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Photoredox-catalyzed deoxyfluorination of activated alcohols with Selectfluor®

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ABSTRACT

Herein we disclose a deoxyfluorination of alcohols with an electrophilic fluorine source via visible-light photoredox catalysis. This radical-mediated C–F coupling is capable of fluorinating secondary and tertiary alcohols efficiently, complementing previously reported nucleophilic deoxyfluorination protocols.

1. Introduction

The deoxyfluorination of alcohols is an attractive method for the ever-challenging synthesis of aliphatic fluorides [1], which are recognized as high-value targets in several industries, such as the pharmaceutical, agrochemical, and materials sciences [2]. From a mechanistic perspective, traditional deoxyfluorination reactions involve the displacement of an *in situ*-activated leaving group by a fluoride ion, generally through a bimolecular S_N2 pathway [3]. Classical nucleophilic deoxyfluorination reagents (e.g., DAST, Deoxo-Fluor) [3a-b] have helped make alkyl fluorides synthetically accessible, although it is widely appreciated that there is significant room for improvement in terms of their functional group tolerance, resistance to elimination, and ease of handling. Several modern alternatives have been developed to these ends, with PhenoFluor [3f] and PyFluor [3g], in particular, making significant progress toward realizing a general and selective protocol for primary and secondary alcohol substrates. In light of these extensive efforts, it is perhaps surprising that deoxyfluorination remains challenging for an appreciable number of alcohols, most notably the tertiary congeners. Ultimately, the common mechanistic feature of these otherwise wide-ranging approaches, the S_N2 fluorination step, may fundamentally limit this chemistry. We hypothesized, therefore, that a new mechanistic approach could expand the scope of this transformation.

We propose an alternative mechanistic strategy based on visible-light photoredox catalysis that would complement the progress of nucleophilic deoxyfluorination methodologies [4]. Photoredox catalysis has permitted the development of fundamentally new reactivity platforms by providing access to reactive radical species under mild conditions from abundant, native functionalities. In this regard, in collaboration with the Overman group, we identified alkyl oxalates as robust alcohol-activating groups for alkyl radical generation via double decarboxylation [5]. During the preparation of this manuscript, the Reisman group as well as Brioche have described select examples of this transformation using the corresponding oxalate half-esters as radical precursors [6].

2. Results and discussion

2.1. Design plan

We envisioned an operationally simple sequence whereby alcohols would be activated as their corresponding oxalate half-esters towards direct electrophilic deoxyfluorination [7]. We expected such a transformation to exhibit broad functional group

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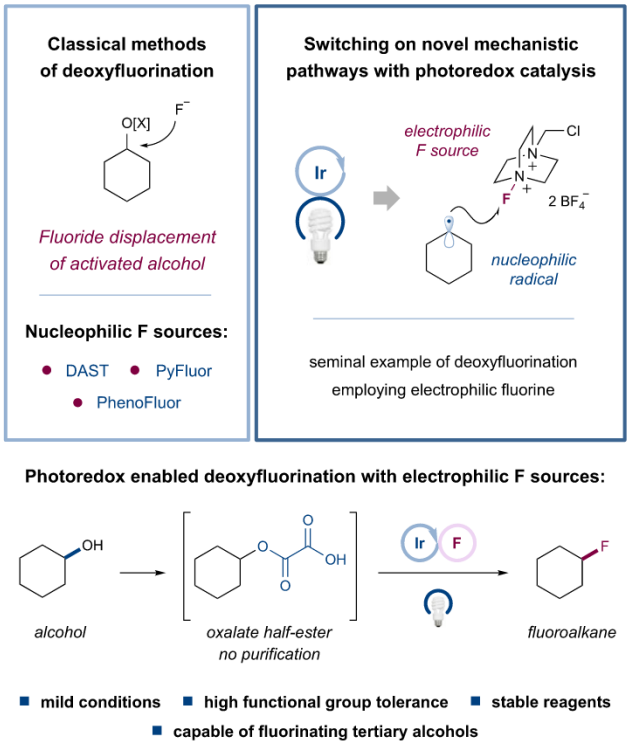
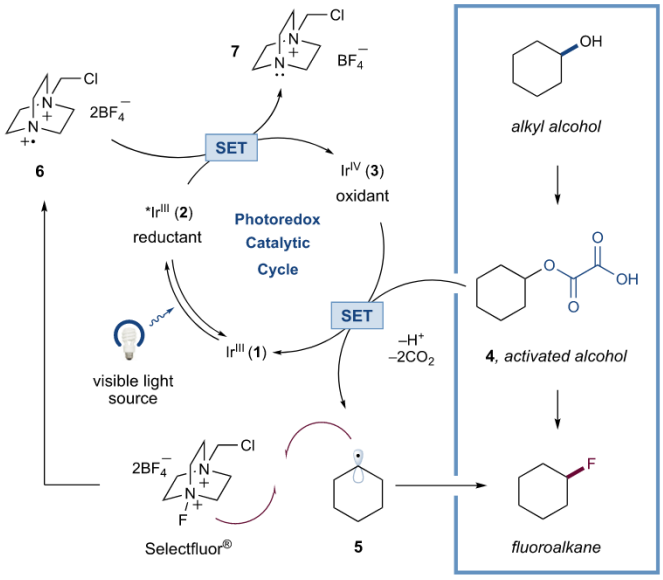




Scheme 1. Proposed Mechanism for the Photoredox-Catalyzed Deoxyfluorination of Alcohols.

tolerance, considering the mild nature of visible-light-mediated single-electron transfer reactions [4]. Furthermore, we postulated that this mechanism could bypass the limitations inherent in bimolecular S_N2 pathways toward obtaining sterically demanding alkyl fluoride products. Moreover, tertiary alkyl radicals are superior nucleophiles in comparison to their secondary and primary analogues [8]. We suspected, therefore, that this manifold would display complementary reactivity to established deoxyfluorination methods, and could be highly efficient for the preparation of tertiary fluorides.

Herein we report the application of visible-light photoredox catalysis towards the first electrophilic deoxyfluorination reaction of alcohols with Selectfluor®, a commercially available, inexpensive, easy-to-handle, and thermally stable electrophilic fluorine source.

As outlined in Scheme 1, irradiation of the heteroleptic Ir(III) photocatalyst Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ (**1**) with visible light leads to the formation of long-lived ($\tau = 2.3$ μs) excited-state species **2** ($E_{1/2}^{red}$ [Ir^{IV}/*Ir^{III}] = −0.89 V vs. SCE in MeCN) [9]. We hypothesized that the initial reduction of a sacrificial amount of Selectfluor® ($E_{1/2}^{red}$ = +0.33 V vs. SCE in MeCN) [10] by **2**, via a single-electron transfer (SET) process, should generate strongly oxidizing Ir(IV) species **3** as the starting point for the active photoredox catalytic cycle. Thereafter, **3** can oxidize the activated alcohol (i.e., half-oxalate **4**) via a second SET process, generating alkyl radical **5** following the loss of two molecules of CO_2. In turn, reduction of **3** would regenerate the ground-state photocatalyst, which is re-excited to **2** by visible light. At this stage, we envisioned direct fluorine-atom transfer from Selectfluor® to alkyl radical **5** would forge the desired C–F bond to afford the fluoroalkane product and radical cation **6**. Finally, SET between **6** and **2** completes the photoredox catalytic cycle, regenerating **3** [11].

Stern-Volmer experiments revealed that a Selectfluor®-mediated oxidation is a plausible initiation step of the photoredox catalytic cycle (i.e., **2** to **3**), as we observed that the emission intensity of the excited-state photocatalyst (**2**) was diminished in the presence of Selectfluor®. In contrast, no quenching occurred in the presence of an activated alcohol [12].

2.2. Optimization studies

Based on our previous investigations on the decarboxylative fluorination of alkyl carboxylic acids [13], we examined the proposed transformation using the oxalate of 2-decanol (formed from the corresponding alcohol in a single step and without purification) with Selectfluor®, using Na_2HPO_4 as the base, and a 34 W blue LED lamp (Table 1). To our delight, the desired deoxyfluorination was observed in 54% yield (entry 1).

The yield could be increased to 72% when using a mixture of acetone/H_2O as solvent (entry 2). Furthermore, the use of

Table 1
Optimization of the Deoxyfluorination Process.[a]

entry	conditions	solvent	yield[b]
1	Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ [**1**]	MeCN/H_2O 4:1	54%
2	photocatalyst **1**	acetone/H_2O 4:1	72%
3	Ir[F(Me)ppy]$_2$(dtbbpy)PF$_6$ [**8**]	acetone/H_2O 4:1	70%
4	Ir[dF(OMe)ppy]$_2$(dtbbpy)PF$_6$ [**9**]	acetone/H_2O 4:1	87%
5	photocatalyst **9**	MeCN/H_2O 4:1	80%
6	photocatalyst **9**	DMF/H_2O 4:1	36%
7	photocatalyst **9**	dioxane/H_2O 4:1	56%
8	photocatalyst **9**	acetone	42%
9	no photocatalyst	acetone/H_2O 4:1	0%
10	no light	acetone/H_2O 4:1	0%

[a] Reactions were performed with photocatalyst (1 mol%), Selectfluor® (2.25 equiv.), oxalate (1.0 equiv.), and NaH_2PO_4 (2.0 equiv.) under blue-light irradiation (34 W LED lamp).
[b] Yields were obtained by ^{19}F NMR analysis of the crude reaction mixtures using 3,5-bis(trifluoromethyl)bromobenzene as an internal standard.

photocatalyst **9** ($E_{1/2}^{red}$ [Ir^{IV}/*Ir^{III}] = −0.82 V vs. SCE in MeCN) [14] afforded the desired product in 87% yield (entry 4). Organic co-solvents other than acetone led to lower yields (entries 5–7). Entry 8 highlights the critical role of water in this transformation, presumably helping to maintain the homogeneity of the reaction mixture, given the poor solubility of Selectfluor® and Na_2HPO_4 in acetone. Consistent with our proposed mechanism, control experiments demonstrated the critical roles of the photocatalyst and visible light in the desired transformation (entries 9–10).

2.3. Substrate scope

With the optimized conditions in hand, we next sought to assess the generality of this transformation. We were pleased to observe that a wide range of differentially substituted secondary and tertiary alcohols could be readily converted to their corresponding alkyl fluorides in good-to-excellent yields (Table 2). Secondary acyclic alcohols were efficiently transformed into the desired alkyl fluorides (**10**–**12**, 67–80% yield). In addition, benzyl-, homobenzyl-, and β-benzyl-substituted oxalates readily underwent deoxyfluorination (**13**–**17**, 62–88% yield). Interestingly, when the oxalate derivatives of secondary alcohols containing a vicinal tertiary benzylic carbon were subjected to our standard deoxyfluorination conditions, tertiary homobenzylic products **16** and **17** were formed (66% and 88% yield, respectively). These products arise from a 1,2-phenyl migration after double decarboxylation [15]. Moreover, oxalates bearing five-, six-, seven-, or twelve-membered rings were found to efficiently undergo deoxyfluorination (**18**–**22**, 71–84% yield). Likewise, monosubstituted cyclohexyl oxalates, as well as bridged polycyclic oxalates, provided the desired products with good selectivity and high efficiency (**21**–**24**, 64–96% yield).

Notably, our deoxyfluorination protocol was also applicable to heterocyclic systems, such as piperidine and proline derivatives (**25** and **26**, 89% and 79% yield, respectively). This transformation could also be accomplished in the presence of a cyano group (**27**, 72% yield). Deoxyfluorination at a propargylic position was also accomplished with good efficiency (**28**, 71% yield). Remarkably, simple diol systems could be selectively activated, after mono-oxalate formation, yielding deoxyfluorinated compounds **29** and **30** [16] in moderate yields and without the need for protecting groups. This result highlights the potential applicability of our deoxyfluorination technology to the selective monofluorination of more complex polyalcohol systems, which are ubiquitous in bioactive molecules.

We next turned our attention to tertiary alcohols, which are a challenging substrate class given the potential formation of elimination side products under established nucleophilic deoxyfluorination conditions. We were pleased to observe that photoredox catalysis enables the efficient deoxyfluorination of differentially substituted tertiary alcohols (**31**–**38**, 46–84% yield), demonstrating the tolerance of this radical mechanism toward increased steric hindrance. The use of a lower-intensity CFL and reduced amounts of Selectfluor® led to improved efficiencies for this series. This procedure could be conducted on gram-scale without loss of efficiency, affording fluoroalkane **31** in 81% yield, which underscores the practical utility of this technology. Notably, product **32** was isolated as a single diastereomer. The electrophilic deoxyfluorination of tertiary alcohols could be carried out in the presence of various functional groups, including protected amines (**34** and **35**), esters (**37**), or amides (**38**). Alkyl fluorides **37** and **38** also highlight the potential of this methodology to access β-fluorocarbonyl derivatives, complementing scarcely reported methodologies to incorporate fluorine into the β-position of this type of system [17]. Moreover, deoxyfluorination could be efficiently conducted at remote positions of unsaturated systems without radical migration to the more stabilized allylic position (**36**, 46% yield), further illustrating the selectivity of this technology. Despite the low stability of primary alkyl radicals, oxalates derived from primary alcohols still afforded the desired fluorinated compounds in synthetically useful yields (**39**–**41,** 36–38% yield).

The utility of this technology was further demonstrated by the deoxyfluorination of a series of natural products and biologically active molecules (Table 3). The reactions proceeded with good yields and selectivities even with substrates containing bridged structures and heteropolycyclic systems (**42**–**45**, 65–86%). Even more impressively, for structures with hindered sites of reaction, such as sclareolide or cedrol, this technology afforded good-to-excellent yields with good levels of selectivity (**46** and **47**, 47% and 93% yield, respectively).

3. Conclusion

In summary, we have developed a new visible-light photoredox-catalyzed method for the deoxyfluorination of alcohols via their corresponding oxalates, which are readily accessible in a single step and without purification. From a mechanistic perspective, this strategy constitutes a distinct approach to the deoxyfluorination of alcohols, employing an electrophilic fluorine source. This technology complements previously reported nucleophilic deoxyfluorination protocols, especially for tertiary alcohols, for which an S_N2-type mechanism is particularly challenging.

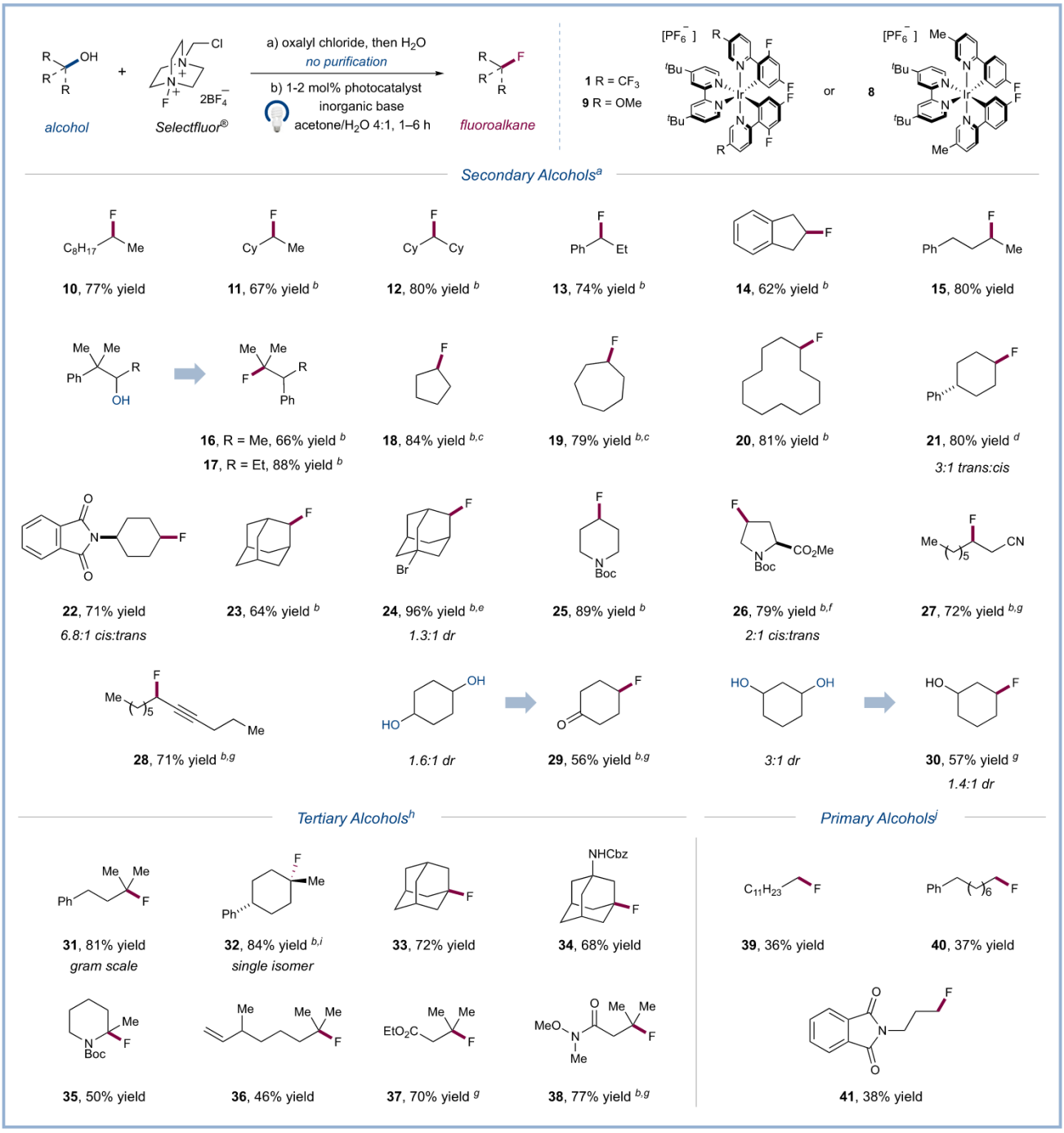
4. Experimental section

General deoxyfluorination procedure. A 40 mL glass vial equipped with a Teflon septum and magnetic stir bar was charged with the oxalic acid or oxalate salt (1.0 equiv), the indicated photocatalyst (1 mol%), Na_2HPO_4 or K_2HPO_4 (2.0 equiv), Selectfluor® (1.1 – 4.5 equiv), and acetone/H_2O (4:1) or acetonitrile/H_2O (4:1). The resulting solution was then sparged with N_2 for 3 min. The vial was sealed and placed between two Kessil® LED illuminators (model H150 blue, http://www.kessil.com/horticulture/H150.php; for primary and secondary oxalates unless otherwise noted) or one 26 W CFL (for tertiary oxalates), approximately 1 inch away from each. The reaction mixture was stirred and irradiated for 1–6 h. Upon completion, the reaction mixture was diluted with Et_2O or ethyl acetate (for less soluble substrates) and washed successively with water and brine. The combined aqueous washings were extracted with the appropriate organic solvent (2 × 25 mL). The combined organic extracts were dried ($MgSO_4$), filtered and concentrated in vacuo. Purification by flash column chromatography over silica gel afforded the pure product.

4.1. Synthesis of 2-fluorodecane (10)

Following the general deoxyfluorination procedure, 2-(decan-2-yloxy)-2-oxoacetic acid (207 mg, 0.9 mmol, 1.0 equiv), Na_2HPO_4 (256 mg, 1.8 mmol, 2.0 equiv), Selectfluor® (638 mg, 1.8 mmol, 2.0 equiv), Ir[dF(OMe)ppy]$_2$(dtbbpy)PF_6 (9.4 mg, 9.0 μmol, 1 mol%) and 4:1 acetone/H_2O (9.0 mL, 0.1 M) provided after 1.5 h the desired product (111 mg, 77% yield) as a colourless liquid. Purification was accomplished via flash column chromatography over silica gel (hexanes). IR (film): ν_{max} 2926, 2856, 1463, 1383, 1341, 1130, 1079 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 4.80-4.47 (m, 1H), 1.80-1.15 (m, 17H), 0.94-0.80 (m, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 91.7, 90.4, 37.0, 36.9, 31.9, 29.5, 29.2, 25.1, 22.7, 21.1, 20.9, 14.1 ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ −171.8 to −172.4 (m, 1F). HRMS (EI) *m/z* calcd. for $C_{10}H_{20}$ [(M − F)$^{*+}$] 140.1560, found 140.1561.

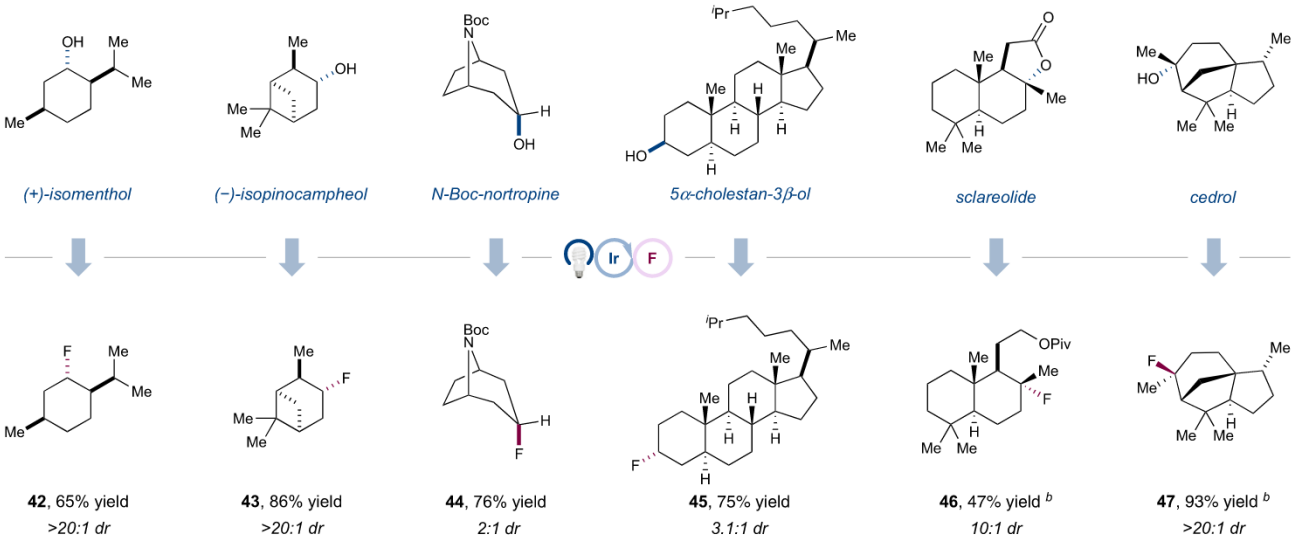
Table 2
From alcohols to fluoroalkanes: Scope of photoredox deoxyfluorination of Oxalates.



4.2. Synthesis of (3-fluoro-3-methylbutyl)benzene (31)

Following the general deoxyfluorination procedure, 2-((2-methyl-4-phenylbutan-2-yl)oxy)-2-oxoacetic acid (1.3 g, 5.4 mmol, 1.0 equiv), Na_2HPO_4 (1.5 g, 10.8 mmol, 2.0 equiv), Selectfluor® (3.3 g, 9.2 mmol, 1.7 equiv), Ir[F(Me)ppy]$_2$(dtbbpy)PF_6 (53 mg, 54 μmol, 1 mol%) and 4:1 acetone/H_2O (54.0 mL, 0.1 M) provided after 1 h the desired product (727 mg, 81% yield) as a colorless oil. Purification was accomplished via flash column chromatography over silica gel (pentane). IR (film): ν_{max} 2971, 2920, 1494, 1453, 1376, 1072, 1030, 734, 696 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.38-7.33 (m, 2H), 7.26 (d, J = 7.3 Hz, 3H), 2.82-2.76 (m, 2H), 2.05-1.93 (m, 2H), 1.47 (d, J = 21.4 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 142.01, 128.40, 128.26, 125.83, 95.23 (d, $J_{C,F}$ = 165.7 Hz), 43.32 (d, $J_{C,F}$ = 22.9 Hz), 30.24 (d, $J_{C,F}$ = 5.4 Hz), 26.66 (d, $J_{C,F}$ = 24.8 Hz) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ −138.80 (dtd, J = 40.9, 21.5, 2.0 Hz, 1F) ppm. HRMS (EI) m/z calcd. for $C_{11}H_{15}$ [$(M - F)^{*+}$] 147.1168, found 147.1131.

Table 3
Late-Stage Deoxyfluorination of Natural Products Containing Alcohol Groups.[a]



4.3. Synthesis of (8-fluorooctyl)benzene (40)

Following the general deoxyfluorination procedure, 2-oxo-2-((8-phenyloctyl)oxy)acetic acid (278 mg, 1.0 mmol, 1.0 equiv), Na_2HPO_4 (284 mg, 2.0 mmol, 2.0 equiv), Selectfluor® (1.6 g, 4.5 mmol, 4.5 equiv), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (11.2 mg, 10.0 μmol, 1 mol%) and $MeCN/H_2O$ (4:1 ratio, 11.0 mL, 0.1 M) provided after 2 h the desired product (76 mg, 37% yield) as a colorless liquid. Purification was accomplished via flash column chromatography over silica gel (pentane). IR (film): ν_{max} 2928, 2856, 1454, 1005, 746, 697 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.30-7.27 (m, 2H), 7.19-7.17 (m, 3H), 4.44 (dt, $J = 47.4$, 6.2 Hz, 2H), 2.61 (t, $J = 7.5$ Hz, 2H), 1.74-1.59 (m, 4H), 1.42-1.33 (m, 8H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 142.8, 128.4, 128.2, 125.6, 84.2 (d, $J_{C,F} = 162.8$ Hz), 35.9, 31.5, 30.4 (d, $J_{C,F} = 19.1$ Hz), 29.4, 29.2, 29.2, 25.1 (d, $J_{C,F} = 5.5$ Hz) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ −218.02 (tt, $J = 48.1$, 24.9 Hz) ppm. HRMS (EI) *m/z* calcd. for $C_{14}H_{21}F$ [$(M)^{*+}$] 208.1627, found 208.1628.

Acknowledgment

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tet.2019.05.043.

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