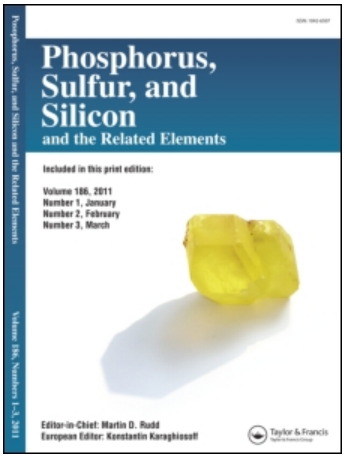

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Weisheng Huang[a]; Yixin Zhang[a]; Chengye Yuan[a]
[a] Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Fenglin Lu, Shanghai, China

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STUDIES ON ORGANOPHOSPHORUS COMPOUNDS 93 REACTION OF TRIVALENT PHOSPHORUS REAGENTS WITH N-SUBSTITUTED TRIFLUOROACETIMIDOYL CHLORIDES. A NOVEL SYNTHESIS OF 1-(N-SUBSTITUTED AMINO)-2,2,2-TRIFLUOROETHYLPHOSPHONATES

WEISHENG HUANG, YIXIN ZHANG and CHENGYE YUAN*
Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Lu, Shanghai, China

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1-(N-substituted amino)-2,2,2-trifluoroethylphosphonates were obtained by the reaction of trialkyl phosphites or diethyl phosphites with trifluoroacetimidoyl chlorides followed by subsequent reduction with sodium cyanoborohydride.

Key words: Trifluoroacetimidoyl chloride, Arbuzov-Michaelis reaction, reduction, trifluoromethylated 1-aminophosphonate.

INTRODUCTION

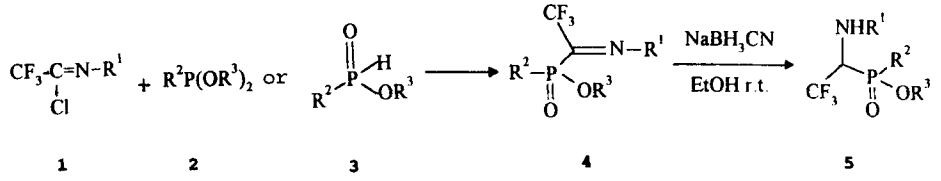
Owing to their biological activities, the preparation of 1-amino-phosphonic acid derivatives has attracted the interest of many chemists.[1] On the other hand, trifluoromethylated compounds have been of great importance and of particular interest in medicinal, agricultural and material sciences.[2] Introduction of a trifluoromethyl group into a molecule is the subject of active investigation. This situation aroused our interest in the synthesis of 1-aminophosphonic acid derivatives bearing a trifluoromethyl moiety.

RESULTS AND DISCUSSION

Two general approaches have been used for the synthesis of 1-aminophosphonic acid derivatives. The first one often involves the performance of an Abramov- or Pudovik-type reaction[3] of a phosphite or phosphorus acid on a Schiff base, preformed or generated *in situ*.[4] Since the imine derivatives of trifluoroacetaldehyde can not be synthesized directly,[5] this approach shows some limitations in the preparation of trifluoromethylated aminophosphonic acid derivatives. The second one involves the initial preparation of the appropriate 1-oxoalkylphosphonate via Michaelis-Arbuzov reaction of a phosphite with an acyl halide,[6] followed by imine formation with the carbonyl group and subsequent reduction of the resultant imine.[7] This synthetic route can not be exploited for our present purpose because the

reaction of perfluoroalkanoic acid chlorides with trialkyl phosphite fails to give perfluoroacylphosphonates.[8]

In connection with our study on the reactions of trifluoroacetimidoyl chlorides with various nucleophiles,[9] we report here the Arbuzov-type reaction of trialkyl phosphite with trifluoroacetimidoyl chloride followed by subsequent reduction to the imine intermediates, leading to 1-(N-aryl/alkyl amino)-2,2,2-trifluoroethylphosphonates, the trifluoromethylated phosphorus analogues of N-protected alanine derivatives.



1 2 3 4 5

R^1 = n-C_8H_{17} (**1a**), cyclo-C_6H_{11} (**1b**), $PhCH_2CH_2$ (**1c**), Ph (**1d**), p-MeC_6H_4 (**1e**), o,p-$Me_2C_6H_3$ (**1f**), p-ClC_6H_4 (**1g**), p-$NO_2C_6H_4$ (**1h**).
R^2 = EtO, R^3 = Et (**2a**, **3a**); R^2 = MeO, R^3 = Me (**2b**); R^2 = i-PrO, R^3 = i-Pr (**2c**); R^2 = Ph, R^3 = Et (**2d**, **3b**); R^2 = PrO, R^3 = Pr (**3c**); R^2 = i-C_4H_9O, R^3 = i-C_4H_9 (**3d**).

We first attempted the reaction of triethyl phosphite with N-phenyl trifluoroacetimidoyl chloride at 80°C without solvent. ^{19}F NMR spectra were used to monitor the reaction course. The ^{19}F chemical shift for the starting imidoyl chloride is 4.8 ppm while for the resulting new compound it is 9.7 ppm. After 6 hrs, the imidoyl chloride disappeared completely and the mixture gave on workup the imino phosphonate **4** in 95% yield. Signals in ^{31}P NMR spectra at δ = 7.37 ppm (q, J = 9.2 Hz) definitely revealed the formation of the Arbuzov-reaction product.

Then we examined the reduction to the imino phosphonate. Usual workup after stirring for 20 hrs at r.t. gave only a 17% yield of the product when sodium borohydride was used as reducing agent and ethanol as solvent. However, the product was obtained in 60% yield using sodium cyanoborohydride instead of sodium borohydride. The reduction product resonated at δ = 15.2 ppm (q, J = 8.7 Hz) in the ^{31}P NMR, much downfield from that of imino phosphonate **4** because the phosphonate moiety in the product is linked to a SP^3 hybridised carbon while in the imino phosphonate it is linked to a SP^2 hybridised carbon.

Thus we extended the above reaction to other trifluoroacetimidoyl chlorides and trivalent phosphorus reagents. N-substituents in the trifluoroacetimidoyl chloride molecules cause a pronounced effect on the reaction. When R^1 was alkyl (entries 1–3), prolongated reaction time was necessary for the completion of the Arbuzov-type reaction. When R^1 was aryl (entries 4–8), the rate of the reaction depended on the substituent on the aryl ring: the more powerful the electron withdrawing group on the aryl ring, the faster the reaction occurred. When N-(p-nitrophenyl)trifluoroacetimidoyl chloride was used, the reaction was performed below 0°C for its high reactivity. Diethyl phenylphosphonite reacted more rapidly than trialkyl phosphite (entry 11). These results indicate that the above Arbuzov-type reaction initiates with the nucleophilic attack of trivalent phosphorus reagents on

TABLE I

Reaction of **2** or **3** with **1** and reduction of **4**

entry	starting material	product	reaction time (h)[a]	overall yield (%)[c]	m.p. (°C)[c]
1	1a and 2a	5a	40/40	44	oil
2	1b and 2a	5b	40/40	40	oil
3	1c and 2a	5c	40/40	48	oil
4	1d and 2a	5d	6/20	59	60
5	1e and 2a	5e	8/20	49	50-52
6	1f and 2a	5f	8/20	42	56-58
7	1g and 2a	5g	5/20	63	72-74
8	1h and 2a	5h	2/4[b]	69	85
9	1d and 2b	5i	6/20	69	58
10	1d and 2c	5j	12/20	50	68-70
11	1d and 2d	5k	1/20	58	76
12	1d and 3a	5d	6/20	49	60
13	1d and 3b	5k	2/20	57	76
14	1d and 3c	5l	6/20	52	48-50
15	1d and 3d	5m	6/20	48	70

a. Arbuzov-Michaelis reaction time/reduction reaction time.

b. The Arbuzov reaction and reduction were performed at 0°C; in other entries, Arbuzov reaction were conducted at 80°C and reduction were carried out at r.t..

c. The isolated yield and m.p. of product **5**.

trifluoroacetimidoyl chlorides. The highly electrophilic imidoyl chloride **1h** and the more nucleophilic phosphorus reagent **2d** promoted the reaction markedly.

Dialkyl phosphites also reacted with trifluoroacetimidoyl chlorides, but triethylamine was essential to remove the hydrochloride generated (entries 12–15). Monoethyl phenylphosphonite reacted similarly (entry 13).

The imino phosphonates thus formed, were subjected to reduction using sodium cyanoborohydride as the reducing agent without purification, since these intermediates were usually obtained quantatitively (based on ^{1}H, ^{19}F and ^{31}P NMR measurement). It was observed that when the highly electrophilic imino phosphonate **4h** was involved, the reduction reaction occurred with extreme violence even at room temperature. This phenomenon is probably due to the reduction resulting from the nucleophilic attack of "negative hydrogen" on the C=N double bonds. In this case the reduction should be conducted under ice-cooling.

EXPERIMENTAL

The melting points are uncorrected. IR spectra were taken on a Shimadzu-440 spectrophotometer. ^{1}H, ^{31}P and ^{13}C NMR spectra were recorded on a Bruker AM-300 spectrometer in $CDCl_3$. Chemical shifts

for ^1H and ^{13}C NMR spectra are reported in ppm downfield from TMS. ^{31}P NMR chemical shifts are reported in ppm downfield from 85% H_3PO_4. ^{19}F NMR spectra were obtained on a Varian EM 360A spectrometer using CF_3CO_2H as an external standard, positive for downfield shifts. EI-MS were recorded on a HP5989A mass spectrometer.

N-substituted trifluoroacetimidoyl chlorides were synthesised by the literature methods.[10] Trialkyl phosphites and dialkyl phosphites were prepared from phosphorus trichloride and the corresponding alcohols in the usual manner. Diethyl phenylphosphonite and monoethyl phenylphosphonite were synthesised similarly from dichlorophenylphosphine. Sodium cyanoborohydride was purchased from Fluka Chemical Co. Other reagents were commercially available from a local source (Shanghai Chemical Co.). THF was freshly distilled from sodium benzophenone ketyl and triethylamine was distilled from CaH_2.

Diethyl 1-(N-phenylimino)-2,2,2-trifluoroethylphosphonates (**4d**): The mixture of triethyl phosphite (0.83 g, 5 mmol) and N-phenyltrifluoroacetimidoyl chloride (1.04 g, 5 mmol) was heated at 80°C for 6 hrs. The volatile components were removed under reduced pressure and the residue was subjected to column chromatography on silical gel (EtOAc: petroleum ether 1:1), giving a pale yellow oil in 95% yield. IR (film): ν 1660 (C=N), 1250 (P=O), 1160 (C—F), 1020 (P—O—C) cm^{-1}. ^1H NMR (CCl_4): δ 1.03 (t, J = 6, 6H, 2Me), 3.77 (q, J = 6, 4H, $2OCH_2$), 6.76–6.96 (m, 2H, Ph), 7.03–7.30 (m, 2H, Ph). ^{19}F NMR (CCl_4): δ 9.7 (s). ^{31}P NMR ($CDCl_3$): δ 7.37 (q, J = 9.2). MS: m/e 309 (M^+), 240 (M—CF_3), 172 (M—P(O) $(OEt)_2$). Anal calcd for $C_{12}H_{15}F_3NO_3P$ (309.44): C, 46.60; H, 4.85; N, 4.59. Found: C, 46.68; H, 4.74; N, 4.62.

Diethyl 1-(N-phenylamino)-2,2,2-trifluoroethylphosphonate (**5d**): *Typical Procedure*: Method A (from triethyl phosphite): Compound **4d** was dissolved in absolute ethanol (5 mL) and sodium cyanoborohydride (0.32 g, 5 mmol) was added. The resulting mixture was stirred at r.t. for 20 hrs then poured into EtOAc (20 mL) and H_2O (15 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (2 × 20 mL). The combined organic layers were dried (Na_2SO_4), filtered, concentrated and purified by column chromatography on silical gel (EtOAc: petroleum 1:1), giving the pure product **5d** as a white solid. Yield: 59%. mp 60°C. Method B (from diethyl phosphite): N-phenyltrifluoroacetimidoyl chloride (1.04 g, 5 mmol) and triethylamine (0.505 g, 5 mmol) was mixed in THF (10 mL). Diethyl phosphite (0.69 g, 5 mmol) was added dropwise and the mixture was stirred for 6 hrs at r.t. The produced triethylamine hydrochloride was filtered off and the filtrate was concentrated to give crude product **4d**, which was subjected to reduction then worked up as described in method A. IR (film): ν 3300 (N—H), 3000, 1610, 1505, 750 (benzene), 1250 (P=O), 1170 (C—F), 1020 (P—O—C) cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.33 (t, J = 7.0, 6H, 2Me), 4.12–4.23 (m, 6H, $2OCH_2$, CH, NH), 6.73 (d, J = 7.1, 2H, Ph), 6.84 (t, J = 7.3, 1H, Ph), 7.20–7.27 (m, 2H, Ph). ^{19}F NMR ($CDCl_3$): δ 9.2 (s). ^{31}P NMR ($CDCl_3$): δ 15.2 (q, J = 8.7). MS: m/e 311 (M^+, 96%), 174 (M—P(O) $(OEt)_2$, 100%). Anal calcd for $C_{12}H_{17}F_3NO_3P$ (311.24): C, 46.30; H, 5.47; N, 4.50. Found: C, 46.46; H, 5.32; N, 4.54.

Diethyl 1-(N-octylamino)-2,2,2-trifluoroethylphosphonate (**5a**): IR (film): ν 2900 (C—H), 1250 (P=O), 1160 (C—F), 1020 (P—O—C) cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.88 (t, J = 7.0, 3H), 1.20–1.50 (m, 18H, $6CH_2$, $2OCH_2CH_3$), 2.87 (t, J = 6.8, 2H, NCH_2), 3.40 (dq, J = 8.4, 21.4, 1H, CHP), 4.15–4.28 (m, 4H, $2OCH_2$). ^{19}F NMR ($CDCl_3$): δ 9.0. ^{31}P NMR ($CDCl_3$): δ 16.9 (q, J = 9.4). MS: m/e 348 (M + 1, 51%), 128 ($C_8H_{17}NH^+$, 100%). Anal calcd for $C_{14}H_{29}F_3NO_3P$ (347.35): C, 48.41; H, 8.36; N, 4.03. Found: C, 48.62; H, 8.30; N, 3.94.

Diethyl 1-(N-cyclohexylamino)-2,2,2-trifluoroethylphosphonate (**5b**): IR (film): ν 3350 (N—H), 2950 (C—H), 1260 (P=O), 1170 (C—F), 1020 (P—O—C) cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.10–1.41 (m, 11H), 1.59–2.19 (m, 6H), 2.71 (br, 1H, NH), 3.52 (dq, J = 8.7, 21.8, 1H, CHP), 4.15–4.28 (m, 4H, $2OCH_2$). ^{19}F NMR ($CDCl_3$): δ 8.6. ^{31}P NMR ($CDCl_3$): δ 17.6 (q, J = 8.6). MS: m/e 318 (M^+ + 1, 100%), 180 (M—P(O) $(OEt)_2$, 28%), 111 (M—CF_3-P(O) $(OEt)_2$, 15%), 98 ($C_6H_{11}NH^+$, 85%), Anal calcd for $C_{12}H_{23}F_3NO_3P$ (317.29): C, 45.42; H, 7.26; N, 4.42. Found: C, 45.54; H, 7.51; N, 4.36.

Diethyl 1-(N-phenylethylamino)-2,2,2-trifluoroethylphosphonate (**5c**): IR (film): ν 3350 (N—H), 1250 (P=O), 1160 (C—F), 1020 (P—O—C) cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.29 (t, J = 7.1, 6H, 2Me), 2.77–2.83 (m, 2H, $PhCH_2$), 3.02–3.06 (m, 1H, NH), 3.18–3.21 (m, 1H, CH), 3.34–3.47 (m, 2H, NCH_2), 4.06–4.18 (m, 4H, $2OCH_2$), 7.18–7.31 (m, 5H, Ph). ^{19}F NMR ($CDCl_3$): δ 9.5. ^{31}P NMR ($CDCl_3$): δ 16.4 (q, J = 8.9). MS: m/e 340 (M^+ + 1, 100%), 248 ($M^+ - PhCH_2$, 93%), 105 ($PhC_2H_4^+$, 38%), 91 ($PhCH_2^+$, 31%). Anal calcd for $C_{14}H_{21}F_3NO_3P$ (339.29): C, 49.56; H, 6.19; N, 4.13. Found: C, 49.78; H, 6.02; N, 4.02.

Diethyl 1-(N-p-tolyalmino)-2,2,2-trifluoroethylphosphonate (**5e**): IR (film): ν 3300 (N—H), 3000, 1620, 1520 (benzene), 1240 (P=O), 1170 (C—F), 1020 (P—O—C) cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.26 (t, J = 7.0, 6H, $2OCH_2\underline{CH_3}$), 2.25 (s, 3H, Me), 4.14–4.21 (m, 6H, $2OCH_2$, NH, CH), 6.63 (d, J = 8.2, 2H, Ph), 7.02 (d, J = 8.2, 2H, Ph). ^{19}F NMR ($CDCl_3$): δ 9.0. ^{31}P NMR ($CDCl_3$): δ 15.5 (q, J = 8.4). MS: m/e 325 (M^+, 57%), 326 (M+1, 34%), 188 (M—P(O) $(OEt)_2$, 100%), 118 (M—CF_3—P(O) $(OEt)_2$, 39%). Anal calcd for $C_{13}H_{19}F_3NO_3P$ (325.26): C, 48.00; H, 5.85; N, 4.31. Found: C, 47.88; H, 5.60; N, 4.54.

Diethyl 1-(N-(3',4'-dimethylphenyl)amino)-2,2,2-trifluoroethylphosphonate (**5f**): IR (film): ν 3400 (N—H), 2980, 1620, 1510, 910, 740 (benzene), 1250 (P=O), 1170 (C—F), 1020 (P—O—C) cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.33 (t, J = 7.1, 6H, $2OCH_2\underline{CH_3}$), 2.16, 2.20 (2s, 6H, 2Me), 4.13–4.27 (m, 6H, $2OCH_2$, NH, CH), 6.48 (dd, J = 2.4, 8.1, 1H, Ph), 6.54 (d, J = 2.3, 1H, Ph), 6.97 (d, J = 8.1, 1H, Ph). ^{19}F NMR ($CDCl_3$): δ 8.6. ^{31}P NMR ($CDCl_3$): δ 15.4 (q, J = 8.6). MS: m/e 339 (M^+, 28%), 202 (M—P(O) $(OEt)_2$, 100%). Anal calcd for $C_{14}H_{21}F_3NO_3P$ (339.29): C, 49.56; H, 6.19; N, 4.13. Found: C, 49.28; H, 6.32; N, 4.18.

Diethyl 1-(N-p-chlorophenylamino)-2,2,2-trifluoroethylphosphonate (**5g**): IR (film): ν 1240 (P=O), 1170 (C—F), 1020 (P—O—C) cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.34 (t, J = 7.0, 6H, 2Me), 4.10–4.27 (m, 5H, CH, $2OCH_2$), 4.55 (br, 1H, NH), 6.68 (d, J = 8.7, 2H, Ph), 7.16 (dd, J = 1.9, 8.8, 2H, Ph). ^{19}F NMR ($CDCl_3$): δ 8.6. ^{31}P NMR ($CDCl_3$): δ 14.8 (q, J = 8.1). MS: m/e 346 (M^+), 208 (M—P(O) $(OEt)_2$). Anal calcd for $C_{12}H_{16}ClF_3NO_3P$ (345.68): C, 41.68; H, 4.63; N, 4.05. Found: C, 41.96; H, 4.52; N, 3.96.

Diethyl 1-(N-p-nitrophenylamino)-2,2,2-trifluoroethylphosphonate (**5h**): IR (film): ν 3280 (N—H), 1600, 1320 (NO_2), 1250 (P=O), 1180 (C—F), 1020 (P—O—C) cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.40 (t, J = 7.0, 6H, 2Me), 4.12–4.44 (m, 5H, $2OCH_2$, CH), 5.99 (br, 1H, NH), 6.82 (dd, J = 2.9, 8.88, 2H, Ph), 8.11–8.16 (m, 2H, Ph). ^{19}F NMR ($CDCl_3$): δ 9.3. ^{31}P NMR ($CDCl_3$): δ 13.7 (q, J = 8.3). MS: m/e 357 (M+1, 100%), 219 (M—P(O) $(OEt)_2$, 33%). Anal calcd for $C_{12}H_{16}F_3N_2O_5P$ (356.24): C, 40.45; H, 4.49; N, 7.87. Found: C, 40.28; H, 4.56; N, 7.54.

Dimethyl 1-(N-phenylamino)-2,2,2-trifluoroethylphosphonate (**5i**): IR (film): ν 3300 (N—H), 1250 (P=O), 1170 (C—F), 1020 (P—O—C) cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.74, 3.79 (2d, J_{P-H} = 10.8, 11.1, 6H, 2Me), 4.28 (br, 2H, NH, CH), 6.68 (m, 2H), 6.79 (m, 1H), 7.18 (m, 2H). ^{19}F NMR ($CDCl_3$): δ 8.17. ^{31}P NMR ($CDCl_3$): δ 17.1 (q, J = 7.3). MS m/e 284 (M^+ + 1, 15%), 283 (M^+, 56%), 174 (M—P(O) $(MeO)_2$, 100%). Anal calcd for $C_{10}H_{13}F_3NO_3P$ (283.18): C, 42.40; H, 4.59; N, 4.95. Found: C, 42.26; H, 4.43; N, 4.69.

Diisopropyl 1-(N-phenylamino)-2,2,2-trifluoroethylphosphonate (**5j**): IR (film): ν 3300 (N—H), 1240 (P=O), 1160 (C—F), 1010 (P—O—C) cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.15–1.40 (md, 12H, 4Me), 4.08–4.35 (br, 2H, NH, CHP), 4.75–4.85 (m, 2H, 2OCH), 6.70–6.84 (m, 3H, Ph), 7.18–7.27 (m, 2H, Ph). ^{19}F NMR ($CDCl_3$): δ 8.6. ^{31}P NMR ($CDCl_3$): δ 13.0 (q, J = 8.4). MS: m/e 339 (M^+, 11%), 174 ($CF_3CHNHPh^+$, 100%). Anal calcd for $C_{14}H_{21}F_3NO_3P$ (339.29): C, 49.58; H, 6.19; N, 4.13. Found: C, 49.82; H, 6.06; N, 4.08.

Ethyl 1-(N-phenylamino)-2,2,2-trifluoroethyl phenylphosphonate (**5k**): IR (film): ν 3400 (N—H), 1250 (P=O), 1170 (C—F), 1020 (P—O—C) cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.26, 1.37 (t, J = 7.1, 7.1, 3H, Me), 4.11–4.52 (m, 4H, OCH_2, NH, CH), 6.52–6.84 (m, 3H, Ph), 7.07–7.23 (m, 2H, Ph), 7.47–7.61 (m, 3H, Ph), 7.83–7.90 (m, 2H, Ph). ^{19}F NMR ($CDCl_3$): δ 9.6, 9.8. ^{31}P NMR ($CDCl_3$): δ 31.2, 32.0 (2q, J = 4.8). MS: m/e 344 (M+1, 55%), 170 (PhP(OH) (OEt), 100%). Anal calcd for $C_{16}H_{17}F_3NO_2P$ (343.28): C, 55.98; H, 4.96; N, 4.08. Found: C, 56.06; H, 5.02; N, 3.86.

Dipropyl 1-(N-phenylamino)-2,2,2-trifluoroethylphosphonate (**5l**): IR (film): ν 3300 (N—H), 3000 (C—H), 1260 (P=O), 1170 (C—F), 1025 (P—O—C) cm $^{-1}$. ^1H NMR ($CDCl_3$): δ 0.97 (t, J = 7.4, 6H, 2Me), 1.57–1.81 (m, 4H, $2\underline{CH_2}CH_3$), 4.00–4.35 (m, 6H, $2OCH_2$, CHP, NH), 6.70–6.85 (m, 2H, Ph), 7.17–7.29 (m, 3H, Ph). ^{19}F NMR ($CDCl_3$): δ 8.2. ^{31}P NMR ($CDCl_3$): δ 15.2 (q, J = 8.7). MS: m/e 339 M^+, 31%), 174 ($CF_3CHNHPh^+$, 100%). Anal calcd for $C_{14}H_{21}F_3NO_3P$ (339.29): C, 49.58; H, 6.19; N, 4.13. Found: C, 49.76; H, 6.06; N, 4.06.

Diisobutyl 1-(N-phenylamino)-2,2,2-trifluoroethylphosphonate (**5m**): IR (film): ν 3300 (N—H), 1240 (P=O), 1170 (C—F), 1020 (P—O—C) cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.85 (d, 6H, J = 6.7, 2Me), 0.93 (d, J = 6.6, 6H, 2Me), 1.85 (m, J = 6.6, 2H, 2CH), 3.79–3.96 (m, 4H, $2OCH_2$), 4.32 (br, 2H, NH,

CHP), 6.71–6.86 (m, 3H, Ph), 7.20–7.60 (m, 2H, Ph). ^{19}F NMR ($CDCl_3$): δ 8.3. ^{31}P NMR ($CDCl_3$): δ 15.3 (q, J = 8.8). MS: m/e 367 (M^+, 13%), 174 ($CF_3CHNHPh^+$, 100%). Anal calcd for $C_{16}H_{25}F_3NO_3P$ (367.34): C, 52.32; H, 6.81; N, 3.81. Found: C, 52.58; H, 6.76; N, 3.52.

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