Supporting Information 1

Rhodium-catalyzed asymmetric hydroalkoxylation and hydrosufenylation of diphenylphosphinylallenes

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General

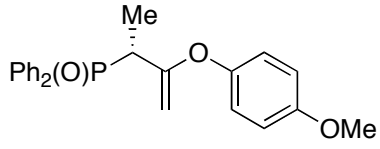
All anaerobic and moisture-sensitive manipulations were carried out with standard Schlenk techniques under predried nitrogen or glovebox techniques under argon. NMR spectra were recorded on a JEOL JNM LA-500 spectrometer (500 MHz for ^{1}H, 125 MHz for ^{13}C, and 202 MHz for ^{31}P). Chemical shifts are reported in δ ppm referenced to an internal $SiMe_4$ standard for ^{1}H NMR, and chloroform-*d* (δ 77.00) for ^{13}C NMR, and external H_3PO_4 standard for ^{31}P NMR: the following abbreviations are used; s: singlet, d: doublet, t: triplet, q: quartet, quint: quintet, sept: septet, m: multiplet, br: broad. 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. *tert*-Butyl alcohol was purchased and used as received. Rhodium complexes, $[Rh(OH)(cod)]_2$[1] and $[Rh(OH)((R)\text{-binap})]_2$, [2] were prepared according to the reported procedures. Diphenylphosphinylallenes were prepared according to the reported procedures.[3,4]

A typical procedure for rhodium-catalyzed asymmetric hydroalkoxylation of diphenylphosphinylallene 1a (Table 2)

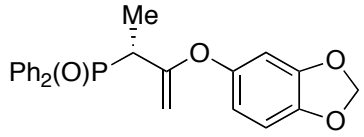
A mixture of $[Rh(OH)(cod)]_2$ (2.3 mg, 5.0 μmol), (*R*)-DTBM-segphos (14.3 mg, 0.012 mmol), and *p*-methoxyphenol (**2m**) (24.8 mg, 0.20 mmol) in *tert*-butyl alcohol (0.4 mL) was stirred at 80 °C for 5 min. After cooling to the room temperature, diphenylphosphinylallene **1a** (101.7 mg, 0.40 mmol) was added, and it was stirred at 80 °C for 24 h. The mixture was passed through a short column of silica gel with ethyl acetate as eluent. After evaporation of the solvent, the residue was subjected to a column chromatography on silica gel (hexane/ethyl acetate) to give **3am** (72.7 mg, 0.19 mmol, 96%).



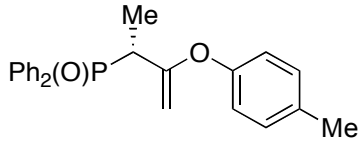
Compound **3am**: White solid; $[\alpha]^{20}_{D}$ +84 (*c* 0.98, $CHCl_3$, 84% ee). Recrystallization of this sample (84% ee) from hexane/ethyl acetate gave 54% recovery of enantiomerically enriched sample (99% ee), whose m.p. is 146–150 ºC. The enantiomeric excess was measured by HPLC (Chiralcel OJ-H column, 0.8 mL/min, hexane/2-propanol = 9/1, 254 nm, t_1 = 12.0 min (*R*), t_2 = 20.1 min (*S*)); ^{1}H

1 R. Usón, L. A. Oro and J. A. Cabeza, *Inorg. Synth.,* 1985, **23**, 126.
2 T. Hayashi, M. Takahashi, Y. Takaya and M. Ogasawara, *J. Am. Chem. Soc.,* 2002, **124**, 5052.
3 (a) A. P. Boisselle and N. A. Meinhardt, *J. Org. Chem.*, 1962, **27**, 1828. (b) M. Rubin, J. Markov, S. Chuprakov, D. J. Wink and V. Gevorgyan, *J. Org. Chem.,* 2003, **68**, 6251.
4 (a) T. Nishimura, S. Hirabayashi, Y. Yasuhara and T. Hayashi, *J. Am. Chem. Soc.,* 2006, **128**, 2556. (b) T. Nishimura, X.-X. Guo and T. Hayashi, *Chem. Asian J.*, 2008, **3**, 1505.

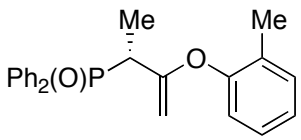
NMR ($CDCl_3$) δ 1.50 (dd, $J_{P\text{-}H}$ = 15.6 Hz, J = 7.3 Hz, 3H), 3.40 (dq, $J_{P\text{-}H}$ = 8.2 Hz, J = 7.3 Hz, 1H), 3.74 (s, 3H), 3.85–3.90 (m, 1H), 4.36–4.42 (m, 1H), 6.42 (d, J = 8.5 Hz, 2H), 6.72 (d, J = 8.5 Hz, 2H), 7.43–7.56 (m, 6H), 7.86–7.97 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 13.7 (d, $J_{P\text{-}C}$ = 2.6 Hz), 39.3 (d, $J_{P\text{-}C}$ = 67.2 Hz), 55.5, 89.5 (d, $J_{P\text{-}C}$ = 6.7 Hz), 114.4, 122.1, 128.1 (d, $J_{P\text{-}C}$ = 11.4 Hz), 128.6 (d, $J_{P\text{-}C}$ = 11.4 Hz), 131.1 (d, $J_{P\text{-}C}$ = 8.3 Hz), 131.5 (d, $J_{P\text{-}C}$ = 2.6 Hz), 131.6 (d, $J_{P\text{-}C}$ = 3.1 Hz), 131.7 (d, $J_{P\text{-}C}$ = 9.3 Hz), 132.27 (d, $J_{P\text{-}C}$ = 83.8 Hz), 132.29 (d, $J_{P\text{-}C}$ = 84.3 Hz), 147.5, 156.3, 160.9 (d, $J_{P\text{-}C}$ = 5.7 Hz); ^{31}P NMR ($CDCl_3$) δ 32.4. Anal. Calcd for $C_{23}H_{23}O_3P$: C, 73.00; H, 6.13. Found: C, 73.21; H, 6.43.



Compound **3an**: White solid; $[\alpha]^{20}_D$ +73 (*c* 1.30, $CHCl_3$, 80% ee). The enantiomeric excess was measured by HPLC (Chiralcel OJ-H column, 1.0 mL/min, hexane/2-propanol = 4/1, 254 nm, t_1 = 8.6 min (*R*), t_2 = 12.2 min (*S*)); ^{1}H NMR ($CDCl_3$) δ 1.49 (dd, $J_{P\text{-}H}$ = 15.5 Hz, J = 7.3 Hz, 3H), 3.38 (dq, J = 8.3, 7.3 Hz, 1H), 3.95 (br s, 1H), 4.41 (br s, 1H), 5.90 (s, 2H), 5.93 (s, 1H), 6.01 (d, J = 8.3 Hz, 1H), 6.61 (d, J = 8.3 Hz, 1H), 7.45–7.54 (m, 6H), 7.86–7.95 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 13.7 (d, $J_{P\text{-}C}$ = 3.1 Hz), 39.2 (d, $J_{P\text{-}C}$ = 67.2 Hz), 89.9 (d, $J_{P\text{-}C}$ = 6.7 Hz), 101.3, 103.3, 107.8, 113.6, 128.1 (d, $J_{P\text{-}C}$ = 11.4 Hz), 128.6 (d, $J_{P\text{-}C}$ = 11.4 Hz), 131.1 (d, $J_{P\text{-}C}$ = 8.8 Hz), 131.57 (d, $J_{P\text{-}C}$ = 3.6 Hz), 131.61 (d, $J_{P\text{-}C}$ = 8.8 Hz), 131.62 (d, $J_{P\text{-}C}$ = 2.6 Hz), 131.9 (d, $J_{P\text{-}C}$ = 98.7 Hz), 132.4 (d, $J_{P\text{-}C}$ = 95.6 Hz), 144.2, 147.3, 148.4, 160.7 (d, $J_{P\text{-}C}$ = 5.7 Hz); ^{31}P NMR ($CDCl_3$) δ 32.0. HRMS (ESI) calcd for $C_{23}H_{22}O_4P$ $(M+H)^+$ 393.1250, found 393.1258.

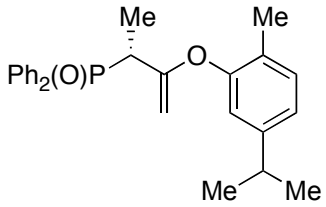


Compound **3ao**: White solid; $[\alpha]^{20}_D$ +83 (*c* 1.02, $CHCl_3$, 80% ee). The enantiomeric excess was measured by HPLC (Chiralcel OJ-H column, 0.8 mL/min, hexane/2-propanol = 95/5, 254 nm, t_1 = 12.6 min (*R*), t_2 = 19.7 min (*S*)); ^{1}H NMR ($CDCl_3$) δ 1.49 (dd, $J_{P\text{-}H}$ = 15.5 Hz, J = 7.3 Hz, 3H), 2.25 (s, 3H), 3.39 (dq, $J_{P\text{-}H}$ = 9.0 Hz, J = 7.3 Hz, 1H), 3.90–3.94 (m, 1H), 4.40 (t, J = 3.0 Hz, 1H), 6.39 (d, J = 8.2 Hz, 2H), 6.98 (d, J = 8.2 Hz, 2H), 7.40–7.53 (m, 6H), 7.85–7.96 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 13.8 (d, $J_{P\text{-}C}$ = 3.1 Hz), 20.7, 39.4 (d, $J_{P\text{-}C}$ = 66.7 Hz), 90.2 (d, $J_{P\text{-}C}$ = 6.2 Hz), 120.9, 128.1 (d, $J_{P\text{-}C}$ = 11.4 Hz), 128.6 (d, $J_{P\text{-}C}$ = 11.4 Hz), 129.9, 131.1 (d, $J_{P\text{-}C}$ = 8.3 Hz), 131.5 (d, $J_{P\text{-}C}$ = 2.6 Hz), 131.6 (d, $J_{P\text{-}C}$ = 2.6 Hz), 131.7 (d, $J_{P\text{-}C}$ = 9.3 Hz), 132.0 (d, $J_{P\text{-}C}$ = 98.2 Hz), 132.6 (d, $J_{P\text{-}C}$ = 96.1 Hz), 133.9, 151.8, 160.4 (d, $J_{P\text{-}C}$ = 5.7 Hz); ^{31}P NMR ($CDCl_3$) δ 32.3. Anal. Calcd for $C_{23}H_{23}O_2P$: C, 76.23; H, 6.40. Found: C, 76.41; H, 6.48.

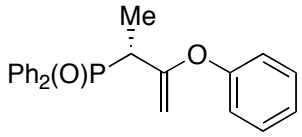


Compound **3ap**: White solid; $[\alpha]^{20}_D$ +72 (*c* 1.07, $CHCl_3$, 87% ee). The enantiomeric excess was measured by HPLC (Chiralpak AS column, 0.5 mL/min, hexane/2-propanol = 95/5, 254 nm, t_1 = 24.0 min (*S*), t_2 = 28.2 min (*R*)); ^{1}H NMR ($CDCl_3$) δ 1.54 (dd, $J_{P\text{-}H}$ = 15.5 Hz, J = 7.3 Hz, 3H), 1.97 (s, 3H), 3.43 (dq, $J_{P\text{-}H}$ =

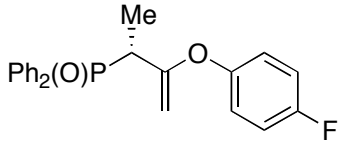
8.1 Hz, J = 7.3 Hz, 1H), 3.73 (t, J = 2.4 Hz, 1H), 4.38 (dd, J = 3.0, 2.8 Hz, 1H), 6.31 (dd, J= 9.1, 1.5 Hz, 1H), 6.96–7.05 (m, 2H), 7.07–7.13 (m, 1H), 7.40–7.55 (m, 6H), 7.83–8.00 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 14.2 (d, $J_{P\text{-}C}$ = 3.1 Hz), 15.7, 39.6 (d, $J_{P\text{-}C}$ = 67.7 Hz), 89.4 (d, $J_{P\text{-}C}$ = 6.3 Hz), 121.6, 124.9, 127.1, 128.3 (d, $J_{P\text{-}C}$ = 11.9 Hz), 128.7 (d, $J_{P\text{-}C}$ = 11.4 Hz), 130.8, 131.20, 131.24 (d, $J_{P\text{-}C}$ = 8.8 Hz), 131.72 (d, $J_{P\text{-}C}$ = 3.1 Hz), 131.74 (d, $J_{P\text{-}C}$ = 3.6 Hz), 131.8 (d, $J_{P\text{-}C}$ = 8.8 Hz), 132.2 (d, $J_{P\text{-}C}$ = 98.7 Hz), 132.8 (d, $J_{P\text{-}C}$ = 95.6 Hz), 152.4, 159.5 (d, $J_{P\text{-}C}$ = 5.6 Hz); ^{31}P NMR ($CDCl_3$) δ 32.2. Anal. Calcd for $C_{23}H_{23}O_2P$: C, 76.23; H, 6.40. Found: C, 76.19; H, 6.57.



Compound **3aq**: White solid; $[\alpha]^{20}_D$ +67 (c 1.16, $CHCl_3$, 85% ee). The enantiomeric excess was measured by HPLC (Chiralcel OJ-H column, 1.0 mL/min, hexane/2-propanol = 99/1, 254 nm, t_1 = 10.1 min (R), t_2 = 14.6 min (S)); ^{1}H NMR ($CDCl_3$) δ 1.110 (d, J = 7.0 Hz, 3H), 1.113 (d, J = 7.0 Hz, 3H), 1.49 (dd, $J_{P\text{-}H}$ = 15.5 Hz, J = 7.4 Hz, 3H), 1.95 (s, 3H), 2.70 (sept, J = 7.0 Hz, 1H), 3.44 (dq, J = 9.1, 7.4 Hz, 1H), 3.69–3.73 (m, 1H), 4.36 (t, J = 2.9 Hz, 1H), 6.03 (d, J= 1.4 Hz, 1H), 6.85 (dd, J = 7.8, 1.4 Hz, 1H), 7.02 (d, J = 7.8 Hz, 1H), 7.40–7.55 (m, 6H), 7.85–8.02 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 14.0 (d, $J_{P\text{-}C}$ = 3.1 Hz), 15.2, 23.8, 23.9, 33.5, 39.4 (d, $J_{P\text{-}C}$ = 67.7 Hz), 88.8 (d, $J_{P\text{-}C}$ = 6.7 Hz), 119.4, 122.9, 127.7, 128.2 (d, $J_{P\text{-}C}$ = 11.9 Hz), 128.6 (d, $J_{P\text{-}C}$ = 11.4 Hz), 130.7, 131.1 (d, $J_{P\text{-}C}$ = 8.8 Hz), 131.56 (d, $J_{P\text{-}C}$ = 3.1 Hz), 131.59 (d, $J_{P\text{-}C}$ = 2.6 Hz), 131.7 (d, $J_{P\text{-}C}$ = 8.8 Hz), 132.0 (d, $J_{P\text{-}C}$ = 98.7 Hz), 132.7 (d, $J_{P\text{-}C}$ = 95.6 Hz), 148.1, 152.0, 159.3 (d, $J_{P\text{-}C}$ = 5.2 Hz); ^{31}P NMR ($CDCl_3$) δ 32.1. HRMS (ESI) calcd for $C_{26}H_{29}NaO_2P$ $(M+Na)^+$ 427.1797, found 427.1782.

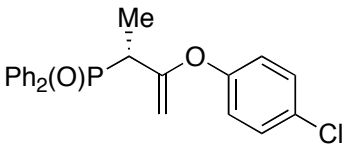


Compound **3ar**: White solid; $[\alpha]^{20}_D$ +89 (c 1.03, $CHCl_3$, 85% ee). The enantiomeric excess was measured by HPLC (Chiralcel OJ-H column, 0.8 mL/min, hexane/2-propanol = 95/5, 254 nm, t_1 = 12.6 min (R), t_2 = 16.1 min (S)); ^{1}H NMR ($CDCl_3$) δ 1.51 (dd, $J_{P\text{-}H}$ = 15.5 Hz, J = 7.4 Hz, 3H), 3.41 (dq, $J_{P\text{-}H}$ = 8.9 Hz, J = 7.4 Hz, 1H), 3.97 (t, J = 2.5 Hz, 1H), 4.46 (t, J = 3.0 Hz, 1H), 6.53 (d, J = 7.6 Hz, 2H), 7.05 (t, J = 7.4 Hz, 1H), 7.20 (t, J = 8.0 Hz, 2H), 7.40–7.55 (m, 6H), 7.83–7.99 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 13.8 (d, $J_{P\text{-}C}$ = 2.6 Hz), 39.5 (d, $J_{P\text{-}C}$ = 66.7 Hz), 91.0 (d, $J_{P\text{-}C}$ = 6.8 Hz), 121.2, 124.5, 128.3 (d, $J_{P\text{-}C}$ = 11.8 Hz), 128.7 (d, $J_{P\text{-}C}$ = 11.3 Hz), 129.5, 131.2 (d, $J_{P\text{-}C}$ = 8.3 Hz), 131.69 (d, $J_{P\text{-}C}$ = 3.1 Hz), 131.73 (d, $J_{P\text{-}C}$ = 8.8 Hz), 131.8 (d, $J_{P\text{-}C}$ = 3.1 Hz), 132.0 (d, $J_{P\text{-}C}$ = 98.7 Hz), 132.6 (d, $J_{P\text{-}C}$ = 95.6 Hz), 154.3, 160.3 (d, $J_{P\text{-}C}$ = 5.8 Hz); ^{31}P NMR ($CDCl_3$) δ 32.3. Anal. Calcd for $C_{22}H_{21}O_2P$: C, 75.85; H, 6.08. Found: C, 75.59; H, 6.03.

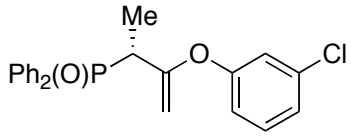


Compound **3as**: White solid; $[\alpha]^{20}_D$ +96 (c 1.00, $CHCl_3$, 84% ee). The enantiomeric excess was measured by HPLC (Chiralcel OJ-H column, 0.8 mL/min, hexane/2-propanol = 95/5, 254 nm, t_1 = 14.8

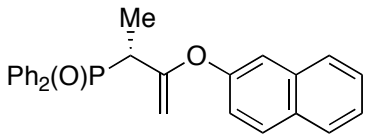
min (*R*), t_2 = 19.1 min (*S*)); ^{1}H NMR ($CDCl_3$) δ 1.50 (dd, $J_{P\text{-}H}$ = 15.5 Hz, *J* = 7.3 Hz, 3H), 3.40 (dq, $J_{P\text{-}H}$ = 8.5 Hz, *J* = 7.3 Hz, 1H), 3.89 (dd, *J* = 3.4, 3.0 Hz, 1H), 4.43 (t, *J* = 3.0 Hz, 1H), 6.45 (dd, *J* = 9.1 Hz, $J_{F\text{-}H}$ = 4.5 Hz, 2H), 6.88 (dd, *J* = 9.1 Hz, $J_{F\text{-}H}$ = 8.1 Hz, 2H), 7.43–7.55 (m, 6H), 7.87–7.96 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 13.7 (d, $J_{P\text{-}C}$ = 3.1 Hz), 39.3 (d, $J_{P\text{-}C}$ = 67.2 Hz), 90.3 (d, $J_{P\text{-}C}$ = 6.7 Hz), 115.9 (d, $J_{F\text{-}C}$ = 23.2 Hz), 122.5 (d, $J_{F\text{-}C}$ = 8.3 Hz), 128.2 (d, $J_{P\text{-}C}$ = 11.4 Hz), 128.6 (d, $J_{P\text{-}C}$ = 11.4 Hz), 131.1 (d, $J_{P\text{-}C}$ = 8.3 Hz), 131.57 (d, $J_{P\text{-}C}$ = 1.5 Hz), 131.61 (d, $J_{P\text{-}C}$ = 9.3 Hz), 131.7 (d, $J_{P\text{-}C}$ = 3.6 Hz), 132.0 (d, $J_{P\text{-}C}$ = 98.2 Hz), 132.4 (d, $J_{P\text{-}C}$ = 96.1 Hz), 149.9 (d, $J_{F\text{-}C}$ = 2.6 Hz), 159.3 (d, $J_{F\text{-}C}$ = 242.3 Hz), 160.6 (d, $J_{P\text{-}C}$ = 6.2 Hz); ^{31}P NMR ($CDCl_3$) δ 32.0. Anal. Calcd for $C_{22}H_{20}FO_2P$: C, 72.12; H, 5.50. Found: C, 72.04; H, 5.53.



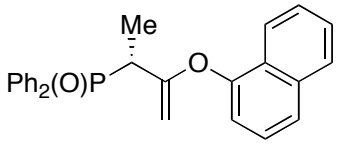
Compound **3at**: White solid; $[\alpha]^{20}_D$ +98 (*c* 0.99, $CHCl_3$, 93% ee). The enantiomeric excess was measured by HPLC (Chiralcel OJ-H column, 0.8 mL/min, hexane/2-propanol = 9/1, 254 nm, t_1 = 8.7 min (*R*), t_2 = 12.0 min (*S*)); ^{1}H NMR ($CDCl_3$) δ 1.49 (dd, $J_{P\text{-}H}$ = 15.6 Hz, *J* = 7.3 Hz, 3H), 3.39 (dq, $J_{P\text{-}H}$ = 8.5 Hz, *J* = 7.3 Hz, 1H), 3.97 (t, *J* = 2.5 Hz, 1H), 4.47 (t, *J* = 3.2 Hz, 1H), 6.44 (d, *J* = 9.0 Hz, 2H), 7.16 (d, *J* = 9.0 Hz, 2H), 7.43–7.54 (m, 6H), 7.86–7.95 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 13.6 (d, $J_{P\text{-}C}$ = 2.6 Hz), 39.3 (d, $J_{P\text{-}C}$ = 66.7 Hz), 91.2 (d, $J_{P\text{-}C}$ = 6.7 Hz), 122.4, 128.2 (d, $J_{P\text{-}C}$ = 11.9 Hz), 128.6 (d, $J_{P\text{-}C}$ = 11.4 Hz), 129.4, 129.5, 131.0 (d, $J_{P\text{-}C}$ = 8.8 Hz), 131.57 (d, $J_{P\text{-}C}$ = 8.8 Hz), 131.59 (d, $J_{P\text{-}C}$ = 2.6 Hz), 131.7 (d, $J_{P\text{-}C}$ = 2.6 Hz), 131.9 (d, $J_{P\text{-}C}$ = 97.7 Hz), 132.3 (d, $J_{P\text{-}C}$ = 96.1 Hz), 152.7, 160.1 (d, $J_{P\text{-}C}$ = 6.2 Hz); ^{31}P NMR ($CDCl_3$) δ 31.8. Anal. Calcd for $C_{22}H_{20}ClO_2P$: C, 69.02; H, 5.27. Found: C, 69.15; H, 5.30. The absolute configuration of **3at** produced by use of (*R*)-DTBM-segphos was determined to be *R,* which was assigned by X-ray analysis (vide infra).



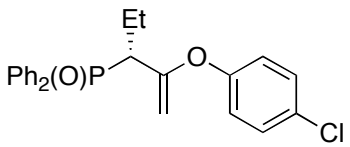
Compound **3au**: White solid; $[\alpha]^{20}_D$ +98 (*c* 1.03, $CHCl_3$, 94% ee). The enantiomeric excess was measured by HPLC (Chiralpak AD-H column, 0.5 mL/min, hexane/2-propanol = 4/1, 254 nm, t_1 = 18.4 min (*R*), t_2 = 19.7 min (*S*)); ^{1}H NMR ($CDCl_3$) δ 1.49 (dd, $J_{P\text{-}H}$ = 15.4 Hz, *J* = 7.3 Hz, 3H), 3.38 (dq, $J_{P\text{-}H}$ = 8.8 Hz, *J* = 7.3 Hz, 1H), 4.04 (dd, *J* = 2.9, 2.4 Hz, 1H), 4.53 (dd, *J* = 3.3, 3.2 Hz, 1H), 6.42 (dd, *J* = 2.2, 1.9 Hz, 1H), 6.46 (ddd, *J* = 8.1, 2.2, 0.8 Hz, 1H), 7.04 (ddd, *J* = 8.0, 1.9, 0.8 Hz, 1H), 7.12 (t, *J* = 8.0 Hz, 1H), 7.44–7.57 (m, 6H), 7.85–7.95 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 13.6 (d, $J_{P\text{-}C}$ = 2.6 Hz), 39.3 (d, $J_{P\text{-}C}$ = 66.6 Hz), 92.0 (d, $J_{P\text{-}C}$ = 6.8 Hz), 119.1, 121.4, 124.5, 128.2 (d, $J_{P\text{-}C}$ = 11.9 Hz), 128.6 (d, $J_{P\text{-}C}$ = 11.4 Hz), 130.1, 131.1 (d, $J_{P\text{-}C}$ = 8.8 Hz), 131.6 (d, $J_{P\text{-}C}$ = 8.8 Hz), 131.70 (d, $J_{P\text{-}C}$ = 3.1 Hz), 131.73 (d, $J_{P\text{-}C}$ = 3.1 Hz), 131.74 (d, $J_{P\text{-}C}$ = 99.1 Hz), 132.2 (d, $J_{P\text{-}C}$ = 95.3 Hz), 134.6, 154.9, 159.7 (d, $J_{P\text{-}C}$ = 6.2 Hz); ^{31}P NMR ($CDCl_3$) δ 31.9. Anal. Calcd for $C_{22}H_{20}ClO_2P$: C, 69.02; H, 5.27. Found: C, 68.79; H, 5.29.



Compound **3av**: White solid; $[\alpha]^{20}_{D}$ +98 (*c* 0.99, $CHCl_3$, 91% ee). The enantiomeric excess was measured by HPLC (Chiralpak AS column, 0.8 mL/min, hexane/2-propanol = 95/5, 254 nm, t_1 = 20.1 min (*S*), t_2 = 23.5 min (*R*)); ^{1}H NMR ($CDCl_3$) δ 1.54 (dd, $J_{P\text{-}H}$ = 15.5 Hz, *J* = 7.3 Hz, 3H), 3.47 (dq, $J_{P\text{-}H}$ = 8.7 Hz, *J* = 7.3 Hz, 1H), 4.00–4.08 (m, 1H), 4.53 (dd, *J* = 3.2, 3.0 Hz, 1H), 6.67 (dd, *J* = 8.8, 2.2 Hz, 1H), 6.91 (d, *J* = 1.9 Hz, 1H), 7.37–7.55 (m, 8H), 7.63 (d, *J* = 7.9 Hz, 1H), 7.67 (d, *J* = 8.8 Hz, 1H), 7.76 (d, *J* = 7.8 Hz, 1H), 7.88–8.02 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 13.9 (d, $J_{P\text{-}C}$ = 3.1 Hz), 39.5 (d, $J_{P\text{-}C}$ = 66.6 Hz), 91.7 (d, $J_{P\text{-}C}$ = 6.8 Hz), 117.4, 121.3, 125.2, 126.4, 127.3, 127.8, 128.3 (d, $J_{P\text{-}C}$ = 11.8 Hz), 128.8 (d, $J_{P\text{-}C}$ = 11.3 Hz), 129.5, 130.9, 131.3 (d, $J_{P\text{-}C}$ = 8.8 Hz), 131.76 (d, $J_{P\text{-}C}$ = 3.1 Hz), 131.82 (d, $J_{P\text{-}C}$ = 2.6 Hz), 131.9 (d, $J_{P\text{-}C}$ = 8.8 Hz), 132.2 (d, $J_{P\text{-}C}$ = 91.4 Hz), 132.7 (d, $J_{P\text{-}C}$ = 95.6 Hz), 134.2, 152.0, 160.3 (d, $J_{P\text{-}C}$ = 5.8 Hz); ^{31}P NMR ($CDCl_3$) δ 32.1. Anal. Calcd for $C_{26}H_{23}O_2P$: C, 78.38; H, 5.82. Found: C, 78.16; H, 6.00.

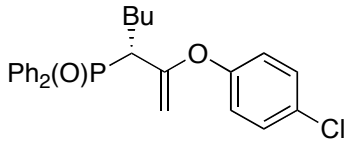


Compound **3aw**: White solid; $[\alpha]^{20}_{D}$ +93 (*c* 1.00, $CHCl_3$, 97% ee). The enantiomeric excess was measured by HPLC (Chiralcel OJ-H column, 0.8 mL/min, hexane/2-propanol = 95/5, 254 nm, t_1 = 19.6 min (*S*), t_2 = 28.1 min (*R*)); ^{1}H NMR ($CDCl_3$) δ 1.62 (dd, $J_{P\text{-}H}$ = 15.7 Hz, *J* = 7.5 Hz, 3H), 3.56 (dq, $J_{P\text{-}H}$ = 8.4 Hz, *J* = 7.5 Hz, 1H), 3.94 (dd, *J* = 2.7, 1.8 Hz, 1H), 4.52 (dd, *J* = 3.3, 2.7 Hz, 1H), 6.58 (d, *J* = 7.3 Hz, 1H), 7.28 (t, *J* = 7.9 Hz, 1H), 7.32 (ddd, *J* = 8.4, 7.0, 1.1 Hz, 1H), 7.43 (ddd, *J* = 8.2, 6.9, 1.1 Hz, 1H), 7.45–7.60 (m, 8H), 7.78 (d, *J* = 8.5 Hz, 1H), 7.90–7.96 (m, 2H), 7.97–8.02 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.2 (d, $J_{P\text{-}C}$ = 3.1 Hz), 39.4 (d, $J_{P\text{-}C}$ = 67.2 Hz), 91.9 (d, $J_{P\text{-}C}$ = 6.2 Hz), 116.3, 121.9, 124.4, 125.6, 125.8, 126.2, 127.0, 127.6, 128.3 (d, $J_{P\text{-}C}$ = 11.4 Hz), 128.7 (d, $J_{P\text{-}C}$ = 11.4 Hz), 131.1 (d, $J_{P\text{-}C}$ = 8.3 Hz), 131.63 (d, $J_{P\text{-}C}$ = 3.1 Hz), 131.66 (d, $J_{P\text{-}C}$ = 2.4 Hz), 131.67 (d, $J_{P\text{-}C}$ = 8.3 Hz), 132.0 (d, $J_{P\text{-}C}$ = 92.6 Hz), 132.4 (d, $J_{P\text{-}C}$ = 94.0 Hz), 134.7, 150.3, 159.9 (d, $J_{P\text{-}C}$ = 5.2 Hz); ^{31}P NMR ($CDCl_3$) δ 32.3. Anal. Calcd for $C_{26}H_{23}O_2P$: C, 78.38; H, 5.82. Found: C, 78.13; H, 5.76.

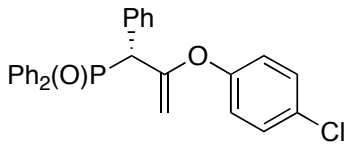


Compound **3bt**: White solid; $[\alpha]^{20}_{D}$ +62 (*c* 1.29, $CHCl_3$, 90% ee). The enantiomeric excess was measured by HPLC (Chiralpak AD-H column, 0.8 mL/min, hexane/2-propanol = 4/1, 254 nm, t_1 = 13.8 min (*S*), t_2 = 16.9 min (*R*)); ^{1}H NMR ($CDCl_3$) δ 1.09 (t, *J* = 7.2 Hz, 3H), 1.80–2.05 (m, 2H), 3.14 (dt, $J_{P\text{-}H}$ = 10.5 Hz, *J* = 3.2 Hz, 1H), 3.91 (s, 1H), 4.45 (t, *J* = 3.0 Hz, 1H), 6.44 (d, *J* = 8.5 Hz, 2H), 7.16 (d, *J* = 8.5 Hz, 2H), 7.40–7.57 (m, 6H), 7.84–7.96 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 12.5 (d, $J_{P\text{-}C}$ = 13.4 Hz), 21.4 (d, $J_{P\text{-}C}$ = 1.5 Hz), 47.4 (d, $J_{P\text{-}C}$ = 67.2 Hz), 90.9 (d, $J_{P\text{-}C}$ = 6.7 Hz), 122.8, 128.2 (d, $J_{P\text{-}C}$ = 11.4 Hz), 128.6 (d, $J_{P\text{-}C}$ = 11.4 Hz), 129.5, 129.8, 131.1 (d, $J_{P\text{-}C}$ = 8.3 Hz), 131.52 (d, $J_{P\text{-}C}$ = 2.1 Hz), 131.57 (d, $J_{P\text{-}C}$ = 8.8 Hz), 131.64 (d, $J_{P\text{-}C}$ = 3.1 Hz), 131.2 (d, $J_{P\text{-}C}$ = 98.2 Hz), 132.6 (d, $J_{P\text{-}C}$ = 95.6 Hz), 152.6, 158.4 (d, $J_{P\text{-}C}$ = 5.7 Hz); ^{31}P NMR ($CDCl_3$) δ 31.7. HRMS (ESI) calcd for $C_{23}H_{22}ClNaO_2P$

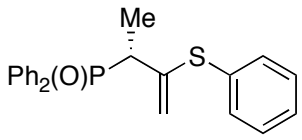
$(M+Na)^+$ 419.0938, found 419.0940.



Compound **3ct**: White solid; $[\alpha]^{20}_D$ +47 (*c* 0.97, $CHCl_3$, 88% ee). The enantiomeric excess was measured by HPLC (Chiralpak AD-H column, 0.8 mL/min, hexane/2-propanol = 4/1, 254 nm, t_1 = 14.8 min (*S*), t_2 = 17.1 min (*R*)); ^{1}H NMR ($CDCl_3$) δ 0.86 (t, *J* = 7.1 Hz, 3H), 1.18–1.46 (m, 3H), 1.52–1.63 (m, 1H), 1.72–1.83 (m, 1H), 1.93–2.06 (m, 1H), 3.23 (dt, $J_{P\text{-}H}$ = 11.1, *J* = 3.7 Hz, 1H), 3.90 (s, 1H), 4.45 (t, *J* = 3.2 Hz, 1H), 6.42 (d, *J* = 8.7 Hz, 2H), 7.16 (d, *J* = 8.7 Hz, 2H), 7.39–7.58 (m, 6H), 7.82–7.97 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 13.8, 22.2, 27.5 (d, $J_{P\text{-}C}$ = 1.5 Hz), 29.9 (d, $J_{P\text{-}C}$ = 12.4 Hz), 45.4 (d, $J_{P\text{-}C}$ = 67.2 Hz), 90.7 (d, $J_{P\text{-}C}$ = 6.7 Hz), 122.9, 128.2 (d, $J_{P\text{-}C}$ = 11.9 Hz), 128.6 (d, $J_{P\text{-}C}$ = 11.4 Hz), 129.5, 129.8, 131.1 (d, $J_{P\text{-}C}$ = 8.3 Hz), 131.52 (d, $J_{P\text{-}C}$ = 3.1 Hz), 131.59 (d, $J_{P\text{-}C}$ = 8.8 Hz), 131.7 (d, $J_{P\text{-}C}$ = 2.6 Hz), 131.2 (d, $J_{P\text{-}C}$ = 98.2 Hz), 132.5 (d, $J_{P\text{-}C}$ = 95.6 Hz), 152.6, 158.7 (d, $J_{P\text{-}C}$ = 5.7 Hz); ^{31}P NMR ($CDCl_3$) δ 31.4. HRMS (ESI) calcd for $C_{25}H_{26}ClNaO_2P$ $(M+Na)^+$ 447.1251, found 447.1253.

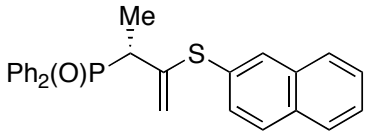


Compound **3dt**: White solid; $[\alpha]^{20}_D$ –83 (*c* 0.98, $CHCl_3$, 74% ee). The enantiomeric excess was measured by HPLC (Chiralpak AD-H column, 0.8 mL/min, hexane/2-propanol = 4/1, 254 nm, t_1 = 21.2 min (*R*), t_2 = 38.7 min (*S*)); ^{1}H NMR ($CDCl_3$) δ 4.09 (dd, *J* = 2.8, 1.8 Hz, 1H), 4.43 (d, *J* = 10.2 Hz, 1H), 4.98 (dd, *J* = 2.8, 1.8 Hz, 1H), 6.57 (d, *J* = 8.9 Hz, 2H), 7.15 (d, *J* = 8.9 Hz, 2H), 7.18–7.60 (m, 11 H), 7.96–8.06 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 53.0 (d, $J_{P\text{-}C}$ = 65.1 Hz), 93.8 (d, $J_{P\text{-}C}$ = 5.2 Hz), 122.3, 127.4 (d, $J_{P\text{-}C}$ = 2.1 Hz), 128.1 (d, $J_{P\text{-}C}$ = 11.9 Hz), 128.3 (d, $J_{P\text{-}C}$ = 1.6 Hz), 128.4 (d, $J_{P\text{-}C}$ = 11.4 Hz), 129.47, 129.54, 130.0 (d, $J_{P\text{-}C}$ = 5.7 Hz), 131.1 (d, $J_{P\text{-}C}$ = 8.8 Hz), 131.4 (d, $J_{P\text{-}C}$ = 2.1 Hz), 131.5 (d, $J_{P\text{-}C}$ = 8.3 Hz), 131.7 (d, $J_{P\text{-}C}$ = 2.6 Hz), 132.1 (d, $J_{P\text{-}C}$ = 102.3 Hz), 132.3 (d, $J_{P\text{-}C}$ = 98.7 Hz), 134.0 (d, $J_{P\text{-}C}$ = 5.2 Hz), 153.0, 158.7 (d, $J_{P\text{-}C}$ = 2.1 Hz); ^{31}P NMR ($CDCl_3$) δ 29.5. HRMS (ESI) calcd for $C_{27}H_{22}ClNaO_2P$ $(M+Na)^+$ 467.0938, found 467.0933.



Compound **6**: White solid; $[\alpha]^{20}_D$ –139 (*c* 1.08, $CHCl_3$, 81% ee). The enantiomeric excess was measured by HPLC (Chiralcel OD-H column, 0.8 mL/min, hexane/2-propanol = 98/2, 254 nm, t_1 = 27.3 min (*R*), t_2 = 30.9 min (*S*)); ^{1}H NMR ($CDCl_3$) δ 1.46 (dd, $J_{P\text{-}H}$ = 15.6 Hz, *J* = 7.3 Hz, 3H), 3.09 (dq, *J* = 7.3, 7.2 Hz, 1H), 4.48 (d, *J* = 1.8 Hz, 1H), 5.70 (d, $J_{P\text{-}H}$ = 1.8 Hz, 1H), 7.16–7.18 (m, 2H), 7.26–7.30 (m, 3H), 7.44–7.53 (m, 6H), 7.80–7.85 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 15.6 (d, $J_{P\text{-}C}$ = 3.1 Hz), 40.1 (d, $J_{P\text{-}C}$ = 66.1 Hz), 115.3 (d, $J_{P\text{-}C}$ = 6.7 Hz), 128.1 (d, $J_{P\text{-}C}$ = 11.4 Hz), 128.5, 128.6 (d, $J_{P\text{-}C}$ = 11.4 Hz), 129.2, 131.0 (d, $J_{P\text{-}C}$ = 8.3 Hz), 131.48 (d, $J_{P\text{-}C}$ = 9.8 Hz), 131.52 (d, $J_{P\text{-}C}$ = 3.1 Hz), 131.6 (d, $J_{P\text{-}C}$ = 2.6 Hz), 132.0, 132.1 (d, $J_{P\text{-}C}$ = 98.7 Hz), 132.6 (d, $J_{P\text{-}C}$ = 93.5 Hz), 133.9, 142.6 (d, $J_{P\text{-}C}$ = 5.7 Hz); ^{31}P NMR

($CDCl_3$) δ 32.5. HRMS (ESI) calcd for $C_{22}H_{21}NaOPS$ $(M+Na)^+$ 387.0943, found 387.0942.



Compound **7**: White solid; $[\alpha]^{20}_D$ –115 (*c* 0.99, $CHCl_3$, 75% ee). The enantiomeric excess was measured by HPLC (Chiralcel OD-H column, 0.8 mL/min, hexane/2-propanol = 98/2, 254 nm, t_1 = 40.7 min (*R*), t_2 = 59.0 min (*S*)); ^{1}H NMR ($CDCl_3$) δ 1.49 (dd, $J_{P\text{-}H}$ = 15.5 Hz, *J* = 7.3 Hz, 3H), 3.15 (quint, *J* = 7.3 Hz, 1H), 4.95 (d, *J* = 3.4 Hz, 1H), 5.74 (d, *J* = 3.4 Hz, 1H), 7.55 (dd, *J* = 8.6, 1.5 Hz, 1H), 7.42–7.58 (m, 7H), 7.68–7.77 (m, 3H), 7.78–7.89 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 15.7 (d, $J_{P\text{-}C}$ = 3.1 Hz), 40.2 (d, $J_{P\text{-}C}$ = 66.2 Hz), 116.0 (d, $J_{P\text{-}C}$ = 7.2 Hz), 126.6, 126.8, 127.6, 127.7, 128.1 (d, $J_{P\text{-}C}$ = 11.9 Hz), 128.7 (d, $J_{P\text{-}C}$ = 11.4 Hz), 128.8, 129.4, 130.5, 131.0 (d, $J_{P\text{-}C}$ = 8.8 Hz), 131.52 (d, $J_{P\text{-}C}$ = 8.8 Hz), 131.57 (d, $J_{P\text{-}C}$ = 2.6 Hz), 131.64 (d, $J_{P\text{-}C}$ = 2.6 Hz), 132.1 (d, $J_{P\text{-}C}$ = 98.7 Hz), 132.3 (d, $J_{P\text{-}C}$ = 94.6 Hz), 132.8, 133.2, 133.7, 142.5 (d, $J_{P\text{-}C}$ = 5.2 Hz); ^{31}P NMR ($CDCl_3$) δ 32.6. HRMS (ESI) calcd for $C_{26}H_{23}NaOPS$ $(M+Na)^+$ 437.1099, found 437.1099.

NMR study of the catalytic reaction in an NMR Sample Tube (Fig. 1)

In an NMR sample tube, $[Rh(OH)((R)\text{-binap})]_2$ (**8**) (14.9 mg, 10 μmol, 20 μmol of Rh) and *p*-cresol (**2o**) (21.6 mg, 0.20 mmol) were placed under argon and C_6D_6 (0.6 mL) was added at room temperature. After shaking the sample tube to dissolve the solid, the mixture was allowed to stand at 30 °C for 1 h. ^{31}P NMR was measured at room temperature to show the complete conversion of **8** with the formation of complex **9** (Figure s1). Complex **9**: ^{31}P NMR (C_6D_6) δ 45.2 (d, $J_{Rh\text{-}P}$ = 207 Hz); ^{1}H NMR (C_6D_6) δ 1.24 (s, 3H) [Me], 3.40 (dd, *J* = 7.3, 1.9 Hz, 1H), 4.02 (dd, *J* = 6.8, 2.1 Hz, 1H), 5.56 (dd, *J* = 6.8, 1.4 Hz, 1H), 6.34 (dd, *J* = 7.3, 1.9 Hz, 1H) [aromatic protons coordinated to a rhodium center]. To the solution was added allene **1a** (25.4 mg, 0.10 mmol) and the mixture was allowed to stand at 30 °C. ^{31}P NMR of the reaction mixture showed two rhodium complexes **9** and **10** with the formation of hydroalkoxylation product **3ao** (Figure s2). Complex **10**: ^{31}P NMR (C_6D_6) δ 35.7 (d, $J_{P\text{-}P}$ = 14 Hz), 39.8 (ddd, $J_{Rh\text{-}P}$ = 193 Hz, $J_{P\text{-}P}$ = 39, 14 Hz), 43.5 (dd, $J_{Rh\text{-}P}$ = 193 Hz, $J_{P\text{-}P}$ = 39 Hz); ^{1}H NMR (C_6D_6) δ 1.35 (dd, $J_{P\text{-}H}$ = 14.9 Hz, *J* = 2.6 Hz, 3H, Me), 2.77 (s, 1H, allylic H), 2.97–3.04 (m, 1H, allylic H) (Figure s3). Allene **1a** was completely converted to **3ao** after 80 h, where hydroxorhodium **8** and π-phenoxorhodium **9** were observed. ^{31}P NMR spectra of the time course of the reaction are shown in Figure 1.

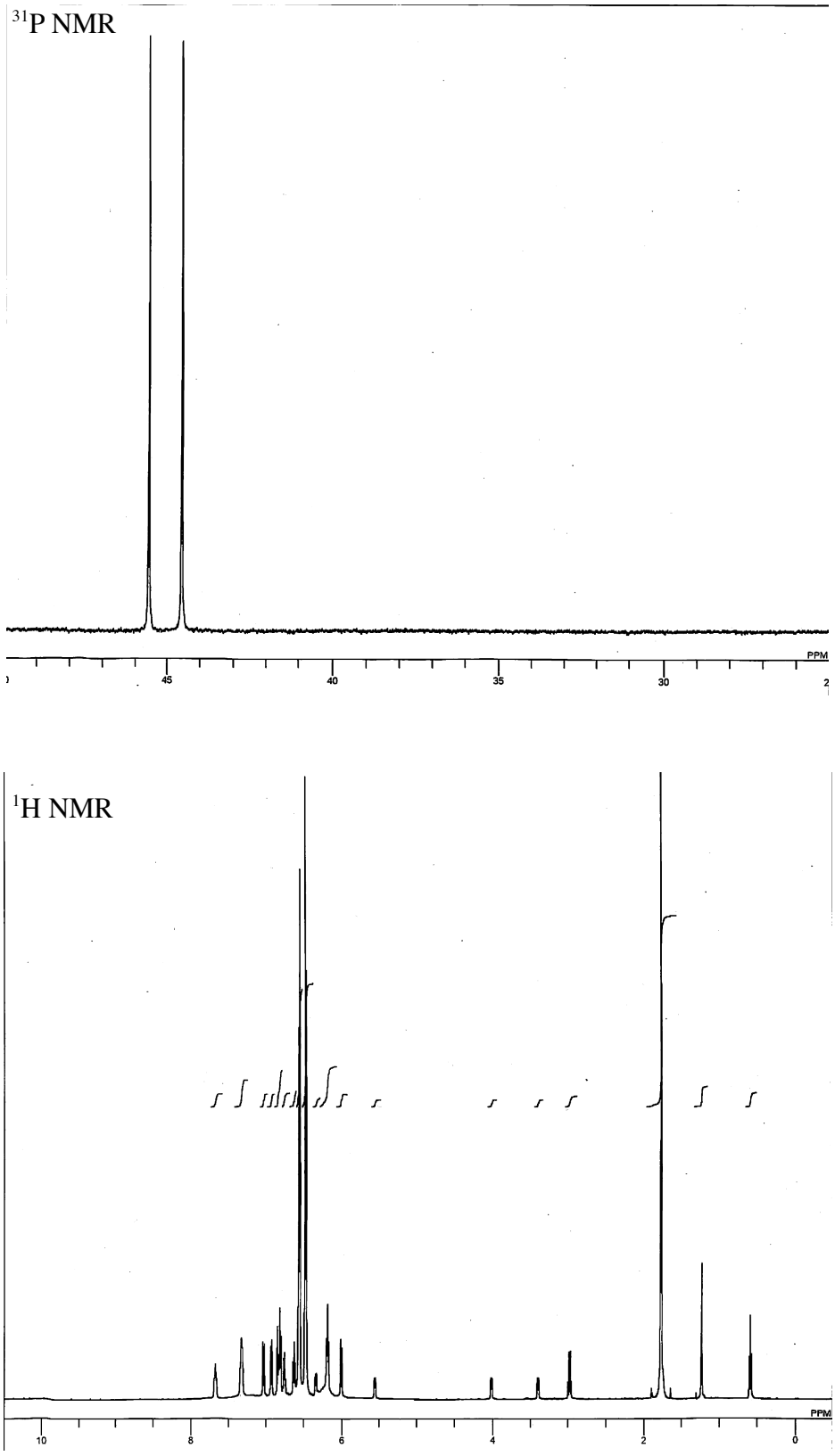


Figure s1. ^{31}P and ^{1}H NMR of complex **9** (containing excess *p*-cresol)

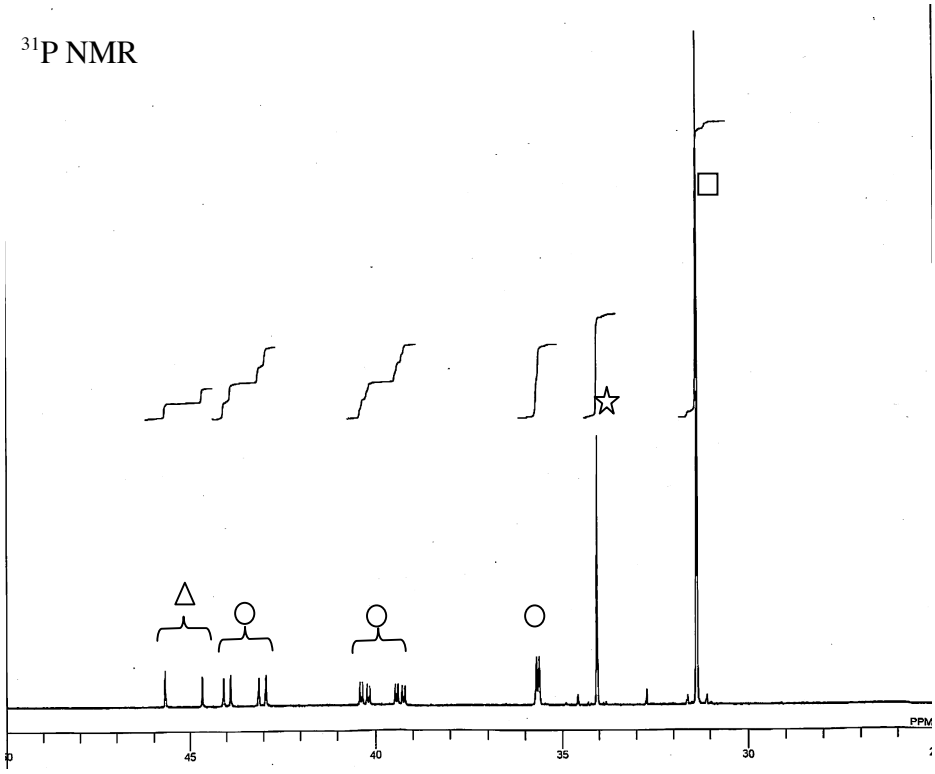


Figure s2. ^{31}P NMR of the reaction mixture after 6 h. △: complex **9**; ○: complex **10**; ☆: **3ao**; □: allene (**1a**)

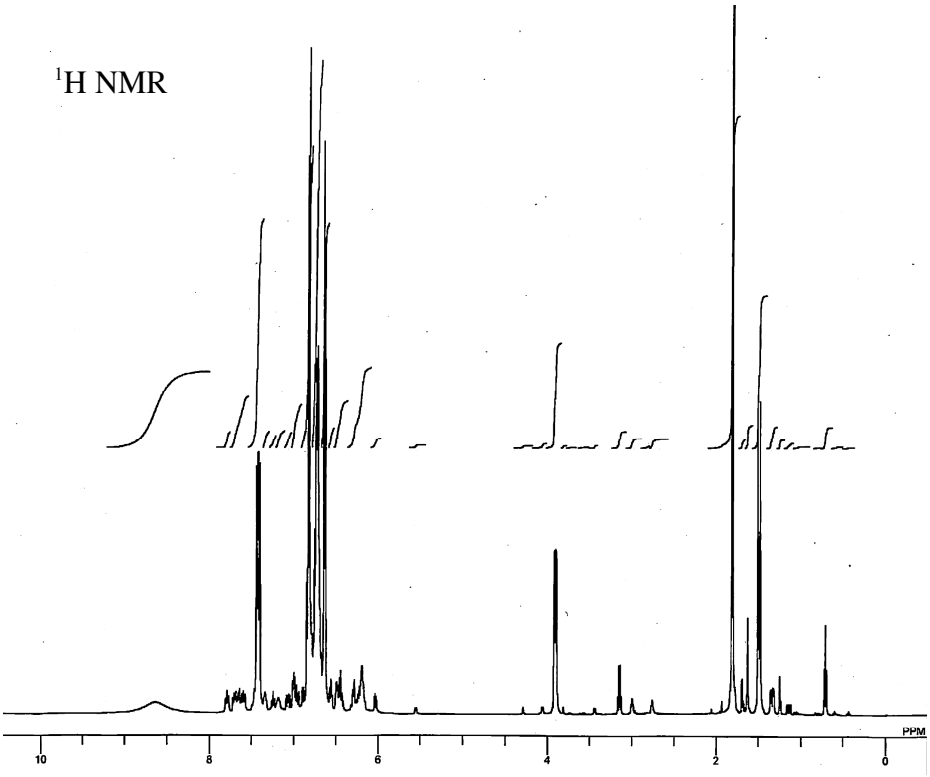


Figure s3. ^{1}H NMR of the reaction mixture containing complex **10**

X-ray crystal structure of 3at

Colorless crystals of **3at** suitable for X-ray crystallographic analysis were obtained by recrystallisation from CH_2Cl_2/hexane. The ORTEP drawing of **3at** is shown in Figure s4. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre (deposition number: CCDC 713591). The data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

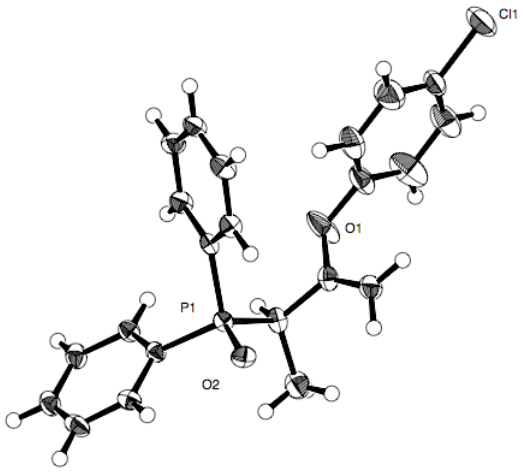


Figure s4. ORTEP illustration of **3at** with thermal ellipsoids drawn at 50% probability level. Crystal data for **3at** (CCDC 713591): $C_{22}H_{20}O_2ClP$, Mw = 382.83, space group $P2_12_12_1$ (#19), a = 5.854(2) Å, b = 16.486(4) Å, c = 20.202(7) Å, V = 1949.5(10) Å^3, Z = 4, D_{calcd} = 1.304 g/cm^3, T = 123 K, R = 0.0364 (I>2.00σ(I)), wR_2 = 0.0940, GOF = 1.055, Flack Parameter = 0.00(6), 19053 reflections measured, 4472 unique (R_{int} = 0.038).