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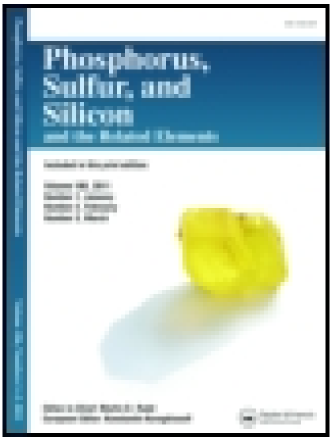

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THE PREPARATION AND CHARACTERIZATION OF SOME FLUORINATED α-AMINOARYLMETHANEPHOSPHONIC ACIDS

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THE PREPARATION AND CHARACTERIZATION OF SOME FLUORINATED α-AMINOARYLMETHANEPHOSPHONIC ACIDS

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Dedicated to Prof. Dr. M. Baudler, Köln

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α-Aminoarylmethanephosphonic acids have been prepared with a range of fluoro, fluoroalkyl, or fluoroalkoxy substituents in the benzene ring (4-F, 3-F, 2-F, 3,4-F_2, F_5, 4-CF_3, 3-CF_3, 4-CF_3O, and 3-CF_3O). These compounds have relatively low aqueous solubility and their NMR spectra (^1H, ^{13}C, ^{31}P and ^{19}F) were therefore recorded in D_2O in the presence of an excess of alkali. Under these conditions, the ring substituents appear to have little effect on δ_P (15–18 ppm), or on the ^1H and ^{13}C parameters for the benzylic group (α-CH), which are mainly in the ranges observed for other types of α-aminoarylmethanephosphonic acids under alkaline conditions (δ_H 3.8–4.0 ppm, $^2J_{PH}$ 15.3–16.5 Hz; δ_C 57–58 ppm, $^1J_{PC}$ 128–132 Hz). For those examples with fluorine in the ortho position (i.e., the 2-fluoro and pentafluoro derivatives) a slightly higher field chemical shift was observed for the benzylic carbon atom (δ_C 50–51 ppm). In the fast-atom bombardment mass spectra, pseudo-molecular ions, MH^+, and ions resulting from the elimination of phosphorous acid $[MH - H_3PO_3]^+$, provide a further useful means of chararacterization for these compounds.

Key words: Fluorinated aminoarylmethanephosphonic acids, dialkyl N-diphenylmethylaminoarylmethanephosphonates, NMR spectroscopy, FAB mass spectrometry.

INTRODUCTION

Aminophosphonic acids are of widespread interest as biologically active molecules,[1–7] as complexing agents for metal ions,[8] and as building blocks in the synthesis of phosphonopeptides.[9,10] α-Aminoarylmethanephosphonic acids and their esters, the phosphonic analogues of α-C-aryl-substituted glycine, have been reported by a number of workers,[11] although derivatives with fluorine or fluorinated substituents in the aromatic ring are uncommon. Such compounds are of interest because of the modified properties (pK_a, lipoidal solubility, etc.), which the introduction of fluorine may engender. The only previous report concerning α-aminofluorophenylmethanephosphonic acids is that of L. Maier *et al.*,[12] who prepared α-amino-4-fluorophenylmethanephosphonic acid and α-amino-3-(4′-fluorophenoxy)phenylmethanephosphonic

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§Part of forthcoming dissertation from U. Gruss, Heinrich-Heine-Universität Düsseldorf 1996.
||Authors for correspondence.

acid via addition of dialkyl phosphites to N-phenylmethyl protected imines (followed by hydrogenation and hydrolysis). The same method was used for the synthesis of diethyl N-phenylmethylamino-2,3-difluoromethylenedioxyphenylmethanephosphonate, which was converted into the corresponding diethyl aminophosphonate.[12] Other derivatives related to α-aminofluorophenylmethanephosphonic acids are the N-protected diethyl amino-4-fluorophenylmethanephosphonates with chiral N-1-phenylethyl[13] and N-2-methoxy-1-phenylethyl groups,[14] prepared by the imine method; and the hydrobromide salt of diphenyl amino-4-fluorophenylmethanephosphonate[16,17] (from N-phosphoryl- and N-thiophosphorylaminoarylmethanephosphonates synthesized by amidoalkylation of triphenyl phosphite with the corresponding amides). But in all these cases conversion to the free α-aminoarylmethanephosphonic acids was not reported. (Another fluorinated derivative, known in the literature, is α-hydroxyamino-4-fluorophenylmethanephosphonic acid,[15] prepared by hydroxyamination of diethyl aroylphosphonate.)

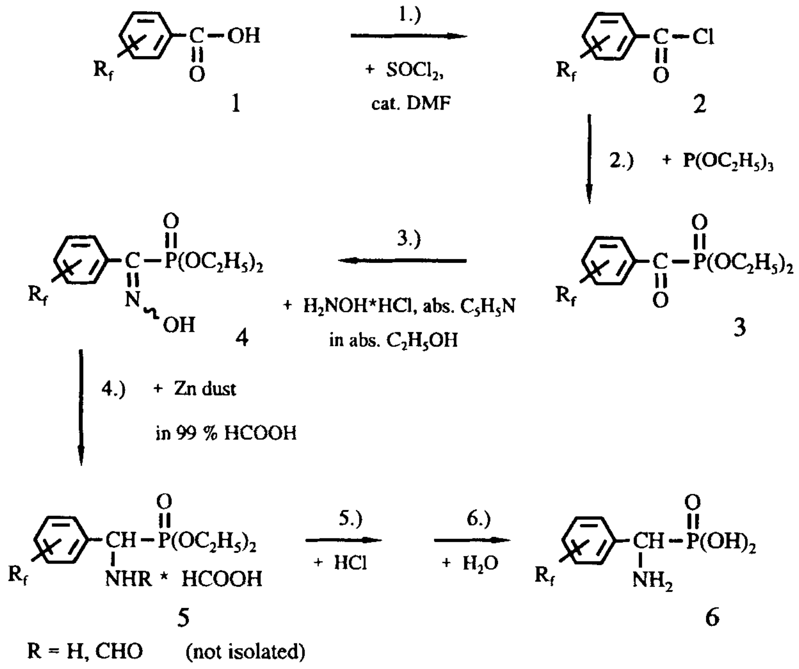
In this paper we describe the preparation of a range of fluorinated α-aminoarylmethanephosphonic acids and we discuss their characterization by NMR spectroscopy (^{1}H, ^{13}C, ^{31}P and ^{19}F) and FAB mass spectrometry.

RESULTS AND DISCUSSION

Preparations

Preparations were carried out by one or more procedures, involving reduction of the corresponding α-oximinophosphonates[19] by zinc in formic acid[21] (method A in Scheme I), amidoalkylation of phosphorus trichloride by a one-step process (method B with the variations a) and b) in Scheme II),[30] or a two-step process (method B with the variation c) in Scheme III,[32,33] or the addition of dialkyl phosphite to an N-protected Schiff base derived from diphenylmethylamine, followed by hydrolysis (method C in Scheme IV).[11,34] These methods have been applied previously in the synthesis of aminoalkanephosphonic acids of various types and were found to be suitable in the present work.

Starting materials for the reaction pathway A, the amination of diethyl aroylphosphonates (Scheme I), are fluorinated benzoic acids **1**, which were converted nearly quantitatively to aroyl chlorides **2** by reaction with an excess of thionyl chloride and catalytic amounts of dimethylformamide at 75°C.[18a,b] Arbuzov reaction with a slight excess of triethyl phosphite at temperatures below 40°C, followed by distillation at oil pump pressure, led to diethyl aroylphosphonates **3**.[15,19] These compounds **3** are sensitive to traces of acids, bases and weak nucleophiles (e.g. water, amines); decomposition of the P—C bond occurs easily. They were therefore converted immediately into the more stable diethyl hydroxyiminoarylmethanephosphonates **4** by reaction with hydroxylamine hydrochloride and pyridine in dry ethanol. These compounds **4** were obtained in the form of highly viscous oils or waxy solids (each consisting of a mixture of E and Z isomers, in which the E form predominates) after extractive work-up and drying under vacuum at room temperature. Purification of the diethyl hydroxyiminoarylmethanephosphonates **4** by distillation was not possible, since decomposition occurs at temperatures above 60°C.[15,19,20] Reduction of the oximes **4** to the corresponding amines **5** was carried out by the use of zinc dust in 99%

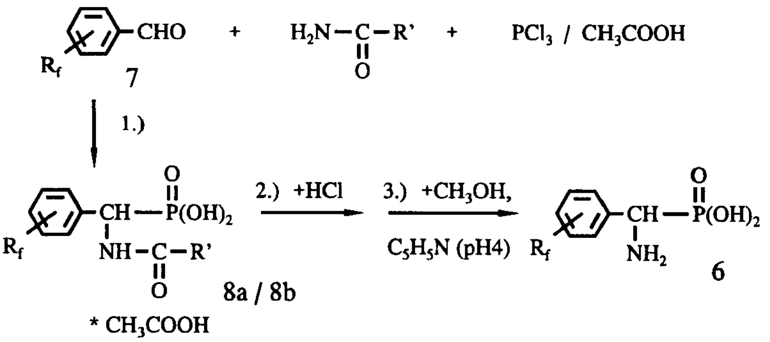


No.	Rf
1, 2, 3, 4, 5, 6 a	4-F
1, 2, 3, 4, 5, 6 c	2-F
1, 2, 3, 4, 5, 6 d	3,4-F_2

SCHEME I Synthesis of α-aminoarylmethanephosphonic acids **6**. Method A: Amination of diethyl aroylphosphonates. In the text hydrochlorides of **6** are designated **6'**.

formic acid at temperatures below 65°C.[21] After filtration and evaporation the remaining oils were used for the following hydrolysis step without further purification. They have not been investigated by ^1H NMR spectroscopy, but comparison with similar processes described in the literature[21,22,23a,23b] and $^{31}P\{^1H\}$ NMR spectroscopy showed that in all cases the oils consisted of mixtures **5** of diethyl aminoarylmethanephosphonates, aminoarylmethanephosphonic acids and analogous N-formylated derivatives. Heating of these products with concentrated hydrochloric acid (6–8 h at 100°C) led to hydrolysis of the phosphonate moiety (and cleavage of the N-formyl groups) and yielded α-aminoarylmethanephosphonic acid hydrochlorides **6'**. After evaporation of the solvent and repeated dissolving of the remaining oils in ethanol/water mixtures followed by evaporation, the α-aminoarylmethanephosphonic acids **6** precipitated during heating in boiling water as fine white crystalline solids.[19]

Method A for the synthesis of fluorinated α-aminoarylmethanephosphonic acids **6** produced very clean microcrystalline products, so that additional recrystallization steps were not necessary. This reaction pathway can be applied for α-aminoarylmethanephosphonic acids **6** with fluorinated substituents at any position in the aromatic system. A negative point is that the reaction procedure involved six steps with very long reaction times in some cases. Only the products of the first and the second step have to be isolated and purified (aroyl chlorides **2** were obtained in nearly



No.	R_f
7, 6 b	3-F
7, 6 e	4-CF_3
7, 6 f	3-CF_3
7, 6 g	4-CF_3O
7, 6 h	3-CF_3O

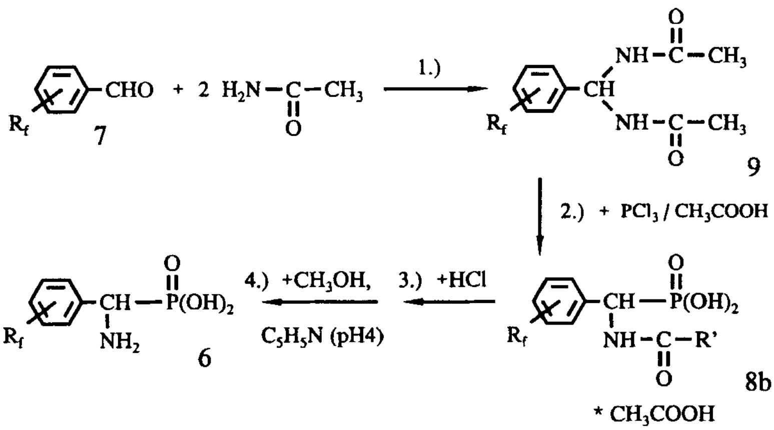
No.	R_f	R'
8 ab	3-F	C_6H_5
8 ae	4-CF_3	C_6H_5
8 af	3-CF_3	C_6H_5
8 ag	4-CF_3O	C_6H_5
8 ah	3-CF_3O	C_6H_5
8 bb	3-F	CH_3
8 be	4-CF_3	CH_3
8 bf	3-CF_3	CH_3
8 bg	4-CF_3O	CH_3
8 bh	3-CF_3O	CH_3

SCHEME II Synthesis of α-aminoarylmethanephosphonic acids **6**. Method B: Amidoalkylation of phosphorus trichloride in one-pot procedures: variation a): with benzamide; variation b): with acetamide.

quantitative yields, while the preparation of the moisture sensitive and high boiling diethyl aroylphosphonates **3** determined the yield of the whole reaction pathway). For the following steps, each product can be used in its crude form.

Other methods for the synthesis of aminoalkanephosphonic acids and aminophosphonates reported in the literature differ only in the techniques for reduction of the dialkyl hydroxyiminoalkanephosphonates. They include the use of a) aluminum amalgam,[19,24,25] b) Zn/Cu couple,[26] c) B_2H_6 gas in THF[24] d) BH_3*THF,[27] e) $TiCl_3$/ NaBH[C(O)CH_3]$_3$ in acetate buffered solution,[28] and f) catalytic hydrogenation.[20,25,29] In the present work the use of zinc dust in formic acid[21] was chosen as this required only simple reactants, avoided working with gases (method c)[24] or f)[20,25,29]), the preparation of reduction catalysts, the generation of the reducing species in a separate preceding reaction step (method a)[19] or b)[26]), or employing expensive complex hydrides (method d)[27] or e)[28]).

A one-pot synthesis for fluorinated α-aminoarylmethanephosphonic acids **6** is the amidoalkylation of phosphorus trichloride in acetic acid solution (method B, variations a) and b) in Scheme II). For this reaction an excess (up to 40%) of a fluorinated benzaldehyde **7** was allowed to react with a mixture of equimolar amounts of benzamide a) or acetamide b) and phosphorus trichloride in acetic acid to give the N-acylaminoarylmethanephosphonic acid **8a,b**. After evaporation of the solution the remaining oil was heated with an excess of concentrated hydrochloric acid to remove the N-protection group to form the aminophosphonic acid hydrochloride **6′**, from which the α-aminoarylmethanephosphonic acid **6** was precipitated by addition of



No.	Rf
7, 9, 8b, 6 a	4-F

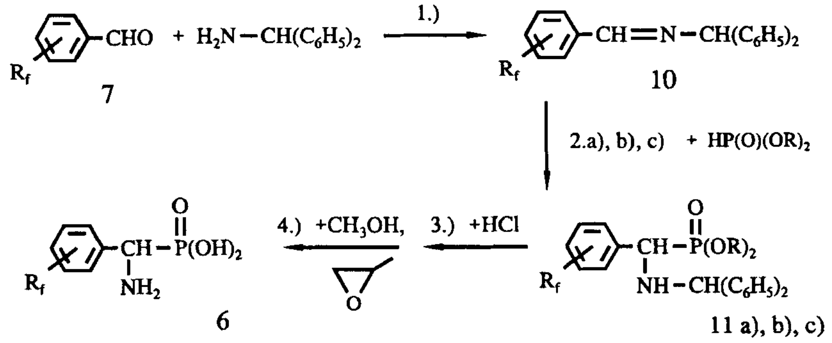
SCHEME III Synthesis of α-aminoarylmethanephosphonic acids **6**. Method B: Amidoalkylation of phosphorus trichloride via a two-step reaction.

pyridine in methanolic solution (pH 4) and cooling to −5 to 0°C. The α-aminoarylmethanephosphonic acids **6** were obtained as amorphous powders which were purified by recrystallization from alcohol/water solutions.[30]

The application of the different amides in this type of reaction showed different advantages: with benzamide the formation of the N-acylated aminophosphonic acids **8a**, and the N-deprotecting reaction were much quicker than with the use of acetamide. The cleavage of the N-benzoyl group was observable by the precipitation of benzoic acid, while the final removal of the N-acetyl group had to be determined by $^{31}P\{^1H\}$ NMR spectroscopy. Nevertheless, the amidoalkylation reaction with acetamide leads in some cases to much better yields for α-aminoarylmethanephosphonic acids **6** (especially for R_f = 4-CF_3 **6e**) than the analogous reaction with benzamide.

Method B (Scheme II) makes it possible to synthesize α-aminoarylmethanephosphonic acids **6** in one step without the use of special apparatus and without purification of intermediate products. Disadvantages are the need to use an excess of the expensive fluorinated benzaldehydes **7**, long reaction times under drastic acid conditions to split off the N-protection groups, and long crystallization times to precipitate the α-aminoarylmethanephosphonic acids **6** from the complex reaction mixtures. By this type of amidoalkylation reaction in a one-pot procedure only meta- and para-substituted benzaldehydes **7** can be converted to α-aminophosphonic acids **6** in moderate to good yields; ortho-substituted compounds do not react in this way (as shown with R_f = 2-CF_3, 2-CF_3O).[30,31]

The third variation of method B for the amidoalkylation of phosphorus trichloride is a two-step reaction (Scheme III). First the fluorinated benzaldehyde **7** was converted into an N,N′-arylidenebis-(acetamide) **9** by heating it with an excess of acetamide, followed by crystallization from methanol.[32] After isolation of this compound it was used for the amidoalkylation reaction under moderate conditions at 0–10°C with equimolar amounts of phosphorus trichloride in acetic acid solution, followed



No.	Rf
7, 10, 6 a	4-F
7, 10, 6 b	3-F
7, 10, 6 c	2-F
7, 10, 6 d	3,4-F_2
7, 10, 6 e	4-CF_3
7, 10, 6 f	3-CF_3
7, 10, 6 g	4-CF_3O
7, 10, 6 h	3-CF_3O
7, 10, 6 i	F_5

No.	Rf	R
11 aa	4-F	CH_3
11 ae	4-CF_3	CH_3
11 ba	4-F	C_2H_5
11 bb	3-F	C_2H_5
11 bd	3,4-F_2	C_2H_5
11 be	4-CF_3	C_2H_5
11 bf	3-CF_3	C_2H_5
11 bg	4-CF_3O	C_2H_5
11 ca	4-F	C_6H_5
11 cb	3-F	C_6H_5
11 cd	3,4-F_2	C_6H_5
11 ce	4-CF_3	C_6H_5
11 cf	3-CF_3	C_6H_5
11 cg	4-CF_3O	C_6H_5

SCHEME IV Synthesis of α-aminoarylmethanephosphonic acids **6**. Method C: Addition of dialkyl phosphites to N-diphenylmethyl protected imines.

by heating at 100°C for completion of the reaction. Work-up and N-deprotection of the N-acetylaminophosphonic acid **8b** was achieved in the same way as described for the one-pot method.[32,33,42]

This two-step procedure is especially suitable for aldehydes sensitive to oxidation, because these compounds were converted first into more stable derivatives, the N,N′-arylidenebis-(acetamides), before the amidoalkylation reaction under drastic acid conditions starts.[32,33,42] This additional step is not a disadvantage, since N,N′-arylidenebis-(acetamides) **9** were obtained in high yields in a crystalline state; they can be employed without purification for the further synthesis, and only equimolar amounts of the expensive fluorinated benzaldehydes **7** are necessary.

Method B, variation c) (Scheme III) was used for one example, namely 4-fluorobenzaldehyde **7a**, and the yield of α-amino-(4-fluorophenyl-)methanephosphonic acid **6a** obtained was noticeably higher than yields for fluorinated α-aminoarylmethanephosphonic acids **6** according to the one-pot procedures (method B, variations a) and b) in Scheme II).

The third method C (Scheme IV) for the preparation of α-aminoarylmethanephosphonic acids **6** uses the addition of substances with P—H bonds to N-protected imines; three steps lead to the desired products. The intermediate compounds, N-substituted imines and N-substituted dialkyl aminophosphonates, are obtained in high to quantitative yields.

In this study the diphenylmethyl group has been chosen for N-protection.[34] Fluorinated benzylidene-1,1-diphenylmethylamines **10** were synthesized in two different ways: In the first route mixing of equimolar amounts of fluorinated benzaldehydes **7** with diphenylmethylamine in dry dichloromethane or dry diethyl ether, and addition of anhydrous potassium carbonate led to the imines **10** under very mild conditions. After filtration and evaporation of the solvents the imines **10** were obtained in the form of waxy solids in nearly quantitative yields.[11,42] In the second variation the compounds **10** were prepared by heating equimolar amounts of benzaldehydes **7** with diphenylmethylamine. The use of dry solvents, the addition of drying agents and catalysts and/or methods to remove water as formed (e.g. Dean and Stark apparatus) were not necessary, because it separated from the oily reaction mixture, and was removed by dissolving the oil in dichloromethane and the addition of anhydrous sodium sulfate.

These imines **10** were converted into α-aminoarylmethanephosphonic acids **6** by a one-pot method: they were stirred with equimolar amounts of dialkyl phosphite (R = CH_3, C_2H_5) at 120–140°C (30–60 min) to yield *in situ* dialkyl N-diphenylmethylaminoarylmethanephosphonates **11**. These oils (without isolation or purification) were heated with concentrated hydrochloric acid at 100°C for N-deprotection and phosphonate hydrolysis at the same time. After extraction of the by-product, diphenylmethyl chloride, with toluene and evaporation of the aqueous solution the remaining oils were dissolved in methanol and the α-aminoarylmethanephosphonic acids **6** were precipitated by the addition of propylene oxide at 40°C.[11,34,35,42,43]

For isolation of dialkyl or diphenyl N-diphenylmethylaminoarylmethanephosphonates **11** (R = CH_3, C_2H_5, C_6H_5) longer reaction times of the imines **10** with the phosphites were required. The oily reaction mixtures crystallized after dissolving them in alcohols followed by addition of diethyl ether at 0°C, to give waxy white solids (R = CH_3, C_2H_5) or fine, white crystalline powders (R = C_6H_5) in high yields. These aminophosphonates **11** were isolated and investigated by NMR spectroscopy in this work for the first time. They represent an air stable storage form for other aminophosphonic acid derivatives. It is possible to convert them to α-aminoarylmethanephosphonic acids **6** as described above, to N-diphenylmethylaminoaryl methanephosphonic acids or to dialkyl aminoarylmethanephosphonates. N-Diphenylmethylaminoarylmethanephosphonic acids can be obtained by transforming the N-protected dialkyl aminoarylmethanephosphonates **11** first to the corresponding bis(trimethylsilyl) aminophosphonates by reaction with an excess of bromotrimethylsilane in chlorinated hydrocarbons at room temperature followed by cleavage of the phosphonic ester groups with water at room temperature.[12] Dialkyl aminoarylmethanephosphonates are prepared by cleaving the N-protection group (without hydrolysis of the phosphonate moiety) by catalytic hydrogenation with Pd/charcoal catalyst in alcoholic solution[12,34,36,43] or by reaction in acid solutions e.g. HBr in acetic acid[16,17,37] or HBr in alcoholic solution[9d,38] under controlled conditions at room temperature, followed by immediate work-up. These derivatives are especially important for phosphonopeptide synthesis.

The α-aminoarylmethanephosphonic acids **6a–6i** were obtained in all cases as anhydrous, microcrystalline solids and were characterized by elemental analysis, NMR spectroscopy and mass spectrometry. Yields and principal NMR parameters are shown in Table I.

NMR Spectroscopy

Because of the low solubility of the α-aminoarylmethanephosphonic acids **6** in water, NMR parameters were determined in the presence of an excess of alkali (NaOD or KOD in D_2O). Under these conditions full deprotonation takes place: the phosphonate is in the bi-negative PO_3^{2-} form and the amino group in the neutral NH_2 form. It has been shown elsewhere for simple α-aminoalkanephosphonic acids, that removal of the proton from nitrogen ($NH_3^+ \rightarrow NH_2$) has the effect of moving the ^{31}P chemical shift to lower field than would be observed for the same aminophosphonic acids, in D_2O alone.[39] While a similar effect may be expected for the α-aminoarylmethanephosphonic acids, our present results are confined to measurements in alkaline conditions only. Under these conditions the ^{31}P chemical shifts for the various fluorinated compounds showed little variation with the substituents present. All were found to lie in the region of δ_P 17–18 ppm (relative to 85% H_3PO_4), except in the case of the pentafluoro derivative **6i** for which the chemical shift was at a slightly higher field (δ_P 15.3 ppm). These chemical shifts are, as a group, all slightly upfield from those reported for other non-fluorinated α-aminoarylmethanephosphonic acids **6** (X = H, 4-MeO, 4-Me, 4-Et, 2-HO, 3-MeO, 4-HO), for which δ_P in all cases was found to lie in the range 18–20 ppm in NaOD/D_2O.[11,40] It is interesting that α-amino-4-nitrophenylmethanephosphonic acid **6** (X = 4-NO_2), with the strongly electron-attracting nitro group present in the para position, also exhibits a chemical shift (δ_P 16.6 ppm) in the same region as the fluorinated compounds.[40] The reason for this uniformly upfield shift in δ_P when electron-attracting substituents are present in the ring is obscure but the effect is small and it is likely that the shielding of phosphorus is dominated more by the electron density associated with the oxygen atoms of the phosphonate anion, PO_3^{2-}, rather than the ring substituents. Conformational and hydrogen-bonding influences may also be involved. Coupling to fluorine broadens the $^{31}P\{^1H\}$ NMR signals in general but distinct doublets were observed for the mono-fluorinated derivatives with 4-, 5-, or 6-bond coupling via the aromatic ring ($^4J_{PF}$ 4.1 Hz, $^5J_{PF}$ 1.4 Hz and $^6J_{PF}$ 3.9 Hz in **6a**, **6b** and **6c**, respectively).

^1H and ^{13}C NMR parameters (see Table I and IX) for the aryl-substituted CH groups of α-aminoarylmethanephosphonic acids **6** also lie, in most cases, within fairly narrow ranges (δ_H 3.8–4.0 ppm, $^2J_{PH}$ 15.3–16.5 Hz; δ_C 57.5–58.3 ppm, $^2J_{PC}$ 128–132 Hz) and are not significantly different from those reported for the non-fluorinated compounds.[11,40] The only compounds whose ^1H and ^{13}C chemical shifts for the CH group lie outside these ranges are those having one or more substituents ortho to the arylmethane carbon **6c**, **6i**, where the inductive effect of fluorine might be expected to have the greatest influence. Even in these cases, the ^1H chemical shift is only slightly downfield, at ca. 4.2 ppm although the ^{13}C chemical shift, surprisingly, is clearly up-field at 50–51 ppm. There is no significant difference in the magnitude of coupling to phosphorus in either case. It is interesting to note that very similar chemical shifts are shown by α-amino-2-hydroxyphenylmethanephosphonic acid (**6**, X = 2-HO) (δ_H 4.3 ppm, δ_C 50.23 ppm), suggesting that the effects observed are steric in origin rather than electronic.

^{19}F NMR chemical shifts for these molecules are similar to those for the starting materials **1** and **7**. The proton-decoupled ^{19}F NMR spectra appear as broad singlets for the trifluoromethyl **6e**, **6f**, and trifluoromethoxy **6g**, **6h** compounds and as un-

TABLE I

$^{31}P\{^1H\}$ and ^1H NMR data, yields and melting points of fluorinated α-aminoarylmethanephosphonic acids **6**. $^{31}P\{^1H\}$ NMR: 10% 1m KOH/D_2O, (**D**), or NaOD(xs)/D_2O, (**L**), vs. 85% H_3PO_4 ext. ^1H NMR: 6% 1m KOH/D_2O, (**D**), or NaOD(xs)/D_2O, (**L**), vs. TSP—d_4—Na, δ [ppm], Mult., $^nJ_{XY}$ [Hz]

No.	δ_H (L) α-CH	δ_H (D) α-CH	δ_P (L)	δ_P (D)	yields [%]	mp. [°C]
6a	3.86, d, $^2J_{PH}$ 15.4	3.80, d, $^2J_{PH}$ 15.3	17.03, d, $^6J_{PF}$ 3.0	18.50, d, $^6J_{PF}$ 3.9	63.3^a, 59.0^d, 55^e	278-282
6b	-	3.93, d, $^2J_{PH}$ 15.6	-	18.03, d, $^5J_{PF}$ 1.4	18.6^b, 25.5^c	289-290
6c	4.41, d, $^2J_{PH}$ 16.1	4.13, d, $^2J_{PH}$ 15.9	17.59, d, $^4J_{PF}$ 4.0	18.14, d, $^4J_{PF}$ 4.1	43.3^a, 28^e	270-273
6d	-	3.79, d, $^2J_{PH}$ 15.7	-	17.86, dd, $^6J_{PF}$ 4.2, $^5J_{PF}$ 1.6	56.1^a	280-282
6e	3.95, d, $^2J_{PH}$ 16.4	3.91, d, $^2J_{PH}$ 16.5	16.96, s	17.71, q, $^7J_{PF}$ 2.1	40.9^b, 74.8^c, 46^e	287-289
6f	-	4.01, d, $^2J_{PH}$ 15.8	-	15.03, s	41.7^b, 35.6^c	253-255
6g	-	3.85, d, $^2J_{PH}$ 15.8	-	18.12, s	31.1^b, 45.1^c,	305-307
6h	3.87, d, $^2J_{PH}$ 16.2	3.91, d, $^2J_{PH}$ 16.0	17.29, s	15.99, s	25.9^b, 35.0^c, 43^e	277-280
6i	4.20, d, $^2J_{PH}$ 17.5	-	15.31, m	-	18^e	268-270

[a] Preparation by method A (Amination of diethyl aroylphosphonates), SCHEME I.

[b] Preparation by method B, variation a) (Amidoalkylation of phosphorus trichloride with benzamide, one-pot procedure), SCHEME II.

[c] Preparation by method B, variation b) (Amidoalkylation of phosphorus trichloride with acetamide, one-pot procedure), SCHEME II.

[d] Preparation by method B, variation c) (Amidoalkylation of phosphorus trichloride with arylmethylidenebisacetamide, two-step method), SCHEME III.

[e] Preparation by method C (addition of dialkyl phosphites to N-protected imines, followed by hydrolysis), SCHEME IV.

resolved multiplets in other cases due to coupling with phosphorus and other fluorine atoms if present (in **6a**, **6b**, **6c**, **6d** and **6i**).

Detailed NMR data are quoted under the experimental section.

Mass Spectroscopy

As reported for other classes of aminophosphonic acids,[6,10b,41] FAB MS (with a primary beam of xenon atoms) or LSIMS (using fast caesium ions) provide additional

TABLE II

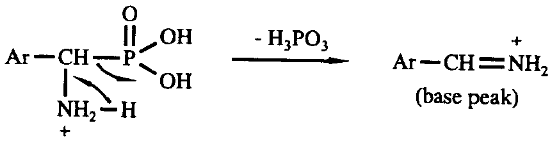
Characteristic ions in the FAB mass spectra of α-aminoarylmethanephosphonic acids **6a**–**6i**

No.	Method[a]	Matrix	m/z [%]			
		(Z)	$[2M + H]^+$	$[MH + Z]^+$	$[MH]^+$	$[MH - H_3PO_3]^+$
6a	Cs^+	glycerol	411 (17.6)	298 (8.9)	206 (33.7)	124 (100)
6b	Cs^+	glycerol	411 (3.8)	298 (5.7)	206 (20.1)	124 (100)
6c	Cs^+	glycerol	-	298 (5.0)	206 (13.5)	124 (71.2)
6d	Cs^+	glycerol	-	-	224 (7.4)	142 (98.7)
6e	Cs^+	glycerol	511 (6.3)	348 (2.2)	256 (14.1)	174 (100)
6e	Xe	thioglycerol	511 (20.6)	-	256 (52.5)	174 (100)[b]
6f	Cs^+	glycerol	-	-	256 (2.9)	174 (100)
6g	Cs^+	glycerol	-	364 (4.2)	272 (10.2)	190 (100)
6h	Cs^+	glycerol	-	-	272 (13.7)	190 (100)
6h	Xe	3-NOBA	-	-	272 (24.6)	190 (6.4)[c]
6i	Cs^+	glycerol	555 (11.4)	370 (10.2)	278 (34.8)	196 (100)
6i	Xe	thioglycerol	555 (40.2)	386 (2.7)	278 (74.6)	196 (100)

[a] Bombardment by primary beam of Cs^+ ions or Xe atoms as indicated.

[b] Also m/z [%] = 176, ($[MH - HPO_3]^+$, 12.1), 155 ($[MH - H_3PO_3 - F]^+$, 29.2).

[c] Peak at m/z [%] = 189 (15.8) corresponds to unexpected $[M - H_3PO_3]^+$; also m/z [%] = 254 ($[MH - H_2O]^+$, 28.5).



SCHEME V Elimination of phosphorous acid from the pseudo-molecular ions of α-aminoarylmethanephosphonic acids **6**.

useful confirmation of identity (Table II). The spectra in most cases show prominent pseudomolecular ions, MH^+, although these are generally weaker in intensity than those observed for aminoalkanephosphonic acids and in one case **6f** this ion was not distinguishable from the background. In those cases in which comparison was made (for **6e**, **6h**, **6i**), more intense pseudomolecular ions were obtained using xenon bombardment with thioglycerol or 3-nitrobenzyl alcohol (3-NOBA) as matrix, than with glycerol and Cs^+ ion bombardment. The base peak in all spectra was generally formed by the elimination of phosphorous acid from the pseudomolecular ion (Scheme V), the so-formed iminium ion being stabilized in these aromatic systems by conjugation with the benzene ring. Cluster ions such as $[MH + Z]^+$ and $[2 M + H]^+$ were also observed in certain cases. In the case of the 4-CF_3 compound **6e** there was evidence for the elimination of metaphosphoric acid from the pseudomolecular ion,[6,10b,41] as shown by the appearance of a peak at m/z = 176 (12.1%), and of the loss of fluorine from the iminium ion to give m/z = 155 (29.2%).

EXPERIMENTAL

Fluorinated benzaldehydes, fluorinated benzoic acids and other reagents were obtained commercially; benzaldehydes and phosphites were distilled before use and solvents were dried according to standard procedures. Melting points were determined using a Reichert Thermopan Kofler Hot Stage or on an Electrothermal Digital Melting Point Apparatus (mp. >250°C); lower melting points were determined on a Büchi Melting Point Apparatus SMP 200; they are all uncorrected. Preparative studies were performed in London and Düsseldorf.

NMR Spectroscopy

Results from ^{31}P-NMR for compounds **6** and **11** are given in Table I and VI–VIII. Compounds **6**, **10** and **11** were characterized by extensive ^{13}C-NMR investigations, corresponding data are listed in Tables IX to XIII. Some ^{1}H-data for **6** and **10** are given in Tables I and V. In general the ^{1}H and ^{19}F-NMR spectra of the aromatic ring systems in all compounds described in this study are of second order character. Labourious analyses and iterations of those high resolution spectra were not performed, but a few, significant, directly accessible parameters are given under the preparative section.

The following spectrometers and referencing techniques were used by the London (L) and Düsseldorf (D) teams: ^{1}H NMR: Perkin Elmer R12B (L), 60 MHz, Bruker AM 250 (L), 250.13 MHz, Bruker AM 200 SY (D), 200.13 MHz. ^{13}C NMR: Bruker WP 80 (L), 20.12 MHz, Bruker AM 250 (L), 62.90 MHz, Bruker AM 200 SY (D), 50.32 MHz. Chemical shifts were recorded relative to TSP-d$_4$ ($Me_3Si—CD_2—CD_2—COONa$) for aqueous solutions of aminophosphonic acids or TMS for solutions of the Schiff bases or dialkyl N-protected aminoarylmethanephosphonates in $CDCl_3$. ^{31}P NMR: WP 80 (L), 32.39 MHz, AM 200 SY (D), 81.02 MHz with 85% H_3PO_4 as an external reference. ^{19}F NMR: Varian VXR 400 (L), 376 MHz with $CFCl_3$ as an external reference, AM 200 SY (D), 188.28 MHz with C_6F_6 as an internal reference for solutions in $CDCl_3$ and C_6D_6 or as an external reference for D_2O solutions. The NMR parameters (δ, given in [ppm] and $^{n}J_{XY}$, given in [Hz]) were taken directly from the spectra.

Mass Spectrometry

Low resolution electron impact mass spectra were obtained on a Kratos Profile mass spectrometer (L) operating at 70 eV. FAB mass spectra were obtained with a VG Micromass ZAB-E mass spectrometer, with a primary beam of xenon atoms operating at 8 kV. LSIMS mass spectra were obtained using the Kratos Profile instrument, equipped with a Cs^+ ion gun operating at 10 kV.

Preparation of Fluorinated α-Aminoarylmethanephosphonic Acids by Method A (Amination of Diethyl Aroylphosphonates) (Scheme I)

Fluorinated Benzoyl Chlorides **2a–d**[44]: 0.50 mol fluorinated benzoic acid **1**, 0.75 mol thionyl chloride and 2 drops of dimethylformamide were mixed under an atmosphere of nitrogen and heated (2–3 h), with stirring at 70–80°C (oil bath temperature). Gas evolution occurred with the formation of a greenish-brown solution. The excess of thionyl chloride was removed by distillation at atmospheric pressure and the fluorinated benzoyl chloride **2** was purified by fractional distillation *in vacuo* (oil pump).

The fluorinated benzoyl chlorides **2** were obtained as colourless, strongly-smelling liquids; they were stored under nitrogen on account of their sensitivity to hydrolysis.

4-Fluorobenzoyl Chloride **2a**
M.Wt. = 158.56, yield: 98.8%, bp. 69–71°C/15 mmHg, n_{20} = 1.5296.
^{1}H NMR (6% $CDCl_3$, TMS), δ: 7.12–7.23 (m, 2H$_{arom.}$, 4-F—C_6H_4—C), 8.09–8.19 (m, 2H$_{arom.}$, 4-F—C_6H_4—C).
^{19}F NMR (6% $CDCl_3$, C_6F_6 int.), δ: 60.92–61.07 (m, 1F, 4-F—C_6H_4—C).

2-Fluorobenzoyl Chloride **2c**
M.Wt. = 158.56, yield: 98.3%, bp. 48–50°C/1.5 mmHg, n_{20} = 1.5369.
^{1}H NMR (6% $CDCl_3$, TMS), δ: 7.14–7.36 (m, 2H$_{arom.}$, 2-F—C_6H_4—C), 7.62–7.73 (m, 1H$_{arom.}$, 2-F—C_6H_4—C), 8.08–8.17 (m, 1H$_{arom.}$, 2-F—C_6H_4—C).
^{19}F NMR (6% $CDCl_3$, C_6F_6 int.), δ: 53.57–53.70 (m, 1F, 2-F—C_6H_4—C).

3,4-Difluorobenzoyl Chloride **2d**
M.Wt. = 176.55, yield: 96.3%, bp. 72–73°C/13 mmHg.
^{1}H NMR (6% $CDCl_3$, TMS), δ: 7.27–7.40 (m, 1H$_{arom.}$, 3,4-F_2—C_6H_3—C), 7.92–8.02 (m, 2H$_{arom.}$, 3,4-F_2—C_6H_3—C).
^{19}F NMR (6% $CDCl_3$, C_6F_6 int.), δ: 27.21–27.44 (m, 1F, 3,4-F_2—C_6H_3—C), C 36.60–36.83 (m, 1F, 3,4-F_2—C_6H_3—C).

Fluorinated Diethyl Benzoylphosphonates **3a–d**: 0.20 mol fluorinated benzoyl chloride **2** was mixed with 0.22 mol triethyl phosphite by dropwise addition (during 2 h), with vigorous stirring under nitrogen. A strongly exothermic reaction occurred with the evolution of ethyl chloride and the reaction mixture became yellow. The temperature of the mixture was maintained at 40°C with the aid of an ice/water bath. Stirring was then continued at room temperature under a gentle stream of nitrogen (4–8 h). After removal of the excess of triethyl phosphite, the fluorinated diethyl benzoylphosphonate **3** was purified by fractional distillation *in vacuo* (oil pump).

The fluorinated diethyl benzoylphosphonates **3** are clear, oily, yellow liquids. As they undergo decomposition in the presence of traces of acids or bases, or weak nucleophiles (like water or amines), they were stored under argon.

Diethyl 4-Fluorobenzoylphosphonate **3a**
M.Wt. = 260.20, yield: 95.1%, bp. 97–99°C/0.1 mmHg.
$^{31}P\{^1H\}$ NMR (10% $CDCl_3$, 85% H_3PO_4 ext.), δ: −0.88 (d, $^6J_{PF}$ 0.6).
^1H NMR (6%, C_6D_6, TMS), δ: 1.00 (dt, $^3J_{HH}$ 7.1, $^4J_{PH}$ 0.5, 6H, 2 × CH_3), 3.99 (qd, $^3J_{HH}$ 7.1, $^3J_{PH}$ 8.1, 4H, 2 × CH_2), 6.56–6.60 (m, $2H_{arom.}$, 4-F—C_6H_4—C), 8.33–8.43 (m, $2H_{arom.}$, 4-F—C_6H_4—C).
^{19}F NMR (6% C_6D_6, C_6F_6 int.), δ: 60.65–60.80 (m, 1F, 4-F—C_6H_4—C).

Diethyl 2-Fluorobenzoylphosphonate **3c**
M.Wt. = 260.20, yield: 68.8%, bp. 108–111°C/0.05 mmHg.
$^{31}P\{^1H\}$ δ: −1.90 (d, $^4J_{PF}$ 1.6).
^1H δ: 1.02 (dt, $^3J_{HH}$ 7.1, $^4J_{PH}$ 0.5, 6H, 2 × CH_3), 4.03 (qd, $^3J_{HH}$ 7.1, $^3J_{PH}$ 8.2, 4H, 2 × CH_2), 6.60–6.76 (m, $2H_{arom.}$, 2-F—C_6H_4—C), 6.81–6.91 (m, $1H_{arom.}$, 2-F—C_6H_4—C), 8.35–8.45 (m, $1H_{arom.}$, 2-F—C_6H_4—C).
^{19}F δ: 51.78–51.91 (m, 1F, 2-F—C_6H_4—C).

Diethyl 3,4-Difluorobenzoylphosphonate **3d**
M.Wt. = 278.19, yield: 83.4%, bp. 116–117°C/0.1 mmHg.
$^{31}P\{^1H\}$ δ: −1.68 (dd, $^6J_{PF}$ 3.3, $^5J_{PF}$ 0.6).
^1H δ: 1.41 (dt, $^3J_{HH}$ 7.1, $^4J_{PH}$ 0.6, 6H, 2 × CH_3), 4.31 (qd, $^3J_{HH}$ 7.1, $^3J_{PH}$ 8.1, 4H, 2 × CH_2), 7.27–7.42 (m, $1H_{arom.}$, 3,4-F_2—C_6H_3—C), 8.05–8.23 (m, $2H_{arom.}$, 3,4-F_2—C_6H_3—C).
^{19}F δ: 26.65–26.89 (m, 1F, 3,$\underline{4}$-F_2—C_6H_3—C), 35.55–35.78 (m, 1F, $\underline{3}$,4-F_2—C_6H_3—C).

Fluorinated Diethyl Benzoyloximinophosphonates **4a–d**: 0.20 mol hydroxylamine hydrochloride was suspended in 130 ml of absolute ethanol, with the exclusion of moisture, and 0.23 mol dry pyridine was added. A solution of 0.15 mol fluorinated diethyl benzoylphosphonate **3** in 50 ml of absolute ethanol was added dropwise (during 2 h). Slight warming occurred to give a clear, yellow solution and the reaction temperature was maintained below 30°C with the aid of an ice/water bath. The mixture was finally stirred at room temperature (55–75 h) and became colourless (the reaction was monitored by $^{31}P\{^1H\}$ NMR). The solvent was then removed on a rotary evaporator under water pump pressure to leave an oil which was taken up in 200 ml of water and extracted five times with dichloromethane. The organic phase was dried over Na_2SO_4 and filtered, and after removal of solvent the yellowish-brown oil was dried *in vacuo* (oil pump) at room temperature.

The oil consists of a mixture of the cis- and trans-isomer of the fluorinated diethyl benzoyloximinophosphonate **4** (with the E-form in excess), contaminated with phosphates. Purification by vacuum distillation is impossible since decomposition occurs above 60°C.

Diethyl 4-Fluorobenzoyloximinophosphonate **4a**
M.Wt = 275.22, yield of the crude oil: 94.8%.
$^{31}P\{^1H\}$ NMR (reaction mixture in C_2H_5OH, D_2O ext., 85% H_3PO_4 ext.), δ: 10.06 (s), (E), 4.93 (s), (Z), (relation E:Z = 1.5:1).

Diethyl 2-Fluorobenzoyloximinophosphonate **4c**
M.Wt. = 275.22, yield of the crude oil: 96.0%.
$^{31}P\{^1H\}$ NMR (10% $CDCl_3$, 85% H_3PO_4 ext.), δ: 8.60 (d, $^4J_{PF}$ 1.9), (E), 3.77 (d, $^4J_{PF}$ 1.1), (Z), (relation E:Z = 1.5:1).

Diethyl 3,4-Difluorobenzoyloximinophosphonate **4d**
M.Wt. = 293.21, yield of the crude oil: 93.2%.
$^{31}P\{^1H\}$ δ: 9.26 (s), (E), 4.64 (s), (Z) (relation E:Z = 2:1).

Fluorinated Diethyl Aminoarylmethanephosphonates and N-Formylated Derivatives **5a–d**: 0.10 mol of the oily fluorinated diethyl benzoyloximinophosphonate **4** was added dropwise (during 1 h), under nitrogen, to a suspension of 0.40 mol zinc dust in 100 ml of 99% formic acid. An exothermic reaction occurred with the vigorous evolution of gas; the reaction temperature was maintained below 65°C by cooling. After addition was complete the suspension was stirred at room temperature (12 h) and the reaction was monitored by $^{31}P\{^1H\}$ NMR. Solids were filtered using a G3-sintered glass filter and washed repeatedly with formic acid to give a yellow filtrate which was evaporated on a rotary evaporator under water pump pressure to give a brownish oil.

From the $^{31}P\{^1H\}$ NMR spectrum it could be seen that in addition to reduction to give diethyl aminoarylmethanephosphonate **5** partial hydrolysis had occurred in the acid solution to give the aminoarylmethanephosphonic acid (in form of its formic acid salt) **6'**.

Diethyl Amino-(4-fluorophenyl-)methanephosphonate **5a**
M.Wt. = 261.23.
$^{31}P\{^1H\}$ NMR (reaction mixture in HCOOH, D_2O ext., 85% H_3PO_4 ext.), δ: 21.27 (s), diethyl aminoarylmethanephosphonate, 16.92 (s), aminoarylmethanephosphonic acid.

Diethyl Amino-(2-fluorophenyl-)methanephosphonate **5c**
M.Wt. = 261.23.
$^{31}P\{^1H\}$ NMR (reaction mixture in HCOOH, D_2O ext., 85% H_3PO_4 ext.), δ: 19.19 (s), diethyl aminoarylmethanephosphonate, 14.72(s), aminoarylmethanephosphonic acid.

Diethyl Amino-(3,4-difluorophenyl-)methanephosphonate **5d**
M.Wt. = 279.22.
$^{31}P\{^1H\}$ NMR (reaction mixture in HCOOH, D_2O ext., 85% H_3PO_4 ext.), δ: 18.43 (s), diethyl aminoarylmethanephosphonate, 11.14 (s), aminoarylmethanephosphonic acid.

Fluorinated α-Aminoarylmethanephosphonic Acids **6a–d**: The brownish oil was heated under reflux (6–8 h) with 50 ml of concentrated hydrochloric acid (oil bath temperature 100–110°C). The hydrolysis gave a clear yellow solution (monitored by $^{31}P\{^1H\}$ NMR), which was evaporated at water pump pressure on a rotary evaporator to leave a yellowish oil of the aminoarylmethanephosphonic acid hydrochloride **6'**. Water was added and the solution was evaporated repeatedly until a white solid was formed. The residue was heated under reflux (2 h) with 50–100 ml of water, and the slightly soluble α-aminoarylmethanephosphonic acid **6** separated as a white crystalline solid. The solid was filtered off (by a Büchner funnel), washed with ethanol, dried in a vacuum desiccator over silicagel, and recrystallized from water/ethanol mixtures.

α-Amino-(4-fluorophenyl-)methanephosphonic Acid **6a**
M.Wt. = 205.13, yield: 63.3% (based on diethyl benzoylphosphonate), mp. 278–282°C.
$^{31}P\{^1H\}$ NMR (10% 1m KOD/D_2O, 85% H_3PO_4 ext.), δ: 18.50 (d, $^6J_{PF}$ 3.9).
^1H NMR (10% 1m KOD/D_2O, TSP—d_4—Na), δ: 3.80 (d, $^2J_{PH}$ 15.3, 1H, PCH), 7.03–7.15 (m, $2H_{arom.}$, 4-F—C_6H_4—C), 7.33–7.45 (m, $2H_{arom.}$, 4-F—C_6H_4—C).
^{19}F NMR (10% 1m KOD/D_2O, C_6F_6 ext.), δ: 45.00–45.18 (m, 1F, 4-F—C_6H_4—C).

α-Amino-(2-fluorophenyl-)methanephosphonic Acid **6c**
M.Wt. = 205.13, yield: 43.3% (based on diethyl benzoylphosphonate), mp. 270–273°C.
$^{31}P\{^1H\}$ δ: 18.14 (d, $^4J_{PF}$ 4.1).
^1H δ: 4.13 (d, $^2J_{PH}$ 15.9, 1H, PCH), 7.06–7.35 (m, $3H_{arom.}$, 2-F—C_6H_4—C), 7.42–7.52 (m, $1H_{arom.}$, 2-F—C_6H_4—C).
^{19}F δ: 45.01–45.21 (m, 1F, 2-F—C_6H_4—C).

α-Amino-(3,4-difluorophenyl-)methanephosphonic Acid **6d**
M.Wt. = 223.12, yield: 56.1% (based on diethyl benzoylphosphonate), mp. 280–282°C.
$^{31}P\{^1H\}$ δ: 17.86 (dd, $^6J_{PF}$ 4.2, $^5J_{PF}$ 1.6).
^1H δ: 3.79 (d, $^2J_{PH}$ 15.7, 1H, CH), 7.09–7.34 (m, $3H_{arom.}$, 3,4-F_2—C_6H_3—C).
^{19}F δ: 23.95–24.18 (m, 1F, 3,$\underline{4}$-F_2—C_6H_3—C), 27.37–27.61 (m, 1F, $\underline{3}$,4-F_2—C_6H_3—C).

Preparation of Fluorinated α-Aminoarylmethanephosphonic Acids by Method B (Amidoalkylation of Phosphorus Trichloride)

One-Pot Procedure: Variation a) with Benzamide; R = C_6H_5 (Scheme II)

Fluorinated N-Benzoylaminoarylmethanephosphonic Acids **8a/b–h**: Under a gentle stream of nitrogen, 0.05 mol benzamide was suspended in 10 ml of acetic acid, and 0.05 mol phosphorus trichloride was added with vigorous stirring. An exothermic reaction occurred with the evolution of hydrogen chloride, and the mixture was stirred until it had cooled to room temperature. 0.07 mol Fluorinated benzaldehyde **7** was added dropwise (during 30 min), so that the reaction temperature did not exceed 40°C. A clear, light yellow solution was formed. In order to complete the conversion, the mixture was heated on a boiling water bath (1–2 h) until gas evolution ceased. Rotary evaporation at water pump pressure gave the N-benzoylaminoarylmethanephosphonic acid **8a** as a yellow oil.

Fluorinated α-Aminoarylmethanephosphonic Acids **6b–h**: In order to remove the benzoyl protecting group from nitrogen, the oil was heated under reflux (6–24 h) with 30 ml of concentrated hydrochloric

TABLE III

Fluorinated α-aminoarylmethanephosphonic acids **6b–h** (Scheme II, variation a)

no.	M.Wt.	yields [%]	mp. [°C]	^{31}P{^{1}H} NMR δ [ppm], Mult., $^{n}J_{PF}$ [Hz]
6b	205.13	18.6	289-290	18.03, d, $^{5}J_{PF}$ 1.4
6e	255.13	40.9	287-289	17.71, q, $^{7}J_{PF}$ 2.1
6f	255.13	41.7	253-255	15.08, bs
6g	271.13	31.1	305-307	18.12, s
6h	271.13	25.9	277-280	15.99, s

acid. After cooling, two phases were formed, the lower being a yellowish oil of the aminoarylmethanephosphonic acid hydrochloride **6'** and the upper being an aqueous phase with needle-like crystals of the resulting benzoic acid. The aqueous phase was separated, filtered to remove benzoic acid and, together with the oily layer, was evaporated at water pump pressure on a rotary evaporator. The residual oil was repeatedly taken up in water and evaporated until a white solid was formed. The residue was dissolved in hot methanol and, after cooling, pyridine was added dropwise until the pH was 4. After several days in a refrigerator the α-aminoarylmethanephosphonic acid **6** separated as a fine, white solid, which was filtered off (on a G3-sintered glass filter), washed with methanol, and dried in a vacuum desiccator over silica gel (Table III).

α-Amino-(3-fluorophenyl-)methanephosphonic Acid **6b**
^{31}P{^{1}H} NMR (10% 1m KOD/D_2O, 85% H_3PO_4 ext), δ: 18.03 (d, $^{5}J_{PF}$ 1.4).
^{1}H NMR (10% 1m KOD/D_2O, TSP—d_4—Na), δ: 3.93 (d, $^{2}J_{PH}$ 15.6, 1H, PCH), 6.99–7.10 (m, $1H_{arom.}$, 3-F—C_6H_4—C), 7.14–7.23 (m, $2H_{arom.}$, 3-F—C_6H_4—C), 7.32–7.43 (m, $1H_{arom.}$, 3-F—C_6H_4—C).
^{19}F NMR (10% 1m KOD/D_2O, C_6F_6 ext.), δ: 48.42–48.61 (m, 1F, 3-F—C_6H_4—C).

α-Amino-(4-trifluoromethylphenyl-)methanephosphonic Acid **6e**
^{31}P{^{1}H} δ: 17.71 (q, $^{7}J_{PF}$ 2.1).
^{1}H δ: 3.91 (d, $^{2}J_{PH}$ 16.5, 1H, PCH), 7.51–7.58 (m, $2H_{arom.}$, 4-F—C_6H_4—C), 7.63–7.72 (m, $2H_{arom.}$, 4-F—C_6H_4—C).
^{19}F δ: 101.16 (bs, 3F, 4-CF_3—C_6H_4—C).

α-Amino-(3-trifluoromethylphenyl-)methanephosphonic Acid **6f**
^{31}P{^{1}H} δ: 15.03 (s).
^{1}H δ: 4.01 (d, $^{2}J_{PH}$ 15.8, 1H, PCH), 7.49–7.68 (m, $3H_{arom.}$, 3-CF_3—C_6H_4—C), 7.73–7.76 (m, $1H_{arom.}$, 3-CF_3—C_6H_4—C).
^{19}F δ: 100.97 (bs, 3F, 3-CF_3—C_6H_4—C).

α-Amino-(4-trifluoromethoxyphenyl-)methanephosphonic Acid **6g**
^{31}P{^{1}H} δ: 18.12 (s).
^{1}H δ: 3.85 (d, $^{2}J_{PH}$ 15.8, 1H, PCH), 7.25–7.32 (m, $2H_{arom.}$, 4-CF_3O—C_6H_4—C), 7.42–7.51 (m, $2H_{arom.}$, 4-CF_3O—C_6H_4—C).
^{19}F δ: 104.94 (bs, 3F, 4-CF_3O—C_6H_4—C).

α-Amino-(3-trifluoromethoxyphenyl-)methanephosphonic Acid **6h**
^{31}P{^{1}H} δ: 15.99 (s).
^{1}H δ: 3.91 (d, $^{2}J_{PH}$ 16.0, 1H, PCH), 7.20–7.26 (m, $1H_{arom.}$, 3-CF_3O—C_6H_4—C), 7.32–7.49 (m, $3H_{arom.}$, 3-CF_3O—C_6H_4—C).
^{19}F δ: 105.54 (bs, 3F, 3-CF_3O—C_6H_4—C).

One-Pot Procedure: Variation b) with Acetamide; R = CH_3 (Scheme II)

Fluorinated N-Acetylaminoarylmethanephosphonic Acids **8b/b–h**: Under a gentle stream of nitrogen, 0.05 mol acetamide was dissolved in 10 ml of acetic acid and 0.05 mol phosphorus trichloride was added with vigorous stirring. Slight warming occurred, with gas evolution, and a white suspension was formed. The mixture was allowed to cool to room temperature and 0.07 mol fluorinated benzaldehyde **7** was added (during 30 min) with the temperature below 40°C. A weakly exothermic reaction occurred with gas evolution and the solid dissolved. In order to complete the reaction, the mixture was heated (2–3 h) on a boiling water bath. Rotary evaporation of the solution at water pump pressure finally gave the N-acetylaminoarylmethanephosphonic acid **8b** as a light yellow oil.

TABLE IV

Fluorinated α-aminoarylmethanephosphonic acids **6b–h**
(Scheme II, variation b)

no.	M.Wt.	mp. [°C]	yields [%]	$^{31}P\{^1H\}$-NMR δ [ppm], Mult., $^nJ_{PF}$ [Hz]
6b	205.13	289-290	25.5	18.03, d, $^5J_{PF}$ 1.4
6e	255.13	287-289	74.8	17.71, q, $^7J_{PF}$ 2.1
6f	255.13	253-255	35.6	15.08, bs
6g	271.13	305-307	45.1	18.12, s
6h	271.13	277-280	35.0	15.99, s

Fluorinated α-Aminoarylmethanephosphonic Acids **6b–h**: The acetyl group was removed from nitrogen by heating the yellowish oil under reflux (12–30 h) with 30 ml of concentrated hydrochloric acid, to give a clear, light yellow solution. After cooling, insoluble components were filtered off, and the aqueous phase was evaporated on a rotary evaporator at water pump pressure to give the aminoarylmethanephosphonic acid hydrochloride **6′** as a yellow oil; this was then repeatedly taken up in water and evaporated until a solid separated in the oil. The residue was dissolved in hot methanol, and after cooling, pyridine was added dropwise until the pH was 4. After several days in a refrigerator the α-aminoarylmethanephosphonic acid separated as a fine, white solid, which was filtered off (on a G3-sintered glass filter), washed with methanol, and dried in a vacuum desiccator over silica gel (Table IV).

Preparation of Fluorinated α-Aminoarylmethanephosphonic Acids by Method B (Amidoalkylation of Phosphorus Trichloride)

Two-Step Procedure (Scheme III)

N,N′-(4-Fluorophenyl-)methylidenebisacetamide **9a**: 0.20 mol 4-Fluorobenzaldehyde **7a** and 0.44 mol acetamide were heated under nitrogen atmosphere on a boiling water bath, with vigorous stirring (4 h). A gelatinous white mass was formed, which solidified on cooling in the form of white needles. These were suspended in methanol and filtered off under suction. The solid was washed with ice-cold methanol and finally dried in a vacuum desiccator over silica gel.

N,N′-(4-Fluorophenyl-)methylidenebisacetamide **9a**
M.Wt. = 224.23, yield: 70.0%, white needles, mp. 165–167°C.
^{1}H NMR (6% $CDCl_3$, TMS), δ: 1.94 (bs, 6H, 2 × CH_3), 6.20 (m, 3H, CH + 2 × NH), 6.98–7.09 (m, $2H_{arom.}$, 4-F—C_6H_4), 7.95–8.05 (m, $2H_{arom.}$, 4-F—C_6H_4).
^{19}F NMR (10% C_6D_6, C_6F_6 int.) δ: 56.02 (m, 1F, 4-F—C_6H_4).

N-Acetylamino-(4′-fluorophenyl-)methanephosphonic Acid **8ba**: Under a gentle stream of nitrogen, 0.10 mol N,N′-(4-fluorophenyl-)methylidenebisacetamide **9a** was suspended in 30 ml of acetic acid and 0.10 mol phosphorus trichloride was added dropwise (during 60 min) at a reaction temperature of 10°C. A strongly exothermic reaction occurred with the evolution of hydrogen chloride and the formation of a white gel. After the addition was complete, the mixture was heated further (2–3 h) on a boiling water bath to give a clear, light yellow solution. Cooling, followed by rotary evaporation at water pump pressure, gave N-acetylamino-(4′-fluorophenyl-)methanephosphonic acid **8ba**, as a light yellow oil.

α-Amino-(4-fluorophenyl-)methanephosphonic Acid **6a**: In order to remove the acetyl group from nitrogen, the oil of N-acetylamino-(4′-fluorophenyl-)methanephosphonic acid **8ba** was heated under reflux (24 h) with 100 ml of concentrated hydrochloric acid. A yellowish solution was formed, with fine needles of acetamide hydrochloride which were filtered off after cooling, and washed with water. The aqueous filtrate was evaporated at water pump pressure on a rotary evaporator to give amino-(4-fluorophenyl-)methanephosphonic acid hydrochloride as a yellow oil. This was repeatedly taken up in water, followed by evaporation, until a solid formed in the oil. The residue was dissolved in a little hot methanol and, after cooling, pyridine was added dropwise until the pH was 4. The solution was allowed to stand for several days in an ice/water bath, when α-amino-(4-fluorophenyl-)methanephosphonic acid **6a** was obtained as a fine white solid which was filtered off (using a G3-sintered glass filter), washed with methanol, and dried in a vacuum desiccator over silica gel.

TABLE V

Fluorinated N-benzylidene-1,1-diphenylmethylamines **10a–g**

no.	M.Wt.	yields [%]	reacting time [h]	^{1}H NMR δ (=CH) [ppm]
10a	289.35	99.5	4	8.35
10b	289.35	97.8	6	8.38
10d	307.34	93.5	6	8.31
10e	339.36	98.2	4	8.43
10f	339.36	93.1	10	8.44
10g	355.36	95.5	8	8.39

TABLE VI

Fluorinated dimethyl N-diphenylmethylaminoarylmethanephosphonates **11aa–ae**

no.	M.Wt.	yields [%]	reacting time [h]	^{31}P{^{1}H} NMR δ [ppm], Mult., $^nJ_{PF}$ [Hz]
11aa	399.40	79.7	4	26.49, d, $^6J_{PF}$ 4.8
11ae	449.41	89.4	5	25.72, q, $^7J_{PF}$ 2.3

α-Amino-(4-fluorophenyl-)methanephosphonic Acid **6a**
M.Wt. = 205.13, yield: 59.0%, fine, white solid, mp. 278–282°C.

Preparation of Fluorinated α-Aminoarylmethanephosphonic Acids by the Method C (Addition of Substances with P—H Bonds to N-Protected Imines, Variation a)) (Scheme IV)

Fluorinated N-Benzylidene-1,1-diphenylmethylamines **10a–h**: The fluorinated benzaldehyde **7** was added dropwise with stirring to a solution of an equimolar quantity of diphenylmethylamine in anhydrous ether (5% w/w) or dichloromethane (10–30% w/w) in the presence of anhydrous potassium carbonate (1–2 mol equiv) at 0°C. The solution was stirred (1–1.5 h) at room temperature and then filtered. Solvent was removed by rotary evaporation, followed by vigorous shaking at 0.1 mmHg (2 h), to leave the Schiff base as follows:

N-4-Fluorobenzylidene-1,1-diphenylmethylamine **10a**
Yield: 97%, bright yellow crystalline solid, C, H, N analysis: $C_{20}H_{16}FN$, M.Wt. = 289.35, requires: C 83.02, H 5.57, N 4.84, found: C 82.91, H 5.60, N 4.89%.
^{1}H NMR ($CDCl_3$), δ 5.57 (s, 1H, NCH), 7.06 (m, $2H_{arom.}$, 4-F—C_6H_4), 7.18–7.40 (m, $10H_{arom.}$, 2 × C_6H_5), 7.81 (m, $2H_{arom.}$, 4-F—C_6H_4), 8.35 (bs, 1H, =CH).
^{19}F NMR ($CDCl_3$), δ: −109.63 – −109.71 (m, 4-F—C_6H_4).
EI ms, m/z [%]: 289 (M^+, 15), 167 ($(C_6H_5)_2CH^+$, 100).

N-2-Fluorobenzylidene-1,1-diphenylmethylamine **10c**
Yield: 99%, sticky, orange-yellow solid, C, H, N analysis: $C_{20}H_{16}FN$, M.Wt. = 289.35, requires: C 83.02, H 5.57, N 4.84, found: C 83.01, H 5.53, N 4.86%.
^{1}H NMR ($CDCl_3$), δ: 5.60 (s, 1H, NCH), 7.02 (m, $1H_{arom.}$, 2-F—C_6H_4), 7.11–7.41 (m, $10H_{arom.}$, 2 × C_6H_5 + $2H_{arom.}$, 2-F—C_6H_4), 8.18 (m, $1H_{arom.}$, 2-F—C_6H_4), 8.74 (bs, 1H, =CH).
^{19}F NMR ($CDCl_3$), δ: − 124.57 (m, 2-F—C_6H_4).
EI ms, m/z [%]: 290 ($[M+1]^+$, 20.6), 289 ($[M]^+$, 49.8), 270 ($[M - F]^+$, 6.3), 212 ($[M - C_6H_5]^+$, 25.9), 182 ($[M - F—C_6H_4C]^+$, 23.2), 181 ($[M - F—C_6H_4CH]^+$, 18.6), 167 ($[M - F—C_6H_4—CH{=}N]^+$, 100), 108 ($[M - (C_6H_5)_2CH—N]^+$, 35.1).

N-4-Trifluoromethylbenzylidene-1,1-diphenylmethylamine **10e**
Yield: 99%, orange solid, C, H, N analysis: $C_{21}H_{16}F_3N$, M.Wt. = 339.36, requires: C 74.33, H 4.75, N 4.13, found: C 74.30, H 4.82, N 4.07%.

N-3-Trifluoromethoxybenzylidene-1,1-diphenylmethylamine **10h**
Yield: 88%, light brown viscous oil, C, H, N analysis: $C_{21}H_{16}F_3NO$, M.Wt. = 355.36, requires: C 70.98, H 4.54, N 3.94, found: C 70.89, H 4.54, N 3.84%.

TABLE VII

Fluorinated diethyl N-diphenylmethylaminoarylmethanephosphonates **11ba–bg**

no.	M.Wt.	yields [%]	reacting time [h]	$^{31}P\{^1H\}$ NMR δ [ppm], Mult., $^nJ_{PF}$ [Hz]
11ba	427.45	90.4	10	24.13, d, $^6J_{PF}$ 4.8
11bb	427.45	81.8	11	23.68, d, $^5J_{PF}$ 1.7
11bd	445.44	87.5	12	23.43, dd, $^6J_{PF}$ 5.5, $^5J_{PF}$ 1.8
11be	477.46	89.3	8	23.39, q, $^7J_{PF}$ 2.3
11bf	477.46	78.6	12	23.30, q, $^7J_{PF}$ 0.6
11bg	493.46	91.6	14	23.79, s

TABLE VIII

Fluorinated diphenyl N-diphenylmethylaminoarylmethanephosphonates **11ca–cg**

no.	M.Wt.	yields [%]	reacting time [h]	$^{31}P\{^1H\}$ NMR: δ [ppm], Mult., $^nJ_{PF}$ [Hz]
11ca	523.54	73.3	4	16.78, d, $^6J_{PF}$ 5.1
11cb	523.54	86.1	8	16.33, d, $^5J_{PF}$ 1.8
11cd	541.53	68.2	6	15.97, dd, $^6J_{PF}$ 5.4, $^5J_{PF}$ 1.8
11ce	573.55	78.6	5	15.95, q, $^7J_{PF}$ 2.3
11cf	573.55	70.3	5	15.87, q, $^7J_{PF}$ 0.7
11cg	589.55	77.8	4	16.37, s

N-Pentafluorobenzylidene-1,1-diphenylmethylamine **10i**
Yield: 99%, bright yellow solid, C, H, N analysis: $C_{20}H_{12}F_5N$, M.Wt. = 361.31, requires: C 66.49, H 3.35, N 3.88, found: C 66.67, H 3.39, N 3.91%.

Fluorinated α-Aminoarylmethanephosphonic Acids **6a–i**: A mixture of the fluorinated benzylidenediphenylamine **10** and an equimolar amount of dimethyl phosphite or diethyl phosphite was heated at 120–140°C (30 min). Concentrated hydrochloric acid (80 ml) was added to the product **11** and the resultant solution was heated under reflux for 3 h. After the removal of by-products by extraction with toluene the aqueous layer was concentrated under reduced pressure, dissolved in methanol, and treated with a moderate excess of propylene oxide at 40–50°C. The crystalline product which separated was filtered off, washed with acetone and dry ether, and dried in vacuo at 80°C to give the following products:

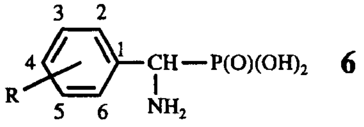
α-Amino-(4′-fluorophenyl-)methanephosphonic Acid **6a**
Yield: 55%, m.p. 278–282°C, C, H, N analysis: $C_7H_9FNO_3P$, M.Wt. = 205.13, requires: C 40.99, H 4.42, N 6.83, found: C 40.98, H 4.93, N 6.80%.
$^{31}P\{^1H\}$ δ: 17.03 (d, $^6J_{PF}$ 3.0).
^1H ($NaOD/D_2O$), δ: 3.86 (d, $^2J_{PH}$ 15.4, 1H, PCH), 7.11 (m, $2H_{arom.}$, 4-F—C_6H_4), 7.40 (m, $2H_{arom.}$, 4-F—C_6H_4).

α-Amino-(2′-fluorophenyl-)methanephosphonic Acid **6c**
Yield: 28%, m.p. 270–273°C, C, H, N analysis: $C_7H_9FNO_3P$, M.Wt. = 205.13, requires: C 40.99, H 4.42, N 6.83, found: C 41.05, H 4.41, N 6.61%.
$^{31}P\{^1H\}$ δ: 17.59 (d, $^4J_{PF}$ 4.0).
^1H ($NaOD/D_2O$), δ: 4.41 (d, $^2J_{PH}$ 16.1, 1H, PCH), 7.07–7.34 (m, $3H_{arom.}$, 2-F—C_6H_4), 7.46 (m, $1H_{arom.}$, 2-F—C_6H_4).
^{19}F ($NaOD/D_2O$), δ: 117.97 (s).

α-Amino-(4′-trifluoromethylphenyl-)methanephosphonic Acid **6e**
Yield: 46%, m.p. 287–289°C, C, H, N analysis: $C_8H_9F_3NO_3P$, M.Wt. = 255.13, requires: C 37.66, H 3.56,

TABLE IX

$^{13}C\{^{1}H\}$ NMR data of the fluorinated α-aminoarylmethanephosphonic acids **6**. $^{13}C\{^{1}H\}$ NMR (10% KOH/D_2O, TSP—d_4—Na), δ [ppm], Mult., $^{n}J_{XY}$ [Hz]. ov.: overlapping



6

No.	α-CH	C1	C2	C3	C4	C5	C6	R
6a	57.52, d, $^{1}J_{PC}$ 131.1	139.82, s	131.90, dd, $^{3}J_{FC}$ 7.8, $^{3}J_{PC}$ 5.1	117.41, d, $^{2}J_{FC}$ 21.6	164.12, d, $^{1}J_{FC}$ 243.5	117.41, d, $^{2}J_{FC}$ 21.6	131.90, dd, $^{3}J_{FC}$ 7.8, $^{3}J_{PC}$ 5.1	-
6b	58.21, dd, $^{4}J_{FC}$ 1.6, $^{1}J_{PC}$ 129.5	147.85, dd, $^{3}J_{FC}$ 7.3, $^{2}J_{PC}$ 2.6	117.03, dd, $^{2}J_{FC}$ 21.8, $^{3}J_{PC}$ 4.7	165.16, dd, $^{1}J_{FC}$ 241.1, $^{4}J_{PC}$ 2.5	115.57, dd, $^{2}J_{FC}$ 21.2, $^{5}J_{PC}$ 2.6	132.29, dd, $^{3}J_{FC}$ 8.5, $^{4}J_{PC}$ 2.1	126.33, dd, $^{4}J_{FC}$ 2.6, $^{3}J_{PC}$ 5.0	-
6c	50.96, dd, $^{3}J_{FC}$ 1.2, $^{1}J_{PC}$ 132.1	131.82, dd, ov. $^{2}J_{PC}$ 1.9	162.69, dd, $^{1}J_{FC}$ 242.6 ov	117.74, d, $^{2}J_{FC}$ 22.8	131.55, dd, $^{3}J_{FC}$ 8.1, ov	126.69, s	130.53, dd, $^{3}J_{FC}$ 8.3, $^{3}J_{PC}$ 2.4	-
6d	57.42, dd, $^{4}J_{FC}$ 0.9, $^{1}J_{PC}$ 129.5	140.98, dd, $^{3}J_{FC}$ 3.0, $^{2}J_{PC}$ 2.9	119.05, dd, $^{2}J_{FC}$ 16.9, $^{3}J_{FC}$ 4.5, ov.	151.49, ddd, $^{1}J_{FC}$ 242.8, $^{2}J_{FC}$ 12.6, $^{4}J_{PC}$ 2.7	152.30, ddd, $^{1}J_{FC}$ 243.2, $^{2}J_{FC}$ 12.6, $^{5}J_{PC}$ 2.3	119.38, dd, $^{2}J_{FC}$ 15.6, $^{4}J_{PC}$ 1.7, ov.	126.63, ddd, $^{3}J_{FC}$ 6.4, $^{4}J_{FC}$ 3.4, $^{3}J_{PC}$ 5.2	-
6e	58.27, d, $^{1}J_{PC}$ 128.1	149.09, s	127.54, s	130.62, d, $^{3}J_{FC}$ 4.7	130.05, q, $^{2}J_{FC}$ 63.8	130.62, d, $^{3}J_{FC}$ 4.7	127.54, s	127.34, q, $^{1}J_{FC}$ 271.2
6f	58.28, d, $^{1}J_{PC}$ 129.3	146.15, d, $^{2}J_{PC}$ 2.6	126.93, dd, $^{3}J_{FC}$ 4.4, $^{3}J_{PC}$ 3.9	131.96, dq, $^{2}J_{FC}$ 31.5, $^{4}J_{PC}$ 2.1	134.04, dd, $^{3}J_{FC}$ 4.8, $^{5}J_{PC}$ 1.2	131.96, d, $^{4}J_{PC}$ 2.0	125.63, dq, $^{5}J_{FC}$ 2.6, $^{3}J_{PC}$ 3.9	127.32, q, $^{1}J_{FC}$ 271.7
6g	57.91, d, $^{1}J_{PC}$ 130.1	144.21, d, $^{2}J_{PC}$ 2.3	131.75, d, $^{3}J_{PC}$ 4.9	123.28, d, $^{4}J_{PC}$ 1.0	150.02, q, $^{3}J_{FC}$ 2.6	123.28, d, $^{4}J_{PC}$ 1.0	131.75, d, $^{3}J_{PC}$ 4.9	123.20, dq, $^{1}J_{FC}$ 255.6, $^{8}J_{PC}$ 1.1
6h	57.93, d, $^{1}J_{PC}$ 129.8	147.46, s	128.90, d, $^{3}J_{PC}$ 4.7	151.24, s	132.00, s	121.13, s	122.69, d, $^{3}J_{PC}$ 4.5	123.03, q, $^{1}J_{FC}$ 255.8
6i	50.23, d, $^{1}J_{PC}$ 130.9	118.45, dd, $^{2}J_{FC}$ 16.2, ov.	147.58, d, $^{1}J_{FC}$ 243.0 ov.	140.14, ddd, $^{1}J_{FC}$ 246.3, ov.	142.09, dm, $^{1}J_{FC}$ 249.4, ov.	140.14, ddd, $^{1}J_{FC}$ 246.3, ov.	147.58, d, $^{1}J_{FC}$ 243.0	

N 5.49, found: C 37.50, H 3.55, N 5.40%.
$^{31}P\{^{1}H\}$ δ: 16.96 (s).
^{1}H (NaOD/D_2O), δ: 3.95 (d, $^{2}J_{PH}$ 16.41, 1H, PCH), 7.57 (m, $2H_{arom.}$, 4-CF_3—C_6H_4), 7.67 (m, $2H_{arom.}$, 4-CF_3—C_6H_4).
^{19}F (NaOD/D_2O), δ: 61.94 (s).
FAB ms (thioglycerol), m/z [%]: 511 (2M + H, 20.6), 256 (M + H, 52.5), 186 (14.6), 176 (M + H − HPO_3, 12.1), 174 (M + H − H_3PO_3, 100), 155 (M + H − F, 29.2), 130 (72.7).

α-Amino-(3′-trifluoromethoxyphenyl-)methanephosphonic Acid **6h**
Yield: 43%, m.p. 277–280°C, C, H, N analysis: $C_8H_9F_3NO_4P$, M.Wt. = 271.13, requires: C 35.44, H 3.35,

TABLE X

Part I: $^{13}C\{^{1}H\}$ NMR data of the fluorinated N-benzylidene-1,1-diphenylmethylamines **10**. $^{13}C\{^{1}H\}$ NMR (10% $CDCl_3$, TMS), δ [ppm], Mult., $^{n}J_{XY}$ [Hz]

No.	δ_C C1	C2	C3	C4	C5	C6	R
10a	132.55, d,	130.32, d,	115.58, d,	164.33, d,	115.58, d,	130.32, d,	-
(L)	$^{4}J_{FC}$ 2.8	$^{3}J_{FC}$ 8.6	$^{2}J_{FC}$ 21.9	$^{1}J_{FC}$ 250.8	$^{2}J_{FC}$ 21.9	$^{3}J_{FC}$ 8.6	
10a	133.28, d,	131.00, d,	116.25, d,	165.02, d,	116.25, d,	131.00, d,	-
(D)	$^{4}J_{FC}$ 3.1	$^{3}J_{FC}$ 8.6	$^{2}J_{FC}$ 21.9	$^{1}J_{FC}$ 250.8	$^{2}J_{FC}$ 21.9	$^{3}J_{FC}$ 8.6	
10b	139.32, d,	115.08, d,	163.70, d,	118.37, d,	130.71, d,	125.27, d,	-
(D)	$^{3}J_{FC}$ 7.3	$^{2}J_{FC}$ 22.2	$^{1}J_{FC}$ 246.4	$^{2}J_{FC}$ 21.7	$^{3}J_{FC}$ 8.0	$^{4}J_{FC}$ 2.9	
10c	123.86, d,	162.33, d,	115.63, d,	124.24, d,	128.07, d,	132.31, d,	-
(L)	$^{2}J_{FC}$ 9.4	$^{1}J_{FC}$ 252.5	$^{2}J_{FC}$ 21.1	$^{3}J_{FC}$ 3.6	$^{4}J_{FC}$ 2.8	$^{3}J_{FC}$ 8.6	
10d	134.24, dd,	117.95, dd,	151.36, dd,	152.72, dd,	117.11, dd,	125.86, dd,	-
(D)	$^{3}J_{FC}$ 5.5,	$^{2}J_{FC}$ 17.8,	$^{1}J_{FC}$ 249.1,	$^{1}J_{FC}$ 252.9,	$^{2}J_{FC}$ 18.0,	$^{3}J_{FC}$ 6.8,	
	$^{4}J_{FC}$ 3.6	$^{3}J_{FC}$ 0.7	$^{2}J_{FC}$ 13.1	$^{2}J_{FC}$ 13.1	$^{3}J_{FC}$ 1.1	$^{4}J_{FC}$ 3.5	
10e	139.35, s	128.65, s	125.49, q,	*	125.49, q,	128.65, s	132.29, q,
(L)			$^{3}J_{FC}$ 3.8		$^{3}J_{FC}$ 3.8		$^{1}J_{FC}$ 259.3
10e	140.07, q,	129.32, s	126.16, q,	133.00, q,	126.16, q,	129.32, s	124.66, q,
(D)	$^{5}J_{FC}$ 1.3		$^{3}J_{FC}$ 3.8	$^{2}J_{FC}$ 32.4	$^{3}J_{FC}$ 3.8		$^{1}J_{FC}$ 272.6
10f	137.68, s	125.78, q,	131.79, q,	127.89, q,	132.26, q,	129.73, s	124.66, q,
(D)		$^{3}J_{FC}$ 3.8	$^{2}J_{FC}$ 32.6	$^{3}J_{FC}$ 3.8	$^{4}J_{FC}$ 1.2		$^{1}J_{FC}$ 272.4
10g	151.61, q,	130.59, s	121.51, q,	129.83, q,	121.51, q,	130.59, s	121.11, q,
(D)	$^{6}J_{FC}$ 1.8		$^{4}J_{FC}$ 1.0	$^{3}J_{FC}$ 89.4	$^{4}J_{FC}$ 1.0		$^{1}J_{FC}$ 257.8
10h	138.37, s	129.92, s	149.58, q,	126.94, s	123.02, s	120.43, s	120.49, q,
(L)			$^{3}J_{FC}$ 1.9				$^{1}J_{FC}$ 257.5
10i	111.34, dd,	146.05, dm,	137.77, dm,	141.89, dm,	137.77, dm,	146.05, dm,	-
(L)	$^{2}J_{FC}$ 11.6,	$^{1}J_{FC}$ 255.4,	$^{1}J_{FC}$ 249.8,	$^{1}J_{FC}$ 268.1,	$^{1}J_{FC}$ 249.8,	$^{1}J_{FC}$ 255.4,	
	overlapping	overlapping	overlapping	overlapping	overlapping	overlapping	

N 5.17, found: C 36.62, H 3.54, N 5.40%.
$^{31}P\{^{1}H\}$ δ: 17.29 (s).
^{1}H ($NaOD/D_2O$), δ: 3.87 (d, $^{2}J_{PH}$ 16.2, 1H, PCH), 7.21 (m, $1H_{arom.}$, 3-CF_3O—C_6H_4), 7.33–7.47 (m, $3H_{arom.}$, 3-CF_3O—C_6H_4).
^{19}F ($NaOD/D_2O$), δ: −57.62 (s).
FAB ms (3-NOBA), m/z [%]: 308 (100), 290 (70.8), 272 (M + H, 24.6), 254 (M + H − H_2O, 28.5), 189 (15.8), 166 (51.7).

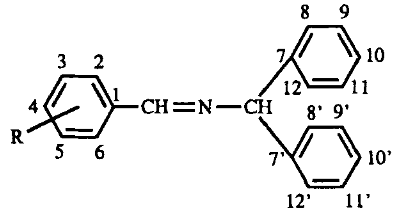
α-Amino-(pentafluorophenyl-)methanephosphonic Acid **6i**
Yield: 18%, m.p. 268–270°C, C, H, N analysis: $C_7H_5F_5NO_3P$, M.Wt. = 277.09, requires: C 30.34, H 1.82, N 5.06, found: C 31.04, H 2.15, N 5.38%.
$^{31}P\{^{1}H\}$ δ: 15.32 (m).
^{1}H ($NaOD/D_2O$), δ: 4.20 (d, $^{2}J_{PH}$ 17.5, 1H, PCH).
^{19}F ($NaOD/D_2O$), δ: −9.47 (m), −25.96 (m), −31.22 (m).
FAB ms (thioglycerol), m/z [%]: 555 (2M + H, 40.2), 386 (M + H + T, 2.7), 278 (M + H, 74.6), 196 (M + H − H_3PO_3, 100), 178 (67.9), 130 (72.7).

Preparation of Fluorinated Dialkyl N-Diphenylmethylaminoarylmethanephosphonates by Method C (Addition of Substances with P—H Bonds to N-Protected Imines, Variation b)) (Scheme IV)

Fluorinated N-Benzylidene-1,1-diphenylmethylamines **10a–g**: 0.05 mol of the fluorinated benzaldehyde **7** was mixed under nitrogen with 0.05 mol diphenylmethylamine. A strongly exothermic reaction oc-

TABLE X

Part II: $^{13}C\{^1H\}$ NMR data of the fluorinated N-benzylidene-1,1-diphenylmethylamines **10**



10

No. δ_C	N-CH	α-CH	C7/7'	C8/8'	C9/9'	C10/10'	C11/11'	C12/12'
10a (L)	77.80, s	159.30, s	143.79, s	*	128.90, s	126.66, s	128.90, s	*
10a (D)	78.47, s	159.96, d, $^5J_{FC}$ 0.6	144.55, s	128.30, s	129,10, s	127.69, s	129,10, s	128.30, s
10b (D)	78.47, s	160.11, d, $^4J_{FC}$ 3.0	144.33, s	128.29, s	129.16, s	127.76, s	129.16, s	128.29, s
10c (L)	78.38, s	154.02, d, $^3J_{FC}$ 4.8	144.19, s	127.59, s	128.45, s	127.03, s	128.45, s	127.59, s
10d (D)	78.36, s	158.95, dd, $^4J_{FC}$ 2.5, $^5J_{FC}$ 1.7	144.25, s	128.25, s	129.18, s	127.80, s	129.18, s	128.25, s
10e (L)	77.98, s	159.37, s	143.49, s	127.61, s	128.55, s	127.19, s	128.55, s	127.61, s
10e (D)	78,65, s	160.02, d, $^6J_{FC}$ 0.4	144.19, s	128.31, s	129.22, s	127.86, s	129.22, s	128.31, s
10f (D)	78.60, s	159.94, s	144.18, s	128.33, s	129.22, s	127.85, s	129.22, s	128.33, s
10g (D)	78.54, s	159.76, s	144.36, s	128.31, s	129.17, s	127.78, s	129.17, s	128.31, s
10h (L)	77.86, s	159.18, s	143.54, s	127.61, s	128.52, s	127.14, s	128.52, s	127.61, s
10i (L)	79.78, s	149.10, d, $^3J_{FC}$ 2.5	143.02, s	127.46, s	128.63, s	127.37, s	128.63, s	127.46, s

TABLE XI

Part I: $^{13}C\{^1H\}$ NMR data of the fluorinated dimethyl N-diphenylmethylaminoarylmethanephosphonates **11a**. $^{13}C\{^1H\}$ NMR (10% $CDCl_3$, TMS), δ [ppm], Mult., $^nJ_{XY}$ [Hz]

No. δ_C	CH_3 (1)	CH_3 (2)	CHP	CHN
11aa (D)	53.91, d, $^2J_{PC}$ 7.0	54.60, d, $^2J_{PC}$ 6.9	57.64, d, $^1J_{PC}$ 156.2	64.30, d, $^3J_{PC}$ 16.8
11ae (D)	54.02, d, $^2J_{PC}$ 7.0	54.76, d, $^2J_{PC}$ 7.0	58.17, d, $^1J_{PC}$ 154.5	64.60, d, $^3J_{PC}$ 16.5

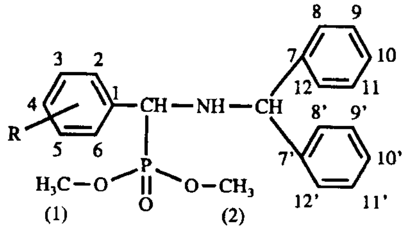
TABLE XI

Part II: $^{13}C\{^1H\}$ NMR data of the fluorinated dimethyl N-diphenylmethylaminoarylmethanephosphonates **11a**

No.	δ_C	C1	C2	C3	C4	C5	C6	R
11aa (D)		132.07, dd, $^4J_{FC}$ 2.0, $^2J_{PC}$ 3.2	130.85, dd, $^3J_{FC}$ 8.1, $^3J_{PC}$ 6.4	116.26, dd, $^2J_{FC}$ 21.5, $^4J_{PC}$ 2.2	163.19, dd, $^1J_{FC}$ 246.7, $^5J_{PC}$ 3.2	116.26, dd, $^2J_{FC}$ 21.5, $^4J_{PC}$ 2.2	130.85, dd, $^3J_{FC}$ 8.1, $^3J_{PC}$ 6.4	-
11ae (D)		141.07, dq, $^2J_{PC}$ 1.3, overlapping	129.62, d, $^4J_{FC}$ 3.7, $^3J_{PC}$ 6.0	126.08, dq, $^3J_{FC}$ 32.4, $^4J_{PC}$ 2.5	130.77, dq, $^2J_{FC}$ 3.7, $^5J_{PC}$ 3.1	126.08, dq, $^3J_{FC}$ 32.4, $^4J_{PC}$ 2.5	129.62, d, $^4J_{FC}$ 3.7, $^3J_{PC}$ 6.0	124.78, dq, $^1J_{FC}$ 272.1, $^6J_{PC}$ 1.2

TABLE XI

Part III: $^{13}C\{^1H\}$ NMR data of the fluorinated dimethyl N-diphenylmethylaminoarylmethanephosphonates **11a**



11a

No.	δ_C	C7/ 7'	C8/ 8',	C9/ 9'	C 10/ 10'	C 11/ 11',	C 12/ 12'
11aa		142.36, s,	127.83, s,	129.12, s,	127.91, s,	127.83, s,	129.12, s,
(D)		144.05, s	128.38, s,	129.36, s	128.17, s	128.38, s,	129.36, s
11ae		142.19, s,	127.84, s,	129.20, s,	128.04, s,	127.84, s,	129.20, s,
(D)		143.81, s	128.37, s,	129.47, s	128.26, s	128.37, s,	129.47, s

curred, with the development of turbidity, and the solution became light yellow. The condensation reaction was completed by heating on a boiling water bath (4–10 h) to give a clear, yellow solution, with water droplets separating on the upper part of the flask. After cooling, the oily reaction mixture was dissolved in dichloromethane and dried over Na_2SO_4. Filtration, followed by rotary evaporation of the filtrate gave a yellow oil which solidified after 1–3 days at room temperature to give a waxy, light yellow solid (Table V).

N-4-Fluorobenzylidene-1,1-diphenylmethylamine **10a**
^1H NMR (6% $CDCl_3$, TMS), δ: 5.57 (bs, 1H, $C\underline{H}Ph_2$), 7.0–7.11 (m, $2H_{arom.}$, 4-F—C_6H_4—C), 7.16–7.41 (m, $10H_{arom.}$, 2 × C_6H_5), 7.71–7.88 (m, $2H_{arom.}$, 4-F—C_6H_4—C), 8.35 (bs, 1H, =CH).
^{19}F NMR (6% $CDCl_3$, C_6F_6 int.), δ: 52.26–52.51 (m, 1F, 4-F—C_6H_4—C).

N-3-Fluorobenzylidene-1,1-diphenylmethylamine **10b**
C, H, N analysis: $C_{20}H_{16}FN$, M.Wt. = 289.35, requires: C 83.02, H 5.57, N 4.84, found: C 82.71, H 5.41, N 4.70.%.
^1H δ: 5.60 (bs, 1H, $C\underline{H}Ph_2$), 7.05–7.15 (m, $1H_{arom.}$, 3-F—C_6H_4—C), 7.18–7.42 (m, $10H_{arom.}$, 2 × C_6H_5 + $1H_{arom.}$, 3-F—C_6H_4—C), 7.49–7.55 (m, $1H_{arom.}$, 3-F—C_6H_4—C), 7.59–7.66 (m, $1H_{arom.}$, 3-F—C_6H_4—C), 8.38 (bs, 1H, =CH).
^{19}F δ: 48.69–48.82 (m, 1F, 3-F—C_6H_4—C).

N-3,4-Difluorobenzylidene-1,1-diphenylmethylamine **10d**
C, H, N analysis: $C_{20}H_{15}F_2N$, M.Wt. = 307.34, requires: C 78.16, H 4.92, N 4.56, found: C 78.12, H 4.84, N 4.44.%.

TABLE XII

Part I: $^{13}C\{^1H\}$ NMR data of the fluorinated diethyl N-diphenylmethylaminoarylmethanephosphonates **11b**. $^{13}C\{^1H\}$ NMR (10% $CDCl_3$, TMS), δ [ppm], Mult., $^nJ_{XY}$ [Hz]

No.	δ_C	CH_3 (1)	CH_3 (2)	CH_2 (3)	CH_2 (4)	CHP	CHN
11ba		16.83, d,	17.16, d,	63.30, d,	63.72, d,	57.92, d,	64.35, d,
(D)		$^3J_{PC}$ 5.9	$^3J_{PC}$ 6.1	$^2J_{PC}$ 6.9	$^2J_{PC}$ 7.0	$^1J_{PC}$ 155.9	$^3J_{PC}$ 16.7
11bb		16.80, d,	17.13, d,	63.36, d,	63.77, d,	58.35, dd,	64.48, d,
(D)		$^3J_{PC}$ 5.9	$^3J_{PC}$ 6.0	$^2J_{PC}$ 6.9	$^2J_{PC}$ 7.0	$^1J_{PC}$ 154.8, $^4J_{FC}$ 1.7	$^3J_{PC}$ 16.5
11bd		16.90, d,	17.18, d,	63.42, d,	63.87, d,	57.86, dd,	64.53, d,
(D)		$^3J_{PC}$ 5.8	$^3J_{PC}$ 6.0	$^2J_{PC}$ 6.9	$^2J_{PC}$ 7.0	$^1J_{PC}$ 155.4, $^4J_{FC}$ 1.2	$^3J_{PC}$ 16.2
11be		16.82, d,	17.15, d,	63.44, d,	63.93, d,	58.48, d,	64.61, d,
(D)		$^3J_{PC}$ 5.9	$^3J_{PC}$ 6.0	$^2J_{PC}$ 7.0	$^2J_{PC}$ 7.0	$^1J_{PC}$ 153.9	$^3J_{PC}$ 16.3
11bf		16.76, d,	17.09, d,	63.50, d,	63.90, d,	58.52, d,	64.70, d,
(D)		$^3J_{PC}$ 6.0	$^3J_{PC}$ 6.0	$^2J_{PC}$ 7.0	$^2J_{PC}$ 7.0	$^1J_{PC}$ 154.3	$^3J_{PC}$ 16.1
11bg		16.79, d,	17.15, d,	63.38, d,	63.84, d,	58.05, d,	64.52, d,
(D)		$^3J_{PC}$ 5.9	$^3J_{PC}$ 6.0	$^2J_{PC}$ 7.0	$^2J_{PC}$ 7.0	$^1J_{PC}$ 155.1	$^3J_{PC}$ 16.4

^1H δ: 5.58 (bs, 1H, $C\underline{H}Ph_2$), 7.09–7.51 (m, $10H_{arom.}$, 2 × C_6H_5 + $2H_{arom.}$, 3,4-F_2—C_6H_3—C), 7.69–7.82 (m, $1H_{arom.}$, 3,4-F_2—C_6H_3—C), 8.31 (bs, 1H, =CH).
^{19}F δ: 24.52–24.75 (m, 1F, 3,$\underline{4}$-F_2—C_6H_3—C), 27.75–27.98 (m, 1F, $\underline{3}$,4-F_2—C_6H_3—C).

N-4-Trifluoromethylbenzylidene-1,1-diphenylmethylamine **10e**
^1H δ: 5.62 (bs, 1H, $C\underline{H}Ph_2$), 7.18–7.42 (m, $10H_{arom.}$, 2 × C_6H_5), 7.60–7.67 (m, $2H_{arom.}$, 4-CF_3—C_6H_4—C), 7.88–7.95 (m, $2H_{arom.}$, 4-CF_3—C_6H_4—C), 8.43 (bs, 1H, =CH).
^{19}F δ: 98.97 (bs, 3F, 4-CF_3—C_6H_4—C).

N-3-Trifluoromethylbenzylidene-1,1-diphenylmethylamine **10f**
C, H, N analysis: $C_{21}H_{16}F_3N$, M.Wt. = 339.36, requires: C 74.33, H 4.75, N 4.13, found: C 74.16, H 4.67, N 4.11.%.
^1H δ: 5.63 (bs, 1H, $C\underline{H}Ph_2$), 7.19–7.43 (m, $10H_{arom.}$, 2 × C_6H_5), 7.46–7.56 (m, $1H_{arom.}$, 3-CF_3—C_6H_4—C), 7.62–7.69 (m, $1H_{arom.}$, 3-CF_3—C_6H_4—C), 7.97–8.02 (m, $1H_{arom.}$, 3-CF_3—C_6H_4—C), 8.09–8.11 (m, $1H_{arom.}$, 3-CF_3—C_6H_4—C), 8.44 (bs, 1H, =CH).
^{19}F δ: 99.09 (bs, 3F, 3-CF_3—C_6H_4—C).

N-4-Trifluoromethoxybenzylidene-1,1-diphenylmethylamine **10g**
C, H, N analysis: $C_{21}H_{16}F_3NO$, M.Wt. = 355.36, requires: C 70.98, H 4.54, N 3.94, found: C 70.73, H 4.49, N 3.92.%.
^1H δ: 5.60 (bs, 1H, $C\underline{H}Ph_2$), 7.17–7.42 (m, $10H_{arom.}$, 2 × C_6H_5 + $2H_{arom.}$, 4-CF_3O—C_6H_4—C), 7.82–7.89 (m, $2H_{arom.}$, 4-CF_3O—C_6H_4—C), 8.39 (bs, 1H, =CH).
^{19}F δ: 104.05 (bs, 3F, 4-CF_3O—C_6H_4—C).

Fluorinated Dimethyl N-Diphenylmethylaminoarylmethanephosphonates **11aa–ae**: 0.02 mol of the fluorinated N-benzylidene-1,1-diphenylmethylamine **10** and 0.03 mol dimethyl phosphite were mixed together under an atmosphere of nitrogen. An endothermic reaction occurred and a yellowish suspension was formed. In order to complete the phosphite-addition reaction the mixture was heated at 100°C (4–5 h) to give a clear, yellowish, oily liquid. Cooling in an ice/water bath gave a highly viscous oil with a white solid. The suspension was dissolved in hot methanol. After cooling the solution was placed in a refrigerator: a white precipitate of the nitrogen protected dimethyl aminophosphonate **11a** formed after a few days, which was filtered off (using a G3-sintered glass filter), washed with ether, dried in a vacuum desiccator over silica gel, and purified by recrystallization from methanol/ether mixtures (Table VI).

Dimethyl N-Diphenylmethylamino-(4'-fluorophenyl-)methanephosphonate **11aa**
C, H, N analysis: $C_{22}H_{23}FNO_3P$, M.Wt. = 399.40, requires: C 66.16, H 5.80, N 3.51, found: C 65.93, H 5.94, N 3.62%.

TABLE XII

Part II: $^{13}C\{^{1}H\}$ NMR data of the fluorinated diethyl N-diphenylmethylaminoarylmethanephosphonates **11b**

No.	δ_C C1	C2	C3	C4	C5	C6	R
11ba	132.36, dd,	130.88, dd,	116.10, dd,	162.70, dd,	116.10, dd,	130.88, dd,	-
(D)	$^{4}J_{FC}$ 2.0,	$^{3}J_{FC}$ 8.1,	$^{2}J_{FC}$ 21.5,	$^{1}J_{FC}$ 246.4,	$^{2}J_{FC}$ 21.5,	$^{3}J_{FC}$ 8.1,	
	$^{2}J_{PC}$ 3.2	$^{3}J_{PC}$ 6.3	$^{4}J_{PC}$ 2.2	$^{5}J_{PC}$ 3.6	$^{4}J_{PC}$ 2.2	$^{3}J_{PC}$ 6.3	
11bb	139.48, dd,	116.11, dd,	163.57, dd,	115.51, dd,	130.59, dd,	124.94, dd,	-
(D)	$^{3}J_{FC}$ 6.8,	$^{2}J_{FC}$ 21.9,	$^{1}J_{FC}$ 246.6,	$^{2}J_{FC}$ 21.2,	$^{3}J_{FC}$ 8.1,	$^{4}J_{FC}$ 2.9,	
	$^{2}J_{PC}$ 2.0	$^{3}J_{PC}$ 6.1	$^{4}J_{PC}$ 2.5	$^{5}J_{PC}$ 3.0	$^{4}J_{PC}$ 2.4	$^{3}J_{PC}$ 6.3	
11bd	133.97, ddd,	118.12, ddd,	150.70, ddd,	151.07, ddd,	117.92, ddd,	125.31, ddd,	-
(D)	$^{4}J_{FC}$ 3.8,		$^{2}J_{FC}$ 12.4,	$^{2}J_{FC}$ 12.4,		$^{4}J_{FC}$ 2.8,	
	$^{3}J_{FC}$ 5.0,	$^{2}J_{FC}$ 17.8,	$^{1}J_{FC}$ 248.3,	$^{1}J_{FC}$ 248.5,	$^{2}J_{FC}$ 17.3,	$^{3}J_{FC}$ 6.4,	
	$^{2}J_{PC}$ 2.3	$^{3}J_{PC}$ 5.9,	$^{4}J_{PC}$ 3.3	$^{5}J_{PC}$ 2.6	$^{4}J_{PC}$ 2.3,	$^{3}J_{PC}$ 3.6	
		overlapping			overlapping		
11be	140.72, dq,	129.59, d,	126.27, dq,	130.96, dq,	126.27, dq,	129.59, d,	124.74, dq,
(D)			$^{3}J_{FC}$ 3.8,	$^{2}J_{FC}$ 32.5,	$^{3}J_{FC}$ 3.8,		$^{1}J_{FC}$ 272.1,
	$^{2}J_{PC}$ = 1.3,	$^{3}J_{PC}$ 6.1	$^{4}J_{PC}$ 2.4	$^{5}J_{PC}$ 3.1	$^{4}J_{PC}$ 2.4	$^{3}J_{PC}$ 6.1	$^{6}J_{PC}$ 1.3
	overlapping						
11bf	138.01, d,	126.24, dq,	131.48, dq,	125.37, dq,	132.46, dq,	129.66, d,	124.72, dq,
(D)		$^{3}J_{FC}$ 3.8,	$^{2}J_{FC}$ 32.3,	$^{3}J_{FC}$ 3.7,	$^{4}J_{FC}$ 5.7,		$^{1}J_{FC}$ 272.3,
	$^{2}J_{PC}$ 2.3	$^{3}J_{PC}$ 6.4	$^{4}J_{PC}$ 2.4	$^{5}J_{PC}$ 3.2	$^{4}J_{PC}$ 1.2	$^{3}J_{PC}$ 2.4	$^{5}J_{PC}$ 0.5
11bg	135.47, d,	130.67, d,	121.54, dq,	149.56, dq,	121.54, dq,	130.67, d,	121.14, dq,
(D)				$^{3}J_{FC}$ 3.5,			$^{1}J_{FC}$ 257.2,
	$^{2}J_{PC}$ 2.1	$^{3}J_{PC}$ 6.2	$^{4}J_{PC}$ 1.1,	$^{5}J_{PC}$ 1.3	$^{4}J_{PC}$ 1.1,	$^{3}J_{PC}$ 6.2	$^{7}J_{PC}$ 1.1
			overlapping		overlapping		

$^{31}P\{^{1}H\}$ NMR (6% $CDCl_3$, 85% H_3PO_4 ext.), δ: 26.49 (d, $^{6}J_{PF}$ 4.8).
^{1}H NMR (6% $CDCl_3$, TMS), δ: 2.50 (bs, 1H, NH), 3.51 (d, $^{3}J_{PH}$ 10.5, 3H, CH_3), 3.86 (d, $^{3}J_{PH}$ 10.6, 3H, CH_3), 3.95 (d, $^{2}J_{PH}$ 21.6, 1H, PCH), 4.64 (d, $^{3}J_{HH}$ 1.2, 1H, $CHPh_2$), 7.00–7.13 (m, $2H_{arom.}$, 4-F—C_6H_4—C), 7.13–7.37 (m, $10H_{arom.}$, 2 × C_6H_5 + $2H_{arom.}$, 4-F—C_6H_4—C).
^{19}F NMR (6% $CDCl_3$, C_6F_6 int.), δ: 47.71–47.89 (m, 1F, 4-F—C_6H_4—C).

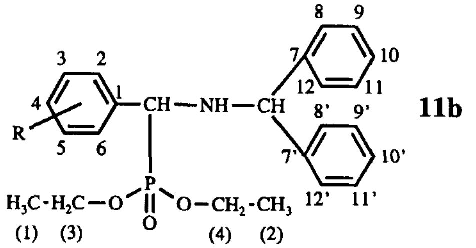
Dimethyl N-Diphenylmethylamino-(4′-trifluoromethylphenyl-)methanephosphonate **11ae**
$^{31}P\{^{1}H\}$ δ: 25.72 (q, $^{7}J_{PF}$ 2.3).
^{1}H δ: 3.55 (d, $^{3}J_{PH}$ 10.6, 3H, CH_3), 3.86 (d, $^{3}J_{PH}$ 10.6, 3H, CH_3), 4.05 (d, $^{2}J_{PH}$ 22.7, 1H, PCH), 4.63 (d, $^{3}J_{HH}$ 1.1, 1H, $CHPh_2$), 7.14–7.36 (m, $10H_{arom.}$, 2 × C_6H_5), 7.43–7.49 (m, $2H_{arom.}$, 4-CF_3—C_6H_4—C), 7.61–7.67 (m, $2H_{arom.}$, 4-CF_3—C_6H_4—C).
^{19}F δ: 99.24 (bs, 3F, 4-CF_3—C_6H_4—C).

Fluorinated Diethyl N-Diphenylmethylaminoarylmethanephosphonates **11ba–bg**: 0.02 mol of the fluorinated N-benzylidene-1,1-diphenylmethylamine **10** was mixed with 0.02 mol diethyl phosphite under nitrogen; with slight cooling a pale yellow suspension resulted. The reaction was completed by heating (8–14 h) at 100°C when an intensively yellow solution was formed. Cooling gave a highly viscous oil, which was dissolved in methanol. After concentration on a rotary evaporator at water pump pressure, the solution was placed in a refrigerator to give the nitrogen protected diethyl aminophosphonate **11b** as a waxy, pale yellow, solid precipitate, which was filtered off (using a G3-sintered glass filter), washed with cooled ether, dried in a vacuum desiccator over silica gel, and purified by recrystallization from methanol/ether mixtures (Table VII).

Diethyl N-Diphenylmethylamino-(4′-fluorophenyl-)methanephosphonate **11ba**
C, H, N analysis: $C_{24}H_{27}FNO_3P$, M.Wt. = 427.45, requires: C 67.44, H 6.37, N 3.28, found: C 67.14, H 6.51, N 3.38%.
$^{31}P\{^{1}H\}$ NMR (6% $CDCl_3$, 85% H_3PO_4 ext.), δ: 24.13 (d, $^{6}J_{PF}$ 4.8).

TABLE XII

Part III: $^{13}C\{^1H\}$ NMR data of the fluorinated diethyl N-diphenylmethylaminoarylmethanephosphonates **11b**



11b

No.	δC C7/7'	C8/8'	C9/9'	C10/10'	C11/11'	C12/12'
11ba	142.52, s,	127.84, s,	129.07, s,	127.84, s,	127.84, s,	129.07, s,
(D)	144.15, s	128.42, s,	129.28, s	128.03, s	128.42, s,	129.28, s
11bb	142.45, s,	127.83, s,	129.07, s,	127.82, s,	127.83, s,	129.07, s,
(D)	144.05, s	128.40, s,	129.28, s	128.05, s	128.40, s,	129.28, s
11bd	142.35, s,	127.85, s,	129.15, s,	127.96, s,	127.85, s,	129.15, s,
(D)	143.92, s	128.39, s,	129.40, s	128.18, s	128.39, s,	129.40, s
11be	142.37, s,	127.84, s,	129.13, s,	127.94, s,	127.84, s,	129.13, s,
(D)	143.92, s	128.39, s,	129.37, s	128.16, s	128.39, s,	129.37, s
11bf	142.31, s,	127.90, s,	129.13, s,	127.94, s,	127.90, s,	129.13, s,
(D)	143.88, s	128.39, s,	129.38, s	128.18, s	128.39, s,	129.38, s
11bg	142.50, s,	127.87, s,	129.12, s,	127.90, s,	127.87, s,	129.12, s,
(D)	144.05, s	128.43, s,	129.34, s	128.12, s	128.43, s,	129.34, s

^1H NMR (6% $CDCl_3$, TMS), δ: 1.20 (dt, $^3J_{HH}$ 7.1, $^4J_{PH}$ 0.5, 3H, CH_3), 1.35 (dt, $^3J_{HH}$ 7.1, $^4J_{PH}$ 0.5, 3H, CH_3), 3.76–4.04 (m, 2H, CH_2), 4.07–4.34 (m, 2H, CH_2), 3.92 (d, $^2J_{PH}$ 22.2, 1H, PCH), 4.65 (d, $^3J_{HH}$ 1.1, 1H, $C\underline{H}Ph_2$), 6.99–7.13 (m, $2H_{arom.}$, 4-F—C_6H_4—C), 7.14–7.36 (m, $10H_{arom.}$, 2 × C_6H_5 + $2H_{arom.}$, 4-F—C_6H_4—C).
^{19}F NMR (6% $CDCl_3$, C_6F_6 int.), δ: 47.37–47.55 (m, 1F, 4-F—C_6H_4—C).

Diethyl N-Diphenylmethylamino-(3'-fluorophenyl-)methanephosphonate **11bb**
C, H, N analysis: $C_{24}H_{27}FNO_3P$, M.Wt. = 427.45, requires: C 67.44, H 6.37, N 3.28, found: C 67.37, H 6.32, N 3.28%.
$^{31}P\{^1H\}$ δ: 23.68 (d, $^5J_{PF}$ 1.7).
^1H δ: 1.11 (dt, $^3J_{HH}$ 7.1, $^4J_{PH}$ 0.5, 3H, CH_3), 1.35 (dt, $^3J_{HH}$ 7.1, $^4J_{PH}$ 0.5, 3H, CH_3), 3.69–4.06 (m, 2H, CH_2), 4.07–4.34 (m, 2H, CH_2), 3.93 (d, $^2J_{PH}$ 22.4, 1H, PCH), 4.67 (d, $^3J_{HH}$ 1.0, 1H, $C\underline{H}Ph_2$), 7.04–7.42 (m, $10H_{arom.}$, 2 × C_6H_5 + $4H_{arom.}$, 3-F—C_6H_4—C)
^{19}F δ: 48.70–48.84 (m, 1F, 3-F—C_6H_4—C).

Diethyl N-Diphenylmethylamino-(3',4'-difluorophenyl-)methanephosphonate **11bd**
C, H, N analysis: $C_{24}H_{26}F_2NO_3P$, M.Wt. = 445.44, requires: C 64.71, H 5.88, N 3.14, found: C 64.55, H 5.91, N 3.18%.
$^{31}P\{^1H\}$ δ: 23.43 (dd, $^6J_{PF}$ 5.1, $^5J_{PF}$ 1.8).
^1H δ: 1.15 (dt, $^3J_{HH}$ 7.1, $^4J_{PH}$ 0.5, 3H, CH_3), 1.35 (dt, $^3J_{HH}$ 7.1, $^4J_{PH}$ 0.5 Hz, 3H, CH_3), 3.74–4.08 (m, 2H, CH_2), 4.07–4.33 (m, 2H, CH_2), 3.90 (d, $^2J_{PH}$ 22.2, 1H, PCH), 4.65 (d, $^3J_{HH}$ 0.9, 1H, $C\underline{H}Ph_2$), 7.00–7.56 (m, $10H_{arom.}$, 2 × C_6H_5 + $3H_{arom.}$, 3,4-F_2—C_6H_3—C).
^{19}F δ: 23.02–23.28 (m, 1F, 3,$\underline{4}$-F_2—C_6H_3—C), 24.57–24.80 (m, 1F, $\underline{3}$,4-F_2—C_6H_3—C).

Diethyl N-Diphenylmethylamino-(4'-trifluoromethylphenyl-)methanephosphonate **11be**
$^{31}P\{^1H\}$ δ: 23.39 (q, $^7J_{PF}$ 2.3).
^1H δ: 1.12 (dt, $^3J_{HH}$ 7.1, $^4J_{PH}$ 0.5, 3H, CH_3), 1.35 (dt, $^3J_{HH}$ 7.1, $^4J_{PH}$ 0.5, 3H, CH_3), 3.72–4.07 (m, 2H, CH_2), 4.07–4.34 (m, 2H, CH_2), 4.02 (d, $^2J_{PH}$ 22.6, 1H, PCH), 4.64 (bs, 1H, $C\underline{H}Ph_2$), 7.20–7.56 (m, $10H_{arom.}$, 2 × C_6H_5 + $2H_{arom.}$, 4-CF_3—C_6H_4—C) 7.59–7.67 (m, $2H_{arom.}$, 4-CF_3—C_6H_4—C).

TABLE XIII

Part I: $^{13}C\{^1H\}$ NMR data of the fluorinated diphenyl N-diphenylmethylaminoarylmethanephosphonates **11c**. $^{13}C\{^1H\}$ NMR (10% $CDCl_3$, TMS), δ [ppm], Mult., $^nJ_{XY}$ [Hz]

No.	δ_C CHP	CHN	C13/ 13'	C14/ 14'	C 15/ 15'	C16/ 16'	C17/ 17'	C 18/ 18'
11ca	57.64, d,	64.30, d,	150.99, d,	120.89, d,	130.18, d,	125.63, d,	130.18, d,	120.89, d,
(D)	$^1J_{PC}$ 156.2	$^3J_{PC}$ 16.8	$^2J_{PC}$ 9.6,	$^3J_{PC}$ 4.4,	$^4J_{PC}$ 0.9,	$^5J_{PC}$ 1.1,	$^4J_{PC}$ 0.9,	$^3J_{PC}$ 4.4,
			151.53, d,	121.10, d,	130.32, d,	125.73, d,	130.32, d,	121.10, d,
			$^2J_{PC}$ 9.6	$^3J_{PC}$ 4.4	$^4J_{PC}$ 0.8	$^5J_{PC}$ 1.1	$^4J_{PC}$ 0.8	$^3J_{PC}$ 4.4
11cb	58.53, dd,	64.68, d,	150.97, d,	120.88, d,	130.20, d,	125.68, d,	130.20, d,	120.88, d,
(D)	$^1J_{PC}$ 158.3,	$^3J_{PC}$ 17.3	$^2J_{PC}$ 9.7,	$^3J_{PC}$ 4.4,	$^4J_{PC}$ 0.9,	$^5J_{PC}$ 1.2,	$^4J_{PC}$ 0.9,	$^3J_{PC}$ 4.4,
	$^4J_{FC}$ 1.8		151.49, d,	121.08, d,	130.33, d,	125.76, d,	130.33, d,	121.08, d,
			$^2J_{PC}$ 9.7	$^3J_{PC}$ 4.5	$^4J_{PC}$ 0.9	$^5J_{PC}$ 1.1	$^4J_{PC}$ 0.9	$^3J_{PC}$ 4.5
11cd	58.23, dd,	64.69, d,	150.92, d,	120.84, d,	130.30, d,	125.81, d,	130.30, d,	120.84, d,
(D)	$^1J_{PC}$ 158.6,	$^3J_{PC}$ 17.1	$^2J_{PC}$ 9.6,	$^3J_{PC}$ 4.4,	$^4J_{PC}$ 0.9,	$^5J_{PC}$ 1.2,	$^4J_{PC}$ 0.9,	$^3J_{PC}$ 4.4,
	$^4J_{FC}$ 1.3		151.42, d,	121.04, d,	130.40, d,	125.88, d,	130.40, d,	121.04, d,
			$^2J_{PC}$ 9.6	$^3J_{PC}$ 4.5	$^4J_{PC}$ 0.9	$^5J_{PC}$ 1.1	$^4J_{PC}$ 0.9	$^3J_{PC}$ 4.5
11ce	58.66, d,	64.79, d,	150.93, d,	120.83, d,	130.26, d,	125.79, d,	130.26, d,	120.83, d,
(D)	$^1J_{PC}$ 157.0	$^3J_{PC}$ 17.1	$^2J_{PC}$ 9.6,	$^3J_{PC}$ 4.4,	$^4J_{PC}$ 0.9,	$^5J_{PC}$ 1.2,	$^4J_{PC}$ 0.9,	$^3J_{PC}$ 4.4,
			151.43, d,	121.07, d,	130.40, d,	125.88, d,	130.40, d,	121.07, d,
			$^2J_{PC}$ 9.7	$^3J_{PC}$ 4.5	$^4J_{PC}$ 0.9	$^5J_{PC}$ 1.1	$^4J_{PC}$ 0.9	$^3J_{PC}$ 4.5
11cf	58.61, d,	64.79, d,	150.93, d,	120.78, d,	130.28, d,	125.76, d,	130.28, d,	120.78, d,
(D)	$^1J_{PC}$ 157.3	$^3J_{PC}$ 17.0	$^2J_{PC}$ 9.6,	$^3J_{PC}$ 4.5,	$^4J_{PC}$ 0.8,	$^5J_{PC}$ 1.1,	$^4J_{PC}$ 0.8,	$^3J_{PC}$ 4.5,
			151.40, d,	121.04, d,	130.41, d,	125.89, d,	130.41, d,	121.04, d,
			$^2J_{PC}$ 9.6	$^3J_{PC}$ 4.5	$^4J_{PC}$ 0.8	$^5J_{PC}$ 1.1	$^4J_{PC}$ 0.8	$^3J_{PC}$ 4.5
11cg	58.25, d,	64.68, d,	150.97, d,	120.82, d,	130.19, d,	125.68, d,	130.19, d,	120.82, d,
(D)	$^1J_{PC}$ 158.0	$^3J_{PC}$ 17.2	$^2J_{PC}$ 9.6,	$^3J_{PC}$ 4.4,	$^4J_{PC}$ 0.9,	$^5J_{PC}$ 1.2,	$^4J_{PC}$ 0.9,	$^3J_{PC}$ 4.4,
			151.47, d,	121.08, d,	130.35, d,	125.80, d,	130.35, d,	121.08, d,
			$^2J_{PC}$ 9.7	$^3J_{PC}$ 4.5	$^4J_{PC}$ 0.9	$^5J_{PC}$ 1.1	$^4J_{PC}$ 0.9	$^3J_{PC}$ 4.5

^{19}F δ: 99.27 (bs, 3F, 4-CF_3—C_6H_4—C).

Diethyl N-Diphenylmethylamino-(3'-trifluoromethylphenyl-)methanephosphonate **11bf**
$^{31}P\{^1H\}$ δ: 23.30 (q, $^6J_{PF}$ 0.6).
^1H δ: 1.12 (dt, $^3J_{HH}$ 7.1, $^4J_{PH}$ 0.5, 3H, CH_3), 1.34 (dt, $^3J_{HH}$ 7.1, $^4J_{PH}$ 0.5, 3H, CH_3), 3.73–4.07 (m, 2H, CH_2), 4.05–4.32 (m, 2H, CH_2), 4.02 (d, $^2J_{PH}$ 22.4, 1H, PCH), 4.65 (bs, 1H, $\mathrm{C\underline{H}Ph_2}$), 7.18–7.64 (m, $10H_{arom.}$, 2 × C_6H_5 + $4H_{arom.}$, 3-CF_3—C_6H_4—C).
^{19}F δ: 99.14 (bs, 3F, 3-CF_3—C_6H_4—C).

Diethyl N-Diphenylmethylamino-(4'-trifluoromethoxyphenyl-)methanephosphonate **11bg**
C, H, N analysis: $C_{25}H_{27}F_3NO_4P$, M.Wt. = 493.46, requires: C 60.85, H 5.51, N 2.84, found: C 60.70, H 5.65, N 2.87%.
$^{31}P\{^1H\}$ δ: 23.79 (s).
^1H δ: 1.10 (dt, $^3J_{HH}$ 7.1, $^4J_{PH}$ 0.5, 3H, CH_3), 1.35 (dt, $^3J_{HH}$ 7.1, $^4J_{PH}$ 0.6, 3H, CH_3), 3.69–4.05 (m, 2H, CH_2), 4.07–4.33 (m, 2H, CH_2), 3.96 (d, $^2J_{PH}$ 22.3, 1H, PCH), 4.66 (d, $^3J_{HH}$ 0.9, 1H, $\mathrm{C\underline{H}Ph_2}$), 7.13–7.40 (m, $10H_{arom.}$, 2 × C_6H_5 + $4H_{arom.}$, 4-CF_3O—C_6H_4—C).
^{19}F δ: 103.96 (bs, 3F, 4-CF_3—C_6H_4—C).

Fluorinated Diphenyl N-Diphenylmethylaminoarylmethanephosphonates **11ca–cg**: 0.02 mol of the fluorinated N-benzylidene-1,1-diphenylmethylamine **10** and 0.02 mol diphenyl phosphite were mixed together under an atmosphere of nitrogen, when a weakly exothermic reaction occurred and a yellowish suspension was formed. In order to complete the phosphite-addition reaction the mixture was heated at 100°C (4–8 h), to give a clear, yellow, oily liquid. Solidification occurred on cooling to give a waxy,

TABLE XIII

Part II: $^{13}C\{^1H\}$ NMR data of the fluorinated diphenyl N-diphenylmethylaminoarylmethanephosphonates **11c**

No.	δ_C	C1	C2	C3	C4	C5	C6	R
11ca (D)		131.28, dd, $^{2}J_{PC}$ 1.4, overlapping	131.24, dd, $^{3}J_{FC}$ 8.2, $^{3}J_{PC}$ 6.9	116.43, dd, $^{2}J_{FC}$ 21.6, $^{4}J_{PC}$ 2.2	163.41, dd, $^{1}J_{FC}$ 247.3, $^{5}J_{PC}$ 3.3	116.43, dd, $^{2}J_{FC}$ 21.6, $^{4}J_{PC}$ 2.2	131.24, dd, $^{3}J_{FC}$ 8.2, $^{3}J_{PC}$ 6.9	-
11cb (D)		138.31, dd, $^{3}J_{FC}$ 6.8, $^{2}J_{PC}$ 1.3	116.49, dd, $^{2}J_{FC}$ 22.2, $^{3}J_{PC}$ 6.6	163.68, dd, $^{1}J_{FC}$ 247.1, $^{4}J_{PC}$ 2.5	116.09, dd, $^{2}J_{FC}$ 21.3, $^{5}J_{PC}$ 3.2	130.94, dd, $^{3}J_{FC}$ 8.2, $^{4}J_{PC}$ 2.3	125.23, dd, $^{4}J_{FC}$ 3.0, $^{3}J_{PC}$ 6.7	-
11cd (D)		132.79, ddd, $^{3}J_{FC}$ 5.0, $^{4}J_{FC}$ 3.8, $^{2}J_{PC}$ 1.5	118.50, ddd, $^{2}J_{FC}$ 17.4, $^{3}J_{PC}$ 7.0, overlapping	151.19, ddd, $^{1}J_{FC}$ 248.9, $^{2}J_{FC}$ 12.0, $^{4}J_{PC}$ 2.5	150.99, ddd, $^{1}J_{FC}$ 249.0, $^{2}J_{FC}$ 12.0, $^{5}J_{PC}$ 3.4	118.25, ddd, $^{2}J_{FC}$ 17.0, $^{4}J_{PC}$ 0.6, overlapping	125.67, ddd, $^{3}J_{FC}$ 6.7, $^{4}J_{FC}$ 3.1, $^{3}J_{PC}$ 3.6, overlapping	-
11ce (D)		139.94, dq, $^{5}J_{FC}$ 1.3, $^{2}J_{PC}$ 1.3	129.96, d, $^{3}J_{PC}$ 6.6	126.38, dq, $^{3}J_{FC}$ 3.8, $^{4}J_{PC}$ 2.4	131.31, dq, $^{2}J_{FC}$ 32.5, $^{5}J_{PC}$ 3.2	126.38, dq, $^{3}J_{FC}$ 3.8, $^{4}J_{PC}$ 2.4	129.96, d, $^{3}J_{PC} = 6.6$	124.71, dq, $^{1}J_{FC}$ 272.2, $^{6}J_{PC}$ 3.2
11cf (D)		136.91, d, $^{2}J_{PC}$ 1.4	126.56, dq, $^{3}J_{FC}$ 3.8, $^{3}J_{PC}$ 7.2	131.76, dq, $^{2}J_{FC}$ 32.5, $^{4}J_{PC}$ 2.3	125.94, dq, overlapping	132.78, dq, $^{4}J_{FC}$ 6.1, $^{4}J_{PC}$ 1.2	130.00, d, $^{3}J_{PC}$ 2.4	124.60, dq, $^{1}J_{FC}$ 272.5, $^{5}J_{PC}$ 0.6
11cg (D)		134.34, d, $^{2}J_{PC}$ 1.3	131.03, d, $^{3}J_{PC}$ 6.7	121.84, dq, $^{4}J_{FC}$ 1.1, overlapping	149.90, q, $^{3}J_{FC}$ 1.8	121.84, dq, $^{4}J_{FC}$ 1.1, overlapping	131.03, d, $^{3}J_{PC}$ 6.7	121.13, dq, $^{1}J_{FC}$ 257.3, $^{7}J_{PC}$ 1.0

yellowish solid, which was dissolved by boiling under reflux in a mixture of ethanol and methanol. On cooling in an ice/water bath, the nitrogen protected diphenyl aminophosphonate **11c** separated as a fine white powder which was filtered off, washed free of oil with cooled ether, and finally dried in a vacuum desiccator over silica gel. The product was purified by recrystallization form THF/ether mixtures (Table VIII).

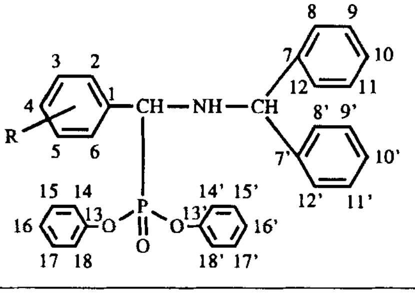
Diphenyl N-Diphenylmethylamino-(4′-fluorophenyl-)methanephosphonate **11ca**
C, H, N analysis: $C_{32}H_{27}FNO_3P$, M.Wt. = 523.54, requires: C 73.41, H 5.20, N 2.68, found: C 73.34, H 5.36, N 2.70%.
$^{31}P\{^1H\}$ NMR (6% $CDCl_3$, 85% H_3PO_4 ext.), δ: 16.78 (d, $^{6}J_{PF}$ 5.1).
^1H NMR (6% $CDCl_3$, TMS), δ: 4.21 (d, $^{2}J_{PH}$ 22.5, 1H, PCH), 4.64 (d, $^{3}J_{HH}$ 1.2, 1H, $C\underline{H}Ph_2$), 6.72–6.80 + 6.92–7.35 (m, $10H_{arom.}$, $CH(C_6\underline{H}_5)_2$ + $10H_{arom.}$, $P(OC_6\underline{H}_5)_2$ + $4H_{arom.}$, 4-F—C_6H_4—$\overline{C}$).
^{19}F NMR (6% $CDCl_3$, C_6F_6 int.), δ: 48.24–48.42 (m, 1F, 4-F—C_6H_4—C).

Diphenyl N-Diphenylmethylamino-(3′-fluorophenyl-)methanephosphonate **11cb**
C, H, N analysis: $C_{32}H_{27}FNO_3P$, M.Wt. = 523.54, requires: C 73.41, H 5.20, N 2.68, found: C 73.30, H 5.30, N 2.76%.
$^{31}P\{^1H\}$ δ: 16.33 (d, $^{5}J_{PF}$ 1.8).
^1H δ: 2.75 (bs, 1H, NH), 4.31 (d, $^{2}J_{PH}$ 22.8, 1H, PCH), 4.75 (d, $^{3}J_{HH}$ 1.1, 1H, $C\underline{H}Ph_2$), 6.83–6.91 + 6.99–7.40 (m, $10H_{arom.}$, $CH(C_6\underline{H}_5)_2$ + $10H_{arom.}$, $P(OC_6\underline{H}_5)_2$ + $4H_{arom.}$, 3-F—C_6H_4—$\overline{C}$).
^{19}F δ: 49.46–49.59 (m, 1F 3-F—C_6H_4—C).

Diphenyl N-Diphenylmethylamino-(3′,4′-difluorophenyl-)methanephosphonate **11cd**
C, H, N analysis: $C_{32}H_{26}F_2NO_3P$, M.Wt. = 541.53, requires: C 70.97, H 4.84, N 2.59, found: C 70.77, H 5.00, N 2.65%.

TABLE XIII

Part III: $^{13}C\{^1H\}$ NMR data of the fluorinated diphenyl N-diphenylmethylaminoarylmethanephosphonates **11c**



11c

No. δ_C	C7/7'	C8/8',	C9/9'	C10/10'	C11/11',	C12/12'
11ca	142.36, s,	127.83, s,	129.12, s,	127.91, s,	127.83, s,	129.12, s,
(D)	144.05, s	128.38, s,	129.36, s	128.17, s	128.38, s,	129.36, s
11cb	142.09, s,	127.81, s,	128.50, s,	128.03, s,	127.81, s,	128.50, s,
(D)	143.82, s	129.19, s,	129.41, s	128.23, s	129.19, s,	129.41, s
11cd	141.96, s,	127.80, s,	129.24, s,	128.12, s,	127.80, s,	129.24, s,
(D)	143.66, s	128.46, s,	129.50, s	128.34, s	128.46, s,	129.50, s
11ce	142.01, s,	127.82, s,	129.24, s,	128.12, s,	127.82, s,	129.24, s,
(D)	143.69, s	128.48, s,	129.49, s	128.33, s	128.48, s,	129.49, s
11cf	141.94, s,	127.85, s,	129.25, s,	128.12, s,	127.85, s,	129.25, s,
(D)	143.65, s	128.47, s,	129.50, s	128.35, s	128.47, s,	129.50, s
11cg	142.12, s,	127.82, s,	128.48, s,	128.05, s,	127.82, s,	128.48, s,
(D)	143.78, s	129.19, s,	129.43, s	128.25, s	129.19, s,	129.43, s

$^{31}P\{^1H\}$ δ: 15.91 (dd, $^6J_{PF}$ 5.4, $^5J_{PF}$ 1.8).
^1H δ: 2.59 (bs, 1H, NH), 4.19 (d, $^3J_{PH}$ 22.4, 1H, PCH), 4.65 (d, $^3J_{HH}$ 1.1, 1H, $C\underline{H}Ph_2$), 6.79–7.31 (m, $10H_{arom.}$, $CH(C_6\underline{H}_5)_2$ + $10H_{arom.}$, $P(OC_6\underline{H}_5)_2$ + $3H_{arom.}$, $3,4\text{-}F_2—C_6H_3—C$).
^{19}F δ: 23.90–24.17 (m, 1F $3,\underline{4}\text{-}F_2—C_6H_3—C$), 25.14–25.39 (m, 1F, $\underline{3},4\text{-}F_2—C_6H_3—C$).

Diphenyl N-Diphenylmethylamino-(4'-trifluoromethylphenyl-)methanephosphonate **11ce**
$^{31}P\{^1H\}$ δ: 15.95 (q, $^7J_{PF}$ 2.3).
^1H δ: 4.39 (d, $^2J_{PH}$ 22.9, 1H, PCH), 4.72 (d, $^3J_{HH}$ 0.7, 1H, $C\underline{H}Ph_2$), 6.81–6.89 + 7.03–7.39 (m, $10H_{arom.}$, $CH(C_6\underline{H}_5)_2$ + $10H_{arom.}$, $P(OC_6\underline{H}_5)_2$), 7.51–7.67 (m, $4H_{arom.}$, $4\text{-}CF_3—C_6H_4—C$).
^{19}F δ: 99.15 (bs, 3F $4\text{-}CF_3—C_6H_4—C$)

Diphenyl N-Diphenylmethylamino-(3'-trifluoromethylphenyl-)methanephosphonate **11cf**
$^{31}P\{^1H\}$ δ: 15.87 (q, $^6J_{PF}$ 0.7).
^1H δ: 4.29 (d, $^2J_{PH}$ 22.8, 1H, PCH), 4.63 (bs, 1H, $C\underline{H}Ph_2$), 6.74–6.82 + 6.91–7.23 (m, $10H_{arom.}$, $CH(C_6\underline{H}_5)_2$ + $10H_{arom.}$, $P(OC_6\underline{H}_5)_2$), 7.37–7.57 (m, $4H_{arom.}$, $3\text{-}CF_3—C_6H_4—C$).
^{19}F δ: 99.16 (bs, 3F, $3\text{-}CF_3—C_6H_4—C$)

Diphenyl N-Diphenylmethylamino-(4'-trifluoromethoxyphenyl-)methanephosphonate **11cg**
C, H, N analysis: $C_{33}H_{27}F_3NO_4P$, M.Wt. = 589.55, requires: C 67.23, H 4.62, N 2.38, found: C 67.30, H 4.69, N 2.38%.
$^{31}P\{^1H\}$ δ: 16.37 (s).
^1H δ: 4.24 (d, $^2J_{PH}$ 22.6, 1H, PCH), 4.65 (d, $^3J_{HH}$ 0.7, 1H, $C\underline{H}Ph_2$), 6.67–6.75 + 6.90–7.38 (m, $10H_{arom.}$, $CH(C_6\underline{H}_5)_2$ + $10H_{arom.}$, $P(OC_6\underline{H}_5)_2$ + $4H_{arom.}$, $4\text{-}CF_3—C_6H_4—C$).
^{19}F δ: 104.01 (bs, 3F, $4\text{-}CF_3O—C_6H_4—C$).

^{13}C-NMR-data of compounds **6**, **10**, and **11** are listed in Tables IX–XIII.

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