Phosphine-Relayed Aldehyde-Olefination and Aza-Wittig Reaction with 2,2,2-Trifluorodiazoethane

Fa-Guang Zhang,*[,†] Ning Lv,[†] Yan Zheng, and Jun-An Ma*

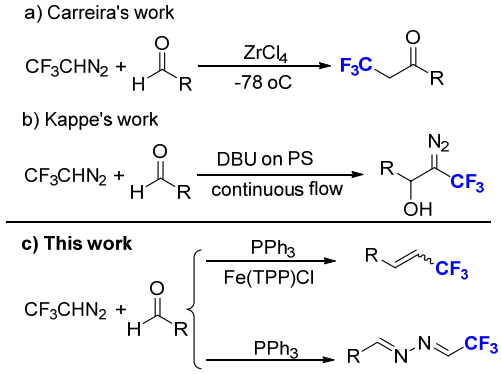
ABSTRACT Phosphine-relayed olefination and aza-Wittig reaction of readily available aldehydes with 2,2,2-trifluorodiazoethane (CF_3CHN_2) have been realized. This protocol enables the facile construction of a series of trifluoromethylated alkenes and hydrazones in good to high yield under mild conditions.

KEYWORDS diazo compounds, olefination, Wittig reactions, 2,2,2-trifluorodiazoethane, phosphine

Introduction

The incorporation of trifluoromethyl group into organic molecules would impart significant alterations to parent compounds such as improved bioavailability, lipophilicity, or metabolic stability.[1] Thus, trifluoromethyl-containing compounds have played an increasingly important role in the area of pharmaceuticals, agrochemicals, and materials.[2] With the demand to prepare various trifluoromethylated compounds in efficient ways, great efforts have been devoted and a number of trifluoromethyl building blocks have been developed over the past decades.[3] In this context, 2,2,2-trifluorodiazoethane (CF_3CHN_2) has emerged as a versatile synthon in the construction of different trifluoromethyl-containing frameworks.[4] Among these studies, Carreira and co-workers developed an elegant protocol for the in situ generation of CF_3CHN_2 and its subsequent utilization in various chemical transformations.[5] For example, the homologation reaction of aldehydes with CF_3CHN_2 employing $ZrCl_4$ as a suitable Lewis acid was reported by Carreira group in 2011 (Scheme 1a).[6] This method allows the straightforward conversion of aldehydes into trifluoromethyl substituted ketones. Very recently, Kappe and co-workers described a convenient generation of CF_3CHN_2 and subsequent aldol-type reaction with aldehydes utilizing continuous flow technology (Scheme 1b).[7] With our continuous interest in the utilization of CF_3CHN_2 in synthetic chemistry,[8] we envisioned that an olefination reaction of aldehydes would be achieved by employing phosphine in carbene relay process with CF_3CHN_2.[9] On the other hand, aza-Wittig process of aldehydes with trifluorodiazoethane to CF_3-hydrazones would also be accomplished when carbene-generating catalyst is absent in reaction media. To realize this proposal, two main challenges need to be addressed: i) to identify a suitable metal catalyst for carbene generation and transferring; ii) to carefully deal with the high reactivity of CF_3CHN_2 toward phosphines. To our delight, the phosphine-relayed olefination of aldehydes has been achieved by employing iron(III) porphyrin complex (Fe(TPP)Cl) as the catalyst (Scheme 1c). This transformation proceeds under mild conditions in a one pot manner, thus providing rapid access to trifluoromethylated olefins from readily available aldehydes.[10] Meanwhile, in the absence of iron catalyst, a wide range of trifluoromethylated hydrazones were afforded via phosphine-relayed aza-Wittig process with CF_3CHN_2 and aldehydes.[11] It should be noted that hydrazones not only serve as useful building block in organic chemistry,[12] but also are considered as important structural motif for their presence in a number of bio-active compounds, natural products, molecular switches and metalo-assemblies.[13] Herein we wish to report our detailed investigation on this subject.

Scheme 1 Different products from the reactions of CF_3CHN_2 with aldehydes



Results and Discussion

We commenced our study by evaluating the olefination of aldehyde **1a** with CF_3CHN_2 in the presence of different metal catalysts (Table1, entries 1–4). It has been found that only Fe(TPP)Cl could deliver the desired product **2a** in the presence of PPh_3 at 40 °C in toluene, albeit with low yield (entry 3). Subsequently, by increasing the amount of PPh_3 and Fe(TPP)Cl (entries 5–7), the yield of **2a** could be dramatically improved to 94% with 2.0:1 of *E*/*Z* ratio (entry 7). Encouraged by this result, a survey of the reaction parameters, such as solvents and reaction temperature, was conducted. Unfortunately, no improvement of the reaction efficiency was observed (entries 8–12). Nevertheless, a stream of gas generation was observed when CF_3CHN_2 was added quickly to the reaction mixture. We speculated that the amount of Fe catalyst could be further reduced if the reaction could be controlled in a slower manner. Indeed, with a syringe pump equipment to add CF_3CHN_2 in one hour, only 1 mol % of Fe(TPP)Cl could still deliver the target product in 93% yield (entries 13–15). Moreover, the amount of PPh_3 could also be reduced to 1.8 equivalents while keeping the high yield of **2a** (entries 16–17). However, it should also be mentioned that further improving the *E*/*Z* ratio of trifluoromethylated alkene appeared to be challenging (entries 18–24). Of note is that when $MePPh_2$ was employed, **2a** was generated with 4.5:1 of the *E*/*Z* ratio, but in dramatically decreasing yield (35%, entry 24). Taken together, optimal conditions for the formation of alkene **2a** from aldehyde with CF_3CHN_2 was established to be performed in toluene at 80 °C with the combination of Fe(TPP)Cl (1 mol %) and PPh_3 (1.8 equiv.).

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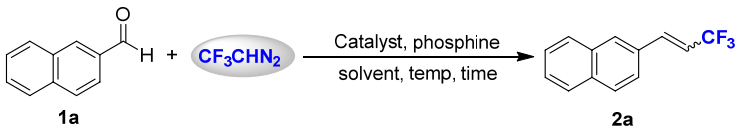
Table 1 Optimization of the reaction conditions for aldehyde olefination [a]



1a **2a**

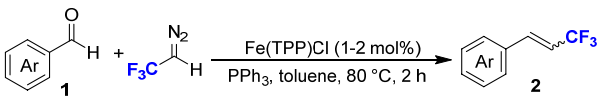
Entry	Solvent	Catalyst (mol %)	Phosphine (equiv.)	Temp (°C) / time (h)	Yield (%)[b] (*E*/*Z*)
1	toluene	Cu(TPP) (2)	PPh_3 (1.5)	40 / 12	nd
2	toluene	Co(TPP) (2)	PPh_3 (1.5)	40 / 12	nd
3	toluene	Fe(TPP)Cl (2)	PPh_3 (1.5)	40 / 12	25 (1.8:1)
4	toluene	Fe(salen)Cl (10)	PPh_3 (1.5)	40 / 12	nd
5	toluene	Fe(TPP)Cl (2)	PPh_3 (1.5)	80 / 8	33 (2.0:1)
6	toluene	Fe(TPP)Cl (2)	PPh_3 (2.4)	80 / 8	61 (2.3:1)
7	toluene	Fe(TPP)Cl (5)	PPh_3 (2.4)	80 / 2	94 (2.0:1)
8	dioxane	Fe(TPP)Cl (5)	PPh_3 (2.4)	80 / 2	41 (2.7:1)
9	CH_3CN	Fe(TPP)Cl (5)	PPh_3 (2.4)	80 / 2	8
10	DMF	Fe(TPP)Cl (5)	PPh_3 (2.4)	80 / 2	nd
11	DCE	Fe(TPP)Cl (5)	PPh_3 (2.4)	80 / 2	35 (2.3:1)
12	toluene	Fe(TPP)Cl (5)	PPh_3 (2.4)	80 / 2	85 (1.3:1)
13	toluene	Fe(TPP)Cl (2)	PPh_3 (2.4)	80 / 2	96 (2.1:1)
14[c]	toluene	Fe(TPP)Cl (1)	PPh_3 (2.4)	80 / 2	93 (2.5:1)
15[c]	toluene	Fe(TPP)Cl (0.5)	PPh_3 (2.4)	80 / 4	81 (2.7:1)
16[c]	**toluene**	**Fe(TPP)Cl (1)**	**PPh_3 (1.8)**	**80 / 2**	**94 (2.5:1)**
17[c]	toluene	Fe(TPP)Cl (1)	PPh_3 (1.5)	80 / 2	82 (2.3:1)
18[c]	toluene	Fe(TPP)Cl (2)	$PtBu_3$ (2.4)	80 / 2	nd
19[c]	toluene	Fe(TPP)Cl (2)	$P(OEt)_3$ (2.4)	80 / 2	nd
20[c, d]	toluene	Fe(TPP)Cl (2)	PPh_3 (2.4)	80 / 2	95 (2.0:1)
21[c]	toluene	Fe(TPP)Cl (2)	$P(4\text{-F-}C_6H_4)_3$ (2.4)	80 / 2	90 (3.5:1)
22[c]	toluene	Fe(TPP)Cl (2)	$P(4\text{-Me-}C_6H_4)_3$ (2.4)	80 / 2	90 (2.3:1)
23[c]	toluene	Fe(TPP)Cl (2)	$P(4\text{-MeO-}C_6H_4)_3$ (2.4)	80 / 2	55 (3.5:1)
24[c]	toluene	Fe(TPP)Cl (2)	$MePPh_2$ (2.4)	80 / 2	35 (4.5:1)

[a] General reaction conditions: 2-naphthaldehyde (0.2 mmol, 1.0 equiv.), phosphine and catalyst under Ar atmosphere, then added CF_3CHN_2 (corresponding solution, 2.5 equiv., 0.5 mmol) slowly and reacted at indicated temperature for appropriate time unless otherwise noted; [b] NMR yields with $PhCF_3$ as the standard reagent; [c] CF_3CHN_2 was added via syringe pump in one hour; [d] 2 equiv. of LiBr was added.

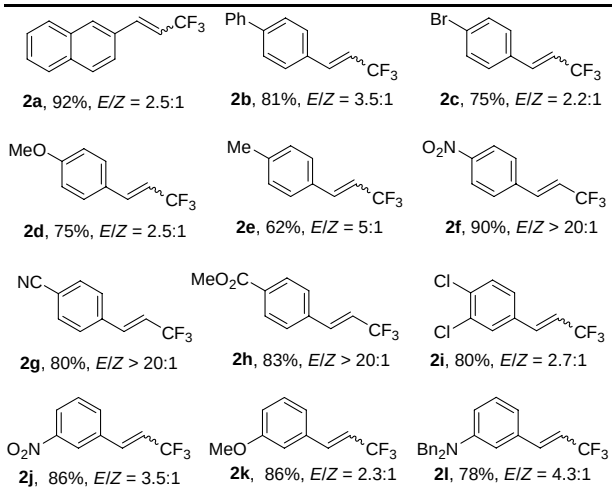
With the optimized reaction conditions in hand (Table 1, entry 16), we then set out to probe the scope of phosphine-relayed olefination with a variety of aldehydes. As depicted in Table 2, various aromatic aldehydes proved to be compatible substrates including the ones with electron-neutral, electron-withdrawing or electron-donating substituents, thus providing corresponding trifluoromethylated olefins in good to high chemical yields. Of note is that aldehydes bearing a strong electron-withdrawing group on the aromatic ring, were transformed to target olefins at room temperature in high yield as a single *E* isomer (Table 2, products **2f–h**). In addition to NO_2, CN, CO_2Me, and halogen functionalities, the olefination could also tolerate amino groups as exemplified with the formation of **2l** in 78% yield. Besides, several alkyl aldehydes and aromatic ketones were also tested in this reaction, however, the conversion was poor even with high loadings of Fe(TPP)Cl or at elevated temperature.

Notably, trifluoromethylated hydrazone **3a** was observed in several cases during afore-mentioned optimization process (Table 1). This hydrazone was assumed to be produced from aza-Wittig reaction of phosphazine intermediate with 2-naphthaldehyde (see the proposed mechanism in Scheme 3).[14] With this hypothesis in mind, **1a** was then treated with CF_3CHN_2 and phosphine in the absence of iron catalyst. Pleasingly, trifluoromethylated hydrazone **3a** could be smoothly obtained as a single isomer in 90% yield. This method could provide a mild, operationally simple and efficient access to trifluoromethylated hydrazones, thus a series of aldehydes were subjected to this transformation to demonstrate the substrate scope. These results are summarized in Table 3. A wide range of aromatic aldehydes could be smoothly transformed into trifluoromethylated hydrazones in good to high yield (Table 3, **3a–n**). It is found that the electronic nature and steric hindrance of substitutents play a crucial role on the reactivity. For instance, for substrate with a strong electron-withdrawing group, the reaction underwent

Table 2 Substrate scope of the trifluoromethylated olefins [a, b]



1 **2**

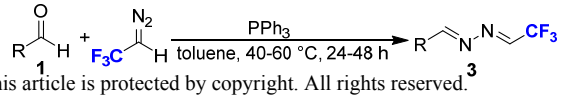


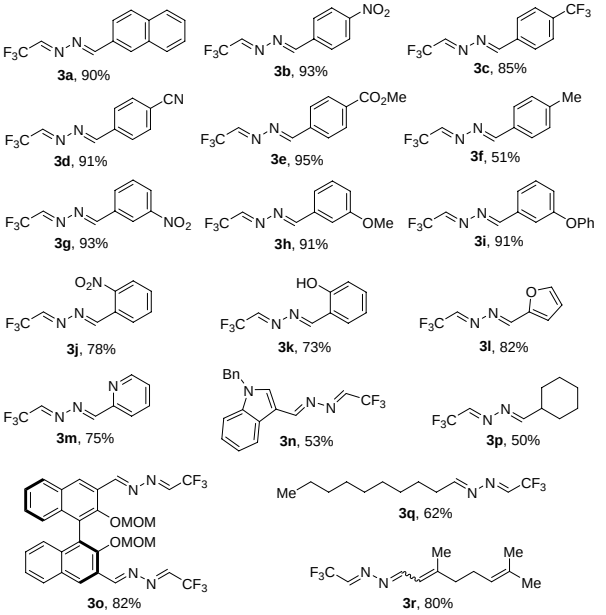
[a] General reaction conditions: aldehyde (0.4 mmol, 1.0 equiv.), PPh_3 (0.72 mmol, 1.8 equiv.), and Fe(TPP)Cl (1–2 mol %) under Ar atmosphere, then added CF_3CHN_2 (2.5 equiv., 0.2 mol/L in toluene) via syringe pump in one hour at indicated temperature and reacted for one hour unless otherwise noted; for compound **2f–h**, reaction was run at rt; [b] Isolated yields, *E/Z* ratio was determined by F-NMR.

at 40–50 °C leading to corresponding product in high yield (**3b–e**). In contrast, for aldehyde bearing an electron-donating group, the desired alkene could still be afforded, but dramatic decrease in yield was observed even at elevated temperature (**3f**). In the light of steric effect, it explains the observation that the yield of **3j** is inferior to that of **3b** and **3g**. To our surprise, despite steric hindrance and free O-H bond, salicylaldehyde is still a compatible substrate in this reaction, thus affording **3k** in 73% yield. The substrate scope could also be expanded to 2-furaldehyde and pyridine-2-aldehyde, along with the generation of **3l** and **3m** in good yield. Notably, we succeeded in obtaining indole derivate **3n** in moderate yield, which was subjected to single crystal X-ray analysis to confirm the molecular structure unambiguously.[15] Moreover, BINOL derivate **3o** was obtained in 82% yield by using this simple aza-Wittig reaction. In addition, alkyl aldehydes, including cyclohexanal, n-decanal and citral, could also participate in the transformation with moderate outcome, highlighting the robustness of current protocol.

Furthermore, with these promising results in hand, we attempted to extend this reaction to ketone substrates. However, no conversion was observed in the case of 4-nitroacetophenone even under harsh conditions, indicating the inert nature of ketones in this reaction. Nevertheless, we speculated that a strong electron-withdrawing group adjacent to the C=O bond would facilitate the reaction to occur. Indeed, aza-Wittig reaction of α-keto esters proceed smoothly under optimized conditions, leading to corresponding products in 76–91% yield (Scheme 2a, **5a–e**). Compounds with hydrazone functional groups are potential useful building blocks in organic synthesis. As illustrated in Scheme 2b, the aza-Wittig product **3** was treated with $LiAlH_4$ and Pd/C respectively in a one-pot procedure. Interestingly, regioselective reduction was observed in both cases, generating corresponding product **6a** and **6b** in good yield. These results displayed the diverse chemical reactivity of the bis-hydrazone

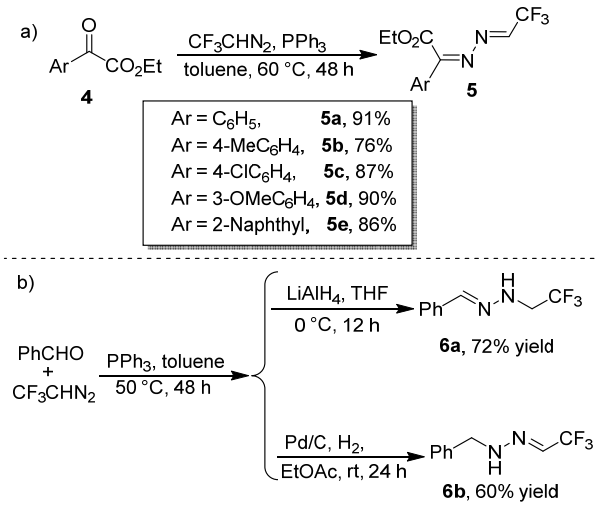
Table 3 Substrate scope of the trifluoromethylated hydrazones from aldehydes [a, b]





[a] General reaction conditions: PPh_3 (0.45 mmol, 1.5 equiv.), CF_3CHN_2 (1.5 equiv., 0.15 mol/L in toluene), rt for 5 minutes under Ar atmosphere, then added aldehyde **1** (0.3 mmol, 1.0 equiv.) in one pot and reacted at 40–60 °C for 24–48 h unless otherwise noted; [b] Isolated yield.

Scheme 2 Aza-Wittig reaction of α-ketoesters with CF_3CHN_2 and reduction of trifluoromethylated hydrazone

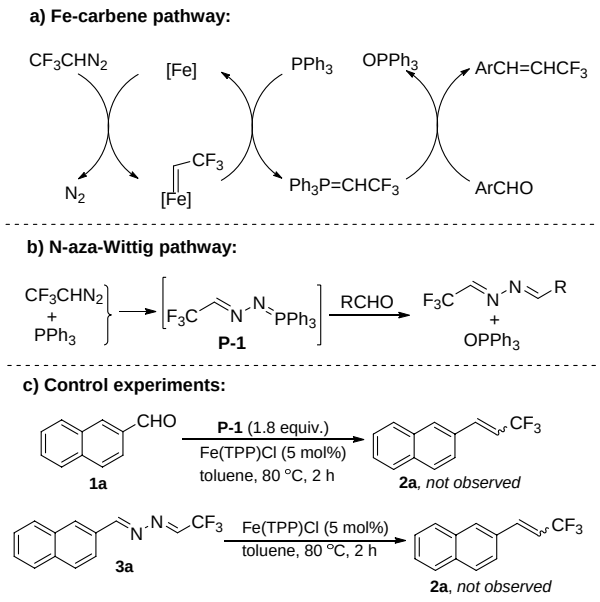


moiety. Furthermore, gram-scale reactions were carried out to demonstrate the scalability of our newly developed method, thereby smoothly furnishing **2a** (1.36 g, 88% yield) and **3a** (1.43 g, 82% yield) respectively (see experimental part for details).

A proposed mechanism is illustrated in Scheme 3 based on our observations and previous studies.[9] When CF_3CHN_2 was added to the reaction mixture (Scheme 3a), Fe(TPP)Cl would be in situ reduced to Fe(II), followed by the fast formation of [Fe]=$CHCF_3$ species via release of N_2. Subsequently, carbene transfer from Fe species to PPh_3 yields the CF_3-Wittig intermediate and releases iron catalyst, implying that the excess of PPh_3 is beneficial for the efficient trapping of active [Fe]-carbene intermediate. Then the Wittig intermediate reacted with aldehyde to furnish the olefin product and triphenylphosphine oxide ($OPPh_3$). The observed poor

stereoselectivity in this transformation contrasts sharply with previous variant of diazoacetates,[9] which likely can be attributed to the lack of stabilizing effects on the generated CF_3-oxaphosphetane intermediates in comparison with CO_2Et-substituted ones.[16] On the other hand, in the absence of iron catalyst (Scheme 3b), phosphazene intermediate **P-1** would be generated while adding CF_3CHN_2 to PPh_3.[14] In this scenario, an aza-Wittig process of this intermediate with aldehyde will proceed to yield trifluoromethylated hydrazone. Control experiments between Fe(TPP)Cl with phosphazene intermediate **P-1** or hydrazone **3a** were performed, while no olefination product **2a** was observed in either case (Scheme 3c). These results not only strongly support the proposed mechanism, but also explain the essentiality of slow addition of CF_3CHN_2 in the procedure.

Scheme 3 Proposed mechanism



Conclusions

In conclusion, by judicious tuning reaction conditions, phosphine-relayed Wittig olefination and aza-Wittig reaction of aldehydes with CF_3CHN_2 have been accomplished. In the presence of Fe(TPP)Cl, a series of aromatic aldehydes were transformed to trifluoromethylated alkenes in good yields under mild conditions. Meanwhile, in the absence of iron catalyst, a wide range of trifluoromethylated hydrazones were readily afforded via aza-Wittig process. α-Keto esters have also been successfully employed in this aza-Wittig reaction to provide corresponding hydrazones in high yield. Further studies including the substrate scope extension, synthetic applications together with detailed mechanistic investigation are underway in our laboratory.

Experimental

General information

^1H, ^{13}C and ^{19}F NMR spectra were recorded on a Bruker AVANCE III 600 M or 400 M spectrometer. Chemical shifts were reported in parts per million (ppm) from the solvent resonance as the internal standard ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.16 ppm). High resolution mass spectrometry (HRMS) spectra were obtained on a Bruker miorOTOF-QII instrument. IR spectra were recorded on an AVATAR 360 FT-IR spectrometer. Melting points (MP) were measured on a WRS-1A digital melting point apparatus and are uncorrected. X-ray structural analysis was conducted on the XtaLAB mini instrument. All purchased reagents were used without further purification unless otherwise noted. Analytical thin layer chromatography was performed on 0.20 mm Qingdao Haiyang silica gel plates. Silica gel (200-300 mesh) (from Qingdao Haiyang Chem. Company, Ltd.) was used for flash chromatography. 2,2,2-Trifluorodiazoethane (CF_3CHN_2) in different solutions was prepared and handled as described in the literature.[8c] α-keto esters were synthesized according to known procedure.[17]

Typical Procedure 1: To a 25 mL Schlenk tube was aldehyde (0.4 mmol, 1.0 equiv.), PPh_3 (0.72 mmol, 189 mg, 1.8 equiv.) and Fe(TPP)Cl (0.004 mmol, 3 mg, 0.01 equiv.) under Ar atmosphere, then CF_3CHN_2 (1.0 mmol, 5 mL, 0.2 mol/L in toluene) was added via a syringe pump to the reaction system in about one hour at 80 °C and reacted for 1 h with stirring. After the reaction was complete detected by TLC, column chromatography on silica gel (ethyl acetate/hexane = 1:100 as the eluent) was directly conducted on the reaction mixture to afford the desired product **2**.

Typical Procedure 2: To a 25 mL Schlenk tube was PPh_3 (0.45 mmol, 118 mg, 1.5 equiv.) under Ar atmosphere, then CF_3CHN_2 (0.45 mmol, 3 mL, 0.15 mol/L in toluene) was added and the mixture was stirred at rt for 5 minutes. Subsequently aldehyde (0.3 mmol, 1.0 equiv.) was added to the reaction system in one pot and the reaction was performed at 60 °C for 30 h with stirring. After the reaction was complete detected by TLC, column chromatography on silica gel (ethyl acetate/hexane = 1:20 as the eluent) was directly conducted on the reaction mixture to afford the desired product **3**.

Typical Procedure 3: To a 10 mL Schlenk tube was PPh_3 (0.45 mmol, 1.5 equiv.) under Ar atmosphere, then CF_3CHN_2 (0.45 mmol, 1.5 equiv.) was added and the mixture was stirred at rt for 5 minutes. Subsequently, carbonyl esters (0.3 mmol, 1.0 equiv.) was added to the reaction system in one pot and the reaction was performed at 60 °C for 48 h with stirring. After the reaction was complete detected by TLC, column chromatography on silica gel (ethyl acetate/petroleum ether = 1:50 as the eluent) was directly conducted on the reaction mixture to afford the desired product **5**.

2a, Typical Procedure 1, 50 mg, 92% yield, white solid, *E*/*Z* = 2.5:1; this compound was also prepared with 7 mmol of 2-naphthaldehyde, 1 mol % of Fe(TPP)Cl, 1.8 equiv. of PPh_3, and 1.5 equiv. of CF_3CHN_2 (0.2 mol/L in toluene) which was added via syringe pump in 6 hours, thus giving 1.36 g of **2a** in 88% yield. ^1H NMR (*E*, 600 MHz, $CDCl_3$) δ 7.82 – 7.80 (m, 4H), 7.50 (dt, *J* = 7.1, 5.4 Hz, 3H), 7.28 (dd, *J* = 16.1, 1.8 Hz, 1H), 6.29 (dq, *J* = 13.1, 6.5 Hz, 1H); ^{19}F NMR (565 MHz, $CDCl_3$) δ –57.27 (*Z*, d, *J* = 9.1 Hz, 3F), –63.10 (*E*, d, J = 6.7 Hz, 3F); ^{13}C NMR (*E*, 150 MHz, $CDCl_3$) δ 137.9 (q, $^3J_{F-C}$ = 6.6 Hz), 134.2, 133.4, 131.0, 129.2, 128.9, 128.5, 127.9, 127.3, 126.9, 123.9 (q, $^1J_{F-C}$ = 267.3 Hz), 123.2, 116.1 (q, $^2J_{F-C}$ = 33.6 Hz).

2b, Typical Procedure 1, 50 mg, 81% yield, light yellow oil, *E*/*Z* = 3.5:1, ^1H NMR (*E*, 600 MHz, $CDCl_3$) δ 7.59 (t, *J* = 7.3 Hz, 5H), 7.49 (d, *J* = 8.3 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.17 (dd, *J* = 16.1, 1.9 Hz, 1H), 6.22 (dq, *J* = 16.1, 6.5 Hz, 1H); ^{19}F NMR (565 MHz, $CDCl_3$) δ –57.45 (*Z*, d, *J* = 9.1 Hz, 3F), –63.13 (*E*, dd, *J* = 6.1, 1.4 Hz, 3F); ^{13}C NMR (*E*, 150 MHz, $CDCl_3$) δ 142.9, 140.2, 137.4 (q, $^3J_{F-C}$ = 6.7 Hz), 132.5, 129.1, 128.1, 128.0, 127.7, 127.2, 123.8 (q, $^1J_{F-C}$ = 267.1 Hz), 115.8 (q, $^2J_{F-C}$ = 33.4 Hz).

2c, Typical Procedure 1, 50 mg, 75% yield, light yellow oil, *E*/*Z* = 2.2:1, ^1H NMR (*E*, 600 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.00 (dd, *J* = 16.1, 1.9 Hz, 1H), 6.11 (dq, *J* = 16.1, 6.4 Hz, 1H); ^{19}F NMR (565 MHz, $CDCl_3$) δ –57.62 (*Z*, d, *J* = 9.0 Hz, 3F), –63.47 (*E*, dd, *J* = 6.3, 1.6 Hz, 3F); ^{13}C NMR (*E*, 150 MHz, $CDCl_3$) δ 136.6 (q, $^3J_{F-C}$ = 6.7 Hz), 132.3, 131.7, 129.1, 124.4, 123.6 (q, $^1J_{F-C}$ = 267.7 Hz), 116.7 (q, $^2J_{F-C}$ = 33.7 Hz).

2d, Typical Procedure 1, 50 mg, 75% yield, light yellow oil, *E*/*Z* = 2.5:1, ^{1}H NMR (*E*, 600 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.6 Hz, 2H), 7.00 (dd, *J* = 16.1, 1.8 Hz, 1H), 6.82 (d, *J* = 8.6 Hz, 2H), 5.97 (dq, *J* = 16.0, 6.6 Hz, 1H), 3.74 (s, 3H); ^{19}F NMR (565 MHz, $CDCl_3$) δ –57.54 (*Z*, d, *J* = 9.3 Hz, 3F), –62.84 (*E*, d, *J* = 6.9 Hz, 3F); ^{13}C NMR (*E*, 150 MHz, $CDCl_3$) δ 161.2, 137.2 (q, $^{3}J_{F\text{-}C}$ = 6.7 Hz), 129.2, 126.2, 124.1 (q, $^{1}J_{F\text{-}C}$ = 266.9 Hz), 114.5, 113.5 (q, $^{2}J_{F\text{-}C}$ = 33.4 Hz), 55.5.

2e, Typical Procedure 1, 46 mg, 62% yield, light yellow oil, *E*/*Z* = 5:1, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.9 Hz, 3H), 7.19 (dd, *J* = 30.9, 11.9 Hz, 4H), 6.18 (dq, *J* = 13.1, 6.5 Hz, 1H), 2.41 (s, 4H).; ^{19}F NMR (377 MHz, $CDCl_3$) δ -57.53 (d, *J* = 9.2 Hz), -63.11 (d, *J* = 6.3 Hz).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.48, 137.76 (q, *J* = 6.7 Hz), 130.91, 129.83, 129.26, 127.67, 124.0 (q, *J* = 270 Hz), 29.91.

2f, Typical Procedure 1, reaction was run at rt with 2 mol% of Fe(TPP)Cl, 50 mg, 90% yield, light yellow oil, *E*/*Z* > 20:1, ^{1}H NMR (*E*, 600 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.7 Hz, 2H), 7.64 (d, *J* = 8.6 Hz, 2H), 7.23 (dd, *J* = 16.2, 1.6 Hz, 1H), 6.37 (dq, *J* = 16.1, 6.3 Hz, 1H); ^{19}F NMR (*E*, 565 MHz, $CDCl_3$) δ –63.98 (d, *J* = 6.1 Hz, 3F); ^{13}C NMR (*E*, 150 MHz, $CDCl_3$) δ 148.7, 139.6, 135.6 (q, $^{3}J_{F\text{-}C}$ = 6.7 Hz), 128.4, 124.3, 123.0 (q, $^{1}J_{F\text{-}C}$ = 267.9 Hz), 120.2 (q, $^{2}J_{F\text{-}C}$ = 34.3 Hz).

2g, Typical Procedure 1, reaction was run at rt with 2 mol% of Fe(TPP)Cl, 50 mg, 80% yield, light yellow oil, *E*/*Z* > 20:1, ^{1}H NMR (*E*, 600 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.2 Hz, 2H), 7.56 (d, *J* = 8.1 Hz, 2H), 7.17 (d, *J* = 16.2 Hz, 1H), 6.32 (dq, *J* = 16.1, 6.3 Hz, 1H); ^{19}F NMR (*E*, 565 MHz, $CDCl_3$) δ –63.89 (d, *J* = 6.7 Hz, 3F); ^{13}C NMR (*E*, 150 MHz, $CDCl_3$) δ 137.8, 136.0 (q, $^{3}J_{F\text{-}C}$ = 6.6 Hz), 132.8, 128.2, 123.1 (q, $^{1}J_{F\text{-}C}$ = 267.9 Hz), 119.6 (q, $^{2}J_{F\text{-}C}$ = 34.2 Hz), 118.3, 113.6.

2h, Typical Procedure 1, reaction was run at rt with 2 mol% of Fe(TPP)Cl, 50 mg, 83% yield, light yellow oil, *E*/*Z* > 20:1, ^{1}H NMR (*E*, 600 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.3 Hz, 2H), 7.43 (d, *J* = 8.3 Hz, 2H), 7.10 (dd, *J* = 16.2, 1.8 Hz, 1H), 6.22 (dq, *J* = 16.1, 6.4 Hz, 1H), 3.85 (s, 3H); ^{19}F NMR (*E*, 565 MHz, $CDCl_3$) δ –63.70 (dd, *J* = 6.2, 1.6 Hz, 3F); ^{13}C NMR (*E*, 150 MHz, $CDCl_3$) δ 166.5, 137.7, 136.7 (q, $^{3}J_{F\text{-}C}$ = 6.7 Hz), 131.5, 130.3, 127.6, 123.4 (q, $^{1}J_{F\text{-}C}$ = 267.4 Hz), 118.3 (q, $^{2}J_{F\text{-}C}$ = 33.9 Hz), 52.4.

2i, Typical Procedure 1, 50 mg, 80% yield, light yellow oil, *E*/*Z* = 2.7:1, ^{1}H NMR (*E*, 600 MHz, $CDCl_3$) δ 7.43 (s, 1H), 7.35 (d, *J* = 5.7 Hz, 1H), 7.18 (d, *J* = 7.7 Hz, 1H), 6.96 (d, *J* = 15.7 Hz, 1H), 6.11 (dq, *J* = 22.3, 6.2 Hz, 1H); ^{19}F NMR (565 MHz, $CDCl_3$) δ –57.70 (*Z*, d, *J* = 8.8 Hz, 3F), –63.69 (*E*, d, *J* = 5.4 Hz, 3F); ^{13}C NMR (*E*, 150 MHz, $CDCl_3$) δ 135.5 (q, $^{3}J_{F\text{-}C}$ = 6.7 Hz), 134.2, 133.5, 131.1, 130.5, 129.4, 126.7, 123.3 (q, $^{1}J_{F\text{-}C}$ = 267.7 Hz), 117.9 (q, $^{2}J_{F\text{-}C}$ = 34.0 Hz).

2j, Typical Procedure 1, 50 mg, 86% yield, light yellow oil, *E*/*Z* = 3.5:1, ^{1}H NMR (*E*, 600 MHz, $CDCl_3$) δ 8.25 (s, 1H), 8.16 (d, *J* = 8.2 Hz, 1H), 7.70 (d, *J* = 7.7 Hz, 1H), 7.53 (t, *J* = 8.0 Hz, 1H), 7.15 (d, *J* = 16.2 Hz, 1H), 6.29 (dq, *J* = 16.1, 6.3 Hz, 1H); ^{19}F NMR (565 MHz, $CDCl_3$) δ –57.75 (*Z*, d, *J* = 8.8 Hz, 3F), –63.88 (*E*, dd, *J* = 6.1, 1.4 Hz, 3F); ^{13}C NMR (*E*, 150 MHz, $CDCl_3$) δ 148.82, 135.5 (q, $^{3}J_{F\text{-}C}$ = 6.7 Hz), 135.25, 133.36, 130.21, 124.62, 123.1 (q, $^{1}J_{F\text{-}C}$ = 267.7 Hz), 122.25, 119.2 (q, $^{2}J_{F\text{-}C}$ = 34.2 Hz).

2k, Typical Procedure 1, 50 mg, 86% yield, light yellow oil, *E*/*Z* = 2.3:1, ^{1}H NMR (*E*, 600 MHz, $CDCl_3$) δ 7.19 (t, *J* = 7.9 Hz, 1H), 7.01 (dd, *J* = 16.1, 2.0 Hz, 1H), 6.93 (d, *J* = 7.6 Hz, 1H), 6.86 (s, 1H), 6.82 (dd, *J* = 8.2, 2.3 Hz, 1H), 6.09 (dq, *J* = 16.1, 6.5 Hz, 1H), 3.71 (s, 3H); ^{19}F NMR (565 MHz, $CDCl_3$) δ –57.40 (*Z*, d, *J* = 8.9 Hz, 3F), –63.32 (*E*, dd, *J* = 6.9, 1.7 Hz, 3F); ^{13}C NMR (*E*, 150 MHz, $CDCl_3$) δ 160.1, 137.8 (q, $^{3}J_{F\text{-}C}$ = 6.6 Hz), 134.9, 130.1, 123.8 (q, $^{1}J_{F\text{-}C}$ = 267.3 Hz), 120.2, 116.2 (q, $^{2}J_{F\text{-}C}$ = 33.4 Hz), 115.8, 112.9, 55.4.

2l, Typical Procedure 1, 50 mg, 78% yield, light yellow oil, *E*/*Z* = 4.3:1, ^{1}H NMR (*E*, 600 MHz, $CDCl_3$) δ 7.24 (q, *J* = 7.3 Hz, 5H), 7.15 (d, *J* = 7.9 Hz, 5H), 7.08 (t, *J* = 8.1 Hz, 1H), 6.93 (d, *J* = 16.1 Hz, 1H), 6.73 (d, *J* = 7.1 Hz, 1H), 6.68 – 6.65 (m, 2H), 6.00 – 5.90 (m, 1H), 4.58 (s, 4H); ^{19}F NMR (565 MHz, $CDCl_3$) δ –57.30 (*Z*, d, *J* = 9.0 Hz, 3F), –63.10 (*E*, d, *J* = 6.3 Hz, 3F); ^{13}C NMR (*E*, 150 MHz, $CDCl_3$) δ 149.7, 138.6 (q, $^{3}J_{F\text{-}C}$ = 6.6 Hz), 138.2, 134.5, 129.9, 128.9, 127.2, 126.7, 123.8 (q, $^{1}J_{F\text{-}C}$ = 267.0 Hz), 115.8, 115.5 (q, $^{2}J_{F\text{-}C}$ = 33.6 Hz), 114.3, 111.8, 54.4.

3a, Typical Procedure 2, 60 °C, 30 h, 68 mg, 90% yield, white solid, mp 68 °C; this compound was also prepared with 7 mmol of 2-naphthaldehyde, 1.5 equiv. of PPh_3, and 1.5 equiv. of CF_3CHN_2 (0.2 mol/L in toluene), thus giving 1.43 g of **3a** in 82% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.52 (s, 1H), 7.95 (s, 1H), 7.90 (d, *J* = 8.6 Hz, 1H), 7.82 (dd, *J* = 8.0, 3.9 Hz, 1H), 7.75 (dd, *J* = 17.0, 8.3 Hz, 3H), 7.43 (dt, *J* = 14.9, 7.0 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.9, 148.6 (q, $^{2}J_{F\text{-}C}$ = 37 Hz), 135.5, 133.0, 132.6, 130.4, 129.0, 129.0, 128.3, 128.1, 127.0, 123.5, 119.9 (q, $^{1}J_{F\text{-}C}$ = 271 Hz); ^{19}F NMR (565 MHz, $CDCl_3$) δ –68.59 (d, *J* = 4.0 Hz, 3F); HRMS (ESI) found: m/z 251.0795 $[M+H]^+$; calcd. for $C_{13}H_9F_3N_2$+H 251.0791; IR (KBr): ν 3467, 1792, 1751, 1604, 1465, 1345, 1208, 1080, 763, 466 cm^{-1}.

3b, Typical Procedure 2, 40 °C, 24 h, 68 mg, 93% yield, light yellow solid, mp 102 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.46 (s, 1H), 8.25 (d, *J* = 8.4 Hz, 2H), 7.93 (d, *J* = 8.5 Hz, 2H), 7.80 (d, *J* = 3.7 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.7, 149.9, 148.9 (q, $^{2}J_{F\text{-}C}$ = 39 Hz), 138.3, 129.9, 124.3, 119.6 (q, $^{1}J_{F\text{-}C}$ = 271 Hz); ^{19}F NMR (565 MHz, $CDCl_3$) δ –68.95 (d, *J* = 3.5 Hz, 3F); HRMS (APCI) found: m/z 246.0490 $[M+H]^+$; calcd. for $C_9H_6F_3N_3O_2$+H 246.0485; IR (KBr): ν 3111, 2958, 1588, 1532, 1349, 1276, 1187, 1139, 967, 880, 668, 503 cm^{-1}.

3c, Typical Procedure 2, 50 °C, 24 h, 68 mg, 85% yield, oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.53 (s, 1H), 7.93 (d, *J* = 8.1 Hz, 2H), 7.88 (q, *J* = 3.9 Hz, 1H), 7.73 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.2, 148.9 (q, $^{2}J_{F\text{-}C}$ = 37 Hz), 136.0, 133.9 (q, $^{2}J_{F\text{-}C}$ = 32 Hz), 129.4, 126.0, 123.8 (q, $^{1}J_{F\text{-}C}$ = 270 Hz), 119.7 (q, $^{1}J_{F\text{-}C}$ = 270 Hz); ^{19}F NMR (565 MHz, $CDCl_3$) δ –63.11 (s, 3F), –68.96 (d, *J* = 4.0 Hz, 3F); HRMS (APCI) found: m/z 269.0516 $[M+H]^+$; calcd. for $C_{10}H_6F_6N_2$+H 269.0508; IR (KBr): ν 2964, 1571, 1325, 1172, 1065, 839, 713, 597 cm^{-1}.

3d, Typical Procedure 2, 50 °C, 24 h, 61 mg, 91% yield, white solid, mp 100 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.48 (s, 1H), 7.92 (d, *J* = 8.1 Hz, 2H), 7.85 (dd, *J* = 7.4, 3.6 Hz, 1H), 7.75 (d, *J* = 8.1 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.3, 148.8 (q, $^{2}J_{F\text{-}C}$ = 37 Hz), 136.6, 132.7, 129.4, 119.5 (q, $^{1}J_{F\text{-}C}$ = 271 Hz), 118.2, 115.5; ^{19}F NMR (565 MHz, $CDCl_3$) δ –68.92 (d, *J* = 3.7 Hz, 3F); HRMS (APCI) found: m/z 226.0695 $[M+H]^+$; calcd. for $C_{10}H_6F_3N_3$+H 226.0587; IR (KBr): ν 2960, 2857, 1593, 1351, 1271, 1139, 872, 829, 707, 483 cm^{-1}.

3e, Typical Procedure 2, 50 °C, 24 h, 74 mg, 95% yield, white solid, mp 90 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.50 (s, 1H), 8.10 (d, *J* = 8.2 Hz, 2H), 7.86 (t, *J* = 6.7 Hz, 3H), 3.93 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.4, 163.8, 148.8 (q, $^{2}J_{F\text{-}C}$ = 37 Hz), 136.6, 134.4, 130.2, 129.1, 119.8 (q, $^{1}J_{F\text{-}C}$ = 271 Hz), 52.6; ^{19}F NMR (565 MHz, $CDCl_3$) δ –68.90 (d, *J* = 3.9 Hz, 3F); HRMS (APCI) found: m/z 259.0695 $[M+H]^+$; calcd. for $C_{11}H_9F_3N_2O_2$+H 259.0689; IR (KBr): ν 2923, 1597, 1371, 1278, 1137, 991, 867, 707, 554 cm^{-1}.

3f, Typical Procedure 2, 60 °C, 48 h, 33 mg, 51% yield, light yellow solid, mp 100 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.54 (s, 1H), 7.91 (q, *J* = 4.1 Hz, 1H), 7.72 (d, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 7.9 Hz, 2H), 2.43 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.2, 148.4 (q, $^{2}J_{F\text{-}C}$ = 37 Hz), 136.5, 130.1, 129.9, 129.4, 119.9 (q, $^{1}J_{F\text{-}C}$ = 271 Hz), 21.9; ^{19}F NMR (565 MHz, $CDCl_3$) δ –69.69 (d, *J* = 4.1 Hz, 3F); HRMS (APCI) found: m/z 215.0797 $[M+H]^+$; calcd. for $C_{10}H_9F_3N_2$+H 215.0791; IR (KBr): ν 2924, 1461, 1375, 1268, 1156, 815, 509 cm^{-1}.

3g, Typical Procedure 2, 50 °C, 24 h, 68 mg, 93% yield, light yellow solid, mp 62 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.68 (s, 1H), 8.57 (s, 1H), 8.37 (d, *J* = 8.1 Hz, 1H), 8.14 (d, *J* = 7.7 Hz, 1H), 7.90 (d, *J* = 3.9 Hz, 1H), 7.69 (t, *J* = 7.9 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.0, 149.1 (q, $^{2}J_{F\text{-}C}$ = 37 Hz), 148.7, 134.6, 134.4, 130.2, 126.6, 122.2, 119.6 (q, $^{1}J_{F\text{-}C}$ = 271 Hz); ^{19}F NMR (565 MHz, $CDCl_3$) δ –68.91 (d, *J* = 3.5 Hz, 3F); HRMS (APCI) found: m/z 246.0490 $[M+H]^+$; calcd. for $C_9H_6F_3N_3O_2$+H 246.0485; IR (KBr): ν 2923, 1534, 1376, 1272, 1173, 991, 880, 735, 527 cm^{-1}.

3h, Typical Procedure 2,60 °C, 48 h, 63 mg, 91% yield, oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.39 (s, 1H), 7.79 (q, *J* = 4.0 Hz, 1H), 7.30 (s, 1H), 7.27 (d, *J* = 7.9 Hz, 1H), 7.23 (d, *J* = 7.5 Hz, 1H), 6.97 (dd, *J* = 8.0, 2.4 Hz, 1H), 3.76 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.5,

159.1, 147.5 (q, $^{2}J_{F-C}$ = 37 Hz), 133.0, 129.1, 121.7, 118.9 (q, $^{1}J_{F-C}$ = 271 Hz), 118.3, 111.4, 54.4; ^{19}F NMR (565 MHz, $CDCl_3$) δ –68.78 (d, *J* = 4.0 Hz, 3F); HRMS (APCI) found: m/z 231.0748 $[M+H]^+$; calcd. for $C_{10}H_9F_3N_2O$+H 231.0740; IR (KBr): ν 2961, 1603, 1463, 1370, 1267, 1161, 1044, 879, 792, 699 cm^{-1}.

3i, Typical Procedure 2, 60 °C, 48 h, 80 mg, 91% yield, oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.34 (s, 1H), 7.72 (d, *J* = 4.0 Hz, 1H), 7.40 – 7.35 (m, 2H), 7.29 (t, *J* = 7.9 Hz, 1H), 7.25 (t, *J* = 7.1 Hz, 2H), 7.03 (t, *J* = 7.9 Hz, 2H), 6.92 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.7, 158.1, 156.6, 148.6 (q, $^{2}J_{F-C}$ = 37 Hz), 134.5, 130.4, 130.1, 124.4, 124.0, 122.7, 119.8 (q, $^{1}J_{F-C}$ = 270 Hz), 119.4, 118.3; ^{19}F NMR (565 MHz, $CDCl_3$) δ –68.75 (d, *J* = 3.6 Hz, 3F); HRMS (APCI) found: m/z 293.0902 $[M+H]^+$; calcd. for $C_{15}H_{11}F_3N_2O$+H 293.0896; IR (KBr): ν 2961, 1573, 1488, 1369, 1258, 1168, 882, 800, 690 cm^{-1}.

3j, Typical Procedure 2, 50 °C, 24 h, 57 mg, 78% yield, light yellow solid, mp 162 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.91 (s, 1H), 8.12 (dd, *J* = 12.5, 8.1 Hz, 2H), 7.82 (d, *J* = 3.8 Hz, 1H), 7.75 (t, *J* = 7.5 Hz, 1H), 7.68 (t, *J* = 7.7 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.4, 149.0, 148.3 (q, $^{2}J_{F-C}$ = 37 Hz), 133.9, 132.3, 129.8, 127.8, 125.0, 119.5 (q, $^{1}J_{F-C}$ = 271 Hz); ^{19}F NMR (565 MHz, $CDCl_3$) δ –68.95 (d, *J* = 3.7 Hz, 3F); HRMS (APCI) found: m/z 246.0489 $[M+H]^+$; calcd. for $C_9H_6F_3N_3O_2$+H 246.0485; IR (KBr): ν 3082, 1528, 1347, 1276, 1141, 849, 742, 645 cm^{-1}.

3k, Typical Procedure 2, 60 °C, 48 h, 47 mg, 73% yield, white solid, mp 70 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.91 (s, 1H), 8.68 (s, 1H), 7.85 (s, 1H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.27 (d, *J* = 7.5 Hz, 1H), 6.95 (d, *J* = 8.3 Hz, 1H), 6.89 (t, *J* = 7.1 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.8, 160.5, 149.5 (q, $^{2}J_{F-C}$ = 37 Hz), 135.0, 133.6, 120.1, 119.7 (q, $^{1}J_{F-C}$ = 271 Hz), 117.5, 116.5; ^{19}F NMR (565 MHz, $CDCl_3$) δ –68.64 (d, *J* = 3.8 Hz, 3F); HRMS (ESI) found: m/z 217.0588 $[M+H]^+$; calcd. for $C_9H_7F_3N_2O$+H 217.0583; IR (KBr): ν 3087, 2963, 1620, 1561, 1489, 1379, 1264, 1133, 1015, 879, 804, 712 cm^{-1}.

3l, Typical Procedure 2, 40 °C, 48 h, 47 mg, 82% yield, oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.44 (s, 1H), 7.95 (q, *J* = 4.1 Hz, 1H), 7.67 (s, 1H), 7.04 (d, *J* = 3.4 Hz, 1H), 6.60 (dd, *J* = 3.3, 1.6 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 154.9, 149.4 (q, $^{2}J_{F-C}$ = 37 Hz), 148.3, 147.3, 119.8 (q, $^{1}J_{F-C}$ = 270 Hz), 119.8, 112.9; ^{19}F NMR (565 MHz, $CDCl_3$) δ –68.68 (d, *J* = 4.1 Hz, 3F); HRMS (APCI) found: m/z 191.0435 $[M+H]^+$; calcd. for $C_7H_5F_3N_2O$+H 191.0427; IR (KBr): ν 2925, 1464, 1262, 1097, 1022, 803, 671 cm^{-1}.

3m, Typical Procedure 2, 50 °C, 48 h, 45 mg, 75% yield, oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.71 (d, *J* = 4.1 Hz, 1H), 8.47 (s, 1H), 8.01 (d, *J* = 7.8 Hz, 1H), 7.83 (d, *J* = 3.9 Hz, 1H), 7.80 (t, *J* = 7.7 Hz, 1H), 7.39 (dd, *J* = 7.4, 4.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.4, 151.7, 150.3, 148.1 (q, $^{2}J_{F-C}$ = 38 Hz), 136.9, 130.0, 123.0, 119.6 (q, $^{1}J_{F-C}$ = 271 Hz); ^{19}F NMR (565 MHz, $CDCl_3$) δ –68.95 (d, *J* = 4.0 Hz, 3F); HRMS (APCI) found: m/z 202.0595 $[M+H]^+$; calcd. for $C_8H_6F_3N_3$+H 202.0587; IR (KBr): ν 2925, 1587, 1467, 1265, 1153, 803, 692 cm^{-1}.

3n, Typical Procedure 2, 60 °C, 48 h, 52 mg, 53% yield, yellow solid, mp 98 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.72 (s, 1H), 8.27 (d, *J* = 6.0 Hz, 1H), 7.92 (d, *J* = 4.2 Hz, 1H), 7.45 (s, 1H), 7.22 (t, *J* = 7.9 Hz, 6H), 7.05 (d, *J* = 6.8 Hz, 2H), 5.22 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.5, 146.8 (q, $^{2}J_{F-C}$ = 36 Hz), 137.8, 135.9, 135.8, 129.2, 128.4, 127.1, 125.9, 124.1, 122.9, 122.5, 120.4 (q, $^{1}J_{F-C}$ = 270 Hz), 111.5, 110.5, 50.8; ^{19}F NMR (565 MHz, $CDCl_3$) δ –68.03 (d, *J* = 4.1 Hz, 3F); HRMS (ESI) found: m/z 330.1218 $[M+H]^+$; calcd. for $C_{18}H_{14}F_3N_3$+H 330.1213; IR (KBr): ν 3107, 2930, 1569, 1465, 1343, 1264, 1168, 995, 881, 744, 698 cm^{-1}; CCDC 993954.

3o, Typical Procedure 2,50 °C, 48 h, 101 mg, 82% yield, light yellow solid, mp 90 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.97 (s, 2H), 8.70 (s, 2H), 7.95 – 7.88 (m, 4H), 7.38 (t, *J* = 6.9 Hz, 2H), 7.27 (t, *J* = 7.0 Hz, 2H), 7.12 (d, *J* = 8.2 Hz, 2H), 4.54 (s, 4H), 2.76 (s, 6H).; ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.5, 153.1, 148.4 (q, $^{2}J_{F-C}$ = 37 Hz), 135.9, 130.4, 130.0, 129.6, 128.8, 126.1, 126.1, 125.8, 119.8 (q, $^{1}J_{F-C}$ = 270 Hz), 100.3, 57.0; ^{19}F NMR (565 MHz, $CDCl_3$) δ –68.64 (d, *J* = 3.9 Hz, 6F); HRMS (ESI) found: m/z 641.1599 $[M+Na]^+$; calcd. for $C_{30}H_{24}F_6N_4O_4$+Na 641.1594; IR (KBr): ν 2927, 1619, 1457, 1351, 1275, 1156, 969, 921, 753 cm^{-1}.

3p, Typical Procedure 2, 50 °C, 48 h, 31 mg, 50% yield, oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (d, *J* = 5.6 Hz, 1H), 7.71 (dd, *J* = 7.8, 3.8 Hz, 1H), 2.37 (d, *J* = 3.8 Hz, 1H), 1.86 (d, *J* = 10.0 Hz, 2H), 1.81 – 1.77 (m, 2H), 1.70 (d, *J* = 12.6 Hz, 1H), 1.32 (dd, *J* = 20.2, 11.3 Hz, 5H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 173.4, 147.7 (q, $^{2}J_{F-C}$ = 37 Hz), 119.7 (q, $^{1}J_{F-C}$ = 271 Hz), 41.2, 29.5, 26.0, 25.4; ^{19}F NMR (565 MHz, $CDCl_3$) δ –69.05 (d, *J* = 3.9 Hz, 3F); HRMS (APCI) found: m/z 207.1114 $[M+H]^+$; calcd. for $C_9H_{13}F_3N_2$+H 207.1104; IR (KBr): ν 2960, 2927, 1457, 1261, 1097, 1023, 802, 699 cm^{-1}.

3q, Typical Procedure 2, 60 °C, 48 h, 46 mg, 62% yield, oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (t, *J* = 5.4 Hz, 1H), 7.72 (d, *J* = 3.9 Hz, 1H), 2.41 (d, *J* = 6.5 Hz, 2H), 1.60 – 1.57 (m, 2H), 1.26 (s, 11H), 0.87 (t, *J* = 6.9 Hz, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.7, 147.9 (q, $^{2}J_{F-C}$ = 37 Hz), 110.7 (q, $^{1}J_{F-C}$ = 271 Hz), 33.0, 32.0, 29.6, 29.5, 29.4, 29.3, 25.9, 22.8, 14.2; ^{19}F NMR (565 MHz, $CDCl_3$) δ –69.07 (d, *J* = 3.6 Hz, 3F); HRMS (APCI) found: m/z 251.1757 $[M+H]^+$; calcd. for $C_{12}H_{21}F_3N_2$+H 251.1730; IR (KBr): ν 2928, 2857, 1463, 1266, 1164, 1022, 804, 701 cm^{-1}.

3r, Typical Procedure 2,50 °C, 48 h, 59 mg, 80% yield, oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.53 (dd, *J* = 32.9, 10.3 Hz, 1H), 7.84 – 7.74 (m, 1H), 6.23 – 6.10 (m, 1H), 5.07 (d, *J* = 6.2 Hz, 1H), 2.37 (t, *J* = 7.5 Hz, 1H), 2.27 – 2.23 (m, 1H), 2.22 – 2.15 (m, 2H), 1.98 (d, *J* = 3.5 Hz, 3H), 1.67 (d, *J* = 14.0 Hz, 3H), 1.59 (d, *J* = 10.7 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.4, 164.1, 157.5, 157.5, 146.9 (q, $^{2}J_{F-C}$ = 37 Hz), 132.4, 131.9, 121.9, 121.7, 121.5, 120.5, 119.0 (q, $^{1}J_{F-C}$ = 271 Hz), 39.8, 32.3, 26.0, 25.2, 24.8, 24.7, 24.1, 17.0, 16.8, 16.8; ^{19}F NMR (565 MHz, $CDCl_3$) δ –68.69 to –68.70 (m, 3F); HRMS (APCI) found: m/z 247.1425 $[M+H]^+$; calcd. for $C_{12}H_{17}F_3N_2$+H 247.1417; IR (KBr): ν 2963, 2926, 1651, 1450, 1264, 1166, 1099, 1022, 803, 705 cm^{-1}.

5a, Typical Procedure 3, 74 mg, 91% yield, oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.9 Hz, 2H), 7.43 (t, *J* = 7.4 Hz, 1H), 7.36 (t, *J* = 7.7 Hz, 2H), 4.35 (q, *J* = 7.1 Hz, 2H), 1.28 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.1, 163.0, 147.1 (q, $^{2}J_{F-C}$ = 37 Hz), 131.8, 129.4, 128.1, 127.2, 118.5 (q, $^{1}J_{F-C}$ = 271 Hz), 61.2, 13.2; ^{19}F NMR (565 MHz, $CDCl_3$) δ –68.88 (d, *J* = 3.7 Hz, 3F); HRMS (APCI) found: m/z 5273.0857 $[M+H]^+$; calcd. for $C_{12}H_{11}F_3N_2O_2$+H 273.0845; IR (KBr): ν 2965, 1741, 1567, 1449, 1352, 1264, 1143, 1020, 800, 691 cm^{-1}.

5b, Typical Procedure 3, 65 mg, 76% yield, oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (q, *J* = 3.9 Hz, 1H), 7.62 (d, *J* = 8.1 Hz, 2H), 7.17 (d, *J* = 7.9 Hz, 2H), 4.35 (q, *J* = 7.1 Hz, 2H), 2.31 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 164.3, 147.9 (q, $^{2}J_{F-C}$ = 37 Hz), 143.8, 129.9, 128.3, 127.8, 119.6 (q, $^{1}J_{F-C}$ = 271 Hz), 62.1, 21.7, 14.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ –68.81 (d, *J* = 3.9 Hz, 3F); HRMS (ESI) found: m/z 287.1004 $[M+H]^+$; calcd. for $C_{13}H_{13}F_3N_2O_2$+H 287.1002; IR (KBr): ν 2987, 1741, 1589, 1352, 1275, 1170, 1038, 821, 742, 498 cm^{-1}.

5c, Typical Procedure 3, 80 mg, 87% yield, oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 (d, *J* = 3.8 Hz, 1H), 7.67 (d, *J* = 8.5 Hz, 2H), 7.36 (d, *J* = 8.5 Hz, 2H), 4.37 (q, *J* = 7.1 Hz, 2H), 1.30 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.7, 162.8, 148.3 (q, $^{2}J_{F-C}$ = 38 Hz), 139.2, 129.5, 129.5, 128.9, 119.5 (q, $^{1}J_{F-C}$ = 271 Hz), 62.5, 14.2; ^{19}F NMR (565 MHz, $CDCl_3$) δ –68.88 (d, *J* = 3.2 Hz, 3F); HRMS (ESI) found: m/z 329.0276 $[M+Na]^+$; calcd. for $C_{12}H_{10}ClF_3N_2O_2$+Na 329.0275; IR (KBr): ν 2987, 1741, 1590, 1352, 1274, 1171, 1035, 834, 690, 501 cm^{-1}.

5d, Typical Procedure 3, 81 mg, 90% yield, oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 (d, *J* = 3.9 Hz, 1H), 7.33 (s, 1H), 7.28 (t, *J* = 7.9 Hz, 1H), 7.23 (d, *J* = 7.6 Hz, 1H), 7.01 (d, *J* = 10.0 Hz, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 3.76 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.0, 163.8, 160.0, 148.1 (q, $^{2}J_{F-C}$ = 37 Hz), 131.7, 130.1, 121.2, 119.4 (q, $^{1}J_{F-C}$ = 271 Hz), 119.3, 112.2, 62.3, 55.5, 14.2; ^{19}F NMR (565 MHz, $CDCl_3$) δ –68.85 (d, *J* = 3.8 Hz, 3F); HRMS

(ESI) found: m/z 325.0779 $[M+Na]^+$; calcd. for $C_{13}H_{13}F_3N_2O_3$+Na 325.0770; IR (KBr): ν 2985, 2841, 1740, 1573, 1464, 1352, 1252, 1171, 1033, 894, 711 cm^{-1}.

5e, Typical Procedure 3, 84 mg, 86% yield, oil; ^1H NMR (600 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.93 (d, *J* = 8.6 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 3H), 7.74 (d, *J* = 8.2 Hz, 1H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.44 – 7.41 (m, 1H), 4.42 (dd, *J* = 14.2, 7.1 Hz, 2H), 1.31 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.4, 164.3, 148.2 (q, $^2J_{F-C}$ = 37 Hz), 135.4, 132.8, 130.6, 129.3, 129.1, 128.6, 128.0, 127.9, 127.1, 123.2, 119.6 (q, $^1J_{F-C}$ = 271 Hz), 62.4, 14.2; ^{19}F NMR (565 MHz, $CDCl_3$) δ –68.85 (d, *J* = 3.8 Hz, 3F); HRMS (ESI) found: m/z 345.0824 $[M+Na]^+$; calcd. for $C_{16}H_{13}F_3N_2O_2$+Na 345.0821; IR (KBr): ν 3061, 2985, 1740, 1585, 1470, 1351, 1272, 1170, 1031, 802, 752, 475 cm^{-1}.

To a 25 mL Schlenk tube was PPh_3 (0.75 mmol, 1.5 equiv.) under Ar atmosphere, then CF_3CHN_2 (0.45 mmol, 1.5 equiv.) was added and the mixture was stirred at rt for 5 minutes. Subsequently benzaldehyde (0.5 mmol, 1.0 equiv.) was added to the reaction system in one pot and the reaction was performed at 50 °C for 48 h with stirring. After the reaction was complete detected by TLC, column chromatography on silica gel (ethyl acetate/ petroleum ether = 1:50 as the eluent) was directly conducted on the reaction mixture to afford the desired product. The product from the previous step was then treated with $LiAlH_4$ at 0 °C for 12 h. After the reaction was completed, the mixture was quenched with aqueous ammonium chloride solution and extracted with ethyl acetate. The combined organic layers were washed with brine and dried over $MgSO_4$. Evaporation of the solvent and purification of the crude mixture by column chromatography. **6a**, 44 mg, 72% yield, oil; ^1H NMR (600 MHz, $CDCl_3$) δ 7.53 (s, 1H), 7.44 (d, *J* = 7.4 Hz, 2H), 7.24 (t, *J* = 7.4 Hz, 2H), 7.19 (t, *J* = 7.2 Hz, 1H), 5.47 (s, 1H), 3.77 – 3.69 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 140.3, 134.9, 128.9, 128.7, 126.4, 124.8 (q, $^1J_{F-C}$ = 279 Hz), 51.6 (q, $^2J_{F-C}$ = 32 Hz); ^{19}F NMR (565 MHz, $CDCl_3$) δ –71.79 (t, *J* = 9.0 Hz, 3F); HRMS (APCI) found: m/z 203.0798 $[M+H]^+$; calcd. for $C_9H_9F_3N_2$+H 203.0791.

To a 25 mL Schlenk tube was PPh_3 (0.75 mmol, 1.5 equiv.) under Ar atmosphere, then CF_3CHN_2 (0.45 mmol, 1.5 equiv.) was added and the mixture was stirred at rt for 5 minutes. Subsequently benzaldehyde (0.5 mmol, 1.0 equiv.) was added to the reaction system in one pot and the reaction was performed at 50 °C for 48 h with stirring. After the reaction was complete detected by TLC, column chromatography on silica gel (ethyl acetate/ petroleum ether = 1:50 as the eluent) was directly conducted on the reaction mixture to afford the desired product. The product from the previous step was transferred to a 50 mL Schlenk tube, Pd/C (40 mg) and ethyl acetate (10 mL) were added under Ar atmosphere, then the system was replaced with a hydrogen atmosphere and maintained at a pressure of 1 atm, and the reaction was performed at room temperature for 24 h. After the reaction was complete, the system was suction-filtered, and the filtrate is concentrated and purified by silica gel column chromatography (petroleum ether/ethyl acetate = 50:1) to obtain the product **6b**. 60 mg, 60% yield; ^1H NMR (600 MHz, $CDCl_3$) δ 7.39 (t, *J* = 7.2 Hz, 2H), 7.35 (d, *J* = 7.2 Hz, 1H), 7.32 (d, *J* = 7.2 Hz, 2H), 6.64 (dd, *J* = 7.6, 3.7 Hz, 1H), 6.31 (s, 1H), 4.31 (d, *J* = 4.0 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 135.1, 129.2, 128.4, 128.2, 121.7 (q, $^1J_{F-C}$ = 267 Hz), 119.4 (q, $^2J_{F-C}$ = 38 Hz), 51.6; ^{19}F NMR (565 MHz, $CDCl_3$) δ –65.02 (d, *J* = 3.4 Hz, 3F); HRMS (ESI) found: m/z 225.0618 $[M+Na]^+$; calcd. for $C_9H_9F_3N_2$+Na 225.0610.

Supporting Information

The supporting information for this article is available on the WWW under https://doi.org/10.1002/cjoc.2018xxxxx.

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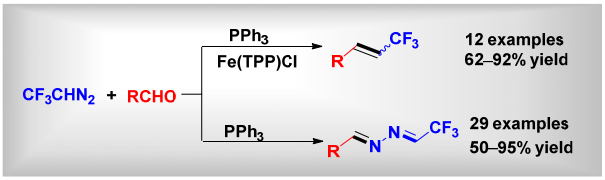

Facile transformations of aldehydes with CF_3CHN_2 to CF_3-alkenes and CF_3-hydrazones have been achieved via phosphine-relay strategy.

Fa-Guang Zhang,*[,†] Ning Lv,[†] Yan Zheng, and Jun-An Ma*