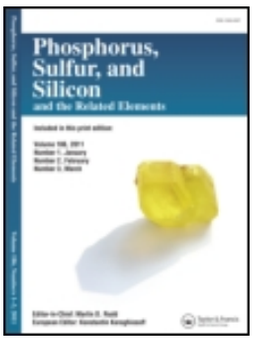


Taylor & Francis
Taylor & Francis Group

Phosphorus, Sulfur, and Silicon and the Related Elements

ISSN: 1042-6507 (Print) 1563-5325 (Online) Journal homepage: http://www.tandfonline.com/loi/gpss20

Reaction of C-silyl-P-chloro-alkylidenephosphoranes with carbonyl compounds

Olga O. Kolodiazhna & Oleg I. Kolodiazhnyi

To cite this article: Olga O. Kolodiazhna & Oleg I. Kolodiazhnyi (2016) Reaction of C-silyl-P-chloro-alkylidenephosphoranes with carbonyl compounds, Phosphorus, Sulfur, and Silicon and the Related Elements, 191:2, 322-328, DOI: 10.1080/10426507.2015.1054932

To link to this article: http://dx.doi.org/10.1080/10426507.2015.1054932

Accepted author version posted online: 02 Dec 2015.

PHOSPHORUS, SULFUR, AND SILICON
2016, VOL. 191, NO. 2, 322–328
http://dx.doi.org/10.1080/10426507.2015.1054932

Taylor & Francis
Taylor & Francis Group

Reaction of C-silyl-P-chloro-alkylidenephosphoranes with carbonyl compounds

Olga O. Kolodiazhna and Oleg I. Kolodiazhnyi

Institute of Bioorganic Chemistry and Petrochemistry of National Academy of Sciences of Ukraine, Kiev, Ukraine

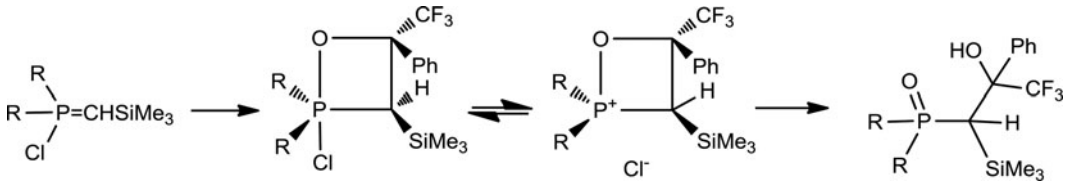
ABSTRACT

Reaction of P-chloroylides with carbonyl compounds leads to the formation of four-membered phosphorus heterocycles—2λ^5-chloro-2,2-oxaphosphetanes. The 2-chloro-2,2-oxaphosphetanes depending on substituent R at α-atom carbon, rearrange with formation of 2-chloroalkylphosphonates (R = H, Alk, Ar) or with elimination of trimethylchlorosilane (R = Me_3Si) convert into trans-phosphorylated alkenes.

ARTICLE HISTORY
Received 21 March 2015
Accepted 2 May 2015

KEYWORDS
C-silylated alkylphosphonites; C-silyl-P-ylides; 1,2λ^5-oxaphosphetanes; vinylphosphonates; dienephosphonates; vinylphosphine oxides

GRAPHICAL ABSTRACT



Introduction

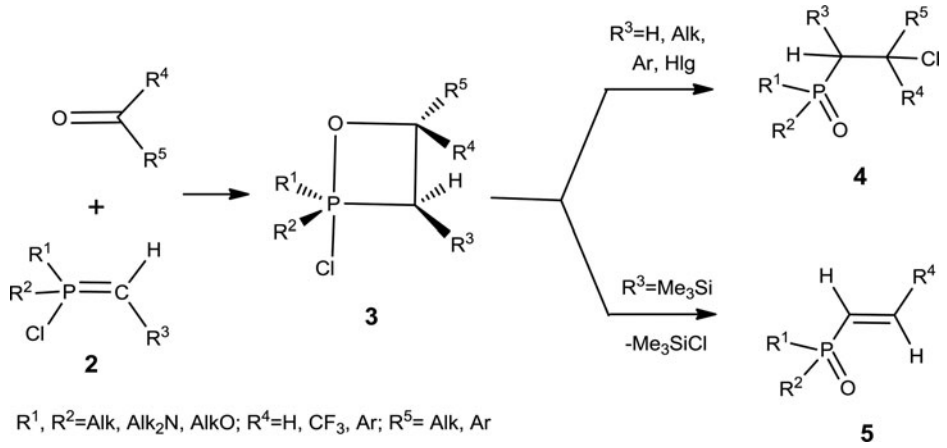
Phosphorus ylides play important roles in modern organic synthesis due to their wide spectrum of synthetic applications.[1–3] Among the different classes of phosphorus ylides, P-halogeneylides are versatile and powerful tools for the synthesis of various compounds.[3,4] P-halogenylides exhibit specific properties which permit to prepare from them synthetically important compounds unavailable through the use of triphenylphosphonium ylides.[5] For example, phosphorus ylides containing chlorine atoms at the phosphorus atom, so-called P-chloroylides, have attracted chemist's attention by their availability, and high reactivity, as well as by interesting chemical properties. [4a,5a] The labile chlorine atom at the phosphorus determine unusual properties of these compounds that are interesting in theoretical, and in preparative relations.[5]

Result and discussion

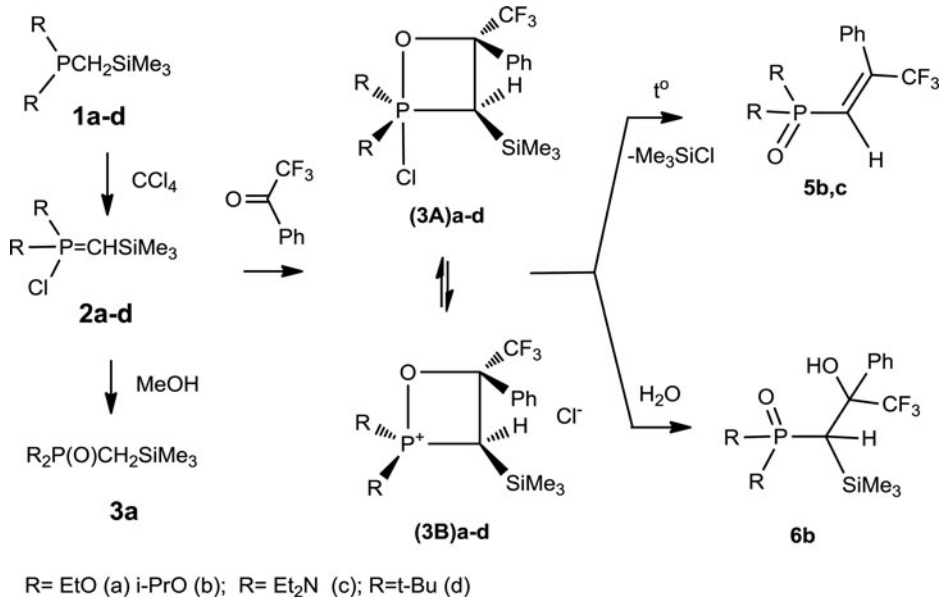
C-Silyl-P-chloroylides **2**, which possess high stability, owing to stabilizing effect of trimethylsilyl group represents the particular interest. The ylides **2** can be obtained by reaction of alkylphosphonites **1** with CCl_4.[6] They were purified by distillation under vacuum and isolated as pure compounds. The ylides **2** represent fuming, flammable on air colorless liquids and very active compounds in the chemical relation. They enter into various chemical transformations. They react with methanol converting into trimethylsilylphosphonates and enter to the [2+2]-cycloaddition reaction with carbonyl compounds with formation of 2-chloro-1,2λ^5-oxaphosphetanes—in general case unstable intermediates.[7] The stability of 2-chlorooxaphosphetanes depends on nature of substituents at C-4 atoms. The 2-chloro-1,2λ^5-oxaphosphetanes bearing H, Alk, or Ar at C-4 atom are unstable, though can be registered by NMR at low temperature. In this case, oxaphosphetanes rearrange to convert into 2-cloroalkylphosphonates **4**.[5d] At the same time, oxaphosphetanes bearing trimethylsilyl group at C-3 atom with elimination of trimethylchlorosilane converted into phosphorylated alkenes **5** (Scheme 1).

The oxaphosphetanes **3a-d** bearing electronegative CF_3 substituent at C-4 are more stable and can be isolated and analyzed by NMR (Scheme 2). For example, the oxaphosphetanes **3a-d** were isolated and their structures were confirmed by NMR spectroscopy and chemical reactions. The NMR spectra of these compounds reveal signals at 0.15–0.20 ppm, singlet (Me_3Si), at 5.4 ppm (PCH), at 7.3–7.8 (aromatic protons).[8–11] The ^{31}P NMR signals of 2-chloro-1,2λ^5-oxaphosphetanes **3a-d** at δ_P +48 ppm (**3**, R^1 = i-PrO) and at δ_P = +60 ppm (**3**, R^1 = Et_2N) respond to tetracoordinate phosphorus included in four-membered phosphetane cycle.[12,13] It is interesting that the δ_P of 2-chloro-1,2λ^5-oxaphosphetane **3d** (R = t-Bu) depends on polarity of solvent (Table 1). In nonpolar solvents

CONTACT Oleg I. Kolodiazhnyi olegkol321@rambler.ru Institute of Bioorganic Chemistry, Murmanskaia Street, 1, Kyiv 02094, Ukraine.



Scheme 1. Convertions of 2-chloro-1,2λ^5-oxaphosphetanes **3**.



Scheme 2. Chemical properties of 2-chloro-1,2λ^5-oxaphosphetanes **3a-d**.

(hexane), the $\delta_P = 10$ ppm of **3d** is typical for phosphorane P(V)-structures. In medium-polar solvents (chloroform, acetonitrile), the δ_P are shifted to weak fields, +40 to +50 ppm, because of oxaphosphetane dissociation **3A** ⇌ **3B**. The addition of chloride aluminium into a solution of oxaphosphetane shifts the value δ_P to +100 ppm, because of full ionization of 2-chloro-1,2λ^5-oxaphosphetane **3d** with formation of tetracoordinated P(IV) structure (see[5f]).

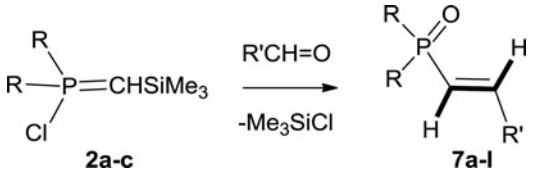
The 2-chloro-1,2λ^5-oxaphosphetanes **3a-d** after evaporation of solvent were obtained as colorless oils. The compounds **3a-d** at room temperature slowly, and at heating faster, eliminates trimethylchlorosilane to convert into alkenephosphonates **5**, which were isolated in good yields and were purified by distillation under vacuum. The 2-chloro-1,2λ^5-oxaphosphetanes not containing CF_3 group are unstable, though in certain cases they were registered by means of ^{31}P NMR spectroscopy. For example, the oxaphosphetane **3b** (R^1 = i-PrO, R^2 = H) was registered by signal at δ_P +40 ppm, which disappeared in course of reaction, and instead of this signal a new signal at δ_P +17 ppm was registered. This signal belongs to vinylphosphonate **5b** which was isolated and analyzed. At heating (40–50°C) the **3b** converts readily and completely into a corresponding vinylphosphonate **5**. The oxaphosphetane **3b** in aqueous ether in the presence of triethylamine was hydrolyzed with formation of crystalline 2-trifluoromethyl-2-hydroxyphosphonate **6b** in good yield.

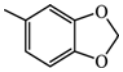
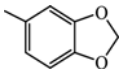
Table 1. Effect of solvents on the δ_P of 2-chloro-1,2λ^5-oxaphosphetane **3d**.

Solvent	Pentane	CCl_4	$CDCl_3$	CD_3CN	$CDCl_3/AlCl_3$
δ_P	10.05	12.0	40.0	50.1	102.1

The P-chloroylides **2** react with carbonyl compounds at equimolecular ratio of reagents in ether solution or without solvent to give alkenes **7a-l** in good yield. The course of reaction was monitored by TLC or NMR. The reaction products were purified by distillation under vacuum or by column chromatography with silica gel. The reaction can be carried out as a one pot two-step synthesis starting from phosphines, CCl_4 and aldehydes without the isolation of ylides. This reaction is a convenient method for the preparation of phosphorylated *trans*-alkenes (Table 2).

Table 2. The synthesis of phosphorylated alkenes **7a-l**.



			Reaction conditions				
Entry	R	R′	Time (h)	(t°C)	Solvent	Product	Yield (%)[a]
1	t-Bu	Ph	0.5	150	[b]	**7a**	80
2	EtO	Ph	2	25–100[e]	Ether	**7b**[c]	80
3	EtO	2-BrC_6H_4	6–8	25–100[e]	Ether	**7c**[d]	60
4	i-PrO	Ph	2	25–100[e]	Ether	**7d**[d]	60
5	Et_2N	Ph	14	25	Ether	**7e**	80
6	Et_2N	2-FC_6H_4	24	25	Ether	**7f**	60
8	Et_2N	CH = CHPh	18	25	Ether	**7g**	80
9	Et_2N		24	25	THF	**7h**	70
9	EtO		48	35	THF	**7i**	65
10	Et_2N	C_6H_4CHO-p	25	18	THF	**7j**	50
11	Et_2N	$R_2P(O)CH = CHC_6H_4$	25	24	THF	**7k**	50
12	i-PrO	$R_2P(O)CH = CHC_6H_4$	25	24	THF	**7l**[e]	50

a) Yield of the isolated product; (b) without solvent; (c) ref.[16–18]; (d) ref.[18,19]; (e) ref.[20]; (f) ref.[21].
(e) After evaporation of solvent the reaction mixture was heated up to 100°C.

The assignment of the stereochemistry of the double bond of diethyl *E*-1-alkenylphosphonates **7a-l** was based on the values of vicinal proton–proton ($^3J_{HH}$) and proton–phosphorus ($^3J_{HP}$) coupling constants. Thus, the values of constants $^3J_{HH}$ = 17–18 Hz and $^3J_{HP}$ = 18–22 Hz for *E*-1-alkenylphosphonates **7a-l**, whereas for Z-7 vicinal-coupling constants $^3J_{hh}$ = 11–14 Hz, and $^3J_{HP}$ are around 47–51 Hz. These results are in agreement with the literature data.[14–19] The *trans*-vinylphosphonates **7a-d, 7l** were earlier synthesized by other methods and their spectroscopic and physical data are identical to those reported in the references cited.[15–19]

The reaction of ylides with aldehydes is regioselective. For example, the reaction of **2c** with terephthalic aldehyde depending on a ratio of initial reactants led to the formation of 1,4-bis-vinylphosphonobenzene **7k,l** or phosphonovinylbenzaldehydes **7j**, that represent interest as reactants for organic synthesis.

Conclusion

In conclusion, we have studied the reaction of C-silyl-P-chloroylides **2** with aldehydes leading to the formation of 2-chloro-1,2λ^5-oxaphosphetanes **3**. The 2-chloro-1,2λ^5-oxaphosphetanes **3** were registered by NMR. The compounds **3**, depending on substituent R at α-carbon atom, rearranged to 2-chloroalkylphosphonates 4 (R = H, Alk, Ar) or with elimination of trimethylchlorosilane (R = Me_3Si) converted into *trans*-phosphorylated alkenes **5**. The reaction is a convenient method for the preparation of phosphorylated alkenes and can be useful for fine organic synthesis.[22]

Experimental

^{1}H and ^{13}C NMR spectra were recorded a Varian VXR-300 (300 MHz for ^{1}H, 60 MHz for ^{13}C, 126.16 (^{31}P) MHz) spectrometer relative to Me_4Si (^{1}H, ^{13}C) or 85% H_3PO_4 (^{31}P) using $CDCl_3$ as solvent. Coupling constants (*J*) are reported in Hertz (Hz). Analytical TLC was carried out on Merck Silica gel 60 F_{254} plates with detection by UV light, anisaldehyde stain solution. Solvents were preliminarily distilled in an inert atmosphere: diethyl ether, hexane, benzene, and carbon tetrachloride over phosphorus pentoxide, methanol, and triethylamine over sodium, and ethyl acetate over calcium chloride. Reagents were purchased from Merck (Germany), Fluka (Buchs, Switzerland), and Acros and were used without further purification. Melting points are uncorrected.

Diethyl trimethylsilylmethylphosphonite (1a)

A solution of trimethylsilylmethylenemagnesium chloride (0.1 mol) in diethyl ether was added at −20°C and stirring to a solution of diethylchlorophosphite (0.1 mol) in diethyl ether (ca.100 mL) After complete addition, the reaction mixture was heated to room temperature and the mixture was stirred for 1 h, a precipitate of magnesium dichloride was filtered off. After filtration, residual $MgCl_2$ was washed thoroughly with ether (3 × 30 cm^3), the extracts were combined and solvent was removed under reduced pressure to afford crude phosphonite **1a**. Distillation at reduced pressure yields pure **1a** as a colorless liquid. Bp 85–90°C (12 mmHg). Yield 75%. ^{1}H NMR ($CDCl_3$): δ 0.01 s (9H, CH_3Si); 1.32 d.t ($^3J_{HH}$ = 6.5 Hz, $^3J_{PH}$ = 1.0 Hz, 6H, CH_3); 1.50 d ($^3J_{PH}$ = 13 Hz, 2H, PCH_2); 3.90 m (4H, OCH_2). ^{31}P NMR ($CDCl_3$), δ_P 184.9 ppm.[6]

Anal. Calcd for $C_8H_{21}O_2PSi$: C, 46.13; H, 10.16; P, 14.87. Found: C, 46.45; H, 10.32; P, 14.61.

Diisopropyl (trimethylsilyl)methylphosphonite (1b)

The phosphonite **1b** was prepared from $(i\text{-PrO})_2PCl$ and trimethylsilylmethylenemagnesium chloride analogously to **1a**. Yield 75%, bp 80–90°C (12 mmHg). ^1H NMR ($CDCl_3$): δ 0.01 s (9H, CH_3Si); 1.40 d ($^3J_{PH}$ = 15 Hz, 2H, PCH_2); 1.25 d.d ($^3J_{HH}$ = 6.0 Hz, $^3J_{PH}$ 1.0, 12H, CH_3); 4.20 m (2H, OCH). ^{31}P NMR ($CDCl_3$): δ_P 185.0 ppm.

Anal. Calcd for $C_{10}H_{25}O_2PSi$: C 50.81; H 10.66; P 13.10. Found: C 50.99; H 10.88; P 12.91.

Bis(diethylamido) trimethylsilylmethylphosphonite (1c)

The phosphonite **1c** was prepared from $(Et_2N)_2PCl$ and trimethylsilylmethylenemagnesium chloride analogously to **1a**. Yield 65%, bp 110°C (10 mmHg). ^{13}C NMR ($CDCl_3$): δ −0.1 d ($^3J_{PC}$ = 7 Hz, CH_3Si); 14.5 d ($^1J_{PC}$ = 28 Hz, PC); 15.1 d ($^3J_{PC}$ = 5.0, CH_3); 43.3 d ($^2J_{PC}$ = 15.0, NC). ^{31}P NMR ($CDCl_3$): δ_P 85.7 ppm.

Anal. Calcd for $C_{12}H_{31}N_2PSi$: C, 54.92; H, 11.91; P, 11.80. Found: C, 54.09; H, 11.96; P, 11.87.

Di-tert-butyl(trimethylsilylmethyl)phosphine (1d)

To a solution of di-tert-butylchlorophosphine (0.1 mol) in pentane (ca.100 mL) in a flask equipped with a water-cooled reflux condenser was added a solution of trimethylsilylmethyllithium (0.1 mol) in pentane at −20°C and stirring. After complete addition, the reaction solution was refluxed for 1.5 h, then the reaction mixture was cooled to room temperature and the mixture was filtered off. After filtration, residual LiCl was washed thoroughly with hexane (3×30 cm^3), the extracts combined and solvent removed under reduced pressure to afford crude phosphine. Distillation at reduced pressure yields pure **1d** as a colorless liquid. Bp 100–104°C (10 mmHg). Yield 75%. ^1H NMR ($CDCl_3$): δ −0.01 s (9H, CH_3Si); 1.15 d ($^3J_{PH}$ = 10 Hz, 18H, CH_3); 1.70 d ($^3J_{PH}$ = 15 Hz, 2H, PCH_2). ^{31}P NMR ($CDCl_3$): δ_P −37.6 ppm.

Anal. Calcd for $C_{12}H_{29}PSi$: C 62.01; H 12.50; P 13.33. Found: C 62.42; H 12.95; P 13.01.

Diethoxychlorphosphonium trimethylsilylmethylide (2a)

In a flask equipped with a magnetic stirrer was placed a solution of diethyl trimethylsilylmethylphosphonite (0.02 mol) in diethyl ether (20 ml), and the carbon tetrachloride (0.04 mol) was added dropwise at stirring and cooling to −70°C. Then, the solvent was removed under reduced pressure to afford crude ylide. The distillation at reduced pressure yields pure **2a** as a colorless liquid. Yield 70%, bp 60°C (0.06 mmHg).[6]

^1H NMR ($CDCl_3$): δ 0.01 d ($^4J_{PH}$ = 0.3 Hz, 9H, CH_3Si); 0.50 d ($^3J_{PH}$ = 3 Hz, 1H, P = CH); 1.25 d.d ($^3J_{HH}$ = 6.5 Hz, $^3J_{PH}$ = 1.0, 6H, CH_3); 4.20 m (4H, OCH_2). ^{13}C NMR (C_6D_6): δ 0.85 d ($^3J_{PC}$ = 6.0 Hz, CH_3Si); 15.00 d ($^1J_{PC}$ = 160 Hz, P = C); 21.30 d ($^3J_{PC}$ = 6 Hz, CH_3C); 71.55 d ($^2J_{PC}$ = 9 Hz, OCH). ^{31}P NMR ($CDCl_3$): δ +65.00 ppm.

Diisopropoxychlorphosphonium trimethylsilylmethylide (2b)

In a flask with a magnetic stirrer was placed a solution of diisopropyl (trimethylsilyl)methylphosphonite (0.02 mol) in 20 mL of diethyl ether and at cooling to −70°C. the carbon tetrachloride (0.04 mol) was added dropwise. Then, the reaction mixture was heated to room temperature and was stirred for 3 h. The solvent was evaporated and the residue was distilled under vacuum. Yield 80%, bp 65°C (0.06 mmHg). ^1H NMR ($CDCl_3$): δ 0.30 d ($^4J_{PH}$ = 0.3 Hz, 9H, CH_3Si); 0.48 d ($^3J_{PH}$ = 3 Hz, 1H, P = CH); 1.65 d.d [$^3J_{HH}$ = 6.5 Hz, $^3J_{PH}$ = 1.0 Hz, 12H $(CH_3)_2CH$]; 4.92 m (2H, OCH). ^{13}C NMR (C_6D_6): δ 0.89 d ($^3J_{PC}$ = 6.0 Hz, CH_3Si); 15.00 d ($^1J_{PC}$ = 155 Hz, P = C); 21.30 d ($^3J_{PC}$ = 6 Hz, CH_3C); 71.55 d ($^2J_{PC}$ 9 = Hz, OCH). ^{31}P NMR ($CDCl_3$): δ_P +59.00 ppm.

Anal. Calcd for: $C_{10}H_{24}ClO_2PSi$: Cl 13.09; P 11.44%. Found: Cl 12.79; P 11.58.

Bis(diethylamino)chlorphosphonium trimethylsilylmeth ylide (2c)

In a flask with a magnetic stirrer was placed a solution of bis(diethylamino) (trimethylsilyl)methylphosphonite (0.02 mol) in diethyl ether (20 mL) and dropwise the carbon tetrachloride (0.04 mol) was added at cooling to −70°C. Then, the reaction mixture was heated to room temperature and was stirred for 0.5 h. The solvent was evaporated and the residue was distilled under vacuum. Yield 70%, bp 105°C (0.08 mmHg). ^1H NMR ($CDCl_3$): δ 0.03 d ($^4J_{PH}$ = 0.3 Hz, 9H, 9H, CH_3Si); 1.30 d ($^3J_{PH}$ = 3 Hz, 1H, P = CH); 1.41 t ($^3J_{HH}$ = 6.5 Hz, 12H, CH_3); 3.54 m (8H, OCH_2). ^{13}C NMR (C_6D_6): δ 2.16 d ($^3J_{PC}$ = 6.0 Hz, CH_3Si); 12.64 s (CH_3); 20.30 d ($^1J_{PC}$ = 144 Hz, P = C); 39.60 d ($^3J_{PC}$ = 4.0 Hz, CH_2N). ^{31}P NMR ($CDCl_3$): δ_P +75.6 ppm.

2-Chloro-2,2-bis(diethylamino)-2,2-dihydro-4-phenyl-4-(trifluoromethyl)-3-(trimethylsilyl)-1,2λ5-oxaphosphetane (3c)

To a solution of bis(diethylamino) trimethylsilylmethylchlorophosphorane (0.02 mol) in diethyl ether (20 mL), was added CCl_4 (0.04 mol) dropwise, at stirring and cooling to −70°C. Then, the reaction mixture was heated to room temperature and was stirred for 20 min. The 2,2,2-trifluoroacetophenone (0.025 mol) was added to the solution and the reaction mixture was stirred for 1–2 h. The course of reaction was monitored by ^{31}P NMR. The solvent was removed under vacuum and at temperature below 0°C. Yield ∼ 90%. Yellowish oil. ^1H NMR ($CDCl_3$): δ 0.15 C (9H, CH_3Si); 1.10 t ($^3J_{HH}$ = 7.0 Hz, 12H, CH_3C); 3.20 m (8H, NCH_2); 5.4 d ($^2J_{PH}$ = 16.0 Hz, 1H, PCH); 7.30 m; 7.80 m (5H, C_6H_5). ^{19}F NMR ($CDCl_3$): δ_F −70.40. ^{31}P NMR ($CDCl_3$): δ_P +60 ppm.

2-Chloro-2,2-diisopropoxy-2,2-dihydro-4-phenyl-4-(trifluoromethyl)-3-(trimethylsilyl)-1,2λ5-oxaphosphetane (3b)

The oxaphosphetane **3b** was prepared from diisopropyl trimethylsylilmethylphosphonite **1b**, CCl_4 and 2,2,2-trifluoroacetophenone analogously to **3c**. Yield 90%, oil.

^{1}H NMR ($CDCl_3$): δ: 0.20 s (9H, CH_3Si); ·0.90 d ($^3J_{HH}$ = 6.0 Hz, 12H, CH_3C); 1.95 d ($^2J_{PH}$ = 18.0 Hz, 1H, PCH); 4.20 m (2H, OCH); 7.30 m; 7.80 m (5H, C_6H_5). ^{19}F NMR ($CDCl_3$), δ_F −68.40. ^{31}P NMR ($CDCl_3$): δ_P +48.3 ppm.

Diisopropyl 2-phenyl-2-(trifluoromethyl) ethenylphosphonate (5b)

Oxaphosphetane **3b** was heated at 60°C for 0.5 h, then the reaction mixture was distilled under vacuum. Yield 77%, bp 130 (0.07 mmHg). The mixture of *E* and *Z*-isomers is in ratio 7:1. We suppose that the major isomer is *E*-alkene **5b**, because δ_H of vinyl proton and δ_P of this compound are shifted to down field relative to those of minor *Z*-isomer (in all ^{31}P NMR spectra, the signals of the Z-isomers **5** appear at higher field than the ones of the *E*-5).[12,13,22,23a–c]

(*E*-isomer): ^{1}H NMR ($CDCl_3$): δ 1.03 d ($^3J_{HH}$ = 6.4 Hz, 6H, CH_3C); 1.12 d ($^3J_{HH}$ = 6.2 Hz, 6H, CH_3C); 4.45 m (2H, OCH); 6.44 d.q ($^4J_{FH}$ = 1.5 Hz, $^2J_{PC}$ = 12.0 Hz, 1H, PCH = C); 7.30 m (5H, C_6H_5). ^{19}F NMR ($CDCl_3$), δ_F −68.40. ^{31}P NMR ($CDCl_3$): δ_P 9.3 ppm.

(*Z*-isomer): ^{1}H NMR ($CDCl_3$): δ 1.28 d ($^3J_{HH}$ = 6.5 Hz, 6H, CH_3C); 1.32 d ($^3J_{HH}$ = 6 Hz, 6H, CH_3C); 4.75 m (2H, OCH); 6.20 d ($^2J_{PH}$ = 8.8 Hz, 1H, PCH = C); 7.30 m (5H, C_6H_5). ^{31}P NMR ($CDCl_3$): δ_P 7.68 ppm.

Anal. Calcd for: $C_{15}H_{20}F_3O_3P$: C 53.57; H 5.99; P 9.21. Found C 54.27; H 5.95; P 9.43.

Bis(diethylamid) 2-phenyl-2-(trifluoromethyl)ethenylphosphonate (5c)

The vinylphosphonate **5c** was prepared from **1c** analogously to **5a**. Yield 70%, b.p. 150°C (0.07 mmHg). ^{1}H NMR ($CDCl_3$): δ 1.38 t ($^3J_{HH}$ = 7 Hz, 12H, CH_3); 3.27 d.q ($^3J_{PH}$ = 10 Hz, 8H, CH_2N); 6.80 d.q ($^2J_{PH}$ = 12 Hz, $^4J_{HF}$ = 1.5 Hz, 1H, C = CH); 7.60 m (5H, C_6H_5). ^{19}F NMR ($CDCl_3$): δ_F −68.11. ^{31}P NMR ($CDCl_3$): δ_P 23.50; 16.20 ppm.

Anal. Calcd for: $C_{17}H_{26}F_3N_2OP$: C 56.35; H 7.23; P 8.55. Found, %: C 56.35; H 7.23; P 8.55.

Diisopropyl (1–trimethylsilyl-2-hydroxyphenyl-3,3, 3-trifluoro)propylphosphonate (6b)

Yield 80%, bp 118°C (0.04 mmHg). ^{1}H NMR ($CDCl_3$): δ 0.5 s (9H, CH_3Si); 0.92 m (12H, CH_3C); 2.82 d ($^2J_{PH}$ = 21.0 Hz, 1H,); 2.87 d ($^2J_{PH}$ = 20.0 Hz, 1H, PCH): 4.48 m; 4.85 m (CHO+OH), 7.17–7.51 m (5H, C_6H_5). ^{19}F NMR ($CDCl_3$): δ_F −77.60. ^{31}P NMR ($CDCl_3$): δ_P +18.70 ppm.

Anal. Calcd for: $C_{18}H_{30}F_3O_4P$. C 50.69; H 7.09. Found C 49.97; H 6.89.

Di-tert.–butyl(2-phenylethenyl)phosphine oxide (7a)

The ylide (I) (0.01 mol) was mixed with benzaldehyde (0.01 mol) and the mixture was heated at 150°C for 30–40 min to the end of trimethylchlorosilane emission. The residue was cooled and recrystallized from heptane. Yield 80%, mp 138°C (heptane).

^{1}H NMR ($CDCl_3$): δ 1.53 d ($^3J_{HH}$ = 13.7 Hz, 9H,CH_3C); 7.08 d.d ($^3J_{HH}$ = 18 Hz, $^2J_{PH}$ = 22.5 Hz, 1H, PCH = C); 7.95 d.d ($^3J_{HH}$ = 18 Hz, 1H, C = CH); 7.8 m (5H, C_6H_5). ^{31}P NMR ($CDCl_3$): δ 50 ppm.

Anal. Calcd for: $C_{16}H_{25}OP$. C 72.70; H 9.53; P 11.72%. Found: C 72.70; H 9.53; P 11.72%

Diethyl (E)-(2-phenylethenyl)phosphonate (7b)

7b was prepared analogously to 7**a**.

Yield 60%, bp 122°C (0.06 mmHg).[13–15] ^{1}H NMR ($CDC1_3$): δ 1.28 t ($^3J_{HH}$ = 7.0 Hz, 3H); 1.30 t ($^3J_{HH}$ = 7.0 Hz, 3H, CH_3); 4.15 d.q ($^3J_{HH}$ = 7.0 Hz, $^3J_{PH}$ = 11.0 Hz, 4H, OCH_2), 6.30 d.d ($^3J_{HH}$ = 17.2 Hz, $^2J_{PH}$ = 17.2 Hz, lH, CH = C), 7.10 d.d ($^3J_{HH}$ = 17.2 Hz, $^3J_{PH}$ = 22 Hz, 1H, C = CH), 7.10–7.40 m (5H, C_6H_5). ^{13}C NMR ($CDCl_3$): δ 16.30, 61.6 d ($^2J_{CP}$ = 6 Hz), 110.70 d ($^1J_{CP}$ = 190 Hz, CH), 128.00, 129.00, 131.10, 136.10, 149.20 d ($^2J_{CP}$ = 6.1 Hz, CH). ^{31}P NMR ($CDCl_3$): δ_P +18.00 ppm.

Diethyl (E)-[2-(2-bromphenyl)ethenyl]phosphonate (7c)

The vinylphosphonate **7c** was prepared from **1b** analogously to **7b**. Yield 75%, mp 82°C (ref.[16] mp 82°C).

^{1}H NMR ($CDC1_3$): δ 1.29 t ($^3J_{HH}$ = 7.0 Hz, 6H, CH_3). 4.07 m ($^3J_{HH}$ = 7.5 Hz, 4H, CH_2O); 6.18 d.d ($^3J_{HH}$ = 17.5 Hz, $^2J_{HP}$ = 17.0 Hz, 1H, PCH = C); 7.30 d ($^3J_{HH}$ = 8.5 Hz, 2H, C_6H_4); 7.37 d.d ($^3J_{HH}$ = 17.5 Hz, $^3J_{HP}$ = 18.2 Hz, 1H, PC = CH); 7.46 d ($^3J_{HH}$ = 8.5 Hz, 2H, o-BrC_6H_4). ^{13}C NMR (C_6D_6): δ 16.40, d (J_{PC} = 7.0 Hz, CH_3); 61.90 d ($^2J_{PC}$ = 5.6 Hz, CH_2O); 114.80 d ($^2J_{PH}$ = 192.0 Hz, P<u>C</u> = C); 124.40; 128.50; 132.60; 133.70 d ($^3J_{PC}$ = 24.0 Hz), 147.30 d ($^2J_{PC}$ = 6.9 Hz, PC = <u>C</u>). ^{31}P NMR ($CDCl_3$): δ_P +19.06 ppm.

Anal. Calcd for: C_{12} H_{16} BrO_3P. C 45.16; H 5.05; P 9.71. Found: C 45.22; H 9.65; P 11.42.

Diisopropyl (E)-(2-phenylethenyl)phosphonate (7d)

The vinylphosphonate **7d** was prepared analogously to **7b**. Yield 60%, b. p.122°C (0.06 mmHg).[13] ^{1}H NMR ($CDC1_3$): δ 1.24 d.d ($^3J_{HH}$ 6.0 Hz, $^3J_{PH}$ 2.5 Hz, 12H, CH_3C); 4.33 m (2H, OCH); 6.10 d.d $^3J_{HH}$ (17.5 Hz, $^2J_{PH}$ 18 Hz, 1H, PCH = C); 7.70 d.d ($^3J_{HH}$ 17.5 Hz, $^3J_{PH}$ 19 Hz, 1H, PC = CH); 7.10 m (5H, C_6H_5). ^{13}C NMR (C_6D_6): δ 23.60, 23.80; 70.21 d ($^2J_{CP}$ 6 Hz, 2H, OCH), 120.80 d ($^1J_{CP}$ 190 Hz), 128.35, 129.00, 131.10, 136.10, 149.20 d ($^2J_{CP}$ = 6.1 Hz, CH). ^{31}P NMR ($CDCl_3$): δ_P +16.00 ppm.

Bis(diethylamido) (E)-(2-phenylethenyl)phosphonate (7e)

To a solution of ylide **1c** (0.01 mol) at −70°C was added benzaldehyde (0.015 mol), the reaction mixture was heated to room temperature and the mixture was stirred for 14 h. The reaction mixture was evaporated in vacuo at +20°C, then the residue was heated at 100°C for 15 min under vacuum (0.05 mm Hg) and the residue was recrystallized in hexane. Yield 80%, mp 103.5°C. ^{1}H NMR ($CDCl_3$): δ 1.38 t (^{3}JHH 7 Hz, 12H, CH_3CH_2); 1.38 ·d.q (^{3}JHH 7 Hz, ^{3}JPH 11 Hz, 8H, CH_2N); 6.60 d.d ($^3J_{HH}$ 17.2 Hz, $^2J_{PH}$ 18 Hz, 1H, PCH = C); 7.75 d.d ($^3J_{HH}$ 17.5 Hz, $^3J_{PH}$ 19 Hz, 1H, C = CH); 7.65 m (5H, C_6H_5). ^{13}C NMR (C_6D_6): δ 13.70; 41.85; 114.50, d ($^1J_{PC}$ 152.0 Hz, PCH = C); 128.70; 131.66 d ($^2J_{PC}$ 24.0 Hz, PC = C), 144.17, 161.90 d ($^3J_{PC}$ 30 Hz). ^{31}P NMR ($CDCl_3$): δ_P +24.50 ppm.

Bis(diethylamid) (E)-[2-(2-fluorophenyl) ethenyl]phosphonate (7f)

Analogously to **7b**, the vinylphosphonate **7f** was prepared from **2c**. Yield 60%, b.p. 130°C (0.1 mmHg), m.p. 114°C (hexane). ^{1}H NMR ($CDC1_3$): δ 1.08 t ($^3J_{HH}$ 7.0 Hz, 12H, CH_3). 3.08 m ($^3J_{HH}$ 7.5 Hz, 4H, CH_2N); 6.25 d.d ($^3J_{HH}$ 17.5 Hz, $^2J_{HP}$ 17.0 Hz, 1H, PCH = C); 7.03 m (2H, C_6H_4); 7.40 d.d (1H, ^3J 17.5 Hz, $^3J_{HP}$ 18.0 Hz, PC = CH); 7.46 d (^3J 8.5 Hz, 2H, C_6H_4). ^{13}C NMR (C_6D_6): δ 13.77; 37.9; 114.50, 118.10 (d, $^1J_{PC}$ 152.0 Hz, P–CH = C); 128.70; 131.66 d ($^2J_{PC}$ 24.0 Hz, PC = C), 144.17, 161.90 d ($^2J_{CF}$ 247.5 Hz). ^{31}P NMR ($CDCl_3$): δ_P +19.06 ppm.

Anal. Calcd for $C_{16}H_{26}FN_2OP$: C 61.52; H 8.39; P 9.92. Found: C 61.81; H 8.42; P 9.61.

Bis(diethylamid) 4-phenyl-(1E,3E)-butadienylphosphonate (7g)

To a solution of ylide **1c** (0.02 mol) in diethyl ether (10 ml) was added cinnamic aldehyde (0.02 mol) at 0 to +5°. The mixture was left for 18 h at room temperature and then was evaporated under vacuum. Yield 70%, bp 170–175°C (0.06 mmHg). ^{1}H NMR ($CDCl_3$): δ 1.4 t ($^3J_{HH}$ 7 Hz, 12H, CH_3); 3.30 d.q ($^3J_{PH}$ 10 Hz, 8H, CH_2N); 6.30 m; 7.30 m (4H, CH = CH); 7.80 m (5H, C_6H_5). ^{31}P NMR ($CDCl_3$): δ_P +23.30 ppm.

Anal. Calcd. for $C_{18}H_{29}N_2OP$: C 67.47; H 9.12; P 9.67. Found C 67.77; H 9.20; P 9.66.

Bis(diethylamid) (E)-2-(1,3-benzodioxol-5-yl) ethenylphosphonate (7h)

The vinylphosphonate **7h** was prepared from **2c**, analogously to **7b**, bp 115–135°C(0.1 mmHg). The product was recrystallized in heptane at −20°C. ^{1}H NMR ($CDCl_3$): δ 1.08 t ($^3J_{HH}$ 7 Hz, 12H, CH_3); 3.07 m (4H, CH_2N); 5.96 s (2H, OCH_2O); 6.14 d.d ($^3J_{HH}$ 17 Hz, $^2J_{PH}$ 17.5 Hz, 1H, PCH = C); 6.78–7.32 m (6H, PC = CH + C_6H_5). ^{13}C NMR ($CDCl_3$): δ 13.86; 38.00, 100.94; 105.63, 107.97; 115.39, 116.63; 122.69, 129.93, 130.03; 145.00, 147.76, 148.32. ^{31}P NMR ($CDCl_3$), δ_P 24.00 ppm.

Anal. Calcd. for $C_{17}H_{27}N_2O_3P$: C 60.34; H 8.04; P 9.15. Found: C 60.66; H 8.21; P 9.05.

Diethyl [(E)-2-(1,3-benzodioxol-5-yl)ethenylphosphonate (7l)

Yield 65%; bp 135 (0.1 mmHg).[21]

^{1}H NMR ($CDCl_3$): δ = 1.30 t ($^3J_{HH}$ = 7.0 Hz, 6 H, CH_3CH_2); 4.23 m (2H, CH_2O), 4.28 m (2H, CH_2O); 6.00 s (2H, CH_2O_2); 6.1 d.d ($^3J_{HH}$ = 17.0 Hz, $^2J_{HP}$ = 17.0 Hz, 1H, PCH = C); 6.78–7.32 m (4H, PC = CH + C_6H_5). ^{13}C NMR ($CDCl_3$): δ = 16.2, 61.9, 101.25, 106.78, 109.2, 119.1 d ($^1J_{CP}$ = 185 Hz, PCH), 123.54, 130.94 d ($^3J_{CP}$ = 20.0 Hz), 147.9, 147.8, 150.1. ^{31}P NMR ($CDCl_3$): δ_P = 20.01 ppm.

Bis(diethylamid) (E)-[2-(4-formylphenyl) ethenyl]phosphonate (7j)

A solution of ylide **1c** (0.02 mol) in diethyl ether (10 ml) was added at stirring to a solution of terephthalic aldehyde (0.025 mol) in THF (3 mL) at 0°C. The reaction mixture was left for a night. Then, the solvent was evaporated under reduced pressure (10 mmHg). The residue was recrystallized in a mixture of ether/pentane at 0°C. Yield 50%, mp 92.5–94°C. After second recrystallization in hexane, mp 98°C. ^{1}H NMR ($CDCl_3$): δ 1.40 t (^3JHH 7 Hz, 12H, CH3CH); 3.41 dd (^3JHH 7 Hz, $^3J_{PH}$ 10.5 Hz, 8H, CH_2N); 8.10 d.d (4H, C_6H_4); 6.80 d.d ($^2J_{HH}$ 17.5 Hz, $^1J_{PH}$ 17.5 Hz, 1H, PCH = C); 7.85, d.d (^3JHH 17.5 Hz, $^3J_{PH}$ 19, 1H, C = CH); 8.00 d; 8.10 d ($^4J_{HH}$ 9 Hz, 4H, C_6H_4); 10.30 s (1H, C(O)H). ^{13}C NMR ($CDCl_3$): δ 14.01; 41.7 d (J 6 Hz); 105.2 d ($^1J_{PC}$ 160 Hz); 130.1; 131.5; 136.0; 142.5; 154.2 d ($^2J_{PC}$ 32 Hz); 191.5. ^{31}P NMR ($CDCl_3$): δ 23.7 ppm.

Anal. Calcd. for $C_{17}H_{27}N_2O_2P$: C 63.34; H 8.44; P 9.61. Found: C 63.13; H 8.41; P 9.52.

(1E,1′E)-Bis-1,4-(tetraethyldiamidophosphono) ethenyl)benzene (7k)

A solution of ylide **1c** (0.025 mol) in diethyl ether (10 ml) was added dropwise at −20°C to a solution of terephthalic aldehyde (0.01 mol) in THF. The temperature was raised to a room and the reaction mixture was left for a night. The solvent was evaporated, the residue was recrystallized in heptane to give a yellow crystalline product in yield of 50%. After second recrystallization in heptane mp 188.5–190°C. ^{1}H NMR ($CDCl_3$): δ 1.05 t (^3JHH 7, 24H, CH_3CH_2); 3.03 d.q (^3JHH 7 Hz, $^3J_{PH}$ 11, 16H, NCH_2); 6.33 d.d (^3JHH 17 Hz, $^2J_{PH}$ 17 Hz, 2H, PCH = C); 7.30 d.d ($^3J_{HH}$ 17 Hz, $^3J_{PH}$ 19 Hz, 2H, C = CH); 7.44 m (4H, C_6H_4). ^{13}C NMR ($CDCl_3$): δ 14.00 d ($^3J_{PC}$ 8 Hz); 41.80 d ($^2J_{PC}$ 6 Hz); 105.70 d ($^1J_{PC}$ 180 Hz, PCH =); 129.80; 137.70; 154.20 d ($^2J_{PC}$ 32 Hz). ^{31}P NMR ($CDCl_3$), δ_P 24.80 ppm. Anal. Calcd. for $C_{20}H_{48}H_2O_2P_2$: C 61.16; H 9.47; N 10.97. Found C 61.31; H 9.66; N10.85.

(1E,1′E)-Bis-1,4-(diisopropylphosphono)ethenyl)-benzene (7l)

7l was prepared analogously to **7k**. Yield 50%. Solid, mp 140–145°C (heptane).[20]

^{1}H NMR ($CDCl_3$): δ 1.25 d ($^2J_{HP}$ = 6.5 Hz, 12H, CH_3); 1.30 d ($^2J_{HP}$ = 6.5 Hz, 12H, CH_3), 4.6 m (4H, OCH), 6.16 dd ($^2J_{HP}$ = 17.0 Hz, $^3J_{HH}$ 17.0 Hz, 2H, PCH = C), 7.30 d.d ($^3J_{HP}$ = 22.3 Hz, $^3J_{HH}$ 17.0 Hz, 2H, C = CH), 7.44 s (4H, H-Ar). ^{13}C NMR ($CDCl_3$): δ 23.60; 23.80; 70.5; 120.0 d ($^1J_{PC}$ = 180.5 Hz), 130.0, 136.0 d ($^3J_{PC}$ = 25 Hz), 148.5. ^{31}P NMR ($CDCl_3$): δ 18.1 ppm.

References

1. Wittig, G. *Science* **1980**, 210, 600.
2. (a)Taillefer, M.; Cristau, H.-J. *Top. Curr. Chem.* **2003**, 229, 41-73; (b)Kolodiazhnyi, O. I. *Russ. Chem. Rev.* **1997**, 225-254; (c)A. E. Nako, A. J. P.; White, M. R.; Crimmin, M. R. *Chem. Sci.*, **2013**, 4, 691-695; (d)Maryanoff, B. E.; Reitz, A. B. *Chem. Rev.* **1989**, 89, 863-927; (e)Edmonds, M.; Abell, A. *The Wittig Reaction* In:T. Takeda (Ed.), *Modern Carbonyl Olefination: Methods and Applications*; Wiley-VCH: Weinheim, **2004**; pp. 1-17.
3. Kolodiazhnyi, O. I. *Phosphorus Ylides. Chemistry and Application in Organic Synthesis*. John Wiley-VCH: Weinheim, **1999**; 565 p.
4. (a)Kolodiazhnyi, O. I. *Tetrahedron Lett.* **1981**, *22*, 1231-1234; (b)Kolodiazhnyi, O. I.; Grishkun, E. V. *Heteroatom. Chem.*, **1998**, 9, 219-228; (c)Kolodiazhnyi, O. I. Hermann/Brauer. In:H. H. Karsch (Ed.), *Synthetic Methods of Organometallic and Inorganic Chemistry*,

Stuttgart: Thieme, **1996**, Vol. 3, p. 90. (d)Fluck, E.; Heckmann, G.; Plass, W.; Spahn, M.; Borrmann, H. *J. Chem. Soc, Perkin Trans*. 1, **1990**, 1223-1224; (e)Soleilhavoup, M.; Baceiredo, A.; Bertrand, G. *Angew. Chem., Int. Edit. Engl.* **1993**, 32, 1167-1169; (f)Igau, A.; Baceiredo, A.; Grutzmacher, H.; Pritzkow, M.; Bertrand, G. *J. Am. Chem. Soc.* **1989**, 111, 6853-6854.

5. (a)Kolodiazhnyi, O. I. *Rus. J. Gen. Chem*. **2005**, 75, 1017-1039; (b)Kolodiazhnyi, O. I.; Schmutzler, R. *Synlett* **2001**, 1065-1078; (c)Kolodiazhnyi, O. I.; Golokhov, D. B. *Russ. J. Gen. Chem*. **1989**, 59, 293-306; (d)Kolodiazhnyi, O. I. *Russ. J. Gen. Chem*. **1986**, 56, 283-298.
6. Kolodiazhnyi, O. I.; Golokhov D. B. *Russ. J. Gen. Chem*. **1987**, 57, 2640-2642.
7. Robiette, R.; Richardson, J.; Aggarwal, V. K.; Harvey, J. N. *J. Am. Chem. Soc*. **2006**, 128, 2394-2409.
8. Vedejs, E.; Marth. C. F. *J. Am. Chem. Soc*., **1990**, 112, 3905-3909
9. Bangerter, F.; Karpf, M.; Meier, L. A.; Rys, P.; Skrabal, P. *J. Am. Chem. Soc*. **1998**, 120, 10653-10659.
10. Lopez, J. G.; Ramallal, A. M.; Gonzalez, J.; Roces, L.; García-Granda, S.; Iglesias, M. J.; Ona-Burgos, P.; Ortiz. F. L. *J. Am. Chem. Soc*. **2012**, 134, 19504-19507.
11. Vedejs, E. *J. Org. Chem*. **2004**, 69, 5159-5167.
12. Kühl O. *Phosphorus-31 NMR Spectroscopy*; Springer: Berlin, **2008**; pp. 31-35.
13. Gorenstein, D. G. (Ed.). *Phosphorous-31 NMR Principles and Applications*. Academic Press: New York, **1984**; 604 p.
14. Lazrek, H.B.; Witvrouw, M.; Pannecouque, C.; De Clerq, E. *Tetrahedron* **1998**, 54, 3807-3816.
15. Zhong, P.; Xiong, Z. X.; Huani, X. *Synth. Commun*. **2000**, 30, 273-278.
16. Xu, Y.; Flavin, M. T.; Xu, Z.-Q. *J. Org. Chem*. **1996**, 61, 7697-7701.
17. Blaszczyk, R.; Gajda, T. *Heteroatom Chem*. **2007**, 18, 732-739.
18. Brunner, H.; Le Cousturier de Courcy, N.; Genêt, J.-P. *Synlett* **2000**, 201-204.
19. Al-Maksoud, W.; Mesnager, J.; Jaber, F.; Pinel, C.; Djakovitch, L. *J. Organometal. Chem*. **2009**, 694, 3222-3231.
20. Jouvin, K.; Coste, A.; Bayle, A.; Legrand, F.; Karthikeyan, G.; Tadiparthi, K.; Evano, G. *Organometallics*, **2012**, 31, 7933-7947.
21. Krawczyk, H.; Łukasz, A. *Synthesis* **2005**, No. 17, 2887-2896.
22. Keglevich G.; Szelke H.: *Alk-1-enyl Phosphorus Compounds*. In:Molander G. A. (Ed.), *Science of Synthesis*, Vol. 33; Thieme Verlag: Stuttgart, **2007**, pp. 737-771.
23. (a)Cristau, H-J.; Pirat, J-L.; Drag, M.; Kafarski, P. *Tetrahedron. Lett*. **2000**, 41, 9781-9785; (b)Cristau, H-J.; Mbianda, X. Y.; Beziat, Y.; Gasc, M. B. *J. Organomet. Chem*. **1997**, 529, 301-311; (c)Sainz-Dıaz, C. I.; Galvez-Ruano, E.; Hernandez-Laguna, A.; Bellanato, J. *J. Org. Chem*. **1995**, 60, 74-83.