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Synthesis of Functionalized *gem*-Difluoroalkenes via a Photocatalytic Decarboxylative/Defluorinative Reaction

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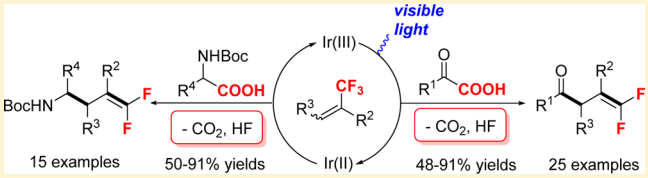
Supporting Information

ABSTRACT: A photocatalytic decarboxylative/defluorinative reaction of α-trifluoromethyl alkenes with α-keto acids and α-amino acids has been developed. The reaction occurs at room temperature under visible light irradiation, affording various γ,γ-difluoroallylic ketones and 1,1-difluorohomoallyl amines in good yields. The synthetic applications of the resulting functionalized *gem*-difluoroalkenes were also described.

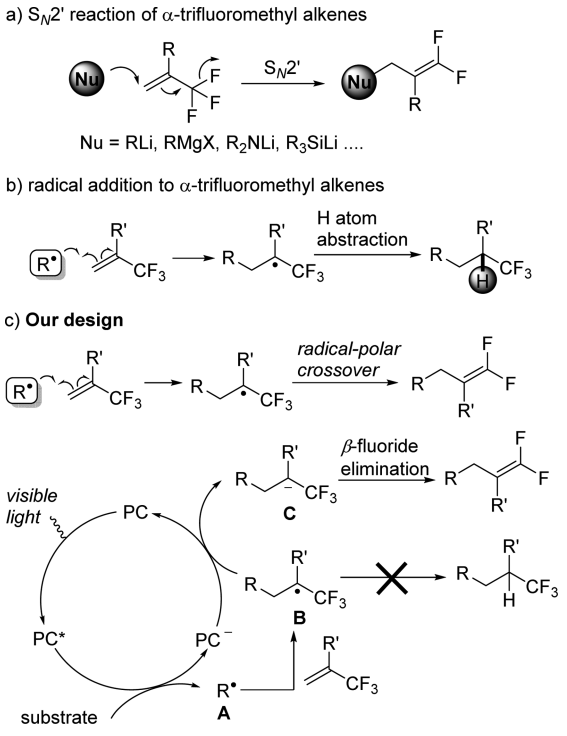


INTRODUCTION

α-Trifluoromethyl alkenes are important building blocks for synthesizing structurally diverse partially fluorinated or non-fluorinated compounds. In the past decades, the addition of carbon and heteroatom nucleophiles to α-trifluoromethyl alkenes followed by β-fluoride elimination in S_N2' manner has been extensively explored, which allows rapid access to functionalized 1,1-difluoroalkenes accompanied by the cleavage of the C−F bond.[1] A variety of nucleophiles, such as organolithiums,[2] Grignard reagents,[3] *N*-lithiated amines,[4,5] ester enolates,[6] and silyl lithium reagents[7] have been investigated (Scheme 1a). However, the high basicity of metal nucleophilic reagents considerably limits the functional group tolerance of this classical S_N2' reaction.

Radical is also a potential nucleophile that undergoes addition to α-trifluoromethyl alkenes. However, the resulting α-CF_3 alkyl radical is typically terminated by the hydrogen abstraction where no defluorination is observed (Scheme 1b).[8] We speculated that, if this hydrogen abstraction process could be intercepted through a radical-polar crossover strategy,[9] it would significantly expand the applications of α-trifluoromethyl alkenes in the synthesis of functionalized 1,1-difluoroalkenes. To this end, we recognized the use of visible-light photoredox catalysis, which has emerged as a powerful tool for developing sustainable chemical processes[10] and features a remarkable ability to facilitate radical-polar crossover reactions under mild conditions.[11] We envisioned that if the excited photocatalyst (PC*) was reductively quenched by a suitable substrate, it would give a one-electron-reduced form of photocatalyst (PC^-) and radical **A**. The addition of **A** to α-trifluoromethyl alkene forms α-CF_3 alkyl radical **B**. Instead of hydrogen abstraction or radical chain propagation, the resulting radical **B** could be single-electron reduced by PC^-, affording key sp^3-hybridized carbanion **C** to facilitate the β-fluoride elimination (Scheme 1c). On the basis of our ongoing interest in the synthesis of fluorinated compounds,[12] we present herein a mild and efficient method to synthesize functionalized *gem*-difluoroalkenes via a visible-light-mediated radical-polar crossover addition−elimination process.

Scheme 1. Reaction Mode for α-Trifluoromethyl Alkene



RESULTS AND DISCUSSION

In considering potential substrates for an experimental test of Scheme 1c, we were initially interested in α-keto acid, which could be engaged as both a good reductive quencher of excited photocatalyst and excellent acyl radical precursor.[13] Moreover,

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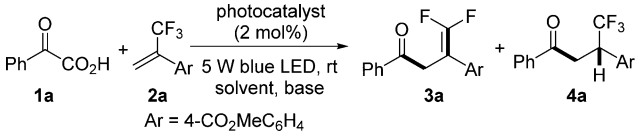
the decarboxylative/defluorinative reaction of α-keto acids and α-trifluoromethyl alkenes would give γ,γ-difluoroallylic ketones, which are versatile synthons for many fluorinated compounds and possess unique reactivity toward intramolecular S_NV reaction.[1a,14] The few reported methods currently available for their preparation require multiple synthetic steps and harsh reaction conditions or utilize hazardous and expensive reagents.[15] Therefore, the success of this photocatalytic reaction will provide a novel and practical method for synthesizing γ,γ-difluoroallylic ketones.

We first explored the proposed reaction using benzoylformic acid **1a** and 4-ester-substituted α-trifluoromethylstyrene **2a** as the model substrates in the presence of photocatalyst and 2,6-lutidine under the irradiation of a 5 W blue LED. It was observed that the strongly oxidizing $Ir(dFCF_3ppy)_2(dtbbpy)PF_6$ ($E_{1/2}^{III*/II}$ = +1.21 V vs SCE) provided the desired *gem*-difluoroalkene **3a** in 21% yield together with 47% yield of no defluorination product **4a** (Table 1, entry 1). Weaker oxidant

Table 1. Photocatalytic Reaction of Benzoylformic Acid 1a and α-Trifluoromethyl Alkene 2a[a]



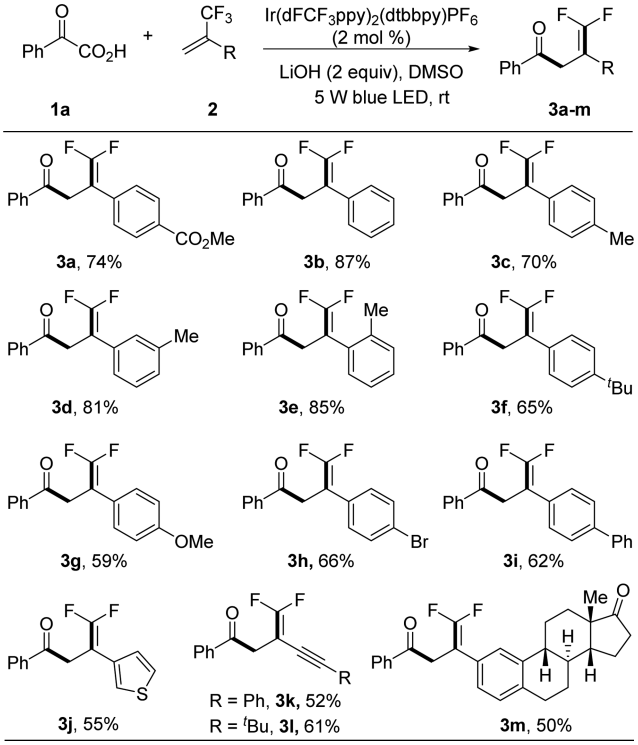
entry	photocatalyst (2 mol %)	base (2 equiv)	solvent	yield [%][b] 3a	4a
1	$Ir(dFCF_3ppy)_2(dtbbpy)PF_6$	2,6-lutidine	DMSO	21	47
2	$Ir(ppy)_2(dtbbpy)PF_6$	2,6-lutidine	DMSO	7	20
3	*fac*-$Ir(ppy)_3$	2,6-lutidine	DMSO	<5	<5
4	$Ir(dFCF_3ppy)_2(dtbbpy)PF_6$	Li_2CO_3	DMSO	61	
5	$Ir(dFCF_3ppy)_2(dtbbpy)PF_6$	Na_2CO_3	DMSO	25	<5
6	$Ir(dFCF_3ppy)_2(dtbbpy)PF_6$	K_2CO_3	DMSO	10	5
7	$Ir(dFCF_3ppy)_2(dtbbpy)PF_6$	LiOH	DMSO	77	
8	$Ir(dFCF_3ppy)_2(dtbbpy)PF_6$	LiCl	DMSO	0	0
9	$Ir(dFCF_3ppy)_2(dtbbpy)PF_6$	LiOH	DMF	52	
10	$Ir(dFCF_3ppy)_2(dtbbpy)PF_6$	LiOH	dioxane	37	
11	$Ir(dFCF_3ppy)_2(dtbbpy)PF_6$	LiOH	toluene	31	

[a]Reaction conditions: benzoylformic acid **1a** (0.4 mmol), α-trifluoromethyl alkene **2a** (0.2 mmol), photocatalyst (2 mol %), base (2 equiv), solvent (1 mL), 5 W blue LED, rt, 24 h. [b]^{1}H NMR yields obtained using mesitylene as the internal standard.

$Ir(ppy)_2(dtbbpy)PF_6$ ($E_{1/2}^{III*/II}$ = +0.66 V vs SCE) was less effective, whereas the strongly reducing *fac*-$Ir(ppy)_3$ ($E_{1/2}^{III*/IV}$ = −1.73 V vs SCE) was unable to promote the reaction (Table 1, entries 2 and 3). We were pleased to find that product **4a** could be completely suppressed when Li_2CO_3 was used as the base (Table 1, entry 4). In contrast, changing the base to Na_2CO_3 or K_2CO_3 dramatically decreased the yield of **3a**, which indicated that the lithium ion could enhance the leaving group ability of the fluorine atom (Table 1, entries 5 and 6).[16] We found the yield of **3a** could be further improved to 77% by using LiOH as the base (Table 1, entry 7), whereas large amounts of substrates remained unreacted when neutral LiCl was employed (Table 1, entry 8). Among various solvents examined, DMF provided a slightly lower yield (Table 1, entry 9). Other conditions employing 1,4-dioxane or toluene resulted in a lowered yield or a longer reaction time because of the poor solubility of **1a** in these solvents (Table 1, entries 10 and 11). A control experiment revealed that no product **3a** was formed when isolated **4a** was treated with LiOH. Because the basicity of LiOH is not enough to deprotonate the hydrogen atom alpha to CF_3 group in **4a**, the formation of **3a** from dehydrofluorination of **4a** seems unlikely.[17]

Having established the optimal reaction conditions (Table 1, entry 7), we examined the scope of the reaction with benzoylformic acid **1a** and a variety of α-trifluoromethyl alkenes **2** (Table 2). The decarboxylative/defluorinative cross-

Table 2. Reaction Scope of α-Trifluoromethyl Alkenes 2[a]



[a]Reaction conditions: benzoylformic acid **1a** (0.4 mmol), α-trifluoromethyl alkene **2** (0.2 mmol), $Ir(dFCF_3ppy)_2(dtbbpy)PF_6$ (2 mol %), and LiOH (2 equiv) in 1 mL of DMSO, irradiated with a 5 W blue LED under N_2 at room temperature for 24 h. Isolated yields.

coupling of **1a** with α-trifluoromethylstyrene led to the formation of γ,γ-difluoroallylic ketone **3b** in 87% yield. The reaction occurs smoothly with *para*-, *meta*-, *ortho*-substituted CF_3-styrenes to afford the corresponding *gem*-difluorostyrenes **3c−i** in moderate to good yields. Moreover, α-trifluoromethyl alkene that incorporates heteroaromatic substituent was found to be viable (**3j**, 55% yield). The reaction is not limited to CF_3-styrenyl reagents, as exemplified by the use of conjugated 2-trifluoromethyl-1,3-enynes to generate 1,1-difluoro-1,3-enyne products (**3k** and **3l**). In addition, α-trifluoromethyl alkene containing estrone moiety could undergo a reaction with **1a** to give desired product **3m** in 50% yield.

Next, various α-keto acids were employed as substrates to react with α-trifluoromethylstyrene **2b** (Table 3). The reaction was found to be not significantly affected by the substituent on

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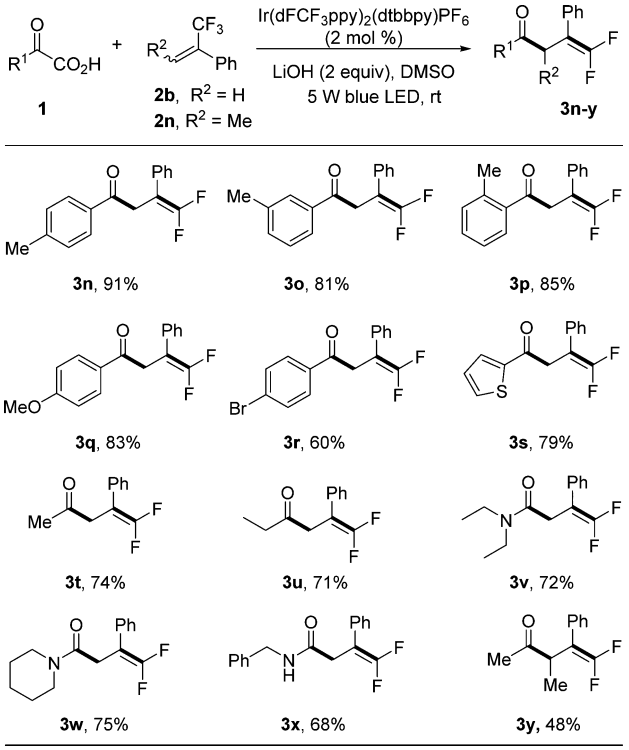
Table 3. Reaction Scope of α-Keto Acids[a]

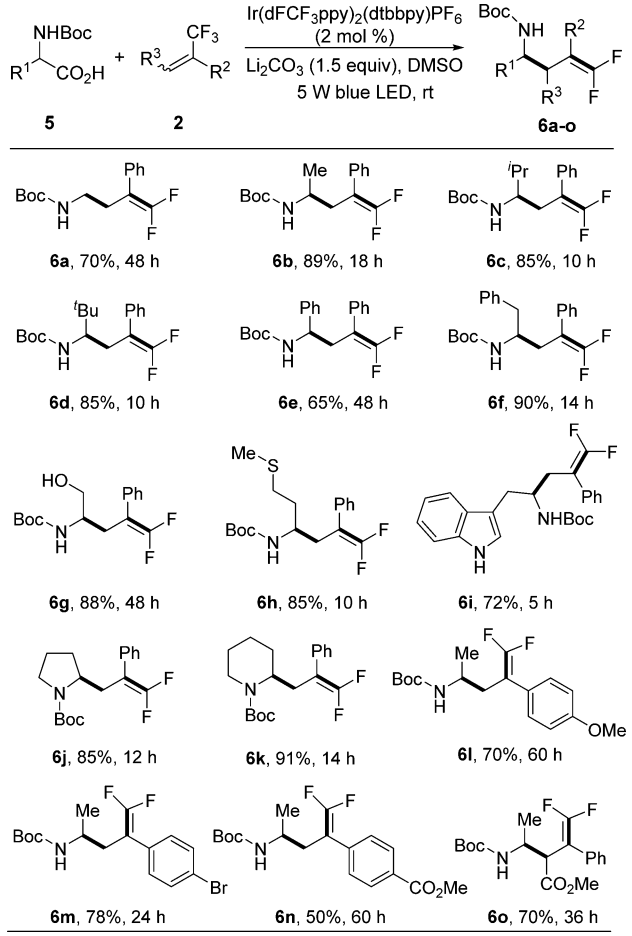


[a]All the reactions were carried out under the conditions as described in Table 2. Isolated yields.

the aromatic ring of 2-oxo-2-arylacetic acids; both electron-rich (**3n**–**q**) and electron-deficient (**3r**) aryl-substituted α-keto acids were effective. We were delighted to find that α-keto acid with a thiophenyl group was also consistent with the optimal conditions, leading to γ,γ-difluoroallylic ketone **3s** in a yield of 79%. It should be noted that aliphatic α-keto acids participated in the reactions with α-trifluoromethylstyrene **2b** to give the anticipated products in good yields (**3t** and **3u**). In addition to aryl- and alkyl-substituted α-keto acids, secondary and primary carbamoyl ketoacids were also examined, and they all smoothly underwent reactions with **2b** to afford the corresponding γ,γ-difluoroallylic amides **3v**–**x** in 68–75% yields. As an additional example, we found α-methyl allylic ketone **3y** could be obtained in 48% yield when *cis*- and *trans*-isomers of β-methyl-α-trifluoromethylstyrene **2n** were employed to react with pyruvic acid. However, the effect of using cyclohexanecarboxylic acid ($E_{1/2}^{red}$ = 1.18 V)[18] as the substrate was unsuccessful; presumably, simple carboxylic acids are significantly more difficult to oxidize than α-keto acids.

α-Amino acids, constituent units of proteins and organisms, have been proven to be good precursors of α-amino radicals through a decarboxylative process under visible-light photoredox conditions.[19] On the basis of the results above, visible-light photocatalytic decarboxylative/defluorinative reactions between α-trifluoromethyl alkenes and *N*-tertbutoxycarbonyl (*N*-Boc) α-amino acids were also tested. We found that desired 1,1-difluorohomoallylic amine **6a** was isolated in 70% yield when *N*-Boc-protected glycine was treated with CF_3-styrene **2b** under slightly modified conditions. A series of natural and non-natural α-amino acids, including alanine (**6b**), valine (**6c**), *tert*-leucine (**6d**), phenylglycine (**6e**), phenylalanine (**6f**), serine (**6g**), methionine (**6h**), tryptophan (**6i**), proline (**6j**), and pipecolinic acid (**6j**) all underwent reaction with **2b** smoothly, affording the corresponding 1,1-difluorohomoallylic amines in good to excellent yields. As detailed in Table 4, these mild

Table 4. Photocatalytic Decarboxylative/Defluorinative Reaction Between α-CF_3 Alkenes and *N*-Boc α-Amino Acids[a]



[a]Reaction conditions: *N*-Boc α-amino acid **5** (0.3 mmol), α-trifluoromethyl alkene **2** (0.2 mmol), Ir(dFCF$_3$ppy)$_2$(dtbbpy)PF$_6$ (2 mol %), and Li_2CO_3 (1.5 equiv) in 1 mL of DMSO, irradiated with a 5 W blue LED under N_2 at room temperature. Isolated yields.

reaction conditions allow the tolerance of functional groups on the aryl ring of α-trifluoromethylstyrene (**6l**–**n**). Remarkably, 3-ester-substituted 1,1-difluorohomoallylic amine **6o** could also be delivered in 72% yield via the reaction of Boc-alanine and 1,2-disubstituted 3,3,3-trifluoropropene that incorporates phenyl-ester groups. It is important to note that 1,1-difluorohomoallylic amines in this section are much less accessible by previous methods.[20]

To test the versatility of functionalized *gem*-difluoroalkenes obtained via the aforementioned sequence, we performed a series of transformations (Scheme 2). We were pleased to find that the carbonyl group in γ,γ-difluoroallylic ketone **3b** underwent smooth reaction with methyl Grignard reagent[21a] or reduction by $NaBH_4$[21b] to give the corresponding γ,γ-difluoro allylic alcohols **7** and **8** in yields of 90 and 80%, respectively. Upon treatment with TABF in DMF, γ,γ-difluoroallylic ketone **3b** was isomerized to α-difluoromethyl α,β-unsaturated ketone **9** with complete *E*-selectivity.[21c] Moreover, we were pleased to find that **3b** could be readily

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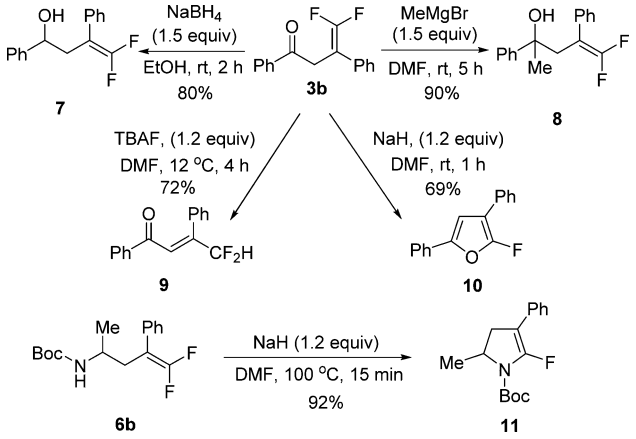
Scheme 2. Synthetic Applications of γ,γ-Difluoroallylic Ketone 3b and 1,1-Difluorohomoallylic Amine 6b



converted to 2-fluorinated furan **10** in a yield of 68% via an intramolecular S_NV reaction. On the other hand, heating the DMF solution of 1,1-difluorohomoallylic amine **6b** in the presence of NaH afforded 2-fluoro-2-pyrroline **11** in excellent yield through a 5-*endo-trig* cyclization process.[20a]

CONCLUSIONS

In conclusion, we have developed a novel visible-light photocatalytic decarboxylative/defluorinative reaction through a radical-polar crossover mechansim. Various γ,γ-difluoroallylic ketones and 1,1-difluorohomoallylic amines, which are difficult to access by existing methods, were obtained in generally good yields from readily available starting materials under mild conditions. The resulting functionalized *gem*-difluoroalkenes can be employed as valuable intermediates for the synthesis of difluoromethylated compounds and monofluorinated heterocycles.

EXPERIMENTAL SECTION

General. All reactions were performed under nitrogen atmosphere in a 10 mL test tube with the irradiation of a 5 W blue LED. For chromatography, 200−300 mesh silica gel was employed. ^{1}H NMR and ^{13}C NMR spectra were measured in $CDCl_3$ on a 400 MHz nuclear magnetic resonance spectrometer. Chemical shifts (δ) were given in ppm, referenced to the residual proton resonance of $CDCl_3$ (7.26) and to the carbon resonance of $CDCl_3$ (77.16). Coupling constants (J) were given in hertz (Hz). The term m, dq, q, t, d, and s referred to multiplet, doublet quartet, quartet, triplet, doublet, and singlet, respectively. Exact masses (HRMS) were recorded on a high-resolution magnetic mass spectrometer using electron impact ionization techniques or an ESI-Q-TQF mass spectrometer. Compounds **2a−j** were prepared according to previously reported procedures.[22]

Typical Procedure for the Synthesis of γ,γ-Difluoroallylic Ketone 3a. A 10 mL test tube equipped with a magnetic stir bar was charged with benzoylformic acid **1a** (0.4 mmol, 60.0 mg), $[Ir(dFCF_3ppy)_2dtbbpy]PF_6$ (2 mol %, 4.0 mg), **2a** (0.2 mmol, 46.0 mg), LiOH (0.4 mmol, 9.6 mg), and 1 mL of DMSO. The solution was stirred at room temperature with the irradiation of a 5 W blue LED under N_2. After completion of the reaction, the resulting solution was quenched with 10 mL of H_2O. The reaction mixture was extracted with ethyl acetate (10 mL × 3), washed with brine, and then dried over anhydrous Na_2SO_4. After the solvent was evaporated, the crude product was purified by column chromatography (hexane/ethyl acetate = 60:1) to give pure product **3a** as a yellow oil (46.8 mg, 74% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (t, J = 6.8 Hz, 4H), 7.60 (t, J = 7.4 Hz, 1H), 7.48 (t, J = 7.5 Hz, 2H), 7.39 (d, J = 8.1 Hz, 2H), 4.10 (s, 2H), 3.89 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.1 (t, J = 2.6 Hz), 166.7, 155.1 (dd, J = 294.6, 289.5 Hz), 138.4 (t, J = 4.3 Hz), 136.2, 133.7, 129.9, 129.2, 128.9, 128.3, 128.0 (t, J = 3.6 Hz), 87.1 (dd, J = 22.5, 16.5 Hz), 52.3, 38.1 (d, J = 2.3 Hz); ^{19}F NMR (377 MHz, $CDCl_3$) δ −85.78 (d, J = 31.7 Hz, 1F), −86.84 (d, J = 31.7 Hz, 1F); EI-MS (m/z, relative intensity) 316 (M^+, 5), 285 (4), 149 (100), 105 (83); HRMS (EI) calcd for $C_{18}H_{14}O_3F_2$ $[M]^+$ 316.0906, found 316.0901.

*4,4-Difluoro-1,3-diphenylbut-3-en-1-one (**3b**).* Colorless oil (44.9 mg, 87% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 8.0 Hz, 2H), 7.60 (t, J = 7.2 Hz, 1H), 7.49 (t, J = 7.6 Hz, 2H), 7.33 (d, J = 4.3 Hz, 4H), 7.26 (dd, J = 8.3, 4.7 Hz, 1H), 4.08 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.5, 154.9 (dd, J = 292.3, 288.3 Hz), 136.4, 133.6, 128.9, 128.6, 128.3, 128.1, 127.6, 87.3 (dd, J = 21.7, 17.5 Hz), 38.5; ^{19}F NMR (377 MHz, $CDCl_3$) δ −88.12 (d, J = 36.7 Hz, 1F), −89.13 (d, J = 36.7 Hz, 1F); EI-MS (m/z, relative intensity) 258 (M^+, 18), 105 (100), 77 (43); HRMS (EI) calcd for $C_{16}H_{12}O_1F_2$ $[M]^+$ 258.0851, found 258.0853.

*4,4-Difluoro-1-phenyl-3-(p-tolyl)but-3-en-1-one (**3c**).* Colorless oil (38.1 mg, 70% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 7.9 Hz, 2H), 7.59 (t, J = 7.0 Hz, 1H), 7.48 (t, J = 7.6 Hz, 2H), 7.21 (d, J = 7.9 Hz, 2H), 7.13 (d, J = 7.9 Hz, 2H), 4.05 (s, 2H), 2.32 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.6 (t, J = 2.6 Hz), 154.8 (dd, J = 292.0, 287.8 Hz), 137.4, 136.5, 133.5, 130.5 (t, J = 3.9 Hz), 129.4, 128.8, 128.3, 128.0 (t, J = 3.3 Hz), 87.2 (dd, J = 21.7, 17.6 Hz), 38.5 (d, J = 2.3 Hz), 21.3; ^{19}F NMR (377 MHz, $CDCl_3$) δ −88.69 (d, J = 38.1 Hz, 1F), −89.52 (d, J = 38.1 Hz, 1F); EI-MS (m/z, relative intensity) 272 (M^+, 11), 257 (4), 105 (100); HRMS (EI) calcd for $C_{17}H_{14}O_1F_2$ $[M]^+$ 272.1007, found 272.1004.

*4,4-Difluoro-1-phenyl-3-(m-tolyl)but-3-en-1-one (**3d**).* Colorless oil (44.1 mg, 81% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 7.7 Hz, 2H), 7.62 (t, J = 7.3 Hz, 1H), 7.51 (t, J = 7.6 Hz, 2H), 7.26 (dd, J = 15.3, 7.6 Hz, 1H), 7.20−7.12 (m, 2H), 7.10 (d, J = 7.5 Hz, 1H), 4.09 (s, 2H), 2.36 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.5 (t, J = 2.9 Hz), 154.8 (dd, J = 292.2, 287.9 Hz), 138.2, 136.4, 133.5, 128.8, 128.8, 128.5, 128.4, 125.2 (t, J = 3.2 Hz), 87.3 (dd, J = 21.5, 17.6 Hz), 38.5, 21.6; ^{19}F NMR (377 MHz, $CDCl_3$) δ −88.33 (d, J = 37.2 Hz, 1F), −89.25 (d, J = 37.2 Hz, 1F); EI-MS (m/z, relative intensity) 272 (M^+, 16), 257 (2), 228 (5), 105 (100); HRMS (EI) calcd for $C_{17}H_{14}O_1F_2$ $[M]^+$ 272.1007, found 272.1004.

*4,4-Difluoro-1-phenyl-2-(m-tolyl)but-3-en-1-one (**3e**).* Colorless oil (46.2 mg, 85% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 7.7 Hz, 2H), 7.56 (t, J = 7.3 Hz, 1H), 7.45 (t, J = 7.6 Hz, 2H), 7.21 (t, J = 6.1 Hz, 3H), 7.16 (d, J = 5.7 Hz, 1H), 3.98 (s, 2H), 2.34 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.4 (t, J = 2.7 Hz), 153.9 (dd, J = 289.7, 287.7 Hz), 137.1, 136.5, 133.5, 132.8 (dd, J = 4.6, 1.7 Hz), 130.5, 129.8 (d, J = 3.2 Hz), 128.8, 128.3, 128.2, 126.0, 85.9 (t, J = 22.1 Hz), 39.5 (d, J = 2.4 Hz), 19.6 (d, J = 2.2 Hz); ^{19}F NMR (377 MHz, $CDCl_3$) δ −87.46 (d, J = 37.9 Hz, 1F), −90.91 (d, J = 37.9 Hz, 1F); EI-MS (m/z, relative intensity) 272 (M^+, 3), 206 (9), 105 (100); HRMS (EI) calcd for $C_{17}H_{14}O_1F_2$ $[M]^+$ 272.1007, found 272.1003.

*3-(4-(tert-Butyl)phenyl)-4,4-difluoro-1-phenylbut-3-en-1-one (**3f**).* Colorless oil (50.8 mg, 81% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 7.7 Hz, 2H), 7.59 (t, J = 7.3 Hz, 1H), 7.48 (t, J = 7.7 Hz, 2H), 7.34 (d, J = 8.3 Hz, 2H), 7.25 (d, J = 7.5 Hz, 2H), 4.06 (s, 2H), 1.29 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.6 (t, J = 2.8 Hz), 154.9 (dd, J = 292.4, 287.8 Hz), 150.5, 136.5, 133.5, 128.9, 128.3, 127.7 (t, J = 3.4 Hz), 125.6, 87.0 (dd, J = 21.6, 17.2 Hz), 38.4 (d, J = 2.3 Hz), 34.6, 31.4; ^{19}F NMR (377 MHz, $CDCl_3$) δ −88.34 (d, J = 37.6 Hz, 1F), −89.25 (d, J = 37.6 Hz, 1F); EI-MS (m/z, relative intensity) 314 (M^+, 4), 299 (3), 255 (6), 105 (100); HRMS (EI) calcd for $C_{20}H_{20}O_1F_2$ $[M]^+$ 314.1477, found 314.1472.

*4,4-Difluoro-3-(4-methoxyphenyl)-1-phenylbut-3-en-1-one (**3g**).* Colorless oil (34.0 mg, 59% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 7.5 Hz, 2H), 7.59 (t, J = 7.3 Hz, 1H), 7.47 (t, J = 7.6 Hz, 2H), 7.24 (d, J = 8.4 Hz, 2H), 6.86 (d, J = 8.7 Hz, 2H), 4.03 (s, 2H), 3.78 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.7 (t, J = 2.5 Hz), 158.9, 154.7 (dd, J = 291.1, 287.6 Hz), 136.4, 133.6, 129.3 (t, J = 3.3 Hz), 128.9, 128.3, 125.7 (t, J = 3.7 Hz), 114.1, 86.8 (dd, J = 21.6, 17.7 Hz), 55.4, 38.6 (d, J = 2.4 Hz); ^{19}F NMR (377 MHz, $CDCl_3$) δ

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−89.28 (d, J = 39.5 Hz, 1F), −90.10 (d, J = 39.5 Hz, 1F); EI-MS (m/z, relative intensity) 288 (M^+, 14), 257 (5), 105 (100), 77 (38); HRMS (EI) calcd for $C_{17}H_{14}O_2F_2$ $[M]^+$ 288.0952, found 288.0956.

3-(4-Bromophenyl)-4,4-difluoro-1-phenylbut-3-en-1-one (**3h**). Colorless oil (44.5 mg, 66% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 7.4 Hz, 2H), 7.60 (t, J = 7.4 Hz, 1H), 7.50−7.44 (m, 4H), 7.19 (d, J = 8.0 Hz, 2H), 4.05 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.3 (t, J = 2.7 Hz), 154.8 (dd, J = 293.1, 288.9 Hz), 136.2, 133.8, 132.5 (t, J = 4.1 Hz), 131.8, 129.8 (t, J = 3.4 Hz), 128.9, 128.3, 121.6, 86.7 (dd, J = 22.7, 17.4 Hz), 38.2 (d, J = 2.2 Hz); ^{19}F NMR (377 MHz, $CDCl_3$) δ −87.27 (d, J = 35.0 Hz, 1F), −88.15 (d, J = 34.9 Hz, 1F); EI-MS (m/z, relative intensity) 338 (^{81}Br, M^+, 4), 336 (^{79}Br, M^+, 4), 105 (100), 77 (32); HRMS (EI) calcd for $C_{16}H_{11}O_1F_2Br_1[M]^+$ 335.9956, found 335.9950.

3-([1,1′-Biphenyl]-4-yl)-4,4-difluoro-1-phenylbut-3-en-1-one (**3i**). White solid (41.4 mg, 62% yield), mp 81−82 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04−7.97 (m, 2H), 7.57 (ddd, J = 8.4, 7.6, 6.0 Hz, 5H), 7.49 (t, J = 7.6 Hz, 2H), 7.42 (dd, J = 15.4, 7.6 Hz, 4H), 7.34 (t, J = 7.3 Hz, 1H), 4.11 (t, J = 2.0 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.5, 154.9 (dd, J = 292.7, 288.5 Hz), 140.6, 140.4, 136.4, 133.6, 132.5, 128.9, 128.4, 128.3, 127.5, 127.3, 127.2, 87.1 (dd, J = 21.9, 17.2 Hz), 38.4; ^{19}F NMR (377 MHz, $CDCl_3$) δ −87.53 (d, J = 35.9 Hz, 1F), −88.49 (d, J = 36.0 Hz, 1F); EI-MS (m/z, relative intensity) 334 (M^+, 9), 272 (8), 149 (74), 119 (100); HRMS (EI) calcd for $C_{22}H_{16}O_1F_2$ $[M]^+$ 334.1164, found 334.1160.

4,4-Difluoro-1-phenyl-3-(thiophen-3-yl)but-3-en-1-one (**3j**). Yellow oil (29.0 mg, 55% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 7.8 Hz, 2H), 7.61 (t, J = 7.3 Hz, 1H), 7.50 (t, J = 7.6 Hz, 2H), 7.31−7.27 (m, 1H), 7.14 (d, J = 3.1 Hz, 2H), 4.06 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.6 (t, J = 2.6 Hz), 155.1 (dd, J = 294.3, 287.3 Hz), 136.4, 133.7, 128.9, 128.3, 126.9 (dd, J = 6.4, 2.1 Hz), 125.9, 122.2 (t, J = 5.4 Hz), 83.9 (dd, J = 24.0, 17.0 Hz), 37.9 (d, J = 2.8 Hz); ^{19}F NMR (377 MHz, $CDCl_3$) δ −85.19 (d, J = 35.5 Hz, 1F), −89.34 (d, J = 35.5 Hz, 1F); EI-MS (m/z, relative intensity) 264 (M^+, 17), 105 (100), 77 (34); HRMS (EI) calcd for $C_{14}H_{10}O_1F_2S_1$ $[M]^+$ 264.0415, found 264.0412.

3-(Difluoromethylene)-1,5-diphenylpent-4-yn-1-one (**3k**). Yellow oil (29.3 mg, 52% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 7.9 Hz, 2H), 7.61 (t, J = 7.4 Hz, 1H), 7.50 (t, J = 7.6 Hz, 2H), 7.39−7.37 (m, 2H), 7.29 (d, J = 5.0 Hz, 3H), 3.85 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.4, 159.9 (dd, J = 297.6, 294.6 Hz), 136.3, 133.7, 131.6, 128.9, 128.6, 128.5, 128.4, 122.8, 93.9 (dd, J = 6.9, 4.9 Hz), 80.7 (dd, J = 7.7, 4.7 Hz), 73.8 (dd, J = 34.8, 20.3 Hz), 37.7; ^{19}F NMR (377 MHz, $CDCl_3$) δ −77.68 (d, J = 10.4 Hz, 1F), −82.58 (d, J = 10.4 Hz, 1F); EI-MS (m/z, relative intensity) 282 (M^+, 11), 105 (100), 77 (41); HRMS (EI) calcd for $C_{18}H_{12}O_1F_2$ $[M]^+$ 282.0851, found 282.0852.

3-(Difluoromethylene)-1-phenylnon-4-yn-1-one (**3l**). Yellow oil (31.9 mg, 61% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98−7.96 (m, 2H), 7.59 (t, J = 7.1 Hz, 1H), 7.48 (t, J = 7.5 Hz, 2H), 3.71 (s, 2H), 2.26 (t, J = 7.0 Hz, 2H), 1.51−1.41 (m, 2H), 1.35 (td, J = 14.0, 6.8 Hz, 2H), 0.87 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.8, 160.0 (dd, J = 295.4, 292.7 Hz), 136.4, 133.6, 128.8, 128.4, 95.4 (t, J = 5.7 Hz), 73.7 (dd, J = 34.3, 20.8 Hz), 71.7 (dd, J = 7.6, 3.9 Hz), 37.9, 30.6, 22.0, 19.2, 13.7; ^{19}F NMR (377 MHz, $CDCl_3$) δ −80.56 (d, J = 16.8 Hz, 1F), −85.09 (d, J = 16.8 Hz, 1F); EI-MS (m/z, relative intensity) 262 (M^+, 4), 251 (2), 238 (3), 220 (1), 105 (100); HRMS (EI) calcd for $C_{16}H_{16}O_1F_2$ $[M]^+$ 262.1164, found 262.1161.

(8S,9R,13S,14R)-2-(1,1-Difluoro-4-oxo-4-phenylbut-1-en-2-yl)-13-methyl-7,8,9,11,12,13,15,16-octahydro-6H-cyclopenta[a]phenanthren-17(14H)-one (**3m**). Yellow solid (43.4 mg, 50% yield), mp 135−137 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 7.8 Hz, 2H), 7.59 (t, J = 7.3 Hz, 1H), 7.48 (t, J = 7.6 Hz, 2H), 7.25 (d, J = 9.5 Hz, 1H), 7.11−7.07 (m, 2H), 4.05 (s, 2H), 2.88 (dd, J = 8.6, 3.7 Hz, 2H), 2.50 (dd, J = 18.8, 8.7 Hz, 1H), 2.39 (d, J = 11.7 Hz, 1H), 2.28 (d, J = 10.3 Hz, 1H), 2.21−1.92 (m, 5H), 1.71−1.38 (m, 9H), 0.90 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.5 (t, J = 2.4 Hz), 192.3, 154.8 (dd, J = 292.0, 287.8 Hz), 139.2, 136.7, 136.4, 133.5, 131.0 (t, J = 3.9 Hz), 128.8, 128.6 (t, J = 3.2 Hz), 128.3, 125.6, 125.4 (t, J = 3.2 Hz), 87.0 (dd, J = 21.4, 17.5 Hz), 50.6, 48.1, 44.4, 38.4 (d, J = 2.3 Hz), 38.1, 36.0, 31.7, 29.5, 26.5, 25.7, 21.7, 13.9; ^{19}F NMR (377 MHz, $CDCl_3$) δ −88.39 (d, J = 37.7 Hz, 1F), −89.27 (d, J = 37.7 Hz, 1F); EI-MS (m/z, relative intensity) 434 (M^+, 17), 104 (100), 77 (20); HRMS (EI) calcd for $C_{28}H_{28}O_2F_2$ $[M]^+$ 434.2052, found 434.2056.

4,4-Difluoro-3-phenyl-1-(p-tolyl)but-3-en-1-one (**3n**). Colorless oil (49.5 mg, 91% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8.1 Hz, 2H), 7.32 (d, J = 4.4 Hz, 4H), 7.26 (t, J = 7.7 Hz, 3H), 4.04 (s, 2H), 2.42 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.1 (t, J = 2.7 Hz), 154.9 (dd, J = 292.3, 287.9 Hz), 144.5, 134.0, 133.7 (t, J = 4.0 Hz), 129.5, 128.6, 128.4, 128.1 (t, J = 3.3 Hz), 127.5, 87.4 (dd, J = 21.8, 17.3 Hz), 38.3 (d, J = 2.3 Hz), 21.8; ^{19}F NMR (377 MHz, $CDCl_3$) δ −88.23 (d, J = 37.0 Hz, 1F), −89.23 (d, J = 36.9 Hz, 1F); EI-MS (m/z, relative intensity) 272 (M^+, 12), 119 (100), 91 (37); HRMS (EI) calcd for $C_{17}H_{14}O_1F_2$ $[M]^+$ 272.1007, found 272.1009.

4,4-Difluoro-3-phenyl-1-(m-tolyl)but-3-en-1-one (**3o**). Colorless oil (44.1 mg, 81% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 6.4 Hz, 2H), 7.39 (dd, J = 12.5, 7.7 Hz, 2H), 7.32 (d, J = 4.1 Hz, 4H), 7.25 (dd, J = 8.6, 4.2 Hz, 1H), 4.06 (s, 2H), 2.41 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.6 (t, J = 2.7 Hz), 154.9 (dd, J = 292.5, 288.1 Hz), 138.7, 136.5, 134.3, 133.7 (t, J = 4.0 Hz), 128.9, 128.7, 128.6, 128.1 (t, J = 3.3 Hz), 127.6, 125.5, 87.4 (dd, J = 21.8, 17.4 Hz), 38.5 (d, J = 2.4 Hz), 21.5; ^{19}F NMR (377 MHz, $CDCl_3$) δ −88.20 (d, J = 36.8 Hz, 1F), −89.17 (d, J = 36.8 Hz, 1F); EI-MS (m/z, relative intensity) 272 (M^+, 18), 119 (100), 91 (44); HRMS (EI) calcd for $C_{17}H_{14}O_1F_2$ $[M]^+$ 272.1007, found 272.1004.

4,4-Difluoro-3-phenyl-1-(m-tolyl)but-3-en-1-one (**3p**). Colorless oil (46.2 mg, 85% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J = 7.6 Hz, 1H), 7.38 (t, J = 7.5 Hz, 1H), 7.36−7.31 (m, 2H), 7.30−7.21 (m, 5H), 3.98 (s, 2H), 2.35 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.7 (t, J = 2.5 Hz), 154.9 (dd, J = 292.7, 288.0 Hz), 138.6, 137.2, 133.4 (t, J = 3.9 Hz), 132.2, 131.7, 128.6, 128.3, 128.1 (t, J = 3.3 Hz), 127.6, 125.8, 87.7 (dd, J = 21.9, 17.1 Hz), 41.1 (d, J = 2.0 Hz), 21.1; ^{19}F NMR (377 MHz, $CDCl_3$) δ −88.26 (d, J = 36.6 Hz, 1F), −89.53 (d, J = 36.6 Hz, 1F); EI-MS (m/z, relative intensity) 272 (M^+, 4), 206 (10), 119 (100), 91 (29); HRMS (EI) calcd for $C_{17}H_{14}O_1F_2$ $[M]^+$ 272.1007, found 272.1005.

4,4-Difluoro-1-(4-methoxyphenyl)-3-phenylbut-3-en-1-one (**3q**). Colorless oil (47.8 mg, 83% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 8.7 Hz, 2H), 7.32 (d, J = 4.3 Hz, 4H), 7.25 (dd, J = 7.7, 3.2 Hz, 1H), 6.95 (d, J = 8.7 Hz, 2H), 4.02 (s, 2H), 3.87 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.0 (d, J = 2.4 Hz), 163.9, 154.8 (dd, J = 292.2, 287.8 Hz), 133.7 (t, J = 3.9 Hz), 130.6, 129.5, 128.6, 128.1 (t, J = 3.3 Hz), 127.5, 114.0, 87.5 (dd, J = 21.8, 17.2 Hz), 55.6, 38.1 (d, J = 2.2 Hz); ^{19}F NMR (377 MHz, $CDCl_3$) δ −88.33 (d, J = 37.1 Hz, 1F), −89.33 (d, J = 37.2 Hz, 1F); EI-MS (m/z, relative intensity) 288 (M^+, 9), 135 (100); HRMS (EI) calcd for $C_{17}H_{14}O_2F_2$ $[M]^+$ 288.0952, found 288.0956.

1-(4-Bromophenyl)-4,4-difluoro-3-phenylbut-3-en-1-one (**3r**). Colorless oil (40.3 mg, 60% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.5 Hz, 2H), 7.62 (d, J = 8.5 Hz, 2H), 7.36−7.29 (m, 4H), 7.28−7.26 (m, 1H), 4.02 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.5, 154.9 (dd, J = 292.6, 288.2 Hz), 135.1, 133.4, 132.2, 129.8, 128.8, 128.7, 128.1, 127.7, 87.2 (dd, J = 21.5, 17.9 Hz), 38.5; ^{19}F NMR (377 MHz, $CDCl_3$) δ −87.89 (d, J = 36.1 Hz, 1F), −88.88 (d, J = 36.1 Hz, 1F); EI-MS (m/z, relative intensity) 338 (^{81}Br, M^+, 5), 336 (^{79}Br, M^+, 5), 185 (100), 183 (99), 157 (26), 155 (25); HRMS (EI) calcd for $C_{16}H_{11}O_1F_2Br_1$ $[M]^+$ 335.9956, found 335.9951.

4,4-Difluoro-3-phenyl-1-(thiophen-2-yl)but-3-en-1-one (**3s**). Yellow oil (41.7 mg, 79% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 3.7 Hz, 1H), 7.66 (d, J = 4.9 Hz, 1H), 7.33 (d, J = 4.4 Hz, 4H), 7.29−7.23 (m, 1H), 7.14 (t, J = 4.4 Hz, 1H), 3.99 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.3 (t, J = 2.5 Hz), 154.9 (dd, J = 292.6, 288.5 Hz), 143.2, 134.2, 132.2, 128.5, 128.2, 128.0 (t, J = 3.3 Hz), 127.6, 87.1 (dd, J = 21.7, 17.7 Hz), 38.9 (d, J = 2.4 Hz); ^{19}F NMR (377 MHz, $CDCl_3$) δ −87.83 (d, J = 35.6 Hz, 1F), −88.84 (d, J = 35.7 Hz, 1F); HRMS (EI) calcd for $C_{14}H_{10}O_1F_2S_1$ $[M]^+$ 264.0415, found 264.0417.

5,5-Difluoro-4-phenylpent-4-en-2-one (**3t**). Colorless oil (29.0 mg, 74% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38−7.32 (m, 2H), 7.28 (dd, J = 11.8, 5.0 Hz, 3H), 3.46 (s, 2H), 2.17 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.6 (t, J = 2.7 Hz), 154.9 (dd, J = 293.5, 288.3 Hz), 133.2 (t, J = 4.0 Hz), 128.8, 127.9 (t, J = 3.5 Hz), 127.7, 87.4 (dd, J =

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22.1, 16.7 Hz), 43.1 (d, J = 1.8 Hz), 29.4; ^{19}F NMR (377 MHz, $CDCl_3$) δ −87.78 (d, J = 35.8 Hz, 1F), −89.10 (d, J = 35.7 Hz, 1F); EI-MS (m/z, relative intensity) 196 (M^+, 8), 180 (7), 167 (41), 149 (100); HRMS (EI) calcd for $C_{11}H_{10}O_1F_2$ $[M]^+$ 196.0694, found 196.0696.

*6,6-Difluoro-5-phenylhex-5-en-3-one (**3u**).* Colorless oil (29.8 mg, 71% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40−7.22 (m, 5H), 3.45 (s, 2H), 2.47 (q, J = 7.3 Hz, 2H), 1.04 (t, J = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.2 (d, J = 2.9 Hz), 154.9 (dd, J = 293.0, 288.1 Hz), 133.4 (t, J = 3.9 Hz), 128.7, 128.0 (t, J = 3.5 Hz), 127.7, 87.4 (dd, J = 22.0, 16.5 Hz), 42.0 (d, J = 1.8 Hz), 35.4, 7.8; ^{19}F NMR (377 MHz, $CDCl_3$) δ −88.07 (d, J = 36.3 Hz, 1F), −89.29 (d, J = 36.3 Hz, 1F); EI-MS (m/z, relative intensity) 210 (M^+, 23), 199 (25), 181 (14), 133 (9), 57 (100); HRMS (EI) calcd for $C_{12}H_{12}O_1F_2$ $[M]^+$ 210.0852, found 210.0851.

*N,N-Diethyl-4,4-difluoro-3-phenylbut-3-enamide (**3v**).* Colorless oil (36.4 mg, 72% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, J = 4.3 Hz, 4H), 7.25 (dd, J = 8.1, 4.0 Hz, 1H), 3.39 (s, 2H), 3.32 (dt, J = 14.1, 7.0 Hz, 4H), 1.18 (t, J = 7.1 Hz, 3H), 1.06 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.1 (t, J = 2.8 Hz), 154.7 (dd, J = 291.1, 287.8 Hz), 133.8 (t, J = 3.8 Hz), 128.5, 128.3 (t, J = 3.1 Hz), 127.5, 88.3 (dd, J = 21.3, 17.5 Hz), 42.1, 40.6, 33.2 (d, J = 2.5 Hz), 14.4, 13.0; ^{19}F NMR (377 MHz, $CDCl_3$) δ −89.39 (d, J = 38.6 Hz, 1F), −90.14 (d, J = 38.6 Hz, 1F); EI-MS (m/z, relative intensity) 253 (M^+, 72), 224 (9), 188 (7), 133 (21), 100 (100), 72 (74); HRMS (EI) calcd for $C_{14}H_{17}O_1N_1F_2$ $[M]^+$ 253.1273, found 253.1270.

*4,4-Difluoro-3-phenyl-1-(piperidin-1-yl)but-3-en-1-one (**3w**).* Colorless oil (39.7 mg, 75% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, J = 6.5 Hz, 4H), 7.27 (dd, J = 11.7, 5.0 Hz, 1H), 3.54−3.47 (m, 2H), 3.39 (d, J = 8.8 Hz, 4H), 1.65−1.58 (m, 2H), 1.51 (dd, J = 11.0, 5.1 Hz, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 154.6 (t, J = 8.1 Hz), 133.7 (t, J = 4.0 Hz), 128.6, 128.3 (d, J = 3.1 Hz), 127.6, 88.3 (dd, J = 20.8, 17.1 Hz), 46.9, 43.2, 33.3, 26.5, 25.6, 24.6; ^{19}F NMR (377 MHz, $CDCl_3$) δ −89.15 (1F, d, J = 38.4 Hz, 1F), −90.08 (1F, d, J = 38.5 Hz, 1F); EI-MS (m/z, relative intensity) 265 (M^+, 100), 188 (12), 149 (34), 112 (87); HRMS (EI) calcd for $C_{15}H_{17}O_1N_1F_2$ $[M]^+$ 265.1273, found 265.1277.

*N-Benzyl-4,4-difluoro-3-phenylbut-3-enamide (**3x**).* Colorless oil (39.0 mg, 68% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, J = 4.2 Hz, 4H), 7.32 (dd, J = 8.2, 4.3 Hz, 1H), 7.24 (d, J = 4.9 Hz, 3H), 7.09−6.99 (m, 2H), 6.03 (br, 1H), 4.37 (d, J = 5.7 Hz, 2H), 3.37 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.8 (t, J = 2.9 Hz), 154.8 (dd, J = 294.5, 289.4 Hz), 137.8, 132.5 (t, J = 3.8 Hz), 130.9, 128.8, 128.6, 127.8, 127.8 (d, J = 3.9 Hz), 127.4, 87.7 (dd, J = 21.0, 15.8 Hz), 43.6, 35.7; ^{19}F NMR (377 MHz, $CDCl_3$) δ −86.80 (d, J = 33.8 Hz, 1F), −87.52 (d, J = 33.8 Hz, 1F); EI-MS (m/z, relative intensity) 287 (M^+, 12), 149 (21), 119 (19), 105 (36), 91 (100), 77 (19); HRMS (EI) calcd for $C_{17}H_{15}O_1N_1F_2$ $[M]^+$ 287.1116, found 287.1111.

*5,5-Difluoro-3-methyl-4-phenylpent-4-en-2-one (**3y**).* Colorless oil (20.1 mg, 48% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38−7.30 (m, 3H), 7.20 (d, J = 7.6 Hz, 2H), 3.54 (q, J = 7.0 Hz, 1H), 2.24 (s, 3H), 1.22 (d, J = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.2, 154.4 (d, J = 291.4 Hz), 132.1, 128.9, 128.7, 128.1, 93.4 (dd, J = 19.5, 15.7 Hz), 47.2, 28.1, 14.2; ^{19}F NMR (377 MHz, $CDCl_3$) δ −88.42 (d, J = 37.5 Hz, 1F), −88.80 (d, J = 37.5 Hz, 1F); EI-MS (m/z, relative intensity) 210 (M^+, 28), 195 (100), 167 (19), 147 (13), 127 (56); HRMS (EI) calcd for $C_{12}H_{12}O_1F_2$ $[M]^+$ 210.0856, found 210.0850.

*Methyl 4-(1,1,1-Trifluoro-4-oxo-4-phenylbutan-2-yl)benzoate (**4a**).* Yellow oil (2,6-lutidine as the base, 26.1 mg, 47%) ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 8.2 Hz, 2H), 7.91 (d, J = 7.6 Hz, 2H), 7.58 (t, J = 7.4 Hz, 1H), 7.46 (dd, J = 13.0, 7.6 Hz, 4H), 4.31 (pd, J = 9.4, 3.9 Hz, 1H), 3.89 (s, 3H), 3.73 (dd, J = 17.9, 9.4 Hz, 1H), 3.63 (dd, J = 17.9, 3.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.1, 166.7, 139.7, 136.2, 133.9, 130.3, 130.1, 129.3, 128.9, 128.9 (q, J = 279.7 Hz), 128.2, 52.3, 45.0 (q, J = 27.7 Hz), 38.3; ^{19}F NMR (377 MHz, $CDCl_3$) δ −69.34 (s, 3F); EI-MS (m/z, relative intensity) 336 (M^+, 1), 316 (34), 105 (100), 77 (34); HRMS (EI) calcd for $C_{18}H_{15}O_3F_3$ $[M]^+$ 336.0968, found 336.0973.

*Typical Procedure for the Synthesis of 1,1-Difluorohomoallylic Amine **6a**.* A 10 mL test tube equipped with a magnetic stir bar was charged with Boc-glycine **5a** (0.3 mmol, 50.0 mg), **2b** (0.2 mmol, 34.4 mg), $[Ir(dFCF_3ppy)_2dtbbpy]PF_6$ (2 mol %, 4.0 mg), Li_2CO_3 (0.3 mmol, 33.3 mg), and 1 mL of DMSO. The solution was stirred at room temperature with the irradiation of a 5 W blue LED under N_2. After completion of reaction, the resulting solution was quenched with 10 mL of H_2O. The reaction mixture was extracted with ethyl acetate (10 mL × 3), washed with brine, and then dried over anhydrous Na_2SO_4. After the solvent was evaporated, the crude product was purified by column chromatography (hexane/ethyl acetate = 60:1) to give pure product **6a** as a white solid (39.6 mg, 70% yield), mp 52−53 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38−7.31 (m, 4H), 7.29−7.25 (m, 1H), 4.59 (s, 1H), 3.15 (d, J = 5.7 Hz, 2H), 2.60 (t, J = 5.9 Hz, 2H), 1.42 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.9, 154.4 (dd, J = 291.6, 287.6 Hz), 133.2, 128.7, 128.3, 127.6, 90.1 (dd, J = 21.4, 13.6 Hz), 79.4, 38.9, 28.5, 28.5. ^{19}F NMR (377 MHz, $CDCl_3$) δ −89.87 (d, J = 40.9 Hz, 1F), −90.53 (d, J = 40.9 Hz, 1F). HRMS (ESI) calcd for $C_{15}H_{19}F_2N_1Na_1O_2$ $[M + Na]^+$ 306.1276, found 306.1272.

*tert-Butyl (5,5-Difluoro-4-phenylpent-4-en-2-yl)carbamate (**6b**).* White solid (52.8 mg, 89% yield), mp 55−56 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38−7.32 (m, 4H), 7.28−7.26 (m, 1H), 4.28 (s, 1H), 3.69 (s, 1H), 2.66−2.60 (m, 1H), 2.47−2.44 (m, 1H), 1.40 (s, 9H), 1.09 (d, J = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.1, 154.6 (t, J = 288.2 Hz), 133.5, 128.7, 128.4 (t, J = 2.8 Hz), 127.6, 90.1 (dd, J = 19.5, 16.5 Hz), 79.2, 45.4, 35.2, 28.5, 20.6; ^{19}F NMR (377 MHz, $CDCl_3$) δ −90.58 (d, J = 42.7 Hz, 1F), −90.73 (d, J = 42.0 Hz, 1F). HRMS (ESI) calcd for $C_{16}H_{21}F_2N_1Na_1O_2$ $[M + Na]^+$ 320.1433, found 320.1434.

*tert-Butyl (6,6-Difluoro-2-methyl-5-phenylhex-5-en-3-yl)-carbamate (**6c**).* White solid (55.2 mg, 85% yield), mp 65−66 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37−7.26 (m, 5H), 4.23 (d, J = 9.3 Hz, 1H), 3.49−3.46 (m, 1H), 2.52−2.41 (m, 2H), 1.74−1.70 (m, 1H), 1.41 (s, 9H), 0.86 (t, J = 6.6 Hz, 6H). At room temperature (RT), this compound appears as an ∼4:1 mixture of rotamers.[23] Peaks corresponding to the minor rotamer are present at δ 4.07 (s, 1H), 3.36 (s, 1H), and 1.32 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.7, 154.4 (dd, J = 290.2, 286.5 Hz), 133.6 (t, J = 3.2 Hz), 128.6, 128.6, 127.6, 90.4 (dd, J = 21.2, 14.7 Hz), 79.0, 54.1, 31.8, 31.6, 28.5, 19.4, 17.4; ^{19}F NMR (377 MHz, $CDCl_3$) δ −90.92 (d, J = 43.3 Hz, 1F), −91.70 (d, J = 43.3 Hz, 1F). Peaks corresponding to the minor rotamer are present at δ −90.25 (d, J = 42.4 Hz, 1F) and −90.87 (d, J = 42.3 Hz, 1F). HRMS (ESI) calcd for $C_{18}H_{25}F_2N_1Na_1O_2$ $[M + Na]^+$ 348.1746, found 348.1750.

*tert-Butyl (6,6-Difluoro-2,2-dimethyl-5-phenylhex-5-en-3-yl)-carbamate (**6d**).* White solid (57.6 mg, 85% yield), mp 67−68 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36−7.32 (m, 2H), 7.29−7.24 (m, 3H), 4.20 (d, J = 10.5 Hz, 1H), 3.40 (t, J = 10.6 Hz, 1H), 3.28 (t, J = 11.0 Hz, 1H), 2.59 (d, J = 13.8 Hz, 1H), 2.26 (t, J = 13.0 Hz, 1H), 1.41 (s, 9H), 0.88 (s, 9H). At RT, this compound appears as an ∼4:1 mixture of rotamers. Peaks corresponding to the minor rotamer are present at δ 4.05 (d, J = 10.4 Hz, 1H), 3.28 (t, J = 11.0 Hz, 1H), and 1.27 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.8, 154.4 (dd, J = 290.0, 285.8 Hz), 133.8 (dd, J = 4.2, 2.7 Hz), 128.7 (t, J = 2.6 Hz), 128.5, 127.5, 90.8 (dd, J = 21.3, 14.9 Hz), 78.9, 57.6, 34.7, 29.9, 28.5, 26.4. Peaks corresponding to the minor rotamer are present at δ 156.0, 128.4 (t, J = 3.0 Hz), 127.4, 79.6, 58.2, 35.1, 28.9, 28.2, and 26.3; ^{19}F NMR (377 MHz, $CDCl_3$) δ −91.26 (d, J = 44.3 Hz, 1F), −92.41 (d, J = 44.3 Hz, 1F). Peaks corresponding to the minor rotamer are present at δ −90.25 (d, J = 43.2 Hz, 1F), −91.10 (d, J = 43.2 Hz, 1F). HRMS (ESI) calcd for $C_{19}H_{27}F_2N_1Na_1O_2$ $[M + Na]^+$ 362.1902, found 362.1916.

*tert-Butyl (4,4-Difluoro-1,3-diphenylbut-3-en-1-yl)carbamate (**6e**).* White solid (43.8 mg, 65% yield), mp 93.2−93.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (t, J = 7.3 Hz, 2H), 7.32−7.23 (m, 6H), 7.18 (d, J = 7.4 Hz, 2H), 4.77 (s, 1H), 4.63 (s, 1H), 2.91 (s, 1H), 2.77 (dd, J = 14.1, 6.3 Hz, 1H), 1.40 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.1, 154.5 (t, J = 289.2 Hz), 141.7, 133.0, 128.7, 128.6 (t, J = 2.8 Hz), 127.7, 127.7, 126.4, 89.9 (t, J = 18.4 Hz), 79.6, 53.5, 35.5, 28.4; ^{19}F NMR (377 MHz, $CDCl_3$) δ −90.63 (s, 2F). HRMS (ESI) calcd for $C_{19}H_{26}F_2N_1O_2$ $[M + H]^+$ 338.1926, found 338.1930.

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*tert-Butyl (5,5-Difluoro-1,4-diphenylpent-4-en-2-yl)carbamate (**6f**).* White solid (67.1 mg, 90% yield), mp 116−117 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (t, J = 7.3 Hz, 2H), 7.29−7.19 (m, 6H), 7.09 (d, J = 7.0 Hz, 2H), 4.29 (s, 1H), 3.82−3.67 (m, 1H), 2.77 (d, J = 5.7 Hz, 2H), 2.55 (d, J = 6.3 Hz, 2H), 1.37 (s, 9H). At RT, this compound appears as an ∼4:1 mixture of rotamers. Peaks corresponding to the minor rotamer are present at δ 4.15−4.10 (m, 1H) and 3.67 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.2, 154.4 (dd, J = 290.9, 287.0 Hz), 137.9, 133.2, 129.4, 128.7, 128.5, 128.5 (t, J = 3.1 Hz), 127.6, 126.6, 90.1 (dd, J = 20.9, 14.1 Hz), 79.3, 50.5, 40.9, 32.9, 28.4; ^{19}F NMR (377 MHz, $CDCl_3$) δ −90.29 (d, J = 41.6 Hz, 1F), −90.70 (d, J = 41.5 Hz, 1F). Peaks corresponding to the minor rotamer are present at δ −89.88 (d, J = 39.9 Hz, 1F) and −90.39 (d, J = 40.1 Hz, 1F). HRMS (ESI) calcd for $C_{22}H_{25}F_2N_1Na_1O_2$ $[M + Na]^+$ 396.1746, found 396.1750.

*tert-Butyl (5,5-Difluoro-1-hydroxy-4-phenylpent-4-en-2-yl)-carbamate (**6g**).* White solid (55.1 mg, 88% yield), mp 69−70 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38−7.32 (m, 4H), 7.29−7.26 (m, 1H), 4.73 (s, 1H), 3.59−3.55 (m, 3H), 2.69−2.57 (m, 2H), 2.47 (s, 1H), 1.41 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.1, 154.5 (dd, J = 291.1, 287.9 Hz), 133.1 (t, J = 3.1 Hz), 128.8, 128.4 (t, J = 2.7 Hz), 127.8, 89.7 (dd, J = 20.9, 15.3 Hz), 79.8, 64.8, 51.3, 29.9, 28.4; ^{19}F NMR (377 MHz, $CDCl_3$), −89.83 (d, J = 40.8 Hz, 1F), −90.32 (d, J = 40.7 Hz, 1F). HRMS (ESI) calcd for $C_{16}H_{21}F_2N_1Na_1O_3$ $[M + Na]^+$ 336.1382, found 336.1386.

*tert-Butyl (6,6-Difluoro-1-(methylthio)-5-phenylhex-5-en-3-yl)-carbamate (**6h**).* White solid (60.7 mg, 85% yield), mp 83−85 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38−7.25 (m, 5H), 4.29 (d, 1H), 3.67−3.56 (m, 1H), 2.63−2.47 (m, 3H), 2.41 (ddd, J = 13.0, 9.3, 6.7 Hz, 1H), 2.03 (s, 3H), 1.77−1.72 (m, 1H), 1.65−1.53 (m, 1H), 1.40 (s, 9H). At RT, this compound appears as an ∼4:1 mixture of rotamers. Peaks corresponding to the minor rotamer are present at δ 4.13 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.4, 154.5 (dd, J = 291.1, 287.5 Hz), 133.4, 128.7, 128.5, 127.7, 89.9 (dd, J = 21.0, 15.4 Hz), 79.4, 49.2, 34.5, 33.8, 30.7, 28.4, 15.7; ^{19}F NMR (377 MHz, $CDCl_3$) δ −90.31 (d, J = 41.2 Hz, 1F), −90.57 (d, J = 41.2 Hz, 1F). Peaks corresponding to the minor rotamer are present at δ −89.78 (d, J = 40.8 Hz) and −90.01 (d, J = 42.1 Hz). HRMS (ESI) calcd for $C_{18}H_{26}O_2N_1F_2S_1$ $[M + H]^+$ 358.1647, found 358.1648.

*tert-Butyl (5,5-Difluoro-1-(1H-indol-3-yl)-4-phenylpent-4-en-2-yl)carbamate (**6i**).* White solid (59.3 mg, 72% yield), mp 112−113 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.47 (s, 1H), 7.33−7.26 (m, 6H), 7.18 (t, J = 7.5 Hz, 1H), 7.08 (d, J = 6.8 Hz, 1H), 6.88 (s, 1H), 4.40−4.21 (m, 1H), 3.97 (s, 1H), 2.97−2.77 (m, 2H), 2.60 (d, J = 6.3 Hz, 2H), 1.40 (s, 9H). At RT, this compound appears as an ∼3.3:1 mixture of rotamers. Peaks corresponding to the minor rotamer are present at δ 4.21 (s, 1H) and 1.20 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.5, 154.4 (dd, J = 290.8, 287.1 Hz), 136.4, 133.4, 128.6, 128.5 (t, J = 2.4 Hz), 127.9, 127.6, 122.8, 122.1, 119.5, 119.0, 111.8, 111.2, 90.3 (dd, J = 21.0, 14.7 Hz), 79.2, 49.8, 33.1, 30.3, 28.5; ^{19}F NMR (377 MHz, $CDCl_3$) δ −90.37 (d, J = 41.8 Hz, 1F), −90.72 (d, J = 41.9 Hz, 1F). Peaks corresponding to the minor rotamer are present at δ −89.97 (d, J = 41.6 Hz, 1F) and −90.30 (d, J = 41.5 Hz, 1F). HRMS (ESI) calcd for $C_{24}H_{25}O_2N_2F_2$ $[M - H]^-$ 411.1890, found 411.1893.

*tert-Butyl 2-(3,3-Difluoro-2-phenylallyl)pyrrolidine-1-carboxylate (**6j**).* White solid (54.9 mg, 85% yield), mp 69−70 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41−7.26 (m, 5H), 3.74 (s, 1H), 3.35 (s, 2H), 2.86 (d, J = 12.1 Hz, 1H), 2.43−2.34 (m, 1H), 1.88−1.74 (m, 3H), 1.67−1.61 (m, 1H), 1.45 (s, 9H). At RT, this compound appears as an ∼1.8:1 mixture of rotamers. Peaks corresponding to the minor rotamer are present at δ 3.85 (s, 1H), 3.25(s, 2H), and 3.01 (d, J = 11.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.6 (t, J = 289.4 Hz), 154.5, 133.2, 128.6, 128.3 (t, J = 3.3 Hz), 127.5, 90.4 (dd, J = 20.4, 14.5 Hz), 79.6, 55.6, 46.4, 31.7, 29.6, 28.7, 22.8. Peaks corresponding to the minor rotamer are present at δ 79.0, 46.8, 30.8, 29.1, and 23.7; ^{19}F NMR (377 MHz, $CDCl_3$) δ −90.09 (d, J = 40.9 Hz, 1F), −90.24 (d, J = 40.8 Hz, 1F). Peaks corresponding to the minor rotamer are present at δ −90.45 (s, 2F). HRMS (ESI) calcd for $C_{18}H_{24}O_2N_1F_2$ $[M + H]^+$ 324.1770, found 324.1772.

*tert-Butyl 2-(3,3-Difluoro-2-phenylallyl)piperidine-1-carboxylate (**6k**).* White solid (57.3 mg, 91% yield), mp 72−74 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37−7.34 (m, 4H), 7.28−7.26 (m, 1H), 4.21 (s, 1H), 3.98 (d, J = 10.5 Hz, 1H), 2.76 (t, J = 13.2 Hz, 1H), 2.65 (s, 2H), 1.78−1.43 (m, 6H), 1.36 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.0, 154.4 (t, J = 289.1 Hz), 133.3, 128.6, 128.4 (t, J = 2.9 Hz), 127.5, 90.2 (t, J = 17.8 Hz), 79.4, 49.0, 39.0, 28.5, 28.0, 27.3, 25.5, 19.0; ^{19}F NMR (377 MHz, $CDCl_3$) δ −90.22 (s, 2F). HRMS (ESI) calcd for $C_{19}H_{26}F_2N_1O_2$ $[M + Na]^+$ 338.1926, found 338.1938.

*tert-Butyl (5,5-Difluoro-4-(4-methoxyphenyl)pent-4-en-2-yl)-carbamate (**6l**).* White solid (45.7 mg, 70% yield), mp 89−90 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, J = 8.4 Hz, 2H), 6.89 (d, J = 8.7 Hz, 2H), 4.28 (s, 1H), 3.80 (s, 3H), 3.67 (s, 1H), 2.63−2.57 (m, 1H), 2.40 (dd, J = 13.3, 6.3 Hz, 1H), 1.41 (s, 9H), 1.08 (d, J = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0, 155.2, 154.5 (dd, J = 289.0, 287.3 Hz), 129.6 (t, J = 2.9 Hz), 125.5, 114.2, 89.5 (dd, J = 20.8, 15.7 Hz), 79.2, 55.4, 45.3, 35.3, 28.5, 20.5; ^{19}F NMR (377 MHz, $CDCl_3$) δ −91.43 (d, J = 43.9 Hz, 1F), −91.66 (d, J = 44.2 Hz, 1F). HRMS (ESI) calcd for $C_{17}H_{23}F_2N_1Na_1O_3$ $[M + Na]^+$ 350.1538, found 350.1550.

*tert-Butyl (4-(4-Bromophenyl)-5,5-difluoropent-4-en-2-yl)-carbamate (**6m**).* White solid (58.5 mg, 78% yield), mp 75−76 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J = 8.4 Hz, 2H), 7.22 (d, J = 8.2 Hz, 2H), 4.27 (s, 1H), 3.66 (s, 1H), 2.62−2.57 (m, 1H), 2.44−2.40 (m, 1H), 1.40 (s, 9H), 1.08 (d, J = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.1, 154.5 (t, J = 289.8 Hz), 132.4, 131.9, 130.1 (t, J = 2.9 Hz), 121.6, 89.4 (t, J = 18.0b Hz), 79.4, 45.3, 35.1, 28.5, 20.5; ^{19}F NMR (377 MHz, $CDCl_3$) δ −89.63 (d, J = 39.8 Hz, 1F), −89.74 (d, J = 40.6 Hz, 1F). HRMS (ESI) calcd for $C_{16}H_{20}Br_1F_2N_1Na_1O_2$ $[M + Na]^+$ 398.0538, found 398.0551.

*Methyl 4-(4-((tert-Butoxycarbonyl)amino)-1,1-difluoropent-1-en-2-yl)benzoate (**6n**).* White solid (35.5 mg, 50% yield), mp 65−66 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 8.3 Hz, 2H), 7.43 (d, J = 8.1 Hz, 2H), 4.27 (s, 1H), 3.91 (s, 3H), 3.68 (s, 1H), 2.66 (ddd, J = 6.8, 5.5, 2.5 Hz, 1H), 2.51−2.47 (m, 1H), 1.39 (s, 9H), 1.09 (d, J = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 155.1, 154.8 (dd, J = 292.3, 289.3 Hz), 138.4, 130.0, 129.2, 128.4 (t, J = 2.9 Hz), 89.9 (dd, J = 21.1, 14.7 Hz), 79.4, 52.3, 45.4, 35.0, 28.5, 20.5; ^{19}F NMR (377 MHz, $CDCl_3$) δ −88.28 (d, J = 36.4 Hz, 1F), −88.43 (d, J = 36.2 Hz, 1F). HRMS (ESI) calcd for $C_{18}H_{23}F_2N_1Na_1O_4$ $[M + Na]^+$ 378.1487, found 378.1485.

*Methyl 2-(1-((tert-Butoxycarbonyl)amino)ethyl)-4,4-difluoro-3-phenylbut-3-enoate (**6o**).* White solid (52.2 mg, 70% yield), mp 72−73 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37−7.30 (m, 5H), 4.66 (s, 1H), 4.04 (s, 1H), 3.70 (s, 3H), 3.59−3.53 (m, 1H), 1.41 (s, 9H), 1.23 (d, J = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.3, 155.3, 155.0 (t, J = 289.3 Hz), 132.2 (d, J = 2.2 Hz), 129.3 (t, J = 2.2 Hz), 128.7, 128.2, 90.7 (t, J = 19.2 Hz), 79.5, 52.2, 50.9, 46.2, 28.5, 19.1; ^{19}F NMR (377 MHz, $CDCl_3$) δ −86.89 (d, J = 35.1 Hz, 1F), −87.22 (d, J = 35.3 Hz, 1F). HRMS (ESI) calcd for $C_{22}H_{25}F_2N_1Na_1O_2$ $[M + Na]^+$ 396.1746, found 396.1750.

*4,4-Difluoro-1,3-diphenylbut-3-en-1-ol (**7**).* Colorless oil (41.6 mg, 80% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42−7.24 (m, 10H), 4.74−4.54 (m, 1H), 2.97−2.66 (m, 2H), 1.94 (br, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.7 (t, J = 289.7 Hz), 143.6, 133.4, 128.7, 128.6, 128.5 (t, J = 3.0 Hz), 128.0, 127.6, 126.0, 89.7 (t, J = 18.1 Hz), 72.4 (t, J = 2.7 Hz), 37.8; ^{19}F NMR (377 MHz, $CDCl_3$) δ −90.03 (s); EI-MS (m/z, relative intensity) 260 (M^+, 6), 242 (4), 193 (21), 154 (29), 107 (89), 79 (100); HRMS (EI) calcd for $C_{16}H_{14}O_1F_2$ $[M]^+$ 260.1007, found 260.1005.

*5,5-Difluoro-2,4-diphenylpent-4-en-2-ol (**8**).* Colorless oil (49.4 mg, 90% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 7.4 Hz, 2H), 7.33 (q, J = 7.8 Hz, 4H), 7.29−7.21 (m, 4H), 2.96 (s, 2H), 1.53 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.9, 154.8 (dd, J = 290.7, 288.7 Hz), 147.2, 134.3 (dd, J = 4.3, 2.6 Hz), 128.7 (d, J = 2.8 Hz), 128.6, 128.2, 127.5, 126.9, 124.8, 89.5 (dd, J = 20.8, 15.3 Hz), 75.6 (t, J = 2.6 Hz), 42.3, 29.6; EI-MS (m/z, relative intensity) 274 (M^+, 2), 240 (7), 154 (9), 121 (100); HRMS (EI) calcd for $C_{17}H_{16}O_1F_2$ $[M]^+$ 274.1164, found 274.1168.

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*(E)-4,4-Difluoro-1,3-diphenylbut-2-en-1-one (**9**).* Colorless oil (37.1 mg, 72% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87−7.81 (m, 2H), 7.51 (t, J = 7.4 Hz, 1H), 7.38 (t, J = 7.6 Hz, 2H), 7.26 (s, 5H), 7.04 (s, 1H), 6.41 (t, J = 55.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.0, 143.3 (t, J = 20.5 Hz), 136.6, 133.8, 132.6, 129.3 (t, J = 8.1 Hz), 129.2, 129.1, 128.8, 128.7, 128.5, 114.7 (t, J = 242.4 Hz); ^{19}F NMR (377 MHz, $CDCl_3$) δ −114.83; EI-MS (m/z, relative intensity) 258 (M^+, 45), 257 (100), 207 (15), 113 (22), 105 (26), 77 (49); HRMS (EI) calcd for $C_{16}H_{12}O_1F_2$ $[M]^+$ 258.0851, found 258.0852.

*2-Fluoro-3,5-diphenylfuran (**10**).* Colorless oil (32.8 mg, 69% yield); ^{1}H NMR (400 MHz, DMSO) δ 7.69 (d, J = 8.0 Hz, 2H), 7.62 (d, J = 7.7 Hz, 2H), 7.54 (d, J = 3.3 Hz, 1H), 7.47 (dd, J = 12.4, 7.5 Hz, 4H), 7.33 (dt, J = 10.7, 5.5 Hz, 2H); ^{13}C NMR (101 MHz, DMSO) δ 153.2 (d, J = 280.8 Hz), 143.9, 129.6 (d, J = 5.5 Hz), 129.5, 129.5, 128.2, 127.6, 126.3, 126.2, 123.3, 106.6, 99.3 (d, J = 6.3 Hz); ^{19}F NMR (377 MHz, DMSO) δ −114.94 (s); EI-MS (m/z, relative intensity) 238 (M^+, 19), 149 (39), 72 (95), 59 (100); HRMS (EI) calcd for $C_{16}H_{11}O_1F_1$ $[M]^+$ 238.0788, found 238.0787.

*tert-Butyl 5-Fluoro-2-methyl-4-phenyl-2,3-dihydro-1H-pyrrole-1-carboxylate (**11**).* Colorless oil (50.9 mg, 92% yield); ^{1}H NMR (400 MHz, DMSO) δ 7.37−7.31 (m, 4H), 7.20−7.17 (m, 1H), 4.25 (ddd, J = 9.3, 6.0, 2.9 Hz, 1H), 3.10 (ddd, J = 14.5, 9.9, 4.7 Hz, 1H), 2.29 (ddd, J = 14.5, 6.4, 2.6 Hz, 1H), 1.46 (s, 9H), 1.29 (d, J = 6.3 Hz, 3H); ^{13}C NMR (101 MHz, DMSO) δ 155.1 (d, J = 4.7 Hz), 151.4 (d, J = 283.4 Hz), 137.8 (d, J = 6.1 Hz), 133.8, 131.1, 130.4 (d, J = 6.5 Hz), 97.3 (d, J = 5.9 Hz), 86.0, 57.0, 37.5 (d, J = 4.5 Hz), 33.1, 26.5; ^{19}F NMR (377 MHz, DMSO) δ −117.42 (s, 1F); EI-MS (m/z, relative intensity) 277 (M^+, 15), 221 (25), 177 (100), 162 (35); HRMS (EI) calcd for $C_{16}H_{20}O_2N_1F_1$ $[M]^+$ 277.1473, found 277.1480.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b01620.

^{1}H, ^{13}C, and ^{19}F NMR spectra of all products (PDF)

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Author Contributions

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Notes

The authors declare no competing financial interest.

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