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I. General Information

Commercial reagents were purified prior to use following the guidelines of Perrin and Armarego.[1] All solvents were purified by column according to the method of Grubbs.[2] Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator. Chromatographic purification of products was accomplished using force-flow chromatography on Aldrich silica gel according to the method of Still.[3] Thin-layer chromatography (TLC) was performed on Aldrich 250 μm silica gel plates. TLC visualization was performed by fluorescence quenching, $KMnO_4$ or iodine stain. All yields reported are averages of at least two experimental runs.

^1H NMR spectra were recorded on a Bruker 500 (500 MHz) and are referenced relative to residual CH_3CN (in CD_3CN) or $CHCl_3$ (in $CDCl_3$) proton signals at δ 1.94 ppm and δ 7.26 ppm, respectively. Data for ^1H spectra are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad, ap = apparent), integration, coupling constant (Hz) and assignment. ^{13}C NMR spectra were recorded on a Bruker 500 (126 MHz) and are referenced relative to residual $CHCl_3$ (in $CDCl_3$) at δ 77.23 ppm. Data for ^{13}C NMR spectra are reported in terms of chemical shift and multiplicity where appropriate. ^{19}F NMR spectra were recorded on a Bruker NanoBay 300 (300 MHz). High Resolution Mass spectra were obtained from the Princeton University Mass Spectral Facility. UV-Vis measurements were acquired using an Agilent 8453 UV-Visible Spectroscopy System.

Reaction Set-up

In a typical experiment, a 36 W high-density blue LED light source (Kessil H150 Blue grow light) was chosen because of the combination of its intense luminosity, compact size, and known spectral irradiance. Placing the light source approximately 5 cm from the reaction ensured efficient photo-excitation. A steady stream of compressed air was directed over the reaction vessels to maintain ambient temperature (23 °C) during irradiation.

Figure S1. Image of a typical reaction apparatus before operation. The LED lamp is placed 5 cm from the stirring reaction vessel and a compressed air stream is directed at the vessel.

Figure S2. The reaction apparatus during operation. As the LED lamp used for this reaction is a high intensity blue light source, it is suggested that precautions be taken to prevent unnecessary ocular exposure to stray light.

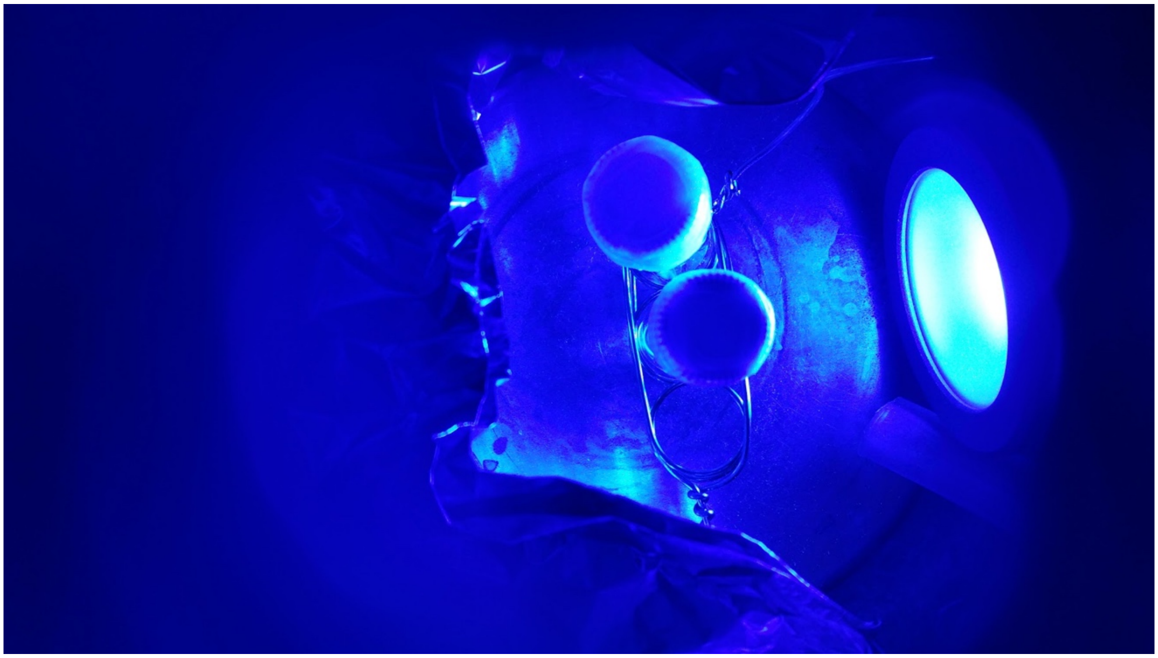


Figure S3. Overhead view inside the reaction apparatus during operation.

II. Fluorination of Unactivated C_{sp3}–H Bonds

$$\text{R}{-}\text{H} \xrightarrow[\text{CH}_3\text{CN, 23 °C, h}\nu\text{, argon}]{\text{1 mol\% UO}_2(\text{NO}_3)_2\text{•6H}_2\text{O} \\ \text{1.5 equiv. NFSI}} \text{R}{-}\text{F}$$

An oven-dried 17 × 60 mm (8 mL) borosilicate vial was equipped with a magnetic stir bar, uranyl nitrate hexahydrate[4] (0.01 equiv), and *N*-fluorobenzenesulfonamide (NFSI) (1.5 equiv). Following the addition of methyl acetate[5] (3-4 drops) and CD_3CN (1.1 mL, ~0.5 M) the vial was fitted with a silicone septa screw cap and sparged with argon for 10 minutes. The substrate (0.5 mmol, 1 equiv, previously sparged with Ar) was added by syringe and stirred vigorously away from UV light sources. A t = 0 aliquot was then removed using a syringe for calibrating the internal standard and the vial was sealed with parafilm and placed approximately 5 cm from a 30 W LED grow light.[6] After 16 hours, the fluorinated product production was assayed using the method described below.

Fluorocyclooctane,[7] Fluorosclareolide (1.6:1 C2/C3 fluorination; C2 4:1 α/β),[8] Ethyl isovalerate[9] all produced products in agreement with the reported literature.

n-Octane and *n*-decane each produced a mixture of fluorinated products consistent with methylene fluorination[10] via NMR analysis.
2-Hexenone, 2-heptenone, 2-octenone, cyclopentanone and methyl valerate each produced trace fluorination products consistent with methylene functionalization not α to the carbonyl.

For the competition experiments between cyclooctane and each of toluene and cyclopentanone, the reaction was set up using the standard conditions outlined above but with both substrates included in an equimolar amount (0.5 mmol, 1 equiv., each).

III. Spectral Output of Lamp

The spectral output of the Kessil H150 Blue grow lamp can be found online at:

http://www.kessil.com/horticulture/H150.php

Importantly, the Kessil lamp has no spectral power below 400 nm, making this a true visible light source.

IV. Absorbance of Reaction Mixture

Due to the known low extinction coefficient of uranyl species, the UV-Vis spectrum was acquired at 10x the normal concentration of $UO_2(NO_3)_2{\bullet}H_2O$, resulting in the catalyst absorbance just barely appearing above the baseline (380 nm < λ < 460 nm).

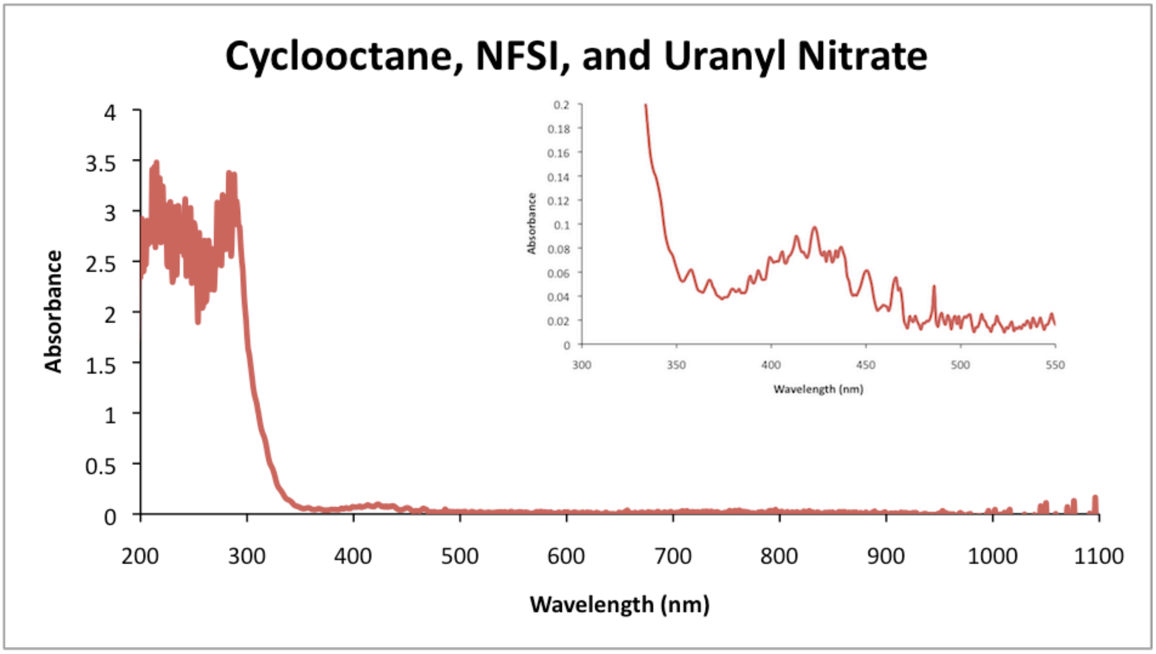


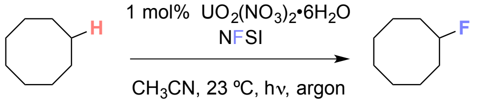
Figure S4. UV-Vis Absorbance of a cyclooctane fluorination reaction mixture containing additional $UO_2(NO_3)_2{\bullet}6H_2O$

As can be seen, there is absorbance of the uranyl species in the spectral output range of the LED lamp (400 – 510 nm) in the presence of the other reaction components

V. Optimization Studies

It was found that reducing the loading of NFSI below 1.5 equivalents led to diminished reaction efficiency (Table S1). Yields are reported after 16 hours of irradiation.

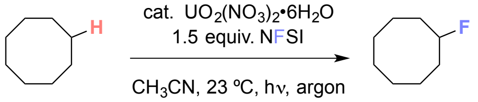
Table S1. NFSI Loading Screen



Entry	NFSI Loading (equiv.)	Yield (%)
1	3	> 95
2	2.5	> 95
3	1.5	> 95
4	1.2	73
5	1	60

Similarly, it was found that catalyst loadings below 1 mol% for uranyl nitrate hexahydrate were deleterious to the reaction. Yields are reported after 16 hours of irradiation (Table S2).

Table S2. Uranyl Catalyst Loading Screen



Entry	$UO_2(NO_3)_2$•$6H_2O$ (mol%)	Yield (%)
1	4	> 95
2	2	> 95
3	1	> 95
4	0.5	52

VI. The Choice of Solvent

Very few solvents are compatible with uranyl photocatalysis; many common solvents serve as competitive substrates (hydrocarbons) or inhibitors (arenes and ethers) for the fluorination reaction and thus were not explored extensively. Acetonitrile's excellent visible light transmission qualities, intertness to the uranyl excited state, and ability to solvate all components of the reaction makes it a natural choice for the transformation. Acetone is also an appropriate choice for this reaction. Water, unfortunately, was unable to dissolve NFSI, nor most of the investigated substrates.

VII. Method For Determining *in situ* yields

An initial t = 0 aliquot (100 μL) of the reaction mixture is diluted to 500 μL using CD_3CN and aerated via vigorous shaking. Integration of a characteristic ^{1}H NMR substrate peak for each alkane followed by normalization to the correct number of protons allows for the integration of the well-resolved methyl acetate O–CH_3 peak (δ 3.59) to serve as the calibrated standard. Following the specified irradiation time, additional aliquots may be removed and prepared using the above procedure to acquire a spectrum. The O–CH_3 peak of the standard is then integrated to the same value as measured in the t = 0 and both the starting material (see above) and product.

The high reactivity of the uranyl excited state precludes the use of many common internal standards as these can serve as competitive substrates for the initial hydrogen atom transfer. Methyl acetate was chosen after determining the very low reactivity of hydrogen atoms alpha to ketones and ester oxygens under uranyl photocatalysis in addition to the paucity of competing peaks in the 3.5–4.0 window of the ^{1}H NMR spectrum.

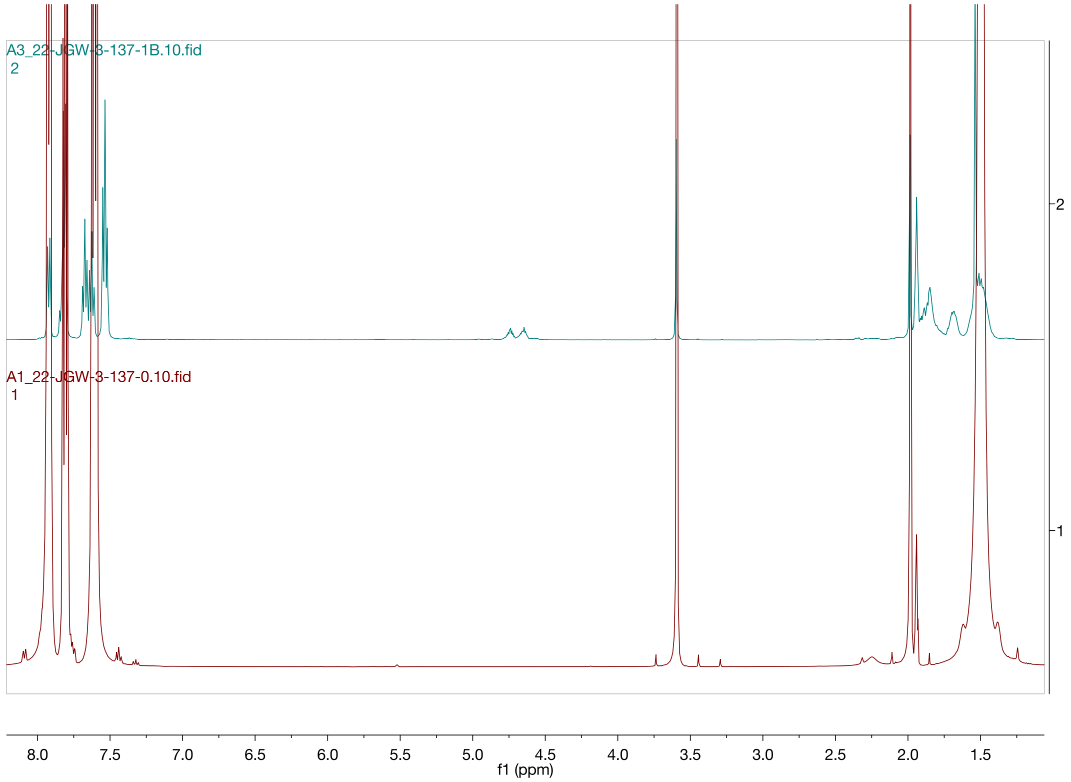


Figure S5. A stacked version of the t = 0 and 16 h spectra. Note the disappearance of the cyclooctane and diminishment of the NFSI resonances with the concomitant appearance of fluorocyclooctane and benzene sulfonimide (“NHSI”) signals.

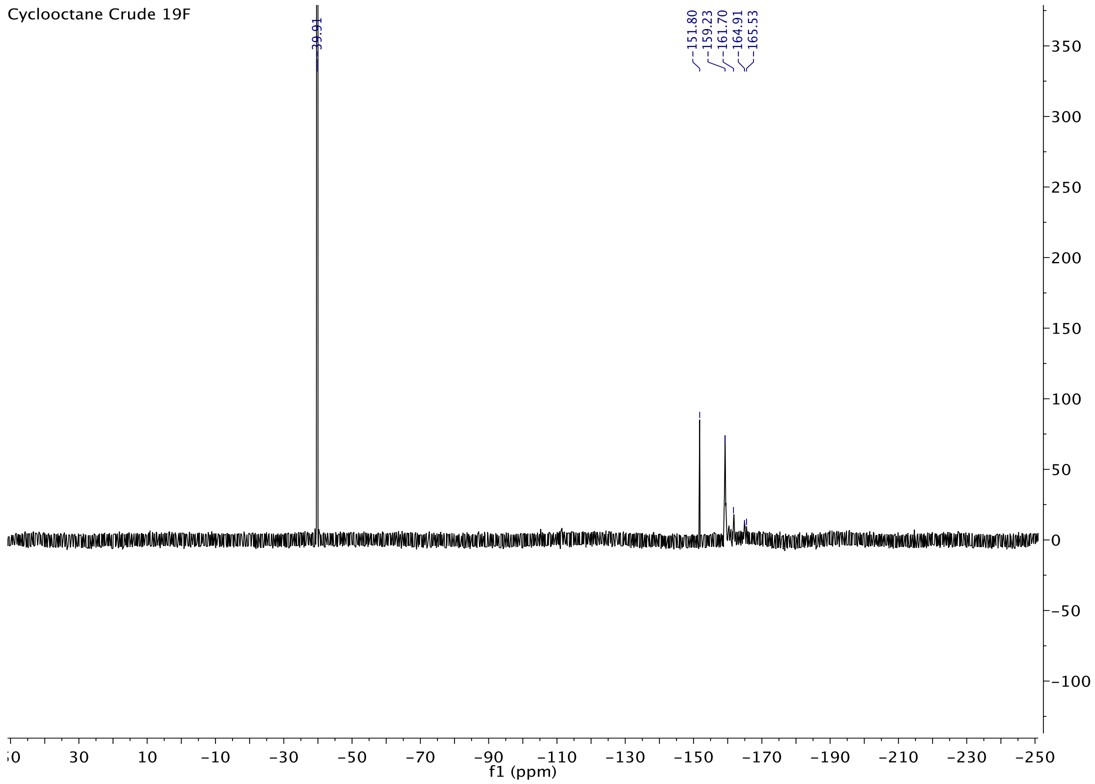


Figure S6. The ^{19}F NMR of the crude reaction mixture shows resonances from residual NFSI (-40 ppm) and fluorocyclooctane (-159 ppm). The peak at -151 ppm likely corresponds to a fluoroborate side product from generation of adventitious fluoride during the course of the reaction and was observed in most reactions; the baseline resonances to the left have not been assigned.

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[1] Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*; 3rd ed., Pergamon Press, Oxford, 1988.

[2] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics,* **1996**, *15*, 1518.

[3] Still, W. C.; Kahn, M.; Mitra, A. J. *J. Org. Chem.* **1978**, *43*, 2923.

[4] $UO_2(NO_3)_2$•$6H_2O$ was supplied by Sigma (cat # 94270 FLUKA) and used as received, as was $UO_2(OAc)_2$•$2H_2O$ (cat # 73943 FLUKA)

[5] Methyl acetate was shown to be inert to the reaction conditions by complete recovery of unreacted starting material.

[6] Kessil H150 Blue 36W LED grow light (Product ID: PT2189)

[7] Lheureux, A.; Bequlieu, F.; Laflamme, F.; Couturier, M.; Bennett, C.; Clayton, S.; Tovell, D.; Bill, D. R.; Mirmehrabi, M.; Tadayon, S. *J. Org. Chem*. **2010,** *75*, 3401-3411.

[8] Liu, W.; Huang, X.; Cheng, M.-J.; Nielsen, R. J.; Goddard, W. A. III; Groves, J. T. *Science* **2012,** *337*, 1322-1325.

[9] S.D. Halperin, H. Fan, S. Chang, R.E. Martin, R. Britton. *Angew. Chem. Int. Ed.* **2014**, *53*, 4690 – 4693.

[10] Kobayashi, S.; Yoneda, A.; Fukuhara, T.; Hara, S. *Tetrahedron* **2004,** *60*, 6923-6930.