

# Supporting Information

## Transition-Metal-Free Amination Phosphoryl Azide for the Synthesis of Phosphoramidates

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## 1. General remarks

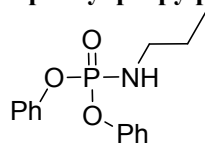
All non-aqueous reactions and manipulations were performed in air atmosphere. All solvents were purchased from Energy Chemical, Aladdin and used without further treatment. The reactions were monitored by GC (7820A, Hubei University of Science and Technology) and GC-MS (QP2010, Hunan University). The electron ionization (EI) method was used as the ionization method for the HRMS measurement, and the mass analyzer type is TOF for EI. The  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker ADVANCE III spectrometer at 400 MHz and 100 MHz, respectively (Hubei University of Science and Technology). Flash column chromatography was performed using silica gel 40-70  $\mu\text{m}$  (200-300  $\mu\text{m}$ ). Amines and azide compounds were purchased from Energy Chemical and used without further treatment.

## 2. General procedure

A 25 ml Schlenk-type tube equipped with a magnetic stir bar was charged with diphenyl phosphoryl azide **1** (0.2 mmol), and *n*-propylamine **2** (0.4 mmol) at room temperature, then the reaction mixture was stirred at 120  $^\circ\text{C}$  for 12 h. The reaction was monitored by GC. After completion of the reaction, the resulting solution was cooled to room temperature, and neutralized with saturated NaCl solution. The product was extracted with EtOAc, dried over anhydrous  $\text{Mg}_2\text{SO}_4$  and concentrated in vacuum. The crude product was purified by flash column chromatography on silica gel and eluted with EtOAc/Petroleum ether (1/5-1/10) give analytically pure product.

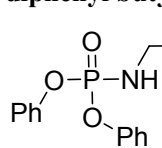
## 3. $^1\text{H}$ NMR, $^{13}\text{C}$ NMR and $^{31}\text{P}$ NMR data of products

### diphenyl propylphosphoramidate (**3a**)<sup>1</sup>



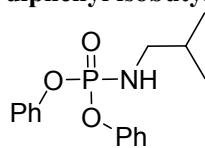
Following the general procedure (EtOAc/Petroleum ether 1:5), **3a** was obtained as a colorless liquid, isolated yield: 84%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  7.24-7.36 (m, 8H), 7.11-7.15 (m, 2H), 3.84 (t, 1H,  $J = 6.4$  Hz), 2.94-3.02 (m, 2H), 1.44 (q, 2H,  $J = 7.2$  Hz), 0.83 (t, 3H,  $J = 7.4$  Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  150.9 (d,  $J_{\text{P-C}} = 6.6$  Hz), 129.6, 124.8 (d,  $J_{\text{P-C}} = 0.9$  Hz), 120.3 (d,  $J_{\text{P-C}} = 5.0$  Hz), 43.6 (d,  $J_{\text{P-C}} = 1.4$  Hz), 24.6 (d,  $J_{\text{P-C}} = 6.3$  Hz), 11.1;  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  0.38; GC-MS:  $m/z = 291$ .

### diphenyl butylphosphoramidate (**3b**)<sup>1</sup>



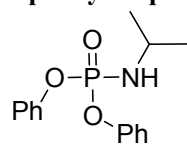
Following the general procedure (EtOAc/Petroleum ether 1:5), **3b** was obtained as a colorless liquid, isolated yield: 81%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 7.33 (t, 4H, *J* = 7.8 Hz), 7.24-7.27 (m, 4H), 7.14-7.18 (m, 2H), 3.03-3.10 (m, 3H, NH and -CH<sub>2</sub>-), 1.41-1.48 (m, 2H), 1.31 (q, 2H, *J* = 7.8 Hz), 0.87 (t, 3H, *J* = 7.2 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 150.9 (d, *J*<sub>P-C</sub> = 6.6 Hz), 129.6, 124.8 (d, *J*<sub>P-C</sub> = 0.9 Hz), 120.3 (d, *J*<sub>P-C</sub> = 5.0 Hz), 43.6 (d, *J*<sub>P-C</sub> = 1.4 Hz), 24.6 (d, *J*<sub>P-C</sub> = 6.3 Hz), 11.1; <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) δ 0.38; GC-MS: *m/z* = 305

### diphenyl isobutylphosphoramidate (**3c**)<sup>1</sup>



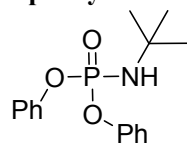
Following the general procedure (EtOAc/Petroleum ether 1:5), **3c** was obtained as a colorless liquid, isolated yield: 90%. δ 7.33 (t, 4H, *J* = 7.8 Hz), 7.24 (d, 4H, *J* = 8.4 Hz), 7.14-7.18 (m, 2H), 3.12-3.18 (m, 1H), 2.86-2.92 (m, 2H), 1.67-1.72 (m, 1H), 0.86 (d, 6H, *J* = 6.8 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 150.9 (d, *J*<sub>P-C</sub> = 6.7 Hz), 129.7, 124.9 (d, *J*<sub>P-C</sub> = 0.9 Hz), 120.2 (d, *J*<sub>P-C</sub> = 5.0 Hz), 49.3, 29.7 (d, *J*<sub>P-C</sub> = 6.2 Hz), 19.8; <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) δ -0.46; GC-MS: *m/z* = 305.

### diphenyl isopropylphosphoramidate (**3d**)<sup>1</sup>



Following the general procedure (EtOAc/Petroleum ether 1:5), **3d** was obtained as a colorless liquid, isolated yield: 81%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 7.31 (t, 4H, *J* = 7.8 Hz), 7.25 (d, 4H, *J* = 8.4 Hz), 7.15 (t, 2H, *J* = 7.0 Hz), 3.54-3.65 (m, 1H), 3.05 (t, 1H, *J* = 10.8 Hz), 1.13 (d, 6H, *J* = 6.4 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 151.0 (d, *J*<sub>P-C</sub> = 6.8 Hz), 129.6, 124.8, 120.2 (d, *J*<sub>P-C</sub> = 5.0 Hz), 44.6, 25.1 (d, *J*<sub>P-C</sub> = 5.7 Hz); <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) δ -1.8; GC-MS: *m/z* = 291.

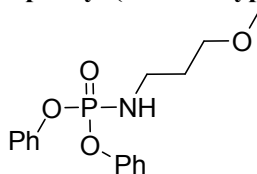
### diphenyl tert-butylphosphoramidate (**3e**)



Following the general procedure (EtOAc/Petroleum ether 1:5), **3e** was obtained as a colorless liquid, isolated yield: 55%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 7.32 (t, 4H, *J* = 7.8 Hz), 7.23-7.26 (m, 4H), 7.13-7.17 (m, 2H), 3.05 (d, 1H, *J* = 8.4 Hz), 1.35 (s, 9H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 151.1 (d, *J*<sub>P-C</sub> = 7.1 Hz), 129.6, 124.7, 120.1 (d, *J*<sub>P-C</sub> = 5.1 Hz), 51.8, 31.3 (d, *J*<sub>P-C</sub> =

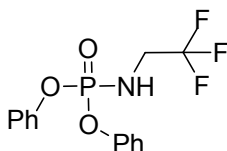
4.9 Hz);  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  -3.4; HRMS (EI): calcd for  $\text{C}_{16}\text{H}_{20}\text{NO}_3\text{P}$ : 305.1181, found: 305.1170.

### diphenyl (3-methoxypropyl)phosphoramidate (**3f**)



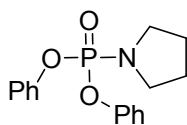
Following the general procedure (EtOAc/Petroleum ether 1:5), **3f** was obtained as a colorless liquid, isolated yield: 85%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  7.25 (t, 4H,  $J = 7.8$  Hz), 7.24-7.27 (d, 4H,  $J = 8.4$  Hz), 7.08 (t, 2H,  $J = 7.4$  Hz), 3.59 (d, 1H,  $J = 5.6$  Hz), 3.32 (t, 2H,  $J = 5.6$  Hz), 3.19 (s, 3H), 3.08-3.15 (m, 2H), 1.61-1.68 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  150.9 (d,  $J_{\text{P-C}} = 6.7$  Hz), 129.67, 124.7, 120.3 (d,  $J_{\text{P-C}} = 4.9$  Hz), 70.9, 58.7, 39.9, 30.8 (d,  $J_{\text{P-C}} = 6.3$  Hz);  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  -0.63; HRMS (EI): calcd for  $\text{C}_{16}\text{H}_{20}\text{NO}_4\text{P}$ : 321.1130, found: 321.1126

### diphenyl (2,2,2-trifluoroethyl)phosphoramidate (**3g**)



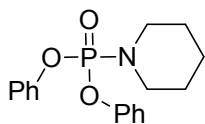
Following the general procedure (EtOAc/Petroleum ether 1:5), **3g** was obtained as a white solid, isolated yield: 52%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  7.25 (t, 4H,  $J = 7.8$  Hz), 7.10-7.19 (m, 6H), 3.55-3.68 (m, 3H, NH and  $-\text{CH}_2-$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  150.5 (d,  $J_{\text{P-C}} = 7.0$  Hz), 129.8, 125.4, 120.1 (d,  $J_{\text{P-C}} = 5.0$  Hz), 43.6 (q,  $J_{\text{C-3F}} = 35.0$  Hz);  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  -2.6; HRMS (EI): calcd for  $\text{C}_{14}\text{H}_{13}\text{F}_3\text{NO}_3\text{P}$ : 331.0585, found: 331.0582.

### diphenyl pyrrolidin-1-ylphosphonate (**3h**)<sup>1</sup>



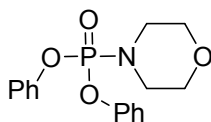
Following the general procedure (EtOAc/Petroleum ether 1:5), **3h** was obtained as a colorless liquid, isolated yield: 85%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  7.32 (t, 4H,  $J = 7.8$  Hz), 7.24 (d, 4H,  $J = 8.8$  Hz), 7.14 (t, 2H,  $J = 7.2$  Hz), 3.29-3.33 (m, 4H), 1.79 (t, 4H,  $J = 6.6$  Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  150.5 (d,  $J_{\text{P-C}} = 6.6$  Hz), 129.7, 124.7, 120.1 (d,  $J_{\text{P-C}} = 5.0$  Hz), 47.2 (d,  $J_{\text{P-C}} = 4.9$  Hz), 26.2 (d,  $J_{\text{P-C}} = 9.5$  Hz);  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  -2.1; GC-MS:  $m/z = 303$ .

### diphenyl piperidin-1-ylphosphonate (**3i**)<sup>1</sup>



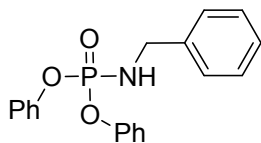
Following the general procedure (EtOAc/Petroleum ether 1:5), **3i** was obtained as a colorless liquid, isolated yield: 78%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 7.42 (t, 4H, *J* = 8.0 Hz), 7.20-7.27 (m, 6H), 3.11-3.16 (m, 4H), 1.43-1.47 (m, 2H), 1.29-1.35 (m, 4H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 150.5 (d, *J*<sub>P-C</sub> = 6.3 Hz), 129.3, 124.3, 119.4 (d, *J*<sub>P-C</sub> = 5.0 Hz), 44.4 (d, *J*<sub>P-C</sub> = 2.2 Hz), 24.7 (d, *J*<sub>P-C</sub> = 4.4 Hz), 23.0; <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) δ -2.1; GC-MS: *m/z* = 317.

#### diphenyl morpholinophosphonate (**3j**)<sup>1</sup>



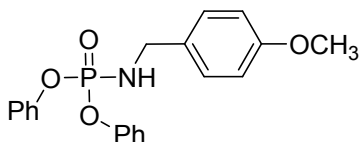
Following the general procedure (EtOAc/Petroleum ether 1:5), **3j** was obtained as a colorless liquid, isolated yield: 90%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 7.34 (t, 4H, *J* = 7.8 Hz), 7.24 (d, 4H, *J* = 8.4 Hz), 7.17 (t, 2H, *J* = 7.4 Hz), 3.56 (t, 4H, *J* = 4.4 Hz), 3.28 (t, 4H, *J* = 4.6 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 150.7 (d, *J*<sub>P-C</sub> = 6.8 Hz), 129.8, 125.1, 120.1 (d, *J*<sub>P-C</sub> = 4.1 Hz), 66.7 (d, *J*<sub>P-C</sub> = 5.3 Hz), 44.8; <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) δ -2.0; GC-MS: *m/z* = 319.

#### diphenyl benzylphosphoramidate (**3k**)<sup>2</sup>



Following the general procedure (EtOAc/Petroleum ether 1:10), **3k** was obtained as a white solid, isolated yield: 90%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 7.31 (t, 4H, *J* = 7.8 Hz), 7.22-7.27 (m, 9H), 7.16 (t, 2H, *J* = 7.2 Hz), 4.25 (q, 2H, *J* = 5.0 Hz), 3.64-3.71 (m, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 150.8 (d, *J*<sub>P-C</sub> = 6.7 Hz), 138.7 (d, *J*<sub>P-C</sub> = 6.6 Hz), 129.7, 128.6, 127.6, 127.4, 124.9, 120.3 (d, *J*<sub>P-C</sub> = 4.9 Hz), 45.7; <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) δ -1.8; GC-MS: *m/z* = 339.

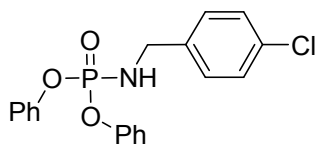
#### diphenyl 4-methoxybenzylphosphoramidate (**3l**)<sup>2</sup>



Following the general procedure (EtOAc/Petroleum ether 1:10), **3l** was obtained as a white solid, isolated yield: 92%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 7.24 (d, 4H, *J* = 7.6 Hz), 7.15-7.18 (m, 4H), 7.04-7.11 (m, 4H), 6.71 (d, 2H, *J* = 8.4 Hz), 4.12 (q, 2H, *J* = 4.6 Hz), 3.70 (s, 3H), 3.32-3.38 (m, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 159.0, 150.9 (d, *J*<sub>P-C</sub> = 6.7

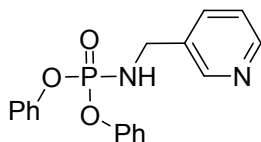
Hz), 130.9 (d,  $J_{P-C} = 6.6$  Hz), 129.7, 128.8, 125.0, 120.3 (d,  $J_{P-C} = 4.9$  Hz), 114.0, 55.3, 45.2;  $^{31}P$  NMR (162 MHz,  $CDCl_3$ )  $\delta$  -1.3; GC-MS:  $m/z = 369$

### diphenyl 4-chlorobenzylphosphoramidate (**3m**)<sup>2</sup>



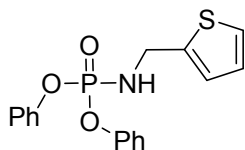
Following the general procedure (EtOAc/Petroleum ether 1:10), **3m** was obtained as a white solid, isolated yield: 85%.  $^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  7.35 (t, 4H,  $J = 7.8$  Hz), 7.26-7.31 (m, 9H), 7.18-7.26 (m, 2H), 4.29 (q, 2H,  $J = 5.0$  Hz), 3.56-3.62 (m, 1H);  $^{13}C$  NMR ( $CDCl_3$ , 100 MHz):  $\delta$  150.8 (d,  $J_{P-C} = 6.8$  Hz), 137.3 (d,  $J_{P-C} = 6.3$  Hz), 133.3, 129.7, 128.8, 128.7, 125.1, 120.2 (d,  $J_{P-C} = 5.0$  Hz), 45.1;  $^{31}P$  NMR (162 MHz,  $CDCl_3$ )  $\delta$  -1.2; GC-MS:  $m/z = 373$

### diphenyl (pyridin-3-ylmethyl)phosphoramidate (**3n**)<sup>1</sup>



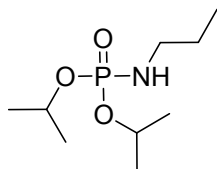
Following the general procedure (EtOAc/Petroleum ether 1:10), **3n** was obtained as a white solid, isolated yield: 81%.  $^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  8.48 (t, 2H,  $J = 4.6$  Hz), 7.53 (d, 1H,  $J = 8.0$  Hz), 7.32 (t, 4H,  $J = 7.8$  Hz), 7.16-7.23 (m, 7H), 4.27 (q, 2H,  $J = 5.4$  Hz), 3.79-3.85 (m, 1H);  $^{13}C$  NMR ( $CDCl_3$ , 100 MHz):  $\delta$  150.7 (d,  $J_{P-C} = 6.8$  Hz), 148.9 (d,  $J_{P-C} = 8.9$  Hz), 135.2, 134.3, 129.8, 125.1, 123.5, 120.1 (d,  $J_{P-C} = 5.0$  Hz), 43.3;  $^{31}P$  NMR (162 MHz,  $CDCl_3$ )  $\delta$  -1.4; GC-MS:  $m/z = 340$

### diphenyl (thiophen-2-ylmethyl)phosphoramidate (**3o**)<sup>2</sup>



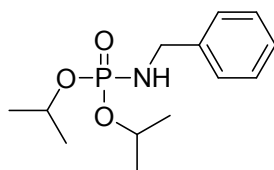
Following the general procedure (EtOAc/Petroleum ether 1:10), **3o** was obtained as a white solid, isolated yield: 78%.  $^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  7.33 (t, 4H,  $J = 7.8$  Hz), 7.23 (d, 4H,  $J = 8.8$  Hz), 7.15-7.20 (m, 3H), 6.90 (d, 2H,  $J = 3.6$  Hz), 4.45 (q, 2H,  $J = 4.8$  Hz), 3.50-3.57 (m, 1H);  $^{13}C$  NMR ( $CDCl_3$ , 100 MHz):  $\delta$  150.8 (d,  $J_{P-C} = 6.8$  Hz), 141.9 (d,  $J_{P-C} = 7.3$  Hz), 129.8, 126.9, 125.7, 125.3, 125.1 (d,  $J_{P-C} = 1.0$  Hz), 120.3 (d,  $J_{P-C} = 4.9$  Hz), 40.8;  $^{31}P$  NMR (162 MHz,  $CDCl_3$ )  $\delta$  -2.1; GC-MS:  $m/z = 345$

### diisopropyl propylphosphoramidate (**3p**)<sup>3</sup>



Following the general procedure (EtOAc/Petroleum ether 1:10), **3p** was obtained as a colorless liquid, isolated yield: 83%. <sup>1</sup>H NMR (DMSO-*d*, 400 MHz): δ 4.49-4.60 (m, 2H), 2.75-2.85 (m, 3H, NH and -CH<sub>2</sub>-), 1.21 (d, 6H, *J* = 6.0 Hz), 1.15 (d, 6H, *J* = 6.4 Hz); <sup>13</sup>C NMR (DMSO-*d*, 100 MHz): δ 70.6 (d, *J*<sub>P-C</sub> = 6.0 Hz), 43.2 (d, *J*<sub>P-C</sub> = 1.0 Hz), 24.8 (d, *J*<sub>P-C</sub> = 6.0 Hz), 23.8, 23.7 (d, *J*<sub>P-C</sub> = 2.0 Hz), 11.2; <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) δ 7.5; GC-MS: *m/z* = 223.

#### diisopropyl benzylphosphoramidate (**3q**)<sup>3</sup>



Following the general procedure (EtOAc/Petroleum ether 1:10), **3q** was obtained as a colorless liquid, isolated yield: 75%. <sup>1</sup>H NMR (DMSO-*d*, 400 MHz): δ 7.27 (d, 2H, *J* = 7.2 Hz), 7.21 (t, 2H, *J* = 7.4 Hz), 7.11 (t, 1H, *J* = 7.0 Hz), 4.45-4.53 (m, 2H), 3.97 (s, s, 3H, NH and -CH<sub>2</sub>-), 1.43-1.51 (m, 2H), 1.27 (t, 12H, *J* = 5.8 Hz), 0.87 (t, 3H, *J* = 7.4 Hz); <sup>13</sup>C NMR (DMSO-*d*, 100 MHz): δ 140.1 (d, *J*<sub>P-C</sub> = 6.4 Hz), 128.2, 127.2, 126.9, 70.4 (d, *J*<sub>P-C</sub> = 4.9 Hz), 45.1, 23.7 (d, *J*<sub>P-C</sub> = 4.3 Hz), 23.6 (d, *J*<sub>P-C</sub> = 5.6 Hz), 11.2; <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) δ 7.1; GC-MS: *m/z* = 271.

#### 4. References

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## 5. Copies of $^1\text{H}$ NMR, $^{13}\text{C}$ NMR and $^{31}\text{P}$ NMR spectra

