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Preparation of Optically Active 2-(Trifluoromethyl)alkan-1-ols by Catalytic Asymmetric Hydrogenation

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The hydrogenation of (*E*)-2-(trifluoromethyl)alk-2-en-1-ols catalyzed by Ru-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (Ru-BINAP) and Rh-BINAP was carried out with good enantiomeric excess (71—83% ee). Ru-BINAP-catalyzed hydrogenation converted 2-(trifluoromethyl)acrylic acid to the corresponding saturated acid whose esterification and reduction provided optically active 2-(trifluoromethyl)propan-1-ol in 80% ee.

Key words asymmetric hydrogenation; asymmetric synthesis; chiral fluorinated compound; 2-(trifluoromethyl)alkan-1-ol; 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl

Selectively fluorinated homochiral compounds have important applications in analytical, biological and medicinal chemistry.[1] Recently, these compounds have become of interest to the optoelectronic industry, *e.g.*, as liquid crystals.[2]

In the case of fluorine-containing molecules with unexpected and generally unusual reactivity, the common methodologies for synthesizing nonfluorinated chiral compounds are frequently inapplicable, giving rise to the term "flustrates" by Seebach.[3] So enantiomerically pure fluorinated compounds have mainly been prepared by chemical or biocatalytic resolution of racemates, selective fluorination of chiral nonfluorinated substances and enzymatic or biological methods. However, much attention has been directed to the asymmetric synthesis of such chiral molecules, and some catalytic asymmetric hydrogenation reactions have been found useful for obtaining optically active fluorinated compounds.[4]

We previously reported the synthesis of chiral 2-(trifluoromethyl)alkan-1-ols (**1**) using stoichiometric amounts of chiral auxiliaries as shown in Chart 1.[5] Here, we present the preparation of optically active **1** by the catalytic asymmetric hydrogenation of (*E*)-2-(trifluoromethyl)alk-2-en-1-ols (**2**).[6]

Results and Discussion

(*E*)-Allylic alcohol (**2**) was prepared in four steps starting from 2-bromo-3,3,3-trifluoropropene (**3**). The conversion of **3** into racemic 2-(trifluoromethyl)alk-1-en-3-ols (**4**) was carried out according to reported methods.[7] The acetylation of **4** with acetic anhydride (Ac_2O) in pyridine in the presence of 4-dimethylaminopyridine (DMAP) at room temperature gave the corresponding acetate **5** in high yield. Treatment of **5** with tetrakis(triphenylphosphine)palladium (0) ($(PPh_3)_4Pd$)[8] in tetrahydrofuran (THF) at room temperature brought about allylic rearrangement followed by deacetylation of the resultant allylic acetate **6** with potassium carbonate (K_2CO_3) in methanol (MeOH) at room temperature to give a separable mixture of **2** and its (*Z*)-isomer (**7**) in 38—80% yield in two steps along with a small amount of compound **4**. The stereochemical assignment of the (*Z*)-alkene **7** was confirmed by the nuclear Overhauser effect (NOE) between H-1 and H-3, while the (*E*)-alkene **2** showed no NOE. The *E*:*Z* ratio in **6** was determined by gas–liquid chromatographic (GLC) analysis.

The hydrogenation of **2** was conducted using 10 mol% of either [(*R*)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl]ruthenium(II) diacetate ($Ru(OAc)_2[(R)\text{-BINAP}]$, A),[9] [(*R*)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl]-rhodium(I) trifluoromethanesulfonate ($Rh^+[(R)\text{-BINAP}]OTf^-$, B),[10] or [(+)-2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane]rhodium(I) trifluoromethanesulfonate ($Rh^+[(+)\text{-DIOP}]OTf^-$, C)[11] as a catalyst, as shown in Table 1. The extent of conversion was measured by GLC analysis. Enantiomeric excess was determined by GLC analysis of the Mosher ester of **1**.[12] Only in the hydrogenation of (*E*)-5-phenyl-2-(trifluoromethyl)prop-2-en-1-ol (**2a**) was Rh-(*R*)-BINAP (B) superior to Ru-(*R*)-BINAP (A) as a catalyst, giving an

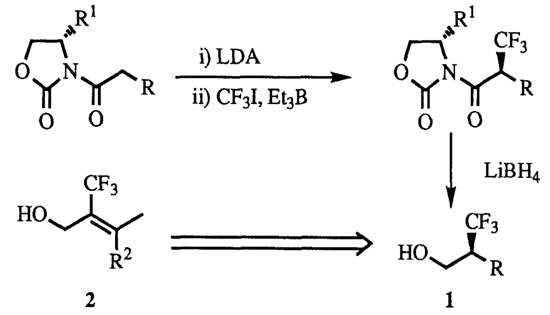

Chart 1

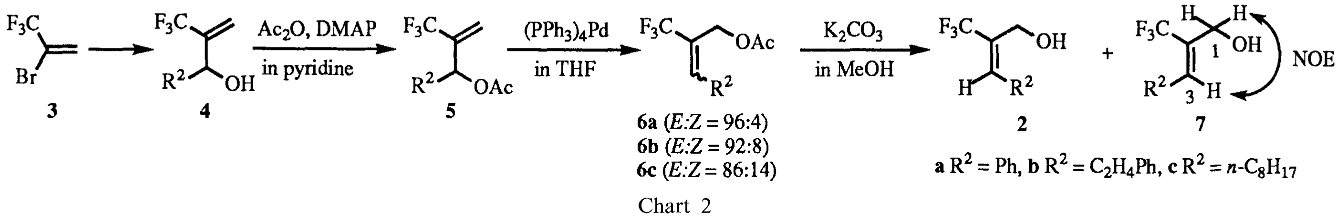

Chart 2

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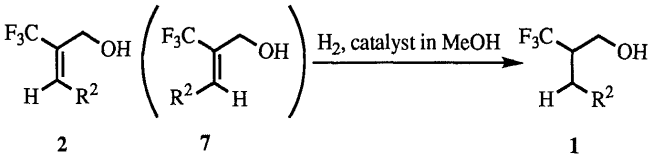
Table 1. Asymmetric Hydrogenation of 2-(Trifluoromethyl)alk-2-en-1-ols (**2**, **7**)



Entry	Olefin **2** R^2	Catalyst[a] (mol%)	H_2 (atm)	Time (h)	Temp. (°C)	Product **1** Conv. (%)	Yield (%)[b]	ee (%)
1	Ph (**2a**)	A (10)	18	240	30	16	13	42
2	Ph (**2a**)	B (10)	5	18	22	32	30	83
3	C_2H_4Ph (**2b**)	A (10)	18	240	30	46	40	71
4	C_2H_4Ph (**2b**)	C (10)	5	18	30	94	77	0
5	*n*-C_8H_{17} (**2c**)	A (10)	18	240	30	94	85	83
6	*n*-C_8H_{17} (**7c**)	A (10)	18	48	30	21	16	15
7	**2c**+**7c** (45:55)	A (10)	18	72	30	44	40	68

a) A = Ru(OAc)$_2$[(*R*)-BINAP]; B = Rh$^+$[(*R*)-BINAP]OTf$^-$; C = Rh$^+$[(+)-DIOP]OTf$^-$. *b*) Isolated yield.

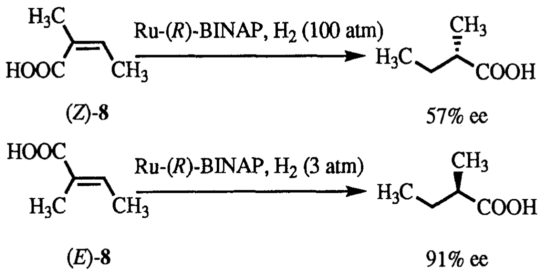
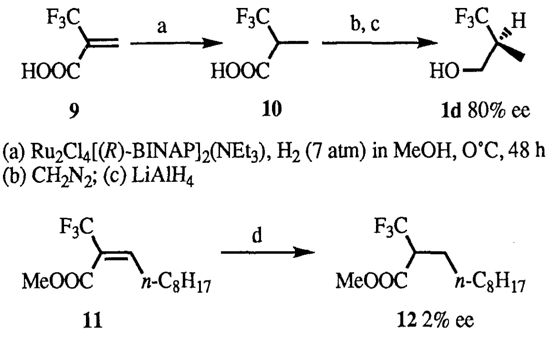


Chart 3



(a) Ru_2Cl_4[(*R*)-BINAP]$_2$(NEt_3), H_2 (7 atm) in MeOH, 0°C, 48 h; (b) CH_2N_2; (c) $LiAlH_4$

(d) Rh$^+$[(R)-BINAP]OTf$^-$, H_2 (5 atm) in MeOH, 45 h

Chart 4

enantiomeric excess of 83% (entries 1 and 2). Ru-(*R*)-BINAP (A)-catalyzed hydrogenation converted (*E*)-5-phenyl-2-(trifluoromethyl)pent-2-en-1-ol (**2b**) to the corresponding saturated alcohol (**1b**) in 71% ee (entry 3). The hydrogenation of **2b** with Rh-(+)-DIOP (C) gave **1b** in 77% yield but with poor enantioselectivity (entry 4). Although the enantiomeric purity of 2-(trifluoromethyl)-undecan-1-ol (**1c**) from the (*E*)-alkene **2c** (83% ee, entry 5) exceeded that from the (*Z*)-alkene **7c** (15% ee, entry 6), the same enantiomer was preferentially formed from **2c** and **7c**, and this is a point of interest.[4d] Thus, it has been shown that Ru-(*R*)-BINAP (A)-catalyzed hydrogenation of the (*E*) and (*Z*) isomers of 2-methyl-2-butenoic acid (**8**) give rise to the antipodal products (Chart 3).[13] The hydrogenation of a mixture of **2c** and **7c** (45:55) for 72 h (entry 7) led to recovery of 56% of the starting material in a ratio of 14:86, indicating **2c** to have been hydrogenated faster than **7c**.

The hydrogenation rate of **2a**—**c** and **7c** was very low. Only 33% of **2c** was hydrogenated after 26 h under the same conditions as in entry 5. In a control experiment with (*E*)-2-methylundec-2-en-1-ol, 100% conversion was observed in the same reaction time. The bulkiness and lipophilicity of the trifluoromethyl group may prevent catalyst A from coordinating **2**.

The hydrogenation of 2-(trifluoromethyl)acrylic acid (**9**) with hydrogen in the presence of 1 mol% of bis[(*R*)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl](triethylamine)-diruthenium(II) tetrachloride (Ru_2Cl_4[(*R*)-BINAP]$_2$-(NEt_3), D)[14] and 1.1 eq of triethylamine (NEt_3) in MeOH at 0 °C and 7 atm for 48 h afforded optically active 2-(trifluoromethyl)propionic acid (**10**) in 100% conversion. The esterification of **10** with diazomethane in ether at 0 °C followed by reduction of the resultant ester with lithium aluminum hydride ($LiAlH_4$) at 0 °C in THF gave (*S*)-2-(trifluoromethyl)propan-1-ol (**1d**) in 80% overall yield.[15] The enantiomeric excess of **1d** was determined to be 80% ee by GLC analysis of the corresponding Mosher ester.[12] The hydrogenation of **9** with hydrogen (7 atm) in the presence of 1 mol% of Ru-(*R*)-BINAP (D) and 1.1 eq of NEt_3 in MeOH at −20 °C or −40 °C for 48 h was completely inhibited. The hydrogenation of methyl (*E*)-2-(trifluoromethyl)-2-undecenoate (**11**) with hydrogen (5 atm) in the presence of Rh-(*R*)-BINAP (B) (10 mol%) at room temperature for 45 h gave the corresponding saturated ester in 69% yield (96% conversion), but only in 2% ee.

In conclusion, the hydrogenation of (*E*)-2-(trifluoromethyl)alk-2-en-1-ols (**2**) catalyzed by Ru-(*R*)-BINAP (A) and Rh-(*R*)-BINAP (B) proceeds with good enantiomeric excess (71—83% ee). Ru-(*R*)-BINAP (D)-catalyzed hydrogenation converted 2-(trifluoromethyl)acrylic acid (**9**) to the corresponding saturated acid **10**, the esterification and reduction of which gave optically active (*S*)-2-(trifluoromethyl)propan-1-ol (**1d**) in 80% ee. Means are presently being sought to improve the hydrogenation rate of **2** and the optical yield of **1** through further investigation on this and related hydrogenations.

Experimental

IR spectra were obtained on a Perkin Elmer 1600 FT-IR. ^{1}H-NMR and ^{19}F-NMR spectra were recorded at 200 MHz and 188 MHz, respectively, on a Varian Gemini-200 instrument. ^{1}H-NMR signals are given in parts per million (ppm) downfield from tetramethylsilane (TMS) as the internal standard. ^{19}F-NMR spectra were given in ppm upfield from CCl_3F as the internal standard. Coupling constants (J values) are given in hertz (Hz). Low- and high-resolution MS analyses were conducted using a Kratos CONCEPT-1H double-focusing magnetic sector spectrometer. GLC analysis was carried out on a Shimadzu GC-14A instrument using a GL Science (30 m × 0.25 mm) Neutrabond-1 capillary column whose film thickness was 1.5 μm. Kieselgel 60 (Merck, 230—400 mesh) was used for column chromatography. Thin-layer chromatography (TLC) was carried out with pre-coated Kieselgel 60 F_{254} plates (Merck). All reactions except for hydrogenation were run under an argon atmosphere. Chiral catalysts (A, B, C and D) were prepared by literature methods.[9—11,14]

Preparation of 2-(Trifluoromethyl)alk-1-en-3-ols (4) 5-Phenyl-2-(trifluoromethyl)prop-1-en-3-ol (**4a**) was prepared according to the literature.[7] 5-Phenyl-2-(trifluoromethyl)pent-1-en-3-ol (**4b**) and 2-(trifluoromethyl)undec-1-en-3-ol (**4c**) were obtained similarly. **4b**: colorless oil, bp 90—94 °C (0.22 mmHg). IR (neat): 3400, 2931, 1604, 1497, 1315, 1167, 1128, 1066, 700 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.80—2.15 (2H, m), 2.61—2.90 (2H, m), 4.87 (1H, m), 5.76 (1H, m), 5.85 (1H, m), 7.15—7.35 (5H, m). ^{19}F-NMR ($CDCl_3$) δ: 66.02 (s). MS m/z: 230 (M^+), 212, 105, 77. High-resolution MS (HRMS) Calcd for $C_{12}H_{13}OF_3$ (M^+): 230.092. Found: 230.092. **4c**: colorless oil, bp 80—87 °C (0.25 mmHg). IR (neat): 3364, 2928, 2857, 1466, 1317, 1170, 1128, 1070, 952 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.88 (3H, t, J=6.8 Hz), 1.15—1.40 (14H, m), 4.35 (1H, m), 5.73 (1H, m), 5.83 (1H, m). ^{19}F-NMR ($CDCl_3$) δ: 66.14 (s). MS m/z: 237 (M−1), 220, 95. HRMS Calcd for $C_{12}H_{20}OF_3$ (M−H): 237.147. Found: 237.145.

***O*-Acetyl-5-phenyl-2-(trifluoromethyl)prop-1-en-3-ol (5a)** To a solution of **4a** (500 mg, 2.47 mmol) in dry pyridine (5.0 ml) were added Ac_2O (1.0 ml, 10.6 mmol) and DMAP (5 mg, 0.04 mmol). The reaction mixture was stirred at room temperature for 12 h and diluted with Et_2O. The organic layer was washed with 1 N aqueous HCl, saturated aqueous $NaHCO_3$ and brine, then dried over $MgSO_4$ and filtered. After evaporation of the solvent, chromatography of the residue with hexane–CH_2Cl_2 (10 : 1, v/v) gave **5a** (576 mg, 95%). **5a**: colorless oil. IR (neat): 1748, 1372, 1229, 1173, 1132, 1025, 700 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.13 (3H, s), 5.62 (1H, m), 5.96 (1H, m), 6.50 (1H, m), 7.30—7.40 (5H, m). ^{19}F-NMR ($CDCl_3$) δ: 65.81 (s). MS m/z: 244 (M^+), 202, 149, 95, 77. HRMS Calcd for $C_{12}H_{11}O_2F_3$ (M^+): 244.071. Found: 244.071.

***O*-Acetyl-5-phenyl-2-(trifluoromethyl)pent-1-en-3-ol (5b)** The procedure for obtaining **5a** was conducted using **4b** (1.79 g, 7.77 mmol). Chromatography with hexane–EtOAc (20 : 1) gave **5b** (2.01 g, 95%). **5b**: colorless oil. IR (neat): 2936, 1750, 1604, 1371, 1171, 1130, 1036, 960, 750, 700 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.08 (3H, s), 2.08 (2H, m), 2.66 (2H, m), 5.47 (1H, m), 5.67 (1H, m), 5.89 (1H, m), 7.13—7.32 (5H, m). ^{19}F-NMR ($CDCl_3$) δ: 65.88 (s). MS m/z: 272 (M^+), 229, 212, 91, 69. HRMS Calcd for $C_{14}H_{15}O_2F_3$ (M^+): 272.102. Found: 272.101.

***O*-Acetyl-2-(trifluoromethyl)undec-1-en-3-ol (5c)** The procedure for **5a** was conducted using **4c** (1.79 g, 7.51 mmol). Chromatography with hexane–EtOAc (20 : 1) gave **5c** (2.02 g, 96%). **5c**: colorless oil. IR (neat): 2929, 2858, 1754, 1470, 1371, 1320, 1231, 1172, 1132, 1026, 954 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.88 (3H, t, J=6.7 Hz), 1.15—1.40 (14H, m), 2.08 (3H, s), 5.43 (1H, m), 5.64 (1H, m), 5.85 (1H, m). ^{19}F-NMR ($CDCl_3$) δ: 66.04 (s). MS m/z: 280 (M^+), 238, 220, 69. HRMS Calcd for $C_{14}H_{23}O_2F_3$ (M^+) 280.165. Found: 280.165.

5-Phenyl-2-(trifluoromethyl)prop-2-en-1-ol (2a) A solution of **5a** (430 mg, 1.76 mmol) and $(PPh_3)_4Pd$ (160 mg, 0.14 mmol) in THF (15 ml) was stirred at room temperature for 7.5 h. After evaporation of the solvent, chromatography of the residue with hexane–CH_2Cl_2 (10 : 1, v/v) gave a mixture of **6a** (E : Z=96 : 4) and **5a** (**6a** : **5a**=96 : 4). A solution of the mixture in MeOH (5 ml) was treated with anhydrous K_2CO_3 (626 mg, 4.53 mmol). After 2 h at room temperature, the mixture was diluted with Et_2O, washed with H_2O and brine, dried over $MgSO_4$ and filtered. The solvent was evaporated off and chromatography of the residue with hexane–EtOAc (10 : 1, v/v) gave **2a** (290 mg, 81%) and **7a** (8.9 mg, 2.5%). **2a**: colorless oil. IR (neat): 3376, 1660, 1305, 1017 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 4.37 (2H, d, J=6.0 Hz), 7.21—7.55 (6H, m). ^{19}F-NMR ($CDCl_3$) δ: 66.81 (s). MS m/z: 202 (M^+), 133, 78, 69. HRMS Calcd for $C_{10}H_9OF_3$ (M^+): 202.061. Found: 202.061.

5-Phenyl-2-(trifluoromethyl)pent-2-en-1-ol (2b) The procedure for **2a** was conducted using **5b** (2.02 g, 7.43 mmol). Allylic rearrangement with $(PPh_3)_4Pd$ gave a mixture of **6b** (E : Z=92 : 8) and **5b** (**6b** : **5b**=81 : 19), the deacetylation of which, followed by chromatography with hexane–EtOAc (10 : 1, v/v), gave **2b** (899 mg, 71%). **2b**: colorless oil. IR (neat): 3378, 1677, 1166, 1044 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.50—2.65 (2H, m), 2.72—2.84 (2H, m), 4.12 (2H, d, J=6.2 Hz), 6.36 (1H, m), 7.11—7.38 (5H, m). ^{19}F-NMR ($CDCl_3$) δ: 66.88 (s). HRMS Calcd for $C_{12}H_{13}OF_3$ (M^+): 230.092. Found: 230.092.

2-(Trifluoromethyl)undec-2-en-1-ol (2c) and Its (*Z*)-Isomer (7c) The procedure for **2a** was conducted using **5c** (300 mg, 1.07 mmol). Allylic rearrangement with $(PPh_3)_4Pd$ gave a mixture of **6c** (E : Z=86 : 14) and **5c** (**6c** : **5c**=82 : 18), whose deacetylation, followed by chromatography with hexane–EtOAc (10 : 1, v/v), afforded **2c** (92 mg, 41%) and **7c** (11 mg, 5%). **2c**: IR (neat): 3343, 2927, 1678, 1332, 895 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.88 (3H, t, J=6.8 Hz), 1.20—1.55 (12H, m), 2.20—2.35 (2H, m), 4.29 (2H, d, J=6.1 Hz), 6.34 (1H, m). ^{19}F-NMR ($CDCl_3$) δ: 66.83 (s). MS m/z: 220 (M−18), 150, 69. HRMS Calcd for $C_{12}H_{19}F_3$ ($M-H_2O$): 220.144. Found: 220.143. **7c**: IR (neat): 3333, 2927, 1672, 1125 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.88 (3H, t, J=6.8 Hz), 1.20—1.55 (12H, m), 2.20—2.35 (2H, m), 4.22 (2H, d, J=6.1 Hz), 6.06 (1H, m). ^{19}F-NMR ($CDCl_3$) δ: 60.07 (s). MS m/z: 220 (M−18), 150, 69. HRMS Calcd for $C_{12}H_{19}F_3$ ($M-H_2O$): 220.144. Found: 220.144.

Asymmetric Hydrogenation of (*E*)-2-(Trifluoromethyl)alk-2-en-1-ols (2) (General Procedure) A solution of **2** (0.42 mmol) and $Ru(OAc)_2$[(R)-BINAP][9] (A, 42 μmol) or Rh^+[(R)-BINAP]OTf^-[10] (B, 42 μmol) in MeOH (3 ml) was placed in an autoclave, pressurized with hydrogen (5 or 18 atm) and stirred at 22 or 30 °C for 18—240 h. Conversion to the corresponding alkanol was measured by GLC analysis. The reaction mixture was concentrated *in vacuo* and the residue was purified by column chromatography with hexane–EtOAc (10 : 1, v/v) to obtain the pure 2-(trifluoromethyl)alkan-1-ol (**1**). The enantiomeric purity of **1** was determined by GLC analysis of the corresponding Mosher ester.

5-Phenyl-2-(trifluoromethyl)propan-1-ol (1a) IR (neat): 3390, 2943, 1498, 1393, 1256, 1160, 1121, 1032, 701 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.40—2.58 (1H, m), 2.78—3.08 (2H, m), 3.61—3.88 (2H, m), 7.20—7.55 (5H, m). ^{19}F-NMR ($CDCl_3$) δ: 69.54 (d, J=9.6 Hz). MS m/z: 204 (M^+), 186, 91, 77. HRMS Calcd for $C_{10}H_{11}OF_3$ (M^+): 204.076. Found: 204.077.

5-Phenyl-2-(trifluoromethyl)pentan-1-ol (1b) IR (neat): 3387, 2945, 1257, 1150, 1120, 1039, 700 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.50—1.90 (4H, m), 2.11—2.39 (1H, m), 2.65 (2H, t, J=7.5 Hz), 3.80 (2H, m). ^{19}F-NMR ($CDCl_3$) δ: 69.42 (d, J=10.1 Hz). MS m/z: 232 (M^+), 214, 104, 91, 69. HRMS Calcd for $C_{12}H_{15}OF_3$ (M^+): 232.108. Found: 232.107.

2-(Trifluoromethyl)undecan-1-ol (1c) IR (neat): 3331, 2936, 1464, 1393, 1257, 1162, 1110, 1043 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.88 (3H, t, J=6.8 Hz), 1.15—1.65 (16H, m), 2.10—2.35 (1H, m), 3.81 (2H, m). ^{19}F-NMR ($CDCl_3$) δ: 69.54 (d, J=10.0 Hz). MS m/z: 222 (M−18), 150, 69. HRMS Calcd for $C_{12}H_{21}F_3$ ($M-H_2O$): 222.160. Found: 222.159.

Asymmetric Hydrogenation of 2-(Trifluoromethyl)acrylic Acid (9) A solution of **9** (140 mg, 1.0 mmol), Ru_2Cl_2[(R)-BINAP]$_2(NEt_3)$[14] (17 mg, 10 μmol) and NEt_3 (153 μl, 1.1 mmol) in MeOH (3 ml) was placed in an autoclave, pressurized with hydrogen (7 atm) and stirred at 0 °C for 48 h. Conversion of **9** was measured by GLC analysis (100%). The reaction mixture was concentrated *in vacuo* and extracted with Et_2O. The extracts were washed with 0.5 N aqueous HCl and brine, dried over anhydrous $MgSO_4$ and filtered. The ethereal solution was treated with diazomethane solution in the same solvent at 0 °C until the yellow color ceased to fade. The reaction mixture was quenched with formic acid, washed with saturated aqueous $NaHCO_3$ and brine, dried over anhydrous $MgSO_4$ and filtered. Following removal of the solvent, the residue was dissolved in Et_2O (5 ml). The ethereal solution was added dropwise to $LiAlH_4$ (38 mg, 1.0 mmol) in the same solvent (5 ml) at 0 °C. The reaction mixture was stirred at 0 °C for 30 min, then quenched with 2 N H_2SO_4 and extracted with Et_2O. The ethereal extracts were washed with H_2O, saturated aqueous $NaHCO_3$ and brine, dried over anhydrous $MgSO_4$ and filtered. After evaporation of the solvent, bulb-to-bulb distillation of the residue gave 4,4,4-trifluoro-3-methylbutanol (**1d**, 102 mg, 80%) which was confirmed identical by IR and ^{1}H-NMR comparisons to be identical with the racemic, 4,4,4-trifluoro-3-methylbutanol.[15] The enantiomeric excess of **1d** was determined to be 80% ee by GLC analysis of the Mosher ester of **1d**.

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