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FICA, a new chiral derivatizing agent for determining the absolute configuration of secondary alcohols by ^{19}F and ^{1}H NMR spectroscopies

Tamiko Takahashi [a,b,*], Hiroaki Kameda [b], Tomoyo Kamei [a], Jyunichi Koyanagi [a], Fabio Pichierri [c], Kenji Omata [d], Miyuki Ishizaki [a], Hiroshi Nakamura [a]

[a] *Faculty of Pharmaceutical Sciences, Josai International University, 1 Gumyo, Togane, Chiba 283-8555, Japan*
[b] *Division of Chemistry, Toyama Medical and Pharmaceutical University, 2630 Sugitani, Toyama 930-0194, Japan*
[c] *Department of Applied Chemistry, Graduate School of Engineering, Tohoku University, Aoba-yama 6-6-07, Sendai 980-8579, Japan*
[d] *Department of Chemistry, Graduate School of Science, Tohoku University, 6-3 Aoba, Aramaki, Aoba-ku, Sendai 980-8578, Japan*

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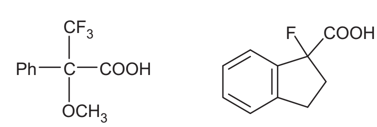
ABSTRACT

Optically active 1-fluoroindan-1-carboxylic acid (FICA) was designed and prepared as its methyl ester for determining the absolute configuration of chiral molecules by both ^{1}H and ^{19}F NMR spectroscopies. Enantiomerically pure isomers of FICA methyl esters (FICA Me esters) were obtained by chromatographic separation using HPLC with a Daicel Chiralcel OJ-H column. The absolute configuration of the (+)-FICA Me ester was deduced to be (*S*) by X-ray crystallographic analysis of the (+)-FICA amide of (*R*)-α-phenethylamine. Both enantiomers were derived to the diastereomeric esters of chiral secondary alcohols by an ester exchange reaction. In the ^{1}H NMR spectra, the signs of $\Delta\delta_H$ ($\delta_R - \delta_S$) were consistent on each side of the FICA molecular plane. Therefore, the concept of the modified Mosher's method could be successfully applied to the FICA-based procedure. Moreover, the consistency in the signs of $\Delta\delta_F$ ($\delta_R - \delta_S$) values suggests that the FICA method would be reliable in assigning the absolute configurations of secondary alcohols based on ^{19}F NMR spectroscopy.

1. Introduction

Techniques for assigning the absolute configuration of chiral molecules have progressed considerably with the development of asymmetric synthesis. Among the available methods that require both reliability and simplicity, ^{1}H NMR-based methods employing a chiral derivatizing agent (CDA) represented by the modified Mosher's method have been widespread because of the simple NMR operations, the small amount of analyzed sample, and their applicability to different types of samples.[1] Among the many CDAs, α-methoxy-α-(trifluoromethyl) phenylacetic acid (MTPA) **1**[2] (Fig. 1) is one of the most widely available agents. However, the ^{1}H NMR spectra of the corresponding diastereomers indicate poor resolution, which was attributed to the presence of three dominant conformers.[3] Moreover, the ^{19}F chemical shifts cannot be generally used for configuration assignments because of inconsistencies in the signs of $\Delta\delta_F$.[2]

In order to develop a CDA that surpasses the capabilities of MTPA, we designed a fluorine-containing CDA, 1-fluoroindan-1-carboxylic acid (FICA) **2** (Fig. 1). This was expected to give larger $\Delta\delta$ values due to the predominance of one NMR-significant conformer, characterized by the fixed orientation of the aromatic ring and restriction of rotation about the C_α–CO bond. We previously reported on the synthesis of racemic FICA methyl esters and suggested that FICA surpasses MTPA as a CDA in all ^{19}F NMR analyses examined with nine alcohols.[4] In particular, the magnitude of $\Delta\delta_F$ values of FICA esters was larger than that of the corresponding MTPA esters. Furthermore, it is noteworthy that the concept of the modified Mosher's method was successfully applied to a (*R*)-(−)-8-phenylmethyl ester in the ^{1}H NMR analyses. Due to the potential interest in using FICA as a CDA, we extended our investigation. Herein we report on the preparation of the FICA methyl ester in enantiomerically pure form and the estimation of its ability as a CDA for the determination of the



1 2

Figure 1. Chemical structures of **1** and **2**.

* Corresponding author. Tel.: +81 475 53 4596; fax: +81 475 53 4556.
E-mail address: tamikot@jiu.ac.jp (T. Takahashi).

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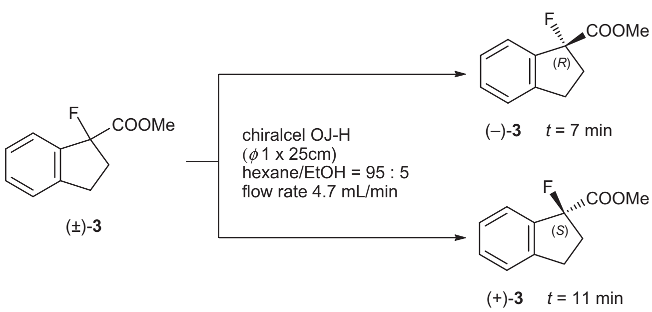
absolute configuration of secondary alcohols by both ^{1}H and ^{19}F NMR spectroscopies.

2. Results and discussion

2.1. Resolution of (±)-FICA methyl ester (±)-3

The (±)-FICA methyl ester (±)-**3** was synthesized according to the reported procedure.[4] The resolution of racemic ester (±)-**3** was performed by HPLC using a Daicel Chiralcel OJ-H column (ϕ 1 × 25 cm, Daicel Co., Japan) (eluent: *n*-hexane/EtOH = 95:5, flow rate: 4.7 mL/min, temp: 25 °C). The first eluted fraction with a retention time of 7 min gave the (−)-FICA methyl ester (−)-**3**, while the second with a retention time of 11 min gave the (+)-isomer (+)-**3** both of which are shown in Scheme 1.



Scheme 1.

2.2. Determination of the absolute configuration of (+) and (−)-FICA methyl ester

The absolute configuration of (+)-FICA methyl ester (+)-**3** was determined to be (*S*) by single-crystal X-ray crystallographic analysis of (*R*)-α-phenethylamide **4** prepared from (+)-FICA methyl ester (+)-**3**.[5] The unit cell of the crystal contains two crystallographically independent molecules, one of which is shown in Figure 2. Therefore, on the basis of this result, the (−)-FICA methyl ester (−)-**3** was confirmed to have an (*R*)-configuration.

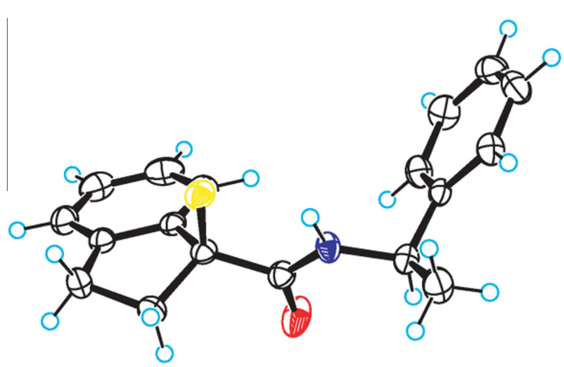
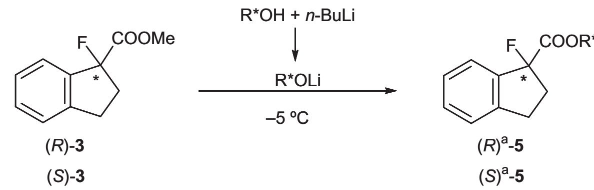


Figure 2. ORTEP drawing for the (+)-FICA amide of (*R*)-α-phenethylamine **4**.

2.3. $\Delta\delta_H$ values for the FICA and MTPA esters of chiral secondary alcohols

The obtained enantiomers (*R*)-**3** and (*S*)-**3** were transformed into their respective diastereomeric esters via an ester exchange reaction[4] where commercially available chiral secondary alcohols with known configurations **5a–m** were employed (Scheme 2).



Scheme 2. [a](*R*) or (*S*) shows the absolute configuration of **3**.

According to the modified Mosher's method, the chemical shift differences between the corresponding protons in the two diastereomers, $\Delta\delta_H$ ($\delta_R - \delta_S$) for the FICA esters and $\Delta\delta_H$ ($\delta_S - \delta_R$) for the MTPA esters,[6] are shown in Fig. 3 and Fig. 4, respectively.

For all of FICA esters examined here, similar magnitudes of $\Delta\delta_H$ values and the systematic distributions for the signs of $\Delta\delta_H$ values to those of the corresponding MTPA esters were obtained. However, in the case of isomenthol **5m**, the FICA ester showed a systematic distribution of the signs of $\Delta\delta_H$ values while the MTPA ester did not. This result indicates that the concept of the modified

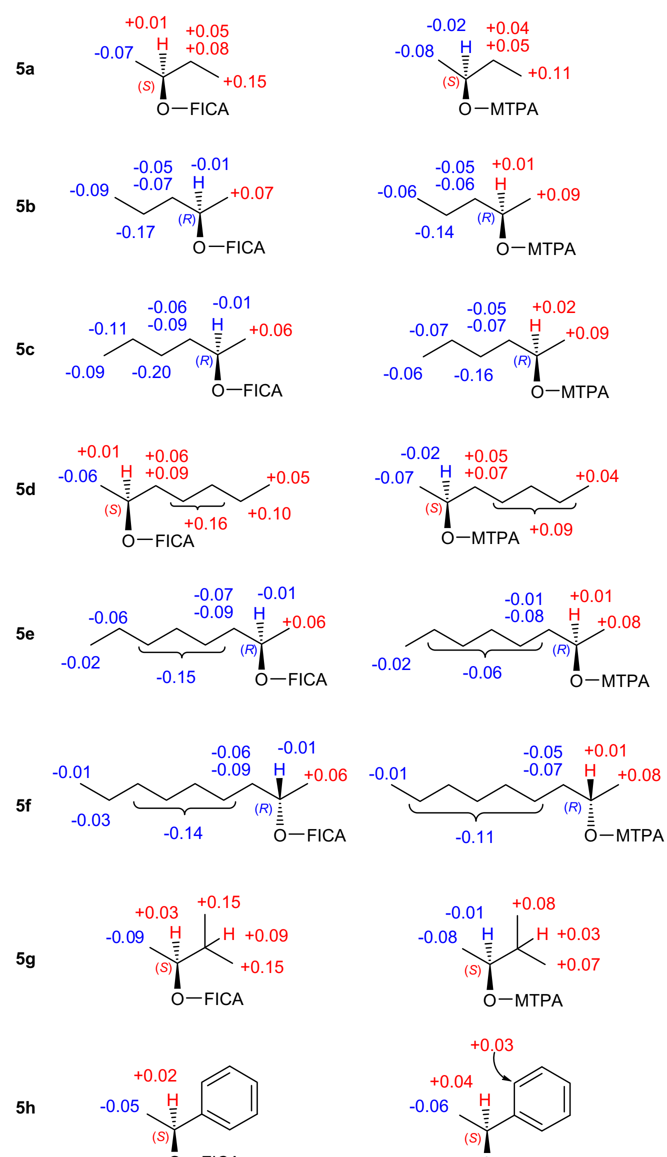


Figure 3. $\Delta\delta_H$ values of the FICA and MTPA[1f] esters of chain alcohols.

5i

5j

5k

5l

5m

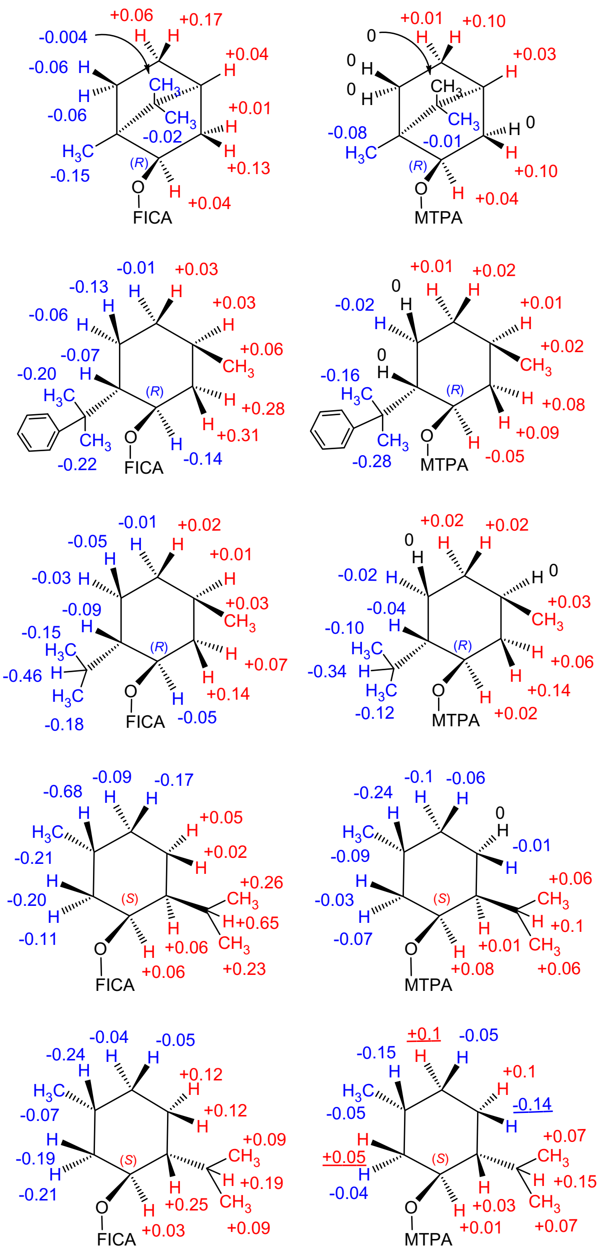


Figure 4. $\Delta\delta_H$ values of the FICA and MTPA[1f] esters of cyclic alcohols.

Mosher's method could be successfully applied to the FICA-based procedure. While FICA and MTPA showed similar performances for acyclic alcohols (Fig. 3), FICA was superior to MTPA when applied to cyclic alcohols (Fig. 4).

2.4. $\Delta\delta_F$ values for the FICA and MTPA esters of chiral secondary alcohols

In order to elucidate the applicability of the FICA-based procedure by ^{19}F NMR, we examined the chemical shift differences $\Delta\delta_F$ between the diastereomers. Table 1 reports the consistent relationship between the signs of $\Delta\delta_F$ values and the absolute configuration for the FICA esters of the chiral secondary alcohols. In other words, the signs of the (*S*)-alcohols were all positive and those of (*R*)-alcohols were all negative. However, such a correlation does not appear among the MTPA esters. Furthermore, the magnitude of the $\Delta\delta_F$ values of the FICA esters was much larger than that of the MTPA esters. Independent of the size of alcohols, the magnitude of the $\Delta\delta_F$ values of the FICA esters was relatively constant. Accordingly, the FICA-based procedure based on ^{19}F NMR spectroscopy was reliable in assigning the absolute configurations of the secondary alcohols.

2.5. DFT calculations on a model of FICA methyl ester

In order to explain the assignment of the absolute configurations, we performed density functional theory (DFT) calculations on the simple FICA methyl ester molecule (Fig. 5). Two molecular models arise upon rotation about the C_α–CO bond: *synperiplanar* (*sp*), with the C–F and C=O bonds oriented in the same direction, and *antiperiplanar* (*ap*), with these same bonds oriented in opposing directions. The geometry optimizations performed at the B3LYP/6-31G(d,p) level of theory[7,8] predicted that the *ap* rotamer is more stable than the *sp* rotamer by 0.67 kcal/mol while the dihedral angle ∠(F–C–C–O) is +18° for the *sp* rotamer and −149° for the *ap* rotamer. The *sp* rotamer displays a folded form and the *ap* rotamer an extended one. In the *sp* rotamer, the aromatic ring is favorably positioned so as to exert a shielding effect on the protons of both the R^1 and R^2 groups of the alcohol, whereas this does not occur in the *ap* rotamer. Therefore, the ^{1}H NMR significant conformer is likely to be mainly the *sp* one. Although the orientation of the aromatic ring was fixed, the comparatively small $\Delta\delta_H$ values were due to the smaller population of the *sp* rotamer.

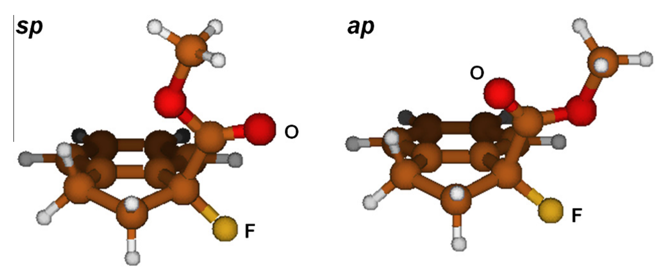


Figure 5. DFT calculations on FICA model (R = Me).

Furthermore, we calculated the differences in ^{19}F chemical shifts differences (δ_F) between the *sp* and the *ap* rotamers at the GIAO-B3LYP/6-31+G(2d,p) level of theory.[9] For the *ap* rotamer we obtained δ_F = −162.1 ppm while for the *sp* one we calculated δ_F = -−157.5 ppm which corresponds to $\Delta\delta_F$ (*syn–anti*) = 5 ppm. The DFT results nicely explain the ^{19}F chemical shift differences experimentally observed (see Table 1).

3. Conclusions

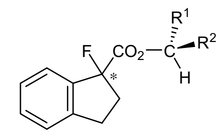
The FICA-based method is reliable in assigning the absolute configurations of secondary alcohols based on both ^{1}H and ^{19}F NMR spectroscopies. The *ap* rotamer was found to be energetically more stable than the *sp* rotamer. However, due to the shielding of the protons by the aromatic moiety of FICA, the NMR-significant conformer is mainly the *sp* one. Despite the fixed orientation of the aromatic ring, the comparatively small $\Delta\delta_H$ values are due to the small population of the *sp* rotamer. The non-equivalence in the measured ^{19}F NMR shifts could be rationalized by the bias associated with the existence of the *sp* and *ap* rotamers.

4. Experimental

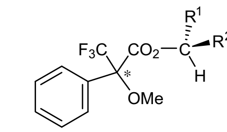
4.1. General

Melting points were measured with a Yanaco micro melting point apparatus and are uncorrected. Microanalyses were performed by

Table 1
$\Delta\delta_F$ values obtained for the FICA and MTPA esters



FICA esters



MTPA esters

	R^1	R^2	Absolute configuration	$\Delta\delta_F$ (ppm) = $\delta_R - \delta_S$	$\Delta\delta_F$ (ppm) = $\delta_S - \delta_R$[a]
5a	Me	Et	*S*	+0.23	−0.00
5b	Pr	Me	*R*	−0.33	−0.02
5c	C_4H_9	Me	*R*	−0.42	−0.06
5d	Me	C_5H_{11}	*S*	+0.32	+0.05
5e	C_6H_{13}	Me	*R*	−0.33	−0.05
5f	C_7H_{15}	Me	*R*	−0.33	−0.06
5g	Me	Pr^i	*S*	+0.56	−0.03
5h	Me	Ph	*S*	+0.52	−0.20
5i	Borneol		*R*	−0.04	+0.10
5j	8-Phenylmenthol		*R*	−0.36	−0.19
5k	Menthol		*R*	−1.02	−0.11
5l	Neomenthol		*S*	+0.13	−0.22
5m	Isomenthol		*S*	+0.24	−0.02

[a] Ref. 1f.

Microanalysis Center of Toyama Medical & Pharmaceutical University and Microanalysis Center of Josai University. Spectroscopic measurements were carried out with the following instruments: optical rotations, JASCO P1020 and JASCO DIP-1000 digital polarimeter; IR, Perkin–Elmer 1600 Series FT-IR, JASCO FT/IR-7300 and JASCO FT/IR-4200; mass (MS), JEOL JMS-700 and JEOL JMS-GCmate; high resolution mass spectra (HRMS), JEOL JMS-700 and JEOL JMS-AX505HAD; ^{1}H NMR, JEOL ECA 500 (500 MHz), Varian Unity 500 (500 MHz) and Varian Gemini 300 (300 MHz) for solutions in $CDCl_3$ with Me_4Si as an internal standard; ^{13}C NMR, JEOL ECA 500 (125.8 MHz) and Varian Gemini 300 (75.46 MHz) for solutions in $CDCl_3$ with $CDCl_3$ as an internal standard (77.2 ppm); ^{19}F NMR, JEOL ECA 500 (470.6 MHz), and JEOL JNM-GX 270 (254 MHz) for solutions in $CDCl_3$ with $CFCl_3$ as an internal standard. Column chromatography, flash column chromatography, and preparative TLC (PLC) were performed on Kieselgel 60 (Merck Art. 7734, Art. 9385, and 7748, respectively). Quantum chemical calculations were performed with Gaussian 03[7] on a Linux-based workstation at Tohoku University.

4.2. Chromatographic separation of (±)-1-fluoroindan-1-carboxylic acid methyl ester (FICA Me ester) (+)-3 and (−)-3

Chromatographic separation of (±)-**3**[4] (804 mg, 4.14 mmol) was carried out by HPLC with a Daicel Chiralcel OJ-H column (ϕ 1.0 × 25 cm, Daicel Co., Japan) (eluent: *n*-hexane/EtOH = 95:5, flow rate 4.7 mL/min, temp: 25 °C). The first fraction to be eluted (retention time t_1 = 7 min) was a colorless oil of (−)-1-fluoroindan-1-carboxylic acid methyl ester (353 mg, 1.82 mmol, 44%, ee >99% by HPLC); $[\alpha]_D^{26} = -39.1$ (*c* 1.58, $CHCl_3$); IR (neat) 2955 (CH), 1756 (C═O) cm^{-1}; ^{1}H NMR (300 MHz) δ 2.49 (dddd, 1H, *J* = 5.0, 8.5, 14.3, 23.4 Hz, 2-H), 2.84 (dddd, 1H, *J* = 5.7, 8.5, 14.3, 20.0 Hz, 2-H), 3.03–3.12 (m, 1H, 3-H), 3.13–3.23 (m, 1H, 3-H), 3.81 (s, 3H, OCH_3), 7.24–7.42 (m, 4H, 4–7-H); ^{13}C NMR (75.46 MHz) δ 30.4 (s, CH_2, 3-C), 36.5 (d, *J* = 23.2 Hz, CH_2, 2-C), 53.0 (s, CH_3, OCH_3), 102.3 (d, *J* = 190.4 Hz, C, 1-C), 124.3 (s, CH, 7-C), 125.3 (s, CH, 4-C), 127.2 (d, *J* = 2.4 Hz, CH, 6-C), 130.6 (d, *J* = 2.4 Hz, CH, 5-C), 139.3 (d, *J* = 20.7 Hz, C, 7a-C), 145.0 (d, *J* = 4.8 Hz, C, 3a-C), 171.1 (d, *J* = 33.0 Hz, C, COO); ^{19}F NMR (254 MHz) δ −139.02 (t, *J* = 22.2 Hz); MS *m*/*z*: 194 (M^+), 174 ($[M-HF]^+$), 135 ($[M-COOMe]^+$), 115 (indenyl cation); HRMS calcd for $C_{11}H_{11}O_2F$ (M^+): 194.0743, found: 194.0736; HPLC (DAICEL CHIRALCEL OJ-H, ϕ 0.46 × 25 cm, Daicel Co., Japan; *n*-hexane/EtOH = 95/5, 1.0 mL/min, 254 nm), t_1 = 9.83 min, k'_1 = 2.23, α = 1.80, *Rs* = 1.45.

The second fraction to be eluted (retention time t_2 = 11 min) was a colorless oil of (+)-1-fluoroindan-1-carboxylic acid methyl ester (348 mg, 1.79 mmol, 43%, ee >99% by HPLC); $[\alpha]_D^{27} = +38.9$ (*c* 1.56, $CHCl_3$); IR (neat) 2955 (CH), 1757 (C═O) cm^{-1}; ^{1}H NMR (300 MHz) δ 2.49 (dddd, 1H, *J* = 5.0, 8.5, 14.3, 23.4 Hz, 2-H), 2.84 (dddd, 1H, *J* = 5.7, 8.5, 14.3, 20.0 Hz, 2-H), 3.03–3.12 (m, 1H, 3-H), 3.13–3.23 (m, 1H, 3-H), 3.81 (s, 3H, OCH_3), 7.24–7.42 (m, 4H, 4–7-H); ^{13}C NMR (75.46 MHz) δ 30.4 (s, CH_2, 3-C), 36.5 (d, *J* = 23.2 Hz, CH_2, 2-C), 53.0 (s, CH_3, OCH_3), 102.3 (d, *J* = 190.4 Hz, C, 1-C), 124.3 (s, CH, 7-C), 125.3 (s, CH, 4-C), 127.2 (d, *J* = 2.4 Hz, CH, 6-C), 130.6 (d, *J* = 2.4 Hz, CH, 5-C), 139.3 (d, *J* = 20.7 Hz, C, 7a-C), 145.0 (d, *J* = 4.8 Hz, C, 3a-C), 171.1 (d, *J* = 33.0 Hz, C, COO); ^{19}F NMR (254 MHz) δ −139.02 (t, *J* = 22.2 Hz); MS *m*/*z*: 194 (M^+), 174 ($[M-HF]^+$), 135 ($[M-COOMe]^+$), 115 (indenyl cation); HRMS calcd for $C_{11}H_{11}O_2F$ (M^+): 194.0743, found: 194.0745; HPLC (DAICEL CHIRALCEL OJ-H, ϕ 0.46 × 25 cm, Daicel Co., Japan; *n*-hexane/EtOH = 95/5, 1.0 mL/min, 254 nm), t_2 = 15.27 min, k'_2 = 4.02, α = 1.80, R_s = 1.45.

4.3. *N*-(*R*)-1-Phenylethyl-(*S*)-1-fluoroindan-1-carboxamide 4

Colorless needles; mp 84 °C; $[\alpha]_D^{26} = +167.2$ (*c* 0.80, $CHCl_3$); IR (neat) 2928 (CH), 1661 (C═O) cm^{-1}; ^{1}H NMR (500 MHz) δ 1.59 (d, 3H, *J* = 7.5 Hz, CH_3), 2.44 (dddd, 1H, *J* = 3.4, 8.0, 14.3, 23.5 Hz, CH_2), 2.90 (dddd, 1H, *J* = 6.9, 8.6, 14.3, 27.5 Hz, CH_2), 3.09 (m, 1H, CH_2), 3.19 (m, 1H, CH_2), 5.24 (qd, 1H, *J* = 1.2, 6.9 Hz, CH), 7.30 (s, 1H, NH), 7.11–7.41 (m, 9H, Ph, Ph′-H); ^{13}C NMR (125.8 MHz) δ 21.7 (s, CH_3), 30.2 (s, CH_2), 36.0 (d, *J* = 24.0 Hz, CH_2), 48.7 (s, CH), 105.2 (d, *J* = 193.2 Hz, C), 123.7 (s, CH), 125.1 (s, CH), 126.1 (s, CH), 127.0 (s, CH), 127.5 (s, CH), 128.7 (s, CH), 130.4 (s, CH), 139.8 (d, *J* = 19.2 Hz, CH), 142.9 (s, CH), 145.6 (s, C), 170.0 (d, *J* = 26.4 Hz, CO); ^{19}F NMR (470.6 MHz) δ −136.54 (t, *J* = 25.2 Hz); MS *m*/*z*: 283 (M^+), 263 ($[M-HF]^+$), 135 ($[M-CONHR^*]^+$); HRMS calcd for $C_{18}H_{18}NOF$ (M^+): 283.1372, found: 283.1362; Anal. Calcd for $C_{18}H_{18}NOF$: C, 76.30; H, 6.40; N, 4.94. Found: C, 76.23; H, 6.42; N, 4.70.

X-ray crystallographic data: $C_{18}H_{18}NOF$, monoclinic, space group C121, *a* = 19.660 (10) Å, *b* = 8.206 (4) Å, *c* = 18.516 (9) Å, *V* = 2928

(2) $Å^3$, $Z = 8$, size = 0.25 × 0.20 × 0.15 mm, μ(MoKα) = 0.088 cm^{-1}, T = 173 K, total data = 21448, unique data = 6712 (R_{int} = 0.042), 416 parameters, R (5707 data with $I > 2.0\sigma(I)$) = 0.0349, wR (all reflections) = 0.0485, GOF = 0.973. The authors have deposited atomic coordinates for the amide with the Cambridge Crystallographic Data Centre, CCDC number 946714. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ (UK).

4.4. General procedure for the ester exchange reaction of 1-fluoroindan-1-carboxylic acid methyl ester with a secondary alcohol

To a solution of a secondary alcohol (0.177 mmol) in dry THF (0.5 mL) was added dropwise *n*-BuLi (1.59 mol/L in hexane, 0.1 mL, 0.159 mmol, at −5 °C) under a nitrogen atmosphere. After being stirred for 30 min, a solution of (*R*)-**3** or (*S*)-**3** (34.3 mg, 0.177 mmol) was added slowly to the mixture. After 15 min, the reaction was quenched with a saturated aqueous NH_4Cl solution (1 mL), and then water (5 mL) and Et_2O (10 mL) were added to the reaction mixture. The organic layer was separated, washed with 2% HCl (5 mL), water (5 mL), and a saturated aqueous $NaHCO_3$ solution (5 mL), and dried over $MgSO_4$. The solvent was evaporated and the residue was purified by column chromatography (hexane/AcOEt = 19:1) to give 1-fluoroindan-1-carboxylic acid ester with a secondary alcohol.

4.4.1. (*S*)-2-Butyl (*R*)-1-fluoroindan-1-carboxylate (*R*)-5a

84%; Colorless oil; $[\alpha]_D^{26} = -6.8$ (*c* 2.29, $CHCl_3$); IR (neat) 2975 (CH), 1751 (C=O) cm^{-1}; ^{1}H NMR (500 MHz) δ 0.92 (t, 3H, *J* = 7.3 Hz, 4′-H), 1.19 (d, 3H, *J* = 6.4 Hz, 1′-H), 1.58 (qdd, 1H, *J* = 7.3, 5.6, 15.0 Hz, 3′-H), 1.65 (qdd, 1H, *J* = 7.3, 6.8, 14.1 Hz, 3′-H), 2.48 (dddd, 1H, *J* = 5.1, 8.5, 14.1, 22.6 Hz, 2-H), 2.83 (dddd, 1H, *J* = 5.6, 8.5, 14.1, 19.7 Hz, 2-H), 3.07 (m, 1H, 3-H), 3.19 (m, 1H, 3-H), 4.98 (qdd, 1H, *J* = 6.4, 6.4, 6.4 Hz, 2′-H), 7.27 (t, 1H, *J* = 7.7 Hz, 6-H), 7.32 (d, 1H, *J* = 7.7 Hz, 4-H), 7.37 (t, 1H, *J* = 7.7 Hz, 5-H), 7.41 (d, 1H, *J* = 7.7 Hz, 7-H); ^{13}C NMR (75.46 MHz) δ 10.1 (s, CH_3, 4′-C), 19.5 (s, CH_3, 1′-C), 28.9 (s, CH_2, 3′-C), 30.4 (s, CH_2, 3-C), 36.5 (d, *J* = 24.4 Hz, CH_2, 2-C), 74.3 (s, CH, 2′-C), 102.1 (d, *J* = 190.4 Hz, C, 1-C), 124.1 (s, CH, 7-C), 125.2 (s, CH, 4-C), 127.1 (d, *J* = 2.4 Hz, CH, 6-C), 130.4 (d, *J* = 3.7 Hz, CH, 5-C), 139.6 (d, *J* = 20.8 Hz, C, 7a-C), 145.0 (d, *J* = 4.9 Hz, C, 3a-C), 170.3 (d, *J* = 31.7 Hz, C, *C*OO); ^{19}F NMR (254 MHz) δ −139.18 (t, *J* = 23.1 Hz); MS *m*/*z*: 236 (M^+), 216 ($[M-HF]^+$), 135 ($[M-COOR^*]^+$), 115 (indenyl cation); HRMS calcd for $C_{14}H_{17}O_2F$ (M^+): 236.1212, found: 236.1167.

4.4.2. (*S*)-2-Butyl (*S*)-1-fluoroindan-1-carboxylate (*S*)-5a

68%; Colorless oil; $[\alpha]_D^{27} = +35.6$ (*c* 1.80, $CHCl_3$); IR (neat) 2975 (CH), 1751 (C=O) cm^{-1}; ^{1}H NMR (500 MHz) δ 0.77 (t, 3H, *J* = 7.3 Hz, 4′-H), 1.26 (d, 3H, *J* = 6.4 Hz, 1′-H), 1.52 (qdd, 1H, *J* = 7.3, 5.6, 15.0 Hz, 3′-H), 1.57 (qdd, 1H, *J* = 7.3, 6.8, 14.1 Hz, 3′-H), 2.48 (dddd, 1H, *J* = 5.1, 8.5, 14.1, 23.1 Hz, 2-H), 2.82 (dddd, 1H, *J* = 5.6, 8.5, 14.1, 19.7 Hz, 2-H), 3.07 (m, 1H, 3-H), 3.19 (m, 1H, 3-H), 4.97 (qdd, 1H, *J* = 6.4, 6.0, 6.4 Hz, 2′-H), 7.26 (t, 1H, *J* = 7.7 Hz, 6-H), 7.31 (d, 1H, *J* = 7.7 Hz, 4-H), 7.37 (tt, 1H, *J* = 1.3, 7.7 Hz, 5-H), 7.42 (d, 1H, *J* = 7.7 Hz, 7-H); ^{13}C NMR (75.46 MHz) δ 9.8 (s, CH_3, 4′-C), 19.7 (s, CH_3, 1′-C), 28.9 (s, CH_2, 3′-C), 30.5 (s, CH_2, 3-C), 36.4 (d, *J* = 23.2 Hz, CH_2, 2-C), 74.2 (s, CH, 2′-C), 102.1 (d, *J* = 189.2 Hz, C, 1-C), 124.2 (s, CH, 7-C), 125.2 (s, CH, 4-C), 127.1 (d, *J* = 2.4 Hz, CH, 6-C), 130.4 (d, *J* = 3.7 Hz, CH, 5-C), 139.7 (d, *J* = 20.8 Hz, C, 7a-C), 144.9 (d, *J* = 4.9 Hz, C, 3a-C), 170.3 (d, *J* = 33.0 Hz, C, *C*OO); ^{19}F NMR (254 MHz) δ −139.41 (t, *J* = 23.1 Hz); MS *m*/*z*: 236 (M^+), 216 ($[M-HF]^+$), 135 ($[M-COOR^*]^+$), 115 (indenyl cation); HRMS calcd for $C_{14}H_{17}O_2F$ (M^+): 236.1212, found: 236.1241.

4.4.3. (*R*)-2-Pentyl (*R*)-1-fluoroindan-1-carboxylate (*R*)-5b

76%; Colorless oil; $[\alpha]_D^{27} = -36.2$ (*c* 2.21, $CHCl_3$); IR (neat) 2961 (CH), 1752 (C=O) cm^{-1}; ^{1}H NMR (500 MHz) δ 0.82 (t, 3H, *J* = 7.3 Hz, 5′-H), 1.19 (m, 2H, 4′-H), 1.26 (d, 3H, *J* = 6.4 Hz, 1′-H), 1.44 (dddd, 1H, *J* = 5.6, 6.4, 9.8, 13.7 Hz, 3′-H), 1.56 (dddd, 1H, *J* = 5.6, 8.1, 9.8, 13.7 Hz, 3′-H), 2.48 (dddd, 1H, *J* = 5.1, 8.5, 14.1, 22.6 Hz, 2-H), 2.82 (dddd, 1H, *J* = 5.6, 8.5, 14.1, 19.7 Hz, 2-H), 3.07 (m, 1H, 3-H), 3.19 (m, 1H, 3-H), 5.04 (qdd, 1H, *J* = 6.4, 5.1, 6.4 Hz, 2′-H), 7.26 (t, 1H, *J* = 7.7 Hz, 6-H), 7.31 (d, 1H, *J* = 7.3 Hz, 4-H), 7.37 (tt, 1H, *J* = 1.3, 7.7 Hz, 5-H), 7.42 (d, 1H, *J* = 8.1 Hz, 7-H); ^{13}C NMR (75.46 MHz) δ 14.0 (s, CH_3, 5′-C), 18.6 (s, CH_2, 4′-C), 20.2 (s, CH_3, 1′-C), 30.4 (s, CH_2, 3-C), 36.4 (d, *J* = 23.2 Hz, CH_2, 2-C), 38.0 (s, CH_2, 3′-C), 72.7 (s, CH, 2′-C), 102.0 (d, *J* = 199.0 Hz, C, 1-C), 124.1 (s, CH, 7-C), 125.1 (s, CH, 4-C), 127.1 (d, *J* = 2.4 Hz, CH, 6-C), 130.4 (d, *J* = 3.7 Hz, CH, 5-C), 139.6 (d, *J* = 19.5 Hz, C, 7a-C), 144.9 (d, *J* = 4.9 Hz, C, 3a-C), 170.3 (d, *J* = 33.0 Hz, C, *C*OO); ^{19}F NMR (254 MHz) δ −139.45 (t, *J* = 23.1 Hz); MS *m*/*z*: 250 (M^+), 230 ($[M-HF]^+$), 135 ($[M-COOR^*]^+$), 115 (indenyl cation); HRMS calcd for $C_{15}H_{19}O_2F$ (M^+): 250.1369, found: 250.1382.

4.4.4. (*R*)-2-Pentyl (*S*)-1-fluoroindan-1-carboxylate (*S*)-5b

71%; Colorless oil; $[\alpha]_D^{27} = +3.5$ (*c* 2.01, $CHCl_3$); IR (neat) 2961 (CH), 1751 (C=O) cm^{-1}; ^{1}H NMR (500 MHz) δ 0.92 (t, 3H, *J* = 7.3 Hz, 5′-H), 1.20 (d, 3H, *J* = 6.0 Hz, 1′-H), 1.35 (m, 2H, 4′-H), 1.49 (dddd, 1H, *J* = 5.6, 6.0, 9.4, 13.7 Hz, 3′-H), 1.63 (dddd, 1H, *J* = 5.6, 7.7, 9.8, 13.7 Hz, 3′-H), 2.48 (dddd, 1H, *J* = 4.7, 8.5, 14.1, 22.6 Hz, 2-H), 2.82 (dddd, 1H, *J* = 5.6, 8.5, 14.1, 20.1 Hz, 2-H), 3.07 (m, 1H, 3-H), 3.19 (m, 1H, 3-H), 5.05 (qdd, 1H, *J* = 6.0, 6.4, 6.8 Hz, 2′-H), 7.27 (t, 1H, *J* = 7.7 Hz, 6-H), 7.32 (d, 1H, *J* = 7.7 Hz, 4-H), 7.37 (tt, 1H, *J* = 1.3, 7.3 Hz, 5-H), 7.40 (d, 1H, *J* = 8.1 Hz, 7-H); ^{13}C NMR (75.46 MHz) δ 14.1 (s, CH_3, 5′-C), 19.0 (s, CH_2, 4′-C), 20.0 (s, CH_3, 1′-C), 30.5 (s, CH_2, 3-C), 36.5 (d, *J* = 23.2 Hz, CH_2, 2-C), 38.1 (s, CH_2, 3′-C), 72.9 (s, CH, 2′-C), 102.1 (d, *J* = 190.4 Hz, C, 1-C), 124.1 (s, CH, 7-C), 125.2 (s, CH, 4-C), 127.2 (d, *J* = 2.4 Hz, CH, 6-C), 130.4 (d, *J* = 3.7 Hz, CH, 5-C), 139.6 (d, *J* = 20.8 Hz, C, 7a-C), 145.0 (d, *J* = 4.9 Hz, C, 3a-C), 170.3 (d, *J* = 31.7 Hz, C, *C*OO); ^{19}F NMR (254 MHz) δ −139.11 (t, *J* = 22.2 Hz); MS *m*/*z*: 250 (M^+), 230 ($[M-HF]^+$), 135 ($[M-COOR^*]^+$), 115 (indenyl cation); HRMS calcd for $C_{15}H_{19}O_2F$ (M^+): 250.1369, found: 250.1352.

4.4.5. (*R*)-2-Hexyl (*R*)-1-fluoroindan-1-carboxylate (*R*)-5c

75%; Colorless oil; $[\alpha]_D^{28} = -38.0$ (*c* 2.31, $CHCl_3$); IR (neat) 2957 (CH), 1752 (C=O) cm^{-1}; ^{1}H NMR (500 MHz) δ 0.81 (t, 3H, *J* = 7.3 Hz, 6′-H), 1.11 (m, 2H, 4′-H), 1.20 (qt, 2H, *J* = 7.3, 6.8 Hz 5′-H), 1.26 (d, 3H, *J* = 6.0 Hz, 1′-H), 1.46 (dddd, 1H, *J* = 5.2, 6.8, 8.5, 15.4 Hz, 3′-H), 1.55 (dddd, 1H, *J* = 6.0, 7.7, 9.0, 13.7 Hz, 3′-H), 2.47 (dddd, 1H, *J* = 5.1, 8.5, 14.1, 23.1 Hz, 2-H), 2.82 (dddd, 1H, *J* = 5.1, 8.5, 14.1, 19.2 Hz, 2-H), 3.07 (m, 1H, 3-H), 3.19 (m, 1H, 3-H), 5.02 (qdd, 1H, *J* = 6.0, 6.4, 6.8 Hz, 2′-H), 7.26 (t, 1H, *J* = 7.7 Hz, 6-H), 7.31 (d, 1H, *J* = 7.7 Hz, 4-H) 7.37 (tt, 1H, *J* = 1.3, 7.7 Hz, 5-H), 7.41 (d, 1H, *J* = 7.7 Hz, 7-H); ^{13}C NMR (75.46 MHz) δ 14.2 (s, CH_3, 6′-C), 20.2 (s, CH_3, 1′-C), 22.6 (s, CH_2, 5′-C), 27.5 (s, CH_2, 4′-C), 30.5 (s, CH_2, 3-C), 35.6 (s, CH_2, 3′-C), 36.4 (d, *J* = 23.2 Hz, CH_2, 2-C), 73.0 (s, CH, 2′-C), 102.1 (d, *J* = 190.4 Hz, C, 1-C), 124.1 (s, CH, 7-C), 125.2 (s, CH, 4-C), 127.1 (d, *J* = 2.4 Hz, CH, 6-C), 130.4 (d, *J* = 2.4 Hz, CH, 5-C), 139.7 (d, *J* = 20.8 Hz, C, 7a-C), 144.9 (d, *J* = 4.9 Hz, C, 3a-C), 170.3 (d, *J* = 31.7 Hz, C, *C*OO); ^{19}F NMR (254 MHz) δ −139.62 (t, *J* = 23.1 Hz); MS *m*/*z*: 264 (M^+), 244 ($[M-HF]^+$), 135 ($[M-COOR^*]^+$), 115 (indenyl cation); HRMS calcd for $C_{16}H_{22}O_2F$ ($[M+H]^+$): 265.1604, found: 265.1622.

4.4.6. (*R*)-2-Hexyl (*S*)-1-fluoroindan-1-carboxylate (*S*)-5c

62%; Colorless oil; $[\alpha]_D^{27} = +2.9$ (*c* 1.84, $CHCl_3$); IR (neat) 2957 (CH), 1751 (C=O) cm^{-1}; ^{1}H NMR (500 MHz) δ 0.89 (t, 3H, *J* = 6.8 Hz, 6′-H), 1.19 (d, 3H, *J* = 6.4 Hz, 1′-H), 1.31 (m, 4H, 4′,5′-H), 1.52 (m, 1H, 3′-H), 1.64 (m, 1H, 3′-H), 2.48 (dddd, 1H, *J* = 5.1, 8.5, 14.1, 23.1 Hz, 2-H), 2.82 (dddd, 1H, *J* = 5.5, 8.5, 14.1, 20.1 Hz, 2-H), 3.07 (m, 1H, 3-H), 3.19 (m, 1H, 3-H), 5.03 (qdd, 1H, *J* = 6.0, 6.4, 6.8 Hz, 2′-H), 7.26 (t, 1H, *J* = 7.3 Hz, 6-H), 7.32 (d, 1H, *J* = 7.7 Hz, 4-H), 7.37 (tt, 1H, *J* = 1.3, 7.3 Hz, 5-H), 7.40 (d, 1H, *J* = 7.7 Hz, 7-H); ^{13}C NMR (75.46 MHz) δ 14.2 (s, CH_3, 6′-C), 20.2 (s, CH_3, 1′-C), 22.7 (s, CH_2, 5′-C), 27.8 (s, CH_2, 4′-C), 30.5 (s, CH_2, 3-C), 35.6 (s, CH_2, 3′-C), 36.5 (d, *J* = 23.2 Hz, CH_2, 2-C), 73.1 (s, CH, 2′-C), 102.1 (d, *J* = 190.4 Hz, C, 1-C), 124.2 (s, CH, 7-C), 125.2 (s, CH, 4-C), 127.1 (d, *J* = 2.4 Hz, CH, 6-C), 130.4 (d, *J* = 3.7 Hz, CH, 5-C), 139.6 (d, *J* = 20.8 Hz, C, 7a-C), 145.0 (d, *J* = 4.9 Hz, C, 3a-C), 170.3 (d, *J* = 33.0 Hz, C, COO); ^{19}F NMR (254 MHz) δ −139.20 (t, *J* = 23.1 Hz); MS *m*/*z*: 264 (M^+), 244 ($[M-HF]^+$), 135 ($[M-COOR^*]^+$), 115 (indenyl cation); HRMS calcd for $C_{16}H_{21}O_2F$ (M^+): 264.1526, found: 264.1492.

4.4.7. (*S*)-2-Heptyl (*R*)-1-fluoroindan-1-carboxylate (*R*)-5d

55%; Colorless oil; $[\alpha]_D^{26} = -2.4$ (*c* 1.80, $CHCl_3$); IR (neat) 2934 (CH), 1752 (C=O) cm^{-1}; ^{1}H NMR (500 MHz) δ 0.88 (t, 3H, *J* = 6.8 Hz, 7′-H), 1.20 (d, 3H, *J* = 6.4 Hz, 1′-H), 1.25–1.38 (m, 6H, 4′–6′-H), 1.52 (m, 1H, 3′-H), 1.63 (m, 1H, 3′-H), 2.48 (dddd, 1H, *J* = 5.1, 8.5, 14.1, 23.1 Hz, 2-H), 2.82 (dddd, 1H, *J* = 5.5, 8.5, 14.1, 19.7 Hz, 2-H), 3.07 (m, 1H, 3-H), 3.20 (m, 1H, 3-H), 5.03 (qdd, 1H, *J* = 6.4, 6.0, 7.3 Hz, 2′-H), 7.26 (t, 1H, *J* = 7.7 Hz, 6-H), 7.32 (d, 1H, *J* = 7.7 Hz, 4-H), 7.37 (t, 1H, *J* = 7.7 Hz, 5-H), 7.40 (d, 1H, *J* = 7.7 Hz, 7-H); ^{13}C NMR (75.46 MHz) δ 14.3 (s, CH_3, 7′-C), 20.2 (s, CH_3, 1′-C), 22.8 (s, CH_2, 6′-C), 25.3 (s, CH_2, 4′-C), 30.4 (s, CH_2, 3-C), 31.8 (s, CH_2, 5′-C), 35.9 (s, CH_2, 3′-C), 36.5 (d, *J* = 23.2 Hz, CH_2, 2-C), 73.1 (s, CH, 2′-C), 102.1 (d, *J* = 190.4 Hz, C, 1-C), 124.1 (s, CH, 7-C), 125.2 (s, CH, 4-C), 127.1 (d, *J* = 2.4 Hz, CH, 6-C), 130.4 (d, *J* = 3.7 Hz, CH, 5-C), 139.6 (d, *J* = 20.8 Hz, C, 7a-C), 145.0 (d, *J* = 4.9 Hz, C, 3a-C), 170.2 (d, *J* = 33.0 Hz, C, COO); ^{19}F NMR (254 MHz) δ −139.21 (t, *J* = 20.4 Hz); MS *m*/*z*: 278 (M^+), 258 ($[M-HF]^+$), 135 ($[M-COOR^*]^+$), 115 (indenyl cation); HRMS calcd for $C_{17}H_{23}O_2F$ (M^+): 278.1682, found: 278.1644.

4.4.8. (*S*)-2-Heptyl (*S*)-1-fluoroindan-1-carboxylate (*S*)-5d

56%; Colorless oil; $[\alpha]_D^{26} = +36.0$ (*c* 1.79, $CHCl_3$); IR (neat) 2934 (CH), 1751 (C=O) cm^{-1}; ^{1}H NMR (500 MHz) δ 0.82 (t, 3H, *J* = 6.8 Hz, 7′-H), 1.14 (m, 4H, 4′,5′-H), 1.20 (m, 2H, 6′-H), 1.26 (d, 3H, *J* = 6.0 Hz, 1′-H), 1.46 (m, 1H, 3′-H), 1.54 (m, 1H, 3′-H), 2.48 (dddd, 1H, *J* = 5.1, 8.5, 14.1, 22.6 Hz, 2-H), 2.82 (dddd, 1H, *J* = 5.1, 8.5, 14.1, 19.2 Hz, 2-H), 3.07 (m, 1H, 3-H), 3.19 (m, 1H, 3-H), 5.02 (qdd, 1H, *J* = 6.0, 6.0, 7.7 Hz, 2′-H), 7.26 (t, 1H, *J* = 7.7 Hz, 6-H), 7.31 (d, 1H, *J* = 7.7 Hz, 4-H), 7.37 (t, 1H, *J* = 7.3 Hz, 5-H), 7.41 (d, 1H, *J* = 7.7 Hz, 7-H); ^{13}C NMR (75.46 MHz) δ 14.2 (s, CH_3, 7′-C), 20.2 (s, CH_3, 1′-C), 22.7 (s, CH_2, 6′-C), 25.0 (s, CH_2, 4′-C), 30.5 (s, CH_2, 3-C), 31.7 (s, CH_2, 5′-C), 35.9 (s, CH_2, 3′-C), 36.4 (d, *J* = 23.2 Hz, CH_2, 2-C), 73.0 (s, CH, 2′-C), 102.1 (d, *J* = 190.4 Hz, C, 1-C), 124.1 (s, CH, 7-C), 125.2 (s, CH, 4-C), 127.1 (d, *J* = 2.4 Hz, CH, 6-C), 130.4 (d, *J* = 2.4 Hz, CH, 5-C), 139.7 (d, *J* = 20.8 Hz, C, 7a-C), 144.9 (d, *J* = 4.9 Hz, C, 3a-C), 170.3 (d, *J* = 33.0 Hz, C, COO); ^{19}F NMR (254 MHz) δ −139.54 (t, *J* = 23.1 Hz); MS *m*/*z*: 278 (M^+), 258 ($[M-HF]^+$), 135 ($[M-COOR^*]^+$); HRMS calcd for $C_{17}H_{24}O_2F$ ($[M+H]^+$): 279.1760, found: 279.1739.

4.4.9. (*R*)-2-Octyl (*R*)-1-fluoroindan-1-carboxylate (*R*)-5e

65%; Colorless oil; $[\alpha]_D^{27} = -36.5$ (*c* 2.23, $CHCl_3$); IR (neat) 2932 (CH), 1752 (C=O) cm^{-1}; ^{1}H NMR (500 MHz) δ 0.86 (t, 3H, *J* = 6.8 Hz, 8′-H), 1.08–1.20 (m, 6H, 4′ 6′-H), 1.23 (m, 2H, 7′-H), 1.26 (d, 3H, *J* = 6.4 Hz, 1′-H), 1.45 (dddd, 1H, *J* = 5.1, 6.4, 9.4, 13.7 Hz, 3′-H), 1.54 (dddd, 1H, *J* = 5.5, 7.7, 9.0, 13.2 Hz, 3′-H), 2.47 (dddd, 1H, *J* = 5.1, 8.5, 14.1, 23.1 Hz, 2-H), 2.82 (dddd, 1H, *J* = 5.1, 8.5, 14.1, 19.2 Hz, 2-H), 3.07 (m, 1H, 3-H), 3.19 (m, 1H, 3-H), 5.02 (qdd, 1H, *J* = 6.4, 5.1, 7.7 Hz, 2′-H), 7.26 (t, 1H, *J* = 7.7 Hz, 6-H), 7.31 (d, 1H, *J* = 7.7 Hz, 4-H), 7.37 (tt, 1H, *J* = 1.3, 7.6 Hz, 5-H), 7.41 (d, 1H, *J* = 7.7 Hz, 7-H); ^{13}C NMR (75.46 MHz) δ 14.4 (s, CH_3, 8′-C), 20.2 (s, CH_3, 1′-C), 22.8 (s, CH_2, 7′-C), 25.3 (s, CH_2, 4′-C), 29.1 (s, CH_2, 5′-C), 30.5 (s, CH_2, 3-C), 31.9 (s, CH_2, 6′-C), 35.9 (s, CH_2, 3′-C), 36.4 (d, *J* = 23.2 Hz, CH_2, 2-C), 73.0 (s, CH, 2′-C), 102.1 (d, *J* = 190.4 Hz, C, 1-C), 124.1 (s, CH, 7-C), 125.2 (s, CH, 4-C), 127.1 (d, *J* = 2.4 Hz, CH, 6-C), 130.4 (d, *J* = 3.6 Hz, CH, 5-C), 139.7 (d, *J* = 22.0 Hz, C, 7a-C), 144.9 (d, *J* = 4.9 Hz, C, 3a-C), 170.3 (d, *J* = 31.7 Hz, C, COO); ^{19}F NMR (254 MHz) δ −139.54 (t, *J* = 23.1 Hz); MS *m*/*z*: 292 (M^+), 272 ($[M-HF]^+$), 135 ($[M-COOR^*]^+$), 115 (indenyl cation); HRMS calcd for $C_{18}H_{25}O_2F$ (M^+): 292.1839, found: 292.1844.

4.4.10. (*R*)-2-Octyl (*S*)-1-fluoroindan-1-carboxylate (*S*)-5e

59%; Colorless oil; $[\alpha]_D^{27} = +1.9$ (*c* 1.98, $CHCl_3$); IR (neat) 2932 (CH), 1752 (C=O) cm^{-1}; ^{1}H NMR (500 MHz) δ 0.88 (t, 3H, *J* = 6.8 Hz, 8′-H), 1.20 (d, 3H, *J* = 6.4 Hz, 1′-H), 1.22–1.36 (m, 8H, 4′–7′-H), 1.52 (m, 1H, 3′-H), 1.63 (m, 1H, 3′-H), 2.48 (dddd, 1H, *J* = 4.7, 8.5, 14.1, 23.1 Hz, 2-H), 2.82 (dddd, 1H, *J* = 5.6, 8.5, 14.1, 20.1 Hz, 2-H), 3.07 (m, 1H, 3-H), 3.19 (m, 1H, 3-H), 5.03 (qdd, 1H, *J* = 6.4, 6.0, 7.3 Hz, 2′-H), 7.26 (t, 1H, *J* = 7.7 Hz, 6-H), 7.32 (d, 1H, *J* = 7.7 Hz, 4-H), 7.37 (tt, 1H, *J* = 1.3, 7.6 Hz, 5-H), 7.40 (d, 1H, *J* = 7.7 Hz, 7-H); ^{13}C NMR (75.46 MHz) δ 14.4 (s, CH_3, 8′-C), 20.2 (s, CH_3, 1′-C), 22.8 (s, CH_2, 7′-C), 25.6 (s, CH_2, 4′-C), 29.3 (s, CH_2, 5′-C), 30.5 (s, CH_2, 3-C), 32.0 (s, CH_2, 6′-C), 36.0 (s, CH_2, 3′-C), 36.5 (d, *J* = 23.2 Hz, CH_2, 2-C), 73.1 (s, CH, 2′-C), 102.1 (d, *J* = 190.4 Hz, C, 1-C), 124.1 (s, CH, 7-C), 125.2 (s, CH, 4-C), 127.1 (d, *J* = 2.4 Hz, CH, 6-C), 130.4 (d, *J* = 3.6 Hz, CH, 5-C), 139.6 (d, *J* = 20.8 Hz, C, 7a-C), 145.0 (d, *J* = 4.9 Hz, C, 3a-C), 170.3 (d, *J* = 33.0 Hz, C, COO); ^{19}F NMR (254 MHz) δ −139.21 (t, *J* = 23.1 Hz); MS *m*/*z*: 292 (M^+), 272 ($[M-HF]^+$), 135 ($[M-COOR^*]^+$); HRMS calcd for $C_{18}H_{25}O_2F$ (M^+): 292.1838, found: 292.1845.

4.4.11. (*R*)-2-Nonyl (*R*)-1-fluoroindan-1-carboxylate (*R*)-5f

57%; Colorless oil; $[\alpha]_D^{27} = -34.4$ (*c* 2.06, $CHCl_3$); IR (neat) 2930 (CH), 1752 (C=O) cm^{-1}; ^{1}H NMR (500 MHz) δ 0.87 (t, 3H, *J* = 7.2 Hz, 9′-H), 1.08–1.22 (m, 8H, 4′–7′-H), 1.26 (m, 2H, 8′-H), 1.26 (d, 3H, *J* = 6.4 Hz, 1′-H), 1.45 (m, 1H, 3′-H), 1.54 (m, 1H, 3′-H), 2.48 (dddd, 1H, *J* = 5.1, 8.5, 14.1, 23.1 Hz, 2-H), 2.82 (dddd, 1H, *J* = 5.1, 8.5, 14.1, 19.2 Hz, 2-H), 3.07 (m, 1H, 3-H), 3.19 (m, 1H, 3-H), 5.02 (qdd, 1H, *J* = 6.0, 6.0, 6.4 Hz, 2′-H), 7.26 (t, 1H, *J* = 7.5 Hz, 6-H), 7.31 (d, 1H, *J* = 7.7 Hz, 4-H), 7.37 (t, 1H, *J* = 7.6 Hz, 5-H), 7.41 (d, 1H, *J* = 7.7 Hz, 7-H); ^{13}C NMR (75.46 MHz) δ 14.4 (s, CH_3, 9′-C), 20.2 (s, CH_3, 1′-C), 22.9 (s, CH_2, 8′-C), 25.3 (s, CH_2, 4′-C), 29.4 (s, CH_2, 6′-C), 29.4 (s, CH_2, 5′-C), 30.5 (s, CH_2, 3-C), 31.9 (s, CH_2, 7′-C), 35.9 (s, CH_2, 3′-C), 36.4 (d, *J* = 23.2 Hz, CH_2, 2-C), 73.0 (s, CH, 2′-C), 102.1 (d, *J* = 191.7 Hz, C, 1-C), 124.2 (s, CH, 7-C), 125.2 (s, CH, 4-C), 127.1 (d, *J* = 2.4 Hz, CH, 6-C), 130.4 (d, *J* = 2.4 Hz, CH, 5-C), 139.7 (d, *J* = 20.8 Hz, C, 7a-C), 144.9 (d, *J* = 4.9 Hz, C, 3a-C), 170.3 (d, *J* = 31.7 Hz, C, COO); ^{19}F NMR (254 MHz) δ −139.54 (t, *J* = 23.1 Hz); MS *m*/*z*: 306 (M^+), 286 ($[M-HF]^+$), 135 ($[M-COOR^*]^+$), 115 (indenyl cation); HRMS calcd for $C_{19}H_{27}O_2F$ (M^+): 306.1995, found: 306.2004.

4.4.12. (*R*)-2-Nonyl (*S*)-1-fluoroindan-1-carboxylate (*S*)-5f

73%; Colorless oil; $[\alpha]_D^{27} = +1.7$ (*c* 2.56, $CHCl_3$); IR (neat) 2930 (CH), 1752 (C=O) cm^{-1}; ^{1}H NMR (500 MHz) δ 0.88 (t, 3H, *J* = 7.3 Hz, 9′-H), 1.20 (d, 3H, *J* = 6.4 Hz, 1′-H), 1.21–1.37 (m, 8H, 4′–7′-H), 1.24–1.34 (m, 2H, 8′-H), 1.51 (m, 1H, 3′-H), 1.63 (m, 1H, 3′-H), 2.48 (dddd, 1H, *J* = 5.1, 8.5, 14.1, 23.1 Hz, 2-H), 2.83 (dddd, 1H, *J* = 5.1, 8.5, 14.1, 19.7 Hz, 2-H), 3.07 (m, 1H, 3-H), 3.19 (m, 1H, 3-H), 5.03 (qdd, 1H, *J* = 6.4, 6.0, 7.3 Hz, 2′-H), 7.26 (t, 1H, *J* = 7.7 Hz, 6-H), 7.32 (d, 1H, *J* = 7.7 Hz, 4-H), 7.37 (t, 1H, *J* = 7.6 Hz, 5-H), 7.40 (d, 1H, *J* = 8.1 Hz, 7-H); ^{13}C NMR (75.46 MHz) δ 14.4 (s, CH_3, 9′-C), 20.0 (s, CH_3, 1′-C), 22.9 (s, CH_2, 8′-C), 25.7 (s, CH_2, 4′-C), 29.4 (s, CH_2, 6′-C), 29.5 (s, CH_2, 5′-C), 30.4 (s, CH_2, 3-C), 32.0 (s, CH_2, 7′-C), 36.0 (s, CH_2, 3′-C), 36.5 (d, *J* = 23.2 Hz, CH_2, 2-C), 73.1 (s, CH, 2′-C), 102.1 (d, *J* = 190.4 Hz, C, 1-C), 124.1 (s, CH, 7-C), 125.2 (s, CH, 4-C), 127.1 (s, CH, 6-C), 130.4 (d, *J* = 3.7 Hz, CH, 5-C), 139.6 (d, *J* = 19.5 Hz, C, 7a-C), 145.0 (d, *J* = 3.7 Hz, C, 3a-C), 170.3 (d, *J* = 33.0 Hz, C, COO); ^{19}F NMR (254 MHz) δ −139.21 (t, *J* = 21.3 Hz); MS *m/z*: 306 (M^+), 286 ($[M-HF]^+$), 135 ($[M-COOR^*]^+$); HRMS calcd for $C_{19}H_{27}O_2F$ (M^+): 306.1995, found: 306.2007.

4.4.13. (*S*)-3-Methyl-2-butyl (*R*)-1-fluoroindan-1-carboxylate (*R*)-5g

71%; Colorless oil; $[\alpha]_D^{27} = -8.0$ (*c* 2.09, $CHCl_3$); IR (neat) 2968 (CH), 1752 (C=O) cm^{-1}; ^{1}H NMR (500 MHz) δ 0.91 (d, 3H, *J* = 6.8 Hz, 4′-H), 0.91 (d, 3H, *J* = 6.8 Hz, 4′-H), 1.12 (d, 3H, *J* = 6.4 Hz, 1′-H), 1.82 (qqd, 1H, *J* = 6.8, 6.8, 6.0 Hz, 3′-H), 2.49 (dddd, 1H, *J* = 5.1, 8.5, 14.1, 22.6 Hz, 2-H), 2.82 (dddd, 1H, *J* = 5.1, 8.5, 14.1, 19.2 Hz, 2-H), 3.07 (m, 1H, 3-H), 3.19 (m, 1H, 3-H), 4.86 (qd, 1H, *J* = 6.4, 6.0 Hz, 2′-H), 7.27 (t, 1H, *J* = 7.7 Hz, 6-H), 7.32 (dd, 1H, *J* = 0.9, 7.7 Hz, 4-H), 7.37 (tt, 1H, *J* = 1.3, 7.7 Hz, 5-H), 7.40 (d, 1H, *J* = 7.7 Hz, 7-H); ^{13}C NMR (75.46 MHz) δ 16.7 (s, CH_3, 1′-C), 18.2 (s, CH_3, 4′-C), 18.4 (s, CH_3, 4′-C), 30.5 (s, CH_2, 3-C), 32.8 (s, CH_2, 3′-C), 36.6 (d, *J* = 23.2 Hz, CH_2, 2-C), 77.2 (s, CH, 2′-C), 102.1 (d, *J* = 190.4 Hz, C, 1-C), 124.1 (s, CH, 7-C), 125.2 (s, CH, 4-C), 127.0 (d, *J* = 3.7 Hz, CH, 6-C), 130.4 (d, *J* = 2.4 Hz, CH, 5-C), 139.7 (d, *J* = 20.8 Hz, C, 7a-C), 144.9 (d, *J* = 4.9 Hz, C, 3a-C), 170.2 (d, *J* = 31.7 Hz, C, COO); ^{19}F NMR (254 MHz) δ −139.43 (t, *J* = 23.1 Hz); MS *m/z*: 250 (M^+), 230 ($[M-HF]^+$), 135 ($[M-COOR^*]^+$), 115 (indenyl cation); HRMS calcd for $C_{15}H_{19}O_2F$ (M^+): 250.1369, found: 250.1383.

4.4.14. (*S*)-3-Methyl-2-butyl (*S*)-1-fluoroindan-1-carboxylate (*S*)-5g

48%; Colorless oil; $[\alpha]_D^{27} = +35.3$ (*c* 1.39, $CHCl_3$); IR (neat) 2967 (CH), 1752 (C=O) cm^{-1}; ^{1}H NMR (500 MHz) δ 0.76 (d, 3H, *J* = 6.8 Hz, 4′-H), 0.76 (d, 3H, *J* = 6.8 Hz, 4′-H), 1.22 (d, 3H, *J* = 6.0 Hz, 1′-H), 1.73 (qqd, 1H, *J* = 6.8, 6.8, 6.4 Hz, 3′-H), 2.48 (dddd, 1H, *J* = 5.6, 8.5, 14.1, 23.1 Hz, 2-H), 2.81 (dddd, 1H, *J* = 5.1, 8.5, 14.1, 17.5 Hz, 2-H), 3.07 (m, 1H, 3-H), 3.20 (m, 1H, 3-H), 4.83 (qd, 1H, *J* = 6.0, 6.4 Hz, 2′-H), 7.26 (t, 1H, *J* = 7.3 Hz, 6-H), 7.31 (d, 1H, *J* = 7.7 Hz, 4-H), 7.36 (tt, 1H, *J* = 1.3, 7.7 Hz, 5-H), 7.42 (d, 1H, *J* = 7.7 Hz, 7-H); ^{13}C NMR (75.46 MHz) δ 17.1 (s, CH_3, 1′-C), 17.9 (s, CH_3, 4′-C), 18.3 (s, CH_3, 4′-C), 30.5 (s, CH_2, 3-C), 32.9 (s, CH_2, 3′-C), 36.4 (d, *J* = 23.2 Hz, CH_2, 2-C), 77.1 (s, CH, 2′-C), 102.1 (d, *J* = 190.4 Hz, C, 1-C), 124.1 (s, CH, 7-C), 125.1 (s, CH, 4-C), 127.1 (d, *J* = 2.4 Hz, CH, 6-C), 130.4 (d, *J* = 2.4 Hz, CH, 5-C), 139.7 (d, *J* = 20.8 Hz, C, 7a-C), 144.8 (d, *J* = 4.9 Hz, C, 3a-C), 170.2 (d, *J* = 33.0 Hz, C, COO); ^{19}F NMR (254 MHz) δ −140.00 (t, *J* = 23.1 Hz); MS *m/z*: 250 (M^+), 230 ($[M-HF]^+$), 135 ($[M-COOR^*]^+$), 115 (indenyl cation); HRMS calcd for $C_{15}H_{19}O_2F$ (M^+): 250.1369, found: 250.1326.

4.4.15. (*S*)-1-Phenylethyl (*R*)-1-fluoroindan-1-carboxylate (*R*)-5h

22%; Colorless oil; $[\alpha]_D^{26} = -50.8$ (*c* 0.74, $CHCl_3$); IR (neat) 2983 (CH), 1751 (C=O) cm^{-1}; ^{1}H NMR (500 MHz) δ 1.53 (d, 3H, *J* = 6.8 Hz, 1′-H), 2.47 (dddd, 1H, *J* = 5.1, 8.5, 14.1, 23.1 Hz, 2-H), 2.81 (dddd, 1H, *J* = 5.6, 8.5, 14.1, 20.1 Hz, 2-H), 3.07 (m, 1H, 3-H), 3.19 (m, 1H, 3-H), 6.01 (q, 1H, *J* = 6.8 Hz, 2′-H), 7.23 (t, 1H, *J* = 7.7 Hz, 6-H), 7.28–7.38 (m, 8H, Ph, Ph′-H); ^{13}C NMR (75.46 MHz) δ 22.3 (s, CH_3, 1′-C), 30.5 (s, CH_2, 3-C), 36.4 (d, *J* = 23.2 Hz, CH_2, 2-C), 74.2 (s, CH, 2′-C), 102.1 (d, *J* = 190.4 Hz, C, 1-C), 124.2 (s, CH, 7-C), 125.2 (s, CH, 4-C), 126.2 (s, CH, 6′-C), 127.2 (d, *J* = 2.4 Hz, CH, 6-C), 128.2, 128.6 (s, CH, 4′,5′-C), 130.5 (d, *J* = 2.4 Hz, CH, 5-C), 139.5 (d, *J* = 20.8 Hz, C, 7a-C), 140.9 (s, C, 3′-C) 145.0 (d, *J* = 4.9 Hz, C, 3a-C), 169.9 (d, *J* = 33.0 Hz, C, COO); ^{19}F NMR (254 MHz) δ −139.35 (t, *J* = 21.3 Hz); MS *m/z*: 284 (M^+), 264 ($[M-HF]^+$), 135 ($[M-COOR^*]^+$), 115 (indenyl cation); HRMS calcd for $C_{18}H_{17}O_2F$ (M^+): 284.1213, found: 284.1216.

4.4.16. (*S*)-1-Phenylethyl (*S*)-1-fluoroindan-1-carboxylate (*S*)-5h

18%; Colorless solid; mp 41 °C; $[\alpha]_D^{27} = -17$ (*c* 0.58, $CHCl_3$); IR (neat) 2982 (CH), 1751 (C=O) cm^{-1}; ^{1}H NMR (500 MHz) δ 1.58 (d, 3H, *J* = 6.8 Hz, 1′-H), 2.49 (dddd, 1H, *J* = 5.1, 8.5, 14.1, 23.1 Hz, 2-H), 2.85 (dddd, 1H, *J* = 5.6, 8.5, 14.1, 19.7 Hz, 2-H), 3.09 (m, 1H, 3-H), 3.20 (m, 1H, 3-H), 5.99 (q, 1H, *J* = 6.8 Hz, 2′-H), 7.17–7.39 (m, 9H, Ph, Ph′-H); ^{13}C NMR (75.46 MHz) δ 22.6 (s, 1′-C), 30.5 (s, 3-C), 36.4 (d, *J* = 23.2 Hz, 2-C), 73.9 (s, 2′-C), 102.1 (d, *J* = 191.7 Hz, 1-H), 124.4 (s, 7-C), 125.2 (s, 4-C), 125.8 (s, 6′-C), 127.1 (s, 6-C), 128.0, 128.5 (s, 4′,5′-C), 130.5 (d, *J* = 3.7 Hz, 5-C), 139.4 (d, *J* = 20.8 Hz, 7a-C), 141.0 (s, 3′-C) 145.0 (d, *J* = 4.9 Hz, 3a-C), 169.8 (d, *J* = 33.0 Hz, COO); ^{19}F NMR (254 MHz) δ −139.35 (t, *J* = 20.3 Hz); MS *m/z*: 284 (M^+), 264 ($[M-HF]^+$), 135 ($[M-COOR^*]^+$), 115 (indenyl cation); HRMS calcd for $C_{18}H_{17}O_2F$ (M^+): 284.1212, found: 284.1209.

4.4.17. (1*S*,2*R*,4*S*)-Bornyl (*R*)-1-fluoroindan-1-carboxylate (*R*)-5i

100%; Colorless oil; $[\alpha]_D^{26} = -39.8$ (*c* 3.85, $CHCl_3$); IR (neat) 2955 (CH), 1754 (C=O) cm^{-1}; ^{1}H NMR (500 MHz) δ 0.70 (s, 3H, 10′-H), 0.84 (s, 3H, 9′-H), 0.89 (s, 3H, 8′-H), 0.99 (dd, 1H, *J* = 3.4, 13.7 Hz, 3′aq-H), 1.19 (m, 2H, 5′aq, 6′aq-H), 1.67 (m, 1H, 6′eq-H), 1.68 (dd, 1H, *J* = 4.7, 4.7 Hz, 4′-H), 1.73 (m, 1H, 5′eq-H), 2.37 (dddd, 1H, *J* = 3.4, 4.7, 9.8, 13.7 Hz, 3′eq-H), 2.48 (dddd, 1H, *J* = 5.6, 8.5, 14.1, 23.5 Hz, 2-H), 2.84 (dddd, 1H, *J* = 5.1, 8.5, 14.1, 16.7 Hz, 2-H), 3.09 (m, 1H, 3-H), 3.20 (m, 1H, 3-H), 5.01 (ddd, 1H, *J* = 2.1, 3.4, 9.8 Hz, 2′eq-H), 7.27 (t, 1H, *J* = 7.7 Hz, 6-H), 7.32 (dd, 1H, *J* = 0.9, 7.7 Hz, 4-H), 7.37 (tt, 1H, *J* = 1.3, 7.7 Hz, 5-H), 7.43 (d, 1H, *J* = 7.7 Hz, 7-H); ^{13}C NMR (75.46 MHz) δ 13.6 (s, CH_3, 10′-C), 19.1 (s, CH_3, 9′-C), 19.9 (s, CH_3, 8′-C), 27.2 (s, CH_2, 6′-C), 28.3 (s, CH_2, 5′-C), 30.5 (s, CH_2, 3-C), 36.4 (d, *J* = 23.2 Hz, CH_2, 2-C), 36.9 (s, CH_2, 3′-C), 45.0 (s, CH, 4′-C), 48.1 (s, C, 7′-C), 49.3 (s, C, 1′-C), 81.4 (s, CH, 2′-C), 102.1 (d, *J* = 191.7 Hz, C, 1-C), 124.1 (s, CH, 7-C), 125.2 (s, CH, 4-C), 127.2 (s, CH, 6-C), 130.4 (d, *J* = 3.7 Hz, CH, 5-C), 139.8 (d, *J* = 22.0 Hz, C, 7a-C), 144.7 (d, *J* = 4.9 Hz, C, 3a-C), 170.8 (d, *J* = 33.0 Hz, C, COO); ^{19}F NMR (254 MHz) δ −140.37 (ddd, *J* = 5.5, 16.7, 24.0 Hz); MS *m/z*: 316 (M^+), 296 ($[M-HF]^+$), 135 ($[M-COOR^*]^+$), 115 (indenyl cation); HRMS calcd for $C_{20}H_{25}O_2F$ (M^+): 316.1839, found: 316.1799.

4.4.18. (1*S*,2*R*,4*S*)-Bornyl (*S*)-1-fluoroindan-1-carboxylate (*S*)-5i

55%; Pale yellow oil; $[\alpha]_D^{25} = -5.6$ (*c* 2.00, $CHCl_3$); IR (neat) 2955 (CH), 1752 (C=O) cm^{-1}; ^{1}H NMR (500 MHz) δ 0.85 (s, 3H, 10′-H), 0.86 (s, 3H, 9′-H), 0.86 (dd, 1H, *J* = 3.0, 13.7 Hz, 3′aq-H), 0.90 (s, 3H, 8′-H), 1.03 (ddd, 1H, *J* = 4.7, 9.4, 11.1 Hz, 5′aq,-H), 1.26 (m, 1H, 6′aq-H), 1.65 (dd, 1H, *J* = 3.8, 3.8 Hz, 4′-H), 1.67 (m, 1H, 5′eq-H), 1.73 (m, 1H, 6′eq-H), 2.36 (dddd, 1H, *J* = 3.8, 4.3, 9.8, 14.1 Hz, 3′eq-H), 2.49 (dddd, 1H, *J* = 5.6, 8.5, 14.1, 23.5 Hz, 2-H), 2.83 (dddd, 1H, *J* = 4.7, 8.5, 14.1, 17.5 Hz, 2-H), 3.09 (m, 1H, 3-H), 3.20 (m, 1H, 3-H), 4.97 (ddd, 1H, *J* = 2.6, 3.0, 9.8 Hz, 2′eq-H), 7.27 (t, 1H, *J* = 7.3 Hz, 6-H), 7.32 (d, 1H, *J* = 7.7 Hz, 4-H), 7.37 (t, 1H, *J* = 7.7 Hz, 5-H), 7.42 (d, 1H, *J* = 7.2 Hz, 7-H); ^{13}C NMR (75.46 MHz) δ 13.9 (s, CH_3, 10′-C), 19.1 (s, CH_3, 9′-C), 19.9 (s, CH_3, 8′-C), 27.3 (s, CH_2, 6′-C), 28.1 (s, CH_2, 5′-C), 30.5 (s, CH_2, 3-C), 36.5 (d, *J* = 23.2 Hz, CH_2, 2-C), 36.8 (s, CH_2, 3′-C), 45.0 (s, CH, 4′-C), 48.1 (s, C, 7′-C), 49.1 (s, C, 1′-C), 81.7 (s, CH, 2′-C), 102.1 (d, *J* = 190.4 Hz, C, 1-C), 124.1 (s, CH, 7-C), 125.2 (s, CH, 4-C), 127.1 (d, *J* = 2.4 Hz, CH, 6-C), 130.4 (d, *J* = 2.4 Hz, CH, 5-C), 139.7 (d, *J* = 20.8 Hz, C, 7a-C), 144.7 (d, *J* = 4.9 Hz, C, 3a-C), 170.8 (d, *J* = 33.0 Hz, C, COO); ^{19}F NMR (254 MHz) δ −140.33 (t, *J* = 23.1 Hz); MS *m/z*: 316 (M^+), 296 ($[M-HF]^+$), 135 ($[M-COOR^*]^+$), 115 (indenyl cation); HRMS calcd for $C_{20}H_{25}O_2F$ (M^+): 316.1839, found: 316.1848.

4.4.19. (1*R*,2*S*,5*R*)-8-Phenylmenthyl (*R*)-1-fluoroindan-1-carboxylate (*R*)-5j

58%; Colorless oil; $[\alpha]_D^{27} = -33.2$ (*c* 2.69, $CHCl_3$); IR (neat) 2954 (CH), 1732 (C=O) cm^{-1}; ^{1}H NMR (500 MHz) δ 0.78 (dddd, 1H,

J = 3.4, 12.0, 12.8, 12.8 Hz, 4′aq-H), 0.86 (d, 3H, J = 6.4 Hz, 10′-H), 0.96 (dddd, 1H, J = 3.4, 12.8, 12.8, 13.2 Hz, 3′aq-H), 1.05 (s, 3H, 9′-H), 1.08 (ddd, 1H, J = 10.7, 12.0, 12.0 Hz, 6′aq-H), 1.16 (s, 3H, 8′-H), 1.37 (dddd, 1H, J = 3.4, 3.4, 3.8, 13.7 Hz, 3′eq-H), 1.45 (m, 1H, 5′aq-H), 1.53 (ddddd, 1H, J = 2.1, 3.4, 3.4, 3.8, 12.8 Hz, 4′eq-H), 1.92 (ddd, 1H, J = 3.4, 10.7, 12.4 Hz, 2′aq-H), 2.01 (dddddd, 1H, J = 1.7, 1.7, 1.7, 2.1, 2.6, 12.0 Hz, 6′eq-H), 2.39 (dddd, 1H, J = 5.6, 8.5, 14.1, 23.5 Hz, 2-H), 2.69 (dddd, 1H, J = 5.1, 8.5, 14.1, 17.9 Hz, 2-H), 3.04 (m, 1H, 3-H), 3.16 (m, 1H, 3-H), 4.87 (ddd, 1H, J = 4.3, 10.7, 10.7 Hz, 1′aq-H), 7.12 (tt, 1H, J = 1.3, 7.3 Hz, *p*′-H), 7.15–7.23 (m, 4H, Ph′-H), 7.26 (t, 1H, J = 7.7 Hz, 6-H), 7.29 (d, 1H, J = 6.8 Hz, 4-H), 7.35 (tt, 1H, J = 1.3, 7.7 Hz, 5-H), 7.43 (d, 1H, J = 7.7 Hz, 7-H); ^{13}C NMR (75.46 MHz) δ 22.0 (s, CH_3, 10′-C), 24.6(s, CH_3, 8′-C), 27.4 (s, CH_2, 3′-C), 29.3 (s, CH_3, 9′-C), 30.5 (s, CH_2, 3-C), 31.6 (s, CH, 5′-C), 34.7 (s, CH_2, 4′-C), 36.1 (d, J = 23.2 Hz, CH_2, 2-C), 40.3 (s, C, 7′-C), 41.7 (s, CH_2, 6′-C), 50.7 (s, CH, 2′-C), 77.1 (s, CH, 1′-C), 102.0 (d, J = 191.7 Hz, C, 1-C), 124.3 (s, CH, 7-C), 125.2 (s, CH, 4-C), 125.4 (s, CH, *p*′-C), 125.7 (s, CH, *o*′ or *m*′-C), 127.1 (s, CH, 6-C), 128.0 (s, CH, *o*′ or *m*′-C), 130.5 (d, J = 3.7 Hz, CH, 5-C), 139.3 (d, J = 22.0 Hz, C, 7a-C), 145.0 (d, J = 3.7 Hz, C, 3a-C), 150.2 (s, C, *ipso*′-C), 169.8 (d, J = 31.7 Hz, C, *C*OO); ^{19}F NMR (254 MHz) δ −139.13 (t, J = 23.1 Hz); MS *m*/*z*: 394 (M^+), 374 ($[M{-}HF]^+$), 135 ($[M{-}COOR^*]^+$), 115 (indenyl cation); HRMS calcd for $C_{26}H_{31}O_2F$ (M^+): 394.2308, found: 394.2266.

4.4.20. (1*R*,2*S*,5*R*)-8-Phenylmenthyl (*S*)-1-fluoroindan-1-carboxylate (*S*)-5j

25%; Colorless solid; mp 88 °C; $[\alpha]_D^{27} = +1.0$ (*c* 1.13, $CHCl_3$); IR (neat) 2957 (CH), 1745 (C=O) cm^{-1}; ^{1}H NMR (500 MHz) δ 0.75 (dddd, 1H, J = 3.0, 12.4, 12.4, 12.4 Hz, 4′aq-H), 0.77 (ddd, 1H, J = 12.4, 12.4, 12.4 Hz, 6′aq-H), 0.80 (d, 3H, J = 6.4 Hz, 10′-H), 1.03 (dddd, 1H, J = 3.4, 12.8, 12.8, 13.2 Hz, 3′aq-H), 1.25 (s, 3H, 9′-H), 1.38 (s, 3H, 8′-H), 1.41 (m, 1H, 5′aq-H), 1.50 (dddd, 1H, J = 3.4, 3.4, 3.4, 13.7 Hz, 3′eq-H), 1.54 (ddddd, 1H, J = 3.0, 3.4, 3.8, 3.8, 12.8 Hz, 4′eq-H), 1.73 (dddddd, 1H, J = 1.7, 2.1, 2.1, 2.1, 2.1, 12.0 Hz, 6′eq-H), 1.99 (ddd, 1H, J = 3.4, 10.7, 12.4 Hz, 2′aq-H), 2.14–2.21 (m, 2H, 2-H), 2.87 (m, 1H, 3-H), 3.07 (m, 1H, 3-H), 5.01 (ddd, 1H, J = 4.3, 10.7, 10.7 Hz, 1′aq-H), 7.14–7.17 (m, 1H, *p*′-H), 7.25 (t, 1H, J = 7.7 Hz, 6-H), 7.27-7.29 (m, 5H, 4, *o*′, *m*′-H), 7.34–7.37 (m, 2H, 5, 7-H); ^{13}C NMR (75.46 MHz) δ 22.0 (s, CH_3, 10′-C), 26.6(s, CH_3, 9′-C), 27.2 (s, CH_2, 3′-C), 27.8 (s, CH_3, 8′-C), 30.4 (s, CH_2, 3-C), 31.5 (s, CH, 5′-C), 34.5 (s, CH_2, 4′-C), 35.5 (d, J = 23.2 Hz, CH_2, 2-C), 40.3 (s, C, 7′-C), 41.3 (s, CH_2, 6′-C), 50.0 (s, CH, 2′-C), 76.8 (s, CH, 1′-C), 102.0 (d, J = 189.2 Hz, C, 1-C), 124.2 (s, CH, 7-C), 125.1 (s, CH, 4-C), 125.4 (s, CH, *p*′-C), 125.6 (s, CH, *o*′ or *m*′-C), 127.0 (d, J = 2.4 Hz, CH, 6-C), 128.2 (s, CH, *o*′ or *m*′-C), 130.3 (d, J = 3.7 Hz, CH, 5-C), 139.5 (d, J = 20.8 Hz, C, 7a-C), 145.1 (d, J = 3.7 Hz, C, 3a-C), 150.9 (s, C, *ipso*′-C), 169.8 (d, J = 33.0 Hz, C, *C*OO); ^{19}F NMR (254 MHz) δ −138.77 (t, J = 22.2 Hz); MS *m*/*z*: 394 (M^+), 374 ($[M{-}HF]^+$); HRMS calcd for $C_{26}H_{31}O_2F$ (M^+): 394.2308, found: 394.2269.

4.4.21. (1*R*,2*S*,5*R*)-Menthyl (*R*)-1-fluoroindan-1-carboxylate (*R*)-5k

89%; Colorless oil; $[\alpha]_D^{27} = -64.5$ (*c* 3.19, $CHCl_3$); IR (neat) 2956 (CH), 1751 (C=O) cm^{-1}; ^{1}H NMR (500 MHz) δ 0.62 (d, 3H, J = 6.8 Hz, 9′-H), 0.72 (d, 3H, J = 6.8 Hz, 8′-H), 0.85 (dddd, 1H, J = 3.4, 11.3, 12.8, 12.8 Hz, 4′aq-H), 0.91 (d, 3H, J = 6.4 Hz, 10′-H), 1.02 (dddd, 1H, J = 3.4, 12.4, 12.8, 13.2 Hz, 3′aq-H), 1.04 (ddd, 1H, J = 11.1, 12.0, 12.4 Hz, 6′aq-H), 1.33 (dddd, 1H, J = 3.0, 3.4, 11.1, 12.4 Hz, 2′aq-H), 1.44 (qqd, 1H, J = 6.8, 7.3, 3.0 Hz, 7′-H), 1.50 (m, 1H, 5′aq-H), 1.63 (dddd, 1H, J = 3.0, 3.4, 3.4, 13.2 Hz, 3′eq-H), 1.67 (ddddd, 1H, J = 2.1, 3.0, 3.4, 3.9, 12.8 Hz, 4′eq-H), 2.03 (dddddd, 1H, J = 1.3, 2.3, 2.3, 2.3, 2.3, 12.0 Hz, 6′eq-H), 2.47 (dddd, 1H, J = 5.6, 8.5, 14.1, 23.5 Hz, 2-H), 2.81 (dddd, 1H, J = 5.1, 8.5, 14.1, 17.9 Hz, 2-H), 3.06 (m, 1H, 3-H), 3.19 (m, 1H, 3-H), 4.76 (ddd, 1H, J = 4.3, 11.1, 11.1 Hz, 1′aq-H), 7.25 (t, 1H, J = 7.7 Hz, 6-H), 7.30 (dd, 1H, J = 0.9, 7.7 Hz, 4-H), 7.36 (tt, 1H, J = 1.3, 7.3 Hz, 5-H), 7.40 (d, 1H, J = 7.3 Hz, 7-H); ^{13}C NMR (75.46 MHz) δ 16.3 (s, CH_3, 9′-C), 20.8 (s, CH_3, 8′-C), 22.3 (s, CH_3, 10′-C), 23.5 (s, CH_2, 3′-C), 26.2 (s, CH, 7′-C), 30.5 (s, CH_2, 3-C), 31.6 (s, CH, 5′-C), 34.4 (s, CH_2, 4′-C), 35.4 (d, J = 22.0 Hz, CH_2, 2-C), 40.9 (s, CH_2, 6′-C), 47.2 (s, CH, 2′-C), 76.1 (s, CH, 1′-C), 102.0 (d, J = 190.4 Hz, C, 1-C), 124.1 (s, CH, 7-C), 125.1 (s, CH, 4-C), 127.0 (d, J = 2.4 Hz, CH, 6-C), 130.4 (d, J = 2.4 Hz, CH, 5-C), 139.6 (d, J = 20.8 Hz, C, 7a-C), 144.8 (d, J = 4.9 Hz, C, 3a-C), 170.2 (d, J = 33.0 Hz, C, *C*OO); ^{19}F NMR (254 MHz) δ −139.83 (t, J = 23.1 Hz); MS *m*/*z*: 318 (M^+), 298 ($[M{-}HF]^+$), 135 ($[M{-}COOR^*]^+$), 115 (indenyl cation); HRMS calcd for $C_{20}H_{27}O_2F$ (M^+): 318.1995, found: 318.2028.

4.4.22. (1*R*,2*S*,5*R*)-Menthyl (*S*)-1-fluoroindan-1-carboxylate (*S*)-5k

94%; Colorless oil; $[\alpha]_D^{28} = -32.5$ (*c* 3.45, $CHCl_3$); IR (neat) 2956 (CH), 1750 (C=O) cm^{-1}; ^{1}H NMR (500 MHz) δ 0.77 (d, 3H, J = 6.8 Hz, 9′-H), 0.83 (dddd, 1H, J = 3.4, 12.8, 12.8, 12.8 Hz, 4′aq-H), 0.88 (d, 3H, J = 6.8 Hz, 10′-H), 0.91 (ddd, 1H, J = 11.7, 11.7, 11.7 Hz, 6′aq-H), 0.90 (d, 3H, J = 6.8 Hz, 8′-H), 1.05 (dddd, 1H, J = 3.4, 12.4, 12.8, 13.7 Hz, 3′aq-H), 1.42 (dddd, 1H, J = 3.0, 3.4, 11.5, 11.5 Hz, 2′aq-H), 1.49 (m, 1H, 5′aq-H), 1.64–1.70 (m, 2H, 3′eq, 4′eq-H), 1.91 (qqd, 1H, J = 6.8, 7.3, 2.6 Hz, 7′-H), 1.96 (br d, 1H, J = 12.0 Hz, 6′eq-H), 2.49 (dddd, 1H, J = 4.7, 8.5, 14.1, 23.1 Hz, 2-H), 2.79 (dddd, 1H, J = 5.5, 8.5, 14.1, 20.1 Hz, 2-H), 3.06 (m, 1H, 3-H), 3.20 (m, 1H, 3-H), 4.81 (ddd, 1H, J = 4.2, 11.1, 11.1 Hz, 1′aq-H), 7.27 (t, 1H, J = 7.7 Hz, 6-H), 7.32 (d, 1H, J = 7.3 Hz, 4-H), 7.35–7.39 (m, 2H, 5, 7-H); ^{13}C NMR (75.46 MHz) δ 16.3 (s, CH_3, 9′-C), 21.1 (s, CH_3, 8′-C), 22.2 (s, CH_3, 10′-C), 23.3 (s, CH_2, 3′-C), 26.5 (s, CH, 7′-C), 30.5 (s, CH_2, 3-C), 31.6 (s, CH, 5′-C), 34.3 (s, CH_2, 4′-C), 36.6 (d, J = 23.2 Hz, CH_2, 2-C), 40.5 (s, CH_2, 6′-C), 47.0 (s, CH, 2′-C), 76.1 (s, CH, 1′-C), 102.1 (d, J = 190.4 Hz, C, 1-C), 124.1 (s, CH, 7-C), 125.2 (s, CH, 4-C), 127.1 (d, J = 2.4 Hz, CH, 6-C), 130.4 (d, J = 2.4 Hz, CH, 5-C), 139.7 (d, J = 20.8 Hz, C, 7a-C), 145.0 (d, J = 4.9 Hz, C, 3a-C), 170.2 (d, J = 33.0 Hz, C, *C*OO); ^{19}F NMR (254 MHz) δ −138.81 (t, J = 22.2 Hz); MS *m*/*z*: 318 (M^+), 298 ($[M{-}HF]^+$), 135 ($[M{-}COOR^*]^+$); HRMS calcd for $C_{20}H_{27}O_2F$ (M^+): 318.1995, found: 318.1953.

4.4.23. (1*S*,2*S*,5*R*)-Neomenthyl (*R*)-1-fluoroindan-1-carboxylate (*R*)-5l

62%; Colorless solid; mp 67 °C; $[\alpha]_D^{27} = -8.7$ (*c* 2.32, $CHCl_3$); IR (neat) 2950 (CH), 1752 (C=O) cm^{-1}; ^{1}H NMR (500 MHz) δ 0.67 (d, 3H, J = 6.4 Hz, 10′-H), 0.79 (dddd, 1H, J = 3.4, 11.5, 11.5, 12.8 Hz, 4′aq-H), 0.88 (d, 3H, J = 6.8 Hz, 9′-H), 0.89 (m, 1H, 5′aq-H), 0.90 (d, 3H, J = 6.8 Hz, 8′-H), 0.95 (m, 1H, 2′aq-H), 0.96 (m, 1H, 6′aq-H), 1.10 (dddd, 1H, J = 3.8, 12.8, 12.8, 12.8 Hz, 3′aq-H), 1.41 (qqd, 1H, J = 6.4, 6.8, 9.0 Hz, 7′-H), 1.56 (ddddd, 1H, J = 3.0, 3.0, 3.4, 3.4, 12.4 Hz, 4′eq-H), 1.69 (dddd, 1H, J = 3.0, 3.4, 3.4, 12.8 Hz, 3′eq-H), 1.82 (dddd, 1H, J = 2.6, 2.6, 3.4, 13.2 Hz, 6′eq-H), 2.48 (dddd, 1H, J = 6.0, 8.5, 14.1, 23.9 Hz, 2-H), 2.79 (dddd, 1H, J = 4.7, 8.5, 14.1, 15.4 Hz, 2-H), 3.08 (m, 1H, 3-H), 3.20 (m, 1H, 3-H), 5.28 (br ddd, 1H, J = 1.7 Hz, 1′aq-H), 7.25 (t, 1H, J = 7.7 Hz, 6-H), 7.31 (d, 1H, J = 6.8 Hz, 4-H), 7.36 (tt, 1H, J = 1.3, 7.7 Hz, 5-H), 7.38 (d, 1H, J = 8.1 Hz, 7-H); ^{13}C NMR (75.46 MHz) δ 20.9 (s, CH_3, 8′-C), 21.3 (s, CH_3, 9′-C), 22.2 (s, CH_3, 10′-C), 25.6 (s, CH_2, 3′-C), 26.4 (s, CH, 7′-C), 29.6 (s, CH, 5′-C), 30.5 (s, CH_2, 3-C), 34.7 (s, CH_2, 4′-C), 36.4 (d, J = 22.0 Hz, CH_2, 2-C), 39.0 (s, CH_2, 6′-C), 46.8 (s, CH, 2′-C), 73.0 (s, CH, 1′-C), 102.0 (d, J = 189.2 Hz, C, 1-C), 123.8 (s, CH, 7-C), 125.2 (s, CH, 4-C), 127.0 (d, J = 2.4 Hz, CH, 6-C), 130.3 (d, J = 3.7 Hz, CH, 5-C), 139.8 (d, J = 20.8 Hz, C, 7a-C), 144.5 (d, J = 4.9 Hz, C, 3a-C), 170.1 (d, J = 34.2 Hz, C, *C*OO); ^{19}F NMR (254 MHz) δ −141.18 (ddd, J = 6.5, 15.7, 23.1 Hz); MS *m*/*z*: 319 ($[M + 1]^+$), 298 ($[M{-}HF]^+$), 135 ($[M{-}COOR^*]^+$); HRMS calcd for $C_{20}H_{28}O_2F$ ($[M{+}H]^+$): 319.2074, found: 319.2045.

4.4.24. (1*S*,2*S*,5*R*)-Neomenthyl (*S*)-1-fluoroindan-1-carboxylate (*S*)-5l

100%; Colorless solid; mp 75 °C; $[\alpha]_D^{28} = +49.3$ (*c* 2.32, $CHCl_3$); IR (neat) 2920 (CH), 1746 (C=O) cm^{-1}; ^1H NMR (500 MHz) δ 0.62 (d, 3H, *J* = 6.4 Hz, 9′-H), 0.67 (d, 3H, *J* = 6.4 Hz, 8′-H), 0.76 (qqd, 1H, *J* = 6.4, 6.8, 9.0 Hz, 7′-H), 0.87 (d, 3H, *J* = 6.4 Hz, 10′-H), 0.88 (m, 1H, 4′aq-H), 0.89 (m, 1H, 2′aq-H), 1.07 (m, 1H, 6′aq-H), 1.08 (m, 1H, 3′aq-H), 1.57 (m, 1H, 5′aq-H), 1.64 (dddd, 1H, *J* = 3.4, 3.4, 3.4, 12.8 Hz, 3′eq-H), 1.73 (ddddd, 1H, *J* = 3.0, 3.0, 3.0, 3.0, 14.5 Hz, 4′eq-H), 2.02 (dddd, 1H, *J* = 2.6, 3.4, 3.4, 14.5 Hz, 6′eq-H), 2.48 (dddd, 1H, *J* = 6.4, 9.0, 14.1, 23.9 Hz, 2-H), 2.81 (dddd, 1H, *J* = 4.3, 8.5, 13.7, 14.1 Hz, 2-H), 3.09 (m, 1H, 3-H), 3.20 (m, 1H, 3-H), 5.22 (br ddd, 1H, *J* = 1.7 Hz, 1′aq-H), 7.25 (t, 1H, *J* = 7.7 Hz, 6-H), 7.30 (d, 1H, *J* = 7.7 Hz, 4-H), 7.35 (tt, 1H, *J* = 1.3, 7.7 Hz, 5-H), 7.40 (d, 1H, *J* = 7.7 Hz, 7-H); ^{13}C NMR (75.46 MHz) δ 20.7 (s, CH_3, 8′-C), 21.0 (s, CH_3, 9′-C), 22.4 (s, CH_3, 10′-C), 25.5 (s, CH_2, 3′-C), 27.1 (s, CH, 7′-C), 29.1 (s, CH, 5′-C), 30.6 (s, CH_2, 3-C), 34.8 (s, CH_2, 4′-C), 36.6 (d, *J* = 22.0 Hz, CH_2, 2-C), 39.2 (s, CH_2, 6′-C), 46.8 (s, CH, 2′-C), 73.1 (s, CH, 1′-C), 101.9 (d, *J* = 190.4 Hz, C, 1-C), 123.9, (s, CH, 7-C) 125.1 (s, CH, 4-C), 127.0 (d, *J* = 2.4 Hz, CH, 6-C), 130.3 (d, *J* = 3.7 Hz, CH, 5-C), 139.7 (d, *J* = 22.0 Hz, C, 7a-C), 144.3 (d, *J* = 4.9 Hz, C, 3a-C), 170.1 (d, *J* = 33.0 Hz, C, *C*OO); ^{19}F NMR (254 MHz) δ −141.32 (ddd, *J* = 6.5, 13.9, 24.0 Hz); MS *m*/*z*: 318 (M^+), 298 ($[M-HF]^+$), 135 ($[M-COOR^*]^+$); HRMS calcd for $C_{20}H_{27}O_2F$ (M^+): 318.1995, found: 318.1987.

4.4.25. (1*R*,2*S*,5*S*)-Isomenthyl (*R*)-1-fluoroindan-1-carboxylate (*R*)-5m

55%; Colorless oil; $[\alpha]_D^{27} = -9.4$ (*c* 2.03, $CHCl_3$); IR (neat) 2957 (CH), 1750 (C=O) cm^{-1}; ^1H NMR (500 MHz) δ 0.86 (d, 3H, *J* = 6.8 Hz, 10′-H), 0.86 (d, 3H, *J* = 6.8 Hz, 9′-H), 0.95 (d, 3H, *J* = 6.4 Hz, 8′-H), 1.16 (dddd, 1H, *J* = 4.7, 8.5, 8.5, 12.8 Hz, 4′aq-H), 1.37 (m, 2H, 4′eq, 6′aq-H), 1.42 (ddd, 1H, *J* = 3.0, 8.1, 13.7 Hz, 6′eq-H), 1.52 (m, 3H, 2′aq, 3′aq, 3′eq-H), 1.62 (m, 1H, 5′eq-H), 1.74 (qqd, 1H, *J* = 6.8, 6.8, 7.3 Hz, 7′-H), 2.48 (dddd, 1H, *J* = 5.6, 8.5, 14.1, 23.1 Hz, 2-H), 2.83 (dddd, 1H, *J* = 5.1, 8.5, 14.1, 17.9 Hz, 2-H), 3.08 (m, 1H, 3-H), 3.19 (m, 1H, 3-H), 5.16 (ddd, 1H, *J* = 3.4, 6.4, 6.4 Hz, 1′aq-H), 7.26 (t, 1H, *J* = 7.7 Hz, 6-H), 7.32 (dd, 1H, *J* = 0.9, 7.7 Hz, 4-H), 7.37 (tt, 1H, *J* = 1.3, 7.7 Hz, 5-H), 7.40 (d, 1H, *J* = 7.7 Hz, 7-H); ^{13}C NMR (75.46 MHz) δ 19.4 (s, CH_3, 10′-C), 20.9 (s, CH_3, 9′-C), 21.2 (s, CH_3, 8′-C), 21.2 (s, CH_2, 3′-C), 26.5 (s, CH, 7′-C), 27.6 (s, CH, 5′-C), 29.9 (s, CH_2, 4′-C), 30.5 (s, CH_2, 3-C), 35.5 (s, CH_2, 6′-C), 36.5 (d, *J* = 22.0 Hz, CH_2, 2-C), 45.5 (s, CH, 2′-C), 73.9 (s, CH, 1′-C), 102.1 (d, *J* = 190.4 Hz, C, 1-C), 124.1 (s, CH, 7-C), 125.2 (s, CH, 4-C), 127.1 (d, *J* = 2.4 Hz, CH, 6-C), 130.4 (d, *J* = 3.7 Hz, CH, 5-C), 139.8 (d, *J* = 20.8 Hz, C, 7a-C), 144.8 (d, *J* = 4.9 Hz, C, 3a-C), 170.0 (d, *J* = 33.0 Hz, C, *C*OO); ^{19}F NMR (254 MHz) δ −139.91 (t, *J* = 23.1 Hz); MS *m*/*z*: 318 (M^+), 298 ($[M-HF]^+$), 135 ($[M-COOR^*]^+$), 115 (indenyl cation); HRMS calcd for $C_{20}H_{27}O_2F$ (M^+): 318.1995, found: 318.2011.

4.4.26. (1*R*,2*S*,5*S*)-Isomenthyl (*S*)-1-fluoroindan-1-carboxylate (*S*)-5m

66%; Colorless oil; $[\alpha]_D^{28} = +39.3$ (*c* 2.39, $CHCl_3$); IR (neat) 2958 (CH), 1749 (C=O) cm^{-1}; ^1H NMR (500 MHz) δ 0.77 (d, 3H, *J* = 6.8 Hz, 9′-H), 0.86 (d, 3H, *J* = 6.8 Hz, 8′-H), 0.93 (d, 3H, *J* = 6.8 Hz, 10′-H), 1.21 (m, 1H, 4′aq-H), 1.27 (m, 1H, 4′eq), 1.40 (m, 3H, 3′aq, 3′eq, 4′eq-H), 1.55 (m, 2H, 6′aq, 7′-H), 1.64 (ddd, 1H, *J* = 4.3, 6.8, 13.7 Hz, 6′eq-H), 1.86 (m, 1H, 5′eq-H), 2.47 (dddd, 1H, *J* = 5.6, 9.0, 14.1, 23.1 Hz, 2-H), 2.82 (dddd, 1H, *J* = 5.1, 8.5, 14.1, 17.5 Hz, 2-H), 3.08 (m, 1H, 3-H), 3.19 (m, 1H, 3-H), 5.12 (ddd, 1H, *J* = 3.4, 6.8, 6.8 Hz, 1′aq-H), 7.26 (t, 1H, *J* = 7.7 Hz, 6-H), 7.31 (d, 1H, *J* = 7.7 Hz, 4-H), 7.36 (t, 1H, *J* = 7.2 Hz, 5-H), 7.41 (d, 1H, *J* = 7.7 Hz, 7-H); ^{13}C NMR (75.46 MHz) δ 19.1 (s, CH_3, 10′-C), 20.7 (s, CH_3, 9′-C), 20.8 (s, CH_2, 3′-C), 21.0 (s, CH_3, 8′-C), 26.4 (s, CH, 7′-C), 27.9 (s, CH, 5′-C), 30.1 (s, CH_2, 4′-C), 30.5 (s, CH_2, 3-C), 36.0 (s, CH_2, 6′-C), 36.5 (d, *J* = 23.2 Hz, CH_2, 2-C), 45.8 (s, CH, 2′-C), 73.7 (s, CH, 1′-C), 102.1 (d, *J* = 190.4 Hz, C, 1-C), 124.1 (s, CH, 7-C), 125.2 (s, CH, 4-C), 127.1 (s, CH, 6-C), 130.4 (d, *J* = 2.4 Hz, CH, 5-C), 139.7 (d, *J* = 20.8 Hz, C, 7a-C), 144.8 (d, *J* = 4.9 Hz, C, 3a-C), 170.0 (d, *J* = 33.0 Hz, C, *C*OO); ^{19}F NMR (254 MHz) δ −140.16 (t, *J* = 23.1 Hz); MS *m*/*z*: 318 (M^+), 298 ($[M-HF]^+$), 135 ($[M-COOR^*]^+$); HRMS calcd for $C_{20}H_{27}O_2F$ (M^+): 318.1995, found: 318.1996.

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