Supporting Information for

Nickel-catalyzed Addition of P(O)–H Bonds to Propargyl Alcohols: One-Pot Generation of Phosphinoyl 1,3-Butadienes

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General. All reactions were carried out under argon atmosphere. Solvents were dried and distilled by the usual manner. ^1H (500 MHz) and ^{31}P (202 MHz) NMR spectra were recorded on a JEOL JA-500 spectrometer using CDCl_3 as the solvent (or a solvent otherwise noted). Chemical shift values for ^1H and ^{31}P were referred to internal TMS and external 85% H_3PO_4 , respectively. Preparative GPC was carried out on a Japan Analytical Industry LC-908 instrument (1H and 2H columns) with CHCl_3 as an eluent. HRMS and elemental analysis were performed by the analytical center of AIST.

Preparation of 1a-b. To a solution of $\text{Ph}_2\text{P(O)H}$ (101 mg, 0.5 mmol) and $\text{Ni}(\text{PPhMe}_2)_4$ (9 mg, 0.015 mmol) in EtOH (1 mL), 2-methyl-3-butyn-2-ol (42 mg, 0.5 mmol) was added. After stirring for 16 h at room temperature, solvent was removed under reduced pressure. The residue was purified by GPC to give 142 mg (99%) of **1a-b** (**1a:1b** = 97:3).

Spectra and analytical data for **1a**

1a: ^1H NMR δ 1.34 (6H, s), 6.53 (1H, dd, $J = 24.8, 16.9$ Hz), 6.84 (1H, td, $J = 18.4, 6.1$ Hz), 7.28–7.43 (4H, m), 7.49 (2H, m), 7.67 (4H, dd, $J = 11.9, 7.9$ Hz); ^1H NMR ($\text{DMSO}-d_6$) δ 1.23 (6H, s), 5.03 (1H, s, OH), 6.61 (1H, dd, $J = 26.5, 17.1$ Hz), 6.75 (1H, dd, $J = 19.9, 16.9$ Hz), 7.50–7.58 (6H, m), 7.67 (4H, dd, $J = 11.7, 6.9$ Hz); ^{31}P NMR δ 24.0. Anal. Calcd for $\text{C}_{17}\text{H}_{19}\text{O}_2\text{P}$: C, 71.32; H, 6.69. Found: C, 71.10; H, 6.61.

Dehydration of 1a-b with acid. A solution of a mixture of **1a** and **1b** (**1a:1b** = **97:3**) (100 mg) with a drop of H_2SO_4 in THF (0.5 mL) was heated at reflux for 20 min. After cooling to room temperature, the mixture was neutralized (aqueous NaHCO_3), extracted (Et_2O), dried (MgSO_4), and evaporated to give **2a** and **2b** in 88% yield (**2a:2b** = **96:4**).

2a: ^1H NMR δ 1.93 (3H, s), 5.29 (1H, s), 5.33 (1H, s), 6.25 (1H, dd, $J = 21.9, 17.2$ Hz), 7.14 (1H, dd, $J = 19.5, 17.2$ Hz); ^{31}P NMR δ 24.6. HRMS Calcd for $\text{C}_{17}\text{H}_{17}\text{OP}$ (M^+): 268.1017. Found: 268.1010.

2b: ^1H NMR δ 1.95 (3H, s), 5.18 (1H, s), 5.41 (1H, d, $J = 20.7$ Hz), 5.55 (1H, s), 6.06 (1H, d, $J = 42.0$ Hz); ^{31}P NMR δ 32.0. HRMS Calcd for $\text{C}_{17}\text{H}_{17}\text{OP}$ (M^+): 268.1017. Found: 268.1012.

General procedure nickel-catalyzed addition of P(O)–H bond to propargyl alcohols forming phosphinoyl 1,3-Butadienes. Propargyl alcohol (1.0 mmol) was added to a mixture of $\text{Z}_2\text{P(O)H}$ (1.0 mmol, $\text{Z}_2 = \text{Ph}_2, \text{Ph(OEt)}, \text{OMe}_2$), $\text{Ni(PPhMe}_2)_4$ (0.05 mmol), and $\text{Ph}_2\text{P(O)OH}$ (0.1 mmol) in THF (1.0 mL). After stirring for 16 h at room temperature, the mixture was evaporated and subjected to NMR analysis to determine the yields and ratios of the products. Isolation of the adducts was performed by using a preparative GPC. Regio isomers were separated by PTLC (silica gel, $\text{CHCl}_3/\text{Et}_2\text{O}$).

^1H NMR δ 1.95 (2H, quint., $J = 7.6$ Hz), 2.48 (4H, br t, $J = 7.6$ Hz), 6.06 (1H, s), 6.08 (1H, dd, $J = 22.6, 17.1$ Hz), 7.26 (1H, t, $J = 18.2$ Hz), 7.45 (4H, td, $J = 7.7, 2.8$ Hz), 7.51 (2H, td, $J = 7.7, 1.5$ Hz), 7.70 (4H, dd, $J = 11.9, 7.7$ Hz); ^{31}P NMR δ 24.8. HRMS Calcd for $\text{C}_{19}\text{H}_{19}\text{OP}$ (M^+): 294.1174. Found: 294.1163.

^1H NMR δ 1.85 (2H, quint., $J = 7.6$ Hz), 2.40 (2H, br s), 2.56 (2H, br t, $J = 7.3$ Hz), 5.27 (1H, d, $J = 20.8$ Hz), 5.86 (1H, d, $J = 42.7$ Hz), 6.24 (1H, s), 7.46 (4H, td, $J = 7.7, 2.5$ Hz), 7.53 (2H, t, $J = 7.7$ Hz), 7.69 (4H, dd, $J = 11.8, 7.7$ Hz); ^{31}P NMR δ 31.7. HRMS Calcd for $\text{C}_{19}\text{H}_{19}\text{OP}$ (M^+): 294.1174. Found: 294.1195

^1H NMR δ 1.59–1.63 (2H, m), 1.66–1.72 (2H, m), 2.18–2.20 (4H, br m), 6.08 (1H, s), 6.10 (1H, dd, $J = 22.2, 17.0$ Hz), 7.04 (1H, dd, $J = 19.7, 17.2$ Hz), 7.42–7.50 (4H, m), 7.51–7.53 (2H, m), 7.69–7.73 (4H m); ^{31}P NMR δ 25.3. HRMS Calcd for $\text{C}_{20}\text{H}_{21}\text{OP}$ (M^+): 308.1330. Found: 308.1330.

^1H NMR δ 1.48–1.51 (2H, br m), 1.61–1.64 (2H, br m), 2.01 (2H, br s), 2.18 (2H, br s), 5.23 (1H, d, $J = 21.3$ Hz), 5.94 (1H, d, $J = 43.3$ Hz), 6.39 (1H, s), 7.41–7.45 (4H, m), 7.48–7.51 (2H, m), 7.67–7.71 (4H, m); ^{31}P NMR δ 32.7.

^1H NMR δ 5.37 (1H, s), 5.68 (1H, s), 5.84 (1H, d, $J = 19.8$ Hz), 5.99 (1H, d, $J = 40.2$ Hz), 7.24 (5H, br s), 7.43 (4H, td, $J = 7.4, 2.9$ Hz), 7.50 (2H, td, $J = 7.4, 1.4$ Hz), 7.76 (4H, dd, $J = 11.9, 7.4$ Hz); ^{31}P NMR δ 29.6. HRMS Calcd for $\text{C}_{22}\text{H}_{19}\text{OP}$: 330.1174. Found: 330.1101

^1H NMR δ 2.31 (3H, s), 5.35 (1H, s), 5.62 (1H, s), 5.84 (1H, d, $J = 20.0$ Hz), 6.00 (1H, d, $J = 40.9$ Hz), 7.05 (2H, d, $J = 8.0$ Hz), 7.12 (2H, d, $J = 8.0$ Hz), 7.43 (4H, td, $J = 7.5, 3.2$ Hz), 7.50 (2H, td, $J = 7.5, 1.3$ Hz), 7.76 (4H, ddd, $J = 11.6, 7.5, 1.3$ Hz); ^{31}P NMR δ 29.6. HRMS Calcd for $\text{C}_{23}\text{H}_{21}\text{OP}$ (M^+): 344.1330. Found: 344.1332.

^1H NMR δ 3.78 (3H, s), 5.32 (1H, s), 5.54 (1H, d, $J = 1.5$ Hz), 5.88 (1H, d, $J = 19.8$ Hz), 6.03 (1H, dd, $J = 40.0, 1.1$ Hz), 6.77 (1H, d, $J = 8.8$ Hz), 7.15 (1H, d, $J = 8.8$ Hz), 7.43 (4H, dt, $J = 7.3, 3.0$ Hz), 7.50 (2H, dt, $J = 7.4, 1.5$ Hz), 7.73–7.77 (4H, m); ^{31}P NMR δ 29.2. HRMS Calcd for $\text{C}_{23}\text{H}_{21}\text{O}_2\text{P}$ (M^+): 360.1279. Found: 360.1277.

^1H NMR δ 2.93 (6H, s), 5.29 (1H, s), 5.42 (1H, s), 5.92 (1H, d, $J = 19.7$ Hz), 6.07 (1H, d, $J = 40.9$ Hz), 6.58 (2H, d, $J = 8.8$ Hz), 7.11 (2H, d, $J = 8.8$ Hz), 7.38–7.50 (6H, m), 7.76 (4H, dd, $J = 11.6, 7.5$ Hz); ^{31}P NMR δ 29.2. HRMS Calcd for $\text{C}_{24}\text{H}_{24}\text{NOP}$ (M^+): 373.1596. Found: 373.1597.

^1H NMR δ 1.88 (3H, s), 3.75 (6H, d, $J = 11.0$ Hz), 5.34 (1H, s), 5.36 (1H, s), 5.64 (1H, td, $J = 18.0, 1.2$ Hz), 7.19 (1H, ddd, $J = 22.1, 17.2, 1.4$ Hz); ^{31}P NMR δ 22.7. HRMS Calcd for $\text{C}_7\text{H}_{13}\text{O}_3\text{P}$ (M^+): 176.0602. Found: 176.0598.

^1H NMR δ 1.95 (3H, s), 3.74 (6H, d, $J = 18.5$ Hz), 5.20 (1H, s), 5.48 (1H, s), 6.03 (1H, d, $J = 46.5$ Hz), 6.21 (1H, d, $J = 22.2$ Hz); ^{31}P NMR δ 20.9. HRMS Calcd for $\text{C}_7\text{H}_{13}\text{O}_3\text{P}$ (M^+): 176.0602. Found: 176.0596.

^1H NMR δ 1.34 (3H, t, $J = 7.0$), 1.86 (3H, s), 3.95–4.14 (2H, m), 5.30 (1H, s), 5.31 (1H, s), 5.91 (1H, dd, $J = 20.4, 17.4$ Hz), 7.16 (1H, dd, $J = 20.0, 17.4$ Hz), 7.48–7.49 (2H, m), 7.55 (1H, t, $J = 7.3$ Hz), 7.81 (2H, dd, $J = 11.9, 7.6$ Hz); ^{31}P NMR δ 20.9. HRMS Calcd for $\text{C}_{13}\text{H}_{17}\text{O}_2\text{P}$: 236.0966. Found: 236.0989.

^1H NMR δ 1.95 (3H, s), 3.74 (6H, d, $J = 18.5$ Hz), 5.20 (1H, s), 5.48 (1H, s), 6.03 (1H, d, $J = 46.5$ Hz), 6.21 (1H, d, $J = 22.2$ Hz); ^{31}P NMR δ 31.7. HRMS Calcd for $\text{C}_{13}\text{H}_{17}\text{O}_2\text{P}$: 236.0966. Found: 236.0961.

PPM

0.000

1.954

3.2350

5.177

5.390

5.432

5.45

6.013

6.097

7.26

7.261

7.461

7.476

7.515

7.529

7.541

7.688

7.705

7.711

7.726

1.0412

1.0485

1.0790

1.0193

1.8390

3.6784

4.0596