Synthesis and Reactions of (2,2,2-Trifluoroethyl)triphenylphosphonium Trifluoromethanesulfonate

Takeshi Hanamoto,*[a] Noriko Morita,[a] and Keiko Shindo[a]

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(2,2,2-Trifluoroethyl)triphenylphosphonium trifluoromethanesulfonate (triflate) (**1**) was readily synthesized in high yield from triphenylphosphane and 2,2,2-trifluoroethyl triflate. The Wittig olefination of **1** with aromatic aldehydes bearing electron-withdrawing groups with CsF as a base in DMF proceeded cleanly, producing the corresponding 3,3,3-trifluoropropenylidene compounds in good yields. On the other hand, the hydrolysis of **1** in methanol containing sodium hydroxide gave (2,2-dimethoxyvinyl)triphenylphosphonium triflate (**6a**) in high yield instead of the corresponding (2,2,2-trifluoroethyl)diphenylphosphane oxide. Furthermore, reactions between **1** and secondary amines exclusively gave the novel (*Z*)-(2-amino-2-fluorovinyl)triphenylphosphonium triflates (**10**) in high yields.

Introduction

Organofluorine compounds bearing trifluoromethyl groups continue to be of great interest, due to their potential for materials science and biological science.[1] The development of new methods through which to introduce the trifluoromethyl group into organic compounds therefore remains an important task. An attractive method for the preparation of such compounds is to use suitable building blocks bearing the trifluoromethyl group.[2] Although much effort towards the preparation of such new building blocks has been made, few studies have been devoted to the synthesis and applications of (2,2,2-trifluoroethyl)triphenylphosphonium salts.[3] One of their attractive potential applications should be the Wittig olefination with aldehydes to introduce the 3,3,3-trifluoropropenyl moiety into organic molecules, but related studies were not explored in detail.[3a] This lack of attention might be due to the difficulty encountered in the preparation of these salts.

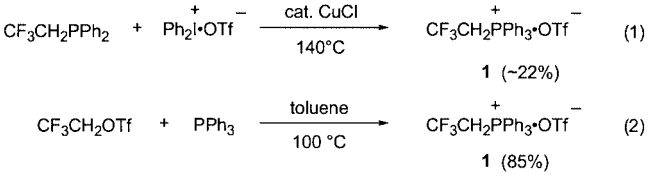
As part of our ongoing research in the development of new fluorinating systems,[4] we became interested in developing a facile synthetic route to (2,2,2-trifluoroethyl)triphenylphosphonium triflate (**1**), with the goal of examining its large potential for the construction of trifluoromethylated organic compounds. This paper describes the facile preparation of **1** and its related Wittig olefination as a useful reaction for introduction of the 3,3,3-trifluoropropenylidene moiety into aldehydes.[5] In addition, the different reactivity of **1** with alkoxides and amines is demonstrated.

[a] Department of Chemistry and Applied Chemistry, Saga University,
Honjyo-machi, Saga 840-8502, Japan
Fax: (internat.) +81-(0)952-288548
E-mail: hanamoto@cc.saga-u.ac.jp

Results and Discussion

1. Preparation of (2,2,2-Trifluoroethyl)triphenylphosphonium Triflate (1)

The reported synthesis of **1** by Umemoto et al. suffered from serious drawbacks such as operational difficulty, requirement for a multistep sequence, and the use of hazardous reagents.[3a] Since this was not acceptable for use as a general synthetic reagent, a new convenient method was required. Previously we had developed an efficient method for the synthesis of (1-fluorovinyl)triphenylphosphonium triflate, using the quaternization of the corresponding (1-fluorovinyl)diphenylphosphane with diphenyliodonium triflate in the presence of Cu^{I}.[4] This method was applied to the preparation of **1**, but our attempt to carry out the quaternization of (2,2,2-trifluoroethyl)diphenylphosphane[6] with diphenyliodonium triflate under similar conditions turned out not to be readily applicable for **1**. The best effort afforded **1** only in low yield (≈22%), as a sticky brown oil (equation 1 in Scheme 1).



Scheme 1. Preparation of **1**

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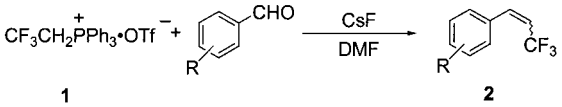
We then turned out attention to an ordinary preparation with triphenylphosphane and 2,2,2-trifluoroethyl triflate. To our delight, this method worked well without any difficulties. The reaction between 2,2,2-trifluoroethyl triflate and triphenylphosphane in dry toluene at 100 °C for 2 days afforded **1** as a white solid in 85% yield (equation 2 in Scheme 1). Its 1H NMR spectrum shows methylene proton signals at δ = 4.83 (ppm) as a double quadruplet attributable to one phosphane and three fluorines. It is also noteworthy that **1** is very stable and easy to handle under standard conditions, in contrast to the corresponding phosphonium iodide described previously.[3b]

2. Wittig Olefination with Aromatic Aldehydes

Although Umemoto et al. had already very briefly reported the Wittig olefination of **1** with benzaldehyde,[3a] we initially performed the Wittig reaction between **1** and 4-methoxybenzaldehyde. The use of conventional bases such as *t*BuOK, LDA, *n*BuLi, and NaH resulted in no formation of olefinic product and the decomposition of **1**, but the use of CsF for this olefination gave some, albeit low, level of success.[3a,7] We therefore conducted the reaction with 2.3 equivalents of CsF both as base and as fluoride ion source in DMF at room temperature to obtain **2** as a mixture of the *E* and *Z* isomers in poor yield.[8] As one solution to this problem, we assumed that certain electronic requirements in the benzene ring might have to be fulfilled for this Wittig reaction. As might be expected, the reaction with aromatic aldehydes bearing strongly electron-withdrawing groups proceeded smoothly, affording the corresponding 3,3,3-trifluoropropenylidene compounds as mixtures of *E* and *Z* isomers in high yields.[9] These results are summarized in Table 1. As some of these products are quite volatile, small losses of material cannot be avoided during the workup and purification. The reaction with benzaldehyde, bearing no electron-withdrawing group on the benzene ring, resulted in a low yield (entry 7), while Wittig olefination with an ordinary aliphatic aldehyde afforded no olefinic product (entry 9). The *E*/*Z* ratios in the products were determined by capillary GC-MS analysis, and the geometrical isomers were characterized by their ^{1}H NMR spectra. A factor of slightly preferential formation of the *Z* isomers might be attributable to the lack of stabilizing effects on the generated betaines, in comparison with the generated β-oxide diphenylphosphane reported by Ishibashi et al.[5] However, the effects of the reaction conditions on these relative *E*/*Z* ratios have not been studied in detail, due to their low selectivity (Scheme 2).

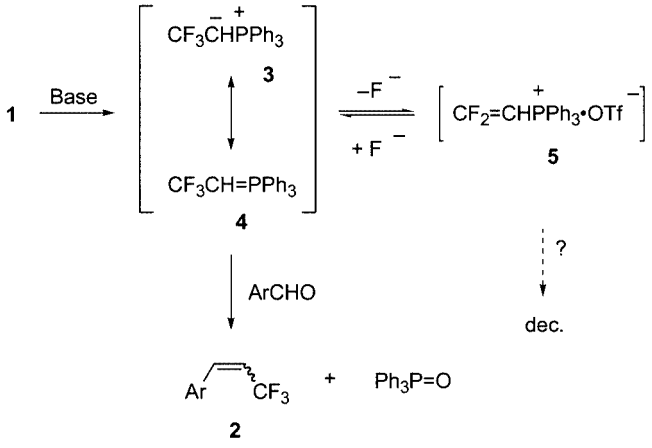
Table 1. Wittig reactions between **1** and various aldehydes



1 **2**

Entry	Aldehyde	Product	Yield (%)[a]	*E*/*Z*[b]
1	4-CF_3-C_6H_4CHO	**2a**	76	41:59
2	4-CN-C_6H_4CHO	**2b**	86	39:61
3	4-Cl-C_6H_4CHO	**2c**	74	40:60
4	2-Cl-C_6H_4CHO	**2d**	64	25:75
5	4-NO_2-C_6H_4CHO	**2e**	90	39:61
6	2-PyCHO[c]	**2f**	85	32:68
7	C_6H_5CHO	**2g**	16	58:42
8	4-MeO-C_6H_4CHO	**2h**	8	55:45
9	$C_6H_5CH_2CH_2$CHO	–	0	–

[a] Isolated yield. [b] Determined by capillary GC-MS analysis. [c] 2-Pyridinecarboxyaldehyde.



Scheme 2. Possible mechanism of Wittig olefination of **1**

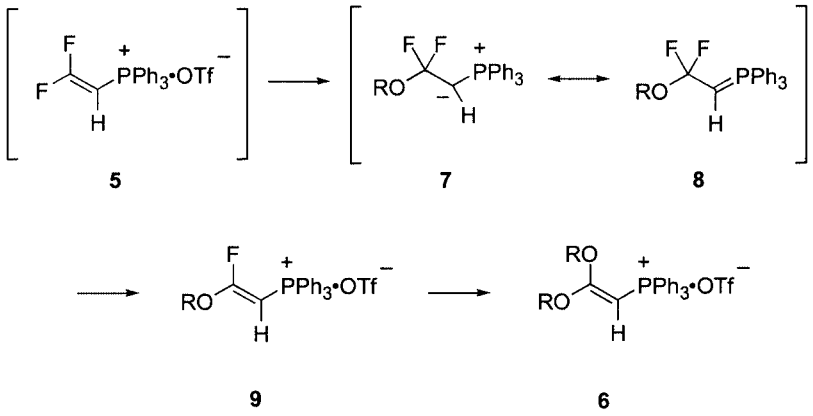
These results suggested the following considerations concerning a possible reaction mechanism:

i. Neither ylide **3** nor phosphorane **4** had lifetimes long enough to react with aldehydes.

ii. As a result, rapid dehydrofluorination (−HF) from **3** or **4** afforded the corresponding (2,2-difluorovinyl)triphenylphosphonium salt **5**, which could not be isolated from the reaction mixture. However, if **5** were to be attacked again by a fluoride anion at the β-position, **3** or **4** should be regenerated in situ. The regenerated species reacted with aldehydes to give the olefinic products.

3. Reactivity of 1 in Aqueous Alcohols Containing Sodium Hydroxide

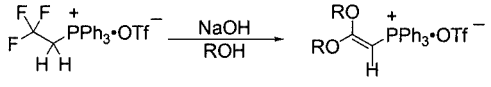
In order to examine other reaction behavior of **1**, we next performed the hydrolysis of **1** with excess sodium hydroxide in methanol. Addition of an excess of aqueous NaOH solution to **1** in methanol afforded not the corresponding (2,2,2-trifluoroethyl)diphenylphosphane oxide, but the (2,2-dimethoxyvinyl)triphenylphosphonium triflate (**6a**) in 95% yield.[10] This finding suggested that the hydroxide or methoxide did not directly attack the phosphorus atom, but abstracted the acidic α proton of **1**. Similar reactions were also observed in alcohols other than methanol, the product yields depending on the alcohols used. These results are shown in Table 2. Ordinary primary aliphatic alcohols gave the (2,2-dialkoxyvinyl)triphenylphosphonium triflates in good yields, but the more acidic 2,2,2-trifluoroethanol gave no corresponding phosphonium salt. The reaction in ethylene glycol, containing a dihydroxy moiety, gave a decreased product yield, while the reaction in bulkier secondary and



Scheme 3. Plausible reaction mechanism for the formation of **6**

tertiary alcohols gave only triphenylphosphane oxide. On the basis of these observations, we considered that good nucleophilicity is essential to the preparation of the (2,2-dialkoxyvinyl)triphenylphosphonium triflates.

Table 2. Preparation of 2,2-dialkoxyvinyl phosphonium salts



1 **6**

Entry	ROH	Product	Yield(%)[a]
1	MeOH	**6a**	95
2	EtOH	**6b**	88
3	CF_3CH_2OH	-	0[b]
4	OH, OH	**6c**	22
5	*i*PrOH	-	0[b]
6	tBuOH	-	0[b]

[a] Isolated yield. [b] Triphenylphosphane oxide was obtained.

Although the detailed reaction path was not clear, we propose the path shown in Scheme 3. As discussed above, the generated salt **5** was attacked by alkoxide to give the new ylide **7** or phosphorane **8**. Subsequently, a second elimination of fluoride ion gave the (2-alkoxy-2-fluorovinyl)triphenylphosphonium triflates (**9**). Repetition of the same process afforded the (2,2-dialkoxyvinyl)triphenylphosphonium triflate (**6**). In consideration of this pathway, we inferred that **5** should be isolable from the reaction between **1** and an equal amount of methoxide. However, treatment of **1** with an equal amount of sodium hydroxide (1 M sodium hydroxide solution in methanol) gave three compounds: **1**, **6**, and **9**, assigned by their ^{1}H NMR spectra. On the basis of these results, we assumed that attack of the methoxide on **5** is faster than abstraction of the α-proton on **1.**

4. Treatment of 1 with Secondary Amines

We next considered that the difference in the nucleophilicity between the alkoxides and the amines might be reflected in single or double addition to fluorinated olefins. The reaction between **1** and diisopropylamine in 1,1,2,2-tetrachloroethane thus proceeded smoothly, exclusively affording the corresponding (*Z*)-(2-fluoro-2-diisopropylaminovinyl)triphenylphosphonium triflate (**10a**) in high yield. The geometric isomer was characterized by its 1H NMR spectrum. As the coupling constant between fluorine and vinyl proton has a value of 42 Hz, we assigned the *Z* form to the isomer. The reason for the exclusive formation of the *Z* isomer could be attributed to the contribution of the stable conformer (**13**) prior to the elimination reaction (Figure 1).

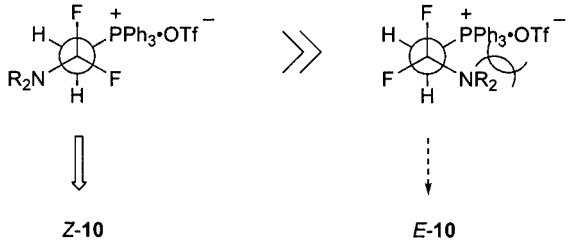
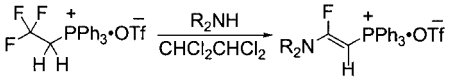


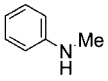
Figure 1. Newman projection of **13**

The reactions between the secondary cyclic alkylamine or the secondary alkyl-arylamines and **1** also worked well to give the corresponding products **10b−10f** in good yields (Table 3). In the case of piperidine (entry 4 in Table 3), the products consisted of the desired fluorinated vinylphosphonium salt **10d** and its hydrolyzed product. Since these two products could not be separated, we isolated them as an amide derivative after subjection to acidic hydrolysis conditions. In further exploration of the scope of this reaction with respect to the primary amine and tertiary amines, we obtained a complex mixture containing none of the desired product in the former case, and the triphenylphosphane oxide in the latter. We have formulated a plausible reaction mechanism, shown in Scheme 4.

Table 3. Preparation of (*Z*)-2-amino-2-fluorovinyl phosphonium salts



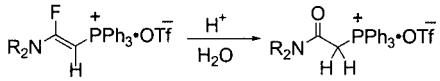
1 **10**

Entry	R_2NH	Product	Yield(%)[a]
1		**10a**	90
2		**10b**	77
3		**10c**	88
4		**(10d)**	-[b]
5		**10e**	93
6		**10f**	70
7	$(Me_3Si)_2NH$	-	0[c]
8		-	0[c]

[a] Isolated yield. [b] The product **10d** was contaminated with the corresponding amide **14d**. These two compounds could not be separated. See text. [c] Triphenylphosphane oxide was obtained.

As mentioned above, we noticed that the fluorinated vinylphosphonium salts **10** are easily susceptible to acidic hydrolysis reactions because of the favorable release of the fluorine atom. Thus, after the $CDCl_3$ solution containing **10** had stood at room temperature for several hours, the solvent was removed to afford the corresponding (2-carbamoylmethyl)triphenylphosphonium triflate (**14**) in good yields.[11] We considered that a trace amount of DCl (or HCl) and H_2O in the $CDCl_3$ solution caused this transformation. These results are shown in Table 4.

Table 4. Hydrolysis of (*Z*)-2-amino-2-fluorovinyl phosphonium salts



10 **14**

Entry	R_2N	Product	Yield(%)[a]
1		**14a**	90
2		**14b**	73
3		**14c**	84
4		**14d**	88[b]

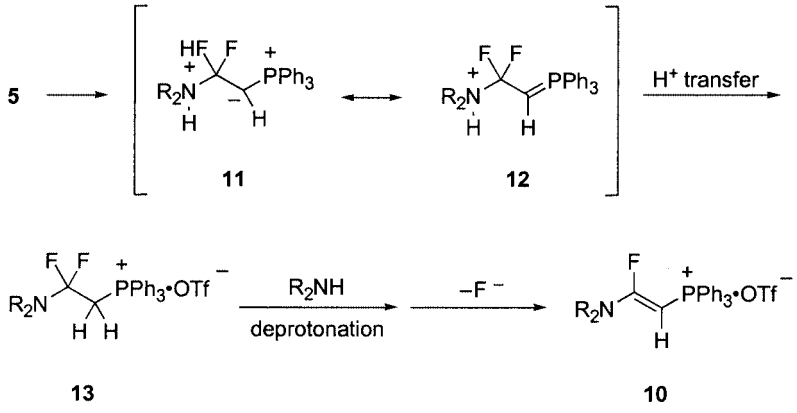
[a] Isolated yield. [b] The overall yield from **1**. See text.

Conclusion

We have developed a new and facile synthetic route to the preparation of (2,2,2-trifluoroethyl)triphenylphosphonium triflate (**1**), which should be utilizable for the preparation of various 3,3,3-trifluoropropenyl compounds. We have also demonstrated the different reactivity of **1** toward alkoxides and amines.

Experimental Section

General: Melting point: Yanako micro melting point apparatus MP-S3. NMR: JEOL JNM-GX 270 and AL-300. Chemical shifts were reported as δ values (ppm) relative to internal tetramethylsilane (^1H) or (trifluoromethyl)benzene (^{19}F) in $CDCl_3$ unless otherwise noted. GC-MS: JEOL JMS-AMII15 mass spectrometer. HRMS and FAB-MS: JEOL JMS-HA100A mass spectrometer at the Institute for Fundamental Research in Organic Chemistry,



Scheme 4. Plausible reaction mechanism for the formation of **10**

Kyushu University. IR: Perkin−Elmer SPECTRUM 2000 FT-IR. Elemental analysis: the Service Center for Elemental Analysis of Organic Compounds affiliated to the Faculty of Science, Kyushu University. Analytical thin-layer chromatography (TLC) and column chromatography were performed on silica gel 60 F_{254} (Merck) and silica gel 60 (40−63 μm), respectively. Toluene, 1,1,2,2-tetrachloroethane, and DMF were used after distillation from CaH_2.

(2,2,2-Trifluoroethyl)triphenylphosphonium Triflate (1):[3a] Triphenylphosphane (3.19 g, 12.1 mmol) was added at room temperature under an argon atmosphere to a solution of 2,2,2-trifluoroethyl triflate (1.88 g, 8.11 mmol) in dry toluene (10 mL). The mixture was heated at 100 °C for 2 days. The precipitate was collected, washed with diethyl ether, and dried in vacuo. The solid was pure enough for microanalysis. Yield 3.39 g (85%). M.p. 205.7−206.6 °C. ^{1}H NMR (270 MHz): δ = 4.83 (dq, *J* = 13.7, 9.8 Hz, 2 H), 7.69−7.86 (m, 15 H) ppm. ^{19}F NMR (283 MHz): δ = −54.7 (3 F, dt, *J* = 7.9, 9.8 Hz), −79.7 (3 F, s) ppm. IR (KBr): ṽ = 2957, 2917, 1589, 1440, 1333, 1290, 1242, 1150, 1130, 1091, 1033, 998, 753, 722, 689 cm^{-1}. FABMS: *m*/*z* = 345 [M^+ − OTf^-]. $C_{21}H_{17}F_6O_3PS$ (494.39): calcd. C 51.01, H 3.47; found C 51.14, H 3.47.

Wittig Reactions between 1 and Aldehydes. General Procedure (Table 1). (*E*)- and (*Z*)-3,3,3-Trifluoro-1-[4-(trifluoromethyl)phenyl]-1-propene (2a) (Table 1, entry 1): CsF (116 mg, 0.76 mmol) was added at room temperature to a solution of **1** (162 mg, 0.33 mmol) and 4-(trifluoromethyl)benzaldehyde (49 μL, 0.36 mmol) in dry DMF (3 mL). After stirring for 8 h, the solution was quenched with H_2O. The mixture was extracted twice with hexane/diethyl ether (3:1), and the combined organic layer was dried over Na_2SO_4. The solution was concentrated in vacuo and the residue was purified by silica gel column chromatography (pentane) to give **2a** (60.1 mg) as a colorless oil.

(*E*)- and (*Z*)-3,3,3-Trifluoro-1-[4-(trifluoromethyl)phenyl]-1-propene (2a): Yield 76%. *E* isomer: R_f = 0.68; hexane/ethyl acetate (20:1); colorless oil. ^{1}H NMR (270 MHz): δ = 6.29 (dq, *J* = 16.1, 6.3 Hz, 1 H), 7.19 (dq, *J* = 16.1, 2.0 Hz, 1 H), 7.57 (d, *J* = 8.3 Hz, 2 H), 7.66 (d, *J* = 8.3 Hz, 2 H) ppm. ^{19}F NMR (283 MHz): δ = −64.2 (3 F, s), −65.0 (3 F, dt, *J* = 6.3, 2.0 Hz) ppm. IR (neat): ṽ = 1669, 1621, 1584, 1420, 1327, 1316, 1286, 1210, 1172, 1127, 1109, 1068, 1018, 974, 860, 840, 819, 690 cm^{-1}. GC-MS: *m*/*z* = 240 (23) [M^+], 171 (53), 151 (100), 150 (12), 75 (11), 69 (11). $C_{10}H_6F_6$ (240.04): calcd. C 50.02, H 2.52; found C 50.31, H 2.67. *Z* isomer: R_f = 0.49; hexane/ethyl acetate(20:1), colorless oil. ^{1}H NMR (270 MHz): δ = 5.90 (dq, *J* = 12.7, 8.8 Hz, 1 H), 6.98 (d, *J* = 12.7 Hz, 1 H), 7.49 (d, *J* = 8.3 Hz, 2 H), 7.64 (d, *J* = 8.3 Hz, 2 H) ppm. ^{19}F NMR (283 MHz): δ = −58.9 (3 F, d, *J* = 8.8 Hz), −64.1 (3 F, s) ppm. IR (neat): ṽ = 1661, 1621, 1407, 1329, 1282, 1227, 1180, 1129, 1068, 1019, 883, 839, 731 cm^{-1}. GC-MS: *m*/*z* = 240 (23) [M^+], 171 (53), 151 (100), 150 (12), 75 (11), 69 (11). HRMS ($C_{10}H_6F_6$): calcd. 240.0373; found 240.0360.

(*E*)- and (*Z*)-1-(4-Cyanophenyl)-3,3,3-trifluoro-1-propene (2b): Yield 86%. *E* isomer: R_f = 0.70; hexane/ethyl acetate (4:1), white solid. M.p. 45.2−46.2 °C. ^{1}H NMR (270 MHz): δ = 6.31 (dq, *J* = 16.1, 6.3 Hz, 1 H), 7.17 (dq, *J* = 16.1, 2.4 Hz, 1 H), 7.56 (d, *J* = 8.3 Hz, 2 H), 7.70 (d, *J* = 8.3 Hz, 2 H) ppm. ^{19}F NMR (283 MHz): δ = −65.2 (3 F, dd, *J* = 6.3, 2.4 Hz) ppm. IR (neat): ṽ = 3066, 2228, 1668, 1609, 1564, 1510, 1416, 1339, 1317, 1279, 1210, 1115, 980, 879, 840, 815, 660 cm^{-1}. GC-MS: *m*/*z* = 197 (100) [M^+], 196 (24), 176 (21), 147 (72), 128 (58), 127 (37), 101 (28), 75 (37), 51 (25), 50 (22). $C_{10}H_6F_3N$ (197.16): calcd. C 60.92, H 3.07, N 7.10; found C 61.26, H 3.16, N 7.06. *Z* isomer: R_f = 0.53; hexane/ethyl acetate (4:1), colorless oil. ^{1}H NMR (270 MHz): δ = 5.93 (dq, *J* = 12.7, 8.8 Hz, 1 H), 6.96 (d, *J* = 12.7 Hz, 1 H), 7.47 (d, *J* = 8.3 Hz, 2 H), 7.67 (d, *J* = 8.3 Hz, 2 H) ppm. ^{19}F NMR (283 MHz): δ = −59.0 (3 F, d, *J* = 8.8 Hz) ppm. IR (neat): ṽ = 3059, 2232, 1659, 1608, 1508, 1405, 1278, 1225, 1189, 1172, 1130, 1021, 883, 837, 753 cm^{-1}. GC-MS: *m*/*z* = 197 (100) [M^+], 196 (23), 176 (20), 147 (74), 128 (53), 127 (32), 101 (25), 75 (34), 51 (23). $C_{10}H_6F_3N$ (197.16): calcd. C 60.92, H 3.07, N 7.10; found C 61.07, H 3.12, N 7.29.

(*E*)- and (*Z*)-1-(4-Chlorophenyl)-3,3,3-trifluoro-1-propene (2c): Yield 74%. *E*/*Z* mixture: R_f = 0.68, 0.54; hexane/ethyl acetate (20:1), colorless oil. ^{1}H NMR (270 MHz): δ = 5.79 (dq, *J* = 12.5, 8.8 Hz, 1 H), 6.18 (dq, *J* = 16.1, 6.3 Hz, 1 H), 6.88 (d, *J* = 12.5 Hz, 1 H), 7.11 (dq, *J* = 16.1, 2.4 Hz, 1 H), 7.34 (s, 4 H), 7.38 (s, 4 H) ppm. ^{19}F NMR (283 MHz): δ = −58.9 (3 F, d, *J* = 8.8 Hz), −64.7 (3 F, ddd, *J* = 6.3, 2.4, 1.2 Hz) ppm. IR (neat): ṽ = 1666, 1597, 1494, 1410, 1332, 1316, 1276, 1225, 1180, 1130, 1015, 973, 877, 831, 809 cm^{-1}. GC-MS: *E* isomer *m*/*z* = 206 (80) [M^+], 171 (32), 151 (100), 102 (34), 101 (43), 75 (39). *Z* isomer *m*/*z* = 206 (72) [M^+], 171 (31), 151 (100), 102 (34), 101 (43), 75 (41). $C_9H_6ClF_3$ (206.59): calcd. C 52.32, H 2.93; found C 52.71, H 3.03.

(*E*)- and (*Z*)-1-(2-Chlorophenyl)-3,3,3-trifluoro-1-propene (2d): Yield 64%. *E*/*Z* mixture: R_f = 0.54, 0.69; hexane/ethyl acetate (20:1), colorless oil. ^{1}H NMR (270 MHz): δ = 5.90 (dq, *J* = 12.7, 8.8 Hz, 1 H), 6.21 (dq, *J* = 16.1, 6.3 Hz, 1 H), 7.07 (d, *J* = 12.7 Hz, 1 H), 7.23−7.61 (m, 9 H) ppm. ^{19}F NMR (283 MHz): δ = −59.2 (3 F, d, *J* = 8.8 Hz), −64.9 (3 F, dd, *J* = 6.3, 2.2 Hz) ppm. IR (neat): ṽ = 1664, 1476, 1439, 1412, 1315, 1275, 1220, 1188, 1130, 1054, 1037, 970, 771, 747 cm^{-1}. GC-MS: *E* isomer *m*/*z* = 206 (82) [M^+], 171 (52), 151 (100), 102 (42), 101 (57), 75 (58), 51 (30). *Z* isomer *m*/*z* = 206 (78) [M^+], 171 (51), 151 (100), 102 (35), 101 (49), 75 (41). $C_9H_6ClF_3$ (206.59): calcd. C 52.32, H 2.93; found C 52.64, H 3.03.

(*E*)- and (*Z*)-3,3,3-Trifluoro-1-(4-nitrophenyl)-1-propene (2e): Yield 90%. *E* isomer: R_f = 0.74; hexane/ethyl acetate (3:1), yellow solid. M.p. 84.0−85.8 °C. ^{1}H NMR (270 MHz): δ = 6.37 (dq, *J* = 16.1, 6.3 Hz, 1 H), 7.23 (dq, *J* = 16.1, 2.4 Hz, 1 H), 7.63 (d, *J* = 8.8 Hz, 2 H), 8.27 (d, *J* = 8.8 Hz, 2 H) ppm. ^{19}F NMR (283 MHz): δ = −65.3 (3 F, dd, *J* = 6.3, 2.4 Hz) ppm. IR (neat): ṽ = 1668, 1652, 1601, 1568, 1557, 1539, 1505, 1417, 1090, 958, 868, 822, 747, 687 cm^{-1}. GC-MS: *m*/*z* = 217 (18) [M^+], 151 (100), 109 (44), 102 (32), 101 (23), 75 (20), 51 (20). HRMS: $C_9H_6F_3NO_2$: calcd. 217.0351; found 217.0361. *Z* isomer: R_f = 0.56; hexane/ethyl acetate (3:1), colorless oil. ^{1}H NMR (270 MHz): δ = 5.98 (dq, *J* = 12.7, 8.8 Hz, 1 H), 7.02 (d, *J* = 12.7 Hz, 1 H), 7.53 (d, *J* = 8.8 Hz, 2 H), 8.24 (d, *J* = 8.8 Hz, 2 H) ppm. ^{19}F NMR (283 MHz): δ = −59.0 (3 F, d, *J* = 8.8 Hz) ppm. IR (neat): ṽ = 3083, 2859, 1661, 1601, 1524, 1497, 1423, 1403, 1348, 1313, 1281, 1227, 1180, 1129, 1016, 976, 888, 857, 783, 766, 747, 726, 688 cm^{-1}. GC-MS: *m*/*z* = 217 (19) [M^+], 151 (100), 109 (42), 102 (21), 101 (21), 75 (21), 51 (17). HRMS ($C_9H_6F_3NO_2$): calcd. 217.0351; found 217.0347. $C_9H_6ClF_3$ (217.15): calcd. C 49.78, H 2.78, N 6.45; found C 50.05, H 2.88, N 6.65.

(*E*)-and (*Z*)-3,3,3-Trifluoro-1-(2-pyridyl)-1-propene (2f): Yield 85%. *E* isomer: R_f = 0.61; hexane/ethyl acetate (3:1), colorless oil. ^{1}H NMR (270 MHz): δ = 6.82 (dq, *J* = 15.6, 6.8 Hz, 1 H), 7.18 (dq, *J* = 15.6, 2.0 Hz, 1 H), 7.29 (ddd, *J* = 7.8, 4.9, 1.0 Hz, 1 H), 7.35 (d, *J* = 7.8 Hz, 1 H), 7.73 (dt, *J* = 2.0, 7.8 Hz, 1 H), 8.61−8.67 (m, 1 H) ppm. ^{19}F NMR (283 MHz): δ = −65.1 (3 F, dd, *J* = 6.8, 2.0 Hz) ppm. IR (neat): ṽ = 2928, 1672, 1590, 1471, 1435, 1334, 1307, 1267, 1204, 1124, 1092, 994, 973, 879, 846, 767, 742, 694 cm^{-1}. GC-MS: *m*/*z* = 173 (25) [M^+], 104 (100), 79 (20), 51 (21). *Z* isomer: R_f = 0.39; hexane/ethyl acetate (3:1), colorless oil. ^{1}H

NMR (270 MHz): δ = 5.96 (dq, *J* = 12.9, 8.8 Hz, 1 H), 7.02 (d, *J* = 12.9 Hz, 1 H), 7.26 (ddd, *J* = 7.8, 4.9, 1.0 Hz, 1 H), 7.50 (d, *J* = 7.8 Hz, 1 H), 7.72 (dt, *J* = 2.0, 7.8 Hz, 1 H), 8.62−8.69 (m, 1 H) ppm. ^{19}F NMR (283 MHz): δ = −59.2 (3 F, d, *J* = 8.8 Hz) ppm. IR (neat): ṽ = 1662, 1588, 1569, 1470, 1438, 1411, 1281, 1220, 1196, 1127, 1093, 994, 874, 803, 746 cm^{-1}. GC-MS: *m*/*z* = 173 (20) [M$^+$], 104 (100), 78 (21), 51 (22). HRMS ($C_9H_6F_3NO_2$): calcd. 173.0452; found 173.0459.

Preparation of (2,2-Dialkoxyvinyl)triphenylphosphonium Triflate. General Procedure (Table 2). (2,2-Dimethoxyvinyl)triphenylphosphonium Triflate (6a): NaOH solution (1 M, 10 mL) was added slowly at 0 °C to a solution of **1** (101 mg, 0.2 mmol) in methanol (2 mL). The mixture was stirred for 12 h at ambient temperature. The organic layer was separated, and the remaining aqueous layer was extracted with CH_2Cl_2 (5 mL × 2). The combined organic layer was dried over Na_2SO_4 and the solution was concentrated in vacuo. The residue was purified by silica gel (containing 6% H_2O) column chromatography (CH_2Cl_2/acetone, 3:1) to give **6a** as a sticky oil. The oil was allowed to stand at room temperature to form the corresponding solid.

(2,2-Dimethoxyvinyl)triphenylphosphonium Triflate (6a): Yield 95%, white solid. M.p. 132.2−133.2 °C. ^{1}H NMR (270 MHz): δ = 3.52 (s, 3 H), 4.21 (s, 3 H), 4.41 (d, *J* = 10.7 Hz, 1 H), 7.62−7.74 (m, 15 H) ppm. IR (KBr): ṽ = 3109, 3063, 1583, 1475, 1436, 1360, 1266, 1149, 1113, 1034, 928, 753, 724, 693 cm^{-1}. $C_{23}H_{22}F_3O_5PS$ (498.44): calcd. C 55.42, H 4.45; found C 55.18, H 4.42.

(2,2-Diethoxyvinyl)triphenylphosphonium Triflate (6b): Yield 88%. ^{1}H NMR (300 MHz): δ = 0.73 (t, *J* = 7.2 Hz, 3 H), 1.48 (t, *J* = 7.2 Hz, 3 H), 4.00 (q, *J* = 7.2 Hz, 2 H), 4.24 (dd, *J* = 1.5, 11.4 Hz, 1 H), 4.46 (q, *J* = 7.2 Hz, 2 H), 7.69−7.86 (m, 15 H) ppm. Since this compound was not easily solidified, we attempted the following procedure. The CH_2Cl_2 solution containing **6b** was slowly added to diethyl ether while being stirred vigorously. A precipitate generally formed with progressing dropwise addition of the CH_2Cl_2 solution, but we found that the generated solid was not **6b** but the corresponding hydrolysis product (**6b′**, see below).

(Ethoxycarbonylmethyl)triphenylphosphonium Triflate (6b′):[12] White solid. M.p. 135.2−137.6 °C. ^{1}H NMR (300 MHz): δ = 1.09 (t, *J* = 7.2 Hz, 3 H), 4.07 (q, *J* = 7.2 Hz, 2 H), 4.83 (dd, *J* = 13.6, 1.1 Hz, 2 H), 7.53−7.84 (m, 15 H) ppm. IR (KBr): ṽ = 3060, 2944, 2885, 1748, 1588, 1475, 1442, 1368, 1258, 1151, 1110, 1031, 756, 722, 692 cm^{-1}. $C_{23}H_{22}F_3O_5PS$ (498.44): calcd. C 55.42, H 4.45; found C 55.47, H 4.23.

([1,3]Dioxolan-2-ylidenemethyl)triphenylphosphonium Triflate (6c): Yield 22%, white solid. M.p. 134.7−136.8 °C. ^{1}H NMR (300 MHz): δ = 4.16 (d, *J* = 10.3 Hz, 1 H), 4.60 (t, *J* = 7.3 Hz, 2 H), 4.76 (t, *J* = 7.3 Hz, 2 H), 7.54−7.79 (m, 15 H) ppm. IR (KBr): ṽ = 3049, 2926, 1615, 1259, 1151, 1110, 1061, 911, 755, 734, 692 cm^{-1}. $C_{23}H_{20}F_3O_5PS$ (496.44): calcd. C 55.65, H 4.06; found C 55.50, H 4.05.

Preparation of (*Z*)-(2-Amino-2-fluorovinyl)triphenylphosphonium Triflate. General Procedure (Table 3). (*Z*)-(2-Fluoro-2-diisopropylaminovinyl)triphenylphosphonium Triflate (10a): Diisopropylamine (43 μL, 0.31 mmol) was added slowly at room temperature to a solution of **1** (100 mg, 0.20 mmol) in 1,1,2,2-tetrachloroethane (3 mL). The mixture was stirred for 12 h at ambient temperature. The organic layer was separated, and the remaining aqueous layer was extracted with CH_2Cl_2 (5 mL × 2). The combined organic layer was dried over Na_2SO_4 and the solution was concentrated in vacuo. The residue was purified by silica gel (containing 6% H_2O) column chromatography (CH_2Cl_2, then CH_2Cl_2/acetone, 3:1) to give **10a** (101 mg) as a solid.

(*Z*)-(2-Fluoro-2-diisopropylaminovinyl)triphenylphosphonium Triflate (10a): Yield 90%, white solid. M.p. 128.5−129.2 °C. ^{1}H NMR (270 MHz): δ = 1.309 (d, *J* = 6.8 Hz, 6 H), 1.313 (d, *J* = 6.8 Hz, 6 H), 3.90−4.10 (m, 2 H), 4.35 (dd, *J* = 43.0, 8.8 Hz, 1 H), 7.58−7.76 (m, 15 H) ppm. ^{19}F NMR (283 MHz): δ = −60.0 (1 F, br. d, *J* = 43.0 Hz), −79.4 (3 F, s) ppm. IR (KBr): ṽ = 3094, 3058, 2986, 2940, 2880, 1600, 1575, 1440, 1266, 1150, 1107, 899, 846, 749, 717, 693 cm^{-1}. $C_{27}H_{30}F_4NO_3PS$ (555.56): calcd. C 58.37, H 5.44, N 2.52; found C 58.77, H 5.42, N 2.40.

(*Z*)-(2-Fluoro-2-molphorylaminovinyl)triphenylphosphonium Triflate (10b): Yield 77%, white solid. M.p. 137.8−139.9 °C. ^{1}H NMR (270 MHz): δ = 3.58 (t, *J* = 5.4 Hz, 4 H), 3.81 (t, *J* = 5.4 Hz, 4 H), 4.69 (dd, *J* = 42.0, 7.3 Hz, 1 H), 7.61−7.77 (m, 15 H) ppm. ^{19}F NMR (283 MHz) δ = −70.0 (1 F, br. d, *J* = 42.0 Hz), −79.5 (3 F, s) ppm. IR (KBr): ṽ = 3589, 3518, 3067, 2920, 2857, 1615, 1452, 1438, 1367, 1253, 1164, 1106, 1033, 878, 836, 756, 722, 692 cm^{-1}. $C_{25}H_{24}F_4NO_4PS$ (541.49): calcd. C 55.45, H 4.47, N 2.59; found C 55.30, H 4.50, N 2.61.

(*Z*)-(2-Diethylamino-2-fluorovinyl)triphenylphosphonium Triflate (10c): Yield 88%, white solid. M.p. 114.2−115.8 °C. ^{1}H NMR (270 MHz): δ = 1.27 (t, *J* = 7.2 Hz, 6 H), 3.49 (q, *J* = 7.2 Hz, 4 H), 4.13 (dd, *J* = 42.0, 8.1 Hz, 1 H), 7.58−7.91 (m, 15 H) ppm. ^{19}F NMR (283 MHz): δ = −68.0 (1 F, dd, *J* = 42.0, 8.3 Hz), −79.4 (3 F, s) ppm. IR (KBr): ṽ = 3072, 2984, 1615, 1574, 1480, 1440, 1258, 1109, 1032, 967, 856, 756, 719, 693 cm^{-1}. $C_{25}H_{26}F_4NO_3PS$ (527.51): calcd. C 56.92, H 4.97, N 2.66; found C 56.92, H 5.00, N 2.61.

4.5.4. (*Z*)-(2-Fluoro-2-*N*-methylanilinovinyl)triphenylphosphonium Triflate (10e): Yield 93%, white solid. M.p. 159.5−161.2 °C. ^{1}H NMR (300 MHz): δ = 3.56 (d, *J* = 2.0 Hz, 3 H), 4.30 (dd, *J* = 39.6, 7.8 Hz, 1 H), 7.31−7.46 (m, 5 H), 7.62−7.77 (m, 15 H) ppm. ^{19}F NMR (283 MHz): δ = −65.2 (1 F, br. d, *J* = 39.6 Hz), −79.4 (3 F, s) ppm. IR (KBr): ṽ = 3060, 2291, 1816, 1634, 1615, 1590, 1574, 1557, 1494, 1464, 1394, 1316, 1265, 1222, 1185, 1153, 1110, 1027, 997, 977, 841, 777, 747, 723, 691 cm^{-1}. $C_{28}H_{24}F_4NO_3PS$ (561.53): calcd. C 59.89, H 4.31, N 2.49; found C 59.88, H 4.35, N 2.48.

(*Z*)-(2-Fluoro-2-indolinylvinyl)triphenylphosphonium Triflate (10f): Yield 70%, white solid. M.p. 151.0−152.0 °C. ^{1}H NMR (300 MHz): δ = 3.36 (t, *J* = 8.3 Hz, 2 H), 4.38 (t, *J* = 8.3 Hz, 2 H), 4.76 (dd, *J* = 40.7, 7.2 Hz, 1 H), 7.01−7.23 (m, 4 H), 7.47−7.78 (m, 15 H) ppm. ^{19}F NMR (283 MHz): δ = −71.5 (1 F, br. d, *J* = 40.7 Hz), −79.5 (3 F, s) ppm. IR (KBr): ṽ = 3423, 3064, 2960, 2853, 1990, 1907, 1823, 1574, 1488, 1471, 1441, 1417, 1369, 1259, 1224, 1189, 1147, 1109, 1032, 997, 844, 753, 722, 693, 669 cm^{-1}. $C_{29}H_{24}F_4NO_3PS$ (573.54): calcd. C 60.73, H 4.22, N 2.44; found C 60.82, H 4.23, N 2.40.

Preparation of [(Carbamoyl)methyl]triphenylphosphonium Triflate − General Procedure (Table 4). [(Diisopropylcarbamoyl)methyl]triphenylphosphonium Triflate (14a): $CDCl_3$ (500 μL) was added slowly at room temperature to a solution of **10a** (51.8 mg, 0.09 mmol) in CH_2Cl_2 (3 mL). The mixture was stirred for 12 h at ambient temperature. After the solution had been concentrated in vacuo, the residue was purified by silica gel (containing 6% H_2O) column chromatography (CH_2Cl_2 then CH_2Cl_2/acetone, 3:1) to give **14a** (46.5 mg) as a white solid.

[(Diisopropylcarbamoyl)methyl]triphenylphosphonium Triflate (14a): Yield 90%, white solid. M.p. 157.6−158.8 °C. ^{1}H NMR (300 MHz): δ = 1.17 (d, *J* = 6.8 Hz, 6 H), 1.26 (d, *J* = 6.4 Hz, 6 H), 3.34−3.48 (m, 1 H), 4.32−4.41 (m, 1 H), 4.94 (d, *J* = 13.0 Hz, 2 H), 7.58−7.79 (m, 15 H) ppm. IR (KBr): ṽ = 2937, 1634, 1440, 1374, 1344, 1261, 1225, 1156, 1112, 1031, 742, 721, 690 cm^{-1}. $C_{27}H_{31}F_3NO_4PS$ (553.58): calcd. C 58.58, H 5.64, N 2.53; found C 58.56, H 5.70, N 2.47.

(2-Morpholino-2-oxoethyl)triphenylphosphonium Triflate (14b): Yield 73%, white solid. M.p. 198.2−200.0 °C. ^{1}H NMR (300 MHz): δ = 3.48 (t, *J* = 4.2 Hz, 2 H), 3.61 (t, *J* = 4.6 Hz, 2 H), 3.75−3.78 (4 H, br. s), 4.95 (d, *J* = 13.2 Hz, 2 H), 7.62−7.80 (m, 15 H) ppm. IR (KBr): ṽ = 3440, 2935, 2892, 1645, 1441, 1388, 1259, 1224, 1154, 1115, 1070, 1030, 998, 869, 749, 718, 690 cm^{-1}. $C_{25}H_{25}F_3NO_5PS$ (539.51): calcd. C 55.66, H 4.67, N 2.60; found C 55.44, H 4.74, N 2.50.

(Diethylcarbamoylmethyl)triphenylphosphonium Triflate (14c): Yield 84%, white solid. M.p. 159.8−162.1 °C. ^{1}H NMR (300 MHz): δ = 1.00 (t, *J* = 7.2 Hz, 3 H), 1.23 (t, *J* = 7.2 Hz, 3 H), 3.28 (q, *J* = 7.2 Hz, 2 H), 3.63 (q, *J* = 7.2 Hz, 2 H), 4.89 (d, *J* = 13.2 Hz, 2 H), 7.61−7.80 (m, 15 H) ppm. IR (KBr): ṽ = 2977, 2926, 2891, 1633, 1469, 1436, 1393, 1259, 1161, 1111, 1029, 997, 957, 914, 872, 751, 717, 691 cm^{-1}. $C_{25}H_{27}F_3NO_4PS$ (525.52): calcd. C 57.14, H 5.18, N 2.67; found C 57.23, H 5.12, N 2.67.

(2-Oxo-2-piperidine-1-yl-ethyl)triphenylphosphonium Triflate (14d): Yield 88%, white solid. M.p. 166.2−167.2 °C. ^{1}H NMR (300 MHz): δ = 1.47−1.50 (m, 2 H), 1.60−1.68 (m, 4 H), 3.42 (t, *J* = 5.7 Hz, 2 H), 3.68 (t, *J* = 5.7 Hz, 2 H), 4.92 (d, *J* = 13.0 Hz, 2 H), 7.60−7.80 (m, 15 H) ppm. IR (KBr): ṽ = 3855, 3448, 2928, 1634, 1437, 1393, 1259, 1159, 1031, 870, 752, 717, 691 cm^{-1}. $C_{26}H_{27}F_3NO_4PS$ (537.53): calcd. C 58.10, H 5.06, N 2.61; found C 57.88, H 4.99, N 2.56.

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