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Enantiopure fluorous amino-derivatives: synthesis and some applications in asymmetric organometallic catalysis

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Abstract—The preparation of (2*R*,3*R*)-1,4-bis[(1*H*,1*H*,2*H*,2*H*,3*H*,3*H*-perfluoroundecyl)oxy]butane-2,3-diol **5** from (4*R*,5*R*)-2,2-dimethyl-1,3-dioxolane-4,5-dimethanol is described. This fluorous diol **5** can be easily converted to the corresponding fluorous enantiopure diamine **8** and amino alcohol **12**. While diamine **8** afforded fluorous diimine **9**, amino alcohol **12** is the precursor of imino alcohol **13** and amino alcohol **14**. Enantioselectivities of up to 31% were obtained in the reduction of acetophenone using iridium or ruthenium complexes associated with these compounds.

1. Introduction

The use of nonconventional media such as water,[1,2] fluorous solvents,[3–6] supercritical fluids,[7] and ionic liquids,[8,9] in organic chemistry and particularly in homogeneous organometallic catalysis has now been thoroughly investigated. In the case of organometallic catalysis, the first investigations in these fields concerned the separation and eventually the recycling of the costly and often toxic organometallic catalyst. However, these new media can also offer the possibility to develop safe and environmentally friendly processes, with the additional advantage that new selectivities could eventually be observed.

Only a few examples of asymmetric organometallic catalysis using chiral fluorous ligands in liquid–liquid fluorous solvent/organic solvent systems, or even under homogeneous conditions in partly fluorinated solvents such as benzotrifluoride have been reported. Literature examples included the epoxidation of alkenes,[10–12] hydrolytic kinetic resolution of terminal epoxides,[13] alkylation of aldehydes,[14–20] hydrogen transfer reduction of ketones,[21,22] ruthenium-catalyzed hydrogenation of ketones[23] and dimethyl itaconate,[24] Heck reaction,[25,26] allylic oxidation of alkenes,[27] ene-reaction,[28] cyclopropanation reaction,[28] and palladium-catalyzed alkylation of allylic acetates.[26,27]

Chiral α-diamines possessing C_2 symmetry[29–31] as well as α-aminoalcohols[32,33] are particularly attractive in asymmetric synthesis. They are potential precursors of chiral ligands for the use in organometallic asymmetric catalysis, and have also been used themselves as ligands. We herein report a very simple and general approach to enantiopure fluorous amino alcohols and diamines starting from tartaric acid and some preliminary results of their use in hydrogen transfer reduction of acetophenone.

2. Results and discussion

The synthesis of the enantiopure fluorous diol **5**, precursor of the fluorous ligands, is described in Scheme 1. Allylation of chiral diol **1** with allyl bromide in DMF in the presence of sodium hydride afforded the bis-allyl ether **2** in 96% yield after column chromatography. Two fluorous ponytails were then introduced using Fish's methodology.[34] A free radical addition of heptadecafluorooctyl iodide to compound **2** in the presence of AIBN gave compound **3** in 84% yield, as a mixture of diastereoisomers. Reduction of compound **3** in dry benzotrifluoride using $HSnBu_3$ in the presence of AIBN afforded fluorous dioxolane **4** in 92% yield. The cleavage

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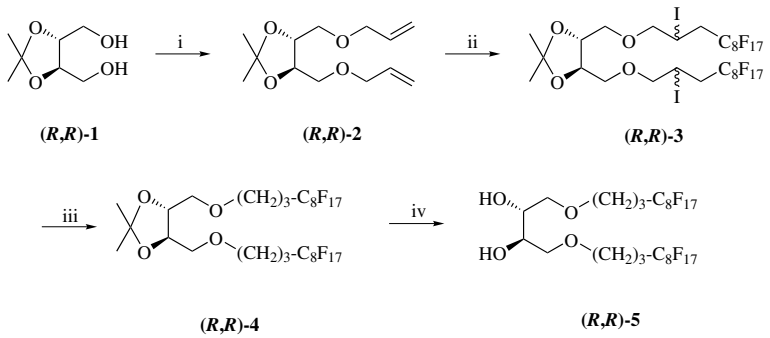


Scheme 1. Synthesis of fluorous diol (*R*,*R*)-**5**. Reagents: (i) CH_2=$CHCH_2Br$, NaH, DMF; (ii) *n*-$C_8F_{17}I$, AIBN; (iii) $HSnBu_3$, $C_6H_5CF_3$; (iv) CH_3OH, H^+.

of the acetonide moiety was performed by heating compound **4** in acidic methanol, allowing the formation of fluorous diol **5** in 81% yield.

The synthesis of fluorous diamine **8**, diimine **9**, aminoalcohol **12** and **14**, and imino alcohol **13**, are described in Scheme 2. Mesylation of diol **5** in a mixture of dichloromethane and trifluorotoluene using 3 equiv of mesyl chloride gave bismesylate **6** in 89% yield, while the use of only 1 equiv of mesyl chloride in dichloromethane as the solvent afforded monomesylate **10** in 39% yield. Reaction of dimesylate **6** with sodium azide in a mixture of DMSO and trifluorotoluene at 80 °C for 24 h gave the bisazido derivative **7** in 76% yield. The fluorous diamine **8** was obtained in 96% yield by the reduction of compound **7** with hydrogen in the presence of palladium. Condensation of this fluorous diamine **8** with 2 equiv of 3,5-bis(perfluorooctyl)benzaldehyde[35] in ethanol afforded the fluorous diimine **9** in 61% yield.

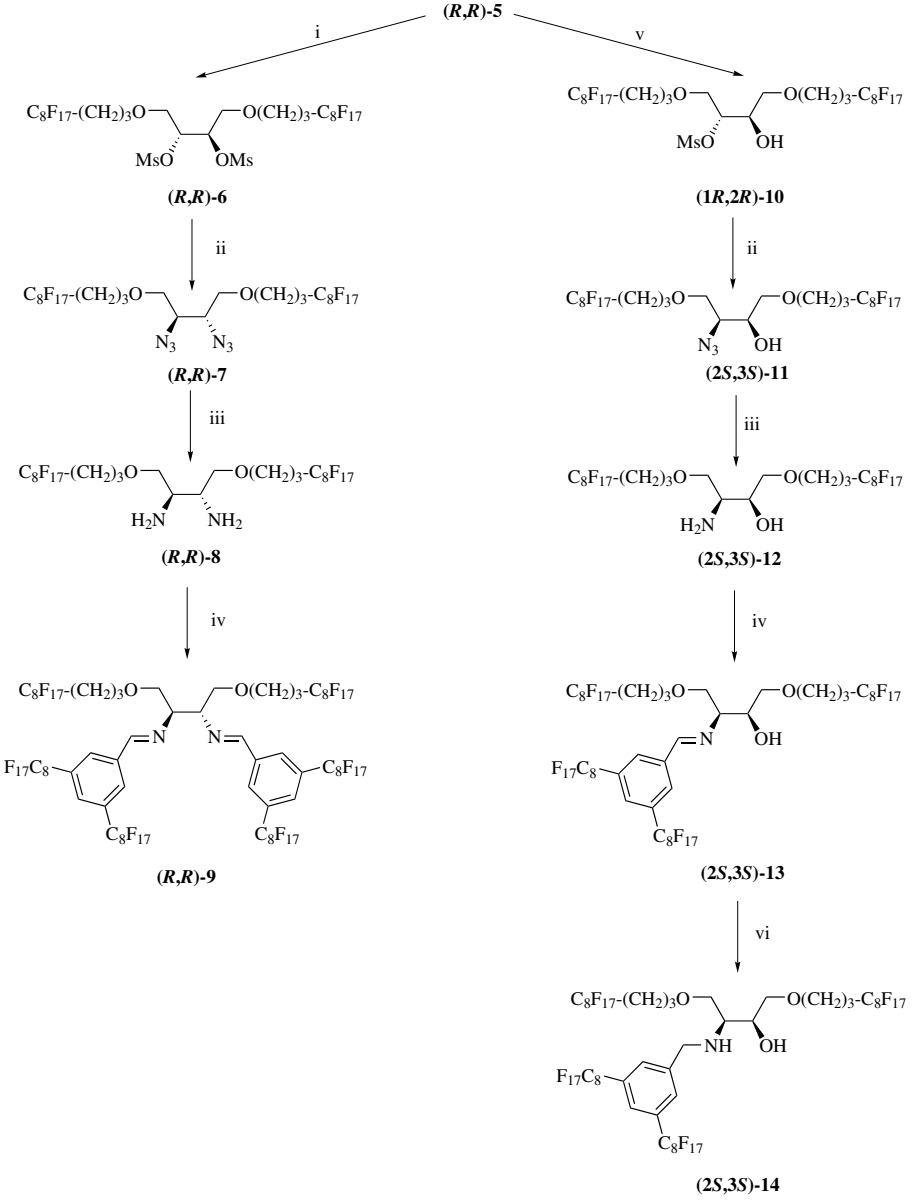
In a similar way, reaction of monomesylate **10** with sodium azide gave the corresponding monoazide **11** in 68% yield, whose reduction gave fluorous amino alcohol **12** in 90% yield. Condensation of amino alcohol **12** with 3,5-bis(perfluorooctyl)benzaldehyde[35] in ethyl alcohol afforded the fluorous imino alcohol **13** in 68% yield, whose reduction with sodium triacetoxyborohydride in a mixture of acetic acid and FC-113 (CCl_2FCF_3Cl) gave the corresponding fluorous amino alcohol **14** in 64% yield.

Following on from our interesting previous results concerning the use of enantiopure fluorous diamines[21] in asymmetric reduction of prochiral ketones, we tried to reduce fluorous diamine **9** using various reagents and in particular sodium triacetoxyborohydride in a mixture of acetic acid and FC-113. The only product formed was the fluorous imidazoline **16**, probably via the intermediate **15** (Scheme 3). The formation of this compound is in agreement with the results concerning the reduction of *N*,*N*′-dibenzylidene-2,3-diamino-2,3-dimethylbutane with $NaBH_4$, leading to the formation of *N*-benzyl-4,4,5,5-tetramethyl-2-phenylimidazoline.[36]

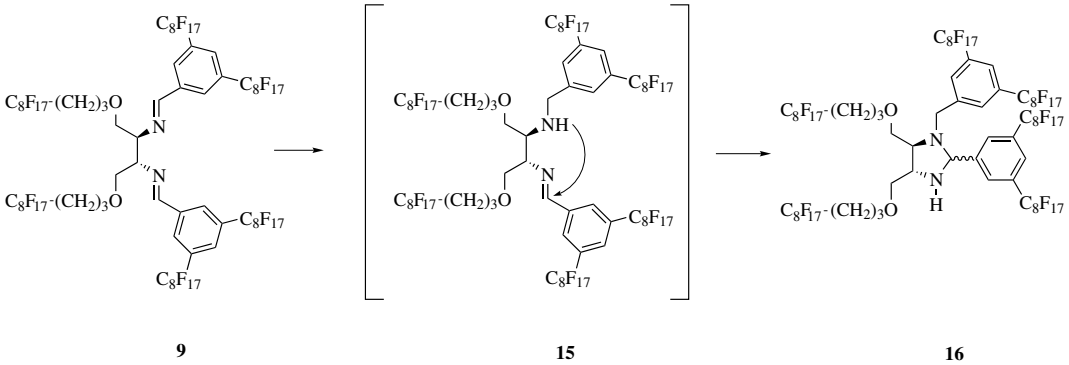
As we expected to use some of these compounds as ligands in the organometallic catalysis, it was important to know the solubility of compounds **9**, **13**, and **14**, in biphasic solvent combinations.[37] The liquid–liquid partition coefficients P ($P = c_{\text{fluorous phase}}/c_{\text{organic phase}}$) for these compounds between FC-72 (a mixture of perfluorohexanes) as the fluorous solvent and various organic solvents are listed in Table 1.

It is noteworthy that fluorous diamine **8** and aminoalcohol **12**, which have a quite similar fluorine content (62.11% and 62.05%, respectively), had almost the same partition coefficients whatever the organic solvent used. The highest partition coefficients were observed for fluorous diimine **9**, having the highest fluorine content (67.08%). Diamine **8** and aminoalcohol **12** were more soluble in ethanol than in FC-72. This was probably due to the presence of hydrogen bonds between the hydroxyl or amino function of these ligands and ethanol, or the formation of an intramolecular hydrogen bond.[38] The higher partition coefficients observed for compounds **9** and **14** going from toluene to acetonitrile could be related to the presence of aromatic rings in these substrates.

In a preliminary study, fluorous compounds **8**, **9**, and **12**–**14**, in association with $[Ir(COD)Cl]_2$ or $[Ru(p\text{-cymene})Cl_2]_2$ were tested in the asymmetric reduction of acetophenone with isopropanol as the hydride source in the presence of perfuoromethylcyclohexane as the fluorous solvent at 70 °C (Table 2). Although the reduction was almost quantitative with all the ligands used and whatever the catalyst precursor, the highest enantioselectivities were obtained in the presence of fluorous diimine **9** associated with $[Ir(COD)Cl]_2$ or the amino alcohol **13** associated with $[Ru(p\text{-cymene})Cl_2]_2$ (31% and 30% ee, respectively) (Table 2, entries 3 and 5). Conversely, fluorous diamine **8**, imino alcohol **13**, or amino alcohol **14**, gave lower enantioselectivities. In order to know the potentiality of these ligands in the recycling of the catalyst, we used the catalyst obtained from $[Ir(COD)Cl]_2$ and ligand **9**. The two phases obtained after the first reduction (Table 2, entry 3) were separated upon cooling at 0 °C, and the fluorous phase containing the catalyst used in a subsequent hydrogen transfer reaction. If almost complete conversion was observed after 24 h reaction, the obtained enantioselectivity was quite low (8% ee) (Table 2, entry 3 bis). The very low ee was probably due to the degradation of the fluorous bisdimine **9**, as shown previously.[22]



Scheme 2. Syntheses of fluorous diimino alcohol (*R*,*R*)-**9**, amino alcohols (2*S*,3*S*)-**12** and (2*S*,3*S*)-**14**, and imino alcohol (2*S*,3*S*)-**13**. Reagents: (i) MsCl (3 equiv), Et_3N, $CH_2Cl_2/C_6H_5CF_3$; (ii) NaN_3, $DMSO/C_6H_5CF_3$; (iii) H_2, Pd/C, CH_3CO_2Et; (iv) 3,5-bis(C_8F_{17})C_6H_3CHO, C_2H_5OH, reflux; (v) MsCl (1 equiv), C_5H_5N; (vi) $NaBH(OAc)_3$, CH_3CO_2H, FC-113.



Scheme 3.

Table 1. Partition coefficients for some fluorous compounds

Compound	F content (wt%)	Solvents	P[a]
8	62.11	$C_6H_5CH_3$/FC-72	2.3
		CH_3CN/FC-72	3.4
		C_2H_5OH/FC-72	0.4
9	67.08	$C_6H_5CH_3$/FC-72	9.8
		CH_3CN/FC-72	32.3
		C_2H_5OH/FC-72	6.4
12	62.05	$C_6H_5CH_3$/FC-72	3.6
		CH_3CN/FC-72	6.0
		C_2H_5OH/FC-72	0.4
13	65.72	$C_6H_5CH_3$/FC-72	12.3
		CH_3CN/FC-72	13.9
		C_2H_5OH/FC-72	6.7
14	65.66	$C_6H_5CH_3$/FC-72	4.9
		CH_3CN/FC-72	11.8
		C_2H_5OH/FC-72	3.5

[a] In a 50:50 (v/v) mixture of FC-72/organic solvent at 25 °C. $P = c_{\text{fluorous phase}}/c_{\text{organic phase}}$.

3. Conclusion

A convenient and ready access to various enantiopure fluorous diamines, amino alcohols, and diimines possessing a high fluorine content has been described. These fluorous compounds have been used in the hydrogen transfer reduction of acetophenone in an asymmetric way in a perfluoromethylcyclohexane/isopropanol mixture in association with rhodium or iridium complexes. Although the conversion was quantitative whatever the ligand used, an enantioselectivity of up to 31% ee was obtained only in the presence of fluorous diimine **9** or fluorous amino alcohol **13**. The application of this methodology for the preparation of similar but more bulky compounds is currently in progress in our laboratory, as well as the application of these fluorous amino alcohols and diamines in other catalytic reactions.

4. Experimental

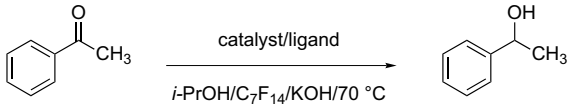
4.1. General

Solvents were purified by standard methods and dried if necessary. All commercially available reagents were used as received. The preparation of 3,5-bis(perfluorooctyl)benzaldehyde has already been described.[35] Reactions involving organometallic catalysis were carried out in a Schlenk tube under an inert atmosphere. Column chromatography was performed on silica gel 60 (230–240 mesh, Merck). Melting points (uncorrected) were determined with a capillary melting point apparatus Büchi SMP-20. Optical rotations were recorded using a Perkin–Elmer 241 polarimeter. The NMR spectra (^{1}H: 300 MHz, ^{13}C: 75.4 MHz, ^{19}F: 282 MHz) were recorded on a Bruker 300 MHz instrument with Me_4Si, $CDCl_3$, $CFCl_3$ as the internal standard, respectively. Conversion and enantiomeric excess were determined by GC using a capillary Quadrex OV1 column (30 m × 0.25 mm) and a capillary Cyclodex-β column (30 m × 0.25 mm), respectively.

4.2. (4*R*,5*R*)-Bis[(allyloxy)methyl]-2,2-dimethyl-1,3-dioxolane 2

To a solution of (4*R*,5*R*)-2,2-dimethyl-1,3-dioxolane-4,5-dimethanol (1.0 g, 6.17 mmol) in dry DMF (20 mL) cooled at 0 °C was added under nitrogen NaH (330 mg, 13.55 mmol). After being stirred for 15 min at 0 °C, allyl bromide (1.28 mL, 14.8 mmol) was slowly added, and the mixture stirred at rt for 2 h. A saturated aqueous solution of ammonium chloride (10 mL) was added, followed by diethyl ether (40 mL). The organic solution was separated and the aqueous phase extracted by diethyl ether (3 × 15 mL). Evaporation of the solvent

Table 2. Catalytic hydrogen transfer reduction of acetophenone using some chiral ligands[a]



Entry	Ligand	Complex	Time (h)	Conversion (%)[b]	Ee (%) (*R*)[b]
1	**8**	$[Ir(COD)Cl]_2$	4	98	8
2	**8**	$[Ru(p\text{-cymene})Cl_2]_2$	24	53	6
3	**9**	$[Ir(COD)Cl]_2$	24	95	31
3 Bis[c]			24	92	8
4	**12**	$[Ir(COD)Cl]_2$	24	97	7
5	**12**	$[Ru(p\text{-cymene})Cl_2]_2$	2	96	30
6	**13**	$[Ir(COD)Cl]_2$	24	98	2
7	**13**	$[Ru(p\text{-cymene})Cl_2]_2$	5	98	14
8	**14**	$[Ir(COD)Cl]_2$	48	69	7
9	**14**	$[Ru(p\text{-cymene})Cl_2]_2$	6	97	12

[a] Reaction conditions: 5 mL perfluoromethylcyclohexane; 5 mL *i*-PrOH; 70 °C; [substrate] = 5×10^{-3} mmol L^{-1}; [substrate]/[catalyst] = 20; [KOH]/[catalyst] = 5.
[b] Determined by capillary GC on a Cyclodex-β chiral column and by comparison with an authentic sample.
[c] Recycling experiment.

under reduced pressure gave a residue that was purified by column chromotography on silica, using petroleum ether/ethyl acetate (9:1) as the eluent, to give compound **2** (1.43 g, 96% yield). Colorless oil; R_f 0.64; $[\alpha]_D^{25} = +13.3$ (c 1, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 1.42 (6H, s, CH_3), 3.56–3.59 (4H, m, CH_2O), 3.98–4.01 (2H, m, CHO), 4.04–4.06 (4H, m, $OCH_2CH=$), 5.19 (2H, ddd, J = 10.5, 2.8, 1.5 Hz, $=CH_2$), 5.27 (2H, ddd, J = 17.1, 3.2, 1.5 Hz, $=CH_2$), 5.84–5.97 (2H, m, –CH=); ^{13}C NMR ($CDCl_3$): δ 27.4 (CH_3), 71.1 (CH_2O), 72.9 ($OCH_2CH=$), 77.9 (CHO), 110.1 (CMe_2), 117.6 ($CH=CH_2$), 134.9 ($CH=CH_2$). Anal. Calcd for $C_{13}H_{22}O_4$: C, 64.44; H, 9.15. Found: C, 63.92; H, 9.10.

4.3. 2,2-Dimethyl-(4*R*,5*R*)-bis{[(2-(*R*,*S*)-iodo-1*H*,1*H*,2*H*,3*H*,3*H*-perfluoroundecyl)oxy]methyl}-1,3-dioxolane 3

A mixture of allylic ether **2** (5.0 g, 20.6 mmol), heptadecafluorooctyl iodide (24.8 g, 45.4 mmol), and AIBN (170 mg, 1.03 mmol) was heated at 75 °C for 1 h. The solution was cooled at rt, at which point AIBN (170 mg, 1.03 mmol) was added, and the mixture then heated again at 75 °C for 1 h. After another addition of AIBN (170 mg, 1.03 mmol), the solution was heated at 75 °C for 12 h. The solution was cooled to rt and the residue purified by flash chromatography on silica, using petroleum ether/ethyl acetate (10:1) as the eluent, to give compound **3** (23.09 g, 84% yield). Colorless oil; R_f 0.48; ^1H NMR ($CDCl_3$): δ 1.42 (6H, s, CH_3), 2.61–2.84 (2H, m, CH_2CF_2), 2.93–3.17 (2H, m, CH_2CF_2), 3.72–3.84 (8H, m, CH_2O), 4.07–4.09 (2H, m, CHO), 4.34–4.44 (2H, m, CHI); ^{13}C NMR ($CDCl_3$): δ 14.4 (CHI), 14.5 (CHI), 27.0 (CH_3), 38.0 (t, J = 20.8 Hz, CH_2CF_2), 71.4 (CH_2O), 71.5 (CH_2O), 76.5 (CHO), 110.1 (CMe_2), 114.4–119.8 (CF_2, CF_3); ^{19}F NMR ($CDCl_3$): δ −127.2 (4F, m, CF_2), −124.5 (4F, m, CF_2), −123.8 (4F, m, CF_2), −123.0 (8F, m, CF_2), −122.6 (4F, m, CF_2), −114.5 (4F, m, CF_2), −82.1 (6F, t, J = 9.6 Hz, CF_3). Anal. Calcd for $C_{29}H_{22}O_4F_{34}I_2$: C, 26.09; H, 1.66. Found: C, 26.28; H, 1.77.

4.4. 2,2-Dimethyl-(4*R*,5*R*)-bis[(1*H*,1*H*,2*H*,2*H*,3*H*,3*H*-perfluoroundecyloxy)methyl]-1,3-dioxolane 4

To a solution of compound **3** (5 g, 3.75 mmol) and AIBN (123 mg, 0.75 mmol) in trifluorotoluene (15 mL) was added under nitrogen $HSnBu_3$ (3.0 mL, 11.25 mmol). After being stirred for 24 h at 80 °C, the solvent was evaporated, and the residue was purified by flash chromatography on silica, using petroleum ether/ethyl acetate (8:1) as the eluent, to give compound **4** (3.73 g, 92% yield). Colorless oil; R_f 0.44; $[\alpha]_D^{25} = +3.2$ (c 0.76, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 1.46 (6H, s, CH_3), 1.85–1.94 (4H, m, CH_2), 2.16–2.20 (4H, m, CH_2CF_2), 3.51–3.63 (8H, m, CH_2O), 3.99 (2H, m, CHO); ^{13}C NMR ($CDCl_3$): δ 20.9 (CH_2), 27.1 (CH_3), 28.1 (t, J = 23.0 Hz, CH_2CF_2), 70.3 (CH_2O), 71.8 (CH_2O), 77.7 (CHO), 110.1 (CMe_2), 117.0–119.6 (CF_2, CF_3); ^{19}F NMR ($CDCl_3$): δ −127.1 (4F, m, CF_2), −124.3 (4F, m, CF_2), −123.7 (4F, m, CF_2), −122.8 (12F, m, CF_2), −115.3 (4F, m, CF_2), −82.0 (6F, t, J = 10.3 Hz, CF_3). Anal. Calcd for $C_{29}H_{24}O_4F_{34}$: C, 32.16; H, 2.24. Found: C, 32.41; H, 2.30.

4.5. (2*R*,3*R*)-1,4-Bis(1*H*,1*H*,2*H*,2*H*,3*H*,3*H*-perfluoroundecyloxy)butane-2,3-diol 5

A solution of compound **4** (3.2 g, 2.96 mmol) in methanol (30 mL) containing 1 M HCl (5 mL) was heated at reflux for 5 h. Then methanol (20 mL) and 1 M HCl (4.3 mL) were added and the solution heated at reflux for 2 h. The solvent was evaporated, a saturated aqueous solution of $NaHCO_3$ added, and the mixture extracted with diethyl ether (4 × 20 mL). Evaporation of the solvent gave a residue that was purified by flash chromatography on silica, using petroleum ether/ethyl acetate (2:1) as the eluent, to give compound **5** (2.5 g, 81% yield). White solid; mp 72–74 °C; R_f 0.26; $[\alpha]_D^{25} = +0.7$ (c 0.4, Et_2O); ^1H NMR ($CDCl_3$): δ 1.85–1.95 (4H, m, CH_2), 2.09–2.24 (4H, m, CH_2CF_2), 2.67 (2H, br s, OH), 3.55–3.59 (8H, m, CH_2O), 3.82 (2H, m, CHO); ^{13}C NMR ($CDCl_3$): δ 21.4 (CH_2), 28.6 (t, J = 23.0 Hz, CH_2CF_2), 70.7 (CH_2O), 71.1 (CH_2O), 73.2 (CHO), 114.0–128.1 (CF_2, CF_3); ^{19}F NMR ($CDCl_3$): δ −126.6 (4F, m, CF_2), −123.9 (4F, m, CF_2), −123.2 (4F, m, CF_2), −122.4 (12F, m, CF_2), −114.8 (4F, m, CF_2), −81.2 (6F, CF_3). Anal. Calcd for $C_{26}H_{20}O_4F_{34}$: C, 29.94; H, 1.93. Found: C, 29.90; H, 1.88.

4.6. (2*R*,3*R*)-1,4-Bis(1*H*,1*H*,2*H*,2*H*,3*H*,3*H*-perfluoroundecyloxy)butane-2,3-diyl dimethanesulfonate 6

To a solution of diol **5** (2.35 g, 2.25 mmol) and triethylamine (0.94 mL, 6.76 mmol) in a 7:3 mixture of CH_2Cl_2 and trifluorotoluene (10 mL) was added at 0 °C mesyl chloride (0.42 mL, 6.41 mmol). After being stirred for 2 h at 0 °C, water (10 mL) was added, and the resulting mixture extracted with diethyl ether (3 × 10 mL). Evaporation of the solvent gave a residue that was purified by flash chromatography on silica, using petroleum ether/ethyl acetate (3:1) as the eluent, to give compound **6** (2.4 g, 89% yield). White solid; mp 82–84 °C; R_f 0.40; $[\alpha]_D^{25} = +6.8$ (c 0.5, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 1.85–1.95 (4H, m, CH_2), 2.16–2.20 (4H, m, CH_2CF_2), 3.11 (6H, s, CH_3), 3.53–3.65 (4H, m, CH_2O), 3.70–3.81 (4H, m, CH_2O), 4.97 (2H, m, CHO); ^{13}C NMR ($CDCl_3$): δ 21.6 (CH_2), 28.6 (t, J = 22.3 Hz, CH_2CF_2), 39.6 (CH_3), 70.2 (CH_2O), 71.0 (CH_2O), 78.7 (CHO), 113.7–126.8 (CF_2, CF_3); ^{19}F NMR ($CDCl_3$): δ −126.6 (4F, m, CF_2), −123.9 (4F, m, CF_2), −123.2 (4F, m, CF_2), −122.4 (12F, m, CF_2), −114.9 (4F, m, CF_2), −81.3 (6F, t, J = 10.3 Hz, CF_3). Anal. Calcd for $C_{28}H_{24}O_8F_{34}S_2$: C, 28.05; H, 2.02. Found: C, 28.19; H, 1.90.

4.7. (2*R*,3*R*)-1,4-Bis(1*H*,1*H*,2*H*,2*H*,3*H*,3*H*-perfluoroundecyloxy)-2,3-diazidobutane 7

A mixture of dimesylate **6** (1.8 g, 1.5 mmol) and sodium azide (340 mg, 5.53 mmol) in DMSO (8 mL)-trifluorotoluene (2 mL) was heated at 80 °C for 24 h. The solution was cooled at rt, a saturated aqueous solution of NaCl (10 mL) was added, and the resulting mixture was extracted with diethyl ether (3 × 10 mL). Evaporation of the solvent gave a residue that was purified by flash chromatography on silica, using petroleum ether/ethyl

acetate (6:1) as the eluent, to give compound **7** (1.24 g, 76% yield). White solid; mp 52–54 °C; R_f 0.66; $[\alpha]_D^{25} = +13.3$ (*c* 0.5, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 1.87–1.96 (4H, m, CH_2), 2.15–2.24 (4H, m, CH_2CF_2), 3.55–3.60 (4H, m, CH_2O), 3.69 (6H, bm, CH_2O, CHN_3); ^{13}C NMR ($CDCl_3$): δ 20.9 (CH_2), 28.0 (t, $J = 22.3$ Hz, CH_2CF_2), 61.2 (CHN_3), 70.2 (CH_2O), 70.9 (CH_2O), 115.6–119.4 (CF_2, CF_3); ^{19}F NMR ($CDCl_3$): δ −127.5 (4F, m, CF_2), −124.6 (4F, m, CF_2), −123.9 (4F, m, CF_2), −123.0 (12F, m, CF_2), −115.6 (4F, m, CF_2), −82.4 (6F, t, $J = 10.3$ Hz, CF_3). Anal. Calcd for $C_{26}H_{18}O_2F_{34}N_6$: C, 28.57; H, 1.66. Found: C, 28.41; H, 1.52.

4.8. (2*R*,3*R*)-1,4-Bis(1*H*,1*H*,2*H*,2*H*,3*H*,3*H*-perfluoroundecyloxy)-2,3-diamino butane 8

A mixture of diazido **7** (2 g, 1.9 mmol) and Pd/C (130 mg) in ethyl acetate (20 mL) was stirred under hydrogen (1 atm) at rt for 24 h. After filtration of the solution on Celite, the solvent was evaporated to give compound **8** (1.9 g, 96% yield) as a solid. White solid; mp 66–68 °C; $[\alpha]_D^{25} = -1.8$ (*c* 0.5, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 1.50 (4H, br s, NH_2), 1.85–1.93 (4H, m, CH_2), 2.11–2.20 (4H, m, CH_2CF_2), 2.93–2.96 (2H, m, C*H*NH_2), 3.6–3.53 (8H, m, CH_2O); ^{13}C NMR ($CDCl_3$): δ 21.1 (CH_2), 28.3 (t, $J = 22.3$ Hz, CH_2CF_2), 52.9 ($CHNH_2$), 70.0 (CH_2O), 74.5 (CH_2O), 114.5–119.4 (CF_2, CF_3); ^{19}F NMR ($CDCl_3$): δ −126.7 (4F, m, CF_2), −124.0 (4F, m, CF_2), −123.3 (4F, m, CF_2), −122.5 (12F, m, CF_2), −115.0 (4F, m, CF_2), −81.5 (6F, t, $J = 10.3$ Hz, CF_3). HRMS (EI) calcd for $C_{26}H_{23}O_2F_{34}N_2$: 1041.1216. Found: 1041.1221.

4.9. (2*R*,3*R*)-*N*,*N*′-Bis{(1*E*)-[3,5-bis(perfluorooctyl)phenyl]methylene}-1,4-bis(1*H*,1*H*,2*H*,2*H*,3*H*,3*H*-perfluoroundecyloxy)butane-2,3-diamine 9

A solution of fluorous diamine **8** (0.50 g, 0.48 mmol) in ethyl alcohol (5 mL) was added to 3,5-bis(*n*-perfluorooctyl)benzaldehyde[35] (0.90 g, 0.96 mmol) dissolved in hot ethyl alcohol (15 mL). After being stirred under reflux for 6 h, the solution was cooled to rt, and the solvent evaporated under reduced pressure. Treatment of the residue with pentane gave a solid that was filtered, washed with cold ethyl alcohol and pentane to afford the fluorous diimine **9** (845.8 mg, 61% yield). White solid; mp 83–85 °C; R_f 0.74 (petroleum ether/ethyl acetate 4:1); $[\alpha]_D^{25} = +16.1$ (*c* 0.5, FC-72); ^1H NMR ($CDCl_3 + CF_2ClCCl_2F$): δ 1.83–1.86 (4H, m, CH_2), 2.07–2.10 (4H, m, CH_2CF_2), 3.48–3.50 (2H, m, >CH–N=), 3.58–3.66 (4H, m, CH_2O), 3.81–3.89 (4H, m, CH_2O), 7.81 (2H, s, H_{arom}), 8.10 (4H, s, H_{arom}), 8.32 (2H, s, –CH=N); ^{13}C NMR ($CDCl_3 + CF_2ClCCl_2F$): δ 21.1 (CH_2), 28.2 (t, $J = 22.3$ Hz, CH_2CF_2), 69.9 (CH_2O), 71.3 (CH_2O), 71.9 (CHN), 127.5 (C_{arom}), 129.8 (C_{arom}), 131.3 (t, $J = 25.3$ Hz, C_{arom}), 138.0 (C_{arom}), 159.8 (HC=N); ^{19}F ($CDCl_3 + CF_2ClCCl_2F$): δ −126.8 (12F, m, CF_2), −124.2 (12F, m, CF_2), −123.4 (12F, m, CF_2), −122.6 (36F, m, CF_2), −115.0 (12F, m, CF_2), −81.5 (18F, t, $J = 10.3$ Hz, CF_3). Anal. Calcd for $C_{72}H_{26}O_2F_{102}N_2$: C, 29.93; H, 0.91. Found: C, 29.46; H, 0.90.

4.10. (1*R*,2*R*)-3-(1*H*,1*H*,2*H*,2*H*,3*H*,3*H*-perfluoroundecyloxy)-1-[(1*H*,1*H*,2*H*,2*H*,3*H*,3*H*-perfluoroundecyloxy)methyl]-2-hydroxypropyl methanesulfonate 10

To a solution of diol **5** (3.2 g, 3.04 mmol) in pyridine (8 mL) was slowly added at 0 °C mesyl chloride (0.22 mL, 2.9 mmol). After being stirred for 30 min at 0 °C, then at rt for 12 h, water (10 mL) was added, and the resulting mixture extracted with CH_2Cl_2 (3 × 20 mL). The combined organic solutions were washed with a saturated aqueous solution of $CuSO_4$ (5 × 10 mL) and then dried over Na_2SO_4. Evaporation of the solvent gave a residue that was purified by flash chromatography on silica, using petroleum ether/ethyl acetate (1:1) as the eluent, to give compound **10** (1.33 g, 39% yield). White solid; mp 74–76 °C; $R_f = 0.72$; $[\alpha]_D^{25} = +6.4$ (*c* 0.45, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 1.85–1.94 (4H, m, CH_2), 2.16–2.20 (4H, m, CH_2CF_2), 2.52 (1H, d, $J = 5.8$ Hz, OH), 3.10 (6H, s, CH_3), 3.51–3.61 (4H, m, CH_2O), 3.71–3.82 (4H, m, CH_2O), 3.99 (1H, m, CHOMs), 4.82 (1H, m, C*H*OH); ^{13}C NMR ($CDCl_3$): δ 21.1 (CH_2), 28.2 (t, $J = 22.3$ Hz, CH_2CF_2), 38.9 (CH_3), 70.1 (CHOMs), 70.4 (CH_2O), 70.7 (CH_2O), 71.2 (CH_2O), 81.1 (CHOH), 115.0–123.1 (CF_2, CF_3); ^{19}F NMR ($CDCl_3$): δ −126.7 (4F, m, CF_2), −124.0 (4F, m, CF_2), −123.3 (4F, m, CF_2), −122.4 (12F, m, CF_2), −114.9 (4F, m, CF_2), −81.4 (6F, t, $J = 10.3$ Hz, CF_3). Anal. Calcd for $C_{27}H_{22}O_6F_{34}S$: C, 28.93; H, 1.98. Found: C, 28.93; H, 1.90.

4.11. (2*S*,3*S*)-3-Azido-1,4-bis(1*H*,1*H*,2*H*,2*H*,3*H*,3*H*-perfluoroundecyloxy)butan-2-ol 11

A mixture of monomesylate **10** (1.2 g, 1.1 mmol) and sodium azide (100 mg, 1.61 mmol) in DMF (6 mL) was heated at reflux for 4 h. The solution was cooled at rt, water (10 mL) added, and the resulting mixture extracted with diethyl ether (3 × 15 mL). Evaporation of the solvent gave a residue that was purified by flash chromatography on silica, using petroleum ether/ethyl acetate (4:1) as the eluent, to give compound **11** (798 mg, 68% yield). White solid; mp 62–64 °C; R_f 0.42; $[\alpha]_D^{25} = +9.8$ (*c* 0.5, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 1.86–1.95 (4H, m, CH_2), 2.12–2.24 (4H, m, CH_2CF_2), 2.49 (1H, d, $J = 5.6$ Hz, OH), 3.52–3.82 (10H, m, CH_2O, CHOH, CHN_3); ^{13}C NMR ($CDCl_3$): δ 21.1 (CH_2), 28.2 (t, $J = 22.3$ Hz, CH_2CF_2), 62.6 (CHN_3), 70.2 (CHOH), 70.3 (CH_2O), 71.3 (CH_2O), 71.9 (CH_2O), 116.0–122.3 (CF_2, CF_3); ^{19}F NMR ($CDCl_3$): δ −126.7 (4F, m, CF_2), −124.0 (4F, m, CF_2), −123.3 (4F, m, CF_2), −122.5 (12F, m, CF_2), −114.9 (4F, m, CF_2), −81.4 (6F, t, $J = 10.3$ Hz, CF_3). Anal. Calcd for $C_{26}H_{19}O_3F_{34}N_3$: C, 29.24; H, 1.79. Found: C, 29.23; H, 1.74.

4.12. (2*S*,3*S*)-3-Amino-1,4-bis(1*H*,1*H*,2*H*,2*H*,3*H*,3*H*-perfluoroundecyloxy)butan-2-ol 12

A mixture of hydroxyazide **11** (1.06 g, 1 mmol) and Pd/C (130 mg) in ethyl acetate (20 mL) was stirred under hydrogen (1 atm) at rt for 24 h. After filtration of the solution on Celite, the solvent was evaporated to give

compound **12** (937 mg, 90% yield) as a solid. White solid; mp 68–70 °C; $[\alpha]_D^{25} = +1.2$ (*c* 0.5, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 1.84–1.82 (4H, m, CH_2), 1.93 (3H, br s, OH, NH_2), 2.04–2.16 (4H, m, CH_2CF_2), 3.00 (1H, m, C*H*NH_2), 3.36–3.50 (8H, m, CH_2O), 3.64 (1H, m, C*H*OH); ^{13}C NMR ($CDCl_3$): δ 21.1 (CH_2), 28.3 (t, $J = 20.3$ Hz, *C*H_2CF_2), 53.3 ($CHNH_2$), 70.1 (CH_2O), 70.3 (CH_2O), 72.2 (CHOH), 72.8 (CH_2O), 73.3 (CH_2O), 115.6–119.9 (CF_2, CF_3); ^{19}F NMR ($CDCl_3$): δ −126.6 (4F, m, CF_2), −123.9 (4F, m, CF_2), −123.1 (4F, m, CF_2), −122.3 (12F, m, CF_2), −114.8 (4F, m, CF_2), −81.3 (6F, t, $J = 9.2$ Hz, CF_3). HRMS (EI) calcd for $C_{26}H_{22}O_3F_{34}N$: 1042.1057. Found: 1042.1055.

4.13. (2*S*,3*S*)-3-({(1*E*)-[3,5-bis(perfluorooctyl)phenyl]-methylene}amino)-1,4-bis(1*H*,1*H*,2*H*,2*H*,3*H*,3*H*-perfluoroundecyloxy)butan-2-ol 13

Fluorous 3,5-bis(*n*-perfluorooctyl)benzaldehyde[35] (0.40 g, 0.42 mmol) and fluorous amino alcohol **12** (0.45 g, 0.43 mmol) were dissolved in hot ethyl alcohol (5 mL). After being stirred at rt for 4 h, the formed solid was filtered, washed with cold ethyl alcohol, and purified by flash chromatography on silica using petroleum ether/ethyl acetate (4:1) as eluent to afford compound **13** (561.4 mg, 68% yield). White solid; mp 88–90 °C; R_f 0.74 (petroleum ether/ethyl acetate 4:1); $[\alpha]_D^{25} = +8.9$ (*c* 0.54, FC-72); ^1H NMR ($CDCl_3$): δ 1.84–1.86 (4H, m, CH_2), 2.04–2.13 (4H, m, CH_2CF_2), 2.53 (1H, d, $J = 5.1$ Hz, OH), 3.41–3.61 (8H, m, OCH_2), 3.94 (1H, m, >CH–N=), 4.02 (1H, m, C*H*OH), 7.85 (1H, s, H_{arom}), 8.16 (2H, s, H_{arom}), 8.34 (1H, s, CH=N); ^{13}C NMR ($CDCl_3$): δ 21.0 (CH_2), 28.0 (t, $J = 22.0$ Hz, *C*H_2CF_2), 69.7 (CH_2O), 70.1 (CH_2O), 71.2 and 71.4 (CHOH, CHN), 72.2 (OCH_2), 72.4 (OCH_2), 126.6 (C_{arom}), 130.1 (C_{arom}), 131.2 (t, $J = 24.7$ Hz, C_{arom}), 137.9 (C_{arom}), 159.8 (HC=N); ^{19}F NMR ($CDCl_3$): δ −126.7 (8F, m, CF_2), −124.0 (4F, m, CF_2), −123.3 (8F, m, CF_2), −122.5 (24F, m, CF_2), −121.8 (4F, m, CF_2), −115.5 (4F, m, CF_2), −111.6 (4F, m, CF_2), −81.3 (12F, m, CF_3). Anal. Calcd for $C_{49}H_{23}O_3F_{68}N$: C, 29.95; H, 1.18. Found: C, 29.55; H, 1.44.

4.14. (2*S*,3*S*)-3-{[3,5-Bis(perfluorooctyl)benzyl]amino}-1,4-bis(1*H*,1*H*,2*H*,2*H*,3*H*,3*H*-perfluoroundecyloxy)-butan-2-ol 14

To imino alcohol **13** (0.3 g, 0.12 mmol) dissolved in Freon (3 mL) was successively added $NaBH(OAc)_3$ (70 mg, 0.32 mmol) and acetic acid (0.01 mL, 0.24 mmol). After being stirred at rt for 7 h, 1 M NaOH (1 mL) was added. After 30 min, the mixture was extracted with diethyl ether (3 × 5 mL). The organic phases were washed with water (5 mL), brine (5 mL), and then dried over anhydrous Na_2SO_4. Evaporation of the solvent under reduced pressure gave a residue that was purified by flash chromatography on silica using petroleum ether/ethyl acetate (2:1) as the eluent to give aminoalcohol **14** (151 mg, 64% yield). White solid; mp 50–52 °C; R_f 0.58 (petroleum ether/ethyl acetate 2:1); $[\alpha]_D^{25} = +5.4$ (*c* 0.37, $C_6H_5CF_3$); ^1H NMR ($CDCl_3$): δ 1.84–1.91 (4H, m, CH_2), 2.07–2.16 (4H, m, CH_2CF_2), 2.80 (1H, d, $J = 5.3$ Hz, OH), 3.51–3.62 (9H, m, OCH_2, CHN=), 3.84–3.85 (1H, m, CHOH), 3.96 (1H, d, $J = 14.3$ Hz, CH_2N), 4.04 (1H, d, $J = 14.3$ Hz, CH_2N), 7.70 (1H, s, H_{arom}), 7.81 (2H, s, H_{arom}); ^{13}C NMR ($CDCl_3$): δ 21.0 (CH_2), 28.1 (t, $J = 22.3$ Hz, *C*H_2CF_2), 50.9 (CH_2N), 58.8 (CHN), 69.8 (CH_2O), 70.1 (CHOH), 70.2 (CH_2O), 70.3 (CH_2O), 72.9 (CH_2O), 130.2–130.6 (m, C_{arom}), 143.3 (C_{arom}); ^{19}F NMR ($CDCl_3$): δ −127.8 (2F, m, CF_2), −126.7 (6F, m, CF_2), −124.1 (6F, m, CF_2), −123.1 (12F, m, CF_2), −122.4 (18F, m, CF_2), −121.8 (4F, m, CF_2), −115.0 (4F, m, CF_2), −111.6 (4F, m, CF_2), −82.9 (3F, m, CF_3), −81.4 (9F, t, $J = 10.3$ Hz, CF_3). Anal. Calcd for $C_{49}H_{25}O_3F_{68}N$: C, 29.89; H, 1.28. Found: C, 29.52; H, 1.49.

4.15. (4*R*,5*R*)-1[3,5-Bis(perfluorooctyl)benzyl]-2(*R*,*S*)-[3,5-bis-(perfluorooctyl)phenyl]-4,5-bis[(1*H*,1*H*,2*H*,2*H*,3*H*,3*H*-perfluoroundecyloxy)methyl]imidazoline 16

Reduction of fluorous diimine **9** (346 mg, 0.12 mmol) under the conditions described previously for the preparation of compound **14** gave fluorous imidazoline **16** (145.6 mg, 42% yield). Colorless oil; R_f 0.60 (petroleum ether/ethyl acetate 4:1); $[\alpha]_D^{25} = -2.4$ (*c* 0.3, FC-72); ^1H NMR ($CDCl_3$): δ 1.80–1.83 (2H, m, CH_2), 1.98–2.00 (4H, m, CH_2, CH_2CF_2), 2.29 (2H, m, CH_2CF_2), 2.50 (1H, br s, NH), 3.08–3.10 (1H, m, CHN), 3.22–3.23 (2H, m, OCH_2), 3.34–3.39 (3H, m, CHN, OCH_2), 3.56–3.62 (4H, m, CH_2O), 3.94 (2H, m, CH_2N), 4.85 (1H, m, N_2CHAr), 7.68 (3H, s, H_{arom}), 7.75 (1H, s, H_{arom}); ^{13}C ($CDCl_3$): δ 20.9 (CH_2), 21.1 (CH_2), 27.9 (t, $J = 22.5$ Hz, *C*H_2CF_2), 28.3 (t, $J = 22.5$ Hz, *C*H_2CF_2), 57.4 (CH_2N), 61.6 (CHNH), 66.8 (CHN), 70.0 (OCH_2), 70.2 (OCH_2), 73.3 (OCH_2), 74.4 (OCH_2), 83.6 (N_2CHAr), 130.1–131.0 (m, C_{arom}), 141.7 (C_{arom}), 144.2 (C_{arom}); ^{19}F NMR ($CDCl_3$): δ −128.0 (8F, m, CF_2), −126.8 (6F, m, CF_2), −124.4 (8F, m, CF_2), −123.4 (28F, m, CF_2), −122.3 (22F, m, CF_2), −121.9 (4F, m, CF_2), −111.9 (8F, m, CF_2), −83.1 (12F, m, CF_3), −81.3 (6F, m, CF_3). Anal. Calcd for $C_{72}H_{28}F_{102}O_2N_2$: C, 29.89; H, 0.97. Found: C, 29.58; H, 1.16.

4.16. Determination of partition coefficients

The partition coefficients were determined by dissolving 20 mg of the fluorous compound in a biphasic system of FC-72 (1 mL) and the organic solvent (1 mL). The resulting mixture was stirred at 50 °C for 30 min and then cooled at room temperature. After 30 min, the two phases were separated and the fluorous compound contained in each layer determined gravimetrically after removal of all volatiles.

4.17. Typical hydrogen transfer reduction

The catalyst was prepared in a Schlenk tube by stirring $[Ir(COD)Cl]_2$ (14 mg, 0.02 mmol), or $[Ru(p\text{-cymene})Cl_2]_2$ (12.2 mg, 0.02 mmol) and the fluorinated ligand (0.04 mmol) in perfluoromethylcyclohexane (5 mL) at 70 °C for 3 h. To this solution cooled to room temperature was added a solution of acetophenone (0.4 mmol) and KOH (5.7 mg, 0.1 mmol) in *i*-PrOH (5 mL). The mixture was then stirred at 70 °C. The conversion and

the enantiomeric excess were determined by gas chromatography using a capillary Cyclodex-β chiral column. For the recycling, the organic phase was separated from the fluorous phase at 0 °C, and a solution of acetophenone and KOH in *i*-PrOH was added.

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