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Rh 催化 *N*-磺酰腙的偕-二氟烯丙基化反应

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摘要 发展了一种铑催化 *N*-磺酰腙和 3,3-二氟烯丙基硫化物的重排反应合成偕-二氟烯丙基化合物的高效方法. 该方法具有中等至优异的收率和良好的官能团耐受性, 并通过两步一锅、克级合成和产物的衍生化验证了其实用性.
关键词 *N*-磺酰腙; 3,3-二氟烯丙基硫化物; 铑催化; 偕-二氟烯丙基化

Rh-Catalyzed *gem*-Difluoroallylation of *N*-Tosylhydrazones

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Abstract A rhodium-catalyzed rearrangement reaction of *N*-tosylhydrazones and 3,3-difluoroallyl sulfides was developed. This protocal provided a facile and efficient synthesis route to *gem*-difluoroallyl compounds with medium to excellent yield and good functional group tolerance. Moreover, the applicability of current method has been demonstrated by one-pot reaction, gram-scale synthesis and further transformations.
Keywords *N*-tosylhydrazones; 3,3-difluoroallyl sulfides; Rh-catalysis; *gem*-difluoroallylation

1 Introduction

Organofluorine compounds show significant effects in improving the properties of functional molecules, which is due to the special physical and chemical properties of fluorine atoms.[1] Among them, *gem*-difluoro methylene (*gem*-CF_2) is a kind of fluorine-containing superior motif, which has attracted extensive attention in the fields of agricultural chemistry and pharmaceutical chemistry.[2] Therefore, the development of highly effective fluorination and fluoroalkylation methods is of great importance. One of the most effective ways to construct these target molecules is the fluoroalkylation of carbene precursors. In 2012, Hu group[3] reported a mild Cu-mediated trifluoromethylation of α-diazo esters with $TMSCF_3$ to produce α-trifluoromethyl esters, which represents the first example of fluoroalkylation of a non-fluorinated carbene precursor. Subsequently, Hu group[4] developed the *gem*-difluoroolefination, trifluoromethylthiolation, deuterotrifluoromethylation and water-promoted regioselective trifluoromethylation of diazo compounds. In 2016, Szabó group[5] disclosed a rhodium-catalyzed geminal-difunctionalization-based fluorination or trifluoromethylation reaction. In 2017, Zhang group[6] developed a Cu-mediated trifluoromethylation of aromatic α-diazo esters with the Yagupolskii-Umemoto reagent. In 2019, Tsui group[7] developed a copper-mediated trifluoromethylation of α-diazoesters and α-diazoketones with fluoroform-derived $CuCF_3$. Recently, we[8] have developed a blue-light mediated formal Doyle-Kirmse reaction for *gem*-difluoroallylation of aryl diazoesters and a rhodium-catalyzed Doyle-Kirmse reaction of 3,3-difluoroallyl sulfides with *N*-sulfonyl-1,2,3- triazoles.

Aldehydes are the basic components of organic synthesis used in various transformations.[9] *N*-Tosylhydrazones, which are easily derived from the simple condensation of aldehydes or ketones, are also a type of useful and versatile synthons in organic synthesis, especially employed as reaction partners in transition-metal-catalyzed carbene based cross coupling reactions, providing powerful synthetic strategies for the formation of carbon-carbon and carbon-heteroatom bonds.[10] In the past few decades, *N*-tosylhydrazones chemistry has developed rapidly in the transition-metal-catalyzed cross coupling reactions, in which diazo compound is generated *in situ* and then reacts with organometallic species to form metal carbene, followed by carbene migratory insertion and subsequent transformations. Numerous valued coupling products were pro-

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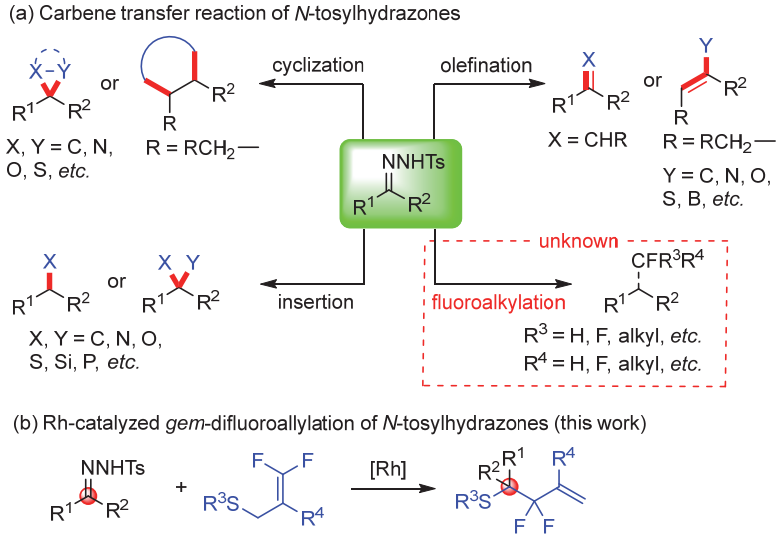
duced under the action of suitable catalysts and coupling partners, including cyclization,[11] insertion,[12] and olefination.[13] However, to our knowledge, direct flouoroalkylation of *N*-tosylhydrazones has not been reported to provide organic fluorides possessing important medicinal value (Scheme 1a). As a continuation of our interest in carbene-based coupling reactions and the synthesis of fluorine-containing compounds,[8,14] herein, we reported a *gem*-difluoroallylation of *N*-tosylhydrazones, which provides an effective method for the synthesis of *gem*-difluoroallyl compounds from readily available *N*-tosylhydrazones (Scheme 1b).

2 Results and discussion

At the beginning of the investigation, basing on our previous work and literature reports,[8] *N*′-(4-chlorobenzylidene)-4-methylbenzenesulfonohydrazide (**1a**, 0.3 mmol), phenyl 2-bromo-3,3-difluoroallyl sulfide (**2a**, 0.2 mmol), $[Rh(OAc)_2]_2$ (2 mol%) and Cs_2CO_3 (0.4 mmol) reacted in 1,2-dichloroethane (DCE) (2 mL) at 100 ℃ for 12 h under an argon atmosphere and the desired *gem*-difluoroallylation product **3a** was isolated in 30% yield (Table 1, Entry 1). A series of catalysts were first examined, and it was observed that $[Rh(esp)]_2$ afforded a satisfactory 81% yield for the reaction (Entries 2～5). Then the bases such as LiO^{t}Bu, NaO^{t}Bu, K_2CO_3 or K_3PO_4, and solvents including MeCN, dioxane or tetrahydrofuran (THF) were also tested, but they could not improve the yield for the reaction (Entries 6～12). When the temperature was reduced or increased, the yields were decreased (Entries 13～15). Further optimization of the molar ratio led to decreased yields (Entries 16, 17). Finally, by lowing the base loading to 1.2 equiv., the desired product was obtained in no significant reduction in yield (Entries 18, 19).

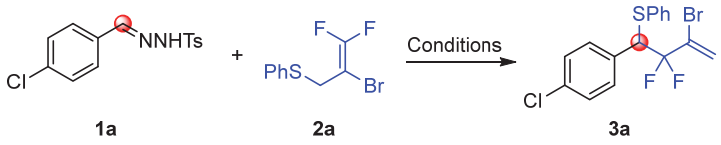
With the optimized conditions in hand (Table 1, Entry 18), the substrate scope of *N*-tosylhydrazones was first screened. As shown in Table 2, *N*-tosylhydrazones of various aromatic aldehydes could react smoothly with **2a**, affording the corresponding *gem*-difluoroallylation products. For the substrates bearing electron-withdrawing substituents in the *para*-position of the aromatic ring, such as chlorine, bromine, cyano, even nitro and sulfonyl, the outcomes were satisfactory (**3a**～**3e**). However, when the substituent was hydrogen atom or electron-donating group, the expected products were isolated in a lower yield (**3f**～**3h**). Surprisingly, only a trace amount of rearrangement product was detected by GC-MS in the reaction of substrate with *p*-$CH_3OC_6H_4$ substituent, presumably due to the reduced stability of ylide intermediate of the extremely electron-rich. To our delight, *N*-tosylhydrazones bearing substituents in *meta*- and *ortho*-positions of aromatic rings with electron-rich or electron-deficient groups all proceeded well to provide the *gem*-difluoroallylation products (**3i**～**3o**) in excellent yields. Substrates bearing naphthyl group were also examined and the products were obtained in excellent yields (**3p**, **3q**). It is noteworthy that cinnamenyl was also well tolerated in the rearrangement with moderate yield (**3r**). In addition, this reaction also occurred smoothly with *N*-tosylhydrazone **1s** derived from trifluoromethyl ketone to produce the corresponding *gem*-difluoroallylation products in good yield (**3s**). *N*-Tosylhydrazones derived from alkyl aldehydes and ketones were also examined; however, only trace rearrangement products were detected by GC-MS in these cases.

Subsequently, the scope of this reaction with a series of 3,3-difluoroallyl sulfides was explored. As shown in Table 3, the substrates bearing substituents with different electronic properties all proceeded well to afford the corresponding products **4a**～**4f** with moderate to excellent yield. Notably, substituents such as benzyl, cyclohexane and thiophene on the 3,3-difluoroallyl sulfides could be well tolerated in the transformation (**4g**～**4i**). Additionally, the reaction also went smoothly with excellent yields when the 2-vinyl bromine atom of sulfide **2a** was replaced by H or *para*-Cl phenyl (**4j** and **4k**).



Scheme 1 Synthetic transformations of *N*-tosylhydrazones

Table 1 Optimization of reaction conditions[a]

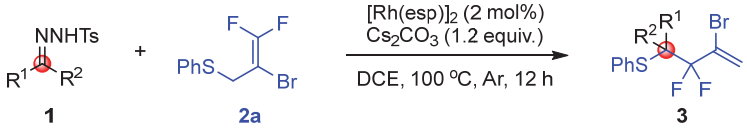


1a **2a** **3a**

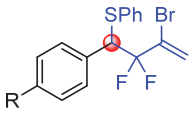
Entry	Catalyst	Base	Solvent	Temperature/℃	Yield[b]/%
1	$[Rh(OAc)_2]_2$	Cs_2CO_3	DCE	100	30
2	$[Rh(esp)]_2$	Cs_2CO_3	DCE	100	81
3	$[Rh(OPiv)_2]_2$	Cs_2CO_3	DCE	100	48
4[c]	$Cu(MeCN)_4PF_6$	Cs_2CO_3	DCE	100	0
5[c]	$AgSbF_6$	Cs_2CO_3	DCE	100	20
6	$[Rh(esp)]_2$	LiO^tBu	DCE	100	53
7	$[Rh(esp)]_2$	NaO^tBu	DCE	100	51
8	$[Rh(esp)]_2$	K_2CO_3	DCE	100	62
9	$[Rh(esp)]_2$	K_3PO_4	DCE	100	36
10	$[Rh(esp)]_2$	Cs_2CO_3	MeCN	100	0
11	$[Rh(esp)]_2$	Cs_2CO_3	Dioxane	100	75
12	$[Rh(esp)]_2$	Cs_2CO_3	THF	100	69
13	$[Rh(esp)]_2$	Cs_2CO_3	DCE	90	70
14	$[Rh(esp)]_2$	Cs_2CO_3	DCE	110	80
15	$[Rh(esp)]_2$	Cs_2CO_3	DCE	120	49
16[d]	$[Rh(esp)]_2$	Cs_2CO_3	DCE	100	78
17[e]	$[Rh(esp)]_2$	Cs_2CO_3	DCE	100	72
18[f]	**$[Rh(esp)]_2$**	**Cs_2CO_3**	**DCE**	**100**	**80**
19[g]	$[Rh(esp)]_2$	Cs_2CO_3	DCE	100	76

[a] Unless otherwise noted, all reactions were carried out with **1a** (0.3 mmol), **2a** (0.2 mmol), catalyst (2.0 mol%), base (0.4 mmol), solvent (2 mL), at temperature (℃) for 12 h under an argon atmosphere. [b] Isolated yields. [c] Catalyst (10.0 mol%), [d] **1a** (0.4 mmol). [e] **1a** (0.2 mmol). [f] Base (0.24 mmol). [g] Base (0.2 mmol).

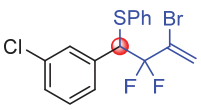
Table 2 Scope of *N*-tosylhydrazones[a,b]



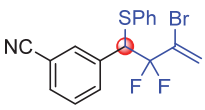
1 **2a** **3**



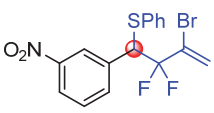
3a, R = Cl, 80%
3b, R = Br, 90%
3c, R = CN, 66%
3d, R = NO_2, 85%
3e, R = SO_2Me, 89%
3f, R = H, 31%
3g, R = Me, 29%
3h, R = ^{i}Pr, 63%



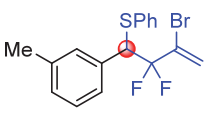
3i, 89%



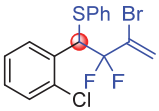
3j, 68%



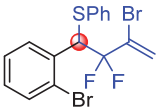
3k, 94%



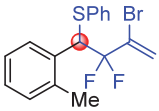
3l, 88%



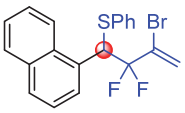
3m, 77%



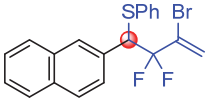
3n, 90%



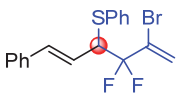
3o, 73%



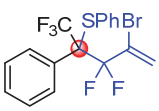
3p, 78%



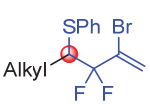
3q, 83%



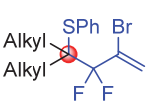
3r, 71%



3s, 78%



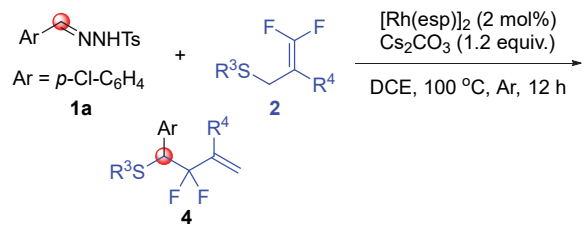
3t, trace

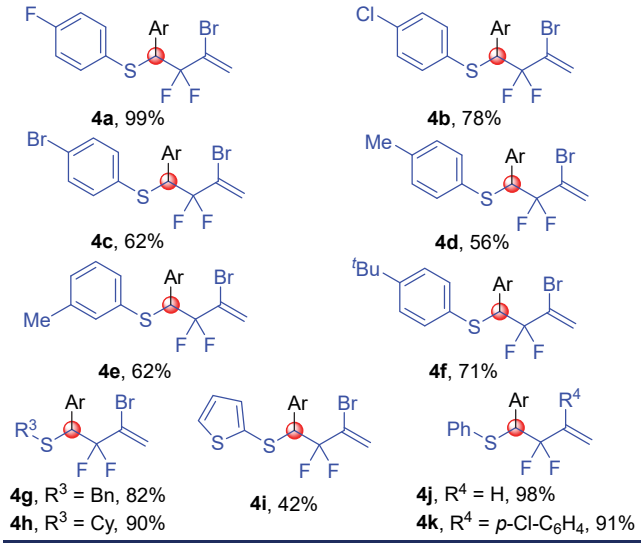


3u, trace

[a] Unless otherwise noted, all reactions were carried out with **1** (0.3 mmol), **2a** (0.2 mmol), $[Rh(esp)]_2$ (2.0 mol%), Cs_2CO_3 (0.24 mmol), DCE (2 mL), at 100 ℃ for 12 h under an argon atmosphere. [b] Isolated yields.

Table 3 Scope of 3,3-difluoroallyl sulfides[a,b]



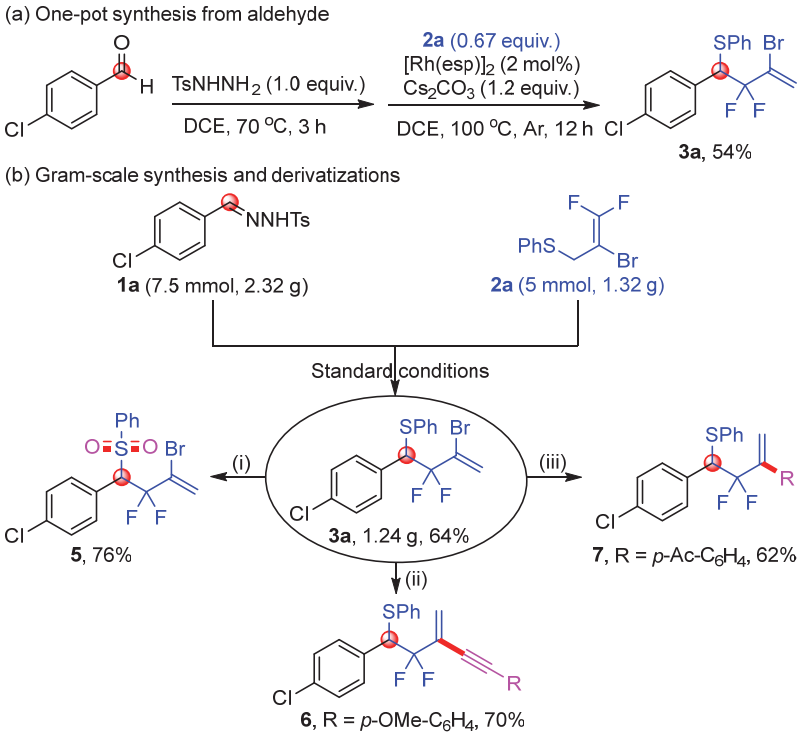


[a] Unless otherwise noted, all reactions were carried out with **1a** (0.3 mmol), **2** (0.2 mmol), $[Rh(esp)]_2$ (2.0 mol%), Cs_2CO_3 (0.24 mmol), DCE (2 mL), at 100 ℃ for 12 h under an argon atmosphere. [b] Isolated yields.

To simplify the reaction protocol, one-pot synthesis was carried out directly from *p*-chlorobenzaldehyde (Scheme 2a). After the complete formation of *N*-tosylhydrazones, the rearrangement worked smoothly to afford the *gem*-difluoroallylation product **3a** in 54% yields. To demonstrate the practical applicability of this method, we also performed the gram scale reaction (Scheme 2b). The *gem*-difluoroallylation product **3a** (1.24 g) was obtained with 64% yield under the standard reaction conditions. The product *gem*-difluoroallyl containing sulfide **3a** could be easily oxidized by *m*-CPBA to the corresponding sulfone derivative **5** in 76% yield through simple operation. Furthermore, we have demonstrated that the vinyl bromine atom of **3a** could smoothly undergo Sonogashira and Suzuki-Miyaura coupling reactions to give the corresponding functionalized products **6** and **7** in yields of 70% and 62%, respectively.

3 Conclusions

In summary, a straightforward fluoroalkylation reaction of *N*-tosylhydrazones using rhodium catalysis has been developed, which allows the synthesis of structurally diverse *gem*-difluoroallylated compounds containing convertible sulfur and bromine groups. The current methods have been verified its practicability through gram reaction, one-pot operation and product derivatization, which may find a wide range of applications in synthetic and pharmaceutical chemistry.



Reaction conditions: (i) **3a** (0.2 mmol), *m*-CPBA (2.5 equiv.), DCM, 0 ℃, 12 h; (ii) **3a** (0.2 mmol), 4-methoxypheny (1.5 equiv.), $Pd(PPh_3)_2Cl_2$ (2.5 mol%), CuI (5.0 mol%), Dry TEA, 50 ℃, Argon, 12 h; (iii) **3a** (0.2 mmol), 4-acetylphenylboronic acid (2.0 equiv.), $Pd(PPh_3)_4$ (5.0 mol%), Toluene/H_2O (*V*∶*V*=4∶1), r.t., 18 h. Yield of the isolated product

Scheme 2 One-pot reaction, gram-scale synthesis and derivatizations of **3a**

4 Experimental section

4.1 Instruments and reagents

^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were measured in $CDCl_3$ and recorded on Brucker ARX 600, 500 or Anasazi Eft 90 spectrometer. Exact masses (HRMS) were recorded on a high resolution magnetic mass spectrometer using electron impact ion source (EI) techniques. Analytical thin layer chromatography (TLC) was carried out using GF254 commercial silica gel plates. Unless otherwise stated, all chemical reagents and solvents (analytical grade) can be used without further purification.

4.2 General procedure for the synthesis of *gem*-difluoroallyl sulfane **3** (**3a** as an example)

Under argon atmosphere, $[Rh(esp)]_2$ (3.0 mg, 0.004 mmol), Cs_2CO_3 (78.2 mg, 0.24 mmol), *N*′-(4-chlorobenzylidene)-4-methylbenzenesulfonohydrazide **1a** (92.6 mg, 0.30 mmol) were successively added to a 10 mL Schlenk tube. The reaction tube was degassed three times with argon, and DCE (2.0 mL) was added, followed by the addition of phenyl 2-bromo-3,3-difluoroallyl sulfide **2a** (53.0 mg, 0.20 mmol) through microinjector. The reaction mixture was stirred at 100 ℃ for 12 h. Upon cooling down to room temperature, the solvent was evaporated under vacuum. The crude product was purified by column chromatography on silica gel with petroleum ether as the eluant, giving the pure product **3a** as a colorless oil liquid (62.3 mg, 80% yield).

(3-Bromo-1-(4-chlorophenyl)-2,2-difluorobut-3-en-1-yl)(phenyl)sulfane (**3a**): Colorless oil, 80% isolated yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.35～7.28 (m, 4H), 7.24 (dd, J=14.1, 7.2 Hz, 5H), 6.21 (s, 1H), 5.81 (s, 1H), 4.74 (t, J=15.1 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 134.44, 133.84 (d, J=2.6 Hz), 133.31, 133.27, 131.01, 129.23, 128.71, 128.40, 123.56 (t, J=31.0 Hz), 123.42 (t, J=6.4 Hz), 118.61 (t, J=251.0 Hz), 57.31 (t, J=25.9 Hz); ^{19}F NMR (471 MHz, $CDCl_3$) δ: −98.99 (dd, J=243.4, 15.0 Hz, 1F), −100.93 (dd, J=243.4, 15.1 Hz, 1F); HRMS (EI) calcd for $C_{16}H_{12}BrClF_2S$ $[M]^+$ 387.9500, found 387.9498.

(3-Bromo-1-(4-bromophenyl)-2,2-difluorobut-3-en-1-yl)(phenyl)sulfane (**3b**): Colorless oil, 90% isolated yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.42 (d, J=8.5 Hz, 2H), 7.33 (d, J=7.7 Hz, 2H), 7.23 (d, J=7.0 Hz, 5H), 6.21 (d, J=2.5 Hz, 1H), 5.81 (d, J=2.4 Hz, 1H), 4.73 (t, J=15.1 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 134.37 (d, J=2.5 Hz), 133.30, 133.24, 131.67, 131.31, 129.23, 128.41, 123.52 (t, J=31.0 Hz), 123.45 (t, J=6.5 Hz), 122.65, 118.54 (t, J=251.0 Hz), 57.38 (t, J=25.9 Hz); ^{19}F NMR (471 MHz, $CDCl_3$) δ: −98.92 (dd, J=243.4, 14.9 Hz, 1F), −100.95 (dd, J=243.4, 15.2 Hz, 1F); HRMS (EI) calcd for $C_{16}H_{12}Br_2F_2S$ $[M]^+$ 433.8974, found 433.8977.

4-(3-Bromo-2,2-difluoro-1-(phenylthio)but-3-en-1-yl)-benzonitrile (**3c**): Colorless oil, 66% isolated yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.58 (d, J=8.4 Hz, 2H), 7.47 (d, J=8.2 Hz, 2H), 7.27 (ddd, J=16.6, 10.9, 6.4 Hz, 5H), 6.27 (d, J=2.1 Hz, 1H), 5.87 (s, 1H), 4.79 (dd, J=16.4, 13.6 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 140.65 (d, J = 2.2 Hz), 133.59, 132.47, 132.21, 130.47, 129.36, 128.79, 123.75 (t, J=6.5 Hz), 123.17 (t, J=30.7 Hz), 118.51, 118.41 (t, J=251.4 Hz), 112.40, 57.73 (t, J=26.1 Hz); ^{19}F NMR (471 MHz, $CDCl_3$) δ: −97.40 (dd, J=244.5, 13.4 Hz, 1F), −101.90 (dd, J=244.6, 16.5 Hz, 1F); HRMS (EI) calcd for $C_{17}H_{12}BrF_2NS$ $[M]^+$ 378.9842, found 378.9838.

(3-Bromo-2,2-difluoro-1-(4-nitrophenyl)but-3-en-1-yl)(phenyl)sulfane (**3d**): Yellow oil, 85% isolated yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.15 (d, J=8.8 Hz, 2H), 7.54 (d, J=8.6 Hz, 2H), 7.32 (d, J=6.7 Hz, 2H), 7.27～7.21 (m, 3H), 6.29 (d, J=2.2 Hz, 1H), 5.88 (d, J=1.2 Hz, 1H), 4.86 (dd, J=16.5, 13.5 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 147.77, 142.58 (d, J=2.1 Hz), 133.60, 132.23, 130.65, 129.40, 128.85, 123.87 (t, J=6.4 Hz), 123.60, 122.98 (t, J=30.6 Hz), 118.33 (t, J=251.5 Hz), 57.41 (t, J=26.1 Hz); ^{19}F NMR (85 MHz, $CDCl_3$) δ: −92.18 (dd, J=244.5, 16.3 Hz, 1F), −97.66 (dd, J=244.5, 13.6 Hz, 1F); HRMS (EI) calcd for $C_{16}H_{12}BrF_2NO_2S$ $[M]^+$ 398.9740, found 398.9738.

(3-Bromo-2,2-difluoro-1-(4-(methylsulfonyl)phenyl)but-3-en-1-yl)(phenyl)sulfane (**3e**): Colorless oil, 89% isolated yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.88 (d, J=8.4 Hz, 2H), 7.58 (d, J=8.3 Hz, 2H), 7.32 (dd, J=8.0, 1.4 Hz, 2H), 7.26 (dt, J=13.9, 5.0 Hz, 3H), 6.30 (d, J=2.1 Hz, 1H), 5.88 (d, J=1.2 Hz, 1H), 4.84 (dd, J=17.0, 13.1 Hz, 1H), 3.06 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 141.56 (d, J=1.9 Hz), 140.33, 133.40, 132.47, 130.67, 129.36, 128.74, 127.51, 123.84 (t, J=6.4 Hz), 123.01 (t, J=30.6 Hz), 118.40 (t, J=251.3 Hz), 57.45 (t, J=26.0 Hz), 44.51; ^{19}F NMR (85 MHz, $CDCl_3$) δ: −93.05 (dd, J=244.4, 16.6 Hz, 1F), −99.02 (dd, J=244.6, 13.3 Hz, 1F); HRMS (EI) calcd for $C_{17}H_{15}BrF_2O_2S_2$ $[M]^+$ 431.9665, found 431.9664.

(3-Bromo-2,2-difluoro-1-phenylbut-3-en-1-yl)(phenyl)-sulfane (**3f**): Colorless oil, 31% isolated yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.35 (dd, J=13.0, 4.2 Hz, 4H), 7.31～7.26 (m, 3H), 7.24～7.20 (m, 3H), 6.17 (d, J=2.4 Hz, 1H), 5.88～5.69 (m, 1H), 4.78 (t, J=15.3 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 135.22, 133.79, 133.03, 129.59, 129.10, 128.49, 128.46, 128.10, 123.73 (t, J=31.1 Hz), 123.24 (t, J=6.4 Hz), 118.81 (t, J=250.8 Hz), 57.74 (t, J=25.7 Hz); ^{19}F NMR (85 MHz, $CDCl_3$) δ: −94.64 (d, J=5.9 Hz, 1F), −94.82 (d, J=6.1 Hz, 1F); HRMS (EI) calcd for $C_{16}H_{13}BrF_2S$ $[M]^+$ 353.9889, found 353.9890.

(3-Bromo-2,2-difluoro-1-(*p*-tolyl)but-3-en-1-yl)(phenyl)sulfane (**3g**): Colorless oil, 29% isolated yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.36 (dd, J=6.4, 3.0 Hz, 2H), 7.28～7.21 (m, 5H), 7.10 (d, J=7.9 Hz, 2H), 6.18 (d, J=2.4 Hz, 1H), 5.77 (d, J=2.3 Hz, 1H), 4.75 (t, J=15.3 Hz, 1H), 2.32 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 138.29, 134.14, 132.92, 132.23, 129.46, 129.24, 129.08, 127.99, 123.94 (t, J=31.2 Hz), 123.14 (t, J=6.4 Hz), 118.88 (t, J=250.7 Hz), 57.51 (t, J=25.8 Hz), 21.31; ^{19}F NMR (471 MHz, $CDCl_3$) δ: −99.59 (dd, J=242.6, 15.6 Hz, 1F),

−100.16 (dd, J=242.4, 14.9 Hz, 1F); HRMS (EI) calcd for $C_{17}H_{15}BrF_2S$ $[M]^+$ 368.0046, found 368.0048.

(3-Bromo-2,2-difluoro-1-(4-isopropylphenyl)but-3-en-1-yl)(phenyl)sulfane (**3h**): Colorless oil, 63% isolated yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.36 (dd, J=6.4, 3.1 Hz, 2H), 7.28 (d, J=8.0 Hz, 2H), 7.24～7.19 (m, 3H), 7.14 (d, J=8.2 Hz, 2H), 6.18 (d, J=2.5 Hz, 1H), 5.77 (d, J=2.4 Hz, 1H), 4.76 (t, J=15.3 Hz, 1H), 3.05～2.67 (m, 1H), 1.23 (d, J=6.9 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 149.12, 134.27, 132.86, 132.48, 129.45, 129.05, 127.94, 126.58, 123.98 (t, J=31.2 Hz), 123.15 (t, J=6.4 Hz), 118.92 (t, J=250.6 Hz), 57.41 (t, J=25.8 Hz), 33.88, 23.99; ^{19}F NMR (471 MHz, $CDCl_3$) δ: −99.27 (dd, J=242.4, 15.5 Hz, 1F), −100.28 (dd, J=242.4, 14.9 Hz, 1F); HRMS (EI) calcd for $C_{19}H_{19}BrF_2S$ $[M]^+$ 396.0359, found 396.0362.

(3-Bromo-1-(3-chlorophenyl)-2,2-difluorobut-3-en-1-yl)(phenyl)sulfane (**3i**): Colorless oil, 89% isolated yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.38 (s, 1H), 7.36～7.31 (m, 2H), 7.28～7.19 (m, 6H), 6.24 (d, J=2.6 Hz, 1H), 5.83 (d, J=2.6 Hz, 1H), 4.77～4.68 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 137.28 (d, J=2.5 Hz), 134.35, 133.34, 133.21, 129.74, 129.68, 129.24, 128.70, 128.46, 127.93, 123.52 (t, J=30.9 Hz), 123.50 (t, J=6.4 Hz), 118.58 (t, J=251.1 Hz), 57.44 (t, J=26.0 Hz); ^{19}F NMR (471 MHz, $CDCl_3$) δ: −98.33 (dd, J=243.7, 14.4 Hz, 1F), −101.22 (dd, J=243.7, 15.7 Hz, 1F); HRMS (EI) calcd for $C_{16}H_{12}BrClF_2S$ $[M]^+$ 387.9500, found 387.9499.

3-(3-Bromo-2,2-difluoro-1-(phenylthio)but-3-en-1-yl)-benzonitrile (**3j**): Colorless oil, 68% isolated yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.65 (s, 1H), 7.59 (dd, J=16.7, 7.8 Hz, 2H), 7.41 (t, J=7.8 Hz, 1H), 7.31 (d, J=6.5 Hz, 2H), 7.28～7.20 (m, 3H), 6.28 (d, J=2.5 Hz, 1H), 5.87 (s, 1H), 4.78 (dd, J=16.7, 13.3 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 136.95 (d, J=2.2 Hz), 134.13, 133.55, 133.22, 132.41, 132.07, 129.36, 129.31, 128.79, 123.75 (t, J=6.5 Hz), 123.16 (t, J=30.7 Hz), 118.47, 118.38 (t, J=251.3 Hz), 112.70, 57.30 (t, J=26.1 Hz); ^{19}F NMR (471 MHz, $CDCl_3$) δ: −97.18 (dd, J=244.7, 13.1 Hz, 1F), −102.31 (dd, J=244.7, 16.7 Hz, 1F); HRMS (EI) calcd for $C_{17}H_{12}BrF_2NS$ $[M]^+$ 378.9842, found 378.9844.

(3-Bromo-2,2-difluoro-1-(3-nitrophenyl)but-3-en-1-yl)-(phenyl)sulfane (**3k**): Yellow oil, 94% isolated yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.24 (s, 1H), 8.16 (d, J=8.2 Hz, 1H), 7.72 (d, J=7.7 Hz, 1H), 7.49 (t, J=8.0 Hz, 1H), 7.33 (dd, J=7.9, 1.4 Hz, 2H), 7.28～7.22 (m, 3H), 6.32 (d, J=1.6 Hz, 1H), 5.90 (d, J=1.6 Hz, 1H), 4.88 (dd, J=17.2, 12.7 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 148.14, 137.37 (d, J=2.1 Hz), 135.80, 133.60, 132.25, 129.47, 129.41, 128.85, 124.72, 123.87 (t, J=6.5 Hz), 123.52, 123.06 (t, J=30.6 Hz), 120.11～116.60 (m), 57.18 (d, J=26.1 Hz); ^{19}F NMR (85 MHz, $CDCl_3$) δ: −92.29 (d, J=244.9 Hz, 1F), −99.00 (d, J=244.7 Hz, 1F); HRMS (EI) calcd for $C_{16}H_{12}BrF_2NO_2S$ $[M]^+$ 398.9740, found 398.9739.

(3-Bromo-2,2-difluoro-1-(*m*-tolyl)but-3-en-1-yl)-(phenyl)sulfane (**3l**): Colorless oil, 88% isolated yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.36 (dd, J=6.3, 3.2 Hz, 2H), 7.24～7.20 (m, 3H), 7.17 (d, J=6.2 Hz, 3H), 7.10 (s, 1H), 6.19 (d, J=2.5 Hz, 1H), 5.77 (d, J=2.5 Hz, 1H), 4.74 (t, J=15.3 Hz, 1H), 2.31 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 138.14, 135.15 (d, J=2.3 Hz), 134.11, 132.97, 130.25, 129.25, 129.07, 128.36, 128.03, 126.69, 123.94 (t, J=31.2 Hz), 123.17 (t, J=6.4 Hz), 118.88 (t, J=250.7 Hz), 57.70 (t, J=25.8 Hz), 21.52; ^{19}F NMR (471 MHz, $CDCl_3$) δ: −99.10 (dd, J=242.7, 15.4 Hz, 1F), −100.26 (dd, J=242.6, 15.0 Hz, 1F); HRMS (EI) calcd for $C_{17}H_{15}BrF_2S$ $[M]^+$ 368.0046, found 368.0047.

(3-Bromo-1-(2-chlorophenyl)-2,2-difluorobut-3-en-1-yl)(phenyl)sulfane (**3m**): Colorless oil, 77% isolated yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.63 (d, J=7.6 Hz, 1H), 7.41～7.35 (m, 2H), 7.33 (dd, J=7.8, 1.5 Hz, 1H), 7.27～7.18 (m, 5H), 6.30 (dd, J=2.5, 1.7 Hz, 1H), 5.86 (dd, J=2.4, 1.9 Hz, 1H), 5.60 (dd, J=18.9, 11.4 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 134.79, 133.28 (d, J=1.8 Hz), 133.13, 133.08, 131.11, 129.56, 129.46, 129.10, 128.26, 127.18, 124.00 (t, J=30.9 Hz), 123.45 (t, J=6.3 Hz), 118.90 (t, J=251.0 Hz), 52.34 (t, J=26.1 Hz); ^{19}F NMR (471 MHz, $CDCl_3$) δ: −95.44 (dd, J=244.8, 11.4 Hz, 1F), −101.53 (dd, J=244.9, 18.8 Hz, 1F); HRMS (EI) calcd for $C_{16}H_{12}BrClF_2S$ $[M]^+$ 387.9500, found 387.9502.

(3-Bromo-1-(2-bromophenyl)-2,2-difluorobut-3-en-1-yl)(phenyl)sulfane (**3n**): Colorless oil, 90% isolated yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.63 (d, J=7.9 Hz, 1H), 7.51 (dd, J=8.0, 1.0 Hz, 1H), 7.41～7.35 (m, 2H), 7.32～7.26 (m, 1H), 7.23 (dd, J=5.1, 1.9 Hz, 3H), 7.12 (td, J=7.9, 1.6 Hz, 1H), 6.38～6.21 (m, 1H), 5.92～5.73 (m, 1H), 5.59 (dd, J=19.6, 10.7 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 134.99 (d, J=1.7 Hz), 133.31, 132.92, 132.83, 131.24 (d, J=2.4 Hz), 129.81, 129.07, 128.30, 127.79, 125.73, 124.04 (t, J=30.9 Hz), 123.58～123.38 (m), 118.91 (t, J=251.1 Hz), 55.05 (t, J=25.9 Hz); ^{19}F NMR (471 MHz, $CDCl_3$) δ: −94.72 (dd, J=245.3, 10.6 Hz, 1F), −101.86 (dd, J=245.3, 19.5 Hz, 1F); HRMS (EI) calcd for $C_{16}H_{12}Br_2F_2S$ $[M]^+$ 433.8974, found 433.8972.

(3-Bromo-2,2-difluoro-1-(*o*-tolyl)but-3-en-1-yl)-(phenyl)sulfane (**3o**): Colorless oil, 73% isolated yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.53 (d, J=5.6 Hz, 1H), 7.34 (dd, J=7.7, 1.6 Hz, 2H), 7.26～7.13 (m, 5H), 7.10 (d, J=8.8 Hz, 1H), 6.29 (d, J=1.7 Hz, 1H), 5.83 (s, 1H), 5.12 (dd, J=18.5, 12.2 Hz, 1H), 2.24 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 136.92, 133.67 (d, J=1.6 Hz), 133.60, 130.30, 129.54, 129.03, 128.29, 128.21, 126.43, 124.25 (t, J=31.2 Hz), 123.23 (t, J=6.3 Hz), 119.21 (t, J=250.5 Hz), 52.55 (t, J=26.1 Hz), 19.88; ^{19}F NMR (471 MHz, $CDCl_3$) δ: −96.11 (dd, J=244.6, 12.0 Hz, 1F), −100.89 (dd, J=244.8, 17.7 Hz, 1F); HRMS (EI) calcd for $C_{17}H_{15}BrF_2S$ $[M]^+$ 368.0046, found 368.0048.

(3-Bromo-2,2-difluoro-1-(naphthalen-1-yl)but-3-en-1-yl)(phenyl)sulfane (**3p**): Colorless oil, 78% isolated yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.01 (d, J=8.4 Hz, 1H), 7.84 (d, J=7.9 Hz, 1H), 7.79 (d, J=8.2 Hz, 2H), 7.48 (ddd, J=19.7, 15.1, 7.4 Hz, 3H), 7.32 (d, J=6.4 Hz, 2H),

7.15 (d, J=7.3 Hz, 3H), 6.30 (s, 1H), 5.80 (t, J=14.9 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 133.99, 133.75, 133.05, 131.93, 131.14, 129.18, 129.09, 129.04, 128.11, 126.81, 125.78, 125.43, 124.35 (t, J=31.2 Hz), 123.35 (t, J=6.1 Hz), 122.76, 119.27 (t, J=250.6 Hz), 51.29 (t, J=26.1 Hz); ^{19}F NMR (471 MHz, $CDCl_3$) δ: −95.62 (dd, J=244.4, 11.5 Hz, 1F), −100.40 (dd, J=244.5, 17.7 Hz, 1F); HRMS (EI) calcd for $C_{20}H_{15}BrF_2S$ $[M]^+$ 404.0046, found 404.0045.

(3-Bromo-2,2-difluoro-1-(naphthalen-2-yl)but-3-en-1-yl)(phenyl)sulfane (**3q**): Colorless oil, 83% isolated yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.79 (d, J=8.7 Hz, 2H), 7.75 (dd, J=10.1, 5.9 Hz, 2H), 7.58 (s, 1H), 7.45 (p, J=5.6 Hz, 2H), 7.35 (dd, J=7.2, 2.4 Hz, 2H), 7.21～7.14 (m, 3H), 6.18 (d, J=2.6 Hz, 1H), 5.74 (d, J=2.6 Hz, 1H), 4.94 (t, J=15.3 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 133.78, 133.22, 133.18, 133.05, 132.67, 129.14, 129.11, 128.41, 128.19 (d, J=0.7 Hz), 127.76, 126.86, 126.56, 126.39, 123.79 (t, J=31.1 Hz), 123.28 (t, J=6.4 Hz), 118.96 (t, J=250.9 Hz), 58.23 (t, J=25.8 Hz); ^{19}F NMR (471 MHz, $CDCl_3$) δ: −99.06 (dd, J=243.0, 15.7 Hz, 1F), −99.74 (dd, J=243.0, 14.8 Hz, 1F); HRMS (EI) calcd for $C_{20}H_{15}BrF_2S$ $[M]^+$ 404.0046, found 404.0046.

(*E*)-(5-Bromo-4,4-difluoro-1-phenylhexa-1,5-dien-3-yl)(phenyl)sulfane (**3r**): Colorless oil, 71% isolated yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.50 (dd, J=6.6, 3.0 Hz, 2H), 7.33～7.21 (m, 8H), 6.35 (dd, J=25.4, 9.1 Hz, 2H), 6.11 (dd, J=15.7, 9.6 Hz, 1H), 5.92 (d, J=2.5 Hz, 1H), 4.32 (td, J=14.3, 9.6 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 136.29, 135.04, 134.72, 132.62, 129.15, 128.71, 128.61, 128.25, 126.76, 123.91 (t, J=30.9 Hz), 122.97 (t, J=6.5 Hz), 121.79 (d, J=2.6 Hz), 118.72 (t, J=250.2 Hz), 56.75 (t, J=26.2 Hz); ^{19}F NMR (471 MHz, $CDCl_3$) δ: −98.79 (dd, J=243.2, 13.8 Hz, 1F), −102.62 (dd, J=243.2, 14.7 Hz, 1F); HRMS (EI) calcd for $C_{18}H_{15}BrF_2S$ $[M]^+$ 380.0046, found 380.0048.

(4-Bromo-1,1,1,3,3-pentafluoro-2-phenylpent-4-en-2-yl)(phenyl)sulfane (**3s**): Colorless oil, 78% isolated yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.86 (s, 2H), 7.46 (d, J=7.6 Hz, 2H), 7.37～7.30 (m, 3H), 7.26 (dd, J=16.2, 8.8 Hz, 1H), 7.17 (t, J=7.7 Hz, 2H), 6.02 (s, 1H), 5.95 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 137.29, 131.08 (d, J=2.0 Hz), 130.46, 129.99, 129.35, 128.64, 128.06, 126.90 (t, J=6.6 Hz), 124.95 (dd, J=286.0, 3.1 Hz), 122.17 (t, J=31.8 Hz), 116.92 (dd, J=260.4, 258.8 Hz), 70.52 (dd, J=50.5, 24.4 Hz); ^{19}F NMR (471 MHz, $CDCl_3$) δ: −58.01 (dd, J=13.4, 10.0 Hz, 1F), −88.34 (dq, J=253.6, 9.6 Hz, 1F), −89.68 (dq, J=253.7, 13.7 Hz, 3F); HRMS (EI) calcd for $C_{17}H_{12}BrF_5S$ $[M]^+$ 421.9763, found 421.9764.

(3-Bromo-1-(4-chlorophenyl)-2,2-difluorobut-3-en-1-yl)(4-fluorophenyl)sulfane (**4a**): Colorless oil, 99% isolated yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.31 (dd, J=8.8, 5.3 Hz, 2H), 7.28～7.23 (m, 4H), 6.92 (t, J=8.7 Hz, 2H), 6.21 (d, J=2.7 Hz, 1H), 5.93～5.72 (m, 1H), 4.65 (t, J=15.2 Hz, 1H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ: 164.19, 162.20, 136.41 (d, J=8.4 Hz), 134.54, 133.57 (d, J=2.5 Hz), 130.98, 128.76, 128.10 (d, J=3.4 Hz), 123.50 (t, J=30.9 Hz), 123.44 (t, J=6.5 Hz), 118.59 (t, J=251.1 Hz), 116.47, 116.30, 57.97 (t, J=25.9 Hz); ^{19}F NMR (471 MHz, $CDCl_3$) δ: −99.36 (dd, J=243.5, 15.3 Hz, 1F), −100.62 (dd, J=243.5, 14.9 Hz, 1F), −111.95～−112.05 (m, 1F); HRMS (EI) calcd for $C_{16}H_{11}BrClF_3S$ $[M]^+$ 405.9405, found 405.9406.

(3-Bromo-1-(4-chlorophenyl)-2,2-difluorobut-3-en-1-yl)(4-chlorophenyl)sulfane (**4b**): Colorless oil, 78% isolated yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.29～7.24 (m, 6H), 7.23～7.19 (m, 2H), 6.20 (d, J=2.7 Hz, 1H), 5.81 (d, J=2.6 Hz, 1H), 4.69 (t, J=15.0 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 134.88, 134.66, 133.45 (d, J=2.2 Hz), 131.63, 130.96, 132.10～129.12 (m), 129.45, 128.84, 123.53 (t, J=6.4 Hz), 123.40 (t, J=30.9 Hz), 118.53 (t, J=251.1 Hz), 57.53 (t, J=26.0 Hz); ^{19}F NMR (471 MHz, $CDCl_3$) δ: −99.59 (dd, J=243.5, 15.3 Hz, 1F), −100.55 (dd, J=243.5, 14.6 Hz, 1F); HRMS (EI) calcd for $C_{16}H_{11}BrCl_2F_2S$ $[M]^+$ 421.9110, found 421.9108.

(3-Bromo-1-(4-chlorophenyl)-2,2-difluorobut-3-en-1-yl)(4-bromophenyl)sulfane (**4c**): Colorless oil, 62% isolated yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.39～7.33 (m, 2H), 7.31～7.25 (m, 4H), 7.21～7.16 (m, 2H), 6.20 (d, J=2.7 Hz, 1H), 5.81 (d, J=2.7 Hz, 1H), 4.70 (t, J=15.0 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 134.95, 134.67, 133.40, 132.38, 132.33, 130.94, 128.84, 123.53 (t, J=6.4 Hz), 123.36 (t, J=30.8 Hz), 122.95, 118.51 (t, J=251.2 Hz), 57.37 (t, J=26.0 Hz); ^{19}F NMR (471 MHz, $CDCl_3$) δ: −99.58 (dd, J=243.5, 15.4 Hz, 1F), −100.48 (dd, J=243.5, 14.5 Hz, 1F); HRMS (EI) calcd for $C_{16}H_{11}Br_2ClF_2S$ $[M]^+$ 467.8584, found 467.8588.

(3-Bromo-1-(4-chlorophenyl)-2,2-difluorobut-3-en-1-yl)(*p*-tolyl)sulfane (**4d**): Colorless oil, 56% isolated yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.27 (q, J=8.8 Hz, 4H), 7.21 (d, J=8.1 Hz, 2H), 7.03 (d, J=7.9 Hz, 2H), 6.21 (d, J=2.6 Hz, 1H), 5.81 (d, J=2.6 Hz, 1H), 4.67 (t, J=15.3 Hz, 1H), 2.29 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 138.75, 134.34, 134.01 (d, J=2.6 Hz), 133.84, 131.03, 130.00, 129.54, 128.66, 123.67 (t, J=31.0 Hz), 123.33 (t, J=6.4 Hz), 118.65 (t, J=250.9 Hz), 57.70 (t, J=25.8 Hz), 21.28; ^{19}F NMR (471 MHz, $CDCl_3$) δ: −98.81 (dd, J=243.4, 14.9 Hz, 1F), −101.08 (dd, J=243.4, 15.5 Hz, 1F); HRMS (EI) calcd for $C_{17}H_{14}BrClF_2S$ $[M]^+$ 401.9656, found 401.9658.

(3-Bromo-1-(4-chlorophenyl)-2,2-difluorobut-3-en-1-yl)(*m*-tolyl)sulfane (**4e**): Colorless oil, 62% isolated yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.33～7.22 (m, 4H), 7.15～7.08 (m, 3H), 7.05 (s, 1H), 6.20 (d, J=2.6 Hz, 1H), 5.81 (d, J=2.5 Hz, 1H), 4.73 (t, J=15.1 Hz, 1H), 2.26 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 139.04, 134.39, 133.98 (d, J=2.5 Hz), 133.82, 133.01, 131.02, 130.13, 129.19, 129.03, 128.67, 123.88～123.35 (m), 123.39 (t, J=6.4 Hz), 118.63 (t, J=250.9 Hz), 57.20 (t, J=25.9 Hz), 21.34; ^{19}F NMR (471 MHz, $CDCl_3$) δ: −98.98 (dd, J=243.3, 15.0 Hz, 1F), −100.84 (dd, J=243.3, 15.1 Hz, 1F); HRMS (EI) calcd for $C_{17}H_{14}BrClF_2S$ $[M]^+$ 401.9656, found 401.9655.

(3-Bromo-1-(4-chlorophenyl)-2,2-difluorobut-3-en-1-yl)(4-(*tert*-butyl)phenyl)sulfane (**4f**): White solid, 71% isolated yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.30 (d, J=8.6 Hz, 2H), 7.28～7.23 (m, 6H), 6.20 (d, J=2.6 Hz, 1H), 5.80 (d, J=2.6 Hz, 1H), 4.70 (t, J=15.3 Hz, 1H), 1.27 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 151.78, 134.34, 134.13 (d, J=2.6 Hz), 133.20, 131.04, 129.78, 128.66, 126.28, 123.68 (t, J=31.1 Hz), 123.35 (t, J=6.4 Hz), 118.66 (t, J=250.8 Hz), 57.43 (t, J=25.9 Hz), 34.73, 31.33; ^{19}F NMR (471 MHz, $CDCl_3$) δ: −98.93 (dd, J=243.5, 15.0 Hz, 1F), −100.80 (dd, J=243.5, 15.3 Hz, 1F); HRMS (EI) calcd for $C_{20}H_{20}BrClF_2S$ $[M]^+$ 444.0126, found 444.0124.

Benzyl(3-bromo-1-(4-chlorophenyl)-2,2-difluorobut-3-en-1-yl)sulfane (**4g**): Colorless oil, 82% isolated yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.33～7.20 (m, 9H), 6.11 (d, J=2.6 Hz, 1H), 5.74 (d, J=2.5 Hz, 1H), 4.26 (t, J=15.0 Hz, 1H), 3.67 (dd, J=110.6, 13.4 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 136.69, 134.42, 133.40 (d, J=3.1 Hz), 131.09, 129.36, 128.77, 128.69, 127.61, 123.64 (t, J=31.1 Hz), 123.08 (t, J=6.4 Hz), 119.00 (t, J=250.2 Hz), 51.26 (t, J=26.2 Hz), 36.63; ^{19}F NMR (471 MHz, $CDCl_3$) δ: −98.87 (dd, J=242.5, 15.0 Hz, 1F), −100.83 (dd, J=242.5, 14.9 Hz, 1F); HRMS (EI) calcd for $C_{17}H_{14}BrClF_2S$ $[M]^+$ 401.9656, found 401.9656.

(3-Bromo-1-(4-chlorophenyl)-2,2-difluorobut-3-en-1-yl)(cyclohexyl)sulfane (**4h**): Colorless oil, 90% isolated yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.38 (d, J=8.4 Hz, 2H), 7.33～7.28 (m, 2H), 6.16 (d, J=2.3 Hz, 1H), 5.79 (d, J=1.3 Hz, 1H), 4.53 (dd, J=15.7, 14.3 Hz, 1H), 2.66～2.55 (m, 1H), 1.94 (d, J=11.5 Hz, 1H), 1.84 (d, J=11.8 Hz, 1H), 1.79～1.64 (m, 2H), 1.56 (d, J=4.7 Hz, 1H), 1.27 (ddd, J=27.2, 21.7, 9.9 Hz, 5H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 134.60 (d, J=2.7 Hz), 134.24, 131.01, 128.70, 123.81 (t, J=31.3 Hz), 123.10 (t, J=6.4 Hz), 118.82 (t, J=250.3 Hz), 50.76 (t, J=26.2 Hz), 44.30, 33.43, 33.30, 25.94, 25.82, 25.80; ^{19}F NMR (471 MHz, $CDCl_3$) δ: −98.26 (dd, J=241.9, 13.8 Hz, 1F), −102.34 (dd, J=241.9, 15.8 Hz, 1F); HRMS (EI) calcd for $C_{16}H_{18}BrClF_2S$ $[M]^+$ 393.9969, found 393.9970.

2-((3-Bromo-1-(4-chlorophenyl)-2,2-difluorobut-3-en-1-yl)thio)thiophene (**4i**): Purple oil, 42% isolated yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.34 (dd, J=5.4, 1.2 Hz, 1H), 7.30～7.23 (m, 4H), 7.00 (dd, J=3.6, 1.2 Hz, 1H), 6.90 (dd, J=5.4, 3.6 Hz, 1H), 6.22 (d, J=2.7 Hz, 1H), 5.82 (d, J=2.6 Hz, 1H), 4.63 (t, J=15.3 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 136.65, 134.61, 133.29, 131.57, 131.02, 130.56, 128.75, 127.71, 123.48 (t, J=6.1 Hz), 123.47 (t, J=30.8 Hz), 118.49 (t, J=251.1 Hz), 59.60 (t, J=25.7 Hz); ^{19}F NMR (471 MHz, $CDCl_3$) δ: −99.54 (dd, J=243.5, 14.6 Hz, 1F), −100.08 (dd, J=242.4, 13.6 Hz, 1F); HRMS (EI) calcd for $C_{14}H_{10}BrClF_2S_2$ $[M]^+$ 393.9064, found 393.9066.

(1-(4-Chlorophenyl)-2,2-difluorobut-3-en-1-yl)(phenyl)-sulfane (**4j**): Colorless oil, 98% isolated yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.31 (dd, J=6.4, 2.9 Hz, 2H), 7.28～7.24 (m, 4H), 7.22 (dd, J=6.0, 3.4 Hz, 3H), 5.93 (dq, J=17.3, 11.3 Hz, 1H), 5.63 (d, J=17.3 Hz, 1H), 5.45 (d, J=11.0 Hz, 1H), 4.37 (t, J=12.9 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 134.55, 134.18, 133.58, 132.93, 130.96, 130.92 (t, J=26.4 Hz), 129.17, 128.64, 128.15, 121.37 (t, J=9.0 Hz), 118.86 (d, J=245.6 Hz), 60.00 (t, J=27.6 Hz); ^{19}F NMR (85 MHz, $CDCl_3$) δ: −93.64～−96.93 (m, 1F), −96.95～−100.56 (m, 1F); HRMS (EI) calcd for $C_{16}H_{13}ClF_2S$ $[M]^+$ 310.0395, found 310.0394.

(1,3-bis(4-chlorophenyl)-2,2-difluorobut-3-en-1-yl)-(phenyl)sulfane (**4k**): Colorless oil, 91% isolated yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.31 (dd, J=6.4, 2.9 Hz, 2H), 7.28～7.24 (m, 4H), 7.22 (dd, J=6.0, 3.4 Hz, 3H), 5.93 (dq, J=17.3, 11.3 Hz, 1H), 5.63 (d, J=17.3 Hz, 1H), 5.45 (d, J=11.0 Hz, 1H), 4.37 (t, J=12.9 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 134.55, 134.18, 133.58, 132.93, 130.96, 130.92 (t, J=26.4 Hz), 129.17, 128.64, 128.15, 121.37 (t, J=9.0 Hz), 118.86 (d, J=245.6 Hz), 60.00 (t, J=27.6 Hz); ^{19}F NMR (85 MHz, $CDCl_3$) δ: −93.64～−96.93 (m, 1F), −96.95～−100.56 (m, 1F); HRMS (EI) calcd for $C_{22}H_{16}Cl_2F_2S$ $[M]^+$ 420.0318, found 420.0320.

1-(3-Bromo-2,2-difluoro-1-(phenylsulfonyl)but-3-en-1-yl)-4-chlorobenzene (**5**): White solid, 76% isolated yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.71 (d, J=7.7 Hz, 2H), 7.62 (t, J=7.4 Hz, 1H), 7.47 (t, J=7.8 Hz, 2H), 7.27 (d, J=6.7 Hz, 4H), 6.21 (s, 1H), 5.74 (s, 1H), 5.02 (dd, J=19.4, 10.1 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 138.41, 136.33, 134.41, 129.30, 129.05, 129.01, 125.66 (d, J=4.3 Hz), 124.00～123.50 (m), 122.62 (t, J=29.7 Hz), 119.48～114.84 (m), 72.24～71.77 (m); ^{19}F NMR (85 MHz, $CDCl_3$) δ: −93.10 (d, J=249.1 Hz, 1F), −101.58 (d, J=248.5 Hz, 1H); HRMS (EI) calcd for $C_{16}H_{12}BrClF_2O_2S$ $[M]^+$ 419.9398, found 419.9398.

(1-(4-Chlorophenyl)-2,2-difluoro-5-(4-methoxyphenyl)-3-methylenepent-4-yn-1-yl)(phenyl)sulfane (**6**): Yellow oil, 70% isolated yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.19～7.11 (m, 6H), 7.06 (d, J=8.4 Hz, 2H), 7.01 (d, J=7.2 Hz, 3H), 6.67 (d, J=8.7 Hz, 2H), 5.65 (s, 1H), 5.55 (s, 1H), 4.59 (t, J=14.8 Hz, 1H), 3.62 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 160.25, 134.35, 134.16 (d, J=4.3 Hz), 133.83, 133.31, 132.94, 131.11, 129.13, 128.56, 128.08, 126.78 (t, J=28.2 Hz), 125.33 (t, J=6.4 Hz), 119.29 (t, J=250.3 Hz), 114.17, 114.00 (dd, J=41.4, 25.2 Hz), 93.12, 83.06, 58.31 (t, J=26.2 Hz), 55.43; ^{19}F NMR (85 MHz, $CDCl_3$) δ: −92.67 (dd, J=240.6, 14.7 Hz, 1F), −96.02 (dd, J=240.6, 14.8 Hz, 1H); HRMS (EI) calcd for $C_{25}H_{19}ClF_2OS$ $[M]^+$ 440.0813, found 440.0814.

1-(4-(4-(4-Chlorophenyl)-3,3-difluoro-4-(phenylthio)-but-1-en-2-yl)phenyl)ethan-1-one (**7**): Colorless oil, 62% isolated yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.92 (d, J=8.5 Hz, 2H), 7.43 (d, J=8.3 Hz, 2H), 7.18 (dd, J=16.0, 7.9 Hz, 3H), 7.10 (dt, J=18.2, 7.9 Hz, 6H), 5.86 (s, 1H), 5.54 (s, 1H), 4.27～4.19 (m, 1H), 2.63 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 197.76, 142.44 (t, J=22.5 Hz), 141.14, 136.91, 134.18, 133.92 (d, J=2.0 Hz), 133.10, 132.90, 131.07, 129.07, 128.77, 128.52, 128.48, 128.21, 121.77 (t, J=8.7 Hz), 120.40 (t, J=249.6 Hz), 58.28 (t, J=26.3 Hz), 26.83; ^{19}F NMR (85 MHz, $CDCl_3$) δ: −

95.95 (d, J=249.7 Hz, 1F), −100.99 (d, J=250.6 Hz, 1F); HRMS (EI) calcd for $C_{24}H_{19}ClF_2OS$ $[M]^+$ 428.0813, found 428.0814.

4.3 Experimental procedure for the one-pot synthesis of (3-bromo-1-(4-chlorophenyl)-2,2-difluorobut-3-en-1-yl)(phenyl)sulfane (**3a**)

To a 10 mL test tube equipped with a magnetic stir bar, 4-chlorobenzaldehyde (0.3 mmol) and 4-methylbenzenesulfonhydrazide (0.3 mmol) were mixed and stirred in DCE (1 mL) at 70 ℃ for 3 h. Upon cooling down to room temperature, the $[Rh(esp)]_2$ (3.0 mg, 0.004 mmol) and Cs_2CO_3 (78.2 mg, 0.24 mmol) were successively added to the above mixture. The reaction tube was degassed three times with argon, and DCE (1.0 mL) was added, followed by the addition of phenyl 2-bromo-3,3-difluoroallyl sulfide **2a** (53.0 mg, 0.20 mmol) through microinjector. The reaction mixture was stirred at 100 ℃ for 12 h. Upon cooling down to room temperature, the solvent was evaporated under vacuum. The crude product was purified by column chromatography on silica gel with petroleum ether as the eluant, giving the pure product **3a** as a colorless oil liquid (42.0 mg, 54% yield).

4.4 Experimental procedure for the gram-scale synthesis of (3-bromo-1-(4-chlorophenyl)-2,2-difluorobut-3-en-1-yl)(phenyl)sulfane (**3a**)

Under argon atmosphere, $[Rh(esp)]_2$ (76.2 mg, 0.1 mmol), Cs_2CO_3 (1.95 g, 6 mmol), *N*′-(4-chlorobenzylidene)-4-methylbenzenesulfonohydrazide (**1a**, 2.32 mg, 7.5 mmol) were successively added to a 250 mL Schlenk tube. The reaction tube was degassed three times with argon, and DCE (50 mL) was added, followed by the addition of phenyl 2-bromo-3,3-difluoroallyl sulfide (**2a**, 1.32 mg, 5.0 mmol) through injector. The reaction mixture was stirred at 100 ℃ for 12 h. Upon cooling down to room temperature, the solvent was evaporated under vacuum. The crude product was purified by column chromatography on silica gel with petroleum ether as the eluant, giving the pure product **3a** as a colorless oil liquid (1.24 g, 64% yield).

4.5 Experimental procedure for the synthesis of 1-(3-bromo-2,2-difluoro-1-(phenylsulfonyl)but-3-en-1-yl)-4-chlorobenzene (**5**)

To a cooled (0 ℃) solution of **3a** (77.9 mg, 0.2 mmol) in 5.0 mL of dry dichloromethane (DCM), was added a solution of *m*-chloroperbenzoic acid (86.3 mg, 0.5 mmol) in 5.0 mL of dry DCM in small portions over 20 min. The reaction was stirred 12 h at 0 ℃. Upon completion of the reaction, the solvent was evaporated under vacuum, the crude product was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (V∶V=10∶1) as the eluant, giving the pure product **5** as a white solid. (63.8 mg, 76% yield).

4.6 Experimental procedure for the synthesis of (1-(4-chlorophenyl)-2,2-difluoro-5-(4-methoxyphenyl)-3-methylenepent-4-yn-1-yl)(phenyl)sulfane (**6**)

Under argon atmosphere, $Pd(PPh_3)_2Cl_2$ (2.8 mg, 0.004 mmol), CuI (1.9 mg, 0.01 mmol), **3a** (83.6 mg, 0.2 mmol), 4-ethynylanisole (39.6 mg, 0.3 mmol) were successively added to a flame-dried 10 mL Schlenk tube. The reaction tube was degassed three times with argon, and dry triethylamine (TEA) (2.0 mL) was added using syringe. The reaction mixture was stirred at 50 ℃ for 12 h. Upon completion of the reaction, the solvent was evaporated under vacuum. The crude product was purified by column chromatography on silica gel with petroleum ether as the eluant, giving the pure product **6** as a yellow oil liquid (61.6 mg, 70% yield).

4.7 Experimental procedure for the synthesis of 1-(4-(4-(4-chlorophenyl)-3,3-difluoro-4-(phenylthio)but-1-en-2-yl)phenyl)ethan-1-one (**7**)

To a 10 mL test tube equipped with a magnetic stir bar was charged with $Pd(PPh_3)_4$ (11.6 mg, 5 mol%), Na_2CO_3 (42.4 mg, 0.4 mmol), **3a** (83.6 mg, 0.2 mmol), (4-acetylphenyl)boronic acid (65.6 mg, 0.4 mmol), and toluene/H_2O (V∶V=4∶1, 2.0 mL). The mixture was stirred at room temperature for 18 h. Upon completion of the reaction, H_2O (15 mL) was added and extracted with EtOAc (15 mL×3). The combined organic layer was washed with brine (5 mL×3), dried over Na_2SO_4 and concentrated under reduced pressure to afford a crude product. Purification by column chromatography on silica gel [eluent: V(petroleum ether)∶V(ethyl acetate)=10∶1] afforded the desired product **7** (53.2 mg, 62%) as a yellow oil liquid.

Supporting Information The structure of unsuccessful *N*-tosylhydrazones substrate; Control experiments; ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra of compounds **3a**～**3s**, **4a**～**4k**, **5**～**7**. The Supporting Information is available free of charge via the Internet at http://sioc-journal.cn/.

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