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Tetrahedron
Tetrahedron 63 (2007) 10059–10066

Reaction of unsaturated phosphonate monoesters with bromo- and iodo(bis-collidine) hexafluorophosphates

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Received 5 April 2007; revised 10 July 2007; accepted 12 July 2007
Available online 19 July 2007

Abstract—Reaction of unsaturated phosphonate monoesters with bromo- and iodo(bis-collidine) hexafluorophosphates are reported to lead to the formation of five- to seven-membered phostones by *exo* mode cyclizations. When the chains of the unsaturated phosphonate monoesters are substituted in α of the double bond by a dioxolane group *endo* mode cyclizations are observed. These cyclizations give rise to the formation of 1,2-oxaphosphepane-2-oxide and 1,2-oxaphosphocane-2-oxide.

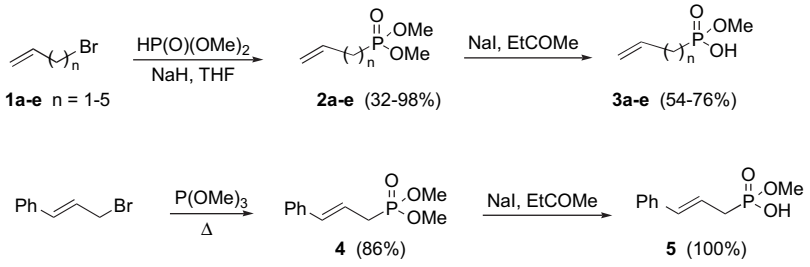
1. Introduction

We have previously reported that reaction of iodo- and bromo(bis-collidine) hexafluorophosphates with ω-ethylenic acids allowed the formation of halo lactones of various ring sizes.[1] Reactions with the corresponding phosphonates have been also examined in the literature. Maas and Hoge reported first the possibility to carry out such cyclizations.[2] They found that cyclic phosphonates could be obtained by reaction of 2-isopropenylcyclopropylphosphonates and phosphinates with bromine.[2] Zhao and co-workers reported that in the case of structurally less favored phosphonates, bromine does not react, and only the reaction with iodine was effective and led to the formation of five- and six-membered cyclic phosphonates.[3] It was subsequently reported that bromine could be also used for these cyclizations if phosphonates monoesters were used.[4] Cyclizations of allenic phosphonic acids and phosphonates into 1,2-oxaphosphol-3-enes have been also reported.[5,6]

The aim of this report is to examine the behavior of unsaturated phosphonate monoesters with iodo and bromo(bis-collidine) hexafluorophosphates, to study the scope of these cyclizations and apply them to the formation of phospho sugar derivatives. The case of α,β-ethylenic phosphonates, which lead to dephosphorylation reactions has been already reported.[7]

2. Results

The substrates studied have been prepared as reported in Scheme 1. Reaction of bromoalkenes **1a–e**[1b] with dimethylphosphite in the presence of sodium hydride in THF[8] gave rise to the formation of dimethylphosphates **2a–e** in satisfactory yields. The monohydrolysis to products **3a–e** were then carried out by reaction with 1 equiv of NaI in butan-2-one at reflux. Methyl 3-phenylallylphosphonate **5** was obtained by heating of cinnamyl bromide with trimethylphosphite,



Scheme 1.

Keywords: Electrophilic cyclization; Phosphocane; Phosphepane; Heterocycle; Halo reagent.
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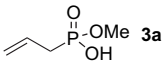
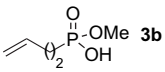
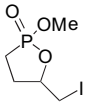
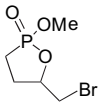
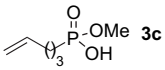
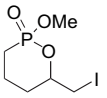
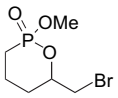
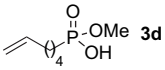
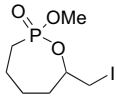
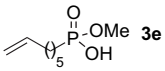
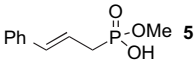
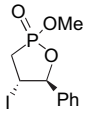
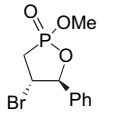
doi:10.1016/j.tet.2007.07.032

Table 1. Reaction of phosphonate monoesters **3a–e** and **5** with iodo- and bromo(bis-collidine) hexafluorophosphates

Entry	Substrate	Iodo phostone (yield, %)	Bromo phostone (yield, %)
a	 **3a**	Degradation	Degradation
b	 **3b**	 **6b** (83) 55:45[a]	 **7b** (46) 60:40[a]
c	 **3c**	 **6c** (76) 66:33[a]	 **7c** (67.5) 70:30[a]
d	 **3d**	 **6d** (64.5) 62:38[a]	See text
e	 **3e**	Degradation	Degradation
f	 **5**	 **8** (57) 65:35[a]	 **9** (44) 45:55[a]

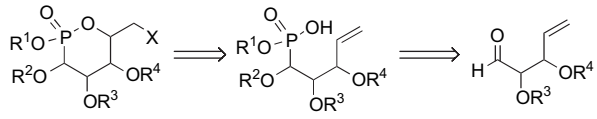
[a] Proportion of the diastereomers.

followed by monohydrolysis. The structure of products **2a–e**, **3a–e**, **4**, and **5** were determined from their NMR, IR, and mass spectra, and by comparison with the literature data when possible (see Section 4).

The reaction of compounds **3a–e** and **5** with 1.3 equiv of iodo- and bromo(bis-collidine) hexafluorophosphates were carried out in dichloromethane at rt. Our results are reported in Table 1.

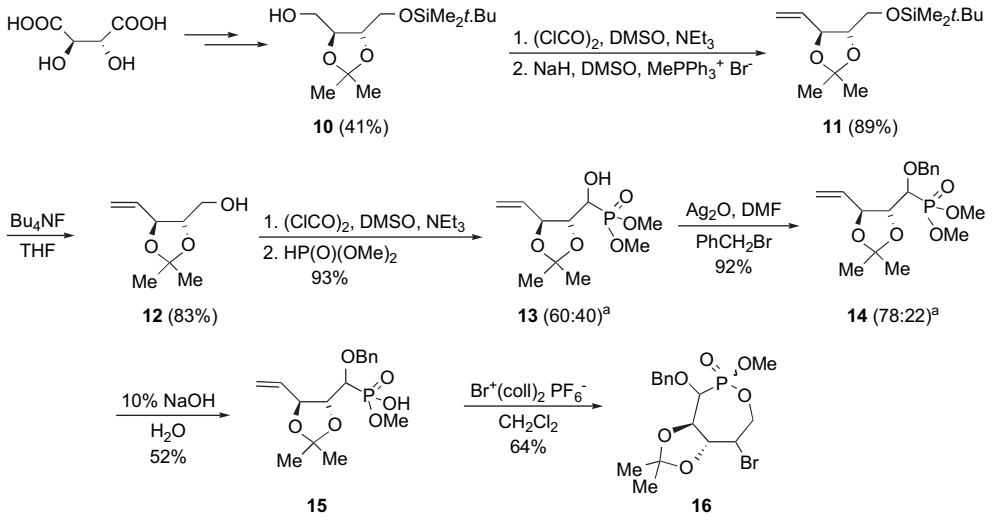
In the case of phosphonate monoesters **3b**,**c**, we observed the formation of the corresponding iodo- and bromo phostones **6b**,**c** and **7b**,**c**, in satisfactory yields. Their structures were deduced from their spectra data and confirmed by comparison with the literature data for the known products. A mixture of two diastereomers, due to the chiral phosphorus atom, is observed in all cases. No product was obtained starting from the allylphosphonate monoester **3a**. These results are not surprising, due to the probable very low stability of the expected 1,2-oxaphosphetanes. Reaction of iodo(bis-collidine) hexafluorophosphate with the phosphonate monoester **3d** led to the iodo phostone **6d** in a satisfactory yield, while reaction of bromo(bis-collidine) hexafluorophosphate led to a complex mixture of products in which the *endo* and *exo* cyclization products could be detected. However, they could not be isolated in an enough pure state to be fully characterized. The formation of the eight-membered phostone was not observed from phosphonate **3e**. This failure, as in the case of the carboxylic acids, is probably due to the fact that higher activation energies are required for this ring size.[1] In the case of the phosphonate monoester **5**, the stable *endo* cyclization products **8** and **9** were obtained. These *endo* cyclizations were favored by the presence of the phenyl group.

We were then interested by application of these cyclizations to the preparation of phospho sugars. Different methods have been developed for their synthesis.[9] However, the possibility to obtain such derivatives by electrophilic cyclization of unsaturated phosphonates has not been yet examined. The aim of our work was thus to apply this methodology to the preparation of such derivatives according to the retro synthetic pathway indicated in Scheme 2.



Scheme 2.

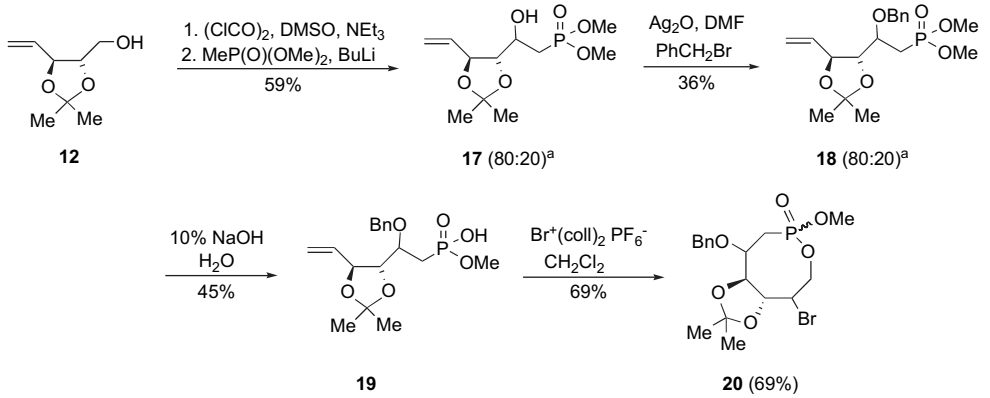
Preparation of phosphonates **15** is outlined in Scheme 3. Starting from L-tartaric acid, monoprotected diol **10** was obtained using a reported procedure.[10] Swern oxidation, followed without purification of the aldehyde, by a Wittig reaction, led to the unsaturated silyl ether **11**.[11] After cleavage of the silyl ether, phosphonate **13** was then obtained as a mixture of two diastereomers in a one-pot procedure by Swern oxidation of alcohol **12** followed by addition of dimethylphosphite. These diastereomers could not be separated by liquid chromatography over silica gel. We were not able to attribute the relative stereochemistry of these diastereomers from their NMR spectra, even if in the literature the major isomer was always reported to have the *anti* stereochemistry.[12] Protection of its alcohol function as benzyl ether,[13] allowed a partial separation of the two diastereomers by liquid chromatography over silica gel. In the conditions used for this reaction, we observed a slight epimerization of the



Scheme 3. Preparation of oxaphosphepane **16**. [a]Proportion of the diastereomers.

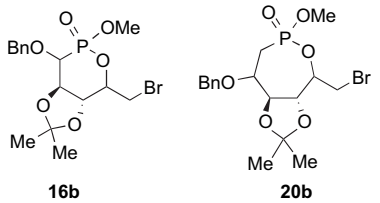
minor diastereomer in favor of the major diastereomer (78:22 ratio for the mixture of diastereomers **14** instead of 60:40 ratio for the mixture of diastereomers **13**). The next two steps were carried out on the major diastereomer and on the mixture of the two diastereomers. Reaction with 10% NaOH led to the desired monoester phosphonate **15**. Subsequent reaction with bromo(bis-collidine) hexafluorophosphate in dichloromethane led to 1,2-oxaphosphepane-2-oxide **16**. From the major phosphonate **15**, a mixture of two diastereomers (68:32) was obtained. The major diastereomer was less polar. Their structures were established without ambiguity from their ^{13}C NMR spectra. The major diastereomer shows in particular using *J*-mode experiments a signal at 67.3 ppm attributed to the carbon in α of the oxygen in the seven-membered cycle, which bears two hydrogen atoms. The signal at 47.2 ppm, attributed to the carbon in α of the bromine atom, bears only one hydrogen atom. If we had the product of 6-*exo* cyclization, (product **16b** in Scheme 5) the carbon in α of the oxygen atom should bear one hydrogen atom, and that in α of the bromine atom should bear two hydrogen atoms. The same observation was made for the minor isomer, for which the carbon shifts were, respectively, of 65.8 and 46.7 ppm. These conclusions were confirmed by HSQC and HMBD experiments. Contrary to our expectation, we did not observe the formation of the six-membered phostones. The fact that in these cyclizations only two diastereomers (corresponding to the chirality induced by the phosphorus atom) were isolated, instead of the four possible diastereomers can be explained by the fact that the oxygen atom in α of the carbon–carbon double bond directs the approach of the bromo reagent. However, we were not able to determine certainly their stereochemistries using NMR experiments (NOESY, COSY, etc.). Attempts to obtain crystal structure were also unsuccessful. The presence of the dioxolane group seems to disfavor, for steric reasons, the 6-*exo* mode cyclizations and favor the 7-*endo* mode ones. Reaction with the mixture of the two diastereomers of compound **15** led to the formation of four diastereomers. The very low stability of the iodo equivalent of compound **16** did not allow its characterization. Some 1,2-oxaphosphepane-2-oxides are known.[14] The good yields observed in these cyclizations seem due to the presence of the dioxolane group, which decreases the activation entropy of these reactions,[1,15] and allows a new preparation of this family of compounds.

This particular behavior of unsaturated phosphonates **15** in their reaction with bromo(bis-collidine) hexafluorophosphate led to examine the case of phosphonates in which one supplementary carbon was introduced in the chain. Such compounds should lead to the formation of still unknown eight-membered heterocycles. The desired ω-ethylenic phosphonate was synthesized as outlined in Scheme 4. As for the formation of α-hydroxyphosphonate



Scheme 4. Preparation of phosphocane **20**. [a]Proportion of the diastereomers.

13, the β-hydroxyphosphonate **17** has been obtained by a one-pot procedure, by Swern oxidation of alcohol **12**, followed by reaction with [(dimethoxyphosphoryl)methyl]-lithium. A mixture of the two diastereomers of compound **17** has been obtained in moderate yield. Here also, the stereochemistry of the major diastereomer of **17** could not be clearly established, even if in the literature, the *anti* stereochemistry between the 3-hydroxyl function and the 4 oxygen of the dioxolane group was reported to be favored.[16] This not very stable phosphonate **17** was protected as stable benzyl ether **18**. The two diastereomers of this ether were partially separated by liquid chromatography over silica gel, so, the next steps were carried out on the major diastereomer of compound **18** and on the mixture of the two diastereomers, in comparable yields. Reaction with 10% aqueous NaOH with the major diastereomer of compound **18** led to the phosphonate monoester **19** and its reaction with bromo(bis-collidine) hexafluorophosphate gave rise to the formation of the phosphocane **20** (60:40 mixture of two diastereomers), which structure was deduced from its NMR spectra. The structural determinations were carried using in ^{13}C NMR *J*-mode experiments. In this case also, an *endo* mode cyclization was observed. The structure of compound **20** was established without ambiguity from its ^{13}C NMR spectra. The major diastereomer shows in particular using *J*-mode experiments a signal at 66.9 ppm attributed to the carbon in α of the oxygen present in the eight-membered cycle. This carbon bears two hydrogen atoms. In the same way, the signal at 51.4 ppm, attributed to the carbon in α of the bromine atom, bears only one hydrogen atom. If we had the product of 7-*exo* cyclization, (product **20b** in Scheme 5) the carbon in α of the oxygen atom should bear one hydrogen atom, and that in α of the bromine atom should bear two hydrogen atoms. The same observation was made for the minor isomer. These conclusions were confirmed by HSQC and HMBD experiments. As in the case of the formation of phostone **16**, we observed only the formation of two diastereomers instead of the four possible diastereomers. Here also the dioxolane group directs the approach of the bromo reagent, favors the *endo* mode cyclization and explains the yield observed in this reaction. Attempts to determine the stereochemistry of this phosphocane by NMR (NOESY, COSY, etc.) were unsuccessful. When the cyclization was carried out on the mixture of the two diastereomers of compound **19**, an inseparable mixture of the expected four diastereomers was obtained.



Scheme 5.

3. Conclusion

We have examined the scope of the reaction of ω-unsaturated phosphonate monoesters with iodo- and bromo(bis-collidine) hexafluorophosphates. Formations of 5- to 7-membered phostones formed by *exo* or *endo* mode cyclizations have been observed for simple phosphonates. Contrary to the results previously reported in the case of unsaturated carboxylic acids,[17] from β,γ-unsaturated phosphonates, 4-membered phostones could not be obtained. In the case of the unsaturated phosphonates **15** and **19**, the formation of *endo* cyclization products seems due to the conjunction of different factors: the presence of the dioxolane group, which favors the formation of the corresponding phostones by *endo* mode cyclizations, the utilization of the bromo reagent, which is known to favor the *endo* cyclizations compared to the iodo reagent,[1] and the phosphonates, which in certain cases, seems also to favor this kind of cyclizations, by comparison with the reactivity of carboxylic acids.[3] For the first time, a phosphocane derivative has been synthesized.

4. Experimental part

4.1. General

ω-Ethylenic bromides **1b–e** have been prepared as previously reported.[1b] Dimethyl allylphosphonate is commercially available. All products were purified by flash liquid chromatography using silica gel columns.

4.2. Preparation of dimethyl phosphonates 2b–e

These compounds were obtained by the Michaelis–Becker reaction of bromides **1b–e** with dimethyl phosphite. Under argon, in a three neck, round-bottomed flask was added successively NaH (60% in mineral oil, 2.54 g, 58 mmol, 1.3 equiv), dry THF (70 mL), and dimethylphosphite (5.3 mL, 1.3 equiv). After stirring at 0 °C (0.5 h), then at reflux (1.5 h), bromides **1b–e** (1 equiv) were introduced at 0 °C. After stirring at rt (24 h), the reaction mixture was quenched by addition of water (50 mL). The aqueous phase was extracted with dichloromethane (3×50 mL). The organic phases were dried ($MgSO_4$), concentrated, and the residue purified by chromatography over silica gel (MeOH–EtOAc). Preparations of dimethyl but-3-enylphosphonate **2b** (94%),[4] dimethyl pent-4-enylphosphonate **2c** (98%),[3a] and dimethyl hex-5-enylphosphonate **2d** (80%),[18] have been reported. Dimethyl hept-6-enylphosphonate **2e**: yield 95%; ^1H NMR (360 MHz, $CDCl_3$): δ=1.36–1.50 (m, 4H), 1.55–1.70 (m, 2H), 1.70–1.80 (m, 2H), 2.00–2.10 (m, 2H), 3.72 (d, J=10 Hz, 6H), 4.44–5.06 (m, 2H), 5.70–5.86 (m, 1H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=21.5 (d, J=5 Hz), 24.8 (d, J=140 Hz), 27.6, 29.3 (d, J=16 Hz), 32.7, 51.5 (d, J=6 Hz), 113.8, 137.9 ppm. HRMS (EI): [M^+] calcd for $C_9H_{19}O_3P$: 206.1072. Found: 206.1073.

4.3. (2*E*)-Dimethyl (3-phenylprop-2-enyl)-phosphonate 4[19]

An oven-dried three neck, round-bottomed flask was charged with a stoichiometric mixture of cinnamyl bromide and trimethyl phosphite. After 2.5 h of heating at reflux, the product was concentrated under vacuum, and purified by liquid chromatography over silica gel (86%). ^1H NMR (250 MHz, $CDCl_3$): δ=2.80 (dd, J=25 and 7 Hz, 2H), 3.78 (d, J=11 Hz, 6H), 6.08–6.25 (m, 1H), 6.55 (dd, J=10 and

5 Hz, 1H), 7.20–7.40 (m, 5H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=30.4 (d, J=139 Hz), 53.1 (d, J=7 Hz), 118.7 (d, J=12 Hz), 126.6, 128.0, 128.9, 135.3 (d, J=9 Hz), 139.0 ppm. ^{31}P NMR (101.25 MHz, $CDCl_3$): δ=22.5 ppm. MS (ES) m/z: 265 (M^++K^+), 249 (M^++Na^+).

4.4. Preparation of methyl hydrogen allylphosphonate 3a

Under argon, in an oven-dried three neck round-bottomed flask, was placed dimethylphosphonate **2a** (50 mmol, 1 equiv), butan-2-one (50 mL), and sodium iodide (51 mmol, 1.05 equiv). The mixture was heated at reflux for 1 day. After cooling at 0 °C, the solid formed was filtered, washed with butan-2-one, and then solubilized in 1 N HCl (50 mL). The solution was extracted with dichloromethane (3×50 mL). The organic phases were dried ($MgSO_4$), and concentrated under vacuum, to give monoester **3a** (90%),[20] which was used without further purification for the cyclization. The monoesters **3b–e** and **5** were prepared using the same procedure. Methyl hydrogen but-3-enylphosphonate **3b** (56%), and methyl hydrogen pent-4-enylphosphonate **3c** (70%) have been already described.[4]

4.5. Methyl hydrogen hex-5-enylphosphonate 3d

Yield 60%; ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.45–1.75 (m, 6H), 2.03 (q, J=7 Hz, 2H), 3.65 (d, J=11 Hz, 3H), 4.87–500 (m, 2H), 5.54–5.83 (m, 1H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=14.8, 27.9 (d, J=140 Hz), 31.4, 33.2, 52.9 (d, J=11 Hz), 114.4, 140.6 ppm. ^{31}P NMR (101.2 MHz, $CDCl_3$): δ=38.6 ppm. HRMS (EI): [M^+] calcd for $C_7H_{15}O_3P$: 178.0759. Found: 178.0758.

4.6. Methyl hydrogen hept-6-enylphosphonate 3e

Yield 95%; ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.30–1.50 (m, 14H), 1.50–1.90 (m, 4H), 1.90–2.05 (m, 2H), 3.72 (d, J=11 Hz, 3H), 4.95–5.05 (m, 2H), 5.70–5.86 (m, 1H), 11.83 (br s, 1H) ppm. HRMS (EI): [M^+] calcd for $C_8H_{17}O_3P$: 192.0915. Found: 192.0916.

4.7. (2*E*)-Methyl hydrogen (3-phenylprop-2-enyl)-phosphonate 5

Yield 90%; ^{1}H NMR (250 MHz, $CDCl_3$): δ=2.73 (dd, J=23 and 6 Hz, 2H), 3.66 (d, J=11 Hz, 3H), 6.13 (m, 1H), 6.52 (dd, J=16 and 5 Hz, 1H), 7.14–7.50 (m, 5H), 10.83 (br s, 1H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=31.2 (d, J=142 Hz), 52.7 (d, J=5 Hz), 118.9 (d, J=12 Hz), 126.8, 128.2, 129.1, 135.5 (d, J=15 Hz), 137.4 ppm. ^{31}P NMR (101.25 MHz, $CDCl_3$) δ=23.24 ppm. IR (film): ν 1638 ($\nu_{C=C}$), 1234.5 ($\nu_{P=O}$) cm^{-1}. HRMS (EI): calcd for $C_{10}H_{13}O_3P$: 212.0602. Found: 212.0603.

4.8. General procedure for the halo cyclizations

To a dichloromethane solution (50 mL) of halo(bis-collidine) hexafluorophosphate[21] (3.6 mmol, 1.3 equiv) was added in the dark, in 2 h, a dichloromethane solution (30 mL) of monoester phosphonate (3 mmol). After 1 h at rt, the solvent was removed under vacuum and 1 N HCl (50 mL) was added. This aqueous phase was then subjected to continuous extraction with diethyl ether (12 h). The ethereal phase was dried ($MgSO_4$), concentrated, and the residue purified by liquid chromatography over silica gel (EtOAc). The results are reported in Table 1. Phostones **6b**,[3b] **6c**,[3a] **7b**,[4] and **7c**[4] have been already described.

4.9. 7-(Iodomethyl)-2-methoxy-1,2-oxaphosphepane-2-oxide 6d

A mixture (62:38) of two diastereomers was isolated. Major isomer (from the mixture) ^{1}H NMR (200 MHz, $CDCl_3$): δ=1.58–2.35 (m, 8H), 3.35 (split AB system, $\Delta\delta_{AB}$= 29.8 Hz), 3.27 (part A, q, J=10.6 and 7.6 Hz, 1H), 3.44 (part B, q, J=4.7 and 10.7 Hz, 1H), 3.82 (d, J=10.6 Hz, 3H), 4.04–4.30 (m, 1H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=8.6 (d, J=5.6 Hz), 21.4 (d, J=4 Hz), 26.0 (d, J=132.5 Hz), 27.1, 35.2, 52.1 (d, J=7.3 Hz), 78.2 (d, J=4.6 Hz) ppm. HRMS (EI): [M^+] calcd for $C_7H_{14}IO_3P$: 304.0625. Found: 304.0626. Minor isomer (from the mixture) ^{1}H NMR (360 MHz, $CDCl_3$): δ=1.56–2.20 (m, 8H), 3.32 (d, J=7.5 Hz, 2H), 3.80 (d, J=11.4 Hz, 3H), 4.26–4.42 (m, 1H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=9.5 (d, J=9.5 Hz), 22.0 (d, J=5 Hz), 26.6, 26.7 (d, J=132 Hz), 25.7, 52.2 (d, J=6.7 Hz), 75.8 (d, J=2H) ppm.

4.10. (4*R**,5*S**)-4-Iodo-2-methoxy-5-phenyl-1,2-oxaphospholane 2-oxide 8

^{1}H NMR (250 MHz, $CDCl_3$) (mixture): δ=2.34–2.97 (m, 2H), 3.85 (d, J=11 Hz, 3H (minor diastereomer)), 3.90 (d, J=11 Hz, 3H (major diastereomer)), 4.17–4.38 (m, 1H), 5.26 (d, J=11 Hz, 1H (minor diastereomer)), 5.42 (dd, J=3 and 11 Hz, 1H (major diastereomer)), 7.35–7.57 (m, 5H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$) major diastereomer (from the mixture): δ=19.5 (d, J=8 Hz), 33.3 (d, J=111 Hz), 54.5, 87.9, 127.0, 129.6, 129.6, 136.7 ppm. Minor diastereomer (from the mixture): δ=19.6 (d, J=8 Hz), 33.3 (d, J=111 Hz), 53.4, 87.8, 125.5, 126.1, 128.7, 135.6 ppm. ^{31}P NMR (101.25 MHz, $CDCl_3$): δ=42.8 ppm. IR (film): ν 1192, 1046 ($\nu_{P=O}$) cm^{-1}.

4.11. (4*R**,5*S**)-4-Bromo-2-methoxy-5-phenyl-1,2-oxaphospholane 2-oxide 9

^{1}H NMR (200 MHz, $CDCl_3$) (mixture): δ=2.31–2.98 (m, 2H), 3.89 (d, J=12 Hz, 3H (minor diastereomer)), 3.95 (d, J=11 Hz, 3H (major diastereomer)), 4.15–4.40 (m, 1H), 5.20 (d, J=8 Hz, 1H), 5.32 (dd, J=2 and 8 Hz, 1H), 7.30–7.60 (m, 5H) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$) major diastereomer (from the mixture): δ=31.6 (d, J=113 Hz), 46.2 (d, J=12 Hz), 53.5 (d, J=6 Hz), 86.2 (d, J=4 Hz), 126.7, 128.7, 129.5, 135.8 ppm. Minor diastereomer (from the mixture): δ=31.3 (d, J=115 Hz), 46.4 (d, J=11 Hz), 53.6 (d, J=6 Hz), 85.9 (d, J=5 Hz), 126.7, 128.7, 129.5, 135.7 ppm. IR (film): ν 1639, 1250, 1042 ($\nu_{P=O}$) cm^{-1}.

4.12. [(4*S*,5*S*)-5-({[*tert*-Butyldimethylsilyl]oxy}methyl)-2,2-dimethyl-1,3-dioxolan-4-yl]methanol 10

This compound has been obtained by a reported procedure, starting from L-tartaric acid.[10]

4.13. {[(4*S*,5*S*)-2,2-Dimethyl-5-vinyl-1,3-dioxolan-4-yl]-methoxy}*tert*-butyldimethylsilane 11

A dichloromethane solution (175 mL) of dimethylsulfoxide (28.1 mL, 0.4 mol, 2.8 equiv) was added slowly at −50 °C to a dichloromethane solution (375 mL) of oxalyl chloride (18.7 mL, 0.213 mol, 1.5 equiv). After the end of the addition the dichloromethane solution was stirred for 15 min, and then a dichloromethane solution (175 mL) of alcohol **10** (0.142 mol, 39.2 g, 1 equiv) was added. After 20 min at −50 °C, triethylamine was added (198 mL, 1.42 mol, 10 equiv), and the solution stirred 15 min at −50 °C. Then, the flask was warmed to rt, and the dichloromethane solution was washed twice with a saturated solution of NaCl, dried (Mg_2SO_4), and concentrated. The crude aldehyde was used without purification for the next step.

To a suspension of NaH (60% in mineral oil, 11.4 g) in THF (190 mL) cooled at 0 °C was added dry dimethylsulfoxide (49.6 mL, 2 equiv). After 30 min at rt, this solution was transferred into a THF solution (870 mL) of methyltriphenylphosphonium bromide (101.5 g, 2 equiv). After stirring 2 h at rt, a THF solution (190 mL) of the aldehyde was added at 0 °C, and the resulting mixture was stirred one night at rt. After addition of ether (1 L), the solid was filtered, and the solution was concentrated under vacuum. The residue was purified by liquid chromatography over silica gel (pentane to pentane–ether (1:1)), to give the desired olefin **11** (16.3 g, 84%).[22]

4.14. [(4*S*,5*S*)-2,2-Dimethyl-5-vinyl-1,3-dioxolan-4-yl]-methanol 12

This compound was prepared as previously reported.[22]

4.15. Dimethyl hydroxy((4*R*,5*S*)-2,2-dimethyl-5-vinyl-1,3-dioxolan-4-yl)methylphosphonate 13

A dichloromethane solution (45 mL) of dimethylsulfoxide (2.78 mL, 39.16 mmol, 3.0 equiv) was added slowly at −50 °C to a dichloromethane solution (40 ml) of oxalyl chloride (1.68 mL, 19.6 mmol, 1.5 equiv). The dichloromethane solution was stirred for 15 min, and then a dichloromethane solution (90 mL) of alcohol **12** (2.06 g, 13 mmol) was added slowly. After 30 min at −50 °C, triethylamine (9.2 mL, 65.25 mmol, 5 equiv) was added. After cooling at rt, dimethylphosphite (2.4 mL, 26.10 mmol, 2 equiv) was added and the resulting mixture was stirred overnight. After addition of water (200 mL), the organic phase was separated, and the aqueous phase was extracted with chloroform (4×200 mL). The organic phases were dried and concentrated under vacuum. The residue was purified by liquid chromatography over silica gel (EtOAc) to give the hydroxyphosphonate **13** as a mixture of two diastereomers (60:40) 2.55 g (73%). ^{1}H NMR (250 MHz, $CDCl_3$) (mixture): δ=1.44 (s, 2.4H), 1.48 (s, 3.6H), 3.83 (d, J=10 Hz, 0.6H), 3.85 (d, J=10 Hz, 0.4H), 4.00–4.19 (m, 2H), 4.47 (t, J=8 Hz, 0.4H), 4.64 (t, J=7 Hz, 0.6H), 5.20–5.53 (m, 2H), 5.73–6.13 (m, 1H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$) minor diastereomer (from the mixture): δ=26.5, 26.9, 53.0 (d, J=6 Hz), 53.6 (d, J=6 Hz), 64.5 (d, J=163 Hz), 77.9 (d, J=14 Hz), 78.7 (d, J=6 Hz), 109.8, 119.8, 134.2 ppm. Major diastereomer (from the mixture): δ=26.7, 26.8, 53.1 (d, J=6 Hz), 53.3 (d, J=6 Hz), 67.9 (d, J=162 Hz), 78.8 (d, J=8 Hz), 80.1 (d, J=5 Hz), 109.4, 117.4, 135.8 ppm. HRMS (ESI): [M$^+$+Na] calcd for $C_{10}H_{19}NaO_6P$: 289.0817. Found: 289.0815.

4.16. Dimethyl (benzyloxy)((4*R*,5*S*)-2,2-dimethyl-5-vinyl-1,3-dioxolan-4-yl)methylphosphonate 14

To a DMF solution (20 mL) of hydroxyphosphonate **13** (1.825 g, 6.86 mmol) was added benzyl bromide (0.896 mL, 7.6 mmol, 1.1 equiv) and Ag_2O (1.756 g). After 48 h at rt, the mixture was filtered over Celite, and the solution was purified by liquid chromatography over silica gel (diethyl ether) to give 2.23 g of benzyl ether **14** as a mixture (92%) of two diastereomers (78:22). A partial separation of the two diastereomers was possible. Major diastereomer: ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.42 (s, 3H), 1.46 (s, 3H), 3.75 (d, J=10 Hz, 3H), 3.78 (d, J=10 Hz, 3H), 4.00 (dd, J=3 and 11 Hz, 1H), 4.10–4.15 (m, 1H), 4.61 (t, J=6 Hz, 1H), 4.80 (AB system, $\Delta\delta$=0.08, J=11 Hz, 2H), 5.19–5.44 (m, 2H), 5.78–5.98 (m, 1H), 7.30–7.47 (m, 5H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=26.5, 27.0, 52.6 (d, J=7 Hz), 53.5 (d, J=6 Hz), 71.2 (d, J=165 Hz), 74.1, 77.7 (d, J=13 Hz), 79.4, 109.5, 119.3, 128.2, 128.4, 128.8, 134.6, 136.6 ppm. ^{31}P NMR (101.12 MHz, $CDCl_3$): δ=21.96 ppm. HRMS (ESI): [M$^+$+Na] calcd for $C_{17}H_{25}NaO_6P$: 379.1286. Found: 379.1288. Minor diastereomer: ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.44 (s, 3H), 3.84 (d, J=11 Hz, 3H), 3.86 (d, J=11 Hz, 3H), 3.70 (dd, J=2 and 8 Hz, 1H), 3.93–4.05 (m, 1H), 4.32 (t, J=8 Hz, 1H), 4.78 (AB system, $\Delta\delta$=0.29, J=11 Hz, 2H), 4.80–5.14 (m, 2H), 5.55–5.76 (m, 1H), 7.28–7.45 (m, 5H) ppm. ^{31}P NMR (101.2 MHz, $CDCl_3$): δ=24.0 ppm. HRMS (ESI): [M$^+$+Na] calcd for $C_{17}H_{25}NaO_6P$: 379.1286. Found: 379.1291.

4.17. Methyl hydrogen (benzyloxy)((4*R*,5*S*)-2,2-dimethyl-5-vinyl-1,3-dioxolan-4-yl)methylphosphonate 15

A solution of the major diastereomer of dimethylphosphonate **14** (0.178 g, 0.5 mmol) in 1 N NaOH (0.86 mL) was heated at reflux (7 h). After cooling, 12 N HCl was added to adjust at pH 5, followed by saturated NaCl solution (2 mL). The aqueous phase was extracted with chloroform (5×3 mL). The organic phases were dried (Na_2SO_4) and concentrated under vacuum. The residue was then purified by liquid chromatography over silica gel (EtOAc–MeOH): ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.38 (s, 3H), 1.42 (s, 3H), 3.60 (br d, J=8 Hz, 3H), 3.93 (br d, J=11 Hz, 1H), 4.05–4.25 (m, 1H), 4.50–5.00 (m, 3H), 5.00–5.50 (m, 2H), 5.80–6.15 (m, 1H), 7.20–7.47 (m, 5H), 7.55 (br s, 1H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=26.9, 27.0, 53.2, 74.2, 75.4, 77.7, 80.9, 109.1, 116.8, 127.8, 128.3, 136.5, 137.8 ppm. ^{31}P NMR (101.2 MHz, $CDCl_3$): δ=16.7 ppm. IR ($CDCl_3$ solution): ν 3412, 3019, 1645, 1265, 1216, 1048, 929 cm^{-1}. HRMS (ESI): [M$^+$+Na] calcd for $C_{16}H_{23}NaO_6P$: 365.1130. Found: 365.1124. The same reaction was carried out with the mixture of diastereomers of phosphonate **14**. Minor diastereomer (from the mixture): ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.36 (s, 6H), 3.40–3.75 (m, 2H), 3.61 (dt, J=1 and 10 Hz, 3H), 4.67 (t, J=11 Hz, 1H), 4.72–5.16 (m, 4H), 5.45–5.65 (m, 1H), 7.17–7.23 (m, 5H), 7.46–7.82 (m, 1H) ppm. ^{31}P NMR (101.2 MHz, $CDCl_3$): δ=20.9 ppm. HRMS (ESI): [M$^+$+Na] calcd for $C_{16}H_{23}NaO_6P$: 365.1130. Found: 365.1130.

4.18. (3a*S*,8a*S*)-4-(Benzyloxy)-8-bromo-5-methoxy-2,2-dimethylhexahydro[1,3]dioxolo[4,5-*d*][1,2]oxaphosphepine 5-oxide 16

To a dichloromethane solution (4 mL) of the major diastereomer of compound **15** (126 mg, 0.37 mmol) was added in 1 h a dichloromethane solution (3 mL) of bromo(bis-collidine) hexafluorophosphate (225 mg, 6.48 mmol). After 12 h at rt, the reaction mixture was concentrated under vacuum, and the residue was purified by liquid chromatography over silica gel (EtOAc–hexanes 60:40). A mixture of two diastereomers (68:32) was obtained. A fraction containing only the less polar diastereomer could be isolated. Major diastereomer (less polar) ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.39 (s, 3H), 1.42 (s, 3H), 3.77 (d, J=11 Hz, 3H), 4.06 (dt, J=4 and 10 Hz, 1H), 4.11–4.42 (m, 5H), 4.71 (s, 2H), 7.21–7.34 (m, 5H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=26.5, 26.9, 47.2, 53.2 (d, J=7 Hz), 67.3 (d, J=7 Hz), 73.0 (d, J=149 Hz), 76.2 (d, J=5 Hz), 78.2 (d, J=19 Hz), 78.7, 109.6, 128.2, 128.3, 128.5, 136.7 ppm. ^{31}P NMR (101.2 MHz, $CDCl_3$): δ=23.7 ppm. IR ($CDCl_3$ solution): ν 3019, 1455, 1256, 1215, 1021 cm^{-1}. HRMS (ESI): [M$^+$+Na] calcd for $C_{16}H_{22}BrNaO_6P$: 443.0235. Found: 443.02360. $[\alpha]_D^{23}$ +19.5 (c 1, $CHCl_3$). Minor diastereomer (more polar): ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.37 (s, 3H), 1.40 (s, 3H), 3.67 (d, J=14 Hz, 3H), 3.72–4.50 (m, 6H), 4.79 (AB system, $\Delta\delta$=0.261 ppm, J=12 Hz, 2H), 7.19–7.30 (m, 5H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=26.3, 27.1, 46.9, 52.6 (d, J=7 Hz), 65.8 (d, J=4 Hz), 71.3 (d, J=150 Hz), 74.8, 78.4, 78.7 (d, J=17 Hz), 109.4, 128.1, 128.3, 128.4, 136.9. ^{31}P NMR (101.2 MHz, $CDCl_3$): δ=23.7. IR ($CDCl_3$ solution): ν 1643, 1455, 1261, 1042, 650 cm^{-1}. HRMS (ESI): [M$^+$+Na] calcd for $C_{16}H_{22}BrNaO_6P$: 443.0235. Found: 443.0230. When the bromo phostonization was carried out on the mixture of the two diastereomers of compound **16**, an inseparable mixture of four diastereomers was obtained.

4.19. Dimethyl 2-hydroxy-2-((4*S*,5*S*)-2,2-dimethyl-5-vinyl-1,3-dioxolan-4-yl)ethylphosphonate 17

The Swern oxidation of alcohol **12** was carried out as reported for the preparation of compound **13**. The dichloromethane solution of the crude aldehyde (5 mmol) was cooled at −78 °C. In a second flask cooled at −78 °C, containing a THF solution (16 mL) of dimethyl methylphosphonate (10 mmol, 2 equiv), was added 1.6 M nBuLi in hexane (10 mmol). After 45 min at this temperature the contents of this flask was cannulated into the flask containing the crude aldehyde. After 15 min, the reaction mixture was warmed to rt. After addition of aqueous ammonium chloride, the organic phase was separated and the aqueous phase extracted with chloroform (3×50 mL). After drying of the organic phases (Na_2SO_4), concentration under vacuum, the residue was purified by liquid chromatography over silica gel (EtOAc). The two diastereomers (80:20) of compound **17** could not be separated. ^{1}H NMR (200 MHz, $CDCl_3$) (mixture): δ=1.42 (s, 3H), 1.44 (s, 3H), 1.80–2.38 (m, 2H), 3.65–3.83 (m, 7H), 3.96–4.20 (m, 1H), 4.40 (t, J=7 Hz, 1H), 5.12–5.43 (m, 2H), 5.73–6.02 (m, 1H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$) major diastereomer (from the mixture): δ=26.9, 29.2 (d, J=140 Hz), 51.9–52.8 (2d), 67.6 (d, J=5 Hz), 79.9, 83.3 (d, J=16 Hz), 109.3, 117.6, 136.4 ppm. Minor diastereomer (from the mixture): δ=26.9, 30.1 (d, J=140 Hz), 51.9–52.8 (2d), 64.6 (d, J=4 Hz), 78.3, 83.2 (d, J=15 Hz), 109.3, 119.3, 135.2 ppm. ^{31}P NMR (101.2 MHz, $CDCl_3$): δ=32.7 (major diastereomer), 33.3 (minor diastereomer) ppm. IR ($CDCl_3$, mixture): ν 3436, 3020, 1476, 1216, 1044, 929 cm^{-1}. HRMS (ESI): [M$^+$+Na] calcd for $C_{11}H_{21}NaO_6P$: 303.0973. Found: 303.0968.

4.20. Dimethyl 2-(benzyloxy)-2-((4*R*,5*S*)-2,2-dimethyl-5-vinyl-1,3-dioxolan-4-yl)ethylphosphonate 18

This compound has been prepared following the method reported for the preparation of compound **14**. A partial separation of the two diastereomers (80:20) could be carried out. Major diastereomer: ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.43 (s, 6H), 2.00–2.30 (m, 2H), 3.60–3.80 (m, 3H), 3.95–4.18 (m, 1H), 4.34 (t, J=2 Hz, 1H), 4.72 (s, 2H), 5.07–5.48 (m, 2H), 5.70–5.98 (m, 1H), 7.20–7.45 (m, 5H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=26.8, 27.4 (d, J=143 Hz), 52.4 (d, J=5 Hz), 74.0 (d, J=4 Hz), 78.8, 82.1 (d, J=17 Hz), 109.2, 118.6, 127.6, 127.9, 128.2, 135.9, 137.5 ppm. ^{31}P NMR (101.2 MHz, $CDCl_3$): δ=31.6 ppm. IR ($CDCl_3$ solution): ν 3401, 3019, 1243, 1216, 1041 cm^{-1}. HRMS (ESI): [M$^+$+Na] calcd for $C_{18}H_{27}NaO_6P$: 393.1443. Found: 393.1444. Minor diastereomer (from the mixture): ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.37 (s, 6H), 1.78–2.32 (m, 2H), 3.50–3.80 (m, 7H), 3.80–4.08 (m, 1H), 4.22–4.85 (m, 3H), 4.85–5.35 (m, 2H), 5.64–5.92 (m, 1H), 7.10–7.20 (m, 5H) ppm. ^{31}P NMR (101.2 MHz, $CDCl_3$): δ=28.0 ppm.

4.21. Methyl hydrogen 2-(benzyloxy)-2-((4*R*,5*S*)-2,2-dimethyl-5-vinyl-1,3-dioxolan-4-yl)ethylphosphonate 19

This compound has been prepared following the method reported for the preparation of compound **15** (34%). Major diastereomer: ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.32 (s, 3H), 1.34 (s, 3H), 1.84–2.20 (m, 2H), 3.55 (d, J=11 Hz, 3H), 3.73–3.87 (m, 1H), 3.87–4.15 (m, 1H), 4.32 (t, J=7 Hz, 1H), 4.63 (AB system, $\Delta\delta$=0.067, J=11 Hz, 2H), 5.02–5.40 (m, 2H), 5.60–5.89 (m, 1H), 7.05–7.35 (m, 5H), 8.10–8.70 (m, 1H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=26.9, 28.4 (d, J=143 Hz), 51.6 (d, J=5.6 Hz), 73.2, 74.2, 78.7, 82.6 (d, J=12 Hz), 109.2, 118.8, 127.6, 128.0, 128.2, 136.2, 138.0 ppm. ^{31}P NMR (101.2 MHz, $CDCl_3$): δ=32.0 ppm. IR ($CDCl_3$ solution): ν 3401, 2981, 1647, 1116.6, 1215, 1054, 987 cm^{-1}. HRMS (ESI): [M$^+$+Na] calcd for $C_{17}H_{25}NaO_6P$: 379.1286. Found: 379.1290.

4.22. (3a*S*,9a*S*)-9-(Benzyloxy)-4-bromo-2,2-dimethyl-7-methoxy-hexahydro-3a*H*-[1,3]dioxolo[4,5-*e*][1,2]oxaphosphocine 7-oxide 20

The reaction was carried out following the method reported for the preparation of phostone **16**. Starting from the major diastereomer of phosphonate **19**, a mixture of two diastereomers of **20** was obtained (60:40), from which the less polar diastereomer could be obtained in pure form. Less polar diastereomer: ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.38 (s, 3H), 1.44 (s, 3H), 1.95–2.45 (m, 2H), 3.67 (d, J=9 Hz, 3H), 4.00–4.20 (m, 3H), 4.22–4.40 (m, 2H), 4.49 (dd, J=2.5 and 7 Hz, 1H), 4.67 (AB system, $\Delta\delta$=0.3, J=12 Hz, 2H),

7.22–7.34 (m, 5H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=26.1 (d, J=130 Hz), 26.6, 26.8, 51.4 (d, J=2 Hz), 52.0 (d, J=7 Hz), 66.9 (d, J=7 Hz), 71.1 (d, J=4 Hz), 74.2, 79.3, 80.4, 109.4, 127.7, 127.9, 128.4, 137.8 ppm. ^{31}P NMR (101.2 MHz, $CDCl_3$): δ=25.8 ppm. IR ($CDCl_3$ solution): ν 1641, 1471, 1261, 1212, 1042, 650 cm^{-1}. HRMS m/z calcd for $C_{17}H_{24}BrNaO_6P$: 457.0392. Found: 457.0392. $[\alpha]_D^{23}$ +4 (c 0.35, $CHCl_3$). More polar diastereomer (from the mixture): ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.35 (s, 3H), 1.37 (s, 3H), 1.99–2.42 (m, 2H), 3.66 (d, J=11 Hz, 3H), 4.00–4.20 (m, 6H), 4.51–4.74 (m, 2H), 7.19–7.35 (m, 5H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=26.6, 26.8, 27.9 (d, J=136 Hz), 50.8 (d, J=3 Hz), 51.7 (d, J=7 Hz), 66.5 (d, J=4 Hz), 72.6 (d, J=4 Hz), 72.9, 78.9, 81.8, 108.3, 127.6, 127.9, 128.4, 137.5 ppm. ^{31}P NMR (101.2 MHz, $CDCl_3$): δ=27.9 ppm. IR ($CDCl_3$ solution): ν 2992, 1639, 1462, 1255, 1050 cm^{-1}. HRMS (ESI): [M$^+$+Na] calcd for $C_{17}H_{24}BrNaO_6P$: 457.0392. Found: 457.0391. When the reaction was carried out with a mixture (2:1) of the two diastereomers of compound **19**, an inseparable mixture (33:33:17:17) of four diastereomers of compound **20** was obtained.

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