Palladium(0)-Catalyzed Highly Regio- and Stereo-selective Addition of Organoboronic Acids with 1,2-Allenylphosphonates Forming Tri- or Tetrasubstituted 1(*E*)-Alkenylphosphonates

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The following starting materials were prepared according to Typical Procedure I in the text.

(1) **Diethyl (propa-1,2-dienyl)phosphonate (1b):**¹ The reaction of prop-2-yn-1-ol (1.401 g, 25 mmol), Et₃N (7.0 mL, 50 mmol), and P(OEt)₂Cl (5.903 g, 38 mmol) in THF (250 mL) afforded 2.261 g (51%) of **1b**: liquid; ¹H NMR (300 MHz, CDCl₃) δ 5.20 (t, *J* = 6.6 Hz, 1 H), 4.91 (dd, *J* = 6.6, 13.5 Hz, 2 H), 4.06-3.93 (m, 4 H), 1.21 (t, *J* = 6.6 Hz, 6 H); ¹³C NMR (CDCl₃, 75.4 MHz): δ 214.4, 79.0 (d, *J*_{PC} = 198.2 Hz), 75.7 (d, *J*_{PC} = 16.3 Hz), 62.1 (d, *J*_{PC} = 5.5 Hz), 15.9 (d, *J*_{PC} = 7.1 Hz); ³¹P NMR (121.5 MHz, CDCl₃) δ 16.3; MS (*m/z*) 177 (13.85), 176 (M⁺, 13.87), 81 (100); IR (neat) 1959, 1944, 1272, 1024 cm⁻¹.

(2) **Diethyl (buta-1,2-dien-3-yl)phosphonate (1c):**¹ The reaction of but-2-yn-1-ol (2.006 g, 29 mmol), Et₃N (6.0 mL, 43 mmol), and P(OEt)₂Cl (7.245 g, 46 mmol) in THF (150 mL) afforded 3.615 g (66%) of **1c**: liquid; ¹H NMR (300 MHz, CDCl₃) δ 4.69 (dq, *J* = 3.0, 13.5 Hz, 2 H), 3.94-3.81 (m, 4 H), 1.62 (dt, *J* = 3.0, 14.1 Hz, 3 H), 1.10 (t, *J* = 7.2 Hz, 6 H); ¹³C NMR (CDCl₃, 75.4 MHz): δ 211.5 (d, *J*_{PC} = 6.9 Hz), 87.7 (d, *J*_{PC} = 189.4 Hz), 75.1 (d, *J*_{PC} = 15.2 Hz), 61.8 (d, *J*_{PC} = 5.9 Hz), 15.7 (d, *J*_{PC} = 6.0 Hz), 14.2 (d, *J*_{PC} = 5.4 Hz); ³¹P NMR (121.5 MHz, CDCl₃) δ 19.3; MS (*m/z*) 190 (M⁺, 24.71), 44 (100); IR (neat) 1946, 1258, 1021 cm⁻¹.

(3) **Diethyl (deca-1,2-dien-3-yl)phosphonate (1d):** The reaction of dec-2-yn-1-ol (0.761 g, 4.9 mmol), Et₃N (0.8 mL, 5.8 mmol), and P(OEt)₂Cl (1.047 g, 6.7 mmol) in THF (30 mL) afforded 0.928 g (69%) of **1d**: liquid; ¹H NMR (300 MHz, CDCl₃) δ 4.76 (dt, *J* = 3.3, 13.5 Hz, 2 H), 3.95-3.83 (m, 4 H), 1.98-1.87 (m, 2 H), 1.36-1.22 (m,

2 H), 1.17-1.01 (m, 14 H), 0.66 (t, $J = 6.6$ Hz, 3 H); ^{13}C NMR (CDCl_3 , 75.4 MHz): δ 211.0 (d, $J_{\text{PC}} = 6.3$ Hz), 93.1 (d, $J_{\text{PC}} = 186.9$ Hz), 76.3 (d, $J_{\text{PC}} = 15.4$ Hz), 61.7 (d, $J_{\text{PC}} = 6.1$ Hz), 31.3, 28.5 (d, $J_{\text{PC}} = 2.9$ Hz), 27.5, 27.4 (d, $J_{\text{PC}} = 1.7$ Hz), 22.1, 15.8 (d, $J_{\text{PC}} = 5.9$ Hz), 13.6; ^{31}P NMR (121.5 MHz, CDCl_3) δ 19.2; MS (m/z) 274 (M^+ , 1.23), 41 (100); IR (neat) 1941, 1257, 1026 cm^{-1} ; HRMS m/z (ESI) calcd for $\text{C}_{14}\text{H}_{27}\text{O}_3\text{PNa}^+$ ($\text{M}^+ + \text{Na}$): 297.1590; Found: 297.1590.

(4) **Diethyl (1-phenylpropa-1,2-dienyl)phosphonate (1e):**² The reaction of 3-phenylprop-2-yn-1-ol (2.055 g, 16 mmol), Et_3N (3.0 mL, 22 mmol), and $\text{P}(\text{OEt})_2\text{Cl}$ (3.802 g, 24 mmol) in THF (140 mL) afforded 2.165 g (54%) of **1e**: liquid; ^1H NMR (300 MHz, CDCl_3) δ 7.39 (d, $J = 7.8$ Hz, 2 H), 7.19-7.02 (m, 3 H), 5.13 (d, $J = 12.9$ Hz, 2 H), 4.06-3.89 (m, 4 H), 1.11 (t, $J = 6.9$ Hz, 6 H); ^{13}C NMR (CDCl_3 , 75.4 MHz): δ 213.3 (d, $J_{\text{PC}} = 4.0$ Hz), 130.8 (d, $J_{\text{PC}} = 7.0$ Hz), 128.1, 127.2 (d, $J_{\text{PC}} = 1.1$ Hz), 127.1 (d, $J_{\text{PC}} = 5.9$ Hz), 96.5 (d, $J_{\text{PC}} = 188.8$ Hz), 77.9 (d, $J_{\text{PC}} = 14.6$ Hz), 62.3 (d, $J_{\text{PC}} = 5.7$ Hz), 15.8 (d, $J_{\text{PC}} = 7.0$ Hz); ^{31}P NMR (121.5 MHz, CDCl_3) δ 16.4; MS (m/z) 252 (M^+ , 68.65), 115 (100); IR (neat) 1948, 1929, 1597, 1494, 1478, 1448, 1248, 1023 cm^{-1} .

(5) **Diethyl (hepta-1,2-dienyl)phosphonate (1f):** The reaction of hept-1-yn-3-ol (2.005 g, 18 mmol), Et_3N (6 mL, 43 mmol), and $\text{P}(\text{OEt})_2\text{Cl}$ (5.544 g, 35 mmol) in THF (150 mL) afforded 2.526 g (60%) of **1f**: liquid; ^1H NMR (300 MHz, CDCl_3) δ 5.47-5.36 (m, 1 H), 5.30-5.24 (m, 1 H), 4.16-4.03 (m, 4 H), 2.14-2.03 (m, 2 H), 1.47-1.29 (m, 10 H), 0.89 (t, $J = 6.6$ Hz, 3 H); ^{13}C NMR (CDCl_3 , 75.4 MHz): δ 210.3 (d, $J_{\text{PC}} = 2.5$ Hz), 90.4 (d, $J_{\text{PC}} = 16.1$ Hz), 78.7 (d, $J_{\text{PC}} = 198.5$ Hz), 60.5 (d, $J_{\text{PC}} = 6.0$

Hz), 29.5 (d, $J_{\text{PC}} = 3.0$ Hz), 25.5 (d, $J_{\text{PC}} = 6.0$ Hz), 20.5, 14.8 (d, $J_{\text{PC}} = 6.5$ Hz), 12.2; ^{31}P NMR (121.5 MHz, CDCl_3) δ 17.1; IR (neat) 1956, 1259, 1027 cm^{-1} ; MS (m/z) 233 ($\text{M}^+ + 1$, 68.28), 81 (100); IR (neat) 1955, 1259, 1027 cm^{-1} ; HRMS m/z (EI) calcd for $\text{C}_{11}\text{H}_{21}\text{O}_3\text{P}^+$ (M^+): 232.1228; Found: 232.1236.

The following compounds were prepared according to Typical Procedure II in the text.

(1) **Diethyl (2-(*p*-methylphenyl)hept-2(*E*)-en-3-yl)phosphonate (*E*-3ab):** The reaction of **1a** (59 mg, 0.25 mmol), **2b** (69 mg, 0.5 mmol), $\text{Pd}(\text{PPh}_3)_4$ (29 mg, 0.025 mmol), and AcOH (14 μL , 0.25 mmol) in THF (3 mL) afforded 73 mg (90%) of ***E*-3ab**: liquid; ^1H NMR (300 MHz, CDCl_3) δ 7.11 (d, $J = 7.8$ Hz, 2 H), 6.94 (d, $J = 7.8$ Hz, 2 H), 4.15-4.05 (m, 4 H), 2.30 (s, 3 H), 2.29 (d, $J = 3.6$ Hz, 3 H), 2.09-1.97 (m, 2 H), 1.36-1.29 (m, 8 H), 1.12-1.00 (m, 2 H), 0.69 (t, $J = 7.2$ Hz, 3 H); ^{13}C NMR (CDCl_3 , 75.4 MHz): δ 153.7 (d, $J_{\text{PC}} = 12.7$ Hz), 140.6 (d, $J_{\text{PC}} = 22.5$ Hz), 136.4, 128.8, 126.4 (d, $J_{\text{PC}} = 171.3$ Hz), 126.4 (d, $J_{\text{PC}} = 1.3$ Hz), 61.1 (d, $J_{\text{PC}} = 6.0$ Hz), 32.2 (d, $J_{\text{PC}} = 1.1$ Hz), 31.5 (d, $J_{\text{PC}} = 10.9$ Hz), 24.7 (d, $J_{\text{PC}} = 7.4$ Hz), 22.4, 21.0, 16.3 (d, $J_{\text{PC}} = 6.2$ Hz), 13.5; ^{31}P NMR (121.5 MHz, CDCl_3) δ 22.6; MS (m/z) 324 (M^+ , 53.62), 143 (100); IR (neat) 1616, 1510, 1444, 1243, 1054 cm^{-1} ; HRMS m/z (ESI) calcd for $\text{C}_{18}\text{H}_{29}\text{O}_3\text{PNa}^+$ ($\text{M}^+ + \text{Na}$): 347.1747; Found: 347.1747.

(2) **Diethyl (2-(*p*-methylphenyl)propa-1(*E*)-enyl)phosphonate (*E*-3bb):** The reaction of **1b** (44 mg, 0.25 mmol), **2b** (68 mg, 0.5 mmol), $\text{Pd}(\text{PPh}_3)_4$ (29 mg, 0.025 mmol), and AcOH (14 μL , 0.25 mmol) in THF (3 mL) afforded 58 mg (87%) of ***E*-3bb**: liquid; ^1H NMR (300 MHz, CDCl_3) δ 7.35 (d, $J = 7.8$ Hz, 2 H), 7.14 (d, $J =$

7.8 Hz, 2 H), 5.86 (d, $J = 16.5$ Hz, 1 H), 4.16-4.02 (m, 4 H), 2.45 (d, $J = 2.7$ Hz, 3 H), 2.33 (s, 3 H), 1.32 (t, $J = 7.2$ Hz, 6 H); ^{13}C NMR (CDCl_3 , 75.4 MHz): δ 157.9 (d, $J_{\text{PC}} = 8.1$ Hz), 139.2, 138.6 (d, $J_{\text{PC}} = 23.7$ Hz), 129.0, 125.7, 112.2 (d, $J_{\text{PC}} = 190.5$ Hz), 61.3 (d, $J_{\text{PC}} = 6.3$ Hz), 21.0, 19.0 (d, $J_{\text{PC}} = 7.2$ Hz), 16.3 (d, $J_{\text{PC}} = 7.2$ Hz); ^{31}P NMR (121.5 MHz, CDCl_3) δ 19.7; MS (m/z) 268 (M^+ , 47.78), 159 (100); IR (neat) 1607, 1566, 1513, 1443, 1248, 1027 cm^{-1} ; HRMS m/z (ESI) calcd for $\text{C}_{14}\text{H}_{21}\text{O}_3\text{PNa}^+$ ($\text{M}^+ + \text{Na}$): 291.1121; Found: 291.1123.

(3) **Diethyl (3-(*p*-methylphenyl)buta-2(*E*)-enyl)phosphonate (*E*-3cb):** The reaction of **1c** (48 mg, 0.25 mmol), **2b** (68 mg, 0.5 mmol), $\text{Pd}(\text{PPh}_3)_4$ (29 mg, 0.025 mmol), and AcOH (14 μL , 0.25 mmol) in THF (3 mL) afforded 60 mg (85%) of ***E*-3cb**: liquid; ^1H NMR (300 MHz, CDCl_3) δ 7.13 (d, $J = 8.0$ Hz, 2 H), 6.98 (d, $J = 8.0$ Hz, 2 H), 4.17-4.04 (m, 4 H), 2.36 (d, $J = 1.2$ Hz, 3 H), 2.32 (s, 3 H), 1.70 (d, $J = 13.8$, 3 H), 1.33 (t, $J = 6.9$ Hz, 6 H); ^{13}C NMR (CDCl_3 , 75.4 MHz): δ 153.6 (d, $J_{\text{PC}} = 13.3$ Hz), 140.5 (d, $J_{\text{PC}} = 22.4$ Hz), 136.7, 128.9, 126.7 (d, $J_{\text{PC}} = 1.4$ Hz), 120.3 (d, $J_{\text{PC}} = 173.4$ Hz), 61.2 (d, $J_{\text{PC}} = 5.1$ Hz), 23.9 (d, $J_{\text{PC}} = 7.1$ Hz), 21.0, 18.3 (d, $J_{\text{PC}} = 11.6$ Hz), 16.3 (d, $J_{\text{PC}} = 6.5$ Hz); ^{31}P NMR (121.5 MHz, CDCl_3) δ 22.4; MS (m/z) 282 (M^+ , 100); IR (neat) 1621, 1510, 1444, 1243, 1027 cm^{-1} ; HRMS m/z (ESI) calcd for $\text{C}_{15}\text{H}_{24}\text{O}_3\text{P}^+$ ($\text{M}^+ + \text{H}$): 283.1458; Found: 283.1459.

(4) **Diethyl (2-(*p*-methylphenyl)deca-2(*E*)-en-3-yl)phosphonate (*E*-3db):** The reaction of **1d** (69 mg, 0.25 mmol), **2b** (68 mg, 0.5 mmol), $\text{Pd}(\text{PPh}_3)_4$ (29 mg, 0.025 mmol), and AcOH (14 μL , 0.25 mmol) in THF (3 mL) afforded 83 mg (91%) of ***E*-3db**: liquid; ^1H NMR (300 MHz, CDCl_3) δ 7.12 (d, $J = 8.0$ Hz, 2 H), 6.96 (d, $J =$

8.0 Hz, 2 H), 4.18-4.04 (m, 4 H), 2.32 (s, 3 H), 2.30 (d, $J = 3.6$ Hz, 3 H), 2.09-1.97 (m, 2 H), 1.40-1.28 (m, 8 H), 1.19-1.06 (m, 8 H), 0.80 (t, $J = 6.9$ Hz, 3 H); ^{13}C NMR (CDCl_3 , 75.4 MHz): δ 153.8 (d, $J_{\text{PC}} = 12.7$ Hz), 140.6 (d, $J_{\text{PC}} = 22.5$ Hz), 136.5, 128.8, 126.44 (d, $J_{\text{PC}} = 171.4$ Hz), 126.40 (d, $J_{\text{PC}} = 1.1$ Hz), 61.1 (d, $J_{\text{PC}} = 5.6$ Hz), 31.8 (d, $J_{\text{PC}} = 11.2$ Hz), 31.5, 30.0 (d, $J_{\text{PC}} = 1.3$ Hz), 29.3, 28.6, 24.8 (d, $J_{\text{PC}} = 7.8$ Hz), 22.5, 21.0, 16.3 (d, $J_{\text{PC}} = 6.6$ Hz), 13.9; ^{31}P NMR (121.5 MHz, CDCl_3) δ 22.7; MS (m/z) 366 (M^+ , 19.65), 143 (100); IR (neat) 1616, 1510, 1457, 1444, 1240, 1027 cm^{-1} ; HRMS m/z (ESI) calcd for $\text{C}_{21}\text{H}_{36}\text{O}_3\text{P}^+$ ($\text{M}^+ + \text{H}$): 367.2397; Found: 367.2395.

(5) Diethyl (1-phenyl-2-(*p*-methylphenyl)propa-1(*E*)-enyl)phosphonate (*E*-3eb):

The reaction of **1e** (64 mg, 0.25 mmol), **2b** (70 mg, 0.5 mmol), $\text{Pd}(\text{PPh}_3)_4$ (30 mg, 0.025 mmol), and AcOH (14 μL , 0.25 mmol) in THF (3 mL) afforded 40 mg (47%) of ***E*-3eb**: liquid; ^1H NMR (300 MHz, CDCl_3) δ 7.14-6.96 (m, 5 H), 6.91-6.80 (m, 4 H), 4.08-3.91 (m, 4 H), 2.59 (d, $J = 3.3$ Hz, 3 H), 2.19 (s, 3 H), 1.20 (t, $J = 6.9$ Hz, 6 H); ^{13}C NMR (CDCl_3 , 75.4 MHz): δ 155.7 (d, $J_{\text{PC}} = 12.1$ Hz), 140.0 (d, $J_{\text{PC}} = 21.3$ Hz), 138.4 (d, $J_{\text{PC}} = 10.5$ Hz), 136.5, 130.6 (d, $J_{\text{PC}} = 4.4$ Hz), 128.5 (d, $J_{\text{PC}} = 178.5$ Hz), 128.3, 127.7 (d, $J_{\text{PC}} = 1.1$ Hz), 127.4 (d, $J_{\text{PC}} = 2.2$ Hz), 126.2 (d, $J_{\text{PC}} = 2.3$ Hz), 61.7 (d, $J_{\text{PC}} = 5.8$ Hz), 24.0 (d, $J_{\text{PC}} = 6.9$ Hz), 21.0, 16.1 (d, $J_{\text{PC}} = 6.7$ Hz); ^{31}P NMR (121.5 MHz, CDCl_3) δ 18.8; MS (m/z) 344 (M^+ , 100); IR (neat) 1602, 1511, 1490, 1442, 1240, 1024 cm^{-1} ; HRMS m/z (ESI) calcd for $\text{C}_{20}\text{H}_{26}\text{O}_3\text{P}^+$ ($\text{M}^+ + \text{H}$): 345.1614; Found: 345.1616.

(6) Diethyl (2-(*p*-methylphenyl)hepta-1(*E*)-enyl)phosphonate (*E*-3fb):³

The reaction of **1f** (56 mg, 0.25 mmol), **2b** (67 mg, 0.5 mmol), $\text{Pd}(\text{PPh}_3)_4$ (30 mg, 0.025

mmol), and AcOH (14 μ L, 0.25 mmol) in THF (3 mL) afforded 42 mg (52%) of **E-3fb**: liquid; ^1H NMR (300 MHz, CDCl_3) δ 7.30 (d, J = 8.1 Hz, 2 H), 7.15 (d, J = 8.1 Hz, 2 H), 5.72 (d, J = 17.4 Hz, 1 H), 4.16-4.05 (m, 4 H), 2.98-2.89 (m, 2 H), 2.35 (s, 3 H), 1.44-1.22 (m, 12 H), 0.82 (t, J = 6.9 Hz, 3 H); ^{13}C NMR (CDCl_3 , 75.4 MHz): δ 163.8 (d, J_{PC} = 8.4 Hz), 139.0, 138.0 (d, J_{PC} = 23.8 Hz), 129.2, 126.3, 112.5 (d, J_{PC} = 190.3 Hz), 61.5 (d, J_{PC} = 6.0 Hz), 32.5 (d, J_{PC} = 7.0 Hz), 31.8, 28.6 (d, J_{PC} = 2.4 Hz), 22.4, 21.1, 16.4 (d, J_{PC} = 6.4 Hz), 14.0; ^{31}P NMR (121.5 MHz, CDCl_3) δ 19.5; MS (m/z) 324 (M^+ , 6.07), 45 (100); IR (neat) 1605, 1565, 1511, 1456, 1247, 1028 cm^{-1} .

(7) **Diethyl (2-(*m*-methoxyphenyl)hept-2(*E*)-en-3-yl)phosphonate (E-3ac)**: The reaction of **1a** (58 mg, 0.25 mmol), **2c** (76 mg, 0.5 mmol), $\text{Pd}(\text{PPh}_3)_4$ (29 mg, 0.025 mmol), and AcOH (14 μ L, 0.25 mmol) in THF (3 mL) afforded 77 mg (91%) of **E-3ac**: liquid; ^1H NMR (300 MHz, CDCl_3) δ 7.20 (t, J = 7.8 Hz, 1 H), 6.77-6.73 (m, 1 H), 6.62 (d, J = 7.8 Hz, 1 H), 6.57 (s, 1 H), 4.13-4.04 (m, 4 H), 3.74 (s, 3 H), 2.28 (d, J = 3.3 Hz, 3 H), 2.07-1.95 (m, 2 H), 1.37-1.25 (m, 8 H), 1.12-0.99 (m, 2 H), 0.67 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (CDCl_3 , 75.4 MHz): δ 159.3, 153.4 (d, J_{PC} = 13.1 Hz), 144.9 (d, J_{PC} = 21.9 Hz), 129.3, 126.6 (d, J_{PC} = 171.2 Hz), 118.8 (d, J_{PC} = 1.5 Hz), 112.2, 112.1 (d, J_{PC} = 1.4 Hz), 61.1 (d, J_{PC} = 6.0 Hz), 55.0, 32.2 (d, J_{PC} = 1.2 Hz), 31.5 (d, J_{PC} = 10.5 Hz), 24.5 (d, J_{PC} = 7.5 Hz), 22.4, 16.2 (d, J_{PC} = 6.6 Hz), 13.5; ^{31}P NMR (121.5 MHz, CDCl_3) δ 22.3; MS (m/z) 340 (M^+ , 43.00), 159 (100); IR (neat) 1597, 1576, 1482, 1465, 1427, 1244, 1028 cm^{-1} ; HRMS m/z (ESI) calcd for $\text{C}_{18}\text{H}_{30}\text{O}_4\text{P}^+$ (M^+ +H): 341.1876; Found: 341.1878.

(8) **Diethyl (2-(*p*-methoxyphenyl)hept-2(*E*)-en-3-yl)phosphonate (E-3ad)**: The

reaction of **1a** (58 mg, 0.25 mmol), **2d** (77 mg, 0.5 mmol), Pd(PPh₃)₄ (29 mg, 0.025 mmol), and AcOH (14 μ L, 0.25 mmol) in THF (3 mL) afforded 75 mg (88%) of **E-3ad**: liquid; ¹H NMR (300 MHz, CDCl₃) δ 6.99 (d, J = 8.4 Hz, 2 H), 6.83 (d, J = 9.0 Hz, 2 H), 4.15-4.03 (m, 4 H), 3.76 (s, 3 H), 2.28 (d, J = 3.6 Hz, 3 H), 2.11-1.97 (m, 2 H), 1.36-1.28 (m, 8 H), 1.12-1.00 (m, 2 H), 0.69 (t, J = 7.2 Hz, 3 H); ¹³C NMR (CDCl₃, 75.4 MHz): δ 158.4, 153.4 (d, J_{PC} = 12.6 Hz), 135.8 (d, J_{PC} = 23.3 Hz), 127.8 (d, J_{PC} = 1.1 Hz), 126.6 (d, J_{PC} = 171.3 Hz), 113.5, 61.1 (d, J_{PC} = 5.6 Hz), 55.1, 32.3 (d, J_{PC} = 1.7 Hz), 31.6 (d, J_{PC} = 11.0 Hz), 24.9 (d, J_{PC} = 7.5 Hz), 22.5, 16.3 (d, J_{PC} = 6.1 Hz), 13.6; ³¹P NMR (121.5 MHz, CDCl₃) δ 22.7; MS (m/z) 340 (M⁺, 53.10), 159 (100); IR (neat) 1610, 1574, 1509, 1464, 1443, 1244, 1028 cm⁻¹; HRMS m/z (ESI) calcd for C₁₈H₃₀O₄P⁺ (M⁺+H): 341.1876; Found: 341.1877.

(9) **Diethyl (2-(*p*-acetylphenyl)hept-2(*E*)-en-3-yl)phosphonate (E-3ae):** The reaction of **1a** (57 mg, 0.25 mmol), **2e** (83 mg, 0.5 mmol), Pd(PPh₃)₄ (29 mg, 0.025 mmol), and AcOH (14 μ L, 0.25 mmol) in THF (3 mL) afforded 75 mg (85%) of **E-3ae**: liquid; ¹H NMR (300 MHz, CDCl₃) δ 7.89 (d, J = 8.3 Hz, 2 H), 7.14 (d, J = 8.3 Hz, 2 H), 4.14-4.02 (m, 4 H), 2.54 (s, 3 H), 2.27 (d, J = 3.6 Hz, 3 H), 2.03-1.89 (m, 2 H), 1.35-1.21 (m, 8 H), 1.07-0.95 (m, 2 H), 0.63 (t, J = 7.5 Hz, 3 H); ¹³C NMR (CDCl₃, 75.4 MHz): δ 197.4, 152.1 (d, J_{PC} = 13.2 Hz), 148.5 (d, J_{PC} = 22.0 Hz), 135.6, 128.4, 127.6 (d, J_{PC} = 172.1 Hz), 126.8 (d, J_{PC} = 1.4 Hz), 61.2 (d, J_{PC} = 6.3 Hz), 32.0 (d, J_{PC} = 1.5 Hz), 31.5 (d, J_{PC} = 10.9 Hz), 26.4, 24.2 (d, J_{PC} = 7.5 Hz), 22.4, 16.2 (d, J_{PC} = 6.4 Hz), 13.5; ³¹P NMR (121.5 MHz, CDCl₃) δ 21.6; MS (m/z) 352 (M⁺, 28.58), 43 (100); IR (neat) 1686, 1600, 1443, 1400, 1241, 1026 cm⁻¹; HRMS m/z (ESI) calcd

for $C_{19}H_{30}O_4P^+$ ($M^+ + H$): 353.1876; Found: 353.1876.

(10) **Diethyl (2-(*m*-nitrophenyl)hept-2(*E*)-en-3-yl)phosphonate (*E*-3af):** The reaction of **1a** (58 mg, 0.25 mmol), **2f** (84 mg, 0.5 mmol), $Pd(PPh_3)_4$ (29 mg, 0.025 mmol), and AcOH (14 μ L, 0.25 mmol) in THF (3 mL) afforded 72 mg (81%) of ***E*-3af**: liquid; 1H NMR (300 MHz, $CDCl_3$) δ 8.13-8.09 (m, 1 H), 7.94 (s, 1 H), 7.52 (t, $J = 7.5$ Hz, 1 H), 7.41 (d, $J = 7.5$ Hz, 1 H), 4.16-4.07 (m, 4 H), 2.32 (d, $J = 3.6$ Hz, 3 H), 2.03-1.91 (m, 2 H), 1.37-1.26 (m, 8 H), 1.10-1.00 (m, 2 H), 0.64 (t, $J = 7.2$ Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 150.3 (d, $J_{PC} = 13.3$ Hz), 148.0, 145.0 (d, $J_{PC} = 23.3$ Hz), 133.0 (d, $J_{PC} = 1.7$ Hz), 129.5, 129.0 (d, $J_{PC} = 172.6$ Hz), 122.0, 121.7 (d, $J_{PC} = 1.4$ Hz), 61.4 (d, $J_{PC} = 6.0$ Hz), 32.0 (d, $J_{PC} = 1.3$ Hz), 31.6 (d, $J_{PC} = 11.2$ Hz), 24.3 (d, $J_{PC} = 7.4$ Hz), 22.4, 16.3 (d, $J_{PC} = 6.5$ Hz), 13.4; ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 20.9; MS (m/z) 355 (M^+ , 26.76), 312 (100); IR (neat) 1610, 1531, 1444, 1241, 1025 cm^{-1} ; HRMS m/z (ESI) calcd for $C_{17}H_{26}NO_5PNa^+$ ($M^+ + Na$): 378.1441; Found: 378.1440.

(11) **Diethyl (6-methyldodeca-5(*E*),7(*E*)-dien-5-yl)phosphonate (*E,E*-3ag):** The reaction of **1a** (58 mg, 0.25 mmol), **2g** (65 mg, 0.5 mmol), $Pd(PPh_3)_4$ (30 mg, 0.025 mmol), and AcOH (14 μ L, 0.25 mmol) in THF (3 mL) afforded 70 mg (89%) of ***E,E*-3ag**: liquid; 1H NMR (300 MHz, $CDCl_3$) δ 6.44 (dd, $J = 2.4, 15.6$ Hz, 1 H), 6.06-5.96 (m, 1 H), 4.08-3.95 (m, 4 H), 2.40-2.29 (m, 2 H), 2.18-2.11 (m, 5 H), 1.43-1.21 (m, 14 H), 0.91-0.85 (m, 6 H); ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 146.9 (d, $J_{PC} = 12.4$ Hz), 136.4, 128.4 (d, $J_{PC} = 22.5$ Hz), 125.0 (d, $J_{PC} = 176.1$ Hz), 61.1 (d, $J_{PC} = 6.0$ Hz), 33.0 (d, $J_{PC} = 2.3$ Hz), 32.6 (d, $J_{PC} = 2.4$ Hz), 31.2, 29.4 (d, $J_{PC} = 11.0$ Hz), 22.8, 22.1, 17.5 (d, $J_{PC} = 7.5$ Hz), 16.2 (d, $J_{PC} = 6.5$ Hz), 13.8 (d, $J_{PC} = 1.1$ Hz); ^{31}P

NMR (121.5 MHz, CDCl₃) δ 23.9; MS (m/z) 316 (M⁺, 34.50), 135 (100); IR (neat) 1633, 1577, 1466, 1237, 1027 cm⁻¹; HRMS m/z (ESI) calcd for C₁₇H₃₄O₃P⁺ (M⁺+H): 317.2240; found: 317.2242.

(12) **Diethyl (1-phenoxy-4-methylnona-2(*E*),4(*E*)-dien-5-yl)phosphonate**

(*E,E*-3ah): The reaction of **1a** (57 mg, 0.25 mmol), **2h** (89 mg, 0.5 mmol), Pd(PPh₃)₄ (29 mg, 0.025 mmol), and AcOH (14 μ L, 0.25 mmol) in THF (3 mL) afforded 65 mg (71%) of ***E, E*-3ah**: liquid; ¹H NMR (300 MHz, CDCl₃) δ 7.28 (t, *J* = 8.1 Hz, 2 H), 6.99-6.88 (m, 3 H), 6.82 (d, *J* = 15.9 Hz, 1 H), 6.20 (dt, *J* = 5.1, 15.9 Hz, 1 H), 4.68 (d, *J* = 5.1 Hz, 2 H), 4.12-3.98 (m, 4 H), 2.45-2.29 (m, 2 H), 2.22 (d, *J* = 3.3 Hz, 3 H), 1.38-1.26 (m, 10 H), 0.88 (t, *J* = 6.9 Hz, 3 H); ¹³C NMR (CDCl₃, 75.4 MHz): δ 158.3, 145.4 (d, *J*_{PC} = 13.0 Hz), 130.3 (d, *J*_{PC} = 23.1 Hz), 129.4, 129.3, 128.4 (d, *J*_{PC} = 175.2 Hz), 120.9, 114.6, 68.1 (d, *J*_{PC} = 2.1 Hz), 61.2 (d, *J*_{PC} = 5.5 Hz), 32.7 (d, *J*_{PC} = 2.4 Hz), 29.7 (d, *J*_{PC} = 10.3 Hz), 22.7, 17.4 (d, *J*_{PC} = 7.5 Hz), 16.3 (d, *J*_{PC} = 6.3 Hz), 13.8; ³¹P NMR (121.5 MHz, CDCl₃) δ 22.8; MS (m/z) 367 (M⁺+1, 15.39), 135 (100); IR (neat) 1599, 1587, 1495, 1456, 1239, 1027 cm⁻¹; HRMS m/z (ESI) calcd for C₂₀H₃₂O₄P⁺ (M⁺+H): 367.2033; Found: 367.2033.

(13) **Diethyl (2-phenylhept-1-en-3-yl)phosphonate (4aa):** The reaction of **1a** (58 mg,

0.25 mmol), **2a** (60 mg, 0.5 mmol), Pd(PPh₃)₄ (29 mg, 0.025 mmol), and AcOH (14 μ L, 0.25 mmol) in CH₃OH (3 mL) afforded 58 mg (71%) of ***E*-3aa** and **4aa** (85:15).

4aa: liquid; ¹H NMR (300 MHz, CDCl₃) δ 7.34-7.30 (m, 2 H), 7.24-7.13 (m, 3 H), 5.44 (d, *J* = 6.3 Hz, 1 H), 5.33 (d, *J* = 6.3 Hz, 1 H), 4.01-3.82 (m, 4 H), 2.88 (ddd, *J* = 3.9, 11.4, 23.4 Hz, 1 H), 1.99-1.81 (m, 1 H), 1.78-1.65 (m, 1 H), 1.40-1.34 (m, 1 H),

1.29-1.09 (m, 9 H), 0.74 (t, $J = 6.9$ Hz, 3 H); ^{13}C NMR (CDCl_3 , 75.4 MHz): δ 144.1 (d, $J_{\text{PC}} = 8.7$ Hz), 143.0 (d, $J_{\text{PC}} = 5.0$ Hz), 128.1, 127.3, 126.3 (d, $J_{\text{PC}} = 1.1$ Hz), 116.2 (d, $J_{\text{PC}} = 9.0$ Hz), 62.4 (d, $J_{\text{PC}} = 6.8$ Hz), 61.6 (d, $J_{\text{PC}} = 7.8$ Hz), 42.5 (d, $J_{\text{PC}} = 136.6$ Hz), 30.2 (d, $J_{\text{PC}} = 3.2$ Hz), 29.7 (d, $J_{\text{PC}} = 14.8$ Hz), 22.4 (d, $J_{\text{PC}} = 1.4$ Hz), 16.3 (d, $J_{\text{PC}} = 3.4$ Hz), 16.2 (d, $J_{\text{PC}} = 2.9$ Hz), 13.7; ^{31}P NMR (121.5 MHz, CDCl_3) δ 30.4; MS (m/z) 310 (M^+ , 10.12), 145 (100); IR (neat) 1623, 1598, 1574, 1494, 1458, 1444, 1247, 1056, 1027 cm^{-1} ; HRMS m/z (MALDI) calcd for $\text{C}_{17}\text{H}_{28}\text{O}_3\text{P}^+$ ($\text{M}^+ + \text{H}$): 311.1771; Found: 311.1776.

^1H , ^{13}C , and ^{31}P NMR spectra of all the new compounds.

Archive directory: /export/home/masm/vnmrsys/data
 Sample directory: gh-2-26-2-ncesy_25Dec2004

Pulse Sequence: NOESY
 Solvent: CDCl3
 Ambient temperature
 File: NOESY
 Mercury-300MB "DMC300"

Relax. delay 2.000 sec
 Mixing 0.300 sec
 Acq. time 9.213 sec
 Width 4607.7 Hz
 2D Width 4607.7 Hz
 32 repetitions
 2 x 128 increments
 OBSERVE H1, 300.0279748 MHz
 DATA PROCESSING
 Gauss apodization 0.056 sec
 F1 DATA PROCESSING
 Gauss apodization 0.025 sec
 FT size 2048 x 2048
 Total time 7 hr, 24 min, 27 sec

18.503

References

- (1) Mark, V. *Tetrahedron Lett.* **1962**, 281-285.
- (2) Pudovik, A. N.; Aladzheva, J. M.; Yakovenko, L. N. *J. Gen. Chem. USSR* (Engl. Transl.), **1965**, 35, 1214-1220. CAS Registry Number: 3095-10-1.
- (3) Pergament, I.; Srebnik, M. *Tetrahedron Lett.* **2001**, 42, 8059-8062. The ^1H NMR data of this compound reported in this paper are the same as what we observed, but the ^{13}C NMR and ^{31}P NMR data are different.