Supplementary Information

[Ru^{IV}(F_{20}-TPP)Cl_2] Efficiently Catalysed Inter- and Intra-Molecular Nitrene Insertion into sp^3 C-H Bonds of Hydrocarbons Using Phosphoryl Azides as Nitrene Source

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I. General Information.................................................................................................................. 1

II. Synthesis of Ruthenium(IV) Porphyrin Catalysts................................................................. 1

III. Synthesis of Phosphoryl Azides............................................................................................ 2

IV. General Procedure for the Reactions in Table 1................................................................. 4

V. General Procedure for the Reactions in Table 2.................................................................. 5

VI. General Procedure for the [Ru^{IV}(F_{20}-TPP)Cl_2]-catalysed Intermolecular C-H Amination of Hydrocarbons with Phosphoryl Azide (Table 3)............................... 5

VII. General Procedure for the [Ru^{IV}(F_{20}-TPP)Cl_2]-catalysed Intramolecular C-H Amination of Phosphorazidates (Scheme 1)............................................................... 5

VIII. Procedure for the Study of Deuterium Kinetic Isotope Effects................................. 6

IX. Characterizations of Products............................................................................................ 7

NMR Spectra............................................................................................................................... 15
I. General Information

Unless otherwise stated, all reactions were performed under argon atmosphere. DPPA was purchased from Acros. [Rh$_2$(esp)$_2$] was purchased from Sigma-Aldrich. Molecular sieves were dried at 400°C for 3 h prior to use. All solvents and hydrocarbons were purified by distillation using standard methods. Metal porphyrin catalysts and other organic azides were synthesized according to previously reported methods. All $^1$H NMR and $^{13}$C NMR spectra were recorded on Bruker AV300, AV400 and AV500 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. ESI mass spectra were obtained on a Waters Micromess Q-Tof Premier quadrapole time-of-flight tandem mass spectrometer.

Caution! Organic azides are potentially explosive and should be handled with great care.

II. Synthesis of Ruthenium(IV) Porphyrin Catalysts

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


Synthesis of $^{[Ru^{IV}(F_{20}-TPP)Cl_2]}$

$[^{[Ru^{II}(F_{20}-TPP)(CO)]} \xrightarrow{m$-CPBA \text{ DCM}}^{[Ru^{IV}(F_{20}-TPP)(O)]} \xrightarrow{\text{HCl} \text{ DCM}}^{[Ru^{IV}(F_{20}-TPP)Cl_2]}$

To a solution of $[^{[Ru^{II}(F_{20}-TPP)(CO)]}$ (66 mg, 0.06 mmol) in 20 mL of dichloromethane was added 202 mg of $m$-CPBA (77%, 0.9 mmol). The reaction mixture was stirred for 20 min until UV spectrum indicated complete consumption of $[^{[Ru^{II}(F_{20}-TPP)(CO)]}$. Then the reaction mixture was flushed through a short alumina column and concentrated by rotary
evaporator to give crude [Ru$^{VI}$(F$_{20}$-TPP)(O)$_{2}$] for the next step.

[Ru$^{VI}$(F$_{20}$-TPP)(O)$_{2}$] was dissolved in 100 mL of anhydrous dichloromethane. Anhydrous HCl was bubbled through the solution for 1 h. After 12 h, the solvent was removed. The obtained solid was washed with diethyl ether to give [Ru$^{IV}$(F$_{20}$-TPP)Cl$_{2}$] (21 mg) in total yield of 30%. $^{1}$H NMR (CDCl$_{3}$, 400MHz): δ -51.1(br, 8H); $^{19}$F NMR (CDCl$_{3}$, 376MHz): δ -129.7, -148.9, -158.9; UV-Vis (CH$_{2}$Cl$_{2}$) $\lambda_{max}$/nm (log $\varepsilon$): 406 (5.01), 507(3.91); LRMS(ESI) m/z Calcd. For C$_{44}$H$_{8}$Cl$_{2}$F$_{20}$N$_{4}$Ru [M]$^{+}$ 1143.9, found 1144.0; [M-Cl]$^{+}$ 1108.9, found 1109.0; [M-2Cl]$^{+}$ 1073.9, found 1074.0.

III. Synthesis of Phosphoryl Azides

Bis(2,2,2-trichloroethyl) phosphorazidate was synthesized according to reported method. (W. Xiao, C.-Y. Zhou and C.-M. Che, Chem. Commun., 2012, 48, 5871-5873)

The general procedure for the synthesis of intramolecular substrates 4a, 4b, 4c and 4d

Step 1)

To a dry flask equipped with an argon inlet and an addition funnel was added phosphorus oxychloride (3.067 g, 20 mmol) and 60 mL of anhydrous diethyl ether under argon atmosphere. The solution was cooled down to -78°C in an acetone-liquid nitrogen bath with stirring. A solution of phenol (1.882 g, 20 mmol) and triethylamine (2.226 g, 22 mmol) in 20 mL of diethyl ether was added dropwise within 1 hour. After the complete addition of phenol and triethylamine, the reaction mixture was slowly warmed up to room temperature and stirred for 12 hours. Subsequently, the reaction mixture was filtered to remove the white solid. The filtrate was concentrated by a rotary evaporator to give the light yellow liquid product in 95% yield. The product was directly used for the next step without further purification.

Step 2)

A dry flask equipped with an argon inlet and an addition funnel was charged with phenyl phosphorodichloridate (422 mg, 2 mmol) and 5 mL of anhydrous diethyl ether under argon
atmosphere. The solution was cooled down to -78°C in an acetone-liquid nitrogen bath with stirring. A solution of alcohol (2 mmol) and triethylamine (223 mg, 2.2 mmol) in 10 mL of diethyl ether was added dropwise within 0.5 hour. After the complete addition of alcohol and triethylamine, the reaction mixture was slowly warmed up to room temperature and stirred for 12 ~ 24 hours. When $^{31}$P NMR indicated the complete consumption of phenyl phosphorodichloridate, the reaction mixture was filtered. The filtrate was concentrated by a rotary evaporator to give the corresponding product in high yield. The product was directly used for the next step without further purification.

Step 3)

The phosphorochloridate (3 mmol) was dissolved in 20 mL of acetone. Sodium azide (3.3 mmol) was added to the solution. The reaction mixture was stirred in darkness for several hours until the phosphorochloridate was completely consumed. The reaction mixture was filtered to remove the precipitated white solid. The filtrate was concentrated and purified by column chromatography (hexane : DCM = 3 : 1) to give the product.

**Phenyl (3-phenylpropyl) phosphorazidate 4a**

![Phenyl (3-phenylpropyl) phosphorazidate 4a](image)

$^1$H NMR (CDCl$_3$, 400MHz): $\delta$ 7.40-7.15 (m, 10H), 4.24 (dd, 2H, $J = 13.8$, 6.4Hz), 2.73 (t, 2H, $J = 7.6$Hz), 2.09-2.02 (m, 2H); $^{13}$C NMR (CDCl$_3$, 125MHz): $\delta$ 150.0(d, $J = 7.5$Hz), 140.5, 130.1, 128.7, 128.6, 126.3, 126.0, 120.3 (d, $J = 4.7$Hz), 68.8 (d, $J = 6.8$Hz), 31.7 (d, $J = 6.9$Hz), 31.5; $^{31}$P NMR (CDCl$_3$,162MHz): $\delta$ -5.2.

HRMS(ESI) m/z Calcd for C$_{15}$H$_{17}$N$_3$O$_3$P [M+H]$^+$ 318.1008, found 317.9998.

**Butyl phenyl phosphorazidate 4b**

![Butyl phenyl phosphorazidate 4b](image)

$^1$H NMR (CDCl$_3$, 500MHz): $\delta$ 7.38 (t, 2H, $J = 7.8$Hz), 7.26-7.22 (m, 3H), 4.27-4.22 (m, 2H), 1.76-1.69 (m, 2H), 1.44-1.40 (m, 2H), 0.94 (t, 3H, $J = 7.4$Hz); $^{13}$C NMR (CDCl$_3$,125MHz): $\delta$
150.0 (d, J = 7.6Hz), 130.0, 125.8, 120.2 (d, J = 4.8Hz), 69.4 (d, J = 6.9Hz), 32.1 (d, J = 6.8Hz), 18.6, 13.5; \( ^{31}P \) NMR (CDCl\(_3\), 162MHz): \( \delta \) -5.2.

HRMS(ESI) m/z Calcd for C\(_{10}\)H\(_{15}\)N\(_3\)O\(_3\)P [M+H]\(^+\) 256.0851, found 256.0869.

**Isobutyl phenyl phosphorazidate 4c**

\[
\begin{align*}
\text{PhO} & \quad \text{O} \\
\text{P} & \quad \text{N}_3 \\
& \quad \text{Ph}
\end{align*}
\]

\( ^1H \) NMR (CDCl\(_3\), 400MHz): \( \delta \) 7.37 (t, 2H, J = 7.7Hz), 7.26-7.21 (m, 3H), 4.00 (t, 2H, J = 6.8Hz), 2.07-1.97 (m, 1H), 0.97 (s, 3H), 0.96 (s, 3H); \( ^{13}C \) NMR (CDCl\(_3\), 125MHz): \( \delta \) 150.1 (d, J = 7.4Hz), 130.0, 125.9, 120.3 (d, J = 4.7Hz), 75.4 (d, J = 7.2Hz), 29.1 (d, J = 7.1Hz), 18.6; \( ^{31}P \) NMR (CDCl\(_3\), 162MHz): \( \delta \) -5.3.

HRMS(ESI) m/z Calcd for C\(_{10}\)H\(_{15}\)N\(_3\)O\(_3\)P [M+H]\(^+\) 256.0851, found 256.0848.

**Phenethyl phenyl phosphorazidate 4d**

\[
\begin{align*}
\text{PhO} & \quad \text{O} \\
\text{P} & \quad \text{N}_3 \\
& \quad \text{Ph}
\end{align*}
\]

\( ^1H \) NMR (CDCl\(_3\), 400MHz): \( \delta \) 7.36-7.14 (m, 10H), 4.42 (dd, 2H, J = 14.7, 7.2Hz), 3.04 (t, J = 6.9Hz); \( ^{13}C \) NMR (CDCl\(_3\), 100MHz): \( \delta \) 149.9(d, J = 7.8Hz), 136.4, 130.0, 129.1, 128.7, 127.0, 125.9, 120.2 (d, J = 4.7Hz), 69.7 (d, J = 6.9Hz), 36.6 (d, J = 6.9Hz); \( ^{31}P \) NMR (CDCl\(_3\), 162MHz): \( \delta \) -5.4.

HRMS(ESI) m/z Calcd for C\(_{14}\)H\(_{15}\)N\(_3\)O\(_3\)P [M+H]\(^+\) 304.0851, found 304.0855.

**IV. General Procedure for the Reactions in Table 1**

To an oven-dried Schlenk flask with a rubber seal was added the corresponding nitrene source (0.1 mmol, 1 equiv.), Ru\(^{IV}(\text{TDCPP})\)Cl\(_2\) (2 mol %) and 50 mg of 4Å molecular sieve.

The flask was evacuated and backfilled with argon three times. Then freshly distilled cyclohexane (2 mmol, 20 equiv.) and 1.5 mL of DCE were added via syringe. The mixture
was stirred at reflux for 12 h. Subsequently, the reaction mixture was allowed to cool down to room temperature and directly purified on a silica gel column with DCM/acetone (50:1, v/v) as eluent to give the pure product.

V. General Procedure for the Reactions in Table 2

An oven-dried Schlenk flask with a rubber seal was charged with bis(2,2,2-trichloroethyl) phosphorazidate (0.1 mmol, 1 equiv.), catalyst (2 mol %) and 50 mg of 4Å molecular sieve. The flask was evacuated and backfilled with argon three times. Then freshly distilled cyclohexane (2 mmol, 20 equiv.) and 1.5 mL of DCE were added via syringe. The mixture was stirred at reflux for 12 h. Subsequently, the reaction mixture was allowed to cool down to room temperature and directly purified on a silica gel column with DCM/acetone (50:1, v/v) as eluent to give the pure product.

VI. General Procedure for the [RuIV(F20-TPP)Cl2]-catalysed Intermolecular C-H Amination of Hydrocarbons with Phosphoryl Azide (Table 3)

To an oven-dried Schlenk flask with a rubber seal was added bis(2,2,2-trichloroethyl) phosphorazidate (77 mg, 0.2 mmol), [RuIV(F20-TPP)Cl2] (4.2 mg, 2 mol %) and 100 mg of 4Å molecular sieve. The flask was evacuated and backfilled with argon three times. Then the substrate (4 mmol, 20 equiv.) and freshly distilled DCE (3 mL) were added via syringe. The mixture was stirred at reflux for 12 h. Upon completion of the reaction, the reaction mixture was allowed to cool to room temperature and purified on a silica gel column with DCM/acetone (50:1, v/v) as eluent to give the pure product.

VII. General Procedure for the [RuIV(F20-TPP)Cl2]-catalysed Intramolecular C-H Amination of Phosphorazidates (Scheme 1)

Phosphorazidate (0.2 mmol), [Ru(F20TPP)Cl2] (0.2 mol %) and 100 mg of 4Å molecular
sieve were added into an oven-dried Schlenk flask which was subsequently evacuated and backfilled with argon three times. Then freshly distilled DCE (3 mL) was added via syringe into the flask. The reaction mixture was stirred at reflux for 12 h until the substrate was completely converted. Subsequently, the reaction mixture was filtered and concentrated by rotary evaporator to give corresponding product. Product 5a and 5b were purified on a short silica gel column with DCM as eluent.

VIII. Procedure for the Study of Deuterium Kinetic Isotope Effects

To an oven-dried Schlenk flask was added 77 mg (1 equiv.) of 2e, 4.2 mg (2 mol %) of [Ru$^{IV}$(TDCPP)Cl$_2$] and 100 mg of 4Å molecular sieve. The flask was sealed with a rubber septum, evacuated and backfilled with argon three times. Cyclohexane (2 mmol, 10 equiv.), cyclohexane-$_{d12}$ (2 mmol, 10 equiv.) and 3 mL of freshly distilled DCE were added via syringe. The reaction mixture was stirred at reflux until azide 2e was completely consumed. Then the reaction mixture was concentrated by rotary evaporator. The residue was purified by column chromatography (silica gel, hexane: EA = 3:1, v/v) to afford a mixture of 3e and 3e-$_{d11}$ (N-D is liable to undergo H-D exchange). The value of $k_H/k_D$ was determined according to the $^1$H NMR spectrum of the product.
IX. Characterizations of Products

Bis(2,2,2-trichloroethyl) cyclohexylphosphoramidate 3e

\[
\text{\begin{tikzpicture}
\end{tikzpicture}}
\]

\(^1\)H NMR (CDCl\(_3\), 400MHz): δ 4.62-4.53 (m, 4H), 3.19-3.13 (m, 1H), 2.98 (t, 1H, J = 10.8Hz), 2.02-1.99 (m, 2H), 1.74-1.72 (m, 1H), 1.60-1.56 (m, 1H), 1.36-1.13 (m, 6H); \(^{13}\)C NMR (CDCl\(_3\), 100MHz): δ 95.3, 95.2, 76.5, 76.4, 51.3, 35.6, 35.6, 25.3, 25.0; \(^{31}\)P NMR (CDCl\(_3\), 162MHz): δ 6.0.

HRMS(EI) m/z Calcd for C\(_{10}\)H\(_{16}\)Cl\(_6\)NO\(_3\)P [M]+ 440.8969, found 440.9071.

Bis(2,2,2-trichloroethyl) cyclopentylphosphoramidate 3f

\[
\text{\begin{tikzpicture}
\end{tikzpicture}}
\]

\(^1\)H NMR (CDCl\(_3\), 300MHz): δ 4.64-4.53 (m, 4H), 3.74-3.64 (m, 1H), 2.93 (t, 1H, J = 10.3Hz), 2.02-1.95 (m, 2H), 1.73-1.68 (m, 2H), 1.59-1.52 (m, 2H), 1.50-1.43 (m, 2H); \(^{13}\)C NMR (CDCl\(_3\), 75MHz): δ 95.3, 95.2, 76.5, 76.4, 53.9, 35.0, 34.9, 23.3; \(^{31}\)P NMR (CDCl\(_3\), 162MHz): δ 6.1.

HRMS(EI) m/z Calcd for C\(_9\)H\(_{14}\)Cl\(_6\)NO\(_3\)P [M]+ 426.8813, found 426.8814.

Bis(2,2,2-trichloroethyl) cyclooctylphosphoramidate 3g

\[
\text{\begin{tikzpicture}
\end{tikzpicture}}
\]
\^1H NMR (CDCl\textsubscript{3}, 400MHz): δ 4.62-4.52 (m, 4H), 3.49-3.39 (m, 1H), 3.19 (t, 1H, J = 11.2Hz), 1.97-1.91 (m, 2H), 1.66-1.52 (m, 12H); \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 75MHz): δ 95.3, 95.2, 76.4, 76.4, 52.3, 34.3, 34.3, 27.3, 25.4, 23.4; \textsuperscript{31}P NMR (CDCl\textsubscript{3}, 162MHz): δ 5.7.

HRMS(EI) m/z Calcd for C\textsubscript{12}H\textsubscript{20}Cl\textsubscript{16}NO\textsubscript{3}P [M]\textsuperscript{+} 468.9282, found 468.9281.

Bis(2,2,2-trichloroethyl) (1-phenylethyl)phosphoramidate 3h

\[
\begin{align*}
\text{HN} & \text{PO} \text{O} \text{CCl}_3 \\
\text{C}_3 & \text{H}_2 \text{Cl}_6 \text{P}
\end{align*}
\]

\^1H NMR (CDCl\textsubscript{3}, 400MHz): δ 7.35-7.34 (m, 4H), 7.28-7.24 (m, 1H), 4.59-4.46 (m, 4H), 4.26-4.22 (dd, 1H, J = 11.0, 5.2Hz), 3.75 (t, 1H, J = 10.6Hz), 1.56 (d, 3H, J = 6.8Hz); \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 100MHz): δ 144.2 (d, J = 4.8Hz), 128.8, 127.6, 126.0, 95.2 (d, J = 12.0Hz), 95.0 (d, J = 12.0Hz), 76.4 (d, J = 4.3Hz), 76.2 (d, J = 3.8Hz), 52.0, 24.9 (d, J = 6.6Hz); \textsuperscript{31}P NMR (CDCl\textsubscript{3}, 162MHz): δ 5.1.

HRMS(EI) m/z Calcd for C\textsubscript{12}H\textsubscript{14}Cl\textsubscript{16}NO\textsubscript{3}P [M]\textsuperscript{+} 462.8813, found 462.8809.

Bis(2,2,2-trichloroethyl) (1-(4-methoxyphenyl)ethyl)phosphoramidate 3i

\[
\begin{align*}
\text{HN} & \text{PO} \text{O} \text{CCl}_3 \\
\text{C}_3 & \text{H}_2 \text{Cl}_6 \text{P}
\end{align*}
\]

\^1H NMR (CDCl\textsubscript{3}, 500MHz): δ 7.27 (d, 2H, J = 8.5Hz), 6.87 (d, 2H, J = 8.4Hz), 4.58-4.47 (m, 4H), 4.31 (dd, 1H, J = 11.0, 5.3Hz), 3.79 (s, 3H), 3.42 (t, 1H, J = 10.4Hz), 1.55 (d, 3H, J = 6.8Hz); \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 125MHz): δ 159.1, 136.2 (d, J = 5.2Hz), 127.2, 114.2, 95.3, 95.2, 76.5 (d, J = 4.1Hz), 76.3 (d, J = 3.9Hz), 55.4, 51.4, 24.8 (d, J = 6.3Hz); \textsuperscript{31}P NMR (CDCl\textsubscript{3}, 162MHz): δ 5.5.

HRMS(ESI) m/z Calcd for C\textsubscript{13}H\textsubscript{17}Cl\textsubscript{16}NO\textsubscript{4}P [M+H]\textsuperscript{+} 493.8997, found 493.9019.
Bis(2,2,2-trichloroethyl) (1,2,3,4-tetrahydronaphthalen-1-yl)phosphoramidate 3j

![Structure](image)

$^1$H NMR (CDCl$_3$, 400MHz): $\delta$ 7.54-7.52 (m, 1H), 7.25-7.17 (m, 2H), 7.09-7.07 (m, 1H), 4.69-4.61 (m, 4H), 4.54-4.52 (m, 1H), 3.29 (t, 1H, $J$ = 11.2Hz), 2.81-2.74 (m, 2H), 2.15-2.12 (m, 1H), 1.92-1.82 (m, 3H); $^{13}$C NMR (CDCl$_3$, 100MHz): $\delta$ 137.2 (d, $J$ = 2.7Hz), 137.1, 129.1, 128.7, 127.5, 126.3, 95.1, 95.0, 76.5, 76.4, 50.4, 32.4 (d, $J$ = 1.4Hz), 29.0, 19.5; $^{31}$P NMR (CDCl$_3$, 162MHz): $\delta$ 5.6.

HRMS(EI) m/z Calcd for C$_{14}$H$_{16}$Cl$_6$NO$_3$P [M]$^+$ 488.8969, found 488.8960.

Bis(2,2,2-trichloroethyl) (2,3-dihydro-1H-inden-1-yl)phosphoramidate 3k

![Structure](image)

$^1$H NMR (CDCl$_3$, 400MHz): $\delta$ 7.47-7.45 (m, 1H), 7.26-7.23 (m, 3H), 4.92-4.83 (m, 1H), 4.69-4.61 (m, 4H), 3.19 (t, 1H, $J$ = 11.6Hz), 3.01-2.94 (m, 1H), 2.87-2.79 (m, 1H), 2.70-2.63 (m, 1H), 1.94-1.84 (m, 1H); $^{13}$C NMR (CDCl$_3$, 100MHz): $\delta$ 143.5 (d, $J$ = 7.9Hz), 142.9, 128.3, 127.0, 125.0, 124.1, 95.2, 95.1, 76.6, 76.6, 57.4, 36.5 (d, $J$ = 3.3Hz), 30.0; $^{31}$P NMR (CDCl$_3$, 162MHz): $\delta$ 5.9.

HRMS(EI) m/z Calcd for C$_{13}$H$_{14}$Cl$_6$NO$_3$P [M]$^+$ 474.8813, found 474.8809.

Bis(2,2,2-trichloroethyl) benzhydrylphosphoramidate 3l

![Structure](image)
\[ {^1}H \text{ NMR (CDCl}_3, 400MHz) : \delta 7.35-7.25 \ (m, 10H), 5.61 \ (t, 1H, J = 9.8Hz), 4.53 \ (dd, 2H, J = 11.0, 6.5Hz), 4.32 \ (dd, 2H, J = 11.0, 5.3Hz), 4.15 \ (dd, 1H, J = 12.2, 9.9 Hz); \]

\[ {^{13}}C \text{ NMR (CDCl}_3, 100MHz) : \delta 142.3, 142.2, 128.8, 127.8, 127.3, 95.1, 94.9, 76.3, 76.3, 59.6; \]

\[ {^{31}}P \text{ NMR (CDCl}_3, 162MHz) : \delta 4.6. \]

HRMS (ESI) m/z Calcd for C\textsubscript{17}H\textsubscript{17}C\textsubscript{6}NO\textsubscript{3}P [M+H]\textsuperscript{+} 525.9048, found 525.9195.

**Bis(2,2,2-trichloroethyl) benzylphosphoramidate 3m**

\[
\begin{align*}
\text{N} & \quad \text{O} & \quad \text{CCl}_3 \\
\text{Cl}_3 & \quad \text{O} & \quad \text{P} & \quad \text{CCl}_3
\end{align*}
\]

\[ {^1}H \text{ NMR (CDCl}_3, 400MHz) : \delta 7.36-7.35 \ (m, 4H), 7.31-7.28 \ (m, 1H), 4.63-4.59 \ (m, 2H), 4.56-4.51 \ (m, 2H), 4.26 \ (d, 1H, J = 7.8Hz), 4.24 \ (d, 1H, J = 7Hz), 3.3 \ (m, 1H); \]

\[ {^{13}}C \text{ NMR (CDCl}_3, 75MHz) : \delta 138.7 \ (d, J = 6.2Hz), 128.9, 127.9, 127.6, 95.2, 95.0, 76.5, 76.5, 45.7; \]

\[ {^{31}}P \text{ NMR (CDCl}_3, 162MHz) : \delta 6.2. \]

HRMS (EI) m/z Calcd for C\textsubscript{11}H\textsubscript{12}C\textsubscript{16}NO\textsubscript{3}P [M]\textsuperscript{+} 448.8656, found 448.8654.

**Bis(2,2,2-trichloroethyl) 3,5-dimethylbenzylphosphoramidate 3n**

\[
\begin{align*}
\text{N} & \quad \text{O} & \quad \text{P} & \quad \text{O} & \quad \text{CCl}_3 \\
\text{Cl}_3 & \quad \text{O} & \quad \text{CCl}_3 & \quad \text{Cl}_3 & \quad \text{CCl}_3
\end{align*}
\]

\[ {^1}H \text{ NMR (CDCl}_3, 400MHz) : \delta 6.97 \ (s, 2H), 6.92 \ (s, 1H), 4.62-4.58 \ (m, 2H), 4.55-4.51 \ (m, 2H), 4.17 \ (d, 1H, J = 6.8Hz), 4.14 \ (d, 1H, J = 6.8Hz), 3.40-3.33 \ (m, 1H), 2.30 \ (s, 6H); \]

\[ {^{13}}C \text{ NMR (CDCl}_3, 100MHz) : \delta 138.6 \ (d, J = 5.9Hz), 138.5, 129.5, 125.4, 95.2, 95.1, 76.5, 76.4, 45.6, 21.3; \]

\[ {^{31}}P \text{ NMR (CDCl}_3, 162MHz) : \delta 6.4. \]

HRMS (ESI) m/z Calcd for C\textsubscript{13}H\textsubscript{17}C\textsubscript{16}NO\textsubscript{3}P [M+H]\textsuperscript{+} 477.9048, found 477.9086.
Bis(2,2,2-trichloroethyl) (naphthalen-2-ylmethyl) phosphoramide 3o

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

\[\text{H NMR (CDCl}_3, 500\text{MHz): } \delta 7.83-7.79 (m, 4H), 7.50-7.46 (m, 3H), 4.63-4.53 (m, 4H), 4.39 (dd, 2H, } J = 11.2, 7.0\text{Hz}), 3.70-3.64 (m, 1H); \text{ } ^{13}\text{C NMR (CDCl}_3, 125\text{MHz): } \delta 136.0 (d, J = 5.9\text{Hz}), 133.4, 132.9, 128.7, 127.9, 127.8, 126.5, 126.3, 126.2, 125.5, 95.2, 95.1, 76.6, 76.5, 45.8; \text{ } ^{31}\text{P NMR (CDCl}_3, 162\text{MHz): } \delta 6.0. \]

HRMS(ESI) m/z Calcd for C_{15}H_{15}Cl_{16}NO_{3}P [M+H]^+ 499.8891, found 499.8882.

Bis(2,2,2-trichloroethyl) cyclohex-2-en-1-ylphosphoramide 3p

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

\[\text{H NMR (CDCl}_3, 400\text{MHz): } \delta 5.85-5.80 (m, 1H), 5.70-5.67 (m, 1H), 4.63-4.55 (m, 4H), 3.85 (br, 1H), 3.10 (t, 1H, } J = 11.6\text{Hz}), 2.02-1.96 (m, 3H), 1.71-1.59 (m, 3H); \text{ } ^{13}\text{C NMR (CDCl}_3, 100\text{MHz): } \delta 130.8, 129.1, 129.0, 95.3, 95.1, 76.5, 76.4, 47.6, 31.8 (d, } J = 4.8\text{Hz}), 24.7, 19.7; \text{ } ^{31}\text{P NMR (CDCl}_3, 162\text{MHz): } \delta 5.9. \]

HRMS(EI) m/z Calcd for C_{10}H_{14}Cl_{9}NO_{3}P [M]^+ 438.8813, found 438.8801.

Bis(2,2,2-trichloroethyl) hexan-2-ylphosphoramide 3q

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

\[\text{H NMR (CDCl}_3, 500\text{MHz): } \delta 4.63-4.53 (m, 4H), 3.40-3.30 (m, 1H), 2.92 (t, 1H, } J = 11.0\text{Hz}), 1.54-1.41 (m, 2H), 1.41-1.28 (m, 4H), 1.23 (d, 3H, } J = 6.5\text{Hz}), 0.90 (t, 3H, } J = 6.9\text{Hz}; \text{ } ^{13}\text{C} \]
NMR (CDCl$_3$, 125MHz): $\delta$ 95.3, 95.2, 76.5 (d, $J = 4.1$Hz), 76.4 (d, $J = 4.3$Hz), 48.7, 38.7 (d, $J = 6.7$Hz), 28.2, 23.3 (d, $J = 3.9$Hz), 22.6, 14.2; $^{31}$P NMR (CDCl$_3$, 162MHz): $\delta$ 6.1.

HRMS(ESI) m/z Calcd for C$_{10}$H$_{19}$Cl$_6$NO$_3$P [M+H]$^+$ 443.9204, found 443.9131.

Bis(2,2,2-trichloroethyl) hexan-2-ylphosphoramidate 3q + Bis(2,2,2-trichloroethyl) hexan-3-ylphosphoramidate 3s

$^1$H NMR (CDCl$_3$, 500MHz): $\delta$ 4.65-4.53 (m, C7–H + C7’–H), 3.40-3.32 (m, C2–H), 3.25-3.15 (m, C3’–H), 2.77-2.65 (m, NH, 3q + 3s), 1.60-1.56 (m, C2’–H), 1.53-1.41 (m, C3–H + C4’–H), 1.40-1.27 (m, C4–H + C5–H + C5’–H), 1.23 (d, $J = 6.5$Hz, C1-H), 0.97-0.88 (m, C6–H + C1’–H + C6’–H); $^{13}$C NMR (CDCl$_3$, 125MHz): $\delta$ 95.3, 95.2, 76.5 (d, $J = 4.1$Hz), 76.4 (d, $J = 4.4$Hz), 54.0, 48.8, 38.7 (d, $J = 6.7$Hz), 38.5 (d, $J = 5.4$Hz), 29.3 (d, $J = 4.9$Hz), 28.3, 23.4 (d, $J = 4.0$Hz), 22.7, 19.0, 14.2, 10.0; $^{31}$P NMR (CDCl$_3$, 162MHz): $\delta$ 6.4, 6.1.

HRMS(ESI) m/z Calcd for C$_{10}$H$_{19}$Cl$_6$NO$_3$P [M+H]$^+$ 443.9204, found 443.9193.

2-Phenoxy-4-phenyl-1,3,2-oxazaphosphinane 2-oxide 5a

$^1$H NMR (CDCl$_3$, 400MHz): $\delta$ 7.31-7.16 (m, 10H), 4.69 (m, 1H), 4.49-4.42 (m, 2H), 3.96 (m, 1H), 2.19(m, 2H); $^{13}$C NMR (CDCl$_3$, 100MHz): $\delta$ 151.3 (d, $J = 7.2$Hz), 142.8 (d, $J = 3.9$Hz), 129.7, 128.8, 127.9, 126.1, 124.6, 120.4 (d, $J = 5.1$Hz), 67.6 (d, $J = 6.6$Hz), 56.6, 33.3(d, $J = 10.5$Hz); $^{31}$P NMR (CDCl$_3$,162MHz): $\delta$ -1.7.

HRMS(ESI) m/z Calcd for C$_{15}$H$_{17}$NO$_3$P [M+H]$^+$ 290.0946, found 290.0949.
4-Methyl-2-phenoxy-1,3,2-oxazaphosphinane 2-oxide 5b

\[
\begin{array}{c}
\text{PhO} \quad \text{O} \\
\text{O} \quad \text{P} \\
\quad \text{NH}
\end{array}
\]

\(^1\)H NMR (CDCl\(_3\), 400MHz): \(\delta\) 7.34-7.30 (t, 2H), 7.24 (t, 2H, \(J = 8.0\)Hz), 7.14 (t, 1H, \(J = 7.2\)Hz), 4.52-4.41 (m, 1H), 4.41-4.32 (m, 1H), 3.73-3.63 (m, 1H), 3.44 (br, 1H), 2.06-2.03 (m, 1H), 1.74-1.66 (m, 1H), 1.24 (d, 3H, \(J = 6.5\)Hz);
\(^{13}\)C NMR (CDCl\(_3\), 100MHz): \(\delta\) 151.3 (d, \(J = 7.4\)Hz), 129.7, 124.6, 120.4 (d, \(J = 4.9\)Hz), 67.1 (d, \(J = 6.9\)Hz), 48.1 (d, \(J = 2.3\)Hz), 31.8 (d, \(J = 9.3\)Hz), 23.3 (d, \(J = 2.0\)Hz);
\(^{31}\)P NMR (CDCl\(_3\), 162MHz): \(\delta\) -1.26.

HRMS(ESI) m/z Calcd for C\(_{10}\)H\(_{15}\)NO\(_3\)P [M+H]\(^+\) 228.0790, found 228.0812.

4,4-dimethyl-2-phenoxy-1,3,2-oxazaphospholidine 2-oxide 5c

\[
\begin{array}{c}
\text{PhO} \quad \text{O} \\
\text{O} \quad \text{P} \\
\quad \text{NH}
\end{array}
\]

\(^1\)H NMR (CDCl\(_3\), 500MHz): \(\delta\) 7.35-7.31 (t, 2H, \(J = 7.3\)Hz), 7.21-7.15 (m, 3H), 4.01 (dd, 1H, \(J = 14.5, 8.6\)Hz), 3.90 (d, 1H, \(J = 15.7\)Hz), 3.72 (t, 1H, \(J = 8.6\)Hz), 1.39 (s, 3H), 1.12 (s, 3H);
\(^{13}\)C NMR (CDCl\(_3\), 125MHz): \(\delta\) 151.0 (d, \(J = 8.1\)Hz), 129.6, 125.1, 121.2 (d, \(J = 4.3\)Hz), 77.9 (d, \(J = 1.9\)Hz), 56.7 (d, \(J = 9.7\)Hz), 28.8 (d, \(J = 3.6\)Hz), 28.0 (d, \(J = 5.7\)Hz);
\(^{31}\)P NMR (CDCl\(_3\), 162MHz): \(\delta\) 19.6.

HRMS(ESI) m/z Calcd for C\(_{10}\)H\(_{15}\)NO\(_3\)P [M+H]\(^+\) 228.0790, found 228.0812.

2-phenoxy-4-phenyl-1,3,2-oxazaphospholidine 2-oxide 5d

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

\(^1\)H NMR (CDCl\(_3\), 500MHz): \(\delta\) 7.38-7.11 (m, 10H), 4.89 (t, 1H, \(J = 8.1\)Hz), 4.55-4.47 (m, 1H), 4.16 (d, \(J = 14.3\)Hz), 3.80 (td, 1H, \(J = 9.1, 2.1\)Hz);
\(^{13}\)C NMR (CDCl\(_3\), 125MHz): \(\delta\) 151.1 (d, \(J =
\( = 8.3\), 139.0 (d, \( J = 9.6\)Hz), 129.8, 128.9, 128.6, 126.4, 125.3, 121.2 (d, \( J = 4.2\)Hz), 73.0, 57.8 (d, \( J = 11.0\)Hz); \(^{31}\)P NMR (CDCl\(_3\), 162MHz): \( \delta \) 19.8.

HRMS(ESI) m/z Calcd for \( \text{C}_{14}\text{H}_{15}\text{NO}_{3}\text{P} \) [M+H]\(^{+}\) 276.0790, found 276.0774.
NMR Spectra
[Ru$^{IV}$ (F$_{20}$·TPP)Cl$_2$]
Phenyl (3-phenylpropyl) phosphorazidate 4a
Butyl phenyl phosphorazidate 4b
Isobutyl phenyl phosphorazidate 4c
Phenethyl phenyl phosphorazidate 4d

**Current Data Parameters**

**NMR**
- p187-1(C)
- p187-2

**FT** - Acquisition Parameters
- Date: 20101731
- Time: 14:27
- TEMPERATURE: 25 °C
- FIELD: 5 mm QNP 10.4150 MHz
- WRAPPED: 5000 Hz
- TMS: Flywheel: 60.0000 sec
- TR: 1.560000 sec
- TE: 294.9 sec
- D1: 0.500000 sec
- D11: 0.500000 sec
- D2: 100.02824 sec
- D12: 315.2 sec
- D22: 9.12 sec
- D22: 90.00 sec
- D22: -1.000000 sec
- D22: -1.000000 sec
- D22: -1.000000 sec

**FT** - Processing parameters
- DF: 100.012740 MHz
- HWB: 0.0150000 sec
- LB: 1.00 Hz
- SB: 1.00 Hz
Bis(2,2,2-trichloroethyl) cyclohexylphosphoramidate 3e
Bis(2,2,2-trichloroethyl) cyclopentylphosphoramidate 3f
Bis(2,2,2-trichloroethyl) cyclooctylphosphoramidate 3g
Bis(2,2,2-trichloroethyl) (1-phenylethyl)phosphoramidate 3h
Bis(2,2,2-trichloroethyl) (1-(4-methoxyphenyl)ethyl)phosphoramidate 3i
Bis(2,2,2-trichloroethyl) (1,2,3,4-tetrahydronaphthalen-1-yl)phosphoramidate 3j
Bis(2,2,2-trichloroethyl) (2,3-dihydro-1H-inden-1-yl)phosphoramidate 3k
Bis(2,2,2-trichloroethyl) benzhydrylphosphoramidate 3l
Bis(2,2,2-trichloroethyl) benzylphosphoramidate 3m
**Bis(2,2,2-trichloroethyl) 3,5-dimethylbenzylphosphoramidate 3n**
Bis(2,2,2-trichloroethyl) (naphthalen-2-ylmethyl)phosphoramide 3o
Bis(2,2,2-trichloroethyl) cyclohex-2-en-1-ylphosphoramidate 3p
Bis(2,2,2-trichloroethyl) hexan-2-ylphosphoramidate 3q
Mixture of 3q and 3s
2-Phenoxy-4-phenyl-1,3,2-oxazaphosphinane 2-oxide 5a
4-Methyl-2-phenoxy-1,3,2-oxazaphosphinane 2-oxide 5b
4,4-dimethyl-2-phenoxy-1,3,2-oxazaphospholidine 2-oxide 5c
2-phenoxy-4-phenyl-1,3,2-oxazaphospholidine 2-oxide 5d
Study of Deuterium Kinetic Isotope Effects