Supporting Information:

Lanthanide anilido complexes: synthesis, characterization, and as highly efficient catalysts for hydrophosphonylation of aldehydes and unactivated ketones

Chengwei Liu, Qinqin Qian, Kun Nie, Yaorong Wang, Qi Shen, Dan Yuan,* and Yingming Yao*

Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry, Chemical Engineering and Materials Science, Dushu Lake Campus, Soochow University, Suzhou215123, People’s Republic of China.
E-mail: yuandan@suda.edu.cn; yaoym@suda.edu.cn

Content

Solid state structures of complexes 2·toluene and 3·toluene ................................. S2
$^{13}$C NMR spectrum of complex 3 in THF-$d_8$ ................................................. S4
$^1$H NMR spectrum of diethyl hydroxy(phenyl)methylphosphonate 6a in THF-$d_8$  S5
Characterization of α-hydroxyphosphonates ..................................................... S6
Fig.S1 ORTEP diagram of complex 2·toluene showing an atom numbering scheme. Thermal ellipsoids are drawn at the 20% probability level. The solvent molecule of toluene and hydrogen atoms are omitted for clarity.
Fig.S2 ORTEP diagram of complex 3-toluene showing an atom numbering scheme. Thermal ellipsoids are drawn at the 20% probability level. The solvent molecule of toluene and hydrogen atoms are omitted for clarity.
$^{13}\text{C}$ NMR spectrum (in THF-$d_8$, 25 °C) of complex 3
$^1$H NMR spectrum (in THF-$d_8$, 25 °C) of diethyl hydroxy(phenyl)methyl phosphonate 6a
Characterization of α-hydroxyphosphonates:

Diethyl hydroxy(phenyl)methylphosphonate (6a).\(^1\)

\(^1\)H NMR (CDCl\(_3\), 400 MHz, ppm): \(\delta 7.49-7.47\) (m, 2H), 7.37-7.28 (m, 3H), 5.03-5.00 (d, J = 10.8 Hz, 1H), 4.08-3.94 (m, 4H), 3.61 (s, 1H), 1.28-1.24 (t, J = 7.1 Hz, 3H), 1.23-1.19 (t, J = 7.1 Hz, 3H).

Diethyl hydroxy(2-methylphenyl)methylphosphonate (6b).\(^2\)

\(^1\)H NMR (CDCl\(_3\), 400 MHz, ppm): \(\delta 7.65-7.63\) (d, J = 7.6 Hz, 1H), 7.24-7.13 (m, 3H), 5.27-5.24 (d, J = 10.9 Hz, 1H), 4.09-3.87 (m, 4H), 3.65 (s, 1H), 2.37 (s, 3H), 1.28-1.25 (t, J = 7.1 Hz, 3H), 1.21-1.17 (t, J = 7.0 Hz, 3H).

Diethyl hydroxy(4-methylphenyl)methylphosphonate (6c).\(^3\)

\(^1\)H NMR (CDCl\(_3\), 400 MHz, ppm): \(\delta 7.37-7.35\) (d, J = 8.1 Hz, 2H), 7.17-7.15 (d, J = 8.0 Hz, 2H), 4.98-4.95 (d, J = 10.5 Hz, 1H), 4.08-3.93 (m, 4H), 3.54 (s, 1H), 2.34 (s, 3H), 1.28-1.25 (t, J = 7.1 Hz, 3H), 1.23-1.19 (t, J = 7.1 Hz, 3H).

Diethyl hydroxy(2-methoxyphenyl)methylphosphonate (6d).\(^2\)

\(^1\)H NMR (CDCl\(_3\), 400 MHz, ppm): \(\delta 7.54-7.50\) (d, J = 7.53 Hz, 1H), 7.28-7.25 (t, J =
7.27 Hz, 1H), 6.99-6.96 (t, J = 6.98 Hz, 1H), 6.88-6.86 (d, J = 6.87 Hz, 1H), 5.43-5.40 (d, J = 12.0 Hz, 1H), 4.14-3.90 (m, 4H), 3.84 (s, 3H), 3.68 (s, 1H), 1.30-1.26 (t, J = 7.1 Hz, 3H), 1.18-1.14 (t, J = 7.0 Hz, 3H).

![Image of compound 6e]

Diethyl hydroxy(3-methoxyphenyl)methylphosphonate (6e).

$^1$H NMR (CDCl$_3$, 400 MHz, ppm): $\delta$ 7.54-7.52 (d, J = 7.6 Hz, 1H), 7.29-7.25 (t, J = 7.7 Hz, 1H), 7.00-6.96 (t, J = 7.5 Hz, 1H), 6.88-6.86 (d, J = 8.3 Hz, 1H), 5.43-5.40 (d, J = 12.0 Hz, 1H), 4.15-3.98 (m, 4H), 3.89 (s, 1H), 3.84 (s, 3H), 1.31-1.27 (t, J = 7.1 Hz, 3H), 1.18-1.15 (t, J = 7.0 Hz, 3H).

![Image of compound 6f]

Diethyl hydroxy(4-methoxyphenyl)methylphosphonate (6f).

$^1$H NMR (CDCl$_3$, 400 MHz, ppm): $\delta$ 7.42-7.39 (d, J = 8.8 Hz, 2H), 6.90-6.88 (d, J = 8.6 Hz, 2H), 4.95-4.93 (d, J = 9.9 Hz, 1H), 4.09-3.91 (m, 4H), 3.80 (s, 3H), 3.01 (s, 1H), 1.29-1.25 (t, J = 7.0 Hz, 3H), 1.23-1.20 (t, J = 7.1 Hz, 3H).

![Image of compound 6g]

Diethyl hydroxy(4-dimethylaminophenyl)methylphosphonate (6g).

$^1$H NMR (CDCl$_3$, 400 MHz, ppm): $\delta$ 7.35-7.33 (d, J = 8.7 Hz, 2H), 6.72-6.70 (d, J = 8.7 Hz, 2H), 4.89-4.87 (d, J = 9.6 Hz, 1H), 4.11-3.90 (m, 4H), 2.95 (s, 6H), 1.31-1.27 (t, J = 7.0 Hz, 3H), 1.23-1.19 (t, J = 7.1 Hz, 3H).
Diethyl hydroxy(4-fluorophenyl)methylphosphonate (6h).^4

^1^H NMR (CDCl$_3$, 400 MHz, ppm): $\delta$ 7.47-7.43 (t, J = 8.0 Hz, 2H), 7.05-7.01 (t, J = 8.6 Hz, 2H), 5.00-4.98 (d, J = 10.4 Hz, 1H), 4.53 (s, 1H), 4.09-3.96 (m, 4H), 1.27-1.24 (t, J = 7.1 Hz, 3H), 1.23-1.20 (t, J = 7.1 Hz, 3H).

Diethyl hydroxy(2-chlorophenyl)methylphosphonate (6i).^5

^1^H NMR (CDCl$_3$, 400 MHz, ppm): $\delta$ 7.76-7.74 (d, J = 7.8 Hz, 1H), 7.36-7.30 (m, 2H), 7.24-7.22 (d, J = 7.4 Hz, 1H), 5.57-5.54 (d, J = 11.6 Hz, 1H), 4.20-3.92 (m, 4H), 3.55 (s, 1H), 1.32-1.29 (t, J = 7.1 Hz, 3H), 1.22-1.18 (t, J = 7.0 Hz, 3H).

Diethyl hydroxy(3-chlorophenyl)methylphosphonate (6j).^6

^1^H NMR (CDCl$_3$, 400 MHz, ppm): $\delta$ 7.47 (s, 1H), 7.33-7.30 (m, 1H), 7.24-7.23 (d, J = 5.0 Hz, 2H), 4.98-4.95 (d, J = 11.3 Hz, 1H), 4.08-3.97 (m, 4H), 3.84 (s, 3H), 1.26-1.22 (t, J = 7.1 Hz, 3H), 1.22-1.18 (t, J = 7.0 Hz, 3H).

Diethyl hydroxy(4-chlorophenyl)methylphosphonate (6k).^6

^1^H NMR (CDCl$_3$, 400 MHz, ppm): $\delta$ 7.41-7.39 (m, 2H), 7.32-7.28 (m, 2H), 4.99-4.96 (d, J = 11.1 Hz, 1H), 4.80 (s, 1H), 4.05-3.96 (m, 4H), 1.27-1.24 (t, J = 6.9 Hz, 3H),
Diethyl hydroxy(4-bromophenyl)methylphosphonate (6l).\(^7\)

\[^1\]H NMR (CDCl\(_3\), 400 MHz, ppm): \(\delta\) 7.49-7.47 (d, J = 8.4 Hz, 2H), 7.37-7.34 (d, J = 8.6 Hz, 2H), 4.99-4.96 (d, J = 10.9 Hz, 1H), 4.47 (s, 1H), 4.10-3.99 (m, 4H), 1.28-1.25 (t, J = 7.0 Hz, 3H), 1.25-1.21 (t, J = 7.1 Hz, 3H).

Diethyl hydroxy(3-nitrophenyl)methylphosphonate (6m).\(^8\)

\[^1\]H NMR (CDCl\(_3\), 400 MHz, ppm): \(\delta\) 8.40 (s, 1H), 8.16-8.14 (d, J = 7.6 Hz, 1H), 7.81-7.80 (d, J = 7.4 Hz, 1H), 7.54-7.50 (t, J = 8.0 Hz, 1H), 5.18-5.15 (d, J = 11.4 Hz, 1H), 4.18-4.06 (m, 4H), 3.71 (s, 1H), 1.31-1.27 (t, J = 7.1 Hz, 3H), 1.27-1.23 (t, J = 7.0 Hz, 3H).

Diethyl hydroxy(4-nitrophenyl)methylphosphonate (6n).\(^5\)

\[^1\]H NMR (CDCl\(_3\), 400 MHz, ppm): \(\delta\) 8.22-8.20 (d, J = 8.7 Hz, 2H), 7.67-7.65 (d, J = 8.8 Hz, 2H), 5.18-5.15 (d, J = 12.3 Hz, 1H), 4.48 (s, 1H), 4.16-4.02 (m, 4H), 3.84 (s, 3H), 1.30-1.27 (t, J = 7.1 Hz, 3H), 1.26-1.23 (t, J = 7.0 Hz, 3H).

Diethyl hydroxy(1-naphthyl)methylphosphonate (6o).\(^9\)

\[^1\]H NMR (CDCl\(_3\), 400 MHz, ppm): \(\delta\) 8.09-8.07 (d, J = 8.3 Hz, 2H), 7.90-7.81 (m, 3H), 7.54-7.46 (m, 3H), 5.88-5.85 (d, J = 11.5 Hz, 1H), 4.08-3.73 (m, 4H), 1.22-1.18 (t, J = 6.8 Hz, 3H).
7.1 Hz, 3H), 1.06-1.03 (t, J = 7.1 Hz, 3H).

Diethyl hydroxy(furan-2-yl)methylphosphonate (6p).\textsuperscript{10}
\(^1\)H NMR (CDCl\textsubscript{3}, 400 MHz, ppm): \(\delta 7.38\) (s, 1H), 6.47 (s, 1H), 6.33 (s, 1H), 4.99-4.96 (d, J = 13.5 Hz, 1H), 4.38 (s, 1H), 4.16-3.98 (m, 4H), 1.29-1.25 (t, J = 7.1 Hz, 3H), 1.22-1.19 (t, J = 7.1 Hz, 3H).

Diethyl 1-hydroxy-2-methyl-propylphosphonate (6q).\textsuperscript{11}
\(^1\)H NMR (CDCl\textsubscript{3}, 400 MHz, ppm): \(\delta 4.33\) (s, 1H), 4.11-3.98 (m, 4H), 3.61-3.47 (m, 1H), 2.01-1.87 (m, 1H), 1.29-1.14 (m, 6H), 1.02-0.87 (m, 6H).

Diethyl hydroxy(benzyl)methylphosphonate (6r).\textsuperscript{12}
\(^1\)H NMR (CDCl\textsubscript{3}, 400 MHz, ppm): \(\delta 6.97-6.88\) (m, 5H), 4.99-4.96 (d, J = 13.5 Hz, 1H), 3.81-3.75 (m, 4H), 3.57 (s, 1H), 2.74-2.63 (m, 2H) 1.01-0.97 (t, J = 7.2 Hz, 3H), 0.95-0.92 (t, J = 6.6 Hz, 3H).

Diethyl 1-hydroxy-1-phenyl-ethylphosphonate (8a).\textsuperscript{13}
\(^1\)H NMR (CDCl\textsubscript{3}, 400 MHz, ppm): \(\delta 7.62-7.59\) (m, 2H), 7.37-7.33 (t, J = 7.8 Hz, 2H), 7.30-7.27 (m, 1H) 4.13-3.84 (m, 4H), 3.45 (s, 1H), 1.84-1.80 (d, J = 15.4 Hz, 3H), 1.27-1.24 (t, J = 7.1 Hz, 3H), 1.21-1.17 (t, J = 7.1 Hz, 3H).
Diethyl 1-hydroxy-1-(2-chloro)phenyl-ethylphosphonate (8b).  
\[^1\text{H}\] NMR (CDCl\textsubscript{3}, 400 MHz, ppm): \(\delta 7.74-7.72\) (d, \(J = 7.8\) Hz, 1H), 7.37-7.35 (d, \(J = 8.3\) Hz, 1H), 7.29-7.20 (m, 2H), 4.17-3.95 (m, 4H), 3.14 (s, 1H), 2.00-1.97 (d, \(J = 15.2\) Hz, 3H), 1.31-1.27 (t, \(J = 7.0\) Hz, 3H), 1.24-1.20 (t, \(J = 7.0\) Hz, 3H).

\[8b\]

Diethyl 1-hydroxy-1-(2-bromo)phenyl-ethylphosphonate (8c).  
\[^1\text{H}\] NMR (CDCl\textsubscript{3}, 400 MHz, ppm): \(\delta 7.74-7.72\) (d, \(J = 8.0\) Hz, 1H), 7.59-7.57 (d, \(J = 7.9\) Hz, 1H), 7.31-7.28 (t, \(J = 7.3\) Hz, 1H), 7.13-7.09 (t, \(J = 7.8\) Hz, 1H), 4.15-3.99 (m, 4H), 3.40 (s, 1H), 2.00-1.96 (d, \(J = 15.2\) Hz, 3H), 1.31-1.27 (t, \(J = 7.0\) Hz, 3H), 1.26-1.22 (t, \(J = 7.1\) Hz, 3H).

\[8c\]

Diethyl 1-hydroxy-1-(2-nitro)phenyl-ethylphosphonate (8d).  
\[^1\text{H}\] NMR (CDCl\textsubscript{3}, 400 MHz, ppm): \(\delta 7.79-7.77\) (d, \(J = 8.0\) Hz, 1H), 7.48-7.44 (t, \(J = 8.3\) Hz, 1H), 7.39-7.34 (m, 2H), 4.23-4.01 (m, 4H), 3.22 (s, 1H), 1.91-1.87 (d, \(J = 15.4\) Hz, 3H), 1.30-1.26 (t, \(J = 7.0\) Hz, 3H), 1.26-1.23 (t, \(J = 7.1\) Hz, 3H).

\[8d\]

Diethyl 1-hydroxy-1-(3-nitro)phenyl-ethylphosphonate (8e).  
\[^1\text{H}\] NMR (CDCl\textsubscript{3}, 400 MHz, ppm): \(\delta 8.51\) (s, 1H), 8.15-8.13 (d, \(J = 8.6\) Hz, 1H), 7.95-7.93 (d, \(J = 8.0\) Hz, 1H), 7.54-7.50 (t, \(J = 8.1\) Hz, 1H), 4.72 (s, 1H), 4.19-4.07 (m, 4H), 1.87-1.84 (d, \(J = 15.4\) Hz, 3H), 1.30-1.28 (t, \(J = 7.1\) Hz, 3H), 1.26-1.24 (t, \(J = 7.1\) Hz, 3H).
Diethyl 1-hydroxy-1-(4-nitro)phenyl-ethylphosphonate (8f).\textsuperscript{16}
$^1$H NMR (CDCl$_3$, 400 MHz, ppm): $\delta$ 8.21-8.19 (d, $J = 9.0$ Hz, 2H), 7.81-7.78 (d, $J = 9.1$ Hz, 2H), 4.29 (s, 1H), 4.18-4.01 (m, 4H), 1.87-1.83 (d, $J = 15.4$ Hz, 3H), 1.28-1.24 (t, $J = 7.0$ Hz, 6H).

Diethyl 1-hydroxy-1-(4-bromo)phenyl-ethylphosphonate (8g).\textsuperscript{14}
$^1$H NMR (CDCl$_3$, 400 MHz, ppm): $\delta$ 7.48 (s, 4H), 4.14-3.90 (m, 4H), 3.49 (s, 1H), 1.81-1.77 (d, $J = 15.4$ Hz, 3H), 1.25-1.25 (t, $J = 7.0$ Hz, 3H), 1.24-1.20 (t, $J = 7.0$ Hz, 3H).

Diethyl 1-hydroxy-1-(4-fluro)phenyl-ethylphosphonate (8h).\textsuperscript{14}
$^1$H NMR (CDCl$_3$, 400 MHz, ppm): $\delta$ 7.60-7.55 (m, 2H), 7.05-7.01 (t, $J = 8.7$ Hz, 2H), 4.14-3.88 (m, 4H), 3.66 (s, 1H), 1.82-1.78 (d, $J = 15.3$ Hz, 3H), 1.28-1.24 (t, $J = 7.1$ Hz, 3H), 1.23-1.19 (t, $J = 7.1$ Hz, 3H).

Diethyl 1-hydroxy-1-(4-trifluoromethyl)phenyl-ethylphosphonate (8i).\textsuperscript{14}
$^1$H NMR (CDCl$_3$, 400 MHz, ppm): $\delta$ 7.75-7.72 (d, $J = 8.6$ Hz, 2H), 7.61-7.59 (d, $J = 8.6$ Hz, 2H), 4.16-4.02 (m, 4H), 3.98 (s, 1H), 1.84-1.81 (d, $J = 15.4$ Hz, 3H), 1.27-1.24 (t, $J = 7.1$ Hz, 3H), 1.25-1.22 (t, $J = 7.1$ Hz, 3H).
Diethyl 1-hydroxy-1-(4-methoxy)phenyl-ethylphosphonate (8j).\textsuperscript{14}

\(^1^H\) NMR (CDCl\textsubscript{3}, 400 MHz, ppm): \(\delta\) 7.52-7.50 (d, \(J = 9.0\) Hz, 2H), 6.89-6.87 (d, \(J = 8.8\) Hz, 2H), 4.12-3.87 (m, 4H), 3.80 (s, 3H), 3.27 (s, 1H), 1.81-1.77 (d, \(J = 15.4\) Hz, 3H), 1.28-1.24 (t, \(J = 7.1\) Hz, 3H), 1.22-1.19 (t, \(J = 7.1\) Hz, 3H).

Diethyl 1-hydroxy-1-(4-methyl)phenyl-ethylphosphonate (8k).\textsuperscript{14}

\(^1^H\) NMR (CDCl\textsubscript{3}, 400 MHz, ppm): \(\delta\) 7.49-7.47 (d, \(J = 7.4\) Hz, 2H), 7.17-7.15 (d, \(J = 7.7\) Hz, 2H), 4.08-3.89 (m, 4H), 2.72 (s, 1H), 2.34 (s, 3H), 1.82-1.78 (d, \(J = 15.2\) Hz, 3H), 1.28-1.25 (t, \(J = 6.8\) Hz, 3H), 1.22-1.19 (t, \(J = 6.5\) Hz, 3H).

Diethyl hydroxy-diphenyl-methylphosphonate (8l).\textsuperscript{15}

\(^1^H\) NMR (CDCl\textsubscript{3}, 400 MHz, ppm): \(\delta\) 7.68-7.66 (d, \(J = 7.4\) Hz, 4H), 7.33-7.23 (m, 6H), 3.98-3.84 (m, 4H), 1.16-1.13 (t, \(J = 6.9\) Hz, 6H).

Diethyl 1-hydroxy-1-(pyridin-3-yl)-ethylphosphonate (8m).\textsuperscript{15}

\(^1^H\) NMR (CDCl\textsubscript{3}, 400 MHz, ppm): \(\delta\) 8.79 (s, 1H), 8.48 (s, 1H), 7.94-7.92 (d, \(J = 8.1\) Hz, 1H), 7.26 (s, 1H), 4.15-3.98 (m, 4H), 2.42 (s, 1H), 1.85-1.81 (d, \(J = 15.5\) Hz, 3H), 1.25-1.21 (t, \(J = 7.0\) Hz, 3H), 1.24-1.21 (t, \(J = 7.0\) Hz, 3H).
Diethyl 1-hydroxy-1-(furan-2-yl)-ethylphosphonate (8n).\textsuperscript{15}

\(^1\)H NMR (CDCl\textsubscript{3}, 400 MHz, ppm): \(\delta 7.37\) (s, 1H), 6.41 (s, 1H), 6.32 (s, 1H), 4.43 (s, 1H), 4.13-3.94 (m, 4H), 1.74-1.71 (d, J = 15.2 Hz, 3H), 1.29-1.25 (t, J = 7.1 Hz, 3H), 1.22-1.19 (t, J = 7.1 Hz, 3H).

Diethyl 1-hydroxy-1-(thiophen-2-yl)-ethylphosphonate (8o).\textsuperscript{15}

\(^1\)H NMR (CDCl\textsubscript{3}, 400 MHz, ppm): \(\delta 7.26-7.25\) (d, J = 5.6 Hz, 1H), 7.14-7.12 (t, J = 3.5 Hz, 1H), 7.00-6.97 (t, J = 4.3 Hz, 1H), 4.17-4.03 (m, 4H), 3.96 (s, 1H), 1.87-1.84 (d, J = 14.9 Hz, 3H), 1.29-1.25 (t, J = 7.1 Hz, 3H), 1.28-1.25 (t, J = 7.1 Hz, 3H).

Diethyl 1-hydroxy-1-methyl-ethylphosphonate (8p).\textsuperscript{17}

\(^1\)H NMR (CDCl\textsubscript{3}, 400 MHz, ppm): \(\delta 4.42\) (s, 1H), 4.06-3.95 (m, 4H), 1.31-1.24 (m, 6H), 1.17-1.14 (t, J = 7.1 Hz, 6H).

Diethyl 1-hydroxy-cyclopentanylphosphonate (8q).\textsuperscript{18}

\(^1\)H NMR (CDCl\textsubscript{3}, 400 MHz, ppm): \(\delta 4.05-3.97\) (m, 4H), 3.80 (s, 1H), 1.87-1.50 (m, 8H), 1.18-1.15 (t, J = 7.1 Hz, 6H).

S14
Diethyl 1-hydroxy-cyclohexanylphosphonate (8r).\textsuperscript{17}

\textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz, ppm): \(\delta 4.20-4.13\) (m, 4H), 2.69 (s, 1H), 1.86-1.57 (m, 10H), 1.35-1.31 (t, \(J = 7.0\) Hz, 6H).

References:
