Supporting Information

Enantioselective Ring Opening of Epoxides by Fluoride Anion Promoted by a Cooperative Dual-Catalyst System

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I. General Information

General Procedures. Unless otherwise noted, reactions were performed without exclusion of air or moisture. Screens were performed in 1-dram borosilicate vials, and all other reactions were performed in round-bottom flasks. Flasks were sealed with rubber septa or Teflon caps. Stainless steel cannulae or syringes were used to transfer air- and moisture-sensitive reagents. Reactions were monitored by GC (see below) or thin-layer chromatography (TLC) on EMD Silica Gel 60 F_{254} plates, visualizing with fluorescence quenching, $KMnO_4$, or ceric ammonium molybdate (CAM). Organic solutions were concentrated under reduced pressure using a Büchi rotary evaporator with an ice-water bath for volatile compounds. Column chromatography was performed using SiliCycle SiliaFlash F60 (40-53 μm, 60 Å).

Materials. Commercial reagents were purchased from Sigma Aldrich, Acros, Alfa Aesar, or TCI, and used as received with the following exceptions. Epoxides were distilled from CaH_2 and stored at 5 ºC. Diethyl ether (Et_2O), dichloromethane (CH_2Cl_2), tetrahydrofuran (THF), toluene, and benzene were dried by passing through activated alumina columns; acetonitrile (CH_3CN) was dried

by passing through a column of activated molecular sieves.[1] (1*R*,2*R*)-(–)-1,2-Cyclohexanediamino-*N,N'*-bis(3,5-di-*t*-butylsalicylidene)cobalt(II) was purchased from Strem and used as received. (–)-Tetramisole hydrochloride was purchased from Sigma; the free base, a white solid, was prepared according to literature procedure[2] and stored at 5 ºC. *Tert*-butyl methyl ether (TBME, anhydrous, >99.8%) was purchased from Aldrich in a Sure/Seal™ bottle and used as received. 2-Methyl-2-butanol (*t*-AmOH, 99%) was purchased from Aldrich and used as received.

Instrumentation. Proton nuclear magnetic resonance (^{1}H NMR) spectra and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Bruker 500 AVANCE spectrometer (500 and 125 MHz, respectively). Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent ($CHCl_3$ = δ 7.27). Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent residual peak ($CDCl_3$ = δ 77.16 ppm). ^{19}F spectra were recorded on a Varian Inova 300 (282 MHz) spectrometer; chemical shifts are reported in parts per millions and are referenced to $CFCl_3$ (δ 0 ppm). NMR data are represented as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant in Hertz (Hz), integration. High-resolution mass spectra were obtained on a Kratos MS 50 using electrospray ionization time-of-flight (ESI-TOF). FT-IR spectra were recorded on a Perkin-Elmer Paragon 500 and are reported in terms of frequency of absorption (cm^{-1}) and intensity (s = strong, m = moderate, w = weak, br = broad). Gas chromatography (GC) was performed on an Agilent 7890A series instrument equipped with a split-mode capillary injection system and flame ionization detectors. Enantiomeric excesses were determined using J&W Scientific Cyclodex-B (30 m x .25 mm) and Macherey-Nagel Hydrodex β-TBDAc (25 m x .25 mm) columns. High-performance liquid chromatography (HPLC) was performed on an Agilent 1200 series instrument with a binary pump and a diode array detector, using a Chiralpak AD-H (25 cm x .46 cm) column. Optical rotations were recorded on a Jasco P-1010 polarimeter using a 1-mL cell with a 0.5 dm path length; concentration (c) is in g/100mL and $[\alpha]_D$ values are in degrees.

[1] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics,* **1996**, *15*, 1518.

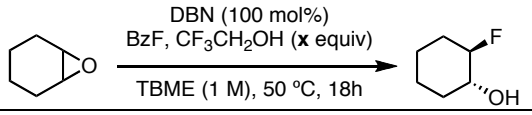
[2] Birman, V. B.; Li, X. *Org. Lett.* **2006***, 8*, 1351.

II. General Procedure for Racemic Fluoride Ring Opening and Related Studies

To a solution of epoxide (1.0 mmol) in 1 mL TBME in a polypropylene vial, benzoyl fluoride (0.218 mL, 2.0 mmol), 1,1,1,3,3,3-hexafluoroisopropanol (0.416 mL, 4.0 mmol), and DBN (24 μL, 0.20 mmol) were added. The vial was sealed, wrapping with Teflon tape, and heated to 50 °C for the designated time. Upon completion, the reaction was cooled, quenched with sat. $NaHCO_3$ (10 mL), extracted with Et_2O (2 x 5 mL), dried over $MgSO_4$, concentrated, and purified by standard methods.

Benzoylated product was not observed by GC analysis of the crude reaction under any conditions.

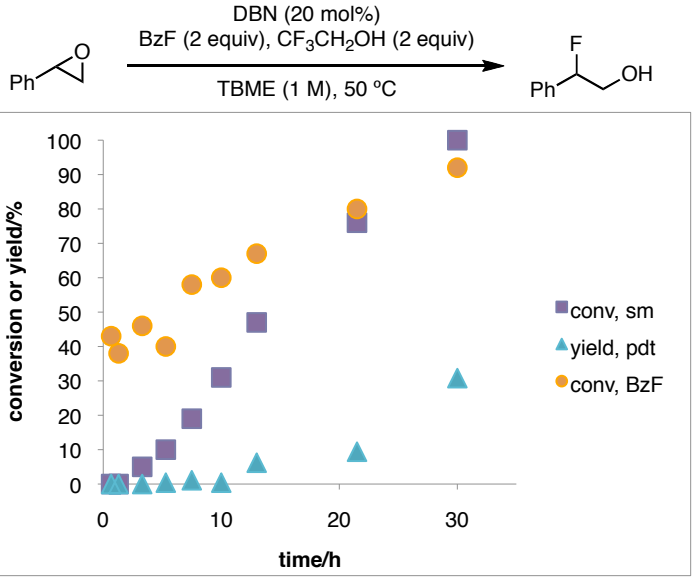
Table S1. Stoichiometry screen with 100 mol% DBN.



equiv	conv. (%)[a]	yield (%)[a]
1	6	0
2	6	0
4	28	19
6	72	58
10	96	82

[a] Determined by GC using dodecane as an internal standard.

Figure S1. The induction period observed in the reaction of styrene oxide corresponds to the formation of the active DBN•$(HF)_4$ complex.



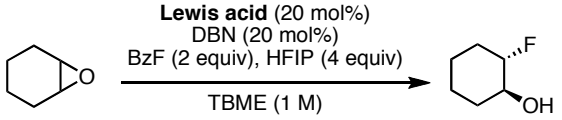
III. General Procedure for Screening

A 1 M stock solution was prepared in the designated solvent (0.2 mL/rxn), containing cyclohexene oxide (20.2 μL/rxn, 0.2 mmol/rxn, 1 equiv), decene (18.9 μL/rxn, 0.5 equiv), and benzoyl fluoride (43.5 μL/rxn, 2 equiv). An aliquot was reserved for measurement of the initial ratio by GC. To undried 1-dram borosilicate vials, catalysts, 1,1,1,3,3,3-hexafluoroisopropanol (83.1 μL, 4 equiv), and 0.8 mL solvent were added, followed by 282 μL stock solution. The vials were stirred open to air for 1–15 minutes then sealed and stirred for the designated time. Upon completion, an aliquot (~0.1 mL) was removed and filtered through a short plug of SiO_2, eluting with Et_2O. Conversion, yield, and enantiomeric excess were determined by GC using commercial columns.

NB: Ratios of amine: Lewis acid greater than 1 result in diminished rates and ee's (see Table S5).

IV. Optimization Studies

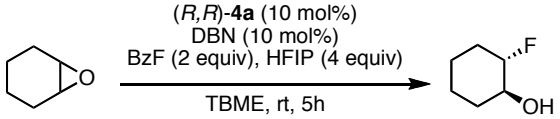
Table S2. Preliminary results in the co-catalytic fluoride ring-opening reaction.



entry	Lewis acid	temp (°C)	time (h)	conv. (%)[a]	yield (%)[a]	ee (%)[b]
1	none	50	3	80	54	-
2	(*R,R*)-**4a**[c]	50	3	100	82	27
3	(*R,R*)-**5**[d]	50	3	96	52	19
4	none	rt	24	31	16	-
5	(*R,R*)-**4a**[c]	rt	24	100	80	49
6	(*R,R*)-**5**[d]	rt	24	57	20	25
7	(*R,R*)-**6**[e]	rt	18	56	23	4

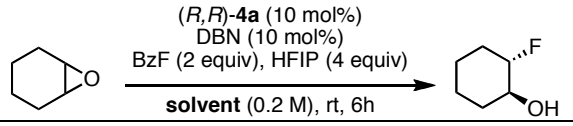
[a] Determined by GC using dodecane as an internal standard. [b] Determined by chiral GC analysis. [c] **4a** = (salen)Co. [d] **5** = (salen)CrCl. [e] **6** = (salen)AlCl. DBN = 1,5-diazabicyclo[4.3.0]non-5-ene. HFIP = 1,1,1,3,3,3-hexafluoroisopropanol.

Table S3. Concentration screen.



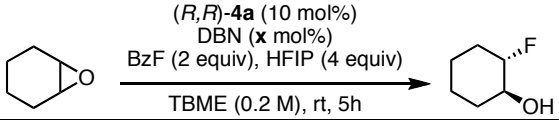
entry	concentration (M)	conv. (%)	yield (%)	ee (%)
1	1.0	97	63	38
2	0.5	93	74	44
3	**0.2**	**73**	**64**	**56**
4	0.05	11	8	59

Table S4. Solvent screen.



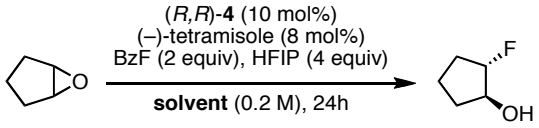
entry	solvent	conv. (%)	yield (%)	ee (%)
1	TBME	67	63	57
2	THF	37	33	16
3	Et_2O	72	70	49
4	dioxane	29	21	40
5	DME	45	33	45
6	*t*-AmOH	43	37	65

Table S5. Effect of amine: Lewis acid (LA) ratio.



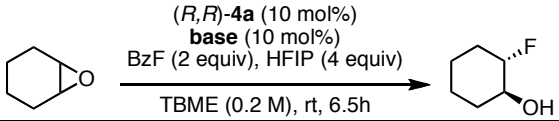
entry	DBN (mol%)	DBN:LA	conv. (%)	yield (%)	ee (%)
1	5	1:2	68	62	63
2	10	1:1	70	62	63
3	20	2:1	57	50	55
4	40	4:1	37	31	42

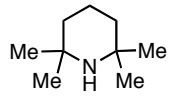
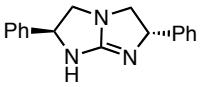
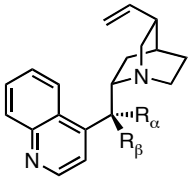
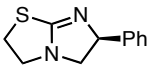
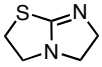
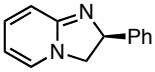
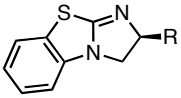
Table S6. Reaction of cyclopentene oxide, varying solvent and counterion.



entry	solvent	LA	conv. (%)	yield (%)	ee (%)
1	*t*-AmOH	**4a**	18	14	86
2	*t*-AmOH	**4b**	5	0	-
3	TBME	**4a**	41	36	84
4	TBME	**4b**	15	11	86
5	Et_2O	**4a**	56	52	81

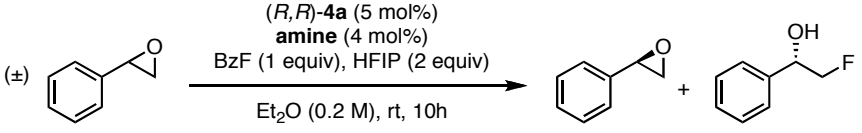
Table S7. Co-catalyst screen.



entry	co-catalyst	conv. (%)	yield (%)	ee (%)
1	none	48	37	54
2	DBN	81	73	61
3	Et_3N	69	61	60
4	DMAP	37	30	33
5		64	50	50
6		76	44	63
7		64	57	62
8		68	59	67
9[a]		61	52	58
10[b]		65	56	54
11	Bu_3P	34	28	45
12		**94**	**86**	**75**
13		54	48	58
14		79	74	73
15[c]		91	83	65
16[d]		81	71	44

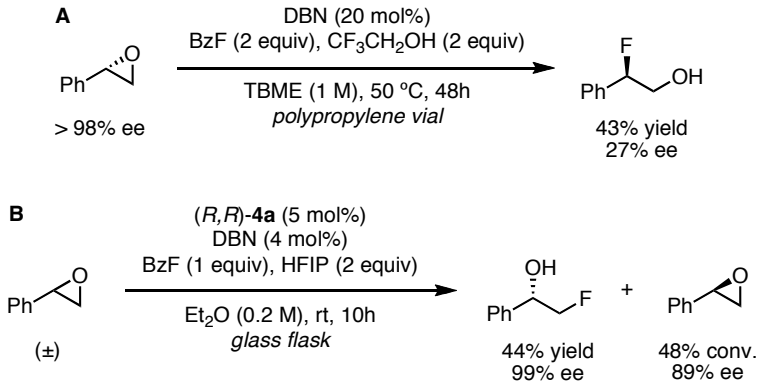
[a] R_β = OBz, R_α = H. [b] R_β = H, R_α = OBz. [c] R = Ph. [d] R = *i*-Pr.

Table S8. Comparison of co-catalysts in the kinetic resolution of styrene oxide.

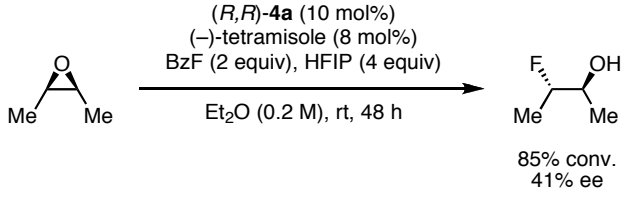


entry	amine	conv. (%)	yield (%)	ee_{sm} (%)	ee_{pdt} (%)	k_{rel}[a]
1	none	21	7	17	>99	>200
2	DBN	53	41	88	99	>300
3	(–)-tetramisole	29	20	32	97	83

[a] Calculated based on ee and yield of product.

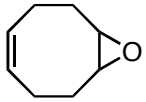


Scheme S1. Comparison of the reaction catalyzed by DBN alone (**A**) to the enantioselective co-catalytic reaction (**B**).

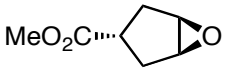


Scheme S2. Acyclic meso substrates react with lower selectivity.

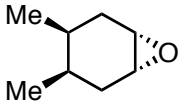
V. Preparation of Epoxides



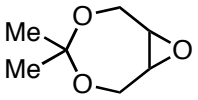
9-oxabicyclo[6.1.0]non-4-ene. Prepared according to a published procedure; spectral data were in agreement with literature values. [3]



***trans* methyl 6-oxabicyclo[3.1.0]hexane-3-carboxylate.** Prepared according to published procedures;[4] spectral data were in agreement with literature values.



(1*R*,3*R*,4*S*,6*S*)-3,4-dimethyl-7-oxabicyclo[4.1.0]heptane. Prepared as a 10:1 mixture of diastereomers according to published procedures;[5] spectral data were in agreement with literature values.



4,4-dimethyl-3,5,8-trioxabicyclo[5.1.0]octane. To 2-methoxypropene (5.74 mL, 60.0 mmol) and Na_2SO_4 (2 g) in a flame-dried flask at 0 ºC, *cis*-2-butene-1,4-diol (1.64 mL, 20.0 mmol) and catalytic *p*-toluenesulfonic acid (10 mg) were added. The reaction was stirred at 0 ºC for 1 hour, then solid Na_2CO_3 (5 g) was added and the slurry stirred vigorously. The reaction mixture was filtered, concentrated *in vacuo*, and the crude residue purified by Kugelrohr distillation (0.5 torr, 80 ºC) to obtain 1.09 g (43% yield) 2,2-dimethyl-4,7-dihydro-1,3-dioxepine. The alkene was epoxidized according to a literature procedure[6] to obtain 0.874 g (71% yield) of the title product. IR (thin film, cm^{-1}) 2991 (m), 2940 (m), 1374 (m), 1220 (s), 1150 (m), 1120 (m), 1086 (m), 1034 (m); ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.03 (dd, J = 28.1, 14.3 Hz, 4H), 3.22 (s, 2H), 1.37 (s, 3H), 1.32 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 102.36, 60.10, 56.51, 24.79, 23.50; HRMS (ESI+) calculated for $C_7H_{12}NaO_3$ ($[M+Na]^+$): 167.06787, found: 167.06797.

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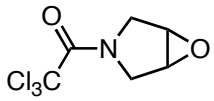
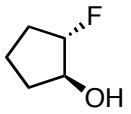
[3] Davies, S. G.; Polywka, M. E. C.; Thomas, S. E. *J. Chem. Soc. Perkin Trans. 1* **1986**, 1277.
[4] (a) Deprés, J.-P.; Greene, A. E. *Org. Synth.* **1998**, *75*, 195. (b) Lizotte, K. E.; Marecki, P. E.; Mertes, M. P. *J. Org. Chem.* **1983**, *48*, 3594.
[5] (a) O'Brien, P.; Tournayre, J. J. *Tetrahedron* **1997**, *53*, 17527. (b) Rickborn, B.; Lwo, S.-Y. *J. Org. Chem.* **1965**, *30*, 2212. (c) Kasai, T.; Watanabe, H.; Mon, K. *Bioorg. Med. Chem.* **1993**, *1*, 67.
[6] Inaba, T.; Birchler, A. G.; Yamada, Y.; Sagawa, S.; Yokota, K.; Ando, K.; Uchida, I. *J. Org. Chem.* **1998**, *63*, 7582.



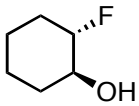
1-(6-oxa-3-azabicyclo[3.1.0]hexan-3-yl)-2,2,2-trichloroethanone. To a solution of diallylamine (1.23 mL, 10.0 mmol) and pyridine (1.21 mL, 15.0 mmol) in dry CH_2Cl_2 (20 mL) at 0 ºC, trichloroacetyl chloride (1.34 mL, 12.0 mmol) was added dropwise and the reaction mixture was warmed to room temperature over 2 hours. The reaction was poured into water (20 mL), washed with 1 M HCl (10 mL), and the aqueous layer extracted with CH_2Cl_2 (1 x 20 mL). The combined organics were washed with sat. $NaHCO_3$ (15 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude residue was diluted with 40% Et_2O/pentane and filtered through a plug of SiO_2, then concentrated to yield *N*,*N*-diallyl-2,2,2-trichloroacetamide (2.41 g, quant.). The diene (10.0 mmol) was degassed in 10 mL dry CH_2Cl_2 by bubbling through argon, then was added to a solution of Grubbs' 1st-generation catalyst (41.1 mg, 0.05 mmol) in degassed CH_2Cl_2 (100 mL). The reaction was stirred under argon at room temperature for 3.5 hours, then quenched by bubbling air through the reaction mixture for 15 minutes. The reaction was concentrated *in vacuo* and purified by Kugelrohr (0.5 torr, 180 ºC) to provide 2,2,2-trichloro-1-(2,5-dihydro-1*H*-pyrrol-1-yl)ethanone (1.93 g, 90% yield). The *N*-trichloroacetyl pyrroline (8.81 mmol) was dissolved in CH_3CN (75 mL) and 0.4 mM aqueous Na_2EDTA solution (45 mL) and cooled to 0 ºC. 1,1,1-Trifluoroacetone (8.69 mL, 88.1 mmol) was charged via a cooled syringe. A mixture of oxone (27.1 g, 44.1 mmol) and $NaHCO_3$ (6.07 g, 70.5 mmol) was added portionwise over 1 hour, and the reaction was stirred, warming to room temperature, for an additional 1 hour. The reaction was diluted with brine (75 mL) and filtered, then extracted with CH_2Cl_2 (3 x 75 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. No further purification of the title product (1.89 g, 93% yield) was necessary. IR (thin film, cm^{-1}) 2876 (w), 1672 (s), 1421 (m), 1391 (m), 1202 (w), 847 (s), 811 (s); ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.50 (d, J = 12.9 Hz, 1H), 4.15 (d, J = 14.0 Hz, 1H), 3.86-3.78 (m, 3H), 3.60 (d, J = 14.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.97, 93.01, 56.11, 53.38, 50.49, 50.06; HRMS (ESI+) calculated for $C_6H_7Cl_3NO_2$ ($[M+H]^+$): 229.95369, found: 229.95363 (100.0%), calculated for $C_6H_6Cl_3NaNO_2$ ($[M+Na]^+$): 251.93563, found: 251.93553 (72.4%).

VI. General Procedure for Enantioselective Fluoride Ring Opening

General Procedure for the Desymmetrization of Meso Epoxides. To an undried 10-mL round-bottom flask were added (1*R*,2*R*)-(–)-1,2-cyclohexanediamino-*N,N'*-bis(3,5-di-*t*-butylsalicylidene)cobalt(II) (**4a**) (60.4 mg, 0.10 mmol, 10 mol%) and (–)-tetramisole (16.3 mg, 0.08 mmol, 8 mol%). 1,1,1,3,3,3-hexafluoroisopropanol (0.416 mL, 4.0 mmol, 4 equiv) was charged and the brown slurry was diluted with 5 mL of Et_2O, TBME, or *t*-AmOH. Epoxide (1.0 mmol, 1 equiv) was then added, followed by benzoyl fluoride (0.218 mL, 2.0 mmol, 2 equiv), and the mixture was stirred, open to air, for 1 minute. The flask was sealed with a Teflon cap, which was secured with Parafilm, and stirred at room temperature for the designated time. Yields and enantiomeric excesses are representative values for two or more reactions.



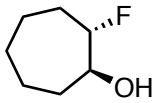
(1*S*,2*S*)-2-fluorocyclopentanol. Cyclopentene oxide (175 μL, 2.0 mmol, 1 equiv) was subjected to the general procedure (scaled by 2x) in Et_2O. After stirring at room temperature for 72 hours, the reaction was quenched with 0.5 M NH_3 in Et_2O (4 mL) and concentrated *in vacuo*, cooling with an ice bath. The reaction was purified by column chromatography on SiO_2, eluting with 5–40% Et_2O in pentane to provide the title product (160 mg, 77% yield). The enantiomeric excess was determined to be 85% by chiral GC analysis (β-TBDAc, 110 ºC isotherm, 1 mL/min, t_R(major) = 12.4 min, t_R(minor) = 14.1 min); $[\alpha]^{22}_D$ = +10.3 ($CHCl_3$, c = 1.1). Spectral data were in agreement with literature values.[7]



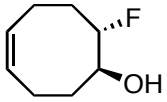
(1*S*,2*S*)-2-fluorocyclohexanol. Modification of the general procedure. To an undried 50-mL round-bottom flask were added (1*R*,2*R*)-(–)-1,2-cyclohexanediamino-*N,N'*-bis(3,5-di-*t*-butylsalicylidene)cobalt(III) tosylate (**4b**) (387 mg, 0.50 mmol, 10 mol%) and (–)-tetramisole (81.7 mg, 0.40 mmol, 8 mol%). 1,1,1,3,3,3-hexafluoroisopropanol (2.1 mL, 20 mmol, 4 equiv) was charged and the brown slurry was diluted with 25 mL *t*-AmOH. Epoxide (506 μL, 5.0 mmol, 1 equiv) was then added, followed by benzoyl fluoride (1.1 mL, 10 mmol, 2 equiv), and the flask was sealed with a Teflon cap, which was secured with Parafilm, and stirred at room temperature. After 24 hours, *t*-AmOH was removed via distillation using a 9-inch Vigreux column (bath temperature, 150 ºC), adding cyclohexane as an azeotrope as needed. The reaction was purified by column chromatography on SiO_2, eluting with 5–30% Et_2O in pentane to provide the title product (384 mg, 65% yield). The enantiomeric excess was determined to be 93% by chiral GC analysis (β-TBDAc, 100 ºC isotherm, 1 mL/min, t_R(major) = 19.6 min, t_R(minor) = 30.8 min); $[\alpha]^{23}_D$ = +19.4 ($CHCl_3$, c = 1.0) (lit.[8] $[\alpha]^{20}_D$ = +16.4 ($CHCl_3$, c = 1.0, >95% ee (*S,S*))). Spectral data were in agreement with

[7] Shellhamer, D. F.; Briggs, A. A.; Miller, B. M.; Prince, J. M.; Scott, D. H.; Healsley, V. L. *J. Chem. Soc., Perkin Trans. 2*. **1996**, 973.
[8] Haufe, G.; Bruns, S. *Adv. Synth. Catal.* **2002**, *344*, 165.

literature values.[9]

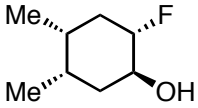


(1*S*,2*S*)-2-fluorocycloheptanol. Cycloheptene oxide (112 mg, 1.0 mmol) was subjected to the general procedure in TBME. After stirring at room temperature for 72 hours, ~7 M NH_3 in MeOH (3 mL) was added and the reaction resealed and stirred for several hours. The mixture was concentrated and purified by column chromatography on SiO_2, eluting with 5–20% Et_2O in pentane to provide the title product (109 mg, 82% yield). The enantiomeric excess was determined to be 90% by chiral GC analysis (β-TBDAc, 120 ºC isotherm, 1 mL/min, t_R(major) = 6.1 min, t_R(minor) = 8.0 min); $[\alpha]^{23}_D$ = –4.0 ($CHCl_3$, c = 1.0). Spectral data were in agreement with literature values.[10]



(1*S*,8*S*,*Z*)-8-fluorocyclooct-4-enol. 9-oxabicyclo[6.1.0]non-4-ene (124 mg, 1.0 mmol) was subjected to the general procedure in TBME. After stirring at room temperature for 72 hours, ~7 M NH_3 in MeOH (3 mL) was added and the reaction resealed and stirred for several hours. The mixture was concentrated and purified by column chromatography on SiO_2, eluting with 5–20% Et_2O in pentane to provide the title product (125 mg, 87% yield). The enantiomeric excess was determined to be 95% by chiral GC analysis (Cyclodex-B, 110 ºC isotherm, 1.2 mL/min, t_R(minor) = 22.2 min, t_R(major) = 23.5 min); $[\alpha]^{23}_D$ = –2.3 ($CHCl_3$, c = 1.0). Spectral data were in agreement with literature values.[11]

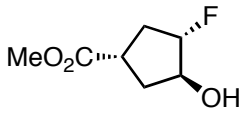
Using (*S*,*S*)-**4a**, product was obtained in 6% GC yield and –32% ee after 24 hours.



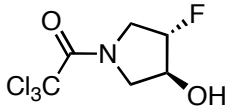
(1*S*,2*S*,4*R*,5*S*)-2-fluoro-4,5-dimethylcyclohexanol. (1*R*,3*R*,4*S*,6*S*)-3,4-dimethyl-7-oxabicyclo[4.1.0]heptane (126 mg, 1.0 mmol, 10:1 dr) was subjected to the general procedure in *t*-AmOH. After stirring at room temperature for 120 hours, the reaction was quenched with 3 mL ~7M NH_3 in MeOH and *t*-AmOH was removed via distillation using a 9-inch Vigreaux column (bath temperature, 150 ºC), adding cyclohexane as an azeotrope as needed. The crude reaction mixture was purified by column chromatography on SiO_2, eluting with 5–30% Et_2O in pentane to provide the title product (123 mg, 10 wt% *t*-AmOH, 75% yield, 10:1 dr). The enantiomeric excess of the major diastereomer was determined to be 90% by chiral GC analysis (β-TBDAc, 110 ºC isotherm, 1 mL/min, t_R(major) = 10.53 min, t_R(minor) = 18.38 min) and that of the minor diastereomer was determined to be 41% (t_R(major) = 11.72 min, t_R(minor) = 20.00 min); $[\alpha]^{24}_D$ = +26.4 ($CHCl_3$, c = 1.0); FTIR (thin film, cm^{-1}) 3992 (br), 2960 (s), 2937 (s), 2876 (s), 1458 (m), 1379 (m), 1099 (m), 1061 (s), 1023 (s), 973 (m); ^{1}H NMR (500 MHz, $CDCl_3$; minor diastereomer indicated

[9] Bruns, S.; Haufe, G. *J. Fluorine Chem.* **2000**, *104*, 247.
[10] Pietz, S.; Frölich, R.; Haufe, G. *Tetrahedron* **1997**, *53*, 17055.
[11] Alvernne, G.; Laurent, A.; Haufe, G. *J. Fluorine Chem.* **1986**, *34*, 147.

by *) δ 4.49 (dddd, J_{HF} = 51.8 Hz, 1H*, C**H**F), 4.29 (dddd, J = 51.9, 11.2, 8.6, 5.2 Hz, 1H C**H**F), 3.68 (m, 1 H*, C**H**OH), 3.85 (dddd, J = ddddd, J = 24.6, 12.8, 8.5, 4.6, 2.7 Hz, 1H, , C**H**OH), 2.34 (d, J = 2.3 Hz, 1H*, O**H**), 2.28 (d, J = 2.4 Hz, O**H**), 1.90–1.72 (m, 4H + 4H*), 1.54–1.40 (m, 2H + 2H*), 0.93 (d, J = 6.8, 3H + 3H*, C**H**$_3$), 0.91 (d, J = 7.2 Hz, 3H + 3H*, C**H**$_3$); ^{13}C NMR (125 MHz, $CDCl_3$; minor diastereomer indicated by *) δ 97.27 (d, ^{1}J = 173.4 Hz), 94.56* (d, ^{1}J = 170.8 Hz), 73.85* (d, ^{2}J = 17.8 Hz), 69.45 (d, ^{2}J = 18.0 Hz), 38.31 (d, ^{3}J = 7.3 Hz), 32.97 (d, ^{2}J = 16.1 Hz), 33.05 (d, ^{3}J = 9.6 Hz), 32.74 (d, ^{4}J = 1.9 Hz), 18.97, 18.91*, 12.63, 12.55*; ^{19}F NMR (282 MHz, $CDCl_3$; minor diastereomer indicated by *) δ –182.0 (d, J_{HF} = 51.8 Hz), –190.6* (d, J_{HF} = 53.6 Hz); HRMS (ESI+) calculated for $C_8H_{15}FNaO$ ([M+Na]$^+$): 169.09991, found: 169.10003.

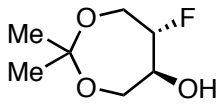


(1*S*,3*S*,4*S*)-methyl 3-fluoro-4-hydroxycyclopentanecarboxylate. *Trans* methyl 6-oxabicyclo[3.1.0]hexane-3-carboxylate (142 mg, 1.0 mmol) was subjected to the general procedure in TBME. After stirring at room temperature for 120 hours, the reaction was quenched with saturated $NaHCO_3$ (10 mL) and extracted with EtOAc (3 x 5 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude residue was purified by column chromatography on SiO_2, 5–40% EtOAc in hexane, to provide the title product (142 mg, 88% yield). The enantiomeric excess was determined to be 86% by chiral GC analysis (Cyclodex-B, 120 °C isotherm, 1 mL/min, t_R(major) = 40.6 min, t_R(minor) = 41.6 min); $[\alpha]^{23}_D$ = –6.0 ($CHCl_3$, c = 1.0); IR (thin film, cm^{-1}) 3448 (br), 2995 (m), 1735 (s), 1438 (m), 1215 (s), 1179 (m), 1073 (s), 968 (m); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.86 (dddd, J = 51.5, 7.2, 3.2, 1.7 Hz, 1H, C**H**F), 4.40 (dddd, 10.8, 7.6, 3.9, 1.9 Hz, 1H, C**H**OH), 3.71 (s, 3H, C**H**$_3$), 3.15-3.08 (m, 1H, C**H**CO_2CH_3), 2.45 (dddd, J = 30.3, 15.1, 9.8, 5.3 Hz, 1H, *c*-Pent**H**), 2.29 (dddd, J = 14.1, 8.8, 5.4, 2.8 Hz, 1H, *c*-Pent**H**), 2.19 (dddd, J = 28.1, 15.1, 6.5, 2.8 Hz, 1H, *c*-Pent**H**), 1.99 (ddd, J = 14.0 Hz, 8.3, 2.1 Hz, 1H, *c*-Pent**H**) 1.91-1.55 (br s, 1H, O**H**); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.71, 98.41 (d, ^{1}J = 178.4 Hz), 76.06 (d, ^{2}J = 27.4 Hz), 52.24, 39.82 (d, ^{3}J = 0.9 Hz), 35.25, 33.68 (d, ^{2}J = 22.1 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ –178.5 (m, J_{HF} = 51.7 Hz); HRMS (ESI+) calculated for $C_7H_{12}FO_3$ ([M+H]$^+$): 163.07650, found: 163.07659 (30.4%), calculated for $C_7H_{11}FNaO_3$ ([M+Na]$^+$): 185.05844, found: 185.05848 (100.0%).



2,2,2-trichloro-1-((3*S*,4*S*)-3-fluoro-4-hydroxypyrrolidin-1-yl)ethanone. 1-(6-oxa-3-azabicyclo[3.1.0]hexan-3-yl)-2,2,2-trichloroethanone (230 mg, 1.0 mmol) was subjected to the general procedure in *t*-AmOH. After stirring at room temperature for 120 hours, the reaction mixture was quenched with sat. $NaHCO_3$ (10 mL) and extracted with EtOAc (3 x 5 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude residue was purified by column chromatography on SiO_2, 10–40% EtOAc in hexane, to provide the title product (211 mg, 84% yield; contains a minor impurity). The enantiomeric excess was determined to be 80% by chiral HPLC analysis (Chiracel AD-H, 90:10 hexane/*i*-PrOH, 1 mL/min, λ = 220 nm, t_R(major) = 10.2 min, t_R(minor) = 8.3 min); $[\alpha]^{23}_D$ = +12.8 ($CHCl_3$, c = 1.1); FTIR (thin film, cm^{-1}) 3449 (br), 2952 (w), 1664 (s), 1418 (m), 1061 (m), 849 (m), 813 (m), 668 (m); ^{1}H NMR (500 MHz, $CDCl_3$; mixture of rotamers, indicated by *) δ 5.07 (d, J = 49.7 Hz, 1H, C**H**F), 5.01 (dd, J

= 50.5, 2.8 Hz, 1H*, C**H**F), 4.58-4.57 (m, 1H, C**H**OH), 4.52-4.50 (m, 1H*, C**H**OH), 4.43–3.78 (m, 4H + 4H*, C$\mathbf{H_2}$), 2.20 (br s, 1H + 1H*, O**H**); ^{13}C NMR (125 MHz, $CDCl_3$; mixture of rotamers, indicated by *) δ 159.76, 159.71*, 95.20* (d, ^1J = 182.7 Hz), 92.96, 92.19 (d, ^1J = 180.4 Hz), 73.91 (d, ^2J = 27.8 Hz), 70.42* (d, ^2J = 28.2 Hz), 55.80*, 54.71, 53.69 (d, ^2J = 22.6 Hz), 52.81* (d, ^2J = 21.7 Hz); ^{19}F NMR (282 MHz, $CDCl_3$; mixture of rotamers, indicated by *) δ –183.2 (m), –185.7* (m); HRMS (ESI+) calculated for $C_6H_8Cl_3FNO_2$ ($[M+H]^+$): 249.95992, found: 249.95999 (100.0%), calculated for $C_6H_7Cl_3FNNaO_2$ ($[M+Na]^+$): 271.94186, found: 271.94117 (44.6%).



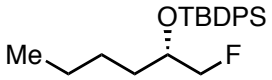
(5*S*,6*S*)-6-fluoro-2,2-dimethyl-1,3-dioxepan-5-ol. 4,4-dimethyl-3,5,8-trioxabicyclo[5.1.0]octane (144 mg, 1.0 mmol) was subjected to the general procedure in TBME. After stirring at room temperature for 120 hours, the reaction mixture was quenched with sat. $NaHCO_3$ (10 mL) and extracted with Et_2O (3 x 5 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude residue was purified by column chromatography on SiO_2, 5–20% acetone in pentane, to provide the title product (90 mg, 55% yield). The enantiomeric excess of the trimethylsilyl ether was determined to be 58% by chiral GC analysis (Cyclodex-B, 110 ºC isotherm, 1.0 mL/min, t_R(major) = 11.0 min, t_R(minor) = 11.5 min); $[\alpha]^{24}_D$ = –21.4 ($CHCl_3$, c = 1.0); FTIR (thin film, cm^{-1}) 3448 (br), 2991 (m), 2944 (m), 1377 (m), 1220 (s), 1159 (m), 1099 (m), 1056 (s), 852 (m); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.44 (ddd, J = 43.9, 3.9, 3.9 Hz, 1H, C**H**F), 4.01 (d, 12.8 Hz, 1H, C$\mathbf{H_2}$), 3.92-3.80 (m, 3H, C$\mathbf{H_2}$), 3.60 (ddd, J = 12.7, 4.3, 1.1 Hz, 1H, C**H**OH), 2.59 (d, J = 8.4 Hz, 1H, O**H**), 1.39 (s, 3H C$\mathbf{H_3}$), 1.36 (s, 3H C$\mathbf{H_3}$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 102.0, 91.7 (d, ^1J = 176.6 Hz), 70.0 (d, ^2J = 29.4 Hz), 60.4, 59.4 (d, ^2J = 20.9 Hz), 25.0, 24.0; ^{19}F NMR (282 MHz, $CDCl_3$) δ –195.7 (m); HRMS (ESI+) calculated for $C_7H_{14}FO_3$ ($[M+H]^+$): 165.09215, found: 165.09219 (9.4%), calculated for $C_7H_{13}FNaO_3$ ($[M+Na]^+$): 187.07409, found: 187.07410 (100.0%).

General Procedure for the Kinetic Resolution of Terminal Epoxides. To an undried 50-mL round-bottom flask were added (1*R*,2*R*)-(–)-1,2-cyclohexanediamino-*N*,*N*'-bis(3,5-di-*t*-butylsalicylidene)cobalt(II) (**4a**) (60.4 or 151 mg, 0.1 or 0.25 mmol, 2 or 5 mol%) and DBN (9.6 or 24 μL, 0.08 or 0.2 mmol, 1.6 or 4 mol%). 1,1,1,3,3,3-hexafluoroisopropanol (1.04 mL, 10.0 mmol, 2 equiv) was charged and the brown slurry was diluted with 25 mL of Et_2O. Epoxide (5.0 mmol, 1 equiv) was then added, followed by benzoyl fluoride (.55 mL, 5.0 mmol, 1 equiv), and the mixture was stirred, open to air, for 15 minutes. The flask was sealed with a Teflon cap, which was secured with Parafilm, and stirred at room temperature until the reaction reached approximately 50% conversion as determined by GC. Yields and enantiomeric excesses are representative values for two or more reactions.

Lower-bound selectivity factors ($k_{rel} = k_{fast}/k_{slow}$) were measured using the equation of Kagan,[12] based on the enantiomeric excess of product (ee) and yield (c, as a surrogate for conversion):

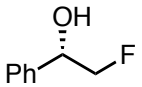
$$k_{rel} = \ln[1 - c(1 + ee)]/\ln[1 - c(1-ee)]$$

[12] Kagan, H. B.; Fiaud, J. C. in *Topics in Stereochemistry*, Vol. 14; Eliel, E. L., Wilen, S. H., Eds., Wiley: New York: 1987; pp 249–330.



(*S*)-1-fluorohexan-2-ol. (±)-Butyloxirane (603 μL, 5.0 mmol) was subjected to the general procedure (using 2 mol% (salen)Co and 1.6 mol% DBN) until the reaction reached 47% conversion (30 hours), as determined by GC analysis using 1-decene as an internal standard. The reaction was quenched with ~7 M NH_3 in MeOH (10 mL), sealed, and stirred for several hours. Solvents, epoxide, and fluorohydrin were purified from nonvolatiles by vacuum transfer. MeOH was removed by diluting the distillate with 20 mL pentane and washing with 1 M NaOH (2 x 10 mL). The aqueous layer was extracted with 1:1 Et_2O/pentane (20 mL) and the combined organics were dried over $MgSO_4$, filtered, and concentrated *in vacuo*, cooling with an ice bath. The residue was diluted with 4 mL CH_2Cl_2 and 1 mL DMF, then treated with imidazole (0.43 g, 6.25 mmol, 1.25 equiv) and TBDPSCl (1.5 mL, 6 mmol, 1.2 equiv). Upon full conversion of the alcohol as determined by GC, the reaction was diluted with 10% LiCl (20 mL) and hexane (40 mL). The layers were separated and the organic layer was washed once more with 10% LiCl (20 mL). The organics were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude residue was filtered through a short plug of SiO_2, eluting with hexane, to provide the silyl-protected title product (0.639 g, 36% yield). The enantiomeric excess of the product (prior to silyl protection) was determined to be 99% by chiral GC analysis (Cyclodex-B, 80 ºC isotherm, 1 mL/min, t_R(major) = 13.6 min, t_R(minor) = 14.2 min); $[\alpha]^{24}_D$ = +18.4 (silyl ether, $CHCl_3$, c = 1.0). Spectral data for the free alcohol were in agreement with literature values.[13]

The unreacted (*R*)-butyloxirane was also isolated during the above sequence and converted to the azido trimethylsilyl ether (azide opening with NaN_3/NH_4Cl[14] followed by silylation with $TMSCl/Et_3N$). The enantiomeric excess was determined to be 96% by chiral GC analysis (Cyclodex-B, 80 ºC isotherm, 1 mL/min t_R(minor) = 52.3 min, t_R(major) = 53.8 min). The major enantiomer was determined by comparison to the literature GC



(*S*)-2-fluoro-1-phenylethanol. (±)-Styrene oxide (572 μL, 5.0 mmol) was subjected to the general procedure (using 5 mol% (salen)Co and 4 mol% DBN) until the reaction reached 48% conversion (10 hours), as determined by GC analysis using 1-decene as an internal standard. The reaction was quenched with ~7M NH_3 in MeOH (7.5 mL) and concentrated, then purified by column chromatography on SiO_2, 5–20% Et_2O in pentane, to provide the title product (305 mg, 44% yield). The enantiomeric excess was determined to be 99% by chiral GC analysis (Cyclodex-B, 100 ºC, 15 min, 15 ºC/min, 150 ºC, 4 min, t_R(major) = 21.0 min, t_R(minor) = 21.3 min); $[\alpha]^{24}_D$ = +60.0 ($CHCl_3$, c = 1.0) (lit.[15] $[\alpha]^{24}_D$ = –67.3 (MeOH, c = 0.94, 85% ee (*R*))). Spectral data were in agreement with literature values.[16]

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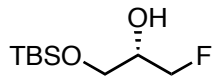
[13] Shellhamer, D. F.; Anstine, D. T.; Gallego, K. M.; Ganesh, B. R.; Hanson, A. A.; Hanson, K. A.; Henderson, R. D.; Prince, J. M.; Healsley, V. L. *J. Chem. Soc. Perkin Trans. 2* **1995**, 861.
[14] Stewart, I. C.; Lee, C. C.; Bergman, R. G.; Toste, F. D. *J. Am. Chem. Soc.* **2005**, *127*, 17676.
[15] Kitazume, T.; Asai, M.; Lin, J. T.; Yamazaki, T. *J. Fluorine Chem.* **1987**, *35*, 477.
[16] DesMarteau, D. D.; Xu, Z.-Q.; Witz, M. *J. Org. Chem.* **1992**, *57*, 629.

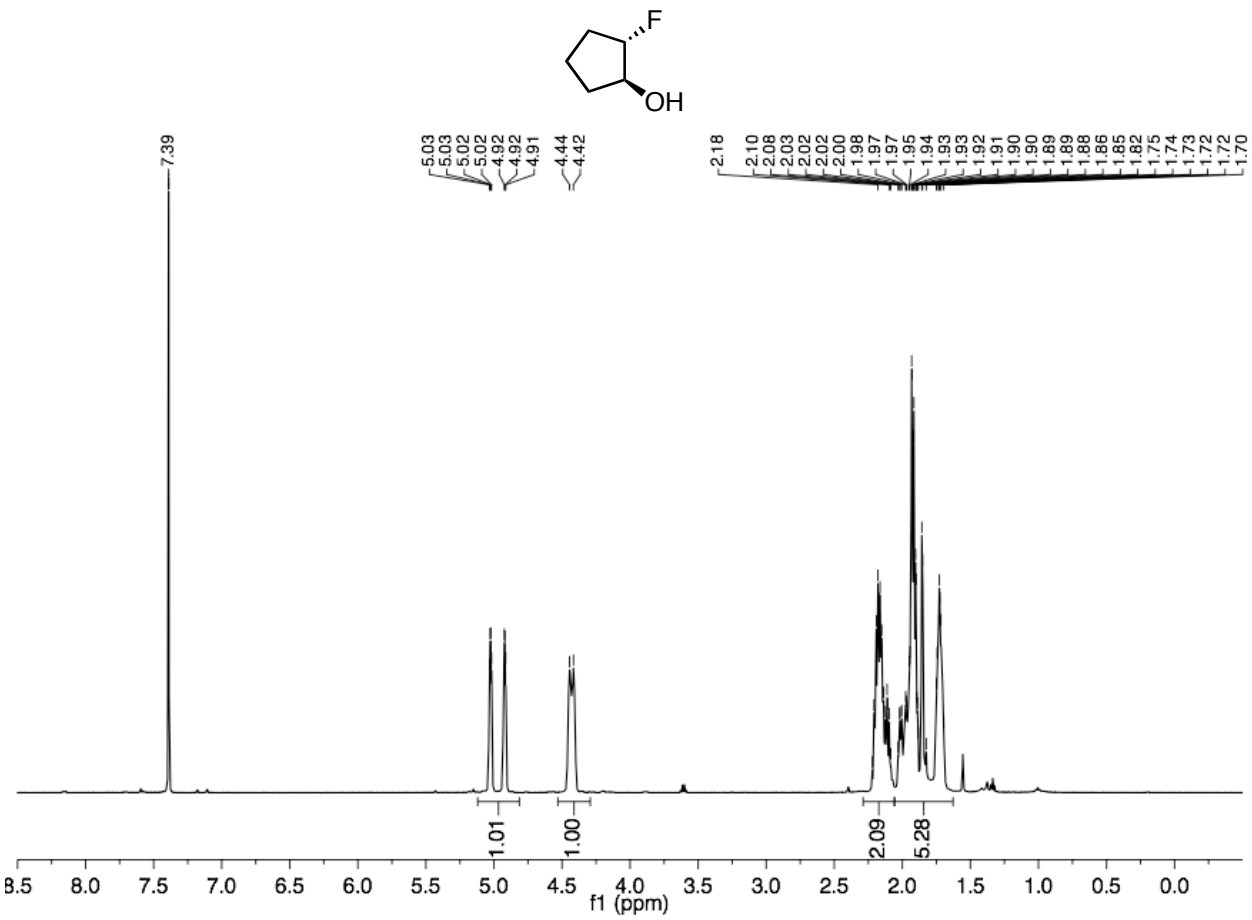
The enantiomeric excess of the unreacted (*R*)-styrene oxide was determined to be 89% by chiral GC analysis (Cyclodex-B, 100 ºC isotherm, t_R(major) = 13.7 min, t_R(minor) = 14.2 min).

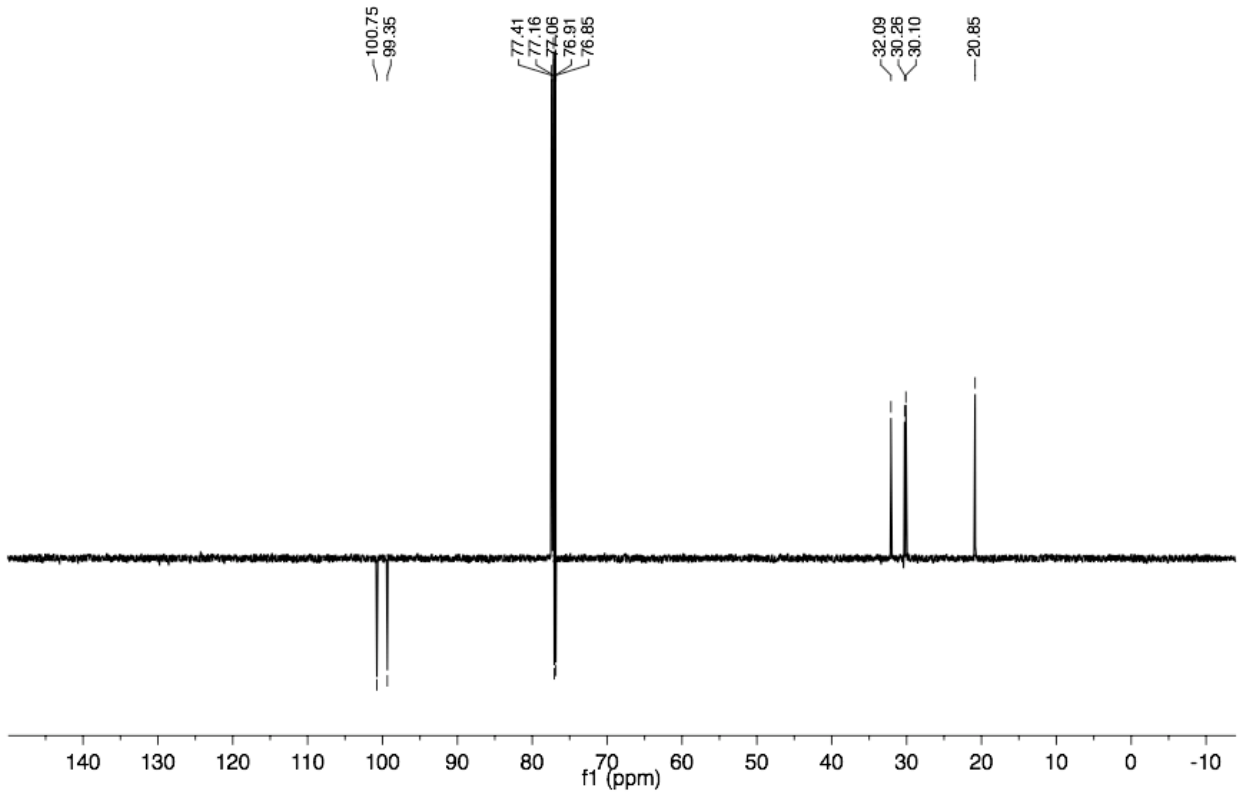


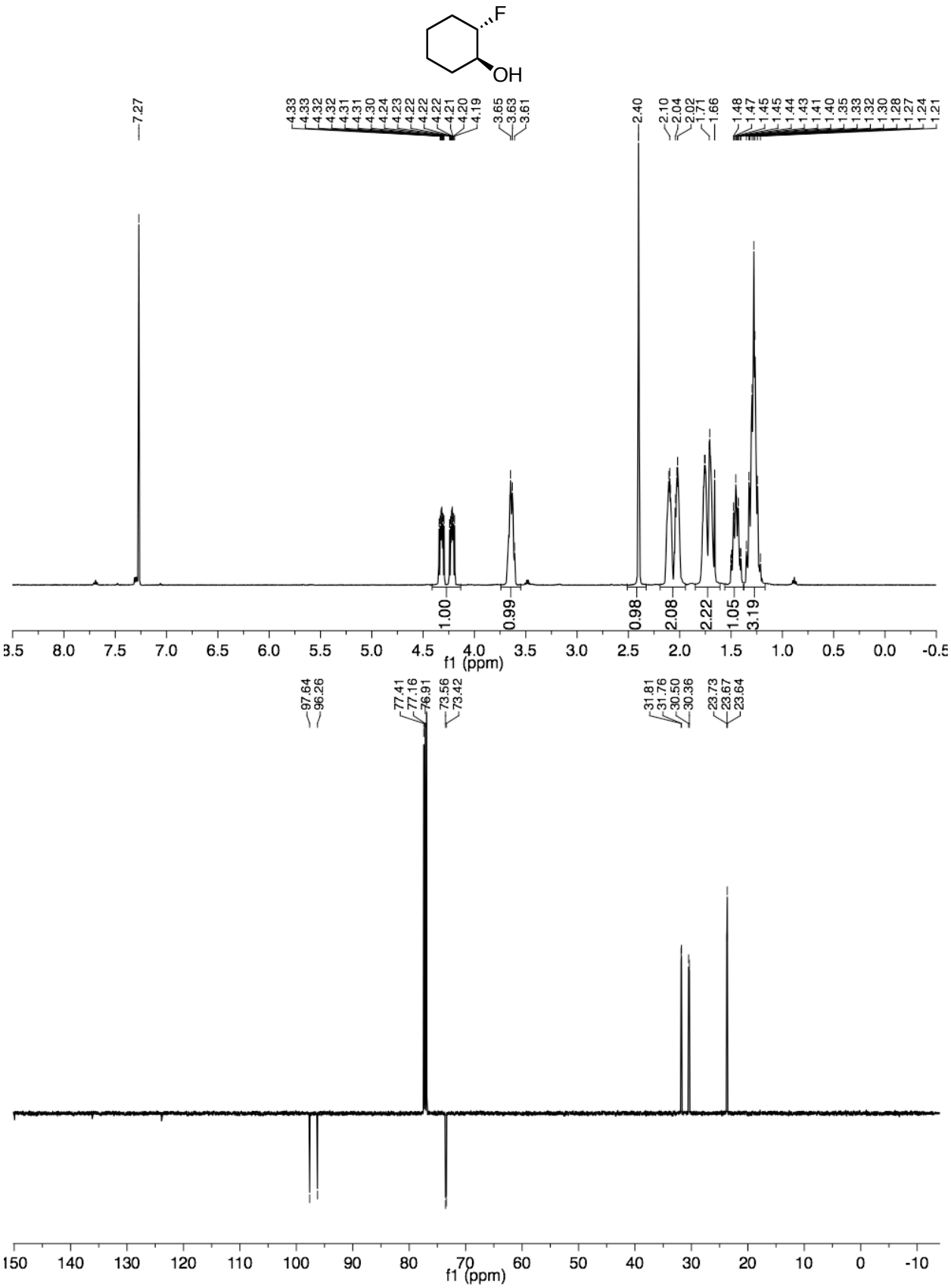
(*S*)-1-(*tert*-butyldimethylsilyloxy)-3-fluoropropan-2-ol. *Tert*-butyldimethylsilyl (±)-glycidyl ether (1.05 mL, 5.0 mmol) was subjected to the general procedure (using 5 mol% (salen)Co and 4 mol% DBN) in a 50-mL polypropylene tube until the reaction reached 52% conversion (24 hours), as determined by GC analysis using 1-decene as an internal standard. The reaction was quenched with sat. $NaHCO_3$ (50 mL) and extracted with Et_2O (2 x 25 mL), then the combined organics were dried over $MgSO_4$, filtered, and concentrated. The crude mixture was purified by column chromatography on SiO_2, 5–20% Et_2O in pentane, to provide the title product (0.460 g, 44% yield). Enantiomeric excess was determined to be 88% by chiral GC analysis (Cyclodex-B, 100 ºC isotherm, t_R(minor) = 20.1 min, t_R(major) = 20.7 min); $[\alpha]^{24}_D$ = +2.3 ($CHCl_3$, c = 1.1); FTIR (thin film, cm^{-1}) 3411 (br), 2956 (s), 2931 (s), 2859 (s), 1472 (m), 1258 (s), 1100 (s), 1019 (s), 838 (s), 779 (s); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.45 (dddd, J = 47.2, 14.7, 9.5, 5.2 Hz, 2H, C**H**$_2$F), 3.90 (ddd, J = 27.1, 10.7, 5.2 Hz, 1H, C**H**OH), 3.71 (dddd, J = 15.6, 10.2, 4.9, 1.4 Hz, 2H, C**H**$_2$OSi), 2.40 (d, J = 6 Hz, 1H, O**H**), 0.91 (s, 9H, SiC(C**H**$_3$)$_3$), 0.09 (s, 6H, SiC**H**$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 83.5 (d, ^{1}J = 169.1 Hz), 70.3 (d, ^{2}J = 20.2 Hz), 62.8 (d, ^{3}J = 6.3 Hz), 26.0, 18.4, –5.3; ^{19}F NMR (282 MHz, $CDCl_3$) δ –194.7 (m); HRMS (ESI+) calculated for $C_9H_{22}FO_2Si$ ($[M+H]^+$): 209.13676, found: 209.13673 (28.8%), calculated for $C_9H_{21}FNaO_2Si$ ($[M+Na]^+$): 231.11871, found: 231.11873 (100.0%).

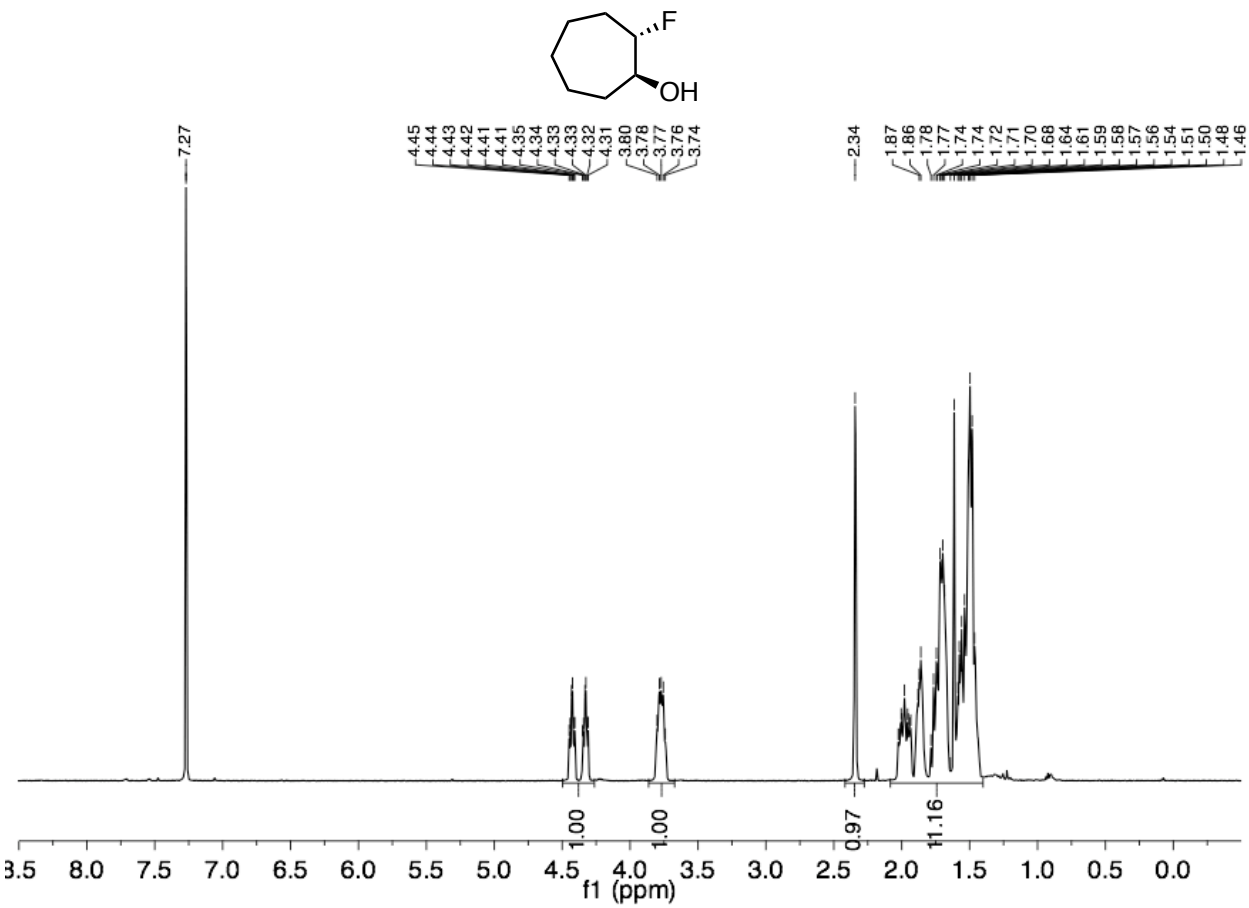
The unreacted TBS (*R*)-glycidyl ether was also isolated during the above sequence and converted to the azido trimethylsilyl ether (azide opening with NaN_3/NH_4Cl followed by silylation with $TMSCl/Et_3N$). The enantiomeric excess was determined to be 95% by chiral GC analysis (Cyclodex-B, 90 ºC isotherm, t_R(minor) = 85.3 min, t_R(major) = 87.4 min).

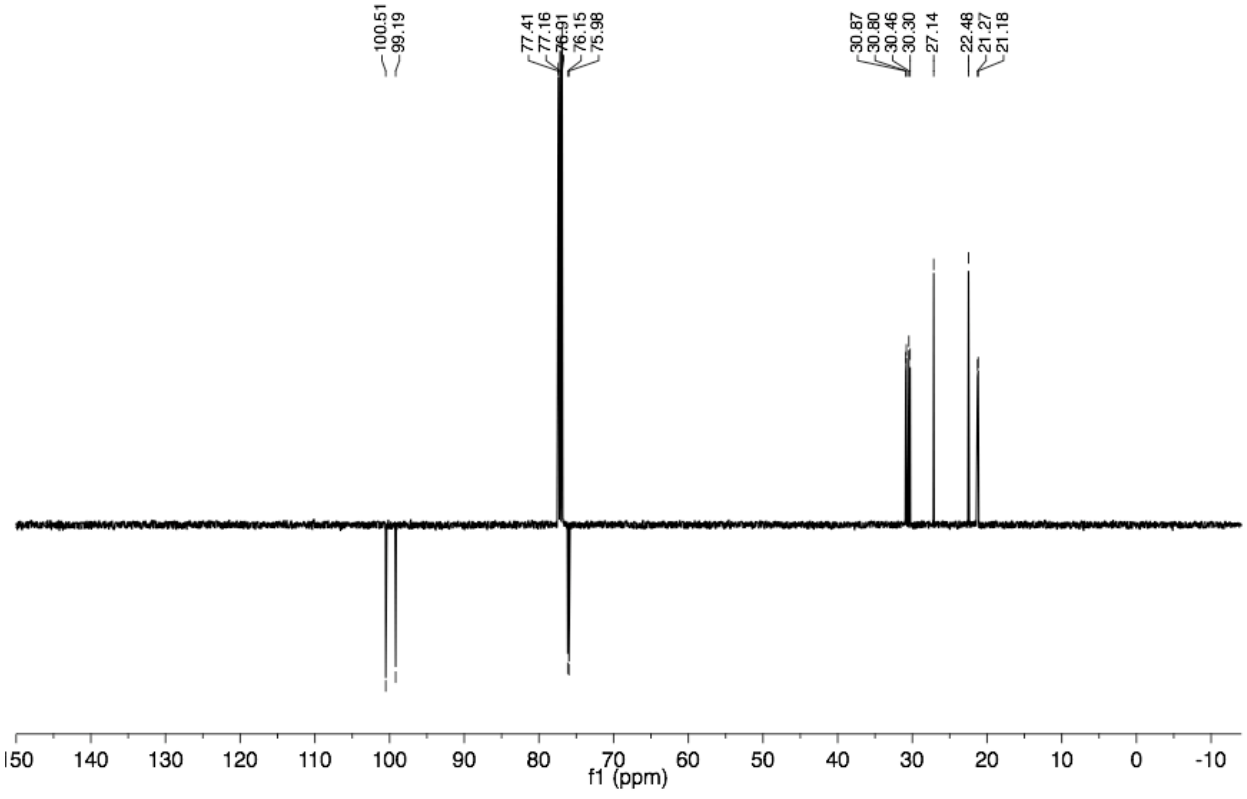
VII. NMR Spectra

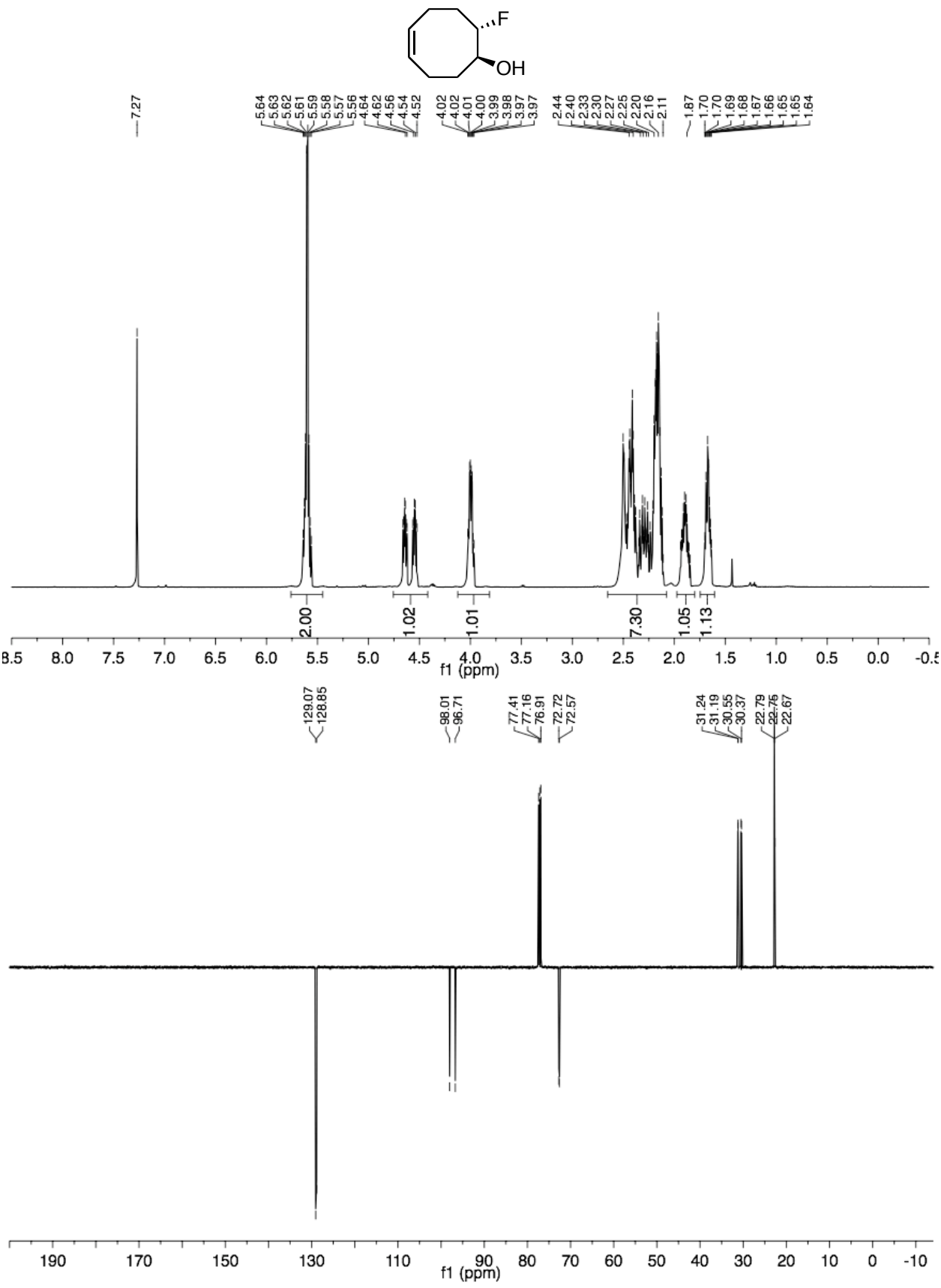


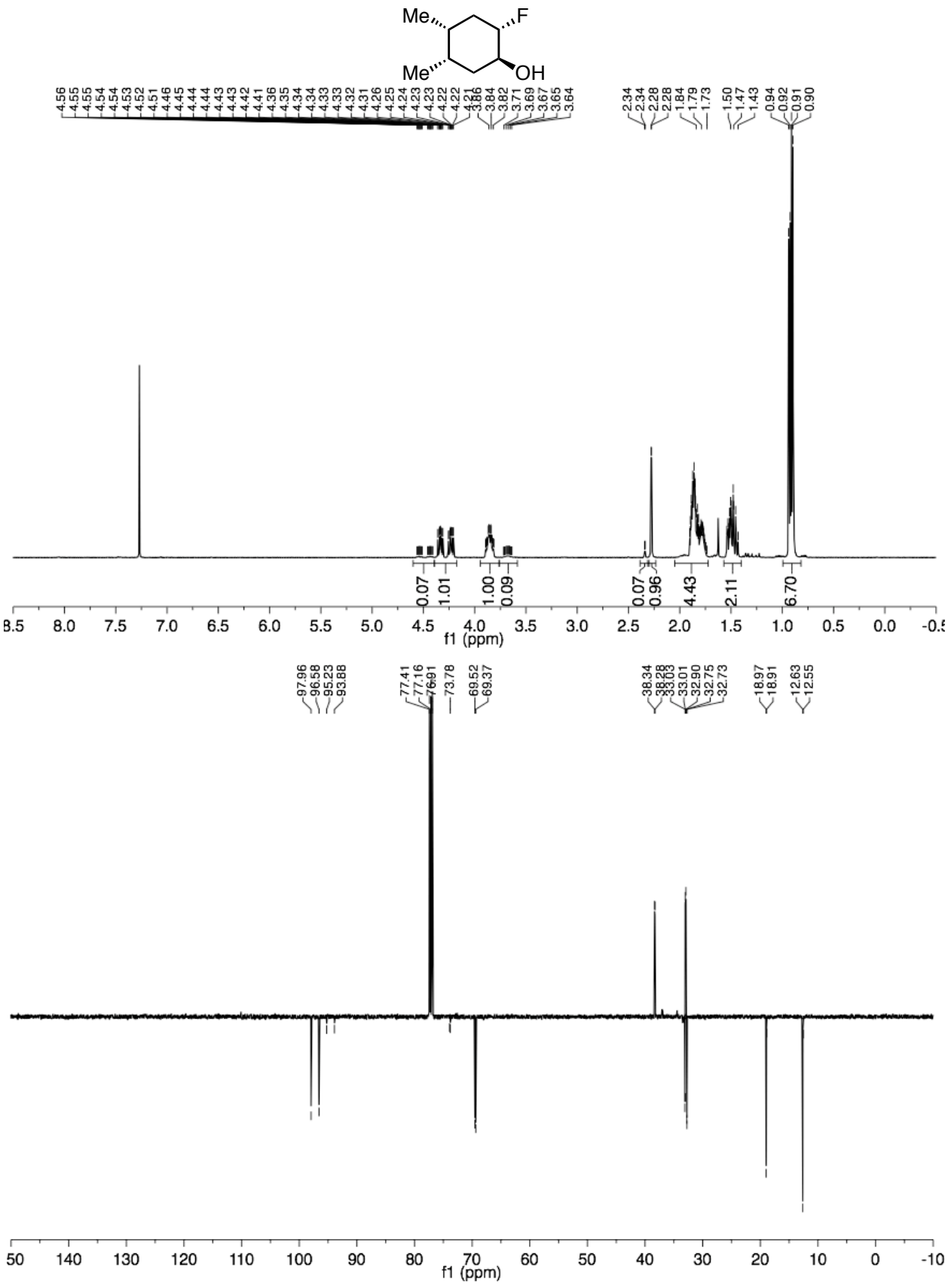


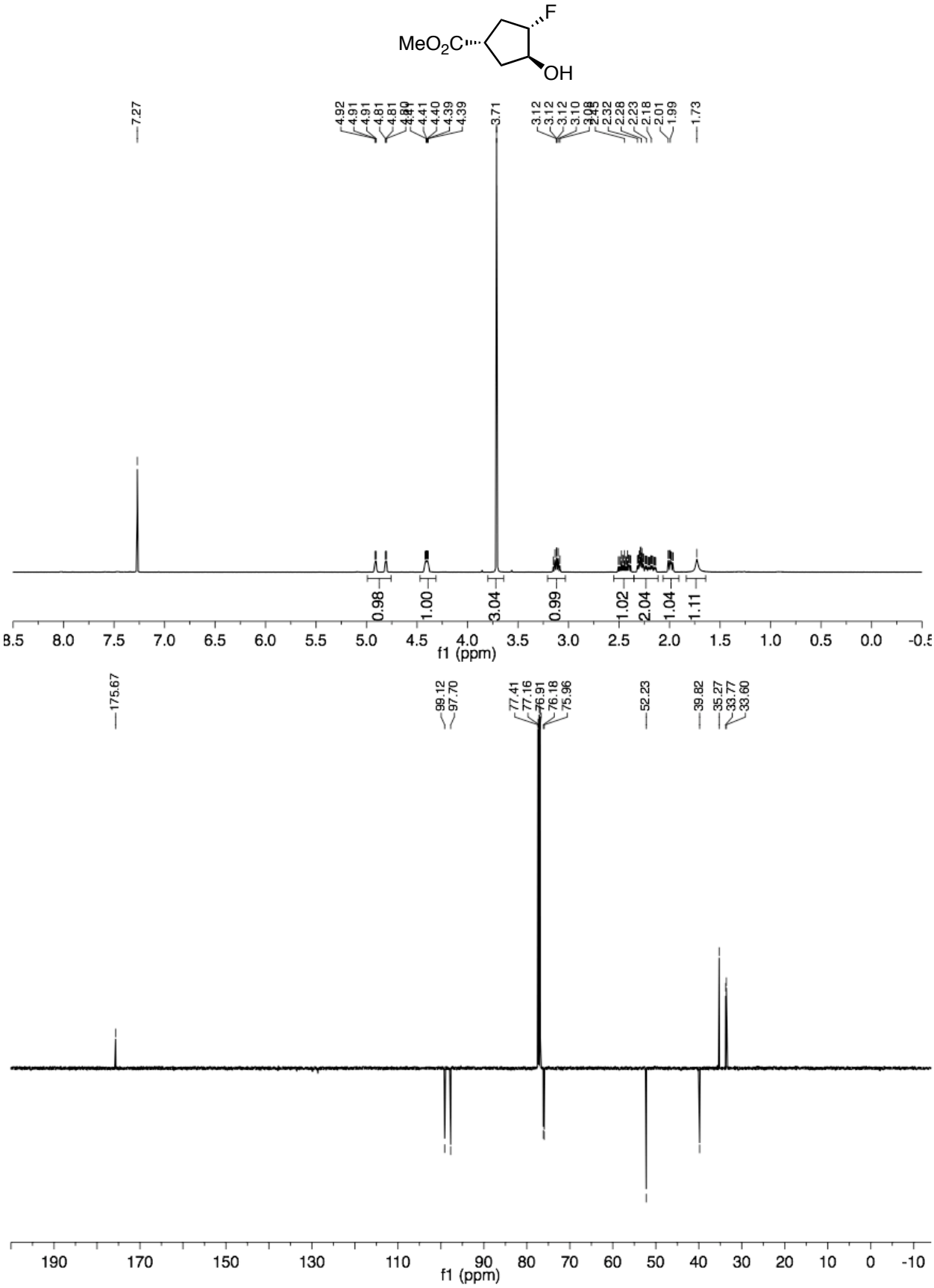

F
OH
7.27
4.33
4.33
4.32
4.32
4.31
4.31
4.30
4.24
4.23
4.22
4.22
4.22
4.21
4.20
4.19
3.65
3.63
3.61
2.40
2.10
2.04
2.02
1.71
1.66
1.48
1.47
1.45
1.45
1.44
1.43
1.41
1.40
1.35
1.33
1.32
1.30
1.28
1.27
1.24
1.21
1.00
0.99
0.98
2.08
2.22
1.05
3.19
f1 (ppm)
97.64
96.26
77.41
77.16
76.91
73.56
73.42
31.81
31.76
30.50
30.36
23.73
23.67
23.64
f1 (ppm)

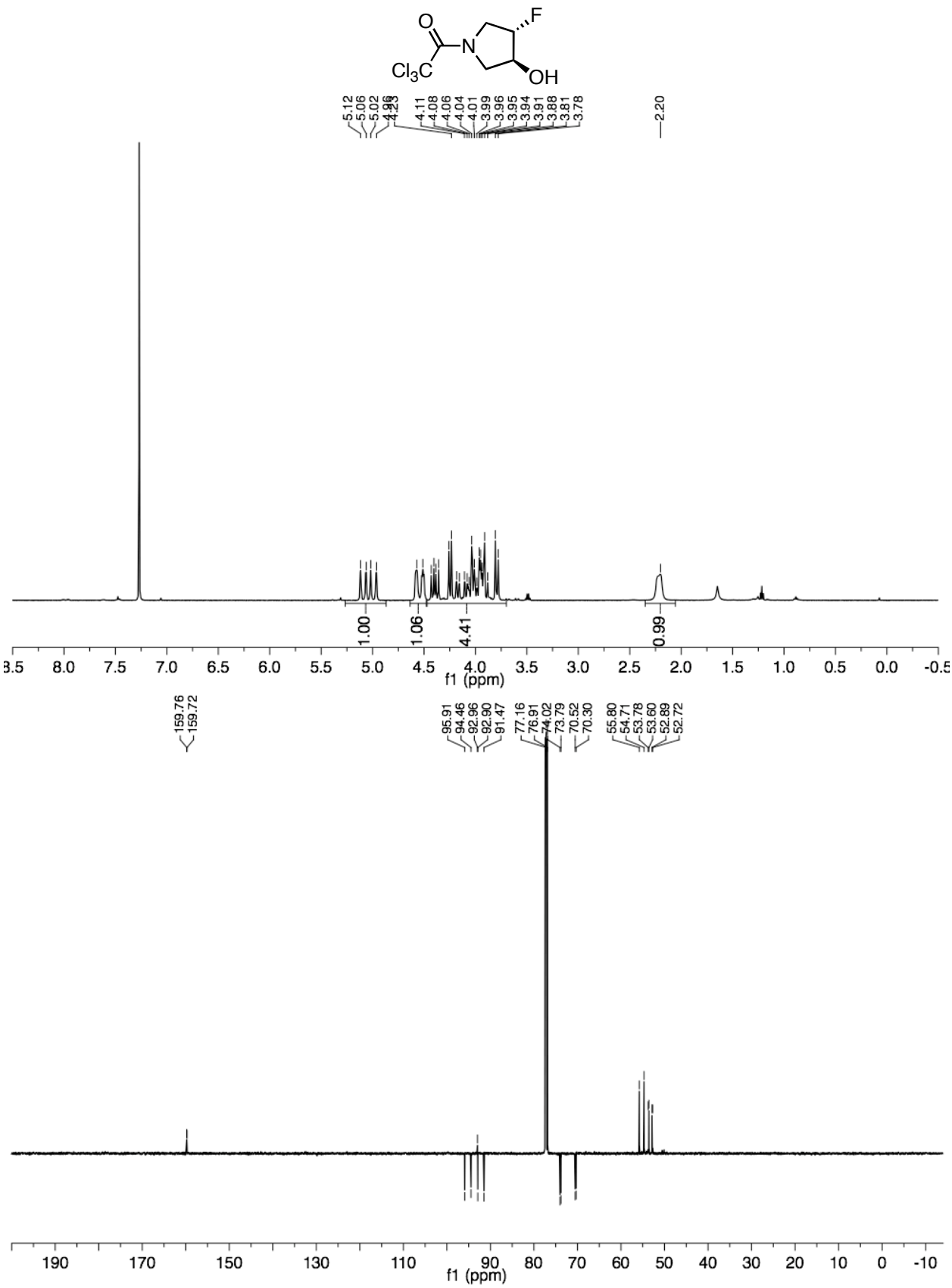

F
OH
7.27
4.45
4.44
4.43
4.42
4.41
4.41
4.35
4.34
4.33
4.33
4.32
4.31
3.80
3.78
3.77
3.76
3.74
2.34
1.87
1.86
1.78
1.77
1.74
1.74
1.72
1.71
1.70
1.68
1.64
1.61
1.59
1.58
1.57
1.56
1.54
1.51
1.50
1.48
1.46
1.00
1.00
0.97
11.16
f1 (ppm)

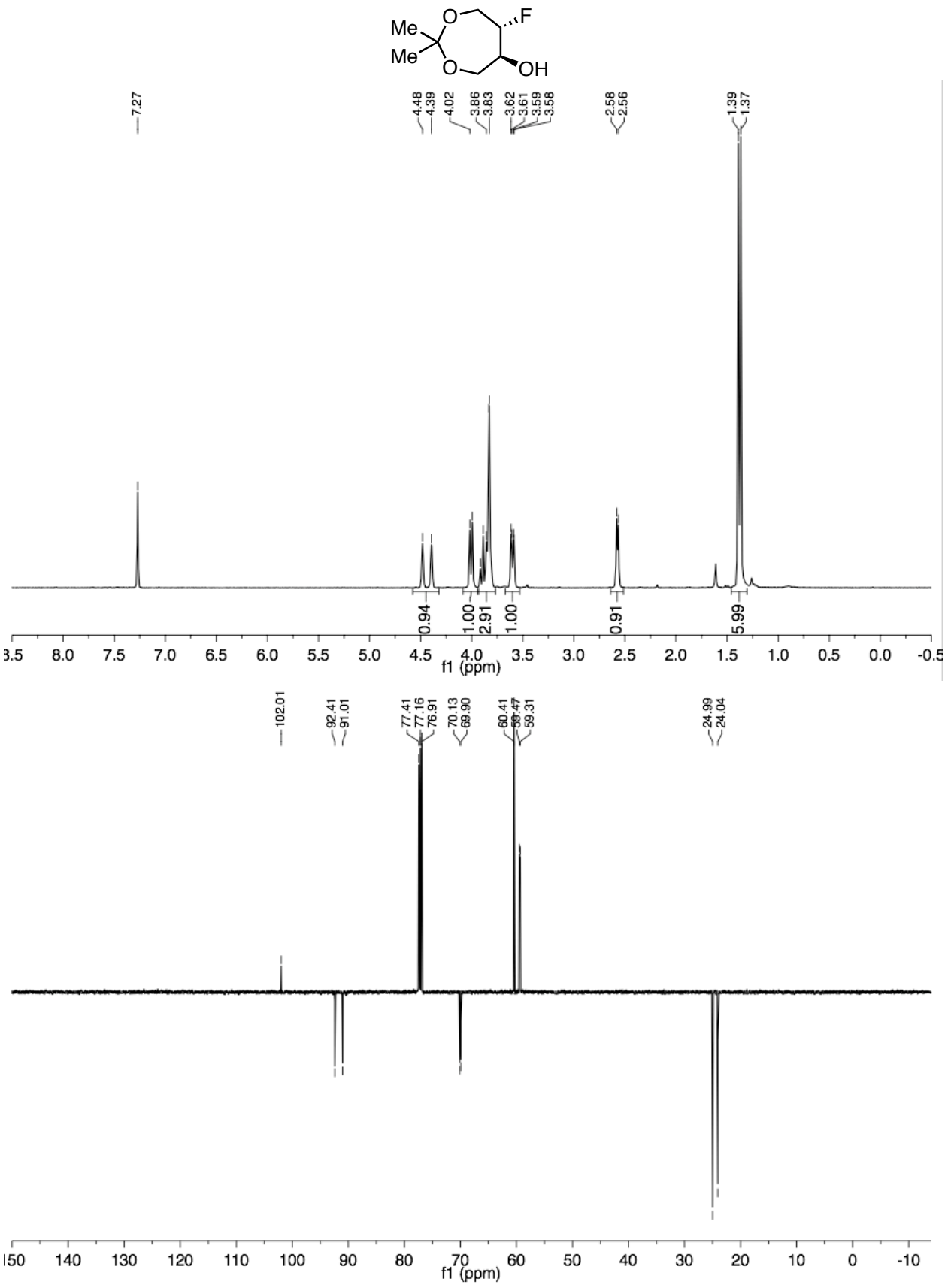

100.51
99.19
77.41
77.16
76.91
76.15
75.98
30.87
30.80
30.46
30.30
27.14
22.48
21.27
21.18
f1 (ppm)

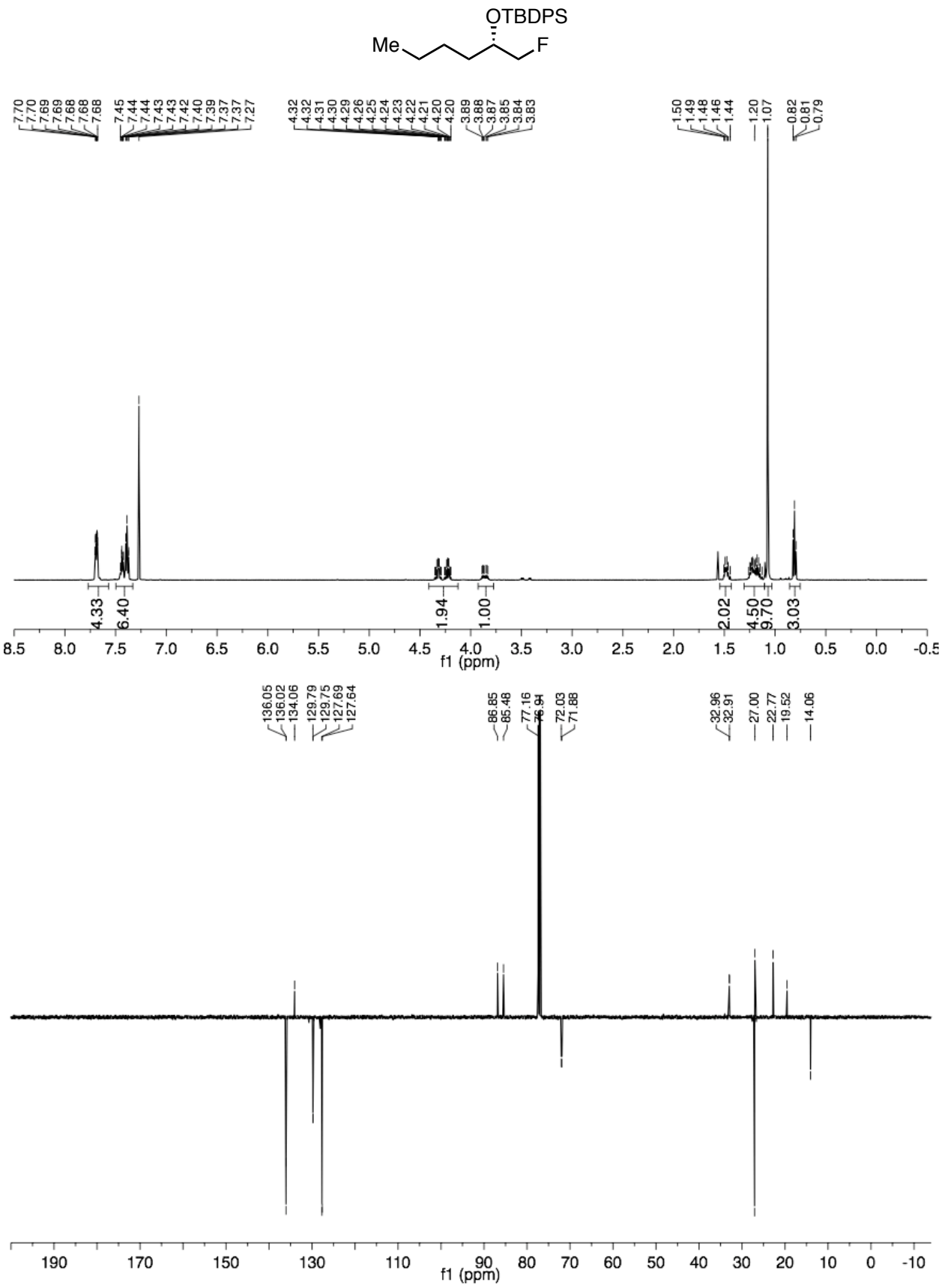

F
OH
7.27
5.64
5.63
5.62
5.61
5.59
5.58
5.57
5.56
4.64
4.62
4.56
4.54
4.52
4.02
4.02
4.01
4.00
3.99
3.98
3.97
3.97
2.44
2.40
2.33
2.30
2.27
2.25
2.20
2.16
2.11
1.87
1.70
1.70
1.69
1.68
1.67
1.66
1.65
1.65
1.64
2.00
1.02
1.01
7.30
1.05
1.13
f1 (ppm)
129.07
128.85
98.01
96.71
77.41
77.16
76.91
72.72
72.57
31.24
31.19
30.55
30.37
22.79
22.76
22.67
f1 (ppm)

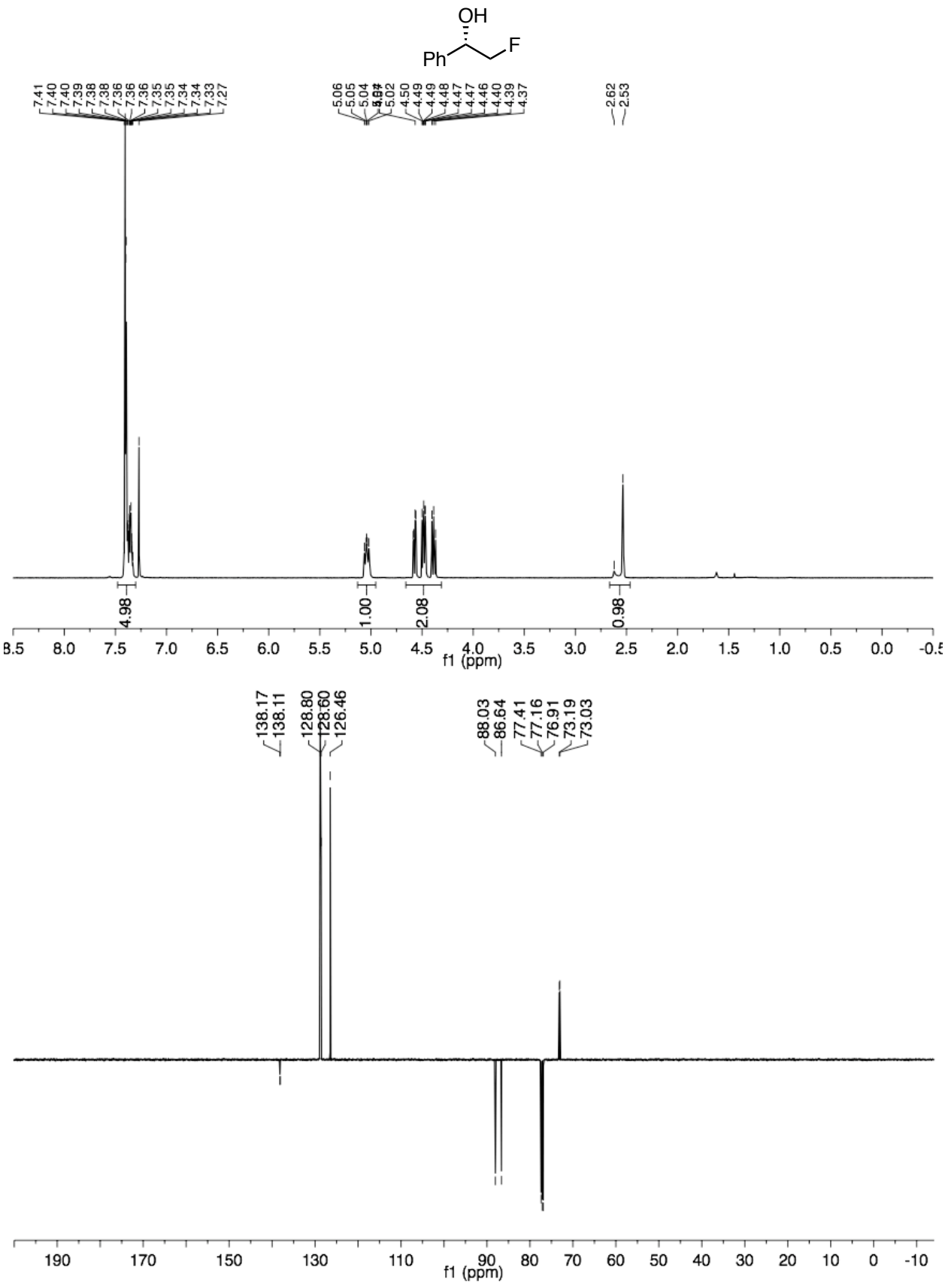

Me
F
Me
OH
f1 (ppm)
f1 (ppm)

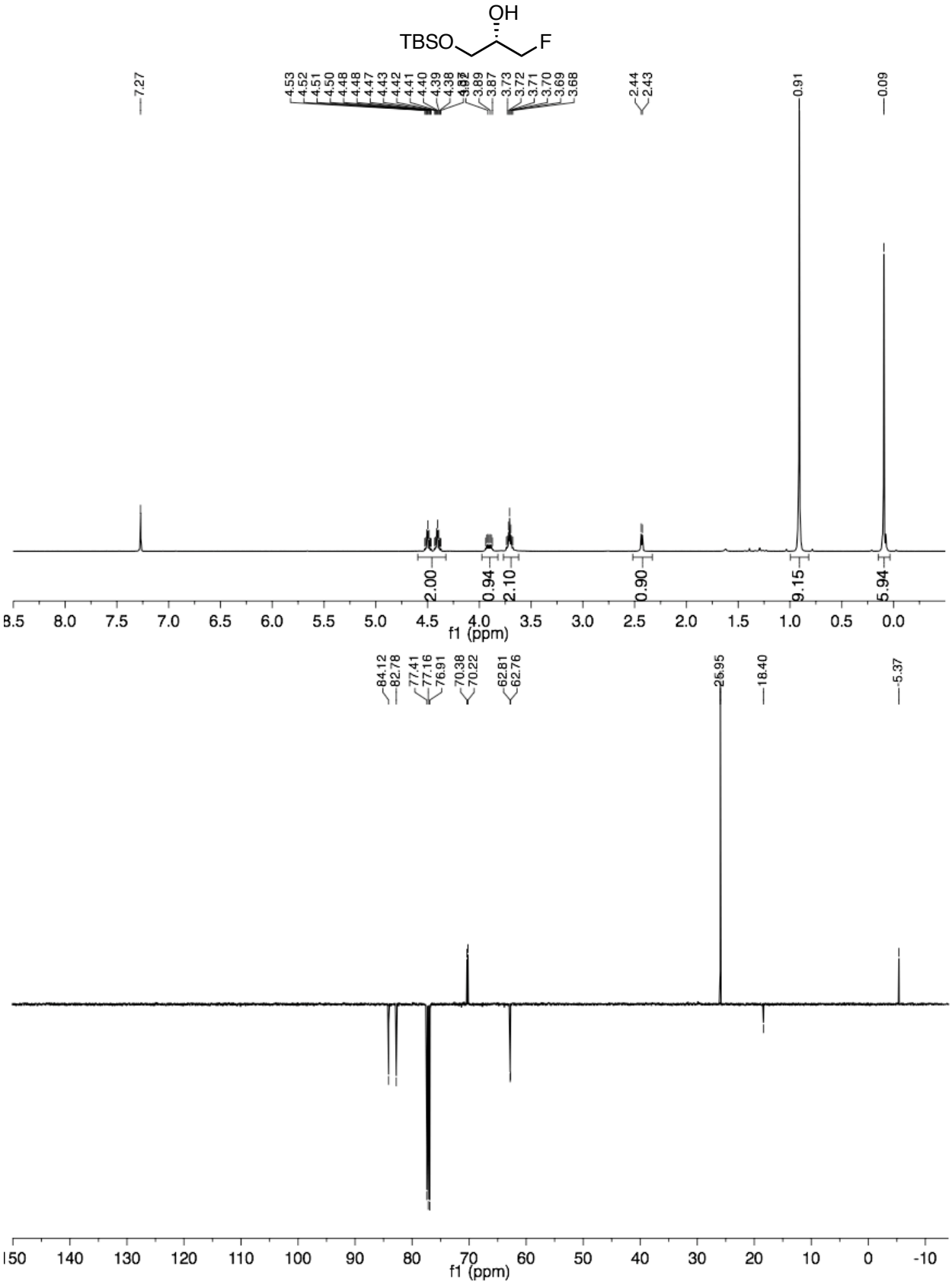

F
MeO2C
OH
7.27
4.92
4.91
4.91
4.81
4.81
4.41
4.40
4.39
4.39
3.71
3.12
3.12
3.12
3.10
2.32
2.28
2.23
2.18
2.01
1.99
1.73
0.98
1.00
3.04
0.99
1.02
2.04
1.04
1.11
f1 (ppm)
175.67
99.12
97.70
77.41
77.16
76.91
76.18
75.96
52.23
39.82
35.27
33.77
33.60
f1 (ppm)


O
N
F
OH
Cl3C
5.12
5.06
5.02
4.96
4.93
4.11
4.08
4.06
4.04
4.01
3.99
3.96
3.95
3.94
3.91
3.88
3.81
3.78
2.20
1.00
1.06
4.41
0.99
f1 (ppm)
159.76
159.72
95.91
94.46
92.96
92.90
91.47
77.16
76.91
74.02
73.79
70.52
70.30
55.80
54.71
53.78
53.60
52.89
52.72
f1 (ppm)

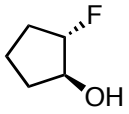

Me
Me
O
O
F
OH
7.27
4.48
4.39
4.02
3.86
3.83
3.62
3.61
3.59
3.58
2.58
2.56
1.39
1.37
0.94
1.00
2.91
1.00
0.91
5.99
f1 (ppm)
102.01
92.41
91.01
77.41
77.16
76.91
70.13
69.90
60.41
59.47
59.31
24.99
24.04
f1 (ppm)


OTBDPS
Me
F
f1 (ppm)
f1 (ppm)


OH
Ph
F
7.41
7.40
7.40
7.39
7.38
7.38
7.36
7.36
7.36
7.35
7.35
7.34
7.34
7.33
7.27
5.06
5.05
5.04
5.02
4.50
4.49
4.49
4.48
4.47
4.47
4.46
4.40
4.39
4.37
2.62
2.53
4.98
1.00
2.08
0.98
f1 (ppm)
138.17
138.11
128.80
128.60
126.46
88.03
86.64
77.41
77.16
76.91
73.19
73.03
f1 (ppm)

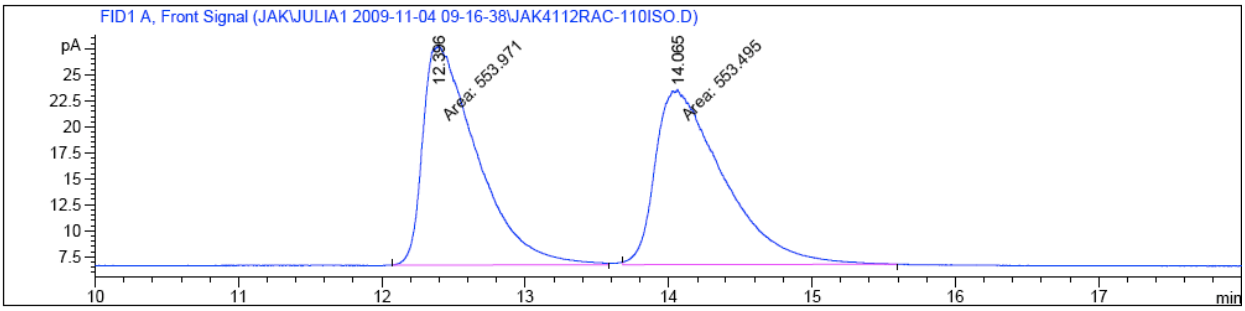

OH
TBSO
F
7.27
4.53
4.52
4.51
4.50
4.48
4.48
4.47
4.43
4.42
4.41
4.40
4.39
4.38
3.89
3.87
3.73
3.72
3.71
3.70
3.69
3.68
2.44
2.43
0.91
0.09
2.00
0.94
2.10
0.90
9.15
5.94
f1 (ppm)
84.12
82.78
77.41
77.16
76.91
70.38
70.22
62.81
62.76
25.95
18.40
-5.37
f1 (ppm)

VIII. GC and HPLC Traces



β-TBDAc, 110 °C isotherm, 1 mL/min

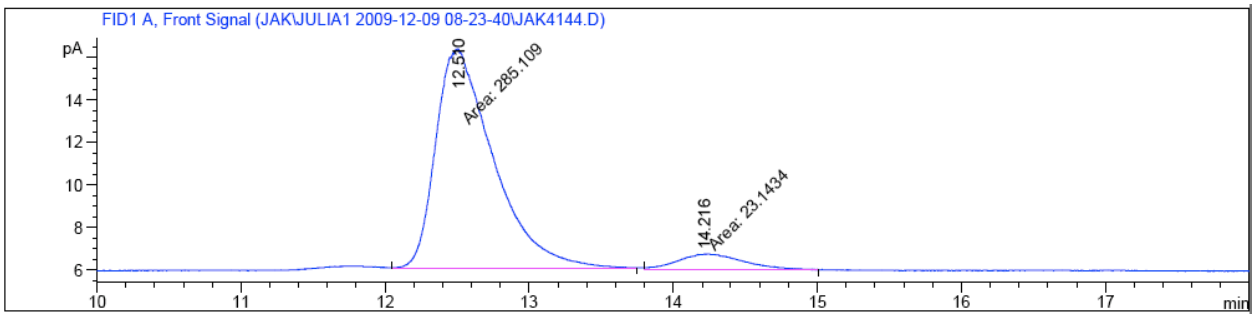
racemic:



Signal 1: FID1 A, Front Signal

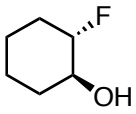
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	12.396	MF	0.4385	553.97131	21.05663	50.02152
2	14.065	FM	0.5477	553.49469	16.84202	49.97848
Totals :				1107.46600	37.89866	

85% ee:



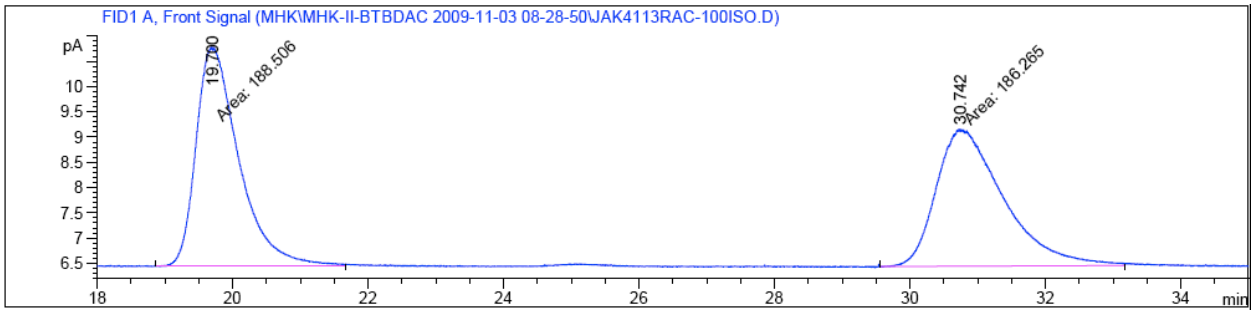
Signal 1: FID1 A, Front Signal

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	12.510	MM	0.4614	285.10861	10.29867	92.49206
2	14.216	MM	0.5221	23.14338	7.38731e-1	7.50794
Totals :				308.25199	11.03740	



β-TBDAc, 100 °C isotherm, 1 mL/min

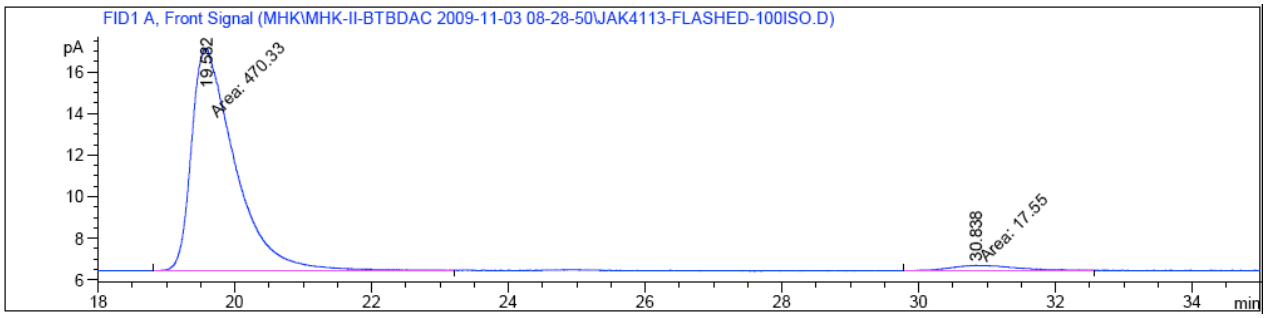
racemic:



Signal 1: FID1 A, Front Signal

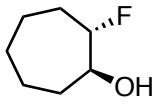
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	19.700	MM	0.7231	188.50551	4.34462	50.29889
2	30.742	MM	1.1428	186.26521	2.71660	49.70111
Totals :				374.77072	7.06123	

93% ee:



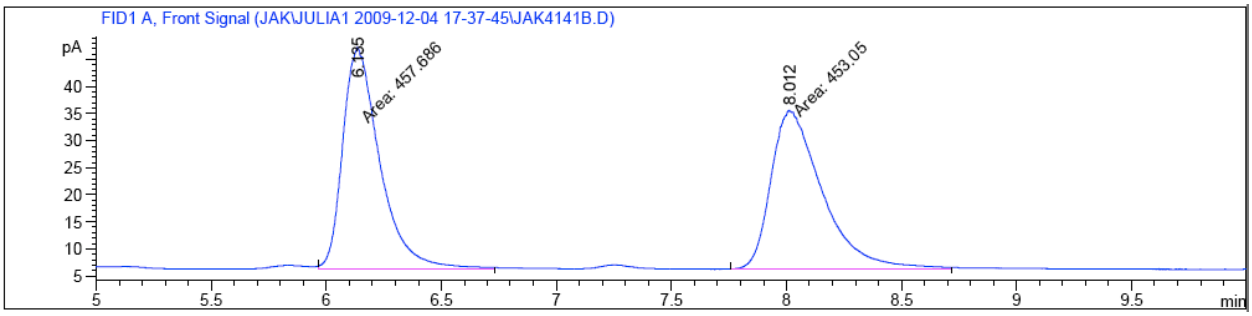
Signal 1: FID1 A, Front Signal

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	19.582	MM	0.7303	470.32996	10.73351	96.40281
2	30.838	MM	1.1161	17.54997	2.62084e-1	3.59719
Totals :				487.87992	10.99560	



β-TBDAc, 120 °C isotherm, 1 mL/min

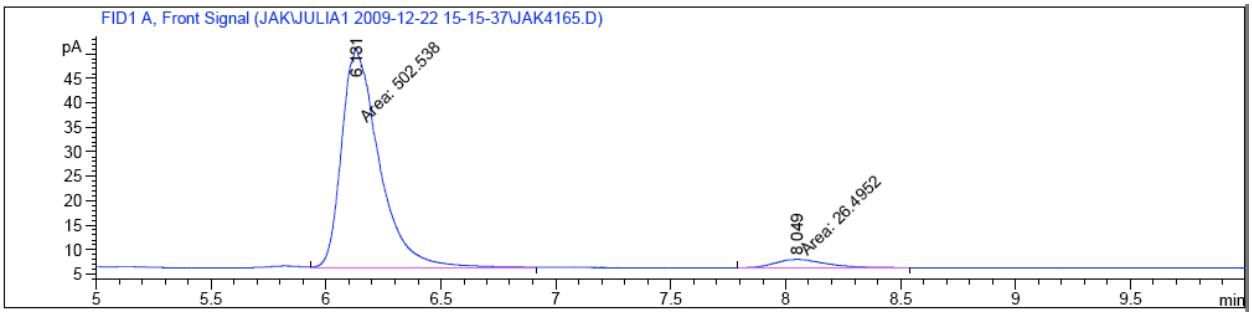
racemic:



Signal 1: FID1 A, Front Signal

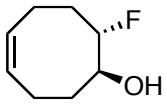
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	6.135	FM	0.1864	457.68604	40.91931	50.25453
2	8.012	MM	0.2576	453.04977	29.31019	49.74547
Totals :				910.73581	70.22950	

90% ee:



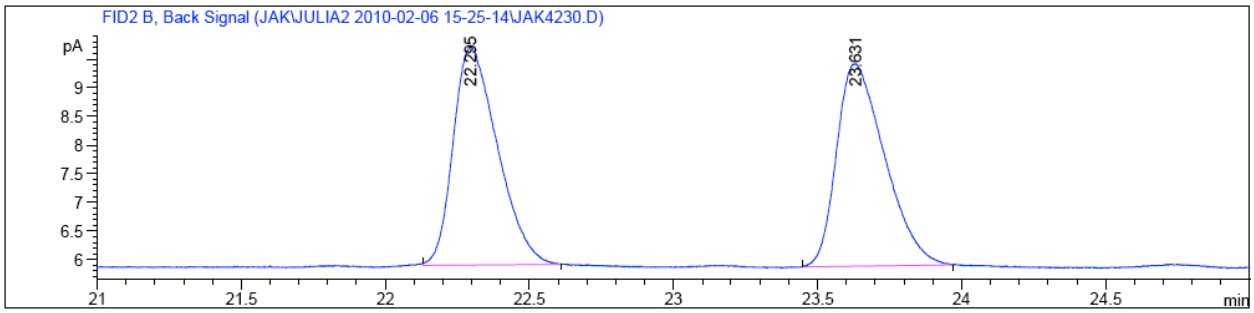
Signal 1: FID1 A, Front Signal

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	6.131	FM	0.1862	502.53827	44.97766	94.99177
2	8.049	MM	0.2539	26.49523	1.73900	5.00823
Totals :				529.03350	46.71666	



Cyclodex-B, 110 ºC isotherm, 1.2 mL/min

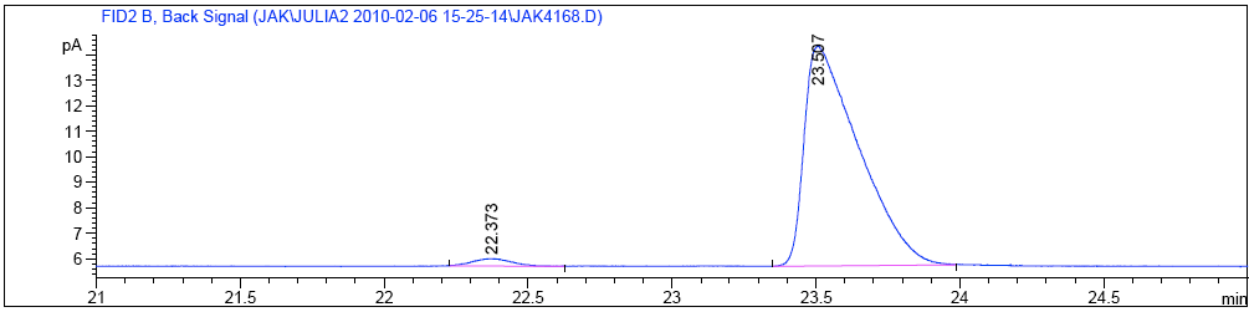
racemic:



Signal 1: FID2 B, Back Signal

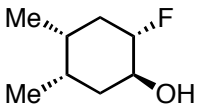
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	22.295	BB	0.1294	40.66261	3.81370	49.74618
2	23.631	BB	0.1437	41.07756	3.53120	50.25382
Totals :				81.74017	7.34491	

95% ee:



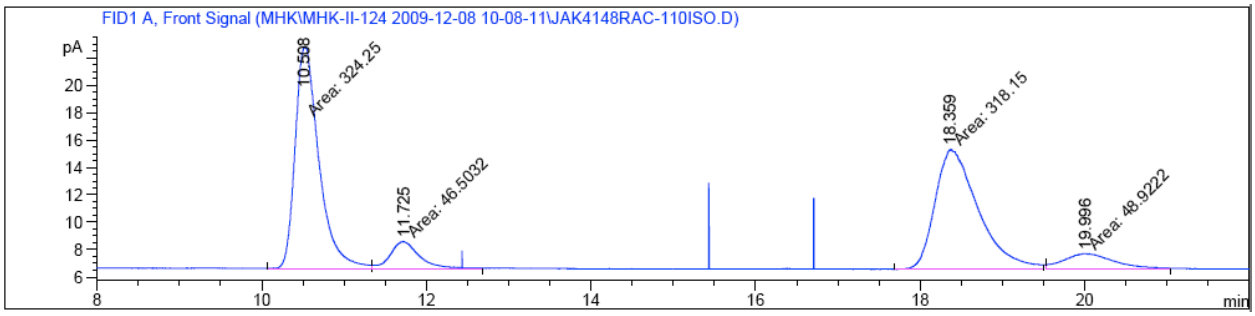
Signal 1: FID2 B, Back Signal

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	22.373	BB	0.1156	2.68675	2.83298e-1	2.30478
2	23.507	BB	0.1722	113.88656	8.64573	97.69522
Totals :				116.57331	8.92903	



β-TBDAc, 110 °C isotherm, 1 mL/min

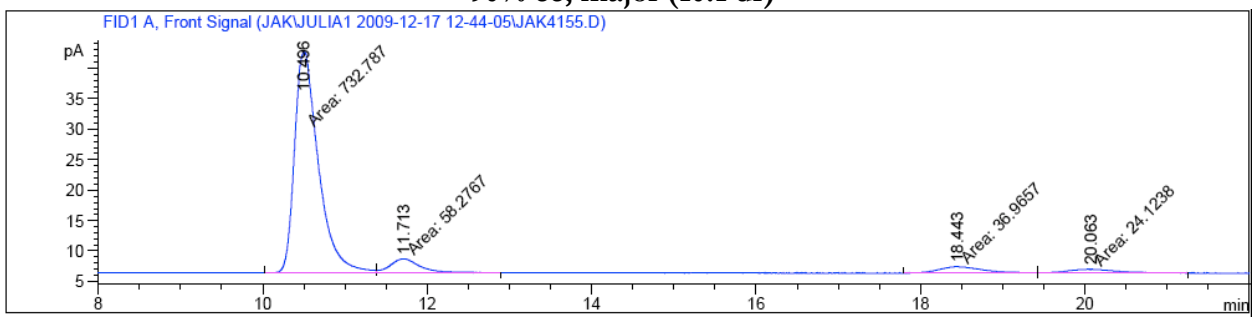
racemic:



Signal 1: FID1 A, Front Signal

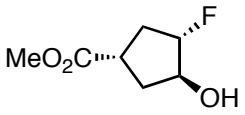
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	10.508	MF	0.3351	324.24985	16.12609	43.94668
2	11.725	FM	0.3974	46.50322	1.95023	6.30274
3	18.359	MF	0.6061	318.15024	8.74794	43.11998
4	19.996	FM	0.7160	48.92225	1.13874	6.63060
Totals :				737.82556	27.96299	

90% ee, major (10:1 dr)



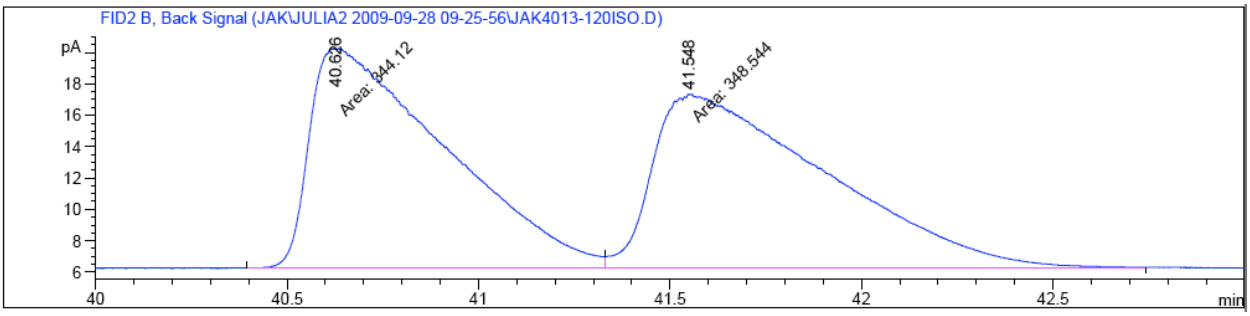
Signal 1: FID1 A, Front Signal

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	10.496	MF	0.3363	732.78680	36.31808	85.99241
2	11.713	FM	0.4233	58.27666	2.29468	6.83876
3	18.443	MF	0.6051	36.96571	1.01820	4.33792
4	20.063	FM	0.6542	24.12375	6.14594e-1	2.83092
Totals :				852.15293	40.24556	



Cyclodex-B, 120 ºC isotherm, 1 mL/min

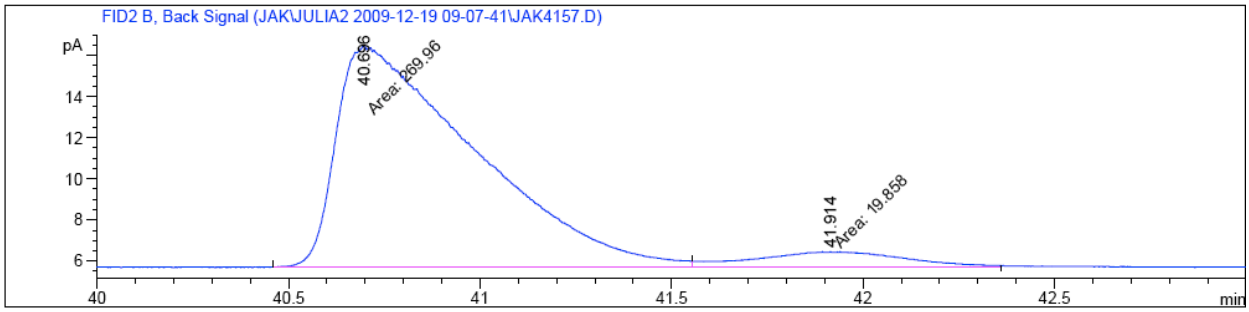
racemic:



Signal 1: FID2 B, Back Signal

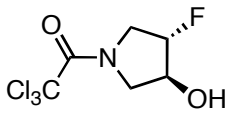
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	40.626	MF	0.4074	344.11960	14.07832	49.68062
2	41.548	FM	0.5239	348.54404	11.08866	50.31938
Totals :				692.66364	25.16698	

86% ee:



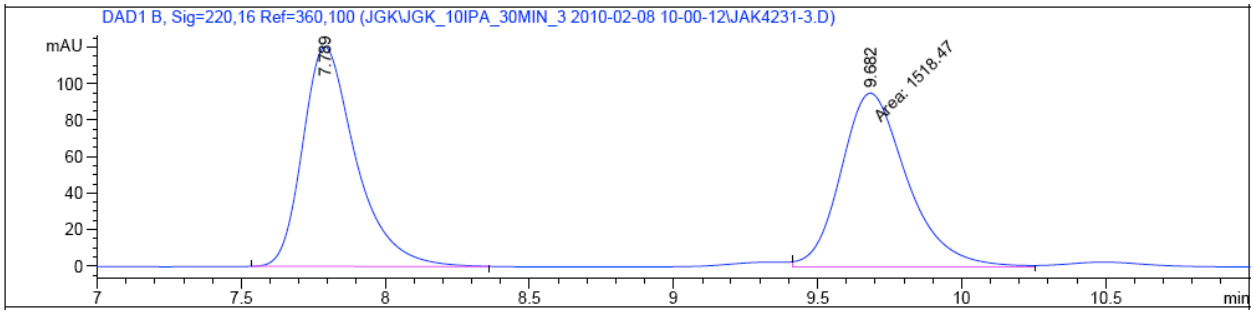
Signal 1: FID2 B, Back Signal

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	40.696	MF	0.4186	269.95950	10.74928	93.14811
2	41.914	FM	0.4532	19.85797	7.30210e-1	6.85189
Totals :				289.81747	11.47949	



Chiracel AD-H, 90% hexane/IPA, 1 mL/min

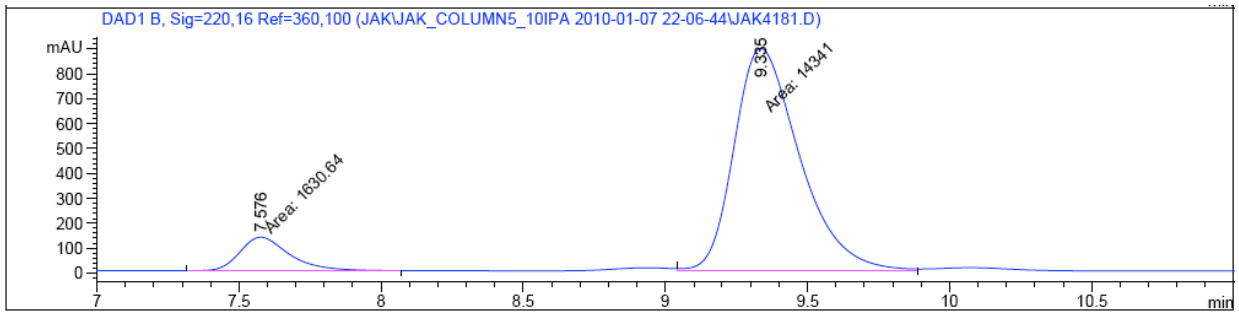
racemic:



Signal 2: DAD1 B, Sig=220,16 Ref=360,100

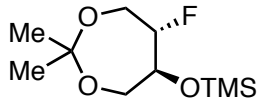
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.789	BB	0.1944	1552.57629	120.45594	50.5553
2	9.682	FM	0.2661	1518.47144	95.10176	49.4447
Totals :				3071.04773	215.55770	

80% ee:



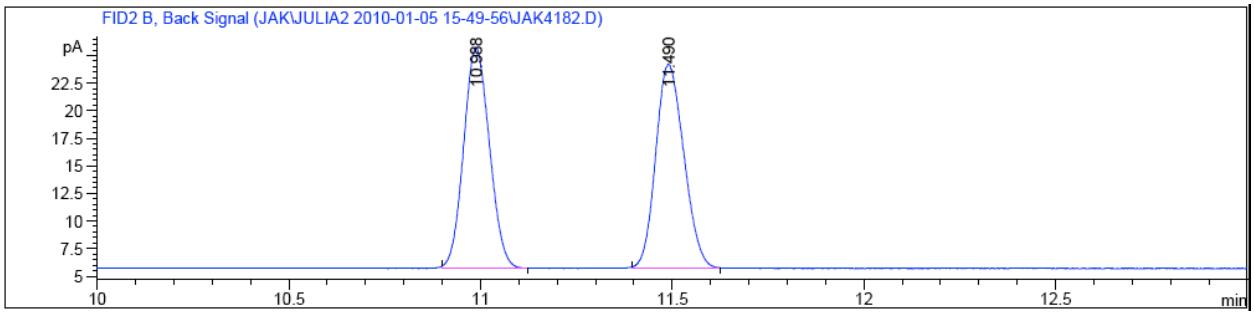
Signal 2: DAD1 B, Sig=220,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.576	MM	0.2019	1630.64185	134.63554	10.2096
2	9.335	MF	0.2675	1.43410e4	893.67841	89.7904
Totals :				1.59716e4	1028.31395	



Cyclodex-B, 110 °C isotherm, 1 mL/min

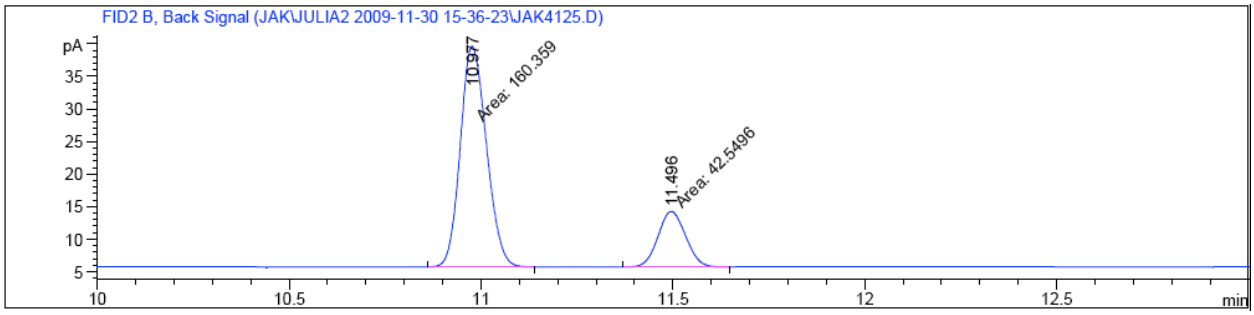
racemic:



Signal 1: FID2 B, Back Signal

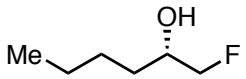
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	10.988	BB	0.0745	93.44767	19.98779	49.80962
2	11.490	BB	0.0794	94.16201	18.48276	50.19038
Totals :				187.60968	38.47055	

58% ee:



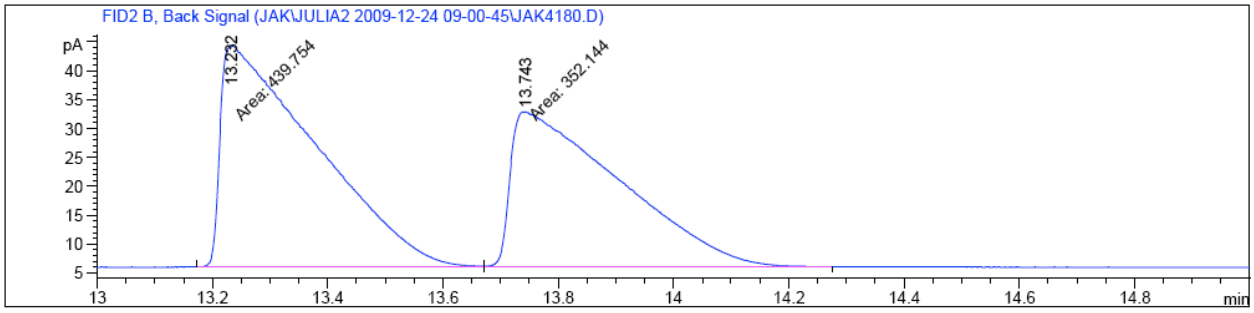
Signal 1: FID2 B, Back Signal

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	10.977	MM	0.0789	160.35948	33.88081	79.03020
2	11.496	MM	0.0830	42.54963	8.54139	20.96980
Totals :				202.90911	42.42220	



Cyclodex-B, 80 ºC isotherm, 1 mL/min

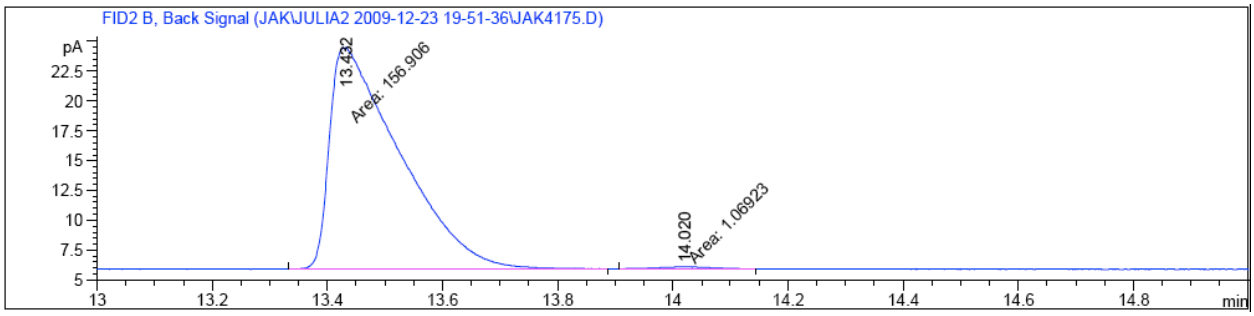
racemic:



Signal 1: FID2 B, Back Signal

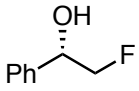
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	13.232	MF	0.1912	439.75385	38.33882	55.53167
2	13.743	FM	0.2189	352.14355	26.81447	44.46833
Totals :				791.89740	65.15329	

99% ee:



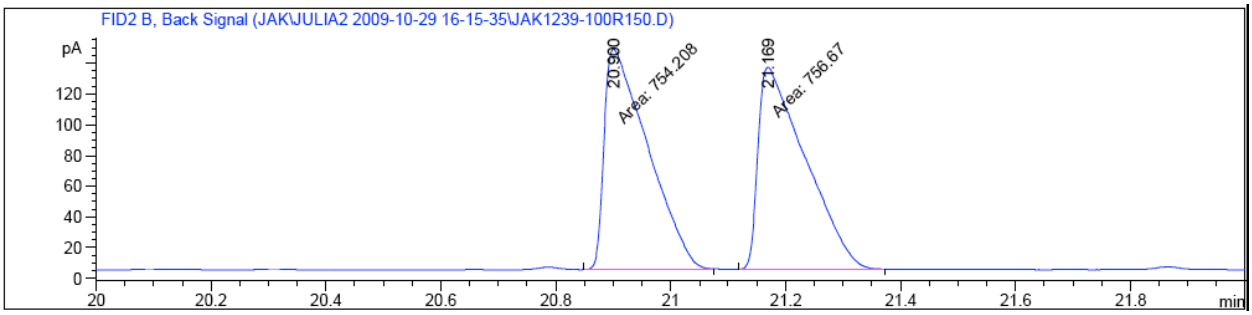
Signal 1: FID2 B, Back Signal

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	13.432	MF	0.1406	156.90572	18.59299	99.32317
2	14.020	MM	0.1120	1.06923	1.59141e-1	0.67683
Totals :				157.97494	18.75213	



Cyclodex-B, 100 ºC, 15 min; 15 ºC/min, 150 ºC, 4 min, 1 mL/min

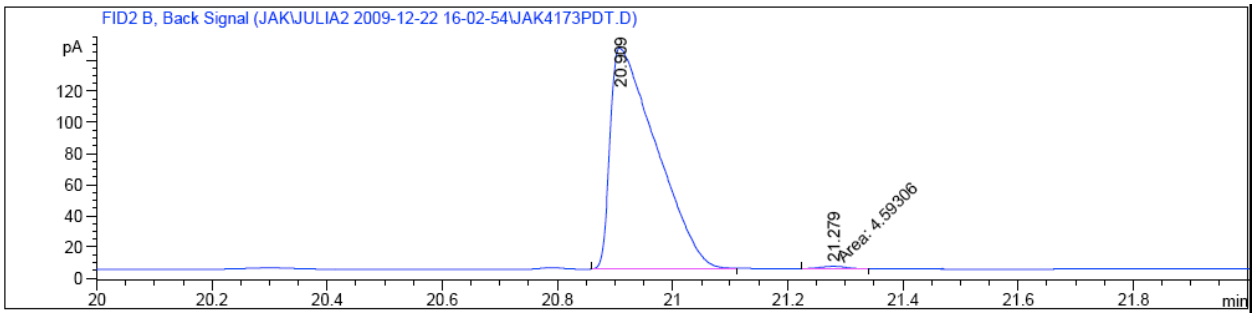
racemic:



Signal 1: FID2 B, Back Signal

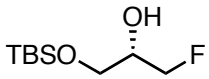
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	20.900	MM	0.0876	754.20819	143.54425	49.91854
2	21.169	MM	0.0957	756.66968	131.80058	50.08146
Totals :				1510.87787	275.34483	

99% ee:



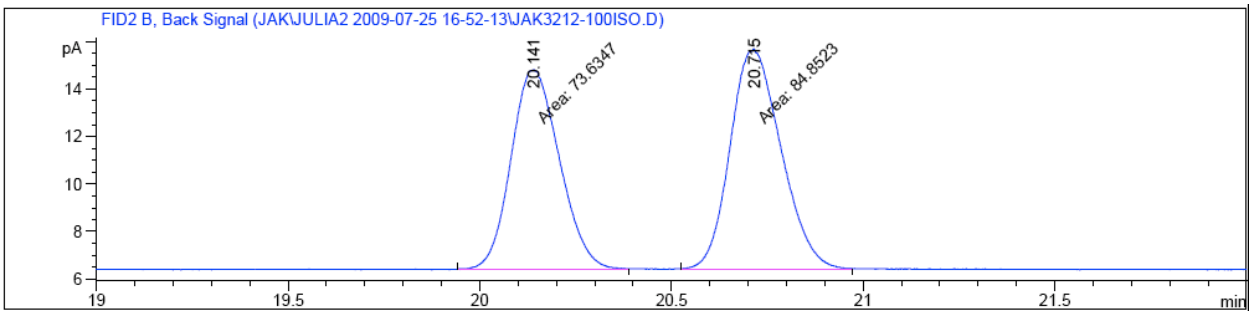
Signal 1: FID2 B, Back Signal

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	20.909	BB	0.0770	789.81348	141.66470	99.42183
2	21.279	MM	0.0506	4.59306	1.51328	0.57817
Totals :				794.40653	143.17798	



Cyclodex-B, 100 ºC isotherm, 1 mL/min

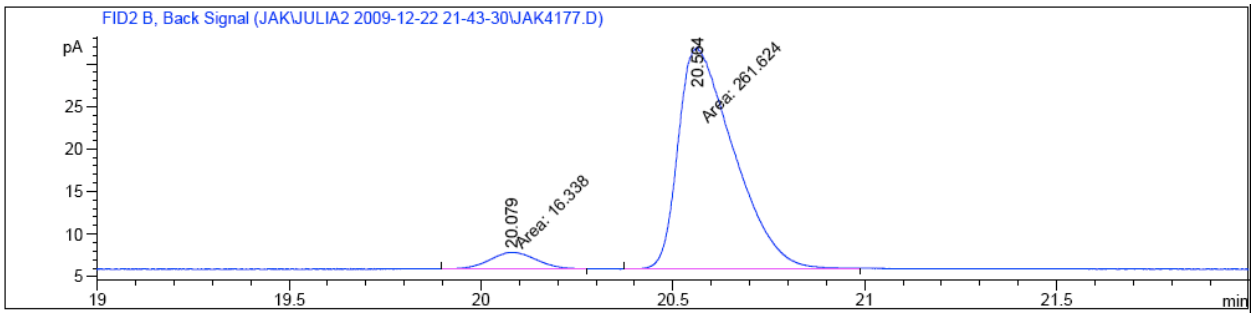
racemic:



Signal 1: FID2 B, Back Signal

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	20.141	MM	0.1460	73.63473	8.40391	46.46105
2	20.715	MM	0.1527	84.85229	9.26158	53.53895
Totals :				158.48701	17.66549	

88% ee:



Signal 1: FID2 B, Back Signal

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	20.079	MM	0.1394	16.33800	1.95310	5.87777
2	20.564	MF	0.1673	261.62445	26.06424	94.12223
Totals :				277.96245	28.01734	