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Chemistry of Difluorocarbene: Synthesis and Conversion of Difluoro(methylene)cyclopropanes

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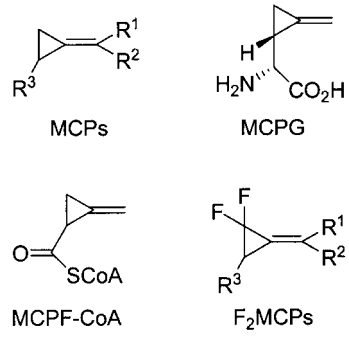
Difluoro(methylene)cyclopropanes (F_2MCPs) were prepared directly by difluorocarbene addition to allenes, and the resulting F_2MCPs were converted into a variety of difluoro(methylene)cyclopropane derivatives through Heck reactions and electrophilic substitutions. The ring-opening reactions of F_2MCPs with I_2 are reported and a plausible reaction mechanism is also discussed.

Introduction

Methylenecyclopropane derivatives (MCPs) have been well documented as useful synthetic intermediates in organic chemistry over the last decade (Scheme 1),[1] while the methylenecyclopropane moiety is also found in biologically active natural substances such as MCPG and its metabolite MCPF-CoA.[2] These compounds' biological activities have also attracted considerable attention.[3] The introduction of fluorine onto the rings of such methylenecyclopropanes should have profound effects on their biological activities and chemical reactivities, due to the strongly electron-withdrawing effect of fluorine, but the synthesis of these fluorinated analogues – difluoro(methylene)cyclopropanes (F_2MCPs) – is rather difficult. Taguchi has developed two efficient methods for the synthesis of F_2MCPs[4] – one through the elimination reaction of the selenoxide-derived (difluorocyclopropyl)methanols and the other through the cyclopropyl anion-promoted β-elimination reaction of silylated difluorocyclopropanes – but multiple reaction steps are needed for both methods. The development of new methods to produce these compounds is therefore of current interest.

Difluorocyclopropane derivatives are usually prepared by difluorocarbene addition to alkenes.[5] A variety of difluorocarbene precursors have been developed, but these precursors are either inefficient or difficult to obtain:[5b] difluorodiazirine, Me_3SnCF_3 and $PhHgCF_3$, for example, require several steps to prepare and involve expensive and/or toxic materials. Hexafluoropropylene oxide (HFPO) is also limited by its availability and its reactions must be carried out in an autoclave, while the most common precursor, $ClCF_2CO_2Na$, is hygroscopic and requires harsh reaction conditions to ensure good yields of products. Recently, though, trimethylsilyl fluorosulfonyldifluoroacetate ($FO_2SCF_2CO_2SiMe_3$, TFDA), which can be easily prepared from considerably less expensive materials, has been reported to be a highly versatile source of difluorocarbene.[6] Dolbier and our group found that difluorocarbene generated from TFDA can add efficiently and effectively to a variety of alkynes and alkenes under mild conditions.[7]



Scheme 1. Structures of various methylenecyclopropanes.

Difluoro(methylene)cyclopropane backbones might be directly accessible by difluorocarbene addition to allenic compounds or their equivalents,[8] and several attempts to explore this possibility have been made.[9] Dolbier found that a mixture of regioisomers and double cyclopropanation products was formed from the reaction between difluorocarbene and simple allene when $PhHgCF_3$ was used as the difluorocarbene source,[9b] while Bargar prepared bioactive F_2MCPs in low yield by treatment of alkyl allenes with difluorocarbene derived from the decomposition of $ClCF_2CO_2Na$, accompanied by the formation of double cyclopropanation products.[9c]

As an extension of our studies on difluorocarbene chemistry and our interest in F_2MCP chemistry, we wish to re-

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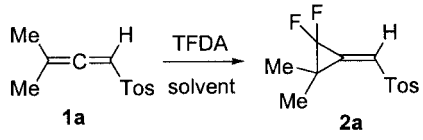
port an improved synthesis of F_2MCPs from TFDA and allenic compounds and describe the chemical conversions of F_2MCPs.

Results and Discussion

Synthesis of Difluoro(methylene)cyclopropanes

The addition of difluorocarbene to allenes was initially investigated by treatment of phenylpropadiene with TFDA in the presence of NaF in diglyme (DG) at 120 °C. Unfortunately, a mixture of rearranged product, starting material and double cyclopropanation product was formed. It had been reported that the introduction of a sulfonyl group into an allene could improve the regioselectivity in its cycloaddition reaction,[10] so sulfonyl allenes were then chosen as the substrates. Treatment of **1a** with TFDA under conditions similar to those described above did give the difluoro(methylene)cyclopropane product **2a** in 22% yield, with the amount of TFDA not significantly affecting the yield of **2a** produced (Table 1, Entries 1 and 2). An improvement was achieved when toluene or xylene was used as the solvent (Table 1, Entries 3 and 4).

Table 1. Conditions for and results of difluorocarbene addition to allenes.



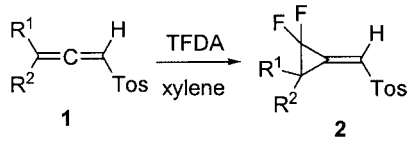
1a **2a**

Entry	Solvent	TFDA (equiv.)	Temp. (°C)[a]	Yield (%)[b]
1	DG	1.5	120	22
2	DG	3	120	20
3	toluene	2	(reflux)	39
4	xylene	2	120	40

[a] External temperature. [b] Isolated yields. They are based on **1a** used.

A series of sulfonyl allenes were then subjected to the optimal reaction conditions described above. In most cases, a wide range of F_2MCPs were obtained in good yield by this methodology. The substituents on the double bond influenced the reactivity significantly: regioselective difluorocarbene addition proceeded smoothly with the allenes possessing geminal dialkyl substituents (**1a** and **1d**–**1g**), while the unsubstituted allene **1b** and the monosubstituted allene **1c** did not give the corresponding F_2MCPs. (Table 2, Entries 2 and 3), with the starting materials **1b** and **1c** being recovered; this is probably because of the relatively low electron density in the double bond. The structure of **2f** was further confirmed by single-crystal X-ray diffraction analysis (Figure 1).

Table 2. Difluorocarbene addition to sulfonyl allenes.[a]



1 **2**

Entry	**1**	R^1	R^2	**2**	Conversion (%)	Yield (%)[b]
1	**1a**	Me	Me	**2a**	63	63
2	**1b**	H	H	**2b**	0	0
3	**1c**	H	Me	**2c**	0	0
4	**1d**	Et	Me	**2d**	57	80
5	**1e**	*t*Bu	Me	**2e**	57	83
6	**1f**	$-(CH_2)_5-$		**2f**	56	88
7	**1g**	Ph	Me	**2g**	60	60

[a] Reactions were carried out with **1**/TFDA/NaF 1:2:0.1 over 3 h. [b] Isolated yields based on the conversion of **1**.

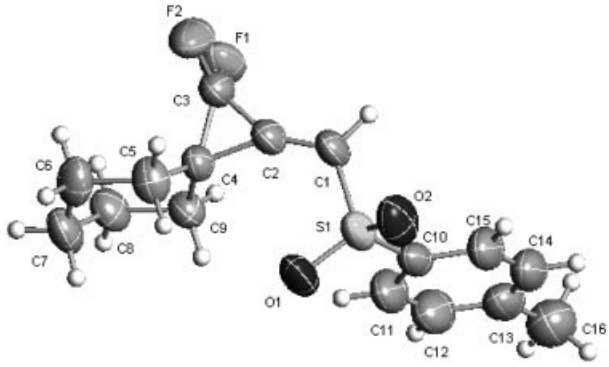


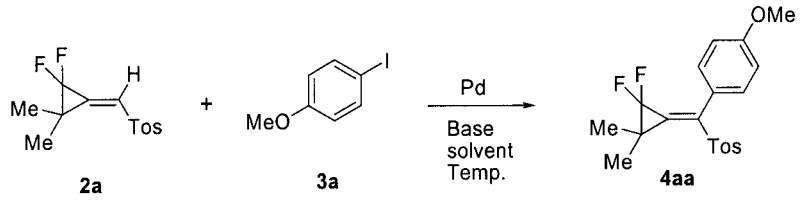
Figure 1. X-ray crystallography for **2f**. Selected bond lengths [Å], bond angles [°] and torsion angles [°]: S(1)–O(1) 1.4251(14), S(1)–C(1) 1.737(2), C(1)–C(2) 1.303(3), C(2)–C(3) 1.446(3), C(1)–H(1) 0.88(2), C(2)–C(4) 1.476(2), C(3)–C(4) 1.491(3); C(1)–C(2)–C(3) 149.30(19), C(3)–C(2)–C(4) 61.35(13), C(2)–C(3)–C(4) 60.34(12); O(1)–S(1)–C(1)–C(2) –3.1(2), S(1)–C(1)–C(2)–C(3) –179.0(3), S(1)–C(1)–C(2)–C(4) –3.8(5), C(1)–C(2)–C(3)–C(4) 177.2(4), C(1)–C(2)–C(4)–C(9) –69.9(4), C(3)–C(2)–C(4)–C(9) 107.29(19), C(1)–C(2)–C(4)–C(5) 74.9(4).

While MCPs have been applied in a wide variety of synthetic transformations, F_2MCPs have so far been less well explored, due to their poor accessibility. With the above difluoro(methylene)cyclopropane derivatives to hand, we next investigated their conversion into diversely functionalized derivatives.

Heck Reactions between F_2MCP and Aryl Iodides

Initial investigations into Heck reactions were made with F_2MCP **2a** and *p*-iodoanisole as the substrates. Of the catalysts, bases, solvents and temperatures screened, the combination of $Pd(PPh_3)_4$ and Ag_2CO_3 in DMF at 120 °C produced the best results for this transformation, with the corresponding coupling product **4aa** being obtained in 74% yield (Table 3). For comparison, no ring-opening products were detected with their nonfluorinated analogues, despite the high conformational strain of **2a**.[11]

Table 3. Conditions and results of Heck reactions.[a]

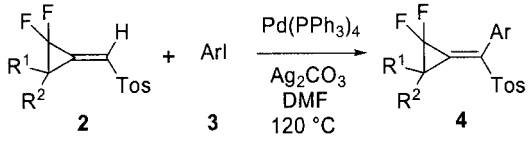


Entry	Catalyst	Base	Solvent	Temp.(°C)	Yield (%)[b]
1	$Pd(OAc)_2$	Ag_2CO_3	CH_3CN	room temp.	0
2	$Pd(OAc)_2$	Ag_2CO_3	DMF	120	50
3	$Pd(OAc)_2$	$NaHCO_3$	DMF	120	0
4[c]	$Pd(PPh_3)_4$	Ag_2CO_3/K_2CO_3	DMF	80	0
5	$Pd(OAc)_2$	Ag_2O	DMF	120	43
6	$PdCl_2(PPh_3)_2$	Ag_2CO_3	DMF	120	18
7	$Pd(PPh_3)_4$	Ag_2CO_3	DMF	120	74

[a] Reactions were carried out in the presence of palladium catalyst (10 mol%). [b] Isolated yields. [c] The ratio of Ag_2CO_3 and K_2CO_3 is 0.05:4.

We then studied the scope of the reaction by allowing the F_2MCPs **2** to react with a variety of aryl iodides **3** under the optimal reaction conditions described above; the results are summarized in Table 4. No desired product was obtained in the case of F_2MCP **2g** (Table 4, Entry 10), which might be a result of the presence of the phenyl group at the allylic position. Neither was any corresponding product was formed in the case of 1-iodo-4-nitrobenzene (**3f**), which contains a strongly electron-withdrawing group on the benzene ring, (Table 4, Entry 6). In other cases the reactions proceeded smoothly to give the arylated F_2MCPs **4** in moderate to good yields. The presence of a bulky group such as *tert*-butyl on the cyclopropane ring had no effect on the yield of **4** (Table 4, Entry 8).

Table 4. Heck reactions between of F_2MCPs **2** and aryl iodides.[a]



2a: R^1 = Me, R^2 = Me
2d: R^1 = Et, R^2 = Me
2e: R^1 = *t*Bu, R^2 = Me
2f: R^1+ R^2 = -$(CH_2)_5$-
2g: R^1 = Ph, R^2 = Me

3a: Ar = 4-MeOPh
3b: Ar = 4-MePh
3c: Ar = Ph
3d: Ar = 4-ClPh
3e: Ar = 4-MeO_2CPh
3f: Ar = 4-NO_2Ph

Entry	2	ArI	4	Yield (%)[b]
1	**2a**	**3a**	**4aa**	74
2	**2a**	**3b**	**4ab**	60
3	**2a**	**3c**	**4ac**	55
4	**2a**	**3d**	**4ad**	37
5	**2a**	**3e**	**4ae**	25
6	**2a**	**3f**	**4af**	0
7	**2d**	**3a**	**4da**	57
8	**2e**	**3a**	**4ea**	60
9	**2f**	**3a**	**4fa**	66
10	**2g**	**3a**	**4ga**	0

[a] **2**/**3**/$Pd(PPh_3)_4$/Ag_2CO_3 = 1:1.1:0.1:4.0. [b] Isolated yields.

Reactions between F_2MCPs and Electrophiles

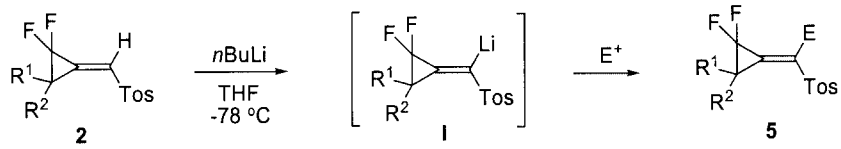
Since the presence of a sulfone group can stabilize the adjacent carbon anion, vinyllithium intermediates generated by direct lithiation of vinyl sulfones have been used in many practical organic syntheses.[12] Application of this method to F_2MCPs **2** was also successful; the results are given in Table 5. Treatment of F_2MCP **2**a with *n*BuLi in THF at –78 °C converted **2a** into the lithiated intermediate **I**, while subsequent treatment (after workup) with benzaldehyde resulted in the formation of **5a** in 75% yield (Table 5, Entry 1).

Similarly to the situation in the Heck reactions, none of the desired product was obtained when **2g**, containing a phenyl substituent on the cyclopropane ring, was used as the starting material (Table 5, Entry 5), but all the other F_2MCPs gave modest to good yields of the desired products. The matter of whether aromatic aldehydes or aliphatic aldehydes were being used had some effect on the yield of **5**: decreased yields of **5** were obtained when aliphatic aldehydes such as propanal were used, for example (Table 5, Entry 6). As well as aldehydes, other electrophiles such as methyl iodide and iodine were also applicable in this conversion (Table 5, Entries 7 and 8). It should be noted that the iodinated product **5h**, an iodoalkene derivative, might be suitable for further transformations.

CuI-Catalyzed Ring-Opening Reactions between F_2MCPs and Iodine

There is a growing interest in ring-opening of MCPs: Huang and co-workers recently reported CuI/I_2-catalyzed ring-opening reactions of MCPs with I_2,[13] whilst Shi's group

Table 5. Reactions between **2** and electrophiles.[a]



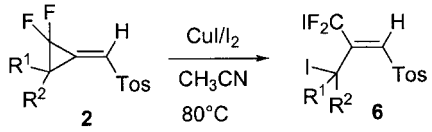
2a: R^1 = Me, R^2 = Me; **2d**: R^1 = Et, R^2 = Me; **2e**: R^1 = *t*Bu, R^2 = Me; **2f**: $R^1 + R^2$ = -$(CH_2)_5$-; **2g**: R^1 = Ph, R^2 = Me

Entry	2	Electrophile	5	Yield (%)[b]
1	**2a**	PhCHO	**5a** [E = CH(OH)Ph]	75
2	**2d**	PhCHO	**5b** [E = CH(OH)Ph]	55
3	**2e**	PhCHO	**5c** [E = CH(OH)Ph]	70
4	**2f**	PhCHO	**5d** [E = CH(OH)Ph]	61
5	**2g**	PhCHO	**5e** [E = CH(OH)Ph]	0
6	**2a**	*n*PrCHO	**5f** [E = CH(OH)*n*Pr]	37
7	**2a**	MeI	**5g** (E = Me)	60
8	**2a**	I_2	**5h** (E = I)	57

[a] Reactions were carried out with **2**/E^+ = 1:1.2. [b] Isolated yields.

found that this reaction can also occur in the absence of CuI.[14] In the next step of our research into F_2MCPs, we investigated their ring-opening reactions. It was found that the reaction between **2a** and I_2 in the presence of CuI readily produced **6a** in 93% yield (Table 6, Entry 1). Other F_2MCPs were studied similarly, and the results are listed in Table 6.

Table 6. Ring-opening reactions between **2** and I_2.[a]

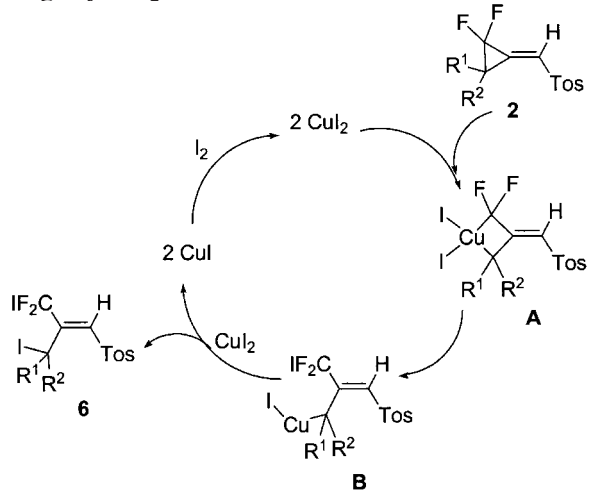


Entry	2	R^1	R^2	6	Yield (%)[b]
1	**2a**	Me	Me	**6a**	93
2	**2d**	Et	Me	**6d**	80
3	**2e**	*t*Bu	Me	**6e**	0
4	**2f**	–$(CH_2)_5$–		**6f**	95
5	**2g**	Ph	Me	**6g**	0

[a] Reactions were carried out with **2**/CuI/I_2 = 1:0.05:3. [b] Isolated yields.

As illustrated in Table 6, the reactions were significantly affected by the substituents on the cyclopropane rings. No reactions occurred, even with prolonged reaction times, with F_2MCPs bearing bulky or aromatic substituents on their cyclopropane rings (Table 6, Entries 3 and 5), while with other F_2MCPs the corresponding ring-opening products were obtained in good to excellent yields.

Ito has proposed a metallocyclic intermediate mechanism to explain the selective distal or proximal C–C bond cleavage of MCPs through Pd- and Pt-catalysed silaboration,[15] while Huang has suggested a copper-containing cyclic intermediate mechanism for CuX_2-mediated ring-opening reactions of MCPs.[13] In view of the similarity of MCPs and F_2MCPs, a plausible mechanism for this reaction is shown in Scheme 2. An equilibrium between CuI and CuI_2 would first be established under the reaction conditions, while the oxidative addition of CuI_2 to the distal C–C bond of F_2MCPs would then result in the formation of intermediate **A**, followed by reductive elimination to give **B**. The final product **6** would be formed after oxidative cleavage by CuI_2.



Scheme 2. Proposed mechanism for CuI-promoted ring-opening reactions of F_2MCPs.

Conclusions

In summary, we have developed a convenient and efficient method for the synthesis of difluoro(methylene)cyclopropanes by addition of difluorocarbene to allenes. Subsequent Heck reactions or electrophilic reactions of the F_2MCPs were investigated. The procedures described here should be adaptable to the synthesis of other difluoro(methylene)cyclopropane derivatives. The ring-opening reactions of F_2MCPs were also studied, providing a novel route to difluoromethylated derivatives. Other synthetically useful transformations of F_2MCPs are under continuing investigation in our laboratory.

Experimental Section

General: ^{1}H NMR spectra were recorded on a Bruker AM 300 (300 MHz) spectrometer with TMS as an internal standard (negative for upfield). ^{19}F NMR spectra were recorded on a Bruker AM 300 (282 MHz) with $CFCl_3$ as an external standard (negative for upfield). The solvent for NMR measurement was $CDCl_3$ or CD_3COCD_3, which were purchased from Cambridge Isotope Laboratories, Aldrich or Acros. MS and HRMS were recorded on a Hewlett–Packard HP-5989A spectrometer and a Finnigan MAT-8483 mass spectrometer. Elementary analyses were obtained on a Perkin–Elmer 2400 Series II Elemental Analyzer. Infrared spectra were measured with a Perkin–Elmer 983 spectrometer. TLC analysis were performed on silica gel plates, column chromatography over silica gel (mesh 300–400), both obtained from Qingdao Ocean Chemicals. Diglyme, THF and CH_3CN were purified by standard methods. $FSO_2CF_2COOSiMe_3$ (TFDA) and sulfonyl allenes were prepared as described in the literature.[7,16] *n*BuLi and aryl iodides were used as commercially available.

Typical Procedure for the Addition of Difluorocarbene to Allenes: Compound **1f** (273 mg, 1.04 mmol), NaF (4 mg, 10 mol%) and xylene (2 mL) were placed under N_2 in a Schlenk tube fitted with a magnetic stirring bar and a pressure-equalizing dropping funnel. The mixture was heated to 120 °C (oil bath), TFDA (530 mg, 2.0 equiv.) was added dropwise with stirring over a period of about 40 min, and the mixture was then stirred for another 2.5 h. at this temperature. After having cooled to room temperature, the reaction mixture was directly purified by flash chromatography on a silica gel column. Compound **2f** (161 mg, 88%) was obtained as a white solid, while **1f** (120 mg, conversion 56%) was recovered.

1,1-Difluoro-2-[(tolyl-4-sulfonyl)methylidene]spiro[2.5]octane (2f): Solid, yield 161 mg (88%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.34–1.44 (m, 3 H), 1.68–1.90 (m, 5 H), 1.96–2.08 (m, 2 H), 2.46 (s, 3 H), 6.95 (s, 1 H), 7.36 (d, J = 9.0 Hz, 2 H), 7.76 (d, J = 8.4 Hz, 2 H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –140.4 (s, 2 F) ppm. IR (film): $\tilde{\nu}$ = 3050, 2939, 2862, 1746, 1598, 1472, 1344, 1321, 1169, 1147, 1115 cm^{-1}. MS (EI): *m*/*z*: 312 [M]$^+$ (15.84), 91 (100). $C_{16}H_{18}F_2O_2S$ (312.1): C 61.52, H 5.81; found: C 61.63, H 5.77.

X-ray Crystallographic Data for 2f: Crystal system: monoclinic, space group: $P21/n$, unit cell dimensions: a = 13.0719(18) Å, b = 5.9925(8) Å, c = 19.815(3) Å, α = 90°, β = 99.478(3)°, γ = 90°; Z = 4, F(000) = 656, $R1$ = 0.0734, wR_2 = 0.1309. CCDC-289229 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

1-{[(2,2-Difluoro-3,3-dimethylcyclopropylidene)methyl]sulfonyl}-4-methylbenzene (2a): Solid, yield 108 mg (63%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.45 (t, J = 1.5 Hz, 6 H), 2.46 (s, 3 H), 7.00 (s, 1 H), 7.37 (d, J = 8.1 Hz, 2 H), 7.80 (d, J = 8.1 Hz, 2 H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –138.7 (s, 2 F) ppm. IR (film): $\tilde{\nu}$ = 2982, 1744, 1594, 1490, 1461, 1394, 1342, 1322, 1298, 1239, 1210, 1154 cm^{-1}. MS (EI): *m*/*z*: 272 (100) [M$^+$]. $C_{13}H_{14}F_2O_2S$ (272.1): C 57.34, H 5.18; found: C 57.37, H 5.17.

1-{[(2-Ethyl-3,3-difluoro-2-methylcyclopropylidene)methyl]sulfonyl}-4-methylbenzene (2d): Solid, yield 130 mg (80%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.09 (t, J = 7.2 Hz, 3 H), 1.44 (s, 3 H), 1.61–1.71 (m, 1 H), 1.99–2.09 (m, 1 H), 2.47 (s, 3 H), 6.99 (s, 1 H), 7.39 (d, J = 7.2 Hz, 2 H), 7.78 (d, J = 8.1 Hz, 2 H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –136.7 (d, J = 181.9 Hz, 1 F), –141.2 (d, J = 184.4 Hz, 1 F) ppm. IR (film): $\tilde{\nu}$ = 2984, 2939, 2883, 1737, 1596, 1462, 1454, 1380, 1357, 1320, 1271, 1152 cm^{-1}. MS (EI): *m*/*z*: 286 [M]$^+$ (8.17), 65 (100). $C_{14}H_{16}F_2O_2S$ (286.1): C 58.72, H 5.63; found: C 58.91, H 5.56.

1-{[(2-*tert*-Butyl-3,3-difluoro-2-methylcyclopropylidene)methyl]-sulfonyl}-4-methylbenzene (2e): Solid, yield 149 mg (83%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.15 (s, 9 H), 1.40 (t, J = 2.1 Hz, 3 H), 2.46 (s, 3 H), 7.08 (s, 1 H), 7.38 (d, J = 8.4 Hz, 2 H), 7.80 (d, J = 8.7 Hz, 2 H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –131.6 (d, J = 188.1 Hz, 1 F), –140.0 (d, J = 188.1 Hz, 1 F) ppm. IR (film): $\tilde{\nu}$ = 2964, 2927, 1839, 1735, 1598, 1468, 1381, 1325, 1239, 1153 cm^{-1}. MS (EI): *m*/*z*: 315 [M + 1]$^+$ (28.76), 139 (100). HRMS (MALDI) calcd. for $C_{16}H_{20}F_2O_2SNa^+$: 337.1056; found: 337.1044.

1-{[(2,2-Difluoro-3-methyl-3-phenylcyclopropylidene)methyl]-sulfonyl}-4-methylbenzene (2g): Solid, yield 120 mg (60%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 2.08 (t, J = 3.3 Hz, 3 H), 2.44 (s, 3 H), 4.17 (s, 1 H), 7.17 (d, J = 6.9 Hz, 2 H), 7.24–7.42 (m, 5 H), 7.79 (d, J = 8.1 Hz, 2 H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –122.3 (s, 2 F) ppm. IR (film): $\tilde{\nu}$ = 2971, 2918, 1641, 1615, 1597, 1462, 1450, 1386, 1361, 1317, 1259, 1137 cm^{-1}. MS (EI): *m*/*z*: 334 [M]$^+$ (1.19), 179 (100). $C_{16}H_{18}F_2O_2S$ (312.1): C 64.65, H 4.82; found: C 64.70, H 4.96.

Typical Procedure for Heck Reactions between Compounds 2 and Aryl Iodides: Compounds **2a** (39 mg) and **3a** (37 mg, 1.1 equiv.), Ag_2CO_3 (170 mg, 4.0 equiv.) and DMF (3 mL) were placed under N_2 in a Schlenk tube containing a magnetic stirring bar. The mixture was cooled to –78 °C with a dry ice/alcohol bath and degassed three times. $Pd(PPh_3)_4$ (17 mg, 10 mol-%) was then added, and the mixture was heated at 120 °C (oil bath) and stirred for 24 h. The reaction mixture was allowed to cool to room temperature and filtered, the solid was washed with ethyl acetate (10 mL), and the combined filtrate was then washed with water and brine and dried with $MgSO_4$. After removal of solvent under reduced pressure, the residue was purified by flash chromatography on a silica gel column to provide **4aa** (40 mg, 74%) as a white solid.

1-{[(2,2-Difluoro-3,3-dimethylcyclopropylidene)(4-methoxyphenyl)-methyl]sulfonyl}-4-methylbenzene (4aa): Solid, yield 40 mg (74%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.54 (s, 3 H), 1.59 (s, 3 H), 2.36 (s, 3 H), 3.79 (s, 3 H), 6.82 (d, J = 9.0 Hz, 2 H), 7.20 (d, J = 7.8 Hz, 2 H), 7.46 (d, J = 9.0 Hz, 2 H), 7.58 (d, J = 8.1 Hz, 2 H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –136.9 (s, 2 F) ppm. IR (film): $\tilde{\nu}$ = 2920, 1716, 1604, 1513, 1463, 1389, 1345, 1324, 1304, 1257, 1183, 1151 cm^{-1}. MS (EI): *m*/*z*: 378 [M]$^+$ (4.12), 135 (100). $C_{20}H_{20}F_2O_3S$ (378.1): C 63.48, H 5.33; found: C 63.57, H 5.12.

1-{[(2,2-Difluoro-3,3-dimethylcyclopropylidene)(tolyl)methyl]-sulfonyl}-4-methylbenzene (4ab): Solid, yield 108 mg (60%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 2.32 (s, 3 H), 2.36 (s, 3 H), 7.10 (d, J = 8.4 Hz, 2 H), 7.20 (d, J = 8.4 Hz, 2 H), 7.38 (d, J = 8.4 Hz, 2 H), 7.58 (d, J = 8.1 Hz, 2 H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –137.02 (s, 2 F) ppm. IR (film): $\tilde{\nu}$ = 2977, 2931, 1715, 1597, 1512, 1458, 1389, 1347, 1319, 1303, 1147 cm^{-1}. MS (EI): *m*/*z*: 362 [M]$^+$ (6.93), 119 (100). $C_{20}H_{20}F_2O_2S$ (362.1): C 66.28, H 5.56; found: C 66.76, H 5.97.

1-{[(2,2-Difluoro-3,3-dimethylcyclopropylidene)(phenyl)methyl]-sulfonyl}-4-methylbenzene (4ac): Solid, yield 191 mg (55%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 2.36 (s, 3 H), 7.22 (d, J = 8.1 Hz, 2 H), 7.30–7.37 (m, 3 H), 7.47–7.52 (m, 2 H), 7.59 (d, J = 8.1 Hz, 2 H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –137.0 (s, 2 F) ppm. IR (film): $\tilde{\nu}$ = 2964, 2926, 2854, 1656, 1456, 1349, 1300, 1262, 1151, 1090 cm^{-1}. MS (EI): *m*/*z*: 348 [M]$^+$ (15.25), 105 (100). $C_{19}H_{18}F_2O_2S$ (348.1): C 65.50, H 5.21; found: C 65.81, H 5.28.

1-{[(4-Chlorophenyl)(2,2-difluoro-3,3-dimethylcyclopropylidene)-methyl]sulfonyl}-4-methylbenzene (4ad): Solid, yield 141 mg (37%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.56 (t, J = 1.5 Hz, 6 H), 2.38 (s, 3 H), 7.22 (d, J = 8.4 Hz, 2 H), 7.28 (d, J = 8.4 Hz, 2 H), 7.43 (d, J = 8.4 Hz, 2 H), 7.56 (d, J = 7.8 Hz, 2 H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –136.97 (s, 2 F) ppm. IR (film): $\tilde{\nu}$ = 2930, 1722, 1594, 1491, 1466, 1388, 1348, 1323, 1203, 1154, 1088 cm^{-1}. MS (EI): m/z: 382 [M]$^+$ (2.94), 139 (100). $C_{19}H_{17}ClF_2O_2S$ (382.1): C 59.61, H 4.48; found: C 59.89, H 4.66.

Methyl 4-[(2,2-Difluoro-3,3-dimethylcyclopropylidene)(tolyl-4-sulfonyl)methyl]benzoate (4ae): Solid, yield 102 mg (25%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.57 (t, J = 2.1 Hz, 6 H), 2.36 (s, 3 H), 3.91 (s, 3 H), 7.21 (d, J = 7.8 Hz, 2 H), 7.55 (d, J = 1.8 Hz, 2 H), 7.57 (d, J = 2.1 Hz, 2 H), 7.97 (d, J = 8.1 Hz, 2 H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –136.9 (s, 2 F) ppm. IR (film): $\tilde{\nu}$ = 2923, 2851, 1724, 1608, 1597, 1459, 1426, 1390, 1347, 1326, 1316, 1276, 1157, 1142 cm^{-1}. MS (EI): m/z: 406 [M]$^+$ (4.62), 163 (100). HRMS (EI) calcd. for $C_{21}H_{20}F_2O_4S$: 406.1046: found: 406.1050.

1-{[(2-Ethyl-3,3-difluoro-2-methylcyclopropylidene)(methoxyphenyl)methyl]sulfonyl}-4-methylbenzene (4da): Solid, yield 223 mg (57%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.14 (t, J = 7.2 Hz, 3 H), 1.55 (t, J = 1.8 Hz, 3 H), 1.69–1.82 (m, 1 H), 2.14–2.25 (m, 1 H), 2.38 (s, 3 H), 3.81 (s, 3 H), 6.84 (d, J = 8.7 Hz, 2 H), 7.22 (d, J = 8.7 Hz, 2 H), 7.47 (d, J = 8.7 Hz, 2 H), 7.59 (d, J = 8.7 Hz, 2 H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –134.7 (d, J = 183.6 Hz, 1 F), –139.4 (d, J = 182.2 Hz, 1 F) ppm. IR (film): $\tilde{\nu}$ = 2926, 1715, 1605, 1512, 1459, 1359, 1322, 1256, 1178, 1150 cm^{-1}. MS (EI): m/z: 392 [M]$^+$ (8.72), 135 (100). HRMS (MALDI) calcd. for $C_{21}H_{22}O_3F_2SNa^+$: 415.1158; found: 415.1150.

1-{[(2-*tert*-Butyl-3,3-difluoro-2-methylcyclopropylidene)(methoxyphenyl)methyl]sulfonyl}-4-methylbenzene (4ea): Liquid, yield 263 mg (60%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.21 (s, 9 H), 1.52 (t, J = 2.1 Hz, 3 H), 2.35 (s, 3 H), 6.81 (d, J = 9.0 Hz, 2 H), 7.20 (d, J = 8.4 Hz, 2 H), 7.38 (d, J = 9 Hz, 2 H), 7.54 (d, J = 8.4 Hz, 2 H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –129.1 (d, J = 184.4 Hz, 1 F), –138.5 (d, J = 186.1 Hz, 1 F) ppm. IR (film): $\tilde{\nu}$ = 2964, 2920, 1715, 1606, 1575, 1512, 1464, 1337, 1324, 1256, 1151 cm^{-1}. MS (ESI): m/z: 438.2 [M + NH_4]$^+$. HRMS (MALDI) calcd. for $C_{23}H_{27}F_2O_3S^+$: 421.1635; found: 421.1643.

1,1-Difluoro-2-[(4-methoxyphenyl)(tolyl-4-sulfonyl)methylidene]-spiro[2.5]octane (4fa): Solid, yield 138 mg (66%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.38–1.49 (m, 3 H), 1.76–1.93 (m, 5 H), 2.12–2.23 (m, 2 H), 2.36 (s, 3 H), 6.82 (d, J = 9.0 Hz, 2 H), 7.20 (d, J = 8.4 Hz, 2 H), 7.45 (d, J = 8.7 Hz, 2 H), 7.57 (d, J = 8.4 Hz, 2 H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –138.4 (s, 2 F) ppm. IR (film): $\tilde{\nu}$ = 2934, 1713, 1607, 1577, 1513, 1456, 1375, 1324, 1305, 1260, 1162, 1148, 1112 cm^{-1}. MS (ESI): m/z: 436.2 [M + NH_4]$^+$. $C_{23}H_{24}F_2O_3S$ (418.1): C 66.01, H 5.78; found: C 66.00, H 5.88.

Typical Procedure for Reactions between Compounds 2 and Electrophiles: Compound **2a** (54 mg, 0.2 mmol) and THF (3 mL) were placed under N_2 in a Schlenk tube containing a magnetic stirring bar, the mixture was cooled to –78 °C with a dry ice/alcohol bath, and *n*BuLi (0.15 mL, 1.6 M, 1.1 equiv.) was added. After the mixture had been stirred for 30 min at this temperature, benzaldehyde (22 mg, 1.2 equiv.) was added, and the reaction mixture was stirred for a further hour at the same temperature. The cool bath was removed, saturated aq. NH_4Cl (5 mL) was added, and the reaction mixture was extracted with ethyl acetate (3 × 10 mL). The combined organic layer was washed with brine and dried with $MgSO_4$. After removal of solvent under reduced pressure, the residue was purified by flash chromatography on a silica gel column to provide **5a** (50 mg, 75%) as a white solid.

2-(2,2-Difluoro-3,3-dimethylcyclopropylidene)-1-phenyl-2-(tolyl-4-sulfonyl)ethanol (5a): Solid, yield 50 mg (75%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.43 (d, J = 8.7 Hz, 6 H), 2.41 (s, 3 H), 2.87 (d, J = 4.5 Hz, 1 H), 5.58 (s, 1 H), 7.13–7.24 (m, 7 H), 7.57 (d, J = 7.8 Hz, 2 H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –135.2 (d, J = 181 Hz, 1 F), –137.1 (d, J = 181 Hz, 1 F) ppm. IR (film): $\tilde{\nu}$ = 3502, 2937, 1737, 1569, 1494, 1463, 1452, 1392, 1349, 1315, 1221, 1146, 1088 cm^{-1}. MS (EI): m/z: 378 [M]$^+$ (1.09), 77(100). $C_{20}H_{20}F_2O_3S$ (378.1): C 63.48, H 5.33; found: C 63.48, H 5.17.

2-(2-Ethyl-3,3-difluoro-2-methylcyclopropylidene)-1-phenyl-2-(tolyl-4-sulfonyl)ethanol (5b): Liquid, yield 216 mg (55%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.02–1.09 (m, 3 H), 1.40 (d, J = 9.3 Hz, 3 H), 1.56–1.69 (m, 1 H), 1.99–2.09 (m, 1 H), 2.41 (s, 3 H), 2.88 (dd, J = 1.2 Hz, 12.6 Hz, 1 H), 5.58 (br., 1 H), 7.12–7.27 (m, 7 H), 7.56 (d, J = 8.1 Hz, 2 H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –132.1 (d, J = 183.6 Hz, 0.25 F), –134.9 (d, J = 184 Hz, 0.25 F), –137.7 (d, J = 181.6 Hz, 0.25 F), –139.5 (d, J = 185.8 Hz, 0.25 F) ppm. IR (film): $\tilde{\nu}$ = 3497, 2975, 2939, 1598, 1495, 1456, 1378, 1361, 1319, 1304, 1199, 1151, 1090 cm^{-1}. MS (ESI): m/z: 409.7 [M + NH_4]$^+$. HRMS (MALDI) calcd. for $C_{21}H_{22}F_2O_3SNa^+$: 415.1154; found: 415.1150.

2-(2-*tert*-Butyl-3,3-difluoro-2-methylcyclopropylidene)-1-phenyl-2-(tolyl-4-sulfonyl)ethanol (5c): Liquid, yield 147 mg (70%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.15 (d, J = 8.4 Hz, 9 H), 1.35 (d, J = 15 Hz, 3 H), 2.40 (d, J = 5.4 Hz, 3 H), 2.82 (dd, J = 5.4, 62.7 Hz, 2 H), 5.59 (d, J = 3.3 Hz, 1 H), 7.07 (m, 1 H), 7.15–7.25 (m, 6 H), 7.35 (d, J = 5.4 Hz, 1 H), 7.61 (d, J = 7.8 Hz, 1 H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –126.5 (d, J = 186 Hz, 0.25 F), –129 (d, J = 187 Hz, 0.25 F), –135.7 (d, J = 188 Hz, 0.25 F), –138.2 (d, J = 187 Hz, 0.25F) ppm. IR (film): $\tilde{\nu}$ = 3500, 2900, 1600, 1450, 1320, 1232, 1149, 1087 cm^{-1}. MS (ESI): m/z: 438.2 [M + NH_4]$^+$. HRMS (MALDI) calcd. for $C_{23}H_{26}F_2O_3SNa^+$: 443.1469; found: 443.1463.

2-(2,2-Difluorospiro[2.5]octylidene)-1-phenyl-2-(tolyl-4-sulfonyl)-ethanol (5d): Solid, yield 127 mg (61%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.85 (t, J = 5.7 Hz, 3 H), 1.19–1.48 (m, 9 H), 1.60–1.70 (m, 2 H), 2.46 (s, 3 H), 4.38 (br., 1 H), 7.37 (d, J = 8.4 Hz, 2 H), 7.77 (d, J = 8.1 Hz, 2 H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –134.8 (m, 0.2 F), –135.5 (m, 0.8 F), –136.1 (m, 0.8 F), –136.7 (m, 0.2F) ppm. IR (film): $\tilde{\nu}$ = 3491, 2964, 2932, 2873, 1597, 1462, 1392, 1351, 1315, 1305, 1224, 1145, 1086 cm^{-1}. MS (ESI): m/z: 436.1 [M + NH_4]$^+$. $C_{23}H_{24}F_2O_3S$ (436.1): C 66.01, H 5.78; found: C 66.30, H 5.58.

1-(2,2-Difluoro-3,3-dimethylcyclopropylidene)-1-(tolyl-4-sulfonyl)-pentan-2-ol (5f): Solid, yield 210 mg (51%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.85 (t, J = 7.2 Hz, 3 H), 1.17–1.39 (m, 2 H), 1.43 (s, 6 H), 1.57–1.72 (m, 2 H), 2.46 (s, 3 H), 4.38 (br., 1 H), 7.37 (d, J = 8.1 Hz, 2 H), 7.77 (d, J = 8.7 Hz, 2 H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –134.8 (m, 0.2 F), –135.5 (m, 0.8 F), –136.1 (m, 0.8 F), –136.7 (m, 0.2F) ppm. IR (film): $\tilde{\nu}$ = 3491, 2964, 2932, 2873, 1597, 1462, 1392, 1351, 1315, 1305, 1224, 1145 cm^{-1}. MS (ESI): m/z: 362.1 [M + NH_4]$^+$. $C_{17}H_{22}F_2O_3S$ (344.1): C 59.30, H 6.40; found: C 59.27, H 6.62.

1-[1-(2,2-Difluoro-3,3-dimethylcyclopropylidene)ethylsulfonyl]-4-methylbenzene (5g): Solid, yield 171 mg (60%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.44 (t, J = 1.8 Hz, 6 H), 2.06 (s, 3 H), 2.46 (s, 3 H), 7.37 (d, J = 8.4 Hz, 2 H), 7.75 (d, J = 8.4 Hz, 2 H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –139.9 (s, 2

F) ppm. IR (film): $\tilde{\nu}$ = 2979, 2930, 2874, 1752, 1597, 1461, 1446, 1392, 1351, 1319, 1227, 1161 cm^{-1}. MS (EI): *m/z*: 286 $[M]^+$ (7.25), 65 (100). HRMS (MALDI) calcd. for $C_{14}H_{16}F_2O_2SNa^+$: 309.0744; found: 309.0731.

1-[(2,2-Difluoro-3,3-dimethylcyclopropylidene)iodomethylsulfonyl]-4-methylbenzene (5h): Solid, yield 147 mg (37%). ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.48 (t, *J* = 1.5 Hz, 6 H), 2.48 (s, 3 H), 7.38 (d, *J* = 8.1 Hz, 2 H), 7.83 (d, *J* = 8.1 Hz, 2 H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –141.8 (s, 2 F) ppm. IR (film): $\tilde{\nu}$ = 2950, 1765, 1700, 1593, 1460, 1446, 1390, 1338, 1321, 1209, 1159, 1149, 879 cm^{-1}. MS (ESI): *m/z*: 399.0 $[M + H^+]$. $C_{13}H_{13}F_2IO_2S$(398.0): C 39.21, H 3.29; found: C 39.36, H 3.47.

Typical Procedure for Ring-Opening Reactions between Compounds 2 and I_2: CuI (3 mg, 10 mol-%) was added under N_2 to a solution of **2a** (20 mg) and I_2 (75 mg, 4.0 equiv.) in CH_3CN (5 mL). The mixture was heated to reflux with stirring and monitored by ^{19}F NMR spectroscopy. After completion, aq. $Na_2S_2O_3$ was added and the reaction mixture was extracted with ethyl acetate (3 × 10 mL). The combined organic layer was washed with brine and dried with $MgSO_4$ and, after removal of solvent under reduced pressure, the residue was purified by flash chromatography on a silica gel column to provide **6a** (36 mg, 93%) as a pale yellow solid.

1-{[2-(Difluoroiodomethyl)-3-iodo-3-methylbut-1-enyl]sulfonyl}-4-methylbenzene (6a): Solid, yield 36 mg (93%). ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 2.10 (s, 3 H), 2.48 (s, 3 H), 7.39 (d, *J* = 8.4 Hz, 2 H), 7.70 (s, 1 H), 7.91 (d, *J* = 8.4 Hz, 2 H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –88.2 (s, 2 F) ppm. IR (film): $\tilde{\nu}$ = 2924, 2852, 1596, 1580, 1494, 1458, 1391, 1317, 1305, 1203, 1155 cm^{-1}. MS (ESI): *m/z*: 544.0 $[M + NH_4]^+$. HRMS (MALDI) calcd. for $C_{13}H_{14}F_2I_2O_2SNa^+$: 548.8681; found: 548.8664.

1-{[2-(Difluoroiodomethyl)-3-iodo-3-methylpent-1-enyl]sulfonyl}-4-methylbenzene (6d): Liquid, yield 216 mg (80%). ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 10.9 (t, *J* = 6.9 Hz, 3 H), 1.44–1.53 (m, 1 H), 2.00 (m, 4 H), 2.47 (s, 3 H), 7.38 (d, *J* = 8.4 Hz, 2 H), 7.73 (s, 1 H), 7.90 (d, *J* = 8.4 Hz, 2 H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –85.3 (s, 2 F) ppm. IR (film): $\tilde{\nu}$ = 2957, 2923, 2852, 1736, 1596, 1581, 1455, 1385, 1328, 1305, 1247, 1199, 1152, 1086 cm^{-1}. MS (MALDI) *m/z*: 541 $[M + H^+]$. HRMS (MALDI) calcd. for $C_{14}H_{16}F_2I_2O_2SNa^+$: 562.8820; found: 562.8821.

1-{[3,3-Difluoro-3-iodo-2-(1-iodocyclohexyl)prop-1-enyl]sulfonyl}-4-methylbenzene (6f): Solid, yield 135 mg (95%). ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.10–1.25 (m, 1 H), 1.37–1.50 (m, 2 H), 1.65–1.81 (m, 5 H), 2.06–2.14 (m, 2 H), 2.49 (s, 3 H), 7.40 (d, *J* = 7.8 Hz, 2 H), 7.80 (s, 1 H), 7.94 (d, *J* = 8.1 Hz, 2 H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –88.8 (s, 2 F) ppm. IR (film): $\tilde{\nu}$ = 3017, 2947, 2926, 2860, 2839, 1593, 1579, 1446, 1428, 1338, 1318, 1304, 1251, 1217, 1156, 1143, 1084 cm^{-1}. $C_{16}H_{18}F_2I_2O_2S$ (565.9): C 33.94, H 3.20; found: C 34.23, H 3.19.

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