Article

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Construction of β-trifluoromethyl enol ether via base-promoted C-O coupling and rearrangement of hydrogen atom

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Abstract: A novel, high-efficiency and high-selectivity construction of β-trifluoromethyl enol ether via base-induced/promoted C-O coupling of trifluoromethylated vinyl chloride and phenols is presented with a broad substrate scope. The reaction mechanism, especially the significantly high selectivity, was excavated and understood via DFT calculation, and is well supported by the experimental observation.

Key Words: β-Trifluoromethyl enol ether, C-O coupling, DFT calculation

Introduction

Owning to the unique properties of the fluorine atom, the introduction of trifluoromethyl group ($-CF_3$) to organic compounds, such as pharmaceuticals, agricultural chemicals and functional materials, may significantly improve their performances.[1] However, most of the synthesis

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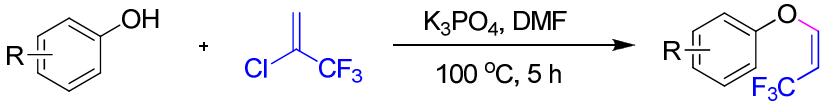
[§] Kun Dai and Kuan Wang contributed equally to this work.

procedures need either expensive substrates or complicated schemes.[2] Thus, there is an urgent need to develop simple and efficient methods to incorporate -CF_3 into the targeted organics.

Enol ethers are a kind of highly important intermediates in fine chemical products, and generally synthesized via C-O bond formation (coupling). So far several ways for C-O coupling have been reported, including the coupling of phenols with arylboronic acids,[3] Ullmann coupling,[4] Williamson ether synthesis,[5] palladium catalyzed coupling of aryl halides,[6] and iron-catalyzed coupling.[7] It is reported that some aliphatic *β*-trifluoromethyl enol ethers could be prepared from 2-bromo-3,3,3-trifluoroprop-1-ene[10] and 2,3,3,3-tetrafluoroprop-1-ene[11]. Puy reported the coupling of 2,4-dichloro-1,1,1-trifluoro-but-2-ene with phenol,[8] via which an aromatic *β*-trifluoromethyl enol ether was synthesized. It was observed that only the chlorine at site 4 (allyl chlorine[9]) can react with phenol, while the chlorine at site 2 (vinyl chlorine) cannot. Interestingly, a vinyl chlorine of (E)-1-chloro-3,3,3-trifluoroprop-1-ene[12] was recently used and coupled with phenols, via which a kind of aromatic (E)-*β*-trifluoromethyl enol ethers were prepared, while the substrate scopes were found to be severely limited. An alternative strategy to synthesize aromatic *β*-trifluoromethyl enol ethers was demonstrated[13], in which trifluoromethyl acetylenes were employed and coupled with phenols. To the best of our knowledge, no example has been reported that directly converting 2-halogeno-3,3,3-trifluoroprop-1-ene into aromatic (Z)-*β*-trifluoromethyl enol ethers.

2-Chloro-3,3,3-trifluoroprop-1-ene (HCFO-1233xf) is a commercially available and low-cost chlorofluorocarbon, and is mainly used as a refrigerant in automotive industry. HCFO-1233xf may also be a promising precursor or synthon in view of its special structure. So far very few publications have been reported about its conversion to other fluorinated fine chemicals.[14-16]



Scheme 1. Conversion of HCFO-1233xf into *β*-trifluoromethyl enol ethers.

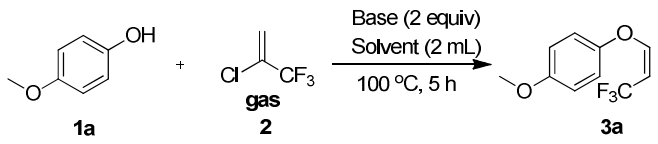
Herein, we develop a simple and efficient reaction route to selectively construct *β*-trifluoromethyl enol ether by using base-induced/promoted C-O coupling of trifluoromethylated vinyl chloride (namely HCFO-1233xf) and phenols (with a broad substrate scope, as shown in Scheme 1). The synthetic mechanism as well as the kinetics for the rate limiting step in the coupling reaction is excavated and understood via density functional theory (DFT) calculations, via which the observed specially high selectivity of the targeted products of (*Z*)-*β*-trifluoromethyl enol ethers is well supported.

Results and discussion

4-Methoxy-phenol **1a** and 2-chloro-3,3,3-trifluoroprop-1-ene **2** were used as the tested substrates via which the reaction conditions were optimized. Typical procedure is described as follows. A solution of 4-methoxy-phenol **1a** and 2-chloro-3,3,3-trifluoroprop-1-ene **2** in DMSO was stirred at 100 ^{o}C for 5 h in the existence of NaOH. The results are shown in Table 1.

As shown in Table 1, it is found that only 1-methoxy-4-(1-trifluoromethyl-vinyloxy)-benzene **3a** was detected in a low yield of 15% and a *Z*/*E* ratio of 95:5 (Table 1, Entry 1). While obvious improvement is obtained by changing the solvent from DMSO to DMF (Table 1, Entry 3). Followed by various bases were explored (Entry 3-15). It is seen that K_3PO_4 may be the best base to promote/catalyze the titled reaction, via which the desired product can be definitely obtained in a yield of 85% and a *Z*/*E* ratio of 93:7 (Table 1, Entry 13). Meanwhile, it is observed that the expected product cannot be detected in some strong base systems, such as LiHMDS and *n*-BuLi (Table 1, Entry 14-15). Clearly, the best reaction conditions may be DMF (2 mL), K_3PO_4 (2 equiv) and at 100 °C for 5 h. It is indicated that the weak base of K_3PO_4 may act as an efficient catalyst and thus significantly promote the titled C-O coupling reaction.

Table 1. Optimization of reaction conditions[a].



Entry	Solvent	Base	Yield (%) [c]	*Z*/*E* ratio [d]
1	DMSO	NaOH	15	95:5
2 [b]	DMSO:DMF	NaOH	46	95:5
3	DMF	NaOH	57	95:5
4	DMF	$NaHCO_3$	18	95:5
5	DMF	Na_2CO_3	0	
6	DMF	KOH	44	95:5
7	DMF	$KHCO_3$	18	96:4
8	DMF	Pyridine	0	
9	DMF	LiOH	0	
10	DMF	$Ca(OH)_2$	0	
11	DMF	DBU	0	
12	DMF	TEA	0	
13	**DMF**	**K_3PO_4**	**85**	**93:7**
14	DMF	LiHMDS	0	
15	DMF	*n*-BuLi	0	

[a] Reaction conditions: 1a (1mmol), 2 (18 mmol), base (2 equiv), solvent (2 mL), 100 °C, 5 h.

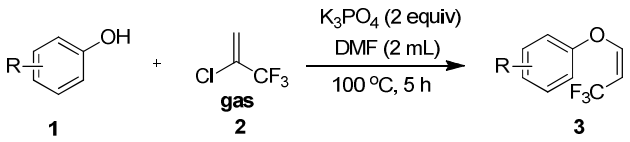
[b] DMSO:DMF=1:1 (2 mL in total)

[c] Yields were determined by ^{19}F NMR integration of products relative to the internal standard of ethyl *p*-fluoroacetophenone.

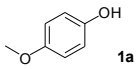
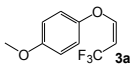
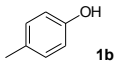
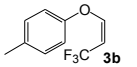
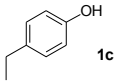
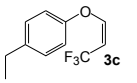
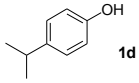
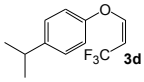
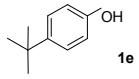
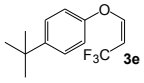
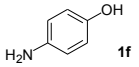
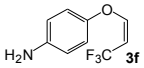
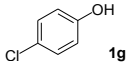
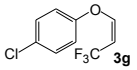
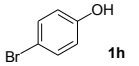
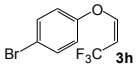
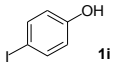
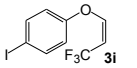
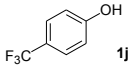
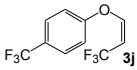
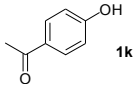
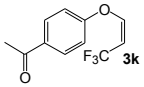
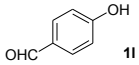
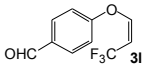
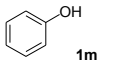
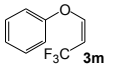
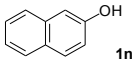
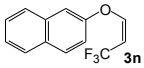
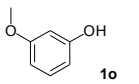
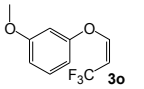
[d] Z/E ratio was determined by ^{19}F NMR.

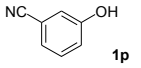
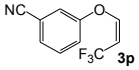
Various substituted phenols were examined to react with 2-chloro-3,3,3-trifluoroprop-1-ene **2** under the optimized conditions so as to investigate the substrate scope of the presented coupling reaction. The results are shown in Table 2.

Table 2. Substrate scope[a]



1 2 3

Entry	Phenol	Product	Yield (%)	*Z*/*E* ratio[b]
1	 1a	 3a	85	93:7
2	 1b	 3b	81	>99:1
3	 1c	 3c	80	>99:1
4	 1d	 3d	83	>99:1
5	 1e	 3e	79	92:8
6	 1f	 3f	82	>99:1
7	 1g	 3g	78	>99:1
8	 1h	 3h	85	>99:1
9	 1i	 3i	84	>99:1
10	 1j	 3j	64	>99:1
11	 1k	 3k	78	>99:1
12	 1l	 3l	93	>99:1
13	 1m	 3m	81	97:3
14	 1n	 3n	83	97:3
15	 1o	 3o	88	97:3

16	 1p	 3p	89	>99:1
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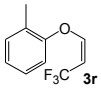
18	 1r	 3r	83	95:5
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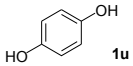
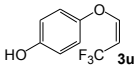
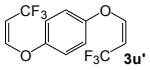
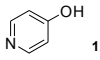
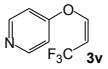
21	 1u	 3u	39	88:12
		 3u'	52 (Total 91)	>99:1
23	 1v	 3v	68	96:4

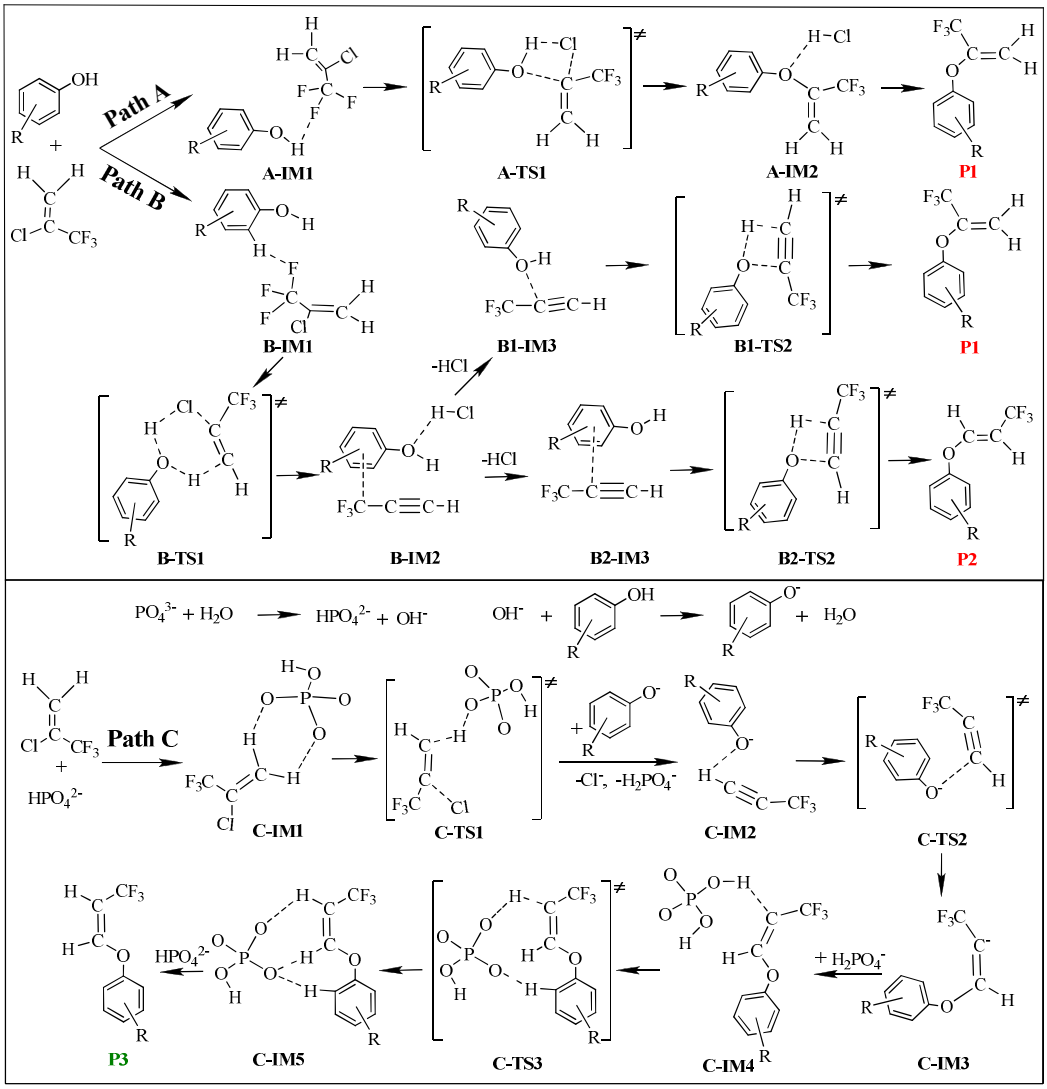
[a] Reaction conditions: phenol (1.0 mmol), 2 (18 mmol), K_3PO_4 (2 equiv), DMF (2 mL), 100 °C, 5 h.

[b] Z/E ratio was determined by ^{19}F NMR.

Interestingly, it is clearly shown that firstly, whenever the phenols are substituted with either electron-donating or electron-withdrawing groups, they can successfully react with 2-chloro-3,3,3-trifluoroprop-1-ene **2** to give the desired products with high reactivity, perfect regioselectivity and excellent stereoselectivity, though phenols with electron-donating substituent generally show (slightly) better reactivity than those with electron-withdrawing one (**3f** versus **3g or 3j)**. Secondly, it is found that the efficiency of the coupling reaction is almost unaffected by the substituent position in phenols. Wherever the phenols are substituted in *para*-, *meta*- or *ortho*-position, the desired products may be definitely obtained in high yields along with excellently high *Z*/*E* ratios under the optimized conditions. Unsurprisingly, non substituted phenol and naphthol (**3m, 3n**) can also efficiently undergo the reaction. Gratifyingly, paradioxybenzene is well-tolerated and got a high yield (**3u, 3u'**). Besides these various substituted phenols, a heterocyclic compound

of 4-pyridinol can also give an acceptable yield of the expected product via the titled coupling reaction and the rearrangement of H atom (**3v**). It is indicated that the presented coupling reaction has a considerably broad substrate scope. In this way, a novel, simple and efficient C-O coupling reaction route to selectively and even stereospecificly construct *β*-trifluoromethyl enol ether is established/demonstrated.

The mechanism of the titled coupling reaction is excavated via DFT calculations, through which the observed significantly high selectivity of the target (Z)-*β*-trifluoromethyl enol ether in the existence of K_3PO_4 is well supported. A schematic description of possible pathway is shown in Scheme 2. The optimized geometries and the corresponding relative energies are shown in Figure 1.



Scheme 2. Schematic depiction of C-O coupling mechnism of HCFO-1233xf with phenols.

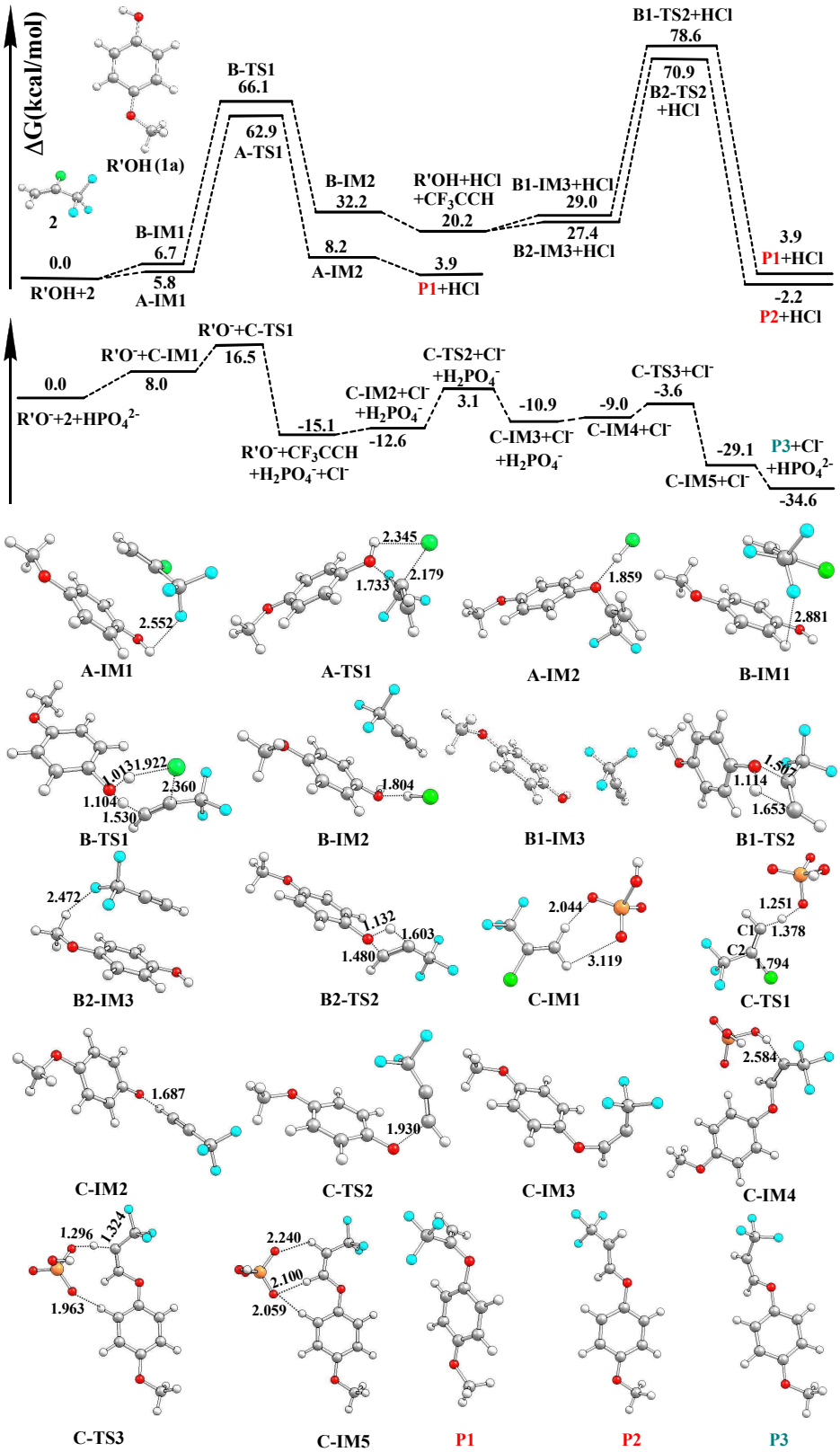


Figure 1. DFT computed schematic energy diagram and the corresponding optimized geometries (bond lengths are in angstrom).

As shown in Figure 1, starting with 4-methoxy-phenol **1a** (R'OH) and 2-chloro-3,3,3-trifluoroprop-1-ene **2**, the reaction may occur though either the direct (nucleophilic) substitution (denoted as path A) or the first elimination HCl of **2** followed by the addition of R'OH (denoted as path B). In path A, with the approaching of R'OH to **2,** a four-membered transition state A-TS1 is formed as the result of the elongation of O-H and C-Cl. The associated activation free energy ($\Delta G^{\neq}$) in this step is 57.1 kcal/mol. Consequently, HCl is eliminated and 1-methoxy-4(1-trifluoromethyl)-benzene (**P1**) is formed. For path B**,** R'OH may assist the H-transferring of **2** via a six-membered transition state B-TS1 with the $\Delta G^{\neq}$ of 59.4 kcal/mol, resulting in the formation of alkyne $CF_3C{\equiv}CH$. Next, the addition reaction of R'OH to $CF_3C{\equiv}CH$ occurs through two transition states of B1-TS2 and B2-TS2 with the $\Delta G^{\neq}$ of 49.6 and 43.5 kcal/mol, respectively. Eventually, **P1** and **P2** are produced. While obviously, so much high $\Delta G^{\neq}$ in paths A and B indicates that these two ways are unlikely to occur.

Since H^+ ion will be continuously produced during the coupling reaction, the existed weak base of PO_4^{3-} will be protonized and transformed to HPO_4^{2-} ($PO_4^{3-} + H^+ \rightarrow HPO_4^{2-}$). In view that there is much excess K_3PO_4, the reaction system must be weakly alkaline due to the hydrolysis of PO_4^{3-} ($PO_4^{3-} + H_2O \rightarrow HPO_4^{2-} + OH^-$), resulting in the production of the active $R'O^-$ ion in reaction system ($R'OH + OH^- \rightarrow R'O^- + H_2O$). Thus, the apparent/whole transformation of PO_4^{3-} and R'OH in the above mentioned reactions may be expressed as:

$$2PO_4^{3-} + R'OH + H^+ \rightarrow 2HPO_4^{2-} + R'O^-$$

We suppose that the increased HPO_4^{2-} may effectively induce/promote the coupling reaction of $R'O^-$ and **2.** After a synergetic rearrangement of H atom, the expected 1-methoxy-4-(1-trifluoromethyl-vinyloxy)-benzene **3a** forms. Such a HPO_4^{2-} induced reaction pathway is denoted as path C, and discussed as follows.

It is seen that the $\Delta G^{\neq}$ for the direct elimination HCl of **2** (shown in Figure S1) is high as 73.7 kcal/mol, which is in good agreement with the experimental observation[14] for that the harsh conditions of 70.0 psi and 500 ^{o}C were needed to realize the conversion of **2** to alkyne $CF_3C{\equiv}CH$. However, it is observed that the elimination HCl of **2** occurs considerably easily when the weak base of PO_4^{3-} was introduced into the reaction system, in which the temperature dramatically decreased to 100 ^{o}C as compared with the direct elimination process[14]. Thus the significant promotion of PO_4^{3-} should be investigated.

As shown in Scheme 2 and Figure 1, the co-existed HPO_4^{2-} (derived from PO_4^{3-}) may abstract H atom on **2** via C-TS1. Followed by that Cl^- ion releases, and the intermediate product of alkyne $CF_3C{\equiv}CH$ forms. The $\Delta G^{\neq}$ associated in this step is merely 8.5 kcal/mol, which is about 65.2 kcal/mol lower than that in the direct elimination HCl of **2** (Figure S1). Furthermore, as compared with the $\Delta G^{\neq}$ in the elimination HCl step in path B (B-IM1→B-IM2), the H-abstracting step in path C is also dramatically lower (by approximately 50.6 kcal/mol), indicating that path C is the most favorable way for the formation of the key intermediate product $CF_3C{\equiv}CH$. Next, the $R'O^-$ ion may preferentially or even selectively approach C1 (instead of C2) atom in $CF_3C{\equiv}CH$ via a transition state of C-TS2 to form the intermediate C-IM3. The $\Delta G^{\neq}$ in this step is 15.7 kcal/mol. The existence of $-CF_3$ may firstly result in larger steric hindrance in C2. More importantly, the biggest electronegativity of F atom along with the almost shortest bond length of C-F may make $-CF_3$ group become a negative charge center in $CF_3C{\equiv}CH$. We believe that it is these two factors that severely hinder the approaching of $R'O^-$ ion to C2 atom in $CF_3C{\equiv}CH$, and preponderantly answer for the high selectivity during the coupling reaction. Finally, H^+ transfers from $H_2PO_4^-$ to C1 atom on C-IM3 via C-TS3 to produce the final product **P3** (namely **3a**, (Z)-1-methoxy-4-(1-trifluoromethyl-vinyloxy)-benzene). The calculated $\Delta G^{\neq}$ in this step is merely 6.4 kcal/mol. Since the calculated $\Delta G^{\neq}$ in the rate-limiting step in path C (15.7 kcal/mol,

C-IM2→C-IM3) is much lower than that in path A (57.1 kcal/mol, A-IM1→A-IM2) and path B (59.4 kcal/mol, B-IM1→B-IM2), it is clear that path C is the most favorable way, namely, **P3** is the most favorable one among the three potential products. Such calculations by M06-2X are in very good agreement with the experimental observations, especially the perfect regio-/stereo-selectivity of the products. We also find that the weak base of K_3PO_4 can neutralize the produced H^+ during the coupling reaction. More importantly, K_3PO_4 (in its protonized form of HPO_4^{2-}) can effectively induce and assist the H-transferring, and thus dramatically promote the formation of not only the key intermediate $CF_3C{\equiv}CH$ but also the final product **P3**. This calculation may well explain the experimental observation why K_3PO_4 is markedly better than the other bases used in the titled coupling reaction.

To further discern the selectivity and understand the formation of the stereospecific Z-alkene, the kinetics of the coupling reaction is intentionally investigated. The pseudo-first-order rate constants (k, s^{-1}) of the rate-limiting steps of paths A-C are calculated at different temperatures and listed in Table 3. As shown in Table 3, the $k_{C\text{-}2}$ for the HPO_4^{2-}-induced coupling reaction is found to be dramatically larger than not only the $k_{A\text{-}1}$ for the direct coupling (in path A), but also the $k_{B\text{-}1}$ for the R'OH-assisted coupling (in path B) in the temperature ranges of 25 to 145 ^oC. Both $k_{A\text{-}1}$ and $k_{B\text{-}1}$ are quite small (1.73×10^{-21} and 1.91×10^{-22} s^{-1}) at 100 ^oC, whereas there is an incredible increase by approximately 18 orders of magnified in the k value when HPO_4^{2-} is introduced into the coupling system. It is clearly suggested that the HPO_4^{2-}-induced path C is the most favorable way in the titled coupling reaction, which is in good agreement with not only the reaction barriers predicted via DFT calculation, but also the experimental observations obtained with a broad substrate scope of phenols. It is expected that the presented mechanism and kinetics may provide a better understanding of the C-O coupling of HCFO-1233xf with phenols, and thus may contribute great to the study of the C-O coupling of similar system.

Table 3. The pseudo-first-order rate constants (k, s^{-1}) computed at different temperatures of the rate-limiting steps in paths A-C.

T/°C	k/s^{-1}		
	Path A (k_{A-1})	Path B (k_{B-1})	Path C (k_{C-2})
25	1.42×10^{-29}	3.34×10^{-31}	2.54×10^{1}
55	6.73×10^{-26}	3.18×10^{-27}	2.02×10^{2}
75	8.48×10^{-24}	6.00×10^{-25}	6.59×10^{2}
85	7.78×10^{-23}	6.62×10^{-24}	1.13×10^{3}
95	6.33×10^{-22}	6.42×10^{-23}	1.90×10^{3}
100	1.73×10^{-21}	1.91×10^{-22}	2.42×10^{3}
105	4.62×10^{-21}	5.53×10^{-22}	3.08×10^{3}
115	3.04×10^{-20}	4.26×10^{-21}	4.89×10^{3}
125	1.82×10^{-19}	2.97×10^{-20}	7.58×10^{3}
145	5.06×10^{-18}	1.09×10^{-18}	1.71×10^{4}

Conclusion

We have developed a novel and effective method to prepareβ-trifluoromethyl enol ether via the C-O coupling of trifluoromethylated vinyl chloride and phenols. High reactivity as well as perfect selectivity is definitely achieved in a quite broad of phenol substrates in the presence of K_3PO_4. The mechanism, kinetics and selectivity are investigated by DFT calculations, which are in very good agreement with what were observed in experiments. It is expected that the present work may contribute great to the construction of β-trifluoromethyl enol ether as well as other fluorinated fine chemicals, providing a promissing way to convert the chlorofluorocarbon of trifluoromethylated vinyl chloride to function materials.

Experimental Section

Materials. Unless otherwise mentioned, solvents and reagents were purchased from commercial sources and used as received. DMF was distilled on CaH_2 before being used.

Synthesis of *β*-trifluoromethyl enol ether. The reaction was carried out in an autoclave containing a 10 mL Teflon reaction tube. Phenols (1 mmol), $7H_2O{\cdot}K_3PO_4$ (676 mg, 2 equiv, 2 mmol), and a magnetic stir bar were placed in the tube, then DMF (2 mL) was added to the tube, which was then capped with a stopper. The autoclave was cooled down to -100 ^oC by liquid nitrogen so as to add 2-chloro-3,3,3-trifluoroprop-1-ene (**2**, 18 mmol). Finally, the autoclave was wormed in an oil bath at 100 °C for 5 h. After the reaction, the autoclave was then cooled to room temperature and vented to discharge the excess 2-chloro-3,3,3-trifluoroprop-1-ene carefully. Water (60 mL) was added, and then the product was extracted with EA (3×15 mL). The organic layers were washed with brine, dried over Na_2SO_4, and evaporated to the organic solvent under reduced pressure. The raw product was purified by column chromatography (silica gel, petroleum ether/ethyl acetate as the eluent). (NOTE: The excess of **2** can be collected and recycled).

Characterization. The FT-IR spectra were measured on a PerkinElmer Spectrum 400 FTIR/FTNIR Spectrophotometer in KBr disks. ^1H, ^{13}C and ^{19}F NMR spectra were recorded on 500 MHz NMR spectrometer in $CDCl_3$ at 25 ^oC. Tetramethylsilane (TMS) and the residual chloroform were used as references of chemical shift for ^1H and ^{13}C NMR spectra. $CFCl_3$ was used as reference of chemical shift for ^{19}F NMR spectra. Data for ^1H, ^{13}C and ^{19}F NMR spectra are expressed as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet). Mass spectra were obtained on a Bruker MAXIS mass spectrometer, via which the high-resolution mass data were recorded in the ESI mode.

The analytic data for the obtained products are shown as follows.

(Z)-1-methoxy-4-(3,3,3-trifluoroprop-1-enyloxy)benzene (3a) 85%, 185 mg; Colorless oil. R_f= 0.8 (petroleum ether); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.98 (d, 2H, *J* = 9.0 Hz), 6.86 (d, 2H, *J* = 9.5 Hz), 6.64 (d, 1H, *J* = 7 Hz), 4.96-4.89 (m, 1H), 3.78 (s, 3H). ^{13}C{1H}NMR (125 MHz, $CDCl_3$) δ 156.6, 150.8, 150.3 (q, *J* =5.3 Hz), 123.0 (q, *J* = 267.8 Hz), 118.5, 114.9, 98.3 (q, *J* = 35 Hz), 55.6. ^{19}F NMR (470 MHz, $CDCl_3$) δ -57.53 (d, *J* = 8.9 Hz, 3F).

IR (KBr): 3009, 2956, 2840, 1671, 1506, 1423, 1274, 1209, 1151, 1121, 1048, 892, 833 cm^{-1}.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{10}H_9F_3O_2Na$ 241.0452; found: 241.0447.

(Z)-1-methyl-4-((3,3,3-trifluoroprop-1-en-1-yl)oxy)benzene (3b) 81%, 163 mg; Colorless oil. R_f= 0.8 (petroleum ether); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15 (dd, *J* = 8.7, 0.6 Hz, 2H), 6.94 (d, *J* = 8.6 Hz, 2H), 6.70 (d, *J* = 6.9 Hz, 1H), 4.98-4.92 (m, 1H), 2.32 (s, 3H). ^{13}C{1H}NMR (125 MHz, $CDCl_3$) δ 154.7, 149.7 (q, *J* = 5.4 Hz), 134.2, 130.3, 122.9 (q, *J* = 267.8 Hz), 117.1, 98.7 (q, *J* = 35.1 Hz), 20.6. ^{19}F NMR (470 MHz, $CDCl_3$) δ -57.63 (d, *J* = 7.5 Hz, 3F).

IR (KBr): 3036, 2928, 1678, 1609, 1508, 1425, 1275, 1216, 1154, 1121, 1049, 892, 827 cm^{-1}.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_9H_{10}F_3ONa$ 225.0553; found: 225.0548.

(Z)-1-ethyl-4-((3,3,3-trifluoroprop-1-en-1-yl)oxy)benzene (3c) 80%, 173 mg; Colorless oil. R_f= 0.8 (petroleum ether); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17 (d, *J* = 8.6 Hz, 2H), 6.96 (d, *J* = 8.6 Hz, 2H), 6.71 (d, *J* = 6.9 Hz, 1H), 4.99 – 4.92 (m, 1H), 2.63 (q, *J* = 7.6 Hz, 2H), 1.22 (t, *J* = 7.6 Hz, 3H). ^{13}C{1H}NMR (125 MHz, $CDCl_3$) δ 154.8, 149.7 (q, *J* = 5.4 Hz), 140.7, 129.2, 122.9 (q, *J* = 267.7 Hz), 117.2, 98.7 (q, *J* = 35 Hz), 28.1, 15.7. ^{19}F NMR (470 MHz, $CDCl_3$) δ -57.57 (d, *J* = 8.9 Hz, 3F).

IR (KBr): 3037, 2970, 2935, 2875, 1678, 1605, 1508, 1458, 1422, 1275, 1216, 1154, 1121, 1049, 893,837 cm^{-1}.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{11}H_{11}F_3ONa$ 239.0660; found: 239.0654.

(Z)-1-isopropyl-4-((3,3,3-trifluoroprop-1-en-1-yl)oxy)benzene (3d) 83%, 191 mg; Colorless oil. R_f= 0.8 (petroleum ether); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.6 Hz, 2H), 6.97 (d, *J* = 8.7 Hz, 2H), 6.71 (d, *J* = 6.9 Hz, 1H), 4.99 – 4.93 (m, 1H), 2.94 – 2.85 (m, 1H), 1.23 (d, *J* = 6.9 Hz, 6H). ^{13}C{1H}NMR (125 MHz, $CDCl_3$) δ 154.8, 149.6 (q, *J* = 5.4 Hz), 145.4, 127.7, 122.9 (q, *J* = 267.7 Hz), 117.1, 98.8 (q, *J* = 35 Hz), 33.5, 24.1. ^{19}F NMR (470 MHz, $CDCl_3$) δ -57.57 (d, *J* = 9.4 Hz, 3F).

IR (KBr): 3037, 2964, 2932, 2874, 1677, 1605, 1508, 1462, 1421, 1275, 1218, 1155, 1121, 1046, 893, 837 cm^{-1}.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{12}H_{13}F_3ONa$ 253.0816; found: 253.0814.

(Z)-1-(tert-butyl)-4-((3,3,3-trifluoroprop-1-en-1-yl)oxy)benzene (3e) 79%, 192 mg; Colorless oil. R_f = 0.8 (petroleum ether); ^1H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.9 Hz, 2H), 6.98 (d, *J* = 8.9 Hz, 2H), 6.73 (d, *J* = 6.9 Hz, 1H), 5.00 – 4.94 (m, 1H), 1.31 (s, 9H). $^{13}C\{1H\}$NMR (125 MHz, $CDCl_3$) δ 154.5, 149.6 (q, *J* = 5.4 Hz), 147.6, 126.7, 122.9 (q, *J* = 267.7 Hz), 116.7, 98.8 (q, *J* = 35.1 Hz).34.4, 31.4. ^{19}F NMR (470 MHz, $CDCl_3$) δ -57.58 (d, *J* = 9.4 Hz, 3F).

IR (KBr): 3043, 2965, 2907, 2872, 1676, 1605, 1510, 1465, 1422, 1274, 1222, 1155, 1118, 1049, 894, 837 cm^{-1}.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{13}H_{15}F_3ONa$ 267.0973; found: 267.0972.

(Z)-4-((3,3,3-trifluoroprop-1-en-1-yl)oxy)aniline (3f) 82%, 166 mg; Dark brown oil. R_f = 0.2 (petroleum ether);^1H NMR (500 MHz, $CDCl_3$) δ 6.86 (d, *J* = 8.8 Hz, 2H), 6.65 – 6.61 (m, 3H), 4.91 – 4.85 (m, 1H), 3.59 (s, 2H). $^{13}C\{1H\}$NMR (125 MHz, $CDCl_3$) δ 150.8 (q, *J* = 5.4 Hz), 149.7, 143.5, 123.1 (q, *J* = 267.6 Hz), 118.6 (s), 116.0 (s), 97.7 (q, *J* = 34.8 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) δ -57.42 (d, *J* = 8.9 Hz, 3F).

IR (KBr): 3454, 3381, 3047, 3018, 1675, 1627, 1509, 1422, 1271, 1212, 1153, 1113, 1048, 890, 832 cm^{-1}.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_9H_9F_3ON$ 204.0636; found: 204.0632.

(Z)-1-chloro-4-((3,3,3-trifluoroprop-1-en-1-yl)oxy)benzene (3g) 78%, 174 mg; Colorless oil. R_f= 0.8 (petroleum ether);^1H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, *J* = 9.0 Hz, 2H), 7.00 (d, *J* = 9.0 Hz, 2H), 6.68 (d, *J* = 6.9 Hz, 1H), 5.07 – 5.01 (m, 1H). $^{13}C\{1H\}$NMR (125 MHz, $CDCl_3$) δ 155.1, 148.7 (q, *J* = 5.4 Hz), 129.9, 129.9, 122.7 (q, *J* = 267.8 Hz), 118.6, 100.0 (q, *J* = 35.2 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) δ -57.77 (d, *J* = 8.9 Hz, 3F).

IR (KBr): 3025, 1650, 1595, 1488, 1422, 1275, 1220, 1154, 1119, 1047, 1011, 890, 832 cm^{-1}.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_9H_7ClF_3O$ 223.0138; found: 223.0140.

(Z)-1-bromo-4-((3,3,3-trifluoroprop-1-en-1-yl)oxy)benzene (3h) 85%, 227 mg; Colorless oil. R_f= 0.8 (petroleum ether); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, 2H, *J* = 9.0 Hz), 6.94 (d, 2H, *J* = 8.5 Hz), 6.68 (d, 1H, *J* = 6.5 Hz), 5.07-5.01 (m, 1H). ^{13}C{1H}NMR (125 MHz, $CDCl_3$) δ 155.6, 148.6 (q, *J* =5.3 Hz), 132.9, 122.6 (q, *J* = 268.0 Hz), 119.0, 117.4, 100.1 (q, *J* = 35.2 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) δ -57.73 (d, *J* = 8.0 Hz, 3F).

IR (KBr): 3025, 1652, 1590, 1482, 1422, 1275, 1220, 1154, 1119, 1047, 1011, 890, 832 cm^{-1}.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_9H_7BrF_3O$ 266.9632; found: 266.9636.

(Z)-1-iodo-4-((3,3,3-trifluoroprop-1-en-1-yl)oxy)benzene (3i) 84%, 264 mg; Colorless oil. R_f= 0.8 (petroleum ether); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 9.0 Hz, 2H), 6.81 (d, *J* = 9.0 Hz, 2H), 6.67 (d, *J* = 6.9 Hz, 1H), 5.07 – 5.01 (m, 1H). ^{13}C{1H}NMR (125 MHz, $CDCl_3$) δ 156.4, 148.4 (q, *J* = 5.4 Hz), 138.9, 122.7 (q, *J* = 268.0 Hz), 119.4, 100.2 (q, *J* = 35.1 Hz), 87.9. ^{19}F NMR (470 MHz, $CDCl_3$) δ -57.70 (d, *J* = 8.9 Hz, 3F).

IR (KBr): 3088, 3025, 1685, 1578, 1481, 1421, 1270, 1221, 1173, 1108, 1039, 1001, 884, 827 cm^{-1}.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_9H_7F_3IO$ 342.9807; found: 342.9803.

(Z)-1-(trifluoromethyl)-4-((3,3,3-trifluoroprop-1-en-1-yl)oxy)benzene (3j) 64%, 164 mg; Colorless oil. R_f= 0.8 (petroleum ether); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.5 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 6.77 (d, *J* = 6.8 Hz, 1H), 5.17 – 5.11 (m, 1H). ^{13}C{1H}NMR (125 MHz, $CDCl_3$) δ 158.6, 147.67 (q, *J* = 5.4 Hz), 127.4 (q, *J* = 3.8 Hz), 126.9 (q, *J* = 32.7 Hz), 123.8 (q, *J* = 270 Hz), 122.5 (q, *J* = 268.1 Hz), 101.2 (q, *J* = 35.2 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) δ -62.07 (s, 3F), -57.93 (d, *J* =8.9 Hz, 3F).

IR (KBr): 3128, 3027, 1682, 1612, 1515, 1419, 1329, 1278, 1227, 1156, 1123, 1069, 1045, 892, 843 cm^{-1}.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{10}H_6F_6ONa$ 279.0021; found: 279.0032.

(Z)-1-(4-((3,3,3-trifluoroprop-1-en-1-yl)oxy)phenyl)ethan-1-one (3k) 78%, 179 mg; Colorless oil. R_f= 0.4 (petroleum ether); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.9 Hz, 2H), 7.12 (d, *J* = 8.9 Hz, 2H), 6.82 (d, *J* = 6.9 Hz, 1H), 5.17 – 5.11 (m, 1H), 2.59 (s, 3H). ^{13}C{1H}NMR (125 MHz,

$CDCl_3$) δ 196.5, 159.6, 147.6 (q, *J* = 5.4 Hz), 133.6, 130.7, 122.5 (q, *J* = 268.1 Hz), 101.1 (q, *J* = 35.2 Hz), 26.5. ^{19}F NMR (470 MHz, $CDCl_3$) δ -57.85 (d, *J* = 8.9 Hz, 3F).

IR (KBr): 1681, 1598, 1504, 1471, 1361, 1262, 1224, 1153, 1117, 1046, 959, 841 cm^{-1}.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{11}H_9F_3O_2Na$ 253.0452; found: 253.0447.

(Z)-4-((3,3,3-trifluoroprop-1-en-1-yl)oxy)benzaldehyde (3l) 93%, 201 mg; Colorless oil. R_f = 0.4 (petroleum ether); ^1H NMR (500 MHz, $CDCl_3$) δ 9.97 (s, 1H), 7.93 (d, *J* = 8.8 Hz, 2H), 7.20 (d, *J* = 8.6 Hz, 2H), 6.84 (d, *J* = 6.8 Hz, 1H), 5.21–5.15 (m, 1H). $^{13}C\{1H\}$NMR (125 MHz, $CDCl_3$) δ 190.5, 160.5, 147.2 (q, *J* = 5.4 Hz), 132.9, 132.0, 122.4 (q, *J* = 268.1 Hz), 101.7 (q, *J* = 35.2 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) δ -57.93 (d, *J* = 8.9 Hz, 3F).

IR (KBr): 1680, 1600, 1506, 1274, 1221, 1156, 1121, 1052, 835 cm^{-1}.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{10}H_7F_3O_2Na$ 239.0296; found: 239.0286.

(Z)-((3,3,3-trifluoroprop-1-en-1-yl)oxy)benzene (3m)[13] 81%, 152 mg; Colorless oil. R_f = 0.7 (petroleum ether); ^1H NMR (500 MHz, $CDCl_3$) δ 7.38-7.34 (m, 2H), 7.18-7.15 (m, 1H), 7.06-7.04 (m, 2H), 6.74 (d, 1H, *J* = 9.0 Hz), 5.03-4.97 (m, 1H).$^{13}C\{1H\}$NMR (125 MHz, $CDCl_3$) δ 156.6, 149.2 (q, *J* =5.3 Hz), 129.9, 122.8 (q, *J* = 267.8 Hz), 117.3, 99.2 (q, *J* = 35.0 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) δ -57.66 (d, *J* = 8.9 Hz, 3F).

IR (KBr): 3007, 2950, 2842, 1670, 1600, 1503, 1423, 1274, 1209, 1151, 1121, 1048, 892 cm^{-1}.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_9H_7F_3ONa$ 211.0347; found: 211.0344.

(Z)-2-((3,3,3-trifluoroprop-1-en-1-yl)oxy)naphthalene (3n) 83%, 198 mg; Colorless oil. R_f = 0.8 (petroleum ether); ^1H NMR (500 MHz, $CDCl_3$) δ 7.84 (t, *J* = 7.7 Hz, 1H), 7.78 (d, *J* = 8.5 Hz, 1H), 7.51 – 7.48 (m, 1H)., 7.46 – 7.42 (m, 1H), 7.39 (d, *J* = 2.5 Hz, 1H), 7.27 (dd, *J* = 8.9, 2.5 Hz, 1H), 6.88 (d, *J* = 6.9 Hz, 1H), 5.11 – 5.04 (m, 1H). $^{13}C\{1H\}$NMR (126 MHz, $CDCl_3$) δ 154.4, 149.1 (q, *J* = 5.4 Hz), 133.9, 130.7, 130.2, 127.8, 127.3, 127.0, 125.4, 122.9 (q, *J* = 267.7 Hz), 118.3, 112.5, 99.7 (q, *J* = 35.1 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) δ -57.61 (d, *J* = 7.1 Hz, 3F).

IR (KBr): 1676, 1630, 1598, 1511, 1273, 1248, 1213, 1155, 1119, 860, 749 cm^{-1}.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{13}H_{10}F_3O$ 239.0684; found: 239.0685.

(Z)-1-methoxy-3-((3,3,3-trifluoroprop-1-en-1-yl)oxy)benzene (3o) 88%, 192 mg; Colorless oil. R_f= 0.8 (petroleum ether); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 (t, *J* = 8.2 Hz, 1H), 6.76 – 6.68 (m, 2H), 6.66 – 6.58 (m, 2H), 5.05 – 4.95 (m, 1H), 3.80 (s, 3H). ^{13}C{1H}NMR (125 MHz, $CDCl_3$) δ 161.0, 157.7, 149.1 (q, *J* = 5.4 Hz), 130.4, 122.8 (q, *J* = 267.8 Hz), 110.5, 109.0, 103.6, 99.3 (q, *J* = 5.4 Hz), 55.5. ^{19}F NMR (470 MHz, $CDCl_3$) δ -57.63 (d, *J* = 7.5 Hz, 3F).

IR (KBr): 2963, 2840, 1675, 1610, 1490, 1456, 1422, 1314, 1259, 1194, 1148, 1043, 940, 767 cm^{-1}.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{10}H_9F_3O_2Na$ 241.0452; found: 241.0451.

(Z)-3-((3,3,3-trifluoroprop-1-en-1-yl)oxy)benzonitrile (3p) 89%, 190 mg; Colorless oil. R_f= 0.4 (petroleum ether); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 – 7.43 (m, 2H), 7.40 – 7.28 (m, 2H), 6.74 (d, *J* = 6.8 Hz, 1H), 5.21 – 5.11 (m, 1H). ^{13}C{1H}NMR (125 MHz, $CDCl_3$) δ 156.3, 147.6 (q, *J* = 5.4 Hz), 131.1, 128.3, 122.4 (q, *J* = 268.1 Hz), 121.9, 120.5, 117.7, 114.0, 101.6 (q, *J* = 35.2 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) δ -57.95 (d, *J* = 8.9 Hz, 3F).

IR (KBr): 2961, 2231, 1675, 1609, 1487, 1456, 1422, 1259, 1194, 1148, 1042, 941, cm^{-1}.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{10}H_6F_3NONa$ 236.0299; found: 236.0299.

(Z)-1-methoxy-2-((3,3,3-trifluoroprop-1-en-1-yl)oxy)benzene (3q) 84%, 183 mg; Colorless oil. R_f= 0.8 (petroleum ether); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.16 – 7.09 (m, 1H), 7.03 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.95 (dd, *J* = 8.2, 1.4 Hz, 1H), 6.91 (td, *J* = 7.7, 1.4 Hz, 1H), 6.59 (d, *J* = 6.9 Hz, 1H), 4.92 – 4.86 (m, 1H), 3.84 (s, 3H). ^{13}C{1H}NMR (125 MHz, $CDCl_3$) δ 151.7 (q, *J* = 5.4 Hz), 150.5, 146.0, 126.0, 123.1 (q, *J* = 267.6 Hz), 121.1, 119.8, 113.4, 97.6 (q, *J* = 34.8 Hz), 56.1. ^{19}F NMR (470 MHz, $CDCl_3$) δ -57.30 (d, *J* = 7.5 Hz, 3F).

IR (KBr): 2946, 2842, 1671, 1606, 1502, 1461, 1420, 1260, 1210, 1107, 1025, 892, 748 cm^{-1}.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{10}H_9F_3O_2Na$ 241.0452; found: 241.0451.

(Z)-1-methyl-2-((3,3,3-trifluoroprop-1-en-1-yl)oxy)benzene (3r) 83%, 168 mg; Colorless oil. R_f= 0.8 (petroleum ether); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 – 7.16 (m, 2H), 7.06 (td, *J* = 7.5, 1.0 Hz, 1H), 6.93 (d, *J* = 8.1 Hz, 1H), 6.69 (d, *J* = 6.8 Hz, 1H), 4.99 – 4.93 (m, 2H), 2.28 (s, 3H). ^{13}C{1H}NMR (126 MHz, $CDCl_3$) δ 155.1, 149.9 (q, *J* = 5.4 Hz), 131.5, 128.7, 127.2, 124.7, 123.1 (q, *J* = 267.8 Hz), 116.1, 98.5 (q, *J* = 35 Hz), 15.6. ^{19}F NMR (470 MHz, $CDCl_3$) δ -57.62 (d, *J* = 9.4 Hz, 3F).

IR (KBr): 2962, 2842, 1679, 1641, 1599, 1491, 1420, 1261, 1224, 1155, 1021, 801, 750 cm^{-1}.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{10}H_{10}F_3O$ 203.0684; found: 203.0683.

(Z)-1-fluoro-2-((3,3,3-trifluoroprop-1-en-1-yl)oxy)benzene (3s) 74%, 152 mg; Colorless oil. R_f= 0.8 (petroleum ether); ^1H NMR (500 MHz, $CDCl_3$) δ 7.22 – 6.97 (m, 4H), 6.66 (dd, *J* = 6.9, 1.8 Hz, 1H), 4.99 – 5.05 (m, 4H). $^{13}C\{1H\}$NMR (125 MHz, $CDCl_3$) δ 153.1 (d, *J* = 248.7 Hz), 154.1, 152.1, 150.1 (qd, *J* = 5.4, 1.9 Hz), 144.2 (d, *J* = 11 Hz), 125.9 (d, *J* = 6.9 Hz), 124.8 (d, *J* = 4.0 Hz), 122.7 (q, *J* = 267.8 Hz), 120.1, 117.3 (d, *J* = 18 Hz), 99.4 (q, *J* = 35.2 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) δ -132.36 (d, *J* = 8.9 Hz, 3F), -57.73 (d, *J* = 8.9 Hz, 3F).

IR (KBr): 2966, 2842, 1680, 1584, 1506, 1478, 1419, 1278, 1227, 1155, 1067, 1044, 893, 753 cm^{-1}.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_9H_6F_4ONa$ 229.0252; found: 229.0248.

(Z)-1-chloro-2-((3,3,3-trifluoroprop-1-en-1-yl)oxy)benzene (3t) 79%, 176 mg; Colorless oil. R_f= 0.8 (petroleum ether); ^1H NMR (500 MHz, $CDCl_3$) δ 7.42 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.26 (td, *J* = 7.8, 1.5 Hz, 1H), 7.13 (td, *J* = 7.7, 1.5 Hz, 1H), 7.08 (dd, *J* = 8.1, 1.4 Hz, 1H), 6.62 (d, *J* = 6.8 Hz, 1H), 5.08 – 5.02 (m, 1H). $^{13}C\{1H\}$NMR (125 MHz, $CDCl_3$) δ 152.4, 149.5 (q, *J*= 5.4 Hz), 130.9, 128.1, 125.9, 125.0, 122.7 (q, *J* = 268 Hz), 118.9, 99.7 (q, *J* = 35 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) δ -57.76 (d, *J* = 7.5 Hz, 3F).

IR (KBr): 2962, 2842, 1680, 1585, 1509, 1479, 1448, 1419, 1280, 1227, 1155, 1211, 1067, 1044, 893, 752,678 cm^{-1}.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_9H_7ClF_3O$ 223.0318; found: 223.0317.

(Z)-4-((3,3,3-trifluoroprop-1-en-1-yl)oxy)phenol (3u) 39%, 80 mg; Colorless oil. ^1H NMR (500 MHz, $CDCl_3$) δ 6.94 (d, *J* = 9.0 Hz, 2H), 6.81 (d, *J* = 9.0 Hz, 2H), 6.64 (d, *J* = 6.9 Hz, 1H), 4.99 (s, 1H), 4.97 - 4.90 (m, 1H). $^{13}C\{1H\}$NMR (126 MHz, $CDCl_3$) δ 152.5, 150.9, 150.2 (q, *J* = 5.4 Hz), 122.9 (q, *J* = 267.8 Hz), 118.8, 116.3, 98.4 (q, *J* = 35.0 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) δ -57.55 (d, *J* = 8.0 Hz, 3F).

IR (KBr): 1677, 1508, 1450, 1275, 1207, 1153, 1117, 1047, 835, 833 cm^{-1}.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_9H_8F_3O_2$ 205.0476; found: 205.0479.

1,4-bis(((Z)-3,3,3-trifluoroprop-1-en-1-yl)oxy)benzene (3u') 52%, 155 mg; Colorless oil. R_f= 0.8

(petroleum ether); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.06 (s, 4H), 6.68 (d, *J* = 6.9 Hz, 2H), 5.10 - 4.92 (m, 2H). ^{13}C{1H}NMR (126 MHz, $CDCl_3$) δ 153.4, 149.2 (q, *J* = 5.4 Hz), 122.7 (q, *J* = 267.8 Hz), 118.7, 99.7 (q, *J* = 35.1 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) δ -57.73 (d, *J* = 8.0 Hz, 3F).

IR (KBr): 1678, 1503, 1424, 1271, 1208, 1152, 1121, 1049, 842, 799, 748 cm^{-1}.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{12}H_9F_6O_2$ 299.0507; found: 299.0505.

(Z)-4-((3,3,3-trifluoroprop-1-en-1-yl)oxy)pyridine (3v) 68%, 128 mg; Colorless oil. R_f= 0.2 (ethyl acetate); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.9 Hz, 2H), 7.14 (dq, *J* = 14.3, 1.9 Hz, 1H), 6.44 (d, *J* = 7.9 Hz, 2H), 5.79 – 5.73 (m, 1H). ^{13}C{1H}NMR (125 MHz, $CDCl_3$) δ 179.4, 136.8 (q, *J* = 7.1 Hz), 136.2, 123.0 (d, *J* = 267.0 Hz), 119.8, 104.3 (q, *J* = 35.3 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) δ -61.45 (d, *J* = 7.5 Hz, 3F).

IR (KBr): 1689, 1639, 1574, 1473, 1418, 1333, 1276, 1195, 1134, 953, 891, 854 cm^{-1}.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_8H_7F_3NO$ 190.0480; found: 190.0481.

Computational Methods.

DFT calculations are performed via Gaussian 09 software at M06-2X[17] method combined with the 6-311+G (d,p) basis sets. Intrinsic reaction coordinate (IRC) computations are employed to validate the connections between reactants, transition states, and products. The conductor-like polarizable continuum model (CPCM)[18,19] is used to evaluate the contribution of the solvent (DMF) to the titled reaction. The theoretical (pseudo-first-order) rate constants at different temperatures for the rate-determining steps of all pathways are calculated by using conventional transition state theory with an asymmetric Eckart tunneling correction (TST/Eckart) [20,21] in the VKLab program[22].

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Supporting Information

Structures for the products. References for the products. ^{1}H NMR, ^{13}C{1H}NMR and ^{19}F NMR spectra of the products. Cartesian coordinates, the number of imaginary frequencies (for transition state only), total energies of target or optimized structures obtained via DFT calculations. DFT computed schematic energy diagram and the structures for the direct eliminating HCl of HCFO-1233xf. These materials are provided free of charge *via* the Internet at http://pubs.acs.org.

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