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# Gold-Catalyzed Simultaneous Formation of C−C, C═O, and C−F bonds in the Presence of Selectfluor: A Synthesis of Fluoroindenes from Allene Esters

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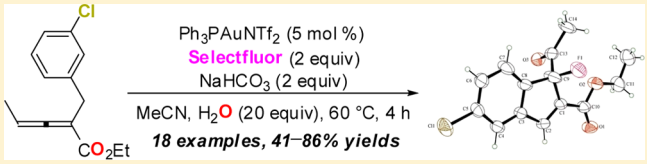
Supporting Information

**ABSTRACT:** An approach for the synthesis of fluorinated indene derivatives has been developed via a gold-catalyzed three-component tandem reaction between allene esters, Selectfluor, and water.




Recently, much attention has been paid to indene derivatives not only because of their broad range of biological and pharmacological activities,[1] but also because of their potential applications in material science.[2] It is reasonable to expect that fluorinated indene derivatives will have interesting biological activities and physical properties since the introduction of the fluorine atom into parent molecules may significantly affect their original properties such as solubility, biological activity, metabolicstability, and physical properties.[3] Indeed, some fluorinated indene derivatives, e.g., fluoroindanols,[4] can be used as appetite depressants. Besides, some fluorinated indene derivatives, e.g., 1,1,6,7-tetrafluoroindanes,[5] can be applied in material science as liquid crystal displaying materials. Regarding their preparation, in contrast to the rich chemistry of the preparation of indenes,[1,2,6,7] efficient methods for the preparation of fluorinated indene derivatives remain quite limited.[8−10] Most of the existing methods for the synthesis of fluorinated indenes[5,11−19] suffer from one or more limitations with respect to multistep procedures, not easy availability of the starting materials, harsh reaction conditions, low chemo- or regioselectivity, and lack of generality. As such, it is still desirable to develop efficient approaches for the preparation of fluoroindenes from simple and readily available substrates.

On the other hand, gold-catalyzed tandem reactions,[20−22] often involving multifold formations of chemical bonds in a single synthetic process, have proven to be a powerful tool for the construction of molecular diversity and structural complexity from simple substrates.[23−31] In this context, recent interest has focused on the development of tandem reactions involving Au(I)/Au(III) redox catalytic systems[29−35] because such catalytic systems open up new avenues for building up complex molecules that are otherwise difficult to accomplish with conventional single Au(I) or Au(III) catalytic systems. For example, Gouverneur et al.[32] have recently reported such a redox reaction involving the gold(I)/Selectfluor[36,37] system-catalyzed intramolecular oxidative cross-couplings using allenoate esters to generate tricyclic dihydroindene derivatives. As our ongoing interest in the gold(I)/Selectfluor system-catalyzed oxidation reactions,[33,29−31] we herein report a gold(I)-catalyzed three-component tandem reaction between allene esters,[38−43] Selectfluor, and water where a simultaneous formation of C−C, C═O, and C−F bonds within a single synthetic step leading to the synthesis of fluorinated indenes has been achieved involving a Au(I)/Au(III) catalytic cycle.

In light of our recent success in the gold(I)-catalyzed fluoroamination of alkynes in the presence of Selectfluor,[33] we envisioned that allenoate esters would undergo the fluorolactonization to give 4-fluorobutenolide derivatives under the gold(I)/Selectfluor catalytic system.[44−46] For an initial study, ethyl 2-benzylpenta-2,3-dienoate **1a** was treated with 2 equiv of Selectfluor and $NaHCO_3$ in the presence of 5 mol % of AuCl in nondehydrated $CH_3CN$ at 60 °C for 4 h. No 4-fluorobutenolide derivative **3a** was obtained, while a fluoroindene product **2a** was isolated in 52% yield (entry 1, Table 1). Our interest in the simultaneous formation of C−C, C═O, and C−F bonds in the reaction leading to the synthesis of fluorinated indenes prompted us to optimize the reaction conditions so as to make the reaction synthetically valuable (Table 1). When the reaction was conducted in the presence of 20 equiv of water under otherwise identical reaction conditions as the entry 1, the yield of **2a** was improved to 57% (entry 2, Table 1). An employment of AuCl/AgOTf catalytic system lowered the yield of **2a** to 50% (entry 3, Table 1). Neutral $Ph_3PAuCl$ and its cationic analogues showed better catalytic activities for the reaction than AuCl (entries 4−10 vs 2, Table 1), among which $Ph_3PAuNTf_2$ was identified as the best

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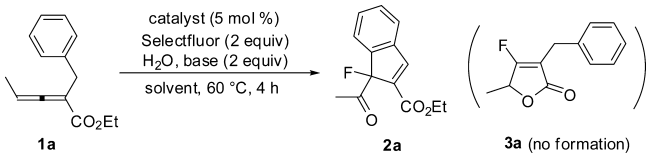
**Table 1. Screening of Catalyst, Solvent, and Base**[a]



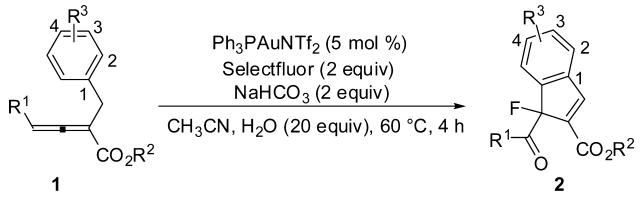

| entry | catalyst | solvent | base | yield (%)[b] |
|---|---|---|---|---|
| 1 | AuCl | $CH_3CN$ | $NaHCO_3$ | 52[c] |
| 2 | AuCl | $CH_3CN$ | $NaHCO_3$ | 57 |
| 3 | AuCl/AgOTf | $CH_3CN$ | $NaHCO_3$ | 50 |
| 4 | $Ph_3PAuCl$ | $CH_3CN$ | $NaHCO_3$ | 68 |
| 5 | $Ph_3PAuCl/AgOTf$ | $CH_3CN$ | $NaHCO_3$ | 64 |
| 6 | $Ph_3PAuCl/AgSbF_6$ | $CH_3CN$ | $NaHCO_3$ | 59 |
| 7 | $Ph_3PAuCl/AgF$ | $CH_3CN$ | $NaHCO_3$ | 62 |
| 8 | $Ph_3PAuCl/AgCN$ | $CH_3CN$ | $NaHCO_3$ | 67 |
| 9 | $Ph_3PAuCl/AgNO_2$ | $CH_3CN$ | $NaHCO_3$ | 69 |
| **10** | **$Ph_3PAuNTf_2$** | **$CH_3CN$** | **$NaHCO_3$** | **73** |
| 11 | $Ph_3PAuNTf_2$ | $CH_3CN$ | $NaHCO_3$ | 40,[d] 42[d,e] |
| 12 | $Ph_3PAuNTf_2$ | $CH_3CN$ | none | 0 |
| 13 | $Ph_3PAuNTf_2$ | $CH_3CN$ | $Na_2CO_3$ | 63 |
| 14 | $Ph_3PAuNTf_2$ | $CH_3CN$ | NaOH | 63 |
| 15 | $Ph_3PAuNTf_2$ | $CH_3CN$ | KOH | 41 |
| 16 | $Ph_3PAuNTf_2$ | $CH_3CN$ | KF | 60 |
| 17 | $Ph_3PAuNTf_2$ | $CH_3CN$ | $CH_3COOK$ | 6 |
| 18 | $Ph_3PAuNTf_2$ | toluene | $NaHCO_3$ | 0 |
| 19 | $Ph_3PAuNTf_2$ | DCE[f] | $NaHCO_3$ | 0 |
| 20 | $Ph_3PAuNTf_2$ | THF | $NaHCO_3$ | 0 |
| 21 | $Ph_3PAuNTf_2$ | 1,4-dioxane | $NaHCO_3$ | 27 |
| 22 | $Ph_3PAuNTf_2$ | $CH_3CN$ | $NaHCO_3$ | 28,[g] 0[h] |
| 23 | (2-biphenyl)$Cy_2PAuCl$ | $CH_3CN$ | $NaHCO_3$ | 67 |
| 24 | $Me_2SAuNTf_2$ | $CH_3CN$ | $NaHCO_3$ | 30 |
| 25 | $IMeSAuNTf_2$ | $CH_3CN$ | $NaHCO_3$ | 0 |
| 26 | $AuCl_3$ | $CH_3CN$ | $NaHCO_3$ | 67 |
| 27 | $AuCl_3/3AgOTf$ | $CH_3CN$ | $NaHCO_3$ | 52 |
| 28 | $AuCl_3/3AgNTf_2$ | $CH_3CN$ | $NaHCO_3$ | 59 |
| 29 | Lewis acids[i,j] | $CH_3CN$ | $NaHCO_3$ | 0 |
| 30 | none | $CH_3CN$ | $NaHCO_3$ | 0 |

[a]All reactions were carried out with **1a** (0.2 mmol), catalyst (5 mol % based on **1a**), Selectfluor (2 equiv), $H_2O$ (20 equiv), and base (2 equiv) in solvent (2 mL) at 60 °C for 4 h unless otherwise noted. [b]Isolated yields. [c]The reaction was conducted in the nondehydrated $CH_3CN$ without addition of water. [d]The reaction was carried out at 40 °C. [e]The reaction time was 10 h. [f]DCE = 1,2-dichloroethane. [g]Only the dehydrated $CH_3CN$ was used without addition of water. [h]In the absence of Selectfluor. [i]Lewis acids, such as CuI, $PdCl_2$, and $FeCl_3$. [j]The amount of catalyst is 30 mol %.

catalyst, affording the desired product **2a** in 73% yield (entry 10, Table 1). Using the same catalyst but running the reaction at 40 °C lowered the yield of **2a** even at a prolonged reaction time (entry 11, Table 1). The catalytic performances of several other gold(I) and gold(III) catalysts including (2-biphenyl)-$Cy_2PAuCl$, $Me_2SAuNTf_2$, $IMeSAuNTf_2$ (IMes = 1,3-bis-(mesityl)imidazol-2-ylidene), $AuCl_3$, $AuCl_3/3AgOTf$, and $AuCl_3/3AgNTf_2$ were investigated; all showed inferior catalytic activities than that of $Ph_3PAuNTf_2$ (entries 23−28 vs 10, Table 1). It was found that both base and solvent had a significant effect on the outcome of the reaction. The reaction gave no desired product **2a** without a base (entry 12, Table 1). Among several bases (entries 10, 13−17, Table 1) and solvents (entries 10, 18−21, Table 1) screened, $NaHCO_3$ was proven to be the best choice of base and $CH_3CN$ to be the best choice of solvent. When the reaction was conducted in the dehydrated $CH_3CN$ without addition of water, a low yield of **2a** was obtained (entry 22, Table 1). Control experiments showed that no desired product was detected in the absence of Selectfluor or a gold catalyst (entries 22, 30, Table 1). Moreover, several conventional Lewis acids such as CuI, $PdCl_2$, and $FeCl_3$ were surveyed as a catalyst for the reaction; all failed to furnish the target product **2a** even at a catalyst loading of 30 mol % (entry 29, Table 1), thus highlighting the unique catalytic activity of gold for the present tandem reaction.

After establishing the optimal reaction conditions, we then devoted our efforts to examine the scope of the reaction, and the results are shown in Table 2. First, a variety of ethyl

**Table 2. Gold(I)-Catalyzed Synthesis of Fluorinated Indenes from Allene Esters**[a]




| entry | $R^1$ | $R^2$ | $R^3$ | product | yield (%)[b] |
|---|---|---|---|---|---|
| 1 | Me | Et | H | **2a** | 73 |
| 2 | Et | Et | H | **2b** | 68 |
| 3 | *n*-Pr | Et | H | **2c** | 84 |
| 4 | *n*-Bu | Et | H | **2d** | 63 |
| 5 | $n$-$C_5H_{11}$ | Et | H | **2e** | 44 |
| 6 | $n$-$C_6H_{13}$ | Et | H | **2f** | 61 |
| 7 | Bn | Et | H | **2g** | 45 |
| 8 | Ph | Et | H | **2h** | 66 |
| 9 | Me | Me | H | **2i** | 64 |
| 10 | Me | *n*-Pr | H | **2j** | 86 |
| 11 | Me | *i*-Pr | H | **2k** | 84 |
| 12 | Me | *n*-Bu | H | **2l** | 81 |
| 13 | Me | allyl | H | **2m** | 71 |
| 14 | *n*-Bu | Me | H | **2n** | 41 |
| 15 | Ph | Me | H | **2o** | 75 |
| 16 | Me | Et | 3-Me | **2p** | 76 |
| 17 | Me | Et | 3-Cl | **2q** | 69 |
| 18 | Me | Et | 3-Br | **2r** | 61 |
| 19 | Me | Et | 2-Me | **2s** | 0 |
| 20 | Me | Et | 4-Me | **2t** | 0 |
| 21 | H | Et | H | **2u** | 0 |

[a]All reactions were carried out with **1** (0.2 mmol), $Ph_3PauNTf_2$ (5 mol % based on **1a**), Selectfluor (2 equiv), $H_2O$ (20 equiv), and $NaHCO_3$ (2 equiv) in $CH_3CN$ (2 mL) at 60 °C for 4 h. [b]Isolated yields.

allenoates were subjected to react with Selectfluor and water under the optimized reaction conditions. In most cases, the reaction proceeded smoothly to give the corresponding fluoroindenes in moderate to good yields regardless of the $R^1$ group being an alkyl (44−84%, **2a**−**2g**, entries 1−7, Table 2) or an aryl group (66%, **2h**, entry 8, Table 2). Unfortunately, a terminal allene ester **1u** failed to give the desired fluoroindene product **2u** (entry 21, Table 2). When ethyl allenoate **1g** bearing two benzyl groups was used as a substrate, only the benzyl group adjacent to the ester group was annulated into an indene ring while leaving the other one intact, demonstrating the high regioselective manner of the reaction (entry 7, Table 2). Then, variation of the ester group of allene **1** was examined.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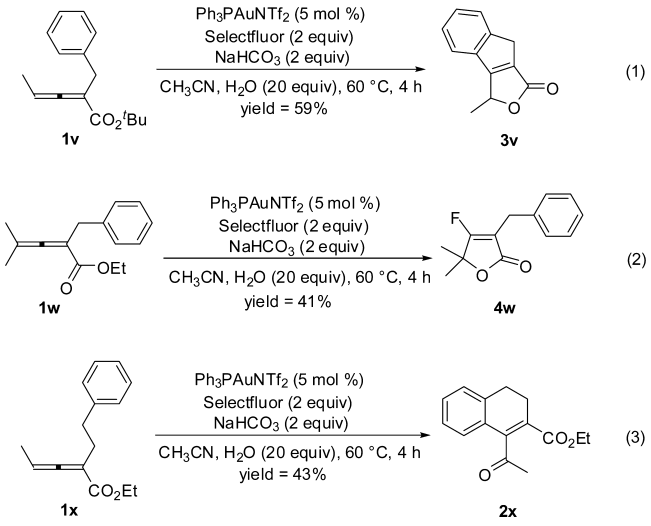
A range of other alkyl groups of $R^2$ including methyl, *n*-propyl, *i*-propyl, *n*-butyl, and even allyl groups could be survived under the reaction conditions, and the desired fluoroindenes were obtained in moderate to good yields (41−86%, **2i**−**2o**, entries 9−15, Table 2). However, when a *tert*-butyl allenoate **1v** was subjected to the reaction conditions, only a butenolide product **3v** rather than a fluoroindene product was isolated in 59% (eq 1, Scheme 1).[32,46] This result was similar to that reported by

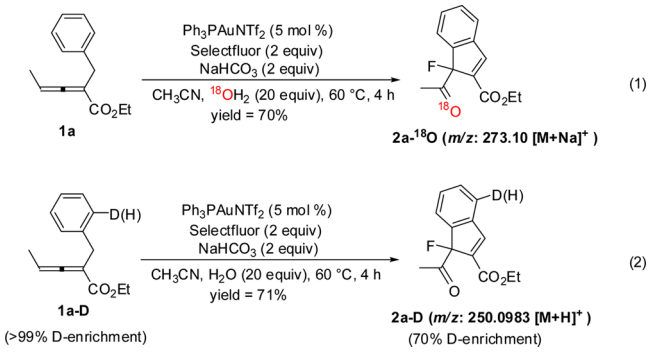
**Scheme 1. Gold(I)-Catalyzed Cyclization of Allene Esters 1v, 1w, and 1x**




Gouverneur et al.[32] in which case 10 mol % of $Ph_3PAuNTf_2$ was used at room temperature. Furthermore, it was found that the benzyl group with 3-position substituted by methyl, Cl, or Br group could also be annulated into an indene ring (**2p**−**2r**, entries 16−18, Table 2), while 2- or 4-position substituted benzyl groups failed to be annulated (**2s**, **2t**, entries 19, 20, Table 2). It was found that a tetrasubstituted allene **1w** failed to furnish the fluoroindene product, while a 4-fluorobutenolide product **4w** was isolated in 41% yield (eq 2, Scheme 1).[44−46] This study together with the works of Gouverneur's group[32] demonstrated that a subtle structural variation of allenoate esters could result in completely different product patterns in the gold(I)/Selectfluor system-catalyzed cyclization of allenoate esters. Finally, when ethyl 2-phenethylpenta-2,3-dienoate **1x** was subjected to the standard reaction conditions, a six-membered cyclic compound **2x** was selectively obtained in 43% yield (eq 3, Scheme 1). The formation of the fluoroindene scaffold was ambiguously established on the basis of the spectral analyses, which was further confirmed by X-ray diffraction analysis of a related derivative **2q** (Figure S1, Supporting Information).

Several experiments were performed to gain a mechanistic insight into the present reaction. An $^{18}OH_2$-labeling experiment unambiguously established that the oxygen atom in the resulting ketone carbonyl group of **2** originated from water (eq 1, Scheme 2; also see the Supporting Information). The reaction exhibited a primary kinetic isotope effect in the intramolecular competition experiment ($k_H/k_D$ = 2.3) (eq 2, Scheme 2; also see the Supporting Information), suggesting a rate-determining cycloauration step.[32,35] On the basis of these results and the previous reports,[29−35,47] a possible mechanism concerning the gold-catalyzed three-component tandem reaction between allene esters **1**, Selectfluor, and water is

**Scheme 2. Preliminary Mechanistic Studies**




proposed (Scheme 3). First, the activation of the allene moiety of **1** by gold(I) species was followed by the nucleophilic addition of $H_2O$ to **1** to form an organogold(I) intermediate **B**.[23,29−35,39−43] The withdrawing ester group was helpful for the regioselective addition of water to the 4-position of **1** rather than the 2-position. Then **B** was oxidized into an organogold(III) species **C** in the presence of Selectfluor (Path I).[29−35] Alternatively, **C** could also be generated by a hydroxyauration reaction of allene **1** with $H_2O$ and a cationic gold(III) species arising from the oxidation of Au(I) with Selectfluor (Path II).[29−34] Cycloauration of **C** followed by reductive elimination of the resulting organogold(III) cycle **D** gave an intermediate **E**.[32−35] A consecutive process of 1,3-H shift of the indene ring[48] and oxidation of hydroxy into carbonyl group[49] of **E** followed by *α*-fluorination[50] of the resulting ketone finally formed fluoroindene **2**.

In summary, a simultaneous formation of C−C, C═O, and C−F bonds has been achieved in the gold-catalyzed three-component tandem reaction between allene esters, Selectfluor, and water. The present reaction allows for the synthesis of a variety of fluoroindenes in moderate to good yields from simple and readily available starting materials.

## EXPERIMENTAL SECTION

**General Methods.** Unless otherwise stated, all reagents were purchased from commercial suppliers and used without purifications. All solvents for the reactions were dried and distilled prior to use according to standard methods. Melting points are uncorrected. The $^1H$ NMR and $^{13}C$ NMR spectra were recorded at 25 °C in $CDCl_3$ at 500 and 125 MHz, respectively, with TMS as the internal standard. $^{19}F$ NMR spectra were recorded at 25 °C in $CDCl_3$ at 376 MHz, with $CF_3COOH$ as external standard. Chemical shifts ($\delta$) are expressed in ppm and coupling constants $J$ are given in Hz. The IR spectra were recorded on an FT-IR spectrometer. GC−MS experiments were performed with EI source, LC−MS experiments were performed with ESI source, and high resolution mass spectra (HRMS) were obtained on a TOF MS instrument with ESI or EI source.

**General Procedure for the Gold-Catalyzed Three-Component Tandem Reaction between Allene Esters (1), Selectfluor, and Water.** In a 10 mL flask, $Ph_3PAuNTf_2$ (7.4 mg, 0.01 mmol), Selectfluor (141 mg, 0.4 mmol), $NaHCO_3$ (34 mg, 0.4 mmol), $H_2O$ (72 mg, 4 mmol), and $CH_3CN$ (1 mL) were added. The mixture was stirred at rt for 5 min before a $CH_3CN$ solution (1 mL) of **1** (0.2 mmol) was added. Then the mixture was stirred at 60 °C for 4 h. Upon completion, the resulting mixture was diluted with $CH_2Cl_2$ (10 mL) and filtered through Celite. After evaporation of the solvent under vacuum, the residue was purified by column chromatography on silica gel (100−200 mesh) using petroleum ether/EtOAc (6/1, v/v) as the eluent to give pure **2**.

*Ethyl 1-Acetyl-1-fluoro-1H-indene-2-carboxylate (**2a**).* Purification by column chromatography (petroleum ether/EtOAc, 6/1) as a pale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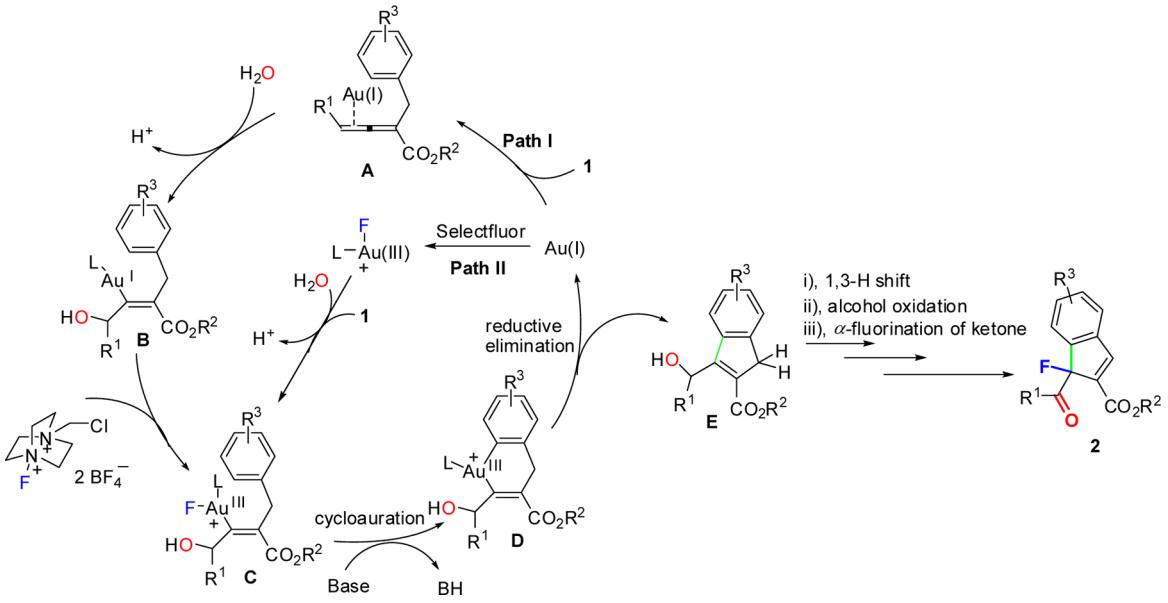
**Scheme 3. Proposed Mechanism**




white solid (36.2 mg, 73%): $R_f$ = 0.68; IR (KBr) $\nu$ = 1715 (C═O) $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 500 MHz) $\delta$ 7.78 (s, 1H), 7.45−7.38 (m, 4H), 4.34−4.26 (m, 2H), 2.30 (d, $J$ = 4.0 Hz, 3H), 1.35 (t, $J$ = 7.0 Hz, 3H); $^{13}C$ NMR ($CDCl_3$, 125 MHz) $\delta$ 201.8 (d, $J$ = 28.8 Hz), 162.2, 146.5 (d, $J$ = 3.8 Hz), 141.8 (d, $J$ = 18.8 Hz), 140.3, 137.4 (d, $J$ = 17.5 Hz), 131.0, 130.0, 124.8, 123.4, 103.0 (d, $J$ = 198.8 Hz), 61.2, 25.4, 14.1; $^{19}F$ NMR ($CDCl_3$, 376 MHz) $\delta$ −177.0 (s); LC−MS (ESI) $m/z$ 271.10 $[M + Na]^+$; HRMS (ESI) for $C_{14}H_{14}FO_3$ $[M + H]^+$ calcd. 249.0927, found 249.0919; mp 63−65 °C.

*Ethyl 1-Fluoro-1-propionyl-1H-indene-2-carboxylate (**2b**).* Purification by column chromatography (petroleum ether/EtOAc, 6/1) as a yellow solid (35.7 mg, 68%): $R_f$ = 0.60; IR (KBr) $\nu$ = 1714 (C═O) $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 500 MHz) $\delta$ 7.77 (s, 1H), 7.44−7.33 (m, 4H), 4.34−4.21 (m, 2H), 2.77−2.60 (m, 2H), 1.32 (t, $J$ = 7.3 Hz, 3H), 1.08 (t, $J$ = 7.0 Hz, 3H); $^{13}C$ NMR ($CDCl_3$, 125 MHz) $\delta$ 204.7 (d, $J$ = 27.5 Hz), 162.3, 146.5 (d, $J$ = 3.8 Hz), 142.1 (d, $J$ = 18.8 Hz), 140.3, 137.5 (d, $J$ = 17.5 Hz), 130.9, 129.9, 124.8, 123.4, 103.1 (d, $J$ = 197.5 Hz), 61.2, 31.1, 14.1, 7.4; $^{19}F$ NMR ($CDCl_3$, 376 MHz) $\delta$ −178.4 (s); LC−MS (ESI) $m/z$ 285.07 $[M + Na]^+$; HRMS (ESI) for $C_{15}H_{16}FO_3$ $[M + H]^+$ calcd. 263.1083, found 263.1075; mp 52−54 °C.

*Ethyl 1-Butyryl-1-fluoro-1H-indene-2-carboxylate (**2c**).* Purification by column chromatography (petroleum ether/EtOAc, 6/1) as a yellow liquid (46.4 mg, 84%): $R_f$ = 0.68; IR (neat) $\nu$ = 1713 (C═O) $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 500 MHz) $\delta$ 7.77 (s, 1H), 7.43−7.28 (m, 4H), 4.34−4.23 (m, 2H), 2.65−2.59 (m, 2H), 1.63−1.61 (m, 2H), 1.32 (t, $J$ = 7.3 Hz, 3H), 0.88 (t, $J$ = 7.0 Hz, 3H); $^{13}C$ NMR ($CDCl_3$, 125 MHz) $\delta$ 203.7 (d, $J$ = 27.5 Hz), 162.3, 146.4 (d, $J$ = 3.8 Hz), 142.0 (d, $J$ = 18.8 Hz), 140.3, 137.6 (d, $J$ = 17.5 Hz), 130.9, 129.9, 124.8, 123.4, 103.1 (d, $J$ = 198.8 Hz), 61.1, 39.4, 30.9, 16.6, 14.1, 13.5; $^{19}F$ NMR ($CDCl_3$, 376 MHz) $\delta$ −178.4 (s); LC−MS (ESI) $m/z$ 277.05 $[M + H]^+$; HRMS (ESI) for $C_{16}H_{18}FO_3$ $[M + H]^+$ calcd. 277.1240, found 277.1237.

*Ethyl 1-Fluoro-1-pentanoyl-1H-indene-2-carboxylate (**2d**).* Purification by column chromatography (petroleum ether/EtOAc, 6/1) as a yellow liquid (36.6 mg, 63%): $R_f$ = 0.60; IR (neat) $\nu$ = 1715 (C═O) $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 500 MHz) $\delta$ 7.77 (s, 1H), 7.44−7.33 (m, 4H), 4.34−4.23 (m, 2H), 2.67−2.58 (m, 2H), 1.60−1.54 (m, 2H), 1.34−1.23 (m, 5H), 0.86 (t, $J$ = 7.3 Hz, 3H); $^{13}C$ NMR ($CDCl_3$, 125 MHz) $\delta$ 203.8 (d, $J$ = 28.8 Hz), 162.3, 146.5 (d, $J$ = 5.0 Hz), 142.1 (d, $J$ = 18.8 Hz), 140.3, 137.6 (d, $J$ = 17.5 Hz), 130.9, 129.9, 124.8, 123.4, 103.1 (d, $J$ = 198.75 Hz), 61.1, 37.2, 25.2, 22.1, 14.1, 13.7; $^{19}F$ NMR ($CDCl_3$, 376 MHz) $\delta$ −178.3 (s); LC−MS (ESI) $m/z$ 313.04 $[M + Na]^+$; HRMS (ESI) for $C_{17}H_{20}FO_3$ $[M + H]^+$ calcd. 291.1396, found 291.1411.

*Ethyl 1-Fluoro-1-hexanoyl-1H-indene-2-carboxylate (**2e**).* Purification by column chromatography (petroleum ether/EtOAc, 6/1) as a yellow liquid (26.8 mg, 44%): $R_f$ = 0.50; IR (neat) $\nu$ = 1717 (C═O) $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 500 MHz) $\delta$ 7.78 (s, 1H), 7.44−7.33 (m, 4H), 4.32−4.24 (m, 2H), 2.63−2.59 (m, 2H), 1.59−1.56 (m, 2H), 1.34−1.23 (m, 7H), 0.86 (t, $J$ = 7.3 Hz, 3H); $^{13}C$ NMR ($CDCl_3$, 125 MHz) $\delta$ 203.9 (d, $J$ = 27.5 Hz), 162.3, 146.6 (d, $J$ = 5.0 Hz), 142.0 (d, $J$ = 18.8 Hz), 140.3, 137.5 (d, $J$ = 17.5 Hz), 130.9, 129.9, 124.8, 123.4, 103.1 (d, $J$ = 198.8 Hz), 61.2, 37.4, 31.1, 22.8, 22.4, 14.2, 13.9; $^{19}F$ NMR ($CDCl_3$, 376 MHz) $\delta$ −178.3 (s); LC−MS (ESI) $m/z$ 327.09 $[M + Na]^+$; HRMS (ESI) for $C_{18}H_{22}FO_3$ $[M + H]^+$ calcd. 305.1553, found 305.1560.

*Ethyl 1-Fluoro-1-heptanoyl-1H-indene-2-carboxylate (**2f**).* Purification by column chromatography (petroleum ether/EtOAc, 6/1) as a yellow liquid (38.8 mg, 61%): $R_f$ = 0.60; IR (neat) $\nu$ = 1716 (C═O) $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 500 MHz) $\delta$ 7.77 (s, 1H), 7.43−7.35 (m, 4H), 4.31−4.26 (m, 2H), 2.65−2.59 (m, 2H), 1.60−1.55 (m, 2H), 1.34−1.22 (m, 9H), 0.85 (t, $J$ = 7.0 Hz, 3H); $^{13}C$ NMR ($CDCl_3$, 125 MHz) $\delta$ 203.8 (d, $J$ = 27.5 Hz), 162.3, 146.5 (d, $J$ = 5.0 Hz), 142.0 (d, $J$ = 18.8 Hz), 140.3, 137.5 (d, $J$ = 17.5 Hz), 130.9, 129.9, 124.8, 123.4, 103.1 (d, $J$ = 197.5 Hz), 61.1, 37.5, 31.5, 28.6, 23.1, 22.4, 14.2, 14.0; $^{19}F$ NMR ($CDCl_3$, 376 MHz) $\delta$ −178.4 (s); LC−MS (ESI) $m/z$ 341.09 $[M + Na]^+$; HRMS (ESI) for $C_{19}H_{24}FO_3$ $[M + H]^+$ calcd. 319.1709, found 319.1700.

*Ethyl 1-Fluoro-1-(2-phenylacetyl)-1H-indene-2-carboxylate (**2g**).* Purification by column chromatography (petroleum ether/EtOAc, 6/1) as a yellow liquid (29.9 mg, 45%): $R_f$ = 0.60; IR (neat) $\nu$ = 1714 (C═O) $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 500 MHz) $\delta$ 7.79 (s, 1H), 7.43−7.26 (m, 6H), 7.19 (d, $J$ = 6.5 Hz, 2H), 6.96 (d, $J$ = 7.5 Hz, 1H), 4.25 (q, $J$ = 7.0 Hz, 2H), 4.06 (dd, $J_1$ = 2.5 Hz, $J_2$ = 15.5 Hz, 1H), 3.90 (dd, $J_1$ = 3.0 Hz, $J_2$ = 15.5 Hz, 1H), 1.32 (t, $J$ = 7.0 Hz, 3H); $^{13}C$ NMR ($CDCl_3$, 125 MHz) $\delta$ 201.5 (d, $J$ = 28.8 Hz), 162.3, 146.6 (d, $J$ = 3.8 Hz), 142.0 (d, $J$ = 18.8 Hz), 140.4, 137.5 (d, $J$ = 17.5 Hz), 132.7, 130.9, 129.9, 128.5, 127.2, 124.8, 123.8, 103.4 (d, $J$ = 200 Hz), 61.2, 44.8, 14.1; $^{19}F$ NMR ($CDCl_3$, 376 MHz) $\delta$ −176.8 (s); LC−MS (ESI) $m/z$ 346.94 $[M + Na]^+$; HRMS (ESI) for $C_{20}H_{18}FO_3$ $[M + H]^+$ calcd. 325.1240, found 325.1231.

*Ethyl 1-Benzoyl-1-fluoro-1H-indene-2-carboxylate (**2h**).* Purification by column chromatography (petroleum ether/EtOAc, 6/1) as a yellow solid (41.0 mg, 66%): $R_f$ = 0.60; IR (KBr) $\nu$ = 1710 (C═O) $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 500 MHz) $\delta$ 7.85−7.81 (m, 3H), 7.56−7.34 (m, 7H), 4.27−4.17 (m, 2H), 1.22 (t, $J$ = 7.0 Hz, 3H); $^{13}C$ NMR ($CDCl_3$, 125 MHz) $\delta$ 194.3 (d, $J$ = 27.5 Hz), 162.1, 146.5 (d, $J$ = 5.0 Hz), 142.7 (d, $J$ = 17.5 Hz), 140.5, 138.9 (d, $J$ = 16.3 Hz), 135.1,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133.1, 131.1, 130.1, 129.0 (d, $J$ = 5.0 Hz), 128.4, 125.1, 124.4, 103.2 (d, $J$ = 196.3 Hz), 61.1, 14.0; $^{19}$F NMR ($CDCl_3$, 376 MHz) $\delta$ −168.4 (s); LC−MS (ESI) $m/z$ 333.05 $[M + Na]^+$; HRMS (ESI) for $C_{19}H_{16}FO_3$ $[M + H]^+$ calcd. 311.1083, found 311.1069; mp 92−95 °C.

*Methyl 1-Acetyl-1-fluoro-1H-indene-2-carboxylate (**2i**).* Purification by column chromatography (petroleum ether/EtOAc, 6/1) as a brown solid (30.0 mg, 64%): $R_f$ = 0.60; IR (KBr) $\nu$ = 1720 (C═O) $cm^{-1}$; $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 7.78 (s, 1H), 7.45−7.38 (m, 4H), 3.84 (s, 3H), 2.29 (d, $J$ = 4.0 Hz, 3H); $^{13}$C NMR ($CDCl_3$, 125 MHz) $\delta$ 201.7 (d, $J$ = 28.8 Hz), 162.7, 146.8 (d, $J$ = 5.0 Hz), 141.8 (d, $J$ = 17.5 Hz), 140.2, 137.0 (d, $J$ = 17.5 Hz), 131.0, 130.1, 124.9, 123.5, 103.0 (d, $J$ = 198.8 Hz), 52.1, 25.3; $^{19}$F NMR ($CDCl_3$, 376 MHz) $\delta$ −177.1 (s); LC−MS (ESI) $m/z$ 257.03 $[M + Na]^+$; HRMS (ESI) for $C_{13}H_{12}FO_3$ $[M + H]^+$ calcd. 235.0770, found 235.0764; mp 67−69 °C.

*Propyl 1-Acetyl-1-fluoro-1H-indene-2-carboxylate (**2j**).* Purification by column chromatography (petroleum ether/EtOAc, 6/1) as a white liquid (45.1 mg, 86%): $R_f$ = 0.50; IR (neat) $\nu$ = 1717 (C═O) $cm^{-1}$; $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 7.77 (s, 1H), 7.43−7.35 (m, 4H), 4.22−4.14 (m, 2H), 2.26 (d, $J$ = 3.5 Hz, 3H), 1.75−1.69 (m, 2H), 0.97 (t, $J$ = 7.5 Hz, 3H); $^{13}$C NMR ($CDCl_3$, 125 MHz) $\delta$ 201.5 (d, $J$ = 28.8 Hz), 162.2, 146.5 (d, $J$ = 3.75 Hz), 141.7 (d, $J$ = 18.8 Hz), 140.2, 137.4 (d, $J$ = 17.5 Hz), 130.9, 129.9, 124.8, 123.3, 102.9 (d, $J$ = 198.8 Hz), 66.7, 25.2, 21.9, 10.3; $^{19}$F NMR ($CDCl_3$, 376 MHz) $\delta$ −177.1 (s); LC−MS (ESI) $m/z$ 285.20 $[M + Na]^+$; HRMS (ESI) for $C_{15}H_{16}FO_3$ $[M + H]^+$ calcd. 263.1083, found 263.1075.

*Isopropyl 1-Acetyl-1-fluoro-1H-indene-2-carboxylate (**2k**).* Purification by column chromatography (petroleum ether/EtOAc, 6/1) as a yellow solid (44.0 mg, 84%): $R_f$ = 0.50; IR (KBr) $\nu$ = 1710 (C═O) $cm^{-1}$; $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 7.73 (s, 1H), 7.40−7.33 (m, 4H), 5.15−5.10 (m, 1H), 2.26 (d, $J$ = 4.0 Hz, 3H), 1.29 (dd, $J_1$ = 6.0 Hz, $J_2$ = 11.5 Hz, 6H); $^{13}$C NMR ($CDCl_3$, 125 MHz) $\delta$ 201.6 (d, $J$ = 30.0 Hz), 161.7, 146.2 (d, $J$ = 5.0 Hz), 141.7 (d, $J$ = 20.0 Hz), 140.3 (d, $J$ = 2.5 Hz), 137.8 (d, $J$ = 17.5 Hz), 130.9, 129.8, 124.7, 123.3, 102.9 (d, $J$ = 197.5 Hz), 68.8, 25.2, 21.69, 21.65; $^{19}$F NMR ($CDCl_3$, 376 MHz) $\delta$ −177.0 (s); LC−MS (ESI) $m/z$ 285.05 $[M + Na]^+$; HRMS (ESI) for $C_{15}H_{16}FO_3$ $[M + H]^+$ calcd. 263.1083, found 263.1077; mp 52−54 °C.

*Butyl 1-Acetyl-1-fluoro-1H-indene-2-carboxylate (**2l**).* Purification by column chromatography (petroleum ether/EtOAc, 6/1) as a yellow liquid (44.7 mg, 81%): $R_f$ = 0.60; IR (neat) $\nu$ = 1715 (C═O) $cm^{-1}$; $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 7.76 (s, 1H), 7.43−7.35 (m, 4H), 4.27−4.19 (m, 2H), 2.26 (d, $J$ = 3.5 Hz, 3H), 1.69−1.65 (m, 2H), 1.42−1.40 (m, 2H), 0.95 (t, $J$ = 7.5 Hz, 3H); $^{13}$C NMR ($CDCl_3$, 125 MHz) $\delta$ 201.5 (d, $J$ = 28.75 Hz), 162.2, 146.5 (d, $J$ = 5.0 Hz), 141.7 (d, $J$ = 18.8 Hz), 140.3 (d, $J$ = 1.3 Hz), 137.4 (d, $J$ = 17.5 Hz), 130.9, 129.9, 124.8, 123.4, 102.9 (d, $J$ = 197.5 Hz), 65.0, 30.5, 25.2, 19.0, 13.6; $^{19}$F NMR ($CDCl_3$, 376 MHz) $\delta$ −177.1 (s); LC−MS (ESI) $m/z$ 299.17 $[M + Na]^+$; HRMS (ESI) for $C_{16}H_{18}FO_3$ $[M + H]^+$ calcd. 277.1240, found 277.1230.

*Allyl 1-Acetyl-1-fluoro-1H-indene-2-carboxylate (**2m**).* Purification by column chromatography (petroleum ether/EtOAc, 6/1) as a yellow liquid (36.9 mg, 71%): $R_f$ = 0.60; IR (neat) $\nu$ = 1720 (C═O) $cm^{-1}$; $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 7.81 (s, 1H), 7.45−7.39 (m, 4H), 6.00−5.94 (m, 1H), 5.39 (dd, $J_1$ = 1.5 Hz, $J_2$ = 17.0 Hz, 1H), 5.29 (dd, $J_1$ = 1.0 Hz, $J_2$ = 17.0 Hz, 1H), 4.76−4.74 (m, 2H), 2.31 (d, $J$ = 3.5 Hz, 3H); $^{13}$C NMR ($CDCl_3$, 125 MHz) $\delta$ 201.8 (d, $J$ = 28.8 Hz), 161.9, 146.9 (d, $J$ = 5.0 Hz), 141.9 (d, $J$ = 18.5 Hz), 140.3, 137.1 (d, $J$ = 17.5 Hz), 131.6, 131.0, 130.1, 124.9, 123.5, 118.8, 103.0 (d, $J$ = 198.8 Hz), 65.7, 25.5; $^{19}$F NMR ($CDCl_3$, 376 MHz) $\delta$ −176.9 (s); LC−MS (ESI) $m/z$ 283.09 $[M + Na]^+$; HRMS (ESI) for $C_{15}H_{14}FO_3$ $[M + H]^+$ calcd. 261.0927, found 261.0934.

*Methyl 1-Fluoro-1-pentanoyl-1H-indene-2-carboxylate (**2n**).* Purification by column chromatography (petroleum ether/EtOAc, 6/1) as a yellow liquid (22.6 mg, 41%): $R_f$ = 0.60; IR (neat) $\nu$ = 1720 (C═O) $cm^{-1}$; $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 7.78 (s, 1H), 7.45−7.34 (m, 4H), 3.83 (s, 3H), 2.67−2.60 (m, 2H), 1.59−1.56 (m, 2H), 1.28−1.25 (m, 2H), 0.86 (t, $J$ = 7.3 Hz, 3H); $^{13}$C NMR ($CDCl_3$, 125 MHz) $\delta$ 203.7 (d, $J$ = 27.5 Hz), 162.7, 146.7 (d, $J$ = 3.8 Hz), 142.0 (d, $J$ = 18.8 Hz), 140.3 (d, $J$ = 1.3 Hz), 137.2 (d, $J$ = 17.5 Hz), 130.9, 129.9, 124.8, 123.4, 103.1 (d, $J$ = 198.8 Hz), 52.0, 37.1, 25.2, 22.1, 13.7; $^{19}$F NMR ($CDCl_3$, 376 MHz) $\delta$ −178.3 (s); LC−MS (ESI) $m/z$ 299.06 $[M + Na]^+$; HRMS (ESI) for $C_{16}H_{18}FO_3$ $[M + H]^+$ calcd. 277.1240, found 277.1232.

*Methyl 1-Benzoyl-1-fluoro-1H-indene-2-carboxylate (**2o**).* Purification by column chromatography (petroleum ether/EtOAc, 6/1) as a yellow solid (44.4 mg, 75%): $R_f$ = 0.60; IR (KBr) $\nu$ = 1713 (C═O) $cm^{-1}$; $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 7.85 (d, $J$ = 7.5 Hz, 2H), 7.81 (s, 1H), 7.57−7.34 (m, 7H), 3.77 (s, 3H); $^{13}$C NMR ($CDCl_3$, 125 MHz) $\delta$ 194.3 (d, $J$ = 27.5 Hz), 162.6, 146.3 (d, $J$ = 5.0 Hz), 142.7 (d, $J$ = 17.5 Hz), 140.5, 138.6 (d, $J$ = 17.5 Hz), 135.2, 133.2, 131.1, 130.2, 129.0 (d, $J$ = 5.0 Hz), 128.5, 125.2, 124.4, 103.3 (d, $J$ = 197.5 Hz), 52.0; $^{19}$F NMR ($CDCl_3$, 376 MHz) $\delta$ −169.7 (s); LC−MS (ESI) $m/z$ 319.10 $[M + Na]^+$; HRMS (ESI) for $C_{18}H_{14}FO_3$ $[M + H]^+$ calcd. 297.0927, found 297.0917; mp 115−117 °C.

*Ethyl 1-Acetyl-1-fluoro-6-methyl-1H-indene-2-carboxylate (**2p**).* Purification by column chromatography (petroleum ether/EtOAc, 6/1) as a yellow solid (39.8 mg, 76%): $R_f$ = 0.60; IR (KBr) $\nu$ = 1714 (C═O) $cm^{-1}$; $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 7.71 (s, 1H), 7.23−7.14 (m, 3H), 4.32−4.21 (m, 2H), 2.36 (s, 3H), 2.24 (d, $J$ = 3.5 Hz, 3H), 1.31 (t, $J$ = 7.3 Hz, 3H); $^{13}$C NMR ($CDCl_3$, 125 MHz) $\delta$ 201.4 (d, $J$ = 30.0 Hz), 161.8, 144.9 (d, $J$ = 5.0 Hz), 142.1 (d, $J$ = 1.3 Hz), 140.0 (d, $J$ = 18.8 Hz), 139.1 (d, $J$ = 17.5 Hz), 137.2, 129.7, 125.1, 124.4, 102.3 (d, $J$ = 200.0 Hz), 61.4, 25.5, 14.1; $^{19}$F NMR ($CDCl_3$, 376 MHz) $\delta$ −176.3 (s); LC−MS (ESI) $m/z$ 284.99 $[M + Na]^+$; HRMS (ESI) for $C_{15}H_{16}FO_3$ $[M + H]^+$ calcd. 263.1083, found 263.1075; mp 76−78 °C.

*Ethyl 1-Acetyl-6-chloro-1-fluoro-1H-indene-2-carboxylate (**2q**).* Purification by column chromatography (petroleum ether/EtOAc, 6/1) as a white solid (38.9 mg, 69%): $R_f$ = 0.60; IR (KBr) $\nu$ = 1717 (C═O) $cm^{-1}$; $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 7.69 (s, 1H), 7.42 (d, $J$ = 1.5 Hz, 1H), 7.36−7.29 (m, 2H), 4.36−4.25 (m, 2H), 2.33 (d, $J$ = 4.0 Hz, 3H), 1.34 (t, $J$ = 7.5 Hz, 3H); $^{13}$C NMR ($CDCl_3$, 125 MHz) $\delta$ 201.4 (d, $J$ = 30 Hz), 161.8, 144.9 (d, $J$ = 3.8 Hz), 142.1 (d, $J$ = 1.3 Hz), 140.0 (d, $J$ = 20.0 Hz), 139.1 (d, $J$ = 17.5 Hz), 137.2, 129.7, 125.1, 124.4, 102.3 (d, $J$ = 200 Hz), 61.4, 25.5, 14.1; $^{19}$F NMR ($CDCl_3$, 376 MHz) $\delta$ −176.5 (s); LC−MS (ESI) $m/z$ 305.02 $[M + Na]^+$; HRMS (ESI) for $C_{14}H_{13}ClFO_3$ $[M + H]^+$ calcd. 283.0537, found 283.0525; mp 135−137 °C.

*Ethyl 1-Acetyl-6-bromo-1-fluoro-1H-indene-2-carboxylate (**2r**).* Purification by column chromatography (petroleum ether/EtOAc, 6/1) as a yellow solid (39.8 mg, 69%): $R_f$ = 0.60; IR (KBr) $\nu$ = 1717 (C═O) $cm^{-1}$; $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 7.67 (s, 1H), 7.56 (d, $J$ = 1.5 Hz, 1H), 7.50 (dd, $J_1$ = 1.5 Hz, $J_2$ = 7.5 Hz, 1H), 7.22 (dd, $J_1$ = 1.0 Hz, $J_2$ = 8.0 Hz, 1H), 4.32−4.27 (m, 2H), 2.31 (d, $J$ = 4.0 Hz, 3H), 1.33 (t, $J$ = 7.0 Hz, 3H); $^{13}$C NMR ($CDCl_3$, 125 MHz) $\delta$ 201.3 (d, $J$ = 28.8 Hz), 161.8, 144.9 (d, $J$ = 5.0 Hz), 142.3, 140.5 (d, $J$ = 18.8 Hz), 138.9 (d, $J$ = 17.5 Hz), 132.6, 127.9, 125.1, 124.7, 102.4 (d, $J$ = 198.8 Hz), 61.4, 25.5, 14.1; $^{19}$F NMR ($CDCl_3$, 376 MHz) $\delta$ −176.7 (s); LC−MS (ESI) $m/z$ 348.92 $[M + Na]^+$; HRMS (ESI) for $C_{14}H_{12}BrFNaO_3$ $[M + H]^+$ calcd. 348.9852, found 348.9846; mp 114−116 °C.

*3-Methyl-3H-indeno[1,2-c]furan-1(8H)-one (**3v**).*[32] Purification by column chromatography (petroleum ether/EtOAc, 6/1) as a white solid (21.9 mg, 59%): $R_f$ = 0.60; IR (KBr) $\nu$ = 1739 (C═O) $cm^{-1}$; $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 7.61 (d, $J$ = 6.5 Hz, 1H), 7.50−7.41 (m, 3H), 5.56−5.50 (m, 1H), 3.61 (d, $J$ = 3.0 Hz, 2H), 1.70 (d, $J$ = 2.0 Hz, 3H); $^{13}$C NMR ($CDCl_3$, 125 MHz) $\delta$ 174.2, 168.6, 149.8, 135.8, 135.3, 128.9, 127.4, 125.9, 121.6, 75.6, 32.2, 19.2; GC−MS (EI, 70 eV) $m/z$ 186 ($M^+$); mp 156−158 °C.

*3-Benzyl-4-fluoro-5,5-dimethylfuran-2(5H)-one (**4w**).* Purification by column chromatography (petroleum ether/EtOAc, 6/1) as a yellow liquid (18.0 mg, 41%): $R_f$ = 0.60; IR (neat) $\nu$ = 1768 (C═O), 1720 (C═O) $cm^{-1}$; $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 7.33−7.23 (m, 5H), 3.57 (s, 2H), 1.55 (s, 6H); $^{13}$C NMR ($CDCl_3$, 125 MHz) $\delta$ 180.5, 178.1, 169.9 (d, $J$ = 22.5 Hz), 136.8 (d, $J$ = 2.5 Hz), 128.6 (d, $J$ = 27.5 Hz), 126.8, 106.6 (d, $J$ = 5.0 Hz), 79.8 (d, $J$ = 22.5 Hz), 29.7, 27.3 (d, $J$ = 2.5 Hz), 23.7 (d, $J$ = 2.5 Hz); $^{19}$F NMR ($CDCl_3$, 376 MHz) $\delta$ −113.1 (s); GC−MS (EI, 70 eV) $m/z$ 220 ($M^+$); HRMS (EI) for $C_{13}H_{13}FO_2$ $[M + H]^+$ calcd. 220.0900, found 220.0907.


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*Ethyl 1-Acetyl-3,4-dihydronaphthalene-2-carboxylate (**2x**).* Purification by column chromatography (petroleum ether/EtOAc, 6/1) as a yellow liquid (21.0 mg, 43%): $R_f$ = 0.61; IR (neat) $\nu$ = 1703 (C═O) $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 500 MHz) $\delta$ 7.32−7.21 (m, 3H), 7.10 (d, $J$ = 8.0 Hz, 1H), 4.27 (q, $J$ = 7.1 Hz, 2H), 2.88 (t, $J$ = 8.0 Hz, 2H), 2.64 (t, $J$ = 8.1 Hz, 2H), 2.49 (s, 3H), 1.34 (t, $J$ = 7.0 Hz, 3H); $^{13}C$ NMR ($CDCl_3$, 125 MHz) $\delta$ 205.3, 166.5, 149.4, 137.3, 130.0, 129.7, 128.2, 127.0, 125.8, 124.3, 61.3, 31.2, 27.6, 22.5, 14.0; GC−MS (EI, 70 eV) $m/z$ 244 ($M^+$); HRMS (EI) for $C_{15}H_{17}O_3$ $[M + H]^+$ calcd. 245.1178, found 245.1174.

*4-Deuterated Ethyl 1-Acetyl-1-fluoro-1H-indene-2-carboxylate (**2a**-d).* Purification by column chromatography (petroleum ether/EtOAc, 6/1) as a pale white solid (35.4 mg, 71%, 70%-Deuterium enrichment at the 4-position): $R_f$ = 0.68; IR (KBr) $\nu$ = 1715 (C═O) $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 500 MHz) $\delta$ 7.78 (s, 1H), 7.44−7.38 (m, 3.30H), 4.34−4.26 (m, 2H), 2.30 (d, $J$ = 4.0 Hz, 3H), 1.34 (t, $J$ = 7.0 Hz, 3H); $^{13}C$ NMR ($CDCl_3$, 125 MHz) $\delta$ 201.8 (d, $J$ = 30.0 Hz), 162.2, 146.4 (d, $J$ = 3.8 Hz), 141.8 (d, $J$ = 18.8 Hz), 140.3 (d, $J$ = 13.8 Hz), 137.5 (d, $J$ = 16.3 Hz), 130.9 (d, $J$ = 13.8 Hz), 130.0, {124.8, 124.7, 124.5, 124.3}(1C, **2a**-*d* plus **2a**), 123.4, 103.0 (d, $J$ = 197.5 Hz), 61.2, 25.4, 14.1; LC−MS (ESI) $m/z$ 272.19 $[M + Na]^+$; HRMS (ESI) for $C_{14}H_{13}DFO_3$ $[M + H]^+$ calcd. 250.0990, found 250.0983; mp 63−65 °C.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

The experimental procedures for the synthesis of starting materials and their characterization, copies of $^1H$ NMR, $^{13}C$ NMR, and $^{19}F$ NMR spectra of the products as well as X-ray structural data (CIF) of compound **2q**. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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