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Perfluoroacetylenephosphonates in Diels–Alder reactions: Synthesis of perfluoroalkylated heterocyclic and carbocyclic phosphonates

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ABSTRACT

Diethyl 3,3,3-trifluoroprop-1-ynylphosphonate and diethyl 3,3,4,4,4-pentafluorobut-1-ynylphosphonate are obtained by the dehydration of the corresponding enols using P_2O_5–Et_3N system as a dehydrating agent, affording acetylenes in 50–60% yield. By the reaction of these perfluoroacetylenephosphonates with acyclic and cyclic 1,3-dienes or diene-like heteroaromatic and aromatic compounds corresponding Diels–Alder cyclo- and bicycloadducts were prepared in good yields (65–90%). The reactivity of the dienes and acetylenes which depends on their structure, as well as the regioselectivity of the reaction are established.

1. Introduction

For many years, the extensive involvement of phosphoric acid derivatives in living systems has been known [1]. These compounds have found important applications in medicine [2], agriculture [3], industry [4], and as reagents in organic synthesis [5]. The incorporation of a fluorine-containing group into such molecules alters dramatically their physical, chemical and biological properties [6–8]. Recently, the regioselective synthesis of fluorinated vinylphosphonates has become significant task in synthetic chemistry [9].

The methods for the preparation of fluorine-containing vinylphosphonates are rather limited [9–15], including Horner–Emmons condensation [10], reactions of fluorinated acid chlorides with phosphites [11,12], or sequential transformations of bisphosphonates [13,14]. The other approach for the synthesis of functionalized vinylphosphonates is the Diels–Alder reaction of 1,3-dienes with substituted acetylenes. However, there are only few examples of reactions with acetylenes containing perfluoroalkyl groups [16–19] or dialkylphosphonate functions [20–29]. In some cases these reactions were accompanied by spontaneous aromatization of primarily formed bicyclic adducts with elimination of low molecular weight compounds, such as: CO [17], C_2H_4 [20] or CO_2 [22,23]. Dienophiles, possessing both the dialkylphosphonate and perfluoroalkyl substituents have been first synthesized in 1985 by Shen's group [30] and used as reagents in dipolar 1,3- [31–33] and 1,2-cycloadditions [34]. However, no example for the application of these compounds in Diels–Alder reactions has been found.

2. Results and discussion

The perfluoroacetylenephosphonates: diethyl 3,3,3-trifluoroprop-1-ynylphosphonate (**3a**) and diethyl 3,3,4,4,4-pentafluorobut-1-ynylphosphonate (**3b**), were prepared according to the known procedure [35]. However, we introduce some improvements which resulted in better yields (87–90%) and purity of the desired acetylenes. Compounds (**3a** and **b**) can be also successfully prepared in 50–60% yield, by the dehydration of the corresponding

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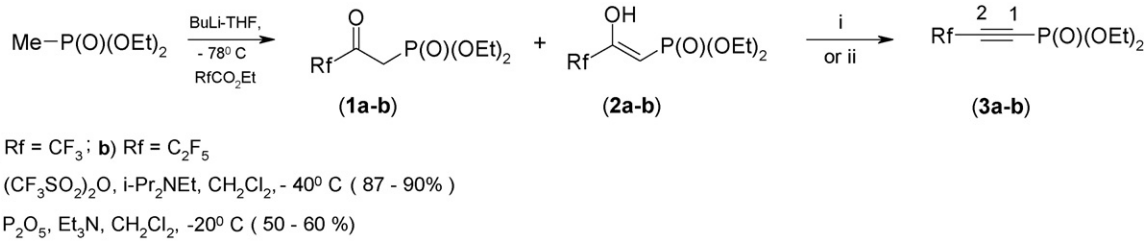


Scheme 1.

enols (**2a** and **b**) [36] using the P_2O_5–Et_3N system in methylene chloride at −20 °C (Scheme 1).

Perfluoroacetylenephosphonates (**3a** and **b**) are versatile and active dienophiles in the diene synthesis with classical donor 1,3-alkadienes, such as isoprene and 2,3-dimethyl-1,3-butadiene. The reaction occurs even at room temperature, affording carbocyclic Diels–Alder adducts (**4a** and **b**, **7a** and **b**, **8a** and **b**). However, complete conversion of the parent tetramethyl acetylene biphosphonate was achieved after 2–3 h of heating at 80 °C (Table 1). The reaction was carried out in a sealed ampoule under dry argon atmosphere with an excess of 1,3-diene using anhydrous benzene as a solvent and a catalytic amount of 1,4-hydroquinone (5 mol%) as a polymerization inhibitor (Scheme 2). With 1-substituted 1,3-dienes such as penta-1,3-diene and hexa-2,4-diene the reaction proceeded smoothly at rather rigid conditions (Table 1) and yields of the targeted carbocyclic perfluorophosphonates (**9a** and **b**, **10a**) were noticeably lower, probably due to the restricted *trans,trans–cis,cis* inversion of the parent 1,3-dienes [37]. With cyclic 1,3-dienes, possessing fixed *cis*-configuration, such as cyclohexa-1,3-diene, cyclopenta-1,3-diene (generated *in situ* upon heating to 190 °C the commercially available bicyclopenta-1,3-diene), the diene synthesis proceeded readily (Table 1) and yields of adducts (**5a** and **b**, **6a** and **b**) were satisfactory (Scheme 2).

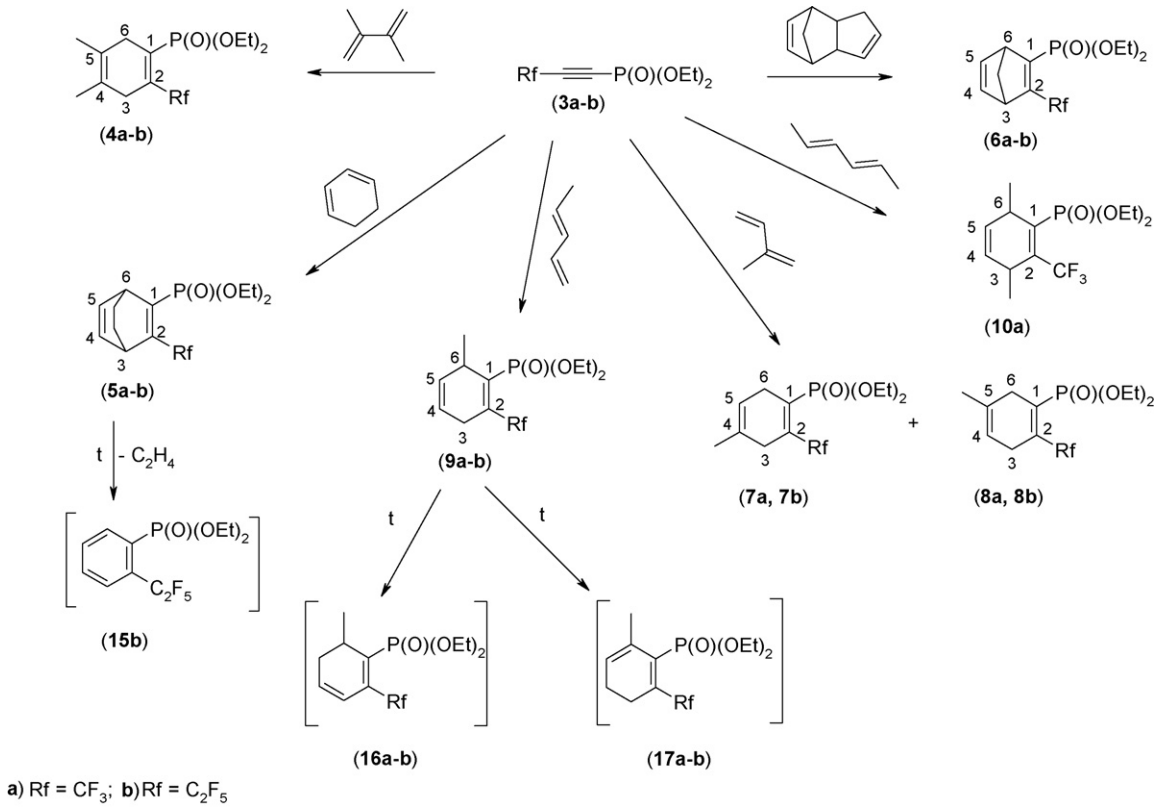
With diethyl 3,3,3-trifluoroprop-1-ynylphosphonate (**3a**) and diethyl 3,3,4,4,4-pentafluorobut-1-ynylphosphonate (**3b**) as examples, we were able to trace the reaction regioselectivity with an unsymmetrical 2-substituted 1,3-diene (isoprene). The electronic control of the reaction was noticed by the predominate formation of isomers (**7a** and **b**) in line with the polarization of the parent compounds [38]. In the case of Rf = CF_3, the (**7a**:**8a)** ratio of isomers, according to ^{31}P, ^{19}F and ^{1}H NMR analysis, was (61:29 mol%) and for Rf = C_2F_5 (**7b**:**8b) =** (56:44 mol%), respectively. Structures of isomers (**7a** and **b)** and (**8a** and **b)** were established by the ^{13}C NMR analysis. The signals of the carbon atoms C(3) and C(6), C(4) and C(5) of the isomers (**7a** and **b)** and (**8a** and **b**) can be assigned, when a set of related compounds is considered. In the case of 1-substituted unsymmetrical 1,3-alkadiene, e.g., piperylene, we confirmed the known regioselectivity of Diels–Alder reaction [39]; only one isomer which responds to the electronic control of reaction has been found (Scheme 2).

The stability of the prepared carbocyclic and bicyclic compounds (**4a** and **b**–**9a** and **b**; **10a**) greatly depends on both: the Rf nature and the presence of substituents in 3 and 6 positions of the formed cyclohexadiene ring. Generally, the carbocyclic and bicyclic adducts containing C_2F_5 substituent at 3 and 6 positions are formed with lower yields and are less thermally stable when compared with related carbocycles having CF_3 substituent at 4 and 5 positions (Table 1). Thus, the diene synthesis with 1,4-disubstituted diene, e.g., hexa-2,4-diene, requires rather harsh conditions; while the cycloadduct (**10a**) was prepared with an appropriate yield (65%). The same reaction with acetylene (**3b**) (Rf = C_2F_5) failed even upon 10–12 h of heating at 200 °C, indicating the extreme instability of the expected cycloadduct. Another example of thermal instability of C_2F_5-substituted adducts is

Table 1
Reaction conditions of 1,4-cycloaddition of conjugated dienes, aromatic and heteroaromatic compounds to perfluoroacetylenephosphonates (**3a** and **b**)

No.	Dienophile	Cycloadduct(s) (ratio of regioisomers, mol%)[a]	Reaction conditions				Yield of isolated Diels–Alder product (%)	Other products
			Temperature (°C)	Duration (h)	Solvent	Ratio of reagents (mol) diene:dienophile		
1	**3a**	**4a**	80	2	Benzene	1.5:1	85	
2	**3b**	**4b**	80	2	Benzene	2:1	82	
3	**3a**	**5a**	70	2	Benzene	1.5:1	80	
4	**3b**	**5b**	75	3	Benzene	1.5:1	73	**15b**[b]
5	**3a**	**6a**	195	4	Benzene	1:1	66	
6	**3b**	**6b**	195	6	Benzene	1.1:1	70	
7	**3a**	**7a + 8a** (61:39)	80	3	Benzene	1.5:1	88	
8	**3b**	**7b + 8b** (56:44)	80	3.5	Benzene	2:1	78	
9	**3a**	**9a**	100	12	1,3-Diene	20:1	74	**16a**, **17a**[c]
10	**3b**	**9b**	120	15	1,3-Diene	25:1	67	**16b**, **17b**[c]
11	**3a**	**10a**	180	12	Benzene	2:1	65	
12	**3a**	**11a**	80	5	Furan	15:1	90	
13	**3b**	**11b**	85	6	Furan	20:1	81	**3b**[d]
14	**3a**	**12a**	80	10	THF	1.1:1	82	
15	**3b**	**12b**	85	15	THF	1.5:1	76	
16	**3a**	**13a + 14a** (66:34)	80	12	Benzene	3:1	81	**3a**[d]
17	**3b**	**13b + 14b** (86:14)	85	15	Benzene	5:1	73	**3b**[d]

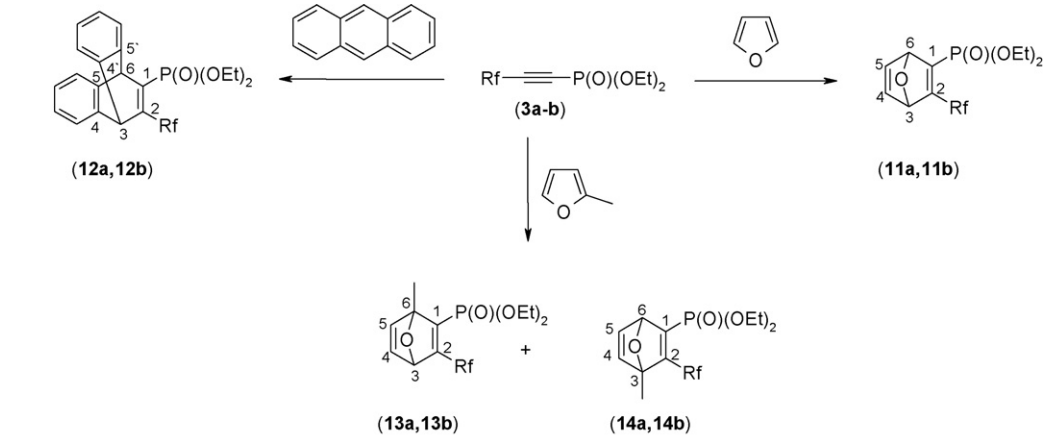
[a] By analysis of the ratio of integral intensity of ^{31}P, ^{19}F and ^{1}H NMR signals.
[b] ~5 mol% in the main compound after distillation.
[c] ~3% and 2% mol of isomeric cyclohexadienes (^{31}P NMR, $\delta \sim 14.7$ and $\delta \sim 14.9$–15.1 ppm) in the main product after distillation.
[d] ~2–5 mol% in the main compound after distillation, determined by analysis of integral intensities of ^{31}P, ^{19}F NMR signals.



Scheme 2.

compound (**5b**), which upon the distillation shows *retro*-Diels–Alder reaction with ethylene elimination and formation of the aromatic compound, diethyl 2-(pentafluoroethyl)phenylphosphonate (**15b**) as an admixture (~5 mol%). The formation of the compound (**15b**) was confirmed by the methods ^{31}P, ^{19}F, and ^{1}H NMR spectroscopy. During the distillation of carbocyclic compounds (**9a** and **b)** (^{31}P, ^{19}F NMR spectroscopy), the C(4) = C(5) double bond migration has been observed and expected product was obtained with traces of isomeric cyclohexa-2,4- (**16a** and **b**, ~3 mol%) and -2,6-dienylperfluoroalkylphosphonates (**17a** and **b,** ~2 mol%) (Scheme 2).

Compounds (**4a** and **b–9a** and **b**; **10a**) are colorless liquids. Their structures were established using ^{1}H, ^{31}P, ^{19}F and ^{13}C NMR spectroscopy. In the ^{1}H NMR spectra the characteristic signals are those of methylene protons in the region of δ 1.1–1.6 ppm and of vinyl protons at δ 5.0–7.0 ppm. The ^{13}C NMR spectra of compounds (**4a** and **b–9a** and **b**; **10a**) are characterized by quadruplet(triplet)–doublet and doublet–quadruplet(triplet) signals of carbon nuclei C(2) and C(1), respectively, in the region of δ 157–131 ppm with the coupling constants $^{1}J_{CP} \sim 180$ Hz, $^{1}J_{CF} \sim 280$ Hz, $^{2}J_{CF} \sim 40$ Hz, $^{2}J_{CP} \sim 4–10$ Hz, and by typical doublet signals of carbon nuclei C(4), C(5) and C(3), C(6) at δ 115–143 ppm ($^{3}J_{CP} \sim 4–6$ Hz) and at δ 57–



Scheme 3.

28 ppm ($^2J_{CP} \sim 6$–11 Hz). The ^{31}P NMR spectra contain characteristic signals in the region of $\delta \sim 9$–15 ppm, the ^{19}F NMR spectra show signals at $\delta \sim -54$ to -64 (~ -83, -112) ppm.

Perfluoroacetylenephosphonates (**3a** and **b**) readily undergo Diels–Alder reaction with furan, anthracene and 2-methylfuran, forming corresponding carbocyclic and (hetero)bicyclic perfluoroalkylphosphonates (**11a** and **b**–**14a** and **b**) in good yields (90–73%). The reactions were conducted by heating in a sealed ampoule with a catalytic amount of 1,4-hydroquinone (5 mol%) as a polymerization inhibitor (Scheme 3), in an appropriate solvent (Table 1) or in an excess of a diene. The reaction conditions, reagent ratio and yields of products are given in Table 1.

The reactivity of 2-methylfuran does not differ from that of unsubstituted furan, contrasting to 1-substituted 1,3-dienes (penta-1,3-diene, hexa-2,4-diene) and unsubstituted 1,3-butadiene (Table 1). This fact could be probably explained by the fixed *cis*-configuration of the diene system in furans; the role of a methyl group is limited to its electron-donor effect. The similar reactivity was observed when anthracene was used as a diene (Table 1).

The stability of carbocyclic and (hetero)bicyclic adducts (**11a** and **b–14a** and **b**) depends mainly on the type of perfluoroalkyl group and on the presence of substituents at the 3 and 6 positions. Compounds (**13a** and **b–14a** and **b)** even at heating to 85–90 °C undergo *retro*-Diels–Alder reaction forming starting reagents: 2-methylfuran and a perfluoroacetylenephosphonate (**3a** and **b**), which in small amounts (2–5%) were identified by ^{31}P, ^{19}F NMR spectroscopy. The most remarkable are traces (5%) of acetylene (**3b**) during the distillation of the mixture of regioisomers (**13b + 14b**) with Rf = C_2F_5. At 180–200 °C the *retro*-Diels–Alder reaction of compounds (**13a** and **b–14a** and **b**) proceeds quantitatively within a few minutes. The bicyclic adducts (**11a** and **11b**) show much higher thermal stability; compound (**11a**) remains intact at short time heating to 200 °C and even at longer heating at 90–100 °C. The distillation of perfluoroalkylphosphonate (**11b**) with Rf = C_2F_5 afford insignificant amount of the alkyne (**3b**) (1–2%). Bicyclic compounds (**12a**, **12b**) show higher thermal stability and compound (**12a**) is resistant to the prolonged heating at 130–150 °C. Only at 170–200 °C compounds (**12b**, **12a**) decompose slowly into substrates: alkynes (**3a** and **b**) and anthracene.

With symmetrical dienes (furan and anthracene) the reaction is regioselective and affords only one regioisomer (**11a** and **b**–**12a** and **b**). In the case of 2-methylfuran the reaction is not regioselective, forming a mixture of regioisomers: (**13a** + **14a**), (**13b** + **14b**) and 6-Me-substituted isomers (**13a** and **13b**) predominantly. With the alkyne (**3b**) the regioselectivity of the reaction is noticeably higher than with (**3a**), giving 86%:14% for the (**13b**:**14b**) and 66%:34% for (**13a**:**14a**). Structures of the regioisomers (**13b**, **14b**) and (**13a**, **14a**) were unequivocally determined by ^{13}C NMR spectra. Chemical shifts and spin–spin coupling constants of carbon nuclei C(3) and C(6), C(4) and C(5) of the isomers (**13b**, **14b**) and (**13a**, **14a**) are quite characteristic and allowed easy identification of these compounds.

Compounds (**11a** and **b–14a** and **b**) are colorless liquids stable under ambient conditions. The cycloadduct (**12a**) is a colorless crystalline substance. Structures of these compounds were established using ^1H, ^{31}P, ^{19}F, and ^{13}C NMR spectroscopy and mass-spectrometry. Structure of compound (**12a**) is confirmed by X-ray structural analysis (Fig. 1).

The ^1H NMR spectra are characterized by the resonance signals of the methylene groups protons at δ 5.5–5.9 ppm, the methyl groups at $\delta \approx 1.8$–1.9 ppm and vinyl protons at δ 5.5–7.5 ppm. The ^{13}C NMR spectra of compounds (**11a** and **b–14a** and **b**) contain quadruplet(triplet)–doublet and doublet–quadruplet(triplet) signals of C(2) and C(1) nuclei at δ 152–157 ppm and δ 145–154 ppm

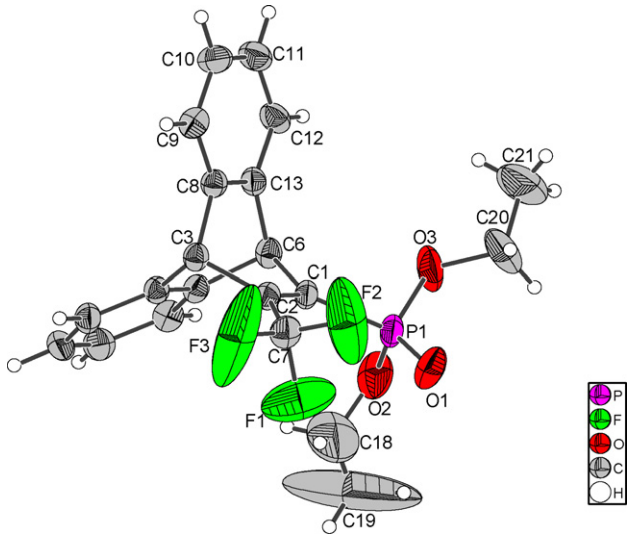


Fig. 1. Molecular structure of compound ***12a***; bond length in pm, bond angle in °[P(1)-O(1) 146.8(3); P(1)-O(2) 158.1(4); P(1)-O(3) 154.7(3); O(2)-C(18) 143.2(10); O(3)-C(20) 143.3(7); C(18)-C(19) 114.9(14); C(20)-C(21) 144.3(11); P(1)-C(1) 179.2(3); C(1)-C(2) 133.8(5); C(2)-C(7) 150.9(5); F(1)-C(7) 133.3(6); C(2)-C(3) 153.6(4); C(3)-C(4) 153.0(4); C(4)-C(5) 139.5(4); C(3)-C(8) 152.3(4); C(6)-C(13) 151.2(5); C(8)-C(9) 139.0(5); C(9)-C(10) 140.1(5); C(10)-C(11) 139.2(6); O(1)-P(1)-O(3) 117.2(2); O(1)-P(1)-O(2) 115.4(2); O(3)-P(1)-O(2) 98.8(3); O(1)-P(1)-C(1) 117.45(18); O(3)-P(1)-C(1) 102.18(19); O(2)-P(1)-C(1) 103.12(18); C(2)-C(1)-C(6) 112.1(3); C(2)-C(1)-P(1) 132.0(3); C(6)-C(1)-P(1) 115.9(2); C(1)-C(2)-C(7) 127.8(3); C(1)-C(2)-C(3) 114.9(3); C(7)-C(2)-C(3) 117.3(3); C(8)-C(3)-C(4) 105.3(2); C(8)-C(3)-C(2) 105.8(3); C(4)-C(3)-C(2) 105.0(3); C(11)-C(10)-C(9) 121.6(4); C(8)-C(13)-C(12) 120.4(3); F(3)-C(7)-F(2) 118.6(6); F(3)-C(7)-F(1) 100.6(7); F(3)-C(7)-C(2) 114.6(4).

with coupling constants $^1J_{CP} \sim 185$–203 Hz, $^1J_{CF} \sim 270$–290 Hz, $^2J_{CF} \sim 26$–37 Hz and $^2J_{CP} \sim 7$–11 Hz, and characteristic signals of C(4), C(5) and C(3), C(6) nuclei at δ 143–147 ppm and δ 84–94 ppm. In the ^{31}P spectra the characteristic signals are those at $\delta \sim 9$–13 ppm, in ^{19}F NMR spectra the signals at $\delta \sim -62$ to -64 (~ -84, -113) ppm.

In conclusion, we demonstrated a new methodology for the synthesis of carbocyclic, carbobicyclic and carbo(hetero)bicyclic 1,2-perfluoroalkyl vinylphosphonates, based on the Diels–Alder reaction of perfluoroacetylenephosphonates (**3a** and **b**) with classical donor acyclic and cyclic 1,3-alkadienes and some aromatic and heteroaromatic compounds.

3. Experimental

All reagents from commercial suppliers, were used without further purification. All solvents were freshly distilled before use from appropriate drying agents THF was distilled from sodium/benzophenone and used immediately. All other reagents were recrystallized or distilled when necessary. Reactions were performed under atmosphere of dry nitrogen. Analytical TLCs were performed with Merck silica gel 60 F_{254} plates. Visualization was accomplished by UV light or spraying by $Ce(SO_4)_2$ solution in 5% H_2SO_4. Column chromatography was carried out using Merck silica gel 60 (230–400 mesh ASTM). Melting points were determined with an Electrothermal IA9100 Digital Melting Point Apparatus without correction. All boiling points are uncorrected. NMR spectra were obtained on a Bruker DPX-200 spectrometer operating at 200.13 MHz for ^1H (TMS), 188.31 MHz for ^{19}F ($CFC1_3$), 80.99 MHz for ^{31}P (H_3PO_4) and 50.32 MHz for ^{13}C (TMS). MS and HRMS spectra were obtained on a Varian MAT CH7A instrument at 70 eV.

3.1. Synthesis of perfluoroalkylacetylene phosphonates (**3a** and **b**) (general procedure)

Method A. To a solution of 69 mmol of corresponding ketone–enol mixture (**1a** and **b**) or (**2a** and **b**) in 100 ml of anhydrous methylene chloride cooled to −40 °C under dry nitrogen atmosphere at vigorous stirring was quickly added diisopropylmethylamine 32.1 g (248 mmol). The solution was stirred for 10 min at this temperature and then trifluoromethanesulfonic acid anhydride 23.4 g (83 mmol) was added dropwise keeping the mixture below −30 °C. The suspension was kept for 3 h at −30 °C and then for 3 h at 5–7 °C. The reaction mixture was diluted with anhydrous ether (1000 ml) and left overnight at −30 °C. The suspension was filtered, the solid was washed with cold ether (3× 50 ml). The filtrate was washed with water (2× 250 ml) and 3% hydrochloric acid (2× 320 ml) and dried over $MgSO_4$. The solvents were evaporated at a reduced pressure and residue was distilled in a vacuum with a 20 cm Vigreux column.

Method B. To a suspension of phosphorus pentoxide 10.79 g (76 mmol) in 50 ml of anhydrous methylene chloride cooled to −20 to −25 °C under dry nitrogen atmosphere with vigorous stirring was added dropwise a solution of 69 mmol of the corresponding ketone–enol mixture (**1a** and **b**) or (**2a** and **b**) and triethylamine 27.93 g (276 mmol) in 70 ml of anhydrous methylene chloride, maintaining the reaction mixture temperature below −20 °C. The suspension was stirred for 3 h at this temperature and then for 4 h at 5–7 °C. Then the reaction mixture was diluted with anhydrous ether (1000 ml) and left overnight at −30 °C. The product was isolated as presented in the *Method A*.

*Diethyl 3,3,3-trifluoroprop-1-ynylphosphonate (**3a**)*. Bp: 81–85 °C (12 mm Hg). Yield: 90% (*Method A*), 50% (*Method B*). ^{31}P NMR($CDCl_3$) δ: −10.19 (q, $^4J_{PF}$ 4.0 Hz). ^{19}F NMR($CDCl_3$) δ: −53.87 (d, 3F, $^4J_{FP}$ 4.0 Hz). ^{13}C NMR($CDCl_3$) δ: 113.29 (qd, C-3, $^1J_{CF}$ 260.5, $^3J_{CP}$ 6.1 Hz), 82.38 (dq, C-2, $^2J_{CP}$ 52.9, $^2J_{CF}$ 53.9 Hz), 77.58 (dq, C-1, $^1J_{CP}$ 275.9, $^3J_{CF}$ 6.1 Hz), 64.87 (d, C-i, $^2J_{CP}$ 5.8 Hz), 16.23 (d, C-j, $^3J_{CP}$ 6.7 Hz). ^{1}H NMR($CDCl_3$) δ: 4.17 (dq, 4H, $^3J_{HH}$ 7.3, $^3J_{HP}$ 8.8 Hz), 1.33(td, 3H, $^3J_{HH}$ 7.2, $^4J_{HP}$ 0.7 Hz). MS (EI) *m*/*e* = 229 ([M–H]$^+$, 2%), 215(5), 203(42), 201(14), 182(40), 175(100), 157(44); HRMS *m*/*e* ([M–H]$^+$) calculated for $C_7H_9O_3F_3P$ 229.02414, found 229.02366.

*Diethyl 3,3,4,4,4-pentafluorobut-1-ynylphosphonate (**3b**)*. Bp: 105–107 °C (12 mm Hg). Yield: 87% (*Method A*), 60% (*Method B*). ^{31}P NMR($CDCl_3$) δ: −10.58 (*t*, $^4J_{PF}$ 6.0 Hz). ^{19}F NMR($CDCl_3$) δ: −86.47 (*t*, 3F, $^3J_{FF}$ 2.6 Hz), −106.05 (m, 2F). ^{13}C NMR($CDCl_3$) δ: 117.69 (qt, C-4, $^1J_{CF}$ 285.3, $^2J_{CF}$ 35.1, $^4J_{CP}$ 1.2 Hz), 104.53 (tq, C-3, $^1J_{CF}$ 249.0, $^2J_{CF}$ 43.4, $^3J_{CP}$ 5.0 Hz), 82.61 (dt, C-1, $^1J_{CP}$ 272.6, $^3J_{CF}$ 6.2 Hz), 81.69 (dt, C-2, $^2J_{CP}$ 46.5, $^2J_{CF}$ 36.9 Hz), 64.93 (d, C-i, $^2J_{CP}$ 5.9 Hz), 16.17 (d, C-j, $^3J_{CP}$ 6.5 Hz). ^{1}H NMR($CDCl_3$) δ: 4.18 (dq, 4H, $^3J_{HH}$ 7.1, $^3J_{HP}$ 8.1 Hz), 1.34 (td, 3H, $^3J_{HH}$ 6.9, $^4J_{HP}$ 0.7 Hz). MS (EI) *m*/*e* = 279 ([M–H]$^+$, 20%), 253(57), 237(20), 225(100), 207(18), 183(21), 157(7); HRMS *m*/*e* ([M–H]$^+$) calculated for $C_8H_9O_3F_5P$ 279.02095, found 279.02190.

3.2. Diels–Alder reaction (typical procedure)

To a preliminary cooled 50 ml ampoule (−30 °C) was placed 5 mmol of corresponding diethyl perfluoroacetylenephosphonate (**3a** and **b**) in 5 ml of appropriate solvent (see Table 1), then required 1,3-diene cooled to 0 °C in amount listed in Table 1 was added and the ampoule was sealed. The mixture was heated at the temperature from 70 to 195 °C for 2–12 h (Table 1). The reaction proceeding was monitored by means of ^{31}P and ^{19}F NMR spectroscopy and it was carried out after complete consumption of the parent alkynephosphonate. Then solvent and 1,3-diene excess were removed in a vacuum and crude product was purified by distillation in a high vacuum, or by crystallization, or by column chromatography.

*Diethyl 4,5-dimethyl-2-(trifluoromethyl)cyclohexa-1,4-dien-1-ylphosphonate (**4a**)*. Bp: 85–87 °C (0.1 mm Hg). Yield: 85%. ^{31}P NMR($CDCl_3$) δ: 14.67 (q, $^4J_{PF}$ 3.5 Hz). ^{19}F NMR($CDCl_3$) δ: −63.46 (d, 3F, $^4J_{FP}$ 3.4 Hz). ^{13}C NMR($CDCl_3$) δ: 136.77 (qd, C-2, $^2J_{CF}$ 32.9, $^2J_{CP}$ 3.7 Hz), 131.30 (dq, C-1, $^1J_{CP}$ 178.3, $^3J_{CF}$ 3.1 Hz), 122.74 (qd, C-7, $^1J_{CF}$ 275.1, $^3J_{CP}$ 10.2 Hz), 122.29 (d, C-5, $^3J_{CP}$ 10.2 Hz), 120.90 (s, C-4), 62.67 (d, C-i, $^2J_{CP}$ 6.2 Hz), 37.00 (d, C-6, $^2J_{CP}$ 7.8 Hz), 33.56 (dq, C-3, $^3J_{CP}$ 13.0, $^3J_{CF}$ 2.8 Hz), 18.01 (s, C-8), 17.94 (s, C-9), 16.49 (d, C-j, $^3J_{CP}$ 6.5 Hz). ^{1}H NMR($CDCl_3$) δ: 4.05 (dq, 4H, $^3J_{HH}$ 7.7, $^3J_{HP}$ 8.4 Hz), 2.94 (m, 2H), 2.82 (d, 2H, $^3J_{HP}$ 8.8 Hz), 1.58 (s, 6H), 1.25 (*t*, 6H, $^3J_{HH}$ 7.0 Hz). MS (EI) *m*/*e* = 311 ([M–H]$^+$, 55%), 291(70), 255(20), 235(100), 215(93), 201(12), 187(5), 155(40); HRMS *m*/*e* ([M–H]$^+$) calculated for $C_{13}H_{19}F_3O_3P$ 311.10239, found 311.10175.

*Diethyl 4,5-dimethyl-2-(pentafluoroethyl)cyclohexa-1,4-dien-1-ylphosphonate (**4b**)*. Bp: 90–92 °C (0.1 mm Hg). Yield: 82%. ^{31}P NMR($CDCl_3$) δ: 15.00 (*t*, $^4J_{PF}$ 4.0 Hz). ^{19}F NMR($CDCl_3$) δ: −82.33 (*t*, 3F, $^3J_{FF}$ 2.2 Hz), −111.19 (m, 2F). ^{13}C NMR($CDCl_3$) δ: 135.16 (td, C-2, $^2J_{CF}$ 22.5, $^2J_{CP}$ 3.7, $^3J_{CF}$ 0.8 Hz), 134.78 (dt, C-1, $^1J_{CP}$ 179.6, $^3J_{CF}$ 3.1 Hz), 122.54 (d, C-5, $^3J_{CP}$ 9.2 Hz), 121.20 (m, C-4), 119.43 (qt, C-8, $^1J_{CF}$ 287.8, $^2J_{CF}$ 38.2, $^4J_{CP}$ 1.7 Hz), 113.41 (tq, C-7, $^1J_{CF}$ 256.3, $^2J_{CF}$ 38.9, $^3J_{CP}$ 1.7 Hz), 62.66 (d, C-i, $^2J_{CP}$ 6.5 Hz), 38.20 (d, C-6, $^2J_{CP}$ 8.5 Hz), 33.84 (dt, C-3, $^3J_{CP}$ 12.9, $^3J_{CF}$ 2.0 Hz), 18.11 (d, C-9, $^4J_{CP}$ 0.9 Hz), 18.00 (d, C-10, $^5J_{CP}$ 0.7 Hz), 16.56 (d, C-j, $^3J_{CP}$ 6.5 Hz). ^{1}H NMR($CDCl_3$) δ: 4.10 (dq, 4H, $^3J_{HH}$ 7.3, $^3J_{HP}$ 8.8 Hz), 3.02 (m, 2H), 2.83 (d, 2H, $^3J_{HP}$ 7.3 Hz), 1.62 (s, 6H), 1.29 (*t*, 6H, $^3J_{HH}$ 7.1 Hz). MS (EI) *m*/*e* = 361 ([M–H]$^+$, 100%), 341(85), 333(20), 313(20), 305(30), 285(85), 265(8), 215(30); HRMS *m*/*e* ([M–H]$^+$) calculated for $C_{14}H_{19}F_5O_3P$ 361.09920, found 361.09922.

*Diethyl 3-(trifluoromethyl)bicyclo[2.2.2]octa-2,5-dien-2-ylphosphonate (**5a**)*. Bp: 82–84 °C (0.1 mm Hg). Yield: 80%. ^{31}P NMR($CDCl_3$) δ: 12.80 (q, $^4J_{PF}$ 4.0 Hz). ^{19}F NMR($CDCl_3$) δ: −62.89 (d, 3F, $^4J_{FP}$ 4.0 Hz). ^{13}C NMR($CDCl_3$) δ: 146.62 (qd, C-2, $^2J_{CF}$ 33.9, $^2J_{CP}$ 6.4 Hz), 139.78 (dq, C-1, $^1J_{CP}$ 185.1, $^3J_{CF}$ 4.2 Hz), 134.45 (d, C-5, $^3J_{CP}$ 4.2 Hz), 133.28 (d, C-4, $^4J_{CP}$ 2.1 Hz), 122.45 (qd, C-7, $^1J_{CF}$ 272.7, $^3J_{CP}$ 7.1 Hz), 62.58 (d, C-i, $^2J_{CP}$ 5.7 Hz), 41.34 (d, C-6, $^2J_{CP}$ 8.5 Hz), 38.59 (dq, C-3, $^3J_{CP}$ 9.9, $^3J_{CF}$ 2.8 Hz), 24.68 (d, C-8, $^3J_{CP}$ 2.1 Hz), 24.22 (s, C-9), 16.50 (d, C-j, $^3J_{CP}$ 6.4 Hz). ^{1}H NMR($CDCl_3$) δ: 6.29 (m, 2H), 4.26 (m, 2H), 3.98 (m, 4H, $^3J_{HP}$ 7.1 Hz), 1.32 (s, 4H), 1.22 (td, 6H, $^3J_{HH}$ 7.2, $^4J_{HP}$ 2.1 Hz). MS (EI) *m*/*e* = 310 ([M]$^+$, 22%), 290(17), 281(20), 255(35), 227(38), 213(100), 207(30), 172(38), 162(36), 153(18); HRMS *m*/*e* ([M]$^+$) calculated for $C_{13}H_{18}F_3O_3P$ 310.09457, found 310.09436.

*Diethyl 3-(pentafluoroethyl)bicyclo[2.2.2]octa-2,5-dien-2-ylphosphonate (**5b**)*. Bp: 86–88 °C (0.1 mm Hg). Yield: 73%. ^{31}P NMR spectrum, δ, ppm ($CDCl_3$): 12.86 (*t*, $^4J_{PF}$ 5.45 Hz). ^{19}F NMR($CDCl_3$) δ: −84.02 (*t*, 3F, $^3J_{FF}$ 3.0 Hz), −112.56 (m, 2F). ^{13}C NMR($CDCl_3$) δ: 145.27 (td, C-2, $^2J_{CF}$ 23.1, $^2J_{CP}$ 6.1 Hz), 143.26 (dt, C-1, $^1J_{CP}$ 186.2, $^3J_{CF}$ 3.6 Hz), 134.53 (d, C-5, $^3J_{CP}$ 3.9 Hz), 133.42 (d, C-4, $^4J_{CP}$ 1.9 Hz), 119.26 (qt, C-8, $^1J_{CF}$ 287.5, $^2J_{CF}$ 39.9, $^4J_{CP}$ 1.6 Hz), 112.83 (tq, C-7, $^1J_{CF}$ 254.0, $^2J_{CF}$ 39.1, $^3J_{CP}$ 5.6 Hz), 62.49 (d, C-i, $^2J_{CP}$ 5.7 Hz), 42.12 (d, C-6, $^2J_{CP}$ 8.5 Hz), 39.28 (dt, C-3, $^3J_{CP}$ 9.6, $^3J_{CF}$ 4.5 Hz), 24.34 (d, C-9, $^4J_{CP}$ 1.2 Hz), 24.11 (s, C-10), 16.41 (d, C-j, $^3J_{CP}$ 6.4 Hz). ^{1}H NMR($CDCl_3$) δ: 6.26 (m, 2H), 4.30 (m, 2H), 3.95 (m, 4H, $^3J_{HP}$ 6.9 Hz), 1.28 (s, 4H), 1.18 (td, 6H, $^3J_{HH}$ 7.3, $^4J_{HP}$ 2.7 Hz). MS (EI) *m*/*e* = 360 ([M]$^+$, 25%), 331(30), 305(38), 277(60), 260(35), 222(25), 213(100), 189(37); HRMS *m*/*e* ([M]$^+$) calculated for $C_{14}H_{18}F_5O_3P$ 360.09137, found 360.09153.

*Diethyl 3-(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-dien-2-ylphosphonate (**6a**)*. Bp: 81–82 °C (0.1 mm Hg). Yield: 66%. ^{31}P NMR($CDCl_3$) δ: 12.26 (q, $^4J_{PF}$ 4.5 Hz). ^{19}F NMR($CDCl_3$) δ: −63.52 (d, 3F, $^4J_{FP}$ 4.3 Hz). ^{13}C NMR($CDCl_3$) δ: 156.44 (qd, C-2, $^2J_{CF}$ 35.9, $^2J_{CP}$ 10.0 Hz), 148.61 (dq, C-1, $^1J_{CP}$ 197.3, $^3J_{CF}$ 4.6 Hz), 142.96 (dq, C-5, $^3J_{CP}$ 3.3, $^5J_{CP}$ 1.5 Hz), 142.05 (dq, C-4, $^4J_{CP}$ 2.7, $^4J_{CF}$ 0.6 Hz), 122.85 (qd, C-7, $^1J_{CF}$ 270.9, $^3J_{CP}$ 4.6 Hz), 73.73 (dq, C-8, $^3J_{CP}$ 5.6, $^4J_{CF}$ 0.8 Hz), 62.60 (d, C-i, $^2J_{CP}$ 6.3 Hz), 56.45 (d, C-6, $^2J_{CP}$ 10.4 Hz), 53.59 (dq, C-3,

$^3J_{CP}$ 13.0, $^3J_{CF}$ 2.1 Hz), 16.50 (d, C-j, $^3J_{CP}$ 6.5 Hz). ^{1}H NMR($CDCl_3$) δ: 6.81 (m, 2H), 4.04 (m, 1H), 3.97 (dq, 4H, $^3J_{HP}$ 8.1, $^3J_{HH}$ 3.2 Hz), 3.84 (m, 1H), 2.04 (dd, 2H, $^2J_{HH}$ 36.0, $^3J_{HH}$ 6.9 Hz), 1.22 (*t*, 6H, $^3J_{HH}$ 7.1 Hz). MS (EI) *m*/*e* = 296 ([M]$^+$, 15%), 267(5), 252(8), 247(10), 227(100), 200(30), 175(45), 159(18), 140(18), 109(25); HRMS *m*/*e* ([M]$^+$) calculated for $C_{12}H_{16}F_3O_3P$ 296.07892, found 296.07845.

Diethyl 3-(pentafluoroethyl)bicyclo[2.2.1]hepta-2,5-dien-2-ylphosphonate (**6b**). Bp: 84–85 °C (0.1 mm Hg). Yield: 70%. ^{31}P NMR($CDCl_3$) δ: 12.20 (*t*, $^4J_{PF}$ 5.2 Hz). ^{19}F NMR($CDCl_3$) δ: −84.39 (*t*, 3F, $^3J_{FF}$ 3.0 Hz), −113.58 (m, 2F). ^{13}C NMR($CDCl_3$) δ: 155.07 (td, C-2, $^2J_{CF}$ 25.0, $^2J_{CP}$ 10.2 Hz), 151.99 (dt, C-1, $^1J_{CP}$ 198.2, $^3J_{CF}$ 3.1 Hz), 142.91 (m, C-4), 141.99 (d, C-5, $^3J_{CP}$ 2.6 Hz), 119.35 (qt, C-8, $^1J_{CF}$ 286.1, $^2J_{CF}$ 39.9, $^4J_{CP}$ 2.0 Hz), 113.09 (tq, C-7, $^1J_{CF}$ 253.9, $^2J_{CF}$ 39.9, $^3J_{CP}$ 3.7 Hz), 73.55 (d, C-9, $^3J_{CP}$ 5.6 Hz), 62.52 (d, C-i, $^2J_{CP}$ 6.1 Hz), 57.04 (dq, C-6, $^2J_{CP}$ 10.1, $^4J_{CF}$ 0.9 Hz), 54.37 (d, C-3, $^3J_{CP}$ 13.3 Hz), 16.45 (d, C-j, $^3J_{CP}$ 6.5 Hz). ^{1}H NMR($CDCl_3$) δ: 6.78 (dd, 1H, $^3J_{HH}$ 4.7, $^3J_{HH}$ 3.2 Hz), 6.76 (dd, 1H, $^3J_{HH}$ 4.7, $^3J_{HH}$ 2.9 Hz), 4.06 (m, 1H), 3.96 (dq, 4H, $^3J_{HP}$ 8.3, $^3J_{HH}$ 3.7 Hz), 3.82 (m, 1H), 2.02 (dd, 2H, $^2J_{HH}$ 34.7, $^3J_{HH}$ 6.9 Hz), 1.21 (*t*, 6H, $^3J_{HH}$ 6.9 Hz). MS (EI) *m*/*e* = 346 ([M]$^+$, 15%), 302(17), 269(25), 250(63), 227(100), 209(8), 189(6), 171(18); HRMS *m*/*e* ([M]$^+$) calculated for $C_{13}H_{16}F_5O_3P$ 346.07572, found 346.07541.

Diethyl 4-methyl-2-(trifluoromethyl)cyclohexa-1,4-dien-1-ylphosphonate (**7a**). Bp: 71–72 °C (0.1 mm Hg). Yield: 88% (together with isomer **8a**). Content in the mixture 61 mol%. ^{31}P NMR($CDCl_3$) δ: 14.90 (q, $^4J_{PF}$ 3.5 Hz). ^{19}F NMR($CDCl_3$) δ: −63.62 (d, 3F, $^4J_{FP}$ 2.9 Hz). ^{13}C NMR($CDCl_3$) δ: 136.36 (qd, C-2, $^2J_{CF}$ 31.6, $^2J_{CP}$ 4.7 Hz), 131.29 (dq, C-1, $^1J_{CP}$ 178.1, $^3J_{CF}$ 3.3 Hz), 122.73 (qd, C-7, $^1J_{CF}$ 275.7, $^3J_{CP}$ 10.6 Hz), 117.20 (d, C-5, $^3J_{CP}$ 10.2 Hz), 115.82 (m, C-4), 62.63 (d, C-i, $^2J_{CP}$ 6.4 Hz), 31.43 (dq, C-3, $^3J_{CP}$ 13.0, $^3J_{CF}$ 3.1 Hz), 31.42 (d, C-6, $^2J_{CP}$ 8.5 Hz), 22.48 (s, C-8), 16.43 (d, C-j, $^3J_{CP}$ 6.5 Hz). ^{1}H NMR($CDCl_3$) δ: 5.26 (m, 1H), 3.98 (dq, 4H, $^3J_{HH}$ 7.1, $^3J_{HP}$ 8.6 Hz), 2.94 (m, 2H), 2.85 (m, 2H), 1.56 (s, 3H), 1.19 (*t*, 6H, $^3J_{HH}$ 7.1 Hz). MS (EI) *m*/*e* = 297 ([M−H]$^+$, 85%), 277(62), 269(10), 249(20), 241(30), 221(100), 201(80), 141(55); HRMS *m*/*e* ([M−H]$^+$) calculated for $C_{12}H_{17}F_3O_3P$ 297.08674, found 297.08685.

Diethyl 5-methyl-2-(trifluoromethyl)cyclohexa-1,4-dien-1-ylphosphonate (**8a**). Bp: 71–72 °C (0.1 mm Hg). Yield: 88% (together with isomer **7a**). Content in the mixture 39 mol%. ^{31}P NMR($CDCl_3$) δ: 14.67 (q, $^4J_{PF}$ 3.2 Hz). ^{19}F NMR($CDCl_3$) δ: −63.33 (d, 3F, $^4J_{FP}$ 2.0 Hz). ^{13}C NMR($CDCl_3$) δ: 136.67 (qd, C-2, $^2J_{CF}$ 31.5, $^2J_{CP}$ 3.7 Hz), 131.09 (dq, C-1, $^1J_{CP}$ 178.0, $^3J_{CF}$ 3.3 Hz), 130.20 (d, C-5, $^3J_{CP}$ 9.5 Hz), 128.89 (m, C-4), 122.86 (qd, C-7, $^1J_{CF}$ 275.7, $^3J_{CP}$ 10.5 Hz), 62.66 (d, C-i, $^2J_{CP}$ 6.4 Hz), 34.77 (d, C-6, $^2J_{CP}$ 8.1 Hz), 28.06 (dq, C-3, $^3J_{CP}$ 12.9, $^3J_{CF}$ 3.4 Hz), 22.47 (d, C-8, $^4J_{CP}$ 2.5 Hz), 16.43 (d, C-j, $^3J_{CP}$ 6.5 Hz). ^{1}H NMR($CDCl_3$) δ: 5.23 (m, 1H), 4.02 (dq, 4H, $^3J_{HH}$ 6.9, $^3J_{HP}$ 8.3 Hz), 2.73 (d, 2H, $^3J_{HP}$ 8.6 Hz), 2.67 (m, 2H), 1.56 (s, 3H), 1.20 (*t*, 6H, $^3J_{HH}$ 7.1 Hz). MS (EI) *m*/*e* = 297 ([M−H]$^+$, 85%), 277(62), 269(10), 249(20), 241(30), 221(100), 201(80), 141(55); HRMS *m*/*e* ([M−H]$^+$) calculated for $C_{12}H_{17}F_3O_3P$ 297.08674, found 297.08685.

Diethyl 4-methyl-2-(pentafluoroethyl)cyclohexa-1,4-dien-1-ylphosphonate (**7b**). Bp: 81–82 °C (0.1 mm Hg). Yield: 78% (together with isomer **8b**). Content in the mixture 56 mol%. ^{31}P NMR($CDCl_3$) δ: 15.21 (q, $^4J_{PF}$ 4.0 Hz). ^{19}F NMR($CDCl_3$) δ: −82.26 (*t*, 3F, $^3J_{FF}$ 2.2 Hz), −111.28 (m, 2F). ^{13}C NMR($CDCl_3$) δ: 134.76 (td, C-2, $^2J_{CF}$ 22.3, $^2J_{CP}$ 4.2, $^3J_{CF}$ 0.6 Hz), 134.53 (dt, C-1, $^1J_{CP}$ 180.0, $^3J_{CF}$ 3.3 Hz), 119.64 (qt, C-8, $^1J_{CF}$ 288.4, $^2J_{CF}$ 38.6, $^4J_{CP}$ 2.0 Hz), 117.36 (d, C-5, $^3J_{CP}$ 10.1 Hz), 115.96 (qd, C-4, $^4J_{CP}$ 1.7, $^3J_{CP}$ 1.2 Hz), 113.51 (tq, C-7, $^1J_{CF}$ 255.9, $^2J_{CF}$ 38.9, $^3J_{CP}$ 7.6 Hz), 62.67 (d, C-i, $^2J_{CP}$ 6.4 Hz), 33.63 (d, C-6, $^2J_{CP}$ 9.2 Hz), 31.76 (dq, C-3, $^3J_{CP}$ 13.0, $^3J_{CF}$ 2.2 Hz), 22.45 (s, C-9), 16.53 (d, C-j, $^3J_{CP}$ 6.7 Hz). ^{1}H NMR($CDCl_3$) δ: 5.36 (m, 1H), 4.10 (dq, 4H, $^3J_{HH}$ 7.1, $^3J_{HP}$ 10.3 Hz), 3.08 (m, 2H), 2.97 (m, 2H), 1.65 (s, 3H), 1.27 (*t*, 6H, $^3J_{HH}$ 7.1 Hz). MS (EI) *m*/*e* = 347 ([M−H]$^+$, 100%), 327(45), 319(20), 299(10), 291(55), 271(58), 251(5), 201(23), 191(22), 141(38); HRMS *m*/*e* ([M−H]$^+$) calculated for $C_{13}H_{17}F_5O_3P$ 347.08355, found 347.08418.

Diethyl 5-methyl-2-(pentafluoroethyl)cyclohexa-1,4-dien-1-ylphosphonate (**8b**). Bp: 81–82 °C (0.1 mm Hg). Yield: 78% (together with isomer **7b**). Content in the mixture 44 mol%. ^{31}P NMR($CDCl_3$) δ: 15.00 (q, $^4J_{PF}$ 4.0 Hz). ^{19}F NMR($CDCl_3$) δ: −82.30 (*t*, 3F, $^3J_{FF}$ 2.2 Hz), −111.00 (m, 2F). ^{13}C NMR($CDCl_3$) δ: 135.08 (td, C-2, $^2J_{CF}$ 22.2, $^2J_{CP}$ 3.6, $^3J_{CF}$ 1.1 Hz), 134.46 (dt, C-1, $^1J_{CP}$ 179.8, $^3J_{CF}$ 3.3 Hz), 130.54 (d, C-5, $^3J_{CP}$ 9.1 Hz), 129.26 (qd, C-4, $^4J_{CF}$ 1.6, $^4J_{CP}$ 1.1 Hz), 119.63 (qt, C-8, $^1J_{CF}$ 288.5, $^2J_{CF}$ 38.6, $^4J_{CP}$ 2.0 Hz), 113.53 (tq, C-7, $^1J_{CF}$ 255.8, $^2J_{CF}$ 39.0, $^3J_{CP}$ 7.6 Hz), 62.69 (d, C-i, $^2J_{CP}$ 6.4 Hz), 36.08 (d, C-6, $^2J_{CP}$ 8.0 Hz), 28.29 (dq, C-3, $^3J_{CP}$ 13.0, $^3J_{CF}$ 2.2 Hz), 22.48 (d, C-9, $^4J_{CP}$ 1.1 Hz), 16.50 (d, C-j, $^3J_{CP}$ 6.7 Hz). ^{1}H NMR($CDCl_3$) δ: 5.32(m, 1H), 4.06 (dq, 4H, $^3J_{HH}$ 7.1, $^3J_{HP}$ 9.5 Hz), 2.79 (d, 2H, $^3J_{HP}$ 8.3 Hz), 2.73 (m, 2H), 1.66 (s, 3H), 1.28 (*t*, 6H, $^3J_{HH}$ 7.1 Hz). MS (EI) *m*/*e* = 347 ([M−H]$^+$, 100%), 327(45), 319(20), 299(10), 291(55), 271(58), 251(5), 201(23), 191(22), 141(38); HRMS *m*/*e* ([M−H]$^+$) calculated for $C_{13}H_{17}F_5O_3P$ 347.08355, found 347.08418.

Diethyl 6-methyl-2-(trifluoromethyl)cyclohexa-1,4-dien-1-ylphosphonate (**9a**). Bp: 64–66 °C (0.1 mm Hg). Yield: 74%. ^{31}P NMR($CDCl_3$) δ: 15.24 (q, $^4J_{PF}$ 3.0 Hz). ^{19}F NMR($CDCl_3$) δ: −63.97 (d, 3F, $^4J_{FP}$ 3.0 Hz). ^{13}C NMR($CDCl_3$) δ: 156.42 (qd, C-2, $^2J_{CF}$ 35.9, $^2J_{CP}$ 10.1 Hz), 148.52 (dq, C-1, $^1J_{CP}$ 197.1, $^3J_{CF}$ 4.4 Hz), 142.93 (d, C-5, $^3J_{CP}$ 6.4 Hz), 142.03 (m, C-4, $^4J_{CP}$ 2.5 Hz), 122.77 (qd, C-7, $^1J_{CF}$ 270.8, $^3J_{CP}$ 4.6 Hz), 73.71 (dq, C-3, $^3J_{CP}$ 5.6, $^3J_{CF}$ 1.0 Hz), 62.58 (d, C-i, $^2J_{CP}$ 6.2 Hz), 56.41 (d, C-8, $^3J_{CP}$ 10.4 Hz), 53.56 (dq, C-6, $^2J_{CP}$ 13.1, $^4J_{CF}$ 1.9 Hz), 16.47 (d, C-j, $^3J_{CP}$ 6.6 Hz). ^{1}H NMR($CDCl_3$) δ: 5.67 (m, 1H), 5.59(m, 1H), 4.03 (dq, 4H, $^3J_{HH}$ 7.1, $^3J_{HP}$ 7.3 Hz), 3.32 (dd, 2H, $^3J_{HH}$ 9.3, $^4J_{HP}$ 5.4 Hz), 2.82 (m, 1H), 1.23 (*t*, 6H, $^3J_{HH}$ 6.9 Hz) 1.10 (d, 3H, $^3J_{HH}$ 6.9 Hz). MS (EI) *m*/*e* = 297 ([M−H]$^+$, 90%), 277(100), 269(20), 249(23), 241(80), 221(85), 201(63), 187(22), 173(15), 141(60); HRMS *m*/*e* ([M−H]$^+$) calculated for $C_{12}H_{17}F_3O_3P$ 297.08674, found 297.08679.

Diethyl 6-methyl-2-(pentafluoroethyl)cyclohexa-1,4-dien-1-ylphosphonate (**9b**). Bp: 68–70 °C (0.1 mm Hg). Yield: 67%. ^{31}P NMR($CDCl_3$) δ: 15.42 (q, $^4J_{PF}$ 4.0 Hz). ^{19}F NMR($CDCl_3$) δ: −81.95 (*t*, 3F, $^3J_{FF}$ 2.2 Hz), −110.82 (m, 2F). ^{13}C NMR($CDCl_3$) δ: 140.74 (dt, C-1, $^1J_{CP}$ 178.2, $^3J_{CF}$ 3.4 Hz), 135.92 (td, C-2, $^2J_{CF}$ 22.5, $^2J_{CP}$ 4.8 Hz), 131.13 (d, C-5, $^3J_{CP}$ 9.5 Hz), 121.08 (m, C-4), 119.34 (qt, C-8, $^1J_{CF}$ 288.4, $^2J_{CF}$ 37.7, $^4J_{CP}$ 1.6 Hz), 113.52 (tq, C-7, $^1J_{CF}$ 259.6, $^2J_{CF}$ 38.5, $^3J_{CP}$ 7.4 Hz), 62.65 (d, C-i, $^2J_{CP}$ 5.6 Hz), 35.97 (d, C-6, $^2J_{CP}$ 8.3 Hz), 27.29 (dq, C-3, $^3J_{CP}$ 11.9, $^3J_{CF}$ 2.6 Hz), 21.46 (m, C-9), 16.53 (d, C-j, $^3J_{CP}$ 6.7 Hz). ^{1}H NMR($CDCl_3$) δ: 5.80 (m, 1H), 5.65 (m, 1H), 4.09 (dq, 4H, $^3J_{HH}$ 7.3, $^3J_{HP}$ 7.1 Hz), 3.45 (d, 2H, $^3J_{HH}$ 10.1 Hz), 2.86 (m, 1H, $^3J_{HP}$ 3.7 Hz), 1.27 (*t*, 6H, $^3J_{HH}$ 7.1 Hz) 1.14 (d, 3H, $^3J_{HH}$ 6.6 Hz). MS (EI) *m*/*e* = 347 ([M−H]$^+$, 100%), 327(71), 319(30), 291(80), 271(68), 251(17), 201(21), 191(36), 173(15), 141(42); HRMS *m*/*e* ([M−H]$^+$) calculated for $C_{13}H_{17}F_5O_3P$ 347.08355, found 347.08413.

Diethyl 3,6-dimethyl-2-(trifluoromethyl)cyclohexa-1,4-dien-1-ylphosphonate (**10a**). Bp: 74–75 °C (0.1 mm Hg). Yield: 65%. ^{31}P NMR($CDCl_3$) δ: 15.22 (q, $^4J_{PF}$ 3.0 Hz). ^{19}F NMR($CDCl_3$) δ: −60.98 (d, 3F, $^4J_{FP}$ 3.0 Hz). ^{13}C NMR($CDCl_3$) δ: 142.84 (qd, C-2, $^2J_{CF}$ 29.6, $^2J_{CP}$ 2.6 Hz), 138.49 (dq, C-1, $^1J_{CP}$ 173.5, $^3J_{CF}$ 3.6 Hz), 130.01 (d, C-5, $^3J_{CP}$ 9.8 Hz), 128.73(dq, C-4, $^4J_{CP}$ 1.9, $^4J_{CF}$ 0.8 Hz), 123.07 (qd, C-7, $^1J_{CF}$ 277.0, $^3J_{CP}$ 10.1 Hz), 62.60 (d, C-i, $^2J_{CP}$ 6.4 Hz), 35.54 (d, C-6, $^2J_{CP}$ 9.0 Hz), 33.10 (dq, C-3 $^3J_{CP}$ 12.3, $^3J_{CF}$ 3.0 Hz), 24.01 (m, C-9), 23.25 (d, C-8, $^3J_{CP}$ 3.3 Hz), 16.51 (d, C-j, $^3J_{CP}$ 6.7 Hz). ^{1}H NMR($CDCl_3$) δ: 5.71 (m, 1H), 5.67 (m, 1H), 4.05 (dq, 4H, $^3J_{HH}$ 7.6, $^3J_{HP}$ 7.1 Hz), 3.29 (m, 1H), 3.05 (m, 1H), 1.26 (*t*, 6H, $^3J_{HH}$ 7.1 Hz), 1.21 (d, 3H, $^3J_{HH}$ 7.3 Hz), 1.17 (d, 3H, $^3J_{HH}$ 7.1 Hz). MS (EI) *m*/*e* = 311 ([M−H]$^+$, 10%), 297(100), 277(7), 241(10), 221(75), 201(70), 173(6), 155(22); HRMS *m*/*e* ([M−H]$^+$) calculated for $C_{13}H_{19}F_3O_3P$ 311.10239, found 311.10240.

Diethyl 3-(trifluoromethyl)-7-oxabicyclo[2.2.1]hepta-2,5-dien-2-ylphosphonate (**11a**). Bp: 74–75 °C (0.1 mm Hg). Yield: 90%. ^{31}P

NMR($CDCl_3$) δ: 8.98 (q, $^4J_{PF}$ 4.2 Hz). ^{19}F NMR($CDCl_3$) δ: −63.66 (d, 3F, $^4J_{FP}$ 4.2 Hz). ^{13}C NMR($CDCl_3$) δ: 156.42 (qd, C-2, $^2J_{CF}$ 36.0, $^2J_{CP}$ 10.7 Hz), 150.45 (dq, C-1, $^1J_{CP}$ 203.2, $^3J_{CF}$ 4.6 Hz), 144.25 (m, C-4), 143.04(d, C-5, $^3J_{CP}$ 2.3 Hz), 122.21 (qd, C-7, $^1J_{CF}$ 268.4, $^3J_{CP}$ 4.6 Hz), 87.63 (d, C-6, $^2J_{CP}$ 13.8 Hz), 84.29 (dq, C-3, $^3J_{CP}$ 12.3, $^3J_{CF}$ 2.3 Hz), 63.13 (d, C-i, $^2J_{CP}$ 5.4 Hz), 16.46 (d, C-j, $^3J_{CP}$ 6.9 Hz). ^{1}H NMR($CDCl_3$) δ: 7.07 (m, 2H), 5.67 (m, 1H), 5.52 (dd, 1H, $^3J_{HH}$ 3.7, $^3J_{HP}$ 3.4 Hz), 3.98 (dq, 4H, $^3J_{HP}$ 7.3, $^3J_{HH}$ 2.7 Hz), 1.95 (*t*, 6H, $^3J_{HH}$ 7.3 Hz). MS (EI) *m*/*e* = 298 ([M]$^+$, 2%), 272(5), 242(6), 229(25), 194(18), 189(20), 175(17), 157(5), 81(10), 68(100); HRMS *m*/*e* ([M]$^+$) calculated for $C_{11}H_{14}F_3O_4P$ 298.05818, found 298.05679.

*Diethyl 3-(pentafluoroethyl)-7-oxabicyclo[2.2.1]hepta-2,5-dien-2-ylphosphonate (***11b***).* Bp: 78–80 °C (0.1 mm Hg). Yield: 81%. ^{31}P NMR($CDCl_3$) δ: 9.10 (*t*, $^4J_{PF}$ 5.0 Hz). ^{19}F NMR($CDCl_3$) δ: −84.45 (*t*, 3F, $^3J_{FF}$ 3.0 Hz), −114.38 (m, 2F). ^{13}C NMR($CDCl_3$) δ: 155.34 (td, C-2, $^2J_{CF}$ 25.9, $^2J_{CP}$ 9.2 Hz), 153.77 (dt, C-1, $^1J_{CP}$ 203.1, $^3J_{CF}$ 3.4 Hz), 144.17 (m, C-4), 143.05 (d, C-5, $^3J_{CP}$ 1.6 Hz), 118.95 (qt, C-8, $^1J_{CF}$ 288.6, $^2J_{CF}$ 37.4, $^4J_{CP}$ 1.7 Hz), 112.74 (tq, C-7, $^1J_{CF}$ 252.8, $^2J_{CF}$ 41.4, $^3J_{CP}$ 3.6 Hz), 88.07 (d, C-6, $^2J_{CP}$ 14.1 Hz), 84.94 (dq, C-3, $^3J_{CP}$ 12.4, $^3J_{CF}$ 2.8 Hz), 63.12 (d, C-i, $^2J_{CP}$ 5.7 Hz), 16.48 (d, C-j, $^3J_{CP}$ 6.2 Hz). ^{1}H NMR($CDCl_3$) δ: 7.15 (dd, 1H, $^3J_{HH}$ 5.1, $^3J_{HH}$ 2.2 Hz), 7.07 (dd, 1H, $^3J_{HH}$ 5.4, $^3J_{HH}$ 2.0 Hz), 5.75 (m, 1H), 5.57 (dd, 1H, $^3J_{HH}$ 3.7, $^3J_{HP}$ 2.5 Hz), 4.05 (dq, 4H, $^3J_{HP}$ 8.3, $^3J_{HH}$ 2.2 Hz), 1.26 (*t*, 6H, $^3J_{HH}$ 6.9 Hz). MS (EI) *m*/*e* = 348 ([M]$^+$, 1%), 320(10), 300(20), 272(5), 253(32), 225(58), 207(10), 183(8), 68(100); HRMS *m*/*e* ([M]$^+$) calculated for $C_{12}H_{14}F_5O_4P$ 348.05499, found 348.05560.

*Diethyl 12-(trifluoromethyl)-9,10-dihydro-9,10-ethenoanthracen-11-ylphosphonate (***12a***).* Crude product was purified by recrystallization from benzene/hexane 1:4, colorless crystals (Yield: 82%, mp 54 °C). ^{31}P NMR($CDCl_3$) δ: 12.44 (q, $^4J_{PF}$ 4.5 Hz). ^{19}F NMR($CDCl_3$) δ: −62.74 (d, 3F, $^4J_{FP}$ 4.3 Hz). ^{13}C NMR($CDCl_3$) δ: 151.68 (qd, C-2, $^2J_{CF}$ 35.4, $^2J_{CP}$ 7.1 Hz), 145.00 (dq, C-1, $^1J_{CP}$ 185.9, $^3J_{CF}$ 4.3 Hz), 144.03 (m, C-4,4′), 144.32(d, C-5,5′, $^3J_{CP}$ 2.6 Hz), 128.80 (s, C-8,8′), 126.10 (d, C-11,11′, $^4J_{CP}$ 4.2 Hz), 124.38(s, C-10,10′), 124.17(s, C-9,9′), 123.16(qd, C-7, $^1J_{CF}$ 272.6, $^3J_{CP}$ 6.7 Hz), 63.10 (d, C-i, $^2J_{CP}$ 5.8 Hz), 55.13 (d, C-6, $^2J_{CP}$ 8.7 Hz), 52.49 (dq, C-3, $^3J_{CP}$ 10.0, $^3J_{CF}$ 2.8 Hz), 16.50 (d, C-j, $^3J_{CP}$ 6.8 Hz). ^{1}H NMR($CDCl_3$) δ: 7.46 (m, 4H), 7.07 (m, 4H), 5.87 (d, 1H, $^3J_{HP}$ 9.2 Hz), 5.52 (d, 1H, $^4J_{HP}$ 4.9 Hz), 4.01 (dq, 4H, $^3J_{HP}$ 6.6, $^3J_{HH}$ 2.6 Hz), 1.24 (*t*, 6H, $^3J_{HH}$ 7.0 Hz). MS (EI) *m*/*e* = 408 ([M]$^+$, 70%), 388(65), 340(7), 270(62), 251(64), 202(44), 178(100), 152(3), 126(2), 109(8); HRMS *m*/*e* ([M]$^+$) calculated for $C_{21}H_{20}F_3O_3P$ 408.11022, found 408.11138.

*Diethyl 12-(pentafluoroethyl)-9,10-dihydro-9,10-ethenoanthracen-11-ylphosphonate (***12b***).* Crude compound was purified by flash column chromatography (EtOAc/hexane 1:6 as eluent), colorless oil (Yield: 76%). Rf (EtOAc/hexane 1:6) 0.38. ^{31}P NMR($CDCl_3$) δ: 12.34 (*t*, $^4J_{PF}$ 4.5 Hz). ^{19}F NMR($CDCl_3$) δ: −83.65 (*t*, 3F, $^3J_{FF}$ 2.6 Hz), −112.77 (m, 2F). ^{13}C NMR($CDCl_3$) δ: 150.59 (td, C-2, $^2J_{CF}$ 24.8, $^2J_{CP}$ 7.4 Hz), 148.57 (dt, C-1, $^1J_{CP}$ 186.7, $^3J_{CF}$ 3.7 Hz), 144.01 (m, C-4,4′), 143.17 (d, C-5,5′, $^3J_{CP}$ 2.5 Hz), 126.14 (s, C-9,9′), 124.27 (m, C-12,12′), 124.16 (m, C-10,10′, 11,11′), 119.16 (qt, C-8, $^1J_{CF}$ 287.8, $^2J_{CF}$ 38.6 Hz), 113.47 (tq, C-7, $^1J_{CF}$ 254.8, $^2J_{CF}$ 39.5, $^3J_{CP}$ 4.3 Hz), 63.07 (d, C-i, $^2J_{CP}$ 6.5 Hz), 55.94 (d, C-6, $^2J_{CP}$ 8.2 Hz), 53.20 (dq, C-3, $^3J_{CP}$ 10.6, $^3J_{CF}$ 5.6 Hz), 16.45 (d, C-j, $^3J_{CP}$ 6.4 Hz). ^{1}H NMR($CDCl_3$) δ: 7.41 (m, 4H), 7.04 (m, 4H), 5.92 (d, 1H, $^3J_{HP}$ 9.8 Hz), 5.51 (d, 1H, $^4J_{HP}$ 5.4 Hz), 4.00 (dq, 4H, $^3J_{HP}$ 7.8, $^3J_{HH}$ 2.5 Hz), 1.22 (*t*, 6H, $^3J_{HH}$ 7.3 Hz). MS (EI) *m*/*e* = 458 ([M]$^+$, 38%), 438(10), 347(22), 320(17), 291(21), 251(15), 202(19), 178(100), 141(12); HRMS *m*/*e* ([M]$^+$) calculated for $C_{22}H_{20}F_5O_3P$ 458.10702, found 458.10808.

*Diethyl 1-methyl-3-(trifluoromethyl)-7-oxabicyclo[2.2.1]hepta-2,5-dien-2-ylphosphonate (***13a***).* Bp: 69–70 °C (0.1 mm Hg). Yield: 82% (together with isomer **14a**). Content in the mixture 66 mol%. ^{31}P NMR($CDCl_3$) δ: 9.45 (q, $^4J_{PF}$ 4.0 Hz). ^{19}F NMR($CDCl_3$) δ: −62.13 (d, 3F, $^4J_{FP}$ 4.0 Hz). ^{13}C NMR($CDCl_3$) δ: 158.67 (qd, C-2, $^2J_{CF}$ 37.7, $^2J_{CP}$ 9.3 Hz), 151.35 (dq, C-1, $^1J_{CP}$ 198.0, $^3J_{CF}$ 5.0 Hz), 147.32(d, C-4, $^4J_{CP}$ 0.8 Hz), 144.23 (d, C-5, $^3J_{CP}$ 3.0 Hz), 122.25 (qd, C-7, $^1J_{CF}$ 270.1, $^3J_{CP}$ 3.7 Hz), 96.72 (d C-6, $^2J_{CP}$ 14.0 Hz), 83.27 (dq, C-3, $^3J_{CP}$ 12.6, $^4J_{CF}$ 2.6 Hz), 62.98 (d, C-i, $^2J_{CP}$ 5.9 Hz), 16.51 (d, C-j, $^3J_{CP}$ 6.5 Hz), 16.44 (d, C-8, $^3J_{CP}$ 6.5 Hz). ^{1}H NMR($CDCl_3$) δ: 7.07 (m, 1H), 6.89 (d, 1H, $^3J_{HH}$ 5.1 Hz), 5.46 (m, 1H), 4.06 (m, 4H), 1.85 (s, 3H), 1.25 (*t*, 6H, $^3J_{HH}$ 7.3 Hz). MS (ESI) *m*/*e* = 311 ([M−H]$^+$, 8%), 263(5), 243(4), 221(2), 201(100), 173(4), 113(7), 93(2), 69(1); Anal. calculated for $C_{12}H_{16}F_3O_4P$ (312.23): C, 46.16; H, 5.17. Found: C, 46.05; H, 5.09%.

*Diethyl 4-methyl-3-(trifluoromethyl)-7-oxabicyclo[2.2.1]hepta-2,5-dien-2-ylphosphonate (***14a***).* Bp: 69–70 °C (0.1 mm Hg). Yield: 82% (together with isomer **13a**). Content in the mixture 34 mol%. ^{31}P NMR($CDCl_3$) δ: 9.30 (q, $^4J_{PF}$ 4.5 Hz). ^{19}F NMR($CDCl_3$) δ: −63.54 (d, 3F, $^4J_{FP}$ 4.6 Hz). ^{13}C NMR($CDCl_3$) δ: 156.90 (qd, C-2, $^2J_{CF}$ 35.4, $^2J_{CP}$ 8.2 Hz), 151.89 (dq, C-1, $^1J_{CP}$ 201.1, $^3J_{CF}$ 4.5 Hz), 146.21 (d, C-5, $^3J_{CP}$ 2.5 Hz), 145.56(d, C-4, $^4J_{CP}$ 0.7 Hz), 122.40 (qd, C-7, $^1J_{CF}$ 270.1, $^3J_{CP}$ 5.0 Hz), 93.82 (dq, C-3, $^3J_{CP}$ 12.9, $^3J_{CF}$ 1.4 Hz), 86.55 (dq, C-6, $^2J_{CP}$ 12.7, $^4J_{CF}$ 0.6 Hz), 63.05 (d, C-i, $^2J_{CP}$ 5.7 Hz), 16.72 (s, C-8), 16.50 (d, C-j, $^3J_{CP}$ 6.5 Hz). ^{1}H NMR($CDCl_3$) δ: 7.10 (m, 1H), 6.86 (d, 1H, $^3J_{HH}$ 6.0 Hz), 5.61(m, 1H), 4.01 (m, 4H), 1.75 (s, 3H), 1.24 (*t*, 6H, $^3J_{HH}$ 7.3 Hz). MS (ESI) *m*/*e* = 311 ([M−H]$^+$, 8%), 263(5), 243(4), 221(2), 201(100), 173(4), 113(7), 93(2), 69(1); Anal. calculated for $C_{12}H_{16}F_3O_4P$ (312.23): C, 46.16; H, 5.17. Found: C, 46.05; H, 5.09%.

*Diethyl 1-methyl-3-(pentafluoroethyl)-7-oxabicyclo[2.2.1]hepta-2,5-dien-2-ylphosphonate (***13b***).* Bp: 79–80 °C (0.1 mm Hg). Yield: 73% (together with isomer **14b**). Content in the mixture 86 mol%. ^{31}P NMR($CDCl_3$) δ: 9.43 (*t*, $^4J_{PF}$ 4.9 Hz). ^{19}F NMR($CDCl_3$) δ: −84.30 (*t*, 3F, $^3J_{FF}$ 3.0 Hz), −112.92 (m, 2F). ^{13}C NMR($CDCl_3$) δ: 157.19 (td, C-2, $^2J_{CF}$ 25.9, $^2J_{CP}$ 10.4 Hz), 154.53 (dt, C-1, $^1J_{CP}$ 201.6, $^3J_{CF}$ 3.1 Hz), 147.19 (m, C-4), 144.21 (d, C-5, $^3J_{CP}$ 2.2 Hz), 118.83 (qt, C-8, $^1J_{CF}$ 286.9, $^2J_{CF}$ 36.1, $^4J_{CP}$ 2.3 Hz), 112.61 (tq, C-7, $^1J_{CF}$ 253.4, $^2J_{CF}$ 39.4, $^3J_{CP}$ 4.0 Hz), 97.06 (d, C-6, $^2J_{CP}$ 14.9 Hz), 83.80 (m, C-3), 16.50 (d, C-j, $^3J_{CP}$ 6.4 Hz), 16.45 (d, C-9, $^3J_{CP}$ 6.5 Hz). ^{1}H NMR($CDCl_3$) δ: 7.03 (m, 1H), 6.90 (d, 1H, $^3J_{HH}$ 5.6 Hz), 5.45 (m, 1H), 4.11 (m, 4H), 1.88 (s, 3H), 1.27 (*t*, 6H, $^3J_{HH}$ 7.3 Hz). MS (ESI) *m*/*e* = 361 ([M−H]$^+$, 10%), 339(8), 311(6), 251(100), 201(4), 141(3), 119(5), 87(3); Anal. calculated for $C_{13}H_{16}F_5O_4P$ (362.24): C, 43.11; H, 4.45. Found: C, 43.01; H, 4.28%.

*Diethyl 4-methyl-3-(pentafluoroethyl)-7-oxabicyclo[2.2.1]hepta-2,5-dien-2-ylphosphonate (***14b***).* Bp: 79–80 °C (0.1 mm Hg). Yield: 73% (together with isomer **14a**). Content in the mixture 14 mol%. ^{31}P NMR($CDCl_3$) δ: 9.32 (*t*, $^4J_{PF}$ 4.0 Hz). ^{19}F NMR($CDCl_3$) δ: −83.79 (*t*, 3F, $^3J_{FF}$ 3.5 Hz), −111.24 (m, 2F). ^{13}C NMR($CDCl_3$) δ: 157.15 (td, C-2, $^2J_{CF}$ 25.7, $^2J_{CP}$ 10.1 Hz), 154.27 (dt, C-1, $^1J_{CP}$ 199.1, $^3J_{CF}$ 3.1 Hz), 146.40 (d, C-5, $^3J_{CP}$ 1.9 Hz), 145.29 (m, C-4), 118.71 (qt, C-8, $^1J_{CF}$ 287.6, $^2J_{CF}$ 36.7, $^4J_{CP}$ 2.0 Hz), 112.73 (tq, C-7, $^1J_{CF}$ 254.3, $^2J_{CF}$ 40.3, $^3J_{CP}$ 3.9 Hz), 95.05 (dt, C-3, $^3J_{CP}$ 12.6, $^3J_{CF}$ 4.5 Hz), 86.77 (dt, C-6, $^2J_{CP}$ 12.6, $^4J_{CF}$ 1.1 Hz), 63.07 (d, C-i, $^2J_{CP}$ 5.3 Hz), 16.84 (s, C-9), 16.52 (d, C-j, $^3J_{CP}$ 6.4 Hz). ^{1}H NMR($CDCl_3$) δ: 7.11 (m, 1H), 6.84 (d, 1H, $^3J_{HH}$ 5.6 Hz), 5.62 (m, 1H), 4.04 (m, 4H), 1.76 (s, 3H), 1.27 (*t*, 6H, $^3J_{HH}$ 7.3 Hz). MS (ESI) *m*/*e* = 361 ([M−H]$^+$, 10%), 339(8), 311(6), 251(100), 201(4), 141(3), 119(5), 87(3); Anal. calculated for $C_{13}H_{16}F_5O_4P$ (362.24): C, 43.11; H, 4.45. Found: C, 43.01; H, 4.28%.

3.3. X-ray structural determination of 12a

The single crystals (colorless prisms) of **12a** suitable for X-ray analysis were obtained from benzene/hexane; $C_{21}H_{20}F_3O_3PC_6H_6$, Mr = 486.45, crystal size 1.0 mm × 0.9 mm × 0.8 mm, triclinic P1 with a = 996.70(10), b = 997.70(10), c = 1399.50(2) pm, α = 89.380(10), β = 75.650(10), δ = 66.530(10)°; V = 1.2306(2) nm^3, Z = 2, D_{calc} = 1.313 Mg/m^3, μ = 0.161 mm^{-1}, difference electron density 0.384 and −0.390 e Å^{-3} was performed at 203(2) K on a Siemens P4 diffractometer using graphite monochromated Mo Kα radiation (λ = 71:073 pm) and a the low temperature device LT2, index range $-12 \le h \le 12$; $-12 \le k \le 12$; $-17 \le l \le 18$, 2θ-range 2.57–27.50°, reflections measured 11260, unique reflections 5627

[R(int) = 0.0258]. Completeness to θ_{max} = 27.50° 99.8%, data/restraints/parameter 5627/57/368. The structure was solved by direct methods and refined by full-matrix least squares at F^2 using the SHELXL-97 (Sheldrick, 1997)-program system. All nonhydrogen atoms were refined anisotropically and the position of the hydrogen atoms were calculated as a riding model. Goodness of fit at F^2 1.030; final R values [$I > 2\sigma(I)$], $R1$ = 0.0551, wR2 = 0.1412; R value (all reflections) $R1$ = 0.0617, wR2 = 0.1467. Crystallographic data have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 674870. Copies of the data can be obtained free of charge via the Internet http://www.ccdc.cam.ac.uk, or on application to the director; CCDC; 12 Union Road, Cambridge CB2 1EZ, UK; Tel. +44-1223-336-408; fax: +44-1223-336-033; deposit@ccdc.cam.ac.uk.

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