Supporting Information
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Supporting information

General Procedure for the Preparation of α-hydroxyphosphonates: A solution of sodium ethoxide (0.786 g, 1.008 mmol, 1.2 eq.) in CH₂Cl₂ (10 ml) was added diethyl phosphite (1.2 ml, 0.912 mmol, 1.05 eq.) via syringe at -35 °C under argon. The reaction was stirred for 30 min and a solution of 4-cyanobenzaldehyde (1 g, 7.6 mmol, 1.0 eq.) in CH₂Cl₂ (5 ml) was added. The mixture was stirred for 3-5 h. The reaction was quenched with 0.1 N HCl and the resulting solution were extracted with ethyl acetate. The organic layers dried with MgSO₄ and the solvents were removed in vacuo. The crude material was purified via flash column chromatography to yield the 1d as white solid (1.96 g, 96%).

Diethyl α-hydroxybenzylphosphonate (1a). ¹H NMR (300 MHz, CDCl₃): δ = 1.18-1.28 (m, 6H), 3.91-4.21 (m, 4H), 5.02 (d, ²JPH = 11.0 Hz, 1H), 7.27-7.37 (m, 3H), 7.49 (d, J = 7.5 Hz, 2H) ppm; ¹³C NMR (75 MHz, CDCl₃): δ= 16.3 (d, ³JPC = 2.0 Hz), 16.4 (d, ³JPC = 2.1 Hz), 63.0 (d, ²JPC = 7.4 Hz), 63.3 (d, ²JPC = 7.0 Hz), 70.6 (d, ¹JPC = 158.8 Hz), 127.1, 127.9, 128.1, 136.9 (d, ²JPC = 158.8 Hz) ppm.

Diethyl α-hydroxy-4-methylbenzylphosphonate (1b). ¹H NMR (300 MHz, CDCl₃): δ = 1.22 (t, J = 7.0 Hz, 3H), 1.28 (t, J = 7.0 Hz, 3H), 2.34 (s, 3H), 3.33 (br, 1H), 3.94-4.10 (m, 4H), 4.98 (d, ²JPH = 10.4 Hz, 1H), 7.17 (d, J = 7.8 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H) ppm; ¹³C NMR (75 MHz, CDCl₃): δ= 16.2 (d, ³JPC = 1.8 Hz), 16.3 (d, ³JPC = 2.0 Hz), 21.1, 62.8 (d, ²JPC = 7.3 Hz), 63.2 (d, ²JPC = 7.0 Hz), 70.4 (d, ¹JPC = 158.9 Hz), 127.0, 127.8, 133.7, 137.5 ppm.

Diethyl α-hydroxy-4-methoxybenzylphosphonate (1c). ¹H NMR (300 MHz, CDCl₃): δ = 1.23 (t, J = 7.0 Hz, 3H), 1.28 (t, J = 7.0 Hz, 3H), 3.81 (s, 3H), 3.92-4.11 (m, 4H), 4.95 (d, ²JPH = 10.4 Hz, 1H), 7.17 (d, J = 7.8 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H) ppm; ¹³C NMR (75 MHz, CDCl₃): δ= 16.2 (d, ³JPC = 2.4 Hz), 16.3 (d, ³JPC = 2.3 Hz), 55.1, 62.8 (d, ²JPC = 6.8 Hz), 63.1 (d, ²JPC = 6.8 Hz), 70.2 (d, ¹JPC = 159.8 Hz), 113.6, 128.4, 128.9, 159.3 ppm.

Diethyl α-hydroxy-4-cyanobenzylphosphonate (1d). ¹H NMR (300 MHz, CDCl₃): δ = 1.23-1.30 (m, 6H), 4.04-4.13 (m, 4H), 5.12 (d, ²JPH = 12.2 Hz, 1H), 7.61 (d, J = 8.7 Hz, 2H), 7.65 (d, J = 8.5 Hz, 2H) ppm; ¹³C NMR (75 MHz, CDCl₃): δ= 16.4 (d, ³JPC = 2.6 Hz), 16.5 (d, ³JPC = 2.4 Hz), 63.3 (d, ²JPC = 7.6 Hz), 63.9 (d, ²JPC = 7.1 Hz), 70.2 (d, ¹JPC = 157.8 Hz), 111.7, 118.8, 127.7, 132.0, 142.5 ppm.

Diethyl α-hydroxy-4-carbobenzyloxybenzylphosphonate (1e). ¹H NMR (300 MHz, CDCl₃): δ = 1.20-1.27 (m, 6H), 3.99-4.12 (m, 4H), 5.11 (d, ²JPH = 12.0 Hz, 1H), 5.18 (br, 1H), 5.36 (s, 2H), 7.34-7.46 (m, 5H), 7.56 (d, J = 6.7 Hz, 2H), 8.06 (d, J = 8.1 Hz, 2H) ppm; ¹³C NMR (75 MHz, CDCl₃): δ= 16.3 (d, ³JPC = 7.4 Hz), 63.6 (d, ²JPC = 7.0 Hz), 66.7, 70.4 (d, ¹JPC = 157.5 Hz), 126.8, 126.9, 128.2, 128.5, 129.4, 129.5, 135.9, 142.1, 166.2 ppm; HRMS (EI) [M]+ 378.1234, Calculated Mass 378.1232.

Diethyl α-hydroxy-4-fluorobenzylphosphonate (1f). ¹H NMR (300 MHz, CDCl₃): δ = 1.21-1.30 (m, 6H), 4.04-4.13 (m, 4H), 5.00 (d, ²JPH = 10.3 Hz, 1H), 7.03-7.09 (m, 2H), 7.44-7.49 (m, 2H) ppm; ¹³C NMR (75 MHz, CDCl₃): δ= 16.1 (d, ³JPC = 5.6 Hz), 62.8 (d, ²JPC = 7.4 Hz), 63.2 (d, ²JPC = 7.1 Hz), 69.7 (d, ¹JPC = 161.0 Hz), 114.8 (d, ²JPC = 21.4 Hz), 128.7, 132.8, 162.2 (d, ¹JPC = 244.6 Hz) ppm.
Diethyl α-hydroxy-4-chlorobenzylphosphonate (1g). $^1$HNMR (300 MHz, CDCl$_3$): δ = 1.22-1.30 (m, 6H), 3.96-4.13 (m, 4H), 5.00 (d, $^2$J$_{PH}$ = 10.7 Hz, 1H), 7.34 (d, J = 8.3 Hz, 2H), 7.43 (d, J = 8.5 Hz, 2H) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$): δ= 16.3 (d, $^3$J$_{PC}$ = 5.5 Hz), 63.0 (d, $^2$J$_{PC}$ = 7.4 Hz), 63.4 (d, $^2$J$_{PC}$ = 7.0 Hz), 69.9 (d, $^1$J$_{PC}$ = 159.6 Hz), 128.3, 128.4, 133.6, 135.5 ppm.

Diethyl α-hydroxy-4-bromobenzylphosphonate (1h). $^1$HNMR (300 MHz, CDCl$_3$): δ = 1.25-1.30 (m, 6H), 4.04-4.07 (m, 4H), 4.98 (d, $^2$J$_{PH}$ = 10.5 Hz, 1H), 7.36 (d, J = 7.4 Hz, 2H), 7.49 (d, J = 7.6 Hz, 2H) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$): δ= 16.3 (d, $^3$J$_{PC}$ = 5.6 Hz), 63.0 (d, $^2$J$_{PC}$ = 7.4 Hz), 63.4 (d, $^2$J$_{PC}$ = 7.2 Hz), 69.9 (d, $^1$J$_{PC}$ = 160.6 Hz), 121.7, 128.7, 131.1, 136.0 ppm.

Diethyl α-hydroxy-2-nitrobenzylphosphonate (1i). $^1$HNMR (300 MHz, CDCl$_3$): δ = 1.20 (t, J = 7.0 Hz, 3H), 1.28 (t, J = 7.0 Hz, 3H), 4.06-4.15 (m, 4H), 6.26 (d, $^2$J$_{PH}$ = 14.2 Hz, 1H), 7.46 (t, J = 7.8 Hz, 1H), 7.69 (t, J = 7.5 Hz, 1H), 8.00 (d, J = 8.0 Hz, 2H) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$): δ = 16.2 (d, $^3$J$_{PC}$ = 8.7 Hz), 63.2 (d, $^2$J$_{PC}$ = 7.5 Hz), 64.1 (d, $^2$J$_{PC}$ = 7.0 Hz), 65.5 (d, $^1$J$_{PC}$ = 159.4 Hz), 124.6, 128.3, 128.9, 133.1, 133.2, 147.5 ppm.

Diethyl α-hydroxy-3-nitrobenzylphosphonate (1j). $^1$HNMR (300 MHz, CDCl$_3$): δ = 1.25-1.33 (m, 6H), 4.04-4.19 (m, 4H), 5.18 (dd, $^2$J$_{PH}$ = 11.3 Hz, J = 5.6 Hz, 1H), 5.47 (br, 1H), 7.53 (t, J = 7.9 Hz, 1H), 7.82 (d, J = 7.5 Hz, 1H), 8.17 (d, J = 8.0 Hz, 1H), 8.42 (s, 1H) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$): δ= 16.0 (d, $^3$J$_{PC}$ = 5.7 Hz), 63.1 (d, $^2$J$_{PC}$ = 7.5 Hz), 63.6 (d, $^2$J$_{PC}$ = 7.2 Hz), 69.3 (d, $^1$J$_{PC}$ = 161.0 Hz), 121.7, 122.4, 128.7, 132.9, 139.5, 147.8 ppm.

Diethyl α-hydroxy-4-nitrobenzylphosphonate (1k). $^1$HNMR (300 MHz, CDCl$_3$): δ = 1.24-1.32 (m, 6H), 4.05-4.18 (m, 4H), 5.18 (dd, $^2$J$_{PH}$ = 12.2 Hz, 1H), 7.68 (d, J = 7.6 Hz, 2H), 8.23 (d, J = 8.3 Hz, 2H) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$): δ= 16.3 (d, $^3$J$_{PC}$ = 5.6 Hz), 63.2 (d, $^2$J$_{PC}$ = 7.6 Hz), 63.9 (d, $^2$J$_{PC}$ = 7.2 Hz), 69.9 (d, $^1$J$_{PC}$ = 158.4 Hz), 123.1, 127.6, 144.5, 147.3 ppm.

General procedure for the preparation of α-fluorobenzylphosphonates from α-hydroxyphosphonates: $^2$ 1d (0.4 g, 1.486 mmol, 1.0 eq.) was dissolved in dry CH$_2$Cl$_2$ (40 ml) at -78 °C and DAST (0.224 ml, 2.228 mmol, 1.2 eq.) was added via syringe under argon. The reaction was stirred for 1 h and then allowed to warm to rt, and quenched with NaHCO$_3$ solution. The resulting solution was extracted with CH$_2$Cl$_2$. The combined organic layer was dried over MgSO$_4$ and removed solvent under reduced pressure. The crude material was purified via flash column chromatography to yield 2d as oil (0.342 g, 85%).

Diethyl α-fluoro-4-methylbenzylphosphonate (2b). $^1$HNMR (300 MHz, CDCl$_3$): δ = 1.25-1.33 (m, 6H), 2.36 (s, 3H), 3.98-4.16 (m, 4H), 5.18 (dd, $^2$J$_{PH}$ = 11.3 Hz, J = 5.6 Hz, 1H), 5.47 (br, 1H), 7.53 (t, J = 7.9 Hz, 1H), 7.82 (d, J = 7.5 Hz, 1H), 8.17 (d, J = 8.0 Hz, 1H), 8.42 (s, 1H) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$): δ= 16.2 (d, $^3$J$_{PC}$ = 8.7 Hz), 63.2 (d, $^2$J$_{PC}$ = 7.5 Hz), 63.6 (d, $^2$J$_{PC}$ = 7.2 Hz), 69.3 (d, $^1$J$_{PC}$ = 161.0 Hz), 121.7, 122.4, 128.7, 132.9, 139.5, 147.8 ppm.

Diethyl α-fluoro-4-cyanobenzylphosphonate (2d). $^1$HNMR (300 MHz, CDCl$_3$): δ = 1.27 (t, J = 7.0 Hz, 3H), 1.33 (t, J = 7.1 Hz, 3H), 4.05-4.22 (m, 4H), 5.78 (dd, $^2$J$_{PH}$ = 9.4 Hz, $^2$J$_{FH}$ = 44.8 Hz, 1H), 7.60 (d, J = 6.9 Hz, 2H), 7.71 (d, J = 8.1 Hz, 2H) ppm;
$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 16.2 (d, $^3$J$_{PC} = 5.5$ Hz), 16.3 (d, $^3$J$_{PC} = 5.6$ Hz), 63.6 (d, $^3$J$_{PC} = 6.8$ Hz), 64.0 (d, $^3$J$_{PC} = 7.0$ Hz), 88.4 (dd, $^1$J$_{PC} = 166.6$ Hz, $^1$J$_{FC} = 185.5$ Hz), 112.7, 118.2, 126.8 (dd, $^3$J$_{PC} = 5.1$ Hz, $^3$J$_{FC} = 7.6$ Hz), 132.1, 138.2 (dd, $^1$J$_{PC} = 1.7$ Hz, $^1$J$_{FC} = 18.4$ Hz) ppm. 

General procedure for the preparation of α-chlorobenzylphosphonates from α-hydroxyphosphonates: A solution of 1k (1.00 g, 3.46 mmol, 1.0 eq.) and triphenylphosphine (1.36 g, 5.19 mmol, 1.5 eq.) in dry CCl$_4$ is refluxed for 8 h under argon. Then, the mixture is evaporated under reduced pressure, and the semisolid residue is extracted with petroleum ether. The combined extracts are filtered, and the solvent is removed under reduced pressure. The crude material was purified by flash column chromatography of silica gel to yield 3k as yellow oil (0.81 g, 76%).

Diethyl α-chlorobenzylphosphonate (3a). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 1.17 (t, $J = 7.0$ Hz, 3H), 1.32 (t, $J = 7.0$ Hz, 3H), 3.85-3.93 (m, 1H), 4.02-4.06 (m, 1H), 4.07-4.23 (m, 2H), 4.91 (d, $^2$J$_{PH} = 14.1$ Hz, 1H), 7.36 (d, $J = 5.9$ Hz, 3H), 7.53 (d, $J = 5.6$ Hz, 2H) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 16.3 (d, $^3$J$_{PC} = 5.8$ Hz), 16.5 (d, $^3$J$_{PC} = 5.8$ Hz), 53.7 (d, $^1$J$_{PC} = 158.7$ Hz), 64.0 (d, $^2$J$_{PC} = 6.8$ Hz), 64.1 (d, $^2$J$_{PC} = 7.2$ Hz), 128.6, 129.0, 129.1, 134.2 ppm.

Diethyl α-chloro-4-methylbenzylphosphonate (3b). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 1.19 (t, $J = 7.0$ Hz, 3H), 1.33 (t, $J = 7.0$ Hz, 3H), 2.35 (s, 3H), 3.88-3.94 (m, 1H), 4.02-4.06 (m, 1H), 4.07-4.24 (m, 2H), 4.87 (d, $^2$J$_{PH} = 13.9$ Hz, 1H), 7.17 (d, $J = 7.8$ Hz, 2H), 7.42 (d, $J = 7.9$ Hz, 2H) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 16.3 (d, $^3$J$_{PC} = 5.8$ Hz), 16.5 (d, $^3$J$_{PC} = 5.8$ Hz), 21.3, 53.7 (d, $^1$J$_{PC} = 158.7$ Hz), 64.0 (d, $^2$J$_{PC} = 6.8$ Hz), 64.1 (d, $^2$J$_{PC} = 7.2$ Hz), 128.6, 129.0, 129.1, 134.2 ppm.

Diethyl α-chloro-4-methoxybenzylphosphonate (3c). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 1.18 (t, $J = 7.0$ Hz, 3H), 1.33 (t, $J = 7.0$ Hz, 3H), 3.81 (s, 3H), 3.84-3.93 (m, 1H), 4.02-4.10 (m, 1H), 4.15-4.22 (m, 2H), 4.86 (d, $^2$J$_{PH} = 13.7$ Hz, 1H), 6.89 (d, $J = 8.6$ Hz, 2H), 7.46 (d, $J = 8.5$ Hz, 2H) ppm.

Diethyl α-chloro-4-cyanobenzylphosphonate (3d). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 1.24 (t, $J = 7.0$ Hz, 3H), 1.33 (t, $J = 7.0$ Hz, 3H), 3.97-4.19 (m, 2H), 4.21-4.26 (m, 2H), 4.97 (d, $^2$J$_{PH} = 15.0$ Hz, 1H), 7.67 (s, 4H) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 16.2 (d, $^3$J$_{PC} = 5.7$ Hz), 16.3 (d, $^3$J$_{PC} = 5.7$ Hz), 52.7 (d, $^1$J$_{PC} = 156.8$ Hz), 64.1 (d, $^2$J$_{PC} = 7.0$ Hz), 64.5 (d, $^2$J$_{PC} = 7.1$ Hz), 112.7, 118.2, 129.6, 132.2, 139.5 ppm; HRMS (EI) [M]$^+$ 278.0479, Calculated Mass 278.0478.

Diethyl α-chloro-4-carboxybenzylphosphonate (3e). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 1.21 (t, $J = 7.1$ Hz, 3H), 1.32 (t, $J = 7.0$ Hz, 3H), 3.97-4.09 (m, 1H), 4.04-4.13 (m, 2H), 4.16-4.23 (m, 2H), 4.94 (d, $^2$J$_{PH} = 14.7$ Hz, 1H), 5.37 (s, 2H), 7.35-7.59 (m, 5H), 7.60 (d, $J = 8.2$ Hz, 2H), 8.08 (d, $J = 8.1$ Hz, 2H) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 16.1 (d, $^3$J$_{PC} = 5.7$ Hz), 16.2 (d, $^3$J$_{PC} = 5.8$ Hz), 53.0 (d, $^1$J$_{PC} = 157.0$ Hz), 63.9 (d, $^2$J$_{PC} = 6.9$ Hz), 64.1 (d, $^2$J$_{PC} = 7.0$ Hz), 66.7, 128.0, 128.1, 128.4, 128.8, 129.7, 130.4, 135.7, 139.1, 165.6 ppm; HRMS (EI) [M]$^+$ 396.0888, Calculated Mass 396.0893.

Diethyl α-chloro-4-fluorobenzylphosphonate (3f). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 1.20 (t, $J = 7.0$ Hz, 3H), 1.33 (t, $J = 7.1$ Hz, 3H), 3.88-3.97 (m, 1H), 4.03-4.07 (m, 1H), 4.08-4.25 (m, 2H), 4.88 (d, $^2$J$_{PH} = 14.1$ Hz, 1H), 7.07 (t, $J = 8.5$ Hz, 2H), 7.50-7.54 (m,
Diethyl α-chloro-4-chlorobenzylphosphonate (3g). $^1$H NMR (300 MHz, CDCl₃): $\delta = 1.21$ (t, $J = 7.1$ Hz, 3H), 1.33 (t, $J = 7.0$ Hz, 3H), 3.90-3.99 (m, 1H), 4.05-4.13 (m, 1H), 4.15-4.25 (m, 2H), 4.87 (d, $^2$Jₚₜ = 14.3 Hz, 1H), 7.35 (d, $J = 8.4$ Hz, 2H), 7.48 (d, $J = 8.4$ Hz, 2H) ppm; $^{13}$C NMR (75 MHz, CDCl₃): $\delta = 16.1$ (d, $^3$Jₚₜ = 5.6 Hz), 16.2 (d, $^3$Jₚₜ = 5.7 Hz), 52.7 (d, $^1$Jₚₜ = 159.2 Hz), 63.8 (d, $^2$Jₚₜ = 6.8 Hz), 64.1 (d, $^2$Jₚₜ = 7.0 Hz), 128.6, 130.1, 132.7, 134.8 ppm.

Diethyl α-chloro-4-bromobenzylphosphonate (3h). $^1$H NMR (300 MHz, CDCl₃): $\delta = 1.22$ (t, $J = 7.0$ Hz, 3H), 1.33 (t, $J = 7.0$ Hz, 3H), 3.91-3.99 (m, 1H), 4.05-4.13 (m, 1H), 4.15-4.25 (m, 2H), 4.85 (d, $^2$Jₚₜ = 14.3 Hz, 1H), 7.41 (d, $J = 7.0$ Hz, 2H), 7.51 (d, $J = 8.3$ Hz, 2H) ppm; $^{13}$C NMR (75 MHz, CDCl₃): $\delta = 16.2$ (d, $^3$Jₚₜ = 5.7 Hz), 16.4 (d, $^3$Jₚₜ = 5.8 Hz), 52.7 (d, $^1$Jₚₜ = 159.0 Hz), 63.9 (d, $^2$Jₚₜ = 6.8 Hz), 64.2 (d, $^2$Jₚₜ = 7.0 Hz), 123.1, 130.5, 131.7, 133.3 ppm.

Diethyl α-chloro-2-nitrobenzylphosphonate (3i). $^1$H NMR (300 MHz, CDCl₃): $\delta = 1.19$ (t, $J = 7.0$ Hz, 3H), 1.36 (t, $J = 7.0$ Hz, 3H), 3.95-4.12 (m, 2H), 4.21-4.31 (m, 2H), 6.18 (d, $^2$Jₚₜ = 16.0 Hz, 1H), 7.53 (t, $J = 7.9$ Hz, 1H), 7.71 (d, $J = 7.5$ Hz, 1H), 7.98 (d, $J = 8.1$ Hz, 2H), 8.10 (d, $J = 7.9$ Hz, 1H) ppm; $^{13}$C NMR (75 MHz, CDCl₃): $\delta = 15.9$ (d, $^3$Jₚₜ = 5.7 Hz), 16.2 (d, $^3$Jₚₜ = 5.7 Hz), 47.0 (d, $^1$Jₚₜ = 157.4 Hz), 63.9 (d, $^2$Jₚₜ = 7.0 Hz), 64.5 (d, $^2$Jₚₜ = 7.0 Hz), 124.6, 129.0, 129.5, 131.5, 133.3, 148.1 ppm; HRMS (EI) [M+H]$^+$ 308.0457, Calculated Mass 308.0455.

Diethyl α-chloro-3-nitrobenzylphosphonate (3j). $^1$H NMR (300 MHz, CDCl₃): $\delta = 1.26$ (t, $J = 7.0$ Hz, 3H), 1.34 (t, $J = 7.0$ Hz, 3H), 4.02-4.28 (m, 4H), 5.00 (d, $^2$Jₚₜ = 14.7 Hz, 1H), 7.58 (t, $J = 8.0$ Hz, 1H), 7.91 (d, $J = 7.6$ Hz, 1H), 7.98 (d, $J = 8.1$ Hz, 1H), 8.23 (d, $J = 8.1$ Hz, 1H), 8.39 (s, 1H) ppm; $^{13}$C NMR (75 MHz, CDCl₃): $\delta = 16.0$ (d, $^3$Jₚₜ = 5.7 Hz), 16.1 (d, $^3$Jₚₜ = 5.7 Hz), 52.1 (d, $^1$Jₚₜ = 157.4 Hz), 63.9 (d, $^2$Jₚₜ = 7.0 Hz), 64.3 (d, $^2$Jₚₜ = 7.0 Hz), 123.5, 129.4, 134.6, 136.3, 147.8 ppm; HRMS (EI) [M+H]$^+$ 308.0462, Calculated Mass 308.0455.

Diethyl α-chloro-4-nitrobenzylphosphonate (3k). $^1$H NMR (300 MHz, CDCl₃): $\delta = 1.26$ (t, $J = 7.0$ Hz, 3H), 1.35 (t, $J = 7.0$ Hz, 3H), 4.00-4.14 (m, 2H), 4.15-4.28 (m, 2H), 5.00 (d, $^2$Jₚₜ = 15.2 Hz, 1H), 7.73 (d, $J = 8.6$ Hz, 2H), 8.25 (d, $J = 8.6$ Hz, 2H) ppm; $^{13}$C NMR (75 MHz, CDCl₃): $\delta = 16.2$ (d, $^3$Jₚₜ = 5.6 Hz), 16.4 (d, $^3$Jₚₜ = 5.7 Hz), 52.5 (d, $^1$Jₚₜ = 156.4 Hz), 64.1 (d, $^2$Jₚₜ = 7.0 Hz), 64.6 (d, $^2$Jₚₜ = 7.0 Hz), 123.6, 129.8, 141.4, 148.0 ppm; HRMS (EI) [M+H]$^+$ 308.0450, Calculated Mass 308.0455.

**General procedure for the preparation of α,α-chlorofluorobenzylphosphonates from α-chlorophosphonates:** To a solution of the α-chlorophosphonates 3k (0.31 g, 0.94 mmol, 1.0 eq.) in dry THF (10 ml) at -78 °C was added dropwise a solution of NaHMD (1.69 mmol, 2.0 M in THF, 1.5 eq.) in dry THF (5 ml) under argon. The resulting dark green solution was stirred for 1 h at -78 °C. A solution of NFSI (0.41 g, 1.31 mmol, 1.3 eq.) in dry THF (5 ml) was added over a period of ten minutes. After addition, the solution was stirred for 1 h and then allowed to warm to -30 °C. The reaction was quenched with 0.01 N HCl and the resulting solution were extracted with CH₂Cl₂. The combined organic layer was dried over MgSO₄ and removed solvent under reduced pressure. The crude material was purified via flash column chromatography of silica gel to yield 4k as yellow oil (0.24 g, 77%).
Diethyl α,α-chlorofluorobenzylphosphonates (4a). $^1$H NMR (300 MHz, CDCl$_3$): δ = 1.20 (t, J = 7.0 Hz, 3H), 1.38 (t, J = 7.0 Hz, 3H), 3.90-3.98 (m, 1H), 4.06-4.14 (m, 1H), 4.26-4.35 (m, 2H), 7.43 (d, J = 3.6 Hz, 3H), 7.67 (d, J = 3.3 Hz, 2H) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$): δ$^1$ = 16.1 (d, $^3$J$_{PC}$ = 5.6 Hz), 16.4 (d, $^3$J$_{PC}$ = 5.6 Hz), 65.1 (d, $^2$J$_{PC}$ = 7.0 Hz), 65.6 (d, $^2$J$_{PC}$ = 7.0 Hz), 106.9 (dd, $^1$J$_{PC}$ = 196.0 Hz, $^1$J$_{FC}$ = 258.2 Hz), 126.2 (d, $^3$J$_{FC}$ = 8.3 Hz), 128.2, 130.0, 135.7 (d, $^2$J$_{FC}$ = 26.5 Hz) ppm; $^{31}$P NMR (121.5 MHz, CDCl$_3$): δ = 6.16 (d, $^2$J$_{PF}$ = 91.2 Hz) ppm; HRMS (EI) [M]+ 280.0435, Calculated Mass 280.0431.

Diethyl α,α-chlorofluoro-4-methylbenzylphosphonates (4b). $^1$H NMR (300 MHz, CDCl$_3$): δ = 1.22 (t, J = 7.0 Hz, 3H), 1.38 (t, J = 7.0 Hz, 3H), 2.38 (s, 3H), 3.94-3.97 (m, 1H), 4.07-4.12 (m, 1H), 4.27-4.34 (m, 2H), 7.23 (d, J = 8.0 Hz, 2H), 7.55 (d, J = 8.0 Hz, 2H) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$): δ$^1$ = 16.3 (d, $^3$J$_{PC}$ = 5.6 Hz), 16.5 (d, $^3$J$_{PC}$ = 5.6 Hz), 21.2, 65.1 (d, $^2$J$_{PC}$ = 6.9 Hz), 65.6 (d, $^2$J$_{PC}$ = 7.1 Hz), 107.3 (dd, $^1$J$_{PC}$ = 197.3 Hz, $^1$J$_{FC}$ = 258.1 Hz), 126.2 (d, $^3$J$_{FC}$ = 8.2 Hz), 129.0, 133.0 (d, $^2$J$_{FC}$ = 20.8 Hz), 140.3 ppm; $^{31}$P NMR (121.5 MHz, CDCl$_3$): δ = 6.24 (d, $^2$J$_{PF}$ = 92.5 Hz) ppm; HRMS (EI) [M]+ 294.0589, Calculated Mass 294.0588.

Diethyl α,α-chlorofluoro-4-methoxybenzylphosphonates (4c). $^1$H NMR (300 MHz, CDCl$_3$): δ = 1.22 (t, J = 7.0 Hz, 3H), 1.38 (t, J = 7.0 Hz, 3H), 3.84 (s, 3H), 3.94-4.00 (m, 1H), 4.07-4.13 (m, 1H), 4.28-4.35 (m, 2H), 6.94 (d, J = 8.6 Hz, 2H), 7.59 (d, J = 7.7 Hz, 2H) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$): δ$^1$ = 16.2 (d, $^3$J$_{PC}$ = 5.6 Hz), 16.4 (d, $^3$J$_{PC}$ = 5.6 Hz), 55.3, 65.1 (d, $^2$J$_{PC}$ = 7.0 Hz), 65.5 (d, $^2$J$_{PC}$ = 6.9 Hz), 107.3 (dd, $^1$J$_{PC}$ = 199.4 Hz, $^1$J$_{FC}$ = 258.2 Hz), 113.6, 127.6, 127.9, 160.9 ppm; $^{31}$P NMR (121.5 MHz, CDCl$_3$): δ = 6.25 (d, $^2$J$_{PF}$ = 93.5 Hz) ppm; HRMS (EI) [M]+ 310.0539, Calculated Mass 310.0537.

Diethyl α,α-chlorofluoro-4-cyanobenzylphosphonates (4d). $^1$H NMR (300 MHz, CDCl$_3$): δ = 1.24 (t, J = 7.0 Hz, 3H), 1.40 (t, J = 7.0 Hz, 3H), 4.01-4.11 (m, 1H), 4.28-4.35 (m, 2H), 7.74 (d, J = 8.3 Hz, 2H), 7.80 (d, J = 8.0 Hz, 2H) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$): δ = 16.2 (d, $^3$J$_{PC}$ = 5.6 Hz), 16.4 (d, $^3$J$_{PC}$ = 5.6 Hz), 55.3, 65.1 (d, $^2$J$_{PC}$ = 7.0 Hz), 65.5 (d, $^2$J$_{PC}$ = 6.9 Hz), 107.3 (dd, $^1$J$_{PC}$ = 195.0 Hz, $^1$J$_{FC}$ = 258.2 Hz), 114.0, 117.9, 127.1 (d, $^3$J$_{FC}$ = 8.5 Hz), 132.0, 140.7 (d, $^2$J$_{FC}$ = 21.1 Hz) ppm; $^{31}$P NMR (121.5 MHz, CDCl$_3$): δ = 5.23 (d, $^2$J$_{PF}$ = 88.1 Hz) ppm; HRMS (EI) [M]+ 280.0435, Calculated Mass 280.0431.

Diethyl α,α-chlorofluoro-4-carbobenzyloxybenzylphosphonates (4e). $^1$H NMR (300 MHz, CDCl$_3$): δ = 1.22 (t, J = 6.9 Hz, 3H), 1.38 (t, J = 6.9 Hz, 3H), 3.94-4.02 (m, 1H), 4.07-4.16 (m, 1H), 4.14-4.22 (m, 2H), 7.74 (d, J = 8.3 Hz, 2H), 7.80 (d, J = 8.0 Hz, 2H) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$): δ = 16.2 (d, $^3$J$_{PC}$ = 5.6 Hz), 16.4 (d, $^3$J$_{PC}$ = 5.6 Hz), 55.3, 65.1 (d, $^2$J$_{PC}$ = 7.1 Hz), 66.0 (d, $^2$J$_{PC}$ = 7.2 Hz), 105.7 (dd, $^1$J$_{PC}$ = 193.9 Hz, $^1$J$_{FC}$ = 259.0 Hz), 114.0, 117.9, 127.1 (d, $^3$J$_{FC}$ = 8.5 Hz), 132.0, 140.7 (d, $^2$J$_{FC}$ = 21.1 Hz) ppm; $^{31}$P NMR (121.5 MHz, CDCl$_3$): δ = 6.25 (d, $^2$J$_{PF}$ = 93.5 Hz) ppm; HRMS (EI) [M]+ 305.0387, Calculated Mass 305.0384.

Diethyl α,α-chlorofluoro-4-fluorobenzylphosphonates (4f). $^1$H NMR (300 MHz, CDCl$_3$): δ = 1.23 (t, J = 7.0 Hz, 3H), 1.39 (t, J = 7.0 Hz, 3H), 3.95-4.03 (m, 1H), 4.08-4.14 (m, 1H), 4.27-4.37 (m, 2H), 7.12 (t, J = 8.5 Hz, 2H), 7.64-7.69 (m, 2H) ppm;
$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 16.2 (d, $^3$J$_{PC}$ = 5.6 Hz), 16.4 (d, $^3$J$_{PC}$ = 5.5 Hz), 65.2 (d, $^2$J$_{PC}$ = 7.0 Hz), 65.8 (d, $^2$J$_{PC}$ = 7.1 Hz), 106.6 (dd, $^1$J$_{PC}$ = 197.5 Hz, $^1$J$_{FC}$ = 258.4 Hz), 115.4 (d, $^2$J$_{FC}$ = 22.0 Hz), 128.5 (d, $^3$J$_{PC}$ = 11.6 Hz), 132.0, 163.6 (d, $^1$J$_{FC}$ = 248.9 Hz) ppm; $^{31}$P NMR (121.5 MHz, CDCl$_3$): $\delta$ = 5.89 (d, $^2$J$_{PF}$ = 91.1 Hz) ppm; HRMS (EI) [M]$^+$ 298.0338, Calculated Mass 298.0337.

Diethyl $\alpha$,$\alpha$-chlorofluoro-4-chlorobenzyl phosphonates (4g). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 1.23 (t, $J$ = 7.0 Hz, 3H), 1.39 (t, $J$ = 7.0 Hz, 3H), 3.92-4.09 (m, 1H), 4.15-4.42 (m, 1H), 4.31-4.34 (m, 2H), 7.41 (d, $J$ = 8.2 Hz, 2H), 7.61 (d, $J$ = 8.4 Hz, 2H) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 16.3 (d, $^3$J$_{PC}$ = 5.5 Hz), 16.5 (d, $^3$J$_{PC}$ = 5.6 Hz), 65.3 (d, $^2$J$_{PC}$ = 7.0 Hz), 65.8 (d, $^2$J$_{PC}$ = 7.1 Hz), 106.5 (dd, $^1$J$_{PC}$ = 196.4 Hz, $^1$J$_{FC}$ = 258.4 Hz), 127.8 (d, $^3$J$_{FC}$ = 8.3 Hz), 128.6, 134.6 (d, $^2$J$_{FC}$ = 21.1 Hz), 136.4 ppm; $^{31}$P NMR (121.5 MHz, CDCl$_3$): $\delta$ = 5.75 (d, $^2$J$_{PF}$ = 90.7 Hz) ppm; HRMS (EI) [M]$^+$ 314.0043, Calculated Mass 314.0042.

Diethyl $\alpha$,$\alpha$-chlorofluoro-4-bromobenzyl phosphonates (4h). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 1.13 (t, $J$ = 7.0 Hz, 3H), 1.28 (t, $J$ = 7.0 Hz, 3H), 3.76-3.90 (m, 1H), 4.01-4.15 (m, 2H), 7.41-7.45 (m, 4H) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 16.3 (d, $^3$J$_{PC}$ = 5.6 Hz), 16.6 (d, $^3$J$_{PC}$ = 5.6 Hz), 65.4 (d, $^2$J$_{PC}$ = 7.1 Hz), 65.9 (d, $^2$J$_{PC}$ = 7.2 Hz), 106.6 (dd, $^1$J$_{PC}$ = 196.3 Hz, $^1$J$_{FC}$ = 258.4 Hz), 124.8, 128.1 (d, $^2$J$_{PC}$ = 8.2 Hz), 128.6, 131.7, 135.1 (d, $^2$J$_{FC}$ = 21.1 Hz) ppm; $^{31}$P NMR (121.5 MHz, CDCl$_3$): $\delta$ = 5.63 (d, $^2$J$_{PF}$ = 90.7 Hz) ppm; HRMS (EI) [M]$^+$ 357.9539, Calculated Mass 357.9536.

Diethyl $\alpha$,$\alpha$-chlorofluoro-2-nitrobenzyl phosphonates (4i). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 1.25 (d, $J$ = 6.4 Hz, 3H), 1.44 (d, $J$ = 6.7 Hz, 3H), 4.06-4.16 (m, 2H), 4.44 (br, 2H), 7.46 (d, $J$ = 6.4 Hz, 1H), 7.57 (d, $J$ = 4.7 Hz, 2H), 7.99 (s, 1H) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 16.1 (d, $^3$J$_{PC}$ = 5.5 Hz), 16.4 (d, $^3$J$_{PC}$ = 5.7 Hz), 65.7 (d, $^2$J$_{PC}$ = 7.4 Hz), 66.6 (d, $^2$J$_{PC}$ = 7.3 Hz), 105.3 (dd, $^1$J$_{PC}$ = 194.2, $^1$J$_{FC}$ = 259.9), 123.4, 127.4 (d, $^2$J$_{FC}$ = 29.1 Hz), 129.9, 130.6, 131.3, 147.9 ppm; $^{31}$P NMR (121.5 MHz, CDCl$_3$): $\delta$ = 3.32 (d, $^2$J$_{PF}$ = 80.5 Hz) ppm;

Diethyl $\alpha$,$\alpha$-chlorofluoro-3-nitrobenzyl phosphonates (4j). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 1.28 (t, $J$ = 7.0 Hz, 3H), 1.41 (t, $J$ = 7.0 Hz, 3H), 4.07-4.22 (m, 2H), 4.31-4.41 (m, 2H), 7.65 (t, $J$ = 8.0 Hz, 1H), 8.03 (d, $J$ = 7.8 Hz, 1H), 8.31 (d, $J$ = 8.1 Hz, 1H), 8.52 (s, 1H) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 16.2 (d, $^3$J$_{PC}$ = 5.6 Hz), 16.3 (d, $^3$J$_{PC}$ = 5.6 Hz), 65.4 (d, $^2$J$_{PC}$ = 7.1 Hz), 66.1 (d, $^2$J$_{PC}$ = 7.2 Hz), 105.5 (dd, $^1$J$_{PC}$ = 195.3, $^1$J$_{FC}$ = 258.8), 121.4 (d, $^3$J$_{PC}$ = 9.4 Hz), 124.8, 129.5, 132.4, 138.1 (d, $^2$J$_{FC}$ = 21.7 Hz), 148.0 ppm; $^{31}$P NMR (121.5 MHz, CDCl$_3$): $\delta$ = 6.63 (d, $^2$J$_{PF}$ = 89.7 Hz) ppm; HRMS (EI) [M]$^+$ 325.0285, Calculated Mass 325.0282.

Diethyl $\alpha$,$\alpha$-chlorofluoro-4-nitrobenzyl phosphonates (4k). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 1.25 (t, $J$ = 7.0 Hz, 3H), 1.41 (t, $J$ = 7.0 Hz, 3H), 4.05-4.19 (m, 2H), 4.32-4.41 (m, 2H), 7.86 (d, $J$ = 8.5 Hz, 2H), 8.29 (d, $J$ = 8.6 Hz, 2H) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 16.3 (d, $^3$J$_{PC}$ = 15.0 Hz), 65.3 (d, $^2$J$_{PC}$ = 7.2 Hz), 66.2 (d, $^2$J$_{PC}$ = 7.1 Hz), 105.6 (dd, $^1$J$_{PC}$ = 193.4 Hz, $^1$J$_{FC}$ = 259.1 Hz), 123.4, 127.5 (d, $^3$J$_{PC}$ = 8.4 Hz), 142.5 (d, $^2$J$_{FC}$ = 21.0 Hz), 148.7 ppm; $^{31}$P NMR (121.5 MHz, CDCl$_3$): $\delta$ = 5.13 (d, $^2$J$_{PF}$ = 88.1 Hz) ppm.
References