

Supporting Information (OL048347K)

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

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List of the Contents of the Supporting Information

1. Ruthenium-Catalyzed Double Phosphinylation of Propargylic Alcohols	Page S2
2. X-ray Crystallographic Studies of 3a·(H₂O)_{0.5}	Page S5
3. X-ray Crystallographic Studies of (S)-3a·(+)-DBTA·(acetone)	Page S6
4. ¹ H NMR Charts of 3c, 3e, 3f , and 3i	Page S9

General Method. ^1H NMR (400, 300, and 270 MHz), ^{13}C NMR (100, 75, and 67.8 MHz), and ^{31}P NMR (161.7 MHz) spectra were recorded using 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 NH_4BF_4 (6 mg, 0.06 mmol) under 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 (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**):**^{S1} IR (KBr, cm^{-1}) 1180 (P=O). ^1H NMR δ 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}C NMR δ 44.1 (d, $J = 73\text{ Hz}$), 126.7, 127.6, 127.7, 128.0, 128.2, 128.3, 128.4, 129.9, 123.0, 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}P NMR δ 29.9 (d, $J = 31\text{ Hz}$), 30.2 (d, $J = 31\text{ Hz}$). Anal. Calcd. for $\text{C}_{33}\text{H}_{29}\text{O}_{2.5}\text{P}_2$: 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, cm^{-1}) 1182 (P=O). ^1H NMR δ 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).

³¹P NMR δ 29.6 (d, J = 24 Hz), 30.1 (d, J = 24 Hz). ¹³C NMR δ 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 C₃₃H₂₈O_{2.5}FP₂: C, 72.66.13; H, 5.17. Found: C, 72.37; H, 5.13. HRMS Calcd for C₃₃H₂₈O₂FP₂ [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, cm⁻¹) 1186 (P=O). ¹H NMR δ 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). ³¹P NMR δ 29.5 (d, J = 24 Hz), 29.7 (d, J = 24 Hz). ¹³C NMR δ 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 C₃₃H₂₇O₂ClP₂: 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, cm⁻¹) 1182 (P=O). ¹H NMR δ 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). ¹³C NMR δ 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). ³¹P NMR δ 29.8 (brs). HRMS Calcd for C₃₃H₂₈O₂BrP₂ [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, cm⁻¹) 1183 (P=O). ¹H NMR δ 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). ¹³C NMR δ 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). ³¹P NMR δ 29.8 (d, J = 28 Hz), 30.1 (d, J = 28 Hz). Anal. Calcd. for C₃₄H₃₀O₃P₂: 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, cm⁻¹) 1176 (P=O). ¹H NMR δ 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). ¹³C NMR δ 20.9, 43.8 (d, J = 74 Hz), 127.6-127.8 (m), 128.1-128.3 (m), 128.4, 12.99, 130.0-132.2 (m), 133.6, 136.2, 140.3 (d, J

= 88 Hz). ^{31}P NMR δ 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, cm^{-1}) 1176 (P=O). ^1H NMR δ 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}C NMR δ 21.0, 44.0 (d, J = 72 Hz), 127.0 (d, J = 5 Hz), 127.3, 127.4-127.8 (m), 1281-128.5 (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}P NMR δ 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, cm^{-1}) 1179 (P=O). ^1H NMR δ 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}C NMR δ 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}P NMR δ 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):^{S1} Yield 72%. White solid, mp 126.5-128.0 °C. IR (KBr, cm^{-1}) 1193 (P=O), 1929, 1953 (C=C=C). ^1H NMR δ 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}C NMR δ 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}P NMR δ 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 $\mathbf{3a}\cdot(\text{H}_2\text{O})_{0.5}$. Colorless crystals of $\mathbf{3a}\cdot(\text{H}_2\text{O})_{0.5}$ suitable for X-ray analysis were obtained by recrystallization from CH_2Cl_2-n -hexane. A single crystal was sealed in a Pyrex glass capillary under N_2 atmosphere and used for data collection. All measurements were made on a Rigaku RAXIS imaging plate area detector with graphite monochromated $\text{Mo-K}\alpha$ 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 **3a** is shown in Figure S1.

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

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

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

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

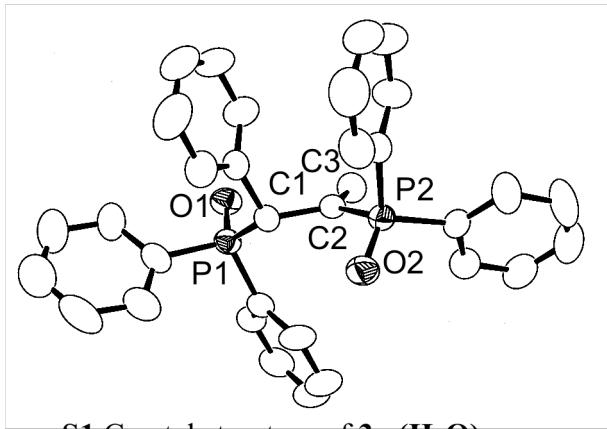


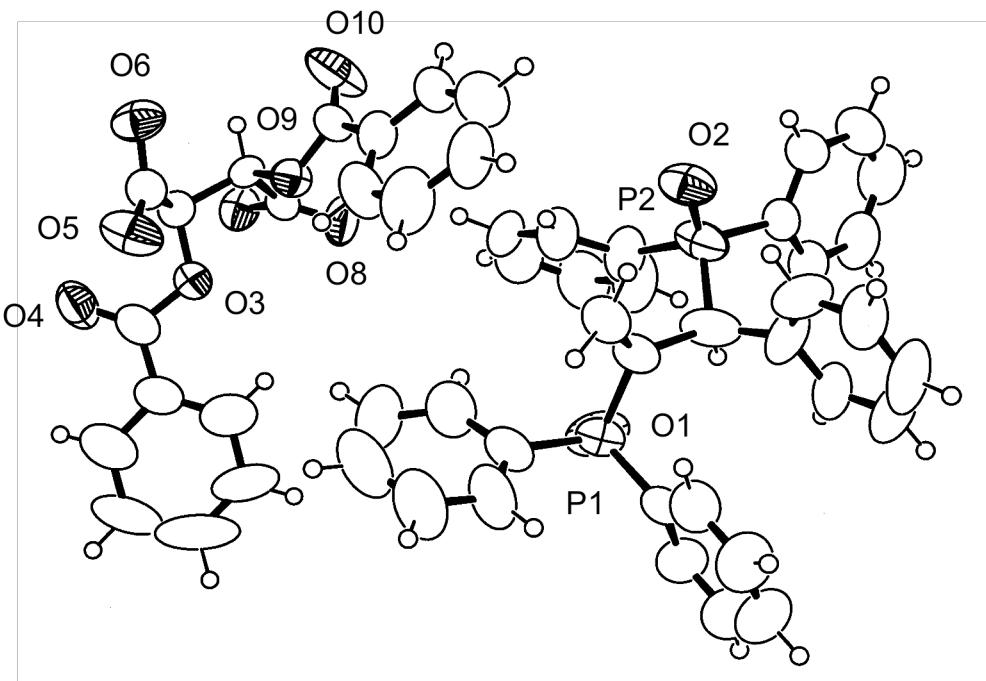
Figure. S1 Crystal structure of **3a·(H₂O)_{0.5}**.

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 N₂ atmosphere and used for data collection. All measurements were made on a Rigaku RAXIS imaging plate area detector with graphite monochromated Mo-K α 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.

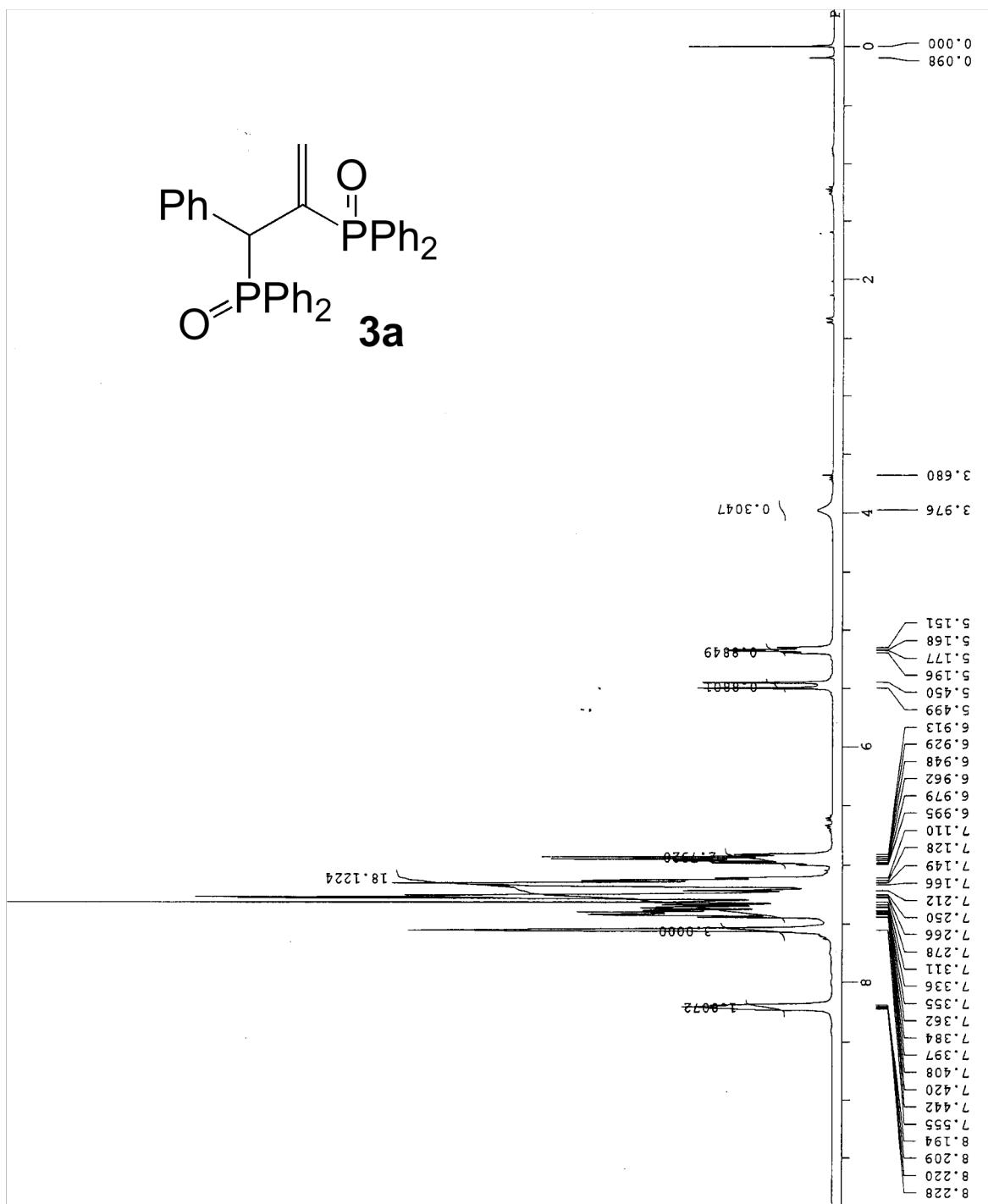
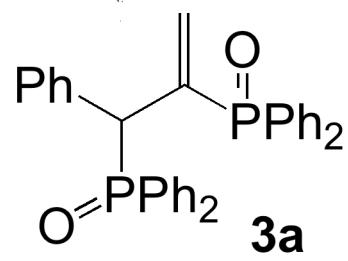
Table S2. Crystallographic Data for **3a**·(+)-DBTA·(Me₂CO).

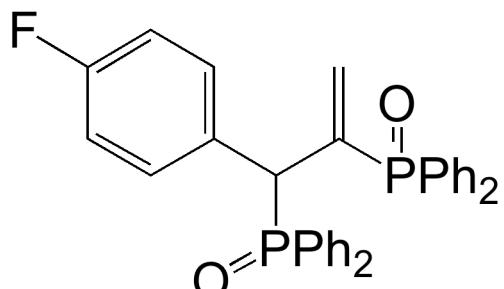
formula	C ₅₄ H ₄₈ O ₁₁ P ₂
formula weigh	934.91
cryst size (mm ³)	0.80 x 0.80 x 0.10
cryst system	triclinic
space group	P ₁ (#1)
cryst color	colorless
<i>a</i> (Å)	10.9283(6)
<i>b</i> (Å)	11.1950(5)
<i>c</i> (Å)	11.5448(9)
α (°)	72.803(1)
β (°)	78.893(2)
γ (°)	67.113(2)
<i>V</i> (Å ³)	1238.2(1)
<i>Z</i>	1
<i>d</i> _{calc} (g cm ⁻¹)	1.254
<i>F</i> (000)	490.00
μ _{calc} (cm ⁻¹)	1.48
no. of unique data	5599
no. of data used	3474
no. of params refined	648
<i>R</i> ^a	0.074
<i>R</i> _w ^b	0.067
goodness of fit indicator	1.52

^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. S2** Crystal structure of **3a**·(+)-DBTA·(Me₂CO). 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.





3b

