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1-*tert*-Butyl-1*H*-tetrazol-5-yl fluoromethyl sulfone ($TBTSO_2CH_2F$): a versatile fluoromethylidene synthon and its use in the synthesis of monofluorinated alkenes via Julia–Kocienski olefination

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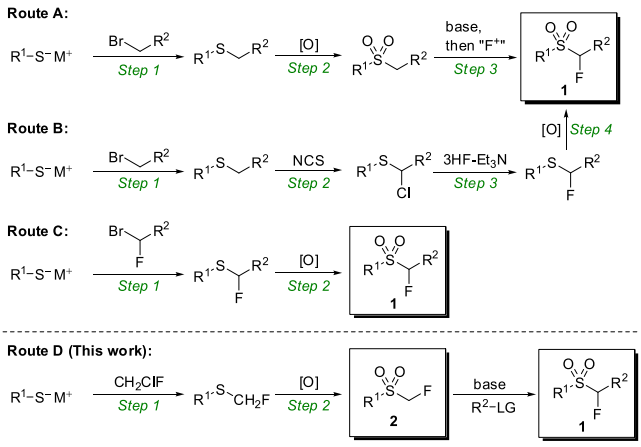
ABSTRACT

1-*tert*-Butyl-1*H*-tetrazol-5-yl fluoromethyl sulfone ($TBTSO_2CH_2F$) has been developed as a new and efficient fluoromethylidene synthon for the synthesis of both terminal and internal monofluoroalkenes via Julia–Kocienski olefination reaction. The base-mediated reaction between $TBTSO_2CH_2F$ and carbonyl compounds (aldehydes and ketones) provided terminal monofluoroalkenes in good yields with moderate *E*/*Z* selectivity. The dominance of *E*- or *Z*-fluoroalkenes could be controlled by selection of proper reaction solvent and temperature. $TBTSO_2CH_2F$ reagent was also found to be readily α-alkylated, acylated, and phenylsulfonylated to give corresponding α-functionalized fluorosulfones, which could be used in the synthesis of alkyl-, acyl-, and phenylsulfonyl-substituted internal monofluoroalkenes via Julia–Kocienski olefination reactions.

1. Introduction

Selective incorporation of fluorine atom(s) into organic compounds can often impart many beneficial properties, which has stimulated the development of highly efficient and practically useful synthetic methods for the preparation of fluorinated organic compounds.[1] Among fluorinated compounds, monofluorinated alkenes are of particular interest, given their broad applications in polymeric materials, agrochemistry, as well as pharmaceutical industry.[2–4] Many methods for their preparation have been developed,[5] including electrophilic fluorination of vinylllithiums[6] or vinylstannanes,[7] Wittig-type reaction with fluorophosphonates,[8] thermal sulfoxide eliminations,[9] and fluoroolefination between fluorinated sulfoximines and nitrones.[10] Recently, Lequeux et al.[11], Zajc and Ghosh [12] and others[13] reported that Julia–Kocienski olefination (sometimes called 'modified Julia olefination'),[14] a one-step reaction between a sulfone and a carbonyl compound, could serve as a convenient and efficient method to prepare monofluorinated alkenes. α-Fluoro sulfones (**1**) required for Julia–Kocienski olefination are commonly prepared according to the following three routes (Scheme 1): (a) S-alkylation, oxidation, followed by electrophilic fluorination (a three-step procedure, Route A),[12,13] (b) S-alkylation, chlorination, fluorination, followed by oxidation (a four-step procedure, Route B),[11a] (c) S-fluoroalkylation, followed by oxidation (a two-step procedure, Route C).[11b–c] Both Routes A and B suffer from long synthetic procedures for each α-fluoro sulfone **1** (with a different R^2 substituent). Route C (a two-step procedure) is attractive for this purpose; however, its applicability was limited by the fact that the functionalized bromofluoromethane compounds (needed for S-fluoroalkylation in the first step) are not easily available.



(R^1 = 1,3-benzothiazol-2-yl (BT), 1-phenyl-1*H*-tetrazol-5-yl (PT), 1-*tert*-butyl-1*H*-tetrazol-5-yl (TBT); R^2 ¡Ù H; LG = leaving group)

Scheme 1.

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Previously, we reported an efficient monofluoromethylation of thiols [such as 1,3-benzothiazol-2-yl thiol (BT-SH), 1-phenyl-1*H*-tetrazol-5-yl thiol (PT-SH), and 1-*tert*-butyl-1*H*-tetrazol-5-yl thiol (TBT-SH)] with chlorofluoromethane, to give corresponding fluoromethyl sulfides (R^1S-CH_2F) in high yields.[15] We envisaged that by simple oxidation, these fluoromethyl sulfides should be readily converted to corresponding fluoromethyl sulfones **2** ($R^1SO_2CH_2F$, R^1=BT, PT, TBT; Scheme 1, Route D). The chemistry of these fluoromethyl heteroaryl sulfones **2** are generally unkown,[16] and they may serve as new type of fluoromethylidenation reagents through Julia–Kocienski olefination reaction. Furthermore, based on our experience in nucleophilic fluoroalkylation with fluorinated sulfones,[17] we envisioned that fluoromethyl sulfones **2** can also be used as a key starting material for the one-step preparation (via nucleophilic fluoroalkylation) of α-functionalized fluorosulfones **1** for other Julia–Kocienski olefinations (Scheme 1, Route D). Therefore, fluoromethyl sulfones **2** could act as a universal reagent to prepare both terminal and internal monofluorinated alkenes via Julia–Kocienski olefinations. In this article, we wish to report our results toward these goals.

2. Results and discussion

2.1. Synthesis of fluoromethyl heteroaryl sulfones

First of all, we carried out the preparation of three fluoromethyl heteroaryl sulfones: 1,3-benzothiazol-2-yl fluoromethyl sulfone **2a** ($BTSO_2CH_2F$), 1-phenyl-1*H*-tetrazol-5-yl fluoromethyl sulfone **2b** ($PTSO_2CH_2F$), and 1-*tert*-butyl-1*H*-tetrazol-5-yl fluoromethyl sulfone **2c** ($TBTSO_2CH_2F$) (Fig. 1).[16] They were conveniently prepared through a two-step procedure from easily available reagents.[18] The monofluoromethylation of mercaptans **3a**–**c** with chlorofluoromethane afforded fluoromethyl sulfides **4a**–**c** in 64–86% yields,[15] and **4a**–**c** were transformed into sulfones **2a**–**c** in 84–97% yields by oxidation with sodium periodate in the presence of catalytic amount of ruthenium(III) chloride (Scheme 2).[19]

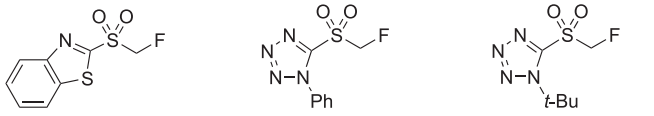
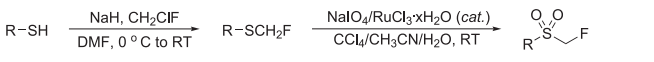


Figure 1. Fluoromethyl sulfones **2a**–**c**.

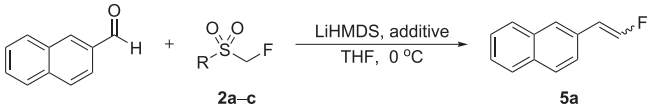


Scheme 2.

2.2. Screening of reaction conditions of Julia–Kocienski olefination

With the sufones **2a**–**c** in hand, we examined their reactivity in Julia–Kocienski olefination reactions, using 2-naphthaldehyde as a model substrate (Table 1). The reactions were performed by adding lithium hexamethyldisilazide (LiHMDS, 2.4 equiv) as a base to the mixture of 2-naphthaldehyde (1.0 equiv) and a sulfone (**2a**–**c**, 1.2 equiv) in THF, according to Berthelette's procedure.[20] It was found that hexamethylphosphoric triamide (HMPA, as an additive) played a crucial role in the reaction (Table 1). In the absence of HMPA, the olefination reaction between sulfone **2a** and 2-naphthaldehyde failed (**2a** decomposed completely; Table 1, entry 1), and the reactions with **2b** and **2c** afforded **5a** in 39% and 31% yield, respectively (entries 3 and 5). However, when HMPA was added, the product yields were significantly improved for all three sulfone reagents **2a**–**c** (entries 2, 4, and 6), with TBT-sulfone **2c** being the most efficient fluoroolefination reagent among **2a**–**c** (with 75% yield).

Table 1
Comparison of the reactivity of the sufones **2a**–**c** in Julia-Kocienski olefination

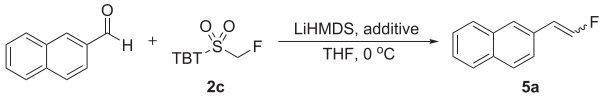


Entry	R	Additive[a]	Yield (%)[b]	*E*/*Z*[b]
1	BT (**2a**)	None	0	—[c]
2	BT (**2a**)	HMPA	68	50:50
3	PT (**2b**)	None	39	36:64
4	PT (**2b**)	HMPA	66	54:46
5	TBT (**2c**)	None	31	22:78
6	**TBT** (**2c**)	**HMPA**	**75**	**45:55**

[a] LiHMDS (2.4 equiv) was added to a solution of 2-naphthaldehyde (1.0 equiv), 2 (1.2 equiv) and additive (2.4 equiv) in THF (*c*=0.2 M) at 0 °C.
[b] Yield and the *E*/*Z* ratio were determined by ^{19}F NMR spectroscopy using $PhCF_3$ as an internal standard.
[c] The sulfone starting material decomposed.

Encouraged by these results, we further optimized the reaction conditions with TBT-sulfone **2c** (Table 2). It was found that when *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) was used as an additive (instead of HMPA), the yield decreased (Table 2, entry 2). Furthermore, after scanning the influence of amount of LiHMDS on the product yield, we found that the addition of 1.5 equiv of LiHMDS led to the optimal yield (88%; Table 2, entry 5).

Table 2
The effects of additives and amount of reagents

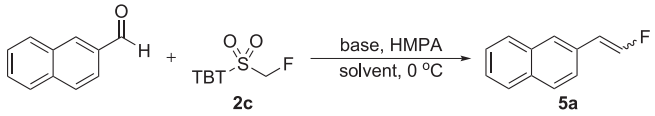


Entry	LiHMDS (equiv)	Additive[a]	Yield (%)[b]	*E*/*Z*[b]
1	2.4	HMPA	75	45:55
2	2.4	TMEDA	46	28:72
3	3.0	HMPA	66	33:67
4	1.8	HMPA	83	45:55
5	**1.5**	**HMPA**	**88**	**42:58**
6	1.3	HMPA	79	47:53

[a] LiHMDS was added to a solution of 2-naphthaldehyde (1.0 equiv), **2c** (1.2 equiv), and additive (equivalent to LiHMDS) in THF (*c*=0.2 M) at 0 °C.
[b] Yield and the *E*/*Z* ratio were determined by ^{19}F NMR spectroscopy using $PhCF_3$ as an internal standard.

Next, we sought to evaluate the influence of bases, solvents, and temperature on the product yield (Table 3). It was found that LiHMDS was the base of choice for the reaction (entries 1–4), and the reaction with KHMDS gave the lowest yield (entry 4). However, the *E*/*Z* selectivity of the reaction increases with the following order of three bases used: LiHMDS<NaHMDS<KHMDS (entries 1, 2, and 4). Among the three solvents used (THF, toluene, and DME), THF was found to be the best one regarding the yield (entries 1, 5, and 6). Furthermore, there was an interesting temperature effect: reactions at lower temperature commonly gave better yields and preferred the formation of *E*-isomer of product **5a**, while the

Table 3
The Effects of bases, solvents, and temperature



Entry	Base[a]	Solvent	Yield (%)[b]	*E*/*Z*[b]
1	**LiHMDS**	**THF**	**88**	**42:58**
2	NaHMDS	THF	63	57:43
3	LDA	THF	49	47:53
4	KHMDS	THF	47	74:26
5	LiHMDS	toluene	66	27:73
6	LiHMDS	DME	84	43:57
7	LiHMDS	THF	57[c]	32:68
8	LiHMDS	THF	87[d]	69:31

[a] Base (1.5 equiv) was added to a solution of 2-naphthaldehyde (1.0 equiv), **2c** (1.2 equiv), and HMPA (1.5 equiv) in various solvents (*c*=0.2 M) at 0 °C.
[b] Yield and the *E*/*Z* ratio were determined by ^{19}F NMR spectroscopy using $PhCF_3$ as an internal standard.
[c] The reaction was carried out at room temperature.
[d] The reaction was carried out at −78 °C.

reactions at higher temperature behaved oppositely (Table 3, entries 1, 7, and 8). Finally, the optimized reaction condition was chosen as follows: LiHMDS (1.5 equiv), **2c** (1.2 equiv), and HMPA (1.5 equiv), THF as solvent, and 0 °C as the reaction temperature (Table 3, entry 1).

2.3. Synthesis of terminal monofluoroalkenes

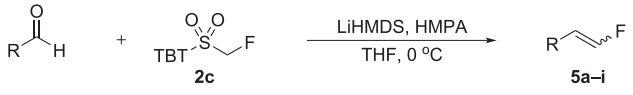
By using the optimized reaction condition (Table 3, entry 1), first of all, we investigated the scope of Julia–Kocienski olefination between **2c** and aldehydes. As shown in Table 4, the reaction was found to be amenable to both aromatic and aliphatic aldehydes. For the reactions with aromatic aldehydes, the product yields were generally high (Table 4, entries 1–8). Although enolizable aliphatic aldehyde also reacted with **2c** to provide **5i**, the yield was merely moderate (51%, Table 4, entry 9). For terminal monofluoroalkenes **5a**–**i**, the *E*- and *Z*-isomers were determined by differences of their $^3J_{H-F}$ coupling constants in ^{19}F NMR spectroscopy ($^3J_{H-F}$ values of *E*-isomers are smaller than those of *Z*-isomers).[21]

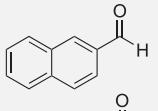
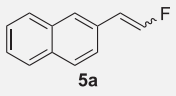
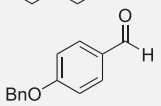
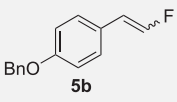
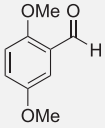
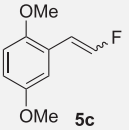
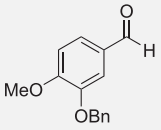
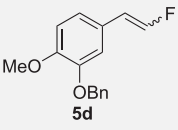
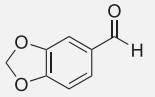
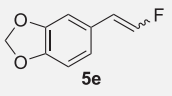
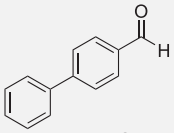
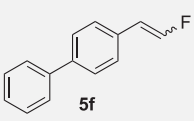
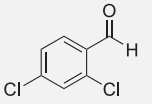
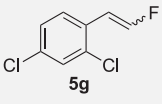
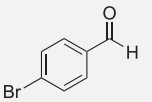
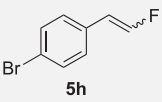
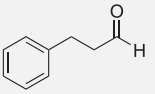
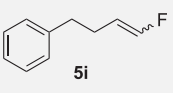
We also extended the fluoroolefination reaction to ketones. By using acetophenone as a model compound, we examined the reaction conditions. As shown in Table 5, when we used the previously optimized reaction condition for aldehydes (as that for Table 4), product **6a** was obtained in 75% yield (Table 5, entry 1). Neither the decrease of reaction temperature nor the increase of the amount of LiHMDS brought further improvement of the yield (Table 5, entries 2–3). With synchronous increase of the amounts of **2c** and LiHMDS, the yield was elevated and reached the highest (88%) when 1.7 equiv of **2c** and 2.0 equiv of LiHMDS were used (Table 5, entry 7).

With this optimized reaction condition (Table 5, entry 7), we examined the scope of Julia–Kocienski olefination between **2c** and ketones. As illustrated in Table 6, all ketones could afford terminal monofluoroalkenes **6a**–**i** in moderate to excellent yields. For acetophenones, the ones with electron-withdrawing substituents gave higher yields than those with electron-donating ones (Table 6, entries 2–5). It is interesting that the *E*/*Z* selectivity for the reactions with cyclic ketones (Table 6, entries 6–7) were opposite to those with acyclic ketones.

Although terminal monofluoroalkenes **5a**–**i** and **6a**–**i** were obtained in one-pot from aldehydes and ketones with reagent **2c**, they were a mixture of *E*- and *Z*-isomers. Therefore, we paid our attention to the *E*/*Z* control of the monofluoroalkene products. During the previous examination of reaction conditions (Table 3),

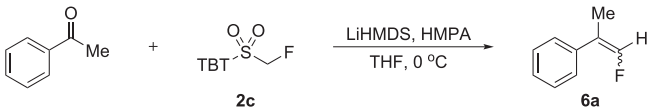
Table 4
Synthesis of terminal monofluoroalkenes **5a**–**i** from aldehydes and **2c**



Entry	RCHO	Product	Isolated yield (%)	*E*/*Z*[a]
1		 **5a**	87	42:58
2		 **5b**	87	34:66
3		 **5c**	90	47:53
4		 **5d**	81	35:65
5		 **5e**	78	34:66
6		 **5f**	86	42:58
7		 **5g**	78	50:50
8		 **5h**	73	47:53
9		 **5i**	51	48:52

[a] The *E*/*Z* ratio was determined by ^{19}F NMR spectroscopy.

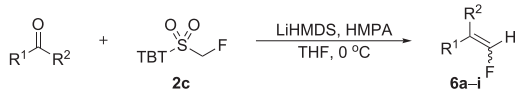
Table 5
Reaction conditions of Julia-Kocienski olefination of ketones

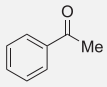
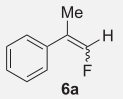
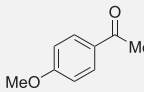
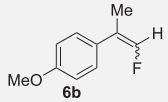
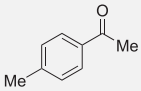
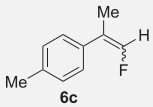
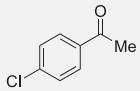
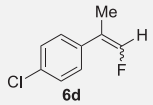
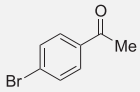
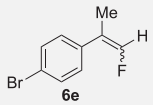
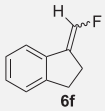
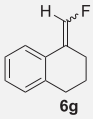
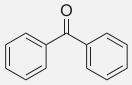
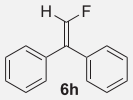
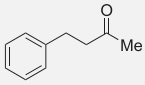
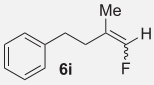


Entry	**2c** (equiv)	LiHMDS (equiv)[a]	Yield (%)[b]	*E*/*Z*[b]
1	1.2	1.5	75	35:65
2	1.2	1.5	70[c]	29:71
3	1.2	1.8	69	34:66
4	1.5	1.8	79	42:58
5	1.5	2.0	78	34:66
6	1.6	1.9	82	35:65
7	**1.7**	**2.0**	**88**	**30:70**
8	1.8	2.1	87	34:66

[a] LiHMDS was added to a solution of ketone (1.0 equiv), **2c**, and HMPA (equivalent to LiHMDS) in THF (*c*=0.2 M) at 0 °C.
[b] Yield and the *E*/*Z* ratio were determined by ^{19}F NMR spectroscopy using $PhCF_3$ as an internal standard.
[c] The reaction was performed at −78 °C.

Table 6
Synthesis of terminal monofluoroalkenes **6a–i** from ketones and **2c**



Entry	R^1COR^2	Product	Isolated yield (%)	E/Z[a]
1		 6a	75[b]	30:70
2		 6b	69[b]	30:70
3		 6c	60[b]	33:67
4		 6d	86	25:75
5		 6e	84	28:72
6		 6f	67	76:24
7		 6g	66	59:41
8		 6h	89	—
9		 6i	52	49:51

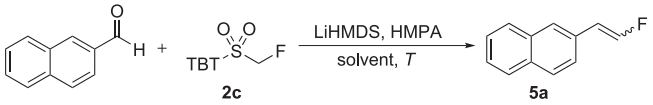
[a] The E/Z ratio was determined by ^{19}F NMR spectroscopy.
[b] The product is volatile.

we found that both solvents and temperature played important roles in the E/Z stereocontrol of the products. So we further investigated the possibility of improving the E/Z selectivity by carefully choosing solvents and reaction temperature. As shown in Table 7, it was found that a good selectivity for either isomer could be achieved, with polar solvent system DMF–HMPA (2:1) (at −78 °C) mainly affording *E*-isomer (Table 7, entry 7), whereas less polar solvent system ether–toluene (1:2) primarily giving *Z*-isomer (Table 7, entry 16). The observed E/Z selectivity was consistent with previous reports.[14b,22]

2.4. Synthesis of alkyl-substituted internal monofluoroalkenes

Previously, we found that α-fluorinated sulfones can act as a class of good nucleophilic fluoroalkylating agent, and $PhSO_2CHF^-$ anion possesses good thermal stability and nucleophilicity.[17b–g] Furthermore, the incorporation of bulky steric *tert*-butyl into tetrazole ring of **2c** enhanced the stability of the corresponding sulfone anion,[14c] as found in optimizing the above mentioned

Table 7
The E/Z control of the monofluoroalkene products

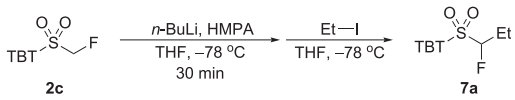


Entry	Solvent	T(°C)	E/Z[a,b]
1	DMF–HMPA(1:1)	0	66:34
2	DMSO–HMPA(1:1)	0	70:30
3	DMSO–HMPA(1:1)	20	66:34
4	HMPA	8	61:39
5	DMF	−60	63:37
6	DMF-HMPA (1:1)	−78	74:26
7	**DMF–HMPA (2:1)**	**−78**	**75:25**
8	DMF–HMPA (3:1)	−78	74:26
9	DMF–DMPU (2:1)	−78	72:28
10	DIPE	0	37:63
11	MTBE	0	38:62
12	Et_2O	0	30:70
13	Et_2O	10	38:62
14	Et_2O	20	41:59
15	Et_2O–toluene (1:1)	0	26:74
16	**Et_2O–toluene (1:2)**	**0**	**25:75**
17	Et_2O–toluene (1:5)	0	25:75

DMPU=*N*,*N*′-dimethylpropylene urea; DIPE=diisopropyl ether; MTBE=methyl *tert*-butyl ether.
[a] Isolated yields in all cases were above 80%.
[b] The E/Z ratio was determined by ^{19}F NMR spectroscopy.

conditions (Table 1). We envisaged that sulfone **2c** could serve as a new fluoroalkylating agent to prepare a variety of structurally diverse α-alkylated fluorinated sulfones. With this consideration, we examined the reaction conditions between **2c** and ethyl iodide in THF (Table 8). By varying the amounts of *n*-butyl lithium and ethyl iodide, we gained optimized reaction condition of α-alkylation of **2c** (Table 8, entry 8).

Table 8
Screening of the condition of α-alkylation of **2c**



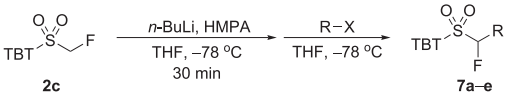
Entry	*n*-BuLi (equiv)	Et–I(equiv)	Yield (%)[a]
1	1.05	1.2	52
2	1.08	1.2	61
3	1.10	1.2	65
4	1.20	1.2	65
5	1.15	1.2	63
6	1.10	2.0	66
7	1.10	3.0	66
8	**1.15**	**2.0**	**71**

[a] The yield was determined by ^{19}F NMR spectroscopy using $PhCF_3$ as an internal standard.

The scope of α-alkylation of **2c** is shown in Table 9. Both long-chain and short-chain alkyl bromides or iodides provided the alkylated sulfones **7a–b** in moderate yields (Table 9, entries 1–4). α-Allylation and benzylation of **2c** were also smoothly accomplished with allyl and benzyl bromides (Table 9, entries 6 and 7). Even secondary alkyl iodide could afford the product **7c** in 62% yield (Table 9, entry 5).

To date, there are few reports about preparation of alkyl-substituted internal monofluoroalkenes utilizing Julia–Kocienski olefination.[11a,12a,b,f] With the α-alkylated sulfones **7a–e** in hand, we set out to prepare alkyl-substituted internal monofluoroalkenes. Based on the above-mentioned olefination reactions with **2c** and

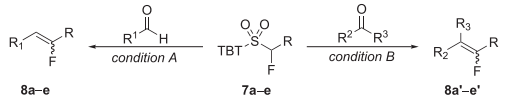
Table 9
Synthesis of α-alkylated sulfones **7a**–**e**



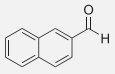
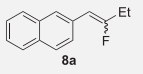
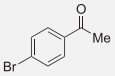
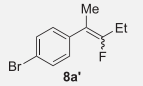
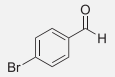
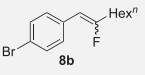
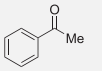
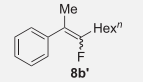
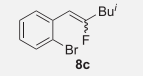
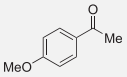
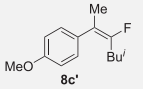
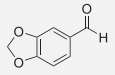
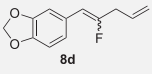
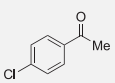
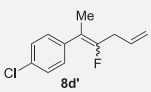
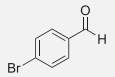
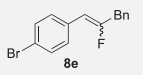
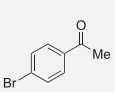
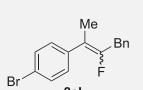
Entry	R	X	Product (**7**)	Isolated yield (%)
1	Et	I	**7a**	67
2	Et	Br	**7a**	64
3	^{n}Hex	I	**7b**	60
4	^{n}Hex	Br	**7b**	68
5	^{i}Bu	I	**7c**	62
6	All	Br	**7d**	57
7	Bn	Br	**7e**	62

previous reports,[12a,20] we performed the reactions between **7a**–**c** and aldehydes (or ketones). The results are summarized in Table 10. It was found that alkyl-substituted internal monofluoroalkenes **8a**–**d** and **8a′**–**c′** were produced in moderate yields, and particularly, **8c′** was obtained with only *E*-configuration due to the steric repulsion. For allylated and benzylated sulfones **7d**–**e**, only **7d** could react with aldehyde to afford the product **8d** in 54% yield, while in other cases the reactions failed (Table 10, entries 7–10).

Table 10
Synthesis of alkyl-substituted internal monofluoroalkenes **8**



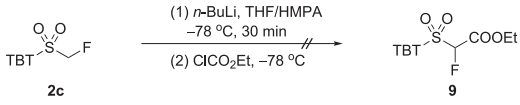
condition A: **7a–e** (1.2 equiv), LiHMDS (2.4 equiv), HMPA (2.4 equiv), THF, 0 °C.
condition B: **7a–e** (1.7 equiv), LiHMDS (3.4 equiv), HMPA (3.4 equiv), THF, 0 °C.

Entry	R	Aldehyde or ketone	Product (**8**)	Yield (%)[a]	*E*/*Z*[b]
1	Et (**7a**)		 **8a**	64	33:67
2			 **8a′**	52	36:64
3	^{n}Hex (**7b**)		 **8b**	70	27:73
4			 **8b′**	66	49:51
5	^{i}Bu (**7c**)		 **8c**	66	51:49
6			 **8c′**	53	100:0
7	Allyl (**7d**)		 **8d**	54	46:54
8			 **8d′**	—[c]	—[c]
9	Bn (**7e**)		 **8e**	—[c]	—[c]
10			 **8e′**	—[c]	—[c]

[a] Isolated yield.
[b] The *E*/*Z* ratio was determined by ^{19}F NMR spectroscopy.
[c] The sulfone decomposed.

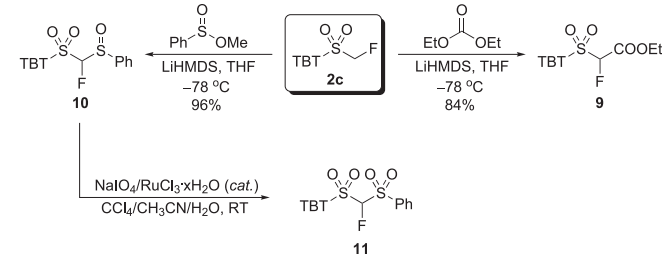
2.5. Synthesis of acyl- and phenylsulfonyl-substituted internal monofluoroalkenes

We also attempted to prepare α-acylated sulfone **9** by treating ethyl chloroformate with **2c**; however, the reaction was not successful (Eq. 1). Inspired by our previous success in the nucleophilic fluoroalkylation of diethyl carbonate with $PhSO_2CH_2F$ (Eq. 2),[17h] we carried out a similar fluoroalkylation reaction between **2c** and diethyl carbonate. To our delight, α-acylation of **2c** was successfully fulfilled to provide product **9** in 84% yield (Scheme 3). Under similar reaction conditions, α-phenylsulfinylated sulfone **10** could also be obtained in 96% yield by nuleophilic fluoroalkylation of methyl benzenesulfinate with **2c**, which was further transformed into α-phenylsulfonylated sulfone **11** by oxidation with sodium periodate (Scheme 3).



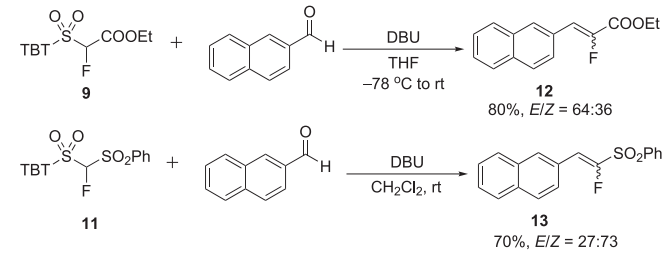
(1)

(2)



Scheme 3.

Having sulfones **9** and **11** in hand, we carried out the Julia–Kocienski olefination using 2-naphthaldehyde as a substrate (Scheme 4). As expected, acyl- and phenylsulfonyl-substituted internal monofluoroalkenes (**12** and **13**) were smoothly obtained in 80% and 70% yield, respectively (Scheme 4). In the course of our investigation, the preparation of a acyl- and phenylsulfonyl-substituted internal monofluoroalkenes were also reported by using other fluorinated sulfone reagents.[11b,c,12c–e,23]



Scheme 4.

3. Conclusion

In summary, 1-*tert*-butyl-1*H*-tetrazol-5-yl fluoromethyl sulfone ($TBTSO_2CH_2F$) has been developed as a new and efficient fluoromethylidene synthon for the synthesis of both terminal and

internal monofluoroalkenes via Julia–Kocienski olefination reaction. The base-mediated reaction between $TBTSO_2CH_2F$ and carbonyl compounds (aldehydes and ketones) provided terminal monofluoroalkenes in good yields and with moderate *E*/*Z* selectivity. The dominance of *E*- or *Z*-fluoroalkenes could be controlled by selection of proper reaction solvent and temperature. Furthermore, $TBTSO_2CH_2F$ reagent was found to be readily α-alkylated, acylated, and phenylsulfonylated to give corresponding α-functionalized fluorosulfones, which could be used in the synthesis of alkyl-, acyl-, and phenylsulfonyl-substituted internal monofluoroalkenes via Julia-Kocienski olefination reactions. Therefore, $TBTSO_2CH_2F$ was demonstrated as a versatile key starting material in the preparation of a variety of structurally diverse monofluoroalkenes, which deserve further elaboration for many potential applications.

4. Experimental section

4.1. General information

Silica gel (200–300 or 300–400 mesh) was used for column chromatography, and in most cases ethyl acetate/petroleum ether combination was used as the eluent. Unless otherwise mentioned, solvents and reagents were purchased from commercial sources and used as received. THF, DME, MTBE, Et_2O, DIPE, and toluene were freshly distilled over sodium. Anhydrous TMEDA, DMF, DMSO, HMPA, and CH_2Cl_2 were distilled over CaH_2.

All the melting points were uncorrected. ^1H, ^{13}C, and ^{19}F NMR spectra were recorded on 400 MHz or 300 MHz NMR spectrometer. ^1H NMR chemical shifts were determined relative to internal $(CH_3)_4Si$ (TMS) at δ 0.0 or to the signal of a residual protonated solvent: $CDCl_3$ δ 7.26. ^{13}C NMR chemical shifts were determined relative to internal TMS at δ 0.0. ^{19}F NMR chemical shifts were determined relative to $CFCl_3$ at δ 0.0. Chemical shifts are reported in part per million. Mass spectra were obtained on a mass spectrometer. High-resolution mass data were recorded on a high-resolution mass spectrometer in the EI, ESI or MALDI mode.

4.2. The preparation of 1-*tert*-butyl-1*H*-tetrazolyl-5-thiol (3c)

Compound **3c** was prepared with sodium azide and *tert*-butyl isothiocyanate,[24] which can be easily prepared in 60 g scale as following procedure.[25]

4.2.1. The preparation of tert-butyl isothiocyanate[25]. Under N_2 atmosphere, a 2-L round-bottomed flask was charged with *tert*-butyl amine (76 mL, 0.72 mol), triethylamine (332 mL, 2.38 mol), and THF (600 mL, used as received), and cooled with an ice-water bath. Carbon disulfide (44 mL, 0.73 mmol) was then added to the reaction mixture via dropping funnel over 1 h. After the addition was completed, the mixture was stirred at room temperature for 4 h, and ^1H NMR of the mixture indicated that conversion into dithiocarbamate salt was completed. The reaction mixture was cooled with an ice-water bath, tosyl chloride (152 g, 0.80 mol) was added in portions, and the mixture was allowed to warm to room temperature and stirred overnight, 2 M HCl (240 mL) and MTBE (200 mL) were added to the mixture. The aqueous layer was separated and extracted with MTBE (3×250 mL). The organic layers were then combined, dried over Na_2SO_4, and filtered. The filtrate was concentrated and distilled under reduced pressure to afford *tert*-butyl isothiocyanate (61.59 g, 74% yield) as colorless oil. ^1H NMR (300 MHz, $CDCl_3$) δ 1.44 (s, 9H).[26]

*4.2.2. The preparation of 1-tert-butyl-1H-tetrazolyl-5-thiol (**3c**)*[24]. To a refluxing solution of NaN_3 (18.64 g, 286.76 mmol) in water (44 mL) was added the solution of *tert*-butyl isothiocyanate (36 mL, 283.75 mmol) in *i*-PrOH (68 mL) via dropping funnel within 45 min. After addition, the mixture was refluxed for 20 h, then cooled to room temperature and in an ice-water bath concd HCl (42 mL) was added carefully. The mixture was then concentrated under reduced pressure and stored in refrigerator. Solid was precipitated, filtered, and washed twice with water, and then dried in vacuo in the presence of P_2O_5 to afford 1-*tert*-butyl-1*H*-tetrazolyl-5-thiol (**3c**, 38.08 g, 85% yield) as pale yellow solid. ^1H NMR (300 MHz, $CDCl_3$) δ 1.86 (s, 9H).

4.3. General procedure for the preparation of fluoromethyl sulfides (4) and fluoromethyl sulfones (2)

To a suspension of NaH (2.10 g, 60% dispersion in mineral oil, 52.50 mmol) in anhydrous DMF (80 mL) was added dropwise a solution of 1-*tert*-butyl-1*H*-tetrazolyl-5-thiol (7.91 g, 50.00 mmol) in anhydrous DMF (35 mL) at 0 °C within 15 min. After addition, the mixture was stirred at 0 °C for 30 min. CH_2FCl (ca. 100 mmol) was then introduced via a needle over 45 min. The mixture was allowed to warm to room temperature and stirred overnight. The reaction was quenched with a saturated aqueous solution of NH_4Cl carefully and diluted with EtOAc. The aqueous layer was extracted with EtOAc. The combined organic layers were washed with water and brine, dried over Na_2SO_4, and concentrated. The residue was purified by flash chromatography (EtOAc/petroleum ether=1:12) to afford 1-*tert*-butyl-1*H*-tetrazol-5-yl fluoromethyl sulfide (**4c**, 8.18 g, 86% yield) as white solid.

To a flask with a magnetic stirring bar were added sulfide **4c** (7.99 g, 42.02 mmol), CCl_4 (50 mL), CH_3CN (50 mL), water (100 mL), and sodium periodate (26.70 g, 126.07 mmol). To the suspension was added ruthenium(III) chloride hydrate (15 mg, 0.055 mmol). The resulting mixture was stirred at room temperature and a white precipitate was formed. After ^{19}F NMR indicated **4c** was disappeared, the precipitate was filtered and washed with Et_2O. The filtrate was diluted with Et_2O and washed successively with a saturated aqueous solution of $NaHCO_3$ and brine, dried over $MgSO_4$. After the removal of half of the solvent under reduced pressure, filtration through a pad of silica gel and concentration afforded the sulfone 1-*tert*-butyl-1*H*-tetrazol-5-yl fluoromethyl sulfone (**2c**, 9.09 g, 97% yield) as colorless oil.

*4.3.1. 1,3-Benzothiazol-2-yl fluoromethyl sulfide (**4a**).* White solid; mp 59–60 °C; IR (KBr): 2930, 1467, 1455, 1431, 1411, 1322, 1311, 1005, 972, 766, 754, 718, 674 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.98–7.80 (m, 2H), 7.50–7.33 (m, 2H), 6.16 (d, $^2J_{F-H}$=50.7 Hz, 2H); ^{19}F NMR (282 MHz, $CDCl_3$): δ −186.7 (t, $^2J_{H-F}$=51.1 Hz, 1F); ^{13}C NMR (75 MHz, $CDCl_3$): δ 162.4 (d, J=4.5 Hz), 152.9, 135.8, 126.4, 125.0, 122.4, 121.2, 84.8 (d, $^1J_{F-C}$=222.2 Hz); MS (EI, *m*/*z*, %): 199 (M^+, 42), 135 (100). Anal. Calcd for $C_8H_6FNS_2$: C, 48.22; H, 3.03; N, 7.03. Found: C, 48.36; H, 7.03; N, 7.04.

*4.3.2. Fluoromethyl 1-phenyl-1H-tetrazol-5-yl sulfide (**4b**).* White solid; mp 86–87 °C; IR (KBr): 2969, 1597, 1591, 1502, 1425, 1396, 1244, 1002, 982, 765, 719, 697, 689, 555 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.61–7.53 (m, 5H), 6.22 (d, $^2J_{F-H}$=50.1 Hz, 2H). ^{19}F NMR (282 MHz, $CDCl_3$): δ −188.4 (t, $^2J_{H-F}$=49.8 Hz, 1F); ^{13}C NMR (75 MHz, $CDCl_3$): δ 151.4, 133.1, 130.7, 130.0, 124.2, 83.9 (d, $^1J_{F-C}$=226.8 Hz); MS (EI, *m*/*z*, %): 211 ($[M+H]^+$, 1), 77 (73), 46 (100). Anal. Calcd for $C_8H_7FN_4S$: C, 45.70; H, 3.36; N, 26.65. Found: C, 45.81; H, 3.38; N, 26.32.

*4.3.3. 1-tert-Butyl-1H-tetrazol-5-yl fluoromethyl sulfide (**4c**).* White solid; mp 54–55 °C; IR (KBr): 2982, 1476, 1399, 1373, 1336, 1289, 1227, 1139, 1104, 985, 720, 591 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 6.25 (d, $^2J_{F-H}$=49.8 Hz, 2H), 1.75 (s, 9H); ^{19}F NMR (282 MHz, $CDCl_3$): δ −187.9 (t, $^2J_{H-F}$=50.0 Hz, 1F); ^{13}C NMR (75 MHz, $CDCl_3$):

δ 149.6, 84.4 (d, $^1J_{F-C}$=225.4 Hz), 61.7, 29.1; MS (EI, *m*/*z*, %): 190 (M^+, 1), 57 (100). Anal. Calcd for $C_6H_{11}FN_4S$: C, 37.88; H, 5.83; N, 29.45. Found: C, 38.06; H, 5.49; N, 29.79.

*4.3.4. 1,3-Benzothiazol-2-yl fluoromethyl sulfone (**2a**)*[11c]. White solid; mp 152–153 °C (lit.[11c]: 144–147 °C); IR (KBr): 3001, 2930, 1467, 1459, 1353, 1347, 1328, 1319, 1155, 1056, 1028, 939, 766, 729, 695, 602, 593, 518 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 8.29–8.26 (m, 1H), 8.07–8.04 (m, 1H), 7.71–7.62 (m, 2H), 5.59 (d, $^2J_{H-F}$=47.4 Hz, 2H); ^{19}F NMR (282 MHz, $CDCl_3$): δ −210.8 (t, $^2J_{H-F}$=47.0 Hz, 1F); ^{13}C NMR (75 MHz, $CDCl_3$): δ 162.3, 152.7, 137.3, 128.6, 128.0, 125.8, 122.4, 90.7 (d, $^1J_{F-C}$=223.3 Hz); MS (EI, *m*/*z*, %): 231 (M^+, 65), 134 (100). Anal. Calcd for $C_8H_6FNO_2S_2$: C, 41.55; H, 2.62; N, 6.06. Found: C, 41.70; H, 2.82; N, 6.13.

*4.3.5. Fluoromethyl 1-phenyl-1H-tetrazol-5-yl sulfone (**2b**).* White needle solid, mp 59–60 °C; IR (KBr): 3002, 1940, 1593, 1496, 1374, 1160, 1079, 945, 780, 769, 696, 688, 568, 528 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.73–7.59 (m, 5H), 5.75 (d, $^2J_{H-F}$=46.3 Hz, 2H); ^{19}F NMR (282 MHz, $CDCl_3$): δ −208.9 (t, $^2J_{H-F}$=46.6 Hz, 1F); ^{13}C NMR (75 MHz, $CDCl_3$): δ 151.6, 132.7, 131.8, 129.9, 125.1, 91.7 (d, J_{F-C}=227.9 Hz); MS (EI, *m*/*z*, %): 243 ($[M+H]^+$, 0.28), 77 (43), 65 (100). Anal. Calcd for $C_8H_7FN_4O_2S$: C, 39.67; H, 2.91; N, 23.13. Found: C, 39.95; H, 2.72; N, 23.23.

*4.3.6. 1-tert-Butyl-1H-tetrazol-5-yl fluoromethyl sulfone (**2c**).* Colorless oil, while standing it sometimes became solid; IR (film): 2995, 2946, 1481, 1378, 1361, 1328, 1209, 1170, 1127, 1082, 937, 764, 635, 585, 552 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 5.84 (d, $^2J_{H-F}$=46.3 Hz, 2H), 1.88 (s, 9H); ^{19}F NMR (282 MHz, $CDCl_3$): δ −207.6 (t, $^2J_{H-F}$=45.9 Hz, 1F); ^{13}C NMR (75 MHz, $CDCl_3$): δ 152.2, 92.1 (d, J_{F-C}=228.6 Hz), 65.8, 29.7; MS (ESI, *m*/*z*): 240 ($[M+NH_4]^+$); HRMS (MALDI/DHB, *m*/*z*): calcd for $C_6H_{11}N_4O_2FSNa^+$ ($[M+Na]^+$): 245.0479; found: 245.0470.

4.4. General procedure for the preparation of terminal monofluoroalkenes (5a–i and 6a–i)

To the solution of **2c** (for aldehydes, 1.2 equiv; for ketones, 1.7 equiv), aldehydes or ketones (1.0 equiv), and HMPA (for aldehydes, 1.5 equiv; for ketones: 2.0 equiv) in THF (*c*=0.2 M) at 0 °C were added dropwise a solution LiHMDS in THF (for aldehydes, 1.5 equiv; for ketones, 2.0 equiv). The mixture was stirred at 0 °C until TLC indicated that the reaction was completed (generally in 1.5–2 h), then quenched with a saturated aqueous solution of NH_4Cl, and extracted with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by silica column chromatography (0–10% EtOAc/petroleum ether) to afford the terminal monofluoroalkenes **5a–i** or **6a–i** (generally as a mixture of *E*- and *Z*-isomers). For monofluoroalkenes **5a–i**, the configuration of the two isomers was determined by differences of their $^3J_{H-F}$ coupling constants in ^{19}F NMR spectroscopy ($^3J_{H-F}$ values of *E*-isomers are smaller than those of *Z*-isomers),[21] and for monofluoroalkenes **6a–i**, the configuration of the two isomers was determined by comparing them with known compounds.[8e,27,28]

*4.4.1. 2-(2-Fluorovinyl)naphthalene (**5a**).* White solid; mp 49–50 °C; A mixture of *E*- and *Z*-isomers (*E*/*Z*=42:58), the *E*/*Z* ratio was determined by ^{19}F NMR spectroscopy; IR (KBr): 3055, 1660, 1593, 1506, 1363, 1242, 1175, 1126, 1100, 1012, 951, 921, 863, 828, 812, 742 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.92 (s, 0.58×1H, *Z*), 7.82–7.75 (m, 3H), 7.68 (dd, J_{H-H}=1.5 Hz, J_{H-H}=8.7 Hz, 0.58×1H, *Z*), 7.63 (s, 0.42×1H, *E*), 7.49–7.43 (m, 2H), 7.38 (dd, J_{H-H}=1.5, 8.7 Hz, 0.42×1H, *E*), 7.27 (dd, $^2J_{F-H}$=83.4 Hz, $^3J_{H-H}$=11.7 Hz, 0.42×1H, *E*), 6.72 (dd, $^2J_{F-H}$=83.0 Hz, $^3J_{H-H}$=5.4 Hz, 0.58×1H, *Z*), 6.54 (dd, $^3J_{F-H}$=20.1 Hz, $^3J_{H-H}$=11.7 Hz, 0.42×1H, *E*), 5.76 (dd, $^3J_{F-H}$=44.9 Hz, $^3J_{H-H}$=5.4 Hz, 0.58×1H, *Z*); ^{19}F NMR (282 MHz, $CDCl_3$): δ −121.7 (dd, $^2J_{H-F}$=83.0 Hz, $^3J_{H-F}$=44.9 Hz, 0.58×1F, *Z*), −129.4 (dd, $^2J_{H-F}$=82.2 Hz, $^3J_{H-F}$=18.9 Hz, 0.42×1F, *E*); ^{13}C NMR (75 MHz, $CDCl_3$): δ 150.5 (d, *J*=259.6 Hz, *Z*), 148.5 (d, *J*=270.7 Hz, *E*), 133.5 (*Z*), 133.4 (*E*), 132.8 (d, *J*=9.7 Hz, *E*), 132.7 (d, *J*=10.0 Hz, *Z*), 130.2, 128.4, 128.03 (d, *J*=1.9 Hz, *Z*), 127.96 (*Z*), 127.9 (*E*), 127.7 (d, *J*=1.6 Hz, *E*), 127.6, 126.7 (d, *J*=6.5 Hz), 126.4, 126.1 (d, *J*=5.6 Hz), 125.9, 125.7 (d, *J*=4.7 Hz), 123.31 (*Z*), 123.29 (*E*), 114.2 (d, *J*=16.8 Hz, *E*), 111.0 (d, *J*=1.4 Hz, *Z*); MS (EI, *m*/*z*, %): 172 (M^+, 100), 171 (37), 151 (7); HRMS (EI, *m*/*z*): calcd for $C_{12}H_9F$ (M^+): 172.0688; found: 172.0692.

*4.4.2. 1-(Benzyloxy)-4-(2-fluorovinyl)benzene (**5b**).* White solid; mp 42–43 °C. A mixture of *E*- and *Z*-isomers (*E*/*Z*=34:66), the *E*/*Z* ratio was determined by ^{19}F NMR spectroscopy; IR (KBr): 3034, 1660, 1608, 1511, 1454, 1249, 1178, 1010, 911, 836, 736, 696 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.46–6.89 (m, 9H+0.34×1H (*E*)), 6.58 (dd, $^2J_{F-H}$=83.2 Hz, $^3J_{H-H}$=5.2 Hz, 0.66×1H, *Z*), 6.35 (dd, $^3J_{H-H}$=11.4 Hz, $^3J_{F-H}$=19.5 Hz, 0.34×1H, *E*), 5.53 (dd, $^3J_{H-H}$=5.7 Hz, $^3J_{F-H}$=45.2 Hz, 0.66×1H, *Z*), 5.06 (s, 0.66×2H, *Z*), 5.04 (s, 0.34×2H, *E*); ^{19}F NMR (282 MHz, $CDCl_3$): δ −125.1 (dd, $^2J_{H-F}$=83.0 Hz, $^3J_{H-F}$=45.2 Hz, 0.66×1F, *Z*), −132.4 (dd, $^2J_{H-F}$=83.1 Hz, $^3J_{H-F}$=19.9 Hz, 0.34×1F, *E*); ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.2 (d, *J*=2.4 Hz, *E*), 158.0 (d, *J*=2.5 Hz, *Z*), 149.0 (d, *J*=256.8 Hz, *E*), 147.1 (d, *J*=267.8 Hz, *Z*), 136.8 (d, *J*=2.6 Hz), 130.2, 130.1, 128.6, 127.99, 127.97, 127.4, 127.3 (d, *J*=3.5 Hz), 125.6 (d, *J*=1.4 Hz), 125.3 (d, *J*=11.8 Hz), 115.2, 114.8, 113.2 (d, *J*=15.9 Hz, *E*), 110.2 (*Z*), 70.0, 69.9; MS (EI, *m*/*z*, %): 228 (M^+, 5), 91 (100), 77 (14); HRMS (EI, *m*/*z*): calcd for $C_{15}H_{13}FO$ (M^+): 228.0950; found: 228.0950.

*4.4.3. 2-(2-Fluorovinyl)-1,4-dimethoxybenzene (**5c**).* Colorless oil. A mixture of *E*- and *Z*-isomers (*E*/*Z*=47:53), the *E*/*Z* ratio was determined by ^{19}F NMR spectroscopy; IR (film): 2946, 2835, 1653,1489, 1645, 1287, 1220, 1181, 1080, 1048, 919, 881, 866, 801, 775, 718 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.39–7.38 (m, 0.53×1H, *Z*), 7.38 (dd, $^2J_{F-H}$=85.8 Hz, $^3J_{H-H}$=11.4 Hz, 0.53×1H, *Z*), 6.82–6.52 (m, 2.47H (Ar*H*)+0.47×1H (*E*)), 6.46 (dd, $^3J_{F-H}$=22.1 Hz, $^3J_{H-H}$=11.3 Hz, 0.47×1H, *E*), 6.04 (dd, $^3J_{F-H}$=46.2 Hz, $^3J_{H-H}$=5.4 Hz, 0.53×1H, *Z*), 3.81 (s, 0.47×3H, *E*), 3.79 (s, 0.53×3H, *Z*), 3.78 (s, 0.47×3H, *E*), 3.76 (s, 0.53×3H, *Z*); ^{19}F NMR (282 MHz, $CDCl_3$): δ −123.1 (dd, $^2J_{F-H}$=84.0 Hz, $^3J_{F-H}$=45.6 Hz, 0.53×1F, *Z*), −124.7 (dd, J_{F-H}=85.8 Hz, $^3J_{F-H}$=22.0 Hz, 0.47×1F, *E*); ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.4, 151.8 (d, *J*=257.7 Hz, *E*), 150.6 (d, *J*=3.7 Hz), 150.5 (d, *J*=1.4 Hz), 148.3 (d, *J*=270.6 Hz, *Z*), 122.4, 122.3, 122.1 (d, *J*=1.5 Hz), 115.7 (d, *J*=12.5 Hz), 114.1 (d, *J*=2.8 Hz), 113.9 (d, *J*=2.4 Hz), 112.8 (d, *J*=2.0 Hz), 111.8, 111.7, 110.4 (d, *J*=18.5 Hz, *E*), 104.4 (d, *J*=2.7 Hz, *Z*), 56.3, 55.9, 55.7; MS (EI, *m*/*z*, %): 182 (M^+, 5), 125 (100), 77 (62); HRMS (EI, *m*/*z*): calcd for $C_{10}H_{11}O_2F$ (M^+): 182.0743; found: 182.0746.

*4.4.4. 2-(Benzyloxy)-4-(2-fluorovinyl)-1-methoxybenzene (**5d**).* White solid; mp 72–73 °C. A mixture of *E*- and *Z*-isomers (*E*/*Z*=35:65), the *E*/*Z* ratio was determined by ^{19}F NMR spectroscopy; IR (KBr): 2932, 2837, 1661, 1603, 1515, 1455, 1418, 1266, 1227, 1141, 1024, 912, 859, 808, 739, 697 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.47–6.78 (m, 8H+0.35×1H (*E*)), 6.56 (dd, $^2J_{F-H}$=82.9 Hz, $^3J_{H-H}$=5.5 Hz, 0.65×1H, *Z*), 6.28 (dd, $^3J_{F-H}$=19.6 Hz, $^3J_{H-H}$=11.3 Hz, 0.35×1H, *E*), 5.48 (dd, $^3J_{F-H}$=45.2 Hz, $^3J_{H-H}$=5.6 Hz, 0.65×1H, *Z*), 5.14 (s, 0.65×2H, *Z*), 5.13 (0.35×2H, *E*), 3.88 (s, 0.65×3H, *Z*), 3.87 (s, 0.35×3H, *E*); ^{19}F NMR (282 MHz, $CDCl_3$): δ −120.9 (dd, $^2J_{H-F}$=81.8 Hz, $^3J_{H-F}$=44.8 Hz, 0.65×1F, *Z*), −128.3 (dd, $^2J_{H-F}$=82.6 Hz, $^3J_{H-F}$=18.9 Hz, 0.35×1F, *E*); ^{13}C NMR (75 MHz, $CDCl_3$): δ 149.2 (d, J_{F-C}=257.6 Hz, *E*), 148.4, 148.0, 147.1 (d, J_{F-C}=267.9 Hz, *Z*), 137.1 (d, J_{F-C}=6.9 Hz), 128.63, 128.56, 128.0, 127.9, 127.5, 127.4, 122.4, 122.3, 114.7, 114.6, 113.6 (d, J_{F-C}=15.9 Hz, *E*), 111.6

(*Z*), 71.2, 71.1, 56.1, 56.0; MS (EI, *m*/*z*, %): 258 (M^+, 5), 91 (100); HRMS (EI, *m*/*z*): calcd for $C_{16}H_{15}O_2F$ (M^+): 258.1056; found: 258.1056.

*4.4.5. 5-(2-Fluorovinyl)benzo[1,3]dioxole (**5e**)*[21]. Colorless oil. A mixture of *E*- and *Z*-isomers (*E*/*Z*=34:66), the *E*/*Z* ratio was determined by ^{19}F NMR spectroscopy; ^1H NMR (300 MHz, $CDCl_3$): δ 7.12–6.67 (m, 3H), 7.06 (dd, $^2J_{F-H}$=83.2 Hz, $^3J_{H-H}$=11.3 Hz, 0.34×1H, *E*), 6.57 (dd, $^2J_{F-H}$=83.1 Hz, $^3J_{H-H}$=5.7 Hz, 0.66×1H, *Z*), 6.31 (dd, $^3J_{F-H}$=18.9 Hz, $^3J_{H-H}$=11.4 Hz, 0.34×1H, *E*), 5.95 (s, 0.66×2H, *Z*), 5.94 (s, 0.34×2H, *E*), 5.51 (dd, $^3J_{F-H}$=44.4 Hz, $^3J_{H-H}$=5.1 Hz, 0.66×1H, *Z*); ^{19}F NMR (282 MHz, $CDCl_3$): δ −124.5 (dd, $^2J_{H-F}$=83.2 Hz, $^3J_{H-F}$=44.2 Hz, 0.66×1F, *Z*), −132.2 (dd, $^2J_{H-F}$=84.1 Hz, $^3J_{H-F}$=19.5 Hz, 0.34×1F, *E*); MS (EI, *m*/*z*, %): 166 (M^+, 100), 107 (56).

*4.4.6. 4-(2-Fluorovinyl)biphenyl (**5f**)*[29]. White solid. A mixture of *E*- and *Z*-isomers (*E*/*Z*=42:58), the *E*/*Z* ratio was determined by ^{19}F NMR spectroscopy; ^1H NMR (300 MHz, $CDCl_3$): δ 7.61–7.05 (m, 9H+0.42×1H (*E*)), 6.67 (dd, $^3J_{H-H}$=5.4 Hz, $^2J_{F-H}$=82.8 Hz, 0.58H, *Z*), 6.75 (dd, $^3J_{F-H}$=19.4 Hz, $^3J_{H-H}$=11.6 Hz, 0.42×1H, *E*), 6.65 (dd, $^3J_{F-H}$=44.7 Hz, $^3J_{H-H}$=5.4 Hz, 0.58×1H, *Z*); ^{19}F NMR (282 MHz, $CDCl_3$): δ −120.6 (dd, $^2J_{H-F}$=82.7 Hz, $^3J_{H-F}$=44.1 Hz, 0.58×1F, *Z*), −128.3 (dd, $^2J_{H-F}$=82.2 Hz, $^3J_{H-F}$=18.6 Hz, 0.42×1F, *E*); MS (EI, *m*/*z*, %): 198 (M^+, 100), 77 (18).

*4.4.7. 2,4-Dichloro-1-(2-fluorovinyl)benzene (**5g**).* Pale yellow oil. A mixture of *E*- and *Z*-isomers (*E*/*Z*=50:50), the *E*/*Z* ratio was determined by ^{19}F NMR spectroscopy; IR (film): 2924, 2854, 1661, 1588, 1553, 1472, 1383, 1208, 1094, 1024, 912, 867, 828, 809, 768 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.76 (d, J_{H-H}=8.7 Hz, 0.50×1H, *E*), 7.40 (s, 0.50×1H, *E*), 7.39 (s, 0.50×1H, *Z*), 7.76–7.17 (m, 1H+0.50×1H (*Z*)), 7.10 (dd, $^2J_{F-H}$=82.5 Hz, $^3J_{H-H}$=11.4 Hz, 0.50×1H, *E*), 6.75 (dd, $^2J_{F-H}$=82.5 Hz, $^3J_{H-H}$=5.4 Hz, 0.50×1H, *Z*), 6.65 (dd, $^3J_{F-H}$=18.3 Hz, $^3J_{H-H}$=11.4 Hz, 0.50×1H, *E*), 6.01 (dd, $^3J_{F-H}$=43.2 Hz, $^3J_{H-H}$=5.4 Hz, 0.50×1H, *Z*); ^{19}F NMR (282 MHz, $CDCl_3$): δ −120.6 (dd, $^2J_{H-F}$=82.7 Hz, $^3J_{H-F}$=44.1 Hz, 0.50×1F, *Z*), −128.3 (dd, J_{H-F}=82.2 Hz, J_{H-F}=18.6 Hz, 0.50×1F, *E*); ^{13}C NMR (75 MHz, $CDCl_3$): δ 151.5 (d, *J*=263.3 Hz, *Z*), 149.6 (d, *J*=274.0 Hz, *E*), 131.5 (d, *J*=12.5 Hz), 129.7, 129.30, 129.28, 127.59, 127.57, 127.3, 127.2, 110.5 (d, *J*=19.2 Hz, *E*), 106.0 (d, J_{F-C}=2.3 Hz, *Z*); MS (EI, *m*/*z*, %): 191 (M^+, 13), 192 (82), 190 (100); HRMS (EI, *m*/*z*): calcd for $C_8H_5FCl_2$ (M^+): 189.9752; found: 189.9757.

*4.4.8. 1-Bromo-4-(2-fluorovinyl)benzene (**5h**).* Pale yellow oil. A mixture of *E*- and *Z*-isomers (*E*/*Z*=47:53), the *E*/*Z* ratio was determined by ^{19}F NMR spectroscopy; IR (film): 2924, 2830, 1660, 1589, 1486, 1400, 1234, 1107, 1087, 1072, 1010, 911, 836, 803 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.47–7.00 (m, 3H), 7.16 (dd, $^2J_{F-H}$=82.4 Hz, $^3J_{H-H}$=5.4 Hz, 0.53×1H, *Z*), 7.11 (d, J_{H-H}=8.4 Hz, 1H), 6.67 (dd, $^3J_{F-H}$=82.2 Hz, $^3J_{H-H}$=5.4 Hz, 0.47×1H, *E*), 6.33 (dd, $^3J_{F-H}$=18.8 Hz, $^3J_{H-H}$=11.9 Hz, 0.47×1H, *E*), 5.53 (dd, $^3J_{F-H}$=44.1 Hz, $^3J_{H-H}$=5.7 Hz, 0.53×1H, *Z*); ^{19}F NMR (282 MHz, $CDCl_3$): δ −120.9 (dd, $^2J_{H-F}$=81.8 Hz, $^3J_{H-F}$=44.8 Hz, 0.53×1F, *Z*), −128.3 (dd, $^2J_{H-F}$=82.6 Hz, $^3J_{H-F}$=18.9 Hz, 0.47×1F, *E*); ^{13}C NMR (75 MHz, $CDCl_3$): δ 150.5 (d, *J*=260.7 Hz, *E*), 148.7 (d, *J*=272.2 Hz, *Z*), 131.9, 131.7, 130.6 (d, *J*=12.0 Hz), 127.7, 127.6, 121.4 (d, *J*=3.5 Hz), 121.3, 121.2, 113.1(d, *J*=16.6 Hz, *E*), 109.9 (d, *J*=1.3 Hz, *Z*); MS (EI, *m*/*z*, %): 201 (M^+, 7), 101 (100), 202 (69), 200 (65); HRMS (EI, *m*/*z*): calcd for C_8H_6FBr (M^+): 199.9637; found: 199.9640.

*4.4.9. 1-(4-Fluorobut-3-enyl)benzene (**5i**)*[8e]. Colorless oil. A mixture of *E*- and *Z*-isomers (*E*/*Z*=48:52), the *E*/*Z* ratio was determined by ^{19}F NMR spectroscopy; ^1H NMR (300 MHz, $CDCl_3$): δ 7.32–7.15 (m, 5H), 6.49 (ddt, $^2J_{F-H}$=85.5 Hz, $^3J_{H-H}$=11.2, 1.5 Hz, 0.48×1H, *E*), 6.44 (ddt, $^2J_{F-H}$=85.5 Hz, $^3J_{H-H}$=6.3, 1.5 Hz, 0.52×1H, *E*), 5.37 (dm, $^3J_{F-H}$=27.0 Hz, 0.48×1H, *E*) 4.75 (ddt, $^3J_{F-H}$=42.6 Hz, $^3J_{H-H}$=11.7, 3.8 Hz, 0.52×1H, *Z*), 2.69 (dd, $^3J_{H-H}$=6.9, 15.0 Hz, 2H), 2.48–2.40 (m, 0.52×2H, *E*), 2.27–2.18 (m, 0.48×2H, *Z*); ^{19}F NMR (282 MHz, $CDCl_3$): δ −129.8 (dd, $^2J_{F-H}$=85.7 Hz, $^3J_{H-H}$=18.8 Hz, 0.48×1F, *E*), −130.1 (dd, $^2J_{F-H}$=85.7 Hz, $^3J_{H-H}$=43.5 Hz, 0.52×1F, *Z*).

*4.4.10. (1-Fluoroprop-1-en-2-yl)benzene (**6a**)*[8e]. Colorless oil. A mixture of *E*- and *Z*-isomers (*E*/*Z*=30:70), the *E*/*Z* ratio was determined by ^{19}F NMR spectroscopy; ^1H NMR (300 MHz, $CDCl_3$): δ 7.51–7.24 (m, 5H), 6.90 (dq, $^2J_{F-H}$=85.1 Hz, $^4J_{H-H}$=1.5 Hz, 0.30×1H, *E*), 6.66 (dq, $^2J_{F-H}$=84.3 Hz, $^4J_{H-H}$=1.5 Hz, 0.70×1H, *Z*), 2.04 (dd, $^4J_{F-H}$=3.6 Hz, $^4J_{H-H}$=1.5 Hz, 0.30×3H, *E*), 1.91 (dd, $^4J_{F-H}$=4.8 Hz, $^4J_{H-H}$=1.5 Hz, 0.70×3H, *Z*); ^{19}F NMR (282 MHz, $CDCl_3$): δ −129.0 (dq, $^2J_{H-F}$=84.7 Hz, $^4J_{H-F}$=4.8 Hz, 0.70×1F, *Z*), −131.2 (dq, $^2J_{H-F}$=85.2 Hz, $^4J_{H-F}$=3.8 Hz, 0.30×1F, *E*).

*4.4.11. 1-(1-Fluoroprop-1-en-2-yl)-4-methoxybenzene (**6b**).* Colorless oil. A mixture of *E*- and *Z*-isomers (*E*/*Z*=30:70), the *E*/*Z* ratio was determined by ^{19}F NMR spectroscopy; IR (film): 2956, 2930, 2837, 1663, 1609, 1574, 1514, 1292, 1251, 1183, 1121, 1101, 1034, 834, 807, 602, 588 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.48–7.20 (m, 2H), 6.92–6.85 (m, 2H), 6.84 (dq, $^2J_{F-H}$=85.5 Hz, $^4J_{H-H}$=1.5 Hz, 0.30×1H, *E*), 6.61 (dq, $^2J_{F-H}$=84.6 Hz, $^4J_{H-H}$=1.5 Hz, 0.70×1H, *Z*), 3.81 (s, 0.70×3H, *Z*), 3.80 (s, 0.30×3H, *E*), 2.01 (dd, $^4J_{F-H}$=3.9 Hz, $^4J_{H-H}$=1.5 Hz, 0.30×3H, *E*), 1.87 (dd, $^4J_{F-H}$=4.8 Hz, $^4J_{H-H}$=1.5 Hz, 0.70×3H, *Z*); ^{19}F NMR (282 MHz, $CDCl_3$): δ −130.3 (dq, $^2J_{H-F}$=84.5 Hz, $^4J_{H-F}$=4.6 Hz, 0.70×1F, *Z*), −132.0 (dq, $^2J_{H-F}$=85.5 Hz, $^4J_{H-F}$=3.8 Hz, 0.30×1F, *E*); ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.1 (d, *J*=1.5 Hz, *E*), 158.8 (d, *J*=2.1 Hz, *Z*), 145.2 (d, *J*=256.1 Hz, *E*), 143.6 (d, *J*=261.6 Hz, *Z*), 129.0 (d, *J*=6.2 Hz, *Z*), 128.3 (d, *J*=1.1 Hz), 127.0 (d, *J*=3.5 Hz, *E*), 119.5 (d, *J*=9.9 Hz, *E*), 116.3 (d, *J*=1.6 Hz, *Z*), 114.0, 113.6, 55.31 (*E*), 55.26 (*Z*), 16.0 (d, *J*=7.2 Hz, *Z*), 12.4 (d, *J*=5.4 Hz, *E*); MS (EI, *m*/*z*, %): 166 (M^+, 100), 107 (14), 77 (27); HRMS (EI, *m*/*z*): calcd for $C_{10}H_{11}OF$ (M^+): 166.0794; found: 166.0786.

*4.4.12. 1-(1-Fluoroprop-1-en-2-yl)-4-methylbenzene (**6c**).* Colorless oil. A mixture of *E*- and *Z*-isomers (*E*/*Z*=33:67), the *E*/*Z* ratio was determined by ^{19}F NMR spectroscopy; IR (film): 2953, 2924, 2859, 1664, 1515, 1441, 1115, 1105, 1064, 823, 808, 718, 602 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.41–7.12 (m, 4H), 6.88 (dq, $^4J_{H-H}$=1.5 Hz, $^2J_{F-H}$=85.2 Hz, 0.33×1H, *E*), 6.62 (dq, $^4J_{H-H}$=1.5 Hz, $^2J_{F-H}$=84.9 Hz, 0.67×1H, *Z*), 2.35 (s, 0.67×3H, *Z*), 2.34 (s, 0.33×3H, *E*), 2.02 (dd, $^4J_{F-H}$=3.9 Hz, $^4J_{H-H}$=1.5 Hz, 0.33×3H, *E*), 1.87 (dd, $^4J_{F-H}$=4.8 Hz, $^4J_{H-H}$=1.5 Hz, 0.67×3H, *Z*); ^{19}F NMR (282 MHz, $CDCl_3$): δ −129.5 (dq, $^2J_{H-F}$=84.6 Hz, $^4J_{H-F}$=5.0 Hz, 0.67×1F, *Z*), −132.2 (dq, $^2J_{H-F}$=85.3 Hz, $^4J_{H-F}$=3.6 Hz, 0.33×1F, *E*); ^{13}C NMR (75 MHz, $CDCl_3$): δ 145.7 (d, *J*=256.8 Hz, *E*), 144.0 (d, *J*=262.3 Hz, *Z*), 137.2 (d, *J*=1.5 Hz, *Z*), 134.7 (d, *J*=8.3 Hz), 133.0 (d, *J*=1.2 Hz, *E*), 129.3, 129.0, 127.7 (d, *J*=6.6 Hz, *Z*) 125.8 (d, *J*=2.9 Hz, *E*), 119.9 (d, *J*=9.7 Hz, *E*), 116.8 (d, *J*=1.4 Hz, Z), 21.2 (*Z*), 21.1 (*E*), 16.0 (d, *J*=7.3 Hz, *Z*), 12.3 (d, *J*=6.2 Hz, *E*); MS (EI, *m*/*z*, %): 150 (M^+, 100), 91 (75); HRMS (EI, *m*/*z*): calcd for $C_{10}H_{11}F$ (M^+): 150.0845; found: 150.0850.

*4.4.13. 1-Chloro-4-(1-fluoroprop-1-en-2-yl)benzene (**6d**).* Colorless oil. A mixture of *E*- and *Z*-isomers (*E*/*Z*=25:75), the *E*/*Z* ratio was determined by ^{19}F NMR spectroscopy; IR (film): 2955, 2926, 2850, 1662, 1596, 1493, 1402, 1122, 1098, 1014, 988, 834, 815, 762, 604 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.44–7.21 (m, 4H), 6.88 (dq, $^2J_{F-H}$=84.3 Hz, $^4J_{H-H}$=1.5 Hz, 0.25×1H, *E*), 6.66 (dq, $^2J_{F-H}$=84.3 Hz, $^4J_{H-H}$=1.5 Hz, 0.75×1H, *Z*), 2.02 (dd, $^4J_{F-H}$=3.9 Hz, $^4J_{H-H}$=1.5 Hz, 0.25×3H, *E*), 1.89 (dd, $^4J_{F-H}$=4.8 Hz, $^4J_{H-H}$=1.5 Hz, 0.75×3H, *Z*); ^{19}F NMR (282 MHz, $CDCl_3$): δ −127.5 (dq, $^2J_{H-F}$=84.0 Hz, $^4J_{H-F}$=4.8 Hz, 0.75×1F, *Z*), −129.8 (dq, $^2J_{H-F}$=84.6 Hz, $^4J_{H-F}$=3.9 Hz, 0.25×1F, *E*); ^{13}C NMR (75 MHz, $CDCl_3$): δ 146.2 (d, *J*=258.4 Hz, *E*), 144.7

(d, J=264.6 Hz, Z), 136.0 (d, J=9.2 Hz, E), 134.2, 133.2, 133.1 (d, J=2.2 Hz), 129.1 (d, J=6.3 Hz, Z), 128.7 (E), 128.4 (Z), 127.2 (d, J=3.3 Hz, E), 119.2 (d, J=10.3 Hz, E), 116.0, 15.9 (d, J=6.9 Hz, Z), 12.2 (d, J=5.9 Hz, E); MS (EI, m/z, %): 170 (M^+, 9), 43 (100); HRMS (EI, m/z): calcd for C_9H_8FCl (M^+): 170.0299; found: 170.0303.

*4.4.14. 1-Bromo-4-(1-fluoroprop-1-en-2-yl)benzene (**6e**).* Colorless oil. A mixture of E- and Z-isomers (E/Z=28:72), the E/Z ratio was determined by ^{19}F NMR spectroscopy; IR (film): 2954, 2925, 2852, 1662, 1489, 1399, 1124, 1100, 1084, 1009, 831, 813, 751, 603 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) 7.51–7.14 (m, 4H), 6.89 (dq, $^2J_{F-H}$=84.3 Hz, $^4J_{H-H}$=1.5 Hz, 0.28×1H, E), 6.66 (dq, $^2J_{F-H}$=84.0 Hz, $^4J_{H-H}$=1.5 Hz, 0.72×1H, Z), 2.01 (dd, $^4J_{F-H}$=3.9 Hz, $^4J_{H-H}$=1.5 Hz, 0.28×3H, E), 1.87 (dd, $^4J_{F-H}$=4.8 Hz, $^4J_{H-H}$=1.5 Hz, 0.72×3H, Z); ^{19}F NMR (282 MHz, $CDCl_3$): δ −127.5 (dq, $^2J_{H-F}$=84.0 Hz, $^4J_{H-F}$=4.8 Hz, 0.72×1F, Z), −129.8 (dq, $^2J_{H-F}$=84.6 Hz, $^4J_{H-F}$=3.9 Hz, 0.28×1F, E); ^{13}C NMR (75 MHz, $CDCl_3$): δ 146.1 (d, J=258.3 Hz, E), 144.6 (d, J=263.8 Hz, Z), 136.5 (d, J=8.4 Hz, E), 134.7 (Z), 131.7 (E), 131.4 (Z), 129.4 (d, J=6.3 Hz, Z), 127.5 (d, J=3.0 Hz, E), 121.4 (d, J=2.3 Hz), 119.3 (d, J=10.2 Hz, E), 116.3 (Z), 15.7 (d, J=7.0 Hz, Z), 12.1 (d, J=6.5 Hz, E); MS (EI, m/z, %): 215 (M^+, 10), 216 (59), 214 (50), 115 (100); HRMS (EI, m/z): calcd for C_9H_8BrF (M^+): 213.9793; found: 213.9798.

*4.4.15. 1-(Fluoromethylene)-indane (**6f**).* Colorless oil. A mixture of E- and Z-isomers (E/Z=76:24), the E/Z ratio was determined by ^{19}F NMR spectroscopy (the configuration of E- and Z-isomers was determined by comparing ^1H NMR spectroscopy with known non-fluoro compound[27]); IR (film): 2930, 2850, 1677, 1473, 1462, 1449, 1360, 1210, 1109, 1079, 1068, 790, 755 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.79–7.75 (m, 0.76×1H, E), 7.31–7.28 (m, 0.24×1H, Z), 7.27–7.12 (m, 3H), 7.23 (dt, $^2J_{F-H}$=83.2 Hz, $^4J_{H-H}$=2.7 Hz, 0.24×1H, Z), 6.58 (dt, $^2J_{F-H}$=83.4 Hz, $^4J_{H-H}$=1.8 Hz, 0.76×1H, E), 3.01 (t, J_{H-H}=6.9 Hz, 2H), 2.90–2.82 (m, 0.24×2H, Z), 2.72–2.65 (m, 0.76×2H, E); ^{19}F NMR (282 MHz, $CDCl_3$): δ −134.1 (d, $^2J_{H-F}$=83.9 Hz, 0.76×1F, E), −139.1 (d, $^2J_{H-F}$=84.1 Hz, 0.24×1F, Z); ^{13}C NMR (75 MHz, $CDCl_3$): δ 145.7, 142.6 (d, J=252.0 Hz, Z), 142.3 (d, J=258.0 Hz, E), 137.7 (E), 137.5 (d, J=7.6 Hz, Z), 128.0 (d, J=2.3 Hz, E), 127.8 (d, J=2.8 Hz, Z), 126.64 (E), 126.55 (Z), 125.5 (d, J=10.0 Hz, E), 125.2 (Z), 124.8 (E), 124.7 (d, J=3.5 Hz), 119.7 (Z), 30.5 (E), 30.2 (Z), 25.4 (d, J=6.5 Hz, E), 25.2 (d, J=2.0 Hz, Z); MS (EI, m/z, %): 148 (M^+, 12), 149 (30), 57 (100); HRMS (EI, m/z): calcd for $C_{10}H_9F$ (M^+): 148.0688; found: 148.0683.

*4.4.16. 1-(Fluoromethylene)-1,2,3,4-tetrahydronaphthalene (**6g**).* Colorless oil.; A mixture of E- and Z-isomers (E/Z=59:41), the E/Z ratio was determined by ^{19}F NMR spectroscopy(the configuration of E- and Z-isomers was determined by comparing ^1H NMR spectroscopy with known non-fluoro compound[28]); IR (film): 2935, 2865, 1655, 1485, 1454, 1433, 1266, 1228, 1113, 1071, 1005, 808, 796, 755, 726 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.93–7.89 (m, 0.41×1H, Z), 7.34–7.32 (m, 0.59×1H, E), 7.21–7.08 (m, 3H), 7.15 (d, $^2J_{F-H}$=84.9 Hz, 0.59×1H, E), 6.65 (d, $^2J_{F-H}$=84.6 Hz, 0.41×1H, Z), 2.85 (t, J_{H-H}=6.5 Hz, 0.41×2H, Z), 2.76 (t, J_{H-H}=6.2 Hz, 0.59×2H, E), 2.62–2.56 (m, 0.59×2H, E), 2.30–2.25 (m, 0.41×2H, Z), 1.92–1.78 (m, 2H); ^{19}F NMR (282 MHz, $CDCl_3$): δ −129.6 (d, $^2J_{H-F}$=84.4 Hz, 0.41×1F, Z), −136.5 (d, $^2J_{H-F}$=85.0 Hz, 0.59×1F, E); ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.3 (d, J=254.5 Hz, E), 143.5 (d, J=269.0 Hz, Z), 137.5 (d, J=5.7 Hz, E), 137.1 (d, J=2.4 Hz, Z), 131.1 (d, J=8.3 Hz, E), 130.7 (d, J=2.9 Hz, Z), 129.2 (E), 129.1 (Z), 129.0 (d, J=13.8 Hz), 127.3 (d, J=2.0 Hz, Z), 127.1 (d, J=2.0 Hz, E), 126.1 (d, J=1.4 Hz, E), 125.8 (Z), 122.6 (d, J=1.4 Hz, E), 119.9 (d, J=11.8 Hz, E), 117.0 (d, J=2.8 Hz, Z), 30.2 (Z), 30.1 (E), 26.9 (d, J=7.5 Hz, Z), 23.6 (d, J=2.7 Hz, Z), 22.3 (d, J=6.2 Hz, E), 22.1 (d, J=1.5 Hz, E); MS (EI, m/z, %): 162 (M^+, 89), 129 (100), 128 (49); HRMS (EI, m/z): calcd for $C_{11}H_{11}F$ (M^+): 162.0845; found: 162.0846.

*4.4.17. 2-Fluoro-1,1-diphenylethene (**6h**)[30a].* Colorless oil; ^1H NMR (300 MHz, $CDCl_3$): δ 7.37–7.22 (m, 10H), 6.96(d, $^2J_{F-H}$=83.7 Hz, 1H); ^{19}F NMR (282 MHz, $CDCl_3$): δ −128.1 (d, $^2J_{H-F}$=83.3 Hz, 1F).

*4.4.18. 1-(4-Fluoro-3-methylbut-3-enyl)benzene (**6i**)[30b].* Colorless oil. A mixture of E- and Z-isomers (E/Z=49:51), the E/Z ratio was determined by ^{19}F NMR spectroscopy; ^1H NMR (300 MHz, $CDCl_3$): δ 7.31–7.14 (m, 5H), 6.36 (dm, J_{F-H}=86.3 Hz, 0.51×1H, Z), 6.35 (dm, J_{F-H}=86.7 Hz, 0.49×1H, E), 2.74–2.67 (m, 2H), 2.44–2.38 (m, 0.51×2H, Z), 2.20–2.14(m, 0.49×2H, E), 1.69 (dd, J=3.2 Hz, J=1.5 Hz, 0.49×3H, E), 1.53 (dd, J=3.9 Hz, J=1.8 Hz, 0.51×3H, Z); ^{19}F NMR (282 MHz, $CDCl_3$): δ −135.3 (dm, $^2J_{H-F}$=86.0 Hz, 0.51×1F, Z), −136.4 (dm, $^2J_{H-F}$=86.1 Hz, 0.49×1F, E).

4.5. General procedure for the preparation of α-alkylated sulfones (7)

Under a nitrogen atmosphere, to the solution of **2c** (267 mg, 1.20 mmol) and HMPA (0.32 mL, 1.83 mmol) in THF (6 mL) was added a solution of n-BuLi in hexane (1.6 M, 0.86 mL, 1.38 mmol) at −78 °C, followed by the addition of iodoethane (0.19 mL, 2.38 mmol) after 30 min. The reaction mixture was stirred for 30 min at −78 °C and then warmed slowly to room temperature. When TLC indicated that **2c** was disappeared, the reaction was quenched by the addition of a saturated NH_4Cl solution (3 mL). The aqueous layer was separated and extracted with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by flash column chromatography (EtOAc/petroleum ether=1:20) to afford the alkylated product **7a** as a colorless oil (208 mg, 67% yield).

*4.5.1. 1-tert-Butyl-5-(1-fluoropropylsulfonyl)-1H-tetrazole (**7a**).* Colorless oil; IR (film): 2988, 2945, 2887, 1480, 1466, 1357, 1273, 1241, 1208, 1171, 1108, 1049, 1023, 981, 906, 817, 661, 627, 584 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 6.14 (ddd, J_{F-H}=47.6 Hz, J_{H-H}=9.0 Hz, J_{H-H}=3.8 Hz, 1H), 2.44–2.15 (m, 2H), 1.87 (s, 9H), 1.27 (t, J_{H-H}=7.5 Hz, 2H); ^{19}F NMR (282 MHz, $CDCl_3$): δ −177.6 (ddd, J_{H-F}=47.7 Hz, J_{H-F}=32.6 Hz, J_{H-F}=17.2 Hz, 1F); ^{13}C NMR (75 MHz, $CDCl_3$): δ 152.4, 104.0 (d, J=225.9 Hz), 65.7, 29.6, 20.2 (d, J=19.9 Hz), 8.6 (d, J=3.4 Hz); MS (EI, m/z, %): 250 (M^+, 0.03), 57 (100). Anal. Calcd for $C_8H_{15}FN_4O_2S$: C, 38.39; H, 6.04; N, 22.38. Found: C, 38.58; H, 6.17; N, 22.54.

*4.5.2. 1-tert-Butyl-5-(1-fluoroheptylsulfonyl)-1H-tetrazole (**7b**).* Colorless oil; IR (film): 2960, 2933, 2861, 1467, 1377, 1355, 1209, 1168, 1119, 1087, 627, 586, 549 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 6.18 (ddd, J_{F-H}=47.7 Hz, J_{H-H}=8.9, 4.2 Hz, 1H), 2.34 (m, 2H), 1.87 (s, 9H), 1.77–1.26 (m, 8H), 0.91 (t, J_{H-H}=6.6 Hz, 3H); ^{19}F NMR (282 MHz, $CDCl_3$): δ −176.1 (ddd, J_{H-F}=48.0, 33.5, 18.5 Hz, 1F); ^{13}C NMR (75 MHz, $CDCl_3$): δ 152.6, 103.5 (d, J=225.5 Hz), 66.0, 31.6, 29.9, 28.9, 26.4 (d, J=19.2 Hz), 24.4 (d, J=2.9 Hz), 22.7, 14.2; MS (ESI, m/z): 307.2 ($[M+H]^+$); HRMS (ESI): calcd for $C_{12}H_{23}FN_4O_2SNa$ ($[M+Na]^+$): 329.1418; found: 329.1417.

*4.5.3. 1-tert-Butyl-5-(1-fluoro-3-methylbutylsulfonyl)-1H-tetrazole (**7c**).* White solid; mp 66–69 °C; IR (KBr): 2962, 2878, 1474, 1380, 1355, 1210, 1171, 1143, 1120, 1088, 618, 584, 547 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 6.23 (ddd, J_{F-H}=48.0 Hz, J_{H-H}=10.2, 2.9 Hz, 1H), 2.17–1.95 (m, 3H), 1.10 (d, J_{H-H}=4.2 Hz, 3H), 1.08 (d, J_{H-H}=4.5 Hz, 3H); ^{19}F NMR (282 MHz, $CDCl_3$): δ −175.8 (ddd, J_{H-F}=47.4 Hz, J_{H-F}=39.5 Hz, J_{H-F}=15.4 Hz, 1F); ^{13}C NMR (75 MHz, $CDCl_3$): δ 152.7, 102.9 (d, J=225.6 Hz), 65.7, 34.4 (d, J=18.7 Hz), 29.7,

24.6, 23.0, 21.4; MS (ESI, *m*/*z*): 279 ([M+H]$^+$); HRMS (ESI): calcd for $C_{10}H_{19}FN_4O_2Sna$ ([M+Na]$^+$): 301.1105; found: 301.1108.

*4.5.4. 1-tert-Butyl-5-(1-fluorobut-3-enylsulfonyl)-1H-tetrazole (**7d**).* Colorless oil; IR (film): 3087, 2989, 2942, 1644, 1480, 1467, 1431, 1408, 1377, 1355, 1241, 1208, 1168, 1121, 1087, 989, 931, 870, 817, 662, 582 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.24 (ddd, J_{F-H}=47.3 Hz, J_{H-H}=9.2, 3.9 Hz, 1H), 5.97–5.83 (m, 1H), 5.41–5.33 (m, 2H), 3.15–2.88 (m, 1H), 1.87 (s, 9H); ^{19}F NMR (282 MHz, $CDCl_3$): δ −176.0 (ddd, J_{H-F}=48.0, 32.0, 18.9 Hz, 1F); ^{13}C NMR (75 MHz, $CDCl_3$): δ 152.6, 128.6 (d, J=2.8 Hz), 121.7, 102.3 (d, J=226.3 Hz), 66.1, 31.2 (d, J=19.3 Hz), 29.9; MS (ESI, *m*/*z*): 263 ([M+H]$^+$). Anal. Calcd for $C_9H_{15}FN_4O_2S$: C, 41.21; H, 5.76; N, 21.36. Found: C, 41.76; H, 5.99; N, 21.32.

*4.5.5. 1-tert-Butyl-5-(1-fluoro-2-phenylethylsulfonyl)-1H-tetrazole (**7e**).* White solid; mp 70–72 °C; IR (KBr): 2984, 2941, 1602, 1494, 1481, 1456, 1432, 1376, 1363, 1353, 1266, 1238, 1208, 1199, 1169, 1079, 1007, 861, 784, 755, 704, 630, 583, 541 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.42–7.31 (m, 5H), 6.33 (ddd, J_{F-H}=47.3 Hz, J_{H-H}=10.3, 2.6 Hz, 1H), 3.69–3.37 (m, 2H), 1.88 (s, 9H); ^{19}F NMR (282 MHz, $CDCl_3$): δ −175.8 (ddd, J_{H-F}=47.7, 37.5, 18.9 Hz, 1F); ^{13}C NMR (75 MHz, $CDCl_3$): δ 152.5, 132.8, 129.9, 129.3, 128.2, 103.5 (d, J=228.5 Hz), 66.1, 32.3 (d J=19.4 Hz), 29.9; MS (ESI, *m*/*z*): 313 ([M+H]$^+$); HRMS (ESI): calcd for $C_{13}H_{17}FN_4O_2Sna^+$ ([M+Na]$^+$): 335.0948; found: 335.0947.

4.6. General procedure for the preparation of alkyl-substituted internal monofluoroalkenes (8)

Under N_2 atmosphere, to a solution of aldehydes (or ketones) and α-alkylated sulfones **7a**–**e** (*condition A*: 1.2 equiv, *condition B*: 1.7 equiv), and HMPA (*condition A*: 2.4 equiv, *condition B*: 3.4 equiv) in THF (*c*=0.2 M) a solution of LiHMDS in THF (*condition A*: 2.4 equiv, *condition B*: 3.4 equiv) was added at 0 °C. When the reaction was completed by TLC, a saturated aqueous NH_4Cl was added to the reaction mixture and the mixture was extracted with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4, and the solvent was evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel (0–5% EtOAc/petroleum ether) to afford the corresponding alkenes **8a**–**d**. and **8a′**–**c′**. For **8a**–**d**, the configuration of *E*- or *Z*-isomers was determined by differences of their $^3J_{H-F}$ coupling constants.[21] For **8a′**–**c′**, the configuration of *E*- or *Z*-isomers was determined by comparing with known compounds.[31]

*4.6.1. 2-(2-Fluorobut-1-enyl)naphthalene (**8a**)[12b].* Colorless oil, while standing it became solid; A mixture of *E*- and *Z*-isomers (*E*/*Z*=33:67), the *E*/*Z* ratio was determined by ^{19}F NMR spectroscopy; IR (film): 3056, 3019, 2977, 2918, 2881, 1687, 1598, 1507, 1462, 1362, 1328, 1271, 1179, 1149, 1371, 973, 895, 837, 816, 746 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.88–7.21 (m, 7H), 6.30 (d, $^3J_{F-H}$=21.6 Hz, 0.33×1H, *E*), 5.60 (d, $^3J_{F-H}$=39.6 Hz, 0.67×1H, *Z*), 2.61–2.33 (m, 2H), 1.22 (t, $^3J_{H-H}$=7.2 Hz, 0.33×3H, *E*), 1.20 (t, $^3J_{H-H}$=7.2 Hz, 0.67×3H, *Z*); ^{19}F NMR (282 MHz, $CDCl_3$): δ −100.1 (*pseudo* q, dt, $^3J_{H-F}$=21.6, 21.6 Hz, 0.33×1F, *E*), −100.4 (dt, $^3J_{H-F}$=39.8, 15.6 Hz, 0.67×1F, *Z*); MS (EI, *m*/*z*, %): 200 (M$^+$, 100); HRMS (EI): calcd for $C_{14}H_{13}F$ (M$^+$): 200.1001; found: 200.1002.

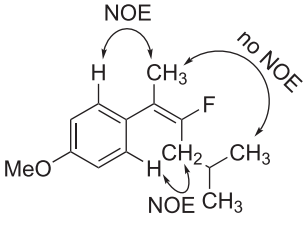
*4.6.2. 1-Bromo-4-(3-fluoropent-2-en-2-yl)benzene (**8a′**).* Colorless oil. A mixture of *E*- and *Z*-isomers (*E*/*Z*=36:64), the *E*/*Z* ratio was determined by ^{19}F NMR spectroscopy; IR (film): 2968, 2925, 2854, 1686, 1489, 1464, 1396, 1187, 1077, 1028, 1010, 963, 828, 720 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.46–7.04 (m, 4H), 2.40 (dq, J_{F-H}=23.2 Hz, J_{H-H}=7.6 Hz, 0.64×2H, *Z*), 2.18 (dq, J_{F-H}=23.0 Hz, J_{H-H}=7.6 Hz, 0.36×2H, *E*), 1.94–1.92 (m, 3H), 1.16 (t, J_{H-H}=7.5 Hz, 0.64×3H, *Z*), 1.07 (t, J_{H-H}=7.4 Hz, 0.36×3H, *E*); ^{19}F NMR (282 MHz, $CDCl_3$): δ −108.7 (t, J_{H-F}=24.3 Hz, 0.64×1F, *Z*), −109.9 (t, J_{H-F}=24.0 Hz, 0.36×1F, *E*); MS (EI, *m*/*z*, %): 243 (M$^+$, 5), 148 (100); HRMS (EI): calcd for $C_{11}H_{12}BrF$ (M$^+$): 242.0106; found: 242.0111.

*4.6.3. 1-Bromo-4-(2-fluorooct-1-enyl)benzene (**8b**).* Colorless oil. A mixture of *E*- and *Z*-isomers (*E*/*Z*=27:73), the *E*/*Z* ratio was determined by ^{19}F NMR spectroscopy; IR (film): 2956, 2929, 2858, 1689, 1488, 1466, 1401, 1151, 1704, 1010, 851, 830, 807 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.45–7.03 (m, 4H), 6.10 (d, $^3J_{F-H}$=21.3 Hz, 0.27×1H, *E*), 5.40 (d, $^3J_{F-H}$=39.0 Hz, 0.73×1H, *Z*), 2.46–2.24 (m, 2H), 1.64–1.53 (m, 2H), 1.41–1.23 (m, 6H), 0.92–0.85 (m, 3H); ^{19}F NMR (282 MHz, $CDCl_3$): δ −97.4 (*pseudo* q, dt, $^3J_{H-F}$=21.9, 21.9 Hz, 0.27×1F, *E*), −99.6 (dt, $^3J_{H-F}$=38.1, =18.8 Hz, 0.73×1F, *Z*); MS (ES, *m*/*z*, %): 285 (M$^+$, 7), 134 (100); HRMS (EI): calcd for $C_{14}H_{18}BrF$ (M$^+$): 284.0576; found: 284.0573.

*4.6.4. 1-(3-Fluoronon-2-en-2-yl)benzene (**8b′**).* Colorless oil. A mixture of *E*- and *Z*-isomers (*E*/*Z*=51:49), the *E*/*Z* ratio was determined by ^{19}F NMR spectroscopy; IR (film): 3024, 2957, 2929, 2858, 1689, 1601, 1494, 1465, 1444, 1379, 1198, 1174, 1053, 1027, 763, 669 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.37–7.17 (m, 5H), 2.39 (dt, $^3J_{F-H}$=23.7, $^3J_{H-H}$=7.2 Hz, 0.49×2H, *Z*), 2.17 (dt, $^3J_{F-H}$=23.4 Hz, $^3J_{H-H}$=7.6 Hz, 0.51×2H, *E*), 1.96 (d, $^4J_{F-H}$=3.3 Hz, 0.49×3H, *Z*), 1.95 (d, $^4J_{F-H}$=3.3 Hz, 0.51×3H, *E*), 1.62–1.16 (m, 8H), 0.90 (t, $^3J_{H-H}$=6.6 Hz, 0.49×3H, *Z*), 0.85 (t, $^3J_{H-H}$=6.9 Hz, 0.51×3H, *E*); ^{19}F NMR (282 MHz, $CDCl_3$): δ −107.7 (t, J_{H-F}=24.0 Hz, 0.49×1F, *Z*), −109.7 (t, J_{H-F}=22.6 Hz, 0.51×1F, *E*); MS (EI, *m*/*z*, %): 220 (M$^+$, 83), 129 (100); HRMS (EI): calcd for $C_{15}H_{21}F$ (M$^+$): 220.1627; found: 220.1632.

*4.6.5. 1-Bromo-2-(2-fluoro-4-methylpent-1-enyl) benzene (**8c**).* Colorless oil. A mixture of *E*- and *Z*-isomers (*E*/*Z*=51:49), the *E*/*Z* ratio was determined by ^{19}F NMR spectroscopy; IR (film): 3068, 2959, 2927, 2871, 1687, 1590, 1561, 1467, 1436, 1369, 1155, 1115, 1025, 750 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.78–7.03 (m, 4H), 6.25 (d, $^3J_{F-H}$=21.0 Hz, 0.51×1H, *E*), 5.82 (d, $^3J_{F-H}$=38.1 Hz, 0.49×1H, *Z*), 2.27–2.24 (m, 0.51×2H, *E*), 2.20–2.16 (m, 0.49×2H, *Z*), 2.04–1.95 (m, 1H), 1.01 (d, $^3J_{H-H}$=6.9 Hz, 0.49×6H, *E*), 0.91 (d, $^3J_{H-H}$=6.6 Hz, 0.51×6H, *E*); ^{19}F NMR (282 MHz, $CDCl_3$): δ −98.0 (*pseudo* q, dt, $^3J_{H-F}$=22.4, 22.4 Hz, 0.51×1F, *E*), −101.0 (*pseudo* q, dt, $^3J_{H-F}$=38.1, 20.0 Hz, 0.49×1F, *Z*); MS (EI, *m*/*z*, %): 257 (M$^+$, 2), 134 (100); HRMS (EI): calcd for $C_{12}H_{14}BrF$ (M$^+$): 256.0263; found: 256.0272.

*4.6.6. 1-(3-Fluoro-5-methylhex-2-en-2-yl)-4-methoxy benzene (**8c′**).* Colorless oil. Only *E*-isomer, the configuration of **8c′** was determined by its NOE spectroscopy (Fig. 2); IR (film): 3035, 2958, 2870, 2836, 1693, 1609, 1513, 1465, 1443, 1288, 1245, 1175, 1037, 859, 832 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.08 (d, J=6.3 Hz, 2H), 6.85 (d, J=6.3 Hz, 2H), 3.81 (s, 3H), 2.06 (dd, $^3J_{F-H}$=22.7 Hz, $^3J_{H-H}$=7.2 Hz, 2H), 1.94 (d, J_{F-H}=3.6 Hz, 3H), 1.92–1.83 (m, 1H), 0.84 (d, $^3J_{H-H}$=6.3 Hz, 6H); ^{19}F NMR (282 MHz, $CDCl_3$): δ −109.1 (t,



8c'

Figure 2. NOE of the product **8c′**.

J_{H-F}=22.7 Hz, 1F, *E*); ^{13}C NMR (75 MHz, $CDCl_3$): 158.3, 156.3 (d, *J*=250.6 Hz), 132.9 (d, *J*=9.5 Hz), 129.6 (d, *J*=2.9 Hz), 114.8 (d, *J*=20.7 Hz), 113.6, 55.1, 38.0 (d, *J*=27.6 Hz), 26.1, 22.2, 16.4 (d, *J*=9.4 Hz); MS (EI, *m*/*z*, %): 222 (M^+, 40), 179 (100); HRMS (EI): calcd for $C_{14}H_{19}OF$ (M^+): 222.1420; found: 222.1421.

*4.6.7. 5-(2-Fluoropenta-1,4-dienyl)benzo[d][1,3] dioxole (**8d**).* Pale yellow oil. A mixture of *E*- and *Z*-isomers (*E*/*Z*=46:54), the *E*/*Z* ratio was determined by ^{19}F NMR spectroscopy; IR (film): 3026, 2961, 2925, 1603, 1503, 1489, 1444, 1336, 1249, 1213, 1103, 1040, 939, 809 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.10–6.64 (m, 3H), 6.20 (d, $^3J_{F-H}$=21.0 Hz, 0.46×1H, *E*), 5.97–5.81 (m, 1H), 5.96 (s, 0.46×2H, *E*), 5.94 (s, 0.54×2H, *Z*), 5.41 (d, $^3J_{F-H}$=39.0 Hz, 0.54×1H, *Z*), 5.28–5.16 (m, 2H), 3.16 (ddt, *J*=1.7, 5.7, 24.3 Hz, 0.46×2H, *E*), 3.06 (dd, *J*=6.6, 15.0, 0.54×2H, *Z*); ^{19}F NMR (282 MHz, $CDCl_3$): δ −99.5 (*pseudo* q, dt, $^3J_{H-F}$=22.9, 22.9 Hz, 0.46×1F, *E*), −102.4 (dt, $^3J_{H-F}$=38.6, 15.5 Hz, 0.54×1F, *Z*); MS (ES, *m*/*z*, %): 206 (M^+, 5), 186 (100); HRMS (EI): calcd for $C_{12}H_{11}FO_2$ (M^+): 206.0743; found: 206.0746.

4.7. The preparation of ethyl 2-(1-*tert*-butyl-1*H*-tetrazol-5-yl-sulfonyl)-2-fluoroacetate (9)[17h]

Under N_2 atmosphere, a solution of LiHMDS in THF (1.06 M, 13.0 mL, 13.78 mmol) was added to the solution of **2c** (1.53 g, 6.88 mmol) and diethyl carbonate (1.67 g, 13.75 mmol) in THF (25 mL) at −78 °C. The mixture was stirred at this temperature until TLC indicated the reaction was completed, and followed by quenching with a saturated aqueous of NH_4Cl. After warming to room temperature, the mixture was extracted with EtOAc, and then the organic layers were washed with brine and dried over Na_2SO_4. After removal of solvent under vacuum, the residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate=10:1) to afford ethyl 2-(1-*tert*-butyl-1*H*-tetrazol-5-yl-sulfonyl)-2-fluoroacetat (**9**, 1.70 g, 84% yield) as colorless oil. IR (film): 2991, 1771, 1469, 1369, 1244, 1172, 1116, 1020, 857, 638, 585 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 6.53 (d, *J*=46.8 Hz, 1H), 4.45 (dq, *J*=7.1, 1.8 Hz, 2H), 1.87 (s, 9H), 1.38 (t, *J*=7.2 Hz, 3H); ^{19}F NMR (282 MHz, $CDCl_3$): δ −179.20 (d, *J*=48.0 Hz, 1F); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.2, 159.0, 151.9, 97.3 (d, *J*=238.2 Hz), 97.2 (d, *J*=237.9 Hz), 66.0, 64.19, 64.18, 29.5, 29.4, 13.7; MS (EI, *m*/*z*, %): 238 ($[M-(CH_3)_3C+H]^+$, 2), 57(100); HRMS (EI): calcd for $C_9H_{15}FN_4O_4S_2$ (M^+): 294.0798; found: 294.0785.

4.8. The preparation of 1-*tert*-butyl-5-(fluoro (phenylsulfonyl)-methyl-sulfonyl)-1*H*-tetrazole (11)

Under N_2 atmosphere, a solution of LiHMDS in THF (1.06 M, 13.21 mL, 14.00 mmol) was added to the solution of **2c** (1.56 g, 7.02 mmol) and methyl benzenesufinate (2.19 g, 14.02 mmol) in THF (25 mL) at −78 °C. The mixture was stirred at this temperature until TLC indicated the reaction was completed, followed by quenching with a saturated aqueous solution of NH_4Cl. After warmed to room temperature, the mixture was extracted with EtOAc, and then the organic layers were washed with brine and dried over Na_2SO_4. After removal of solvent under vacuum, the residue was purified by silica gel column chromatography (EtOAc/petroleum ether=1:5) to afford **10** (2.32 g, 96% yield) as white solid.

Into a flask equipped with a magnetic stirrer were sequentially added **10** (696 mg, 2.01 mmol), CCl_4 (4 mL), CH_3CN (4 mL), water (8 mL), and sodium periodate (651 mg, 3.04 mmol). Thereafter, ruthenium trichloride hydrate (5 mg, 0.018 mmol) was added to the reaction flask. The resulting mixture was stirred at room temperature and a white precipitate was formed. The completion of the reaction was monitored by ^{19}F NMR (the signal of compound **10** disappeared), and the precipitate was filtered and washed with Et_2O. The filtrate was diluted with Et_2O and washed successively with a saturated aqueous solution of $NaHCO_3$ and brine, dried over $MgSO_4$. After the removal of half of the solvent under vacuum, filtration through a pad of silica gel and concentration afforded **11** (599 mg, 82% yield) as white solid.

*4.8.1. 1-tert-Butyl-5-(fluoro(phenylsulfinyl)methyl sulfinyl)-1H-tetrazole (**10**).* White solid; mp 135–136 °C. A mixture of two diastereomers (downfield/upfield=8:92); IR (KBr): 2997, 2950, 1476, 1445, 1358, 1169, 1122, 1104, 1086, 691, 613, 582 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.88–7.85 (m, 2H), 7.66–7.61 (m, 3H), 6.68 (d, *J*=45.3 Hz, 0.92×1H), (d, *J*=46.2 Hz, 0.08×1H), 1.87 (s, 0.92×9H), 1.86 (s, 0.08×9H); ^{19}F NMR (282 MHz, $CDCl_3$): δ −166.19 (d, *J*=48.6 Hz, 0.08×1F), −182.78 (d, *J*=47.1 Hz, 0.92×1F); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.1, 137.69 (d, *J*=3.0 Hz), 137.67, 133.4, 133.1, 129.8, 129.5, 126.0 (d, *J*=1.4 Hz), 125.3, 109.8 (d, *J*=283.6 Hz), 66.0, 29.4; MS (EI, *m*/*z*, %): 346 (M^+, 0.24), 125 (100); HRMS (EI): calcd for $C_{12}H_{15}FN_4O_3S_2$ (M^+): 346.0570; found: 346.0571.

*4.8.2. 1-tert-Butyl-5-(fluoro(phenylsulfonyl)methyl sulfonyl)-1H-tetrazole (**11**).* White solid; mp 141–142 °C; IR (KBr): 3074, 2984, 2952, 1585, 1484, 1450, 1367, 1353, 1192, 1178, 1098, 1077, 803, 760, 751, 562 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 8.07 (d, *J*=8.1 Hz, 2H), 7.84 (t, *J*=7.5 Hz, 1H), 7.67 (t, *J*=8.0 Hz, 2H), 7.02 (d, *J*=45.0 Hz, 1H), 1.83 (s, 9H); ^{19}F NMR (282 MHz, $CDCl_3$): δ −167.8 (d, *J*=44.9 Hz, 1F); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.6, 136.3, 134.8, 130.3, 129.7, 105.2 (d, *J*=269.5 Hz), 66.2, 29.5; MS (EI, *m*/*z*, %): 306 ($[M-(CH_3)_3C+H]^+$, 1), 57 (100). Anal. Calcd for $C_{12}H_{15}FN_4O_4S_2$: C, 39.77; H, 4.17; N, 15.46. Found: C, 39.59; H, 4.10; N, 15.39.

4.9. The preparation of acyl-substituted internal monofluoroalkene 12[11b]

Under N_2 atmosphere, to a stirred solution of sulfone **9** (589 mg, 2.00 mmol) and 2-naphthaldehyde (375 mg, 2.40 mmol) in THF (10 mL), DBU (0.42 mL, 2.85 mmol) was added dropwise at −78 °C. After addition the mixture was stirred for 30 min at −78 °C and then 2 h at room temperature. The reaction was quenched with a saturated aqueous solution of NH_4Cl (5 mL) and then extracted with EtOAc (30 mL). The organic layers were combined and washed with brine, dried over Na_2SO_4, filtered, and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography (EtOAc/petroleum ether=1:120) to afford ethyl 2-fluoro-3-(naphthalen-2-yl)acrylate (**12**, 391 mg, 80% yield) as colorless oil. A mixture of *E*- and *Z*-isomers (*E*/*Z*=64:36), the *E*/*Z* ratio was determined by ^{19}F NMR spectroscopy; ^1H NMR (300 MHz, $CDCl_3$): δ 8.10 (s, 0.36×1H, *Z*), 7.93 (s, 0.64×1H, *E*), 7.87–7.76 (m, 3H), 7.59–7.47 (m, 3H), 7.08 (d, *J*=35.1 Hz, 0.36×1H, *Z*), 7.06 (d, *J*=22.8 Hz, 0.64×1H, *E*), 4.38 (q, *J*=7.1 Hz, 0.36×2H, *Z*), 4.26 (q, *J*=7.1 Hz, 0.64×2H, *E*), 1.41 (t, *J*=7.2 Hz, 0.36×3H, *Z*), 1.22 (t, *J*=7.5 Hz, 0.64×3H, *Z*); ^{19}F NMR (282 MHz, $CDCl_3$): δ −115.9 (d, *J*=21.5 Hz, 0.64×1F, *E*), −124.4 (d, *J*=35.0 Hz, 0.36×1F, *Z*).

4.10. The preparation of phenylsulfonyl-substituted internal monofluoroalkene 13[12d]

Under N_2 atmosphere, to a stirred solution of 2-naphthaldehyde (100 mg, 0.64 mmol) and sulfone **11** (302 mg, 0.83 mmol) in freshly distilled CH_2Cl_2 (4 mL), DBU was added (0.15 mL, 0.97 mmol) at room temperature. The reaction was continued at room temperature until the aldehyde was consumed and quenched with a saturated aqueous solution of NH_4Cl (4 mL) and then extracted with EtOAc (20 mL). The organic layers were combined and washed with brine, dried over Na_2SO_4, filtered, and evaporated under reduced pressure. The crude product was purified by silica gel chromatography (EtOAc/petroleum ether=1:50) to afford 2-(2-fluoro-2-(phenylsulfonyl)vinyl)naphthalene (**13**, 140 mg, 70% yield) as pale

yellow oil. A mixture of *E*- and *Z*-isomers (*E*/*Z*=27:73), the *E*/*Z* ratio was determined by ^{19}F NMR spectroscopy; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.06–7.81 (m, 6H), 7.70–7.48 (m, 6H), 7.22 (d, *J*=35.1 Hz, 0.27×1H, *E*), 7.06 (d, *J*=21.9 Hz, 0.73×1H, *Z*); ^{19}F NMR (282 MHz, $CDCl_3$): δ −111.5 (d, *J*=23.7 Hz, 0.73×1F, *Z*), −125.1 (d, *J*=33.0 Hz, 0.27×1F, *E*).

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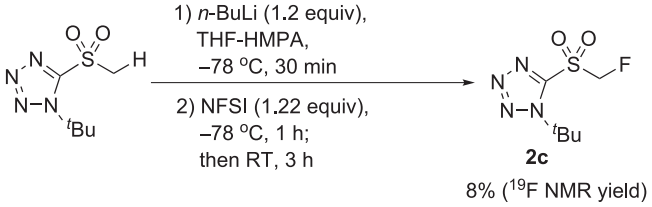
Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2010.04.113. These data include MOL files and InChiKeys of the most important compounds described in this article.

References and notes

1. (a) Uneyama, K. *Organofluorine Chemistry*; Blackwell: Oxford, UK, 2006; (b) Kirsch, P. Modern Fluoroorganic Chemistry: Synthesis, Reactivity, Applications; Wiley-VCH: Weinheim. (c) Chambers, R. D. *Fluorine in Organic Chemistry*; Blackwell: Oxford, 2004; (d) Bégué, J.-P.; Bonnet-Delpon, D. *Bioorganic and Medicinal Chemistry of Fluorine*; Wiley: Hoboken, USA, 2008; (e) *Organofluorine Compounds. Chemistry and Applications*; Hiyama, T., Ed.; Springer: New York, NY, 2000; (f) *Organofluorine Chemistry: Principles and Commercial Applications*; Banks, R. E., Smart, B. E., Tatlow, J. C., Eds.; Plenum: New York, NY, 1994.
2. Ameduri, B.; Boutevin, B. *J. Fluorine Chem.* **2000**, *104*, 53–62.
3. McCarthy, J. R.; Matthews, D. P.; Stemerick, D. M.; Huber, E. W.; Bey, P.; Lippert, B. J.; Snyder, R. D.; Sunkara, P. S. *J. Am. Chem. Soc.* **1991**, *113*, 7439–7440; (b) Welch, J. T. *Slective Fluorination in Organic and Bioorganic Chemistry*; American Chemical Society: Washington, D.C, 1991; (c) Weintraub, P. M.; Holland, A. K.; Gates, C. A.; Moore, W. R.; Resvick, R. J.; Beye, P.; Peet, N. P. *Bioorg. Med. Chem.* **2003**, *11*, 427–431.
4. *Fluorine-Containing Synthons*; Soloshonok, V. A., Ed.; American Chemical Society: Washington, DC, 2005.
5. Steenis, J. H.; Gen, A. *J. Chem. Soc., Perkin Trans. 1* **2002**, 2117–2133.
6. Lee, S. H.; Schwartz, J. *J. Am. Chem. Soc.* **1986**, *108*, 2445–2447.
7. (a) Tius, M. A.; Kawakami, J. K. *Synlett* **1993**, 207–208; (b) Tius, M. A.; Kawakami, J. K. *Tetrahedron* **1995**, *51*, 3997–4010.
8. (a) Manfre, F.; Kern, J. M.; Biellmann, J.-F. *J. Org. Chem.* **1992**, *57*, 2060–2065; (b) Burton, D. J.; Cox, D. G. *J. Am. Chem. Soc.* **1983**, *105*, 650–651; (c) Cox, D. G.; Gurusamy, N.; Burton, D. J. *J. Am. Chem. Soc.* **1985**, *107*, 2811–2812; (d) Wheaton, G. A.; Burton, D. J. *J. Org. Chem.* **1983**, *48*, 917–927; (e) van Steenis, J. H.; van der Gen, A. *Eur. J. Org. Chem.* **2001**, 897–910.
9. (a) McCarthy, J. R.; Matthews, D. P.; Edwards, M. L.; Stemerick, D. M.; Jarvi, E. T. *Tetrahedron Lett.* **1990**, *31*, 5449–5452; (b) Khrimian, A. P.; DeMilo, A. B.; Waters, R. M.; Liquido, N. J.; Nicholson, J. M. *J. Org. Chem.* **1994**, *59*, 8034–8039.
10. Zhang, W.; Huang, W.; Hu, J. *Angew. Chem., Int. Ed.* **2009**, *48*, 9858–9861.
11. (a) Chevrie, D.; Lequeux, T.; Demoute, J. P.; Pazenok, S. *Tetrahedron Lett.* **2003**, *44*, 8127–8130; (b) Pfund, E.; Lebargy, C.; Rouden, J.; Lequeux, T. *J. Org. Chem.* **2007**, *72*, 7871–7877; (c) Calata, C.; Catel, J.-M.; Pfund, E.; Lequeux, T. *Tetrahedron* **2009**, *65*, 3967–3973; (d) Calata, C.; Pfund, E.; Lequeux, T. *J. Org. Chem.* **2009**, *74*, 9399–9405.
12. (a) Ghosh, A. K.; Zajc, B. *Org. Lett.* **2006**, *8*, 1553–1556; (b) Zajc, B.; Kake, S. *Org. Lett.* **2006**, *8*, 4457–4460; (c) del Solar, M.; Ghosh, A. K.; Zajc, B. *J. Org. Chem.* **2008**, *73*, 8206–8211; (d) He, M.; Ghosh, A. K.; Zajc, B. *Synlett* **2008**, 999–1004; (e) Ghosh, A. K.; Banerjee, S.; Sinha, S.; Kang, S. B.; Zajc, B. *J. Org. Chem.* **2009**, *74*, 3689–3697; (f) Ghosh, A. K.; Zajc, B. *J. Org. Chem.* **2009**, *74*, 8531–8540.
13. Alonso, D. A.; Fuensanta, M.; Gomez-Bengoa, E.; Najera, C. *Adv. Synth. Catal.* **2008**, *350*, 1823–1829.
14. (a) Baudin, J. B.; Hareau, G.; Julia, S. A.; Ruel, O. *Tetrahedron Lett.* **1991**, *32*, 1175–1178; (b) Blakemore, P. R.; Cole, W. J.; Kocienski, P. J.; Morley, A. *Synlett* **1998**, 26–28; (c) Kocienski, P. J.; Bell, A.; Blakemore, P. R. *Synlett* **2000**, 365–366; (d) Blakemore, P. R. *J. Chem. Soc., Perkin Trans. 1* **2002**, 2563–2585; (e) Aissa, C. *Eur. J. Org. Chem.* **2009**, 1831–1844; (f) Takeda, T. *Modern Carbonyl Olefination*; Wiley-VCH: Weinheim, 2004.
15. Zhang, W.; Zhu, L.; Hu, J. *Tetrahedron* **2007**, *63*, 10569–10575.
16. Both PTSO2CH2F (**2b**) and TBTSO2CH2F (**2c**) are previously unknown, and BTSO2CH2F (**2a**) was recently reported as an undesired product [see Ref. 11c]. We found that fluoromethyl heteroaryl sulfone compounds were difficult to be prepared by electrophilic fluorination of corresponding methyl sulfones (see below).



8% (^{19}F NMR yield)

17. (a) Li, Y.; Hu, J. *Angew. Chem., Int. Ed.* **2005**, *44*, 5882–5886; (b) Li, Y.; Ni, C.; Liu, J.; Zhang, L.; Zheng, J.; Zhu, L.; Hu, J. *Org. Lett.* **2006**, *8*, 1693–1696; (c) Ni, C.; Li, Y.; Hu, J. *J. Org. Chem.* **2006**, *71*, 6829–6833; (d) Ni, C.; Liu, J.; Zhang, L.; Hu, J. *Angew. Chem., Int. Ed.* **2007**, *46*, 786–789; (e) Prakash, G. K. S.; Hu, J. *Acc. Chem. Res.* **2007**, *40*, 921–930; (f) Liu, J.; Li, Y.; Hu, J. *J. Org. Chem.* **2007**, *72*, 3119–3121; (g) Ni, C.; Zhang, L.; Hu, J. *J. Org. Chem.* **2008**, *73*, 5699–5713; (h) Ni, C.; Zhang, L.; Hu, J. *J. Org. Chem.* **2009**, *74*, 3767–3771; (i) Hu, J. *J. Fluorine Chem.* **2009**, *130*, 1130–1139.
18. Please see experimental section.
19. Su, W. *Tetrahedron Lett.* **1994**, *35*, 4955–4958.
20. Surprenant, S.; Chan, W. Y.; Berthelette, C. *Org. Lett.* **2003**, *5*, 4851–4854.
21. Kataoka, K.; Tsuboi, S. *Synthesis* **1999**, 452–456.
22. Liu, P.; Jacobsen, E. N. *J. Am. Chem. Soc.* **2001**, *123*, 10772–10773.
23. Prakash, G. S. K.; Chacko, S.; Vaghoo, H.; Shao, N.; Gurung, L.; Mathew, T.; Olah, G. A. *Org. Lett.* **2009**, *11*, 1127–1130.
24. (a) Quast, H.; Bieber, L. *Chem. Ber.* **1981**, *114*, 3253–3272; (b) Aïssa, C. *J. Org. Chem.* **2006**, *71*, 360–363.
25. Wang, R.; Dolman, S. J. *J. Org. Chem.* **2007**, *72*, 3969–3971.
26. Adam, W.; Bargon, R. M.; Bosio, S. G.; Schenk, W. A.; Stalke, D. *J. Org. Chem.* **2002**, *67*, 7037–7041.
27. Pearson, W. H.; Fang, W.-K. *J. Org. Chem.* **2000**, *65*, 7158–7174.
28. Oku, A.; Harada, T.; Hattori, K.; Nozaki, Y.; Yamaura, Y. *J. Org. Chem.* **1988**, *53*, 3089–3098.
29. Uno, H.; Sakamoto, K.; Semba, F.; Suzuki, H. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 210–217.
30. (a) Asakura, N.; Usuki, Y.; Iio, H. *J. Fluorine Chem.* **2003**, *124*, 81–88; (b) McCarthy, J. R.; Huber, E. W.; Le, T.-B.; Laskovics, M. F.; Matthews, D. P. *Tetrahedron* **1996**, *52*, 45–58.
31. Andrei, D.; Wnuk, S. F. *J. Org. Chem.* **2006**, *71*, 405–408.