Supporting Information for

Cu-Catalyzed Hydrophosphorylative Ring Opening of Propargyl Epoxides: Highly Selective Access to 4-Phosphoryl 2,3-Allenols

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**General Information.** Unless otherwise specified, all reactions were performed under dry N₂ atmosphere. Anhydrous solvents were distilled prior to use: THF was distilled from sodium using benzophenone as the indicator; DCM and DMF were distilled from CaH₂; MeOH was commercially available and used after degass. Propargyl epoxides 1 were prepared following known procedures. ¹ Typical procedure was given below. H-phosphonates 2a-2d diphenylphosphine oxide 2e were purchased from commercial sources and used as received. Flash chromatography was performed on silica gel using petroleum ether and EtOAc as eluent. ¹H, ¹³C and ³¹P NMR spectra were recorded on Bruke-Advance 400 Ultra NMR spectrometer. Chemical shifts (ppm) were recorded with tetramethylsilane (TMS) as the internal reference standard. Chemical shifts are expressed in ppm and J values are given in Hz. HRMS analysis of the products (EI-TOF) was performed at the Analytical Center of the Department of Chemistry of Zhejiang University, China.

**Typical procedure for the preparation of the starting materials 1¹**

\[
\begin{align*}
\text{Me}_3\text{Si} & \equiv & & n-\text{BuLi} & \text{THF, -78 °C} & \left[\text{Me}_3\text{Si} \equiv \text{Li}\right] \\
\text{Ph} & \equiv & & \text{O} & \text{Br} & \text{THF, -78 °C-r}t \\
\text{SiMe}_3 & \equiv & & \text{Ph} & \text{Bu}_4\text{NF} & \rightarrow 1a
\end{align*}
\]

\(n\)-Butyl lithium (4 mL, 2.5 M in hexane) was added to a solution of ethynyltrimethylsilane (1.08 g, 11 mmol) in THF (15 mL) at –78 °C under N₂ atmosphere. The reaction mixture was allowed to stir at this temperature for 30 min. 2-bromo-1-phenylethan-1-one (1.99 g, 10 mmol) in THF (10 mL) was then slowly added at –78 °C. The reaction mixture was naturally warmed to room temperature and kept stirring overnight. After quenched by aq. NaHCO₃ solution, extracted with EtOAc and concentrated to dryness, the residue was dissolved in THF and cooled to 0 °C. A solution of tetrabutylammonium fluoride (ca. 10 mmol, 85% purity containing water) in THF was dropwise added. After completion of the reaction (monitored by TLC), the reaction mixture was quenched with water and extracted with EtOAc. The organic layers were dried with MgSO₄, and concentrated under vacumm. Pure 2-ethynyl-2-phenyloxirane 1a (1.04 g, yield 72%) was obtained after column chromatography on silica gel (petroleum ether–ethyl acetate 60:1 v/v). Propargyl epoxides 1b-1g, 1k and 1l were prepared from the corresponding alkynes and bromides with a similar procedure.

**Synthetic procedure for the propargyl acetate 1q²**

\[
\begin{align*}
\equiv & \text{CH₂Cl₂, 0 °C} & \equiv \\
1h & \text{m-CPBA}
\end{align*}
\]

To a solution of 1-ethynylcyclohex-1-ene (2.120 g, 20 mmol) in CH₂Cl₂ (60 mL) at 0°C was

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added *m*-CPBA (85%, 22 mmol). The mixture was stirred at 0°C. The reaction was monitored by TLC until completion. The reaction mixture was filtered and the solution was washed with aq K$_2$CO$_3$ solution, brine, dried over Na$_2$SO$_4$ and concentrated. Pure product 1h (976 mg, 40%) was obtained by distillation under a reduced pressure. Substrates 1i and 1j were prepared via the epoxidation of the corresponding olefins with a similar procedure.

General procedure for the Cu-catalyzed preparation of 4-phosphoryl 2,3-allenols via reactions of propargyl epoxides with P(O)H compounds

An oven-dried Schlenk tube containing a Teflon-coated stir bar was charged with CuI (2.9 mg, 5 mol %). The Schlenk tube was sealed and then evacuated and backfilled with N$_2$ (3 cycles). 1.0 mL of MeOH was injected, followed by the injection of *i*Pr$_2$NEt (5 uL) upon stirring. The mixture was cooled to 0 °C. Then 1 (0.36 mmol) and 2 (0.3 mmol) dissolved in 1.0 mL of MeOH was injected. The reaction was kept stirring at the same temperature. After the reaction was complete (monitored by TLC), removal of the solvent under vacuum left a slurry residue, which was purified by flash chromatography on silica (petroleum ether/ethyl acetate) to afford the product 3.

Characterization data of the products

![Image of 3a](image-url)

**dimethyl (4-hydroxy-3-phenylbuta-1,2-dien-1-yl)phosphonate (3a).** [Eluent for silica-gel column chromatography: PE/EtOAc = 1/1 to 1/3. Obtained amount and yield: 69.9 mg, 92%]. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.41–7.33 (m, 4H), 7.29–7.26 (m, 1H), 5.76 (s, 1H), 4.61 (s, 2H), 3.93 (br, 1H), 3.76 (dd, $J_1 = 7.2$ Hz, $J_2 = 2.0$ Hz, 6H). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 213.0, 131.9 (d, $J_{P-C} = 8.4$ Hz), 128.8, 128.1 (d, $J_{P-C} = 1.6$ Hz), 126.6 (d, $J_{P-C} = 2.7$ Hz), 108.8 (d, $J_{P-C} = 16.5$ Hz), 83.1 (d, $J_{P-C} = 195.9$ Hz), 60.8 (d, $J_{P-C} = 6.5$ Hz), 53.17 (d, $J_{P-C} = 6.8$ Hz), 53.07 (d, $J_{P-C} = 5.6$ Hz). $^{31}$P NMR (CDCl$_3$, 162 MHz): $\delta$ 17.5. HRMS (EI-TOF) (m/z): calcd for C$_{12}$H$_{15}$O$_4$P [M$^+$] 254.0708 found 254.0710.

![Image of 3b](image-url)

**dimethyl (3-(4-chlorophenyl)-4-hydroxybuta-1,2-dien-1-yl)phosphonate (3b).** [Eluent for silica-gel column chromatography: PE/EtOAc = 1/1 to 1/3. Obtained amount and yield: 85.5 mg, 99%]. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.33–7.27 (m, 4H), 5.74 (s, 1H), 4.53 (dd, $J_1 = 5.6$ Hz, $J_2 = 2.8$ Hz, 2H), 3.75 (dd, $J_1 = 7.2$ Hz, $J_2 = 4.0$ Hz, 6H). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 212.8, 133.6 (d, $J_{P-C} = 1.3$ Hz), 130.4 (d, $J_{P-C} = 8.0$ Hz), 128.8, 127.7 (d, $J_{P-C} = 2.7$ Hz), 107.6 (d, $J_{P-C} = 17.5$ Hz), 82.9 (d, $J_{P-C} = 195.4$ Hz), 60.5 (d, $J_{P-C} = 6.5$ Hz), 53.06 (d, $J_{P-C} = 5.4$ Hz), 52.95 (d,
$J_{P,C} = 6.3$ Hz). $^{31}$P NMR (CDCl$_3$, 162 MHz): $\delta$ 17.3. HRMS (El-TOF) (m/z): calcd for C$_{12}$H$_{14}$ClO$_4$P [M$^+$] 288.0318 found 288.0320.

**dimethyl (3-(4-bromophenyl)-4-hydroxybuta-1,2-dien-1-yl)phosphonate (3c).** [Eluent for silica-gel column chromatography: PE/EtOAc = 1/1 to 1/3. Obtained amount and yield: 93.2 mg, 94%]: $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.46 (d, $J = 8.8$ Hz, 2H), 7.26 (d, $J = 8.0$ Hz, 2H), 5.74 (s, 1H), 4.54 (dd, $J_1 = 5.2$ Hz, $J_2 = 2.0$ Hz, 2H), 3.76 (dd, $J_1 = 7.2$ Hz, $J_2 = 2.0$ Hz, 6H). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 212.9, 131.8 (d, $J_{P,C} = 1.5$ Hz), 130.9 (d, $J_{P,C} = 8.3$ Hz), 128.1 (d, $J_{P,C} = 2.5$ Hz), 121.9 (d, $J_{P,C} = 1.6$ Hz), 107.8 (d, $J_{P,C} = 17.0$ Hz), 83.2 (d, $J_{P,C} = 195.5$ Hz), 60.7 (d, $J_{P,C} = 6.6$ Hz), 53.1 (d, $J_{P,C} = 5.4$ Hz), 53.0 (d, $J_{P,C} = 6.3$ Hz). $^{31}$P NMR (CDCl$_3$, 162 MHz): $\delta$ 17.1. HRMS (El-TOF) (m/z): calcd for C$_{12}$H$_{14}$BrO$_4$P [M$^+$] 331.9813 found 331.9816.

**dimethyl (4-hydroxy-3-(4-(trifluoromethyl)phenyl)buta-1,2-dien-1-yl)phosphonate (3d).** [Eluent for silica-gel column chromatography: PE/EtOAc = 1/1 to 1/3. Obtained amount and yield: 80.7 mg, 84%]: $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.58 (d, $J = 8.4$ Hz, 2H), 7.51 (d, $J = 8.4$ Hz, 2H), 5.79 (s, 1H), 4.59 (br, 2H), 3.77 (d, $J_1 = 7.6$ Hz, 6H). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 213.1, 135.9 (d, $J_{P,C} = 7.9$ Hz), 129.8 (dd, $J_1 = 64.9$ Hz, $J_2 = 31.5$ Hz), 126.8 (d, $J_{P,C} = 2.1$ Hz), 125.6 (d, $J_{P,C} = 2.9$ Hz), 123.9 (q, $J_{P,C} = 270.1$ Hz), 107.7 (d, $J_{P,C} = 16.9$ Hz), 83.3 (d, $J_{P,C} = 195.7$ Hz), 60.6 (d, $J_{P,C} = 5.9$ Hz), 53.16 (d, $J_{P,C} = 6.7$ Hz), 53.06 (d, $J_{P,C} = 5.4$ Hz). $^{31}$P NMR (CDCl$_3$, 162 MHz): $\delta$ 16.9. HRMS (El-TOF) (m/z): calcd for C$_{13}$H$_{14}$F$_3$O$_4$P [M$^+$] 322.0582 found 322.0578.

**dimethyl (3-([1,1'-biphenyl]-4-yl)-4-hydroxybuta-1,2-dien-1-yl)phosphonate (3e).** [Eluent for silica-gel column chromatography: PE/EtOAc = 3/1 to 1/1. Obtained amount and yield: 90.0 mg, 91%]: $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.57-7.55 (m, 4H), 7.47-7.40 (m, 4H), 7.36-7.32 (m, 1H), 5.79 (s, 1H), 4.63 (br, 2H), 3.77 (dd, $J_1 = 7.2$ Hz, $J_2 = 4.0$ Hz, 6H). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 213.1, 140.7, 140.3, 130.7 (d, $J_{P,C} = 7.7$ Hz), 128.8, 127.45, 127.37, 126.9 (d, $J_{P,C} = 2.0$ Hz), 126.9, 108.4 (d, $J_{P,C} = 16.3$ Hz), 83.1 (d, $J_{P,C} = 197.1$ Hz), 60.7 (d, $J_{P,C} = 6.6$ Hz), 53.1 (d, $J_{P,C} = 5.4$ Hz), 53.0 (d, $J_{P,C} = 6.5$ Hz). $^{31}$P NMR (CDCl$_3$, 162 MHz): $\delta$ 17.3. HRMS (El-TOF) (m/z): calcd for C$_{15}$H$_{19}$O$_4$P [M$^+$] 330.1021 found 330.1021.
dimethyl (3-(hydroxymethyl)-4,4-dimethylpenta-1,2-dien-1-yl)phosphonate (3f).

[Eluent for silica-gel column chromatography: PE/EtOAc = 1/1. Obtained amount and yield: 66.9 mg, 95%]: ¹H NMR (CDCl₃, 400 MHz): δ 5.35 (t, J = 2.8 Hz, 1H), 4.19-4.15 (m, 2H), 4.00 (br, 1H), 3.70 (d, J = 7.2 Hz, 6H), 1.08 (s, 9H). ¹³C NMR (CDCl₃, 100 MHz): δ 209.8, 116.8 (d, J_P-C = 16.8 Hz), 81.4 (d, J_P-C = 197.8 Hz), 59.0 (d, J_P-C = 6.6 Hz), 52.8 (d, J_P-C = 5.9 Hz), 52.6 (d, J_P-C = 6.0 Hz), 32.8 (d, J_P-C = 4.5 Hz), 29.2 (d, J_P-C = 2.8 Hz). ³¹P NMR (CDCl₃, 162 MHz): δ 19.8. HRMS (EI-TOF) (m/z): calcd for C₁₀H₁₉O₄P [M⁺] 234.1021 found 234.1025.

diethyl (4-hydroxy-3-phenylbuta-1,2-dien-1-yl)phosphonate (3g).

[Eluent for silica-gel column chromatography: PE/EtOAc = 1/1 to 1/3. Obtained amount and yield: 75.2 mg, 89%]: ¹H NMR (CDCl₃, 400 MHz): δ 7.41–7.32 (m, 4H), 7.28–7.25 (m, 1H), 5.78 (s, 1H), 4.59 (dd, J₁ = 4.4 Hz, J₂ = 1.2 Hz, 2H), 4.16-4.08 (m, 4H), 3.69 (br, 1H), 1.33-1.28 (m, 6H). ¹³C NMR (CDCl₃, 100 MHz): δ 212.4, 132.0 (d, J_P-C = 7.5 Hz), 128.7 (d, J_P-C = 1.6 Hz), 127.9 (d, J_P-C = 1.4 Hz), 126.5 (d, J_P-C = 2.7 Hz), 108.6 (d, J_P-C = 16.6 Hz), 84.3 (d, J_P-C = 195.2 Hz), 62.66 (d, J_P-C = 5.6 Hz), 62.59 (d, J_P-C = 5.7 Hz), 60.9 (d, J_P-C = 6.6 Hz), 16.2 (d, J_P-C = 6.9 Hz). ³¹P NMR (CDCl₃, 162 MHz): δ 14.6. HRMS (EI-TOF) (m/z): calcd for C₁₄H₁₉O₄P [M⁺] 282.1021 found 282.1020.

dibutyl (4-hydroxy-3-phenylbuta-1,2-dien-1-yl)phosphonate (3h).

[Eluent for silica-gel column chromatography: PE/EtOAc = 1/1. Obtained amount and yield: 67.0 mg, 66%]: ¹H NMR (CDCl₃, 400 MHz): δ 7.40 (d, J_P-C = 8.0 Hz, 2H), 7.36–7.32 (m, 2H), 7.28–7.26 (m, 1H), 5.77 (s, 1H), 4.58 (dd, J₁ = 5.6 Hz, J₂ = 2.4 Hz, 2H), 4.07-4.02 (m, 4H), 3.63 (br, 1H), 1.67-1.58 (m, 4H), 1.40-1.33 (m, 4H), 0.89 (td, J₁ = 7.2 Hz, J₂ = 3.2 Hz, 6H). ¹³C NMR (CDCl₃, 100 MHz): δ 212.46 (d, J_P-C = 1.5 Hz), 132.1 (d, J_P-C = 7.4 Hz), 128.7 (d, J_P-C = 1.5 Hz), 127.9 (d, J_P-C = 1.4 Hz), 126.5 (d, J_P-C = 1.8 Hz), 108.6 (d, J_P-C = 16.7 Hz), 84.2 (d, J_P-C = 195.1 Hz), 66.4 (d, J_P-C = 5.4 Hz), 66.3 (d, J_P-C = 7.1 Hz), 60.9 (d, J_P-C = 5.5 Hz), 32.3 (d, J_P-C = 6.2 Hz), 18.6, 13.5. ³¹P NMR (CDCl₃, 162 MHz): δ 14.7. HRMS (EI-TOF) (m/z): calcd for C₁₈H₂₉O₄P [M⁺] 338.1647 found 338.1650.
(4-hydroxy-3-phenylbuta-1,2-dien-1-yl)diphenylphosphine oxide (3j). [Eluent for silica-gel column chromatography: PE/EtOAc = 1/1 to 1/3. Obtained amount and yield (0.6 mmol scale): 184.8 mg, 89%]: $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.80-7.72 (m, 4H), 7.52-7.47 (m, 2H), 7.43-7.39 (m, 4H), 7.28-7.20 (m, 5H), 6.26 (s, 1H), 4.41 (dd, $J_1 = 4.8$ Hz, $J_2 = 2.8$ Hz, 2H). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 212.1 (d, $J_{P-C} = 2.4$ Hz), 132.36 (d, $J_{P-C} = 127.8$, 127.6). $^{31}$P NMR (CDCl$_3$, 162 MHz): $\delta$ 24.8. HRMS (EI-TOF) ($m/z$): calcd for C$_{22}$H$_{19}$O$_2$P [M$^+$] 346.1123 found 346.1124.

(3-(4-bromophenyl)-4-hydroxybuta-1,2-dien-1-yl)diphenylphosphine oxide (3k). [Eluent for silica-gel column chromatography: PE/EtOAc = 1/1 to 1/3. Obtained amount and yield (0.6 mmol scale): 223.8 mg, 88%]: $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.76-7.68 (m, 4H), 7.54-7.48 (m, 2H), 7.44-7.34 (m, 6H), 7.06 (d, dd, $J = 8.0$ Hz, 2H), 6.23-6.21 (m, 1H), 4.37 (s, 2H). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 212.0 (d, $J_{P-C} = 2.8$ Hz), 132.33 (d, $J_{P-C} = 128.4$), 128.7 (d, $J_{P-C} = 1.8$ Hz), 128.6 (d, $J = 2.0$ Hz), 128.1 (d, $J = 0.8$ Hz), 121.8, 109.6 (d, $J_{P-C} = 13.9$ Hz), 89.7 (d, $J_{P-C} = 117.6$ Hz), 60.8 (d, $J_{P-C} = 5.9$ Hz). $^{31}$P NMR (CDCl$_3$, 162 MHz): $\delta$ 24.2. HRMS (EI-TOF) ($m/z$): calcd for C$_{22}$H$_{18}$O$_2$PBr [M$^+$] 424.0228 found 424.0230.

(3-(hydroxymethyl)-4,4-dimethylpenta-1,2-dien-1-yl)diphenylphosphine oxide (3l). [Eluent for silica-gel column chromatography: PE/EtOAc = 1/1 to 1/3. Obtained amount and yield: 66.5 mg, 68%]: $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.83-7.73 (m, 4H), 7.50-7.39 (m, 6H), 5.96-5.93 (m, 1H), 4.15-4.02 (m, 2H), 3.72 (br, 1H), 0.84 (s, 9H). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 208.6, 133.0 (d, $J_{P-C} = 78.5$ Hz), 132.6, 131.8 (d, $J_{P-C} = 1.8$ Hz), 131.5, 131.44 (d, $J_{P-C} = 2.0$ Hz), 131.36, 128.4 (d, $J = 9.4$ Hz), 128.3 (d, $J = 9.4$ Hz), 117.6 (d, $J_{P-C} = 13.7$ Hz), 88.5 (d, $J_{P-C} = 104.6$ Hz), 59.1 (d, $J_{P-C} = 6.4$ Hz), 32.9 (d, $J_{P-C} = 4.6$ Hz), 29.0 (d, $J_{P-C} = 2.3$ Hz). $^{31}$P NMR (CDCl$_3$, 162 MHz): $\delta$ 25.3. HRMS (EI-TOF) ($m/z$): calcd for C$_{20}$H$_{23}$O$_2$P [M$^+$] 326.1436 found 326.1438.
dimethyl (2-(2-hydroxycyclohexylidene)vinyl)phosphonate (3m). Obtained as a 56:44 diastereoisomer mixture. The dr value was determined from the $^{31}$P NMR analysis. [Eluent for silica-gel column chromatography: PE/EtOAc = 1/3. Obtained amount and yield: 53.4 mg, 77%]. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 5.36-5.29 (m, 1H), 4.17-4.13 (m, 1H), 4.03 (br, 1H), 3.74-3.70 (m, 6H), 2.47-2.41 (m, 1H), 2.08-1.39 (m, 7H). $^{31}$P NMR (CDCl$_3$, 162 MHz): $\delta$ 19.4, 19.3. HRMS (EI-TOF) (m/z): calcd for C$_{10}$H$_{17}$O$_4$P [M$^+$] 232.0864; found 232.0869.

(2-(2-hydroxycyclohexylidene)vinyl)diphenylphosphine oxide (3n). The compound was obtained as a 75:25 diastereoisomer mixture. [Eluent for silica-gel column chromatography: PE/EtOAc = 3/1. Obtained amount and yield: 70.2 mg, 72%]. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.85-7.78 (m, 2H), 7.62-7.67 (m, 2H), 7.49-7.38 (m, 6H), 5.85-5.83 (m, 1H), 4.02-3.98 (m, 1H), 4.00 (br, 1H), 2.26-2.16 (m, 1H), 1.90-1.78 (m, 2H), 1.58-1.55 (m, 1H), 1.45-1.39 (m, 1H), 1.30-1.06 (m, 3H). $^{31}$P NMR (CDCl$_3$, 162 MHz): $\delta$ 26.2. $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 206.6, 206.1, 132.8, 132.7 131.7, 131.6, 131.5, 131.4, 131.3, 131.2, 128.3 (d, $J_{P-C} = 8.7$ Hz), 128.2 (d, $J_{P-C} = 8.8$ Hz), 109.5 (d, $J_{P-C} = 12.9$ Hz), 109.3 (d, $J_{P-C} = 13.8$ Hz), 87.0 (d, $J_{P-C} = 105.8$ Hz), 86.2 (d, $J_{P-C} = 105.7$ Hz), 68.3 (d, $J_{P-C} = 2.7$ Hz), 68.0 (d, $J_{P-C} = 3.3$ Hz), 34.8, 34.6, 28.2 (d, $J_{P-C} = 4.7$ Hz), 27.5 (d, $J_{P-C} = 4.7$ Hz), 25.8, 25.5, 22.9, 22.3. HRMS (EI-TOF) (m/z): calcd for C$_{20}$H$_{21}$O$_2$P [M$^+$] 324.1279; found 324.1282.

NOTE: The diastereomeric ratio of 3n can not be directly determined from its $^1$H and $^{31}$P NMR spectra due to the overlap of the signals. Performing the esterification of 3n with HOAc (1.2 equiv) in the presence of DMAP (0.1 equiv) and DCC (1.2 equiv) afforded the esterified derivative, namely 2-(2-(diphenylphosphoryl)vinylidene)cyclohexyl acetate (3n-SI). From the $^1$H and $^{31}$P NMR spectra (see below, Figure S1), we got the dr value of ca. 3/1.
$^1$H NMR spectra of 2-(2-(diphenylphosphoryl)vinylidene)cyclohexyl acetate (3n-SI)

$^{31}$P NMR spectra of 2-(2-(diphenylphosphoryl)vinylidene)cyclohexyl acetate (3n-SI)

Figure S1. $^1$H and $^{31}$P NMR spectra of 2-(2-(diphenylphosphoryl)vinylidene)cyclohexyl acetate (3n-SI)
dimethyl (4-hydroxy-3-methylnona-1,2-dien-1-yl)phosphonate (3o).

The compound was obtained as a 55:45 diastereoisomer mixture. [Eluent for silica-gel column chromatography: PE/EtOAc = 3/1. Obtained amount and yield: 44.1 mg, 56%]: 1H NMR (CDCl3, 400 MHz): δ 5.23–5.21 (m, 0.55H), 5.16–5.13 (m, 0.45H), 4.14–4.11 (m, 0.45), 4.05–4.00 (m, 0.55H), 3.70–3.67 (m, 7H), 1.76–1.71 (m, 3H), 1.57–1.49 (m, 2H), 1.40–1.20 (m, 6H), 0.85–0.82 (m, 3H). 31P NMR (CDCl3, 162 MHz): δ 19.38, 19.27. HRMS (EI-TOF) (m/z): calcd for C12H23O4P [M+] 262.1334 found 262.1337.

dimethyl (5-hydroxy-3-(hydroxymethyl)penta-1,2-dien-1-yl)phosphonate (3p). [Eluent for silica-gel column chromatography: EtOAc. Obtained amount and yield: 42.6 mg, 64%]: 1H NMR (CDCl3, 400 MHz): δ 5.31 (s, 1H), 4.19–4.08 (m, 4H), 3.72 (d, J = 11.6 Hz, 6H), 3.71 (br 2H), 2.42–2.24 (m, 2H). 13C NMR (CDCl3, 100 MHz): δ 211.3, 104.7 (d, JP-C = 16.7 Hz), 79.5 (d, Jp-C = 196.5 Hz), 62.1 (d, Jp-C = 7.6 Hz), 60.2 (d, Jp-C = 4.2 Hz), 52.95 (d, Jp-C = 5.6 Hz), 52.89 (d, Jp-C = 6.0 Hz), 32.1 (d, Jp-C = 6.9 Hz). 31P NMR (CDCl3, 162 MHz): δ 20.3. HRMS (EI-TOF) (m/z): calcd for C8H15O5P [M+] 222.0657 found 222.0659.

dimethyl (1-hydroxy-2-phenyldeca-2,3-dien-4-yl)phosphonate (4a).

[Eluent for silica-gel column chromatography: PE/EtOAc = 10/1 to 1/1. Obtained amount and yield: 79.7 mg, 79%]: 1H NMR (CDCl3, 400 MHz): δ 7.42–7.34 (m, 4H), 7.29–7.25 (m, 1H), 4.65–4.56 (m, 2H), 3.76–3.72 (m, 6H), 2.65 (br, 1H), 2.32–2.26 (m, 2H), 1.56–1.49 (m, 2H), 1.35–1.25 (m, 6H), 0.85 (t, J = 6.0 Hz, 3H). 13C NMR (CDCl3, 100 MHz): δ 208.7 (d, Jp-C = 4.5 Hz), 132.9 (d, Jp-C = 7.4 Hz), 128.7 (d, Jp-C = 1.4 Hz), 127.7 (d, Jp-C = 1.4 Hz), 126.3 (d, Jp-C = 3.4 Hz), 109.5 (d, Jp-C = 16.7 Hz), 98.2 (d, Jp-C = 183.8 Hz), 61.4 (d, Jp-C = 6.6 Hz), 53.05 (d, Jp-C = 3.4 Hz), 52.98 (d, Jp-C = 3.5 Hz), 31.5, 29.0 (d, Jp-C = 5.6 Hz), 28.8, 28.2 (d, Jp-C = 6.6 Hz), 22.6, 14.0. 31P NMR (CDCl3, 162 MHz): δ 20.2. HRMS (EI-TOF) (m/z): calcd for C18H27O4P [M+] 338.1647; found 338.1645.

dimethyl (4-hydroxy-1,3-diphenylbuta-1,2-dien-1-yl)phosphonate (4b).

[Eluent for silica-gel column chromatography: PE/EtOAc = 10/1 to 1/1. Obtained amount and yield: 19.4 mg, 20%]: 1H NMR (CDCl3, 400 MHz): δ 7.60 (d, J = 7.6 Hz, 2H), 7.46 (d, J = 7.6 Hz, 2H),
7.39-7.27 (m, 6H), 4.74 (d, J = 5.2 Hz, 2H), 3.79 (dd, J₁ = 20.4 Hz, J₂ = 7.6 Hz, 6H), 2.62 (br, 1H).

$\text{${}^{13}$C NMR (CDCl₃, 100 MHz): } \delta 212.0, 132.1 \text{ (d, } J_{P,C} = 7.1 \text{ Hz), } 131.2 \text{ (d, } J_{P,C} = 7.5 \text{ Hz), } 129.0, 128.8, 128.2 \text{ (d, } J_{P,C} = 3.3 \text{ Hz), } 127.6 \text{ (d, } J_{P,C} = 6.0 \text{ Hz), } 126.5, 110.9 \text{ (} J_{P,C} = 15.1 \text{ Hz), } 101.0 \text{ (d, } J_{P,C} = 187.3 \text{ Hz), } 61.3 \text{ (d, } J_{P,C} = 5.8 \text{ Hz), } 55.3 \text{ (t, } J_{P,C} = 5.2 \text{ Hz).}$

$\text{${}^{31}$P NMR (CDCl₃, 162 MHz): } \delta 17.8.$

HRMS (EI-TOF) (m/z): calcd for C$_{18}$H$_{19}$O$_4$P [M⁺] 330.1021; found 330.1025.

![5a](image)

1-methoxy-2-phenyldec-3-yn-2-ol (5a). [Eluent for silica-gel column chromatography: PE/EtOAc = 10/1]: $^1$H NMR (CDCl₃, 400 MHz): $\delta$ 7.57 (d, J = 7.6 Hz, 2H), 7.39-7.30 (m, 3H), 7.33-3.59 (m, 2H), 3.26 (s, 3H), 2.39 (br, 1H), 2.38 (t, J = 7.2 Hz, 2H), 1.65-1.58 (m, 2H), 1.49-1.44 (m, 2H), 1.33-1.30 (m, 4H), 0.90 (t, J = 6.8 Hz, sH). $^{13}$C NMR (CDCl₃, 100 MHz): $\delta$ 139.0, 132.0, 128.3, 128.2, 90.4, 81.1, 71.9, 52.4, 31.3, 28.7, 28.6, 22.6, 18.9, 14.1.

HRMS (EI-TOF) (m/z): calcd for C$_{17}$H$_{24}$O$_2$ [M⁺] 260.1776; found 260.1776.

![5b](image)

1-methoxy-2,4-diphenylbut-3-yn-2-ol (5b). [Eluent for silica-gel column chromatography: PE/EtOAc = 10/1]: $^1$H NMR (CDCl₃, 400 MHz): $\delta$ 7.65 (d, J = 8.0 Hz, 2H), 7.57-7.55 (m, 2H), 7.43-7.35 (m, 6H), 3.84-3.75 (m, 2H), 3.36 (s, 3H), 2.47 (br, 1H). $^{13}$C NMR (CDCl₃, 100 MHz): $\delta$ 138.4, 132.0, 128.8, 128.42, 128.38, 127.0, 122.2, 89.4, 86.1, 81.4, 71.8, 52.7.

HRMS (EI-TOF) (m/z): calcd for C$_{17}$H$_{16}$O$_2$ [M⁺] 252.1150; found 252.1150.
Competition experiment

The reaction of 1a (0.2 mmol), 2a (0.2 mmol) and 2e (0.2 mmol) was performed in CH₃OH (2 mL) for 2 h. Removal of the solvent under reduced pressure afforded a slurry liquid, a small amount of which was dissolved in CDCl₃. The ³¹P NMR of the mixture was then recorded (Figure S2). Four peaks at 24.5, 21.7, 17.4 and 10.5 ppm were identified as the ³¹P NMR signals of 3j, 2e, 3a, and 2a. Yields of 3a and 3j were calculated based on the integration of the peaks.

Figure S2
Deuterium labeling experiments

The reaction of 1a-d (D% = ca. 93%, 0.24 mmol, 34.8 mg) and 2a (0.2 mmol, 22.1 mg) in CH₃OH (2 mL) afforded 3a (46.3 mg) in 91% yield (eq. s2).

On the other hand, the reaction of 1a (0.24 mmol, 34.6 mg) and 2a (0.2 mmol, 22.2 mg) in CH₃OD (D% > 99.5%, 2 mL) afforded the α-deuterated allenylphosphonate 3a-d (46.2 mg) in 90% yield (eq. s3). D% = 91%, determined from the ¹H NMR analysis (Figure S3). *Dimethyl (4-hydroxy-3-phenyl buta-1,2-dien-1-yl-1-d) phosphonate* (3a-d): ¹H NMR (CDCl₃, 400 MHz): δ 7.42–7.34 (m, 4H), 7.30–7.26 (m, 1H), 5.76-5.75 (m, 0.09H), 4.66-4.57 (m, 2H), 3.77 (d, J =11.6 Hz, 6H).

Figure S3
Synthetic transformations of 3a

To a solution of 3a (0.274 mmol, 69.5 mg) in CH₂Cl₂ (3 mL) at room temperature was added 2.0 equiv of I₂ (139.2 mg). The mixture was stirred overnight, then quenched with aq. Na₂S₂O₃ and extracted with CH₂Cl₂. The combined organic layers were washed with brine, dried over Na₂SO₄ and concentrated. The product 6 (61.1 mg, 61%) was obtained by purification by flash chromatography on silica (petroleum ether/ethyl acetate). The compound 6 was obtained as a diastereoisomers (dr: ca.4/1, determined from ³¹P NMR analysis). ¹H NMR (CDCl₃, 400 MHz): δ 7.51-7.39 (m, 5H), 6.76-6.65 (m, 1H), 4.37-4.20 (m, 3H), 3.96-3.90 (m, 3H). ³¹P NMR (CDCl₃, 162 MHz): δ 37.8, 37.2. HRMS (EI-TOF) (m/z): calcd for C₁₁H₂₂O₄PI [M⁺] 365.9518; found 365.9515.

To a mixture of 3a (0.257 mmol, 65.3 mg), [1,1'-biphenyl]-4-ylboronic acid (0.514 mmol, 101.8 mg) and water (2 mL) was added a catalytic amount of (Ph₃P)₂PdCl₂ (9 mg) under an atmosphere of N₂. After heated to reflux for 3 h, the reaction mixture was cooled down and extracted with EtOAc. The combined organic layers were washed with brine, dried with Na₂SO₄ and concentrated under reduced pressure. The pure product 7 (89.1 mg, 89%) was obtained by purification by flash chromatography on silica (petroleum ether/ethyl acetate). The exact configuration referring to the C-C double bonds in the product 7 has not been determined. We reason that this reaction proceeds with high stereoselectivity since the ¹H, ¹³C and ³¹P NMR data of 7 all indicate that only one of the stereoisomers is formed. ¹H NMR (CDCl₃, 400 MHz): δ 7.63 (d, J = 8.0 Hz, 4H), 7.52 (d, J = 8.0 Hz, 2H), 7.37-7.32 (m, 6H), 5.80 (d, J = 16.8 Hz, 1H), 5.54 (s, 1H), 5.24 (s, 1H), 3.46 (d, J = 11.2 Hz, 6H). ¹³C NMR (CDCl₃, 100 MHz): δ 160.1 (d, J = 6.7 Hz), 151.3 (J = 23.6 Hz), 141.0, 140.3, 139.6, 136.8 (J = 7.9 Hz), 129.7 (d, J = 1.9 Hz), 128.8, 128.4 (d, J = 5.0 Hz), 127.9, 127.5, 127.0, 126.4, 122.0, 118.1, 116.2, 52.1 (d, J = 6.5 Hz). ³¹P NMR (CDCl₃, 162 MHz): δ 19.5. HRMS (EI-TOF) (m/z): calcd for C₂₄H₂₃O₃P [M⁺] 390.1385; found 390.1389.

To a solution containing 3a (0.348 mmol, 88.3 mg), 3-phenylpropionic acid (0.383 mmol, 56.0 mg) and N, N-dimethylpyridin-4-amine (DMAP, 0.0348 mmol, 4.3 mg) in dry CH₂Cl₂ (3 mL) was added
a solution of dicyclohexylmethanediimine (DCC, 0.388 mmol, 80.1 mg) in CH₂Cl₂ (2 mL) at 0 °C. After the addition was complete, the reaction was naturally warmed to room temperature. Upon the consumption of 3a (monitored by TLC), the reaction mixture was filtrated and concentrated. The obtained residue was purified by column chromatography on silica gel (petroleum ether – ethyl acetate 3:1 to 1:1) to afford 8b (94.3 mg, 71%). 8a was obtained following a similar procedure.

\[
\begin{align*}
\text{AcO} & \quad \text{MeO} \\
\text{P} & \quad \text{O} \\
\text{MeO} & \quad \text{P} \\
\text{O} & \quad \text{MeO} \\
\text{Ph} & \quad \text{MeO} \\
\end{align*}
\]

\[8a\]

\[\text{\textsuperscript{1}H NMR (CDCl}_3, 400 \text{MHz}): \delta 7.38–7.37 (m, 4H), 7.32–7.28 (m, 1H), 5.85 (s, 1H), 5.08 (dd, J₁ = 5.6 Hz, J₂ = 2.8 Hz, 2H), 3.78 (t, J = 12.0 Hz, 6H), 2.10 (s, 3H). \text{\textsuperscript{13}C NMR (CDCl}_3, 100 \text{MHz}): \delta 212.4 (d, J_P-C = 1.3 Hz), 170.3, 131.2 (d, J_P-C = 7.0 Hz), 128.8 (d, J_P-C = 1.8 Hz), 128.1 (d, J_P-C = 1.9 Hz), 126.1 (d, J_P-C = 1.8 Hz), 104.0 (d, J_P-C = 16.8 Hz), 83.7 (d, J_P-C = 19.5 Hz), 61.3 (d, J_P-C = 6.5 Hz), 53.0 (d, J_P-C = 6.4 Hz), 20.7. \text{\textsuperscript{31}P NMR (CDCl}_3, 162 \text{MHz}): \delta 15.7. \text{HRMS (EI-TOF) (m/z): \text{calcd for } C_{14}H_{17}O_{5}P \text{ [M\textsuperscript{+}]} = 296.0814 \text{ found 296.0819.}}\]

\[\text{\textsuperscript{1}H NMR (CDCl}_3, 400 \text{MHz}): \delta 7.57 (d, J = 8.0 Hz, 2H), 7.48–7.32 (m, 8H), 5.90 (s, 1H), 5.29-5.18 (m, 2H), 3.80 (dd, J₁ = 11.6 Hz, J₂ = 7.6 Hz, 6H). \text{\textsuperscript{13}C NMR (CDCl}_3, 100 \text{MHz}): \delta 212.8 (d, J_P-C = 1.3 Hz), 153.5, 133.0, 131.1 (d, J_P-C = 8.1 Hz), 130.9, 129.0, 128.6, 128.4, 126.3 (d, J_P-C = 2.3 Hz), 119.3, 103.4 (d, J_P-C = 17.0 Hz), 87.4, 84.1 (d, J_P-C = 194.3 Hz), 80.1, 62.9 (d, J_P-C = 6.3 Hz), 53.2 (d, J_P-C = 6.1 Hz). \text{\textsuperscript{31}P NMR (CDCl}_3, 162 \text{MHz}): \delta 15.5. \text{HRMS (EI-TOF) (m/z): \text{calcd for } C_{21}H_{19}O_{5}P \text{ [M\textsuperscript{+}]} = 382.0970 \text{ found 382.0971.}}\]

A solution of 50.0 mg of 8b in toluene (3 mL) was heated to 110 °C for 48 h in a sealed tube. After removal of the solvent under a reduced pressure, the residue was passed through a short silica-gel column with PE-EtOAc as eluent. Pure product 9 was obtained by recrystallization from methol (20.3 mg, 41%). \[\text{\textsuperscript{1}H NMR (CDCl}_3, 400 \text{MHz}): \delta 8.23 (d, J = 7.6 Hz, 2H), 7.48–7.26 (m, 8H), 5.76 (d, J = 24.4 Hz, 1H), 5.38 (d, J = 16.4 Hz, 1H), 4.78 (d, J = 16.0 Hz, 1H), 3.46 (dd, J₁ = 11.6 Hz, J₂ = 11.2 Hz, 6H). \text{\textsuperscript{13}C NMR (CDCl}_3, 100 \text{MHz}): \delta 156.1, 150.4 (d, J_P-C = 9.7 Hz), 131.2, 131.4, 131.2, 129.6, 128.7, 128.6, 128.4, 126.9, 118.2, 74.5, 53.5 (d, J_P-C = 7.4 Hz), 52.8 (d, J_P-C = 7.7 Hz), 49.1 (d, J_P-C = 146.1 Hz). \text{\textsuperscript{31}P NMR (CDCl}_3, 162 \text{MHz}): \delta 23.4. \text{HRMS (EI-TOF) (m/z): \text{calcd for } C_{21}H_{19}O_{5}P \text{ [M\textsuperscript{+}]} = 382.0970 \text{ found 382.0971.}}\]
$^1$H NMR spectrum of dimethyl (4-hydroxy-3-phenylbuta-1,2-dien-1-yl)phosphonate (3a)

CDCl$_3$, 400 MHz
$^{13}$C NMR spectrum of dimethyl (4-hydroxy-3-phenylbuta-1,2-dien-1-yl)phosphonate (3a)

CDCl$_3$, 100 MHz
$^{31}$P NMR spectrum of dimethyl (4-hydroxy-3-phenylbuta-1,2-dien-1-yl)phosphonate (3a)
$CDCl_3$, 162 MHz
$^1$H NMR spectrum of dimethyl (3-(4-chlorophenyl)-4-hydroxybuta-1,2-dien-1-yl)phosphonate (3b)

CDCl$_3$, 400 MHz
$^{13}$C NMR spectrum of dimethyl (3-(4-chlorophenyl)-4-hydroxybuta-1,2-dien-1-yl)phosphonate (3b)

CDCl$_3$, 100 MHz
$^{31}P$ NMR spectrum of dimethyl (3-(4-chlorophenyl)-4-hydroxybuta-1,2-dien-1-yl)phosphonate (3b)

CDCl$_3$, 162 MHz
$^1$H NMR spectrum of dimethyl (3-(4-bromophenyl)-4-hydroxybuta-1,2-dien-1-yl)phosphonate (3c)

CDCl$_3$, 400 MHz
$^{13}$C NMR spectrum of dimethyl (3-(4-bromophenyl)-4-hydroxybuta-1,2-dien-1-yl)phosphonate (3c)

CDCl$_3$, 100 MHz
$^{31}P$ NMR spectrum of dimethyl (3-(4-bromophenyl)-4-hydroxybuta-1,2-dien-1-yl)phosphonate (3c)
CDCl$_3$, 162 MHz
$^1$H NMR spectrum of dimethyl (4-hydroxy-3-(4-(trifluoromethyl)phenyl)buta-1,2-dien-1-yl)phosphonate (3d)
CDCl$_3$, 400 MHz
$^{13}C$ NMR spectrum of dimethyl (4-hydroxy-3-(4-(trifluoromethyl)phenyl)buta-1,2-dien-1-yl)phosphonate (3d)
$CDCl_3$, 100 MHz
$^{31}$P NMR spectrum of dimethyl (4-hydroxy-3-(4-(trifluoromethyl)phenyl)buta-1,2-dien-1-yl)phosphonate (3d)
CDCl$_3$, 162 MHz
$^1H$ NMR spectrum of dimethyl (3-([1,1'-biphenyl]-4-yl)-4-hydroxybuta-1,2-dien-1-yl)phosphonate (3e)

CDCl$_3$, 400 MHz
$^{13}$C NMR spectrum of dimethyl (3-([1,1'-biphenyl]-4-yl)-4-hydroxybuta-1,2-dien-1-yl)phosphonate (3e)
CDCl$_3$, 100 MHz
$^{31}$P NMR spectrum of dimethyl (3-((1,1'-biphenyl)-4-yl)-4-hydroxybuta-1,2-dien-1-yl)phosphonate (3e)
CDCl$_3$, 162 MHz
$^1$H NMR spectrum of dimethyl (3-(hydroxymethyl)-4,4-dimethylpenta-1,2-dien-1-yl)phosphonate (3f)
CDCl$_3$, 400 MHz
$^{13}$C NMR spectrum of dimethyl (3-(hydroxymethyl)-4,4-dimethylpenta-1,2-dien-1-yl)phosphonate (3f)
$CDCl_3$, 100 MHz
$^{31}$P NMR spectrum of dimethyl (3-(hydroxymethyl)-4,4-dimethylpenta-1,2-dien-1-yl)phosphonate (3f)

CDCl$_3$, 162 MHz
$^1$H NMR spectrum of diethyl (4-hydroxy-3-phenylbuta-1,2-dien-1-yl)phosphonate (3g)

$CDCl_3$, 400 MHz
$^{13}$C NMR spectrum of diethyl (4-hydroxy-3-phenylbuta-1,2-dien-1-yl)phosphonate (3g)

CDCl$_3$, 100 MHz
$^{31}$P NMR spectrum of diethyl (4-hydroxy-3-phenylbuta-1,2-dien-1-yl)phosphonate (3g)
$CDCl_3$, 162 MHz
$^1$H NMR spectrum of dibutyl (4-hydroxy-3-phenylbuta-1,2-dien-1-yl)phosphonate (3h)

CDCl$_3$, 400 MHz
$^{13}$C NMR spectrum of dibutyl (4-hydroxy-3-phenylbuta-1,2-dien-1-yl)phosphonate (3h)

CDCl$_3$, 100 MHz
$^{31}$P NMR spectrum of dibutyl (4-hydroxy-3-phenylbuta-1,2-dien-1-yl)phosphonate (3h)

CDCl$_3$, 162 MHz
$^1$H NMR spectrum of (4-hydroxy-3-phenylbuta-1,2-dien-1-yl)diphenylphosphine oxide (3j)

CDCl$_3$, 400 MHz
$^{13}C$ NMR spectrum of (4-hydroxy-3-phenylbuta-1,2-dien-1-yl)diphenylphosphine oxide (3j)

CDCl$_3$, 100 MHz
$^{31}$P NMR spectrum of (4-hydroxy-3-phenylbuta-1,2-dien-1-yl)diphenylphosphine oxide (3j)

$CDCl_3$, 162 MHz
$^1$H NMR spectrum of (3-(4-bromophenyl)-4-hydroxybuta-1,2-dien-1-yl)diphenylphosphine oxide (3k)
CDCl$_3$, 400 MHz
$^{13}$C NMR spectrum of (3-(4-bromophenyl)-4-hydroxybuta-1,2-dien-1-yl)diphenylphosphine oxide (3k) 
$CDCl_3$, 100 MHz
$^{31}$P NMR spectrum of (3-(4-bromophenyl)-4-hydroxybuta-1,2-dien-1-yl)diphenylphosphine oxide (3k)

CDCl$_3$, 162 MHz
$^1$H NMR spectrum of (3-(hydroxymethyl)-4,4-dimethylpenta-1,2-dien-1-yl)diphenylphosphine oxide (3I)
CDCl₃, 400 MHz
$^{13}$C NMR spectrum of (3-(hydroxymethyl)-4,4-dimethylpenta-1,2-dien-1-yl)diphenylphosphine oxide (3l)
$CDCl_3$, 100 MHz
$^{31}P$ NMR spectrum of (3-(hydroxymethyl)-4,4-dimethylpenta-1,2-dien-1-yl)diphenylphosphine oxide (3I)
$CDCl_3$, 162 MHz
$^1$H NMR spectrum of dimethyl (2-(2-hydroxycyclohexyldene)vinyl)phosphonate (3m). The compound was obtained as a diastereoisomer mixture.

CDCl$_3$, 400 MHz
$^{13}$C NMR spectrum of dimethyl (2-(2-hydroxycyclohexylidene)vinyl)phosphonate (3m). The compound was obtained as a diastereoisomer mixture.

CDCl$_3$, 100 MHz
$^31$P NMR spectrum of dimethyl (2-(2-hydroxycyclohexylidene)vinyl)phosphonate (3m). The compound was obtained as a diastereoisomer mixture.

CDCl$_3$, 162 MHz
$^1$H NMR spectrum of (2-(2-hydroxycyclohexylidene)vinyl)diphenylphosphine oxide (3n)
CDCl$_3$, 400 MHz
$^{13}$C NMR spectrum of (2-(2-hydroxycyclohexylidene)vinyl)diphenylphosphine oxide (3n)
$CDCl_3$, 100 MHz
$^{31}P$ NMR spectrum of (2-(2-hydroxycyclohexylidene)vinyl)diphenylphosphine oxide (3n)

$CDCl_3$, 162 MHz
$^1$H NMR spectrum of dimethyl (4-hydroxy-3-methylnona-1,2-dien-1-yl)phosphonate (3o)

CDCl$_3$, 400 MHz
$^{31}$P NMR spectrum of dimethyl (4-hydroxy-3-methylnona-1,2-dien-1-yl)phosphonate (3o)

CDCl$_3$, 162 MHz
$^1$H NMR spectrum of dimethyl (5-hydroxy-3-(hydroxymethyl)penta-1,2-dien-1-yl)phosphonate (3p)

CDCl$_3$, 400 MHz
$^{13}$C NMR spectrum of dimethyl (5-hydroxy-3-(hydroxymethyl)penta-1,2-dien-1-yl)phosphonate (3p)
$CDCl_3$, 400 MHz
$^{31}$P NMR spectrum of dimethyl (5-hydroxy-3-(hydroxymethyl)penta-1,2-dien-1-yl)phosphonate (3p)

CDCl$_3$, 162 MHz
$^1$H NMR spectrum of dimethyl (1-hydroxy-2-phenyldeca-2,3-dien-4-yl)phosphonate (4a)

CDCl$_3$, 400 MHz
$^{13}$C NMR spectrum of dimethyl (1-hydroxy-2-phenyldeca-2,3-dien-4-yl)phosphonate (4a)

CDCl$_3$, 100 MHz
$^31$P NMR spectrum of dimethyl (1-hydroxy-2-phenyldeca-2,3-dien-4-yl)phosphonate (4a)
$CDCl_3, 160 MHz$
$^1$H NMR spectrum of dimethyl (4-hydroxy-1,3-diphenylbuta-1,2-dien-1-yl)phosphonate (4b)
CDCl$_3$, 400 MHz
$^{13}$C NMR spectrum of dimethyl (4-hydroxy-1,3-diphenylbuta-1,2-dien-1-yl)phosphonate (4b)

$CDCl_3, 100 MHz$
$^{31}$P NMR spectrum of dimethyl (4-hydroxy-1,3-diphenylbuta-1,2-dien-1-yl)phosphonate (4b)
$CDCl_3, 162 MHz$
$^1$H NMR spectrum of 1-methoxy-2-phenyldodec-3-yn-2-ol (5a)
CDCl$_3$, 400 MHz
$^{13}$C NMR spectrum of 1-methoxy-2-phenyldec-3-yn-2-ol (5a)
CDCl$_3$, 100 MHz
$^1$H NMR spectrum of 1-methoxy-2,4-diphenylbut-3-yn-2-ol (5b)

CDCl$_3$, 400 MHz
$^{13}$C NMR spectrum of 1-methoxy-2,4-diphenylbut-3-yn-2-ol (5b)
$CDCl_3$, 100 MHz
$^1$H NMR spectrum of compound 6
CDCl$_3$, 400 MHz
$^{31}P$ NMR spectrum of compound 6

CDCl$_3$, 162 MHz
$^1$H NMR spectrum of compound 7

CDCl₃, 400 MHz
$^{13}$C NMR spectrum of compound 7
$CDCl_3$, 100 MHz
$^{31}P$ NMR spectrum of compound 7
$CDCl_3, 162 MHz$
$^1$H NMR spectrum of compound 8a

CDCl$_3$, 400 MHz
$^{13}$C NMR spectrum of compound 8a

CDCl$_3$, 100 MHz
$^{31}$P NMR spectrum of compound 8a

CDCl$_3$, 162 MHz
$^1$H NMR spectrum of compound 8b

CDCl$_3$, 400 MHz
$^{13}$C NMR spectrum of compound 8b

CDCl$_3$, 100 MHz
$^{31}$P NMR spectrum of compound 8b

CDCl$_3$, 162 MHz
$^1$H NMR spectrum of compound 9

CDCl$_3$, 400 MHz
$^{13}$C NMR spectrum of compound 9
CDCl$_3$, 100 MHz
$^{31}P$ NMR spectrum of compound 9
$CDCl_3, 162 MHz$