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Synthesis of secondary α-perfluoroalkyl- and tertiary α,α-bis(perfluoroalkyl)-*N*-methylprolinols and their catalytic activities in the acyl transfer reaction

Kazumasa Funabiki *, Akitsugu Shibata, Keisuke Hatano, Masaki Matsui

Department of Materials Science and Technology, Faculty of Engineering, Gifu University, 1-1, Yanagido, Gifu 501-1193, Japan

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ABSTRACT

Various chiral α-perfluoroalkyl-*N*-methylprolinols were prepared and their organocatalytic activities in an acyl transfer reaction of 4-nitrophenyl 2-methoxyacetate with methanol-d_4 in chloroform-*d* were examined. As a result, α-trifluoromethyl-*N*-methylprolinol was a more effective acyl transfer catalyst than not only secondary α-perfluorobutyl- and *n*-butyl-*N*-methylprolinols but also tertiary α,α-bis(perfluorobutyl)-*N*-methylprolinol.

1. Introduction

Chiral prolinol derivatives have been used in asymmetric synthesis as powerful chiral auxiliaries [1] or chiral ligands for the reduction of ketones [2] and for the alkylation [3] and arylation [4] of aldehydes. Very recently, considerable attention has been paid to chiral prolinol derivatives as effective organocatalysts for various asymmetric reactions [5]. However, there have been only a few reports on the asymmetric synthesis [6] of α-polyfluoroalkylated prolinol derivatives and their use as chiral ligands or organocatalysts [7], although it has been reported that dialkylamino-α-trifluoromethylated alcohols could be used as chiral ligands [8a–c], a chiral auxiliary [8d], and organocatalysts [9]. Those papers showed that dialkylamino-α-trifluoromethylated alcohols gave better catalytic activities than their non-fluorinated counterparts.

Furthermore, although there have been several reports on the introduction of long perfluoroalkyl groups into catalysts to recover them from the reaction mixture through the use of their flourous properties [10], to the best of our knowledge there have been only a few reports on *the differences in catalytic activity between trifluoromethylated and longer perfluoroalkylated catalysts* [11]. We describe here the asymmetric synthesis of α-trifluoromethyl- and α-perfluorobutyl-*N*-methylprolinols with a secondary alcohol unit as well as α,α-bis(perfluorobutyl)-*N*-methylprolinols with a tertiary alcohol unit and estimate their organocatalytic activities in the acyl transfer reaction [12] of 4-nitrophenyl 2-methoxyacetate with 10 equiv. of methanol-d_4 (CD_3OD) in chloroform-*d* ($CDCl_3$).

2. Results and discussion

2.1. Synthesis of various α-perfluoroalkylated *N*-methylprolinols 3

As previously reported by us [6a], (*S*)-*tert*-butyl 2-((*R*)-2,2,2-trifluoro-1-hydroxyethyl)pyrrolidine-1-carboxylate ((α*R*)-**2a**), (*S*)-*tert*-butyl 2-((*S*)-2,2,2-trifluoro-1-hydroxyethyl)pyrrolidine-1-carboxylate ((α*S*)-**2a**), (*S*)-*tert*-butyl 2-(2,2,3,3,4,4,5,5,5-nonafluoropentanoyl)pyrrolidine-1-carboxylate ((α*R*)-**2b**), and (*S*)-*tert*-butyl 2-((*S*)-1-hydroxypentyl)pyrrolidine-1-carboxylate ((α*S*)-**2c**) were prepared by perfluoroalkylation or *n*-butylation of methyl (*S*)-*N*-*tert*-butyloxycarbonyl (Boc)-pyrrolidine-2-dicarboxylate and stereoselective reduction of the obtained chiral ketones **1a–c** (Scheme 1). (*S*)-*Tert*-butyl 2-(1,1,1,2,2,3,3,4,4,6,6,7,7,8,8,9,9,9-octadecafluoro-5-hydroxynonan-5-yl)pyrrolidine-1-carboxylate (**2d**) was prepared by second perfluorobutylation of the obtained ketone **1b** in 55% yield.

Conversion of the Boc-groups in (*S*)-*tert*-butyl 2-((*R*)-2,2,2-trifluoro-1-hydroxyethyl)pyrrolidine-1-carboxylate ((α*R*)-**2a**), (*S*)-*tert*-butyl 2-((*S*)-2,2,2-trifluoro-1-hydroxyethyl)pyrrolidine-1-carboxylate ((α*S*)-**2a**), (*S*)-*tert*-butyl 2-(2,2,3,3,4,4,5,5,5-nonafluoropentanoyl)pyrrolidine-1-carboxylate ((α*R*)-**2b**), (*S*)-*tert*-butyl 2-((*S*)-1-hydroxypentyl)pyrrolidine-1-carboxylate ((α*S*)-**2c**), and (*S*)-*tert*-butyl 2-(1,1,1,2,2,3,3,4,4,6,6,7,7,8,8,9,9,9-octadecafluoro-5-hydroxynonan-5-yl)pyrrolidine-1-carboxylate (**2d**) into methyl groups was achieved by treatment with lithium aluminum hydride (LAH) at reflux temperature in anhydrous THF to produce (*R*)-2,2,2-

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* Corresponding author. Tel.: +81 58 293 2599; fax: +81 58 293 2794.
E-mail address: funabiki@gifu-u.ac.jp (K. Funabiki).

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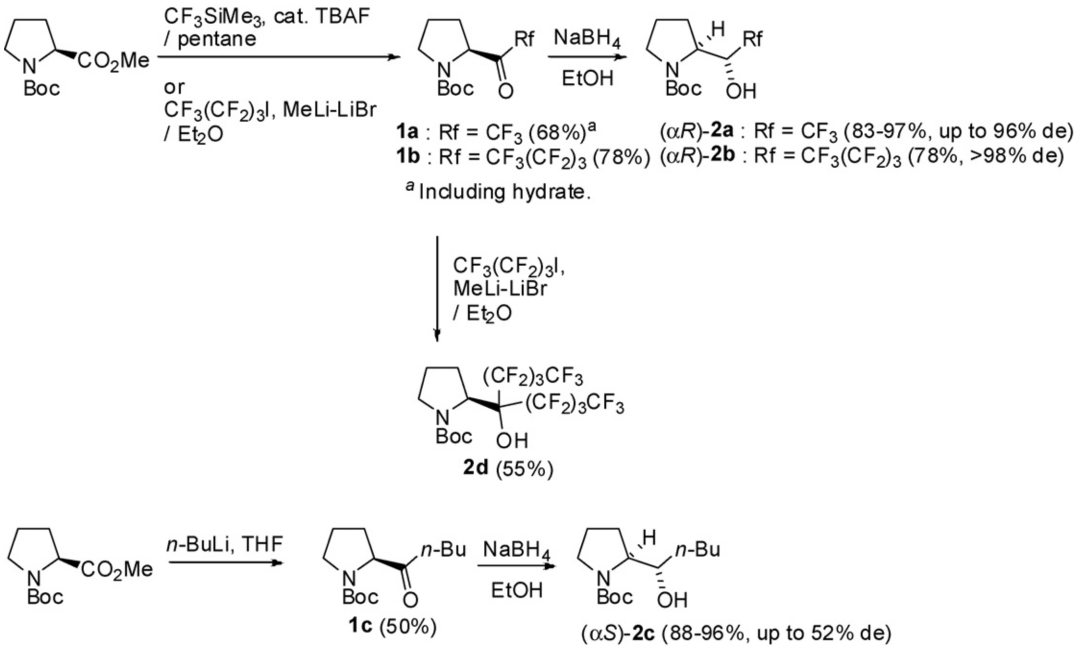


Scheme 1. Previous our reports on asymmetric synthesis of *N*-Boc prolinols **2**.

trifluoro-1-((*S*)-1-methylpyrrolidin-2-yl)ethanol ((α*R*)-**3a**), (*S*)-2,2,2-trifluoro-1-((*S*)-1-methylpyrrolidin-2-yl)ethanol ((α*S*)-**3a**), (*R*)-2,2,3,3,4,4,5,5,5-nonafluoro-1-((*S*)-1-methylpyrrolidin-2-yl) pentan-1-ol ((α*R*)-**3b**), (*S*)-1-((*S*)-1-methylpyrrolidin-2-yl)pentan-1-ol ((α*S*)-**3c**), and (*S*)-1,1,1,2,2,3,3,4,4,6,6,7,7,8,8,9,9,9-octadecafluoro-5-(1-methylpyrrolidin-2-yl)nonan-5-ol (**3d**) in 44-96% yields, as shown in Scheme 2. Lowering of the yields of (α*R*)- and (α*S*)-**3a** may be due to their high volatility.

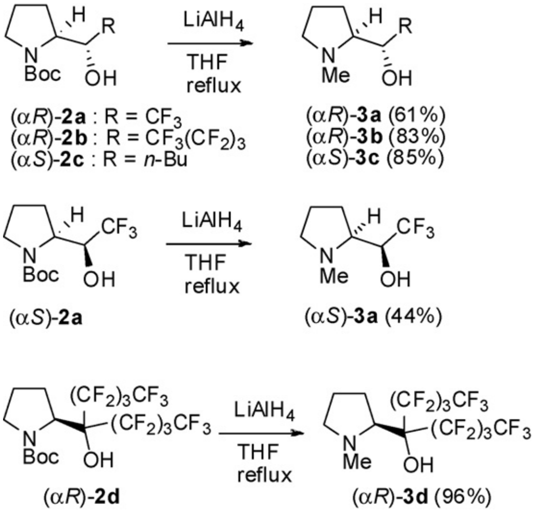
2.2. α-Trifluoromethyl, perfluorobutyl, n-butyl, and α,α-bis(perfluorobutyl)-N-methylprolinol 3-catalyzed acyl transfer reaction

The catalytic activity of the obtained α-perfluorobutyl-*N*-methylprolinol (α*R*)-**3b** in an acyl transfer reaction of 4-nitrophenyl 2-methoxyacetate (**4**) using 10 equiv. of CD_3OD at 25 ± 2 °C was examined and the percentages of methyl-d_3 2-methoxyacetate (**5**) and 4-nitrophenyl 2-methoxyacetate (**4**) were plotted as a function of time to analyze the pseudo-zero-order reactions, as shown in Fig. 1.

Fig. 1 shows that the product **5** was obtained in 31% yield after 10 h in the acyl transfer reaction. The turnover number (TON) using (α*R*)-**3b** was calculated to be 1.6.

The results of various other *N*-methylprolinol **3a,c,d**-catalyzed acyl transfer reactions of 4-nitrophenyl 2-methoxyacetate (**4**) using 10 equiv of CD_3OD, including TONs, are summarized in Table 1.

Interestingly, α-trifluoromethyl-*N*-methylprolinol (α*R*)-**3a** is the most effective catalyst and gave the product **5** in 89% yield (TON = 4.5). In the case of α-perfluorobutyl-*N*-methylprolinol (α*R*)-**3b**, the product **5** was obtained in only 31% yield (TON = 1.6). α-*n*-Butyl-*N*-methylprolinol (α*S*)-**3c** was less effective in the reaction than α-perfluorobutyl-*N*-methylprolinol (α*R*)-**3b**



Scheme 2. Synthesis of α-trifluoromethyl, perfluorobutyl, *n*-butyl, and α,α-bis(perfluorobutyl)-*N*-methylprolinol **3**.

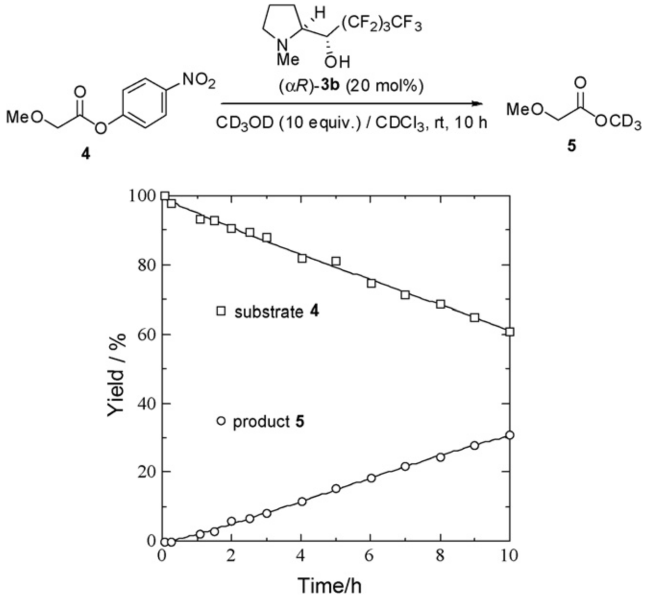
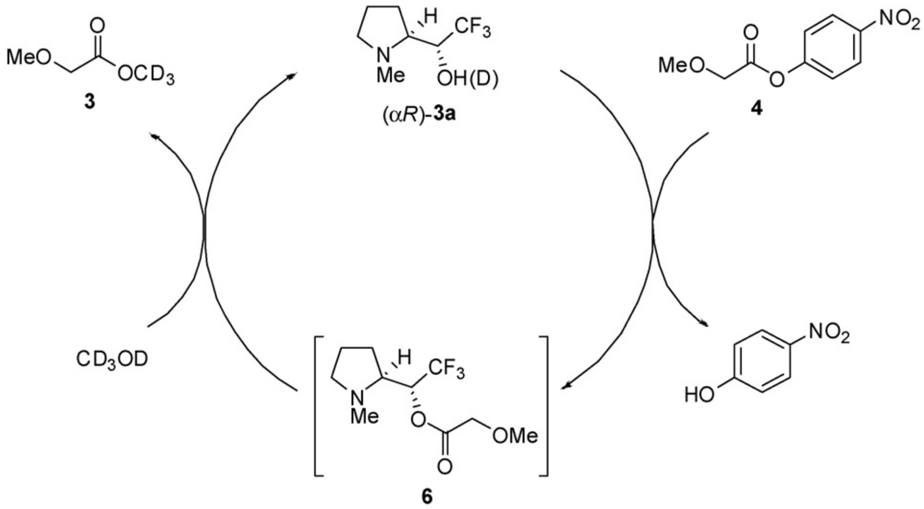


Fig. 1. Kinetics of α-perfluorobutyl-*N*-methylprolinol (α*R*)-**3b**-catalyzed acyl transfer reaction.



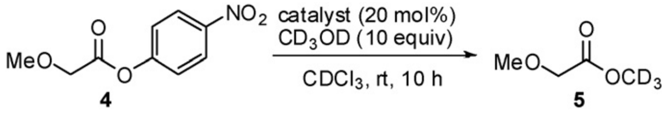
Scheme 3. Plausible reaction mechanism for the *N*-methylprolinol (α*R*)-**3a**–catalyzed acyl transfer reaction.

(22% yield, TON = 1.1). With α,α-bis(perfluorobutyl)-*N*-methylprolinol **3d**, the reaction did not progress at all (0% yield, TON = 0). When other diastereomer of (α*S*)-**3a** was used, conspicuous difference in the reaction rate was not observed (84% yield, TON = 4.3). The ester-exchange reactions using the catalysts **3a** and **3c** also obeyed the pseudo-zero-order kinetics.

Although, unfortunately, we could not detect the intermediate **6** in ^{1}H NMR measurement, based on the report by Sammakia [9a], a plausible reaction mechanism for the *N*-methylprolinol **3a**-catalyzed acyl transfer reaction may be considered as shown in Scheme 3.

4-Nitrophenyl 2-methoxyacetate (**4**) was nucleophilic-attacked by catalyst **3a** to produce the intermediate (*R*)-2,2,2-trifluoro-1-((*S*)-1-methylpyrrolidin-2-yl)ethyl 2-methoxyacetate (**6**). As soon as the formation of intermediate **6**,**6** may be nucleophilic-attacked by CD_3OD to afford methyl-d_3 2-methoxyacetate (**5**) and regenerate the catalyst **3a**. The introduction of a perfluoroalkyl group to the α-position of the prolinol would seem to have two effects. First, the acidity of the hydroxyl group of the catalyst **3** should increase, and consequently the alcoholate would be easily generated. Second, the leaving ability of catalyst **3** should increase and the elimination of catalyst **3** from the intermediate **6** should be accelerated in the catalytic acyl transfer reaction. In fact, α-trifluoromethyl- and perfluorobutyl-*N*-methylprolinols **3a,b** promoted the acyl transfer reaction more than *n*-butyl-*N*-methylprolinol **3c**. However, the introduction of two perfluorobutyl groups to the α-position was not effective. This result could be ascribed to the large steric hindrance of the tertiary alcohol moiety [9a]. Consequently, the acyl transfer reaction with α,α-bis(perfluorobutyl)-*N*-methylprolinol **3d** did not proceed, even though the hydroxyl group of *N*-methylprolinol **3d** is much more acidic than that of (α*R*)-perfluorobutyl-*N*-methylprolinol **3b**. In summary, as a potent electron-withdrawing group at the α-position of the hydroxyl group in the nucleophilic organocatalyst for the acyl transfer reaction, a trifluoromethyl group is much more suitable than a longer perfluorobutyl group, since the perfluorobutyl group may be too bulky to allow nucleophilic-attack to the ester carbonyl group.

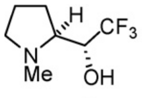
Table 1
N-Methylprolinol **3**-catalyzed acyl transfer reaction.



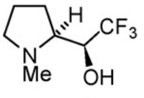
Catalyst	Product[a] (%)	Recovery of **4**[a] (%)	TON[b]
(α*R*)-**3a**	89	11	4.5
(α*S*)-**3a**	84	16	4.3
(α*R*)-**3b**	31	61	1.6
(α*S*)-**3c**	22	71	1.1
3d	0	97	0

[a] ^{1}H NMR yield.

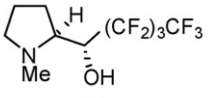
[b] Turn over number (mol of product/mol of catalyst).



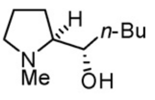
(α*R*)-**3a**



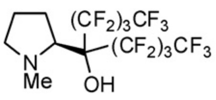
(α*S*)-**3a**



(α*R*)-**3b**



(α*S*)-**3c**



3d

3. Conclusion

In conclusion, various α-perfluoroalkylated *N*-methylprolinols **3** were prepared and their catalytic activities in the acyl transfer reaction of 4-nitrophenyl 2-methoxyacetate (**4**) were examined. As a result, introduction of trifluoromethyl group at α-position of *N*-methylprolinol **3** remarkably promoted the acyl transfer reaction of 4-nitrophenyl 2-methoxyacetate (**4**) with methanol-d_4. Catalytic asymmetric reactions using the α-perfluoroalkylprolinol derivatives are currently being investigated in our laboratory.

4. Experimental

Optical rotations were measured in Uvasol grade $CHCl_3$ (Merck) on a HORIBA SEPA-300. Melting points were obtained on a Yanagimoto MP-S2 micro-melting point apparatus and are uncorrected. IR spectra were measured on a SHIMADZU FT-IR 8100A spectrometer. ^{1}H NMR spectra were measured with a JEOL α-400 (400 MHz) FT-NMR spectrometer, a JNM-AL400 (400 MHz) FT-NMR spectrometer in deuteriochloroform ($CDCl_3$) solutions with tetramethylsilane (Me_4Si) as the internal standard. ^{13}C NMR spectra were measured with a JEOL α-400 (100 MHz) FT-NMR spectrometer, a JNM-AL400 (100 MHz) FT-NMR spectrometer in deuteriochloroform ($CDCl_3$) solutions with tetramethylsilane (Me_4Si) as the internal standard. ^{19}F NMR spectra were recorded on a JEOL α-400 (376 MHz) FT-NMR spectrometer, a JNM-AL400 (372 MHz) FT-NMR spectrometer in $CDCl_3$ solutions using trifluoroacetic acid (TFA) as the external standard. HRMS were measured on a JEOL JMS-700 mass spectrometer. All solvents were distilled over calcium hydride under argon. Anhydrous tetrahydrofuran (THF) and diethyl ether were purchased from Kanto Chemical Co., Inc. and directly used without any treatment. Trifluoromethyltrimethylsilane (CF_3SiMe_3) was gifted from the Tosoh F-Tech, Inc. (*S*)-*Tert*-butyl 2-((*R*)-2,2,2-trifluoro-1-hydroxyethyl)pyrrolidine-1-carboxylate ((α*R*)-**2a**), (*S*)-*tert*-butyl 2-((*S*)-2,2,2-trifluoro-1-hydroxyethyl)pyrrolidine-1-carboxylate ((α*S*)-**2a**), (*S*)-*tert*-butyl 2-(2,2,3,3,4,4,5,5,5-nonafluoropentanoyl)pyrrolidine-1-carboxylate ((α*R*)-**2b**), (*S*)-*tert*-butyl 2-((*S*)-1-hydroxypentyl)pyrrolidine-1-carboxylate ((α*S*)-**2c**), and (*S*)-*tert*-butyl 2-(1,1,1,2,2,3,3,4,4,6,6,7,7,8,8,9,9,9-octadecafluoro-5-hydroxynonan-5-yl)pyrrolidine-1-carboxylate (**2d**) were prepared by our previous report [6a].

4.1. Preparation of (R)-2,2,2-trifluoro-1-((S)-1-methylpyrrolidin-2-yl)ethanol ((αR)-3a) [6b]

To a suspension of $LiAlH_4$ (2 mmol, 0.076 g) in dry THF was added a dry THF solution of (α*R*)-**3c** (1 mmol, 0.269 g) at 0 °C under argon. After stirring at room temperature for 10 min, and reaction mixture was refluxed for 24 h. After the reaction mixture was cooled to 0 °C, water (5 ml) was added to the reaction mixture, followed by acidification to pH 2 with 10% HCl aq., washing with Et_2O (20 ml, 2×). After the reaction mixture was alkalified with conc. NaOH aq., extraction with CH_2Cl_2 (30 ml, 3×). The organic layer was washed with brine (70 ml), dried over Na_2SO_4, concentrated by distillation under reduced pressure. Purification of the residue by silica gel column chromatography (hexane–Et_2O = 1:1) gave (α*R*)-**3a** (61%, 0.112 g).

4.1.1. (R)-2,2,2-Trifluoro-1-((S)-1-methylpyrrolidin-2-yl)ethanol ((αR)-3a)

Yield 61%; $[\alpha]_D^{23}$ 15.6 (*c* = 1.01, $CHCl_3$); IR (KBr) 3092.6 (OH) cm^{-1}; HRMS (EI) found: *m*/*z* 182.0798. Calcd for $C_7H_{12}F_3NO$: M−H, 182.0793; mp 46.2–47.3 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 1.69–1.82 (3H, m), 2.05–2.18 (1H, m), 2.24–2.30 (1H, m), 2.49 (3H, s), 2.54–2.59 (1H, m), 3.09–3.14 (1H, m), 3.96 (1H, q, *J* = 7.48 Hz), 5.85 (1H, br s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.7 (s), 23.9 (s), 40.8 (s), 56.7 (s), 65.2 (s), 68.0 (q, *J* = 28.7 Hz), 125.01 (q, *J* = 282.7 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ −1.2 (3F, m).

4.1.2. (S)-Tert-butyl 2-((S)-2,2,2-trifluoro-1-hydroxyethyl)pyrrolidine-1-carboxylate ((αS)-2a)

Yield 44%; $[\alpha]_D^{22}$ −18.8 (*c* = 0.99, $CHCl_3$); IR (KBr) 3092.6 (OH) cm^{-1}; HRMS (EI) found: *m*/*z* 182.0798. Calcd for $C_7H_{12}F_3NO$: M−H, 182.0793; ^1H NMR (400 MHz, $CDCl_3$) δ 1.60–1.76 (3H, m), 2.02–2.13 (1H, m), 2.38–2.45 (1H, m), 2.41 (3H, s), 2.81–2.85 (1H, m), 3.05–3.09 (1H, m), 3.38–3.49 (1H, m), 5.13 (1H, br s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.9 (s), 32.6 (s), 43.0 (s), 57.4 (s), 62.5 (s), 72.1 (q, *J* = 29.5 Hz), 125.2 (q, *J* = 282.30 Hz) ^{19}F NMR (376 MHz, $CDCl_3$) δ −0.2 (3F, m).

4.1.3. (R)-2,2,3,3,4,4,5,5,5-Nonafluoro-1-((S)-1-methylpyrrolidin-2-yl)pentan-1-ol ((αR)-3b)

Yield 83%; $[\alpha]_D^{25}$ −0.25 (*c* = 1.00, $CHCl_3$); IR (KBr) 3077.2 (OH) cm^{-1}; HRMS (EI) found: *m*/*z* 332.0694. Calcd for $C_{10}H_{12}F_9NO$: M−H, 332.0697; ^1H NMR (400 MHz, $CDCl_3$) δ 1.64–1.82 (3H, m), 2.09–2.20 (1H, m), 2.46–2.52 (1H, m), 2.47 (3H, s), 3.04 (1H, ddd, *J* = 9.1, 4.5, 2.7 Hz), 3.11–3.16 (1H, m), 3.65 (1H, dt, *J* = 23.8, 3.1 Hz), 5.38 (1H, br s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.0 (s), 33.4 (s), 42.6 (s), 57.2 (s), 61.8 (s), 70.9 (dd, *J* = 28.7, 21.3 Hz), 105.2–121.9 (4C, m); ^{19}F NMR (376 MHz, $CDCl_3$) δ −52.1 to −51.2 (1F, m), −51.8 to −49.4 (2F, m), −47.4 to −47.3 (2F, m), −46.6 to −45.7 (1F, m), −5.3 (3F, tt, *J* = 9.9, 3.2 Hz).

4.1.4. (S)-1-((S)-1-Methylpyrrolidin-2-yl)pentan-1-ol ((αS)-3c)

Yield 85%, $[\alpha]_D^{25}$ −4.45 (*c* = 1.00, $CHCl_3$); IR (KBr) 3441.6 (OH) cm^{-1}; HRMS (EI) found: *m*/*z* 170.1554. Calcd for $C_{10}H_{21}NO$: M−H, 170.1546; ^1H NMR (400 MHz, $CDCl_3$) δ 0.91 (3H, t, *J* = 7.08 Hz), 1.26–1.97 (10H, m), 2.31–2.39 (2H, m), 2.45 (3H, s), 3.01–3.06 (1H, m), 3.16–3.20 (1H, m), 4.01 (1H, br s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0 (s), 22.8 (s), 24.5 (s), 28.4 (s), 29.11 (s), 35.0 (s), 44.6 (s), 57.4 (s), 70.0 (s) and 74.3 (s).

4.1.5. (S)-1,1,1,2,2,3,3,4,4,6,6,7,7,8,8,9,9,9-Octadecafluoro-5-(1-methylpyrrolidin-2-yl)nonan-5-ol (3d)

Yield 96%; $[\alpha]_D^{25}$ 6.23 (*c* = 1.00, $CHCl_3$); IR (KBr) 3493 (OH) cm^{-1}; HRMS (CI) Found *m*/*z* 552.0627. Calcd for $C_{14}H_{12}ONF_{18}$: M+H, 552.0631; ^1H NMR (400 MHz, $CDCl_3$) δ 1.82–1.89 (1H, m), 1.91–2.00 (1H, m), 2.09–2.14 (1H, m), 2.44 (3H, s), 2.52–2.58 (1H, m), 2.97–3.05 (1H, m), 3.32 (1H, t, *J* = 7.32 Hz), 6.47 (1H, br s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.5 (s), 27.1 (s), 46.3 (s), 55.1 (s), 71.0 (s), 80.8 (quint, *J* = 25.02 Hz), 106.0–121.9 (8C, m); ^{19}F NMR (376 MHz, $CDCl_3$) δ −49.8 to −45.3 (4F, m), −44.0 to −39.2 (4F, m), −35.9 to −30.6 (4F, m), −3.5 to −3.2 (6F, m).

4.2. A typical procedure of transesterification

Transesterification of *p*-nitrophenyl methoxyacetate were monitored by ^1H NMR at 400 MHz using a JEOL α-400 FT-NMR spectrometer. Chloroform-*d* was freshly distilled from calcium hydride immediately prior to each experiment. Samples were prepared from stock solutions of the ester and the catalyst, neat methanol-d_4, and *p*-methylanisole (as a standard). The chloroform-*d* solutions were 0.1 M in ester, 1.0 M in methanol, and 0.01 M in catalyst at total volume of 750 μL, plus 3 μL of standard. Reactants were combined directly into NMR tubes. Reactions were run at 25 ± 2 °C. An NMR spectrum was taken before the catalyst was added, and reaction progress was monitored by the disappearance of aromatic resonances of *p*-nitrophenyl methoxyacetate (**4**) and the appearance of methylene protons of methyl-d_3 methoxyacetate (**5**).

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