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A novel approach of cycloaddition of difluorocarbene to α,β-unsaturated aldehydes and ketones: synthesis of *gem*-difluorocyclopropyl ketones and 2-fluorofurans

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A series of *gem*-difluorocyclopropyl acetals and ketals are easily obtained in moderate yields from the [1+2] cycloaddition of difluorocarbene to 1,3-dioxolanes of α,β-unsaturated aromatic aldehydes and ketones. Hydrolysis of these fluorinated compounds under acidic conditions either gives the corresponding *gem*-difluorocyclopropyl ketones or 1-aryl-2-fluorofuran derivatives through intramolecular carbonium rearrangement with simultaneous ring cleavage.

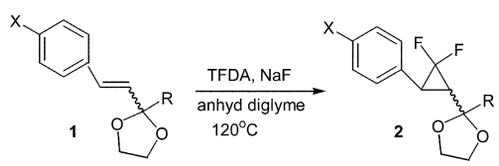
Introduction

Difluorocarbene addition to an olefin is a fundamental reaction for the preparation of difluorocyclopropane derivatives.[1] Although electron-rich alkenes react readily with difluorocarbene under mild conditions, there are only a few difluorocarbene reagents that have been found to react with electron-deficient alkenes to give reasonable yields of *gem*-difluorocyclopropanes.[2] Using electron-poor steroidal enones and dienones, Beard *et al*. first carried out their cycloaddition with difluorocarbene generated from high temperature (150–180 °C) thermolysis of a large excess (50 equiv.) of sodium chlorodifluoroacetate.[3] Due to the inconvenience and low yields of this method, Kobayashi *et al*. prepared *gem*-difluorocyclopropyl ketones through a three-step procedure, *i.e.* addition of difluorocarbene to the allyl acetate, alkaline hydrolysis and Jones oxidation, instead of the direct difluoromethylenation of α,β-unsaturated ketones.[4] Recently, a highly efficient difluorocarbene precursor, $FSO_2CF_2COOSiMe_3$ (TFDA) was reported, by which an unprecedented difluorocarbene addition to electron-poor *n*-butyl acrylate proceeded in 73% yield.[5] The superiority of the new reagent over $ClCF_2COONa$ was also demonstrated in the synthesis of bis- and oligo-*gem*-difluorocyclopropanes.[6] However, we found that TFDA did not react with α,β-unsaturated aldehydes and ketones under the reaction conditions used (*i.e.* in the presence of 10 mol% of NaF in diglyme at 120 °C).[7] It is not surprising that the nucleophilic character of the enone carbon–carbon double bond is considerably reduced by electron delocalization with the carbonyl group, resulting in lower reactivity towards the electrophilic difluorocarbene species.[8] In order to overcome the difficulty, a protection and deprotection of enone carbonyl group might be an alternative choice.

We, herein, present the results of cycloaddition of difluorocarbene generated from decomposition of TFDA to protected α,β-unsaturated aldehydes and ketones followed by deprotection with acidic hydrolysis.

Results and discussion

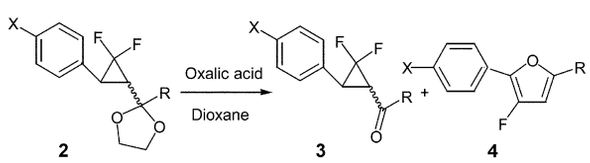
Treatment of 1,3-dioxolanes of α,β-unsaturated aromatic aldehydes and ketones (**1**) with TFDA (3 equiv.) in diglyme in the presence of 10 mol% anhydrous NaF at 110–130 °C for about 2 h gave the corresponding [1+2] adducts (**2**) in moderate to good yields (Scheme 1).



Scheme 1 X = H, R = H (**a**); X = Cl, R = H (**b**); X = CH_3O, R = H (**c**); X = CH_3, R = H (**d**); X = CF_3, R = H (**e**); X = H, R = CH_3 (**f**); X = Cl, R = CH_3 (**g**); X = CH_3O, R = CH_3 (**h**); X = CH_3, R = CH_3 (**i**); X = CF_3, R = CH_3 (**j**); X = CH_3O, R = C_6H_5 (**k**); X = CH_3, R = C_6H_5 (**l**); X = H, R = C_6H_5 (**m**); X = Cl, R = C_6H_5 (**n**); X = CF_3, R = C_6H_5 (**o**); X = C_6H_5, R = 4-CH_3–C_6H_4 (**p**); X = C_6H_5, R = 4-CH_3O–C_6H_4 (**q**).

The results are listed in Table 1.

Unexpectedly, the following deprotection step was not easy. Employing usual deprotection conditions for 1,3-dioxolanes, *e.g.* HCl–acetone/rt, HCl–methanol/rt, HCl–THF/rt, **2** could not be converted to the corresponding aldehydes and ketones and were recovered completely. Interestingly, it was found that deprotection was achieved by treatment with saturated oxalic acid solution in dioxane at 110 °C for 6 h.[9] The products based on ^1H, ^{19}F NMR, MS as well as elemental analysis were *gem*-difluorocyclopropyl ketones (**3**) and /or 1-aryl-2-fluorofurans (**4**) (Scheme 2).



Scheme 2

The results are listed in Table 2.

Compound **4k** was crystallized from a mixture of petroleum ether and dichloromethane, and its structure was confirmed by single crystal X-ray analysis (Fig. 1).

The results shown in Table 2 demonstrated that the normal products **3** after acidic hydrolysis were obtained for almost all of the β-aryl-*gem*-difluorocyclopropyl ketals (Table 2, entries 13–17) except for those compounds having an electron-donating group (CH_3O, CH_3) on the β-phenyl ring (Table 2, entries 11,12). 1-Aryl-2-fluorofurans (**4**) were the only isolated products derived from the hydrolysis of β-aryl *gem*-difluorocyclopropylacetals (**2**, R = H) (Table 2, entries 1–4) except the compound possessing a strong electron withdrawing group

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Table 1 Cycloaddition of difluorocarbene to acetals and ketals of α,β-unsaturated aromatic aldehydes and ketones

Entry	Substrate	X	R	T/°C[a]	Time/h	Product	Isolated yield (%)
1	**1a**	H	H	118	1	**2a**	68
2	**1b**	Cl	H	126	2	**2b**	59
3	**1c**	CH_3O	H	124	0.5	**2c**	72
4	**1d**	CH_3	H	120	1	**2d**	67
5	**1e**	CF_3	H	128	1	**2e**	51
6	**1f**	H	CH_3	112	0.5	**2f**	49
7	**1g**	Cl	CH_3	118	2	**2g**	48
8	**1h**	CH_3O	CH_3	115	0.5	**2h**	54
9	**1i**	CH_3	CH_3	122	1	**2i**	62
10	**1j**	CF_3	CH_3	124	2	**2j**	42
11	**1k**	CH_3O	C_6H_5	120	0.5	**2k**	61
12	**1l**	CH_3	C_6H_5	122	1.5	**2l**	65
13	**1m**	H	C_6H_5	118	1	**2m**	42
14	**1n**	Cl	C_6H_5	128	1	**2n**	48
15	**1o**	CF_3	C_6H_5	126	1	**2o**	40
16	**1p**	C_6H_5	4-$CH_3C_6H_4$	128	0.5	**2p**	60
17	**1q**	C_6H_5	4-$CH_3OC_6H_4$	132	2	**2q**	64

[a] Oil bath temperature

Table 2 Hydrolysis of *gem*-difluorocyclopropyl acetals and ketals with saturated oxalic acid solution in dioxane at 110 °C for 6 h

Entry	Substrate	X	R	Product	Yield (%)
1	**2a**	H	H	**4a**	21
2	**2b**	Cl	H	**4b**	21
3	**2c**	CH_3O	H	**4c**	26
4	**2d**	CH_3	H	**4d**	27
5	**2e**	CF_3	H	**4e**, **3e**	1 (**4e**), 55 (**3e**)
6	**2f**	H	CH_3	**4f**	47
7	**2g**	Cl	CH_3	**4g**, **3g**	1(**4g**), 64 (**3g**)
8	**2h**	CH_3O	CH_3	**4h**	52
9	**2i**	CH_3	CH_3	**4i**	50
10	**2j**	CF_3	CH_3	**3j**	69
11	**2k**	CH_3O	C_6H_5	**4k**	55
12	**2l**	CH_3	C_6H_5	**4l**, **3l**	15 (**4l**), 36 (**3l**)
13	**2m**	H	C_6H_5	**3m**	78
14	**2n**	Cl	C_6H_5	**3n**	54
15	**2o**	CF_3	C_6H_5	**3o**	43
16	**2p**	C_6H_5	4-$CH_3C_6H_4$	**4p**, **3p**	2(**4p**), 60(**3p**)
17	**2q**	C_6H_5	4-$CH_3OC_6H_4$	**4q**, **3q**	2(**4q**), 58(**3q**)

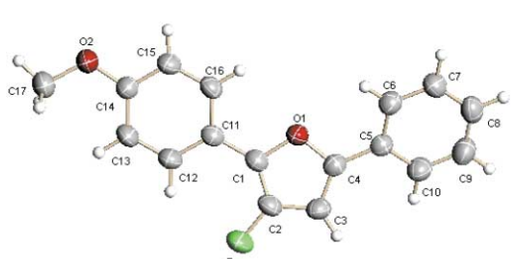
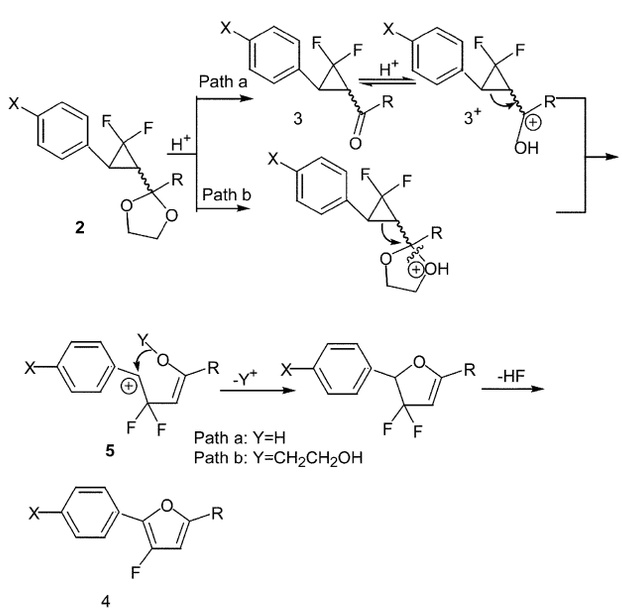


Fig. 1 X-Ray structure of **4k**. Selected bond lengths (Å), bond angles (°) and torsion angles (°): C (1)–C(2), 1.351(2); C(1)–C(11), 1.4474 (19); C(2)–C(3), 1.391(2); O(1)–C(1), 1.3770(16); O(1)–C(4), 1.3740(16); F–C(2), 1.3525(17); C(2)–C(3), 1.391(2); C(3)–C(4), 1.347(2); C(4)–C(5) 1.4523(19); C(4)–O(1)–C(1), 108.35(11); C(14)–O(2)–C(17), 117.70(13); C(2)–C(1)–O(1), 106.03(12); C(1)–C(2)–F, 124.62(14); F–C(2)–C(3), 124.79(14).

(CF_3) at the *para* position of the β-phenyl ring (Table 2, entry 5), As for the β-aryl-*gem*-difluorocyclopropylmethyl ketals (**2**, R = CH_3), the ratio of normal products (**3**) to furan derivatives (**4**) obtained is dependent on the electronic property of the substitute on the β-phenyl ring; *i.e.* for an electron-donating group, furan derivatives (**4**, R = CH_3, Table 2, entries 6, 8, 9) were the sole products, whereas for an electron-withdrawing group, the normal ketone was dominantly, if not exclusively, produced (Table 2, entries 5, 7, 10).

All these results might be rationalized as follows: after deprotection of **2**, β-aryl-*gem*-difluorocyclopropyl aldehydes and ketones (**3**) might be protonated on carbonyl oxygen to give a carbonium ion ($\mathbf{3}^+$) whose reactivity depends on the properties of R and the substituent X on the β-phenyl ring (Scheme 3).

The carbocation of aldehyde (R = H) and methyl ketones (R = CH_3), ($\mathbf{3}^+$) generated undergoes an intramolecular shift easily with simultaneous collapse of the carbon–carbon bond



Scheme 3 Proposed mechanism.

opposite to the *gem*-difluoromethyl group[10] followed by an attack of enol oxygen on the resultant carbonium ion **5** (Y = H) to yield β-fluorofuran derivatives after HF elimination (Path a).

An alternative mechanism suggested by one of the referees of this manuscript is that cyclopropane ring opening occurs during the protonation of **2** with the direct formation of a new cation **5** (Y = CH_2CH_2OH) instead of $\mathbf{3}^+$ (Path b).

This process, apparently, proceeds readily when the substituent on the β-phenyl ring is an electron-donating or even a weak electron-withdrawing group (X = CH_3, CH_3O, H, Cl). On the contrary, if a strong electron-withdrawing group (X = CF_3, Cl) is present on the β-phenyl ring, the carbocation intramolecular shift does not take place or proceeds with difficultly.

As for the aryl ketones (R = C_6H_5, *p*-$CH_3C_6H_4$, *p*-$CH_3OC_6H_4$), due to the participation of the aryl group, their carbocations ($\mathbf{3}^+$) are stable and do not rearrange, therefore, aryl ketones are regenerated unless an electron-donating group (CH_3, CH_3O) on the β-phenyl ring is present, in which case the β-fluorofuran derivative is also formed and even becomes the only product.

The study on the reaction of simple α,β-unsaturated aliphatic aldehydes and ketones (RCH=CHCRO, R = H, alkyl) with TFDA is in progress.

In conclusion, we have developed a simple method for the synthesis of β-aryl *gem*-difluorocyclopropyl ketones and 1-aryl-2-fluorofurans from the reactions of protected α,β-unsaturated aldehydes and ketones with an easily available difluorocarbene precursor, $FSO_2CF_2COOSiMe_3$.

Experimental section

^{1}H NMR spectra were recorded with TMS as an internal standard (positive for upfield). ^{19}F NMR spectra were recorded with $CFCl_3$ as an external standard (negative for upfield). The solvent for NMR measurement was $CDCl_3$. Diglyme was dried with sodium, $FSO_2CF_2COOSiMe_3$ (TFDA) was prepared according to the literature.[5] Aldehydes are commercially available, whereas all α,β-unsaturated ketones were prepared following published procedures.[11] 1,3-Dioxane of α,β-unsaturated aldehydes are prepared according to published methods.[12,13]

Synthesis of 1,3-dioxane of α,β-unsaturated ketones[14]

A typical procedure: in a 250 ml flask equipped with a Dean–Stark adaptor and a condenser was placed 4-phenyl-3-butene-2-one (1.56 g, 10.7 mmol), ethylene glycol (9.3 ml), 2-ethyl-2-methyl-1,3-dioxolane[15] (9.3 ml), PTSA (93 mg) and benzene (150 ml). The mixture was heated to reflux for 12 h. After the mixture was cooled to room temperature, saturated Na_2CO_3 (20 ml) was added and stirred for 15 minutes. The organic layer was separated and the aqueous was extracted with ether. The combined organic phase was washed with brine and dried over Na_2SO_4. The solvent was removed and the residue was purified by flash chromatography on a silica gel column. Ketal **1f** was obtained as a pale yellow liquid (1.24 g, 61%) with spectroscopic data identical to that reported previously.[16] Compound **1m** (71% yield) was determined by the published spectroscopic data.[17]

Compound **1g**: yellow liquid, 64%. IR (film) (cm^{-1}): 2987, 2885, 1655, 1594, 1492, 1406, 1374, 1215, 1195, 1095, 1043. ^{1}H NMR ($CDCl_3$) δ 1.55 (s, 3H), 3.93–4.02 (m, 4H), 6.13 (d, J = 16.2 Hz, 1H), 6.66 (d, J = 16.5 Hz, 1H), 7.26–7.31 (m, 4H). MS *m*/*z* (relative intensity) 224 (M^+, 5.14), 209 (100.00), 174 (1.54), 165 (41.73), 137 (14.92), 102 (13.16), 87 (13.04). Anal. Calcd for $C_{12}H_{13}ClO_2$: C, 64.15; H, 5.83. Found, C, 64.33; H, 6.50%.

Compound **1h**: white solid, mp 50–51 °C, 65% yield. IR (film) (cm^{-1}): 2989, 2934, 2896, 1655, 1606, 1578, 1512, 1442, 1307, 1274, 1247, 1175, 1101, 1031. ^{1}H NMR ($CDCl_3$) δ 1.56 (s, 3H), 3.81 (s, 3H), 3.94–4.02 (m, 4H), 6.02 (d, J = 18.6 Hz, 1H), 6.65 (d, J = 15.9 Hz, 1H), 6.84–6.87 (m, 2H), 7.32–7.35 (m, 2H). MS *m*/*z* (relative intensity) 220 (M^+, 7.59), 205 (100.00), 189 (1.82), 175 (2.87), 161 (40.34), 148 (11.09), 133 (14.93), 102 (3.57), 87 (13.04). Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32. Found, C, 70.92; H, 7.39%.

Compound **1i**: yellow liquid, 88% yield. IR (film) (cm^{-1}): 2987, 2885, 1515, 1373, 1297, 1197, 1100, 1074, 1042. ^{1}H NMR ($CDCl_3$) δ 1.58 (s, 3H), 2.35 (s, 3H), 3.93–4.05 (m, 4H), 6.12 (d, J = 16.2 Hz, 1H), 6.69 (d, J = 15.9 Hz, 1H), 7.14 (d, J = 7.8 Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H). MS *m*/*z* (relative intensity) 204 (M^+, 1.53), 189 (100.00), 173 (0.89), 159 (2.93), 145 (35.95), 117 (16.36), 91 (10.09). Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found, C, 76.65; H, 8.31%.

Compound **1j**: yellow liquid, 95% yield. IR (film) (cm^{-1}): 2986, 2886, 1618, 1415, 1376, 1327, 1201, 1167, 1127, 1069, 1043. ^{1}H NMR ($CDCl_3$) δ 1.57 (s, 3H), 3.92–4.04 (m, 4H), 6.25 (d, J = 15.9 Hz, 1H), 6.74 (d, J = 15.9 Hz, 1H), 7.47–7.59 (m, 4H). MS *m*/*z* (relative intensity) 258 (M^+, 5.12), 243 (100.00), 199 (47.10), 171 (20.18), 87 (18.04). Anal. Calcd for $C_{13}H_{13}F_3O_2$: C, 60.46; H, 5.07. Found: C, 60.51; H, 4.94%.

Compound **1k**: solid, mp 76–77 °C, 75% yield. IR (film) (cm^{-1}): 2980, 2965, 2895, 1654, 1606, 1575, 1514, 1310, 1285, 1245, 1176, 1152, 1046, 1023. ^{1}H NMR ($CDCl_3$) δ 3.80 (s, 3H), 3.98–4.12 (m, 4H), 6.22 (d, J = 15.9 Hz, 1H), 6.61 (d, J = 15.9 Hz, 1H), 6.83 (d, J = 8.7 Hz, 2H), 7.30–7.37 (m, 5H), 7.54–7.57 (m, 2H). MS *m*/*z* (relative intensity) 282 (M^+, 10.82), 251 (1.20), 221 (51.04), 210 (100.00), 205 (25.77), 195 (11.03), 149 (30.15), 105 (34.19), 77 (21.94). Anal. Calcd for $C_{18}H_{18}O_3$: C, 76.57; H, 6.43. Found: C, 76.53; H, 6.41%.

Compound **1l**: solid, mp 61–62 °C, 77% yield. IR (film) (cm^{-1}): 2895, 1665, 1600, 1514, 1447, 1338, 1223, 1155, 1044. ^{1}H NMR ($CDCl_3$) δ 2.32 (s, 3H), 3.99–4.13 (m, 4H), 6.30 (d, J = 16.2 Hz, 1H), 6.65 (d, J = 15.9 Hz, 1H), 7.09–7.58 (m, 9H). MS *m*/*z* (relative intensity) 266 (M^+, 36.59), 251 (0.78), 221 (47.89), 207 (100.00), 194 (84.58), 189 (35.67), 179 (46.81), 145 (42.81), 105 (39.68), 91 (22.03), 77 (50.20). Anal. Calcd for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81; Found: C, 81.04; H, 6.87%.

Compound **1n**: pale yellow solid, mp 66–67 °C, 90% yield. IR (film) (cm^{-1}): 2890, 1658, 1592, 1489, 1332, 1219, 1160, 1049. ^{1}H NMR ($CDCl_3$) δ 3.96–4.14 (m, 4H), 6.33 (d, J = 15.9 Hz, 1H), 6.64 (d, J = 15.6 Hz, 1H), 7.23–7.60 (m, 9H). MS *m*/*z* (relative intensity) 286 (M^+, 12.86), 241 (6.84), 214 (49.63), 189 (18.38), 179 (46.58), 165 (31.57), 149 (28.95), 105 (55.48), 77 (100.00). HRMS. Calcd for $C_{17}H_{15}ClO_2$: 286.0761. Found: 286.0766.

Compound **1o**: white solid, mp 79–80 °C, 82% yield. IR (film) (cm^{-1}): 2897, 1664, 1615, 1448, 1416, 1324, 1168, 1110, 1067. ^{1}H NMR ($CDCl_3$) δ 3.98–4.14 (m, 4H), 6.45 (d, J = 15.9 Hz, 1H), 6.73 (d, J = 15.6 Hz, 1H), 7.36–7.58 (m, 9H). ^{19} F NMR ($CDCl_3$) δ −62.5 (s, 3F). MS *m*/*z* (relative intensity) 320 (M^+, 45.41), 276 (17.89), 248 (52.70), 207 (19.99), 189 (27.60), 175 (19.98), 149 (85.63), 105 (100.00), 77 (77.41). Anal. Calcd for $C_{18}H_{15}F_3O_2$: C, 67.50; H, 4.72. Found: C, 67.80; H, 4.40%.

Compound **1p**, white solid, mp 70–71 °C, 82% yield. IR (film) (cm^{-1}): 2984, 2949, 2891, 1650, 1614, 1577, 1511, 1495, 1450, 1278, 1246, 1182, 1143, 1054, 1020. ^{1}H NMR ($CDCl_3$) δ 2.36 (s, 3H), 3.99–4.12 (m, 4H), 6.35 (d, J = 15.9 Hz, 1H), 6.69 (d, J = 15.9 Hz, 1H), 7.17–7.49 (m, 9H). MS *m*/*z* (relative intensity) 266 (M^+, 21.26), 251 (0.95), 221 (51.04), 194 (100.00), 179 (55.16), 131(26.64), 119 (44.69). Anal. Calcd for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 81.16; H, 6.91%.

Compound **1q**: colorless liquid, 42%. ^{1}H NMR ($CDCl_3$) δ 3.81 (s, 3H), 3.97–4.13 (m, 4H), 6.35 (d, J = 15.9 Hz, 1H), 6.67 (d, J = 15.9 Hz, 1H), 6.88–6.91 (m, 2H), 7.23–7.40 (m, 5H), 7.47–7.50 (m, 2H). MS *m*/*z* (relative intensity) 282 (M^+, 15.17), 210 (100.00), 205 (7.91), 179 (18.50), 175 (9.25), 131 (8.21), 103 (11.11), 77 (19.22). Anal. Calcd for $C_{18}H_{18}O_3$: C, 76.57; H, 6.43. Found: C, 81.16; H, 6.91%.

Synthesis of *gem*-difluoropropyl acetals and ketals

A typical procedure: under a nitrogen atmosphere, in a 10 ml side-armed Pyrex tube with a magnetic stirring bar and a pressure-equalized addition funnel, was placed acetal (**1a**) (1.82 g, 10.33 mmol), sodium fluoride (43 mg, 1.03 mmol) and diglyme (1 ml). After heating the mixture to about 120 °C (bath), TFDA (7.76 g, 30.98 mmol) was added dropwise. The mixture was stirred at this temperature for 1 h. Then the reaction was cooled to room temperature and directly purified by flash chromatography on a silica gel column. Title product (**2a**) (1.60 g, 68%) was obtained as a pale yellow liquid (eluent: petroleum ether–ether = 10 : 1).

Compound **2a**: liquid, IR (film) (cm^{-1}): 2893, 1679, 1504, 1475, 1448, 1259, 1217, 1176, 1021, 1003. ^1H NMR ($CDCl_3$) δ 2.10–2.16 (m, 1H), 2.85–2.91 (m, 1H), 3.90–4.06 (m, 4H), 5.00 (d, J = 6.0 Hz, 1 H), 7.24–7.34 (m, 5H). ^{19}F NMR ($CDCl_3$) δ −134.6 (dd, J = 163.3, 15.8 Hz, 1 F), −137.0 (dd, J = 164.4, 15.5 Hz, 1 F). MS *m*/*z* (relative intensity) 226 (M^+, 1.60), 207 (1.56), 183 (0.58), 164 (4.83), 153 (2.97), 133 (16.04), 77 (6.51), 73 (100.00). HRMS. Calcd for $C_{12}H_{12}F_2O_2$: 226.0805, Found 226.0805.

Compound **2b**: liquid, IR (film) (cm^{-1}): 2894, 1683, 1500, 1400, 1260, 1176, 1093, 1004. ^1H NMR ($CDCl_3$) δ 2.05–2.14 (m, 1H), 2.81–2.97 (m, 1H), 3.90–4.06 (m, 4H), 4.46 (d, J = 8.1 Hz, 0.31 H), 4.99 (d, J = 5.7 Hz, 0.69 H), 7.17–7.39 (m, 4H). ^{19}F NMR ($CDCl_3$) δ −134.6 (dd, J = 163.3, 15.8 Hz, 1 F), −137.0 (dd, J = 164.4, 15.5 Hz, 1 F). MS *m*/*z* (relative intensity) 260 (M^+, 0.55), 225 (1.76), 187 (3.67), 165 (17.66), 137 (10.63), 131 (50.33), 103 (25.60), 73 (100.00). HRMS. Calcd for $C_{12}H_{11}ClF_2O_2$: 260.0416, Found 260.0371. Anal. Calcd for $C_{12}H_{11}F_2O_2$: C, 55.29; H, 4.25; F, 14.58. Found: C, 55.49; H, 4.24; F, 14.36%.

Compound **2c**: pale yellow liquid, IR (film) (cm^{-1}): 2897, 1614, 1519, 1251, 1178, 1033. ^1H NMR ($CDCl_3$) δ 2.04–2.10 (m, 1H), 2.79–2.87 (m, 1H), 3.78 (s, 3H), 3.90–4.08 (m, 4H), 4.49 (d, J = 8.1 Hz, 0.32 H), 4.97 (d, J = 6.3 Hz, 0.68 H), 6.84–6.87 (m, 2H), 7.16–7.36 (m, 2H). ^{19}F NMR ($CDCl_3$) δ −122.5 (dd, J = 165.3, 14.4 Hz, 0.32 F), −134.9 (dd, J = 159.0, 13.5 Hz, 0.68 F), −137.1 (dd, J = 163.6, 13.5 Hz, 0.68 F), −145.8 (d, J = 165.0 Hz, 0.32 F). MS *m*/*z* (relative intensity) 256 (M^+, 1.73), 183 (4.48), 139 (49.32), 77 (8.52), 73 (100.00). Anal. Calcd for $C_{13}H_{14}F_2O_3$: C, 60.93; H, 5.51; F, 14.83. Found: C, 60.59; H, 6.02; F, 14.55%.

Compound **2d**: pale yellow liquid, IR (film) (cm^{-1}): 2959, 2893, 1521, 1473, 1402, 1328, 1259, 1220, 1175, 1098, 1026, 1004. ^1H NMR($CDCl_3$) δ 2.05–2.14 (m, 1H), 2.33 (s, 3H), 2.81–2.88 (m, 1H), 3.90–4.07 (m, 4H), 4.98 (d, J = 6.0 Hz, 1H), 7.15 (s, 4H). ^{19}F NMR ($CDCl_3$) δ −134.3 (dd, J = 159.6 Hz, 15.2 Hz, 1F), −136.6 (dd, J = 159.3 Hz, 14.4 Hz, 1F). MS *m*/*z* (relative intensity) 240 (M^+, 1.04), 225 (0.33), 167 (1.37), 147 (4.97), 73 (100.00). Anal. Calcd for $C_{13}H_{14}F_2O_2$: C, 64.99; H, 5.87; F, 15.82. Found: C, 65.07; H, 5.96; F, 15.84%.

Compound **2e**: yellow liquid, IR (film) (cm^{-1}): 2964, 2897, 1686, 1623, 1584, 1525, 1476, 1413, 1329, 1262, 1169, 1127, 1070, 1021. ^1H NMR($CDCl_3$) δ 2.12–2.22 (m, 1H), 2.89–2.97 (m, 1H), 3.83–4.10 (m, 4H), 7.35–7.60 (m, 4H). ^{19}F NMR ($CDCl_3$) δ −134.1 (dd, J = 161.6 Hz, 13.0 Hz, 1F), −136.2 (dd, J = 162.7, 13.8 Hz, 1F), −62.60 (s, 3F). MS *m*/*z* (relative intensity) 294 (M^+, 0.55), 293 (0.61), 275 (2.23), 232 (1.78), 221 (1.73), 201 (6.48), 145 (2.24), 73 (100.00), 69 (2.03). Anal. Calcd for $C_{13}H_{11}F_5O_2$: C, 53.07; H, 3.77; F, 32.29. Found: C, 52.60; H, 3.63; F, 32.53%.

Compound **2f**: liquid, IR (film) (cm^{-1}): 2989, 2891, 1670, 1609, 1504, 1446, 1327, 1221, 1039. ^1H NMR ($CDCl_3$) δ 1.56 (s, 3H), 2.11–2.19 (m, 1H), 2.91–2.98 (m, 1H), 3.93–4.08 (m, 4H), 7.23–7.39 (m, 5H). ^{19}F NMR ($CDCl_3$) δ −133.6 (dd, J = 159.3, 17.2 Hz, 1 F), −135.9 (dd, J = 162.2, 14.9 Hz, 1 F). MS *m*/*z* (relative intensity) 240 (M^+, 0.84), 225 (1.58), 190 (0.50), 175 (7.83), 133 (12.14), 87 (89.56), 43 (100.00). HRMS. Calcd for $C_{13}H_{14}F_2O_2$: 240.0962, Found 240.0925.

Compound **2g**: liquid, IR (film) (cm^{-1}): 2988, 1891, 1672, 1612, 1593, 1493, 1464, 1220, 1091, 1039. ^1H NMR ($CDCl_3$) δ 1.35 (s, 3H), 2.07–2.15 (m, 1H), 2.87–2.94 (m, 1H), 3.91–4.06 (m, 4H), 7.12–7.33 (m, 4H). ^{19}F NMR ($CDCl_3$) δ −133.8 (dd, J = 159.3, 15.2 Hz, 1 F), −136.5 (dd, J = 159.0, 14.1 Hz, 1 F). MS *m*/*z* (relative intensity) 274 (M^+, 2.19), 259 (1.78), 209 (12.75), 165 (14.64), 101 (8.89), 87 (100.00). HRMS. Calcd for $C_{13}H_{13}ClF_2O_2$: 274.0572, Found 274.0587.

Compound **2h**: liquid, IR (film) (cm^{-1}): 2989, 2895, 1614, 1519, 1466, 1250, 1180, 1037. ^1H NMR ($CDCl_3$) δ 1.55 (s, 3H), 2.03–2.11 (m, 1H), 2.85–2.93 (m, 1H), 3.79 (s, 3H), 3.92–4.06 (m, 4H), 6.85–6.88 (m, 2 H), 7.14–7.17 (d, J = 8.7 Hz, 2 H). ^{19}F NMR ($CDCl_3$) δ −135.0 (dd, J = 158.4, 14.7 Hz, 1 F), −137.5 (dd, J = 158.3, 13.8 Hz, 1 F). MS *m*/*z* (relative intensity) 270 (M^+, 1.12), 255 (1.96), 235 (1.58), 183 (3.99), 163 (6.84), 87 (100.00). HRMS. Calcd for $C_{14}H_{16}F_2O_3$: 270.1068, Found 270.1063.

Compound **2i**: pale yellow liquid, IR (film) (cm^{-1}): 2988, 2891, 1522, 1466, 1410, 1378, 1328, 1278, 1244, 1221, 1172, 1039, 993. ^1H NMR ($CDCl_3$) δ 1.55 (s, 3H), 2.11 (dddd, J = 14.7, 8.7, 1.2 Hz, 1H), 2.90 (dddd, J = 14.7, 9.0, 1.2 Hz, 1H), 3.90–4.07 (m, 4H), 7.3 (s, 4H). ^{19}F NMR ($CDCl_3$) δ −133.7 (dd, J = 159.0, 14.7 Hz, 1F), −136.0 (dd, J = 157.4, 14.4 Hz, 1F). MS *m*/*z* (relative intensity) 254 (M^+, 2.60), 239 (2.08), 189 (1.94), 167 (2.10), 147 (5.79), 115 (4.80), 87 (100.00). HRMS. Calcd for $C_{14}H_{16}F_2O_2$: 254.1118, Found: 254.1102. Anal. Calcd for $C_{14}H_{16}F_2O_2$: F, 14.94. Found: F, 15.14%.

Compound **2j**: liquid, IR (film) (cm^{-1}): 2990, 1620, 1468, 1169, 1127, 1068. ^1H NMR ($CDCl_3$) δ 1.55 (s, 3H), 2.15–2.23 (m, 1H), 2.95–3.03 (m, 1H), 3.92–4.09 (m, 2H), 7.34–7.60 (m, 4H). ^{19}F NMR ($CDCl_3$) δ −62.5 (s, 3F), −133.3 (dd, J = 161.0, 14.4 Hz, 1F), −136.7 (dd, J = 160.5, 13.5 Hz, 1F). MS *m*/*z* (relative intensity) 308 (M^+, 1.68), 293 (6.87), 243 (100.00), 199 (49.54), 171 (18.43), 145 (11.73), 87 (93.49). Anal. Calcd for $C_{19}H_{18}F_2O_3$: C, 68.67; H, 5.46; F, 11.43. Found: C, 68.67; H, 5.42; F, 11.61%.

Compound **2k**: white solid, mp 59–60 °C. IR (film) (cm^{-1}): 2895, 1654, 1513, 1460, 1421, 1285, 1245, 1152, 1046. ^1H NMR ($CDCl_3$) δ 2.26–2.33 (m, 1H), 3.09–3.17 (m, 1H), 3.76 (s, 3H), 3.83–4.18 (m, 4H), 6.79–6.83 (m, 2H), 7.05–7.09 (m, 2H). ^{19}F NMR ($CDCl_3$) δ −133.3 (dd, J = 158.1, 14.5 Hz, 1F), 136.7 (dd, J = 158.3, 14.3 Hz, 1F). MS *m*/*z* (relative intensity) 332 (M^+, 1.11), 238 (2.30), 210 (16.79), 205 (4.99), 149 (100.00), 105 (31.77), 77 (21.96). Anal. Calcd for $C_{19}H_{18}F_2O_3$: C, 68.67; H, 5.46; F, 11.43. Found: C, 68.67; H, 5.42; F, 11.61%.

Compound **2l**: solid, mp 40–41 °C. IR (film) (cm^{-1}): 2895, 1654, 1513, 1460, 1421, 1285, 1245, 1152, 1046. ^1H NMR ($CDCl_3$) δ 2.30 (s, 3H), 2.31–2.37 (m, 1H), 3.11–3.19 (m, 1H), 3.83–4.18 (m, 4H), 7.03–7.08 (m, 4H), 7.33–7.41 (m, 3H), 7.54–7.58 (m, 2H). ^{19}F NMR ($CDCl_3$) δ −132.3 (dd, J = 157.9, 14.7 Hz, 1F), −135.4 (dd, J = 158.5, 13.3 Hz, 1F). MS *m*/*z* (relative intensity) 316 (M^+, 3.04), 266 (28.87), 239 (0.80), 194 (70.88), 149 (100.00), 105 (91.34), 77 (60.80). Anal. Calcd for $C_{19}H_{18}F_2O_2$: C, 72.14; H, 5.74; F, 12.01. Found: C, 72.48; H, 5.92; F, 12.02%.

Compound **2m**: yellow liquid, ^1H NMR ($CDCl_3$) δ 2.33–2.41 (m, 1H), 3.15–3.23 (m, 1H), 3.81–4.18 (m, 4H), 7.15–7.66 (m, 10H). ^{19}F NMR ($CDCl_3$) δ −131.8 (dd, J = 159.9, 14.1 Hz, 1F), −135.7 (dd, J = 161.9, 15.2 Hz, 1F). MS *m*/*z* (relative intensity) 302 (M^+, 4.70), 252 (3.29), 207 (14.47), 149 (45.39), 105 (100.00), 77 (57.90). HRMS Calcd. for $C_{18}H_{16}F_2O_2$: 302.1118. Found: 302.1128.

Compound **2n**: liquid. ^1H NMR ($CDCl_3$) δ 2.28–2.36 (m, 1H), 3.57–3.64 (m, 1H), 3.78–4.16 (m, 4H), 7.07–7.70 (m, 9H). ^{19}F NMR ($CDCl_3$) δ −131.9 (dd, J = 160.7, 13.8 Hz, 1F), −135.3 (dd, J = 158.9, 13.5 Hz, 1F). MS *m*/*z* (relative intensity) 336 (M^+, 5.18), 317 (0.53), 287 (16.09), 242 (11.29), 214 (40.56), 149 (100.00), 105 (94.22), 77 (35.81). Anal. Calcd

for $C_{18}H_{15}ClF_2O_2$: C, 64.20; H, 4.49; F, 11.28. Found: C, 64.50; H, 4.11; F, 11.15%.

Compound **2o**: liquid, IR (film) (cm^{-1}): 2896, 1686, 1621, 1486, 1413, 1327, 1168, 1127, 1069. ^1H NMR ($CDCl_3$) δ 2.28–2.36 (m, 1 H), 3.11–3.19 (m, 1 H), 3.76–4.12 (m, 4 H), 7.18–7.61 (m, 9 H). ^{19}F NMR ($CDCl_3$) δ −62.6 (s, 3F), −131.7 (dd, J = 159.3, 16.1 Hz, 1F), −135.2 (dd, J = 159.3, 13.8 Hz, 1F). MS *m*/*z* (relative intensity) 370 (M^+, 10.73), 320 (25.20), 248 (30.46), 149 (90.49), 105 (100.00), 77 (63.03). Anal. Calcd for $C_{19}H_{15}F_5O_2$: C, 61.62; H, 4.08. Found: C, 62.81; H, 3.75%.

Compound **2p**: liquid, IR (film) (cm^{-1}): 3030, 2895, 1608, 1504, 1469, 1446, 1328, 1275, 1168, 1074, 1011. ^1H NMR ($CDCl_3$) δ 2.33 (s, 3H), 2.33–2.41 (m, 1H), 3.14–3.21 (m, 1H), 3.82–4.14 (m, 4H), 7.16–7.32 (m, 7H), 7.43–7.46 (m, 2H). ^{19}F NMR ($CDCl_3$) δ −132.2 (dd, J = 159.9, 14.4 Hz, 1F), −135.3 (dd, J = 159.3, 14.4 Hz, 1F). Anal. Calcd for $C_{19}H_{18}F_2O_2$: C, 72.14; H, 5.74; F, 12.01. Found: C, 72.35; H, 5.70; F, 12.26%.

Compound **2q**: white solid, mp 111–112 °C. IR (film) (cm^{-1}): 3024, 2964, 1612, 1584, 1511, 1467, 1302, 1276, 1255, 1168, 1175, 1076, 1014. ^1H NMR ($CDCl_3$) δ 2.37 (dddd, J = 14.4, 8.4, 0.6 Hz, 1H), 3.14 (dd, J = 14.1, 9.0 Hz, 1H), 3.82 (s, 3H), 3.85–4.14 (m, 4H), 6.88–6.92 (m, 2H), 7.16–7.32 (m, 5H), 7.46–7.50 (m, 2H). ^{19}F NMR ($CDCl_3$) δ −132.2 (dd, J = 158.2, 14.7 Hz, 1F), −135.3 (dd, J = 158.2, 14.7 Hz, 1F). MS *m*/*z* (relative intensity) 332 (M^+, 0.59), 301 (2.38), 252 (0.58), 237 (2.72), 221 (0.98), 192 (100.00), 179 (78.48), 135 (62.57), 107 (6.53), 77 (13.35). Anal. Calcd for $C_{19}H_{18}F_2O_3$: C, 68.67; H, 5.46; F, 11.43. Found: C, 68.57; H, 5.39; F, 11.36%.

Hydrolysis of *gem*-difluorocyclopropyl derivatives 2 under acidic conditions

A typical procedure: a 25 ml flask with a water condenser and a magnetic stirring bar was charged with **2a** (1.54 g, 6.8 mmol), 5 ml of saturated oxalic solution and 5 ml of dioxane, the mixture was heated to 110 °C and stirred for 6 h. After cooling to room temperature the content was extracted with ether. The organic layer was dried over Na_2SO_4. After removal of solvent under reduced pressure, the residue was purified by flash chromatography on silica gel column. 3-Fluoro-2-phenylfuran (**4a**) (0.23 g, 21%) was obtained as pale yellow liquid.

Compound **4a**: liquid, IR (film) (cm^{-1}): 3059, 1633, 1602, 1510, 1490, 1433, 1281, 1267, 1113, 1066. ^1H NMR ($CDCl_3$) δ 6.40–6.41 (m, 1H), 7.21–7.27 (m, 2H), 7.37–7.43 (m, 2 H), 7.67–7.70 (m, 2H). ^{19}F NMR ($CDCl_3$) δ −165.3 (s, 1F). MS *m*/*z* (relative intensity) 162 (M^+, 6.62), 133 (11.83), 121 (6.75), 105 (100.00), 77 (93.15). Anal. Calcd for $C_{10}H_7FO$: C, 74.07; H, 4.35; F, 11.72. Found: C, 73.90; H, 4.24; F, 11.43%.

Compound **4b**: liquid, IR (film) (cm^{-1}): 1631, 1568, 1507, 1486, 1435, 1400, 1278, 1265, 1168, 1086. ^1H NMR ($CDCl_3$) δ 6.42–6.43 (m, 1H), 7.23–7.26 (m, 1H), 7.36–7.39 (m, 2 H), 7.58–7.62 (m, 2H). ^{19}F NMR ($CDCl_3$) δ −164.4 (s, 1F). MS *m*/*z* (relative intensity) 196 (M^+, 100.00), 167 (31.74), 161 (2.09), 133 (52.59), 77 (93.15). Anal. Calcd for $C_{10}H_6ClFO$: C, 61.09; H, 3.08; F, 9.66. Found: C, 61.14; H, 2.94; F, 9.47%.

Compound **4c**: liquid, IR (film) (cm^{-1}): 2960, 2839, 1639, 1608, 1575, 1520, 1496, 1437, 1301, 1252, 1118, 1087, 1037. ^1H NMR ($CDCl_3$) δ 3.82 (s, 3H), 6.39–6.40 (m, 1H), 6.93–6.96 (m, 2H), 7.18–7.20 (m, 1H), 7.60–7.63 (m, 2H). ^{19}F NMR ($CDCl_3$) δ −168.0 (s, 1F). MS *m*/*z* (relative intensity) 192 (M^+, 100.00), 177 (10.83), 151 (46.75), 107 (13.15). HRMS Calcd for $C_{11}H_9FO_2$: 192.0587; Found: 192.0590.

Compound **4d**: liquid, IR (film) (cm^{-1}): 2924, 1683, 1635, 1607, 1520, 1436, 1410, 1327, 1266, 1228, 1185, 1089. ^1H NMR ($CDCl_3$) δ 2.36 (s, 3H), 6.40–6.41 (m, 1H), 7.20–7.23 (m, 3H), 7.58 (d, J = 8.1 Hz, 2H). ^{19}F NMR ($CDCl_3$) δ −166.0 (s, 1F). MS *m*/*z* (relative intensity) 176 (M^+, 100.00), 147 (35.31), 133 (29.21). Anal. Calcd for $C_{11}H_9FO$: C, 74.99; H, 5.15; F, 10.78. Found: C, 74.78; H, 4.94; F, 10.74%.

Compound **4e**: liquid, ^1H NMR ($CDCl_3$) δ 6.39 (m, 1H), 7.19 (d, J = 0.6 Hz, 1H), 7.24 (m, 1H), 7.57–7.60 (m, 2H), 7.70–7.73 (m, 2H). ^{19}F NMR ($CDCl_3$) δ −161.8 (d, J = 4.2 Hz).

Compound **3e**: liquid, IR (film) (cm^{-1}): ^1H NMR ($CDCl_3$) δ 2.97–3.06 (m, 1H), 3.63–3.69 (m, 1H), 7.37–7.40 (m, 2H), 7.62–7.69 (m, 2H), 9.55 (m, 1H). ^{19}F NMR ($CDCl_3$) δ −166. MS *m*/*z* (relative intensity) 250 (M^+, 0.51), 231 (4.04), 221 (100.00), 201 (83.71), 181 (12.22), 151 (68.41), 131 (73.80), 69 (3.01). Anal. Calcd for $C_{11}H_7F_5O$: C, 52.81; H, 2.82. Found: C, 53.31; H, 3.57%.

Compound **4f**: liquid, IR (film) (cm^{-1}): 2924, 1683, 1635, 1607, 1520, 1436, 1410, 1327, 1266, 1228, 1185, 1089. ^1H NMR ($CDCl_3$) δ 2.31 (s, 3H), 6.03–6.05 (m, 1H), 7.18–7.25 (m, 1H), 7.35–7.40 (m, 2H), 7.62–7.66 (m, 2H). ^{19}F NMR ($CDCl_3$) δ −162.8 (s, 1F). MS *m*/*z* (relative intensity) 176 (M^+, 100.00), 147 (15.30), 133 (40.55), 105 (24.20), 77 (29.77). HRMS Calcd for $C_{11}H_9FO$: 176.0637; Found: 176.0654.

Compound **4g**: liquid, ^1H NMR ($CDCl_3$) δ 2.31 (s, 3H), 6.04–6.05 (m, 1H), 7.33–7.37 (m, 2H), 7.55–7.59 (m, 2H). ^{19}F NMR ($CDCl_3$) δ −162.3 (s, 1F).

Compound **3g**: liquid, IR (cm^{-1}): 1716, 1500, 1453, 1402, 1362, 1331, 1286, 1221, 1181, 1155, 1092, 1016. ^1H NMR (300 MHz, $CDCl_3$): δ 2.40 (s, 3H), 2.95–3.02 (m, 1H), 3.52–3.60 (m, 1H), 7.15–7.18 (m, 2H), 7.30–7.34 (m, 2H). MS *m*/*z* (relative intensity) 230 (M^+, 0.91), 210 (4.51), 187 (79.13), 167 (57.40), 151 (27.80), 111 (2.76), 43 (100.00). Anal. Calcd for $C_{11}H_9ClF_2O$: C, 57.28; H, 3.93; F, 16.47. Found: C, 57.32; H, 4.03; F, 16.74%.

Compound **4h**: liquid. IR (cm^{-1}): 3003, 2957, 1646, 1611, 1583, 1570, 1511, 1463, 1442, 1410, 1303, 1255, 1180, 1145, 1040. ^1H NMR (300 MHz, $CDCl_3$): δ 2.29 (s, 3H), 3.82 (s, 3H), 6.01 (s, 1H), 6.91–6.94 (m, 2H), 7.55–7.58 (m, 2H). ^{13}C NMR (500 MHz, $CDCl_3$): δ 14.11, 55.11, 100.43, 114.01, 122.36, 124.20, 134.55, 148.52. MS *m*/*z* (relative intensity) 206, 191, 175, 163. HRMS Calcd for $C_{12}H_{11}FO_2$: 206.0743. Found: 206.0714.

Compound **4i**: colorless liquid, IR (film) (cm^{-1}): 2923, 1640, 1580, 1511, 1451, 1406, 1300, 1255, 1146. ^1H NMR ($CDCl_3$) δ 2.32 (s, 3H), 2.37 (3, 3H), 6.04 (t, J = 1.2 Hz, 1H), 7.21 (d, J = 7.8 Hz, 2H), 7.54–7.57 (m, 2H). ^{19}F NMR ($CDCl_3$) δ −163.9 (s, 1F). MS *m*/*z* (relative intensity) 190 (M^+, 100.00), 189 (47.53), 175 (8.55), 147 (38.82), 91 (17.65). Anal. Calcd for $C_{12}H_{11}FO$: C, 75.77; H, 5.83; F, 9.99. Found C, 75.73; H, 5.82; F, 10.09%.

Compound **3j**: yellow liquid, IR (film) (cm^{-1}): 3017, 1718, 1623, 1526, 1456, 1411, 1364, 1328, 1287, 1224, 1168, 1128, 1071, 1018. ^1H NMR ($CDCl_3$) δ 2.43 (s, 3H), 3.03–3.11 (m, 1H), 3.61–3.69 (m, 1H), 7.36 (d, J = 8.4 Hz, 2H), 7.61 (d, J = 8.1 Hz, 2H). ^{19}F NMR ($CDCl_3$) δ −32.5–−132.4 (m, 2F), −62.7 (s, 3F). MS *m*/*z* (relative intensity) 265 (M^+ + 1, 0.56), 245 (0.46), 221 (3.19), 201 (7.71), 195 (1.08), 151 (6.98), 43 (100.00). Anal. Calcd for $C_{12}H_9F_5O$: C, 54.56; H, 3.43; F, 35.96. Found: C, 54.25; H, 3.28; F, 35.80%.

Compound **4k**, white solid, mp 70–71 °C. IR (film) (cm^{-1}): 2965, 1633, 1574, 1507, 1412, 1247, 1179, 1041. ^1H NMR ($CDCl_3$) δ 3.85 (s, 3H), 6.64 (d, J = 0.9 Hz, 1H), 6.90–7.00 (m, 2H), 7.25–7.43 (m, 3H), 7.67–7.71 (m, 4H). ^{19}F NMR ($CDCl_3$) δ −164.2 (s, 1F). MS *m*/*z* (relative intensity) 268 (M^+, 100.00), 253 (85.33), 225 (29.78), 196 (6.43), 176 (8.15), 77 (9.64). Anal. Calcd for $C_{17}H_{13}FO_2$: C, 76.11; H, 4.88; F, 7.08. Found: C, 76.12; H, 4.88; F, 6.99%. X-Ray crystallographic data: † $C_{17}H_{13}FO_2$, M_r = 268.27; crystal system, monoclinic; space group, $P2(1)/c$; unit cell dimensions, a = 3.9188 (8) Å, b = 30.250 (6) Å, c = 11.013 (2) Å, α = 90°, β = 100.187 (4)°, γ = 90°; V = 1284.9 (5) Å^3; Z = 4; D_x = 1.387 g cm^{-3}; λ(Mo-Kα) = 0.7153 Å; μ = 1.00 cm^{-1}; F(000) = 560; T = 293 (2) K; GoF = 0.823; R_{int} = 0.0775;

† CCDC reference numbers 200171. See http://www.rsc.org/suppdata/ob/b2/b212232d/ for crystallographic data in .cif or other electronic format.

$wR(F^2)$ = 0.0803 for 7845 reflections and 234 parameters and $R(F)$ = 0.0425. †

Compound **4l**: solid, mp 88–89 °C. IR (film) (cm^{-1}): 2921, 1631, 1596, 1508, 1483, 1451, 1429, 1406, 1317, 1261, 1149, 1110. ^{1}H NMR ($CDCl_3$) δ 2.31 (s, 3H), 6.59 (d, J = 0.9 Hz, 1H), 7.16–7.25 (m, 3H), 7.31–7.36 (m, 2H), 7.60–7.64 (m, 3H). ^{19}F NMR ($CDCl_3$) δ −162.4 (s, 1F). MS *m*/*z* (relative intensity) 252 (M^+, 100.00), 237 (1.87), 223 (3.84), 209 (11.17), 191 (5.16), 175 (0.57), 147 (7.34), 133 (8.05), 77 (2.89). HRMS. Calcd for $C_{17}H_{13}FO$: 252.0950. Found: 252.0972. Anal. Calcd for $C_{17}H_{14}F_2O$: C, 80.93; H, 5.19. Found: C, 80.77; H, 5.32%.

Compound **3l**: solid, mp 92–93 °C. IR (film) (cm^{-1}): 3030, 2927, 1679, 1597, 1521, 1450, 1407, 1326, 1286, 1226, 1164, 1043. ^{1}H NMR ($CDCl_3$) δ 2.35 (s, 3H), 3.58–3.65 (m, 1H), 3.79–3.85 (m, 1H), 7.16–7.23 (m, 2H), 7.51–7.67 (m, 3H), 8.03–8.06 (m, 2H). ^{19}F NMR ($CDCl_3$) δ −132.2 (m, 2F). MS *m*/*z* (relative intensity) 272 (M^+, 0.87), 252 (0.66), 225 (29.78), 167 (6.29), 105 (100.00), 91 (2.61), 77 (25.94). Anal. Calcd for $C_{17}H_{14}F_2O$: C, 74.99; H, 5.18; F, 13.95. Found: C, 74.88; H, 5.15; F, 13.70%.

Compound **3m**: solid, mp 60–61 °C. IR (film) (cm^{-1}):. ^{1}H NMR ($CDCl_3$) δ 3.61–3.69 (m, 1H), 3.82–3.91 (m, 1H), 7.29–7.67 (m, 8H), 8.03–8.07 (m, 2H). ^{19}F NMR ($CDCl_3$) δ −132.6 (d, J = 5.1 Hz, 2F). MS *m*/*z* (relative intensity) 258 (M^+, 0.71), 238 (0.63), 209 (0.76), 105 (100.00), 77 (40.33). HRMS. Calcd for $C_{16}H_{12}F_2O$: 258.0856. Found: 258.0877.

Compound **3n**: mp 84–85 °C. IR (film) (cm^{-1}): 3030, 1680, 1596, 1498, 1449, 1400, 1324, 1289, 1226, 1116, 1097, 1053, 1017. ^{1}H NMR ($CDCl_3$) δ 3.57–3.65 (m, 1H), 3.79–3.86 (m, 1H), 7.24–7.28 (m, 2H), 7.32–7.36 (m, 2H), 7.51–7.57 (m, 4H), 8.03–8.06 (m, 1H). ^{19}F NMR ($CDCl_3$) δ −131.8 (t, J = 6.9 Hz, 2F). MS *m*/*z* (relative intensity) 292 (M^+, 1.54), 272 (0.58), 187 (1.11), 167 (3.60), 151 (9.33), 105 (100.00), 77 (39.30). Anal. Calcd for $C_{16}H_{11}ClF_2O$: C, 65.65; H, 3.79; F, 12.98. Found: C, 65.51; H, 3.84; F, 13.24%.

Compound **3o**: solid, mp 61–62 °C. IR (film) (cm^{-1}): 1687, 1621, 1452, 1329, 1169, 1069, 1137. ^{1}H NMR ($CDCl_3$) δ 3.67–3.72 (m, 1H), 3.89–4.92 (m, 1H), 7.44–7.69 (m, 7H), 8.04–8.07 (m, 2H). ^{19}F NMR ($CDCl_3$) δ −62.6 (s, 3 F), −132.0 (m, 2F). MS *m*/*z* (relative intensity) 326 (M^+, 1.52), 307 (1.24), 221 (1.07), 208 (6.50), 151 (13.29), 105 (100.00), 77 (42.49), 69 (1.22). Anal. Calcd for $C_{17}H_{11}F_5O$: C, 62.58; H, 3.40; F, 29.11. Found: C, 61.91; H, 3.34; F, 29.44%.

Compound **4p**: solid, mp 60–61 °C. IR (film) (cm^{-1}): 2920, 1632, 1598, 1501, 1428, 1318, 1150, 1043, 1009. ^{1}H NMR ($CDCl_3$) δ 2.38 (s, 3H), 6.61 (d, J = 1.2 Hz, 1H), 7.20–7.28 (m, 3H), 7.40–7.45 (m, 2H), 7.74–7.77 (m, 2H). ^{19}F NMR ($CDCl_3$) δ −161.4 (s, 1F). MS *m*/*z* (relative intensity) 252 (M^+, 100.00), 237 (1.72), 223 (1.72), 209 (12.74), 147 (9.43), 77 (7.57). HRMS. Calcd for $C_{17}H_{13}FO$: 252.0950. Found: 252.0978.

Compound **3p**: white solid, mp 98–99 °C. IR (film) (cm^{-1}): 3045, 1673, 1607, 1506, 1462, 1436, 1333, 1285, 1231, 1185, 1170, 1048, 1000. ^{1}H NMR ($CDCl_3$) δ 2.45 (s, 3H), 3.59–3.66 (m, 1H), 3.80–3.89 (m, 1H), 7.29–7.39 (m, 7H), 7.94–7.96 (m, 2H). ^{19}F NMR ($CDCl_3$) δ −132.3–−132.2 (m, 2F). MS *m*/*z* (relative intensity) 272 (M^+, 2.87), 257 (1.29), 237 (0.54), 222 (0.30), 151 (6.84), 119 (100.00), 91 (27.36), 77 (3.06). Anal. Calcd for $C_{17}H_{14}F_2O$: C, 74.99; H, 5.18; F, 13.95. Found: C, 74.94; H, 5.10; F, 13.79%.

Compound **4q**: solid, mp 66–67 °C. IR (film) (cm^{-1}): 2961, 1630, 1583, 1501, 1431, 1305, 1253, 1046. ^{1}H NMR ($CDCl_3$) δ 3.86 (s, 3H), 6.54 (d, J = 0.6 Hz, 1H), 6.94–6.97 (m, 2H), 7.25–7.27 (m, 1H), 7.40–7.45 (m, 2H), 7.62–7.76 (m, 4H). ^{19}F NMR ($CDCl_3$) δ −161.4 (s, 1F). MS *m*/*z* (relative intensity) 268 (M^+, 100.00), 253 (66.00), 225 (13.34), 196 (9.86), 176 (5.36), 134 (9.91), 105 (7.40), 77 (16.51). HRMS. Calcd for $C_{17}H_{13}FO_2$: 268.0900. Found: 268.0930.

Compound **3q**: solid, mp 79–80 °C. IR (film) (cm^{-1}): 3030, 1668, 1601, 1573, 1511, 1459, 1452, 1318, 1291, 1260, 1172, 1028. ^{1}H NMR ($CDCl_3$) δ 3.56–3.62 (m, 1H), 3.80–3.85 (m, 1H), 3.90 (s, 3H), 6.99–7.01 (m, 2H), 7.31–7.39 (m, 4H), 8.02–8.05 (m, 2H). ^{19}F NMR ($CDCl_3$) δ −132.4–−132.3 (m, 2F). MS *m*/*z* (relative intensity) 288 (M^+, 7.44), 257 (0.28), 221 (0.82), 182 (6.31), 167 (2.56), 135 (100.00), 107 (7.63), 77 (19.12). Anal. Calcd for $C_{17}H_{14}F_2O_2$: C, 70.83; H, 4.89; F, 13.18. Found: C, 70.81; H, 4.93; F, 13.02%.

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