# *N*-(Arylsulfonyl)trihaloacetimidoyl Chlorides and Their Reactions with Phosphites

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We have developed a convenient synthetic approach to highly reactive *N*-(arylsulfonyl)trichloro- and -trifluoroacetimidoyl chlorides **2** by reacting the corresponding *N*-acylsulfonamides with $PCl_5$. The interaction of the imidoyl chlorides with phosphites proceeds through different pathways depending on the substituents in the reagents, and leads to *N*-arylsulfonyl-*N*-trichlorovinylphosphoramidates **4**, 1-arylsulfonylamino-1-chlorotrifluoroethylphosphonate **5**, *C*,*N*-bis(phosphorylated) *N*-dihalovinylsulfonamides **8** and α-(arylsulfonylamino)trifluoroethylidenebis(phosphonates) **10**. A rare example of an aza-Perkow reaction involving a trifluoromethyl group was discovered.


## Introduction

Trihaloacetimidoyl chlorides are useful reagents for the synthesis of various acyclic and heterocyclic compounds having trihalomethyl groups.[1,2] The reagents having electron-withdrawing acyl or phosphoryl groups (EWG) at the imine nitrogen atom are of particular preparative interest.[1c,2] The imidoyl chlorine atom in these compounds is easily substituted by another group (Y) and, in this way, a wide series of highly reactive imines $X_3C-C(Y)=N-EWG$ (**I**) can be obtained. This strategy has already been used in the synthesis of imidoylphosphonates **I** (Y = $R_2PO$; X = F, Cl; EWG = COR, $R_2PO$), which are starting compounds for the preparation of biologically active aminophosphonic acid derivatives.[1c,2–4] The possibility of using this approach to obtain compounds with fluorine-containing substituents and α-aminophosphonic acid residues in the same molecule seems very attractive since fluorine substituents are widely used in the design of new drugs to improve their lipophilicity and to modify their pharmacological properties.[1a,1b,5]

In contrast to *N*-acyl- and *N*-phosphoryl-substituted trihaloacetimidoyl chlorides, their analogs having sulfonyl groups at the nitrogen atom are less well known. Only two representative examples of such compounds, i.e., $CF_3C(Cl)=NSO_2X$ (X = F, Cl)[6] have been reported and no information about *N*-sulfonyltrichloroacetimidoyl chlorides is available in the literature. Almost nothing is known about the properties of the imidoyl chlorides, even though — because of the very strong electron-withdrawing ability of the sulfonyl group — they are unquestionably of interest as potential building blocks in the synthesis of functionalized nitrogen-containing compounds and as convenient models to study the specific effects that *N*-sulfonyl substituents have on the reactivity of these molecules. The recently discovered N-to-C transfer of sulfonyl groups in reactions of trifluoroiminopyruvates with phosphites, which leads to biologically important *C*-sulfonylated derivatives of trifluoroalanine,[7] illustrates the specificity of the chemistry of *N*-sulfonylated imines and the considerable preparative opportunities they offer. The present work is dedicated to the synthesis of the first representative examples of *N*-arylsulfonyltrihaloacetimidoyl chlorides and to their reactions with tervalent phosphorus nucleophiles.

The following dominant or competing routes are known for the reactions of phosphites with trihaloacetimidoyl chlorides activated by EWGs other than sulfonamide ones: Arbuzov reactions involving the imidoyl chlorine atom,[1c,2a,2b,3c,3d,4,8a–8c] aza-Perkow reactions with participation of the trihalomethyl group,[1c,3d,8a] and cycloadditions leading to phosphoranes.[2b,3c,9] The relative importance of these pathways for the reactions of *N*-sulfonylated trihaloacetimidoyl chlorides has not been studied previously.

## Results and Discussion

*N*-Arylsulfonyltrihaloacetimidoyl chlorides were prepared by the sequence of reactions shown in Scheme 1.

Easily accessible *N*-arylsulfonyltrihaloacetamides **1** react readily with phosphorus pentachloride upon heating in benzene to give imidoyl chlorides **2** in almost quantitative yields. The products are crystalline solids that are stable un-

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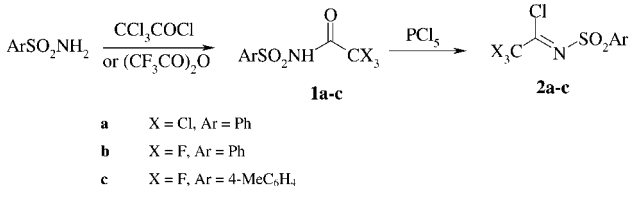
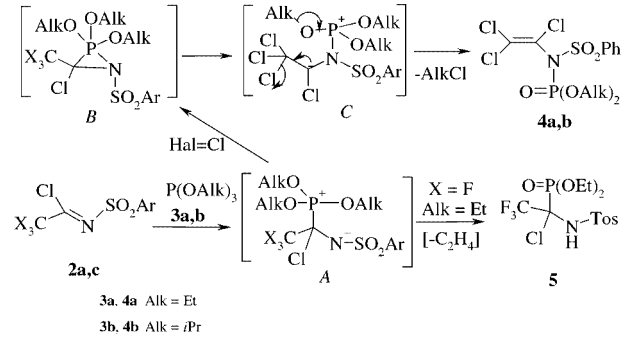



Scheme 1

der a dry atmosphere but are readily hydrolyzed in humid air. Their spectroscopic data and elemental analyses confirm the structure proposed and show that the theoretically possible chlorination of the sulfur atom — with the formation of isomeric compounds containing C(O)N=S(Cl) groups (cf.[6b,10]) — did not take place in this case.

The presence of several reaction centers in compounds **2,** and the umpolung of some of them, results in a variety of pathways and products in the reactions of the imidoyl chlorides with nucleophilic phosphorus agents. Substituents at the C=N bond and at the phosphorus atom in the reagents also have a substantial effect on the pathway taken[1c,2b,3,11] and, thus, the final results of these reactions are often difficult to predict a priori.

We have found that trichloroacetimidoyl chloride **2a** reacts smoothly and regiospecifically with trialkyl phosphites under mild conditions to form *N*-phosphorylated vinylsulfonamides **4** in high yields (Scheme 2).



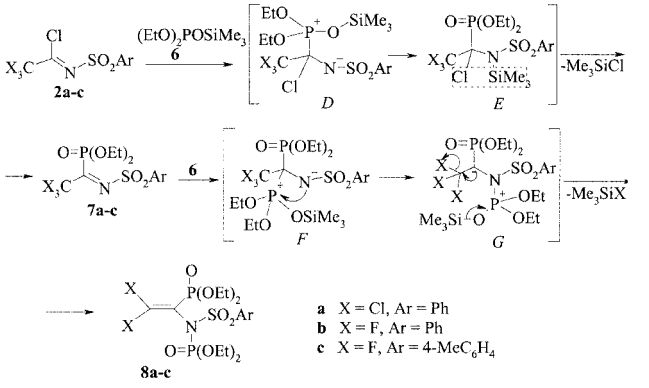

Scheme 2

Thus, the interaction follows the aza-Perkow reaction route[1c] involving a chlorine atom of the trichloromethyl group, while the imidoyl chlorine atom remains unaltered. Monitoring of the process by $^{31}P$ NMR spectroscopy indicates the absence of any *C*-phosphorylation products. The reaction is most likely to begin with the nucleophilic attack of the phosphite at the most electrophilic center: the imidoyl carbon atom. The subsequent C−N migration of the phosphorus group in the bipolar intermediate *A*, via the cyclic phosphorane *B*, results in the formation of carbanion *C*, which undergoes elimination of an alkyl chloride. $^{31}P$ and $^{13}C$ NMR spectra prove the structure of the vinylsulfonamides **4** unequivocally. The latter compounds do not react with phosphites **3**, as is expected for compounds having such structures.[1c,3]

Substituting the chlorine atoms of trichloroacetimidoyl chloride **2a** by fluorine atoms in the trifluoro analog **2c** changes the course of its reaction with triethyl phosphite drastically. In the latter case, a *C*-phosphorylated product is formed, rather than an *N*-phosphorylated one (Scheme 2), but the imidoyl chlorine atom remains unreactive. The primary steps in the reactions of **2a** and **2c** are apparently similar and lead to the same intermediate *A*. In view of similar electronic characteristics of $CCl_3$ and $CF_3$ groups ($\sigma_p$ = 0.46 and 0.54, respectively),[12] it is likely that what distinguishes the transformations of *A* that follow is determined by steric factors: the bulky trichloromethyl group causes the neighboring phosphorus residue to migrate rapidly to the nitrogen atom whereas, in the case of the trifluoromethyl analog, the bipolar ion *A* is stabilized through elimination of an ethylene molecule and protonation of the nitrogen atom. Compound **5** is formally an addition product of diethyl phosphite and imidoyl chloride **2c**, but, as established by independent experiments, the interaction of these reagents under the above reaction conditions does not produce phosphonate **5**. The equilibrium formation of similar compounds having $(EtO)_2P(O)$[13] or $CCl_3C(O)$[2b,11] substituents at the imino nitrogen atom, rather than sulfonyl groups, has been suggested previously, but these compounds have not been isolated from solutions because of their strong propensity to eliminate HCl or $(EtO)_2P(O)H$. Thus, phosphonate **5** is the first representative example of such a compound to be obtained in a pure state and to be completely characterized by elemental analysis and spectroscopic data.

α-Chloro-α-(tosylamino)trifluoroethylphosphonate **5** is a white crystalline solid that is stable at room temperature under an inert anhydrous atmosphere. Being an activated halide, it reacts with triethyl phosphite even at room temperature, but it forms a complex mixture of products.

Silyl phosphites often behave specifically and provide good preparative results in reactions with electrophilic agents.[14] We have studied the interaction of imidoyl chlorides **2** also with diethyltrimethylsilyl phosphite (**6**). These reactions follow a completely different course, involving two equivalents of phosphite **6**, and furnish *C*,*N*-bis(phosphorylated) products **8** (Scheme 3).



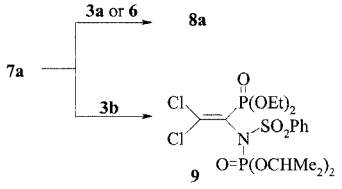

Scheme 3

Therefore, in contrast to the reactions with trialkyl phosphites presented in Scheme 2, silyl phosphite **6** reacts with trichloro- and trifluoroacetimidoyl chlorides by the same mechanism; the nature of the halogen substituents in substrates **2** has no effect on the direction of the reaction.

The first step of this reaction is most likely similar to that shown in Scheme 2. It results in the formation of a bipolar ion *D*, but, because of the high migratory aptitude of the $Me_3Si$ group, the former is stabilized by elimination of $Me_3SiCl$ from the intermediate *E* after the fast O−N shift of the $Me_3Si$ group (or immediately from betaine *D*) to give imidoylphosphonates **7** rather than through the C−N transfer of the phosphorus residue. These products are more reactive than the starting imidoyl chlorides **2** because of the strong activating effect of the phosphoryl group[2b,15] and, for this reason, they react quickly with a second molecule of phosphite **6** to form a bipolar ion *F*. The C−N migration of the phosphorus group in the latter species (possibly via a cyclic phosphorane of type *B*) produces carbanion *G*, which undergoes elimination of the halide ion and is transformed into the stable bis(phosphorylated) product **8**; that is, an aza-Perkow reaction occurs in the second step. We note that only one example of an aza-Perkow transformation involving a $CF_3$ group has been reported to date.[1c,16] The reaction shown in Scheme 3 occurs readily with both trifluoro- and trichloroacetimidoylphosphonates **7** apparently because of the umpolung of the adjacent C and N reaction centers during the C−N shift of the phosphorus group.

The intermediacy of imidoylphosphonates was confirmed by additional experiments. Thus, when chloride **2a** is reacted with one equivalent of phosphite **6** at −70 °C, a 1:1 mixture of **7a** ($\delta_P$ = −3.7 ppm) and **8a** ($\delta_P$ = −4.4 and 9.3 ppm) is formed, as evidenced by $^{31}P$ NMR spectra. If one equivalent of triethyl phosphite **3a** or diethyl trimethylsilyl phosphite **6** is added to this reaction mixture, **7a** is completely transformed into **8a**, whereas the addition of triisopropyl phosphite **3b** leads to the formation of vinylamide **9** ($\delta_P$ −6.0 and 9.5 ppm), which bears different phosphoryl groups at its C and N atoms (Scheme 4).



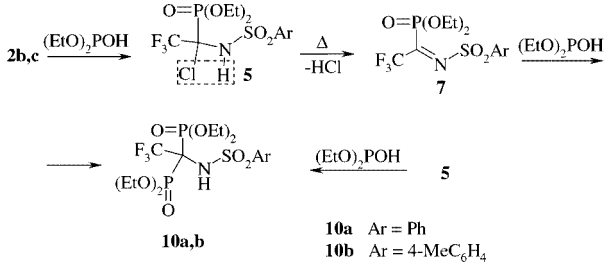

Scheme 4

Thus, imidoylphosphonates **7** react with trialkyl phosphites or diethyl trimethylsilyl phosphite by the same mechanism and the differences found in the reactions of imidoyl chlorides **2a−c** with these nucleophiles are determined by the different course of the first monophosphorylation step.

The spectral and analytical data of compounds **8** are in complete agreement with their structures. Of crucial importance to structural identification is the presence of the signal in the $^{13}C$ NMR spectrum that corresponds to the =CP carbon atom ($\delta_C$ = 126.4 and 89.3 ppm for **8a** and **8c**, respectively) that is coupled to its directly bonded phosphorus atom ($^1J_{C,P}$ = 220−230 Hz) and also the presence of signals of equal intensity from the phosphonate ($\delta_P$ = 9.3−9.8 ppm) and phosphate groups ($\delta_P$ between −3.0 and −4.4 ppm) in the $^{31}P$ NMR spectra.

Taking into account the high yields obtained for the preparation of compounds **8**, the reactions represented in Scheme 3 can be considered as a convenient preparative approach to the little-studied *N*-dichlorovinylamides and the almost-unknown *N*-difluorovinylamides,[17] which may serve as useful starting substrates for further functionalization.[18,19]

As is seen in Schemes 2 and 3, the reactions of imidoyl chlorides **2** with neutral esters of phosphorous acid occur mostly with the participation of the $CX_3$ groups and are driven by the transformation of the latter into dihalomethylene residues. This process is due to the formation of intermediate bipolar ions *A* or *F*, umpolung of the C and N reaction centers therein, and generation of carbanions *C* or *G*. It could be assumed that the intermediacy of the bipolar ions is unlikely when acid phosphites are used as nucleophilic agents, and it could be expected that $CX_3$ groups in substrates **2** would remain unaltered. This concept would be particularly important for the preparation of functionalized derivatives having trifluoromethyl groups.[1a,1b,5] Indeed, we have established that the reaction of trifluoroacetimidoyl chlorides **2b,c** with diethyl phosphite takes a new course, namely the nucleophilic addition of two phosphite molecules to the C=N bond leading to the previously unknown α-(sulfonylamino)trifluoroethylidenebis(phosphonates) **10** (Scheme 5).




Scheme 5

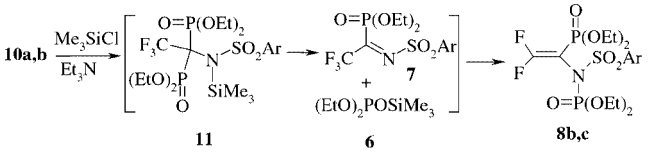
Whatever the ratio of the reagents is, the reaction does not stop after the first monophosphorylation step. The probable reason for this observation is that under the reaction conditions (reflux in benzene) the initially formed adduct **5** readily eliminates HCl and transforms into imidoylphosphonate **7**. The latter species, being more reactive than the starting imidoyl chlorides,[2b,15] reacts rapidly with a second molecule of dialkyl phosphite to give the end product **10**. Judging from the experimental findings, the rate-limiting step of the process is the addition of the phosphite to the C=N bond with the formation of adduct **5**. The reaction path proposed for the transformation of **2** into **10** was

corroborated by the fact that phosphonate **5**, obtained independently by the process in Scheme 2, reacted with diethyl phosphite to yield bis(phosphonate) **10b**. Compounds **10** are stable and crystalline. NMR spectra clearly indicate that the phosphoryl groups are equivalent and attached to the same carbon atom in the molecule.

The simple preparative access to fluorinated bis(phosphonates) of the type **10**, as represented in Scheme 5, is of special importance when the wide spectrum of physiological activities exhibited by compounds containing a P−C−P triad is taken into consideration, particularly that of the aminomethylenebis(phosphonates).[20]

As can be seen in Scheme 3, the vicinal disposition of the nucleofuge and trimethylsilyl group in the intermediate *E* promotes fast elimination of chlorotrimethylsilane and transformation of *E* into **7**. In principle, the dialkoxyphosphoryl group in bis(phosphonates) **10** can also act as a nucleofuge. Hence, it follows that silylation of the nucleophilic nitrogen center in **10** and subsequent abstraction of the phosphoryl group may lead to the corresponding imidoylphosphonate. We have found that bis(phosphonates) **10a,b** do undergo silylation at room temperature in the presence of triethylamine, but the end products of these reactions are the C,N-bis(phosphorylated) difluorovinylsulfonamides **8b,c**, rather than the expected imidoylphosphonates **7**. Such a surprising result can be readily explained by considering Scheme 6.




Scheme 6

It is likely that trimethylsilylamides **11** bearing two phosphoryl groups in the α-position are unstable[21] and readily eliminate diethyl silyl phosphite **6** to form the highly electrophilic imidoylphosphonates **7**, which react rapidly with the nucleophile **6** by the sequence of transformations depicted in the second part of Scheme 3 to give the indicated sulfonamides **8b,c**. The latter compounds are identical to the compounds obtained by reacting imidoyl chlorides **2b,c** with two equivalents of phosphite **6** (Scheme 3).

Considering Scheme 6 as a whole, we may infer that the system $Me_3SiCl + Et_3N$ is formally a catalyst for the transformation **10→8** via the C−N shift of the phosphoryl group.

## Conclusion

In summary, we have developed a simple synthetic approach to previously unknown *N*-(arylsulfonyl)trihaloacetimidoyl chlorides. The unusual reactivity of these compounds clearly reveals itself in the interactions with phosphites, which proceed through the following reaction pathways: (i) aza-Perkow conversion involving a halogen atom of the $CHal_3$ group, but not the imidoyl chlorine atom; (ii) the substitution of the imidoyl chlorine atom with a phosphorus-containing group, followed by transformations of the resulting imidoylphosphonates in which the $CHal_3$ group takes part; (iii) the addition of a phosphite molecule to the C=N bond and subsequent transformations of the primary adduct. The preferred reaction route depends on the nature of the phosphorus agent and the halogen in the $CHal_3$ group. Despite the complexity and multistep character of the process, these reactions are highly regioselective and preparatively acceptable. The high and versatile reactivity of the imidoyl chlorides **2** renders them convenient reagents for the synthesis of pharmacologically promising *N*-phosphorylated and *C,N*-bis(phosphorylated) halovinylsulfonamides **4** and **8**, α-sulfonamido-substituted ethylphosphonate (**5**), and ethylidenebis(phosphonates) (**10**) bearing trifluoromethyl groups. The umpolung of the C and N reaction centers mediated by the phosphorus reagents allows unusual transformations to be accomplished. The revealed effects of the substituents in these reagents can aid the choice of conditions for conducting syntheses of important functionalized organophosphorus compounds having fluorine-containing groups. The study of additional synthetic applications of imidoyl chlorides **2** in reactions with other nucleophiles is now in progress.

## Experimental Section

**General Remarks:** IR spectra were obtained using a UR-20 spectrophotometer. $^1H$, $^{13}C$, $^{19}F$, and $^{31}P$ NMR spectra were recorded with a Varian VXR−300 spectrometer at 299.95, 75.43, 282.20, and 121.42 MHz, respectively, with internal TMS ($^1H$, $^{13}C$), $CFCl_3$ ($^{19}F$), and external 85% $H_3PO_4$ ($^{31}P$) as standards.

***N*-(Trichloroacetyl)benzenesulfonamide (1a):** A mixture of benzenesulfonamide (5 g, 31.8 mmol) and trichloroacetyl chloride (6.36 g, 35.0 mmol) was heated at 130 °C for 4 h. The precipitate that formed was filtered off and washed with petroleum ether to give **1a** (9.6 g, 86%) as a white solid. M.p. 150−151 °C. IR (KBr): $\tilde{\nu}$ = 1180, 1375 (S=O), 1790 (C=O), 3270 (NH) $cm^{-1}$. $^1H$ NMR ($CDCl_3$): δ = 7.61 (t, $^3J_{HH}$ = 8 Hz, 2 H, *m*-C−H, Ph), 7.72 (t, $^3J_{HH}$ = 8 Hz, 1 H, *p*-C−H, Ph), 8.12 (d, $^3J_{HH}$ = 8 Hz, 2 H, *o*-C−H, Ph), 8.95 (s, 1 H, NH) ppm. $C_8H_6Cl_3NO_3S$ (302.56): calcd. C 31.76, H 2.00, Cl 35.15, N 4.63, S 10.60; found C 31.71, H 1.95, Cl 35.38, N 4.72, S 10.86.

**General Procedure for Preparation of *N*-(Trifluoroacetyl)arenesulfonamides 1b,c:** A solution of benzenesulfonamide or *p*-toluenesulfonamide (38.2 mmol) and trifluoroacetic anhydride (45.8 mmol) in benzene (25 mL) was heated under reflux for 6 h. The mixture was cooled and the precipitate was filtered off and washed with benzene and petroleum ether.

***N*-(Trifluoroacetyl)benzenesulfonamide (1b):** White solid, 9.5 g (98%). M.p. 135 °C. IR ($CCl_4$): $\tilde{\nu}$ = 1180, 1370 (S=O), 1780 (C=O), 3260 (NH) $cm^{-1}$. $^1H$ NMR ($CDCl_3$): δ = 7.63 (t, $^3J_{HH}$ = 8 Hz, 2 H, *m*-C−H, Ph), 7.76 (t, $^3J_{HH}$ = 8 Hz, 1 H, *p*-C−H, Ph), 8.13 (d, $^3J_{HH}$ = 8 Hz, 2 H, *o*-C−H, Ph), 9.07 (s, 1 H, NH) ppm. $^{19}F$ NMR ($CDCl_3$): δ = −75.30 ppm. $C_8H_6F_3NO_3S$ (253.20): calcd. C 37.95, H 2.39, N 5.53, S 12.66; found C 37.81, H 2.37, N 5.49, S 12.77.

***N*-Trifluoroacetyl-*p*-toluenesulfonamide (1c):** White solid, 10 g (98%). M.p. 155 °C (ref.[22] m.p. 155.5−156.5 °C). IR (KBr): $\tilde{\nu}$ = 1160, 1375 (S=O), 1790 (C=O), 3270 (NH) $cm^{-1}$. $^1H$ NMR ($CDCl_3$): δ = 2.49 (s, 3 H, $CH_3$), 7.43 (d, $^3J_{HH}$ = 8 Hz, 2 H, Ar), 7.97 (d, $^3J_{HH}$ = 8 Hz, 2 H, Ar), 9.11 (s, 1 H, NH) ppm. $^{19}F$ NMR ($CDCl_3$): δ = −76.30 ppm. $C_9H_8F_3NO_3S$ (267.23): calcd. C 40.45, H 3.02, N 5.24, S 12.00; found C 40.62, H 3.13, N 5.16, S 11.86.

**General Procedure for Preparation of *N*-(Arylsulfonyl)trihaloacetimidoyl Chlorides 2a−c:** A mixture of the appropriate sulfonamide **1** and a small excess of $PCl_5$ was heated under reflux in benzene (15−20 mL) for 6 h (for **2a**) or 2 h (for **2b** and **2c**). The solvent was evaporated under a reduced pressure and the residue was washed with diethyl ether (**2a**, **2c**) or distilled in vacuo (**2b**).

***N*-(Phenylsulfonyl)trichloroacetimidoyl Chloride (2a):** White solid prepared from **1a** (7.0 g, 23.0 mmol) and $PCl_5$ (5.0 g, 24.0 mmol) in 96% yield (7.1 g). M.p. 100−101 °C. IR ($CCl_4$): $\tilde{\nu}$ = 1175, 1365 (S=O), 1640 (C=N) $cm^{-1}$. $^1H$ NMR ($CDCl_3$): δ = 7.61 (t, $^3J_{HH}$ = 8 Hz, 2 H, *m*-C−H, Ph), 7.71 (t, $^3J_{HH}$ = 8 Hz, 1 H, *p*-C−H, Ph), 8.03 (d, $^3J_{HH}$ = 8 Hz, 2 H, *o*-C−H, Ph) ppm. $^{13}C$ NMR ($CDCl_3$): δ = 94.97 (s, $CCl_3$), 127.59 (s, *o*-C, Ph), 129.25 (s, *m*-C, Ph), 134.34 (s, *p*-C, Ph), 138.34 (s, *ipso*-C, Ph), 152.71 (s, C=N) ppm. $C_8H_5Cl_4NO_2S$ (321.00): calcd. C 29.93, H 1.57, Cl 44.18, N 4.36, S 9.99; found C 30.10, H 1.47, Cl 43.88, N 4.29, S 9.85.

***N*-(Phenylsulfonyl)trifluoroacetimidoyl Chloride (2b):** White solid prepared from **1b** (4.0 g, 15.8 mmol) and $PCl_5$ (3.45 g, 16.6 mmol) in 90% yield (3.9 g). B.p. 75−76 °C (0.07 Torr). M.p. 29−30 °C. IR ($CCl_4$): $\tilde{\nu}$ = 1180, 1370 (S=O), 1670 (C=N) $cm^{-1}$. $^1H$ NMR ($CDCl_3$): δ = 7.62 (t, $^3J_{HH}$ = 8 Hz, 2 H, *m*-C−H, Ph), 7.74 (t, $^3J_{HH}$ = 8 Hz, 1 H, *p*-C−H, Ph), 8.02 (d, $^3J_{HH}$ = 8 Hz, 2 H, *o*-C−H, Ph) ppm. $^{13}C$ NMR ($CDCl_3$): δ = 116.20 (q, $^1J_{C,F}$ = 281 Hz, $CF_3$), 127.96 (s, *o*-C, Ph), 129.40 (s, *m*-C, Ph), 134.72 (s, *p*-C, Ph), 137.89 (s, *ipso*-C, Ph), 144.48 (q, $^2J_{C,F}$ = 46 Hz, C=N) ppm. $^{19}F$ NMR ($CDCl_3$): δ = −72.60 ppm. $C_8H_5ClF_3NO_2S$ (271.63): calcd. C 35.37, H 1.86, Cl 13.05, S 11.80; found C 35.52, H 1.47, Cl 13.12, S 11.68.

***N*-(Tosyl)trifluoroacetimidoyl Chloride (2c):** A crystalline solid prepared from **1c** (5.5 g, 20.0 mmol) and $PCl_5$ (4.7 g, 22.0 mmol) in nearly quantitative yield (5.7 g). M.p. 41−42 °C. IR ($CCl_4$): $\tilde{\nu}$ = 1180, 1370 (S=O), 1670 (C=N) $cm^{-1}$. $^1H$ NMR ($CDCl_3$): δ = 2.4 (s, 3 H, $CH_3$), 7.33 (d, $^3J_{HH}$ = 8 Hz, 2 H, Ar), 7.81 (d, $^3J_{HH}$ = 8 Hz, 2 H, Ar) ppm. $^{19}F$ NMR ($CDCl_3$): δ = −72.60 ppm. $C_9H_7ClF_3NO_2S$ (285.67): calcd. C 37.84, H 2.47, Cl 12.41, N 4.90, S 11.22; found C 37.81, H 2.55, Cl 12.43, N 4.85, S 11.31.

**General Procedure for Preparation of Dialkyl *N*-Phenylsulfonyl-*N*-(trichloroethenyl)phosphoramidates 4a,b:** The appropriate phosphite (1.5 mmol) was added to a stirred solution of imidoyl chloride **2a** (1.5 mmol) at 0 °C and then reacted for 2 h at room temperature. The reaction mixture was concentrated in vacuo and the residue was washed with petroleum ether.

**Diethyl *N*-Phenylsulfonyl-*N*-(trichloroethenyl)phosphoramidate (4a):** Colorless oil, 0.57 g (90%). IR ($CCl_4$): $\tilde{\nu}$ = 1040 (POC), 1180, 1380 (S=O), 1290 (P=O) $cm^{-1}$. $^1H$ NMR ($CDCl_3$): δ = 1.32 (t, $^3J_{HH}$ = 7 Hz, 3 H, $CH_3$), 1.36 (t, $^3J_{HH}$ = 7 Hz, 3 H, $CH_3$), 4.13−4.30 (m, 4 H, $OCH_2$), 7.56 (t, $^3J_{HH}$ = 8 Hz, 2 H, Ph), 7.68 (t, $^3J_{HH}$ = 8 Hz, 1 H, Ph), 8.09 (d, $^3J_{HH}$ = 8 Hz, 2 H, Ph) ppm. $^{13}C$ NMR ($CDCl_3$): δ = 15.77 (d, $^3J_{C,P}$ = 6.5 Hz, $CH_3$), 15.80 (d, $^3J_{C,P}$ = 6.5 Hz, $CH_3$), 65.15 (d, $^2J_{C,P}$ = 6 Hz, $CH_2O$), 65.42 (d, $^2J_{C,P}$ = 6 Hz, $CH_2O$), 124.11 (s, $CCl_2$), 128.74 (s, *o*-C, Ph), 128.80 (s, =CCl), 128.94 (s, *m*-C, Ph), 134.26 (s, *p*-C, Ph), 138.31 (s, *ipso*-C, Ph) ppm. $^{31}P$ NMR ($CDCl_3$): δ = −5.1 ppm. $C_{12}H_{15}Cl_3NO_5PS$ (422.65): calcd. C 34.10, H 3.58, Cl 25.16, P 7.33; found C 33.95, H 3.52, Cl 25.11, P 7.38.

**Diisopropyl *N*-Phenylsulfonyl-*N*-(trichloroethenyl)phosphoramidate (4b):** Colorless oil, 0.51 g (76%). IR ($CCl_4$): $\tilde{\nu}$ = 1040 (POC), 1180, 1380 (S=O), 1280 (P=O) $cm^{-1}$. $^1H$ NMR ($CDCl_3$): δ = 1.31 (m, 12 H, $CH_3$), 4.71−4.85 (m, 2 H, OCH), 7.47 (t, $^3J_{HH}$ = 8 Hz, 2 H, *m*-C−H, Ph), 7.59 (t, $^3J_{HH}$ = 8 Hz, 1 H, *p*-C−H, Ph), 8.01 (d, $^3J_{HH}$ = 8 Hz, 2 H, *o*-C−H, Ph) ppm. $^{31}P$ NMR ($CDCl_3$): δ = −8.0 ppm. $C_{14}H_{19}Cl_3NO_5PS$ (450.70): calcd. C 37.31, H 4.25, P 6.87, S 7.11; found C 37.18, H 4.08, P 6.93, S 6.98.

**Diethyl 1-Chloro-2,2,2-trifluoro-1-tosylaminoethylphosphonate (5):** Triethyl phosphite (0.37 g, 2.25 mmol) was added dropwise to a stirred and cooled (−70 °C) solution of imidoyl chloride **2c** (0.64 g, 2.25 mmol) in diethyl ether (10 mL). The precipitated product **5** was isolated by filtration (0.48 g, 45%). M.p. 90−91 °C. IR ($CCl_4$): $\tilde{\nu}$ = 1045 (POC), 1180, 1375 (S=O), 1280 (P=O) $cm^{-1}$. $^1H$ NMR ($CDCl_3$): δ = 1.35 (t, $^3J_{HH}$ = 7 Hz, 3 H, $CH_3CH_2$), 1.38 (t, $^3J_{HH}$ = 7 Hz, 3 H, $CH_3CH_2$), 2.45 (s, 3 H, $CH_3Ar$), 4.28−4.35 (m, 4 H, $OCH_2$), 6.33 (d, $^3J_{HP}$ = 11 Hz, 1 H, NH), 7.33 (d, $^3J_{HH}$ = 8 Hz, 2 H, Ar), 7.82 (d, $^3J_{HH}$ = 8 Hz, 2 H, Ar) ppm. $^{13}C$ NMR ($CDCl_3$): δ = 16.03 (d, $^3J_{C,P}$ = 6.5 Hz, $CH_3CH_2$), 16.12 (d, $^3J_{C,P}$ = 6.5 Hz, $CH_3CH_2$), 21.58 (s, $CH_3Ar$), 66.70 (d, $^2J_{C,P}$ = 8 Hz, $CH_2O$), 67.62 (d, $^2J_{C,P}$ = 8 Hz, $CH_2O$), 75.02 (dq, $^1J_{C,P}$ = 166.7, $^2J_{C,F}$ = 36.7 Hz, CP), 120.96 (q, $^1J_{C,F}$ = 286 Hz, $CF_3$), 128.29, 129.59, 136.71, 144.85 (Ar) ppm. $^{19}F$ NMR ($CDCl_3$): δ = −68.54 ppm. $^{31}P$ NMR ($CDCl_3$): δ = 8.66 ppm. $C_{13}H_{18}ClF_3NO_5PS$ (423.77): calcd. C 36.84, H 4.28, Cl 8.37, P 7.31, S 7.57; found C 36.89, H 4.25, Cl 8.34, P 7.42, S 7.43.

**General Procedure for Preparation of *C*,*N*-Bis(phosphorylated) Compounds 8:** Phosphite **6** (4.4 mmol) was added dropwise to a stirred solution of the appropriate imidoyl chloride **2** (2.2 mmol) in diethyl ether (10 mL) preliminarily cooled to −70 °C. The stirred mixture was warmed to room temperature, the solvent was evaporated in vacuo, and then the oily residue was washed with petroleum ether.

**Diethyl *N*-(2,2-Dichloro-1-diethoxyphosphorylethenyl)-*N*-(phenylsulfonyl)phosphoramidate (8a):** Colorless oil, 0.92 g (80%). IR ($CCl_4$): $\tilde{\nu}$ = 1020 (POC), 1180, 1380 (S=O), 1280 (P=O) $cm^{-1}$. $^1H$ NMR ($CDCl_3$): δ = 1.27 (m, 12 H, $CH_3CH_2$), 4.06−4.27 (m, 8 H, $OCH_2$), 7.47 (t, $^3J_{HH}$ = 8 Hz, 2 H, *m*-H, Ph), 7.58 (t, $^3J_{HH}$ = 8 Hz, 1 H, *p*-H, Ph), 7.99 (d, $^3J_{HH}$ = 8 Hz, 2 H, *o*-H, Ph) ppm. $^{13}C$ NMR ($CDCl_3$): δ = 14.35−16.53 (br, $CH_3$), 63.15 (d, $^2J_{C,P}$ = 6 Hz, $CH_2O$), 63.23 (d, $^2J_{C,P}$ = 6 Hz, $CH_2O$), 64.76 (d, $^2J_{C,P}$ = 6 Hz, $CH_2O$), 64.96 (d, $^2J_{C,P}$ = 6 Hz, $CH_2O$), 126.42 (d, $^1J_{C,P}$ = 221 Hz, CP), 128.13 (s, *o*-Ph), 128.58 (s, *m*-Ph), 133.58 (s, *p*-Ph), 138.16 (s, *ipso*-Ph), 143.73 (dd, $^2J_{C,P}$ = 34, $^3J_{C,P}$ = 6 Hz, $=CCl_2$) ppm. $^{31}P$ NMR ($CDCl_3$): δ = −4.4 (m, 1 P, PN), 9.30 (m, 1 P, PC) ppm. $C_{16}H_{25}Cl_2NO_8P_2S$ (524.29): calcd. C 36.65, H 4.81, Cl 13.52, P 11.82, S 6.12; found C 36.82, H 4.68, Cl 13.49, P 11.74, S 6.31.

**Diethyl *N*-(1-Diethoxyphosphoryl-2,2-difluoroethenyl)-*N*-(phenylsulfonyl)phosphoramidate (8b):** Colorless oil, 0.9 g (83%). IR ($CCl_4$): $\tilde{\nu}$ = 1050 (POC), 1180, 1375 (S=O), 1280 (P=O) $cm^{-1}$. $^1H$ NMR ($CDCl_3$): δ = 1.32 (t, $^3J_{HH}$ = 7 Hz, 6 H, $CH_3$), 1.36 (t, $^3J_{HH}$ = 7 Hz, 6 H, $CH_3$), 4.2 (m, 8 H, $OCH_2$), 7.54 (t, $^3J_{HH}$ = 8 Hz, 2 H, *m*-H, Ph), 7.66 (t, $^3J_{HH}$ = 8 Hz, 1 H, *p*-H, Ph), 8.08 (d, $^3J_{HH}$ = 8 Hz, 2 H, *o*-H, Ph) ppm. $^{19}F$ NMR ($CDCl_3$): δ = −69.92 (ddd, $^2J_{FF}$ = 17.2, $^3J_{FP}$ = 17.2, $^4J_{FP}$ = 8 Hz, 1 F), −64.68 (ddd, $^2J_{FF}$ = 17.2, $^3J_{FP}$ = 21.5, $^4J_{FP}$ = 6 Hz, 1 F) ppm. $^{31}P$ NMR ($CDCl_3$): δ = −3.0 (1 P, PN), 9.76 (1 P, PC) ppm. $C_{16}H_{25}F_2NO_8P_2S$ (491.38): calcd. C 39.11, H 5.13, N 2.85, P 12.61, S 6.53; found C 38.96, H 5.24, N 2.76, P 12.74, S 6.49.

**Diethyl *N*-(1-Diethoxyphosphoryl-2,2-difluoroethenyl)-*N*-tosylphosphoramidate (8c):** Colorless oil, 0.97 g (87%). IR ($CCl_4$): $\tilde{\nu}$ = 1020 (POC), 1180, 1380 (S=O), 1280 (P=O) $cm^{-1}$. $^1H$ NMR ($CDCl_3$): δ = 1.14 (m, 12 H, $CH_3CH_2$), 2.22 (s, 3 H, $CH_3Ar$), 3.95−4.21 (m, 8 H, $OCH_2$), 7.11 (d, $^3J_{HH}$ = 8 Hz, 2 H, Ar), 7.72 (d, $^3J_{HH}$ = 8 Hz, 2 H, Ar) ppm. $^{13}C$ NMR ($CDCl_3$): δ = 15.80 (d, $^3J_{C,P}$ = 6 Hz, $CH_3CH_2$), 15.90 (d, $^3J_{C,P}$ = 6 Hz, $CH_3CH_2$), 16.01 (d, $^3J_{C,P}$ = 6 Hz, $CH_3CH_2$), 16.10 (d, $^3J_{C,P}$ = 6 Hz, $CH_3CH_2$), 21.54 (s, $CH_3Ar$), 63.25 (d, $^2J_{C,P}$ = 6 Hz, $CH_2O$), 63.33 (d, $^2J_{C,P}$ = 6 Hz, $CH_2O$), 64.71 (d, $^2J_{C,P}$ = 6 Hz, $CH_2O$), 65.23 (d, $^2J_{C,P}$ = 6 Hz, $CH_2O$), 89.29 (ddd, $^1J_{C,P}$ = 230, $^2J_{C,F}$ = 41.5, $^2J_{C,F}$ = 7.7 Hz, CP), 128.89 (s, Ar), 129.15 (s, Ar), 135.29 (s, $CSO_2$), 144.96 (s, $CCH_3$), 162.41 (dddd, $^1J_{C,F}$ = 315, $^1J_{C,F}$ = 305, $^2J_{C,P}$ = 35, $^3J_{C,P}$ = 4 Hz, = $CF_2$) ppm. $^{19}F$ NMR ($CDCl_3$): δ = −69.40 (ddd, $^2J_{FF}$ = 17.2, $^3J_{FP}$ = 17.2, $^4J_{FP}$ = 8 Hz, 1 F), −64.20 (ddd, $^2J_{FF}$ = 17.2, $^3J_{FP}$ = 21.2, $^4J_{FP}$ = 5 Hz, 1 F) ppm. $^{31}P$ NMR ($CDCl_3$): δ = −3.0 (dd, $^4J_{PF}$ = 8, $^4J_{PF}$ = 5 Hz, 1 P, PN), 9.85 (dd, $^3J_{PF}$ = 21.2, $^3J_{PF}$ = 17.2 Hz, 1 P, PC) ppm. $C_{17}H_{27}F_2NO_8P_2S$ (505.41): calcd. C 40.40, H 5.38, P 12.26, S 6.34; found C 40.58, H 5.33, P 12.32, S 6.31.

**General Procedure for Preparation of Bis(phosphonates) 10a,b:** A solution of imidoyl chloride **2b,c** (2.2 mmol) and diethyl phosphite (4.4 mmol) in benzene (10 mL) was heated under reflux for 1 h, cooled, and then concentrated in vacuo. The residue was washed with petroleum ether.

**Tetraethyl 2,2,2-Trifluoro-1-(phenylsulfonylamino)ethylidenebis(phosphonate) (10a):** White powder, 0.7 g (63%). M.p. 82 °C. IR ($CCl_4$): $\tilde{\nu}$ = 1050 (POC), 1180, 1360 (S=O), 1275 (P=O) $cm^{-1}$. $^1H$ NMR ($CDCl_3$): δ = 1.31 (t, $^3J_{HH}$ = 7 Hz, 6 H, $CH_3$), 1.34 (t, $^3J_{HH}$ = 7 Hz, 6 H, $CH_3$), 4.21−4.32 (m, 8 H, $OCH_2$), 5.69 (t, $^3J_{HP}$ = 14 Hz, 1 H, NH), 7.49 (t, $^3J_{HH}$ = 8 Hz, 2 H, *m*-H, Ph), 7.53 (t, $^3J_{HH}$ = 8 Hz, 1 H, *p*-H, Ph), 8.04 (d, $^3J_{HH}$ = 8 Hz, 2 H, *o*-H, Ph) ppm. $^{19}F$ NMR ($CDCl_3$): δ = −64.31 (t, $^3J_{FP}$ = 8 Hz) ppm. $^{31}P$ NMR ($CDCl_3$): δ = 11.76 ppm. $C_{16}H_{26}F_3NO_8P_2S$ (511.38): calcd. C 37.58; H 5.12; P 12.11; S 6.27; found C 37.35; H 5.23; P 11.98; S 6.34.

**Tetraethyl 2,2,2-Trifluoro-1-(tosylamino)ethylidenebis(phosphonate) (10b):** White powder, 0.65 g (58%). M.p. 83 °C. IR ($CCl_4$): $\tilde{\nu}$ = 1050 (POC), 1180, 1360 (S=O), 1280 (P=O) $cm^{-1}$. $^1H$ NMR ($CDCl_3$): δ = 1.32 (t, $^3J_{HH}$ = 7 Hz, 6 H, $CH_3CH_2$), 1.34 (t, $^3J_{HH}$ = 7 Hz, 6 H, $CH_3CH_2$), 2.41 (s, 3 H, $CH_3Ar$), 4.18−4.33 (m, 8 H, $OCH_2$), 5.66 (t, $^3J_{HP}$ = 14 Hz, 1 H, NH), 7.30 (d, $^3J_{HH}$ = 8 Hz, 2 H, Ar), 7.91 (d, $^3J_{HH}$ = 8 Hz, 2 H, Ar) ppm. $^{19}F$ NMR ($CDCl_3$): δ = −64.23 (t, $^3J_{FP}$ = 8 Hz) ppm. $^{31}P$ NMR ($CDCl_3$): δ = 11.07 ppm. $C_{17}H_{28}F_3NO_8P_2S$ (525.41): calcd. C 38.86, H 5.37, P 11.79, S 6.10; found C 39.00, H 5.20, P 11.59, S 6.37.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