# **Rhodium-Catalyzed Reaction of 1-Alkynylphosphines with** Water Yielding (*E*)-1-Alkenylphosphine Oxides

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Table 1. Optimization of Reaction Conditions

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Treatment of 1-alkynylphosphines with a rhodium catalyst in 1,4-dioxane/ $H_2O$  at reflux provides (*E*)-1-alkenylphosphine oxides in good yields with perfect stereoselectivity. The reaction proceeds as follows. Oxidative addition of 1-alkynylphosphine to rhodium followed by hydrolysis yields the corresponding terminal alkyne and diphenylphosphine oxide. Rhodium-catalyzed hydrophosphinylation of the terminal alkyne then proceeds to afford (*E*)-1-alkenylphosphine oxide.

We have been interested in the use of 1-alkynylphosphines as precursors of new phosphines.<sup>1</sup> Here, we report a new transformation of 1-alkynylphosphines. 1-Alkynylphosphines react with water in the presence of a rhodium catalyst to provide the corresponding (*E*)-1-alkenylphosphine oxides<sup>2</sup> with perfect stereoselectivity. This is an interesting formal hydration reaction of 1-alkynylphosphines from mechanistic and synthetic points of view.

### **Results and Discussion**

Treatment of 1-octynyldiphenylphosphine (1a) under [RhCl-

 $(cod)]_2$  catalysis in 1,4-dioxane/H<sub>2</sub>O (10/1) at reflux provided (*E*)-1-octenyldiphenylphosphine oxide (**2a**) in 84% NMR yield and 73% isolated yield (Table 1, Entry 1). Other rhodium complexes such as [Rh(OH)(cod)]<sub>2</sub> also showed catalytic activity (Entry 2). Addition of PPh<sub>3</sub> (2 mol. amt. to Rh) as a ligand had no effect on the reaction (Entry 3). In contrast, when BINAP (1 mol. amt. to Rh) or P(OEt)<sub>3</sub> (2 mol. amt. to Rh) was used instead of PPh<sub>3</sub>, the reaction was completely inhibited (Entries 4 and 5). Rh(acac)<sub>3</sub> and an iridium catalyst, [IrCl-(cod)]<sub>2</sub>, were inactive (Entries 6 and 7).

1,4-Dioxane/H<sub>2</sub>O was the choice of solvent. Although the

<i>n</i> -C <sub>6</sub> H <sub>13</sub> −CΞC−PPh <sub>2</sub> 1a		0.015 mol. amt additive	t. catalyst e n-C <sub>6</sub> H <sub>13</sub>	<sub>3</sub> H
		solvent / H <sub>2</sub> O = reflux, 3	=10 / 1 H h	H PPh <sub>2</sub> O 2a
Entry	Catalyst	Additive	Solvent <sup>f)</sup>	Yield <sup>a)</sup> /%
1	[RhCl(cod)] <sub>2</sub>	None	1,4-Dioxane	84 (73)
2	$[Rh(OH)(cod)]_2$	None	1,4-Dioxane	75
3	[RhCl(cod)]2	PPh3 <sup>b)</sup>	1,4-Dioxane	85
4	[RhCl(cod)] <sub>2</sub>	BINAP <sup>c)</sup>	1,4-Dioxane	0
5	[RhCl(cod)] <sub>2</sub>	P(OEt) <sub>3</sub> <sup>b)</sup>	1,4-Dioxane	0
6	$Rh(acac)_3$	None	1,4-Dioxane	0
7	$[IrCl(cod)]_2$	None	1,4-Dioxane	0
8	[RhCl(cod)] <sub>2</sub>	None	Toluene <sup>g)</sup>	0-84
9	[RhCl(cod)] <sub>2</sub>	None	THF	0
10	[RhCl(cod)] <sub>2</sub>	None	CH <sub>3</sub> CN	0
11	[RhCl(cod)]2	None	ClCH <sub>2</sub> CH <sub>2</sub> Cl <sup>g)</sup>	0
12 <sup>d)</sup>	[RhCl(cod)] <sub>2</sub>	None	1,4-Dioxane	0
13 <sup>e)</sup>	[RhCl(cod)]	None	1 4-Dioxane	0-84

a) Based on <sup>31</sup>PNMR with a sufficient first decay period. Isolated yields are in parentheses. b) 2 mol. amt. to Rh. c) 1 mol. amt. to Rh. d) The reaction was performed without  $H_2O$ . e) The reaction was performed with  $H_2O$  (3 mol. amt. to **1a**). f) The reaction is homogeneous unless otherwise noted. g) The reaction proceeded in a two-phase medium.

Table 2. Synthesis of (E)-1-Alkenylphosphine Oxide<sup>a)</sup>

	0.015 mol. amt. [RhCl(cod)]2	R H
R-C=C-PPn <sub>2</sub> 1	1,4-Dioxane / H <sub>2</sub> O =10 / 1 reflux	H PPh <sub>2</sub> O
		2
R	Yield <sup>b)</sup> /%	Time/h
Ph (1b)	72	6
<i>i</i> -Pr ( <b>1c</b> )	69	8
<i>t</i> -Bu (1d)	0	8
$o-MeOC_6H_4$ (1)	e) 72	21
p-MeOC <sub>6</sub> H <sub>4</sub> (1	<b>f</b> ) 75	7
<i>p</i> -AcC <sub>6</sub> H <sub>4</sub> ( <b>1g</b>	) 62	5
2-Pyridyl (1h)	0	12
PhCH(OH) (1i	) 0	12

a) Reaction conditions: **1** (0.50 mmol), [RhCl(cod)]<sub>2</sub> (0.0075 mmol), 1,4-dioxane (3 mL), H<sub>2</sub>O (0.30 mL). b) Isolated yields.

reaction proceeded in a toluene/H<sub>2</sub>O mixed solvent, the reaction suffered from poor reproducibility (Entry 8). When toluene was used, the reaction proceeded in a two-phase medium. The erratic amount of water in the nonpolar organic phase would be responsible for the poor reproducibility. When THF or acetonitrile was used instead of 1,4-dioxane, the reaction did not proceed, albeit the reaction is homogeneous (Entries 9 and 10). The reaction in a 1,2-dichloroethane/H<sub>2</sub>O biphasic medium failed, probably because of the highly hydrophobic nature of 1,2-dichloroethane (Entry 11). The use of 1,4-dioxane without H<sub>2</sub>O resulted in complete recovery of **1a** (Entry 12). When the amount of H<sub>2</sub>O was reduced to three molar amounts to the alkynylphosphine, poor reproducibility was observed (Entry 13). The amount of water in the organic phase is the key for reproducibility.

The scope of 1-alkynylphosphines was investigated (Table 2). Although a bulky *t*-butyl group of **1d** completely suppressed the reaction,<sup>3</sup> phenyl- and isopropyl-substituted alkynylphosphines **1b** and **1c** underwent the reaction. The reactions of methoxyphenyl-substituted **1e** and **1f** and *p*-acetylphenyl-substituted **1g** proceeded smoothly. However, neither pyridine-containing **1h**, hydroxy group-containing **1i**, nor 1-octynyldicyclohexylphosphine reacted.

To reveal the mechanism of this reaction, we carried out the following two experiments. First,  $D_2O$  was used instead of  $H_2O$ . As a result, a product deuterated at the two alkenyl positions was obtained as the sole product (eq 1). From a mechanistic point of view, it is worth noting that the reaction in 1,4dioxane/ $D_2O$  was slow (vide infra). Next, a mixture of **1f** and **1j** was exposed to the reaction conditions. In this case, four 1-alkenylphosphine oxides were obtained in almost equal amounts (eq 2). This result suggests that cleavage of the  $C_{sp}$ -P bonds of 1-alkynylphosphines would occur.





Based on these results, we assume that the reaction mechanism is as follows (Scheme 1). This reaction seems to consist of two steps. In the first step, C-P bond cleavage proceeds. Oxidative addition of 1-alkynylphosphine to a Rh<sup>I</sup> complex occurs to yield 4. The oxidative addition would be reversible because no reaction took place in the absence of water (vide supra). Protonation with H<sub>2</sub>O followed by reductive elimination provides 1-alkyne 5 and diphenylphosphine oxide. In the second step, rhodium-catalyzed hydrophosphinylation of 1-alkyne with diphenylphosphine oxide proceeds to yield 1alkenylphosphine oxide. Oxidative addition of diphenylphosphine oxide occurs to afford 7. Hydrorhodation of alkyne 5 followed by reductive elimination provides the product 2. Such a rhodium-catalyzed hydrophosphinylation reaction has been reported.<sup>4</sup> Actually, treatment of 1-octyne with diphenylphosphine oxide under the reaction conditions provided (E)-1-octenyldiphenylphosphine oxide in high yield (eq 3). This result supports the proposed mechanism. During the reaction, accumulation of neither diphenylphosphine oxide, 1-alkyne, nor rhodium hydride 7 was observed. Therefore, oxidative addition of diphenylphosphine oxide to a Rh<sup>I</sup> complex is not rate-determining. The protonolysis of 4 would be the rate-determining step, since the use of  $D_2O$  retarded the reaction (eq 1).





Scheme 1. Plausible reaction mechanism.

#### Conclusion

We have found a reaction for the synthesis of (E)-1-alkenylphosphine oxides from 1-alkynylphosphines. The reaction is an interesting formal hydration reaction that involves carbon– phosphorus bond cleavage with a rhodium complex. Transition metal-mediated carbon–phosphorus bond cleavage has been an attractive topic in organometallic chemistry.<sup>5,6</sup> The present reaction gives new information on the reactivity of 1-alkynylphosphine under rhodium catalysis.

#### Experimental

 $^{1}$ H NMR (500 MHz) and  $^{13}$ C NMR (125.7 MHz) General. spectra were taken on a Varian UNITY INOVA 500 spectrometer and were obtained in CDCl3 or C6D6 with tetramethylsilane as an internal standard. <sup>31</sup>PNMR (121.5 MHz) spectra were taken on a Varian GEMINI 300 spectrometer and were obtained in  $CDCl_3$  or  $C_6D_6$  with 85%  $H_3PO_4$  solution as an external standard. NMR yields were determined by fine <sup>31</sup>PNMR spectra with (MeO)<sub>3</sub>P=O as an internal standard. The first delay of <sup>31</sup>P NMR measurements was set for 15 s to make integrals for signals accurate. IR spectra were taken on a SHIMADZU FTIR-8200PC spectrometer. Mass spectra were determined on a JEOL Mstation 700 spectrometer. TLC analyses were performed on commercial glass plates bearing 0.25-mm layer of Merck Silica gel 60F<sub>254</sub>. Silica gel (Wakogel 200 mesh) was used for column chromatography. Elemental analyses were carried out at the Elemental Analysis Center of Kyoto University.

Materials obtained from commercial suppliers were used without further purification. 1-Alkynylphosphines were prepared according to the literature.<sup>1a</sup>

Typical Procedure for Rhodium-Catalyzed Reaction to Yield (*E*)-1-Alkenylphosphine Oxides. Synthesis of 2a is representative. [RhCl(cod)]<sub>2</sub> (3.7 mg, 0.0075 mmol) was placed in a 20-mL reaction flask under argon. 1,4-Dioxane (3.0 mL), H<sub>2</sub>O (0.30 mL), and 1-octynyldiphenylphosphine (1a, 0.15 g, 0.50 mmol) were sequentially added. The resulting solution was stirred for 4 h at reflux. After the mixture was cooled to room temperature, water (10 mL) was added, and the product was extracted with dichloromethane ( $10 \text{ mL} \times 3$ ). The combined organic layer was dried over anhydrous sodium sulfate and concentrated under re-

duced pressure. Chromatographic purification on silica gel yielded **2a** (0.11 g, 0.37 mmol, 73%) as a white solid.

**Characterization Data.** Phosphines **1a**,<sup>7</sup> **1b**,<sup>7</sup> **1c**,<sup>1a</sup> **1d**,<sup>8</sup> **1e**,<sup>1c</sup> **1f**,<sup>9</sup> **1g**,<sup>1a</sup> **1h**,<sup>10</sup> and **1i**,<sup>1a</sup> and phosphine oxides **2a**,<sup>11</sup> **2b**,<sup>11</sup> **2c**,<sup>12</sup> and **2f**<sup>13</sup> showed the same spectroscopic data as those described in the literature.

**Bis(4-methylphenyl)-1-octynylphosphine (1j):** IR (neat) 3015, 2928, 2853, 2178, 1905, 1598, 1496, 1456, 1395, 1184, 1094, 1019, 803, 624 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 0.91 (t, *J* = 7.0 Hz, 3H), 1.27–1.37 (m, 4H), 1.46 (dd, *J* = 7.5, 7.5 Hz, 2H), 1.61 (dd, *J* = 7.5, 7.5 Hz, 2H), 2.33 (s, 6H), 2.43 (dt, *J* = 1.5, 7.5 Hz, 2H), 7.13–7.17 (m, 4H), 7.47–7.53 (m, 4H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 14.30, 20.64, 21.53, 22.81, 28.53, 28.55, 31.29, 76.23 (d, *J* = 1.6 Hz), 109.94 (d, *J* = 3.9 Hz), 129.24 (d, *J* = 7.6 Hz), 132.36 (d, *J* = 21.0 Hz), 133.84 (d, *J* = 4.9 Hz), 138.68; <sup>31</sup>P NMR (CDCl<sub>3</sub>) δ –36.38. Found: C, 82.18; H, 8.62%. Calcd for C<sub>22</sub>H<sub>27</sub>P: C, 81.95; H, 8.44%.

(*E*)-1-Diphenylphosphinyl-2-(2-methoxyphenyl)ethene (2e): IR (nujol) 2923, 2853, 1598, 1484, 1461, 1247, 1181, 1004, 821, 744, 665 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  3.82 (s, 3H), 6.90 (d, *J* = 8.5 Hz, 1H), 6.94 (dd, *J* = 18.0, 24.0 Hz, 1H), 6.95 (dd, *J* = 8.5, 8.5 Hz, 1H), 7.33 (dd, *J* = 8.5, 8.5 Hz, 1H), 7.44–7.55 (m, 7H), 7.73– 7.83 (m, 5H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  55.41, 111.16, 119.69 (d, *J* = 104.1 Hz), 120.57, 124.12 (d, *J* = 17.1 Hz), 128.49 (d, *J* = 11.9 Hz), 128.76 (d, *J* = 1.0 Hz), 131.20, 131.43 (d, *J* = 10.0 Hz), 131.65 (d, *J* = 2.4 Hz), 133.35 (d, *J* = 104.5 Hz), 143.00 (d, *J* = 4.9 Hz), 158.08; <sup>31</sup>P NMR (CDCl<sub>3</sub>)  $\delta$  23.09. Found: C, 75.11; H, 5.62%. Calcd for C<sub>21</sub>H<sub>19</sub>O<sub>2</sub>P: C, 75.44; H, 5.73%. Mp: 150.5– 152.0 °C.

**4-**[*(E*)-2-(**Diphenylphosphinyl**)ethenyl]acetophenone (2g): IR (nujol) 2924, 2853, 1678, 1603, 1438, 1359, 1270, 1182, 1107, 1000, 806, 746, 728, 665 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 2.59 (s, 3H), 6.97 (dd, J = 17.5, 22.0 Hz, 1H), 7.44–7.57 (m, 7H), 7.60 (d, J = 8.0 Hz, 2H), 7.70–7.79 (m, 4H), 7.95 (d, J = 8.0 Hz, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 26.63, 122.45 (d, J = 101.8 Hz), 127.83, 128.66 (d, J = 11.9 Hz), 128.79, 131.29 (d, J = 10.0 Hz), 132.01 (d, J = 2.5 Hz), 132.47 (d, J = 105.9 Hz), 137.80, 139.24 (d, J = 17.6 Hz), 145.93 (d, J = 3.4 Hz), 197.26; <sup>31</sup>P NMR (CDCl<sub>3</sub>) δ 22.00. Found: C, 76.23; H, 5.54%. Calcd for C<sub>22</sub>H<sub>19</sub>O<sub>2</sub>P: C, 76.29; H, 5.53%. Mp: 176.0–177.5 °C.

(*E*)-1-Bis(4-methylphenyl)phosphinyl-1-octene (2j): IR (neat) 2927, 2856, 1629, 1603, 1453, 1400, 1182, 1118, 1101, 807,

656 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 0.85 (t, J = 7.0 Hz, 3H), 1.21–1.34 (m, 6H), 1.45 (tt, J = 7.0, 7.5 Hz, 2H), 2.26 (dt, J = 6.5, 7.5 Hz, 2H), 2.36 (s, 6H), 6.17 (dd, J = 17.0, 24.0 Hz, 1H), 6.66 (ddt, J = 17.0, 19.5, 6.5 Hz, 1H), 7.21–7.26 (m, 4H), 7.51–7.59 (m, 4H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 13.95, 21.48 (d, J = 1.0 Hz), 22.46, 27.80 (d, J = 1.0 Hz), 28.73, 31.47, 34.40 (d, J = 16.8 Hz), 122.00 (d, J = 102.6 Hz), 129.11 (d, J = 12.5 Hz), 130.05 (d, J = 106.4 Hz), 131.24 (d, J = 10.5 Hz), 141.92 (d, J = 2.9 Hz), 152.24 (d, J = 1.4 Hz); <sup>31</sup>P NMR (CDCl<sub>3</sub>) δ 22.02. HRMS (EI<sup>+</sup>) (m/z) Observed: 340.1954 ( $\Delta = -0.7$  ppm). Calcd for C<sub>22</sub>H<sub>29</sub>OP [M<sup>+</sup>]: 340.1956.

(*E*)-1,2-Dideuterio-1-diphenylphosphinyl-1-octene (2a-D): IR (nujol) 2923, 2854, 1593, 1546, 1438, 1180, 1120, 722, 665 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.86 (t, J = 7.0 Hz, 3H), 1.20–1.36 (m, 6H), 1.46 (tt, J = 7.5, 7.5 Hz, 2H), 2.27 (dt, J = 2.0, 7.5 Hz, 2H), 7.40–7.53 (m, 6H), 7.64–7.71 (m, 4H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ 13.96, 22.48, 27.76, 28.74, 31.48, 34.27 (d, J = 16.3 Hz), 121.09 (dt, J = 101.3, 24.8 Hz), 128.42 (d, J = 12.0 Hz), 131.23 (d, J = 10.0 Hz), 131.58 (d, J = 2.9 Hz), 133.22 (d, J = 104.5 Hz), 152.46 (t, J = 23.4 Hz); <sup>31</sup>P NMR (CDCl<sub>3</sub>)  $\delta$  21.78. <sup>2</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  6.20, 6.73. HRMS (EI<sup>+</sup>) (m/z) Observed: 314.1767 ( $\Delta$  = -0.4 ppm). Calcd for C<sub>20</sub>H<sub>23</sub>D<sub>2</sub>OP [M<sup>+</sup>]: 314.1769. Mp: 58.0–60.0 °C.

(*E*)-2-Bis(4-methylphenyl)phosphinyl-1-(4-methoxyphenyl)ethene (2k): IR (nujol) 2924, 2855, 1602, 1511, 1464, 1438, 1378, 1307, 1257, 1176, 1100, 1020, 1002, 823, 756 cm<sup>-1</sup>; <sup>1</sup>HNMR (CDCl<sub>3</sub>)  $\delta$  2.39 (s, 6H), 2.82 (s, 3H), 6.64 (dd, J =17.5, 22.0 Hz, 1H), 6.88 (d, J = 8.5 Hz, 2H), 7.23–7.31 (m, 4H), 7.39 (dd, J = 17.5, 19.5 Hz, 1H), 7.46 (d, J = 8.5 Hz, 2H), 7.59– 7.67 (m, 4H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  21.53 (d, J = 1.0 Hz), 55.31, 114.13, 116.78 (d, J = 105.9 Hz), 128.06 (d, J = 18.1 Hz), 129.21 (d, J = 12.4 Hz), 129.14, 130.10 (d, J = 107.4 Hz), 131.36 (d, J = 10.5 Hz), 142.06 (d, J = 2.4 Hz), 146.51 (d, J = 3.8 Hz), 161.01; <sup>31</sup>P NMR (CDCl<sub>3</sub>)  $\delta$  23.19. HRMS (EI<sup>+</sup>) (m/z) Observed: 362.1433 ( $\Delta = -0.8$  ppm). Calcd for C<sub>23</sub>H<sub>23</sub>O<sub>2</sub>P [M<sup>+</sup>]: 362.1436. Mp: 148.0–149.5 °C.

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#### References

1 a) A. Kondoh, H. Yorimitsu, K. Oshima, J. Am. Chem. Soc.

2007, 129, 4099. b) A. Kondoh, H. Yorimitsu, K. Oshima, Org. Lett. 2007, 9, 1383. c) S. Kanemura, A. Kondoh, H. Yorimitsu, K. Oshima, Org. Lett. 2007, 9, 2031. d) A. Kondoh, H. Yorimitsu, K. Oshima, J. Am. Chem. Soc. 2007, 129, 6996.

2 1-Alkenylphosphine oxides are useful in organic chemistry: M. Niu, H. Fu, Y. Jiang, Y. Zhao, *Chem. Commun.* **2007**, 272, and references cited therein.

3 The *t*-butyl group would retard the oxidative addition (Scheme 1). Treatment of *t*-butylacetylene with diphenylphosphine oxide under conditions similar to those in eq 3 led to smooth hydrophosphinylation.

4 L.-B. Han, C.-Q. Zhao, M. Tanaka, J. Org. Chem. 2001, 66, 5929.

5 a) P. E. Garrou, *Chem. Rev.* **1985**, 85, 171. b) J. V. Ortiz, Z. Havlas, R. Hoffmann, *Helv. Chim. Acta* **1984**, 67, 1. c) S. A. Macgregor, *Chem. Soc. Rev.* **2007**, *36*, 67. d) A. W. Parkins, *Coord. Chem. Rev.* **2006**, 250, 449.

6 a) A. Inoue, H. Shinokubo, K. Oshima, J. Am. Chem. Soc. 2003, 125, 1484. b) L. K. Hwang, Y. Na, J. Lee, Y. Do, S. Chang, Angew. Chem., Int. Ed. 2005, 44, 6166. c) M. Sakamoto, I. Shimizu, A. Yamamoto, Chem. Lett. 1995, 1101. d) B. E. Segelstein, T. W. Butler, B. L. Chenard, J. Org. Chem. 1995, 60, 12. e) D. K. Morita, J. K. Stille, J. R. Norton, J. Am. Chem. Soc. 1995, 117, 8576. f) F. E. Goodson, T. I. Wallow, B. M. Novak, J. Am. Chem. Soc. 1997, 119, 12441. g) H. Nakazawa, Y. Matsuoka, Y. Nakagawa, K. Miyoshi, Organometallics 1992, 11, 1385.

7 P. Bharathi, M. Periasamy, Organometallics 2000, 19, 5511.

8 F.-E. Hong, Y.-C. Lai, Y.-J. Ho, Y.-C. Chang, J. Organomet. Chem. 2003, 688, 161.

9 M. Bernechea, N. Lugan, B. Gil, E. Lalinde, G. Lavigne, *Organometallics* **2006**, *25*, 684.

10 V. V. Afanasiev, I. P. Beletskaya, M. A. Kazankova, I. V. Efimova, M. U. Antipin, *Synthesis* **2003**, 2835.

11 L.-B. Han, N. Choi, M. Tanaka, *Organometallics* **1996**, *15*, 3259.

12 P. Mauleón, A. A. Núñez, I. Alonso, J. C. Carretero, *Chem. Eur. J.* **2003**, *9*, 1511.

13 N. Vinokurov, A. Michrowska, A. Szmigielska, Z. Drzazga, G. Wójciuk, O. M. Demchuk, K. Grela, K. M. Pietrusiewicz, H. Butenschön, *Adv. Synth. Catal.* **2006**, *348*, 931.