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Cu-Catalyzed Aminodifluoroalkylation of Alkynes and α-Bromodifluoroacetamides

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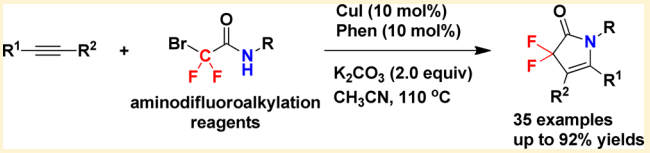
Supporting Information

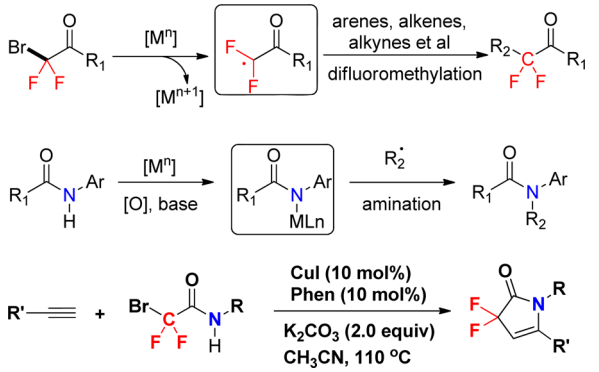
ABSTRACT: The copper-catalyzed highly regioselective aminodifluoroalkylation of alkynes and α-bromodifluoroacetamides was realized for the first time. With this method, 3,3-difluoro-1*H*-pyrrol-2(3*H*)-ones were constructed in a single step from various alkynes and α-bromodifluoroacetamides substrates without using any extra oxidant.



The introduction of fluorine atoms or fluorinated moieties can alter molecular physical and chemical properties and biological activities in a dramatic way.[1] Nitrogen-containing heterocycles are the key core of bioactive molecules.[2] Therefore, efficient synthesis of fluorinated nitrogen-containing heterocycles is highly desirable for exploration of new pharmaceuticals.[3] As part of our ongoing study on amino-fluorination reaction of alkenes and aminoarylation of alkynes using *N*-fluorobenzenesulfonimide (NFSI) as nitrogen source and the fluorine or aryl source,[4] we try to synthesize fluorinated nitrogen-containing heterocycles directly from alkynes by seeking a reagent with both fluorine and nitrogen moieties. Our literature survey showed that α-bromodifluoroacetamides might be suitable reagents for this purpose.[5] As we know, the gem-difluoromethylene group (CF_2) not only acts as lipophilic hydrogen bond donors and as bioisosteres of alcohols and thiols but also may significantly improve the biological stability.[6] Very recently, via reductive cleavage of C−Br bond, α-bromodifluoroacetamides were successfully utilized as a fluoroalkyl radical reagent which can be trapped by a series of unsaturated compounds.[5c,d] On the other hand, in the presence of transition metal, oxidant, and base, α-bromodifluoroacetamides may also be used as a suitable reagent for amination via cleavage of N−H bond in *N*-aryl amides.[7] Therefore, we reasoned that in the presence of one suitable catalyst, the above two processes could be consequentially realized to fulfill a catalytic cycle. Thus, the gem-difluoro group and nitrogen atom can be simultaneously installed into an unsaturated C−C bond, which will lead a gem-difluorinated aza-heterocycle (Scheme 1).

In contrast to the recent significant progress in the difluoromethylation of arenes[5b,8] and difluoromethylation difunctionalization of alkenes,[5d,9] efficient difluoroalkylation of less reactive alkynes are less abundant. Recently, examples of metal-catalyzed difluoromethylation difunctionalization of alkynes such as halodifluoroalkylation, aryldifluoromethylation, cyanodifluoroalkylation, and carbodifluoroalkylation was realized to provide molecules with important difluoroalkyl units (C═CCF$_2$R).[10] However, to our knowledge, aminodifluoroalkylation of simple alkynes has never been reported. Herein, we report the first example of a copper-catalyzed highly regioselective aminodifluoroalkylation of alkynes with α-bromodifluoroacetamides as both fluorine and nitrogen sources for facile access to a series of fluorinated aza-heterocycles 3,3-difluoro-1*H*-pyrrol-2(3*H*)-ones[11] (Scheme 1).

Scheme 1. Aminodifluoromethylation of Alkynes and Our Strategy



We began our investigation utilizing the reaction between ethynylbenzene **1a** and 2-bromo-2,2-difluoro-*N*-(*p*-tolyl)-acetamide **2a** as the model reaction (Table 1). With CuI as the catalyst in the presence of K_2CO_3 in MeCN, the model reaction was performed at 110 °C for 2 h under air, and no desired aminodifluoroalkylation product was observed (Table 1, entry 1). When 10 mol % pyridine was added to the above reaction, intermolecular aminodifluoroalkylation product **3a** was obtained in 18% yield (Table 1, entry 2). We were pleased to discover that 1,10-phenanthroline (Phen) was an extremely

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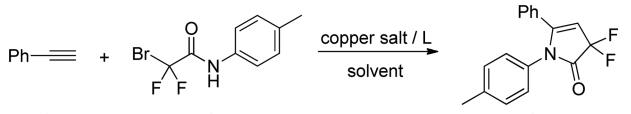
Table 1. Optimization of the Reaction Conditions[a]



1a 2a 3a

entry	metal	ligand	additive	solvent	yield (%)[b]
1	CuI	none	K_2CO_3	CH_3CN	0
2	CuI	pyridine	K_2CO_3	CH_3CN	18
3	CuI	bipy	K_2CO_3	CH_3CN	9
4	CuI	Ph_3P	K_2CO_3	CH_3CN	7
5	**CuI**	**Phen**	**K_2CO_3**	**CH_3CN**	**92**
6	CuI	Phen	none	CH_3CN	trace
7	none	Phen	K_2CO_3	CH_3CN	trace
8	CuI	Phen	KO^{t}Bu	CH_3CN	15
9	CuI	Phen	Et_3N	CH_3CN	29
10	CuBr	Phen	K_2CO_3	CH_3CN	86
11	CuCl	Phen	K_2CO_3	CH_3CN	90
12	$Cu(OTf)_2$	Phen	K_2CO_3	CH_3CN	41
13	$Cu(OAc)_2$	Phen	K_2CO_3	CH_3CN	45
14	CuI	Phen	K_2CO_3	EtOH	6
15	CuI	Phen	K_2CO_3	DMF	8
16	CuI	Phen	K_2CO_3	EtOAc	19
17[c]	CuI	Phen	K_2CO_3	CH_3CN	24

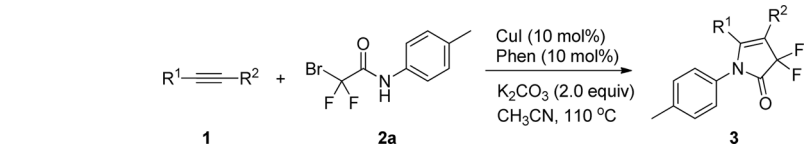
[a]Reactions were carried out with **1a** (0.45 mmol), **2a** (0.3 mmol), metal (10 mol %), ligand (10 mol %), and additive (2.0 equiv) in 3 mL of solvent under an air atmosphere at 110 °C for 2 h unless noted otherwise. [b]Yield of the isolated product. [c]The reaction was performed at 90 °C. Phen = 1,10-phenanthroline, Tf = trifluoromethanesulfonyl, bipy = 2,2′-bipyridine.

efficient ligand for promoting the reaction, affording **3a** in 92% yield (Table 1, entries 3−5). Control reactions demonstrated that base and catalyst were essential to the reaction (Table 1, entries 6 and 7). Other bases such as KO^{t}Bu and Et_3N were not as effective as K_2CO_3 (Table 1, entries 8 and 9). Further investigation on different copper salts revealed that CuBr and CuCl were also efficient catalysts for this transformation, affording product **3a** in satisfying 86 and 90% yields, respectively (Table 1, entries 10 and 11). With $Cu(OTf)_2$ and $Cu(OAc)_2$ as catalysts, **3a** was provided in 41 and 45% yields, respectively (Table 1, entries 12 and 13). Other solvents (e.g., EtOH, DMF, and EtOAc) were examined but did not lead to any significant improvement (Table 1, entries 14−16). When the reaction was performed at 90 °C, **3a** was isolated in 24% yield (Table 1, entry 17). It should be noted that the transformation from **1a** into **3a** represents the first direct aminodifluoroalkylation from alkynes.

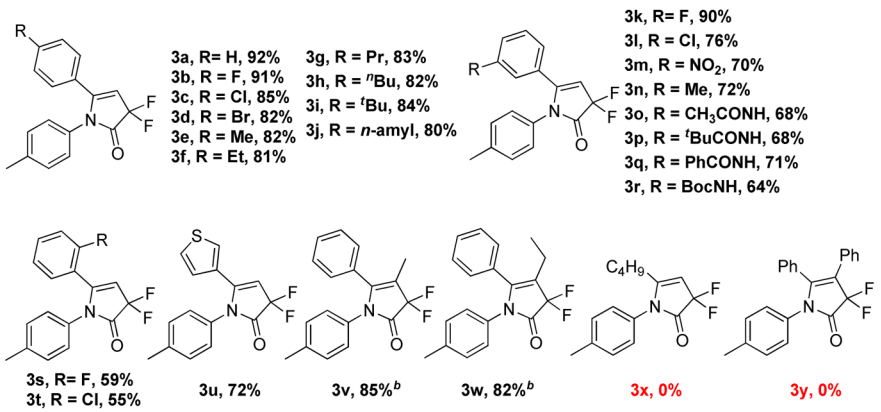
With the optimized reaction conditions in hand (Table 1, entry 5), the scope of the aminodifluoroalkylation of alkynes was examined, and the results are shown in Table 2. The reaction of **2a** and a variety of alkynes derivatives afforded the desired aminodifluoroalkylation products **3** in 55−92% yields. Halo-substituted phenylacetylenes (**1b**−**1d**, **1k**, **1l**, **1s**, and **1t**) were tolerated in the aminodifluoroalkylation reaction and could be very useful for further transformations. Phenylacetylene substrates bearing electron-withdrawing substituents such as F, Cl, Br, and nitro were effectively converted into the corresponding products in moderate to excellent yields. Substrates with electron-donating substituents on the aromatic ring underwent aminodifluoroalkylation smoothly to afford the desired products (**3e**−**3j** and **3n**−**3r**) in good yields. In addition, heteroaromatic alkynes such as 3-ethynylthiophene **1u** were also effective to provide **3u** in 72% yield. Internal alkynes were subsequently examined. Starting from prop-1-yn-1-ylbenzene **1v** and but-1-yn-1-ylbenzene **1w**, **3v** and **3w** were obtained in 85 and 82% yields, respectively. However, from the substrates hex-1-yne **1x** and diphenylacetylene **1y**, no reactions occurred, and the substrate **2a** was completely recovered. Remarkably, in all cases, the reactions proceeded smoothly under air, and high regioselectivities were observed.

To further explore the potential of this efficient aminodifluoroalkylation reaction, a variety of α-bromodifluoroacetamides was investigated. As shown in Table 3, α-bromodi-

Table 2. Reactions of Alkynes 1 with 2a[a]



1 2a 3



[a]Reactions were carried out with **1** (0.45 mmol), **2a** (0.3 mmol), CuI (10 mol %), Phen (10 mol %), and K_2CO_3 (2.0 equiv) in CH_3CN (3 mL) under air atmosphere at 110 °C for 2 h. Yield of the isolated product. [b]The reaction was run for 4 h.

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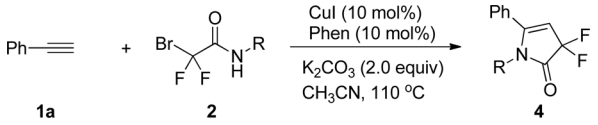
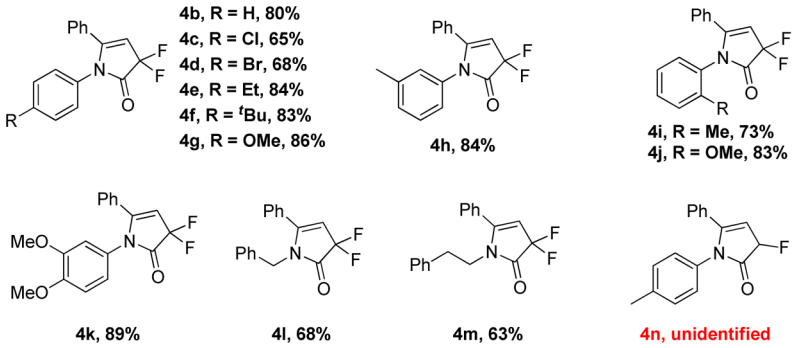
Table 3. Reactions of Ethynylbenzene 1a with α-Bromodifluoroacetamides 2[a]

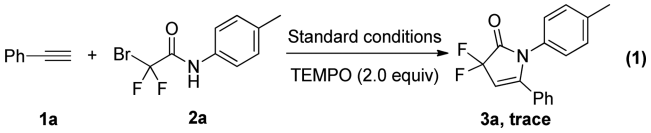




[a]Reactions were carried out with **1a** (0.45 mmol), **2** (0.3 mmol), CuI (10 mol %), Phen (10 mol %), and K_2CO_3 (2.0 equiv) in CH_3CN (3 mL) under air atmosphere at 110 °C for 2 h. Yield of the isolated product.

fluoroacetamides with different substituents at the aromatic ring could be converted to the desired products **4b**−**4k** in moderate to good yields. Slightly decreased but acceptable yields were also achieved for reactions starting from *ortho*-substituted aryl amides (**2i** and **2j**). Remarkably, we found that not only *N*-aryl substrates but also *N*-alkyl substrates worked well, affording **4l** and **4m** in 68 and 63% yields, respectively. However, the desired annulation product was not observed between the reaction of ethynylbenzene with monofluoroacetamide 2-bromo-2-fluoro-*N*-(*p*-tolyl)acetamide **2n**.[12]

To gain insight into the mechanism of this transformation, a radical trapping experiment was performed. When the radical scavenger 2,2,6,6-tetramethylpiperidine *N*-oxide (TEMPO, 2.0 equiv) was added to the aminodifluoroalkylation reaction of **1a** under the optimal conditions, no desired products were isolated, and 80% **2a** was recovered (eq 1). The results indicate

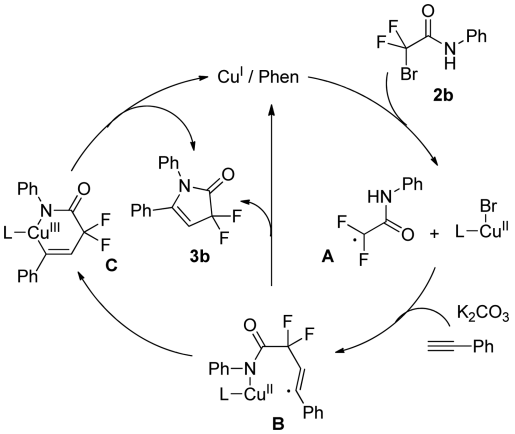


(1)

that a radical pathway may be involved under the catalytic system. On the basis of the present experimental results and literature precedent, a possible mechanism was proposed as described in Scheme 2. Initially, the reaction of CuI and **2b** gave a radical intermediate **A** and Cu^{II} species via a single electron transfer (SET) process.[5c] Subsequently, addition of the in situ generated fluoroalkyl radical **A** to the C−C triple bond of alkyne leads to the formation of vinyl radical[10c,e] which, with Cu^{II} species, gave the intermediate **B** in the presence of K_2CO_3. Nitrogen atom transfer from Cu^{II} to the adduct radical produces the aminodifluoroalkylation product and regenerates Cu^{I},[13] which enters into the next catalytic circle. On the other hand, we could not exclude another pathway: Cu^{II}-amido species reacts with vinyl radicals to form vinyl-Cu^{III}-amido species **C**, which then undergoes the final reductive elimination to give the desired annulation product.[7a,10c,e,14]

In summary, we developed the first example of copper-catalyzed radical aminodifluoroalkylation reaction of alkynes for the synthesis of 3,3-difluoro-1*H*-pyrrol-2(3*H*)-ones. The high

Scheme 2. Plausible Reaction Mechanism



regioselectivity, broad substrate scope, no extra oxidant, and low loading of the copper catalyst make the aminodifluoroalkylation reactions very attractive. We believe that it should prompt further research in the area of transition-metal catalyzed aminodifluoroalkylation reactions and related chemistry using α-bromodifluoroacetamides as both difluoroalkyl and nitrogen sources.

EXPERIMENTAL SECTION

All reagents were purchased from commercial sources and used without further treatment unless otherwise indicated. All reactions were run under air with no precautions taken to exclude moisture. ^1H NMR, ^{13}C NMR, and ^{19}F NMR spectra were recorded at 25 °C on a Varian instrument (400, 100, and 376 MHz). Melting points were obtained with a micro melting point XT4A Beijing Keyi electrooptic apparatus and are uncorrected. High resolution mass spectra were recorded on Bruck microTof. All reactions were monitored by TLC with Taizhou GF254 silica gel coated plates. Flash column chromatography was carried out using 200−300 mesh silica gel at increased pressure.

General Procedure for the Preparation of 1o−1r. Substrates **1o**−**1q** were prepared by the reaction of corresponding anilines (1 mmol) and acyl chlorides (1.1 mmol) in CH_2Cl_2 at room temperature. Substrates **1r** was prepared according to literature procedure.[15]

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General Procedure for the Preparation of 2 (2a as Example). In a nitrogen-filled glovebox, *p*-toluidine (535.8 mg, 5.0 mmol), ethyl bromodifluoroacetate (785.1 μL, 6.0 mmol), and $La(OTf)_3$ (146.5 mg, 0.25 mmol) were combined in screw-cap test tube. The reaction mixture was stirred at 50 °C and monitored by TLC. After the amine was exhausted, the mixture was purified by silica gel column chromatography to give the corresponding products **2a** (1.21 g, 92%).

General Procedure for the Preparation of 3 and 4 (3a as Example). To a solution of the 2-bromo-2,2-difluoro-*N*-(*p*-tolyl)-acetamide **2a** (79.2 mg, 0.3 mmol) in CH_3CN (3.0 mL) was added the ethynylbenzene **1a** (49 μL, 0.45 mmol), Phen (5.4 mg, 0.03 mmol), CuI (5.7 mg, 0.03 mmol), and K_2CO_3 (82.9 mg, 0.6 mmol) in screw-cap test tube. The reaction mixture was stirred at 110 °C for 2.0 h. After the reaction finished, the reaction mixture was cooled to room temperature and quenched by water. The mixture was extracted with EtOAc (5.0 mL × 3); the combined organic phases were dried over anhydrous Na_2SO_4, and the solvent was evaporated under vacuum. The residue was purified by column chromatography to give the corresponding products **3a** (78.7 mg, 92%).

N-(3-Ethynylphenyl)acetamide ***1o***. White solid (149.5 mg, 94%). Petroleum ether/ethyl acetate = 40/1 as eluent for column chromatography. Mp: 86−88 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.13 (s, 3H), 3.04 (s, 1H), 7.20 (d, *J* = 6.8 Hz, 2H), 7.48−7.49 (m, 1H), 7.67 (s, 1H), 8.60 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.2, 77.4, 83.1, 120.7, 122.5, 123.6, 127.8, 128.8, 138.0, 169.4. HRMS (ESI-TOF) calcd for $C_{10}H_{10}NO$, $[M + H]^+$ *m*/*z* 160.0762, found 160.0764.

N-(3-Ethynylphenyl)pivalamide ***1p***. White solid (189.0 mg, 94%). Petroleum ether/ethyl acetate = 40/1 as eluent for column chromatography. Mp: 144−146 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.27 (s, 9H), 3.03 (s, 1H), 7.17−7.20 (m, 2H), 7.50−7.53 (m, 1H), 7.56 (s, 1H), 7.64 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 27.4, 39.5, 77.3, 83.1, 120.8, 122.5, 123.7, 127.7, 128.7, 138.0, 176.8. HRMS (ESI-TOF) calcd for $C_{13}H_{16}NO$, $[M + H]^+$ *m*/*z* 202.1232, found 202.1230.

N-(3-Ethynylphenyl)benzamide ***1q***. White solid (198.9 mg, 90%). Petroleum ether/ethyl acetate = 40/1 as eluent for column chromatography. Mp: 122−124 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.08 (s, 1H), 7.26−7.31 (m, 2H), 7.44 (t, *J* = 7.2 Hz, 2H), 7.53 (t, *J* = 7.2 Hz, 1H), 7.68 (d, *J* = 7.2 Hz, 1H), 7.77 (s, 1H), 7.84 (d, *J* = 7.6 Hz, 2H), 8.12 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 77.5, 83.1, 120.9, 122.8, 123.8, 127.0, 128.2, 128.7, 129.0, 131.9, 134.6, 138.0, 166.0. HRMS (ESI-TOF) calcd for $C_{15}H_{12}NO$, $[M + H]^+$ *m*/*z* 222.0919, found 222.0926.

tert-Butyl (3-Ethynylphenyl)carbamate ***1r***. White solid (173.7 mg, 80%). Petroleum ether/ethyl acetate = 40/1 as eluent for column chromatography. Mp: 70−72 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.50 (s, 9H), 3.04 (s, 1H), 6.75 (s, 1H), 7.13 (d, *J* = 7.6 Hz, 1H), 7.20 (t, *J* = 7.6 Hz, 1H), 7.34 (d, *J* = 7.6 Hz, 1H), 7.53 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 28.2, 77.1, 80.6, 83.3, 119.0, 121.9, 122.6, 126.6, 128.8, 138.4, 152.6. HRMS (ESI-TOF) calcd for $C_{13}H_{16}NO_2$, $[M + H]^+$ *m*/*z* 218.1181, found 218.1171.

2-Bromo-2,2-difluoro-N-(p-tolyl)acetamide ***2a***. White solid (1.21 g, 92%). Petroleum ether/ethyl acetate = 90/1 as eluent for column chromatography. Mp: 118−120 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.35 (s, 3H), 7.18 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.97 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.9, 111.6 (t, *J* = 315.0 Hz), 120.5, 129.8, 132.7, 136.1, 157.4 (t, *J* = 28.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ −60.4. HRMS (ESI-TOF) calcd for $C_9H_9BrF_2NO$, $[M + H]^+$ *m*/*z* 263.9836, found 263.9828.

2-Bromo-2,2-difluoro-N-phenylacetamide ***2b***. White solid (1.12 g, 90%). Petroleum ether/ethyl acetate = 90/1 as eluent for column chromatography. Mp: 46−48 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (d, *J* = 7.6 Hz, 1H), 7.40 (t, *J* = 8.0 Hz, 2H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.86 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 111.4 (t, *J* = 315.0 Hz), 120.6, 126.2, 129.3, 135.2, 157.6 (t, *J* = 28.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ −60.6. HRMS (ESI-TOF) calcd for $C_8H_7BrF_2NO$, $[M + H]^+$ *m*/*z* 249.9679, found 249.9680.

2-Bromo-N-(4-chlorophenyl)-2,2-difluoroacetamide ***2c***. White solid (1.16 g, 82%). Petroleum ether/ethyl acetate = 90/1 as eluent for column chromatography. Mp: 136−138 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (d, *J* = 8.8 Hz, 2H), 7.53 (d, *J* = 8.8 Hz, 2H), 7.88 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 111.3 (t, *J* = 315.0 Hz), 121.7, 129.5, 131.6, 133.8, 157.5 (t, *J* = 28.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ −60.7. HRMS (ESI-TOF) calcd for $C_8H_6BrClF_2NO$, $[M + H]^+$ *m*/*z* 283.9289, found 283.9287.

2-Bromo-N-(4-bromophenyl)-2,2-difluoroacetamide ***2d***. White solid (1.36 g, 83%). Petroleum ether/ethyl acetate = 90/1 as eluent for column chromatography. Mp: 144−146 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (d, *J* = 8.8 Hz, 2H), 7.52 (d, *J* = 8.8 Hz, 2H), 7.87 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 111.3 (t, *J* = 315.0 Hz), 119.2, 122.0, 132.4, 134.3, 157.4 (t, *J* = 28.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ −60.7. HRMS (ESI-TOF) calcd for $C_8H_6Br_2F_2NO$, $[M + H]^+$ *m*/*z* 329.8764, found 329.8770.

2-Bromo-N-(4-ethylphenyl)-2,2-difluoroacetamide ***2e***. White solid (1.26 g, 91%). Petroleum ether/ethyl acetate = 90/1 as eluent for column chromatography. Mp: 98−99 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.24 (t, *J* = 7.6 Hz, 3H), 2.65 (q, *J* = 7.6 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.84 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.5, 28.3, 111.6 (t, *J* = 315.0 Hz), 120.5, 128.7, 132.9, 142.4, 157.4 (t, *J* = 28.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ −60.4. HRMS (ESI-TOF) calcd for $C_{10}H_{11}BrF_2NO$, $[M + H]^+$ *m*/*z* 277.9992, found 277.9999.

2-Bromo-N-(4-(tert-butyl)phenyl)-2,2-difluoroacetamide ***2f***. White solid (1.37 g, 90%). Petroleum ether/ethyl acetate = 90/1 as eluent for column chromatography. Mp: 115−117 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.32 (s, 9H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 8.8 Hz, 2H), 7.81 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 31.2, 34.5, 111.5 (t, *J* = 315.0 Hz), 120.3, 126.1, 132.6, 149.4, 157.6 (t, *J* = 27.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ −60.4. HRMS (ESI-TOF) calcd for $C_{12}H_{15}BrF_2NO$, $[M + H]^+$ *m*/*z* 306.0305, found 306.0309.

2-Bromo-2,2-difluoro-N-(4-methoxyphenyl)acetamide ***2g***. White solid (1.31 g, 94%). Petroleum ether/ethyl acetate = 90/1 as eluent for column chromatography. Mp: 117−119 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.81 (s, 3H), 6.91 (d, *J* = 8.8 Hz, 2H), 7.47 (d, *J* = 8.8 Hz, 2H), 7.84 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.5, 111.7 (t, *J* = 315.0 Hz), 114.5, 122.2, 128.1, 157.4 (t, *J* = 28.0 Hz), 157.7; ^{19}F NMR (376 MHz, $CDCl_3$): δ −60.4. HRMS (ESI-TOF) calcd for $C_9H_9BrF_2NO_2$, $[M + H]^+$ *m*/*z* 279.9785, found 279.9782.

2-Bromo-2,2-difluoro-N-(m-tolyl)acetamide ***2h***. White solid (1.18 g, 90%). Petroleum ether/ethyl acetate = 90/1 as eluent for column chromatography. Mp: 60−61 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.36 (s, 3H), 7.06 (d, *J* = 7.2 Hz, 1H), 7.27 (t, *J* = 8.0 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.43 (s, 1H), 8.14 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.3, 111.5 (t, *J* = 315.0 Hz), 117.7, 121.2, 127.0, 129.0, 135.1, 139.3, 157.6 (t, *J* = 28.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ −60.5. HRMS (ESI-TOF) calcd for $C_9H_9BrF_2NO$, $[M + H]^+$ *m*/*z* 263.9836, found 263.9833.

2-Bromo-2,2-difluoro-N-(o-tolyl)acetamide ***2i***. White solid (1.12 g, 85%). Petroleum ether/ethyl acetate = 90/1 as eluent for column chromatography. Mp: 72−74 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.35 (s, 3H), 7.06 (d, *J* = 7.6 Hz, 1H), 7.27 (t, *J* = 7.6 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 2H), 8.29 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.2, 111.5 (t, *J* = 315.0 Hz), 117.8, 121.3, 127.0, 129.0, 135.1, 139.2, 157.7 (t, *J* = 28.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ −60.4. HRMS (ESI-TOF) calcd for $C_9H_9BrF_2NO$, $[M + H]^+$ *m*/*z* 263.9836, found 263.9830.

2-Bromo-2,2-difluoro-N-(2-methoxyphenyl)acetamide ***2j***. White solid (1.26 g, 90%). Petroleum ether/ethyl acetate = 90/1 as eluent for column chromatography. Mp: 78−79 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.93 (s, 3H), 6.93 (d, *J* = 8.0 Hz, 1H), 7.01 (t, *J* = 8.0 Hz, 1H), 7.16 (t, *J* = 8.0 Hz, 1H), 8.31 (d, *J* = 8.0 Hz, 1H), 8.54 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.9, 110.2, 111.6 (t, *J* = 315.0 Hz), 120.0, 121.2, 125.2, 125.8, 148.4, 157.0 (t, *J* = 27.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ −60.2. HRMS (ESI-TOF) calcd for $C_9H_9BrF_2NO_2$, $[M + H]^+$ *m*/*z* 279.9785, found 279.9778.

2-Bromo-N-(3,4-dimethoxyphenyl)-2,2-difluoroacetamide ***2k***. White solid (1.45 g, 94%). Petroleum ether/ethyl acetate = 90/1 as eluent for column chromatography. Mp: 138−140 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.89 (s, 3H), 3.91 (s, 3H), 6.86 (d, *J* = 8.8 Hz, 1H), 6.98 (dd, J_1 = 2.4 Hz, J_2 = 8.8 Hz, 1H), 7.32 (d, *J* = 2.4 Hz, 1H), 7.72 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.9, 56.0, 105.0, 111.3,

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111.6 (t, J = 315.0 Hz), 112.8, 128.7, 147.2, 149.2, 157.4 (t, J = 28.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ −60.3. HRMS (ESI-TOF) calcd for $C_{10}H_{11}BrF_2NO_3$, $[M + H]^+$ m/z 309.9890, found 309.9881.

N-Benzyl-2-bromo-2,2-difluoroacetamide ***2l***. White solid (1.25 g, 95%). Petroleum ether/ethyl acetate = 100/1 as eluent for column chromatography. Mp: 44−45 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.49 (d, J = 6.0 Hz, 2H), 6.98 (s, 1H), 7.28−7.31 (m, 2H), 7.33−7.39 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 43.9, 111.7 (t, J = 314.0 Hz), 127.7, 128.0, 128.9, 136.1, 160.0 (t, J = 27.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ −60.5. HRMS (ESI-TOF) calcd for $C_9H_9BrF_2NO$, $[M + H]^+$ m/z 263.9836, found 263.9831.

2-Bromo-2,2-difluoro-N-phenethylacetamide ***2m***. White solid (1.32 g, 95%). Petroleum ether/ethyl acetate = 100/1 as eluent for column chromatography. Mp: 92−94 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.91 (t, J = 6.8 Hz, 2H), 3.62 (q, J = 6.8 Hz, 2H), 6.50 (s, 1H), 7.22 (d, J = 6.8 Hz, 2H), 7.26−7.29 (m, 1H), 7.35 (t, J = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 34.9, 41.3, 111.7 (t, J = 314.0 Hz), 126.9, 128.7, 128.8, 137.7, 160.0 (t, J = 27.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ −60.4. HRMS (ESI-TOF) calcd for $C_{10}H_{11}BrF_2NO$, $[M + H]^+$ m/z 277.9992, found 277.9983.

3,3-Difluoro-5-phenyl-1-(p-tolyl)-1H-pyrrol-2(3H)-one ***3a***. White solid (78.7 mg, 92%). Petroleum ether/ethyl acetate = 50/1 as eluent for column chromatography. Mp: 106−108 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.32 (s, 3H), 5.63 (t, J = 1.2 Hz, 1H), 6.91 (d, J = 8.4 Hz, 2H), 7.11 (d, J = 8.0 Hz, 2H), 7.18 (d, J = 7.6 Hz, 2H), 7.29 (t, J = 7.6 Hz, 2H), 7.38 (t, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.1, 99.8 (t, J = 23.0 Hz), 112.9 (t, J = 244.0 Hz), 126.5, 127.9, 128.5, 128.8, 129.6, 130.6, 130.9, 137.9, 154.6 (t, J = 11.0 Hz), 166.9 (t, J = 30.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ −110.1. HRMS (ESI-TOF) calcd for $C_{17}H_{14}F_2NO$, $[M + H]^+$ m/z 286.1043, found 286.1042.

3,3-Difluoro-5-(4-fluorophenyl)-1-(p-tolyl)-1H-pyrrol-2(3H)-one ***3b***. Colorless oil (82.7 mg, 91%). Petroleum ether/ethyl acetate = 70/1 as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.33 (s, 3H), 5.61 (d, J = 1.6 Hz, 1H), 6.90 (d, J = 8.4 Hz, 2H), 6.98 (t, J = 8.4 Hz, 2H), 7.13 (d, J = 8.0 Hz, 2H), 7.16−7.20 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.1, 99.7 (t, J = 23.0 Hz), 112.8 (t, J = 244.0 Hz), 115.8 (d, J = 22.0 Hz), 124.9 (d, J = 3.0 Hz), 126.6, 129.8, 130.1 (d, J = 8.0 Hz), 130.8, 138.1, 153.5 (t, J = 11.0 Hz), 163.8 (d, J = 251.0 Hz), 166.7 (t, J = 30.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ −110.0, −108.3. HRMS (ESI-TOF) calcd for $C_{17}H_{13}F_3NO$, $[M + H]^+$ m/z 304,0949, found 304,0944.

5-(4-Chlorophenyl)-3,3-difluoro-1-(p-tolyl)-1H-pyrrol-2(3H)-one ***3c***. Colorless oil (81.3 mg, 85%). Petroleum ether/ethyl acetate = 70/1 as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.33 (s, 3H), 5.64 (s, 1H), 6.90 (d, J = 8.0 Hz, 2H), 7.11−7.14 (m, 4H), 7.27 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.1, 100.1 (t, J = 23.0 Hz), 112.7 (t, J = 244.0 Hz), 126.5, 127.2, 128.9, 129.2, 129.8, 130.7, 136.9, 138.2, 153.4 (t, J = 11.0 Hz), 166.7 (t, J = 30.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ −110.1. HRMS (ESI-TOF) calcd for $C_{17}H_{13}ClF_2NO$, $[M + H]^+$ m/z 320.0654, found 320.0649.

5-(4-Bromophenyl)-3,3-difluoro-1-(p-tolyl)-1H-pyrrol-2(3H)-one ***3d***. Colorless oil (89.3 mg, 82%). Petroleum ether/ethyl acetate = 60/1 as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.33 (s, 3H), 5.64 (s, 1H), 6.90 (d, J = 8.0 Hz, 2H), 7.05 (d, J = 8.0 Hz, 2H), 7.13 (d, J = 8.0 Hz, 2H), 7.43 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.1, 100.1 (t, J = 23.0 Hz), 112.6 (t, J = 244.0 Hz), 125.2, 126.5, 127.7, 129.4, 129.8, 130.7, 131.9, 138.2, 153.5 (t, J = 11.0 Hz), 166.7 (t, J = 30.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ −110.2. HRMS (ESI-TOF) calcd for $C_{17}H_{13}BrF_2NO$, $[M + H]^+$ m/z 364.0149, found 364.0156.

3,3-Difluoro-1,5-di-p-tolyl-1H-pyrrol-2(3H)-one ***3e***. Colorless oil (73.6 mg, 82%). Petroleum ether/ethyl acetate = 70/1 as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.33 (s, 6H), 5.58 (s, 1H), 6.91−6.93 (m, 2H), 7.07−7.13 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.1, 21.4, 99.1 (t, J = 23.0 Hz), 113.0 (t, J = 244.0 Hz), 125.9, 126.6, 127.9, 129.2, 129.6, 131.1, 137.8, 141.0, 154.6 (t, J = 11.0 Hz), 167.0 (t, J = 30.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ −109.8. HRMS (ESI-TOF) calcd for $C_{18}H_{16}F_2NO$, $[M + H]^+$ m/z 300.1200, found 300.1218.

5-(4-Ethylphenyl)-3,3-difluoro-1-(p-tolyl)-1H-pyrrol-2(3H)-one ***3f***. Colorless oil (76.1 mg, 81%). Petroleum ether/ethyl acetate = 70/1 as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.21 (t, J = 7.6 Hz, 3H), 2.33 (s, 3H), 2.63 (q, J = 7.6 Hz, 2H), 5.59 (s, 1H), 6.93 (d, J = 8.0 Hz, 2H), 7.08−7.13 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.0, 21.1, 28.6, 99.1 (t, J = 23.0 Hz), 113.0 (t, J = 244.0 Hz), 126.1, 126.6, 127.9, 128.0, 129.6, 131.1, 137.8, 147.2, 154.6 (t, J = 11.0 Hz), 167.0 (t, J = 30.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ −109.7. HRMS (ESI-TOF) calcd for $C_{19}H_{18}F_2NO$, $[M + H]^+$ m/z 314.1356, found 314.1353.

3,3-Difluoro-5-(4-propylphenyl)-1-(p-tolyl)-1H-pyrrol-2(3H)-one ***3g***. Colorless oil (81.4 mg, 83%). Petroleum ether/ethyl acetate = 70/1 as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.91 (t, J = 7.2 Hz, 3H), 1.57−1.63 (m, 2H), 2.33 (s, 3H), 2.56 (t, J = 7.6 Hz, 2H), 5.59 (s, 1H), 6.92 (d, J = 8.0 Hz, 2H), 7.08−7.12 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.7, 21.1, 24.1, 37.8, 99.1 (t, J = 23.0 Hz), 113.0 (t, J = 244.0 Hz), 126.1, 126.6, 127.9, 128.6, 129.6, 131.1, 137.8, 145.8, 154.6 (t, J = 11.0 Hz), 167.0 (t, J = 30.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ −109.8. HRMS (ESI-TOF) calcd for $C_{20}H_{20}F_2NO$, $[M + H]^+$ m/z 328.1513, found 328.1506.

5-(4-Butylphenyl)-3,3-difluoro-1-(p-tolyl)-1H-pyrrol-2(3H)-one ***3h***. Colorless oil (83.9 mg, 82%). Petroleum ether/ethyl acetate = 70/1 as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.91 (t, J = 7.6 Hz, 3H), 1.30−1.37 (m, 2H), 1.52−1.60 (m, 2H), 2.33 (s, 3H), 2.56 (t, J = 7.6 Hz, 2H), 5.90 (d, J = 1.2 Hz, 1H), 6.92 (d, J = 8.4 Hz, 2H), 7.06−7.12 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.8, 21.1, 22.3, 33.1, 35.4, 99.1 (t, J = 23.0 Hz), 113.0 (t, J = 244.0 Hz), 126.0, 126.5, 127.8, 128.5, 129.6, 131.1, 137.8, 146.0, 154.6 (t, J = 11.0 Hz), 167.0 (t, J = 30.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ −109.8. HRMS (ESI-TOF) calcd for $C_{21}H_{22}F_2NO$, $[M + H]^+$ m/z 342.1669, found 342.1677.

5-(4-(tert-Butyl)phenyl)-3,3-difluoro-1-(p-tolyl)-1H-pyrrol-2(3H)-one ***3i***. Yellow oil (85.9 mg, 84%). Petroleum ether/ethyl acetate = 70/1 as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.28 (s, 9H), 2.34 (s, 3H), 5.59 (s, 1H), 6.93 (d, J = 8.4 Hz, 2H), 7.11 (t, J = 8.4 Hz, 4H), 7.29 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.1, 31.1, 34.9, 99.2 (t, J = 23.0 Hz), 113.0 (t, J = 244.0 Hz), 125.4, 125.8, 126.6, 127.7, 129.6, 131.2, 137.8, 154.2, 154.5 (t, J = 11.0 Hz), 167.0 (t, J = 30.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ −109.8. HRMS (ESI-TOF) calcd for $C_{21}H_{22}F_2NO$, $[M + H]^+$ m/z 342.1669, found 342.1664.

3,3-Difluoro-5-(4-pentylphenyl)-1-(p-tolyl)-1H-pyrrol-2(3H)-one ***3j***. Yellow oil (85.2 mg, 80%). Petroleum ether/ethyl acetate = 70/1 as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.89 (t, J = 6.8 Hz, 3H), 1.28−1.35 (m, 4H), 1.55−1.62 (m, 2H), 2.33 (s, 3H), 2.58 (t, J = 7.6 Hz, 2H), 5.60 (s, 1H), 6.93 (d, J = 8.0 Hz, 2H), 7.09−7.19 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.9, 21.1, 22.4, 30.6, 31.4, 35.7, 99.1 (t, J = 23.0 Hz), 113.0 (t, J = 244.0 Hz), 126.0, 126.5, 127.8, 128.5, 129.6, 131.1, 137.8, 146.0, 154.6 (t, J = 11.0 Hz), 167.0 (t, J = 30.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ −109.7. HRMS (ESI-TOF) calcd for $C_{22}H_{24}F_2NO$, $[M + H]^+$ m/z 356.1826, found 356.1821.

3,3-Difluoro-5-(3-fluorophenyl)-1-(p-tolyl)-1H-pyrrol-2(3H)-one ***3k***. White solid (81.8 mg, 90%). Petroleum ether/ethyl acetate = 60/1 as eluent for column chromatography. Mp: 109−110 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.33 (s, 3H), 5.66 (d, J = 1.6 Hz, 1H), 6.89−6.92 (m, 3H), 6.97 (d, J = 8.0 Hz, 1H), 7.06−7.10 (m, 1H), 7.13 (d, J = 8.4 Hz, 2H), 7.24−7.30 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.1, 100.6 (t, J = 23.0 Hz), 112.6 (t, J = 244.0 Hz), 115.1 (d, J = 23.0 Hz), 117.7 (d, J = 21.0 Hz), 123.8 (d, J = 1.0 Hz), 126.4, 129.8, 130.3 (d, J = 9.0 Hz), 130.7, 130.8 (d, J = 8.0 Hz), 138.2, 153.3 (t, J = 11.0 Hz), 162.3 (d, J = 246.0 Hz), 166.6 (t, J = 30.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ −111.3, −110.4. HRMS (ESI-TOF) calcd for $C_{17}H_{13}F_3NO$, $[M + H]^+$ m/z 304,0949, found 304,0939.

5-(3-Chlorophenyl)-3,3-difluoro-1-(p-tolyl)-1H-pyrrol-2(3H)-one ***3l***. Colorless oil (72.7 mg, 76%). Petroleum ether/ethyl acetate = 60/1 as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.32 (s, 3H), 5.65 (s, 1H), 6.91 (d, J = 8.4 Hz, 2H), 6.98 (d, J = 8.0

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Hz, 1H), 7.13 (d, J = 8.0 Hz, 2H), 7.20 (t, J = 8.0 Hz, 1H), 7.26 (s, 1H), 7.35 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.1, 100.7 (t, J = 23.0 Hz), 112.6 (t, J = 245.0 Hz), 126.1, 126.5, 128.0, 129.7, 129.8, 130.5, 130.6, 130.7, 134.7, 138.2, 153.1 (t, J = 11.0 Hz), 166.6 (t, J = 30.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ −110.4. HRMS (ESI-TOF) calcd for $C_{17}H_{13}ClF_2NO$, $[M + H]^+$ m/z 320.0654, found 320.0649.

3,3-Difluoro-5-(3-nitrophenyl)-1-(p-tolyl)-1H-pyrrol-2(3H)-one ***3m***. Colorless oil (69.3 mg, 70%). Petroleum ether/ethyl acetate = 60/1 as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.32 (s, 3H), 5.78 (t, J = 1.2 Hz, 1H), 6.92 (d, J = 8.0 Hz, 2H), 7.14 (d, J = 8.4 Hz, 2H), 7.45−7.51 (m, 2H), 8.12 (s, 1H), 8.22−8.24 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.1, 101.6 (t, J = 23.0 Hz), 112.3 (t, J = 245.0 Hz), 123.0, 125.2, 126.2, 129.7, 130.1, 130.2, 130.4, 133.5, 138.7, 148.1, 152.1 (t, J = 11.0 Hz), 166.3 (t, J = 30.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ −110.6. HRMS (ESI-TOF) calcd for $C_{17}H_{13}F_2N_2O_3$, $[M + H]^+$ m/z 331.0894, found 331.0903.

3,3-Difluoro-5-(m-tolyl)-1-(p-tolyl)-1H-pyrrol-2(3H)-one ***3n***. Colorless oil (64.6 mg, 72%). Petroleum ether/ethyl acetate = 60/1 as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.28 (s, 3H), 2.32 (s, 3H), 5.61 (s, 1H), 6.88−6.93 (m, 3H), 7.07−7.19 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.1, 21.3, 99.6 (t, J = 23.0 Hz), 112.9 (t, J = 244.0 Hz), 125.1, 126.5, 128.2, 128.5, 128.7, 129.6, 131.0, 131.4, 137.8, 138.4, 154.7 (t, J = 11.0 Hz), 166.9 (t, J = 30.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ −110.1. HRMS (ESI-TOF) calcd for $C_{18}H_{16}F_2NO$, $[M + H]^+$ m/z 300.1200, found 300.1193.

N-(3-(4,4-Difluoro-5-oxo-1-(p-tolyl)-4,5-dihydro-1H-pyrrol-2-yl)-phenyl)acetamide ***3o***. White solid (69.8 mg, 68%). Petroleum ether/ethyl acetate = 40/1 as eluent for column chromatography. Mp: 136−138 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.12 (s, 3H), 2.29 (s, 3H), 5.60 (s, 1H), 6.75 (d, J = 7.2 Hz, 1H), 6.89 (d, J = 8.0 Hz, 2H), 7.08 (d, J = 7.6 Hz, 2H), 7.15 (t, J = 8.0 Hz, 1H), 7.49 (d, J = 8.0 Hz, 1H), 7.56 (s, 1H), 7.69 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.0, 24.4, 100.2 (t, J = 23.0 Hz), 112.8 (t, J = 244.0 Hz), 118.9, 121.6, 123.5, 126.4, 129.0, 129.4, 129.7, 130.8, 138.0, 138.5, 154.2 (t, J = 11.0 Hz), 167.0 (t, J = 30.0 Hz), 168.6; ^{19}F NMR (376 MHz, $CDCl_3$): δ −110.2. HRMS (ESI-TOF) calcd for $C_{19}H_{17}F_2N_2O_2$, $[M + H]^+$ m/z 343.1258, found 343.1251.

N-(3-(4,4-Difluoro-5-oxo-1-(p-tolyl)-4,5-dihydro-1H-pyrrol-2-yl)-phenyl)pivalamide ***3p***. White solid (78.4 mg, 68%). Petroleum ether/ethyl acetate = 40/1 as eluent for column chromatography. Mp: 178−179 °C. ^{1}H NMR (400 MHz, DMSO): δ 1.21 (s, 9H), 2.27 (s, 3H), 6.07 (s, 1H), 6.70 (d, J = 7.6 Hz, 1H), 7.03 (d, J = 8.0 Hz, 2H), 7.18 (t, J = 8.0 Hz, 3H), 7.67 (d, J = 8.0 Hz, 1H), 7.89 (s, 1H), 9.34 (s, 1H); ^{13}C NMR (100 MHz, DMSO): δ 25.8, 32.3, 44.4, 104.5 (t, J = 23.0 Hz), 118.5 (t, J = 243.0 Hz), 124.8, 127.2, 127.7, 132.3, 133.6, 133.8, 134.7, 136.0, 142.9, 145.0, 160.0 (t, J = 11.0 Hz), 171.6 (t, J = 30.0 Hz), 181.8; ^{19}F NMR (376 MHz, DMSO): δ −108.9. HRMS (ESI-TOF) calcd for $C_{22}H_{23}F_2N_2O_2$, $[M + H]^+$ m/z 385.1728, found 385.1729.

N-(3-(4,4-Difluoro-5-oxo-1-(p-tolyl)-4,5-dihydro-1H-pyrrol-2-yl)-phenyl)benzamide ***3q***. White solid (86.1 mg, 71%). Petroleum ether/ethyl acetate = 40/1 as eluent for column chromatography. Mp: 170−171 °C. ^{1}H NMR (400 MHz, DMSO): δ 2.28 (s, 3H), 6.10 (s, 1H), 6.82 (d, J = 7.6 Hz, 1H), 7.06 (d, J = 8.0 Hz, 2H), 7.19 (d, J = 8.0 Hz, 2H), 7.28 (t, J = 8.0 Hz, 1H), 7.55 (t, J = 7.6 Hz, 2H), 7.61 (t, J = 7.2 Hz, 1H), 7.79 (d, J = 8.0 Hz, 1H), 7.94 (d, J = 7.2 Hz, 2H), 8.00 (s, 1H), 10.39 (s, 1H); ^{13}C NMR (100 MHz, DMSO): δ 21.0, 99.9 (t, J = 23.0 Hz), 113.8 (t, J = 243.0 Hz), 120.1, 122.7, 123.6, 127.5, 128.1, 128.9, 129.2, 129.3, 130.0, 131.3, 132.2, 135.1, 138.1, 140.0, 155.2 (t, J = 11.0 Hz), 166.2, 166.9 (t, J = 30.0 Hz); ^{19}F NMR (376 MHz, DMSO): δ −108.8. HRMS (ESI-TOF) calcd for $C_{24}H_{19}F_2N_2O_2$, $[M + H]^+$ m/z 405.1415, found 405.1423.

tert-Butyl (3-(4,4-Difluoro-5-oxo-1-(p-tolyl)-4,5-dihydro-1H-pyrrol-2-yl)phenyl)carbamate ***3r***. White solid (76.8 mg, 64%). Petroleum ether/ethyl acetate = 40/1 as eluent for column chromatography. Mp: 147−148 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.51 (s, 9H), 2.31 (s, 3H), 5.63 (s, 1H), 6.48 (s, 1H), 6.69 (d, J = 7.6 Hz, 1H), 6.92 (d, J = 8.0 Hz, 2H), 7.10 (d, J = 8.0 Hz, 2H), 7.15 (d, J = 8.0 Hz, 1H), 7.29 (d, J = 8.0 Hz, 1H), 7.45 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.1, 28.3, 81.1, 100.1 (t, J = 23.0 Hz), 112.8 (t, J = 244.0 Hz), 117.6, 120.3, 122.4, 126.5, 129.0, 129.7, 130.9, 137.8, 138.8, 152.4, 154.3 (t, J = 11.0 Hz), 166.9 (t, J = 30.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ −110.2. HRMS (ESI-TOF) calcd for $C_{22}H_{23}F_2N_2O_3$, $[M + H]^+$ m/z 401.1677, found 401.1676.

3,3-Difluoro-5-(2-fluorophenyl)-1-(p-tolyl)-1H-pyrrol-2(3H)-one ***3s***. Colorless oil (53.6 mg, 59%). Petroleum ether/ethyl acetate = 60/1 as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.29 (s, 3H), 5.70 (s, 1H), 6.91 (d, J = 8.0 Hz, 2H), 7.00 (t, J = 9.2 Hz, 1H), 7.07 (d, J = 8.4 Hz, 2H), 7.11 (d, J = 7.6 Hz, 1H), 7.20 (t, J = 6.8 Hz, 1H), 7.35−7.40 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.1, 102.5 (dt, J_1 = 3.0 Hz, J_2 = 23.0 Hz), 112.5 (t, J = 245.0 Hz), 116.2 (d, J = 21.0 Hz), 117.3 (d, J = 14.0 Hz), 124.3 (d, J = 3.0 Hz), 126.1, 129.5, 130.2 (d, J = 2.0 Hz), 130.7, 132.6 (d, J = 8.0 Hz), 137.9, 149.7 (t, J = 11.0 Hz), 159.5 (d, J = 251.0 Hz), 166.1 (t, J = 30.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ −111.2, −110.0. HRMS (ESI-TOF) calcd for $C_{17}H_{13}F_3NO$, $[M + H]^+$ m/z 304,0949, found 304,0950.

5-(2-Chlorophenyl)-3,3-difluoro-1-(p-tolyl)-1H-pyrrol-2(3H)-one ***3t***. Colorless oil (52.6 mg, 55%). Petroleum ether/ethyl acetate = 60/1 as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.26 (s, 3H), 5.64 (d, J = 1.2 Hz, 1H), 6.90 (d, J = 6.8 Hz, 2H), 7.03 (d, J = 7.6 Hz, 2H), 7.24−7.32 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.0, 102.5 (t, J = 23.0 Hz), 112.6 (t, J = 245.0 Hz), 126.3, 126.9, 128.5, 129.4, 130.0, 130.4, 130.7, 131.6, 133.1, 137.9, 152.4 (t, J = 11.0 Hz), 165.9 (t, J = 30.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ −111.7. HRMS (ESI-TOF) calcd for $C_{17}H_{13}ClF_2NO$, $[M + H]^+$ m/z 320.0654, found 320.0652.

3,3-Difluoro-5-(thiophen-3-yl)-1-(p-tolyl)-1H-pyrrol-2(3H)-one ***3u***. White solid (62.9 mg, 72%). Petroleum ether/ethyl acetate = 60/1 as eluent for column chromatography. Mp: 76−78 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.39 (s, 3H), 5.66 (s, 1H), 6.95 (d, J = 5.2 Hz, 1H), 6.99 (s, 1H), 7.04 (d, J = 8.0 Hz, 2H), 7.21 (d, J = 8.0 Hz, 2H), 7.28 (d, J = 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.2, 98.0 (t, J = 23.0 Hz), 113.0 (t, J = 244.0 Hz), 126.4, 126.6, 127.3, 127.5, 129.4, 129.9, 131.1, 138.7, 149.2 (t, J = 11.0 Hz), 166.9 (t, J = 30.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ −109.6. HRMS (ESI-TOF) calcd for $C_{15}H_{12}F_2NOS$, $[M + H]^+$ m/z 292.0608, found 292.0610.

3,3-Difluoro-5-phenyl-1-(p-tolyl)-1H-pyrrol-2(3H)-one ***3v***. White solid (76.3 mg, 85%). Petroleum ether/ethyl acetate = 60/1 as eluent for column chromatography. Mp: 112−113 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.91 (t, J = 2.4 Hz, 3H), 2.27 (s, 3H), 6.84 (d, J = 8.4 Hz, 2H), 7.04 (d, J = 8.0 Hz, 2H), 7.11−7.13 (m, 2H), 7.28−7.36 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 7.1, 21.0, 108.5 (t, J = 22.0 Hz), 113.0 (t, J = 246.0 Hz), 126.4, 128.0, 128.4, 129.1, 129.5, 129.7, 131.0, 137.4, 146.2 (t, J = 10.0 Hz), 166.3 (t, J = 30.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ −116.8. HRMS (ESI-TOF) calcd for $C_{18}H_{16}F_2NO$, $[M + H]^+$ m/z 300.1200, found 300.1200.

3,3-Difluoro-5-phenyl-1-(p-tolyl)-1H-pyrrol-2(3H)-one ***3w***. Colorless oil (77.0 mg, 82%). Petroleum ether/ethyl acetate = 60/1 as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.20 (t, J = 7.6 Hz, 3H), 2.26 (s, 3H), 2.34 (q, J = 7.6 Hz, 3H), 6.85 (d, J = 8.0 Hz, 2H), 7.03 (d, J = 8.0 Hz, 2H), 7.13 (d, J = 6.4 Hz, 2H), 7.28−7.36 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.8, 16.4, 21.0, 113.8 (t, J = 246.0 Hz), 113.9 (t, J = 20.0 Hz), 126.4, 128.1, 128.4, 128.9, 129.4, 129.7, 130.9, 137.4, 146.6 (t, J = 10.0 Hz), 166.2 (t, J = 30.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ −114.4. HRMS (ESI-TOF) calcd for $C_{19}H_{18}F_2NO$, $[M + H]^+$ m/z 314.1356, found 314.1356.

3,3-Difluoro-1,5-diphenyl-1H-pyrrol-2(3H)-one ***4b***. Colorless oil (65.1 mg, 80%). Petroleum ether/ethyl acetate = 60/1 as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.66 (s, 1H), 7.04 (d, J = 6.8 Hz, 2H), 7.18 (d, J = 7.2 Hz, 2H), 7.27−7.33 (m, 5H), 7.38 (t, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 100.0 (t, J = 23.0 Hz), 112.8 (t, J = 244.0 Hz), 126.7, 127.8, 127.9, 128.5, 128.7, 129.0, 130.7, 133.5, 154.5 (t, J = 11.0 Hz), 166.7 (t, J = 30.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ −109.9. HRMS (ESI-TOF) calcd for $C_{16}H_{12}F_2NO$, $[M + H]^+$ m/z 272.0887, found 272.0888.

1-(4-Chlorophenyl)-3,3-difluoro-5-phenyl-1H-pyrrol-2(3H)-one ***4c***. Colorless oil (59.5 mg, 65%). Petroleum ether/ethyl acetate = 60/

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1 as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.66 (s, 1H), 6.96 (d, J = 8.4 Hz, 2H), 7.17 (d, J = 7.6 Hz, 2H), 7.27−7.34 (m, 4H), 7.41 (d, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 100.4 (t, J = 24.0 Hz), 112.7 (t, J = 244.0 Hz), 127.8, 127.9, 128.4, 128.7, 129.2, 130.9, 132.1, 133.6, 154.0 (t, J = 11.0 Hz), 166.5 (t, J = 30.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ −109.7. HRMS (ESI-TOF) calcd for $C_{16}H_{11}ClF_2NO$, $[M + H]^+$ m/z 306.0497, found 306.0487.

1-(4-Bromophenyl)-3,3-difluoro-5-phenyl-1H-pyrrol-2(3H)-one ***4d***. Colorless oil (71.0 mg, 68%). Petroleum ether/ethyl acetate = 60/1 as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.66 (s, 1H), 6.90 (d, J = 8.8 Hz, 2H), 7.17 (d, J = 7.6 Hz, 2H), 7.32 (d, J = 7.6 Hz, 2H), 7.40−7.45 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 100.5 (t, J = 24.0 Hz), 112.7 (t, J = 244.0 Hz), 121.6, 127.9, 128.1, 128.4, 128.7, 130.9, 132.2, 132.6, 154.0 (t, J = 11.0 Hz), 166.5 (t, J = 30.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ −109.7. HRMS (ESI-TOF) calcd for $C_{16}H_{11}BrF_2NO$, $[M + H]^+$ m/z 349.9992, found 349.9987.

1-(4-Ethylphenyl)-3,3-difluoro-5-phenyl-1H-pyrrol-2(3H)-one ***4e***. Colorless oil (75.3 mg, 84%). Petroleum ether/ethyl acetate = 60/1 as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.21 (t, J = 7.6 Hz, 3H), 2.62 (q, J = 7.6 Hz, 2H), 5.63 (s, 1H), 6.94 (d, J = 8.4 Hz, 2H), 7.14 (d, J = 8.0 Hz, 2H), 7.19 (d, J = 7.6 Hz, 2H), 7.29 (t, J = 7.6 Hz, 2H), 7.38 (t, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.2, 28.4, 99.8 (t, J = 23.0 Hz), 112.9 (t, J = 244.0 Hz), 126.5, 127.9, 128.4, 128.5, 128.8, 130.6, 131.1, 144.1, 154.6 (t, J = 11.0 Hz), 166.9 (t, J = 30.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ −110.0. HRMS (ESI-TOF) calcd for $C_{18}H_{16}F_2NO$, $[M + H]^+$ m/z 300.1200, found 300.1190.

1-(4-(tert-Butyl)phenyl)-3,3-difluoro-5-phenyl-1H-pyrrol-2(3H)-one ***4f***. White solid (81.4 mg, 83%). Petroleum ether/ethyl acetate = 60/1 as eluent for column chromatography. Mp: 121−123 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.29 (s, 9H), 5.65 (s, 1H), 6.96 (d, J = 8.4 Hz, 2H), 7.20 (d, J = 7.6 Hz, 2H), 7.28−7.34 (m, 4H), 7.39 (t, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 31.2, 34.6, 99.8 (t, J = 23.0 Hz), 112.9 (t, J = 244.0 Hz), 125.9, 126.1, 127.9, 128.4, 128.8, 130.6, 130.8, 151.0, 154.6 (t, J = 11.0 Hz), 166.9 (t, J = 30.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ −110.0. HRMS (ESI-TOF) calcd for $C_{20}H_{20}F_2NO$, $[M + H]^+$ m/z 328.1513, found 328.1518.

3,3-Difluoro-1-(4-methoxyphenyl)-5-phenyl-1H-pyrrol-2(3H)-one ***4g***. White solid (77.7 mg, 86%). Petroleum ether/ethyl acetate = 60/1 as eluent for column chromatography. Mp: 142−143 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.78 (s, 3H), 5.62 (s, 1H), 6.82 (d, J = 8.8 Hz, 2H), 6.96 (d, J = 8.8 Hz, 2H), 7.18 (d, J = 7.6 Hz, 2H), 7.29 (t, J = 7.6 Hz, 2H), 7.38 (t, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.4, 99.6 (t, J = 23.0 Hz), 112.8 (t, J = 244.0 Hz), 114.3, 126.2, 128.0, 128.0, 128.5, 128.7, 130.6, 154.6 (t, J = 11.0 Hz), 159.0, 167.0 (t, J = 30.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ −110.2. HRMS (ESI-TOF) calcd for $C_{17}H_{14}F_2NO_2$, $[M + H]^+$ m/z 302.0993, found 302.0984.

3,3-Difluoro-5-phenyl-1-(m-tolyl)-1H-pyrrol-2(3H)-one ***4h***. Colorless oil (71.9 mg, 84%). Petroleum ether/ethyl acetate = 60/1 as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.30 (s, 3H), 5.65 (s, 1H), 6.77 (d, J = 7.6 Hz, 1H), 6.94 (s, 1H), 7.10 (d, J = 7.2 Hz, 1H), 7.16−7.21 (m, 3H), 7.30 (t, J = 7.6 Hz, 2H), 7.39 (t, J = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.2, 99.8 (t, J = 23.0 Hz), 112.8 (t, J = 244.0 Hz), 123.7, 127.3, 127.9, 128.4, 128.7, 128.8, 130.6, 133.5, 139.1, 154.6 (t, J = 11.0 Hz), 166.8 (t, J = 30.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ −110.0. HRMS (ESI-TOF) calcd for $C_{17}H_{14}F_2NO$, $[M + H]^+$ m/z 286.1043, found 286.1033.

3,3-Difluoro-5-phenyl-1-(o-tolyl)-1H-pyrrol-2(3H)-one ***4i***. Colorless oil (62.4 mg, 73%). Petroleum ether/ethyl acetate = 60/1 as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.19 (s, 3H), 5.66 (d, J = 2.0 Hz, 1H), 6.95 (d, J = 8.0 Hz, 1H), 7.14 (d, J = 7.2 Hz, 3H), 7.23−7.27 (m, 4H), 7.35 (t, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.9, 99.3 (t, J = 23.0 Hz), 112.8 (t, J = 244.0 Hz), 126.8, 127.6, 128.5, 128.5, 128.8, 129.1, 130.7, 131.3, 132.8, 136.3, 154.9 (t, J = 11.0 Hz), 166.7 (t, J = 30.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ −110.6. HRMS (ESI-TOF) calcd for $C_{17}H_{14}F_2NO$, $[M + H]^+$ m/z 286.1043, found 286.1045.

1-(3,4-Dimethoxyphenyl)-3,3-difluoro-5-phenyl-1H-pyrrol-2(3H)-one ***4j***. Colorless oil (75.0 mg, 83%). Petroleum ether/ethyl acetate = 60/1 as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.52 (s, 3H), 5.59 (s, 1H), 6.80 (d, J = 8.4 Hz, 1H), 6.98 (t, J = 7.6 Hz, 1H), 7.19−7.35 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.3, 98.5 (t, J = 23.0 Hz), 112.1, 113.0 (t, J = 244.0 Hz), 120.8, 122.5, 127.1, 128.1, 129.5, 129.6, 130.2, 130.2, 154.9, 155.7 (t, J = 11.0 Hz), 167.2 (t, J = 30.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ −111.1 (d, J = 304.6 Hz, 1F), −109.4 (d, J = 300.8 Hz, 1F) calcd for $C_{17}H_{14}F_2NO_2$, $[M + H]^+$ m/z 302.0993, found 302.0991.

1-(3,4-Dimethoxyphenyl)-3,3-difluoro-5-phenyl-1H-pyrrol-2(3H)-one ***4k***. White solid (88.4 mg, 89%). Petroleum ether/ethyl acetate = 60/1 as eluent for column chromatography. Mp: 130−131 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.68 (s, 3H), 3.84 (s, 3H), 5.63 (d, J = 2.0 Hz, 1H), 6.51 (d, J = 2.4 Hz, 1H), 6.61 (dd, J_1 = 2.4 Hz, J_2 = 8.8 Hz, 1H), 6.77 (d, J = 8.4 Hz, 1H), 7.19 (t, J = 7.2 Hz, 2H), 7.29 (t, J = 7.6 Hz, 2H), 7.38 (t, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.9, 55.9, 99.5 (t, J = 23.0 Hz), 110.4, 110.9, 112.8 (t, J = 244.0 Hz), 119.3, 126.3, 127.9, 128.4, 128.8, 130.5, 148.5, 149.0, 154.6 (t, J = 11.0 Hz), 166.8 (t, J = 30.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ −110.2. HRMS (ESI-TOF) calcd for $C_{18}H_{16}F_2NO_3$, $[M + H]^+$ m/z 332.1098, found 332.1096.

1-Benzyl-3,3-difluoro-5-phenyl-1H-pyrrol-2(3H)-one ***4l***. Colorless oil (58.2 mg, 68%). Petroleum ether/ethyl acetate = 70/1 as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.65 (s, 2H), 5.42 (s, 1H), 6.89−6.92 (m, 2H), 7.20−7.23 (m, 5H), 7.38 (t, J = 7.2 Hz, 2H), 7.47 (t, J = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 44.4, 100.0 (t, J = 23.0 Hz), 113.0 (t, J = 244.0 Hz), 127.2, 127.7, 127.9, 128.7, 128.7, 129.0, 130.7, 135.8, 155.0 (t, J = 11.0 Hz), 168.1 (t, J = 30.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ −112.2. HRMS (ESI-TOF) calcd for $C_{17}H_{14}F_2NO$, $[M + H]^+$ m/z 286.1043, found 286.1037.

3,3-Difluoro-1-phenethyl-5-phenyl-1H-pyrrol-2(3H)-one ***4m***. Colorless oil (56.6 mg, 63%). Petroleum ether/ethyl acetate = 70/1 as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.68 (t, J = 7.2 Hz, 2H), 3.70 (t, J = 7.2 Hz, 2H), 5.33 (s, 1H), 6.91−6.93 (m, 2H), 7.20−7.26 (m, 5H), 7.43−7.53 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 34.3, 42.3, 99.7 (t, J = 23.0 Hz), 112.8 (t, J = 244.0 Hz), 126.7, 127.7, 128.6, 128.8, 128.9, 129.0, 130.6, 137.3, 154.9 (t, J = 11.0 Hz), 167.9 (t, J = 30.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ −112.8. HRMS (ESI-TOF) calcd for $C_{18}H_{16}F_2NO$, $[M + H]^+$ m/z 300.1200, found 300.1204.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.7b01313.

^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra for compounds **1**, **2**, **3**, and **4** (PDF)

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The authors declare no competing financial interest.

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