A Photoredox-Catalyzed Approach for Formal Hydride Abstraction to Enable a General C_{sp^3}–H Fluorination with HF

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ABSTRACT: While a great number of C–H functionalization methods have been developed in recent years, new mechanistic paradigms to deconstruct such bonds have been comparatively rare. Amongst possible strategies for breaking a C_{sp^3}–H bond are deprotonation, oxidative addition with a metal catalyst, direct insertion via a nitrene intermediate, hydrogen atom transfer (HAT) with both organic and metal-based abstractors, and lastly, hydride abstraction. The latter is a relatively unexplored approach due to the unfavorable thermodynamics of such an event, and thus has not been developed as a general way to target both activated and unactivated C_{sp^3}–H bonds on hydrocarbon substrates. Herein, we report our successful efforts in establishing a catalytic C–H functionalization manifold for accessing an intermediate carbocation by formally abstracting hydride from unactivated C_{sp^3}–H bonds. The novel catalytic design relies on a stepwise strategy driven by visible light photoredox catalysis and is demonstrated in the context of a C–H fluorination employing nucleophilic fluorine sources. Difluorination of methylene groups is also demonstrated, and represents the first C–H difluorination with nucleophilic fluoride. Additionally, the formal hydride abstraction is shown to be amenable to several other classes of nucleophiles, allowing for the construction of C–C or C–heteroatom bonds.

INTRODUCTION

Methods that can derivatize C_{sp^3}–H bonds to different functional groups have great potential to increase synthetic efficiency in the construction of complex small molecules or new therapeutic targets, and is particularly applicable towards the goal of 'late-stage functionalization' (LSF).[1] The abundance of unactivated C_{sp^3}–H bonds in small molecules makes them the ideal precursors for LSF, but direct C–H functionalization transformations remain a challenging feat.[2] Current well-established mechanistic designs for derivatizing C–H bonds include: 1) deprotonation[3], 2) oxidative addition into a C–H bond via a metal catalyst[4–6], 3) insertion via a carbene or nitrene species[7–9], 4) HAT to access nucleophilic carbon-centered radicals[10–12], and lastly, 5) hydride abstraction[13–18].

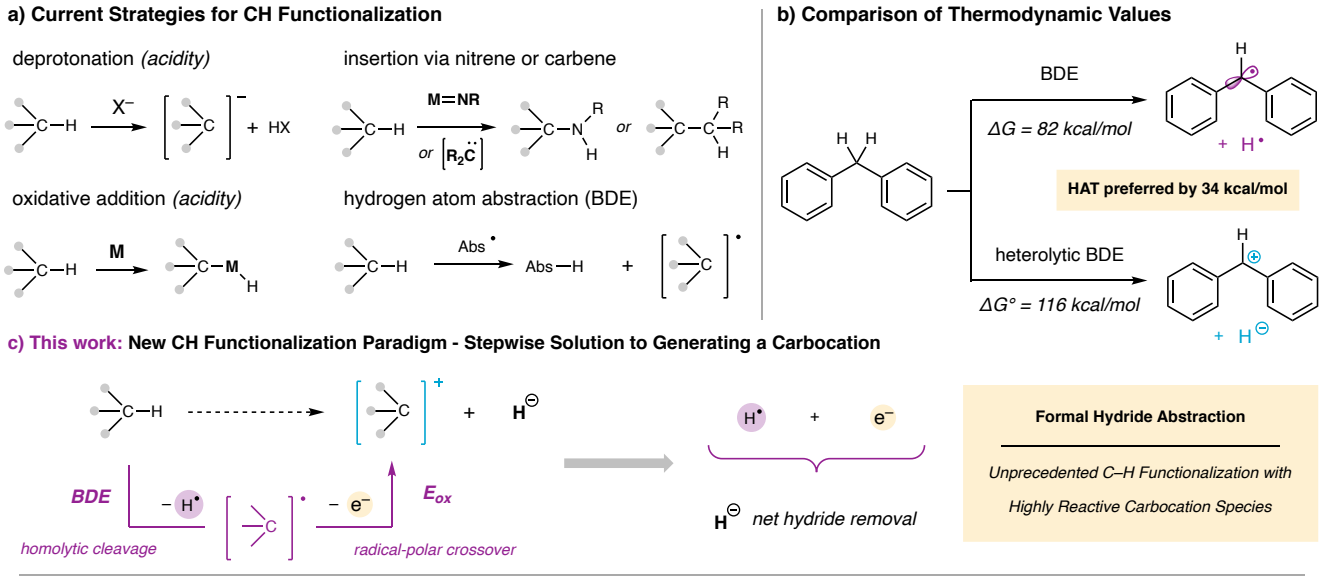


Figure 1. Strategies for Deconstructing C_{sp^3}–H bonds. a) Current mechanistic approaches to breaking a C_{sp^3}–H bond b) Contrasting bond dissociation energies of homolytic and heterolytic breaking events c) Demonstrating of the initial concept on CH nucleophilic fluorination and proposed mechanism with peroxides.

While the first four strategies are widespread and fairly general (Fig. 1a)[19,20], development of the latter has focused primarily on functionalization at α-heteroatom C–H sites through the use of strong Lewis acids to access stabilized iminium and oxocarbenium ions. Herein, we describe a new mechanistic platform for dismantling C_{sp^3}–H bonds of hydrocarbons that achieves a formal hydride abstraction (FHA). This novel approach generalizes hydride abstraction with respect to the nature of the targeted C_{sp^3}–H bond and provides a hydride abstraction platform that can target unprecedented C–H positions in a given molecule. The intermediacy of an all-carbon carbocation is underutilized, or essentially non-existent, amongst the number of C–H derivatization methodologies a chemist has at their disposal, despite carbocations being highly reactive intermediates that can readily engage an expansive array of nucleophilic coupling partners.

In recent years, HAT-based methods have been widespread as a powerful approach to functionalize unactivated C_{sp^3}–H sites to a plethora of different functional groups via coupling of open-shell intermediates. In contrast, hydride abstraction-based mechanisms are rare, with carbocations a wholly underleveraged intermediate in C–H functionalization. This discrepancy can plausibly be rationalized by the differences in thermodynamic requirements for the two bond cleavage processes. For example, the benzylic C_{sp^3}–H bond of diphenylmethane has a homolytic bond dissociation energy (BDE) of 82 kcal/mol[21], whereas its heterolytic bond dissociation energy to give a carbocation and hydride species requires 116 kcal/mol[22], a 34 kcal/mol difference (Fig. 1b). Accordingly, existing heterolytic cleavage methods in the field of C–H functionalization are typically gated by acidity, where activated C_{sp^3}–H bonds can be targeted via deprotonation or metal-mediated oxidative addition. Recently, we hypothesized that a highly reactive carbocation intermediate could be obtained from a C_{sp^3}–H bond through a stepwise mechanistic process: first, a hydrogen atom abstraction followed by a radical-polar crossover (RPC) event via oxidation of the carbon radical to a carbocation (Fig. 1c). Our proposed design would establish a new C_{sp^3}–H functionalization approach that is gated by hydricity of the desired C–H bond, but ultimately delivers a polar intermediate. Such a design would provide a platform that can readily engage a diverse array of nucleophilic coupling partners without altering their electronic nature. We showcase the potential utility of our formal hydride abstraction in the area of fluorine chemistry by presenting a new C_{sp^3}–H nucleophilic fluorination methodology.

Incorporating C–F bonds into the structures of viable drug scaffolds has become a routine endeavor for the medicinal chemist.[23–25] Due to the small size of fluorine (van der Waals radius, 1.47 Å)[26] and large electronegativity (3.98 Pauling scale)[27], the introduction of a fluorine atom can dramatically impact ligand-target interaction, compound conformation, pK_a, and lipophilicity. The unique ability of fluorine to extensively alter the biological activity and metabolic stability of a drug candidate has resulted in the synthetic community placing a high value on the development of new fluorination reactions. However, the bottleneck of synthetic routes to organofluorines is often the fluorination step due to relatively few existing chemical technologies.[28,29] The development of fluorination strategies that utilize nucleophilic fluorine sources offers many advantages, and has become highly desirable, primarily due to its potential application in fluorine-18 endeavors as well as the lower costs and higher safety features relative to common electrophilic fluorinating reagents such as SelectFluor™. Seminal work from Groves and coworkers have established a platform for C_{sp^3}–H fluorination via generation of carbon-centered radicals and subsequent fluorination by reaction with an *in-situ* generated electrophilic Mn-F bond derived from nucleophilic fluoride.[30,31] The herein proposed abstraction-RPC mechanistic strategy would, in contrast, access a highly reactive carbocation intermediate that can be utilized to engage nucleophilic fluoride, as well as other classes of nucleophiles that are not amenable to such a metal-mediated polarity reversal strategy (Fig. 2). Radical-polar crossover has in recent years emerged as a powerful strategy in the field of photoredox catalysis. Specifically, the radical-*cationic* crossover has been demonstrated as an enabling element by the groups of Chen & Xiao[32], Kim[33], Ragains[34], Zhou[35], Akita[36], Doyle[37], Aggarwal[38], and Nagib[12] for a variety of C–C and C–heteroaom bond forming transformations. The Doyle group recently described the direct oxidation of carbon radicals generated via a reductively-induced decarboxylation event in the context of a

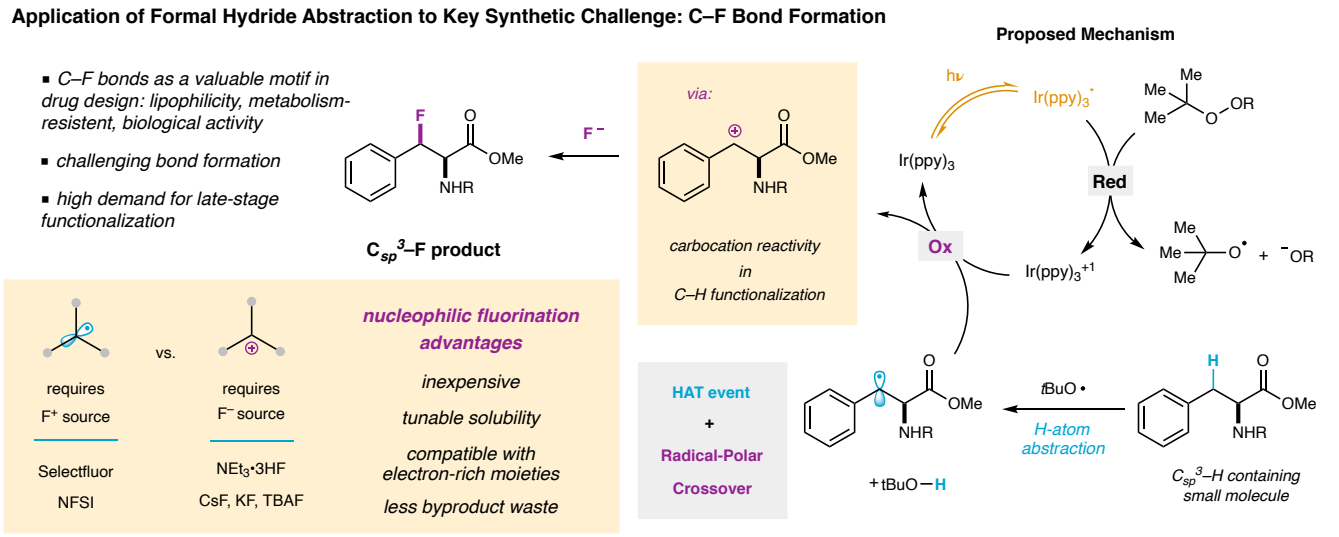


Figure 2. Proposed Mechanism for Stepwise Formal Hydride Abstraction. Demonstration of the initial concept on C–H nucleophilic fluorination and proposed mechanism with peroxides.

net redox-neutral photoredox cycle. A recent publication from the groups of Song and Li combined hydrogen-atom abstraction with radical-polar crossover through the use of iron salts and an organophotocatalyst, albeit in a 3-component coupling strategy[39]. To the best of our knowledge, the combination of a HAT event with RPC at the same C–H site of a hydrocarbon to achieve a net hydride abstraction has not been previously reported for intermolecular coupling reactions.

RESULTS AND DISCUSSION

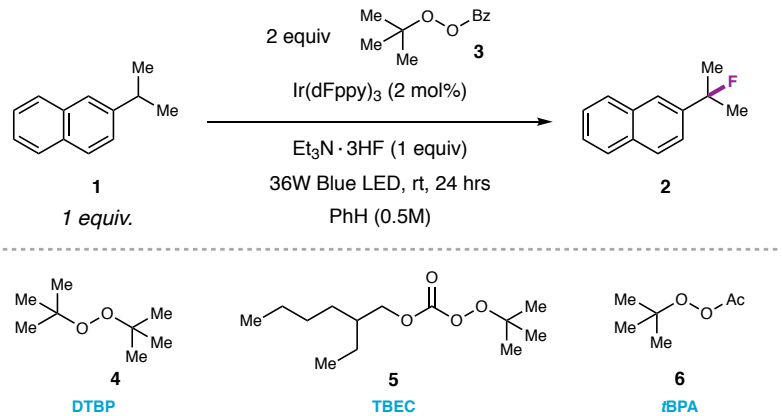
Reaction Design. A critical element of the proposed formal hydride abstraction platform is the identification of an appropriate hydrogen atom abstractor that could be generated in a single-electron reduction event. Such a mechanistic element would provide a net redox neutral catalytic cycle with a visible-light photoredox catalyst. To satisfy this requirement, readily available organic peroxides that can generate known hydrogen atom abstractor *tert*-butoxy radical (*t*BuO•)[40] were examined. Figure 2 details our proposed mechanism with such peroxide reagents. Upon visible-light excitation of a photocatalyst, single-electron reduction of an organic peroxide can lead to fragmentation of the weak O–O bond, to give alkoxy radical and alkoxide anion intermediates. H-atom abstraction of a C_{sp^3}–H bond on a hydrocarbon substrate by *t*BuO• would generate the corresponding alkyl radical, and *tert*-butanol as a benign, easily removable byproduct. Subsequent single-electron oxidation crossover of the alkyl radical to a carbocation is proposed to occur through a single-electron oxidation by the oxidized photocatalyst. The oxidation of a carbon radical is quite facile, ranging from -0.11V for tertiary radicals to +0.68 V for primary (vs. SCE).[41] Generation of the carbocation in the presence of nucleophilic partners will lead to a rapid S_N1-type substitution, thereby furnishing the desired C-F bond, effectively avoiding unproductive olefin formation that is observed in classical S_N2 settings due to the requirement for more basic fluoride sources.

Gratifyingly, with 1-isopropyl naphthalene as our model substrate, we tested the commercially-available reductively-triggered hydrogen atom abstractor peroxide – *tert*-butyl peroxybenzoate (TBPB, **3**), which was found to work in combination with reducing photoredox catalyst, $Ir(dFppy)_3$, and triethylamine-trihydrofluoride to afford 69% yield of the desired C–H fluorination product **2** (Table 1, **entry 1**). Control experiments in the absence of photocatalyst and light demonstrated the dependence of the reaction on the photochemistry design element (**entries 2 and 3**). While benzene was found to provide the highest yields of fluorinated product, the reaction also proceeded in ethyl acetate or acetonitrile (**entries 4 and 5**). We hypothesize the use of benzene assists in reducing the competitive side pathway of β-scission of the *t*BuO radical. This fragmentation has been studied and is known to be controlled by the polarity of the solvent and concentration effects, with the rates of HAT being 2-3 orders of magnitude faster than the rate of fragmentation.[42,43] Other mild peroxides were tested but were not comparable to TBPB (**entries 6-8**). Basic fluoride sources were found to give lower yields (**entries 9 and 10**). Gratifyingly, use of the fluoride reagent in limiting quantities still results in appreciable yields of the fluorinated product, an indication the platform could be amenable to fluorine-18 chemistry (**entry 11**). Analysis of crude reaction mixtures did not detect styrene products, again highlighting the S_N1-type mechanistic design.

Scope. With a successful photoredox catalyst/peroxide system in hand, we next turned to investigating the scope of this reaction. We were delighted to find the reaction was amenable to a diverse assortment of hydrocarbon substrates (Scheme 1). Successful fluorination of cumene was observed under optimized conditions, and the presence of an electron-withdrawing group at the para position of the aryl ring was well-tolerated (**7, 8**). Diphenyl and triphenyl C–H positions were also viable substrates that produced excellent yields (**9, 10**). Aryl-substituted heterocycles were amenable to fluorination at the benzylic position, as both 5- and 6-membered rings were fluorinated in modest yields (**11-14**). Excitingly, benzylic sites adjacent to electron-withdrawing groups successfully provided α-fluoro products in one step (**14, 15**). Lastly, isopropyl-substituted heteroarenes, including pyridine, pyrimidine, and pyrazole worked modestly well in the formal hydride abstraction platform (**16-18**).

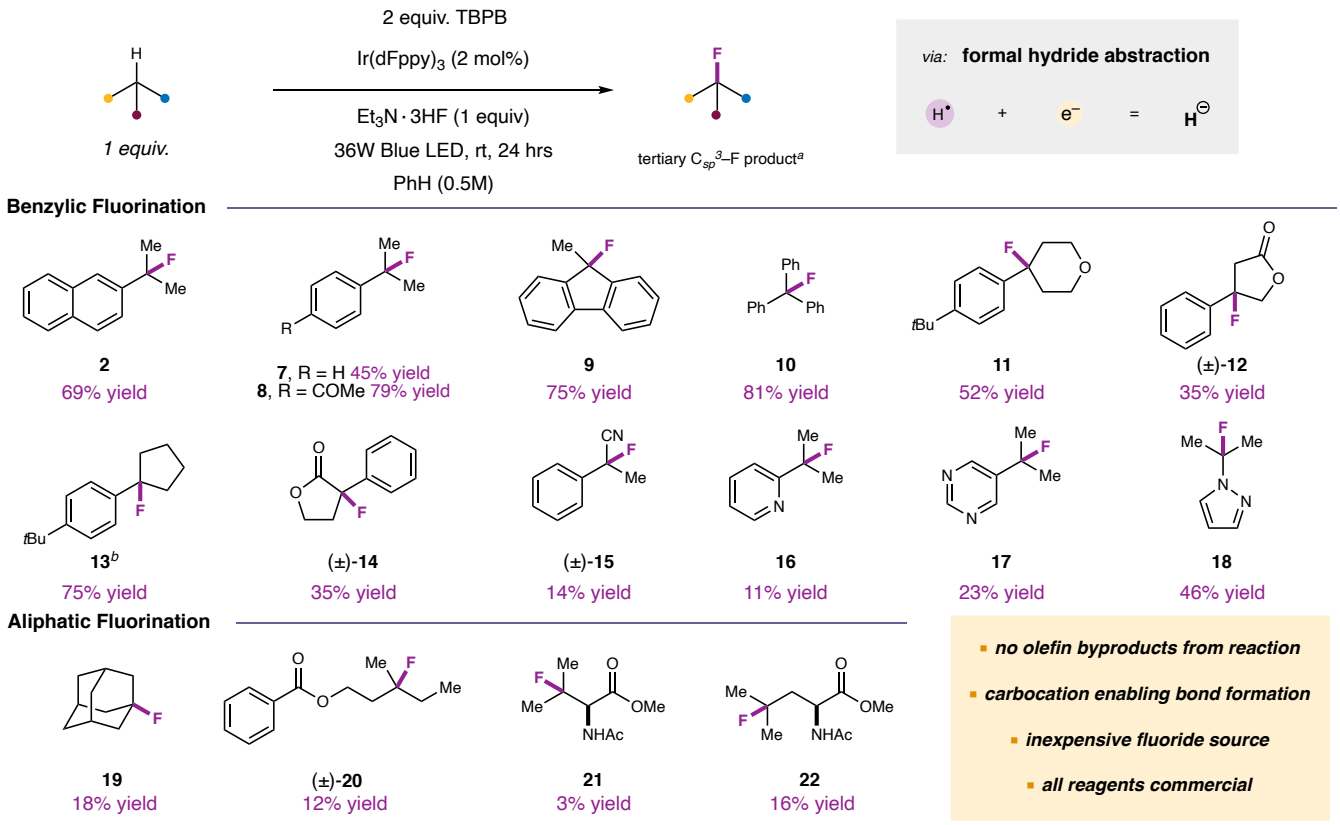
Precursors containing aliphatic tertiary C–H sites were evaluated next. Aliphatic C_{sp^3}–H bonds represent a more uphill hydride abstraction than benzylic positions, with the cited heterolytic BDE being 234 kcal/mol[44] for isobutane, compared to a homolytic BDE value of 100 kcal/mol. Hence, we were elated to observe the formal hydride abstraction design successfully functionalized the tertiary position of adamantane in 18% yield (**19**). Notably, no 2-fluoroadamantane product is observed, indicating our system provides complementary regioselectivities to the Groves fluorination.[45] Long-chain aliphatic substrate **20** also afforded fluorinated product in 12% yield

Table 1. Optimization of reaction conditions and control studies.



entry	deviation from standard conditions	Yield of 2[a]
1	none	69%
2	no photocatalyst	0%
3	no light	0%
4	EtOAc instead of PhH	38%
5	MeCN instead of PhH	33%
6	DTBP instead of TBPB	5%
7	TBEC instead of TBPB	14%
8	*t*BPA instead of TBPB	1%
9	CsF instead of $Et_3N \cdot 3HF$	9%
10	NH_4F or AgF	5%
11	0.1 equiv $Et_3N \cdot 3HF$	10%

[a] Reactions were performed on 0.20 mmol scale of the hydrocarbon. Fluorobenzene added as an external standard for determining ^{19}F NMR yields.

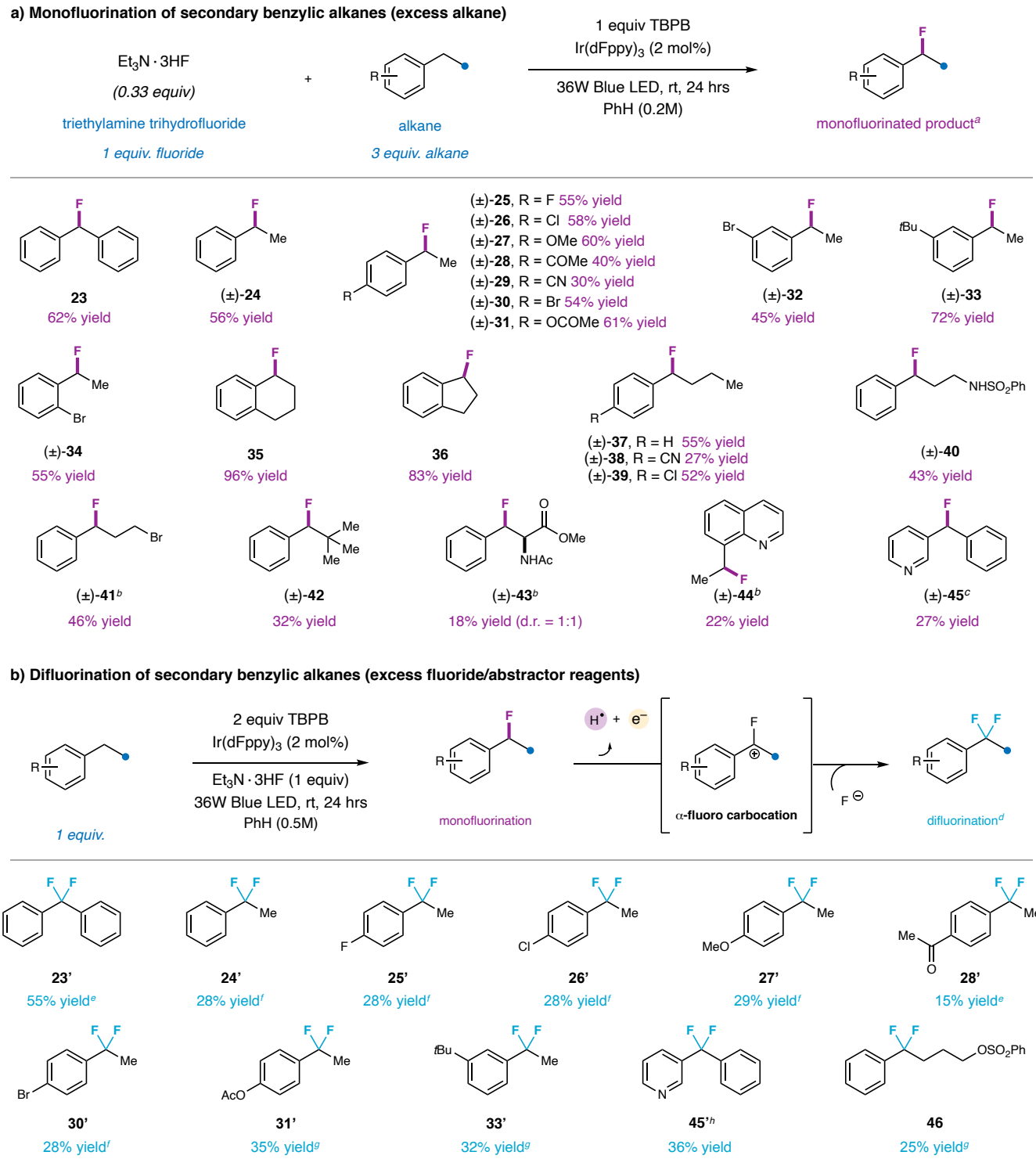


Scheme 1. Scope of benzylic and aliphatic tertiary C–H positions. [a] Reaction conditions: C_{sp^3}–H precursor (1 equiv., 0.50 mmol), TBPB (2 equiv.), $Et_3N{\bullet}3HF$ (1 equiv.), benzene (0.5M), and $Ir(dFppy)_3$ (2 mol%). ^{19}F NMR yields with fluorobenzene as the external standard and are calculated relative to the hydrocarbon precursor. [a] Reaction was run on 0.20 mmol scale of hydrocarbon.

selectively at the tertiary position. Fluorination of amino acids with aliphatic side chains demonstrated the impact of proximal electron-withdrawing functionality, as fluorination of leucine worked to a greater extent than that of valine (**21, 22**).

We next turned to investigating the scope of our mechanistic platform with secondary benzylic C–H substrates (Scheme 2a). Inversion of the stoichiometry of the reaction provided good yields of monofluorinated benzylic products with fluoride anion as the limiting reagent. Diphenylmethane was found to work in good yield and afforded 62% yield of the monofluorinated product (**23**). Fluorination of ethylbenzene (**24**) also resulted in good yield and provided a scaffold for interrogation of substituent effects on the success of the fluorination. An examination of various electron-donating and electron-withdrawing groups on the phenyl ring found higher yields for electron-donating functionality, potentially due to the ability to better stabilize a benzylic carbocation, and thus a more facile RPC oxidation (**25-31**). The formal hydride abstraction was not deterred by meta (**32, 33**) or ortho (**34**) substitution. Excellent yields were obtained at the benzylic position of fused 5- and 6-membered rings (**35, 36**). For substrates containing long-chain alkyl groups, complete selectivity for the benzylic methylene position over other methylene carbons was observed, even in the case of electronically-activated α-heteroatom positions (**37-41**). Additional steric bulk with neopentyl substrate **42** saw diminished yields. To our satisfaction, the benzylic position of phenyl alanine was successfully fluorinated in 18% yield (**43**), highlighting possibilities of this reactivity platform on amino acids for protein modification applications. Lastly, we found alkyl pyridine-based substrates could be fluorinated with compounds **44** and **45** working in modest yields upon a switch in fluoride reagent to silver fluoride. Interestingly, when triethylamine trihydrofluoride was used as the fluoride source, 1% or less of fluorinated product was observed for these substrates, offering some site selectivity opportunities on more complex substrates.

Next, we questioned whether or not difluorination products could be accessed directly from this class of substrates, which possess two abstractable C_{sp^3}–H bonds at the benzylic position. The importance of difluoromethylene groups (CF_2) in medicinal chemistry scaffolds has received recent attention due to their numerous benefits in drug design such as locked substrate conformations, alcohol, sulfone, and sulfamide isosteres, modulation of basicity and dipole moments, and increased metabolic stability.[46] We envision our stepwise hydride abstraction design could be utilized to achieve an *in-situ* double formal hydride abstraction via a sequential abstraction on the monofluorinated product that would involve the intermediacy of an α-fluoro carbocation (Scheme 2b). Classically, α-fluoro carbocations are generated either through the nucleophilic nature of a vinyl fluoride moiety, a strong Lewis acid association to a multifluorinated substrate, or the use of fluorooxidants, and have been ideal intermediates for access to a plethora of alternative organofluorine compounds.[47,48] This stepwise formal hydride abstraction paradigm could offer a C–H functionalization strategy to directly accessing valuable α-fluoro carbocation species from methylene sites under mild conditions. Excitingly, difluoromethylene products were observed when the hydrocarbon precursor was employed as the limiting reagent with excess fluoride and



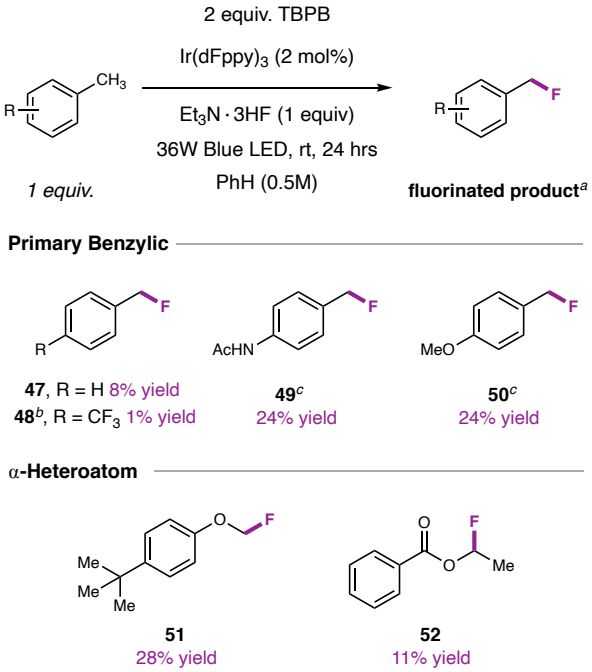
Scheme 2. Secondary benzylic scope with mono- and difluorination. a) Monofluorination Conditions. [a] Reaction conditions: C_{sp^3}–H precursor (3 equiv., 1.50 mmol), TBPB (1 equiv., 0.5mmol), Et_3N•3HF (0.33 equiv., 0.165 mmol), and $Ir(dFppy)_3$ (2 mol%). ^{19}F NMR yields with fluorobenzene as the external standard. Monofluorination yields are shown in purple. [b] Excess of alkane not needed. Reaction stoichiometry was reversed with 1 equiv. C_{sp^3}–H precursor, TBPB (2 equiv. 1.0 mmol), Et_3N•3HF (1.0 equiv., 0.5 mmol), and $Ir(dFppy)_3$ (2 mol%). [c] Silver fluoride, AgF (1 equiv., 0.5 mmol) used instead of Et_3N•3HF b) Difluorination conditions. [d] Reaction conditions: C_{sp^3}–H precursor (1 equiv., 0.50 mmol), TBPB (2 equiv.), Et_3N•3HF (1 equiv.), benzene (0.5M), and $Ir(dFppy)_3$ (2 mol%). ^{19}F NMR yields with fluorobenzene as the external standard. Difluorination yields are shown in blue. [e] 32-35% of **23** and **28**. [f] 41-50% of **24**-**27**, **30**. [g] 55-58% of **31**, **33**, and **46**. [g] 3 equiv. of AgF were used instead of Et_3N•3HF. 50% of **45** was observed.

hydrogen-atom abstractor. Difluorination of diphenylmethane worked well, providing 55% yield of **23'**. We were encouraged to observe difluoromethylene products of ethylbenzene scaffolds (**24'**-**33'**). Modest yields were maintained with electron-rich sub-

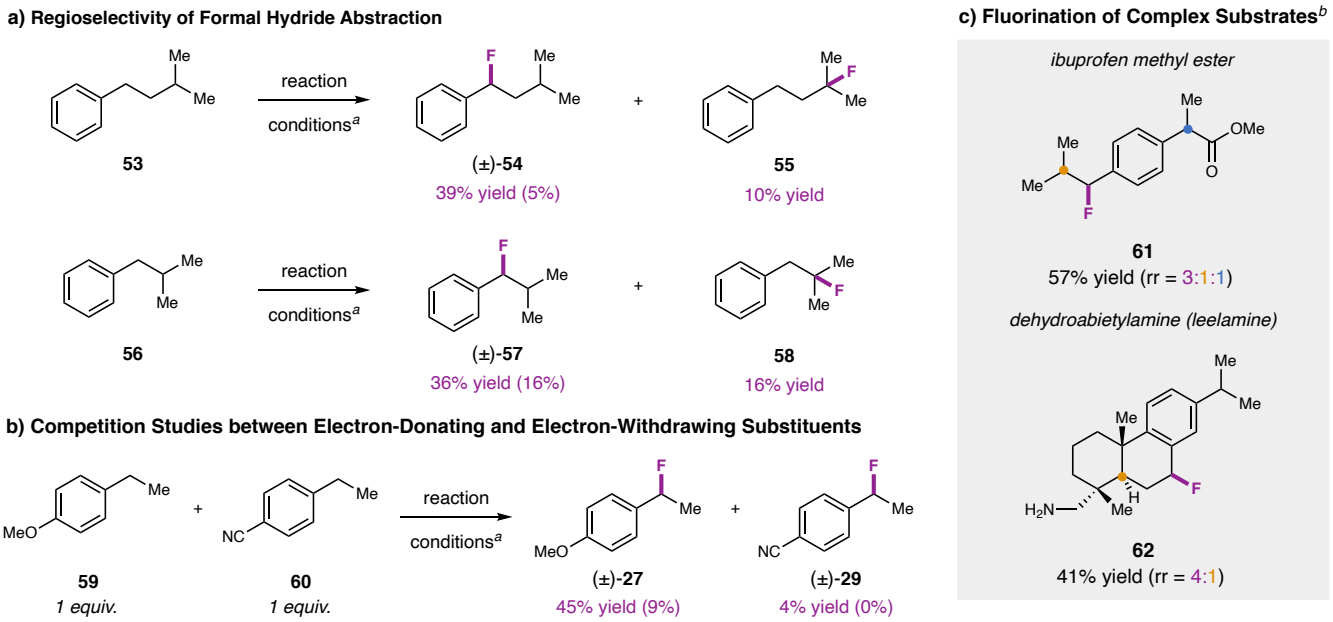
stituents on the arene, while electron-deficient groups lowered the efficiency of the system. Meta substitution was tolerated (**33'**), while ortho substitution shut down the difluorination (See SI). Heterocycle-containing diarylmethanes also worked under the difluorination conditions, again, only when silver fluoride was present (**45'**). Additional length in the alkyl chain of secondary benzylic substrates was tolerated for the difluorination (**46**). It should be noted that the monofluorinated intermediate is still present at the end of the reaction. While studies are ongoing to achieve full conversion to the difluorinated products, to the best of our knowledge, this work represents the first methylene difluorination with nucleophilic fluoride reagents. Additionally, this work provides a direct entry way to fluoro carbocation intermediate, which have been used to access a variety of other . Judicious choice of the relative stoichiometry of the hydrocarbon to fluoride/abstractor reagents allows for access to either monofluorinated or difluorinated products.

Given the electronic demands of the mechanistic design, we were pleased to find primary benzylic C–H bonds were viable precursors in the formal hydride abstraction (Scheme 3). Electron-donating groups at the para position of toluene motifs were necessary for achieving modest yields, with electron-withdrawing groups preventing fluorination almost entirely (**47-50**). Encouragingly, hydridic C–H sites adjacent to heteroatoms were amenable to fluorination in the reaction, including ester and ether functionality (**51,52**).

Finally, we aimed to investigate the regioselectivity of our formal hydride abstraction with competition studies and the examination of complex small molecules (Scheme 4). Substrates **53** and **56** contain secondary benzylic, aliphatic tertiary, and secondary and primary C_{sp^3}–H bonds. Upon treatment with the standard reaction conditions in benzene, both substrates were preferentially fluorinated at the secondary benzylic position in >2:1 ratio relative to the tertiary aliphatic site. High regioselectivity was observed in a competition study between an electron-rich and electron-deficient ethylbenzene substrate, with great preference (>11:1) for functionalization on the electron-rich substrate (Scheme 4b). Lastly, we evaluated on the electron-rich substrate (Scheme 4b). Lastly, we evaluated the amenability of the formal hydride abstraction C_{sp^3}–H fluorination on complex small molecules (Scheme 4c). For the methyl ester of Ibuprofen (**61**), fluorination was observed at three positions, with the benzylic methylene site being favored. Excitingly, leelamine (**62**) was also successfully fluorinated in 41% yield –



Scheme 3. Primary Benzylic and α–Heteroatom Scope [a] Reaction was run on 0.50 mmol scale of the alkane. [b] Reaction was run on 0.20 mmol scale of the alkane. [c] 9% of difluoro product was observed.

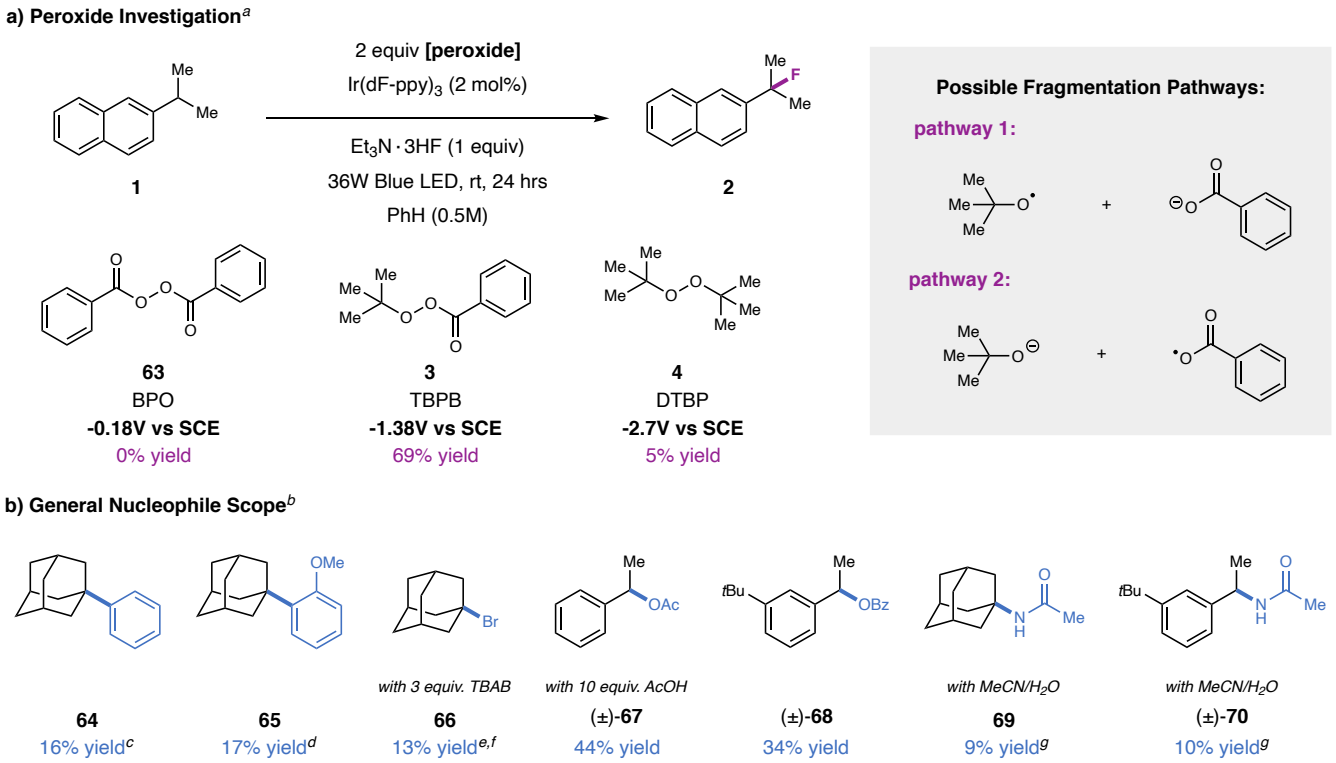


Scheme 4. Multi-site fluorination studies and examples. Reaction conditions: C_{sp^3}–H precursor (1 equiv.), TBPB (2 equiv.), Et3N•3HF (1 equiv.), and Ir(dFppy)3 (2 mol%). ^{19}F NMR yields. Values in parentheses represent the yield of difluorination product. a) Intramolecular Regioselectivity Studies. [a] Reactions run on 0.20 mmol scale. b) Selectivity study between electronically different ethylbenzene derivatives. c) Fluorination on Complex Substrates. [b] Reactions run on 0.50 mmol scale.

without needing to protect the primary amine – and demonstrating preferential regioselectivity also for the secondary benzylic site. In all substrate situations, secondary aliphatic fluorination products were undetectable.

FURTHER CONSIDERATIONS

Next, we considered the identity of the electrophilic hydrogen atom abstractor (Scheme 5a). While we hypothesize TBPB[49] fragments upon SET reduction to provide tBuO• and benzoate, recent work by Glorius and co-workers demonstrates that benzoxy radical, •OCOPh, could also be a viable catalytic H-atom abstractor species.[50] Thus, Scheme 5 shows two possible fragmentation pathways of the perester upon reduction. In order to interrogate pathway 1 vs. pathway 2, we tested symmetrical peroxide benzoyl peroxide (BPO), which fragments to give benzoxy radical and benzoate anion, under our reaction conditions. No fluorination product was observed with BPO, suggestion the benzoxy radical is unlikely to be a HAT catalyst under our reaction conditions. Next, di-*tert*-butyl peroxide (DTBP) was investigated as the peroxide, which provided only 5% yield of the fluorinated product. Stern-Volmer experiments showed relatively weak quenching of the photocatalyst in the presence of DTBP, which suggests the lack of success of DTBP may be due to a high reduction potential (-2.7V v SCE)[51] that is not within the reducing ability of the photocatalyst. As shown in Table 1, use of TBEC as the peroxide also resulted in fluorinated product, which if fragmentation following pathway 2 occurred upon single-electron reduction, would generate an alkoxycarbonyloxy radical that has not been cited as a H-atom abstractor. Together, this data suggests the identity of the hydrogen atom abstractor to be *t*BuO• (pathway 1).



Scheme 5. Further considerations of the formal hydride abstraction protocol a) Peroxide fragmentation pathways. [a] Reactions run on 0.20 mmol scale. b) Other Viable Nucleophile Classes. [b] Reaction conditions: C_{sp^3}–H precursor (1 equiv., 0.50 mmol), TBPB (2 equiv.), Et_3N•3HF (1 equiv.), benzene (0.5M) and $Ir(dFppy)_3$ (2 mol%) with isolated yields. [c] TBEC was used instead of TBPB [d] Anisole (0.17M) instead of benzene [e] TBAB = tetrabutylammonium bromide, benzene (0.17M) [f] ^{1}H NMR yield. [g] MeCN (0.5M) instead of benzene, H_2O (50 mol%), H_2SO_4 (20-40 mol%)

To probe the intermediacy of a reactive carbocation, we proposed that this platform could be amenable to C–H functionalization with a variety of general nucleophile classes, both carbon- and heteroatom-based (Scheme 5b). A quick investigation of other nucleophiles revealed that Friedel-Crafts (**64, 65**), halogenation (**66**), esterification (**67, 68**) and Ritter products (**69, 70**) were obtained, simply through replacement of the fluoride source with an appropriate nucleophile. Benzoate compound **68** demonstrates the ability of TBPB to provide dual functionality as both the abstractor source and the nucleophile. Notably, the arylation reaction represents a formal dehydrogenative coupling between two C–H sites.

CONCLUSION

Current late-stage functionalization technologies of C_{sp^3}–H bonds often rely on electrophilic polar groups that invert the inherent nucleophilic nature of the nitrogen, oxygen, or halogen atoms. We have identified a broadly applicable reaction platform for achieving a formal hydride abstraction that utilizes commercially-available peresters in conjunction with photoredox catalysis. Our strategy involves a stepwise sequence of HAT followed by a radical-cationic crossover event to enable a net hydride removal from general C_{sp^3}–H bonds. We have demonstrated the initial success of the novel C_{sp^3}–H functionalization platform in the realm of C–H fluorination, specifically leveraging the platform to take advantage of the benefits of nucleophilic fluoride sources. Moreover, the mechanistic design detailed here takes advantage of highly reactive carbocations without paying the energetic penalty needed to achieve a direct hetero-

lytic bond cleavage. In addition, we have also successfully demonstrated the interception of the carbocation intermediate by other nucleophile classes, furthering the potential impact of this formal hydride abstraction on practicing chemists.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

PDF includes descriptions of experiments and spectral data.

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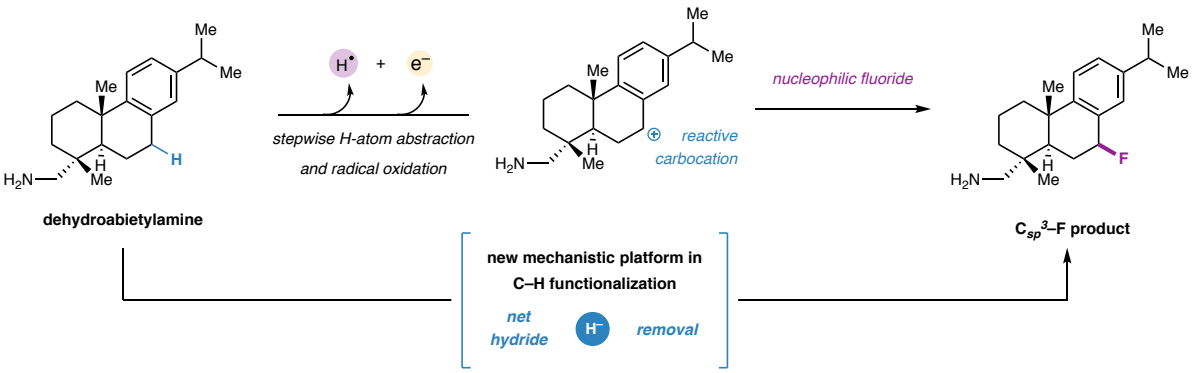
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