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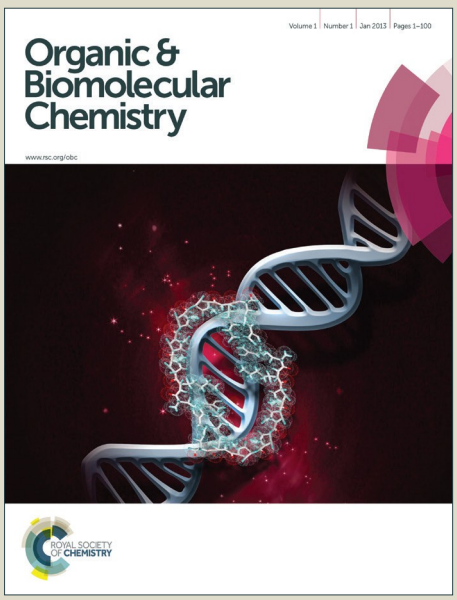

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Synthesis of 1,4-dihydrophosphinoline 1-oxides by acid-promoted cyclization of 1-(diphenylphosphoryl)allenes

Alexander S. Bogachenkov,[a] Albina V. Dogadina,[b] Irina A. Boyarskaya,[a] Vadim P. Boyarskiy,[a] Aleksander V. Vasilyev*[a,c]

[a]Department of Organic Chemistry, Institute of Chemistry, Saint Petersburg State University, Universitetskaya nab., 7/9, Saint Petersburg, 199034, Russia.

[b]Department of Organic Chemistry, Saint Petersburg Institute of Technology (Technical University), Moskovskiy pr. 26, 190013, Saint Petersburg, Russia

[c]Department of Chemistry, Saint Petersburg State Forest Technical University, Institutsky per., 5, Saint Petersburg, 194021, Russia. E-mail: aleksvasil@mail.ru.

*Corresponding author: A.V. Vasilyev

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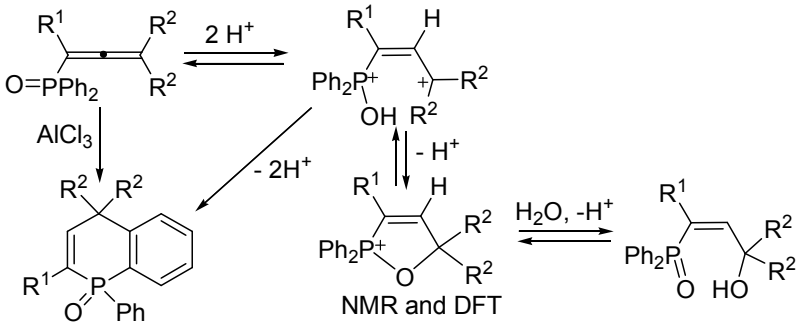
Abstract: 1-(Diphenylphosphoryl)alka-1,2-dienes (phosphonoallenes) in Brønsted (super)acids (TfOH, FSO_3H, H_2SO_4) gave corresponding 1,2-oxaphosphol-3-enium ions, that were studied by means of NMR and DFT calculations. Upon hydrolysis of reaction solution, these cations afforded 3-hydroxyalk-2-en-1-yl-diphenylphosphine oxides (phosphonoallyl alcohols). But in (super)acids the cations were slowly transformed into O-protonated forms of 1-phenyl-1,4-dihydrophosphinoline 1-oxides, which were monitored by NMR. The latter phosphaheterocycles can be directly obtained from phosphonoallenes under the action of Lewis acid $AlCl_3$.

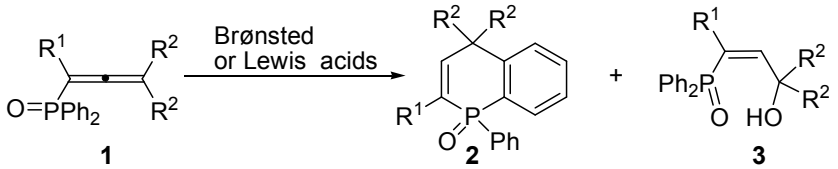
Graphical Abstract:



Introduction

Allenes are useful and interesting building blocks and targets in organic chemistry.[1] The synthetic potential of allenes has been explored extensively in recent years, and this has led to development of novel methods for construction of a variety of carbo- and hetero-cycles.[2] One of the most important reactions of allenes is electrophilic addition. The interactions of electrophiles, including the hydrohalogenic acids, with dialkyl allenephosphonates[3] or allenylphosphine oxides[4] give 2,5-dihydro-1,2-oxaphosphole derivatives or expected 2,1- and 2,3-adducts, depending on substituents at the allene triad. Recently various phosphonoallenes have been widely explored in intra- and inter-molecular synthesis of cyclobutenes, indenes, indenones, naphthalenes, phenanthrenes, furans, indols, (iso)chromenes, isocoumarins, thiochromanes.[5]

In our preliminary short communication[6] we have shown that 1-(diphenylphosphoryl)alka-1,2-dienes (phosphonoallenes) **1** in Brønsted or Lewis acids afforded 1-phenyl-1,4-dihydrophosphinoline 1-oxides **2** and/or 3-hydroxyalk-2-en-1-yl-diphenylphosphine oxides **3** (Scheme 1).



Scheme 1. Synthesis of compounds **2** and **3** from phosphonoallenes **1**.

To the best of our knowledge, at the moment there are only a few methods for synthesis of such rare phosphaheterocycles **2**. They are based on reactions of 1-chloro-1,2,3,4-tetrahydrophosphinoline 1-oxide[7] and benzophosphole ring expansion.[8] The compounds **2** may be in great demand as corresponding new phosphine precursors in coordination chemistry of transition metals.

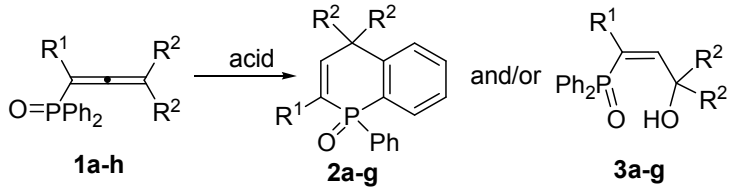
This work is a continuation of our initial study.[6] Herein we have involved more phosphonoallenes **1** in this reaction, and have investigated intermediate species and mechanism of the reaction by means of NMR and DFT calculations.

Results and discussion

Table 1 contains the data on transformations of allenes **1a-h** into phosphinoline oxides **2a-g** and/or allyl alcohols **3a-g** under action of various Brønsted (super)acids (TfOH, FSO_3H, H_2SO_4) and strong Lewis acid $AlCl_3$. Acid-promoted transformations of allenes **1a-h** give two kinds of reaction products, phosphinoline oxides **2a-g** and alcohols **3a-g**, depending on the structure of starting allene, acid (Brønsted or Lewis), and reaction conditions (time, temperature) (Table 1). This

reaction does not proceed in weaker Brønsted acid CF_3CO_2H, in which starting allenes **1a-h** remain unreacted.

Table 1. Acid promoted transformations of allenes **1a-h** into compounds **2a-g** and/or **3a-g**.



1a-h **2a-g** **3a-g**

Entry	Substituents in **1**, **2**, **3**		Allene **1**	Reaction conditions			Reaction products (yield, %)	
	R^1	R^2		Acid	Temperature (°C)	Time (h)	**2**	**3**
1[a]	H	Me	**1a**	$AlCl_3$	r.t.	0.17	**2a** (98)	-
2[a]				H_2SO_4	r.t.	0.5	**2a** (14)	**3a** (84)
3[a]				TfOH	r.t.	0.5	**2a** (5)	**3a** (94)
4[a]				TfOH	120	4	**2a** (88)	-
5[a]	H	$(CH_2)_4$	**1b**	$AlCl_3$	r.t.	0.17	**2b** (57)	-
6[a]				H_2SO_4	r.t.	0.5	-	**3b** (47)
7[a]				FSO_3H	-70	1	-	**3b** (70)
8[a]	H	$(CH_2)_5$	**1c**	$AlCl_3$	r.t.	0.17	**2c** (50)	-
9[a]				H_2SO_4	r.t.	0.5	-	**3c** (52)
10[a]				TfOH	-40	3	-	**3c** (51)
11[a]				FSO_3H	-40	3	-	**3c** (90)
12[a]	Br	Me	**1d**	$AlCl_3$	r.t.	0.17	**2d** (80)	-
13[a]				H_2SO_4	r.t.	0.5	**2d** (14)	**3d** (85)
14[a]				TfOH	r.t.	0.5	**2d** (17)	**3d** (81)
15[a]				TfOH	120	1	**2d** (91)	-
16[a]				FSO_3H	-40	3	**2d** (31)	**3d** (67)
17[a]	Ph	Me	**1e**	$AlCl_3$	r.t.	2	**2e** (62)	-
18[a]				H_2SO_4	r.t.	0.5	**2e** (26)	**3e** (72)
19[a]				TfOH	r.t.	0.5	**2e** (14)	**3e** (80)
20[a]				TfOH	120	1	**2e** (34)	-
21[a]				FSO_3H	-40	3	**2e** (18)	**3e** (80)
22	n-Pr	Me	**1f**	$AlCl_3$	r.t.	0.17	**2f** (93)	-
23				H_2SO_4	r.t.	0.5	**2f** (27)	**3f** (70)
24				TfOH	120	4	**2f** (95)	-
25	t-Bu	Me	**1g**	$AlCl_3$	r.t.	0.5	**2g** (17)	-
26				TfOH	120	1	**2g** (68)	-
27	$n\text{-}C_6F_{13}$	Me	**1h**	$AlCl_3$	r.t.	0.5	oligomers	
28				TfOH	120	4	-	**3g** (80)

[a]Data from ref. 6.

Structures of reaction products were determined by ^1H, ^{13}C, ^{19}F, ^{31}P NMR, IR spectroscopy, HRMS (see Experimental and Supplementary information) and X-ray analysis for compounds **2a**,**c**,**d**[6] and **2f** (see Figure 1). Compounds **3a-g** were exclusively formed as *Z*-isomers, that was

proved by values of coupling constants ^3J ~12 Hz for vinyl protons at C=C bond (see Experimental and Supplementary information).

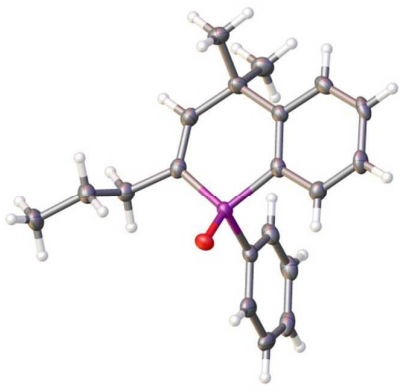


Figure 1. X-ray crystal structure of compound **2f** (ORTEP diagram, ellipsoid contour of probability levels is 50%, CCDC reference number – 1426281).

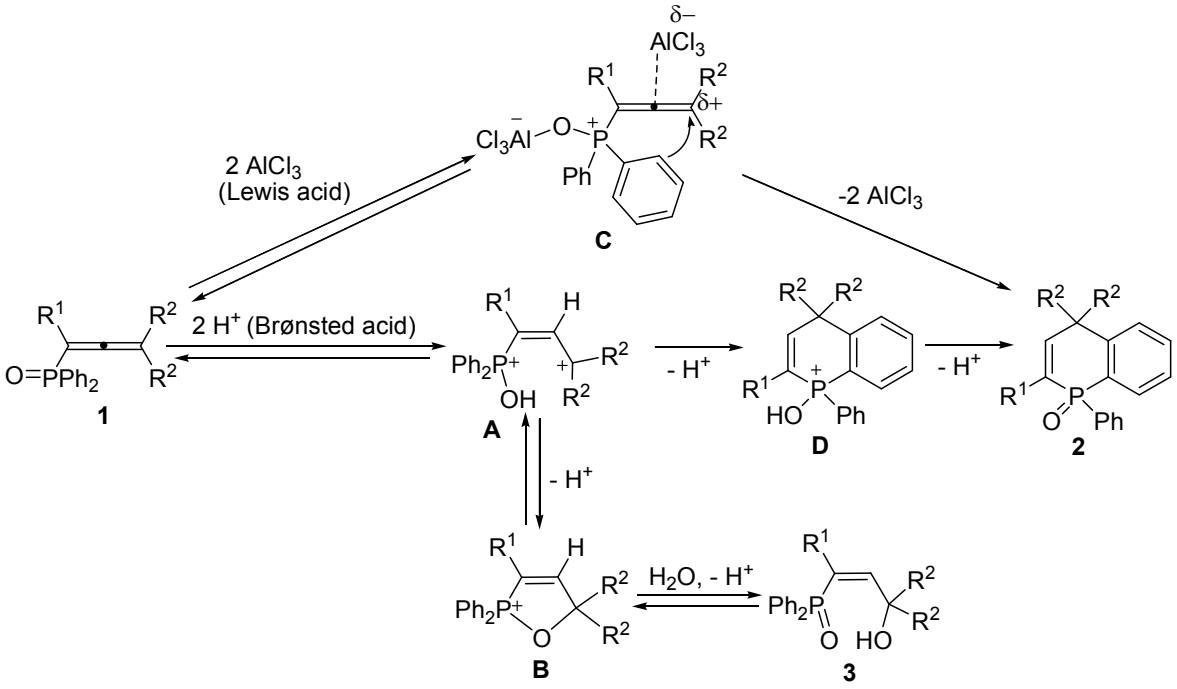
The data obtained allow to note some regularities and features of the reaction. Transformations in Brønsted (super)acids (TfOH, FSO_3H, H_2SO_4) at low temperature (-70, -40 °C) for 1-3 h (entries 7, 10, 11, 16, 21) or at room temperature for short time 0.5 h (entries 2, 3, 6, 9, 13, 14, 18, 19, 23) yielded only alcohols **3**, with small amount of phosphinoline oxides **2** in some cases. The increase of reaction temperature to 120 °C along with time to 4 h in TfOH afforded only compounds **2** (entries 4, 15, 20, 24). Moreover, individually isolated alcohols **3** upon heating in TfOH at 120°C for 4 h were completely converted into compounds **2**. These data revealed that formation of alcohols **3** was kinetically favorable and reversible, and it went to more thermodynamically stable phosphinoline oxides **2**.

Contrary to that, reactions under the action of $AlCl_3$ at room temperature for 10 min resulted in the formation of compounds **2** only (entries 1, 5, 8, 12, 17, 22, 25). Effect of $AlCl_3$ may be explained by strong coordination of this Lewis acid at oxygen atom of the P=O group, that deactivates this oxygen for further electrophilic attack on it.

One may propose the following acid-promoted transformations of allene **1** under action of Brønsted or Lewis acids (Scheme 2). Protonation of oxygen atom of the P=O group and central carbon of allene triad results in the formation of cation **A**, which may react in two different ways: a) cyclization into phenyl ring, leading to cation **D** and then to phosphinoline oxide **2**; b) interaction with oxygen atom of the P=O group, giving 1,2-oxaphosphol-3-enium ion **B** (it is a reversible stage), hydrolytic cleavage of the latter forms alcohol **3**. It should be noted that dications **A** belong to superelectrophiles[9] which are very reactive species in miscellaneous Friedel-Crafts reactions. In

weaker acid CF_3CO_2H only O-protonation of P=O group of compounds **1** takes place with no further protonation of allene system and no reaction occurs (*vide supra*).

Coordination of $AlCl_3$ at oxygen atom and allene system gives species **C** (Scheme 2). Such a strong coordination with oxygen atom of the P=O group occurs, leading to substantial deactivation of nucleophilic properties of this oxygen. As a result, formation of cation **B** and alcohol **3** is fully suppressed, and phospinoline oxide **2** is formed as the only reaction product.

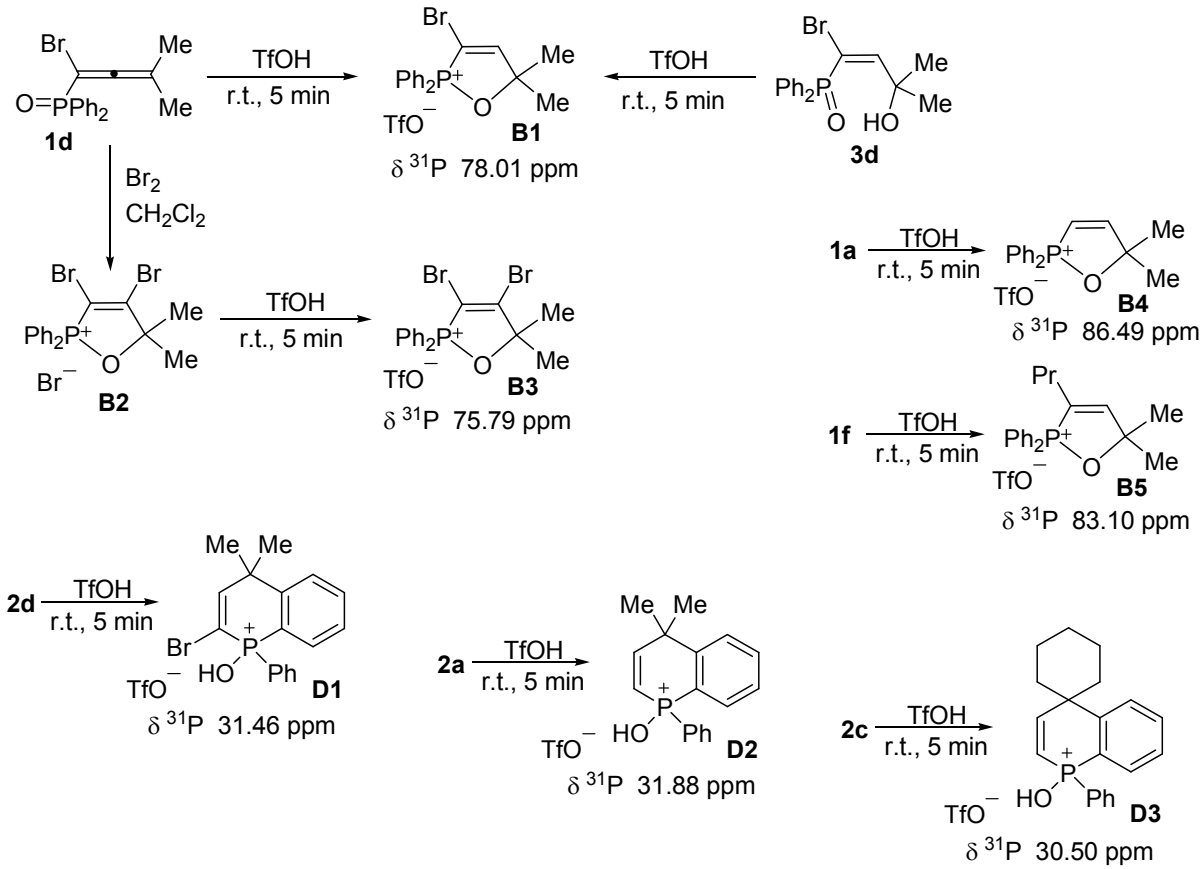


Scheme 2. Acid-promoted transformations of allenes **1**.

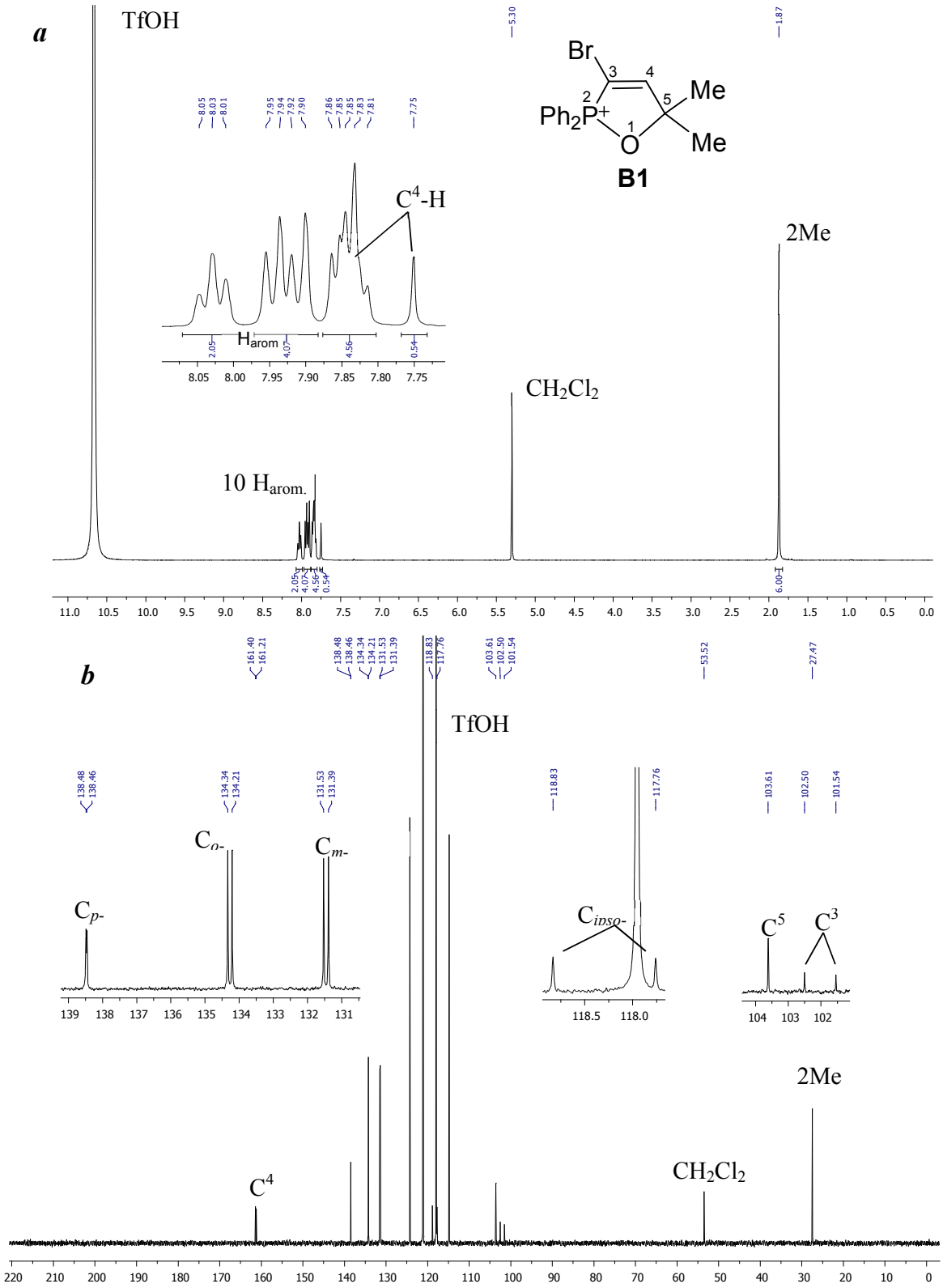
It is important to trace effect of substituent R^1 to ratio of reaction products **2** : **3**. Thus, allenes **1a,d,e,f** with R^2 = Me, differing in groups R^1 = H, Br, Ph, Pr correspondingly, give mixtures of phosphinoline oxides **2a,d,e,f** and alcohols **3a,d,e,f** at the same reaction conditions in H_2SO_4 at r.t. for 0.5 h (see Table 1, entries 2, 13, 18, 23). For the compounds **1a (**R^1 = H) and **1d** (R^1 = Br) the ratio of **2** : **3** is 1 : 6 (entries 2, 13). But in case of better cation stabilizing groups R^1 = Ph for allene **1e** and R^1 = Pr for allene **1f** amounts of the corresponding alcohols are reduced, and the ratio of **2e** : **3e** is 1 : 2.7 (entry 18) and for **2f** : **3f** is 1 : 2.6 (entry 23). In terms of the intermediate cations **A** (Scheme 2), positive charge may be partially delocalized into substituent R^1 in these species. When R^1 = Ph, Pr this delocalization may play a big role, leading to a substantial decrease of charge on reactive carbocationic center, that hampers nucleophilic attack from oxygen to cation **B** (Scheme 1). That finally results in the decrease of amount of the corresponding alcohol **3**. On the other hand, introduction of powerful electron withdrawing group $R^1 = C_6F_{13}$ in allene **1h** led to the solely formation of alcohol **3g**, which is not transformed into the corresponding phosphinoline oxides **2**

even at 120 °C for 4 h in TfOH (entry 28). Moreover, this allene **1h** did not give compound **2** with $AlCl_3$ (entry 27).

To investigate this reaction deeper we undertook NMR study of intermediate species of this transformation. Upon dissolving of allene **1d** or alcohol **3d** in TfOH directly in NMR tube, an immediate formation of one and the same species, having chemical shift at 78.01 ppm in ^{31}P NMR spectrum, was observed. We suspected that this species was triflate of 1,2-oxaphosphol-3-enium **B1** (see Scheme 3 and Figure 2). To prove that we specially prepared another cation of this type by bromination of allene **1d**, leading to bromide **B2** (according to literature procedure[10]), which then was converted in TfOH into triflate **B3**, having signal at 75.79 ppm in ^{31}P NMR, that is very close to cation **B1** (Scheme 3). The species **B1** and **B3** have very similar ^{1}H, ^{13}C, and ^{31}P NMR spectra in TfOH (compare spectra in Figure 2, Experimental, and Supplementary information). Thus, one may conclude that compounds **1d** and **3d** in TfOH do form cation **B1**. That also means that there are equilibriums between **1**, **A**, **B**, and **3** (Scheme 2). It should be noted that there are not so many data in literature[10-12] on such oxaphospholenium ions **B**.



Scheme 3. Generating of cations **B1-B5** and **D1-D3** in TfOH.



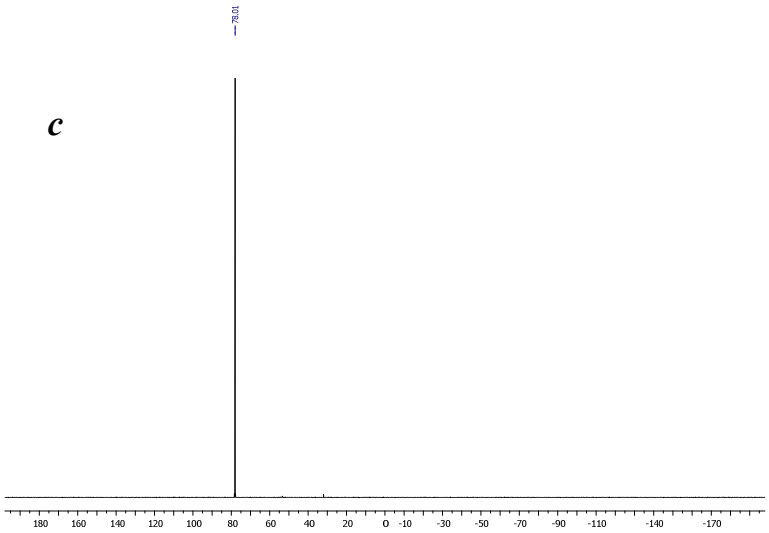
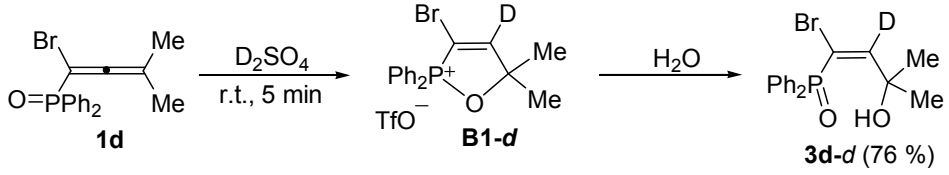


Figure 2. ^{1}H (***a***), ^{13}C (***b***), and ^{31}P (***c***) NMR spectra of cation **B1**, generated from allene **1d** or alcohol **3d** in TfOH at r.t. (see Scheme 3), CH_2Cl_2 – internal standard.

Then the monitoring of the behavior of cation **B1** in TfOH in time and at elevated temperature by ^{1}H, ^{13}C, and ^{31}P NMR was done (see Figure 3). At room temperature new signals increasing on time (till to 14 days) appeared in spectra. Thus, in ^{31}P NMR this new species had signal in completely different region at 31.5 ppm. The same was observed with increase of temperature, but much faster, heating of the solution of **B1** in TfOH at 100 °C for 5 h led to quantitative formation of this new species. And this ion was O-protonated form **D1** of phospinoline oxide **2d** (see Scheme 3 and Figure 3). **D1** was also independently generated from **2d** in TfOH and detected by NMR (Scheme 3). That again proves that formation of compounds **2** is thermodynamically favorable.

We additionally generated 1,2-oxaphosphol-3-enium ions **B4**, **B5** from allenes **1a**, **1f**, and cations **D2**, **D3** from phosphinoline oxides **2a**, **2c** respectively (Scheme 3). In ^{31}P NMR both types of these species have specific absorbance, **B1-B5** at ~75 – 87 ppm, and **D1-D3** at ~30 – 32 ppm (see Scheme 3, and full spectral data in Experimental and Supporting Information).

To go deeper in the reaction mechanism we carried out reaction of allene **1d** in deuterated sulfuric acid D_2SO_4, that afforded 3-^{2}H alcohol **3d-*d*** proving addition of deuteron in central carbon atom of allene triad with no deuteron-proton exchange upon quenching with H_2O (Scheme 4). Concerning cleavage of five-membered ring in species **B**, using hydrolysis of these species with ^{18}O- labeled water it was shown recently, that P–O bond was cleaved rather than C–O one. [12]



Scheme 4. Reaction of allene **1d** with D_2SO_4.

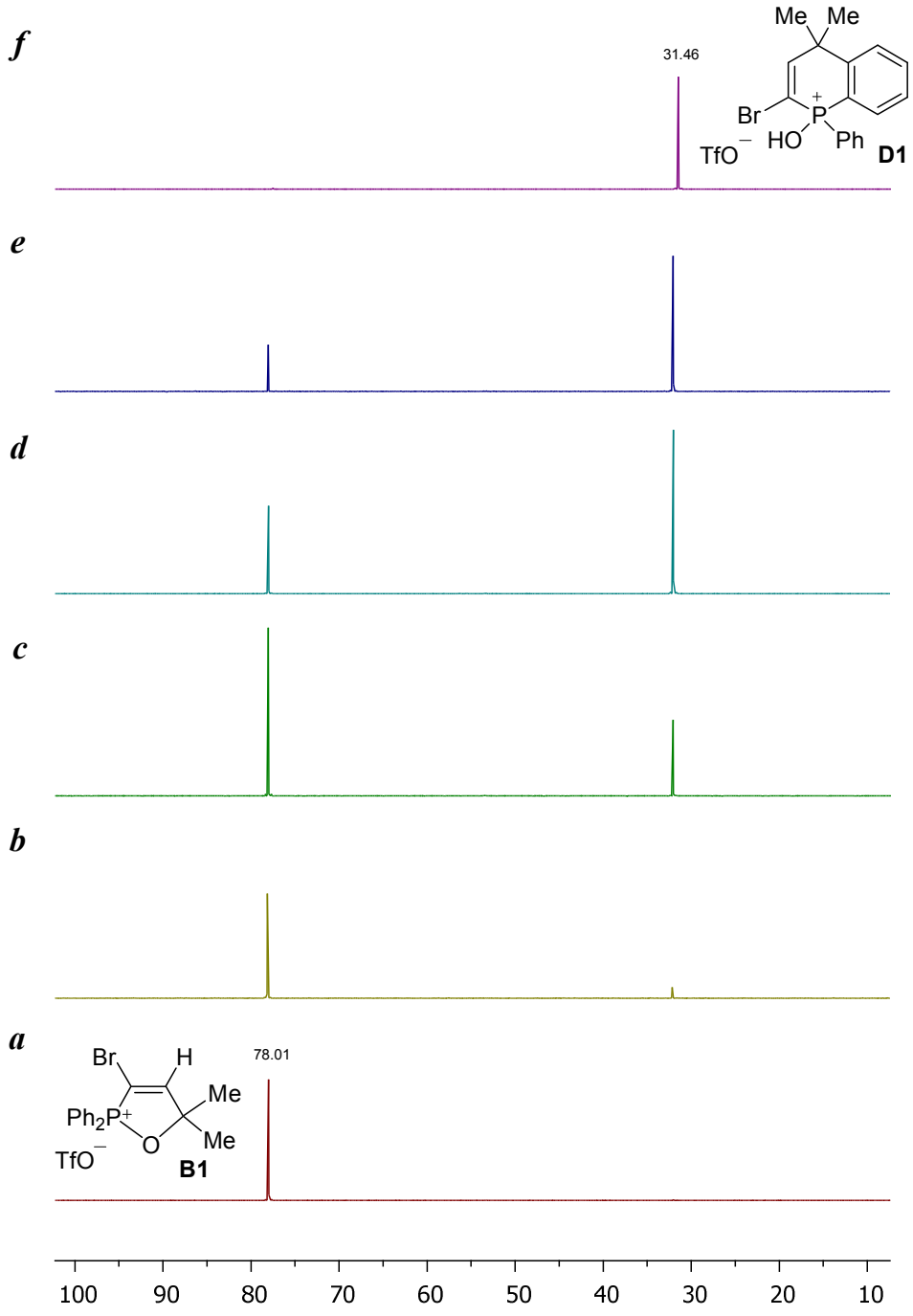
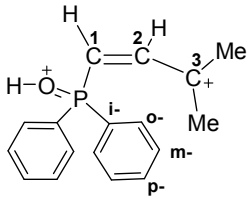


Figure 3. ^{31}P NMR monitoring of the progress of the transformation of **B1** into **D1** in TfOH: (***a***) r.t., 5 min; (***b***) r.t., 28 h; (***c***) r.t., 5 days; (***d***) r.t., 14 days; (***e***) 50°C, 5 h; (***f***) 100°C, 5 h.

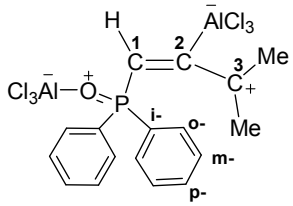
We performed DFT calculations of intermediate species and thermodynamics of this reaction. Selected electronic characteristics of species **A1** and **C1** derived from allene **1a** at the protonation or coordination with $AlCl_3$ respectively (see Scheme 2) are given in Table 2. Calculations have shown that carbon C^3 bears large positive charge in both species **A1** and **C1** that makes it electrophilic reactive center. But, in dication **A1** the charge is bigger that makes atom C^3 "harder" electrophilic center, which interacts more preferably with "hard" oxygen atom of the P=O group, giving cations **B**. That is contrary to species **C1**, bearing less charge on this atom, that leads to more favorite interaction with "softer" π-nucleophilic phenyl ring, resulting in formation compounds **2**. Apart from that, *ortho*-carbons in phenyl rings have negative charge, that facilitates cyclization in these positions.

Calculations predict that positive charge is substantially localized on phosphorus atom of the P=O group, and oxygen atom of this group possesses negative charge, that also explains its interaction with electrophilic center C^3. The species **A1** and **C1** have been characterized in terms of HOMO and LUMO energies and global electrophilicity index ω.[13] The high ω values reveal that these species are strong electrophiles, especially dication **A1**.

Table 2. Selected electronic characteristics of species **A1** and **C1** obtained by DFT calculations.



A1



C1

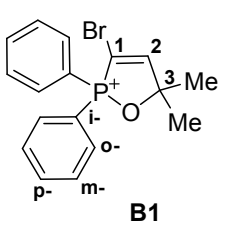
Species	E_{HOMO}, eV	E_{LUMO}, eV	ω,[a] eV	q(C^1),[b] e	q(C^3),[b] e	q(C_o-),[b] e	q(P),[b] e	q(O),[b] e
A1	-7.92	-5.17	7.8	-0.35	0.46	-0.16	1.91	-0.97
C1	-7.65	-3.08	3.1	-0.56	0.23	-0.16	1.97	-1.19

[a]Global electrophilicity index $\omega = (E_{HOMO} + E_{LUMO})^2/8(E_{LUMO} - E_{HOMO})$. [b]Natural charges.

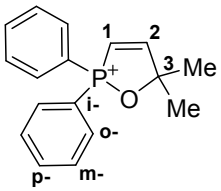
Then, we estimated charge distribution in intermediate cations **B1**, **B4**, **D1**, **D2**, generated from allenes **1a** and **1d** (see Scheme 3), by DFT calculations (Table 3). Positive charge in these species is mainly localized on phosphorus atom. That is reflected in changes in NMR spectra of cations **D** and their neutral precursors **2**. Thus, in ^{31}P NMR the signal of phosphorus in cation **D1** is ~20-30 ppm down-field shifted compare to the same signals of compounds **2**. Despite the triad P–

$C^1=C^2$ in species **B1**, **B4**, **D1**, **D2** is pseudo-allyl type, delocalization of the positive charge on carbon C^2 is very weak. Positive charge is also very slightly delocalized into phenyl rings (Table 3).

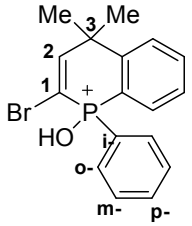
Table 3. Selected electronic characteristics of cations **B1**, **B4**, **D1**, **D2** obtained by DFT calculations.



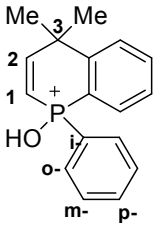
B1



B4



D1



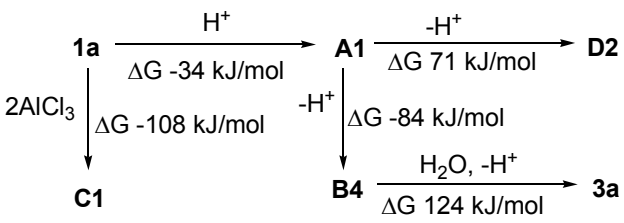
D2

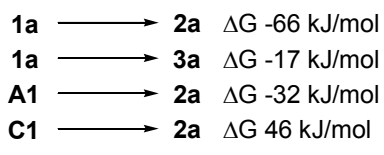
Cation	q(P),[a] e	q(C^1),[a] e	q(C^2),[a] e	q(C^3),[a] e	q($C_{i\text{-}}$),[a] e	q($C_{o\text{-}}$),[a] e	q($C_{m\text{-}}$),[a] e	q($C_{p\text{-}}$),[a] e
B1	1.89	-0.51	-0.16	0.27	-0.45	-0.16	-0.18	-0.14
B4	1.91	-0.56	-0.10	0.26	-0.44	-0.16	-0.19	-0.16
D1	1.89	-0.53	-0.07	-0.13	-0.43	-0.17	-0.18	-0.15
D2	1.91	-0.60	-0.03	-0.14	-0.43	-0.17	-0.19	-0.16

[a]Natural charges.

Calculations on thermodynamic parameters of transformation of allene **1a** into compounds **2a** and **3a** involving key intermediate species **A1**, **B4**, **C1**, **D2** are given in Scheme 5. Reaction Gibb's energies reveal that coordination of **1a** with two molecules of $AlCl_3$ affording species **C1** is extremely energetically favorable (ΔG -108 kJ/mol). Reaction pathway from **1a** through **A1** into **B4** has a gain in energy as well. But formation of **D2** and **3a** from **A1** and **B4** respectively is not favorable, especially the last reaction with ΔG 124 kJ/mol (Scheme 5). In general, ΔG values for conversions of **1a** into **2a** and **3a** are negative showing energy benefit in these processes.

Apart from that, calculations show that **D2** is 19 kJ/mol thermodynamically more stable than **B4**. This is an additional prove of the shift of equilibrium (see Scheme 2) to the formation of **D2** (compare with NMR data in Figure 3).





Scheme 5. Calculated Gibb's energies of reactions.

Conclusions

In conclusion, novel and efficient syntheses of 1-phenyl-1,4-dihydrophosphinoline 1-oxides and 3-hydroxyalk-2-en-1-yl-diphenyl phosphine oxides based on Brønsted or Lewis acid-promoted transformations of 1-(diphenylphosphoryl)alka-1,2-dienes have been developed. Mechanism and intermediate species of this reaction have been investigated by means of NMR and DFT calculations.

Experimental

General Remarks. The NMR spectra of solutions of compounds in $CDCl_3$ were recorded on Bruker AVANCE III 400 spectrometers at 25 °C (at 400, 100, 376 and 162 MHz for ^{1}H, ^{13}C, ^{19}F and ^{31}P NMR spectra respectively). Chemical shifts are given in δ-values [ppm] referenced to the residual signals of non-deuterated solvent ($CHCl_3$): δ 7.26 (^{1}H), 77.2 (^{13}C), or to the signals of $CFCl_3$ δ 0.0 ppm (^{13}F) and 85% H_3PO_4 δ 0.0 ppm (^{31}P). NMR experiments in the superacid TfOH at room temperature were performed on Bruker AVANCE III 400 spectrometer (at 400, 100 and 162 MHz for ^{1}H, ^{13}C and ^{31}P NMR spectra respectively). NMR spectra in TfOH were referenced to the signal of CH_2Cl_2 added as internal standard: δ 5.32 ppm (^{1}H), and δ 53.84 ppm (^{13}C). High-resolution mass spectra were recorded on Bruker Micro-TOF mass spectrometer (ESI-MS) and Varian 902-MS Mass Spectrometer (MALDI-MS). IR spectra of compounds in KBr were taken with Bruker spectrometer. Melting points were measured on a Kofler hot-stage (VEB Wägetechnik Rapido, PHMK 81/2969).The reactions were monitored by thin-layer chromatography carried out on silica gel plates (Alugram SIL G/UV-254), using UV light for detection. Preparative column chromatography was performed on silica gel Fluka 40-63 with eluation by petroleum ether-ethyl acetate or dichloromethane-methanol mixtures.

X-ray crystallography. Single crystal X-ray analysis was performed at single crystal diffractometer Agilent Technologies (Oxford Diffraction) «Supernova». A suitable crystal was selected and studied on the diffractometer. The crystal was kept at 100(2) K during data collection. Using Olex2,[14] the structure was solved with the ShelXS[15] structure solution program using Direct Methods and refined with the ShelXL refinement package using Least Squares minimization.

CCDC 1426281 (**2f**) contains the supplementary crystallographic data, which can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk.

DFT calculations. All computations has been carried out at the DFT/HF hybrid level of theory using Becke's three-parameter hybrid exchange functional in combination with the gradient-

corrected correlation functional of Lee, Yang, and Parr (B3LYP) by using GAUSSIAN 09 program packages.[16] Solvation effect was taken into account within the frameworks of Polarizable Continuum Model. The geometries optimization were performed using the 6-311+G(2d,2p) basis set. The Hessian matrix was calculated analytically for the optimized structures in order to prove the location of correct minima (no imaginary frequencies) and to estimate the thermodynamic parameters. Enthalpies and Gibbs free energies were calculated for 25°C.

Synthesis of starting allenes. The necessary allenes **1a-h** were obtained in reaction of the corresponding propargyl alcohols with chloro diphenyl phosphine $PClPh_2$ in yields of 55-65% as it was described by us previously,[5f,g] allenes **1a-e** are known compounds.[5f,g]

2-Methyl-4-(diphenylphosphoryl)hepta-2,3-diene (**1f**).

Colorless oil; **IR** (KBr), cm^{-1}: 688, 720, 758, 875, 952, 1020, 1076, 1116, 1144, 1190, 1260, 1365, 1426, 1479, 1638, 1825, 1862, 1900, 1942, 1975, 2012, 2928, 2943, 3058; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ, ppm: 0.87 t (3H, C^7H_3, $^3J_{HH}$ 8.0 Hz), 1.40 d (6H, C^1H_3, C^8H_3, $^5J_{HP}$ 8.0 Hz), 1.48 sext (2H, C^6H_2, $^3J_{HH}$ 8.0 Hz), 2.17 dt (2H, C^5H_2, $^3J_{HH}$ 8.0 Hz, $^3J_{HP}$ 8.0 Hz), 7.38–7.48 m (6H, $H_{arom.}$), 7.65–7.70 m (4H, $H_{arom.}$); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ, ppm: 13.7 s (C^7), 19.3 d (C^1, C^8, $^4J_{CP}$ 6.0 Hz), 21.8 d (C^6, $^3J_{CP}$ 5.0 Hz), 29.7 d (C^5, $^2J_{CP}$ 8.0 Hz), 96.4 d (C^4, $^1J_{CP}$ 102.6 Hz), 98.5 d (C^2, $^3J_{CP}$ 15.1 Hz), 128.2 d ($C^{3'}$, $C^{5'}$, $^3J_{CP}$ 12.1 Hz), 131.6 s ($C^{4'}$), 131.6 d ($C^{2'}$, $C^{6'}$, $^2J_{CP}$ 10.1 Hz), 132.7 d ($C^{1'}$, $^1J_{CP}$ 103.6 Hz), 207.7 d (C^3, $^2J_{CP}$ 6.0 Hz); **^{31}P NMR** ($CDCl_3$, 162 MHz) δ, ppm: 31.7; **HRMS** (ESI): m/z calcd for $C_{20}H_{23}OPH$ $[M+H]^+$ 311.1559, found 311.1563; m/z calcd for $C_{20}H_{23}OPNa$ $[M+Na]^+$ 333.1373, found 333.1385.

2,5,5-Trimethyl-4-(diphenylphosphoryl)hexa-2,3-diene (**1g**).

Colorless solid; mp 87–88°C; **IR** (KBr), cm^{-1}: 660, 693, 718, 763, 878, 948, 1018, 1080, 1115, 1140, 1192, 1258, 1369, 1428, 1485, 1599, 1635, 1822, 1860, 1899, 1940, 1973, 2010, 2921, 2948, 3060; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ, ppm: 1.21 s (9H, C^6H_3, C^7H_3, C^8H_3), 1.37 d (6H, C^1H_3, C^9H_3, $^5J_{HP}$ 4.0 Hz), 7.39–7.49 m (6H, $H_{arom.}$), 7.65–7.71 m (4H, $H_{arom.}$); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ, ppm: 19.3 d (C^1, C^9, $^4J_{CP}$ 6.0 Hz), 31.0 d (C^6, C^7, C^8, $^3J_{CP}$ 3.0 Hz), 36.4 d (C^5, $^2J_{CP}$ 7.0 Hz), 98.4 d (C^2, $^3J_{CP}$ 15.1 Hz), 105.6 d (C^4, $^1J_{CP}$ 99.6 Hz), 128.1 d ($C^{3'}$, $C^{5'}$, $^3J_{CP}$ 12.1 Hz), 131.2 ($C^{4'}$, $^4J_{CP}$ 3.0 Hz), 131.5 d ($C^{2'}$, $C^{6'}$, $^2J_{CP}$ 9.1 Hz), 134.9 d ($C^{1'}$, $^1J_{CP}$ 103.6 Hz), 207.4 d (C^3, $^2J_{CP}$ 8.0 Hz); **^{31}P NMR** ($CDCl_3$, 162 MHz) δ, ppm: 31.5; **HRMS** (ESI): m/z calcd for $C_{21}H_{25}OPH$ $[M+H]^+$ 325.1716, found 325.1720; m/z calcd for $C_{21}H_{25}OPNa$ $[M+Na]^+$ 347.1530, found 347.1543.

2-Methyl-4-(diphenylphosphoryl)-5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluorodeca-2,3-diene (**1h**) was obtained from 5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluorodeca-3-yn-2-ol (4) (see below).

Colorless solid; mp 82–84°C; **IR** (KBr), cm^{-1}: 662, 698, 723, 764, 868, 881, 945, 1026, 1078, 1113, 1142, 1186, 1258, 1366, 1437, 1481, 1597, 1638, 1825, 1859, 1906, 1938, 1973, 2014, 2926, 2951, 3065; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ, ppm: 1.50 d (6H, C^1H_3, $C^{11}H_3$, $^5J_{HP}$ 1.0 Hz), 7.45–7.56

m (6H, $H_{arom.}$), 7.71–7.76 m (4H, $H_{arom.}$); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ, ppm: 18.4 d (C^1, C^{11}, $^4J_{CP}$ 4.0 Hz), 92.6 d (C^4, $^1J_{CP}$ 100.6 Hz, $^2J_{CF}$ 29.2 Hz), 104.2 d (C^2, $^3J_{CP}$ 11.1 Hz), 128.6 d ($C^{3'}$, $C^{5'}$, $^3J_{CP}$ 13.1 Hz), 131.7 d ($C^{2'}$, $C^{6'}$, $^2J_{CP}$ 10.1 Hz), 132.0 d ($C^{1'}$, $^1J_{CP}$ 109.7 Hz), 132.3 ($C^{4'}$, $^4J_{CP}$ 3.0 Hz), 212.7 d (C^3, $^2J_{CP}$ 2.0 Hz); **^{31}P NMR** ($CDCl_3$, 162 MHz) δ, ppm: 26.7; **^{19}F NMR** ($CDCl_3$, 376 MHz) δ, ppm: (-126.2)–(-126.0) m (2F, CF_2), (-122.9)–(-122.7) m (2F, CF_2), (-121.4)–(-121.2) m (2F, CF_2), (-120.9)–(-120.7) m (2F, CF_2), (-101.1)–(-100.9) m (2F, C^5F_2), (-80.9)–(-80.7) m (3F, $C^{10}F_3$); **HRMS** (ESI): m/z calcd for $C_{23}H_{16}F_{13}OPH$ $[M+H]^+$ 587.0804, found 587.0805; m/z calcd for $C_{23}H_{16}F_{13}OPNa$ $[M+Na]^+$ 609.0618, found 609.0639.

5,5,6,6,7,7,8,8,9,9,10,10,10-Tridecafluoro-2-methyldec-3-yn-2-ol (4).[17] **^{1}H NMR** ($CDCl_3$, 400 MHz) δ, ppm: 1.58 s (6H, C^1H_3, $C^{11}H_3$), 2.11 s (1H, OH); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ, ppm: 30.4 s (C^1, C^{11}), 65.3 s (C^2), 69.0 t (C^4, $^2J_{CF}$ 36.0 Hz), 97.4 t (C^3, $^3J_{CF}$ 6.0 Hz), 104.5–113.5 m (C^5, C^6, C^7, C^8, C^9), 117.5 qt ($C^{10}F_3$, $^1J_{CF}$ 286.0 Hz, $^2J_{CF}$ 33.0 Hz); **^{19}F NMR** ($CDCl_3$, 376 MHz) δ, ppm: (-126.4)–(-126.3) m (2F, CF_2), (-123.0)–(-122.9) m (4F, $2CF_2$), (-121.6)–(-121.5) m (2F, CF_2), (-98.3)–(-98.2) m (2F, C^5F_2), (-81.3)–(-81.1) m (3F, $C^{10}F_3$).

General procedure for transformation of allenes 1a-h in Brønsted acids (TfOH, FSO_3H, H_2SO_4). Synthesis of compounds 2a-g, 3a-g.

A solution of allene **1** (0.3 mmol) in TfOH (1 mL) was stirred at temperature for the time as indicated in Table 1. The mixture was poured into ice water (30 mL) and extracted with chloroform (3×30 mL). The extracts were combined, washed with water, a saturated aqueous solution of $NaHCO_3$, and water again, and dried over Na_2SO_4, the solvent was distilled off under reduced pressure, and the residue was subjected to chromatographic separation on silica gel using CH_2Cl_2–MeOH (up to 5 %) as an eluent.

Analogously the reactions were carried out in H_2SO_4 (see Table 1). Reaction mixture in FSO_3H was quenched with frozen hydrochloric acid at -80 °C and worked-up as described above.

General procedure for transformation of compounds 1a-h under the action of $AlCl_3$. Synthesis of compounds 2a-g.

$AlCl_3$ (2.5 mmol) was added to solution of allene **1 (**0.5 mmol) in CH_2Cl_2 (10 mL). Reaction mixture was stirred at room temperature for 10-120 min as indicated in Table 1. The mixture was quenched with ice water (50 mL), extracted, and worked-up as described above.

Physical-chemical characteristics of compounds **2a-e** and **3a-e** were reported by us previously.[6]

1-Phenyl-2-propyl-4,4-dimethyl-1,4-dihydrophosphinoline 1-oxide (**2f**).

Colorless solid; mp 170–171°C; **IR** (KBr), cm^{-1}: 656, 695, 724, 744, 779, 860, 918, 962, 1082, 1115, 1248, 1295, 1366, 1442, 1487, 1590, 1624, 2878, 2929, 2967, 2980, 3054; **^{1}H NMR**

($CDCl_3$, 400 MHz) δ, ppm: 0.83 t (3H, $C^{13}H_3$, $^3J_{HH}$ 8.0 Hz), 1.39–1.54 m (2H, $C^{12}H_2$), 1.53 d (6H, $C^{14}H_3$, $C^{15}H_3$, $^5J_{HP}$ 8.0 Hz), 2.08–2.19 m (1H, $C^{11}H_2$), 2.27–2.39 m (1H, $C^{11}H_2$), 6.36 d (1H, C^3H, $^3J_{HP}$ 32.0 Hz), 7.22–7.26 m (1H, $H_{arom.}$), 7.37–7.50 m (5H, $H_{arom.}$), 7.59–7.67 m (3H, $H_{arom.}$); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ, ppm: 13.7 s (C^{13}), 21.8 d (C^{12}, $^3J_{CP}$ 4.0 Hz), 31.9 d (C^{14}, $^4J_{CP}$ 3.0 Hz), 32.5 d (C^{15}, $^4J_{CP}$ 2.0 Hz), 33.1 d (C^{11}, $^2J_{CP}$ 8.0 Hz), 38.8 d (C^4, $^3J_{CP}$ 12.0 Hz), 126.8 d (C^7, $^3J_{CP}$ 9.1 Hz), 127.0 d (C^5, $^3J_{CP}$ 12.1 Hz), 127.9 d (C^9, $^1J_{CP}$ 101.6 Hz), 128.1 d (C^2, $^1J_{CP}$ 94.6 Hz), 128.5 d ($C^{3'}C^{5'}$, $^3J_{CP}$ 12.1 Hz), 131.3–131.6 m (C^6, C^8, $C^{4'}$), 131.4 d ($C^{2'}$, $C^{6'}$, $^2J_{CP}$ 10.1 Hz), 134.4 d ($C^{1'}$, $^1J_{CP}$ 104.6 Hz), 149.0 d (C^{10}, $^2J_{CP}$ 8.0 Hz), 150.9 d (C^3, $^2J_{CP}$ 8.0 Hz); **^{31}P NMR** ($CDCl_3$, 162 MHz) δ, ppm: 9.7; **HRMS** (ESI): m/z calcd for $C_{20}H_{23}OPH$ $[M+H]^+$ 311.1559, found 311.1565; m/z calcd for $C_{20}H_{23}OPNa$ $[M+Na]^+$ 333.1373, found 333.1381.

1-Phenyl-2-tert-butyl-4,4-dimethyl-1,4-dihydrophosphinoline 1-oxide (**2g**).

Colorless solid; mp 167–168 °C; **IR** (KBr), cm^{-1}: 650, 700, 718, 740, 775, 856, 918, 962, 1076, 1116, 1248, 1298, 1369, 1443, 1480, 1595, 1620, 2878, 2940, 2965, 2980, 3048; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ, ppm: 1.20 s (9H, $C^{12}H_3$, $C^{13}H_3$, $C^{14}H_3$), 1.54 s (6H, $C^{15}H_3$, $C^{16}H_3$), 6.56 d (1H, C^3H, $^3J_{HP}$ 36.0 Hz), 7.22–7.26 m (1H, $H_{arom.}$), 7.37–7.45 m (5H, $H_{arom.}$), 7.67–7.72 m (3H, $H_{arom.}$); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ, ppm: 31.3 d (C^{12}, C^{13}, C^{14}, J_{CP} 4.0 Hz), 32.1 d (C^{15}, $^4J_{CP}$ 2.0 Hz), 32.1 d (C^{15}, $^4J_{CP}$ 2.0 Hz), 32.5 d (C^{16}, $^4J_{CP}$ 3.0 Hz), 37.2 d (C^{11}, $^2J_{CP}$ 7.0 Hz), 38.9 d (C^4, $^3J_{CP}$ 12.1 Hz), 126.4 d (C^7, $^3J_{CP}$ 8.1 Hz), 127.0 d (C^5, $^3J_{CP}$ 11.1 Hz), 128.4 d ($C^{3'}$, $C^{5'}$, $^3J_{CP}$ 12.1 Hz), 129.9 d (C^9, $^1J_{CP}$ 101.6 Hz), 130.8 d ($C^{2'}$, $C^{6'}$, $^2J_{CP}$ 10.1 Hz), 130.9–131.2 m (C^6, C^8, $C^{4'}$), 135.6 d (C^2, $^1J_{CP}$ 90.5 Hz), 137.3 d ($C^{1'}$, $^1J_{CP}$ 103.6 Hz), 147.4 d (C^{10}, $^2J_{CP}$ 7.0 Hz), 150.1 d (C^3, $^2J_{CP}$ 8.0 Hz); **^{31}P NMR** ($CDCl_3$, 162 MHz) δ, ppm: 9.1; **HRMS** (ESI): m/z calcd for $C_{21}H_{25}OPH$ $[M+H]^+$ 325.1716, found 325.1725; m/z calcd for $C_{21}H_{25}OPNa$ $[M+Na]^+$ 347.1530, found 347.1546.

(3*E*)-4-Bromo-4-(diphenylphosphoryl)-2-methyl(3-^{2}H)but-3-en-2-ol (3d-*d*).

Colorless solid; mp 96–97°C; **IR** (KBr), cm^{-1}: 691, 704, 748, 814, 970, 1096, 1117, 1161, 1186, 1215, 1315, 1356, 1369, 1437, 1566, 1589, 2926, 2970, 3057, 3252; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ, ppm: 1.50 s (6H, $2CH_3$), 6.97 s (1H, OH), 7.50–7.60 m (6H, $H_{arom.}$), 7.83–7.87 m (4H, $H_{arom.}$); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ, ppm: 31.0 s ($2CH_3$), 71.8 d (C^2, $^3J_{CP}$ 3.0 Hz), 111.7 d (C^4, $^1J_{CP}$ 76.5 Hz), 128.7 d ($C^{3'}$, $C^{5'}$, $^3J_{CP}$ 11.1 Hz), 129.3 d ($C^{1'}$, $^1J_{CP}$ 90.6 Hz), 132.8 d ($C^{2'}$, $C^{6'}$, $^2J_{CP}$ 8.0 Hz), 132.9 d ($C^{4'}$, $^2J_{CP}$ 2.0 Hz), 165 m (C^3); **^{31}P NMR** ($CDCl_3$, 162 MHz) δ, ppm: 31.5; **HRMS** (ESI): m/z calcd for $C_{17}H_{17}DBrO_2PH$ $[M+H]^+$ 366.0363, found 366.0361; m/z calcd for $C_{17}H_{17}DBrO_2PNa$ $[M+Na]^+$ 388.0177, found 388.0193.

(*Z*)-2-Methyl-4-(diphenylphosphoryl)hept-3-en-2-ol (3f).

Colorless oil; **IR** (KBr), cm^{-1}: 648, 696, 710, 723, 752, 968, 997, 1070, 1117, 1169, 1219, 1356, 1377, 1437, 1464, 1609, 2870, 2932, 2965, 2978, 3057; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ, ppm: 0.62 t (3H, C^7H_3, $^3J_{HH}$ 8.0 Hz), 1.02 sext (2H, C^6H_2, $^3J_{HH}$ 8.0 Hz), 1.46 s (6H, C^1H_3, C^8H_3),

1.82–1.89 m (2H, C^5H_2, $^3J_{HH}$ 8.0 Hz), 6.68 d (1H, C^3H, $^3J_{HP}$ 40.0 Hz), 6.99 s (1H, OH), 7.45–7.48 m (4H, $H_{arom.}$), 7.52–7.57 m (2H, $H_{arom.}$), 7.65–7.70 m (4H, $H_{arom.}$); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ, ppm: 13.7 s (C^7H_3), 23.2 d (C^6H_2, $^3J_{CP}$ 3.0 Hz), 31.3 d (C^1H_3, C^8H_3, $^4J_{CP}$ 1.0 Hz), 37.3 d (C^5H_2, $^2J_{CP}$ 14.0 Hz), 70.1 d (C^3, $^3J_{CP}$ 6.0 Hz), 128.2 d (C^4, $^1J_{CP}$ 88.5 Hz), 128.7 d ($C^{3'}$, $C^{5'}$, $^3J_{CP}$ 12.1 Hz), 131.9 d ($C^{1'}$, $^1J_{CP}$ 103.6 Hz), 132.2 d ($C^{4'}$), 132.3 d ($C^{2'}$, $C^{6'}$, $^2J_{CP}$ 11.1 Hz), 159.4 s (C^3, $^2J_{CP}$ 6.0 Hz); **^{31}P NMR** ($CDCl_3$, 162 MHz) δ, ppm: 34.8; **HRMS** (ESI): m/z calcd for $C_{20}H_{25}O_2PH$ $[M+H]^+$ 329.1665, found 329.1667; m/z calcd for $C_{20}H_{25}O_2PNa$ $[M+Na]^+$ 351.1479, found 351.1488.

***(Z)*-2-Methyl-4-(diphenylphosphoryl)-5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluorodec-3-en-2-ol (3g).**

Colorless oil; **IR** (KBr), cm^{-1}: 652, 698, 708, 720, 750, 966, 998, 1072, 1115, 1170, 1217, 1354, 1374, 1438, 1462, 1612, 2872, 2930, 2968, 2980, 3055; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ, ppm: 1.53 s (6H, C^1H_3, $C^{11}H_3$), 7.02 s (1H, OH), 7.37 d (1H, C^3H, $^3J_{HP}$ 36.0 Hz), 7.46–7.51 m (4H, $H_{arom.}$), 7.56–7.61 m (2H, $H_{arom.}$), 7.68–7.73 m (4H, $H_{arom.}$); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ, ppm: 30.5 s (C^1H_3, $C^{11}H_3$), 71.1 d (C^2, $^3J_{CP}$ 5.0 Hz), 128.6 d ($C^{3'}$, $C^{5'}$, $^3J_{CP}$ 13.1 Hz), 131.3 d ($C^{1'}$, $^1J_{CP}$ 110.7 Hz), 132.2 d ($C^{4'}$), 128.7 d ($C^{3'}$, $C^{5'}$, $^3J_{CP}$ 12.1 Hz), 132.6 d ($C^{2'}$, $C^{6'}$, $^2J_{CP}$ 11.1 Hz), 132.9 s ($C^{4'}$, $^4J_{CP}$ 3.0 Hz), 171.5 d (C^3, $^2J_{CP}$ 6.0 Hz); **^{31}P NMR** ($CDCl_3$, 162 MHz) δ, ppm: 31.5; **^{19}F NMR** ($CDCl_3$, 376.50 MHz) δ, ppm: (-126.3)–(-126.1) m (2F, CF_2), (-123.0)–(-122.9) m (2F, CF_2), (-122.0)–(-121.9) m (2F, CF_2), (-119.7)–(-119.4) m (2F, CF_2), (-97.8)–(-97.6) m (2F, C^5F_2), (-81.0)–(-80.7) m (3F, $C^{10}F_3$); **HRMS** (ESI): m/z calcd for $C_{23}H_{18}F_{13}O_2PH$ $[M+H]^+$ 605.0910, found 605.0916; m/z calcd for $C_{23}H_{18}F_{13}O_2PNa$ $[M+Na]^+$ 627.0724, found 627.0735.

NMR spectra of cations B1-B5, D1-D3 in superacid TfOH.

3-Bromo-5,5-dimethyl-2,2-diphenyl-1,2-oxaphosphol-3-enium (B1).

^{1}H NMR (TfOH, 400 MHz) δ, ppm: 1.87 s (6H, $2CH_3$), 7.78 d (1H, C^4H, $^3J_{HP}$ 28.0 Hz), 7.81–7.86 m (4H, $H_{arom.}$), 7.90–7.95 m (4H, $H_{arom.}$), 8.01–8.05 m (2H, $H_{arom.}$); **^{13}C NMR** (TfOH, 100 MHz) δ, ppm: 27.5 s ($2CH_3$), 102.0 d (C^3, $^1J_{CP}$ 96.6 Hz), 103.6 s (C^5), 118.3 d (2 *ipso*-C, $^1J_{CP}$ 107.7 Hz), 131.5 d (4 *m*-C, $^3J_{CP}$ 14.1 Hz), 134.3 d (4 *o*-C, $^2J_{CP}$ 13.1 Hz), 138.5 d (2 *p*-C, $^4J_{CP}$ 2.0 Hz), 161.3 d (C^4, $^2J_{CP}$ 19.1 Hz); **^{31}P NMR** (TfOH, 162 MHz) δ, ppm: 78.0.

3,4-Dibromo-5,5-dimethyl-2,2-diphenyl-1,2-oxaphosphol-3-enium (B2) with bromide counter-ion was obtained according to literature procedure.[10]

3,4-Dibromo-5,5-dimethyl-2,2-diphenyl-1,2-oxaphosphol-3-enium (B3).

^{1}H NMR (TfOH, 400 MHz) δ, ppm: 1.98 s (6H, $2CH_3$), 7.70–8.10 m (10H, $H_{arom.}$); **^{13}C NMR** (TfOH, 100 MHz) δ, ppm: 27.6 s ($2CH_3$), 103.3 d (C^3, $^1J_{CP}$ 99.6 Hz), 104.1 d (C^5, $^3J_{CP}$ 4.0 Hz), 117.9 d (2 *ipso*-C, $^1J_{CP}$ 108.7 Hz), 131.5 d (4 *m*-C, $^3J_{CP}$ 15.1 Hz), 134.3 d (4 *o*-C, $^2J_{CP}$ 13.1 Hz), 138.8 d (2 *p*-C, $^4J_{CP}$ 2.0 Hz), 154.7 d (C^4, $^2J_{CP}$ 34.2 Hz); **^{31}P NMR** (TfOH, 162 MHz) δ, ppm: 75.8.

2,2-Diphenyl-5,5-dimethyl-1,2-oxaphosphol-3-enium (B4).

^{1}H NMR (TfOH, 400 MHz) δ, ppm: 1.85 s (6H, $2CH_3$), 6.78 dd (1H, C^4H, $^3J_{HH}$ 8.0 Hz, $^3J_{HP}$ 40.0 Hz), 7.73–7.99 m (11H, $10H_{arom.}$, C^3H); **^{13}C NMR** (TfOH, 100 MHz) δ, ppm: 27.1 s ($2CH_3$), 102.6 d (C^5, $^3J_{CP}$ 3.0 Hz), 111.8 d (C^3, $^1J_{CP}$ 83.0 Hz), 121.2 d (2 *ipso*-C, $^1J_{CP}$ 106.0 Hz), 131.1 d (4 *m*-C, $^3J_{CP}$ 14.1 Hz), 133.5 d (4 *o*-C, $^2J_{CP}$ 13.1 Hz), 137.5 d (2 *p*-C, $^4J_{CP}$ 3.0 Hz), 164.4 d (C^4, $^2J_{CP}$ 6.0 Hz); **^{31}P NMR** (TfOH, 162 MHz) δ, ppm: 86.5.

3-Propyl-2,2-diphenyl-5,5-dimethyl-1,2-oxaphosphol-3-enium (B5).

^{1}H NMR (TfOH, 400 MHz) δ, ppm: 1.00 t (3H, C^8H_3, $^3J_{HH}$ 8.0 Hz), 1.68 m (2H, C^7H_2), 1.84 s (6H, $2CH_3$), 2.50 m (2H, C^6H_2), 7.34 d (1H, C^4H, $^3J_{HP}$ 36.0 Hz), 7.82–8.01 m (10H, $H_{arom.}$); **^{13}C NMR** (TfOH, 100 MHz) δ, ppm: 13.0 s (C^8), 21.8 d (C^7, $^3J_{CP}$ 7.0 Hz), 27.6 s ($2CH_3$), 28.9 d (C^6, $^2J_{CP}$ 12.0 Hz), 101.3 d (C^5, $^3J_{CP}$ 2.0 Hz), 120.4 d (2 *ipso*-C, $^1J_{CP}$ 102.0 Hz), 127.2 d (C^3, $^1J_{CP}$ 74.0 Hz), 131.2 d (4 *m*-C, $^3J_{CP}$ 14.1 Hz), 133.7 d (4 *o*-C, $^2J_{CP}$ 13.1 Hz), 137.6 d (2 *p*-C, $^4J_{CP}$ 3.0 Hz), 156.1 d (C^4, $^2J_{CP}$ 14.0 Hz); **^{31}P NMR** (TfOH, 162 MHz) δ, ppm: 83.1.

(2-Bromo-4,4-dimethyl-1-phenyl-1,4-dihydro-1λ^5-phosphinolin-1-ylidene)oxonium (D1).

^{1}H NMR (TfOH, 400 MHz) δ, ppm: 1.75 s (3H, CH_3), 1.79 s (3H, CH_3), 7.63–8.00 m (10H, $9H_{arom}$, C^3H); **^{13}C NMR** (TfOH, 100 MHz) δ, ppm: 29.9 s (CH_3), 31.2 s (CH_3), 45.0 d (C^4, $^3J_{CP}$ 11.1 Hz), 100.8 d (C^2, $^1J_{CP}$ 102.6 Hz), 115.0 d (C^9, $^1J_{CP}$ 102.6 Hz), 120.1 d ($C^{1'}$, $^1J_{CP}$ 128.8 Hz), 129.6 d (C^7, $^3J_{CP}$ 11.1 Hz), 129.9 d (C^5, $^3J_{CP}$ 12.1 Hz), 131.0 d ($C^{3'}$, $C^{5'}$, $^3J_{CP}$ 15.1 Hz), 133.2 d (C^8, $^2J_{CP}$ 9.1 Hz), 133.5 d ($C^{2'}$, $C^{6'}$, $^2J_{CP}$ 13.1 Hz), 137.2 d (C^6, $^4J_{CP}$ 3.0 Hz), 137.7 d ($C^{4'}$, $^4J_{CP}$ 2.0 Hz), 152.7 d (C^{10}, $^2J_{CP}$ 11.1 Hz), 168.0 d (C^3, $^2J_{CP}$ 13.1 Hz); **^{31}P NMR** (TfOH, 162 MHz) δ, ppm: 31.5.

(1-Phenyl-4,4-dimethyl-1,4-dihydro-1λ^5-phosphinolin-1-ylidene)oxonium (D2).

^{1}H NMR (TfOH, 400 MHz) δ, ppm: 1.73 s (3H, CH_3), 1.79 s (3H, CH_3), 6.53 dd (1H, C^2H, $^3J_{HH}$ 12.0 Hz, $^2J_{HP}$ 12.0 Hz), 7.61–7.98 m (9H, H_{arom}), 7.63 dd (1H, C^3H, $^3J_{HH}$ 12.0 Hz, $^3J_{HP}$ 44.0 Hz); **^{13}C NMR** (TfOH, 100 MHz) δ, ppm: 30.0 d (CH_3, $^4J_{CP}$ 2.0 Hz), 31.0 d (CH_3, $^4J_{CP}$ 2.0 Hz), 40.9 d (C^4, $^3J_{CP}$ 14.1 Hz), 107.5 d (C^2, $^1J_{CP}$ 97.0 Hz), 115.9 d (C^9, $^1J_{CP}$ 103.0 Hz), 122.5 d ($C^{1'}$, $^1J_{CP}$ 123.0 Hz), 129.3 s (C^5), 129.4 d (C^7, $^3J_{CP}$ 2.0 Hz), 130.9 d ($C^{3'}$, $C^{5'}$, $^3J_{CP}$ 15.0 Hz), 132.5 d (C^8, $^2J_{CP}$ 6.0 Hz), 132.5 d ($C^{2'}$, $C^{6'}$, $^2J_{CP}$ 15.0 Hz), 136.4 d (C^6, $^4J_{CP}$ 3.0 Hz), 137.0 d ($C^{4'}$, $^4J_{CP}$ 2.0 Hz), 152.9 d (C^{10}, $^2J_{CP}$ 10.0 Hz), 169.8 d (C^3, $^2J_{CP}$ 3.0 Hz); **^{31}P NMR** (TfOH, 162 MHz) δ, ppm: 31.9.

(1-Phenyl-4-hexan-1,6-diyl-1,4-dihydro-1λ^5-phosphinolin-1-ylidene)oxonium (D3).

^{1}H NMR (TfOH, 400 MHz) δ, ppm: 1.66 - 2.42 m (10H, $C^{11\text{-}15}H_2$), 6.63 dd (1H, C^2H, $^3J_{HH}$ 12.0 Hz, $^2J_{HP}$ 12.0 Hz), 7.59–8.08 m (9H, H_{arom}), 8.43 dd (1H, C^3H, $^3J_{HH}$ 12.0 Hz, $^3J_{HP}$ 40.0 Hz); **^{13}C NMR** (TfOH, 100 MHz) δ, ppm: 22.5 s (C^{12}), 22.6 s (C^{14}), 25.7 s (C^{13}), 39.6 s (C^{15}), 40.5 s (C^{11}), 44.1 d (C^4, $^3J_{CP}$ 13.1 Hz), 108.0 d (C^2, $^1J_{CP}$ 97.0 Hz), 116.6 d (C^9, $^1J_{CP}$ 103.0 Hz), 122.6 d ($C^{1'}$, $^1J_{CP}$ 124.0 Hz), 129.2 d (C^5, $^3J_{CP}$ 13.0 Hz), 129.4 d (C^7, $^3J_{CP}$ 10.0 Hz), 130.9 d ($C^{3'}$, $C^{5'}$, $^3J_{CP}$ 15.0 Hz), 132.5 d (C^8, $^2J_{CP}$ 9.0 Hz), 132.7 d ($C^{2'}$, $C^{6'}$, $^2J_{CP}$ 13.0 Hz), 136.4 d (C^6, $^4J_{CP}$ 3.0 Hz), 136.9

d ($C^{4'}$, $^{4}J_{CP}$ 2.0 Hz), 154.2 d (C^{10}, $^{2}J_{CP}$ 10.0 Hz), 166.6 d (C^{3}, $^{2}J_{CP}$ 2.0 Hz); **^{31}P NMR** (TfOH, 162 MHz) δ, ppm: 30.5.

Supplementary information: ^{1}H, ^{13}C, ^{19}F, ^{31}P NMR spectra, X-ray data, DFT calculations.

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