Tetrahedron 66 (2010) 758–764

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Oxaphospholene and oxaphosphinene heterocycles via RCM using unsymmetrical phosphonates or functional phosphinates

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ARTICLE INFO

Article history:
Received 7 September 2009
Received in revised form
6 November 2009
Accepted 10 November 2009
Available online 14 November 2009

ABSTRACT

New phosphorus heterocycles were synthesized using RCM reaction. They were prepared from unsymmetrical or polyfunctional insaturated precursor in 50 to 87% yields solving the problem of possible competitive side reactions. In parallel hydroxyphosphinate scaffolds represent a versatile starting material and could be of great interest for the synthesis of phosphosugar libraries.

1. Introduction

Due to their key roles in cells metabolism and their potential to serve as pharmaceuticals and agricultural agents, phosphorus molecules are popular targets for the development of new biologically active compounds.[1] General methods to synthesize phosphorus heterocycles (P–heterocycles) employing functional group-compatible transition-metal catalyzed processes were a key achievement of the last few years.[2] Among them, the advent of ring-closing metathesis (RCM)[3] as a core synthetic tool has led to numerous advances in the preparation of small phosphorus molecules.[4] However, synthesis of *P*-heterocycles by such way is sometimes clearly impeded by competitive side reactions: So far if diallyl allylphosphonates mainly furnished the more favored six-membered oxaphospholenes, symmetrical diallyl vinylphosphonates led competitively to the formation of both five- and six-membered *P*-heterocycles and were consequently not easily purified.[5] Besides in an interesting piece of work, Hanson synthesized phosphonosugars (cyclic phosphonates) utilizing the RCM reaction. Then, subsequent epoxidation followed by opening of the epoxide resulted in the formation of the oxaphosphinene containing a hydroxyl group which required two more linear steps from the ring formation.[6]

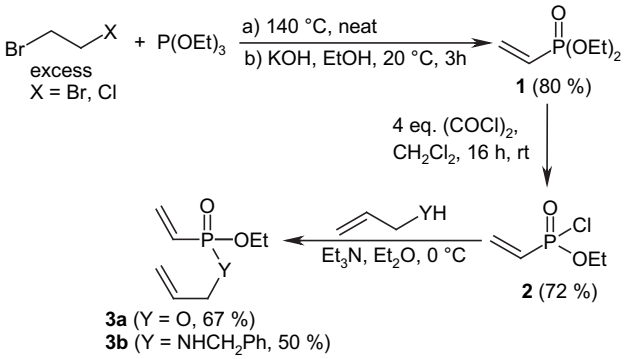
These findings suggest that the search for novel unsymmetrical and/or functional unsaturated phosphorus precursors is highly desirable as illustrated by recently patented anticancer oxaphosphinanes.[7] As part of a program aimed at developing the construction of diverse phosphorus-containing heterocycles as potential fungicides, we herein report the RCM reaction of unsymmetrical phosphonates or functional 1-hydroxyphosphinates with as features the presence of two different functional alkenyl groups directly linked to the phosphorus atom.

2. Results and discussion

2.1. Preparation of unsaturated functional precursors

Vinyl- or allylphosphonochloridates were the key intermediates and they constituted a really affordable unsymmetrical phosphorus reagent.

The synthesis of unsymmetrical allyl vinylphosphonates was performed according to the Scheme 1. Firstly the reaction of triethyl phosphite with 1-bromo-2-chloroethane led to diethyl 2-chloroethylphosphonate which was reacted with alcoholic potassium hydroxide affording diethyl vinylphosphonate **1** in 80% yield. Then, selective monochlorination using oxalyl chloride gave ethyl



Scheme 1. Synthesis of unsymmetrical allyl vinylphosphonates **3a**, **b**.

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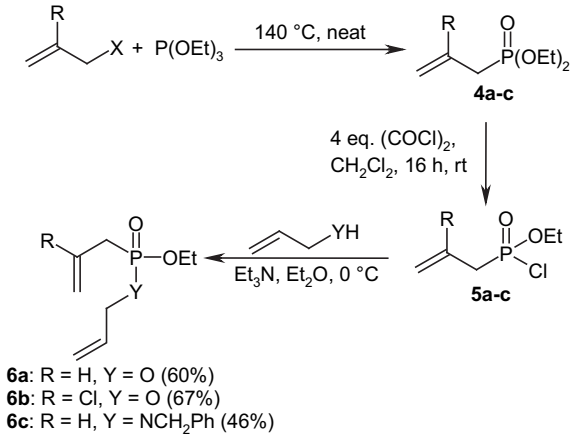
doi:10.1016/j.tet.2009.11.049

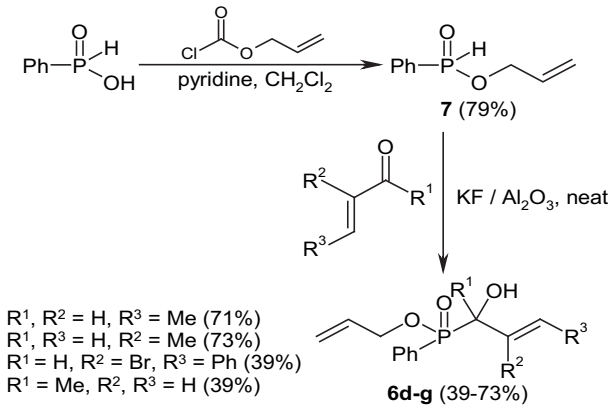
vinylphosphonochloridate **2** in 96% yield. The final step used either allylic alcohol or *N*-allyl-*N*-benzylamine in order to obtain the precursors **3a**, **b,** respectively in 67% and 50% yields.

Allyl allylphosphonates were obtained using a similar approach. The Arbuzov reaction of triethyl phosphite with commercial allyl halides afforded the corresponding allylphosphonates **4a–c** in yields ranging from 58 to 85%. After the quantitative formation of phosphonochloridate **5a–c**, their reactions with allylic alcohols or *N*-allyl-*N*-benzylamine gave precursors **6a–c** in 46–67% yields, Scheme 2.



Scheme 2. Synthesis of unsymmetrical allyl allylphosphonates **6a–c**.

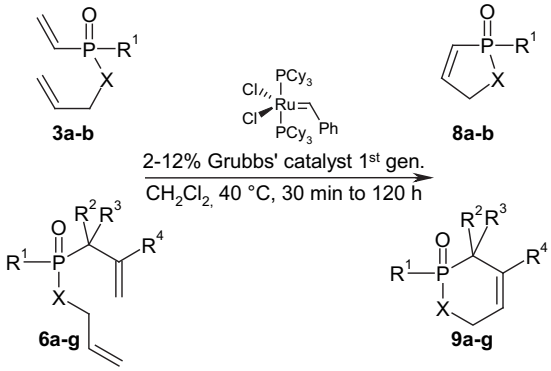
Synthesis of functional allyl allylphosphinates **8a–d** was performed by another way starting from phenylphosphinic acid. The esterification of acid took place using a modified Hewitt reaction in 79% yield.[8] Then, the Pudovik additions of H–phenylphosphinate to α,β-unsaturated ketones or aldehydes, using potassium fluoride as a base, led to the functional α–hydroxyphosphinates **6d–g** in 39–73% yields.[9] No diastereoselectivity was observed during those reactions and the resulting products were obtained with low diastereomeric excess. On the other hand, the competitive Michael addition product was only obtained in 21% yield when methylvinylketone was reacted with **7**. However, it was easily removed after purification by flash chromatography on silica, Scheme 3.



Scheme 3. Synthesis of allyl α-hydroxyallylphosphinates **6d–g**.

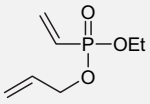
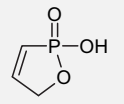
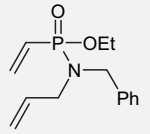
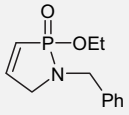
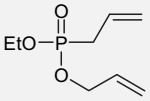
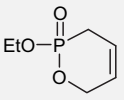
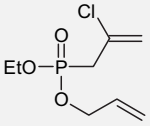
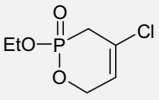
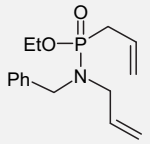
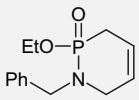
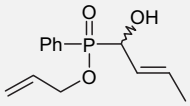
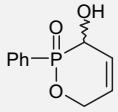
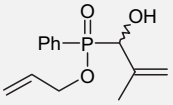
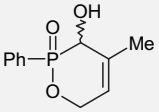
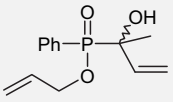
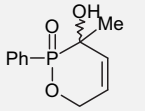
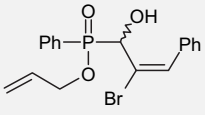
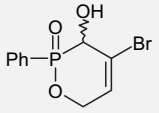
2.2. Ring closure metathesis reactions

The first generation Grubbs' catalyst was used in refluxing dichloromethane to perform the RCM reaction. Scope and limitations were given in Scheme 4 and Table 1. The reaction of alkenylphosphonates or phosphinates was sometimes tricky but the yields were ranging from 50 and up to 87%. When the reaction failed, starting material was recovered after chromatography showing that no reaction and no degradation occurred.



Scheme 4. RCM reaction of unsymmetrical and functional precursors **3a**, **b** or **6a–g**.

Table 1
RCM reaction products from unsymmetrical and hydroxy precursors

	Precursor	Product	% Catalyst	Time	Yield (%)
8a			7	2 h	64
8b			2	30 min	80
9a			5	2 h 30 min	87
9b			10	48 h	0
9c			2.5	30 min	75
9d			7.5	2 h	70
9e			12	76 h	0
9f			10	3 h	50
9g			12	120 h	0

Five membered oxaphospholene ester **8a** was not stable and was readily hydrolyzed by air moisture into its acid form in 64% yield as Machida observed with similar structures.[10] Surprisingly, azaphospholene ester **8b** was quite stable on fast chromatography but it was transformed on storage through a phosphorus–nitrogen bond cleavage.

Substrates having halogen on double bond did not undergo the RCM reaction. This was consistent with the fact that only few examples of ring closure metathesis on vinyl or allyl halide substrates succeeded using the second generation Grubbs' catalyst.[11]

Concerning 3-hydroxyoxaphosphinanes, we were aware that the Lewis basicity of both phosphoryl group and hydroxy group may result in catalyst deactivation.[12] We were pleased to see that functional oxaphosphinanes **9d** and **9f** were obtained, respectively in 70 and 50% as probably the result of a weak and/or reversible chelation. However, reactions failed with substituted precursors **6e** and **6g**. The course of the RCM reaction was monitored by ^{31}P NMR to check the difference of behavior between the two diastereoisomers. Unfortunately, the reaction occurred nearly at the same rate resulting in no possible kinetic resolution. By the way, we managed to separate the diastereomers of **9d** by chromatography.

3. Conclusion

In conclusion, we have demonstrated a new way to synthesize diverse functionalized unsaturated phosphinates and phosphonates solving the problem of possible competitive side reactions. In parallel hydroxyphosphinate scaffolds represent a versatile starting material and could be of great interest for the synthesis of phosphosugar libraries. Perspective work will be devoted to control the chirality on α–hydroxyphosphonate or phosphinate precursors during the RCM[13] or from the Pudovik reaction.[14] These studies are underway and will be reported in due course.

4. Experimental section

4.1. General remarks

All reactions were carried under nitrogen atmosphere using Schlenk techniques. The solvents were dried using standard methods, distilled and stored under nitrogen. Reactions were monitored by ^{31}P NMR using DMSO-d_6 as internal references. Column chromatographies were performed on silica gel (Merck 60 AC.C 35–70 μm).

^{31}P, ^{1}H and ^{13}C NMR spectra were recorded on a BRUKER AVANCE 250 and BRUKER AVANCE 400 spectrometers. MS and HRMS were recorded on a JEOL JMS DX-300 using NBA as matrix in FAB$^+$ ionization mode. IR spectra were measured on a PERKIN-ELMER spectrum 1000.

4.2. Synthesis of unsaturated precursors

*4.2.1. Diethyl vinylphosphonate (**1**).* First step: synthesis of diethyl 2-chloroethylphosphonate. Triethyl phosphite (15.0 g, 90 mmol) and 1-bromo-2-chloroethane (51.8 g, 0.36 mol, 4 equiv) were heated at 140 °C for 24 h. Remaining starting materials were removed under vacuum. The residue was purified by column chromatography (AcOEt 100%) to give a colorless liquid (17.0 g, 94%); ^{31}P NMR (101.25 MHz, $CDCl_3$): δ 26.7. ^{1}H NMR (250.13 MHz, $CDCl_3$): δ 4.05–3.93 (m, 4H, 2POCH_2), 3.78–3.66 (m, 2H, CH_2Cl), 2.25–2.15 (m, 2H, P-CH_2), 1.32 (t, $^{3}J_{HH}$=7.0 Hz, 6H, 2CH_3); ^{13}C NMR (62.90 MHz, $CDCl_3$): δ 61.5 (d, $^{2}J_{PC}$=6.5 Hz, OCH_2), 34.8 (s, CH_2Cl), 29.9 (d, $^{1}J_{PC}$=140.0 Hz, *P*-CH_2), 15.3 (d, $^{3}J_{PC}$=7.0 Hz, CH_3).

Second step: synthesis of diethyl vinylphosphonate (**1**). Diethyl 2-chloroethylphosphonate (10.0 g, 50.0 mmol) was slowly added to a cold solution of potassium hydroxide in ethanol (50 mmol, 75 mL). The reaction mixture was stirred during one hour then heated to reflux for 15 min. The solid was filtered off and washed with ethanol. Ethanol was removed under vacuum and the remaining oil was distilled under vacuum (Bp 93–97 °C/16 Torr). Yield: 6.19 g (85%).

^{31}P NMR (101.25 MHz, $CDCl_3$): δ 17.9; ^{1}H NMR (250.13 MHz, $CDCl_3$): δ 6.31 (ddd, $^{3}J_{HH}$=18.7 Hz, $^{2}J_{HH}$=−1.9 Hz, $^{3}J_{PH}$=25.3 Hz, 1H, =CH_2), 6.14 (ddd, $^{3}J_{HH}$=12.8 Hz, $^{2}J_{HH}$=−1.9 Hz, $^{3}J_{PH}$=51.1 Hz, 1H, =CH_2), 6.07 (ddd, $^{3}J_{HH}$=12.8 Hz, $^{3}J_{HH}$=18.7 Hz, $^{2}J_{PH}$=21.9 Hz, 1H, PC*H*), 4.17–4.02 (m, 4H, 2CH_2), 1.29 (t, $^{3}J_{HH}$=7.6 Hz, 6H, 2CH_3); ^{13}C NMR (62.90 MHz, $CDCl_3$): δ 135.0 (d, $^{2}J_{PC}$=1.9 Hz, CH_2), 126.0 (d, $^{1}J_{PC}$=184.2 Hz, PC*H*), 61.7 (d, $^{2}J_{PC}$=5.6 Hz, OCH_2), 16.2 (s, CH_3).

*4.2.2. Ethyl vinylphosphonochloridate (**2**).* Diethyl vinylphosphonate (6.0 g, 36 mmol) in dry CH_2Cl_2 (100 mL) and oxalyl chloride (18.5 g, 146 mmol, 4.05 equiv) were stirred at room temperature for 24 h and refluxed for 1 h. Solvent and remaining oxalyl chloride were removed under vacuum at room temperature. Residue was purified by distillation (Bp 85 °C/15 Torr). Yield: 4.0 g (72%).

^{31}P NMR (101.25 MHz, DMSO-d_6): δ 26.9; ^{13}C NMR (62.90 MHz, DMSO-d_6): δ 135.6 (s, CH_2), 128.5 (d, $^{1}J_{PC}$=169.3 Hz, *CH*), 62.9 (d, $^{2}J_{PC}$=7.8 Hz, CH_2), 15.1 (d, $^{3}J_{PC}$=7.1 Hz, CH_3).

*4.2.3. Allyl ethyl vinylphosphonate (**3a**).* Ethyl vinylphosphonochloridate **2** (1.68 g, 10.9 mmol) in dry Et_2O (10 mL) was added dropwise to a cold mixture of anhydrous allylic alcohol (1.13 g 19.4 mmol, 1.8 equiv) and triethylamine (2.0 g, 19.8 mmol, 1.8 equiv) in dry Et_2O (40 mL). The mixture was then stirred for 3 h at room temperature. The solid was removed by filtration and washed with Et_2O (3×10 mL). Solvents were removed under vacuum and the residue was purified by column chromatography (AcOEt 100%) Yield: 1.28 g (67%).

^{31}P NMR (81.02 MHz, $CDCl_3$): δ 18.2; ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 6.20 (ddd, $^{3}J_{HH}$=18.2 Hz, $^{2}J_{HH}$=−1.8 Hz, $^{3}J_{PH}$=25.1 Hz, 1H, =CH_2), 6.04 ($^{3}J_{HH}$=12.9 Hz, $^{2}J_{HH}$=−1.8 Hz, $^{3}J_{PH}$=52.7 Hz, 1H, =CH_2), 5.99 (m, $^{3}J_{HH}$=5.8 Hz, $^{3}J_{HH}$=5.6 Hz, $^{3}J_{HH}$=10.4 Hz, $^{3}J_{HH}$=17.2 Hz, 1H, =C*H*), 5.98 ($^{3}J_{HH}$=12.9 Hz, $^{3}J_{HH}$=18.2 Hz, $^{2}J_{PH}$=20.1 Hz, 1H, PC*H*), 5.24 (m, $^{2}J_{HH}$=−1.5 Hz, $^{4}J_{HH}$=1.5 Hz, $^{4}J_{HH}$=1.1 Hz, $^{3}J_{HH}$=17.2 Hz, 1H, CH_2), 5.12 (m, $^{2}J_{HH}$=−1.5 Hz, $^{4}J_{HH}$=1.5 Hz, $^{4}J_{HH}$=1.5 Hz, $^{3}J_{HH}$=10.4 Hz, 1H, CH_2), 4.42 (m, $^{3}J_{PH}$=8.2 Hz, $^{2}J_{HH}$=−23.6 Hz, $^{4}J_{HH}$=1.1 Hz, $^{4}J_{HH}$=1.5 Hz, $^{3}J_{HH}$=5.8 Hz, 1H, OCH_2), 4.38 (m, $^{3}J_{PH}$=8.0 Hz, $^{2}J_{HH}$=−23.6 Hz, $^{4}J_{HH}$=1.1 Hz, $^{4}J_{HH}$=1.5 Hz, $^{3}J_{HH}$=5.6 Hz, 1H, OCH_2), 3.99 (qd, $^{3}J_{HH}$=7.1 Hz, $^{3}J_{PH}$=8.1 Hz, 2H, OCH_2), 1.22 (t, $^{3}J_{HH}$=7.1 Hz, 3H, CH_3); ^{13}C NMR (62.90 MHz, $CDCl_3$): δ 136.0 (s, CH_2), 133.0 (d, $^{3}J_{PC}$=6.7 Hz, *CH*), 126.0 (d, $^{1}J_{PC}$=184.0 Hz, *CH*), 118.3 (s, CH_2), 66.6 (d, $^{2}J_{PC}$=5.3 Hz, CH_2), 62.4 (d, $^{2}J_{PC}$=5.8 Hz, CH_2), 16.6 (d, $^{3}J_{PC}$=6.2 Hz, CH_3); FABMS (NBA, *m*/*z*, I, %): 177 [(M+H)$^+$, 100%]MS FAB(+); HRMS *m*/*z* (MH$^+$) 177.0693 (calcd for $C_7H_{13}O_3P$: 177.0680); IR (NaCl): ν 3000, 2280, 1400, 1260, 1110, 1070, 1050, 980, 920, 750, 660 cm^{-1}.

*4.2.4. Ethyl N-allyl-N-benzylvinylphosphonamidate (**3b**).* A solution of ethyl vinylphosphonochloridate **2** (1.68 g, 10.9 mmol) in dry Et_2O (10 mL) was added dropwise to a cold mixture of anhydrous allylbenzylamine (1.6 g 10.9 mmol) and triethylamine (2.0 g, 19.8 mmol) in dry Et_2O (40 mL). The mixture was then stirred 44 h at room temperature. The solid was removed by filtration and washed with Et_2O (3×10 ml). Solvents were removed under vacuum and the residue was purified by column chromatography (AcOEt 100%). Yield 1.44 g (50%).

^{31}P NMR (81.02 MHz, $CDCl_3$): δ 21.3; ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 7.42–7.21 (m, 5H, CH_{Ar}), 6.18 (m, $^{3}J_{HH}$=18.6 Hz, $^{2}J_{HH}$=−2.0 Hz, $^{3}J_{PH}$=23.7 Hz, 1H, =CH_2), 6.14 (m, $^{3}J_{HH}$=12.7 Hz, $^{3}J_{HH}$=18.6 Hz, $^{2}J_{PH}$=22.3 Hz, 1H, *CH*), 6.04 (m, $^{2}J_{HH}$=−2.0 Hz, $^{3}J_{HH}$=12.7 Hz, $^{3}J_{PH}$=48.2 Hz, 1H, =CH_2), 5.72 (tdd, $^{3}J_{HH}$=6.4 Hz, $^{3}J_{HH}$=10.2 Hz, $^{3}J_{HH}$=17.1 Hz, 1H, *CH*), 5.22–5.16 (m, $^{2}J_{HH}$=−1.3 Hz, $^{3}J_{HH}$=10.2 Hz, 1H, CH_2), 5.12 (dddd, $^{2}J_{HH}$=−1.3 Hz, $^{4}J_{HH}$=1.4 Hz,

$^4J_{HH}$=1.3 Hz, $^3J_{HH}$=17.1 Hz, 1H, *CH*$_2$), 4.23 (dd, $^2J_{HH}$=−15.2 Hz, $^2J_{PH}$=9.2 Hz, 1H, NC*H*$_2$), 4.21 (dd, $^2J_{HH}$=−15.2 Hz, $^2J_{PH}$=9.2 Hz, 1H, NC*H*$_2$), 4.12 (qdd, $^2J_{HH}$=−10.1 Hz, $^3J_{HH}$=7.2 Hz, $^3J_{PH}$=7.2 Hz, 1H, OC*H*$_2$), 3.82 (qdd, $^2J_{HH}$=−10.1 Hz, $^3J_{HH}$=7.2 Hz, $^3J_{PH}$=7.4 Hz, 1H, OC*H*$_2$), 3.50 (m, $^2J_{HH}$=−9.7 Hz, $^4J_{HH}$=1.4 Hz, $^4J_{HH}$=1.3 Hz, $^3J_{HH}$=6.4 Hz, $^3J_{PH}$=10.9 Hz, 1H, *CH*$_2$), 3.49 (m, $^2J_{HH}$=−9.7 Hz, $^4J_{HH}$=1.4 Hz, $^4J_{HH}$=1.3 Hz, $^3J_{HH}$=6.4 Hz, $^3J_{PH}$=10.7 Hz, 1H, NC*H*$_2$), 1.32 (t, $^3J_{HH}$=7.2 Hz, 3H, *CH*$_3$); ^{13}C NMR (100.61 MHz, $CDCl_3$): δ 138.2 (d, $^3J_{PC}$=2.4 Hz, *CH*$_{Ar}$), 135.2 (d, $^3J_{PC}$=1.8 Hz, =*CH*), 135.0 (d, $^2J_{PC}$=1.9 Hz, =*CH*$_2$), 128.3 and 128.6 (s, *CH*$_{Ar}$), 127.3 (s, *CH*), 126.0 (d, $^1J_{PC}$=184.0 Hz, *PCH*=), 118.3 (s, =*CH*$_2$), 59.9 (d, $^2J_{PC}$=6.7 Hz, *OCH*$_2$), 48.1 (d, $^2J_{PC}$=4.3 Hz, *NCH*$_2$), 47.1 (d, $^2J_{PC}$=4.3 Hz, *NCH*$_2$), 16.6 (d, $^3J_{PC}$=6.7 Hz, *CH*$_3$); FABMS (NBA, *m*/*z*, I, %): 266 [(M+H)$^+$, 100%]; HRMS *m*/*z* (MH$^+$) 266.1321 (calcd for $C_{14}H_{21}NO_2P$: 266.1310); IR (NaCl): ν 3057, 2977, 2954, 1618, 1215, 1070, 1017, 722, 695, 670, 626, 598, 528, 500 cm^{-1}.

*4.2.5. Diethyl allylphosphonate (**4a**).* Triethylphosphite (20 mL, 120 mmol) and allyl bromide (11 mL g, 130 mmol) were heated at 140 °C for 4 h. Remaining allyl bromide was removed under vacuum. The product was purified by column chromatography (AcOEt 100%). Yield: 21.38 g (99%).

^{31}P NMR (81.02 MHz, $CDCl_3$): δ 27.7; ^{1}H NMR (250.13 MHz, $CDCl_3$): δ 5.92–5.70 (m, 1H, =*CH*), 5.35–5.12 (m, 2H, =*CH*$_2$), 4.20–4.06 (m, 4H, *OCH*$_2$), 2.64 (m, $^2J_{PH}$=21.9 Hz, $^3J_{HH}$=7.4 Hz, $^4J_{HH}$=1.2 Hz, $^4J_{HH}$=1.2 Hz, 2H, *PCH*$_2$), 1.34 (t, $^3J_{HH}$=7.0 Hz, 6H, 2*CH*$_3$); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ 127.3 (d, $^2J_{PC}$=11.2 Hz, =*CH*), 119.5 (d, $^3J_{PC}$=14.5 Hz, =*CH*$_2$), 61.7 (d, $^2J_{PC}$=6.7 Hz, *OCH*$_2$), 31.5 (d, $^1J_{PC}$=139.0 Hz, *PCH*$_2$), 16.2 (d, $^3J_{PC}$=6.0 Hz, *CH*$_3$).

*4.2.6. Diethyl 2-chloroallylphosphonate (**4b**).* Triethyl phosphite (20 mL, 120 mmol), 2-chloroallyl chloride (16.0 g, 140 mmol), and sodium bromide (14.8 g, 144 mmol) were heated at 140 °C for 18 h. Solid was filtered off and washed with AcOEt (3×10 mL). The product was purified by column chromatography (AcOEt/CH_2Cl_2 1/1). Yield: 14.9 g (58%).

^{31}P NMR (101.25 MHz, $CDCl_3$): δ 23.9; ^{1}H NMR (250.13 MHz, $CDCl_3$): δ 5.40–5.37 (m, =*CH*$_2$), 4.16 (qd, $^3J_{HH}$=7.1 Hz, $^3J_{PH}$=8.1 Hz, 4H, *OCH*$_2$), 2.94 (dd, 2H $^2J_{PH}$=21.4 Hz, $^4J_{HH}$=0.7 Hz, *PCH*$_2$), 1.35 (t, $^3J_{HH}$=7.1 Hz, 6H, *CH*$_3$); ^{13}C NMR (62.90 MHz, $CDCl_3$): δ 132.0 (d, $^2J_{PC}$=11.4 Hz, =*CCl*), 117,0 (d, $^3J_{PC}$=10.1 Hz, =*CH*$_2$), 62.7 (d, $^2J_{PC}$=6.6 Hz, *OCH*$_2$), 37.5 (d, $^1J_{PC}$=141.0 Hz, *PCH*$_2$), 16.5 (d, $^3J_{PC}$=6.2 Hz, *CH*$_3$); FABMS (NBA, *m*/*z*, I, %): 213 [(M+H)$^+$, 100%]; HRMS *m*/*z* (MH$^+$) 213.0431 (calcd for $C_7H_{15}ClO_3P$: 213.0447); IR (NaCl): ν 3680, 3440, 3020, 1680, 1400, 1260, 1210, 1100, 750, 660 cm^{-1}.

*4.2.7. Ethyl allylphosphonochloridate (**5a**).* Diethyl allylphosphonate (10.0 g, 56.0 mmol) in dry CH_2Cl_2 (40 mL) and oxalyl chloride (21.3 g, 168.0 mmol) were stirred at room temperature for 24 h and refluxed for 1 h. CH_2Cl_2 and remaining oxalyl chloride were removed under vacuum and the residue was used without further purification. Yield: 9.21 g (97%).

^{31}P NMR (81.02 MHz, DMSO-d_6): δ 39.3; ^{1}H NMR (250.13 MHz, DMSO-d_6): δ 5.59 (m, $^3J_{PH}$=9.1 Hz, $^3J_{HH}$=12.0 Hz, $^3J_{HH}$=13.3 Hz, $^3J_{HH}$=7. 3 Hz, 1H, =*CH*), 5.16 (m, $^4J_{PH}$=5.5 Hz, $^2J_{HH}$=−1.3 Hz, $^4J_{HH}$=1.2 Hz, $^3J_{HH}$=12.4 Hz, 1H, =*CH*$_2$), 5.12 (m, $^4J_{PH}$=4.8 Hz, $^2J_{HH}$=−1.2 Hz, $^4J_{HH}$=1.1 Hz, $^3J_{HH}$=13.3 Hz, 1H, =*CH*$_2$), 4.20–3.96 (m, 2H, *OCH*$_2$), 2.92 (m, $^2J_{PH}$=22.4 Hz, $^4J_{HH}$=1.1 Hz, $^4J_{HH}$=1.2 Hz, $^3J_{HH}$=7.3 Hz, 1H, *PCH*$_2$), 2.83 (m, $^2J_{PH}$=21.3 Hz, $^4J_{HH}$=1.1 Hz, $^4J_{HH}$=1.2 Hz, $^3J_{HH}$=7.3 Hz, 1H, *PCH*$_2$), 1.16 (t, $^3J_{HH}$=7.1 Hz, 3H, *CH*$_3$); ^{13}C NMR (50.32 MHz, DMSO-d_6): δ 126.3 (d, $^2J_{PC}$=12.9 Hz, =*CH*), 121.8 (d, $^3J_{PC}$=16.8 Hz, =CH$_2$), 63.5 (d, $^2J_{PC}$=8.6 Hz, *OCH*$_2$), 39.0 (d, $^1J_{PC}$=121.9 Hz, *PCH*$_2$), 16.0 (d, $^3J_{PC}$=7.2 Hz, *CH*$_3$).

*4.2.8. Ethyl 2-chloroallylphosphonochloridate (**5b**).* Diethyl 2-chloroallylphosphonate (9.66 g, 45 mmol) in dry CH_2Cl_2 (80 mL) and oxalyl chloride (23.7 g, 186 mmol) were stirred at room temperature for 10 h and refluxed for 24 h. CH_2Cl_2 and remaining oxalyl chloride were removed under vacuum. Product was used without further purification. Yield: 8.86 g (97%).

^{31}P NMR (101.25 MHz, DMSO-d_6): δ 33.8; ^{1}H NMR (250.13 MHz, DMSO-d_6): δ 4.92–5.14 (m, 2H, =*CH*$_2$), 3.70–3.91 (m, 2H, *OCH*$_2$), 2.84–2.88 (m, 2H, *PCH*$_2$), 0.94 (t, $^3J_{HH}$=7.1 Hz, 3H, *CH*$_3$); ^{13}C NMR (62.90 MHz, DMSO-d_6): δ 130.0 (d, $^2J_{PC}$=13.0 Hz, *CCl*), 118.9 (d, $^3J_{PC}$=12.3 Hz, =*CH*$_2$), 64.0 (d, $^2J_{PC}$=8.4 Hz, *OCH*$_2$), 44.0 (d, $^1J_{PC}$=125.7 Hz, *PCH*$_2$), 15.8 (d, $^3J_{PC}$=6.9 Hz, *CH*$_3$).

*4.2.9. Allyl ethyl allylphosphonate (**6a**).* A solution of ethyl allylphosphonochloridate (1.84 g, 10.9 mmol) in dry diethylether (10 mL) was added dropwise to a cold mixture of anhydrous allylic alcohol (1.13 g, 19.4 mmol) and triethylamine (2.0 g, 19.8 mmol) in dry diethylether (40 mL). The mixture was then stirred for 3 h at room temperature. The solid was removed by filtration and washed with ether (3×10 ml). Solvents were removed under vacuum and the residue was purified by column chromatography (AcOEt 100%). Yield: 1.28 g (67%).

^{31}P NMR (81.02 MHz, $CDCl_3$): δ 28.0; ^{1}H NMR (250.13 MHz, $CDCl_3$): δ 6.02–5.60 (m, 2H, 2 =*CH*), 5.41–5.07 (m, 4H, 2 =*CH*$_2$), 4.53–4.44 (m, 2H, *OCH*$_2$), 4.15–3.98 (m, 2H, *OCH*$_2$), 2.91–2.75 (m, $^2J_{PH}$=21.3 Hz, $^4J_{HH}$=1.1 Hz, $^4J_{HH}$=1.2 Hz, $^3J_{HH}$=7.3 Hz, 2H, *PCH*$_2$), 1.16 (t, $^3J_{HH}$=7.1 Hz, 3H, *CH*$_3$); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ 135.4 (d, $^3J_{PC}$=6.7 Hz, =*CH*), 127.5 (d, $^2J_{PC}$=13.2 Hz, =*CH*), 123.2 (d, $^3J_{PC}$=16.4 Hz, =*CH*$_2$), 118.3 (s, =*CH*$_2$), 66.6 (d, $^2J_{PC}$=5.3 Hz, *OCH*$_2$), 62.4 (d, $^2J_{PC}$=5.8 Hz, *OCH*$_2$), 39.2 (d, $^1J_{PC}$=126.6 Hz, *PCH*$_2$), 16.6 (d, $^3J_{PC}$=6.2 Hz, *CH*$_3$); FABMS (NBA, *m*/*z*, I, %): 219 [(M+H)$^+$, 100%]; HRMS *m*/*z* (MH$^+$) 219.1165 (calcd for $C_{10}H_{20}O_3P$: 219.1150); IR (NaCl): ν 3330, 3000, 2280, 1690, 1400, 1210, 1110, 1070, 1050, 980, 920, 750, 660 cm^{-1}.

*4.2.10. Allyl ethyl 2-chloroallylphosphonate (**6b**).* A solution of ethyl 2-chloroallylphosphonochloridate (1.13 g, 10.9 mmol) in dry Et_2O (10 mL) was added dropwise to a cold mixture of anhydrous allyl alcohol (1.13 g 19.4 mmol) and triethylamine (2.0 g, 19.8 mmol) in dry Et_2O (40 mL). The mixture was then stirred for 3 h at room temperature. The solid was removed by filtration and washed with Et_2O (3×10 mL). Solvents were removed under vacuum and the residue was purified by column chromatography (AcOEt 100%). Yield 1.28 g (67%).

^{31}P NMR (81.02 MHz, $CDCl_3$): δ 23.8; ^{1}H NMR (250.13 MHz, $CDCl_3$): δ 6.00–5.83 (m,1H =*CH*), 5.43–5.21 (m, 4H, =*CH*$_2$), 4.59–4.52 (m, *OCH*$_2$), 4.20–4.02 (m, *OCH*$_2$), 2.94 (dd, $^2J_{PH}$=21.4 Hz, $^4J_{HH}$=0.7 Hz, 2H, *PCH*$_2$), 1.32 (t, $^3J_{HH}$=7.1 Hz, 3H, *CH*$_3$); ^{13}C NMR (62.90 MHz, $CDCl_3$): δ 132.6 (d, $^2J_{PC}$=10.8 Hz, *CCl*), 131.7 (d, $^3J_{PC}$=6.2 Hz, =*CH*), 117.8 (s, =*CH*$_2$), 116.8 (d, $^3J_{PC}$=10.0 Hz, =*CH*$_2$), 66.5 (d, $^2J_{PC}$=5.8 Hz, *OCH*$_2$), 62.3 (d, $^2J_{PC}$=6.8 Hz, *OCH*$_2$), 37.1 (d, $^1J_{PC}$=141.0 Hz, *PCH*$_2$), 16.2 (d, $^3J_{PC}$=6.2 Hz, *CH*$_3$); FABMS (NBA, *m*/*z*, I, %): 225 [(M+H)$^+$, 100%]; HRMS *m*/*z* (MH$^+$) 225.0435 (calcd for $C_8H_{15}ClO_3P$: 225.0447); IR (NaCl): ν 3680, 3440, 3020, 1680, 1400, 1260, 1210, 1100 cm^{-1}.

*4.2.11. Ethyl N-allyl-N-benzyl-allylphosphonamidate (**6c**).* A solution of ethyl allylphosphonochloridate (1.0 g, 5.9 mmol) in dry diethylether (10 mL) was added dropwise to a cold mixture of anhydrous allylbenzylamine (0.80 g, 5.45 mmol) and triethylamine (1.0 g, 9.9 mmol) in dry diethylether (40 mL). The mixture was then stirred for 48 h at room temperature. The solid was removed by filtration and washed with ether (3×10 ml). Solvents were removed under vacuum and the residue was purified by column chromatography (AcOEt 100%). Yield 0.785 g (46%).

^{31}P NMR (81.02 MHz, $CDCl_3$): δ 27.1; ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 7.47–7.23 (m, 5H, *CH*$_{Ar}$), 5.84 (m, $^3J_{HH}$=7.5 Hz, $^3J_{HH}$=7.4 Hz, $^3J_{HH}$=9.4 Hz, $^3J_{HH}$=17.7 Hz, $^3J_{PH}$=6.0 Hz, 1H, =*CH*), 5.72 (tdd,

$^3J_{HH}$=7.1 Hz, $^3J_{HH}$=5.9 Hz, $^3J_{HH}$=10.3 Hz, $^3J_{HH}$=17.0 Hz, 1H, =*CH*), 5.20 (m, $^2J_{HH}$=−1.7 Hz, $^4J_{HH}$=1.3 Hz, $^4J_{HH}$=1.4 Hz, $^3J_{HH}$=9.4 Hz, $^4J_{PH}$ undetermined, 1H, =CH_2), 5.18 (m, $^2J_{HH}$=−1.7 Hz, $^4J_{HH}$=1.2 Hz, $^4J_{HH}$=1.4 Hz, $^3J_{HH}$=17.7 Hz, $^4J_{PH}$ undetermined, 1H, =CH_2), 5.17 (m, $^2J_{HH}$=−1.5 Hz, $^4J_{HH}$=1.2 Hz, $^4J_{HH}$=1.2 Hz, $^3J_{HH}$=10.3 Hz, 1H, =CH_2), 5.12 (m, $^2J_{HH}$=−1.5 Hz, $^4J_{HH}$=1.4 Hz, $^4J_{HH}$=1.4 Hz, $^3J_{HH}$=17.0 Hz, 1H, =CH_2), 4.25 (dd, $^2J_{HH}$=−15.0 Hz, $^3J_{PH}$=8.8 Hz, 1H, *NCH*$_2$*Ph*), 4.16 (dd, $^2J_{HH}$=−15.0 Hz, $^3J_{PH}$=9.4 Hz, 1H, *NCH*$_2$*Ph*), 4.12 (qdd, $^2J_{HH}$=−10.0 Hz, $^3J_{HH}$=7.0 Hz, $^3J_{PH}$=7.0 Hz, 1H, *OCH*$_2$), 3.88 (qdd, $^2J_{HH}$=−10.0 Hz, $^3J_{HH}$=7.2 Hz, $^3J_{PH}$=7.2 Hz, 1H, *OCH*$_2$), 3.50 (m, $^2J_{HH}$=−17.2 Hz, $^4J_{HH}$=1.2 Hz, $^4J_{HH}$=1.4 Hz, $^3J_{HH}$=7.1 Hz, $^3J_{PH}$=10.4 Hz, 1H, *NCH*$_2$), 3.49 (m, $^2J_{HH}$=−17.2 Hz, $^4J_{HH}$=1.2 Hz, $^4J_{HH}$=1.4 Hz, $^3J_{HH}$=5.9 Hz, $^3J_{PH}$=10.4 Hz, 1H, *NCH*$_2$), 2.67 (m, $^2J_{HH}$=−14.9 Hz, $^4J_{HH}$=1.4 Hz, $^4J_{HH}$=1.4 Hz, $^3J_{HH}$=7.4 Hz, $^2J_{PH}$=21.3 Hz, 1H, *PCH*$_2$), 2.62 (m, $^2J_{HH}$=−14.9 Hz, $^4J_{HH}$=1.2 Hz, $^4J_{HH}$=1.3 Hz, $^3J_{HH}$=7.5 Hz, $^2J_{PH}$=20.1 Hz, 1H, *PCH*$_2$), 1.28 (t, $^3J_{HH}$=7.1 Hz, 3H, *CH*$_3$); ^{13}C NMR (100.61 MHz, $CDCl_3$): δ 138.2 (d, $^3J_{PC}$=2.4 Hz, C_{Ar}), 135.2 (d, $^3J_{PC}$=1.8 Hz, *CH*=), 128.4 and 128.6 (s, CH_{Ar}), 128.4 (d, $^2J_{PC}$=10.4 Hz, =*CH*), 127.3 (s, CH_{Ar}), 119.6 (d, $^3J_{PC}$=14.1 Hz, =CH_2), 118.3 (s, =CH_2), 59.9 (d, $^2J_{PC}$=6.7 Hz, *OCH*$_2$), 48.1 (d, $^2J_{PC}$=4.3 Hz, *NCH*$_2$), 47.1 (d, $^2J_{PC}$=4.3 Hz, *NCH*$_2$), 33.5 (d, $^1J_{PC}$=128.7 Hz, *PCH*$_2$), 16.2 (d, $^3J_{PC}$=6.7 Hz, *CH*$_3$); FABMS (NBA, *m*/*z*, I, %): 280 [(M+H)$^+$, 100%]; HRMS *m*/*z* (MH^+) 280.1474 (calcd for $C_{15}H_{23}NO_2P$: 280.1466); IR (NaCl): ν 3060, 2978, 2960, 1600, 1222, 1076, 1025, 723, 690, 671, 540, 500 cm^{-1}.

*4.2.12. Allyl phenylphosphinate (**7**).* Pyridine (9.5 g, 120 mmol) was added dropwise to a mixture of allyl chloroformate (14.5 g, 120 mmol) and phenylphosphinic acid (16.8 g, 120 mmol) in CH_2Cl_2 (250 mL). Once gas evolution has stopped, the reaction mixture was heated to reflux for 15 min, and then cooled to room temperature and 100 mL of HCl 0.1 N were added and stirred for 30 min. Organic layer was extracted twice with 70 mL of water, dried with Na_2SO_4, filtered and solvent was removed under vacuum. The remaining oil is distilled under vacuum (T=121 °C, 1 mmHg). Yield 14.12 g (65%).

^{31}P NMR (161.97 MHz, $CDCl_3$): δ 25.1; ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 7.60 (d, $^1J_{PH}$=564.9 Hz, 1H, *PH*), 7.79–7.73 (m, 2H, CH_{Ar}), 7.59–7.55 (m, 1H, CH_{Ar}), 7.50–7.47 (m, 2H, CH_{Ar}), 5.93 (m, $^3J_{HH}$=5.6 Hz, $^3J_{HH}$=5.6 Hz, $^3J_{HH}$=10.3 Hz, $^3J_{HH}$=17.2 Hz, 1H, =*CH*), 5.36 (m, $^2J_{HH}$=−1.6 Hz, $^4J_{HH}$=1.5 Hz, $^4J_{HH}$=1.5 Hz, $^3J_{HH}$=17.2 Hz, 1H, =CH_2), 5.24 (m, $^2J_{HH}$=−1.6 Hz, $^4J_{HH}$=1.1 Hz, $^4J_{HH}$=1.5 Hz, $^3J_{HH}$=10.3 Hz, 1H, =CH_2), 4.59 (m, $^3J_{PH}$=8.7 Hz, $^2J_{HH}$=−13.6 Hz, $^4J_{HH}$=1.1 Hz, $^4J_{HH}$=1.5 Hz, $^3J_{HH}$=5.6 Hz, H, *OCH*$_2$), 4.53 (m, $^3J_{PH}$=8.3 Hz, $^2J_{HH}$=−13.6 Hz, $^4J_{HH}$=1.1 Hz, $^4J_{HH}$=1.5 Hz, $^3J_{HH}$=5.6 Hz, 1H, *OCH*$_2$); ^{13}C NMR (100.61 MHz, $CDCl_3$): δ 133.17 (d, $^4J_{PC}$=3.1 Hz, CH_{Ar}), 132.33 (d, $^2J_{PC}$=6.7 Hz, CH_{Ar}), 130.8 (d, $^3J_{PC}$=11.9 Hz, CH_{Ar}), 129.6 (d, $^1J_{PC}$=132.4 Hz, C_{Ar}), 128.7 (d, $^3J_{PC}$=14.3 Hz, =*CH*), 118.6 (s, =CH_2), 66.1 (d, $^2J_{PC}$=6.3 Hz, *OCH*$_2$).

4.3. General procedure for Pudovik reaction compounds 6d–g

In a schlenck tube under N_2, potassium fluoride on alumina (5–10% w/w) was added to a mixture of 1 equiv of allyl phenylphosphinate and 1 equiv of α,β-unsaturated carbonyl compound until no liquid phase remained. The mixture was left for 30 min at room temperature and then extracted with CH_2Cl_2. The solid phase was washed with 3×10 mL of CH_2Cl_2. Solvent was removed under reduced pressure and the resulting oil was purified through column chromatography on silica gel.

*4.3.1. Allyl 1-hydroxybut-2-enylphenylphosphinate (**6d**).* α,β-unsaturated carbonyl compound: crotonaldehyde (0.384 mg). Chromatography eluent: AcOEt 100%. Yield 0.985 g (71%).

^{31}P NMR (161.97 MHz, $CDCl_3$): δ 39.3 (50%), 40.0 (50%); ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 7.85–7.75 (m, 2H, CH_{Ar}), 7.60–7.55 (m, 1H, CH_{Ar}), 7.50–7.46 (m, 2H, CH_{Ar}), 5.96 (m, $^3J_{HH}$=7.2 Hz, $^3J_{HH}$=6.6 Hz, $^3J_{HH}$=10.4 Hz, $^3J_{HH}$=17.2 Hz, 1H, =*CH*), 5.75 (m, 1H, =*CH*–CH_3), 5.74 (m, 1H, =*CH*–CH_3), 5.62 (m, $^3J_{PH}$=4.6 Hz, $^3J_{HH}$=16.8 Hz, $^4J_{HH}$=1.5 Hz, $^3J_{HH}$=5.5 Hz, 1H, =*CH*), 5.52 (m, $^3J_{PH}$=4.56 Hz, $^3J_{HH}$=15.03 Hz, $^4J_{HH}$=1.5 Hz, $^3J_{HH}$=4.8 Hz, 1H, =*CH*), 5.36 (m, $^2J_{HH}$=−2.8 Hz, $^4J_{HH}$=2.4 Hz, $^4J_{HH}$=1.4 Hz, $^3J_{HH}$=17.20 Hz, H, =CH_2), 5.24 (m, $^2J_{HH}$=−2.8 Hz, $^4J_{HH}$=2.4 Hz, $^4J_{HH}$=1.4 Hz, $^3J_{HH}$=10.4 Hz, 1H, =CH_2), 4.63 (m, $^2J_{PH}$=9.6 Hz, $^4J_{HH}$=13.0 Hz, $^3J_{HH}$=4.8 Hz, $^5J_{HH}$=1.6 Hz, 1H, *CHOH*), 4.60 (m, $^2J_{HH}$=−12.9 Hz, $^4J_{HH}$=1.3 Hz, $^4J_{HH}$=1.4 Hz, $^3J_{HH}$=6.6 Hz, 1H, *OCH*$_2$), 4.54 (m, $^3J_{HH}$=0.4 Hz, $^4J_{HH}$=2.4 Hz, $^4J_{HH}$=2.4 Hz, $^3J_{HH}$=7.2 Hz, 1H, *CHOH*), 4.47 (m, $^2J_{PH}$=9.6 Hz, $^2J_{HH}$=−12.9 Hz, $^3J_{HH}$=5.5 Hz, $^5J_{HH}$=1.3 Hz, 1H, *OCH*$_2$), 1.72 (m, $^5J_{PH}$=5.0 Hz, $^5J_{HH}$=1.6 Hz, $^4J_{HH}$=1.5 Hz, $^3J_{HH}$=6.6 Hz, 3H, *CH*$_3$), 1.69 (m, $^5J_{PH}$=5.0 Hz, $^5J_{HH}$=1.6 Hz, $^4J_{HH}$=1.5 Hz, $^3J_{HH}$=6.58 Hz, 3H, *CH*$_3$); ^{13}C NMR (100.61 MHz, $CDCl_3$): δ 133.1 (d, $^3J_{PC}$=2.4 Hz, =*CH*), 133.0 (d, $^3J_{PC}$=1.8 Hz, =*CH*), 132.7 (d, $^2J_{PC}$=9.2 Hz, CH_{Ar}), 132.6 (d, $^4J_{PC}$=3.1 Hz, CH_{Ar}), 132.5 (d, $^2J_{PC}$=9.2 Hz, CH_{Ar}), 132.5 (d, $^4J_{PC}$=3.7 Hz, CH_{Ar}), 128.6 (d, $^1J_{PC}$=120.7 Hz, C_{Ar}), 128.1 (d, $^1J_{PC}$=122.6 Hz, C_{Ar}), 130.5 (d, $^3J_{PC}$=12.2 Hz, =*CH*–CH_3), 129.6 (d, $^3J_{PC}$=12.2 Hz, =*CH*–CH_3), 128.3 (d, $^3J_{PC}$=12.3 Hz, CH_{Ar}), 128.2 (d, $^3J_{PC}$=12.2 Hz, CH_{Ar}), 125.4 (d, $^2J_{PC}$=1.8 Hz, =*CH*), 125.3 (d, $^2J_{PC}$=2.4 Hz, =*CH*), 117.7 (s, =CH_2), 117.7 (s, =CH_2), 71.6 (d, $^1J_{PC}$=114.6 Hz, *PCH*), 65.8 (d, $^3J_{PC}$=6.8 Hz, *OCH*$_2$), 65.7 (d, $^3J_{PC}$=6.8 Hz, *OCH*$_2$), 22.9 (d, $^4J_{PC}$=1.8 Hz, *CH*$_3$), 17.9 (d, $^4J_{PC}$=2.4 Hz, *CH*$_3$); FABMS (NBA, *m*/*z*, I, %): 253 [(M+H)$^+$, 100%]; HRMS *m*/*z* (MH^+) 253.0991 (calcd for $C_{13}H_{18}O_3P$: 253.0993); IR (NaCl): ν 3266, 2900, 1722, 1649, 1592, 1439, 1424, 1377, 1214, 1121, 1092, 1050, 925, 845, 820, 748, 695, 550 cm^{-1}.

*4.3.2. Allyl 1-hydroxy-2-methylprop-2-enylphenyl-phosphinate (**6e**).* α,β-unsaturated carbonyl compound: methylacroleine (0.384 g). Chromatography eluent: AcOEt 100%. Yield 1.00 g (73%).

^{31}P NMR (161.97 MHz, $CDCl_3$): δ 39.5 (51%), 40.0 (49%); ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 7.85–7.75 (m, 2H, CH_{Ar}), 7.60–7.55 (m, 1H, CH_{Ar}), 7.50–7.46 (m, 2H, CH_{Ar}), 5.95 (m, $^3J_{HH}$=7.1 Hz, $^3J_{HH}$=2.6 Hz, $^3J_{HH}$=10.4 Hz, $^3J_{HH}$=17.0 Hz, 1H, =*CH*), 5.36 (m, $^2J_{HH}$=−1.8 Hz, $^4J_{HH}$=1.5 Hz, $^4J_{HH}$=1.6 Hz, $^3J_{HH}$=17.0 Hz, H, =CH_2), 5.34 (m, $^2J_{HH}$=−1.8 Hz, $^4J_{HH}$=1.5 Hz, $^4J_{HH}$=1.6 Hz, $^3J_{HH}$=17.0 Hz, H, =CH_2), 5.25 (m, $^2J_{HH}$=−1.8 Hz, $^4J_{HH}$=1.5 Hz, $^4J_{HH}$=2.6 Hz, $^3J_{HH}$=10.4 Hz, 1H, =CH_2), 5.23 (m, $^2J_{HH}$=−1.8 Hz, $^4J_{HH}$=1.5 Hz, $^4J_{HH}$=2.6 Hz, $^3J_{HH}$=10.4 Hz, 1H, =CH_2), 4.96 (m, $^4J_{PH}$=5.7 Hz, $^4J_{HH}$=1.2 Hz, $^2J_{HH}$=−2.9 Hz, $^4J_{HH}$=0.8 Hz, 1H, =CH_2), 4.93 (m, $^4J_{PH}$=4.2 Hz, $^4J_{HH}$=1.2 Hz, $^2J_{HH}$=−2.8 Hz, $^4J_{HH}$=1.5 Hz, 1H, =CH_2), 4.92 (m, $^4J_{PH}$=5.7 Hz, $^4J_{HH}$=1.2 Hz, $^2J_{HH}$=−2.8 Hz, $^4J_{HH}$=0.8 Hz, 1H, =CH_2), 4.90 (m, $^4J_{PH}$=4.2 Hz, $^4J_{HH}$=1.2 Hz, $^2J_{HH}$=−2.8 Hz, $^4J_{HH}$=1.5 Hz, 1H, =CH_2), 4.63 (m, $^2J_{HH}$=−12.4 Hz, $^4J_{HH}$=1.5 Hz, $^4J_{HH}$=1.6 Hz, $^3J_{HH}$=7.1 Hz, 1H, *OCH*$_2$), 4.60 (m, $^3J_{PH}$=undetermined, $^2J_{HH}$=−12.4 Hz, $^4J_{HH}$=1.5 Hz, $^4J_{HH}$=1.6 Hz, $^3J_{HH}$=7.1 Hz, 1H, *OCH*$_2$), 4.48 (m, $^3J_{PH}$=undetermined, $^2J_{HH}$=−12.4 Hz, $^4J_{HH}$=1.5 Hz, $^4J_{HH}$=1.1 Hz, $^3J_{HH}$=2.6 Hz, 1H, *OCH*$_2$), 4.46 (m, $^3J_{PH}$=undetermined, $^2J_{HH}$=−12.4 Hz, $^4J_{HH}$=1.5 Hz, $^4J_{HH}$=1.1 Hz, $^3J_{HH}$=2.6 Hz, 1H, *OCH*$_2$), 4.57 (m, $^2J_{PH}$=9.3 Hz, $^4J_{HH}$=1.5 Hz, $^4J_{HH}$=0.8 Hz, 1H, *PCH*), 1.85 (m, $^4J_{PH}$=2.7 Hz, $^4J_{HH}$=1.2 Hz, $^4J_{HH}$=1.2 Hz, 3H, *CH*$_3$), 1.76 (m, $^4J_{PH}$=2.7 Hz, $^4J_{HH}$=1.2 Hz, $^4J_{HH}$=1.2 Hz, 3H, *CH*$_3$); ^{13}C NMR (100.61 MHz, $CDCl_3$): δ 140.6 (d, $^2J_{PC}$=5.1 Hz, =*C*), 140.6 (d, $^2J_{PC}$=5.1 Hz, =*C*), 133.0 (d, $^3J_{PC}$=6.6 Hz, =*CH*), 132.9 (d, $^3J_{PC}$=6.6 Hz, =*CH*), 132.7 (d, $^2J_{PC}$=9.5 Hz, CH_{Ar}), 132.7 (d, $^4J_{PC}$=2.2 Hz, CH_{Ar}), 128.3 (d, $^3J_{PC}$=12.4 Hz, CH_{Ar}), 128.2 (d, $^3J_{PC}$=12.4 Hz, CH_{Ar}), 127.7 (d, $^1J_{PC}$=122.9 Hz, C_{Ar}), 127.5 (d, $^1J_{PC}$=122.9 Hz, C_{Ar}), 118.0 (s, =CH_2), 114.4 (d, $^3J_{PC}$=10.2 Hz, =CH_2), 114.3 (d, $^3J_{PC}$=9.5 Hz, =CH_2), 74.6 (d, $^1J_{PC}$=109.0 Hz, *PCH*), 74.5 (d, $^1J_{PC}$=109.8 Hz, *PCH*), 65.9 (d, $^3J_{PC}$=7.3 Hz, *OCH*$_2$), 65.8 (d, $^3J_{PC}$=6.6 Hz, *OCH*$_2$), 20.1 (d, $^3J_{PC}$=2.2 Hz, *CH*$_3$), 19.9 (d, $^3J_{PC}$=2.2 Hz, *CH*$_3$); MS FAB$^+$ (NBA) *m*/*z* (%): 253 (M+H)$^+$ (100) MS HR$^+$ (NBA) $C_{13}H_{18}O_3P$: 253.0993 found: 253.1025; IR (NaCl): ν 3280, 3060–2800, 1695, 1592, 1450, 1224, 1130, 1050, 925, 760, 682 cm^{-1}.

*4.3.3. Allyl 1-hydroxy-1-methylprop-2-enylphenyl-phosphinate (**6f**).* α,β-unsaturated carbonyl compound: methylvinylketone (0.384 g). Chromatography eluent: AcOEt 100%, Yield 0.510 g (39%).

^{31}P NMR (161.97 MHz, $CDCl_3$): δ 41.8 (50%, dia 1), 41.9 (50%, dia 2); ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 7.92–7.75 (m, 2H, CH_{Ar}), 7.64–7.50 (m, 1H, CH_{Ar}), 7.53–7.42 (m, 2H, CH_{Ar}), 6.10–5.89 (m, 2H, =*CH*), 5.40–5.19 (m, 4H, =CH_2), 4.72–4.66 (m, 2H, OCH_2), 4.42–4.36 (m, 2H, OCH_2), 3.80 (sl, *OH*), 3.70 (sl, *OH*), 1.56 (d, $^{3}J_{PH}$=14.8 Hz, 3H, CH_3), 1.49 (d, $^{3}J_{PH}$=15.0 Hz, 3H, CH_3); ^{13}C NMR (100.61 MHz, $CDCl_3$): δ 137.5 (d, $^{2}J_{PC}$=0.9 Hz, =*CH*), 138.1 (d, $^{2}J_{PC}$=1.5 Hz, =*CH*), 133.0 (d, J_{PC}=3.1 Hz, =*CH*), 133.1 (d, J_{PC}=2.4 Hz, =*CH*), 132.6 (d, J_{PC}=9.1 Hz, CH_{Ar}), 132.6 (d, J_{PC}=3.7 Hz, CH_{Ar}), 128.2 (d, $^{3}J_{PC}$=12.3 Hz, CH_{Ar}), 128.1 (d, $^{3}J_{PC}$=11.0 Hz, CH_{Ar}), 127.4 (d, $^{1}J_{PC}$=119.5 Hz, C_{Ar}), 127.1 (d, $^{1}J_{PC}$=120.1 Hz, C_{Ar}), 117.8 (s, =CH_2), 117.7 (s, =CH_2), 116.0 (d, $^{3}J_{PC}$=9.2 Hz, =CH_2), 115.5 (d, $^{3}J_{PC}$=9.2 Hz, =CH_2), 74.5 (d, $^{1}J_{PC}$=112.4 Hz, *PC*), 74.3 (d, $^{1}J_{PC}$=114.6 Hz, *PC*), 66.1 (d, $^{3}J_{PC}$=7.1 Hz, OCH_2), 65.9 (d, $^{3}J_{PC}$=7.4 Hz, OCH_2), 22.9 (d, $^{2}J_{PC}$=2.6 Hz, CH_3), 22.6 (d, $^{2}J_{PC}$=2.6 Hz, CH_3); FABMS (NBA, *m/z*, I, %): 253 [(M+H)$^+$, 100%]; HRMS *m/z* (MH^+) 253.0997 (calcd for $C_{13}H_{18}O_3P$: 253.0993); IR (NaCl): ν 3239, 1590, 1646, 1438, 1364, 1200, 1119, 1020, 855, 832, 744, 680, 552 cm^{-1}.

*4.3.4. Allyl 2-bromo-1-hydroxy-3-phenylprop-2-enylphenylphosphinate (**6g**).* α,β-unsaturated carbonyl compound: 2-bromocinnamaldehyde (1.16 g). Chromatography eluent: AcOEt/CH_2Cl_2 4/6. Yield 0.260 g and 0.280 g (39% for both stereoisomers).

4.3.4.1. First diastereomer. ^{31}P NMR (161.97 MHz, $CDCl_3$): δ 39.7; ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 7.89–7.83 (m, 2H, CH_{Ar}), 7.37–7.28 (m, 5H, CH_{Ar}), 7.61–7.56 (m, 1H, CH_{Ar}), 7.49–7.44 (m, 2H, CH_{Ar}), 6.92 (dd, $^{4}J_{PH}$=4.8 Hz, $^{3}J_{HH}$=0.4 Hz, 1H, =*CHPh*), 6.00 (m, $^{3}J_{HH}$=5.3 Hz, $^{3}J_{HH}$=5.4 Hz, $^{3}J_{HH}$=10.5 Hz, $^{3}J_{HH}$=17.1 Hz, 1H, =*CH*), 5.45 (m, $^{2}J_{HH}$=−1.4 Hz, $^{4}J_{HH}$=1.5 Hz, $^{4}J_{HH}$=1.5 Hz, $^{3}J_{HH}$=17.1 Hz, 1H, =CH_2), 5.27 (m, $^{2}J_{HH}$=−1.4 Hz, $^{4}J_{HH}$=1.4 Hz, $^{4}J_{HH}$=1.4 Hz, $^{3}J_{HH}$=10.5 Hz, 1H, =CH_2), 5.02 (dd, $^{2}J_{PH}$=12.1 Hz, $^{3}J_{HH}$=1.1 Hz, 1H, *CHOH*), 4.74 (m, $^{3}J_{PH}$=6.9 Hz, $^{2}J_{HH}$=−12.9 Hz, $^{4}J_{HH}$=1.5 Hz, $^{4}J_{HH}$=1.4 Hz, $^{3}J_{HH}$=5.3 Hz, H, OCH_2), 4.61 (m, $^{3}J_{PH}$=7.2 Hz, $^{2}J_{HH}$=−12.9 Hz, $^{4}J_{HH}$=1.5 Hz, $^{4}J_{HH}$=1.4 Hz, $^{3}J_{HH}$=5.3 Hz, 1H, OCH_2); ^{13}C NMR (100.61 MHz, $CDCl_3$): δ 135.1 (d, $^{4}J_{PC}$=3.1 Hz, CH_{Ar}), 133.1 (d, $^{4}J_{PC}$=3.1 Hz, CH_{Ar}), 133.0 (d, $^{6}J_{PC}$=9.8 Hz, CH_{Ar}), 132.7 (d, $^{3}J_{PC}$=6.7 Hz, =*CH*), 131.1 (d, $^{2}J_{PC}$=9.8 Hz, CH_{Ar}), 128.9 (d, $^{3}J_{PC}$=2.4 Hz, =*CH*), 128.3 (d, $^{3}J_{PC}$=12.9 Hz, CH_{Ar}), 128.0 (d, $^{5}J_{PC}$=1.8 Hz, CH_{Ar}), 128.0 (s, CH_{Ar}), 126.4 (d, $^{1}J_{PC}$=127.4 Hz, *C*), 120.0 (s, *CBr*), 118.2 (s, =CH_2), 76.4 (d, $^{1}J_{PC}$=100.9 Hz, *CHOH*), 66.5 (d, $^{2}J_{PC}$=7.3 Hz, OCH_2); FABMS (NBA, *m/z*, I, %): 393 [(M+H)$^+$, 100%]; HRMS *m/z* (MH^+) 393.0262 (calcd for $C_{18}H_{19}BrO_3P$: 393.0255); IR (NaCl): ν 3207, 2826, 1712, 1590, 1492, 1439, 1217, 1200, 1122, 1092, 1016, 923, 693, 563 cm^{-1}.

4.3.4.2. Second diastereomer. ^{31}P NMR (161.97 MHz, $CDCl_3$): δ 39.9; ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 7.89–7.83 (m, 2H, CH_{Ar}), 7.61–7.56 (m, 1H, CH_{Ar}), 7.49–7.44 (m, 2H, CH_{Ar}), 7.37–7.28 (m, 5H, CH_{Ar}), 6.92 (dd, $^{4}J_{PH}$=4.8 Hz, $^{3}J_{HH}$=0.44 Hz, 1H, =*CH*), 6.00 (m, $^{3}J_{HH}$=5.3 Hz, $^{3}J_{HH}$=5.4 Hz, $^{3}J_{HH}$=10.5 Hz, $^{3}J_{HH}$=17.1 Hz, 1H, =*CH*), 5.45. (m, $^{2}J_{HH}$=−1.4 Hz, $^{4}J_{HH}$=1.5 Hz, $^{4}J_{HH}$=1.5 Hz, $^{3}J_{HH}$=17.1 Hz, 1H, =CH_2), 5.27 (m, $^{2}J_{HH}$=−1.4 Hz, $^{4}J_{HH}$=1.4 Hz, $^{4}J_{HH}$=1.4 Hz, $^{3}J_{HH}$=10.5 Hz, 1H, =CH_2), 5.02. (dd, $^{2}J_{PH}$=12.1 Hz, $^{3}J_{HH}$=1.1 Hz, 1H, *CHOH*), 4.74 (m, $^{3}J_{PH}$=6.9 Hz, $^{2}J_{HH}$=−12.9 Hz, $^{4}J_{HH}$=1.5 Hz, $^{4}J_{HH}$=1.4 Hz, $^{3}J_{HH}$=5.3 Hz, 1H, OCH_2), 4.61 (m, $^{3}J_{PH}$=7.2 Hz, $^{2}J_{HH}$=−12.9 Hz, $^{4}J_{HH}$=1.5 Hz, $^{4}J_{HH}$=1.4 Hz, $^{3}J_{HH}$=5.3 Hz, 1H, OCH_2); ^{13}C NMR (100.61 MHz, $CDCl_3$): δ 135.1(d, $^{4}J_{PC}$=3.1 Hz, CH_{Ar}), 133.1 (d, $^{4}J_{PC}$=3.1 Hz, CH_{Ar}), 133.0 (d, $^{6}J_{PC}$=9.8 Hz, CH_{Ar}), 132.7 (d, $^{3}J_{PC}$=6.7 Hz, =*CH*), 131.1 (d, $^{2}J_{PC}$=9.8 Hz, CH_{Ar}), 128.9 (d, $^{3}J_{PC}$=2.4 Hz, =*CHPh*), 128.3 (d, $^{3}J_{PC}$=12.9 Hz, CH_{Ar}), 128.0 (d, $^{5}J_{PC}$=1.8 Hz, CH_{Ar}), 128.04 (s, CH_{Ar}), 126.4 (d, $^{1}J_{PC}$=127.4 Hz, *PC*), 120.0 (s, *CBr*), 118.2 (s, =CH_2), 76.4 (d, $^{1}J_{PC}$=100.9 Hz, *CHOH*), 66.5 (d, $^{2}J_{PC}$=7.3 Hz, OCH_2); FABMS (NBA, *m/z*, I, %): 393 [(M+H)$^+$, 100%]; HRMS *m/z* (MH^+) 393.0260 (calcd for $C_{18}H_{19}BrO_3P$: 393.0255); IR (NaCl): ν 3210, 1712, 1594, 1490, 1432, 1220, 1188, 1118, 1095, 1013, 920, 748, 699, 570 cm^{-1}.

4.4. General procedure for RCM reactions compounds 8a–b and 9a–g

To a solution of precursor **3a**, **b** or **6a–g** in dry CH_2Cl_2 (0.02 M) was added Grubb's first generation catalyst (2% mol). The mixture was stirred under reflux. The reaction was monitored by ^{31}P NMR. If after 30 min starting material remained, the reaction was stirred one more hour. If no evolution occurred, 1% mol of catalyst was added. After consumption of unsaturated precursor, solvent was removed under vacuum and the residue was purified by chromatography.

*4.4.1. 2-Hydroxy-2-oxo-1,2-oxaphosphol-3-ene (**8a**).* Catalyst: 5%, Eluent: AcOEt/Hexane 8/2 then AcOEt 100%. Yield: 0.215 g (65%).

^{31}P NMR (81.02 MHz, Acetone-D_6): δ 42.9; ^{1}H NMR (400.13 MHz, Acetone-D_6): δ 7.72 (sl, 1H, OH), 7.31 (tdd, $^{3}J_{PH}$=44.7 Hz, $^{3}J_{HH}$=8.6 Hz, $^{3}J_{HH}$=1.7 Hz, 1H, =*CH*), 6.33 (tdd $^{2}J_{PH}$=34.6 Hz, $^{3}J_{HH}$=8.6 Hz, $^{4}J_{HH}$=2.4 Hz, 1H *PCH*), 4.82 (ddd, $^{3}J_{PH}$=6.4 Hz, $^{3}J_{HH}$=1.7 Hz, $^{4}J_{HH}$=2.4 Hz, 2H, OCH_2); ^{13}C NMR (100.61 MHz, Acetone-D_6): δ 148.7 (d, $^{2}J_{PC}$=17.2 Hz, =*CH*), 116.7 (d, $^{1}J_{PC}$=166.1 Hz, *PCH*), 70.6 (d, $^{2}J_{PC}$=14.7 Hz, OCH_2); FABMS (NBA, *m/z*, I, %): 121 [(M+H)$^+$, 100%]; HRMS *m/z* (MH^+) 121.0054 (calcd for $C_3H_6O_3P$: 121.0054); IR (KBr): ν 3425, 3086, 1595, 1322, 1212, 1105, 930, 738, 622 cm^{-1}. Melting point 119 °C (Lit. 110–111 °C).[10]

*4.4.2. 1-Benzyl-2-ethoxy-2-oxo-1,2-azaphosphol-3-ene (**8b**).* Catalyst: 2%, Eluent: AcOEt 100%. Yield: 0.250 g (80%).

^{31}P NMR (81.02 MHz, $CDCl_3$): δ 38.4; ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 7.48–7.21 (m, 5H, CH_{Ar}), 6.90–6.80 (m, 1H, =*CH*), 6.12–6.04 (m, 1H, *PCH*), 4.40–4.35 (m, 2H, NCH_2), 4.23 (dd, $^{2}J_{HH}$=−15.2 Hz, $^{2}J_{PH}$=9.2 Hz, 1H, NCH_2Ph), 4.21 (dd, $^{2}J_{HH}$=−15.2 Hz, $^{2}J_{PH}$=9.2 Hz, 1H, NCH_2Ph), 4.20–4.11 (m, 2H, OCH_2), 1.35 (t, $^{3}J_{HH}$=7.1 Hz, 3H, CH_3); ^{13}C NMR (100.61 MHz, $CDCl_3$): δ 148.7 (d, $^{2}J_{PC}$=17.2 Hz, =*CH*), 138.2 (d, $^{3}J_{PC}$=2.4 Hz, C_{Ar}), 128.6 and 128.9 (s, CH_{Ar}), 127 (s, CH_{Ar}), 122.9 (d, $^{1}J_{PC}$=164.2 Hz, *PCH*), 61.2 (d, $^{2}J_{PC}$=6.7 Hz, OCH_2), 53.1 (d, $^{2}J_{PC}$=4.3 Hz, NCH_2), 49.1 (d, $^{2}J_{PC}$=4.3 Hz, NCH_2), 16.3 (d, $^{3}J_{PC}$=6.7 Hz, CH_3); FABMS (NBA, *m/z*, I, %): 238 [(M+H)$^+$, 100%]; HRMS *m/z* (MH^+) 238.1005 (calcd for $C_{12}H_{17}NO_2P$: 238.0997); IR (NaCl): ν 2977, 1623, 1222, 1074, 1012, 725, 693, 660 cm^{-1}.

*4.4.3. 4,5-Dehydro-2-ethoxy-2-oxo-1,2-oxaphosphinane (**9a**).* Catalyst: 3.5%, Eluent: AcOEt/Hexane 8/2 then AcOEt 100%. Yield: 0.700 g (87%).

^{31}P NMR (101.25 MHz, $CDCl_3$): δ 20.8; ^{1}H NMR (250.13 MHz, $CDCl_3$): δ 5.74–5.67 (m, 2H, *CH*=*CH*), 4.89–4.71 (m, 2H, OCH_2), 4.20–4.11 (m, 2H, CH_2), 2.59–2.46 (m, 2H, PCH_2), 1.35 (t, $^{3}J_{HH}$=7.1 Hz, 3H, CH_3); ^{13}C NMR (62.90 MHz, $CDCl_3$): δ 125.3 (d, $^{3}J_{PC}$=17.2 Hz, =*CH*), 120.7 (d, $^{2}J_{PC}$=9.6 Hz, =*CH*), 69.2 (d, $^{2}J_{PC}$=7.7 Hz, OCH_2), 61.7 (d, $^{2}J_{PC}$=6.6 Hz, OCH_2), 22.7 (d, $^{1}J_{PC}$=133.4 Hz, PCH_2), 16.7 (d, $^{3}J_{PC}$=5.7 Hz, CH_3); FABMS (NBA, *m/z*, I, %): 163 [(M+H)$^+$, 100%]; HRMS *m/z* (MH^+) 163.0547 (calcd for $C_6H_{12}O_3P$: 163.0524); IR (NaCl): ν 3512, 3070, 2873, 1452, 1230, 1181, 1063, 954, 840 cm^{-1}.

*4.4.4. 1-Benzyl-2-ethoxy-4,5-dehydro-2-oxo-1,2-azaphosphinane (**9c**).* Catalyst: 2.5%, Eluent: CH_2Cl_2/EtOH 97/3. Yield: 0.802 g (88%).

^{31}P NMR (101.25 MHz, $CDCl_3$): δ 25.4; ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 7.36–7.25. (m, 5H, CH_{Ar}), 5.72–5.55 (m, 2H, *CH*=*CH*), 4.61 (dd, $^{3}J_{PH}$=10.6 Hz, $^{2}J_{HH}$=−14.7 Hz, 1H, NCH_2), 4.08–4.00 (m, 3H,OCH_2 and NCH_2), 3.47–3.66 (m, 2H, NCH_2), 2.69–2.39 (m, 2H, PCH_2), 1.32 (t, $^{3}J_{HH}$=7.0 Hz, CH_3); ^{13}C NMR (62.90 MHz, $CDCl_3$): δ 138.2 (d, $^{3}J_{PC}$=5.4 Hz, C_{Ar}), 128.8 (s, CH_{Ar}), 128.7 (s, CH_{Ar}), 126.2 (d,

J_{PC}=15.0 Hz, =*CH*), 127.7 (s, CH_{Ar}), 120.6 (d, J_{PC}=10.3 Hz, =*CH*), 61.0 (d, $^{2}J_{PC}$=6.5 Hz, OCH_2), 50.2 (s, NCH_2), 49.5 (s, NCH_2), 24.7 (d, $^{1}J_{PC}$=126.9 Hz, PCH_2), 16.9 (d, $^{3}J_{PC}$=6.1 Hz, CH_3); FABMS (NBA, *m*/*z*, I, %): 252 [(M+H)$^+$, 100%]; HRMS *m*/*z* (MH^+) 252.1148 (calcd for $C_{13}H_{19}O_2NP$: 252.1143); IR (NaCl): ν 3070, 2988, 2960, 1612, 1219,1085, 1022, 724, 690 cm^{-1}.

*4.4.5. 4,5-Dehydro-3-hydroxy-2-phenyl-2-oxo-1,2-oxaphosphinane (**9d**).* Catalyst: 7%, Eluent: CH_2Cl_2/EtOH 98/2 Yield: two fractions of diastereomers 0.408 g and 0.320 mg (87%).

4.4.5.1. First diastereomer. ^{31}P NMR (161.97 MHz, $CDCl_3$): δ 29.3; ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 7.82–7.77 (m, 2H, CH_{Ar}), 7.55–7.51 (m, 1H, CH_{Ar}), 7.45–7.40 (m, 2H, CH_{Ar}), 5.88 (m, $^{3}J_{PH}$=19.0 Hz, $^{3}J_{HH}$=11.2 Hz, $^{3}J_{HH}$=2.5 Hz, $^{4}J_{HH}$=2.4 Hz, $^{4}J_{HH}$=2.4 Hz, 1H, =*CH*), 5.75 (m, $^{4}J_{PH}$=3.0 Hz, $^{3}J_{HH}$=11.2 Hz, $^{4}J_{HH}$=2.6 Hz, $^{3}J_{HH}$=2.4 Hz, $^{3}J_{HH}$=2.6 Hz, 1H, =*CH*), 4.89 (m, $^{3}J_{PH}$=3.1 Hz, $^{2}J_{HH}$=−16.7 Hz, $^{3}J_{HH}$=2.6 Hz, $^{4}J_{HH}$=2.4 Hz, $^{5}J_{HH}$=2.7 Hz, 1H, OCH_2), 4.63 (m, $^{3}J_{PH}$=15.4 Hz, $^{2}J_{HH}$=−16.7 Hz, $^{3}J_{HH}$=2.4 Hz, $^{4}J_{HH}$=2.4 Hz, $^{5}J_{HH}$=2.6 Hz, 1H, OCH_2), 4.45 (m, $^{2}J_{PH}$=3.1 Hz, $^{4}J_{HH}$=2.6 Hz, $^{3}J_{HH}$=2.5 Hz, $^{5}J_{HH}$=2.6 Hz, $^{5}J_{HH}$=2.7 Hz, 1H, *CHOH*); ^{13}C NMR (100.61 MHz, $CDCl_3$): δ 133.1 (d, $^{4}J_{PC}$=2.9 Hz, CH_{Ar}), 131.7 (d, $^{3}J_{PC}$=10.2 Hz, CH_{Ar}), 128.7 (d, $^{3}J_{PC}$=13.9 Hz, CH_{Ar}), 128.5 (d, $^{1}J_{PC}$=134.7 Hz, C_{Ar}), 128.0 (d, $^{2}J_{PC}$=2.9 Hz, =*CH*), 125.4 (d, $^{2}J_{PC}$=11.7 Hz, =*CH*), 65.6 (d, $^{2}J_{PC}$=7.3 Hz, OCH_2), 62.5 (d, $^{1}J_{PC}$=102.4 Hz, *CHOH*); FABMS (NBA, *m*/*z*, I, %): 211 [(M+H)$^+$, 100%], 193 [(M-OH)$^+$, 25%]; HRMS *m*/*z* (MH^+) 211.0527 (calcd for $C_{10}H_{12}O_3P$: 211.0524); IR (NaCl): ν 3252, 3063, 2880, 1443, 1272, 1234, 1175, 1119, 1099, 1063, 954, 743, 696 cm^{-1}.

4.4.5.2. Second diastereomer. ^{31}P NMR (161.97 MHz, $CDCl_3$): δ 34.5; ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 7.81–7.76 (m, 2H, CH_{Ar}), 7.50–7.45 (m, 1H, CH_{Ar}), 7.37–7.33 (m, 2H, CH_{Ar}), 5.96–5.86 (m, 1H, =*CH*), 5.79–5.75 (m, 1H, =*CH*), 4.83–4.76 (m, 1H, OCH_2), 4.62–4.57 (m, 1H, OCH_2), 4.32–4.21 (m, 1H, *CHOH*); ^{13}C NMR (100.61 MHz, $CDCl_3$): δ 133.0 (d, $^{4}J_{PC}$=2.2 Hz, CH_{Ar}), 132.5 (d, $^{2}J_{PC}$=9.5 Hz, CH_{Ar}), 128.4 (d, $^{3}J_{PC}$=12.4 Hz, CH_{Ar}), 127.9 (d, J_{PC}=13.5 Hz, =*CH*), 126.9 (d, $^{1}J_{PC}$=133.9 Hz, C_{Ar}), 126.4 (d, J_{PC}=2.2 Hz, =*CH*), 66.5 (d, $^{2}J_{PC}$=7.3 Hz, OCH_2), 61.7 (d, $^{1}J_{PC}$=106.1 Hz, *CHOH*); FABMS (NBA, *m*/*z*, I, %): 211 [(M+H)$^+$, 100%]; HRMS *m*/*z* (MH^+) 211.0527 (calcd for $C_{10}H_{12}O_3P$: 211.0524); IR (NaCl): ν 3300, 1523, 1225, 1163, 1121, 1084, 1063, 922, 726 cm^{-1}; Melting point 158 °C.

*4.4.6. 4,5-Dehydro-3-hydroxy-3-methyl-2-phenyl-2-oxo-1,2-oxaphosphinane (**9f**).* Catalyst: 10%, Eluent: CH_2Cl_2/EtOH 98/2. Yield: 0.444 g (50%).

^{31}P NMR ($CDCl_3$, 161.97 MHz): δ 38.5 (55% dia. 1), 32.1 (45% dia. 2); ^{1}H NMR ($CDCl_3$, 400.13 MHz): δ 7.81–7.76 (m, 2H, CH_{Ar}), 7.50–7.45 (m, 1H, CH_{Ar}), 7.37–7.33 (m, 2H, CH_{Ar}), 5.96–5.86 (m, 2H, *CH*=*CH*), 5.10–5.02 (m, 1H, OCH_2), 4.90–4.76 (m, 1H, OCH_2), 1.56 (d, $^{3}J_{PH}$=14.8 Hz, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100.61 MHz): *diastereomer 1*: δ 133.1 (d, $^{4}J_{PC}$=2.2 Hz, CH_{Ar}), 132.4 (d, $^{2}J_{PC}$=9.5 Hz, CH_{Ar}), 129.0 (d, $^{3}J_{PC}$=12.5 Hz, CH_{Ar}), 128.0 (d, J_{PC}=13.5 Hz, =*CH*), 126.9 (d, $^{1}J_{PC}$=136.3 Hz, C_{Ar}), 126.4 (d, J_{PC}=2.2 Hz, =*CH*), 66.5 (d, $^{2}J_{PC}$=7.4 Hz, OCH_2), 63.4 (d, $^{1}J_{PC}$=112.9 Hz, *PCOH*), 22.6 (d, $^{2}J_{PC}$=3.9 Hz, CH_3); *diastereomer 2*: δ 134.1 (d, $^{4}J_{PC}$=2.2 Hz, CH_{Ar}), 133.2 (d, $^{2}J_{PC}$=10.2 Hz, CH_{Ar}), 130.2 (d, $^{3}J_{PC}$=11.3 Hz, CH_{Ar}), 128.5 (d, J_{PC}=14.2 Hz, =*CH*), 127.2 (d, $^{1}J_{PC}$=132.5 Hz, C_{Ar}), 126.2 (d, J_{PC}=2.2 Hz, =*CH*), 64.2 (d, $^{2}J_{PC}$=7.3 Hz, OCH_2), 61.7 (d, $^{1}J_{PC}$=114.5 Hz, *PCOH*), 24.2 (d, $^{2}J_{PC}$=4.4 Hz, CH_3); FABMS (NBA, *m*/*z*, I, %): 225 [(M+H)$^+$, 100%]; HRMS *m*/*z* (MH^+) 225.0701 (calcd for $C_{11}H_{14}O_3P$: 225.0680); IR (NaCl): ν 3300, 3100, 2900, 1550, 1272, 1225, 1172, 1130, 1099, 1050, 954, 743, 696 cm^{-1}.

Acknowledgements

This research was supported by Bayer CropScience SA and the Région Languedoc-Roussillon.

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