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Stereocontrolled access to α-fluoro-β-ketoesters

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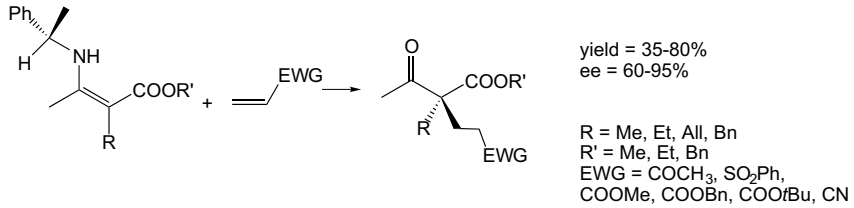
Abstract—The effect of a fluorine atom on the asymmetric Michael reaction between a chiral α-fluoro-β-enaminoester derived from (*S*)-1-phenylethylamine and various electrophilic alkenes is studied. α-Fluoro-α-substituted ketoesters are obtained in good yields with fairly good enantioselectivity.

1. Introduction

Michael reaction is known to be one of the simplest and most efficient methods for the construction of quaternary carbon centres. The use of an asymmetric variant of this reaction is well documented in the literature by the stereocontrolled synthesis of quaternary carbon still being a challenge for organic chemists. Asymmetric Michael addition on cyclic or acyclic β-ketoesters has been considered by various methods in the literature and particularly via enaminoester derivatives.[1–8] As part of a systematic study on asymmetric Michael reaction between chiral acyclic enaminoesters derived from (*S*)-1-phenylethylamine and various Michael acceptors, our team has already considered the effect of α-substituent or ester substituent of the β-enaminoester on reactivity and enantioselectivity obtained using this method.[3,4,7–9] Michael adducts were obtained after hydrolysis in good yields (>50% yield) and excellent enantioselectivity (ee > 90%) whatever the alkyl substituents at the α-position and with a majority of esters of the β-enaminoester (Scheme 1).

Moreover, the fluorine atom presents a unique set of chemical and physical properties conferring to fluoro-derivatives particular behaviour in terms of chemical, biological activity and/or bioavailability.[10–12] Particular characteristics of fluorine derivatives are due to the combination of high electronegativity, small size and low polarizability of the fluorine atom with high stability of the C–F bond.[13,14] As a result, a large set of pharmaceutical compounds presently possess a fluorine atom in their structure with some famous examples such as fluorouracil or fluoroquinolones.[15,16]



Scheme 1. Asymmetric Michael reaction of β-ketoesters.

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The introduction of a fluorine atom to generate a fluorinated quaternary carbon centre was generally realized by catalytic asymmetric electrophilic fluorination: α-fluoro-β-ketoesters have been obtained with modest to excellent enantiomeric excesses.[17] Nevertheless, this introduced the fluorine atom at a tertiary carbon centre, and only few examples have been described starting from acyclic β-ketoesters.[18] As a result it seems very interesting to apply our expertise on the asymmetric Michael addition starting from acyclic β-ketoesters to α-fluoro-β-ketoesters and to study the effect of a fluorine atom in terms of both enantioselectivity and efficiency.

Herein we report the reaction between chiral α-fluoro-β-enaminoesters and various electrophilic alkenes. In this approach, contrary to the catalytic asymmetric electrophilic fluorinations, the fluorine atom was present in the starting material and we studied the asymmetric introduction of the alkyl substituent.

2. Results and discussion

A condensation between ethyl 2-fluoroacetoacetate and (*S*)-1-phenylethylamine in refluxing toluene furnished compound **1** in quantitative yield (Scheme 2).

Fluoroenaminoester **1** exists in two diastereomeric forms *E* and *Z* in a 4/1 ratio. This ratio was determined by using 1D ^{1}H NMR and 2D HeteronOe ^{1}H–^{19}F experiments. The correlation between the fluorine atom and methyl directly branched on the alkene moiety was observed in the major product, while a correlation between fluorine atom and NH group was observed in the minor product (Fig. 1). This result is in agreement with other literature data, where the *E*/*Z* ratio ranged from 1:1 to 8:1 for α-fluoro- and α-perfluoroalkyl enamines.[19,20] This ratio can be explained by chelation between the hydrogen atom bearing the nitrogen of the enamine and the carbonyl group of the ester function, which favours the *E* configuration. This was already observed by Prié et al. with perfluorinated β-enaminoesters, where the (*E*)-derivative was highly favoured for primary and secondary amines (*E*/*Z* ratio 100:0) thanks to an intramolecular hydrogen bond. However for the tertiary amines, the *E*/*Z* ratio decreased in favour of the *Z* diastereomer (*E*/*Z* ratio from 95:5 to 50:50).[20] In our case, the high electronegativity of the fluorine atom destabilized this intramolecular hydrogen bonding leading to the 4:1 *E*/*Z* ratio.

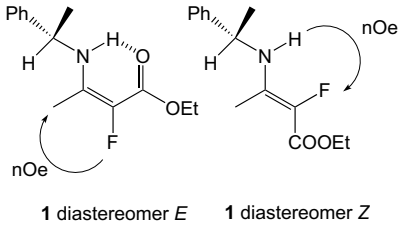


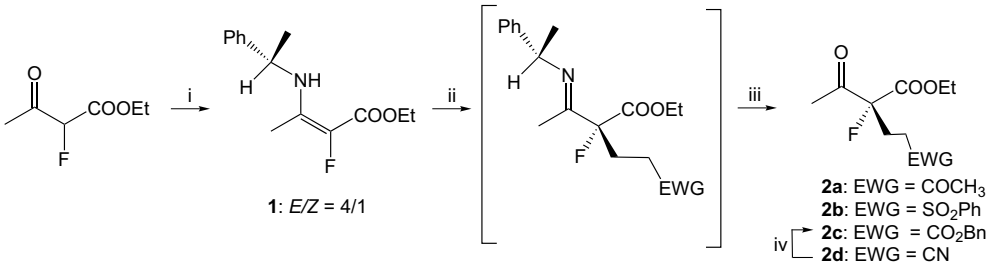
Figure 1. HeteronOe ^{1}H–^{19}F correlations in the two diastereomers of compound **1**.

Attempts to improve this ratio were carried out by refluxing compound **1** in THF or in toluene for 24 h, but no change was observed. ^{1}H NMR experiment was carried out in DMSO-d_6 with increasing temperature. No change in the *E*/*Z* ratio was observed until 120 °C. Above this temperature, we observed an irreversible decline of the *E*/*Z* ratio to 55:45. Attempts at the isolation of the two diastereoisomers by column chromatography proved to be unsuccessful.

Additions of this crude fluoroenaminoester **1** to Michael acceptors, such as methylvinylketone (MVK), phenylvinylsulfone, benzyl acrylate and acrylonitrile were performed under neutral conditions in THF. Reaction evolution was followed by ^{19}F NMR and the reaction conditions are summarized in Table 1.

Michael adducts **2a**–**2d** were obtained, after hydrolytic work-up (10% AcOH in water, rt, 1 h), in moderate to good yields (35–73% over three steps). The presence of the fluorine atom has no influence on the reactivity: yields are similar to those obtained for other enaminoesters.[8] Concerning compound **2a**, a retro-Michael reaction was observed during hydrolysis, but not for other compounds **2b**–**2d**, which explained the lower yield obtained with the MVK acceptor (entry 1).

The enantiomeric excesses (ees) of compounds **2a**–**2d** were determined either by ^{1}H NMR with a chiral shift agent or by HPLC with a Daicel Chiralcel AD column (Table 1). For compound **2d**, it was necessary to transform it into



Scheme 2. Synthesis of Michael adducts **2a**–**d**. Reagents and conditions: (i) (*S*)-1-phenylethylamine, APTS catal., toluene, Dean-Stark, reflux overnight; (ii) CH_2=CH–EWG, $ZnCl_2$ (0 or 1 equiv), hydroquinone catal., THF, rt, 60 °C or reflux, 6 h to 6 days; (iii) AcOH 10%, rt, 1 h; (iv) HCl(g), BnOH, −20 °C, 72 h then HCl 6 M, 15 min.

Table 1. Reaction conditions, yields and enantiomeric excesses for compounds **2a–d**

Entry	Compd	CH_2=CH–EWG (equiv)	Reaction time	T (°C)	Lewis acid	Yield (%)	ee (%)
1	**2a**	EWG = $COCH_3$ (3)	6 h	20	—	46	60[a]
2	**2b**	EWG = SO_2Ph (1.2)	16 h	67	—	71	77[b]
3	**2b**	EWG = SO_2Ph (1.2)	16 h	67	$ZnCl_2$	57	77[b]
4	**2c**	EWG = CO_2Bn (2)	16 h	67	—	73	75[a]
5	**2d**	EWG = CN (6[c])	6 days	60	—	35	74[d]
6	**2d**	EWG = CN (3)	24 h	60	$ZnCl_2$	66	54[d]

[a] Determined by ^{1}H NMR with Eu(hfc)$_3$ as chiral shift reagent.
[b] Determined by chiral HPLC.
[c] Acrylonitrile was added in two portions of 3 equiv, one at the beginning and the other after 3 days.
[d] Determined by chiral HPLC via derivative **2c**.

benzyl ester **2c** thanks to a Pinner reaction in benzyl alcohol (Scheme 2).[21] Enantiomeric excesses of compounds **2a–2d** were fairly good (60–77%) (Table 1, entries 1–5). A major difference is a partial loss of enantioselectivity, only around 75% for adducts **2b–2c** (and 60% ee for **2a**) against 95% for other enaminoesters.[8] The loss of enantioselectivity is to be explained below.

It is noteworthy that the introduction of $ZnCl_2$ caused an important decrease in reaction time when the reaction was carried out with the poorly reactive Michael acceptor acrylonitrile, but also led to a large decrease in enantioselectivity with only 54% ee (entry 6). When used with a good Michael acceptor such as phenylvinylsulfone, $ZnCl_2$ had no influence neither on the reactivity nor on enantioselectivity of the reaction (entries 2 and 3).

The absolute configuration in compound **2b** was determined by means of a single-crystal X-ray analysis, on the basis of the anomalous diffusion of the sulfur atom, and was shown to be an (*R*)-absolute configuration (Fig. 2).[22,23] The absolute configuration of other adducts **2a**, **2c** and **2d** was assigned by analogy, considering the same mechanism.

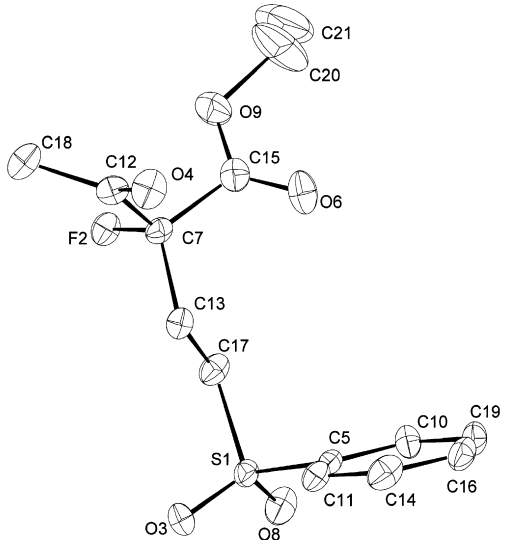


Figure 2. X-ray crystal structure of adduct **2b** with labelled heteroatoms. All hydrogens atoms have been omitted for clarity.

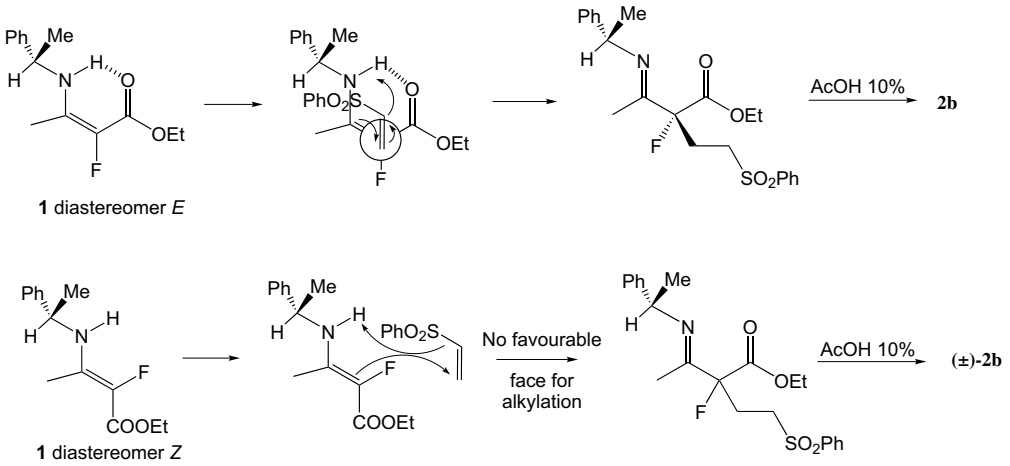
This result is in accordance with the proposed mechanism implicating a highly ordered transition state associated with a pericyclic process, thus ensuring a predictable stereochemical course and a high enantioselectivity. The nucleophilic partner implicated in this reaction is assumed to be the more substituted secondary enamine secured by hydrogen bonding between the NH group and the carbonyl moiety of the ester group. A *syn*-approach between compound **1** and the phenylvinylsulfone combined with the related six-membered 'aza-ene-synthesis-like' transition state can be invoked. According to this model, the alkylation takes place predominantly on the less hindered *Si* π-face, *anti*- to the bulky phenyl group of the chiral amine moiety portrayed in its energetically preferred conformation, in which the H atom is *anti* to the H atom of the amino group (Scheme 3).[3,4,24]

This mechanism is acceptable for the *E*-diastereomer of compound **1**, however, with fluoroenaminoester **1** existing in the *E*- and *Z*-configuration, the Michael reaction could be realized on the *Z*-diastereomer where no intramolecular hydrogen bonding could secure the six-membered transition state. As a result the *Z*-diastereomer led to racemic **2b** (Scheme 1).

It is important to note that isomerization of compound **1** from the *E*-diastereomer into the *Z*-diastereomer did not occur below 120 °C in DMSO (reaction monitored by ^{1}H NMR). It could thus be assumed that, in refluxing THF (67 °C), there is no isomerization of compound **1**, which could modify the ratio between *Z*- and *E*-diastereomers during the Michael reaction process. Such a process thus led to a 90:10 *R*/*S* ratio which gave an ee of around 80%. This is approximately the value of the ee obtained for compound **2b** and for other adducts **2c–2d**, confirming our hypothesis. The existence of the two diastereomers, *Z*- and *E*-, in fluoroenaminoester **1** explained the decrease in the enantioselectivity observed when the fluoro substituent was introduced in place of an alkyl substituent. For adduct **2a**, retro-Michael reaction during hydrolysis caused an additional loss of enantioselectivity with an ee of only 60%.

3. Conclusion

In conclusion, we have demonstrated that the asymmetric Michael addition of α-fluoro-β-enaminoester to Michael acceptors could be carried out under the same conditions



Scheme 3. Transition state of the reaction involving compound **1** and phenylvinylsulfone.

as those described for α-alkyl-β-enaminoesters. Yields are similar (>40% yield) but we observed a decrease in enantioselectivity, due to the existence of α-fluoro-β-enaminoester **1** under the *Z*- and *E*-configurations. The study of a Michael reaction on fluoroenaminoester **1** with α-substituted Michael acceptors is currently in progress.

4. Experimental

4.1. General

Commercial reagents were used without purification. Prior to use, THF was freshly distilled from sodium-benzophenone, toluene from CaH_2. All anhydrous reactions were carried out under an argon atmosphere. Analytical thin layer chromatography was performed on Merck 60F-254 precoated silica (0.2 mm) on glass and was revealed by UV-light or Kägi-Misher reagent. All flash chromatography separations were performed with Merck Kieselgel (40–63 μm). Melting points were recorded on an Electrothermal digital apparatus and are uncorrected. Infrared (IR) spectra were obtained as neat films and were recorded on Bruker Vector 22 spectrophotometer. ^1H, ^{19}F and ^{13}C spectra were recorded, respectively, at 300 MHz, 188 MHz and 75 MHz unless otherwise specified. $CDCl_3$ was used as internal reference. Specific rotations $[\alpha]_D^{20}$ were measured on a PolAAr32 polarimeter with sodium (589 nm) lamp at 20 °C in a 1 dm-cell. Elemental analyses were performed by the Service de Microanalyse, Centre d'Etudes Pharmaceutiques, Châtenay-Malabry, France, with a Perkin–Elmer 2400 analyser. Enantiomeric excesses (ees) were evaluated either by ^1H NMR spectroscopy using $Eu(hfc)_3$ as chiral shift reagent or by chiral HPLC on a Spectrasystem P1000XR with a Spectraseries UV100 spectrophotometer and a chiral column Chiralcel AD, spectra being treated with AZUR program.

4.2. Ethyl (*S*)-2-fluoro-3-(1-phenyl-ethylamino)-but-2-enoate 1

To a solution of ethyl fluoroacetoacetate (1.5 g, 10 mmol, 1 equiv) in toluene (20 mL) were added under an inert atmosphere, a catalytic amount of *para*-toluenesulfonic acid and (*S*)-1-phenylethylamine (1.55 mL, 12 mmol, 1.2 equiv). After stirring at reflux overnight using a Dean-Stark apparatus and cooling, the mixture was concentrated, diluted with anhydrous Et_2O, filtered and then the filtrate was concentrated to yield compound **1** as a yellow oil (quantitative yield) as a *Z*/*E* 20:80 mixture; ^1H NMR (400 MHz, $CDCl_3$) δ: 1.30 (t, $^3J = 7.2$ Hz, 3H, $COOCH_2$-CH_3 *E*), 1.36 (t, $^3J = 7.3$ Hz, 3H, $COOCH_2CH_3$ *Z*), 1.50 (d, $^3J = 7.0$ Hz, 3H, CH_3 *Z* + *E*), 1.87 (d, $^4J_F = 4.0$ Hz, 3H, $CH_3C=$ *E*), 2.16 (d, $^4J_F = 2.5$ Hz, 3H, $CH_3C=Z$), 4.21 (q, $^3J = 7.3$ Hz, 2H, $COOCH_2CH_3$ *Z*), 4.29 (q, $^3J = 7.1$ Hz, 2H, $COOCH_2CH_3$ *E*), 4.56 (qt, $^3J = 7.3$ Hz, 1H, CH*E*), 4.63 (qt, $^3J = 7.3$ Hz, 1H, CH*E*), 4.89 (br s, 1H, NH *Z*), 7.20–7.50 (m, 5H, H_{ar} *Z* + *E*), 7.84 (br s, 1H, NH *E*); ^{19}F NMR ($CDCl_3$) δ: −163.35 (*Z*), −177.62 (*E*); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 11.78 (d, $^3J_F = 6.8$ Hz, CH_3), 14.35 ($COOCH_2CH_3$), 24.54 (CH_3 *Z*), 24.87 (CH_3 *E*), 51.25 (CH *Z*), 52.66 (CH *E*), 59.44 ($COOCH_2CH_3$), 125.17 + 126.96 + 128.63 (CH_{ar} *E*), 125.56 + 127.00 + 128.45 (CH_{ar} *Z*), 129.76 (d, $^1J_F = 215$ Hz, =*C*–F *E*), 144.85 (C_{qar} *E*), 144.49 (C_{qar} *Z*), 147.22 (d, $^2J_F = 23.9$ Hz, =*C*–NH), 164.15 (*C*OO); IR (cm^{-1}): 3303, 2978, 1663, 1616, 1450, 1368, 1269, 1213, 1119, 1075, 1059.

4.3. General procedure for the Michael reaction between the enaminoester derivative 1 and electrophilic alkenes

To a solution of compound **1** (1 equiv) in THF (0.2 M) were added, under inert atmosphere, catalytic amount of hydroquinone and a solution of electrophilic alkene (1.2–3 equiv) in a minimum of THF dropwise. After stirring the mixture at room temperature for methylvinylketone, 60 °C for acrylonitrile or reflux otherwise (evolution reaction was monitored by ^{19}F NMR) and cooling, a solution of AcOH 10% was added. After further stirring at room temperature for 1 h, THF was evaporated and the aqueous layer extracted three times with dichloromethane. The organic layers were then combined, washed with HCl 1 M and brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified by column chromatography (cyclohexane/EtOAc 9:1–7:3) to yield the desired compound.

4.3.1. Ethyl (*R*)-2-acetyl-2-fluoro-5-oxo-hexanoate 2a. Yellowish oil (46% yield); ee = 60%, R_f: 0.30 (cyclohexane/EtOAc 7:3); ^{1}H NMR ($CDCl_3$) δ: 1.26 (t, $^3J = 7.1$ Hz, 3H, $COOCH_2CH_3$), 2.11 (s, 3H, CH_3CO), 2.26 (d, $^4J_F = 4.5$ Hz, 3H, CH_3CO), 2.25–2.45 (m, 2H, CH_2C_q), 2.50 (t, $^3J = 7.4$ Hz, 2H, CH_2CO), 4.22 (q, $^3J = 7.1$ Hz, 2H, $COO\ CH_2CH_3$); ^{19}F NMR ($CDCl_3$) δ: −164.63; ^{13}C NMR ($CDCl_3$) δ: 13.85 ($COOCH_2CH_3$), 25.36 (CH_3CO), 27.27 (d, $^2J_F = 21.1$ Hz, CH_2Cq), 29.71 (CH_3CO), 36.52 (d, $^3J_F = 3.0$ Hz, CH_2CO), 62.65 ($COOCH_2CH_3$), 98.98 (d, $^1J_F = 196$ Hz, CqF), 165.91 (d, $^2J_F = 25.6$ Hz, COO), 201.20 (d, $^2J_F = 28.2$ Hz, CO), 206.02 (CO); IR (cm^{-1}): 2983, 1752, 1718, 1420, 1359, 1263, 1191, 1168, 1097, 1016; $[\alpha]_D^{20} = -23$ (c 1.0, CH_2Cl_2). Anal. Calcd for $C_{10}H_{15}FO_4$: C, 55.04; H, 6.93. Found: C, 55.21; H, 7.06.

4.3.2. Ethyl (*R*)-2-acetyl-4-benzenesulfonyl-2-fluoro-butanoate 2b. White solid (71% yield); ee = 77%; R_f: 0.45 (cyclohexane/EtOAc 7:3); mp = 49 °C; ^{1}H NMR ($CDCl_3$) δ: 1.17 (t, $^3J = 7.1$ Hz, 3H, $COOCH_2CH_3$), 2.19 (d, $^4J_F = 4.6$ Hz, 3H, CH_3CO), 2.25–2.60 (m, 2H, CH_2C_q), 3.10 (t, $^4J_F = 8.3$ Hz, 2H, CH_2SO_2), 4.16 (q, $^3J = 7.1$ Hz, 2H, $COOCH_2CH_3$), 7.45–7.60 (m, 3H, H_{ar}), 7.85 (m, 2H, H_{ar}); ^{19}F NMR ($CDCl_3$) δ: −164.16; ^{13}C NMR ($CDCl_3$) δ: 13.75 ($COOCH_2CH_3$), 24.98 (CH_3CO), 26.53 (d, $^2J_F = 21.4$ Hz, CH_2Cq), 49.73 (d, $^3J_F = 3.2$ Hz, CH_2SO_2), 62.84 ($COOCH_2CH_3$), 97.55 (d, $^1J_F = 199$ Hz, CqF), 127.71 + 129.17 + 133.80 (CH_{ar}), 138.14 (Cq_{ar}), 164.72 (d, $^2J_F = 25.3$ Hz, COO), 200.06 (d, $^2J_F = 28.1$ Hz, CO); IR (cm^{-1}): 2986, 1753, 1734, 1447, 1305, 1266, 1144, 1086; $[\alpha]_D^{20} = -33$ (c 1.1, CH_2Cl_2). Anal. Calcd for $C_{14}H_{17}FO_5S$: C, 53.15; H, 5.42. Found: C, 53.24; H, 5.58; HPLC (hexane/*i*-PrOH 96/4, 1.5 mL/min, $\lambda = 217$ nm): $t_R = 28.7$ min (for the *S* enantiomer, $t_R = 35.6$ min).

4.3.3. Ethyl (*R*)-2-acetyl-4-benzyloxycarbonyl-2-fluoro-butanoate 2c. Yellowish oil (73% yield); ee = 75%; R_f: 0.45 (cyclohexane/EtOAc 8:2); ^{1}H NMR ($CDCl_3$) δ: 1.29 (t, $^3J = 7.1$ Hz, 3H, $COOCH_2CH_3$), 2.30 (d, $^4J_F = 4.6$ Hz, 3H, CH_3CO), 2.30–2.40 (m, 4H, $CqCH_2CH_2CO_2$), 4.26 (q, $^3J = 7.1$ Hz, 2H, $COOCH_2CH_3$), 5.12 (s, 2H, $COOCH_2Ph$), 7.35 (m, 5H, H_{ar}); ^{19}F NMR ($CDCl_3$) δ: −165.30; ^{13}C NMR ($CDCl_3$) δ: 13.61 ($COOCH_2CH_3$), 25.09 (CH_3CO), 27.55 (d, $^3J_F = 3.8$ Hz, CH_2COOBn), 28.37 (d, $^2J_F = 20.9$ Hz, CH_2Cq), 62.42 ($COOCH_2CH_3$), 66.22 ($COOCH_2Ph$), 98.79 (d, $^1J_F = 197$ Hz, CqF), 127.93 + 128.23 (CH_{ar}), 135.50 (Cq_{ar}), 165.41 (d, $^2J_F = 25.5$ Hz, $COOEt$), 171.32 ($COOBn$), 200.81 (d, $^2J_F = 28.3$ Hz, CO); IR (cm^{-1}): 2984, 1732, 1168, 1015; $[\alpha]_D^{20} = -30$ (c 1.3, CH_2Cl_2). Anal. Calcd for $C_{16}H_{19}FO_5$: C, 61.93; H, 6.17. Found: C, 61.99; H, 6.24.

4.3.4. Ethyl (*R*)-2-acetyl-4-cyano-2-fluoro-butanoate 2d. Yellowish oil (35% yield); ee = 74%; R_f: 0.30 (cyclohexane/EtOAc 7:3); ^{1}H NMR ($CDCl_3$) δ: 1.30 (t, $^3J = 7.1$ Hz, 3H, $COOCH_2CH_3$), 2.32 (d, $^4J_F = 4.6$ Hz, 3H, CH_3CO), 2.30–2.40 (m, 4H, $CqCH_2CH_2CO_2$), 4.26 (q, $^3J = 7.1$ Hz, 2H, $COOCH_2CH_3$); ^{19}F NMR ($CDCl_3$) δ: −166.17; ^{13}C NMR ($CDCl_3$) δ: 11.38 (d, $^3J_F = 5.5$ Hz, CH_2CN), 13.82 ($COOCH_2CH_3$), 25.30 (CH_3CO), 29.06 (d, $^2J_F = 20.9$ Hz, CH_2Cq), 63.23 ($COOCH_2CH_3$), 98.03 (d, $^1J_F = 198$ Hz, CqF), 117.88 (CN), 164.89 (d, $^2J_F = 24.5$ Hz, $COOEt$), 200.38 (d, $^2J_F = 27.9$ Hz, CO); IR (cm^{-1}): 2985, 2252, 1752, 1713, 1361, 1265, 1147, 1092, 1015; $[\alpha]_D^{20} = -60$ (c 1.1, CH_2Cl_2). Anal. Calcd for $C_9H_{12}FNO_3$: C, 53.73; H, 6.01; N, 6.96. Found: C, 53.95; H, 6.17; N, 6.94.

4.4. Pinner reaction of compound 2d into compound 2c

Anhydrous HCl(g) was bubbled into benzyl alcohol maintained in an ice bath over a period of 5 min to saturation. Compound **2d** (140 mg, 0.7 mmol, 1 equiv) was diluted into 0.5 mL of this solution under inert atmosphere and the flask was capped with a septum and kept at −20 °C for 70 h. The mixture was then diluted at 0 °C with 0.5 mL of HCl 6 M. After stirring for 20 min at 0 °C, the mixture was diluted with 2 mL of water, extracted with 3 × 5 mL of DCM. The organic layers were combined, washed with 10 mL of brine, dried over Na_2SO_4, filtered and then concentrated and the residue purified by column chromatography (cyclohexane/EtOAc 100:0 to 90:10) to yield compound **2c** (80 mg, 37% yield).

4.5. Crystal data of compound 2b

White crystal of 0.20 × 0.23 × 0.30 mm. $C_{14}H_{17}F_1O_5S_1$, $M = 316.35$: monoclinic, space group $P21$, $Z = 2$, $a = 11.140(2)$, $b = 6.033(2)$, $c = 11.884(2)$ Å, $\alpha = \gamma = 90°$ $\beta = 91.73(2)°$, $V = 798.3(3)$ Å^3, $d = 1.316$ g cm^{-3}, $F(000) = 332$, $\lambda = 0.710693$ Å (Mo Kα), $\mu = 0.230$ mm^{-1}; 4427 reflections measured ($-15 \leqslant h \leqslant 15$, $-8 \leqslant k \leqslant 0$, $0 \leqslant l \leqslant 16$) on a Nonius CAD4 diffractometer. The structure was solved with SIR97 and refined with CRYSTALS. Hydrogen atoms riding. Refinement converged to $R(gt) = 0.0622$ for the 1386 reflections having $I \geqslant 2\sigma(I)$, and $wR(gt) = 0.0726$, goodness-of-fit $S = 1.1078$, Residual electron density: −0.25 and 0.46 e Å^3. Crystallographical data is being deposited with Cambridge Crystallographic Data Centre (CCDC 636340).

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