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Supporting Information

Preparation and Functionalization of Mono- and Polyfluoroepoxides via Fluoroalkylation of Carbonyl Electrophiles

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Supporting Information

This PDF file includes:

Experimental Details and Spectroscopic Characterization

Figures. S1 to S250

Table S1 to S22

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Table of Contents:

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General considerations

Hexamethylborazine and KCH_2Ph,[1] and **1-CF_2H**[2] were prepared according to the literature.

1-CF_2Ph was prepared according to a modified procedure in the literature.[3]

Tetrahydrofuran (THF) and dichloromethane (DCM) were purified using a Glass Contour solvent purification system through percolation through a Cu catalyst, molecular sieves, and alumina and finally stored over sodium metal and activated molecular sieves for a minimum of 48 hours. Toluene was freshly distilled over sodium metal, freeze-pump-thawed, and stored over sodium metal and activated molecular sieves for a minimum of 48 hours prior to use. 1,2-Dichloroethane (DCE) was dried with CaH_2 over 12 h and distilled and freeze-pump-thawed, and stored over activated molecular sieves for a minimum of 48 hours prior to use.

All other solid reagents were obtained from commercial sources and subjected to dynamic vacuum for 4-24 h prior to use. All other liquid ketones were dried with anhydrous $CaCl_2$ or $MgSO_4$ for 24 h and then distilled and subjected to three freeze-pump-thaw cycles prior to further use. All liquid aroyl chlorides were distilled and subjected to three freeze-pump-thaw cycles prior to further use. 4-iodobenzoyl chloride was sublimed under dynamic vacuum prior to further use. Unless otherwise noted, all manipulations were performed under an inert nitrogen atmosphere.

Flash column chromatography was conducted on a chromatography column with silica as the stationary phase or using or a Biotage Isolera One flash chromatography system. All eluents used in this paper for manual column chromatography was 10:1 hexanes:EtOAc (v/v) containing 5 vol% Et_3N.

NMR spectra were recorded on a Varian NMR Systems 700 MHz, Varian NMR Systems 600 MHz, Varian NMR Systems 500 MHz, Bruker Avance Neo 500 MHz, or Agilent MR-400 spectrometer. ^1H, ^{13}C, ^{19}F, and ^{11}B shifts are reported in parts per million (ppm) relative to TMS, with the residual solvent peak used as an internal reference. ^{19}F NMR spectra are referenced to 1,2-difluorobenzene or, in spectra lacking internal standard, on a unified scale, where the single primary reference is the frequency of the residual solvent peak in the ^1H NMR spectrum. Peaks not listed in the peak assignment correspond to residual solvent. Multiplicities are reported as follows: singlet (*s*), doublet (*d*), triplet (*t*), quartet (*q*), and multiplet (*m*). Compounded splitting patterns are denoted through combinations of the above letters, e.g. dd for a doublet of doublets. NMR spectra were processed using MestReNova version 10.0.2. For the purpose of labeling atoms for spectral assignments, hydrogen atoms and carbon atoms are labeled with Greek letters. In ^{19}F NMR spectra of *in situ* reactions, 1,2-difluorobenzene (internal standard) appears as a triplet peak at -140.18 (THF), -139.85 (toluene), or -142.66 (DCE) ppm, respectively. Impurities including water, solvent residule and grease also appear as trace contaminants in the ^1H-NMR spectra of isolated organic compounds and they were annotated according to the literature.[4]

In situ kinetic data using ^{19}F NMR spectroscopy were acquired on a Varian NMR Systems 500 MHz spectrometer and processed in VnmrJ. Data were fit using Origin 2018.

High resolution mass spectra (HR-MS) were obtained on an electrospray Agilent Q-TOF mass spectrometer. GC-MS data were collected on a Shimadzu QP-2010 GCMS.

IR spectra were collected on a Thermo-Nicolet IS-50 spectrometer equipped with an ATR accessory. Data were plotted using Origin 2018.

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Crystals were mounted on a Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer equipped with Micromax-007HF Cu-target microfocus rotating anode (λ = 1.54187 Å) operated at 1.2 kW power (40 kV, 30 mA). The X-ray intensities were measured at 293 K with the detector placed at a distance 42.00 mm from the crystal. Rigaku d*trek images were exported to CrysAlisPro[5] and CrystalClear Expert 2.0 r16[6] for processing and corrected for absorption. The structures were solved and refined with the Bruker SHELXTL (version 2022/5) software package.[7] Images of X-ray structures were generated using Mercury.

Comments on the stability of the fluoroepoxides: Several of the isolated α-fluoroepoxides (**2f** and **3a**) decomposed (the major decomposed product was found to be the 1,2-F migration products) when exposed to silica gel and water. General stability of the α-fluoroepoxides: the more electron deficient at the β-C corresponds to higher stability of the α-fluoroepoxides, consistent with previous literature reports.[8] For example, 18% **2f** (filtered from the crude solution without other purification) was found to slowly convert to **5c** after storing in a glass vial for 8 days under ambient air atmosphere. **2f** and **3a** completely converted to the corresponding 1,2-F migration products after storage in a vial outside of a glovebox after 3 months. The other α-fluoroepoxides reported in this work are stable in the air at room temperature indefinitely when stored in glass vials.

Experimental Procedures

1. Synthesis and characterization of **1-CF_2Ph**[3]

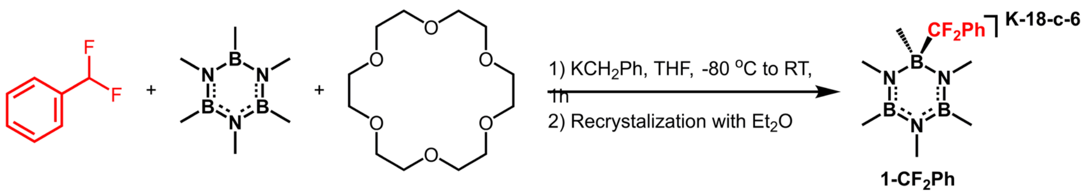


Figure S1. Scheme for the synthesis of **1-CF_2Ph**.

Compound **1-CF_2Ph** was prepared by a modified procedure (below) that afforded higher chemical yield, compared to the prior report.[3]

18-crown-6 (2.99 g, 11.3 mmol) and hexamethylborazine (1.87 g) were dissolved in 45 mL THF and cooled to –78 °C in a cold trap with stirring for 30 min. Solid benzyl potassium (1.48 g, 11.4 mmol) was gradually added to the solution. 5 mL THF was used to wash the vial used for weighing benzyl potassium and the solution was combined. After stirring for another 10 min, $PhCF_2H$ (1.45 g, 11.3 mmol) was added. The mixture was taken out of the cold trap and allowed to warm to room temperature with stirring (1 h). After the reaction, THF was removed by vacuum. Fresh THF (~3 mL) was added to the paste until all the solid was fully dissolved followed by 50-100 mL of Et_2O was added to precipitate the solid product. The mixture solid product was collected by filtration and washed with Et_2O until the eluent became colorless (~100 mL). The solid was dissolved in minimal amount of THF (~3 mL) and precipitated with Et_2O. This process was repeated for 2 additional cycles to obtain a white solid. The product was dried under vacuum for ~3 h. The obtained **1-CF_2Ph** was kept in a -30 °C freezer for further use. Isolated yield: 85%. The spectral characterization was consistent with literature.[3] ^{19}F NMR (377 MHz, THF) δ -106.18 ppm (*dd*, *J* = 38.9, 19.3 Hz, 2F).

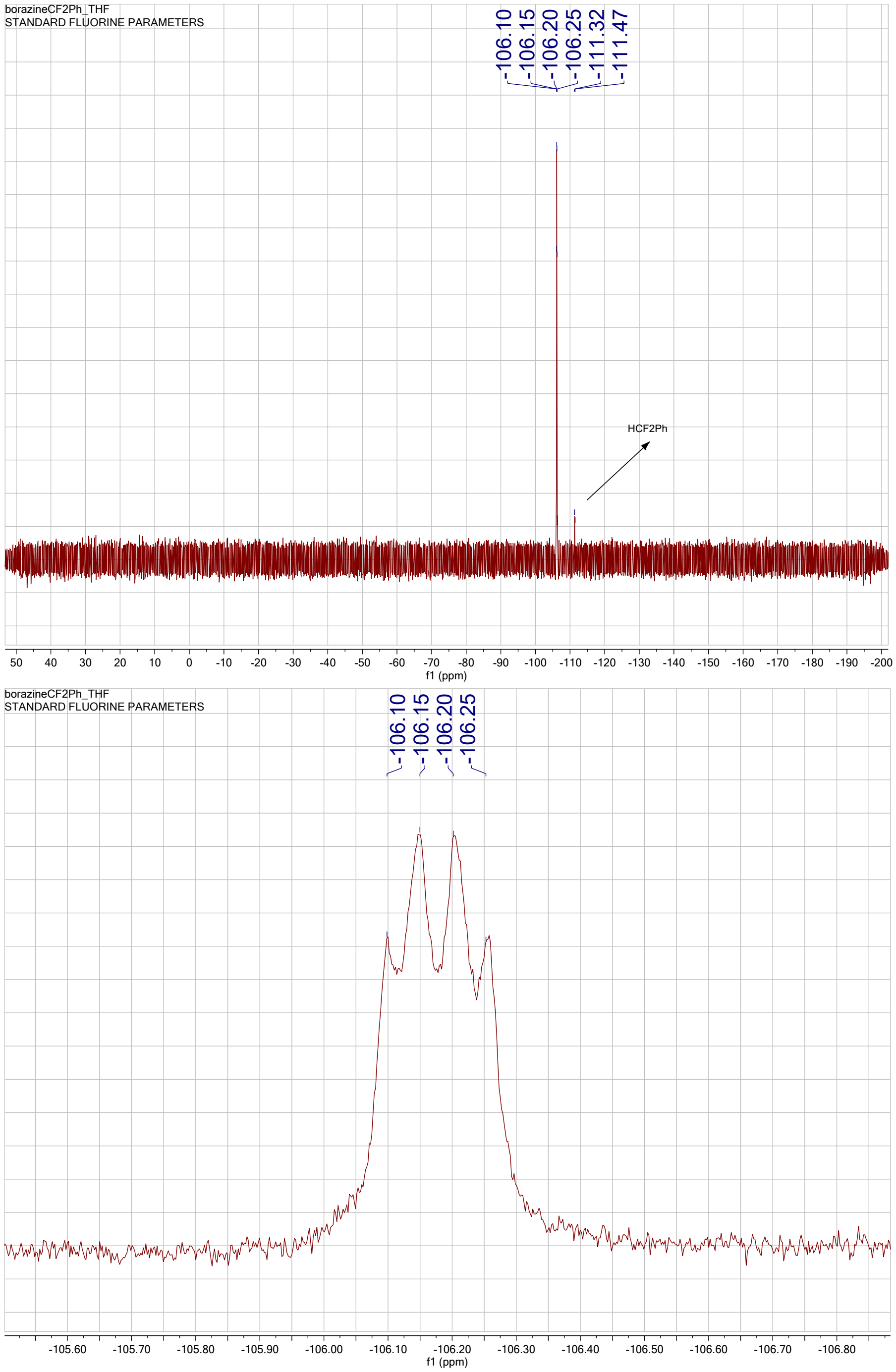


Figure S2. ^{19}F NMR (in THF) spectra of **1-CF$_2$Ph**. Top: full spectra and bottom: zoom-in spectra.

Computational details

Calculations were performed with the Gaussian 16 suite of programs[9] using the M062X functional,[10] the integral equation formalism variant polarizable continuum model (IEFPCM) for toluene,[11] and an ultrafine (150,974 point) integration grid for all atoms. All reported compounds underwent gas-phase geometry optimization with the M062X/6-311++g(d,p) basis set[12]–[14] followed by vibrational frequency calculations. These were used to verify that the structures were truly local energetic minima by the absence of imaginary vibrational modes. The coordinates of the reported 9 optimized geometries are shown at the end of the Supporting Information.

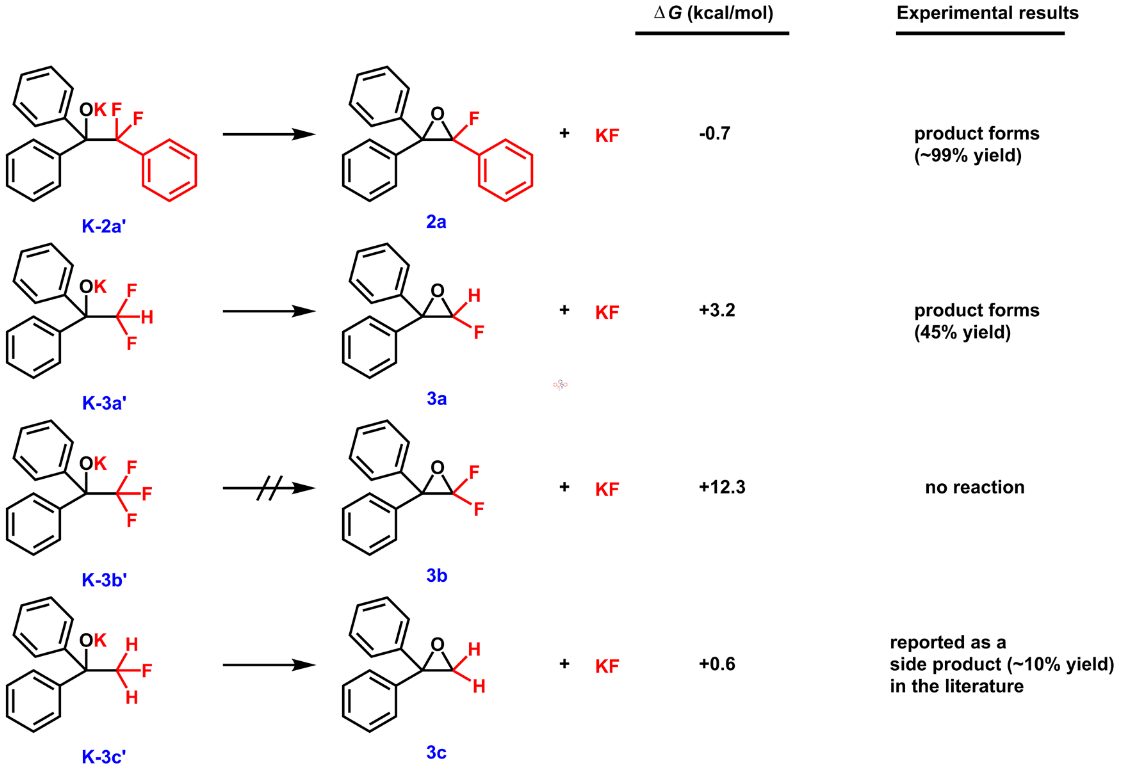


Figure S3. Scheme for the synthesis of fluorinated epoxides from potassium alkoxides. Synthesis of **2a, 3a** and **3b**: 0.08 M in toluene, 90 ºC for 30 min. Observed formation of **3c**: -40 ºC in THF, 10% reported.[15]

Compound	SP (toluene, hartree)	*G* correction (hartree)	Corrected *G* (hartree)
K-2a'	-1645.929115	0.246789	-1645.682326
2a	-946.073542	0.247374	-945.826168
K-3b'	-1514.173491	0.162700	-1514.010791
3b	-814.298794	0.164976	-814.133818
K-3a'	-1414.913350	0.171194	-1414.742156
3a	-715.0522222	0.17244	-714.879782
K-3c'	-1315.662210	0.180716	-1315.481494
3c	-615.8041524	0.180844	-615.623308
KF	-699.857305	-0.021108	-699.836197

Table S1. Calculated *G* (with solvent correction in toluene) of the compounds in **Figure S3**. SP: single point energy.

Mechanistic studies

1. Reaction of benzophenone and **1-CF$_2$Ph** in THF at room temperature.

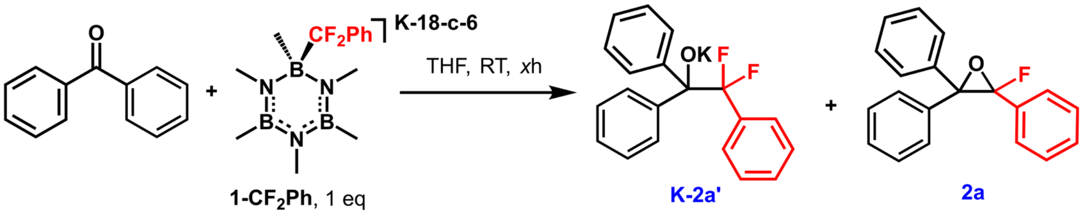


Figure S4. Reaction of benzophenone with **1-CF$_2$Ph** at RT in THF for *x* h (*x* = 1-168).

Protocol

Benzophenone (7.3 mg, 0.04 mmol), **1-CF$_2$Ph** (23.6 mg, 0.04 mmol), and 1,2-difluorobenzene (6.4 mg, 6 µL, 0.056 mmol) were measured in an 8 mL vial with 1 mL THF under N_2 atmosphere. After all reagents dissolved, the solution was transferred into a screwed NMR tube. The NMR tube was rotated at RT for 168 h. ^{19}F NMR spectra were collected after various time period.

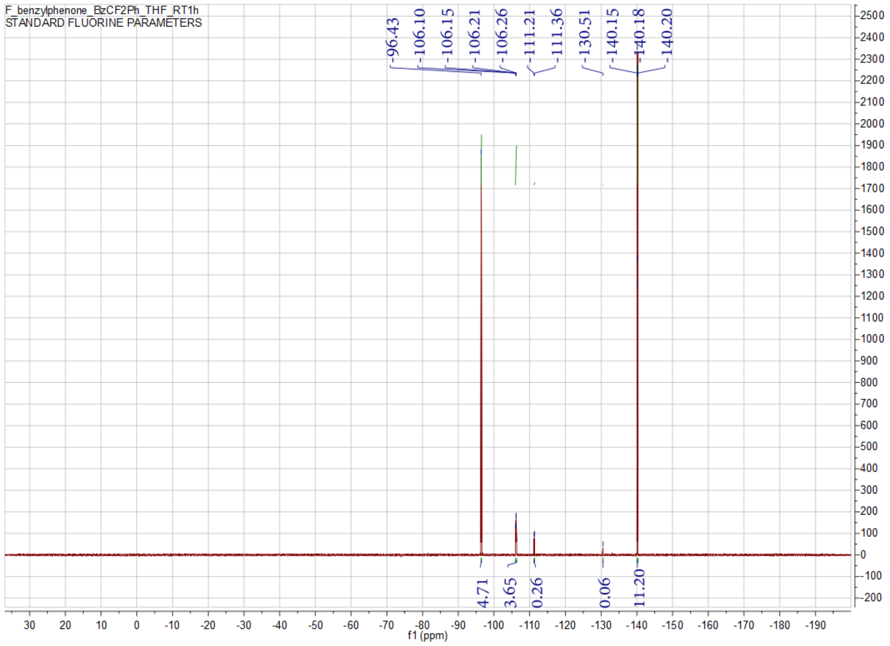


Figure S5. Reaction of benzophenone and **1-CF$_2$Ph** at RT in THF after 1 h. ^{19}F NMR (377 MHz, THF) δ -96.43 (s, 2F, **K-2a'**), -106.18 (dd, $J_{F\text{-}F}$ = 41.0 Hz, $J_{F\text{-}B}$ = 18.9 Hz, 2F, **1-CF2Ph**), -111.28 (d, $J_{F\text{-}H}$ = 56.2 Hz, 2F, PhCF$_2$H), -130.51 (s, 1F, **2a**), -140.18 (t, J = 9.5 Hz, 2F).

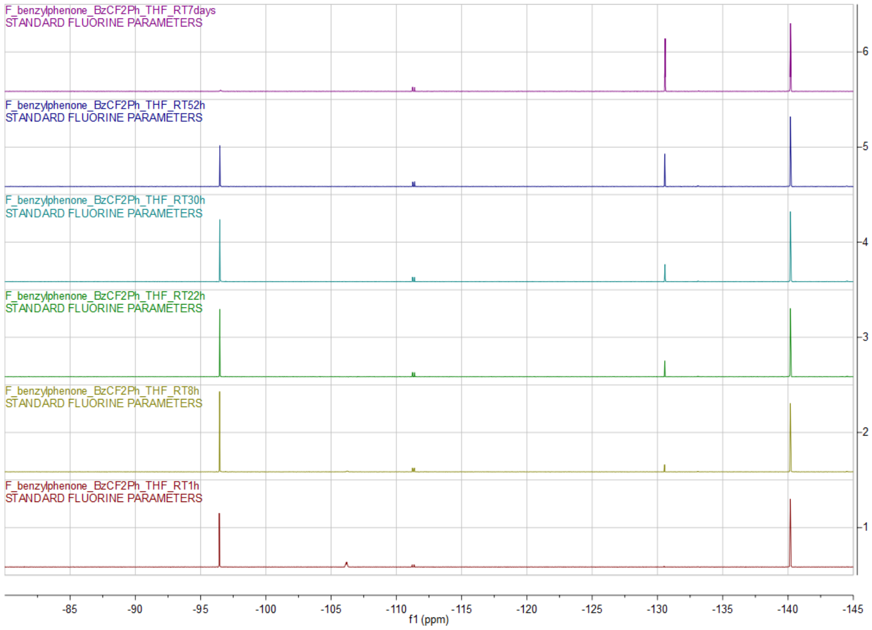


Figure S6. Reaction of benzophenone with **1-CF₂Ph** at RT in THF for 1-168 h.

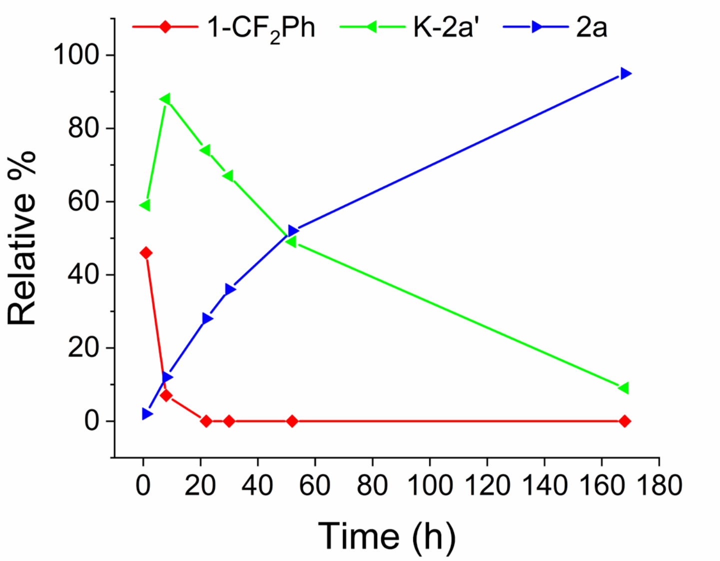


Figure S7. Plot of the conversion from **1-CF₂Ph** into **K-2a'** and **2a** at RT in THF for 1-168 h.

2. Synthesis and isolation of **H-2a'**[3]

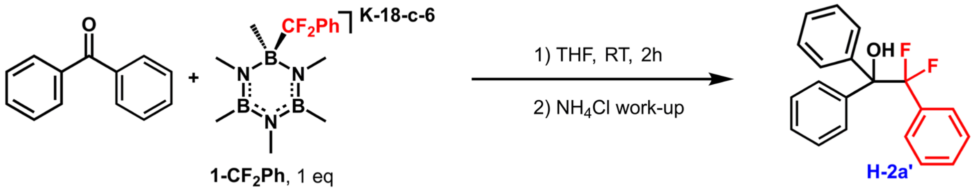


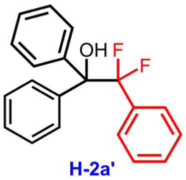
Figure S8. Scheme for the synthesis of **H-2a'**.

Protocol

This compound has been previously reported using THF solvent.[3] The modified procedure was shown below:

Benzophenone (0.4 mmol, 73 mg) and **1-CF$_2$Ph** (0.4 mmol, 238 mg) were measured in an 8 mL vial and 5 mL THF was added, then sealed. The sealed vials were stirred under N_2 atmosphere at room temperature for 2h. Saturated NH_4Cl (~1 mL) was then added to the mixture, and the organic layer was collected. The aqueous layer was extracted with THF (3 x 3 mL), and the THF layers were removed, combined, and dried with anhydrous $MgSO_4$. Solvent was removed under vacuum, and then subjected to column chromatography (eluent = hexanes: EtOAc = 10:1, v/v), which afforded **H-2a'** as a colorless oil in 44% yield.

3. Characterization of H-**2a'**



H-2a'

White solid (0.4 mmol scale, 44% isolated, 55 mg). ^{1}H, ^{13}C, and ^{19}F NMR spectroscopic data matched with the literature.[3] ^{19}F NMR (377 MHz, $CDCl_3$) δ -101.39 (s, 2F). ^{1}H NMR (401 MHz, $CDCl_3$) δ 7.50 – 7.41 (m, 4H), 7.32 (t, J = 7.4 Hz, 1H), 7.29-7.24 (6H, overlapping with $CDCl_3$), 7.20 (t, J = 7.7 Hz, 2H), 7.07 (d, J = 7.7 Hz, 2H), 2.76 (s, 1H). ^{13}C-NMR (126 MHz, $CDCl_3$): 141.67 (s), 134.40 (t, $J_{C\text{-}F}$=26.2 Hz), 129.70 (t, $J_{C\text{-}F}$=1.9 Hz,), 128.16 (t, $J_{C\text{-}F}$=2.1 Hz), 127.94 (s), 127.89 (s), 127.55 (t, $J_{C\text{-}F}$=6.6 Hz), 127.18, 123.36 (t, $J_{C\text{-}F}$=255.9 Hz), 81.04 (t, $J_{C\text{-}F}$=28.9 Hz).

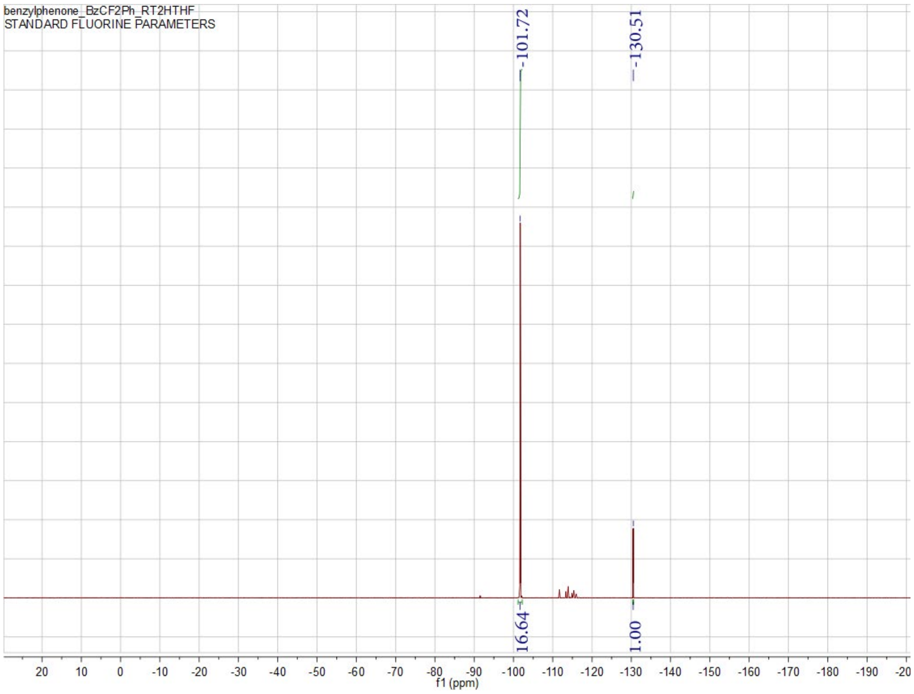


Figure S9. *In situ* ^{19}F NMR spectra (THF) of **H-2a'**. ^{19}F NMR (471 MHz, THF) δ -101.72 (s, 2F, **H-2a'**), -130.51 (s, 1F, **2a**).

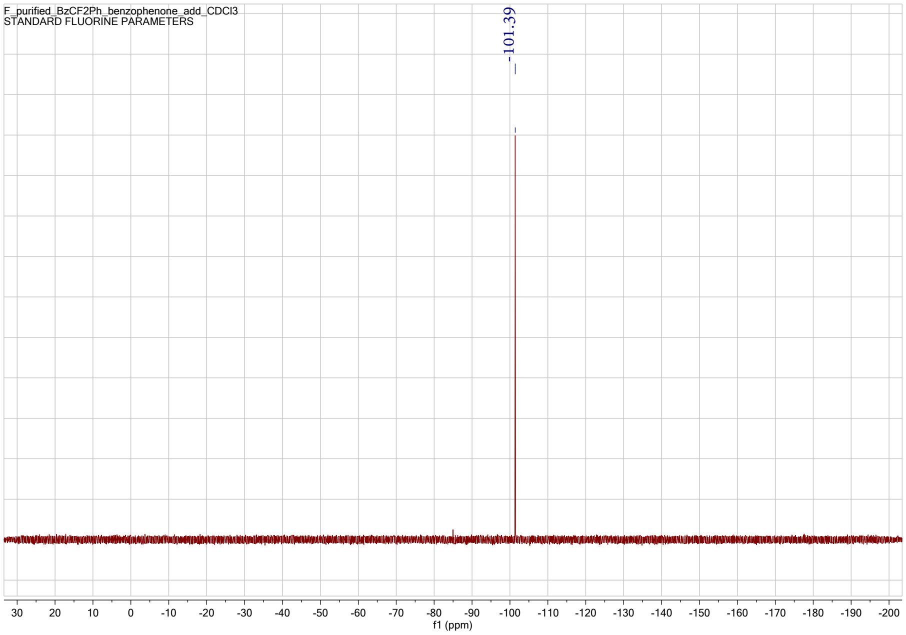


Figure S10. ^{19}F NMR spectra ($CDCl_3$) of the isolated **H-2a’**.

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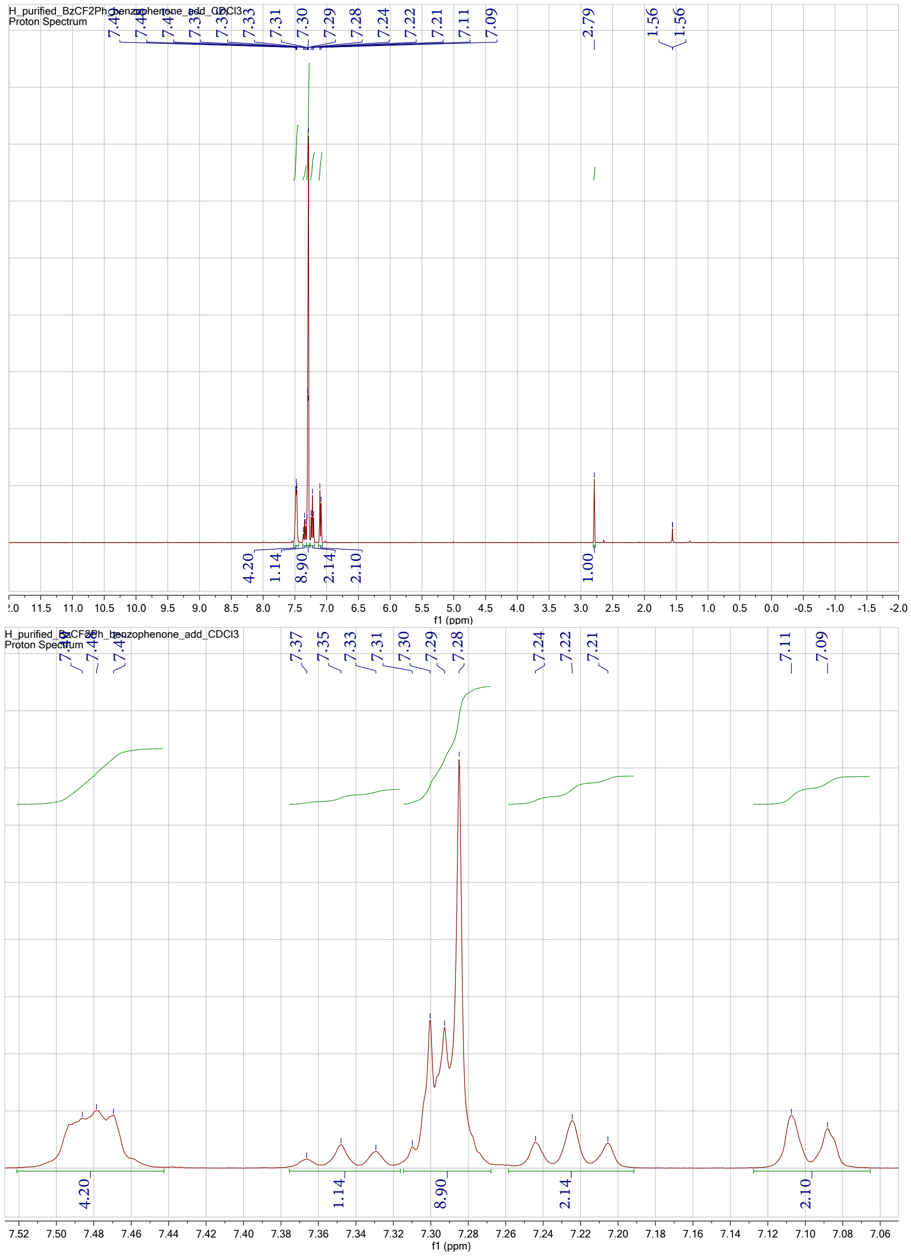

Figure S11. ^{1}H NMR spectra ($CDCl_3$) of the isolated **H-2a'**. Top: full spectra and bottom: zoom-in spectra.

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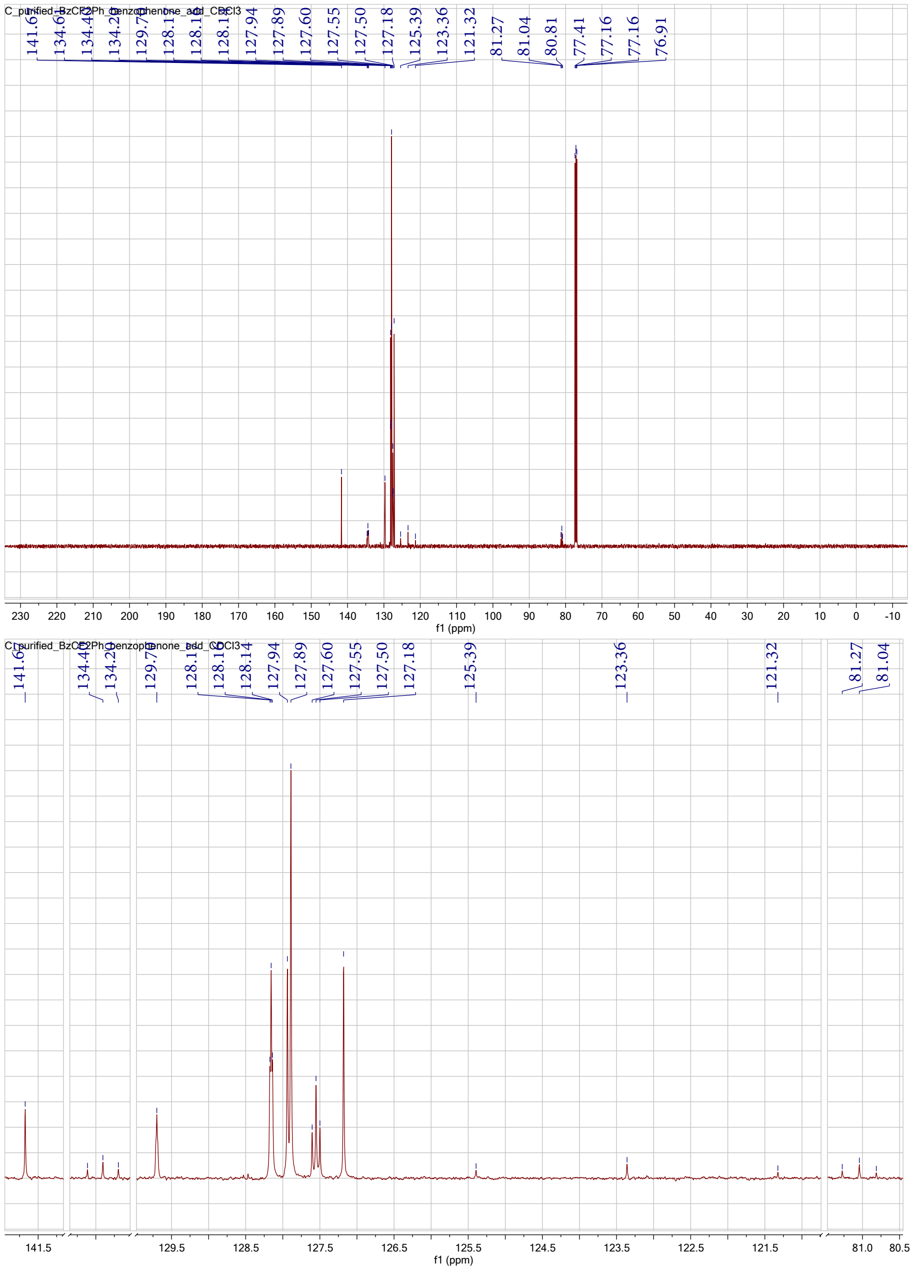

Figure S12. ^{13}C NMR spectra (CDCl$_3$) of isolated **H-2a’**. Top: full spectra and bottom: zoom-in spectra.

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4. Detection of F^- in the aqueous phase after the work-up

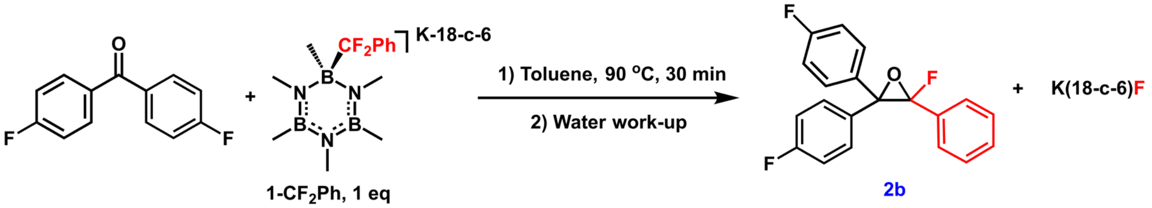

Figure S13. Scheme of the reaction for the detection of F^-.

Protocol

4,4'-Difluorobenzophenone (0.04 mmol, 8.7 mg) and **1-CF₂Ph** (0.04 mmol, 23.6 mg) were measured in an 8 mL vial with 0.5 mL toluene under N_2 atmosphere. The mixture was heated on bench at 90 ºC for 30 min. Then the reaction was worked-up with ~ 1 mL H_2O and ^{19}F NMR spectra of the aqueous phase was collected with KOTf as an internal standard. Then authentic KF (4.2 mg) was added to the aqueous solution and ^{19}F NMR spectra was collected again.

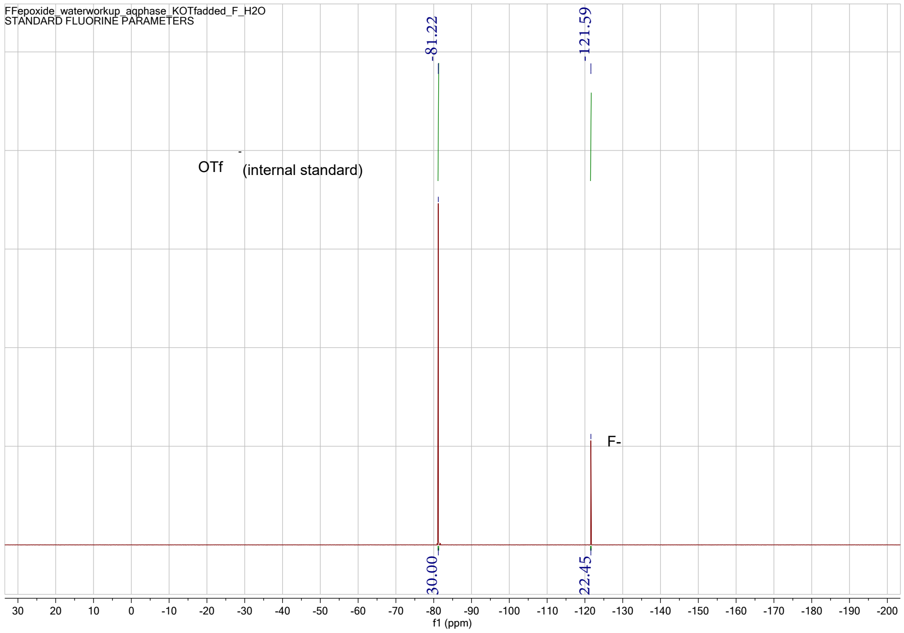

Figure S14. ^{19}F NMR spectra (H_2O) of the aqueous phase after work-up.

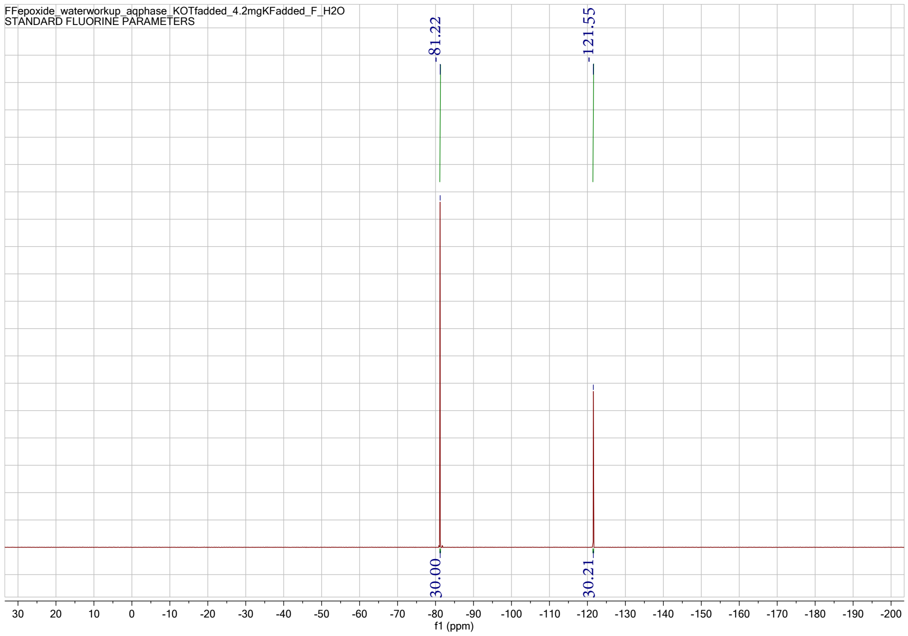

Figure S15. ^{19}F NMR spectra (H_2O) of the aqueous phase after work-up and the addition of authentic KF.

Discussion: After work-up of the reaction, KF was dissolved in the aqueous phase evidenced by ^{19}F NMR spectroscopy (-121.6 ppm). Addition of authentic KF increased the intensity of the same peak (-121.6 ppm), confirming the species dissolved in the aqueous phase is F⁻.

5. *In situ* ^{19}F NMR experiment for kinetic study

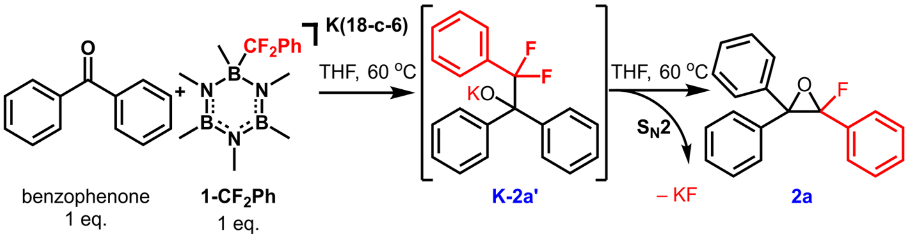

Figure S16. Scheme of the model reaction for kinetic study.

Protocol

Benzophenone (0.04 mmol, 7.3 mg), **1-CF₂Ph** (0.04 mmol, 23.6 mg), and 1,2-difluorobenzene (internal standard, 0.056 mmol, 6.4 mg, 6 µL) were measured in an 8 mL vial with 1 mL THF under N_2 atmosphere. After forming a homogeneous solution, the liquid was transferred into a screwcap NMR tube and immediately cooled at -80 ºC. After the NMR instrument reached 60 ºC for 5 min, ^{19}F NMR spectra was collected every 1 min for 90 min in total. The concentrations of each species in the solution were calculated based on the integration of peaks relative to that of the internal standard.

6. Fitting of the kinetic data

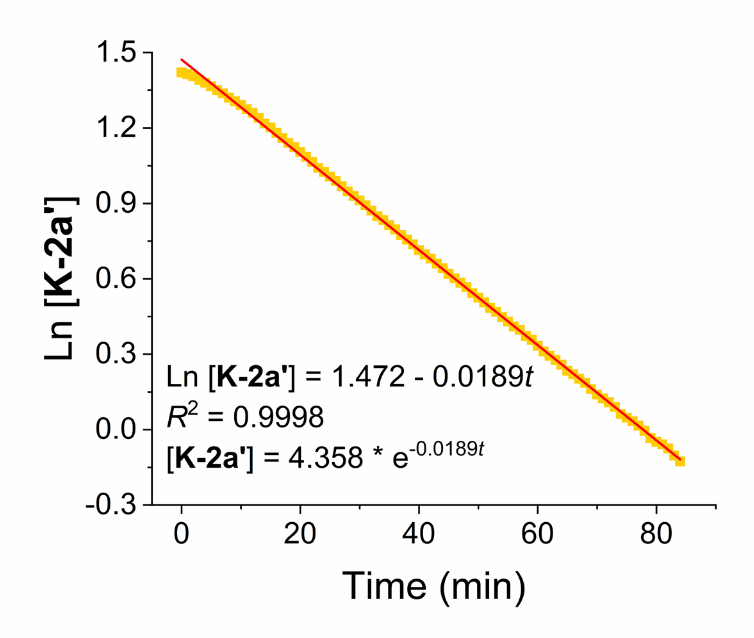

Figure S17. First order fitting of [**K-2a'**] vs time.

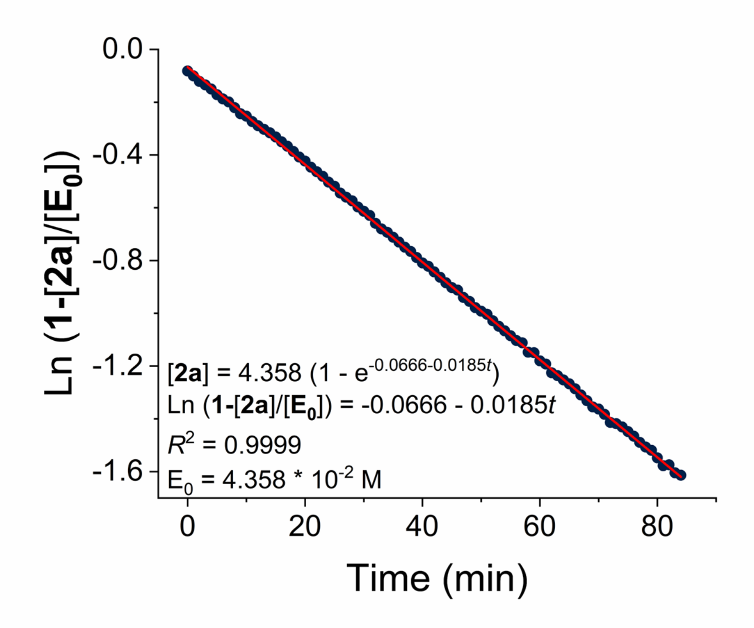

Figure S18. Fitting of [**2a**] vs time. **[E$_0$]** is the maximum [**2a**] and was obtained from results in **Figure S17**.

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7. TBAF as an additive

Protocol

Benzophenone (0.04 mmol, 7.3 mg), **1-CF$_2$Ph** (0.04 mmol, 23.6 mg), and TBAF (0.04 mmol, 10.5 mg) were measured in an 8 mL vial with 0.5 mL toluene under N_2 atmosphere. The vial was heated at 90 ºC for 30 min with stirring. 1,2-difluorobenzene (internal standard, 0.056 mmol, 6.4 mg, 6 µL) was added after the mixture cooled down and ^{19}F NMR spectra was collected.

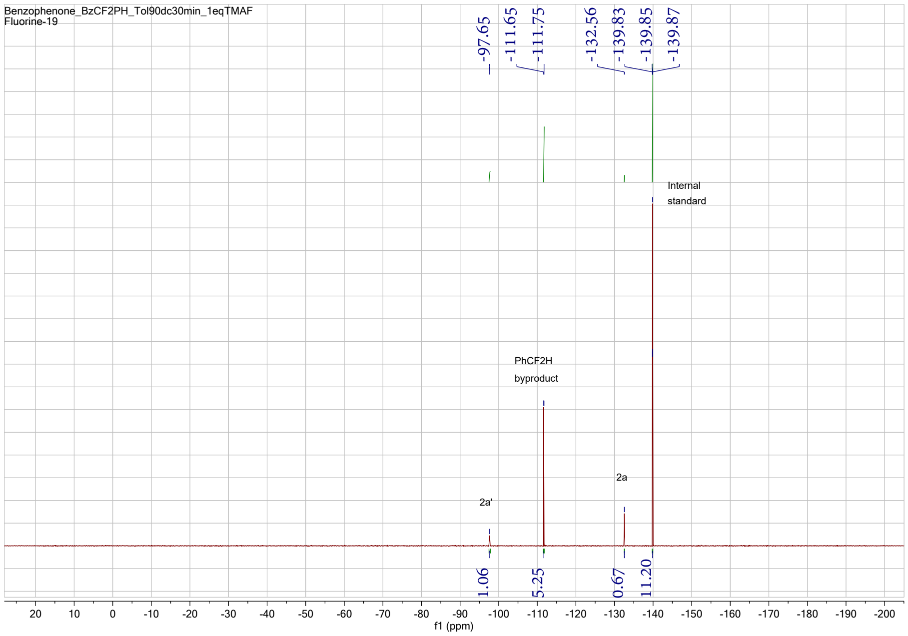


Figure S19. ^{19}F NMR spectra of the reaction mixture with TBAF as an additive. Conversion from **2a'** to **2a** was incomplete after 30 minutes.

Ketone scope (2a-2j)

Figure S20. Scheme for the synthesis of mono α-fluoroepoxides from ketones.

1. Protocols for the synthesis and isolation:

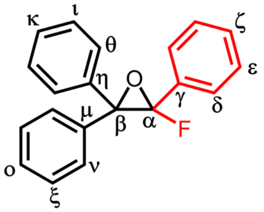
Protocol (0.04 mmol scale, for substrate screening)

(0.04 mmol scale, for substrate scope): The ketone electrophile (0.04 mmol) and **1-CF$_2$Ph** (0.04 mmol, 23.8 mg) were measured in an 8 mL vial, and 0.5 mL toluene was added, followed by a stir bar. The sealed vial was heated and stirred (600 rpm) at 90 ºC for 30 min. 6 µL 1,2-difluorobenzene (0.056 mmol) was added as the internal standard for quantification of the chemical yield of the afforded α-fluoroepoxides using ^{19}F NMR spectroscopy.

Protocol (0.4 mmol scale, for isolation)

The ketone electrophile (0.4 mmol) and **1-CF$_2$Ph** (0.4 mmol, 238 mg) were measured in an 8 mL vial with 5 mL toluene and a stir bar under N_2 atmosphere. The sealed vial was heated and stirred at 90 ºC for 30 min. 60 µL 1,2-difluorobenzene (0.56 mmol, 64 mg) was added as the internal standard and 0.5 mL of the mixture was used for quantification of the chemical yields of the afforded α-fluoroepoxides using ^{19}F NMR spectroscopy. After confirming purity by NMR spectroscopy, ~1 mL water was added and the organic phase was extracted with EtOAc (3 x 2 mL). The combined organic portions were dried with anhydrous $MgSO_4$ and the solvent was removed under vacuum. The resulting residue was further purified by flash column chromatography on silica gel (eluent: hexanes:EtOAc = 10:1, v/v, containing 5 vol% Et_3N) affording the pure compound.

2. Characterization (NMR spectra and LC-MS):



2a: 85%
(93 ± 7%, n=4)

White solid (0.4 mmol, 98.7 mg, 85% isolated, >99% purity). ^{19}F NMR (377 MHz, $CDCl_3$) δ -130.61 (s, 1F). ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.62 (d, J = 7.3 Hz, 3H), 7.46 (t, J = 6.7 Hz, 3H), 7.43 – 7.36 (m, 6H), 7.34 – 7.29 (m, 3H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 136.45 (d, J = 4.5 Hz), 135.89 (d, J = 2.8 Hz), 132.14 (d, J = 32.4 Hz, γC), 129.63 (s), 128.34 (s), 128.26 (s), 128.20 (s), 128.12 (s), 128.10 (s), 127.83 (s), 127.32 (s), 127.30 (s), 100.02 (d, J = 266.3 Hz, αC), 73.22 (d, J = 22.8 Hz, βC). HR-MS (ESI): calcd. for [M-CFO]$^+$ ($C_{19}H_{15}^+$) = 243.1168, found: 243.1158.

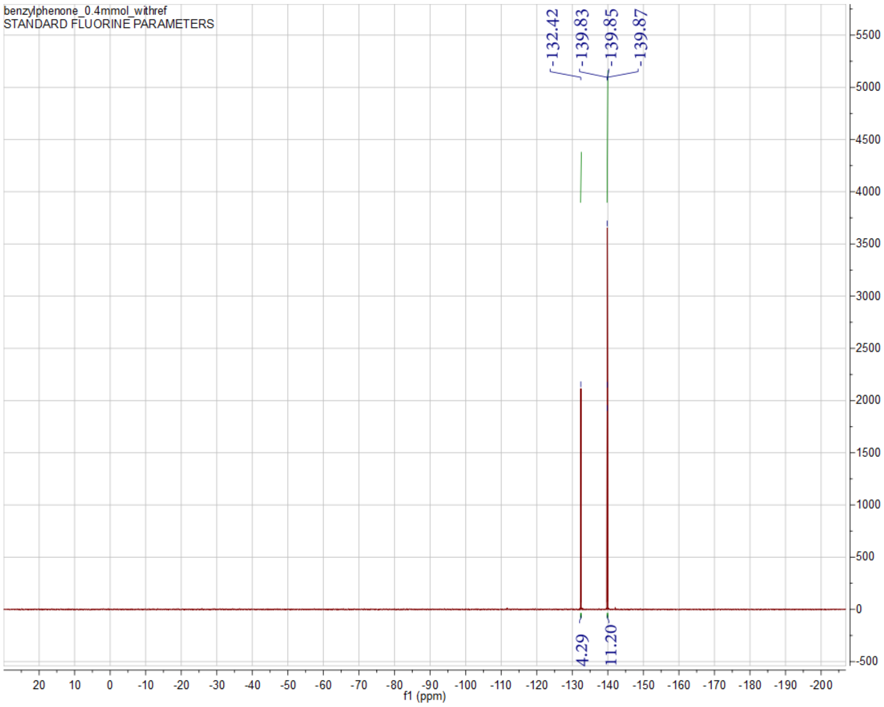


Figure S21. Representative *in situ* ^{19}F NMR spectra of **2a**. ^{19}F NMR (377 MHz, Toluene) δ -132.42 (s, 1F).

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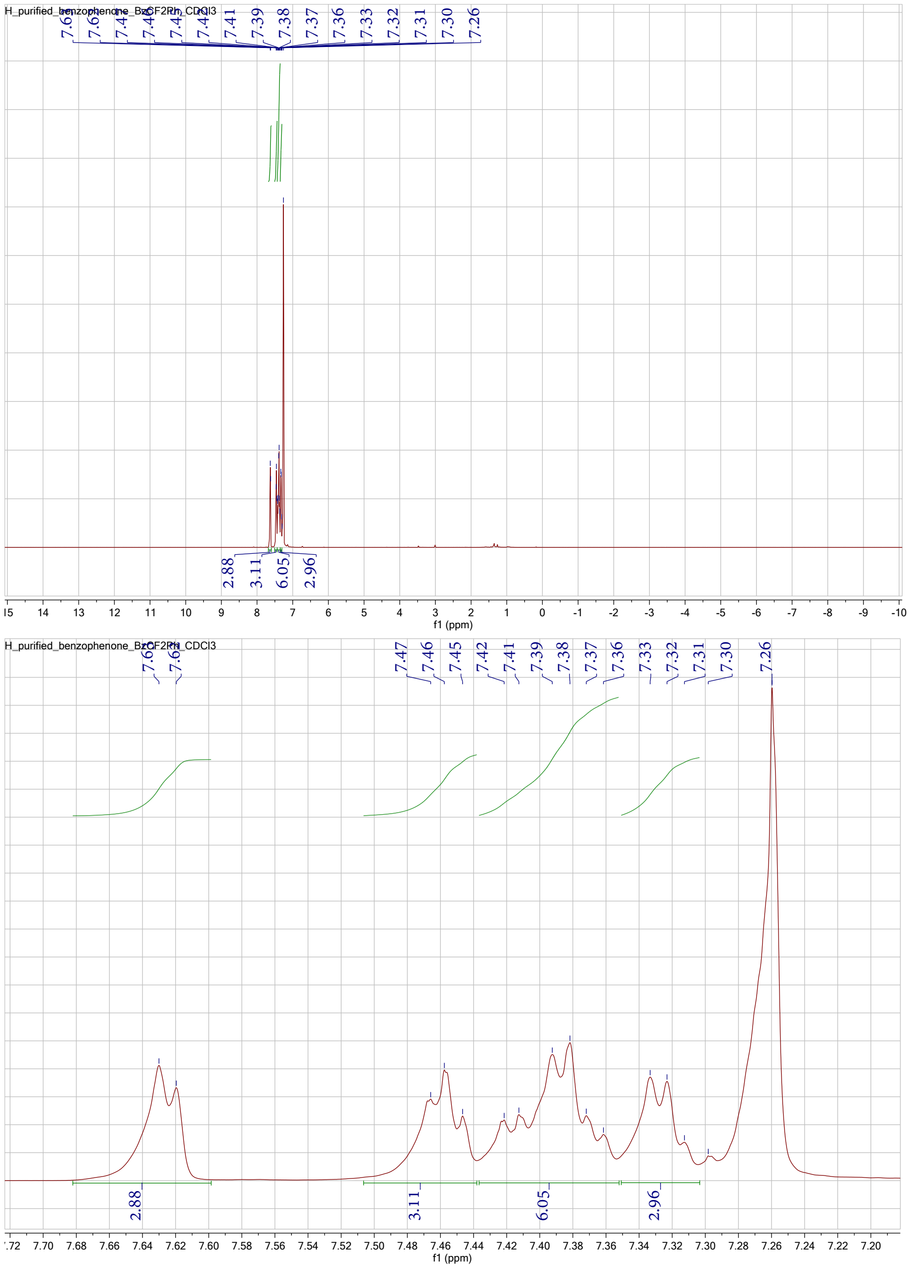

Figure S22. ^{1}H NMR spectra ($CDCl_3$) of isolated **2a**. Top: full spectra and bottom: zoom-in spectra.

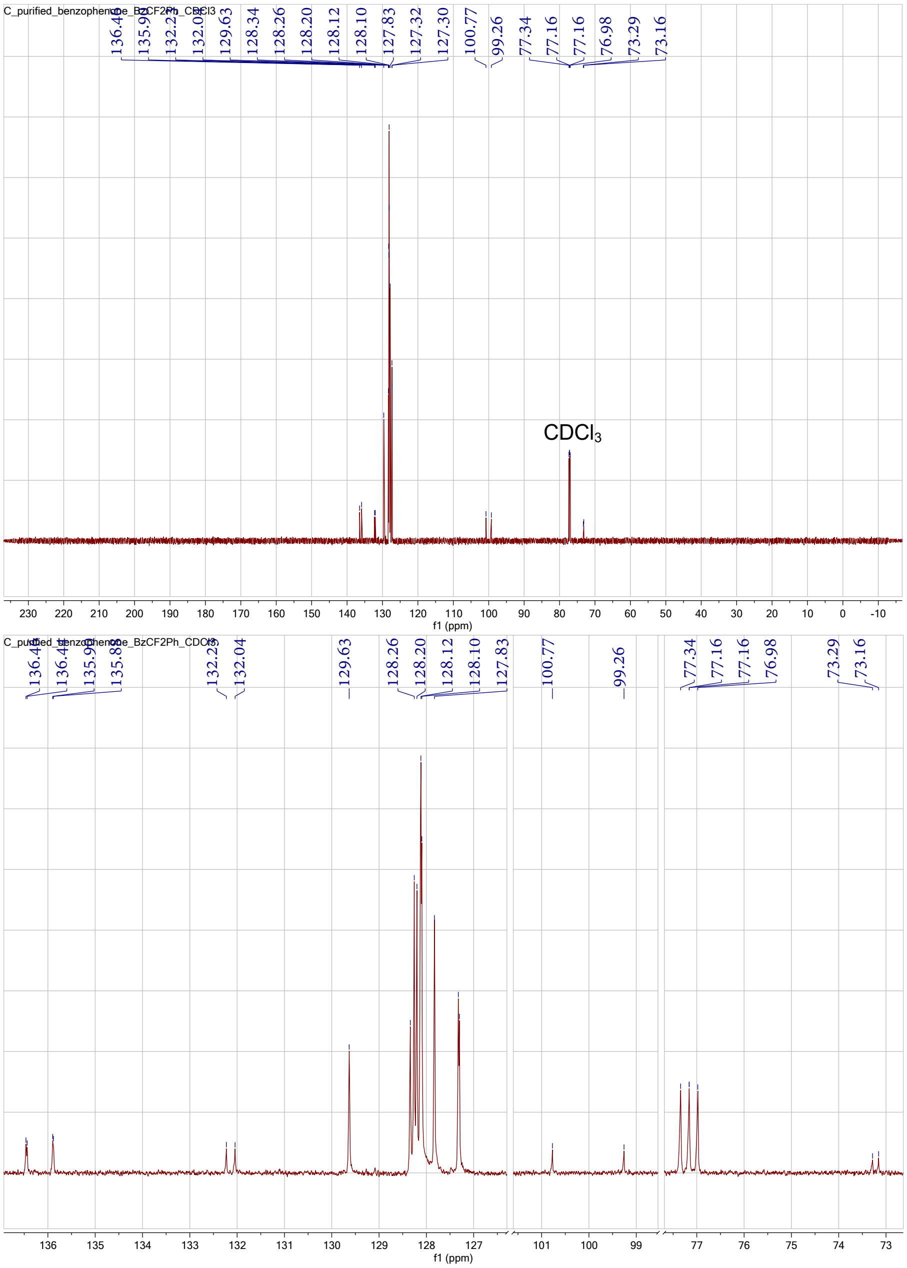

Figure S23. ^{13}C NMR spectra (CDCl$_3$) of isolated **2a**. Top: full spectra and bottom: zoom-in spectra.

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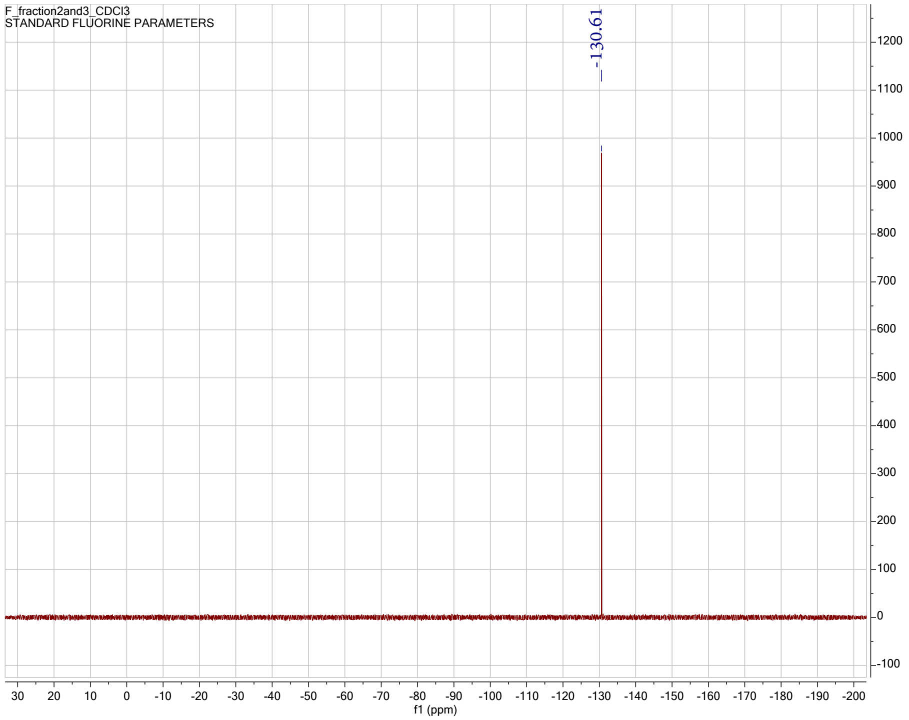
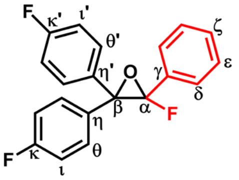


Figure S24. ^{19}F NMR spectra (CDCl$_3$) of isolated **2a**.



2b: 93%
(95 ± 5%, n=2)

White solid (0.4 mmol, 121 mg isolated, >99% purity). ^{19}F NMR (564 MHz, CDCl$_3$) δ -112.68 – -112.72 (m, Ar-F, 1F), -113.37 – -113.44 (m, Ar-F, 1F), -130.96 (s, αF, 1F). ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.46 (dd, *J* = 8.6, 5.4 Hz, 2H, 2θH or 2θ’H), 7.33 (tt, *J* = 8.4, 4.0 Hz, 1H, 1ζH), 7.30 – 7.27 (m, 4H, 2δH + 2εH), 7.12 (dd, *J* = 8.6, 5.3 Hz, 2H, 2θH or 2θ’H), 7.07 (t, *J* = 8.7 Hz, 2H, 2ιH or 2ι’H), 6.89 (t, *J* = 8.6 Hz, 2H, 2ιH or 2ι’H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 162.83 (d, *J* = 247.9 Hz, κC or κ’C), 162.41 (d, *J* = 248.1 Hz, κC or κ’C), 132.08 (t, *J* = 3.2 Hz, ηC or η’C), 131.71 (d, *J* = 32.2 Hz, γC), 131.63 (t, *J* = 3.2 Hz, ηC or η’C), 130.05 (dd, *J* = 8.3, 1.1 Hz, θC or θ’C), 129.88 (d, *J* = 1.2 Hz, ζC), 129.80 (d, *J* = 8.4 Hz, θC or θ’C), 128.28 (s, εC), 127.28 (d, *J* = 4.1 Hz, δC), 115.45 (d, *J* = 21.7 Hz, ιC or ι’C), 115.32 (d, *J* = 21.7 Hz, ιC or ι’C), 99.89 (d, *J* = 266.9 Hz, αC), 72.13 (d, *J* = 22.9 Hz, βC). HR-MS (ESI): calcd. for [M-CFO]$^+$ ($C_{19}H_{13}F_2^+$) = 279.0980, found: 279.0959.

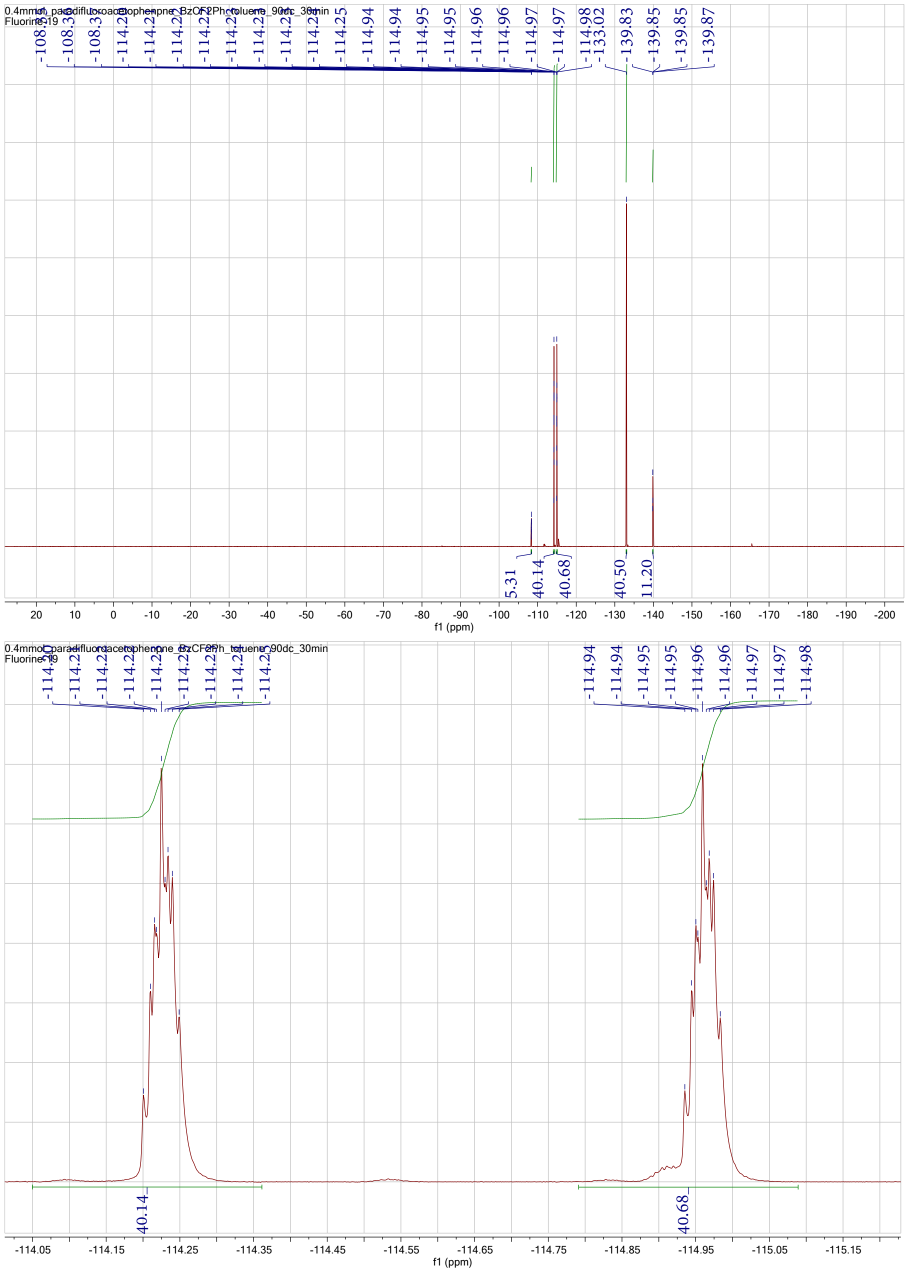


Figure S25. Representative *in situ* ^{19}F NMR spectra (in toluene) of **2b**. Top: full spectra and bottom: zoom-in spectra.

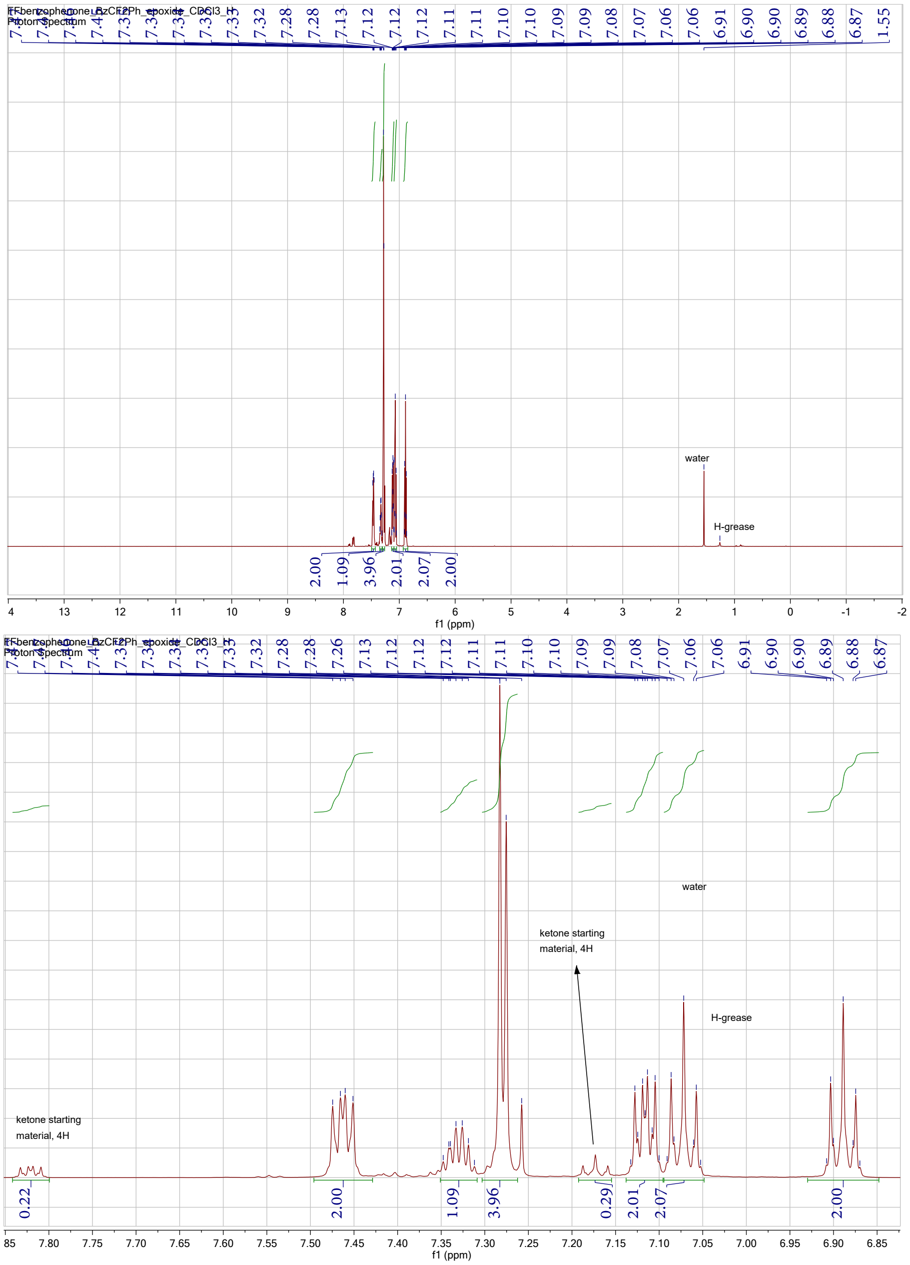


Figure S26. ^{1}H NMR spectra (CDCl$_3$) of isolated **2b**. Top: full spectra and bottom: zoom-in spectra. Small amount of the ketone starting material was found in the isolated **2b**. According to the ^{1}H NMR spectra, The molar ratio of **2b** : ketone starting material = 100 : 5.5, in agreement with the ^{19}F NMR spectra (**Figure S25**).

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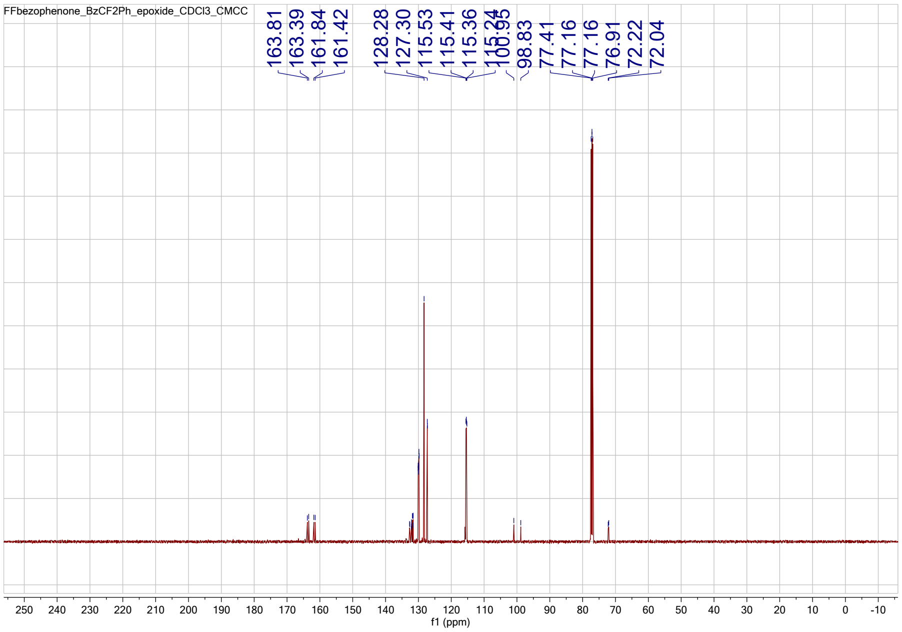

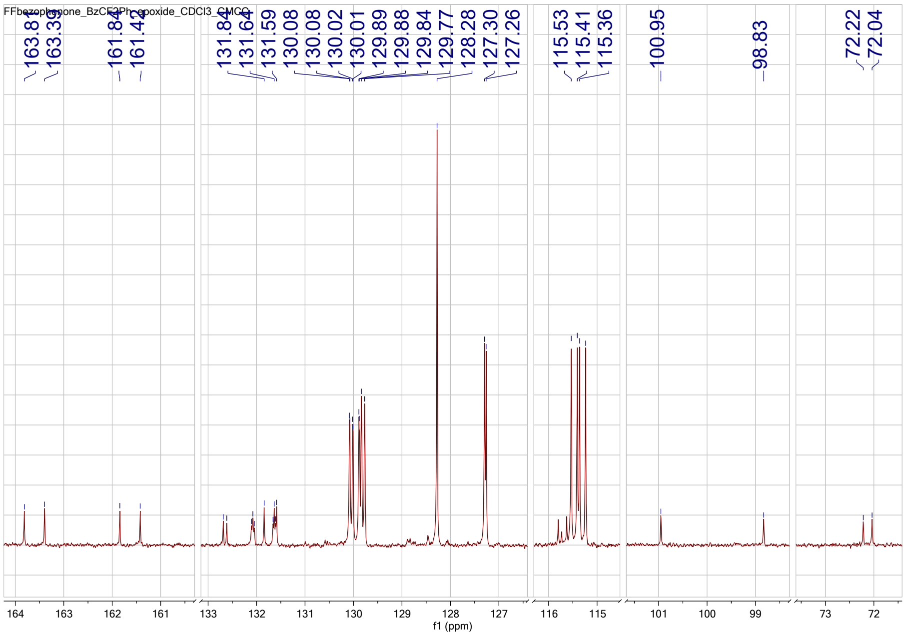

Figure S27. ${}^{13}C$ NMR spectra ($CDCl_3$) of isolated **2b**. Top: full spectra and bottom: zoom-in spectra.

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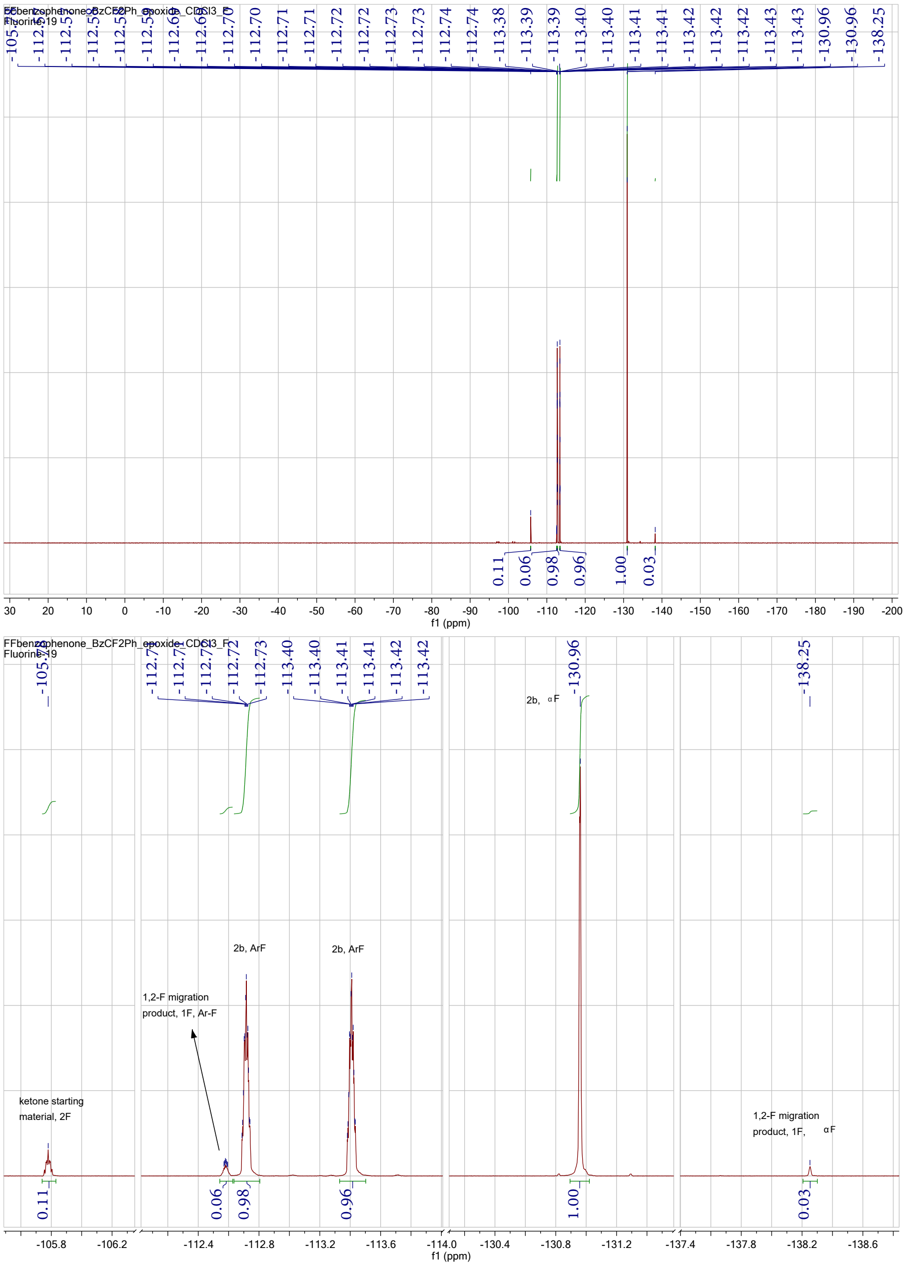
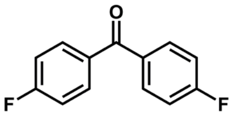
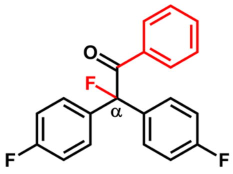


Figure S28. ^{19}F NMR spectra ($CDCl_3$) of isolated **2b**. Top: full spectra and bottom: zoom-in spectra. Small amount of the ketone starting material and decomposed 1,2-F migration product were found in the isolated **2b**. According to the ^{19}F NMR spectra, The molar ratio of **2b** : ketone starting material : 1,2-F migration product = 100 : 5.5 : 3.

Structures of the impurities:



ketone starting material



1,2-F migration product

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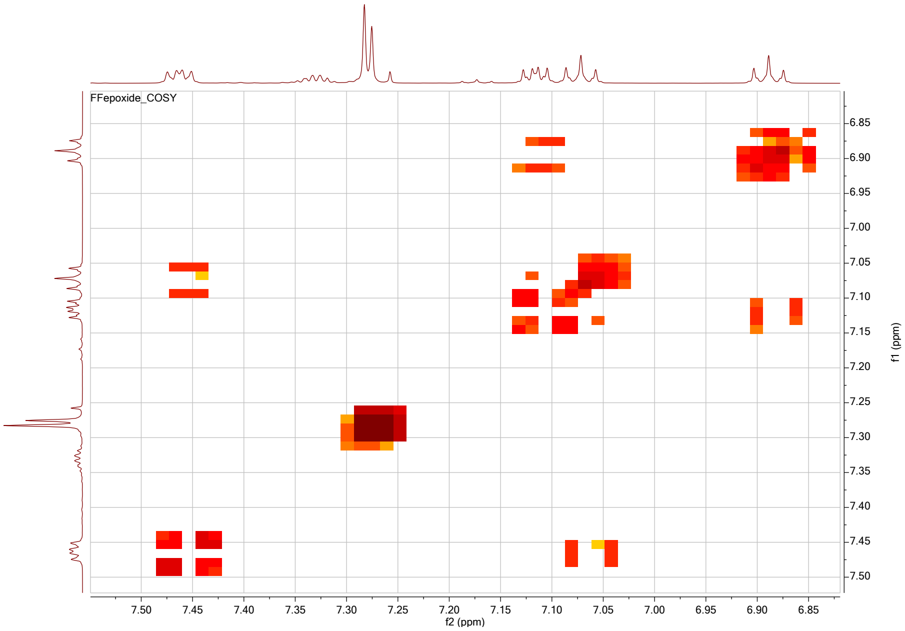

Figure S29. ^{1}H-^{1}H COSY spectra (CDCl$_3$) of isolated **2b**

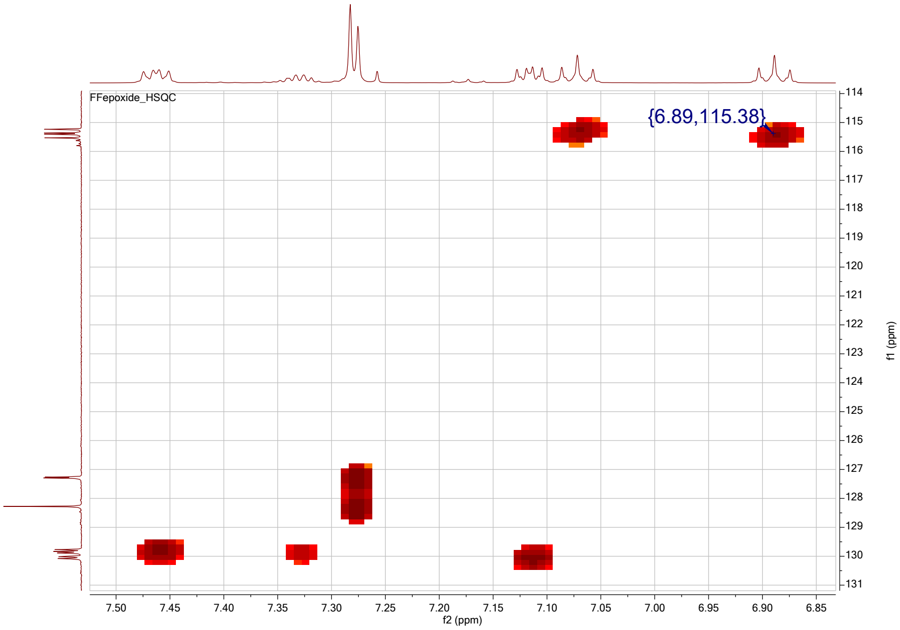

Figure S30. ^{1}H-^{13}C HSQC spectra (CDCl$_3$) of isolated **2b.**

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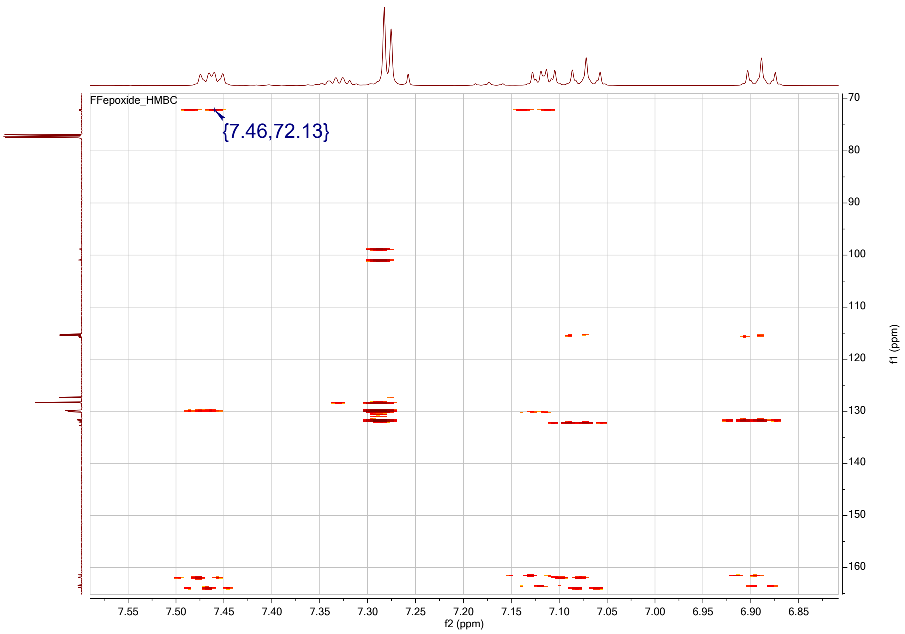
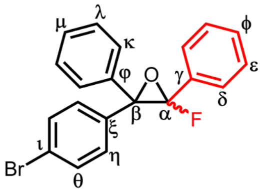


Figure S31. ^{1}H-^{13}C HMBC spectra (CDCl$_3$) of isolated **2b.**



2c: 89%, d.r. = 59:41
(94 ± 1%, d.r. = 59:41, n=2)

Colorless oil (0.4 mmol, 131 mg isolated, 95% purity). Inseparable mixture of diastereoisomers. ^{19}F NMR (377 MHz, CDCl$_3$) δ -129.75 (s, 1F, minor isomer), -131.34 (s, 1F, major isomer). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.55 – 7.50 (m), 7.44 – 7.39 (m), 7.37 – 7.27 (m, overlapping with CDCl$_3$), 7.25 – 7.19 (m), 7.19 – 7.14 (m), 7.10 – 7.05 (m, 2H, 2ηH, minor). ^{13}C NMR (126 MHz, CDCl$_3$), major, δ 135.58 (d, J = 4.5 Hz), 135.30 (d, J = 2.8 Hz), 131.49 (s), 131.43 (s), 129.83 (d, J = 1.3 Hz), 129.79 (d, J = 1.5 Hz), 129.63 (s), 128.40 (s), 128.26 (d, J = 24.1 Hz, γC), 127.79 (s), 127.30 (d, J = 4.3 Hz), 122.68 (s, ιC), 99.87 (d, J = 266.7 Hz, αC), 72.76 (d, J = 22.6 Hz, βC). HR-MS (ESI): calcd. for [M-CFO]$^+$ ($C_{19}H_{14}Br^+$) = 321.0273, found: 321.0250. HR-MS (EI): calcd. for [M]$^+$ ($C_{20}H_{14}BrFO^+$) = 368.0212, found: 368.0005.

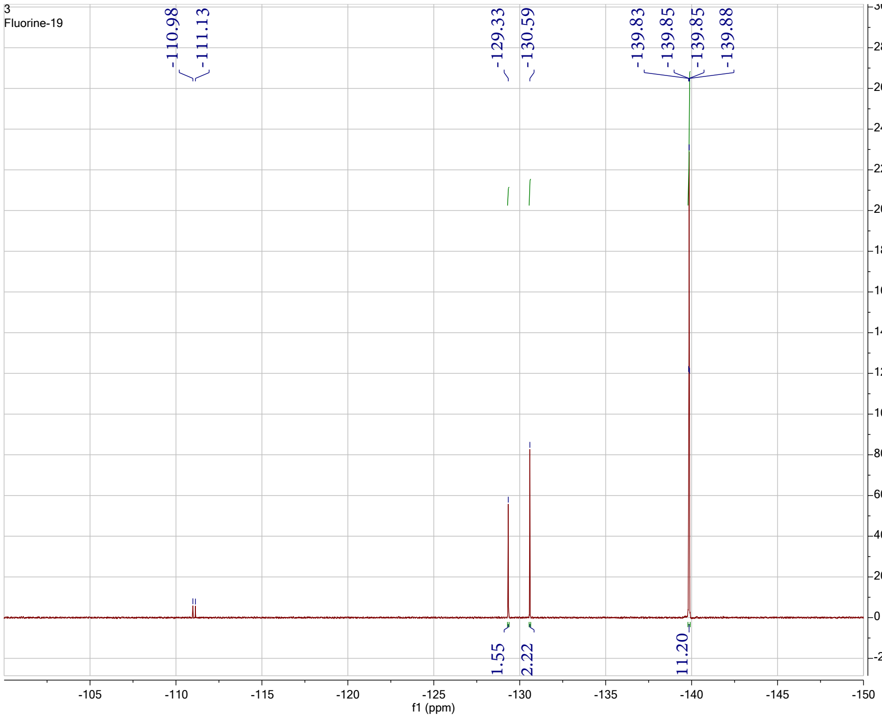


Figure S32. Representative *in situ* ^{19}F NMR spectra (in toluene) of **2c**.

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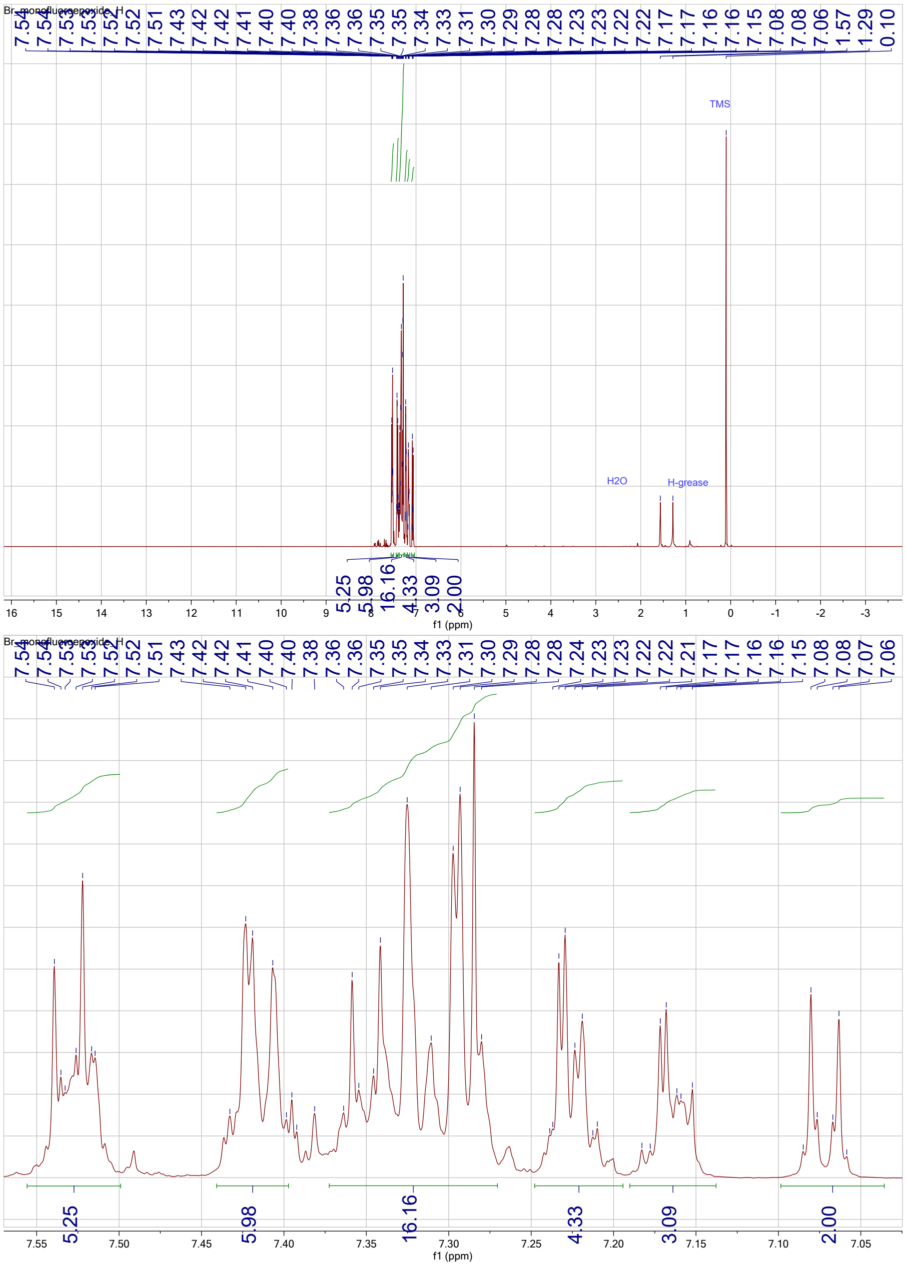

Figure S33. ^{1}H NMR spectra (CDCl$_3$) of isolated **2c**. d.r. (59:41) was determined by ^{19}F NMR spectroscopy, so the total integration of Ar-H is expected to be 14+14/41*59 =34.15, which is close to the observed value (36.81). Top: full spectra and bottom: zoom-in spectra.

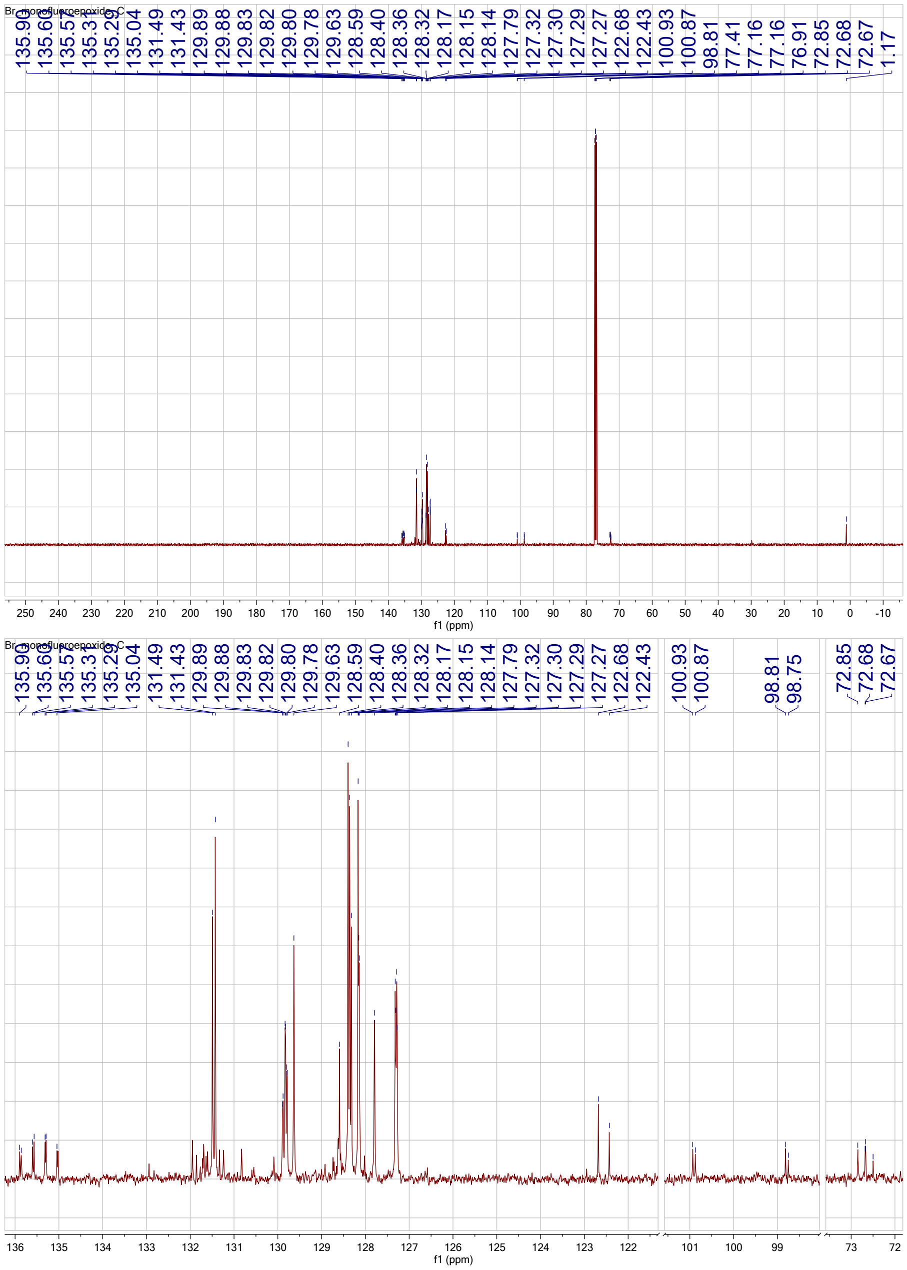

Figure S34. ^{13}C NMR spectra (CD_2Cl_2) of isolated **2c**. Top: full spectra and bottom: zoom-in spectra.

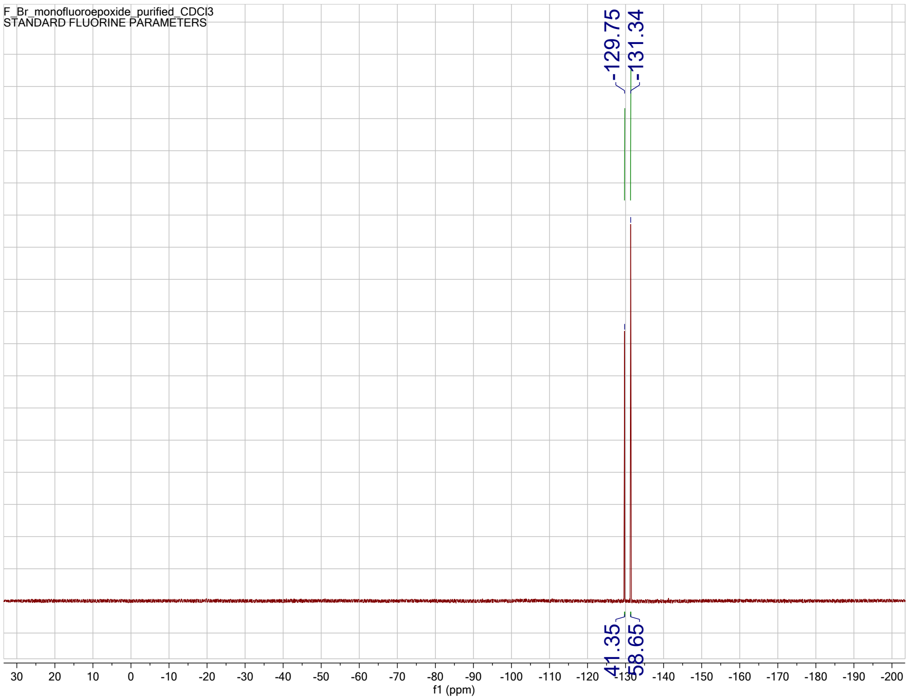

Figure S35. ^{19}F NMR spectra (CDCl$_3$) of isolated **2c**.

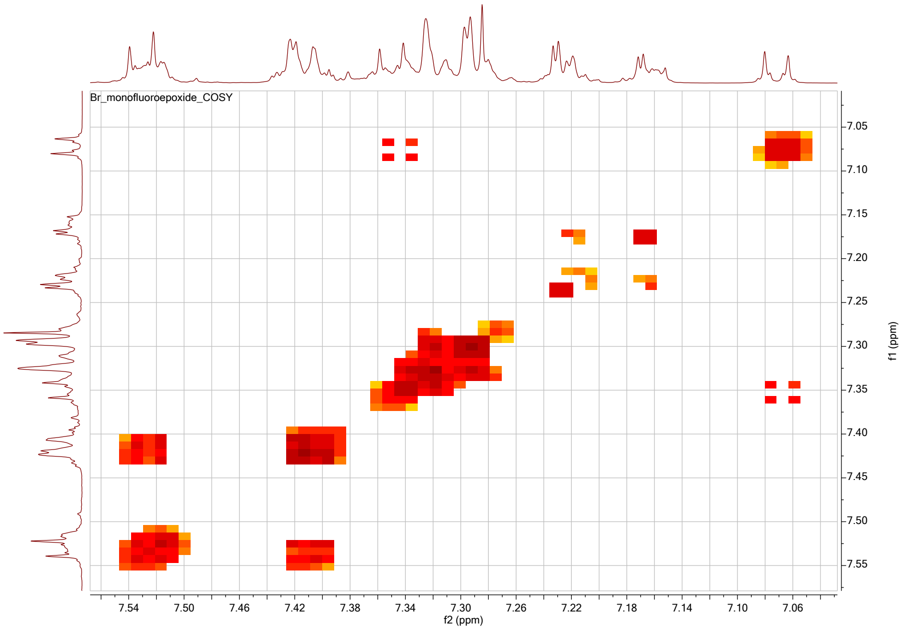

Figure S36. ^{1}H-^{1}H COSY spectra (CDCl$_3$) of isolated **2c**.

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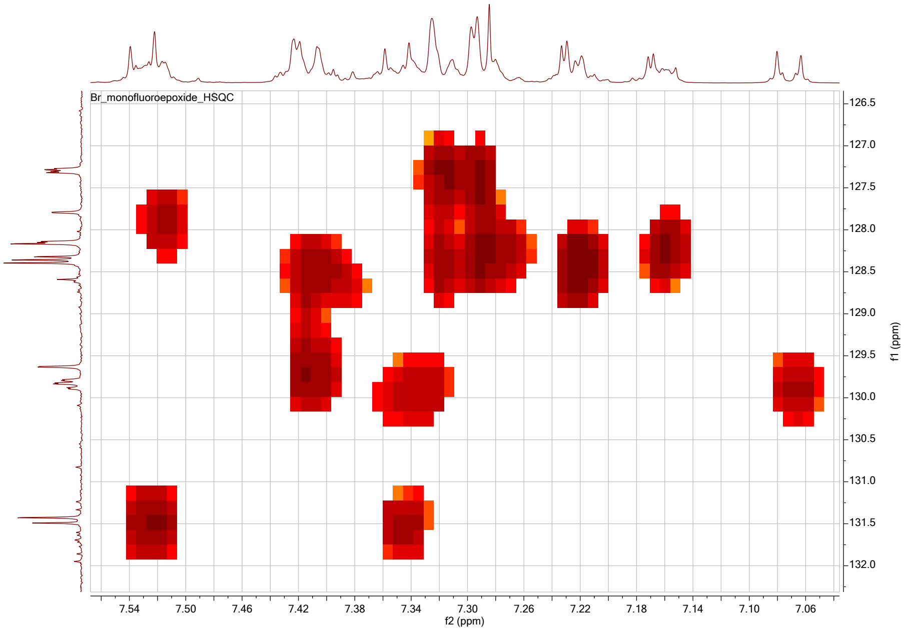

Figure S37. ^{1}H-^{13}C HSQC spectra (CDCl$_3$) of isolated **2c**.

Figure S38. ^{1}H-^{13}C HMBC spectra (CDCl$_3$) of isolated **2c.**

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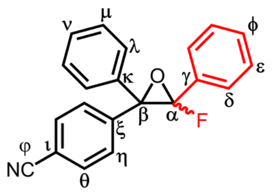

2d: 57%, d.r. = 60:40
(81 ± 6%, d.r. = 60:40, n=4)

Yellow oil (0.4 mmol, 72 mg isolated, 91% purity). Inseparable mixture of diastereoisomers. ^{13}C NMR (126 MHz, CDCl$_3$) δ 141.58 (d, *J* = 4.6 Hz), 140.99 (d, *J* = 3.1 Hz), 134.93 (d, *J* = 4.6 Hz), 134.48 (d, *J* = 2.8 Hz), 132.09 (s), 132.01 (s), 131.31 (d, *J* = 31.9 Hz, major isomer, γC), 131.11 (d, *J* = 31.9 Hz, minor isomer, γC), 130.10 (d, *J* = 1.4 Hz), 129.99 (d, *J* = 1.2 Hz), 128.89 (s), 128.72 (s), 128.57 (s), 128.52 (s), 128.40 (s), 128.21 (s), 128.15 (d, *J* = 1.2 Hz), 127.72 (s), 127.25 (d, *J* = 4.4 Hz), 127.09 (d, *J* = 3.8 Hz), 118.67 (s, major isomer, φC), 118.34 (s, minor isomer, φC), 112.15 (s), 99.78 (d, *J* = 267.7 Hz, major isomer, αC), 99.65 (d, *J* = 268.8 Hz, minor isomer, αC), 72.49 (d, *J* = 22.8 Hz, major isomer, βC), 72.27 (d, *J* = 23.0 Hz, minor isomer, βC). ^{19}F NMR (471 MHz, CDCl$_3$) δ -128.29 (s, 1F, minor isomer), -131.74 (s, 1F, major isomer). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.65 – 7.59 (m), 7.50 – 7.44 (m), 7.41 – 7.34 (m), 7.32 – 7.17 (m, overlapping with CDCl$_3$), 7.15 – 7.08 (m).

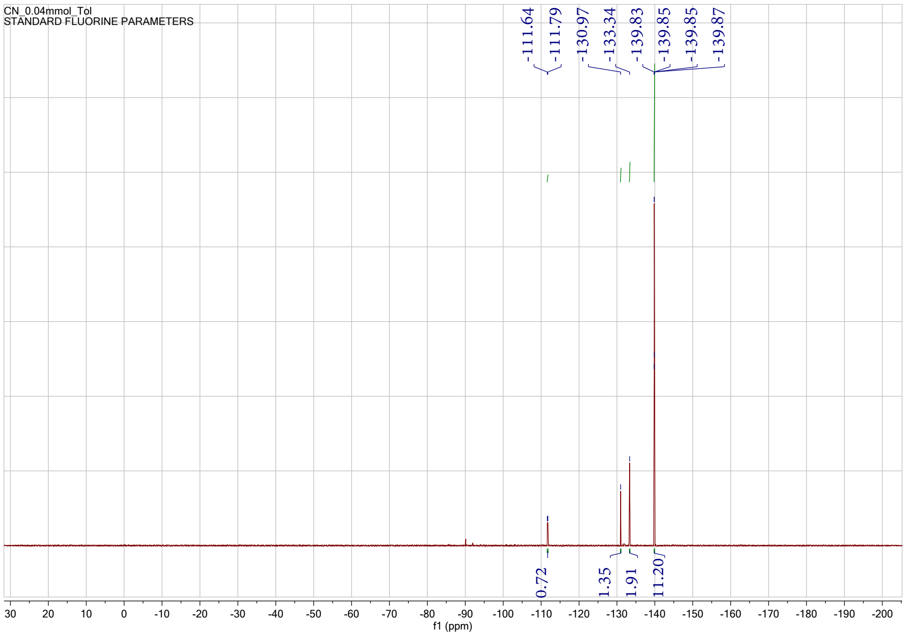

Figure S39. Representative *in situ* ^{19}F NMR spectra (in toluene) of **2d**. ^{19}F NMR (377 MHz, toluene) δ -130.97 (s), -133.34 (s).

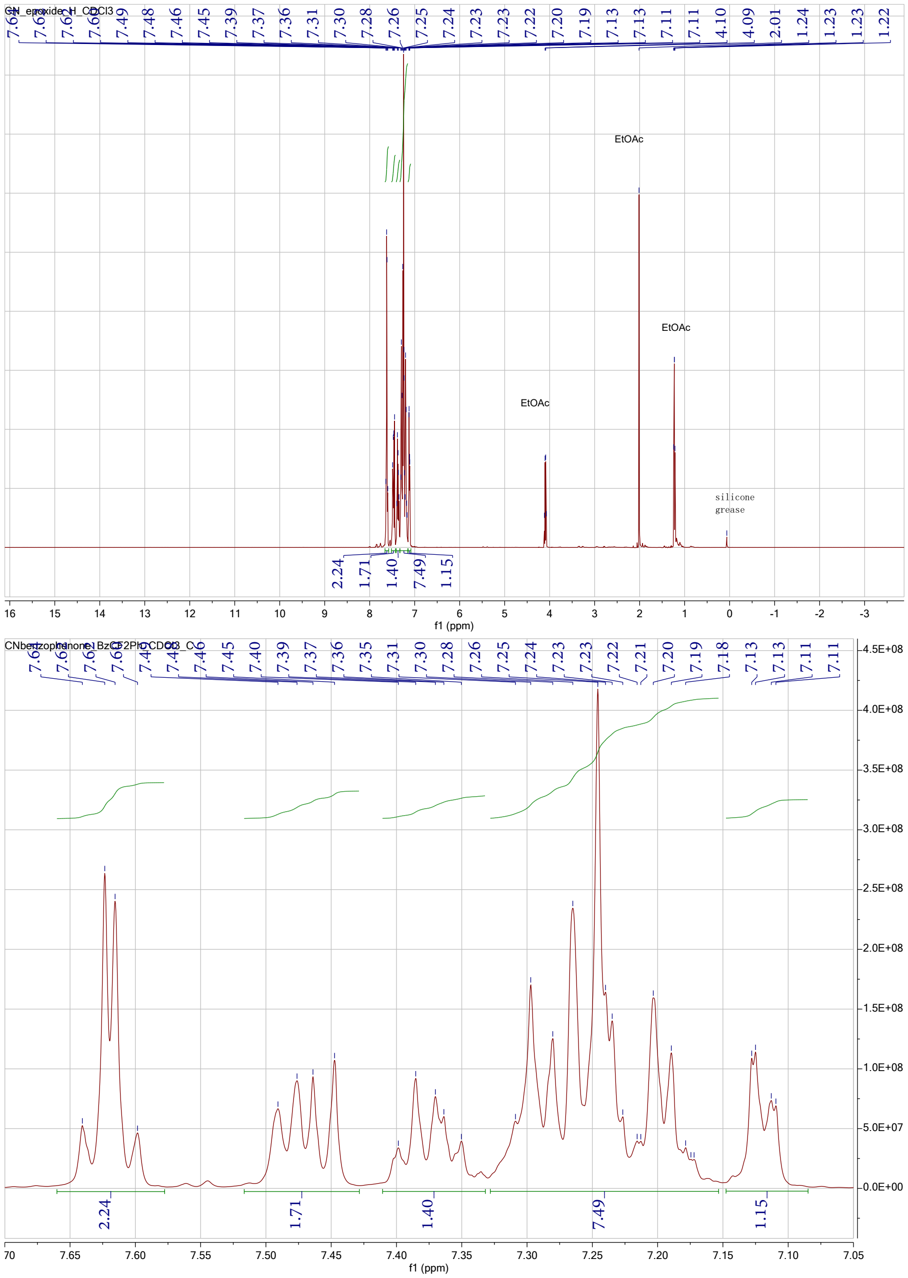

Figure S40. ^{1}H NMR spectra ($CDCl_3$) of isolated **2d**. Top: full spectra and bottom: zoom-in spectra.

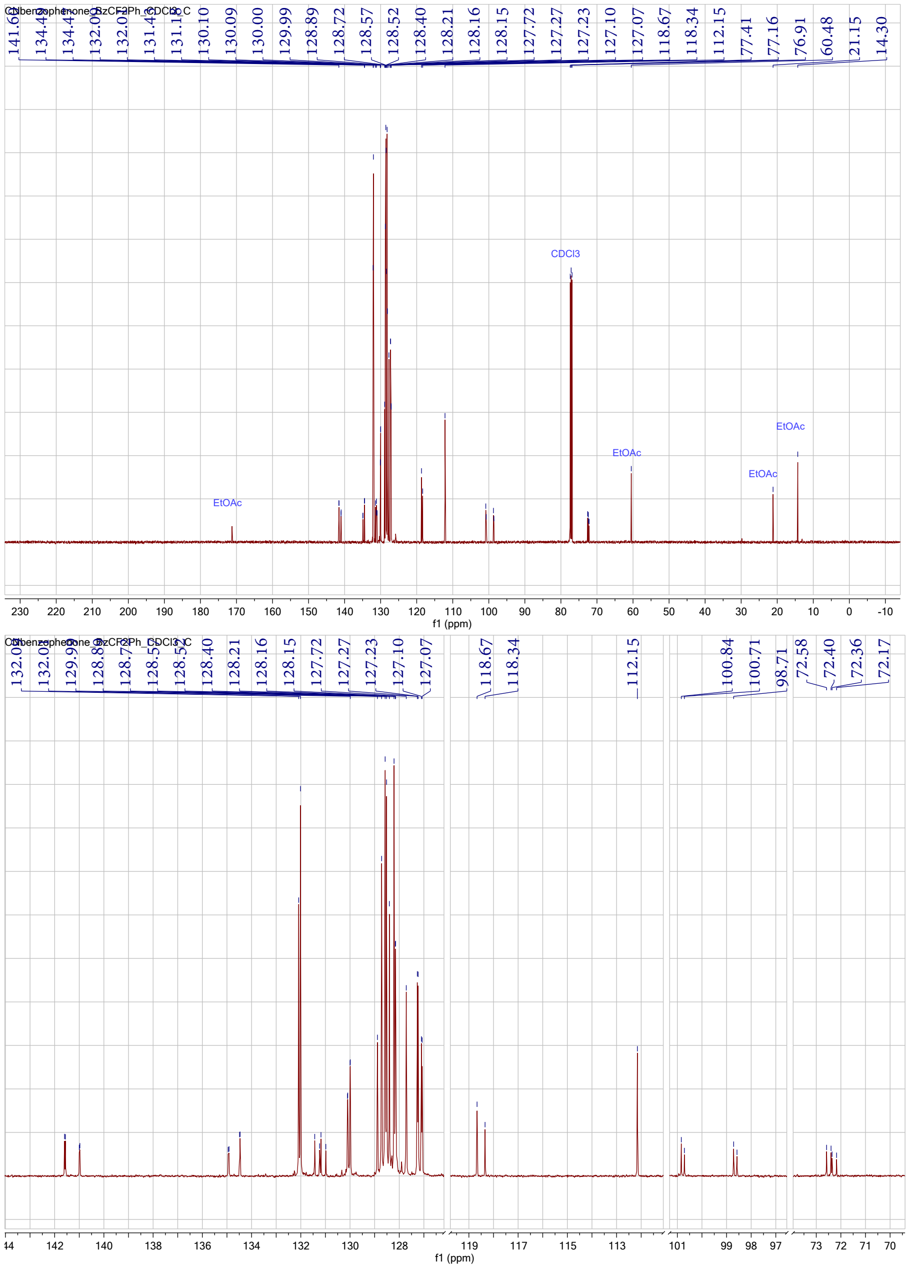

Figure S41. ^{13}C NMR spectra (CDCl$_3$) of isolated **2d**. Top: full spectra and bottom: zoom-in spectra.

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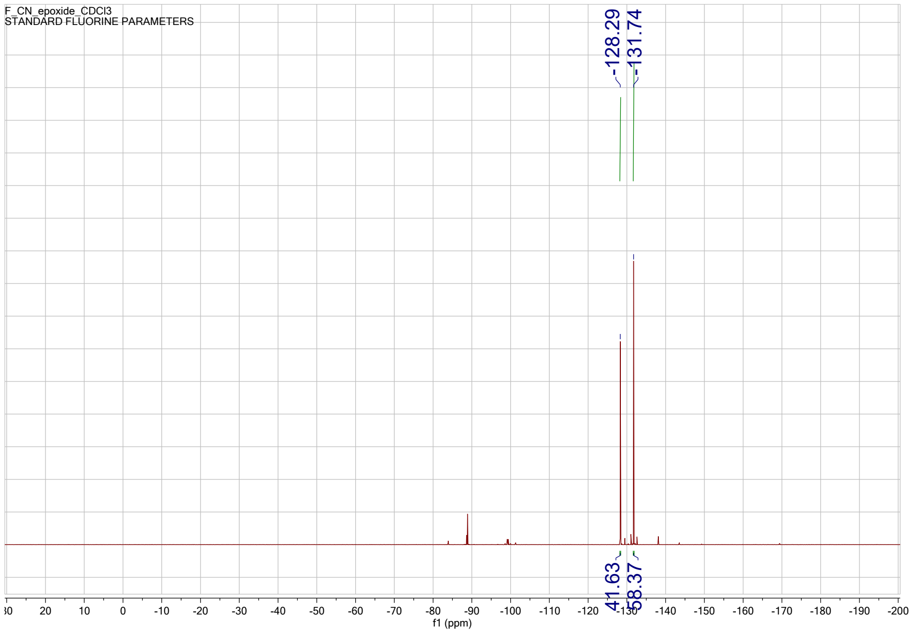

Figure S42. ^{19}F NMR spectra ($CDCl_3$) of isolated **2d**. The unlabeled small peaks were from unknown impurities.

Figure S43. ^{1}H-^{13}C HSQC spectra ($CDCl_3$) of isolated **2d.**

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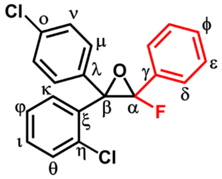
Figure S44. ^{1}H-^{13}C HMBC spectra (CDCl$_3$) of isolated **2d.**



2e: 73%, d.r. = 60:40

White solid (0.4 mmol, 105 mg isolated, 85% purity). Inseparable mixture of diastereoisomers. ^{19}F NMR (564 MHz, CDCl$_3$) δ -117.56 (broad), -135.45 (broad). ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.75 (dd, J = 7.6, 1.7 Hz, 1H, minor isomer), 7.55 (d, J = 7.2 Hz, 2H, minor isomer), 7.52 (d, J = 7.7 Hz, 2H, major isomer), 7.46 (dd, J = 7.9, 1.2 Hz, 1H, minor isomer), 7.41 – 7.30 (m, 7H major isomer), 7.30 – 7.18 (m, overlapping with CDCl$_3$, 7H minor isomer + 4H major isomer), 7.15 – 7.11 (m, 2H, minor isomer). ^{13}C NMR (126 MHz, CDCl$_3$) δ 135.72 (s), 134.68 (s), 134.32 (s), 133.39 (d, J = 3.5 Hz), 132.54 (s), 131.41 (d, J = 33.0 Hz, γC, minor isomer), 130.81 (d, J = 31.2 Hz, γC, major isomer), 130.36 (s), 130.18 (s), 130.12 (d, J = 1.8 Hz), 130.06 (d, J = 3.4 Hz), 129.87 (s), 129.82 (s), 129.73 (s), 129.06 (s), 128.39 (s), 128.35 (s), 128.31 (s), 127.80 (s), 127.57 (d, J = 3.1 Hz), 127.51 (s), 127.40 (s), 127.36 (s), 100.05 (d, J = 266.1 Hz, αC, minor isomer), 99.67 (d, J = 269.0 Hz, αC, major isomer), 71.69 (d, J = 22.9 Hz, βC, major isomer), 70.54 (d, J = 23.2 Hz, βC, minor isomer). Structure confirmed by single crystal X-ray crystallography.

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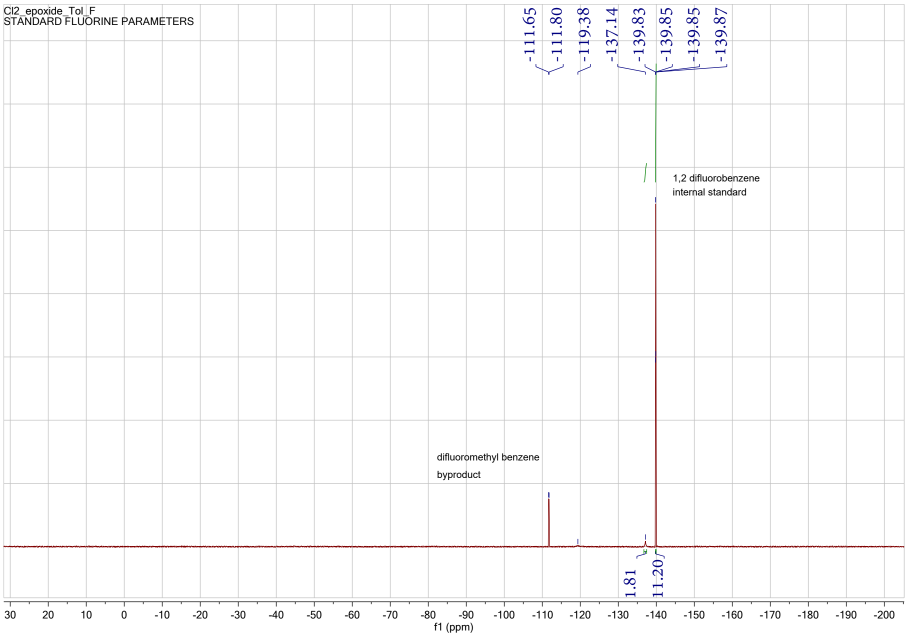

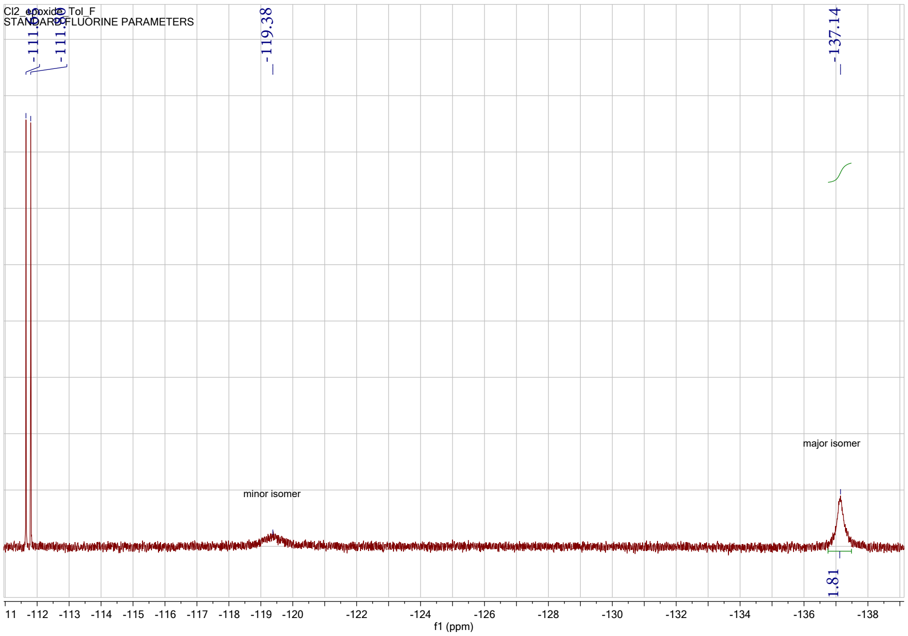

Figure S45. Representative *in situ* ^{19}F NMR spectra (in toluene) of **2e**. Top: full spectra and bottom: zoom-in spectra. The 2 peaks (137.14 and 119.38 ppm) from the desired α-fluoroepoxides were broad, resulting in inaccurate in situ yield and d.r. ratio.

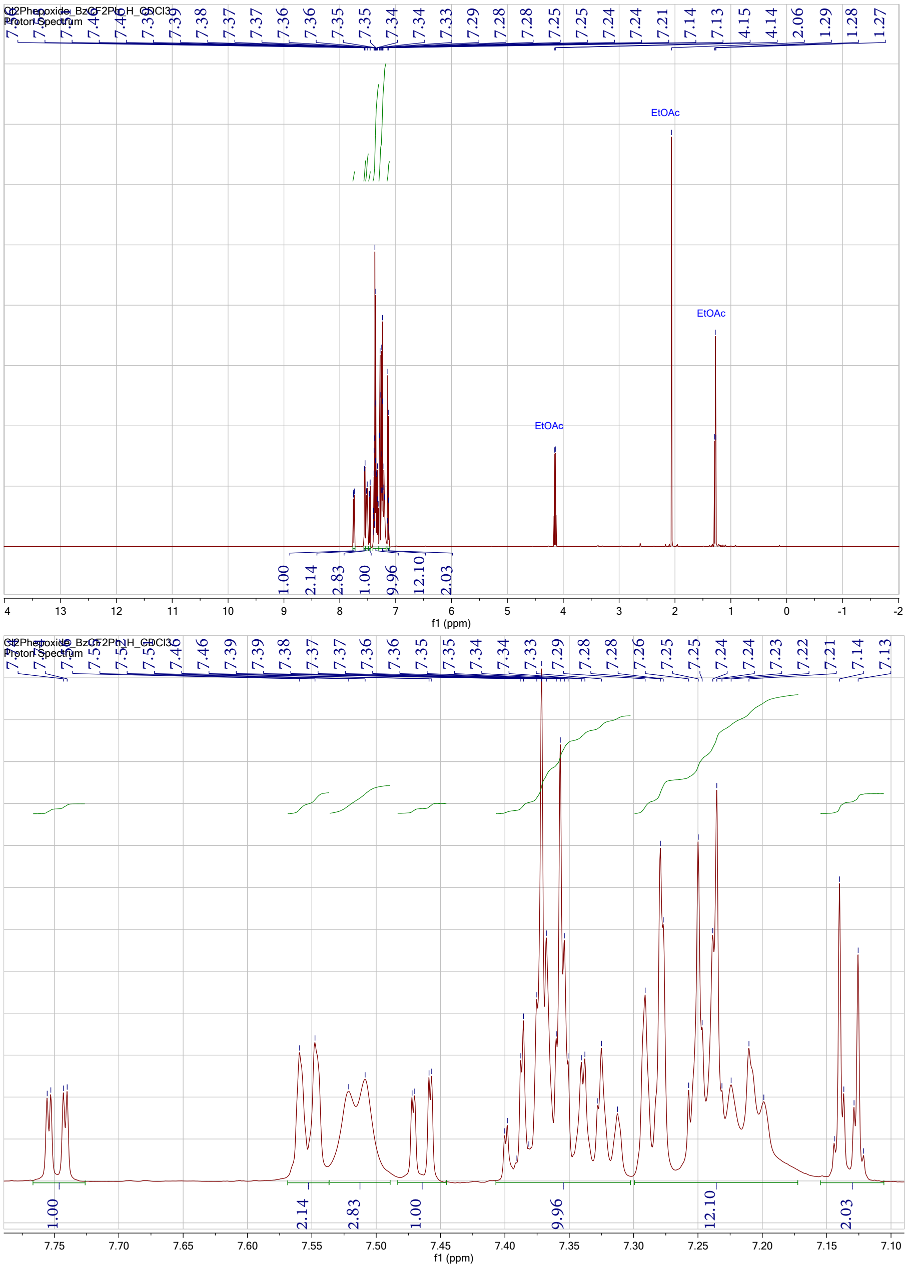

Figure S46. ^{1}H NMR spectra ($CDCl_3$) of isolated **2e**. d.r. = 1 : (2.83/2) = 42:58 determined by ^{1}H NMR spectroscopy. Top: full spectra and bottom: zoom-in spectra. Based on the d.r., the total H integration is expected to be 13+ 13/42*58 =30.95, found: 31.07.

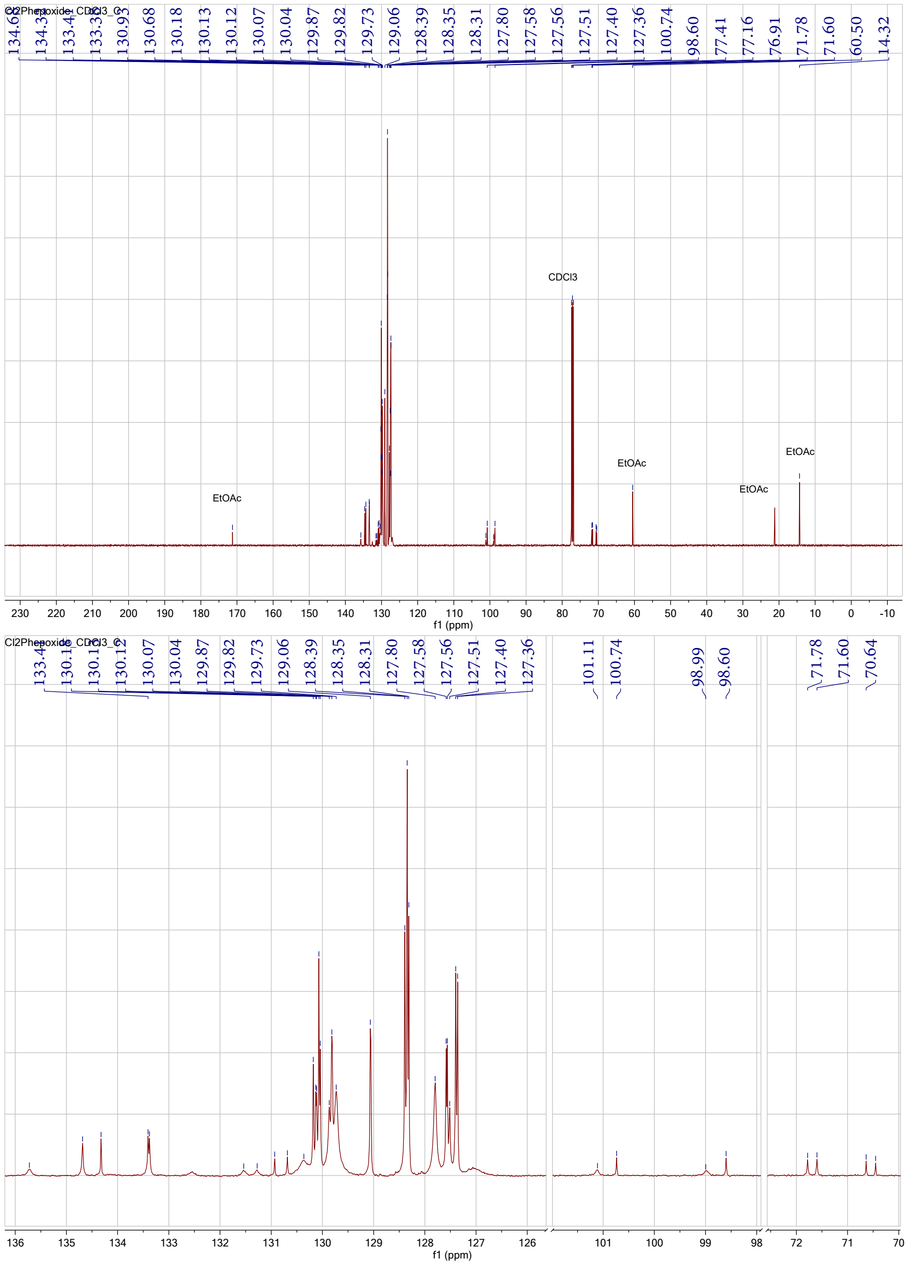

Figure S47. ^{13}C NMR spectra (CDCl$_3$) of isolated **2e**. Top: full spectra and bottom: zoom-in spectra.

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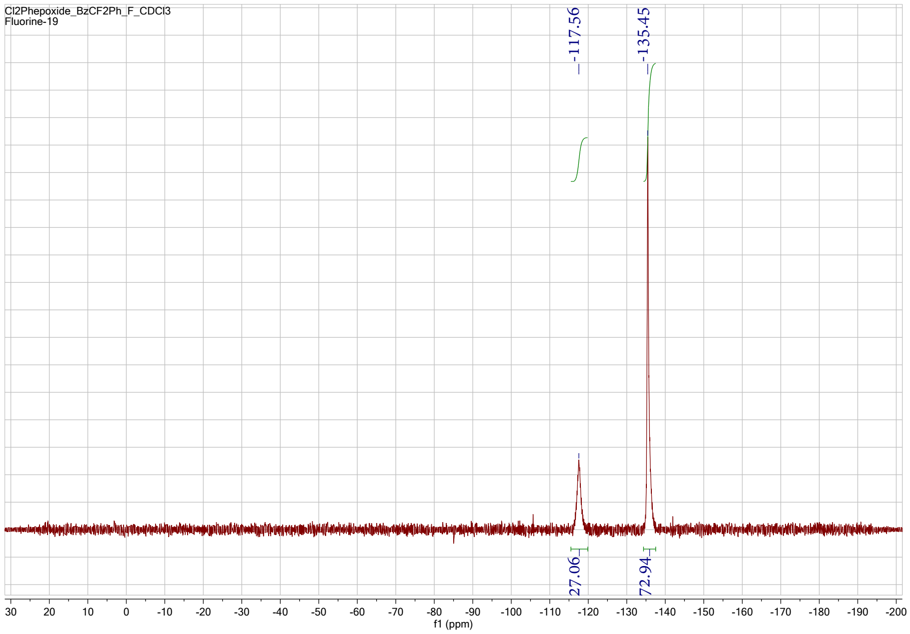

Figure S48. ^{19}F NMR spectra (CDCl$_3$) of isolated **2e**. d.r. = 73:27 determined by ^{19}F NMR spectroscopy.

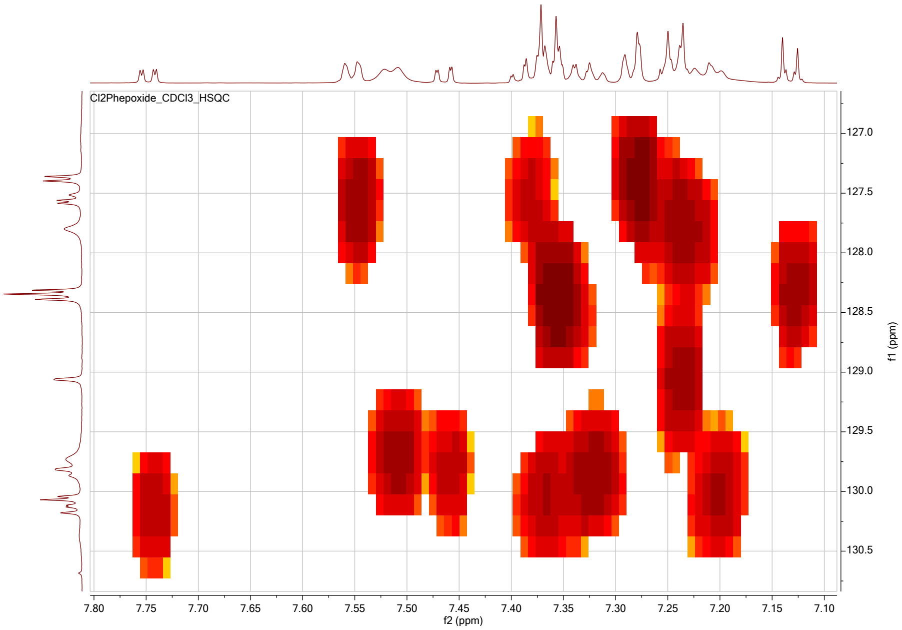

Figure S49. ^{1}H-^{13}C HSQC spectra (CDCl$_3$) of isolated **2e.**

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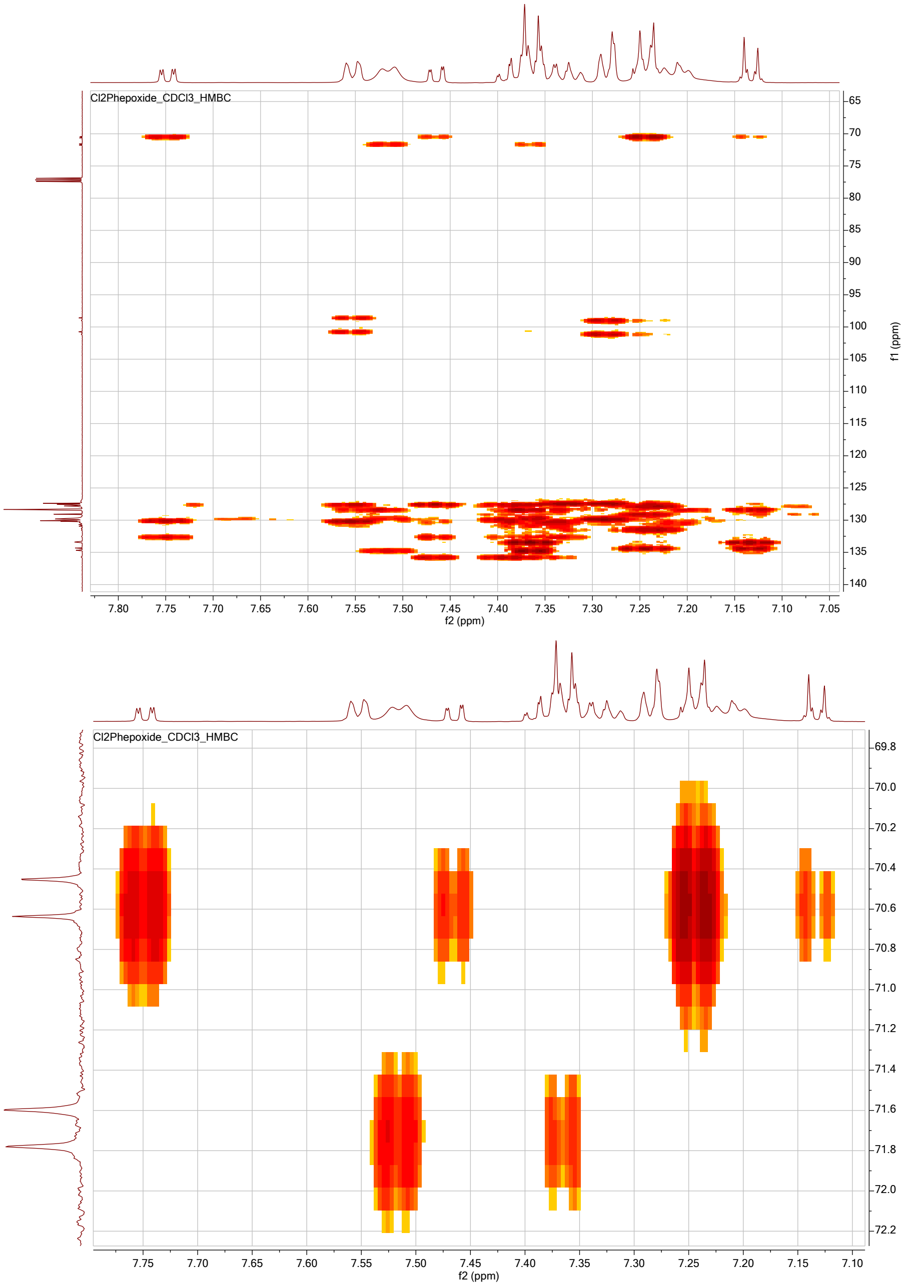

Figure S50. ^{1}H-^{13}C HMBC spectra (CDCl$_3$) of isolated **2e.** Top: full spectra and bottom: zoom-in spectra.

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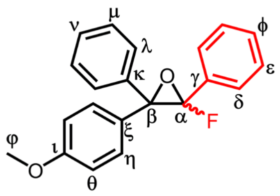

2f: 84%, d.r. = 52:48
(92 ± 5%, d.r. = 52:48, n=2)

Pale yellow oil (0.4 mmol, 108 mg isolated, 81% purity). Inseparable mixture of diastereoisomers. ^{19}F NMR (564 MHz, CD$_2$Cl$_2$) δ -128.96 (s, 1F, major isomer), -129.43 (s, 1F, minor isomer). ^{1}H NMR (600 MHz, CD$_2$Cl$_2$) δ 7.53 (d, *J* = 7.7 Hz), 7.46 (d, *J* = 8.4 Hz), 7.43 – 7.27 (m), 7.24 – 7.18 (m), 7.10 (d, *J* = 8.9 Hz, 2θH), 6.93 (d, *J* = 8.9 Hz, 2θH), 6.76 – 6.71 (m), 3.82 (s, 3φH, minor isomer), 3.72 (s, 3φH, major isomer). ^{13}C NMR (126 MHz, CD$_2$Cl$_2$) δ 160.10 (s, ιC), 159.71 (s, ιC), 137.29 (d, *J* = 4.5 Hz, κC), 136.47 (d, *J* = 3.1 Hz, κC), 132.81 (s), 132.45 (d, *J* = 32.5 Hz, γC), 132.43 (d, *J* = 32.5 Hz, γC), 132.21 (s), 129.98 (d, *J* = 1.7 Hz), 129.92 (d, *J* = 1.7 Hz), 129.54 (d, *J* = 1.4 Hz), 129.44 (d, *J* = 0.8 Hz), 128.81 (d, *J* = 4.6 Hz, ξC), 128.54 (s), 128.51 (s), 128.44 (s), 128.38 (s), 128.31 (s), 128.17 (d, *J* = 1.4 Hz), 127.97 (s), 127.62 (d, *J* = 4.0 Hz), 127.51 (d, *J* = 4.0 Hz), 113.93 (s, θC), 113.85 (s, θC), 100.65 (d, *J* = 265.2 Hz, αC), 100.57 (d, *J* = 265.2 Hz, αC), 73.39 (d, *J* = 22.8 Hz, βC), 73.31 (d, *J* = 23.1 Hz, βC), 55.69 (s, φC), 55.52 (s, φC).

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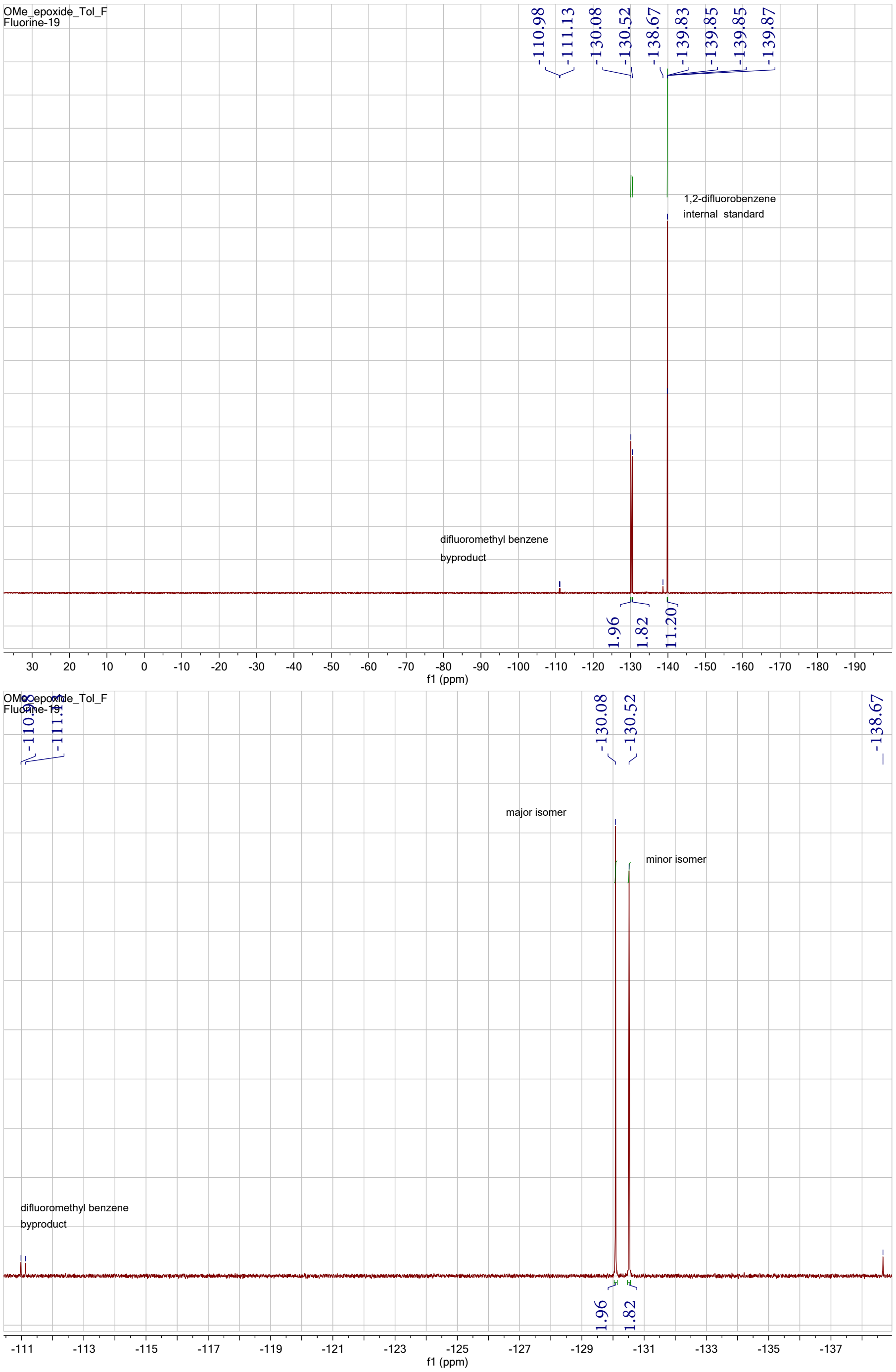

Figure S51. Representative *in situ* ^{19}F NMR spectra (in toluene) of **2f**. Top: full spectra and bottom: zoom-in spectra. The peak located at -138.67 ppm was assigned to be the 1,2-F migration product (**5c**) due to the instability of **2f**.

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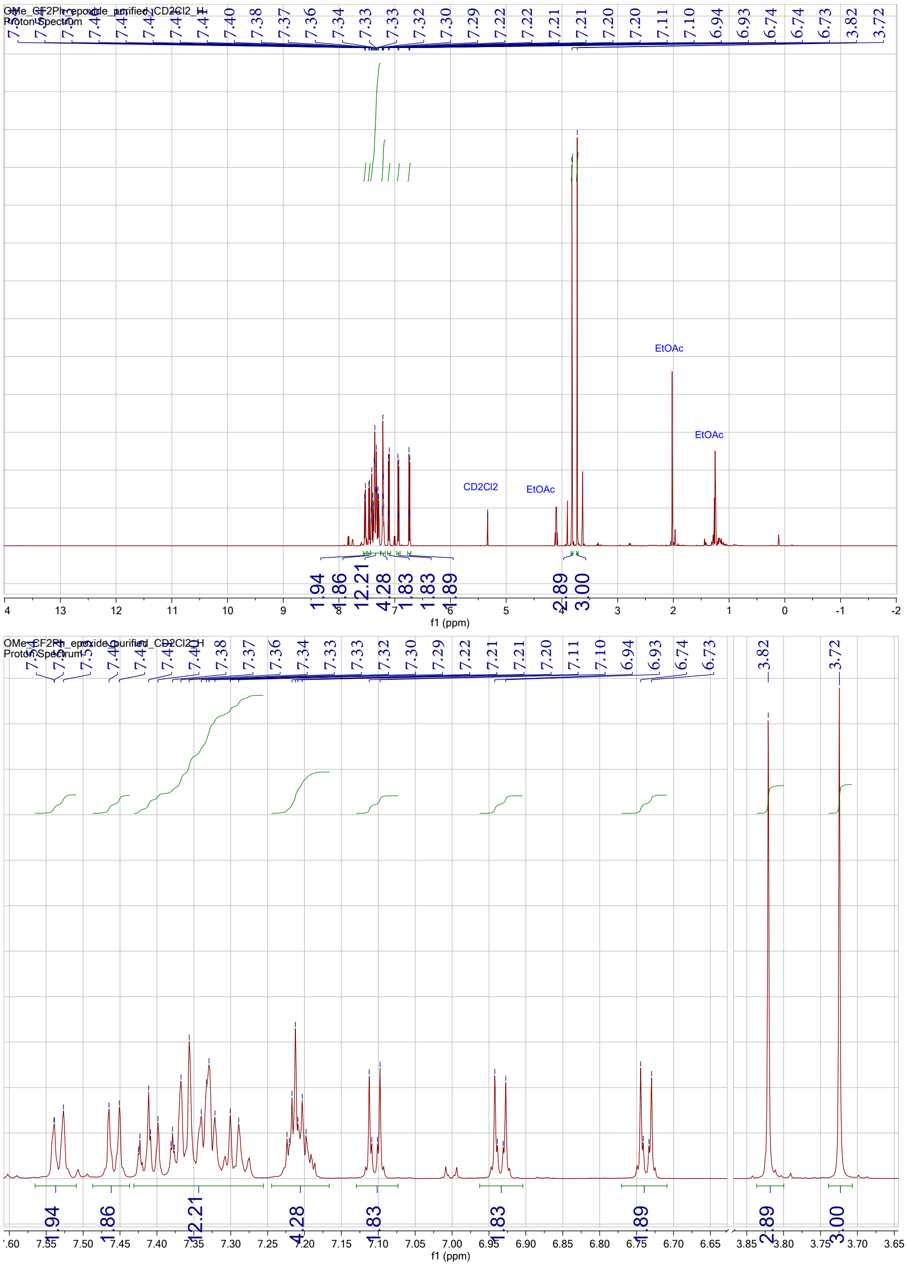

Figure S52. ^{1}H NMR spectra (CD_2Cl_2) of isolated **2f** (major isomer). Top: full spectra and bottom: zoom-in spectra. d.r. value obtained from the ^{1}H NMR spectra is 49:51, consistent with that calculated from ^{19}F NMR results (**Figure S54**, 52:48). Observed total integration of H (31.73) is similar to the predicted value 17*(1+48/52) = 32.69.

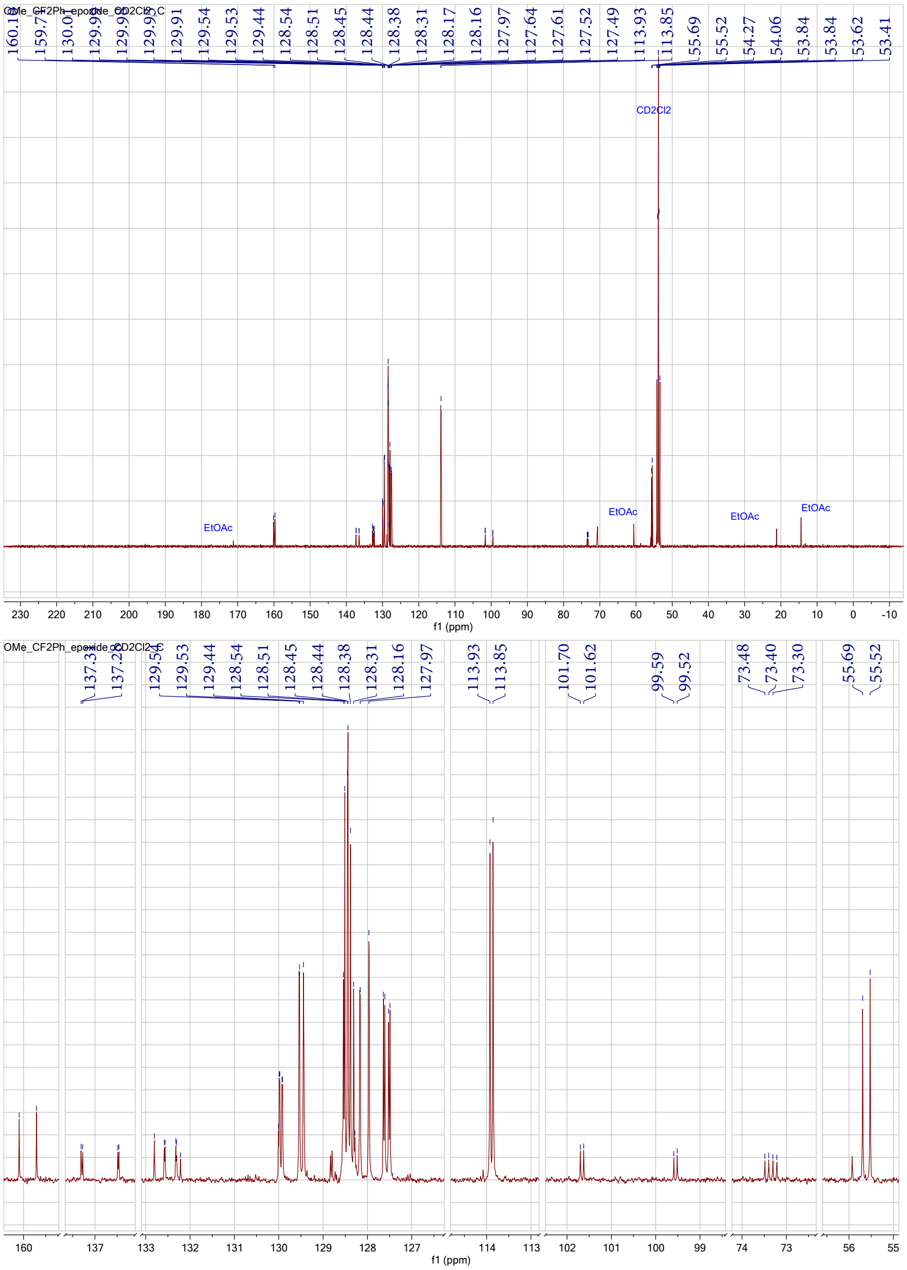

Figure S53. ^{13}C NMR spectra (CD_2Cl_2) of isolated **2f**. Top: full spectra and bottom: zoom-in spectra.

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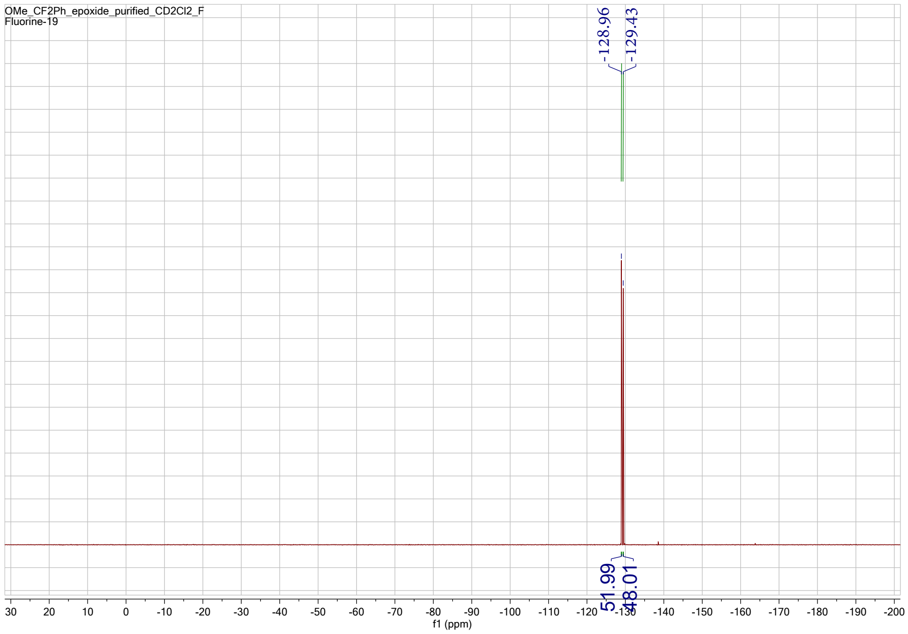

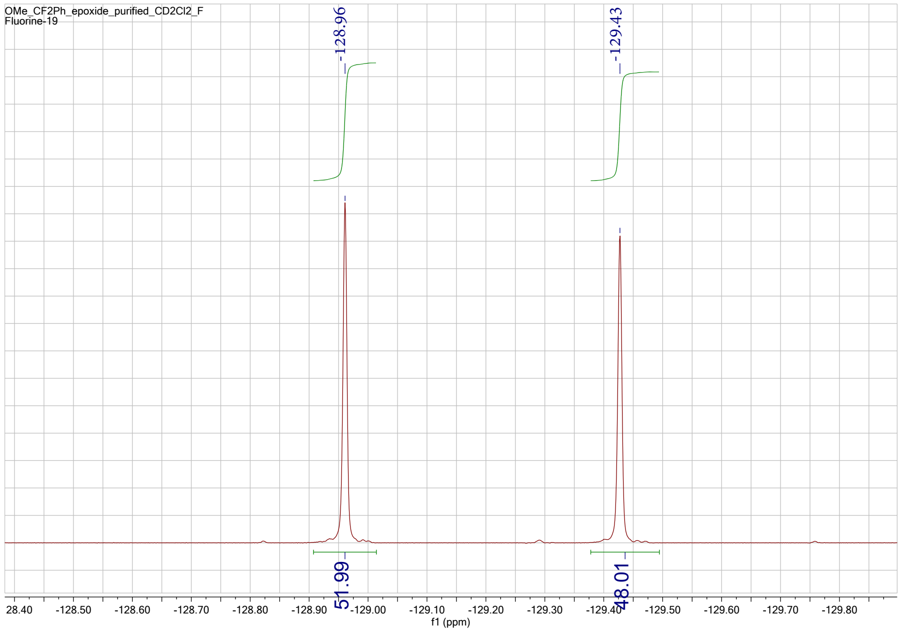

Figure S54. ^{19}F NMR spectra (CD_2Cl_2) of isolated **2f**. Top: full spectra and bottom: zoom-in spectra.

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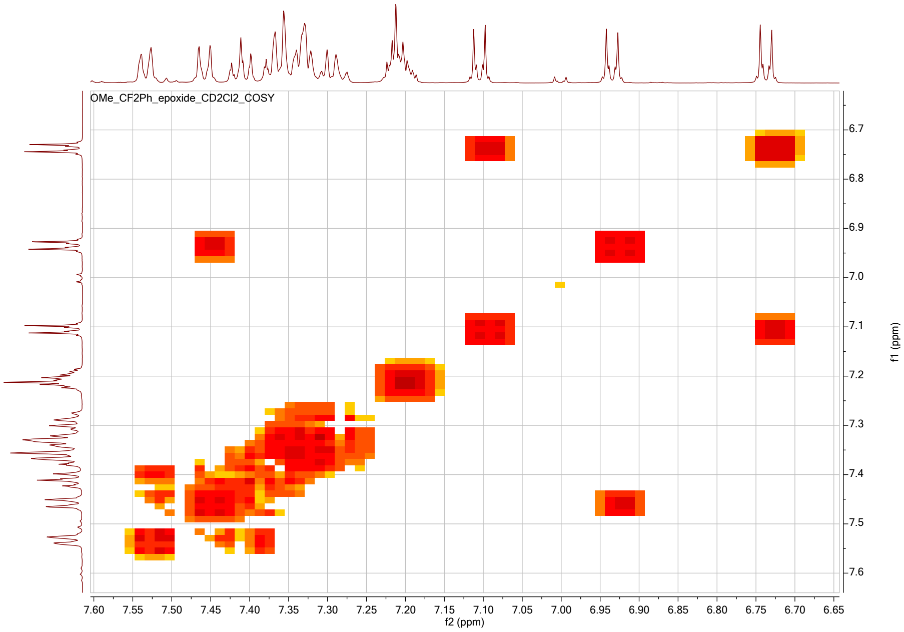

Figure S55. ^1H-^1H COSY spectra ($CDCl_3$) of isolated **2f**

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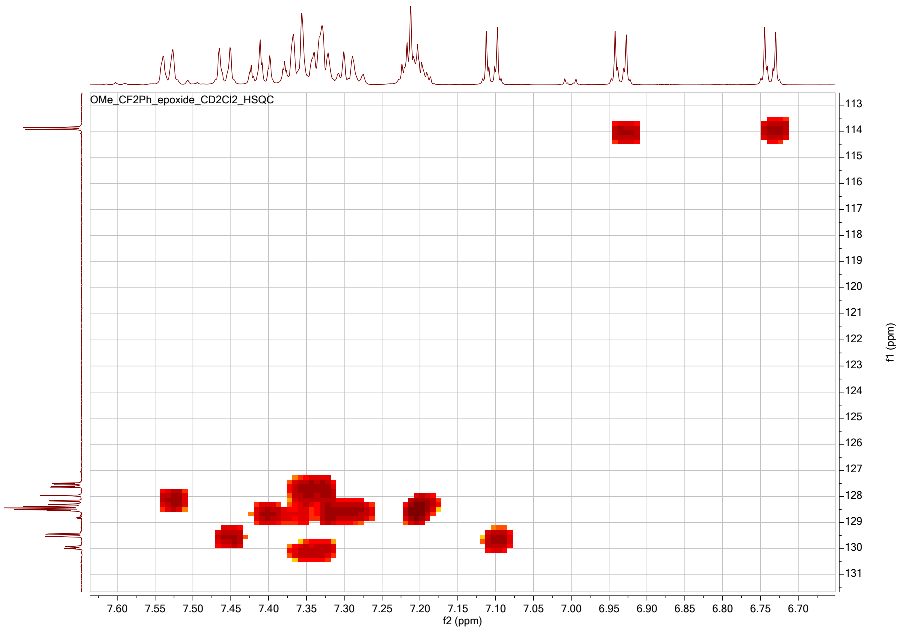

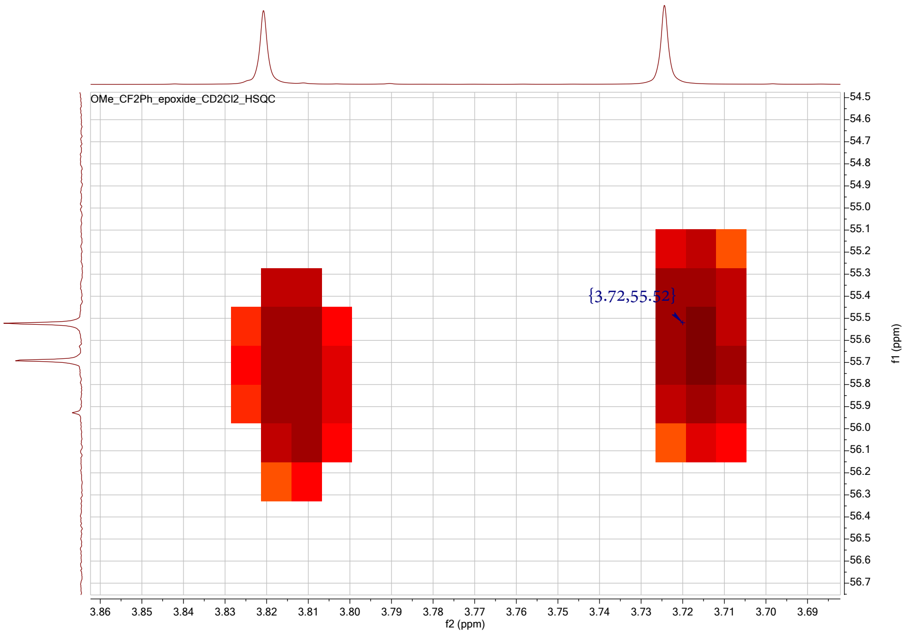

Figure S56. ^{1}H-^{13}C HSQC spectra (CDCl$_3$) of isolated **2f.** Top: full spectra and bottom: zoom-in spectra.

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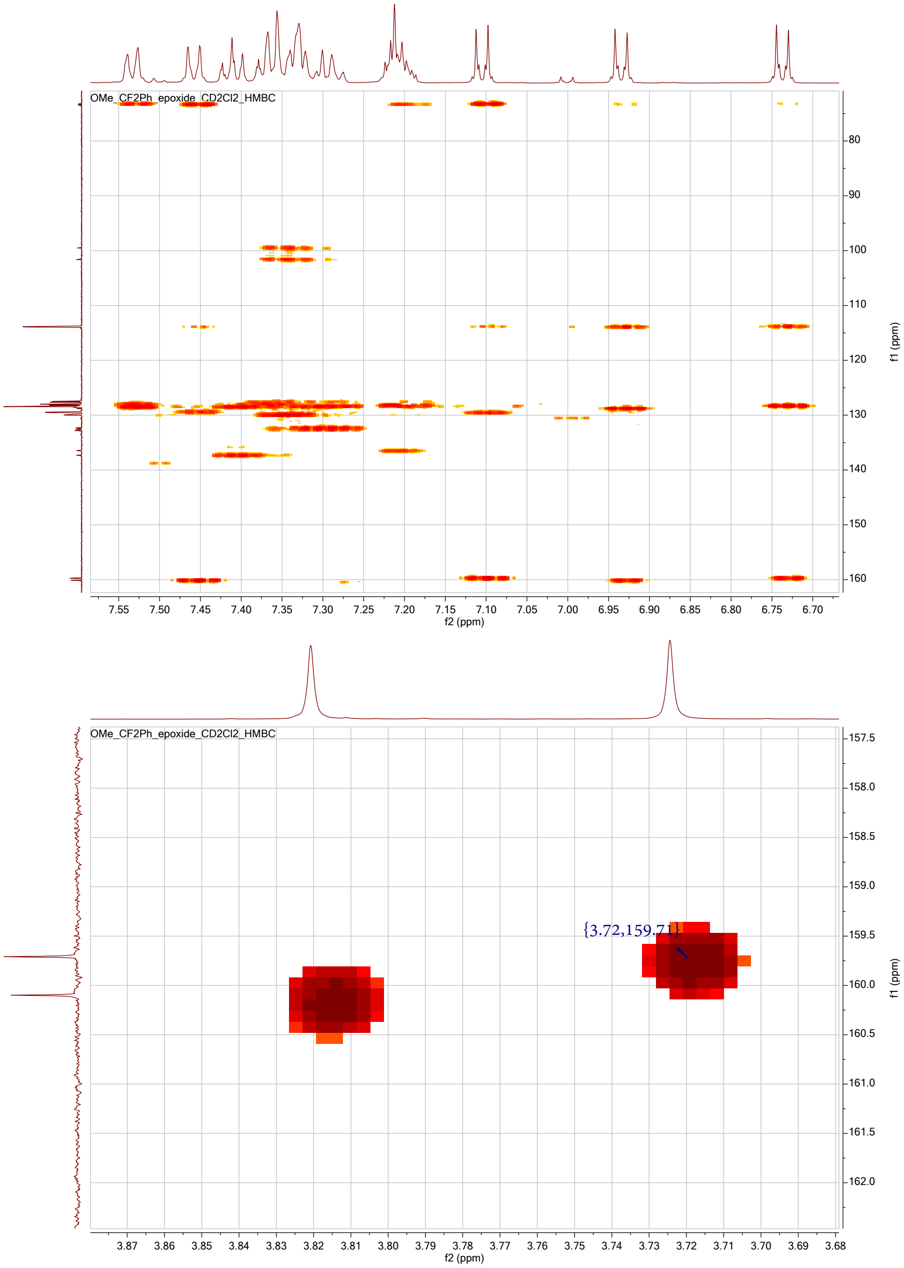
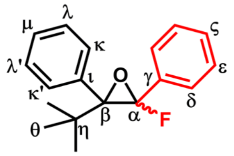


Figure S57. ^1H-^{13}C HMBC spectra ($CDCl_3$) of isolated **2f.** Top: full spectra and bottom: zoom-in spectra.



2g: 56%, d.r. = 87:13
(94 ± 4% d.r. = 90:10, n=2)

Colorless oil (0.4 mmol, 61 mg isolated, >99% purity), volatile under high vacuum. Inseparable mixture of diastereoisomers. ^{19}F NMR (471 MHz, CDCl$_3$) δ -96.83 (s, 1αF, minor isomer), -132.72 (s, 1αF, major isomer). Major isomer: ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.41 (d, *J* = 7.8 Hz, 1H, 1κH), 7.28 (t, *J* = 7.6 Hz, 1H, 1λH), 7.21 – 7.12 (m, 5H, 2δH + 2εH + 1ζH), 7.10 (tt, *J* = 7.4, 1.2 Hz, 1H, 1μH), 6.93 (t, *J* = 7.6, 1H, 1λ'H), 6.73 (d, *J* = 7.7 Hz, 1H, 1κ'H), 1.21 (m, 9H, 9θH). ^{13}C NMR (126 MHz, CDCl$_3$) δ 136.38 (d, *J* = 2.4 Hz, ιC), 133.42 (d, *J* = 33.4 Hz, γC), 128.96 (d, *J* = 1.8 Hz, εC), 128.56 (d, *J* = 3.4 Hz, κC), 127.80 (s, κ'C and λC), 127.71 (s, ζC), 127.18 (s, μC), 126.86 (d, *J* = 8.4 Hz, δC), 126.86 (s, λ'C), 101.47 (d, *J* = 267.7 Hz, αC), 77.62 (d, *J* = 20.6 Hz, βC), 35.64 (d, *J* = 5.6 Hz, ηC), 28.37 (d, *J* = 3.9 Hz, θC).

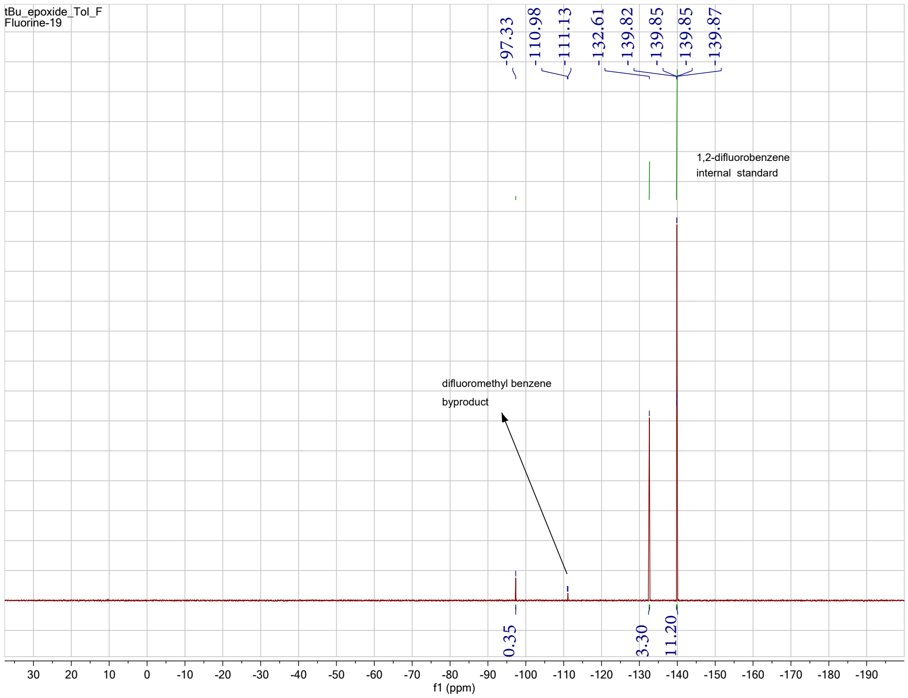


Figure S58. Representative *in situ* ^{19}F NMR spectra (in toluene) of **2g**. Top: full spectra and bottom: zoom-in spectra.

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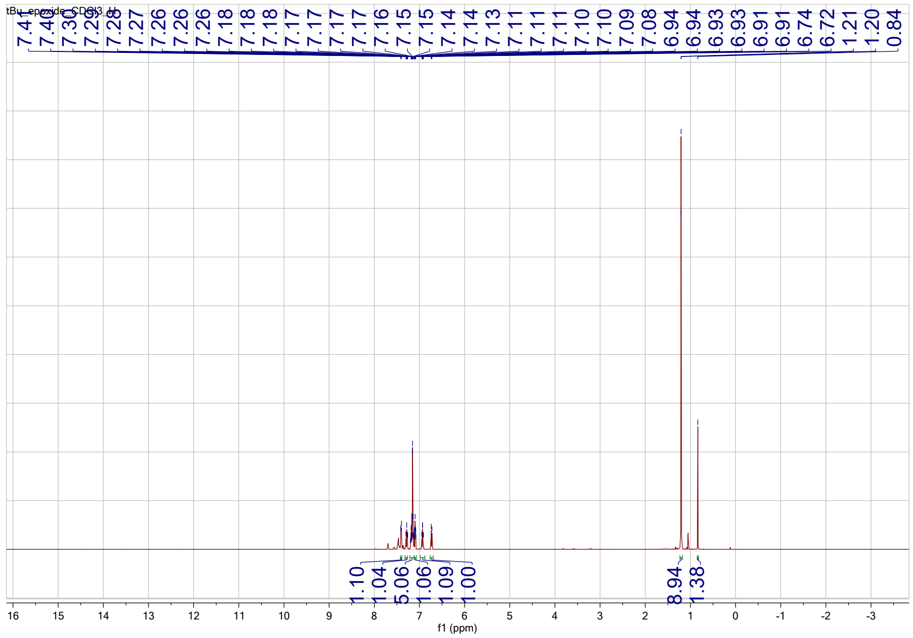

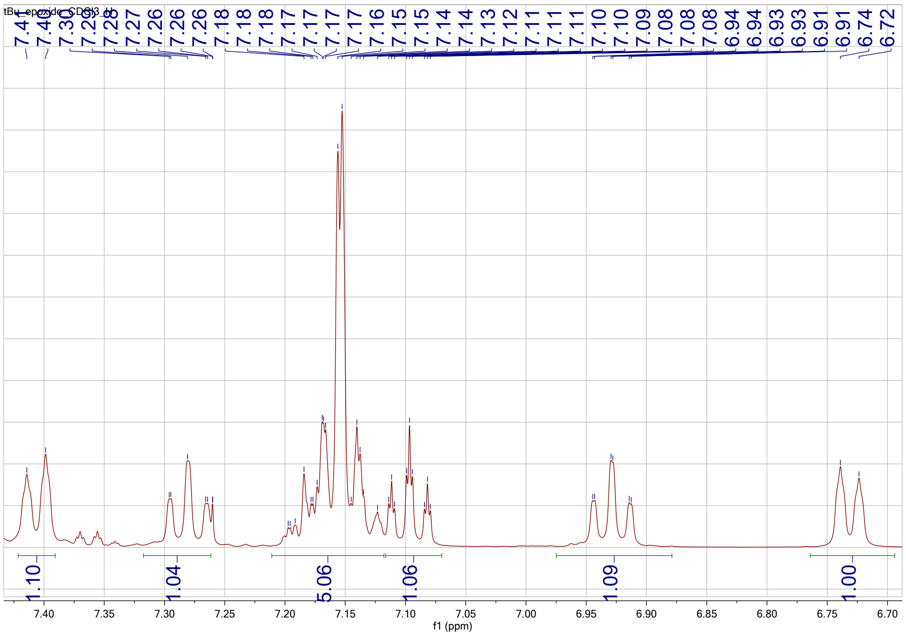

Figure S59. ^{1}H NMR spectra (CD_2Cl_2) of isolated **2g**. Top: full spectra and bottom: zoom-in spectra. Only Ar-H from the major isomer were labeled and integrated. The d.r. was calculated from the ^{1}H NMR spectra = 8.94 : 1.38 = 87:13.

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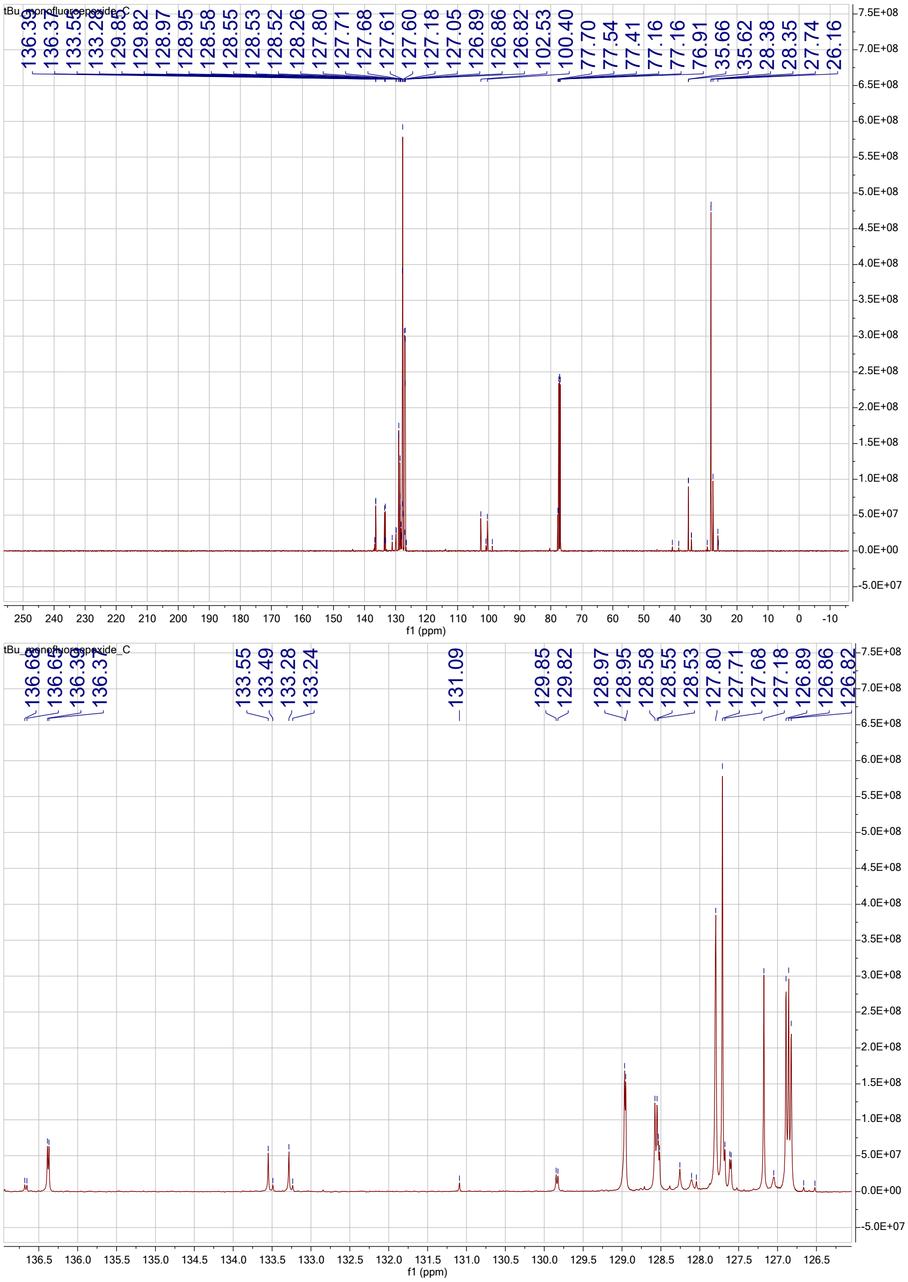

Figure S60. ^{13}C NMR spectra (CDCl$_3$) of isolated **2g**. Top: full spectra and bottom: zoom-in spectra.

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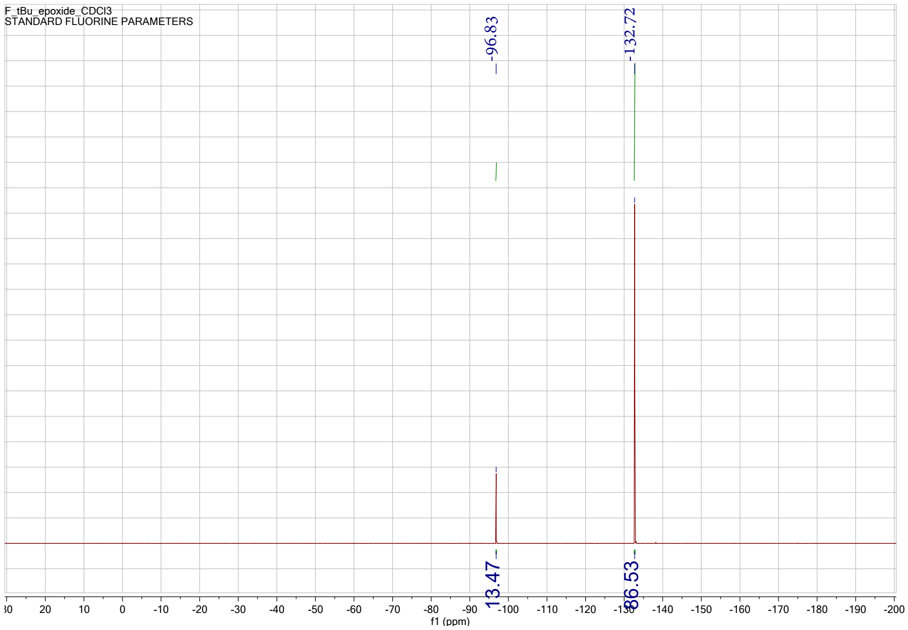


Figure S61. ^{19}F NMR spectra (CDCl$_3$) of isolated **2g**. d.r. = 87:13, in agreement with that determined by ^{1}H NMR (**Figure S59**).

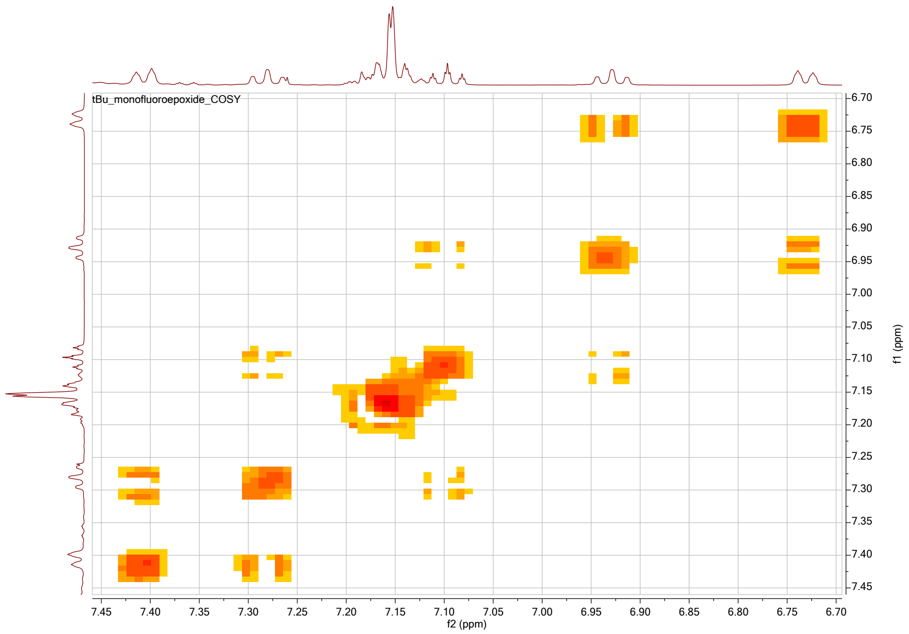
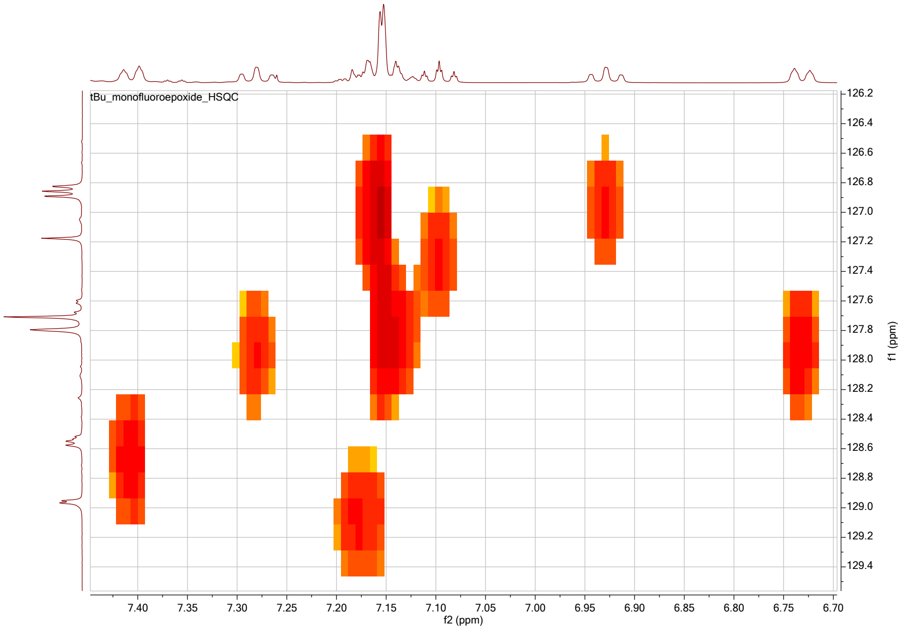


Figure S62. ^{1}H-^{1}H COSY spectra (CDCl$_3$) of isolated **2g**.



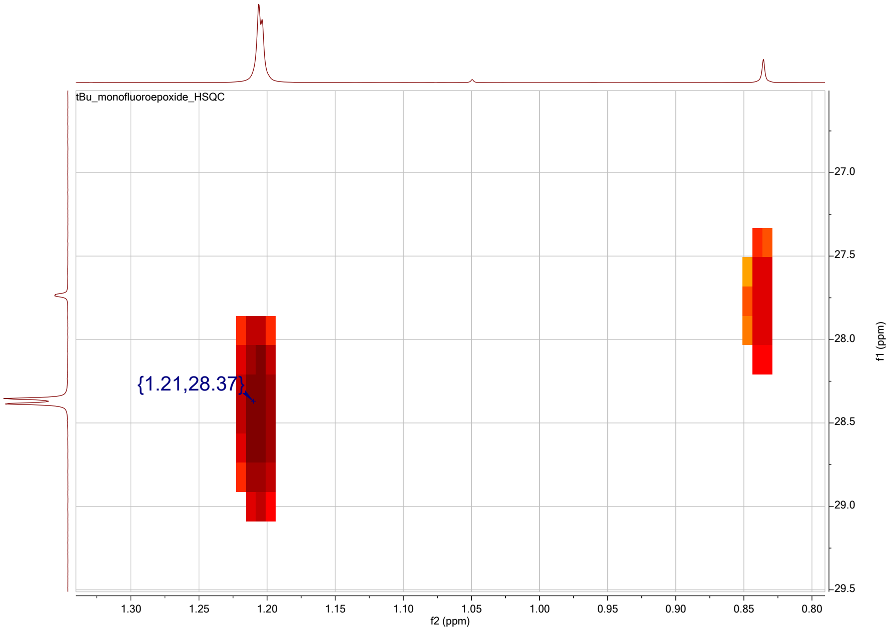


Figure S63. ^{1}H-^{13}C HSQC spectra ($CDCl_3$) of isolated **2g**. Top: full spectra and bottom: zoom-in spectra.

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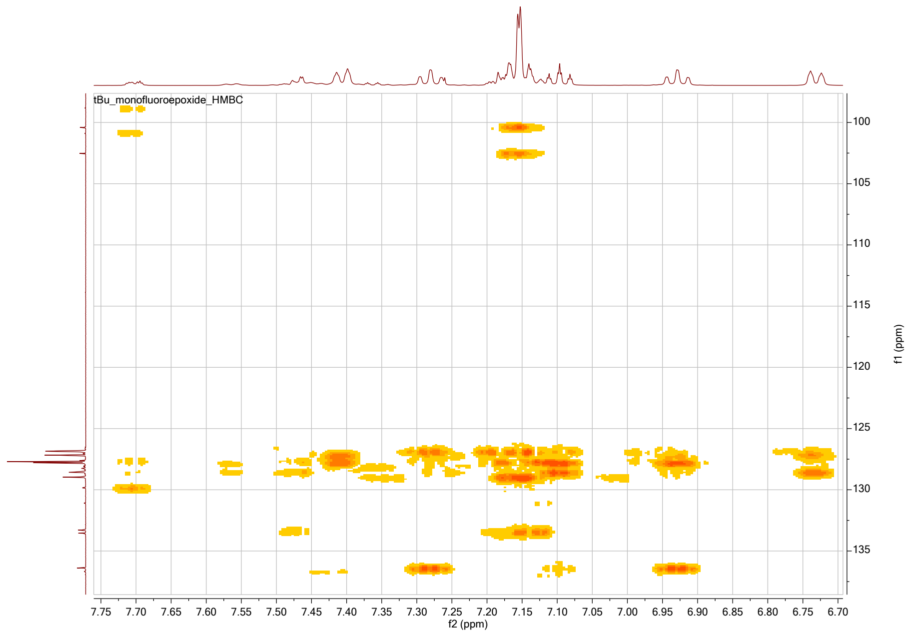

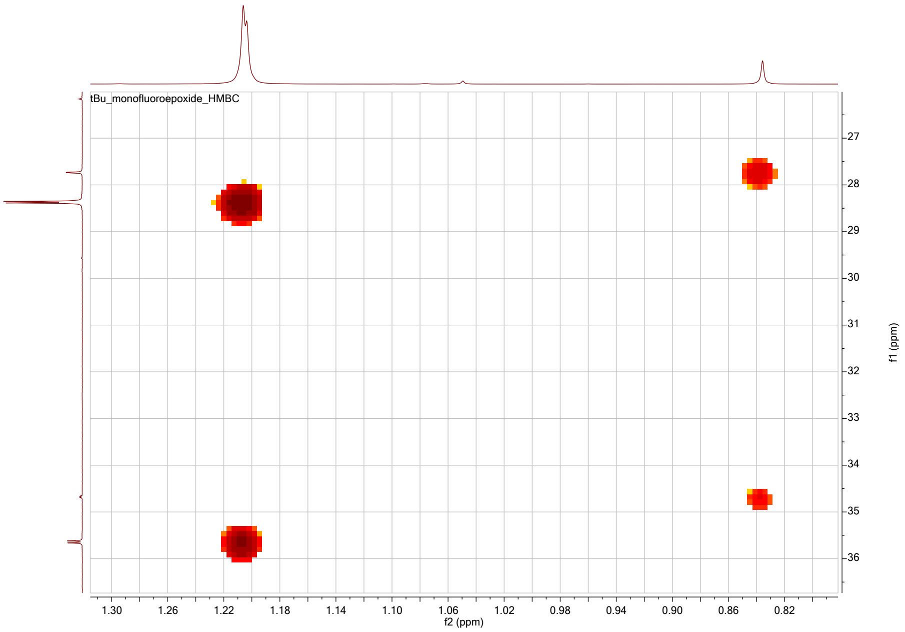

Figure S64. ^{1}H-^{13}C HMBC spectra (CDCl$_3$) of isolated **2g**. Top: full spectra and bottom: zoom-in spectra.

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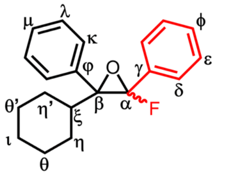

2h: 90%, d.r. = 81:19
(91 ± 9%, d.r. = 80:20, n=2)[
enolizable ketone]

White solid (0.4 mmol, 107 mg isolated, >99 % purity). Inseparable mixture of diastereoisomers. <u>Major isomer</u>: ^{19}F NMR (564 MHz, CD$_2$Cl$_2$) δ -136.90 (s, 1F). ^{1}H NMR (600 MHz, CD$_2$Cl$_2$) δ 7.27 – 7.23 (m, 1H), 7.22 – 7.15 (m, 7H), 7.06 (dd, *J* = 4.4, 2.6 Hz, 2H), 2.20 – 2.12 (m, 1H, ζH), 2.03 (dd, *J* = 24.3, 12.5 Hz, 2H), 1.81 – 1.74 (m, 2H), 1.71 – 1.62 (m, 1H, overlapping with the minor isomer), 1.57 – 1.44 (m, 1H), 1.43 – 1.32 (m, 2H), 1.11 (qd, *J* = 12.6, 3.7 Hz, 1H), 1.06 – 0.97 (m, 1H). ^{13}C NMR (126 MHz, CD$_2$Cl$_2$) δ 134.16 (d, *J* = 2.8 Hz), 133.05 (d, *J* = 32.7 Hz, γC), 129.50 (d, *J* = 1.7 Hz), 128.60 (d, *J* = 1.4 Hz), 128.15 (s), 127.90 (s), 127.73 (s), 127.14 (d, *J* = 4.3 Hz), 101.51 (d, *J* = 263.2 Hz, αC), 76.26 (d, *J* = 21.3 Hz, βC), 42.20 (d, *J* = 2.9 Hz, ζC), 29.75 (s), 28.60 (s), 26.55 (s), 26.48 (s), 26.34 (s). <u>Minor isomer</u>: ^{19}F NMR (564 MHz, CD$_2$Cl$_2$) δ -118.82 (s, 1F). ^{13}C NMR (126 MHz, CD$_2$Cl$_2$) δ 134.69 (d, *J* = 3.8 Hz), 132.41 (d, *J* = 32.4 Hz, γC), 130.24 (d, *J* = 2.1 Hz), 128.76 (d, *J* = 1.0 Hz), 128.31 (s), 128.15 (s), 128.13 (s), 127.67 (t, *J* = 3.7 Hz), 100.94 (d, *J* = 261.2 Hz, αC), 75.37 (d, *J* = 22.3 Hz, βC), 41.62 (d, *J* = 3.4 Hz, ζC), 29.36 (s), 27.49 (d, *J* = 2.0 Hz, ηC), 26.23 (s), 26.19 (s), 25.98 (s).

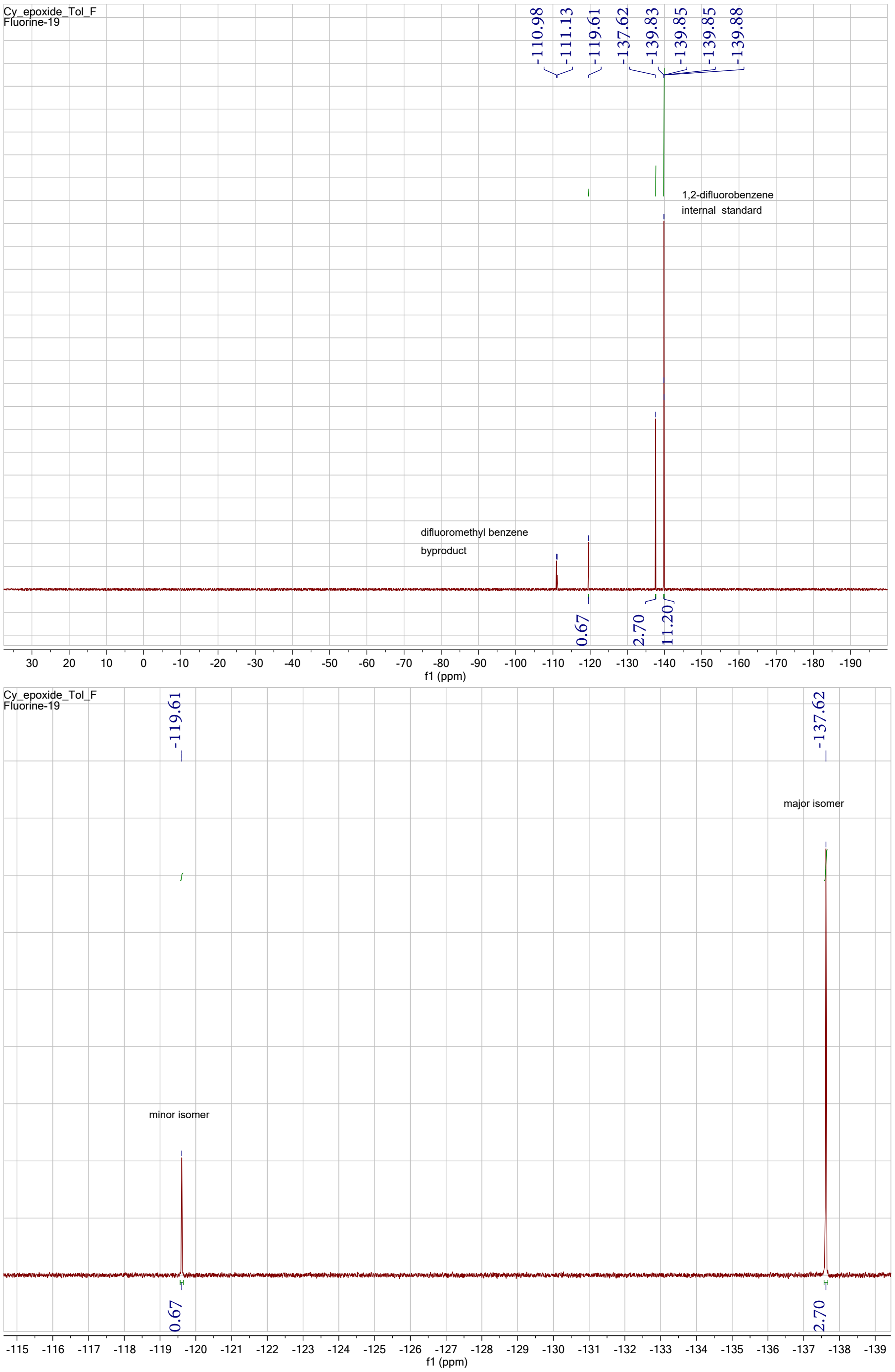

Figure S65. Representative *in situ* ^{19}F NMR spectra (in toluene) of **2h**. Top: full spectra and bottom: zoom-in spectra.

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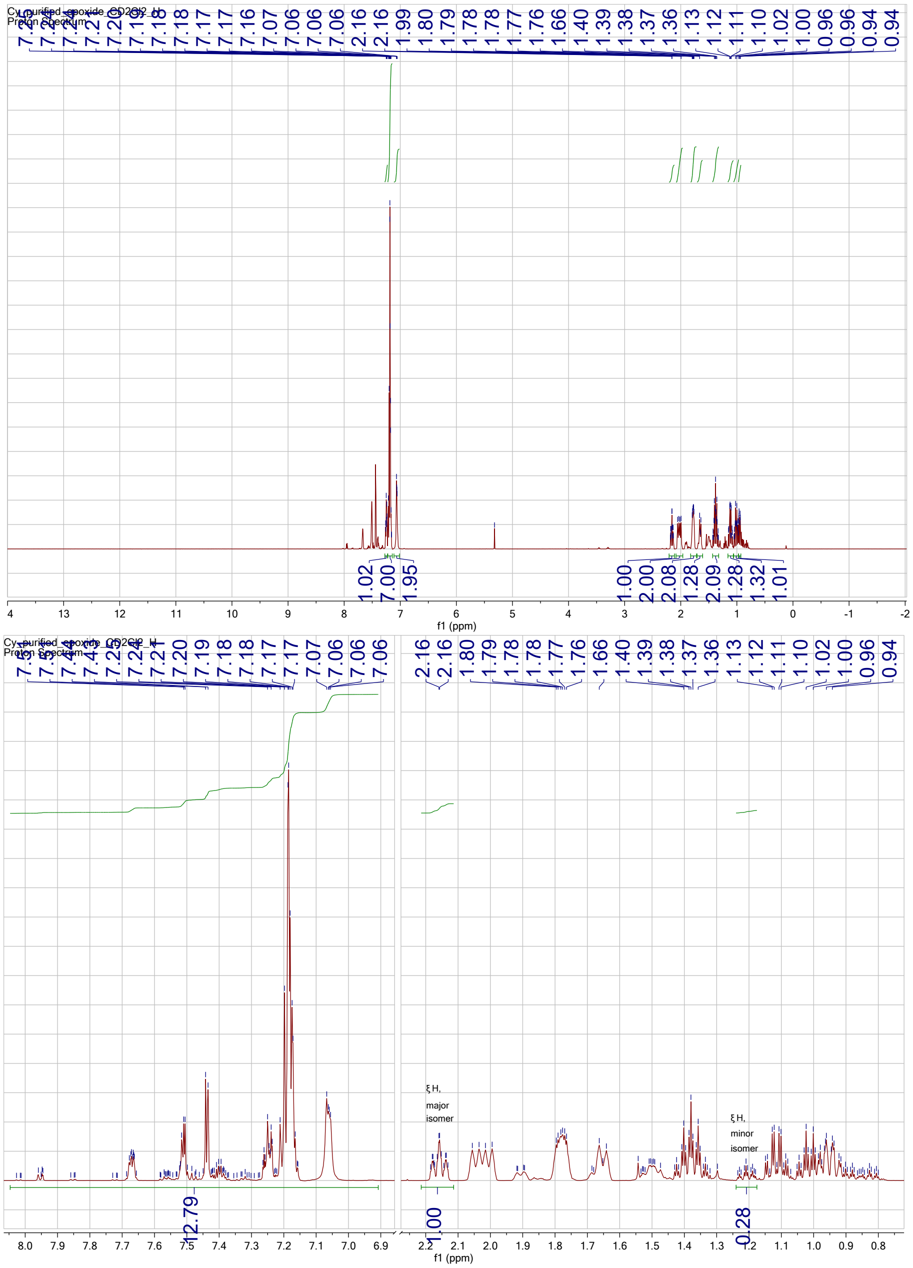

Figure S66. ^{1}H NMR spectra (CD_2Cl_2) of isolated **2h**. Top: full spectra and bottom: zoom-in spectra. The d.r. obtained from the ^{1}H NMR spectra is 78:22 based on the integration of ξH, consistent with that calculated from the ^{19}F NMR spectra (80:20). The integration of the total Ar-H is expected to be 10 + (10 * 22/78) = 12.82, close to the observed integration (12.79). Peaks and integration of the major isomer was selectively labelled in the right figure.

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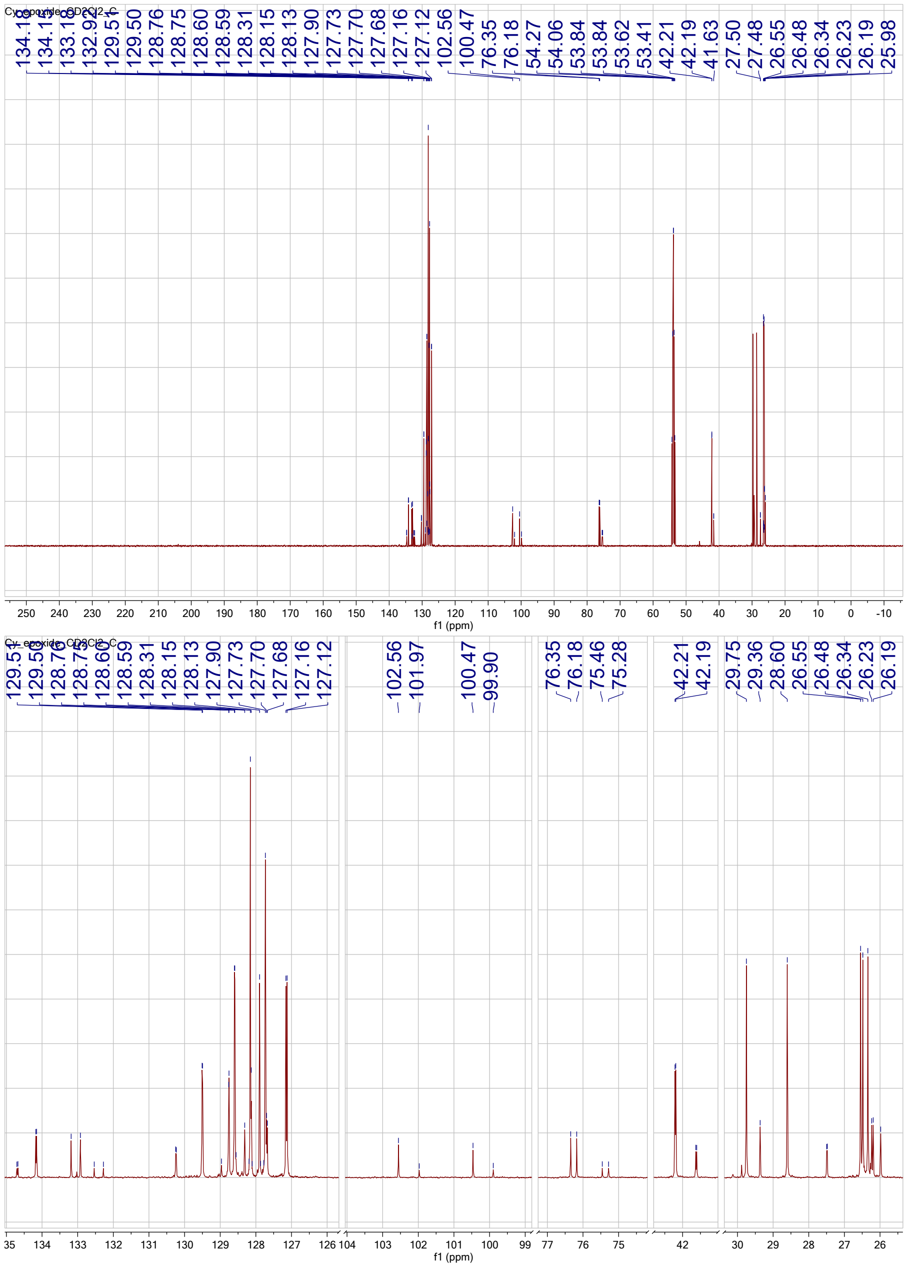

Figure S67. ^{13}C NMR spectra (CD_2Cl_2) of isolated **2h**. Top: full spectra and bottom: zoom-in spectra.

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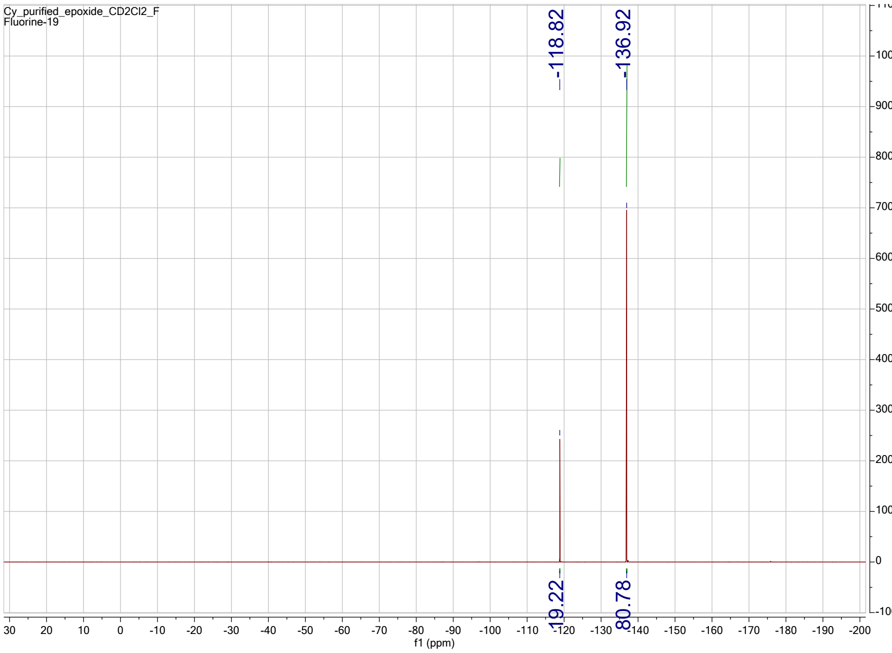

Figure S68. ^{19}F NMR spectra (CD_2Cl_2) of isolated **2h**.

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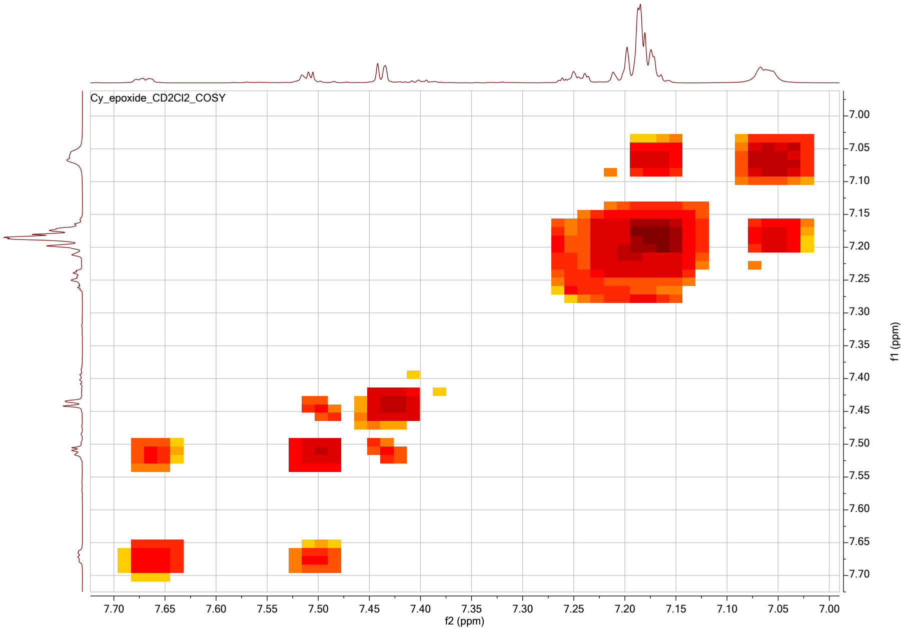

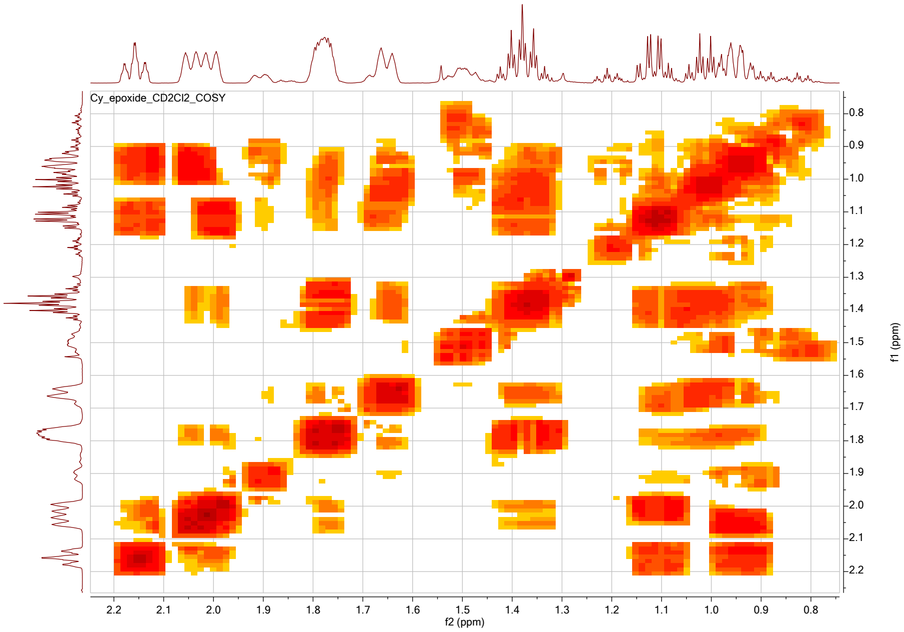

Figure S69. ^{1}H-^{1}H COSY spectra ($CDCl_3$) of isolated **2h**. Top: full spectra and bottom: zoom-in spectra.

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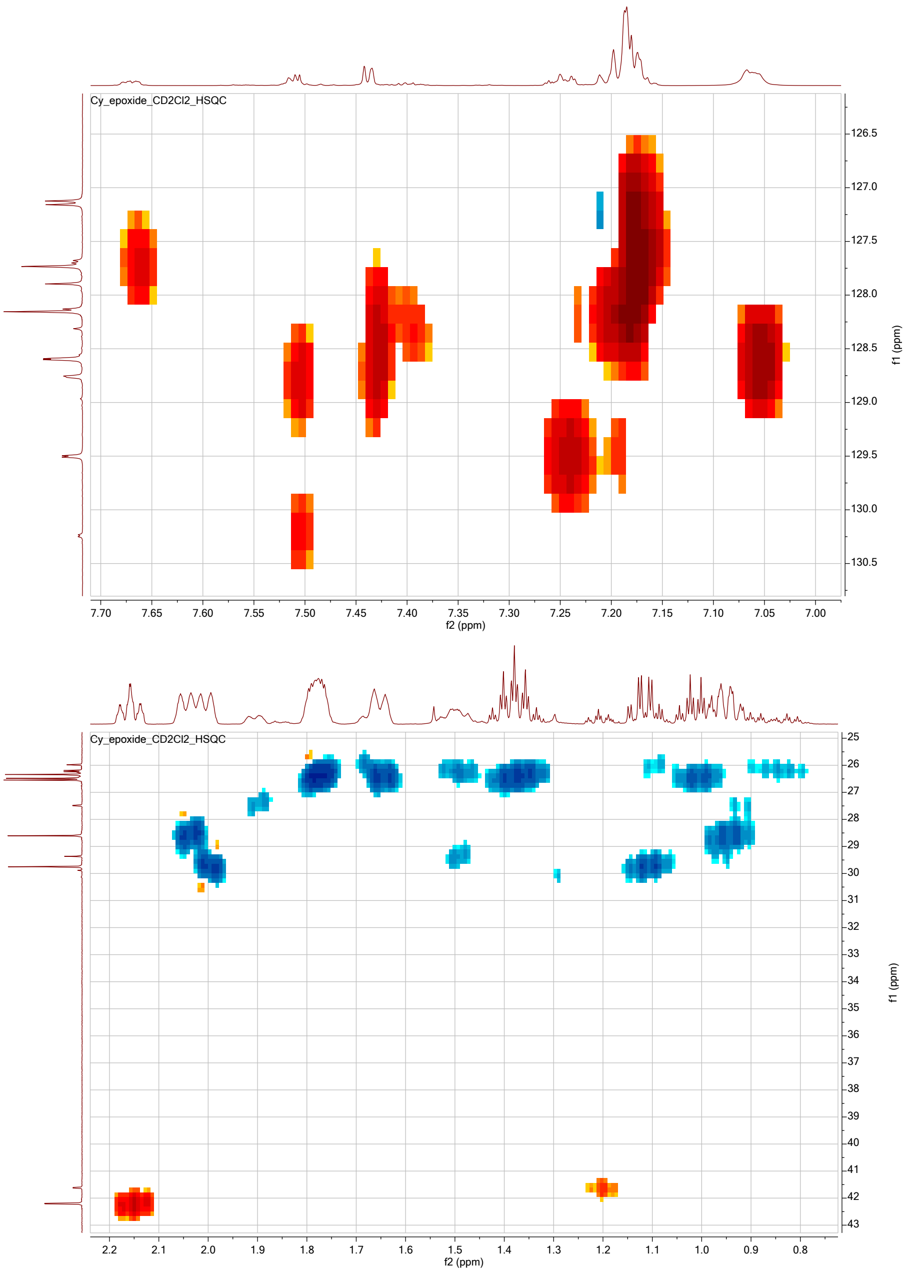

Figure S70. ^{1}H-^{13}C HSQC spectra (CD_2Cl_2) of isolated **2h**. Top: full spectra and bottom: zoom-in spectra.

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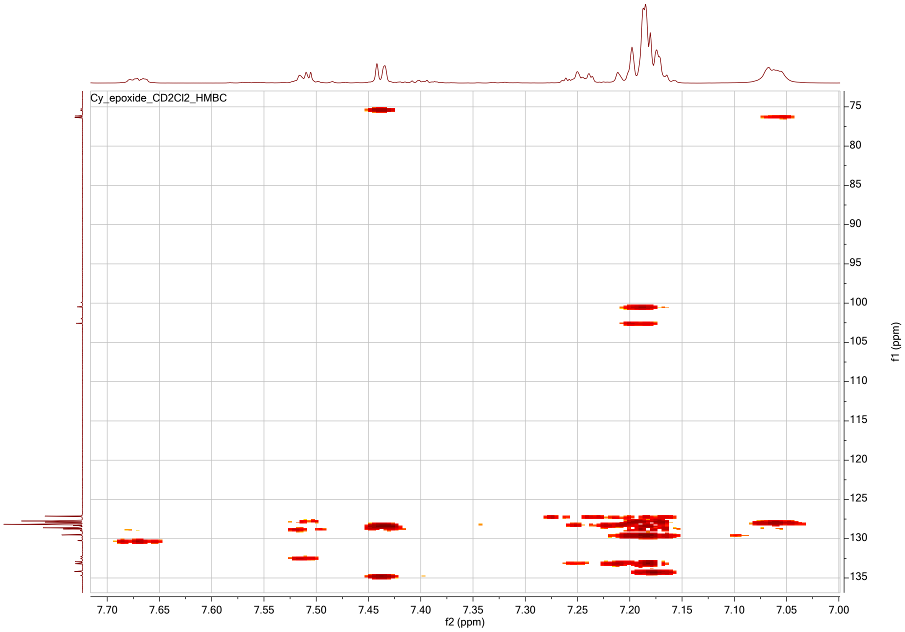

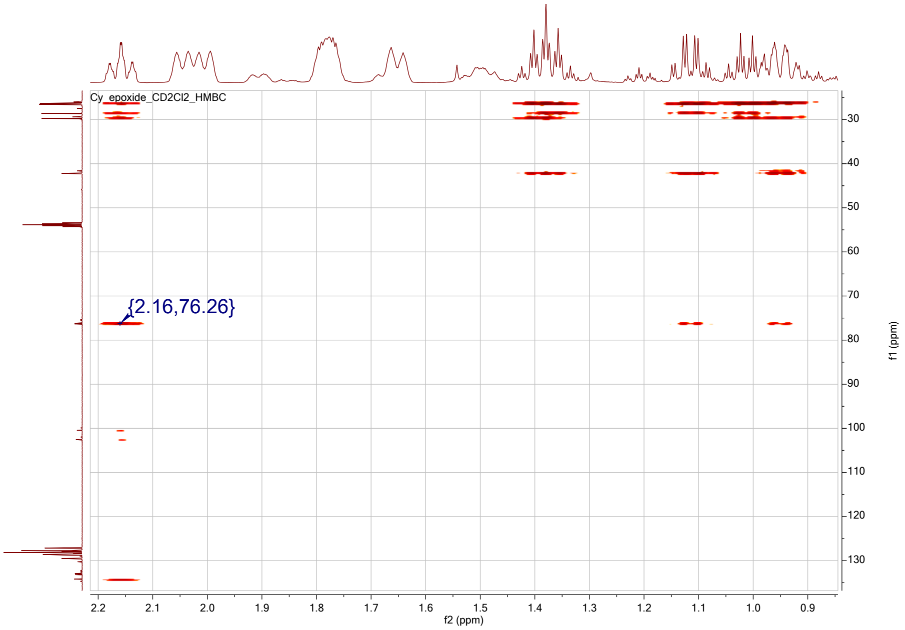

Figure S71. ^{1}H-^{13}C HMBC spectra (CD_2Cl_2) of isolated **2h.**

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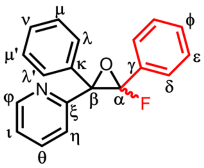

2i: 88%, d.r. = 60:40
(93 ± 1%, d.r. = 60:40, n=2)

Yellow oil (0.4 mmol, 102.4 mg isolated, >99% purity). Inseparable mixture of diastereoisomers. ^{19}F NMR (564 MHz, CD$_2$Cl$_2$) δ -128.06 (s, minor isomer, 1F), -128.84 (s, major isomer, 1F). ^{1}H NMR (600 MHz, cd$_2$cl$_2$) δ 8.61 (dt, *J* = 4.8, 1.3 Hz, 1H, φH major isomer), 8.44 – 8.41 (m, 1H, φH minor isomer), 7.82 – 7.77 (m, 3H major isomer + 1H minor isomer), 7.59 (td, *J* = 7.7, 1.8 Hz, 1H, θH minor isomer), 7.49 – 7.20 (m, 10H major isomer + 10H minor isomer), 7.10 (ddd, *J* = 7.6, 4.8, 1.1 Hz, 1H, ιH minor isomer). ^{13}C NMR (126 MHz, CD$_2$Cl$_2$) δ 156.35 (d, *J* = 4.6 Hz, ξC, major isomer), 155.63 (d, *J* = 3.3 Hz, ξC, minor isomer), 149.47 (s, φC, major isomer), 149.46 (s, φC, minor isomer), 137.01 (s, θC, major isomer), 136.76 (s, θC, minor isomer), 135.49 (d, *J* = 4.4 Hz, κC, minor isomer), 135.02 (d, *J* = 3.0 Hz, κC, major isomer), 131.86 (d, *J* = 31.9 Hz, γC, minor isomer), 131.63 (d, *J* = 31.8 Hz, γC, major isomer), 130.18 (d, *J* = 1.7 Hz), 130.09 (d, *J* = 1.7 Hz), 128.81 (s), 128.53 (s), 128.47 (s), 128.45 (s), 128.35 (s), 128.33 (s), 128.20 (s), 128.04 (s), 127.56 (d, *J* = 4.0 Hz, δC, major isomer), 127.37 (d, *J* = 3.8 Hz, δC, minor isomer), 123.44 (s, ιC, major isomer), 123.18 (s, ιC, minor isomer), 122.38 (d, *J* = 2.3 Hz), 121.92 (d, *J* = 1.2 Hz), 100.47 (d, *J* = 266.6 Hz, αC, major isomer), 100.27 (d, *J* = 267.0 Hz, αC, minor isomer), 73.25 (d, *J* = 23.2 Hz, βC, major isomer), 73.04 (d, *J* = 23.1 Hz, βC, minor isomer). HR-MS (ESI): calcd. for [M - F]$^+$ = 272.1070 (C$_{19}$H$_{14}$NO$^+$), found: 272.1065; calcd. for [M - COF]$^+$ = 244.1121 (C$_{18}$H$_{14}$N$^+$), found: 244.1115.

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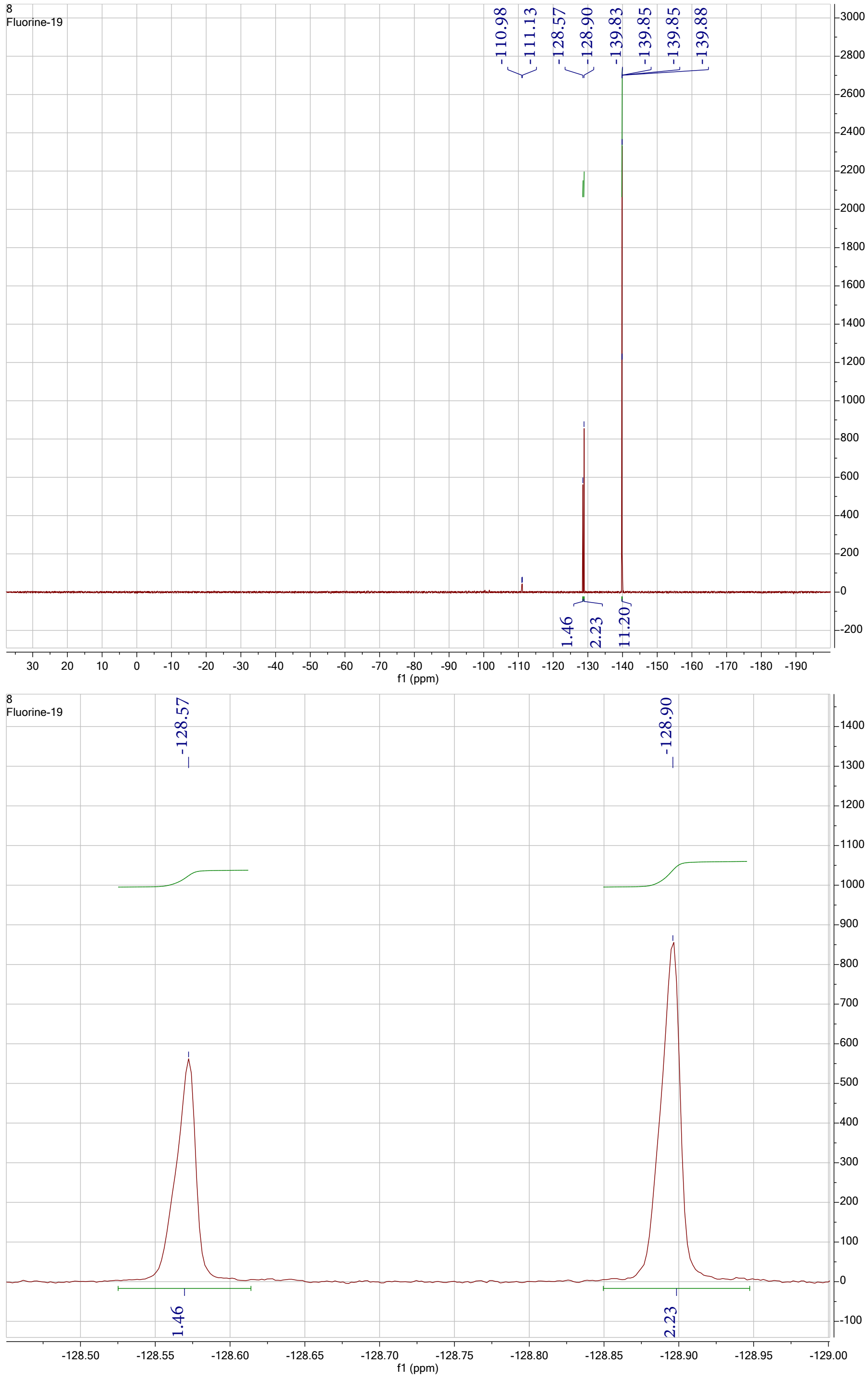

Figure S72. Representative *in situ* ^{19}F NMR spectra (in toluene) of **2i**. Top: full spectra and bottom: zoom-in spectra.

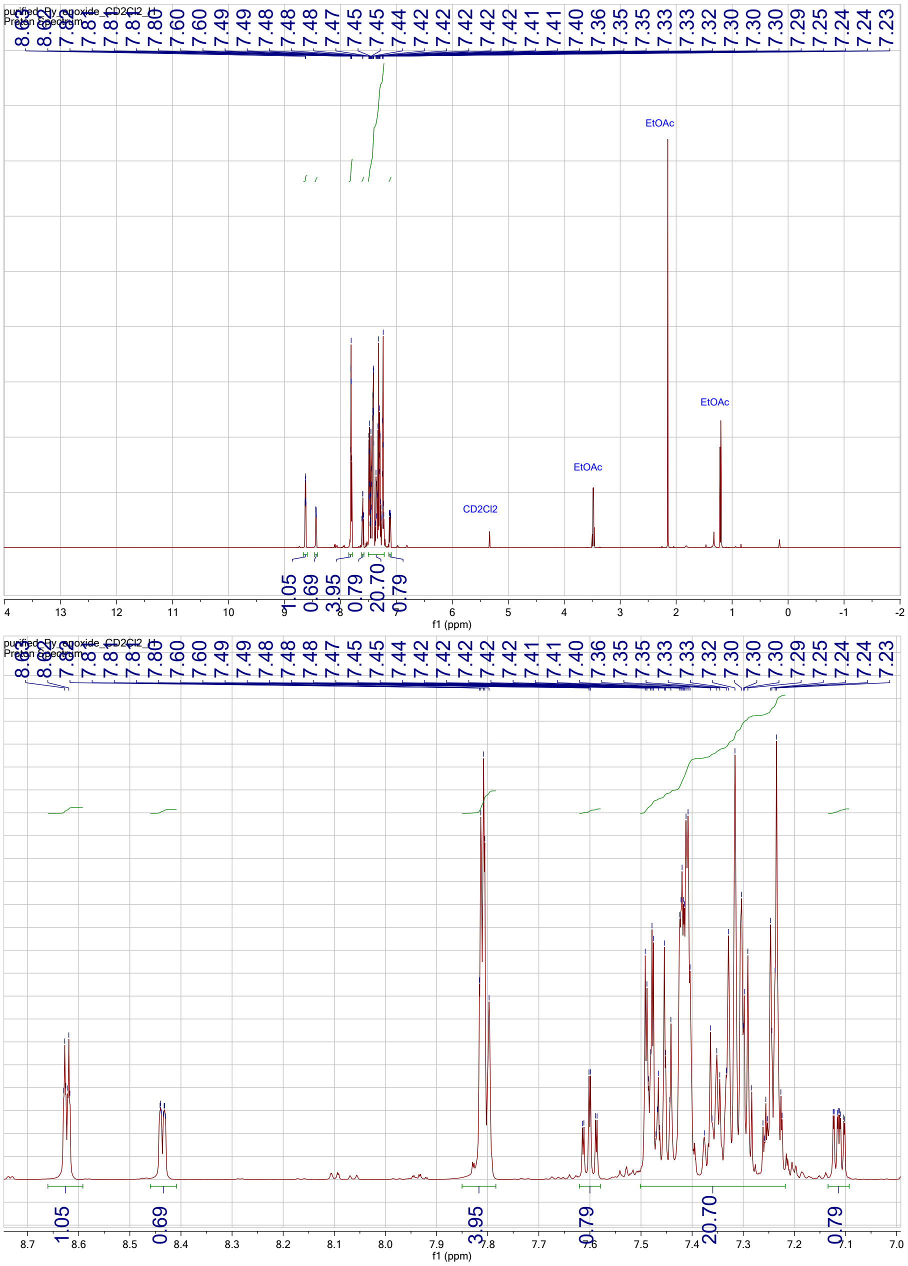

Figure S73. ^1H NMR spectra (CD_2Cl_2) of isolated **2i**. Top: full spectra and bottom: zoom-in spectra. d.r. determined by ^1H NMR spectroscopy = 1.05:0.69 = 60:40.

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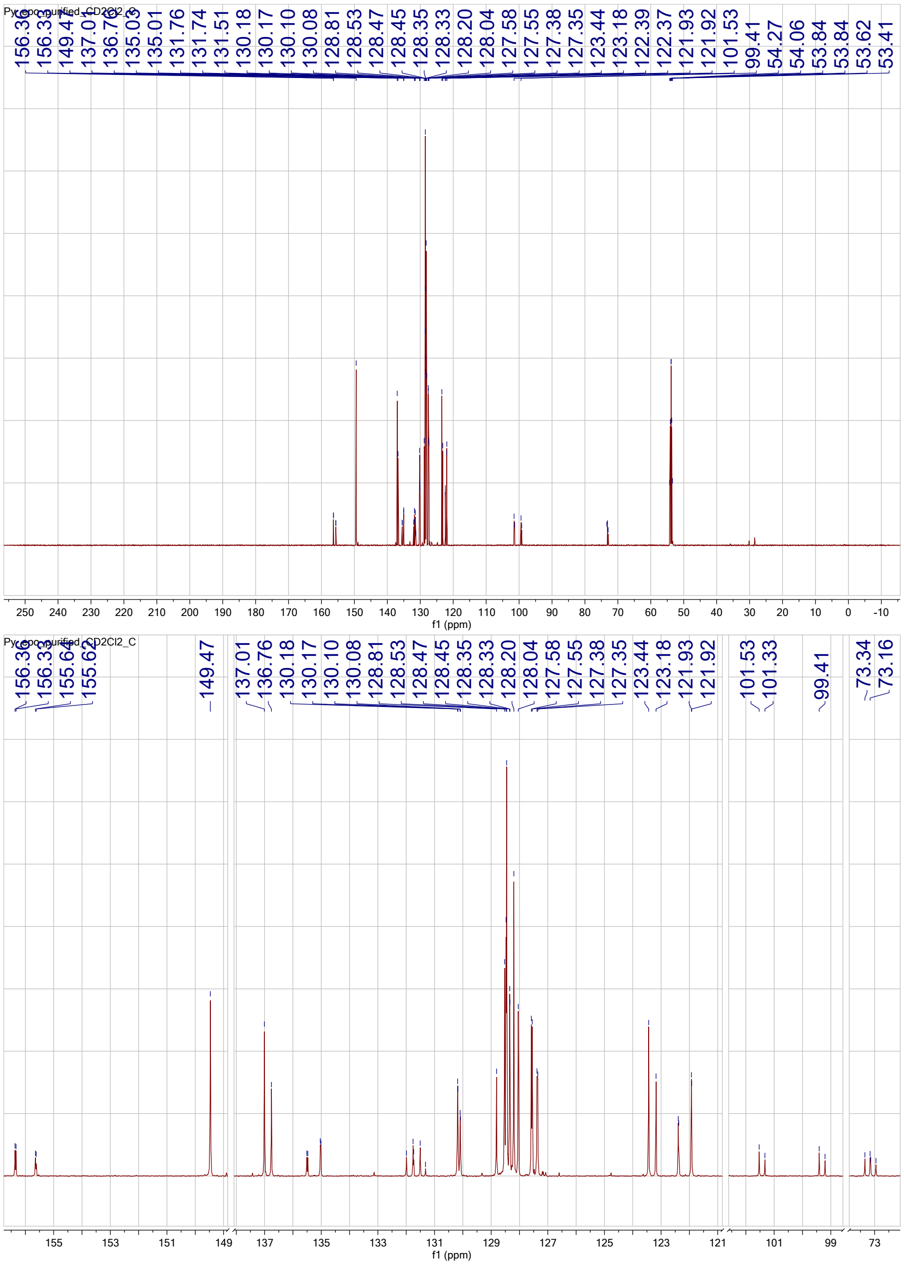

Figure S74. ^{13}C NMR spectra (CD_2Cl_2) of isolated **2i**. Top: full spectra and bottom: zoom-in spectra.

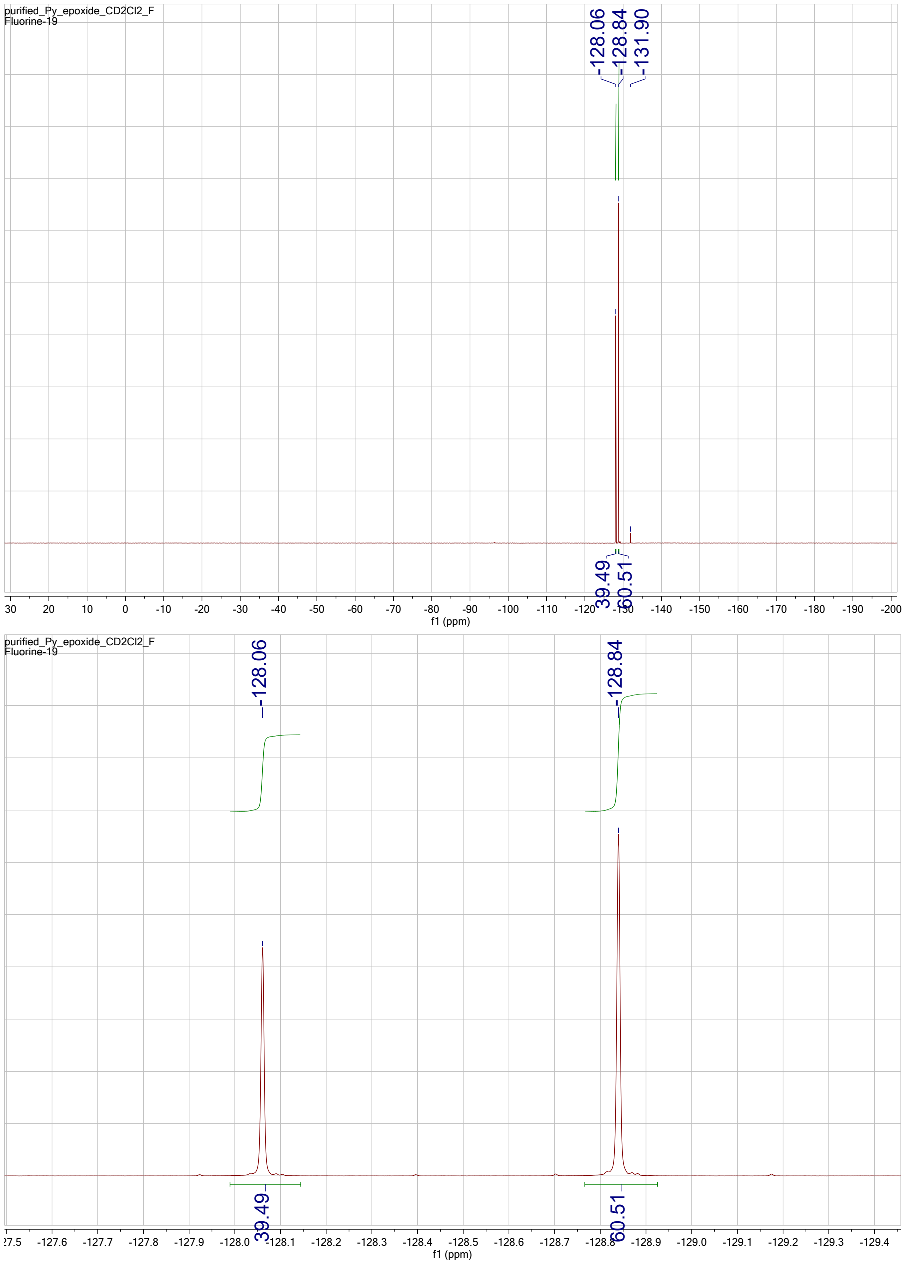

Figure S75. ^{19}F NMR spectra (CD_2Cl_2) of isolated **2i**. Top: full spectra and bottom: zoom-in spectra. d.r. determined by ^{19}F NMR spectroscopy = 60:40, consistent with the results from ^{1}H NMR spectroscopy (**Figure S73**).

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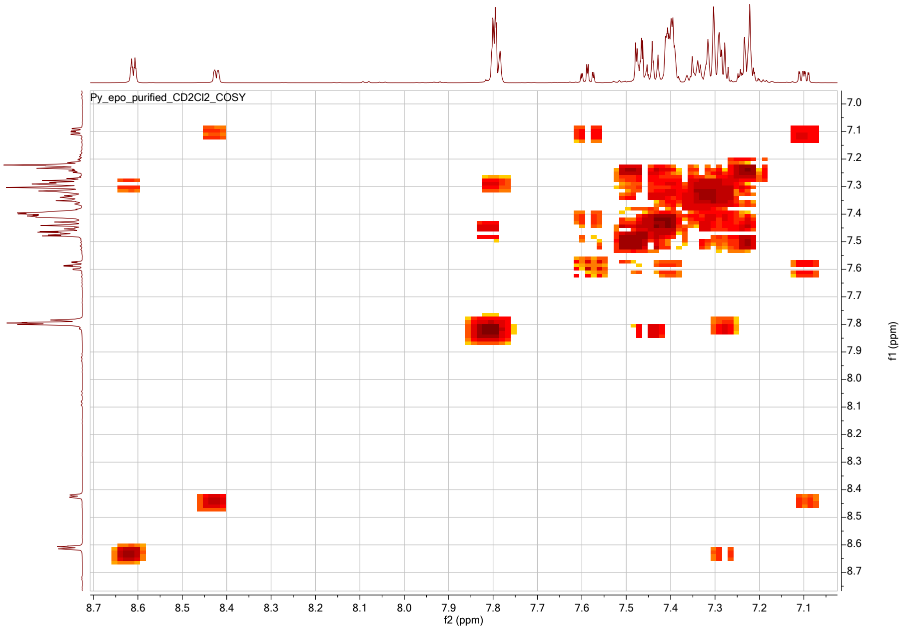

Figure S76. ^{1}H-^{1}H COSY spectra (CD_2Cl_2) of isolated **2i**.

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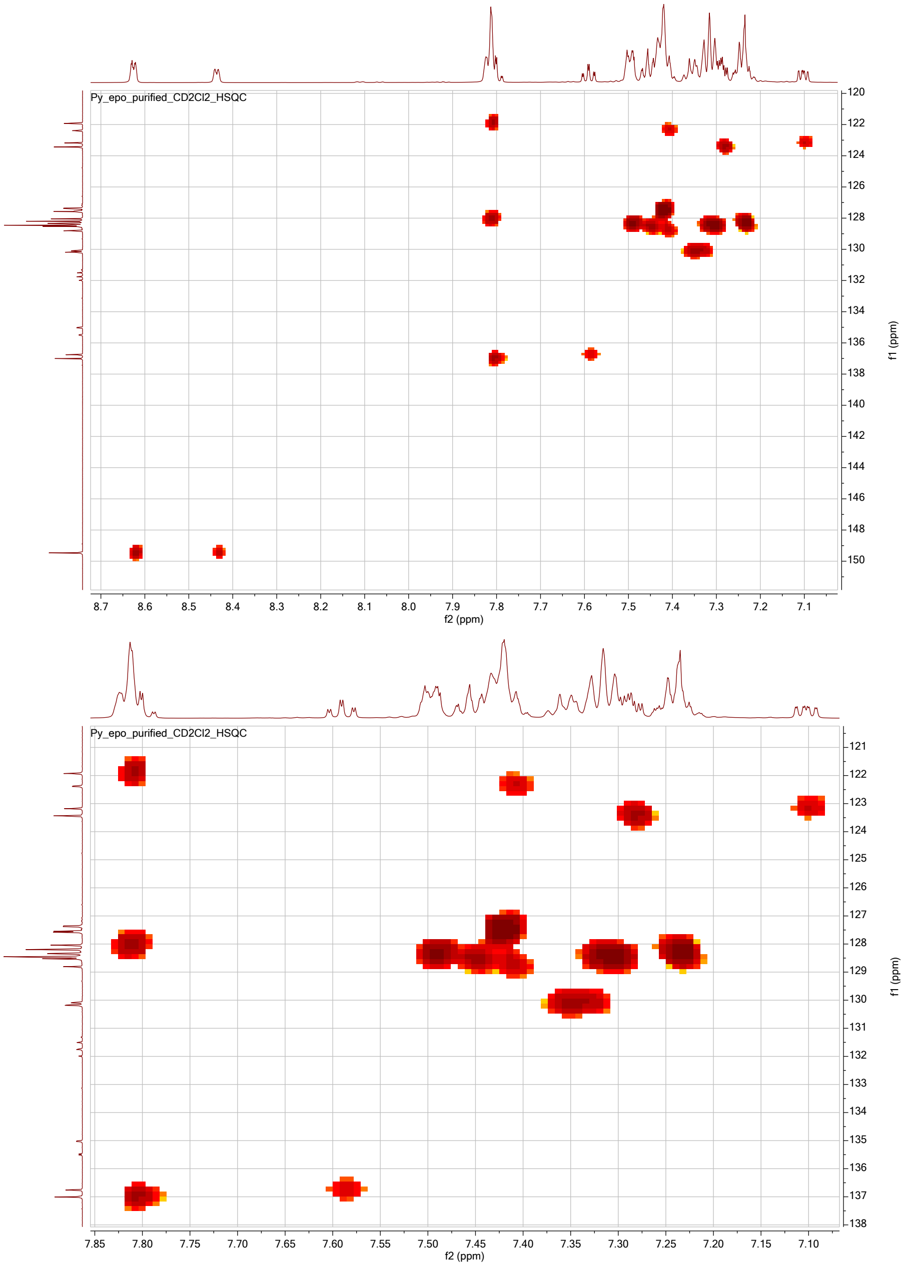


Figure S77. ^{1}H-^{13}C HSQC spectra (CD_2Cl_2) of isolated **2i**.

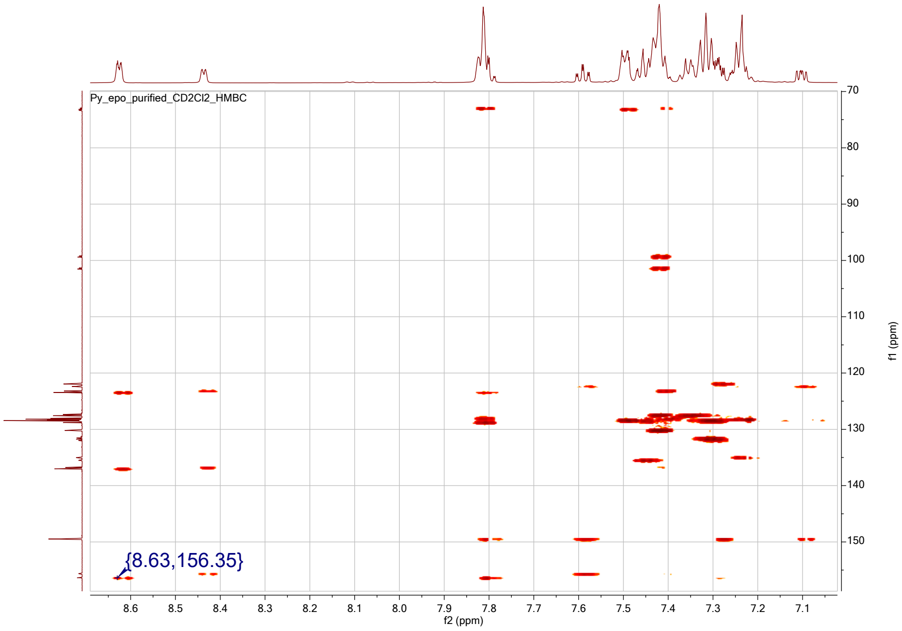
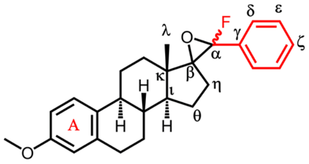
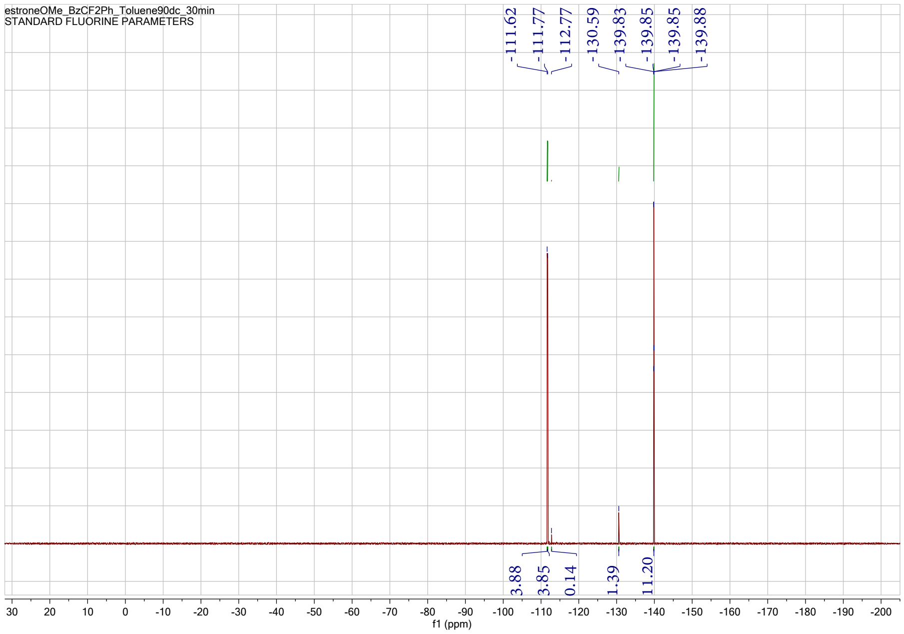


Figure S78. ^{1}H-^{13}C HMBC spectra (CD_2Cl_2) of isolated **2i.**



2j: 36%, d.r. = 82:18
(40 ± 5%, d.r.=91:9, n=2)
[from Estrone]

Yellow oil (0.4 mmol, 56.5 mg isolated, >99% purity). Inseparable mixture of diastereoisomers. ^{19}F NMR (564 MHz, CD_2Cl_2) δ -110.73 (s, 1F, minor isomer), -128.19 (s, 1F, major isomer). Major isomer: ^{13}C NMR (126 MHz, CD_2Cl_2) δ 157.95 (s, A ring -OMe), 138.27 (s, A ring substituted C), 133.63 (d, J = 33.6 Hz, γC), 132.81 (s, A ring substituted C), 129.79 (d, J = 1.6 Hz, εC), 128.60 (s, A ring substituted C), 127.07 (d, J = 3.7 Hz, δC), 126.65 (s, A ring unsubstituted C), 114.02 (s, A ring unsubstituted C), 111.74 (s, A ring unsubstituted C), 103.17 (d, J = 265.3 Hz, αC), 80.67 (d, J = 19.9 Hz, βC), 55.47 (s), 52.73 (s), 44.34 (s), 43.92 (s), 39.51 (s), 34.56 (d, J = 9.8 Hz), 30.10 (s), 28.77 (d, J = 2.2 Hz), 27.55 (s), 26.83 (d, J = 3.0 Hz), 23.52 (s), 15.14 (s). ^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.53 – 7.39 (m, 1H), 7.23 (d, J = 8.6 Hz, 1H), 6.70 (dt, J = 9.5, 4.8 Hz, 1H), 6.66 – 6.62 (m, 1H), 3.77 (d, J = 1.7 Hz, 1H), 2.94 – 2.79 (m, 1H), 2.43 – 2.33 (m, 1H), 2.31 – 2.24 (m, 1H), 2.09 – 1.82 (m, 1H), 1.74 – 1.62 (m, 1H), 1.61 – 1.31 (m, 1H), 1.14 (s, 1H). HR-MS (ESI): calcd. for $[M + H]^+$ = 393.2224 ($C_{26}H_{30}FO_2^+$), found: 393.2220; calcd. for $[M - COPh]^+$ = 287.1806 ($C_{19}H_{24}FO^+$), found: 287.1491.



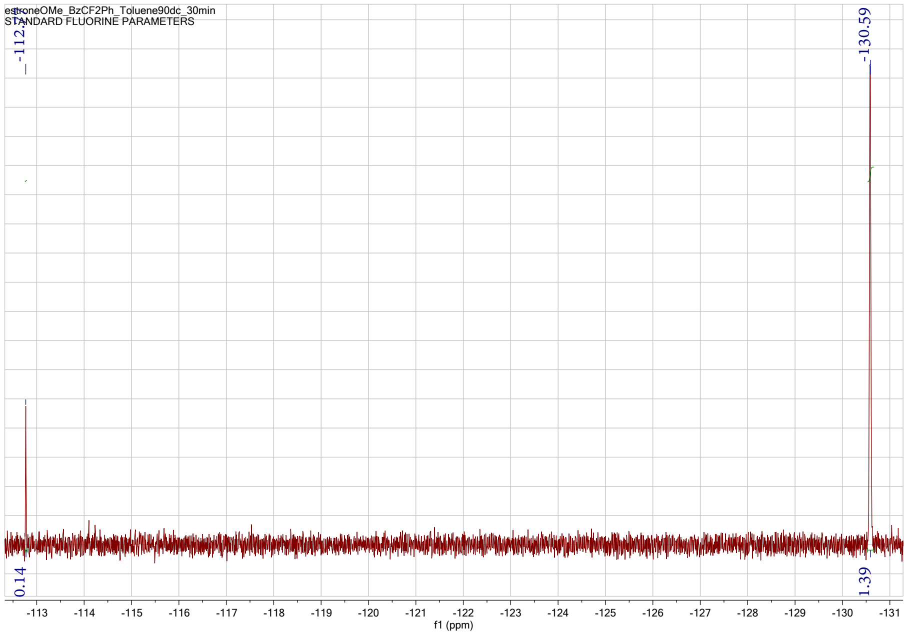


Figure S79. Representative *in situ* ^{19}F NMR spectra (in toluene) of **2k**. Top: full spectra and bottom: zoom-in spectra.

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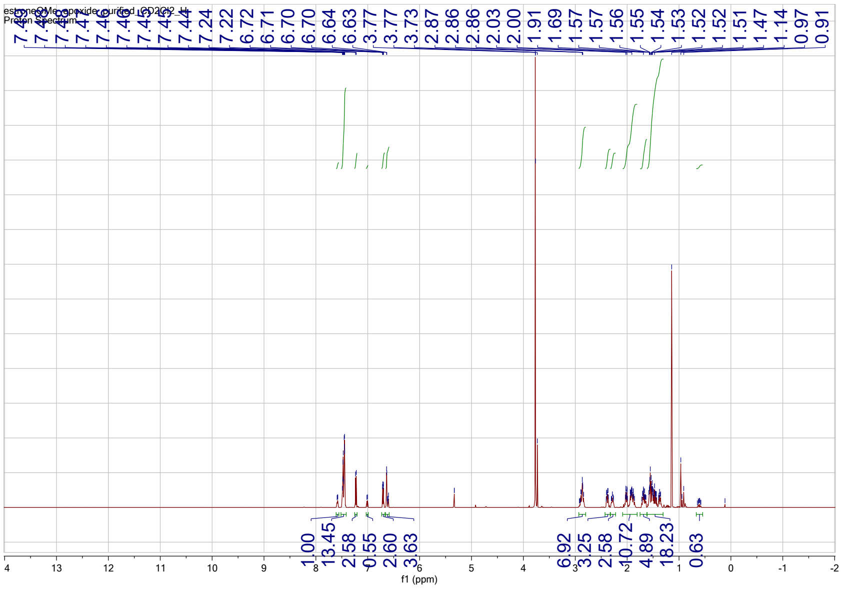

Figure S80. ^{1}H NMR spectra (CD_2Cl_2) of isolated **2j**.

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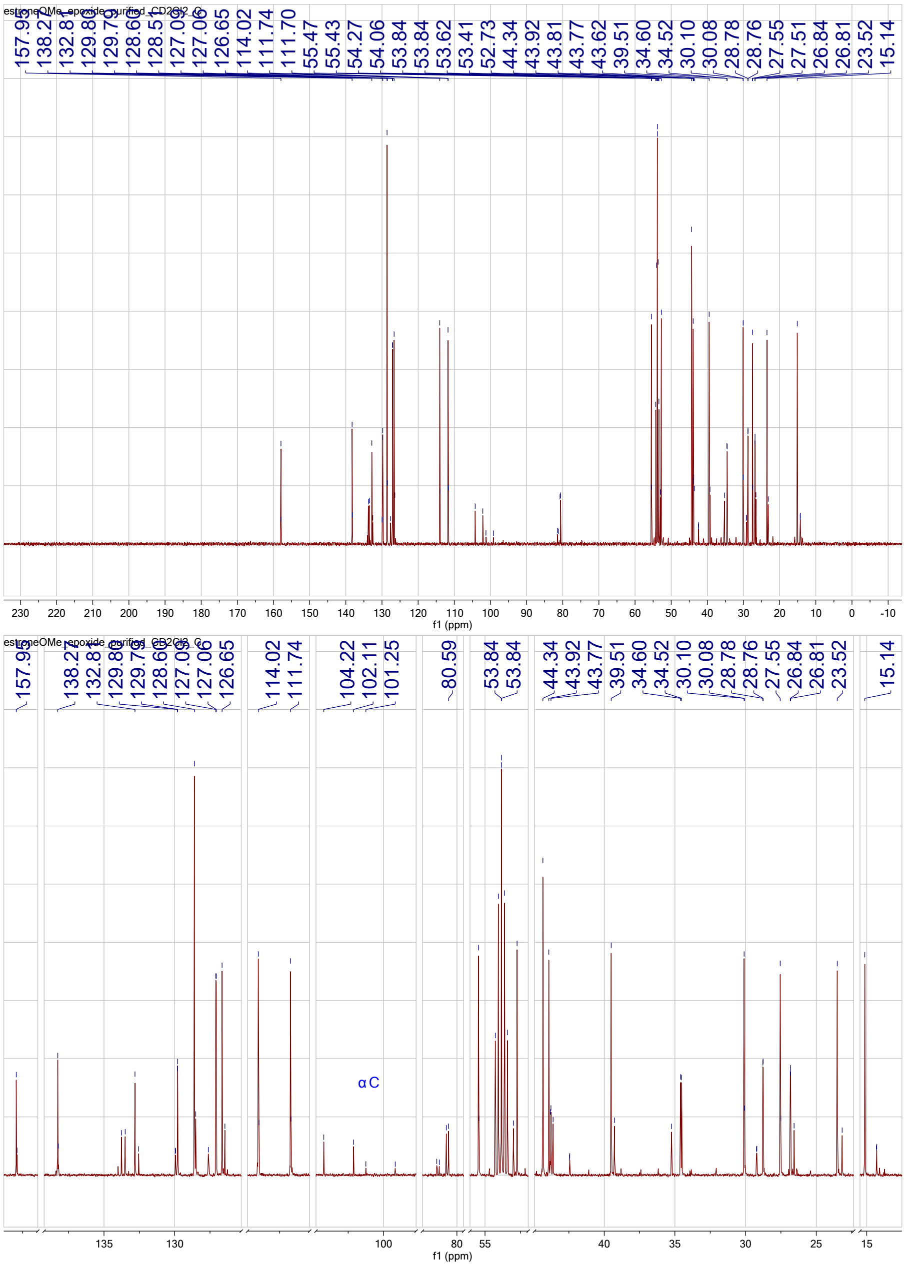

Figure S81. ^{13}C NMR spectra (CD_2Cl_2) of isolated **2k**. Top: full spectra and bottom: zoom-in spectra.

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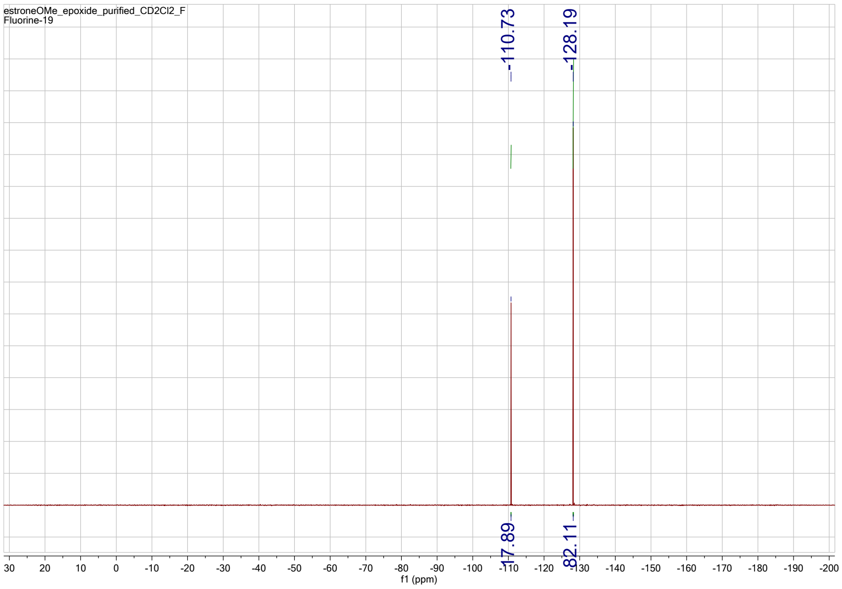

Figure S82. ^{19}F NMR spectra (CD_2Cl_2) of isolated **2k**.

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3. Other selected enolizable ketones or benzaldehyde as substrates

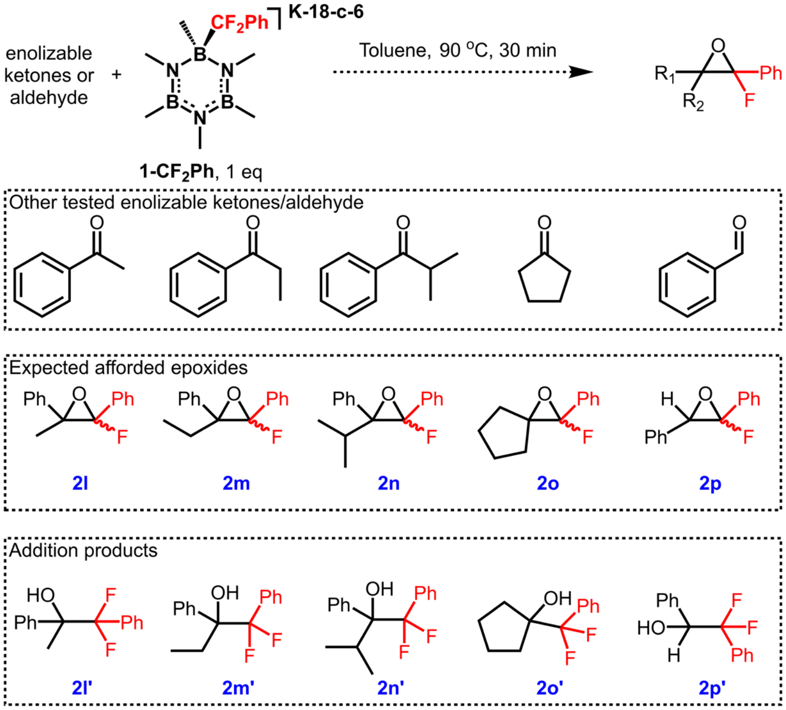

Figure S83. Evaluation of the synthesis of fluorinated epoxides from enolizable ketones and benzaldehyde.

Note: We found that the water content and purity of the enolizable ketones significantly decreases yield. To minimize water content, the ketones were stored over sieves. However, aldol addition/condensation reactions are promoted by molecular sieves, and it is possible that lower purity of the ketones may have contributed to lower chemical conversions.

Entry	Epoxide (%)	d.r.	Addition product (%)	$PhCF_2H$ (%)
1	**2l**, 5	-	**2l'**, 31	44
2	**2m**, 19	76:24	**2m'**, 19	72
3	**2n**, 39	76:24	**2n'**, 11	52
4	**2o**, 0	-	**2o'**,44	55
5	**2p**, 6	-	**2p'**, 55	11

Table S2. Evaluation of the synthesis of fluorinated epoxides from enolizable ketones. Yields and d.r were determined by ^{19}F NMR spectroscopy.

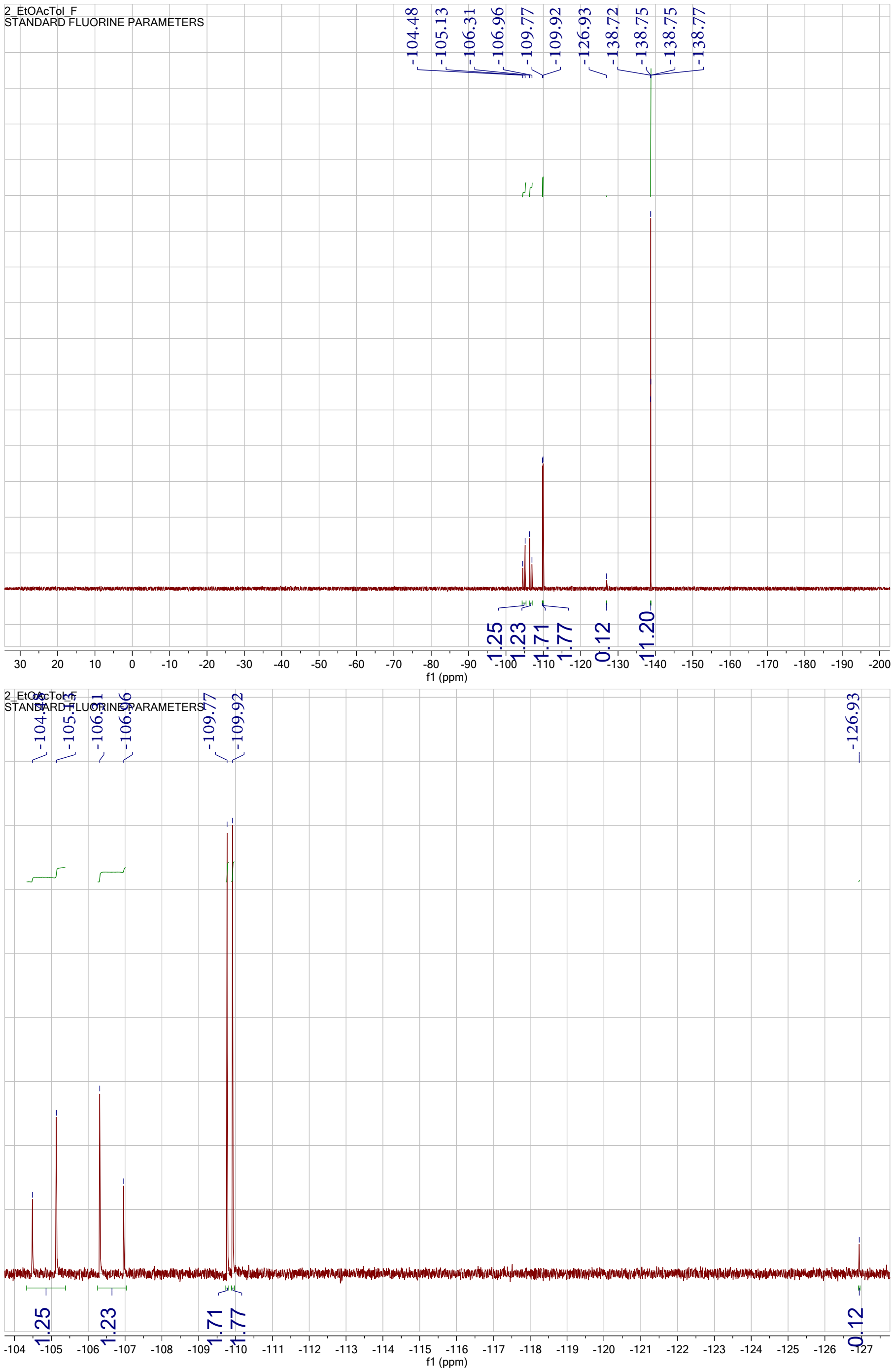

Figure S84. Representative *in situ* ^{19}F NMR spectra (in toluene + EtOAc) of **2l** and **2l’**. Top: full spectra and bottom: zoom-in spectra. ^{19}F NMR (377 MHz, toluene + EtOAc) δ -104.81 (d, *J* = 245.0 Hz, **2l’**, 1F), -106.64 (d, *J* = 245.1 Hz, **2l’**, 1F), -126.93 (s, **2l**, 1F).

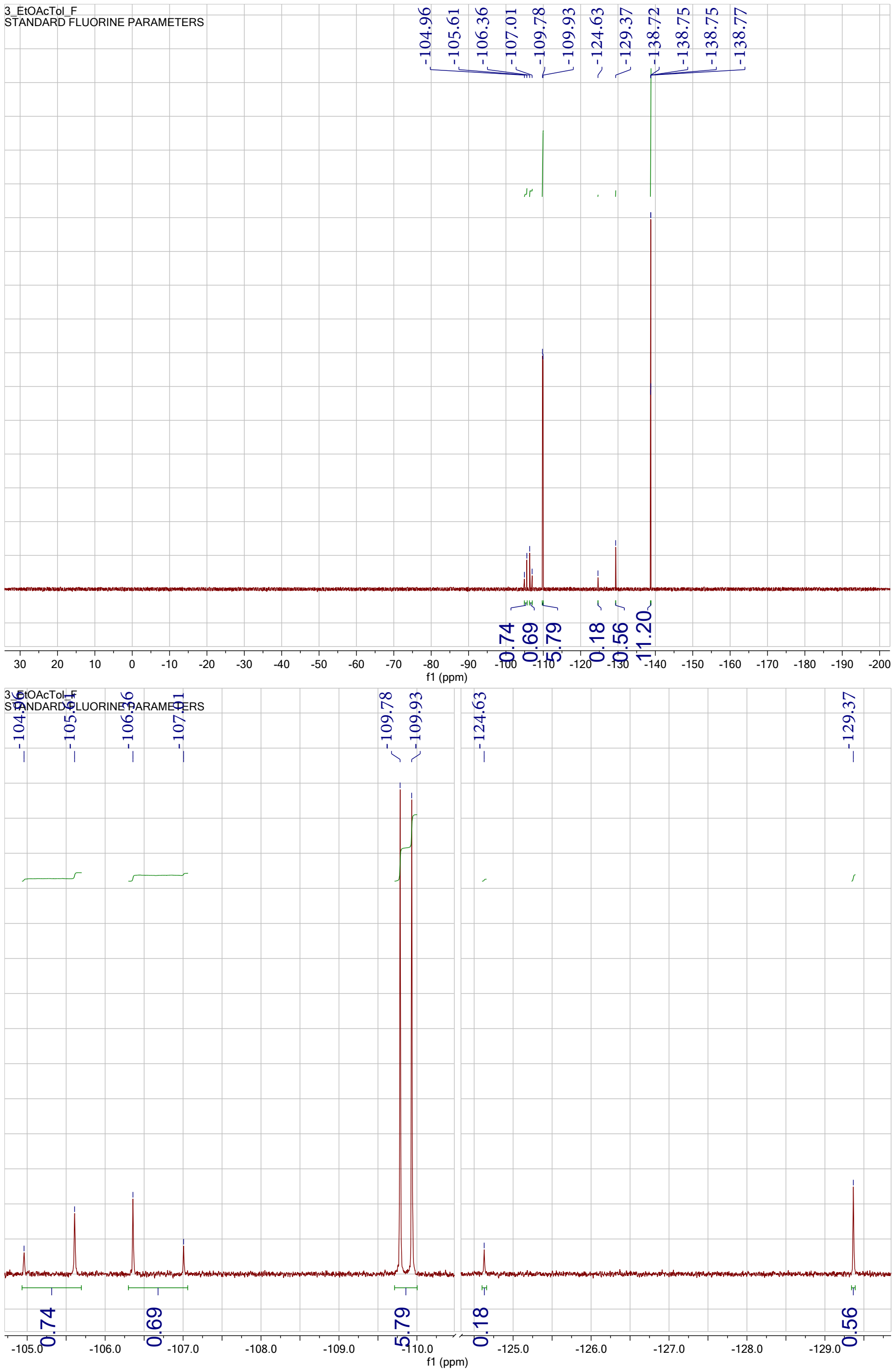

Figure S85. Representative *in situ* ^{19}F NMR spectra (in toluene + EtOAc) of **2m** and **2m'**. Top: full spectra and bottom: zoom-in spectra. ^{19}F NMR (377 MHz, toluene + EtOAc) δ -105.28 (d, J = 244.4 Hz, **2m'**, 1F), -106.68 (d, J = 244.7 Hz, **2m'**, 1F), -124.63 (s, **2m**, 1F, minor isomer), -129.37 (s, **2m**, 1F, major isomer).

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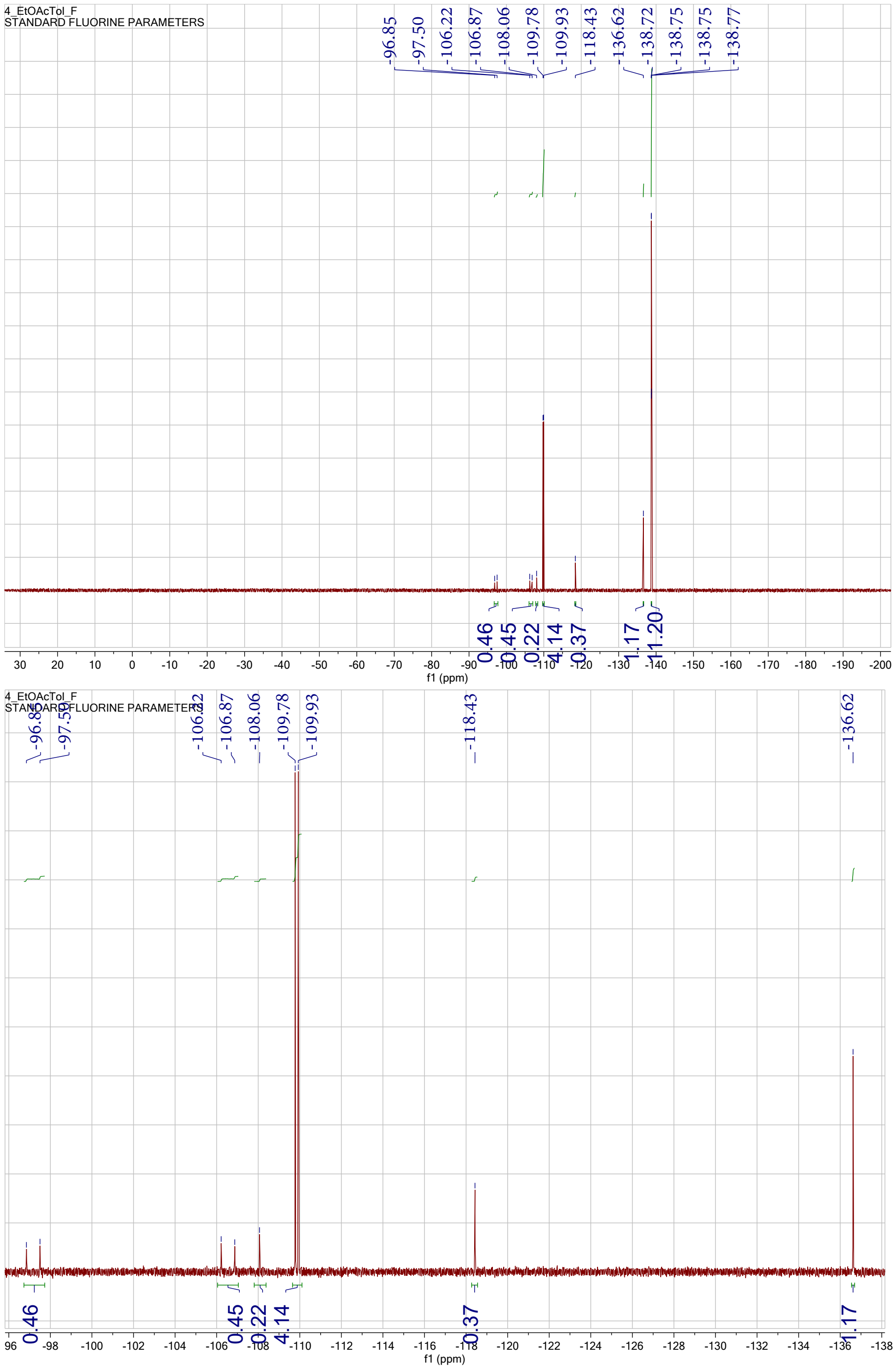

Figure S86. Representative *in situ* ^{19}F NMR spectra (in toluene + EtOAc) of **2n** and **2n'**. Top: full spectra and bottom: zoom-in spectra. ^{19}F NMR (377 MHz, toluene + EtOAc) δ -97.18 (d, *J* = 246.8 Hz, **2n'**, 1F), -106.55 (d, *J* = 245.9 Hz, **2n'**, 1F), -118.43 (s, **2n**, 1F, minor isomer), -136.62 (s, **2m**, 1F, major isomer).

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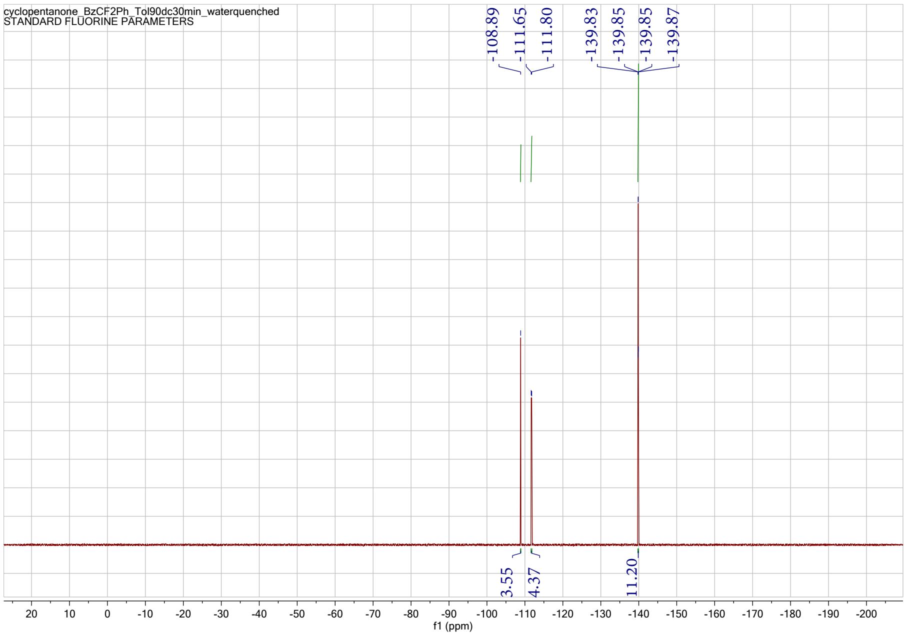

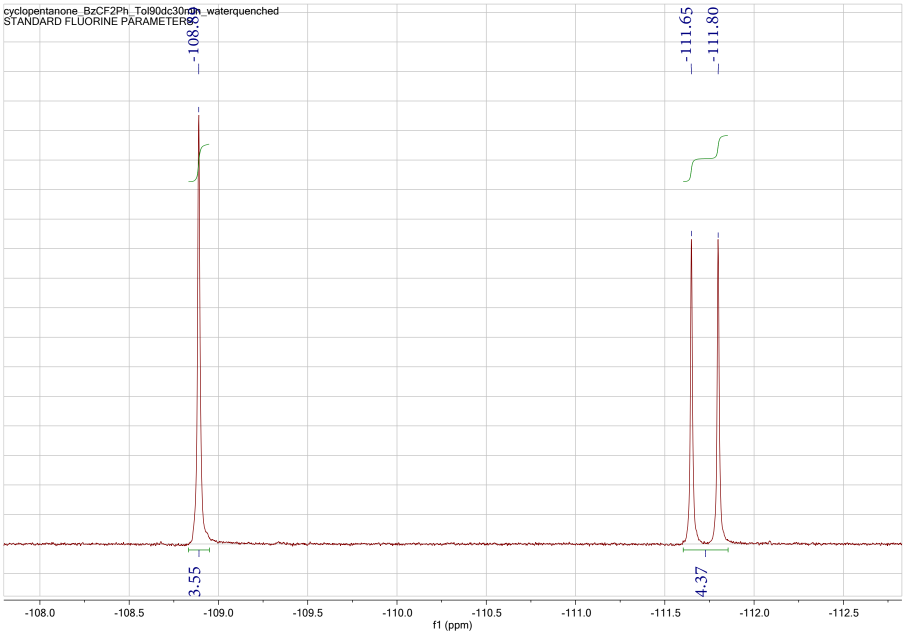

Figure S87. Representative *in situ* ^{19}F NMR spectra (in toluene + EtOAc) of **2o'**. Top: full spectra and bottom: zoom-in spectra. ^{19}F NMR (377 MHz, toluene + EtOAc) δ -108.89 (s, **2o'**, 2F).

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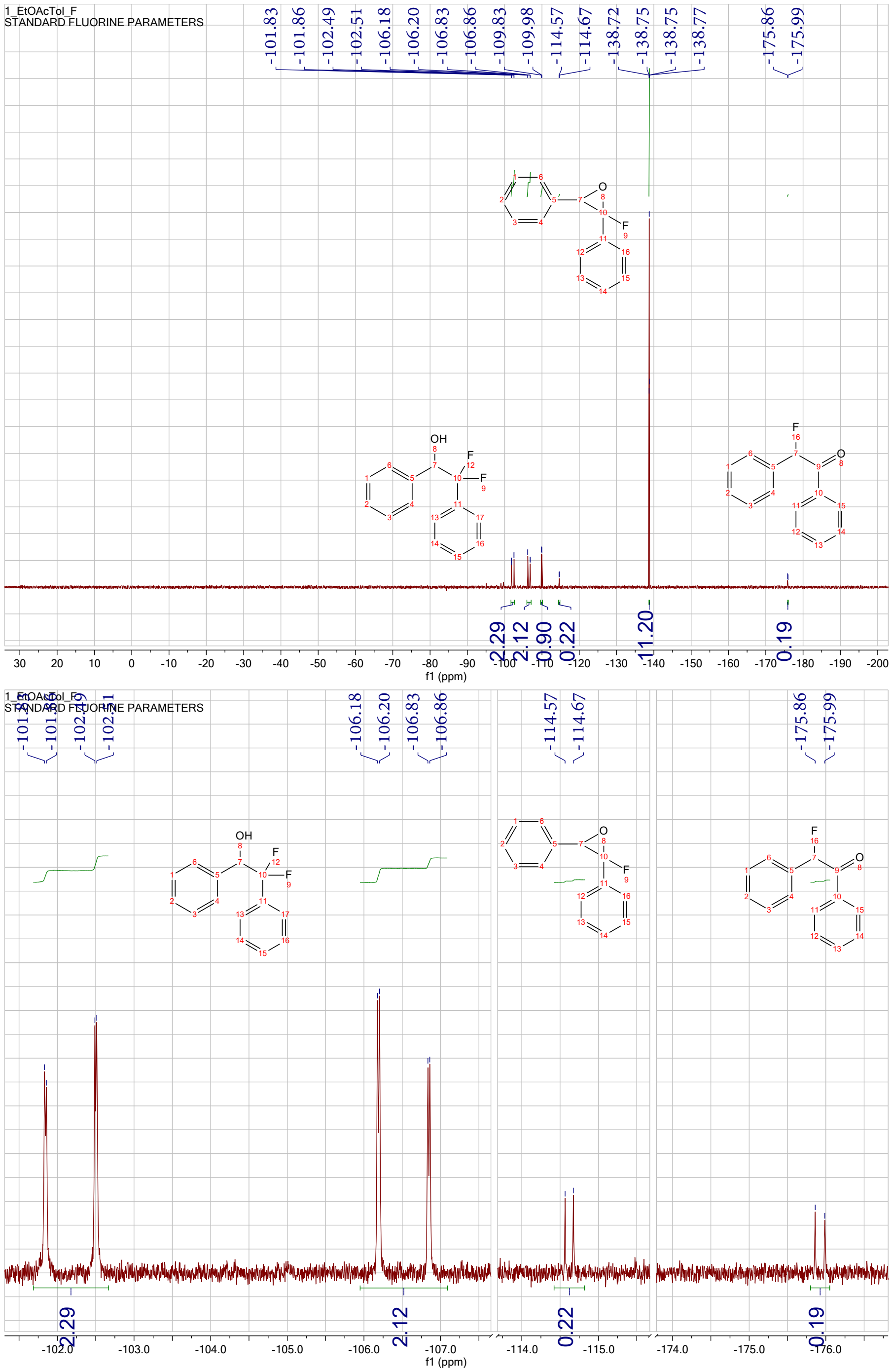

Figure S88. Representative *in situ* ^{19}F NMR spectra (in toluene + EtOAc) of **2p** and **2p'**. Top: full spectra and bottom: zoom-in spectra. ^{19}F NMR (377 MHz, toluene + EtOAc) δ -102.17 (dd, J = 247.5, 9.2 Hz, **2p'**, 1F), -106.52 (dd, J = 247.5, 9.5 Hz, **2p'**, 1F), -114.62 (d, J = 40.6 Hz, **2p**, 1F), -175.92 (d, J = 47.2 Hz, 1F, 1,2-F migration product, structure shown in the spectra).

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4. Other tested ketone substrates which did not afford the fluorinated epoxides

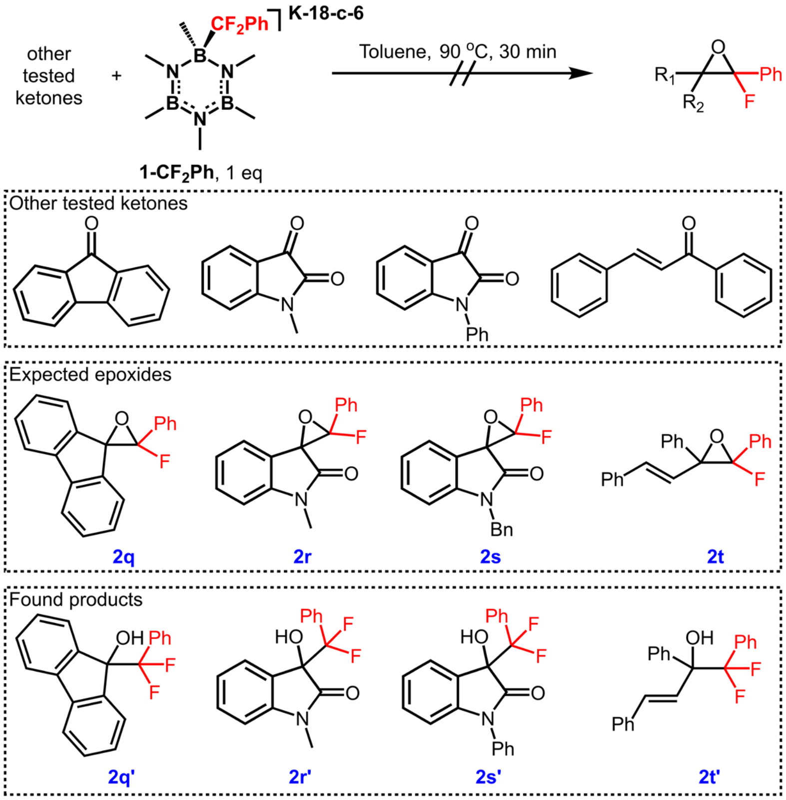

Figure S89. Evaluation of the synthesis of fluorinated epoxides from other tested ketone substrates.

Entry	Epoxide (%)	Addition product (%)	$PhCF_2H$ (%)
1	**2q**, 0	**2q'**, 62	8
2	**2r**, 0	**2r'**, 96	13
3	**2s**, 0	**2s'**, 42	26
4	**2t**, 0	**2t'**, 32	17

Table S3. Evaluation of the synthesis of fluoroepoxides from other tested ketone substrates. Yields determined by ^{19}F NMR spectroscopy.

Note: The attempting synthesis of **2q-2t** were performed at 0.04 mmol scale. identification of the addition product was based on the chemical shift and mass balance of the major product in the ^{19}F NMR spectra. Selected compounds (**2r'** and **2t'**) were purified and characterized by ^{1}H, ^{19}F and ^{13}C NMR spectroscopy.

Purification of **2r'**: 1-2 mL water was added to the crude reaction mixture. 1-2 mL EtOAc was added to extract the organic species for 3 times. The organic portions (top layers) were combined and dried with anhydrous $MgSO_4$. After removal of the $MgSO_4$ by filtration, the solvents were removed under vacuum. A few drops of EtOAc was added to dissolve the product and hexanes were added until no more solids coming out from the solution. The solid (**2r'**) was collected by filtration and washed with hexanes. ^{13}C, ^{19}F, and ^{1}H NMR spectra were collected after drying the sample under high vacuum overnight.

Purification of **2t'**: 1-2 mL water was added to the crude reaction mixture. 1-2 mL EtOAc was added to extract the organic species for 3 times. The organic portions (top layers) were combined and dried with anhydrous $MgSO_4$. After removal of the $MgSO_4$ by filtration, the solvents were removed under vacuum. **2o'** was purified by a flash column (eluent: hexanes:EtOAc = 10:1 (v/v) containing 5 vol% Et_3N).

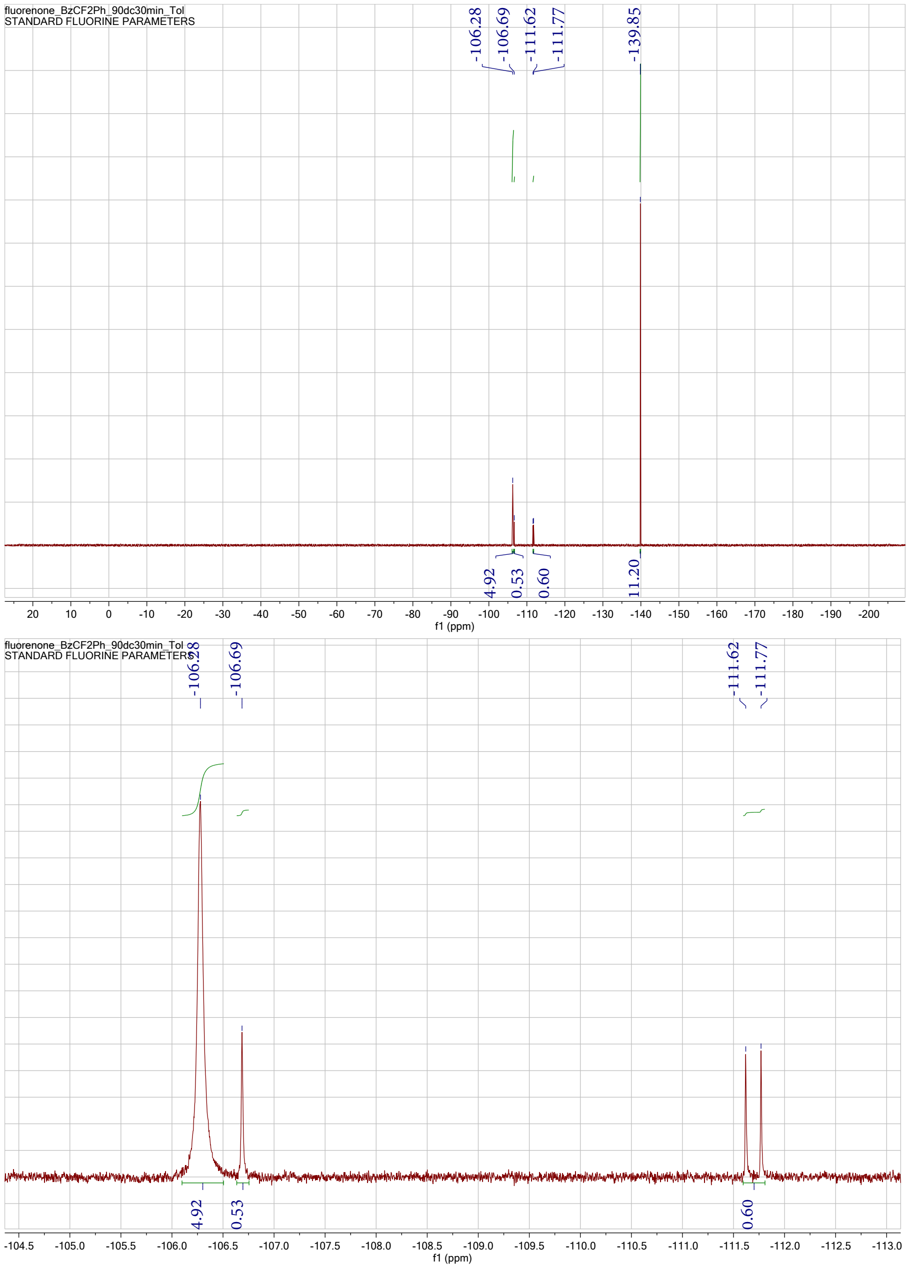

Figure S90. Representative *in situ* ^{19}F NMR spectra (in toluene) of **2q'**. Top: full spectra and bottom: zoom-in spectra. ^{19}F NMR (377 MHz, toluene) δ -106.28 (s, 2F).

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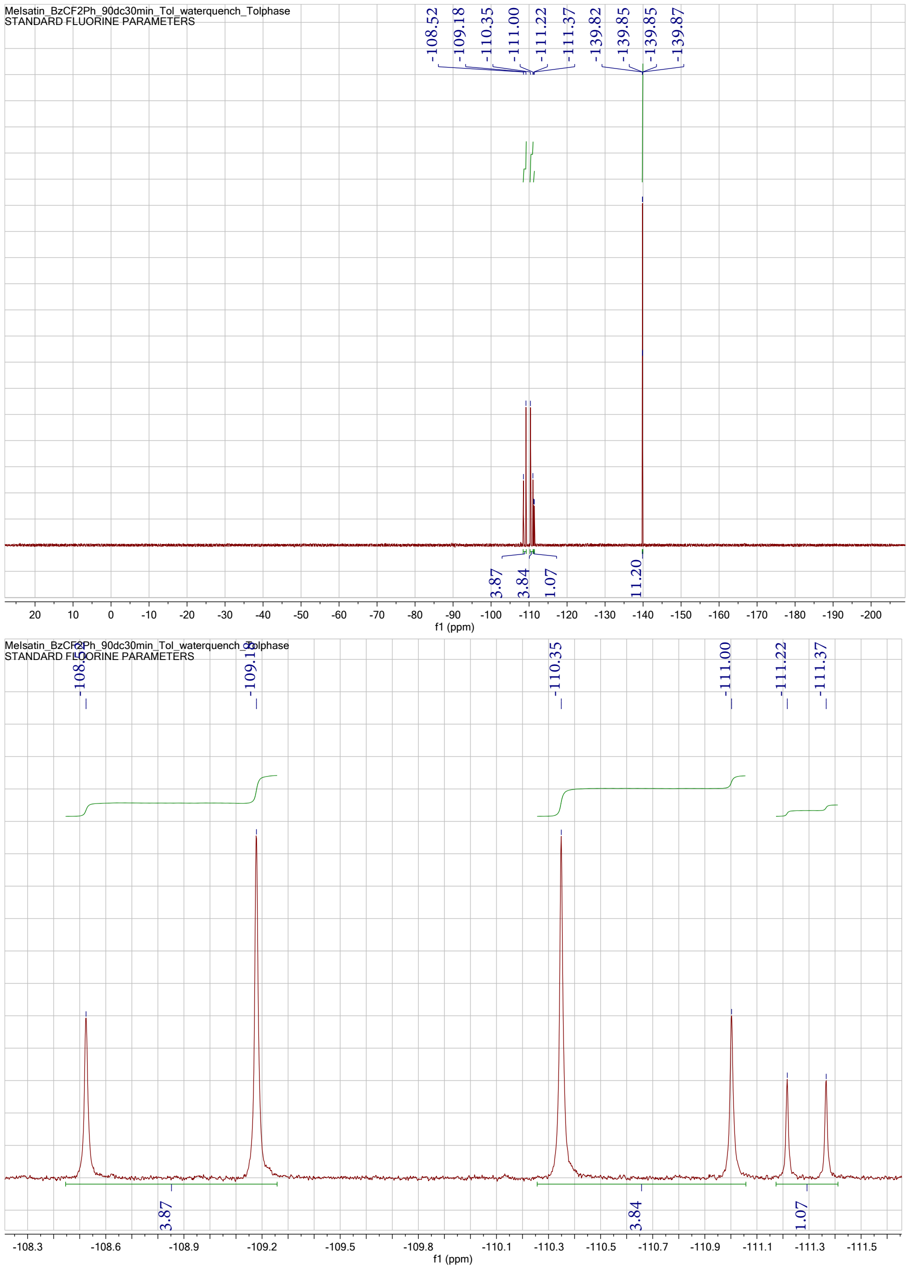

Figure S91. Representative *in situ* ^{19}F NMR spectra (in toluene) of **2r**’. Top: full spectra and bottom: zoom-in spectra. ^{19}F NMR (377 MHz, toluene) δ -108.85 (d, J = 246.5 Hz, 1F), -110.68 (d, J = 246.4 Hz, 1F).

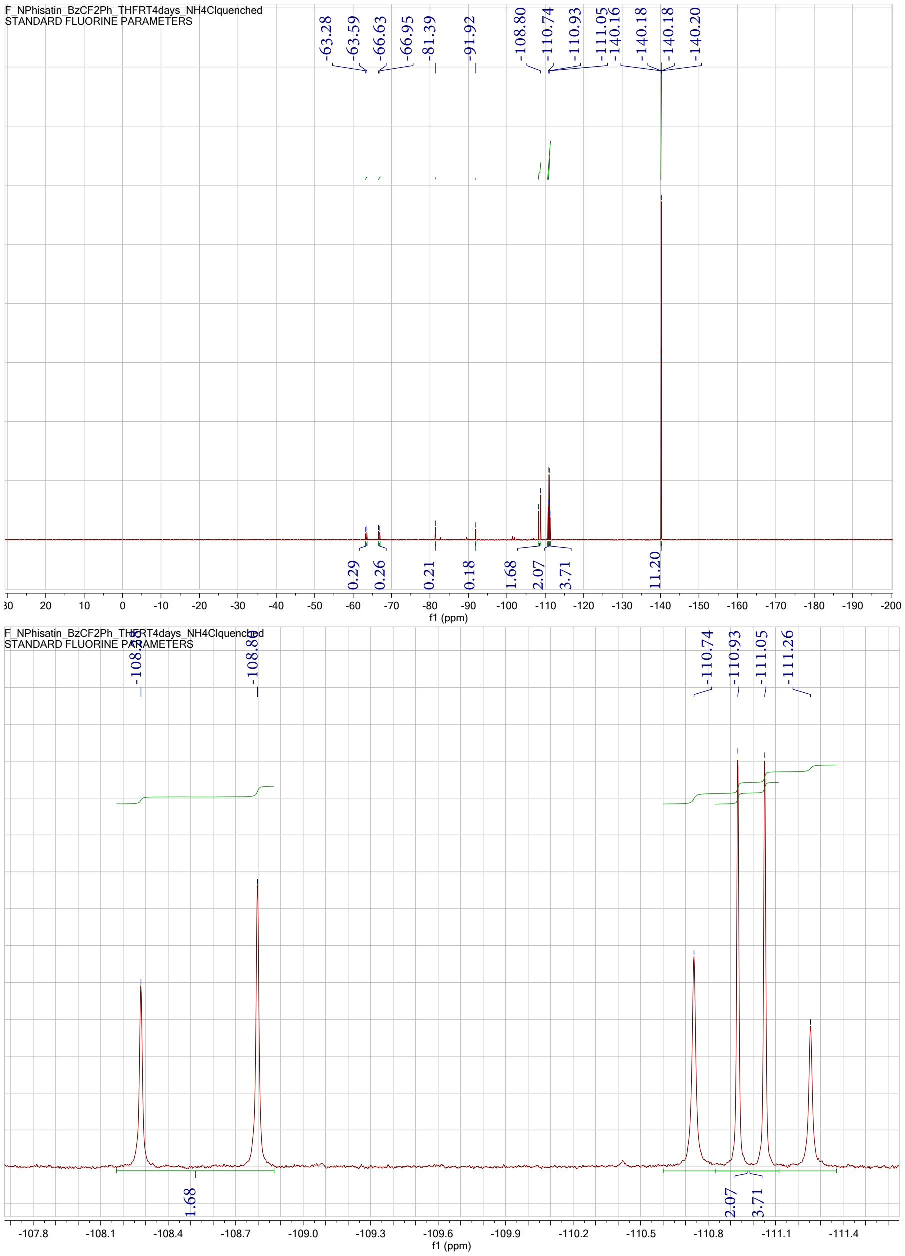

Figure S92. Representative *in situ* ^{19}F NMR spectra (in THF) of **2s**'. Top: full spectra and bottom: zoom-in spectra. ^{19}F NMR (471 MHz, THF) δ -108.54 (d, *J* = 243.8 Hz, 1F), -111.00 (d, *J* = 243.8 Hz, 1F).

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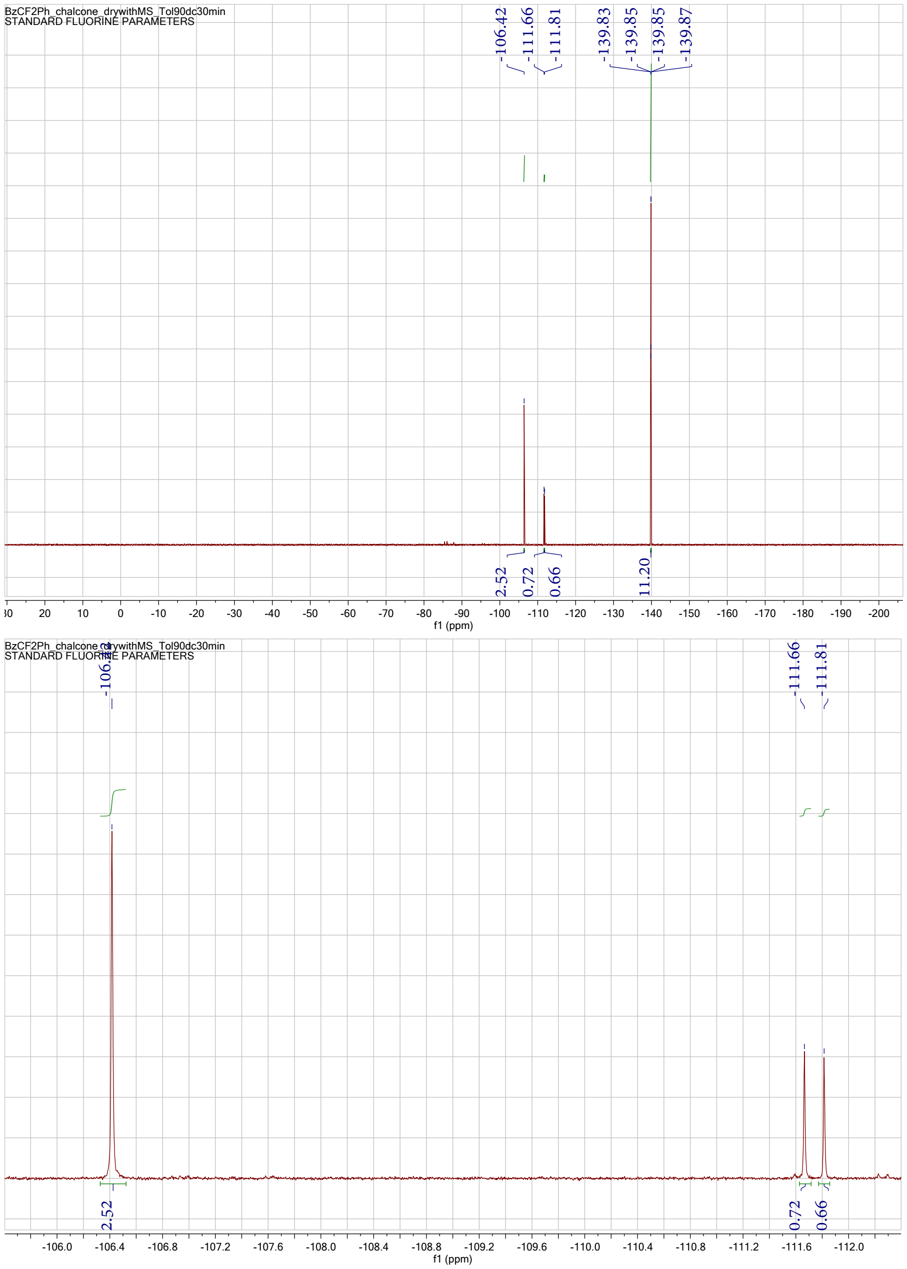

Figure S93. Representative *in situ* ^{19}F NMR spectra (in toluene) of **2t**'. Top: full spectra and bottom: zoom-in spectra. ^{19}F NMR (377 MHz, Toluene) δ -106.42 (s, 2F).

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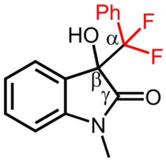

2r'

Yellow solid. ^{19}F NMR (471 MHz, CDCl$_3$) δ -108.51 (d, *J* = 245.6 Hz, 1F), -110.55 (d, *J* = 245.6 Hz, 1F). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.39 – 7.31 (m, 3H), 7.29 – 7.20 (m, 5H), 7.08 (t, *J* = 7.5 Hz, 1H), 6.65 (d, *J* = 7.8 Hz, 1H), 3.68 (s, 1H), 2.98 (s, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 173.44 (s, γC), 144.47 (s), 131.89 (t, *J* = 25.6 Hz), 131.15 (s), 130.53 (s), 127.76 (s), 126.89 (t, *J* = 6.3 Hz), 126.51 (s), 124.20 (s), 123.23 (s), 119.98 (t, *J* = 254.8 Hz, αC), 108.48 (s), 78.72 (t, *J* = 28.6 Hz, βC), 26.31 (s).

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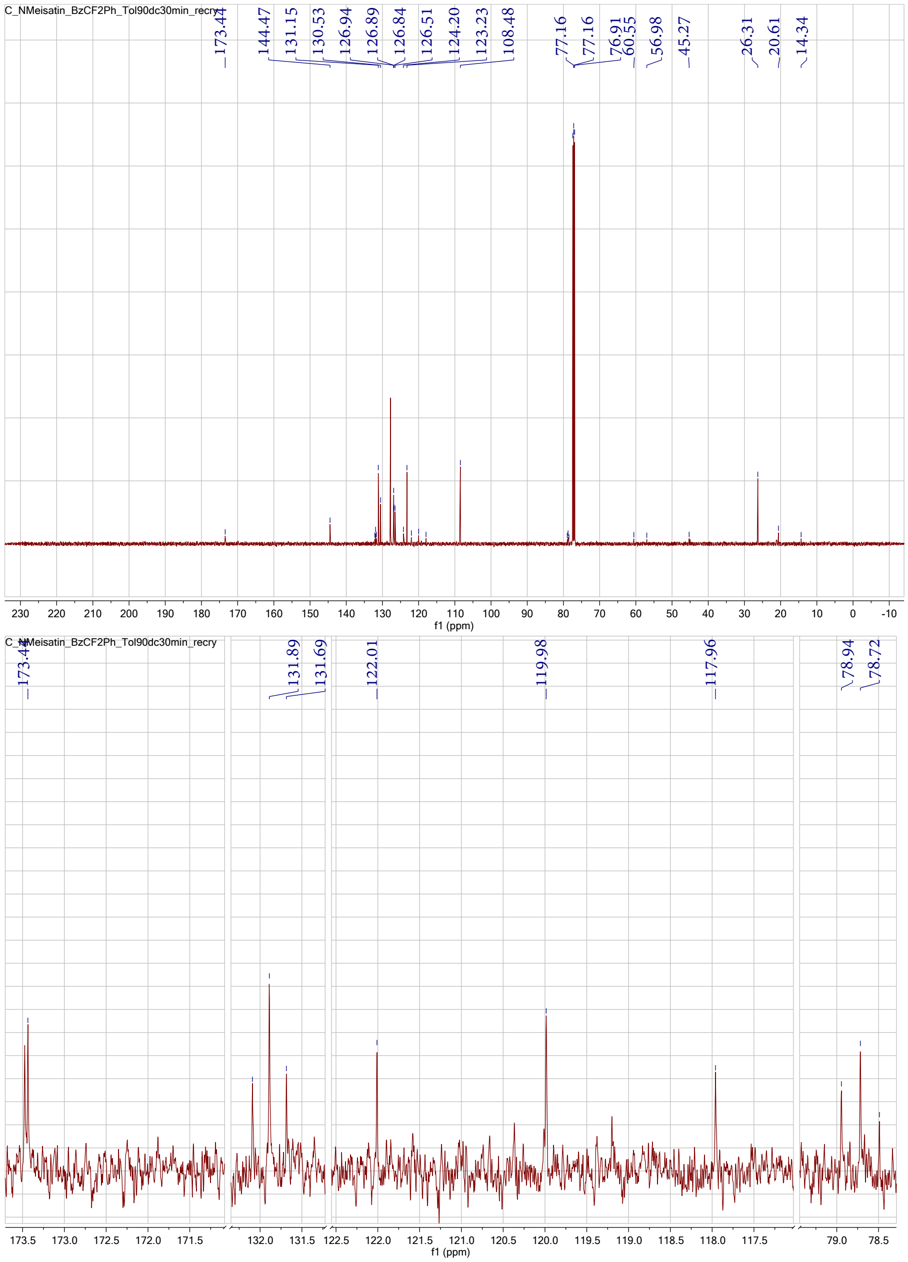

Figure S94. ^{13}C NMR spectra of the isolated **2r’** (CDCl$_3$). Diagnostic peaks were enlarged in the bottom spectra.

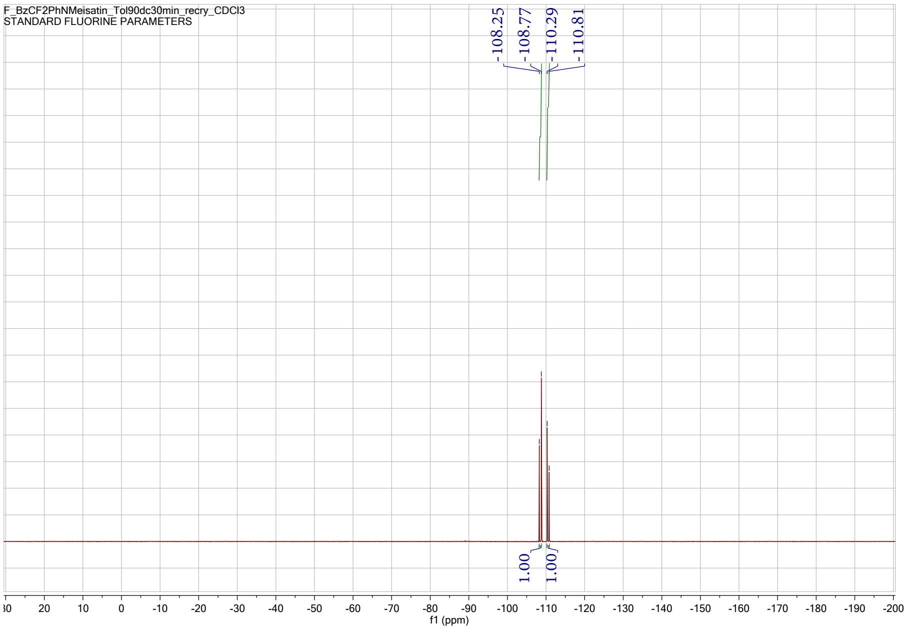

Figure S95. ^{19}F NMR spectra of the isolated **2r’** ($CDCl_3$).

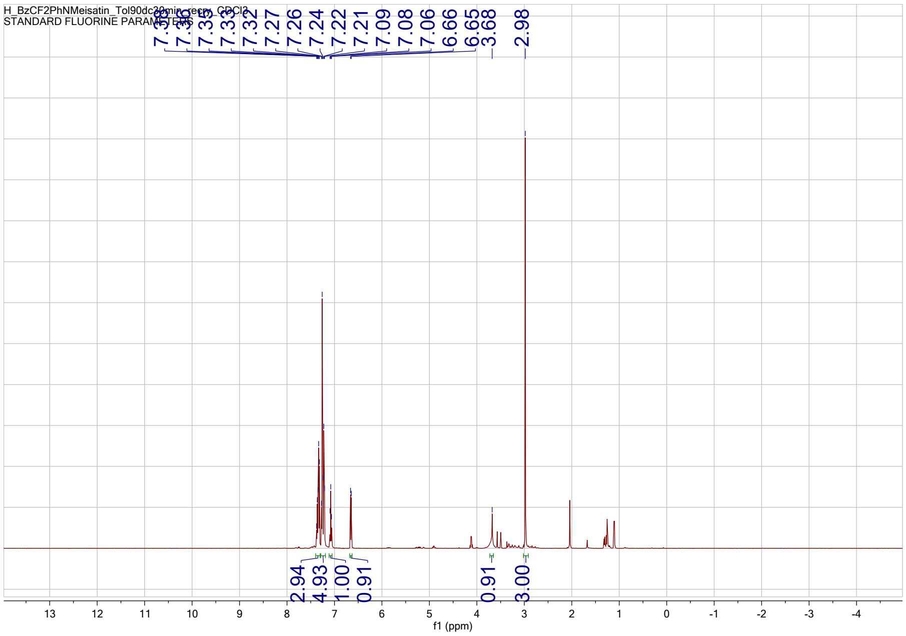

Figure S96. ^{1}H NMR spectra of the isolated **2r’** ($CDCl_3$).

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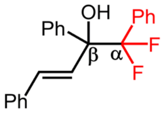

2t'

Yellow solid. ^{19}F NMR (564 MHz, CDCl$_3$) δ -105.13 (d, *J* = 246.8 Hz, 1F), -105.62 (d, *J* = 246.7 Hz, 1F). ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.47 – 7.40 (m, 4H), 7.38 – 7.31 (m, 3H), 7.30 – 7.24 (m, 6H), 7.21 (d, *J* = 7.4 Hz, 2H), 7.07 (d, *J* = 16.0 Hz, 1H), 6.78 (d, *J* = 16.1 Hz, 1H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 139.35 (s), 136.33 (s), 133.58 (t, *J* = 26.1 Hz), 132.38 (s), 129.86 (s), 129.18 (s), 128.68 (s), 128.16 (s), 128.00 (s), 127.78 (s), 127.42 (s), 127.26 (s), 127.17 (t, *J* = 6.4 Hz), 126.80 (s), 122.06 (t, *J* = 253.7 Hz, αC), 79.26 (t, *J* = 28.7 Hz, βC).

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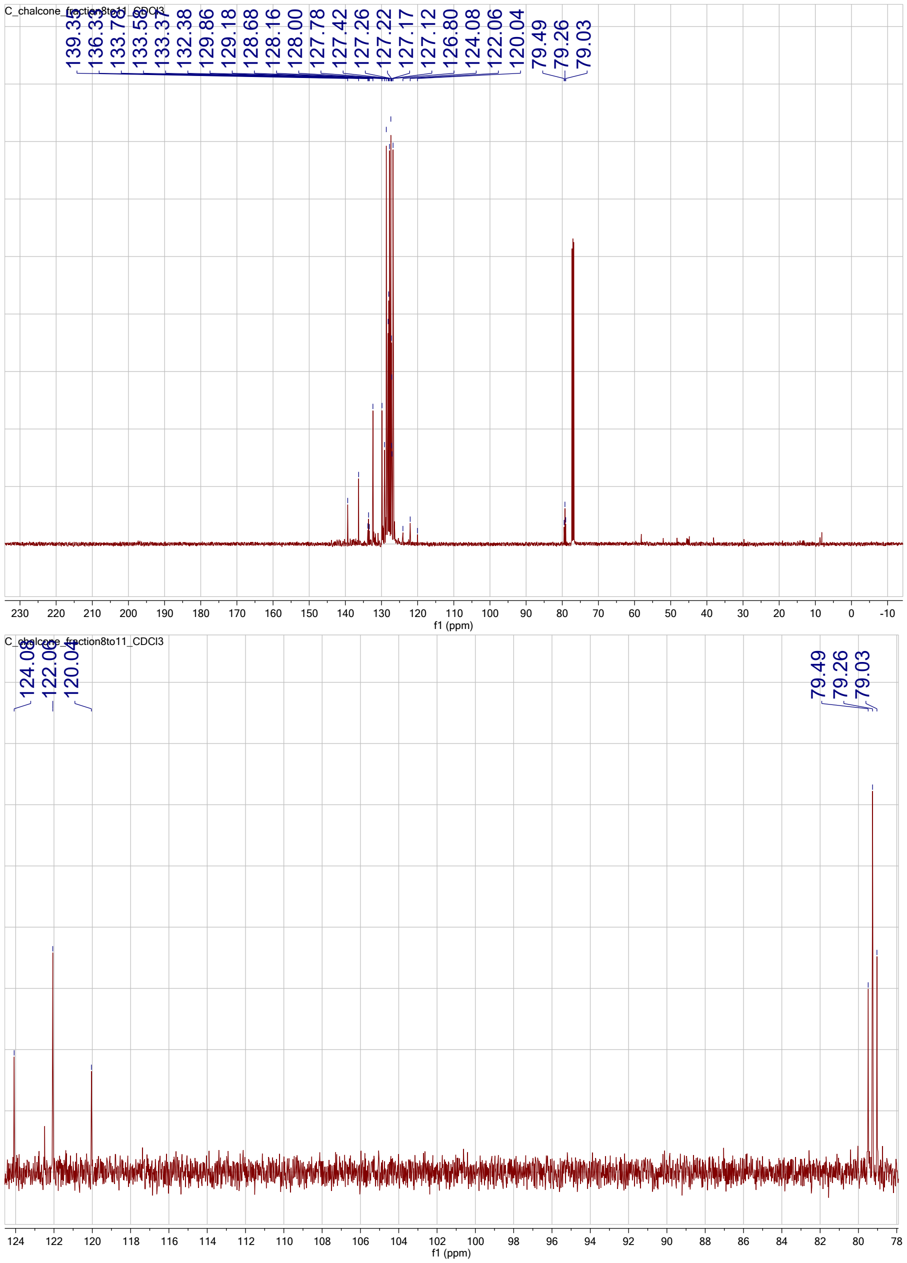

Figure S97. ^{13}C NMR spectra of **2t'** ($CDCl_3$). Diagnostic peaks were enlarged in the bottom spectra: 122.06 (t, *J* = 253.7 Hz, αC), 79.26 (t, *J* = 28.7 Hz, βC).

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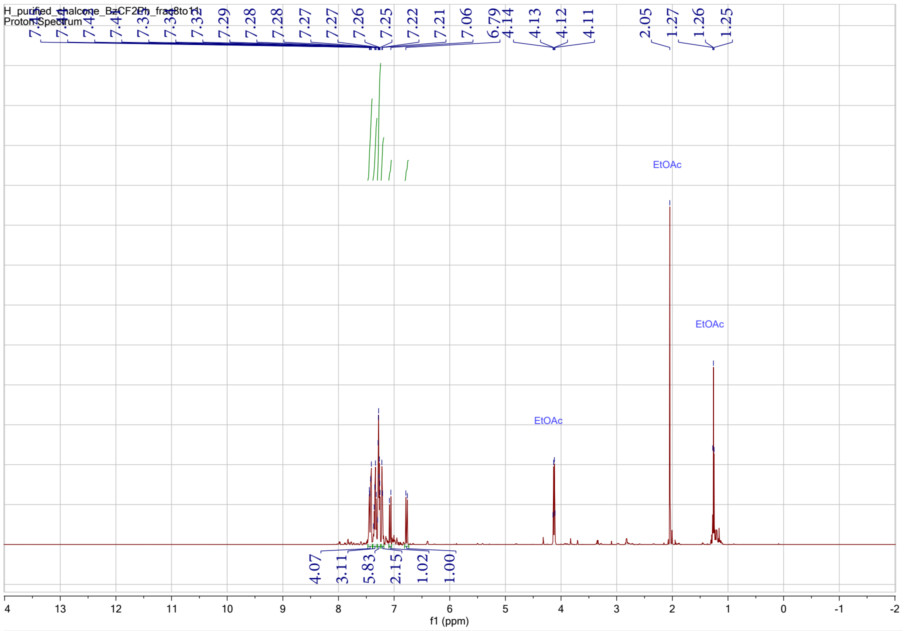

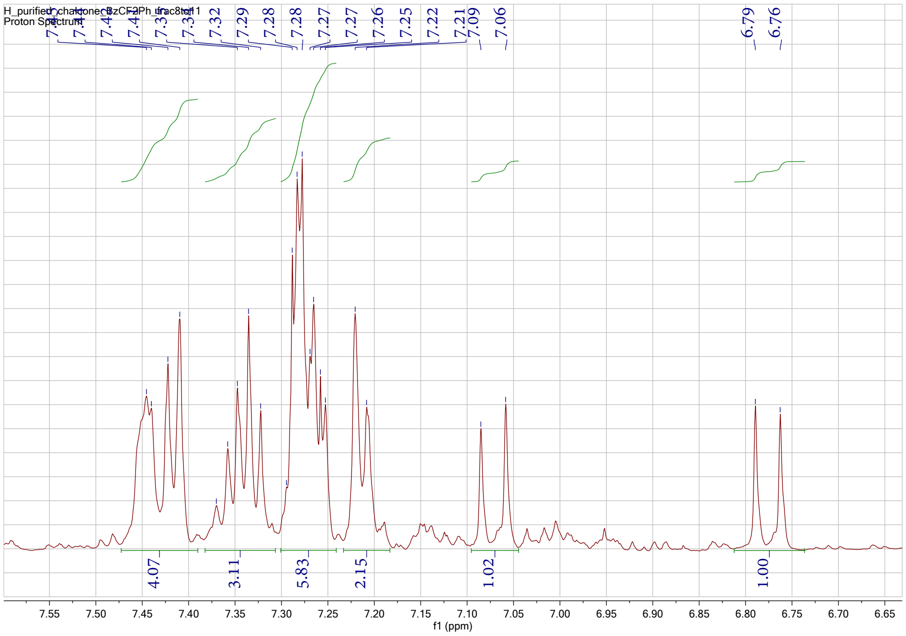

Figure S98. ^{1}H NMR spectra of **2t'** ($CDCl_3$). Aromatic H and the diagnostic 2 alkene H were enlarged in the bottom spectra: 7.07 (d, *J* = 16.0 Hz, 1H), 6.78 (d, *J* = 16.1 Hz, 1H).

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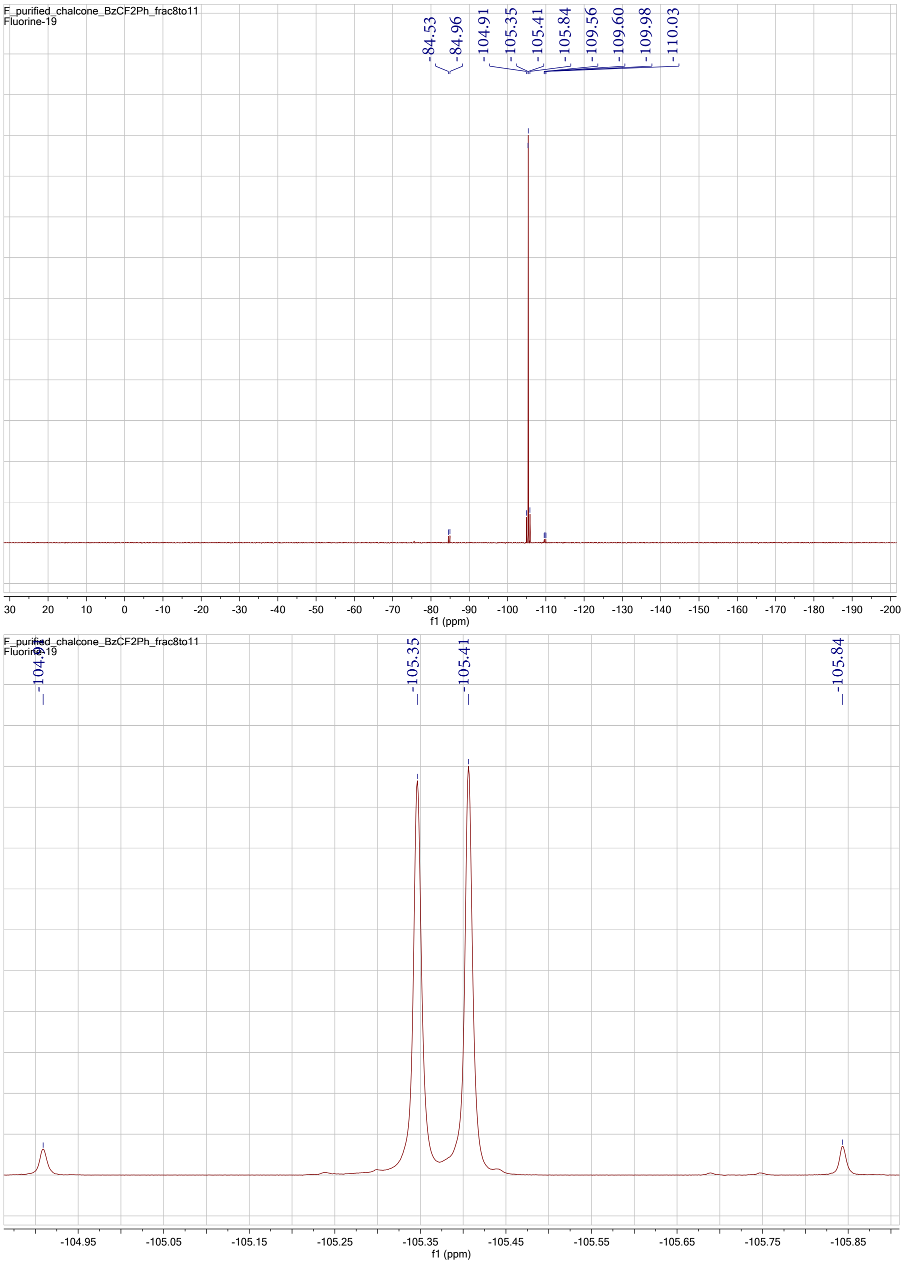

Figure S99. ^{19}F NMR spectra of **2t'** ($CDCl_3$). Top: full spectra and bottom: zoom-in spectra.

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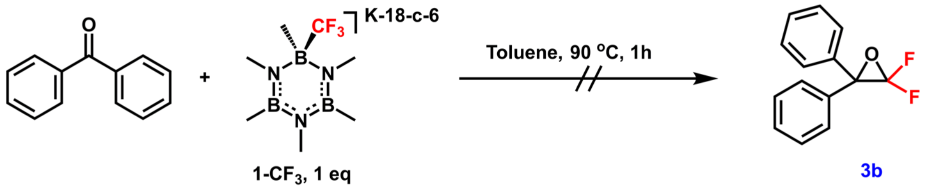
Extended fluoroalkyl scope (3a and 3b)

1. Attempted synthesis of **3b**



Protocol

Benzophenone (0.01 mmol, 1.8 mg) and 1.5 eq **1-CF₃** (0.4 M in THF, 25 μL containing PhF as internal standard) were mixed under N_2. Additional THF was added until the total volume reached 0.5 mL. The mixture was sealed and heated at 90 ºC for 30 min with stirring. Then all the volatile species were removed under vacuum and 0.5 mL toluene was added to dissolve the residual. The toluene solution was heated at 90 ºC for 7 days and another identical reaction was evaluated at 120 ºC for 30 min.

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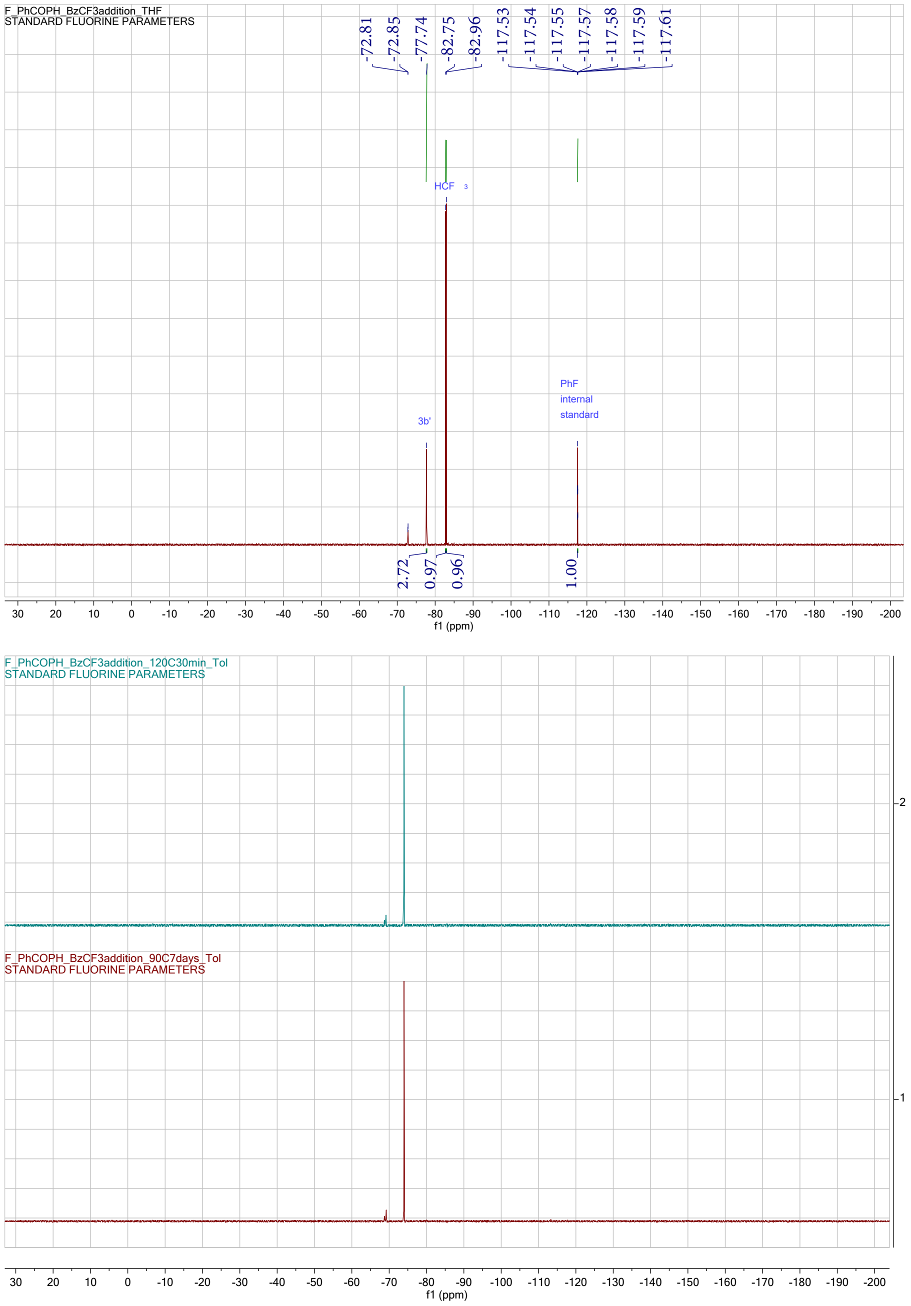

Figure S100. ^{19}F NMR spectra (THF) showing the in situ yield of K-**3b'** = 91%. Top: full spectra and bottom: zoom-in spectra. Even after heating the mixture in toluene at 90 ºC for 7 days or 120 ºC for 30 min, **3b'** remained intact, which indicates the high stability of **H-3b'**.

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2. Synthesis and isolation of **H-3b’** from benzophenone and **1-CF**$_3$[16]

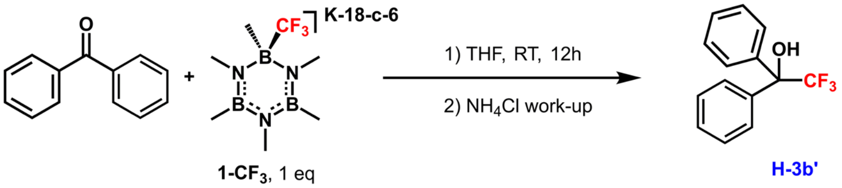
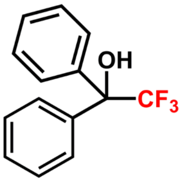


Figure S101. Scheme for the synthesis of **H-3b’**.

Protocol

Benzophenone (0.4 mmol, 73 mg) and 1 equiv. of **1-CF**$_3$ (0.4 M in THF, 1 mL) were measured in an 8 mL vial. THF was added until a total volume of 2 mL. The sealed vials were stirred at room temperature overnight. The mixture was then worked-up with saturated NH_4Cl solution (~3 mL) and the organic layer was extracted with THF (3 x 3 mL) and dried with anhydrous $MgSO_4$. After removal of the solvent under vacuum, **H-3b’** was produced in 68% yield and isolated in 53% yield as a colorless oil using Biotage (eluent = hexanes : EtOAc = 10:1, v/v).

2.2 Characterization of **H-3b’**



H-3b'

Colorless oil. ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.45 (s), 128.80 (s), 128.41 (s), 127.52 (q, J = 1.6 Hz), 125.41 (q, J = 286.3 Hz) 79.57 (q, J = 28.6 Hz). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 – 7.46 (m, 4H), 7.41 – 7.32 (m, 6H), 2.83 (s, 1H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -74.32 (s, 3F). Characterization data are consistent with that reported in the literature.[16]

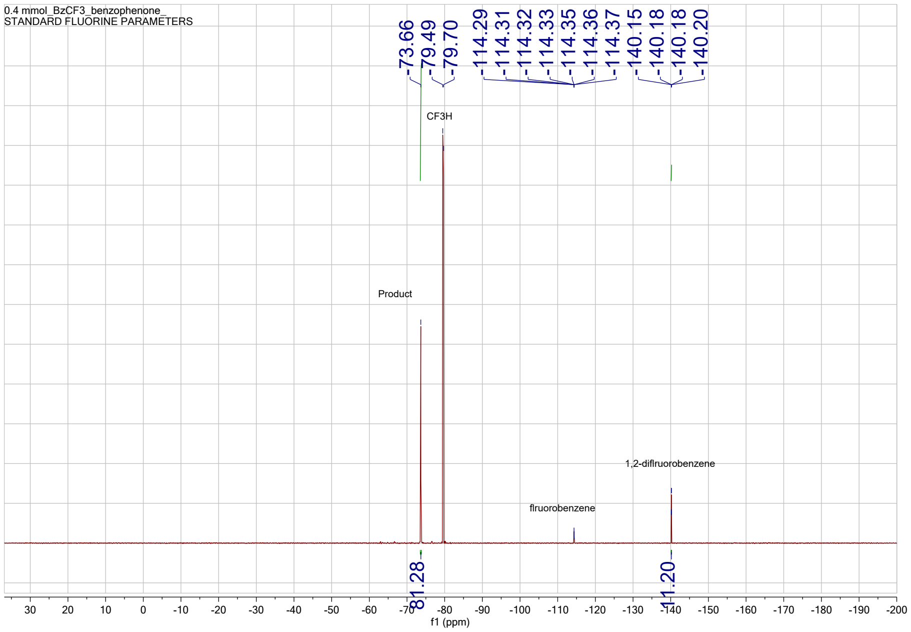


Figure S102. *In situ* ^{19}F NMR spectra (THF) showing the in situ yield of K-**3b**' = 68%.

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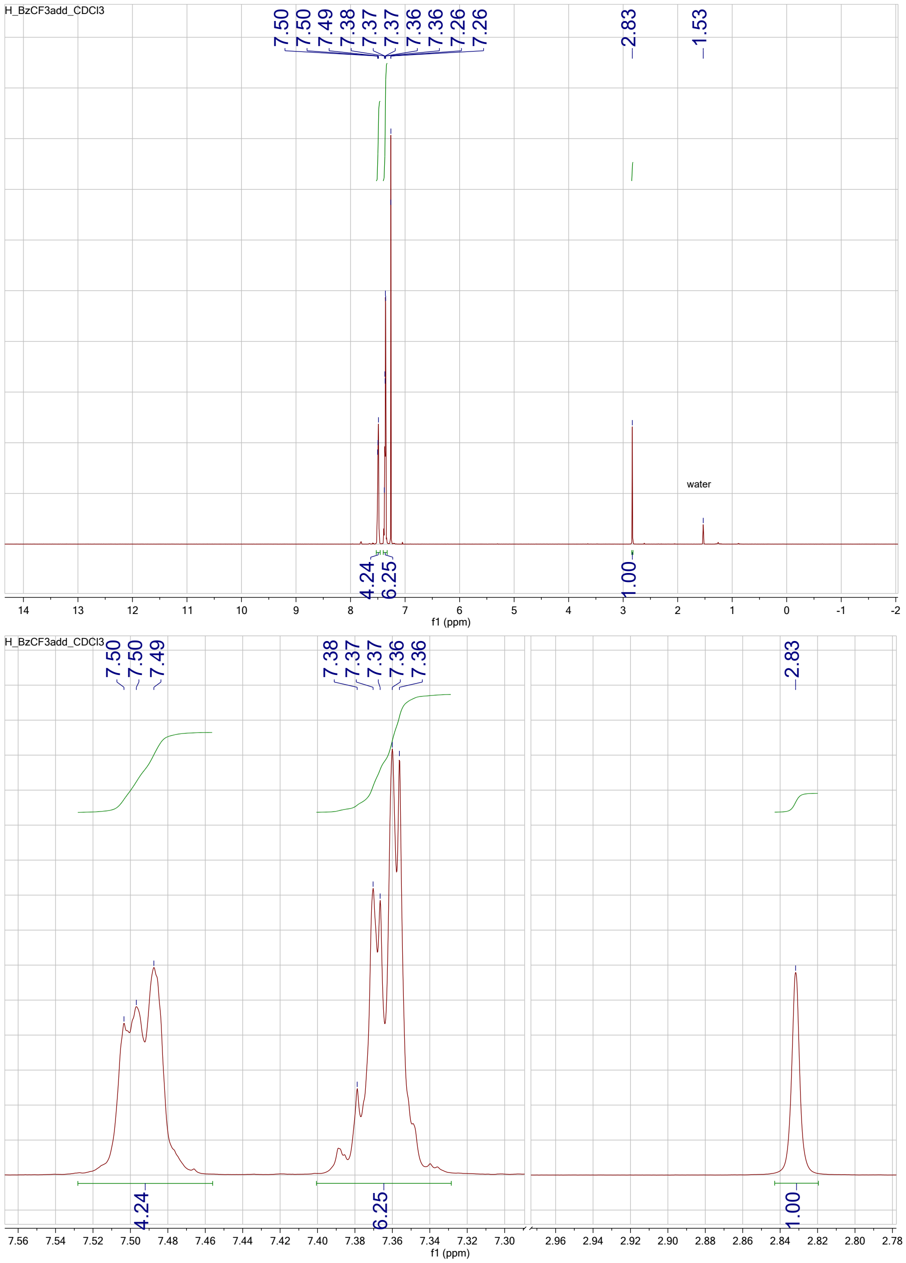

Figure S103. ^{1}H NMR spectra ($CDCl_3$) of isolated **H-3b'**. Top: full spectra and bottom: zoom-in spectra.

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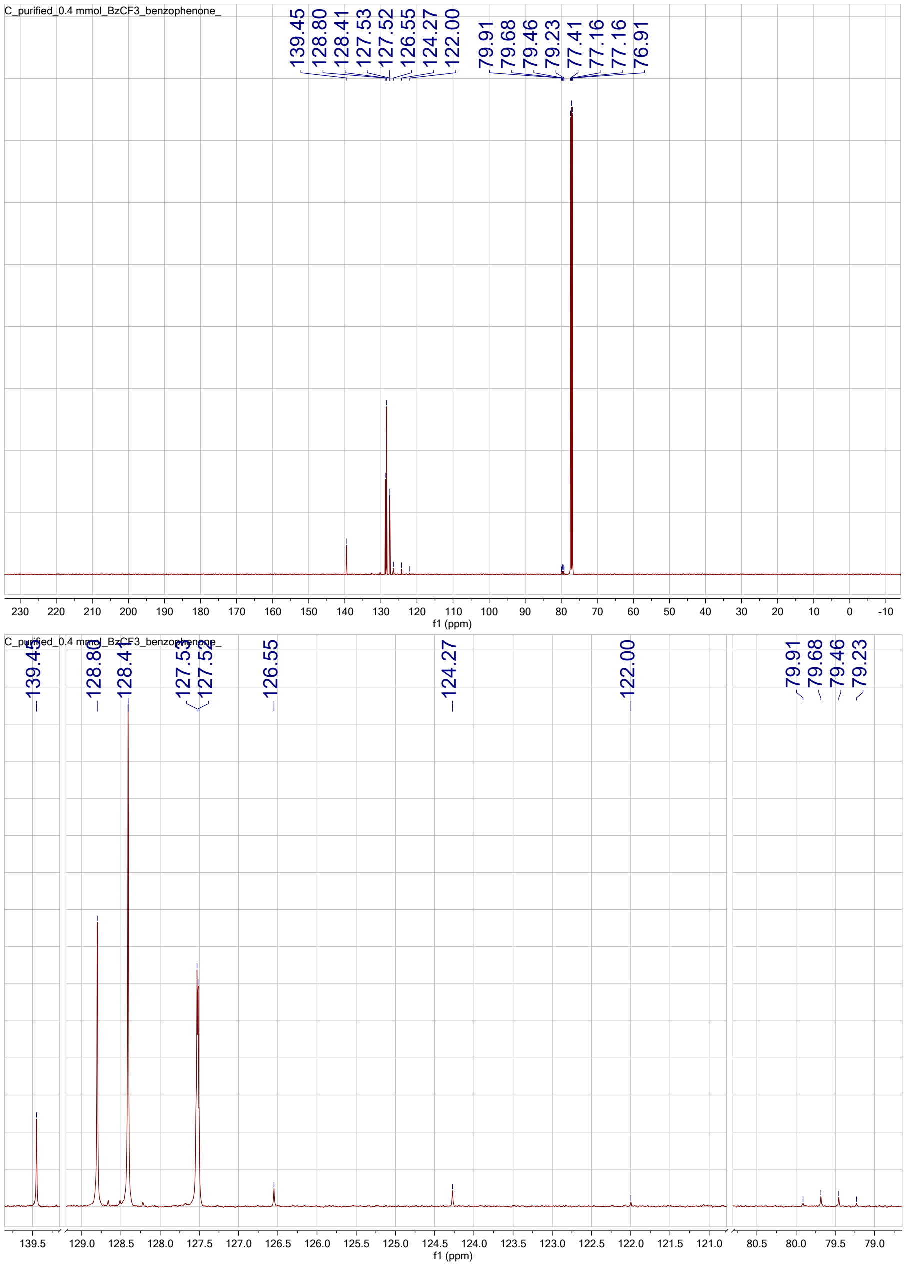


Figure S104. ^{13}C NMR spectra ($CDCl_3$) of isolated **H-3b’**. Top: full spectra and bottom: zoom-in spectra.

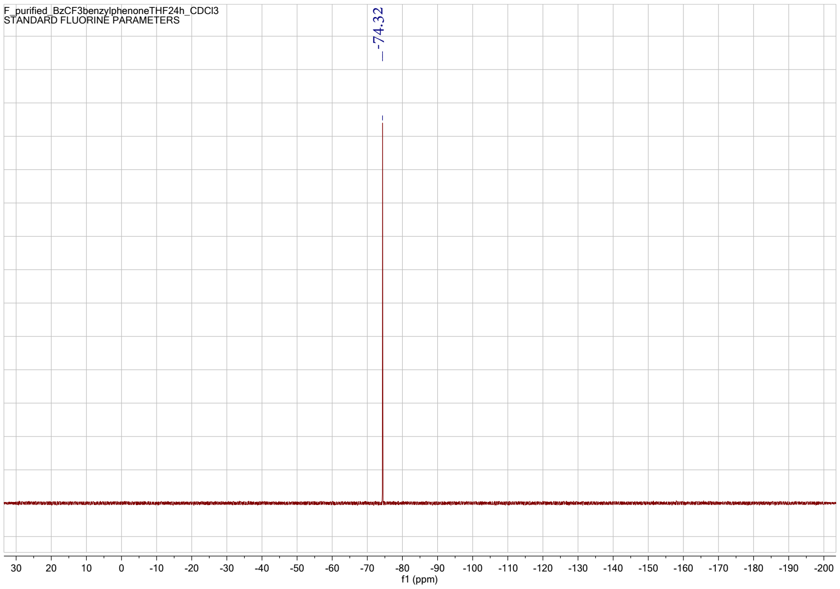
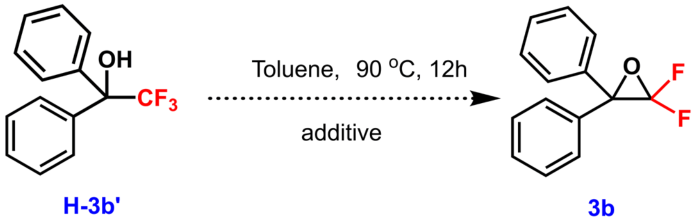


Figure S105. ^{19}F NMR spectra ($CDCl_3$) of isolated **H-3b'**.

2.3 Attempt at the synthesis of **3b** using authentic **H-3b'**

Protocol

Authentic **H-3b'** (0.01 mmol, mg) and various additives were dissolved in 0.5 mL toluene under N_2 atmosphere. The sealed vials were heated on the bench and 6 uL 1,2-difluorobenzene was added for quantification using ^{19}F NMR spectroscopy.



Entry	Additive	Unconverted H-3b' (%)	Yield of 3b (%)
1	-	100	0
2	1 eq tBuOK	100	0
3	1 eq tBuONa	21	0
4	1 eq tBuOLi	15	0
5	0.5 eq $tBuO_2Mg$	18	0
6	0.5 eq $CaOTf_2$	39	0
7	1 eq TMSOTf	100	0

Table S4. Additive screening for the synthesis of **3b**. None of the tested additives gave product **3b**.

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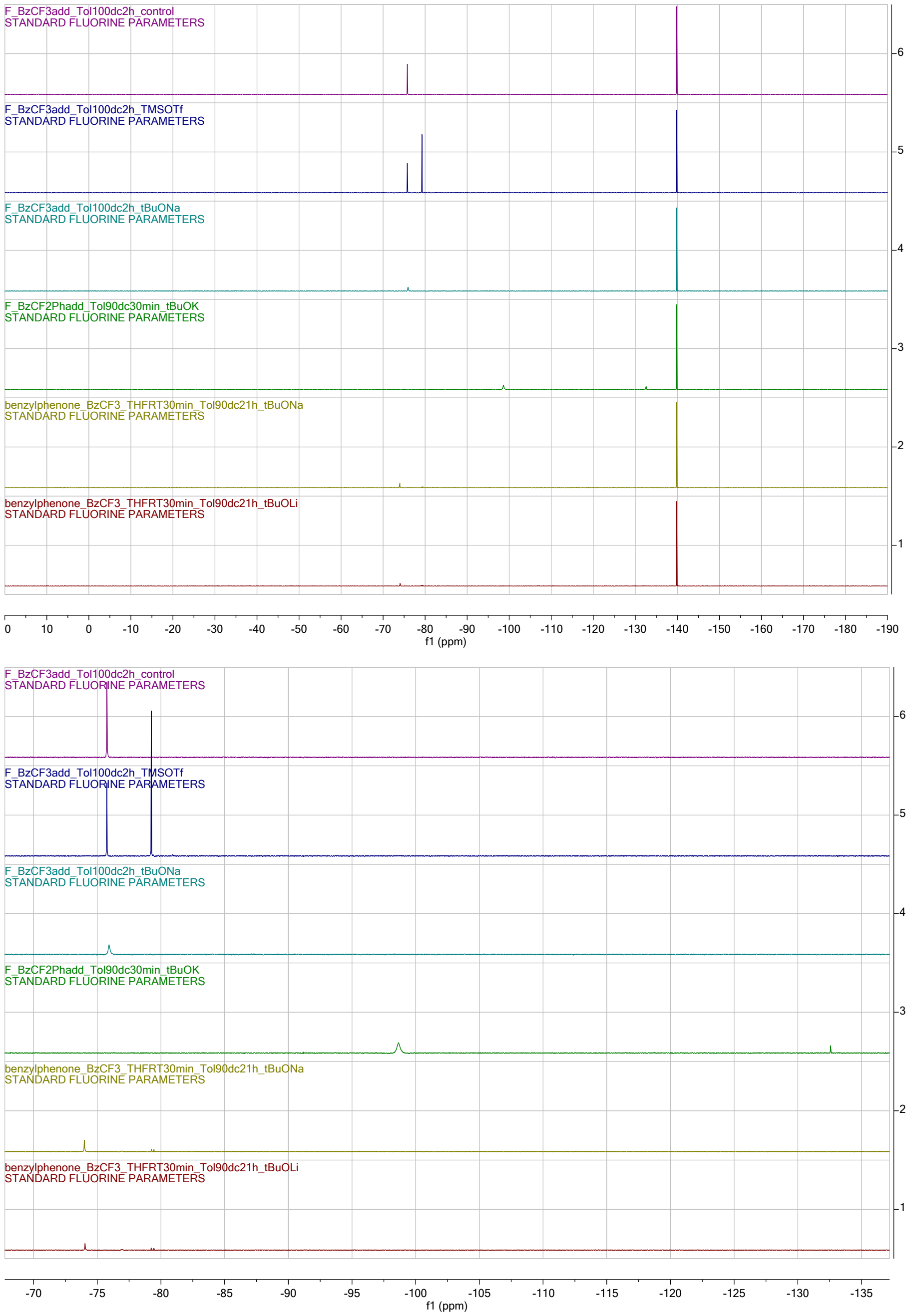

Figure S106. ^{19}F NMR spectra (in Toluene) of F-abstracting additive screening results. Top: full spectra and bottom: zoom-in spectra.

3. Synthesis and isolation of **3a** from benzophenone and **1-CF$_2$H**

3.1 Optimization of the reaction condition

Figure S107. Optimized condition for the synthesis of **3a**.

Solvent	**^{19}F NMR yield of 3a (%)**
Toluene (0.5 mL)	31
Toluene (1 mL)	34
Toluene (2 mL)	**39**
Toluene (4 mL)	37
THF	18
Dioxane	30
dichlorobenzene	4

Table S5. Solvent and concentration optimization. 0.02 M in toluene gave the highest yield of **3a**.

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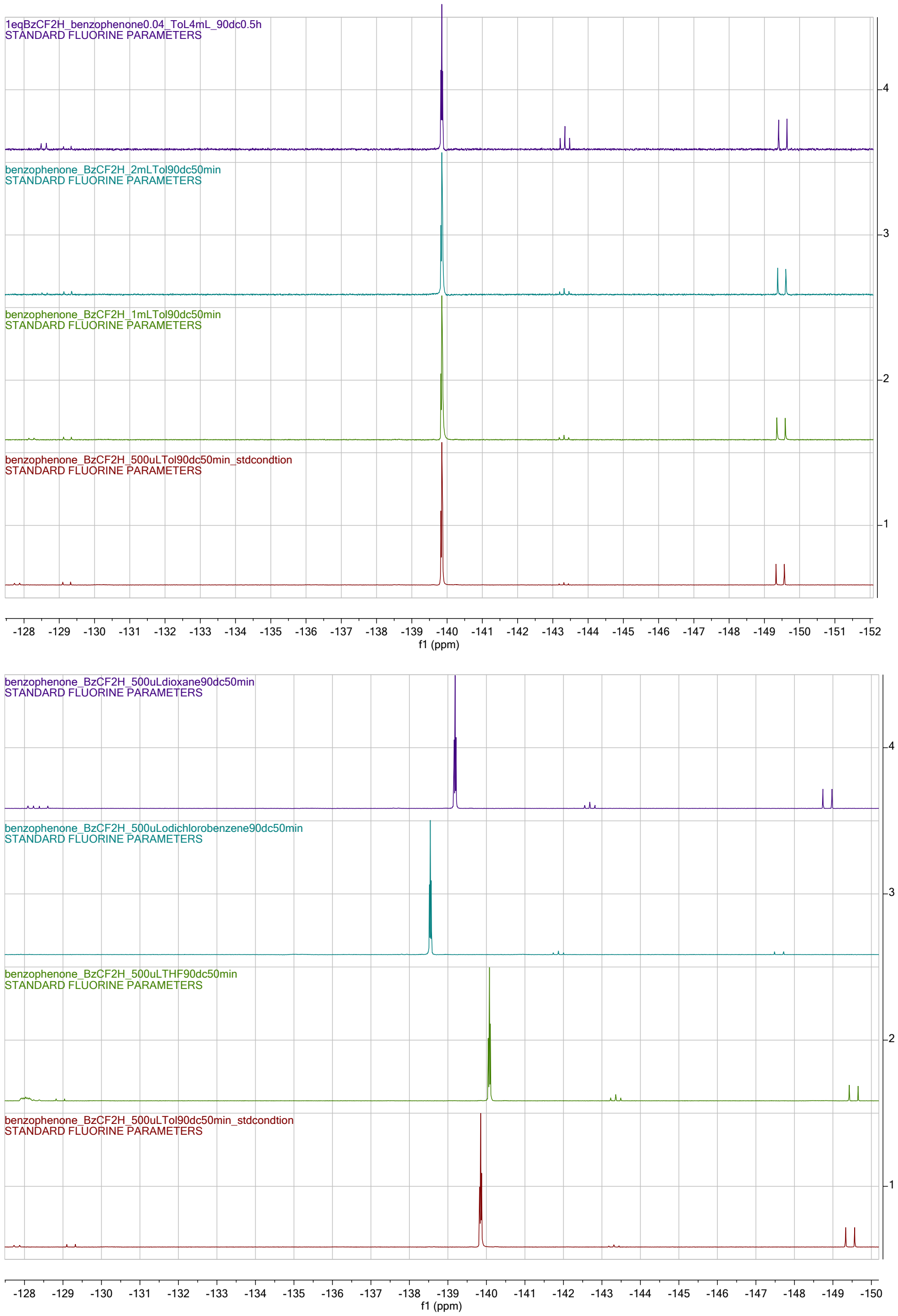

Figure S108. ^{19}F NMR spectra of the reaction between benzophenone and **1-CF$_2$H** at various concentrations in toluene (left) or in different solvents (right). Top: full spectra and bottom: zoom-in spectra.

`

1-CF₂H equiv.	^{19}F NMR yield of 3a (%)
1	36
2	36

Table S6. **1-CF₂H** equivalent optimization (equiv. relative to benzophenone). 0.5 mL toluene, 0.04 mmol scale, heating 30 min, 6 μL internal standard. Increasing the equiv. of **1-CF₂H** did not improve the yield of **3a** and thus 1 equiv. of **1-CF₂H** was considered as the optimized amount.

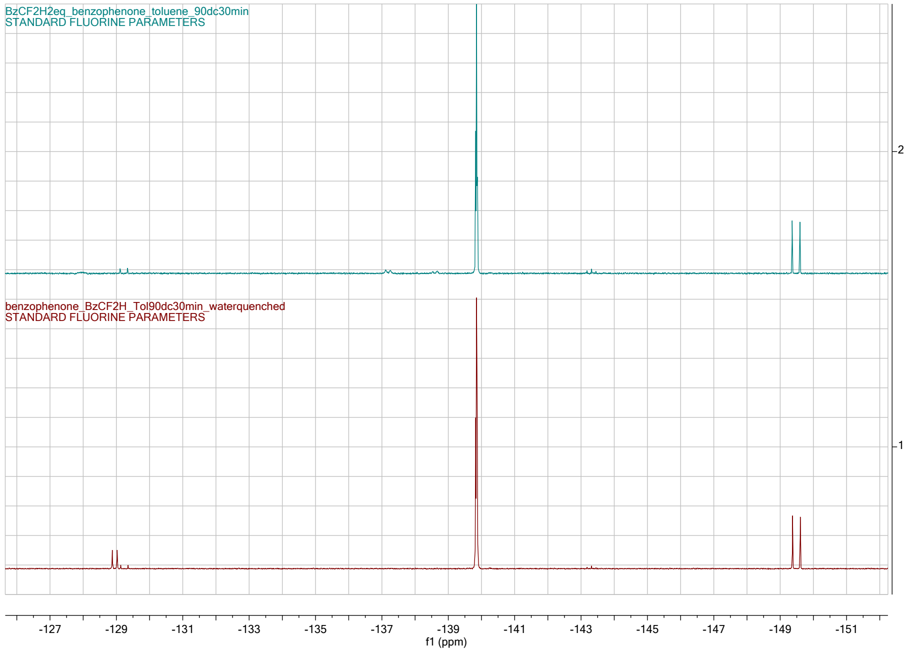

Figure S109. ^{19}F NMR spectra of the reaction between benzophenone and various equivalents of **1-CF₂H**.

Additive	Equiv.	^{19}F NMR yield of 3a (%)
-	-	36
KOTf	0.5	19
KOTf	1	7
KBARF$_{20}$	0.5	0
KBARF$_{20}$	1	0

Table S7. Effects of K$^+$ additives. Although we previous found that addition of K$^+$ source can activate the fluoroalkyl anion,[17] the 2 tested K$^+$ sources significantly decreased the yield of **3a**.

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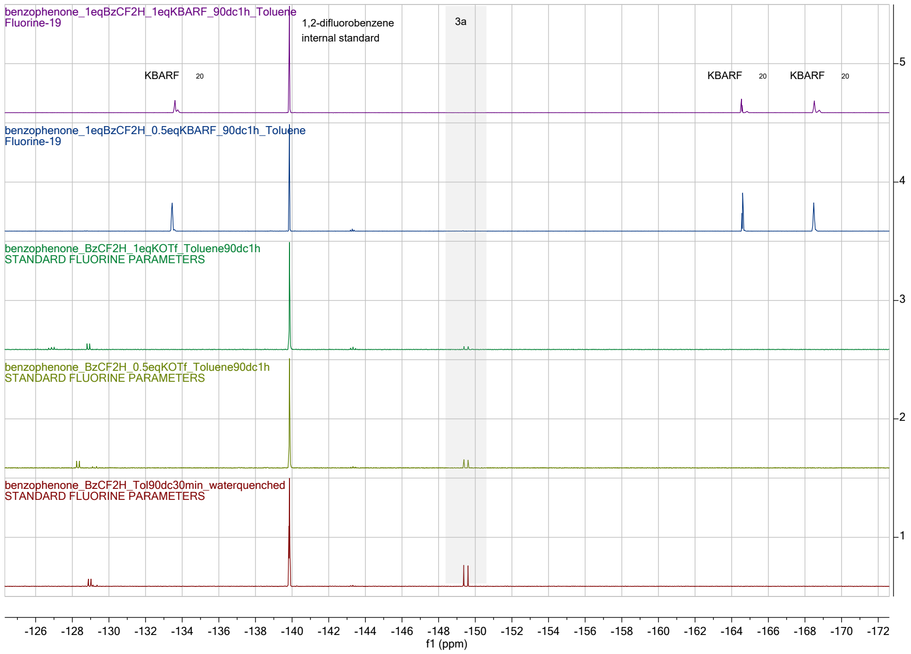

Figure S110. ^{19}F NMR spectra of the reaction between benzophenone and **1-CF$_2$H** with various K$^+$ additives.

Temperature (ºC)	^{19}F NMR yield of 3a (%)
70	32
80	**52**
90	39

Table S8. Temperature optimization. 2 mL toluene, 0.04 mmol scale.

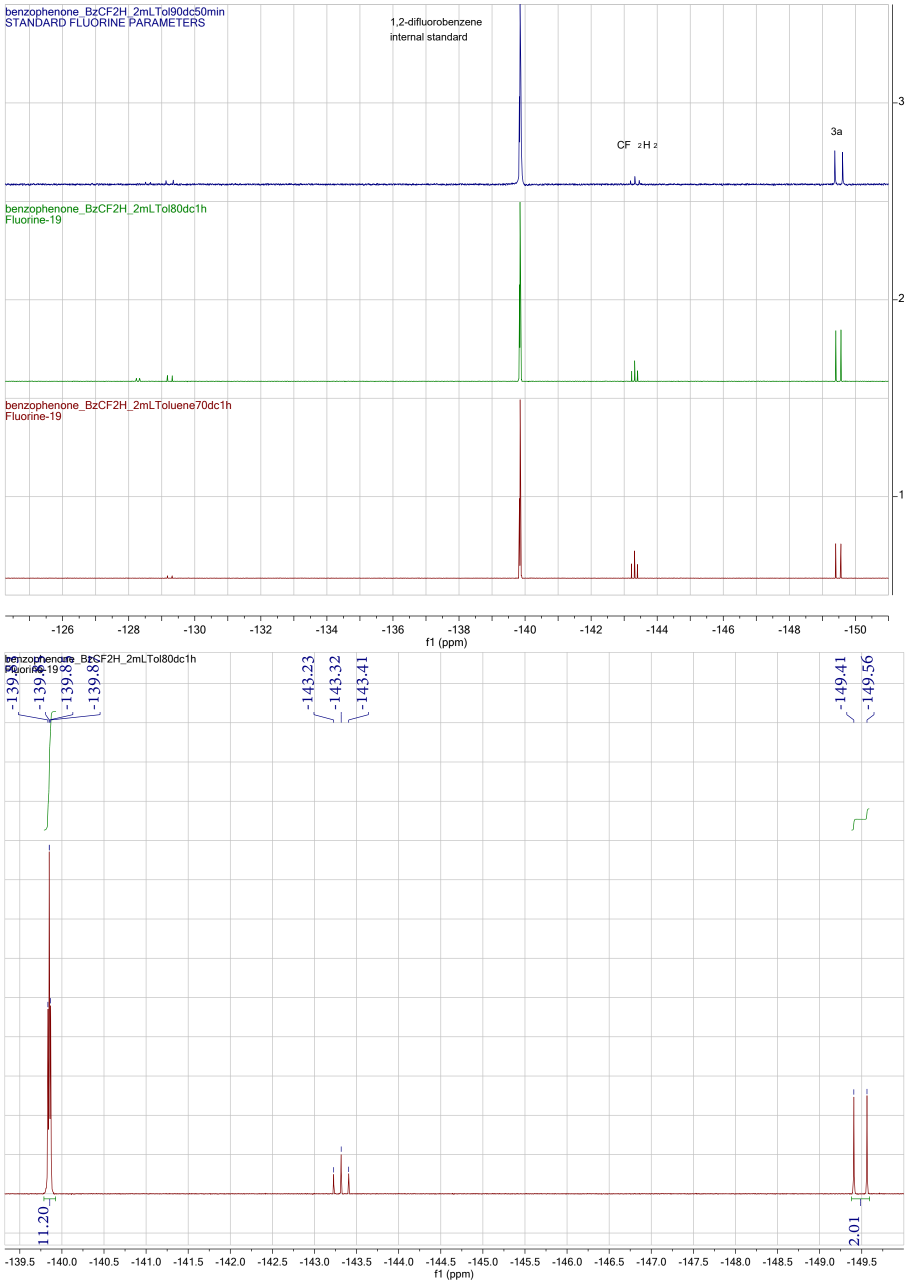

Figure S111. ^{19}F NMR spectra of the reaction between benzophenone and **1-CF₂H** at 90, 80, and 70 ºC, respectively (top, from top to bottom) and the zoom-in spectra of the reaction at 80 ºC (bottom).

`

Heating time (h)	**^{19}F NMR yield of 3a (%)**
0.5	**36**
1	**38**
1.5	32
2	32
24	17

Table S9. Heating time optimization. 1 mL Toluene, 90ºC, 0.04 mmol scale, 12 µL internal standard. Heating the reaction between 30 min – 1 h gave comparable yields of **3a**. However, heating 24 h decreased the yield of **3a**.

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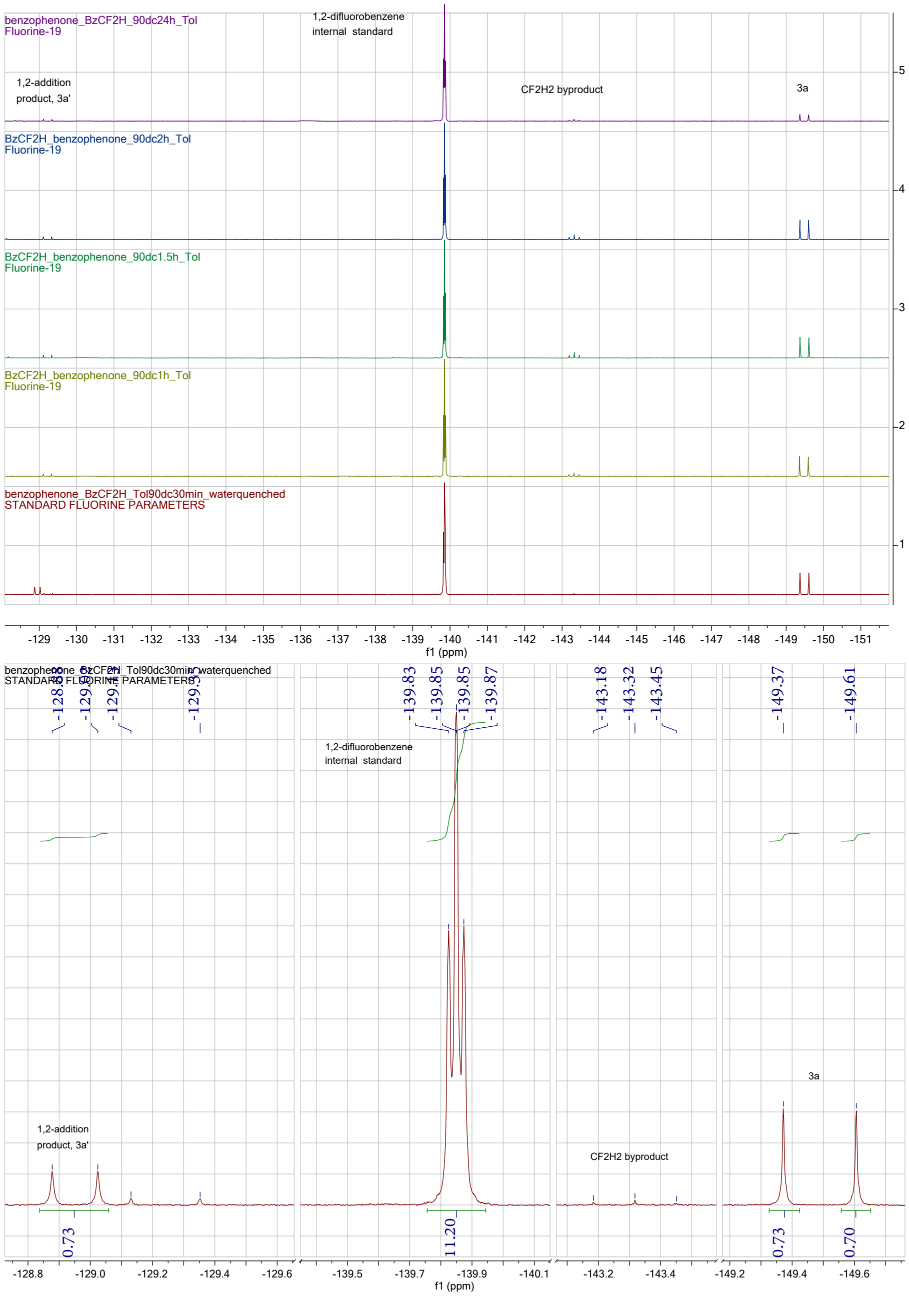
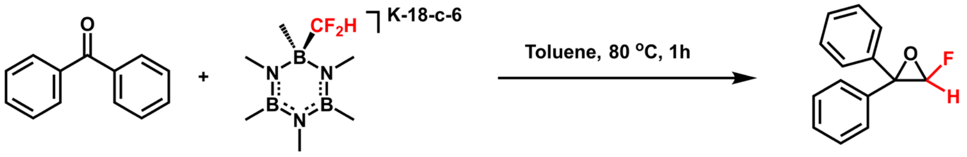


Figure S112. ^{19}F NMR spectra of the reaction between benzophenone and **1-CF$_2$H**. Optimized condition for the synthesis of **3a**. The chemical shifts and coupling constants of **H-3a'** (-128.95 ppm, d, *J* = 55.2 Hz, 2F) and **3a** (-149.49, d, *J* = 88.2 Hz, 1F) are consistent with those reported in the literature.[18],[19]

Discussion: based on the optimization above, we the optimal conditions for the synthesis of **3a** are 1 eq. **1-CF$_2$H** and benzophenone, 0.02 M in toluene, 80 ºC for 1h.

`

2.2 Synthesis and isolation of **3a**



1-CF$_2$H, 1 eq

3a

Figure S113. Optimized condition for the synthesis of **3a**.

Protocol (for condition optimization)

Benzophenone (0.04 mmol, 7.3 mg) and **1-CF$_2$H** (0.04 mmol, 21 mg) were measured in an 8 mL vial with 2 mL toluene and a stir bar under N_2 atmosphere. The sealed vials were heated and stirred at 80 °C for 1h. 6 µL (0.056 mmol) 1,2-difluorobenzene was added as the internal standard for quantification of the chemical yields of the afforded fluoroepoxides.

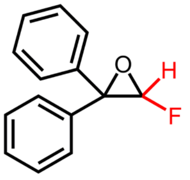
Protocol (for isolation)

Benzophenone (0.4 mmol, 73 mg) and **1-CF$_2$H** (0.4 mmol, 210 mg) were measured in a 20 mL vial with 20 mL toluene and a stir bar under N_2 atmosphere. The sealed vials were heated and stirred at 80 °C for 1h. 60 µL (0.56 mmol) 1,2-difluorobenzene was added as the internal standard and 0.5 mL of the solution was transferred to an NMR tube for quantifying the chemical yields of the afforded fluorinated epoxides. Then ~1 mL water was added to the same vial to work-up and the organic phase was extracted with EtOAc (3 x 3mL). The combined organic portions were dried with anhydrous $MgSO_4$ and the solvent was removed under vacuum.

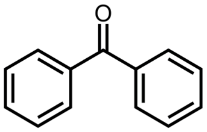
The resulting residual was further purified by flash column chromatography on silica gel (eluent: hexanes:EtOAc = 10:1, v/v, containing 5 vol% Et_3N) affording the pure compound.

Note: After 3 months storage on bench, **3a** was observed to slowly transform into the corresponding 1,2-F migration product **5c**.

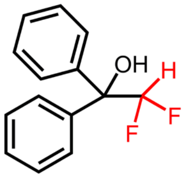
3.3 Characterization of **3a** (NMR spectra)



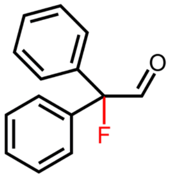
3a: (45% ± 4, n = 2), impurities:



benzophenone

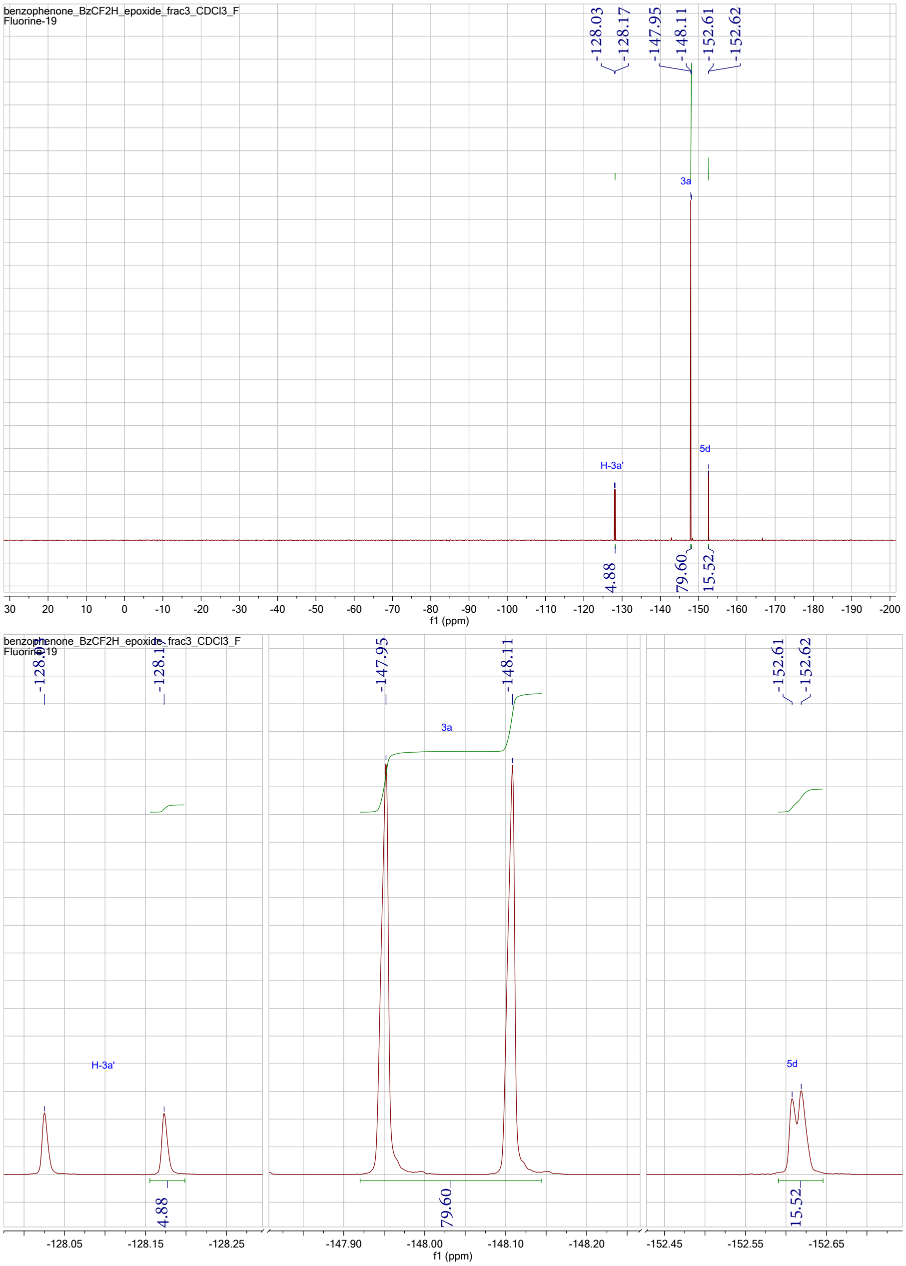


H-3a'



5d

Yellow oil (0.4 mmol, 29 mg isolated, 46.3% purity). ^{19}F NMR (564 MHz, $CDCl_3$) δ -148.03 (d, J = 88.1 Hz). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 – 7.32 (m, 10H), 5.80 (d, J = 88.1 Hz, 1H). The ^{1}H and ^{19}F NMR characterization results are similar to that reported in the literature.[19] Due to the low purity of the isolated compound, the isolated yield is not listed.


benzophenone_BzCF2H_epoxide_frac3_CDCl3_F
Fluorine-19
-128.03
-128.17
-147.95
-148.11
-152.61
-152.62
3a
5d
H-3a'
4.88
79.60
15.52
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)
-128.05 -128.15 -128.25
-147.90 -148.00 -148.10 -148.20
-152.45 -152.55 -152.65

`

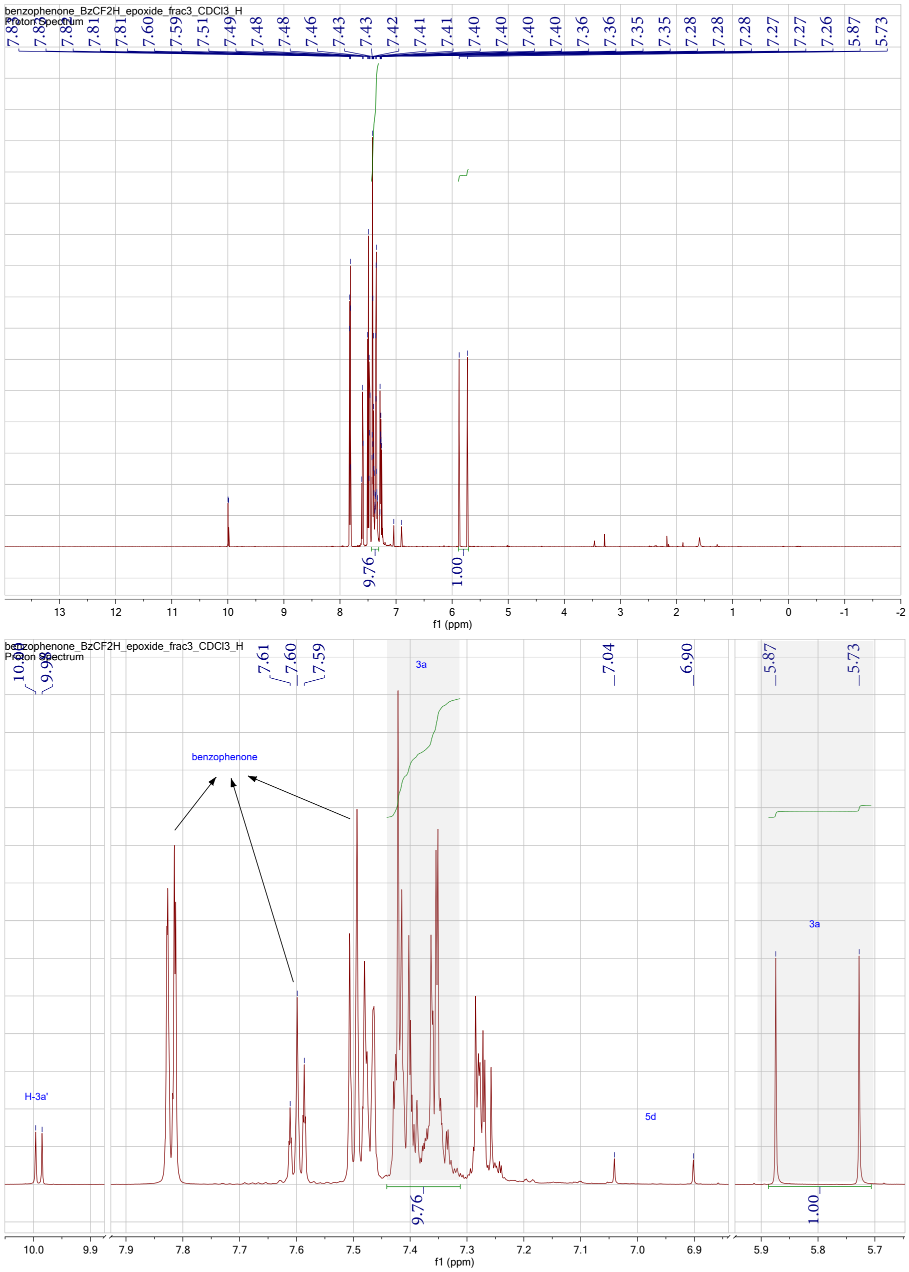


Figure S114. ^{19}F (2 top) and ^{1}H (2 bottom) NMR spectra (in CDCl$_3$) of isolated **3a**.

Aroyl chloride scope (4a-4e)

1. Detection of the intermediates

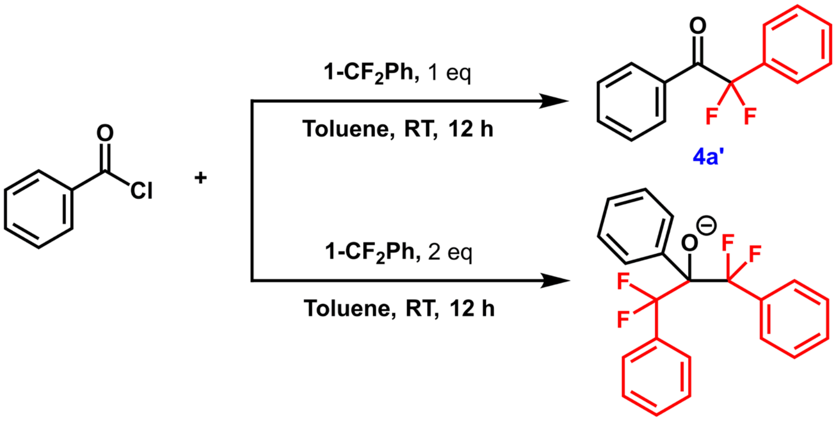


Figure S115. Scheme for probing the intermediates toward **4a**.

Protocol

Benzoyl chloride (0.04 mmol, 4.3 mg) and 1 eq. **1-CF$_2$Ph** (0.04 mmol, 23.8 mg) or 2 eq. (0.08 mmol, 47.6 mg) were measured in 8 mL vials with 1 mL toluene and a stir bar under N_2 atmosphere, respectively. The sealed vials were stirred at RT for 12 h. 6 µL (0.056 mmol) 1,2-difluorobenzene was then added as the internal standard. The chemical yields of the fluorinated species were quantified by ^{19}F NMR spectroscopy.

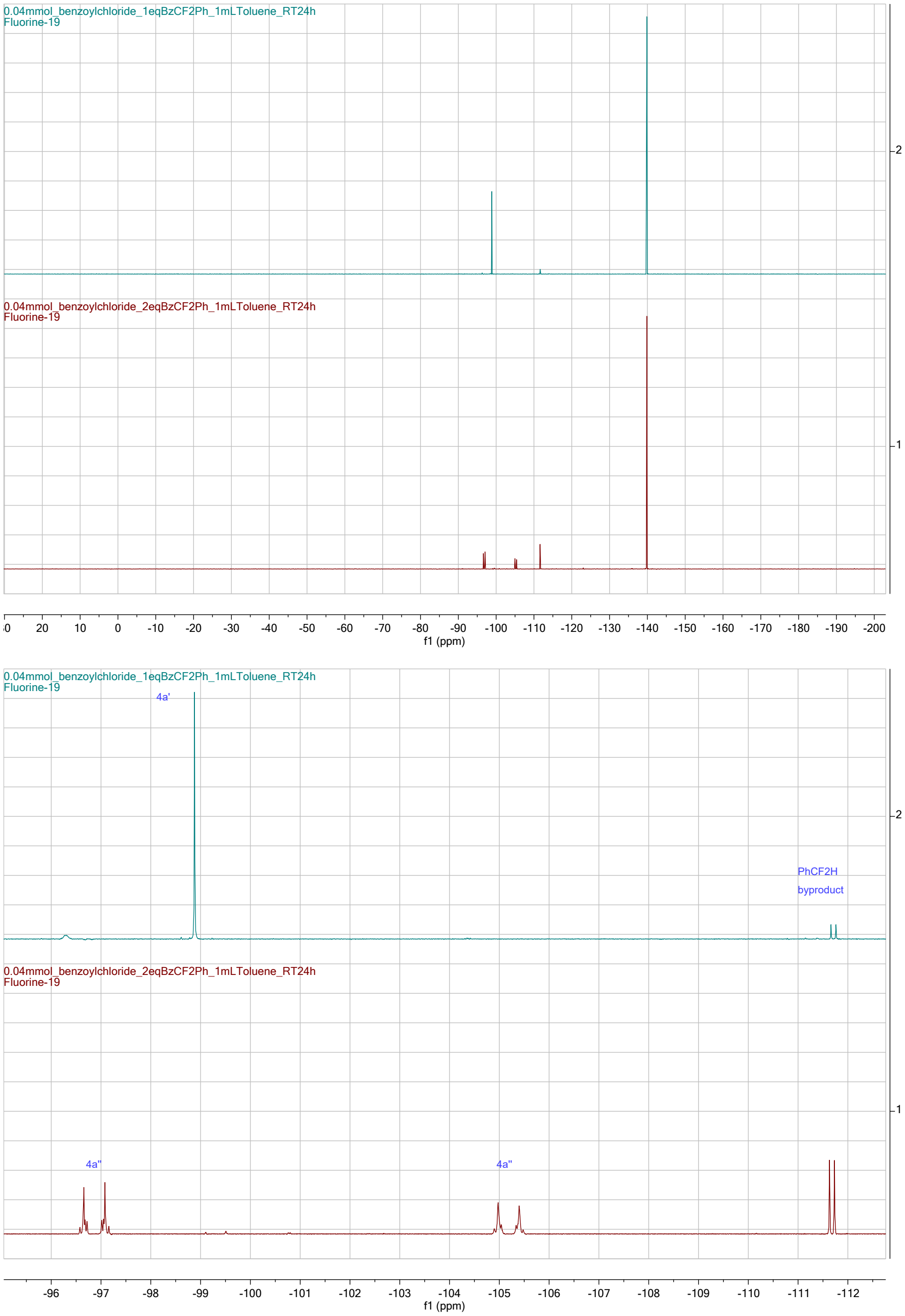


Figure S116. ^{19}F NMR spectra (in toluene) of benzoyl chloride and 1 eq. (top spectra) or 2 eq. (bottom spectra) **1-CF$_2$Ph**. **4a'**: ^{19}F NMR (564 MHz, toluene) -98.88 ppm (s, 2F), *in situ* yield of 95%; **4a''**: ^{19}F NMR (564 MHz, toluene) δ -96.54 – -97.19 (m, 2F), -104.80 – -105.56 (m, 2F), *in situ* yield of 99%.

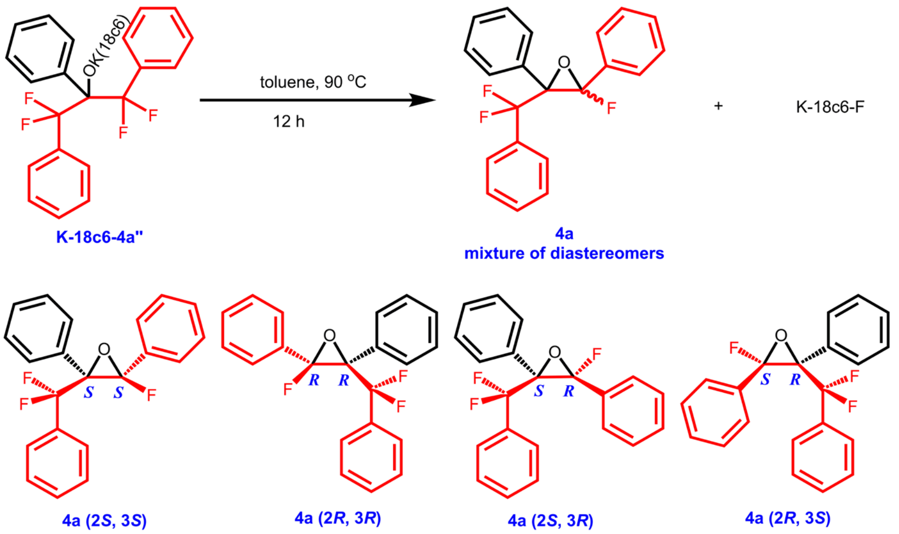


Figure S117. There are 4F on the intermediate **4a''**, leading to 4 possible absolute configurations of the afforded **4a** as shown above, giving 2 types of ^{19}F NMR signals. Due to the fact that –CF$_2$Ph > –Ph and –Ph > –F in size, we propose that the product would favor the formation of *trans* configuration of –CF$_2$Ph and –Ph: **4a (2*S*, 3*S*)** and **4a (2*R*, 3*R*)**. This is in agreement with the ^{19}F NMR (**Figure S119**) and X-ray single crystal diffraction results (**Figure 4b**, **4a (2*R*, 3*R*)**).

2. Synthesis of multi-fluoroepoxides from **1-CF$_2$Ph** and aroyl chlorides

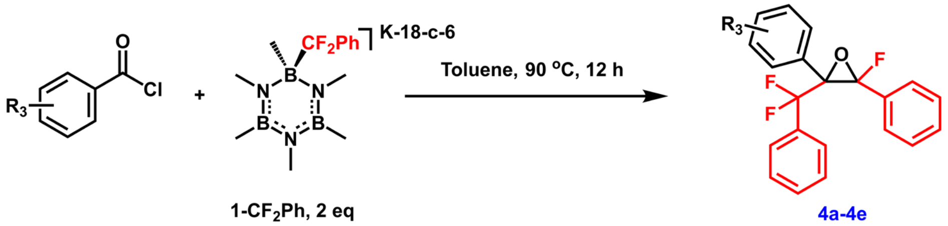


Figure S118. Scheme for the synthesis of multi-fluoroepoxides from **1-CF$_2$Ph** and aroyl chlorides.

Protocol (for optimization)

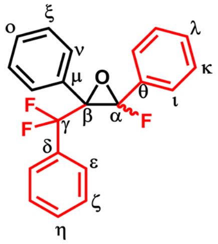
The acyl chloride electrophile (0.04 mmol) and **1-CF$_2$Ph** (0.08 mmol, 47.6 mg) were measured in an 8 mL vial with 0.5 mL toluene and a stir bar under an N$_2$ atmosphere. The sealed vials were heated and stirred at 90 °C for 12 h. 6 µL (0.056 mmol) 1,2-difluorobenzene was added as the internal standard for quantification of the chemical yields of the afforded multi-fluoroepoxides.

Protocol (for isolation)

The acyl chloride electrophile (0.4 mmol) and **2** (0.8 mmol, 476 mg) were measured in an 8 mL vial with 5 mL toluene and a stir bar under an N$_2$ atmosphere. The sealed vials were heated and stirred at 90 °C for 12 h. 1 mL of the mixture was filtered through glass microfiber, then characterized by ^{19}F NMR spectroscopy (with added 6 µL, 0.056 mmol, 1,2-difluorobenzene as the internal standard) for quantification of the chemical yields. The NMR sample was added back to the original reaction sample, followed by ~1 mL water, then the organic phase was extracted with EtOAc (3 x 3 mL). The combined organic portions were dried with anhydrous MgSO$_4$ and the solvent was removed under vacuum.

The resulting residue was further purified by flash column chromatography on silica gel (eluent: hexanes:EtOAc = 10:1, v/v, containing 5 vol% Et$_3$N) affording the purified compounds. Crystals suitable for X-ray diffraction were obtained by vapor diffusion of pentane into a toluene solution of 4a at -30 °C.

3. Characterization of **4a-4e** (NMR spectra and LC-MS)



4a: 83%, d.r. = 88:12
(84 ± 6%, d.r. = 88:12, n=4)

White solid (0.4 mmol, 113 mg isolated, 83% purity). Inseparable mixture of diastereoisomers. ^{19}F NMR (564 MHz, CDCl$_3$) δ -93.80 (dd, J = 252.8, 27.4 Hz, major isomer, γF, 1F), -95.44 (d, J = 256.3 Hz, minor isomer, γF, 1F), -96.63 (d, J = 256.6 Hz, minor isomer, γF, 1F), -97.97 (dd, J = 252.8, 23.1 Hz, major isomer, γF, 1F), -104.66 (s, minor isomer, αF, 1F), -130.92 (dd, J = 27.4, 23.1 Hz, major isomer, αF, 1F). Major isomers: ^{13}C NMR (126 MHz, CDCl$_3$) δ 134.67 (t, J = 26.3 Hz, δC), 130.90 (d, J = 31.3 Hz, θC), 130.47 (unresolved triplet, ζC), 130.31 (d, J = 2.5 Hz, μC), 129.91 (d, J = 1.7 Hz, κC), 128.88 (s, νC), 128.73 (s, oC), 128.28 (s, ηC), 128.05 (s, λC), 127.64 (s, ξC), 127.04 (d, J = 4.3 Hz, ιC), 126.19 (t, J = 6.1 Hz, εC), 118.80 (ddd, J = 251.8, 250.1, 5.7 Hz, γC), 98.80 (dd, J = 274.7, 2.5 Hz, αC), 71.57 (ddd, J = 33.3, 31.9, 19.8 Hz, βC). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.46 – 7.40 (m, 3H), 7.40 – 7.35 (m, 2H), 7.23 – 7.20 (m, 1H), 7.18 (m, 4H), 7.15 – 7.10 (m, 1H, 1oH), 7.04 (t, J = 7.8 Hz, 2H, 2ξH), 6.88 (d, J = 6.5 Hz, 2H, 2νH). HR-MS (ESI): calcld. for [M – 3F + 4H]$^+$ (C$_{21}$H$_{19}$O)$^+$ = 287.1430, found 287.1464. Product confirmed by single crystal X-ray diffraction, which was used to benchmark subsequent spectroscopic characterization.

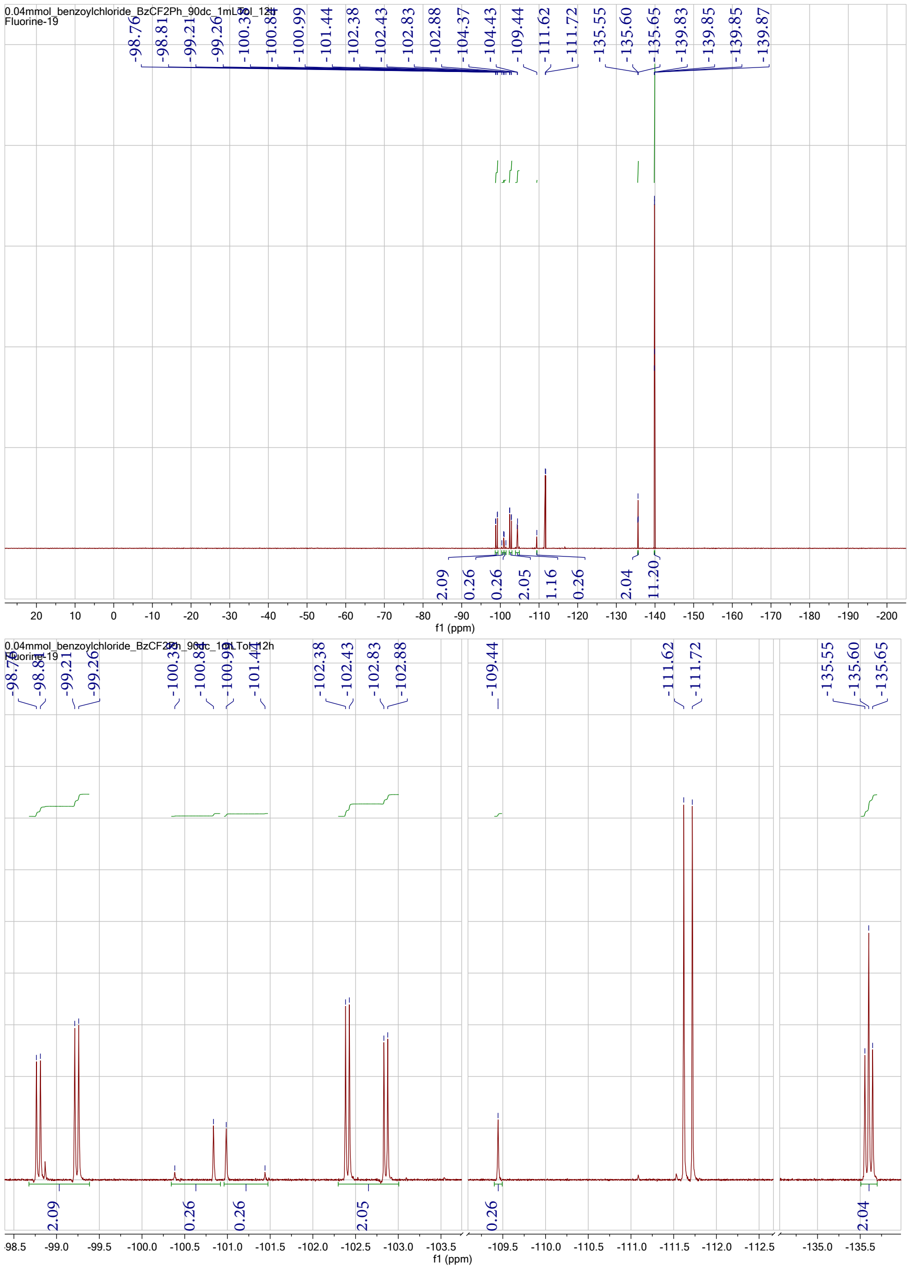
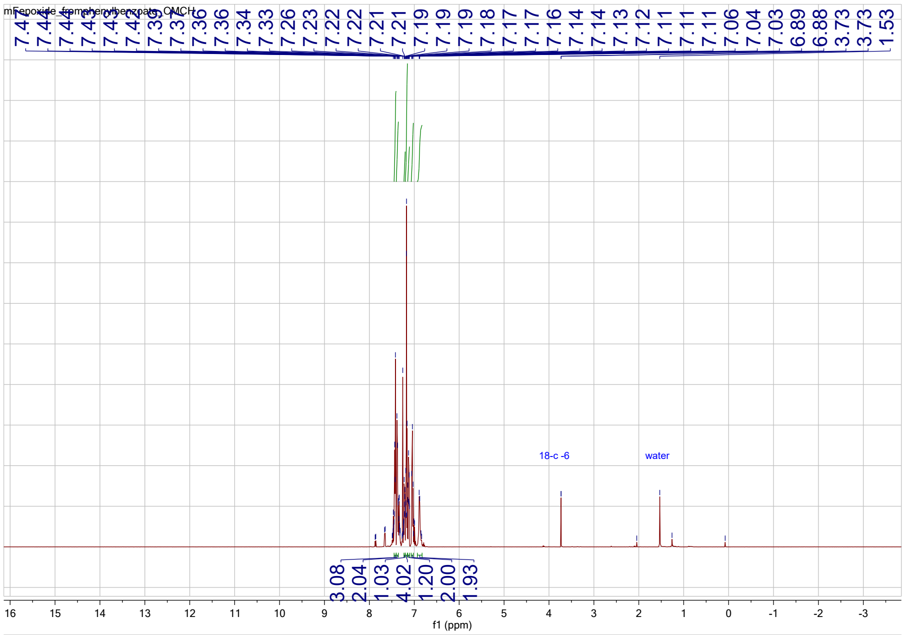


Figure S119. Representative *in situ* ^{19}F NMR spectra (in toluene) of **4a**. Top: full spectra and bottom: zoom-in spectra.



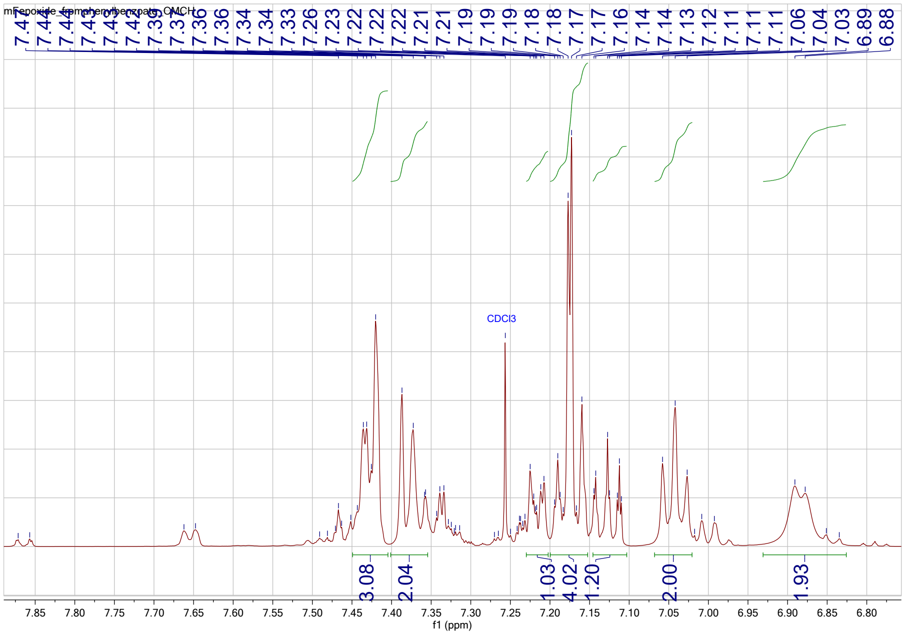


Figure S120. ^{1}H NMR spectra ($CDCl_3$) of isolated **4a**. Top: full spectra and bottom: zoom-in spectra.

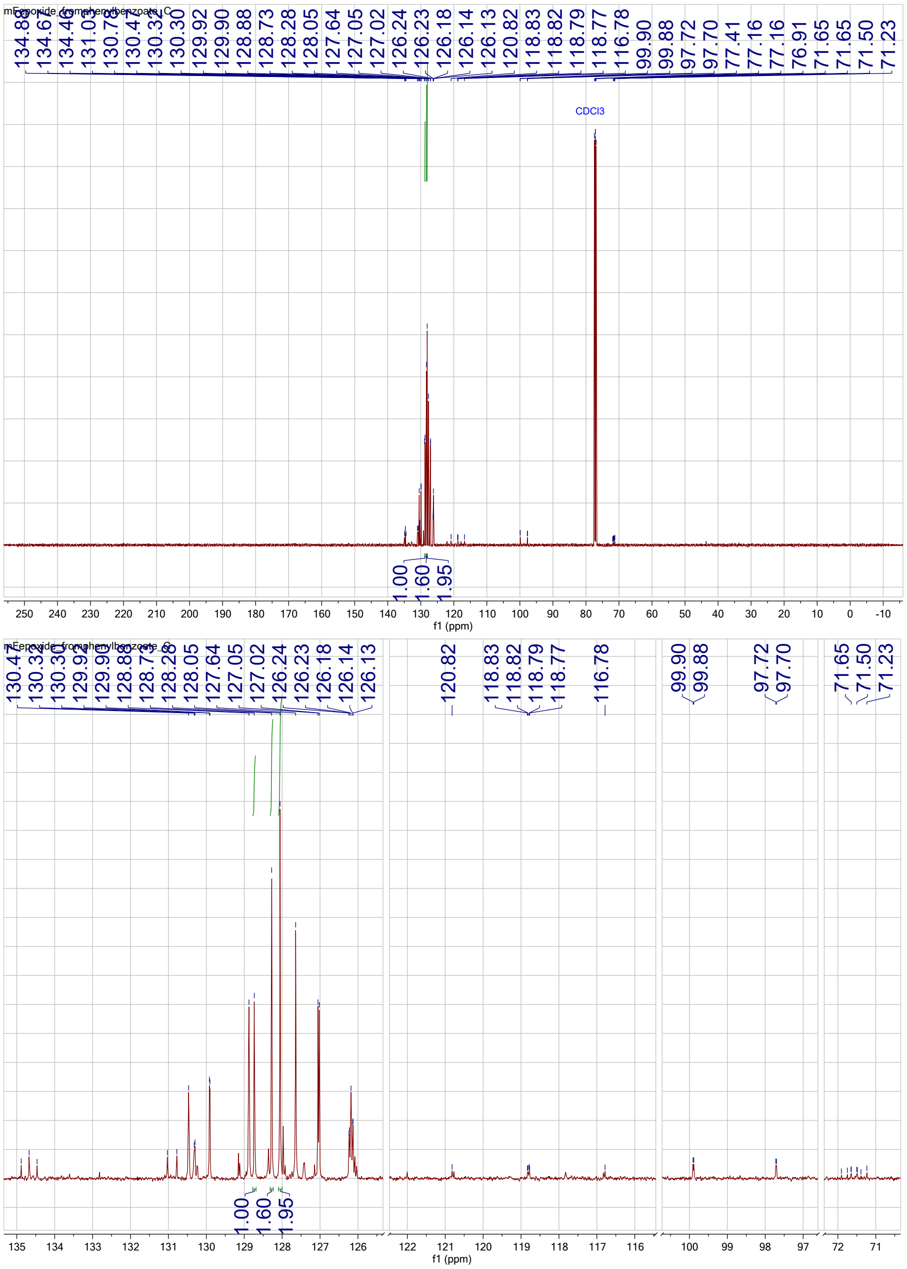


Figure S121. ^{13}C NMR spectra (CDCl$_3$) of isolated **4a**. Top: full spectra and bottom: zoom-in spectra.

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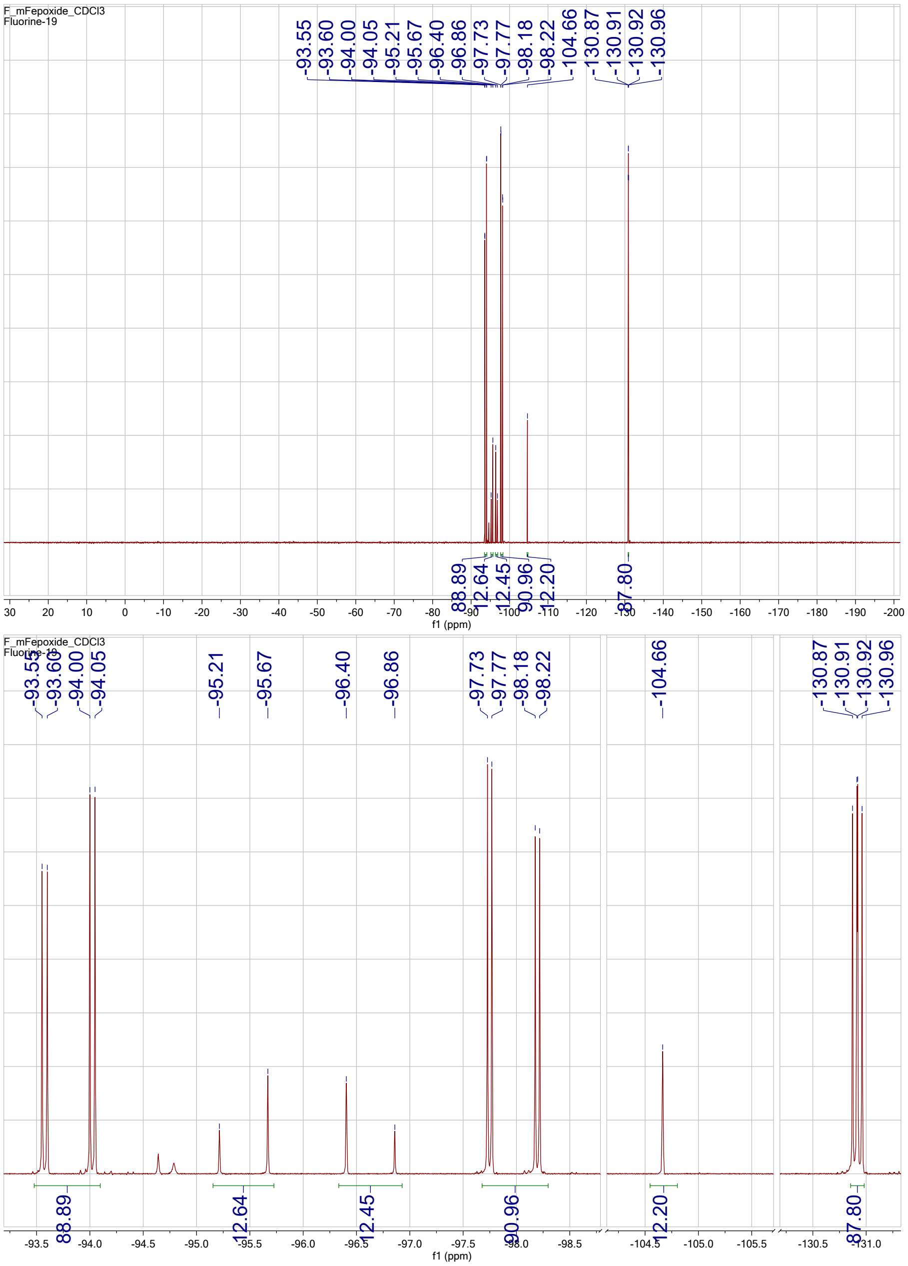

Figure S122. ^{19}F NMR spectra (CDCl$_3$) of isolated **4a**. Top: full spectra and bottom: zoom-in spectra.

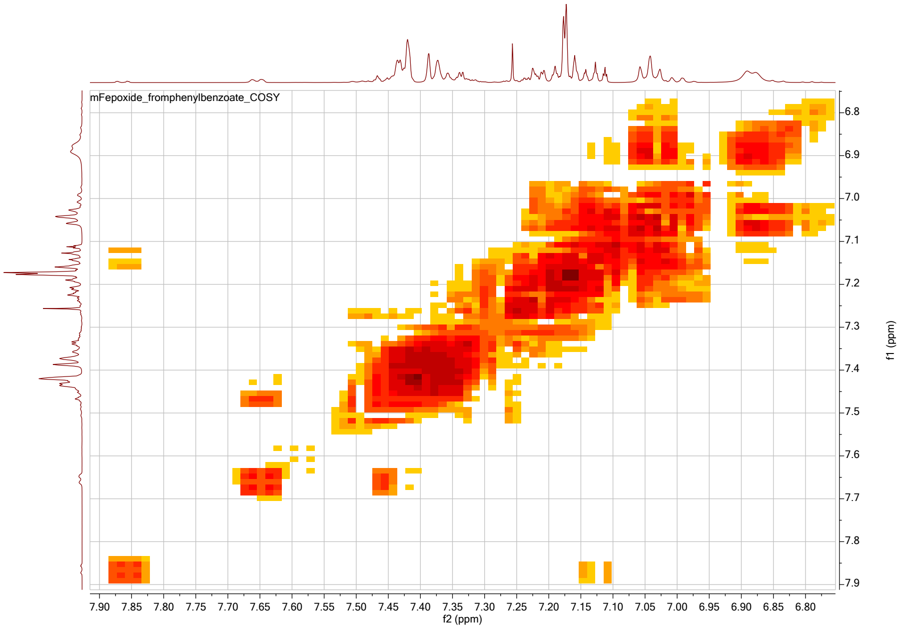

Figure S123. ^{1}H-^{1}H COSY spectra (CDCl$_3$) of isolated **4a**.

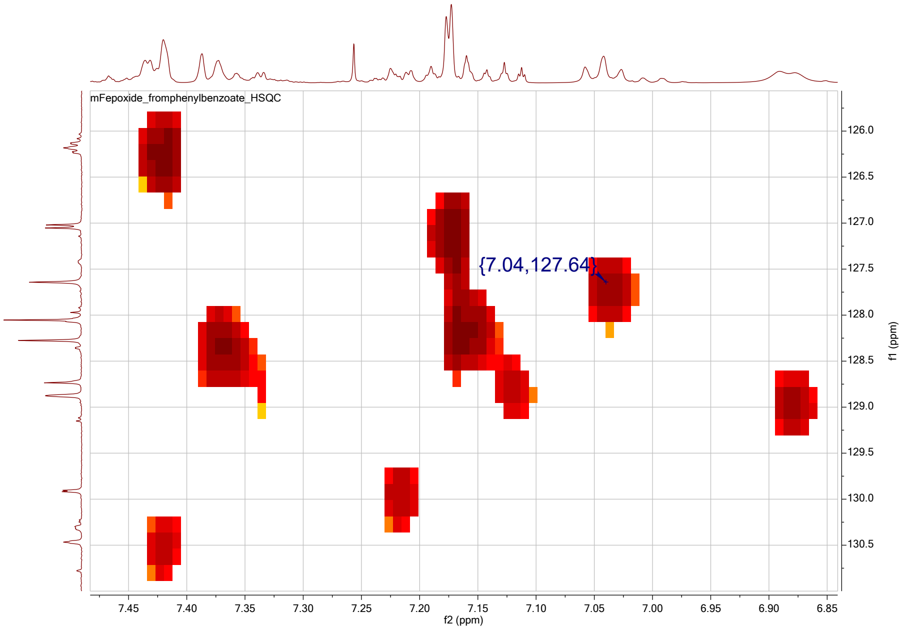

Figure S124. ^{1}H-^{13}C HSQC spectra (CDCl$_3$) of isolated **4a.**

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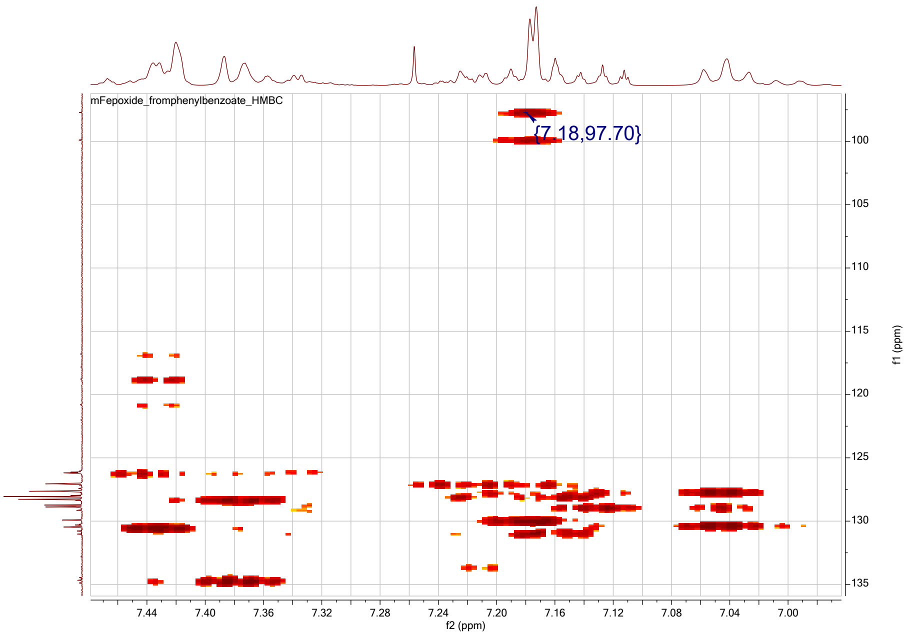
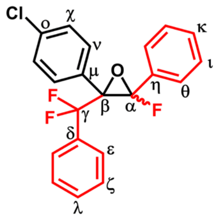


Figure S125. ^{1}H-^{13}C HMBC spectra (CDCl$_3$) of isolated **4a**.



R_3 = Ph(*p*-Cl)
4b: 23%, d.r. = 85:15
(59 ± 4%, d.r. = 85:15, n=2)

Yellow oil (0.4 mmol, 34 mg isolated, 33% purity). Inseparable mixture of diastereoisomers. ^{19}F NMR (564 MHz, CD$_2$Cl$_2$) δ -97.47 (dd, *J* = 252.7, 28.1 Hz, major isomer, γF, 1F), -99.21 (d, *J* = 256.3 Hz, minor isomer, γF, 1F), -100.17 (d, *J* = 256.3 Hz, minor isomer, γF, 1F), -101.71 (dd, *J* = 252.7, 22.9 Hz, major isomer, γF, 1F), -108.13 (s, minor isomer, αF, 1F), -133.56 (dd, *J* = 28.1, 22.9 Hz, major isomer, αF, 1F). Major isomer: ^{1}H NMR (600 MHz, CD$_2$Cl$_2$) δ 7.48 – 7.45 (m, 1H), 7.43 – 7.41 (m, 4H), 7.25 – 7.18 (m, 5H), 7.05 (d, *J* = 8.7 Hz, 2H), 6.83 (d, *J* = 7.0 Hz, 2H). ^{13}C NMR (126 MHz, CD$_2$Cl$_2$) δ 167.91 (s, oC), 135.13 (s), 134.47 (t, *J* = 26.1 Hz), 131.32 (s), 131.03 (s), 130.48 (s), 128.78 (s), 128.55 (s), 128.30 (s), 127.21 (d, *J* = 4.1 Hz), 126.25 (t, *J* = 5.3 Hz), 119.02 (ddd, *J* = 249.7, 248.8, 4.8 Hz, γC), 99.03 (dd, *J* = 275.0, 2.5 Hz, αC), 66.38 (d, *J* = 39.1 Hz, βC). HR-MS: calcld. For [M – O + H]$^+$ ($C_{21}H_{15}ClF_3^+$) = 359.0809, found: 359.1304.

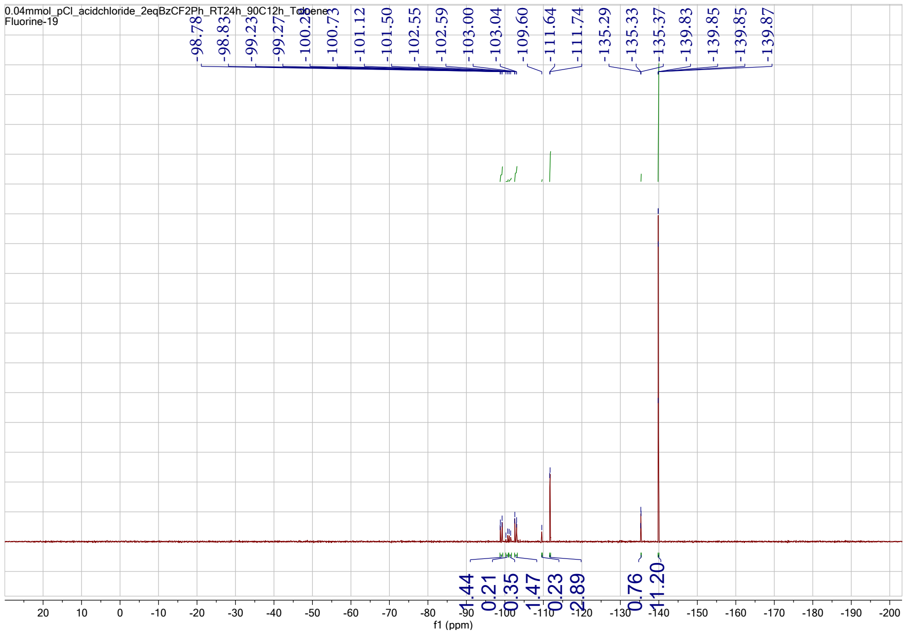


Figure S126. Representative *in situ* ^{19}F NMR spectra (in toluene) of **4b** showing the chemical yield.

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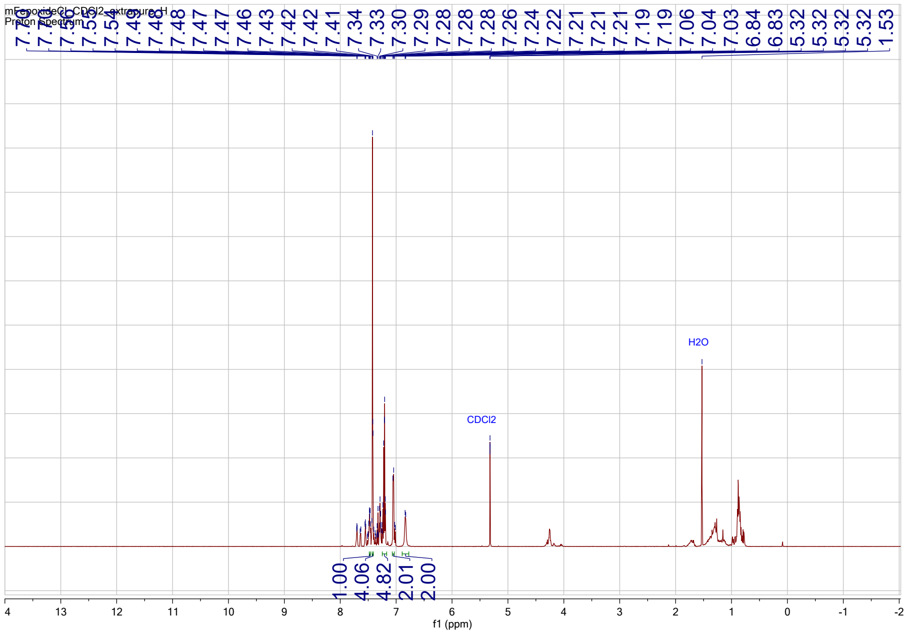

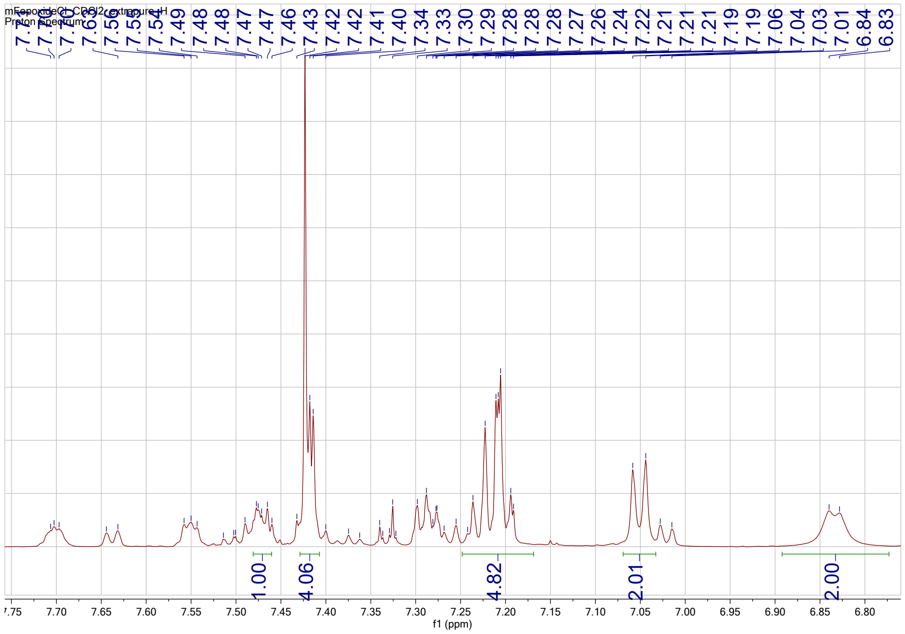

Figure S127. ^{1}H NMR spectra (CD_2Cl_2) of isolated **4b**. Top: full spectra and bottom: zoom-in spectra.

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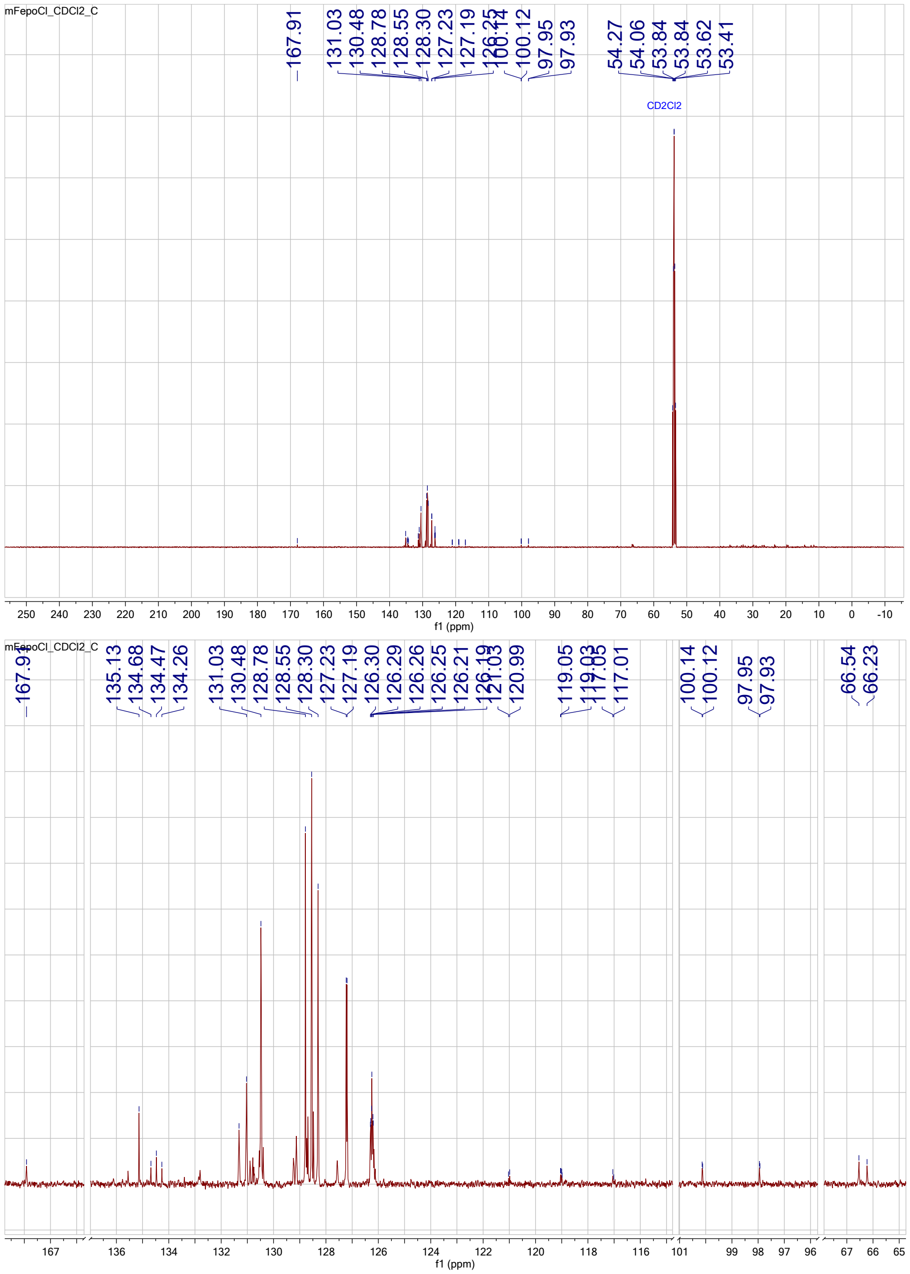

Figure S128. ^{13}C NMR spectra (CD_2Cl_2) of isolated **4b**. Top: full spectra and bottom: zoom-in spectra.

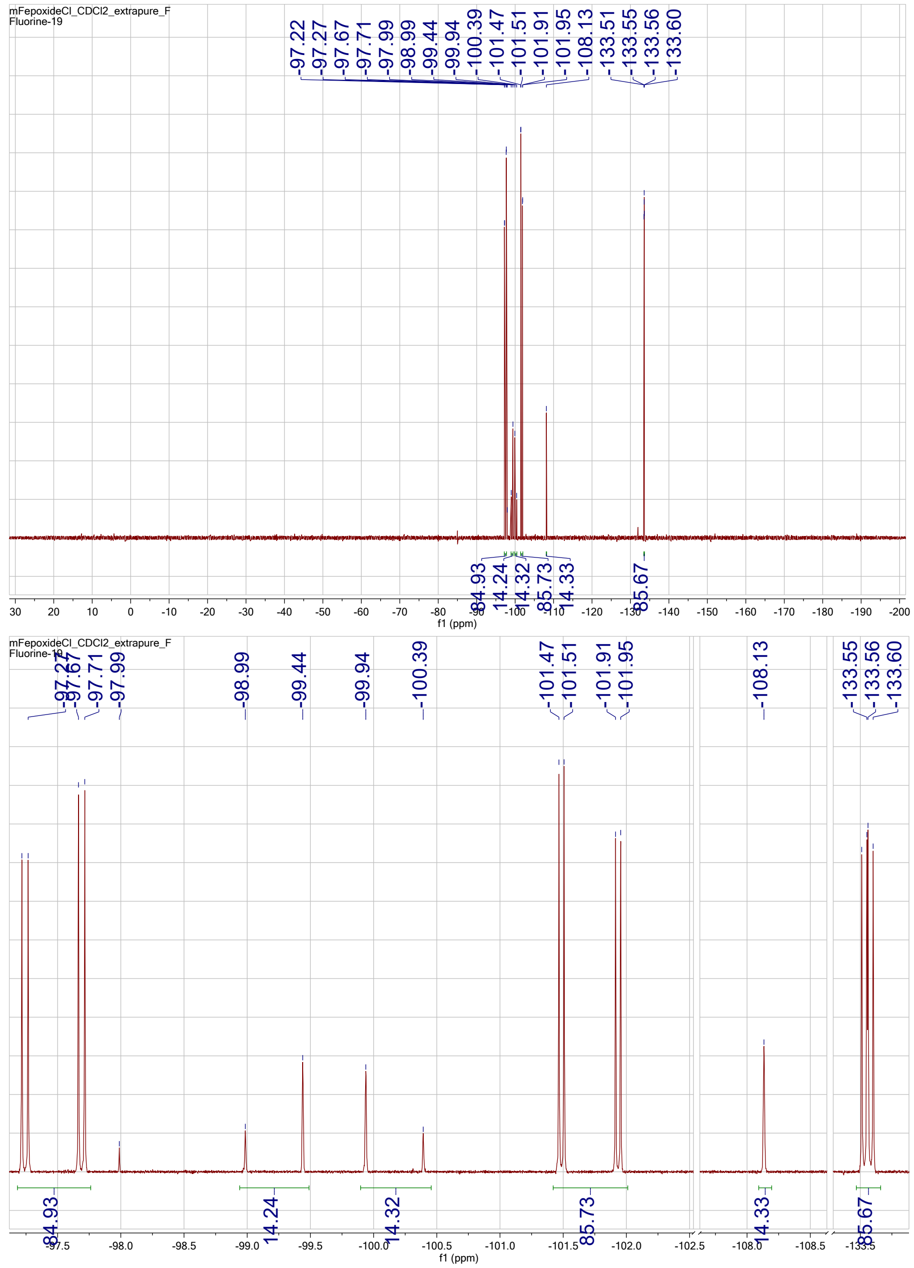

Figure S129. ^{19}F NMR spectra (CD_2Cl_2) of isolated **4b**. Top: full spectra and bottom: zoom-in spectra.

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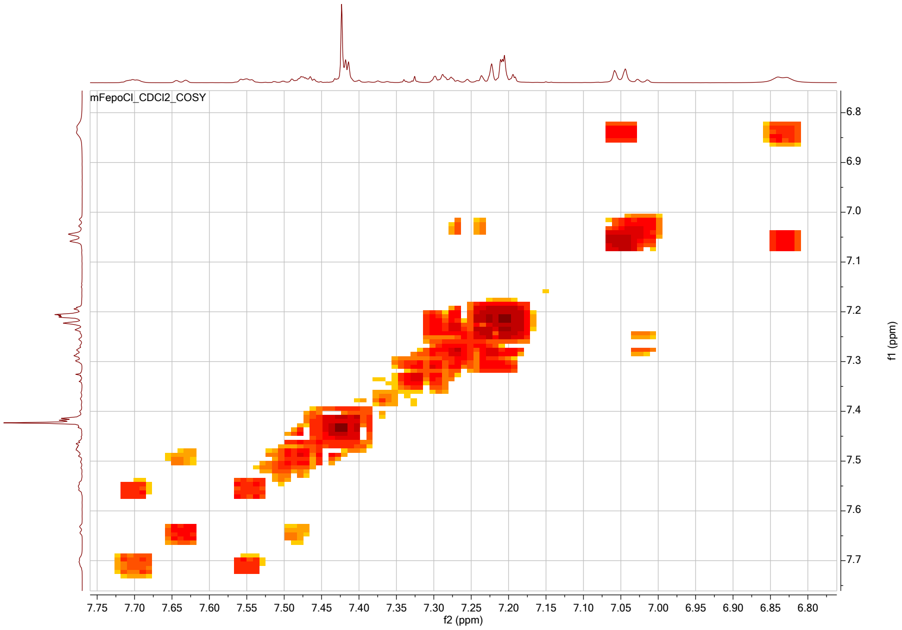

Figure S130. ^{1}H-^{1}H COSY spectra (CD_2Cl_2) of isolated **4b**.

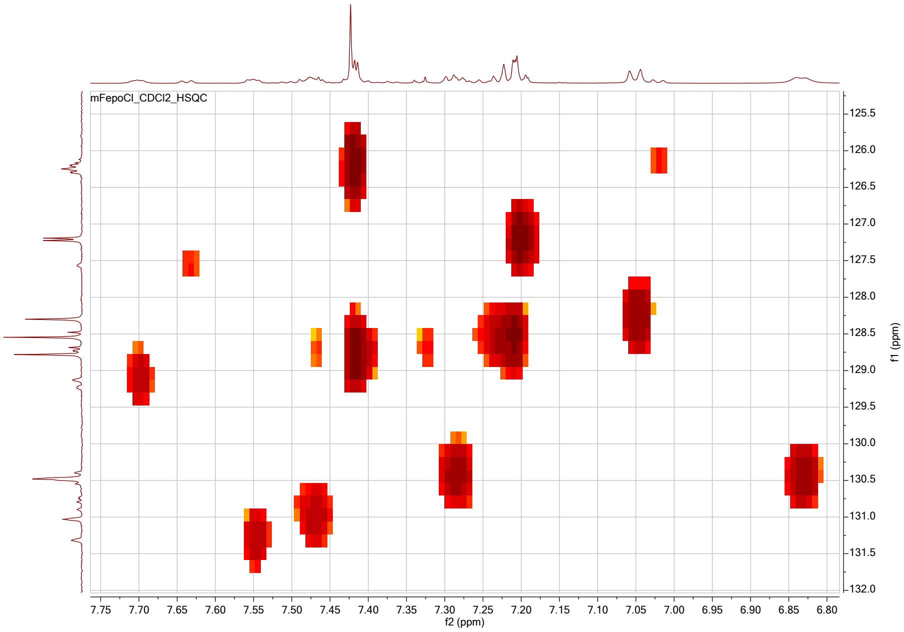

Figure S131. ^{1}H-^{13}C HSQC spectra (CD_2Cl_2) of isolated **4b**.

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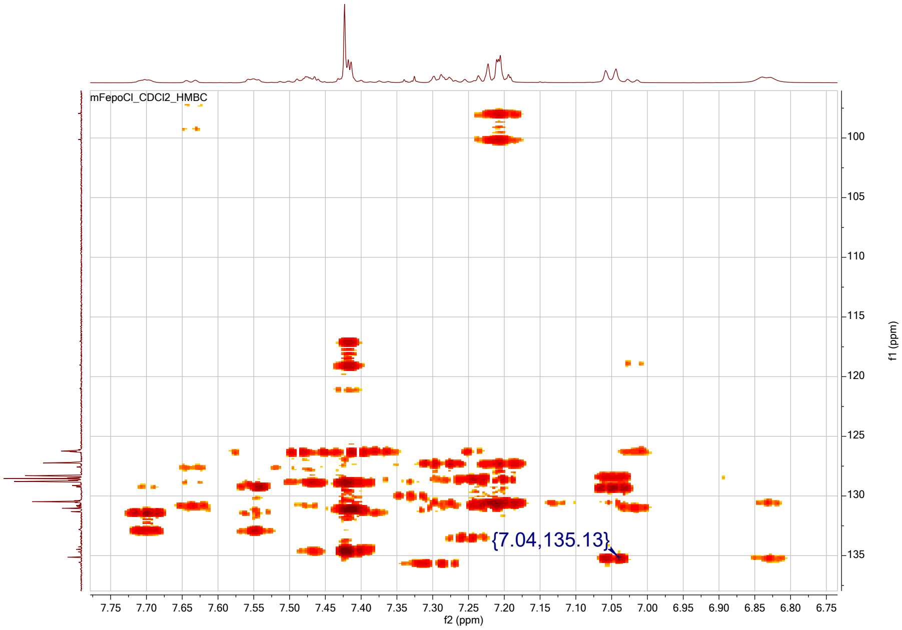
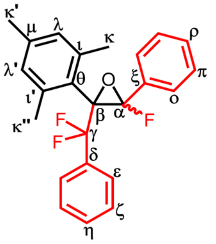


Figure S132. ^{1}H-^{13}C HMBC spectra (CD_2Cl_2) of isolated **4b**.



R₃ = Mesityl

4c: 58%, d.r. =94:6

(62 ± 7%, d.r. = 94:6, n=3)

Yellow oil (0.4 mmol, 89 mg isolated, 98% purity). Inseparable mixture of diastereoisomers. ^{19}F NMR (564 MHz, CD_2Cl_2) δ -92.06 (dd, J = 254.1, 24.1 Hz, major isomer, 1F, γF), -95.12 (d, J = 253.8 Hz, minor isomer, 1F, γF), -98.07 (d, J = 253.6 Hz, minor isomer, 1F, γF), -98.80 (dd, J = 254.1, 18.2 Hz, major isomer, 1F, γF), -108.11 (s, minor isomer, 1F, αF), -138.59 (dd, J = 23.9, 18.4 Hz, major isomer, 1F, αF). Major isomer: ^{13}C NMR (126 MHz, CD_2Cl_2) δ 140.63 (d, J = 2.3 Hz, ιC or ι'C), 139.24 (s, μC), 138.14 (s, ιC or ι'C), 135.14 (t, J = 26.7 Hz, δC), 131.50 (d, J = 31.9 Hz, ξC), 130.77 (s, ηC), 130.28 (d, J = 1.2 Hz, ρC), 130.17 (s, λC or λ'C), 128.74 (s, λC or λ'C), 128.47 (s, ζC), 127.97 (s, πC), 127.71 (d, J = 5.7 Hz, oC), 127.06 (ddd, εC, unresolved), 123.73 (d, J = 2.0 Hz, θC), 120.49 (ddd, J = 251.6, 249.9, 6.3 Hz, γC), 99.41 (dd, J = 273.0, 2.4 Hz, αC), 71.81 (td, J = 34.9, 20.0 Hz, βC), 21.08 (s, κ'C), 20.22 (d, J = 4.2 Hz, κC or κ''C), 19.53 (t, J = 2.1 Hz, κC or κ''C). ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.52 – 7.47 (m, 3H, 2εH + 1ηH), 7.45 – 7.40 (m, 2H, 2ζH), 7.30 (t, J = 7.3 Hz, 1H, 1ρH), 7.18 (t, J = 7.6 Hz, 2H, 2πH), 7.13 (dd, J = 8.4, 1.1 Hz, 2H, 2oH), 6.88 (s, 1H, 1λH or 1λ'H), 6.48 (s, 1H, 1λH or 1λ'H), 2.50 (s, 3H, 3κH or 3κ''H), 2.20 (s, 3H, 3κ'H), 1.44 (s, 3H, 3κH or 3κ''H). HR-MS (ESI): calcd. for $[M - 3F + 2H]^+$ ($C_{24}H_{23}O^+$) = 327.1743, found: 327.1742.

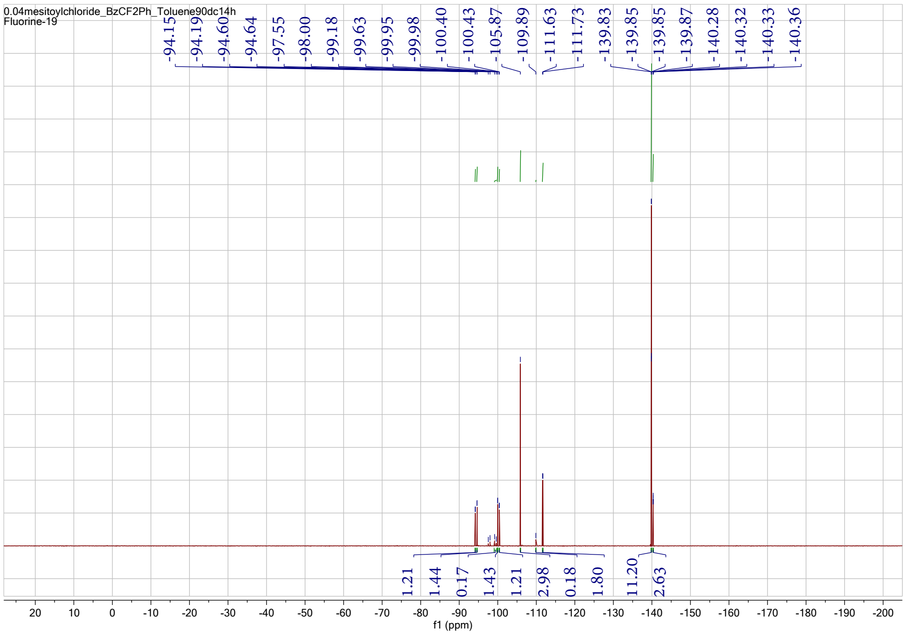


Figure S133. Representative *in situ* ^{19}F NMR spectra (in toluene) of **4c**. ^{19}F NMR (564 MHz, toluene) δ -94.39 (dd, J = 254.3, 24.7 Hz, major isomer, γF, 1F), -97.77 (d, J = 252.3 Hz, minor isomer, γF, 1F), -99.40 (d, J = 253.3 Hz, minor isomer, γF, 1F), -100.19 (dd, J = 254.3, 20.0 Hz, major isomer, γF, 1F), -109.89 (s, minor isomer, αF, 1F), -111.68 (d, J = 56.4 Hz, PhCF$_2$H byproduct, 2F), -140.32 (dd, J = 24.6, 20.2 Hz, major isomer, αF, 1F).

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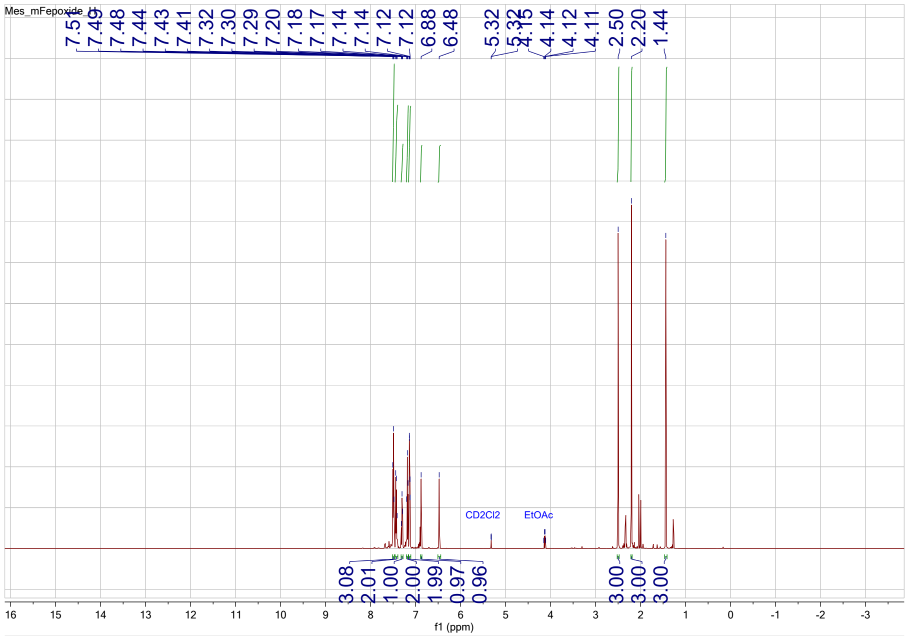

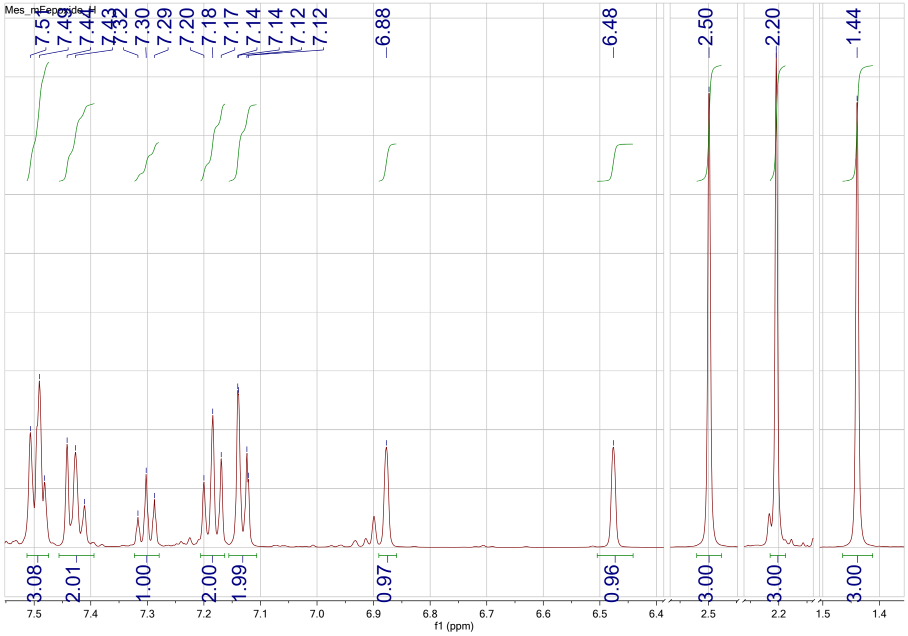

Figure S134. ^{1}H NMR spectra (CD_2Cl_2) of isolated **4c**. Top: full spectra and bottom: zoom-in spectra. The integration of the major isomer was labeled in the ^{1}H NMR spectra.

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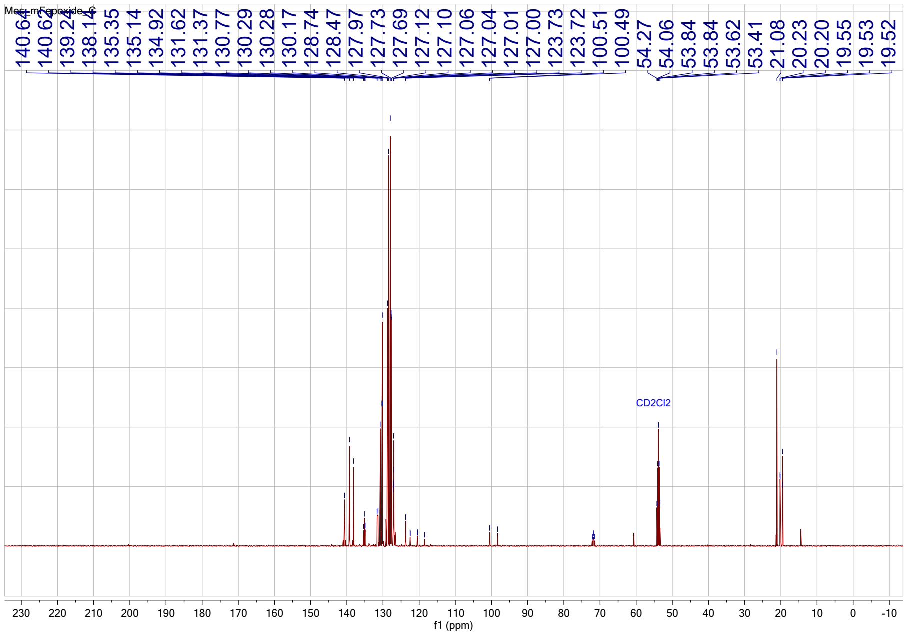
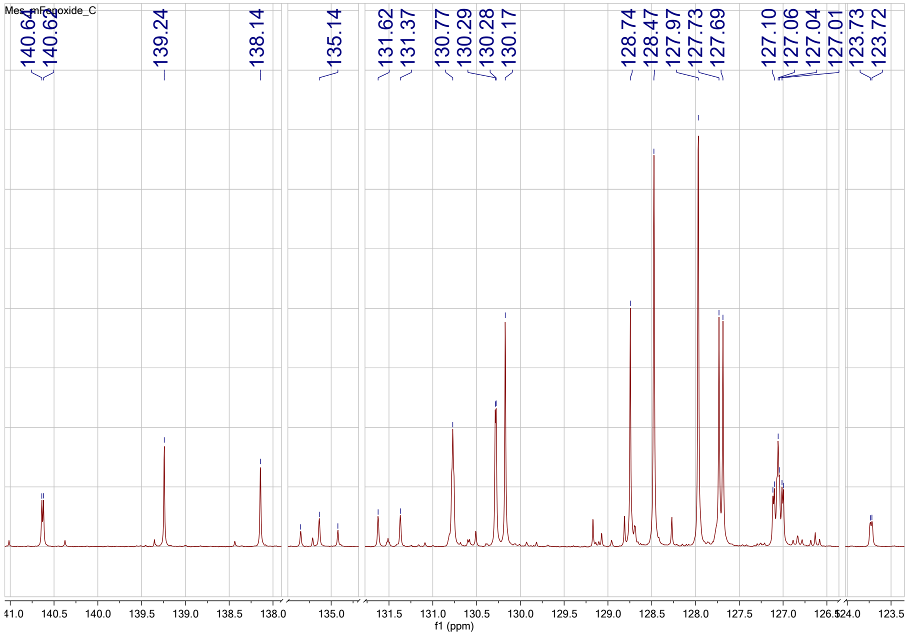

Mes-mFepoxide_C
140.64
140.62
139.24
138.14
135.35
135.14
134.92
131.62
131.37
130.77
130.29
130.28
130.17
128.74
128.47
127.97
127.73
127.69
127.12
127.10
127.06
127.04
127.01
127.00
123.73
123.72
100.51
100.49
54.27
54.06
53.84
53.84
53.62
53.41
21.08
20.23
20.20
19.55
19.53
19.52
CD2Cl2
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Mes-mFepoxide_C
140.64
140.62
139.24
138.14
135.14
131.62
131.37
130.77
130.29
130.28
130.17
128.74
128.47
127.97
127.73
127.69
127.10
127.06
127.04
127.01
123.73
123.72
41.0 140.5 140.0 139.5 139.0 138.5 138.0 135.0 131.5 131.0 130.5 130.0 129.5 129.0 128.5 128.0 127.5 127.0 126.5 124.0 123.5
f1 (ppm)

`

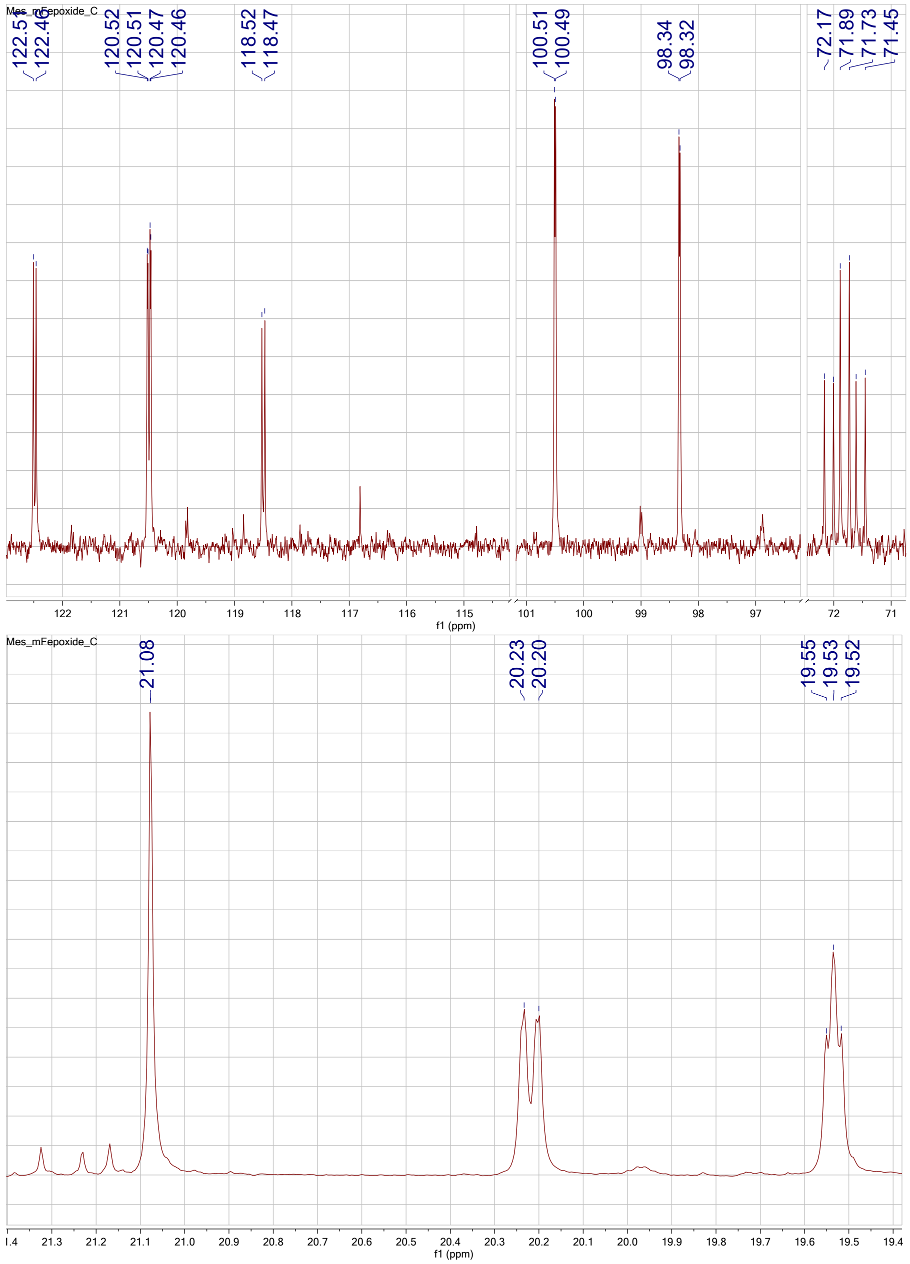


Figure S135. ^{13}C NMR spectra (CD_2Cl_2) of isolated **4c**. From top to bottom: full spectra; zoom-in spectra for the Ar-C, α/β/γ C, and methyl C.

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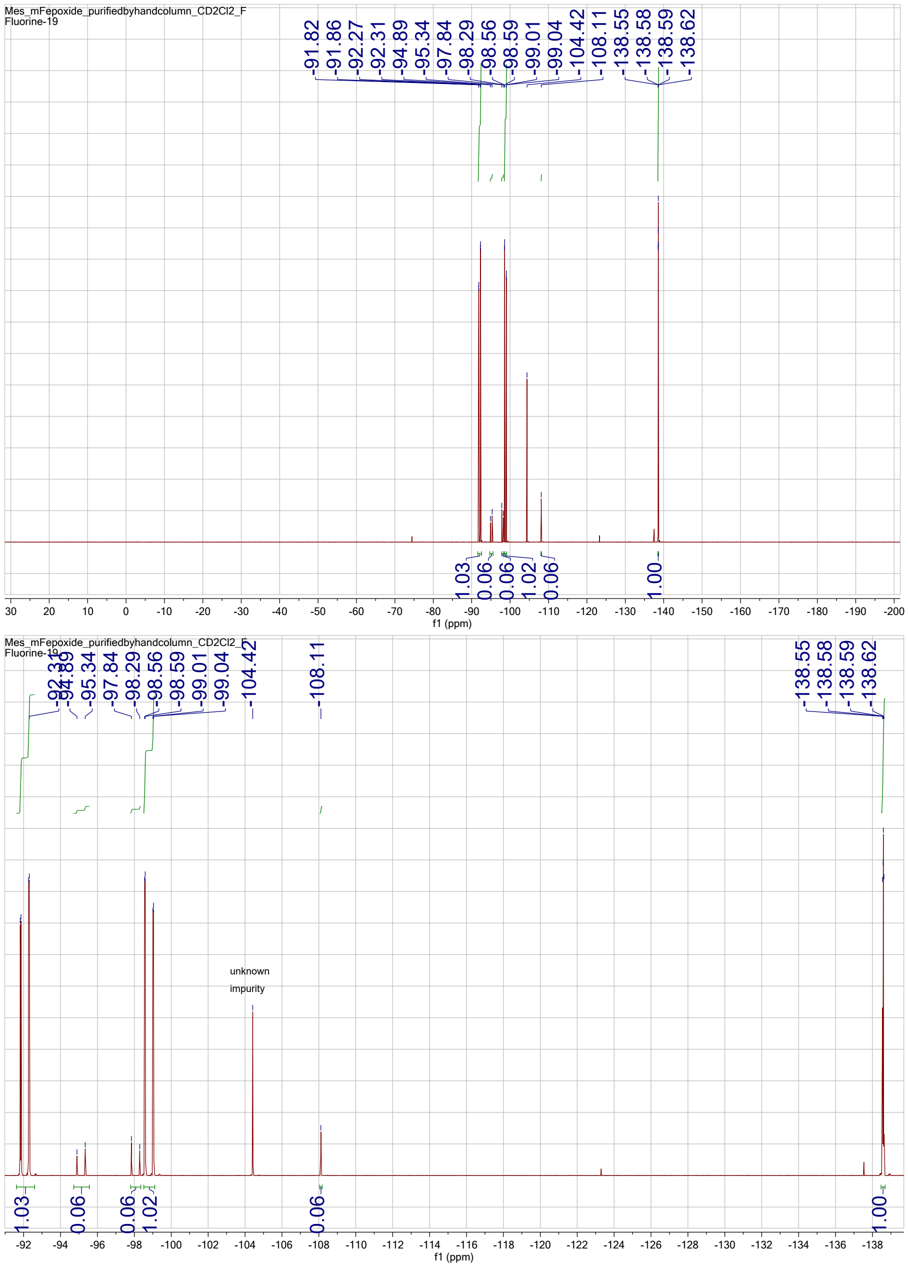
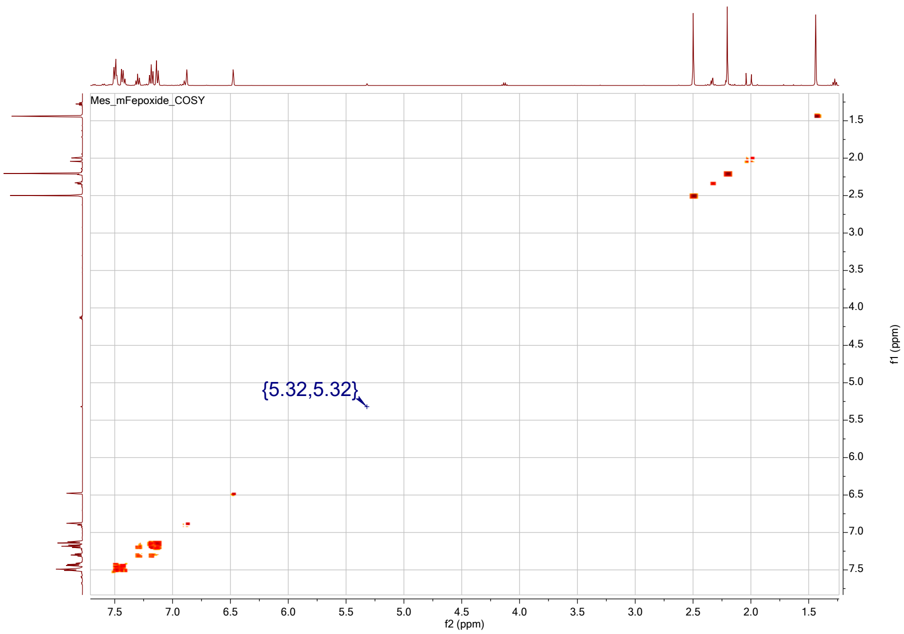


Figure S136. ^{19}F NMR spectra (CD_2Cl_2) of isolated **4c**. Top: full spectra and bottom: zoom-in spectra.



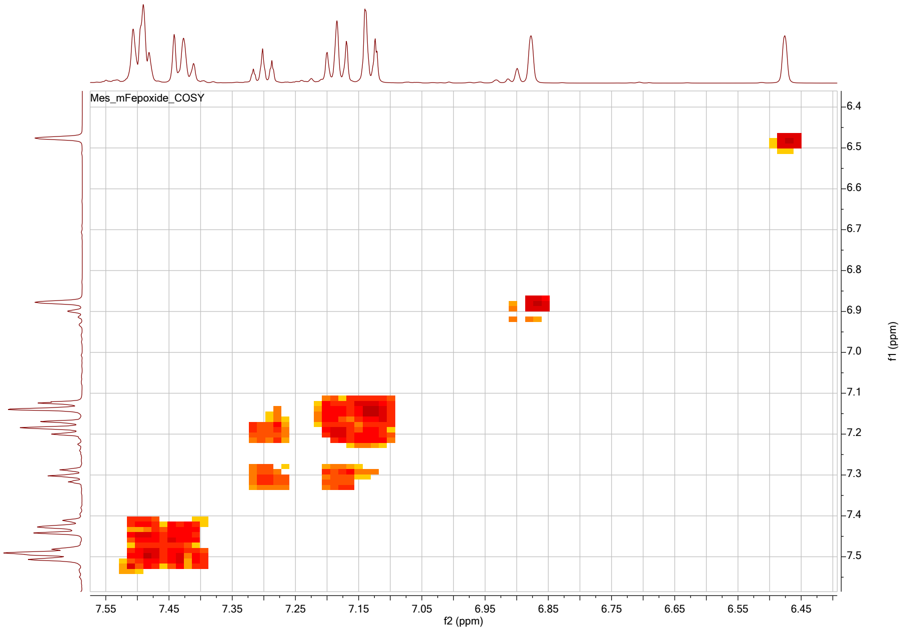


Figure S137. ^{1}H-^{1}H COSY spectra (CD_2Cl_2) of isolated **4c**. Top: full spectra and bottom: zoom-in spectra.

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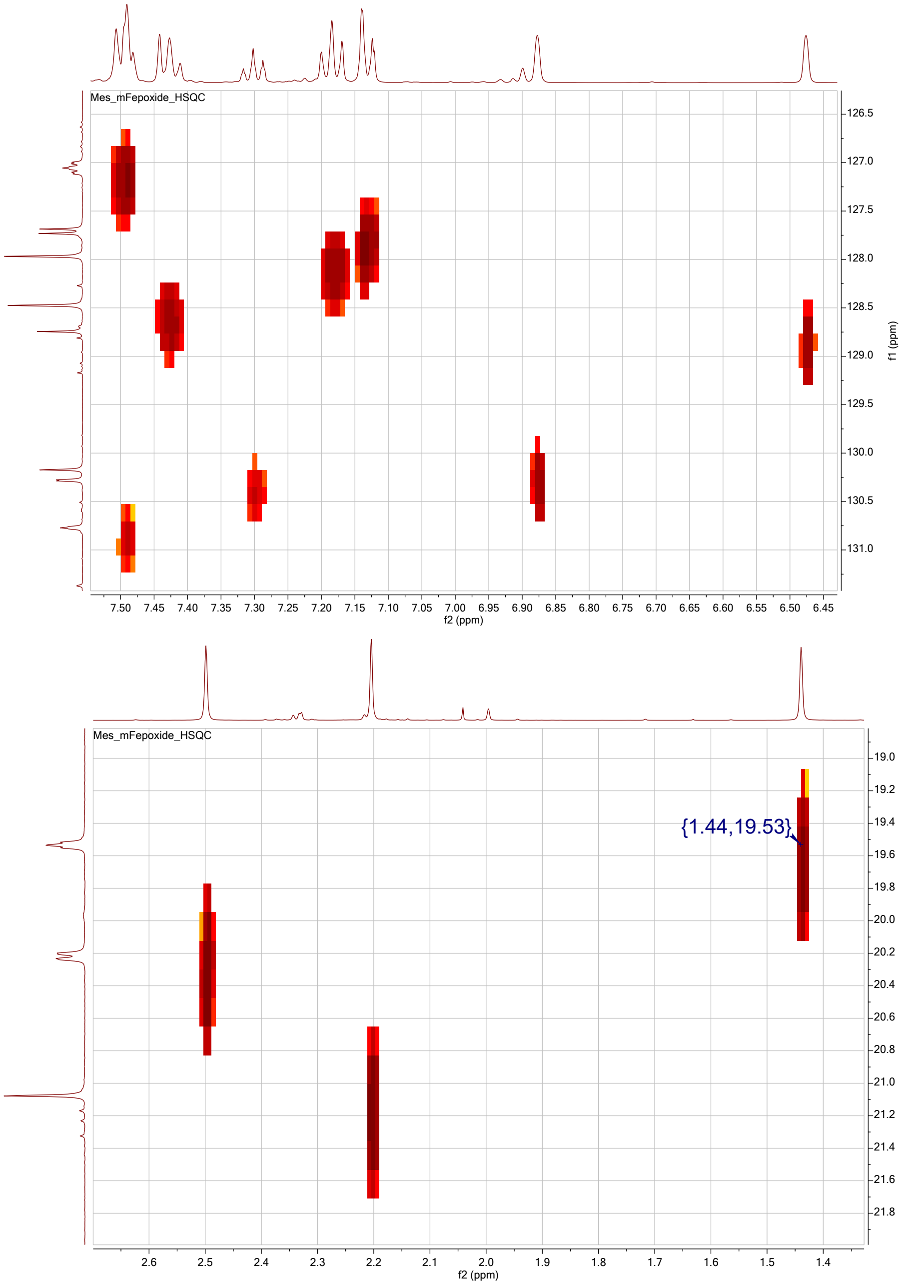
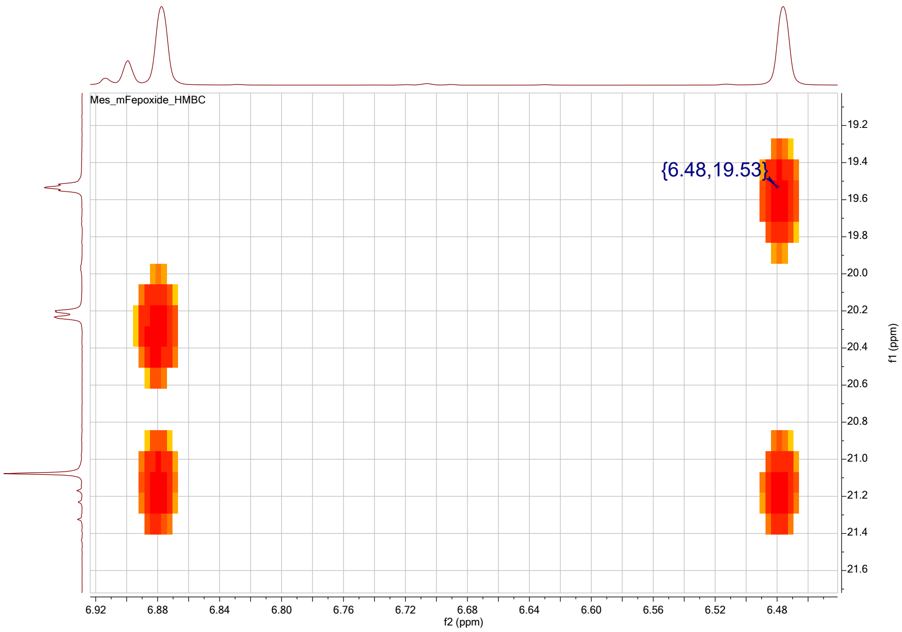
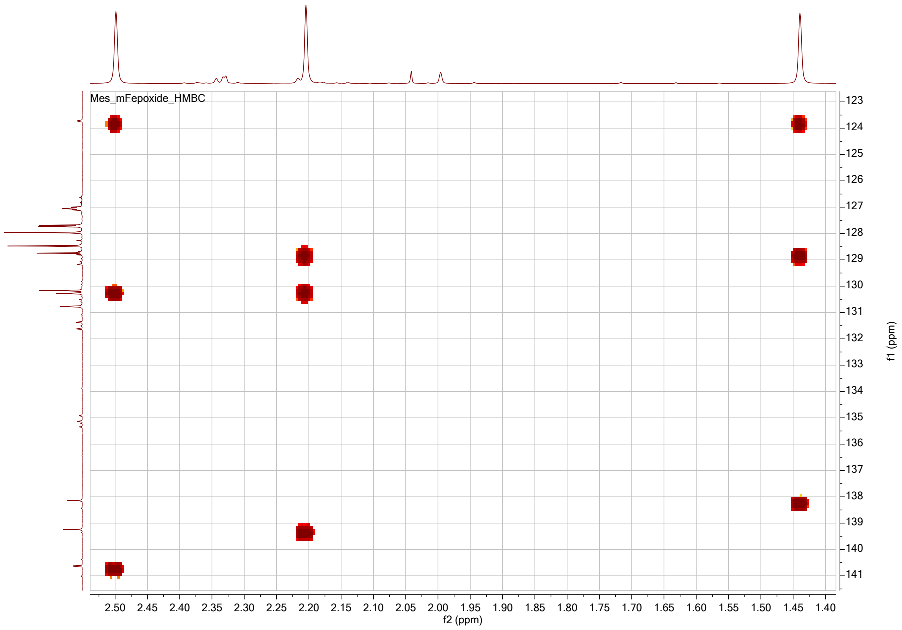


Figure S138. ^{1}H-^{13}C HSQC spectra (CD_2Cl_2) of isolated **4c**. Top: full spectra and bottom: zoom-in spectra.


Mes_mFepoxide_HMBC
{6.48,19.53}
f2 (ppm)
f1 (ppm)


Mes_mFepoxide_HMBC
f2 (ppm)
f1 (ppm)

`

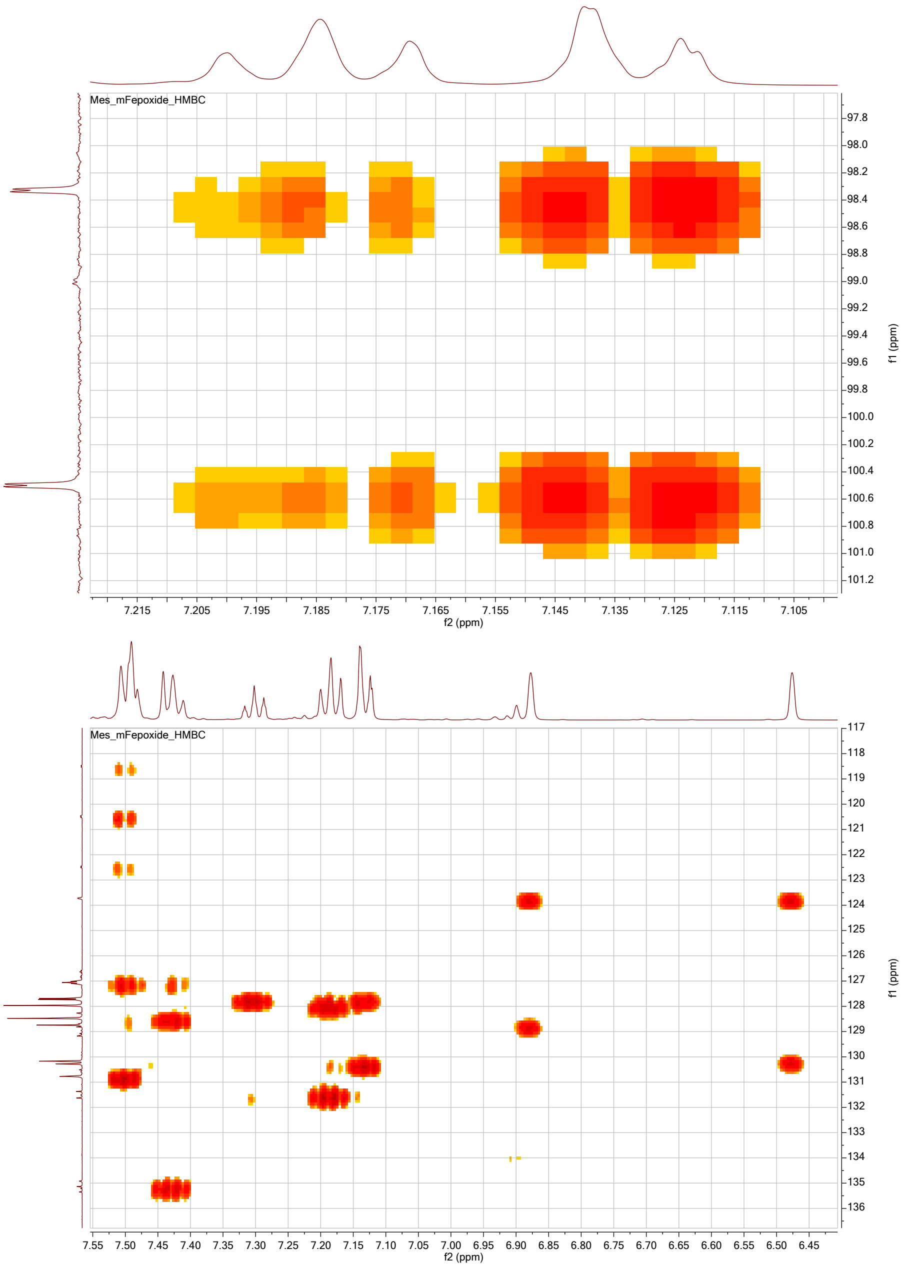
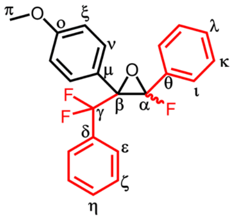


Figure S139. ^{1}H-^{13}C HMBC spectra (CDCl$_3$) of isolated **4c**.



R$_3$ = Ph(*p*-OMe)
4d: 70%, d.r. = 90:10
(90 ± 14%, d.r. = 90:10, n=3)

Yellow oil (0.4 mmol, 104 mg isolated, >99% purity). Inseparable mixture of diastereoisomers. ^{19}F NMR (564 MHz, CD$_2$Cl$_2$) δ -97.30 (dd, *J* = 251.1, 29.4 Hz, major isomer, 1F, γF), -99.26 (d, *J* = 254.5 Hz, minor isomer, 1F, γF), -99.91 (d, *J* = 254.4 Hz, minor isomer, 1F, γF), -101.54 (dd, *J* = 251.1, 22.6 Hz, major isomer, 1F, γF), -107.97 (s, minor isomer, 1F, αF), -133.85 – -133.97 (dd, *J* = 29.3, 29.4 Hz, major isomer, 1F, αF). Major isomer: ^{13}C NMR (126 MHz, CD$_2$Cl$_2$) δ 160.17 (s, oC), 134.97 (t, *J* = 26.2 Hz, δC), 131.31 (d, *J* = 31.3 Hz, θC), 130.86 (s, ηC), 130.48 (s, νC), 130.29 (d, *J* = 1.6 Hz, κC), 128.69 (s, ζC), 128.43 (s, λC), 127.39 (d, *J* = 4.2 Hz, ιC), 126.36 (t, *J* = 6.7 Hz, εC), 122.40 (s, μC), 119.31 (ddd, *J* = 251.8, 249.3, 5.8 Hz, γC), 113.41 (s, ξC), 99.35 (dd, *J* = 273.8, 2.5 Hz, αC), 71.65 (ddd, *J* = 32.8, 31.2, 19.7 Hz, βC), 55.43 (s, πC). ^{1}H NMR (500 MHz, CD$_2$Cl$_2$) δ 7.51 – 7.41 (m, 5H, 2εH + 2ζH + 1ηH), 7.30 – 7.21 (m, 5H, 2ιH + 2κH + 1λH), 6.86 (d, *J* = 8.0 Hz, 2H, 2νH), 6.62 (d, *J* = 9.0 Hz, 2H, 2ξH), 3.67 (s, 3H, 3πH). HR-MS (ESI): calcd. for $[M – 3F + 2H]^+$ ($C_{24}H_{23}O^+$) = 327.1743, found: 327.1742.

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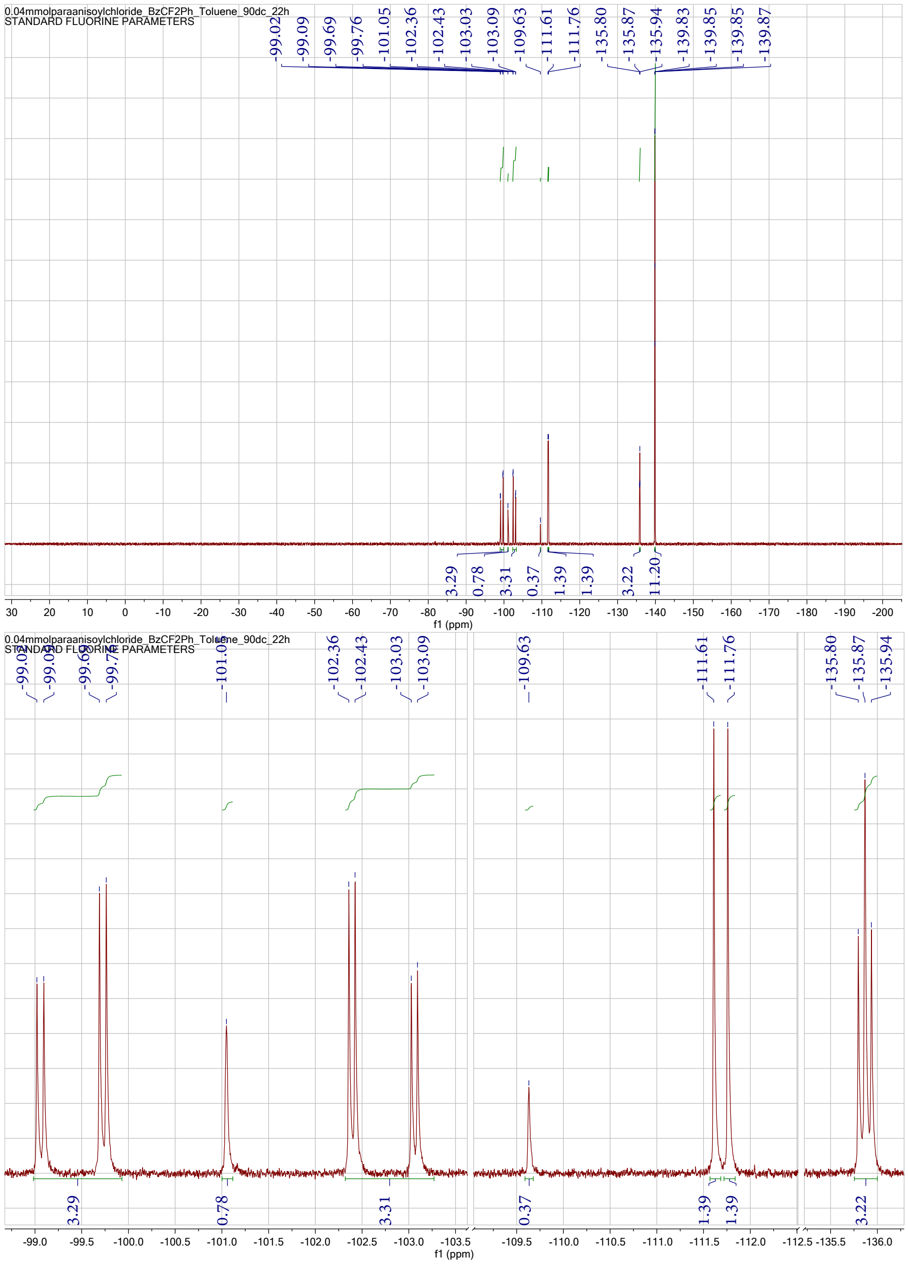

Figure S140. Representative *in situ* ^{19}F NMR spectra (in toluene) of **4d**. Top: full spectra and bottom: zoom-in spectra. ^{19}F NMR (377 MHz, toluene) δ -99.43 (dd, *J* = 251.9, 27.8 Hz, major isomer, γF, 1F), -101.10 (s, minor isomer, γF, 2F), -102.75 (dd, *J* = 251.9, 25.0 Hz, major isomer, γF, 1F), -109.66 (s, minor isomer, 1F, αF), -111.68 (d, *J* = 56.4 Hz, byproduct, PhCF$_2$H, 2F), -135.91 (t, *J* = 26.4 Hz, major isomer, 1F, αF).

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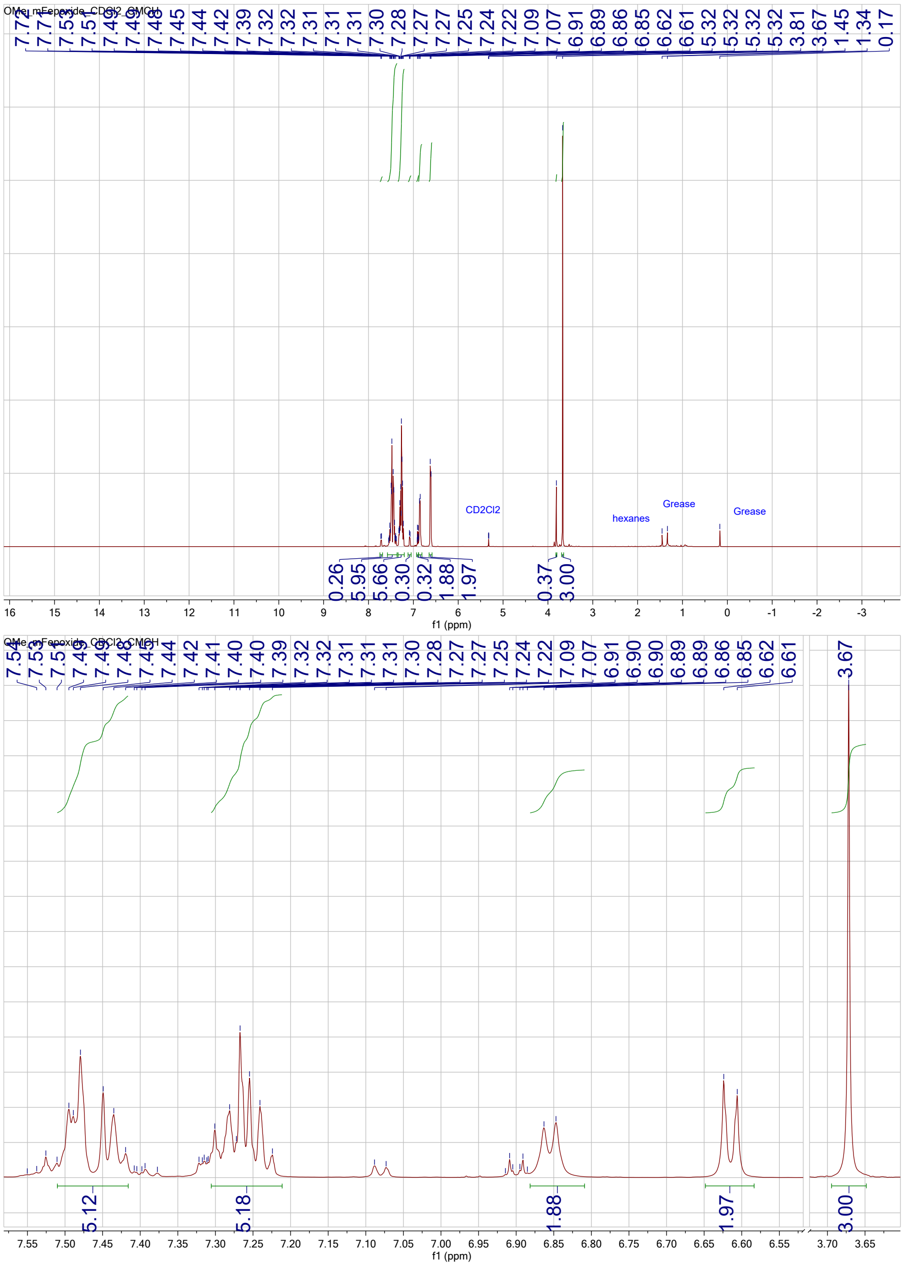

Figure S141. ^{1}H NMR spectra (CD$_2$Cl$_2$) of isolated **4d**. d.r. (3:0.37=89:11) determined by ^{1}H NMR spectroscopy is consistent with the ^{19}F NMR results (**Figure S143**). In addition, the total integration in the aromatic region (6.5-8 ppm) is expected to be 19.10, close to the observed number (19.71) shown in the left spectra. Integration of the major isomer was shown in the right spectra.

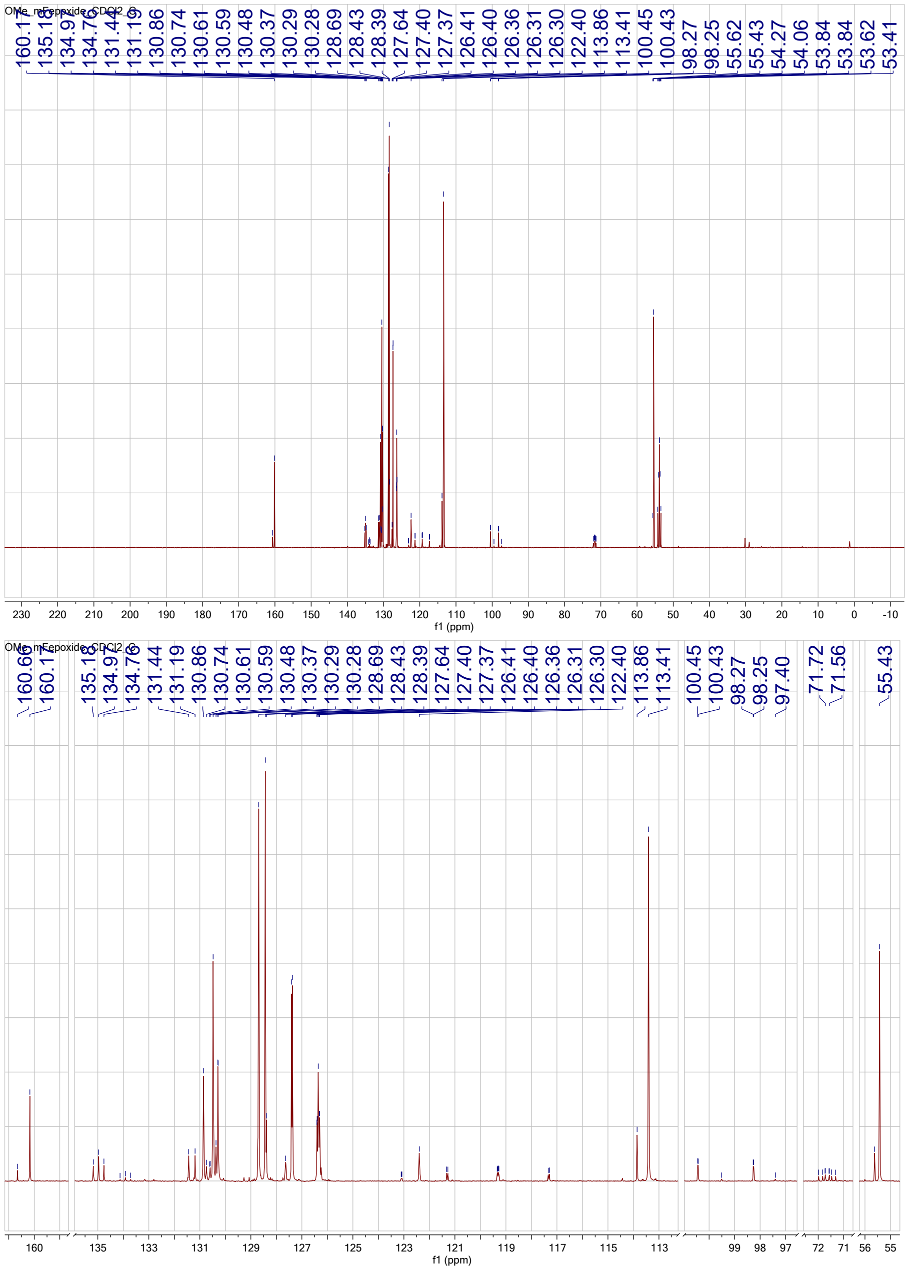

Figure S142. ^{13}C NMR spectra (CD_2Cl_2) of isolated **4d**.

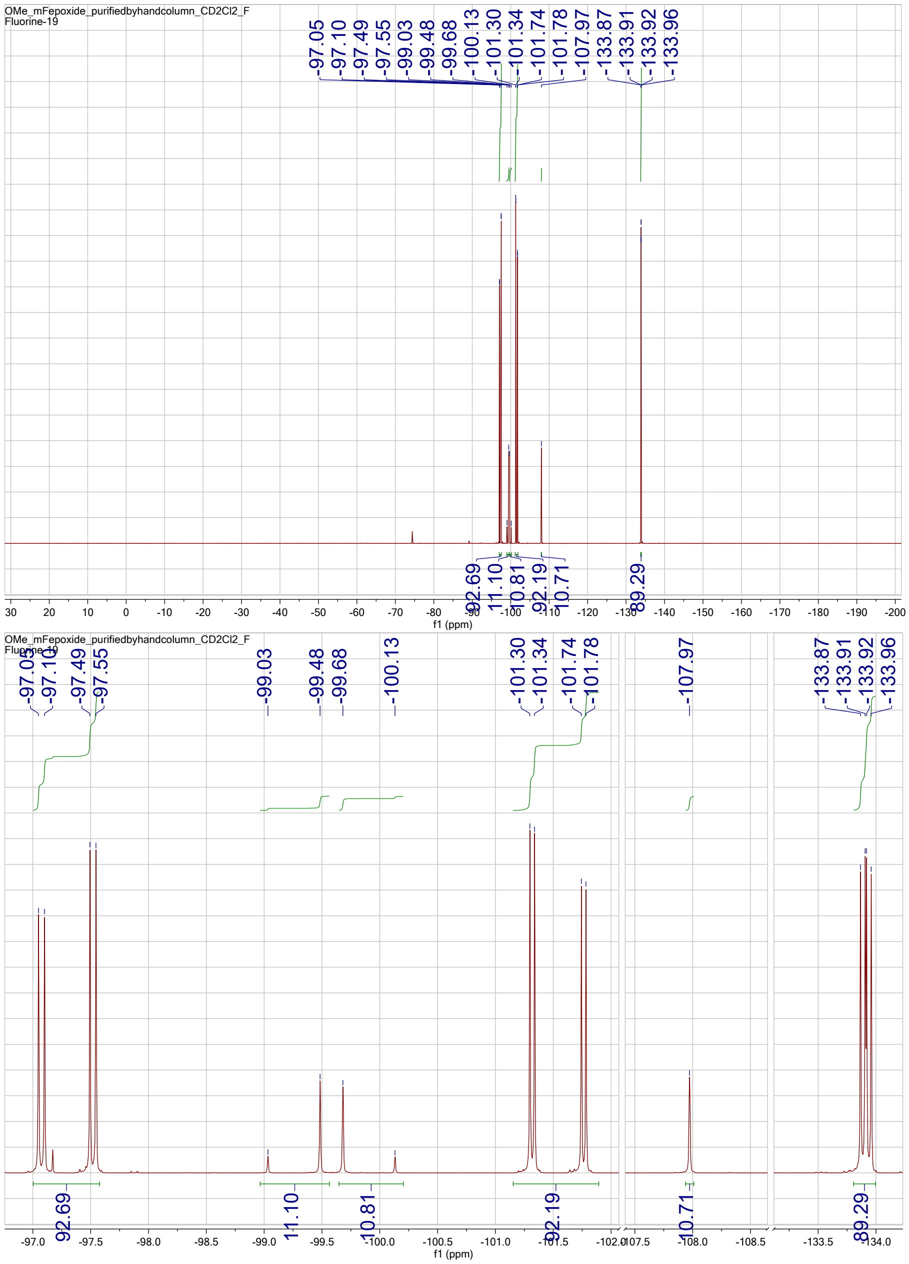

Figure S143. ^{19}F NMR spectra (CD_2Cl_2) of isolated **4d**. Top: full spectra and bottom: zoom-in spectra.

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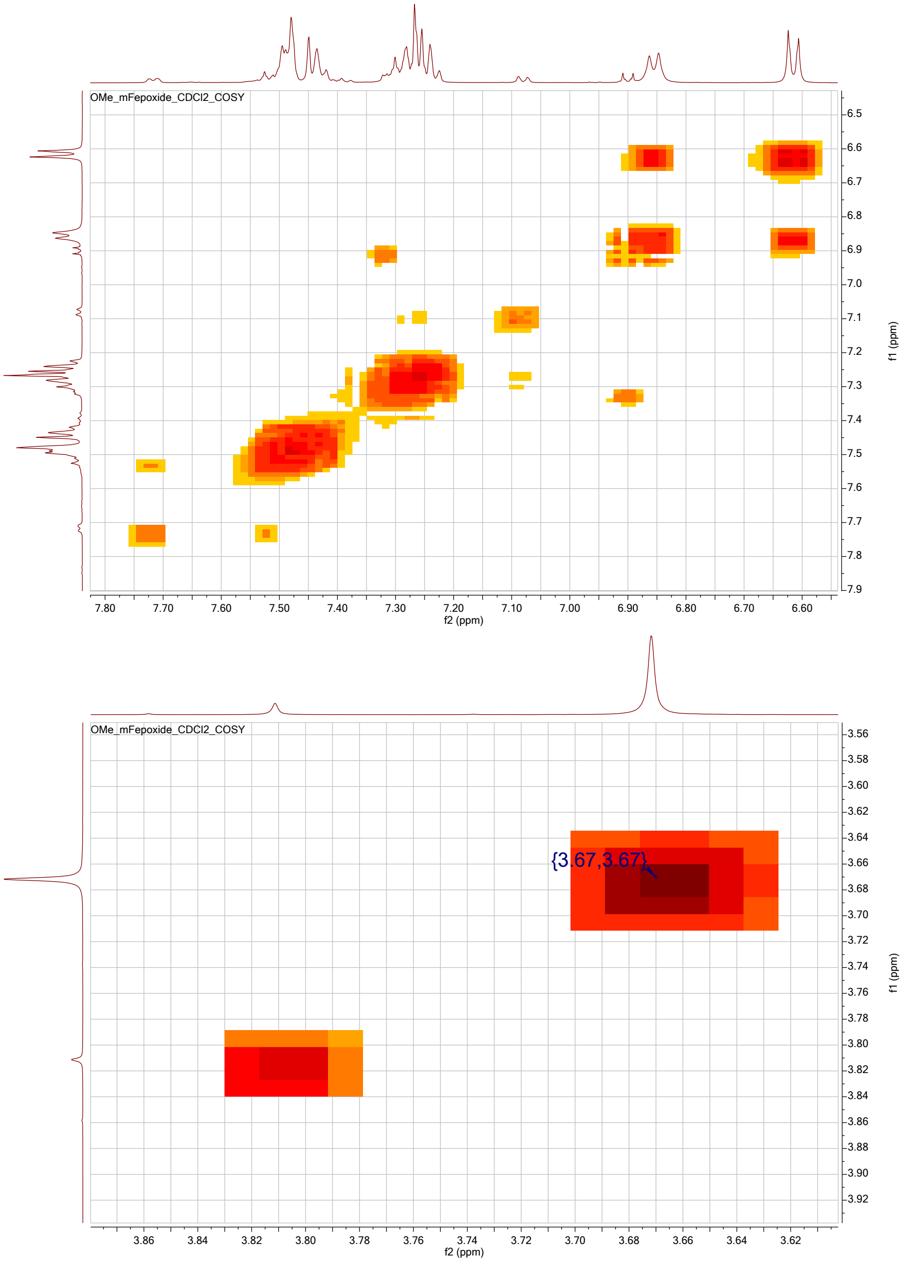


Figure S144. ^{1}H-^{1}H COSY spectra (CDCl$_3$) of isolated **4d**. Top: full spectra and bottom: zoom-in spectra.

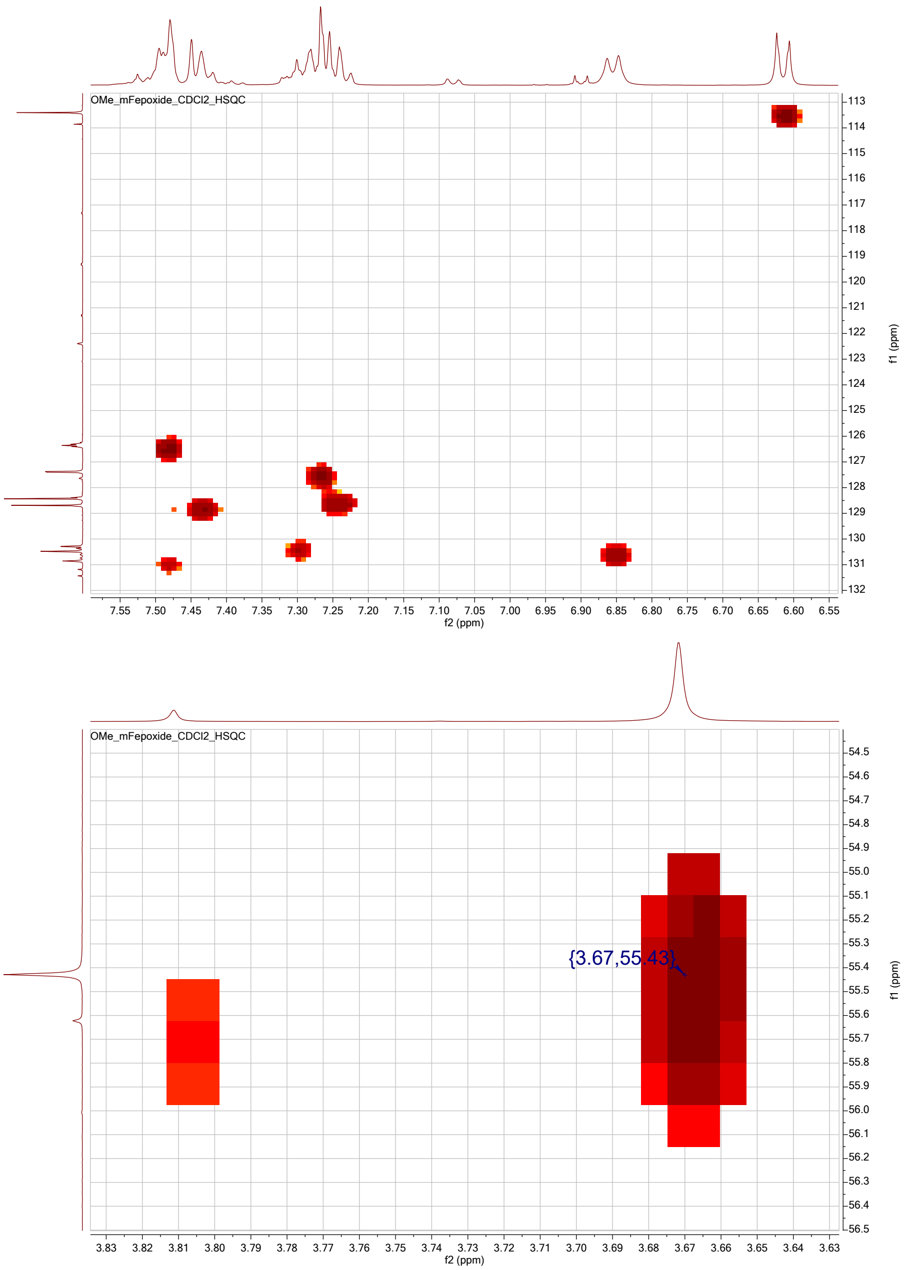


Figure S145. ^{1}H-^{13}C HSQC spectra (CDCl$_3$) of isolated **4d**.

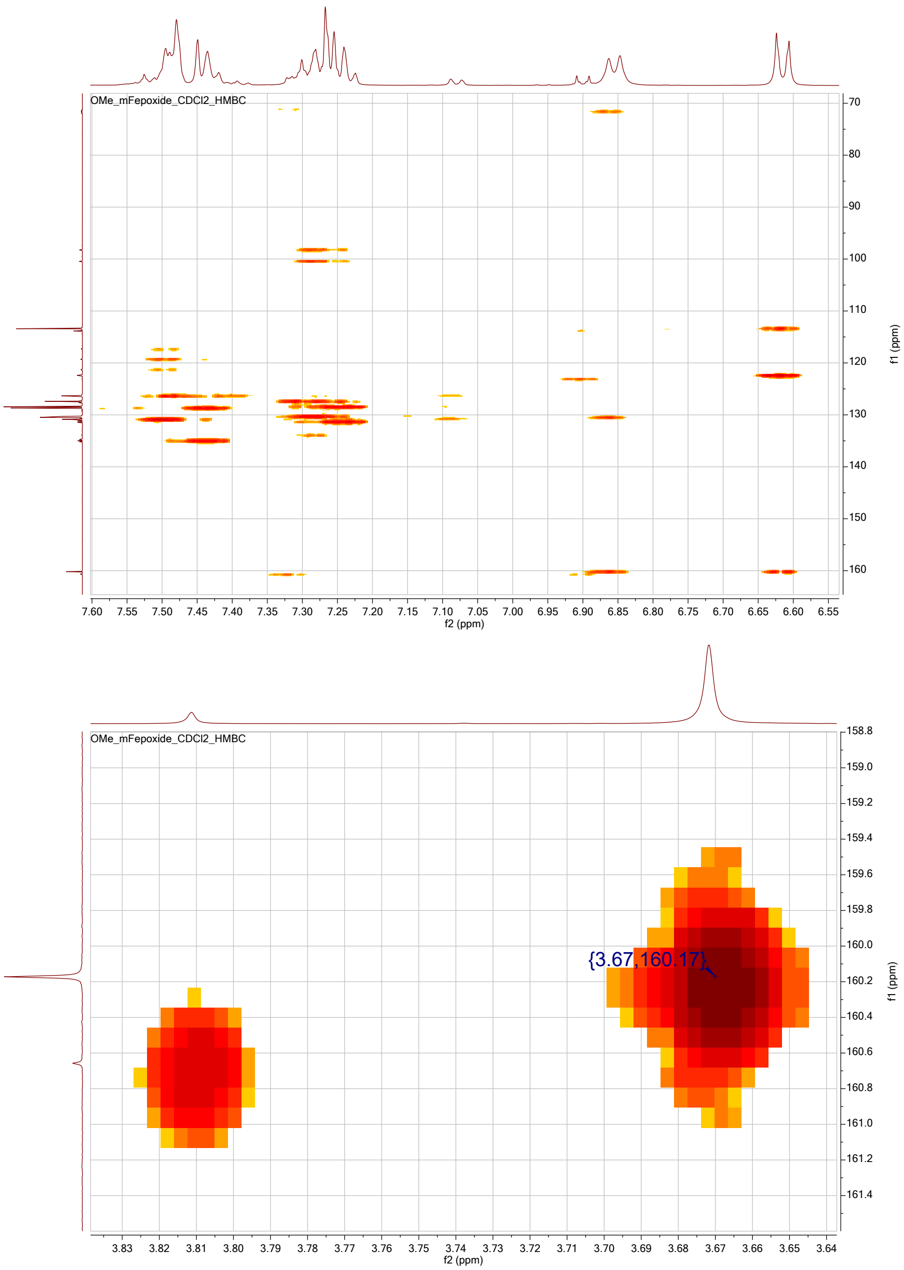
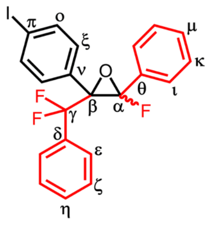


Figure S146. ^{1}H-^{13}C HMBC spectra (CDCl$_3$) of isolated **4d**. Top: full spectra and bottom: zoom-in spectra.



R_3 = Ph(*p*-I)

4e: 36%, d.r. = 84:16

(71%, d.r. = 83:17 , n=1)

Pale yellow oil (0.1 mmol, 17 mg isolated, 89% purity). ^{19}F NMR (564 MHz, CD$_2$Cl$_2$) δ -97.21 (dd, *J* = 252.9, 28.2 Hz, major isomer, γF, 1F), -99.06 (d, *J* = 256.0 Hz, minor isomer, γF, 1F), -100.07 (d, *J* = 257.2 Hz, minor isomer, γF, 1F), -101.66 (dd, *J* = 252.8, 22.5 Hz, major isomer, γF, 1F), -108.11 (s, minor isomer, αF, 1F), -133.29 (dd, *J* = 28.1, 22.6 Hz, major isomer, αF, 1F). Major isomer: ^{1}H NMR (500 MHz, CD$_2$Cl$_2$) δ 7.49 – 7.47 (m, 1H, 1ηH), 7.45 – 7.38 (m, 6H, 2ξH + 2εH + 2ζH), 7.32 – 7.27 (m, 1H, 1μH), 7.25 – 7.20 (m, 4H, 2ιH + 2κH), 6.64 (d, *J* = 7.5 Hz, 2H, 2oH). ^{13}C NMR (126 MHz, CD$_2$Cl$_2$) δ 137.22 (s), 134.44 (t, *J* = 26.1 Hz, δC), 131.71 (t, *J* = 3.1 Hz,), 131.41 (d, *J* = 33.8 Hz, θC), 131.04 (s, νC, unresolved triplet), 130.76 (s, ξC), 130.51 (d, *J* = 1.7 Hz, κC), 128.79 (s, ζC), 128.56 (s), 127.20 (d, *J* = 4.1 Hz, ιC), 126.25 (t, *J* = 5.3 Hz, εC), 118.95 (ddd, *J* = 252.2, 249.8, 5.9 Hz, γC), 98.95 (dd, *J* = 275.2, 2.6 Hz, αC), 95.34 (s, πC), 71.44 (ddd, *J* = 33.6, 31.7, 19.9 Hz, βC). HR-MS (ESI): calcd. for [M – F]$^+$ ($C_{21}H_{14}F_2IO^+$) = 447.0052, found: 447.2926.

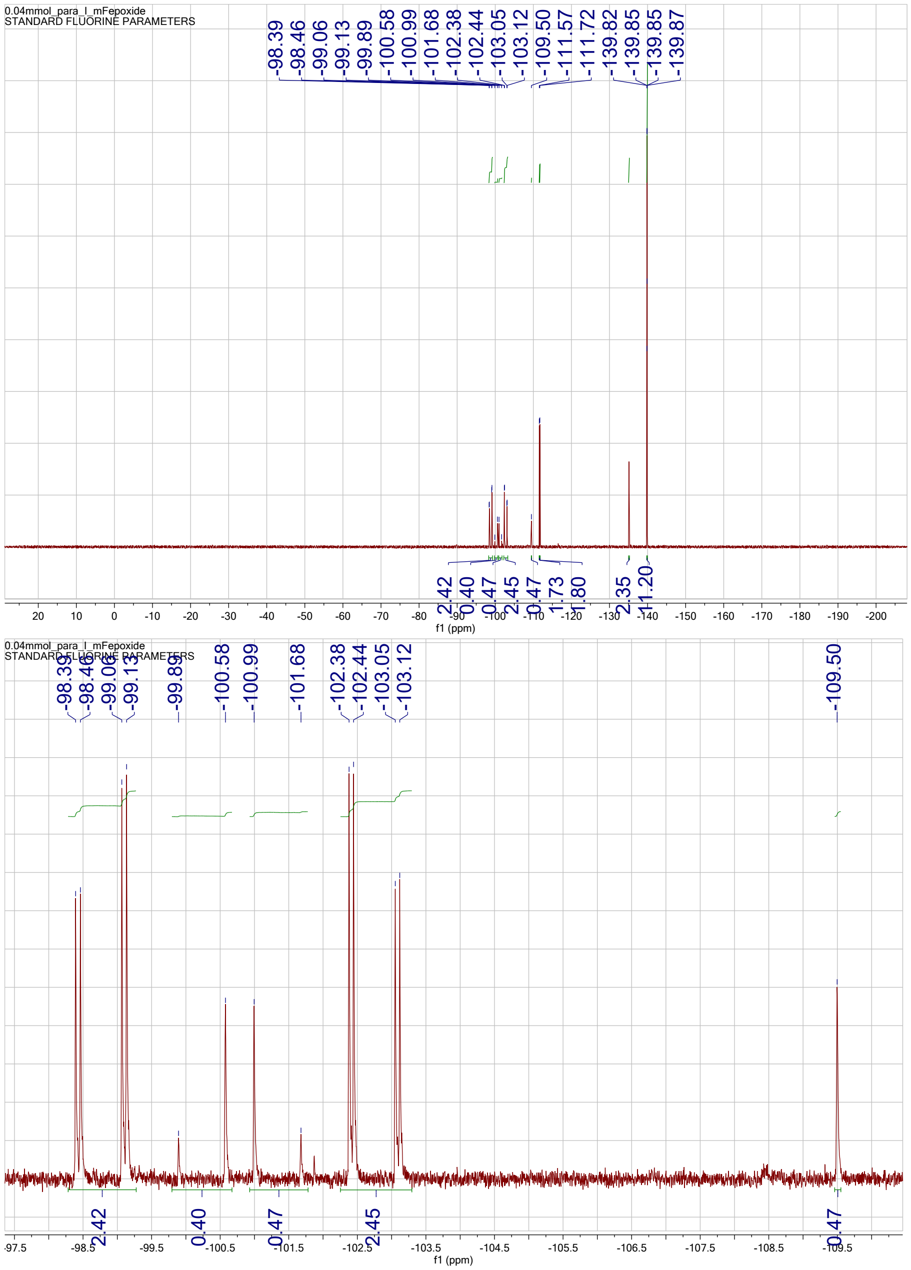
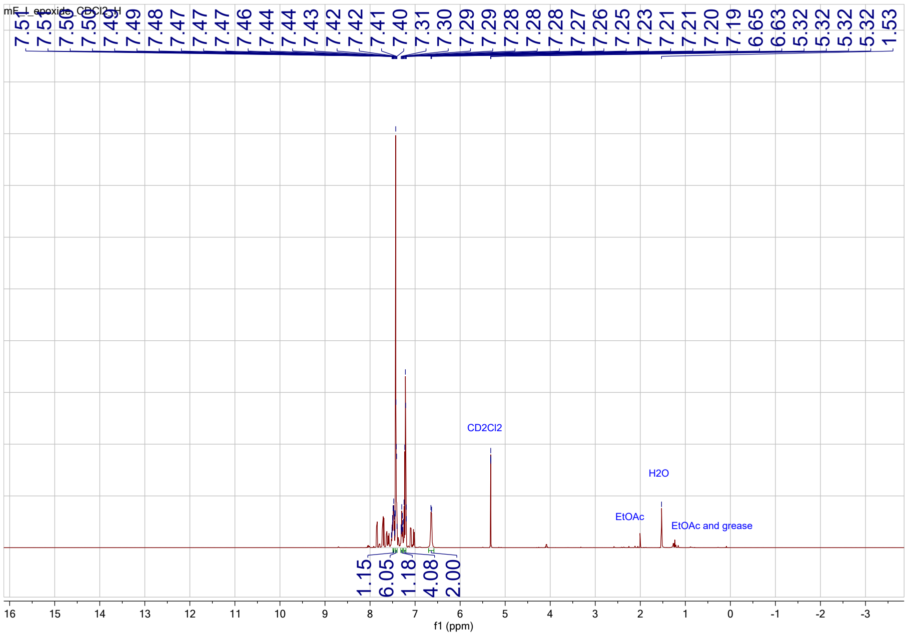


Figure S147. Representative *in situ* ^{19}F NMR spectra (in toluene) of **4f**. Top: full spectra and bottom: zoom-in spectra. ^{19}F NMR (377 MHz, toluene) δ -98.76 (dd, *J* = 253.7, 26.4 Hz, major isomer, γF, 1F), -100.23 (d, *J* = 258.0 Hz, minor isomer, γF, 1F), -101.34 (d, *J* = 257.4 Hz, minor isomer, γF, 1F), -102.75 (dd, *J* = 253.8, 24.7 Hz, major isomer, γF, 1F), -109.50 (s, minor isomer, αF, 1F), -111.64 (d, *J* = 56.4 Hz, byproduct, $PhCF_2H$, 2F), -135.12 (t, *J* = 25.5 Hz, major isomer, αF, 1F).



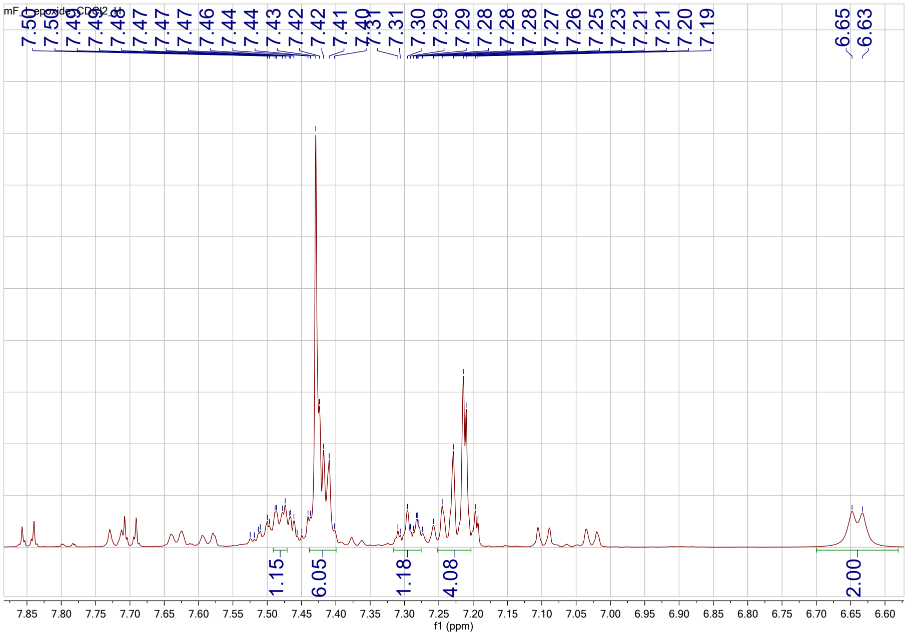


Figure S148. ^{1}H NMR spectra (CD_2Cl_2) of isolated **4f**. Top: full spectra and bottom: zoom-in spectra. d.r. determined by ^{1}H NMR spectroscopy is (0.45+2.00) : 0.45 = 82 : 18, consistent with that calculated form ^{19}F NMR spectroscopy (86:14, **Figure S150**).

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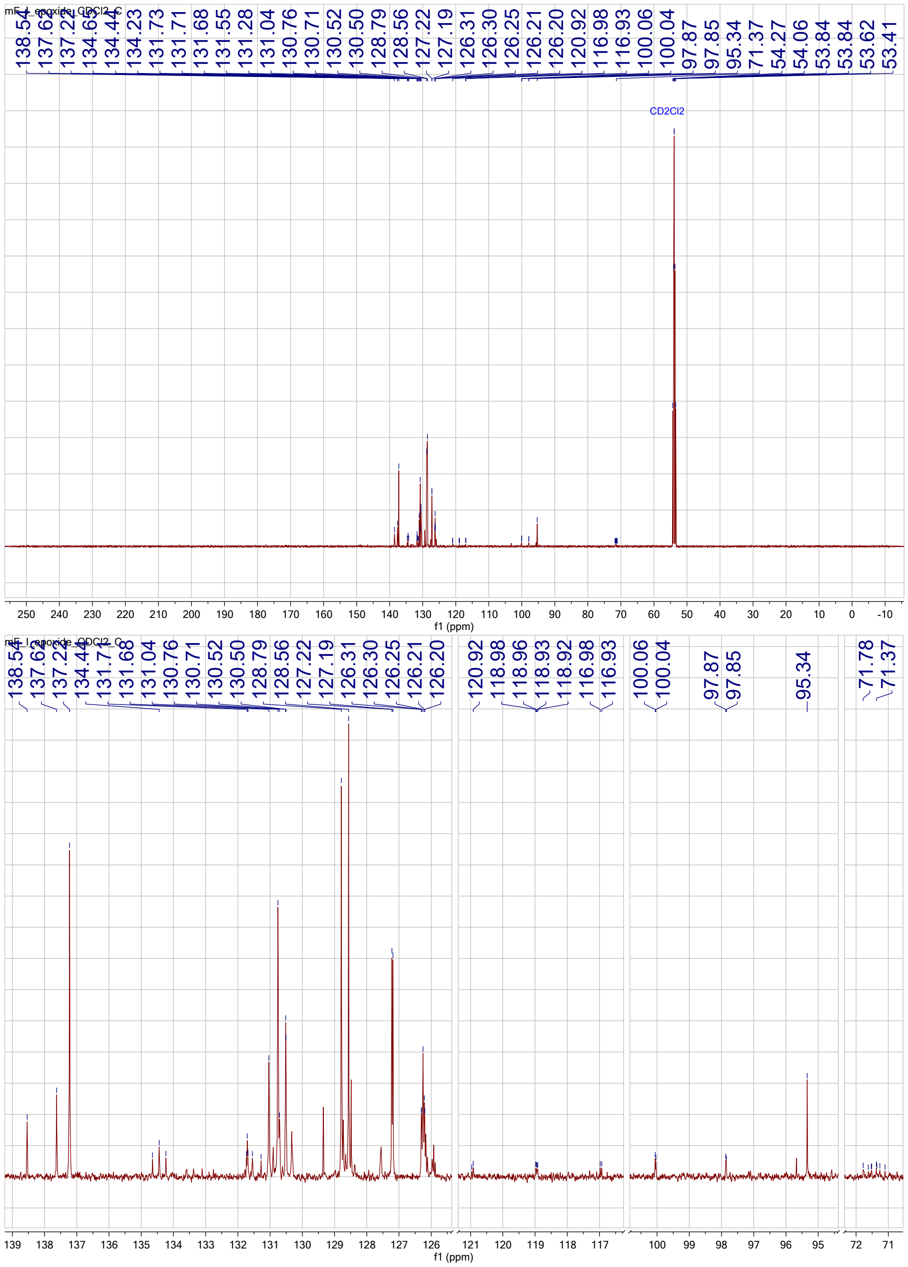

Figure S149. ^{13}C NMR spectra (CD_2Cl_2) of isolated **4f**. Top: full spectra and bottom: zoom-in spectra.

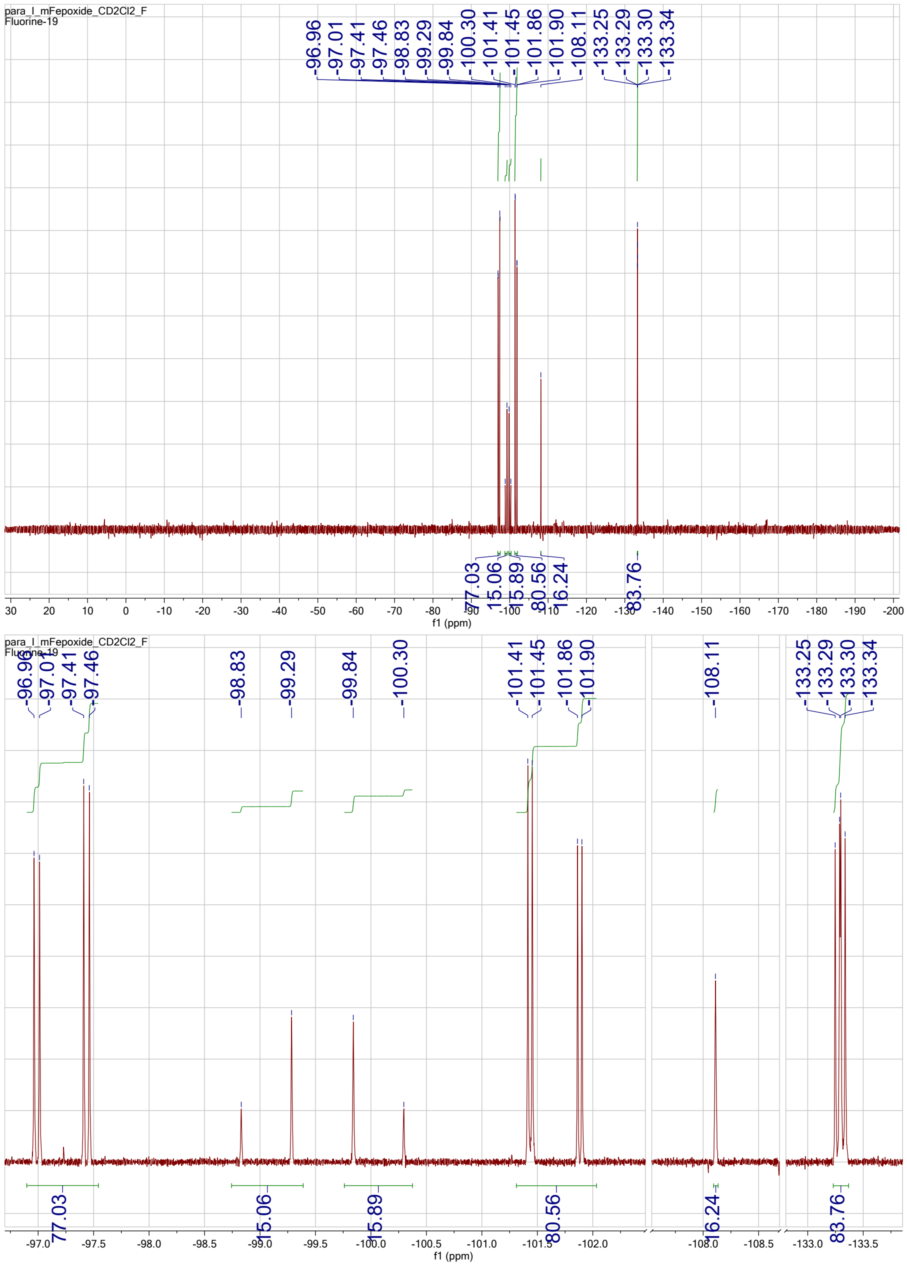

Figure S150. ^{19}F NMR spectra (CD_2Cl_2) of isolated **4f**. Top: full spectra and bottom: zoom-in spectra.

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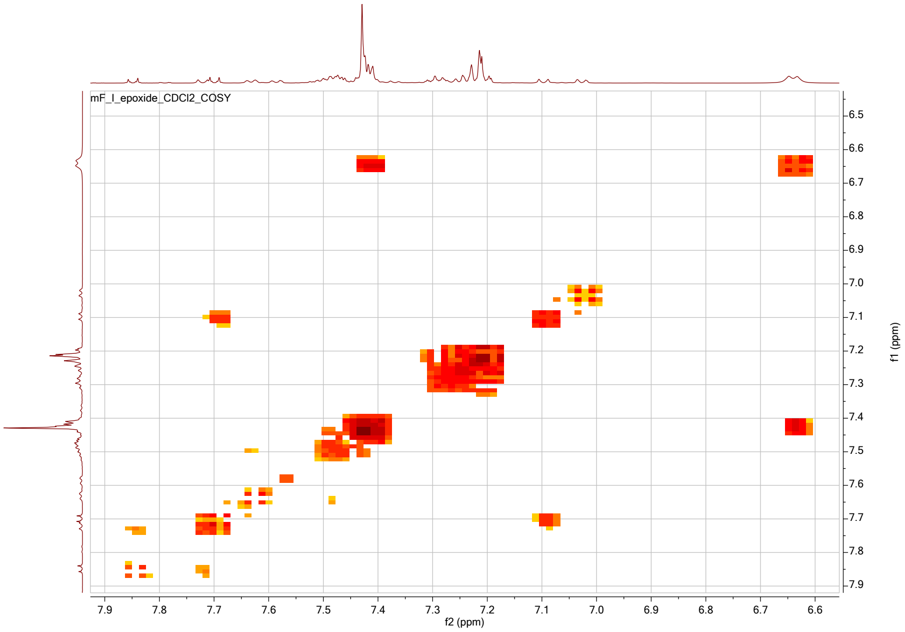

Figure S151. ^{1}H-^{1}H COSY spectra (CD_2Cl_2) of isolated **4f**.

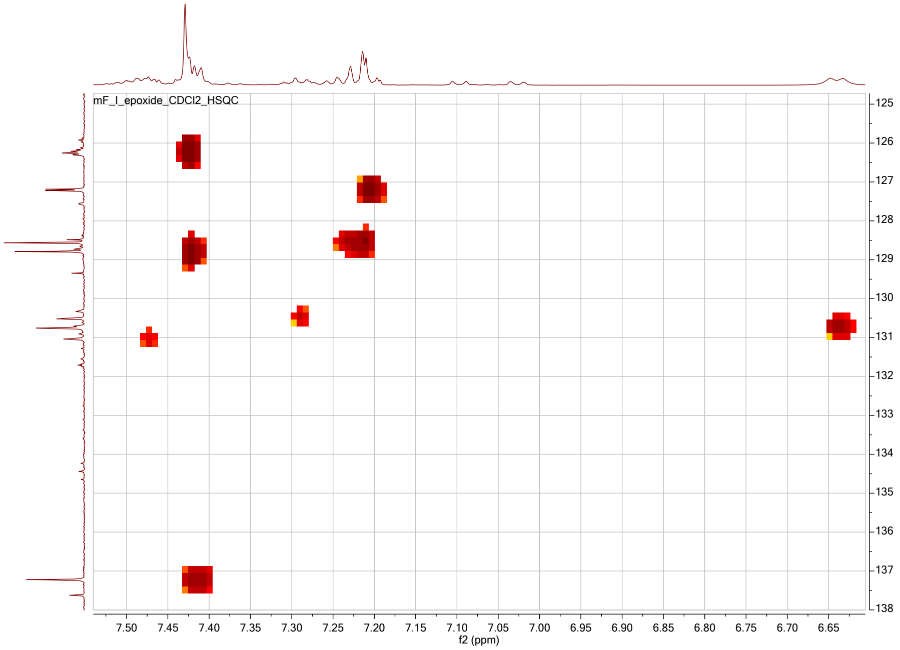

Figure S152. ^{1}H-^{13}C HSQC spectra (CD_2Cl_2) of isolated **4f**.

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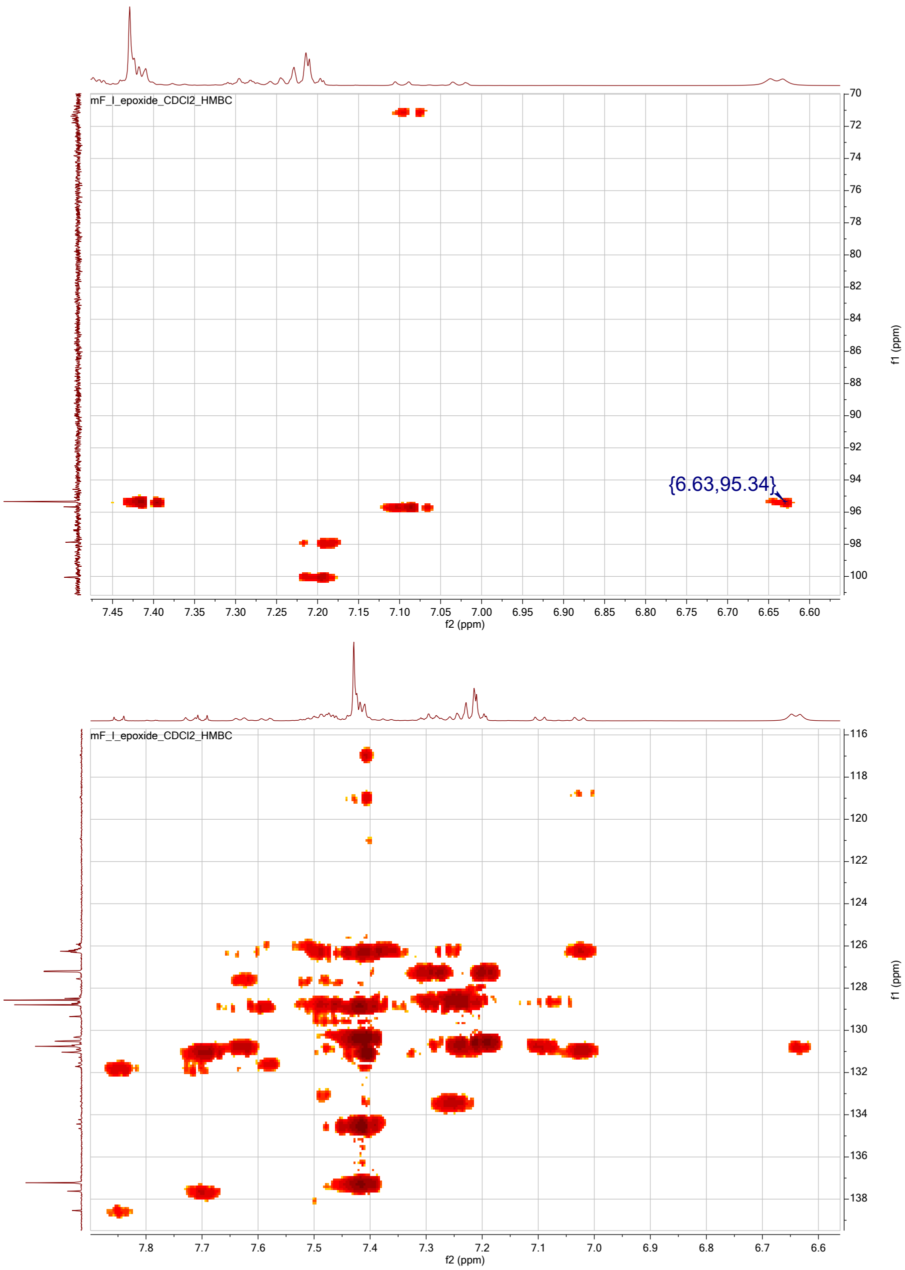

Figure S153. ^{1}H-^{13}C HMBC spectra (CD_2Cl_2) of isolated **4f**. Top: full spectra and bottom: zoom-in spectra.

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Ester scope (4a)

1. Detection of the intermediates

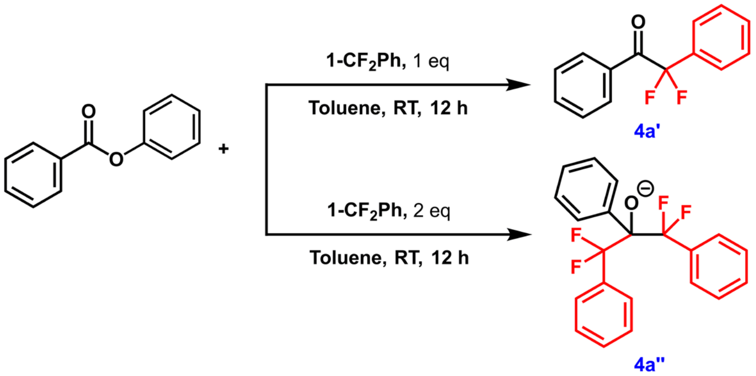

Figure S154. Scheme for probing the intermediates toward **4a** from phenyl benzoate.

Protocol

Phenyl benzoate (0.04 mmol, 7.9 mg) and 1 eq. **1-CF$_2$Ph** (0.04 mmol, 23.8 mg) or 2 eq. (0.08 mmol, 47.6 mg) were measured in 8 mL vials with 1 mL toluene and a stir bar under N_2 atmosphere, respectively. The sealed vials were stirred at RT for 12 h. 6 μL (0.056 mmol) 1,2-difluorobenzene was added as the internal standard for quantification of the chemical yields of the fluorinated species.

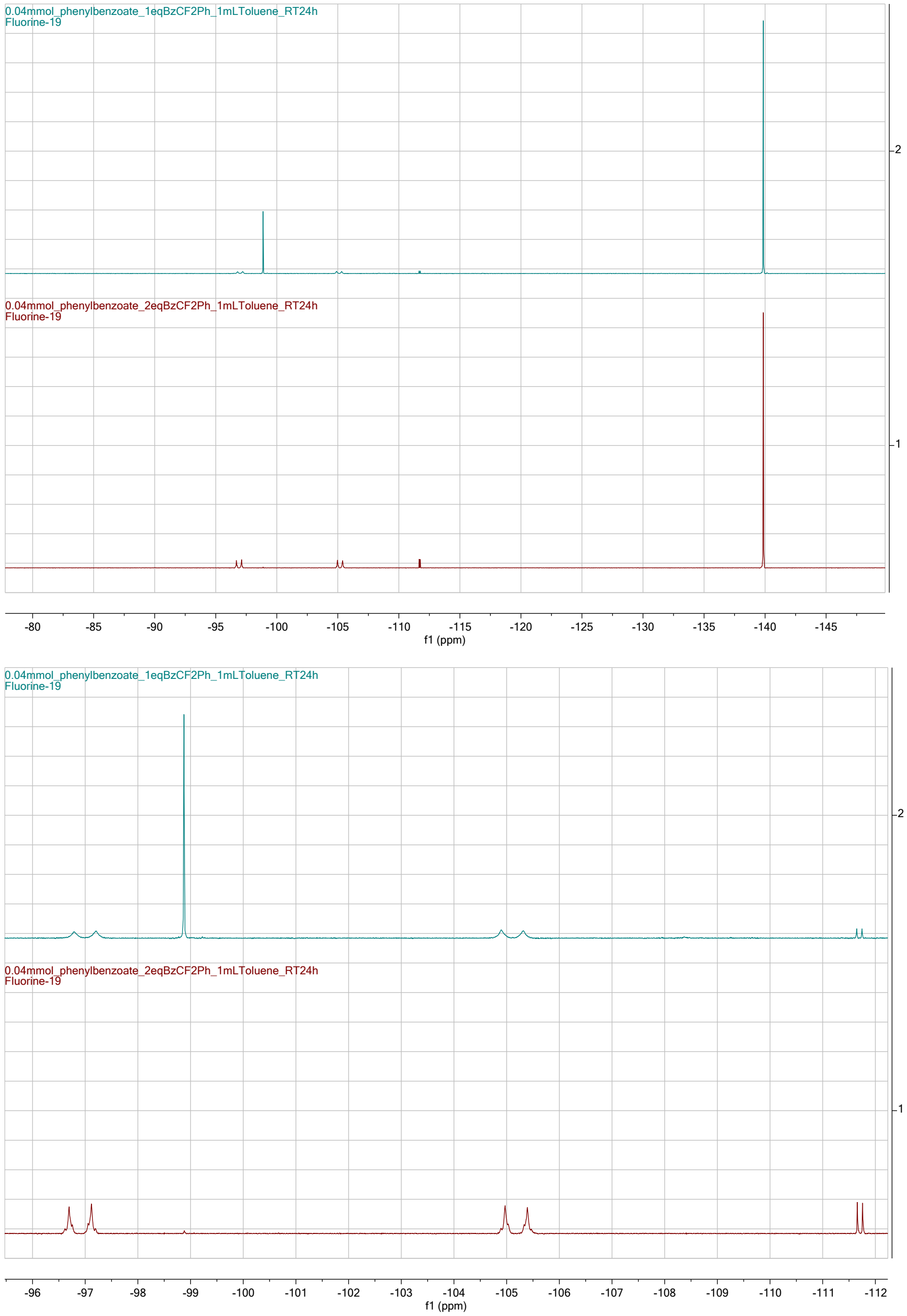

Figure S155. ^{19}F NMR spectra (in toluene) of phenyl benzoate and 1 or 2 eq. **1-CF$_2$Ph**. **4a'**: ^{19}F NMR (564 MHz, toluene) δ -98.87 (s), quantitative *in situ* yield. **4a''**: ^{19}F NMR (564 MHz, toluene) δ -96.39 – -97.38 (m), -104.75 – -105.61 (m), quantitative *in situ* yield.

2. Synthesis and isolation of the multi-fluoroepoxide **4a** from **1-CF$_2$Ph** and esters

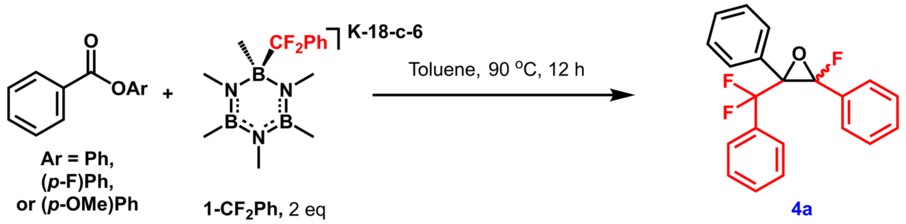

Figure S156. Scheme for the synthesis of multi-fluoroepoxide **4a** from **1-CF$_2$Ph** and esters.

Protocol (for optimization)

The ester substrates (0.04 mmol) and **1-CF$_2$Ph** (0.08 mmol, 47.6 mg) were measured in an 8 mL vial with 0.5 mL toluene and a stir bar under an N_2 atmosphere. The sealed vials were heated and stirred at 90 °C for 12 h. 6 µL (0.056 mmol) 1,2-difluorobenzene was added as the internal standard for quantification of the chemical yields of the afforded multi-fluoroepoxides.

Protocol (for isolation)

The ester substrates (0.4 mmol) and **1-CF$_2$Ph** (0.8 mmol, 476 mg) were measured in an 8 mL vial with 5 mL toluene and a stir bar under N_2 atmosphere. The sealed vials were heated and stirred at 90 °C for 12 h. 0.5 mL of the mixture was filtered through glass microfiber, then characterized by ^{19}F NMR spectroscopy (with added 6 µL, 0.056 mmol, 1,2-difluorobenzene as the internal standard) for quantification of the chemical yields. The NMR sample was added back to the original reaction sample, followed by ~1 mL water, then the organic phase was extracted with EtOAc (3 x 3 mL). The combined organic portions were dried with anhydrous $MgSO_4$ and the solvent was removed under vacuum.

The resulting residue was further purified by flash column chromatography on silica gel (eluent: hexanes:EtOAc = 10:1, v/v, containing 5 vol% Et_3N) affording the purified compounds. Crystals suitable for X-ray diffraction were obtained by vapor diffusion of pentane into a toluene solution of **4a** at -30 °C.

3. Characterization (^{19}F NMR spectra)

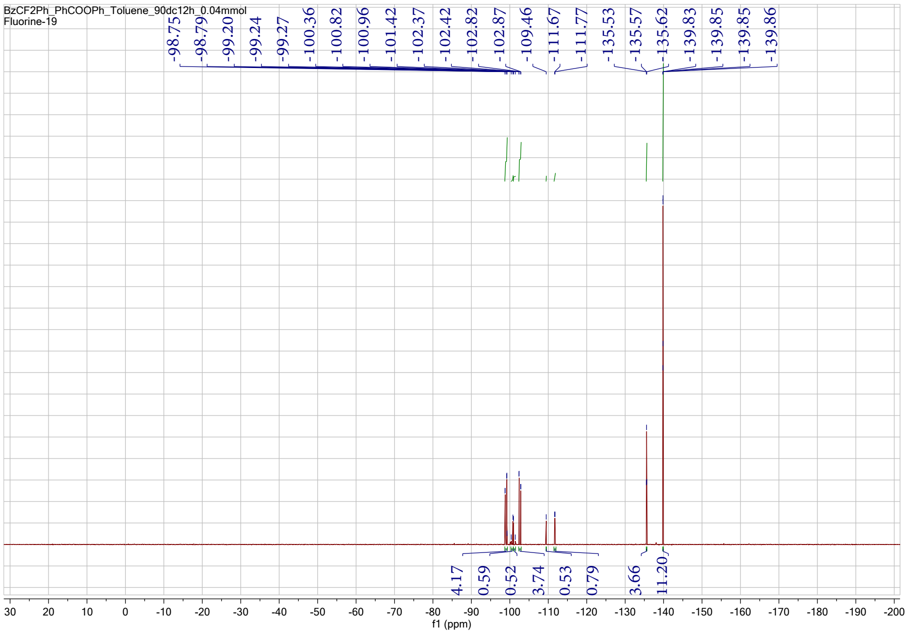

Figure S157. Representative *in situ* ^{19}F NMR spectra (in toluene) of **4a** (from phenyl benzoate, Ar = Ph).

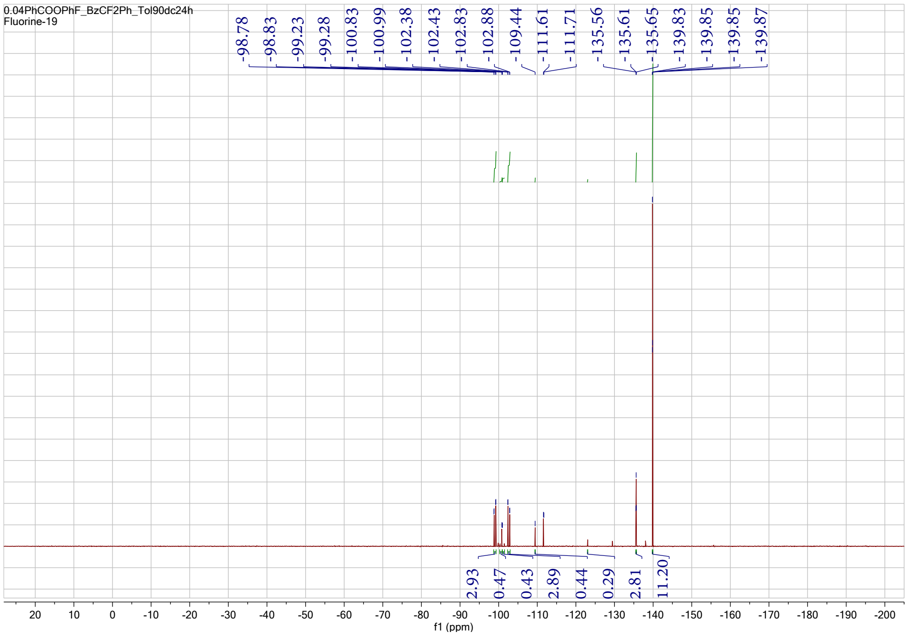

Figure S158. Representative *in situ* ^{19}F NMR spectra (in toluene) of **4a** (from *p*-fluorophenyl benzoate, Ar = (*p*-F)Ph).

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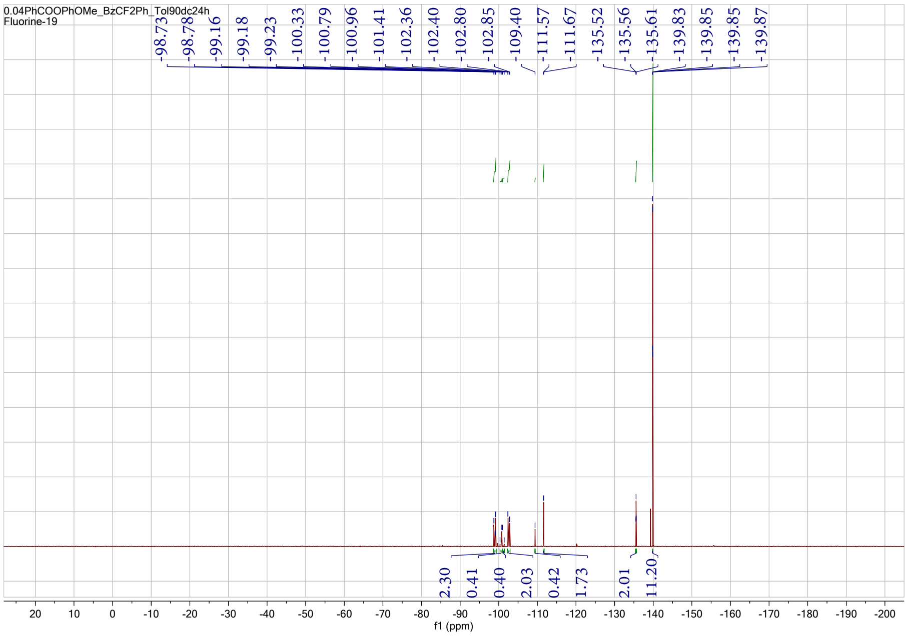

Figure S159. Representative *in situ* ^{19}F NMR spectra (in toluene) of **4a** (from *p*-methoxyphenyl benzoate, Ar = (*p*-OMe)Ph).

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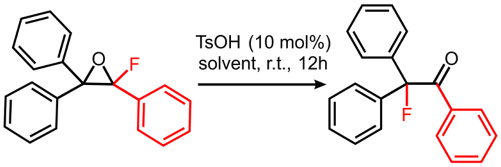
1,2-F migration (5a-5f)

1. Optimization of 1,2-F migration reactions of the prepared fluoroepoxides

1.1 Solvent screen



2a **5a**

Protocol

Purified **2a** (0.01 mmol, 100 μL 29 mg/mL stock solution) and 900 μL of solvent were measured in an 8 mL vial with 0.5 mL toluene and a stir bar under an N_2 atmosphere. The sealed vials were heated and stirred at 90 ºC for 12 h. 6 μL (0.056 mmol) 1,2-difluorobenzene was added as the internal standard for quantification of the chemical yields of the afforded 1,2-F migration products.

Solvent	**2a conversion (%)**	**^{19}F NMR yield of 5a (%)**
DCM	100	42
Toluene	100	43

Table S10. Solvent screening for the 1,2-F migration reaction of α-fluoroepoxides. The results showed similar outcome in toluene compared with in DCM.

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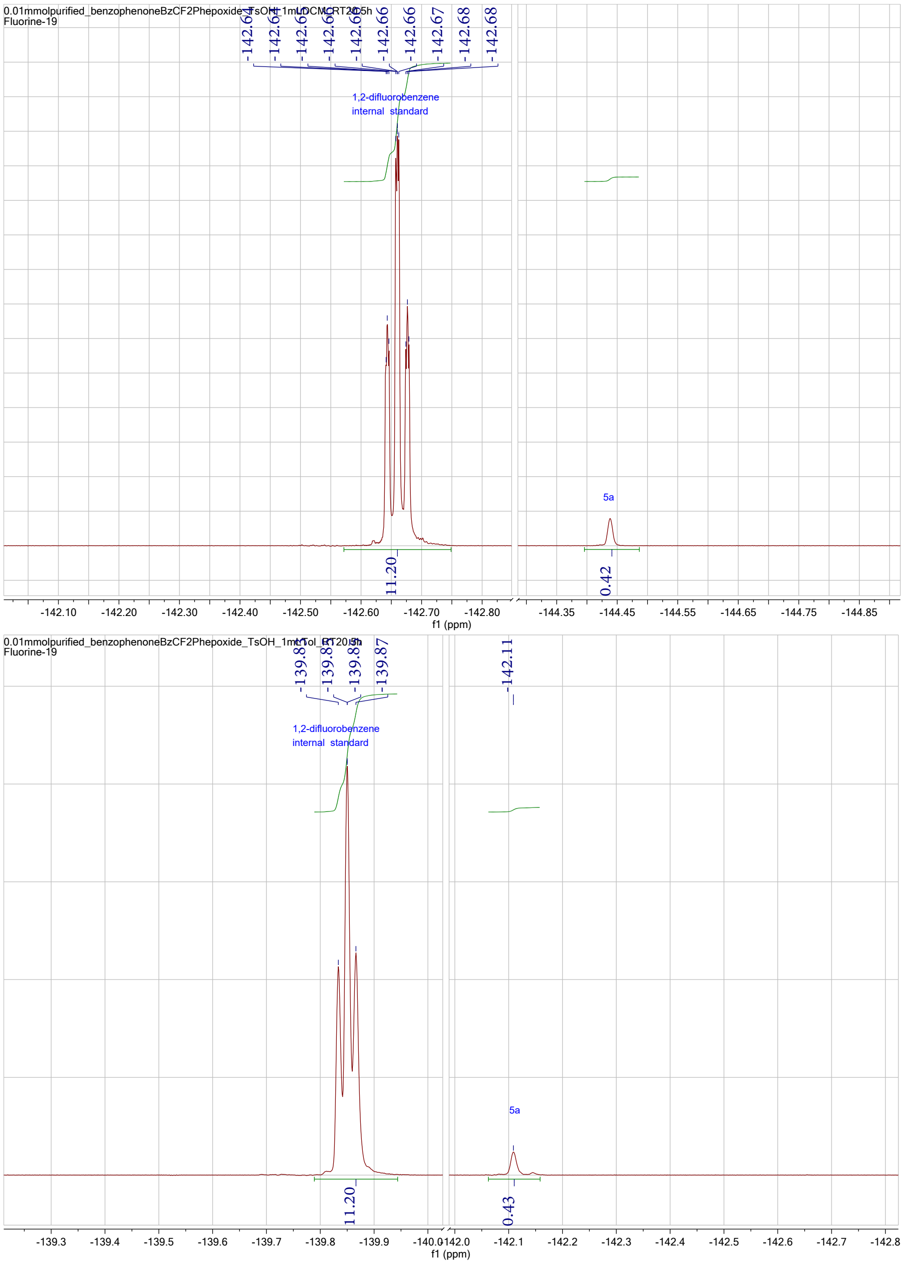

Figure S160. ^{19}F NMR spectra of **5a** in DCM (top) and toluene (bottom).

1.2 Catalyst screening

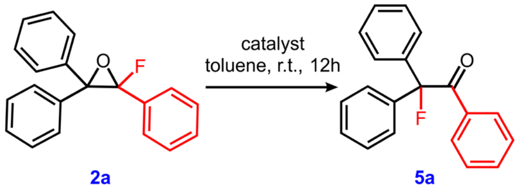

Figure S161. Scheme of the catalyst screening for the 1,2-F migration reactions.

Protocol

Purified **2a** (0.01 mmol, 100 µL 29 mg/mL stock solution in toluene) and 900 µL of toluene were measured in an 8 mL vial with 0.5 mL toluene and a stir bar under an N_2 atmosphere. The sealed vials were heated and stirred at 90 °C for 12 h. 6 µL (0.056 mmol) 1,2-difluorobenzene was added as the internal standard for quantification of the chemical yields of the afforded 1,2-F migration products. 6 µL 1,2-difluorobenzene was added to each entry as the internal standard for quantification using ^{19}F NMR spectroscopy.

Entry	**Catalyst (mol%)**	**2a conversion (%)**	**^{19}F NMR yield of 5a (%)**
1	**TsOH·H_2O (1%)**	**100**	**64**
2	TsOH·H_2O (5%)	100	50
3	TsOH·H_2O (10%)	100	39
4	**HCl-dioxane (100%)**	**100**	**72**

Table S11. Catalyst screening for the 1,2-F migration reaction of the α-fluoroepoxide **2a**. The used HCl-dioxane is diluted from a 4 M HCl stock solution in dioxane.

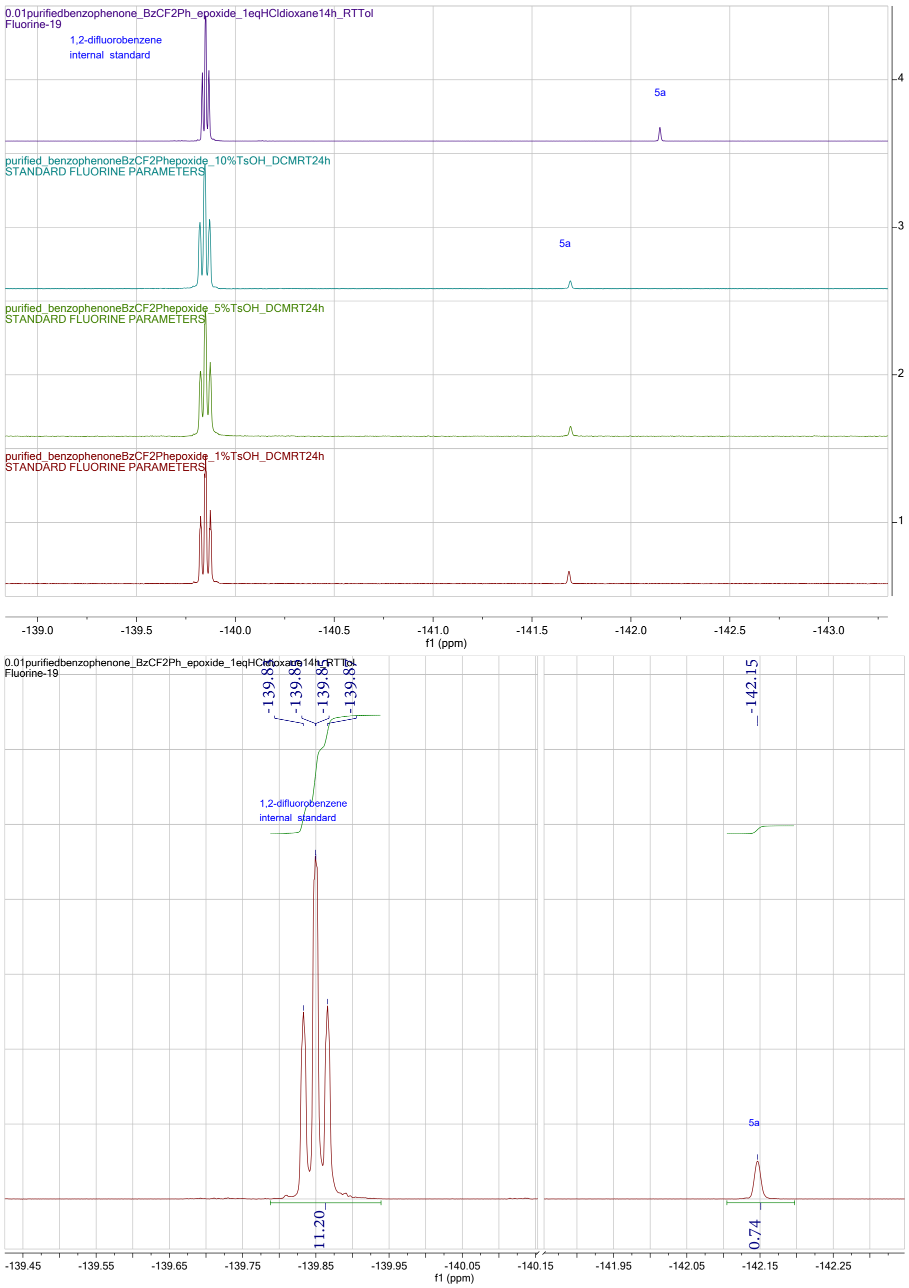

Figure S162. ^{19}F NMR spectra of **5a** obtained from entry 1-4 (from top to bottom) and HCl-dioxane (entry 4, bottom).

1.3 Feasibility of one-pot reaction

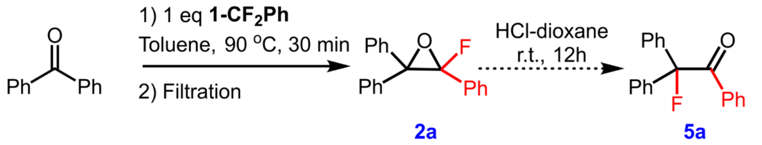

Figure S163. Scheme for one-pot synthesis of **5a**.

Protocol:
Under N_2 atmosphere, benzophenone (0.08 mmol, 14.6 mg), **1-CF$_2$Ph** (0.08 mmol, 48 mg), and 1 mL toluene were set up in 8 mL vials with a stir bar. The sealed vials were heated and stirred (600 rpm) at 90 ºC for 30 min. After cooling to RT, the toluene solution was filtered through glass microfiber under ambient atmosphere. For each entry, 125 μL of the filtered solution was diluted to 1 mL with toluene and various amount of HCl-dioxane (4 M HCl in dioxane) was added to the crude toluene solution of **2a**. 6 μL 1,2-difluorobenzene was added to each entry as the internal standard for quantification using ^{19}F NMR spectroscopy.

Discussion: the in situ yield of **2a** is quantitative under the above condition. Thus, the filtered toluene solution exclusively contains hexamethylborazine, **2a**, and small amount of K(18-crow-6)F. We thus evaluated the feasibility of one-pot reaction converting benzophenone to the 1,2-F migration product **5a**.

Entry	Catalyst (mol%)	2a conversion (%)	^{19}F NMR yield of 5a (%)
1	HCl-dioxane (50%)	0	0
2	HCl-dioxane (100%)	0	0
3	HCl-dioxane (300%)	26	6
4	HCl-dioxane (400%)	74	5

Table S12. Feasibility of one-pot reaction test. The used HCl-dioxane is diluted from a 4 M HCl stock solution in dioxane.

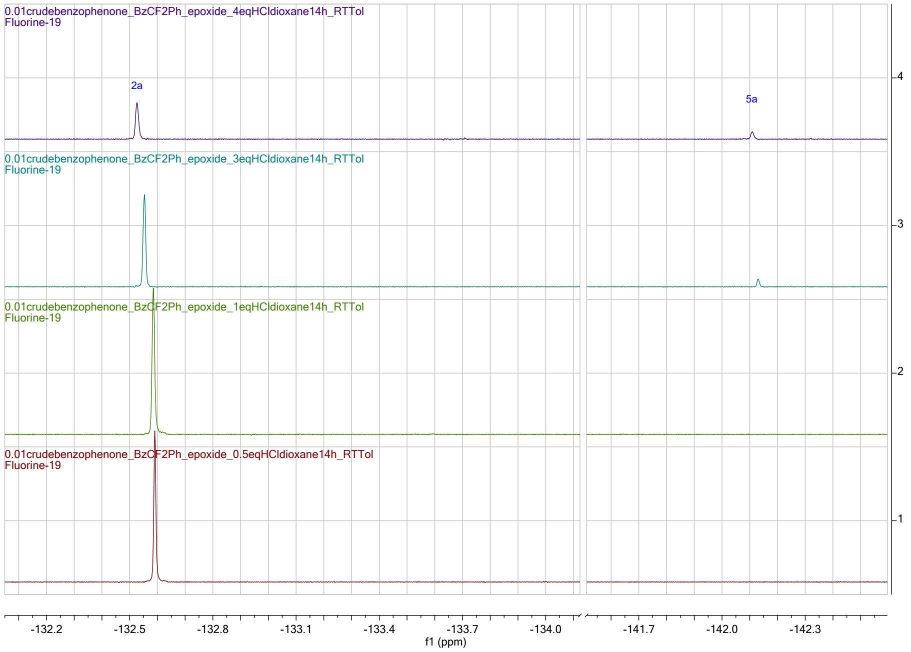

Figure S164. ^{19}F NMR spectra (in toluene) for the feasibility of one-pot reaction test. 1,2-difluorobenzne internal standard peak (not shown in the spectra) was adjusted to the same intensity. From bottom to top: entry 1-4.

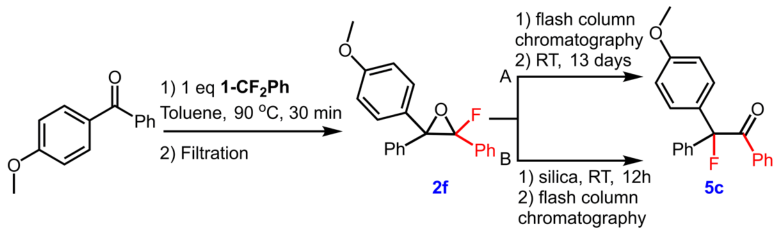

Figure S165. 2 methods for the synthesis of **5c** from **2f**. a) synthesis of **5c** from purified **2f** (no extra catalyst needed) and b) one-pot synthesis of **5c** (silica as the catalyst).

Protocol:

Under N_2 atmosphere (2 parallel reactions), 4-methoxybenzophenone (0.1 mmol, 21 mg), **1-CF$_2$Ph** (0.1 mmol, 59 mg), and 1 mL toluene were set up in an 8 mL vial with a stir bar. The sealed vials were heated and stirred (600 rpm) at 90 °C for 30 min. After cooling to RT, the toluene solution was filtered through glass microfiber under ambient atmosphere affording crude **2f**.

Method A: crude **2f** was purified by flash column chromatography (eluent = hexanes:EtOAc = 10:1, v/v, containing 5vol% Et_3N). The purified **2f** was dissolved in CD_2Cl_2 and characterized by ^{19}F NMR spectroscopy immediately and after 13 days storage under ambient air atmosphere with 6 µL 1,2-difluorobenzene added as the internal standard for quantification.

Method B: ~5 mg silica was added to the crude **2f** and the mixture was stirred for 12 h at RT under ambient atmosphere. The mixture was then purified by flash column chromatography (eluent = hexanes:EtOAc = 10:1, v/v, containing 5vol% Et_3N). The purified **5c** was dissolved in CD_2Cl_2 and characterized by ^{19}F NMR spectroscopy.

Discussion: **2f** was less stable under ambient conditions compared with **2a**, making the one-pot synthesis of **5c** possible. The above 2 methods gave similar yield of **5c**. We assumed that the glass vial served as the catalyst for method A. **3a** was found to have similar stability to **2f**.

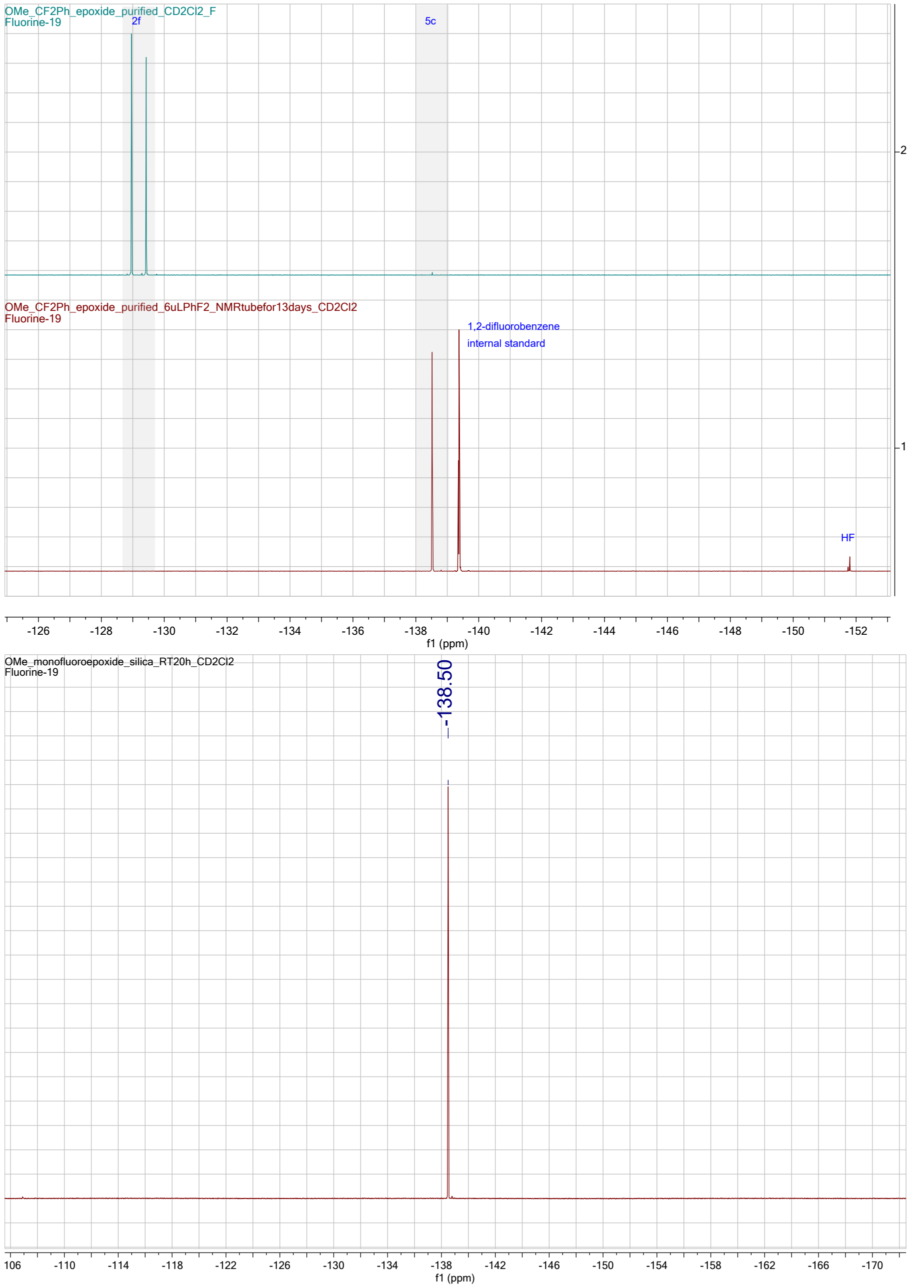

Figure S166. ^{19}F NMR spectra (in CD_2Cl_2) of **5c** afforded from the 2 methods. top: **5c** afforded from the method A (no extra catalyst added). Top panel, spectra collected immediately after purification; bottom panel, spectra collected after 13 days storage under ambient atmosphere with 6 µL 1,2-difluorobenzene added as the internal standard for quantification). Bottom: **5c** afforded from the method B (silica as the catalyst).

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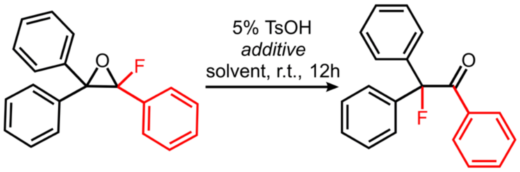
1.4 Additive effect



2a **5a**

Protocol:

All the reactions were at 0.01 mmol scale. Various additives were mixed with 100 μL purified **2a** (in DCM or toluene stock solution, 1 M) and 900 μL of the corresponding solvents (DCM or toluene). Then 5 mol% TsOH·H_2O (0.1 mg, 100 μL of 1mg/mL DCM stock solution) was added. All the reactions were stirred overnight (> 12h) at RT under N_2 atmosphere. 6 μL 1,2-difluorobenzene was added to each entry as the internal standard for quantification using ^{19}F NMR spectroscopy.

Entry (solvent)	Additive	2a conversion (%)	^{19}F NMR yield of 5a (%)
1 (DCM)	-	100	50
2 (toluene)	-	100	43
3 (toluene)	1eq KF	0	0
4 (toluene)	1eq KF + 1eq 18-c-6	0	0
5 (DCM)	1eq hexamethylborazine	0	0
6 (toluene)	1eq hexamethylborazine	0	0

Table S13. Additive effects on the 1,2-F migration reaction of α-fluoroepoxides.

Discussion: The results showed that 1,2-F migration reactions were similarly efficient in either DCM or toluene. However, components of **1-CF$_2$Ph** (hexamethylborazine) or reagent generated during the synthesis of **2a** (KF) completely prevent the 1,2-F migration reaction under our tested conditions. As a result, purified fluoroepoxides were used for the 1,2-F migration reactions.

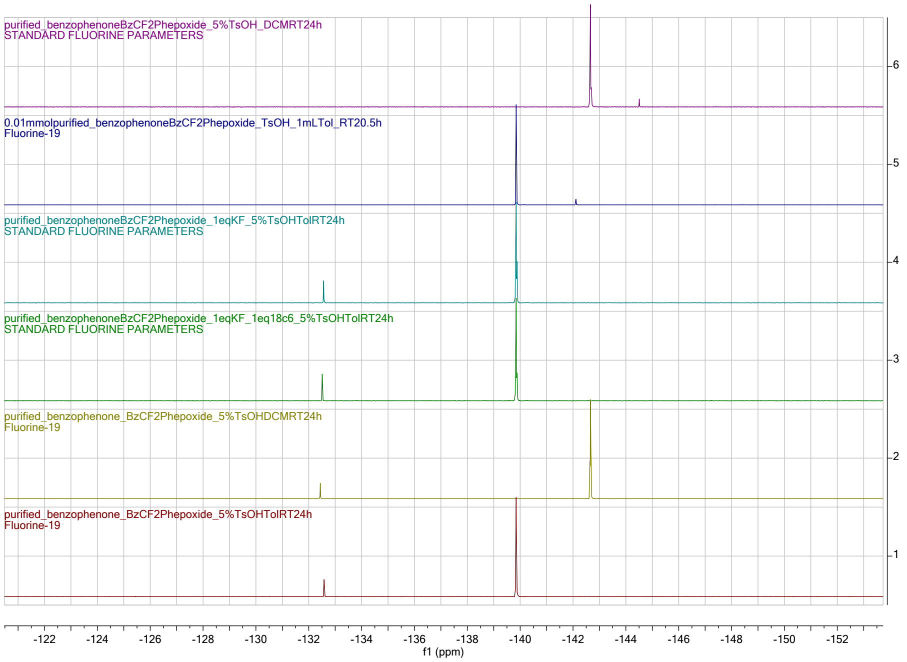
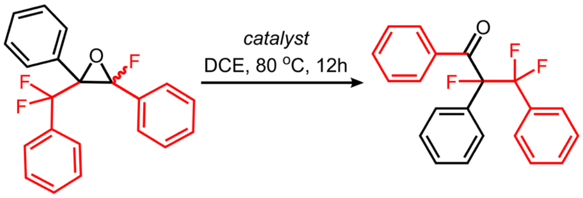


Figure S167. ^{19}F NMR spectra showing the additive effects for the 1,2-F migration reaction of **2a**. From top to bottom: entry 1-6.

1.5 Optimization of the 1,2-F migration reaction using the multi-fluoroepoxide



4a **5e**

Figure S168. Scheme for 1,2-F migration reaction from the multi-fluoroepoxide **4a**.

Protocol

All the reactions were set up at 0.01 mmol scale except entry 4 (0.04 mmol). Under N_2 atmosphere, **4a** (0.1 M stock solution in DCE, 100 µL for entries 1, 2, 3, 5 and 400 µL for entry 4) solution was diluted with DCE. Then various catalyst additives were added (DCE stock solution). All the reactions were 1 mL in total in volume. The reactions were stirred overnight (> 12h) at 80 °C under N_2 atmosphere. 6 µL 1,2-difluorobenzene was added to each entry as the internal standard for quantification using ^{19}F NMR spectroscopy.

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Entry	Catalyst (mol%)	4a conversion (%)	^{19}F NMR yield of 5e (%)
1	TsOH·H_2O (2%)	0	0
2	TsOH·H_2O (5%)	0	0
3	TsOH·H_2O (10%)	0	0
4	$FeCl_3$ (20%)	100	37
5	$GaCl_3$ (10%)	100	57

Table S14. Catalytic activity of TsOH·H_2O or various Lewis acids. 10 mol% $GaCl_3$ is optimal.

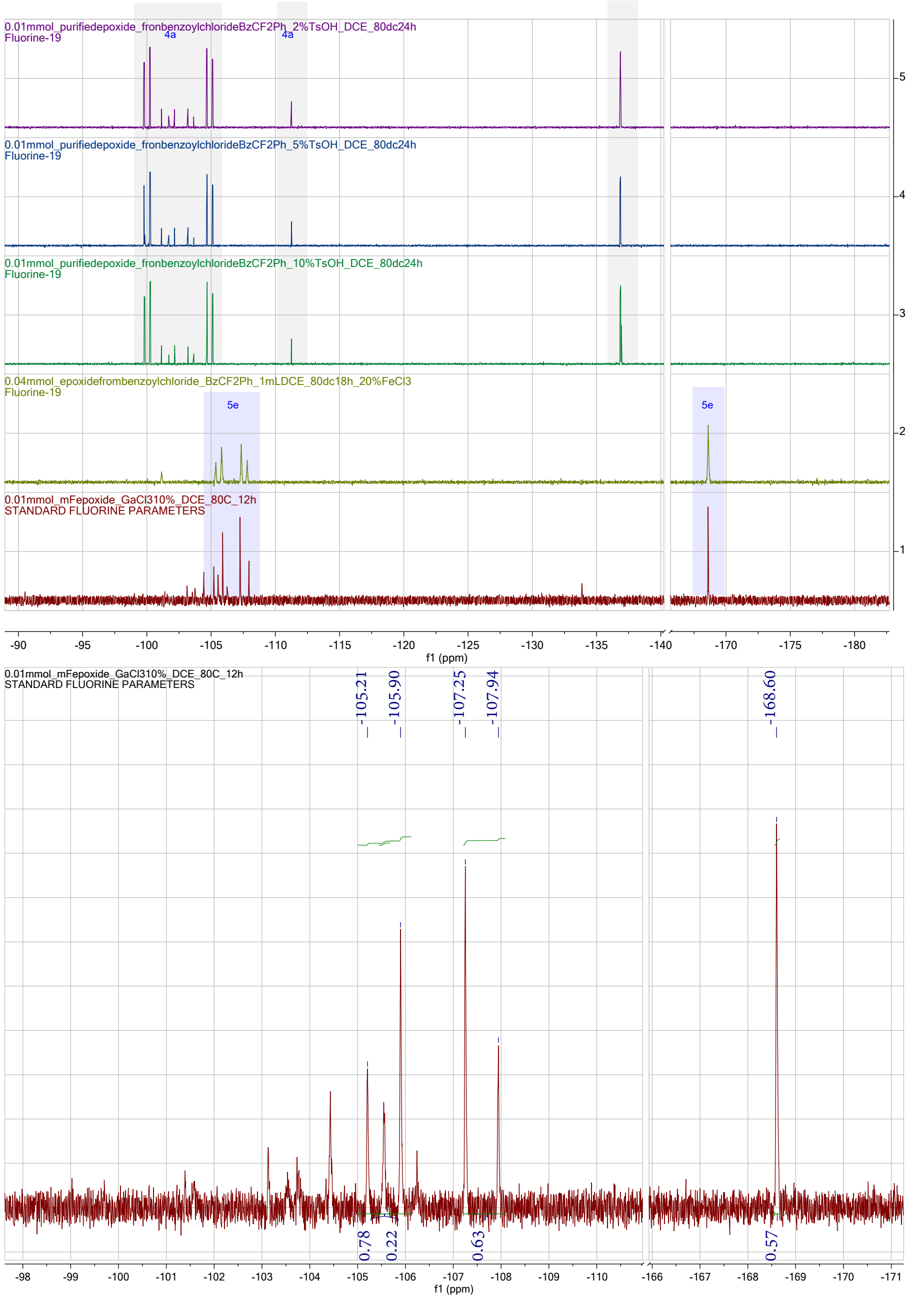

Figure S169. ^{19}F NMR spectra (in DCE) of entry 1-5 (top) and entry 5 (bottom, $GaCl_3$ as additive).

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2. Synthesis and purification of **5a-5e**

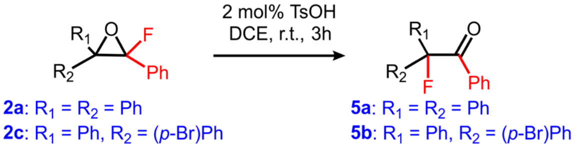


Figure S170. Scheme for the synthesis of **5a-5b**.

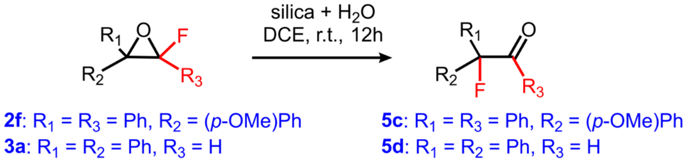


Figure S171. Scheme for the one-pot synthesis of **5c-5d**.

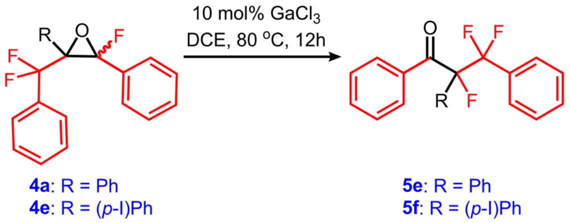


Figure S172. Scheme for the synthesis of **5e-5f**.

Protocol (Synthesis of ***5a*** *and* ***5b*** *for isolation)*

Purified fluoroepoxides (**2a** and **2c**, 0.1 M stock solution in DCE, 1 mL) and TsOH·H_2O (2 mol%, 344 µL 1 mg/mL stock solution in DCE) were mixed in an 8 mL vial with a stir bar under an N_2 atmosphere. The sealed vials were stirred at RT for ~3 h. 6 µL (0.056 mmol) 1,2-difluorobenzene was added as the internal standard for quantification of the chemical yields of the afforded 1,2-F migration products.

Protocol (Synthesis of ***5c*** *for isolation)*

Crude **2f** toluene solution (0.4 mmol scale, see the detailed synthesis protocol in "Ketone scope (**2a-2k**)") was filtered through glass microfiber. Water (100 µL) and silica (~ 5 mg) was added to the solution in an 8 mL vial with a stir bar under ambient atmosphere. The reaction was stirred at RT overnight (>12 h). The mixture was then passed a celite plug and the solvent was removed by vacuum. The residue was purified using flash column chromatography.

Protocol (Synthesis of ***5d*** *for isolation)*

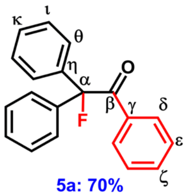
Crude **3a** toluene solution (0.1mmol scale, see the detailed synthesis protocol in "Extended fluoroalkyl scope (**3a** and **3b**)") was filtered through glass microfiber. Water (100 µL) and silica (~ 5 mg) was added to the solution in an 8 mL vial with a stir bar under ambient atmosphere. The reaction was stirred at RT overnight (>12 h). The mixture was then passed a celite plug and the solvent was removed by vacuum. The residue was dissolved in 1 mL DCE and 6 µL (0.056 mmol)

1,2-difluorobenzene was added as the internal standard for quantification of the chemical yields. After removal of the solvent, the sample was purified using preparative TLC.

Protocol (Synthesis of ***5e*** *and* ***5f*** *for isolation)*
Purified multi-fluoroepoxides (**4a**, 0.1 M stock solution in DCE, 1 mL; or 17 mg of **4e**) and $GaCl_3$ (10 mol%) were mixed in an 8 mL vial with a stir bar under an N_2 atmosphere. The sealed vials were heated at 80 °C and stirred for >12 h. After cooling, 6 μL (0.056 mmol) 1,2-difluorobenzene was added as the internal standard for quantification of the chemical yields.

Purification of **5a**, **5b**, **5d**, and **5e** was carried out on preparative TLC plates with 10:1 hexanes:EtOAc (v/v) as the developing solvent. **5c** was purified by flash column chromatography with 10:1 hexanes:EtOAc (v/v) as the eluent.

3. Characterization of **5a-5e** (NMR spectra and MS)



5a: 70%
(quant.)

Yellow oil (0.1 mmol, 20.3 mg isolated, 96% purity). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.4 Hz, 2H), 7.53 (t, *J* = 7.2 Hz, 1H, 1ζH), 7.43 – 7.36 (m, 11H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 197.65 (d, *J* = 30.4 Hz, βC), 139.29 (d, *J* = 23.1 Hz, ηC), 135.27 (s, ζC), 133.17 (s), 130.46 (d, *J* = 5.5 Hz, γC), 128.81 (s), 128.45 (s, ιC), 128.26 (s), 126.78 (d, *J* = 6.9 Hz, θC), 103.02 (d, *J* = 186.9 Hz, αC). ^{19}F NMR (565 MHz, $CDCl_3$) δ -140.70 (s, 1F). GC-MS (EI): calcld. for $[M\text{-}PhCO]^+$ ($C_{13}H_{10}F^+$) = 185.0767, $[M\text{-}Ph_2CF]^+$ ($C_7H_5O^+$) = 105.0340. Found: 185.07, 105.04.

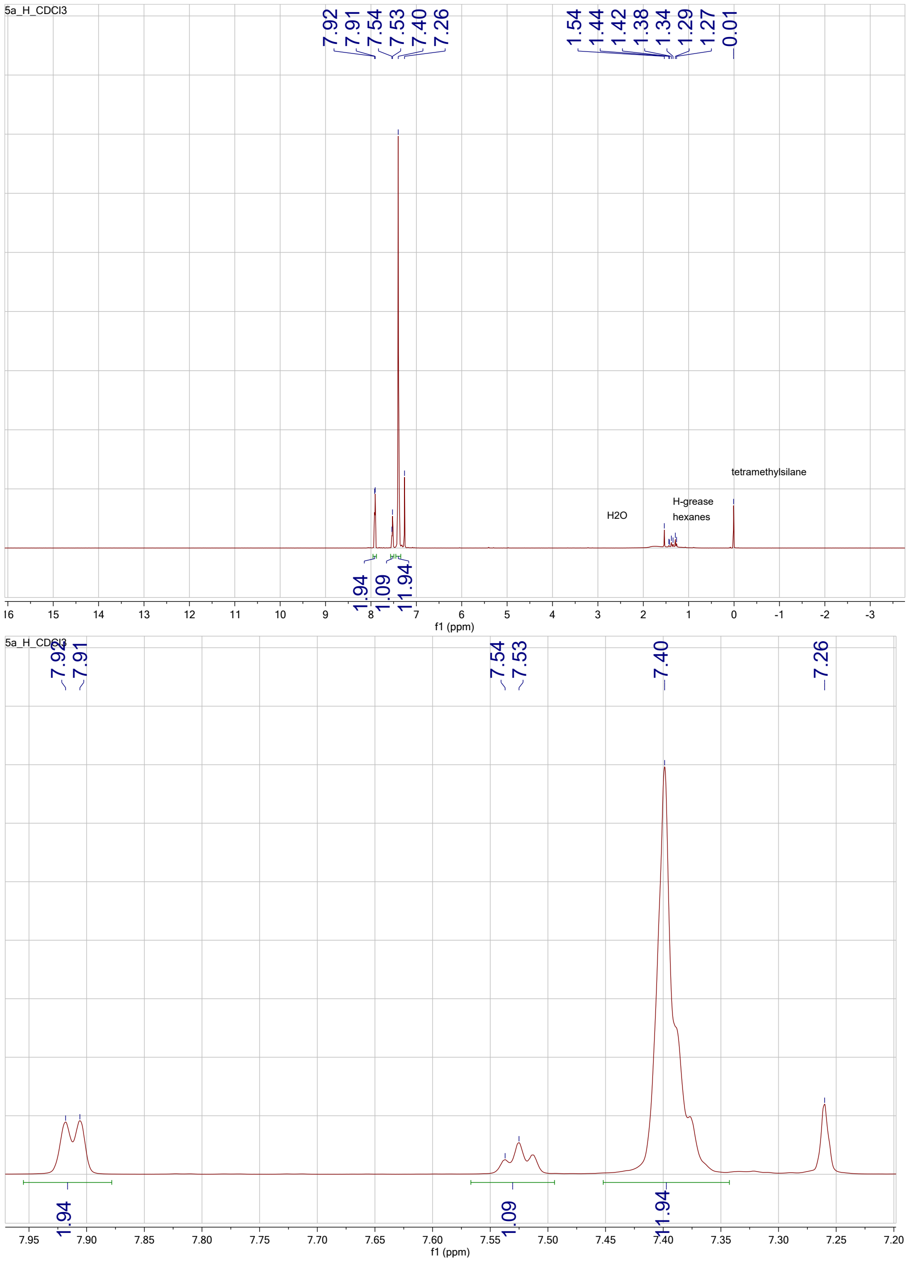


Figure S173. ^{1}H NMR spectra ($CDCl_3$) of isolated **5a**. Top: full spectra and bottom: zoom-in spectra.

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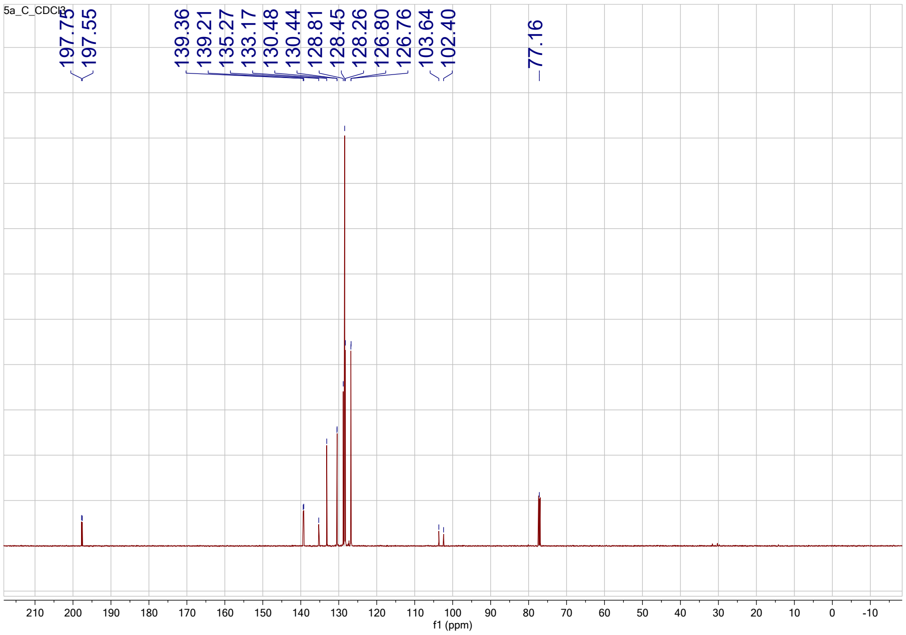

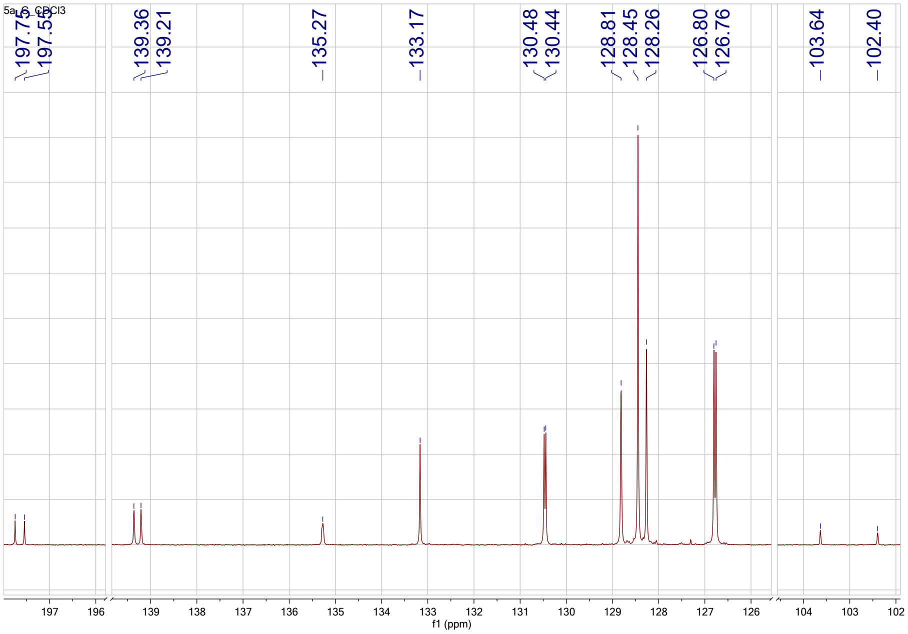

Figure S174. ^{13}C NMR spectra (CDCl$_3$) of isolated **5a**. Top: full spectra and bottom: zoom-in spectra.

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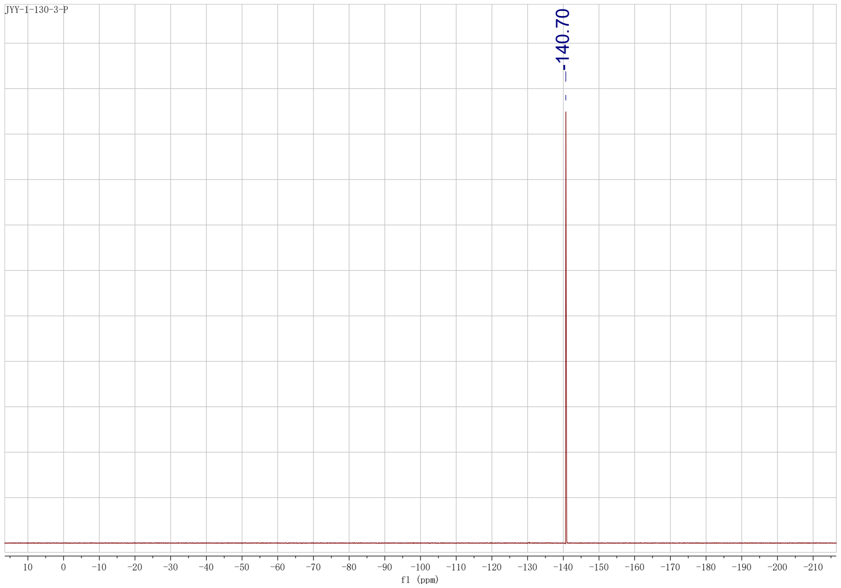
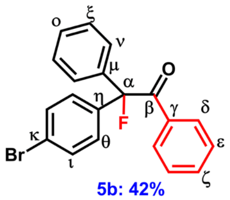


Figure S175. ^{19}F NMR spectra ($CDCl_3$) of isolated **5a**.



5b: 42%
(quant.)

Colorless oil (0.1 mmol, 15.5 mg isolated, 81% purity) ^{19}F NMR (564 MHz, CD_2Cl_2) δ -141.60 (s, 1F). ^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.87 (d, *J* = 8.3 Hz, 2H, 2δH), 7.57–7.52 (m, 3H, 2ιH + 1oH), 7.44 – 7.38 (m, 5H, 1ζH + 2ξH + 2νH), 7.38 – 7.36 (m, 2H, 2εH), 7.26 (d, *J* = 8.5 Hz, 2H, 2θH). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 197.35 (d, *J* = 29.9 Hz, βC), 139.03 (d, *J* = 22.7 Hz, μC), 138.83 (d, *J* = 23.8 Hz, ηC), 135.31 (d, *J* = 3.7 Hz, γC), 133.75 (s, oC), 131.85 (s, ιC), 130.69 (d, *J* = 5.6 Hz, δC), 129.41 (d, *J* = 1.7 Hz, ζC), 128.97 (s), 128.96 (d, *J* = 7.2 Hz, θC), 128.68 (s), 126.86 (d, *J* = 7.1 Hz, εC), 123.39 (d, *J* = 2.4 Hz, κC), 102.94 (d, *J* = 187.7 Hz, αC). HR-MS (ESI): calcld. for $[M – F]^+$ ($C_{20}H_{14}BrO^+$) = 349.0223, found: 349.0226; $[M\text{-}F\text{-}CO]^+$ ($C_{19}H_{14}Br^+$) = 321.0273, found: 321.0267.

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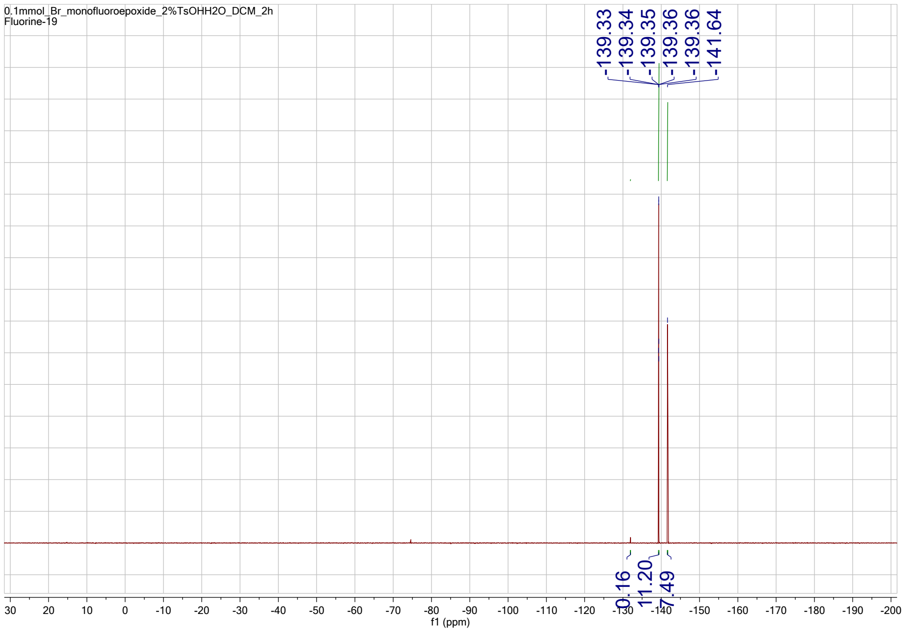

Figure S176. Representative *in situ* ^{19}F NMR spectra (in DCM) of **5b** (δ -141.64 ppm).

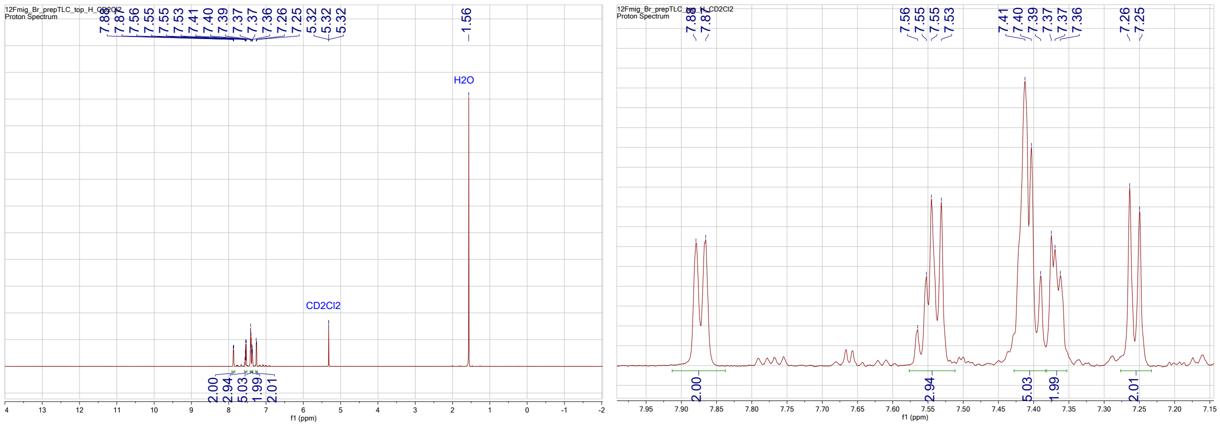

Figure S177. ^{1}H NMR spectra (CD_2Cl_2) of isolated **5b**.

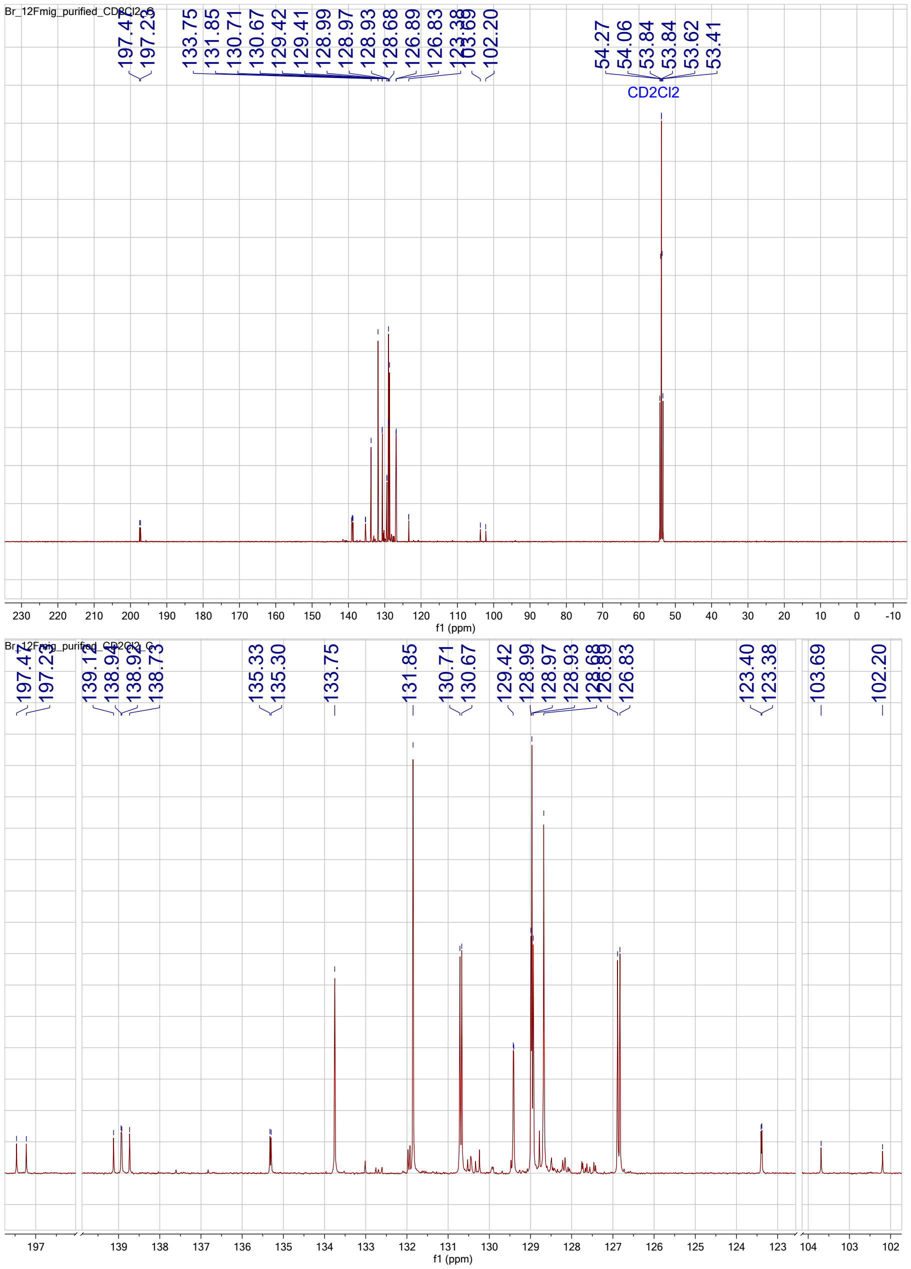

Figure S178. ^{13}C NMR spectra (CD_2Cl_2) of isolated **5b**. Top: full spectra and bottom: zoom-in spectra.

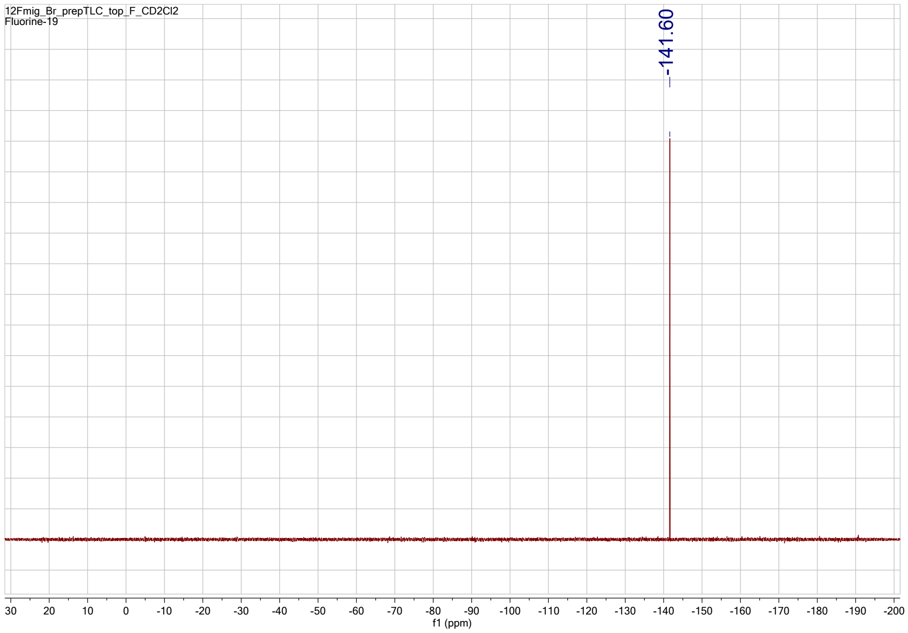

Figure S179. ^{19}F NMR spectra (CD_2Cl_2) of isolated **5b**.

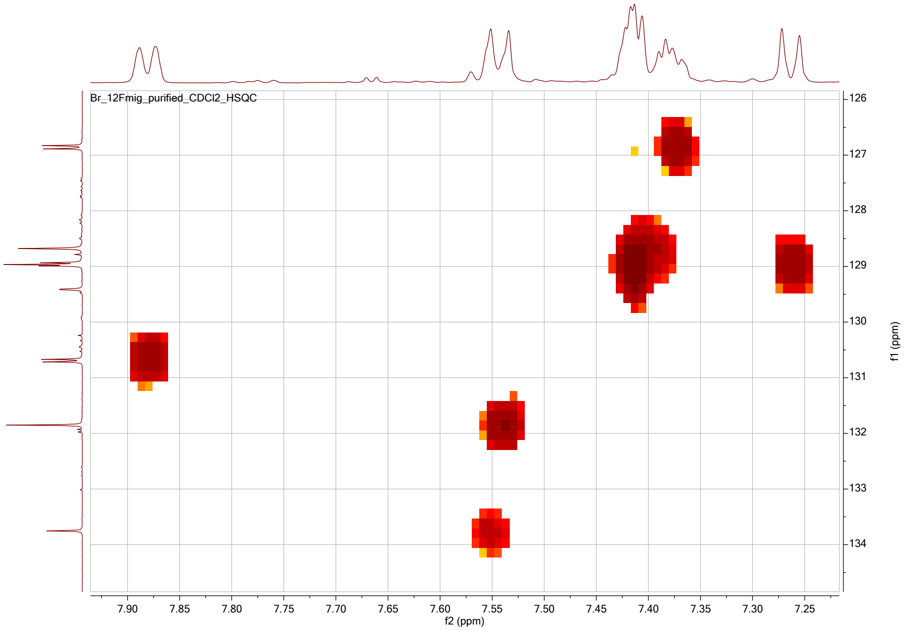

Figure S180. ^{1}H-^{13}C HSQC NMR spectra (CD_2Cl_2) of isolated **5b**.

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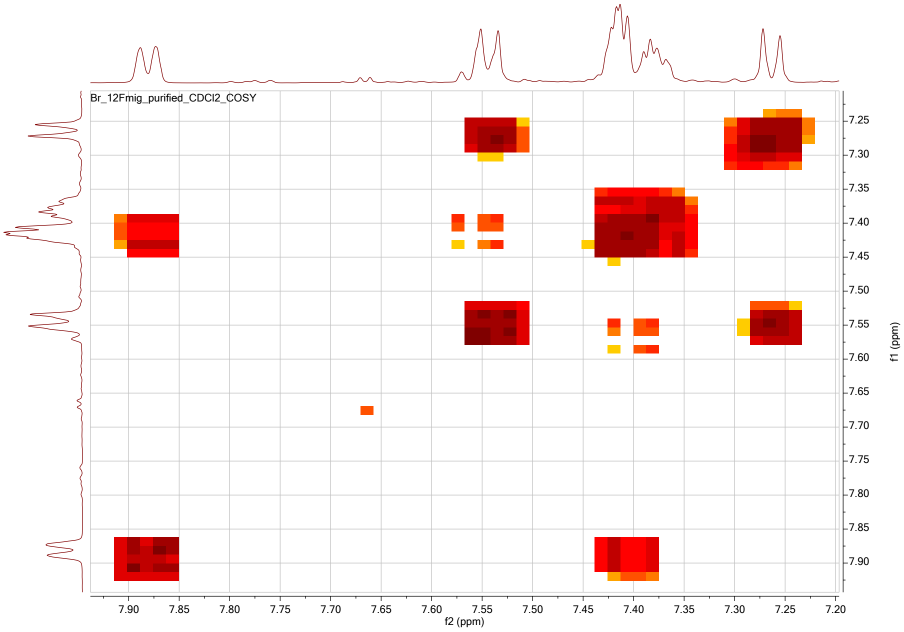

Figure S181. ^{1}H-^{1}H COSY NMR spectra (CD_2Cl_2) of isolated **5b**.

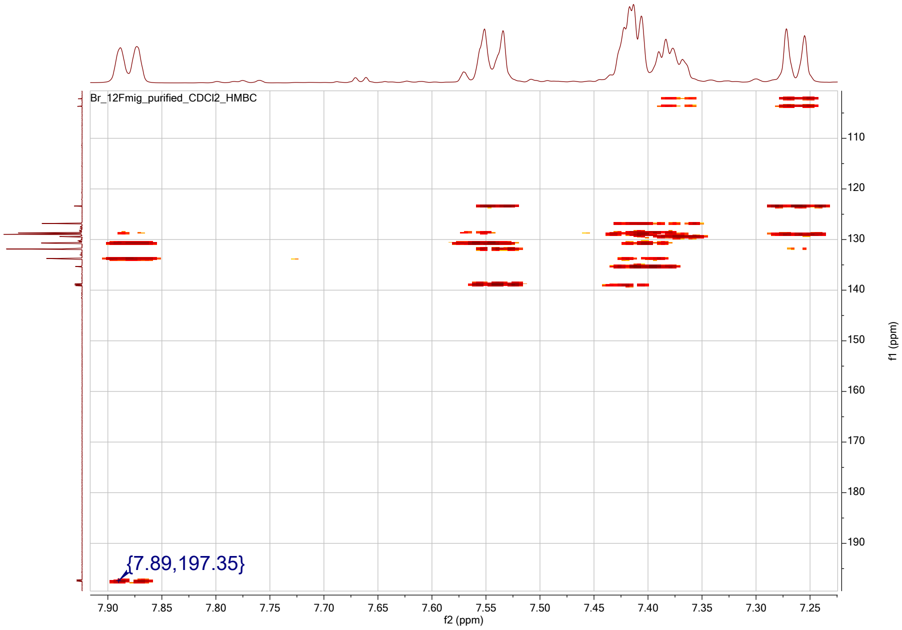

Figure S182. ^{1}H-^{13}C HMBC NMR spectra (CD_2Cl_2) of isolated **5b**.

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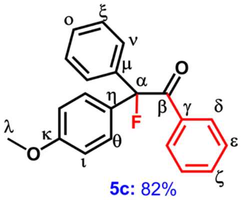


5c: 82%
2 steps

Colorless oil (0.4 mmol scale, 105 mg isolated over 2 steps, 75% purity). ^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.89 (d, *J* = 8.0 Hz, 2H, 2δH), 7.54 (t, *J* = 7.4 Hz, 1H, 1οH), 7.44 – 7.35 (m, 7H, 2εH + 2νH + 2ξH + 1ζH), 7.26 (d, *J* = 8.7 Hz, 2H, 2θH), 6.92 (d, *J* = 8.7 Hz, 2H, 2ιH), 3.81 (s, 3H, 3λH). ^{19}F NMR (564 MHz, CD_2Cl_2) δ -138.54 (s, 1F). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 198.17 (d, *J* = 30.7 Hz, βC), 160.42 (d, *J* = 1.9 Hz, κC), 139.77 (d, *J* = 23.3 Hz, μC), 135.73 (d, *J* = 3.7 Hz, γC), 133.49 (s, ζC), 131.76 (d, *J* = 23.4 Hz, ηC), 130.67 (d, *J* = 5.6 Hz, δC), 129.09 (d, *J* = 1.7 Hz, ξC), 128.73 (s), 128.67 (d, *J* = 6.6 Hz), 128.58 (s), 127.06 (d, *J* = 7.0 Hz, νC), 114.08 (s, ιC), 103.36 (d, *J* = 185.7 Hz, αC), 55.70 (s, λC). HR-MS (ESI): calcd. for $[M - F]^+$ ($C_{21}H_{17}O_2^+$) = 301.1223, found: 301.1218; $[M - FCO]^+$ ($C_{20}H_{17}O^+$) = 273.1274, found: 273.1323.

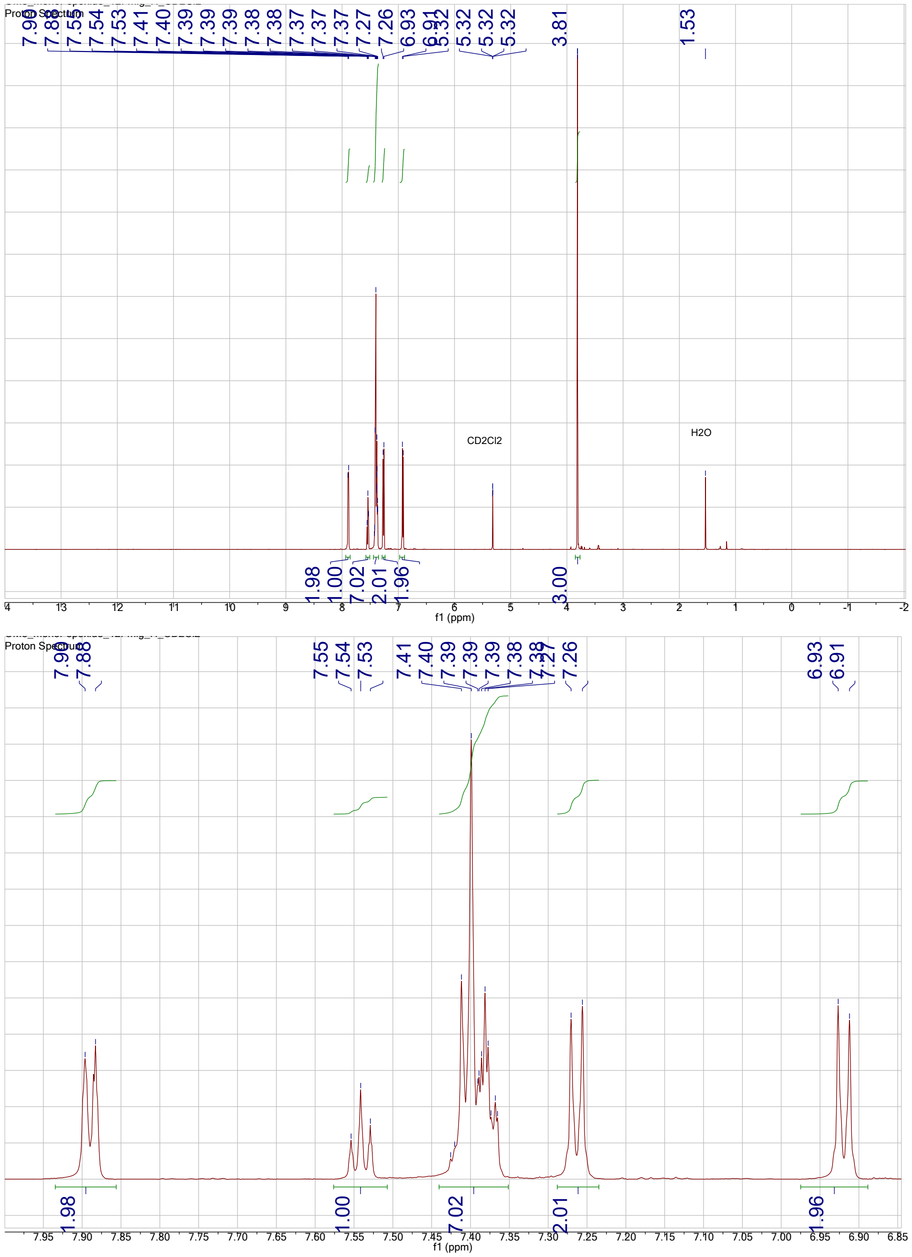


Figure S183. ^{1}H NMR spectra (CD_2Cl_2) of isolated **5c**. Top: full spectra and bottom: zoom-in spectra.

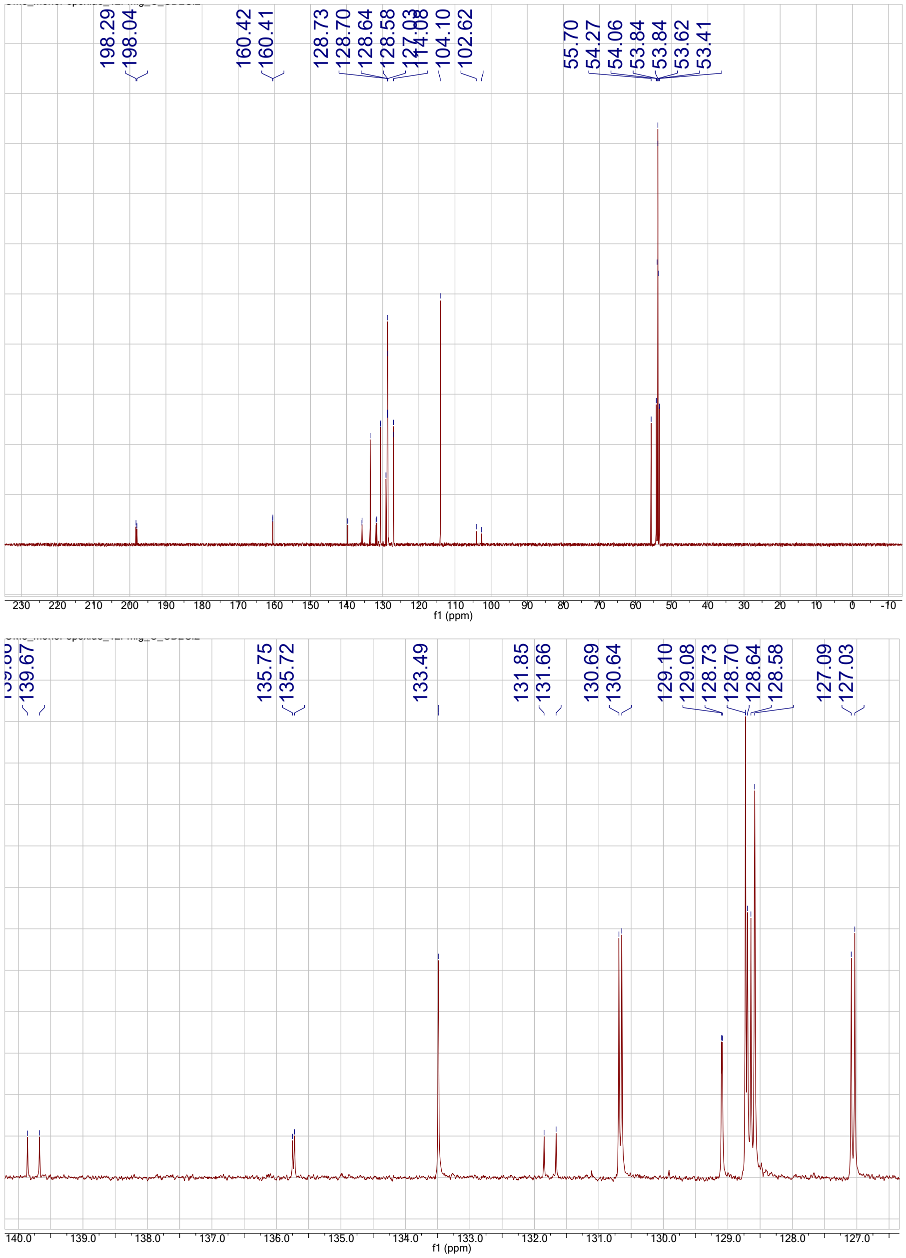


Figure S184. ^{13}C NMR spectra (CD_2Cl_2) of isolated **5c**. Top: full spectra and bottom: zoom-in spectra.

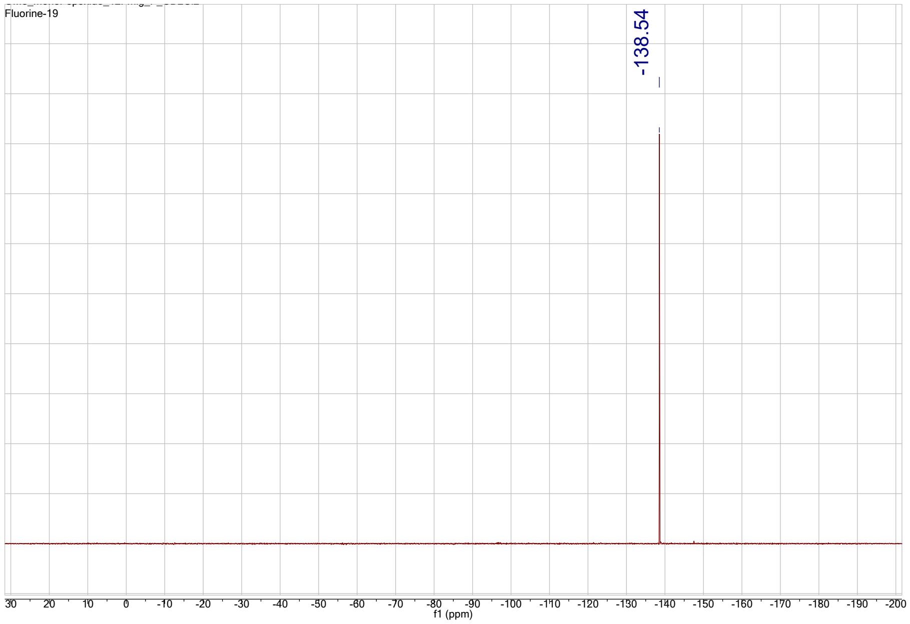


Figure S185. ^{19}F NMR spectra (CD_2Cl_2) of isolated **5c**.

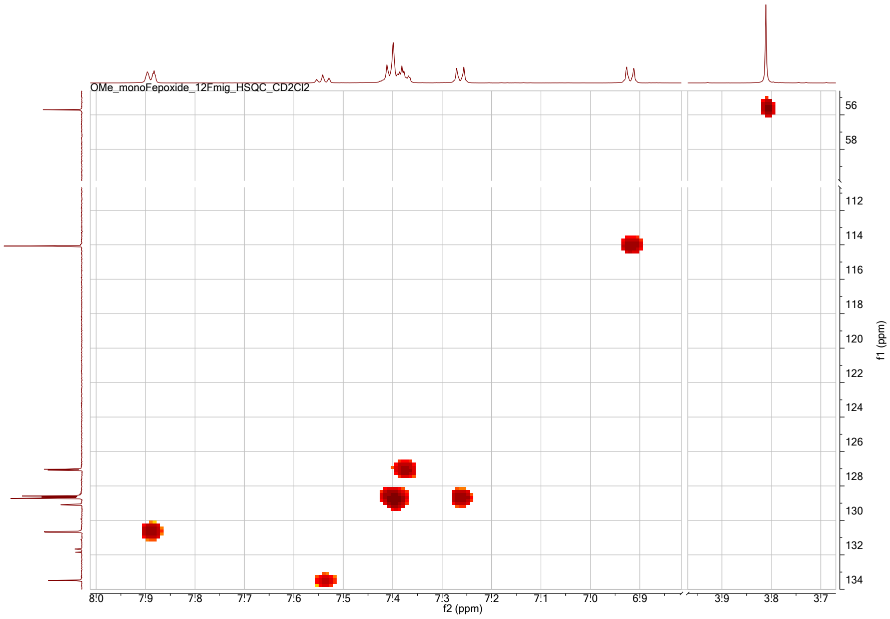
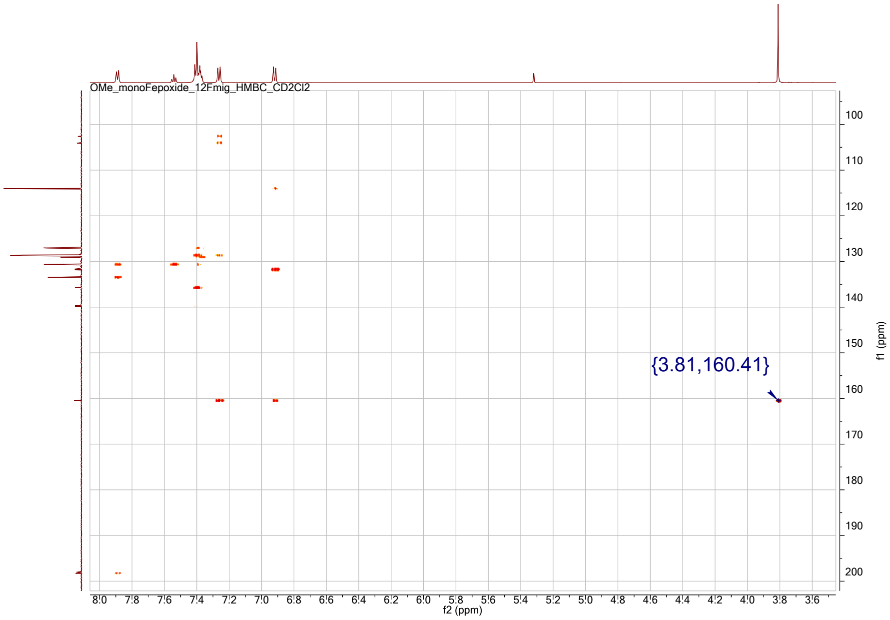


Figure S186. ^{1}H-^{13}C HSQC NMR spectra (CD_2Cl_2) of isolated **5c**.



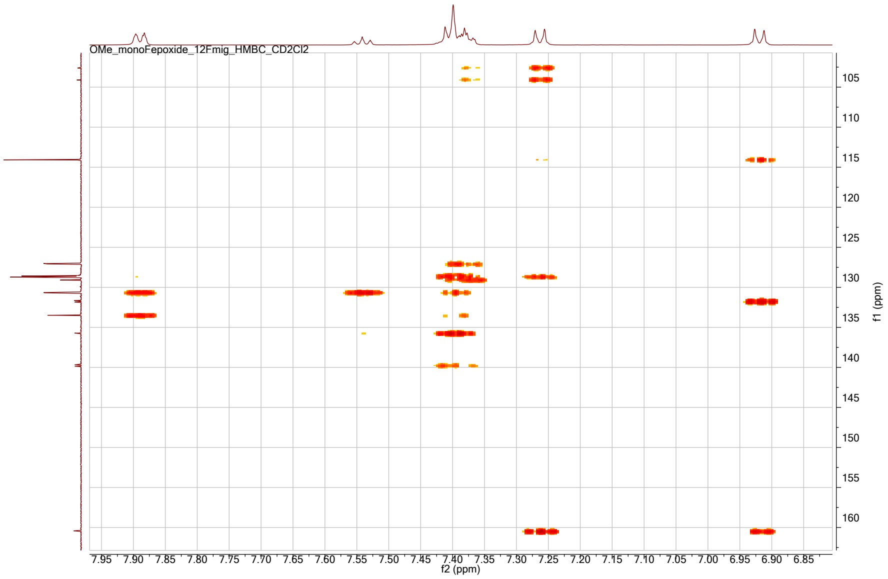


Figure S187. ^{1}H-^{13}C HMBC NMR spectra (CD_2Cl_2) of isolated **5c**. Top: full spectra and bottom: zoom-in spectra.

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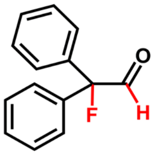

5d: (42%)
2 steps

Yellow oil (0.1 mmol, isolated yield was not determined due to the volatility). ^{19}F NMR (564 MHz, CD_2Cl_2) δ -153.02 (d, J = 6.9 Hz, 1F). ^{1}H NMR (600 MHz, CD_2Cl_2) δ 9.99 (d, J = 6.9 Hz, 1H), 7.46 – 7.39 (m, 10H). The ^{1}H, and ^{19}F NMR results are consistent with the reported data in the literature.[20] The isolated compound is volatile under high vacuum (0.08 Torr) at room temperature.

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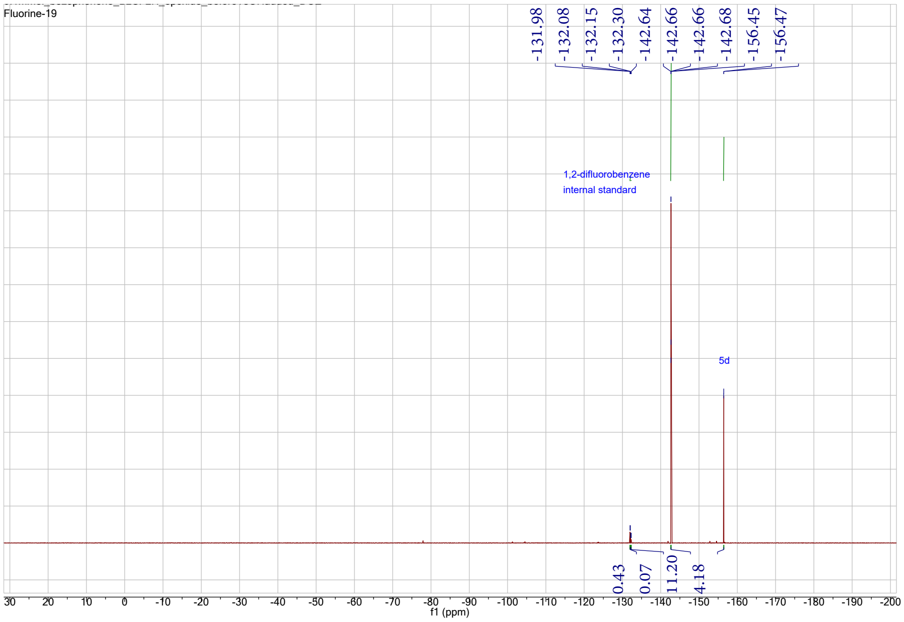

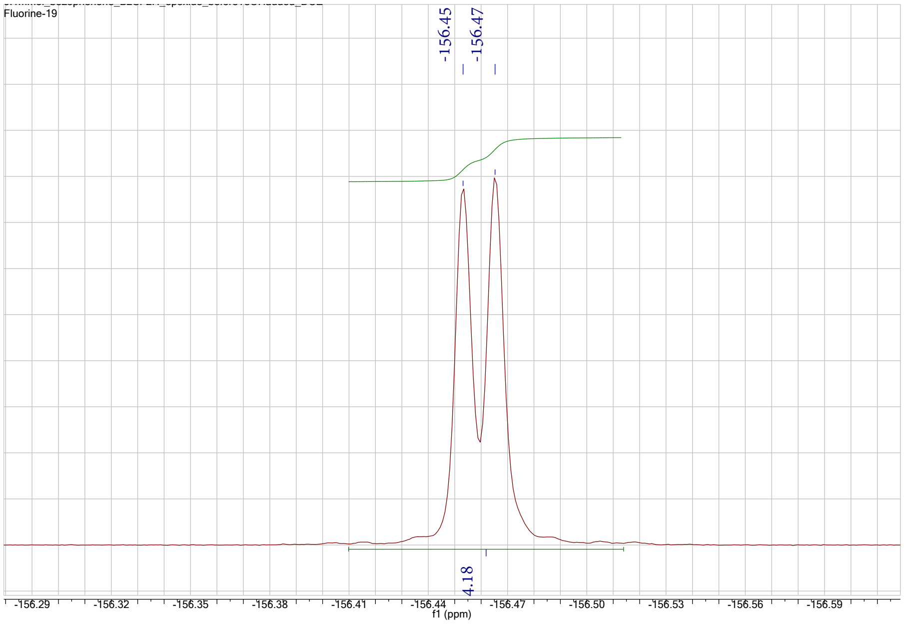

Figure S188. Representative *in situ* ^{19}F NMR spectra (in DCE) of **5d**. Top: full spectra and bottom: zoom-in spectra.

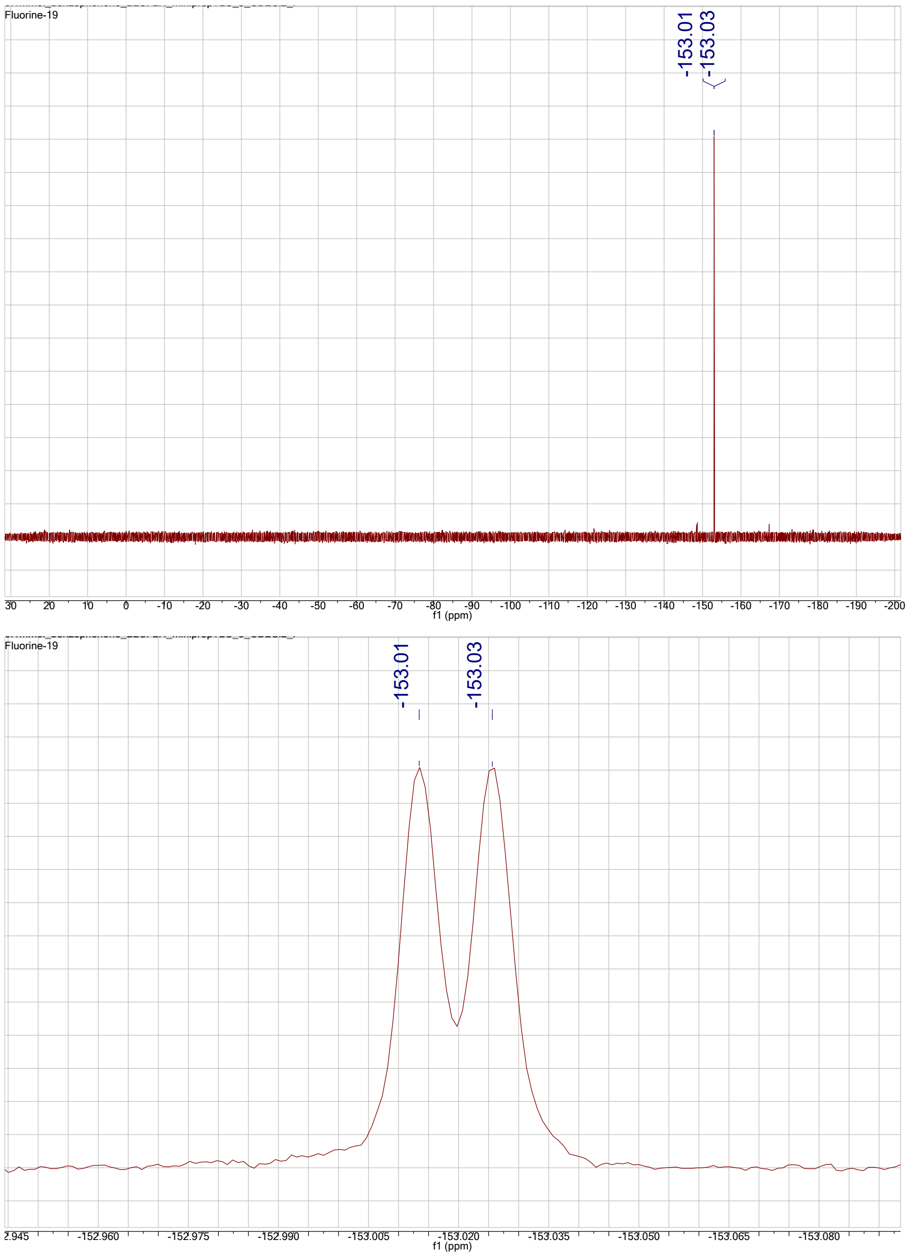

Figure S189. ^{19}F NMR spectra (in CD_2Cl_2) of the isolated **5d**. Top: full spectra and bottom: zoom-in spectra.

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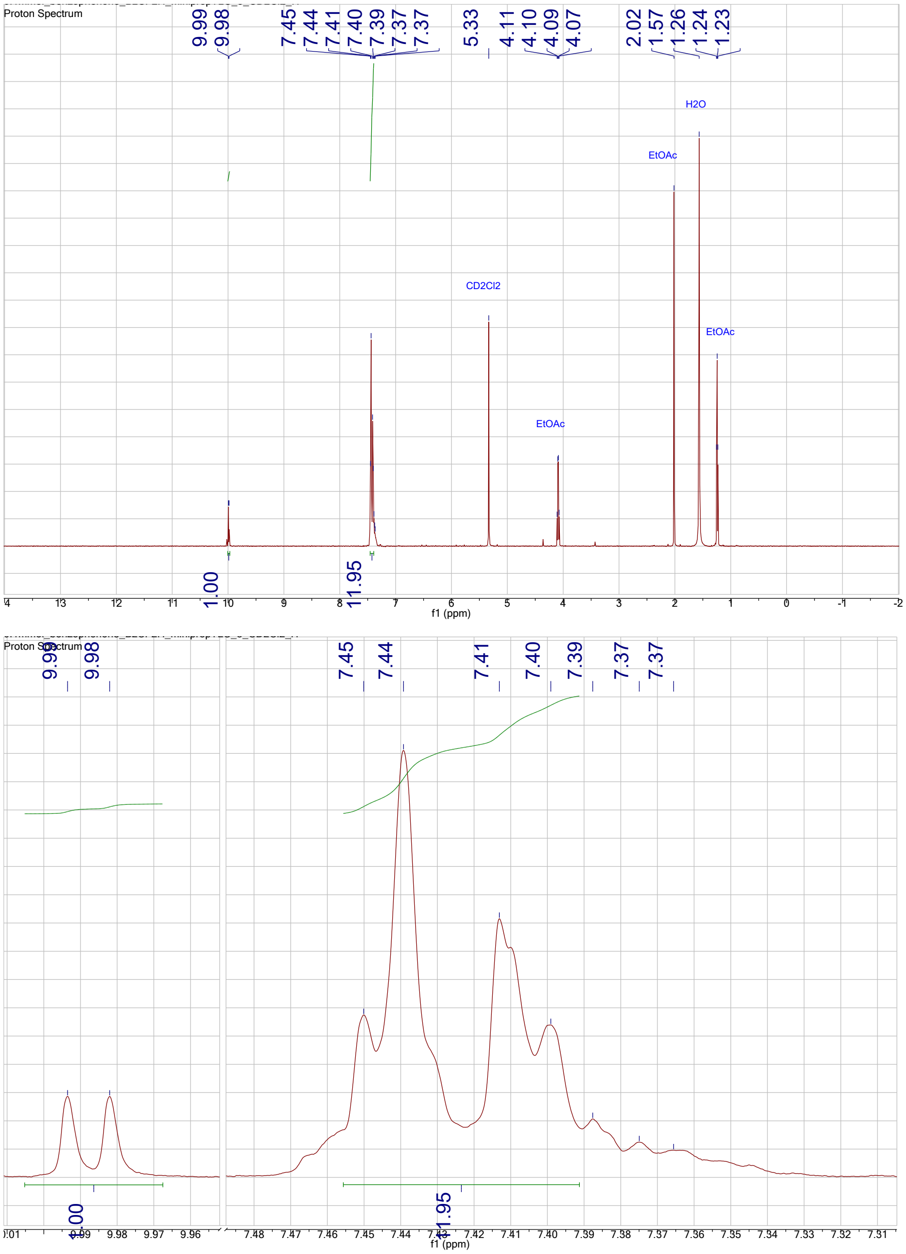

Figure S190. ^{1}H NMR spectra (in CD_2Cl_2) of the isolated **5d**. Top: full spectra and bottom: zoom-in spectra.

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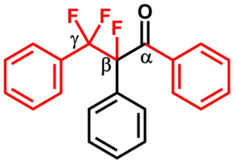

5e: 39%
(57%)

Yellow oil (0.1 mmol, 13 mg isolated, 46% purity). ^{19}F NMR (564 MHz, CD_2Cl_2) δ -102.32 (d, *J* = 261.2 Hz, γF, 1F), -104.22 (dd, *J* = 260.3, 4.2 Hz, γF, 1F), -165.07 (s, βF, 1F). ^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.68 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 7.6 Hz, 1H), 7.54 (d, *J* = 7.4 Hz, 2H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.38 – 7.31 (m, 7H), 7.26 – 7.22 (m, 2H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 193.94 (d, *J* = 27.0 Hz, αC), 135.39 (d, *J* = 2.7 Hz), 133.70 (s), 132.09 (dd, *J* = 21.4, 2.0 Hz), 131.00 (s), 129.94 (d, *J* = 6.0 Hz), 128.89 (d, *J* = 1.8 Hz), 128.61 (s), 128.09 (s), 127.75 (td, *J* = 6.4, 2.4 Hz), 127.33 (s), 127.08 (dd, *J* = 17.3, 7.1 Hz), 126.46 (d, *J* = 9.2 Hz), 120.13 (ddd, *J* = 285.5, 260.4, 32.1 Hz, γC), 99.64 (dd, *J* = 227.4, 30.2 Hz, βC). HR-MS (ESI): calcd. for $C_{21}H_{19}O^+$, $[M-3F+4H]^+$: 287.1430 Found: 287.1451. GC-MS (EI): Retention time = 17.325-17.375 min. 214.1: $[PhCFHCOPh]^+$, calcd. ($C_{14}H_{11}FO^+$) = 214.0794, 127.1: $[PhCF_2]^+$, calcd. ($C_7H_5F_2^+$) = 127.0359, 105.0: $[PhCO]^+$, calcd. ($C_7H_5O^+$) = 105.0340, 77: $[Ph]^+$, calcd. ($C_6H_5^+$) = 77.0391, 51: $[CF_2H]^+$, calcd. (CF_2H) = 51.0041.

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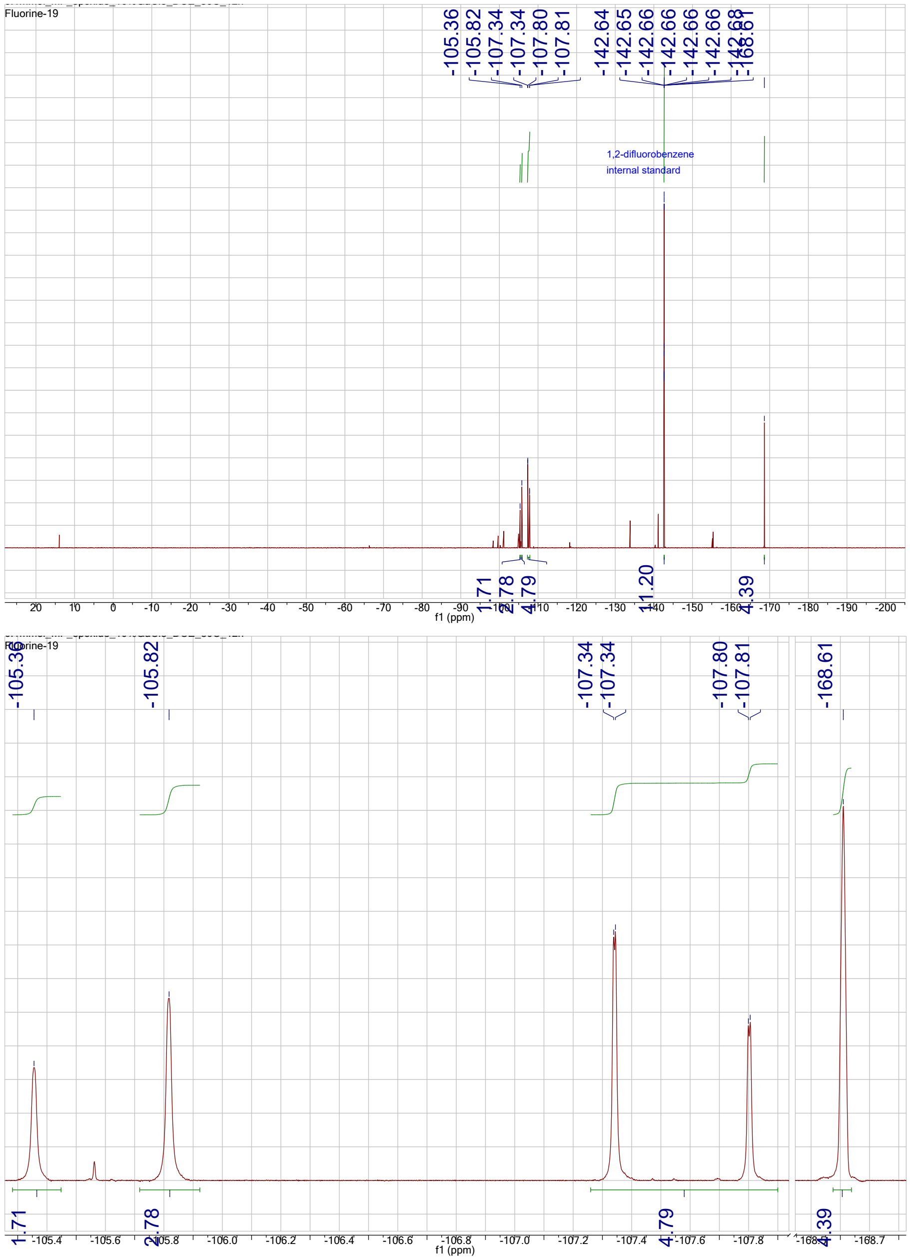

Figure S191. Representative *in situ* ^{19}F NMR spectra (in DCE) of **5e** showing the chemical yield. Top: full spectra and bottom: zoom-in spectra.

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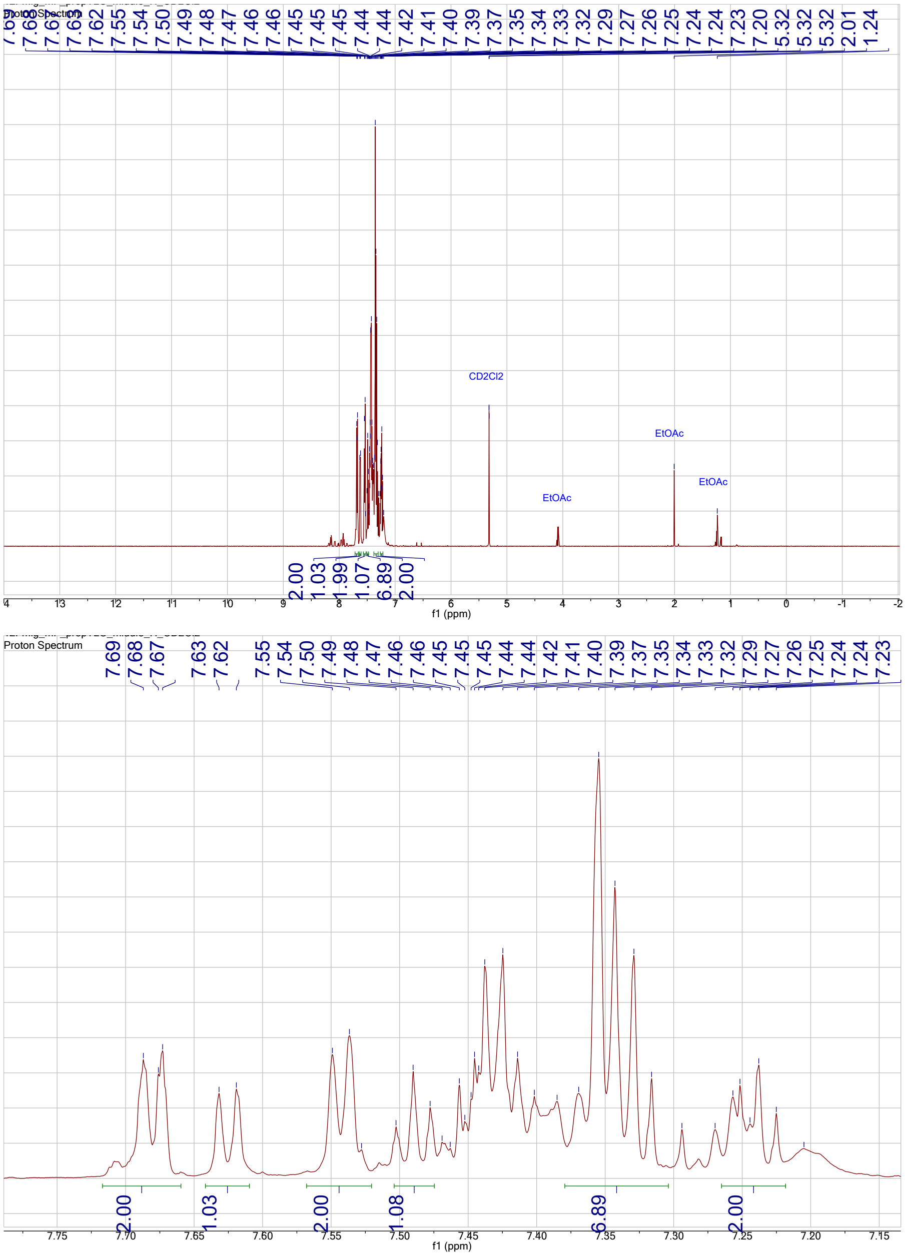


Figure S192. ^{1}H NMR spectra (CD_2Cl_2) of isolated **5e**. Top: full spectra and bottom: zoom-in spectra.

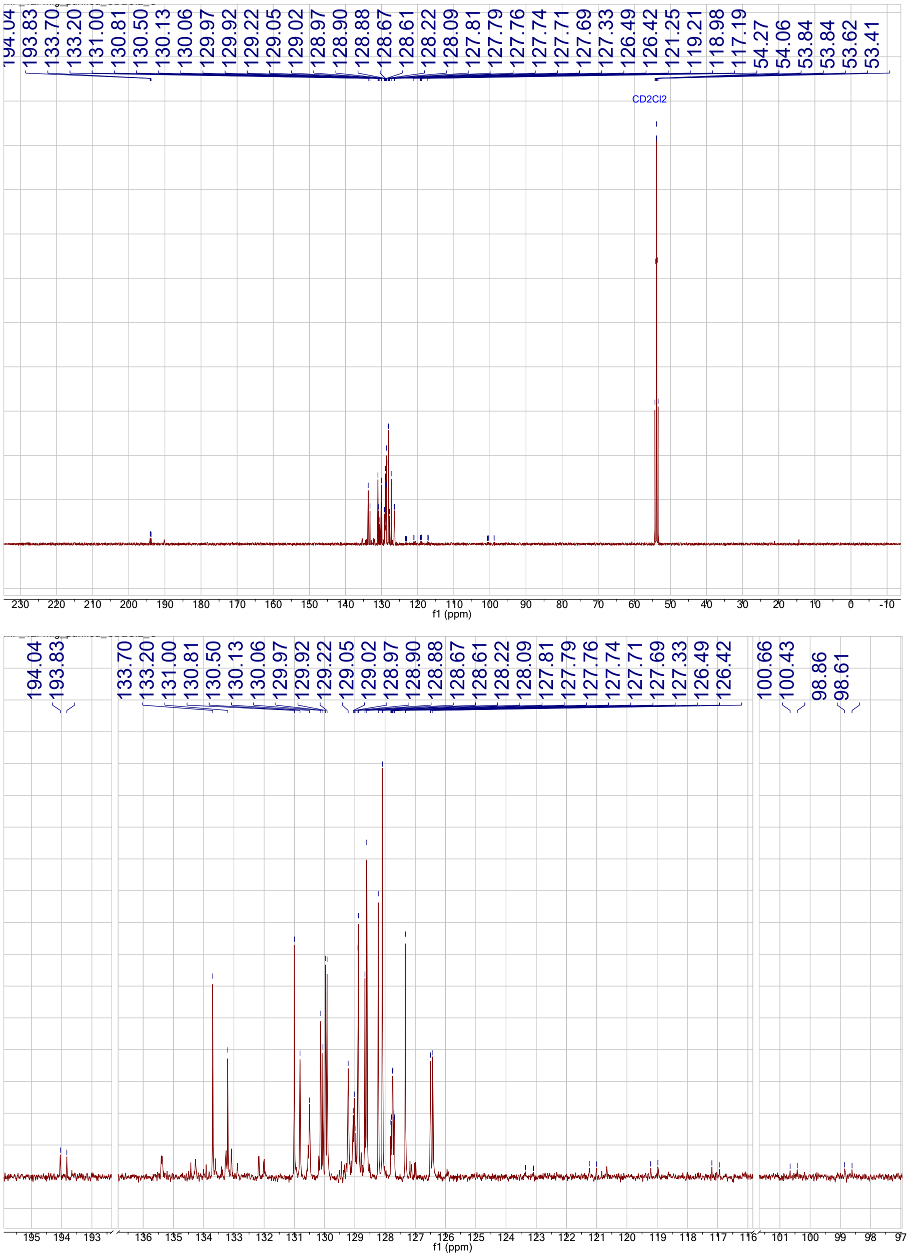


Figure S193. ^{13}C NMR spectra (CD_2Cl_2) of isolated **5e**. Top: full spectra and bottom: zoom-in spectra. Diagnostic peaks including 193.94 (d, $J = 27.0$ Hz, αC), 120.13 (ddd, $J = 285.5$, 260.4, 32.1 Hz, γC), and 99.64 (dd, $J = 227.4$, 30.2 Hz, βC) were shown in the zoom-in figure.

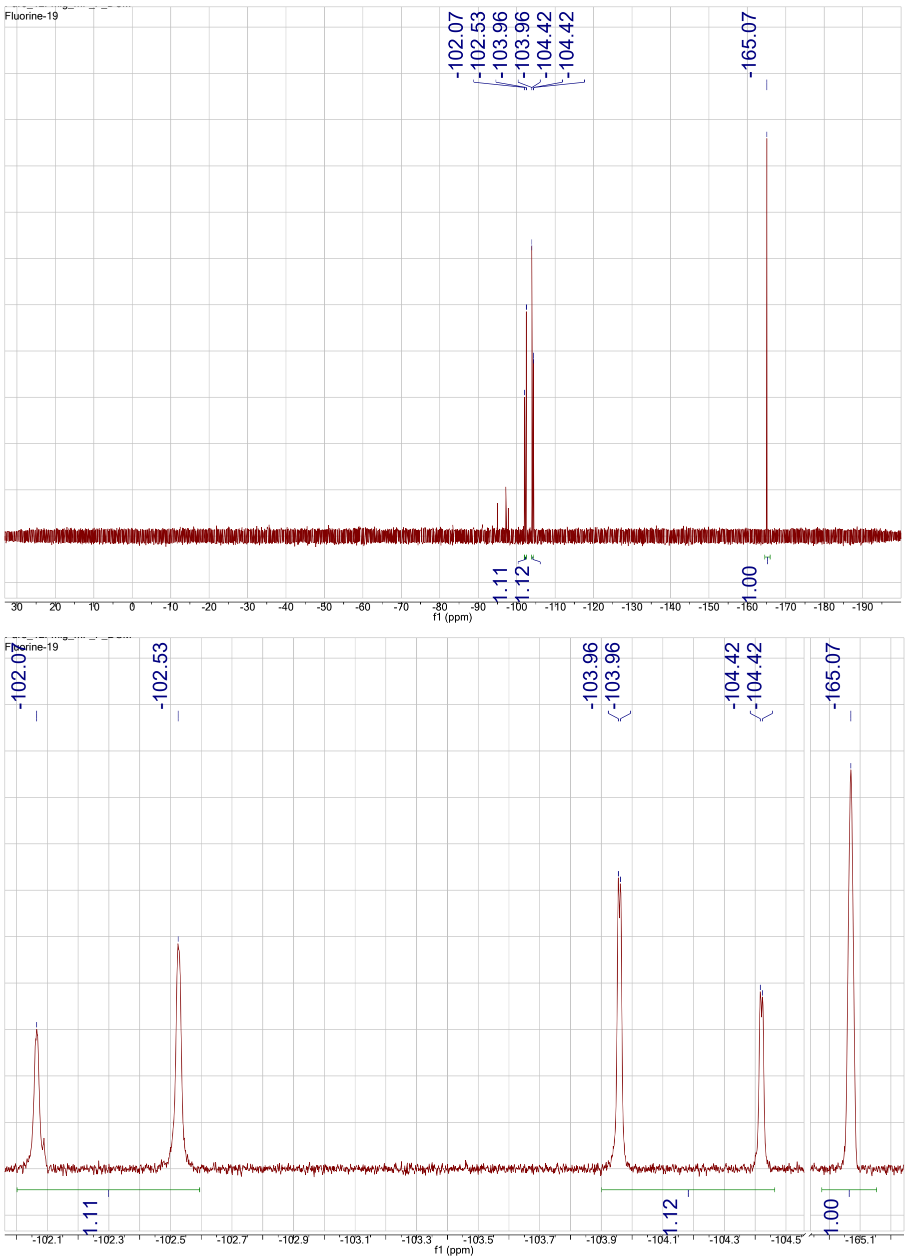


Figure S194. ^{19}F NMR spectra (CD_2Cl_2) of isolated **5e**. Top: full spectra and bottom: zoom-in spectra.

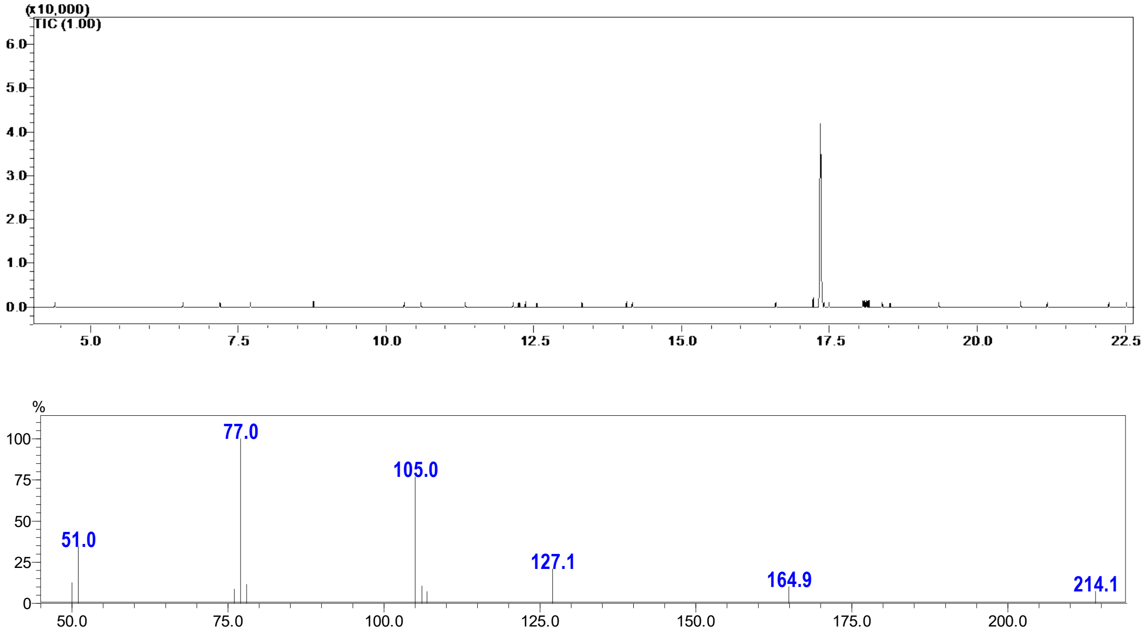
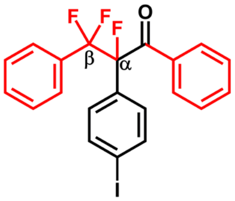


Figure S195. GC-MS spectra of isolated **5e**.



5f: (11%)

^{19}F NMR (564 MHz, 1,2-dichloroethane) δ -105.66 (d, *J* = 259.5 Hz, 1F, βF), -107.48 (d, *J* = 257.8 Hz, 1F, βF), -168.81 (s, 1F, αF).

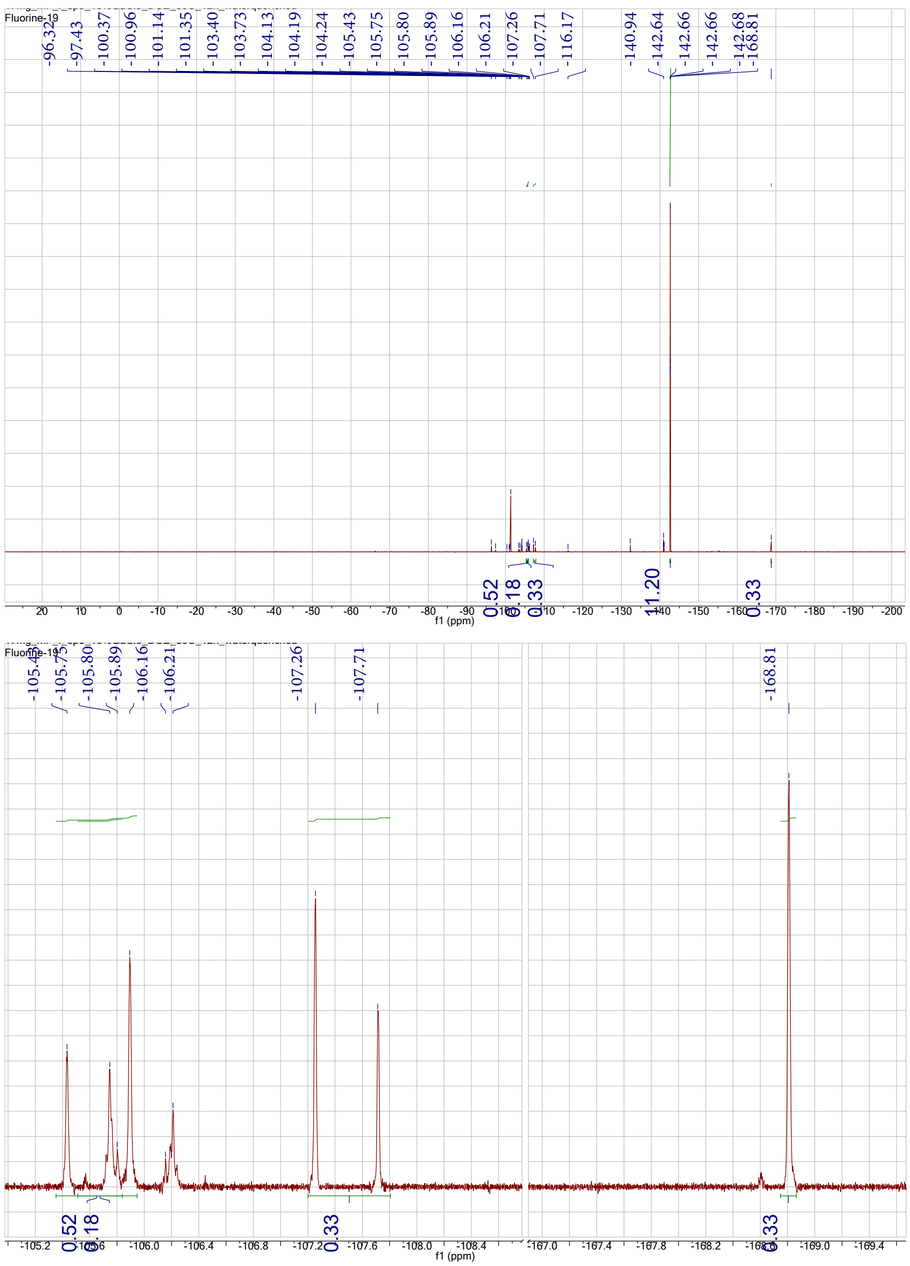


Figure S196. Representative *in situ* ^{19}F NMR spectra (in DCE) of **5f** showing the chemical yield. Top: full spectra and bottom: zoom-in spectra.

Ring Opening Defluorinative Functionalization (6a-6c, 6c' and 7b)

1. Optimization for the synthesis of **6a**

Protocol A (0.01 mmol, for optimization)

The optimization reactions were carried out in 1 mL DCE with a concentration of 0.01 M of purified fluoroepoxides (**2b**). The catalyst was added from a freshly prepared stock solution in DCE. 1.5 equv. Trimethylsilyl azide ($TMSN_3$) was used in all cases.

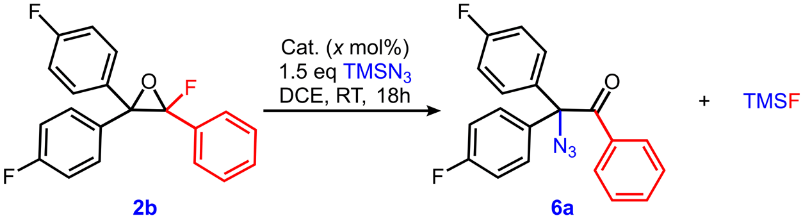


Figure S197. Scheme for the synthesis of **6a**.

Catalyst (mol%)	^{19}F NMR yield of 6a(%)	2b not converted (%)
$FeCl_3$ (2%)	23	70
$FeCl_3$ (5%)	92	9
$FeCl_3$ (10%)	**97**	**3**
$GaCl_3$ (5%)	**Quant.**	**0**

Table S15. Catalyst optimization for the synthesis of **6a**. 5% $GaCl_3$ or 10% $FeCl_3$ is optimal.

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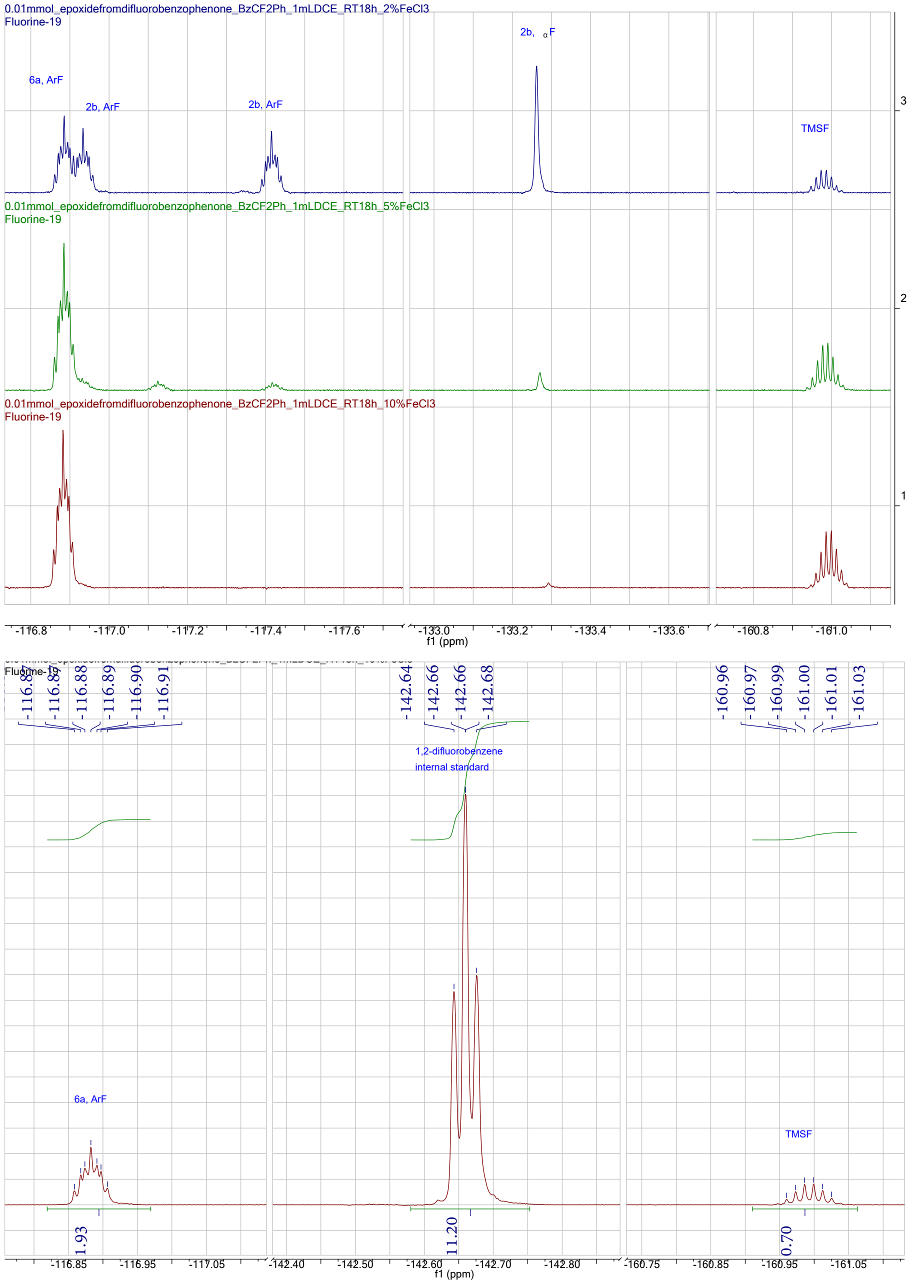

Figure S198. Catalyst loading optimization. Top spectra: bottom to top FeCl$_3$ = 10 mol%, 5 mol%, and 2 mol% respectively. Bottom spectra: zoom-in spectra of 10 mol% FeCl$_3$ loading.

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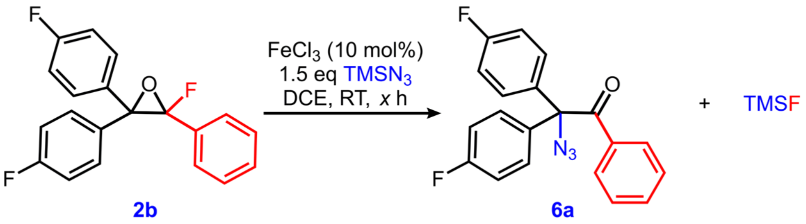

Time	**^{19}F NMR yield of 6a(%)**	**2b not converted (%)**
20 min	0	100
1 h 20 min	22	78
2 h 30 min	38	62
3 h 30 min	53	47
5 h 30 min	63	37
23 h	95	5
27 h	97	3

Table S16. Reaction time optimization for the synthesis of **6a**. 10 mol% FeCl$_3$ was used as the catalyst.

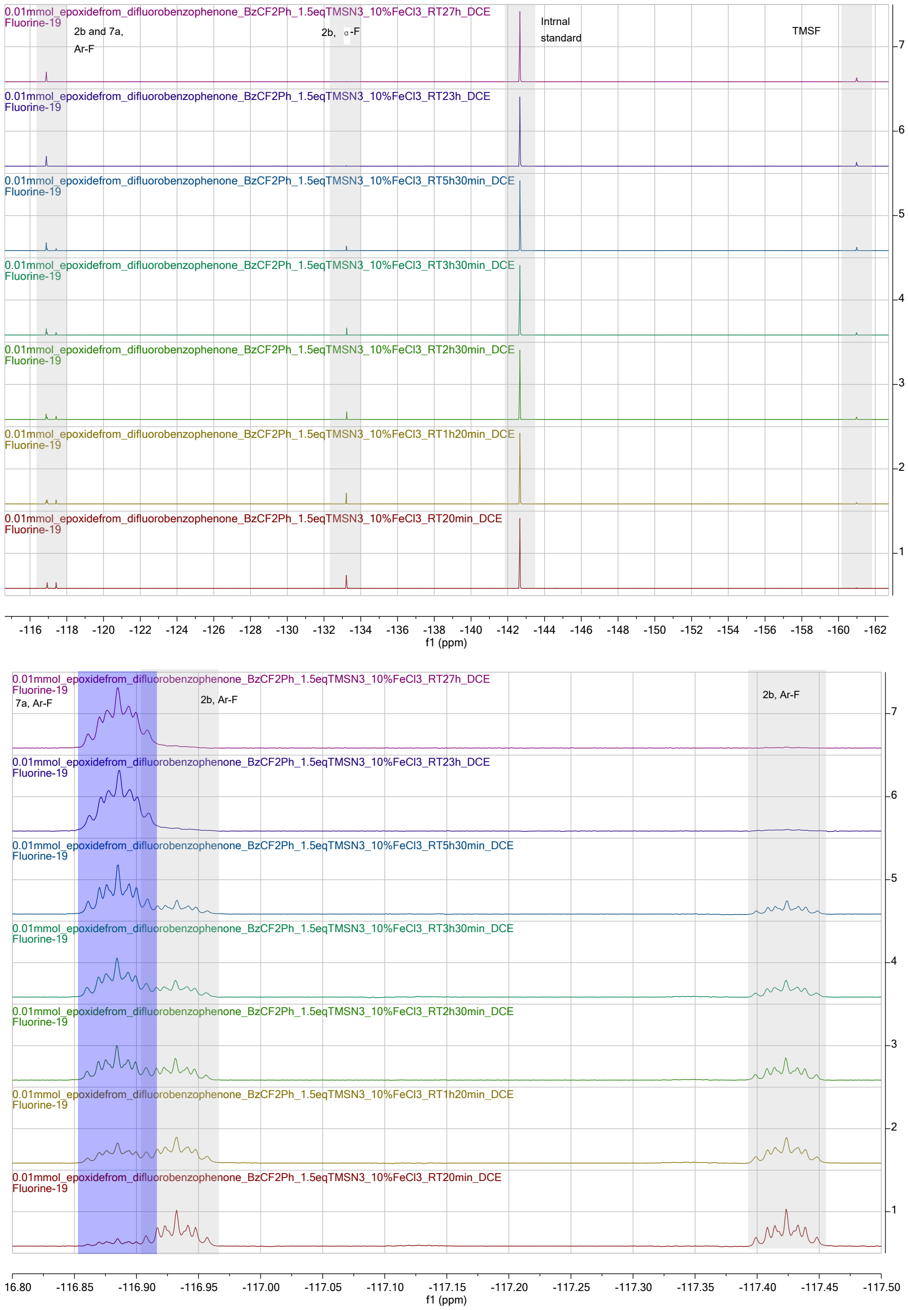

Figure S199. Reaction time optimization (bottom to top = 20 minute, 1 h 20 min, 2 h 30 min, 3 h 30 min, 5 h 30 min, 23 h, and 27 h, respectively). As the reaction proceeded, the 2 asymmetrical Ar-F peaks in the ^{19}F NMR spectra of **2b** were converted to one Ar-F peak in **6a**. The reaction was finished after 23 h.

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2. Optimization for the synthesis of **6b**

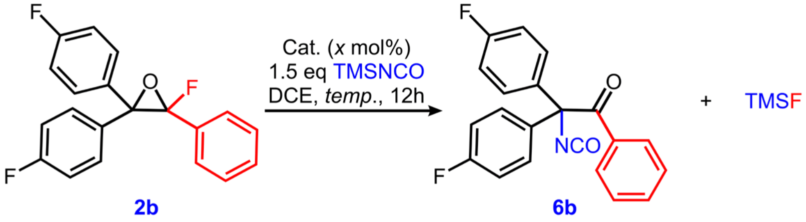

Figure S200. Scheme for the synthesis of **6b**.

Protocol

The optimization reactions were carried out in 1 mL DCE with a concentration of 0.01 M of purified fluoroepoxides (**2b**). The catalyst was added from a freshly prepared stock solution in DCE. 1.5 equv. Trimethylsilyl isocyanate (TMSNCO) was used in all cases.

Catalyst (mol%)	Temperature (°C)	^{19}F NMR yield of 6b(%)
-	80	0
$FeCl_3$ (10%)	20	0
$FeCl_3$ (10%)	80	27
$GaCl_3$ (5%)	**80**	**72**
$GaCl_3$ (10%)	80	53
$GaCl_3$ (20%)	80	26

Table S17. Optimization for the synthesis of **6b**. 5% $GaCl_3$ is optimal.

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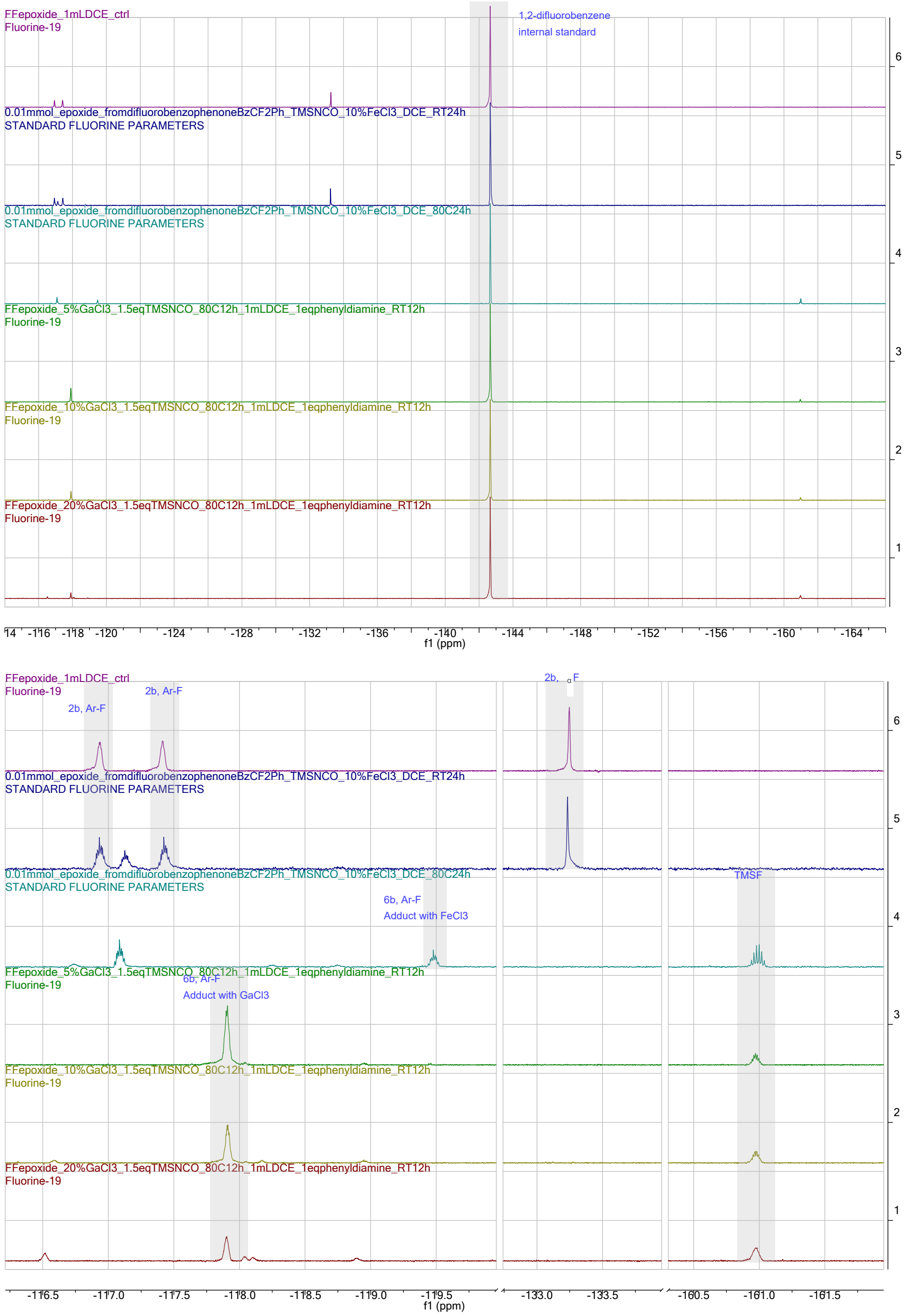

Figure S201. ^{19}F NMR spectra (in DCE) of the optimization results for the synthesis of **6b** (from bottom to top: 80ºC 20 mol% $GaCl_3$, 80ºC 10 mol% $GaCl_3$, 80ºC 5 mol% $GaCl_3$, 80ºC 10 mol% $FeCl_3$, RT 10 mol% $FeCl_3$, respectively). **2b** in DCE heated at 80 ºC without catalyst was used as the control (top row). 80ºC 5 mol% $GaCl_3$ is optimal.

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3. Optimization for the synthesis of **6c**

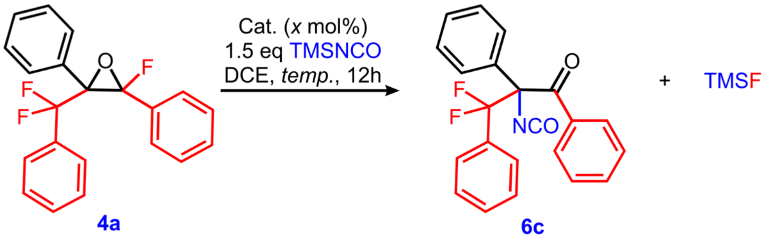

Figure S202. Scheme for the synthesis of **6c**.

Protocol

The optimization reactions were carried out in 1 mL DCE with a concentration of 0.01 M of purified fluoroepoxides (**4a**). The catalyst was added from a freshly prepared stock solution in DCE. 1.5 equv. TMSNCO was used in all cases.

Entry	Catalyst (mol%)	Unconverted Epoxide (%)	5e (%)	6c (%)
1	$FeCl_3$ (5%)	81	7	0
2	$FeCl_3$ (10%)	50	20	12
3	**$FeCl_3$ (20%)**	**0**	**27**	**15**
4	**$GaCl_3$ (10%)**	**0**	**39**	**14**
5	$Sc(OTf)_3$	50	21	0
6	$BF_3 \cdot Et_2O$	75	7	0
7	BCF	100	0	0
8	$AlCl_3$	100	0	0
9	$InCl_3$	81	21	0
10	$Fe(OTf)_3$	100	0	0
11	FeF_3	100	0	0

Table S18. Catalyst optimization for the synthesis of **6c**. 10 mol% $GaCl_3$ or 20 mol% $FeCl_3$ are optimal. Fluoroepoxide (**4a**) conversion, yield of **5e** and **6c** were determined by ^{19}F NMR spectroscopy.

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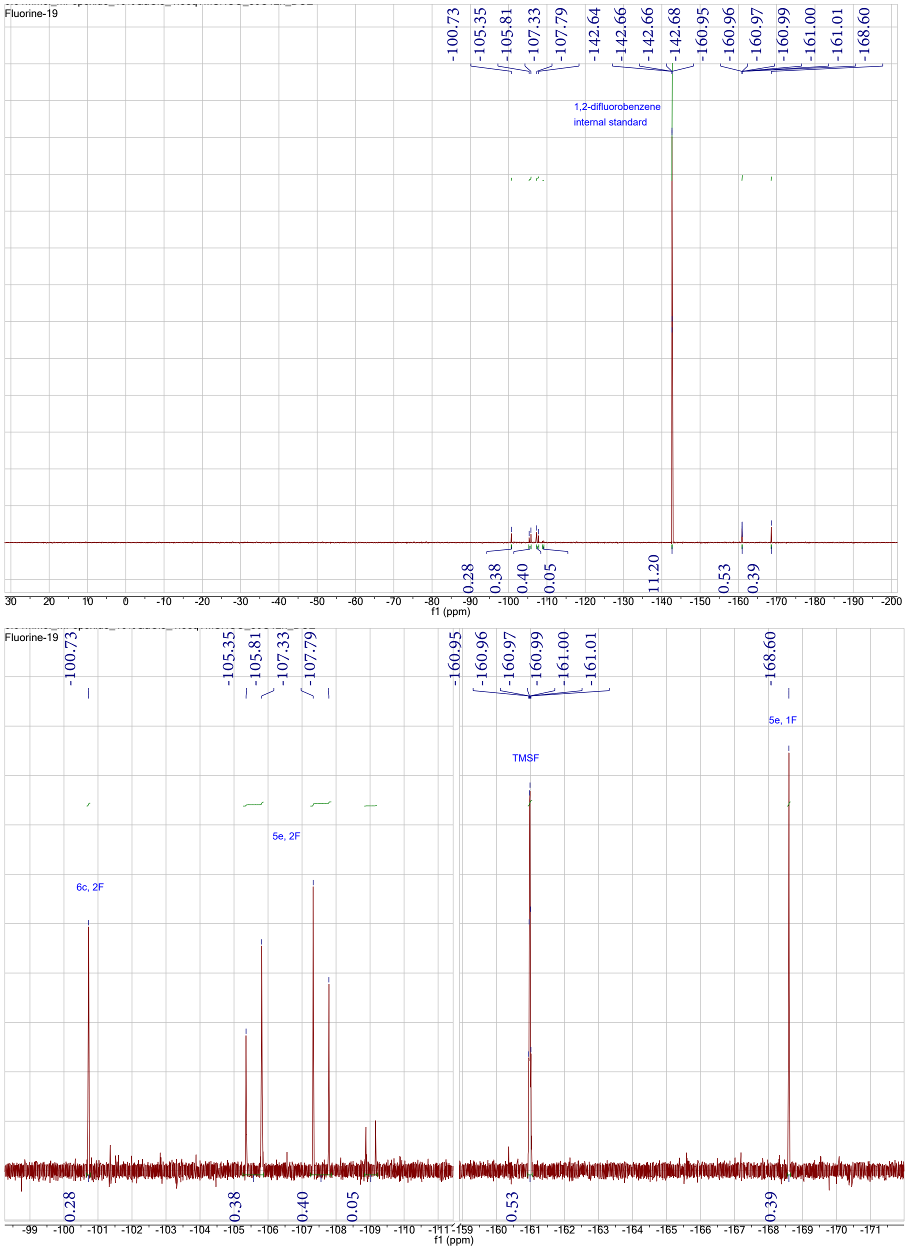


Figure S203. ^{19}F NMR spectra (in DCE) of entry 4. Top: full spectra and bottom: zoom-in spectra.

4. Synthesis and isolation of **6a** and **6c’**

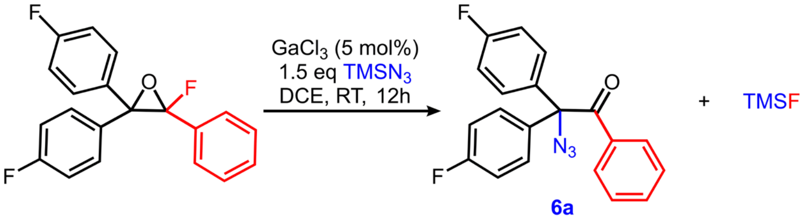


Figure S204. Scheme for the synthesis of **6a**.

Protocol (0.1 mmol, for isolation)

6a: Purified **2b** (0.1 mmol, 33 mg) and $TMSN_3$ (0.15 mmol, 17 mg) were dissolved in DCE in an 8 mL vial with a stir bar under N_2 atmosphere. Then $GaCl_3$ (added from a freshly prepared stock solution in DCE, 5 mol%) was injected to the solution. Total volume was 1 mL. The solution was stirred for 12 h at RT.

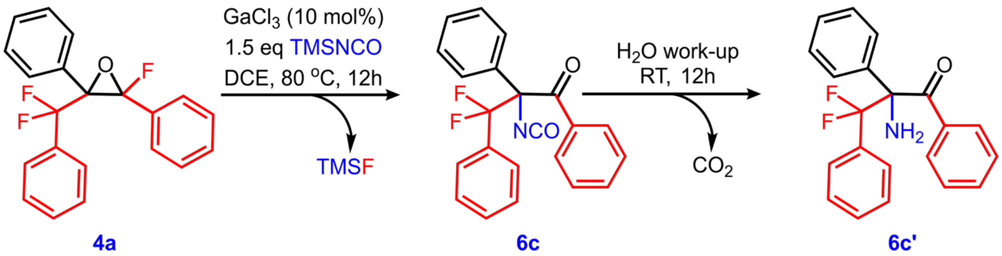


Figure S205. Scheme for the synthesis of **6c'**.

6c': Purified **4a** (0.1 mmol, 34 mg) and TMSNCO (0.15 mmol, 17 mg) were dissolved in DCE in an 8 mL vial with a stir bar under N_2 atmosphere. Then $GaCl_3$ (added from a freshly prepared stock solution in DCE, 10 mol%) was injected to the solution. Total volume was 1 mL. The solution was stirred for 12 h at 80 °C. After the reaction cooled to RT, 500 μL water was added to the solution under ambient atmosphere and the mixture was stirred at RT for 12 h.

6a was purified by preparative TLC using hexanes : EtOAc = 10:1 (v/v) as the developing solvent. The isolated **6a** on silica was washed off with EtOAc. EtOAc was then removed under vacuum affording the purified **6a**.

6c' was purified by preparative TLC using hexanes : EtOAc = 1:1 (v/v) as the developing solvent.

5. Synthesis and isolation of **7b**

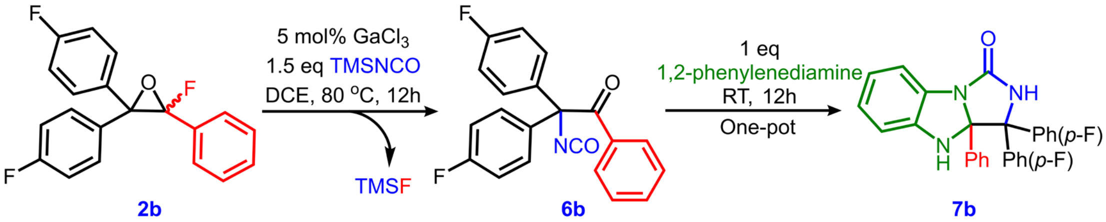


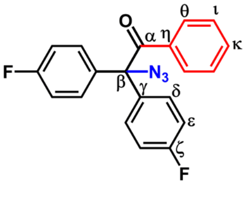
Figure S206. Scheme for the synthesis of **7b**.

Protocol

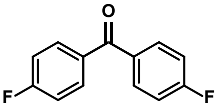
Purified **2b** (0.1 mmol, 33 mg) and TMSNCO (0.15 mmol, 17 mg) were dissolved in DCE in an 8 mL vial with a stir bar under N_2 atmosphere. Then $GaCl_3$ (added from a freshly prepared stock solution in DCE, 5 mol%) was injected to the solution. Total volume was 1 mL. The solution was stirred for 12 h at 80 °C. After the reaction cooled to RT, 1,2-phenylenediamine (0.1 mmol, 11 mg) was added to the solution under ambient atmosphere and the mixture was stirred at RT for 12 h.

7b was purified by preparative TLC using hexanes : EtOAc = 1:1 (v/v) as the developing solvent.

6. Characterization of **6a-6c**, **6c'**, and **7b** (NMR spectra and ESI-MS)



6a: 67% (quant.)



ketone starting material impurity

Colorless oil (0.1 mmol scale, 23.4 mg, 67% isolated, 95% purity). ^{19}F NMR (564 MHz, CD_2Cl_2) δ -113.55 – -113.48 (m, 2F). ^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.81 (d, *J* = 7.6 Hz, 2H, θH), 7.50 (t, *J* = 7.4 Hz, 1H, κH), 7.39 – 7.31 (m, 6H, 4δH (*m*) + 2ιH (*t*)), 7.12 (t, *J* = 8.7 Hz, 4H, εH). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 197.00 (s, αC), 163.05 (d, *J* = 248.5 Hz, ζC), 135.76 (s, ηC), 135.04 (d, *J* = 3.3 Hz, γC), 133.33 (s, κC), 130.63 (d, *J* = 8.4 Hz, δC), 130.55 (s, θC), 128.55 (s, ιC), 116.01 (d, *J* = 21.7 Hz, εC), 79.59 (s, βC). HR-MS (ESI), m/z = 307.1027 (calculated for $[M\text{-}N_3]^+$ = $[C_{20}H_{13}F_2O]^+$ = 307.0929), 279.0974 (calculated for $[M\text{- }N_3\text{-}CO]^+$ = $[C_{19}H_{13}F_2]^+$ = 279.0980). IR: 2105 cm^{-1} ($-N_3$), 1685 cm^{-1} (-C=O). The IR results and MS fragmentation pattern were consistent with a similar compound reported in the literature.[21]

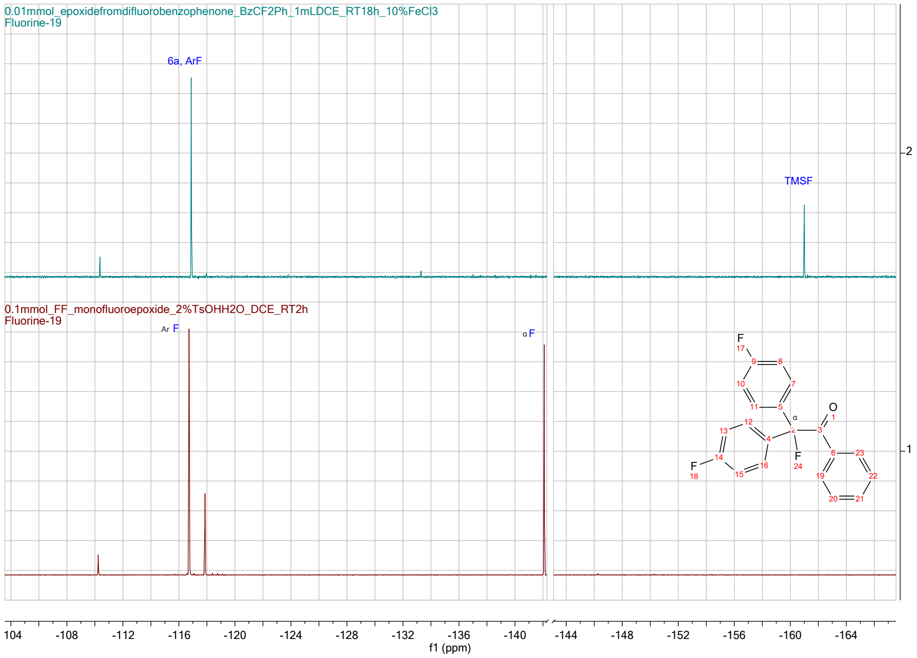


Figure S207. Representative *in situ* ^{19}F NMR spectra (in DCE) comparing the reaction profiles of 1,2-F migration (affording α-fluoroketone, structure shown in the bottom panel) and ring opening defluorinative functionalization (affording **6a**) from **2b**. Top panel: synthesis of **6a** (0.01 mmol scale; 1 mL 0.01 M **2b**, 1.5 equv. $TMSN_3$, 10 mol% $FeCl_3$, DCE, RT, 12 h). Bottom panel: 1,2-F migration reaction (0.1 mmol scale; 1 mL 0.1 M **2b**, 2 mol% TsOH, DCE, RT, 2 h).

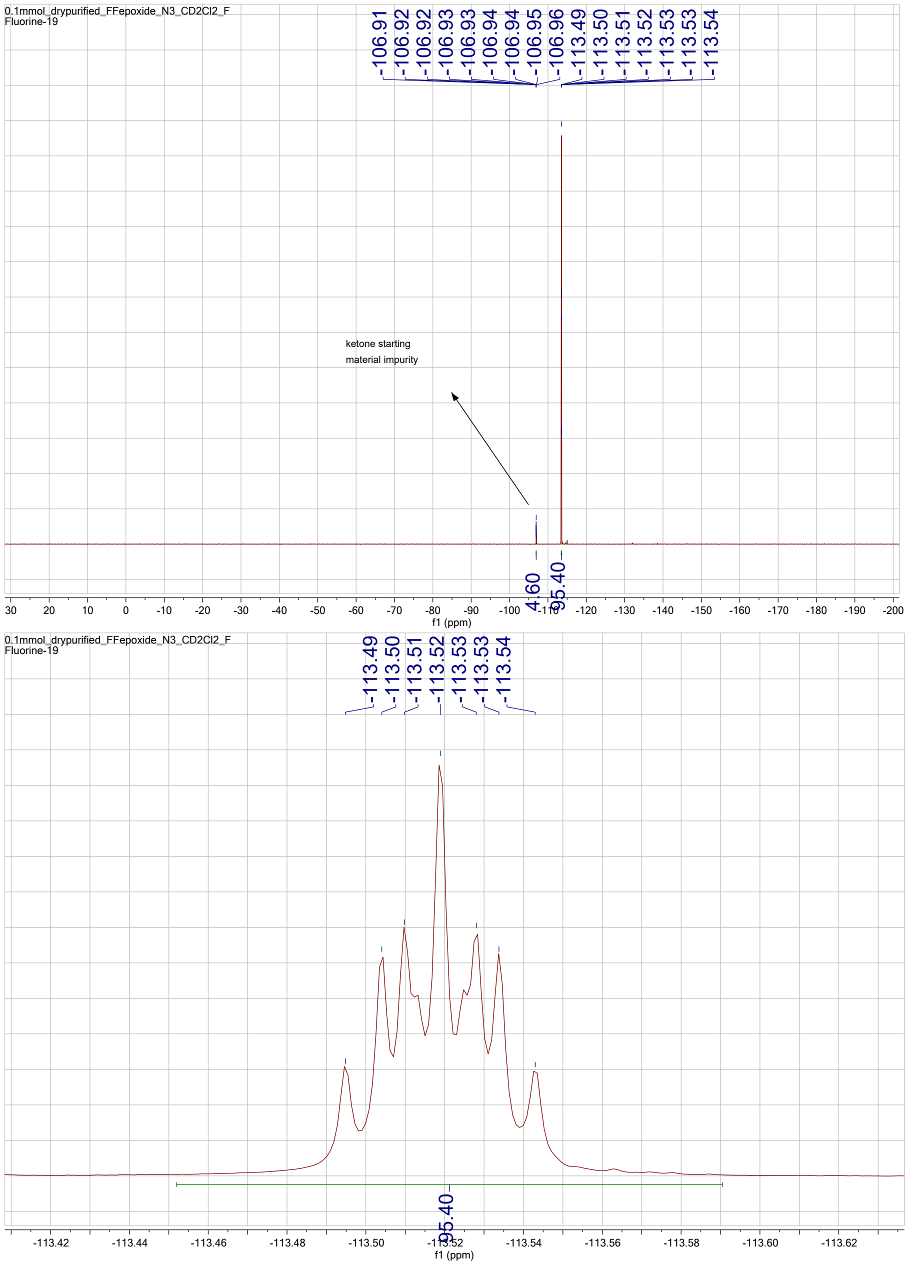


Figure S208. ^{19}F NMR spectra (CD_2Cl_2) of isolated **6a**. Top: full spectra and bottom: zoom-in spectra. 5% ketone starting material impurity was found in the purified sample.

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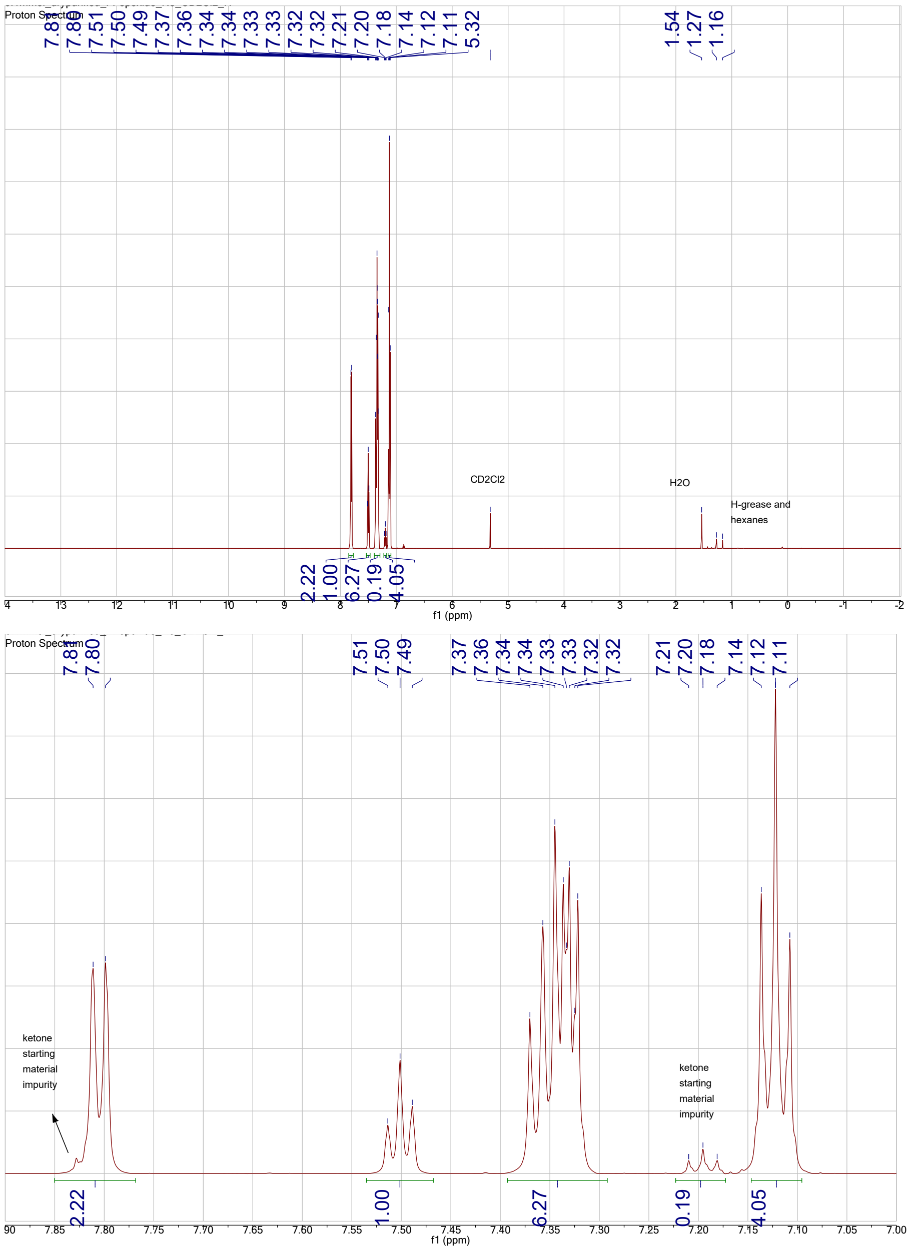

Figure S209. ^{1}H NMR spectra (CD_2Cl_2) of isolated **6a**. Top: full spectra and bottom: zoom-in spectra. The ketone starting material impurity was quantified by ^{1}H NMR spectroscopy, 0.19/4/1 * 100% = 5%, in agreement with that calculated from the ^{19}F NMR spectroscopy (5%).

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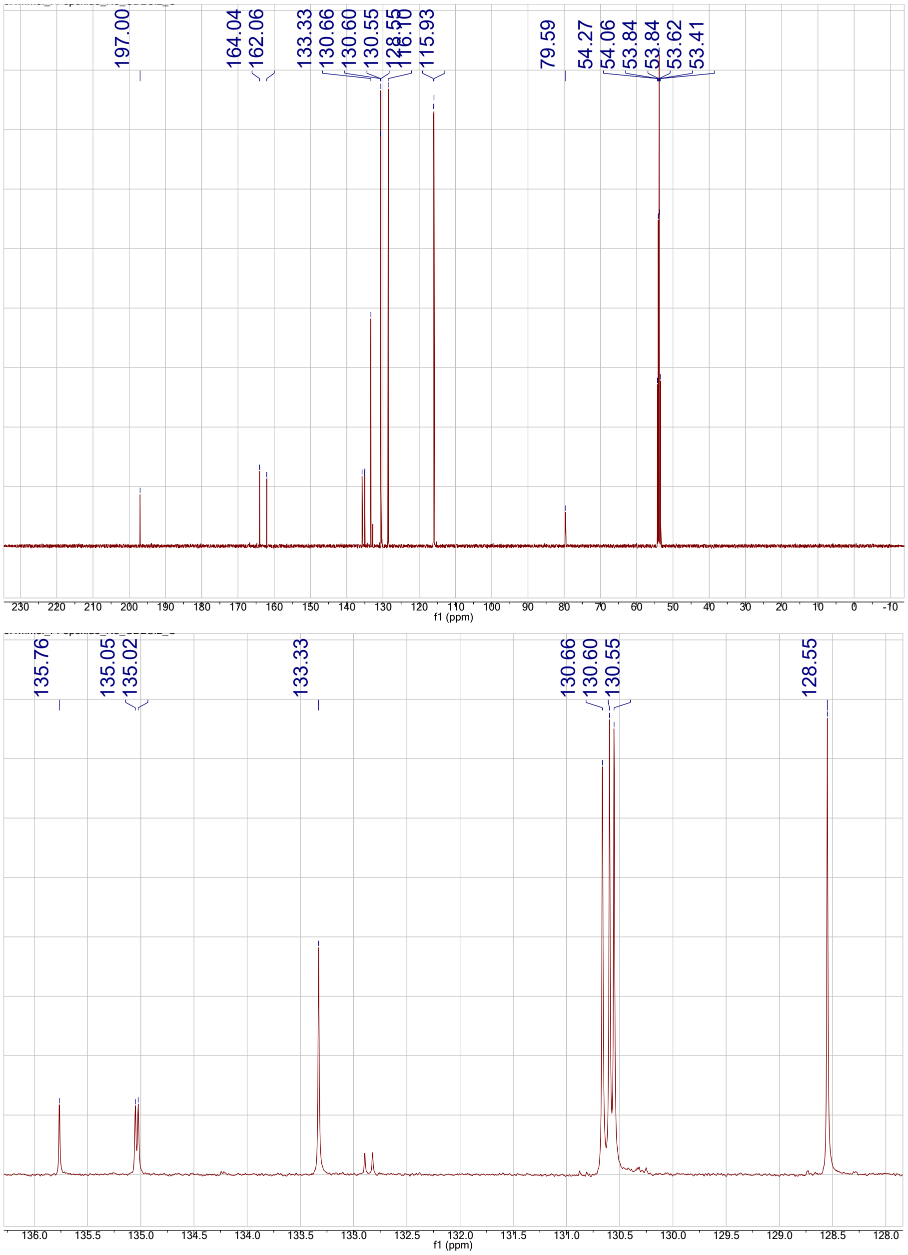

Figure S210. ^{13}C NMR spectra (CD_2Cl_2) of isolated **6a**. Top: full spectra and bottom: zoom-in spectra.

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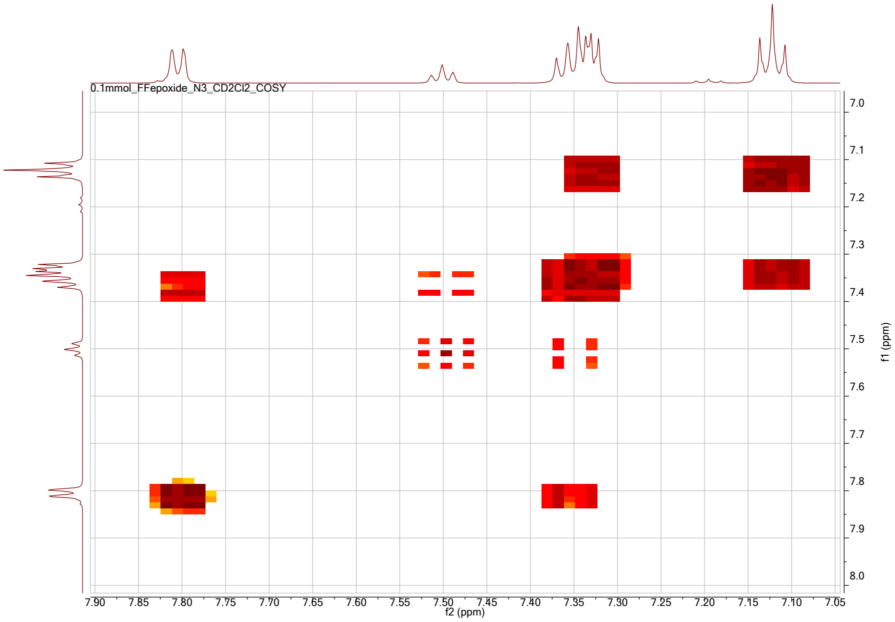

Figure S211. ^{1}H-^{1}H COSY spectra (CD_2Cl_2) of isolated **6a**.

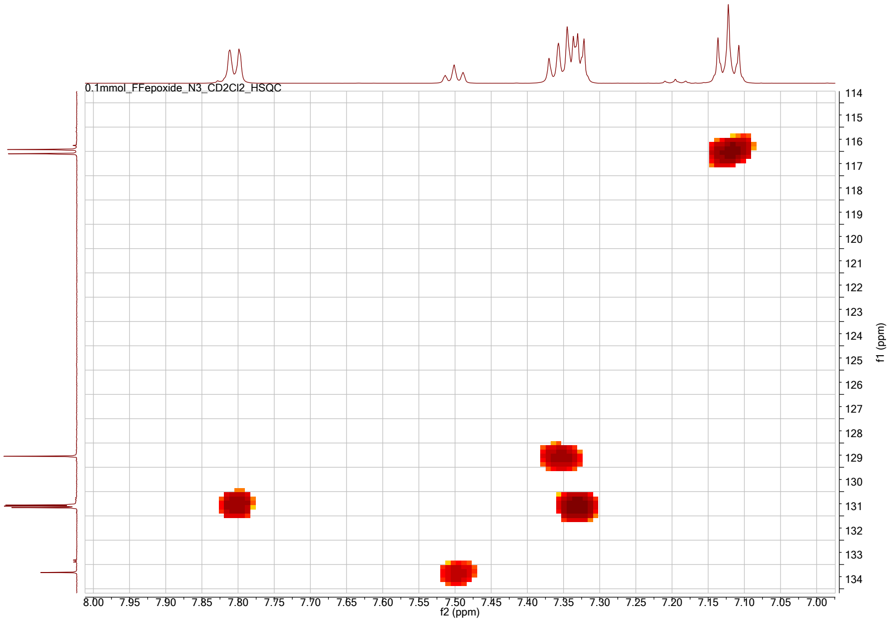

Figure S212. ^{1}H-^{13}C HSQC spectra (CD_2Cl_2) of isolated **6a**.

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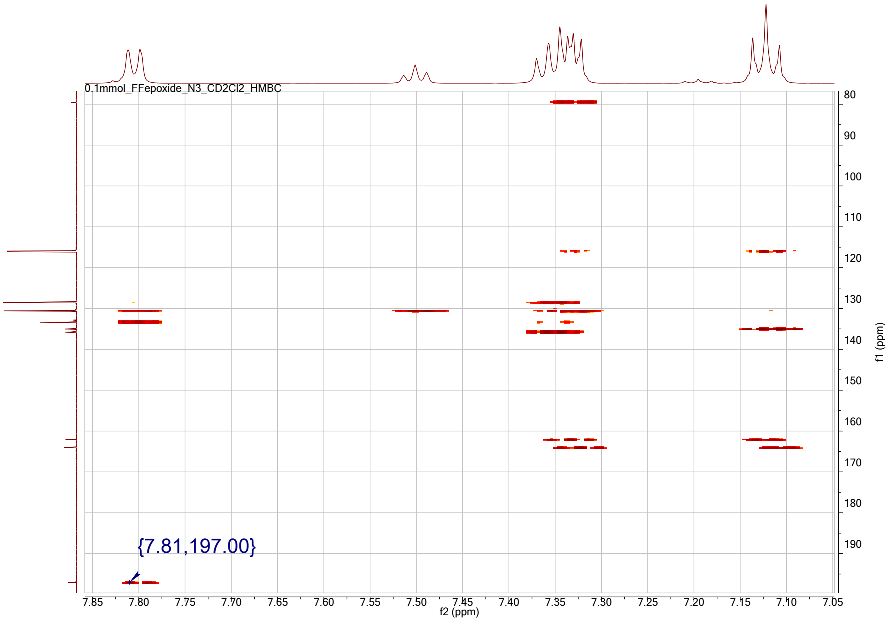

Figure S213. ^{1}H-^{13}C HMBC spectra (CD_2Cl_2) of isolated **6a**.

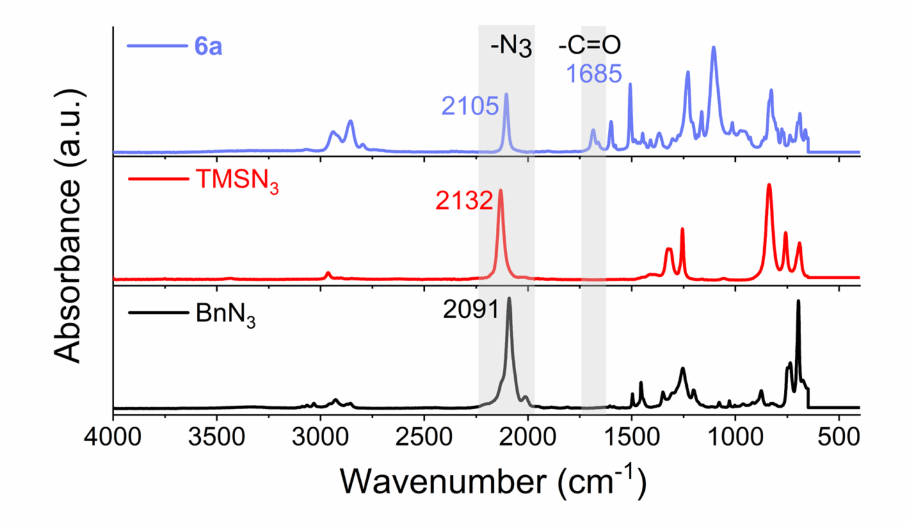

Figure S214. IR spectra of isolated **6a** (top row). $TMSN_3$ (middle row) and benzyl azide (BnN_3, bottom row) were used for comparison.

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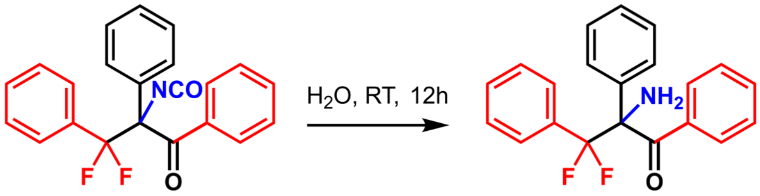

6c **6c'**

Due to the water sensitivity of **6c**, the hydrolyzed **6c'** were isolated and characterized with ^{19}F NMR spectroscopy and LC-MS.

6c': ^{19}F NMR (564 MHz, CD_2Cl_2) δ -97.27 (s, 2F). HR-MS (ESI): calcd. for $[M + H]^+$ ($C_{21}H_{18}F_2NO^+$) = 338.1356, found: 338.1350.

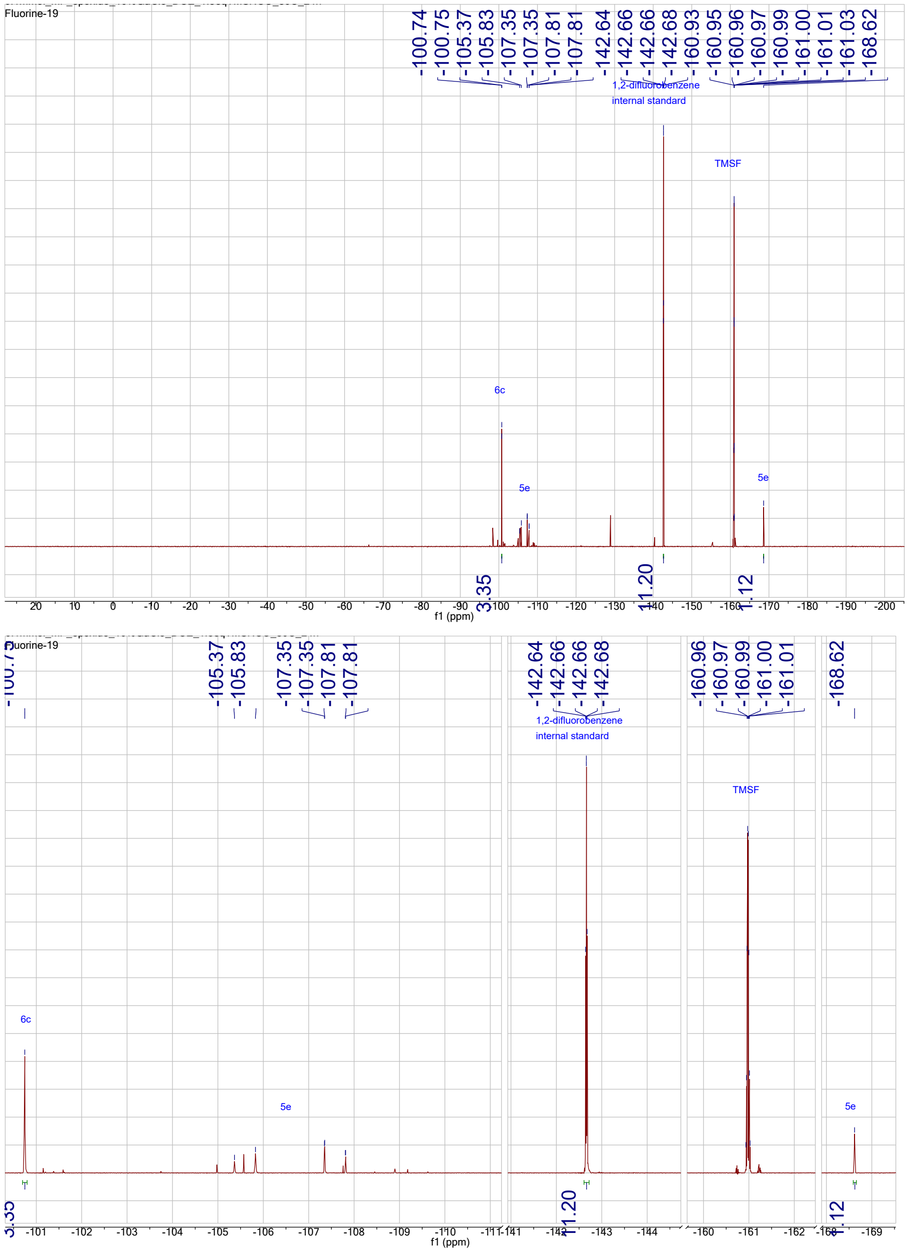

Figure S215. Representative *in situ* ^{19}F NMR spectra (in DCE) of **6c**. Top: full spectra and bottom: zoom-in spectra. ^{19}F NMR (564 MHz, DCE) δ -100.75 (s, 2F).

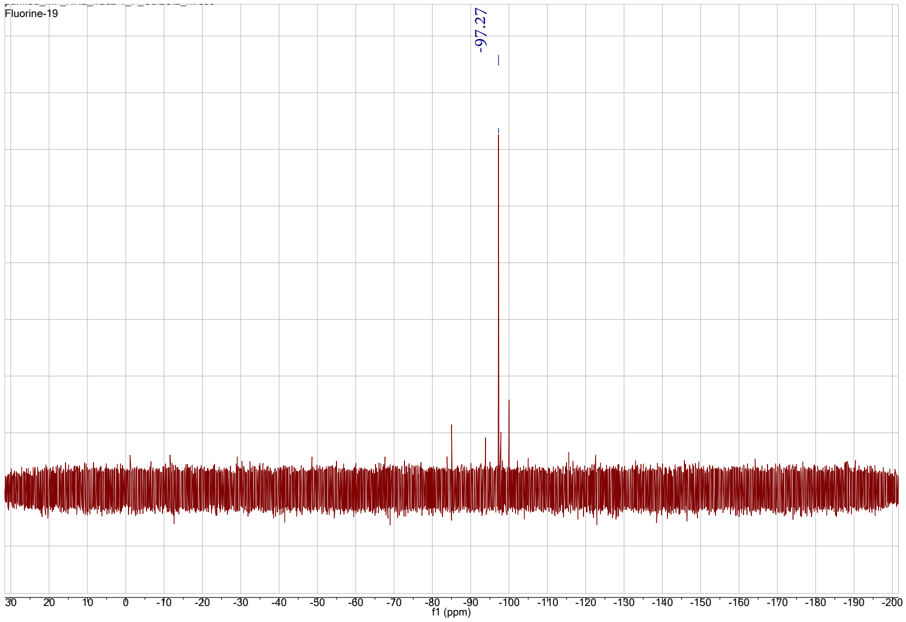

Figure S216. ^{19}F NMR spectra (in CD_2Cl_2) of the isolated **6c'**.

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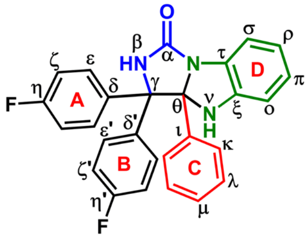

7b: 50% (62%)
[from **6b**]

Yellow solids (0.1 mmol, 22 mg isolated, 56% purity). ^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.52 – 7.47 (m, 2H, A or B ring), 7.27 – 7.22 (m, 2H, 2κH), 7.21 (s, broad, 1H, βH), 7.14 – 6.95 (m, 10H, 2H D ring + 2H A ring + 2H B ring + 2λH + 1μH + 1νH), 6.80 (t, *J* = 8.7 Hz, 2H, A or B ring), 6.70 (dd, *J* = 8.0, 1.2 Hz, 1H, σH), 6.57 (td, *J* = 8.0, 1.3 Hz, 1H, ρH). ^{19}F NMR (564 MHz, CD_2Cl_2) δ -115.03 – -115.10 (m, 1F, ηF or η'F), -115.57 – -115.63 (m, 1F, ηF or η'F). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 162.42 (d, *J* = 247.3 Hz, ηC or η'C), 162.26 (d, *J* = 247.2 Hz, ηC or η'C), 159.72 (s, αC), 144.77 (s), 137.40 (d, *J* = 3.0 Hz, δC or δ'C), 136.34 (d, *J* = 2.5 Hz, δC or δ'C), 130.26 (d, *J* = 8.0 Hz, εC or ε'C), 129.76 (d, *J* = 8.2 Hz, εC or ε'C), 129.03 (s), 128.97 (s), 128.82 (s, κC), 128.64 (s), 127.61 (s), 123.86 (s), 119.96 (s), 118.68 (s, πC), 115.37 (d, *J* = 21.4 Hz, ζC or ζ'C), 114.93 (d, *J* = 21.5 Hz, ζC or ζ'C), 97.79 (s, θC), 74.40 (s, γC). HR-MS (ESI): $[M + H]^+$ calcd. for $[C_{27}H_{20}F_2N_3O]^+$: 440.1569 Found: 440.1547.

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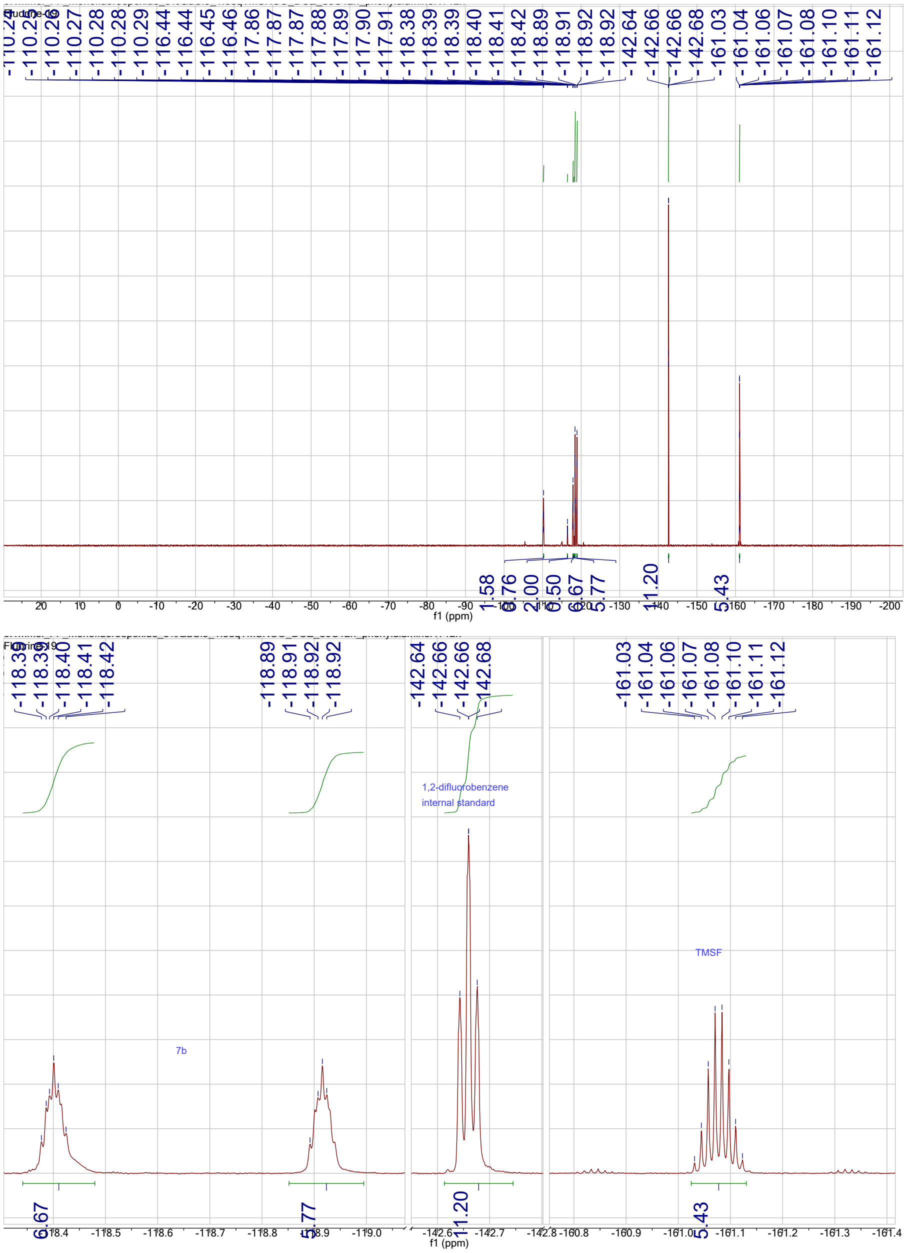

Figure S217. Representative *in situ* ^{19}F NMR spectra (in DCE) of **7b**. Top: full spectra and bottom: zoom-in spectra.

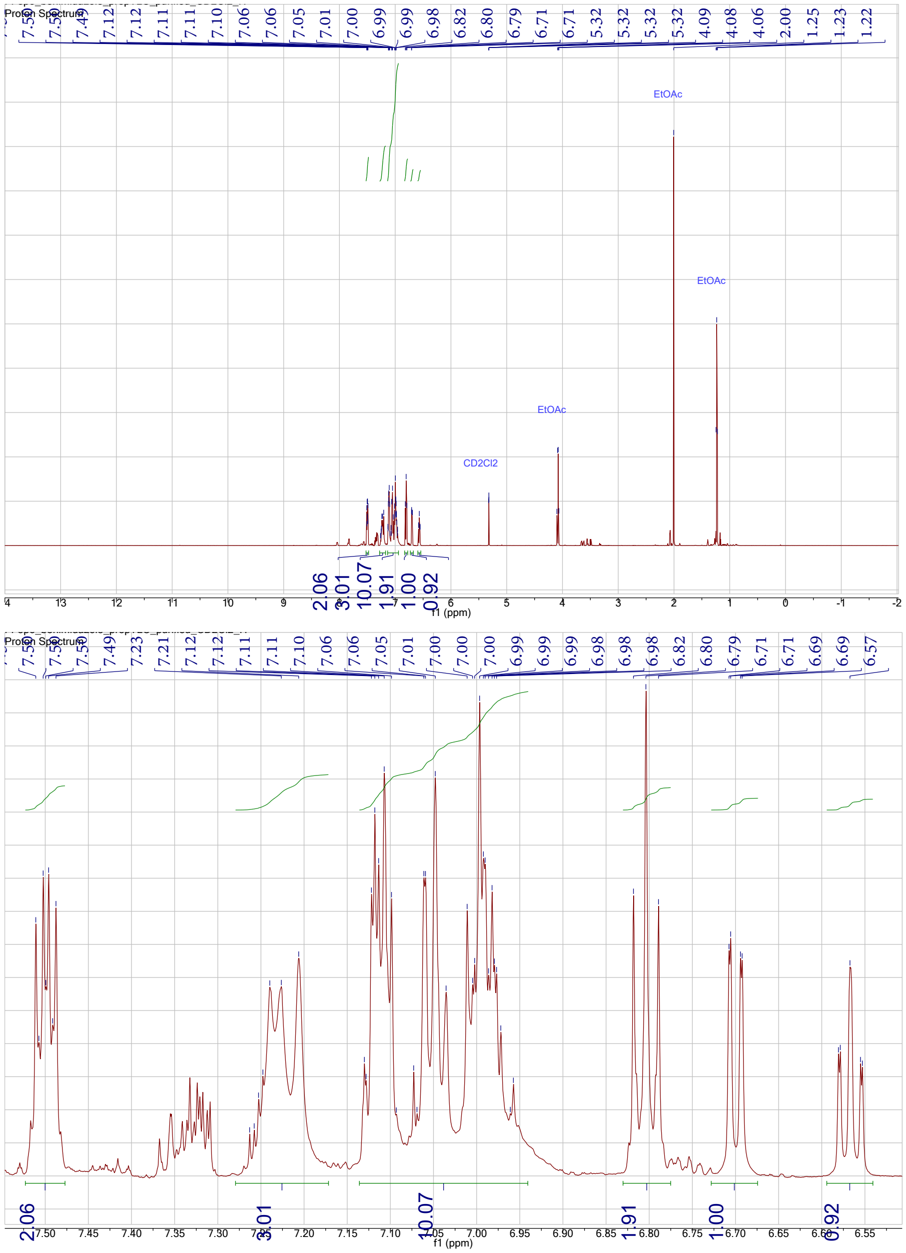

Figure S218. ^{1}H NMR spectra (CD_2Cl_2) of isolated **7b**. Top: full spectra and bottom: zoom-in spectra.

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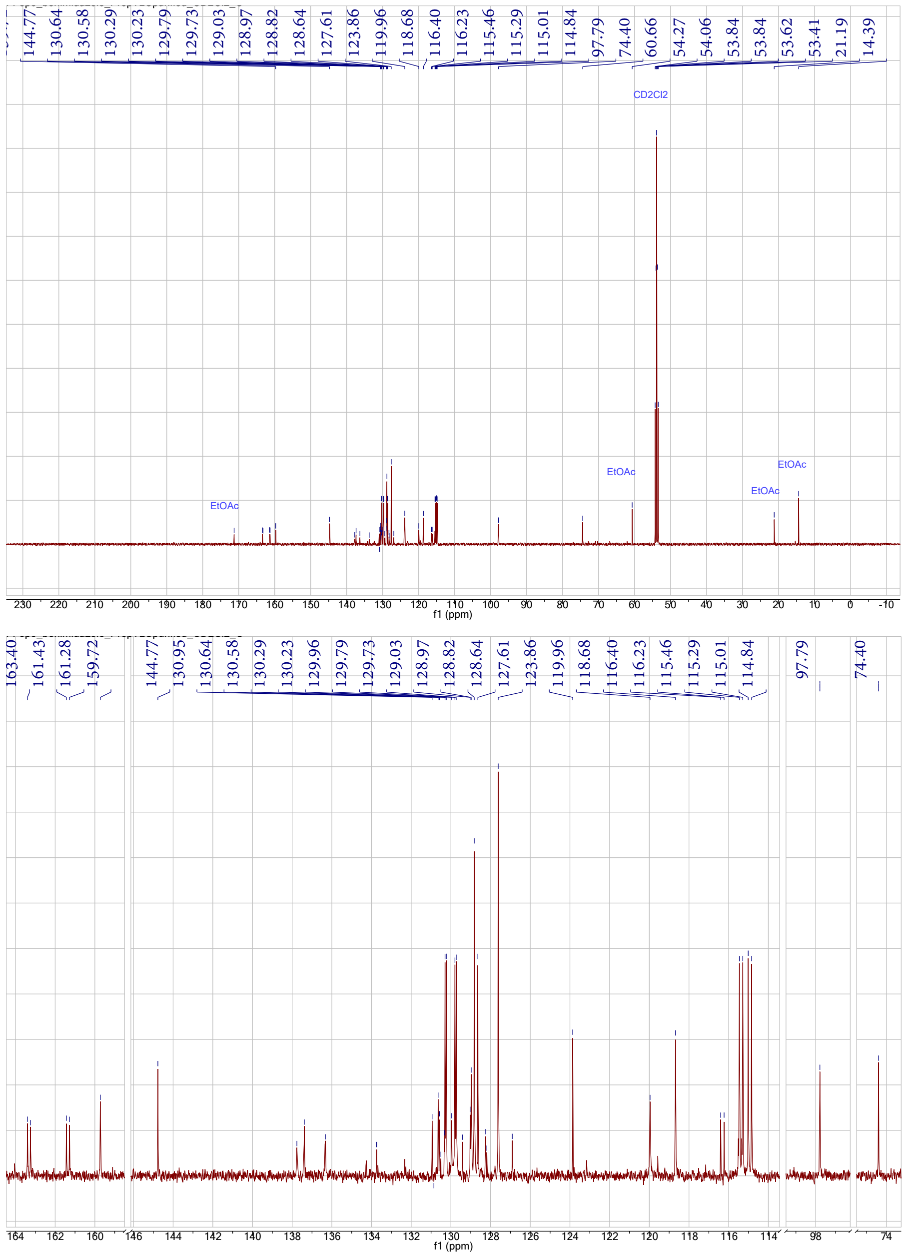


Figure S219. ^{13}C NMR spectra (CD_2Cl_2) of isolated **7b**. Top: full spectra and bottom: zoom-in spectra.

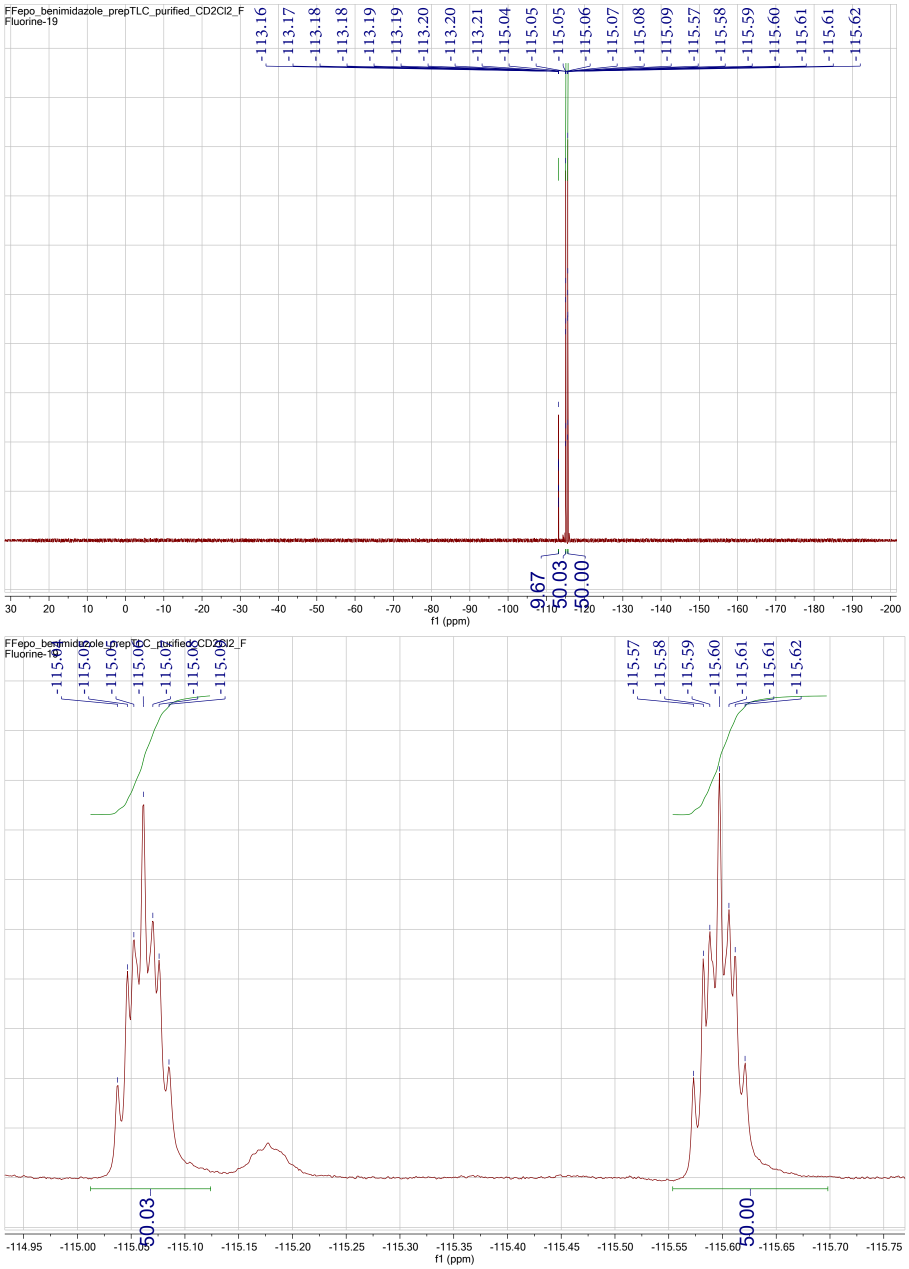


Figure S220. ^{19}F NMR spectra (CD_2Cl_2) of isolated **7b**. 9% unknown impurity was found.

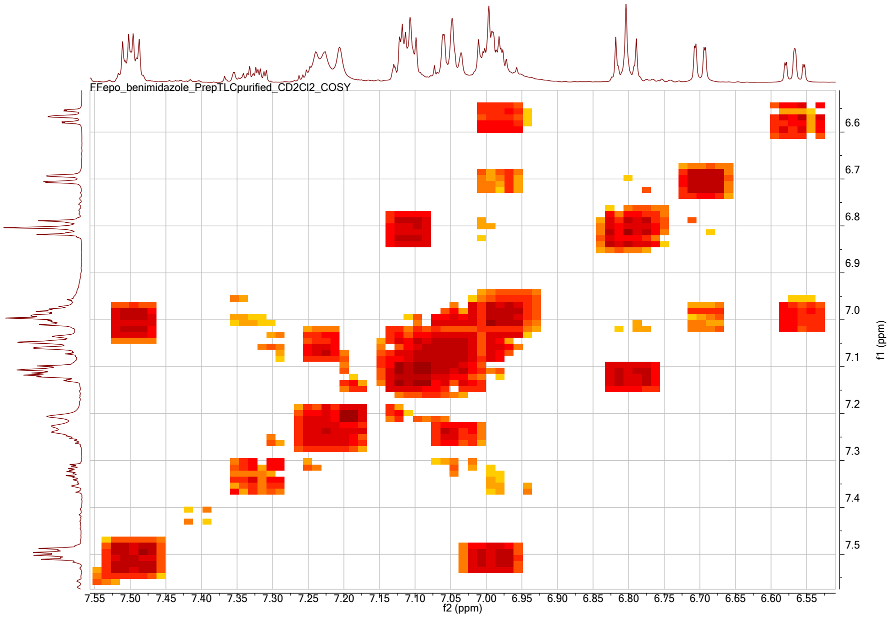


Figure S221. ^{1}H-^{1}H COSY spectra (CD_2Cl_2) of isolated **7b**.

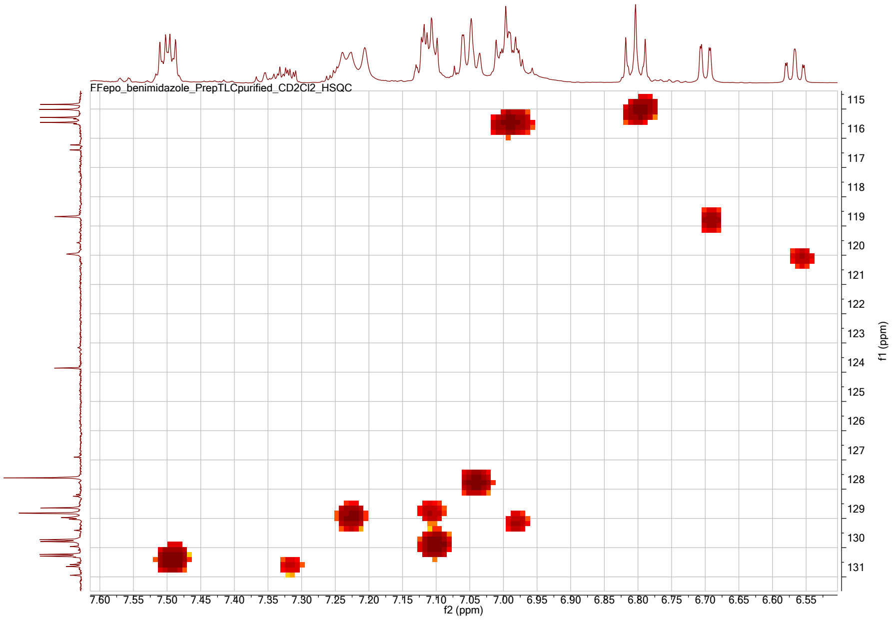


Figure S222. ^{1}H-^{13}C HSQC spectra (CD_2Cl_2) of isolated **7b**.

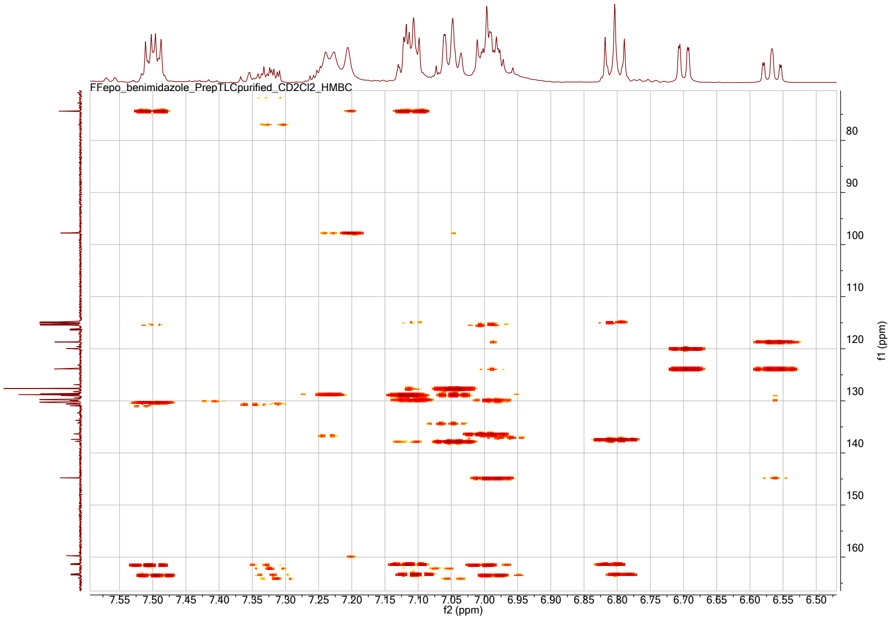


Figure S223. ^{1}H-^{13}C HMBC spectra (CD_2Cl_2) of isolated **7b**.

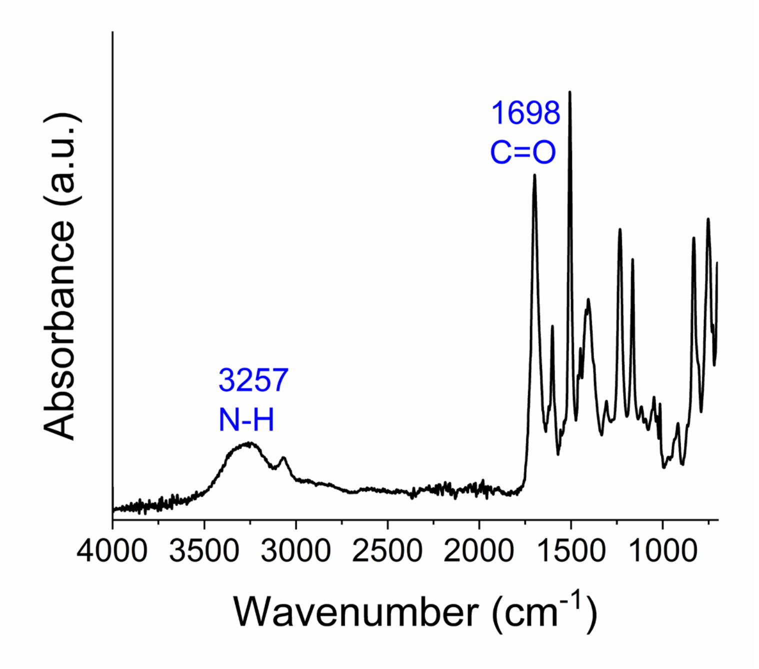
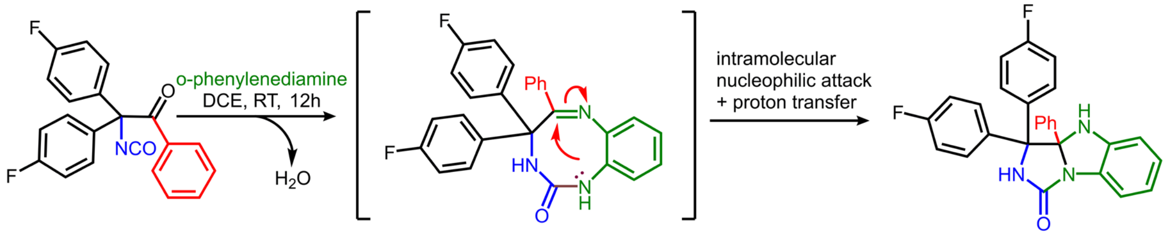


Figure S224. IR spectra of isolated **7b**.



6b

7b

Figure S225. Plausible mechanism for the formation of **7b**.

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Purity Information

General protocol: the purity of most isolated compounds were quantified by ^{19}F NMR spectroscopy using 1,2-difluorobenzene as the internal standard. Unless otherwise noted, 6 μL (6.4 mg, 0.056 mmol) 1,2-difluorobenze were added to ~0.01 mmol of samples (assuming 100% purity; generally corresponding to 100 μL of a 0.1 M stock solution) and mixed with 900 μL solvent and ^{19}F NMR spectra were collected. Purity (%) of each compound was calculated by the following equation after analyzing the integration values of the standard: sample. 6.4 mg internal standard (0.056 mmol 1,2-difluorobenzene, i.e. 0.112 mmol F) was used. Thus, when the integration of the internal standard was normalized to 11.2, the absolute amount (mmol) of the tested sample is (integration of the sample signal)/(number of F for the corresponding integration).

Compound	Purity (%)
1-CF$_2$Ph	93
1-CF$_2$H	>99
2a	>99
2b	91
2c	95
2d	91
2e	85
2f	81
2g	>99
2h	>99
2i	>99
2j	>99
3a	46
4a	83
4b	33
4c	98
4d	>99
4e	89
5a	96
5b	81
5c	75
5e	46
6a	95
7b	56

Table S19. Purity of the synthesized compounds in this work determined by ^{19}F NMR spectroscopy (except **2e**, **3a**, and **7b** which used ^{1}H NMR spectroscopy). All purity numbers measured above 100% were given as > 99%.

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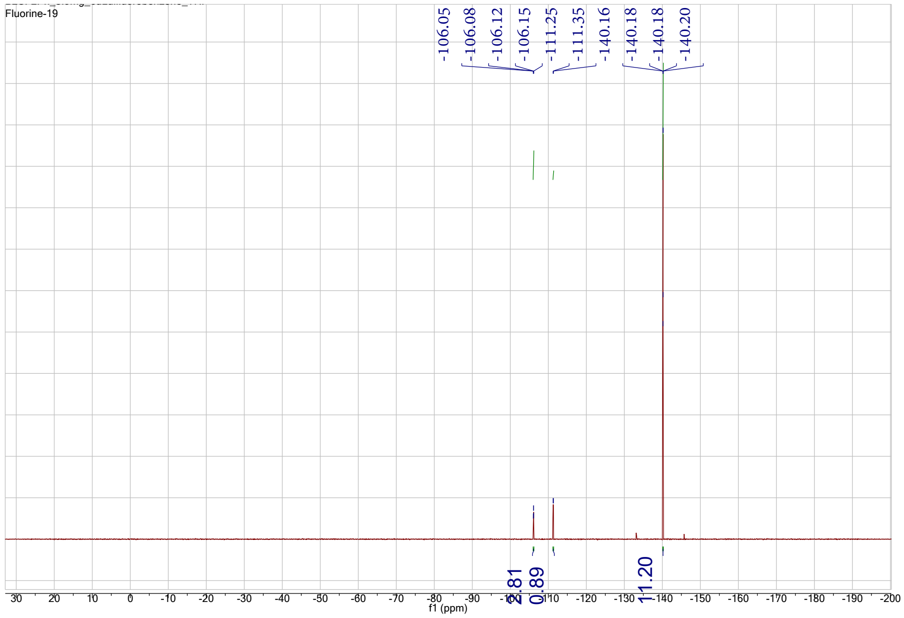

Figure S226. ^{19}F NMR spectra showing the purity of **1-CF$_2$Ph**. 9 mg (0.015 mmol in theory) of sample was used. Measured: 0.014 mmol. Purity = 0.014/0.015 = 93%.

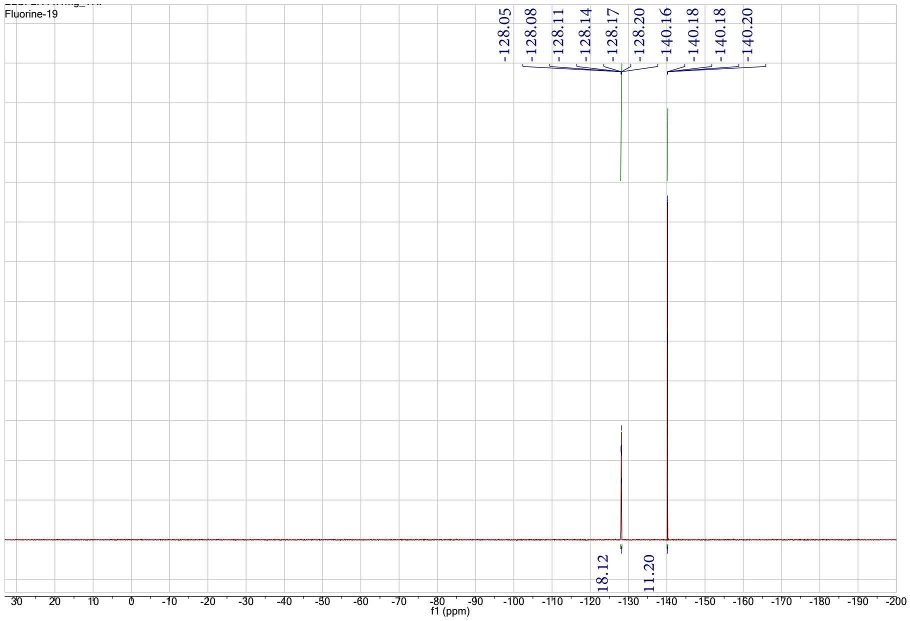

Figure S227. ^{19}F NMR spectra showing the purity of **1-CF$_2$H** (44.1 mg of the sample used). Theoretical 44.1 mg/519.1 g/mol = 0.085 mmol. Observed: 18.12/2/100=0.091 mmol.

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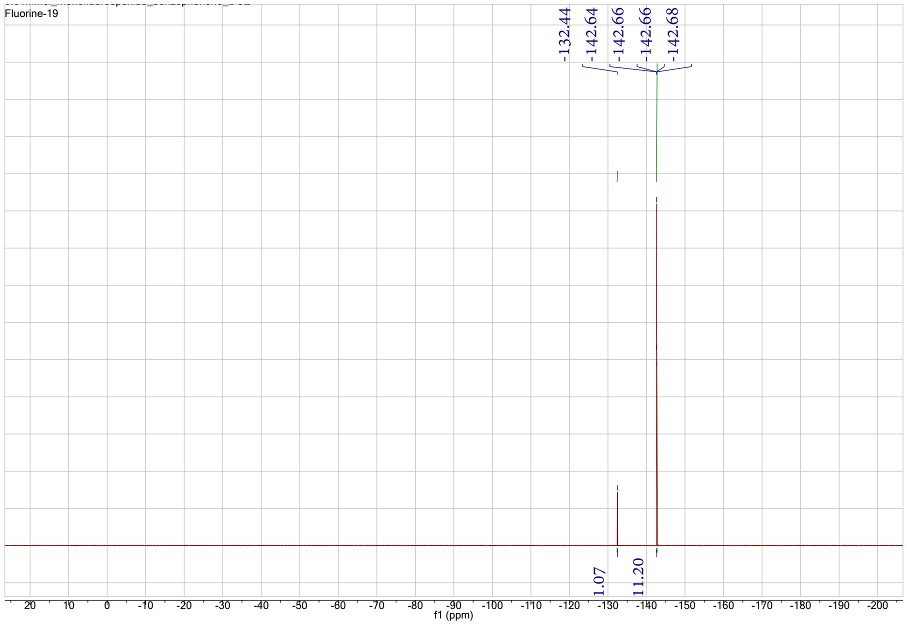

Figure S228. ^{19}F NMR spectra showing the purity of **2a**.

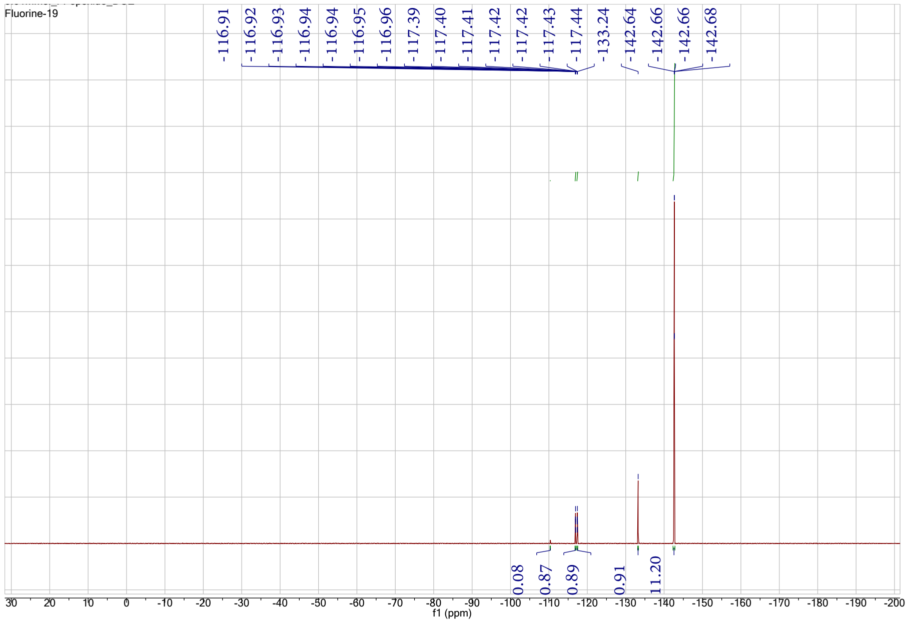

Figure S229. ^{19}F NMR spectra (in DCE) showing the purity of **2b**.

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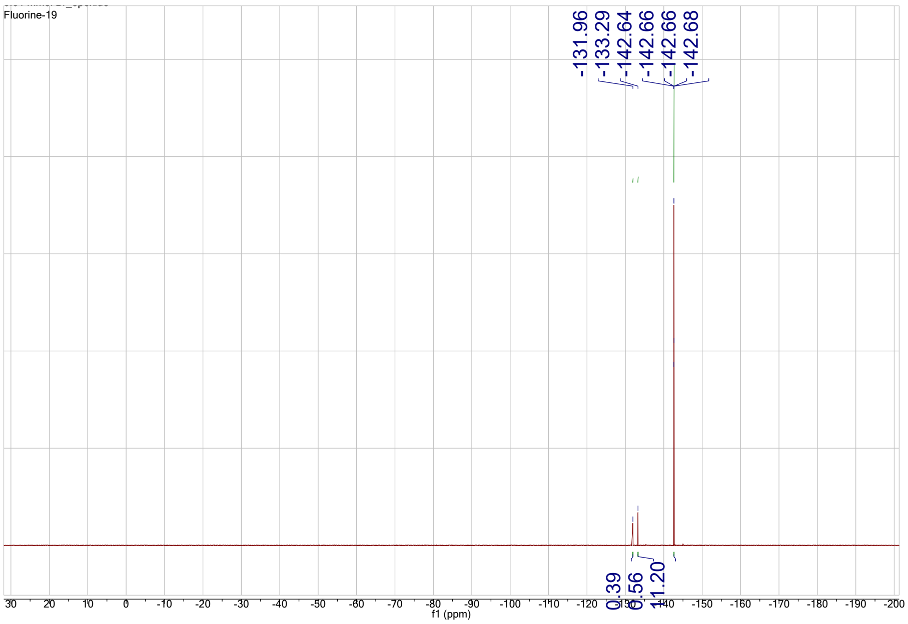

Figure S230. ^{19}F NMR spectra showing the purity of **2c**.

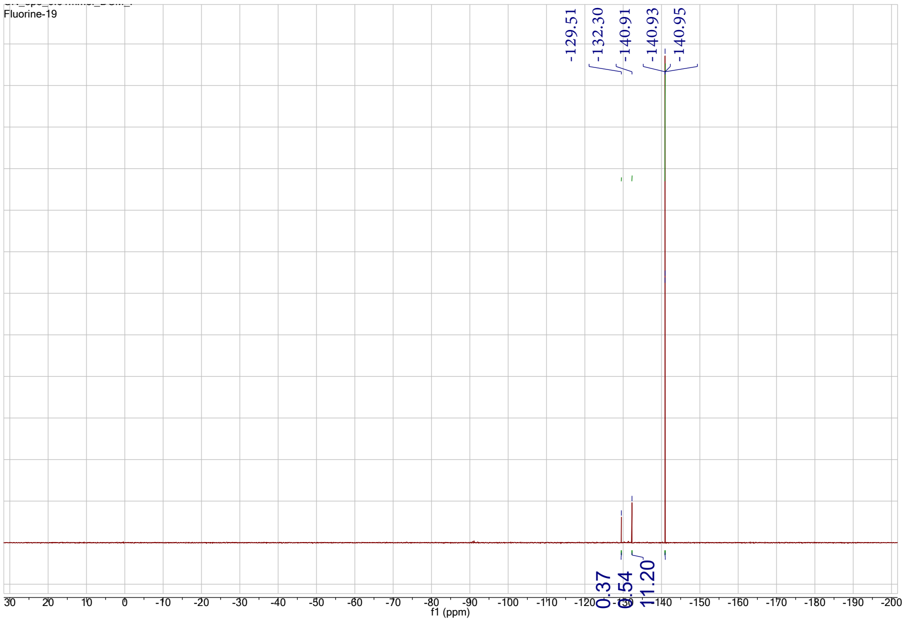

Figure S231. ^{19}F NMR spectra showing the purity of **2d**.

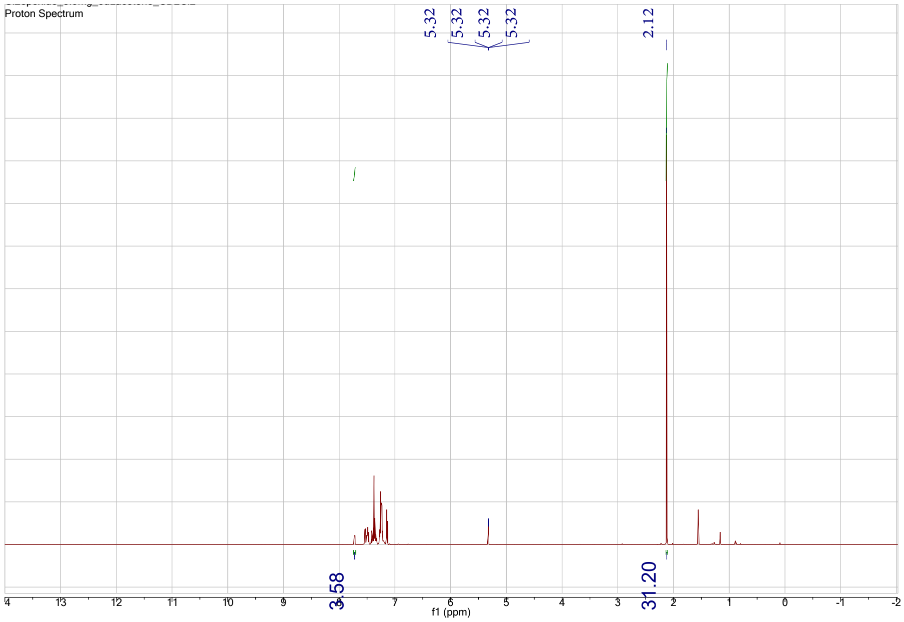

Figure S232. ^{1}H NMR spectra (CD_2Cl_2) showing the purity of **2e** (5 µL, 3 mg, acetone was used as the internal standard). 4 mg of sample (0.01 mmol in theory) was tested. Measured: [3.58 + 3.58/42*58]/10 = 85%.

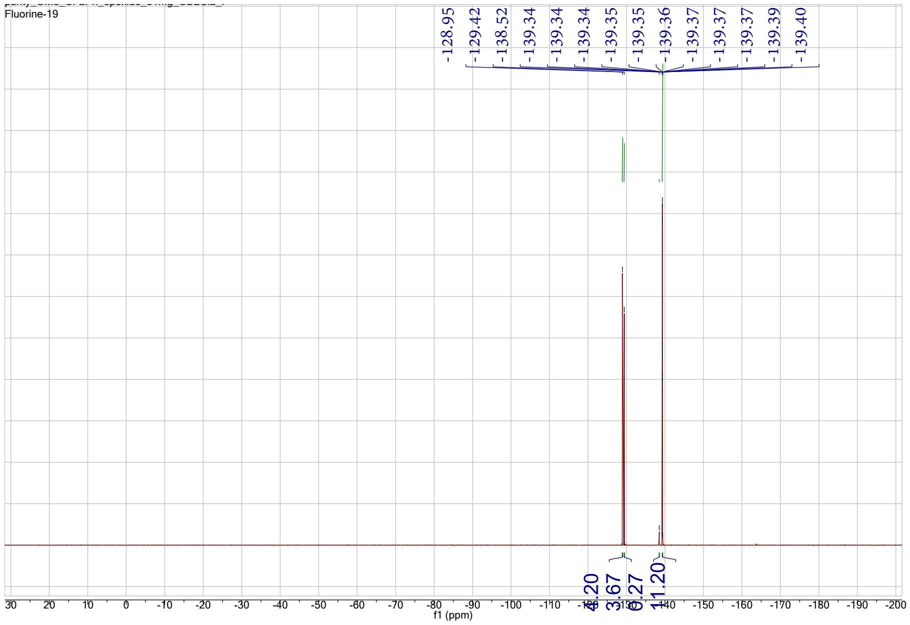

Figure S233. ^{19}F NMR spectra showing the purity of **2f**. 31 mg of purified sample was tested.

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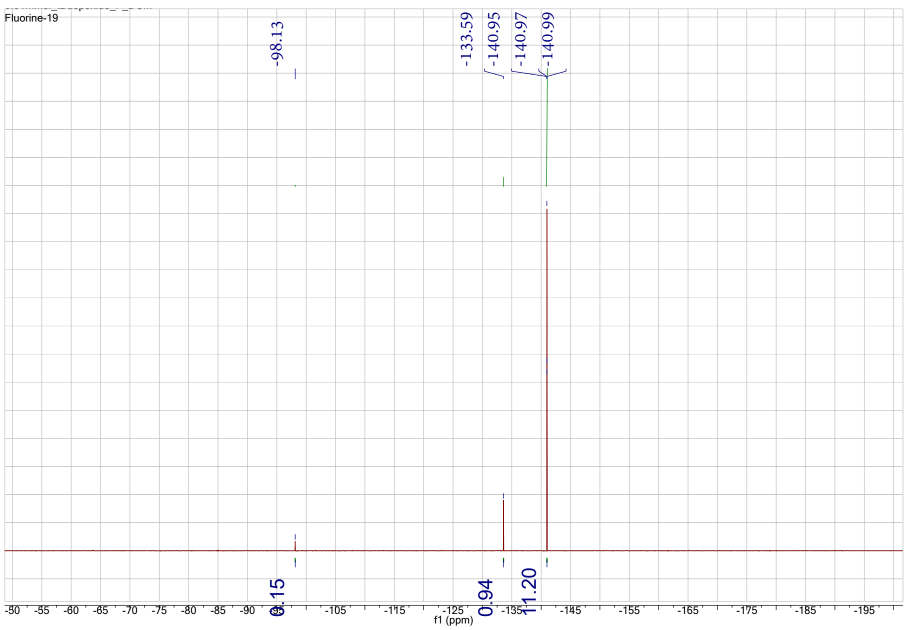

Figure S234. ^{19}F NMR spectra showing the purity of **2g**.

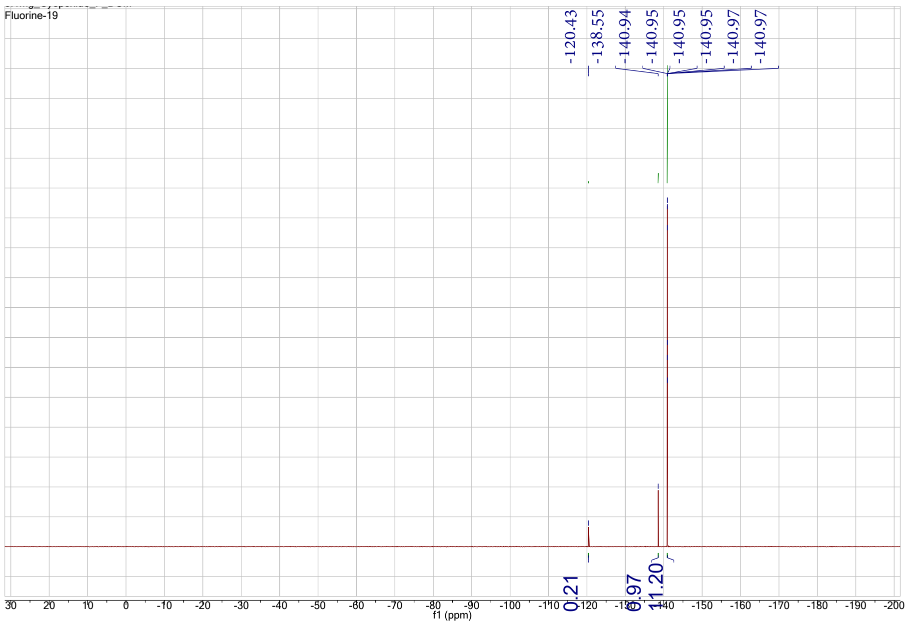

Figure S235. ^{19}F NMR spectra showing the purity of **2h**. 3.1 mg of purified sample was tested.

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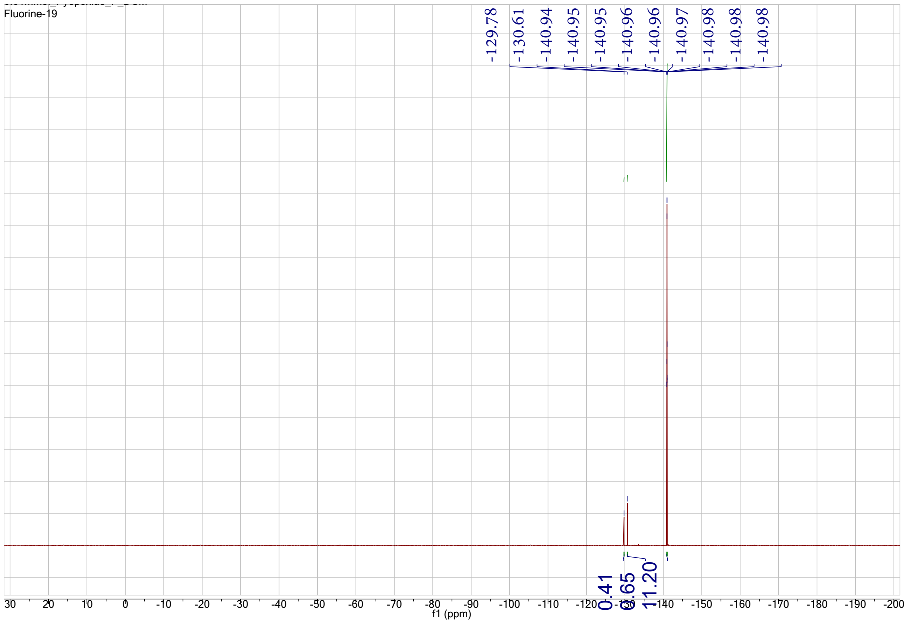

Figure S236. ^{19}F NMR spectra showing the purity of **2i**.

Figure S237. ^{19}F NMR spectra (in DCE) showing the purity of **2j**.

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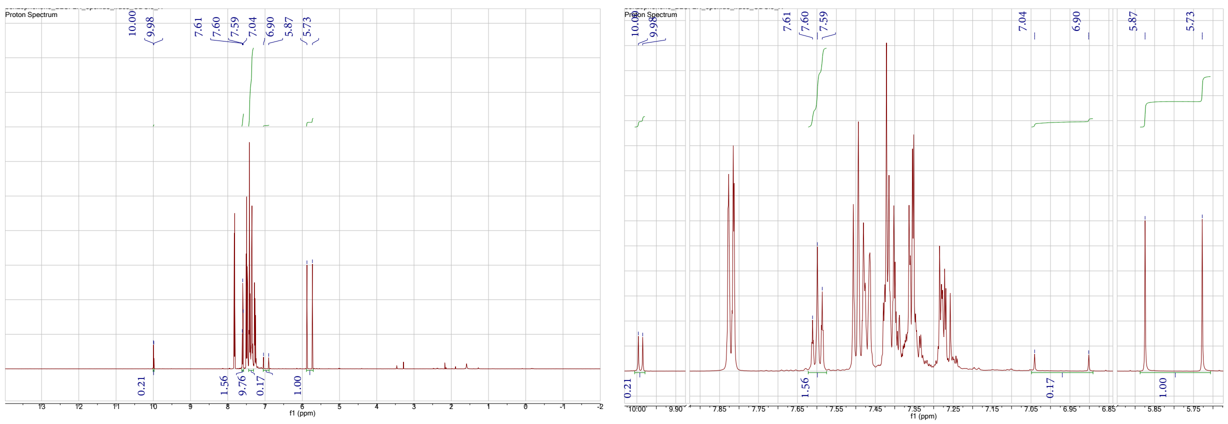

Figure S238. ^{1}H NMR spectra (600 MHz, $CDCl_3$) showing the purity of **3a**. For this sample, no external standard was added and purity was estimated by integration of resonances. The labeled integration corresponds to δ 9.99 (d, *J* = 6.7 Hz, 1H, **5d**), 7.60 (t, *J* = 7.4 Hz, 2H, benzophenone), 6.97 (d, *J* = 83.4 Hz, 1H, **H-3a**'), 5.80 (d, *J* = 88.1 Hz, 1H, **3a**), respectively. We conclude that the molar ratio of **3a**: **H-3a**': benzophenone: **5d** = 1:0.17:0.78:0.21. After normalization, the purity of **3a** was calculated to be 1/(1+0.17+0.78+0.21) = 46%.

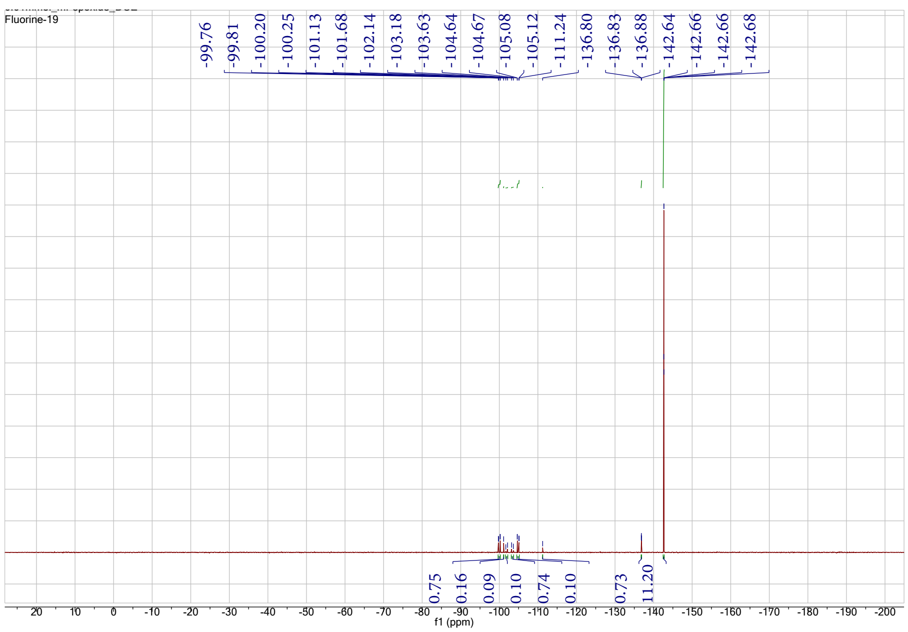

Figure S239. ^{19}F NMR spectra (in DCE) showing the purity of **4a**.

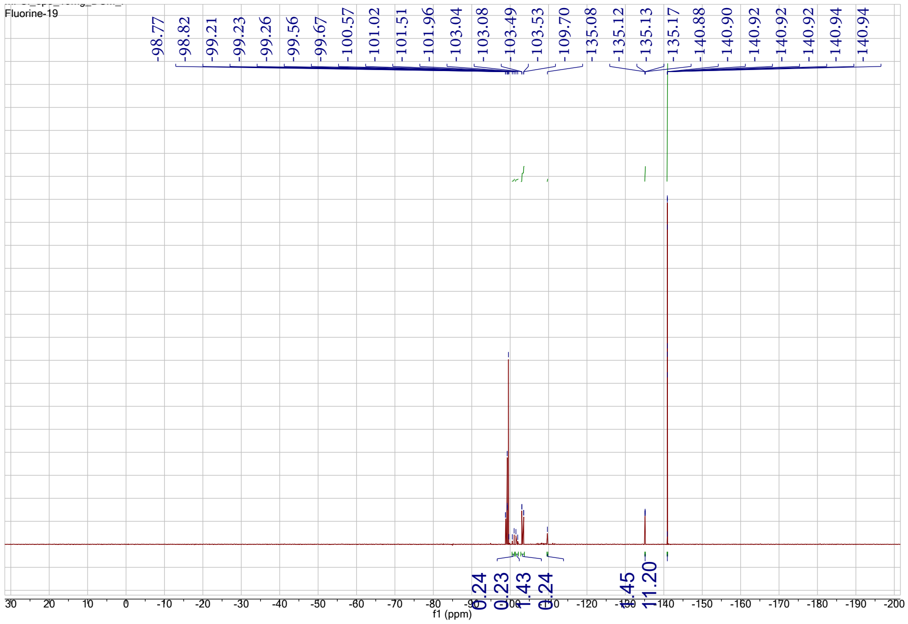

Figure S240. ^{19}F NMR spectra showing the purity of **4b**. 19 mg isolated sample was tested.

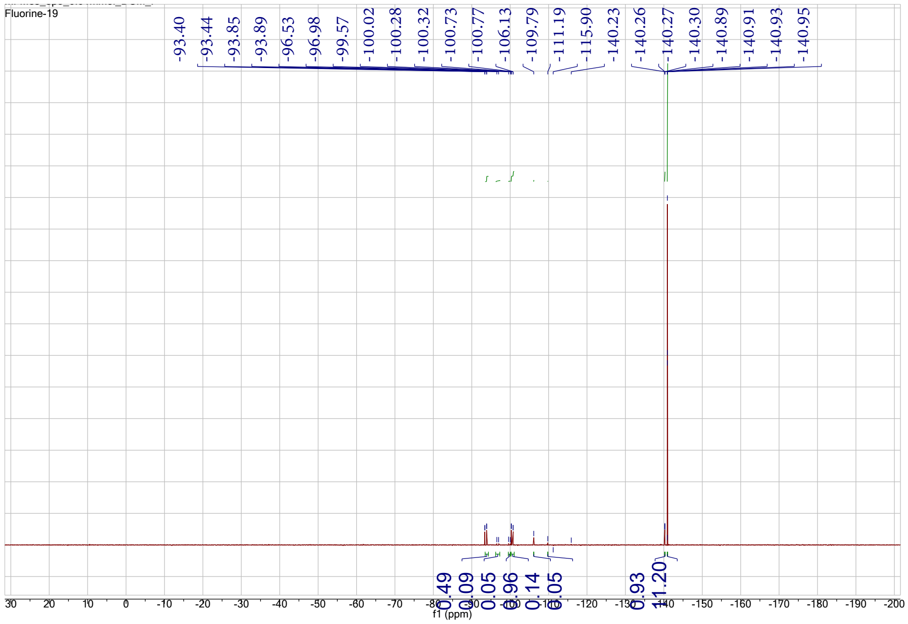

Figure S241. ^{19}F NMR spectra showing the purity of **4c**.

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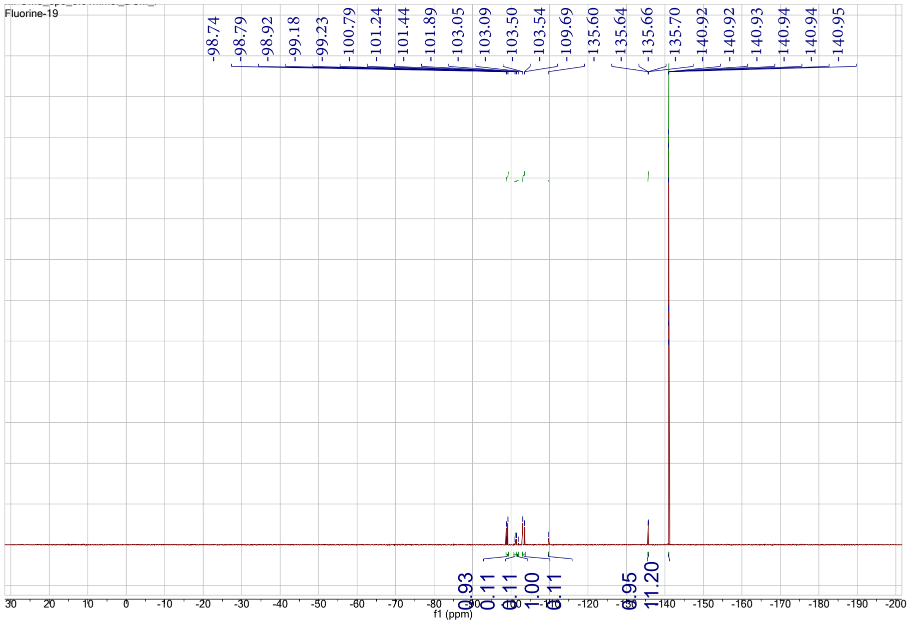

Figure S242. ^{19}F NMR spectra showing the purity of **4d**.

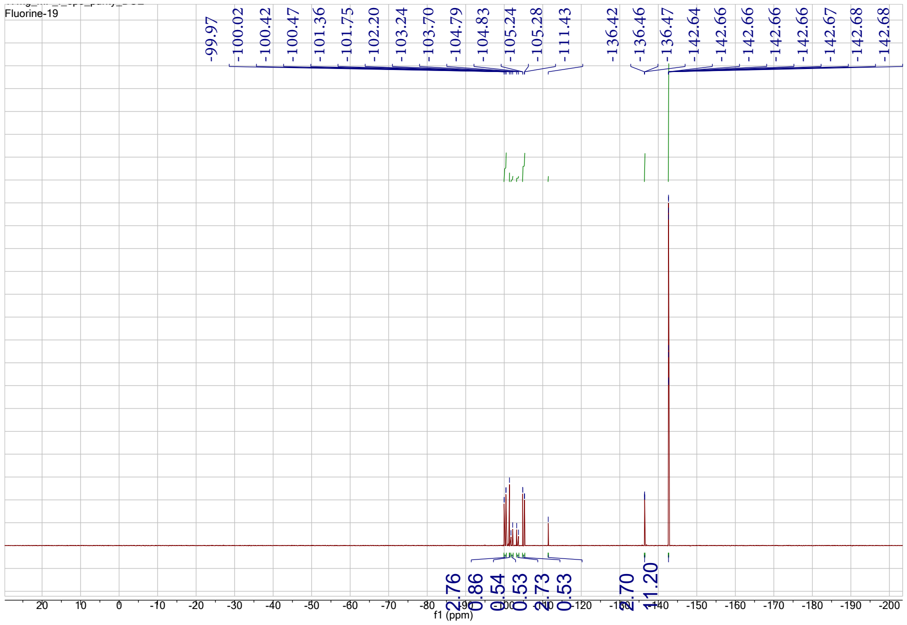

Figure S243. ^{19}F NMR spectra showing the purity of **4e** (in DCE). 17 mg of purified sample was used.

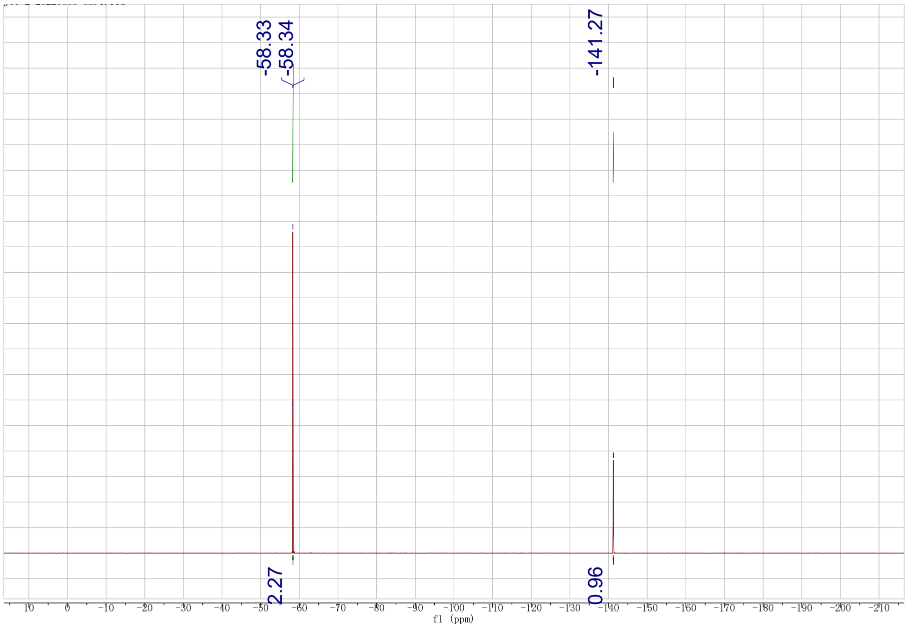

Figure S244. ^{19}F NMR spectra showing the purity of **5a**. 15 mg of purified sample was used. α,α,α-trifluorotoluene was used as the internal standard (-58.33 ppm).

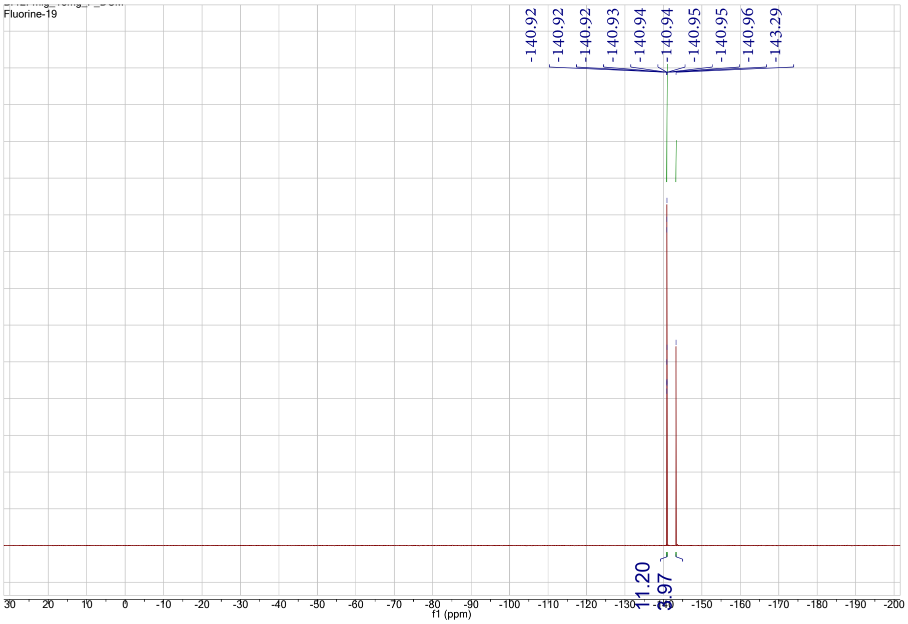

Figure S245. ^{19}F NMR spectra showing the purity of **5b**. 18 mg of purified sample was used.

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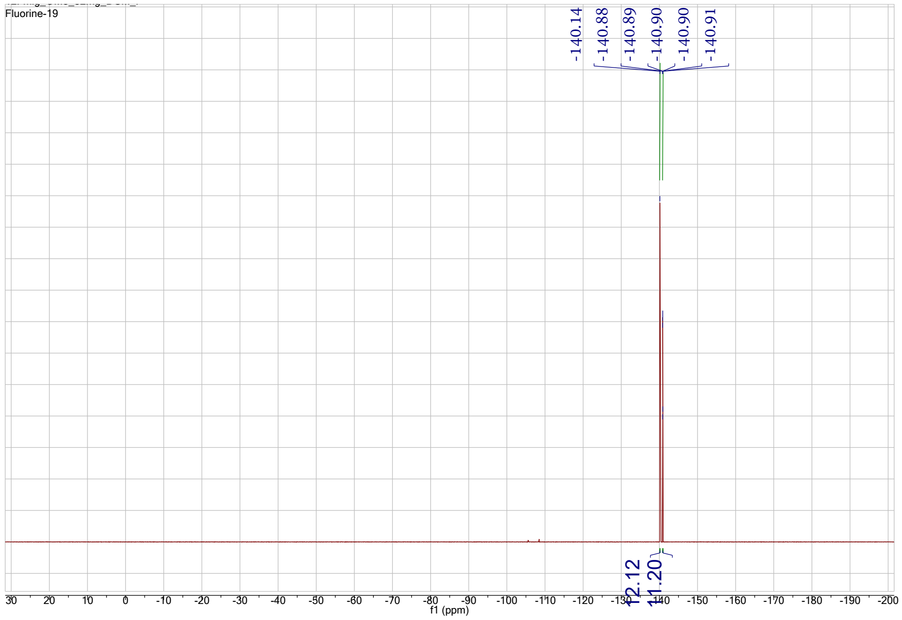

Figure S246. ^{19}F NMR spectra showing the purity of **5c**. 52 mg sample was tested.

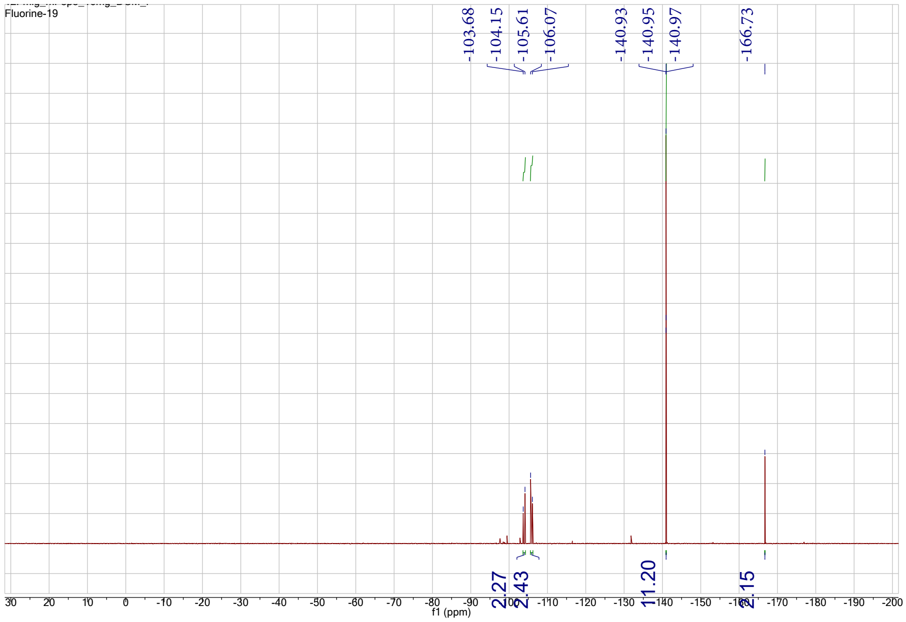

Figure S247. ^{19}F NMR spectra showing the purity of **5e**. 16 mg sample was tested.

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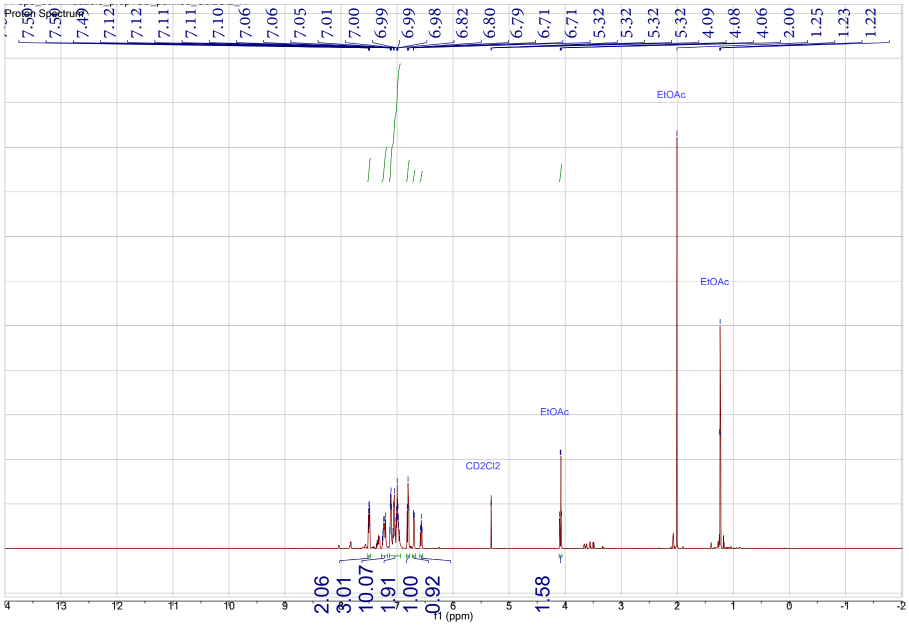

Figure S248. ^{1}H NMR spectra showing the purity of **7b**. The major impurity of the purified **7b** is EtOAc based on ^{1}H NMR spectra. Assuming the tested sample is a 2-component mixture of **7b** and EtOAc, the purity of **7b** is estimated to be 1/(1.58/2+1) = 56 %.

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X-Ray Crystallographic Analysis (2e and 4a)

Protocol

Crystal of the α-fluoroepoxide (**2e**), 2-(2-chlorophenyl)-2-(4-chlorophenyl)-3-fluoro-3-phenyloxirane, was grown from a super-saturated solution (pentane + DCM) of the purified sample (**2e**, ~20 mg, 0.06 mmol) at -30 °C over 3 days and colorless crystals were formed. The setup was kept in dry ice when sent for X-ray single crystal diffraction experiment.

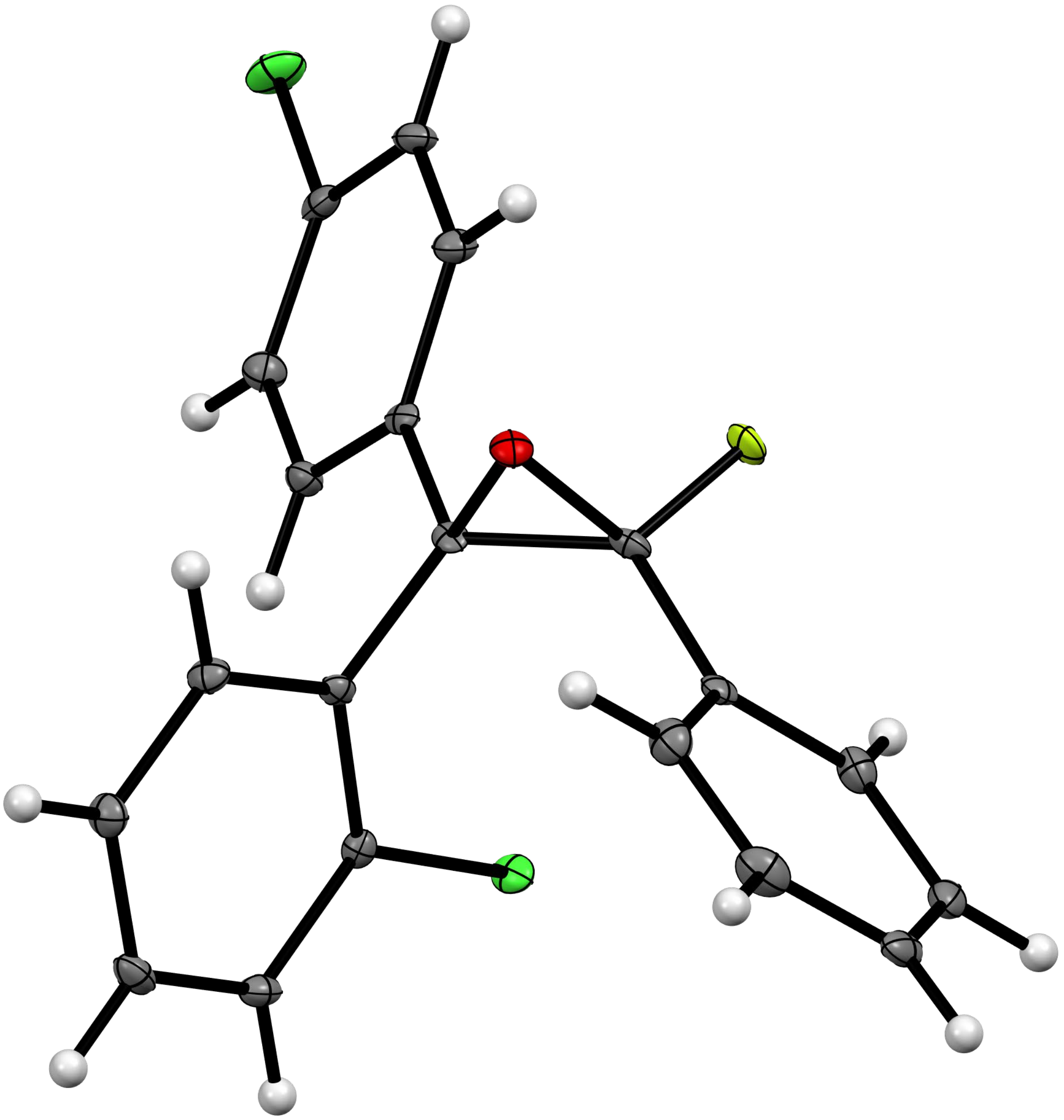

Figure S249. ORTEP diagram (50% probability level) of **2e**. The crystallographic data are summarized in **Table S21**.

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Sample ID	ws04
Chemical formula	$C_{20}H_{13}Cl_2FO$
Crystal system, space group	triclinic, P-1
Temperature (K)	293
M_r	359.20
a, b, c (Å)	8.5079(4), 9.6156(4), 10.3022(3)
α, β, γ (°)	83.401(3), 88.993(3), 79.248(4)
V ($Å^3$)	822.51(5)
Z	2
Radiation type	Cu Kα (λ = 1.54184)
μ /mm^{-1}	3.669
F(000)	368.0
Crystal size/mm^3	0.351 × 0.231 × 0.131
2θ range for data collection/°	8.64 to 138.884
Index ranges	$-10 \leqslant h \leqslant 9$, $-11 \leqslant k \leqslant 11$, $-12 \leqslant l \leqslant 12$
Reflections collected	11516
Independent reflections	2958 [R_{int} = 0.0397, R_{sigma} = 0.0235]
Data/restraints/parameters	2958/0/217
Goodness-of-fit on F^2	1.641
Final R indexes [I>=2σ (I)]	R_1 = 0.0647, wR_2 = 0.1750
Final R indexes [all data]	R_1 = 0.0651, wR_2 = 0.1756
Largest diff. peak/hole / e $Å^{-3}$	0.81/-1.26

Table S21. Crystal data and structure refinement for **2e** (CCDC 2204633).

Protocol

Crystal of the multi-fluoroepoxide (**4a**), 2-(difluoro(phenyl)methyl)-3-fluoro-2,3-diphenyloxirane, was obtained by dissolving the purified sample (**4a**, 3.4 mg, 0.01 mmol) at room temperature with 10-20 μL toluene in a 0.25 mL glass vial (inner vial). The setup was cooled at -30 ºC over 24 h while pentane (the outer solvent) was diffused into the toluene solution in the inner vial and colorless crystals were formed. The setup was kept in dry ice when sent for X-ray single crystal diffraction experiment.

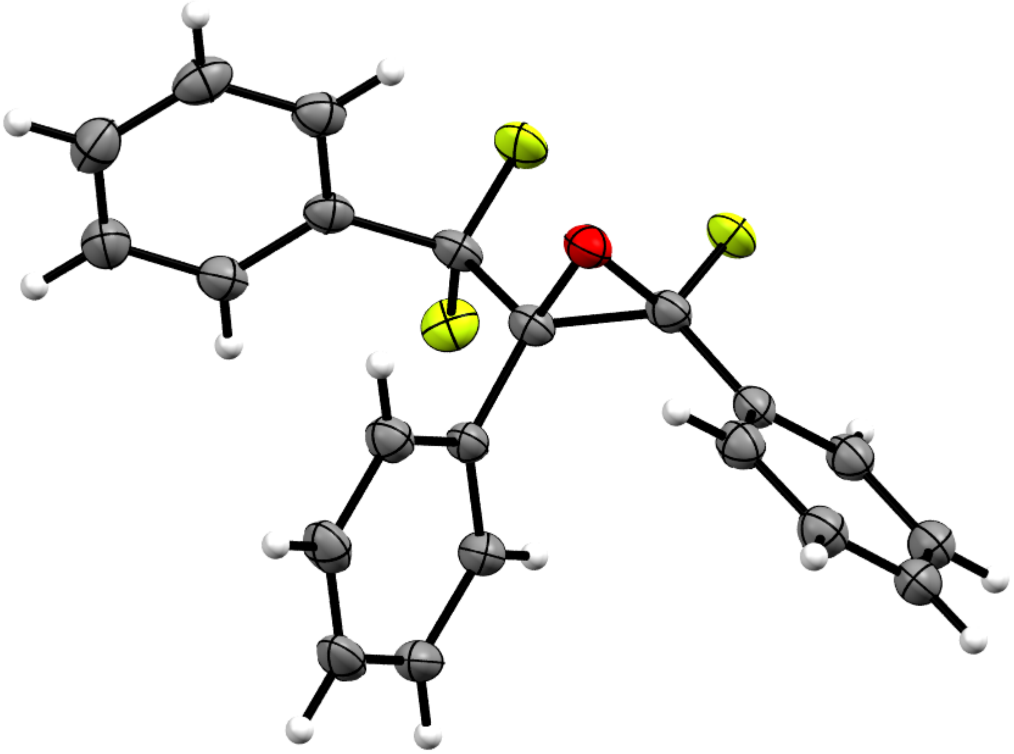

Figure S250. ORTEP diagram (50% probability level) of **4a**. The crystallographic data are summarized in **Table S22**.

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Sample ID	ws03-oP
Chemical formula	$C_{21}H_{15}F_3O$
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Temperature (K)	293
M_r	340.33
a, b, c (Å)	5.79557(11), 16.5797(4), 17.1963(4)
α, β, γ (°)	90, 90, 90
V (Å^3)	1652.38(6)
Z	4
Radiation type	Cu Kα (λ = 1.54184)
μ /mm^{-1}	0.895
F(000)	704.0
Crystal size/mm^3	0.134 × 0.088 × 0.062
2θ range for data collection/°	7.406 to 139.054
Index ranges	$-7 \leqslant h \leqslant 6$, $-20 \leqslant k \leqslant 20$, $-20 \leqslant l \leqslant 20$
Reflections collected	24762
Independent reflections	3071 [$R_{int} = 0.0695$, $R_{sigma} = 0.0345$]
Data/restraints/parameters	3071/0/226
Goodness-of-fit on F^2	1.053
Final R indexes [I>=2σ (I)]	$R_1 = 0.0403$, $wR_2 = 0.1034$
Final R indexes [all data]	$R_1 = 0.0427$, $wR_2 = 0.1060$
Largest diff. peak/hole / e Å^{-3}	0.20/-0.24
Flack parameter	-0.07(8)

Table S22. Crystal data and structure refinement for **4a** (CCDC 2195232).

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