

Convenient access to stable β -fluorovinyl-substituted 1,2-benziodoxolones

Tsugio Kitamura,^{*a} Rinka Sato,^a Hikari Morita,^a Daichi Kitamura,^a Juzo Oyamada,^a Masahiro Higashi,^b and Yosuke Kishikawa^b

^aDepartment of Chemistry and Applied Chemistry, Saga University, Honjo-machi, Saga 840-8502, Japan;

²Daikin Industries, Ltd., Settsu, Osaka 566-8585, Japan

Email: kitamura@cc.saga-u.ac.jp

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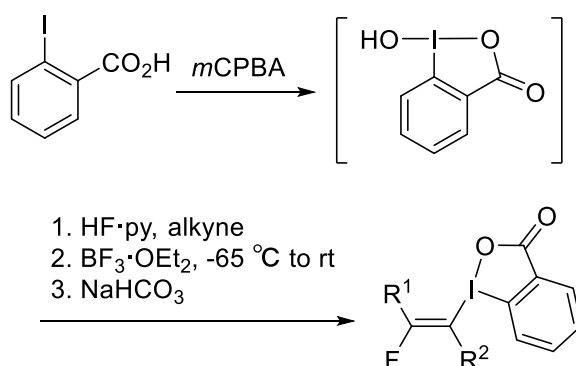
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Abstract

A convenient synthesis of 1-(2-fluorovinyl)-1,2-benziodoxol-3(1*H*)-ones was described. Fluorination reaction of alkynes with the reagent from *o*-iodobenzoic acid, *m*CPBA and HF·py was conducted in DCM and followed by addition of BF₃·OEt₂ at -65 °C. Treatment of the reaction mixture with NaHCO₃ gave 1-(2-fluorovinyl)benziodoxolones as stable solids. The similar fluorination reaction of alkynes using 1-hydroxy-1,2-benziodoxol-3(1*H*)-one and HF·py also gave the same products.

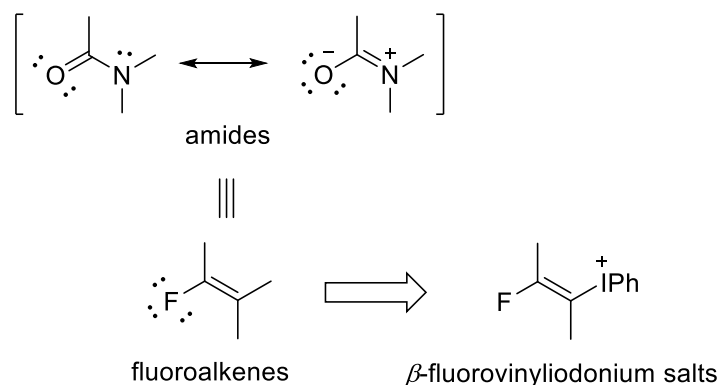


Keywords: Fluorination; hypervalent iodine; hydrogen fluoride; alkyne; 1-(β -fluorovinyl)-1,2-benziodoxol-3(1*H*)-one

Introduction

Substance P (SP) is an undecapeptide member of the tachykinin neuropeptide family, containing a chain of eleven amino acid residues, and it acts as a neurotransmitter and as a neuromodulator.¹ However, major problem is rapid degradation by peptidases in the use of peptides as therapeutic agents. To overcome the drawback, non-hydrolysable amide isosteres are used as an established approach. In 1990, Allmendinger and his coworkers reported that a fluoroalkene unit is an excellent amide bond substitute mimicking both steric and electronic features of the peptide bond.²⁻⁴ Fluoroalkenes have a similarity in chemical and structural properties to amide groups and are stable enough against hydrolysis. When the amide bond of SP between Phe (phenylalanine)-Gly (glycine) is replaced by an isosteric fluorovinyl unit, the isosteres cannot be cleaved by peptidases, causing a significant biological activity. Particularly, in receptor binding assays, the fluoroalkene isostere is nearly as active as SP itself.^{2,3}

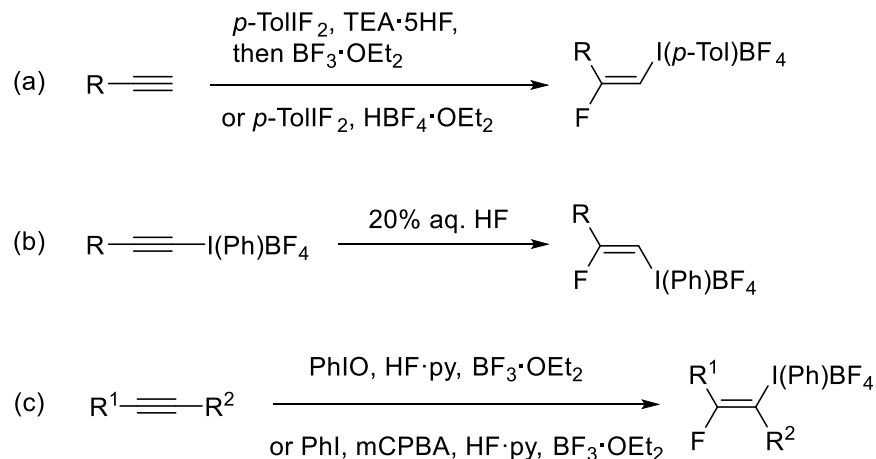
Recently hypervalent iodine compounds have received much attention due to their synthetically useful nature such as mild oxidation property, chemical behavior similar to transition metals, and excellent leaving ability.⁵⁻⁹ As the building block for fluoroalkene synthesis, as shown in Scheme 1, a β -fluorovinylidonium salt is an excellent candidate because phenyliodonio group (PhI^+) is readily replaceable with many functional groups under mild conditions due to its superleaving ability, which is nearly 10^6 times more reactive than triflate group.¹⁰ Therefore, the synthetic conditions of fluoroalkenes become milder than those of conventional methods.



Scheme 1. Fluorovinylidonium salts as the building block of fluoroalkenes

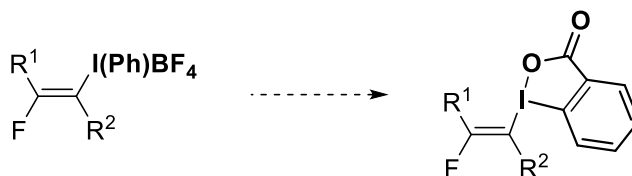
There are some applications as the building block. Hara and his coworkers demonstrated the utility of β -fluorovinylidonium salts as the building block for fluorine-containing compounds,¹¹⁻¹⁶ where the utility has been shown by several coupling reactions such as carbomethoxylation, Heck coupling, Stille coupling, Sonogashira coupling, and Suzuki coupling.

Scheme 2 shows the synthetic methods of β -fluorovinylidonium salts reported previously, including (a) the reaction of terminal alkynes with *p*-(difluoroiodo)toluene in the presence of HF or HBF_4 ,^{16,18} (b) the reaction of alkynylidonium salts with aqueous hydrofluoric acid,^{15,17} and (c) the reaction of alkynes with PhIO/HF reagent.¹⁹



Scheme 2. Previous works on synthesis of β -fluorovinylidonium salts

Although β -fluorovinylidonium salts are stable enough to handle, they lack stability enough to be stored for long periods under atmospheric conditions. Also, some idonium salts have poor crystallinity and are oils, so handling is troublesome. Therefore, we envisioned incorporation of a rigid structure into the β -fluorovinylidonium salts to increase their crystallinity and stability (Scheme 3). Benziodoxolones bearing a 5-membered ring fit this purpose because they show a high thermal stability due to the bridging of the equatorial and apical positions by the 5-membered ring and the overlap of the lone pair electrons with the p-orbitals of the benzene ring.^{8,20}

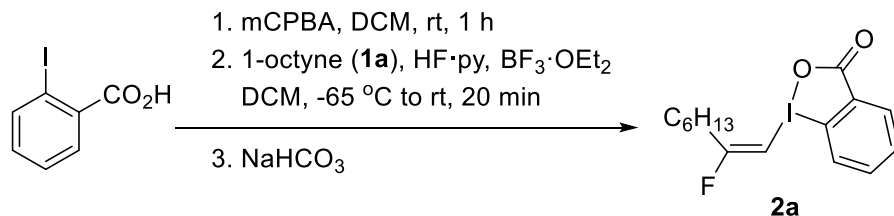


Scheme 3. Introduction of a stable cyclic structure into β -fluorovinylidonium salts

Since we previously developed a convenient synthesis of β -fluorovinylidonium salts using the in-situ preparation of iodosylbenzene from iodobenzene,¹⁹ we applied this procedure to the synthesis of β -fluorovinylidonium salts bearing the benziodoxolone structure. Thus, we thought to be able to prepare β -fluorovinylbenziodoxolones from *o*-iodobenzoic acid.

Results and Discussion

The synthesis of β -fluorovinylbenziodoxolones from *o*-iodobenzoic acid was examined using 1-octyne as a model substrate according to the similar procedure reported before.¹⁹ *o*-Iodobenzoic acid was treated with mCPBA and then reacted with HF-pyridine complex and 1-octyne (**1a**). The reaction mixture was treated with $\text{BF}_3\cdot\text{OEt}_2$ complex, and finally quenched with sodium hydrogen carbonate. The molar ratios of $\text{BF}_3\cdot\text{OEt}_2$ and **1a** were examined to optimize the conditions. The results are given in Table 1. The best result (Table 1, entry 2) was obtained using *o*-iodobenzoic acid (0.75 mmol), **1a** (0.5 mmol), HF-py (10 mmol HF), and $\text{BF}_3\cdot\text{OEt}_2$ (5 mmol), giving 2-fluoro-1-octenylbenziodoxolone **2a** in 84% yield.

Table 1. Optimization of Fluorination of **1a**^a

Entry	BF ₃ ·OEt ₂ (mmol)	1a (mmol)	Yield (%) ^b
1	2	0.5	42
2	5	0.5	84
3	10	0.5	78
4	5	0.75	66

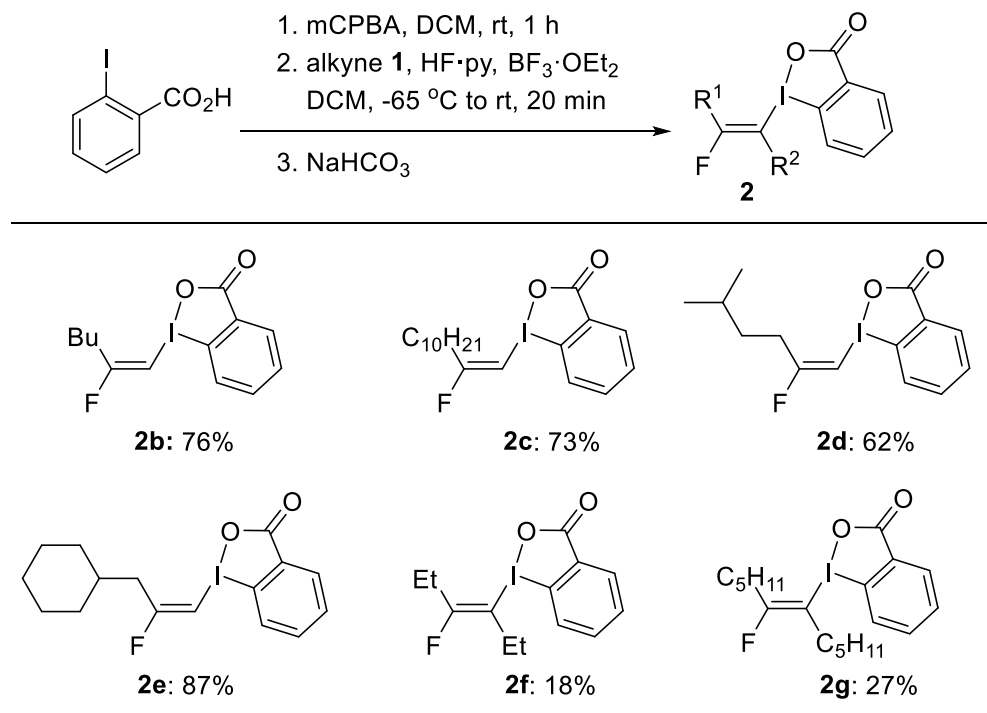
^a Conditions: *o*-iodobenzoic acid (0.75 mmol), DCM (1 mL), 1 h; 1-octyne (**1a**), HF·py (10 mmol HF), DCM (1 mL); BF₃·OEt₂, -65 °C to rt, 20 min. ^b Yields are determined by ¹⁹F NMR.

The stereochemistry of 2-fluoro-1-octenylbenziodoxolone **2a** was determined by ¹H NMR. The vinylic proton appeared at 6.59 ppm and coupled with fluorine atom. The coupling constant ³J_{H-F} was 18 Hz. This value was in good agreement with the (*E*) geometry of (*E*)-2-fluoro-1-octenyl(phenyl)iodonium tetrafluoroborate, ³J_{H-F} = 15 Hz.¹⁹ There is an obvious difference in melting point between non-cyclic 2-fluoro-1-octenyl(phenyl)iodonium tetrafluoroborate and benziodoxolone **2a**, 52-53 °C¹⁹ and 118-119 °C. The melting point of the benziodoxolone **2a** is much higher. In addition, to evaluate the thermal stability, the mass change of the samples was measured by TG. The temperatures at which 1% weight loss occurred were compared under a nitrogen atmosphere. As shown in Table 2, the 1% weight loss temperature of **2a** was 194.6 °C, and that of 2-fluoro-1-octenyl(phenyl)iodonium tetrafluoroborate was 135.6 °C. Clearly, **2a** was found to be more thermally stable than 2-fluoro-1-octenyl(phenyl)iodonium tetrafluoroborate.

Table 2. Thermal stability of β-fluorovinylidonium salts

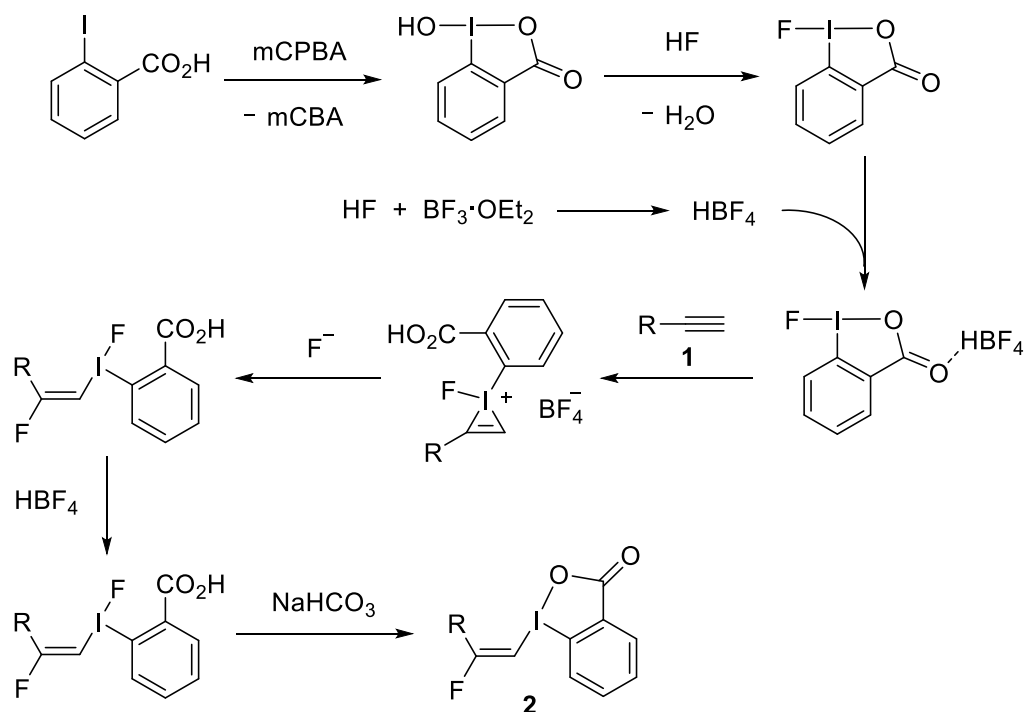
Entry	Iodonium salts	Mp (°C)	1%Weight loss temperature (°C)
1	2a	118-119	194.6
2		52-53	135.6

The fluorination reaction of other alkynes **1** with *o*-iodobenzoic acid was conducted. The results are given in Table 3. Terminal alkynes worked well to give good yields of the products **2** but the reaction for the internal alkynes resulted in lower yields. This may be attributed to the steric hindrance of the benziodoxolone structure.

Table 3. Fluorination of Alkynes **1**^a

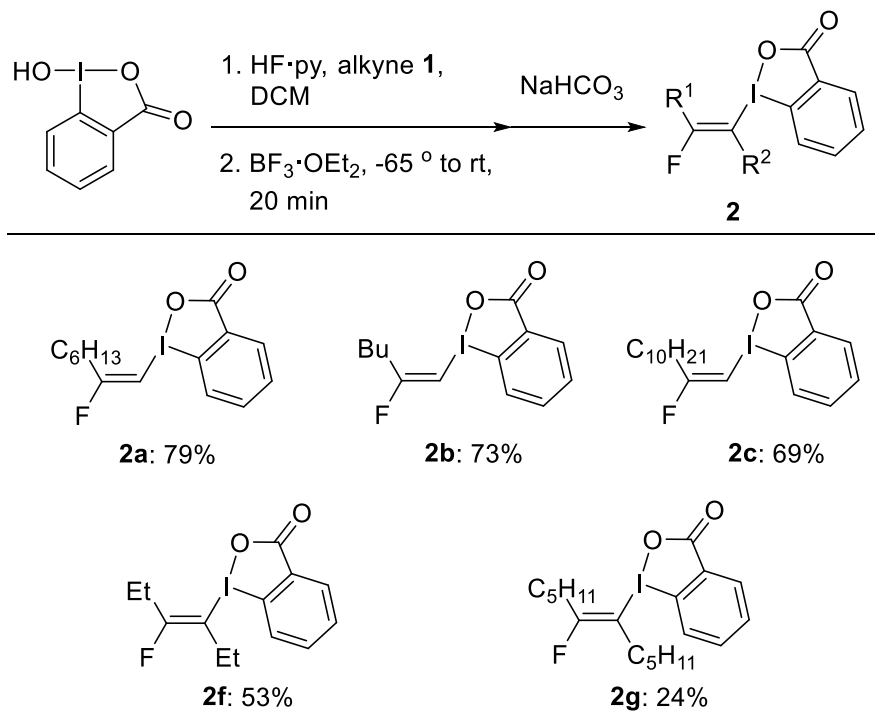
^a Conditions: *o*-iodobenzoic acid (0.75 mmol), DCM (1 mL), 1 h; **1** (0.5 mmol), HF·py (10 mmol HF), DCM (1 mL); BF₃·OEt₂ (5 mmol), -65 °C to rt, 20 min. Isolated yields are given.

The reaction of alkynes **1** with HF in the presence of *o*-iodobenzoic acid and mCPBA is considered to proceed as reported previously in the fluorination with reagents combined of hypervalent iodine and HF (Scheme 4).²¹⁻²⁸ First, *o*-iodobenzoic acid is oxidized by mCPBA to form 1-hydroxy-1,2-benziodoxolone and then reacts with HF to generate 1-fluoro-1,2-benziodoxolone, which is activated by tetrafluoroboric acid formed from HF and BF₃.¹⁶ The activated fluorobenziodoxolone reacts with an alkyne **1** to give a β -fluorovinylidonium salts. Treatment with sodium hydrogen carbonate affords a cyclized β -fluorovinylbenziodoxolone **2**.



Scheme 4. A possible mechanism

In the synthesis of β -fluorovinylbenziodoxolone **2**, 1-hydroxybenziodoxolone is expected to be a key intermediate which is formed in situ by oxidation of *o*-iodobenzoic acid with mCPBA. Thus, we re-examined the fluorination of alkynes **1** using 1-hydroxybenziodoxolone. Synthesis of 1-hydroxybenziodoxolone was conducted according to the literature methods.^{29,30} The reaction of alkynes **1** in the presence of HF·py was conducted using 1.5 equiv of 1-hydroxybenziodoxolone. Treatment of **1** with 1-hydroxybenziodoxolone in the presence of HF·py followed by addition of $\text{BF}_3 \cdot \text{OEt}_2$ gave the desired 2-fluoroalkenylbenziodoxolones **2** after treatment with aqueous NaHCO_3 . The results are given in Table 4.

Table 4. Fluorination of **1** Using 1-Hydroxy-1,2-benziodoxolone^a

^a Conditions: 1-hydroxy-1,2-benziodoxolone (0.3 mmol), HF·py (4 mmol HF), alkyne **1** (0.2 mmol), DCM (0.5 mL); BF₃·OEt₂ (2 mmol), -65 °C to rt, 20 min. Isolated yields are given.

The similar results were obtained in the case of the reaction with 1-hydroxy-1,2-benziodoxolone. The fluorination of terminal alkynes **1a-1c** gave the desired products **2** in good yields, while that of internal alkynes **1f** and **1g** resulted in moderate yields of the products **2**. These results clearly indicate that 1-hydroxy-1,2-benziodoxolone is a key intermediate.

Conclusions

In conclusion, we have developed convenient methods for synthesis of stable 1-(2-fluorovinyl)-1,2-benziodoxolones. The fluorination reaction is achieved in the presence of HF·py using *o*-iodobenzoic acid in the presence of mCPBA or 1-hydroxy-1,2-benziodoxolone. Compared with non-cyclic 2-fluorovinylidonium salts, 1-(2-fluorovinyl)-1,2-benziodoxolones **2** indicate a considerable advantage in the ease of handling and the stability for storage. In addition to good yields of the products, the convenient procedure facilitates the approach to synthesis of valuable fluoroalkanes as the building block.

Experimental Section

General. All solvents and starting materials were used as received without further purification unless otherwise indicated. ¹H NMR (400 MHz), ¹³C NMR (100 MHz), and ¹⁹F NMR (376 MHz) spectra were recorded on an Agilent 400-MR NMR spectrometer. High-resolution mass spectra were measured by the Analytical

Center, Institute for Materials Chemistry, Kyushu University. TG was analyzed by Technology and Innovation Center, Daikin Industries. Melting points were measured with a YANACO micro melting apparatus and are uncorrected. Column chromatographic separation was carried out using Silica Gel 60. Pre-coated plates (silica gel 60 F₂₅₄, MERCK) were used for TLC examination.

1-(2-Fluorovinyl)-1,2-benziodoxol-3(1H)-ones 2 using *o*-iodobenzoic acid/mCPBA. To a Teflon tube were placed *o*-iodobenzoic acid (186 mg, 0.75 mmol), mCPBA (65%, 199 mg, 0.75 mmol), and DCM (1 mL). The mixture was stirred at room temperature for 1 h, and then HF·py (0.26 mL, 10 mmol HF), alkyne **1** (0.5 mmol), DCM (1 mL) were added at this temperature. After cooling to -65 °C, BF₃·Et₂O (0.62 mL, 5.0 mmol) was added and stirred for 10 min. The reaction mixture was stirred at room temperature for 20 min. The reaction mixture was poured into water (10 mL) containing NaHCO₃ (1.26 g, 15 mmol) and extracted with DCM (10 mL × 3). The combined organic layer was dried over anhydrous Na₂SO₄. Evaporation of the solvent gave crude viscous crystalline products **2**, which was submitted to column chromatography on silica gel. Elution with 5% MeOH/EtOAc gave pure crystalline products.

1-(2-Fluorovinyl)-1,2-benziodoxol-3(1H)-ones 2 using 1-hydroxy-1,2-benziodoxol-3(1H)-one. To a Teflon tube were placed 1-hydroxy-1,2-benziodoxol-3(1H)-one (73.8 mg, 0.3 mmol), HF·py (0.1 mL, 4 mmol HF), alkyne **1** (0.2 mmol), DCM (0.5 mL) were added and stirred at room temperature for 10 min. After cooling to -65 °C, BF₃·Et₂O (0.25 mL, 2.0 mmol) was added and stirred for 10 min. The reaction mixture was stirred at room temperature for 20 min. The reaction mixture was poured into water (10 mL) containing NaHCO₃ (0.5 g, 6 mmol) and extracted with DCM (10 mL × 3). The combined organic layer was dried over anhydrous Na₂SO₄. Evaporation of the solvent gave crude viscous crystalline products **2**, which was submitted to column chromatography on silica gel. Elution with 5% MeOH/EtOAc gave pure crystalline products.

1-[(*E*)-2-Fluoro-1-octen-1-yl]-1,2-benziodoxol-3(1H)-one (2a). The product was obtained as white solids, mp 118-119 °C. ¹H NMR (400 MHz, CD₃OD): δ 0.80 (t, *J* 7 Hz, 3H), 1.17-1.35 (m, 6H), 1.57-1.64 (m, 2H), 2.75 (dt, *J* 7, 23 Hz, 2H), 6.59 (d, *J* 18 Hz, 1H), 7.71-7.76 (m, 3H), 8.27 (d, *J* 7 Hz, 2H). ¹³C{¹H} NMR (100 MHz, DMSO-*d*₆): δ 5.0, 14.1, 17.8, 20.2, 23.1, 23.2 (d, *J* 26 Hz), 72.6 (d, *J* 29 Hz), 105.9, 119.2, 122.7, 124.0, 124.8, 126.2, 160.7, 166.9 (d, *J* 283 Hz). ¹⁹F NMR (376 MHz, CD₃OD): δ -68.2. HRMS (FAB, double focusing): *m/z* [MH]⁺ calcd for C₁₅H₁₉FIO₂: 377.0408; found: 377.0414.

1-[(*E*)-2-Fluoro-1-hexen-1-yl]-1,2-benziodoxol-3(1H)-one (2b). The product was obtained as white solids; mp 138 °C. ¹H NMR (400 MHz, CD₃OD): δ 0.87 (t, *J* 7 Hz, 3H), 1.31-1.40 (m, 2H), 1.56-1.63 (m, 2H), 2.75 (dt, *J* 7, 22 Hz, 2H), 6.58 (d, *J* 19 Hz, 1H), 7.70-7.78 (m, 3H), 8.27 (d, *J* 7 Hz, 1H). ¹³C{¹H} NMR (100 MHz, CD₃OD): δ = 14.3, 23.3, 29.6, 32.6 (d, *J* 26 Hz), 82.1 (d, *J* 28 Hz), 115.5, 132.8, 132.3, 133.6, 134.4, 135.8, 170.3, 176.5 (d, *J* 283 Hz). ¹⁹F NMR (376 MHz, CD₃OD): δ = -63.3. HRMS (FAB, double focusing): *m/z* [MH]⁺ calcd for C₁₃H₁₅FIO₂: 349.0095; found: 349.0101.

1-[(*E*)-2-Fluoro-1-dodecen-1-yl]-1,2-benziodoxol-3(1H)-one (2c). The product was obtained as white solids, mp 98 °C. ¹H NMR (400 MHz, CD₃OD): δ 0.87 (t, *J* 7 Hz, 3H), 1.20-1.30 (m, 14H), 1.57-1.64 (m, 2H), 2.68 (dt, *J* 7, 22 Hz, 2H), 6.17 (d, *J* 19 Hz, 1H), 7.54 (d, *J* 8 Hz, 1H), 7.64-7.71 (m, 2H), 8.46 (dd, *J* 2, 7 Hz, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 14.8, 24.0, 27.4, 30.1, 30.5, 30.7, 30.8, 30.9, 32.7 (d, *J* 26 Hz), 33.3, 82.3 (d, *J* 28 Hz), 115.6, 128.8, 132.3, 133.6, 134.4, 135.7, 170.2, 176.4 (d, *J* 283 Hz). ¹⁹F NMR (376 MHz, CDCl₃): δ = -62.7. HRMS (FAB, double focusing): *m/z* [MH]⁺ calcd for C₁₉H₂₇FIO₂: 433.1034; found: 433.1040.

1-[(*E*)-2-Fluoro-5-methyl-1-hexen-1-yl]-1,2-benziodoxol-3(1H)-one (2d). The product was obtained as white solids, mp 148 °C. ¹H NMR (400 MHz, DMSO-*d*₆): δ 0.79 (d, *J* 7 Hz, 6H), 1.41 (q, *J* 7 Hz, 2H), 1.48-1.57 (m, 1H), 2.67 (dt, *J* 7, 23 Hz, 2H), 6.72 (d, *J* 20 Hz, 1H), 7.63-7.76 (m, 3H), 8.12 (dd, *J* 2, 7 Hz, 1H). ¹³C{¹H} NMR (100 MHz, DMSO-*d*₆): δ = 22.2, 27.0, 29.3 (d, *J* 26 Hz), 34.7, 83.8 (d, *J* 24 Hz), 114.8, 127.3, 130.6, 131.6, 133.8, 134.2,

165.9, 172.7 (d, *J* 279 Hz). ¹⁹F NMR (376 MHz, DMSO-*d*₆): δ = -68.0. HRMS (FAB, double focusing): *m/z* [MH]⁺ calcd for C₁₄H₁₇FIO₂: 363.0252; found: 363.0258.

1-[(*E*)-3-Cyclohexyl-2-fluoro-1-propen-1-yl]-1,2-benziodoxol-3(1*H*)-one (2e). The product was obtained as white solids, mp 139 °C. ¹H NMR (400 MHz, DMSO-*d*₆): δ 0.88-1.19 (m, 5H), 1.52-1.67 (m, 6H), 2.58 (dd, *J* 7, 24 Hz, 2H), 6.77 (d, *J* 20 Hz, 1H), 7.63-7.75 (m, 3H), 8.12 (dd, *J* 1, 7 Hz, 1H). ¹³C{¹H} NMR (100 MHz, DMSO-*d*₆): δ = 25.6, 25.7, 32.1, 35.3, 38.4 (d, *J* 25 Hz), 85.0 (d, *J* 24 Hz), 114.8, 127.4, 130.6, 131.6, 133.7, 134.2, 165.9, 171.6 (d, *J* 279 Hz). ¹⁹F NMR (376 MHz, DMSO-*d*₆): δ = -65.4. HRMS (FAB, double focusing): *m/z* [MH]⁺ calcd for C₁₆H₁₉FIO₂: 389.0408; found: 389.0412.

1-[(*E*)-4-Fluoro-3-hexen-3-yl]-1,2-benziodoxol-3(1*H*)-one (2f). The product was obtained as white solids; mp 208 °C. ¹H NMR (400 MHz, CD₃OD): δ 1.14 (t, *J* 7 Hz, 3H), 1.16 (t, *J* 7 Hz, 3H), 2.74 (q, *J* 7 Hz, 2H), 2.80 (q, *J* 7 Hz, 2H), 7.69-7.74 (m, 3H), 8.29 (d, *J* 8 Hz, 1H). ¹³C{¹H} NMR (100 MHz, CD₃OD): δ = 11.6, 14.4, 26.7 (d, *J* 7 Hz), 28.3 (d, *J* 28 Hz), 105.3 (d, *J* 23 Hz), 114.2, 128.8, 132.3, 133.9, 135.0, 135.9, 170.0, 171.2 (d, *J* 279 Hz). ¹⁹F NMR (376 MHz, CD₃OD): δ = -79.9. HRMS (FAB, double focusing): *m/z* [MH]⁺ calcd for C₁₃H₁₅FIO₂: 349.0095; found: 349.0101.

1-[(*E*)-7-Fluoro-6-dodecen-6-yl]-1,2-benziodoxol-3(1*H*)-one (2g). The product was obtained as white solids; mp 106-107 °C; yield. ¹H NMR (400 MHz, CD₃OD): δ 0.70-0.85 (m, 6H), 1.05-1.23 (m, 4H), 1.43-1.50 (m, 4H), 2.61-2.67 (m, 4H), 7.57-7.66 (m, 3H), 8.19 (d, *J* 6 Hz, 1H). ¹³C{¹H} NMR (100 MHz, CD₃OD): δ = 14.4, 14.6, 23.58, 23.64, 27.6, 30.0, 32.41, 32.43, 33.2 (d, *J* 6 Hz), 34.6 (d, *J* 27 Hz), 104.4 (d, *J* 24 Hz), 114.1, 128.8, 132.4, 134.0, 135.0, 135.9, 170.1, 171.0 (d, *J* 279 Hz). ¹⁹F NMR (376 MHz, CD₃OD): δ = -76.8. HRMS (FAB, double focusing): *m/z* [MH]⁺ calcd for C₁₉H₂₇FIO₂: 433.1034; found: 433.1040.

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