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The first enzymatic desymmetrizations of prochiral phosphine oxides

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Abstract—Prochiral bis(methoxycarbonylmethyl)phenylphosphine oxide was subjected to PLE-mediated hydrolysis to give a chiral monoacetate in 92% yield and 72% e.e. In turn, prochiral bis(hydroxymethyl)phenylphosphine oxide was desymmetrized, using either a lipase-catalyzed acetylation or hydrolysis of the corresponding diacetyl derivative, to give a chiral monoacetate in the yield up to 76% and with e.e.s up to 79%. Absolute configurations of the products were determined by means of chemical correlation.

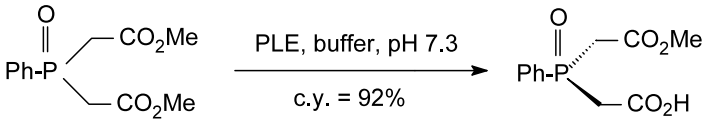
1. Introduction

Chemoenzymatic methodologies have recently become powerful tools for the synthesis of chiral, nonracemic compounds.[1] Of several enzymes used for such purposes, hydrolases are of particular importance, since most of them combine a high reaction stereoselectivity with a broad substrate tolerance.[2] Thus, it has recently been shown that commercially available hydrolases (esterases, lipases, proteases) are also capable of recognizing heteroatom stereogenic centres which makes them useful in the synthesis of chiral heteroorganic compounds.[3] As a result of our own studies on the use of hydrolytic enzymes in the synthesis of chiral phosphorus compounds, we have so far reported the kinetic resolution of racemic, P-stereogenic phosphinylacetates,[4] phosphonyl- and phosphorylacetates,[5] hydroxymethanephosphinates, -phosphonates,[6,7] and phosphine oxides, including using ionic liquids as solvents.[8] In connection with our ongoing work focused on a search for new P-stereogenic phosphorus-containing catalysts for asymmetric synthesis, we have become interested in the preparation of certain new types of optically active, functionalized organophosphorus derivatives. Herein we disclose the details of our investigations on the enzymatic asymmetric synthesis of nonracemic P-stereogenic phosphine oxides **2** and **5**, starting from the appropriate prochiral substrates: bis(methoxy-carbonylmethyl)phenylphosphine oxide **1** and bis(hydroxymethyl)phenylphosphine oxide **4** or its diacetyl derivative **6**.[9] It should be stressed that such an approach has never been used for the preparation of optically active phosphorus derivatives, although there were precedents created by the desymmetrization of other prochiral heteroatom substrates, viz. sulfinyldicarboxylates,[10] bis(hydroxymethyl)silanes[11] and bis(hydroxymethyl)germanes.[12]

2. Results and discussion

2.1. Desymmetrization of bis(methoxycarbonylmethyl)-phenylphosphine oxide 1

Bis(methoxycarbonylmethyl)phenylphosphine oxide **1**, which was synthesized according to the procedure pre-



1

(*R*)-(+)-**2**, $[\alpha]_D$ = +3.9 (MeOH)

ee = 72%

(1)

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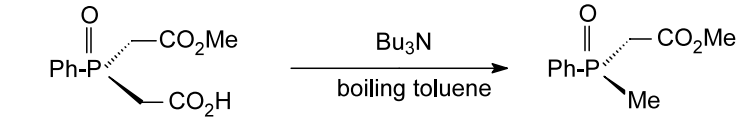
viously described by us,[13] was subjected to hydrolysis in a phosphate buffer in the presence of several hydrolases, of which only pig liver esterase (PLE) proved to be efficient. The expected product, viz. the monoacetate **2** was isolated after acidification and purification by column chromatography in 92% yield and 72% e.e. (Eq. (1)).

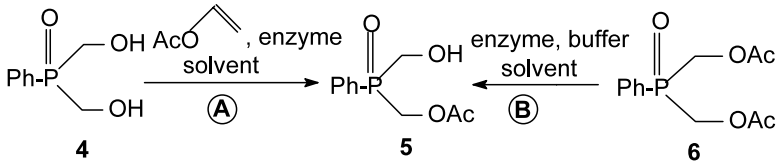
The absolute configuration of the product was easily determined by a simple chemical correlation shown in Eq. (2).



(2)

(*R*)-(+)-**2**, $[\alpha]_D$ = +3.9 (MeOH)
ee = 72%

(*R*)-(+)-**3**, $[\alpha]_D$ = +17 (MeOH)
ee = 65 %



(3)

When the monoacetate (+)-**2** was refluxed in toluene, decarboxylation took place to give the phosphine oxide (+)-**3** whose absolute configuration was known from the literature to be (*R*).[4] As the transformation did not involve the phosphorus stereogenic centre, its absolute configuration was not changed; hence (+)-**2** has the (*R*) configuration.

Having established the stereoselectivity of the above reaction, we decided to check whether the Jones model of the PLE active site[14] is also applicable to prochiral phosphoryl substrates as it is for a prochiral sulfinyl analog[10b] as well as for racemic phosphoryl derivatives.[4,5] Thus, according to this model the diacetate **1** should be located in the PLE active site as follows (Fig. 1). The ester group which undergoes hydrolysis should be placed in the neighbourhood of serine, the second ester group in the front polar pocket (P_F), the phosphoryl oxygen atom in the back polar pocket (P_B) and finally the large organic substituent (phenyl) in the large hydrophobic pocket (H_L). This mode of location clearly shows that the (*R*) enantiomer of **1** should be produced, which is in agreement with the experiment and establishes the applicability of the Jones model also to these types of substrates.

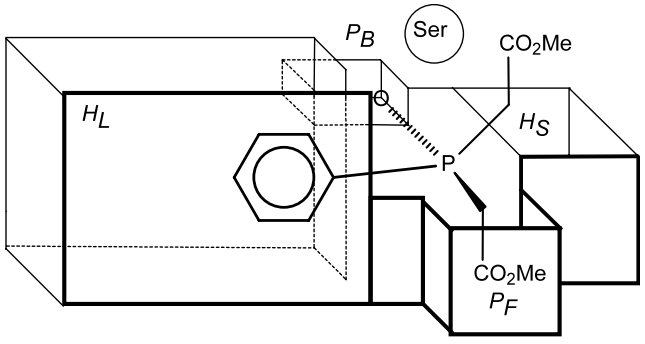


Figure 1. Preferred binding orientation of **1** in the active site of PLE.

2.2. Desymmetrization of bis(hydroxymethyl)phenyl phosphine oxide 4 and bis(acetoxymethyl)phenylphosphine oxide 6

The phosphine oxide **4** was synthesized according to literature procedures,[15,16] and the diacetyl derivative **6** was obtained by acetylation of **4** with acetic anhydride in the presence of $Yb(OTf)_3$.[17] Two procedures were used to obtain the desired optically active (acetoxymethyl)(hydroxymethyl)phenylphosphine oxide **5**: a lipase-catalyzed acetylation of the prochiral substrate **4** (**A**) and a reverse reaction i.e. lipase-catalyzed hydrolysis of the corresponding prochiral diacetyl derivative **6** (**B**) (Eq. (3)).

In the latter case the reaction was always performed in an organic solvent saturated with a phosphate buffer (pH 7.2). Several lipases proved to be suitable for these transformations and gave **5** in reasonable yields and with moderate to good ee. The results are summarized in Table 1. It should be noted that the application of the two reverse procedures enabled us to obtain both enantiomerically enriched forms of **5**. This is due to a common feature of enzymes which exhibit the same sense of stereoselectivity towards substrates, irrespective of the direction of the reversible reaction they catalyze (e.g. ester formation versus ester hydrolysis). Considering the influence of solvents and certain additives on the yield and stereoselectivity of the reaction, no particular regularity could be seen. Thus, application of ionic liquids instead of common organic solvents did not exert a profound influence on the reaction, which was in contrast to the kinetic resolution of racemic hydroxymethanephosphonates where the stereoselectivity was markedly enhanced.[8]

Moreover, the yields of the product were usually lower, most probably due to some difficulties in its isolation from the highly polar medium. In turn, amines were added with the hope of increasing enantioselectivity of the lipase-mediated transformations.[18] However, the effect was generally opposite to expectations. The addi-

Table 1. Enzymatic desymmetrization of **4** and **6**

Enzyme/solvent	Method	Monoacetate **5**			
		Yield (%)	$[\alpha]_D$ ($CHCl_3$)	E.e. (%)	Abs. conf.
PFL/$CHCl_3$	**A**	50	+3.9	79	*R*
PFL/DPE[a]	**B**	50	−3.4	68	*S*
PFL/DPE[a,b]	**B**	40	−1.8	37	*S*
PS/THF[b]	**A**	57	+1.8	37	*R*
PS/THF/Et_3N	**A**	30	0	0	
AHS/DPE[a]	**B**	40	−2.4	50	*S*
AK/$CHCl_3$	**A**	76	+0.7	15	*R*
AK/THF	**A**	40	+2.6	53	*R*
PFL/BMIM·PF_6	**A**	35	+0.6	14	*R*
PFL/BMIM·PF_6[b]	**A**	60	+1.1	22	*R*
PFL/BMIM·PF_6[a]	**B**	18	−3.3	65	*S*
PFL/BMIM·PF_6[a,b]	**B**	25	−1.0	20	*S*

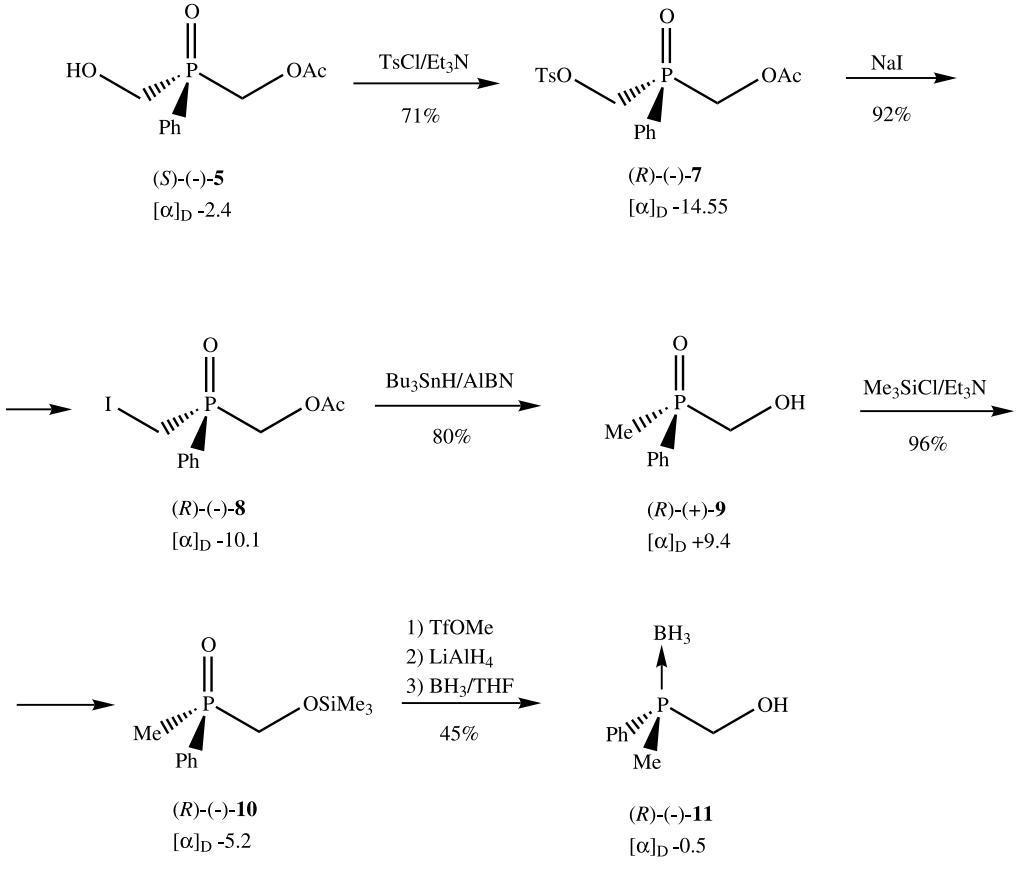
Enzymes: PFL: lipase from *Pseudomonas flourescens*; AHS: lipase AHS (AMANO); AK: lipase AK (AMANO); PS: lipase PS (AMANO).
Solvents: DPE: diisopropyl ether; BMIM·PF_6-ionic liquid: 1-butyl-3-methylimidazolium hexafluorophosphate.[8]

[a] The solvent saturated with a phosphate buffer.

[b] Pyridine added.

tion of triethylamine resulted in a complete loss of stereoselectivity, with a concomitant decrease of the yield (due to the preferential formation of the product of exhaustive acetylation). The addition of pyridine, on the one hand decreased the enantioselectivity of the reaction performed in organic solvents, on the other hand slightly improved the result of the hydrolysis carried out in the ionic liquid.

To establish the absolute configuration of **5**, the chemical correlation shown in Scheme 1 was carried out. Thus, (−)-**5** was transformed into the tosyl derivative



Scheme 1.

(−)-**7** and then into the iodomethylphosphine oxide (−)-**8**. The latter was reduced using the conditions developed by Bałczewski[19] to give the corresponding hydroxymethylphosphine oxide (+)-**9**. So far, none of the transformations involved the phosphorus stereogenic center nor did the silylation procedure leading to (−)-**10**, which was performed to protect the hydroxy group during the ensuing transformations. Thus, (−)-**10** was subjected to an O-alkylation followed by a reduction with $LiAlH_4$ and a quench with borane. This reaction was carried out according to a procedure described by Imamoto et al.[20] who proved that it proceeds with inversion of configuration at phosphorus. The levorotatory adduct **11**, whose absolute configuration is known to be (*R*),[21] was obtained by us, however, with a fairly low enantiomeric excess equal to 7%. This is in contrast to very high stereoselectivities of this reaction found for alkylarylmethylphosphine oxides.[20] Nevertheless, knowing the absolute configuration of the final product of the chemical correlation, (*R*)-(−)-**11**, and assuming the inversion of configuration at phosphorus in the last step, we were able to assign the absolute configurations to all the intermediary compounds and ultimately to the monoacetate **5**, which is (*S*)-(−) (Scheme 1).

3. Experimental

3.1. General

The enzymes were purchased from AMANO or FLUKA. NMR spectra were recorded on Bruker instruments at 200 MHz for ^1H and 81 MHz for ^{31}P, with C_6D_6 or $CDCl_3$ as solvents. The enantiomeric excess (e.e.) values of all the products were determined by ^1H NMR, using (−)-(*S*) or (+)-(*R*)-*t*-butylphenylphosphinothioic acid as a chiral solvating agent.[22] Optical rotations were measured on a Perkin–Elmer 241 MC photopolarimeter. Column chromatography was carried out using Merck 60 silica gel. TLC was performed on Merck 60 F_{254} silica gel plates.

3.2. Synthesis of bis(acetoxymethyl)phenylphosphine oxide 6

Bis(hydroxymethyl)phenylphosphine oxide **4** (2 g, 10.7 mmol) was dissolved in hot dichloromethane (100 mL) and ytterbium triflate, $Yb(OTf)_3$ (0.66 g, 1.07 mmol) was added followed by acetic anhydride (3.28 g, 32.2 mmol). The resulting suspension was stirred overnight at room temperature and the conversion was followed by TLC (acetone:petroleum ether, 2:1). When the reaction was completed, the dichloromethane solution was washed with diluted sodium bicarbonate, dried over magnesium sulfate and, after evaporation, purified by column chromatography using acetone:petroleum ether (2:1) as eluent. Yield: 2.5 g (86%). ^{31}P NMR ($CDCl_3$): $\delta = 29.24$. ^1H NMR ($CDCl_3$): $\delta = 2.11$ (s, 6H), 4.60–4.70 (2×AB, 4H), 7.5–7.9 (m, 5H). ^{13}C NMR ($CDCl_3$): $\delta = 20.10$, 58.78 (d, $J = 83.25$), 125.69, 128.63, 128.86, 130.71, 130.84, 133.08, 169.58 (d, $J = 7.0$). MS (EI): m/z 271 (M+H). HRMS calcd for $C_{12}H_{16}PO_5$ (M+H), 271.0737; found 271.0735.

3.3. Enzymatic desymmetrization of bis(methoxycarbonylmethyl)phosphine oxide 1

To a stirred solution of **1** (100 mg, 0.37 mmol) in a phosphate buffer (pH 7.2, 11 mL) pig liver esterase, PLE (45 μL) was added and the mixture was stirred at 30°C. The pH was maintained by a continuous addition of 0.2 M aqueous NaOH using an automatic titrator. When the appropriate amount of NaOH·aq (1.85 mL) was dropped in (after ca. 5 days), the reaction solution was acidified with diluted sulfuric acid to pH 2.1. Then methanol was added (100 mL) and, after 0.5 h, the resulted cloudy solution was filtered through Celite. The filtrate was evaporated and the residue was purified by column chromatography, using chloroform–methanol (2:1) as solvent, to give **2** (87 mg, 92%), $[\alpha]_D^{20} = +3.9$ (*c* 1.1, MeOH), e.e. = 72%. ^{31}P NMR ($CDCl_3$): $\delta = 34.66$. ^1H NMR ($CDCl_3$): $\delta = 3.58$ (s, 3H), 3.25–3.75 (m, 4H), 7.31–7.81 (m, 5H), 10.38 (s, 1H). ^{13}C NMR ($CDCl_3$): $\delta = 36.96$ (d, $J = 32.6$), 38.23 (d, $J = 33.3$), 52.33, 128.5, 128.77, 130.42, 130.6, 130.84, 132.6, 166.64 (d, $J = 3.6$), 169.34.

3.4. Enzymatic acetylation of bis(hydroxymethyl)phenylphosphine oxide 4—general procedure

A mixture of **4** (1 mmol), a lipase (10–20 mg) and vinyl acetate (1 mL) in an appropriate solvent (10 mL) was stirred at room temperature. In some cases a few drops of an amine were added (see Table 1). As the substrate **4** was hardly soluble in any organic solvent, the reaction mixture was at the beginning usually cloudy and became more clear when the reaction proceeded (a suspension of the enzyme remained). The reaction was monitored by ^{31}P NMR and stopped at the optimal conversion: usually, in addition to the expected monoacetyl product **5**, the bisacetyl derivative **6** was also formed. The average reaction time exceeded 10 days. The enzyme was filtered off and the solvent was removed under vacuum. The residue was purified by preparative TLC (acetone:hexane, 2:1) to give optically active **5**. ^{31}P NMR ($CDCl_3$): $\delta = 33.8$. ^1H NMR ($CDCl_3$): $\delta = 2.1$ (s, 3H), 4.17–4.33 (m, 2H), 4.59–4.79 (2×AB, 2H), 7.51–7.85 (m, 5H). ^{13}C NMR ($CDCl_3$): $\delta = 20.29$, 58.93 (d, $J = 81.0$), 58.50 (d, $J = 80.0$), 126.59, 128.54, 128.77, 130.74, 130.91, 132.68, 170.01 (d, $J = 6.7$). MS (EI): m/z 229 (M+H). HRMS calcd for $C_{10}H_{14}PO_4$ (M+H) 229.0626; found 229.0629.

3.5. Enzymatic hydrolysis of bis(acetoxymethyl)-phenylphosphine oxide 6—general procedure

A mixture of **6** (1 mmol) and a lipase (ca. 10 mg) was stirred in a solvent (10 mL) saturated with a phosphate buffer (pH 7.2). In some cases a few drops of pyridine were added (Table 1). The reaction was monitored by ^{31}P NMR. After completion of the hydrolysis (which usually resulted in the concomitant formation of certain amounts of the bis-hydroxy derivative **4**) magnesium sulfate was added to remove water. The precipitates were filtered off, the solvents were removed under vacuum and the residue was purified by preparative TLC (conditions as above) to give pure **5**.

3.6. Chemical correlation and absolute configuration of 5

3.6.1. Synthesis of (*R*)-(−)-7. To a solution of **5** (60 mg, 0.26 mmol, ($[\alpha]_D = -2.39$, 48% e.e.) in dichloromethane (4 mL) were added tosyl chloride (56 mg, 0.29 mmol) and triethylamine (35 mg, 0.35 mmol) and the mixture was stirred overnight. Then, the solution was washed with water, dried with magnesium sulfate and the solvent was removed under vacuum. The residue was chromatographed on a preparative plate (acetone:hexane, 2:1) to give pure **7** (71 mg, 71%), $[\alpha]_D^{20} = -14.55$ (*c* 1.12, $CHCl_3$). ^{31}P NMR ($CDCl_3$): $\delta = 27.76$. ^1H NMR ($CDCl_3$): $\delta = 2.06$ (s, 3H), 2.42 (s, 3H), 4.63–4.74 (4×AB, 4H), 7.29–7.81 (m, 9H). MS (CI): *m*/*z* 383 (M+H).

3.6.2. Synthesis of (*R*)-(−)-8. A mixture of **7** (70 mg, 0.18 mmol), sodium iodide (110 mg, 0.73 mmol) in acetone (10mL) was stirred at room temperature for 4 days (TLC control: $CHCl_3$–methanol, 15:1). Acetone was removed under vacuum, the residue was dissolved in chloroform and washed with water and an aqueous solution of sodium thiosulfate. The chloroform solution was dried and evaporated to dryness. The crude product was purified by preparative TLC ($CHCl_3$–methanol, 15:1) to give pure **8** (89.5 mg, 92%), $[\alpha]_D^{20} = -10.1$ (*c* 1.39, $CHCl_3$). ^{31}P NMR ($CDCl_3$): $\delta = 29.64$. ^1H NMR ($CDCl_3$): $\delta = 2.13$ (s, 3H), 3.29–3.51 (2×AB, 2H),4.66–4.84 (2×AB, 2H), 7.48–7.85 (m, 5H). MS (CI): *m*/*z* 339 (M+H).

3.6.3. Synthesis of (*R*)-(+)-9. A mixture of **8** (160 mg, 0.473 mmol), AIBN (a few milligrams), and tributyltin hydride, *n*-Bu_3SnH (165 mg, 0.567 mmol) in dry benzene (20 mL) was refluxed for 2 days. After evaporation of the solvent the residue was purified by preparative TLC (acetone). The product was eluted from the silica gel with methanol, which caused removal of the acetyl group. The solvent was evaporated to give pure **9**, 64 mg (80%), $[\alpha]_D^{20} = +9.4$ (*c* 1.33, $CHCl_3$). ^{31}P NMR ($CDCl_3$): $\delta = 37.45$. ^1H NMR ($CDCl_3$): $\delta = 1.79$ (d, $J = 12.88$, 3H), 4.03–4.14 (2×AB, 2H), 4.98 (b. s, 1H), 7.45–7.78 (m, 5H). MS (CI): *m*/*z* 171 (M+H).

3.6.4. Synthesis of (*R*)-(−)-10. A sample of **9** (44 mg, 0.26 mmol) was dissolved in diethyl ether (3 mL) and triethylamine (63 mg, 0.62 mmol) and chlorotrimethylsilane (67.5 mg, 0.62 mmol) were subsequently added. The solution was stirred overnight at room temperature and then the triethylammonium hydrochloride was filtered off. After evaporation of the liquids, crude **10** was obtained (60 mg, 96%) which without further purification was used as a substrate in the next reaction. $[\alpha]_D^{20} = -5.2$ (*c* 1.05, $CHCl_3$). ^{31}P NMR ($CDCl_3$): $\delta = 36.85$. ^1H NMR ($CDCl_3$): $\delta = 0.15$ (s, 9H), 1.77 (d, $= 12.88$, 3H), 3.84–4.07 (m, 2H), 7.43–7.85 (m, Ph). MS (CI): *m*/*z* 243 (M+H).

3.6.5. Synthesis of (*R*)-(−)-11. To a solution of **10** (50.7 mg, 0.21 mmol) in THF (2 mL) methyl triflate (37.8 mg, 0.23 mmol) was added under argon and the mixture was stirred for 2 h at room temperature. Then it was cooled to 0°C, $LiAlH_4$ (20 mg, 0.52 mmol) was added and stirring was continued for the next 5 h. After this time, a BH_3–THF complex (2 M solution in THF, 0.15 mL) was added and the mixture was stirred for 15 min. Water was added and the aqueous layer was extracted with ethyl acetate. The organic layers were dried over $MgSO_4$ and the solvents evaporated under vacuum. The residue was purified by preparative TLC (ethyl acetate:hexane, 1:3) to give pure **11** (15.7 mg, 45%). $[\alpha]_D^{20} = -0.5$ (*c* 1.57, $CHCl_3$). ^{31}P NMR ($CDCl_3$): $\delta = 11.42$. ^1H NMR ($CDCl_3$): $\delta = -0.2$–0.96 (br.q, 3H), 1.65 (d, $J = 10.46$, 3H), 1.85 (br.s, 1H), 4.08 (s, 2H), 7.43–7.80 (m, 5H). MS (CI): *m*/*z* 167 (M−H), 137 (M−CH_2OH). HRMS calcd for $C_8H_{13}BOP$ (M−H) 167.0792; found 167.0798.

Acknowledgements

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