

Supporting Information

Electrochemical phosphorylation of arenols and anilines leading to organophosphates and phosphoramidates

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General experimental procedures

Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. The instrument for electrolysis was dual display potentiostat (QJ3005T) (made in China). The anodic electrode was platinum plate (10 mm×10 mm×1 mm) and cathodic electrode was platinum plate (10 mm×10 mm×1 mm). Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel in petroleum (boiling point was between 60-90 °C). Gradient flash chromatography was conducted eluting with a continuous gradient from petroleum to the indicated solvent, and they were listed as volume/volume ratios. ¹H- and ¹³C-NMR spectra were recorded on a Bruker DRX-400 spectrometer operating at 400 MHz and 100 MHz respectively. HRMS spectrometry (LC-HRMS) was recorded on a LXQ Spectrometer (Thermo Scientific) operating on ESI-TOF (MeOH as a solvent).

General procedure for the synthesis of compounds **3a-r**.

In an oven-dried undivided three-necked bottle (25 mL) equipped with a stir bar, P(O)H compounds **1a** (0.5 mmol), phenol **2a** (0.6 mmol), sodium iodide (0.2 equiv), MeCN (5 mL) was added. The bottle was equipped with platinum plate (10 mm×10 mm×1 mm) as the anode and platinum plate (10 mm×10 mm×1 mm) as the cathode. The reaction mixture was stirred and electrolyzed at a constant current of 20 mA under air at room temperature for 2 h. After completion of the reaction, as indicated by TLC and GC-MS, the pure product was obtained by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 20-5 : 1). The same procedure was applied to the production of other compounds **3a-r**.

General procedure for the synthesis of compounds **5a-p**.

In an oven-dried undivided three-necked bottle (25 mL) equipped with a stir bar, P(O)H compounds **1a** (0.5 mmol), aniline **4a** (0.6 mmol), potassium iodide (0.2 equiv), MeCN (5 mL) was added. The bottle was equipped with platinum plate (10 mm×10 mm×1 mm) as the anode and platinum plate (10 mm×10 mm×1 mm) as the cathode. The reaction mixture was stirred and electrolyzed at a constant current of 10 mA under air at 50°C for 2 h. After completion of the reaction, as indicated by TLC and GC-MS, the pure product was obtained by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 40-30 : 1). The same procedure was applied to the production of other compounds **5a-p**.

General procedure for cyclic voltammetry (CV)

Cyclic voltammetry was performed in a three-electrode cell connected to a schlenk line under air at room temperature. The working electrode was a glassy carbon electrode, the counter electrode a platinum wire. The reference was a SCE electrode submerged in saturated aqueous KCl solution. 10 mL of CH₃CN containing 0.01 M nBu₄NBF₄ were poured into the electrochemical cell in all experiments. The scan rate is 0.1 V/s, ranging from 0 V to 3.5 V. The peak potentials vs. SCE for used. From figure 1, it can be seen that an obvious oxidation peak of phenol (**2a**) was observed at 1.82 V. The oxidation peak of aniline (**4a**) could also be observed at 1.15 V. Meanwhile, the oxidation peak of aniline KI could be seen at 1.05 V.

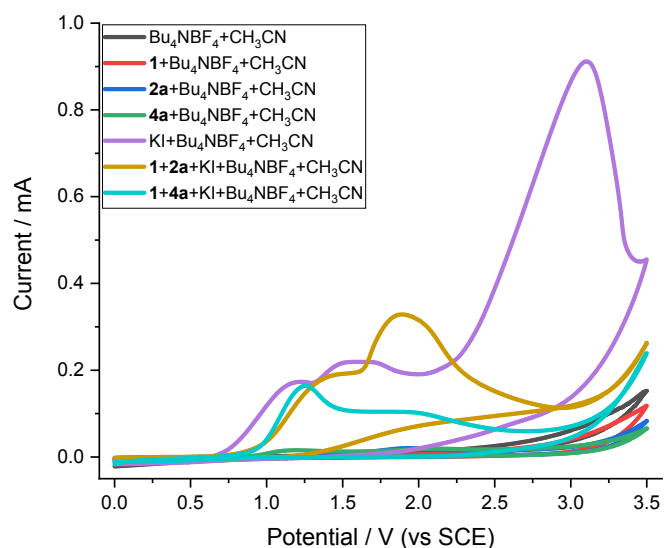
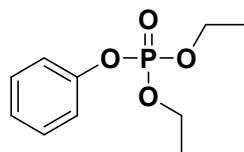


Figure 1 Cyclic voltammetry

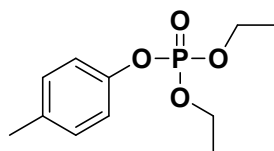
Detail descriptions for products

Diethyl phenyl phosphate (3a)



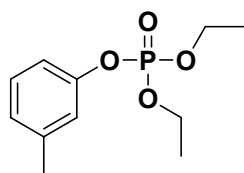
¹H NMR (400 MHz, Chloroform-d) δ 7.37 – 7.30 (m, 2H), 7.22 (dt, J = 8.7, 1.2 Hz, 2H), 7.17 (td, J = 7.4, 1.1 Hz, 1H), 4.27 – 4.16 (m, 4H), 1.35 (td, J = 7.1, 1.1 Hz, 6H). **¹³C NMR** (101 MHz, Chloroform-d) δ 129.68, 124.95, 119.99, 119.94, 64.60, 64.54, 16.11, 16.04. **³¹P NMR** (162 MHz, Chloroform-d) δ -6.33. **HRMS** (ESI-TOF) m/z calculated for C₁₀H₁₆O₄P⁺ 231.0781 (M+H)⁺, found 231.0777.

Diethyl *p*-tolyl phosphate (3b)



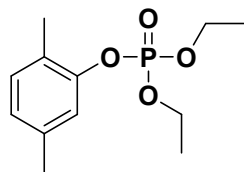
¹H NMR (400 MHz, Chloroform-d) δ 7.10 (d, J = 2.3 Hz, 4H), 4.25 – 4.14 (m, 4H), 2.30 (s, 3H), 1.33 (td, J = 7.1, 1.1 Hz, 6H). **¹³C NMR** (101 MHz, Chloroform-d) δ 148.60, 148.53, 134.47, 130.08, 119.69, 119.64, 64.48, 64.41, 20.65, 16.08, 16.02. **HRMS** (ESI-TOF) m/z calculated for C₁₁H₁₈O₄P⁺ 245.0937 (M+H)⁺, found 245.0927.

Diethyl *m*-tolyl phosphate (3c)



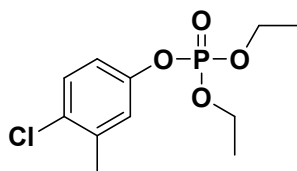
¹H NMR (400 MHz, Chloroform-d) δ 7.22 (t, J = 7.8 Hz, 1H), 7.07 – 6.96 (m, 3H), 4.27 – 4.17 (m, 4H), 2.35 (s, 3H), 1.36 (td, J = 7.1, 1.1 Hz, 6H). **¹³C NMR** (101 MHz, Chloroform-d) δ 139.92, 129.33, 125.72, 120.58, 120.53, 116.89, 116.85, 64.53, 64.47, 21.30, 16.11, 16.04. **HRMS** (ESI-TOF) m/z calculated for C₁₁H₁₈O₄P⁺ 245.0937 (M+H)⁺, found 245.0927.

2,5-Dimethylphenyl diethyl phosphate (3d)



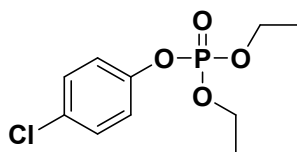
¹H NMR (400 MHz, Chloroform-d) δ 7.12 (s, 1H), 7.07 (d, $J = 7.6$ Hz, 1H), 6.88 (d, $J = 7.5$ Hz, 1H), 4.22 (dddd, $J = 11.0, 7.0, 3.5, 1.5$ Hz, 4H), 2.31 (s, 3H), 2.27 (s, 3H), 1.36 (td, $J = 7.1, 1.1$ Hz, 6H). **¹³C NMR** (101 MHz, Chloroform-d) δ 148.98, 136.97, 130.93, 125.84, 125.61, 120.30, 64.49, 64.43, 20.95, 16.14, 16.07, 15.92. **HRMS** (ESI-TOF) m/z calculated for $C_{12}H_{20}O_4P^+$ 259.1094 (M+H)⁺, found 259.1088.

4-Chloro-3-methylphenyl diethyl phosphate (3e)



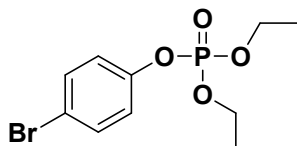
¹H NMR (400 MHz, Chloroform-d) δ 7.28 (s, 1H), 7.13 (d, $J = 2.9$ Hz, 1H), 7.04 – 6.99 (m, 1H), 4.23 (dq, $J = 8.3, 7.1, 2.5$ Hz, 4H), 2.37 (s, 3H), 1.37 (td, $J = 7.1, 1.1$ Hz, 6H). **¹³C NMR** (101 MHz, Chloroform-d) δ 137.68, 130.45, 129.90, 122.37, 122.32, 118.67, 118.62, 64.73, 64.67, 20.22, 16.13, 16.06. **HRMS** (ESI-TOF) m/z calculated for $C_{11}H_{17}ClO_4P^+$ 279.0547 (M+H)⁺, found 279.0541.

4-Chlorophenyl diethyl phosphate (3f)



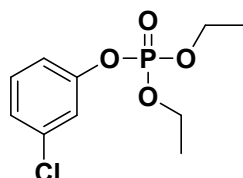
¹H NMR (400 MHz, Chloroform-d) δ 7.27 (d, $J = 8.7$ Hz, 2H), 7.19 – 7.10 (m, 2H), 4.23 – 4.14 (m, 4H), 1.32 (td, $J = 7.1, 1.1$ Hz, 6H). **¹³C NMR** (101 MHz, Chloroform-d) δ 149.26, 130.25, 129.66, 124.93, 121.33, 119.97, 64.76, 64.70, 16.08, 16.02. **HRMS** (ESI-TOF) m/z calculated for $C_{10}H_{15}ClO_4P^+$ 265.0391 (M+H)⁺, found 265.0381.

4-Bromophenyl diethyl phosphate (3g)



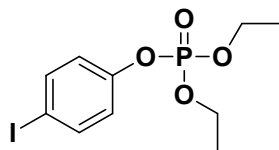
¹H NMR (400 MHz, Chloroform-d) δ 7.45 (d, $J = 8.6$ Hz, 2H), 7.16 – 7.08 (m, 2H), 4.27 – 4.17 (m, 4H), 1.35 (td, $J = 7.1, 1.1$ Hz, 6H). **¹³C NMR** (101 MHz, Chloroform-d) δ 149.83, 132.68, 121.78, 117.88, 64.79, 64.73, 16.12, 16.05. **HRMS** (ESI-TOF) m/z calculated for $C_{10}H_{15}BrO_4P^+$ 308.9886 (M + H)⁺, found 308.9879.

3-Chlorophenyl diethyl phosphate (3h)



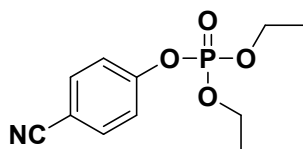
¹H NMR (400 MHz, Chloroform-d) δ 7.29 – 7.20 (m, 2H), 7.12 (ddq, $J = 9.3, 7.2, 1.1$ Hz, 2H), 4.20 (dq, $J = 10.2, 7.1, 1.9$ Hz, 4H), 1.33 (td, $J = 7.0, 1.1$ Hz, 6H). **¹³C NMR** (101 MHz, Chloroform-d) δ 151.15, 134.85, 130.41, 125.25, 120.56, 118.32, 64.81, 64.75, 16.06, 15.99. **HRMS** (ESI-TOF) m/z calculated for $C_{10}H_{15}ClO_4P^+$ 265.0391 (M+H)⁺, found 265.0381.

Diethyl (4-iodophenyl) phosphate (3i)



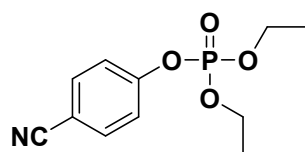
¹H NMR (400 MHz, Chloroform-d) δ 7.61 (td, $J = 6.0, 2.5$ Hz, 2H), 7.01 – 6.94 (m, 2H), 4.24 – 4.14 (m, 4H), 1.33 (q, $J = 6.6$ Hz, 6H). **¹³C NMR** (101 MHz, Chloroform-d) δ 150.65, 138.67, 122.23, 88.56, 64.77, 64.71, 16.12, 16.05. **HRMS** (ESI-TOF) m/z calculated for $C_{10}H_{15}IO_4P^+$ 356.9747 (M+H)⁺, found 356.9733.

4-Cyanophenyl diethyl phosphate (3j)



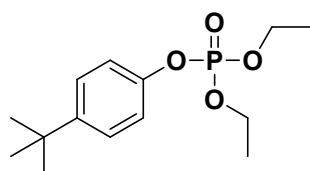
¹H NMR (400 MHz, Chloroform-d) δ 7.60 (dd, $J = 8.9, 2.9$ Hz, 2H), 7.30 – 7.26 (m, 2H), 4.23 – 4.12 (m, 4H), 1.33 – 1.27 (m, 6H). **¹³C NMR** (101 MHz, Chloroform-d) δ 154.05, 134.04, 120.93, 118.13, 108.73, 65.06, 65.00, 16.03, 15.96. **HRMS** (ESI-TOF) m/z calculated for $C_{11}H_{15}NO_4P^+$ 256.0733 (M+H)⁺, found 256.0722.

[1,1'-Biphenyl]-2-yl diethyl phosphate (3k)



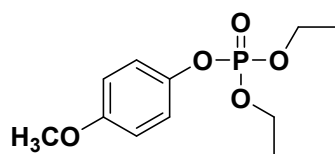
¹H NMR (400 MHz, Chloroform-d) δ 7.50 (ddt, $J = 14.3, 8.1, 1.5$ Hz, 3H), 7.45 – 7.32 (m, 5H), 7.25 (tt, $J = 7.4, 1.1$ Hz, 1H), 4.03 – 3.86 (m, 4H), 1.21 (td, $J = 7.1, 1.1$ Hz, 6H). **¹³C NMR** (101 MHz, Chloroform-d) δ 147.75, 137.52, 133.63, 133.56, 131.15, 129.51, 128.69, 128.68, 128.05, 127.36, 125.17, 120.48, 64.38, 64.32, 15.99, 15.92. **HRMS** (ESI-TOF) m/z calculated for $C_{16}H_{20}O_4P^+$ 307.1094 (M+H)⁺, found 307.1081.

4-(*tert*-Butyl)phenyl diethyl phosphate (3l)



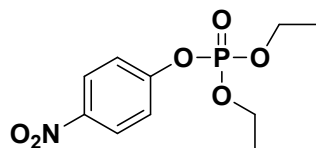
¹H NMR (400 MHz, Chloroform-d) δ 7.36 – 7.30 (m, 2H), 7.12 (dt, $J = 8.8, 1.5$ Hz, 2H), 4.20 (td, $J = 7.3, 2.2$ Hz, 4H), 1.34 (dd, $J = 8.2, 6.3$ Hz, 6H), 1.29 (d, $J = 2.0$ Hz, 9H). **¹³C NMR** (101 MHz, Chloroform-d) δ 148.44, 148.37, 147.72, 147.71, 126.47, 119.31, 119.26, 64.44, 64.39, 34.32, 31.37, 16.09, 16.02. **HRMS** (ESI-TOF) m/z calculated for $C_{14}H_{24}O_4P^+$ 287.1407 (M+H)⁺, found 287.1395.

Diethyl (4-methoxyphenyl) phosphate (3m)



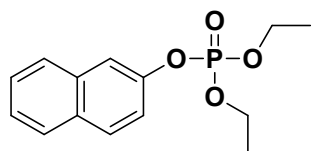
¹H NMR (400 MHz, Chloroform-d) δ 7.17 – 7.12 (m, 2H), 6.85 (d, $J = 9.0$ Hz, 2H), 4.25 – 4.16 (m, 4H), 3.78 (s, 3H), 1.35 (td, $J = 7.1, 1.1$ Hz, 6H). **¹³C NMR** (101 MHz, Chloroform-d) δ 156.65, 120.89, 120.85, 114.60, 64.51, 64.45, 55.59, 16.12, 16.06. **HRMS** (ESI-TOF) m/z calculated for $C_{11}H_{18}O_5P^+$ 261.0886 (M+H)⁺, found 261.0876.

Diethyl (4-nitrophenyl) phosphate (3n)



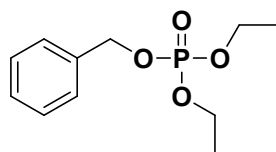
¹H NMR (400 MHz, Chloroform-d) δ 8.25 (d, $J = 8.8$ Hz, 2H), 7.39 (dd, $J = 9.2, 1.0$ Hz, 2H), 4.26 (dq, $J = 8.7, 7.1, 1.8$ Hz, 4H), 1.38 (td, $J = 7.1, 1.1$ Hz, 6H). **¹³C NMR** (101 MHz, Chloroform-d) δ 155.60, 144.64, 125.67, 120.51, 65.21, 65.15, 16.10, 16.04. **HRMS** (ESI-TOF) m/z calculated for $C_{10}H_{15}NO_6P^+$ 276.0632 (M+H)⁺, found 276.0621.

Diethyl naphthalen-2-yl phosphate (3o)



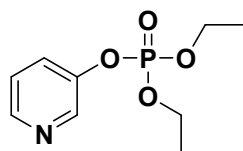
¹H NMR (400 MHz, Chloroform-d) δ 7.83 – 7.74 (m, 3H), 7.68 (t, $J = 1.8$ Hz, 1H), 7.44 (dddd, $J = 19.6, 8.1, 6.9, 1.4$ Hz, 2H), 7.35 (dd, $J = 8.9, 2.5$ Hz, 1H), 4.23 (dtd, $J = 15.3, 7.1, 2.9$ Hz, 4H), 1.34 (td, $J = 7.1, 1.0$ Hz, 6H). **¹³C NMR** (101 MHz, Chloroform-d) δ 148.33, 133.88, 130.89, 129.85, 127.71, 127.52, 126.72, 125.47, 120.06, 116.41, 64.73, 64.67, 16.15, 16.09. **HRMS** (ESI-TOF) m/z calculated for $C_{14}H_{18}O_4P^+$ 281.0937 (M+H)⁺, found 281.0924.

Benzyl diethyl phosphate (3p)



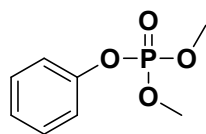
¹H NMR (400 MHz, Chloroform-d) δ 7.43 – 7.34 (m, 5H), 5.08 (d, $J = 8.1$ Hz, 2H), 4.14 – 4.06 (m, 4H), 1.32 (td, $J = 7.1, 1.1$ Hz, 6H). **¹³C NMR** (101 MHz, Chloroform-d) δ 136.07 (d, $J = 7.1$ Hz), 128.51 (d, $J = 9.8$ Hz), 127.87, 69.04, 63.83 (d, $J = 5.8$ Hz), 16.08 (d, $J = 6.7$ Hz). **HRMS** (ESI-TOF) m/z calculated for $C_{11}H_{18}O_4P^+$ 245.0937 (M+H)⁺, found 245.0924.

Dimethyl pyridin-3-yl phosphate (3q)



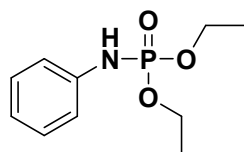
¹H NMR (400 MHz, Chloroform-d) δ 8.52 (dd, $J = 2.7, 1.3$ Hz, 1H), 8.46 – 8.39 (m, 1H), 7.61 (ddt, $J = 8.4, 2.6, 1.2$ Hz, 1H), 7.32 – 7.28 (m, 1H), 4.23 (dq, $J = 8.7, 7.1, 1.7$ Hz, 4H), 1.36 (td, $J = 7.1, 1.1$ Hz, 6H). **¹³C NMR** (101 MHz, Chloroform-d) δ 147.74, 146.14, 142.14, 127.39, 124.13, 64.98 (d, $J = 6.1$ Hz), 16.06 (d, $J = 6.6$ Hz). **HRMS** (ESI-TOF) m/z calculated for $C_9H_{15}NO_4P^+$ 232.0733 (M+H)⁺, found 232.0716.

Dimethyl phenyl phosphate (3r)



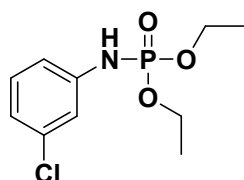
¹H NMR (400 MHz, Chloroform-d) δ 7.37 – 7.31 (m, 2H), 7.23 – 7.14 (m, 3H), 3.87 (s, 3H), 3.84 (s, 3H). **¹³C NMR** (101 MHz, Chloroform-d) δ 150.62, 129.77, 125.15, 119.87, 54.88 (d, $J = 6.2$ Hz). **HRMS** (ESI-TOF) m/z calculated for $C_8H_{12}O_4P^+$ 203.0468 (M+H)⁺, found 203.0456.

Diethyl phenylphosphoramidate (5a)



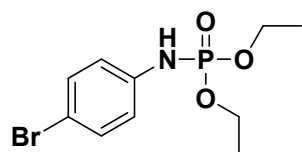
¹H NMR (400 MHz, Chloroform-d) δ 7.29 – 7.22 (m, 2H), 7.08 – 7.00 (m, 2H), 6.99 – 6.92 (m, 1H), 6.76 (d, $J = 9.5$ Hz, 1H), 4.26 – 4.04 (m, 4H), 1.33 (td, $J = 7.1, 0.9$ Hz, 6H). **¹³C NMR** (101 MHz, Chloroform-d) δ 139.94, 129.21, 121.39, 117.24, 62.70, 62.65, 16.13, 16.06. **³¹P NMR** (162 MHz, Chloroform-d) δ 2.73. **HRMS** (ESI-TOF) m/z calculated for $C_{10}H_{17}NO_3P^+$ 271.0399 (M+H)⁺, found 271.0395.

Diethyl (3-chlorophenyl)phosphoramidate (5b)



¹H NMR (400 MHz, Chloroform-d) δ 7.54 – 7.43 (m, 1H), 7.16 (t, $J = 8.1$ Hz, 1H), 7.07 (t, $J = 2.1$ Hz, 1H), 6.96 – 6.89 (m, 2H), 4.23 – 4.06 (m, 4H), 1.33 (td, $J = 7.1, 0.9$ Hz, 6H). **¹³C NMR** (101 MHz, Chloroform-d) δ 141.51, 134.80, 130.17, 121.39, 117.40, 115.55, 62.91, 62.86, 16.10, 16.03. **HRMS** (ESI-TOF) m/z calculated for $C_{10}H_{16}ClNO_3P^+$ 264.0551 (M+H)⁺, found 264.0544.

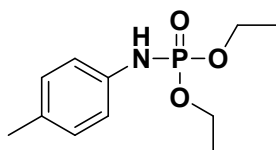
Diethyl (4-bromophenyl)phosphoramidate (5c)



¹H NMR (400 MHz, Chloroform-d) δ 7.37 – 7.32 (m, 2H), 7.30 – 7.26 (m, 1H), 6.94 (d, $J = 8.8$ Hz, 2H), 4.23 – 4.03 (m, 4H), 1.32 (td, $J = 7.1, 0.8$ Hz, 6H). **¹³C NMR** (101 MHz, Chloroform-d) δ 139.29, 132.07, 118.99, 118.91, 113.75, 62.84, 62.79,

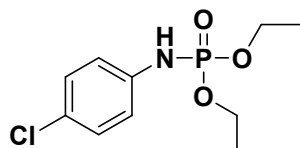
16.12, 16.05. **HRMS** (ESI-TOF) m/z calculated for $C_{10}H_{16}BrNO_3P^+$ 208.0046 ($M+H$)⁺, found 308.0038.

Diethyl *p*-tolylphosphoramidate (**5d**)



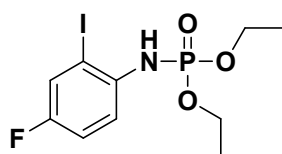
¹H NMR (400 MHz, Chloroform-d) δ 7.06 (d, $J = 8.1$ Hz, 2H), 6.97 – 6.93 (m, 2H), 6.71 (q, $J = 8.4, 7.6$ Hz, 1H), 4.22 – 4.05 (m, 4H), 2.29 (s, 3H), 1.32 (td, $J = 7.1, 0.9$ Hz, 6H). ¹³C NMR (101 MHz, Chloroform-d) δ 137.34, 130.72, 129.73, 117.33, 117.26, 62.59, 62.54, 20.56, 16.13, 16.06. **HRMS** (ESI-TOF) m/z calculated for $C_{11}H_{19}NO_3P^+$ 244.1097 ($M+H$)⁺, found 244.1092.

Diethyl (4-chlorophenyl)phosphoramidate (**5e**)



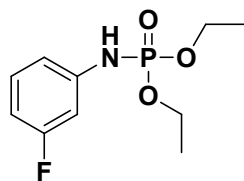
¹H NMR (400 MHz, Chloroform-d) δ 7.60 – 7.45 (m, 1H), 7.19 (d, $J = 8.8$ Hz, 2H), 7.00 (d, $J = 8.8$ Hz, 2H), 4.21 – 4.03 (m, 4H), 1.31 (t, $J = 7.1$ Hz, 6H). ¹³C NMR (101 MHz, Chloroform-d) δ 138.87, 129.12, 126.31, 118.57, 62.78, 62.74, 16.10, 16.03. **HRMS** (ESI-TOF) m/z calculated for $C_{10}H_{16}ClNO_3P^+$ 264.0551 ($M+H$)⁺, found 264.0544.

Diethyl (4-fluoro-2-iodophenyl)phosphoramidate (**5f**)



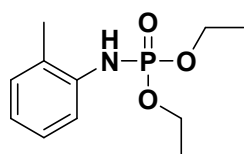
¹H NMR (400 MHz, Chloroform-d) δ 7.47 (ddd, $J = 7.7, 2.9, 1.3$ Hz, 1H), 7.32 – 7.27 (m, 1H), 7.02 (ddd, $J = 9.1, 7.8, 2.9$ Hz, 1H), 5.32 (d, $J = 7.9$ Hz, 1H), 4.24 – 4.07 (m, 4H), 1.33 (td, $J = 7.1, 0.9$ Hz, 6H). ¹³C NMR (101 MHz, Chloroform-d) δ 158.42, 155.97, 136.85, 125.70, 125.45, 117.73, 117.65, 116.36, 116.15, 63.29, 63.24, 16.12, 16.05. **HRMS** (ESI-TOF) m/z calculated for $C_{10}H_{15}FINO_3P^+$ 373.9813 ($M+H$)⁺, found 373.9805.

Diethyl (3-fluorophenyl)phosphoramidate (**5g**)



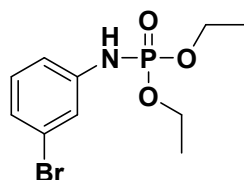
¹H NMR (400 MHz, Chloroform-d) δ 7.29 (d, J = 9.1 Hz, 1H), 7.19 (td, J = 8.3, 6.7 Hz, 1H), 6.84 – 6.78 (m, 2H), 6.68 – 6.61 (m, 1H), 4.23 – 4.07 (m, 4H), 1.34 (td, J = 7.1, 0.9 Hz, 6H). **¹³C NMR** (101 MHz, Chloroform-d) δ 130.39, 130.30, 113.06, 112.98, 108.03, 104.52, 62.94, 62.89, 16.10, 16.03. **HRMS** (ESI-TOF) m/z calculated for C₁₀H₁₆FNO₃P⁺ 248.0846 (M+H)⁺, found 248.0841.

Diethyl *o*-tolylphosphoramidate (5h)



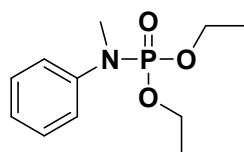
¹H NMR (400 MHz, Chloroform-d) δ 7.22 (dd, J = 8.1, 1.3 Hz, 1H), 7.19 – 7.11 (m, 2H), 6.92 (td, J = 7.4, 1.4 Hz, 1H), 4.96 (d, J = 8.4 Hz, 1H), 4.26 – 4.04 (m, 4H), 2.25 (s, 3H), 1.33 (td, J = 7.1, 0.9 Hz, 6H). **¹³C NMR** (101 MHz, Chloroform-d) δ 137.73, 130.59, 127.12, 124.96, 121.87, 116.98, 62.90, 62.85, 17.70, 16.13, 16.05. **HRMS** (ESI-TOF) m/z calculated for C₁₁H₁₉NO₃P⁺ 244.1097 (M+H)⁺, found 244.1092.

Diethyl (3-bromophenyl)phosphoramidate (5i)



¹H NMR (400 MHz, Chloroform-d) δ 7.28 – 7.20 (m, 2H), 7.15 – 7.04 (m, 2H), 6.98 (dt, J = 7.4, 2.0 Hz, 1H), 4.27 – 4.03 (m, 4H), 1.34 (td, J = 7.1, 0.9 Hz, 6H). **¹³C NMR** (101 MHz, Chloroform-d) δ 141.58, 130.49, 124.37, 122.90, 120.26, 115.97, 62.96, 62.91, 16.13, 16.06. **HRMS** (ESI-TOF) m/z calculated for C₁₀H₁₆BrNO₃P⁺ 208.0046 (M+H)⁺, found 308.0038.

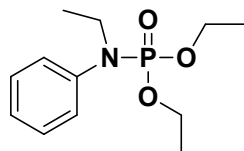
Diethyl methyl(phenyl)phosphoramidate (5j)



¹H NMR (400 MHz, Chloroform-d) δ 7.34 – 7.26 (m, 4H), 7.08 (tt, J = 6.6, 1.9 Hz, 1H), 4.18 – 3.98 (m, 4H), 3.21 (d, J = 8.8 Hz, 3H), 1.29 (td, J = 7.1, 1.0 Hz,

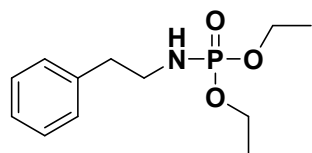
6H). ^{13}C NMR (101 MHz, Chloroform-d) δ 144.22, 128.88, 123.56, 121.93, 121.89, 62.63, 62.58, 36.88, 36.83, 16.09, 16.02. **HRMS** (ESI-TOF) m/z calculated for $\text{C}_{11}\text{H}_{19}\text{NO}_3\text{P}^+$ 244.1097 ($\text{M}+\text{H}^+$), found 244.1092.

Diethyl ethyl(phenyl)phosphoramidate (5k)



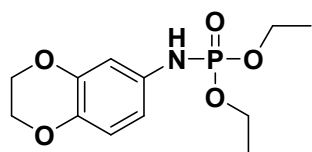
^1H NMR (400 MHz, Chloroform-d) δ 7.35 – 7.25 (m, 4H), 7.16 (ddt, $J = 8.2, 6.3, 1.1$ Hz, 1H), 4.16 – 3.98 (m, 4H), 3.65 (dq, $J = 10.3, 7.1$ Hz, 2H), 1.27 (td, $J = 7.1, 0.9$ Hz, 6H), 1.12 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 128.98, 125.62, 125.58, 124.91, 62.52, 62.47, 44.79, 44.74, 16.13, 16.05, 14.56, 14.54. **HRMS** (ESI-TOF) m/z calculated for $\text{C}_{12}\text{H}_{21}\text{NO}_3\text{P}^+$ 258.1254 ($\text{M}+\text{H}^+$), found 258.1248.

Diethyl phenethylphosphoramidate (5l)



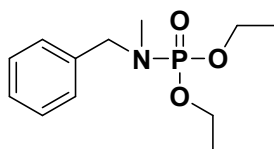
^1H NMR (400 MHz, Chloroform-d) δ 7.32 (dd, $J = 8.0, 6.5$ Hz, 2H), 7.26 – 7.19 (m, 3H), 4.12 – 3.92 (m, 4H), 3.19 (dq, $J = 9.9, 6.9$ Hz, 2H), 2.81 (t, $J = 6.9$ Hz, 2H), 2.62 (d, $J = 9.1$ Hz, 1H), 1.32 (td, $J = 7.0, 0.8$ Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-d) δ 138.69, 128.88, 128.62, 126.54, 62.28, 62.22, 42.65, 37.96, 37.91, 16.25, 16.18. **HRMS** (ESI-TOF) m/z calculated for $\text{C}_{12}\text{H}_{21}\text{NO}_3\text{P}^+$ 258.1254 ($\text{M}+\text{H}^+$), found 258.1248.

Diethyl (2,3-dihydrobenzo[b][1,4]dioxin-6-yl)phosphoramidate (5m)



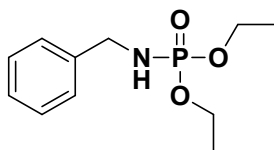
^1H NMR (400 MHz, Chloroform-d) δ 6.74 (d, $J = 8.6$ Hz, 1H), 6.59 (d, $J = 2.7$ Hz, 1H), 6.51 (dd, $J = 8.7, 2.7$ Hz, 1H), 6.27 – 6.12 (m, 1H), 4.25 – 4.05 (m, 8H), 1.35 – 1.30 (m, 6H). ^{13}C NMR (101 MHz, Chloroform-d) δ 143.77, 138.52, 133.71, 117.51, 111.08, 106.73, 64.55, 64.17, 62.68, 62.63, 16.14, 16.07. **HRMS** (ESI-TOF) m/z calculated for $\text{C}_{12}\text{H}_{19}\text{NO}_5\text{P}^+$ 288.0995 ($\text{M}+\text{H}^+$), found 288.1064.

N-Benzyl-*N*-methyl-*P,P*-dipropylphosphinic amide (5m)



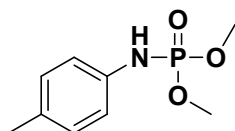
¹H NMR (400 MHz, Chloroform-d) δ 7.37 – 7.24 (m, 3H), 4.20 (d, J = 8.8 Hz, 1H), 4.15 – 3.97 (m, 2H), 2.55 (d, J = 9.8 Hz, 2H), 1.34 (td, J = 7.1, 0.9 Hz, 3H). **¹³C NMR** (101 MHz, Chloroform-d) δ 137.96, 137.91, 128.42, 128.19, 127.31, 62.28, 62.23, 53.00, 52.95, 33.13, 33.09, 16.21, 16.14. **HRMS** (ESI-TOF) m/z calculated for $C_{14}H_{25}NOP^+$ 258.1254 (M+H)⁺, found 258.1248.

Diethyl benzylphosphoramidate (5m)



¹H NMR (400 MHz, Chloroform-d) δ 7.35 – 7.18 (m, 5H), 4.09 – 3.91 (m, 6H), 3.51 (t, J = 9.2 Hz, 1H), 1.26 (td, J = 7.4, 6.9, 2.1 Hz, 6H). **¹³C NMR** (101 MHz, Chloroform-d) δ 139.83, 139.77, 128.47, 127.32, 127.23, 62.30, 62.25, 45.23, 16.16, 16.09. **HRMS** (ESI-TOF) m/z calculated for $C_{11}H_{19}NO_3P^+$ 244.1097 (M+H)⁺, found 244.1092.

Dimethyl p-tolylphosphoramidate (5p)



¹H NMR (400 MHz, Chloroform-d) δ 7.07 (d, J = 8.1 Hz, 2H), 6.96 – 6.91 (m, 2H), 6.58 (d, J = 9.5 Hz, 1H), 3.80 (s, 3H), 3.77 (s, 3H), 2.29 (s, 3H). **¹³C NMR** (101 MHz, Chloroform-d) δ 136.89, 131.18, 129.86, 117.37, 53.11 (d, J = 4.9 Hz), 20.58. **HRMS** (ESI-TOF) m/z calculated for $C_9H_{15}NO_3P^+$ 216.0784 (M+H)⁺, found 216.0771.

