Nucleophilic 5-*endo-trig* Cyclization of 3,3-Difluoroallylic Metal Enolates and Enamides: Facile Synthesis of Ring-Fluorinated Dihydroheteroles

Takeshi Fujita,[a] Masahiro Ikeda,[a] Masahiro Hattori,[a] Kotaro Sakoda,[b] Junji Ichikawa*[a]

[a] Division of Chemistry, Faculty of Pure and Applied Sciences, University of Tsukuba, Tsukuba, Ibaraki 305-8571, Japan
Fax +81(29)8534237; E-mail: junji@chem.tsukuba.ac.jp

[b] Department of Chemistry, Graduate School of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

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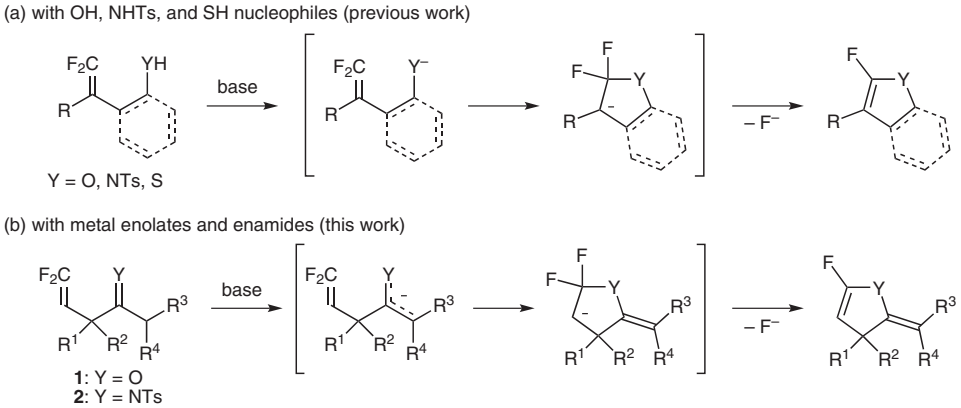
Abstract: Metal enolates and enamides bearing difluoroallylic moieties underwent nucleophilic 5-*endo-trig* cyclization, a process considered to be disfavored according to Baldwin's rules. Whereas no C-cyclization was observed in these reactions, O- and N-cyclization proceeded exclusively to afford 5-fluorinated 2-alkylidene-2,3-dihydrofurans and -2,3-dihydropyrroles, respectively.

Key words: cyclizations, fluorine, heterocycles, furans, pyrroles, ring closure

According to Baldwin's rules, the 5-*endo-trig* cyclization is a disfavored process, because the transition state of this cyclization mode involves a profound distortion of the bond angles.[1] Although the number of reported examples of the 5-*endo-trig* cyclization is gradually increasing, well-designed cyclization precursors are still required in most cases.[2–5] As a result, in practice, the 5-*endo-trig* cyclization process is rarely adopted for the construction of five-membered rings. Therefore, a version of this anti-Baldwin process with wider application is highly desirable.

We have previously achieved nucleophilic 5-*endo-trig* cyclization of *gem*-difluoroalkenes (1,1-difluoro-1-alkenes).[5] The high reactivity of 1,1-difluoro-1-alkenes, arising from their electron-deficient and highly polarized nature, facilitates intramolecular nucleophilic vinylic substitution (S_NV), in which a fluorine substituent is simultaneously installed on the resulting cyclized product.[5,6] The unique properties of 1,1-difluoro-1-alkenes make even a nucleophilic 5-*endo-trig* approach feasible. Specifically, it seems that (i) the highly polarized difluorovinylidene double bond permits initial ring formation by electrostatic attraction between the CF_2 carbon and the internal nucleophile, and (ii) the successive elimination of fluoride ion suppresses the reverse ring opening, thereby functioning as a 'lock' to afford the 5-*endo-trig* product. In a series of our studies, hydroxy (–OH), sulfonylamino (–$NHSO_2R$), and sulfanyl (–SH) groups have been successfully employed as nucleophiles under basic conditions to afford a variety of fluorine-containing five-membered heterocycles (Scheme 1, a).

We recently reported the 5-*endo-trig* cyclization of rotationally restricted 3,3-difluoroallylic metal enolates (Scheme 1, b).[7] In this reaction, 5-*endo-trig* ring closure is exclusively effected in an O-cyclization fashion to provide 2-alkylidene-2,3-dihydrofurans,[8] despite the extra steric constraint associated with the planarity of enolates. Furthermore, we have achieved 5-*endo-trig* cyclization of 3,3-difluoroallylic imines via their metal enamides, prepared in situ by treatment with an appropriate base (Scheme 1, b). Notably, the 3,3-difluoroallylic metal enamides appear to be more restricted than the corresponding metal enolates because of the presence of an extra substituent on the nitrogen atom. Intriguingly, the 5-*endo-*



Scheme 1 The 5-*endo-trig* cyclization of 1,1-difluoro-1-alkenes

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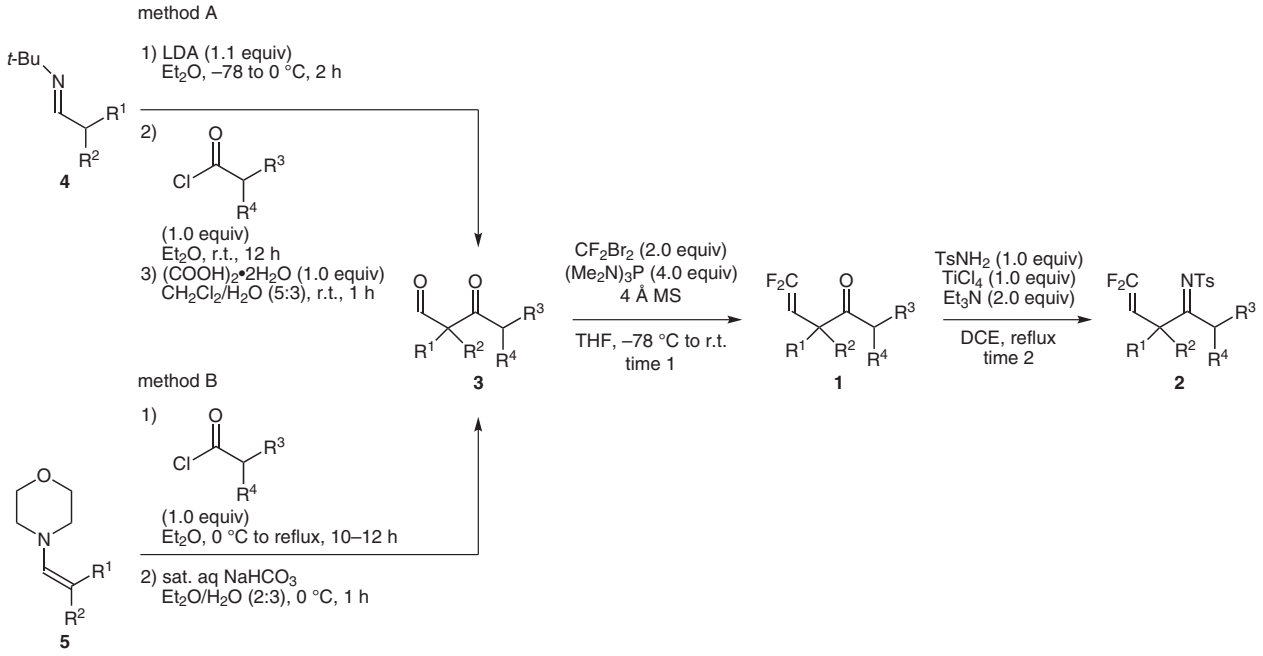
trig cyclization of enamides bearing 1,1-difluoro-1-alkene moieties readily proceeds in an N-cyclization fashion, similar to the O-cyclization of enolates, to give 2-alkylidene-2,3-dihydropyrroles. Here, we report the full details of the 5-*endo*-*trig* cyclization of 3,3-difluoroallylic ketones **1** and imines **2**, and we discuss the stereochemistry of exocyclic double-bond formation in both products.

The enolate precursors, the 3,3-difluoroallylic ketones **1**, were synthesized by a Wittig-type difluoromethylenation of 1,3-keto aldehydes **3** (Table 1),[9] which, in turn, were prepared either by acylation of the *N*-*tert*-butyl enamides generated by deprotonation of the imines **4** (method A) or by acylation of the morpholine enamines **5** (method B), with subsequent hydrolysis in each case.[10] Keto aldehydes **3a**, **3c**–**g**, and **3j** were obtained by method A, whereas keto aldehydes **3b**, **3h**, and **3i** were prepared by method B (Table 1). When the 1,3-keto aldehydes **3** were treated with a triaminophosphonium difluoromethylide generated by the reaction of dibromodifluoromethane with tris(dimethylamino)phosphine,[9] the corresponding 3,3-difluoroallylic ketones **1** were obtained in moderate to high yields (Table 1).[11] Furthermore, the enamide precursors, the 3,3-difluoroallylic *N*-(4-methylbenzenesulfonyl)(tosyl)imines **2**, were prepared by treating the ketones **1** with 4-toluensulfonamide in the presence of titanium(IV) chloride and triethylamine (Table 1).[12]

The resulting 3,3-difluoroallylic ketones **1** were subjected to basic conditions to effect the normally disfavored 5-*endo*-*trig* cyclization (Table 2). When sodium hydride and sodium methoxide were used as bases in tetrahydrofuran, no cyclization occurred (Table 2, entries 1 and 2). Upon treatment with an equimolar amount of lithium diisopro-

Table 1 Preparation of 3,3-Difluoroallylic Ketones **1** and Imines **2**[a]

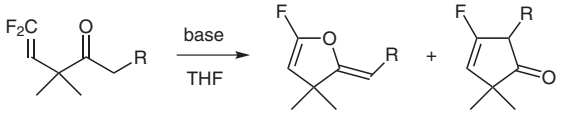


Entry	R^1	R^2	R^3	R^4	Method	Yield of **3** (%)	Time 1 (h)	Yield of **1** (%)	Time 2	Yield of **2** (%)
1	Me	Me	$(CH_2)_7Me$	H	A	**3a** 32	10	**1a** 86	3 d	**2a** 61
2	Me	Me	Bn	H	B	**3b** 58	16	**1b** 87	1 d	**2b** 68
3	Me	Me	Cy	H	A	**3c** 45	7	**1c** 82	7 h	**2c** 82
4	Me	Me	*t*-Bu	H	A	**3d** 85	10	**1d** 58	–	
5	Me	Me	Ph	H	A	**3e** 44	10	**1e** 63	1 d	**2e** 60
6	Me	Me	4-$MeOC_6H_4$	H	A	**3f** 54	5	**1f** 58	2 d	**2f** 54
7	Me	Me	$–(CH_2)_5–$		A	**3g** 90	12	**1g** 71	–	
8	$–(CH_2)_5–$		H	H	B	**3h** –[18]	10	**1h** 66	1 d	**2h** 67
9	$–(CH_2)_5–$		*t*-Bu	H	B	**3i** 29	8	**1i** 68	–	
10	$–(CH_2)_5–$		$–(CH_2)_5–$		A[a]	**3j** 41	10	**1j** 27	–	

[a] Reaction conditions: 1. **4**, *t*-BuLi (1.0 equiv), pentane–THF, –78 °C to 0 °C, 1 h; 2. CyCOCl (1.0 equiv), pentane–THF, –78 °C to reflux, 2 h; 3. AcOH (50 equiv), NaOAc (50 equiv), H_2O–pentane–THF, 0 °C, 1 h.

pylamide (LDA), **1a** gave the 5-fluorinated 2-alkylidene-2,3-dihydrofuran **6a** in 29% yield (entry 3) as a single diastereomer (*Z*-form; see below). O-Cyclization of the enolate generated from **1a** proceeded exclusively in a 5-*endo-trig* fashion, and the C-cyclized product, the 3-fluoro-2-octylcyclopent-3-en-1-one **7a**, was not detected. The use of two equivalents of LDA improved the yield of dihydrofuran **6a** to 42% (entry 4). Potassium *tert*-butoxide and potassium hydride were found to be much more effective bases than LDA (entries 5 and 6). Finally, the use of two equivalents of potassium hydride led to a 91% yield of dihydrofuran **6a** without the formation of cyclopentenone **7a** (entry 7).

Table 2 Optimization of Base-Mediated 5-*endo-trig* Cyclization of Ketone **1a**[a]



1a **6a** **7a**

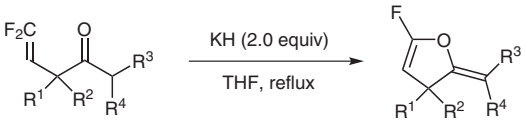
R = *n*-C_8H_{17}

Entry	Base (equiv)	Time (h)	Yield (%) of **6a**	Yield (%) of **7a**
1	NaH (1.0)	2	–[b]	–[b]
2	NaOMe (1.0)	2	–[b]	–[b]
3	LDA (1.0)	5	29	–[b]
4	LDA (2.0)	4	42	–[b]
5	*t*-BuOK (1.0)	2	63	–[b]
6	KH (1.0)	2	79	–[b]
7	KH (2.0)	2	91	–[b]

[a] Reaction conditions: THF, reflux.
[b] Not detected.

Having identified the optimal conditions, we then investigated the substrate scope for the 5-*endo-trig* cyclization of 3,3-difluoroallylic ketones **1** (Table 3). Ketones **1b**–**f** and **1i** bearing benzyl (entry 2), secondary alkyl (entry 3), tertiary alkyl (entries 4 and 9), or aryl groups (entries 5 and 6) on the α-carbon participated in the cyclization to produce the corresponding 2-alkylidene-5-fluoro-2,3-dihydrofurans **6b**–**f** and **6i** in high to excellent yields with exclusive stereoselectivity. The reaction was therefore unaffected by substituents on the α-carbon of the carbonyl group distal to the difluoroalkene moiety. In addition, the cyclization proceeded successfully even when the α-carbon was disubstituted (entries 7 and 10) or unsubstituted (entry 8). When ketones **1h**–**j** bearing a cyclohexane ring at the allylic position were used, the corresponding spirocyclic products **6h**–**j** were obtained (entries 8–10). In all cases, the 5-*endo-trig* cyclization afforded the appropriate 5-fluorinated 2-alkylidene-2,3-dihydrofuran **6** without the formation of a C-cyclization product. As Baldwin previously noted, in the intramolecular nucleophilic cyclization

Table 3 5-*endo-trig* Cyclization of 3,3-Difluoroallylic Ketones **1** via Their Metal Enolates



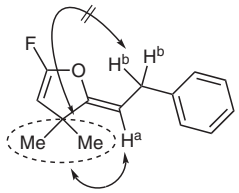
1 **6**

Entry	Time (h)	Product	Yield (%)
1	2	**6a**	91
2	2	**6b**	97
3	2	**6c**	83
4	2	**6d**	75
5	2	**6e**	98
6	2	**6f**	97
7	21	**6g**	94
8	5	**6h**	91
9	2	**6i**	94
10[a]	3	**6j**	97

[a] Pyridine was used as the solvent instead of THF.

of enolates, C-cyclization requires a perpendicular approach of the electrophilic moiety to the plane of the enolate, whereas O-cyclization allows the electrophilic moiety to approach in the plane of the enolate, so that the reaction can proceed more readily.[13]

In this series of experiments, the 2-alkylidene-2,3-dihydrofurans **6a**–**f** and **6i** were obtained as single stereoisomers. To determine the configuration of the alkylidene moieties of **6**, we performed nuclear Overhauser effect (NOE) experiments with dihydrofuran **6b** (Figure 1). A substantial correlation was observed between the vinylic proton (H^a in Figure 1) and the protons of the two methyl groups attached to the dihydrofuran ring, whereas no NOE correlation was detected between the allylic protons (H^b in Figure 1) and the methyl protons. Therefore, the stereochemistry of dihydrofurans **6a**–**f** and **6i** was determined to be *Z*. This can be rationalized as follows: steric repulsion between the substituents on both the α-carbons of the ketone **1** facilitates selective formation of the *Z*-enolate, which undergoes subsequent cyclization without inversion to give (*Z*)-**6**.



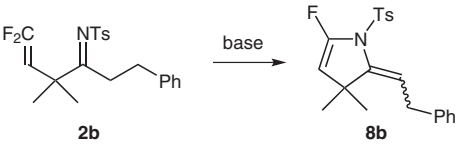
(*Z*)-**6b**

Figure 1 Stereochemistry of **6b** determined by NOE experiments

In an attempt to broaden the range of applicability of the 5-*endo*-*trig* cyclization of 1,1-difluoro-1-alkenes, we attempted a similar reaction with the 3,3-difluoroallylic imines **2** in the hope of obtaining the corresponding ring-fluorinated dihydropyrroles (Table 4). However, when we initially applied the optimal conditions determined for the cyclization of 3,3-difluoroallylic ketones **1** to the reaction of the 3,3-difluoroallylic imine **2b**, we obtained no cyclized products (Table 4, entry 1). Instead, the corresponding *Z*-enamine was formed, presumably through protonation of the intermediary metal enamide (See below; Scheme 2). However, the use of *N*,*N*-dimethylformamide instead of tetrahydrofuran as the solvent induced the desired 5-*endo*-*trig* cyclization at 90 °C to afford the 5-fluorinated 2-alkylidene 2,3-dihydropyrrole **8b** in 68% yield with a diastereomeric ratio of 74:26 (entry 2). As with ketones **1**, no C-cyclized product was obtained and N-cyclization occurred exclusively. Among the bases examined, potassium *tert*-butoxide was found to be the most effective, and the use of 1.2 equiv at 90 °C gave the highest yield of **8b** (78%) with a diastereomeric ratio of approximately 4:1 (entry 5).

The optimal conditions for the cyclization of imine **2b** were successfully applied to other 3,3-difluoroallylic imines **2**. This resulted in the formation of the corresponding

Table 4 Optimization of the Base-Mediated 5-*endo*-*trig* Cyclization of Imine **2b**



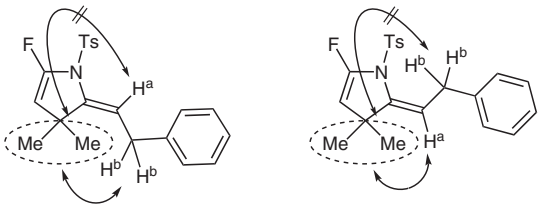
2b **8b**

Entry	Base (equiv)	Conditions	Yield of **8b** (%)	*E*/*Z*
1	KH (2.0)	THF, reflux, 2 h	–[a]	–
2	KH (1.2)	DMF, 90 °C, 3 h	68	74:26
3	NaH (1.2)	DMF, 90 °C, 4 h	69	61:39
4	NaOMe (1.2)	DMF, 90 °C, 5.5 h	57	75:25
5	*t*-BuOK (1.2)	DMF, 90 °C, 4 h	78	79:21
6	*t*-BuOK (1.2)	DMF, 100 °C, 3 h	69	78:22
7	*t*-BuOK (2.0)	DMF, 90 °C, 4 h	59	80:20

[a] Not detected.

2-alkylidene-5-fluoro-2,3-dihydropyrroles **8** (Table 5). Imines **2a** and **2c** bearing primary and secondary alkyl substituents on the α-carbon of the imino group distal to the difluoroalkene moiety readily underwent the 5-*endo*-*trig* cyclization to give dihydropyrroles **8a** and **8c**, respectively (Table 5, entries 1 and 3). Note that the cyclization of α-arylated imines **2e** and **2f** proceeded with exclusive stereoselectivity to afford products **8e** and **8f**, respectively (entries 4 and 5). Furthermore, in the case of imine **2h** bearing a cyclohexane ring in the allylic position, the corresponding spirocyclic product **8h** was obtained almost quantitatively (entry 6).

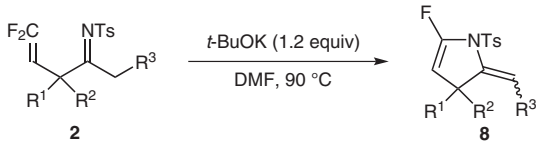
As in the case of the 2-alkylidene-2,3-dihydrofurans **6**, the stereochemistry of **8** was determined by NOE experiments using an *E*/*Z* mixture of dihydropyrrole **8b** (Figure 2). The major product exhibited a correlation between the allylic protons (H^b in Figure 2) and the protons of the two methyl groups attached to the dihydropyrrole ring, whereas the minor product exhibited correlation between the vinylic proton (H^a in Figure 2) and the methyl protons. These observations suggested that the major and minor products were the *E*- and *Z*-isomers of **8b**, respectively, which is in sharp contrast to the *Z*-selectivity observed in the O-cyclization of ketones **1**. The change in stereoselec-

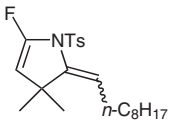
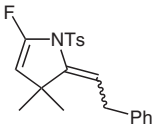
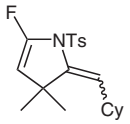
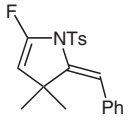
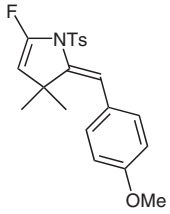
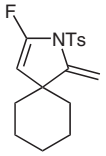


(*E*)-**8b** (major) (*Z*)-**8b** (minor)

Figure 2 Stereochemistry of **8b** determined by NOE experiments

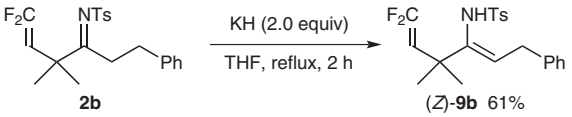
Table 5 5-*endo-trig* Cyclization of 3,3-Difluoroallylic Imines **2** via Their Metal Enamides



Entry	Time (h)	Product	Yield (%)	*E*/*Z*
1	4	**8a** 	74	89:11
2	4	**8b** 	78	79:21
3	6	**8c** 	63	93:7
4	4	**8e** 	86	–
5[a]	3	**8f** 	77	–
6[a]	4	**8h** 	99	–

[a] Amount of *t*-BuOK used was increased to 1.3 equiv.

tivity can be explained as follows. It is likely that the *Z*-enamides are initially formed by deprotonation of 3,3-difluoroallylic imines **2**, presumably as a result of steric repulsion between the substituents on the two α-carbons of imines **2**. This speculation is supported by the fact that the reaction of **2b** with potassium hydride in tetrahydrofuran gave the *Z*-enamine **9b** exclusively (Scheme 2; see also Table 4, entry 1). The stereochemistry of **9b** was confirmed by NOE experiments. Cyclization of the *Z*-enamide derived from **2b** appears to be retarded by the presence on the nitrogen atom of the tosyl group, which is repelled by the benzyl group, thereby hindering the reaction. As a result, cyclization occurs preferentially from the *E*-enamide after stereo inversion, leading to the selective formation of dihydropyrrole **8b** bearing an *E*-alkylidene moiety. In particular, for imines **8e** and **8f**, the steric repulsion between the tosyl group and the aryl substituents on the carbon α to the imino groups is of sufficient magnitude to induce exclusive formation of the *E*-isomers as a result of the planarity of the enamide system.



Scheme 2 Confirmation of the stereochemistry of the metal enamide

In summary, we succeeded in cyclizing 3,3-difluoroallylic ketones **1** and imines **2** in a 5-*endo-trig* fashion, a process predicted to be disfavored by Baldwin's rules. The corresponding metal enolates and enamides undergo exclusive O- and N-cyclization to afford 2-alkylidene-5-fluoro-2,3-dihydrofurans **6** and 2-alkylidene-5-fluoro-2,3-dihydropyrroles **8**, respectively. The 5-*endo-trig* cyclization of 1,1-difluoro-1-alkenes therefore has broad applicability. Note that this protocol simultaneously introduces a fluorine substituent and an *exo*-alkylidene unit onto the dihydroheterole rings. Because ring-fluorinated compounds bearing such unique heteronuclei are unprecedented, these compounds have significant potential as key synthetic intermediates for the preparation of fluorinated functional heteroles, which constitute an important class of bioactive molecules.[14]

^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra were recorded on a Bruker Avance 500 or a Bruker DRX 500 spectrometer. Chemical shift values are given in ppm relative to internal TMS (for ^{1}H NMR: δ = 0.00 ppm), $CDCl_3$ (for ^{13}C NMR: δ = 77.0 ppm), or C_6F_6 (for ^{19}F NMR: δ = 0.00 ppm). IR spectra were recorded on a Horiba FT-300S spectrometer by the attenuated total reflectance (ATR) method. Mass spectra were measured on a JEOL MS-700M or a JEOL JMS-T100GCV spectrometer. Elemental analyses were carried out at the Elemental Analysis Laboratory, Division of Chemistry, Faculty of Pure and Applied Sciences, University of Tsukuba. All reactions were carried out under argon. THF and DMF were purified by using a solvent-purification system (GlassContour) equipped with columns of activated alumina and supported copper catalyst (Q-5) before use. Column chromatography was performed on Silica Gel 60 (Kanto Chemical Co. Inc.). Preparative TLC was performed on B5-F silica gal (Wako Pure Chemical Industries, Ltd. 4-(Cyclohexylidenemethyl)morpholine,[15] 4-(2-methylprop-1-en-1-yl)morpholine,[15] 2-methyl-*N*-(2-methylpropylidene)propan-2-amine,[16] *N*-(cyclohexylmethylene)-2-methylpropan-2-amine,[17] and 1-acetylcyclohexanecarbaldehyde (**3h**)[18] were prepared according to literature procedures.

2,2-Dimethyl-3-oxododecanal (3a); Typical Procedure A (Method A)

A 2.4 M solution of BuLi in hexane (16.4 mL, 43.3 mmol) was added to a solution of *i*-Pr_2NH (6.35 mL, 45.3 mmol) in Et_2O (98 mL) at –78 °C, and the mixture was stirred for 10 min at –78 °C and then for 10 min at 0 °C. 2-Methyl-*N*-(2-methylpropylidene)propan-2-amine (5.01 g, 39.4 mmol) was added dropwise at –78 °C, and the solution was stirred for 10 min at –78 °C, warmed to 0 °C, and stirred for 2 h at 0 °C. $Me(CH_2)_8COCl$ (8.00 mL, 39.4 mmol) was added at –78 °C, and the mixture was stirred for 15 min at –78 °C, warmed to r.t., and stirred for 12 h. Phosphate buffer (pH 7; 50 mL) was added, and the organic materials were extracted with Et_2O (3 × 150 mL). The combined extracts were washed with brine (300 mL),

dried (Na_2SO_4), and concentrated under reduced pressure. The residue was dissolved in CH_2Cl_2 (78 mL) and the solution was treated with a solution of oxalic acid dihydrate (4.91 g, 39.4 mmol) in H_2O (47 mL) with stirring for 1 h at r.t. Organic materials were extracted with CH_2Cl_2 (3 × 150 mL), and the extracts were combined, washed with brine (300 mL), dried ($MgSO_4$), and concentrated under reduced pressure. The residue was purified by column chromatography [silica gel, EtOAc–hexane (1:5)] to give a colorless oil; yield: 2.47 g (32%).

IR (neat): 2924, 2854, 1734, 1700, 1466, 1366, 1072, 1035, 914, 838, 722 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 7.0 Hz, 3 H), 1.21–1.32 (m, 12 H), 1.33 (s, 6 H), 1.45 (tt, *J* = 7.3, 7.3 Hz, 2 H), 2.44 (t, *J* = 7.3 Hz, 2 H), 9.62 (s, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.0, 19.1, 22.6, 23.3, 29.0, 29.2, 29.3, 29.3, 31.8, 39.0, 60.3, 201.1, 209.3.

HRMS (FAB): *m*/*z* $[M + H]^+$ calcd for $C_{14}H_{27}O_2$: 227.2011; found: 227.2006.

1-(3,3-Dimethylbutanoyl)cyclohexanecarbaldehyde (3i); Typical Procedure B (Method B)

t-$BuCH_2COCl$ (3.65 g, 27.1 mmol) was dissolved in Et_2O (7 mL) with vigorous stirring at 0 °C. 4-(Cyclohexylidenemethyl)morpholine (4.92 g, 27.1 mmol) was added over 1 h at 0 °C, and the solution was then refluxed for 10 h. Sat. aq $NaHCO_3$ (10 mL) was added at 0 °C and the mixture was stirred for 1 h at 0 °C. Organic materials were extracted with Et_2O (3 × 100). The combined were combined, washed with brine (150 mL), dried (Na_2SO_4), and concentrated under reduced pressure. The residue was purified by column chromatography [silica gel, EtOAc–hexane (1:20)] to give a colorless oil; yield: 1.65 g (29%).

IR (neat): 2935, 2866, 1730, 1699, 1450, 1363, 1217, 1124, 1016, 908, 829, 741, 690 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.99 (s, 9 H), 1.26–1.42 (m, 3 H), 1.47–1.61 (m, 3 H), 1.78–1.87 (m, 2 H), 2.04–2.11 (m, 2 H), 2.32 (s, 2 H), 9.48 (s, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 22.3, 25.1, 28.4, 29.4, 30.6, 50.7, 66.7, 201.9, 206.8.

LRMS (FAB): *m*/*z* (%) = 211 (11) $[M + H]^+$.

2,2-Dimethyl-3-oxo-5-phenylpentanal (3b)

This was prepared by following the typical procedure B from $Ph(CH_2)_2COCl$ (4.41 mL, 28.3 mmol) and 4-(2-methylprop-1-enyl)morpholine (4.00 g, 28.3 mmol) in Et_2O (7.0 mL). The mixture was refluxed for 12 h, and sat. aq $NaHCO_3$ (10 mL) was added. Purification by column chromatography [silica gel, EtOAc–hexane (1:5)] gave a colorless oil; yield: 3.34 g (58%).

IR (neat): 3028, 2975, 2935, 2823, 2717, 1726, 1699, 1604, 1496, 1454, 1365, 1065, 987, 912, 819, 748, 698 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.29 (s, 6 H), 2.77 (t, *J* = 7.4 Hz, 2 H), 2.89 (t, *J* = 7.4 Hz, 2 H), 7.15–7.23 (m, 3 H), 7.26–7.29 (m, 2 H), 9.55 (s, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 19.1, 29.5, 40.8, 60.2, 126.2, 128.3, 128.5, 140.7, 201.0, 208.4.

Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.31; H, 8.14.

4-Cyclohexyl-2,2-dimethyl-3-oxobutanal (3c)

Compound **3c** was prepared by following typical procedure A from *i*-Pr_2NH (1.30 mL, 9.28 mmol), Et_2O (71 mL), a 2.64 M soln of BuLi in hexane (3.40 mL, 8.98 mmol), 2-methyl-*N*-(2-methylpropylidene)propan-2-amine (1.04 g, 8.20 mmol), and $CyCH_2COCl$ (1.32 g, 8.20 mmol). The mixture was stirred at r.t. for 12 h, and then pH 7 phosphate buffer (40 mL) was added. After workup, the crude product was treated with CH_2Cl_2 (16 mL) and oxalic acid dihydrate (1.03 g, 8.19 mmol) in H_2O (9.8 mL), and the mixture was stirred for 1 h at r.t. Purification by column chromatography [silica gel, EtOAc–hexane (1:3)] gave a colorless liquid; yield: 716 mg (45%).

IR (neat): 2973, 2924, 2852, 2715, 1731, 1701, 1658, 1448, 1365, 1286, 1195, 1045, 914, 827 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.88 (m, 2 H), 1.07–1.18 (m, 1 H), 1.20–1.34 (m, 2 H), 1.31 (s, 6 H), 1.60–1.70 (m, 5 H), 1.82–1.95 (m, 1 H), 2.31 (d, *J* = 6.7 Hz, 2 H), 9.61 (s, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 19.0, 26.0, 26.1, 26.1, 33.1, 46.6, 60.5, 201.2, 208.8.

HRMS (EI): *m*/*z* $[M - CO]^+$ calcd for $C_{11}H_{20}O$: 168.1514; found: 168.1515.

2,2,5,5-Tetramethyl-3-oxohexanal (3d)

Compound **3d** was prepared by following typical procedure A from *i*-Pr_2NH (4.61 mL, 32.9 mmol), Et_2O (71 mL), a 2.64 M soln of BuLi in hexane (11.5 mL, 31.4 mmol), 2-methyl-*N*-(2-methylpropylidene)propan-2-amine (3.64 g, 28.6 mmol), and *t*-$BuCH_2COCl$ (4.00 mL, 28.6 mmol). The mixture was stirred at r.t. for 12 h, and then pH 7 phosphate buffer (40 mL) was added. After workup, the crude product was treated with CH_2Cl_2 (28 mL) and oxalic acid dihydrate (1.80 g, 14.3 mmol) in H_2O (17 mL). The reaction mixture was stirred for 1 h at r.t. Purification by column chromatography [silica gel, EtOAc–hexane (1:4)] gave a colorless liquid; yield: 2.04 g (85%).

IR (neat): 2954, 2870, 2715, 1731, 1703, 1466, 1365, 1246, 1061, 912, 835 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.01 (s, 9 H), 1.30 (s, 6 H), 2.35 (s, 2 H), 9.61 (s, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 19.0, 29.4, 30.7, 50.6, 61.0, 201.3, 208.3.

HRMS (EI): *m*/*z* $[M - CO]^+$ calcd for $C_9H_{18}O$: 142.1358; found: 142.1356.

2,2-Dimethyl-3-oxo-4-phenylbutanal (3e)

Compound **3e** was prepared by following typical procedure A from *i*-Pr_2NH (0.371 mL, 2.64 mmol), Et_2O (5.8 mL), a 2.64 M soln of BuLi in hexane (0.93 mL, 2.5 mmol), 2-methyl-*N*-(2-methylpropylidene)propan-2-amine (293 mg, 2.30 mmol), and $PhCH_2COCl$ (0.31 mL, 2.3 mmol). The mixture was stirred at r.t. for 12 h, and then pH 7 phosphate buffer (5 mL) was added. After workup, the crude product was treated with CH_2Cl_2 (4.6 mL) and oxalic acid dihydrate (290 mg, 2.30 mmol) in H_2O (2.8 mL), and the mixture was stirred for 1 h at r.t. Purification by column chromatography [silica gel, EtOAc–hexane (1:5)] gave a colorless liquid; yield: 192 mg (44%).

IR (neat): 2978, 1729, 1700, 1497, 1455, 1051, 827, 728, 696, 549 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.36 (s, 6 H), 3.77 (s, 2 H), 7.14 (d, *J* = 7.4 Hz, 2 H), 7.24 (tt, *J* = 7.4, 1.7 Hz, 1 H), 7.30 (dd, *J* = 7.4, 7.4 Hz, 2 H), 9.56 (s, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 19.1, 45.5, 60.5, 127.0, 128.5, 129.5, 133.0, 200.6, 206.3.

HRMS (FAB): *m*/*z* $[M + H]^+$ calcd for $C_{12}H_{15}O_2$: 191.1072; found: 191.1077.

4-(4-Methoxyphenyl)-2,2-dimethyl-3-oxobutanal (3f)

Compound **3f** was prepared by following typical procedure A from *i*-Pr_2NH (5.19 mL, 37.0 mmol), Et_2O (80 mL), a 2.64 M soln of BuLi in hexane (13.0 mL, 35.5 mmol), 2-methyl-*N*-(2-methylpropylidene)propan-2-amine (4.09 g, 32.2 mmol), and 4-$MeOC_6H_4CH_2COCl$ (5.94 g, 32.2 mmol). The mixture was stirred at r.t. for 12 h, and then pH 7 phosphate buffer (50 mL) was added. After workup, the crude product was treated with CH_2Cl_2 (64 mL)

and oxalic acid dihydrate (4.06 g, 32.2 mmol) in H_2O (39 mL), and the mixture was stirred for 1 h at r.t. Purification by column chromatography [silica gel, EtOAc–hexane (1:3 to 1:2 to 1:1)] gave a colorless liquid; yield: 3.85 g (54%).

IR (neat): 2972, 2935, 2836, 2717, 1701, 1612, 1512, 1464, 1246, 1033, 815, 787 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.37 (s, 6 H), 3.72 (s, 2 H), 3.79 (s, 3 H), 6.73 (d, *J* = 8.6 Hz, 2 H), 7.06 (d, *J* = 8.6 Hz, 2 H), 9.55 (s, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 19.3, 44.8, 55.2, 60.6, 114.1, 124.8, 130.6, 158.7, 200.6, 206.6.

HRMS (EI): *m*/*z* [M^+] calcd for $C_{13}H_{16}O_3$: 220.1099; found: 220.1106.

3-Cyclohexyl-2,2-dimethyl-3-oxopropanal (3g)

Compound **3g** was prepared by following typical procedure A from *i*-Pr_2NH (4.60 mL, 32.9 mmol), Et_2O (71 mL), a 2.64 M soln of BuLi in hexane (11.5 mL, 31.4 mmol), 2-methyl-*N*-(2-methylpropylidene)propan-2-amine (3.64 g, 28.6 mmol), and CyCOCl (4.00 mL, 28.6 mmol). The mixture was stirred at r.t. for 12 h, and then pH 7 phosphate buffer (50 mL) was added. After workup, the crude product was treated with CH_2Cl_2 (57 mL) and oxalic acid dihydrate (3.60 g, 28.6 mmol) in H_2O (34 mL), and the mixture was stirred for 1 h at r.t. Purification by column chromatography [silica gel, EtOAc–hexane (1:4)] gave a colorless liquid; yield: 4.70 g (90%).

IR (neat): 2975, 2931, 2856, 2715, 1732, 1699, 1450, 1367, 1141, 1066, 987, 831, 733, 667 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.17–1.29 (m, 3 H), 1.33 (s, 6 H), 1.35–1.41 (m, 2 H), 1.64–1.79 (m, 5 H), 2.65 (tt, *J* = 11.4, 3.3 Hz, 1 H), 9.62 (s, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 19.0, 25.4, 25.5, 29.1, 47.1, 60.9, 201.1, 212.2.

HRMS (EI): *m*/*z* [M – CO]$^+$ calcd for $C_{10}H_{18}O$: 154.1358; found: 154.1362.

1-(Cyclohexanecarbonyl)cyclohexanecarbaldehyde (3j)

N-(Cyclohexylmethylene)-2-methylpropan-2-amine (983 mg, 5.87 mmol) was dissolved in THF (35 mL) and *t*-BuLi (1.59 M, 3.69 mL, 5.87 mmol) was added over 1 min at –78 °C. The mixture was stirred at 0 °C for 1 h then CyCOCl (861 mg, 5.87 mmol) was added at –78 °C. The mixture was refluxed for 2 h, and then treated with AcOH (17.6 g, 293 mmol), NaOAc (24.1 g, 293 mmol), and H_2O (70 mL) at 0 °C with stirring for 1 h. The organic materials were extracted with Et_2O (3 × 20 mL), and the organic layers were combined and washed sequentially with aq $NaHCO_3$ (10 × 30 mL) and brine (50 mL), then dried (Na_2SO_4). Purification by column chromatography [silica gel, Et_3N–EtOAc–hexane (1:2:50)] gave a colorless liquid; yield: 533 mg (41%).

IR (neat): 2927, 2854, 1728, 1701, 1450, 1367, 1246, 1163, 1132, 987, 893, 773 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.18–1.69 (m, 14 H), 1.72–1.80 (m, 2 H), 1.80–1.90 (m, 2 H), 2.05–2.13 (m, 2 H), 2.67 (tt, *J* = 12.7, 3.3 Hz, 1 H), 9.53 (s, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 22.4, 25.1, 25.4, 25.5, 28.2, 29.1, 46.9, 66.4, 201.6, 211.0.

HRMS (FAB): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{23}O_2$: 223.1698; found: 223.1693.

1,1-Difluoro-3,3-dimethyltridec-1-en-4-one (1a); Typical Procedure C

$P(NMe_2)_3$ (7.0 mL, 37.0 mmol) was added to a mixture of CF_2Br_2 (1.77 mL, 18.6 mmol) and microwave-dried 4 Å MS (3.0 g) in THF (31 mL) at –78 °C. The mixture was stirred for 15 min at –78 °C and then warmed to r.t. Aldehyde **3a** (2.10 g, 9.28 mmol) was added, and the mixture was stirred for 10 h. The reaction was then quenched with pH 7 phosphate buffer (20 mL) at 0 °C. After suction filtration, the organic materials were extracted with EtOAc (3 × 50 mL). The combined extracts were washed with brine (100 mL), dried (Na_2SO_4), and concentrated under reduced pressure. The residue was purified by TLC [silica gel, EtOAc–hexane (1:5)] to give a colorless oil; yield: 2.07 g (86%).

IR (neat): 2925, 2854, 1738, 1716, 1508, 1456, 1331, 1223, 1001, 771 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.9 Hz, 3 H), 1.26–1.31 (m, 18 H), 1.56 (tt, *J* = 7.1, 7.1 Hz, 2 H), 2.49 (t, *J* = 7.1 Hz, 2 H), 4.37 (dd, J_{HF} = 27.9, 4.4 Hz, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.0, 22.6, 24.1, 24.9 (d, J_{CF} = 3 Hz), 29.2, 29.2, 29.4, 29.4, 31.8, 37.0, 45.1 (dd, J_{CF} = 4, 4 Hz), 83.9 (dd, J_{CF} = 23, 15 Hz), 155.7 (dd, J_{CF} = 294, 287 Hz), 211.7.

^{19}F NMR (470 MHz, $CDCl_3$): δ = 76.9 (dd, J_{FF} = 44 Hz, J_{FH} = 4 Hz, 1 F), 78.2 (dd, J_{FF} = 44 Hz, J_{FH} = 28 Hz, 1 F).

Anal. Calcd for $C_{15}H_{26}F_2O$: C, 69.20; H, 10.07. Found: C, 69.10; H, 10.14.

6,6-Difluoro-4,4-dimethyl-1-phenylhex-5-en-3-one (1b)

Compound **1b** was prepared by following typical procedure C from CF_2Br_2 (2.37 mL, 25.7 mmol), microwave-dried 4 Å MS (1.3 g), THF (40 mL), $P(NMe_2)_3$ (9.32 mL, 51.3 mmol), and aldehyde **3b** (2.62 g, 12.8 mmol). The mixture was stirred for 16 h and then the reaction was quenched with pH 7 phosphate buffer (20 mL) at 0 °C. Purification by column chromatography [silica gel, EtOAc–hexane (1:10)] gave a colorless oil; yield: 2.28 g (87%).

IR (neat): 3028, 2979, 2937, 1736, 1712, 1329, 1227, 997, 700 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.25 (dd, J_{HF} = 1.0, 0.6 Hz, 6 H), 2.80–2.83 (m, 2 H), 2.87–2.90 (m, 2 H), 4.30 (dd, J_{HF} = 27.8, 4.4 Hz, 1 H), 7.17–7.20 (m, 3 H), 7.26–7.30 (m, 2 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 24.8 (d, J_{CF} = 2.2 Hz), 30.2, 39.1, 45.2 (dd, J_{CF} = 4, 3 Hz), 83.8 (dd, J_{CF} = 24, 15 Hz), 126.1, 128.4, 128.5, 141.3, 155.8 (dd, J_{CF} = 294, 288 Hz), 210.6.

^{19}F NMR (470 MHz, $CDCl_3$): δ = 77.2 (dd, J_{FF} = 43 Hz, J_{FH} = 4 Hz, 1 F), 78.3 (dd, J_{FF} = 43 Hz, J_{FH} = 28 Hz, 1 F).

Anal. Calcd for $C_{14}H_{16}F_2O$: C, 70.57; H, 6.77. Found: C, 70.24; H, 6.96.

1-Cyclohexyl-5,5-difluoro-3,3-dimethylpent-4-en-2-one (1c)

Compound **1c** was prepared by following typical procedure C from CF_2Br_2 (2.7 mL, 29 mmol), microwave-dried 4 Å MS (4.5 g), THF (48 mL), $P(NMe_2)_3$ (10.9 mL, 57.6 mmol), and aldehyde **3c** (2.82 g, 14.4 mmol). The mixture was stirred for 7 h and then the reaction was quenched with pH 7 phosphate buffer (20 mL) at 0 °C. Purification by column chromatography [silica gel, EtOAc–hexane (1:5)] gave a colorless oil; yield: 2.71 g (82%).

IR (neat): 2978, 2923, 2852, 1735, 1712, 1469, 1448, 1328, 1286, 1226, 1136, 1045, 1001, 962, 943, 906 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.84–0.92 (m, 2 H), 1.11–1.17 (m, 1 H), 1.24–1.32 (m, 3 H), 1.27 (dd, J_{HF} = 1.0, 0.6 Hz, 6 H), 1.61–1.69 (m, 4 H), 1.85–1.90 (m, 1 H), 2.36 (d, *J* = 6.7 Hz, 2 H), 4.35 (dd, J_{HF} = 28.0, 4.5 Hz, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 24.8 (dd, J_{CF} = 3, 1 Hz), 26.1, 26.2, 33.1, 33.4, 44.8, 45.2 (dd, J_{CF} = 4, 4 Hz), 83.8 (dd, J_{CF} = 23, 15 Hz), 155.8 (dd, J_{CF} = 294, 288 Hz), 211.0.

^{19}F NMR (470 MHz, $CDCl_3$): δ = 77.0 (dd, J_{FF} = 44 Hz, J_{FH} = 4 Hz, 1 F), 77.8 (dd, J_{FF} = 44 Hz, J_{FH} = 28 Hz, 1 F).

Anal. Calcd for $C_{13}H_{20}F_2O$: C, 67.80; H, 8.75. Found: C, 67.57; H, 8.78.

1,1-Difluoro-3,3,6,6-tetramethylhept-1-en-4-one (1d)

Compound **1d** was prepared by following typical procedure C from CF_2Br_2 (0.80 mL, 8.4 mmol), microwave-dried 4 Å MS (0.42 g),

THF (3.2 mL), $P(NMe_2)_3$ (3.2 mL, 17 mmol), and aldehyde **3d** (714 mg, 4.20 mmol). The mixture was stirred for 10 h, and then the reaction was quenched with pH 7 phosphate buffer (5 mL) at 0 °C. Purification by column chromatography [silica gel, EtOAc–hexane (1:5)] gave a colorless oil; yield: 500 mg (58%).

IR (neat): 2956, 2927, 2856, 1738, 1716, 1466, 1365, 1330, 1225, 1128, 1061, 1005 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.02 (s, 9 H), 1.26 (dd, J_{HF} = 1.3, 0.8 Hz, 6 H), 2.40 (s, 2 H), 4.34 (dd, J_{HF} = 28.0, 4.5 Hz, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 24.9 (d, J_{CF} = 2 Hz), 29.6, 30.6, 45.7 (dd, J_{CF} = 4, 4 Hz), 48.8, 83.9 (dd, J_{CF} = 23, 15 Hz), 155.7 (dd, J_{CF} = 295, 288 Hz), 210.9.

^{19}F NMR (470 MHz, $CDCl_3$): δ = 76.9 (dd, J_{FF} = 44 Hz, J_{FH} = 4 Hz, 1 F), 77.8 (dd, J_{FF} = 45 Hz, J_{FH} = 28 Hz, 1 F).

Anal. Calcd for $C_{11}H_{18}F_2O$: C, 64.68; H, 8.88. Found: C, 64.67; H, 9.10.

5,5-Difluoro-3,3-dimethyl-1-phenylpent-4-en-2-one (1e)

Compound **1e** was prepared by following typical procedure C from CF_2Br_2 (491 mg, 2.34 mmol), microwave-dried 4 Å MS (0.23 g), THF (1.8 mL), $P(NMe_2)_3$ (763 mg, 4.68 mmol), and aldehyde **3e** (222 mg, 1.17 mmol). The mixture was stirred for 10 h, and then the reaction was quenched with pH 7 phosphate buffer (5 mL) at 0 °C. Purification by TLC [silica gel, EtOAc–hexane (1:5)] gave a colorless oil; yield: 166 mg (63%).

IR (neat): 2964, 1809, 1682, 1211, 1192, 1174, 1055, 935, 771, 694 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.34 (s, 6 H), 3.81 (s, 2 H), 4.41 (dd, J_{HF} = 27.8, 4.3 Hz, 1 H), 7.18 (d, J = 7.2 Hz, 2 H), 7.25 (t, J = 7.2 Hz, 1 H), 7.30 (dd, J = 7.2, 7.2 Hz, 2 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 24.9, 43.8, 45.6 (dd, J_{CF} = 4, 4 Hz), 83.8 (dd, J_{CF} = 23, 15 Hz), 126.8, 128.4, 129.4, 134.4, 155.8 (dd, J_{CF} = 294, 288 Hz), 208.5.

^{19}F NMR (470 MHz, $CDCl_3$): δ = 77.5 (dd, J_{FF} = 43 Hz, J_{FH} = 4 Hz, 1 F), 78.3 (dd, J_{FF} = 43 Hz, J_{FH} = 28 Hz, 1 F).

HRMS (FAB): m/z $[M + H]^+$ calcd for $C_{13}H_{15}F_2O$: 225.1091; found: 225.1087.

5,5-Difluoro-1-(4-methoxyphenyl)-3,3-dimethylpent-4-en-2-one (1f)

Compound **1f** was prepared by following typical procedure C from CF_2Br_2 (3.5 mL, 37 mmol), microwave-dried 4 Å MS (6.0 g), THF (62 mL), $P(NMe_2)_3$ (13.5 mL, 71.3 mmol), and aldehyde **3f** (4.1 g, 19 mmol). The mixture was stirred for 5 h, and then the reaction was quenched with pH 7 phosphate buffer (10 mL) at 0 °C. Purification by column chromatography [silica gel, EtOAc–hexane (1:4)] gave a colorless oil; yield: 2.72 g (58%).

IR (neat): 2978, 2939, 1736, 1726, 1514, 1248, 1178, 1047, 1003 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.34 (dd, J_{HF} = 1.0, 0.7 Hz, 6 H), 3.76 (s, 2 H), 3.79 (s, 3 H), 4.41 (dd, J_{HF} = 27.8, 4.3 Hz, 1 H), 6.85 (d, J = 8.7 Hz, 2 H), 7.09 (d, J = 8.7 Hz, 2 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 25.1 (dd, J_{CF} = 3, 1 Hz), 42.9, 45.6 (dd, J_{CF} = 4, 3 Hz), 55.2, 83.9 (dd, J_{CF} = 24, 15 Hz), 113.9, 126.5, 130.4, 155.8 (dd, J_{CF} = 295, 288 Hz), 158.5, 209.0.

^{19}F NMR (470 MHz, $CDCl_3$): δ = 77.4 (dd, J_{FF} = 43 Hz, J_{FH} = 4 Hz, 1 F), 78.2 (dd, J_{FF} = 43 Hz, J_{FH} = 28 Hz, 1 F).

Anal. Calcd for $C_{14}H_{16}F_2O_2$: C, 66.13; H, 6.34. Found: C, 66.19; H, 6.46.

1-Cyclohexyl-4,4-difluoro-2,2-dimethylbut-3-en-1-one (1g)

Compound **1g** was prepared by following typical procedure C from CF_2Br_2 (3.6 mL, 37 mmol), microwave-dried 4 Å MS (1.9 g), THF (15 mL), $P(NMe_2)_3$ (14 mL, 75 mmol), and aldehyde **3g** (3.40 g, 18.7 mmol). The mixture was stirred for 12 h and then the reaction was quenched with pH 7 phosphate buffer (20 mL) at 0 °C. Purification by column chromatography [silica gel, EtOAc–hexane (1:10)] gave a colorless oil; yield: 2.86 g (71%).

IR (neat): 2977, 2933, 2857, 1736, 1709, 1452, 1331, 1227, 1134, 1063, 989, 933, 798 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.22–1.28 (m, 3 H), 1.30 (dd, J_{HF} = 0.6, 0.6 Hz, 6 H), 1.38–1.46 (m, 2 H), 1.62–1.65 (m, 2 H), 1.76–1.79 (m, 3 H), 2.76 (tt, J = 11.6, 3.3 Hz, 1 H), 4.39 (dd, J_{HF} = 27.8, 4.6 Hz, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 24.6 (d, J_{CF} = 2 Hz), 25.6, 25.7, 30.2, 45.6 (dd, J_{CF} = 4, 3 Hz), 46.0, 83.3 (dd, J_{CF} = 23, 15 Hz), 155.9 (dd, J_{CF} = 295, 288 Hz), 214.4.

^{19}F NMR (470 MHz, $CDCl_3$): δ = 77.5 (dd, J_{FF} = 44 Hz, J_{FH} = 4 Hz, 1 F), 78.2 (dd, J_{FF} = 44 Hz, J_{FH} = 28 Hz, 1 F).

Anal. Calcd for $C_{12}H_{18}F_2O$: C, 66.64; H, 8.39. Found: C, 66.40; H, 8.34.

1-[1-(2,2-Difluorovinyl)cyclohexyl]ethanone (1h)

Compound **1h** was prepared by following typical procedure C from CF_2Br_2 (5.12 g, 24.4 mmol), microwave-dried 4 Å MS (1.89 g), THF (55 mL), $P(NMe_2)_3$ (7.99 g, 49.0 mmol), and aldehyde **3h** (1.89 g, 12.3 mmol). The mixture was stirred for 10 h, and then the reaction was quenched with pH 7 phosphate buffer (30 mL) at 0 °C. Purification by column chromatography [silica gel, Et_2O–hexane (1:20)] gave a colorless oil; yield: 1.52 g (66%).

IR (neat): 2935, 2858, 1732, 1709, 1333, 1211, 1180, 1136, 987, 920, 887, 798, 590 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.29–1.40 (m, 1 H), 1.44–1.62 (m, 5 H), 1.68–1.80 (m, 4 H), 2.15 (s, 3 H), 4.21 (dd, J_{HF} = 28.2, 4.8 Hz, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 22.2, 25.2, 25.4, 32.8 (d, J_{CF} = 1 Hz), 49.4 (dd, J_{CF} = 3, 3 Hz), 82.0 (dd, J_{CF} = 23, 16 Hz), 155.7 (dd, J_{CF} = 295, 289 Hz), 209.0.

^{19}F NMR (470 MHz, $CDCl_3$): δ = 78.3 (dm, J_{FF} = 41 Hz, 1 F), 78.6 (dd, J_{FF} = 41 Hz, J_{FH} = 29 Hz, 1 F).

HRMS (FAB): m/z $[M + H]^+$ calcd for $C_{10}H_{15}F_2O$: 189.1091; found: 189.1100.

1-[1-(2,2-Difluorovinyl)cyclohexyl]-3,3-dimethylbutan-1-one (1i)

Compound **1i** was prepared by following typical procedure C from CF_2Br_2 (452 mg, 2.15 mmol), microwave-dried 4 Å MS (0.22 g), THF (1.6 mL), $P(NMe_2)_3$ (702 mg, 4.30 mmol), and aldehyde **3i** (226 mg, 1.08 mmol). The mixture was stirred for 8 h, and then the reaction was quenched with sat. aq $NaHCO_3$ (5 mL) at 0 °C. Purification by TLC [silica gel, EtOAc–hexane (1:20)] gave a colorless oil; yield: 178 mg (68%).

IR (neat): 2937, 1732, 1711, 1363, 1333, 1223, 1184, 1009, 908, 812 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.94 (s, 9 H), 1.15–1.24 (m, 2 H), 1.31–1.41 (m, 2 H), 1.42–1.53 (m, 2 H), 1.55–1.64 (m, 2 H), 1.59–1.69 (m, 2 H), 2.29 (s, 2 H), 4.09 (dd, J_{HF} = 28.8, 4.6 Hz, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 22.3, 25.5, 29.5, 30.5, 32.7, 49.0, 49.9 (dd, J_{CF} = 4, 3 Hz), 81.9 (dd, J_{CF} = 23, 15 Hz), 155.7 (dd, J_{CF} = 295, 288 Hz), 210.0.

^{19}F NMR (470 MHz, $CDCl_3$): δ = 78.2 (d, J_{FF} = 41 Hz, 1 F), 78.9 (dd, J_{FF} = 41 Hz, J_{FH} = 29 Hz, 1 F).

LRMS (FAB): m/z (%) = 245 (11) $[M + H]^+$.

Cyclohexyl[1-(2,2-difluorovinyl)cyclohexyl]methanone (1j)

Compound **1j** was prepared by following typical procedure C from CF_2Br_2 (897 mg, 4.27 mmol), microwave-dried 4 Å MS (0.43 g), THF (3.2 mL), $P(NMe_2)_3$ (1.39 g, 8.53 mmol), and aldehyde **3j** (823

mg, 3.70 mmol). The mixture was stirred for 10 h, and then the reaction was quenched with pH 7 phosphate buffer (5 mL) at 0 °C. Purification by column chromatography [silica gel, EtOAc–hexane (1:20)] gave a colorless oil; yield: 252 mg (27%).

IR (neat): 2929, 2854, 1728, 1705, 1450, 1331, 1225, 1186, 1151, 985, 901, 804, 735 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.12–1.25 (m, 4 H), 1.29–1.42 (m, 4 H), 1.45–1.74 (m, 12 H), 2.63 (tt, *J* = 11.6, 3.3 Hz, 1 H), 4.14 (dd, J_{HF} = 28.5, 4.6 Hz, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 22.3, 25.5, 25.6, 25.7, 30.3, 32.4, 46.5, 49.8 (dd, J_{CF} = 3, 3 Hz), 81.3 (dd, J_{CF} = 23, 15 Hz), 155.9 (dd, J_{CF} = 296, 289 Hz), 214.0.

^{19}F NMR (470 MHz, $CDCl_3$): δ = 78.6 (d, J_{FF} = 40 Hz, 1 F), 79.2 (dd, J_{FF} = 40 Hz, J_{FH} = 28 Hz, 1 F).

LRMS (FAB): *m*/*z* (%) = 257 (17) $[M + H]^+$.

N-(4,4-Difluoro-2,2-dimethyl-1-nonylbut-3-en-1-ylidene)-4-methylbenzenesulfonamide (2a); Typical Procedure D

Et_3N (110 μL, 0.79 mmol) was added to a solution of ketone **1a** (104 mg, 0.40 mmol) and $TsNH_2$ (68 mg, 0.40 mmol) in DCE (4 mL) at 0 °C, and the mixture was stirred for 5 min at 0 °C. $TiCl_4$ (44 μL, 0.40 mmol) was added dropwise at 0 °C, and the mixture was refluxed for 3 d then cooled to r.t. The reaction was quenched with pH 7 phosphate buffer (5 mL), and the mixture was filtered through a pad of Celite under reduced pressure. The organic materials were extracted with EtOAc (3 × 10 mL). The extracts were combined, washed with brine (20 mL), dried (Na_2SO_4), and concentrated under reduced pressure. The residue was purified by column chromatography [silica gel, EtOAc–hexane (1:5)] to give a pale-yellow oil; yield: 101 mg (61%).

IR (neat): 2954, 2925, 2871, 2854, 1735, 1616, 1467, 1458, 1319, 1303, 1290, 1222, 1157, 1093, 1004, 813, 746, 680 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 7.0 Hz, 3 H), 1.26–1.35 (m, 16 H), 1.43 (tt, *J* = 7.4, 7.4 Hz, 2 H), 1.73–1.80 (m, 2 H), 2.43 (s, 3 H), 2.85–2.89 (m, 2 H), 4.30 (dd, J_{HF} = 27.4, 4.8 Hz, 1 H), 7.31 (d, *J* = 8.2 Hz, 2 H), 7.84 (d, *J* = 8.2 Hz, 2 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1, 21.5, 22.6, 26.3 (d, J_{CF} = 3 Hz), 29.0, 29.0, 29.2, 29.4, 30.5, 31.8, 34.2, 44.5 (dd, J_{CF} = 5, 3 Hz), 84.3 (dd, J_{CF} = 24, 14 Hz), 126.9, 129.4, 138.6, 143.3, 155.8 (dd, J_{CF} = 295, 288 Hz), 193.8 (dd, J_{CF} = 2, 2 Hz).

^{19}F NMR (470 MHz, $CDCl_3$): δ = 77.9 (dd, J_{FF} = 42 Hz, J_{FH} = 5 Hz, 1 F), 78.5 (dd, J_{FF} = 42 Hz, J_{FH} = 27 Hz, 1 F).

Anal. Calcd for $C_{22}H_{33}F_2NO_2S$: C, 63.89; H, 8.04. Found: C, 63.78; H, 8.24.

N-[4,4-Difluoro-2,2-dimethyl-1-(2-phenylethyl)but-3-en-1-ylidene]-4-methylbenzenesulfonamide (2b)

Compound **2b** was prepared by following typical procedure D from ketone **1b** (213 mg, 0.895 mmol), $TsNH_2$ (153 mg, 0.89 mmol), DCE (9 mL), Et_3N (249 μL, 1.79 mmol), and $TiCl_4$ (98 μL, 0.89 mmol). Purification by TLC [silica gel, EtOAc–hexane (1:5)] gave a pale-yellow solid; yield: 238 mg (68%); mp 43.2–44.5 °C.

IR (neat): 3064, 3028, 2981, 2938, 2873, 1736, 1614, 1496, 1456, 1317, 1219, 1155, 1092, 1002, 814, 760, 737, 681, 584, 551 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.33 (s, 6 H), 2.45 (s, 3 H), 3.09–3.20 (m, 4 H), 4.28 (dd, J_{HF} = 27.2, 4.7 Hz, 1 H), 7.22–7.25 (m, 1 H), 7.32–7.34 (m, 6 H), 7.89 (d, *J* = 8.3 Hz, 2 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 21.6, 26.2 (d, J_{CF} = 3 Hz), 34.9, 36.4, 44.7 (dd, J_{CF} = 5, 3 Hz), 84.1 (dd, J_{CF} = 24, 14 Hz), 126.5, 127.0, 128.4, 128.7, 129.4, 138.4, 140.5, 143.6, 155.9 (dd, J_{CF} = 295, 289 Hz), 192.1 (dd, J_{CF} = 2, 2 Hz).

^{19}F NMR (470 MHz, $CDCl_3$): δ = 78.3 (dd, J_{FF} = 42 Hz, J_{FH} = 5 Hz, 1 F), 78.8 (dd, J_{FF} = 42 Hz, J_{FH} = 27 Hz, 1 F).

Anal. Calcd for $C_{21}H_{23}F_2NO_2S$: C, 64.43; H, 5.92. Found: C, 64.43; H, 6.00.

N-[1-(Cyclohexylmethyl)-4,4-difluoro-2,2-dimethylbut-3-en-1-ylidene]-4-methylbenzenesulfonamide (2c)

Compound **2c** was prepared by following typical procedure D from ketone **1c** (538 mg, 2.34 mmol), $TsNH_2$ (400 mg, 2.34 mmol), DCE (23 mL), Et_3N (0.65 mL, 4.66 mmol), and $TiCl_4$ (0.22 mL, 2.00 mmol). Purification by column chromatography [silica gel, EtOAc–hexane (1:5)] gave a pale-yellow oil; yield: 733 mg (82%).

IR (neat): 2927, 2852, 1739, 1616, 1448, 1319, 1218, 1157, 1093, 1004, 813, 738, 678, 584 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.05–1.20 (m, 3 H), 1.25–1.33 (m, 8 H), 1.65–1.67 (m, 1 H), 1.73–1.75 (m, 4 H), 2.11–2.18 (m, 1 H), 2.43 (s, 3 H), 2.83 (d, *J* = 7.5 Hz, 2 H), 4.28 (dd, J_{HF} = 27.2, 5.0 Hz, 1 H), 7.31 (d, *J* = 8.2 Hz, 2 H), 7.83 (d, *J* = 8.2 Hz, 2 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 21.5, 26.0, 26.4, 26.8 (d, J_{CF} = 3 Hz), 33.7, 38.2, 41.6, 44.7 (dd, J_{CF} = 5, 3 Hz), 84.6 (dd, J_{CF} = 24, 14 Hz), 126.9, 129.4, 138.8, 143.2, 155.7 (dd, J_{CF} = 295, 288 Hz), 193.6.

^{19}F NMR (470 MHz, $CDCl_3$): δ = 77.9 (dd, J_{FF} = 43 Hz, J_{FH} = 5 Hz, 1 F), 78.4 (dd, J_{FF} = 43 Hz, J_{FH} = 27 Hz, 1 F).

Anal. Calcd for $C_{20}H_{27}F_2NO_2S$: C, 62.64; H, 7.10. Found: C, 62.72; H, 7.33.

N-(1-Benzyl-4,4-difluoro-2,2-dimethylbut-3-en-1-ylidene)-4-methylbenzenesulfonamide (2e)

Compound **2e** was prepared by following typical procedure D from ketone **1e** (132 mg, 0.59 mmol), $TsNH_2$ (101 mg, 0.59 mmol), DCE (6 mL), Et_3N (165 μL, 1.2 mmol), and $TiCl_4$ (65 μL, 0.59 mmol). Purification by TLC [silica gel, EtOAc–hexane (1:5)] gave pale-yellow crystals; yield: 133 mg (60%); mp 75.0–76.0 °C.

IR (neat): 2983, 2927, 1738, 1616, 1321, 1240, 1155, 1092, 914, 687 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.24 (d, J_{HF} = 1.4 Hz, 6 H), 2.45 (s, 3 H), 4.13 (dd, J_{HF} = 27.4, 5.0 Hz, 1 H), 4.44 (s, 2 H), 7.24 (m, 3 H), 7.33 (m, 4 H), 7.88 (d, *J* = 8.4 Hz, 2 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 21.6, 27.5 (d, J_{CF} = 4 Hz), 40.2, 44.7 (dd, J_{CF} = 5, 4 Hz), 84.9 (dd, J_{CF} = 25, 14 Hz), 126.9, 127.1, 128.8, 129.0, 129.5, 134.6, 138.3, 143.7, 155.5 (dd, J_{CF} = 295, 288 Hz), 191.0.

^{19}F NMR (470 MHz, $CDCl_3$): δ = 77.9 (dd, J_{FF} = 42 Hz, J_{FH} = 5 Hz, 1 F), 78.5 (dd, J_{FF} = 42 Hz, J_{FH} = 27 Hz, 1 F).

Anal. Calcd for $C_{20}H_{21}F_2NO_2S$: C, 63.64; H, 5.61. Found: C, 63.89; H, 5.76.

N-[4,4-Difluoro-1-(4-methoxybenzyl)-2,2-dimethylbut-3-en-1-ylidene]-4-methylbenzenesulfonamide (2f)

Compound **2f** was prepared by following typical procedure D from ketone **1f** (679 mg, 2.67 mmol), $TsNH_2$ (457 mg, 2.67 mmol), DCE (26 mL), Et_3N (0.744 mL, 5.34 mmol), and $TiCl_4$ (0.293 mL, 2.67 mmol). Purification by column chromatography [silica gel, EtOAc–hexane (1:4)] gave a pale-yellow oil; yield: 584 mg (54%).

IR (neat): 2983, 2937, 2836, 1738, 1614, 1511, 1465, 1319, 1247, 1180, 1155, 1092, 1034, 1004, 814, 782, 683 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.23 (d, J_{HF} = 1.3 Hz, 6 H), 2.45 (s, 3 H), 3.79 (s, 3 H), 4.15 (dd, J_{HF} = 27.4, 5.0 Hz, 1 H), 4.36 (s, 2 H), 6.86 (d, *J* = 8.7 Hz, 2 H), 7.18 (d, *J* = 8.7 Hz, 2 H), 7.34 (d, *J* = 8.2 Hz, 2 H), 7.88 (d, *J* = 8.2 Hz, 2 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 21.6, 27.6 (d, J_{CF} = 3 Hz), 39.5, 44.6 (dd, J_{CF} = 5, 3 Hz), 55.2, 85.0 (dd, J_{CF} = 25, 14 Hz), 114.1, 126.5, 127.1, 129.4, 130.2, 138.4, 143.6, 155.5 (dd, J_{CF} = 295, 288 Hz), 158.5, 191.6 (dd, J_{CF} = 2, 2 Hz).

^{19}F NMR (470 MHz, $CDCl_3$): δ = 77.8 (dd, J_{FF} = 43 Hz, J_{FH} = 5 Hz, 1 F), 78.5 (dd, J_{FF} = 43 Hz, J_{FH} = 27 Hz, 1 F).

Anal. Calcd for $C_{21}H_{23}F_2NO_3S$: C, 61.90; H, 5.69. Found: C, 62.14; H, 5.82.

_N_-{1-[1-(2,2-Difluorovinyl)cyclohexyl]ethylidene}-4-methylbenzenesulfonamide (2h)

Compound **2h** was prepared by following typical procedure D from ketone **1h** (209 mg, 1.11 mmol), $TsNH_2$ (190 mg, 1.11 mmol), DCE (11 mL), Et_3N (0.309 mL, 2.22 mmol), and $TiCl_4$ (0.122 mL, 1.11 mmol). Purification by column chromatography [silica gel, EtOAc–hexane (1:5)] gave a yellow solid; yield: 253 mg (67%); mp 59.1–61.0 °C.

IR (neat): 2935, 2860, 1730, 1614, 1315, 1149, 1092, 696, 552 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.18–1.28 (m, 1 H), 1.36–1.46 (m, 2 H), 1.50–1.66 (m, 5 H), 1.74–1.79 (m, 2 H), 2.43 (s, 3 H), 2.52 (s, 3 H), 4.19 (dd, J_{HF} = 28.1, 4.6 Hz, 1 H), 7.32 (d, J = 8.4 Hz, 2 H), 7.85 (d, J = 8.4 Hz, 2 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 20.2, 21.5, 22.2, 25.3, 47.9 (dd, J_{CF} = 4, 3 Hz), 81.9 (dd, J_{CF} = 23, 15 Hz), 126.9, 129.3, 138.5, 143.4, 156.0 (dd, J_{CF} = 296, 290 Hz), 190.6.

^{19}F NMR (470 MHz, $CDCl_3$): δ = 79.3 (dd, J_{FF} = 39 Hz, J_{FH} = 5 Hz, 1 F), 79.7 (dd, J_{FF} = 39 Hz, J_{FH} = 28 Hz, 1 F).

HRMS (EI): m/z [M^+] calcd for $C_{17}H_{21}F_2NO_2S$: 341.1261; found: 341.1265.

(2*Z*)-5-Fluoro-3,3-dimethyl-2-nonylidene-2,3-dihydrofuran (6a); Typical Procedure E

KH (oil-free, 38 mg, 0.94 mmol) was added to a solution of difluoroallylic ketone **1a** (122 mg, 0.47 mmol) in THF (9 mL) at r.t. The mixture was refluxed for 2 h and then cooled to r.t. The reaction was quenched with pH 7 phosphate buffer (5 mL), and the organic materials were extracted with Et_2O (3 × 10 mL). The extracts were combined, washed with brine (20 mL), dried ($MgSO_4$), and concentrated under reduced pressure. The residue was purified by TLC [silica gel, Et_2O–pentane (1:10)] to give a colorless oil; yield: 102 mg (91%).

IR (neat): 2922, 2854, 1726, 1689, 1458, 1327, 1281, 1138, 993, 731 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, J = 7.0 Hz, 3 H), 1.22 (d, J_{HF} = 1.1 Hz, 6 H), 1.24–1.36 (m, 12 H), 2.07 (td, J = 7.3, 7.3 Hz, 2 H), 4.14 (d, J_{HF} = 5.2 Hz, 1 H), 4.50 (td, J = 7.3 Hz, J_{HF} = 3.6 Hz, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1, 22.7, 24.7, 29.1, 29.3, 29.4, 29.6, 30.3 (d, J_{CF} = 3 Hz), 31.9, 44.0 (d, J_{CF} = 3 Hz), 79.4 (d, J_{CF} = 8 Hz), 100.8, 157.7 (d, J_{CF} = 274 Hz), 159.8.

^{19}F NMR (470 MHz, $CDCl_3$): δ = 46.1 (dd, J_{FH} = 5, 4 Hz).

HRMS (FAB): m/z [M + H]$^+$ calcd for $C_{15}H_{26}FO$: 241.1968; found: 241.1966.

(2*Z*)-5-Fluoro-3,3-dimethyl-2-(2-phenylethylidene)-2,3-dihydrofuran (6b)

Compound **6b** was synthesized by typical procedure E from difluoroallylic ketone **1b** (138 mg, 0.58 mmol), THF (11 mL), and KH (oil-free, 46 mg, 1.2 mmol). The mixture was refluxed for 2 h. Purification by TLC [silica gel, EtOAc–pentane (1:5)] gave a colorless oil; yield: 122 mg (97%).

IR (neat): 3028, 2970, 2931, 1801, 1726, 1703, 1454, 1279, 1219, 1126, 1088, 993, 976, 748, 698 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.26 (d, J_{HF} = 1.1 Hz, 6 H), 3.45 (d, J = 7.5 Hz, 2 H), 4.20 (d, J_{HF} = 5.4 Hz, 1 H), 4.73 (td, J = 7.5, J_{HF} = 3.4 Hz, 1 H), 7.18–7.22 (m, 3 H), 7.27–7.30 (m, 2 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 30.1 (d, J_{CF} = 2 Hz), 30.9, 44.2 (d, J_{CF} = 2 Hz), 79.7 (d, J_{CF} = 8 Hz), 99.4, 125.9, 128.2, 128.4, 141.0, 157.5 (d, J_{CF} = 276 Hz), 160.6 (d, J_{CF} = 3 Hz).

^{19}F NMR (470 MHz, $CDCl_3$): δ = 46.2 (s).

Anal. Calcd for $C_{14}H_{15}FO$: C, 77.04; H, 6.93. Found: C, 76.80; H, 7.16.

(2*Z*)-2-(Cyclohexylmethylene)-5-fluoro-3,3-dimethyl-2,3-dihydrofuran (6c)

Compound **6c** was synthesized by typical procedure E from difluoroallylic ketone **1c** (194 mg, 0.84 mmol), THF (15 mL), and KH (oil-free, 68 mg, 1.7 mmol). The mixture was refluxed for 2 h. Purification by column chromatography [silica gel, Et_2O–pentane (1:10)] gave a colorless oil; yield: 147 mg (83%).

IR (neat): 2962, 2923, 2850, 1724, 1689, 1448, 1342, 1309, 1280, 1255, 1227, 1138, 1039, 993, 890, 730 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.01–1.09 (m, 2 H), 1.10–1.19 (m, 1 H), 1.21 (d, J_{HF} = 1.2 Hz, 6 H), 1.25–1.40 (m, 2 H), 1.61–1.70 (m, 5 H), 2.32–2.37 (m, 1 H), 4.13 (d, J_{HF} = 5.3 Hz, 1 H), 4.38 (dd, J = 9.1, J_{HF} = 3.6 Hz, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 25.9, 26.1, 30.3 (d, J_{CF} = 2 Hz), 33.4, 34.2, 43.9 (d, J_{CF} = 2 Hz), 79.3 (d, J_{CF} = 8 Hz), 106.7, 157.6 (d, J_{CF} = 275 Hz), 158.5 (d, J_{CF} = 3 Hz).

^{19}F NMR (470 MHz, $CDCl_3$): δ = 46.0 (s).

Anal. Calcd for $C_{13}H_{19}FO$: C, 74.25; H, 9.11. Found: C, 74.37; H, 9.24.

(2*Z*)-2-(2,2-Dimethylpropylidene)-5-fluoro-3,3-dimethyl-2,3-dihydrofuran (6d)

Compound **6d** was synthesized by typical procedure E from difluoroallylic ketone **1d** (115 mg, 0.56 mmol), THF (11 mL), and KH (oil-free, 45 mg, 1.1 mmol). The mixture was refluxed for 2 h. Purification by column chromatography [silica gel, Et_2O–pentane (1:10)] gave a colorless oil; yield: 77 mg (75%).

IR (neat): 2952, 2927, 2868, 1705, 1464, 1363, 1247, 1059, 808 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.12 (s, 9 H), 1.19 (d, J_{HF} = 1.2 Hz, 6 H), 4.12 (d, J_{HF} = 5.3 Hz, 1 H), 4.42 (d, J_{HF} = 3.7 Hz, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 30.5, 30.5, 30.5, 44.8 (d, J_{CF} = 2 Hz), 79.0 (d, J_{CF} = 8 Hz), 110.4 (d, J_{CF} = 1 Hz), 157.6 (d, J_{CF} = 274 Hz), 158.1 (d, J_{CF} = 3 Hz).

^{19}F NMR (470 MHz, $CDCl_3$): δ = 46.2 (s).

HRMS (EI): m/z [M – CH_3]$^+$ calcd for $C_{10}H_{14}FO$: 169.1029; found: 169.1032.

(2*Z*)-2-Benzylidene-5-fluoro-3,3-dimethyl-2,3-dihydrofuran (6e)

Compound **6e** was synthesized by typical procedure E from difluoroallylic ketone **1e** (51 mg, 0.23 mmol), THF (5 mL), and KH (30% dispersion in mineral oil, 60 mg, 0.45 mmol). The mixture was refluxed for 2 h. Purification by TLC [silica gel, EtOAc–pentane (1:5)] gave a colorless oil; yield: 45 mg (98%).

IR (neat): 2925, 1724, 1682, 1279, 1261, 1059, 989, 750, 692 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.35 (d, J_{HF} = 1.1 Hz, 6 H), 4.30 (d, J_{HF} = 5.5 Hz, 1 H), 5.47 (d, J_{HF} = 3.3 Hz, 1 H), 7.17 (tt, J = 7.6, 1.1 Hz, 1 H), 7.32 (dd, J = 7.6, 7.6 Hz, 2 H), 7.53 (dd, J = 7.6, 1.1 Hz, 2 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 29.9 (d, J_{CF} = 2 Hz), 45.9 (d, J_{CF} = 2 Hz), 80.0 (d, J_{CF} = 7 Hz), 101.0, 126.2, 128.0, 128.4, 134.5, 157.4 (d, J_{CF} = 277 Hz), 160.6 (d, J_{CF} = 3 Hz).

^{19}F NMR (470 MHz, $CDCl_3$): δ = 46.5 (m).

HRMS (FAB): m/z [M + H]$^+$ calcd for $C_{13}H_{14}FO$: 205.1029; found: 205.1022.

(2*Z*)-5-Fluoro-2-(4-methoxybenzylidene)-3,3-dimethyl-2,3-dihydrofuran (6f)

Compound **6f** was synthesized by typical procedure E from difluoroallylic ketone **1f** (105 mg, 0.41 mmol), THF (8 mL), and KH (oil-free, 33 mg, 0.83 mmol). The mixture was refluxed for 2 h. Purifi-

cation by TLC [silica gel, EtOAc–hexane (1:10)] gave a colorless oil; yield: 93 mg (97%).

IR (neat): 3134, 2964, 2929, 1809, 1720, 1674, 1606, 1510, 1458, 1350, 1245, 1176, 1140, 1059, 1030, 989, 844, 733 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.34 (d, J_{HF} = 0.3 Hz, 6 H), 3.80 (s, 3 H), 4.28 (d, J_{HF} = 5.5 Hz, 1 H), 5.42 (d, J_{HF} = 3.3 Hz, 1 H), 6.87 (d, J = 8.8 Hz, 2 H), 7.47 (d, J = 8.8 Hz, 2 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 29.9 (d, J_{CF} = 2 Hz), 45.7 (d, J_{CF} = 2 Hz), 55.2, 79.8 (d, J_{CF} = 8 Hz), 100.4, 113.8, 127.3, 129.2, 157.4 (d, J_{CF} = 277 Hz), 157.9, 159.0 (d, J_{CF} = 3 Hz).

^{19}F NMR (470 MHz, $CDCl_3$): δ = 46.4 (s).

Anal. Calcd for $C_{14}H_{15}FO_2$: C, 71.78; H, 6.45. Found: C, 71.61; H, 6.70.

2-Cyclohexylidene-5-fluoro-3,3-dimethyl-2,3-dihydrofuran (6g)

Compound **6g** was synthesized by typical procedure E from difluoroallylic ketone **1g** (67 mg, 0.31 mmol), THF (8 mL), and KH (oil-free, 25 mg, 0.62 mmol). The mixture was refluxed for 21 h. Purification by column chromatography [silica gel, Et_2O–pentane (1:10)] gave a colorless oil; yield: 57 mg (94%).

IR (neat): 2966, 2925, 2854, 1724, 1687, 1327, 1313, 1047, 725, 584 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.36 (d, J_{HF} = 1.3 Hz, 6 H), 1.51–1.56 (m, 6 H), 2.14–2.23 (m, 4 H), 4.01 (d, J_{HF} = 4.9 Hz, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 26.5, 27.2, 27.9 (d, J_{CF} = 1 Hz), 27.9, 28.3, 28.4, 44.2 (d, J_{CF} = 3 Hz), 79.8 (d, J_{CF} = 9 Hz), 115.1, 150.1 (d, J_{CF} = 2 Hz), 157.1 (d, J_{CF} = 273 Hz).

^{19}F NMR (470 MHz, $CDCl_3$): δ = 45.0 (d, J_{HF} = 5 Hz).

Anal. Calcd for $C_{12}H_{17}FO$: C, 73.44; H, 8.73. Found: C, 73.64; H, 8.95.

3-Fluoro-1-methylene-2-oxaspiro[4.5]dec-3-ene (6h)

Compound **6h** was synthesized by typical procedure E from difluoroallylic ketone **1h** (50 mg, 0.27 mmol), THF (5 mL), and KH (30% dispersion in mineral oil, 71 mg, 0.53 mmol). The mixture was refluxed for 2 h. Purification by TLC [silica gel, Et_2O–hexane (1:10)] gave a colorless oil; yield: 41 mg (91%).

IR (neat): 2922, 2852, 1716, 1684, 1647, 1458, 1375, 1294, 1230, 997, 721, 667 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.29–1.46 (m, 6 H), 1.68 (d, J = 11.5 Hz, 2 H), 1.74 (d, J = 11.5 Hz, 2 H), 4.22 (dd, J_{HF} = 3.1 Hz, J = 3.0 Hz, 1 H), 4.34 (d, J_{HF} = 5.4 Hz, 1 H), 4.60 (d, J = 3.0, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 23.0, 25.6, 29.7, 39.7 (d, J_{CF} = 2 Hz), 76.0 (d, J_{CF} = 8 Hz), 84.7, 158.0 (d, J_{CF} = 275 Hz), 167.9 (d, J_{CF} = 3 Hz).

^{19}F NMR (470 MHz, $CDCl_3$): δ = 46.7–46.8 (m).

HRMS (FAB): m/z $[M + H]^+$ calcd for $C_{10}H_{14}FO$: 169.1029; found: 169.1034.

(1*Z*)-1-(2,2-Dimethylpropylidene)-3-fluoro-2-oxaspiro[4.5]dec-3-ene (6i)

Compound **6i** was synthesized by typical procedure E from difluoroallylic ketone **1i** (49 mg, 0.20 mmol), THF (2 mL), and KH (30% dispersion in mineral oil, 53 mg, 0.40 mmol). The mixture was refluxed for 2 h. Purification by TLC [silica gel, Et_2O–hexane (1:10)] gave a colorless oil; yield: 42 mg (94%).

IR (neat): 2924, 2854, 1724, 1684, 1462, 1346, 1283, 1225, 995, 731 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.12 (s, 9 H), 1.18–1.37 (m, 6 H), 1.61–1.72 (m, 4 H), 4.42 (d, J_{HF} = 3.4 Hz, 1 H), 4.50 (d, J_{HF} = 5.0 Hz, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 23.2, 25.7, 29.7, 30.6, 40.3 (d, J_{CF} = 2 Hz), 49.9 (d, J_{CF} = 3 Hz), 75.1 (d, J_{CF} = 9 Hz), 111.0, 158.4 (d, J_{CF} = 274 Hz), 158.4 (d, J_{CF} = 3 Hz).

^{19}F NMR (470 MHz, $CDCl_3$): δ = 46.9 (dd, J_{FH} = 5, 3 Hz).

HRMS (FAB): m/z $[M + H]^+$ calcd for $C_{14}H_{22}FO$: 225.1655; found: 225.1649.

1-Cyclohexylidene-3-fluoro-2-oxaspiro[4.5]dec-3-ene (6j)

Compound **6j** was synthesized by typical procedure E from difluoroallylic ketone **1j** (25 mg, 0.099 mmol), pyridine (5 mL), and KH (30% dispersion in mineral oil, 49 mg, 0.36 mmol). The mixture was refluxed for 3 h. Purification by TLC [silica gel, EtOAc–hexane (1:10)] gave a colorless oil; yield: 23 mg (97%).

IR (neat): 2921, 2852, 1793, 1685, 1446, 1335, 1261, 1198, 1161, 1146, 1113, 1041, 1014, 847 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.17–1.40 (m, 5 H), 1.49–1.60 (br s, 4 H), 1.60–1.75 (m, 5 H), 1.80–1.89 (m, 2 H), 2.16–2.21 (m, 2 H), 2.25–2.30 (m, 2 H), 4.51 (d, J_{HF} = 4.9 Hz, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 23.1, 25.7, 26.6, 27.4, 28.1, 28.2, 28.3, 29.7, 36.6 (d, J_{CF} = 2 Hz), 75.1 (d, J_{CF} = 9 Hz), 115.6, 150.1 (d, J_{CF} = 2 Hz), 157.9 (d, J_{CF} = 272 Hz).

^{19}F NMR (470 MHz, $CDCl_3$): δ = 45.7 (dt, J_{FH} = 4, 3 Hz).

HRMS (FAB): m/z $[M + H]^+$ calcd for $C_{15}H_{22}FO$: 237.1655; found: 237.1646.

(2*E*)-5-Fluoro-2-(4-methoxybenzylidene)-3,3-dimethyl-1-[(4-tolyl)sulfonyl]-2,3-dihydro-1*H*-pyrrole (8f); Typical Procedure F

t-BuOK (32 mg, 0.28 mmol) was added to a solution of difluoroallylic imine **2f** (87 mg, 0.21 mmol) in DMF (5 mL) at r.t., and the mixture was heated to 90 °C for 3 h then cooled to r.t. The reaction was quenched with pH 7 phosphate buffer (5 mL), and the organic materials were extracted with EtOAc (3 × 10 mL). The extracts were combined, washed with brine (20 mL), dried (Na_2SO_4), and concentrated under reduced pressure. The residue was purified by TLC [silica gel, EtOAc–hexane (1:2)] to give a colorless solid; yield: 63 mg (77%); mp 108.1–109.8 °C.

IR (neat): 3103, 2966, 2931, 2868, 2837, 1703, 1608, 1510, 1464, 1371, 1290, 1248, 1171, 1082, 1034, 814, 673, 615, 557, 540 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.62 (d, J_{HF} = 0.9 Hz, 6 H), 2.48 (s, 3 H), 3.81 (s, 3 H), 4.41 (d, J_{HF} = 2.6 Hz, 1 H), 6.84 (d, J = 8.5 Hz, 2 H), 7.07 (d, J = 8.5 Hz, 2 H), 7.18 (s, 1 H), 7.40 (d, J = 8.1 Hz, 2 H), 7.79 (d, J = 8.1 Hz, 2 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 21.7, 28.1 (d, J_{CF} = 3 Hz), 43.6, 55.2, 97.5 (d, J_{CF} = 9 Hz), 113.3, 121.1, 127.8, 128.5, 129.5, 130.3, 132.8, 144.9, 144.9, 149.6 (d, J_{CF} = 280 Hz), 158.7.

^{19}F NMR (470 MHz, $CDCl_3$): δ = 43.2 (s).

Anal. Calcd for $C_{21}H_{22}FNO_3S$: C, 65.10; H, 5.72. Found: C, 65.22; H, 5.90.

5-Fluoro-3,3-dimethyl-2-nonylidene-1-[(4-tolyl)sulfonyl]-2,3-dihydro-1*H*-pyrrole (8a)

Compound **8a** was synthesized by typical procedure F from difluoroallylic imine **2a** (53 mg, 0.13 mmol), DMF (3 mL), and *t*-BuOK (18 mg, 0.16 mmol). The mixture was heated to 90 °C for 4 h. Purification by TLC [silica gel, EtOAc–hexane (1:5)] gave a pale-yellow oil; yield: 38 mg (74%; *E*/*Z* = 89:11).

IR (neat): 2958, 2925, 2856, 1705, 1664, 1599, 1458, 1377, 1298, 1174, 1081, 910, 813, 706, 667, 619, 561 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ (major) = 0.82 (d, J_{HF} = 1.2 Hz, 6 H), 0.90 (t, J = 7.0 Hz, 3 H), 1.26–1.36 (m, 12 H), 2.15 (dt, J = 8.0, 7.7 Hz, 2 H), 2.43 (s, 3 H), 4.40 (d, J_{HF} = 2.4 Hz, 1 H), 6.06 (t, J = 8.0 Hz, 1 H), 7.31 (d, J = 8.2 Hz, 2 H), 7.66 (d, J = 8.2 Hz, 2 H); δ (minor) = 0.89 (d, J_{HF} = 1.2 Hz, 6 H), 0.88 (t, J = 7.0 Hz, 3 H), 1.39–1.46 (m, 12 H), 2.32 (td, J = 7.3, 7.2 Hz, 2 H), 2.43 (s, 3 H),

4.59 (d, J_{HF} = 2.9 Hz, 1 H), 5.16 (td, J = 7.2, J_{HF} = 2.1 Hz, 1 H), 7.33 (d, J = 8.2 Hz, 2 H), 7.76 (d, J = 8.2 Hz, 2 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ (mixture) = 14.1, 21.6, 22.7, 27.2 (d, J_{CF} = 3 Hz), 27.4, 28.6 (d, J_{CF} = 3 Hz), 28.9, 29.2, 29.3, 29.4, 29.4, 29.4, 29.6, 30.1, 31.9, 42.6 (d, J_{CF} = 2 Hz), 43.5 (d, J_{CF} = 1 Hz), 97.5 (d, J_{CF} = 9 Hz), 98.5 (d, J_{CF} = 9 Hz), 119.9, 120.4, 128.5, 129.2, 129.4, 132.2, 134.2, 142.5, 144.3, 144.7, 149.8 (d, J_{CF} = 279 Hz), 151.2 (d, J_{CF} = 279 Hz).

^{19}F NMR (470 MHz, $CDCl_3$): δ (major) = 43.9 (s); δ (minor) = 45.3 (s).

Anal. Calcd for $C_{22}H_{32}FNO_2S$: C, 67.14; H, 8.20. Found: C, 67.21; H, 8.37.

5-Fluoro-3,3-dimethyl-1-2-(2-phenylethylidene)-[(4-tolyl)sulfonyl]-2,3-dihydro-1*H*-pyrrole (8b)

Compound **8b** was synthesized by typical procedure F from difluoroallylic imine **2b** (47 mg, 0.12 mmol), DMF (3 mL), and *t*-BuOK (17 mg, 0.15 mmol). The mixture was heated to 90 °C for 4 h. Purification by TLC [silica gel, EtOAc–hexane (1:5)] gave a colorless solid; yield: 35 mg (78%; *E*/*Z* = 79:21); mp 103.2–105.8 °C.

IR (neat): 3027, 2964, 2927, 2868, 1705, 1670, 1597, 1496, 1454, 1373, 1273, 1172, 1089, 800, 700, 586, 540 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ (major) = 0.92 (s, 6 H), 2.43 (s, 3 H), 3.54 (d, J = 8.4 Hz, 2 H), 4.45 (d, J_{HF} = 2.6 Hz, 1 H), 6.29 (t, J = 8.4 Hz, 1 H), 7.18–7.37 (m, 7 H), 7.55 (d, J = 8.3 Hz, 2 H); δ (minor) = 0.92 (s, 6 H), 2.44 (s, 3 H), 3.71 (d, J = 6.9 Hz, 2 H), 4.65 (d, J_{HF} = 2.4 Hz, 1 H), 5.35 (td, J = 6.9, J_{HF} = 1.8 Hz, 1 H), 7.18–7.37 (m, 7 H), 7.80 (d, J = 8.3 Hz, 2 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ (major) = 21.6, 27.6 (d, J_{CF} = 3 Hz), 33.2, 42.7 (d, J_{CF} = 2 Hz), 97.2 (d, J_{CF} = 9 Hz), 117.7, 126.4, 128.3, 128.5, 128.6, 129.3, 132.1, 139.8, 143.4, 144.7, 149.8 (d, J_{CF} = 280 Hz); δ (minor) = 21.6, 28.5 (d, J_{CF} = 3 Hz), 35.1, 43.7, 98.6 (d, J_{CF} = 9 Hz), 118.9, 126.1, 128.4, 128.5, 128.5, 129.5, 134.1, 141.0, 144.9, 145.2, 151.1 (d, J_{CF} = 279 Hz).

^{19}F NMR (470 MHz, $CDCl_3$): δ (major) = 44.0 (s); δ (minor) = 45.3 (s).

Anal. Calcd for $C_{21}H_{22}FNO_2S$: C, 67.90; H, 5.97. Found: C, 67.82; H, 6.09.

2-(Cyclohexylmethylene)-5-fluoro-3,3-dimethyl-1-[(4-tolyl)sulfonyl]-2,3-dihydro-1*H*-pyrrole (8c)

Compound **8c** was synthesized by typical procedure F from difluoroallylic imine **2c** (77 mg, 0.20 mmol), DMF (5 mL), and *t*-BuOK (27 mg, 0.24 mmol). The mixture was heated to 90 °C for 6 h. Purification by TLC [silica gel, EtOAc–hexane (1:5)] gave a pale-yellow oil; yield: 46 mg (63%; *E*/*Z* = 93:7).

IR (neat): 2960, 2927, 2850, 1705, 1662, 1448, 1377, 1290, 1174, 1141, 1089, 1062, 673, 579, 542 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ (major) = 0.80 (d, J_{HF} = 1.1 Hz, 6 H), 1.18–1.29 (m, 5 H), 1.63–1.68 (m, 3 H), 1.76 (br s, 2 H), 2.24–2.27 (m, 1 H), 2.43 (s, 3 H), 4.41 (d, J_{HF} = 2.5 Hz, 1 H), 5.93 (d, J = 11.4 Hz, 1 H), 7.32 (d, J = 8.1 Hz, 2 H), 7.65 (d, J = 8.1 Hz, 2 H); δ (minor) = 0.84 (d, J_{HF} = 0.9 Hz, 6 H), 0.97–1.05 (m, 2 H), 1.13–1.34 (m, 3 H), 1.66–1.75 (m, 3 H), 1.79–1.83 (m, 2 H), 2.43 (s, 3 H), 2.64–2.72 (m, 1 H), 4.58 (d, J_{HF} = 2.9 Hz, 1 H), 4.96 (dd, J = 10.4, J_{HF} = 2.1 Hz, 1 H), 7.33 (d, J = 8.2 Hz, 2 H), 7.76 (d, J = 8.2 Hz, 2 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ (major) = 21.6, 25.7, 25.8, 27.7 (d, J_{CF} = 3 Hz), 33.3, 36.9, 42.7 (d, J_{CF} = 2 Hz), 97.4 (d, J_{CF} = 9.2 Hz), 125.2, 128.6, 129.2, 131.8, 141.4, 144.7, 149.7 (d, J_{CF} = 279 Hz); δ (minor) = 21.6, 25.8, 26.2, 28.7 (d, J_{CF} = 3 Hz), 32.8, 37.0, 43.3, 98.7 (d, J_{CF} = 9 Hz), 125.9, 128.5, 129.4, 134.2, 142.6, 144.6, 151.1 (d, J_{CF} = 279 Hz).

^{19}F NMR (470 MHz, $CDCl_3$): δ (major) = 43.9 (s); δ (minor) = 45.6 (s).

Anal. Calcd for $C_{20}H_{26}FNO_2S$: C, 66.09; H, 7.21. Found: C, 65.93; H, 7.35.

(2*E*)-2-Benzylidene-5-fluoro-3,3-dimethyl-1-[(4-tolyl)sulfonyl]-2,3-dihydro-1*H*-pyrrole (8e)

Compound **8e** was synthesized by typical procedure F from difluoroallylic imine **2e** (49 mg, 0.13 mmol), DMF (3 mL), and *t*-BuOK (20 mg, 0.18 mmol). The mixture was heated to 90 °C for 4 h. Purification by TLC [silica gel, EtOAc–hexane (1:5)] gave a colorless solid; yield: 40 mg (86%); mp 124.0–126.0 °C.

IR (neat): 2983, 2931, 2867, 1704, 1652, 1597, 1373, 1292, 1174, 1088, 1026, 706, 673, 621 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.61 (d, J_{HF} = 1.2 Hz, 6 H), 2.48 (s, 3 H), 4.40 (d, J_{HF} = 2.7 Hz, 1 H), 7.14 (d, J = 7.9 Hz, 2 H), 7.24–7.32 (m, 4 H), 7.41 (d, J = 8.1 Hz, 2 H), 7.80 (d, J = 8.1 Hz, 2 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 21.7, 28.2 (d, J_{CF} = 3 Hz), 43.7 (d, J_{CF} = 2 Hz), 97.3 (d, J_{CF} = 9 Hz), 121.1, 127.2, 127.9, 128.5, 129.1, 129.5, 132.8, 135.5, 145.0, 145.4, 149.6 (d, J_{CF} = 280 Hz).

^{19}F NMR (470 MHz, $CDCl_3$): δ = 43.2 (s).

Anal. Calcd for $C_{20}H_{20}FNO_2S$: C, 67.20; H, 5.64. Found: C, 67.16; H, 5.77.

3-Fluoro-1-methylene-2-[(4-tolyl)sulfonyl]-2-azaspiro[4.5]dec-3-ene (8h)

Compound **8h** was synthesized by typical procedure F from difluoroallylic imine **2h** (65 mg, 0.19 mmol), DMF (5 mL), and *t*-BuOK (27 mg, 0.24 mmol). The mixture was heated to 90 °C for 4 h. Purification by column chromatography [silica gel, EtOAc–hexane (1:5)] gave a pale-yellow solid; yield: 61 mg (99%); mp 88.3–89.4 °C.

IR (neat): 2929, 2858, 1699, 1647, 1367, 1288, 1171, 677, 559 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.92–0.99 (m, 2 H), 1.08–1.21 (m, 5 H), 1.45–1.52 (m, 2 H), 1.58–1.63 (m, 1 H), 2.42 (s, 3 H), 4.67 (dd, J_{HF} = 2.3 Hz, J = 2.0 Hz, 1 H), 4.89 (br s, 1 H), 5.61 (d, J = 2.0 Hz, 1 H), 7.31 (d, J = 8.3 Hz, 2 H), 7.68 (d, J = 8.3 Hz, 2 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 21.6, 22.7, 25.4, 39.2 (d, J_{CF} = 3 Hz), 47.5 (d, J_{CF} = 2 Hz), 90.8 (d, J_{CF} = 8 Hz), 97.3, 128.0, 129.4, 132.7, 144.8, 150.4 (d, J_{CF} = 280 Hz), 152.9.

^{19}F NMR (470 MHz, $CDCl_3$): δ = 42.8 (s).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{17}H_{20}FNO_2S$: 321.1199; found: 321.1198.

***N*-[(1*Z*)-4,4-Difluoro-2,2-dimethyl-1-(2-phenylethylidene)but-3-en-1-yl]-4-methylbenzenesulfonamide [(*Z*)-9b]**

KH (30% dispersion in mineral oil, 25 mg, 0.19 mmol) was added to a solution of difluoroallylic imine **2b** (37 mg, 0.095 mmol) in THF (2 mL) at r.t., and the mixture was refluxed for 2 h then cooled to r.t. The reaction was quenched with pH 7 phosphate buffer (5 mL), and the organic materials were extracted with Et_2O (3 × 10 mL). The extracts were combined, washed with brine (20 mL), dried ($MgSO_4$), and concentrated under reduced pressure. The residue was purified by TLC [silica gel, EtOAc–hexane (1:5)] to give a colorless solid; yield: 23 mg (61%); mp 87.5–90.2 °C.

IR (neat): 3267, 3028, 2976, 1736, 1414, 1329, 1221, 1153, 1092, 995, 771, 677, 557 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.23 (d, J_{HF} = 0.7 Hz, 6 H), 2.40 (s, 3 H), 3.35 (d, J = 6.9 Hz, 2 H), 4.05 (dd, J_{HF} = 27.2, 5.3 Hz, 1 H), 5.60 (br s, 1 H), 5.62 (t, J = 6.9 Hz, 1 H), 7.07 (d, J = 7.5 Hz, 2 H), 7.19 (t, J = 7.3 Hz, 1 H), 7.25–7.28 (m, 4 H), 7.78 (d, J = 8.3 Hz, 2 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 21.5, 27.6 (d, J_{CF} = 3 Hz), 34.8, 38.6 (dd, J_{CF} = 5, 3 Hz), 85.7 (dd, J_{CF} = 22, 13 Hz), 125.2, 126.1, 126.8, 128.4, 128.4, 129.5, 138.7, 138.9, 140.4, 143.5, 155.5 (dd, J_{CF} = 296, 287 Hz).

^{19}F NMR (470 MHz, $CDCl_3$): δ = 77.8 (dd, J_{FF} = 44 Hz, J_{FH} = 27 Hz, 1 F), 78.2 (dd, J_{FF} = 44 Hz, J_{FH} = 5 Hz, 1 F).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{21}H_{23}F_2NO_2S$: 391.1418; found: 391.1405.

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