

Supporting information

Rhodium (III)-Catalyzed *ortho*-Olefination of Aryl Phosphonates

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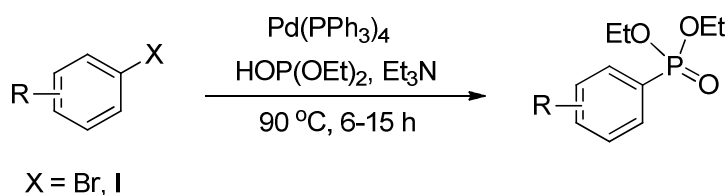
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1. Experimental Section:

General: Reactions were carried out in oven-dried glassware under a nitrogen atmosphere. All commercial reagents were used without purification, and all solvents were reagent grade. All reaction mixtures were stirred magnetically and were monitored by thin-layer chromatography using Merck silica gel 60 F₂₅₄ percolated glass plates, which were visualized with UV light and then developed using either iodine or a solution of anisaldehyde. Flash column chromatography was carried out using Merck silica gel 60 (0.040-0.063 mm, 230-400 mesh). ¹H NMR (400MHz) and ¹³C NMR spectra were recorded on a ECA 400 MHz and ECA 400SL) spectrometer. Deuterated chloroform was used as the solvent, and chemical shift values (δ) are reported in parts per million relative to the residual signals of this solvent (δ 7.24 for ¹H and δ 77.2 for ¹³C). Infrared spectra were recorded on a FTIR spectrometer as either a thin film pressed between two sodium chloride plates or as a solid suspended in a potassium bromide disk. High-resolution mass spectra were recorded on a LC/ HRMS mass spectrometer.

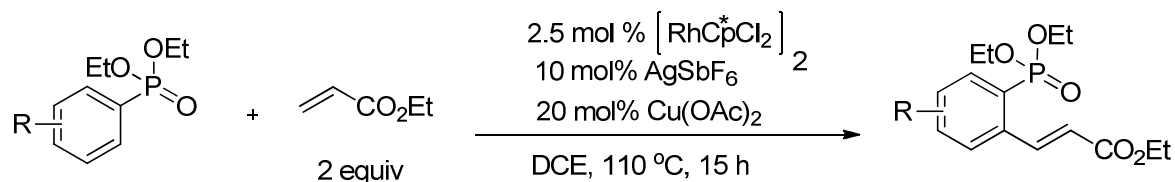
2. Analytical data:

General experimental procedure for the preparation of aryl phosphonate:¹

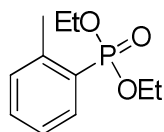


To a stirred solution of diethyl phosphite (2.0 mmol) and triethylamine (2.0 mmol) in presence of a catalytic amount of Pd(PPh₃)₄ (0.08 mmol, 5 mol % equiv), aryl bromide or aryl iodide (1.6 mmol) was added under nitrogen, and the reaction mixture was stirred at 90 °C for 6-15 h. When the aryl halide used was solid, toluene (1 ml) was added as solvent. After the addition of ether, the reaction mixture was filtered. After evaporation of the solvent, the crude product was purified by silica gel column chromatography.

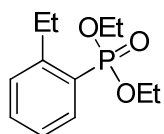
General experimental procedure for the Rh-catalyzed C-H alkenylation:



(RhCp*Cl₂)₂ (3.4 mg, 0.005 mmol, 2.5mol % equiv), AgSbF₆ (7.5 mg, 0.02 mmol, 10 mol % equiv) and Cu(OAc)₂ (7.9 mg, 0.04 mmol, 20 mol % equiv) was carefully weighed to a vial equipped with a magnetic stirrer bar and a tightly-screwed cap. Aryl phosphonate (0.22 mmol, 1.0 equiv) in dichloroethane (0.5 mL) was then added, followed by ethyl acrylate (0.44 mmol, 2.0 equiv). The reaction mixture was flushed with oxygen for 30 second and stirred at 110 °C for 15 h, and cooled to room temperature. The crude product was concentrated *in vacuo* and purified by flash column chromatography (ethyl acetate:hexane = 1:1) to afford the desired alkenylated product.

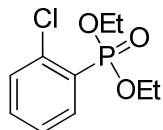


Diethyl o-tolyl phosphonate (1):² ¹H NMR (400 MHz, CDCl₃): δ 7.94-7.88 (m, 1H), 7.44-7.40 (m, 1H), 7.28-7.24 (m, 2H), 4.18-4.05 (m, 4H), 2.57 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 6H); ¹³C NMR (400 MHz, CDCl₃) δ 155.2, 134.1 (d, *J*_{C-P} = 10.5 Hz), 132.8, 131.5, 131.3, 130.9, 126.8, 125.6, 119.7, 115.1, 62.3, 21.3, 16.4 (d, *J*_{C-P} = 6.8 Hz); ³¹P NMR (400 MHz, CDCl₃): δ = 20.1288; IR (film) 3053.32, 2304.94, 1712.79, 1421.54, 1361.74, 1265.30, 1222.87, 894.97, 727.16 cm⁻¹; HRMS (EI) calcd for C₁₁H₁₇O₃P (M⁺) 229.0994, found 229.0990.

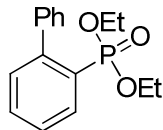


Diethyl (2-ethylphenyl) phosphonate (3a): ¹H NMR (400 MHz, CDCl₃): δ 7.92-7.86 (m, 1H), 7.49-7.43 (m, 1H), 7.34-7.21 (m, 2H), 4.21-4.04 (m, 4H), 2.97 (q, *J* = 7.8 Hz, 2H), 1.35-1.23 (m, 9H); ¹³C NMR (400 MHz, CDCl₃) δ 148.4 (d, *J*_{C-P} = 10.5 Hz), 134.0, 132.8, 129.8

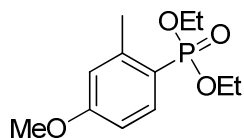
(d, J_{C-P} = 15.3 Hz), 125.5 (d, J_{C-P} = 15.3 Hz), 62.1 (d, J_{C-P} = 5.7 Hz), 27.3, 16.5 (d, J_{C-P} = 5.7 Hz), 15.8; ^{31}P NMR (400 MHz, CDCl_3): δ = 20.3413; IR (film) 2983.88, 1712.79, 1595.13, 1568.13, 1475.54, 1392.61, 1361.74, 1246.02, 1143.79, 964.41 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{12}\text{H}_{19}\text{O}_3\text{P}(\text{M}^+)$ 243.1150, found 243.1151.



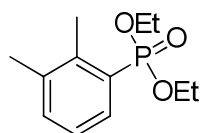
Diethyl (2-chlorophenyl) phosphonate (3b): ^1H NMR (400 MHz, CDCl_3): δ 8.03-7.97 (m, 1H), 7.50-7.31 (m, 3H), 4.24-4.08 (m, 4H), 1.21-1.29 (m, 6H); ^{13}C NMR (400 MHz, CDCl_3) δ 136.9, 136.0 (d, J_{C-P} = 7.6 Hz), 133.7, 130.9 (d, J_{C-P} = 10.5 Hz), 128.3, 126.5 (d, J_{C-P} = 13.4 Hz), 62.7 (d, J_{C-P} = 5.7 Hz), 16.4 (d, J_{C-P} = 6.7 Hz); ^{31}P NMR (400 MHz, CDCl_3): δ = 15.1435; IR (film) 2983.88, 1712.79, 1583.56, 1566.20, 1456.26, 1392.61, 1367.53, 1163.08, 1060.85, 758.02 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{10}\text{H}_{14}\text{O}_3\text{PCl}(\text{M}^+)$ 249.0447, found 249.0441.



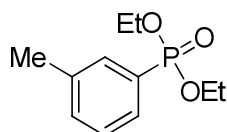
Diethyl [1,1'-biphenyl]-2-yl phosphonate (3c): ^1H NMR (400 MHz, CDCl_3): δ 8.07-8.01(m, 1H), 7.57-7.26 (m, 8H), 3.96-3.80 (m, 4H), 1.11 (t, J = 7.1 Hz, 6H); ^{13}C NMR (400 MHz, CDCl_3) δ 146.3 (d, J_{C-P} = 9.6 Hz), 141.6, 134.0 (d, J_{C-P} = 9.6 Hz), 132.1, 131.5 (d, J_{C-P} = 14.4 Hz), 129.5 (d, J_{C-P} = 10.5 Hz), 127.9, 127.6, 127.5, 127.4, 127.1, 126.9, 126.1, 62.0 (d, J_{C-P} = 5.7 Hz), 16.2 (d, J_{C-P} = 6.7 Hz); ^{31}P NMR (400 MHz, CDCl_3): δ = 18.7995; IR (film) 3016.67, 2399.45, 1712.79, 1591.27, 1562.34, 1469.76, 1444.68, 1392.61, 1367.53, 1217.08, 1139.93, 1095.57, 1028.06, 974.05 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{16}\text{H}_{19}\text{O}_3\text{P}(\text{M}^+)$ 291.1150, found 291.1148.



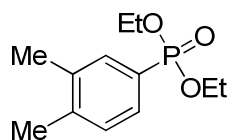
Diethyl (4-methoxy-2-methylphenyl) phosphonate (3d): ^1H NMR (400 MHz, CDCl_3): δ 7.88-7.85 (m, 1H), 6.78-6.75 (m, 2H), 4.13- 4.06 (m, 4H), 2.53 (s, 3H), 1.33-1.30 (m, 6H); ^{13}C NMR (400 MHz, CDCl_3) δ 163.4, 144.2, 136.4 (d, $J_{\text{C-P}} = 12.4$ Hz), 132.2, 128.6, 117.3 (d, $J_{\text{C-P}} = 15.3$ Hz), 61.9 (d, $J_{\text{C-P}} = 4.8$ Hz), 55.4, 21.5, 16.4 (d, $J_{\text{C-P}} = 6.7$ Hz); ^{31}P NMR (400 MHz, CDCl_3): $\delta = 21.0401$; IR (film) 3412.08, 2985.81, 1699.29, 1637.56, 1591.27, 1363.67, 1166.93, 1109.07, 1022.27, 530.42 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{12}\text{H}_{19}\text{O}_4\text{P}(\text{M}^+)$ 259.1099, found 259.1097.



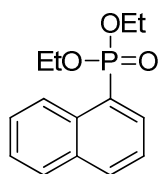
Diethyl (2,3-dimethylphenyl) phosphonate (3e): ^1H NMR (400 MHz, CDCl_3): δ 7.79-7.75 (m, 1H), 7.44-7.31 (m, 2H), 4.14-4.09 (m, 4H), 2.49 (s, 3H), 2.31 (s, 3H), 1.32 (t, $J = 7.3$ Hz, 6H); ^{13}C NMR (400 MHz, CDCl_3) δ 140.3 (d, $J_{\text{C-P}} = 10.5$ Hz), 138.1 (d, $J_{\text{C-P}} = 14.4$ Hz), 135.0, 134.2, 131.9 (d, $J_{\text{C-P}} = 10.5$ Hz), 127.9, 126.1, 125.3, 125.2, 61.9 (d, $J_{\text{C-P}} = 5.7$ Hz), 20.5, 17.7, 16.4 (d, $J_{\text{C-P}} = 6.7$ Hz); ^{31}P NMR (400 MHz, CDCl_3): $\delta = 20.0167$; IR (film) 3018.60, 2399.45, 1708.93, 1521.84, 1444.68, 1215.15, 1161.15, 1053.13, 1026.13, 968.27, 848.68, 759.95 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{12}\text{H}_{19}\text{O}_3\text{P}(\text{M}^+)$ 243.1150, found 243.1149.



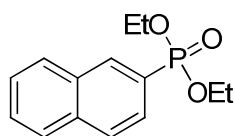
Diethyl *m*-tolyl phosphonate (3f): ^1H NMR (400 MHz, CDCl_3): δ 7.66-7.57 (m, 2H), 7.36-7.35 (m, 2H), 4.18-4.04 (m, 4H), 2.39 (s, 3H), 1.34-1.30 (m, 6H); ^{13}C NMR (400 MHz, CDCl_3) δ 138.4 (d, $J_{\text{C-P}} = 15.3$ Hz), 133.3, 132.4 (d, $J_{\text{C-P}} = 10.5$ Hz), 129.0, 128.9, 128.8, 128.6, 128.4, 127.2, 62.1 (d, $J_{\text{C-P}} = 5.7$ Hz), 21.4, 16.4 (d, $J_{\text{C-P}} = 6.7$ Hz); ^{31}P NMR (400 MHz, CDCl_3): $\delta = 19.9356$; IR (film) 3435.88, 2983.88, 1708.93, 1442.75, 1363.67, 1313.52, 1247.94, 1120.64, 1022.27, 968.27, 569.00, 547.78 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{11}\text{H}_{17}\text{O}_3\text{P}(\text{M}^+)$ 229.0994, found 229.0994.



Diethyl (3,4-dimethylphenyl) phosphonate (3g):³ ¹H NMR (400 MHz, CDCl₃): δ 7.59-7.46 (m, 2H), 7.24-7.16 (m, 1H), 4.18-4.00 (m, 4H), 2.30-2.23 (m, 6H), 1.35-1.26 (m, 6H); ¹³C NMR (400 MHz, CDCl₃) δ 141.9, 141.5, 137.4, 132.9, 132.3, 130.3, 129.9, 129.6, 126.4, 124.3, 62.2 (d, *J*_{C-P} = 5.7 Hz), 20.1, 19.8 (d, *J*_{C-P} = 4.8 Hz), 16.5 (d, *J*_{C-P} = 13.4 Hz); ³¹P NMR (400 MHz, CDCl₃): δ = 20.5848; IR (film) 2987.74, 1606.70, 1446.61, 1215.15, 1111.00, 1026.13, 968.27, 754.17, 667.17 cm⁻¹; HRMS (EI) calcd for C₁₂H₁₉O₃P(M⁺) 243.1150, found 243.1150.



Diethyl naphthalen-1-yl phosphonate (3h):⁴ ¹H NMR (400 MHz, CDCl₃): δ 8.55-8.49 (m, 1H), 8.27-8.17 (m, 1H), 8.04-7.84 (m, 2H), 7.63-7.39 (m, 3H), 4.23-4.03 (m, 4H), 1.35-1.21 (m, 6H); ¹³C NMR (400 MHz, CDCl₃) δ 134.9 (d, *J*_{C-P} = 8.6 Hz), 133.7 (d, *J*_{C-P} = 15.3 Hz), 128.8 (d, *J*_{C-P} = 19.2 Hz), 127.6, 127.4, 126.8, 126.4, 124.7 (d, *J*_{C-P} = 16.3 Hz), 62.5, 16.5 (d, *J*_{C-P} = 6.7 Hz); ³¹P NMR (400 MHz, CDCl₃): δ = 19.8274; IR (film) 2983.88, 1712.79, 1508.33, 1363.67, 1222.87, 1045.42, 804.32, 777.31 cm⁻¹; HRMS (EI) calcd for C₁₄H₁₇O₃P(M⁺) 265.0994, found 265.0995.

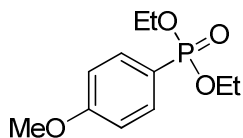


Diethyl naphthalen-2-yl phosphonate (3i):² ¹H NMR (400 MHz, CDCl₃): δ 8.35 (d, *J* = 16.0 Hz, 1H), 7.86-7.78 (m, 3H), 7.70-7.65 (m, 1H), 7.53-7.45 (m, 3H), 4.14-3.99 (m, 4H), 1.25 (t, *J* = 7.1 Hz, 6H); ¹³C NMR (400 MHz, CDCl₃) δ 135.1, 134.1 (d, *J*_{C-P} = 10.5 Hz), 132.4 (d, *J*_{C-P} = 17.2 Hz), 129.1, 128.6, 128.4, 127.9, 127.0, 126.6, 126.5, 126.4, 124.5, 62.3 (d, *J*_{C-P} = 4.8 Hz), 16.5 (d, *J*_{C-P} = 5.7 Hz); ³¹P NMR (400 MHz, CDCl₃): δ = 19.7462; IR (film) 2987.74, 1710.86, 1627.92, 1438.90, 1392.61, 1236.37, 1163.08, 1097.50, 1024.20,

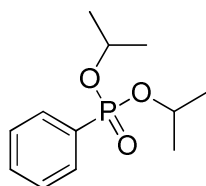
968.27, 864.11, 819.75, 651.94, 540.07 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{14}\text{H}_{17}\text{O}_3\text{P}(\text{M}^+)$ 265.0994, found 265.0996.



Dimethyl phenyl phosphonate (3j):^{2, 4} ^1H NMR (400 MHz, CDCl_3): δ 7.77-7.71(m, 2H), 7.71-7.39 (m, 3H), 3.72-3.68 (m, 6H); ^{13}C NMR (400 MHz, CDCl_3) δ 132.7, 131.9, 131.9, 128.7, 128.5; ^{31}P NMR (400 MHz, CDCl_3): δ = 22.1807; IR (film) 2953.02, 2850.79, 1714.72, 1593.20, 1438.90, 1234.44, 1134.14, 835.18, 798.53, 752.24 cm^{-1} ; HRMS (EI) calcd for $\text{C}_8\text{H}_{11}\text{O}_3\text{P}(\text{M}^+)$ 187.0524, found 187.0522.

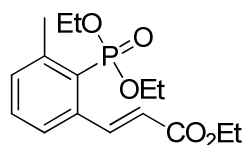


Diethyl (4-methoxyphenyl) phosphonate (3k):⁴ ^1H NMR (400 MHz, CDCl_3): δ 7.79-7.72 (m, 3H), 6.99-6.96 (m, 2H), 4.17-4.02 (m, 4H), 3.85 (d, J = 9.2 Hz, 3H), 1.38-1.26 (m, 6H); ^{13}C NMR (400 MHz, CDCl_3) δ 162.9, 133.8 (d, $J_{\text{C-P}}$ = 11.5 Hz), 132.0, 128.6 (d, $J_{\text{C-P}}$ = 12.4 Hz), 114.1 (d, $J_{\text{C-P}}$ = 16.2 Hz), 62.0 (d, $J_{\text{C-P}}$ = 4.8 Hz), 55.3, 16.3 (d, $J_{\text{C-P}}$ = 6.7Hz); ^{31}P NMR (400 MHz, CDCl_3): δ = 20.3684; IR (film) 2985.81, 1710.86, 1600.92, 1571.99, 1506.41, 1440.83, 1392.61, 1298.09, 1242.16, 1130.29, 968.27, 808.17 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{11}\text{H}_{17}\text{O}_4\text{P}(\text{M}^+)$ 245.0943, found 245.0941.

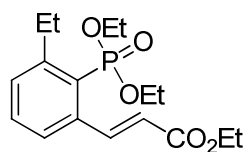


Diisopropyl phenylphosphonate (3l):^{2, 4} ^1H NMR (400 MHz, CDCl_3): δ 7.85-7.79 (m, 2H), 7.55-7.51 (m, 1H), 7.47-7.42 (m, 2H), 4.73-4.65 (m, 2H), 1.38 (s, 3H), 1.37 (s, 3H), 1.23 (s, 3H), 1.22 (s, 3H); ^{13}C NMR (400 MHz, CDCl_3) δ 132.2, 131.9, 128.6, 128.4, 70.9 (d, $J_{\text{C-P}}$ = 5.7 Hz), 24.2 (d, $J_{\text{C-P}}$ = 3.8 Hz), 24.0 (d, $J_{\text{C-P}}$ = 4.8 Hz); ^{31}P NMR (400 MHz, CDCl_3): δ = 17.2847; IR (film) 2981.95, 1438.90, 1386.82, 1242.16, 1178.51, 1132.21, 1103.28, 987.55,

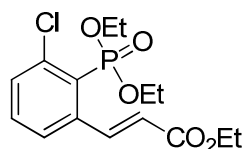
885.33, 748.38, 694.37, 565.14 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{12}\text{H}_{19}\text{O}_3\text{P}(\text{M}^+)$ 243.1150, found 243.1154.



(E)-Ethyl 3-(2-(diethoxyphosphoryl)-3-methylphenyl)acrylate (2): ^1H NMR (400 MHz, CDCl_3): δ 8.56 (d, $J = 16.0$ Hz, 1H), 7.40-7.38 (m, 2H), 7.28-7.27 (m, 1H), 6.17 (d, $J = 15.6$ Hz, 1H), 4.29-4.04 (m, 6H), 2.69 (s, 3H), 1.35-1.30 (m, 9H); ^{13}C NMR (400 MHz, CDCl_3) δ 166.9, 146.4, 144.4 (d, $J_{\text{C-P}} = 10.5$ Hz), 140.5, 133.1 (d, $J_{\text{C-P}} = 15.3$ Hz), 132.2, 126.4 (d, $J_{\text{C-P}} = 13.4$ Hz), 120.8, 62.1 (d, $J_{\text{C-P}} = 4.8$ Hz), 60.7, 23.2, 16.4 (d, $J_{\text{C-P}} = 6.7$ Hz), 14.5; ^{31}P NMR (400 MHz, CDCl_3): $\delta = 18.3330$; IR (film) 2981.95, 1712.79, 1633.71, 1581.63, 1454.33, 1367.53, 1307.74, 1168.86, 1138.00, 966.34, 867.97 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{16}\text{H}_{23}\text{O}_5\text{P}(\text{M}^+)$ 327.1361, found 327.1368.

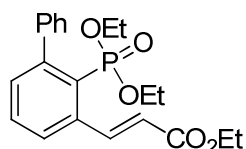


(E)-Ethyl 3-(2-(diethoxyphosphoryl)-3-ethylphenyl)acrylate (4a): ^1H NMR (400 MHz, CDCl_3): δ 8.53 (d, $J = 16.0$ Hz, 1H), 7.47-7.28 (m, 3H), 6.16 (d, $J = 15.6$ Hz, 1H), 4.29-3.69 (m, 6H), 3.18-3.13 (m, 2H), 1.36-1.24 (m, 12H); ^{13}C NMR (400 MHz, CDCl_3) δ 166.9, 151.2 (d, $J_{\text{C-P}} = 11.5$ Hz), 146.7, 140.4 (d, $J_{\text{C-P}} = 9.6$ Hz), 132.3, 131.9, 131.8, 126.4 (d, $J_{\text{C-P}} = 14.4$ Hz), 120.5, 62.0 (d, $J_{\text{C-P}} = 5.7$ Hz), 60.6, 28.5, 17.1, 16.4 (d, $J_{\text{C-P}} = 6.7$ Hz), 14.5; ^{31}P NMR (400 MHz, CDCl_3): $\delta = 18.2314$; IR (film) 2983.88, 1708.93, 1635.64, 1581.63, 1454.33, 1392.61, 1367.53, 1309.67, 1172.72, 1138.00, 966.34, 808.17 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{17}\text{H}_{25}\text{O}_5\text{P}(\text{M}^+)$ 341.1518, found 341.1515.

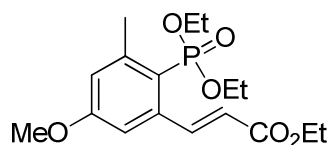


(E)-Ethyl 3-(3-chloro-2-(diethoxyphosphoryl)phenyl)acrylate (4b): ^1H NMR (400 MHz, CDCl_3): δ 8.61 (d, $J = 16.0$ Hz, 1H), 7.74-7.42 (m, 3H), 6.15 (d, $J = 16.0$ Hz, 1H), 4.30-4.11 (m, 6H), 1.37-1.32 (m, 9H); ^{13}C NMR (400 MHz, CDCl_3) δ 166.5, 145.4, 143.0 (d, $J_{\text{C-P}} = 8.6$

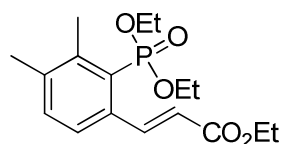
Hz), 138.9, 132.9, 132.3, 132.2, 125.4, 121.9, 62.7 (d, J_{C-P} = 5.7 Hz), 60.9, 16.4 (d, J_{C-P} = 6.7 Hz), 14.5; ^{31}P NMR (400 MHz, CDCl_3): δ = 13.9576; IR (film) 2995.45, 1701.22, 1637.56, 1554.63, 1438.90, 1367.53, 1309.67, 1238.30, 1178.51, 1124.50, 1024.20, 974.05, 798.53, 665.44, 621.08, 567.07 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{15}\text{H}_{20}\text{O}_5\text{P}(\text{M}^+)$ 347.0816, found 347.0816.



(E)-Ethyl 3-(2-(diethoxyphosphoryl)-[1,1'-biphenyl]-3-yl)acrylate (4c): ^1H NMR (400 MHz, CDCl_3): δ 8.54 (d, J = 16.0 Hz, 1H), 7.59-7.26 (m, 8H), 4.32-4.26 (m, 2H), 3.96-3.88 (m, 2H), 3.79-3.72 (m, 2H), 1.37-1.26 (m, 3H), 1.13-1.09 (m, 6H); ^{13}C NMR (400 MHz, CDCl_3) δ 166.7, 147.9, 145.7, 142.6, 140.5, 140.4, 132.9, 132.8, 131.5, 129.2, 127.8, 127.6, 127.4, 121.1, 61.9 (d, J_{C-P} = 6.7 Hz), 60.8, 29.9, 16.1 (d, J_{C-P} = 6.7 Hz), 14.5; ^{31}P NMR (400 MHz, CDCl_3): δ = 16.8249; IR (film) 1708.93, 1309.67, 1276.88, 1047.35, 1026.13, 972.12, 557.43 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{21}\text{H}_{25}\text{O}_5\text{P}(\text{M}^+)$ 389.1518, found 389.1520.

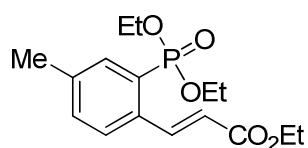


(E)-Ethyl 3-(2-(diethoxyphosphoryl)-5-methoxy-3-methylphenyl)acrylate (4d): ^1H NMR (400 MHz, CDCl_3): δ 8.56 (d, J = 15.6 Hz, 1H), 6.89-6.87 (m, 1H), 6.79-6.77 (m, 1H), 6.16 (d, J = 15.6 Hz, 1H), 4.29-3.84 (m, 6H), 2.66 (s, 3H), 1.35-1.26 (m, 9H); ^{13}C NMR (400 MHz, CDCl_3) δ 166.8, 161.9, 146.5, 142.8, 120.8, 118.3 (d, J_{C-P} = 16.3 Hz), 111.7 (d, J_{C-P} = 14.4 Hz), 61.8 (d, J_{C-P} = 5.7 Hz), 55.5, 23.4, 16.4 (d, J_{C-P} = 6.7 Hz), 14.5; ^{31}P NMR (400 MHz, CDCl_3): δ = 19.0700; IR (film) 2985.81, 1699.29, 1591.27, 1363.67, 1166.93, 1045.42, 966.34, 530.42 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{17}\text{H}_{25}\text{O}_6\text{P}(\text{M}^+)$ 357.1467, found 357.1465.

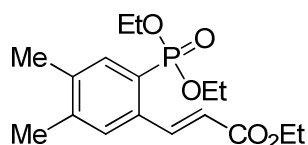


(E)-Ethyl 3-(2-(diethoxyphosphoryl)-3,4-dimethylphenyl)acrylate (4e): ^1H NMR (400 MHz, CDCl_3): δ 8.56 (d, J = 15.6 Hz, 1H), 7.30-7.27 (m, 2H), 6.12 (d, J = 15.6 Hz, 1H),

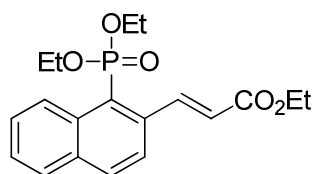
4.28-4.04 (m, 6H), 2.60 (s, 3H), 2.32 (s, 3H), 1.36-1.30 (m, 9H); ^{13}C NMR (400 MHz, CDCl_3) δ 167.0, 146.5 (d, $J_{\text{C-P}} = 3.8$ Hz), 142.9 (d, $J_{\text{C-P}} = 11.4$ Hz), 139.8 (d, $J_{\text{C-P}} = 15.3$ Hz), 138.5 (d, $J_{\text{C-P}} = 10.5$ Hz), 133.8 (d, $J_{\text{C-P}} = 2.9$ Hz), 127.2, 126.3 (d, $J_{\text{C-P}} = 15.2$ Hz), 125.4, 119.7, 62.0 (d, $J_{\text{C-P}} = 5.7$ Hz), 60.6, 21.3, 18.7, 16.4 (d, $J_{\text{C-P}} = 6.7$ Hz), 14.5; ^{31}P NMR (400 MHz, CDCl_3): $\delta = 19.9897$; IR (film) 2985.81, 1712.79, 1633.71, 1444.68, 1365.60, 1307.74, 1226.73, 1166.93, 1022.27, 966.34, 827.46, 761.88, 624.94, 549.71 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{17}\text{H}_{25}\text{O}_5\text{P}(\text{M}^+)$ 341.1518, found 341.1512.



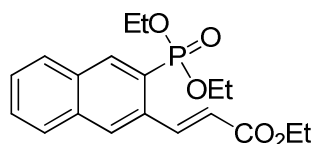
(E)-Ethyl 3-(2-(diethoxyphosphoryl)-4-methylphenyl)acrylate (4f): ^1H NMR (400 MHz, CDCl_3): δ 8.31 (d, $J = 16.0$ Hz, 1H), 7.88-7.84 (m, 1H), 7.60-7.58 (m, 1H), 7.35-7.33 (m, 1H), 6.32 (d, $J = 16.0$ Hz, 1H), 4.26-4.08 (m, 4H), 2.39 (s, 3H), 1.33-1.31 (m, 9H); ^{13}C NMR (400 MHz, CDCl_3) δ 166.8, 142.9, 140.0 (d, $J_{\text{C-P}} = 13.4$ Hz), 135.4 (d, $J_{\text{C-P}} = 9.6$ Hz), 133.6, 128.7, 127.3 (d, $J_{\text{C-P}} = 14.4$ Hz), 120.3, 62.4, 60.7, 21.4, 16.4 (d, $J_{\text{C-P}} = 6.7$ Hz), 14.4 (d, $J_{\text{C-P}} = 11.5$ Hz); ^{31}P NMR (400 MHz, CDCl_3): $\delta = 18.5560$; IR (film) 2981.95, 1438.90, 1242.16, 1132.21, 1008.77, 748.38, 694.37, 565.14, 540.07 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{16}\text{H}_{23}\text{O}_5\text{P}(\text{M}^+)$ 327.1361, found 327.1362.



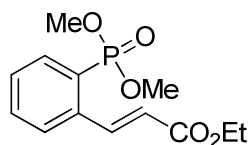
(E)-Ethyl 3-(2-(diethoxyphosphoryl)-4,5-dimethylphenyl)acrylate (4g): ^1H NMR (400 MHz, CDCl_3): δ 8.31 (d, $J = 16.0$ Hz, 1H), 7.81 (d, $J = 14.6$ Hz, 1H), 7.47-7.48 (m, 1H), 6.34 (d, $J = 16.0$ Hz, 1H), 4.28-4.05 (m, 6H), 2.32-2.30 (m, 6H), 1.35-1.30 (m, 9H); ^{13}C NMR (400 MHz, CDCl_3) δ 166.9, 143.1 (d, $J_{\text{C-P}} = 19.1$ Hz), 142.1 (d, $J_{\text{C-P}} = 11.5$ Hz), 138.7 (d, $J_{\text{C-P}} = 10.5$ Hz), 136.0, 135.9, 135.3, 128.6, 125.9, 120.1, 62.3 (d, $J_{\text{C-P}} = 5.7$ Hz), 60.7, 20.1, 19.7, 16.4 (d, $J_{\text{C-P}} = 6.7$ Hz), 14.5; ^{31}P NMR (400 MHz, CDCl_3): $\delta = 19.0429$; IR (film) 2983.88, 1712.79, 1637.56, 1446.61, 1367.53, 1242.16, 1028.06, 765.74 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{17}\text{H}_{25}\text{O}_5\text{P}(\text{M}^+)$ 341.1518, found 341.1521.



(E)-Ethyl 3-(1-(diethoxyphosphoryl)naphthalen-2-yl)acrylate (4h): ^1H NMR (400 MHz, CDCl_3): δ 9.10 (d, $J = 2.2$ Hz, 1H), 8.90 (d, $J = 16.0$ Hz, 1H), 8.01 (d, $J = 9.2$ Hz, 1H), 7.84 (d, $J = 8.2$ Hz, 1H), 7.67-7.26 (m, 3H), 6.34 (d, $J = 16.0$ Hz, 1H), 4.33-4.22 (m, 4H), 4.12-4.05 (m, 2H), 1.38-1.29 (m, 9H); ^{13}C NMR (400 MHz, CDCl_3) δ 166.7, 146.0, 140.2, 133.8, 133.6, 128.5, 128.0, 127.8, 126.9, 125.1 (d, $J_{\text{C-P}} = 15.3$ Hz), 121.9, 62.2, 60.7, 16.3 (d, $J_{\text{C-P}} = 6.7$ Hz), 14.4; ^{31}P NMR (400 MHz, CDCl_3): $\delta = 17.9880$; IR (film) 3008.95, 1708.93, 1419.61, 1363.67, 1224.80, 1091.71, 1022.27, 765.74, 665.44, 530.42 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{19}\text{H}_{23}\text{O}_5\text{P}(\text{M}^+)$ 363.1361, found 363.1364.

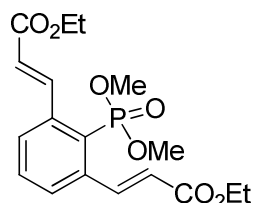


(E)-Ethyl 3-(3-(diethoxyphosphoryl)naphthalen-2-yl)acrylate (4i): ^1H NMR (400 MHz, CDCl_3): δ 8.63 (d, $J = 16.5$ Hz, 1H), 8.42 (d, $J = 15.6$ Hz, 1H), 8.14 (d, $J = 5.0$ Hz, 1H), 7.95-7.87 (m, 2H), 7.63-7.56 (m, 2H), 6.48 (d, $J = 16.0$ Hz, 1H), 4.33-4.09 (m, 6H), 1.36-1.32 (m, 9H); ^{13}C NMR (400 MHz, CDCl_3) δ 166.9, 143.6, 137.2, 134.8, 129.0, 128.4, 127.8, 127.4, 120.9, 62.1, 60.1, 29.7, 16.2, 14.5; ^{31}P NMR (400 MHz, CDCl_3): $\delta = 18.5560$; IR (film) 3005.10, 1712.79, 1363.67, 1222.87, 1180.44, 1024.20, 970.19, 763.81, 530.42 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{19}\text{H}_{23}\text{O}_5\text{P}(\text{M}^+)$ 363.1361, found 363.1360.

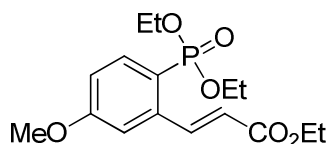


(E)-Ethyl 3-(2-(diethoxyphosphoryl)phenyl)acrylate (4j): ^1H NMR (400 MHz, CDCl_3): δ 8.30 (d, $J = 16.0$ Hz, 1H), 8.05-7.99 (m, 1H), 7.60-7.56 (m, 1H), 7.50-7.26 (m, 1H), 6.38 (d, $J = 16.0$ Hz, 1H), 4.26 (q, $J = 7.3$ Hz, 2H), 3.80 (s, 3H), 3.78 (s, 3H), 1.34 (t, $J = 7.1$ Hz, 3H), 6.75 (m, 1H), 4.23-4.03 (m, 4H), 1.31 (q, $J = 7.3$ Hz, 6H); ^{13}C NMR (400 MHz, CDCl_3) δ

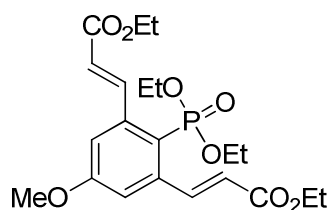
166.6, 142.7, 138.1 (d, J_{C-P} = 9.5 Hz), 134.8 (d, J_{C-P} = 9.5 Hz), 133.0, 132.0 (d, J_{C-P} = 9.5 Hz), 129.3 (d, J_{C-P} = 15.3 Hz), 128.7, 127.6, 127.4 (d, J_{C-P} = 13.3 Hz), 125.8, 121.7, 60.9, 52.9 (d, J_{C-P} = 5.7 Hz), 14.5; ^{31}P NMR (400 MHz, CDCl_3): δ = 21.1205; IR (film) 1710.86, 1315.45, 1247.94, 1182.36, 1138.00, 1033.85, 775.38, 557.43 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{15}\text{H}_{21}\text{O}_5\text{P}(\text{M}^+)$ 313.1205, found 313.1206.



(2E,2'E)-Diethyl 3,3'-(2-(diethoxyphosphoryl)-1,3-phenylene)diacrylate (5j): ^1H NMR (400 MHz, CDCl_3): δ 8.53 (m, J = 16.0 Hz, 2H), 7.58-7.57 (m, 3H), 6.23 (d, J = 16.0 Hz, 2H), 4.28 (q, J = 7.1 Hz, 4H), 3.79 (s, 3H), 3.78 (s, 3H), 1.34 (t, J = 7.3 Hz, 6H); ^{13}C NMR (400 MHz, CDCl_3) δ 166.6 (d, J_{C-P} = 3.8 Hz), 144.8 (d, J_{C-P} = 8.6 Hz), 141.2 (d, J_{C-P} = 9.6 Hz), 132.9, 129.5 (d, J_{C-P} = 14.4 Hz), 60.7, 52.7, 14.5 (d, J_{C-P} = 4.8 Hz); ^{31}P NMR (400 MHz, CDCl_3): δ = 19.3783; IR (film) 3410.15, 1708.93, 1629.85, 1363.67, 1273.02, 1028.06, 1028.06, 977.91, 555.50 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{18}\text{H}_{23}\text{O}_7\text{P}(\text{M}^+)$ 383.1260, found 383.1255.

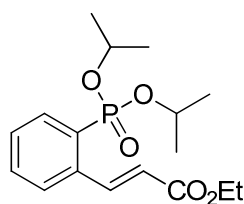


(E)-Ethyl 3-(2-(diethoxyphosphoryl)-5-methoxyphenyl)acrylate (4k): ^1H NMR (400 MHz, CDCl_3): δ 8.32 (d, J = 15.6 Hz, 1H), 8.01-7.95 (m, 1H), 7.18-7.16 (m, 1H), 6.98-6.94 (m, 1H), 6.34 (d, J = 16.0 Hz, 1H), 4.31-4.04 (m, 6H), 3.88 (s, 3H), 1.36-1.30 (m, 9H); ^{13}C NMR (400 MHz, CDCl_3) δ 166.6, 163.1, 143.0, 140.1, 136.9 (d, J_{C-P} = 11.5 Hz), 121.5, 114.5 (d, J_{C-P} = 15.3 Hz), 113.2 (d, J_{C-P} = 14.4 Hz), 62.4 (d, J_{C-P} = 5.7 Hz), 60.8, 55.7, 16.5 (d, J_{C-P} = 6.7 Hz), 14.5; ^{31}P NMR (400 MHz, CDCl_3): δ = 18.9495; IR (film) 2983.88, 1712.79, 1637.56, 1595.13, 1560.41, 1477.47, 1367.53, 1234.44, 966.34 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{16}\text{H}_{23}\text{O}_6\text{P}(\text{M}^+)$ 343.1311, found 343.1310.

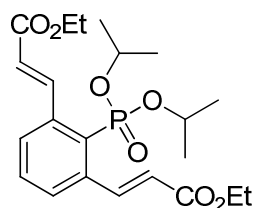


(2E,2'E)-Diethyl 3,3'-(2-(diethoxyphosphoryl)-5-methoxy-1,3-phenylene)diacrylate (5k):

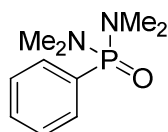
^1H NMR (400 MHz, CDCl_3): δ 8.58 (d, J = 16.0 Hz, 2H), 7.06 (d, J = 3.6 Hz, 2H), 6.21 (d, J = 16.0 Hz, 2H), 4.30-4.02 (m, 8H), 3.89 (s, 3H), 1.39-1.11 (m, 12H); ^{13}C NMR (400 MHz, CDCl_3) δ 166.6, 162.2, 145.3, 143.1 (d, $J_{\text{C-P}}$ = 10.5 Hz), 121.8, 114.8 (d, $J_{\text{C-P}}$ = 14.3 Hz), 62.3 (d, $J_{\text{C-P}}$ = 5.7 Hz), 60.9, 55.8, 16.4 (d, $J_{\text{C-P}}$ = 6.7 Hz), 14.5; ^{31}P NMR (400 MHz, CDCl_3): δ = 17.1537; IR (film) 3016.67, 1712.79, 1639.49, 1589.34, 1417.68, 1361.74, 1224.80, 1180.44, 1109.07, 1024.20, 765.74 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{21}\text{H}_{29}\text{O}_8\text{P}(\text{M}^+)$ 441.1678, found 441.1674.



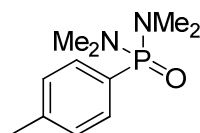
(E)-Ethyl 3-(2-(diisopropoxyphosphoryl)phenyl)acrylate (4l): ^1H NMR (400 MHz, CDCl_3): δ 8.40 (d, J = 16.5 Hz, 1H), 8.11-8.05 (m, 1H), 7.85-7.57 (m, 1H), 7.48-7.46 (m, 1H), 7.45-7.28 (m, 2H), 6.36 (d, J = 16 Hz, 1H), 4.78-4.67 (m, 2H), 4.28 (q, J = 7.1 Hz, 2H), 1.42-1.20 (m, 15H); ^{13}C NMR (400 MHz, CDCl_3) δ 166.7, 143.5, 134.6 (d, $J_{\text{C-P}}$ = 9.5 Hz), 132.6 (d, $J_{\text{C-P}}$ = 2.9 Hz), 131.9 (d, $J_{\text{C-P}}$ = 10.1 Hz), 129.4 (d, $J_{\text{C-P}}$ = 14.3 Hz), 128.5 (d, $J_{\text{C-P}}$ = 15.1 Hz), 127.2 (d, $J_{\text{C-P}}$ = 13.4 Hz), 121.0, 71.5 (d, $J_{\text{C-P}}$ = 6.7 Hz), 70.9, 60.7, 24.2, 24.0, 23.9, 14.5; ^{31}P NMR (400 MHz, CDCl_3): δ = 15.8240; IR (film) 3018.60, 2983.88, 1710.86, 1467.83, 1386.82, 1313.52, 1242.16, 1103.28, 991.41, 781.17, 736.81, 667.37, 565.14 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{17}\text{H}_{25}\text{O}_5\text{P}(\text{M}^+)$ 341.1518, found 341.1522.



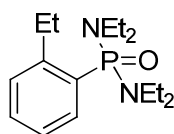
(2*E*,2'*E*)-Diethyl 3,3'-(2-(diisopropoxyphosphoryl)-1,3-phenylene)diacrylate (5l): ^1H NMR (400 MHz, CDCl_3): δ 8.67 (d, $J = 16.0$ Hz, 2H), 7.59-7.52 (m, 3H), 6.21 (d, $J = 15.6$ Hz, 2H), 4.82-4.74 (m, 2H), 4.74-4.25 (m, 4H), 1.41-1.32 (m, 12H), 1.27-1.19 (m, 6H); ^{13}C NMR (400 MHz, CDCl_3) δ 166.7, 145.6 (d, $J_{\text{C-P}} = 3.8$ Hz), 140.7 (d, $J_{\text{C-P}} = 9.6$ Hz), 132.3, 129.4, 129.3, 121.4, 71.8 (d, $J_{\text{C-P}} = 6.7$ Hz), 60.8, 24.1, 14.5; ^{31}P NMR (400 MHz, CDCl_3): $\delta = 13.8764$; IR (film) 2981.95, 1712.79, 1635.64, 1454.33, 1367.53, 1311.59, 1238.30, 1174.65, 1103.28, 991.41, 650.01, 561.29 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{22}\text{H}_{31}\text{O}_7\text{P}(\text{M}^+)$ 439.1886, found 439.1879.



Aryl phosphinic acid bis(dimethylamide) (6): ^1H NMR (400 MHz, CDCl_3): δ 7.68-7.64 (m, 2H), 7.40-7.35 (m, 2H), 2.56 (s, 6H), 2.54 (s, 6H); ^{13}C NMR (400 MHz, CDCl_3) δ 132.1, 131.9, 131.2, 130.9, 129.4, 128.3, 128.2, 36.2 (d, $J_{\text{C-P}} = 2.9$ Hz); ^{31}P NMR (400 MHz, CDCl_3): $\delta = 30.4038$; IR (film) 2304.94, 1712.78, 1265.30, 894.97, 727.16 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{10}\text{H}_{17}\text{N}_2\text{OP}(\text{M}^+)$ 213.1157, found 213.1158.

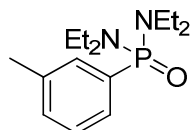


4-Methyl-aryl phosphinic acid bis(dimethylamide) (6a): ^1H NMR (400 MHz, CDCl_3): δ 7.65-7.61 (m, 2H), 7.28-7.23 (m, 2H), 2.64 (s, 6H), 2.62 (s, 6H), 2.39 (s, 3H); ^{13}C NMR (400 MHz, CDCl_3) δ 141.7 (d, $J_{\text{C-P}} = 2.9$ Hz), 132.4, 132.3, 132.2, 132, 130, 129.4, 129.3, 129.2, 120 (d, $J_{\text{C-P}} = 4.8$ Hz), 36.4, 21.6; ^{31}P NMR (400 MHz, CDCl_3): $\delta = 30.8636$; IR (film) 2376.30, 1734.01, 1602.85, 1456.26, 1217.08, 1114.86, 771.53 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{15}\text{H}_{27}\text{N}_2\text{OP}(\text{M}^+)$ 283.1939, found 283.1933.

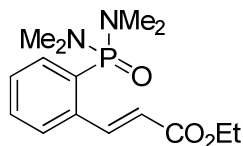


2-Ethyl-aryl phosphinic acid bis(diethylamide) (6b): ^1H NMR (400 MHz, CDCl_3): δ 7.49-7.31 (m, 3H), 7.19-7.16 (m, 1H), 3.18-3.04 (m, 10H), 1.27 (t, $J = 3.7$ Hz, 3H), 1.09-1.06 (m

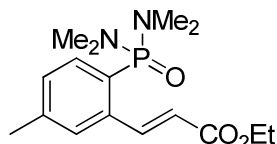
12H); ^{13}C NMR (400 MHz, CDCl_3) δ 149.9, 132.5 (d, $J_{\text{C-P}} = 10.5$ Hz), 131.3, 129.9 (d, $J_{\text{C-P}} = 13.4$ Hz), 125.1 (d, $J_{\text{C-P}} = 13.4$ Hz), 39.2 (d, $J_{\text{C-P}} = 4.8$ Hz), 26.9, 15.6, 14.2; ^{31}P NMR (400 MHz, CDCl_3): $\delta = 30.9838$; IR (film) 3197.98, 2987.74, 1710.86, 1604.77, 1500.62, 1419.61, 1230.95, 1033.85, 774.46 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{12}\text{H}_{21}\text{N}_2\text{OP}(\text{M}^+)$ 241.1470, found 241.1477.



3-Methyl-aryl phosphinic acid bis(dimethylamide) (6c): ^1H NMR (400 MHz, CDCl_3): δ 7.66-7.62 (m, 1H), 7.54-7.49 (m, 1H), 7.32-7.25 (m, 2H), 3.14-3.03 (m, 8H), 2.38 (s, 3H), 1.04 (t, $J = 7.1$ Hz); ^{13}C NMR (400 MHz, CDCl_3) δ 138.1, 134.3, 132.9, 132.8, 131.7, 128.8, 128.1, 128, 38.4 (d, $J_{\text{C-P}} = 3.8$ Hz), 21.5, 13.8; ^{31}P NMR (400 MHz, CDCl_3): $\delta = 29.0242$; IR (film) 1714.72, 1640.23, 1390.68, 1020.34, 866.04, 655.80 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{15}\text{H}_{27}\text{N}_2\text{OP}(\text{M}^+)$ 283.1939, found 283.1938.

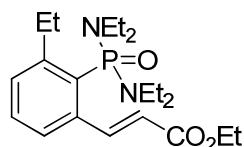


(E)-ethyl 3-(2-(bis(dimethylamino)phosphoryl)phenyl)acrylate (7): ^1H NMR (400 MHz, CDCl_3): δ 8.56 (d, $J = 16.0$ Hz, 1H), 7.17-7.42 (m, 4H), 6.34 (d, $J = 16.0$ Hz), 4.25 (q, $J = 7.1$ Hz, 6H), 2.69 (s, 6H), 2.67 (s, 6H), 1.33 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (400 MHz, CDCl_3) δ 166.9, 143.7, 139.2, 133.4 (d, $J_{\text{C-P}} = 8.6$ Hz), 131.9, 129.5, 129.4, 127.8, 127.7, 120.8, 60.8, 36.6 (d, $J_{\text{C-P}} = 4.8$ Hz), 14.5; ^{31}P NMR (400 MHz, CDCl_3): $\delta = 29.9385$; IR (film) 1643.35, 1463.97, 1436.97, 1292.31, 1192.01, 979.84, 786.81 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{15}\text{H}_{23}\text{N}_2\text{O}_3\text{P}(\text{M}^+)$ 311.1525, found 311.1524.

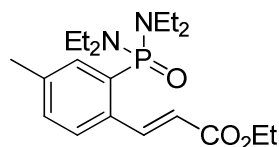


(E)-ethyl 3-(2-(bis(dimethylamino)phosphoryl)-5-methylphenyl)acrylate (9): ^1H NMR (400 MHz, CDCl_3): δ 8.51 (d, $J = 16.0$ Hz, 1H), 7.58-7.49 (m, 2H), 7.27-7.23 (m, 1H), 6.32

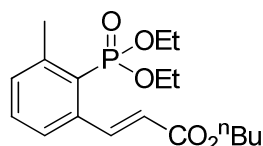
(d, $J = 16.0$ Hz, 1H), 4.25 (q, $J = 7.1$ Hz, 2H), 2.69 (s, 6H), 2.67 (s, 6H), 1.33 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (400 MHz, CDCl_3) δ 166.9, 143.7, 138.6 (d, $J_{\text{C-P}} = 8.6$ Hz), 133.4 (d, $J_{\text{C-P}} = 8.6$ Hz), 130.2 (d, $J_{\text{C-P}} = 13.4$ Hz), 128.4 (d, $J_{\text{C-P}} = 12.4$ Hz), 120.5, 60.6, 36.6 (d, $J_{\text{C-P}} = 4.8$ Hz), 14.3; ^{31}P NMR (400 MHz, CDCl_3): $\delta = 30.1333$; IR (film) 2841.08, 1710.86, 1598.99, 1506.41, 1296.16, 1132.21 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{16}\text{H}_{25}\text{N}_2\text{O}_3\text{P}(\text{M}^+)$ 325.1681, found 325.1673.



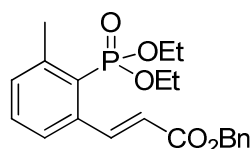
(E)-ethyl 3-(2-(bis(diethylamino)phosphoryl)-3-methylphenyl)acrylate (10): ^1H NMR (400 MHz, CDCl_3): δ 8.30 (d, $J = 16.0$ Hz, 1H), 7.49-7.26 (m, 3H), 6.11 (d, $J = 16.0$ Hz, 1H), 4.24 (q, $J = 7.3$ Hz, 2H), 3.15-2.99 (m, 10H), 1.33-1.24 (m, 3H), 1.14-1.06 (m, 15H); ^{13}C NMR (400 MHz, CDCl_3) δ 167.1, 147.7, 139.8, 132.6 (d, $J_{\text{C-P}} = 9.6$ Hz), 132.1 (d, $J_{\text{C-P}} = 12.4$ Hz), 131.4, 131.1, 129.9 (d, $J_{\text{C-P}} = 12.5$ Hz), 126.7 (d, $J_{\text{C-P}} = 11.5$ Hz), 125.1 (d, $J_{\text{C-P}} = 13.4$ Hz), 119.3, 60.6, 39.9 (d, $J_{\text{C-P}} = 4.8$ Hz), 39.3, 27.9, 16.4, 14.5, 14.3, 14.2; ^{31}P NMR (400 MHz, CDCl_3): $\delta = 28.2939$; IR (film) 2 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{17}\text{H}_{39}\text{N}_2\text{O}_2\text{P}(\text{M}^+)$ 335.2827, found 335.2818.



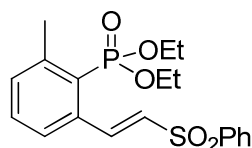
(E)-ethyl 3-(2-(bis(diethylamino)phosphoryl)-4-methylphenyl)acrylate (11): ^1H NMR (400 MHz, CDCl_3): δ 8.68 (d, $J = 16$ Hz, 1H), 7.63-7.25 (m, 3H), 6.28 (d, $J = 16.0$ Hz, 1H), 4.25-4.20 (m, 2H), 3.12-3.03 (m, 8H), 2.37 (s, 3H), 1.31-1.28 (m, 3H), 1.09-1.01 (m, 12H); ^{13}C NMR (400 MHz, CDCl_3) δ 167.0, 143.9, 139.4 (d, $J_{\text{C-P}} = 12.4$ Hz), 138.2 (d, $J_{\text{C-P}} = 12.5$ Hz), 132.9, 132.3, 131.8, 128.9, 128.2, 127.7, 119.6, 60.6, 39.4 (d, $J_{\text{C-P}} = 4.8$ Hz), 38.5 (d, $J_{\text{C-P}} = 6.9$ Hz), 21.6 (d, $J_{\text{C-P}} = 5.7$ Hz), 14.2, 13.9, 13.8; ^{31}P NMR (400 MHz, CDCl_3): $\delta = 29.5111$; IR (film) 1712.79, 1583.56, 1456.26, 1242.16, 1022.27, 758.02 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{20}\text{H}_{33}\text{N}_2\text{O}_3\text{P}(\text{M}^+)$ 381.2307, found 381.2303.



(E)-Butyl 3-(2-(diethoxyphosphoryl)-3-methylphenyl)acrylate (12a): ^1H NMR (400 MHz, CDCl_3): δ 8.56 (d, $J = 16.0$ Hz, 1H), 7.40-7.38 (m, 2H), 7.28-7.25 (m, 1H), 6.17 (d, $J = 16.0$ Hz, 1H), 4.23-4.04 (m, 6H), 2.69 (s, 3H), 1.73-1.66 (m, 2H), 1.47-1.42 (m, 2H), 1.31 (t, $J = 7.1$ Hz, 6H), 0.96 (t, $J = 7.6$ Hz, 6H); ^{13}C NMR (400 MHz, CDCl_3) δ 166.9, 146.4, 144.5, 140.5 (d, $J_{\text{C-P}} = 10.5$ Hz), 133.2 (d, $J_{\text{C-P}} = 15.3$ Hz), 132.1, 126.3 (d, $J_{\text{C-P}} = 13.4$ Hz), 120.7, 64.6, 62.0 (d, $J_{\text{C-P}} = 4.8$ Hz), 30.9, 23.2, 19.4, 16.4 (d, $J_{\text{C-P}} = 6.7$ Hz), 13.9; ^{31}P NMR (400 MHz, CDCl_3): $\delta = 18.3667$; IR (film) 2962.66, 1712.79, 1635.64, 1581.63, 1454.33, 1390.68, 1309.67, 1238.30, 1168.86, 1138.00, 1022.27, 968.27, 754.17, 640.37, 570.93, 532.35 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{18}\text{H}_{27}\text{O}_5\text{P}(\text{M}^+)$ 355.1674, found 355.1675.

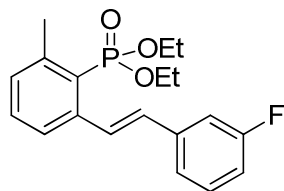


(E)-Benzyl 3-(2-(diethoxyphosphoryl)-3-methylphenyl)acrylate (12b): ^1H NMR (400 MHz, CDCl_3): δ 8.62 (d, $J = 16.0$ Hz, 1H), 7.43-7.26 (m, 8H), 6.22 (d, $J = 16.0$ Hz, 1H), 5.25 (s, 2H), 4.19-4.01 (m, 4H), 2.69 (s, 3H), 1.31-1.26 (m, 6H); ^{13}C NMR (400 MHz, CDCl_3) δ 166.6, 146.9, 144.1, 140.5, 136.1, 132.9, 132.0, 129.1, 128.6, 128.3, 127.8, 119.9, 78.4, 77.5, 76.7, 67.7, 66.3, 61.8, 23.0, 16.2 (d, $J_{\text{C-P}} = 6.7$ Hz); ^{31}P NMR (400 MHz, CDCl_3): $\delta = 18.2585$; IR (film) 3018.60, 1708.93, 1417.68, 1361.74, 1222.87, 1089.78, 1024.20, 966.34, 748.38, 667.37, 530.42 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{21}\text{H}_{25}\text{O}_5\text{P}(\text{M}^+)$ 389.1518, found 389.1495.

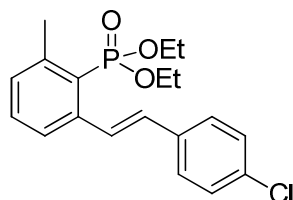


(E)-Diethyl (2-methyl-6-(2-(phenylsulfonyl)vinyl)phenyl) phosphonate (12c): ^1H NMR (400 MHz, CDCl_3): δ 8.66 (d, $J = 16.0$ Hz, 1H), 8.02 (d, $J = 7.3$ Hz, 1H), 7.63-7.26 (m, 7H), 6.59 (d, $J = 15.6$ Hz, 1H), 4.19-4.02 (m, 4H), 2.68 (s, 3H), 1.35-1.25 (m, 6H); ^{13}C NMR (400 MHz, CDCl_3) δ 145.1, 140.6, 138.2, 133.9, 133.8, 133.5, 132.3, 129.5, 129.4, 129.3, 128.1,

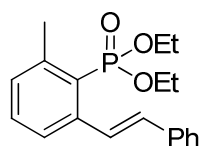
126.6, 62.2, 29.9, 23.0, 16.5 (d, $J_{C-P} = 5.7$ Hz); ^{31}P NMR (400 MHz, CDCl_3): $\delta = 17.9068$; IR (film) 2993.52, 1710.86, 1446.61, 1361.74, 1307.74, 1147.65, 1022.27, 970.19, 850.61, 686.66, 594.08 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{19}\text{H}_{23}\text{O}_5\text{PS}(\text{M}^+)$ 395.1082, found 395.1077.



(E)-Diethyl (2-(3-fluorostyryl)-6-methylphenyl) phosphonate (12d): ^1H NMR (400 MHz, CDCl_3): δ 8.63 (d, $J = 16.0$ Hz, 1H), 8.58-7.25 (m, 7H), 6.21 (d, $J = 15.6$ Hz, 1H), 4.21-4.01 (m, 4H), 2.69 (s, 3H), 1.27 (t, $J = 6.2$ Hz, 6H); ^{13}C NMR (400 MHz, CDCl_3) δ 166.6, 147.0 (d, $J_{C-P} = 3.8$ Hz), 144.5 (d, $J_{C-P} = 11.5$ Hz), 141.4, 140.4 (d, $J_{C-P} = 9.6$ Hz), 136.3, 133.3, 133.1, 132.1, 128.8, 128.7, 128.6, 128.5, 128.4, 126.4, 126.3, 120.2, 66.5, 62.0 (d, $J_{C-P} = 5.7$ Hz), 23.1 (d, $J_{C-P} = 2.9$ Hz), 16.4 (d, $J_{C-P} = 6.7$ Hz); ^{31}P NMR (400 MHz, CDCl_3): $\delta = 18.2585$; IR (film) 1712.79, 1419.61, 1363.67, 1224.80, 1165.00, 1091.71, 756.10, 698.23, 530.42 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{19}\text{H}_{22}\text{O}_3\text{PF}(\text{M}^+)$ 349.1369, found 349.1360.



(E)-Diethyl (2-(4-chlorostyryl)-6-methylphenyl) phosphonate (12e): ^1H NMR (400 MHz, CDCl_3): δ 8.19 (d, $J = 16.0$ Hz, 1H), 7.54-7.19 (m, 7H), 6.81 (d, $J = 16.0$ Hz, 1H), 4.21-4.03 (m, 4H), 2.69 (s, 3H), 1.32-1.27 (m, 6H); ^{13}C NMR (400 MHz, CDCl_3) δ 144.5, 143.3, 136.7, 132.1, 129.5, 129.0, 128.1 (d, $J_{C-P} = 4.8$ Hz), 125.4, 123.7, 61.8, 23.5, 16.5 (d, $J_{C-P} = 6.7$ Hz); ^{31}P NMR (400 MHz, CDCl_3): $\delta = 19.8815$; IR (film) 2991.59, 1710.86, 1490.97, 1452.40, 1363.67, 1217.08, 1091.71, 1022.27, 970.19, 815.89, 767.67, 665.44 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{19}\text{H}_{23}\text{O}_3\text{PCl}(\text{M}^+)$ 365.1073, found 365.1068.



(E)-Diethyl (2-methyl-6-styrylphenyl) phosphonate (12f): ^1H NMR (400 MHz, CDCl_3): δ 8.16 (d, $J = 16.0$ Hz, 1H), 7.56-7.17 (m, 8H), 6.85 (d, $J = 16.0$ Hz, 1H), 4.21-4.02 (m, 4H), 2.68 (s, 3H), 1.33-1.22 (m, 6H); ^{13}C NMR (400 MHz, CDCl_3) δ 138.4, 131.3, 130.9, 130.1, 128.9, 127.8, 127.0, 125.6, 125.4, 61.7, 23.5, 16.5 (d, $J_{\text{C-P}} = 6.7$ Hz); ^{31}P NMR (400 MHz, CDCl_3): $\delta = 20.0167$; IR (film) 3408.22, 2991.59, 1710.86, 1450.47, 1363.67, 1024.20, 968.27, 596.00, 530.42 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{19}\text{H}_{23}\text{O}_3\text{P}(\text{M}^+)$ 331.1463, found 331.1453.

3. References:

1. (a) T. Hirao, T. Masunaga, Y. Ohshiro and T. Agawa, *Synthesis*, 1981, 56; (b) Y. Xu and J. Zhang, *Synthesis*, 1984, 778.
2. R.-Q. Zhang, J. Xu, Z.-S. Cai, *Org. Lett.* 2011., **13**, 2110.
3. Y. Guoqiang, S. Chaoren, Z. Liang, Z. Wanbin, *Tetrahedron Lett.*, 2011, **52**, 5032.
4. M. Kalek, M. Jezowska, J. Stawinskia, *Org. Lett.*, 2008, **10**, 4637.

4. Spectra of compounds:

