

## Synthesis of Amido- and Diamidophosphites with Polyfluoroalkyl Substituents

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**Abstract**—Bis(polyfluoroalkyl) chlorophosphites and polyfluoroalkyl dichlorophosphites react easily with secondary amines (from –40 to –22°C, 1–3 h, CH<sub>2</sub>Cl<sub>2</sub>) in the presence or absence of triethylamine to form the corresponding bis(polyfluoroalkyl) diorganylamidophosphites or bis(diorganylamido) polyfluoroalkyl phosphites in the yield of up to 74%. Bis(polyfluoroalkyl) diorganylamidophosphites were also synthesized from diorganylamidodichlorophosphites and polyfluoroalkanols (–25 to –22°C, 2 h, Et<sub>3</sub>N–CH<sub>2</sub>Cl<sub>2</sub>) with a yield of 56–60%.

**Keywords:** polyfluoroalkyl dichlorophosphites, bis(polyfluoroalkyl) chlorophosphites, secondary amines, diorganylamidodichlorophosphites, polyfluoroalkanols

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Amido and diamidophosphites are widely used as ligands for metal complexes [1–7], starting compounds for nucleotide synthesis [8–13] and biomedical materials [14], and also as building blocks for organic synthesis [15–17]. Of special interest are fluorine-containing organic phosphites, which are promising precursors of drugs [18–20], including for the treatment of socially significant diseases [21, 22]. Amidopolyfluoroalkylphosphites are also used as components for the creation of innovative materials, for example, as effective non-combustible and oxidative additives to electrolytes for Li-ion chemical current sources [23, 24].

In this regard, the development of convenient methods for the preparation of amido and diamidophosphites containing polyfluoroalkyl substituents is an urgent task. For the synthesis of new representatives of bis(polyfluoroalkyl) diorganylamidophosphites, we proposed two approaches based on the reaction of diorganylamidodichlorophosphites with polyfluoroalkanols and the reaction of bis(polyfluoroalkyl) chlorophosphites with secondary amines. Thus, diallylamidodichloro- and diphenylamidodichlorophosphites **1a**, **1b** reacted with 2,2,2-trifluoro-1-ethanol **2** (molar ratio of reactants is 1 : 2) in the presence of triethylamine at a low temperature

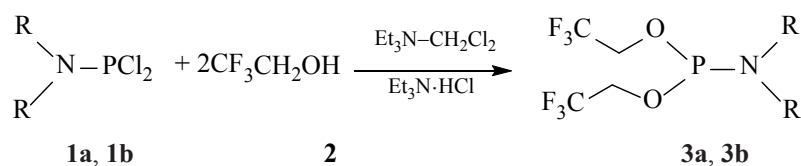
(from –25 to –22°C, 2 h, CH<sub>2</sub>Cl<sub>2</sub>) to form bis(2,2,2-trifluoroethyl) diallylamido- and bis(2,2,2-trifluoroethyl) diphenylamidophosphites **3a** and **3b** with a yield of 60 and 56%, respectively (Scheme 1).

Under similar conditions (from –25 to –22°C, 3 h, CH<sub>2</sub>Cl<sub>2</sub>), bis(2,2,2-trifluoroethyl) chlorophosphite reacted with an excess of dimethylamine, which is involved into this process not only in the formation of bis(2,2,2-trifluoroethyl) dimethylamidophosphite **4** (yield 42%), but is also a dehydrochlorinating agent (Scheme 2).

The use of polyfluoroalkyl dichlorophosphites **5–7** in the reaction with secondary amines **8–10** led to the formation of bis(diorganylamido) polyfluoroalkylphosphites **11a–11e**. The reaction proceeded in a triethylamine–dichloromethane medium (from –40 to –22°C, 1–3 h); the yield of diamidophosphites **11a–e** reaches 74% (Scheme 3).

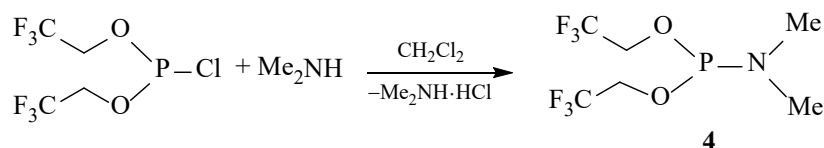
It should be noted that the reaction of amidodichlorophosphites **1a** and **1b** with trifluoroethanol **2** (Scheme 1), as well as the reaction of polyfluoroalkyl dichlorophosphites **5–7** with secondary amines **8–10** (Scheme 3) proceed selectively and practically quantitatively, as evidenced by <sup>31</sup>P NMR spectra of the reaction mixtures. Further work-up and isolation of the reaction products **3** and **11** by vacuum distillation led to a decrease in their preparative yield.

Scheme 1.

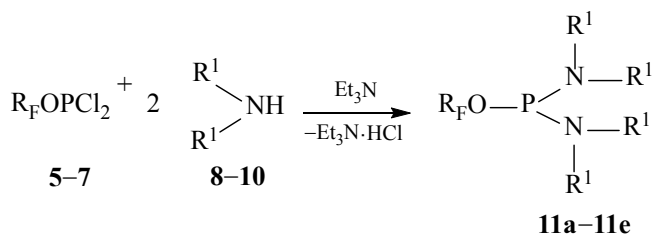


R<sup>1</sup> = CH<sub>2</sub>=CHCH<sub>2</sub> (a), Ph (b).

Scheme 2.



Scheme 3.



R<sub>F</sub> = CF<sub>3</sub>CH<sub>2</sub>, R<sup>1</sup> = Et (**11a**, 56%); R<sub>F</sub> = CF<sub>3</sub>CH<sub>2</sub>, R<sup>1</sup> = H<sub>2</sub>C=CHCH<sub>2</sub> (**11b**, 67%);  
 R<sub>F</sub> = H(CF<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>, R<sup>1</sup> = Me (**11c**, 52%); R<sub>F</sub> = H(CF<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>, R<sup>1</sup> = H<sub>2</sub>C=CHCH<sub>2</sub> (**11d**, 68%);  
 R<sub>F</sub> = H(CF<sub>2</sub>)<sub>4</sub>CH<sub>2</sub>, R<sup>1</sup> = H<sub>2</sub>C=CHCH<sub>2</sub> (**11e**, 74%).

In summary, the convenient methods were developed for the synthesis of previously unknown functional organophosphites with amido and polyfluoroalkyl substituents, which are promising intermediates for drug design.

## EXPERIMENTAL

<sup>1</sup>H, <sup>13</sup>C, <sup>19</sup>F, <sup>31</sup>P NMR spectra were registered on a Bruker DPX 400 and a Bruker AV-400 spectrometers (400.13, 101.61, 376.50, and 161.98 MHz, respectively) from CDCl<sub>3</sub> solution relative to internal HMDS (<sup>1</sup>H, <sup>13</sup>C) or CFCl<sub>3</sub> (<sup>19</sup>F), and external 85% H<sub>3</sub>PO<sub>4</sub> (<sup>31</sup>P). To signals assignment in the <sup>1</sup>H, <sup>13</sup>C NMR spectra, two-dimensional homo- and heteronuclear NMR spectroscopy techniques were used (COSY, HSQC, HMBC). IR spectra were recorded on a Bruker IFS 25 spectrometer from a thin layer.

The starting *N,N*-diallylamidodichlorophosphite **1a** was obtained by an improved procedure [25] from *N,N*-diallylamine and PCl<sub>3</sub> (1 : 1) in the presence of triethylamine (3 mol %) in dichloromethane. Using the same procedure [25], *N,N*-diphenylamidodichlorophosphite **1b** was synthesized from *N,N*-diphenylamine and PCl<sub>3</sub> in dichlo-

romethane. In similar manner, bis(2,2,2-trifluoroethyl) chlorophosphite was prepared from PCl<sub>3</sub> and bis(2,2,2-trifluoroethyl) *H*-phosphonate in dichloromethane [25]. The starting bis(2,2,2-trifluoroethyl) *H*-phosphonate was obtained from PCl<sub>3</sub> and trifluoroethanol in the presence of water [26]. Polyfluoroalkyl dichlorophosphites **5–7** were synthesized from PCl<sub>3</sub> and polyfluoroalkanols according to the procedure [27]. Dimethylamine was generated in a separate flask from dimethylamine hydrochloride and aqueous KOH and used to synthesize compounds **4** and **11c** as a solution in CH<sub>2</sub>Cl<sub>2</sub>. All the experiments were carried out in a dry inert atmosphere (argon).

**General procedure for the synthesis of bis(2,2,2-trifluoroethyl) organylamidophosphites 3a, 3b.** A solution of 0.1 mol of diorganylamidodichlorophosphite **1a** or **1b** in 50 mL of CH<sub>2</sub>Cl<sub>2</sub> was added dropwise with stirring over 1 h at a temperature from –25 to –20°C (dry ice–acetone) to a solution of 0.2 mol (20.01 g) of 2,2,2-trifluoro-1-ethanol **2** and 0.2 mol (20.24 g) of triethylamine in 20 mL of CH<sub>2</sub>Cl<sub>2</sub>. In this case, a white precipitate was formed (triethylammonium hydrochloride). Cooling

was removed, the reaction mixture was stirred at room temperature for another 1 h, then 100 mL of hexane was added. The resulting mixture kept overnight, after which it was analyzed by  $^{31}\text{P}$  NMR. The spectra record the disappearance of signals of the starting dichlorophosphites (at 163.1 ppm for **1a** and at 150.4 ppm for **1b**) and the appearance of signals of the final reaction products **3a** or **3b**. Triethylammonium hydrochloride was filtered off and washed with hexane ( $5 \times 30$  mL). Hexane washing solution and the solvent from the filtrate were combined, the solvents were distilled off under reduced pressure, the residue was distilled in vacuum.

**Bis(2,2,2-trifluoroethyl) *N,N*-diallylamido-phosphite (3a).** Yield 19.6 g (60%), clear liquid, bp  $53^\circ\text{C}$  (1 mmHg),  $d_4^{20}$  1.3918,  $n_D^{20}$  1.2514. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 3085 m, 2995 s, 2936 s, 2918 m, 2865 m, 1643 m, 1455 m, 1444 m, 1419 s, 1360 m, 1300 s, 1282 s, 1168 s, 1100 m, 1074 s, 994 m, 965 s, 927 s, 890 m, 848 s, 795 m, 772 s, 730 m, 652 m, 588 m, 553 m, 536 m, 509 w, 435 m, 422 m.  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 3.63 d. d. t (4H,  $\text{NCH}_2$ ,  $^3J_{\text{HP}} = 9.4$ ,  $^3J_{\text{HH}} = 6.2$ ,  $^4J_{\text{HH}} = 1.0$  Hz), 3.98 d. d. q and 4.07 d. d. q (4H,  $\text{OCH}_2$ ,  $^2J_{\text{HH}} = 12.4$ ,  $^3J_{\text{HP}} = 6.6$ ,  $^3J_{\text{HF}} = 8.8$  Hz), 5.15 d. d. t (2H,  $\text{CH}_2=$ ,  $H_{\text{trans}}$ ,  $^3J_{\text{HH}} = 16.8$ ,  $^2J_{\text{HH}} = 1.5$ ,  $^4J_{\text{HH}} = 1.0$  Hz), 5.17 d. m (2H,  $\text{CH}_2=$ ,  $H_{\text{cis}}$ ,  $^3J_{\text{HH}} = 10.6$  Hz), 5.67 d. d. t (2H,  $\text{CH}=$ ,  $^3J_{\text{HH}} = 16.8$ ,  $^3J_{\text{HH}} = 10.6$ ,  $^3J_{\text{HH}} = 6.2$  Hz).  $^{13}\text{C}$  NMR spectrum,  $\delta_{\text{C}}$ , ppm: 46.2 d ( $\text{CH}_2\text{N}$ ,  $^2J_{\text{CP}} = 20.1$  Hz), 61.5 q. d ( $\text{CH}_2\text{O}$ ,  $^2J_{\text{CF}} = 36.1$ ,  $^2J_{\text{CP}} = 16.1$  Hz), 117.7 ( $\text{CH}_2=$ ), 123.9 q. d ( $\text{CF}_3$ ,  $^1J_{\text{CF}} = 278.1$ ,  $^3J_{\text{CP}} = 8.7$  Hz), 135.3 d ( $\text{CH}=$ ,  $^3J_{\text{CP}} = 2.7$  Hz).  $^{19}\text{F}$  NMR spectrum,  $\delta_{\text{F}}$ , ppm:  $-75.5$  t. d ( $\text{CF}_3$ ,  $^3J_{\text{FH}} = 8.8$ ,  $^4J_{\text{FP}} = 6.1$  Hz).  $^{31}\text{P}$  NMR spectrum:  $\delta_{\text{P}}$  151.3 ppm. Found, %: C 37.08; H 4.61; F 35.23; N 4.53; P 9.50.  $\text{C}_{10}\text{H}_{14}\text{F}_6\text{NO}_2\text{P}$ . Calculated, %: C 36.93; H 4.34; F 35.05; N 4.31; P 9.52.

**Bis(2,2,2-trifluoroethyl) *N,N*-diphenylamido-phosphite (3b).** Yield 22.2 g (56%), clear liquid, bp  $103\text{--}104^\circ\text{C}$  (1 mmHg). IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 3402 m, 3087 w, 3039 m, 2938 m, 2888 w, 1594 s, 1510 m, 1490 s, 1451 m, 1416 m, 1301 s, 1281 s, 1258 m, 1168 s, 1096 s, 1067 s, 1030 m, 1007 w, 964 s, 915 w, 889 m, 847 m, 797 m, 751 s, 693 s, 655 m, 611 w, 555 m, 532 m, 487 w.  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 4.10 d. d. q and 4.14 d. d. q (4H,  $\text{OCH}_2$ ,  $^2J_{\text{HH}} = 12.4$ ,  $^3J_{\text{HP}} = 6.0$ ,  $^3J_{\text{HF}} = 8.4$  Hz), 7.24 m (4H, *o*-Ph), 7.36 m (4H, *m*-Ph), 7.33 m (2H, *p*-Ph).  $^{13}\text{C}$  NMR spectrum,  $\delta_{\text{C}}$ , ppm: 61.9 q. d ( $\text{CH}_2\text{O}$ ,  $^2J_{\text{CF}} = 36.3$ ,  $^2J_{\text{CP}} = 16.8$  Hz), 123.4 q. d ( $\text{CF}_3$ ,  $^1J_{\text{CF}} = 278.4$ ,  $^3J_{\text{CP}} = 8.0$  Hz), 125.2 (*Cp*), 125.9 d (*C<sup>o</sup>*,  $^3J_{\text{CP}} = 6.9$  Hz), 129.3 (*C<sup>m</sup>*), 143.6 d (*C<sup>ipso</sup>*,  $^2J_{\text{CP}} = 10.3$  Hz).  $^{19}\text{F}$  NMR spectrum,  $\delta_{\text{F}}$ , ppm:  $-75.0$  t. d ( $\text{CF}_3$ ,  $^3J_{\text{FH}} = 8.4$ ,  $^4J_{\text{FP}} = 6.5$  Hz).  $^{31}\text{P}$

NMR spectrum:  $\delta_{\text{P}}$  141.8 ppm. Found, %: C 48.54; H 3.38; F 28.55; N 3.37; P 7.68.  $\text{C}_{16}\text{H}_{14}\text{F}_6\text{NO}_2\text{P}$ . Calculated, %: C 48.38; H 3.55; F 28.69; N 3.53; P 7.80.

**Bis(2,2,2-trifluoroethyl) *N,N*-dimethylamido-phosphite (4).** To a solution of bis(2,2,2-trifluoroethyl) chlorophosphite (0.08 mol, 21.16 g) in 120 mL of  $\text{CH}_2\text{Cl}_2$  cooled to from  $-25$  to  $-20^\circ\text{C}$  (dry ice–acetone) was added a freshly prepared solution of dimethylamine (0.44 mol, 19.84 g) in 60 mL of  $\text{CH}_2\text{Cl}_2$  for 1 h with stirring. The reaction mixture was stirred for another 1 h at  $-20^\circ\text{C}$  and 1 h at room temperature, then kept overnight. Dimethylamine hydrochloride was filtered off and washed with 30 mL of  $\text{CH}_2\text{Cl}_2$ . Washings and the solvent from the filtrate were combined,  $\text{CH}_2\text{Cl}_2$  was removed under reduced pressure, and the residue was distilled in vacuum. Yield 9.18 g (42%), clear liquid, bp  $24\text{--}25^\circ\text{C}$  (1 mmHg) (bp  $25^\circ\text{C}$  (1 mmHg) [23]),  $n_D^{20}$  1.3820 ( $n_D^{20}$  1.3823 [21]).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 2.67 d (6H, Me,  $^3J_{\text{HP}} = 9.2$  Hz), 3.99 quintet (2H,  $\text{CH}_2$ ,  $^3J_{\text{HF}} = ^3J_{\text{HP}} = 8.4$  Hz), 4.00 quintet (2H,  $\text{CH}_2$ ,  $^3J_{\text{HF}} = ^3J_{\text{HP}} = 8.7$  Hz).  $^{31}\text{P}$  NMR spectrum:  $\delta_{\text{P}}$  51.0 ppm. Found, %: C 26.17; H 3.44; F 41.91; P 11.12.  $\text{C}_6\text{H}_{10}\text{F}_6\text{NO}_2\text{P}$ . Calculated, %: C 26.39; H 3.69; F 41.74; P 11.34.

**General procedure for the synthesis of polyfluoroalkyl bis(diorganylamido)phosphites 11a–11e.** A solution of 0.25 mol of the secondary amine **8–10** and 0.25 mol (25.30 g) of triethylamine in 50 mL of  $\text{CH}_2\text{Cl}_2$  was cooled to from  $-40$  to  $-35^\circ\text{C}$  (in the case of diethylamine), from  $-25$  to  $-20^\circ\text{C}$  (when using dimethylamine) or from  $-10$  to  $-5^\circ\text{C}$  (in the case of diallylamine). A solution of 0.125 mol of polyfluoroalkyl dichlorophosphite **5–7** in 20 mL of  $\text{CH}_2\text{Cl}_2$  was added dropwise to the resulting solution at the indicated temperature over 20 min (using 2,2,2-trifluoroethyl dichlorophosphite or 2,2,3,3,4,4,5,5-octafluoropentyl dichlorophosphite) or 1 h (in the case of 2,2,3,3-tetrafluoropropyl phosphite). A precipitate of triethylamine hydrochloride was formed. The temperature of the reaction mixture was brought to room temperature for 1 h with stirring, then 100 mL of hexane was added. The mixture was kept overnight, after which it was analyzed by  $^{31}\text{P}$  NMR. In the spectra, the disappearance of signals of the initial dichlorophosphites **5–7** in the range of 180–182 ppm and the appearance of signals of the final products **11a–11e** at 137–142 ppm were recorded. The precipitate was filtered off and washed with hexane ( $5 \times 30$  mL). Hexane washings were combined with the filtrate solvent. The solvents were distilled off under reduced pressure, and the residue was distilled in vacuum.

**2,2,2-Trifluoroethyl bis(diethylamido)phosphite (11a).** Yield 19.2 g (56%), clear liquid, bp 78–80°C (1 mmHg). Compound **11a** crystallizes when distilled, colorless crystals, mp 56–69°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 2971 s, 2934 s, 2871 s, 2726 w, 1463 s, 1415 m, 1377 s, 1345 w, 1281 s, 1190 m, 1189 m, 1162 s, 1100 s, 1074 s, 1024 s, 1011 s, 965 s, 923 m, 845 m, 789 m, 768 w, 672 m, 649 w, 560 w, 533 w, 526 w, 496 w, 479 w.  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 1.02 t (12H, Me,  $^3J_{\text{HH}} = 7.1$  Hz), 2.93 and 3.05 d. d. q (8H,  $\text{NCH}_2$ ,  $^2J_{\text{HH}} = 16.6$ ,  $^3J_{\text{HP}} = 9.7$ ,  $^3J_{\text{HH}} = 7.1$  Hz), 3.86 d. q (2H,  $\text{CH}_2\text{O}$ ,  $^3J_{\text{HP}} = 7.7$ ,  $^3J_{\text{HF}} = 8.8$  Hz).  $^{13}\text{C}$  NMR spectrum,  $\delta_{\text{C}}$ , ppm: 14.6 d (Me,  $^3J_{\text{CP}} = 2.3$  Hz), 38.9 d ( $\text{NCH}_2$ ,  $^2J_{\text{CP}} = 19.5$  Hz), 61.9 q. d ( $\text{CH}_2\text{O}$ ,  $^2J_{\text{CF}} = 35.2$ ,  $^2J_{\text{CP}} = 21.0$  Hz), 124.3 q. d ( $\text{CF}_3$ ,  $^1J_{\text{CF}} = 278.4$ ,  $^3J_{\text{CP}} = 10.7$  Hz).  $^{19}\text{F}$  NMR spectrum,  $\delta_{\text{F}}$ , ppm: –75.2 t. d ( $\text{CF}_3$ ,  $^3J_{\text{FH}} = 8.8$ ,  $^4J_{\text{FP}} = 6.8$  Hz).  $^{31}\text{P}$  NMR spectrum:  $\delta_{\text{P}}$  140.7 ppm. Found, %: C 43.54; H 8.18; F 20.55; N 10.07; P 11.38.  $\text{C}_{10}\text{H}_{22}\text{F}_3\text{N}_2\text{OP}$ . Calculated, %: C 43.79; H 8.09; F 20.78; N 10.21; P 11.29.

**2,2,2-Trifluoroethyl bis(diallylamido)phosphite (11b).** Yield 26.9 g (67%), clear liquid, bp 82–83°C (1 mmHg),  $d_4^{20}$  1.0981,  $n_D^{20}$  1.4520. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 3080 m, 3009 w, 2981 m, 2903 m, 2848 m, 1640 m, 1439 m, 1417 s, 1349 m, 1280 s, 1162 s, 1095 s, 1049 m, 993 s, 921 s, 846 m, 759 s, 648 w, 585 w, 555 m.  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 3.46 d. d. d (4H,  $\text{NCH}_2$ ,  $^2J_{\text{HH}} = 15.2$ ,  $^3J_{\text{HP}} = 8.9$ ,  $^3J_{\text{HH}} = 6.1$  Hz), 3.61 d. d. d (4H,  $\text{NCH}_2$ ,  $^2J_{\text{HH}} = 15.2$ ,  $^3J_{\text{HP}} = 8.4$ ,  $^3J_{\text{HH}} = 6.1$  Hz), 3.92 d. q (2H,  $\text{CH}_2\text{O}$ ,  $^3J_{\text{HP}} = 8.2$ ,  $^3J_{\text{HF}} = 8.7$  Hz), 5.10 d (4H,  $\text{CH}_2=$ ,  $\text{H}_{\text{trans}}$ ,  $^3J_{\text{HH}} = 17.9$  Hz), 5.10 d (4H,  $\text{CH}_2=$ ,  $\text{H}_{\text{cis}}$ ,  $^3J_{\text{HH}} = 9.7$  Hz), 5.67 d. d. t (4H,  $\text{CH}=$ ,  $^3J_{\text{HH}} = 17.9$ ,  $^3J_{\text{HH}} = 9.7$ ,  $^3J_{\text{HH}} = 6.1$  Hz).  $^{13}\text{C}$  NMR spectrum,  $\delta_{\text{C}}$ , ppm: 47.7 d ( $\text{NCH}_2$ ,  $^2J_{\text{CP}} = 18.4$  Hz), 62.4 q. d ( $\text{CH}_2\text{O}$ ,  $^2J_{\text{CF}} = 35.6$ ,  $^2J_{\text{CP}} = 20.8$  Hz), 117.0 ( $\text{CH}_2=$ ), 124.1 q. d ( $\text{CF}_3$ ,  $^1J_{\text{CF}} = 278.0$ ,  $^3J_{\text{CP}} = 10.8$  Hz), 136.0 d ( $\text{CH}=$ ,  $^3J_{\text{CP}} = 2.4$  Hz).  $^{19}\text{F}$  NMR spectrum:  $\delta_{\text{F}}$  –75.1 ppm.  $^{31}\text{P}$  NMR spectrum:  $\delta_{\text{P}}$  139.7 ppm. Found, %: C 52.02; H 6.78; F 17.48; N 8.54; P 9.98.  $\text{C}_{14}\text{H}_{22}\text{F}_3\text{N}_2\text{OP}$ . Calculated, %: C 52.17; H 6.88; F 17.68; N 8.69; P 9.61.

**2,2,3,3-Tetrafluoropropyl bis(dimethylamido)phosphite (11c).** Yield 16.3 g (52%), clear liquid, bp 30–31°C (1 mmHg),  $d_4^{20}$  1.1619,  $n_D^{20}$  1.4067. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 2994 m, 2972 m, 2923 s, 2884 s, 2839 s, 2795 s, 1484 m, 1462 s, 1454 s, 1409 w, 1352 w, 1277 s, 1229 s, 1201 s, 1134 m, 1121 s, 1082 s, 976 s, 955 s, 832 s, 771 s, 685 s, 659 m, 584 w, 548 s, 532 w, 506 w, 456 w, 409 m.  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 2.52 s and 2.55 s (12H, Me), 3.87 t. d. t (2H,  $\text{CH}_2$ ,  $^3J_{\text{HF}} = 12.6$ ,  $^3J_{\text{HP}} = 6.9$ ,  $^4J_{\text{HF}} = 1.6$  Hz),

5.90 t. t (1H,  $\text{HCF}_2$ ,  $^2J_{\text{HF}} = 53.3$ ,  $^3J_{\text{HF}} = 5.1$  Hz).  $^{13}\text{C}$  NMR spectrum,  $\delta_{\text{C}}$ , ppm: 36.2 and 36.4 (Me), 61.4 t. d ( $\text{CH}_2$ ,  $^2J_{\text{CF}} = 29.5$ ,  $^2J_{\text{CP}} = 17.6$  Hz), 109.2 t. t ( $\text{HCF}_2$ ,  $^1J_{\text{CF}} = 249.3$ ,  $^2J_{\text{CF}} = 34.80$  Hz), 115.2 t. t. d ( $\text{CF}_2$ ,  $^1J_{\text{CF}} = 249.9$ ,  $^2J_{\text{CF}} = 26.4$ ,  $^3J_{\text{CP}} = 8.5$  Hz).  $^{19}\text{F}$  NMR spectrum,  $\delta_{\text{F}}$ , ppm: –149.3 d ( $\text{HCF}_2$ ,  $^2J_{\text{HF}} = 53.3$  Hz), –126.3 ( $\text{CF}_2$ ).  $^{31}\text{P}$  NMR spectrum:  $\delta_{\text{P}}$  142.0 ppm. Found, %: C 33.59; H 6.13; F 30.58; N 11.09; P 12.33.  $\text{C}_7\text{H}_{15}\text{F}_4\text{N}_2\text{OP}$ . Calculated, %: C 33.61; H 6.04; F 30.38; N 11.20; P 12.38.

**2,2,3,3-Tetrafluoropropyl bis(diallylamido)phosphite (11d).** Yield 30.1 g (68%), viscous pale yellow liquid, bp 98–99°C (1 mmHg),  $d_4^{20}$  1.1390,  $n_D^{20}$  1.4527. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 3082 m, 3009 m, 2982 m, 2917 m, 2858 m, 2793 w, 2732 w, 2670 w, 2423 w, 1679 w, 1642 m, 1442 m, 1419 s, 1359 m, 1280 s, 1259 s, 1231 s, 1207 s, 1109 s, 1049 m, 993 s, 927 s, 833 m, 762 m, 670 w, 548 m.  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 3.47 d. d. d (4H,  $\text{NCH}_2$ ,  $^2J_{\text{HH}} = 15.2$ ,  $^3J_{\text{HP}} = 9.0$ ,  $^3J_{\text{HH}} = 6.1$  Hz), 3.60 d. d. d (4H,  $\text{NCH}_2$ ,  $^2J_{\text{HH}} = 15.2$ ,  $^3J_{\text{HP}} = 8.7$ ,  $^3J_{\text{HH}} = 6.4$  Hz), 3.92 t. d (2H,  $\text{CH}_2\text{O}$ ,  $^3J_{\text{HF}} = 12.5$ ,  $^3J_{\text{HP}} = 6.1$  Hz), 5.12 br. d (4H,  $\text{CH}_2=$ ,  $\text{H}_{\text{trans}}$ ,  $^3J_{\text{HH}} = 17.9$  Hz), 5.13 br. d (4H,  $\text{CH}_2=$ ,  $\text{H}_{\text{cis}}$ ,  $^3J_{\text{HH}} = 9.4$  Hz), 5.68 m (4H,  $\text{CH}=$ ), 5.92 t. t (1H,  $\text{HCF}_2$ ,  $^2J_{\text{HF}} = 53.3$ ,  $^3J_{\text{HF}} = 5.4$  Hz).  $^{13}\text{C}$  NMR spectrum,  $\delta_{\text{C}}$ , ppm: 47.8 d ( $\text{NCH}_2$ ,  $^2J_{\text{CP}} = 18.8$  Hz), 61.9 t. d ( $\text{CH}_2\text{O}$ ,  $^2J_{\text{CF}} = 30.3$ ,  $^2J_{\text{CP}} = 19.9$  Hz), 109.2 t. t ( $\text{HCF}_2$ ,  $^1J_{\text{CF}} = 249.6$ ,  $^2J_{\text{CF}} = 34.3$  Hz), 115.2 t. t. d ( $\text{CF}_2$ ,  $^1J_{\text{CF}} = 250.0$ ,  $^2J_{\text{CF}} = 26.5$ ,  $^3J_{\text{CP}} = 10.2$  Hz), 116.8 ( $\text{CH}_2=$ ), 136.0 ( $\text{CH}=$ ).  $^{19}\text{F}$  NMR spectrum,  $\delta_{\text{F}}$ , ppm: –139.9 d ( $\text{HCF}_2$ ,  $^2J_{\text{HF}} = 53.3$  Hz), –125.9 ( $\text{CF}_2$ ).  $^{31}\text{P}$  NMR spectrum:  $\delta_{\text{P}}$  137.5 ppm. Found, %: C 50.81; H 6.53; F 21.40; N 7.89; P 8.71.  $\text{C}_{15}\text{H}_{23}\text{F}_4\text{N}_2\text{OP}$ . Calculated, %: C 50.85; H 6.54; F 21.45; N 7.91; P 8.74.

**2,2,3,3,4,4,5,5-Octafluoropentyl bis(diallylamido)phosphite (11e).** Yield 42.0 g (74%), yellow liquid, bp 123–124°C (1 mmHg),  $d_4^{20}$  1.2302,  $n_D^{20}$  1.4318. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 3082 m, 3010 m, 2983 m, 2909 m, 2852 m, 1641 m, 1441 m, 1419 s, 1359 m, 1289 m, 1259 m, 1233 m, 1172 s, 1132 s, 1094 m, 1046 m, 993 s, 923 s, 905 m, 848 w, 808 m, 763 m, 672 w, 547 m.  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 3.46 d. d. d and 3.59 d. d. d (8H,  $\text{NCH}_2$ ,  $^2J_{\text{HH}} = 15.3$ ,  $^3J_{\text{HP}} = 8.3$ ,  $^3J_{\text{HH}} = 6.1$ ,  $^3J_{\text{HH}} = 6.6$  Hz), 4.02 t. d. t (2H,  $\text{CH}_2\text{O}$ ,  $^3J_{\text{HF}} = 14.0$ ,  $^3J_{\text{PH}} = 6.8$ ,  $^4J_{\text{HF}} = 1.4$  Hz), 5.10 br. d (4H,  $\text{CH}_2=$ ,  $\text{H}_{\text{trans}}$ ,  $^3J_{\text{HH}} = 17.7$  Hz), 5.10 br. d (4H,  $\text{CH}_2=$ ,  $\text{H}_{\text{cis}}$ ,  $^3J_{\text{HH}} = 9.5$  Hz), 5.65 d. d. d. d (4H,  $\text{CH}=$ ,  $^3J_{\text{HH}} = 17.7$ ,  $^3J_{\text{HH}} = 9.5$ ,  $^3J_{\text{HH}} = 6.1$ ,  $^3J_{\text{HH}} = 6.6$  Hz), 6.03 t. t (1H,  $\text{HCF}_2$ ,  $^2J_{\text{HF}} = 52.0$ ,  $^3J_{\text{HF}} = 5.6$  Hz).  $^{13}\text{C}$  NMR spectrum,  $\delta_{\text{C}}$ , ppm: 47.7 d ( $\text{NCH}_2$ ,  $^2J_{\text{CP}} = 19.0$  Hz), 61.6 t. d ( $\text{CH}_2\text{O}$ ,  $^2J_{\text{CF}} = 25.9$ ,  $^2J_{\text{CP}} = 21.6$  Hz),



107.7 t. t (HCF<sub>2</sub>, <sup>1</sup>J<sub>CF</sub> = 253.5, <sup>2</sup>J<sub>CF</sub> = 31.0 Hz), 109.9 m (CF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>), 111.0 t. quintet (HCF<sub>2</sub>CF<sub>2</sub>, <sup>1</sup>J<sub>CF</sub> = 264.2, <sup>2</sup>J<sub>CF</sub> = 30.6 Hz), 115.6 t. t. d (CF<sub>2</sub>CH<sub>2</sub>, <sup>1</sup>J<sub>CF</sub> = 256.5, <sup>2</sup>J<sub>CF</sub> = 30.2, <sup>3</sup>J<sub>CP</sub> = 9.5 Hz), 116.9 (CH<sub>2</sub>=), 136.0 d (CH=, <sup>3</sup>J<sub>CP</sub> = 2.6 Hz). <sup>19</sup>F NMR spectrum, δ<sub>F</sub>, ppm: –137.2 d. m (2F, HCF<sub>2</sub>, <sup>2</sup>J<sub>HF</sub> = 51.9 Hz), –130.3 m (2F, HCF<sub>2</sub>CF<sub>2</sub>), –125.2 m (2F, HCF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>), –120.0 m (2F, CF<sub>2</sub>CH<sub>2</sub>). <sup>31</sup>P NMR spectrum: δ<sub>P</sub> 139.8 ppm. Found, %: C 44.83; H 5.09; F 33.18; N 6.04; P 6.76. C<sub>17</sub>H<sub>23</sub>F<sub>8</sub>N<sub>2</sub>OP. Calculated, %: C 44.94; H 5.10; F 33.45; N 6.17; P 6.82.

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#### CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

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