Supplementary Information

Ruthenium(IV) porphyrin catalyzed phosphoramidation of aldehyde with phosphoryl azide as nitrene source

Wenbo Xiao, Cong-Ying Zhou and Chi-Ming Che*

Department of Chemistry, State Key Laboratory of Synthetic Chemistry, and Open Laboratory of Chemical Biology of the Institute of Molecular Technology for Drug Discovery and Synthesis, The University of Hong Kong, Pokfulam Road, Hong Kong, China.

Fax: (852) 2857-1586  Tel: (852) 2859-2154  E-mail: cmche@hku.hk

Table of contents

I. General Information  S1

II. Synthesis of Ruthenium(IV) Porphyrins  S2

III. Synthesis of Phosphoryl Azides  S2

IV. General procedure for the phosphoramidation of aldehyde with phosphoryl azide catalyzed by [RuIV(TTP)Cl2]  S4

V. Procedure for the Scale-up Synthesis  S4

VI. Kinetic Isotope Effect Experiment  S5

VII. Characterizations of Products  S6

NMR Spectra  S20

S1
I. General Information

Unless otherwise stated, all reactions were performed under argon atmosphere. DPPA and aldehydes were obtained commercially and used without further purification unless acid impurities were identified in aldehydes. Molecular sieves were dried at 400°C for 3 h prior to use. All solvents were purified by distillation using standard methods. Metal porphyrins and organic azides were synthesized according to previously reported methods. All $^1$H NMR and $^{13}$C NMR spectra were recorded on Bruker AV300 or AV400 NMR spectrometers with tetramethylsilane (TMS) as internal reference. $^{31}$P NMR spectra were recorded on Bruker AV400 NMR spectrometer with 85% H$_3$PO$_4$ as external reference. Mass spectra were recorded on Finnigan MAT 95 mass spectrometer. Elemental analysis was conducted on Flash EA 1112 analyzer by Analysis & Test Center of Institute of Chemistry of Chinese Academy of Sciences. Caution! Organic azides are potentially explosive and should be handled with great care.

II. Synthesis of Ruthenium(IV) Porphyrins

Ruthenium(IV) porphyrins were synthesized according to the following references.


III. Synthesis of Phosphoryl Azides

Dimethyl phosphorazidate $3b$, diethyl phosphorazidate $3e$ and bis(2, 2, 2-trichloroethyl) phosphorazidate $3d$ were prepared according to the literature with minor modification.
General procedure for the synthesis of phosphoryl azides:

To a stirred solution of phosphorochloridate (3 mmol) in acetone (20 mL), was added sodium azide (4.5 mmol) in one portion at room temperature. The reaction mixture was stirred for 3h, during this period white solid precipitated. Then the mixture was filtered through a short celite, washed with 20ml of acetone. The filtrate was dried by a rotary evaporator at room temperature with a foil cover on the flask to prevent from light. The residue was purified by column chromatography (silica gel, DCM) to give pure product.

Bis(2, 2, 2-trichloroethyl) phosphorazidate 3d

White solid, 78% yield.

$^1$H NMR (CDCl$_3$,400MHz): $\delta$4.71-4.65(m, 4H); $^{13}$C NMR (CDCl$_3$,100MHz): $\delta$94.2, 94.1, 77.5, 77.5; $^{31}$P NMR (CDCl$_3$,162MHz): $\delta$-2.3(s); HRMS(EI) m/z Calcd. for C4H4Cl6N3O3P [M]$^+$ 382.8121, found 382.8103.

References for the synthesis of phosphoryl azides:


IV. General procedure for the phosphoramidation of aldehyde with phosphoryl azide catalyzed by $[\text{Ru}^{IV}(\text{TTP})\text{Cl}_2]$ 

To an oven-dried schlenk flask with a rubber seal was added aldehyde (0.2 mmol), DPPA (0.24 mmol), 3ÅMS (25 mg) and $[\text{Ru}^{IV}(\text{TTP})\text{Cl}_2]$ (5 mmol%). The flask was evacuated and backfilled with argon three times. Freshly distilled dichloromethane (1 mL) was added via syringe. The reaction mixture was stirred under reflux for 12h. After cooled down to room temperature, the reaction mixture was filtered through a short celite. The filtrate was concentrated by a rotary evaporator and purified by column chromatography (silica gel, DCM) to give pure product.

V. Procedure for the Scale-up Synthesis

![Chemical reaction diagram]

Yield: 92%

To an oven-dried schlenk flask was added $[\text{Ru}^{IV}(\text{TTP})\text{Cl}_2]$ (42 mg, 0.05 mmol, 5 mol%) and 125 mg of 3Å molecular sieve. The sealed flask was degassed for 20min and backfilled with argon. The freshly distilled DCM (3 mL) and $p$-anisaldehyde (136 mg, 1 mmol, 1 equiv.) were added via syringe. The mixture was heated to reflux. A solution of DPPA (330 mg, 1.2 mmol, 1.2 equiv.) in 2.5 mL of DCM was added dropwise via syringe pump within 5h. After addition, the reaction mixture was stirred for another 7h. Then the reaction mixture was concentrated by a rotary evaporator and the residue was purified by column chromatography to give the pure product $2c$ in 92% yield.
VI. Kinetic Isotope Effect Experiment

To an oven-dried schlenk flask with a rubber seal was added bis(2,2,2-trichloroethyl) phosphorazidate 3d (77 mg, 0.2 mmol), [Ru$^{IV}$(TTP)Cl$_2$] (8.4 mg, 0.01 mmol, 5 mol%) and 50 mg of 3Å molecular sieve. The flask was evacuated and backfilled with argon three times. Then benzaldehyde 1b (32 mg, 0.3 mmol) and benzaldehyde-$d_6$ 1p (34 mg, 0.3 mmol) were added. The reaction mixture was stirred under reflux for 12h. Upon the completion of the reaction, the mixture was allowed to cool and purified by a column chromatography (silica gel, hexane:EA=3:1) to give a mixture of bis(2,2,2-trichloroethyl) benzoylphosphoramidate 2t and bis(2,2,2-trichloroethyl) benzoylphosphoramidate-$d_5$ 2u (the labile D of N-D was replaced by H during purification). The ratio of $k_{H}/k_{D}$ was determined by $^1$H NMR.
VII. Characterizations of Products

Diphenyl (4-methylbenzoyl)phosphoramidate 2a

\[
\begin{align*}
\text{1H NMR (CDCl}_3\text{,400MHz): } & \delta 9.49(d, 1H, NH, J_{H-P}=10.3Hz), 7.86(d, 2H, J=7.8Hz), 7.25-7.22(m, 8H), 7.18(d, 2H, J=7.9Hz), 7.14-7.11(m, 2H), 2.38(s, 3H); \\
\text{13C NMR (CDCl}_3\text{,100MHz): } & \delta 167.5(d, C5, J_{C-P}=3.6Hz), 150.2(C4 or C4'), 150.1(C4 or C4'), 143.8, 129.8(C2 & C2'), 129.5(d, C6, J_{C-P}=11.4Hz), 129.3, 128.5, 125.6(C1 & C1'), 120.7(C3 or C3'), 120.6(C3 or C3'), 21.7; \\
\text{31P NMR (CDCl}_3\text{,162MHz): } & \delta -9.1(d, J_{P-H}=10.3Hz). \\
\text{HRMS(EI) m/z Calcd. for C20H18NO4P } [M]^+ & 367.0973, \text{ found 367.0957.}
\end{align*}
\]

Diphenylbenzoylphosphoramidate 2b

\[
\begin{align*}
\text{1H NMR (CDCl}_3\text{,400MHz): } & \delta 9.62(d, 1H, NH, J_{H-P}=9.6Hz), 7.97(d, 2H, J=8.6Hz), 7.54(t, 1H, J=7.4Hz), 7.39(t, 2H, J=7.8Hz), 7.25(m, 8H), 7.17-7.11(m, 2H); \\
\text{13C NMR (CDCl}_3\text{,100MHz): } & \delta 167.6(d, C5, J_{C-P}=3.4Hz), 150.2(C4 or C4'), 150.1(C4 or C4'), 133.1, 132.3(d, C6, J_{C-P}=11.2Hz), 129.8(C2 & C2'), 128.6, 128.5,
\end{align*}
\]
125.7(C1 & C1'), 120.6(C3 or C3'), 120.6(C3 or C3'); $^{31}$P NMR (CDCl$_3$, 162MHz): δ-9.1(d, $J_{P-H}$=9.6Hz).

HRMS(EI) m/z Calcd. for C19H16NO4P [M]$^+$ 353.0817, found 353.0810.

Anal. Calcd. for C19H16NO4P: C, 64.59; H, 4.56; N, 3.96. Found: C, 64.59; H, 4.52; N, 3.92.

**Diphenyl (4-methoxybenzoyl)phosphoramidate 2c**

![Chemical Structure](Image)

$^1$H NMR (CDCl$_3$, 400MHz): δ8.79(d, 1H, NH, $J_{H-P}$=10.3Hz), 7.90(d, 2H, $J$=8.9Hz), 7.28-7.26(m, 8H), 7.17-7.13(m, 2H), 6.88(d, 2H, $J$=8.9Hz), 3.85(s, 3H); $^{13}$C NMR (CDCl$_3$, 100MHz): δ167.0(d, C5, $J_{C-P}$=3.2Hz), 163.5 (C-OMe), 150.3(C4 or C4'), 150.2(C4 or C4'), 131.1, 129.8(C2 & C2'), 125.6(C1 & C1'), 124.6(d, C6, $J_{C-P}$=11.3Hz), 120.7(C3 or C3'), 120.6(C3 or C3'), 113.8, 55.6; $^{31}$P NMR (CDCl$_3$, 162MHz): δ-8.8(d, $J_{P-H}$=10.3Hz).

HRMS(EI) m/z Calcd. for C20H18NO5P [M]$^+$ 383.0923, found 383.0912.

**Diphenyl (4-hydroxybenzoyl)phosphoramidate 2d**

\[ \text{HO-} \overset{3}{\overset{4}{\overset{4'}{\overset{3'}{\text{N}}}}} \overset{2}{\overset{1}{\overset{2'}{\text{P}}}}} \overset{O}{\overset{1'}{\text{O}}} \overset{O}{\overset{2'}{\text{O}}} \overset{3'}{\text{O}}} \overset{4}{\overset{3}{\text{O}}} \overset{1}{\overset{2}{\text{O}}} \overset{5}{\overset{6}{\text{O}}} \]

\( ^1\text{H NMR (d6-DMSO,400MHz):} \ \delta 10.41(s, 1H), 10.37(s, 1H), 7.87(d, 2H, J=8.4Hz), 7.45(t, 4H, J=7.3Hz), 7.29-7.27(m, 6H), 6.85(d, 2H, J=7.9Hz); \ ^{13}\text{C NMR (d6-Acetone,100MHz):} \ \delta 167.5 (C5), 162.7 (C-OH), 151.5(C4 or C4'), 151.4(C4 or C4'), 131.4, 130.6(C2 & C2'), 126.2(C1 & C1'), 124.8(d, C6, J_{C-P} =11.1Hz), 121.5(C3 or C3'), 121.4(C3 or C3'), 116.1; \ ^{31}\text{P NMR (CDCl}_3,162MHz): \ \delta -9.7(s). \)

HRMS(EI) m/z Calcd. for C19H16NO5P [M]\(^+\) 369.0766, found 369.0748.


**Diphenylbenzo[d][1,3]dioxole-5-carbonylphosphoramidate 2e**

\[ \text{HO-} \overset{3}{\overset{4}{\overset{4'}{\overset{3'}{\text{N}}}}} \overset{2}{\overset{1}{\overset{2'}{\text{P}}}}} \overset{O}{\overset{1'}{\text{O}}} \overset{O}{\overset{2'}{\text{O}}} \overset{3'}{\text{O}}} \overset{4}{\overset{3}{\text{O}}} \overset{1}{\overset{2}{\text{O}}} \overset{5}{\overset{6}{\text{O}}} \]

\( ^1\text{H NMR (CDCl}_3,400MHz): \ \delta 9.58(d, 1H, NH, J_{H-P}=10.1Hz), 7.56(dd, 1H, J=8.2, 1.8Hz), 7.50(d, 1H, J=1.7Hz), 7.25-7.21(m, 8H), 7.15-7.13(m, 2H), 6.72(d, 1H, J=8.2Hz), 6.02(s, 2H); \ ^{13}\text{C NMR (CDCl}_3,100MHz): \ \delta 166.7(d, C5, J_{C-P}=3.1Hz), 151.7(C-O-dioxolane), 150.2(C4 or C4'), 150.1(C4 or C4'), 148.1(C-O-dioxolane), 129.8(C2 & C2'), 126.3(d, C6, J_{C-P}=11.3Hz), 125.7(C1 & C1'), 124.3, \)

S8
120.6(C3 or C3′), 120.6(C3 or C3′), 108.8, 108.1, 101.9(O-CH2-O); $^{31}$P NMR
(CDCl$_3$,162MHz): δ-9.0(d, $J_{P-H}$=9.9Hz).

HRMS(EI) m/z Calcd. for C20H16NO6P [M]$^+$ 397.0715, found 397.0708.

**Diphenyl(4-chlorobenzoyl)phosphoramidate 2f**

![Diphenyl(4-chlorobenzoyl)phosphoramidate 2f](image)

$^1$H NMR (CDCl$_3$,400MHz): δ9.65(d, 1H, NH, $J_{H-P}$=10.1Hz), 7.88(d, 2H, $J$=8.6Hz), 7.32(d, 2H, $J$=8.5Hz), 7.27-7.19(m, 8H), 7.15-7.13(m, 2H); $^{13}$C NMR
(CDCl$_3$,75MHz): δ166.6(d, C5, $J_{C-P}$=3.3Hz), 150.2(C4 or C4′), 150.1(C4 or C4′),
139.6(C-Cl), 130.6(d, C6, $J_{C-P}$=11.4Hz), 130.0, 129.9(C2 & C2′), 128.9, 125.8(C1 or C1′), 125.8(C1 or C1′), 120.6(C3 or C3′), 120.5(C3 or C3′); $^{31}$P NMR
(CDCl$_3$,162MHz): δ-9.2(d, $J_{P-H}$=9.9Hz).

HRMS(EI) m/z Calcd. for C19H15ClNO4P [M]$^+$ 387.0427 , found 387.0417.

Anal. Calcd. for C19H15ClNO4P: C, 58.85; H, 3.90; N, 3.61. Found: C, 58.38;
H, 3.84; N, 3.68.

**Diphenyl (4-nitrobenzoyl)phosphoramidate 2g**

![Diphenyl (4-nitrobenzoyl)phosphoramidate 2g](image)
$^1$H NMR (CDCl$_3$, 400MHz): $\delta$10.22(d, 1H, NH, $J_{H,p}$=9.4Hz), 8.16(d, 2H, $J$=8.6Hz), 8.11(d, 2H, $J$=8.8Hz), 7.28(t, 4H, $J$=7.9Hz), 7.20-7.16(m, 6H); $^{13}$C NMR (CDCl$_3$, 75MHz): $\delta$166.2 (d, C5, $J_{C,p}$=3.2Hz), 150.9(C-NO$_2$), 150.5(C4 or C4$'$), 150.4(C4 or C4$'$), 137.8(d, C6, $J_{C,p}$=11.7Hz), 130.4(C2 & C2$'$), 130.2, 126.5(C1 or C1$'$), 126.5(C1 or C1$'$), 124.2, 120.9(C3 or C3$'$), 120.9(C3 or C3$'$); $^{31}$P NMR (CDCl$_3$, 162MHz): $\delta$-9.7 (d, $J_{P,H}$=9.4Hz).

HRMS(EI) m/z Calcd. for C19H15N2O6P [M]$^+$ 398.0668 , found 398.0658.

Anal. Calcd. for C19H15N2O6P: C, 57.29; H, 3.80; N, 7.03. Found: C, 57.30; H, 3.87; N, 6.94.

**Diphenyl 2-naphthoylphosphoramidate 2h**

$^1$H NMR (CDCl$_3$, 400MHz): $\delta$10.00(d, 1H, NH, $J_{H,p}$=10.2Hz), 8.61(s, 1H), 8.06(dd, 1H, $J$=8.6, 1.7Hz), 7.85(d, 1H, $J$=8.0Hz), 7.84(d, 1H, $J$=8.6Hz), 7.72(d, 1H, $J$=8.0Hz), 7.58(t, 1H, $J$=7.0Hz), 7.49(t, 1H, $J$=7.1Hz), 7.27-7.15(m, 8H), 7.08(t, 2H, $J$=7.1Hz); $^{13}$C NMR (CDCl$_3$, 100MHz): $\delta$167.8(d, C5, $J_{C,p}$=3.4Hz), 150.2(C4 or C4$'$), 150.1(C4 or C4$'$), 135.5, 132.5, 129.9, 129.8(C2 & C2$'$), 129.6, 129.4(d, C6, $J_{C,p}$=11.2Hz), 128.5, 128.4, 127.7, 126.8, 125.6(C1 & C1$'$), 124.5, 120.7(C3 or C3$'$), 120.6(C3 or C3$'$); $^{31}$P NMR (CDCl$_3$, 162MHz): $\delta$-8.8 (d, $J_{P,H}$=9.9Hz).

HRMS(EI) m/z Calcd. for C23H18NO4P [M]$^+$ 403.0973 , found 403.0964.
Diphenyl furan-2-carbonylphosphoramidate 2i

\[
\begin{align*}
\text{1}^1\text{H NMR (CDCl}_3\text{,}400\text{MHz): } & \delta 8.71(\text{d, 1H, NH, } J_{\text{H-P}}=10.3\text{Hz}), 7.48(\text{dd, 1H, H9, } J_{\text{H9-H8}}=1.7\text{Hz}, J_{\text{H9-H7}}=0.7\text{Hz}), 7.31(\text{d, 1H, H7, } J_{\text{H7-H8}}=3.6\text{Hz}), 7.28-7.26(\text{m, 8H, } J_{\text{H8-H9}}=1.7\text{Hz}, J_{\text{H8-H7}}=3.6\text{Hz}); \\
\text{13C NMR (CDCl}_3\text{,}100\text{MHz): } & \delta 165.4 (C5), 157.4 (C6), 150.1(C4 or C4'), 150.0(C4 or C4'), 146.1(C9), 129.8(C2 & C2'), 125.7(C1 & C1'), 120.6(C3 or C3'), 120.6(C3 or C3'), 117.7(C7), 112.7(C8); \\
\text{31P NMR (CDCl}_3\text{,}162\text{MHz): } & \delta -10.7(\text{d, } J_{\text{P-H}}=10.1\text{Hz}).
\end{align*}
\]

HRMS(EI) m/z Calcd. for C17H14NO5P [M]+ 343.0610 , found 343.0599.

Anal. Calcd. for C17H14NO5P: C, 59.48; H, 4.11; N, 4.08. Found: C, 59.54; H, 4.12; N, 4.03.

Diphenylcinnamoylphosphoramidate 2j

\[
\begin{align*}
\text{1}^1\text{H NMR (CDCl}_3\text{,}400\text{MHz): } & \delta 9.21(\text{d, 1H, NH, } J_{\text{H-P}}=11.5\text{Hz}), 7.73(\text{d, 1H, } J_{\text{trans}}=15.8\text{Hz}), 7.46(\text{d, 1H, } J=7.12\text{Hz}), 7.45(\text{d, 1H, } J=7.64\text{Hz}), 7.39-7.36(\text{m, 3H, } J_{\text{trans}}=15.7\text{Hz}); \\
\text{13C NMR (CDCl}_3\text{,}100\text{MHz): } & \delta 166.4 (C5), 150.1(C4 or C4'), 150.0(C4 or C4'), 144.8 (C7), 134.2(C8), 130.6, 129.9(C2 & C2'), 129.0, 128.4, 125.8(C1 & C1'), 120.6(C3 or
\end{align*}
\]

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C3′), 120.6 (C3 or C3′), 119.4 (d, C6, J_{C,P}=12.9\text{Hz}); ^{31}\text{P} NMR (CDCl\textsubscript{3}, 162MHz): δ-8.8 (d, J_{P,H}=11.2\text{Hz}).

HRMS (EI) m/z Calcd. for C21H18NO4P [M]^+ 379.0973, found 379.0956.

Anal. Calcd. for C21H18NO4P: C, 66.49; H, 4.78; N, 3.69. Found: C, 66.46; H, 4.76; N, 3.68.

Diphenyl (3-methylbut-2-enoyl)phosphoramidate 2k

\[ \text{\begin{tikzpicture}
\draw (0,0) circle (0.5cm);
\draw (1,0) circle (0.5cm);
\draw (0,1) circle (0.5cm);
\draw (1,1) circle (0.5cm);
\draw (0,0) -- (1,1);
\draw (0,1) -- (1,0);
\draw (0,0) -- (0,1);
\draw (1,0) -- (1,1);
\draw (0,0) -- (1,0);
\draw (0,1) -- (1,1);
\draw (0,0) -- (0,1);
\draw (1,0) -- (1,1);
\draw (0,0) -- (1,1);
\draw (0,1) -- (1,0);
\draw (0,0) -- (1,1);
\draw (0,1) -- (1,0);
\end{tikzpicture}} \]

\[^1\text{H} \text{NMR (CDCl}_3, 400MHz): δ8.66 (d, 1H, NH, J_{H,P}=11.3\text{Hz}), 7.31-7.21 (m, 8H), 7.19-7.15 (m, 2H), 5.61 (s, 1H), 2.17 (s, 3H), 1.83 (s, 3H); ^{13}\text{C} \text{NMR (CDCl}_3, 100MHz): δ166.3 (d, C5, J_{C,P}=2.6\text{Hz}), 158.4 (d, C7, J_{C,P}=2.4\text{Hz}), 150.2 (C4 or C4′), 150.1 (C4 or C4′), 129.8 (C2 & C2′), 125.6 (C1 & C1′), 120.7 (C3 or C3′), 120.6 (C3 or C3′), 117.3 (d, C6, J_{C,P}=12.9\text{Hz}), 27.7, 20.5; ^{31}\text{P} \text{NMR (CDCl}_3, 162MHz): δ-9.1 (d, J_{P,H}=11.8\text{Hz}).\]

HRMS (EI) m/z Calcd. for C17H18NO4P [M]^+ 331.0973, found 331.0964.

Diphenyl (5,6-dihydro-2H-pyran-3-carbonyl)phosphoramidate 2l

\[ \text{\begin{tikzpicture}
\draw (0,0) circle (0.5cm);
\draw (1,0) circle (0.5cm);
\draw (0,1) circle (0.5cm);
\draw (1,1) circle (0.5cm);
\draw (0,0) -- (1,1);
\draw (0,1) -- (1,0);
\draw (0,0) -- (0,1);
\draw (1,0) -- (1,1);
\draw (0,0) -- (0,1);
\draw (1,0) -- (1,1);
\draw (0,0) -- (1,1);
\draw (0,1) -- (1,0);
\draw (0,0) -- (1,1);
\draw (0,1) -- (1,0);
\end{tikzpicture}} \]
\[ \delta 9.34 (d, 1H, NH, J_{H-P}=10.0Hz), 7.32-7.27 (m, 4H), 7.22-7.16 (m, 6H), 6.87-6.85 (m, 1H), 4.30 (dd, 2H, J=4.4, 2.5Hz), 3.68 (t, 2H, J=5.5Hz), 2.17-2.11 (m, 2H); \]
\[ \delta 166.6 (d, C5, J_{C-P}=3.3Hz), 150.6 (C4 or C4'), 150.5 (C4 or C4'), 135.9 (C8), 132.5 (d, C6, J_{C-P}=10.4Hz), 130.2 (C2 & C2'), 126.1 (C1 & C1'), 120.9 (C3 or C3'), 64.8 (C7), 63.6, 25.9; \]
\[ \delta -9.1 (d, J_{P-H}=9.9Hz). \]

HRMS (EI) m/z Calcd. for C18H18NO5P [M]^{+} 359.0923, found 359.0911.

**Diphenyloctanoylphosphoramidate 2m**

\[ \delta 9.06 (d, 1H, NH, J_{H-P}=11.0Hz), 7.32-7.26 (m, 4H), 7.21-7.16 (m, 6H), 2.19 (t, 2H, J=7.3Hz), 1.50 (m, 2H), 1.24 (m, 8H), 0.88-0.84 (m, 3H); \]
\[ \delta 174.6 (d, C5, J_{C-P}=4.8Hz), 150.1 (C4 or C4'), 150.0 (C4 or C4'), 129.8 (C2 & C2'), 125.7 (C1 & C1'), 120.6 (C3 or C3'), 120.5 (C3 or C3'), 37.2 (d, C6, J_{C-P}=9.5Hz), 31.7, 29.0, 28.9, 24.8, 22.7, 14.1; \]
\[ \delta -10.4 (d, J_{P-H}=11.1Hz). \]

HRMS (EI) m/z Calcd. for C20H26NO4P [M]^{+} 375.1599, found 375.1593.

Anal. Calcd. for C20H26NO4P: C, 63.99; H, 6.98; N, 3.73. Found: C, 64.14; H, 7.07; N, 3.63.
Diphenyl (3-phenylpropanoyl)phosphoramidate 2n

\[ \begin{array}{c}
\text{Ph} \quad \text{N} \quad \text{O} \\
\text{\text{Ph}} \quad \text{P} \quad \text{O} \\
\end{array} \]

$^1$H NMR (CDCl$_3$, 400MHz): $\delta$9.15(d, 1H, NH, $J_{H,P}$=11.4Hz), 7.25-7.11(m, 15H), 2.84(t, 2H, $J$=7.7Hz), 2.50(t, 2H, $J$=7.7Hz); $^{13}$C NMR (CDCl$_3$, 100MHz): $\delta$173.58(d, C5, $J_{C-P}$=4.8Hz), 150.0(C4 or C4′), 149.9(C4 or C4′), 140.3(C8), 129.8(C2 & C2′), 128.5, 128.5, 126.3, 125.7(C1 & C1′), 120.6(C3 or C3′), 120.5(C3 or C3′), 38.6(d, C6, $J_{C-P}$=9.9Hz), 30.5(C7); $^{31}$P NMR (CDCl$_3$, 162MHz): $\delta$-9.8(d, $J_{P-H}$=11.6Hz).

HRMS(EI) m/z Calcd. for C21H20NO4P [M]$^+$ 381.1130, found 381.1118.

Diphenyl (1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazole-4-carbonyl)-phosphoramidate 2o

\[ \begin{array}{c}
\text{Ph} \quad \text{N} \quad \text{O} \\
\text{\text{Ph}} \quad \text{N} \quad \text{O} \\
\end{array} \]

$^1$H NMR (CDCl$_3$, 400MHz): $\delta$10.30(d, 1H, NH, $J_{H,P}$=14.0Hz), 7.52(t, 2H, $J$=7.5Hz), 7.47(t, 1H, $J$=7.4Hz), 7.30-7.27(m, 10H), 7.16-7.13(m,2H), 3.33(s, 3H), 2.70(s, 3H); $^{13}$C NMR (CDCl$_3$, 100MHz): $\delta$163.9(C5), 163.1(C8), 154.9(C7), 150.6(C4 or C4′), 150.5(C4 or C4′), 132.7(C9), 129.9, 129.7(C2 & C2′), 129.5, 127.0, 125.3(C1 & C1′), 120.8(C3 or C3′), 120.7(C3 or C3′), 98.3(d,
C6, J_{C-P} =12.5Hz), 33.4(N-CH₃), 12.1; ³¹P NMR (CDCl₃,162MHz): δ-10.3(d, Jₚ-H =13.9Hz).

HRMS(EI) m/z Calcd. for C24H22N₃O₅P [M]+ 463.1297 , found 463.1285.

**Dimethyl (4-methylbenzoyl)phosphoramidate 2p**

![Chemical structure of 2p](image)

¹H NMR (CDCl₃,400MHz): δ9.01(d, 1H, NH, Jₕ₋ₚ=9.1Hz), 7.96(d, 2H, J=6.7Hz), 7.28(d, 2H, J=6.8Hz), 3.91(s, 3H), 3.88(s, 3H), 2.41(s, 3H); ¹³C NMR (CDCl₃,100MHz): δ167.9(d, C₂, Jₚ-C₂=2.0Hz), 143.8(C₄), 129.6(d, C₃, J_{C-P} =10.5Hz) 129.4, 128.4, 54.6(C1 or C1'), 54.5(C1 or C1'), 21.7; ³¹P NMR (CDCl₃,162MHz): δ1.8(d, Jₚ-H=9.6Hz).

HRMS(EI) m/z Calcd. for C10H14NO₄P [M]+ 243.0660 , found 243.0649.

Anal. Calcd. for C10H14NO₄P: C, 49.39; H, 5.80; N, 5.76. Found: C, 49.09; H, 5.78; N, 5.61.

**Diethyl (4-methylbenzoyl)phosphoramidate 2q**

![Chemical structure of 2q](image)

¹H NMR (CDCl₃,400MHz): δ8.83(d, 1H, NH, Jₕ₋ₚ=9.0Hz), 7.93(d, 2H, J=8.2Hz), 7.27(d, 2H, J=7.9Hz), 4.34-4.20(m, 4H), 2.41(s, 3H), 1.37(t, 6H, Jₕ₋ₚ=7.0Hz); ¹³C NMR (CDCl₃,100MHz): δ167.4(C₃), 143.3(C₅), 129.6(d, C₄, J_{C-P}=10.4Hz), 129.1, 128.0, 64.0(C2 or C2'), 63.9(C2 or C2'), 21.3, 15.9(C1 or C1'), 15.8(C1 or C1'); ³¹P NMR (CDCl₃,162MHz): δ-1.5(q, Jₚ-H=8.0Hz).
HRMS(EI) m/z Calcd. for C12H18NO4P [M]+ 271.0973, found 271.0968.

**Bis(2,2,2-trichloroethyl) (4-methylbenzoyl)phosphoramidate 2r**

\[
\begin{array}{c}
\text{O} \quad \text{O} \\
\text{N} \quad \text{O} \\
\text{CCl}_3 \\
\end{array}
\]

\(^1\)H NMR (CDCl\textsubscript{3},400MHz): \(\delta\)9.46(d, 1H, NH, \(J\text{H-P}=10.1\text{Hz}\)), 7.94(d, 2H, \(J=8.1\text{Hz}\)), 7.27(d, 2H, \(J=7.7\text{Hz}\)), 4.84(s, 2H), 4.82(s,2H), 2.42(s,3H); \(^{13}\)C NMR (CDCl\textsubscript{3},75MHz): \(\delta\)168.2(C3), 144.5(C5), 129.7, 128.8(d, C4, \(J\text{C-P}=10.9\text{Hz}\)), 128.5, 94.8(C1 or C1'), 94.7(C1 or C1'), 77.9(C2 or C2'), 77.9(C2 or C2'), 21.8; \(^{31}\)P NMR (CDCl\textsubscript{3},162MHz): \(\delta\)-3.7(q, \(J\text{P-H}= 7.9\text{Hz}\)).

HRMS(EI) m/z Calcd. for C12H12Cl\textsubscript{6}NO4P [M]+ 474.8635, found 474.8626.

Anal. Calcd. for C12H12Cl\textsubscript{6}NO4P: C, 30.16; H, 2.53; N, 2.93. Found: C, 30.33; H, 2.59; N, 3.04.

**Bis(4-nitrophenyl) (4-methylbenzoyl)phosphoramidate 2s**

\[
\begin{array}{c}
\text{O} \quad \text{O} \\
\text{N} \quad \text{O} \\
\text{NO}_2 \\
\end{array}
\]

\(^1\)H NMR (CDCl\textsubscript{3},400MHz): \(\delta\)8.97(s, 1H, NH), 8.18(d, 4H, \(J=8.4\text{Hz}\)), 7.81(d, 2H, \(J=7.9\text{Hz}\)), 7.42(d, 4H, \(J=8.7\text{Hz}\)), 7.25(d, 2H, \(J=7.5\text{Hz}\)), 2.43(s,3H); \(^{13}\)C NMR (CDCl\textsubscript{3},100MHz): \(\delta\)161.7 (C5), 154.2(C4 or C4'), 154.2(C4 or C4'), 145.6(C6), 145.3(C1 & C1'), 129.8, 128.3, 126.3, 125.9(C2 & C2'), 121.4(C3 or C3'), 121.3(C3 or C3'), 115.8, 21.7; \(^{31}\)P NMR (CDCl\textsubscript{3},162MHz): \(\delta\)-10.4(s).
Bis(2,2,2-trichloroethyl) benzoylphosphoramidate 2t

\[ \text{C}=\text{N} \quad \text{O} \quad \text{P} \quad \text{O} \quad \text{O} \quad \text{CCl}_3 \quad \text{CCl}_3 \]

$^1$H NMR (CDCl$_3$, 400MHz): $\delta$9.49(d, 1H, NH, $J_{H-P}$=8.6Hz), 8.05(d, 2H, $J$=7.5Hz), 7.60(t, 1H, $J$=7.4Hz), 7.48(t, 2H, $J$=7.6Hz), 4.85(s,2H), 4.83(s,2H); $^{13}$C NMR (CDCl$_3$, 100MHz):$\delta$168.2(C3), 133.5, 131.5(d, C4, $J_{C-P}$=10.9Hz), 128.8, 128.3, 94.6(C1 or C1’), 94.5(C1 or C1’), 77.8(C2 or C2’), 77.8(C2 or C2’); $^{31}$P NMR (CDCl$_3$, 162MHz): $\delta$-3.8(m).

HRMS(EI) m/z Calcd. for C$_{11}$H$_{10}$C$_6$NO$_4$P [M]$^+$ 460.8479, found 460.8468.

X-Ray Data of Diphenyl(4-methylbenzoyl)phosphoramidate 2a

Fig. S1 X-ray crystal structure of 2a (CCDC 862823 for 2a contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from
The Cambridge Crystallographic Data Centre via
www.ccdc.cam.ac.uk/data_request/cif).

**Computing details**

Program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008).

**Crystal data**

[C_{20}H_{18}NO_4P]

\( F(000) = 768 \)

\( M_r = 367.32 \)

\( D_x = 1.294 \text{ Mg m}^{-3} \)

Monoclinic, \( P2_1/n \)

Cu K\( \alpha \) radiation, \( \lambda = 1.54178 \text{ Å} \)

\( a = 10.0023 \) (7) Å

Cell parameters from 216 reflections

\( b=10.6631(7)\text{Å} \)

\( c=17.6975(12)\text{Å} \)

\( \beta=92.303(2)^\circ \)

\( V=1886.0(2)\text{Å}^3 \)

\( Z=4 \)

0.04×0.04×0.03 mm

**Data collection**

Radiation source: fine-focus sealed 3061 reflections with \( I > 2\sigma(I) \)

graphite

\( R_{int}=0.047 \)

Absorption correction: Multi-scan

\( SADABS \)

\( \theta_{max}=65.9^\circ, \theta_{min}=4.8^\circ \)

\( T_{min}=0.942, T_{max}=0.956 \)

\( h=-11 \rightarrow 10 \)

S18
23806 measured reflections \( k=-12 \rightarrow 12 \)
3232 independent reflections \( l=-20 \rightarrow 20 \)

**Refinement**

Refinement on \( F^2 \)

Primary atom site location: Structure-invariant direct methods

Least-square smatrix: Full

Secondary atom site location: Difference Fourier map

\[ R[F^2 > 2\sigma(F^2)] = 0.038 \]

Hydrogen site location: Inferred from neighbouring sites

\[ wR(F^2) = 0.109 \]

H-atom parameters constrained

\[ S = 1.04 \]

\[ w = 1/[\sigma^2(F_o^2) + (0.0697P)^2 + 0.352P] \]

where \( P = (F_o^2 + 2F_c^2)/3 \)

3232 reflections \( (\Delta/\sigma)_{\text{max}} = 0.002 \)

236 parameters \( \Delta \rho_{\text{max}} = 0.18e\AA^{-3} \)

0 restraints \( \Delta \rho_{\text{min}} = -0.44e\AA^{-3} \)
NMR Spectra
Bis(2,2,2-trichloroethyl)phosphorazidate3d
Diphenyl (4-methylbenzoyl)phosphoramidate 2a
Diphenylbenzoylphosphoramide 2b
Diphenyl (4-methoxybenzoyl)phosphoramidate 2c
Diphenyl (4-hydroxybenzoyl)phosphoramidate 2d
Diphenylbenzo[d][1,3]dioxole-5-carbonylphosphoramidate 2e
Diphenyl(4-chlorobenzoyl)phosphoramidate 2f
Diphenyl (4-nitrobenzoyl)phosphoramidate 2g
Electronic Supplementary Material (ESI) for Chemical Communications
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**HSQC**

1H - 13C correlations

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### S43

**Bruker**

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**1H NMR**

**13C NMR**

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**ESI**

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Diphenyl 2-naphthoylphosphoramidate 2h
Diphenyl furan-2-carbonylphosphoramidate 2i
Diphenylcinnamoylphosphoramidate 2j
Diphenyl (3-methylbut-2-enoyl)phosphoramidate 2k
Current data parameters
NAME 13C=H-N=O-11
EXPER 1
PROCID 1

F2 - Acquisition parameters
Date 03/18/05
Time 0.87
INSTRUM HP-380
MODE 1 DUAL S/N

PULPROF 90° ;
TD 30760
SOLVENT DMSO-d6
NS 5776
GS 3

SM 10030.360 MHz
FIDRES 0.577151 Hz
AB 0.700000 Hz
RG 8192
DW 25.550 us
TE 6.00 us
T1 300.0 K
T1 2.00000000 us
T1 0.0300000000 us

************** CHANNEL F1 **************
MAC1 130
M1 7.00 us
FL1 4.00 dB
FP1 75.478024 MHz

************** CHANNEL F2 **************
C1D102 wait1/2
NAC2 1 T
POP02 0.00 us/c
PL2 320.00 dB
PL0 18.00 dB
SP2D 300.151000 MHz

F2 - Processing parameters
ST 03/18/05
SF 75.478772 MHz
KON EX
SSB 1
LS 1.0 M
BS 9
PC 1.40

3D NMR plot parameters
CX 26.50 cm
F1P 210.000 ppm
F1 125.00 ppm
F2P -0.100 ppm
F2 -0.50 ppm

PMCH 0.0577 ppm/°C
H2CH 805.85740 Hz/cm

ppm 200 180 160 140 120 100 80 60 40 20 0
Diphenyl (5,6-dihydro-2H-pyran-3-carbonyl)phosphoramidate 2l
Diphenyloctanoylphosphoramidate 2m
Diphenyl (3-phenylpropanoyl)phosphoramidate 2n
Diphenyl (1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazole-4-carbonyl)-
phosphoramidate 2o
Dimethyl (4-methylbenzoyl)phosphoramidate 2p
Diethyl (4-methylbenzoyl)phosphoramidate 2q
Bis(2,2,2-trichloroethyl) (4-methylbenzoyl)phosphoramidate 2r
Bis(4-nitrophenyl) (4-methylbenzoyl)phosphoramide 2s
Bis(2,2,2-trichloroethyl) benzoylphosphoramidate 2t