Simple and Efficient Generation of α-Fluoromalonaldehyde from Fluorinated Enol Sulfonate and Its Reaction with Acyl Chlorides Leading to (*Z*)-*β*-Acyloxy-α-fluoroacrylaldehydes†

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Introduction

Malonaldehyde is a naturally occurring three-carbon dialdehyde formed as an end-product of the peroxidation of unsaturated lipids[1] or a byproduct of the biosynthesis of prostaglandins in animal tissues.[2] The reactions of malonaldehyde with DNA and proteins are an ongoing interest in biochemistry,[3] because it is not only a toxic, mutagenic, and carcinogenic substrate[4] but also one involved in cell aging[5] and the deterioration of foods.[6] In organic synthesis, malonaldehyde has also been used as a potential C-3 building block for the construction of complex organic molecules.[7]

On the other hand, the development of efficient and stereoselective synthetic methods of organofluorine compounds continues to be of crucial importance within the field of medicinal and agricultural chemistries due to their unique physical, chemical, and biological properties.[8] Despite its versatile synthetic utility, to the best of our knowledge, two preparations of α-fluoromalonaldehyde and its acetals have been reported, which suffer from the toxicity of the starting material, poor overall yields, and multistage manipulations.[9] In our continuing studies aiming at expanding the utilization of fluorinated enol sulfonate **1**,[10] we now describe the simple and efficient generation of α-fluoromalonaldehyde sodium salt **2** from **1** and its reaction with a number of acid chlorides leading predominantly to the corresponding (*Z*)-*β*-acyloxy-α-fluoroacrylaldehydes **3**.

Results and Discussion

Table 1 summarizes the results for the generation of α-fluoromalonaldehyde sodium salt **2** from **1** and its successive reaction with benzoyl chloride providing the corresponding *β*-benzoyloxy-α-fluoroacrylaldehydes (**3a**).

Treatment of sulfonate **1a** in the presence of 3.3 equiv of sodium hydroxide (NaOH) in a mixed solvent of DMSO−H_2O (1:1) at room temperature for 1 h resulted in the generation of α-fluoromalonaldehyde sodium salt **2**. The reaction of **2** with 2 equiv of benzoyl chloride (PhCOCl) at room temperature for 1 h afforded (*Z*)-*β*-benzoyloxy-α-fluoroacrylaldehyde **3a** in 92% yield (Table 1, entry 3). The geometry of **3a** was assigned on the basis of magnitudes of couplings between the fluorine and vinylic hydrogen.[11]

The use of 1.1−2.2 equiv of NaOH gave **3a** in only 17−57% yield (entries 1 and 2). Employment of other solvents, such as DMF, acetonitrile (MeCN), and THF, decreased the yield of **3a** (entries 4−6). Neither the reaction in benzene nor in hexane proceeds at all, and starting material **1a** is recovered in quantitative yield even for a longer reaction time (entries 7 and 8). Among the bases examined, such as potassium hydroxide (KOH), potassium *tert*-butoxide (*t*-BuOK), sodium carbonate (Na_2CO_3), and triethylamine (Et_3N), NaOH was the most suitable base for the reaction. KOH and *t*-BuOK could also be used (entries 9 and 10), whereas Na_2CO_3 and Et_3N were ineffective for the reaction, and a quantitative amount of sulfonate **1a** was recovered (entries 11 and 12). The reaction of 2,2,3-trifluoro-1-propenyl *p*-chlorobenzenesulfonate (**1b**) instead of **1a** provided **3a** in 84% yield (entry 13).

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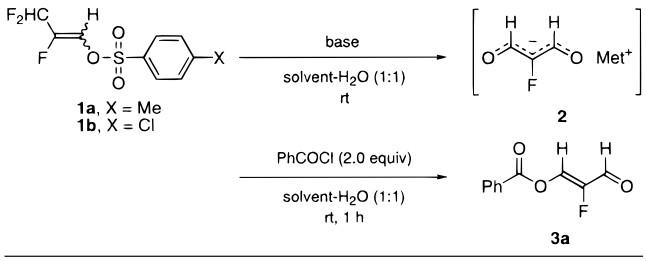
Table 1. Screening of the Conditions for the Generation of Malonaldehyde Metal Salt and Its Reaction with Benzoyl Chloride[a]



entry	sulfonate	base (equiv)	solvent	time (h)	product **3a** yield (%)[b]	ratio (*Z*/*E*)[c]
1	**1a**	NaOH (1.1)	DMSO	1	17 (69)	>99/<1
2	**1a**	NaOH (2.2)	DMSO	1	57 (40)	>99/<1
3	**1a**	NaOH (3.3)	DMSO	1	92 (−)	>99/<1
4	**1a**	NaOH (3.3)	DMF	1	43 (35)	>99/<1
5	**1a**	NaOH (3.3)	MeCN	1	38 (60)	>99/<1
6	**1a**	NaOH (3.3)	THF	1	12 (71)	>99/<1
7	**1a**	NaOH (3.3)	benzene	3	0 (100)	−
8	**1a**	NaOH (3.3)	hexane	3	0 (99)	−
9	**1a**	KOH (3.3)	DMSO	1	87 (9)	>99/<1
10	**1a**	*t*-BuOK (3.3)	DMSO	1	77 (19)	>99/<1
11	**1a**	Na_2CO_3 (1.65)	DMSO	1	3 (93)	>99/<1
12	**1a**	Et_3N (3.3)	DMSO	1	0 (92)	−
13	**1b**	NaOH (3.3)	DMSO	1	84 (14)	>99/<1

[a] All reactions were carried out as described in Experimental Section. [b] Isolated yields. Values in parentheses stand for the recovered **1**. [c] Determined by ^{19}F NMR of the crude products prior to isolation.

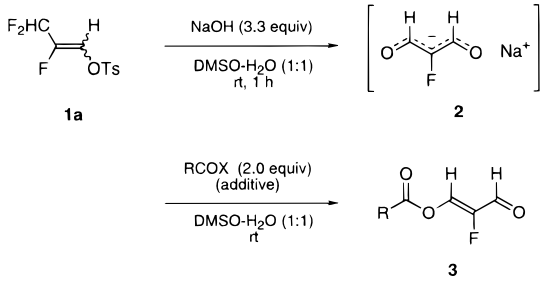
The results of the reaction of **1a** with various carboxylic acid derivatives are summarized in Table 2.

Benzoic anhydride was used as a substitute for benzoyl chloride to give **3a** in 75% yield (Table 2, entry 2), whereas the use of benzoyl bromide resulted in a remarkable decrease in the yield (entry 3). The substituent on the aromatic ring of carboxylic acid derivatives significantly affects the yield of **3**. The reaction between **2** and acid chlorides carrying an electron-donating group, such as 4-methylphenyl, 4-methoxyphenyl, or (*E*)-styryl group, provided **3b,d,g** in 35−57% yield (entries 4, 7, and 21) under optimized conditions, which could be improved by longer reaction time (entries 5 and 8). On the contrary, the reaction of **2** with the electron-withdrawing substituted aromatic acid chlorides, such as 4-chloro- and 4-(trifluoromethyl)benzoyl chlorides, as well as dodecanoyl chloride, only gave **3e,f,h** in low yield (4−17%) (entries 15, 19, and 23).

As a result of a more detailed study of the reaction conditions and additives, it was found that the addition of a phase transfer catalyst (PTC) to the reaction mixture was very crucial for the increase in the yield (entries 9, 10, 11, 12, 13, 16, 17, 20, 22, and 24). Thus, the use of a catalytic amount (10−30 mol %) of PTC, such as *n*-tetrabutylammonium chloride (n-$Bu_4N^+Cl^-$), *n*-tetrabutylammonium bromide (n-$Bu_4N^+Br^-$), *n*-tetrabutylammonium iodide (n-$Bu_4N^+I^-$), and *n*-tetrabutylammonium hydrogensulfate (n-$Bu_4N^+HSO_4^-$), were extremely effective for the reaction, giving **3d** in higher yield for the shorter reaction time (1 h) (entries 9−13). Among them, a catalytic amount (30 mol %) of n-$Bu_4N^+Br^-$ produced the most satisfactory results (entry 10). On the other hand, the addition of 18-crown-6 (3.3 equiv) did not affect the yield (entry 14).

The reaction of **2** with cinnamoyl chloride in the presence of a catalytic amount of n-$Bu_4N^+Br^-$ smoothly proceeded to give **3g** in 73% yield (entry 22). However,

Table 2. Synthesis of β-Acyloxy-α-fluoroacrylaldehydes 3[a]



entry	RCOX	time (h)	additive (mol %)	product **3**	yield (%)[b]
1	PhCOCl	1	none	**3a**	92
2	$(PhCO)_2O$	1	none	**3a**	75
3	PhCOBr	1	none	**3a**	19
4	4-MeC_6H_4COCl	1	none	**3b**	57
5		3	none	**3b**	75
6	2-MeC_6H_4COCl	1	none	**3c**	89
7	4-$MeOC_6H_4COCl$	1	none	**3d**	35
8		3	none	**3d**	65
9		1	n-$Bu_4N^+Br^-$ (10)	**3d**	73
10		1	n-$Bu_4N^+Br^-$ (30)	**3d**	80
11		1	n-$Bu_4N^+Cl^-$ (30)	**3d**	52
12		1	n-$Bu_4N^+I^-$ (30)	**3d**	70
13		1	n-$Bu_4N^+HSO_4^-$ (30)	**3d**	75
14		1	18-crown-6 (330)	**3d**	38
15	4-ClC_6H_4COCl	1	none	**3e**	17
16		1	n-$Bu_4N^+Br^-$ (30)	**3e**	29
17	$(4\text{-}ClC_6H_4CO)_2O$	1	n-$Bu_4N^+Br^-$ (30)	**3e**	28
18	4-$ClC_6H_4CO_2Me$	1	none	**3e**	0
19	4-$CF_3C_6H_4COCl$	1	none	**3f**	5
20		1	n-$Bu_4N^+Br^-$ (30)	**3f**	26
21	(*E*)-PhCH=CHCOCl	1	none	**3g**	35
22		1	n-$Bu_4N^+Br^-$ (30)	**3g**	73
23	$CH_3(CH_2)_{10}COCl$	1	none	**3h**	4
24		1	n-$Bu_4N^+Br^-$ (30)	**3h**	22

[a] All reactions were carried out as described in Experimental Section. [b] Isolated yields.

in the case of 4-chloro- and 4-(trifluoromethyl)benzoyl chlorides as well as dodecanoyl chloride, the addition of PTC was not effective and resulted in only a slight increase in the yield (entries 16, 20, and 24), probably because of their high reactivities under these conditions. To improve the yield of **3e**, we examined the reaction of **2** with 4-chlorobenzoic anhydride in the presence of n-$Bu_4N^+Br^-$ that merely gave a similar yield (28%) (entry 17). The reaction of **2** with methyl 4-chlorobenzoate also did not proceed at all (entry 18). Noteworthy is that only (*Z*)-isomer was produced in the reaction, irrespective of the substituents of carboxylic acid derivatives.

Unfortunately, other electrophiles, such as phenyl isocyanate, benzenesulfonyl chloride, diphenyl chlorophosphate, chlorodiphenylphosphine, chlorodimethylphenylsilane, *tert*-butyldimethylsilyl chloride, benzaldehyde, and 1-iodohexane, did not react at all with **2**, even if n-BuN^+Br^-, 18-crown-6, or 4,7,13,16,21,24-hexaoxa-1,-10-diazabicyclo[8.8.8]hexacosane was added.[12]

Regarding the α-fluoromalonaldehyde sodium salt **2**, three resonance structures could be illustrated such as the dialdehyde form **2A**, the (*Z*)-enol form **2B**, and the (*E*)-enol form **2C** (Figure 1).

(12) The reaction of fluorine-free malonaldehyde with tosyl chloride or alkyl chloride in the presence of 18-crown-6, see: (a) Vatèle, J.-M. *Tetrahedron* **1986**, *42*, 4443. (b) David, S.; Eustache, J. *J. Chem. Soc., Perkin. Trans. 1* **1979**, 2521. (c) David, S.; Lubineau, A.; Vatèle, J.-M. *New. J. Chem.* **1980**, *4*, 547. (d) D'Angelo, J.; Maddaluno, J. *Tetrahedron Lett.* **1983**, *24*, 895.

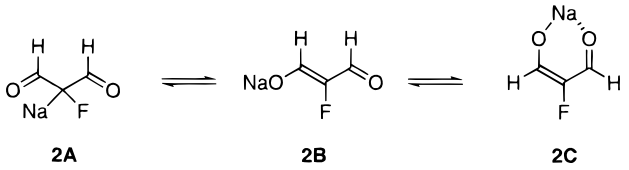


Figure 1.

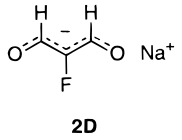


Figure 2.

To confirm the structure of **2**, we measured the in situ-generated **2** using the ^{1}H NMR and ^{19}F NMR spectra.[13] According to the chemical shift (δ −96.71) in the ^{19}F NMR spectrum as well as the coupling constants ($^3J_{HF}$ = 25.12 Hz) between the vicinal fluorine and hydrogen in the ^{1}H NMR spectrum, it was found that the in situ-generated **2** is stabilized in the W-shaped structure, **2D** ((*Z*)-enol, *s-trans*) in the highly coordinating solvent (DMSO−D_2O (H_2O)) at room temperature (Figure 2).[14]

Although exact elucidation of the reaction mechanism awaits further investigation, the reaction seems to proceed as follows. The enol sulfonate **1a** may undergo cleavage of the enol oxygen−sulfur bond with hydroxide ion, followed by the loss of a fluorine atom to generate α,β-difluoroacrylaldehyde, which reacts with hydroxide ion to give the α-fluoromalonaldehyde sodium salt **2**. Then, **2** reacts with various acid chlorides to afford the corresponding (*Z*)-β-acyloxy-α-fluoroacrylaldehydes **3**.

In summary, we have found a novel and effective generation of the α-fluoromalonaldehyde sodium salt **2** from fluorinated enol sulfonates **1**, and the subsequent reaction of **2** with various acid chlorides that exclusively provide the corresponding (*Z*)-β−acyloxy-α-fluoroacrylaldehydes **3** in good to excellent yields.

Experimental Section

^{1}H NMR spectra were measured with a JEOL α-400 (400 MHz) FT-NMR spectrometer in deuteriochloroform ($CDCl_3$) solutions with tetramethylsilane (Me_4Si) as the internal standard. ^{13}C NMR spectra were obtained on a JEOL α-400 (100 MHz) FT-NMR spectrometer in $CDCl_3$ solutions relative to $CDCl_3$ (77.0 ppm). ^{19}F NMR spectra were recorded on a JEOL α-400 (376 MHz) FT-NMR in $CDCl_3$ solutions using trifluoroacetic acid as the external standard. The isolation of pure products was carried out by column chromatography using silica gel (Wakogel C-200, 100−200 mesh, Wako Pure Chemical Ind., Ltd.). The sulfonate **1** was prepared according to our previously reported procedure.[10h]

A Typical Procedure for the Synthesis of 3. To a solution of sodium hydroxide (NaOH) (3.3 mmol, 0.138 g) in H_2O (2 mL) was added a DMSO (2 mL) solution of the sulfonate **1a** (1.0 mmol, 0.266 g) at 0 °C. After the mixture was stirred at room temperature for 1 h, benzoyl chloride (2.0 mmol, 0.280 g) was slowly added. After it was stirred at room temperature for 1 h, the mixture was quenched with cold brine (30 mL), followed by extraction with diethyl ether (Et_2O) (30 mL × 3), dried over anhydrous Na_2SO_4, and concentrated under vacuum. After the distribution of the isomer ratio of the products were determined by ^{19}F NMR, the residue was subjected to chromatography on a column of silica gel using benzene as the eluent, giving (*Z*)-2-fluoro-3-oxo-1-propenyl benzoate (**3a**) as a white solid (0.178 g, 92%).

(*Z*)-2-Fluoro-3-oxo-1-propenyl benzoate (3a): mp 106.3−107.0 °C (hexane); IR ($CHCl_3$) 1681.9 (C═C), 1702.1 (C═O), 1755.2 (C═O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.51−7.60 (m, 2H), 7.68−7.75 (m, 1H), 8.06 (d, J = 19.03 Hz, 1H), 8.18−8.22 (m, 2H), 9.30 (d, J = 17.81 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 126.70, 128.97, 130.73, 135.04, 135.31, 136.26 (d, J = 4.13 Hz), 146.04 (d, J = 263.83 Hz), 161.37, 181.81 (d, J = 18.2 Hz); ^{19}F NMR ($CDCl_3$) δ-69.46 (dd, J = 19.03, 17.81 Hz, 1F); MS (CI) *m/z* (rel intensity) 195 (M^+ + H; 23.8); HRMS (CI) Calcd for $C_{10}H_8FO_3$: M + H, 195.0457. Found: *m/z* 195.0450. Anal. Calcd: C, 61.86; H, 3.63. Found: C, 61.85; H, 3.71.

(*Z*)-2-Fluoro-3-oxo-1-propenyl 4-methylbenzoate (3b): mp 135.8−136.1 °C (hexane); IR ($CHCl_3$) 1681.0 (C═C), 1702.1 (C═O), 1750.9 (C═O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.47 (s, 3H), 7.34 and 8.09 (AB quartet, J = 8.17 Hz, 1H), 8.06 (d, J = 19.03 Hz, 1H), 9.29 (d, J = 17.81 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 21.85, 123.85, 129.69, 130.78, 136.49 (d, J = 3.31 Hz), 145.94 (d, J = 263.00 Hz), 161.34, 181.84 (d, J = 19.02 Hz); ^{19}F NMR ($CDCl_3$) δ −69.84 (dd, J = 19.03, 17.81 Hz, 1F); MS (CI) *m/z* (rel intensity) 209 (M^+ + H; 100.0); HRMS (CI) Calcd for $C_{11}H_{10}FO_3$: M + H, 209.0614. Found: *m/z* 209.0615. Anal. Calcd: C, 63.46; H, 4.36. Found: C, 63.47; H, 4.39.

(*Z*)-2-Fluoro-3-oxo-1-propenyl 2-methylbenzoate (3c). mp 101.9−102.5 °C (hexane); IR ($CHCl_3$) 1678.6 (C═C), 1701.8 (C═O), 1752.1 (C═O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.65 (s, 3H), 7.43−7.49 (m, 2H), 7.69−7.75 (m, 2H), 8.06 (d, J = 19.27 Hz, 1H), 9.28 (d, J = 18.05 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 21.85, 125.26, 126.12, 131.63, 132.14, 134.10, 136.35 (d, J = 4.14 Hz), 142.58, 145.84 (d, J = 262.99 Hz), 161.02, 181.84 (d, J = 18.20 Hz); ^{19}F NMR ($CDCl_3$) δ −70.00 (dd, J = 19.27, 18.05 Hz, 1F); MS (CI) *m/z* (rel intensity) 209 (M^+ + H; 1.6); Anal. Calcd: C, 63.46; H, 4.36. Found: C, 63.51; H, 4.46.

A Typical Procedure for the Synthesis of 3 in the Presence of Phase Transfer Catalyst. To a solution of sodium hydroxide (3.3 mmol, 0.138 g) in H_2O (2 mL) was added a DMSO (2 mL) solution of the sulfonate **1a** (1.0 mmol, 0.266 g) at 0 °C. After stirring at room temperature for 1 h, *n*-tetrabutylammonium bromide (n-$Bu_4N^+Br^-$) (0.67 mmol, 0.193 g) and 4-anisoyl chloride (2.0 mmol, 0.340 g) were successively introduced into the reaction mixture. After stirring at room temperature for 1 h, the entire mixture was quenched with cold brine (30 mL), followed by extraction with ethyl acetate (EtOAc) (30 mL × 3), dried over anhydrous Na_2SO_4, and concentrated. After the distribution of the isomer ratio of the products were determined by ^{19}F NMR, the residue was subjected to chromatography on a column of silica gel using chloroform as the eluent, giving (*Z*)-2-fluoro-3-oxo-1-propenyl 4-methoxybenzoate (**3d**) as a white solid (0.179 g, 80%).

(*Z*)-2-Fluoro-3-oxo-1-propenyl 4-methoxybenzoate (3d): mp 149.2−150.1 °C (hexane); IR ($CHCl_3$) 1679.5 (C═C), 1700.4 (C═O), 1746.4 (C═O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.89, 7.02 and 7.89 (AB quartet, J = 8.78 Hz, 4H), 8.48 (d, J = 21.22 Hz, 1H), 9.42 (d, J = 20.49 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 55.60, 114.31, 118.70, 133.04, 136.66 (d, J = 4.13 Hz), 145.87 (d, J = 262.17 Hz), 160.89, 165.08, 181.84 (d, J = 18.20 Hz); ^{19}F NMR ($CDCl_3$) δ −71.96 (d, J = 21.22, 20.49 Hz, 1F); MS (CI) *m/z* (rel intensity) 225 (M^+ + H; 78.6); HRMS (CI) Calcd for: $C_{11}H_{10}FO_4$: M + H, 225.0605. Found: *m/z* 225.0570. Anal. Calcd: C, 58.93; H, 4.05. Found: C, 58.92; H, 4.09.

(*Z*)-2-Fluoro-3-oxo-1-propenyl 4-chlorobenzoate (3e): mp 135.3−135.8 °C (hexane); IR ($CHCl_3$) 1683.1 (C═C), 1701.8 (C═O), 1752.5 (C═O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.96 (d, J = 18.79 Hz, 1H), 7.74 and 8.05 (AB quartet, J = 8.78 Hz, 4H), 9.23 (d, J = 17.81 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 125.12, 129.41, 132.00, 135.93 (d, J = 4.97 Hz), 141.83, 146.05 (d, J = 263.82 Hz), 160.59, 181.71 (d, J = 19.02 Hz); ^{19}F NMR ($CDCl_3$) δ −68.94 (dd, J = 18.79, 17.81 Hz, 1F); MS (CI) *m/z* (rel intensity) 231 (M^++ 2 + H; 3.1), 229 (M^+ + H; 8.7); Anal. Calcd for: C, 52.54; H, 2.65. Found: C, 52.29; H, 2.75.

(13) At present, unfortunately, sodium salt **2** could not be isolated from the reaction mixture by column chromatography, reprecipitation, and/or recrystallization.

(14) In polar solvents, fluorine-free malonaldehyde exists entirely as β-hydroxy acrolein, see: Kwon, T.-W.; VanderVeen, J. *J. Agric. Food Chem.* **1968**, *16*, 639.

(*Z*)-2-Fluoro-3-oxo-1-propenyl 4-trifluoromethylbenzoate (3f): mp 125.3−125.9 °C (hexane); IR ($CHCl_3$) 1683.9 (C═C), 1698.1 (C═O), 1760.2 (C═O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.96 (d, J = 18.79 Hz, 1H), 7.74 and 8.25 (AB quartet, J = 8.30 Hz, 4H), 9.26 (d, J = 17.32 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 29.69, 126.04 (d, J = 3.31 Hz), 131.13, 135.55 (d, J = 4.96 Hz), 146.24 (d, J = 264.24 Hz), 160.41, 181.64 (d, J = 19.85 Hz); ^{19}F NMR ($CDCl_3$) δ −68.23 (dd, J = 18.79, 17.32 Hz, 1F); MS (CI) m/z (rel intensity) 263 ($M^+ + H$; 10.9). Anal. Calcd: C, 50.40; H, 2.31. Found: C, 50.41; H, 2.44.

(*Z*)-2-Fluoro-3-oxo-1-propenyl (*E*)-3-phenyl-2-ethenoate (3g): mp 110.3−110.8 °C (hexane); IR ($CHCl_3$) 1630.6 (C═C), 1677.4 (C═C), 1703.4 (C═O), 1749.8 (C═O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.58 (d, J = 15.86 Hz, 1H), 7.43−7.50 (m, 3H), 7.60−7.62 (m, 2H), 7.96 (d, J = 19.76 Hz, 1H), 7.97 (d, J = 15.98 Hz, 1H), 9.26 (d, J = 17.81 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 114.04, 126.69, 129.11, 131.69, 133.36, 136.35 (d, J = 4.13 Hz), 145.67 (d, J = 263.00 Hz), 150.15, 161.43, 181.79 (d, J = 19.02 Hz); ^{19}F NMR ($CDCl_3$) δ −70.03 (dd, J = 19.76, 17.81 Hz, 1F); MS (CI) m/z (rel intensity) 220 ($M^+ + H$; 0.7); HRMS (CI) Calcd for: $C_{12}H_{10}FO_3$: M + H, 220.0536. Found: m/z 220.0529. Anal. Calcd: C, 65.45; H, 4.12. Found: C, 65.27; H, 4.11.

(*Z*)-2-Fluoro-3-oxo-1-propenyl dodecanoate (3h): mp 37.8−38.1 °C (hexane); IR ($CHCl_3$) 1678.4 (C═C), 1702.7 (C═O), 1781.6 (C═O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.80 (t, J = 6.56 Hz, 3H), 1.12−1.34 (m, H), 1.65 (quintet, J = 7.26 Hz, 2H), 2.51 (t, J = 7.44 Hz, 2H), 7.76 (d, J = 19.27 Hz, 1H), 9.14 (d, J = 17.81 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.09, 22.66, 24.33, 28.88, 29.09, 29.29, 29.34, 29.52, 29.55, 29.69, 31.87, 33.64, 135.94 (d, J = 4.96 Hz), 145.52 (d, J = 263.00 Hz), 168.63, 181.83 (d, J = 19.02 Hz); ^{19}F NMR ($CDCl_3$) δ −70.13 (dd, J = 19.27, 17.81 Hz, 1F); MS (CI) m/z (rel intensity) 273 ($M^+ + H$; 2.5). Anal. Calcd for: C, 66.15; H, 9.25. Found: C, 65.90; H, 9.18.

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