Convenient Synthesis of 3,3,3-Trifluoropropenyl Compounds from Aromatic Aldehydes by Means of the TBAF-Mediated Horner Reaction

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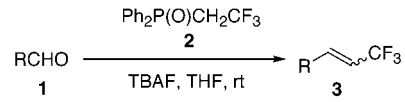
Abstract: A simple synthesis of 3,3,3-trifluoropropenyl compounds by means of the TBAF-mediated Horner reaction is described. The reagent, 2,2,2-trifluoroethyldiphenylphosphine oxide, was readily prepared either by Arbuzov reaction of ethyl diphenylphosphinite with 2,2,2-trifluoroethyl iodide or by treating chlorodiphenylphosphine with trifluoroacetic acid and water. Treatment of the phosphine oxide with aromatic aldehydes in the presence of TBAF at room temperature afforded the corresponding 3,3,3-trifluoropropenyl compounds in good yields. The present method is very convenient for preparing 3,3,3-trifluoropropenyl compounds from aromatic aldehydes in terms of availability of the reagent, operational simplicity, and good yields of the products.

It is well-known that the introduction of a fluorine atom into biologically active compounds often intensifies their activities and chemical and/or biological stabilities.[1] Among fluorine-containing groups, a 3,3,3-trifluoropropenyl structure ($CF_3CH{=}CH-$) has been found in candidates for medicines[2] or agricultural chemicals.[3] In a series of pyrethroid-type insecticides, the 3,3,3-trifluoropropenyl group contributes to their volatility, which is essential for exhibiting their activity.[3a−d] Reactions of the unsaturated moiety of 3,3,3-trifluoropropenyl compounds have also been widely investigated.[4] While a variety of methods have been developed for synthesizing 3,3,3-trifluoropropenyl compounds, the methods have several disadvantages, such as the requirement of a multistep sequence of reactions and the use of expensive and/or low-boiling reagents.[5] One of the most direct routes to synthesize the trifluoropropenyl structure seems to be the use of a Wittig-type reaction of an aldehyde with a trifluoromethyl-containing reagent. Indeed, the Wittig reaction of 2,2,2-trifluoroethyltriphenylphosphonium triflate with benzaldehyde in the presence of CsF was reported.[6] However, the preparation of the phosphonium salt requires a multistep sequence of reactions involving the use of a hypervalent iodine compound.[6] The reaction of triphenylphosphine with 2,2,2-trifluoroethyl iodide giving phosphonium iodide does not proceed within the preparative time scale (9 months, 9%).[7,8] In this paper, we report a convenient method for synthesizing 3,3,3-trifluoropropenyl compounds **3** using the TBAF-mediated Horner reaction of 2,2,2-trifluoroethyldiphenylphosphine oxide (**2**) with aldehydes **1** (Scheme 1).

Scheme 1



Results and Discussions

The starting phosphine oxide **2** could readily be prepared from ethyl diphenylphosphinite (**4**) by Michaelis−Arbuzov reaction with 2,2,2-trifluoroethyl iodide (**5**) in 81% yield (Scheme 2). Sartori and Mosler reported an alternative method for the preparation of **2** that consisted of treating chlorodiphenylphosphine (**6**) with trifluoroacetic acid and water at 180 °C for 80 h.[9] So, we then examined the modification of Sartori's procedure and found that treatment of **6** with a mixture of trifluoroacetic acid and water at 0 °C to room temperature for 30 min, followed by heating around 100 °C for 2 h, afforded **2** in

(1) For reviews, see: (a) Schlosser, M. *Tetrahedron* **1978**, *34*, 3. (b) Kobayashi, Y.; Kumadaki, I. *Acc. Chem. Res.* **1978**, *11*, 197. (c) Ishikawa, N. *Kagaku No Ryoiki* **1981**, *35*, 441. (d) Filler, R.; Kobayashi, Y. *Biomedicinal Aspects of Fluorine Chemistry*; Kodansha, Elsevier Biomedical: Tokyo, 1982. (e) Welch, J. T. *Tetrahedron* **1987**, *43*, 3123. (f) Resnati, G. *Tetrahedron* **1993**, *49*, 9385. (g) Hiyama, T. *Organofluorine Compounds—Chemistry and Applications*; Springer: Berlin, 2000.

(2) (a) Wataya, Y.; Matsuda, A.; Santi, D. V.; Bergstrom, D. E.; Ruth, J. L. *J. Med. Chem.* **1979**, *22*, 339. (b) Bergstrom, D. E.; Ruth, J. L.; Reddy, P. A.; Clercq, E. D. *J. Med. Chem.* **1984**, *27*, 279. (c) Noyori, R.; Morisawa, Y.; Maeda, T.; Yasuda, S.; Uchida, K. JP-02056462, 1990.

(3) (a) Bentley, P. D.; Cheetham, R.; Huff, R. K.; Pascoe, R.; Sayle, J. D. *Pestic. Sci.* **1980**, *11*, 156. (b) Mack, H.; Hanack, M. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 184. (c) Mack, H.; Hanack, M. *Liebigs Ann. Chem.* **1989**, 833. (d) Nägele, U. M.; Hanack, M. *Liebigs Ann. Chem.* **1989**, 847. (e) Scheiblich, S.; Maier, T.; Baltruschat, H. S.; Hoellmueller, T. US-6130188, 2000.

(4) For leading references, see: (a) Morikawa, T.; Nishiwaki, T.; Kobayashi, Y. *Tetrahedron Lett.* **1989**, *30*, 2407. (b) Hanzawa, Y.; Suzuki, M.; Kobayashi, Y.; Taguchi, T.; Iitaka, Y. *J. Org. Chem.* **1991**, *56*, 1718. (c) Tanaka, K.; Mori, T.; Mitsuhashi, K. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 263. (d) Bouvet, D.; Sdassi, H.; Ourévitch, M.; Bonnet-Delpon, D. *J. Org. Chem.* **2000**, *65*, 2104. (e) Kuroki, Y.; Asada, D.; Sakamaki, Y.; Iseki, K. *Tetrahedron Lett.* **2000**, *41*, 4603.

(5) (a) Drakesmith, F. G.; Stewart, O. J.; Tarrant, P. *J. Org. Chem.* **1968**, *33*, 280. (b) Sakai, T. T.; Santi, D. V. *J. Med. Chem.* **1973**, *16*, 1079. (c) Eliseenkov, E. V.; Koginov, A. S.; Dneprovskii, A. S. *Zh. Org. Khim.* **1978**, *14*, 781. (d) Fuchikami, T.; Yatabe, M.; Ojima, I. *Synthesis* **1981**, 365. (e) Dolbier, W. R., Jr.; Medinger, K. S. *Tetrahedron* **1982**, *38*, 2411. (f) Kitazume, T.; Ishikawa, N. *J. Am. Chem. Soc.* **1985**, *107*, 5186. (g) Yamazaki, T.; Ishikawa, N. *Chem. Lett.* **1985**, 889. (h) Wiemers, D. M.; Burton, D. J. *J. Am. Chem. Soc.* **1986**, *108*, 832. (i) Fujita, M.; Hiyama, T. *Tetrahedron Lett.* **1986**, *27*, 3659. (j) Urata, H.; Fuchikami, T. *Tetrahedron Lett.* **1991**, *32*, 91. (k) Su, D.-B.; Duan, J.-X.; Chen, Q.-Y. *Tetrahedron Lett.* **1991**, *32*, 7689. (l) Tellier, F.; Sauvetre, R. *J. Fluorine Chem.* **1993**, *62*, 183. (m) Mizutani, K.; Yamazaki, T.; Kitazume, T. *J. Chem. Soc., Chem. Commun.* **1995**, 51. (n) Furuta, S.; Kuroboshi, M.; Hiyama, T. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 805. (o) Zang, X.; Qing, F. L.; Yang, Y.; Yu, J.; Fu, X.-K. *Tetrahedron Lett.* **2000**, *41*, 2953. (p) Shimizu, M.; Fujimoto, T.; Minezaki, H.; Hata, T.; Hiyama, T. *J. Am. Chem. Soc.* **2001**, *123*, 6947. See also ref 3a.

(6) (a) Umemoto, T.; Gotoh, Y. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 3307. (b) Umemoto, T.; Gotoh, Y. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 2008. The method for the preparation of phosphonium salt is as follows. CF_3CH_2I + TFAA + TFA + H_2O_2 → $CF_3CH_2I(OCOCF_3)_2$; $CF_3CH_2I(OCOCF_3)_2$ + TfOH + PhH → $CF_3CH_2I(OTf)Ph$; $CF_3CH_2I(OTf)Ph$ + Ph_3P → $Ph_3P^+CH_2CF_3$ TfO^-.

(7) Henry, R. A. *J. Chem. Eng. Spectrum* **1976**, *21*, 503.

(8) The S_N2 reaction scarcely occurs on the carbon α to a trifluoromethyl group due to the strong electron-withdrawing nature of the trifluoromethyl group. See: Shinohara, N.; Yamazaki, T.; Kitazume, T. *Reviews on Heteroatom Chemistry*; Oae, S., Ed.; MYU: Toyko, 1996; pp 165−182. This is the reason the hypervalent iodine compound was used for the preparation of the phosphonium salt bearing trifluoromethyl group; see ref 6.

(9) (a) Sartori, P.; Mosler, G. *Phosphorus Sulfur* **1980**, *8*, 115. See also: (b) Smith, D. J. H.; Trippett, S. *J. Chem. Soc., Perkin Trans. 1* **1975**, 963.

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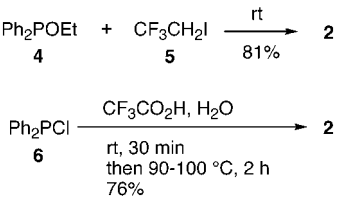
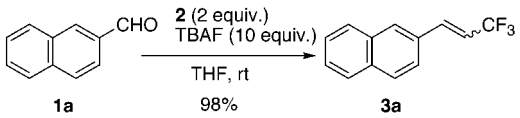
Scheme 2



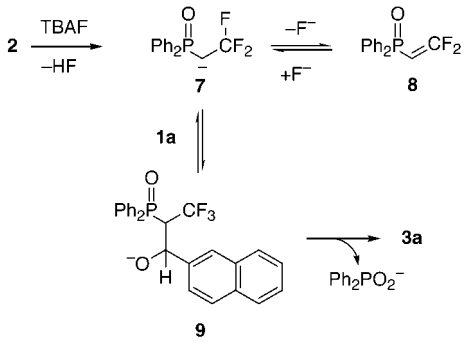
76% yield without any chromatographic separation (see the Experimental Section). This modified Sartori's procedure is recommended for a large-scale preparation of **2** due to the low prices of the starting materials.

With the phosphine oxide **2** in hand, we initiated our investigation by examining the reaction of **2** with 2-naphthaldehyde (**1a**). Reaction of equimolar amounts of **2** with **1a** in the presence of TBAF (10 equiv) (pre-dehydrated with MS 4A in THF) at room temperature for 2 h gave 2-(3,3,3-trifluoropropenyl)naphthalene (**3a**)[5d,n] in 73% yield with recovery of 14% yield of **1a**. A similar reaction



using 1.5 equiv of **2** gave **3a** in high yield (81%), but a small amount of the aldehyde was still recovered. The most satisfactory result was obtained by using 2 equiv of **2**: these conditions gave **3a** (*E*/*Z* = 85:15) in 98% yield after 1 h of reaction. Attempts to reduce the amount of TBAF gave unsatisfactory results: for example, treatment of **2** (2 equiv) with **1a** in the presence of 5 equiv of TBAF afforded **3a** in 50% yield with recovery of 45% yield of **1a**.

A possible mechanism for the Horner reaction of **2** with **1a** is as follows. A fluoride anion of TBAF deprotonates from **2** to generate the phosphinoxy carbanion **7**.[10,11] The anion **7** reacts with aldehyde **1a** to give the adduct **9**, whose elimination of phosphinate affords the product **3a**. It is assumed that the anion **7** having a trifluoromethyl group is unstable[12,13] and rapidly gives the elimination product difluorovinylphosphine oxide **8**.[14] However, the Michael addition of fluoride anion to **8** can regenerate **7**.[13a] In fact, treatment of difluorovinyl compound **8** (1 equiv), prepared according to the reported procedure,[14] with **1a** (10 equiv) in the presence of TBAF (10 equiv) gave **3a** in 47% yield.



In contrast to the use of TBAF, the use of common bases such as BuLi, KHMDS, KH, *t*-BuOK, and Triton B for the reaction of **1a** gave no 3,3,3-trifluoropropenyl compound **3a**. These results are rationalized in terms of the short lifetime of the anionic intermediate **7** as mentioned above. For instance, treatment of the phosphine oxide **2** with KH gave only the difluorovinyl compound **8** even in the presence of **1a**.[15] Compound **8** can no longer regenerate anion **7** due to an insufficient quantity of fluoride anion. In addition, neither KF nor CeF worked as a fluoride anion.

The results of Horner reaction of **2** with several aldehydes **1** giving 3,3,3-trifluoropropenyl compounds **3** are summarized in Table 1 [**2** (2 equiv), TBAF (10 equiv), rt, 1 h]. Benzaldehydes **1b**−**d** also gave the desired trifluoropropenyl compounds **3b**,[5c,d,f] **3c**,[5d,n] and **3d** in good yields (Table 1, entries 1−3). Reactions of benzaldehydes having electron-withdrawing groups **1e** and **1f** gave the corresponding products **3e** and **3f** in 64 and 65 yields, respectively (Table 1, entries 4 and 5). Reaction of 4-acetylbenzaldehyde (**1g**) also provided trifluoropropenyl compound **3g**, although the yield was low (Table 1, entry 6). Heteroaromatic aldehydes **1h**−**j** yielded products **3h**, **3i**,[5d] and **3j** in good yields (Table 1, entries 7−9). The reaction of *trans*-cinnamaldehyde (**1k**) gave **3k**[5d,n] in 83% yield (Table 1, entry 10). However, 3-phenylpropanal (**1l**) gave no expected compound **3l** ($PhCH_2CH_2CH{=}CHCF_3$) but afforded ester **10** in 60% yield (Table 1, entry 11). This might be because the deprotonation of the enolizable aldehyde **1l** with fluoride anion competed with that of phosphine oxide **2** (Scheme 3). Reactions with ketones such as the benzophenone and 4-*tert*-butylcyclohexanone afforded no 3,3,3-trifluoropropenyl compounds.

In summary, the present Horner reaction is quite convenient for preparing 3,3,3-trifluoropropenyl compounds from aldehydes in terms of availability of reagent **2**, operational simplicity, and generally good yields of the products, although the scope is somewhat limited. A control of *E*/*Z* selectivity of the products and application to the synthesis of biologically active compounds are currently under investigation.

Experimental Section

Melting points are uncorrected. ^1H and ^{13}C NMR spectra were measured for solutions in $CDCl_3$, CCl_4, or benzene-d_6. Column chromatography was performed on Silica gel 60 PF_{254} under pressure.

Preparation of 2,2,2-Trifluoroethyldiphenylphosphine Oxide (2). (a) From ethyl diphenylphosphinite (4). A mixture of ethyl diphenylphosphinite (**4**) (1.98 g, 5.79 mmol) and 2,2,2-trifluoroethyl iodide (**5**) (3.60 g, 17.2 mmol) was stirred at room temperature for 3 h under an argon atmosphere. After removal of excess **5** by evaporation, the residue was chromatographed on silica gel (AcOEt) to give crude **2**. Recrystallization

(10) For other fluoride anion-mediated Wittig and Horner reactions, see: (a) Schiemenz, G. P.; Becker, J.; Stöckigt, J. *Chem. Ber.* **1970**, *103*, 2077. (b) Texier-Boullet, F.; Villemin, D.; Ricard, M.; Moison, H.; Foucaud, A. *Tetrahedron* **1985**, *41*, 1259.

(11) For a review of synthetic application utilizing the fluoride anion as a base, see: Clark, J. H. *Chem. Rev.* **1980**, *80*, 429.

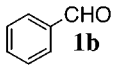
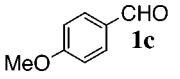
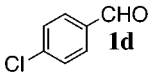
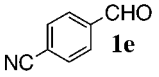
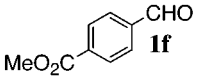
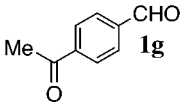
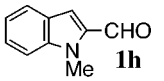
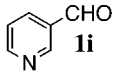
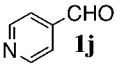
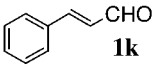
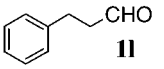
(12) (a) Nakai, T.; Tanaka, K.; Ishikawa, N. *Chem. Lett.* **1976**, 1263. (b) Nakai, T.; Tanaka, K.; Setoi, H.; Ishikawa, N. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 3069. (c) Aktaev, N. P.; Eremin, O. G.; Sokol'skii, G. A.; Knunyants, I. L. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1977**, 1117. (d) Bergstrom, D. E.; Ng, M. W.; Wong, J. J. *J. Org. Chem.* **1983**, *48*, 1902.

(13) For generation of an anion α to a trifluoromethyl group, see: (a) Ishikawa, N.; Yokozawa, T. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 724. (b) Fuchigami, T.; Nakagawa, Y. *J. Org. Chem.* **1987**, *52*, 5276. (c) Uneyama, K.; Momota, M. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 3378.

(14) Ichikawa, J.; Jyono, H.; Yonemaru, S.; Okauchi, T.; Minami, T. *J. Fluorine Chem.* **1999**, *97*, 109.

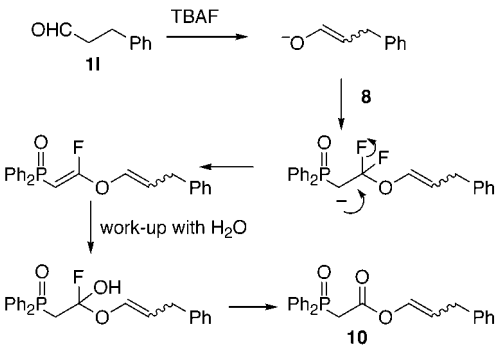
(15) Treatment of phosphine oxide **2** with *t*-BuOK in THF also gave difluorovinylphosphine oxide **8** in 25% yield.

Table 1. Horner Reaction of Aldehydes 1 with Phosphine Oxide 2

Entry	RCHO	Product	Yield (%)	*E*/*Z* ratio
1	 **1b**	**3b**[a]	63	78 : 22
2	 **1c**	**3c**	75	95:5
3	 **1d**	**3d**	74	82 : 18
4	 **1e**	**3e**	64	100 : 0
5	 **1f**	**3f**	65	95 : 5
6[b]	 **1g**	**3g**	24[c]	38 : 62
7	 **1h**	**3h**	73	100 : 0
8	 **1i**	**3i**	66	73 : 27
9	 **1j**	**3j**	58	100 : 0
10	 **1k**	**3k**	83	62 : 38
11	 **1l**	**10**[d]	60	20 : 80

[a] Volatile compound. [b] This reaction was carried out by using **2** (2 equiv) and TBAF (6 equiv) at −40 °C. [c] 44% of **1g** was recovered. [d] $Ph_2P(O)CH_2CO_2CH{=}CHCH_2Ph$ (**10**).

Scheme 3



from AcOEt−hexane gave **2** (1.98 g, 81%) as colorless needles: mp 160−161 °C (lit.[9a] mp 155−157 °C); ^{1}H NMR (270 MHz, $CDCl_3$) δ 3.25 (2 H, dq, J = 11.8, 10.5 Hz), 7.40−7.64 (6 H, m), 7.72−7.87 (4 H, m). The ^{1}H NMR spectrum was identical with that reported.[9a] **(b) From chlorodiphenylphosphine (6).** To a stirred mixture of trifluoroacetic acid (21.9 mL, 0.284 mol) and water (15.3 mL, 0.851 mol) was added dropwise phosphine **6** (203.8 mL, 1.135 mol) at 0 °C for 30 min, and the mixture solidified gradually. When the mixture was allowed to warm to room temperature, it turned to a pale yellow solution. After 30 min, the mixture was heated within the range between 90 and 100 °C for 2 h. After cooling, the mixture was diluted with $CHCl_3$ (200 mL) and concentrated under reduced pressure. To the residue were added $CHCl_3$ (400 mL) and an aqueous saturated solution of $NaHCO_3$ (400 mL), and the mixture was stirred vigorously for 1 h. The organic phase was separated, and the aqueous phase was extracted with $CHCl_3$ (400 mL × 2). The combined organic phase was washed successively with an aqueous saturated solution of $NaHCO_3$ (300 mL × 2) followed by brine (200 mL × 2) and dried over $MgSO_4$. After filtration, the filtrate was concentrated under reduced pressure, and the residue was recrystallized from AcOEt (300 mL) to afford **2** (50.4 g), mp 160−161 °C. The mother liquor was concentrated under reduced pressure, and the residue was further recrystallized from AcOEt (80 mL) to afford the second crop of **2** (11.4 g, total 76%), which was sufficiently pure for use.

General Procedure for Horner Reaction. MS 4A (powder, 2.4 g) was added to a 1 M solution of TBAF in THF (3.0 mL, 3.0 mmol), and the mixture was stirred at room-temperature overnight under an argon atmosphere. To the mixture were added a solution of aldehyde **1** (0.3 mmol) and phosphine oxide **2** (0.6 mmol) in THF (5 mL). After the mixture was stirred for 1 h, MS 4A was removed by filtration. Water (30 mL) was added to the filtrate, and the whole was extracted with AcOEt. The extract was washed with brine, dried ($MgSO_4$), and concentrated. The residue was chromatographed on silica gel (AcOEt−hexane) to give **3**.

2-(3,3,3-Trifluoroprop-1-enyl)naphthalene (3a): colorless crystals; mp 108−109 °C (**3a-*E*** from hexane) (lit.[5n] mp 108−109 °C, lit.[5d] mp 108−108.5 °C); ^{1}H NMR (500 MHz, benzene-d_6) δ 5.38 (15/100 H, dq, J = 12.7, 9.3 Hz, *Z*), 5.91 (85/100 H, dq, J = 16.1, 6.8 Hz, *E*), 6.44 (15/100 H, d, J = 12.7 Hz, *Z*), 7.00 (85/100 H, dq, J = 14.6, 2.0 Hz, *E*), 7.10 (85/100 H, dd, J = 9.3, 2.0 Hz, *E*), 7.17−7.55 (6 H, m, *E* + *Z*), 7.60 (15/100 H, br s, *Z*); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.85 (15/100 H, dq, J = 12.6, 9.2 Hz, *Z*), 6.32 (85/100 H, dq, J = 16.1, 6.4 Hz, *E*), 7.08 (15/100 H, d, J = 12.6 Hz, *Z*), 7.31 (85/100 H, dq, J = 16.1, 2.4 Hz, *E*), 7.49−7.55 (15/100 + 2 × 85/100 H, m, *E* + *Z*), 7.59 (85/100 H, dd, J = 8.8, 2.0 Hz, *E*), 7.81−7.88 (4 H, m, *E* + *Z*); ^{13}C NMR (67.8 MHz, $CDCl_3$) for *E*-isomer δ 116.0 (q, J = 34.2 Hz), 123.1, 123.7 (q, J = 268.5 Hz), 126.8, 127.2, 127.8, 128.4, 128.8, 129.1, 130.9, 133.3, 134.1, 137.7 (q, J = 7.4 Hz). The ^{1}H NMR spectrum (in $CDCl_3$) was identical with that reported.[5d,n]

(3,3,3-Trifluoroprop-1-enyl)benzene (3b): colorless oil; ^{1}H NMR (500 MHz, benzene-d_6) δ 5.29 (22/100 H, dq, J = 12.2, 8.8 Hz, *Z*), 5.82 (78/100 H, dq, J = 16.1, 6.3 Hz, *E*), 6.30 (22/100 H, d, J = 12.2 Hz, *Z*), 6.82−7.05 [(4 + 2 × 78/100) H, m], 7.20 (22/100 H, d, J = 6.8 Hz, *Z*); ^{1}H NMR (500 MHz, CCl_4) δ 5.65 (22/100 H, dq, J = 12.2, 8.8 Hz, *Z*), 6.10 (78/100 H, dq, J = 15.6, 6.3 Hz, *E*), 7.06 (78/100 H, dq, J = 15.6, 1.9 Hz, *E*), 7.21−7.35 (5 H, m, *E* + *Z*); ^{13}C NMR (67.8 MHz, $CDCl_3$) for *E*-isomer δ 115.9 (q, J = 34.2 Hz), 123.6 (q, J = 268.6 Hz), 127.5, 128.9, 130.0, 133.4. The ^{1}H NMR spectrum (in CCl_4) was identical with that reported.[5c,d,f]

1-(3,3,3-Trifluoroprop-1-enyl)-4-methoxybenzene (3c): colorless oil; ^{1}H NMR (270 MHz, benzene-d_6) δ 3.19 (3 × 5/100 H, s, *Z*), 3.21 (3 × 95/100 H, s, *E*), 5.27 (5/100 H, dq, J = 12.9, 9.6 Hz, *Z*), 5.77 (95/100 H, dq, J = 16.3, 6.8 Hz, *E*), 6.28 (5/100 H, d, J = 12.9 Hz, *Z*), 6.58 (2 H, br d, J = 11.0 Hz, *E* + *Z*), 6.85 (2 H, br d, J = 11.0 Hz, *E* + *Z*), 6.91 (95/100 H, dq, J = 16.1, 2.3 Hz, *E*). **3c-*E*:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.84 (3 H, s, OMe), 6.06 (1 H, dq, J = 16.1, 6.5 Hz), 6.91 (2 H, d, J = 8.8 Hz) δ 7.09 (1 H, dq, J = 16.1, 2.3 Hz), 7.39 (2 H, d, J = 8.8 Hz); ^{13}C NMR (67.8 MHz, $CDCl_3$) for *E*-isomer δ 55.3, 113.4 (q, J = 34.2 Hz), 114.3, 123.9 (q, J = 268.6 Hz), 126.1, 129.0, 137.1 (q, J = 7.3 Hz). The ^{1}H NMR spectrum (in $CDCl_3$) was identical with that reported.[5d,n]

1-Chloro-4-(3,3,3-trifluoroprop-1-enyl)benzene (3d): pale yellow oil; ^{1}H NMR (500 MHz, benzene-d_6) δ 5.24 (18/100 H, dq, J = 12.7, 8.8 Hz, *Z*), 5.64 (82/100 H, dq, J = 16.1, 6.4 Hz, *E*), 6.09 (18/100 H, d, J = 12.7 Hz, *Z*), 6.53 (2 × 82/100 H, br d, J = 8.3 Hz, *E*), 6.65 (82/100 H, dq, J = 16.1, 2.4 Hz, *E*), 6.87 (2 × 18/100 H, br d, J = 8.3 Hz, *Z*), 6.91 (2 × 82/100 H, br d, J = 8.3 Hz, *E*), 6.94 (2 × 18/100 H, br d, J = 8.3 Hz, *Z*); HRMS calcd for $C_9H_6{}^{35}ClF_3$ 206.0111, found 206.0115.

4-(3,3,3-Trifluoroprop-1-enyl)benzenecarbonitrile (3e): colorless crystals; mp 37−39 °C; ^{1}H NMR (270 MHz, benzene-d_6) δ 5.55 (1 H, dq, J = 16.0, 6.8 Hz), 6.35 (2 H, br d, J

= 8.4 Hz), 6.49 (1 H, dq, J = 16.0, 21 Hz), 6.81 (2 H, br d, J = 8.4 Hz); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 113.6, 118.2, 119.4 (q, J = 34.7 Hz), 123.0 (q, J = 268.2 Hz), 128.1, 132.8, 135.9 (q, J = 6.9 Hz), 137.7; HRMS calcd for $C_{10}H_6F_3N$ 197.0453, found 197.0450.

Methyl 4-(3,3,3-trifluoroprop-1-enyl)benzoate (3f): colorless crystals; mp 70−72 °C; ^{1}H NMR (500 MHz, benzene-d_6) δ 3.46 (3 × 5/100 H, s, *Z*), 3.49 (3 × 95/100 H, s, *E*), 5.26 (5/100 H, dq, J = 12.6, 9.3 Hz, *Z*), 5.73 (95/100 H, dq, J = 16.7, 6.0 Hz, *E*), 6.16 (5/100 H, d, J = 12.6 Hz, *Z*), 6.73 (95/100 H, dq, J = 16.7, 2.1 Hz, *E*), 6.75 (2 × 95/100 H, br d, J = 8.5 Hz, *E*), 7.07 (2 × 5/100 H, br d, J = 8.6 Hz, *Z*), 7.95 (2 × 95/100 H, br d, J = 8.5 Hz, *E*), 7.97 (2 × 5/100 H, br d, J = 8.6 Hz, *Z*); ^{13}C NMR (67.8 MHz, $CDCl_3$) for *E*-isomer δ 52.3, 118.2 (q, J = 34.2 Hz), 123.2 (q, J = 34.2 Hz), 127.5, 130.2, 131.4, 136.6 (q, J = 6.1 Hz), 137.6, 166.4; HRMS calcd for $C_{11}H_9F_3O$ 230.0554, found 230.0552.

1-[4-(3,3,3-Trifluoroprop-1-enyl)-4-acetylbenzene (3g): pale yellow oil; ^{1}H NMR (500 MHz, benzene-d_6) δ 2.03 (3 × 62/100 H, s, *Z*), 2.05 (3 × 38/100 H, s, *E*), 5.29 (62/100 H, dq, J = 12.7, 9.3 Hz, *Z*), 5.78 (38/100 H, dq, J = 16.1, 6.3 Hz, *E*), 6.18 (62/100 H, d, J = 12.7 Hz, *Z*), 6.77 (38/100 H, dq, J = 16.1, 2.4 Hz, *E*), 6.78 (2 × 38/100 H, br d, J = 8.3 Hz, *E*), 7.07 (2 × 62/100 H, br d, J = 8.3 Hz, *Z*), 7.61 (2 × 38/100 H, br d, J = 8.3 Hz, *E*), 7.62 (2 × 62/100 H, J = 8.3 Hz, *Z*); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 26.6 (*E* and *Z*), 118.3 (q, J = 34.6 Hz, *E*), 120.0 (q, J = 34.7 Hz, *Z*), 122.5 (q, J = 270.5 Hz, *Z*), 123.2 (q, J = 268.2 Hz, *E*), 136.5 (q, J = 6.9 Hz, *E*), 138.5 (q, J = 6.9 Hz, *Z*), 197.2 (*E*), 197.4 (*Z*); HRMS calcd for $C_{11}H_9F_3O$ 214.0605, found 214.0606.

2-(3,3,3-Trifluoroprop-1-enyl)-1-methylindole (3h): colorless crystals; mp 92−93 °C; ^{1}H NMR (500 MHz, benzene-d_6) δ 2.66 (3 H, s), 5.90 (1 H, dq, J = 16.2, 6.6 Hz), 6.45 (1 H, br s), 6.84 (1 H, dq, J = 16.2, 2.0 Hz), 6.87 (1 H, br d, J = 7.8 Hz), 7.12 (1 H, br t, J = 7.8 Hz), 7.17 (1 H, br t, J = 7.8 Hz), 7.56 (1 H, br d, J = 7.8 Hz); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 29.9, 102.7, 109.5, 116.3 (q, J = 34.6 Hz), 120.4, 121.2, 123.3, 123.5 (q, J = 268.2 Hz), 126.3 (q, J = 6.9 Hz), 127.3, 133.7, 138.7; HRMS calcd for $C_{12}H_{10}NF_3$ 225.0766, found 225.0767.

3-(3,3,3-Trifluoroprop-1-enyl)pyridine (3i): pale yellow oil; ^{1}H NMR (500 MHz, benzene-d_6) δ 5.28 (27/100 H, dq, J = 12.7, 8.8 Hz, *Z*), 5.70 (73/100 H, dq, J = 16.1, 6.8 Hz, *E*), 6.04 (27/100 H, d, J = 12.7 Hz, *Z*), 6.56 (73/100 H, dd, J = 7.8, 4.4 Hz, *E*), 6.61 (27/100 H, dd, J = 7.8, 4.4 Hz, *Z*), 6.63 (73/100 H, dq, J = 16.1, 2.5 Hz, *E*), 6.81 (73/100 H, dt, J = 7.8, 2.0 Hz, *E*), 7.29 (27/100 H, dt, J = 7.8, 2.0 Hz, *Z*), 8.29 (73/100 H, d, J = 2.0 Hz, *E*), 8.35 (27/100 H, dd, J = 4.4, 2.0 Hz, *Z*), 8.36 (73/100 H, dd, J = 4.4, 2.0 Hz, *E*), 8.46 (27/100 H, d, J = 2.0 Hz, *Z*); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.92 (27/100 H, dq, J = 12.5, 9.4 Hz, *Z*), 6.30 (73/100 H, dq, J = 16.0, 6.3 Hz, *E*), 6.92 (27/100 H, d, J = 12.5 Hz, *Z*), 7.17 (73/100 H, dq, J = 16.0, 2.0 Hz, *E*), 7.32 (27/100 H, dd, J = 7.8, 5.0 Hz, *Z*), 7.35 (73/100 H, dd, J = 7.8, 5.0 Hz, *E*), 7.75 (27/100 H, dt, J = 7.8, 2.0 Hz, *Z*), 7.78 (73/100 H, dt, J = 7.8, 2.0 Hz, *E*), 8.58 (27/100 H, dd, J = 5.0, 2.0 Hz, *Z*), 8.60 (27/100 H, d, J = 2.0 Hz, *Z*), 8.62 (73/100 H, dd, J = 5.0, 2.0 Hz, *E*), 8.70 (73/100 H, d, J = 2.0 Hz, *E*); ^{13}C NMR (67.8 MHz, $CDCl_3$) for *E*-isomer δ 117.9 (q, J = 34.2 Hz), 123.0 (q, J = 268.5 Hz), 123.1, 123.6, 133.8, 135.9 (q, J = 6.1 Hz), 149.1, 150.9. The ^{1}H NMR spectrum (in $CDCl_3$) was identical with that reported.[5d]

4-(3,3,3-Trifluoroprop-1-enyl)pyridine (3j): yellow oil; ^{1}H NMR (270 MHz, benzene-d_6) δ 5.75 (1H, dq, J = 16.2, 6.6 Hz), 6.38 (2H, br d, J = 4.4 Hz), 6.52 (1H, dq, J = 16.2, 2.2 Hz), 8.41 (2H, br d, J = 4.4 Hz). Anal. Calcd for $C_8H_6F_3N$: C, 55.50; H, 3.49; N, 8.09. Found: C, 55.21; H, 3.59; N, 8.02.

(5,5,5-Trifluoropenta-1,3-dienyl)benzene (3k): colorless oil; ^{1}H NMR (500 MHz, benzene-d_6) d 5.16 (38/100 H, dq, J = 11.7, 8.8 Hz, *Z*), 5.34 (62/100 H, dq, J = 15.1, 7.3 Hz, *E*), 5.99 (38/100 H, td, J = 11.7, 1.0 Hz, *Z*), 6.18−6.25 (2 × 64/100 H, m, *E*), 6.30 (38/100 H, br d, J = 15.6 Hz, *Z*), 6.55−6.62 (62/100 H, m, *E*), 6.99−7.14 (5 H, m, *E* + *Z*), 7.21 (38/100 H, ddq, J = 15.6, 11.7, 1.2 Hz, *Z*); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.55 (38/100 H, dqdd, J = 11.7, 8.8, 1.2, 1.0 Hz, *Z*), 5.80 (62/100 H, dq, J = 15.1, 6.8 Hz, *E*), 6.57 (38/100 H, ddd, J = 12.2, 11.7, 1.2 Hz, *Z*), 6.76 (62/100 H, dd, J = 15.1, 9.8 Hz, *E*), 6.78 (38/100 H, ddd, J = 15.1, 1.2, 1.0 Hz, *Z*), 6.82 (62/100 H, br d, J = 15.1 Hz, *E*), 6.90 (62/100 H, ddq, J = 15.1, 9.8, 2.0 Hz, *E*), 7.17 (38/100 H, ddqn, J = 15.1, 12.2, 1.2 Hz, *Z*), 7.31 (1 H, br t, J = 6.8 Hz, *E*+*Z*), 7.36 (2 H, br t, J = 6.8 Hz, *E*+*Z*), 7.44 (2 × 62/100 H, br d, J = 6.8 Hz, *E*), 7.46 (2 × 38/100 H, br d, J = 6.8 Hz, *Z*); ^{13}C NMR (67.8 MHz, $CDCl_3$) for *E*-isomer δ 118.3 (q, J = 34.7 Hz), 123.5 (q, J = 268.2 Hz), 124.9, 128.8, 128.9, 129.1, 135.8, 137.5 (q, J = 6.9 Hz), 139.3. The ^{1}H NMR spectral data (in benzene-d_6 and in $CDCl_3$) were identical with those reported.[5d,n]

3-Phenylpropenyl diphenylphosphorosoacetate (10): colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.18 (2 × 80/100 H, d, J = 7.3 Hz, *Z*), 3.24 (2 × 20/100 H, J = 7.3 Hz, *E*), 3.54 (2 × 20/100 H, J = 15.6 Hz, *E*), 3.61 (2 × 80/100 H, J = 15.6 Hz, *Z*), 5.00 (80/100 H, br q, J = 7.3 Hz, *Z*), 5.37 (20/100 H, dt, J = 15.6, 7.3 Hz, *E*), 6.94−7.84 (16 H, m); HRMS calcd for $C_{23}H_{21}O_3P$ 336.1228, found 336.1234.

Supporting Information Available: ^{1}H NMR spectra for **3d**−**h** and **10** and ^{13}C NMR spectra for **3e**−**h**. This material is available free of charge via the Internet at http://pubs.acs.org.

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