

Supporting information

A regio- and stereoselective synthesis of trisubstituted alkenes via gold(I)-catalyzed hydrophosphoryloxylation of haloalkynes

Bathoju Chandra Chary,^a Sunggak Kim,^{a*} Doosup Shin,^b and Phil Ho Lee^{b*}

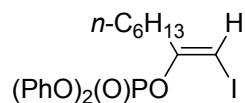
^aDivision of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore 637371, Singapore

^bDepartment of Chemistry, Institute of Molecular Science and Fusion Technology, Kangwon National University, Chuncheon 200-701, Republic of Korea

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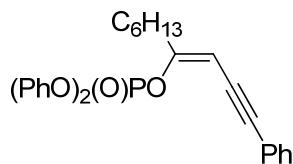
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General procedure of Au-catalyzed addition reactions



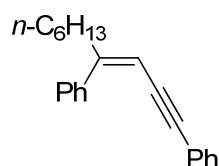
(Z)-1-iodooct-1-en-2-yl diphenyl phosphate (2a): To a suspension of Ph₃PAuCl (114.0 mg, 0.23 mmol), AgOTf (59.0 mg, 0.23 mmol) and diphenyl phosphate (1373 mg, 5.5 mmol) in toluene (22 mL) was added 1-iodooct-1-yne (1.080 g, 4.57 mmol) at room temperature. After being stirred at room temperature for 4 h, the solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography (EtOAc:hexane = 1:10) to give **2a** (159.0 mg, 80%) as a yellowish oil. ¹H NMR (400 MHz, CDCl₃) δ 7.19-7.38 (m, 10H), 5.65 (s, 1H), 2.49 (t, *J* = 7.6 Hz, 2H), 1.50-1.47 (m, 2H), 1.29-1.19 (m, 6H), 0.86 (t, *J* = 6.9 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 156.9, 150.6, 130, 125.8, 120.5 (d, *J*_{cp} = 4.8 Hz), 62.1 (d, *J*_{cp} = 10.5 Hz), 35.3, 31.6, 28.6, 26.7, 22.7, 14.2; IR (film) 2954, 2929, 1591, 1490, 1189, 963, 772, 687, 514 cm⁻¹; HRMS (EI) calcd. for C₂₀H₂₄IO₄P: *m/z* 486.0457 [M⁺], found: *m/z* 486.0460.

General procedure of Pd-catalyzed cross-coupling reactions

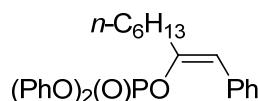


Diphenyl (Z)-1-phenyldec-3-en-1-yn-4-yl phosphate (3a): To a suspension of Pd(PPh₃)₄ (13.86 mg, 0.012 mmol) and CuI (5.71 mg, 0.03 mmol) in 1,4-dioxane (1.5 mL) was added (Z)-1-iodooct-1-en-2-yl diphenyl phosphate (145.8 mg, 0.3 mmol) at room temperature. After 15 min, Et₃N (91.07 mg, 0.9 mmol) and phenylacetylene (36.76 mg, 0.36 mmol) was added. After being stirred for 2 h at room temperature, the reaction mixture was quenched with saturated aqueous NaHCO₃. The aqueous layer was extracted with ether (3 × 20 mL), dried with MgSO₄, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (EtOAc:hexane = 1:10) to give **3a** (116.0 mg, 84%) as a brown oil. ¹H NMR (400 MHz, CDCl₃) δ 7.30-7.19 (m, 13H), 7.16-7.12 (m, 2H), 5.33 (s, 1H), 2.42 (t, *J* = 7.6 Hz, 2H), 1.49 (quint, *J* = 7.5 Hz, 2H), 1.32-1.20 (m, 6H), 0.87 (t, *J* = 6.9 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 159.0 (d, *J*_{cp} = 8.8 Hz), 151.0 (d, *J*_{cp} = 7.7 Hz), 131.9,

130.2, 128.6, 125.8, 123.7, 120.6, 96.7, 96.6, 94.6, 83.6 (d, $J_{cp} = 2.9$ Hz), 34.8, 31.9, 28.9, 26.8, 22.9, 14.5; IR (film) 3061, 2930, 1489, 1188, 1160, 1010, 961, 689 cm⁻¹; HRMS (EI) calcd. for C₂₈H₂₉O₄P: *m/z* 460.1803 [M⁺], found: *m/z* 460.1803.

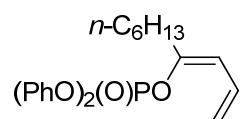


(Z)-1,4-diphenyldec-3-en-1-yne (4a): To a suspension of PdCl₂ (1.773 mg, 0.010 mmol) and (Z)-diphenyl 1-phenyldec-3-en-1-yn-4-yl phosphate (92.1 mg, 0.2 mmol) in THF (1.0 mL) was added phenyl magnesium bromide 1.0 M in THF (39.9 mg, 0.22 mmol) at room temperature. After being stirred for 15 min at room temperature, the reaction mixture was, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane) to give **4a** (37.0 mg, 70%) as a yellowish oil. ¹H NMR (400 MHz, CDCl₃) δ 7.59 (d, $J = 8.0$ Hz, 2H), 7.38 (t, $J = 7.4$ Hz, 2H), 7.33-7.29 (m, 1H), 7.28-7.22 (m, 5H), 5.80 (s, 1H), 2.55(td, $J = 7.5$ Hz, $J = 1.0$ Hz, 2H), 1.43-1.37 (m, 2H), 1.34-1.22 (m, 6H), 0.86 (t, $J = 6.9$ Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 154.3, 140.0, 131.7, 128.6, 128.5, 128.3, 128.14, 128.11, 124.3, 106.2, 91.5, 89.1, 38.3, 32.0, 29.3, 28.8, 23.0, 14.5; IR (film) 2025, 2855, 1489, 755, 690, 441, 427 cm⁻¹; HRMS (EI) calcd. for C₂₂H₂₄: *m/z* 288.1878 [M⁺], found: *m/z* 288.1880.

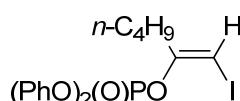


diphenyl (Z)-1-phenyloct-1-en-2-yl phosphate (5a): To a suspension of Pd(PPh₃)₄ (11.56 mg, 0.010 mmol) in 1,4-dioxane (1.0 mL) was added (Z)-1-iodooct-1-en-2-yl diphenyl phosphate (97.26 mg, 0.2 mmol) at room temperature. After 15 min, Et₃N (40.48 mg, 0.4 mmol), 3.0 M K₃PO₄ (138.6 mg, 0.6 mmol) and phenylboronic acid (29.27 mg, 0.24 mmol) was added. After being stirred for 1 h at 70 °C, the reaction mixture was quenched with saturated aqueous NaHCO₃. The aqueous layer was extracted with ether (3 × 20 mL), dried with MgSO₄, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (EtOAc:hexane = 1:10) to give **5a** (55.0 mg, 63%) as a brown oil. ¹H NMR (400 MHz, CDCl₃) δ 7.42 (d, $J = 8.4$ Hz, 2H), 7.28 (t, $J = 7.9$ Hz, 4H),

7.22-7.11 (m, 9H), 5.81 (s, 1H), 2.54 (t, $J = 7.5$ Hz, 2H), 1.61 (quint, $J = 7.5$ Hz, 2H), 1.38-1.24 (m, 6H), 0.87 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 150.9 (d, $J_{cp} = 6.9$ Hz), 149.3 (d, $J_{cp} = 8.7$ Hz), 134.2, 130.1, 129.2, 128.6, 127.4, 125.7, 120.4 (d, $J_{cp} = 4.9$ Hz), 114.5 (d, $J_{cp} = 8.6$ Hz), 35.4, 32.0, 29.0, 27.4, 22.9, 14.5; IR (film) 2954, 2929, 1591, 1290, 1190, 1010, 776, 402 cm^{-1} ; HRMS (EI) calcd. for $\text{C}_{26}\text{H}_{29}\text{O}_4\text{P}$: m/z 436.1803 [M^+], found: m/z 436.1806.

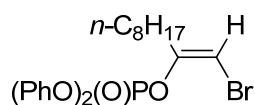


(Z)-deca-1,3-dien-4-yl diphenyl phosphate (7c): To a suspension of $\text{PdCl}_2(\text{PPh}_3)_2$ (10.52 mg, 0.015 mmol) and (Z)-1-iodooct-1-en-2-yl diphenyl phosphate (145.8 mg, 0.3 mmol) in DMF (1.5 mL) was added tributyl(vinyl)tin (142.6 mg, 0.45 mmol) at room temperature. After being stirred for 16 h at room temperature, the reaction mixture was quenched with saturated aqueous NaHCO_3 . The aqueous layer was extracted with ether (3×20 mL), dried with MgSO_4 , filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (EtOAc:hexane = 1:10) to give **7c** (110.0 mg, 95%) as a yellow oil. ^1H NMR (600 MHz, CDCl_3) δ 7.35 (t, $J = 7.9$ Hz, 4H), 7.25 (d, $J = 7.9$ Hz, 4H), 7.20 (t, $J = 7.4$ Hz, 2H), 6.53 (td, $J = 10.5$ Hz, $J = 7.1$ Hz, 1H), 5.58 (d, $J = 10.7$ Hz, 1H), 5.15 (d, $J = 17.1$ Hz, 1H), 4.97 (d, $J = 10.4$ Hz, 1H), 2.36 (t, $J = 7.5$ Hz, 2H), 1.47 (quint, $J = 7.5$ Hz, 2H), 1.28-1.20 (m, 6H), 0.86 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 151.0 (d, $J_{cp} = 7.6$ Hz), 149.6 (d, $J_{cp} = 9.4$ Hz), 130.2, 130.0, 125.9, 120.6 (d, $J_{cp} = 4.9$ Hz), 117.3, 116.3 (d, $J_{cp} = 7.9$ Hz), 34.6, 31.9, 29.0, 26.9, 22.9, 14.4; IR (film) 2956, 2929, 2857, 1490, 1188, 1009, 955, 632 cm^{-1} ; HRMS (EI) calcd. for $\text{C}_{22}\text{H}_{27}\text{O}_4\text{P}$: m/z 386.1647 [M^+], found: m/z 386.1646.

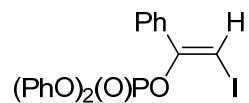


(Z)-1-iodohex-1-en-2-yl diphenyl phosphate (2b): ^1H NMR (400 MHz, CDCl_3) δ 7.37-7.18 (m, 10H), 5.64 (s, 1H), 2.49 (t, $J = 7.8$ Hz, 2H), 1.49-1.43 (m, 2H), 1.31-1.25 (m, 2H), 0.85 (t, $J = 6.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 157 (d, $J_{cp} = 6.7$ Hz), 150.6 (d, $J_{cp} = 7.7$

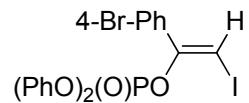
Hz), 129.9, 125.8, 120.4 (d, $J_{cp} = 4.8$ Hz), 62.1 (d, $J_{cp} = 11.5$ Hz), 34.9, 28.7, 22.0, 13.8; IR (film) 3012, 2958, 2931, 1637, 1591, 1489, 1296, 1188, 1122, 966; HRMS (EI) calcd for C₁₈H₂₀IO₄P: *m/z* 459.0222 [M⁺], found: *m/z* 459.0218.



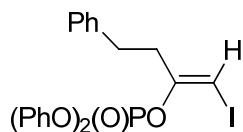
(Z)-1-bromodec-1-en-2-yl diphenyl phosphate (2c): ¹H NMR (400 MHz, CDCl₃) δ 7.37-7.19 (m, 10H), 5.66 (s, 1H), 2.38 (t, $J = 7.6$ Hz, 2H), 1.47-1.44 (m, 2H), 1.27-1.22 (m, 10H), 0.87 (t, $J = 6.9$ Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 152.5, 150.6, 129.9, 125.7 (d, $J_{cp} = 10.5$ Hz), 120.4, 91.79, 34.4, 32.0, 29.3, 28.9, 26.4, 22.8, 14.3; IR (film) 3018, 2927, 2856, 1653, 1591, 1489, 1296, 1215, 1188, 1139, 1010, 968, 756, 667 cm⁻¹; HRMS (EI) calcd for C₂₂H₂₈BrO₄P: *m/z* 467.0987 [M⁺], found: *m/z* 467.0981.



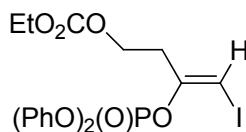
(Z)-2-iodo-1-phenylvinyl diphenyl phosphate (2d): ¹H NMR (400 MHz, CDCl₃) δ 7.49-7.47 (m, 2H), 7.35-7.25 (m, 7H), 7.18-7.13 (m, 6H), 6.38 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 155.0 (d, $J_{cp} = 8.6$ Hz), 150.6 (d, $J_{cp} = 7.7$ Hz), 133.9, 129.9 (d, $J_{cp} = 13.4$ Hz), 128.6, 125.6, 120.3 (d, $J_{cp} = 4.8$ Hz), 66.4 (d, $J_{cp} = 9.6$ Hz); IR (film) 3018, 1591, 1489, 1298, 1215, 1188, 1053, 1024, 966, 756 cm⁻¹; HRMS (EI) calcd for C₂₀H₁₆IO₄P: *m/z* 477.9831 [M⁺], found: *m/z* 477.9834.



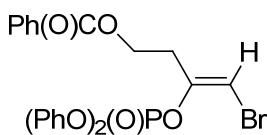
(Z)-1-(4-bromophenyl)-2-iodovinyl diphenyl phosphate (2e): ¹H NMR (400 MHz, CDCl₃) δ 7.43-7.41 (m, 2H), 7.34-7.19 (m, 6H), 7.18-7.16 (m, 6H), 6.42 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 154.0 (d, $J_{cp} = 8.6$ Hz), 150.5 (d, $J_{cp} = 7.6$ Hz), 132.9, 131.9, 129.9, 128.0, 125.8, 124.2, 120.3 (d, $J_{cp} = 4.8$ Hz), 67.2 (d, $J_{cp} = 9.5$ Hz); IR (film) 3068, 3014, 1589, 1487, 1394, 1307, 1215, 1188, 1043, 947, 754 cm⁻¹; HRMS (EI) calcd for C₂₀H₁₅IO₄PBrNa: *m/z* 578.8834 [M⁺], found: *m/z* 578.8836.



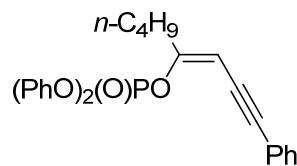
(Z)-1-iodo-4-phenylbut-1-en-2-yl diphenyl phosphate (2f): ^1H NMR (400 MHz, CDCl_3) δ 7.38-7.30 (m, 8H), 7.28-7.17 (m, 5H), 7.10 (d, $J = 6.9$ Hz, 2H), 5.63 (s, 1H), 2.82 (s, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 155.7 (d, $J_{cp} = 7.1$ Hz), 150.4 (d, $J_{cp} = 7.6$ Hz), 139.9, 129.9, 128.5, 128.4, 126.3, 125.7, 120.3 (d, $J_{cp} = 4.8$ Hz), 63.1 (d, $J_{cp} = 10.5$ Hz), 37.0, 32.9; IR (film) 3075, 1590, 1488, 1297, 1185, 960, 688, 639 cm^{-1} ; HRMS (EI) calcd. for $\text{C}_{22}\text{H}_{20}\text{IO}_4\text{P}$: m/z 506.0144 [M^+], found: m/z 506.0145.



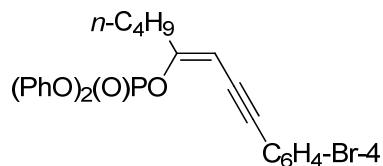
(Z)-3-(diphenoxypyrophosphoryloxy)-4-iodobut-3-enyl ethyl carbonate (2g): ^1H NMR (400 MHz, CDCl_3) 7.37-7.19 (m, 10H), 5.85 (s, 1H), 4.24-4.15 (m, 4H), 2.90-2.89 (m, 2H), 1.31-1.26 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 154.9, 152.4 (d, $J_{cp} = 7.6$ Hz), 150.4 (d, $J_{cp} = 7.6$ Hz), 130.0, 125.9, 120.4 (d, $J_{cp} = 4.8$ Hz), 65.2, 64.4, 63.5, 34.7, 14.4; IR (film) 3076, 2981, 1735, 1641, 1589, 1487, 1384, 1367, 1184, 1120, 1070, 763, 638 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{19}\text{H}_{20}\text{IO}_7\text{P}$: m/z 519.0070 [M^+], found: m/z 519.0071.



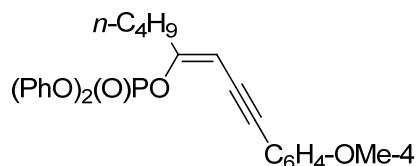
(Z)-4-(benzoyloxy)-1-bromobut-1-en-2-yl diphenyl phosphate (2h): ^1H NMR (400 MHz, CDCl_3) δ 8.01-7.98 (m, 2H), 7.45-7.19 (m, 15H), 5.85 (s, 1H), 4.39 (t, $J = 6.6$ Hz, 2H), 2.89-2.86 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.7, 151.0, 148.1, 133.3, 130.0, 128.5, 125.9, 120.2, 94.1, 60.6, 33.9; IR (film) 3070, 2962, 1732, 1678, 1589, 1487, 1454, 1382, 1070, 773, 711 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{23}\text{H}_{21}\text{O}_6\text{BrP}$: m/z 503.0259 [M^+], found: m/z 503.0255.



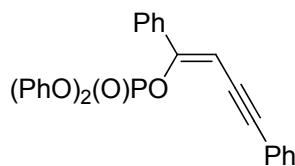
Diphenyl (Z)-1-phenyloct-3-en-1-yn-4-yl phosphate (3b): ^1H NMR (400 MHz, CDCl_3) δ 7.34-7.14 (m, 15H), 5.34 (s, 1H), 2.43 (t, $J = 7.8$ Hz, 2H), 1.49-1.45 (m, 2H), 1.35-1.29 (m, 2H), 0.87 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 158.6, 150.8, 131.7, 129.9, 128.3, 125.6, 120.4 (d, $J_{cp} = 4.8$ Hz), 96.4, 94.9, 84.1, 34.2, 28.7, 22.2, 13.9; IR (film) 3053, 2958, 2872, 1653, 1591, 1489, 1296, 1265, 1219, 1188, 1161, 1008, 688 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{26}\text{H}_{25}\text{O}_4\text{P}$: m/z 433.1569 [M^+], found: m/z 433.1566.



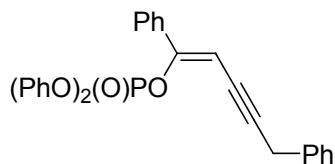
(Z)-1-(4-bromophenyl)oct-3-en-1-yn-4-yl diphenyl phosphate (3c): ^1H NMR (400 MHz, CDCl_3) δ 7.35-7.09 (m, 14H), 5.31 (s, 1H), 2.40 (t, $J = 7.8$ Hz, 2H), 1.49-1.45 (m, 2H), 1.34-1.28 (m, 2H), 0.87 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 159.1, 150.6, 133.1, 131.6, 129.9, 125.7, 122.4 (d, $J_{cp} = 14.4$ Hz), 96.3 (d, $J_{cp} = 7.7$ Hz), 93.2, 84.5, 34.3, 28.6, 22.1, 13.9; IR (film) 3018, 2399, 1591, 1489, 1294, 1215, 1161, 1010, 966, 767, 669 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{26}\text{H}_{25}\text{O}_4\text{PBr}$: m/z 511.0674 [M^+], found: m/z 511.0668.



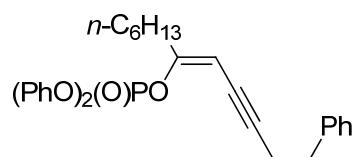
(Z)-1-(4-methoxyphenyl)oct-3-en-1-yn-4-yl diphenyl phosphate (3d): ^1H NMR (400 MHz, CDCl_3) δ 7.31-7.12 (m, 12H), 6.76-6.73 (m, 2H), 5.32 (s, 1H), 3.77 (s, 3H), 2.40 (t, $J = 7.8$ Hz, 2H), 1.49-1.43 (m, 2H), 1.33-1.28 (m, 2H), 0.86 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 159.7, 157.9 (d, $J_{cp} = 9.6$ Hz), 150.7 (d, $J_{cp} = 7.7$ Hz), 133.1, 129.9, 125.6, 120.3 (d, $J_{cp} = 4.8$ Hz), 115.6, 113.9, 96.6 (d, $J_{cp} = 8.6$ Hz), 82.0, 55.4, 34.2, 28.7, 22.1, 13.9; IR (film) 3016, 2960, 2399, 1602, 1508, 1489, 1292, 1247, 1215, 1026, 966, 771, 667 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{27}\text{H}_{28}\text{O}_5\text{P}$: m/z 463.1674 [M^+], found: m/z 463.1666.



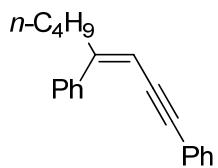
Diphenyl (Z)-1,4-diphenylbut-1-en-3-ynyl phosphate (3e): ^1H NMR (400 MHz, CDCl_3) δ 7.57-7.55 (m, 2H), 7.36-7.55 7.09 (m, 18H), 6.08 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 154.5, 150.7 (d, $J_{cp} = 7.7$ Hz), 133.6, 131.8, 129.9, 128.7, 128.3, 125.6 (d, $J_{cp} = 16.3$ Hz), 120.3 (d, $J_{cp} = 4.8$ Hz), 97.7 (d, $J_{cp} = 8.6$ Hz), 84.2; IR (film) 3016, 2399, 1593, 1489, 1294, 1215, 1070, 1010, 966, 771, 669 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{28}\text{H}_{22}\text{O}_4\text{P}$: m/z 453.1256 [M^+], found: m/z 453.1262.



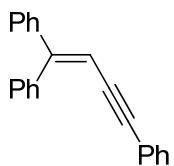
Diphenyl (Z)-1,5-diphenylpent-1-en-3-ynyl phosphate (3f): ^1H NMR (400 MHz, CDCl_3) δ 7.52-7.50 (m, 2H), 7.33-7.12 (m, 18H), 5.88 (s, 1H), 3.58 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 155.0, 150.8 (d, $J_{cp} = 7.6$ Hz), 136.5, 133.8, 129.8 (d, $J_{cp} = 4.8$ Hz), 128.7 (d, $J_{cp} = 5.7$ Hz), 120.3 (d, $J_{cp} = 5.7$ Hz), 98.1 (d, $J_{cp} = 6.7$ Hz), 96.4, 26.2; IR (film) 3053, 2985, 2252, 1489, 1421, 1265, 1219, 910, 771, 650 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{29}\text{H}_{24}\text{O}_4\text{P}$: m/z 467.1412 [M^+], found: m/z 467.1418.



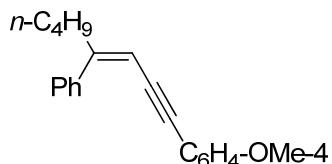
Diphenyl (Z)-1-phenyldodec-5-en-3-yn-6-yl phosphate (3g): ^1H NMR (400 MHz, CDCl_3) δ 7.35-7.24 (m, 10H), 7.18 (t, $J = 6.8$ Hz, 3H), 7.12 (d, $J = 7.1$ Hz, 2H), 5.09 (s, 1H), 2.70 (t, $J = 7.8$ Hz, 2H), 2.43 (t, $J = 7.2$ Hz, 2H), 2.32 (t, $J = 7.6$ Hz, 2H), 1.43(quint, $J = 7.0$ Hz, 2H), 1.30-1.17 (m, 6H), 0.86 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 157.6 (d, $J_{cp} = 9.5$ Hz), 150.6 (d, $J_{cp} = 7.5$ Hz), 140.7, 129.8 (d, $J_{cp} = 8.3$ Hz), 128.3 (d, $J_{cp} = 2.7$ Hz), 126.2, 125.4, 120.2(d, $J_{cp} = 4.9$ Hz), 96.5 (d, $J_{cp} = 7.8$ Hz), 94.7, 74.4, 35.0, 34.2, 31.4, 28.5, 26.3, 22.5, 21.7, 14.0; IR (film) 2953, 2928, 1591, 1490, 1010, 961, 774, 415 cm^{-1} ; HRMS (EI) calcd. for $\text{C}_{30}\text{H}_{33}\text{O}_4\text{P}$: m/z 488.2116 [M^+], found: m/z 488.2115.



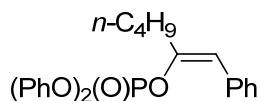
(Z)-1,4-diphenyloct-3-en-1-yne (4b): ^1H NMR (400 MHz, CDCl_3) δ 7.61-7.59 (m, 2H), 7.40-7.22 (m, 8H), 5.80 (s, 1H), 2.56 (t, $J = 7.5$ Hz, 2H), 1.42-1.26 (m, 4H), 0.88 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 154.0, 139.7, 131.4, 128.4, 128.3, 128.0, 127.9, 124.1, 106.0, 91.3, 88.9, 37.8, 30.7, 22.5, 14.1; IR (film) 3078, 3014, 2956, 2194, 1591, 1489, 1440, 1377, 1215, 1068, 914, 839, 767, 690 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{20}\text{H}_{20}$: m/z 261.1643 [M^+], found: m/z 261.1653.



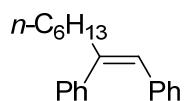
1,1,4-triphenylbut-1-en-3-yne (4c): ^1H NMR (400 MHz, CDCl_3) δ 7.60-7.00 (m, 15H), 6.23 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 152.9, 141.6, 139.4, 131.6, 130.4, 128.7, 128.5, 128.5, 128.0, 127.5, 107.3, 93.9, 89.4; IR (film) 3053, 2985, 2252, 1265, 1219, 910, 771, 734, 650 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{22}\text{H}_{16}$: m/z 281.1330 [M^+], found: m/z 281.1336.



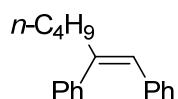
1-methoxy-4-((Z)-4-phenyloct-3-en-1-ynyl)benzene (4d): ^1H NMR (400 MHz, CDCl_3) δ 7.60-7.58 (m, 2H), 7.39-7.19 (m, 6H), 6.79-6.77 (m, 2H), 5.77 (s, 1H), 3.77 (s, 3H), 2.54 (t, $J = 7.5$ Hz, 2H), 1.38-1.26 (m, 4H), 0.88 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 159.4, 152.9, 139.9, 132.9, 128.3, 128.0, 127.8, 116.3, 114.1, 106.2, 91.5, 87.5, 55.5, 37.7, 30.8, 22.5, 14.1; IR (film) 3012, 2956, 1604, 1508, 1463, 1247, 1170, 1035, 831, 756, 667 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{21}\text{H}_{23}\text{O}$: m/z 291.1749 [M^+], found: m/z 291.1752.



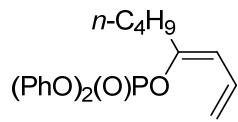
Diphenyl (Z)-1-phenylhex-1-en-2-yl phosphate (5b): ^1H NMR (400 MHz, CDCl_3) δ 7.42-7.39 (m, 2H), 7.29-6.78 (m, 13H), 5.81 (s, 1H), 2.54 (t, $J = 7.3$ Hz, 2H), 1.61-1.57 (m, 2H), 1.39-1.33 (m, 2H), 0.89 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 156.4, 150.6 (d, $J_{cp} = 7.7$ Hz), 149.0 (d, $J_{cp} = 8.6$ Hz), 133.9, 129.9, 129.6, 129.0, 128.4, 127.2, 125.6, 120.2 (d, $J_{cp} = 4.8$ Hz), 115.5, 114.4 (d, $J_{cp} = 8.6$ Hz), 34.9, 29.3, 22.2, 14.0; IR (film) 3059, 2956, 2870, 1672, 1591, 1489, 1296, 1188, 1095, 960, 754, 688 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{24}\text{H}_{25}\text{O}_4\text{P}$: m/z 409.1569 [M^+], found: m/z 409.1563.



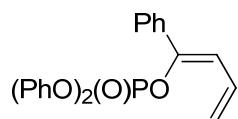
(Z)-1,2-diphenyloct-1-ene (6a): ^1H NMR (400 MHz, CDCl_3) δ 7.59 (d, $J = 7.5$ Hz, 1H), 7.44 (t, $J = 7.5$ Hz, 1H), 7.36-7.21 (m, 3H), 7.14 (d, $J = 6.6$ Hz, 2H), 7.09.-7.01 (m, 2H), 6.91 (d, $J = 6.5$ Hz, 1H), 6.42 (s, 1H), 2.48 (t, $J = 7.2$ Hz, 2H), 1.50-1.21 (m, 8H), 0.87 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR (400 MHz, CDCl_3) δ 144.0, 141.9, 138.0, 129.4, 129.0, 128.9, 128.2, 127.6, 127.2, 126.4, 41.2, 32.1, 29.3, 28.3, 23.1, 14.5; IR (film) 2928, 1593, 1439, 1187, 962, 693, 541 cm^{-1} ; HRMS (EI) calcd. for $\text{C}_{20}\text{H}_{24}$: m/z 264.1878 [M^+], found: m/z 264.1874.



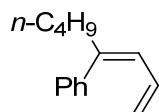
(Z)-1,2-diphenylhex-1-ene (6b): ^1H NMR (400 MHz, CDCl_3) δ 7.59 (d, $J = 7.3$ Hz, 1H), 7.42 (t, $J = 7.8$ Hz, 1H), 7.30-7.04 (m, 6H), 6.90 (d, $J = 6.4$ Hz, 2H), 6.43 (s, 1H), 2.49 (t, $J = 6.7$ Hz, 2H), 1.41-1.25 (m, 4H), 0.88 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 143.6, 141.6, 137.5, 129.0, 128.8, 128.6, 127.9, 127.2, 126.1, 40.5, 30.2, 22.4, 14.0, 139.7, 131.4, 128.4, 128.3, 128.0, 127.9, 124.1, 106.0, 91.3, 88.9, 37.8, 30.7, 22.5, 14.1; IR (film) 3153, 2958, 2252, 1791, 1548, 1379, 1219, 906, 732, 650 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{18}\text{H}_{20}\text{Na}$: m/z 259.1463 [M^+], found: m/z 259.1466.



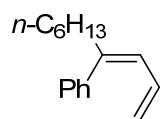
(Z)-octa-1,3-dien-4-yl diphenyl phosphate (7a): ^1H NMR (400 MHz, CDCl_3) δ 7.36-7.17 (m, 10H), 6.57-6.48 (m, 1H), 5.57 (d, $J = 11$ Hz, 1H), 5.15 (d, $J = 17.4$ Hz, 1H), 4.96 (d, $J = 10.5$ Hz, 1H), 2.36 (t, $J = 7.3$ Hz), 1.49-1.42 (m, 2H), 1.34-1.22 (m, 2H), 0.86 (t, $J = 7.6$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 150.7 (d, $J_{cp} = 7.7$ Hz), 149.4, 129.9, 129.8, 125.7, 120.4, 120.3, 117.1, 116.1 (d, $J_{cp} = 7.7$ Hz), 34.0, 28.8, 22.2, 13.9; IR (film) 2956, 2929, 1668, 1591, 1489, 1417, 1290, 1217, 1188, 960, 771, 688 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{20}\text{H}_{23}\text{O}_4\text{PNa}$: m/z 381.1232 [M^+], found: m/z 381.1235.



Diphenyl (Z)-1-phenylbuta-1,3-dienyl phosphate (7b): ^1H NMR (400 MHz, CDCl_3) δ 7.54-7.51 (m, 2H), 7.34-7.11 (m, 13H), 6.86-6.35 (m, 1H), 6.33 (d, $J = 1.8$ Hz, 1H), 5.38 (d, $J = 17.4$ Hz, 1H), 5.19 (d, $J = 10.5$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 150.7 (d, $J = 6.7$ Hz), 145.9, 134.5, 130.3, 129.9, 129.1, 128.6, 125.7 (d, $J = 10.5$ Hz), 120.3 (d, $J = 4.8$ Hz), 117.6 (d, $J = 6.7$ Hz); IR (film) 3043, 2926, 1732, 1643, 1591, 1487, 1456, 1415, 1296, 1217, 1045, 960, 769, 688, 648 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{22}\text{H}_{19}\text{O}_4\text{P}$: m/z 379.1099 [M^+], found: m/z 379.1105.



1-((Z)-octa-1,3-dien-4-yl)benzene (8a): ^1H NMR (400 MHz, CDCl_3) δ 7.37-7.18 (m, 5H), 6.38-6.28 (m, 1H), 6.12 (d, $J = 11.4$ Hz, 1H), 5.16 (d, $J = 17.4$ Hz, 1H), 4.94 (d, $J = 10.4$ Hz, 1H), 2.42 (t, $J = 7.1$ Hz, 2H), 1.34-1.25 (m, 4H), 0.88 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.7, 140.9, 134.8, 128.8, 128.4, 127.4, 127.0, 126.8, 116.1, 39.0, 30.5, 22.5, 14.1; IR (film) 2925, 1642, 1415, 1217, 961, 769, 688, 647 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{14}\text{H}_{18}$: m/z 187.1490 [M^+], found: m/z 187.1490.



1-((Z)-deca-1,3-dien-4-yl)benzene (8b): ¹H NMR (400 MHz, CDCl₃) δ 7.36-7.16 (m, 5H), 6.37-6.28 (m, 1H), 6.12 (d, *J* = 10.9 Hz, 1H), 5.18 (dd, *J* = 16.9 Hz, *J* = 1.9 Hz, 1H), 4.94 (dd, *J* = 10.1 Hz, *J* = 1.9 Hz, 1H), 2.41 (t, *J* = 7.1 Hz, 2H), 1.52-1.21 (m, 8H), 0.85 (t, *J* = 6.9 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 144.6, 140.8, 134.6, 128.6, 128.0, 127.2, 126.8, 115.9, 39.1, 31.7, 28.9, 28.1, 22.6, 14.1; IR (film) 3061, 3034, 2926, 1477, 1429, 1005, 725, 693 cm⁻¹; HRMS (EI) calcd. for C₁₆H₂₂: *m/z* 214.1722 [M⁺], found: *m/z* 214.1722.

