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# EWG assisted nucleophilic fluorination using PPHF: a strategy for the synthesis of 1,2,2-triaryl-2-fluoroethanones

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ABSTRACT

The nucleophilic fluorination of 1,2,2-triaryl-2-hydroxyethanones by fluoride ion has been carried out using pyridinium poly(hydrogen fluoride) (PPHF) to give 1,2,2-triaryl-2-fluoroethanones in fairly good yield. The presence of electron withdrawing group (EWG), such as −COAr at the carbon bearing hydroxyl group facilitates such nucleophilic fluorination. The intermediacy of bridged oxiranyl ion and α-keto-carbenium ion has been proposed for the formation of various α-fluoroketones and benzofuran derivatives respectively.



## 1. Introduction

Fluorine containing organic compounds have important role in biochemistry, material science and medicinal chemistry.[1] Approximately 20% of drugs in the market contain fluorine and this number is expected to grow.[2] The enhanced biological activity, binding interaction and stability of C−F bond in these compounds make them suitable as drug molecules.[3] In particular, α-fluoro acetophenone (1-aryl-2-fluoroethanone) and its derivatives can produce a number of interesting molecules used in pharmaceutical and agrochemical industry.[4] A number of reagents have been discovered for fluorination of organic compounds depending on the type of functionality.[5] Fluorination at α-position of acetophenone and its derivatives can occur by replacing hydrogen or hetero atoms (O, N) using either electrophilic or nucleophilic source of fluorine respectively. The electrophilic methods use $F_2$, $CF_3OF$, $CsSO_4F$ or reagents such as *N*-fluoro-*o*-benzenedisulfonimide (NFOBS), *N*-fluorodiphenyldisulfonimide (NFSi), 1-fluoro-4-hydroxy-1,4-diazoniabicyclo [2.2.2] octane bis(tetrafluoroborate) (Accufluor-NFTh) and 1-fluoro-4-chloromethyl-1,4-diazoniabicyclo [2.2.2] octane bis(tetrafluoroborate) (Selectfluor).[4b,6] The intermediate involved in these reactions is either an enol or trialkylsilylenol ether. In the later case, a strong base is used to generate an enolate, which is trapped by trialkylchlorosilane. Both intermediates form α-fluoroketones with electrophilic fluorine. Similarly, a few methods have been reported using nucleophilic sources of fluorine, such as KF in 18-crown-6, tetraethylammonium fluoride (TEAF), $TlF_3$ and pyridinium poly(hydrogen fluoride) (PPHF) with HgO or NCS or NBS.[4b,7] The leaving group, such as halogen or $N_2^+$ in these reactions has been introduced before fluorination.

Since a large number of natural and synthetic compounds are alcohols, carboxylic acids and hydroxyketones, the fluorinating agent, which can react selectively with oxygen functionality would be a suitable one. The direct replacement of hydroxyl group by nucleophilic fluorine has been carried out using reagents, such as PPHF, diethylaminosulphur trifluoride (DAST) and Ishikawa reagent ($CF_3CHFCF_2NEt_2$+$CF_3CF{=}CFNEt_2$).[7e,8–10] Keeping in view of the nature of substrate, reaction, work up conditions, commercial availability and handling, PPHF is a reagent of choice. In this backdrop, we envisaged that, if it becomes viable to replace the hydroxyl group in 1,1-diaryl methanols or α-hydroxyketones with PPHF, it would be an important and effective strategy for the fluorodehydroxylation in these classes of compounds. It is further anticipated that the end products of such fluorodehydroxylation can function as versatile synthetic intermediates, which may find applications in fluorine substituted bioactive compounds.[11] In this paper, such advances leading to the desired α-fluoroketones and the role of different electron withdrawing groups (EWG) present at the carbon bearing hydroxyl group are presented.

## 2. Results and discussion

1,2,2-Triaryl-2-hydroxyethanones can be considered as having 1,1-diaryl methanol and benzoyl moieties (EWG). Since fluorination

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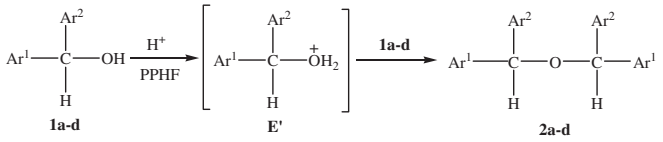
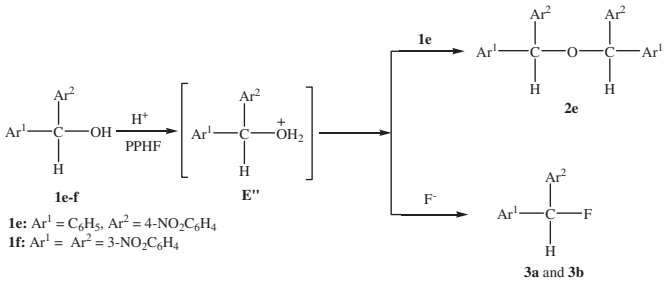
of 1,1-diaryl methanol derivatives[12] using PPHF has not been reported, attempts have been made towards their fluorodehydroxylation.[13a] The positive outcome of such a reaction would provide us an effective methodology to replace –OH group with $F^-$ in these class of compounds. Towards this objective, **1a**–**f** were treated with PPHF at ambient temperature. The compounds **1a**–**d** gave only corresponding bis (1,1-diphenylmethyl) ethers, **2a**–**d**[13] (Scheme 1, Table 1). 1-(4-Nitrophenyl)-1-phenyl methanol (**1e**) yielded both ether and fluoroalkane; bis[1-(4-nitrophenyl)-1-phenylmethyl] ether (**2e**, 33%) and 1-fluoro-1-(4-nitrophenyl)-1-phenyl methane, (**3a**, 43%). While the treatment of bis[1-(3-nitrophenyl)] methanol (**1f**) with PPHF under similar conditions gave only 1-fluoro-bis[1-(3-nitrophenyl)] methane (**3b**, 62%) (Scheme 2, Table 1). These compounds were characterised by various spectral data (See Experimental section).




**Scheme 1.** Formation of **2a**–**d**, from the reaction of 1,1-diaryl methanols, **1a**–**d** with PPHF.

**Table 1**
Isolated yields of ethers, **2a**–**e** and fluoro compounds, **3a**, **b**

| Compound | $Ar^1$ | $Ar^2$ | Yield (%) |
|---|---|---|---|
| **2a** | $C_6H_5$ | $C_6H_5$ | 72 |
| **2b** | $C_6H_5$ | 4-$CH_3C_6H_4$ | 67 |
| **2c** | $C_6H_5$ | 4-$OCH_3C_6H_4$ | 49 |
| **2d** | $C_6H_5$ | 2-$FC_6H_4$ | 43 |
| **2e** | $C_6H_5$ | 4-$NO_2C_6H_4$ | 33 |
| **3a** | $C_6H_5$ | 4-$NO_2C_6H_4$ | 43 |
| **3b** | 3-$NO_2C_6H_4$ | 3-$NO_2C_6H_4$ | 62 |

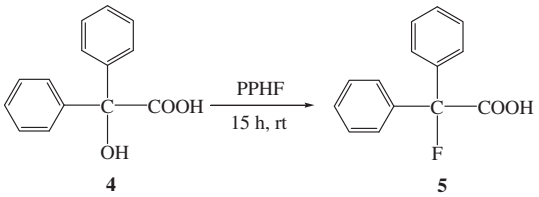



**Scheme 2.** Formation of **2e**, **3a** and **3b**, from the reaction of **1e** and **1f** with PPHF.

$^1$H NMR spectra of ethers (**2a**–**e**) displayed characteristic singlet at $\delta$ 5.26–5.67 (s, 2H) for benzhydrylic protons and multiplets at $\delta$ 6.78–7.98 for the aromatic protons, whereas in fluoro compounds **3a** and **3b**, benzhydrylic proton appeared as a doublet at $\delta$ 6.48 (d, 1H, $^2J_{HF}$=47 Hz) and $\delta$ 6.54 (d, 1H, $^2J_{HF}$=47.1 Hz) respectively due to the presence of fluorine on the same carbon atom. The aromatic protons displayed signal quite downfield upto $\delta$ 8.24. The presence of a doublet at $\delta$ 94.5 (d, $^1J_{CF}$=174.6 Hz) and $\delta$ 90.4 (d, $^1J_{CF}$=178.6 Hz) for the carbon bearing fluorine in $^{13}$C NMR spectra of **3a** and **3b**, respectively further supports their structure formulae.

It is interesting to note that secondary alcohols **1a**–**d** do not give the corresponding fluoro compounds but gave bis(diarylmethyl) ethers. In the first step, the alcohol may get protonated to give electrophile **E**′, which would be attacked by **1a**–**d** to give ethers **2a**–**d** in the second step (Scheme 1). The electrophilicity of **E**′ may be just sufficient towards the attack of alcoholic nucleophiles, **1a**–**d** and not for the $F^-$. Interestingly **1e** on treatment with PPHF gave both products, ether (**2e**) as well as corresponding fluoro compound (**3a**). In this case nitro group (being electron withdrawing) is expected to increase the electrophilicity of **E**″ to such an extent that both the nucleophiles **1e** and fluoride ion attack the electrophile **E**″ to give ether **2e** as well as fluoro product **3a**. The presence of two nitro groups in case of **1f** further increases the electrophilicity of **E**″ to greater extent. As the nucleophilicity of fluoride ion is more than that of alcohols, the electrophile has been attacked by the fluoride ion only to give the corresponding fluoro compound (**3b**) exclusively (see also Scheme 6). In a nutshell, more the presence of EWGs at any position of the aromatic ring(s), more will be the fluoride ion attack. It may thus be inferred from the above observations that the alcohols bearing electron withdrawing group(s) under the prevailing reaction conditions can produce the desired fluorinated product. It is further envisaged that alcohols bearing an electron withdrawing group (EWG) like –COAr or –COOH bonded directly to carbon bearing hydroxyl group may be capable of providing fluoro product.

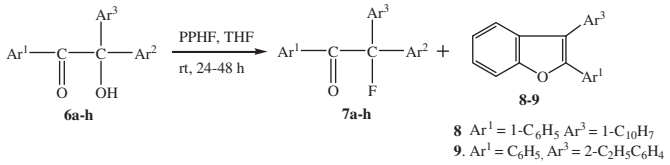
In order to investigate this hypothesis that nucleophilic substitution of hydroxyl group by fluoride ion ($F^-$) using PPHF is activated by electron withdrawing group present at the carbon bearing hydroxyl group, benzilic acid, which has the required positioning of carboxylic group, was selected. To benzilic acid in dry THF was added PPHF at 0 °C and was stirred at room temperature for 15 h (Scheme 3). The organic compound was extracted with DCM, washed with water, brine and dried. Removal of solvent yielded only 2-fluoro-2,2-diphenylethanoic acid **5** in 53% yield. The formation of any other product including corresponding ether was not detected by TLC analysis of the crude reaction mixture. The compound **5** was characterised by IR, $^1$H NMR, $^{13}$C NMR, $^{19}$F NMR and mass spectral data. The IR showed absorption bands at 1720 cm$^{-1}$ and 3350 cm$^{-1}$ for carbonyl and hydroxyl group, respectively. $^{19}$F NMR spectrum showed a signal at $\delta$ –139 (s).




**Scheme 3.** Fluorodehydroxylation of benzilic acid, **4**, using PPHF.

The successful fluorodehydroxylation of benzilic acid, which delineated the role of EWG like –COOH leading to the desired product prompted us to investigate the reaction of α-hydroxyketones, such as **6a**–**h** (Scheme 4). In these reactions, the electron withdrawing group is –COAr. 1,2,2-Triaryl-2-hydroxyoethanones **6a**–**h**[14] were reacted with PPHF in ice-cold solution in dry THF. The contents were stirred at room temperature for appropriate time period. The reaction was quenched with ice-cold liquor ammonia and products were obtained by usual work up. These were purified by flash chromatography to give products **7a**–**h**. The time for fluorination, yield of products and physical state of the α-fluoroketones are summarised in Table 2. The benzofuran derivative **8** (yield 22%) and **9** (yield 14%) were also obtained from the reaction of **6b** and **6d** under the above mentioned reaction conditions. 1,2,2-Triaryl-2-fluoroethanones have been characterised using various spectral data (See experimental).

The IR spectra of α-fluoroketones showed absorption bands for the carbonyl stretching in the range of 1675–1695 cm$^{-1}$. The compound **6a** absorbs at 1665 cm$^{-1}$ and **7a** at 1675 cm$^{-1}$. Electron withdrawing group (F) attached to α-carbon generally increases C=O stretching frequency. The planar geometry between phenyl and carbonyl groups have also been affected by steric factors, which reduces conjugation between phenyl and carbonyl groups to give




**Scheme 4.** Products, **7a**–**h** and **8**, **9** formed in the reaction of α-hydroxyketones, **6a**–**h**, with PPHF.

**Table 2**
Reaction time, isolated yields and melting point of α-fluoroketones, **7a**–**h**

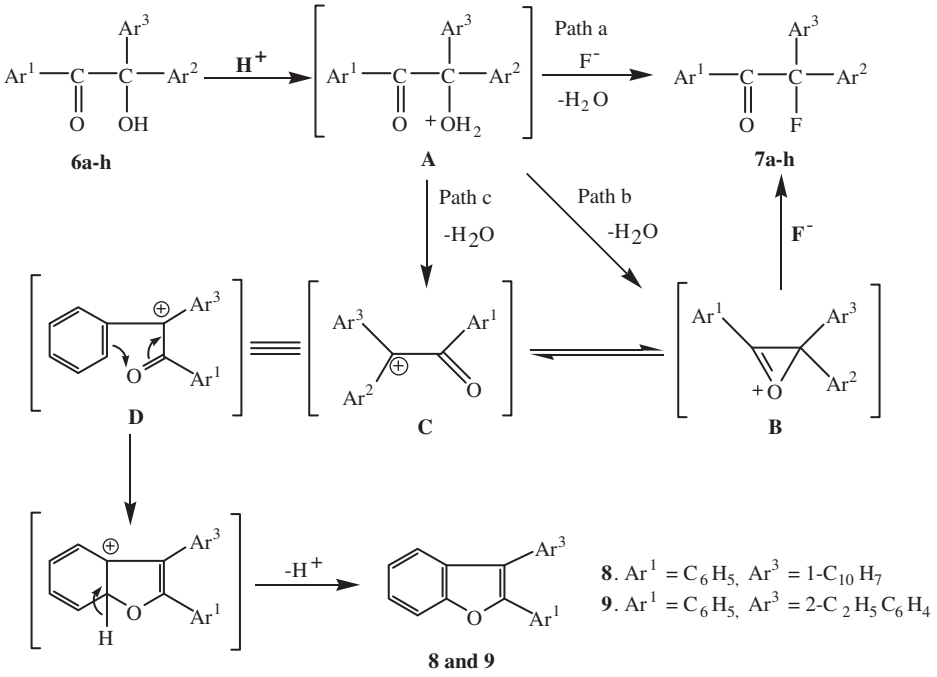
| Entry | $Ar^1$ | $Ar^2$ | $Ar^3$ | Time (h) | Yield (%) | Mp (°C) |
|---|---|---|---|---|---|---|
| **7a** | $C_6H_5$ | $C_6H_5$ | $C_6H_5$ | 24 | 76 | 73–74 |
| **7b** | $C_6H_5$ | $C_6H_5$ | 1-$C_{10}H_7$ | 48 | 37 (22)[a] | 114–115 |
| **7c** | $C_6H_5$ | $C_6H_5$ | 2-$CH_3C_6H_4$ | 28 | 80 | 66–68 |
| **7d** | $C_6H_5$ | $C_6H_5$ | 2-$C_2H_5C_6H_4$ | 25 | 46 (14)[a] | 42–44 |
| **7e** | $C_6H_5$ | $C_6H_5$ | 4-$CH_3C_6H_4$ | 48 | 57 | Oil |
| **7f** | 2-$CH_3C_6H_4$ | $C_6H_5$ | $C_6H_5$ | 24 | 69 | 39–40 |
| **7g** | 2-$C_2H_5C_6H_4$ | $C_6H_5$ | $C_6H_5$ | 24 | 55 | Oil |
| **7h** | 4-$CH_3C_6H_4$ | 4-$CH_3C_6H_4$ | $C_6H_5$ | 24 | 60 | Oil |

[a] The yields given in parentheses are for rearranged products **8** and **9**.

rise to more double bond character for >C=O group and results in higher value of $\nu_{C=O}$. The planarity remains undisturbed in α-fluoroketones, such as **7a**, which shows $\nu_{C=O}$ at 1675 $cm^{-1}$, while other compounds show in between 1680–1690 $cm^{-1}$.

The $^1H$ NMR spectra of all α-fluoroketones exhibited multiplet for aromatic protons in the range of δ 6.68–7.99. Compounds **7a**–**e** and **7h** showed their *ortho* aromatic protons (2H) downfield in the range of δ 7.80–7.99, whereas in case of **7f** and **7g**, alkyl group has occupied one *ortho* position on the phenyl group and it seems that it shields the *ortho* proton and consequently *ortho* protons merge into multiplets for other aromatic protons. Therefore, **7f** and **7g** do not exhibit separate signals for *ortho* protons. α-Fluoroketones have also been analysed by $^{19}F$ NMR spectra, which showed chemical shift as singlet confirm the presence of fluorine. $^{13}C$ NMR spectra of all α-fluoroketones showed splitting of carbonyl carbon due to coupling between fluorine and carbonyl carbon atom and it appeared as doublet. The compounds **7a**–**e** and **7h** showed at δ 198 while **7f** and **7g** displayed it at δ 202.8. The higher chemical shift for C=O in **7f** and **7g** may be due to presence of alkyl group on the phenyl ring attached to the carbonyl group. Fluorine bearing carbon (C–F) showed intensive splitting and high coupling constant values (d, $J_{CF}$ ~ 180–189 Hz). The molecular ion is absent in almost all α-fluoroketones. The high resolution mass spectra of fragment ion of **7a**–**h** however showed exact masses, which supported their molecular formulae. $^1H$ NMR spectrum of **8** and **9** showed multiplet for aromatic protons in the range of δ 7.07–7.83. $^{13}C$ NMR did not give indication for the presence of fluorine ($J_{C-F}$ is missing) and carbonyl group. The mass spectra of **8** showed molecular ion at *m*/*z* 320 and at *m*/*z* 298 for **9** as a base peak. Based on the above data (along with that given in the Experimental section), **8** and **9** were assigned as 3-(1-naphthyl)-2-phenyl benzofuran and 3-(2-ethylphenyl)-2-phenyl benzofuran, respectively.

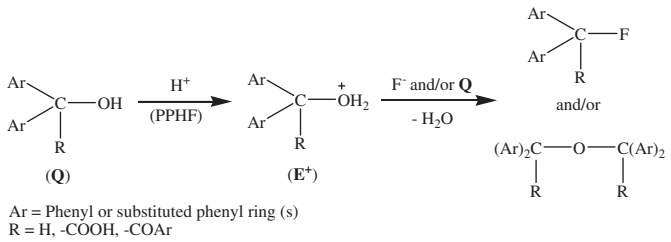
The excess of HF in PPHF (30% pyridine, 70% hydrogen fluoride) is capable of protonating the 3° alcoholic group to give protonated 1,2,2-triaryl-2-hydroxyethanones (**A**) (Scheme 5). One would expect that the attack of nucleophile ($F^-$) is involved in the rate determining step as in $S_N2$ mechanism. If the nucleophile has little bonding to the transition state of **A**, it has almost the full loss of leaving group $H_2O$ (analogous to $S_N1$ type mechanism).[15] The protonated α-hydroxyketones (**A**) may be attacked by the fluoride ion to give α-fluoroketones **7a**–**h** (path a). Alternatively the loss of water molecule in **A** can lead to either bridged oxiranyl ion **B** (Path b) or α-ketocarbenium ion **C** (Path c). These intermediates can either exist exclusively as one of themselves or in varying proportions (which may be in equilibrium). The intermediate **B** may also be attacked by the fluoride ion to give α-fluoroketones **7a**–**h**. The intermediate **C** (depending upon the conformational stability and subtle stereoelectronic factors) may adopt the conformation **D**, which can undergo 4π-electrocyclization to give benzofuran derivatives (**8** and **9**).[16] Though such cyclizations are reported by Reynolds[17] and Creary,[18] their plausible existence in fluorodehydroxylation using PPHF is reported here for the first time. However, it is to be noted that the formation of benzofuran derivatives is not always mutually exclusive, in two cases (**6b** and **6d**), both products




**Scheme 5.** Mechanism for the formation of α-fluoroketones, **7a**–**h** and benzofuran derivatives, **8**, **9**, by the reaction of α-hydroxyketones, **6a**–**h**, with PPHF.

are isolated. The formation of benzofuran derivatives only in two cases suggests that the intermediate of **C** type does not exist in other cases (**6a**, **6c** and **6e**–**h**). Therefore, all the α-fluoroketones may form from **A** or **B**, which indicates that reaction proceeds via $S_N2$ type mechanism. Though we still do not have any concrete evidence for the existence of **B** and **C**, from the above mentioned observations and literature,[8] it is proposed that the reaction is of $S_N2$ type. Scheme 5 explains the formation of α-fluoroketones **7a**–**h** and benzofuran derivatives **8** and **9**.

In general, the formation of fluoro compounds and/or ethers can be explained by the Scheme 6. The protonation of (**Q**) by PPHF would generate an electrophile ($\mathbf{E}^+$), which can react with nucleophile, such as $F^-$ and/or (**Q**) to form corresponding fluoro compound and/or ether. Water is the other product of the reaction.




**Scheme 6.** Plausible product distribution in the fluorodehydroxylation reaction using PPHF.

The fluoride anion has the higher nucleophilicity parameter than alcohols[19] and the EWG increases the electrophilicity of $\mathbf{E}^+$ present either in aromatic ring (s) or when it is attached to carbon bearing hydroxyl group (R=–COOH, –COAr). Considering the reaction as the combination of nucleophile and electrophile and using the nucleophilicity and electrophilicity parameters, it is predicted that the attack of fluoride ion relative to **Q** is more facile on $\mathbf{E}^+$ having EWG.[20] Thus, EWG favors the formation of the fluoro compounds and not the ethers.

## 3. Conclusion

It has been shown in this paper that it is possible to fluorodehydroxylate the family of 1,2,2-triaryl-2-hydroxyoethanones (**6a**–**h**) with PPHF leading to their corresponding fluoro compounds (**7a**–**h**). The nucleophilic fluorination by fluoride ion is facilitated by increasing the electrophilicity of $\mathbf{E}^+$, which can be achieved by the presence of electron withdrawing groups, such as $-NO_2$, –COOH and –COAr. Compounds like 1,1-diaryl methanols (**1a**–**d**), which lack the assistance of such electron withdrawing group yield only dimer like products, such as their ethers (**2a**–**d**). Formation of benzofuran derivatives **8** and **9** along with α-fluoroketones **7b** and **7d**, points towards the fact that the reactive intermediate **C** may adopt requisite conformational positioning (**D**) that can lead to 4π-electrocyclization. Such suitable topological positioning may be dictated by stereoelectronic factors. Even in such instances, the fluoride attack on reactive species is energetically feasible and it is evidenced by the formation of both, the cyclised product as well as the corresponding fluoro compounds.

## 4. Experimental

### 4.1. Equipments and chemicals

Melting points were taken in open capillaries and are uncorrected. The IR spectra were recorded on Perkin–Elmer IR 1800 spectrophotometer. The $^1$H NMR and $^{13}$C NMR spectra were recorded in $CDCl_3$ on JEOL ECX 300 spectrometer operating at 300 MHz and 75.53 MHz, respectively, with TMS as an internal standard. $^{19}$F NMR spectra were performed on JEOL ECX 300 spectrometer operating at 282.56 MHz. For $^1$H NMR and $^{13}$C NMR spectra, chemical shifts are in parts per million relative to TMS while for $^{19}$F NMR spectra, the chemical shift values are relative to $CFCl_3$. Coupling constants are in hertz. Mass spectra were recorded at 70 eV using VG analytical 11–250-J 70S. The relative intensities are given in parentheses. CHN analyses were recorded using Flash EA 1112 series CHNS-O Analyser. Flash chromatography was performed by using 40–63 μ (230–400 mesh) silica gel. PPHF was obtained from Sigma–Aldrich.

### 4.2. General procedure for the reaction of 1,1-diaryl methanols (1a–f) with PPHF

A solution of 1,1-diaryl methanol, **1a**–**f** (0.2–1.0 g, 0.73–5.43 mmol) was taken in a plastic bottle (13.4 cm×5.6 cm) in dry THF. PPHF (1.5–3.0 mL) was added to the stirred solution at ice-cold temperature. The contents were further stirred for 6–24 h and the reaction mixture was quenched with liquor ammonia at ice-cold temperature. The organic compound was extracted with DCM, washed with $Na_2CO_3$ (10%) solution, water, brine and dried over anhydrous $Na_2SO_4$. The solvent was removed under reduced pressure to afford viscous oil, which was purified by flash column chromatography to give products **2a**–**e**, **3a** and **3b** in varying yields of 33–72%.

*4.2.1. Bis(1,1-diphenylmethyl) ether (**2a**).* Yield 0.68 g (72%). Colourless solid, mp: 109–110 °C (lit.[13a] mp 107–109 °C).

*4.2.2. Bis[1-(4-methylphenyl)-1-phenylmethyl] ether (**2b**)[13b].* Yield 0.64 g (67%). Viscous oil. $^1$H NMR ($CDCl_3$, 300 MHz): δ 6.98–7.27 (m, 18H, ArH), 5.26 (s, 2H, OCH) 2.18 (s, 6H, $CH_3$). $^{13}$C NMR ($CDCl_3$, 75.53 MHz): δ 143.9, 140.9, 136.9, 129.0, 128.3, 127.2, 126.5, 126.4, 71.2, 21. LRMS *m*/*z*: 378 ($M^+$, 0), 199 (14), 198 (80.6), 197 (24.7), 183 (47.2), 181 (10.5), 166 (11.3), 165 (23.9), 152 (8.4), 121 (25.7), 120 (19.1), 107 (11.2), 106 (11.5), 105 (100), 93 (52.8), 92 (67.6), 79 (20.9), 78 (19.4), 77 (68.1), 76 (6.4).

*4.2.3. Bis[1-(4-methoxyphenyl)-1-phenylmethyl] ether (**2c**)[13c].* Yield 0.28 g (49%). Colourless solid. Mp: 121–122 °C. $^1$H NMR ($CDCl_3$, 300 MHz): δ 7.21–7.36 (m, 14H, ArH), 6.86 (d, 4H, ArH), 5.33 (s, 2H, OCH), 3.78 (s, 6H, $OCH_3$). $^{13}$C NMR ($CDCl_3$, 75.53 MHz): δ 158.9, 142.7, 142.5, 134.5, 134.3, 128.7, 127.8, 113.8, 69.1, 55.3. LRMS *m*/*z*: 410 ($M^+$, 0.6), 214 (4.1), 213 (26.6), 198 (42.5), 197 (100), 196 (10), 182 (7.3), 166 (2.7), 165 (18.8), 154 (12), 153 (25.2), 152 (10.9), 135 (11.5), 105 (7.2), 106 (0.6), 92 (4.2), 77 (12.3).

*4.2.4. Bis[1-(2-fluorophenyl)-1-phenylmethyl] ether (**2d**).* Yield 0.42 g (43%). Viscous oil. $R_f$ (5% hexane/EtOAc) 0.66. $^1$H NMR ($CDCl_3$, 300 MHz): δ 7.51–7.57 (m, 2H, ArH), 7.22–7.31 (m, 12H, ArH), 7.03–7.20 (m, 2H, ArH), δ 6.86–7.93 (m, 2H, ArH) 5.67 (d, 2H, $^4J_{HF}$=2.1 Hz OCH). $^{13}$C NMR ($CDCl_3$, 75.53 MHz): δ 161.8 ($^1J_{CF}$=245.2 Hz), 141.1, 129.1, 128.5, 128.2, 127.7, 127.2, 127.0, 124.4, 115.5 ($^4J_{CF}$=19 Hz), 65.5. $^{19}$F NMR ($CDCl_3$, 282.56 MHz): δ −115.9 (m, ArF).

*4.2.5. Bis[1-(4-nitrophenyl)-1-phenylmethyl] ether (**2e**)[13d,e].* Yield 0.31 g (33%). Colourless solid. Mp: 56–58 °C. $R_f$ (10% hexane/EtOAc) 0.80. $^1$H NMR ($CDCl_3$, 300 MHz): δ 8.06–8.12 (m, 4H, ArH), 7.43–7.48 (m, 4H, ArH), 7.10–7.21 (m, 10H, ArH), 5.38 (s, 2H, OCH). $^{13}$C NMR ($CDCl_3$, 75.53 MHz): δ 149.2, 147.4, 147.2, 140.1, 139.7, 129.0, 128.7, 128.4, 127.5, 123.6, 79.7. LRMS *m*/*z*: 410 ($M^+$, 0.6), 214 (4.8), 213 (26.6), 198 (42.5), 197 (100), 196 (10.0), 182 (7.3), 166 (2.7), 165 (18.8), 154 (12.0), 149 (25.2), 152 (10.9), 135 (11.5), 105 (7.2), 106 (0.6), 92 (4.2), 77 (12.3).

*4.2.6. 1-Fluoro-1-(4-nitrophenyl)-1-phenyl methane (**3a**).* Yield 0.42 g (43%). Colourless solid, Mp: 38–40 °C. $R_f$ (10% hexane/EtOAc) 0.68. $^1$H NMR ($CDCl_3$, 300 MHz): δ 8.12–8.15 (d, 2H, $^3J_{HH}$=8.4 Hz, ArH),

7.42–7.45 (m, 2H, $^3J_{HH}$=8.4 Hz, ArH), 7.22–7.32 (m, 5H, ArH), 6.48 (d, 1H, $^2J_{HF}$=47 Hz, CH). $^{13}$C NMR ($CDCl_3$, 75.53 MHz): δ 147.6 ($^2J_{CF}$=23.2 Hz), 138.6 ($^2J_{CF}$=20.5 Hz), 129.2, 128.9, 126.9, 126.8, 123.7, 94.5 ($^1J_{CF}$=174.6 Hz). $^{19}$F NMR ($CDCl_3$, 282.56 MHz): δ −166.6 (d, $^2J_{FH}$=47.1 Hz). LRMS *m/z*: 231 ($M^+$, 100), 232 (18), 230 (26), 214 (15.0), 185 (32), 184 (43), 183 (48), 166 (15), 165 (51), 152 (13), 109 (63), 108 (14), 107 (35), 101 (24), 83 (19), 77 (40). Anal. Calcd for $C_{13}H_{10}FNO_2$: C, 67.53; H, 4.36; N, 6.06. Found: C, 67.55; H, 4.35; N, 6.05.

*4.2.7. 1-Fluoro-bis[1-(3-nitrophenyl)] methane (**3b**).* Yield 0.125 g 62%. Colourless solid. Mp 95–96 °C. $R_f$ (10% hexane/EtOAc) 0.54. $^1$H NMR ($CDCl_3$, 300 MHz): δ 6.54–6.70 (d, 1H, $^2J_{HF}$=47.1 Hz, CHF), 7.57–7.69 (m, 4H, ArH), 8.21–8.24 (m, 4H, ArH). $^{13}$C NMR ($CDCl_3$, 75.53 MHz): δ 148.5, 140.3 (d, $^2J_{CF}$=22.9 Hz), 132.1 (d, $^3J_{CF}$=6.3 Hz), 130.2, 124.0 (d, $J_{CF}$=1.8 Hz), 121.4 (d, $^3J_{CF}$=6.8 Hz), 90.4 (d, $^1J_{CF}$=178.6). $^{19}$F NMR ($CDCl_3$, 282.56 MHz): δ −167.7 (d, $^2J_{FH}$=46.5 Hz). Anal. Calcd for $C_{13}H_9FN_2O_4$: C, 56.52; H, 3.28; N, 10.14. Found: C, 56.48; H, 3.22; N, 10.19.

### 4.3. 2-Fluoro-2,2-diphenyl ethanoic acid (5)

A saturated solution of 2-hydroxy-2,2-diphenyl ethanoic acid, **4** (0.8 g, 3.5 mmol) in dry THF was taken in a plastic bottle. PPHF (2 mL) was added to the stirred solution at ice-cold temperature. The contents were further stirred for 15 h and the reaction mixture was quenched with liquor ammonia at ice-cold temperature. The organic compound was extracted with DCM, washed with water, brine and dried over anhydrous $Na_2SO_4$. The solvent was removed under reduced pressure to afford a viscous oil, which was purified by flash chromatography (hexane/ethylacetate, 96:4) to yield a white solid **5**. Yield 0.42 g (53%). Mp: 135–136 °C. IR (Nujol) $\nu_{max}$: 3350 $cm^{-1}$ (OH), 1720 $cm^{-1}$ (CO). $^1$H NMR ($CDCl_3$, 300 MHz): δ 6.80–7.70 (m, 10H, ArH). $^{13}$C NMR ($CDCl_3$, 75.53 MHz): δ 80.9 (d, $^1J_{CF}$=187.2 Hz, CF), 126.6, 128.5, 129.4, 141.3 (d, $^2J_{CF}$=22.1 Hz), 178.5 (d, $^2J_{CF}$=18.7 Hz). $^{19}$F NMR ($CDCl_3$, 282.56 MHz): δ −139 (s). LRMS *m/z*: 230 ($M^+$, 0), 224 (46), 166 (100), 165 (94), 105 (49), 77 (37). Anal. Calcd for $C_{14}H_{11}FO_2$: C, 73.03; H, 4.82. Found: C, 73.10; H, 4.80.

### 4.4. General procedure for the fluorodehydroxylation of α-hydroxyketones (6a–h)

A saturated solution of α-hydroxyketone **6a**–**h** (1.0–3.0 g, 3.2–9.6 mmol) in dry THF was taken in a plastic bottle (13.4 cm×5.6 cm). To this solution, PPHF (2.0–6.0 mL) was added at ice-cold temperature. The temperature was allowed to rise to ambient temperature and the contents were stirred for 24–48 h. The reaction mixture was quenched with ice-cold liquor ammonia. The organic compound was extracted with DCM, washed with HCl (10%), $Na_2CO_3$ (10%), water, brine and dried over anhydrous $Na_2SO_4$. The solvent was removed under reduced pressure to yield brown viscous oil, which was purified by flash column chromatography (hexane/ethylacetate, 98:2) to give colourless product **7a**–**h** and **8**, **9** in varying yields.

*4.4.1. 2-Fluoro-1,2,2-triphenylethanone (**7a**).* Yield 2.30 g (76%). Colourless solid, Mp: 73–74 °C; $R_f$ (10% hexane/EtOAc) 0.41. IR (KBr): 1675 $cm^{-1}$ (CO). $^1$H NMR ($CDCl_3$, 300 MHz): δ 7.96–7.99 (m, 2H, ArH), 7.26–7.58 (m, 13H, ArH). $^{13}$C NMR ($CDCl_3$, 75.53 MHz): δ 197.9 (d, $^2J_{CF}$=30.5 Hz, CO), 139.4, 135.2, 133.2, 130.5, 128.8, 128.4, 128.3, 126.7, 104.2 (d, $^1J_{CF}$=186.2 Hz, CF). $^{19}$F NMR ($CDCl_3$, 282.56 MHz): δ −140.6 (s). LRMS *m/z*: 290 ($M^+$, 0.2), 272 (0.2), 271 (0.3), 270 (0.2), 186 (9.3), 185 (54.3), 183 (15.7), 165 (17.5), 106 (9.7), 105 (100.0), 77 (22.2). HRMS: calcd for $C_{13}H_{10}F$ ($M^+$−$C_6H_5CO$) *m/z* 185.0766. Found 185.0761.

*4.4.2. 2-Flouro-2-(1-naphthyl)-1,2-diphenylethanone (**7b**).* Yield 1.0 g (37%). Colourless solid, Mp: 114–115 °C; $R_f$ (10% hexane/EtOAc) 0.35. IR (KBr): 1680 $cm^{-1}$ (CO). $^1$H NMR ($CDCl_3$, 300 MHz): δ 7.87–7.96 (m, 2H, ArH), 7.25–7.58 (m, 15H, ArH). $^{13}$C NMR ($CDCl_3$, 75.53 MHz): δ 198.3 (d, $^2J_{CF}$=30.2 Hz, CO), 137.9, 137.6, 135.9, 135.3, 134.6, 133.3, 130.7, 129.0, 128.9, 128.7, 128.4, 128.0, 126.7, 126.5, 125.9, 124.3, 122.3, 105.6 ($^1J_{CF}$=180.4 Hz, CF). $^{19}$F NMR ($CDCl_3$, 282.56 MHz): δ −136.8 (s). LRMS *m/z*: 340 ($M^+$, 5.0), 320 (1.6), 235 (100.0), 216 (11.7), 215 (48.2), 106 (6.1), 105 (39), 77 (20.7). HRMS: calcd for $C_{24}H_{17}OF$ *m/z* 340.1263. Found 340.1290.

*4.4.3. 3-(1-Naphthyl)-2-phenyl benzofuran (**8**)[21].* Yield 0.52 g (22%). Colourless solid, Mp: 94–95 °C. $^1$H NMR ($CDCl_3$, 300 MHz): δ 7.11–7.83 (m, 16H, ArH). $^{13}$C NMR ($CDCl_3$, 75.53 MHz): δ 151.5, 150.1, 134.8, 130.9, 130.6, 129.4, 129.0, 128.4, 127.8, 126.9, 126.8, 126.6, 126.2, 126.0, 124.3, 123.7, 123.1, 119.6, 112.2. LRMS: *m/z* 320 ($M^+$, 33.6), 289 (3.3), 141 (11.0), 116 (5.6), 102 (6.0), 101 (100), 99 (5.1), 98 (28.5), 95 (4.7), 94 (46.5), 85 (10.1), 84 (7.0), 83 (80.6), 82 (11.9), 77 (2.4).

*4.4.4. 2-Fluoro-2-(2-methylphenyl)-1,2-diphenylethanone (**7c**).* Yield 2.40 g (80%). Colourless solid, Mp: 66–68 °C; $R_f$ (10% hexane/EtOAc) 0.39. IR (KBr): 1680 $cm^{-1}$ (CO). $^1$H NMR ($CDCl_3$, 300 MHz): δ 7.89–7.92 (m, 2H, ArH), 7.04–7.50 (m, 12H, ArH), 2.27 (d, $^5J_{HF}$=3.2 Hz, 3H, $CH_3$). $^{13}$C NMR ($CDCl_3$, 75.53 MHz): δ 198.2 (d, $^2J_{CF}$=30 Hz, CO), 138.0, 137.7, 135.3, 133.0, 132.1, 130.5, 129.3, 128.9, 128.8, 128.5, 126.7, 126.6, 125.3, 105.4 (d, $^1J_{CF}$=184.7 Hz, CF), 21.5. $^{19}$F NMR ($CDCl_3$, 282.56 MHz): δ −140.3 (s). LRMS *m/z*: 304 ($M^+$, 0), 199 (33), 197 (0), 196 (5.7), 134 (7.0), 183 (12.3), 179 (12.9), 178 (12.1), 106 (9.7), 105 (100), 77 (19.9). HRMS: calcd for $C_{14}H_{12}F$ ($M^+$−$C_6H_5CO$) *m/z* 199.0923. Found 199.0922.

*4.4.5. 2-Fluoro-2-(2-ethylphenyl)-1,2-diphenylethanone (**7d**).* Yield 1.10 g (46%). Colourless solid, Mp: 42–44 °C; $R_f$ (10% hexane/EtOAc) 0.40. IR (KBr): 1675 $cm^{-1}$ (CO). $^1$H NMR ($CDCl_3$, 300 MHz): δ 7.83–7.86 (m, 2H, ArH), 7.45–6.68 (m, 12H, ArH), 2.50–2.58 (q, 2H, $CH_2$), 1.10–1.15 (t, 3H, $CH_3$). $^{13}$C NMR ($CDCl_3$, 75.53 MHz): δ 198.2 (d, $^2J_{CF}$=29.6 Hz, CO), 143.9, 138.2, 137.9, 137.6, 135.3, 133.0, 130.4, 129.4, 128.9, 128.7, 128.5, 128.3, 126.7, 125.1, 105.2 (d, $^1J_{CF}$=184.7 Hz, CF), 27.1, 15.6. $^{19}$F NMR ($CDCl_3$, 282.56 MHz): δ −140.9 (s). LRMS *m/z*: 318 ($M^+$, 0.8), 299 (2.5), 214 (15.0), 213 (81.9), 193 (10.3), 192 (9.3), 183 (4.0), 178 (13.6), 165 (4.4), 115 (9.9), 106 (7.8), 105 (100), 91 (2.4), 77 (2.8), 76 (19.1). HRMS: calcd for $C_{15}H_{14}F$ ($M^+$−$C_6H_5CO$) *m/z* 213.1113. Found 213.1109.

*4.4.6. 3-(2-Ethylphenyl)-2-phenyl benzofuran (**9**).* Yield 0.32 g (14%). Colourless oil. $^1$H NMR ($CDCl_3$, 300 MHz): δ 7.07–7.63 (m, 13H, ArH), 2.97–3.05 (q, 2H, $CH_2$), 1.40–1.46 (t, 3H, $CH_3$). $^{13}$C NMR ($CDCl_3$, 75.53 MHz): δ 152.7, 150.1, 133.4, 131.1, 130.0, 129.0, 128.5, 128.3, 127.7, 127.2, 126.7, 126.2, 124.1, 123.3, 120.3, 117.8, 111.2, 23.2, 14.6. LRMS: *m/z* 298 ($M^+$, 100), 299 (26.5), 284 (5.9), 283 (27.5), 241 (63.2), 211 (11.8), 178 (3.6), 141 (4.9), 134 (4.0), 126 (4.5), 105 (10.5), 77 (78.2).

*4.4.7. 2-Fluoro-2-(4-methylphenyl)-1,2-diphenylethanone (**7e**).* Yield 1.15 g (57%). Colourless oil; $R_f$ (10% hexane/EtOAc) 0.41. IR (KBr): 1687 $cm^{-1}$ (CO). $^1$H NMR ($CDCl_3$, 300 MHz): δ 7.89–7.91 (d, 2H, ArH), 7.48–7.52 (t, 1H, ArH), 7.36–7.40 (m, 7H, ArH), 7.21–7.24 (d, 2H, ArH), 7.14–7.16 (d, 2H, ArH), 2.15 (s, 3H, $CH_3$). $^{13}$C NMR ($CDCl_3$, 75.53 MHz): δ 198.0 (d, $^2J_{CF}$=30.1 Hz, CO), 139.3, 138.7, 136.3, 135.2, 133.1, 130.5, 129.1, 128.7, 128.3, 128.2, 126.7, 126.7, 102.0 (d, $^1J_{CF}$=185.2 Hz, CF), 21.22. $^{19}$F NMR ($CDCl_3$, 282.56 MHz): δ −139.8 (s). HRMS: calcd for $C_{14}H_{12}F$ ($M^+$−$C_6H_5CO$) *m/z* 199.0923. Found 199.0918.

*4.4.8. 2-Fluoro-1-(2-methylphenyl)-2,2-diphenylethanone (**7f**).* Yield 1.38 g (69%). Colourless solid, Mp: 39–40 °C; $R_f$ (10% hexane/EtOAc) 0.42. IR (KBr): 1685 $cm^{-1}$ (CO). $^1$H NMR ($CDCl_3$,

300 MHz): δ 7.06–7.48 (m, 14H, ArH), 2.29 (s, 3H, $CH_3$). $^{13}C$ NMR ($CDCl_3$, 75.53 MHz): δ 202.8 (d, $^2J_{CF}$=30.2 Hz, CO), 139.4, 139.0, 137.8, 136.6, 131.3, 130.9, 128.7, 128.4, 126.7, 126.6, 124.8, 103.6 (d, $^1J_{CF}$=187.6 Hz, CF), 20.5; $^{19}F$ NMR ($CDCl_3$, 282.56 MHz): δ −140.2 (s). LRMS *m*/*z*: 304 ($M^+$, 0), 284 (1.4), 186 (4.1), 185 (22.6), 184 (3.7), 183 (10.8), 165 (15.3), 120 (12.9), 119 (100.0), 91 (31.8). HRMS: calcd for $C_{13}H_{10}F$ ($M^+$−$C_7H_7CO$) *m*/*z* 185.0766. Found 185.0761.

*4.4.9. 2-Fluoro-1-(2-ethylphenyl)-2,2-diphenylethanone (**7g**).* Yield 0.60 g (55%). Colourless oil; $R_f$ (10% hexane/EtOAc) 0.41. IR (KBr): 1680 $cm^{-1}$ (CO). $^1H$ NMR ($CDCl_3$, 300 MHz): δ 7.51–6.75 (m, 14H, ArH), 2.55–2.62 (q, 2H, $CH_2$), 1.14–1.11 (t, 3H, $CH_3$). $^{13}C$ NMR ($CDCl_3$, 75.53 MHz): δ 202.7 (d, $^2J_{CF}$=33.9 Hz, CO), 143.9, 139.4, 139.1, 137.6, 136.4, 133.0, 131.0, 130.4, 129.8, 129.4, 128.7, 128.2, 126.6, 125.1, 124.8, 103.5 (d, $^1J_{CF}$=189.3 Hz, CF), 26.6, 15.5. $^{19}F$ NMR ($CDCl_3$, 282.56 MHz): δ −140.2 (s). LRMS *m*/*z*: 318 ($M^+$, 0), 299 (4.5), 298 (15.6), 283 (4.9), 214 (19.3), 213 (31.7), 197 (7.5), 196 (9.6), 193 (12.6), 185 (49.9), 179 (4.4), 178 (17.8), 165 (5.5), 152 (1.8), 135 (10.8), 133 (100), 116 (1.7), 115 (13.2), 106 (11.2), 105 (52.2), 91 (5.4), 77 (22.4). HRMS: calcd for $C_{13}H_{10}F$ ($M^+$−$C_8H_9CO$) *m*/*z* 185.0766. Found 185.0760.

*4.4.10. 2-Fluoro-1,2-bis(4-methylphenyl)-2-phenylethanone (**7h**).* Yield 1.20 g (60%). Colourless oil; $R_f$ (10% hexane/EtOAc) 0.42. IR (KBr): 1690 $cm^{-1}$ (CO). $^1H$ NMR ($CDCl_3$, 300 MHz): δ 7.80–7.84 (m, 2H, ArH), 7.12–7.28 (m, 11H, ArH), 2.40 (s, 6H, $CH_3$). $^{13}C$ NMR ($CDCl_3$, 75.53 MHz): δ 197.4 (d, $^2J_{CF}$=29.0 Hz, CO), 144.0, 139.7, 139.4, 138.6, 136.4, 132.6, 130.7, 130.3, 130.0, 129.7, 129.1, 128.9, 128.6, 128.2, 126.7, 121.1, 104.3 (d, $^1J_{CF}$=185.8 Hz, CF), 21.3, 21.2. $^{19}F$ NMR ($CDCl_3$, 282.56 MHz): δ −139.8 (s). LRMS *m*/*z*: 318 ($M^+$, 0), 199 (46.0), 183 (12.3), 165 (5.6), 120 (12.3), 119 (100.0), 105 (7.1), 97 (9.2), 91 (25.4), 85 (15.8), 71 (21.7). HRMS: calcd for $C_{14}H_{12}F$ ($M^+$−$C_7H_7CO$) *m*/*z* 199.0923. Found 199.0907.

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20. Although the trend of electrophilicities of $E^+$ formed during the proposed mechanism is not known, the increasing trend of electrophilic reactivities of a few Michael acceptors with EWG (−CN, $NO_2$) have been calculated by using equation log $K_{20^\circ C}=s_N(N+E)$, where $s_N$, sensitivity parameter; *N*, nucleophilicity and *E* stands for electrophilicity. This equation has also been used to predict the rates (*k*) and reactivities: Appel, R.; Mayr, H. *J. Am. Chem. Soc.* **2011**, *133*, 8240 and references cited therein.
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