



Supporting Information

for

Copper-catalyzed *O*-alkenylation of phosphonates

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Experimental procedures and characterization data of enol phosphonates 3

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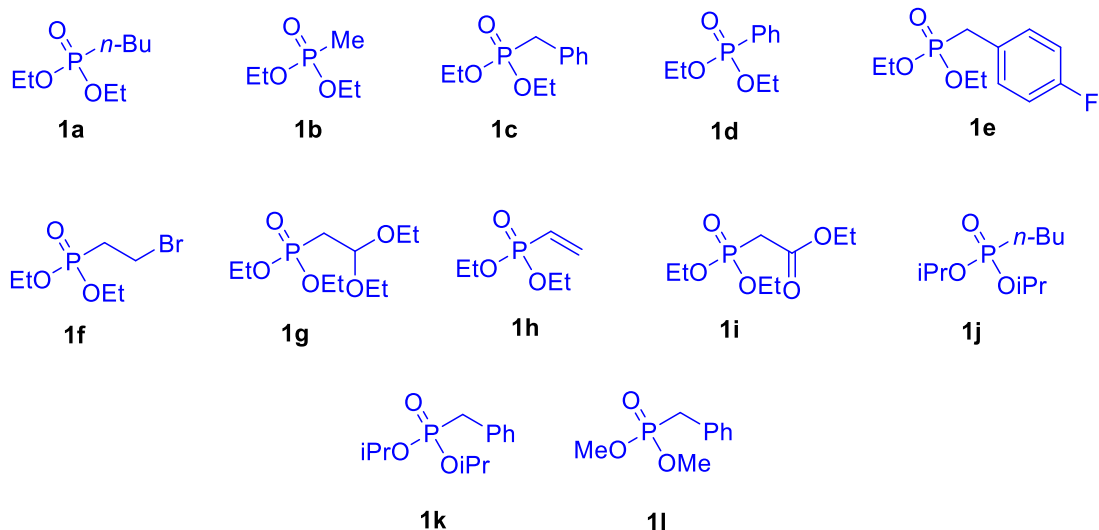
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1. General methods

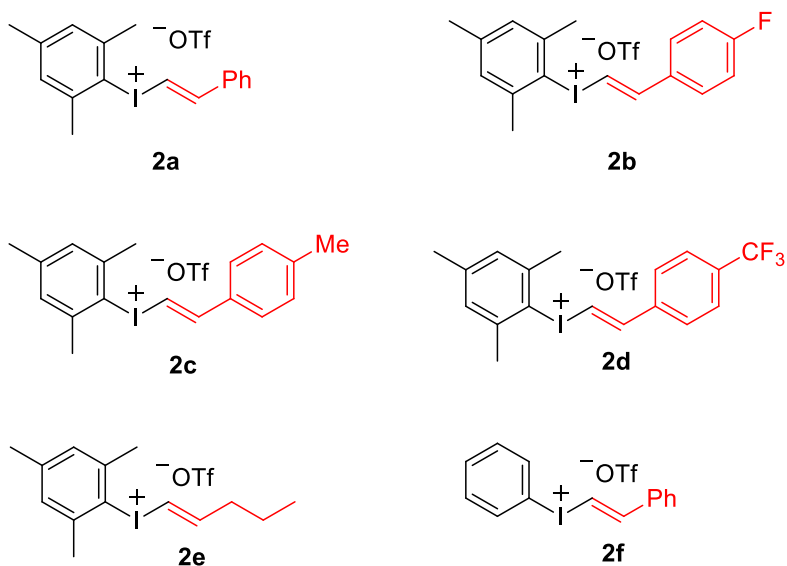
- All reactions were performed under argon atmosphere using oven dried glassware and using a sealed tube. Solvents were dried using an MBraun SPS 800 system. All chemicals and copper complexes were purchased from Acros Organics Ltd., Aldrich Chemical Co. Ltd., Alfa Aesar, Apollo, Strem Chemicals Inc., Fluorochem Ltd. or TCI Europe N.V. chemical companies and used without further purification, unless otherwise noted.
- Analytical thin layer chromatography was carried out on silica-coated aluminium plates (silica gel 60 F254 Merck) and components were visualized by UV light, I₂ and KMnO₄ staining. Flash column chromatography was performed on silica gel 60 (Merck, 230–400 mesh) without previous deactivation, unless otherwise stated.
- High resolution mass spectrometry was carried out on a Bruker microTOF spectrometer using APCI.
- ¹H and ¹³C NMR experiments were carried out using a Varian Inova 500 MHz or a Varian Mercury 300MHz NMR spectrometers. Chemical shift values are reported in ppm with the solvent resonance as the internal standard (CHCl₃: δ 7.26 for ¹H, δ 77.16 for ¹³C). Coupling constants (*J*) are given in Hertz (Hz). Multiplicities are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet or as a combination of them.

2. List of starting materials

- Phosphonates **1a**, **1b**, **1d-1j** were obtained from commercial sources. **1c**, **1k**, **1l** were prepared according to described procedures.¹



- Alkenyl(mesityl)iodonium salts **2** were prepared according to described procedures.^{2,3}



¹ Huang, T.; Chen, T.; Han, L., *J. Org. Chem.* **2018**, *83*, 2959–2965.

² Suero, M. G.; Bayle, E. D.; Collins, B. S. L.; Gaunt, M. J. *J. Am. Chem. Soc.* **2013**, *135*, 5332–5335.

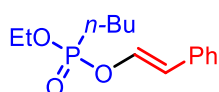
³ Ren, W.; Xiang, H.; Peng, C.; Musha, Z.; Chen, J.; Huang, R.; Hu, Y. *RCS Adv.* **2018**, *8*, 5542–5549.

3. General procedure for the copper-catalyzed oxygen-alkenylation of dialkyl phosphonates

CuTC (0.02 mmol, 0.10 equiv), the corresponding alkenyl(aryl)iodonium salt **2** (0.6 mmol, 2 equiv) and a stirring bar were charged in a sealed tube. A solution of phosphonate **1** (0.2 mmol, 1 equiv) in dry dichloromethane (2 ml) and 2,6-di-*tert*-butylpyridine (0.22 mmol, 1 equiv) was added and the resulting mixture was stirred at 50 °C under an argon atmosphere for 16 h. After this time, the reaction was quenched by addition of saturated aqueous solution of NH₄Cl (10 ml) and extracted with CH₂Cl (2 × 10 ml). The organic layer was dried over Na₂SO₄, filtered and solvent was removed under vacuum. The final product was purified by column chromatography on silica gel using *n*-hexane/AcOEt (1:1) as eluent.

4. Compound characterization

(*E*)-Ethyl styryl butylphosphonate (**3a**)



Obtained from **1a** and **2a** following the general procedure as a yellow oil after column chromatography following the general procedure in 78% yield.

¹H NMR (300 MHz, CDCl₃) δ 7.3 – 7.17 (m, 6H), 6.34 (dd, *J* = 12.4, 1.5 Hz, 1H), 4.29 – 4.08 (m, 2H), 1.93 – 1.77 (m, 2H), 1.73 – 1.53 (m, 2H), 1.49 – 1.38 (m, 2H), 1.34 (t, *J* = 7.1 Hz, 3H), 0.92 (t, *J* = 7.4 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 137.1 (d, *J* = 6.0 Hz, CH), 134.2 (C), 128.7 (2 x CH), 127.2 (CH), 126.0 (2 x CH), 116.7 (d, *J* = 9.5 Hz, CH), 62.0 (d, *J* = 7.1 Hz, CH₂), 25.3 (d, *J* = 140.2 Hz, CH₂), 24.1 (d, *J* = 5.3 Hz, CH₂), 23.6 (d, *J* = 17.5 Hz, CH₂), 16.4 (d, *J* = 6.0 Hz, CH₃), 13.5 (CH₃). ³¹P NMR (202 MHz, CDCl₃) δ 32.65. HRMS (APCI) Calc. for C₁₄H₂₂O₃P [M+H⁺]: 269.1300, found 269.1301.

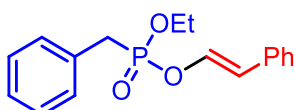
(*E*)-Ethyl styryl methylphosphonate (**3b**)



Obtained from **1b** and **2a** following the general procedure as a yellow oil after column chromatography following the general procedure in 60% yield.

¹H NMR (500 MHz, CDCl₃) δ 7.33 – 7.29 (m, 4H), 7.26 – 7.21 (m, 2H), 6.40 (dd, *J* = 12.4, 1.5 Hz, 1H), 4.29 – 4.15 (m, 2H), 1.62 (d, *J* = 17.8 Hz, 3H), 1.39 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 136.7 (d, *J* = 6.1 Hz, CH), 134.0 (C), 128.5 (2 x CH), 127.3 (CH), 126.0 (2 x CH), 117.3 (d, *J* = 9.6 Hz, CH), 62.2 (d, *J* = 6.7 Hz, CH₂), 16.3 (d, *J* = 6.3 Hz, CH₃), 11.2 (d, *J* = 145.3 Hz, CH₃). ³¹P NMR (202 MHz, CDCl₃) δ 30.52. HRMS (APCI) Calc. for C₁₁H₁₆O₃P [M+H⁺]: 227.0832, found 227.0832.

(*E*)-Ethyl styryl benzylphosphonate (**3c**)



Obtained from **1c** and **2a** following the general procedure as a yellow oil after column chromatography following the general procedure in 64% yield.

¹H NMR (300 MHz, CDCl₃) δ 7.36 – 7.18 (m, 10H), 7.09 (dd, *J* = 12.3, 6.4 Hz, 1H), 6.30 (dd, *J* = 12.1, 1.3 Hz, 1H), 4.20 – 4.06 (m, 2H), 3.28 (d, *J* = 21.8 Hz, 2H), 1.28 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 137.0 (d, *J* = 6.5 Hz, CH), 134.0 (C), 130.4 (d, *J* = 9.5 Hz, C), 129.9 (d, *J* = 6.7 Hz, CH), 128.7 (d, *J* = 3.2 Hz, 2 x CH), 128.8 (2 x CH), 127.3 (2 x CH), 127.2 (d, *J* = 3.8 Hz, CH), 126.0 (2 x CH), 117.1 (d, *J* = 9.5 Hz, CH), 62.94 (d, *J* = 7.3 Hz, CH₂), 33.6 (d, *J* = 138.0 Hz, CH₂), 16.3 (d, *J* = 5.8 Hz, CH₃). HRMS (APCI) Calc. for C₁₇H₂₀O₃P [M+H⁺]: 303.1145, found 303.1145.

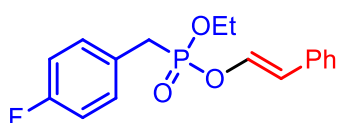
(E)-Ethyl styryl phenylphosphonate (3d)



Obtained from **1d** and **2a** following the general procedure as a yellow oil after column chromatography following the general procedure in 69% yield.

¹H NMR (500 MHz, CDCl₃) δ 7.89 (ddd, *J* = 13.7, 8.3, 1.5 Hz, 2H), 7.64 – 7.59 (tq, *J* = 7.4, 1.4 Hz, 1H), 7.55 – 7.50 (m, 2H), 7.32 – 7.28 (m, 4H), 7.27 – 7.20 (m, 2H), 6.41 (dd, *J* = 12.3, 1.2 Hz, 1H), 4.32 – 4.24 (m, 2H), 1.42 (t, *J* = 7.1 Hz, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 136.8 (d, *J* = 5.3 Hz, CH), 134.0 (C), 133.0 (d, *J* = 3.1 Hz, CH), 131.8 (d, *J* = 10.2 Hz, 2 x CH), 128.7 (2 x CH), 128.7 (d, *J* = 15.4 Hz, 2 x CH), 127.3 (CH), 127.1 (d, *J* = 191.3 Hz, C), 126.0 (2 x CH), 117.6 (d, *J* = 9.9 Hz, CH), 62.9 (d, *J* = 6.0 Hz, CH₂), 16.4 (d, *J* = 6.4 Hz, CH₃). **³¹P NMR** (202 MHz, CDCl₃) δ 18.19. **HRMS** (APCI) Calc. for C₁₆H₁₈O₃P [M+H⁺]: 289.0990, found 289.0988.

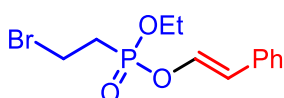
(E)-Ethyl styryl 4-fluorobenzylphosphonate (3e)



Obtained from **1e**, **2a** following the general procedure as a yellow oil after column chromatography following the general procedure in 41% yield.

¹H NMR (500 MHz, CDCl₃) δ 7.33 – 7.28 (m, 4H), 7.27 – 7.23 (m, 3H), 7.12 (dd, *J* = 12.3, 6.4 Hz, 1H), 7.04 (t, *J* = 8.5 Hz, 2H), 6.33 (dd, *J* = 12.3, 1.4 Hz, 1H), 4.20 – 4.12 (m, 2H), 3.27 (d, *J* = 21.3 Hz, 2H), 1.31 (t, *J* = 6.9 Hz, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 162.1 (dd, *J* = 246.0, 4.1 Hz, C), 136.9 (d, *J* = 6.4 Hz, 2 x CH), 133.9 (C), 131.4 (dd, *J* = 8.0, 6.8 Hz, 2 x CH), 128.7 (2 x CH), 127.3 (2 x CH), 126.3 (dd, *J* = 9.4, 3.3 Hz, C), 126.0 (2 x CH), 117.2 (d, *J* = 9.6 Hz, CH), 115.6 (dd, *J* = 21.6, 3.1 Hz, CH), 62.9 (d, *J* = 7.3 Hz, CH₂), 32.7 (d, *J* = 139.2 Hz, CH₂), 16.3 (d, *J* = 5.9 Hz, CH₃). **³¹P NMR** (202 MHz, CDCl₃) δ 24.49. **¹⁹F NMR** (282 MHz, CDCl₃) δ -115.45. **HRMS** (APCI) Calc. for C₁₇H₁₉FO₃P [M+H⁺]: 321.1050 found 321.1048.

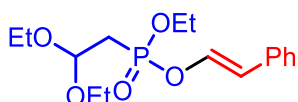
(E)-Ethyl styryl (2-bromoethyl)phosphonate (3f)



Obtained from **1f** and **2a** as a yellow oil after column chromatography following the general procedure in 55% yield.

¹H NMR (500 MHz, CDCl₃) δ 7.33 – 7.26 (m, 4H), 7.22 (dd, *J* = 12.3, 6.6 Hz, 1H), 6.42 (dd, *J* = 12.4, 1.5 Hz, 1H), 4.32 – 4.17 (m, 2H), 3.65 – 3.56 (m, 2H), 2.60 – 2.49 (m, 2H), 1.39 (t, *J* = 7.08 Hz, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 136.4 (d, *J* = 6.2 Hz, CH), 133.7 (C), 128.8 (2 x CH), 127.5 (CH), 126.1 (2 x CH), 117.8 (d, *J* = 9.7 Hz, CH), 62.8 (d, *J* = 7.1 Hz, CH₂), 30.5 (d, *J* = 135.3 Hz, CH₂), 22.9 (CH₂), 16.4 (d, *J* = 6.0 Hz, CH₃). **³¹P NMR** (202 MHz, CDCl₃) δ 25.35. **HRMS** (APCI) Calc. for C₁₂H₁₇BrO₃P [M+H⁺]: 319.0095, found 319.0093.

(E)-Ethyl styryl (2,2-diethoxyethyl)phosphonate (3g)



3g

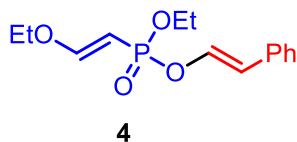
Obtained from **1g** and **2a** as a yellow oil after column chromatography following the general procedure in 52% yield. Reaction time: 10 h.*

¹H NMR (500 MHz, CDCl₃) δ 7.34 – 7.28 (m, 4H), 7.26 – 7.21 (m, 2H), 6.37 (dd, *J* = 12.4, 1.4 Hz, 1H), 4.98 (q, *J* = 5.7 Hz, 1H), 4.27 – 4.17 (m, 2H), 3.72 – 3.67 (m, 2H), 3.62 – 3.55 (m, 2H), 2.36 (dd, *J* = 18.8, 5.8 Hz, 2H), 1.39 (t, 7.1 Hz, 3H), 1.24 (t, *J* = 7.1 Hz, 3H), 1.21 (t, *J* = 7.1 Hz, 3H). **¹³C NMR** (75 MHz, CDCl₃) δ 137.2 (d, *J* = 13.5 Hz, CH), 134.3 (C), 128.9 (2 x CH), 127.5 (CH), 126.3 (2 x CH), 117.2 (d, *J* = 8.6 Hz, CH), 98.2 (d, *J* = 19.9 Hz, CH), 62.63 (d, *J* = 6.4 Hz, CH₂), 62.0 (2 x CH₂), 32.0 (d, *J* = 140.4 Hz, CH₂), 16.6 (d, *J* = 6.9 Hz, CH₃), 15.4 (CH₃). **³¹P**

NMR (202 MHz, CDCl₃) δ 25.28. **HRMS (APCI)** Calc. for C₁₆H₂₆O₅P [M+H⁺]: 329.1512 found 329.1515.

*Note: when reaction was stirred over 18 h a 1:1 mixture of **3g** and **4** was obtained.

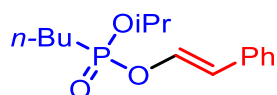
Ethyl (*E*)-styryl ((*E*)-2-ethoxyvinyl)phosphonate (**4**)



¹H NMR (500 MHz, CDCl₃) δ 7.34 – 7.28 (m, 6H), 7.18 (dd, *J* = 12.4, 6.9 Hz, 1H), 6.37 (dd, *J* = 12.4, 1.4 Hz, 1H), 4.80 (dd, *J* = 13.6, 10.5 Hz, 1H), 4.27 – 4.17 (m, 2H), 3.94 (q, *J* = 7.0 Hz, 2H), 1.42 – 1.34 (m, 6H).

¹³C NMR (126 MHz, CDCl₃) δ 164.2 (d, *J* = 22.2 Hz, CH), 136.9 (d, *J* = 5.9 Hz, CH), 134.1 (C), 128.7 (2 x CH), 127.2 (CH), 125.9 (2 x CH), 116.9 (d, *J* = 9.9 Hz, CH), 87.0 (d, *J* = 205.2 Hz, CH), 66.5 (CH₂), 62.3 (d, *J* = 6.8 Hz, CH₂), 16.3 (d, *J* = 4.6 Hz, CH₃), 14.3 (CH₃). **³¹P NMR** (202 MHz, CDCl₃) δ 21.43. **HRMS (APCI)** Calc. for C₁₄H₂₀O₄P [M+H⁺]: 283.1094 found 283.1095.

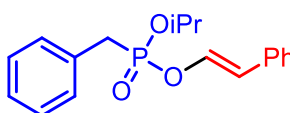
(*E*)-Isopropyl styryl butylphosphonate (**3j**)



Obtained from **1j** and **2a** as a yellow oil after column chromatography following the general procedure in 51% yield.

¹H NMR (300 MHz, CDCl₃) δ 7.28 – 7.18 (m, 6H), 6.33 (dd, *J* = 12.4, 1.4 Hz, 1H), 4.86 – 4.75 (m, 1H), 1.90 – 1.77 (m, 2H), 1.71 – 1.55 (m, 2H), 1.42 (sext, *J* = 7.4 Hz, 2H), 1.35 (dd, *J* = 6.2, 3.8 Hz, 6H), 0.92 (t, *J* = 7.3 Hz, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 137.4 (d, *J* = 6.0 Hz, CH), 134.5 (C), 128.9 (2 x CH), 127.4 (CH), 126.2 (2 x CH), 116.9 (d, *J* = 9.5 Hz, CH), 71.3 (d, *J* = 7.2 Hz, CH), 26.0 (d, *J* = 141.0 Hz, CH₂), 24.4 (d, *J* = 5.5 Hz, CH₂), 24.3 (d, *J* = 5.0 Hz, CH₃), 24.2 (d, *J* = 4.8 Hz, CH₃), 23.9 (d, *J* = 17.7 Hz, CH₂), 13.81 (d, *J* = 1.3 Hz, CH₃). **³¹P NMR** (202 MHz, CDCl₃) δ 31.70. **HRMS (APCI)** Calc. for C₁₅H₂₄O₃P [M+H⁺]: 283.1458, found 283.1460.

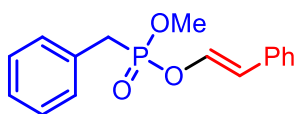
(*E*)-Isopropyl styryl benzylphosphonate (**3k**)



Obtained from **1k** and **2a** as a yellow oil after column chromatography following the general procedure in 84% yield.

¹H NMR (500 MHz, CDCl₃) δ 7.36 – 7.34 (m, 4H), 7.32 – 7.28 (m, 3H), 7.26 – 7.22 (m, 3H), 7.12 (dd, *J* = 12.3, 6.4 Hz, 1H), 6.32 (dd, *J* = 12.4, 1.3 Hz, 1H), 4.81 – 4.72 (m, 1H), 3.28 (dd, *J* = 21.7, 3.2 Hz, 2H), 1.34 (d, *J* = 6.2 Hz, 3H), 1.26 (d, *J* = 6.3 Hz, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 137.13 (d, *J* = 6.3 Hz, CH), 134.1 (C), 130.7 (d, *J* = 9.3 Hz, C), 129.9 (d, *J* = 6.7 Hz, CH), 128.7 (2 x CH), 128.6 (CH), 128.6 (CH), 127.2 (CH), 127.1 (d, *J* = 3.7 Hz, 2 x CH), 126.0 (2 x CH), 116.9 (d, *J* = 9.5 Hz, CH), 72.0 (d, *J* = 7.5 Hz, CH), 34.0 (d, *J* = 138.8 Hz, CH₂), 23.99 (d, *J* = 3.6 Hz, CH₃), 23.81 (d, *J* = 5.4 Hz, CH₃). **³¹P NMR** (202 MHz, CDCl₃) δ 24.17. **HRMS (APCI)** Calc. for C₁₈H₂₂O₃P [M+H⁺]: 317.1301, found 317.1298.

(*E*)-Methyl styryl benzylphosphonate (**3l**)

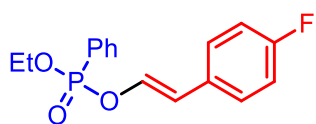


Obtained from **1l** and **2a** as a yellow oil after column chromatography following the general procedure in 31% yield.

¹H NMR (500 MHz, CDCl₃) δ 7.36 – 7.23 (m, 10H), 7.12 (dd, *J* = 12.3, 6.4 Hz, 1H), 6.34 (dd, *J* = 12.4, 1.4 Hz, 1H), 3.78 (d, *J* = 11.1 Hz, 3H), 3.32 (d, *J* = 21.8 Hz, 2H). **¹³C NMR** (126 MHz, CDCl₃) δ 137.1 (d, *J* = 6.3 Hz, CH), 134.0 (C), 130.3 (d, *J* = 9.3 Hz, C), 130.0 (d, *J* = 6.8 Hz, 2 x CH), 128.8 (d, *J* = 3.2 Hz, CH), 128.7 (2 x CH), 127.3 (2 x CH), 127.4 (CH), 126.0 (2 x CH),

117.2 (d, $J = 9.6$ Hz, CH), 53.0 (d, $J = 7.3$ Hz, CH₃), 33.2 (d, $J = 138.1$ Hz, CH₂). ³¹P NMR (202 MHz, CDCl₃) δ 27.07. HRMS (APCI) Calc. for C₁₆H₁₈O₃P [M+H⁺]: 289.098, found 289.0991.

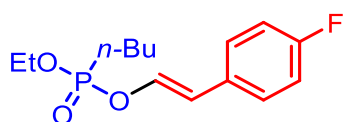
(E)-Ethyl 4-fluorostyryl phenylphosphonate (3m)



Obtained from **1d** and **2b** as a yellow oil after column chromatography following the general procedure in 75% yield.

¹H NMR (500 MHz, CDCl₃) δ 7.88 (dd, $J = 13.7, 8.2, 1.3$ Hz, 2H), 7.62 (tq, $J = 7.4, 1.4$ Hz, 1H), 7.52 (td, $J = 7.8, 4.5$ Hz, 2H), 7.23 (dd, $J = 8.7, 5.3$ Hz, 2H), 7.16 (dd, $J = 12.2, 6.8$ Hz, 1H), 6.99 (t, $J = 8.7$ Hz, 2H), 6.37 (dd, $J = 13.5, 1.2$ Hz, 1H), 4.32 – 4.24 (m, 2H), 1.42 (t, $J = 7.1$ Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 162.1 (d, $J = 246.6$ Hz, C), 136.5 (dd, $J = 5.3, 2.2$ Hz, 2 x CH), 133.0 (d, $J = 3.1$ Hz, CH), 131.8 (d, $J = 10.2$ Hz, 2 x CH), 130.1 (d, $J = 3.4$ Hz, C), 128.7 (d, $J = 15.5$ Hz, 2 x CH), 127.5 (d, $J = 8.0$ Hz, 2 x CH), 127.1 (d, $J = 192.5$ Hz, C), 116.5 (d, $J = 10.0$ Hz, CH), 115.6 (d, $J = 21.7$ Hz, 2 x CH), 63.0 (d, $J = 6.0$ Hz, CH₂), 16.3 (d, $J = 6.3$ Hz, CH₃). ³¹P NMR (202 MHz, CDCl₃) δ 18.26. ¹⁹F NMR (282 MHz, CDCl₃) δ -114.9. HRMS (APCI) Calc. for C₁₆H₁₇FO₃P [M+H⁺]: 307.0894 found 307.0902.

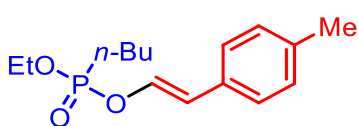
(E)-Ethyl 4-fluorostyryl butylphosphonate (3n)



Obtained from **1a** and **2b** as a yellow oil after column chromatography following the general procedure in 65% yield.

¹H NMR (300 MHz, CDCl₃) δ 7.26 (dd, $J = 8.7, 5.4$ Hz, 2H), 7.18 (dd, $J = 12.4, 6.6$ Hz, 1H), 7.00 (t, $J = 8.7$ Hz, 2H), 6.33 (dd, $J = 12.3, 1.4$ Hz, 1H), 4.29 – 4.12 (m, 2H), 1.93 – 1.81 (m, 2H), 1.71 – 1.58 (m, 2H), 1.46 (sext, $J = 7.4$ Hz, 2H), 1.37 (t, $J = 7.1$ Hz, 3H), 0.95 (t, $J = 7.4$ Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 162.0 (d, $J = 246.5$ Hz, C), 136.8 (dd, $J = 5.9, 2.2$ Hz, 2 x CH), 130.2 (d, $J = 3.3$ Hz, C), 127.5 (d, $J = 7.7$ Hz, 2 x CH), 115.6 (d, $J = 21.7$ Hz, 2 x CH), 115.7 (s, CH), 62.1 (d, $J = 7.0$ Hz, CH₂), 25.3 (d, $J = 140.3$ Hz, CH₂), 24.1 (d, $J = 5.3$ Hz, CH₂), 23.6 (d, $J = 17.6$ Hz, CH₂), 16.4 (d, $J = 6.1$ Hz, CH₃), 13.5 (CH₃). ³¹P NMR (202 MHz, CDCl₃) δ 32.73. ¹⁹F NMR (282 MHz, CDCl₃) δ -115.4. HRMS (APCI) Calc. for C₁₄H₂₁FO₃P [M+H⁺]: 287.1112 found 287.1115.

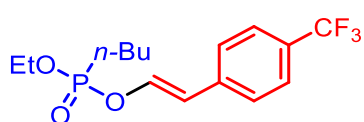
(E)-Ethyl 4-methylstyryl butylphosphonate (3o)



Obtained from **1a** and **2c** as a yellow oil after column chromatography following the general procedure in 94% yield.

¹H NMR (300 MHz, CDCl₃) δ 7.26 – 7.16 (m, 3H), 7.11 (d, $J = 7.8$ Hz, 2H), 6.34 (dd, $J = 12.5, 2.1$ Hz, 1H), 4.30 – 4.09 (m, 2H), 2.34 (s, 3H), 1.95 – 1.81 (m, 2H), 1.72 – 1.59 (m, 2H), 1.46 – 1.39 (m, 2H), 1.37 (t, $J = 6.9$ Hz, 3H), 0.94 (t, $J = 7.2$ Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 136.0 (C), 135.3 (d, $J = 6.0$ Hz, CH), 130.1 (C), 128.4 (2 x CH), 124.9 (2 x CH), 115.7 (d, $J = 9.5$ Hz, CH), 61.0 (d, $J = 7.2$ Hz, CH₂), 24.3 (d, $J = 140.3$ Hz, CH₂), 23.1 (d, $J = 5.4$ Hz, CH₂), 22.6 (d, $J = 17.4$ Hz, CH), 20.1 (CH₃), 15.4 (d, $J = 6.1$ Hz, CH₃), 12.5 (CH₃). ³¹P NMR (202 MHz, CDCl₃) δ 31.56. HRMS (APCI) Calc. for C₁₅H₂₃O₃P [M+H⁺]: 283.1458 found 283.1454.

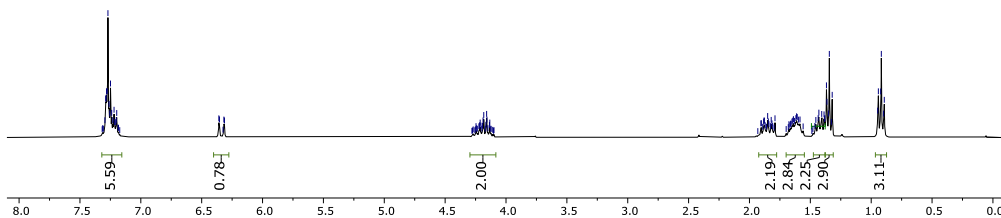
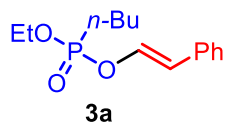
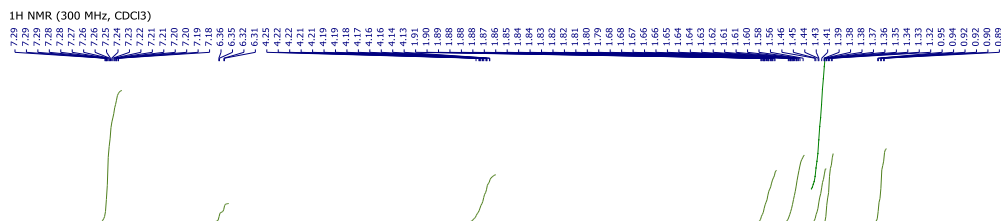
(E)-Ethyl 4-(trifluoromethyl)styryl butylphosphonate (3p)



Obtained from **1a** and **2d** as a yellow oil after column chromatography following the general procedure in 70% yield.

¹H NMR (500 MHz, CDCl₃) δ 7.54 (d, *J* = 8.2 Hz, 2H), 7.38 (d, *J* = 8.5 Hz, 2H), 7.35 (dd, *J* = 12.4, 6.9 Hz, 1H), 6.36 (d, *J* = 12.3 Hz, 1H), 4.26 – 4.14 (m, 2H), 1.92 – 1.84 (m, 2H), 1.69 – 1.62 (m, 2H), 1.45 (sext, *J* = 7.3 Hz, 2H), 1.37 (t, *J* = 7.1 Hz, 3H), 0.94 (t, *J* = 7.3 Hz, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 139.3 (d, *J* = 5.8 Hz, C), 138.2 (d, *J* = 1.28 Hz, CH), 129.3 (q, *J* = 32.5 Hz, C), 126.3 (2 x CH), 125.9 (q, *J* = 3.8 Hz, 2 x CH), 124.4 (q, *J* = 271.9 Hz, C), 115.5 (d, *J* = 9.6 Hz, CH), 62.4 (d, *J* = 7.1 Hz, CH₂), 26.6 (d, *J* = 138 Hz, CH₂), 24.4 (d, *J* = 5.4 Hz, CH₂), 23.9 (d, *J* = 16.08 Hz, CH₂), 16.6 (d, *J* = 12.5 Hz, CH₃), 13.8 (d, *J* = 1.2 Hz, CH₃). **³¹P NMR** (202 MHz, CDCl₃) δ 31.95. **¹⁹F NMR** (282 MHz, CDCl₃) δ -62.66. **HRMS (APCI)** Calc. for C₁₅H₂₁F₃O₃P [M+H⁺]: 337.1181 found 337.1176.

6. ^1H NMR and ^{13}C NMR spectra



^{13}C NMR (126 MHz, CDCl_3)

