Supplementary Materials: Palladium-Catalyzed Isomerization-Coupling Reactions of Allyl Chloride with Amines to Generate Functionalized Phosphorus Derivatives

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General Chemistry:

The $^1$H NMR spectrum was recorded on a 400-MHz spectrometer. The chemical shift for $^1$H NMR spectra is reported (in parts per million) relative to internal tetramethylsilane (Me$_4$Si, $\delta = 0.00$ ppm) with CDCl$_3$. $^{13}$C NMR spectra were recorded at 101 mHz. Chemical shifts for $^{13}$C NMR spectra are reported (in parts per million) relative to CDCl$_3$ ($\delta = 77.0$ ppm). $^{31}$P NMR spectra were recorded at 162 MHz, and chemical shifts are reported (in parts per million) relative to external 85% phosphoric acid ($\delta = 0.0$ ppm). TLC plates were visualized by UV. All starting materials were purchased from commercial sources and used as received. The solvents were distilled under N$_2$ and dried according to standard procedures. $^{31}$P NMR spectra were referenced to phosphoric acid. The NMR yields of the articles are determined by integration of all of the resonances in the $^{31}$P spectra. The yields obtained by the approach are generally accurate and reproducible.
Part 1. Crystallographic Information.

Table S1. (S)-menthyl 3-oxo-3-phenylpropyl phenylphosphinate, 5a

<table>
<thead>
<tr>
<th>Empirical formula</th>
<th>C$<em>{25}$ H$</em>{33}$ O$_{3}$ P</th>
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<tbody>
<tr>
<td>Crystal system</td>
<td>Orthorhombic</td>
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<tr>
<td>Space group</td>
<td>P212121</td>
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<tr>
<td>Formula weight</td>
<td>412.48</td>
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<td>a, Å</td>
<td>8.4732(9)</td>
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<td>b, Å</td>
<td>11.1296(11)</td>
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<tr>
<td>c, Å</td>
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<tr>
<td>β, deg</td>
<td>90</td>
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<tr>
<td>γ, deg</td>
<td>90</td>
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<tr>
<td>V, Å³</td>
<td>2375.1(4)</td>
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<tr>
<td>Z</td>
<td>4</td>
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<tr>
<td>T, K</td>
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<tr>
<td>λ, Å</td>
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<td>ρ, g cm$^{-3}$</td>
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<td>R1 [I N 2σ(I)]</td>
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Table S2. Diphenyl 3-oxo-3-phenyl propylphosphonate, 5f

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Figure S3. ORTEP drawing of 5a with thermal ellipsoids at the 50% probability.

Figure S4. ORTEP drawing of 5f with thermal ellipsoids at the 50% probability.
Part 2. The NMR spectrum for the mechanism of 1f with benzyl amine.

$^{31}$P-NMR spectroscopy of crude 7f/5f=93:7

$^1$H-NMR spectroscopy of crude 7f/5f
$^{31}$P-NMR spectroscopy of crude 7f/5f=30:70

$^1$H-NMR spectroscopy of crude 7f/5f
$^{31}$P-NMR spectroscopy of crude 7f/5f=10:90

$^1$H-NMR spectroscopy of crude 7f/5f
**31P-NMR spectroscopy of crude 5f**

![31P-NMR spectrum]

**1H-NMR spectroscopy of crude 5f**

![1H-NMR spectrum]
Part 3. Selected $^{31}$P, $^{1}$H and $^{13}$C NMR spectroscopy of 1, 2, 4, 5, 11, 12 and 13.

$(Sr)$-Menthyl-1-hydroxy-3-phenylallyl phenylphosphinate, 2a, $^{31}$P NMR spectroscopy
Ethyl 1-hydroxy-3-phenylallyl phenylphosphinate, 2b, 31P NMR spectroscopy
Diethyl 1-hydroxy-3-phenylallylphosphonate, 2c, 31P NMR spectroscopy

\[ \text{\textsuperscript{1}H NMR spectroscopy of 2c} \]
Dimethyl 1-hydroxy-3-phenylallylphosphonate, 2d, 31P NMR spectroscopy

31P NMR spectroscopy of 2d

1H NMR spectroscopy of 2d
Diethyl 1-hydroxy-3-p-tolyl allylphosphonate, 2e, 31P NMR spectroscopy

\[ \text{Diethyl 1-hydroxy-3-p-tolyl allylphosphonate, 2e} \]

\[ 31P \text{ NMR spectroscopy of 2e} \]

\[ ^1H \text{ NMR spectroscopy of 2e} \]
Diphenyl 1-hydroxy-3-phenylallylphosphine oxide, 2f, 31P NMR spectroscopy

$^1$H NMR spectroscopy of 2f
(Sr)-Menthy 1-hydroxy-3-phenylallylphenylphosphine oxide, 2g, $^31$P NMR spectroscopy

$^1$H NMR spectroscopy of 2g
(S)-Menthy1 3-chloro-3-phenylprop-1-en-1-ylphenylphosphinate, 1a, $^{31}$P NMR spectroscopy
Ethyl 3-chloro-3-phenylprop-1-en-1-ylphenylphosphinate, 1b, 31P NMR spectroscopy

1H NMR spectroscopy of 1b
Diethyl 3-chloro-3-phenylprop-1-en-1-ylphosphonate, 1c, 31P NMR spectroscopy

$^{31}$P NMR spectroscopy of 1c

$^1$H NMR spectroscopy of 1c
13C NMR spectroscopy of 1c

Dimethyl 3-chloro-3-phenylprop-1-en-1-ylphosphonate, 1d, 31P NMR spectroscopy
$^1$H NMR spectroscopy of 1d

$^{13}$C NMR spectroscopy of 1d
Diethyl 3-chloro-3-p-tolylprop-1-en-1-ylphosphonate, 1e, 31P NMR spectroscopy
$^{13}$C NMR spectroscopy of 1e

Diphenyl 3-chloro-3-phenylprop-1-en-1-ylphosphine oxide, 1f, 31P NMR spectroscopy
$^1$H NMR spectroscopy of 1f

$^{13}$C NMR spectroscopy of 1f
(S)-Menthyl-3-chloro-3-phenylprop-1-en-1-yl phenylphosphine oxide, 1g, $^{31}$P NMR spectroscopy

$^1$H NMR spectroscopy of 1g
$^{13}$C NMR spectroscopy of 1g

$^{31}$P NMR spectroscopy of 4g
$^1$H NMR spectroscopy of 4g

$^{13}$C NMR spectroscopy of 4g
Dimethyl 1-chloro-3-phenylprop-1-en-1-ylphosphonate, 4d', 31P NMR spectroscopy

'H NMR spectroscopy of 4d'

\[
\begin{align*}
\text{Dimethyl 1-chloro-3-phenylprop-1-en-1-ylphosphonate, 4d', 31P NMR spectroscopy} \\
\text{'H NMR spectroscopy of 4d'}
\end{align*}
\]
gCOSY NMR spectroscopy of 4d'

13C NMR spectroscopy of 4d'
(Sr)-Methyl 3-oxo-3-phenylpropyl phenylphosphinate, 5a, $^{31}$P NMR spectroscopy

$^{1}$H NMR spectroscopy of 5a
13C NMR spectroscopy of 5a

Ethyl 3-oxo-3-phenylpropyl phenylphosphinate, 5b, 31P NMR spectroscopy
$^1$H NMR spectroscopy of 5b

Diethyl 3-oxo-3-phenyl propylphosphonate, 5c, $^{31}$P NMR spectroscopy
\[ ^1H \text{NMR spectroscopy of 5c} \]

\[ ^13C \text{NMR spectroscopy of 5c} \]
Dimenthyl 3-oxo-3-phenylpropyl phenylphosphonate, 5d, $^{31}$P NMR spectroscopy
$^{13}$C NMR spectroscopy of 5d

Diethyl 3-oxo-3-p-tolyl propylphosphonate, 5e, $^{31}$P NMR spectroscopy
$^1$H NMR spectroscopy of 5e

Diphenyl 3-oxo-3-phenyl propylphosphonate, 5f, $^{31}$P NMR spectroscopy
$^1$H NMR spectroscopy of 5f

$^{13}$C NMR spectroscopy of 5f
(Sr)-Menthy1 3-oxo-3-phenylpropyl phenylphosphinate, 5g/5g’, \textsuperscript{31}P NMR spectroscopy

\[ \text{\textsuperscript{1}H NMR spectroscopy of 5g/5g’} \]
$^{13}$C NMR spectroscopy of 5g/5g’

(Sr)-Menthy1-3-butylamino-3-phenylpropyl phenylphosphinate, 11aa, $^{31}$P NMR spectroscopy
'H NMR spectroscopy of 11aa

13C NMR spectroscopy of 11aa
(S)-Menthyl-3-phenethylamino-3-phenylpropyl phenylphosphinate, 11ab, $^{31}$P NMR spectroscopy

$^1$H NMR spectroscopy of 11ab
(S)-Menthy1-3-phenyl-3-pyrrolidin-1-yl propylphosphinate, 11ac, $^3$P NMR spectroscopy
$^1$H NMR spectroscopy of 11ac

$^{13}$C NMR spectroscopy of 11ac
Ethyl 3-butylamino-3-phenylpropyl phenylphosphinate, 11ba, $^{31}$P NMR spectroscopy

$^1$H NMR spectroscopy of 11ba
$^{13}$C NMR spectroscopy of 11ba

Ethyl 3-phenethylamino-3-phenylpropyl phenylphosphinate, 11bb, $^{31}$P NMR spectroscopy
$^1$H NMR spectroscopy of 11bb

$^{13}$C NMR spectroscopy of 11bb
Diethyl 3-butylamino-3-phenyl propylphosphonate, 11ca, $^{31}$P NMR spectroscopy

$^{1}$H NMR spectroscopy of 11ca
$^{13}$C NMR spectroscopy of 11ca

Diethyl 3-phenethylamino-3-phenyl propylphosphonate, 11cb, $^{31}$P NMR spectroscopy
$^{1}H$ NMR spectroscopy of 11cb

$^{13}C$ NMR spectroscopy of 11cb
Dimethyl 3-butyramino-3-phenyl propylphosphonate, 11da, $^{31}$P NMR spectroscopy

$^1$H NMR spectroscopy of 11da
$^{13}$C NMR spectroscopy of 11da

Dimethyl 3-phenylethylamino-3-phenyl propylphosphonate, 11db, $^{31}$P NMR spectroscopy
$^1$H NMR spectroscopy of 11db

$^{13}$C NMR spectroscopy of 11db
Dimethyl 3-phenyl-3-pyrrolidin-1-yl propylphosphonate, 11dc, $^{31}$P NMR spectroscopy
$^{13}$C NMR spectroscopy of 11dc

Dimethyl-3-methyl phenylamino-3-phenyl propylphosphonate, 11dd, $^{31}$P NMR spectroscopy
$^1$H NMR spectroscopy of 11dd

$^{13}$C NMR spectroscopy of 11dd
Diethyl 3-butylamino-3-p-tolyl propylphosphonate, 11ea, $^{31}$P NMR spectroscopy

$^{1}$H NMR spectroscopy of 11ea
Diethyl 3-phenethlamino-3-\(p\)-tolyl propylphosphonate, 11eb, \(^{31}\)P NMR spectroscopy
$^1$H NMR spectroscopy of 11eb

$^{13}$C NMR spectroscopy of 11eb
Diphenyl 3-butilamino-3-phenylpropyl phosphine oxide, 11fa, $^{31}$P NMR spectroscopy
$^{13}$C NMR spectroscopy of 11fa

Diphenyl 3-phenethylamino-3-phenylpropyl phosphine oxide, 11fb, $^{31}$P NMR spectroscopy
$^1$H NMR spectroscopy of 11fb

$^{13}$C NMR spectroscopy of 11fb
(S)-Menthyl-3-butylamino-3-phenylpropyl phenylphosphine oxide, 11gaA/11gaB, $^{31}$P NMR spectroscopy
**13C NMR spectroscopy of 11ga\textsubscript{A}/11ga\textsubscript{B}**

(S\textsubscript{P})-Menthyl-3-phenethylamino-3-phenylpropyl phenylphosphine oxide, 11gb\textsubscript{A}/11gb\textsubscript{B}, 11gb\textsubscript{A’}/11gb\textsubscript{B’}, \textsuperscript{31}P NMR spectroscopy
'H NMR spectroscopy of 11gb\textsubscript{A}/11gb\textsubscript{B}, 11gb\textsubscript{A'}/11gb\textsubscript{B'}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{1H_NMR_spectrum}
\end{figure}

\[13C\text{ NMR spectroscopy of 11gb\textsubscript{A}/11gb\textsubscript{B}, 11gb\textsubscript{A'}/11gb\textsubscript{B'}}\]

\begin{figure}
\centering
\includegraphics[width=\textwidth]{13C_NMR_spectrum}
\end{figure}
Diphenyl 3-hydroxy-3-phenylprop-1-en-1-ylphosphine oxide, 12a, $^{31}$P NMR spectroscopy
\textbf{\( ^{13} \text{C} \) NMR spectroscopy of 12a}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{13C_NMR_spectrum_12a}
\caption{\( ^{13} \text{C} \) NMR spectrum of compound 12a.}
\end{figure}

\textbf{Dimethyl 3-hydroxy-3-phenylprop-1-en-1-ylphosphonate, 12b, \( ^{31} \text{P} \) NMR spectroscopy}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{31P_NMR_spectrum_12b}
\caption{\( ^{31} \text{P} \) NMR spectrum of compound 12b.}
\end{figure}
$^1$H NMR spectroscopy of 12b

$^{13}$C NMR spectroscopy of 12b
Dimenthoxyl 2-benzoyl-4-cyanobutylphosphonate, 13a, $^{31}$P NMR spectroscopy
$^{13}$C NMR spectroscopy of 13a

Ethyl 4-dimethoxyphosphorylmethyl-5-oxo-5-phenylpentanoate, 13b, $^{31}$P NMR spectroscopy
\[ ^1\text{H NMR spectroscopy of 13b} \]

\[ ^{13}\text{C NMR spectroscopy of 13b} \]