Experimental Procedure:

The synthesis of diethyl (E)-2-phenylethenyl-phosphonate is representative. Pinacolato (E)-2-phenylethenylboronate (230 mg, 1.0 mmol), $P(OEt)_3$ (332 mg. 2.0 mmol) and $Pd(OAc)_2$ (9 mg, 0.04 mmol) were heated at 95 ^oC in a 10 mL round-bottomed flask under an oxygen atomosphere. The reaction mixture was dissolved in EtOAc, washed with H_2O (10 mL) dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. Silica gel chromatography (40% EtOAc-hexane) afforded diethyl (E)-2-phenylethenylphosphonate (187 mg, 78% yield). ^1H NMR (250 MHz) and ^{13}C NMR (62.5 MHz) spectra were run in $CDCl_3$. ^{31}P NMR spectra were run in $CDCl_3$ using H_3PO_4 (85 Wt. % solution in water, available commercially) as reference.

1. Diethyl (*E*)-2-phenylethenylphosphonate [5i, 6] (entry 1)

^1H NMR (250 MHz, $CDCl_3$): δ 1.36 (t, J = 6.94 Hz, 6H, C<u>H</u>$_3$), 4.08–4.19 (m, 4H, C<u>H</u>$_2$), 6.27 (t, $^2J_{P\text{-}H} = {}^3J_{H\text{-}H}$ = 17.58 Hz, 1H, C<u>H</u>P), 7.37–7.59 (m, 6H, C<u>H</u>Ph and aromatic protons). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 16.23 (2<u>C</u>H$_3$), 61.67 (d, $^2J_{P\text{-}C}$ = 4.94 Hz, 2<u>C</u>H$_2$), 113.78 (d, $^1J_{P\text{-}C}$ = 190.18 Hz, <u>C</u>HP), 127.53 (2<u>C</u>H, aromatic *meta*), 128.68 (2 <u>C</u>H, aromatic *ortho*), 130.07 (<u>C</u>H, aromatic *para*), 134.67 (d, $^3J_{P\text{-}C}$ = 22.87 Hz, aromatic <u>C</u>), 148.54 (<u>C</u>HPh). ^{31}P NMR (400 MHz, $CDCl_3$): δ 20.15 (s).

2. Diethyl (*Z*)-2-phenylethenylphosphonate [5e, 5i, 6, 8] (entry 2)

^1H NMR (250 MHz, $CDCl_3$): δ 1.18 (t, J = 7.10 Hz, 6H, C<u>H</u>$_3$), 3.94–4.05 (m, 4H, C<u>H</u>$_2$), 5.81 (dd, $^2J_{P\text{-}H}$ = 15.41, $^3J_{H\text{-}H}$ = 14.36, 1H, C<u>H</u>P), 7.16–7.70 (m, 6H, C<u>H</u>Ph and aromatic protons). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 16.04 (2<u>C</u>H$_3$), 61.74 (d, $^2J_{P\text{-}C}$ = 5.18 Hz, 2 <u>C</u>H$_2$), 116.58 (d, $^1J_{P\text{-}C}$ = 184.81 Hz, <u>C</u>HP), 128.11 (2<u>C</u>H, aromatic *meta*), 129.30 (<u>C</u>H, aromatic para), 129.54 (<u>C</u>H, aromatic *ortho*), 135.27 (d, $^3J_{P\text{-}C}$ = 9.19 Hz, aromatic <u>C</u>), 148.37 (<u>C</u>HPh). ^{31}P NMR (400 MHz, $CDCl_3$): δ 16.63 (s).

3. Diethyl (*E*)-2-(4'-chlorophenyl)ethenylphosphonate [5i] (entry 3)

^1H NMR (250 MHz, $CDCl_3$): δ 1.35 (t, J = 6.88 Hz, 6H, C<u>H</u>$_3$), 4.08–4.20 (m, 4H, C<u>H</u>$_2$), 6.23 (t, $^2J_{P\text{-}H} = {}^3J_{H\text{-}H}$ = 17.23 Hz, 1H, C<u>H</u>P), 7.29–7.53 (m, 5H, aromatic protons and ArC<u>H</u>). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 16.30 (2<u>C</u>H$_3$), 61.88 (d, $^2J_{P\text{-}C}$ = 5.18 Hz, 2<u>C</u>H$_2$), 114.74 (d, $^1J_{P\text{-}C}$ = 190.81 Hz, <u>C</u>HP), 128.84 (2<u>C</u>H, aromatic, *ortho* to –Cl), 129.07 (2<u>C</u>H, aromatic, *meta* to –Cl), 133.31 (d, $^3J_{P\text{-}C}$ = 23.31 Hz, aromatic <u>C</u>-CH=CH) 136.06 (aromatic <u>C</u>-Cl), 147.16 (d, $^2J_{P\text{-}C}$ = 6.37 Hz, Ar<u>C</u>H). ^{31}P NMR (400 MHz, $CDCl_3$): δ 19.56 (s).

4. Diethyl (*Z*)-2- (4'-chlorophenyl)ethenylphosphonate [5i] (entry 4)

^1H NMR (250 MHz, $CDCl_3$): δ 1.22 (t, J = 7.00 Hz, 6H, 2C<u>H</u>$_3$), 3.96–4.07 (m, 4H, 2C<u>H</u>$_2$), 5.83 (t, $^2J_{P\text{-}H} = {}^3J_{H\text{-}H}$ = 14.47 Hz, 1H, C<u>H</u>P), 7.11 (d, $^3J_{H\text{-}H}$ = 14.23 Hz , ArC<u>H</u>), 7.35 (d, J = 8.51 Hz, aromatic C<u>H</u>, *ortho* to –Cl), 7.65 (d, J = 8.49 Hz, aromatic C<u>H</u>, *meta* to –Cl). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 16.25 (2 <u>C</u>H$_3$), 61.92 (2 <u>C</u>H$_2$), 117.42 (d, $^1J_{P\text{-}C}$ = 185.74 Hz, <u>C</u>HP), 128.40 (2 <u>C</u>H, aromatic, *ortho* to –Cl), 131.02 (2 <u>C</u>H, aromatic, *meta* to –Cl), 134.87 (d, $^3J_{P\text{-}C}$ = 13.26 Hz, aromatic <u>C</u>-CH), 136.04 (aromatic <u>C</u>-Cl), 146.86 (<u>C</u>HAr). ^{31}P NMR (400 MHz, $CDCl_3$): δ 18.00 (s).

5. Diethyl (*E*)- octenylphosphonate [5b] (entry 5)

^1H NMR (300 MHz, $CDCl_3$): δ 0.88 (t, J = 6.72 Hz, 3H, C<u>H</u>$_3$(CH$_2$)$_5$), 1.23–1.63 (m, 14H, CH$_2$(C<u>H</u>$_2$)$_4$CH$_3$, C<u>H</u>$_3$CH$_2$O), 2.18–2.23 (m, 2H, C<u>H</u>$_2$CH=CH), 4.01–4.13 (m, 4H, OC<u>H</u>$_2$CH$_3$), 5.64 (dd, $^2J_{P\text{-}H}$ = 19.20 Hz, $^3J_{H\text{-}H}$ = 17.16 Hz, 1H, C<u>H</u>P), 6.68–6.86 (m, 1H, C<u>H</u>=CHP). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 13.99 (<u>C</u>H$_3$(CH$_2$)$_5$), 16.30 (2CH$_3$, <u>C</u>H$_3$CH$_2$O), 22.54 (CH$_3$<u>C</u>H$_2$(CH$_2$)$_4$), 27.70 (CH$_3$CH$_2$<u>C</u>H$_2$(CH$_2$)$_3$), 28.96 (CH$_3$(CH$_2$)$_2$<u>C</u>H$_2$(CH$_2$)$_2$), 31.66 (CH$_3$(CH$_2$)$_3$<u>C</u>H$_2$CH$_2$), 34.10 (d, $^3J_{P\text{-}C}$ = 21.43 Hz, <u>C</u>H$_2$CH=CHP), 61.50 (d, $^2J_{P\text{-}C}$ = 4.62 Hz, 2CH$_2$, OC<u>H</u>$_2$CH$_3$), 116.61 (d, $^1J_{P\text{-}C}$ = 186.37, <u>C</u>HP), 154.00 (d, $^2J_{P\text{-}C}$ = 3.81 Hz, <u>C</u>H=CHP). ^{31}P NMR (400 MHz, $CDCl_3$): δ 19.58 (s).

6. Diethyl (*Z*)-octenylphosphonate [13a] (entry 6)

^1H NMR (250 MHz, $CDCl_3$): δ 0.88 (br s, 3H, C<u>H</u>$_3$(CH$_2$)$_5$), 1.25–1.67 (m, 14H, CH$_3$(C<u>H</u>$_2$)$_4$CH$_2$, OCH$_2$C<u>H</u>$_3$), 2.31–2.53 (m, 2H, C<u>H</u>$_2$CH=CH), 3.99–4.17 (m, 4H, OC<u>H</u>$_2$CH$_3$), 5.57 (dd, $^2J_{P\text{-}H}$ = 19.91 Hz, $^3J_{H\text{-}H}$ = 12.88 Hz, 1H, C<u>H</u>P), 6.35–6.39 (m), 6.56– 6.61 (m) (1H, C<u>H</u>=CHP). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 14.04 (<u>C</u>H$_3$(CH$_2$)$_5$), 16.35 (2CH$_3$, <u>C</u>H$_3$CH$_2$O), 22.57 (CH$_3$<u>C</u>H$_2$(CH$_2$)$_4$), 28.91 (CH$_3$CH$_2$<u>C</u>H$_2$(CH$_2$)$_3$), 29.71 (CH$_3$(CH$_2$)$_2$<u>C</u>H$_2$(CH$_2$)$_2$), 30.46 (d, $^3J_{P\text{-}C}$ = 32.00 Hz, <u>C</u>H$_2$CH=CHP), 31.65 (<u>C</u>H$_2$CH$_2$CH=CHP), 61.32 (2CH$_2$, CH$_3$<u>C</u>H$_2$O), 116.32 (d, $^1J_{P\text{-}C}$ = 183.44 Hz, <u>C</u>HP), 154.37 (<u>C</u>H=CHP). ^{31}P NMR (400 MHz, $CDCl_3$): δ 15.95 (s).

7. Diethyl (*E*)-2-(4'-fluorophenyl)ethenylphosphonate[13b] (entry 7)

^{1}H NMR (250 MHz, $CDCl_3$): δ 1.35 (t, J = 6.98 Hz, 6H, C$\underline{H}_3$), 4.08–4.20 (m, 4H, C$\underline{H}_2$), 6.18 (t, $^{2}J_{P\text{-}H}$ = $^{3}J_{H\text{-}H}$ = 17.32 Hz, 1H, C$\underline{H}$P), 7.08 (t, J = 8.5 Hz, 2H, aromatic C$\underline{H}$ *ortho* to –F), 7.39–7.54 (m, 3H, aromatic C$\underline{H}$, *meta* to –F and C$\underline{H}$=CHP). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 16.35 (2 $\underline{C}H_3$), 61.83 (2 $\underline{C}H_2$), 113.64 (d, $^{1}J_{P\text{-}C}$ = 191.50 Hz, $\underline{C}$HP), 115.87 (d, J = 21.69 Hz, 2CH, aromatic $\underline{C}$H *ortho* to –F), 129.49 (d, J = 8.12 Hz, 2CH, aromatic $\underline{C}$H *meta* to –F), 131.00 (d, $^{3}J_{P\text{-}C}$ = 22.87 Hz, aromatic $\underline{C}$-CH=CHP), 147.26 ($\underline{C}$H=CHP), 163.56 (d, $^{1}J_{C\text{-}F}$ = 246.06 Hz, aromatic $\underline{C}$-F). ^{31}P NMR (400 MHz, $CDCl_3$): δ 19.95 (s).

8. Diethyl (*E*)-2-phenyl-1-methylethenylphosphonate[13c] (entry 8)

^{1}H NMR (250 MHz , $CDCl_3$): δ 1.34 (t, J = 7.10 Hz, 6H, $\underline{C}H_3CH_2O$), 2.08 (dd, $^{3}J_{P\text{-}H}$ = 15.33 Hz, $^{4}J_{H\text{-}H}$ = 1.40 Hz, 3H, C$\underline{H}_3$-C=CH), 4.07–4.23 (m, 4H, OC$\underline{H}_2$CH$_3$), 7.30–7.62 (m, 5H, aromatic), 8.11 (d, $^{3}J_{P\text{-}H}$ = 8.65 Hz, PhC$\underline{H}$=C). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 14.24 (d, $^{2}J_{P\text{-}C}$ = 9.81 Hz, $\underline{C}H_3$-C=CH), 16.35 (2CH$_3$, $\underline{C}H_3CH_2O$), 61.94 (d, $^{2}J_{P\text{-}C}$ = 5.31 Hz, 2CH$_2$, O$\underline{C}H_2CH_3$), 128.36 (4 aromatic $\underline{C}$H), 129.45 (aromatic $\underline{C}$H), 131.69 (d, $^{1}J_{P\text{-}C}$ = 202.69 Hz, CH$_3\underline{C}$-P), 135.61 (d, $^{3}J_{P\text{-}C}$ = 30.31 Hz, aromatic $\underline{C}$), 142.83 (d, $^{2}J_{P\text{-}C}$ = 11.69 Hz, $\underline{C}$H=C-P). ^{31}P NMR (400 MHz, $CDCl_3$): δ 22.81 (s).

9. Dimethyl (*E*)-octenylphosphonate[5b]

^{1}H NMR (250 MHz, $CDCl_3$): δ 0.88 (t, J = 6.75 Hz, 3H, C$\underline{H}_3$(CH$_2$)$_5$), 1.28–1.46 (m, 8H, CH$_3$(C$\underline{H}_2$)$_4$CH$_2$), 2.19–2.27 (m, 2H, C$\underline{H}_2$CH=CH), 3.72 (d, J = 11.08 Hz, 2 OC$\underline{H}_3$) 5.62 (ddd, $^{2}J_{P\text{-}H}$ = 21.33 Hz, $^{3}J_{H\text{-}H}$ = 17.14 Hz, $^{4}J_{H\text{-}H}$ = 1.39 Hz, 1H, C$\underline{H}$P), 6.71–6.92 (m, 1H, C$\underline{H}$=CHP). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 13.93 ($\underline{C}H_3$(CH$_2$)$_5$), 22.43 ($\underline{C}H_2CH_3$), 27.60 ($\underline{C}H_2CH_2CH_3$), 28.63 ($\underline{C}H_2$(CH$_2$)$_2$CH$_3$), 31.46 ($\underline{C}H_2$(CH$_2$)$_3$CH$_3$), 34.11 (d, $^{3}J_{P\text{-}C}$ = 21.37 Hz, $\underline{C}H_2$CH=CH), 52.13 (d, $^{2}J_{P\text{-}C}$ = 4.25 Hz, 2CH$_3$, O$\underline{C}H_3$), 115.12 (d, $^{1}J_{P\text{-}C}$ = 186.87 Hz, $\underline{C}$HP), 155.03 (d, $^{2}J_{P\text{-}C}$ = 3.37 Hz, $\underline{C}$H=CHP). ^{31}P NMR (400 MHz, $CDCl_3$): δ 22.33 (s).