

## **Supporting Information (OL048347K)**

### **Double Phosphinylation of Propargylic Alcohols: a Novel Synthetic Route to 1,2-Bis(diphenylphosphino)ethane Derivatives**

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**General Method.**  $^1\text{H}$  NMR (400, 300, and 270 MHz),  $^{13}\text{C}$  NMR (100, 75, and 67.8 MHz), and  $^{31}\text{P}$  NMR (161.7 Mhz) spectra were recorded using  $\text{CDCl}_3$  as solvent. Quantitative GLC analyses were performed on a Shimadzu GC-14A instrument equipped with a flame ionization detector using a 25 m x 0.25 mm CBP10 fused silica capillary column. GC-MS analyses were carried out on a Shimadzu GC-MS QP-5000 spectrometer. Elemental analyses were performed at Microanalytical Center of Kyoto University. Mass spectra were measured on a JEOL JMS600H mass spectrometer. All reactions were carried out under a dry nitrogen atmosphere. Solvents were dried by the usual methods and distilled before use.

**Ruthenium-Catalyzed Double Phosphinylation of Propargylic Alcohols with Diphenylphosphine Oxide.** A typical experimental procedure for the reaction of 1-phenyl-2-propyn-1-ol (**2a**) with diphenylphosphine oxide catalyzed by  $[\text{Cp}^*\text{RuCl}(\mu_2\text{-SMe})_2\text{RuCp}^*\text{Cl}]$  (**1a**) is described below. In a 20 mL flask were placed **1a** (19 mg, 0.03 mmol) and  $\text{NH}_4\text{BF}_4$  (6 mg, 0.06 mmol) under  $\text{N}_2$ . Anhydrous  $\text{ClCH}_2\text{CH}_2\text{Cl}$  (10 mL) was added, and then the mixture was magnetically stirred at room temperature. After the addition of **2a** (79 mg, 0.60 mmol) and diphenylphosphine oxide (607 mg, 3.00 mmol), the reaction flask was kept at 60 °C for 18 h. The solvent was concentrated under reduced pressure by an aspirator, and then the residue was purified by HPLC ( $\text{CHCl}_3$ ) to give **3a** as pale yellow solid, 194.2-195.0 °C (280 mg, 0.54 mmol, 90% yield).

**2,3-Bis(diphenylphosphinyl)-3-phenyl-1-propene (3a):**<sup>S1</sup> IR (KBr,  $\text{cm}^{-1}$ ) 1180 (P=O).  $^1\text{H}$  NMR  $\delta$  5.15 (q, 1H,  $J = 7.2\text{Hz}$ ), 5.45 (d, 1H,  $^2J_{\text{PH}} = 19.6\text{ Hz}$ ), 6.91-6.99 (m, 3H), 7.11-7.44 (m, 18H), 7.55 (s, 3H), 8.19-8.23 (m, 2H).  $^{13}\text{C}$  NMR  $\delta$  44.1 (d,  $J = 73\text{ Hz}$ ), 126.7, 127.6, 127.7, 128.0, 128.2, 128.3, 128.4, 129.9, 130.0 (d,  $J = 5\text{ Hz}$ ), 130.8, 131.4-131.7 (m), 132.1 (d,  $J = 53\text{ Hz}$ ), 140.2 (d,  $J = 87\text{ Hz}$ ).  $^{31}\text{P}$  NMR  $\delta$  29.9 (d,  $J = 31\text{ Hz}$ ), 30.2 (d,  $J = 31\text{ Hz}$ ). Anal. Calcd. for  $\text{C}_{33}\text{H}_{29}\text{O}_2\text{P}_2$ : C, 75.13; H, 5.54. Found: C, 75.09; H, 5.56. HRMS Calcd for  $\text{C}_{33}\text{H}_{29}\text{O}_2\text{P}_2$  [M+H] 519.1643. Found 519.1642.

Spectroscopic data and isolated yield of other products are as follows.

**2,3-Bis(diphenylphosphinyl)-3-(4-fluorophenyl)-1-propene (3b):** Yield 71%. Pale yellow solid, mp 173.4-174.2 °C. IR (KBr,  $\text{cm}^{-1}$ ) 1182 (P=O).  $^1\text{H}$  NMR  $\delta$  5.18 (br, 1H), 5.44 (d, 1H,  $J = 19.2\text{ Hz}$ ), 6.60 (t, 2H,  $J = 8.2\text{ Hz}$ ), 7.17-7.56 (m, 21H), 8.20 (br, 2H).

$^{31}\text{P}$  NMR  $\delta$  29.6 (d,  $J$  = 24 Hz), 30.1 (d,  $J$  = 24 Hz).  $^{13}\text{C}$  NMR  $\delta$  43.3 (d,  $J$  = 72 Hz), 114.3 (d,  $J$  = 22 Hz), 127.6-127.8 (m), 130.5 (d,  $J$  = 7 Hz), 131.1, 131.4-131.6 (m), 133.4, 140.4 (d,  $J$  = 86 Hz), 160.2 (d,  $J$  = 249 Hz). Anal. Calcd. for  $\text{C}_{33}\text{H}_{28}\text{O}_{2.5}\text{FP}_2$ : C, 72.66.13; H, 5.17. Found: C, 72.37; H, 5.13. HRMS Calcd for  $\text{C}_{33}\text{H}_{28}\text{O}_2\text{FP}_2$  [M+H] 537.1479. Found 537.1547.

**2,3-Bis(diphenylphosphinyl)-3-(4-chlorophenyl)-1-propene (3c):** Yield 96%. Pale yellow solid, mp 186.5-187.8 °C. IR (KBr,  $\text{cm}^{-1}$ ) 1186 (P=O).  $^1\text{H}$  NMR  $\delta$  5.08 (br, 1H), 5.33 (s, 1H,  $J$  = 18.8 Hz), 6.76 (d, 2H,  $J$  = 8.0 Hz), 7.00-7.42 (m, 21H), 8.08 (br, 2H).  $^{31}\text{P}$  NMR  $\delta$  29.5 (d,  $J$  = 24 Hz), 29.7 (d,  $J$  = 24 Hz).  $^{13}\text{C}$  NMR  $\delta$  43.3 (d,  $J$  = 72 Hz), 127.5-127.7 (m), 127.9 (d,  $J$  = 12 Hz), 128.1 (d,  $J$  = 12 Hz), 130.2 (d,  $J$  = 8 Hz), 130.7-131.5 (m), 132.1 (d,  $J$  = 3 Hz), 132.4, 133.3 (t,  $J$  = 9 Hz), 140.0 (d,  $J$  = 87 Hz). Anal. Calcd. for  $\text{C}_{33}\text{H}_{27}\text{O}_2\text{ClP}_2$ : C, 71.68; H, 4.92. Found: C, 71.59; H, 4.87.

**2,3-Bis(diphenylphosphinyl)-3-(4-bromophenyl)-1-propene (3d):** Yield 88%. Pale yellow solid, mp 190.8-192.0 °C. IR (KBr,  $\text{cm}^{-1}$ ) 1182 (P=O).  $^1\text{H}$  NMR  $\delta$  5.16 (q, 1H,  $J$  = 6.3 Hz), 5.42 (d, 1H,  $J$  = 18.8 Hz), 6.99-7.19 (m, 4H), 7.21-7.48 (m, 16H,  $J$  = 6.3 Hz), 7.56-7.58 (m, 3H), 8.13-8.21 (m, 2H).  $^{13}\text{C}$  NMR  $\delta$  43.3 (d,  $J$  = 73 Hz), 127.7-127.9 (m), 128.0-128.4 (m), 130.4-130.8 (m), 131.1-131.8 (m), 132.6 (d,  $J$  = 4 Hz), 133.4, 133.5, 133.6, 140.1 (d,  $J$  = 86 Hz).  $^{31}\text{P}$  NMR  $\delta$  29.8 (brs). HRMS Calcd for  $\text{C}_{33}\text{H}_{28}\text{O}_2\text{BrP}_2$  [M+H] 597.0733. Found 597.0747.

**2,3-Bis(diphenylphosphinyl)-3-(4-methoxyphenyl)-1-propene (3e):** Yield 15%. Pale yellow solid, mp 200.1-201.0 °C. IR (KBr,  $\text{cm}^{-1}$ ) 1183 (P=O).  $^1\text{H}$  NMR  $\delta$  3.66 (s, 3H), 5.12 (br, 1H), 5.41 (d, 1H,  $J$  = 18.8 Hz), 6.47 (d, 2H,  $J$  = 8.8 Hz), 7.05 (d, 2H,  $J$  = 8.4 Hz), 7.14-7.55 (m, 19H), 8.17 (br, 2H).  $^{13}\text{C}$  NMR  $\delta$  44.0 (d,  $J$  = 75 Hz), 55.1, 113.3, 127.7-128.6 (m), 130.4-132.2 (m), 140.4 (d,  $J$  = 86 Hz).  $^{31}\text{P}$  NMR  $\delta$  29.8 (d,  $J$  = 28 Hz), 30.1 (d,  $J$  = 28 Hz). Anal. Calcd. for  $\text{C}_{34}\text{H}_{30}\text{O}_3\text{P}_2$ : C, 74.44; H, 5.51. Found: C, 74.34; H, 5.56.

**2,3-Bis(diphenylphosphinyl)-3-(4-methylphenyl)-1-propene (3f):** Yield 54%. White solid, mp 183.1-183.9 °C. IR (KBr,  $\text{cm}^{-1}$ ) 1176 (P=O).  $^1\text{H}$  NMR  $\delta$  2.14 (s, 3H), 5.14 (d, 1H,  $J$  = 4.0 Hz), 5.42 (d, 1H,  $J$  = 19.2 Hz), 6.75 (d, 2H,  $J$  = 7.6 Hz), 7.03 (d, 2H,  $J$  = 7.6 Hz), 7.12-7.61 (m, 19H), 8.16-8.19 (m, 2H).  $^{13}\text{C}$  NMR  $\delta$  20.9, 43.8 (d,  $J$  = 74 Hz), 127.6-127.8 (m), 128.1-128.3 (m), 128.4, 129.9, 130.0-132.2 (m), 133.6, 136.2, 140.3 (d,  $J$

= 88 Hz).  $^{31}\text{P}$  NMR  $\delta$  30.1 (brs). Anal. Calcd. for  $\text{C}_{34}\text{H}_{30}\text{O}_2\text{P}_2$ : C, 76.68; H, 5.68. Found: C, 76.77; H, 5.73.

**2,3-Bis(diphenylphosphinyl)-3-(3-methylphenyl)-1-propene (3g):** Yield 46%. White solid, mp 167.1-168.8 °C. IR (KBr,  $\text{cm}^{-1}$ ) 1176 (P=O).  $^1\text{H}$  NMR  $\delta$  2.01 (s, 3H), 5.11 (d, 1H,  $J = 3.5$  Hz), 5.43 (d, 1H,  $J = 18.9$  Hz), 6.76-6.90 (m, 3H), 7.04-7.55 (m, 20H), 8.19 (br, 2H).  $^{13}\text{C}$  NMR  $\delta$  21.0, 44.0 (d,  $J = 72$  Hz), 127.0 (d,  $J = 5$  Hz), 127.3, 127.4-127.8 (m), 128.1-128.5 (m), 128.6 (d,  $J = 13$  Hz), 130.4-131.8 (m), 133.5-133.8 (m), 137.0, 139.9 (d,  $J = 88$  Hz).  $^{31}\text{P}$  NMR  $\delta$  29.8 (d,  $J = 28$  Hz), 30.1 (d,  $J = 28$  Hz). Anal. Calcd. for  $\text{C}_{34}\text{H}_{31}\text{O}_{2.5}\text{P}_2$ : C, 75.41; H, 5.77. Found: C, 75.36; H, 5.87. HRMS Calcd for  $\text{C}_{34}\text{H}_{31}\text{O}_2\text{P}_2$  [M+H] 533.1799. Found 533.1799.

**2,3-Bis(diphenylphosphinyl)-3-(2-naphthyl)-1-propene (3i):** Yield 80%. White solid, mp 212.2-212.8 °C. IR (KBr,  $\text{cm}^{-1}$ ) 1179 (P=O).  $^1\text{H}$  NMR  $\delta$  5.35 (d, 1H,  $J = 3.2$  Hz), 5.48 (d, 1H,  $J = 18.8$  Hz), 6.88-7.64 (m, 26H), 8.23 (br, 2H).  $^{13}\text{C}$  NMR  $\delta$  44.4 (d,  $J = 74$  Hz), 125.4 (d,  $J = 18$  Hz), 127.1-128.58 (m), 129.6 (d,  $J = 7$  Hz), 130.8 (d,  $J = 8$  Hz), 131.2-131.9 (m), 132.1, 132.8, 133.9, 140.4 (brs).  $^{31}\text{P}$  NMR  $\delta$  29.7 (d,  $J = 28$  Hz), 29.9 (d,  $J = 28$  Hz). Anal. Calcd. for  $\text{C}_{37}\text{H}_{30}\text{O}_2\text{P}_2$ : C, 78.16; H, 5.32. Found: C, 78.32; H, 5.38.

**1-Diphenyl-1-phenyl-1,2-propadiene (5a):**<sup>S1</sup> Yield 72%. White solid, mp 126.5-128.0 °C. IR (KBr,  $\text{cm}^{-1}$ ) 1193 (P=O), 1929, 1953 (C=C=C).  $^1\text{H}$  NMR  $\delta$  4.87 (d, 2H,  $^4J_{\text{PH}} = 11.2$  Hz), 7.16-7.27 (m, 3H), 7.40-7.44 (m, 4H), 7.47-7.51 (m, 2H), 7.59 (d, 2H,  $J = 8.4$  Hz), 7.73-7.78 (m, 4H).  $^{13}\text{C}$  NMR  $\delta$  78.1 (d,  $J = 12$  Hz), 99.5 (d,  $J = 100$  Hz), 127.2, 127.7-127.8 (m), 130.9, 131.2-131.5 (m), 132.5, 212.8 (d,  $J = 7$  Hz).  $^{31}\text{P}$  NMR  $\delta$  27.5 (brs). HRMS Calcd for  $\text{C}_{21}\text{H}_{17}\text{OP}$  [M] 316.1017. Found 316.1015.

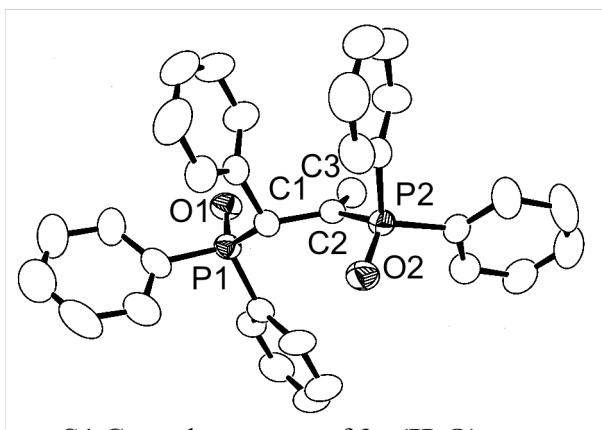
**X-ray Crystallographic Studies of  $3\mathbf{a} \cdot (\text{H}_2\text{O})_{0.5}$ .** Colorless crystals of  $3\mathbf{a} \cdot (\text{H}_2\text{O})_{0.5}$  suitable for X-ray analysis were obtained by recrystallization from  $\text{CH}_2\text{Cl}_2$ –*n*-hexane. A single crystal was sealed in a Pyrex glass capillary under  $\text{N}_2$  atmosphere and used for data collection. All measurements were made on a Rigaku RAXIS imaging plate area detector with graphite monochromated Mo- $\text{K}\alpha$  radiation. Details of crystal and data collection parameters are summarized in Table S1. The positions of non-hydrogen atoms were determined by direct methods (SIR97) and subsequent Fourier syntheses (DIRDIF99). An ORTEP drawing of  $3\mathbf{a}$  is shown in Figure S1.

**Table S1.** Crystallographic Data for  $3\mathbf{a} \cdot (\text{H}_2\text{O})_{0.5}$ .

formula	$\text{C}_{33}\text{H}_{29}\text{O}_{2.5}\text{P}_2$
formula weigh	527.54
cryst size ( $\text{mm}^3$ )	0.60 x 0.40 x 0.80
cryst system	monoclinic
space group	$\text{C}2/\text{c}$ (#15)
cryst color	colorless
$a$ (Å)	32.114(2)
$b$ (Å)	8.7757(3)
$c$ (Å)	22.7056(7)
$\beta$ (°)	118.400(1)
$V$ (Å <sup>3</sup> )	5628.9(4)
$Z$	8
$d_{\text{calc}}$ ( $\text{g cm}^{-3}$ )	1.245
$F(000)$	2216.00
$\mu_{\text{calc}}$ ( $\text{cm}^{-1}$ )	1.84
no. of unique data	23114
no. of data used	18863
no. of params refined	371
$R^a$ (all reflections)	0.076
$R_w^b$ (all reflections)	0.183
goodness of fit indicator	1.439

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|.$$

$$^b R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}.$$



**Figure. S1** Crystal structure of **3a·(H<sub>2</sub>O)<sub>0.5</sub>**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected distances (Å): P(1)–O(1), 1.4807; C(1)–P(1), 1.8369; C(1)–C(2), 1.5376; C(2)–C(3), 1.3299; C(2)–P(2), 1.8094; P(2)–O(2), 1.4839.

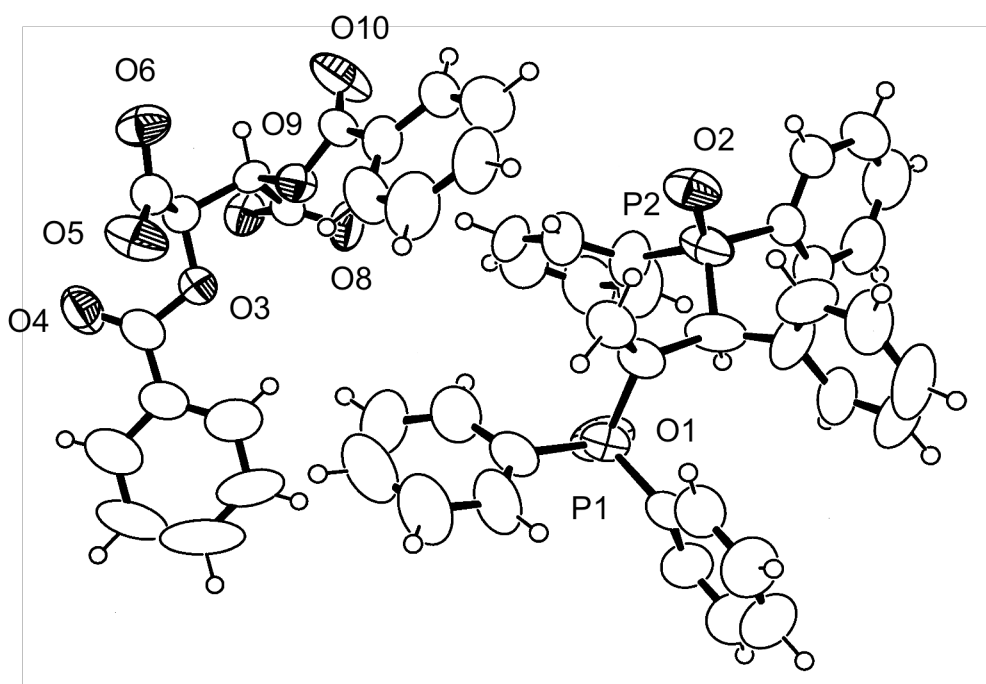
**X-ray Crystallographic Studies of (S)-3a·(+)-DBTA·(acetone).** Colorless crystals of **(S)-3a·(+)-DBTA·(acetone)** suitable for X-ray analysis were obtained by recrystallization from acetone–*n*-hexane. A single crystal was sealed in a Pyrex glass capillary under N<sub>2</sub> atmosphere and used for data collection. All measurements were made on a Rigaku RAXIS imaging plate area detector with graphite monochromated Mo-K $\alpha$  radiation. Details of crystal and data collection parameters are summarized in Table S2. The positions of non-hydrogen atoms were determined by direct methods (SIR97) and subsequent Fourier syntheses (DIRDIF99). An ORTEP drawing of **(S)-3a·(+)-DBTA·(acetone)** is shown in Figure S2.

**Table S2.** Crystallographic Data for **3a<sup>+</sup>(+)-DBTA<sup>+</sup>·(Me<sub>2</sub>CO)**.

formula	C <sub>54</sub> H <sub>48</sub> O <sub>11</sub> P <sub>2</sub>
formula weigh	934.91
cryst size (mm <sup>3</sup> )	0.80 x 0.80 x 0.10
cryst system	triclinic
space group	P <sub>1</sub> (#1)
cryst color	colorless
<i>a</i> (Å)	10.9283(6)
<i>b</i> (Å)	11.1950(5)
<i>c</i> (Å)	11.5448(9)
$\alpha$ (°)	72.803(1)
$\beta$ (°)	78.893(2)
$\gamma$ (°)	67.113(2)
<i>V</i> (Å <sup>3</sup> )	1238.2(1)
<i>Z</i>	1
<i>d</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.254
<i>F</i> (000)	490.00
$\mu$ <sub>calc</sub> (cm <sup>-1</sup> )	1.48
no. of unique data	5599
no. of data used	3474
no. of params refined	648
<i>R</i> <sup>a</sup>	0.074
<i>R</i> <sub>w</sub> <sup>b</sup>	0.067
goodness of fit indicator	1.52

<sup>a</sup>  $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ .

<sup>b</sup>  $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w F_o^2]^{1/2}$ .



**Figure. S2** Crystal structure of **3a<sup>+</sup>(+)-DBTA<sup>+</sup>·(Me<sub>2</sub>CO)**. Thermal ellipsoids are drawn at the 50% probability level. Acetone is omitted for clarity.

## Reference

(S1) Savage, M. P.; Trippett, S. *J. Chem. Soc. (C)* **1968**, 591.



