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Facile synthesis of 1,7,8-trifluoro-2-naphthol *via* DMAP catalyzed cycloaromatization

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ABSTRACT

A facile synthesis of 1,7,8-trifluoro-2-naphthol, an important synthetic intermediate for liquid crystal compounds with a 1,7,8-trifluoronaphthalene structure, was developed starting from 4-bromo-1,2-difluorobenzene *via* DMAP catalyzed intramolecular cycloaromatization in 51% overall yield for the 6 steps.

1. Introduction

Recently, many liquid crystal (LC) compounds for active matrix liquid crystal displays (AM-LCDs) contain fluorine atoms. The introduction of fluorine atoms into LC compounds dramatically improve their physical properties, such as broadening the nematic range, increasing the dielectric anisotropy value ($\Delta\varepsilon$), and decreasing the ion solvation ability, which are beneficial for high performance AM-LCDs in terms of attaining wide view-angle, fast switching time, and low power consumption [1]. During exploration of laterally fluorinated LC compounds with large negative dielectric anisotropy, Manero et al. first reported LC compounds possessing a 1,7,8-trifluoronaphthalene moiety as a novel core structure in 1995 [2]. Since then, Kusumoto et al. has intensively developed their derivatives such as compounds **A** and **B** (Fig. 1), exhibiting high absolute dielectric anisotropy values (−7.5 for **A**) [3].

Most of LC compounds with the 1,7,8-trifluoronaphtahlene unit have been synthesized from a common intermediate, 1,7,8-trifluoro-2-naphthol (**1**), because **1** can be easily functionalized to introduce alkyl, alkoxy, and aryl groups at the C2 and C6 positions [4]. Several synthetic procedures for **1** were reported by Kusumoto et al. [5a,5c] and Yokota et al. [5b] and they demonstrated an intermolecular cycloaromatization between 2-(2,3-difluorophenyl)acetyl chloride and acetylene equivalents such as acetylene, vinyl chloride, and (trimethylsilyl)acetylene in the presence of $AlCl_3$ to produce 7,8-difluoro-2-naphthol, which was then fluorinated at the C-1 position with a *N*-fluoropyridinium salt. Although these patent procedures are a straightforward way to construct the 2-naphthol skeleton, it was difficult to avoid difluorination at the C-1 fluorination step of 7,8-difluoro-2-naphthol. Therefore, it was required to reduce the resulting over fluorinated product (1,1,7,8-tetrafluoro-1,2-dihydronaphthalene-2-one) by $NaBH_4$ to the desired 1,7,8-trifluoro-2-naphthol (**1**) [4]. Since there still remains a requirement to improve the synthetic method of **1**, we initiated a project for the synthesis of **1**. Herein, we wish to disclose a facile synthesis of 1,7,8-trifluoro-2-naphthol (**1**) from 4-bromo-1,2-difluorobenzene (**4**) *via* DMAP catalyzed intramolecular cycloaromatization.

2. Results and discussion

Our synthetic plan for 1,7,8-trifluoro-2-naphthol (**1**) is outlined in Scheme 1. The key element in this scheme consists of the intramolecular cycloaromatization [6–9] of (2-vinylaryl)acetic acid **2** that already contains three requisite fluorine atoms to elaborate the core 2-naphthol structure. In this reaction, we expected that activation of the carboxylic acid residue of **2** with $(COCl)_2$ or Ac_2O in the presence of a base would lead to intermediate **I**, which would give rise to **1** through intramolecular

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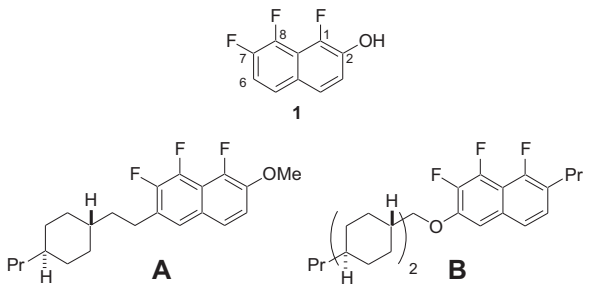


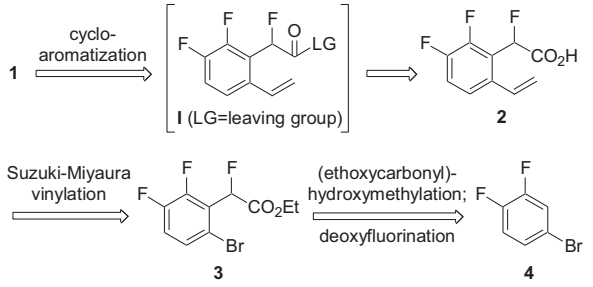
Fig. 1. 1,7,8-Trifluoro-2-naphthol (**1**) and its LC derivatives.

acylation followed by tautomerization. The vinyl group in **2** would be introduced by Suzuki–Miyaura vinylation [10,11] of arylfluoroacetate **3**, which would be synthesized from 4-bromo-1,2-difluorobenzene (**4**), *via* (ethoxycarbonyl)hydroxymethylation at the C-3 position and deoxyfluorination of the resulting alcohol.

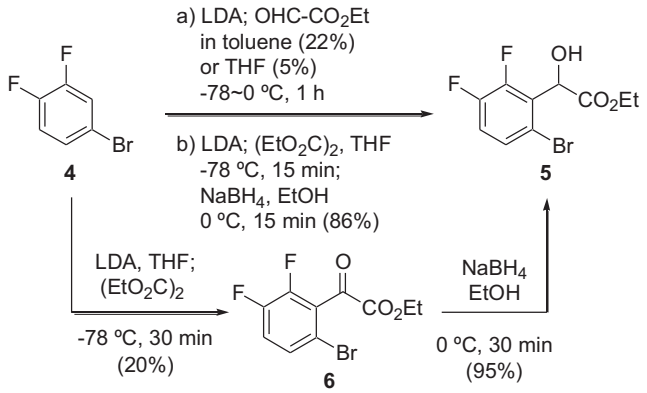
On the basis of these tactics, our synthesis commenced with the reaction of 4-bromo-1,2-difluorobenzene (**4**) and an ethyl glyoxalate equivalent. As shown in Scheme 2, we initially pursued the coupling reaction of an aryllithium, generated by lithiation at the C-3 position of **4** with LDA [12], with ethyl glyoxalate in toluene or THF. Unfortunately, only a low amount of the desired product **5** was obtained (22% and 5% yield, respectively). On the other hand, treatment of the aryllithium reagent with diethyl oxalate gave a 20% yield of the corresponding arylglyoxylate **6**, which was then reduced by $NaBH_4$ to furnish the desired arylglycolate **5** in 95%. Since the low yield of **6** from **4** was due to the instability of **6**, the one-pot acylation–reduction procedure improved the yield, producing **5** in 86% yield.

With the desired arylglycolate **5** in hand, we next explored deoxyfluorination of the resulting hydroxyl group of **5**. We undertook deoxyfluorination of **5** with several commercially available deoxyfluorinating reagents, such as DAST (Et_2NSF_3) [13], Deoxo-Fluor [$(MeOCH_2CH_2)_2NSF_3$] [14], Ishikawa reagent (Et_2N-CF_2-CHF-CF_3) [15], TFEMDA (Me_2N-CF_2-CHF_2) [16], and Yarovenko reagent (Et_2N-CF_2-CHClF) [17], as shown in Table 1. Each deoxyfluorination except using Ishikawa reagent (entry 3) proceeded to produce the desired arylfluoroacetate **3** in moderate to good yield (47–78%). Especially, the addition of HF-pyridine into the reaction mixture was effective (entries 4–6) [18] and the best result was obtained by treatment of **5** with TFEDMA in the presence of HF-pyridine, affording a 78% yield of **3** (entry 5).

Succeeded in the synthesis of arylfluoroacetate **3**, we turned our attention to introduce the requisite vinyl group by Suzuki–Miyaura cross-coupling reaction as depicted in Table 2. In 2002, Molander et al. reported the facile preparation of potassium vinyltrifluoroborate ($vinylBF_3K$) and the usage of it to various Suzuki–Miyaura vinylations [10a]. Taking advantage of their original condition [$PdCl_2(dppf)\cdot(CH_2Cl_2)_2$, and Et_3N], **3** was allowed to react with $vinylBF_3K$ to furnish the desired (2-vinylaryl)acetate **7** in 75% (entry 1). To improve the reaction



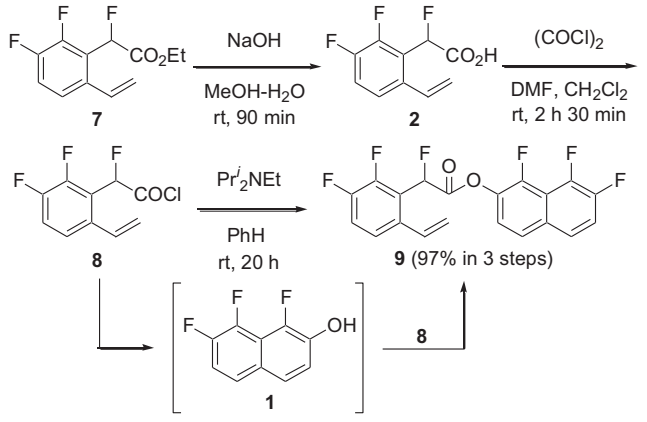
Scheme 1. Synthetic strategy for 1,7,8-trifluoro-2-naphthol (**1**).



Scheme 2. Synthesis of arylglycolate **5**.

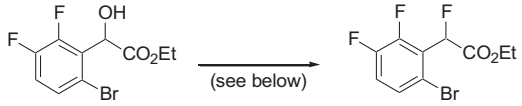
yield and use a cheaper catalyst/phosphine ligand combination, we next applied Molander's modified condition [$PdCl_2$-PPh_3, Cs_2CO_3 in THF-H_2O (9:1)] [10b] to the reaction, giving a 47% yield of **7** (entry 2). After carrying out detailed investigation of bases (Et_3N, Na_2CO_3, K_3PO_4, and K_2CO_3) (entries 3–6), the reaction proceeded most effectively by using 5 mol% of $PdCl_2$ and 15 mol% of PPh_3 in the presence of 3 eq. of K_2CO_3 in THF–H_2O (9:1), offering (2-vinylaryl)acetate **7** in 91% yield (entry 5). To further improve the reaction efficiency, we performed the reaction with a less amount of catalyst (2 mol% of $PdCl_2$) in THF-H_2O (9:1), however, the yield was decreased to 74% (entry 7). Fortunately, in a solvent system of THF-H_2O (1:1) the reaction catalyzed by 1 mol% of $PdCl_2$ and 3 mol% of PPh_3 proceeded to give **7** in 90% yield (entry 8). Using 2,4,6-trivinylcyclotriboroxane-pyridine complex [19] instead of $vinylBF_3K$ was ineffective (entry 9).

Having obtained the key intermediate **7**, a synthetic equivalent of (2-vinylaryl)acetic acid **2**, in hand, the stage was now set to test the crucial intramolecular cycloaromatization. In 1997, Myers [6] and Hirama [7] coincidentally reported the cycloaromatization of 2-(2-vinylphenyl)acetyl chloride derivatives with Pr^i_2NEt to produce the corresponding 2-naphthol derivatives in good yield. Thus, we initially prepared acid chloride **8** by hydrolysis of (2-vinylaryl)acetate **7** in aq. NaOH–MeOH, followed by treatment of the resulting (2-vinylaryl)acetic acid **2** with oxalyl chloride in the presence of DMF as shown in Scheme 3. We then attempted the cycloaromatization upon treatment of **8** with Pr^i_2NEt in benzene, unfortunately yielding no desired product **1** at all. Instead, unwanted dimer **9** was isolated in 97% yield from **7**. Presumably, this result can be attributed to the prompt esterification of **1**, formed through the expected cycloaromatization, with unreacted acid chloride **8**.



Scheme 3. Intramolecular cycloaromatization of acid chloride **8**.

Table 1
Deoxyfluorination of arylglycolate **5**.

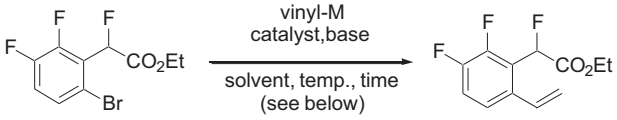


5 **3**

Entry	Condition	Yield[a]
1	DAST[b] (2.0 eq.), CH_2Cl_2, rt, 19 h	67%
2	Deoxo-Fluor[c] (1.5 eq.), CH_2Cl_2, rt, 19 h	47%
3	Ishikawa reagent[d] (2.5 eq.), CH_2Cl_2, rt, 24 h	0%
4	Deoxo-Fluor[c] (1.2 eq.), HF-py (3.5 eq.), CH_2Cl_2, rt, 22 h	76%
5	TFEDMA[e] (1.0 eq.), HF-py (3.8 eq.), 1,2-dichloroethane, 80 °C, 7 h	78%
6	Yarovenko reagent[f] (1.5 eq.), HF-py (7.0 eq.), 1,2-dichloroethane, 80 °C, 7 h	68%

[a] Isolated yield.
[b] DAST = Et_2N-SF_3.
[c] Deoxo-Fluor = $(MeOCH_2CH_2)_2N$-SF_3.
[d] Ishikawa reagent = Et_2N-CF_2-CHF-CF_3.
[e] TFEDMA = Me_2N-CF_2-CHF_2.
[f] Yarovenko reagent = Et_2N-CF_2-CHClF.

Table 2
Suzuki–Miyaura vinylation of arylfluoroacetate **3**.

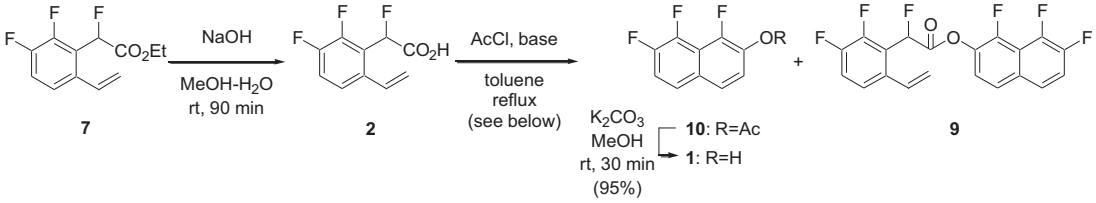


3 **7**

Entry	Vinyl-M	Catalyst	Base	Solvent, temperature, time	Yield[a]
1	vinylBF_3K (1.2 eq.)	Pd(dppf)Cl_2·(CH_2Cl_2)$_2$ (0.05 eq.)	Et_3N (1.2 eq.)	EtOH, 85 °C, 13 h	75%
2	vinylBF_3K (1.2 eq.)	$PdCl_2$ (0.05 eq.), PPh_3 (0.15 eq.)	Cs_2CO_3 (3.0 eq.)	THF-H_2O (9:1), 85 °C, 19 h	47%
3	vinylBF_3K (1.2 eq.)	$PdCl_2$ (0.05 eq.), PPh_3 (0.15 eq.)	Et_3N (1.2 eq.)	EtOH, 85 °C, 13 h	24%
4	vinylBF_3K (1.2 eq.)	$PdCl_2$ (0.05 eq.), PPh_3 (0.15 eq.)	K_3PO_4 (3.0 eq.)	THF-H_2O (9:1), 85 °C, 19 h	20%
5	vinylBF_3K (1.2 eq.)	$PdCl_2$ (0.05 eq.), PPh_3 (0.15 eq.)	K_2CO_3 (3.0 eq.)	THF-H_2O (9:1), 85 °C, 12 h	91%
6	vinylBF_3K (1.2 eq.)	$PdCl_2$ (0.05 eq.), PPh_3 (0.15 eq.)	Na_2CO_3 (3.0 eq.)	THF-H_2O (9:1), 85 °C, 12 h	58%
7	vinylBF_3K (1.2 eq.)	$PdCl_2$ (0.02 eq.), PPh_3 (0.06 eq.)	K_2CO_3 (3.0 eq.)	THF-H_2O (9:1), 85 °C, 12 h	74%
8	vinylBF_3K (1.2 eq.)	$PdCl_2$ (0.01 eq.), PPh_3 (0.03 eq.)	K_2CO_3 (3.0 eq.)	THF-H_2O (1:1), 85 °C, 24 h	90%
9	2,4,6-trivinylcyclotriboroxane-pyridine complex (1.2 eq.)	$PdCl_2$ (0.05 eq.), PPh_3 (0.15 eq.)	K_2CO_3 (3.0 eq.)	THF-H_2O (9:1), 85 °C, 15 h	1.3%

[a] Isolated yield.

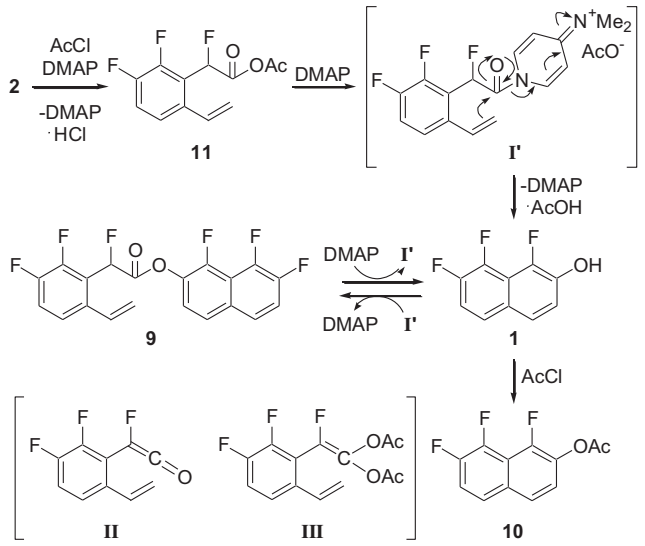
Table 3
Cycloaromatization of (2-vinylphenyl)acetic acid **2**.



7 **2** **9**

Entry	AcCl (eq.)	Base	Time (h)	Yield of **10** (from **7**)[a]	Yield of **9** (from **7**)[a]
1	3.0	DMAP (3.0 eq.)	18	87%	0%
2	5.0	DMAP (5.0 eq.)	13	98%	0%
3	2.0	DMAP (2.0 eq.)	24	86%	0%
4	1.0	DMAP (1.0 eq.)	18	20%[b]	45%[b]
5	3.0	Et_3N (3.0 eq.)	17	26%[b]	71%[b]
6	3.0	Pyridine (3.0 eq.)	20	54%[b]	22%[b]
7	3.0	Et_3N (3.0 eq.), DMAP (0.1 eq.)	12	50%	0%
8	3.0	Pyridine (3.0 eq.), DMAP (0.1 eq.)	12	89%	0%
9	2.0	Pyridine (2.0 eq.), DMAP (0.1 eq.)	12	38%[b]	24%[b]

[a] Isolated yield.
[b] Due to the difficulty of separation of **10** and **9**, the yields of **10** and **9** were calculated based on the isolated yield and the ^1H NMR ratio of a mixture of **10** and **9**.

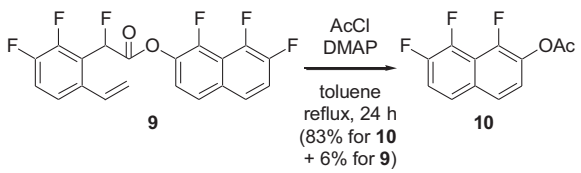


Scheme 4. Plausible mechanism of the formation of naphthyl acetate **10** from (2-vinylaryl)acetic acid **2**.

Encouraged by this result, we then planned to use naphthol protecting reagents to inhibit the unwanted dimer formation. During the synthesis of furaquinocins, Suzuki et al. constructed their 2-naphthol moiety by the cycloaromatization of a (2-vinylphenyl)acetic acid derivative with 3 eq. of acetyl chloride (AcCl) and 3 eq. of 4-(dimethylamino)pyridine (DMAP) [8]. We envisaged that a combination of AcCl and DMAP would serve as naphthol capture reagents as well as carboxylic acid activating reagents. Accordingly, as depicted in Table 3, we carried out cycloaromatization by treatment of (2-vinylphenyl)acetic acid **2** with 3 eq. of AcCl and 3 eq. of DMAP in toluene under reflux for 18 h, which resulted in the formation of the expected naphthyl acetate **10** in 87% yield from **7** (entry 1). Increasing amounts of AcCl (5 eq.) and DMAP (5 eq.) improved the yield to 98% (entry 2). While the reaction with 2 eq. of AcCl and DMAP gave the same result (entry 3), decreasing amounts of AcCl (1 eq.) and DMAP (1 eq.) lowered the yield to 20% with the formation of **9** in 45% (entry 4). We next surveyed bases such as Et_3N and pyridine, however, the yield of **10** decreased and undesired dimer **9** formed (entries 5–6). Since we realized DMAP is essential for this reaction, a DMAP catalyzed cycloaromatization (0.1 eq. of DMAP and 3 eq. of Et_3N) was examined, affording a 50% yield of **10** (entry 7). After further investigation, we fortunately found that the reaction in the presence of a catalytic amount of DMAP (0.1 eq.) and pyridine (3 eq.) produced **10** in good yield (89%, entry 8). An attempt of the direct cycloaromatization of ester **7** by exposure to DMAP in the absence of AcCl in refluxing toluene was failed.

Finally, methanolysis of the resulting acetate **10** with K_2CO_3 in MeOH provided 1,7,8-trifluoro-2-naphthol (**1**) as a white solid in 95% (51% overall yield for the 6 steps from **4**).

As shown in Scheme 4, we assumed that the key intramolecular cycloaromatization was initiated by the formation of acid anhydride **11** from **2** with AcCl and DMAP, followed by the DMAP mediated formation of acylammonium salt **I′** as a reactive intermediate. The intramolecular electrophilic acylation of **I'**, followed by tautomerization furnished 2-naphthol **1**. Then, the resultant 2-naphthol **1** was immediately acetylated in the presence of AcCl to furnish **10**, however, as a competitive reaction **1** was also acylated with **I′** to produce the undesired product **9**. Since we treated ester **9** with AcCl (3 eq.) and DMAP (3 eq.) in refluxing toluene to give rise to **10** in 83% yield (Scheme 5), the formation of **9** from **1** should be regarded as a reversible reaction. Therefore, even while undesired dimer **9** formed during the cycloaromatization, **9** was transformed to phenol **1** in the presence of a sufficient amount of AcCl and DMAP, which was eventually acetylated to give **10**. As Suzuki et al. suggested [8], there might be other possible reactive intermediates involved in this reaction. The acid anhydride **11** underwent elimination by DMAP to form ketene **II**, which was cyclized *via* Cope rearrangement followed by acetylation to produce **10**. Alternatively, Cope cyclization of ketene diacetate **III**, generated *via* enol acetylation of acid anhydride **11**, followed by aromatization might produce 1,7,8-trifluoro-2-naphthyl acetate (**10**).



Scheme 5. Conversion of dimer **9** to naphthyl acetate **10**.

3. Conclusion

In summary, we have established the facile synthetic route to 1,7,8-trifluoro-2-naphthol (**1**), an important synthetic precursor for liquid crystal (LC) compounds, from 4-bromo-1,2-difluorobenzene (**4**) in 51% overall yield for the 6 steps. (Ethoxycarbonyl)hydroxymethylation of **4**, followed by deoxyfluorination of the resulting arylglycolate **5** in the presence of TFEDMA and HF-pyridine furnished arylfluoroacetate **3**, which was subjected to Suzuki–Miyaura vinylation with vinylBF_3K catalyzed by 1 mol% of $PdCl_2$ and 3 mol% of PPh_3 in THF-H_2O (1:1), affording (2-vinylphenyl)acetate **7**. Exposure of (2-vinylaryl)acetic acid **2**, obtained by hydrolysis of **7**, to acetyl chloride, pyridine, and a catalytic amount of DMAP gave rise to 2-naphthyl acetate **10** *via* cycloaromatization. Finally, methanolysis of **10** produced the desired 1,7,8-trifluoro-2-naphthol (**1**). Since this developed method was short and efficient, it could be applicable to the industrial scale preparation of **1**.

4. Experimental

4.1. General

All reactions involving air- and moisture-sensitive reagents were carried out using oven-dried glassware and standard syringe-septum cap techniques. Routine monitoring of reaction was carried out using glass-supported Merck silica gel 60 F_{254} TLC plates. Flash column chromatography was performed on Kanto Chemical Silica Gel 60 N (spherical, neutral 40–50 μm). All solvents and reagents were obtained from commercial suppliers and were used without further purification. Melting points were taken on a Mettler Toledo MP70 melting point system and were uncorrected. Infrared (IR) spectral measurements were carried out with a HORIBA FT-720 spectrometer. ^1H, ^{13}C, and ^{19}F NMR spectra were measured with a Bruker AVANCE III spectrometer. Chemical shifts are expressed in parts per million using tetramethylsilane (δ = 0, ^1H NMR) and $CFCl_3$ (δ = 0, ^{19}F NMR) as standard substances. ^{19}F NMR spectra were recorded with ^1H decoupling. Chemical shifts are expressed in ppm. Multiplicities are indicated by s (singlet), brs (broad singlet), d (doublet), brd (broad doublet), t (triplet), q (quartet), dd (doublet of doublet), brdd (broad doublet of doublet), ddd (doublet of doublet of doublet), dddd (doublet of doublet of doublet of doublet) and m (multiplet).

4.2. Preparation of ethyl 2-(6-bromo-2,3-difluorophenyl)-2-hydroxyacetate (**5**)

4.2.1. Preparation of ethyl 2-(6-bromo-2,3-difluorophenyl)-2-oxoacetate (**6**)

To a stirred solution of *N*,*N*-diisopropylamine (0.7 mL, 5.0 mmol) in THF (5.0 mL) was added dropwise a solution of *n*-BuLi in *n*-hexane (1.59 M, 3.1 mL, 5.0 mmol) at 0 °C under Ar and the resulting solution was stirred at 0 °C for 20 min to prepare lithium diisopropylamide (LDA). To the prepared solution of LDA was added dropwise a solution of 4-bromo-1,2-difluorobenzene (**4**) (965 mg, 5.0 mmol) in THF (5.0 mL) at −78 °C over 15 min and the resulting mixture was stirred at −78 °C for 1 h. To the resulting mixture was added dropwise diethyl oxalate (0.68 mL, 5.0 mmol) and the reaction mixture was stirred at −78 °C for 30 min. The reaction mixture was quenched with 1.0 M HCl (5.0 mL) and the aqueous layer was extracted with ether (5.0 mL × 3). The extract was washed with water (5.0 mL) and brine (5.0 mL), then dried over $MgSO_4$. Concentration of the solvent *in vacuo* afforded a residue, which was purified by silica gel column chromatography (hexane/ethyl acetate) to give **6** (170 mg, 20%) as a white solid. mp. 49.5–51.6 °C. IR (neat): 3080, 2993, 2960, 2924, 2854, 2362, 2339, 1743, 1716, 1464, 1274, 1255, 1215, 1167, 1122, 1092, 1061, 872, 827, 744, 739 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.39 (ddd, J = 9.0, 4.0, 2.0 Hz, 1H), 7.24 (brdd, J = 9.0, 8.5 Hz, 1H), 4.43 (q, J = 7.0 Hz, 2H), 1.41 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 182.1 (d, J_{CF} = 1.5 Hz, 1C), 159.6 (s, 1C), 149.7 (dd, J_{CF} = 252, 13 Hz, 1C), 149.1 (dd, J_{CF} = 258, 15 Hz, 1C), 128.9 (dd, J_{CF} = 5.9, 4.4 Hz, 1C), 127.8 (d, J_{CF} = 14 Hz, 1C), 120.9 (brd, J_{CF} = 18 Hz, 1C), 114.1 (dd, J_{CF} = 3.7, 2.2 Hz, 1C), 63.5 (s, 1C), 13.8 (s, 1C). ^{19}F NMR (376 MHz, $CDCl_3$): δ −135.6 (d, J_{FF} = 20 Hz, 1F), −137.0 (d, J_{FF} = 20 Hz, 1F). Anal. Calcd for $C_{10}H_7BrF_2O_3$: C, 40.98; H, 2.41. Found: C, 41.27; H, 2.55.

4.2.2. Preparation of ethyl 2-(6-bromo-2,3-difluorophenyl)-2-hydroxyacetate (**5**) by reduction of **6**

To a stirred solution of ethyl 2-(6-bromo-2,3-difluorophenyl)-2-oxoacetate (**6**) (290 mg, 0.99 mmol) in EtOH (1.0 mL) was added $NaBH_4$ (37.8 mg, 1.0 mmol) at 0 °C under Ar and the resulting solution was stirred at 0 °C for 30 min. The reaction mixture was quenched with 13% NH_4Cl aq. (2.0 mL) and the aqueous layer was extracted with ethyl acetate (5.0 mL × 3). The extract was washed with water (2.0 mL) and brine (2.0 mL), then dried over $MgSO_4$. Concentration of the solvent *in vacuo* afforded a residue, which was purified by silica gel column chromatography (hexane/ethyl acetate) to give **5** (276 mg, 95%) as a light yellow solid. mp. 40.3–41.8 °C. IR (neat): 3467 (br), 2985, 1736, 1712, 1475, 1277, 1209, 1088, 1022, 885, 860, 810, 644 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.36 (ddd, J = 8.9, 4.5, 2.1 Hz, 1H), 7.08 (dd, J = 8.9, 0.7 Hz, 1H), 5.62 (d, J = 4.9 Hz, 1H), 4.30 (q, J = 7.3 Hz, 2H), 3.63 (d, J = 4.9 Hz, 1H), 1.26 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.84 (d, J_{CF} = 1.5 Hz, 1C), 149.9 (dd, J_{CF} = 250, 13 Hz, 1C), 149.7 (dd, J_{CF} = 254, 14 Hz, 1C), 128.5 (dd, J_{CF} = 5.9, 4.4 Hz, 1C), 128.3 (d, J_{CF} = 13 Hz, 1C), 118.3 (brd, J_{CF} = 18 Hz, 1C), 118.2 (brs, 1C), 68.8 (dd, J_{CF} = 2.6, 2.6 Hz, 1C), 62.8 (s, 1C), 13.9 (s, 1C). ^{19}F NMR (376 MHz, $CDCl_3$): δ −137.0 (d, J_{FF} = 20 Hz, 1F), −137.7 (d, J_{FF} = 20 Hz, 1F). Anal. Calcd for $C_{10}H_9BrF_2O_3$: C, 40.70; H, 3.07. Found: C, 40.65; H, 2.77.

4.2.3. One pot acylation–reduction procedure for **5** from **4**

To a stirred solution of *N*,*N*-diisopropylamine (0.7 mL, 5.0 mmol) in THF (5.0 mL) was added dropwise a solution of *n*-BuLi in *n*-hexane (2.69 M, 1.9 mL, 5.0 mmol) at 0 °C under Ar and the resulting solution was stirred at 0 °C for 20 min to prepare lithium diisopropylamide (LDA). To the prepared solution of LDA was added dropwise a solution of 4-bromo-1,2-difluorobenzene (**4**) (964 mg, 5.0 mmol) in THF (5.0 mL) at −78 °C over 15 min and the resulting mixture was stirred at −78 °C for 1 h. To the reaction mixture was added dropwise diethyl oxalate (0.68 mL, 5.0 mmol) and the resulting mixture was stirred at −78 °C for 15 min. $NaBH_4$ (188 mg, 5.0 mmol) and ethanol (5.0 mL) were added sequentially, then the reaction mixture was warmed to 0 °C and stirred at 0 °C for 15 min. The reaction mixture was quenched with saturated NH_4Cl aq. (5.0 mL) and the resulting mixture was stirred at room temperature for 15 min. The reaction mixture was extracted with ethyl acetate (10 mL × 1, 5.0 mL × 2). The extract was washed with water (5.0 mL) and brine (5.0 mL), then dried over $MgSO_4$. Concentration of the solvent *in vacuo* afforded a residue, which was purified by silica gel column chromatography (hexane/ethyl acetate) to give **5** (1.27 g, 86%) as a light yellow solid.

4.3. Preparation of ethyl 2-(6-bromo-2,3-difluorophenyl)-2-fluoroacetate (**3**)

To a stirred solution of 2-(6-bromo-2,3-difluorophenyl)-2-hydroxyacetate (**5**) (148 mg, 0.50 mmol) in HF-py (70%, 0.05 mL, 1.9 mmol) and CH_2Cl_2 (0.95 mL) was added *N*,*N*-dimethyl-1,1,2,2-tetrafluoroethylamine (TFEDMA) (0.12 mL, 0.50 mmol) at room temperature under Ar and the resulting solution was stirred at 80 °C for 7 h. The reaction mixture was cooled to 0 °C and the reaction mixture was quenched with saturated $NaHCO_3$ aq. (2.0 mL) and the aqueous layer was extracted with ethyl acetate (5.0 mL × 1, 2.0 mL × 2). The extract was washed with water (3.0 mL) and brine (3.0 mL), then dried over $MgSO_4$. Concentration of the solvent *in vacuo* afforded a residue, which was purified by silica gel column chromatography (hexane/ethyl acetate) to give **3** (116 mg, 78%) as a yellow oil. IR (neat): 2987, 1766, 1477, 1279, 1216, 1066, 1028, 887, 814 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.41 (dddd, J = 9.0, 4.5, 2.3, 1.0 Hz, 1H), 7.17 (ddd, J = 9.0, 8.0, 1.8 Hz, 1H), 6.23 (d, J = 46 Hz, 1H), 4.34 (q, J = 7.4 Hz, 2H), 1.31 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.9 (d, J_{CF} = 27 Hz, 1C), 150.0 (ddd, J_{CF} = 257, 13, 2.9 Hz, 1C), 149.8 (ddd, J_{CF} = 251, 13, 2.2 Hz, 1C), 128.8 (ddd, J_{CF} = 5.8, 4.4, 1.5 Hz, 1C), 124.7 (dd, J_{CF} = 19, 12 Hz, 1C), 119.8 (brd, J_{CF} = 18 Hz, 1C), 118.7 (brdd, J_{CF} = 6.6, 3.5 Hz, 1C), 84.4 (ddd, J_{CF} = 188, 2.6, 2.5 Hz, 1C), 62.4 (s, 1C), 13.9 (s, 1C). ^{19}F NMR (376 MHz, $CDCl_3$): δ −134.5 (dd, J_{FF} = 20, 5.4 Hz, 1F), −137.0 (d, J_{FF} = 20 Hz, 1F), −183.2 (d, J_{FF} = 5.4 Hz, 1F). Anal. Calcd for $C_{10}H_8BrF_3O_2$: C, 40.43; H, 2.71. Found: C, 40.54; H, 2.65.

4.4. Preparation of ethyl 2-(2,3-difluoro-6-vinylphenyl)-2-fluoroacetate (**7**)

4.4.1. Suzuki–Miyaura vinylation of **3** catalyzed by 5 mol% of $PdCl_2$ in THF/H_2O (9:1)

To a stirred solution of ethyl 2-(6-bromo-2,3-difluorophenyl)-2-fluoroacetate (**3**) (297 mg, 1.0 mmol) in THF/H_2O (2.0 mL, 9:1) was sequentially added potassium vinyltrifluoroborate (161 mg, 1.2 mmol), potassium carbonate (415 mg, 3.0 mmol), triphenylphosphine (39.3 mg, 0.15 mmol) and palladium(II) chloride (8.9 mg, 0.05 mmol). The resulting suspension was degassed in three times and stirred at 85 °C for 12 h. To the reaction mixture was added 2.4 M HCl (2.5 mL) at room temperature and the aqueous layer was extracted with ethyl acetate (5.0 mL × 3). The extract was washed with water (5.0 mL) and brine (5.0 mL), then dried over $MgSO_4$. Concentration of the solvent *in vacuo* afforded a residue, which was purified by silica gel column chromatography (hexane/ethyl acetate) to give **7** (221 mg, 91%) as a colorless oil. IR (neat): 2985, 1763, 1743, 1500, 1292, 1219, 1207, 1065, 1030, 825 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.30–7.17 (m, 2H), 6.96 (ddd, J = 17, 11, 2.0 Hz, 1H), 6.20 (d, J = 46 Hz, 1H), 5.64 (d, J = 17 Hz, 1H), 5.41 (d, J = 11 Hz, 1H), 4.34–4.21 (m, 2H), 1.27 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.7 (dd, J_{CF} = 27, 1.5 Hz, 1C), 149.6 (ddd, J_{CF} = 250, 13, 1.2 Hz, 1C), 149.0 (ddd, J_{CF} = 251, 14,

4.4 Hz, 1C), 135.4 (d, J_{CF} = 3.7 Hz, 1C), 132.0 (brs, 1C), 122.5 (ddd, J_{CF} = 5.9, 4.4, 2.2 Hz, 1C), 121.2 (dd, J_{CF} = 19, 9.5 Hz, 1C), 119.1 (s, 1C), 118.5 (brd, J_{CF} = 17 Hz, 1C), 81.6 (ddd, J_{CF} = 186, 5.9, 2.2 Hz, 1C), 62.2 (s, 1C), 13.9 (s, 1C). ^{19}F NMR (376 MHz, $CDCl_3$): δ −138.1 (d, J_{FF} = 21 Hz, 1F), −141.1 (dd, J_{FF} = 21, 2.7 Hz, 1F), −182.2 (d, J_{FF} = 2.7 Hz, 1F). Anal. Calcd for $C_{12}H_{11}F_3O_2$: C, 59.02; H, 4.54. Found: C, 59.17; H, 4.73.

4.4.2. Suzuki–Miyaura vinylation of **3** catalyzed by 1 mol% of $PdCl_2$ in THF/H_2O (1:1)

To a stirred solution of ethyl 2-(6-bromo-2,3-difluorophenyl)-2-fluoroacetate (**3**) (891 mg, 3.0 mmol) in THF/H_2O (6.0 mL, 1:1) was sequentially added potassium vinyltrifluoroborate (482 mg, 3.6 mmol), potassium carbonate (1.24 g, 9.0 mmol), triphenylphosphine (23.6 mg, 0.089 mmol) and palladium(II) chloride (5.3 mg, 0.030 mmol). The resulting suspension was degassed in three times and stirred at 85 °C for 24 h. To the reaction mixture was added 2.4 M HCl (7.5 mL) at room temperature and the aqueous layer was extracted with ethyl acetate (8.0 mL × 3). The extract was washed with water (5.0 mL) and brine (5.0 mL), then dried over $MgSO_4$. Concentration of the solvent *in vacuo* afforded a residue, which was purified by silica gel column chromatography (hexane/ethyl acetate) to give **7** (656 mg, 90%) as a colorless oil.

4.5. Preparation of 1,7,8-trifluoro-2-naphthyl 2-(2,3-difluoro-6-vinylphenyl)-2-fluoroacetate (**9**)

To a stirred solution of ethyl 2-(2,3-difluoro-6-vinylphenyl)-2-fluoroacetate (**7**) (244 mg, 1.0 mmol) in MeOH/H_2O (4.0 mL, 1:1) was added sodium hydroxide (112 mg, 2.8 mmol) at room temperature. The resulting solution was stirred at room temperature for 1 h 30 min. The reaction mixture was quenched with 2.4 M HCl (2.5 mL) and extracted with diethyl ether (3.0 mL × 3). The extract was washed with water (2.0 mL) and brine (2.0 mL), then dried over $MgSO_4$. Concentration of the solvent *in vacuo* afforded crude 2-(2,3-difluoro-6-vinylphenyl)-2-fluoroacetic acid (**2**) (248 mg), which was used in the next step without further purification. To a stirred solution of 2-(2,3-difluoro-6-vinylphenyl)-2-fluoroacetic acid (**2**) (248 mg) in CH_2Cl_2 (4.0 mL) was added *N*,*N*-dimethylformamide (0.025 mL, 0.32 mmol) and oxalyl chloride (0.13 mL, 1.5 mmol) at room temperature. The resulting solution was stirred at room temperature for 2 h 30 min and concentrated *in vacuo* to afford crude 2-(2,3-difluoro-6-vinylphenyl)-2-fluoroacetyl chloride (**8**). To a stirred solution of 2-(2,3-difluoro-6-vinylphenyl)-2-fluoroacetyl chloride (**8**) in benzene (5.0 mL) was added *N*,*N*-diisopropylethylamine (0.52 mL, 3.0 mmol) and the resulting suspension was stirred at room temperature for 20 h. The reaction mixture was quenched with 1.7 M HCl (3.5 mL) and the aqueous layer was extracted with ethyl acetate (3.0 mL × 3). The extract was dried over $MgSO_4$, then concentration of the solvent *in vacuo* afforded a residue, which was purified by silica gel column chromatography (hexane/ethyl acetate) to give **9** (192 mg, 97%) as an orange solid. mp. 115.5 °C (dec.). IR (neat): 2360, 2343, 2328, 1792, 1784, 1649, 1633, 1502, 1483, 1456, 1356, 1292, 1263, 1242, 1211, 1169, 1076, 1055, 1026, 1014, 931, 849, 825, 706, 654 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62–7.57 (m, 2H), 7.40–7.25 (m, 3H), 7.21 (dd, J = 9.0, 6.7 Hz, 1H), 7.07 (ddd, J = 17, 11, 2.0 Hz, 1H), 6.57 (d, J = 46 Hz, 1H), 5.75 (d, J = 17 Hz, 1H), 5.53 (d, J = 11 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.4 (d, J_{CF} = 28 Hz, 1C), 149.7 (brdd, J_{CF} = 251, 13 Hz, 1C), 149.2 (ddd, J_{CF} = 252, 14, 4.4 Hz, 1C), 147.8 (ddd, J_{CF} = 249, 12, 1.5 Hz, 1C), 147.6 (ddd, J_{CF} = 261, 6.6, 1.5 Hz, 1C), 143.8 (ddd, J_{CF} = 258, 15, 1.5 Hz, 1C), 135.8 (d, J_{CF} = 3.8 Hz, 1C), 134.4 (d, J_{CF} = 12 Hz, 1C), 131.7 (s, 1C), 130.7 (s, 1C), 124.3 (m, 1C), 124.2 (m, 1C), 122.9 (brs, 1C), 121.2 (s, 1C), 120.3 (dd, J_{CF} = 19, 9.5 Hz, 1C), 120.1 (s, 1C), 119.2 (d, J_{CF} = 17 Hz, 1C), 117.9 (brd, J_{CF} = 21 Hz, 1C), 115.7 (brdd, J_{CF} = 9.5, 9.5 Hz, 1C). 81.5 (ddd, J_{CF} = 189, 6.6, 3.0 Hz, 1C). ^{19}F NMR (376 MHz, $CDCl_3$): δ −134.1 (ddd, J_{FF} = 52, 5.5, 2.7 Hz, 1F), −137.6 (d, J_{FF} = 20 Hz, 1F), −139.0 (dd, J_{FF} = 16, 5.5 Hz, 1F), −140.5 (brd, J_{FF} = 20 Hz, 1F), −145.2 (dd, J_{FF} = 52, 16 Hz, 1F), −181.8 (d, J_{FF} = 2.7 Hz, 1F). Anal. Calcd for $C_{20}H_{10}F_6O_2$: C, 60.62; H, 2.54. Found: C, 60.41; H, 2.64.

4.6. Preparation of 1,7,8-trifluoro-2-naphthyl acetate (**10**)

To a stirred solution of ethyl 2-(2,3-difluoro-6-vinylphenyl)-2-fluoroacetate (**7**) (244 mg, 1.0 mmol) in MeOH/H_2O (3.0 mL, 2:1) was added sodium hydroxide (100 mg, 2.5 mmol) at room temperature. The resulting solution was stirred at room temperature for 1 h 30 min. The reaction mixture was quenched with 2.4 M HCl (2.5 mL) and extracted with diethyl ether (4.0 mL × 3). The extract was washed with water (2.0 mL) and brine (2.0 mL), then dried over $MgSO_4$. Concentration of the solvent *in vacuo* afforded crude 2-(2,3-difluoro-6-vinylphenyl)-2-fluoroacetic acid (**2**) (246 mg) as a white solid, which was used in the next step without further purification. To a stirred solution of 2-(2,3-difluoro-6-vinylphenyl)-2-fluoroacetic acid (**2**) (246 mg) in toluene (5.0 mL) was sequentially added 4-(dimethylamino)pyridine (12.2 mg, 0.10 mmol), pyridine (0.24 mL, 3.0 mmol) and acetyl chloride (0.21 mL, 3.0 mmol). The resulting suspension was stirred under reflux for 12 h 30 min. The reaction mixture was cooled to room temperature and quenched with 1.1 M HCl (2.2 mL), then the aqueous layer was extracted with ethyl acetate (5.0 mL × 3). The extract was washed with water (3.0 mL) and brine (3.0 mL), then dried over $MgSO_4$. Concentration of the solvent *in vacuo* afforded a residue, which was purified by silica gel column chromatography (hexane/ethyl acetate) to give **10** (214 mg, 89%) as a white solid. mp. 119.0–120.4 °C. IR (neat): 2359, 2343, 2328, 1759, 1631, 1481, 1373, 1356, 1261, 1250, 1203, 1173, 910, 849, 829, 679, 652 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62–7.56 (m, 2H), 7.35 (ddd, J = 9.8, 9.1, 7.2 Hz, 1H), 7.24 (dd, J = 9.3, 7.2 Hz, 1H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.2 (s, 1C), 147.9 (ddd, J_{CF} = 252, 6.6, 1.5 Hz, 1C), 147.8 (ddd, J_{CF} = 248, 12, 2.2 Hz, 1C), 143.9 (ddd, J_{CF} = 257, 15, 2.2 Hz, 1C), 135.4 (brd, J_{CF} = 12 Hz, 1C), 130.5 (brs, 1C), 124.2 (ddd, J_{CF} = 7.3, 5.1, 2.2 Hz, 1C), 124.0 (brs, 1C), 122.1 (brs, 1C), 117.5 (dd, J_{CF} = 21, 1.5 Hz, 1C), 115.9 (brdd, J_{CF} = 9.5, 9.5 Hz, 1C), 20.4 (s, 1C). ^{19}F NMR (376 MHz, $CDCl_3$): δ −134.8 (dd, J_{FF} = 53, 5.4 Hz, 1F), −139.6 (dd, J_{FF} = 18, 5.4 Hz, 1F), −145.6 (dd, J_{FF} = 53, 18 Hz, 1F). Anal. Calcd for $C_{12}H_7F_3O_2$: C, 60.01; H, 2.94. Found: C, 60.02; H, 2.82.

4.7. Preparation of 1,7,8-trifluoro-2-naphthol (**1**)

To a stirred solution of 1,7,8-trifluoro-2-naphthyl acetate (**10**) (181 mg, 0.75 mmol) in MeOH (10 mL) was added potassium carbonate (208 mg, 1.61 mmol) and the resulting suspension was stirred at room temperature for 30 min. The reaction mixture was quenched with 13% NH_4Cl aq. (2.0 mL) and extracted with ethyl acetate (3.0 mL × 3). The extract was washed with water (3.0 mL) and brine (3.0 mL), then dried over $MgSO_4$. Concentration of the solvent *in vacuo* afforded a residue, which was purified by silica gel column chromatography (hexane/ethyl acetate) to give **1** (143 mg, 95%) as a white solid. mp. 104.0–105.7 °C. IR (neat): 3344 (brs), 1647, 1633, 1487, 1464, 1373, 1348, 1261, 1244, 1234, 1200, 1176, 1014, 845, 825, 820, 651 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54–7.48 (m, 2H), 7.24–7.16 (m, 2H), 5.59 (brs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.9 (ddd, J_{CF} = 247, 12, 2.2 Hz, 1C), 143.1 (ddd, J_{CF} = 242, 7.3, 1.5 Hz, 1C), 142.8 (ddd, J_{CF} = 255, 15, 1.5 Hz, 1C), 141.3 (brd, J_{CF} = 14 Hz, 1C), 127.2 (brs, 1C), 124.5 (ddd, J_{CF} = 5.1, 2.2, 2.2 Hz, 1C), 124.2 (ddd, J_{CF} = 8.0, 5.1, 2.2 Hz, 1C), 118.3 (brs, 1C), 115.6 (ddd, J_{CF} = 9.5, 9.5, 2.2 Hz, 1C), 115.0 (dd, J_{CF} = 21, 1.4 Hz, 1C). ^{19}F NMR (376 MHz, $CDCl_3$): δ −140.3 (dd, J_{FF} = 18, 4.1 Hz, 1F), −148.3

(dd, J_{FF} = 48, 18 Hz, 1F), −151.7 (dd, J_{FF} = 48, 4.1 Hz, 1F). Anal. Calcd for $C_{10}H_5F_3O$: C, 60.62; H, 2.54. Found: C, 60.72; H, 2.59.

4.8. Conversion of **9** to **10**

To a stirred solution of 1,7,8-trifluoro-2-naphthyl 2-(2,3-difluoro-6-vinylphenyl)-2-fluoroacetate (**9**) (79.2 mg, 0.20 mmol) in toluene (4.0 mL) was sequentially added 4-(dimethylamino)-pyridine (73.3 mg, 0.60 mmol) and acetyl chloride (0.043 mL, 0.60 mmol). The resulting suspension was stirred under reflux for 24 h. The reaction mixture was cooled to room temperature and quenched with 1.0 M HCl (1.0 mL), then the aqueous layer was extracted with ethyl acetate (10 mL × 1, 5.0 mL × 3). The extract was washed with water (10 mL) and brine (10 mL), then dried over $MgSO_4$. Concentration of the solvent *in vacuo* afforded a residue, which was purified by preparative layer chromatography (chloroform) to give a 29:1 mixture (calculated by ^{1}H NMR) of **10** and **9** (83.8 mg, 83% for **10** and 6% for **9**).

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