Visible-Light–Driven Photoreductive Complete Degradation of Sulfur Hexafluoride under Ambient Conditions

Hu Zhang,[1] Yi-Ming Chen,[1] Sheng-Ye Zhang,*[2] Yan-Biao Kang*[,1]

1. Department of Chemistry and Materials Science, University of Science and Technology of China, Hefei 230026, China, E-mail: ybkang@ustc.edu.cn

2. State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai, 200032, China, E-mail: zhangshengye@sioc.ac.cn

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1. General information

Materials

Sulfur hexafluoride (99.999%) was purchased from Nanjing Special Gas Plant Co., LTD. All other compounds were purchased from commercial sources without purification unless otherwise noted. Inorganic salts (commercial source): Potassium tert-butanol (99%; J&K); Sodium tert-butanol (99%; Macklin); Lithium tert-butanol (99%; Macklin); potassium hydroxide (90%; General-Reagent); cesium carbonate (99.9%; Energy chemical); potassium phosphate (99%; General-Reagent); potassium carbonate (99%; Keshi); potassium methoxide (98%, Energy chemical). The solvent is purified according to Purification of Laboratory Chemicals, Sixth Edition, 2009 Wilfred L.F. Armarego and Christina Li Lin Chai.

Methods

Unless otherwise noted, reactions were performed with rigorous exclusion of air and moisture. Solvents were pre-dried over activated 4 Å molecular sieves and distilled over calcium hydride under argon atmosphere or degassed prior to use unless otherwise noted.

Organic solutions were concentrated under reduced pressure using a rotary evaporator unless otherwise noted. All work-up and purification procedures were carried out with reagent-grade solvents in air.

Instruments

NMR:

Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Bruker Magnet System 400'54 Ascend with a cryoprobe (400 MHz), Magnet System 500'54 Ascend with a cryoprobe (500 MHz) and JNM-ECZ600R/S1 with a cryoprobe (600 MHz) unless otherwise noted. Carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Bruker Magnet System 400'54 Ascend with a cryoprobe (100 MHz), Magnet System 500'54 Ascend with a cryoprobe (125 MHz) and JNM-ECZ600R/S1 with a cryoprobe (150 MHz) unless otherwise noted. Fluorine nuclear magnetic resonance (^{19}F NMR) spectra were recorded on a Bruker Magnet System 400'54 Ascend with a cryoprobe (376 MHz) or Magnet System 500'54 Ascend with a cryoprobe (471 MHz) or JNM-ECZ600R/S1 with a cryoprobe (565 MHz) unless otherwise noted. All NMR spectra were taken at 25 °C. Chemical shifts for protons are reported in parts per million (ppm) downfield from tetramethyl silane and are referenced to residual protium in the NMR solvent ($CDCl_3$ = 7.26 ppm, d6-DMSO = 2.50 ppm). Chemical shifts for carbon are reported in parts per million downfield from tetramethyl silane and are referenced to the carbon resonance of the solvent peak ($CDCl_3$ = 77.16 ppm, d6-DMSO = 39.5 ppm). NMR data are represented as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad, dq = doublet of quartets), coupling constant (J) in Hertz (Hz), integration.

IC:

Ion chromatography (IC) was performed using a Thermo Scientific Dionex ICS-3000 equipped with a Dionex AS-DV autosampler and using a Dionex IonPac AS19/AG19 4 mm. The analysis was run using an eluent of 20 mM potassium hydroxide and a Dionex ADRS 600 4 mm RFICTM Dynamically Regenerated Suppressor. A flow rate of 1.0 mL/min was used, giving the following retention times: fluoride = 3.8 min. Elemental standards containing 1000 ug/mL fluoride anion were mixed to make quantitative standards consisting of 10, 20 ug/mL of each anion in ultra-pure H2O (18.2 MΩ·cm). Ultra pure H_2O was used as the calibration blank. Validation experiments indicated an error of approximately 10% for ion chromatography.

Light Sources and Reaction setup

All photoreactions were performed with four 9 W Semi-LEDs lamps (C35L-U-60, λmax = 407 nm) unless otherwise noted. The lamps were placed on an aluminum cylinder evenly. The three necks electrochemical device is in the middle of this cylinder approximately 3 cm away from each LED beams. (**Figure S1**) Emission plot of this light source was reported in our earlier article [1].

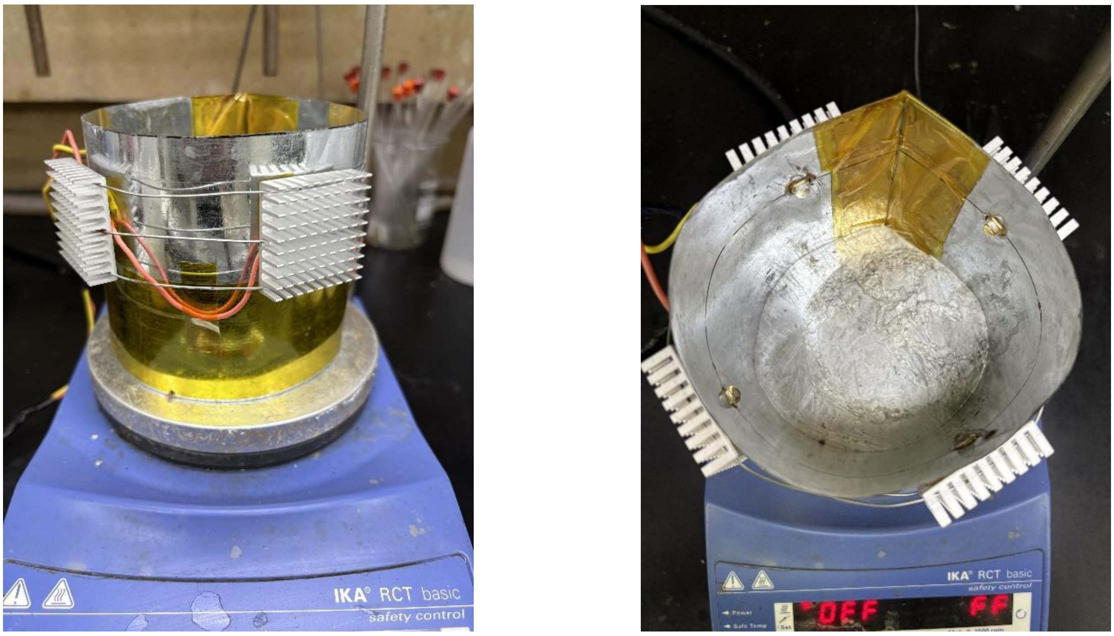
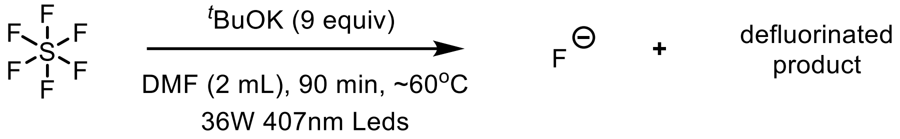


Figure S1. Light reaction device. 36W 407nm LEDs.

2. Verification of the Reaction Conditions for the Defluorination of SF_6

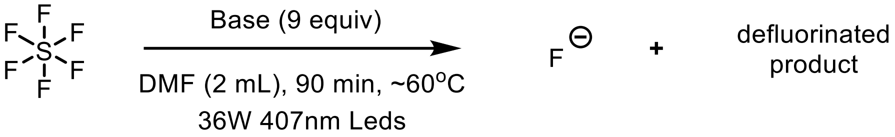
Table S1. Control experiments for defluorination of SF_6



Entry	Variations of reaction conditions[a]	deF(%)
1	Standard Conditions	99
2	w/o light	0
3	w/o ^{t}BuOK	0

[a] Reaction conditions: SF_6 (gas, 29.2 mg, 0.2 mmol repeat unit), ^{t}BuOK (1.8 mmol, 9 equiv) in 2.0 mL of DMF under the irradiation of 36W LEDs (λmax = 407 nm), reacted for 90 minutes at about 60 °C. Fluoride recovery yield was determined by ^{19}F NMR analysis using hexafluoroisopropanol (33.6 mg, 0.2 mmol, 1.2 mmol F) as an internal standard.

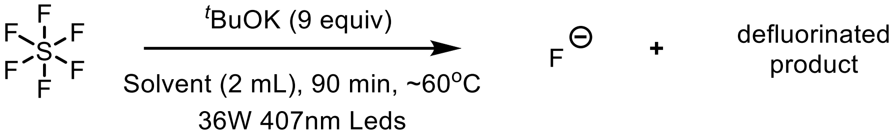
Table S2. Base screening using DMF as solvent



Entry	Base[a]	deF(%)
1	^{t}BuOK	99
2	^{t}BuONa	53
3	^{t}BuOLi	44
4	KOH	28
5	K_2CO_3	Trace
6	K_3PO_4	5
7	MeOK	37
8	Cs_2CO_3	17

[a] Reaction conditions: SF_6 (gas, 29.2 mg, 0.2 mmol repeat unit), Base (1.8 mmol, 9 equiv) in 2.0 mL of DMF under the irradiation of 36W LEDs (λmax = 407 nm), reacted for 90 minutes at about 60 °C. Fluoride recovery yield was determined by ^{19}F NMR analysis using hexafluoroisopropanol (33.6 mg, 0.2 mmol, 1.2 mmol F) as an internal standard.

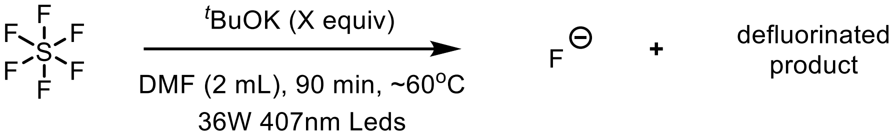
Table S3. Solvent screening using ^{t}BuOK as Base



Entry	Solvent[a]	deF(%)
1	DMF	99
2	DMSO	92
3	DMAc	96
4	NMP	98
5	1,4-Dioxane	0
6	Toluene	0
7	H_2O	0

[a] Reaction conditions: SF_6 (gas, 29.2 mg, 0.2 mmol repeat unit), ^{t}BuOK (1.8 mmol, 9 equiv) in 2.0 mL of Solvent under the irradiation of 36W LEDs (λmax = 407 nm), reacted for 90 minutes at about 60 °C. Fluoride recovery yield was determined by ^{19}F NMR analysis using hexafluoroisopropanol (33.6 mg, 0.2 mmol, 1.2 mmol F) as an internal standard.

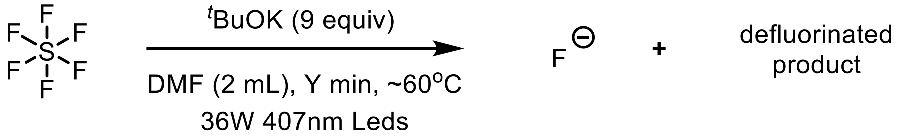
Table S4. Effects of the amount of tBuOK for defluorination of SF_6



Entry	^{t}BuOK (X equiv)[a]	deF(%)
1	1 equiv	8
2	3 equiv	42
3	5 equiv	63
4	7 equiv	89
5	9 equiv	99

[a] Reaction conditions: SF_6 (gas, 29.2 mg, 0.2 mmol repeat unit), ^{t}BuOK (0.2X mmol, X equiv) in 2.0 mL of DMF under the irradiation of 36W LEDs (λmax = 407 nm), reacted for 90 minutes at about 60 °C. Fluoride recovery yield was determined by ^{19}F NMR analysis using hexafluoroisopropanol (33.6 mg, 0.2 mmol, 1.2 mmol F) as an internal standard.

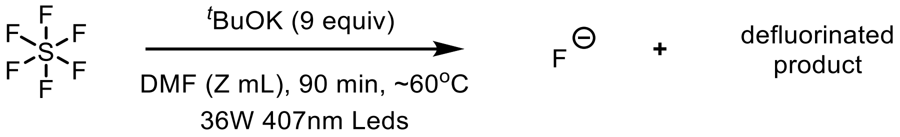
Table S5. Effects of the rection time for defluorination of SF_6



Entry	Time (Y min)[a]	deF(%)
1	15 min	35
2	30 min	51
3	45 min	77
4	60 min	88
5	75 min	92
6	90 min	99

[a] Reaction conditions: SF_6 (gas, 29.2 mg, 0.2 mmol repeat unit), ^{t}BuOK (1.8 mmol, 9 equiv) in 2.0 mL of DMF under the irradiation of 36W LEDs (λmax = 407 nm), reacted for Y minutes at about 60°C. Fluoride recovery yield was determined by ^{19}F NMR analysis using hexafluoroisopropanol (33.6 mg, 0.2 mmol, 1.2 mmol F) as an internal standard.

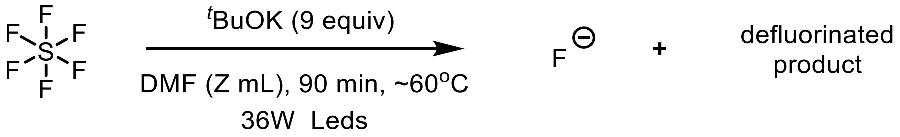
Table S6. Effects of reaction concentration for defluorination of SF_6



Entry	DMF (Z mL)[a]	deF(%)
1	1 mL	79
2	2 mL	99
3	3 mL	86
4	4 mL	89

[a] Reaction conditions: SF_6 (gas, 29.2 mg, 0.2 mmol repeat unit), ^{t}BuOK (1.8 mmol, 9 equiv) in Z mL of DMF under the irradiation of 36W LEDs (λmax = 407 nm), reacted for 90 minutes at about 60°C. Fluoride recovery yield was determined by ^{19}F NMR analysis using hexafluoroisopropanol (33.6 mg, 0.2 mmol, 1.2 mmol F) as an internal standard.

Table S7. Effects of wavelength of the light source for defluorination of SF_6



Entry	wavelength[a]	deF(%)
1	365nm	99
2	390nm	99
3	407nm	99
4	440nm	55

[a] Reaction conditions: SF_6 (gas, 29.2 mg, 0.2 mmol repeat unit), ^{t}BuOK (1.8 mmol, 9 equiv) in 2 mL of DMF under the irradiation of 36W LEDs (λ_{max} = 365、390、407 or 440nm), reacted for 90 minutes at about 60°C. Fluoride recovery yield was determined by ^{19}F NMR analysis using hexafluoroisopropanol (33.6 mg, 0.2 mmol, 1.2 mmol F) as an internal standard.

3. Defluorination of SF_6

In a 50 mL round-bottom Schlenk flask, place a 1 cm long glass-coated magnetic stir bar and add potassium tert-butoxide (1.8 mmol, 202 mg, 9 equiv). After purging the reaction flask with argon three times, evacuate the flask under vacuum for 15 minutes. Then, use a syringe to draw dry DMF (2 mL). With the same syringe, draw sulfur hexafluoride (0.2 mmol repeat unit, 29.2 mg, 1 equiv) from a balloon filled with sulfur hexafluoride gas (the sulfur hexafluoride gas can be weighed on a balance using the syringe). Subsequently, inject the sulfur hexafluoride and DMF together into the reaction flask, which is under negative pressure at this point. The reaction mixture was stirred vigorously under irradiation of 36 W LEDs (λmax = 407 nm). (**Figure S2**). The reaction temperature was monitored by a thermometer demonstrated. It is shown that the reaction temperature kept around 60 °C.

The reaction suspension was first slightly yellow, then turned to yellowish-brown after half an hour, turns brown after 60 minutes, When the reaction stops at 90 minutes, it can be observed that the brown color has deepened (**Figure S3**) . After that, the solvent was removed by vacuum at 110 °C. 20 mL of deionized water was added to the reaction system, and HFIP (33.6 mg, 0.2 mmol, 1.2 mmol F) was added as the internal standard for determing the fluoride recovery yield.

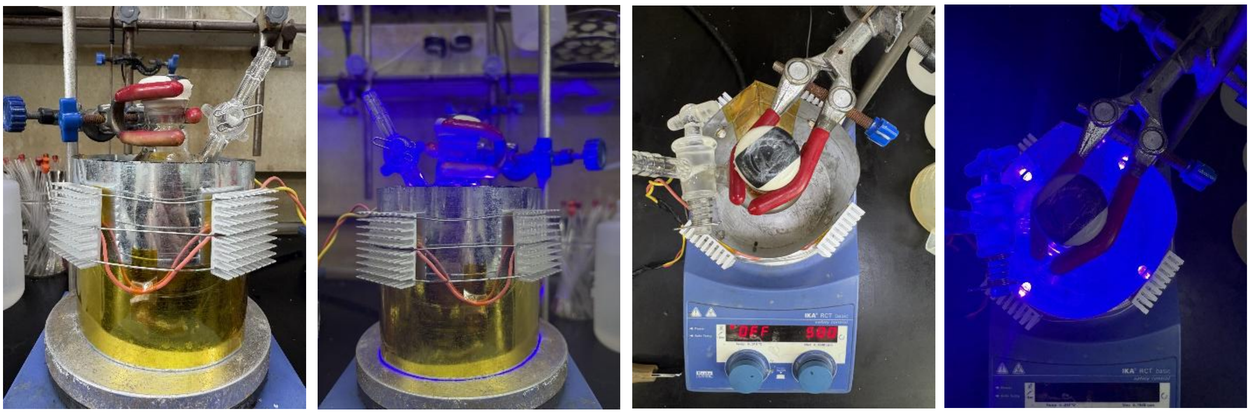
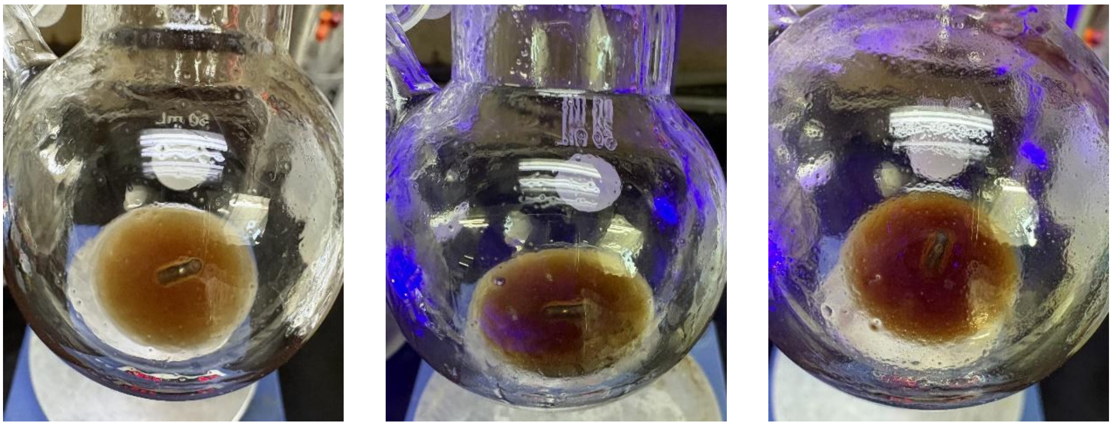


Figure S2. Representative reaction setup.



30min **60min** **90min**

Figure S3. The reaction color changed over time. The reaction suspension was first slightly yellow, then turned to yellowish-brown after half an hour, turns brown after 60 minutes, When the reaction stops at 90 minutes, it can be observed that the brown color has deepened.

4. Identification and Characterization of Defluorinated Products

Characterization of fluoride anion by ^{19}F NMR.

Fluorine decoupled carbon nuclear magnetic resonance (^{19}F NMR) spectra were recorded on a JEOL 600 MHz system.

Quantitation of fluoride anion by ^{19}F NMR analysis.

The results of nuclear magnetic resonance fluorine spectrum detection of fluoride anions match with the results of ion chromatography. Fluoride anion yield is calculated as mols fluorine in the products per mol fluorine in SF_6 reactant by ^{19}F NMR analysis (**Figure S4**) of the aqueous solution using HFIP as an internal standard and the equations as follows:

$$\textbf{Fluoride (mol\%)} = \frac{a \times 6}{b \times c} \times 100$$

Where

a is the integral of fluoride anion when the integral of HFIP is set to 0.2

b is the number of moles of HFIP standard

c is the number of moles of the fluorine atom in one mole of HFIP

6 is the number of moles of the fluorine atom in one mole of SF_6

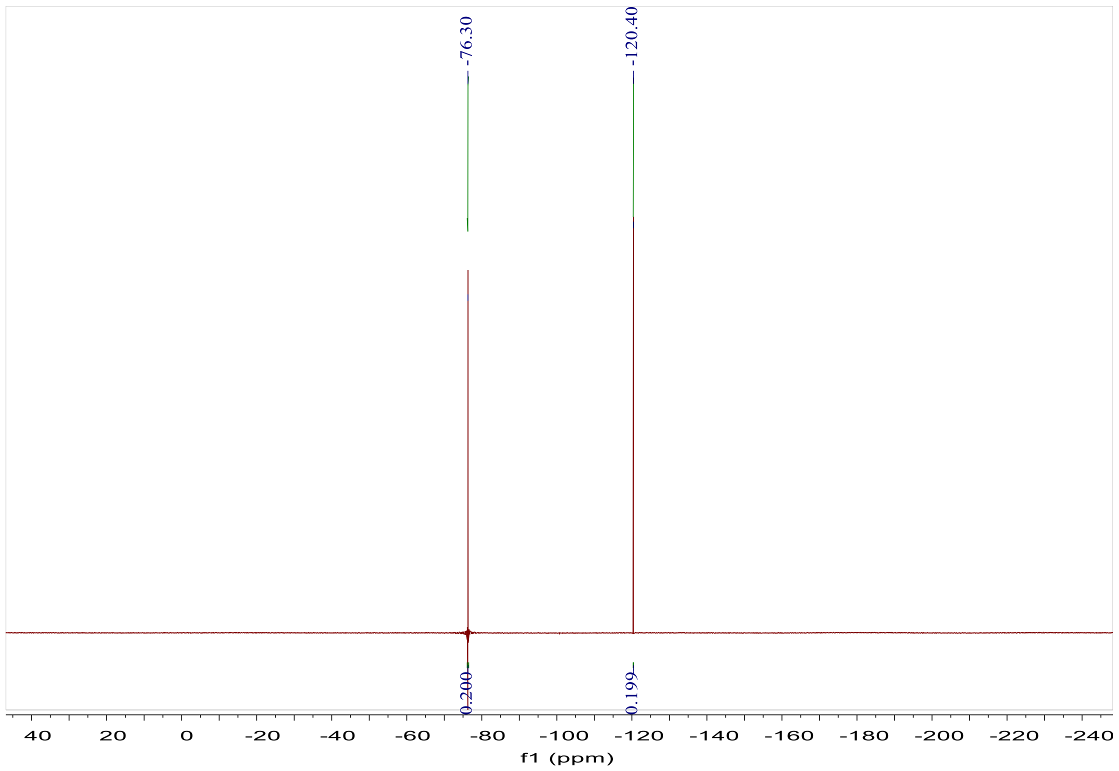


Figure S4. Quantitation of fluoride anion (-120.40 ppm) by ^{19}F NMR (565 MHz) analysis using HFIP (33.6 mg, 0.2 mmol, 1.2 mmol F, -76.3 ppm) as an internal standard in D_2O.

Fluoride anion recovery yield is calculated as 99%, as 0.2 mmol SF6 was subjected to the reaction, 0.2 mmol of HFIP (b) was used as the internal standard, and the integral of fluoride anion is 0.199 (a) (**Figure S4**).

Characterization of defluorinated product by XPS.

X-ray photoelectron spectroscopy (XPS) measurements were performed on a Kratos Axis supra$^+$ X-ray photoelectron spectrometer.

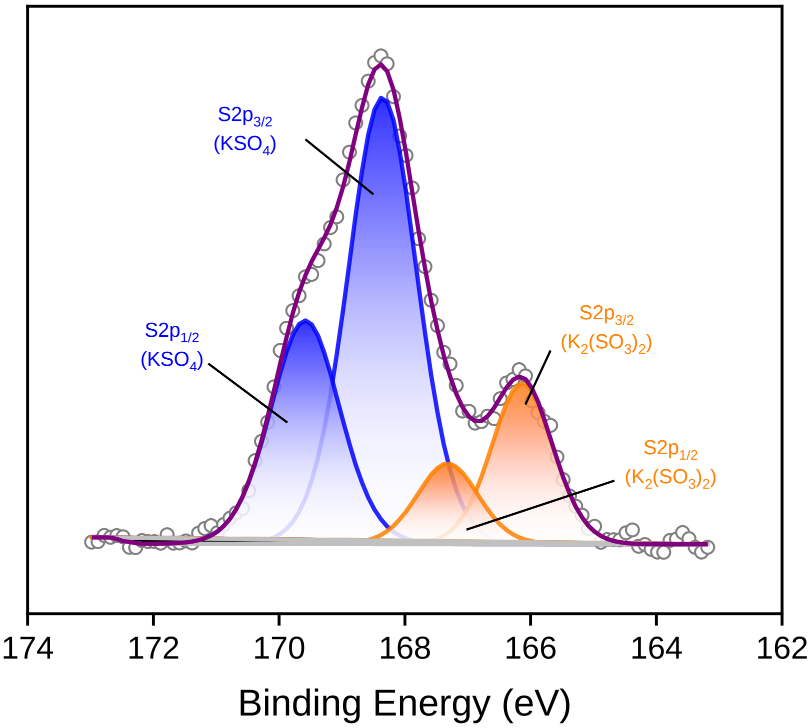


Figure S5. S(2p) XPS spectra of the product after a reaction time of 30 minutes.

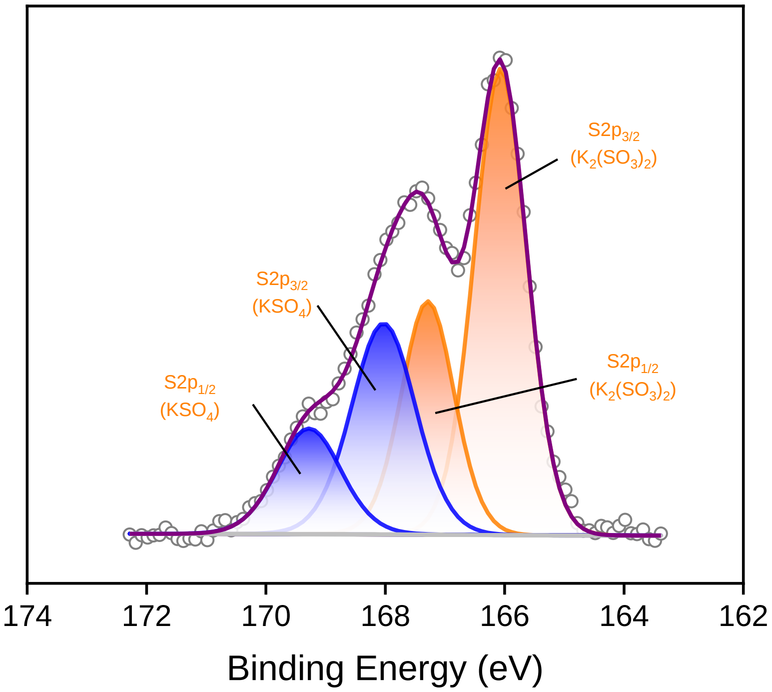


Figure S6. S(2p) XPS spectra of the product after a reaction time of 60 minutes.

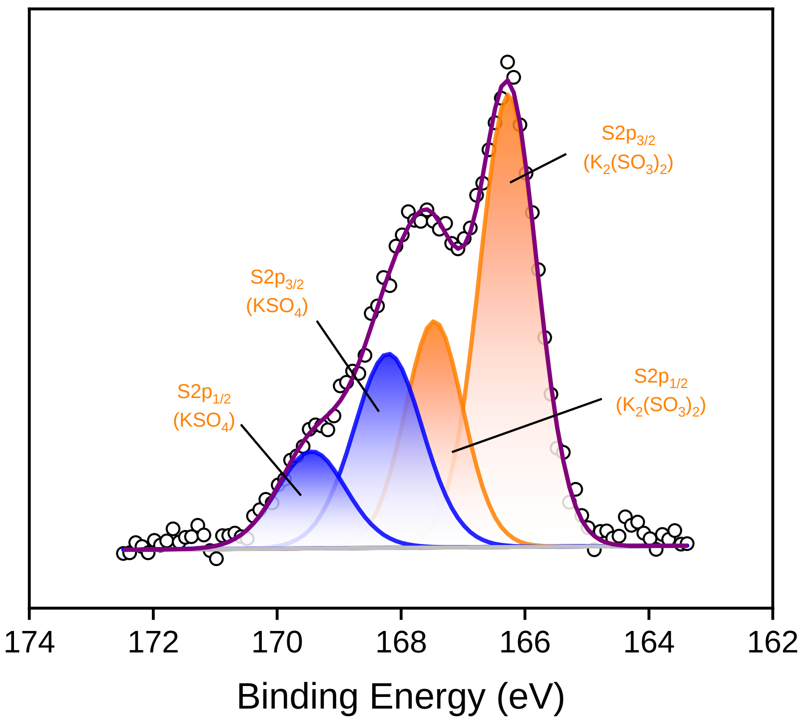


Figure S7. S(2p) XPS spectra of the product after a reaction time of 90 minutes.

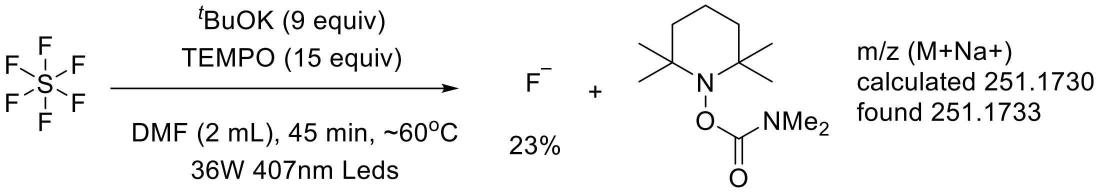
Characterization of the de-fluorination product by ion chromatography

After the reaction was complete, the organic solvent was removed from the system. Then, 10 mL of deionized water was added, and 100 μL of the resulting solution was taken and diluted into 50 mL of deionized water. Ion chromatography analysis yielded the following results: it can be observed that SF6 was almost completely converted into fluoride ions and sulfate ions.

Table S8. The detection results of the de-fluorination products by ion chromatography

Ion	F^-, mg/L	SO_4^{2-}, mg/L	SO_3^{2-}, mg/L	$S_2O_3^{2-}$, mg/L	S^{2-}, mg/L
Content	4.5223	3.7988	0.0116	0.0116	0.0035
Yield	99.2%	98.9%	0.4%	0.5%	0.3%

5. Radical trapping experiment



In a 50 mL round-bottom Schlenk flask, place a 1 cm long glass-coated magnetic stir bar and add potassium tert-butoxide (1.8 mmol, 202 mg, 9 equiv), TEMPO (3.0 mmol, 469 mg, 15equiv). After purging the reaction flask with argon three times, evacuate the flask under vacuum for 15 minutes. Then, use a syringe to draw dry DMF (2 mL). With the same syringe, draw sulfur hexafluoride (0.2 mmol, 29.2 mg, 1 equiv) from a balloon filled with sulfur hexafluoride gas (the sulfur hexafluoride gas can be weighed on a balance using the syringe). Subsequently, inject the sulfur hexafluoride and DMF together into the reaction flask, which is under negative pressure at this point. The reaction mixture was stirred vigorously under irradiation of 36 W LEDs (λmax = 407 nm) for 45min. After that, the solvent was removed by vacuum at 110 °C. 20 mL of deionized water was added to the reaction system, and HFIP (33.6 mg, 0.2 mmol, 1.2 mmol F) was added as the internal standard for determing the fluoride recovery yield. 23% of fluoride recovery yield was calculated.

HRMS (ES-TOF) m/z(TEMPO-CONMe₂): $[M+Na]^+$ calcd for $C_{12}H_{24}N_2O_2Na^+$ 251.1730, found 251.1733. (**Figure S8**)

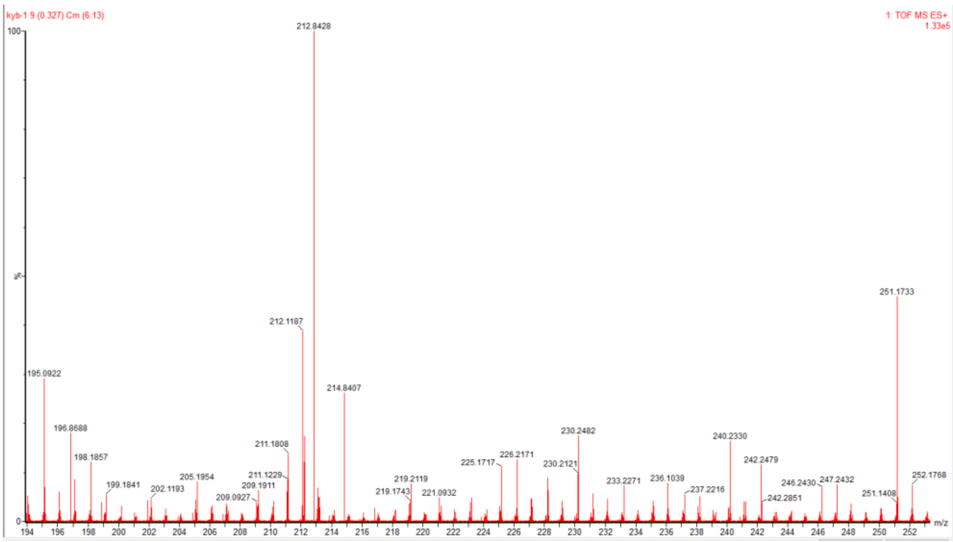


Figure S8. HRMS (ES-TOF) m/z of TEMPO-CONMe₂.

6. Kinetic studies

The dependence of the initial on ^{t}BuOK

In a 50 mL round-bottom Schlenk flask, place a 1 cm long glass-coated magnetic stir bar and add potassium tert-butoxide (0.6-1.8 mmol, 67.2mg-202 mg, 3-9 equiv). After purging the reaction flask with argon three times, evacuate the flask under vacuum for 15 minutes. Then, use a syringe to draw dry DMF (2 mL). With the same syringe, draw sulfur hexafluoride (0.2 mmol repeat unit, 29.2 mg, 1 equiv) from a balloon filled with sulfur hexafluoride gas (the sulfur hexafluoride gas can be weighed on a balance using the syringe). Subsequently, inject the sulfur hexafluoride and DMF together into the reaction flask, which is under negative pressure at this point. The reaction mixture was stirred vigorously under irradiation of 36 W LEDs (λmax = 407 nm). The reactions ended after each had been carried out for 3 min, 6 min, 9 min, 12 min, 16 min, 20 min, 25 min, 35 min, 45 min. After that, the solvent was removed by vacuum at 110 ºC. 20 mL of deionized water was added to the reaction system, and HFIP (33.6 mg, 0.2 mmol, 1.2 mmol F) was added as the internal standard for determining the fluoride recovery yield. The results are shown in **Fig. S9** and **Table S7**.

Table S9. Dependence of ^{t}BuOK: KF vs. time.

Time （min)	KF yield			
	3 equiv	5 equiv	7 equiv	9 equiv
0	0	0	0	0
3	6%	7%	8%	9%
6	10%	12%	15%	18%
9	14%	17%	19%	23%
12	17%	20%	25%	30%
16	19%	24%	30%	36%
20	26%	31%	35%	41%
25	30%	37%	41%	46%
35	34%	46%	54%	62%
45	39%	52%	62%	77%

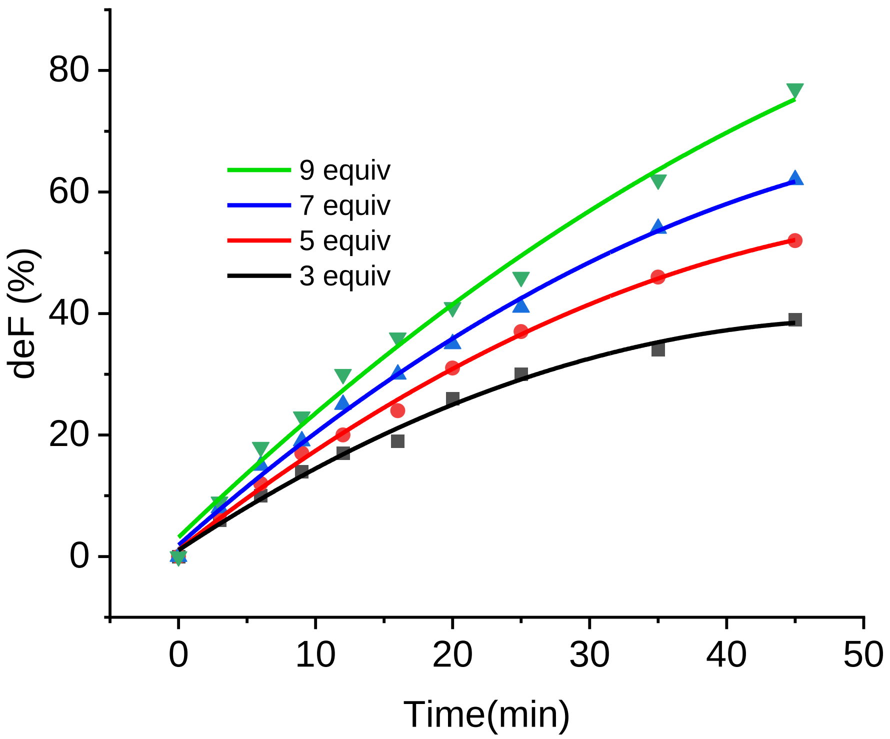


Figure S9. Dependence of the intial rate on tBuOK (equiv) : plots of KF vs. time.

7. Defluorination of SF_6 in 2 mmol Scale Reaction

In a 250 mL round-bottom Schlenk flask, place a 2 cm long glass-coated magnetic stir bar and add potassium tert-butoxide (18 mmol, 2.02 g, 9 equiv). After purging the reaction flask with argon three times, evacuate the flask under vacuum for 15 minutes. Then, use a syringe to draw dry DMF (20 mL). With the same syringe, draw sulfur hexafluoride (2 mmol, 292 mg, 1 equiv) from a balloon filled with sulfur hexafluoride gas (the sulfur hexafluoride gas can be weighed on a balance using the syringe). Subsequently, inject the sulfur hexafluoride and DMF together into the reaction flask, which is under negative pressure at this point. The reaction mixture was stirred vigorously under irradiation of 36 W LEDs (λmax = 407 nm) for 3h. After that, the solvent was removed by vacuum at 110 °C. 40 mL of deionized water was added to the reaction system, and HFIP (33.6 mg, 0.2 mmol, 1.2 mmol F) was added as the internal standard for determing the fluoride recovery yield. 98.5% of fluoride recovery yield was calculated.(**Figure S10**)

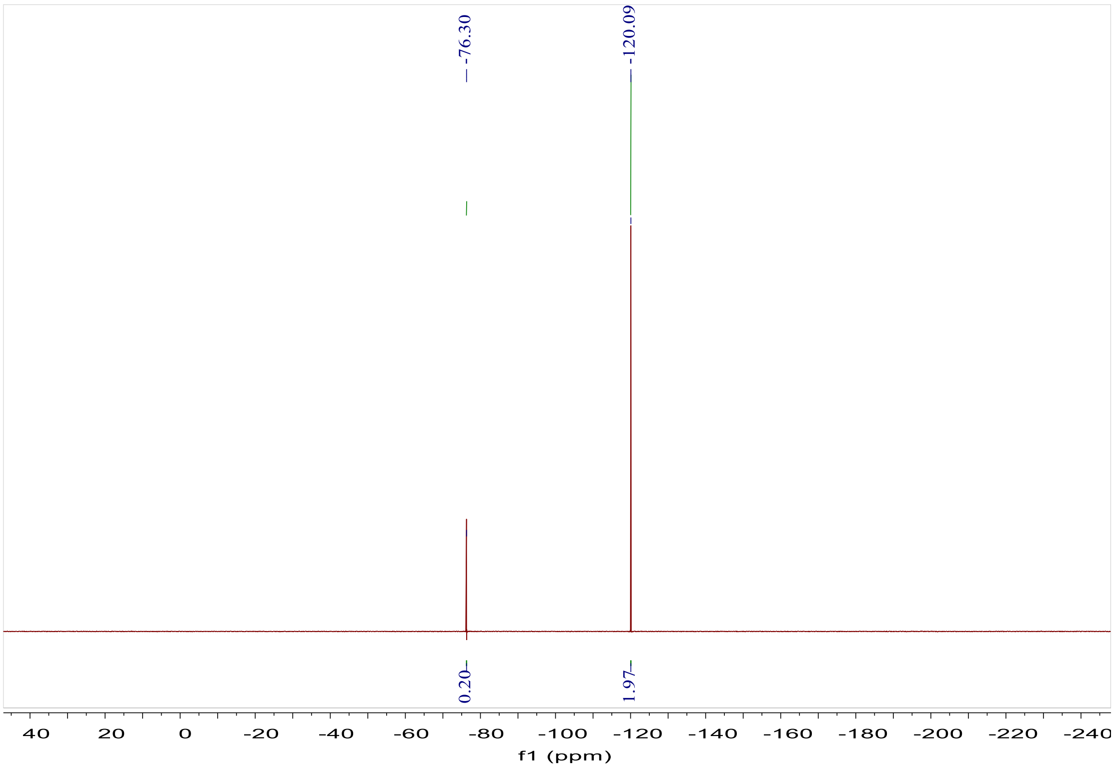


Figure S10. Quantitation of fluoride anion (-120.09 ppm) by ^{19}F NMR (565 MHz) analysis using HFIP (33.6 mg, 0.2 mmol, 1.2 mmol F, -76.3 ppm) as an internal standard in D_2O.

8. Separation and recovery of KF

At the end of the 2.4 mmol sulfur hexafluoride reaction, the solvent was removed by vacuum at 110 °C. 40 mL of deionized water was added to the reaction system. At this point, the aqueous solution should contain hydroxide ions, sulfate ions, sulfite ions, fluoride ions, etc. To the solution, 4 mmol of barium fluoride solid was added, and the reaction is stirred overnight at room temperature. The resulting barium sulfate and barium sulfite precipitates are filtered and washed with 20 ml of deionized water. The filtered and washed aqueous solution was then evaporated to dryness using a rotary evaporator at 70°C, followed by drying in an oven at 120°C. A solid weighted 1040 mg is obtained. The solid was dissolved in 20 ml of deionized water, and HFIP (0.4 mmol, 67.2mg) is added as an internal standard to determine the purity of KF in the treated solid inorganic salt. Through ^{19}F NMR calculation, the solid inorganic salt contains 16.6 mmol of KF (963 mg),(**Figure S11**) resulting in a purity of 92.6% for KF.

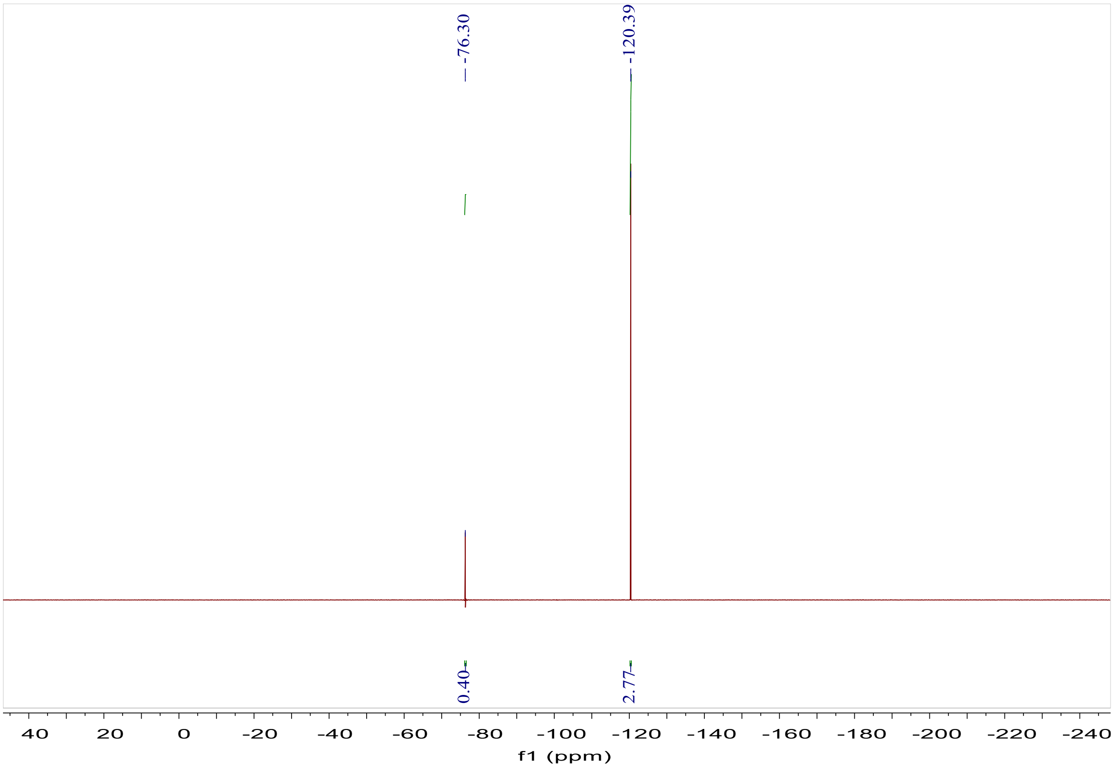


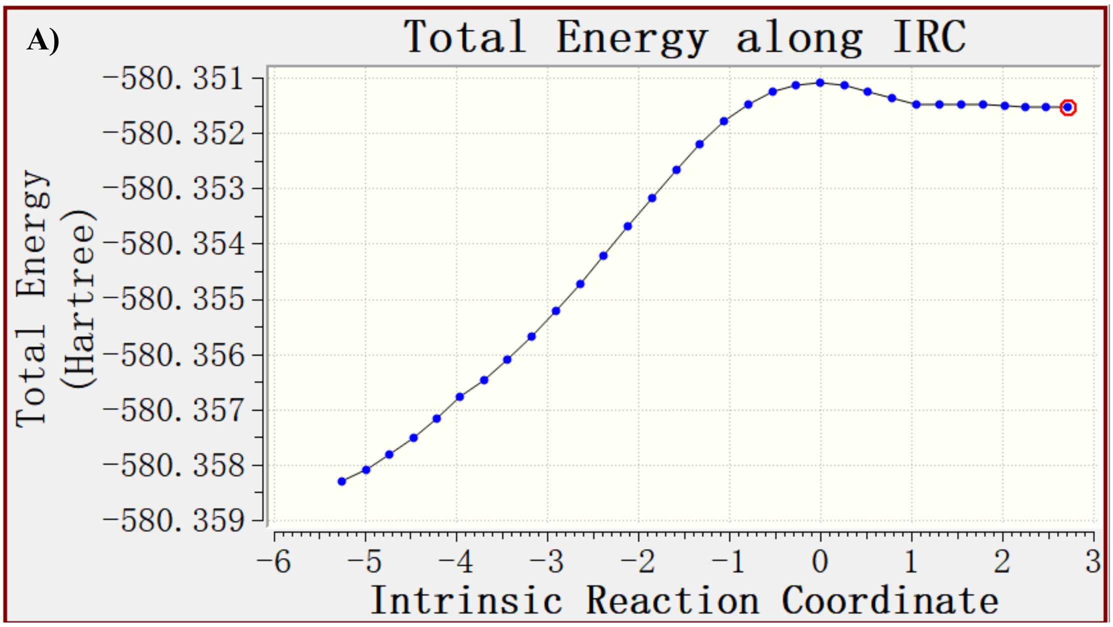
Figure S11. Quantitation of fluoride anion (-120.39 ppm) by ^{19}F NMR (565 MHz) analysis using HFIP (67.2 mg, 0.4 mmol, 2.4 mmol F, -76.3 ppm) as an internal standard in D_2O.

9. DFT calculation

Computation details

DFT calculations were performed with the Gaussian 16 [2] programs. Geometry optimization and frequency calculations were performed using ωB97XD [3] functional together with the def2-SVP [4-5] basis set. The polarizable continuum model (PCM) [6] implicit solvation model was used to account for the solvation effects. The frequency calculations confirmed that the optimized structures corresponded to either energy minima (no imaginary frequency) or transition structures (one imaginary frequency). Intrinsic reaction coordinates (IRC) calculations at the same level verified the connectivity of located intermediates and transition states. To enhance the accuracy of electronic energies, single-point energy was calculated at ωB97XD/def2-TZVPP [4-5]-PCM level of theory using the optimized structures. The determination of standard enthalpies and Gibbs free energies (at a concentration of 1 mol·L^{-1} and a temperature of 298.15 K) involved the use of Grimme's quasi-harmonic approximation and Head-Gordon's method [7-8], implemented in GoodVibes version 3.2. Three-dimensional molecular structures were visualized using CYLview20.

A)



B)

C)

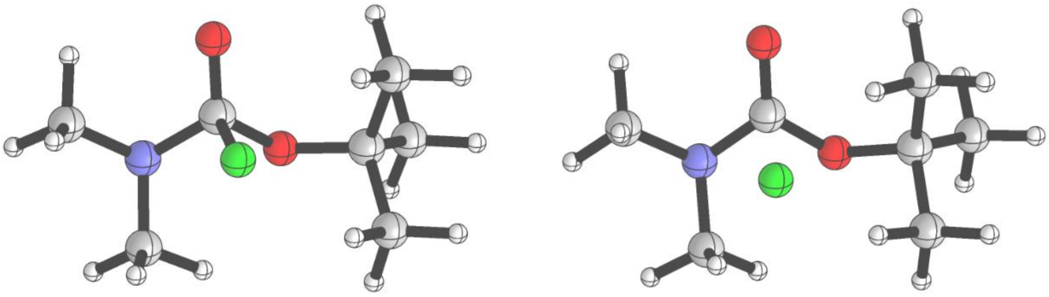


Figure S12. IRC of **TS3**. A) Total energy along IRC. B) Initial form of **TS3**. C) Final form of **TS3**. The IRC calculation showed the barrierless between **Int4** and **Int5**.

10. Thermochemical data

Table S10. Energies of the Optimized Structures[a].

Name	E/(a.u.)	ZPE/(a.u.)	H/(a.u.)[b]	-TS/(a.u.)[bc]	G/(a.u.)[b]
SF6	-997.306898	0.021678	-997.278778	0.036142	-997.314921
SF6$^{\cdot -}$	-997.428664	0.012392	-997.406299	0.044342	-997.450641
SF5^{-}	-897.625332	0.012796	-897.605427	0.037105	-897.642532
SF5$^{\cdot}$	-897.40389	0.015331	-897.382139	0.036478	-897.418617
Int1	-247.986851	0.088251	-247.891795	0.035452	-247.927247
Int1*	-247.865755	0.087095	-247.77172	0.035826	-247.807546
Int2	-247.879662	0.09072	-247.781968	0.036608	-247.818576
Int3	-347.815115	0.095747	-347.711524	0.038556	-347.75008
Int4	-581.016023	0.220842	-580.781106	0.051348	-580.832454
Int5	-481.056556	0.219993	-480.822956	0.050958	-480.873914
TS1	-1245.309579	0.105588	-1245.187839	0.057627	-1245.245466
TS2	-580.994494	0.219472	-580.761196	0.051086	-580.812282
TS3	-581.017991	0.220788	-580.783614	0.050456	-580.83407
tBuO^{-}	-233.179865	0.120637	-233.0519	0.036044	-233.087944
F^{-}	-99.983174	0	-99.980814	0.016519	-99.997333

[a] Single-point energies were obtained at the PCM(DMF), ωB97XD/def2-TZVPP level of theory based on the structure optimized at the ωB97XD/def2-SVP level.

[b] The sum of the thermal correction to the entropy and enthalpy was obtained from Grimme's quasi-harmonic approximation and Head-Gordon's method, respectively.

[c] T = 298.15 K

Cartesian coordinates and energies for all optimized compounds and transition states:

SF_6

0 1

F	-1.04322379	0.05575764	-1.18656361
S	0.00000255	-0.00000329	-0.00001249
F	-1.10449676	-0.62700184	0.94144385
F	-0.43744888	1.45017862	0.45267534
F	1.04321182	-0.05575085	1.18655318
F	1.10451430	0.62702800	-0.94143187
F	0.43743878	-1.45020572	-0.45265468

$SF_6^{\cdot-}$

-1 2

S	0.03288501	0.00005915	0.00013306
F	-0.00957187	1.62962004	-0.54206177
F	0.05188882	-0.54059168	-1.62917483
F	1.77812161	0.03703222	0.02315731
F	0.04538997	-1.63073169	0.54049200
F	-1.66156077	-0.03621272	-0.02353407
F	-0.01627061	0.54098605	1.63137673

SF_5^-

-1 1

F	0.09412010	1.71961367	-0.17255971
S	-0.00014103	-0.00005466	-0.33942697
F	-1.71937958	0.09381106	-0.17266685
F	0.00001372	0.00037042	1.29357065
F	-0.09410292	-1.71929016	-0.17223336
F	1.71959939	-0.09440782	-0.17268500

$SF_5^{\cdot}$

0 2

F	-1.16094327	-1.13505265	-0.24759882
S	0.00019122	-0.00005551	-0.20920535
F	1.13536938	-1.16112188	-0.24719022
F	-0.00061237	0.00007609	1.36159255
F	1.16098345	1.13542347	-0.24722177
F	-1.13513714	1.16077366	-0.24766112

Int1

-1 1

C	0.86182411	-0.83992547	-0.00017913

O	1.92093822	-0.17122863	-0.00027861
N	-0.32590700	-0.05240408	-0.00002001
C	-1.60165995	-0.69739134	0.00019768
C	-0.31690124	1.38493388	0.00014629
H	-1.42515148	-1.78519046	0.00022587
H	-2.21441916	-0.44163028	0.88970516
H	-2.21471263	-0.44173777	-0.88914078
H	0.74167355	1.68761695	0.00036869
H	-0.81638665	1.81608362	-0.89059012
H	-0.81673784	1.81581315	0.89081115

Int1*

-1 1

C	0.99388823	-0.00048642	0.39460830
O	2.15164151	-0.00013623	-0.15323924
N	-0.29590765	-0.00012341	-0.19593897
C	-1.10075837	-1.20010086	-0.00398691
C	-1.09997313	1.20064881	-0.00388136
H	-0.50774612	-2.08693615	-0.26778234
H	-1.43994376	-1.32416329	1.04812849
H	-2.00447886	-1.17967993	-0.64191418
H	-0.50640174	2.08680477	-0.26866446
H	-2.00411292	1.18040598	-0.64116310
H	-1.43803555	1.32515320	1.04844217

Int2

0 2

C	0.86547430	-0.65307240	-0.00004413
O	1.98077972	-0.20534767	-0.00003980
N	-0.31644141	-0.04567463	-0.00001685
C	-1.54814908	-0.81140632	0.00001206
C	-0.42748793	1.40754754	0.00005830
H	-1.31037862	-1.88206724	-0.00017607
H	-2.14771150	-0.57790176	0.89375432
H	-2.14789957	-0.57763218	-0.89353176
H	0.57797474	1.84398282	0.00005976
H	-0.97109672	1.74889888	-0.89435796
H	-0.97105997	1.74881034	0.89453076

Int3

0 1

C	-0.78025091	-0.14790549	-0.00005378
N	0.55388720	-0.00326031	-0.00003068
O	-1.42323160	-1.16151652	-0.00007267

C	1.24471219	1.27387985	0.00007805
C	1.39105247	-1.18830009	-0.00010142
F	-1.41655040	1.03988887	0.00014509
H	0.53019979	2.10081212	-0.00004416
H	1.88319926	1.35502520	0.89328496
H	1.88347517	1.35500365	-0.89293140
H	0.75984863	-2.08242141	-0.00000673
H	2.03379435	-1.19928137	-0.89402108
H	2.03399633	-1.19922934	0.89367161

Int4

-1 1

C	0.69993334	-0.50266225	-0.10518238
N	1.85609942	0.27895811	-0.48497450
O	0.74744666	-1.73211856	-0.28484186
C	1.88747445	1.66016128	-0.06991744
C	3.11354394	-0.39280786	-0.27807929
F	0.57998109	-0.21140924	1.47185051
O	-0.40663033	0.21972469	-0.61681373
C	-1.73091656	0.10053858	-0.10741984
C	-2.04734288	-1.26590795	0.50890403
C	-2.63103411	0.33140010	-1.32423297
C	-1.96122992	1.20882973	0.92788975
H	2.64270115	2.21334355	-0.65422380
H	0.90800345	2.12024707	-0.24659329
H	2.13375763	1.78069755	1.00520589
H	3.91357969	0.11987844	-0.83776262
H	3.03529108	-1.42735674	-0.63221958
H	3.41978569	-0.42044019	0.79143018
H	-3.10474001	-1.28734943	0.81726519
H	-1.40836392	-1.44172332	1.38167683
H	-1.86716297	-2.07274955	-0.21299166
H	-3.69312393	0.34199793	-1.03450057
H	-2.39077160	1.29504017	-1.79905831
H	-2.47963163	-0.46533799	-2.06843854
H	-1.78168349	2.19555660	0.47237195
H	-2.99373341	1.18889156	1.31146458
H	-1.25553379	1.07112183	1.75601423

Int5

0 1

O	0.27511610	0.47589481	-0.01117569
C	-0.72276994	-0.41667551	0.00833329
N	-1.94017440	0.19427339	0.03446890

O	-0.57015154	-1.62650691	0.00599225
C	-3.14074187	-0.61061995	-0.01806112
C	-2.13059032	1.62929040	-0.00251327
C	1.67441210	0.08697746	-0.00212936
C	2.40239956	1.42801351	-0.01367810
C	2.00089233	-0.68530718	1.27469156
C	2.00808396	-0.71146754	-1.26094583
H	-3.79736403	-0.37984504	0.83650826
H	-3.70385017	-0.41391314	-0.94605353
H	-2.86971094	-1.67044723	0.01553320
H	-1.18912064	2.14584190	0.20157934
H	-2.50932044	1.95474012	-0.98680170
H	-2.86860274	1.92392272	0.76008621
H	3.48990041	1.26766397	-0.01246512
H	2.13526667	2.00439882	-0.91140514
H	2.13577859	2.02001753	0.87402983
H	3.08529097	-0.86005464	1.33088353
H	1.48524163	-1.65271810	1.29435722
H	1.70085623	-0.10255109	2.15856865
H	1.71697595	-0.14508284	-2.15832573
H	3.09215837	-0.89165805	-1.30535603
H	1.48788963	-1.67659903	-1.26513682

TS1

-1 1

C	2.50773268	0.90553540	-0.38260347
N	2.85522230	-0.34970721	-0.10896897
O	3.04488409	1.94230478	-0.09875373
C	2.04559709	-1.47269751	-0.53924847
C	4.06140187	-0.64479616	0.65035228
F	0.17671130	0.76458427	-0.27706690
S	-1.64556498	0.02891454	0.04060470
F	-1.03918770	-1.16973947	1.07927489
F	-1.48916905	-1.04600296	-1.27652600
F	-1.94474955	1.03021899	1.37808302
F	-3.11589057	-0.61267696	0.28583159
F	-2.40102455	1.16307606	-0.97741113
H	1.14340784	-1.09597801	-1.02868722
H	2.61674030	-2.12059338	-1.22368656
H	1.73551518	-2.07005660	0.33238947
H	4.56150118	0.29565801	0.90999447
H	3.80851293	-1.18747984	1.57517849
H	4.74913471	-1.26806040	0.05727754

TS2

-1 1

C	1.18980591	-0.74386159	-0.30543727
N	2.09448891	0.23403391	0.02234129
O	0.89056483	-1.09605272	-1.42135762
C	2.20027999	0.63270778	1.41589517
C	2.17294147	1.31975388	-0.93220626
F	1.06049383	-1.63166274	0.71729827
O	-0.49526208	0.48802127	0.42824980
C	-1.77694540	0.20532555	0.07636197
C	-2.05188552	0.56722769	-1.40758472
C	-2.75877664	1.02292333	0.95446290
C	-2.11411966	-1.29771731	0.26405166
H	2.45312677	-0.23107041	2.04350055
H	3.00774780	1.37192583	1.51236258
H	1.24290807	1.05755294	1.75522570
H	1.28604801	1.97097774	-0.84383890
H	2.20897799	0.91454646	-1.95058626
H	3.08511509	1.90651230	-0.75234737
H	-3.08854655	0.35828826	-1.72851267
H	-1.35952606	-0.00100827	-2.04660591
H	-1.85285962	1.64132421	-1.56497053
H	-3.82135160	0.84807129	0.70720112
H	-2.60298173	0.76876698	2.01638728
H	-2.54767642	2.09904027	0.83615849
H	-1.92225259	-1.58863400	1.30984996
H	-3.16545132	-1.53855706	0.02461035
H	-1.45936764	-1.90491362	-0.37890600

TS3

-1 1

C	1.18980600	0.74386200	0.30543700
N	2.09448900	-0.23403400	-0.02234100
O	0.89056500	1.09605300	1.42135800
C	2.20028000	-0.63270800	-1.41589500
C	2.17294100	-1.31975400	0.93220600
F	1.06049400	1.63166300	-0.71729800
O	-0.49526200	-0.48802100	-0.42825000
C	-1.77694500	-0.20532600	-0.07636200
C	-2.05188600	-0.56722800	1.40758500
C	-2.75877700	-1.02292300	-0.95446300
C	-2.11412000	1.29771700	-0.26405200
H	2.45312700	0.23107000	-2.04350100
H	3.00774800	-1.37192600	-1.51236300

H	1.24290800	-1.05755300	-1.75522600
H	1.28604800	-1.97097800	0.84383900
H	2.20897800	-0.91454600	1.95058600
H	3.08511500	-1.90651200	0.75234700
H	-3.08854700	-0.35828800	1.72851300
H	-1.35952600	0.00100800	2.04660600
H	-1.85286000	-1.64132400	1.56497100
H	-3.82135200	-0.84807100	-0.70720100
H	-2.60298200	-0.76876700	-2.01638700
H	-2.54767600	-2.09904000	-0.83615800
H	-1.92225300	1.58863400	-1.30985000
H	-3.16545100	1.53855700	-0.02461000
H	-1.45936800	1.90491400	0.37890600

tBuO$^-$

-1 1

O	0.00347710	-0.00005959	1.48828968
C	-0.00015967	-0.00054009	0.15339571
C	0.26441878	1.42330878	-0.43540232
C	1.09968260	-0.94123847	-0.43702239
C	-1.36702614	-0.48181897	-0.43249903
H	0.26575388	1.47381153	-1.54025023
H	-0.50585551	2.11755649	-0.05654985
H	1.24033487	1.78742645	-0.06987715
H	1.13714518	-0.97346623	-1.54197304
H	0.93199841	-1.96700624	-0.06535019
H	2.08663227	-0.61590906	-0.06494696
H	-2.17020551	0.17878332	-0.06290489
H	-1.41463091	-0.50131480	-1.53739649
H	-1.58048292	-1.49767227	-0.05790044

F$^-$

-1 1

F	0.00000000	0.00000000	0.00000000

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