Synthesis of Precursors of *gem*-Difluorodiols and Amino Alcohols Using Electrochemical and Photochemical Reactions

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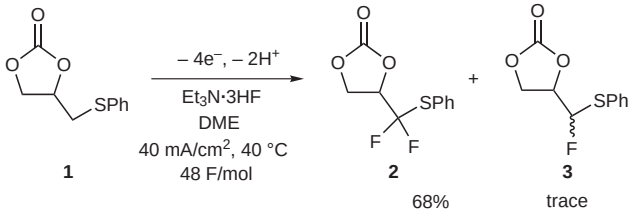
Abstract: Photo-initiated S–CF_2 bond cleavage of electrochemically prepared 4-[difluoro(phenylthio)methyl]-1,3-dioxolanone and 4-[difluoro(phenylthio)methyl]-1,3-oxazolidinone in the presence of olefins provided the corresponding radical addition products, while the photolysis in the presence of aromatics and heteroaromatics provided radical substitution products in moderate yields.

Key words: radical addition, radical aromatic substitution, photoreaction, difluoromethyl radical, sulfide



Scheme 1

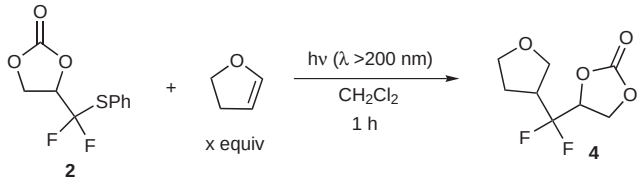
As a kind of building block for constructing biologically active compounds, organofluorine compounds hold high promise for the pharmaceutical and agrochemical industries due to high electronegativity and the small van der Waals radius of a fluorine atom.[1] In particular, difluoromethylene compounds have attracted a great deal of interest due to their being isosteric with an ether oxygen,[2] and synthesis of these compounds has thus become a subject of investigation in organic chemistry. On the other hand, fluorine-containing 1,2-diols are useful building blocks for the preparation of valuable organofluorine compounds and many papers have reported on the synthesis of 1,2-diol analogues having a difluoromethylene group.[3]

Recently, electrochemical partial fluorination of organic compounds has been shown to be a powerful method for selective fluorination.[4] Previously, we successfully carried out anodic difluorination of 4-[(phenylthio)methyl]-1,3-dioxolan-2-one (**1**) to provide the corresponding *gem*-difluorinated product **2** in ca. 70% yield (Scheme 1).[5] Since **2** has multiple functional groups, we expected that **2** can be converted to other useful organofluorine compounds. Although metal[6] and AIBN/organostannane-catalyzed,[7] and electrocatalytic[8] radical addition of difluorohalo esters and ketones across alkenes has been studied intensively, photochemical radical addition has been rarely reported.[9]

With this background in mind, we studied photolysis of **2** for generating the corresponding difluoromethyl radical, which can be trapped with unsaturated compounds to form new CF_2-containing building blocks.

At first, we investigated the homolytic dissociation of the S–CF_2 bond of **2** using ultraviolet light in the presence of olefins. The photolysis of **2** was carried out in the presence of an electron-rich olefin, 2,3-dihydrofuran, as a model olefin in CH_2Cl_2 using a 6-W low-pressure mercury-vapor lamp through a quartz filter until **2** was completely consumed. The results are summarized in Table 1.

Table 1 Photochemical Reaction of **2** with 2,3-Dihydrofuran



Entry	X	Yield (%)[a]
1	5	38
2	10	49
3	20	67 (58)[b]

[a] Determined by ^{19}F NMR analyses. Isolated yield is shown in parentheses.
[b] Diastereomeric mixture.

In all cases, the expected radical addition took place and the difluoromethylene group was introduced exclusively to the 3-position of 2,3-dihydrofuran. The yield increased with the amount of 2,3-dihydrofuran used, and the best result was obtained by using 20 equivalents amounts of 2,3-dihydrofuran to **2** (run 3). Thus, we achieved photoinduced cleavage of the S–CF_2 bond followed by regioselective radical addition to 2,3-dihydrofuran. Next, we extended this photoreaction to various substrates. The results are shown in Table 2.

Regardless of the molecular structures of olefins employed, the expected radical adducts **5**–**7** were formed in moderate yields. Notably, the difluoromethylene group was introduced to the terminal position of acyclic vinyl ether and olefin exclusively (runs 2 and 4). Previously, we

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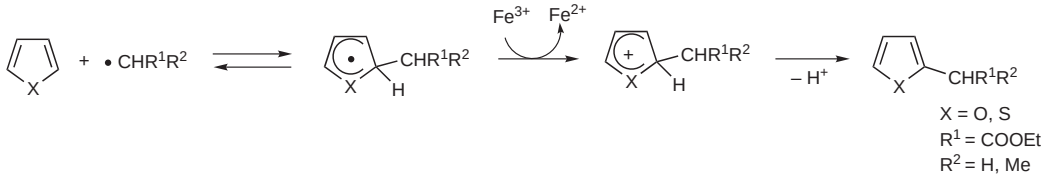
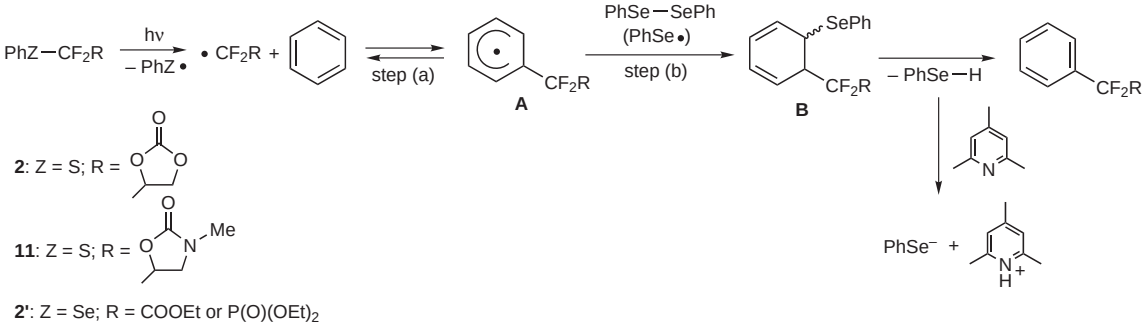


Scheme 2



Scheme 3

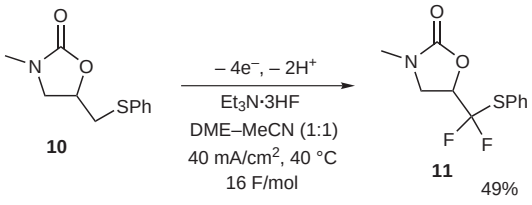
found that photochemical reaction of α,α-difluoro-α-(phenylseleno)acetate with olefins always provided mixtures of the corresponding saturated (radical adducts) and unsaturated products (substituted products).[10] In sharp contrast, in these reactions, saturated radical adducts were obtained exclusively and no unsaturated product was formed. Lequex, Piettre and co-workers also reported homolytic cleavage of the S–CF_2 bond of sulfanyldifluoromethylphosphonate using AIBN/*n*-Bu_3SnH in the presence of various olefins and they always obtained saturated adducts:[11] The reaction with 2,3-dihydrofuran provided the adduct to its 3-position exclusively in 47% yield. In this case, a hydrogen atom source is *n*-Bu_3SnH. However, in our case, the hydrogen atom source has not been specified at present.

Next, photoreaction of **2** with aromatic compounds like benzene and furan was carried out similarly. Interestingly, aromatic substitution took place and the corresponding cross-coupling products **8** and **9**[18] were obtained (runs 5 and 7). Notably, the substitution with the difluoromethyl group at the α-position of furan proceeded regioselectively to provide the corresponding product **9**. However, the yields of **8** and **9** were low. Baciocchi et al. reported aromatic substitution with electrophilic carbon radicals generated by alkyl halides and triethylborane.[12] Since the radical addition step is reversible, an oxidizing reagent like Fe^{3+} is necessary to shift the equilibrium to the right side as shown in Scheme 2.

In the case of our aromatic substitution using **2**, the cleavage of the aryl–CF_2 bond of radical σ-complex **A** probably occurred similarly to Baciocchi's case as shown in Scheme 3 [step (a)]. On the other hand, we found recently that the aromatic substitution of α,α-difluoroselenides **2′** having ester and phosphonate groups under photoirradiation provided the corresponding substitution products in moderate yields.[13] This reaction seemed to involve phenylselenyl transfer [Scheme 3, step (b)] followed by the elimination of a phenylselenol from the group transfer adduct **B** once formed to provide aromatized products. In this reaction, we found that the yields increased by the addition of diphenyl diselenide and 2,4,6-trimethylpyridine.[14] So, we tried to improve the yields of photolytic aromatic substitution using **2** by the addition of diphenyl diselenide to form phenylselenyl group transfer adduct **B** and 2,4,6-trimethylpyridine to suppress the generation of phenylselenol as a hydrogen atom source (Scheme 3).

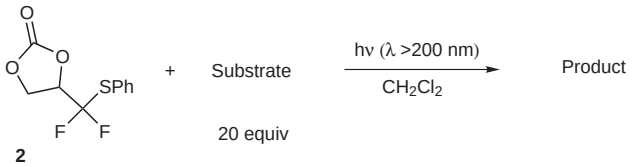
As expected, the yields increased twice for both benzene and furan (runs 6 and 8) although much longer photoirradiation was required to complete the reaction. Thus, the yields increased appreciably, but they are still moderate because of considerable formation of unidentified byproducts detected by TLC.

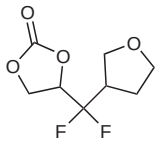
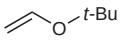
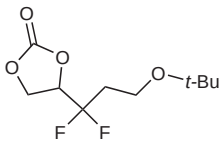
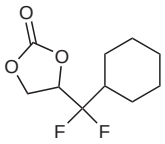
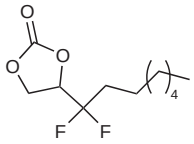
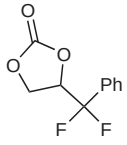
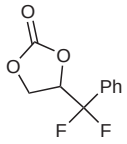
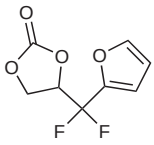
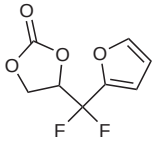
Furthermore, we extended this photochemical reaction to an oxazolidinone analogue having a difluoromethylene unit in order to prepare precursors to difluorinated amino alcohols. At first, we carried out anodic difluorination of 4-[(phenylthio)methyl]-*N*-methyloxazolidinone (**10**) in $Et_3N{\cdot}3HF$/DME–MeCN (1:1) to provide the corresponding *gem*-difluorinated product **11** in moderate yield (Scheme 4).



Scheme 4

Table 2 Photoreaction of **2** with Various Olefins and Aromatics



Run	Substrate	Time (h)	Product (%)[a]
1		1	 **4** 67(58)
2		2	 **5** 45 (40)
3		2	 **6** 43 (38)
4		2	 **7** 48 (40)
5		4	 **8** 22 (20)
6[b]		8	 **8** 46 (44)
7		4	 **9** 24 (20)
8[b]		8	 **9** 44 (41)

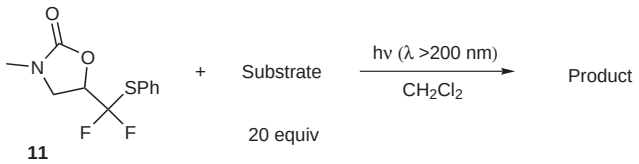
[a] Determined by ^{19}F NMR analyses. Isolated yields are shown in parentheses.
[b] In the presence of 1 equiv of PhSe–SePh and 5 equiv of 2,4,6-trimethylpyridine.

Next, the photochemical reaction of **11** was carried out similarly with cyclic and acyclic olefins, and aromatics. The results are summarized in Table 3.

The expected radical addition and aromatic substitution also took place and the corresponding products **12**–**17**[19] were obtained in moderate yields (runs 1–5, and 7). Notably, the corresponding regioselective addition and substitution products were obtained similarly to the case of 1,3-dioxolanone **2** (runs 1, 2, 4, and 7). Although the yields of aromatic substitution were low, the yields were considerably increased by the addition of diphenyl diselenide and 2,4,6-trimethylpyridine (runs 6 and 8).

Although heteroaryl-substituted difluoroketons,[15,16] acetates,[13] and phosphonate[13] have been prepared, such multifunctional difluoromethylene compounds have never been prepared so far.

Table 3 Photoreaction of **11** with Various Olefins and Aromatics[17]



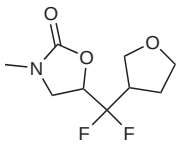
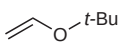
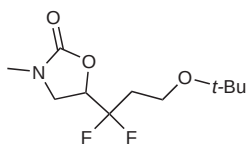
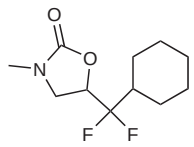
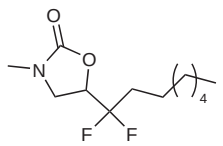
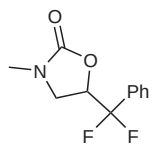
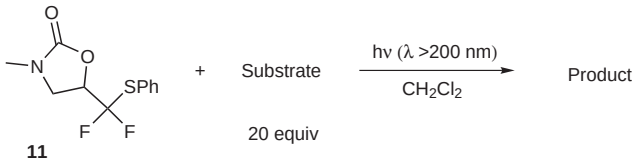
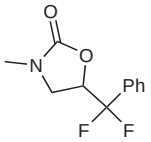
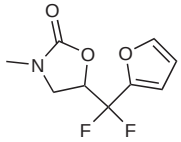
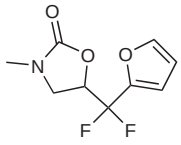
Run	Substrate	Time (h)	Product (%)[a]
1		2	 **12** 66 (61)[c]
2		2	 **13** 58 (52)
3		2	 **14** 66 (57)
4		2	 **15** 50 (45)
5		4	 **16** 22 (19)

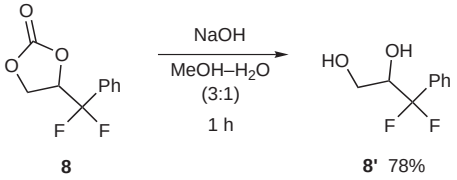
Table 3 Photoreaction of **11** with Various Olefins and Aromatics[17] (continued)



Run	Substrate	Time (h)	Product (%)[a]
6[b]		8	 **16** 40 (37)
7		4	 **17** 19 (16)
8[b]		8	 **17** 43 (39)

[a] Determined by ^{19}F NMR analyses. Isolated yields are shown in parentheses.
[b] In the presence of 1 equiv of PhSe–SePh and 5 equiv of 2,4,6-trimethylpyridine.
[c] Diastereomeric mixture ca. 1:1.

Finally, the deprotection of the carbonate group of **8** as a model substrate was demonstrated (Scheme 5). Alkaline hydrolysis of **8** readily proceeded to provide difluorinated diol **8′**[21] in good yield.



Scheme 5

In conclusion, we have successfully carried out the electrochemical difluorination of 4-[(phenylthio)methyl]-*N*-methyloxazolidinone similarly to the case of 4-[(phenylthio)methyl]-1,3-dioxolanone.[20] The photoinitiated S–CF_2 bond cleavage in the presence of various unsaturated compounds such as olefins and aromatics provided regioselective addition and substitution products, respectively. Moreover, the corresponding aromatic product was converted to a difluoro diol in good yield. This method seems to be highly useful for the preparation of various new CF_2-containing building blocks.

References and Notes

(1) Hiyama, T. *Organofluorine Compounds*; Springer-Verlag: Berlin, **2000**.
(2) (a) *Biomedicinal Aspects of Fluorine Chemistry*; Filler, R.; Kobayashi, Y., Eds.; Kodansya and Elsevier Biomedical: Tokyo, **1982**. (b) Tozer, M. J.; Herpin, T. F. *Tetrahedron* **1996**, *52*, 8619.
(3) (a) Audouard, C.; Gerry, A. J. F.; Kerouredan, E.; Miah, A.; Percy, J. M.; Yang, H. *Org. Lett.* **2004**, *6*, 4269. (b) Kornilov, A. M.; Sorochinsky, A. E.; Kukhar, V. P. *Tetrahedron: Asymmetry* **1994**, *5*, 1015. (c) Hanazawa, Y.; Inazawa, K.; Kon, A.; Aoki, H.; Kobayashi, Y. *Tetrahedron Lett.* **1987**, *28*, 659.
(4) (a) Fuchigami, T.; Tajima, T. In *Fluorine-Containing Synthons*, *ACS Symposium Series 911*; Soloshonok, V. A., Ed.; American Chemical Society: Washington, DC, **2005**, 276. (b) Fuchigami, T. *Organic Electrochemistry*, 4th ed.; Lund, H.; Hammerich, O., Eds.; Marcel Dekker: New York, **2001**, Chap. 25. (c) Fuchigami, T. In *Advances in Electron-Transfer Chemistry*, Vol. 6; Mariano, P. S., Ed.; JAI Press: CT, **1999**, 41.
(5) Suzuki, K.; Ishii, H.; Fuchigami, T. *Tetrahedron Lett.* **2001**, *42*, 4861.
(6) (a) Kitagawa, O.; Miura, A.; Kobayashi, Y.; Taguchi, T. *Chem. Lett.* **1990**, 1011. (b) Yang, Z.-Y.; Burton, D. J. *J. Org. Chem.* **1992**, *57*, 5144. (c) Qiu, Z.-M.; Burton, D. J. *J. Org. Chem.* **1995**, *60*, 5570.
(7) Roberts, J. L.; Borgese, J.; Chan, C.; Keith, D. D.; Wei, C.-C. *Heterocycles* **1993**, *35*, 115.
(8) Médebielle, M. *Tetrahedron Lett.* **1995**, *36*, 2071.
(9) Qiu, Z.-M.; Burton, D. J. *Tetrahedron Lett.* **1994**, *35*, 1813.
(10) Murakami, S.; Ishii, H.; Fuchigami, T. *J. Fluorine Chem.* **2001**, *42*, 4861.
(11) Lequeux, T.; Lebouc, F.; Lopin, C.; Yang, H.; Gouhier, G.; Piettre, S. R. *Org. Lett.* **2001**, *3*, 185.
(12) Baciocchi, E.; Muraglia, E. *Tetrahedron Lett.* **1993**, *34*, 5015.
(13) Murakami, S.; Kim, S.; Ishii, H.; Fuchigami, T. *Synlett* **2004**, 815.
(14) Murakami, S.; Ishii, H.; Tajima, T.; Fuchigami, T. *Tetrahedron* **2006**, in press.
(15) Eto, H.; Kaneko, Y.; Sakamoto, T. *Chem. Pharm. Bull.* **2000**, *48*, 982.
(16) Uneyama, K.; Tanaka, H.; Kobayashi, S.; Shinoyama, M.; Amii, H. *Org. Lett.* **2004**, *6*, 2733.
(17) **Typical Procedure for Photochemical Reaction.** A solution of **2** or **11** (0.17 mmol) and olefin (3.40 mmol) in CH_2Cl_2 (40 mL) or aromatic compounds (40 mL) without any solvents was bubbled with Ar at r.t. for 0.5 h and then photolyzed for 2 h or 4 h with 6-W low-pressure mercury-vapor lamp. The reaction was conducted using a quartz vessel inside the light source. After the photolysis, the resulting solution was evaporated under vacuum and the residue was purified by preparative thin-layer chromatography (MERCK Silica gel 60 GF_{254}, 33% or 50% EtOAc in hexane) and by HPLC (Develosil ODS-5, MeCN as eluent) to provide pure products.
(18) (a) **4-[Difluoro-(3-tetrahydrofuryl)methyl]-1,3-dioxolan-2-one (4):** ^1H NMR (270 MHz, $CDCl_3$): δ = 4.86–4.54 (m, 3 H), 4.02–3.74 (m, 4 H), 3.09–2.83 (m, 1 H), 2.20–1.89 (m, 2 H). ^{19}F NMR (254 MHz, $CDCl_3$): δ = –41.91 to –44.34 (m, 2 F). MS: *m/z* = 207 [M^+ – H], 189 [M^+ – F], 87 [M^+ – F_2C – C_4H_7O]. (b) **4-[(3-*tert*-Butoxy-1,1-difluoro)propyl]-1,3-dioxolan-2-one (5):** ^1H NMR (270 MHz, $CDCl_3$): δ = 5.10–4.97 (m, 1 H), 4.59–4.48 (m, 2 H), 3.55 (t, 2 H, *J* = 5.8 Hz), 2.44–2.09 (m, 2 H), 1.19 (s, 9H). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ =

153.82, 120.56 (dd, *J* = 247.0, 243.1 Hz), 74.89 (dd, *J* = 34.7, 26.3 Hz), 73.63, 64.26 (dd, *J* = 5.0, 2.8 Hz), 54.76 (t, *J* = 6.7 Hz), 34.54 (dd, *J* = 23.5, 22.9 Hz), 27.41. ^{19}F NMR (254 MHz, $CDCl_3$): δ = –33.90 to –35.17 (m, 1 F), –36.78 to –37.93 (m, 1 F). FAB-MS: *m/z* = 239 [M^+ + H]. FAB–HRMS: *m/z* calcd for $C_{10}H_{17}F_2O_4$: 239.1095; found: 239.1091.

(c) **4-[(Cyclohexyl)difluoromethyl]-1,3-dioxolan-2-one (6):** ^{1}H NMR (270 MHz, $CDCl_3$): δ = 4.92–4.78 (m, 1 H), 4.69–4.50 (m, 2 H), 2.01–1.74 (m, 6 H), 1.31–1.24 (m, 5 H). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ = 153.61, 121.25 (dd, *J* = 249.8, 243.7 Hz), 72.36 (dd, *J* = 41.4, 28.5 Hz), 64.02 (dd, *J* = 5.6, 3.9 Hz), 40.80 (t, *J* = 21.8 Hz), 25.76 (dd, *J* = 5.6, 2.8 Hz), 25.69, 25.46 (d, *J* = 1.1 Hz), 25.29, 24.04 (dd, *J* = 4.5, 3.9 Hz). ^{19}F NMR (254 MHz, $CDCl_3$): δ = –54.11 (ddd, 1 F, *J* = 303.3, 53.6, 3.7 Hz), –59.75 (ddd, 1 F, *J* = 303.3, 55.5, 16.6 Hz). FAB-MS: *m/z* = 221 [M^+ + H]. FAB–HRMS: *m/z* calcd for $C_{10}H_{15}F_2O_3$: 221.0989; found: 221.0986.

(d) **4-(1,1-Difluorooctyl)-1,3-dioxolan-2-one (7):** ^{1}H NMR (270 MHz, $CDCl_3$): δ = 4.80–4.51 (m, 3 H), 2.18–1.81 (m, 2 H), 1.60–1.48 (m, 2 H), 1.39–1.23 (m, 8 H), 0.89 (t, 3 H, *J* = 7.1 Hz). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ = 153.49, 120.72 (dd, *J* = 249.3, 241.5 Hz), 74.16 (dd, *J* = 40.8, 27.9 Hz), 63.96 (dd, *J* = 5.0, 3.4 Hz), 33.11 (dd, *J* = 23.5, 22.4 Hz), 31.65, 29.18, 28.98, 22.65, 21.25 (dd, *J* = 5.6, 2.8 Hz), 14.41. ^{19}F NMR (254 MHz, $CDCl_3$): δ = –35.57 to –36.76 (m, 1 F), –40.22 to –41.43 (m, 1 F). MS: *m/z* = 236 [M^+], 149. HRMS: *m/z* calcd for $C_{11}H_{18}F_2O_3$: 236.1224; found: 236.1232.

(e) **4-[Difluoro(phenyl)methyl]-1,3-dioxlan-2-one (8):** ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.56–7.45 (m, 5 H), 5.04–4.92 (m, 1 H), 4.68–4.43 (m, 2 H). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ = 153.32, 131.36 (dd, *J* = 25.2, 24.6 Hz), 131.21 (dd, *J* = 2.2, 1.7 Hz), 128.83, 125.59 (t, *J* = 6.1 Hz), 118.15 (dd, *J* = 249.3, 244.3 Hz), 75.88 (dd, *J* = 39.7, 32.4 Hz), 64.21 (t, *J* = 3.3 Hz). ^{19}F NMR (254 MHz, $CDCl_3$): δ = –30.95 (dd, 1 F, *J* = 262.6, 5.5 Hz), –37.90 (dd, 1 F, *J* = 262.6, 12.9 Hz). MS: *m/z* = 214 [M^+], 127. HRMS: *m/z* calcd for $C_{10}H_8F_2O_3$: 214.0442; found: 214.0443.

(f) **4-[Difluoro(2-furyl)methyl]-1,3-dioxolan-2-one (9):** ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.55–7.54 (m, 1 H), 6.83–6.81 (m, 1 H), 6.51–6.50 (m, 1 H), 5.23–5.11 (m, 1 H), 4.72–4.56 (m, 2 H). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ = 153.24, 144.97 (dd, *J* = 2.2, 1.7 Hz), 143.58 (dd, *J* = 37.4, 33.0 Hz), 113.82 (dd, *J* = 243.7, 240.3 Hz), 112.33 (dd, *J* = 3.4, 2.8 Hz), 111.00 (t, *J* = 1.1 Hz), 74.21 (dd, *J* = 37.4, 29.6 Hz), 63.94 (t, *J* = 3.4 Hz). ^{19}F NMR (254 MHz, $CDCl_3$): δ = –28.80 (dd, 1 F, *J* = 280.0, 5.5 Hz), –38.17 (dd, 1 F, *J* = 280.0, 11.1 Hz). MS: *m/z* = 204 [M^+], 117. HRMS: *m/z* calcd for $C_8H_6F_2O_4$: 204.0234; found: 204.0237.

(19) (a) **5-[Difluoro(3-tetrahydrofuryl)methyl]-3-methyloxazolidinone (12):** ^{1}H NMR (270 MHz, $CDCl_3$): δ = 4.67–4.44 (m, 1 H), 4.01–3.63 (m, 6 H), 3.18–2.92 (m, 4 H), 2.22–1.87 (m, 2 H). ^{19}F NMR (254 MHz, $CDCl_3$): δ = –43.16 (ddd, 1 F, *J* = 262.6, 18.5, 12.9 Hz), –44.43 (ddd, 1 F, *J* = 262.4, 20.2, 3.7 Hz). MS: *m/z* = 222 [M^+ + H]. FAB–HRMS: *m/z* calcd for $C_9H_{14}F_2NO_3$: 222.0942; found: 222.0945.

(b) **5-[(3-*tert*-Butoxy-1,1-difluoro)propyl]-3-methyloxazol-idinone (13):** ^{1}H NMR (270 MHz, $CDCl_3$): δ = 4.81–4.67 (m, 1 H), 3.64–3.54 (m, 4 H), 2.90 (s, 3 H), 2.44–2.06 (m, 2 H), 1.19 (s, 9 H). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ = 156.82, 121.00 (dd, *J* = 246.5, 244.3 Hz), 73.36, 71.69 (dd, *J* = 34.1, 30.2 Hz), 54.91 (dd, *J* = 6.7, 6.1 Hz), 46.10 (dd, *J* = 4.5, 3.4 Hz), 34.37 (dd, *J* = 23.5, 22.9 Hz), 30.95, 27.45. ^{19}F NMR (254 MHz, $CDCl_3$): δ = –35.48 to –37.81 (m, 2 F). FAB–MS: *m/z* 252 [M^+ + H]. FAB-HRMS: *m/z* calcd for $C_{11}H_{20}F_2NO_3$: 252.1411; found: 252.1407.

(c) **5-[(Cyclohexyl)difluoromethyl]-3-methyloxazol-idinone (14):** ^{1}H NMR (270 MHz, $CDCl_3$): δ = 4.73–4.59 (m, 1 H), 3.74–3.58 (m, 2 H), 2.91 (s, 3 H), 2.14–1.62 (m, 6 H), 1.33–1.13 (m, 5 H). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ = 156.69, 121.84 (dd, *J* = 250.1, 244.3 Hz), 69.41 (dd, *J* = 39.17, 29.1 Hz), 45.79 (dd, *J* = 5.3, 3.4 Hz), 40.66 (t, *J* = 21.8 Hz), 30.94, 29.77, 25.95 (dd, *J* = 6.1, 2.8 Hz), 25.84, 25.43, 24.06 (dd, *J* = 5.0, 3.9 Hz). ^{19}F NMR (254 MHz, $CDCl_3$): δ = –45.35 (ddd, 1 F, *J* = 258.9, 20.3, 3.7 Hz), –46.72 (ddd, 1 F, *J* = 258.9, 18.5, 9.2 Hz). MS: *m/z* = 233 [M^+], 100. HRMS: *m/z* calcd for $C_{11}H_{17}F_2NO_2$: 233.1227; found: 233.1222.

(d) **5-(1,1-Difluorooctyl)-3-methyloxazolidinone (15):** ^{1}H NMR (270 MHz, $CDCl_3$): δ = 4.60–4.446 (m, 1 H), 3.71–3.60 (m, 2 H), 2.91 (s, 3 H), 2.17–1.84 (m, 2 H), 1.58–1.46 (m, 2 H), 1.37–1.25 (m, 8 H), 0.89 (t, 3 H, *J* = 6.8 Hz). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ = 156.65, 121.36 (dd, *J* = 248.2, 239.8 Hz), 71.22 (dd, *J* = 40.2, 27.9 Hz), 45.81 (dd, *J* = 4.5, 3.4 Hz), 33.07 (dd, *J* = 23.5, 22.9 Hz), 31.67, 30.94, 29.25, 29.03, 22.65, 21.36 (dd, *J* = 5.6, 2.8 Hz), 14.14. ^{19}F NMR (254 MHz, $CDCl_3$): δ = –35.55 to –36.72 (m, 1 F), –40.22 to 41.43 (m, 1 F). MS: *m/z* = 249 [M^+], 149, 100. HRMS: *m/z* calcd for $C_{12}H_{21}F_2NO_2$: 249.1540; found: 249.1539.

(e) **5-[Difluoro(phenyl)methyl]-3-methyloxazolidinone (16):** ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.55–7.42 (m, 5 H), 4.85–4.73 (m, 1 H), 3.67 (d, 2 H, *J* = 7.4 Hz), 2.82 (s, 3H). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ = 156.45, 132.20 (dd, *J* = 25.7, 25.2 Hz), 130.72 (t, *J* = 1.7 Hz), 128.51, 125.69 (t, *J* = 6.1 Hz), 118.65 (dd, *J* = 248.7, 244.3 Hz), 72.93 (dd, *J* = 39.13, 32.42 Hz), 46.32 (t, *J* = 3.35 Hz), 30.83. ^{19}F NMR (254 MHz, $CDCl_3$): δ –30.25 (dd, 1 F, *J* = 258.9, 5.5 Hz), –38.53 (dd, 1 F, *J* = 258.9, 14.8 Hz). MS: *m/z* = 227 [M^+]. HRMS: *m/z* calcd for $C_{11}H_{11}F_2NO_2$: 227.0758; found: 227.0748.

(f) **5-[Difluoro(2-furyl)methyl]-3-methyloxazolidinone (17):** ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.52–7.49 (m, 1 H), 6.79–6.76 (m, 1 H), 6.48–6.45 (m, 1 H), 5.04–4.91 (m, 1 H), 3.73 (d, 2 H, *J* = 7.6 Hz), 2.89 (s, 3 H). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ = 156.36, 144.31 (dd, *J* = 2.2, 1.7 Hz), 144.45 (dd, *J* = 35.8, 33.0 Hz), 114.38 (dd, *J* = 243.7, 240.3 Hz), 111.78 (dd, *J* = 3.9, 2.8 Hz), 110.78 (t, *J* = 1.1 Hz), 71.22 (dd, *J* = 36.3, 29.6 Hz), 45.97 (t, *J* = 3.4 Hz), 30.87. ^{19}F NMR (254 MHz, $CDCl_3$): δ = –28.77 (dd, 1 F, *J* = 277.4, 5.5 Hz), –39.12 (dd, 1 F, *J* = 277.4, 12.9 Hz). MS: *m/z* = 217 [M^+], 117, 100. HRMS: *m/z* calcd for $C_9H_9F_2NO_3$: 217.0550; found: 217.0551.

(20) **Electrochemical Difluorination of 5-(Phenylthio)methyl-3-methyloxazolidinone (10):**

Constant current electrolysis (40 mA/cm^{-2}) of **10** was carried out at platinum electrodes (2 × 2 cm^2) at 40 °C in DME–MeCN (5 mL each) containing 0.3 M $Et_3N{\cdot}3HF$ using undivided cell. After electrolysis, the supporting electrolyte was removed by silica gel short column chromatography. The product **11** was isolated by silica gel column chromatography (EtOAc–hexane, 1:3).

5-[Difluoro(phenylthio)methyl]-3-methyloxazolidinone (11): ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.63–7.60 (m, 2 H), 7.49–7.35 (m, 3 H), 4.71–4.57 (m, 1 H), 3.74–3.61 (m, 2 H), 2.88 (s, 3 H). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ = 156.09, 138.46 (dd, *J* = 8.9, 0.6 Hz), 136.34, 130.23, 129.11, 126.41 (dd, *J* = 282.3, 280.6 Hz), 71.86 (dd, *J* = 31.9, 27.9 Hz), 46.48 (t, *J* = 2.8 Hz), 30.67. ^{19}F NMR (254 MHz, $CDCl_3$): δ = –11.22 (dd, 1 F, *J* = 218.2, 9.2 Hz), –12.91 (dd, 1 F, *J* = 218.2, 9.2 Hz). MS: *m/z* = 259 [M^+], 159, 77. HRMS: *m/z* calcd for $C_{11}H_{11}F_2NO_2S$: 259.0479; found: 259.0485.

(21) **3,3-Difluoro-3-phenylpropan-1,2-diol (8′):** ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.55–7.45 (m, 5 H), 4.14–4.02 (m, 1 H), 3.78–3.64 (m, 2 H), 3.22–1.93 (br, 2 H). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ = 133.98 (t, *J* = 25.7 Hz), 130.23 (t, *J* = 1.7 Hz), 128.40, 125.50 (t, *J* = 6.7 Hz), 120.72 (t, *J* = 247.0 Hz), 74.23 (dd, *J* = 30.2, 29.1 Hz), 61.14 (t, *J* = 3.4 Hz). ^{19}F NMR (254 MHz, $CDCl_3$): δ = –29.62 (dd, 1 F, *J* = 253.4, 9.2 Hz), –32.57 (dd, 1 F, *J* = 253.4, 12.9 Hz). MS: *m*/*z* = 188 [M^+], 127, 77. HRMS: *m*/*z* calcd for $C_9H_{10}F_2O_2$: 188.0649; found: 188.0652.