# Supporting Information

# A Simple Primary Amine Catalyst for Enantioselective α-Hydroxylations and α-Fluorinations of Branched Aldehydes

Michael R. Witten and Eric N. Jacobsen*

*Department of Chemistry & Chemical Biology, Harvard University, Cambridge, Massachusetts 02138*

Email: jacobsen@chemistry.harvard.edu

**Contents**



## 1. General Information

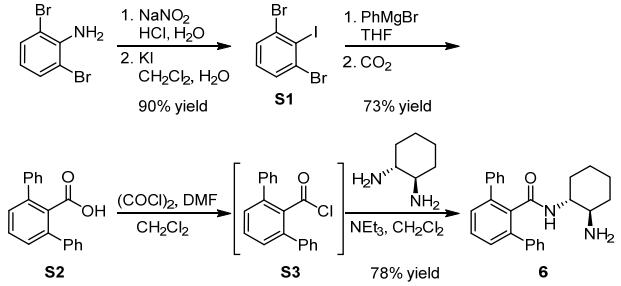
Unless otherwise noted, all reactions were performed in oven- or flame-dried round-bottom flasks. Vials were capped and flasks were fitted with rubber septa. Reactions were conducted under air unless noted. Stainless steel syringes were used to transfer air- and moisture-sensitive liquids. Flash chromatography was performed using silica gel 60 (230-400 mesh) from EM Science. Commercial reagents were purchased from Sigma-Aldrich, Alfa Aesar, Oakwood Chemical, Matrix Chemical, or TCI America, and used as received with the following exceptions: dichloromethane, toluene, tetrahydrofuran, *N*,*N*-dimethylformamide, and diethyl ether were dried by passing through columns of activated alumina. Triethylamine was distilled from $CaH_2$ at 760 torr. 2-phenylpropionaldehyde (**1a**) and 3-(4-*tert*-butylphenyl)isobutyraldehyde (**1o**) were purchased from Sigma-Aldrich and TCI America respectively, and distilled from $CaH_2$ at 50 torr prior to use. *n*-Butyllithium was titrated using *N*-benzylbenzamide as an indicator. Proton nuclear magnetic resonance ($^{1}$H NMR) spectra, fluorine nuclear magnetic resonance ($^{19}$F NMR) spectra, and carbon nuclear magnetic resonance ($^{13}$C NMR) spectra were recorded on Varian-Mercury-300 (300 MHz), Varian-Mercury-400 (400 MHz), or Inova-500 (500 MHz) spectrometers. 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 ($CDCl_3$ = δ 77.0). Data are represented as follows: chemical shift (multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, m = multiplet), coupling constants in Hertz (Hz), integration). Infrared (IR) spectra were obtained using a Bruker Alpha Platinum ATR FTIR spectrometer. Optical rotations were measured using a Jasco DIP 370 digital polarimeter. The mass spectral data were obtained on a Bruker micrOTOF-Q II time-of-flight LC/MS spectrometer (ESI-TOF). Chiral HPLC analysis was performed using an Agilent analytical chromatograph with commercial ChiralPak or ChiralCel columns.

Abbreviations: *ee* – enantiomeric excess, GC – gas chromatography, HPLC – high performance liquid chromatography, GC – gas chromatography, *n*-BuLi – butyllithium, $CH_2Cl_2$ – dichloromethane, THF – tetrahydrofuran, DMF – *N*,*N*-dimethylformamide, EtOAc – ethyl acetate, $Et_2O$ – diethyl ether, MeCN – acetonitrile, MeOH – methanol, EtOH – ethanol, *i*PrOH – isopropanol, $NEt_3$ – triethylamine, $CHCl_3$ – chloroform, $C_6H_6$ – benzene, AcOH – acetic acid, BzOH – benzoic acid, TFA – trifluoroacetic acid, TCA – dichloroacetic acid, DCA – dichloroacetic acid, $N_2$ – nitrogen, $CO_2$ – carbon dioxide, $H_2O$ – water, HCl – hydrochloric acid, HBr – hydrobromic acid, $Na_2SO_4$ – sodium sulfate, $NaHCO_3$ – sodium bicarbonate, $NH_4Cl$ – ammonium chloride, $NaBH_4$ – sodium borohydride, NFSI – *N*-fluorobenzenesulfonimide, DIAD – diisopropyl azodicarboxylate, DEAD – diethyl azodicarboxylate, sat. – saturated, aq. – aqueous, conc. – concentrated, h – hours, min – minutes, diast. – diastereomer, N.D. – not determined.

## 2. Synthesis and Characterization of Catalyst 6

**Scheme S1.** Synthesis of catalyst **6**.




**1,3-dibromo-2-iodobenzene (S1):**

Following a reported procedure,[1] 2,6-dibromoaniline (5.002 g, 19.93 mmol) was dissolved in 37% HCl (10 mL) and $H_2O$ (27 mL) in a 500-mL round-bottom flask. The reaction mixture was cooled to 0 ˚C in an ice bath then a solution of sodium nitrite (1.435 g, 20.79 mmol, 1.04 equiv) in $H_2O$ (22 mL) was slowly added. The flask was sealed with a septum under an atmosphere of $N_2$, and the mixture was

[1] Mao, G.; Orita, A.; Matsuo, D.; Hirate, T.; Iwanaga, T.; Toyota, S.; Otera, J. *Tetrahedron Lett.* **2009**, *50*, 2860–2864.

stirred at 0 ˚C. After 1 h of stirring, the flask was opened again, and an ice cold solution of potassium iodide (33.10 g, 199 mmol, 10.0 equiv) in $H_2O$ (46 mL) was slowly and carefully added at 0 ˚C. The yellow mixture rapidly turned red and began to bubble. If potassium iodide is added too quickly, the solution will bubble over. After addition of all potassium iodide, $CH_2Cl_2$ (40 mL) was also added to the reaction and the biphasic mixture was stirred under an atmosphere of $N_2$ at 23 ˚C for 4.5 h. Then, solid sodium sulfite (0.750 g, 5.95 mmol, 0.3 equiv) was added to quench the oxidant and the red color rapidly dissipated. This mixture was stirred at 23 ˚C under an atmosphere of $N_2$ for an additional 15 min, then the phases were separated. The aqueous phase was extracted with $CH_2Cl_2$ (2 x 25 mL) and the pooled organic layers were washed with brine (30 mL). The organic phase was dried over $Na_2SO_4$, filtered, and concentrated. The crude orange powder was dissolved in hexanes with minimal $CH_2Cl_2$, and purified by silica plug, eluting with hexanes to afford **S1** as a white powder (6.457 g, 90%).
Spectroscopic results agree with previously reported data.[1]

**[1,1':3',1''-terphenyl]-2'-carboxylic acid (S2):**
Following a reported procedure,[2] aryl iodide **S1** (5.919 g, 16.36 mmol) was dissolved in anhydrous THF (12 mL). Dropwise by syringe, under an atmosphere of $N_2$, phenylmagnesium bromide (49 mL of a 1.0 M solution in THF, 49 mmol, 3.0 equiv) was added to the stirring **S1** solution at 23 ˚C. The reaction began to get cloudy. After 2.5 h, dry $CO_2$ gas was bubbled from a balloon directly into the stirring reaction mixture by needle, with a gas outlet line from the flask attached to an oil bubbler to prevent moisture from entering the reaction. The solution rapidly clarified. The balloon was refilled as necessary, and after 3.5 h, the reaction was quenched with $H_2O$ (50 mL) and 1M aq. HCl (10 mL). The aqueous layer was extracted with $Et_2O$ (4 x 50 mL). Then the pooled organic layers were washed with $H_2O$ (50 mL). The organic solution was dried over $Na_2SO_4$, filtered, and concentrated. The crude product was purified by flash chromatography (silica gel, 19:1 to 3:2 hexanes/EtOAc) to afford **S2** as a white powder (3.257g, 73%).
$\mathbf{R_f}$ = 0.22 (silica gel, 2:1 hexanes/EtOAc);
**IR** (film) $\nu_{max}$ 1695, 1458, 1292, 1275, 909, 757, 732, 699 $cm^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.53 (dd, *J* = 7.3, 8.3 Hz, 1H), 7.45 – 7.38 (m, 12H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 174.5, 140.3, 140.2, 131.6, 129.6, 128.9, 128.4, 128.3, 127.6;
**MS** (ESI-TOF) calcd. for $C_{19}H_{14}O_2$ $[M + H]^+$ 275.1067, found 275.1067.

**[1,1':3',1''-terphenyl]-2'-carbonyl chloride (S3):**
Following a reported procedure,[3] benzoic acid **S2** (3.257 g, 11.87 mmol) was dissolved in anhydrous $CH_2Cl_2$ (16 mL, 0.74 M) and the resultant mixture was cooled to 0 ˚C in an ice bath. Under an atmosphere of $N_2$, oxalyl chloride (2.8 mL, 4.06 g, 32.0 mmol, 2.7 equiv) was then added by syringe to

[2] Dickie, D. A.; Chan, A. Y. C.; Jalali, H.; Jenkins, H. A.; Yu, H.-Z.; Clyburne, J. A. C. *Chem. Commun.* **2004**, 2432–2433.
[3] Branca, M.; Pena, S.; Guillot, R.; Gori, D.; Alezra, V.; Kouklovsky, C. *J. Am. Chem. Soc.* **2009**, *131*, 10711–10718.

the stirring solution, followed by catalytic anhydrous DMF (0.05 mL, 0.047 g, 0.646 mmol, 5 mol%). The reaction was stirred under an atmosphere of $N_2$ for 90 min, and slowly allowed to warm to 23 ˚C. The organic solution was then washed sequentially with 5% aq. $NaHCO_3$ (2 x 10 mL) and $H_2O$ (2 x 10 mL). The organic solution was dried over $Na_2SO_4$, filtered, and concentrated to afford **S3** as a fluffy, pale yellow powder which was used without further purification (3.504 g, 100%).

**$^1$H NMR** (400, $CDCl_3$) δ 7.64 – 7.59 (m, 1H), 7.52 – 7.45 (m, 12H).

***N*-((1*R*,2*R*)-2-aminocyclohexyl)-[1,1':3',1''-terphenyl]-2'-carboxamide (6):**

(*R,R*)-1,2-*trans*-diaminocyclohexane[4] (2.781 g, 24.36 mmol, 4.0 equiv) was dissolved in anhydrous $CH_2Cl_2$ (30 mL, 0.2 M) and the resultant mixture was cooled to 0 ˚C in an ice bath. Under an atmosphere of $N_2$, $NEt_3$ (0.83 mL, 0.603 g, 5.95 mol, 1.0 equiv) was added by syringe, followed by benzoyl chloride **S3** (1.752 g, 5.98 mmol) in minimal anhydrous $CH_2Cl_2$ (~5 mL). Complete transfer of acyl chloride was ensured with an additional aliquot of $CH_2Cl_2$ (~5 mL). The reaction was stirred under an atmosphere of $N_2$ for 12 h, during which time it was slowly allowed to warm to 23 ˚C. The mixture was then concentrated by rotary evaporation and the crude white residue was purified by flash chromatography (silica gel, 99:1 to 9:1 $CH_2Cl_2$/MeOH) to afford **6** as a white powder (1.7306g, 78%).

**$R_f$** = 0.31 (silica gel, 9:1 $CH_2Cl_2$/MeOH);

**IR** (film) $\nu_{max}$ 3251, 2932, 2855, 1623, 1549, 1328, 758, 730, 699 $cm^{-1}$;

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.8 Hz, 4H), 7.47 (d, *J* = 6.8 Hz, 1H), 7.42 – 7.38 (m, 4H), 7.37 – 7.34 (m, 4H), 5.20 (d, *J* = 8.8 Hz, 1H), 3.24 – 3.15 (m, 1H), 1.98 (td, *J* = 10.5, 3.9 Hz, 1H), 1.78 (d, *J* = 12.2 Hz, 1H), 1.58 (d, *J* = 10.2 Hz, 1H), 1.53 – 1.47 (m, 1H), 1.31 – 1.21 (m, 2H), 1.12 – 1.01 (m, 2H), 0.93 – 0.86 (m, 2H), 0.63 (qd, *J* = 12.2, 3.4 Hz, 1H);

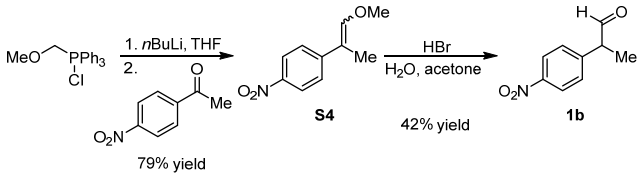
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 168.9, 140.4, 139.8, 136.3, 129.0, 128.9, 128.8, 128.2, 127.7, 56.4, 54.9, 34.2, 31.4, 24.9, 24.8;

**MS** (ESI-TOF) calcd. for $C_{25}H_{26}N_2O$ [M + $H^+$] 371.2118, found 371.2121;

**$[\alpha]_D^{25}$** = –36.0 (*c* = 2.0, $CHCl_3$).

## 3. Synthesis and Characterization of Substrates

**Scheme S2.** Synthesis of substrate **1b**.



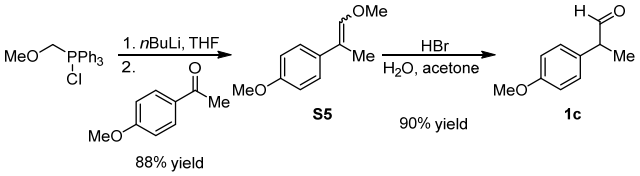

**1-(1-methoxyprop-1-en-2-yl)-4-nitrobenzene (S4):**

[4] (*R,R*)-1,2-*trans*-diaminocyclohexane was resolved according to: a) Larrow, J. F.; Jacobsen, E. N.; Gao, Y.; Hong, Y.; Nie, X.; Zepp, C. M. *J. Org. Chem.* **1994**, *59*, 1939–1942; b) Larrow, J. F.; Jacobsen, E. N. *Org. Synth.* **1998**, *75*, 1–6.

Following a general procedure,[5] (methoxymethyl)triphenylphosphonium chloride (6.231 g, 18.18 mmol, 1.5 equiv) was suspended in anhydrous THF (144 mL, 0.084 M) and the resultant mixture was cooled to –78 ˚C in a dry ice/acetone bath. Slowly by syringe, *n*BuLi (9.5 mL of a 1.92 M solution in hexanes, 18.24 mmol, 1.5 equiv) was added to the stirring phosphonium chloride solution under an atmosphere of $N_2$. The reaction was allowed to stir under $N_2$ at –78 ˚C for 30 min, then at 23 ˚C for 30 min, at which point the solution turned deep red. Then, the mixture was recooled to –78 ˚C, and 4'-nitroacetophenone (2.001 g, 12.11 mmol) in minimal anhydrous THF (~5 mL) was added dropwise by syringe. After stirring under $N_2$ for 16 h, the reaction was quenched with $H_2O$ (75 mL). The layers were separated and the aqueous phase was extracted with $Et_2O$ (2 x 45 mL). The pooled organic solutions were washed with brine (60 mL), dried over $Na_2SO_3$, filtered, and concentrated. The crude product was purified by flash chromatography (silica gel, 19:1 to 2:1 hexanes/EtOAc) to afford **S4** as an orange oil (1.850 g, 79%) in a 1.35:1 ratio of *E*/*Z*-enol ether isomers.
Spectroscopic results agree with previously reported data.[6]

**2-(4-nitrophenyl)propanal (1b):**
Following a general procedure,[5] enol ether **S4** (0.810 g, 4.19 mmol) was dissolved in a 4:1 mixture of acetone and $H_2O$ (4.9 mL, 0.86 M) and the resultant solution was cooled to 0 ˚C in an ice bath. Conc. HBr (48%, 0.45 mL) was added to the solution and the reaction mixture was stirred at 23 ˚C for 46 h. The acetone was removed by rotary evaporation and the remaining aqueous residue was neutralized with sat. aq. $NaHCO_3$, as determined by pH paper. This aqueous solution was then extracted with $Et_2O$ (3 x 10 mL). The pooled organic layers were dried over $Na_2SO_3$, filtered, and concentrated. The crude product was purified by flash chromatography (silica gel, 19:1 to 3:2 hexanes/EtOAc) to afford **1b** as an orange oil (0.312 g, 42%).
Spectroscopic results agree with previously reported data.[5,6]

**Scheme S3.** Synthesis of substrate **1c**.




**1-methoxy-4-(1-methoxyprop-1-en-2-yl)benzene (S5):**
Reaction of 4'-methoxyacetophenone (2.007 g, 13.36 mmol), (methoxymethyl)triphenylphosphonium chloride (6.851 g, 19.99 mmol, 1.5 equiv), and *n*BuLi (10.4 mL of a 1.92 M solution in hexanes, 19.97 mmol, 1.5 equiv) in anhydrous THF (159 mL, 0.084 M) according to **S4** above afforded **S5** as a colorless oil after column chromatography (silica gel, 19:1 to 2:1 hexanes/EtOAc) in a 1.29:1 ratio of -*E*/*Z*-enol ether isomers (2.098 g, 88%).
Spectroscopic results agree with previously reported data.[6,7]

---

[5] Fu, J.-Y.; Xu, X.-Y.; Li, Y.-C.; Huang, Q.-C.; Wang, L.-X. *Org. Biomol. Chem.* **2010**, *8*, 4524–4526.

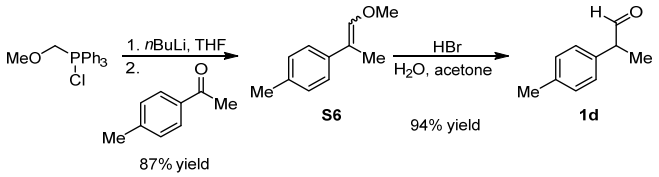
[6] Baumann, T.; Vogt, H.; Bräse, S. *Eur. J. Org. Chem.* **2007**, *2007*, 266–282.

**2-(4-methoxyphenyl)propanal (1c):**

Reaction of enol ether **S5** (2.098 g, 11.77 mmol) and conc. HBr (48%, 1.3 mL) in 4:1 acetone/$H_2O$ (13.7 mL, 0.86 M) according to **1b** above afforded **1c** as a colorless oil after column chromatography (silica gel, 19:1 to 3:2 hexanes/EtOAc) (1.731 g, 90%).

Spectroscopic results agree with previously reported data.[5–8]

**Scheme S4.** Synthesis of substrate **1d**.




**1-(1-methoxyprop-1-en-2-yl)-4-methylbenzene (S6):**

Reaction of 4'-methylacetophenone (0.70 mL, 0.704 g, 5.24 mmol), (methoxymethyl)triphenylphosphonium chloride (2.690 g, 7.85 mmol, 1.5 equiv), and *n*BuLi (4.5 mL of a 1.72 M solution in hexanes, 7.74 mmol, 1.5 equiv) in anhydrous THF (61 mL, 0.086 M) according to **S4** above afforded **S6** as a colorless oil after column chromatography (silica gel, 19:1 to 2:1 hexanes/EtOAc) in a 1:1 ratio of *E*/*Z*-enol ether isomers (0.738 g, 87%).

$\mathbf{R}_f$ = 0.81 (silica gel, 4:1 hexanes/$Et_2O$);

**IR** (film) $\nu_{max}$ 2931, 1652, 1514, 1454, 1258, 1221, 1204, 1131, 1115, 1009, 812 $cm^{-1}$;

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.63 – 7.58 (m, 1H), 7.33 – 7.27 (m, 1H), 7.26 – 7.17 (m, 2H), 6.47 (diast., s, 0.5H), 6.16 (diast., s, 0.5H), 3.79 – 3.77 (diast., m. 1.5H), 3.74 – 3.72 (diast., m, 1.5H), 2.44 – 2.41 (m, 3H), 2.10 – 2.08 (diast., m, 1.5H), 2.02 – 1.99 (diast., m, 1.5H);

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 144.5, 144.0, 137.6, 135.5, 135.4, 129.0, 128.5, 127.3, 124.8, 114.3, 110.7, 59.9, 59.7, 34.6, 34.5, 25.2, 22.6, 21.0, 20.9, 18.2, 14.1, 12.5;

**MS** (ESI-TOF) calcd. for $C_{11}H_{14}O$ [M + $H^+$] 163.1117, found 163.1093.

**2-(p-tolyl)propanal (1d):**

Reaction of enol ether **S6** (1.650 g, 10.17 mmol) and conc. HBr (48%, 1.1 mL) in 4:1 acetone/$H_2O$ (11.9 mL, 0.86 M) according to **1b** above afforded **1d** as a pale yellow oil after column chromatography (silica gel, 19:1 to 3:2 hexanes/EtOAc) (1.412 g, 94%).

Spectroscopic results agree with previously reported data.[5,7,9]

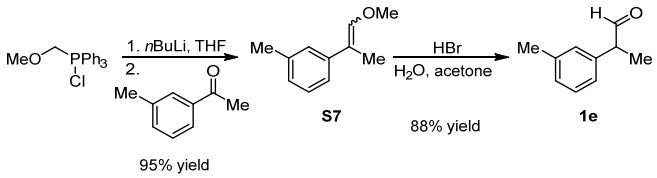
**Scheme S5.** Synthesis of substrate **1e**.

---

[7] Hoffmann, S.; Nicoletti, M.; List, B. *J. Am. Chem. Soc.* **2006**, *128*, 13074–13075.

[8] Vyas, D. J.; Larionov, E.; Besnard, C.; Guénée, L.; Mazet, C. *J. Am. Chem. Soc.* **2013**, *135*, 6177–6183.

[9] List, B.; Čorić, I.; Grygorenko, O. O.; Kaib, P. S. J.; Komarov, I.; Lee, A.; Leutzsh, M.; Pan, S. C.; Tymtsunik, A. V.; Van Gammeren, M. *Angew. Chem. Int. Ed.* **2014**, *53*, 282–285.




**1-(1-methoxyprop-1-en-2-yl)-3-methylbenzene (S7):**

Reaction of 3'-methylacetophenone (0.60 mL, 0.592 g, 4.41 mmol), (methoxymethyl)triphenylphosphonium chloride (2.268 g, 6.62 mmol, 1.5 equiv), and *n*BuLi (3.2 mL of a 2.05 M solution in hexanes, 6.56 mmol, 1.5 equiv) in anhydrous THF (52 mL, 0.085 M) according to **S4** above afforded **S7** as a colorless oil after column chromatography (silica gel, 19:1 to 2:1 hexanes/EtOAc) in a 1.5:1 ratio of *E*/*Z*-enol ether isomers (0.682 g, 95%).

$\mathbf{R}_f$ = 0.75 (silica gel, 4:1 hexanes/$Et_2O$);

**IR** (film) $\nu_{max}$ 2931, 1652, 1603, 1489, 1222, 1134, 782, 699 $cm^{-1}$;

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.48 (major diast., s, 0.6H), 7.40 (minor diast., dd, *J* = 1.8, 3.3 Hz, 0.4H), 7.31 – 7.22 (m, 1H), 7.19 – 7.15 (m, 1H), 7.07 (d, *J* = 5.9 Hz, 1H), 6.47 (major diast., td, *J* = 2.9, 1.4 Hz, 0.6H), 6.18 – 6.14 (minor diast., m, 0.4H), 3.78 – 3.75 (major diast., m. 1.8H), 3.73 – 3.70 (minor diast., m, 1.2H), 2.44 – 2.39 (m, 3H), 2.06 (major diast., dt, *J* = 4.5, 1.3 Hz, 1.8H), 1.98 (minor diast., dt, *J* = 4.2, 1.2 Hz, 1.2H);

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 145.0, 144.4, 140.5, 138.3, 137.8, 137.2, 128.2, 128.1, 127.8, 126.8, 126.6, 125.7, 124.6, 122.1, 114.4, 110.9, 60.0, 59.8, 21.6, 21.5, 18.4, 12.6;

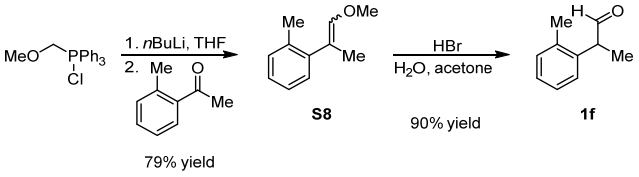
**MS** (ESI-TOF) calcd. for $C_{11}H_{14}O$ [M + $H^+$] 163.1117, found 163.1085.

**2-(m-tolyl)propanal (1e):**

Reaction of enol ether **S7** (1.499 g, 9.24 mmol) and conc. HBr (48%, 0.99 mL) in 4:1 acetone/$H_2O$ (10.7 mL, 0.86 M) according to **1b** above afforded **1e** as a pale yellow oil after column chromatography (silica gel, 19:1 to 3:2 hexanes/EtOAc) (1.206 g, 88%).

Spectroscopic results agree with previously reported data.[9]

**Scheme S6.** Synthesis of substrate **1f**.




**1-(1-methoxyprop-1-en-2-yl)-2-methylbenzene (S8):**

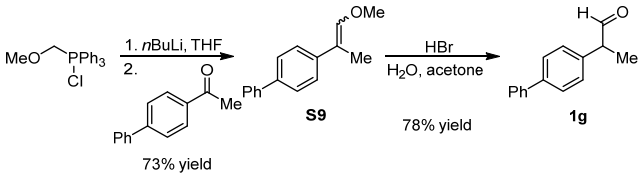
Reaction of 2'-methylacetophenone (1.7 mL, 1.744 g, 13.00 mmol), (methoxymethyl)triphenylphosphonium chloride (6.679 g, 19.48 mmol, 1.5 equiv), and *n*BuLi (10.0 mL of a 1.92 M solution in hexanes, 19.20 mmol, 1.5 equiv) in anhydrous THF (155 mL, 0.084 M) according to **S4** above afforded **S8** as a colorless oil after column chromatography (silica gel, 19:1 to 2:1 hexanes/EtOAc) in a 4.5:1 ratio of *E*/*Z*-enol ether isomers (1.661 g, 79%).

$\mathbf{R}_f$ = 0.80 (silica gel, 4:1 hexanes/$Et_2O$);

**IR** (film) $\nu_{max}$ 2930, 1664, 1486, 1455, 1220, 1130, 1069, 758, 727 $cm^{-1}$;
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.76 (minor diast., d, *J* = 2.3 Hz, 0.18H), 7.44 – 7.38 (major diast., m, 0.82H), 7.28 – 7.16 (m, 3H), 6.10 – 6.05 (minor diast., m. 0.18H), 6.04 – 5.98 (major diast., m, 0.82H), 3.76 – 3.71 (major diast., m, 2.46H), 3.63 – 3.58 (minor diast., m, 0.54H), 2.67 – 2.60 (minor diast., m, 0.54H), 2.42 – 2.33 (major diast., m, 2.46H), 2.03 – 1.97 (major diast., m, 2.46H), 1.95 – 1.89 (minor diast., m, 0.54H);
**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 145.2, 142.3, 140.9, 136.3, 133.7, 133.5, 131.9, 131.4, 130.0, 129.4, 128.7, 126.6, 125.4, 115.0, 113.1, 59.4, 59.3, 29.4, 21.5, 20.0, 19.5, 14.9;
**MS** (ESI-TOF) calcd. for $C_{11}H_{14}O_3$ [M + $Na^+$] 185.0937, found 185.0535.

**2-(o-tolyl)propanal (1f):**
Reaction of enol ether **S8** (1.661 g, 10.24 mmol) and conc. HBr (48%, 1.1 mL) in 4:1 acetone/$H_2O$ (11.9 mL, 0.86 M) according to **1b** above afforded **1f** as a pale yellow oil after column chromatography (silica gel, 19:1 to 3:2 hexanes/EtOAc) (1.365 g, 90%).
Spectroscopic results agree with previously reported data.[5,8]

**Scheme S7.** Synthesis of substrate **1g**.

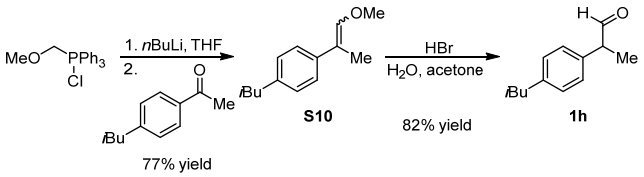



**4-(1-methoxyprop-1-en-2-yl)-1,1'-biphenyl (S9):**
Reaction of 4-acetylbiphenyl (2.299 g, 11.71 mmol), (methoxymethyl)triphenylphosphonium chloride (6.030 g, 17.59 mmol, 1.5 equiv), and *n*BuLi (9.0 mL of a 1.92 M solution in hexanes, 17.28 mmol, 1.5 equiv) in anhydrous THF (140 mL, 0.084 M) according to **S4** above afforded **S9** as a white powder after column chromatography (silica gel, 19:1 to 2:1 hexanes/EtOAc) in a 1.2:1 ratio of *E*/*Z*-enol ether isomers (1.910 g, 73%).
$\mathbf{R}_f$ = 0.73 (silica gel, 4:1 hexanes/$Et_2O$);
**IR** (film) $\nu_{max}$ 2931, 1648, 1486, 1223, 1133, 1078, 1007, 907, 848, 831, 764, 728, 696 $cm^{-1}$;
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.82 – 7.77 (m, 1H), 7.72 – 7.64 (m, 3H), 7.64 – 7.60 (m, 1H), 7.54 – 7.45 (m, 3H), 7.44 – 7.38 (m, 1H), 6.58 (major diast., d, *J* = 1.2 Hz, 0.55H), 6.23 (minor diast., d, *J* = 1.6 Hz, 0.45H), 3.80 (major diast., s, 1.65H) 3.77 (minor diast., s, 1.35H), 2.13 (major diast., d, *J* = 1.2 Hz, 1.65H), 2.04 (minor diast., d, *J* = 1.6 Hz, 1.35H);
**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 145.3, 144.9, 141.1, 140.8, 139.6, 138.6, 137.4, 128.7, 128.6, 127.8, 127.0, 126.9, 126.8, 126.5, 125.2, 113.9, 110.2, 60.1, 59.9, 31.6, 22.6, 18.2, 14.1, 12.4;
**MS** (ESI-TOF) calcd. for $C_{16}H_{16}O$ [M + $H^+$] 225.1274, found 225.1325.

**2-([1,1'-biphenyl]-4-yl)propanal (1g):**
Reaction of enol ether **S9** (1.910 g, 8.52 mmol) and conc. HBr (48%, 0.92 mL) in 4:1 acetone/$H_2O$ (9.9 mL, 0.86 M) according to **1b** above afforded **1g** as a white powder after column chromatography (silica

gel, 19:1 to 3:2 hexanes/EtOAc) (1.405 g, 78%).
Spectroscopic results agree with previously reported data.[9]

**Scheme S8.** Synthesis of substrate **1h**.

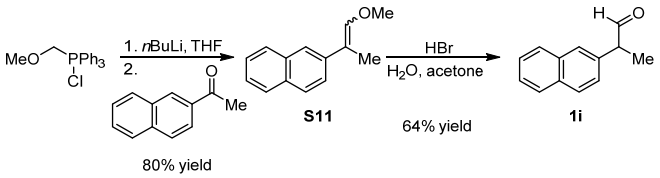



**1-isobutyl-4-(1-methoxyprop-1-en-2-yl)benzene (S10):**
Reaction of 4'-isobutylacetophenone (2.2 mL, 2.094 g, 11.88 mmol), (methoxymethyl)triphenylphosphonium chloride (6.112 g, 17.83 mmol, 1.5 equiv), and *n*BuLi (10.0 mL of a 1.78 M solution in hexanes, 17.80 mmol, 1.5 equiv) in anhydrous THF (141 mL, 0.084 M) according to **S4** above afforded **S10** as a colorless oil after column chromatography (silica gel, 19:1 to 2:1 hexanes/EtOAc) in a 2:1 ratio of *E*/*Z*-enol ether isomers (1.874 g, 77%).
$\mathbf{R}_f$ = 0.60, 0.72 (both diast., silica gel, 4:1 hexanes/$Et_2O$);
**IR** (film) $\nu_{max}$ 2952, 1652, 1513, 1465, 1223, 1133, 1074, 838, 798 $cm^{-1}$;
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.55 (minor diast., d, *J* = 8.2 Hz, 0.67H), 7.24 (major diast., d, *J* = 8.2 Hz, 1.33H), 7.13 (minor diast., *J* = 8.2 Hz, 0.67H), 7.09 (major diast., d, *J* = 7.8 Hz, 1.33H), 6.42 (major diast., s, 0.67H), 6.11 (minor disat., s, 0.33H), 3.73 (major diast., s, 2H), 3.69 (minor diast., s, 1H), 2.47 (d, *J* = 7.0 Hz, 2H), 2.01 (major diast., s, 2H), 1.93 (minor diast., s, 1H), 1.87 (dt, *J* = 13.3, 6.6 Hz, 1H), 0.93 (d, *J* = 6.6 Hz, 3H);
**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 144.6, 144.2, 139.4, 139.3, 137.9, 135.6, 129.1, 128.7, 127.1, 124.6, 114.3, 110.7, 60.0, 59.8, 45.2, 45.0, 30.2, 22.4, 18.3, 15.5;
**MS** (ESI-TOF) calcd. for $C_{14}H_{20}O$ [M + $H^+$] 205.1587, found 205.1607.

**2-(4-isobutylphenyl)propanal (1h):**
Reaction of enol ether **S10** (1.874 g, 9.17 mmol) and conc. HBr (48%, 1.0 mL) in 4:1 acetone/$H_2O$ (10.6 mL, 0.86 M) according to **1b** above afforded **1h** as a pale yellow oil after column chromatography (silica gel, 19:1 to 3:2 hexanes/EtOAc) (1.427 g, 82%).
Spectroscopic results agree with previously reported data.[10]

**Scheme S9.** Synthesis of substrate **1i**.

[10] Friest, J. A.;. Maezato, Y; Broussy, S.; Blum, P.; Berkowitz, D. B. *J. Am. Chem. Soc.* **2010**, *132*, 5930–5931.




**2-(1-methoxyprop-1-en-2-yl)naphthalene (S11):**

Reaction of 2-acetonaphthone (2.006 g, 11.78 mmol), (methoxymethyl)triphenylphosphonium chloride (6.041 g, 17.62 mmol, 1.5 equiv), and *n*BuLi (11.0 mL of a 1.60 M solution in hexanes, 17.60 mmol, 1.5 equiv) in anhydrous THF (140 mL, 0.084 M) according to **S4** above afforded **S11** as a white solid after column chromatography (silica gel, 19:1 to 2:1 hexanes/EtOAc) in a 1.3:1 ratio of *E*/*Z*-enol ether isomers (1.860 g, 80%).

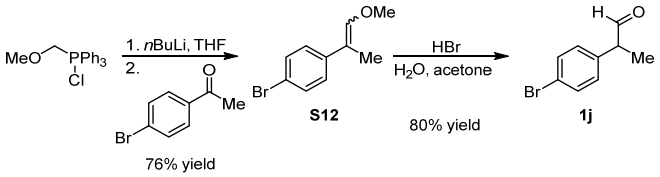
Spectroscopic results agree with previously reported data.[6]

**2-(naphthalen-2-yl)propanal (1i):**

Reaction of enol ether **S11** (1.860 g, 9.38 mmol) and conc. HBr (48%, 1.0 mL) in 4:1 acetone/$H_2O$ (10.9 mL, 0.86 M) according to **1b** above afforded **1i** as a white powder after column chromatography (silica gel, 19:1 to 3:2 hexanes/EtOAc) (1.106 g, 64%).

Spectroscopic results agree with previously reported data.[5,6,8]

**Scheme S10.** Synthesis of substrate **1j**.




**1-bromo-4-(1-methoxyprop-1-en-2-yl)benzene (S12):**

Reaction of 4'-bromoacetophenone (2.002 g, 10.06 mmol), (methoxymethyl)triphenylphosphonium chloride (5.173 g, 15.09 mmol, 1.5 equiv), and *n*BuLi (7.7 mL of a 1.96 M solution in hexanes, 15.09 mmol, 1.5 equiv) in anhydrous THF (120 mL, 0.084 M) according to **S4** above afforded **S12** as a colorless oil after column chromatography (silica gel, 19:1 to 2:1 hexanes/EtOAc) in a 1.3:1 ratio of -*E*/*Z*-enol ether isomers (1.732 g, 76%).

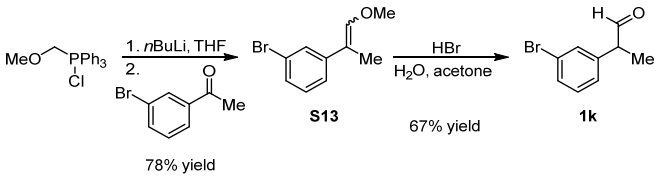
Spectroscopic results agree with previously reported data.[6]

**2-(4-bromophenyl)propanal (1j):**

Reaction of enol ether **S12** (1.732 g, 7.63 mmol) and conc. HBr (48%, 0.83 mL) in 4:1 acetone/$H_2O$ (8.9 mL, 0.86 M) according to **1b** above afforded **1j** as a pale yellow oil after column chromatography (silica gel, 19:1 to 3:2 hexanes/EtOAc) (1.295 g, 80%).

Spectroscopic results agree with previously reported data.[5–9]

**Scheme S11.** Synthesis of substrate **1k**.




**1-bromo-3-(1-methoxyprop-1-en-2-yl)benzene (S13):**

Reaction of 3'-bromoacetophenone (1.5 mL, 2.258 g, 11.34 mmol), (methoxymethyl)triphenylphosphonium chloride (5.831 g, 17.01 mmol, 1.5 equiv), and *n*BuLi (8.7 mL of a 1.96 M solution in hexanes, 17.05 mmol, 1.5 equiv) in anhydrous THF (135 mL, 0.084 M) according to **S4** above afforded **S13** as a colorless oil after column chromatography (silica gel, 19:1 to 2:1 hexanes/EtOAc) in a 1.5:1 ratio of *E*/*Z*-enol ether isomers (1.997 g, 78%).

$\mathbf{R}_f$ = 0.72 (silica gel, 4:1 hexanes/$Et_2O$);

**IR** (film) $\nu_{max}$ 2931, 1651, 1590, 1555, 1476, 1261, 1224, 1136, 1068, 993, 779, 689 $cm^{-1}$;

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.80 (minor diast., dt, *J* = 3.7, 2 Hz, 0.4H), 7.55 (minor diast., ddd, *J* = 4.7, 3.1, 1.2 Hz, 0.4H), 7.49 – 7.44 (major diast., m, 0.6H), 7.37 – 7.29 (m, 1H), 7.26 – 7.22 (major diast., m, 0.6H), 7.21 – 7.14 (m, 1H), 6.45 (major diast., d, *J* = 1.6 Hz, 0.6H), 6.17 (minor diast., d, *J* = 1.2 Hz, 0.4H), 3.77 – 3.74 (major diast., m, 1.8H), 3.73 – 3.70 (minor diast., m, 1.2H), 1.98 (major diast., dd, *J* = 3.1, 1.6 Hz, 1.8H), 1.91 (minor diast., d, *J* = 1.2 Hz, 1.2H);

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 146.0, 145.7, 142.9, 140.4, 130.4, 129.8, 129.3, 128.8, 128.6, 127.8, 125.9, 123.4, 122.6, 122.2, 113.2, 109.3, 60.3, 60.0, 18.1, 12.4;

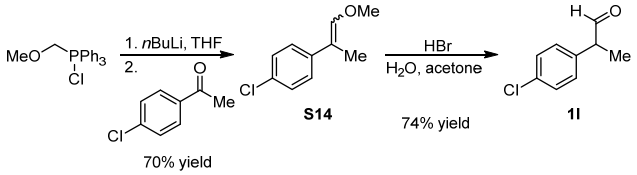
**MS** (ESI-TOF) calcd. for $C_{10}H_{11}BrO$ [M + $H^+$] 227.0066 and 229.0046, found 227.0064 and 229.0033.

**2-(3-bromophenyl)propanal (1k):**

Reaction of enol ether **S13** (1.997 g, 8.79 mmol) and conc. HBr (48%, 0.96 mL) in 4:1 acetone/$H_2O$ (10.2 mL, 0.86 M) according to **1b** above afforded **1k** as a yellow oil after column chromatography (silica gel, 19:1 to 3:2 hexanes/EtOAc) (1.252 g, 67%).

Spectroscopic results agree with previously reported data.[8]

**Scheme S12.** Synthesis of substrate **1l**.




**1-chloro-4-(1-methoxyprop-1-en-2-yl)benzene (S14):**

Reaction of 4'-chloroacetophenone (1.6 mL, 1.907 g, 12.34 mmol), (methoxymethyl)triphenylphosphonium chloride (6.344 g, 18.51 mmol, 1.5 equiv), and *n*BuLi (10.4 mL of a 1.78 M solution in hexanes, 18.51 mmol, 1.5 equiv) in anhydrous THF (147 mL, 0.084 M) according to **S4** above afforded **S14** as a colorless oil after column chromatography (silica gel, 19:1 to 2:1 hexanes/EtOAc) in a 1.1:1 ratio of *E*/*Z*-enol ether isomers (1.580 g, 70%).

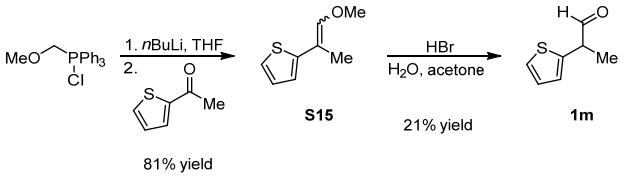
Spectroscopic results agree with previously reported data.[6]

**2-(4-chlorophenyl)propanal (1l):**

Reaction of enol ether **S14** (1.580 g, 8.65 mmol) and conc. HBr (48%, 0.97 mL) in 4:1 acetone/$H_2O$ (10.0 mL, 0.87 M) according to **1b** above afforded **1l** as a yellow oil after column chromatography (silica gel, 19:1 to 3:2 hexanes/EtOAc) (1.072 g, 74%).

Spectroscopic results agree with previously reported data.[6,8,9]

**Scheme S13.** Synthesis of substrate **1m**.




**2-(1-methoxyprop-1-en-2-yl)thiophene (S15):**

Reaction of 2-acetylthiophene (0.50 mL, 0.584 g, 4.63 mmol), (methoxymethyl)triphenylphosphonium chloride (2.381 g, 6.95 mmol, 1.5 equiv), and *n*BuLi (3.0 mL of a 2.30 M solution in hexanes, 6.90 mmol, 1.5 equiv) in anhydrous THF (55 mL, 0.084 M) according to **S4** above afforded **S15** as a colorless oil after column chromatography (silica gel, 19:1 to 2:1 hexanes/EtOAc) in a 1.1:1 ratio of -*E*/*Z*-enol ether isomers (0.5803 g, 81%).

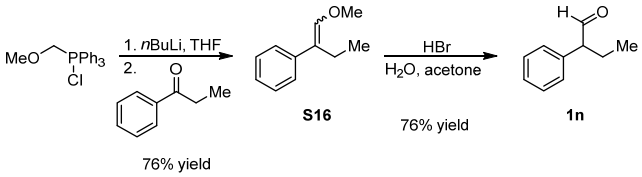
Spectroscopic results agree with previously reported data.[6,7]

**2-(thiophen-2-yl)propanal (1m):**

Reaction of enol ether **S15** (1.126 g, 7.30 mmol) and conc. HBr (48%, 0.82 mL) in 4:1 acetone/$H_2O$ (8.5 mL, 0.86 M) according to **1b** above afforded **1m** as a volatile, pale yellow oil after column chromatography (silica gel, 19:1 to 3:2 hexanes/EtOAc) (0.215 g, 21%).

Spectroscopic results agree with previously reported data.[6,7]

**Scheme S14.** Synthesis of substrate **1n**.




**(1-methoxybut-1-en-2-yl)benzene (S16):**

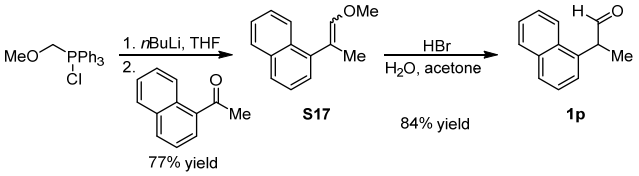
Reaction of propriophenone (1.6 mL, 1.614 g, 12.03 mmol), (methoxymethyl)triphenylphosphonium chloride (6.189 g, 18.05 mmol, 1.5 equiv), and *n*BuLi (10.1 mL of a 1.78 M solution in hexanes, 17.98 mmol, 1.5 equiv) in anhydrous THF (143 mL, 0.084 M) according to **S4** above afforded **S16** as a pale yellow oil after column chromatography (silica gel, 19:1 to 2:1 hexanes/EtOAc) in a 1.3:1 ratio of -*E*/*Z*-enol ether isomers (1.480 g, 76%).

Spectroscopic results agree with previously reported data.[6]

**2-phenylbutanal (1n):**

Reaction of enol ether **S16** (1.480 g, 9.12 mmol) and conc. HBr (48%, 1.0 mL) in 4:1 acetone/$H_2O$ (10.6 mL, 0.86 M) according to **1b** above afforded **1n** as a pale yellow oil after column chromatography (silica gel, 19:1 to 3:2 hexanes/EtOAc) (1.030 g, 76%).
Spectroscopic results agree with previously reported data.[6–8]

**Scheme S15.** Synthesis of substrate **1p**.




**1-(1-methoxyprop-1-en-2-yl)naphthalene (S17):**
Reaction of 1-acetonaphthone (1.8 mL, 2.016 g, 11.84 mmol), (methoxymethyl)triphenylphosphonium chloride (6.091 g, 17.77 mmol, 1.5 equiv), and *n*BuLi (11.1 mL of a 1.60 M solution in hexanes, 17.76 mmol, 1.5 equiv) in anhydrous THF (141 mL, 0.084 M) according to **S4** above afforded **S17** as a colorless oil after column chromatography (silica gel, 19:1 to 2:1 hexanes/EtOAc) in a 1:1 ratio of -*E*/*Z*-enol ether isomers (1.812 g, 77%).
$\mathbf{R}_f$ = 0.63 (silica gel, 4:1 hexanes/$Et_2O$);
**IR** (film) $\nu_{max}$ 2931, 1666, 1220, 1126, 801, 777 $cm^{-1}$;
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.16 – 8.10 (diast., m, 0.5H), 8.05 – 7.98 (diast., m, 0.5H), 7.95 – 7.88 (m, 1H), 7.85 – 7.79 (m, 1H), 7.57 – 7.45 (m, 3H), 7.43 – 7.34 (m, 1H), 6.32 – 6.27 (diast., m, 0.5H), 6.21 – 6.17 (diast., m, 0.5H, 3.79 – 3.76 (diast., m, 1.5H), 3.58 – 3.55 (diast., m, 1.5H), 2.20 – 2.15 (diast., m, 1.5H), 2.09 – 2.03 (diast., m, 1.5H);
**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 146.1, 143.4, 139.5, 138.0, 133.8, 133.6, 132.4, 130.9, 128.7, 128.5, 128.4, 128.3, 127.03, 126.96, 126.3, 125.93, 125.86, 125.7, 125.62, 125.55, 125.4, 113.9, 112.3, 59.7, 59.6, 20.4, 16.1;
**MS** (ESI-TOF) calcd. for $C_{14}H_{14}O$ [M + $H^+$] 199.1117, found 199.1161.

**2-(naphthalen-1-yl)propanal (1p):**
Reaction of enol ether **S17** (1.812 g, 9.14 mmol) and conc. HBr (48%, 1.0 mL) in 4:1 acetone/$H_2O$ (10.6 mL, 0.86 M) according to **1b** above afforded **1p** as a colorless oil after column chromatography (silica gel, 19:1 to 3:2 hexanes/EtOAc) (1.409 g, 84%).
Spectroscopic results agree with previously reported data.[7]

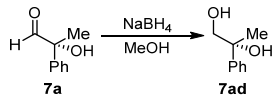
## 4. Procedures for α-Functionalizations and Characterization of Products

**General Procedure for Primary Amine-Catalyzed α-Hydroxylations (Optimization Studies, Table 1):**

A 1.0-dram vial was charged with primary amine catalyst (**3**–**6**, 20 mol% as indicated). No precautions were taken to ensure dryness of vial or to exclude air or moisture. THF (1.0 mL, 0.15 M in aldehyde substrate as indicated) was added to the catalyst. Next, dodecane (3.4 μL, 2.55 mg, 0.015 mmol, 10 mol%) was added by syringe as an internal standard for GC conversion analysis. Then, aldehyde **1a** (20 μL, 20.0 mg, 0.15 mmol) was added by syringe, followed by the indicated additives (e.g. TFA, 2.4 μL, 3.5 mg, 0.031 mmol, 20 mol%; $NaHCO_3$, 18.8 mg, 0.224 mmol, 1.5 equiv). Last, oxaziridine **2** was added as a solid (46.3 mg, 0.179 mmol, 1.2 equiv). The mixture was stirred at 23 ˚C and conversion was monitored by GC of small aliquots every 30 min for the first 4 h, then every 2 h for the next 6 h, then every 16 h.

**General Procedure for Reduction of α-Hydroxyaldehydes to Diols (Optimization Studies, Table 1):**

**Scheme S16.** Reduction of **7a** to diol **7ad**.




**7a** **7ad**

α-Hydroxyaldehydes **7a** were directly reduced to diols **7ad** for HPLC analysis of *ee*. The crude reaction mixture was transferred to a 20-mL vial with MeOH (2 mL, 0.075M in aldehyde), then $NaBH_4$ (56 mg, 1.49 mmol, 10 equiv) was added. The reaction mixture was stirred, open to air, for 90 min at 23 ˚C, then quenched with sat. aq. $NH_4Cl$ (4 mL) and EtOAc (4 mL). After an additional 30 min of stirring open to air at 23 ˚C, the layers were separated and the aqueous phase was extracted with EtOAc (3 x 6 mL). The pooled organic layers were dried over $Na_2SO_4$, filtered, and concentrated by rotary evaporation. Enantiomeric excess was determined by chiral HPLC after chromatographic purification on silica gel.

**General Procedure for Primary Amine-Catalyzed α-Fluorinations (Optimization Studies, Table 2):**

A 1.0-dram vial was charged with primary amine catalyst (**3**–**6**, 20 mol% as indicated). No precautions were taken to ensure dryness of vial or to exclude air or moisture. THF (1.0 mL, 0.15 M in aldehyde substrate as indicated) was added to the catalyst. Next, dodecane (3.4 μL, 2.55 mg, 0.015 mmol, 10 mol%) was added by syringe as an internal standard for GC conversion analysis. Then, aldehyde **1a** (20 μL, 20.0 mg, 0.15 mmol) was added by syringe, followed by the indicated additives (e.g. TFA, 2.4 μL, 3.5 mg, 0.031 mmol, 20 mol%; $NaHCO_3$, 18.8 mg, 0.224 mmol, 1.5 equiv). Last, NFSI **8** was added as a solid (56.5 mg, 0.179 mmol, 1.2 equiv). The mixture was stirred at 23 ˚C and conversion was monitored by GC of small aliquots every 30 min for the first 4 h, then every 2 h for the next 6 h, then every 16 h.

**General Procedure for Reduction of α-Fluoroaldehydes to Fluorohydrins (Optimization Studies,**

**Table 2):**

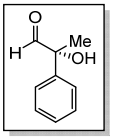
α-Fluoroaldehydes **9a** were directly reduced to fluorohydrins **10a** for HPLC analysis of *ee*. The crude reaction mixture was transferred to a 20-mL vial with MeOH (2 mL, 0.075M in aldehyde), then $NaBH_4$ (56 mg, 1.49 mmol, 10 equiv) was added. The reaction mixture was stirred, open to air, for 90 min at 23 ˚C, then quenched with sat. aq. $NH_4Cl$ (4 mL) and EtOAc (4 mL). After an additional 30 min of stirring open to air at 23 ˚C, the layers were separated and the aqueous phase was extracted with EtOAc (3 x 6 mL). The pooled organic layers were dried over $Na_2SO_4$, filtered, and concentrated by rotary evaporation. Enantiomeric excess was determined by chiral HPLC after chromatographic purification on silica gel (19:1 to 3:2 hexanes/EtOAc).

**General Procedure for Primary Amine-Catalyzed α-Hydroxylations (Substrate Scope, Table 3):**

A 2.0-dram vial was charged with aldehyde substrate **1a**–**o** (1.00 mmol as indicated). No precautions were taken to ensure dryness of vial or to exclude air or moisture. The aldehyde was then dissolved in THF (0.3 M in aldehyde as indicated). Solid catalyst **6** (20 mol% as indicated) was added, followed by TFA (20 mol% as indicated) by syringe. Last, dry reagents $NaHCO_3$ (1.0 equiv as indicated) and oxaziridine **2** (1.0 equiv as indicated) were added to the vial sequentially. The vial was sealed and the mixture was allowed to stir for the designated amount of time (4 or 20 h) at 23 ˚C. The reaction starts out heterogeneous, but eventually becomes homogeneous. The mixture was concentrated by rotary evaporation, and the resultant residue was purified directly by silica gel flash chromatography. Racemic standards were synthesized as described, with racemic catalyst **(±)-6**.

**General Procedure for Reduction of α-Hydroxyaldehydes to Diols (Substrate Scope, Table 3):**

A 20-mL vial was charged with α-hydroxyaldehyde **7a**–**o** (~0.1 mmol as indicated), then dissolved in MeOH (0.075 M as indicated). Solid $NaBH_4$ (10 equiv as indicated) was added and the reaction mixture was stirred, open to air, for 90 min at 23 ˚C, then quenched with sat. aq. $NH_4Cl$ (4 mL) and EtOAc (4 mL). After an additional 30 min of stirring open to air at 23 ˚C, the layers were separated and the aqueous phase was extracted with EtOAc (3 x 6 mL). The pooled organic layers were dried over $Na_2SO_4$, filtered, and concentrated by rotary evaporation. The crude product was purified by silica gel flash chromatography.




**(*R*)-2-hydroxy-2-phenylpropanal (7a):**

According to the general procedure, **1a** (134 µL, 134 mg, 1.00 mmol), **2** (258 mg, 1.00 mmol, 1.0 equiv), **6** (74 mg, 0.20 mmol, 20 mol%), TFA (15.4 µL, 22.8 mg, 0.20 mmol, 20 mol%), and $NaHCO_3$ (84 mg, 1.00 mmol, 1.0 equiv) were allowed to react in a THF solution (3.3 mL, 0.3 M) for 4 h to afford **7a** (142 mg, 95%) as a colorless oil after column chromatography (silica gel, 19:1 to 3:2 hexanes/$Et_2O$).

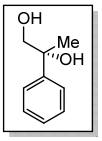
$\mathbf{R}_f$ = 0.59 (silica gel, 2:1 hexanes/$Et_2O$);

**IR** (film) $\nu_{max}$ 3448 (br), 1732, 1492, 1448, 1336, 1071, 859, 758, 699 $cm^{-1}$;

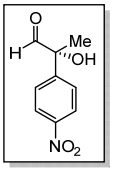
$^{1}$**H NMR** (500 MHz, $CDCl_3$) δ 9.57 (s, 1H), 7.48 (d, *J* = 7.8 Hz, 2H), 7.42 (td, *J* = 7.3, 1.0 Hz, 2H), 7.37 – 7.33 (m, 1H), 3.89 (d, *J* = 6.4 Hz, 1H), 1.72 (s, 3H);

$^{13}$**C NMR** (126 MHz, $CDCl_3$) δ 199.8, 139.2, 128.9, 128.2, 125.8, 79.1, 23.6;

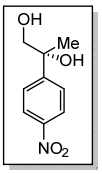
**MS** (ESI-TOF) calcd. for $C_9H_{10}O_3$ [M + $H^+$ – $H_2O$] 149.0597, found 149.0561;
$[\alpha]_D^{23}$ = –257.6° (*c* = 1.3, $CHCl_3$).[11]




**(*R*)-2-phenylpropane-1,2-diol (7ad):**
According to the general procedure, **7a** (22 mg, 0.15 mmol) and $NaBH_4$ (55 mg, 1.47 mmol, 10 equiv) were allowed to react in a MeOH solution (2.0 mL, 0.075 M) for 90 min to afford **7ad** (14 mg, 66%) as a colorless oil after column chromatography (silica gel, 9:1 to 2:3 hexanes/$Et_2O$). This material was determined to be of 90% *ee* by chiral HPLC analysis (ChiralPak AS-H, 5% *i*PrOH in hexanes, 1 mL/min, 210 nm).
$\mathbf{R}_f$ = 0.21 (silica gel, 2:1 hexanes/$Et_2O$);
**IR** (film) $\nu_{max}$ 3385 (br), 1446, 1044, 1027, 763, 700 $cm^{-1}$;
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.5 Hz, 2H), 7.38 (t, *J* = 7.5 Hz, 2H), 7.30 (dt, *J* = 7.3, 1.6 Hz, 1H), 3.81 (d, *J* = 11.3 Hz, 1H), 3.65 (d, *J* = 10.9 Hz, 1H), 2.63 (br s, 1H), 1.89 (br s, 1H), 1.55 (s, 3H);
**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 144.9, 128.4, 127.2, 125.1, 74.8, 71.7, 26.0;
**MS** (ESI-TOF) calcd. for $C_9H_{12}O_2$ [M + $Na^+$] 175.0730, found 175.0686;
$[\alpha]_D^{24}$ = –8.1 (*c* = 1.1, $CHCl_3$).[12]




**(*R*)-2-hydroxy-2-(4-nitrophenyl)propanal (7b):**
According to the general procedure, **1b** (179 mg, 1.00 mmol), **2** (258 mg, 1.00 mmol, 1.0 equiv), **6** (74 mg, 0.20 mmol, 20 mol%), TFA (15.4 μL, 22.8 mg, 0.20 mmol, 20 mol%), and $NaHCO_3$ (84 mg, 1.00 mmol, 1.0 equiv) were allowed to react in a THF solution (3.3 mL, 0.3 M) for 4 h to afford **7b** (114 mg, 58%) as a yellow oil after column chromatography (silica gel, 19:1 to 3:2 hexanes/$Et_2O$).
$\mathbf{R}_f$ = 0.24 (silica gel, 2:1 hexanes/$Et_2O$);
**IR** (film) $\nu_{max}$ 3485 (br), 1733, 1606, 1521, 1348, 855, 702 $cm^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 9.63 (s, 1H), 8.28 (d, *J* = 8.8 Hz, 2H), 7.70 (d, *J* = 8.8 Hz, 2H), 3.93 (s, 1H), 1.76 (s, 3H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 198.5, 146.4, 126.8, 124.0, 79.2, 24.3;
**MS** (ESI-TOF) calcd. for $C_9H_9NO_4$ [M + $H^+$ – $H_2O$] 178.0499, found 178.0512;
$[\alpha]_D^{23}$ = –146.0 (*c* = 0.8, $CHCl_3$).



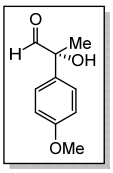

**(*R*)-2-(4-nitrophenyl)propane-1,2-diol (7bd):**
According to the general procedure, **7b** (12.8 mg, 0.07 mmol) and $NaBH_4$ (25 mg, 0.66 mmol, 10 equiv) were allowed to react in a MeOH solution (0.87 mL, 0.075 M) for 90 min to afford **7bd** (8.3 mg, 64%) as a yellow oil after column chromatography (silica gel, 9:1 to 2:3 hexanes/$Et_2O$). This material was determined to be of 84% *ee* by chiral HPLC analysis (ChiralPak AS-H, 10% *i*PrOH in hexanes, 1 mL/min, 210 nm).

---

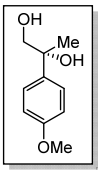
[11] For comparison: Du, Z.; Kawatani, T.; Kataoka, K.; Omatsu, R.; Nokami, J. *Tetrahedron* **2012**, *68*, 2471–2480.

[12] For comparison: DeBergh, J. R.; Spivey, K. M.; Ready, J. M. *J. Am. Chem. Soc.* **2008**, *130*, 7828–7829.

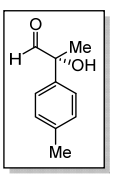
$\mathbf{R}_f$ = 0.07 (silica gel, 2:1 hexanes/$Et_2O$);
**IR** (film) $\nu_{max}$ 3373 (br), 1604, 1514, 1347, 1042, 854, 701 $cm^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.8 Hz, 2H), 7.66 (d, *J* = 8.8 Hz, 2H), 3.83 (dd, *J* = 11.0, 4.6 Hz, 1H), 3.72 (dd, *J* = 11.0 , 6.0 Hz, 1H), 2.75 (s, 1H), 1.90 (t, *J* = 5.6 Hz, 1H), 1.58 (s, 3H);
**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 152.5, 126.2, 123.6, 74.8, 70.6, 26.1;
**MS** (ESI-TOF) calcd. for $C_9H_{11}NO_4$ [M + $Na^+$] 220.0580, found 220.0593;
$[\alpha]_D^{24}$ = –14.6 (*c* = 0.5, $CHCl_3$).




**(*R*)-2-hydroxy-2-(4-methoxyphenyl)propanal (7c):**
According to the general procedure, **1c** (164 mg, 1.00 mmol), **2** (258 mg, 1.00 mmol, 1.0 equiv), **6** (74 mg, 0.20 mmol, 20 mol%), TFA (15.4 μL, 22.8 mg, 0.20 mmol, 20 mol%), and $NaHCO_3$ (84 mg, 1.00 mmol, 1.0 equiv) were allowed to react in a THF solution (3.3 mL, 0.3 M) for 4 h to afford **7c** (140 mg, 78%) as a white solid after column chromatography (silica gel, 19:1 to 3:2 hexanes/$Et_2O$).
$\mathbf{R}_f$ = 0.22 (silica gel, 4:1 hexanes/$Et_2O$);
**IR** (film) $\nu_{max}$ 3444 (br), 1729, 1609, 1511, 1302, 1252, 1030, 864, 832 $cm^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 9.51 (s, 1H), 7.37 (d, *J* = 9.0, 1.7 Hz, 2H), 6.96 – 6.92 (m, 2H), 3.82 (s, 3H), 3.81 (s, 1H), 1.96 (s, 3H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 199.6, 159.5, 131.0, 127.2, 114.3, 78.7, 55.3, 23.3;
**MS** (ESI-TOF) calcd. for $C_{10}H_{12}O_3$ [M + $H^+$ – $H_2O$] 163.0754, found 163.0749;
$[\alpha]_D^{24}$ = –62.8 (*c* = 0.9, $CHCl_3$).




**(*R*)-2-(4-methoxyphenyl)propane-1,2-diol (7cd):**
According to the general procedure, **7c** (10.8 mg, 0.06 mmol) and $NaBH_4$ (23 mg, 0.60 mmol, 10 equiv) were allowed to react in a MeOH solution (0.80 mL, 0.075 M) for 90 min to afford **7cd** (2.8 mg, 26%) as a white solid after column chromatography (silica gel, 9:1 to 2:3 hexanes/$Et_2O$). This material was determined to be of 92% *ee* by chiral HPLC analysis (ChiralCel OD-H, 5% *i*PrOH in hexanes, 1 mL/min, 224 nm).
$\mathbf{R}_f$ = 0.14 (silica gel, 2:1 hexanes/$Et_2O$);
**IR** (film) $\nu_{max}$ 3388 (br), 2929, 1612, 1513, 1463, 1301, 1248, 1180, 1032, 869 $cm^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.8 Hz, 2H), 6.29 (d, *J* = 8.8 Hz, 2H), 3.82 (s, 3H), 3.78 (dd, *J* = 10.7, 4.4 Hz, 1H), 3.62 (d, *J* = 11.2, 7.8 Hz, 1H), 2.46 (s, 1H), 1.73 (dd, *J* = 8.3, 4.9 Hz, 1H), 1.54 (s, 3H);
**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 137.0, 126.3, 113.8, 74.5, 71.2, 55.3, 26.1;
**MS** (ESI-TOF) calcd. for $C_{10}H_{14}O_3$ [M + $Na^+$] 205.0835, found 205.0835;
$[\alpha]_D^{23}$ = –4.0 (*c* = 0.1, $CHCl_3$).




**(*R*)-2-hydroxy-2-(*p*-tolyl)propanal (7d):**
According to the general procedure, **1d** (148 mg, 1.00 mmol), **2** (258 mg, 1.00 mmol, 1.0 equiv), **6** (74 mg, 0.20 mmol, 20 mol%), TFA (15.4 μL, 22.8 mg, 0.20 mmol, 20 mol%), and $NaHCO_3$ (84 mg, 1.00 mmol, 1.0 equiv) were allowed to react in a THF solution (3.3

mL, 0.3 M) for 4 h to afford **7d** (113 mg, 69%) as a white solid after column chromatography (silica gel, 19:1 to 3:2 hexanes/$Et_2O$).

**$R_f$** = 0.63 (silica gel, 2:1 hexanes/$Et_2O$);

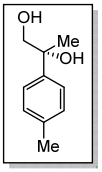
**IR** (film) $\nu_{max}$ 3442 (br), 2929, 1730, 1511, 1350, 1093, 863, 816, 537 $cm^{-1}$;

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 9.54 (s, 1H), 7.36 (d, *J* = 8.2 Hz, 2H), 7.23 (d, *J* = 8.2 Hz, 2H), 3.83 (s, 1H), 2.36 (s, 3H), 1.70 (s, 3H);

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 199.8, 138.0, 136.1, 129.6, 125.7, 78.9, 23.4, 21.0;

**MS** (ESI-TOF) calcd. for $C_{10}H_{12}O_2$ [M + $Na^+$] 187.0730, found 187.0726;

**$[\alpha]_D^{24}$** = –150.5 (*c* = 1.7, $CHCl_3$).




**(*R*)-2-(*p*-tolyl)propane-1,2-diol (7dd):**

According to the general procedure, **7d** (10.6 mg, 0.07 mmol) and $NaBH_4$ (24 mg, 0.65 mmol, 10 equiv) were allowed to react in a MeOH solution (0.86 mL, 0.075 M) for 90 min to afford **7dd** (9.1 mg, 85%) as a white solid after column chromatography (silica gel, 9:1 to 2:3 hexanes/$Et_2O$). This material was determined to be of 90% *ee* by chiral HPLC analysis (ChiralPak AD-H, 5% *i*PrOH in hexanes, 1 mL/min, 212 nm).

**$R_f$** = 0.23 (silica gel, 2:1 hexanes/$Et_2O$);

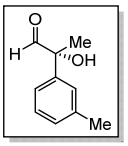
**IR** (film) $\nu_{max}$ 3377 (br), 2925, 1514, 1041, 866, 527 $cm^{-1}$;

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.2 Hz, 2H), 7.19 (d, *J* = 7.8 Hz, 2H), 3.76 (d, *J* = 10.1 Hz, 1H), 3.63 (dd, *J* = 10.5, 7.0 Hz, 1H), 2.54 (s, 1H), 2.36 (s, 3H), 1.80 (br s, 1H), 1.53 (s, 3H);

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 141.9, 136.9, 129.2, 125.0, 74.7, 71.2, 26.0, 21.0;

**MS** (ESI-TOF) calcd. for $C_{10}H_{14}O_2$ [M + $Na^+$] 189.0886, found 189.0883;

**$[\alpha]_D^{24}$** = –8.1 (*c* = 0.4, $CHCl_3$).[13]




**(*R*)-2-hydroxy-2-(*m*-tolyl)propanal (7e):**

According to the general procedure, **1e** (148 mg, 1.00 mmol), **2** (258 mg, 1.00 mmol, 1.0 equiv), **6** (74 mg, 0.20 mmol, 20 mol%), TFA (15.4 μL, 22.8 mg, 0.20 mmol, 20 mol%), and $NaHCO_3$ (84 mg, 1.00 mmol, 1.0 equiv) were allowed to react in a THF solution (3.3 mL, 0.3 M) for 4 h to afford **7e** (157 mg, 95%) as a pale yellow oil after column chromatography (silica gel, 19:1 to 3:2 hexanes/$Et_2O$).

**$R_f$** = 0.72 (silica gel, 2:1 hexanes/$Et_2O$);

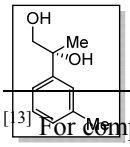
**IR** (film) $\nu_{max}$ 3451 (br), 2980, 2928, 1732, 1077, 830, 787, 703 $cm^{-1}$;

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 9.56 (s, 1H), 7.33 – 7.26 (m, 3H), 7.16 (d, *J* = 7.3 Hz, 1H), 3.82 (d, *J* = 1.0 Hz, 1H), 2.43 – 2.37 (m, 3H), 1.71 (s, 3H);

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 199.8, 139.0, 138.7, 128.9, 128.8, 126.4, 122.8, 79.0, 23.5, 21.6;

**MS** (ESI-TOF) calcd. for $C_{10}H_{12}O_2$ [M + $Na^+$] 187.0730, found 187.0730;

**$[\alpha]_D^{24}$** = –53.5 (*c* = 0.3, $CHCl_3$).




**(*R*)-2-(*m*-tolyl)propane-1,2-diol (7ed):**

[13] For comparison: Chavan, S. P.; Khatod, H. S. *Tetrahedron: Asymmetry* **2012**, *23*, 1410–1415.

According to the general procedure, **7e** (11.4 mg, 0.07 mmol) and $NaBH_4$ (26 mg, 0.69 mmol, 10 equiv) were allowed to react in a MeOH solution (0.93 mL, 0.075 M) for 90 min to afford **7ed** (5.8 mg, 50%) as a pale yellow oil after column chromatography (silica gel, 9:1 to 2:3 hexanes/$Et_2O$). This material was determined to be of 89% *ee* by chiral HPLC analysis (ChiralPak AD-H, 5% *i*PrOH in hexanes, 1 mL/min, 220 nm).

$\mathbf{R_f}$ = 0.19 (silica gel, 2:1 hexanes/$Et_2O$);

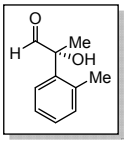
**IR** (film) $\nu_{max}$ 3383 (br), 2976, 2928, 1459, 1375, 1167, 1042, 786, 705 $cm^{-1}$;

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.30 – 7.23 (m, 3H), 7.11 (d, *J* = 6.6 Hz, 1H), 3.81 (dd, *J* = 11.1, 4.5 Hz, 1H), 3.64 (dd, *J* = 10.9, 8.2 Hz, 1H), 2.56 (s, 1H), 2.38 (s, 3H), 1.77 (dd, *J* = 8.4, 4.5 Hz, 1H), 1.53 (s, 3H);

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 144.9, 138.1, 128.4, 128.0, 125.8, 122.1, 74.8, 71.2, 26.1, 21.6;

**MS** (ESI-TOF) calcd. for $C_{10}H_{14}O_2$ [M + $Na^+$] 189.0886, found 189.0885;

$\mathbf{[\alpha]_D^{24}}$ = –7.1 (*c* = 0.3, $CHCl_3$).




**(*R*)-2-hydroxy-2-(*o*-tolyl)propanal (7f):**

According to the general procedure, **1f** (148 mg, 1.00 mmol), **2** (258 mg, 1.00 mmol, 1.0 equiv), **6** (74 mg, 0.20 mmol, 20 mol%), TFA (15.4 μL, 22.8 mg, 0.20 mmol, 20 mol%), and $NaHCO_3$ (84 mg, 1.00 mmol, 1.0 equiv) were allowed to react in a THF solution (3.3 mL, 0.3 M) for 20 h to afford **7f** (132 mg, 80%) as a yellow oil after column chromatography (silica gel, 19:1 to 3:2 hexanes/$Et_2O$).

$\mathbf{R_f}$ = 0.71 (silica gel, 2:1 hexanes/$Et_2O$);

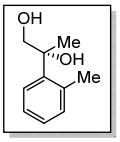
**IR** (film) $\nu_{max}$ 3440 (br), 2979, 1731, 1487, 1459, 1092, 1050, 805, 758, 726 $cm^{-1}$;

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 9.58 (s, 1H), 7.51 – 7.48 (m, 1H), 7.31 – 7.28 (m, 2H), 7.22 – 7.20 (m, 1H), 3.59 (s, 1H), 2.32 (s, 3H), 1.75 (s, 3H);

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 200.4, 137.8, 136.0, 132.4, 128.9, 126.9, 126.2, 79.9, 23.2, 21.0;

**MS** (ESI-TOF) calcd. for $C_{10}H_{12}O_2$ [M + $H^+$] 187.0730, found 187.0706;

$\mathbf{[\alpha]_D^{23}}$ = –100.5 (*c* = 0.4, $CHCl_3$).




**(*R*)-2-(*o*-tolyl)propane-1,2-diol (7fd):**

According to the general procedure, **7f** (11.3 mg, 0.07 mmol) and $NaBH_4$ (26 mg, 0.69 mmol, 10 equiv) were allowed to react in a MeOH solution (0.92 mL, 0.075 M) for 90 min to afford **7fd** (8.9 mg, 78%) as a yellow oil after column chromatography (silica gel, 9:1 to 2:3 hexanes/$Et_2O$). This material was determined to be of 55% *ee* by chiral HPLC analysis (ChiralPak AS-H, 5% *i*PrOH in hexanes, 1 mL/min, 210 nm).

$\mathbf{R_f}$ = 0.21 (silica gel, 2:1 hexanes/$Et_2O$);

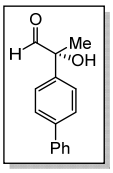
**IR** (film) $\nu_{max}$ 3380 (br), 2974, 2934, 1459, 1165, 1035, 759, 727 $cm^{-1}$;

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.47 – 7.43 (m, 1H), 7.21 – 7.18 (m, 3H), 4.04 (dd, *J* = 11.1, 3.7 Hz, 1H), 3.70 (dd, *J* = 11.1, 8.0 Hz, 1H), 2.58 (s, 1H), 2.57 (s, 3H), 1.91 (dd, *J* = 7.4, 4.3 Hz, 1H), 1.61 (s, 3H);

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 141.9, 136.0, 132.9, 127.5, 126.2, 125.9, 75.9, 69.5, 25.4, 22.3;

**MS** (ESI-TOF) calcd. for $C_{10}H_{14}O_2$ [M + $Na^+$] 189.0886, found 189.0880;

$\mathbf{[\alpha]_D^{24}}$ = –0.3 (*c* = 0.6, $CHCl_3$).



**(*R*)-2-([1,1'-biphenyl]-4-yl)-2-hydroxypropanal (7g):**

According to the general procedure, **1g** (210 mg, 1.00 mmol), **2** (258 mg, 1.00 mmol, 1.0 equiv), **6** (74 mg, 0.20 mmol, 20 mol%), TFA (15.4 μL, 22.8 mg, 0.20 mmol, 20 mol%), and $NaHCO_3$ (84 mg, 1.00 mmol, 1.0 equiv) were allowed to react in a THF solution (3.3 mL, 0.3 M) for 4 h to afford **7g** (222 mg, 98%) as a white solid after column chromatography (silica gel, 19:1 to 3:2 hexanes/$Et_2O$).

$\mathbf{R}_f$ = 0.54 (silica gel, 2:1 hexanes/$Et_2O$);

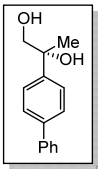
**IR** (film) $\nu_{max}$ 3493 (br), 2917, 2849, 1723, 1486, 1318, 1094, 865, 767, 736, 695 $cm^{-1}$;

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 9.61 (s, 1H), 7.65 (d, *J* = 7.7 Hz, 2H), 7.60 (d, *J* = 7.3 Hz, 2H), 7.55 (d, *J* = 8.3 Hz, 2H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.38 (t, *J* = 7.3 Hz, 1H), 3.88 (s, 1H), 1.76 (s, 3H);

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 199.6, 141.2, 140.4, 138.1, 128.8, 127.61, 127.57, 127.1, 126.3, 79.0, 23.6;

**MS** (ESI-TOF) calcd. for $C_{15}H_{14}O_2$ [M + $Na^+$] 249.0886, found 249.0871;

$\mathbf{[\alpha]_D^{24}}$ = –223.3 (*c* = 0.2, $CHCl_3$).



**(*R*)-2-([1,1'-biphenyl]-4-yl)propane-1,2-diol (7gd):**

According to the general procedure, **7g** (11.7 mg, 0.05 mmol) and $NaBH_4$ (20 mg, 0.52 mmol, 10 equiv) were allowed to react in a MeOH solution (0.69 mL, 0.075 M) for 90 min to afford **7gd** (6.1 mg, 52%) as a white solid after column chromatography (silica gel, 9:1 to 2:3 hexanes/$Et_2O$). This material was determined to be of 90% *ee* by chiral HPLC analysis (ChiralPak AS-H, 5% *i*PrOH in hexanes, 1 mL/min, 210 nm).

$\mathbf{R}_f$ = 0.19 (silica gel, 2:1 hexanes/$Et_2O$);

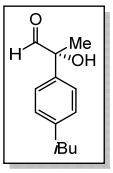
**IR** (film) $\nu_{max}$ 3383 (br), 1487, 1401, 1021, 839, 766, 733, 697 $cm^{-1}$;

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.61 (td, *J* = 6.6, 2.0 Hz, 4H), 7.54 (d, *J* = 8.6 Hz, 2H), 7.48 – 7.43 (m, 2H), 7.38 – 7.34 (m, 1H), 3.87 (dd, *J* = 10.9, 4.7 Hz, 1H), 3.70 (dd, *J* = 11.1, 8.0 Hz, 1H), 2.60 (s, 1H), 1.81 (dd, *J* = 7.8, 4.7 Hz, 1H), 1.59 (s, 3H);

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 144.0, 140.7, 140.2, 128.8, 127.3, 127.2, 127.1, 125.6, 74.8, 74.1, 26.1;

**MS** (ESI-TOF) calcd. for $C_{15}H_{16}O_2$ [M + $Na^+$] 251.1043, found 251.1026;

$\mathbf{[\alpha]_D^{24}}$ = –8.2 (*c* = 0.5, $CHCl_3$).



**(*R*)-2-hydroxy-2-(4-isobutylphenyl)propanal (7h):**

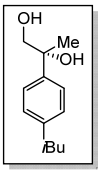
According to the general procedure, **1h** (190 mg, 1.00 mmol), **2** (258 mg, 1.00 mmol, 1.0 equiv), **6** (74 mg, 0.20 mmol, 20 mol%), TFA (15.4 μL, 22.8 mg, 0.20 mmol, 20 mol%), and $NaHCO_3$ (84 mg, 1.00 mmol, 1.0 equiv) were allowed to react in a THF solution (3.3 mL, 0.3 M) for 4 h to afford **7h** (202 mg, 98%) as a colorless oil after column chromatography (silica gel, 19:1 to 3:2 hexanes/$Et_2O$).

$\mathbf{R}_f$ = 0.58 (silica gel, 2:1 hexanes/$Et_2O$);

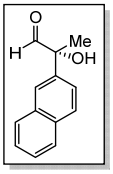
**IR** (film) $\nu_{max}$ 3485 (br), 2955, 2926, 2869, 1733, 1536, 1466, 1383, 1170, 1097, 865, 796, 740, 672 $cm^{-1}$;

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 9.54 (s, 1H), 7.36 (d, *J* = 8.3 Hz, 2H), 7.19 (d, *J* = 7.8 Hz, 2H), 3.82 (s,

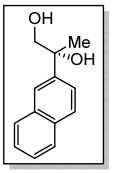
1H), 2.48 (d, $J$ = 7.3 Hz, 2H), 1.86 (dt, $J$ = 13.7, 6.8 Hz, 1H), 1.71 (s, 3H), 0.91 (d, $J$ = 6.8 Hz, 6H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 199.8, 141.8, 136.3, 129.6, 125.6, 79.0, 45.0, 30.2, 23.4, 22.3;
**MS** (ESI-TOF) calcd. for $C_{13}H_{18}O_2$ [M + $Na^+$] 229.1199, found 229.1209;
**$[\alpha]_D^{24}$** = –141.9 ($c$ = 0.5, $CHCl_3$).




**(*R*)-2-(4-isobutylphenyl)propane-1,2-diol (7hd):**
According to the general procedure, **7h** (15.8 mg, 0.08 mmol) and $NaBH_4$ (29 mg, 0.77 mmol, 10 equiv) were allowed to react in a MeOH solution (1.0 mL, 0.075 M) for 90 min to afford **7hd** (16.0 mg, 99%) as a colorless oil after column chromatography (silica gel, 9:1 to 2:3 hexanes/$Et_2O$). This material was determined to be of 86% *ee* by chiral HPLC analysis (ChiralPak AS-H, 5% *i*PrOH in hexanes, 1 mL/min, 218 nm).
**$R_f$** = 0.24 (silica gel, 2:1 hexanes/$Et_2O$);
**IR** (film) $\nu_{max}$ 3363 (br), 2954, 2925, 2868, 1531, 1465, 1348, 1167, 1042, 797, 616, 560 $cm^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.36 (d, $J$ = 8.3 Hz, 2H), 7.16 (d, $J$ = 8.3 Hz, 2H), 3.80 (dd, $J$ = 11.0, 2.7 Hz, 1H), 3.64 (dd, $J$ = 11.0, 7.6 Hz, 1H), 2.51 (s, 1H), 2.47 (d, $J$ = 7.3 Hz, 2H), 1.87 (dt, $J$ = 13.7, 6.8 Hz, 1H), 1.77 (br s, 1H), 1.54 (s, 3H), 0.91 (d, $J$ = 10.7 Hz, 6H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 142.1, 140.7, 129.2, 124.8, 74.7, 71.2, 45.0, 30.2, 26.0, 22.4;
**MS** (ESI-TOF) calcd. for $C_{13}H_{20}O_2$ [M + $Na^+$] 231.1356, found 231.1352;
**$[\alpha]_D^{25}$** = –1.8 ($c$ = 0.6, $CHCl_3$).[14]




**(*R*)-2-hydroxy-2-(naphthalen-2-yl)propanal (7i):**
According to the general procedure, **1i** (184 mg, 1.00 mmol), **2** (258 mg, 1.00 mmol, 1.0 equiv), **6** (74 mg, 0.20 mmol, 20 mol%), TFA (15.4 μL, 22.8 mg, 0.20 mmol, 20 mol%), and $NaHCO_3$ (84 mg, 1.00 mmol, 1.0 equiv) were allowed to react in a THF solution (3.3 mL, 0.3 M) for 4 h to afford **7i** (194 mg, 97%) as a white solid after column chromatography (silica gel, 19:1 to 3:2 hexanes/$Et_2O$).
**$R_f$** = 0.56 (silica gel, 2:1 hexanes/$Et_2O$);
**IR** (film) $\nu_{max}$ 3461 (br), 1730, 1130, 826, 751, 478 $cm^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 9.66 (s, 1H), 7.99 (s, 1H), 7.90 – 7.95 (m, 3H), 7.56 (dd, $J$ = 8.8, 2.0 Hz, 1H), 7.54 – 7.51 (m, 2H), 3.95 (s, 1H), 1.83 (s, 3H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 199.7, 136.5, 133.3, 132.9, 128.7, 128.2, 127.6, 126.6, 126.5, 125.2, 123.3, 79.3, 23.6;
**MS** (ESI-TOF) calcd. for $C_{13}H_{12}O_2$ [M + $K^+$] 239.0469, found 239.1281;
**$[\alpha]_D^{24}$** = –249.2 ($c$ = 0.4, $CHCl_3$).




**(*R*)-2-(naphthalen-2-yl)propane-1,2-diol (7id):**
According to the general procedure, **7i** (22 mg, 0.11 mmol) and $NaBH_4$ (41 mg, 1.07 mmol, 10 equiv) were allowed to react in a MeOH solution (1.4 mL, 0.075 M) for 90 min to afford

[14] For comparison: Ishibashi, H.; Maeki, M.; Yagi, J.; Ohba, M.; Kanai, T. *Tetrahedron* **1999**, *55*, 6075–6080.

**7id** (10.5 mg, 48%) as a white solid after column chromatography (silica gel, 9:1 to 2:3 hexanes/$Et_2O$). This material was determined to be of 91% *ee* by chiral HPLC analysis (ChiralPak AD-H, 5% *i*PrOH in hexanes, 1 mL/min, 210 nm).

**$R_f$** = 0.16 (silica gel, 2:1 hexanes/$Et_2O$);

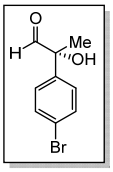
**IR** (film) $\nu_{max}$ 3371 (br), 2974, 1128, 858, 820, 747, 480 $cm^{-1}$;

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.85 (td, *J* = 8.3, 1.0 Hz, 3H), 7.54 (dt, *J* = 8.5, 1.6 Hz, 1H), 7.52 – 7.47 (m, 2H), 3.93 (dt, *J* = 11.2, 2.2 Hz, 1H), 3.74 (td, *J* = 8.3, 1.5 Hz, 1H), 2.71 (s, 1H), 1.79 (dd, *J* = 7.3, 4.9 Hz, 1H), 1.64 (s, 3H);

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 142.3, 133.2, 132.5, 128.2, 128.1, 127.5, 126.3, 126.0, 124.0, 123.3, 75.0, 71.0, 26.1;

**MS** (ESI-TOF) calcd. for $C_{13}H_{14}O_2$ [M + $Na^+$] 225.0886, found 225.0910;

**$[\alpha]_D^{24}$** = –6.2 (*c* = 0.7, $CHCl_3$).




**(*R*)-2-(4-bromophenyl)-2-hydroxypropanal (7j):**

According to the general procedure, **1j** (213 mg, 1.00 mmol), **2** (258 mg, 1.00 mmol, 1.0 equiv), **6** (74 mg, 0.20 mmol, 20 mol%), TFA (15.4 μL, 22.8 mg, 0.20 mmol, 20 mol%), and $NaHCO_3$ (84 mg, 1.00 mmol, 1.0 equiv) were allowed to react in a THF solution (3.3 mL, 0.3 M) for 4 h to afford **7j** (209 mg, 91%) as a white solid after column chromatography (silica gel, 19:1 to 3:2 hexanes/$Et_2O$).

**$R_f$** = 0.56 (silica gel, 2:1 hexanes/$Et_2O$);

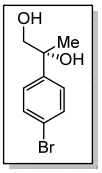
**IR** (film) $\nu_{max}$ 3459 (br), 1731, 1488, 1397, 1081, 1009, 863, 821, 788, 545, 493 $cm^{-1}$;

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 9.54 (s, 1H), 7.55 (d, *J* = 7.8 Hz, 2H), 7.36 (d, *J* = 8.3 Hz, 2H), 3.82 (s, 1H), 1.70 (s, 3H);

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 199.2, 138.3, 132.0, 127.6, 122.5, 78.9, 23.7;

**MS** (ESI-TOF) calcd. for $C_9H_9BrO_2$ [M + $H^+$ – $H_2O$] 210.9753 and 212.9733, found 210.9782 and 212.9763;

**$[\alpha]_D^{23}$** = –184.8 (*c* = 0.3, $CHCl_3$).




**(*R*)-2-(4-bromophenyl)propane-1,2-diol (7jd):**

According to the general procedure, **7j** (13.6 mg, 0.06 mmol) and $NaBH_4$ (22 mg, 0.59 mmol, 10 equiv) were allowed to react in a MeOH solution (0.79 mL, 0.075 M) for 90 min to afford **7jd** (3.3 mg, 24%) as a colorless oil after column chromatography (silica gel, 9:1 to 2:3 hexanes/$Et_2O$). This material was determined to be of 88% *ee* by chiral HPLC analysis (ChiralPak AS-H, 5% *i*PrOH in hexanes, 1 mL/min, 220 nm).

**$R_f$** = 0.10 (silica gel, 2:1 hexanes/$Et_2O$);

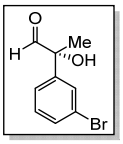
**IR** (film) $\nu_{max}$ 3369 (br), 1489, 1396, 1040, 1009, 867, 822, 526 $cm^{-1}$;

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 3.78 (dd, *J* = 10.9, 4.7 Hz, 1H), 3.64 (dd, *J* = 10.9, 7.4 Hz, 1H), 2.54 (s, 1H), 1.73 (dd, *J* = 7.2 , 5.3, 1H), 1.53 (s, 3H);

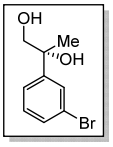
**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 131.5, 127.0, 74.6, 70.9, 26.0;

**MS** (ESI-TOF) calcd. for $C_9H_{11}BrO_2$ [M + $Na^+$] 252.9835 and 254.9814, found 252.9880 and 954.9854;

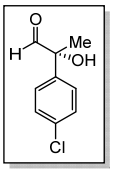
$[\alpha]_D^{25}$ = –40.0 (*c* = 0.1, $CHCl_3$).[15]




**(*R*)-2-(3-bromophenyl)-2-hydroxypropanal (7k):**
According to the general procedure, **1k** (213 mg, 1.00 mmol), **2** (258 mg, 1.00 mmol, 1.0 equiv), **6** (74 mg, 0.20 mmol, 20 mol%), TFA (15.4 μL, 22.8 mg, 0.20 mmol, 20 mol%), and $NaHCO_3$ (84 mg, 1.00 mmol, 1.0 equiv) were allowed to react in a THF solution (3.3 mL, 0.3 M) for 4 h to afford **7k** (188 mg, 82%) as a pale yellow oil after column chromatography (silica gel, 19:1 to 3:2 hexanes/$Et_2O$).
$\mathbf{R}_f$ = 0.52 (silica gel, 2:1 hexanes/$Et_2O$);
**IR** (film) $\nu_{max}$ 3461 (br), 1734, 1568, 1475, 1418, 1069, 902, 785, 719, 650 $cm^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 9.56 (s, 1H), 7.66 – 7.64 (m, 1H), 7.49 – 7.46 (m, 1H), 7.40 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.30 (d, *J* = 11.7 Hz, 1H), 3.85 (s, 1H), 1.70 (s, 3H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 199.1, 141.6, 131.3, 130.4, 129.0, 124.4, 123.2, 78.8, 23.8;
**MS** (ESI-TOF) calcd. for $C_9H_9BrO_2$ [M + $H^+$ – $H_2O$] 210.9753 and 212.9733, found 210.9781 and 212.9764;
$[\alpha]_D^{24}$ = –118.5 (*c* = 0.4, $CHCl_3$).



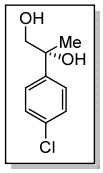

**(*R*)-2-(3-bromophenyl)propane-1,2-diol (7kd):**
According to the general procedure, **7k** (14.6 mg, 0.06 mmol) and $NaBH_4$ (24 mg, 0.64 mmol, 10 equiv) were allowed to react in a MeOH solution (0.85 mL, 0.075 M) for 90 min to afford **7kd** (3.6 mg, 56%) as a pale yellow oil after column chromatography (silica gel, 9:1 to 2:3 hexanes/$Et_2O$). This material was determined to be of 87% *ee* by chiral HPLC analysis (ChiralPak AD-H, 5% *i*PrOH in hexanes, 1 mL/min, 210 nm).
$\mathbf{R}_f$ = 0.20 (silica gel, 2:1 hexanes/$Et_2O$);
**IR** (film) $\nu_{max}$ 3356 (br), 2977, 2931, 1594, 1566, 1474, 1417, 1041, 878, 784, 762, 697 $cm^{-1}$;
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.65 (t, *J* = 1.8 Hz, 1H), 7.42 (ddd, *J* = 7.8, 2.0, 1.2 Hz, 1H), 7.39 (ddd, *J* = 7.8, 1.8, 1 Hz, 1H), 7.25 (t, *J* = 7.8 Hz, 1H), 3.79 (dd, *J* = 11.3, 4.3 Hz, 1H), 3.64 (dd, *J* = 10.9, 7.4 Hz, 1H), 2.62 (s, 1H), 1.80 (dd, *J* = 7.4, 5.1 Hz, 1H), 1.53 (s, 3H);
**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 147.4, 130.3, 130.0, 128.5, 123.7, 122.8, 74.5, 70.9, 26.0;
**MS** (ESI-TOF) calcd. for $C_9H_{11}BrO_2$ [M + $Na^+$] 252.9835 and 254.9814, found 252.9880 and 954.9854;
$[\alpha]_D^{25}$ = –10.0 (*c* = 0.4, $CHCl_3$).



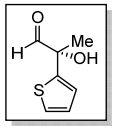

**(*R*)-2-(4-chlorophenyl)-2-hydroxypropanal (7l):**
According to the general procedure, **1l** (169 mg, 1.00 mmol), **2** (258 mg, 1.00 mmol, 1.0 equiv), **6** (74 mg, 0.20 mmol, 20 mol%), TFA (15.4 μL, 22.8 mg, 0.20 mmol, 20 mol%), and $NaHCO_3$ (84 mg, 1.00 mmol, 1.0 equiv) were allowed to react in a THF solution (3.3 mL, 0.3 M) for 4 h to afford **7l** (177 mg, 96%) as a white solid after column chromatography (silica gel, 19:1 to 3:2 hexanes/$Et_2O$).
$\mathbf{R}_f$ = 0.63 (silica gel, 2:1 hexanes/$Et_2O$);

[15] For comparison: Cleji, M.; Archelas, A.; Furstoss, R. *Tetrahedron: Asymmetry* **1998**, *9*, 1839–1842.

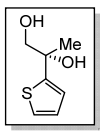
**IR** (film) $\nu_{max}$ 3445 (br), 2982, 1733, 1491, 1401, 1094, 1013, 863, 826, 788, 753 $cm^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 9.54 (s, 1H), 7.44 – 7.38 (m, 4H), 3.84 (s, 1H), 1.70 (s, 3H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 199.2, 137.7, 134.3, 129.0, 127.2, 78.8, 23.7;
**MS** (ESI-TOF) calcd. for $C_9H_9ClO_2$ [M + $H^+$ – $H_2O$] 167.0258, found 167.0244;
**$[\alpha]_D^{23}$** = –196.2 (*c* = 0.4, $CHCl_3$).




**(*R*)-2-(4-chlorophenyl)propane-1,2-diol (7ld):**
According to the general procedure, **7l** (19.0 mg, 0.10 mmol) and $NaBH_4$ (39 mg, 1.03 mmol, 10 equiv) were allowed to react in a MeOH solution (1.4 mL, 0.075 M) for 90 min to afford **7ld** (8.6 mg, 45%) as a colorless oil after column chromatography (silica gel, 9:1 to 2:3 hexanes/$Et_2O$). This material was determined to be of 90% *ee* by chiral HPLC analysis (ChiralPak AS-H, 5% *i*PrOH in hexanes, 1 mL/min, 210 nm).
**$R_f$** = 0.18 (silica gel, 2:1 hexanes/$Et_2O$);
**IR** (film) $\nu_{max}$ 3374 (br), 2977, 2932, 1492, 1400, 1375, 1096, 1041, 1013, 828, 545 $cm^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.42 – 7.39 (m, 2H), 7.36 – 7.33 (m, 2H), 3.77 (dd, *J* = 11.0, 3.2 Hz, 1H), 3.64 (dd, *J* = 11.2, 6.8 Hz, 1H), 2.58 (s, 1H), 1.81 (br s, 1H), 1.53 (s, 3H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 143.5, 133.1, 128.5, 126.6, 74.5, 70.9, 26.0;
**MS** (ESI-TOF) calcd. for $C_9H_{11}ClO_2$ [M + $Na^+$] 209.0340, found 209.0324;
**$[\alpha]_D^{25}$** = –10.4 (*c* = 0.5, $CHCl_3$).

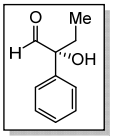



**(*S*)-2-hydroxy-2-(thiophen-2-yl)propanal (7m):**
According to the general procedure, **1m** (100 mg, 0.71 mmol), **2** (184 mg, 0.71 mmol, 1.0 equiv), **6** (53 mg, 0.14 mmol, 20 mol%), TFA (11.0 μL, 16 mg, 0.14 mmol 20 mol%), and $NaHCO_3$ (60 mg, 0.71 mmol, 1.0 equiv) were allowed to react in a THF solution (3.3 mL, 0.3 M) for 4 h to afford **7m** (80 mg, 72%) as a yellow oil after column chromatography (silica gel, 19:1 to 3:2 hexanes/$Et_2O$).
**$R_f$** = 0.71 (silica gel, 2:1 hexanes/$Et_2O$);
**IR** (film) $\nu_{max}$ 3435 (br), 2980, 1731, 1450, 1350, 1240, 1097, 858, 704 $cm^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 9.49 (s, 1H), 7.34 (d, *J* = 4.9 Hz, 1H), 7.08 – 7.05 (m, 1H), 7.03 (dd, *J* = 2.7, 1.7 Hz, 1H), 4.06 (s, 1H), 1.76 (s, 3H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 197.4, 143.7, 127.7, 126.4, 124.7, 78.0, 24.1;
**MS** (ESI-TOF) calcd. for $C_7H_8O_2S$ [M + $H^+$ – $H_2O$] 139.0212, found 139.0185;
**$[\alpha]_D^{23}$** = –158.8 (*c* = 0.5, $CHCl_3$).

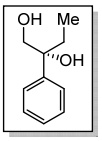



**(*S*)-2-(thiophen-2-yl)propane-1,2-diol (7md):**
According to the general procedure, **7m** (12.3 mg, 0.08 mmol) and $NaBH_4$ (30 mg, 0.79 mmol, 10 equiv) were allowed to react in a MeOH solution (1.1 mL, 0.075 M) for 90 min to afford **7md** (7.5 mg, 60%) as a yellow oil after column chromatography (silica gel, 9:1 to 2:3 hexanes/$Et_2O$). This material was determined to be of 77% *ee* by chiral HPLC analysis (ChiralPak AD-H, 5% *i*PrOH in hexanes, 1 mL/min, 234 nm).
**$R_f$** = 0.16 (silica gel, 2:1 hexanes/$Et_2O$);

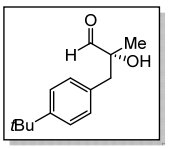
**IR** (film) $\nu_{max}$ 3371 (br), 2977, 2929, 2875, 1458, 1374, 1237, 1123, 1043, 702 $cm^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.26 (dd, *J* = 5.1, 1.5 Hz, 1H), 7.01 – 6.97 (m, 2H), 3.82 (d, *J* = 11.2 Hz, 1H), 3.66 (d, *J* = 11.2 Hz, 1H), 2.81 (br s, 1H), 1.94 (br s, 1H), 1.63 (s, 3H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 149.9, 127.0, 124.6, 123.1, 74.0, 71.5, 26.6;
**MS** (ESI-TOF) calcd. for $C_7H_{10}O_2S$ [M + $Na^+$] 181.0294, found 181.0292;
**$[\alpha]_D^{25}$** = –1.4 (*c* = 0.7, $CHCl_3$).




**(*R*)-2-hydroxy-2-phenylbutanal (7n):**
According to the general procedure, **1n** (148 mg, 1.00 mmol), **2** (258 mg, 1.00 mmol, 1.0 equiv), **6** (74 mg, 0.20 mmol, 20 mol%), TFA (15.4 μL, 22.8 mg, 0.20 mmol, 20 mol%), and $NaHCO_3$ (84 mg, 1.00 mmol, 1.0 equiv) were allowed to react in a THF solution (3.3 mL, 0.3 M) for 4 h to afford **7n** (161 mg, 98%) as a white solid after column chromatography (silica gel, 19:1 to 3:2 hexanes/$Et_2O$).
**$R_f$** = 0.68 (silica gel, 2:1 hexanes/$Et_2O$);
**IR** (film) $\nu_{max}$ 3494 (br), 2974, 2938, 1725, 1448, 1351, 1315, 1203, 1171, 1023, 987, 740, 700 $cm^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 9.60 (s, 1H), 7.52 – 7.49 (m, 2H), 7.44 – 7.40 (m, 2H), 7.33 (tt, *J* = 7.3, 1.2 Hz, 1H), 3.79 (s, 1H), 2.16 – 2.03 (m, 2H), 0.92 (t, *J* = 7.6 Hz, 3H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 200.5, 138.3, 128.8, 127.9, 125.8, 82.1, 29.7, 7.0;
**MS** (ESI-TOF) calcd. for $C_{10}H_{12}O_2$ [M + $H^+$ – $H_2O$] 147.0804, found 147.0759;
**$[\alpha]_D^{24}$** = –123.0 (*c* = 0.5, $CHCl_3$).




**(*R*)-2-phenylbutane-1,2-diol (7nd):**
According to the general procedure, **7n** (13.8 mg, 0.08 mmol) and $NaBH_4$ (32 mg, 0.84 mmol, 10 equiv) were allowed to react in a MeOH solution (1.1 mL, 0.075 M) for 90 min to afford **7nd** (5.6 mg, 40%) as a white solid after column chromatography (silica gel, 9:1 to 2:3 hexanes/$Et_2O$). This material was determined to be of 68% *ee* by chiral HPLC analysis (ChiralPak AD-H, 5% *i*PrOH in hexanes, 1 mL/min, 208 nm).
**$R_f$** = 0.26 (silica gel, 2:1 hexanes/$Et_2O$);
**IR** (film) $\nu_{max}$ 3388 (br), 2969, 2936, 28801531, 1447, 1348, 1166, 1050, 760, 701 $cm^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.44 – 7.36 (m, 4H), 7.29 (dt, *J* = 7.3, 1.7 Hz, 1H), 3.87 (dd, *J* = 11.2, 4.4 Hz, 1H), 3.72 (dd, *J* = 11.0, 8.1 Hz, 1H), 2.56 (s, 1H), 1.92 – 1.80 (m, 2H), 1.61 (dd, *J* = 8.1, 4.6 Hz, 1H), 0.79 (t, *J* = 7.3 Hz, 3H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 143.1, 128.4, 127.0, 125.6, 70.5, 31.1, 17.4;
**MS** (ESI-TOF) calcd. for $C_{10}H_{14}O_2$ [M + $Na^+$] 189.0886, found 189.0885;
**$[\alpha]_D^{25}$** = +2.2 (*c* = 0.4, $CHCl_3$).[16]




**(*R*)-3-(4-(*tert*-butyl)phenyl)-2-hydroxy-2-methylpropanal (7o):**
According to the general procedure, **1o** (216 μL, 204 mg, 1.00 mmol), **2** (258 mg, 1.00 mmol, 1.0 equiv), **6** (74 mg, 0.20 mmol, 20 mol%), TFA (15.4 μL, 22.8 mg, 0.20

[16] For comparison: Agami, C.; Couty, F.; Lequesne, C. *Tetrahedron* **1995**, *51*, 4043–4056.

mmol, 20 mol%), and $NaHCO_3$ (84 mg, 1.00 mmol, 1.0 equiv) were allowed to react in a THF solution (3.3 mL, 0.3 M) for 20 h to afford **7o** (214 mg, 97%) as a pale yellow oil after column chromatography (silica gel, 19:1 to 3:2 hexanes/$Et_2O$).

$\mathbf{R_f}$ = 0.63 (silica gel, 2:1 hexanes/$Et_2O$);

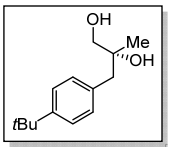
**IR** (film) $\nu_{max}$ 3457 (br), 2965, 2868, 1734, 1364, 1269, 1126, 1109, 838, 816 $cm^{-1}$;

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 9.63 (s, 1H), 7.32 (d, *J* = 8.3 Hz, 2H), 7.11 (d, *J* = 8.3 Hz, 2H), 3.04 – 2.98 (m, 2H), 2.87 (d, *J* = 14.2 Hz, 1H), 1.36 (s, 3H), 1.31 (s, 9H);

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 203.7, 150.0, 131.7, 129.9, 125.4, 78.1, 43.2, 34.4, 31.3, 22.4;

**MS** (ESI-TOF) calcd. for $C_{14}H_{20}O_2$ [M + $H^+$ – $H_2O$] 203.1340, found 203.1421;

$\mathbf{[\alpha]_D^{23}}$ = –10.6 (*c* = 0.3, $CHCl_3$).




**(*R*)-3-(4-(*tert*-butyl)phenyl)-2-methylpropane-1,2-diol (7od):**
According to the general procedure, **7o** (36 mg, 0.16 mmol) and $NaBH_4$ (62 mg, 1.63 mmol, 10 equiv) were allowed to react in a MeOH solution (2.2 mL, 0.075 M) for 90 min to afford **7od** (11.2 mg, 31%) as a pale yellow oil after column chromatography (silica gel, 9:1 to 2:3 hexanes/$Et_2O$). This material was determined to be of 60% *ee* by chiral HPLC analysis (ChiralCel OD-H, 4% *i*PrOH in hexanes, 1 mL/min, 210 nm).

$\mathbf{R_f}$ = 0.20 (silica gel, 2:1 hexanes/$Et_2O$);

**IR** (film) $\nu_{max}$ 3385 (br), 2963, 2869, 1514, 1462, 1364, 1269, 1124, 1049, 838 $cm^{-1}$;

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.3 Hz, 2H), 7.17 (d, *J* = 8.3 Hz, 2H), 3.48 (ddd, *J* = 31.2, 10.7, 5.9, 2H), 2.80 (dd, *J* = 40.5, 13.2, 2H), 1.92 (t, *J* = 5.9 Hz, 1H), 1.86 (s, 1H), 1.33 (s, 9H), 1.17 (s, 3H);

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 149.5, 133.7, 130.1, 125.3, 72.9, 69.4, 44.1, 34.4, 31.4, 23.7;

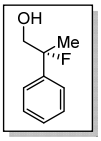
**MS** (ESI-TOF) calcd. for $C_{14}H_{22}O_2$ [M + $Na^+$] 245.1512, found 245.1521;

$\mathbf{[\alpha]_D^{25}}$ = +0.6 (*c* = 1.1, $CHCl_3$).

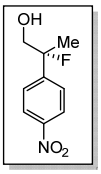
**General Procedure for Primary Amine-Catalyzed α-Fluorinations (Substrate Scope, Table 4):**
A 2.0-dram vial was charged with aldehyde substrate **1a**–**p** (1.00 mmol as indicated). No precautions were taken to ensure dryness of vial or to exclude air or moisture. The aldehyde was then dissolved in THF (0.3 M in aldehyde as indicated). Solid catalyst **6** (20 mol% as indicated) was added, followed by TFA (20 mol% as indicated) by syringe. Last, dry reagents $NaHCO_3$ (1.0 equiv as indicated) and NFSI **8** (1.0 equiv as indicated) were added to the vial sequentially. The vial was sealed and the mixture was allowed to stir for the designated amount of time (4 or 20 h) at 23 ˚C. A white precipitate forms as the reaction proceeds. Racemic standards were synthesized as described, with racemic catalyst **(±)-6**.

**General Procedure for Reduction of α-Fluoroaldehydes to Fluorohydrins (Substrate Scope, Table 4):**
α-Fluoroaldehydes **9a**–**p** were directly reduced to fluorohydrins **10a**–**p** as follows. The crude reaction mixture was transferred to a 200-mL round-bottom flask with MeOH (7 mL), and the vial was rinsed with 2 additional aliquots of MeOH (2 x 3 mL, 13 mL total, 0.075 M overall) to ensure complete transfer. Solid $NaBH_4$ (10 equiv as indicated) was added in 3 portions over the course of 10 min, then the reaction mixture was stirred, open to air, at 23 ˚C. After 90 min, the reaction was quenched with sat. aq. $NH_4Cl$

(30 mL) and EtOAc (30 mL). After an additional 30 min of stirring open to air at 23 ˚C, the layers were separated and the aqueous phase was extracted with EtOAc (4 x 25 mL). The pooled organic layers were dried over $Na_2SO_4$, filtered, and concentrated by rotary evaporation. The crude product was purified by silica gel flash chromatography. Several fluorohydrins could be recrystallized to increased *ee*. Recrystallization procedures are described below where appropriate.



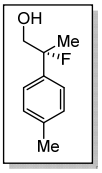

**(*R*)-2-fluoro-2-phenylpropan-1-ol (10a):**
According to the general procedures, **1a** (134 μL, 134 mg, 1.00 mmol), **8** (316 mg, 1.00 mmol, 1.0 equiv), **6** (74 mg, 0.20 mmol, 20 mol%), TFA (15.4 μL, 22.8 mg, 0.20 mmol, 20 mol%), and $NaHCO_3$ (84 mg, 1.00 mmol, 1.0 equiv) were allowed to react in a THF solution (3.3 mL, 0.3 M) for 4 h to afford crude **9a**. The mixture was then reacted with $NaBH_4$ (380 mg, 10.0 mmol, 10 equiv) in MeOH (13 mL, 0.075 M) for 90 min to afford **10a** (153 mg, 99%) as a colorless oil after column chromatography (silica gel, 19:1 to 3:2 hexanes/$Et_2O$). This material was determined to be of 80% *ee* by chiral HPLC analysis (ChiralPak AS-H, 5% *i*PrOH in hexanes, 1 mL/min, 210 nm).
$\mathbf{R}_f$ = 0.46 (silica gel, 2:1 hexanes/$Et_2O$);
**IR** (film) $\nu_{max}$ 3359 (br), 2986, 2931, 1496, 1447, 1381, 1053, 1029, 856, 762, 669, 546 $cm^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.44 – 7.37 (m, 4H), 7.36 – 7.32 (m, 1H), 3.89 – 3.71 (m, 2H), 2.23 – 2.13 (m, 1H), 1.72 (d, *J* = 22.5, 3H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 141.5 (d, *J* = 21.0 Hz), 127.1, (d, *J* = 75.3), 124.4, (d, *J* = 9.5 Hz), 97.8, (d, *J* = 172.6 Hz), 69.4 (d, *J* = 24.8 Hz), 23.1 (d, *J* = 24.8 Hz);
**$^{19}$F NMR** (282 MHz, $CDCl_3$) δ –157.0;
**MS** (ESI-TOF) calcd. for $C_9H_{11}FO$ [M + $Na^+$] 177.0686, found 177.0662;
$[\alpha]_D^{23}$ = –9.4 (*c* = 1.1, $CHCl_3$).[17]



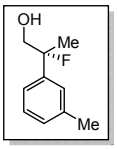

**(*R*)-2-fluoro-2-(4-nitrophenyl)propan-1-ol (10b):**
According to the general procedures, **1b** (179 mg, 1.00 mmol), **8** (315 mg, 1.00 mmol, 1.0 equiv), **6** (74 mg, 0.20 mmol, 20 mol%), TFA (15.4 μL, 22.8 mg, 0.20 mmol, 20 mol%), and $NaHCO_3$ (84 mg, 1.00 mmol, 1.0 equiv) were allowed to react in a THF solution (3.3 mL, 0.3 M) for 4 h to afford crude **9b**. The mixture was then reacted with $NaBH_4$ (378 mg, 10.0 mmol, 10 equiv) in MeOH (13 mL, 0.075 M) for 90 min to afford **10b** (179 mg, 90%) as a pale green oil after column chromatography (silica gel, 19:1 to 3:2 hexanes/$Et_2O$). This material was determined to be of 74% *ee* by chiral HPLC analysis (ChiralCel OD-H, 5% *i*PrOH in hexanes, 1 mL/min, 210 nm).
$\mathbf{R}_f$ = 0.14 (silica gel, 4:1 hexanes/$Et_2O$);
**IR** (film) $\nu_{max}$ 3372 (br), 1606, 1519, 1348, 1053, 854, 700 $cm^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 8.26 (d, *J* = 10.3 Hz, 2H), 7.56 (d, *J* = 8.8 Hz, 2H), 3.91 – 3.84 (m, 2H), 1.90 (t, *J* = 6.6 Hz, 1H), 1.73 (d, *J* = 22.9 Hz, 3H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 148.7 (d, *J* = 23.0 Hz), 125.6 (d, *J* = 10.5 Hz), 123.5 (d, *J* = 1.9 Hz), 97.5 (d, *J* = 174.5 Hz), 69.1 (d, *J* = 24.9 Hz), 23.3 (d, *J* = 24.0 Hz);

[17] For comparison: Brandes, S.; Niess, B.; Bella, M.; Prieto, A.; Overgaard, J.; Jørgensen, K. A. *Chem.—Eur. J.* **2006**, *12*, 6039–6052.

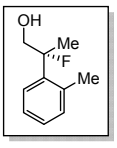
**$^{19}$F NMR** (376 MHz, $CDCl_3$) δ –157.7;
**MS** (ESI-TOF) calcd. for $C_9H_{10}FNO_3$ [M + $Na^+$] 222.1706, found 222.0562;
**$[\alpha]_D^{23}$** = –9.9 (*c* = 1.0, $CHCl_3$).




**(*R*)-2-fluoro-2-(*p*-tolyl)propan-1-ol (10d):**
According to the general procedures, **1d** (148 mg, 1.00 mmol), **8** (315 mg, 1.00 mmol, 1.0 equiv), **6** (74 mg, 0.20 mmol, 20 mol%), TFA (15.4 μL, 22.8 mg, 0.20 mmol, 20 mol%), and $NaHCO_3$ (84 mg, 1.00 mmol, 1.0 equiv) were allowed to react in a THF solution (3.3 mL, 0.3 M) for 4 h to afford crude **9d**. The mixture was then reacted with $NaBH_4$ (378 mg, 10.0 mmol, 10 equiv) in MeOH (13 mL, 0.075 M) for 90 min to afford **10d** (142 mg, 85%) as a colorless oil after column chromatography (silica gel, 19:1 to 3:2 hexanes/$Et_2O$). This material was determined to be of 79% *ee* by chiral HPLC analysis (ChiralPak AD-H, 5% *i*PrOH in hexanes, 1 mL/min, 212 nm).
**$R_f$** = 0.46 (silica gel, 2:1 hexanes/$Et_2O$);
**IR** (film) $\nu_{max}$ 3390 (br), 2987, 2925, 1516, 1450, 1379, 1189, 1050, 859, 816, 546 $cm^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.3 Hz, 2H), 7.21 (d, *J* = 8.3 Hz, 2H), 3.90 – 3.70 (m, 2H), 2.37 (s, 1H), 1.80 (t, *J* = 6.6 Hz, 1H), 1.70 (d, *J* = 22.5 Hz, 3H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 138.5 (d, *J* = 22.1 Hz), 137.6, 129.1, 124.4 (d, *J* = 8.6 Hz), 97.8 (d, *J* = 171.7 Hz), 69.6 (d, *J* = 24.9 Hz), 23.2 (d, *J* = 24.9 Hz), 21.0;
**$^{19}$F NMR** (376 MHz, $CDCl_3$) δ –156.7;
**MS** (ESI-TOF) calcd. for $C_{10}H_{13}FO_2$ [M + $Na^+$] 191.0843, found 191.0844;
**$[\alpha]_D^{23}$** = –11.7 (*c* = 0.8, $CHCl_3$).




**(*R*)-2-fluoro-2-(*m*-tolyl)propan-1-ol (10e):**
According to the general procedures, **1e** (148 mg, 1.00 mmol), **8** (315 mg, 1.00 mmol, 1.0 equiv), **6** (74 mg, 0.20 mmol, 20 mol%), TFA (15.4 μL, 22.8 mg, 0.20 mmol, 20 mol%), and $NaHCO_3$ (84 mg, 1.00 mmol, 1.0 equiv) were allowed to react in a THF solution (3.3 mL, 0.3 M) for 4 h to afford crude **9e**. The mixture was then reacted with $NaBH_4$ (378 mg, 10.0 mmol, 10 equiv) in MeOH (13 mL, 0.075 M) for 90 min to afford **10e** (147 mg, 88%) as a colorless oil after column chromatography (silica gel, 19:1 to 3:2 hexanes/$Et_2O$). This material was determined to be of 78% *ee* by chiral HPLC analysis (ChiralPak AS-H, 5% *i*PrOH in hexanes, 1 mL/min, 210 nm).
**$R_f$** = 0.68 (silica gel, 2:1 hexanes/$Et_2O$);
**IR** (film) $\nu_{max}$ 3382 (br), 2989, 2923, 1449 1378, 1189, 1051, 889, 787, 704 $cm^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.8 Hz, 1H), 7.20 – 7.13 (m, 3H), 3.90 – 3.71 (m, 2H), 2.39 (s, 1H), 1.81 (t, *J* = 6.6 Hz, 1H), 1.70 (d, *J* = 22.5 Hz, 3H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 141.4 (d, *J* = 21.1 Hz), 138.1, 133.8, 128.5 (d, *J* = 29.7 Hz), 125.1 (d, *J* = 8.6 Hz), 121.5 (d, *J* = 9.6 Hz), 97.9 (d, *J* = 171.7 Hz), 69.6 (d, *J* = 24.9 Hz), 23.2 (d, *J* = 24.9 Hz), 21.6;
**$^{19}$F NMR** (376 MHz, $CDCl_3$) δ –157.1;
**MS** (ESI-TOF) calcd. for $C_{10}H_{13}FO_2$ [M + $Na^+$] 191.0843, found 191.0842;
**$[\alpha]_D^{24}$** = –7.7 (*c* = 1.1, $CHCl_3$).




**(*R*)-2-fluoro-2-(*o*-tolyl)propan-1-ol (10f):**

According to the general procedures, **1f** (148 mg, 1.00 mmol), **8** (315 mg, 1.00 mmol, 1.0 equiv), **6** (74 mg, 0.20 mmol, 20 mol%), TFA (15.4 μL, 22.8 mg, 0.20 mmol, 20 mol%), and $NaHCO_3$ (84 mg, 1.00 mmol, 1.0 equiv) were allowed to react in a THF solution (3.3 mL, 0.3 M) for 20 h to afford crude **9f**. The mixture was then reacted with $NaBH_4$ (378 mg, 10.0 mmol, 10 equiv) in MeOH (13 mL, 0.075 M) for 90 min to afford **10f** (138 mg, 82%) as a colorless oil after column chromatography (silica gel, 19:1 to 3:2 hexanes/$Et_2O$). This material was determined to be of 73% *ee* by chiral HPLC analysis (ChiralPak AS-H, 5% *i*PrOH in hexanes, 1 mL/min, 210 nm). Purified fluorohydrin **10f** (104 mg) was dissolved in 3:1 hexanes/$Et_2O$ (0.3 mL) and gently heated in a 40 ˚C water bath for 2 min to ensure complete dissolution. The solution was cooled to 23 ˚C on the benchtop for 1 h, during which time white needles crystallized. The crystals were isolated by filtration and washed with cold hexanes to afford **10f** (33 mg, 32% recovery), which was determined to be of 99% *ee* by chiral HPLC analysis as above.

$\mathbf{R_f}$ = 0.55 (silica gel, 2:1 hexanes/$Et_2O$);

**IR** (film) $\nu_{max}$ 3338 (br), 2981, 2938, 1457, 1382, 1061, 1042, 857, 759, 726 $cm^{-1}$;

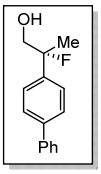
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.33 – 7.31 (m, 1H), 7.23 – 7.18 (m, 3H), 4.08 – 4.00 (m, 1H), 3.90 – 3.81 (m, 1H), 2.49 (d, *J* = 3.4 Hz, 3H), 1.88 (t, *J* = 6.3 Hz, 1H), 1.76 (d, *J* = 22.9 Hz, 3H);

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 138.8 (d, *J* = 20.1 Hz), 135.2, 132.6, 128.0, 125.9 (d, *J* = 1.9 Hz), 125.7 (d, *J* = 11.5 Hz), 99.3 (d, *J* = 171.7 Hz), 68.3 (d, *J* = 24.9 Hz), 23.0 (d, *J* = 25.9 Hz), 21.7 (d, *J* = 7.7 Hz);

**$^{19}$F NMR** (282 MHz, $CDCl_3$) δ –150.7;

**MS** (ESI-TOF) calcd. for $C_{10}H_{13}FO_2$ [M + $Na^+$] 191.0843, found 191.0852;

$\mathbf{[\alpha]_D^{23}}$ = –1.1 (*c* = 0.9, $CHCl_3$).




**(*R*)-2-([1,1'-biphenyl]-4-yl)-2-fluoropropan-1-ol (10g):**

According to the general procedures, **1g** (210 mg, 1.00 mmol), **8** (315 mg, 1.00 mmol, 1.0 equiv), **6** (74 mg, 0.20 mmol, 20 mol%), TFA (15.4 μL, 22.8 mg, 0.20 mmol, 20 mol%), and $NaHCO_3$ (84 mg, 1.00 mmol, 1.0 equiv) were allowed to react in a THF solution (3.3 mL, 0.3 M) for 4 h to afford crude **9g**. The mixture was then reacted with $NaBH_4$ (378 mg, 10.0 mmol, 10 equiv) in MeOH (13 mL, 0.075 M) for 90 min to afford **10g** (204 mg, 89%) as a colorless oil after column chromatography (silica gel, 19:1 to 3:2 hexanes/$Et_2O$). This material was determined to be of 81% *ee* by chiral HPLC analysis (ChiralPak AD-H, 5% *i*PrOH in hexanes, 1 mL/min, 210 nm). Purified fluorohydrin **10g** (204 mg) was dissolved in 3:1 hexanes/$Et_2O$ (7.0 mL) and gently heated in a 50 ˚C water bath for 5 min to ensure complete dissolution. The solution was cooled to –10 ˚C in a freezer for 1 h, during which time white crystals formed. The crystals were isolated by filtration and washed with cold hexanes to afford **10g** (105 mg, 52% recovery), which was determined to be of 93% *ee* by chiral HPLC analysis as above.

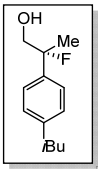
$\mathbf{R_f}$ = 0.46 (silica gel, 2:1 hexanes/$Et_2O$);

**IR** (film) $\nu_{max}$ 3370 (br), 1488, 1449, 1404, 1051, 763, 727, 692 $cm^{-1}$;

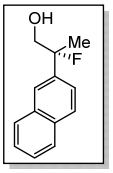
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.65 – 7.58 (m, 4H), 7.48 – 7.44 (m, 4H), 7.39 – 7.33 (m, 1H), 3.96 – 3.76 (m, 2H), 1.88 (t, *J* = 6.6 Hz, 1H), 1.75 (d, *J* = 22.5 Hz, 3H);

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 140.8, 140.53, 140.49 (d, *J* = 21.0 Hz), 128.8, 127.5, 127.2, 127.1, 124.9 (d, *J* = 8.6 Hz), 97.8 (d, *J* = 172.6), 69.6 (d, *J* = 24.9 Hz), 23.2 (d, *J* = 24.9 Hz);

**$^{19}$F NMR** (282 MHz, $CDCl_3$) δ –156.9;
**MS** (ESI-TOF) calcd. for $C_{15}H_{15}FO$ [M + $Na^+$] 253.0999, found 253.1021;
**$[\alpha]_D^{23}$** = –17.1 (*c* = 0.8, $CHCl_3$).



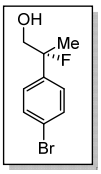

**(*R*)-2-fluoro-2-(4-isobutylphenyl)propan-1-ol (10h):**
According to the general procedures, **1h** (190 mg, 1.00 mmol), **8** (315 mg, 1.00 mmol, 1.0 equiv), **6** (74 mg, 0.20 mmol, 20 mol%), TFA (15.4 μL, 22.8 mg, 0.20 mmol, 20 mol%), and $NaHCO_3$ (84 mg, 1.00 mmol, 1.0 equiv) were allowed to react in a THF solution (3.3 mL, 0.3 M) for 4 h to afford crude **9h**. The mixture was then reacted with $NaBH_4$ (378 mg, 10.0 mmol, 10 equiv) in MeOH (13 mL, 0.075 M) for 90 min to afford **10h** (176 mg, 84%) as a colorless oil after column chromatography (silica gel, 19:1 to 3:2 hexanes/$Et_2O$). This material was determined to be of 76% *ee* by chiral HPLC analysis (ChiralPak AS-H, 3% *i*PrOH in hexanes, 1 mL/min, 210 nm). Purified fluorohydrin **10h** (151 mg) was dissolved in 3:1 hexanes/$Et_2O$ (0.3 mL). The solution was cooled to –10 ˚C in a freezer for 2 h, during which time white crystals formed. The crystals were isolated by filtration and washed with cold hexanes to afford **10h** (115 mg, 75% recovery), which was determined to be of 97% *ee* by chiral HPLC analysis as above.
**$R_f$** = 0.66 (silica gel, 2:1 hexanes/$Et_2O$);
**IR** (film) $\nu_{max}$ 3370 (br), 2954, 2925, 2969, 1466, 1367, 1189, 1051, 846, 796, 588, 561 $cm^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.31 – 7.26 (m, 2H), 7.19 – 7.12 (m, 2H), 3.90 – 3.69 (m, 2H), 2.50 – 2.47 (m, 2H), 1.92 – 1.83 (m, 2H), 1.71 (d, *J* = 22.5 Hz, 3H), 0.92 (d, *J* = 6.4 Hz, 6H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 141.4, 138.7 (d, *J* = 22.1 Hz), 129.1, 124.2 (d, *J* = 9.6 Hz), 97.9 (d, *J* = 170.7 Hz), 69.6 (d, *J* = 24.9 Hz), 45.0, 30.2, 23.1 (d, *J* = 24.9 Hz), 22.4;
**$^{19}$F NMR** (376 MHz, $CDCl_3$) δ –156.3;
**MS** (ESI-TOF) calcd. for $C_{13}H_{19}FO$ [M + $Na^+$] 233.1312, found 233.1337;
**$[\alpha]_D^{24}$** = –7.0 (*c* = 1.4, $CHCl_3$).[18]



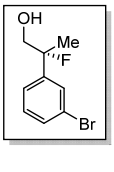

**(*R*)-2-fluoro-2-(naphthalen-2-yl)propan-1-ol (10i):**
According to the general procedures, **1i** (184 mg, 1.00 mmol), **8** (315 mg, 1.00 mmol, 1.0 equiv), **6** (74 mg, 0.20 mmol, 20 mol%), TFA (15.4 μL, 22.8 mg, 0.20 mmol, 20 mol%), and $NaHCO_3$ (84 mg, 1.00 mmol, 1.0 equiv) were allowed to react in a THF solution (3.3 mL, 0.3 M) for 4 h to afford crude **9i**. The mixture was then reacted with $NaBH_4$ (378 mg, 10.0 mmol, 10 equiv) in MeOH (13 mL, 0.075 M) for 90 min to afford **10i** (179 mg, 88%) as a white solid after column chromatography (silica gel, 19:1 to 3:2 hexanes/$Et_2O$). This material was determined to be of 82% *ee* by chiral HPLC analysis (ChiralCel OD-H, 5% *i*PrOH in hexanes, 1 mL/min, 210 nm). Purified fluorohydrin **10i** (142 mg) was dissolved in 3:1 hexanes/$Et_2O$ (2.0 mL) and gently heated in a 50 ˚C water bath for 3 min to ensure complete dissolution. The solution was cooled to –10 ˚C in a freezer for 1 h, during which time white needles crystallized. The crystals were isolated by filtration and washed with cold hexanes to afford **10i** (74 mg, 52% recovery), which was determined to be of 91% *ee* by chiral HPLC analysis as above.

[18] For comparison: Goj, O.; Burchardt, A.; Haufe, G. *Tetrahedron: Asymmetry* **1997**, *8*, 399–408.

**$R_f$** = 0.46 (silica gel, 2:1 hexanes/$Et_2O$);
**IR** (film) $\nu_{max}$ 3368 (br), 1382, 1195, 1113, 1050, 858, 819, 748, 478 $cm^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.90 – 7.84 (m, 4H), 7.54 – 7.50 (m, 2H), 7.46 (dd, *J* = 8.8, 2.0 Hz, 1H), 4.01 – 3.80 (m, 2H), 1.88 (t, *J* = 6.6 Hz, 1H), 1.81 (d, *J* = 22.9 Hz, 3H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 138.8 (d, *J* = 21.1 Hz), 132.9 (d, *J* = 28.8 Hz), 128.2 (d, *J* = 15.3 Hz), 127.6, 126.4, 126.3, 123.6 (d, *J* = 10.5 Hz), 122.4 (d, *J* = 8.6 Hz), 98.0 (d, *J* = 172.6 Hz), 69.5 (d, *J* = 24.9 Hz), 23.3 (d, *J* = 24.9 Hz);
**$^{19}$F NMR** (282 MHz, $CDCl_3$) δ –156.7;
**MS** (ESI-TOF) calcd. for $C_{13}H_{13}FO$ [M + $Na^+$] 227.0843, found 227.0872;
**$[\alpha]_D^{24}$** = –13.4 (*c* = 1.0, $CHCl_3$).




**(*R*)-2-(4-bromophenyl)-2-fluoropropan-1-ol (10j):**
According to the general procedures, **1j** (213 mg, 1.00 mmol), **8** (315 mg, 1.00 mmol, 1.0 equiv), **6** (74 mg, 0.20 mmol, 20 mol%), TFA (15.4 μL, 22.8 mg, 0.20 mmol, 20 mol%), and $NaHCO_3$ (84 mg, 1.00 mmol, 1.0 equiv) were allowed to react in a THF solution (3.3 mL, 0.3 M) for 4 h to afford crude **9j**. The mixture was then reacted with $NaBH_4$ (378 mg, 10.0 mmol, 10 equiv) in MeOH (13 mL, 0.075 M) for 90 min to afford **10j** (186 mg, 79%) as a white solid after column chromatography (silica gel, 19:1 to 3:2 hexanes/$Et_2O$). This material was determined to be of 82% *ee* by chiral HPLC analysis (ChiralPak AD-H, 5% *i*PrOH in hexanes, 1 mL/min, 220 nm). Purified fluorohydrin **10j** (158 mg) was dissolved in 3:1 hexanes/$Et_2O$ (3.5 mL) and gently heated in a 50 ˚C water bath for 3 min to ensure complete dissolution. The solution was cooled to –10 ˚C in a freezer for 1 h, during which time white needles crystallized. The crystals were isolated by filtration and washed with cold hexanes to afford **10j** (64 mg, 40% recovery), which was determined to be of 99% *ee* by chiral HPLC analysis as above.
**$R_f$** = 0.49 (silica gel, 2:1 hexanes/$Et_2O$);
**IR** (film) $\nu_{max}$ 3390 (br), 2998, 2926, 1399, 1052, 851, 820, 745, 539 $cm^{-1}$;
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.8 Hz, 2H), 7.26 (d, *J* = 14.2 Hz, 2H), 3.89 – 3.72 (m, 2H), 1.86 (t, *J* = 5.9 Hz, 1H), 1.70 (d, *J* = 22.5 Hz, 3H);
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 140.6 (d, *J* = 22.1 Hz), 131.6, 126.3 (d, *J* = 8.6 Hz), 122.0, 97.5 (d, *J* = 173.6 Hz), 69.3 (d, *J* = 24.9 Hz), 23.1 (d, *J* = 24.9 Hz);
**$^{19}$F NMR** (376 MHz, $CDCl_3$) δ –157.2;
**MS** (ESI-TOF) calcd. for $C_9H_{10}BrFO$ [M + $Na^+$] 254.9791 and 256.9771, found 254.9849 and 256.9831;
**$[\alpha]_D^{24}$** = –13.8 (*c* = 0.7, $CHCl_3$).




**(*R*)-2-(3-bromophenyl)-2-fluoropropan-1-ol (10k):**
According to the general procedures, **1k** (213 mg, 1.00 mmol), **8** (315 mg, 1.00 mmol, 1.0 equiv), **6** (74 mg, 0.20 mmol, 20 mol%), TFA (15.4 μL, 22.8 mg, 0.20 mmol, 20 mol%), and $NaHCO_3$ (84 mg, 1.00 mmol, 1.0 equiv) were allowed to react in a THF solution (3.3 mL, 0.3 M) for 4 h to afford crude **9k**. The mixture was then reacted with $NaBH_4$ (378 mg, 10.0 mmol, 10 equiv) in MeOH (13 mL, 0.075 M) for 90 min to afford **10k** (205 mg, 88%) as a colorless oil after

column chromatography (silica gel, 19:1 to 3:2 hexanes/$Et_2O$). This material was determined to be of 80% *ee* by chiral HPLC analysis (ChiralPak AS-H, 5% *i*PrOH in hexanes, 1 mL/min, 210 nm).

**$R_f$** = 0.51 (silica gel, 2:1 hexanes/$Et_2O$);

**IR** (film) $\nu_{max}$ 3353 (br), 2986, 2937, 1568, 1477, 1418, 1247, 1053, 865, 786, 759, 695 $cm^{-1}$;

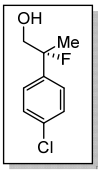
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.56 – 7.55 (m, 1H), 7.49 (dt, *J* = 7.0, 1.9 Hz, 1H), 7.32 – 7.28 (m, 2H), 3.90 – 3.74 (m, 2H), 1.88 (t, *J* = 6.6 Hz, 1H), 1.71 (d, *J* = 23.2 Hz, 3H);

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 143.9 (d, *J* = 22.1 Hz), 131.0, 130.0, 127.8 (d, *J* = 9.6 Hz), 123.1 (d, *J* = 8.6 Hz), 122.7 (d, *J* = 1.9 Hz), 97.3 (d, *J* = 174.5 Hz), 69.3 (d, *J* = 24.9 Hz), 23.2 (d, *J* = 24.9 Hz);

**$^{19}$F NMR** (376 MHz, $CDCl_3$) δ –157.2;

**MS** (ESI-TOF) calcd. for $C_9H_{10}BrFO$ [M + $Na^+$] 254.9791 and 256.9771, found 254.9854 and 256.9834;

**$[\alpha]_D^{24}$** = –9.7 (*c* = 1.2, $CHCl_3$).




**(*R*)-2-(4-chlorophenyl)-2-fluoropropan-1-ol (10l):**

According to the general procedures, **1l** (169 mg, 1.00 mmol), **8** (315 mg, 1.00 mmol, 1.0 equiv), **6** (74 mg, 0.20 mmol, 20 mol%), TFA (15.4 μL, 22.8 mg, 0.20 mmol, 20 mol%), and $NaHCO_3$ (84 mg, 1.00 mmol, 1.0 equiv) were allowed to react in a THF solution (3.3 mL, 0.3 M) for 4 h to afford crude **9l**. The mixture was then reacted with $NaBH_4$ (378 mg, 10.0 mmol, 10 equiv) in MeOH (13 mL, 0.075 M) for 90 min to afford **10l** (139 mg, 74%) as a white solid after column chromatography (silica gel, 19:1 to 3:2 hexanes/$Et_2O$). This material was determined to be of 86% *ee* by chiral HPLC analysis (ChiralPak AD-H, 5% *i*PrOH in hexanes, 1 mL/min, 220 nm). Purified fluorohydrin **10l** (122 mg) was dissolved in 3:1 hexanes/$Et_2O$ (2.5 mL) and gently heated in a 50 ˚C water bath for 3 min to ensure complete dissolution. The solution was cooled to –10 ˚C in a freezer for 1 h, during which time white needles crystallized. The crystals were isolated by filtration and washed with cold hexanes to afford **10l** (40 mg, 33% recovery), which was determined to be of 99% *ee* by chiral HPLC analysis as above.

**$R_f$** = 0.67 (silica gel, 2:1 hexanes/$Et_2O$);

**IR** (film) $\nu_{max}$ 3410 (br), 2924, 1404, 1079, 1056, 1013, 853, 824, 543 $cm^{-1}$;

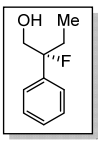
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.8 Hz, 2H), 7.32 (d, *J* = 8.8 Hz, 2H), 3.88 – 3.71 (m, 2H), 1.82 (ddd, *J* = 7.7, 6.0, 1.5 Hz, 1H), 1.69 (d, *J* = 22.9 Hz, 3H);

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 140.1 (d, *J* = 22.1 Hz), 133.8, 128.6, 126.0 (d, *J* = 8.6 Hz), 97.5 (d, *J* = 172.6 Hz), 69.4 (d, *J* = 24.9 Hz), 23.2 (d, *J* = 24.9 Hz);

**$^{19}$F NMR** (282 MHz, $CDCl_3$) δ –158.9;

**MS** (ESI-TOF) calcd. for $C_9H_{10}ClFO$ [M + $Na^+$] 211.0296, found 211.0281;

**$[\alpha]_D^{25}$** = –14.1 (*c* = 1.1, $CHCl_3$).




**(*R*)-2-fluoro-2-phenylbutan-1-ol (10n):**

According to the general procedures, **1n** (166 mg, 1.00 mmol), **8** (315 mg, 1.00 mmol, 1.0 equiv), **6** (74 mg, 0.20 mmol, 20 mol%), TFA (15.4 μL, 22.8 mg, 0.20 mmol, 20 mol%), and $NaHCO_3$ (84 mg, 1.00 mmol, 1.0 equiv) were allowed to react in a THF solution (3.3 mL, 0.3 M) for 4 h to afford crude **9n**. The mixture was then reacted with $NaBH_4$ (378 mg, 10.0 mmol, 10

equiv) in MeOH (13 mL, 0.075 M) for 90 min to afford **10n** (149 mg, 88%) as a colorless oil after column chromatography (silica gel, 19:1 to 3:2 hexanes/$Et_2O$). This material was determined to be of 48% *ee* by chiral HPLC analysis (ChiralPak AD-H, 2% *i*PrOH in hexanes, 1 mL/min, 210 nm).

**$R_f$** = 0.53 (silica gel, 2:1 hexanes/$Et_2O$);

**IR** (film) $\nu_{max}$ 3359 (br), 2974, 2937, 1448, 1058, 913, 876, 759, 700 $cm^{-1}$;

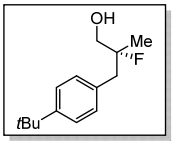
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.42 – 7.38 (m, 2H), 7.35 – 7.32 (m, 3H), 3.93 – 3.74 (m, 2H), 2.23 – 2.12 (m, 1H), 1.99 – 1.84 (m, 2H), 1.72 (t, *J* = 6.6 Hz, 1H), 0.83 (t, *J* = 7.3 Hz, 3H);

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 139.8 (d, *J* = 22.1 Hz), 128.40 (d, *J* = 1.9 Hz), 128.38 (d, *J* = 67.2 Hz), 127.6, 124.8 (d, *J* = 9.6 Hz), 100.3 (d, *J* = 175.5 Hz), 68.8 (d, *J* = 24.0 Hz), 28.9 (d, *J* = 23.0 Hz), 7.2 (d, *J* = 5.8 Hz);

**$^{19}$F NMR** (282 MHz, $CDCl_3$) δ –170.5;

**MS** (ESI-TOF) calcd. for $C_{10}H_{13}FO$ [M + $Na^+$] 191.0843, found 191.0860;

**$[\alpha]_D^{24}$** = –2.0 (*c* = 0.7, $CHCl_3$).[19]




**(*R*)-3-(4-(*tert*-butyl)phenyl)-2-fluoro-2-methylpropan-1-ol (10o):**

According to the general procedures, **1o** (216 µL, 204 mg, 1.00 mmol), **8** (315 mg, 1.00 mmol, 1.0 equiv), **6** (74 mg, 0.20 mmol, 20 mol%), TFA (15.4 µL, 22.8 mg, 0.20 mmol, 20 mol%), and $NaHCO_3$ (84 mg, 1.00 mmol, 1.0 equiv) were allowed to react in a THF solution (3.3 mL, 0.3 M) for 20 h to afford crude **9o**. The mixture was then reacted with $NaBH_4$ (378 mg, 10.0 mmol, 10 equiv) in MeOH (13 mL, 0.075 M) for 90 min to afford **10o** (214 mg, 95%) as a colorless oil after column chromatography (silica gel, 19:1 to 3:2 hexanes/$Et_2O$). This material was determined to be of 69% *ee* by chiral HPLC analysis (ChiralPak AS-H, 3% *i*PrOH in hexanes, 1 mL/min, 218 nm).

**$R_f$** = 0.75 (silica gel, 2:1 hexanes/$Et_2O$);

**IR** (film) $\nu_{max}$ 3342 (br), 2960, 2869, 1510, 1460, 1363, 1269, 1034, 841, 572 $cm^{-1}$;

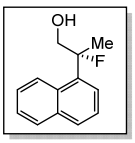
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.31 (d, *J* = 7.8 Hz, 2H), 7.12 (d, *J* = 8.3 Hz, 2H), 3.56 (dd, *J* = 10.5, 6.1 Hz, 1H), 3.50 (dd, *J* = 9.8, 5.9 Hz, 1H), 2.72 (dd, *J* = 13.7, 6.4 Hz, 1H), 2.42 (dd, *J* = 13.5, 8.1 Hz, 1H), 2.00 – 1.92 (m, 1H), 1.33 (s, 9H), 0.94 (d, *J* = 6.8 Hz, 3H);

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 148.7, 137.5, 128.8, 125.1, 67.8, 39.2, 37.8, 34.3, 31.4, 16.6;

**$^{19}$F NMR** (376 MHz, $CDCl_3$) δ –154.3;

**MS** (ESI-TOF) calcd. for $C_{14}H_{21}FO$ [M + $Na^+$] 247.1469, found 247.1474;

**$[\alpha]_D^{24}$** = –1.7 (*c* = 0.7, $CHCl_3$).




**(*R*)-2-fluoro-2-(naphthalen-1-yl)propan-1-ol (10p):**

According to the general procedures, **1p** (184 mg, 1.00 mmol), **8** (315 mg, 1.00 mmol, 1.0 equiv), **6** (74 mg, 0.20 mmol, 20 mol%), TFA (15.4 µL, 22.8 mg, 0.20 mmol, 20 mol%), and $NaHCO_3$ (84 mg, 1.00 mmol, 1.0 equiv) were allowed to react in a THF solution (3.3 mL, 0.3 M) for 20 h to afford crude **9p**. The mixture was then reacted with $NaBH_4$ (378 mg, 10.0 mmol, 10 equiv) in MeOH (13 mL, 0.075 M) for 90 min to afford **10p** (191 mg, 94%) as a colorless

[19] For comparison: Lee, S. Y.; Neufeind, S.; Fu, G. C. *J. Am. Chem. Soc.* **2014**, *136*, 8899–8902.

oil after column chromatography (silica gel, 19:1 to 3:2 hexanes/$Et_2O$). This material was determined to be of 69% *ee* by chiral HPLC analysis (ChiralPak AS-H, 5% *i*PrOH in hexanes, 1 mL/min, 210 nm). Purified fluorohydrin **10p** (158 mg) was dissolved in 3:1 hexanes/$Et_2O$ (1.5 mL) and gently heated in a 40 ˚C water bath for 3 min to ensure complete dissolution. The solution was cooled to –10 ˚C in a freezer for 24 h, during which time white crystals formed. The crystals were isolated by filtration and washed with cold hexanes to afford **10p** (61 mg, 39% recovery), which was determined to be of 90% *ee* by chiral HPLC analysis as above.

$\mathbf{R}_f$ = 0.50 (silica gel, 2:1 hexanes/$Et_2O$);

**IR** (film) $\nu_{max}$ 3354 (br), 1511, 1242, 1111, 865, 804, 776 $cm^{-1}$;

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 8.33 (d, *J* = 8.3 Hz, 1H), 7.90 (d, *J* = 7.8 Hz, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.60 (dd, *J* = 7.3, 1.0 Hz), 7.55 – 7.45 (m, 3H), 4.30 (ddd, *J* = 18.4, 13.1, 4.6, 1H), 4.15 – 4.06 (m, 1H), 2.02 (d, *J* = 1.0 Hz, 1H), 1.97 (d, *J* = 1.79 Hz, 3H);

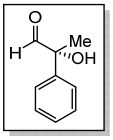
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 136.4 (d, *J* = 20.2 Hz), 134.6, 129.5, 129.3, 126.1, 125.5, 125.4, 124.9, 123.9 (d, *J* = 12.5 Hz), 99.5 (d, *J* = 171.7 Hz), 68.7 (d, *J* = 24.9 Hz), 23.7 (d, *J* = 25.9 Hz);

**$^{19}$F NMR** (376 MHz, $CDCl_3$) δ –146.5;

**MS** (ESI-TOF) calcd. for $C_{13}H_{13}FO$ [M + $Na^+$] 227.0843, found 227.0911;

**$[\alpha]_D^{24}$** = +0.9 (*c* = 1.4, $CHCl_3$).

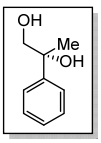
**Gram-Scale Reactions (Scheme 2a,b):**




**(*R*)-2-hydroxy-2-phenylpropanal (7a):**

A 200-mL round-bottom flask was charged with aldehyde substrate **1a** (1.50 mL, 1.50 g, 11.2 mmol). No precautions were taken to ensure dryness of flask or to exclude air or moisture. The aldehyde was then dissolved in THF (37 mL, 0.3 M). Solid catalyst **6** (0.831 g, 2.24 mmol, 20 mol%) was added, followed by TFA (170 μL, 0.252 g, 2.21 mmol, 20 mol%) by syringe. Last, dry reagents $NaHCO_3$ (0.941 g, 11.2 mmol, 1.0 equiv) and oxaziridine **2** (2.892 g, 11.2 mmol, 1.0 equiv) were added to the flask sequentially. The flask was capped and the mixture was allowed to stir for 4 h at 23 ˚C. The reaction started out heterogeneous, but eventually became homogeneous. The mixture was concentrated by rotary evaporation, and the resultant residue was purified directly by flash chromatography (silica gel, 19:1 to 3:2 hexanes/EtOAc) to afford **7a** as a colorless oil which solidifies when stored at –78 ˚C (1.102 g, 66%).

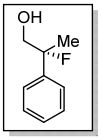
Spectroscopic results agree with those reported above.




**(*R*)-2-phenylpropane-1,2-diol (7ad):**

According to the general procedure, **7a** (27.3 mg, 0.18 mmol) and $NaBH_4$ (69 mg, 1.81 mmol, 10 equiv) were allowed to react in a MeOH solution (2.4 mL, 0.075 M) for 90 min to afford **7ad** (20.5 mg, 74%) as a colorless oil after column chromatography (silica gel, 9:1 to 2:3 hexanes/$Et_2O$). This material was determined to be of 89% *ee* by chiral HPLC analysis (ChiralPak AS-H, 5% *i*PrOH in hexanes, 1 mL/min, 210 nm).

Spectroscopic results agree with those reported above.

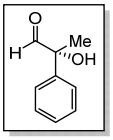


**(*R*)-2-fluoro-2-phenylpropan-1-ol (10a):**

A 200-mL round-bottom flask was charged with aldehyde substrate **1a** (1.00 mL, 1.00 g, 7.5 mmol). No precautions were taken to ensure dryness of flask or to exclude air or moisture. The aldehyde was then dissolved in THF (25 mL, 0.3 M). Solid catalyst **6** (0.138 g, 0.37 mmol, 5 mol%) was added, followed by TFA (115 μL, 0.170 g, 1.49 mmol, 20 mol%) by syringe. Last, dry reagents $NaHCO_3$ (0.628 g, 7.5 mmol, 1.0 equiv) and NFSI **8** (2.356 g, 7.5 mmol, 1.0 equiv) were added to the flask sequentially. The flask was capped and the mixture was allowed to stir for 4 h at 23 ˚C. A white precipitate formed as the reaction proceeded. After 4 h, the crude reaction mixture was transferred to a 1-L round-bottom flask with MeOH (70 mL), and the 200-mL flask was rinsed with 2 additional aliquots of MeOH (2 x 15 mL, 100 mL total, 0.075 M overall) to ensure complete transfer. The flask was cooled to 0 ˚C in an ice bath, then solid $NaBH_4$ (2.830 g, 74.8 mmol, 10 equiv) was added in 3 portions over the course of 10 min. The reaction mixture was stirred, open to air, at 23 ˚C. After 90 min, the reaction was quenched with sat. aq. $NH_4Cl$ (200 mL) and EtOAc (200 mL). After an additional 30 min of stirring open to air at 23 ˚C, the layers were separated and the aqueous phase was extracted with EtOAc (4 x 150 mL). The pooled organic layers were dried over $Na_2SO_4$, filtered, and concentrated by rotary evaporation. The crude product was purified by flash chromatography (silica gel, 19:1 to 3:2 hexanes/EtOAc) to afford **10a** as a colorless oil which solidifies when stored at –10 ˚C (1.152 g, 100%). This material was determined to be of 80% *ee* by chiral HPLC analysis (ChiralPak AS-H, 5% *i*PrOH in hexanes, 1 mL/min, 210 nm). Purified fluorohydrin **10a** (1.151 g) was dissolved in hexanes (1.0 mL) and gently heated in a 40 ˚C water bath for 5 min to ensure complete dissolution. The solution was cooled to –10 ˚C in a freezer for 1 h, during which time white crystals formed. The crystals were isolated by filtration and washed with cold hexanes to afford **10a** (0.706 g, 61% recovery), which was determined to be of 89% *ee* by chiral HPLC analysis as above.

Spectroscopic results agree with those reported above.

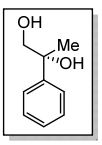
**Low Temperature α-Hydroxylation (Scheme 2c):**



**(*R*)-2-hydroxy-2-phenylpropanal (7a):**

A 2-dram vial was charged with aldehyde substrate **1a** (134 μL, 134 mg, 1.00 mmol). No precautions were taken to ensure dryness of vial or to exclude air or moisture. The aldehyde was then dissolved in THF (3.3 mL, 0.3 M). Solid catalyst **6** (74 mg, 0.20 mmol, 20 mol%) was added, followed by TFA (15.4 μL, 22.8 mg, 0.20 mmol, 20 mol%) by syringe. $NaHCO_3$ (84 mg, 1.00 mmol, 1.0 equiv) was added to the vial, which was then sealed and placed in a –78 ˚C dry ice/acetone bath. After 30 minutes, oxaziridine **2** (258 mg, 1.00 mmol, 1.0 equiv) was added to the vial, which was then resealed and placed in a bath at –25 ˚C. After stirring for 24 h at –25 ˚C, the mixture was concentrated by rotary evaporation at 23 ˚C, and the resultant residue was purified directly by flash chromatography (silica gel, 19:1 to 3:2 hexanes/EtOAc) to afford **7a** as a colorless oil (98 mg, 65%).

Spectroscopic results agree with those reported above.

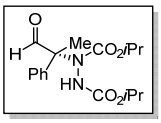


**(*R*)-2-phenylpropane-1,2-diol (7ad):**

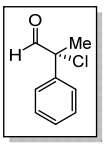
According to the general procedure, **7a** (15.3 mg, 0.10 mmol) and $NaBH_4$ (39 mg, 1.02

mmol, 10 equiv) were allowed to react in a MeOH solution (1.36 mL, 0.075 M) for 90 min to afford **7ad** (10.2 mg, 66%) as a colorless oil after column chromatography (silica gel, 9:1 to 2:3 hexanes/$Et_2O$). This material was determined to be of 93% *ee* by chiral HPLC analysis (ChiralPak AS-H, 5% *i*PrOH in hexanes, 1 mL/min, 210 nm).
Spectroscopic results agree with those reported above.

**Reactions with Alternative Electrophiles (Scheme 3):**



**Diisopropyl (*R*)-1-(1-oxo-2-phenylpropan-2-yl)hydrazine-1,2-dicarboxylate (13):**
A 2-dram vial was charged with aldehyde substrate **1a** (134 μL, 134 mg, 1.00 mmol). No precautions were taken to ensure dryness of vial or to exclude air or moisture. The aldehyde was then dissolved in THF (3.3 mL, 0.3 M). Solid catalyst **6** (74 mg, 0.20 mmol, 20 mol%) was added, followed by TFA (15.4 μL, 22.8 mg, 0.20 mmol, 20 mol%) by syringe. Last, DIAD **12** (195 μL, 202 mg, 1.00 mmol, 1.0 equiv) was added to the vial, which was then sealed. The mixture was allowed to stir for 4 h at 23 ˚C, after which the solution was concentrated by rotary evaporation. The resultant residue was purified directly by flash chromatography (silica gel, 9:1 to 2:3 hexanes/EtOAc) to afford **13** as a thick, colorless oil (319 mg, 95%). This material was determined to be of 85% *ee* by chiral HPLC analysis (ChiralPak AD-H, 5% *i*PrOH in hexanes, 0.5 mL/min, 210 nm). A racemic standard was synthesized as described, with racemic catalyst **(±)-6**.
$\mathbf{R}_f$ = 0.60 (silica gel, 2:1 hexanes/$Et_2O$);
**IR** (film) $\nu_{max}$ 3304 (br), 2982, 1733, 1703, 1376, 1321, 1245, 1107 $cm^{-1}$;
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 9.77 (minor rotamor, s, 0.24H), 9.61 (major rotamer, s, 0.76H), 7.61 – 7.30 (m, 5H), 6.32 (br s, 1H), 5.04 – 4.82 (m, 2H), 1.84 – 1.70 (m, 3H), 1.34 – 1.11 (m, 12H);
**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 194.2, 192.8, 156.0, 155.6, 137.1, 128.9, 128.1, 127.3, 73.0, 71.4, 21.7, 18.1;
**MS** (ESI-TOF) calcd. for $C_{17}H_{24}N_2O_5$ [M + $H^+$] 337.1758, found 337.1769;
$\mathbf{[\alpha]_D^{24}}$ = +42.3 (*c* = 1.1, $CHCl_3$).[20]



**(*R*)-2-chloro-2-phenylpropanal (15):**
A 2-dram vial was charged with aldehyde substrate **1a** (134 μL, 134 mg, 1.00 mmol). No precautions were taken to ensure dryness of vial or to exclude air or moisture. The aldehyde was then dissolved in THF (3.3 mL, 0.3 M). Solid catalyst **6** (74 mg, 0.20 mmol, 20 mol%) was added, followed by TFA (15.4 μL, 22.8 mg, 0.20 mmol, 20 mol%) by syringe. Last, $NaHCO_3$ (84 mg, 1.00 mmol, 1.0 equiv) and 2,3,4,5,6,6-hexachlorocyclohexa-2,4-dienone **14** (301 mg, 1.00 mmol, 1.0 equiv) were sequentially added to the vial, which was then sealed. The mixture was allowed to stir for 4 h at 23 ˚C, after which the solution was concentrated by rotary evaporation. The resultant residue was purified directly by flash chromatography (silica gel, 19:1 to 3:2 hexanes/EtOAc) to afford **15** as a yellow oil (120 mg, 71%). This material was determined to be of 66% *ee* by chiral HPLC analysis (ChiralPak AD-H, 2% *i*PrOH in hexanes, 0.5 mL/min, 210 nm). A racemic standard was synthesized as

[20] For comparison: Theodorou, A.; Papadopoulos, G. N.; Kokotos, C. G. *Tetrahedron* **2013**, *69*, 5438–5443.

described, with racemic catalyst **(±)-6**.

**$R_f$** = 0.80 (silica gel, 2:1 hexanes/$Et_2O$);

**IR** (film) $\nu_{max}$ 1729, 1492, 1445, 1383, 1165, 1112, 1055, 890, 759, 695, 531 $cm^{-1}$;

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 9.47 (s), 7.51 – 7.47 (m, 2H), 7.46 – 7.37 (m, 3H), 2.00 (s, 3H);

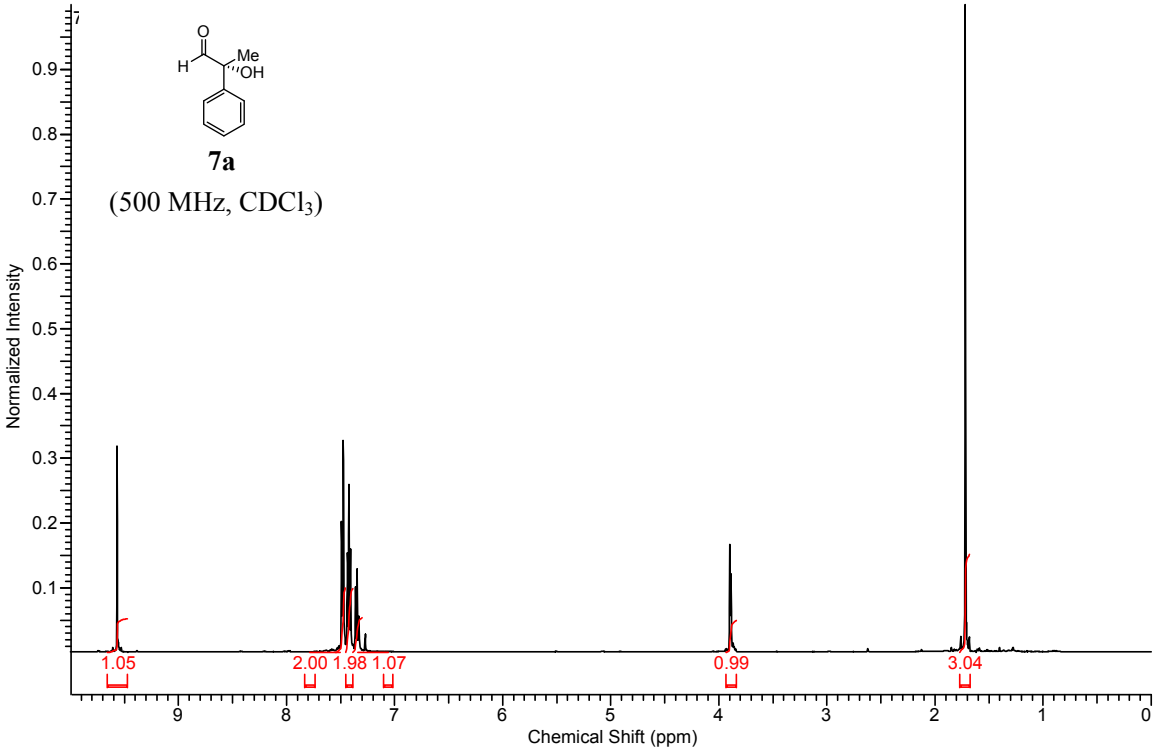
**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 191.7, 137.1, 128.9, 128.8, 126.7, 73.6, 25.5;

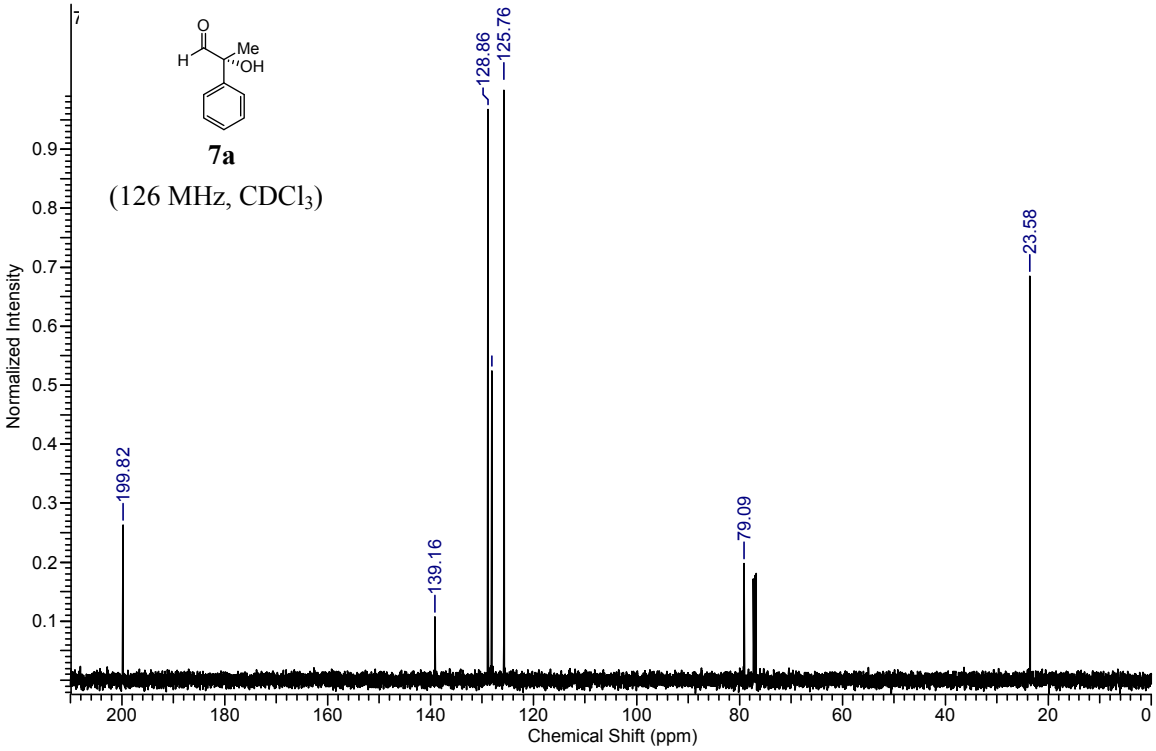
**MS** (ESI-TOF) calcd. for $C_9H_9ClO$ [M + $H^+$ – $H_2O$] 151.0309, found 151.0288;

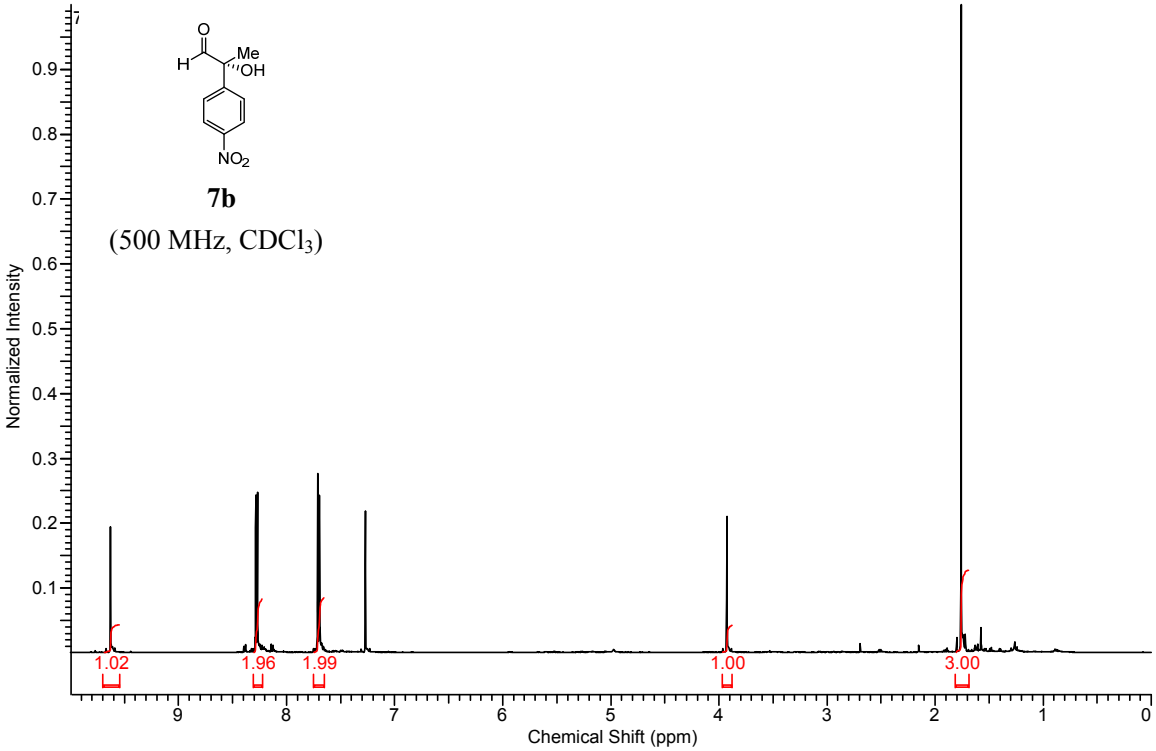
**$[\alpha]_D^{24}$** = +33.7 (*c* = 1.0, $CHCl_3$).[21]

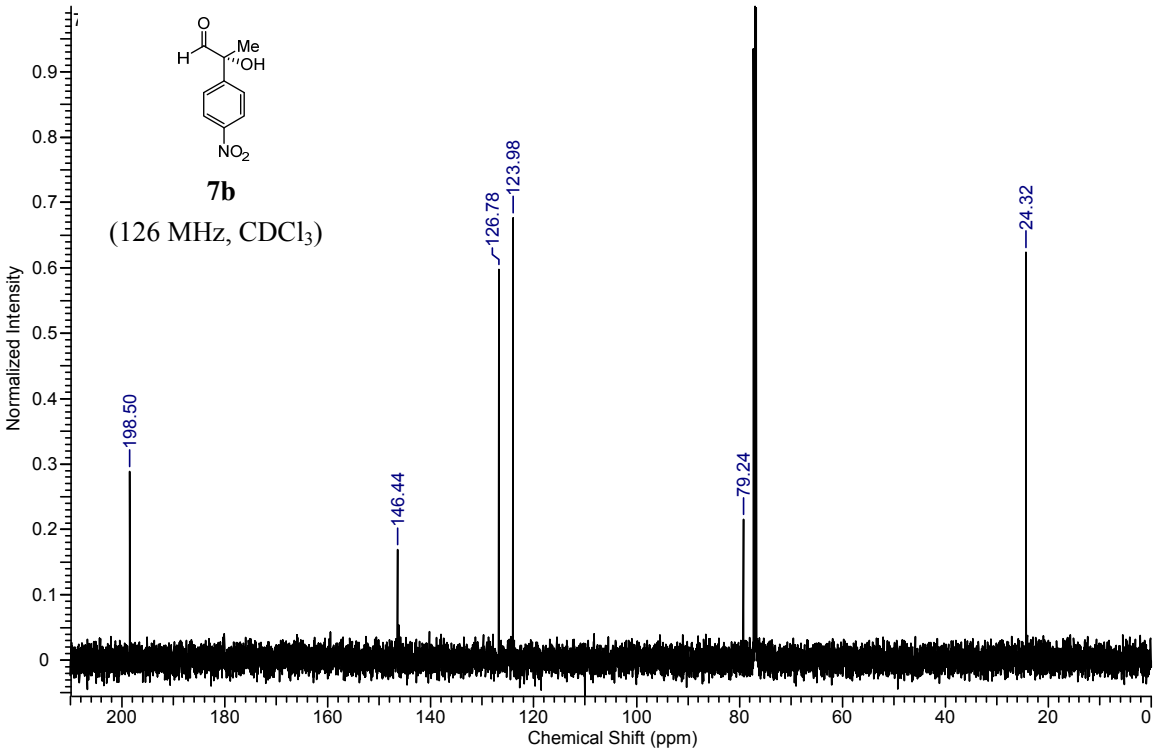
## 5. $^1$H and $^{13}$C NMR Spectra of α-Functionalization Products

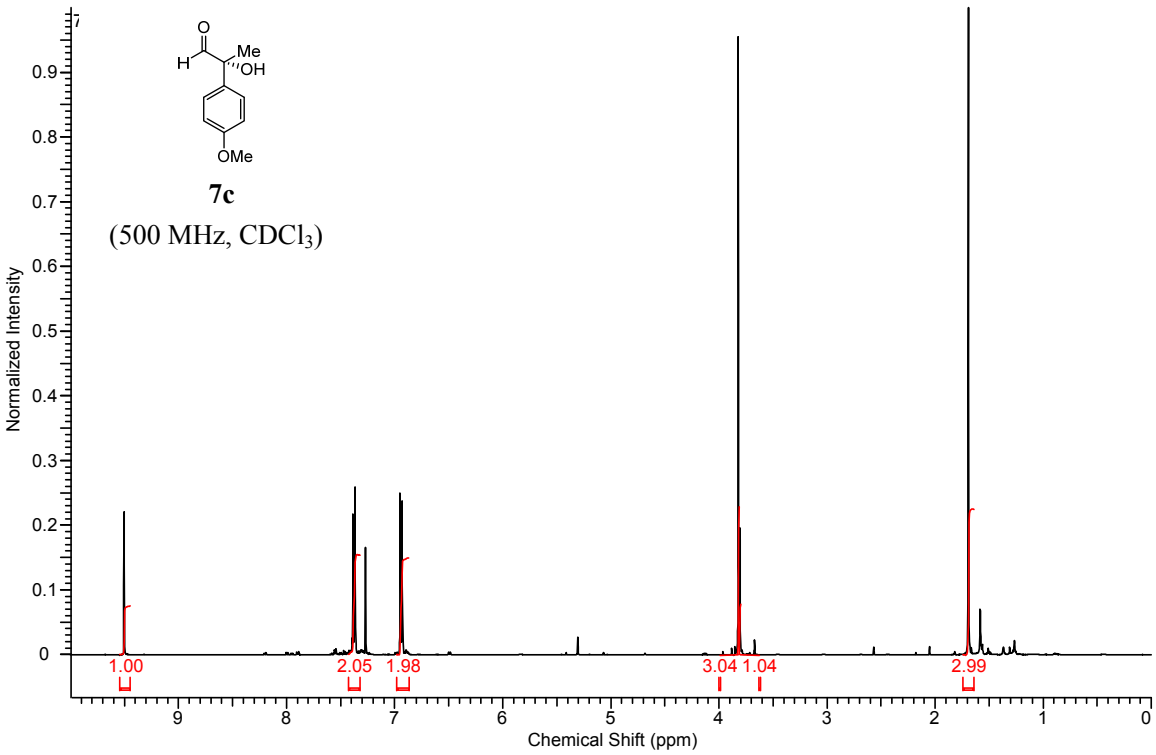
[21] For comparison: Paulmier, C.; Outurquin, F.; Plaquevant, J.-C. *Tetrahedron Lett.* **1988**, *29*, 5889–5891.

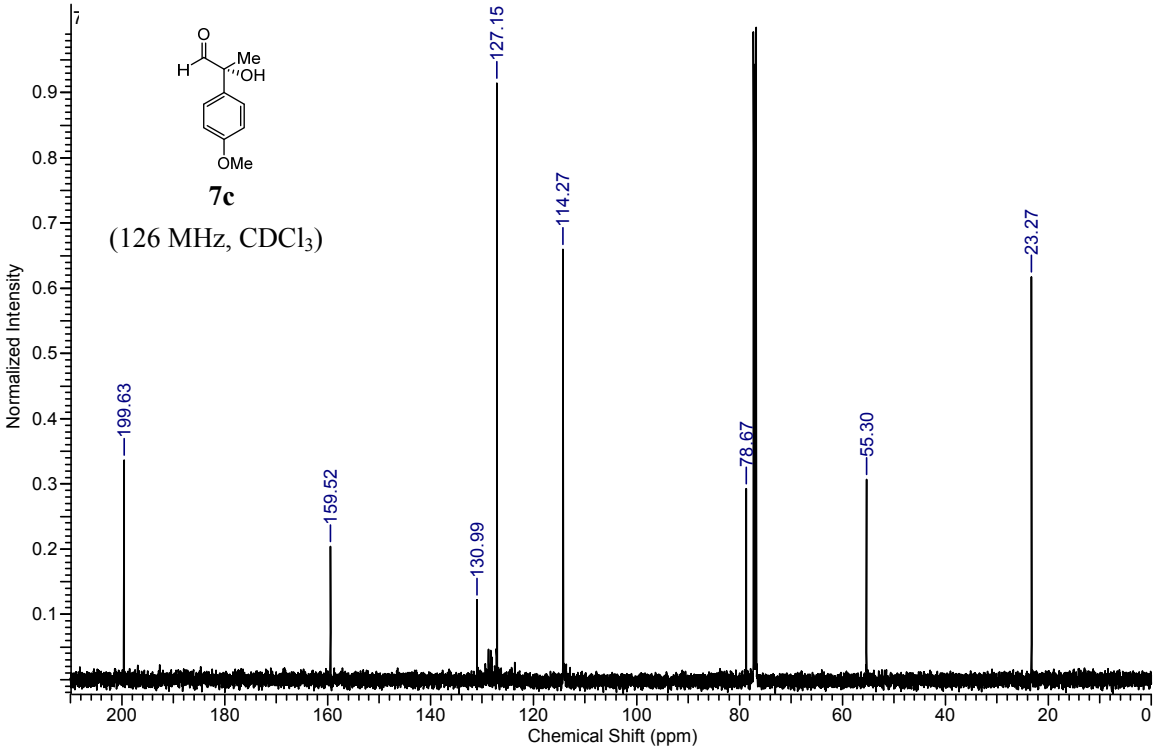

O
H
Me
OH
7a
(500 MHz, CDCl3)
Normalized Intensity
1.05
2.00
1.98
1.07
0.99
3.04
Chemical Shift (ppm)

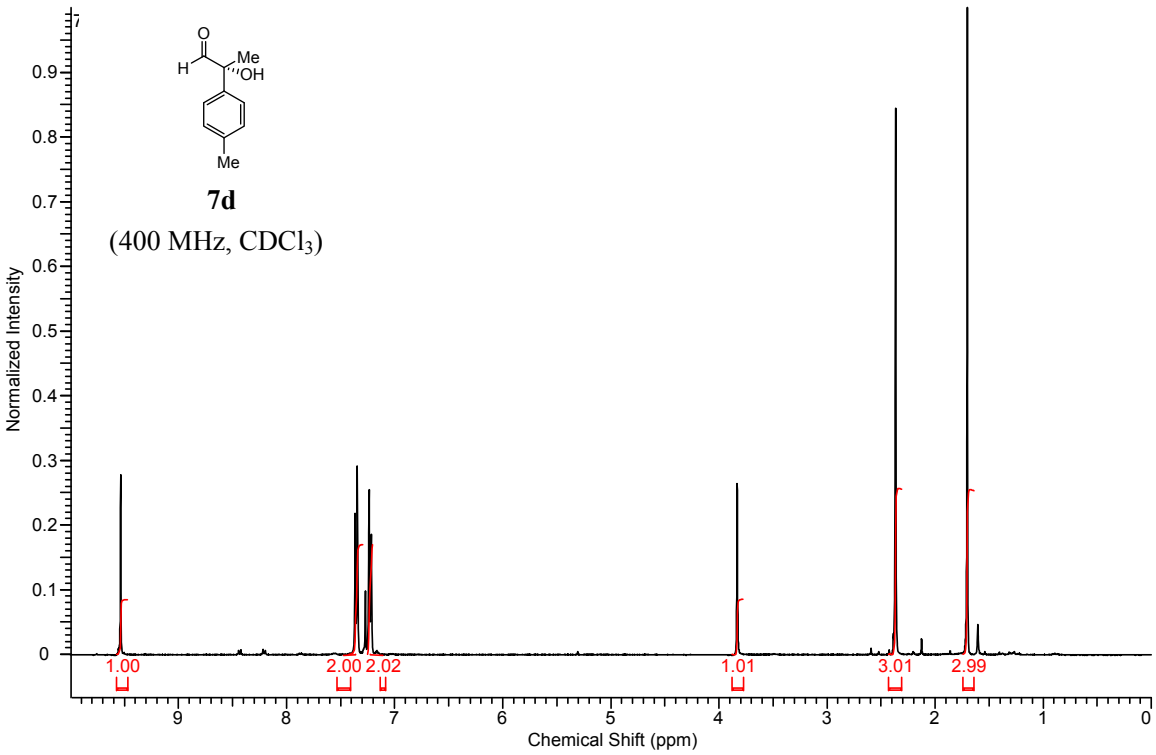

O
H
Me
OH
7a
(126 MHz, CDCl3)
Normalized Intensity
199.82
139.16
128.86
125.76
79.09
23.58
Chemical Shift (ppm)

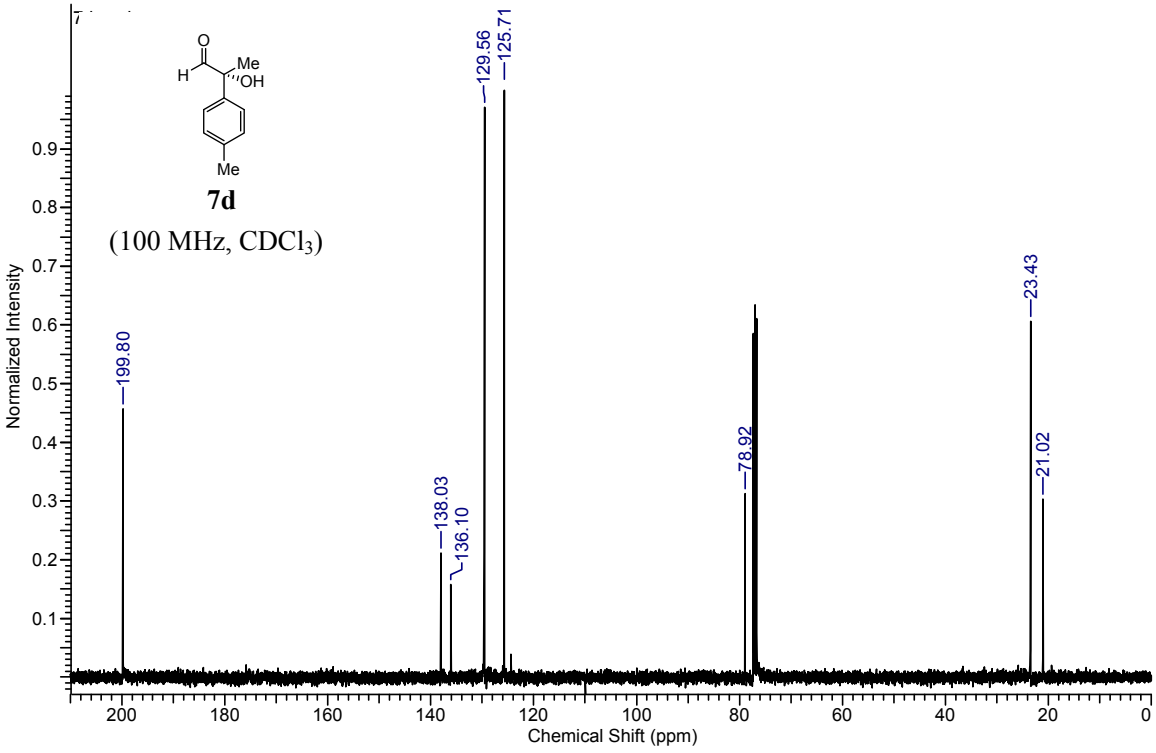

O
H
Me
OH
NO2
7b
(500 MHz, CDCl3)
Normalized Intensity
1.02
1.96
1.99
1.00
3.00
Chemical Shift (ppm)

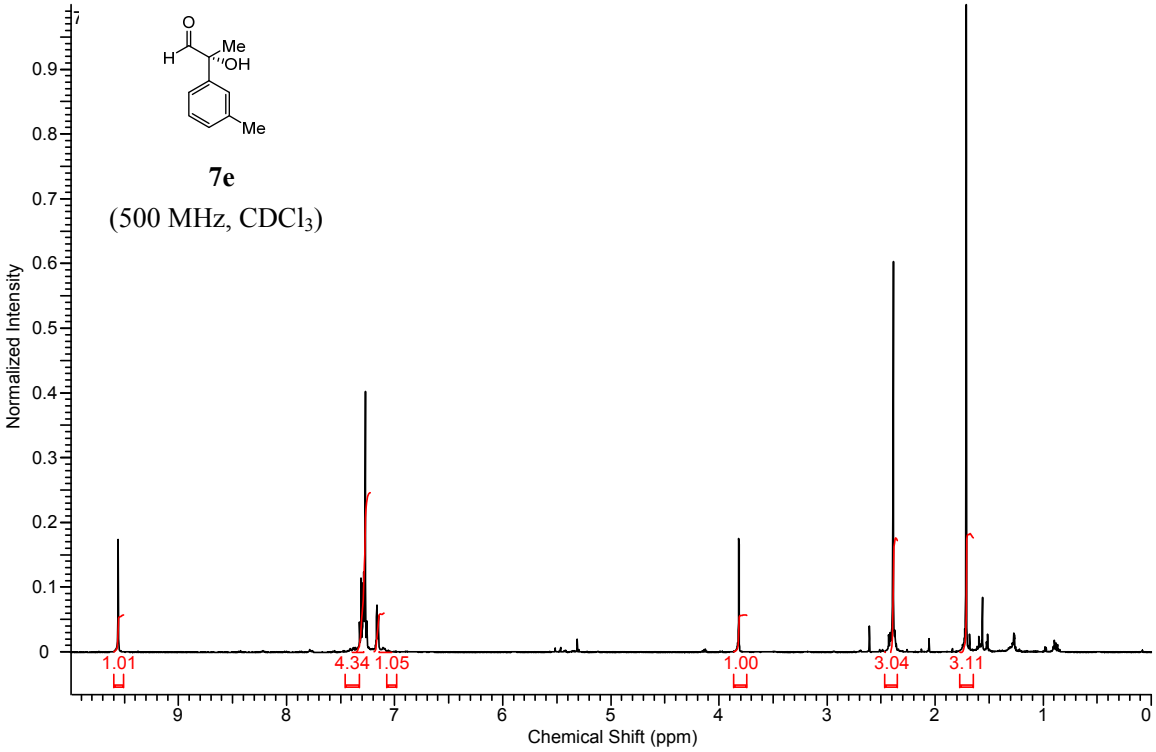

O
H
Me
OH
NO2
7b
(126 MHz, CDCl3)
Normalized Intensity
198.50
146.44
126.78
123.98
79.24
24.32
Chemical Shift (ppm)

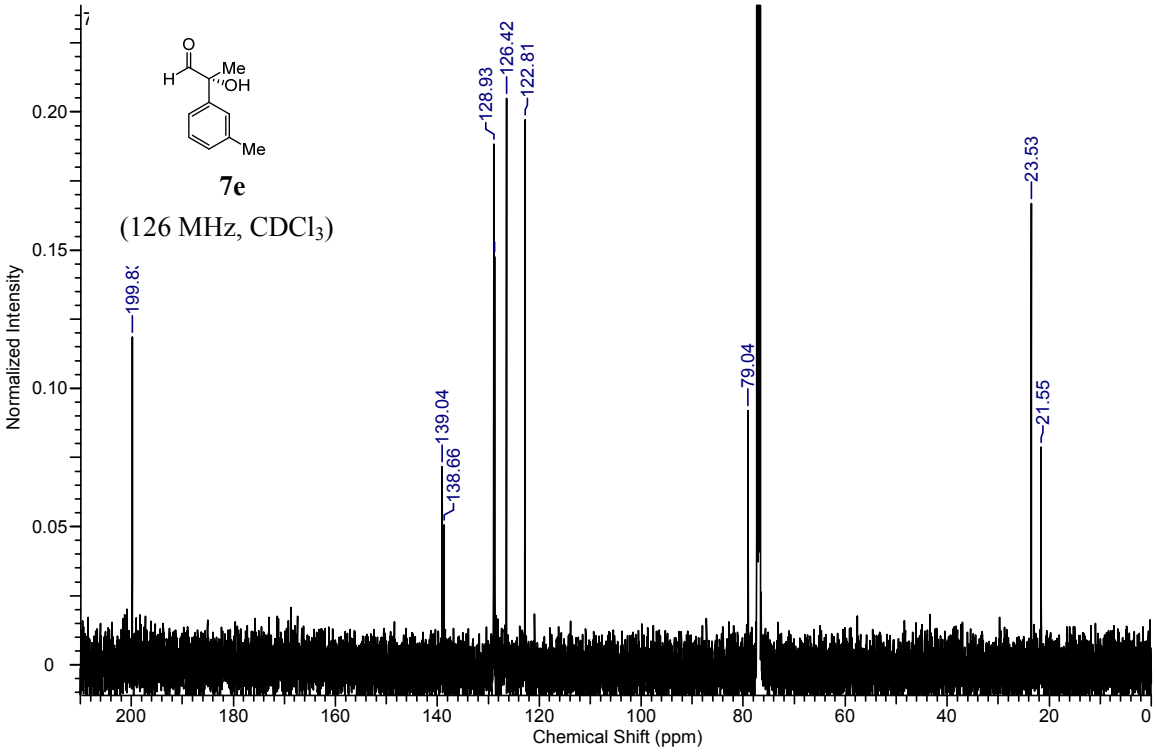

O
H
Me
OH
OMe
7c
(500 MHz, CDCl3)
Normalized Intensity
1.00
2.05
1.98
3.04
1.04
2.99
Chemical Shift (ppm)

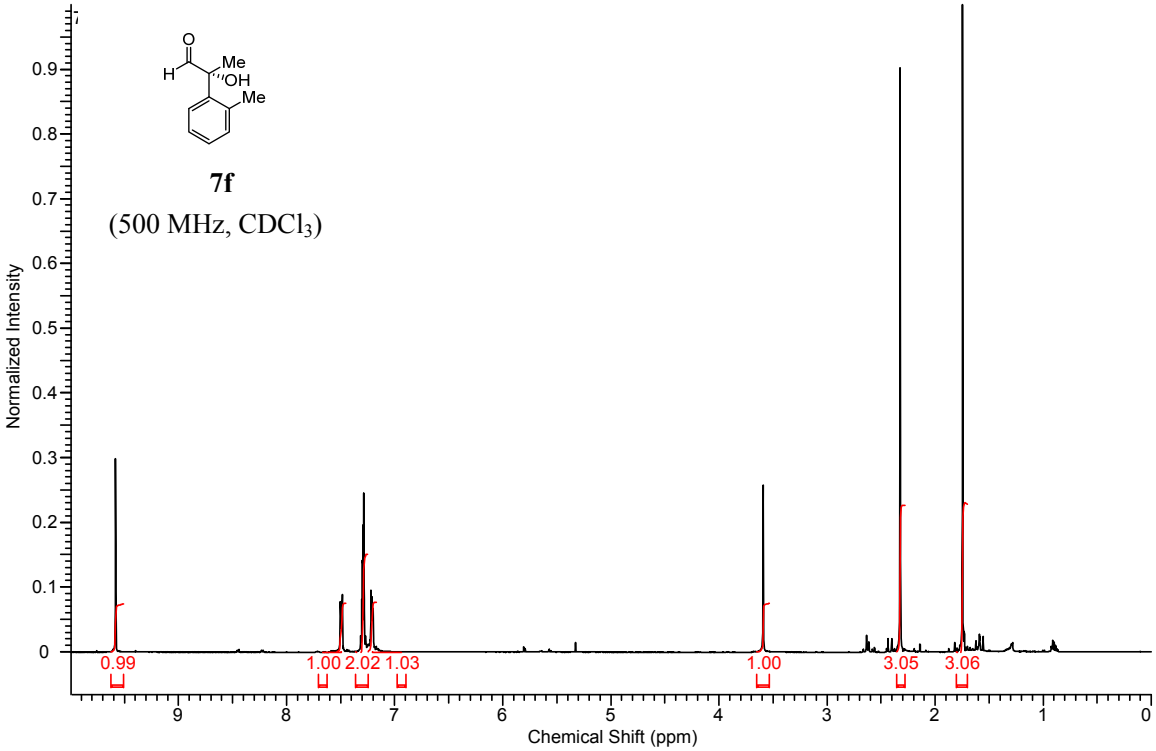

O
H
Me
OH
OMe
7c
(126 MHz, CDCl3)
Normalized Intensity
199.63
159.52
130.99
127.15
114.27
78.67
55.30
23.27
Chemical Shift (ppm)

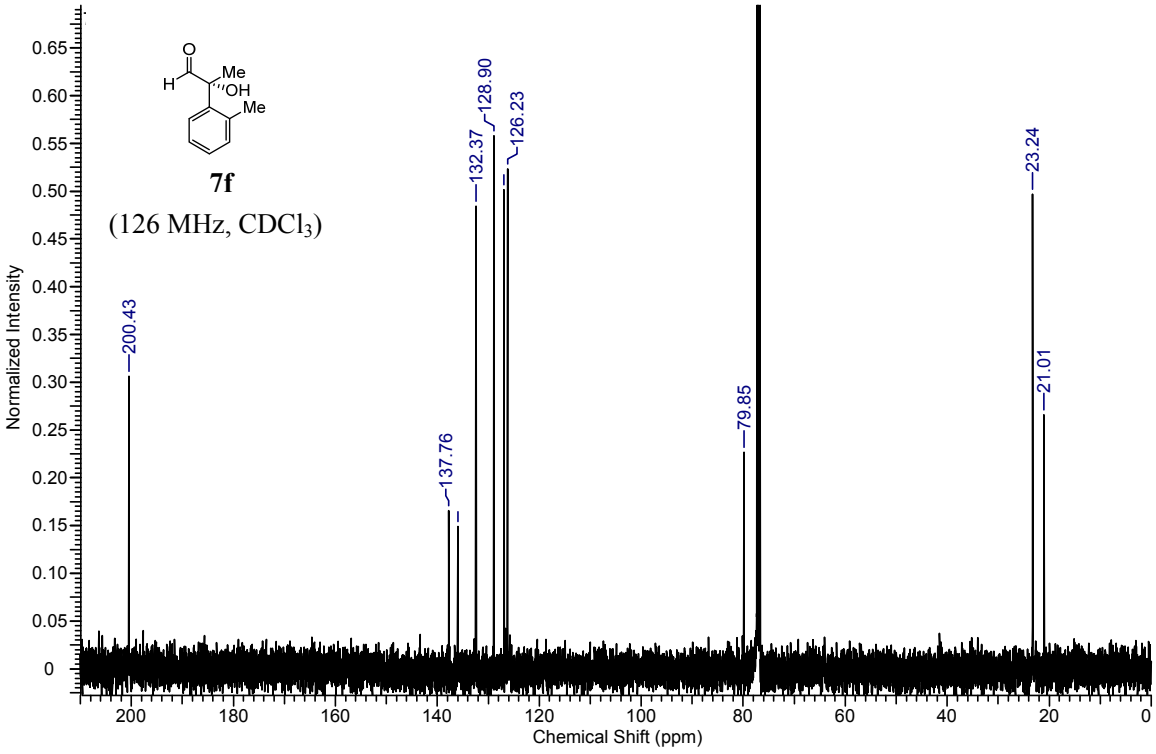

7d
(400 MHz, CDCl3)
Normalized Intensity
Chemical Shift (ppm)
1.00
2.00
2.02
1.01
3.01
2.99

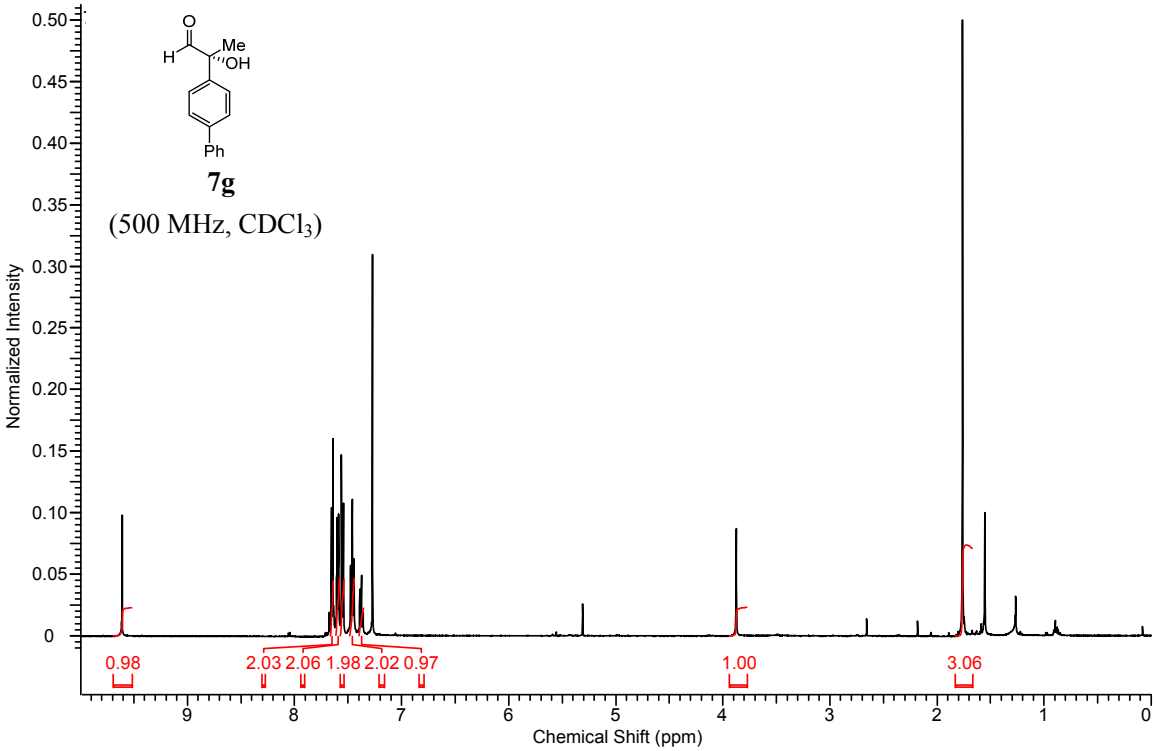

7d
(100 MHz, CDCl3)
Normalized Intensity
Chemical Shift (ppm)
199.80
138.03
136.10
129.56
125.71
78.92
23.43
21.02

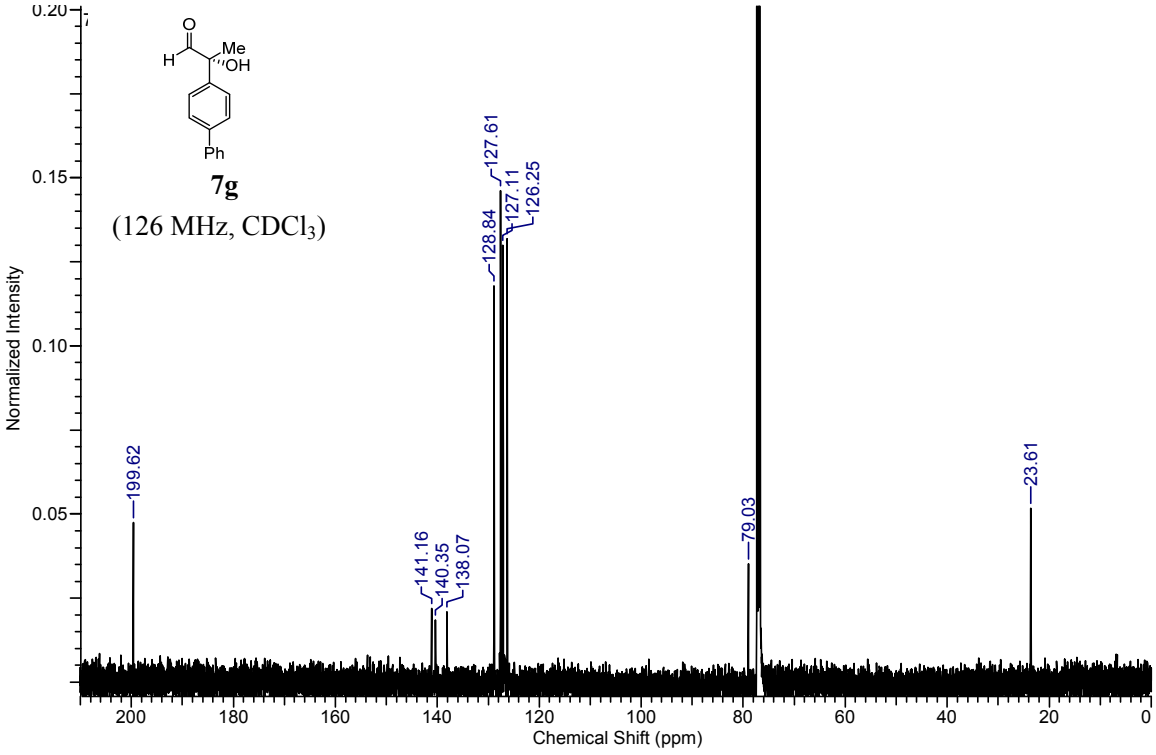

O
H
Me
OH
Me
7e
(500 MHz, CDCl3)
Normalized Intensity
1.01
4.34
1.05
1.00
3.04
3.11
Chemical Shift (ppm)

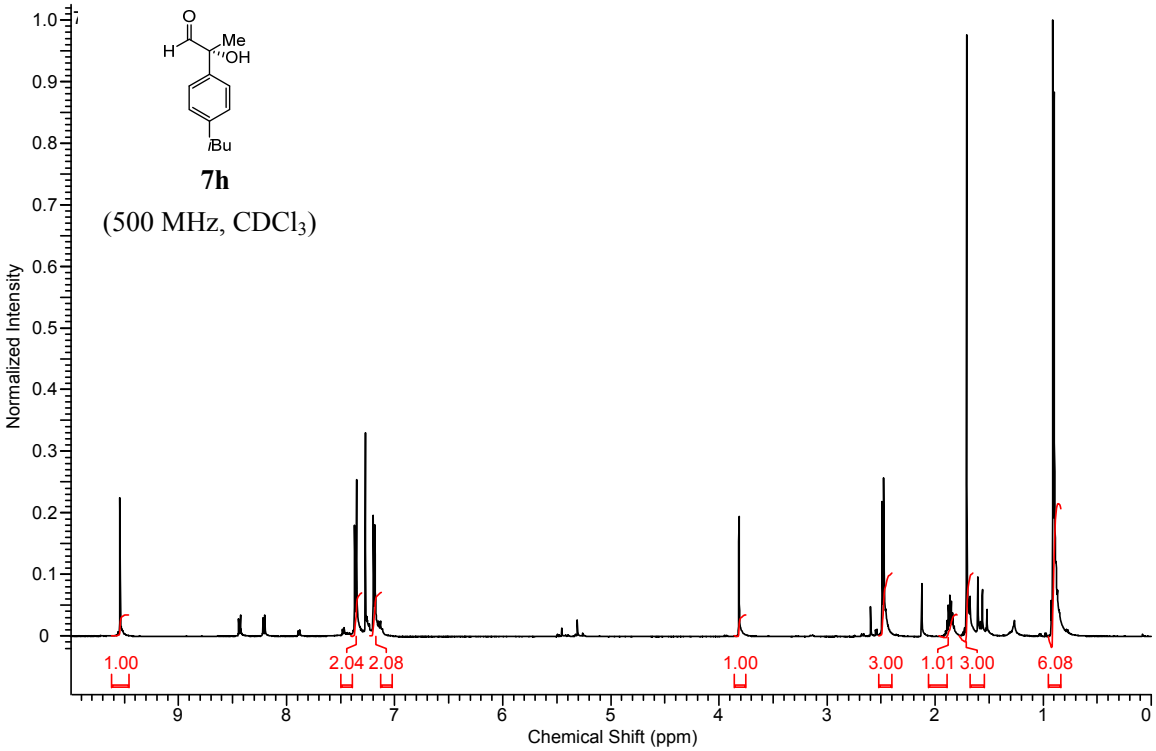

O
H
Me
OH
Me
7e
(126 MHz, CDCl3)
Normalized Intensity
199.8
139.04
138.66
128.93
126.42
122.81
79.04
23.53
21.55
Chemical Shift (ppm)

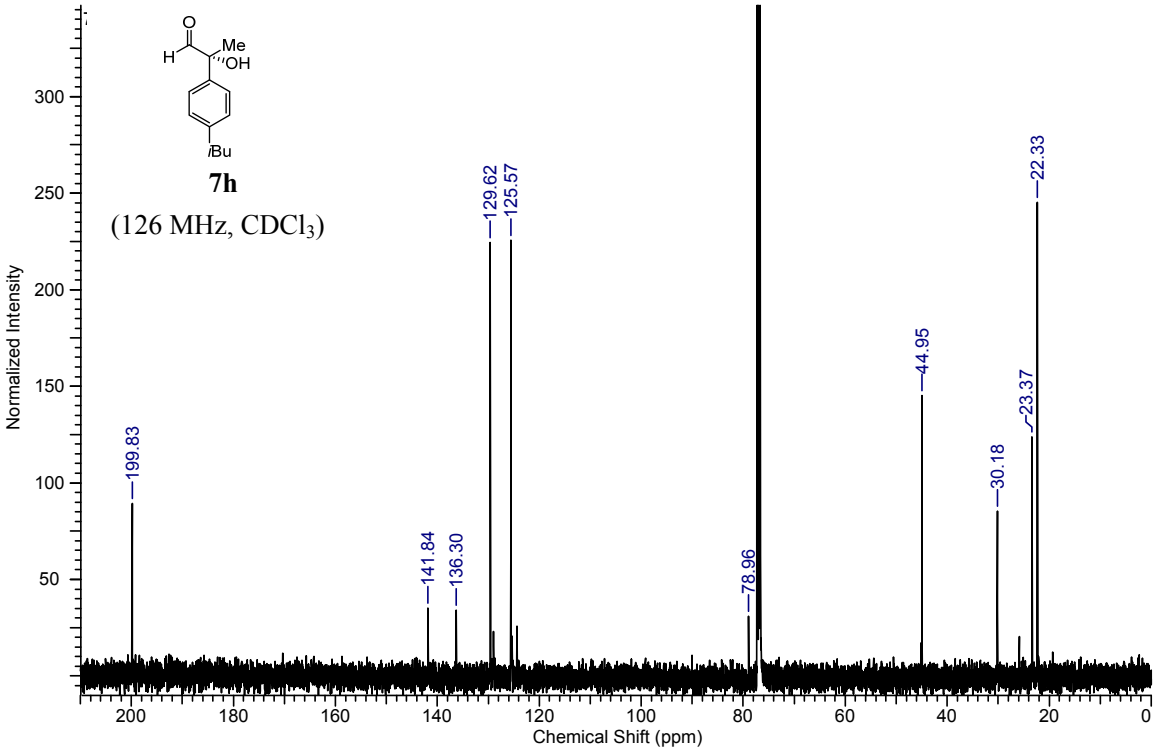

O
H
Me
OH
Me
7f
(500 MHz, CDCl3)
Normalized Intensity
0.99
1.00
2.02
1.03
1.00
3.05
3.06
Chemical Shift (ppm)

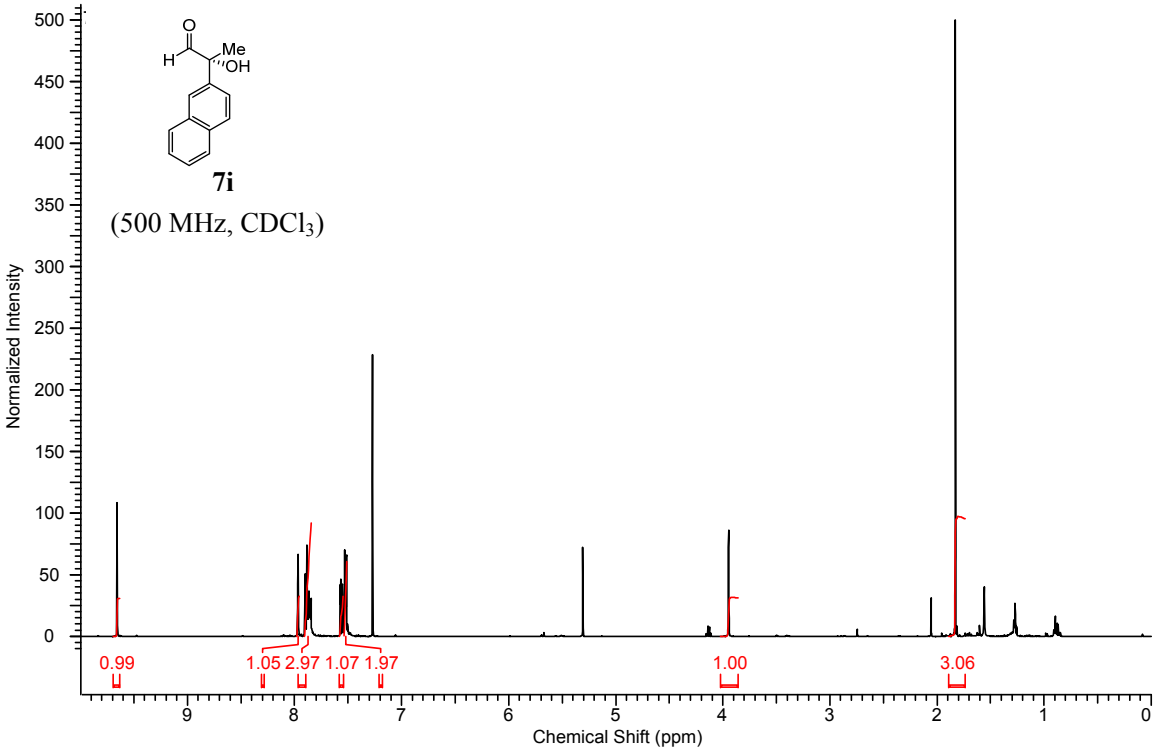

O
H
Me
OH
Me
7f
(126 MHz, CDCl3)
Normalized Intensity
200.43
137.76
132.37
128.90
126.23
79.85
23.24
21.01
Chemical Shift (ppm)

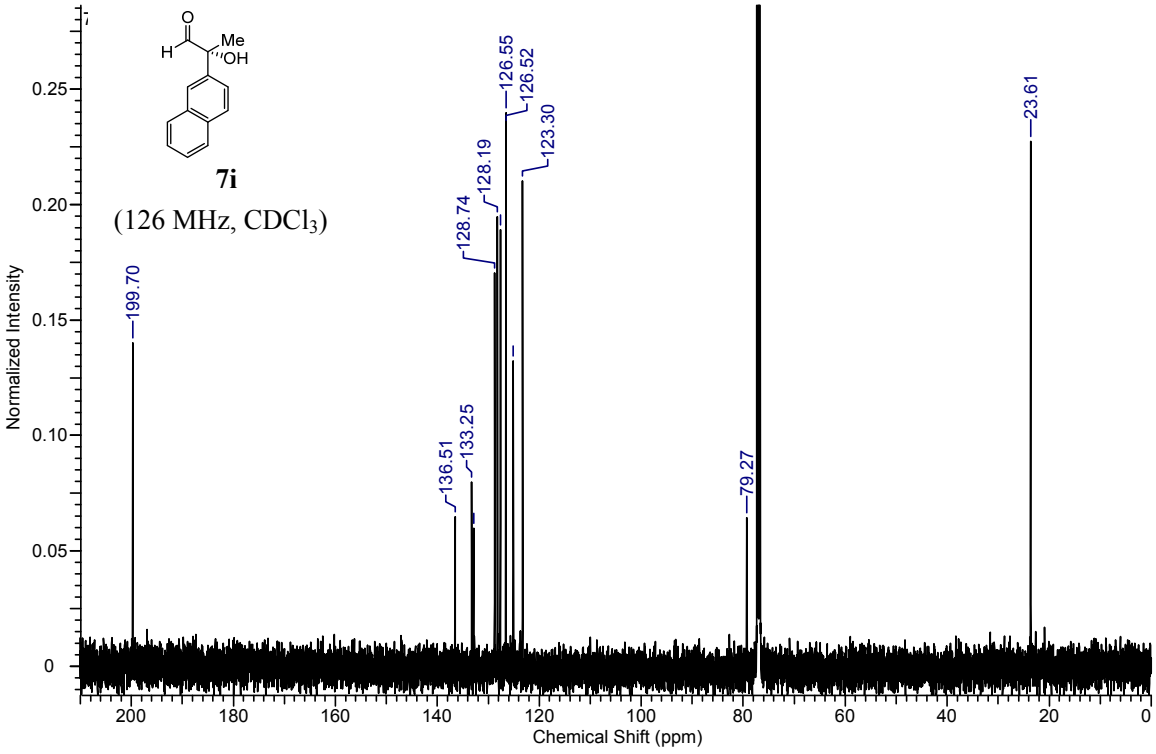

O
H
Me
OH
Ph
7g
(500 MHz, CDCl3)
Normalized Intensity
0.98
2.03 2.06 1.98 2.02 0.97
1.00
3.06
Chemical Shift (ppm)

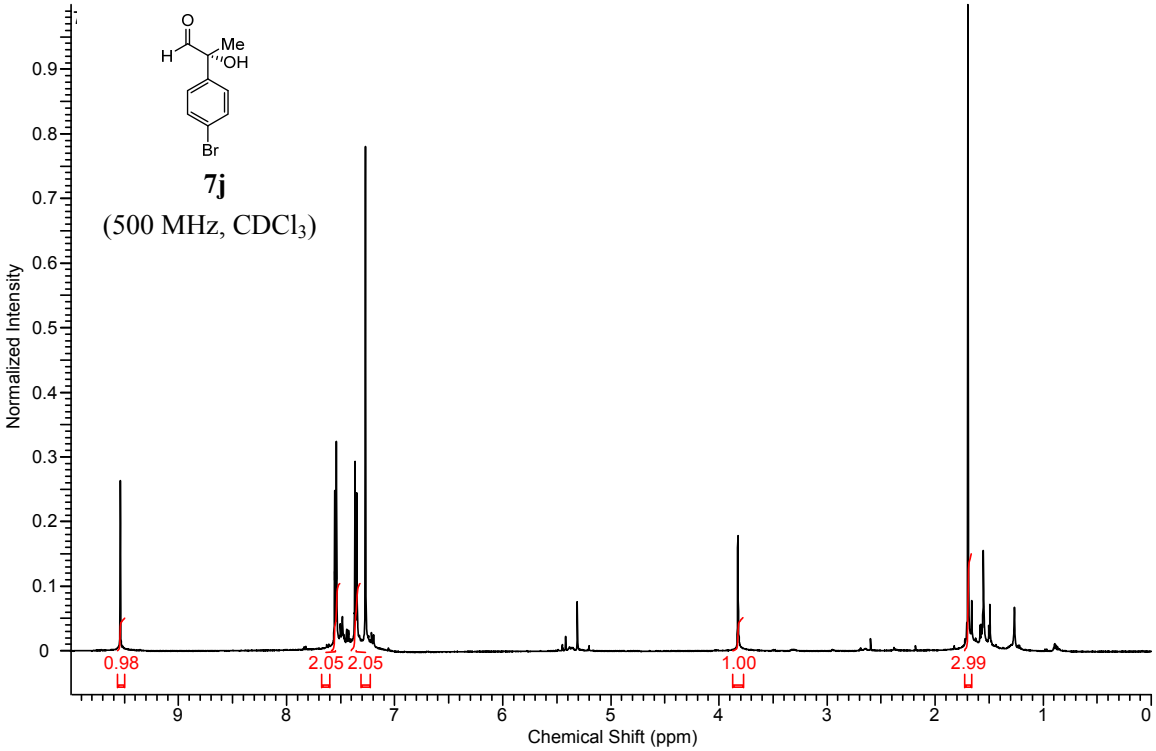

O
H
Me
OH
Ph
7g
(126 MHz, CDCl3)
Normalized Intensity
199.62
141.16
140.35
138.07
128.84
127.61
127.11
126.25
79.03
23.61
Chemical Shift (ppm)

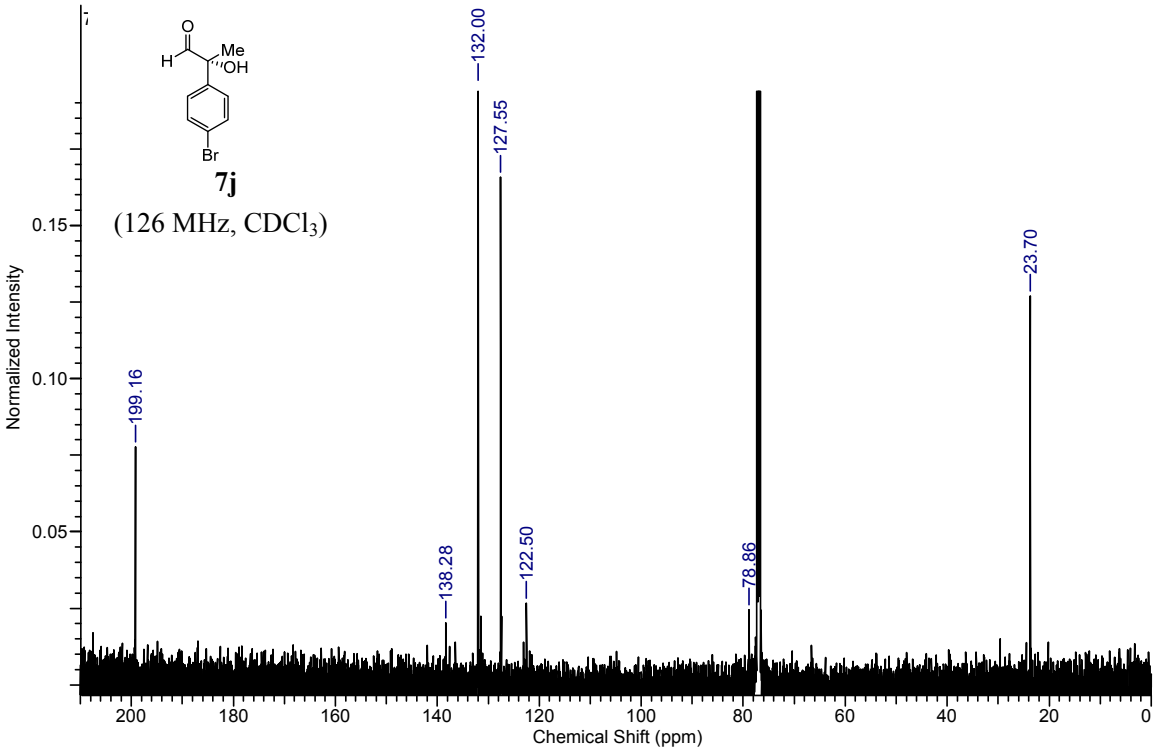

7h
(500 MHz, CDCl3)
Normalized Intensity
Chemical Shift (ppm)
1.00
2.04
2.08
1.00
3.00
1.01
3.00
6.08

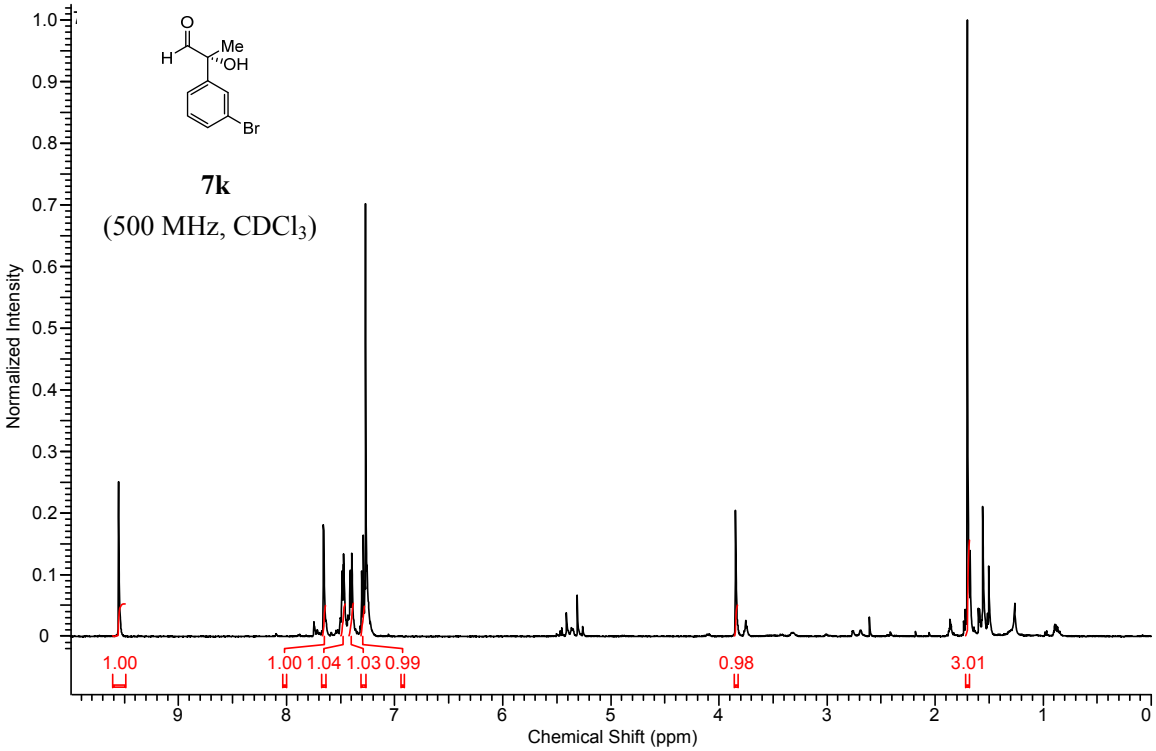

7h
(126 MHz, CDCl3)
Normalized Intensity
Chemical Shift (ppm)
199.83
141.84
136.30
129.62
125.57
78.96
44.95
30.18
23.37
22.33

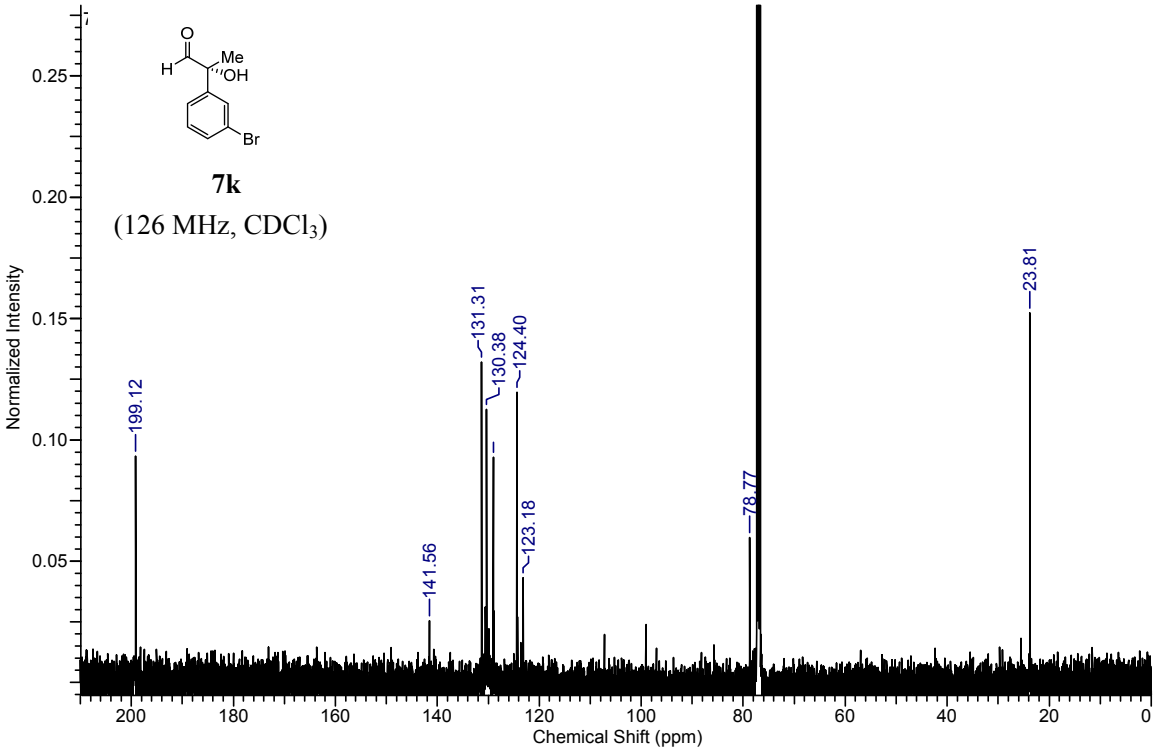

7i
(500 MHz, CDCl3)
Normalized Intensity
0.99
1.05
2.97
1.07
1.97
1.00
3.06
Chemical Shift (ppm)

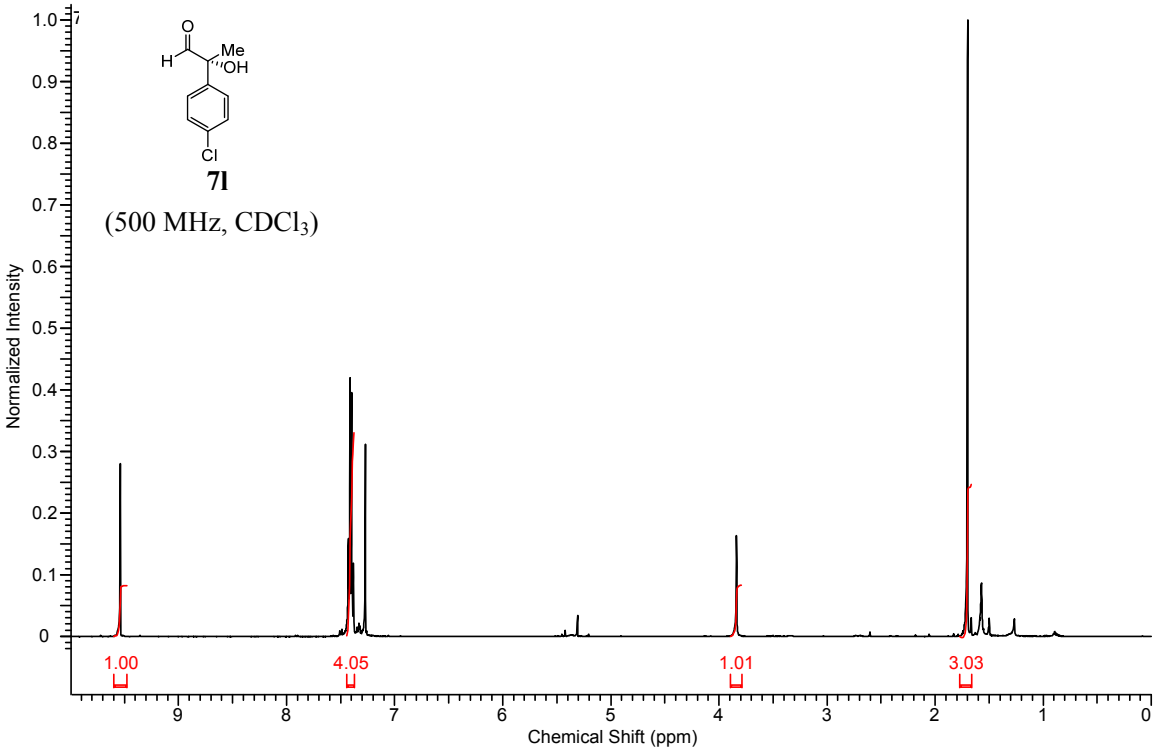

7i
(126 MHz, CDCl3)
Normalized Intensity
199.70
136.51
133.25
128.74
128.19
126.55
126.52
123.30
79.27
23.61
Chemical Shift (ppm)

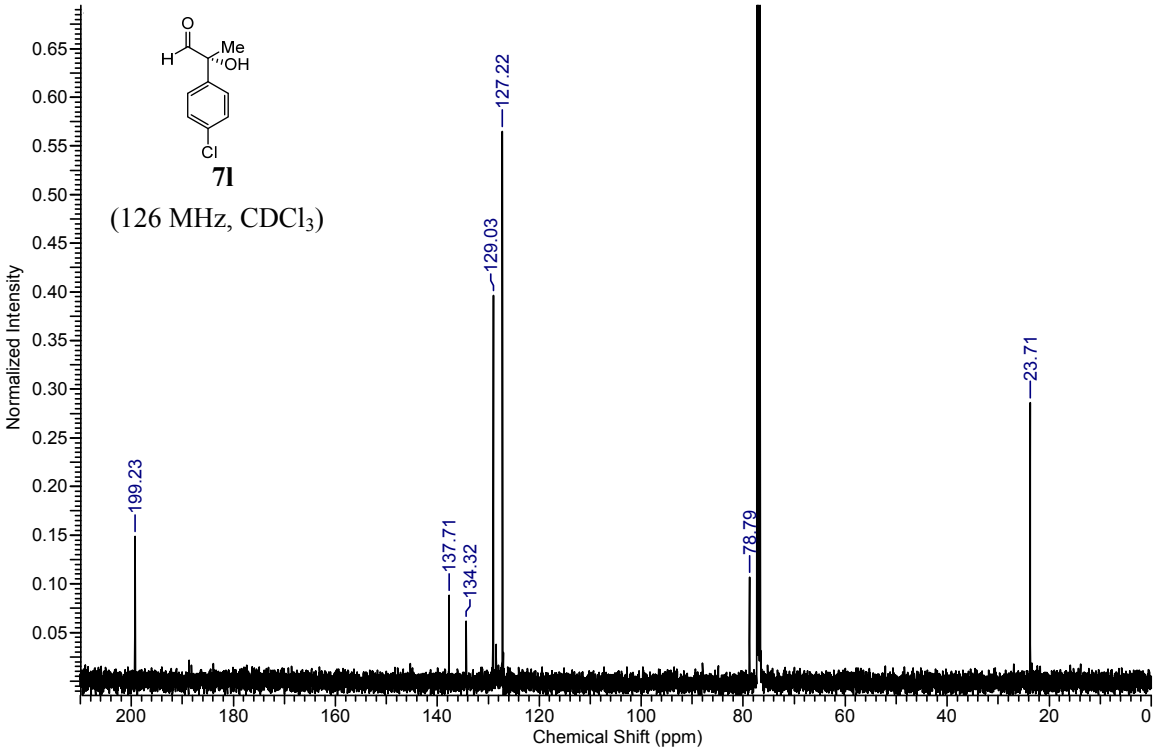

O
H
Me
OH
Br
7j
(500 MHz, CDCl3)
Normalized Intensity
0.98
2.05
2.05
1.00
2.99
Chemical Shift (ppm)

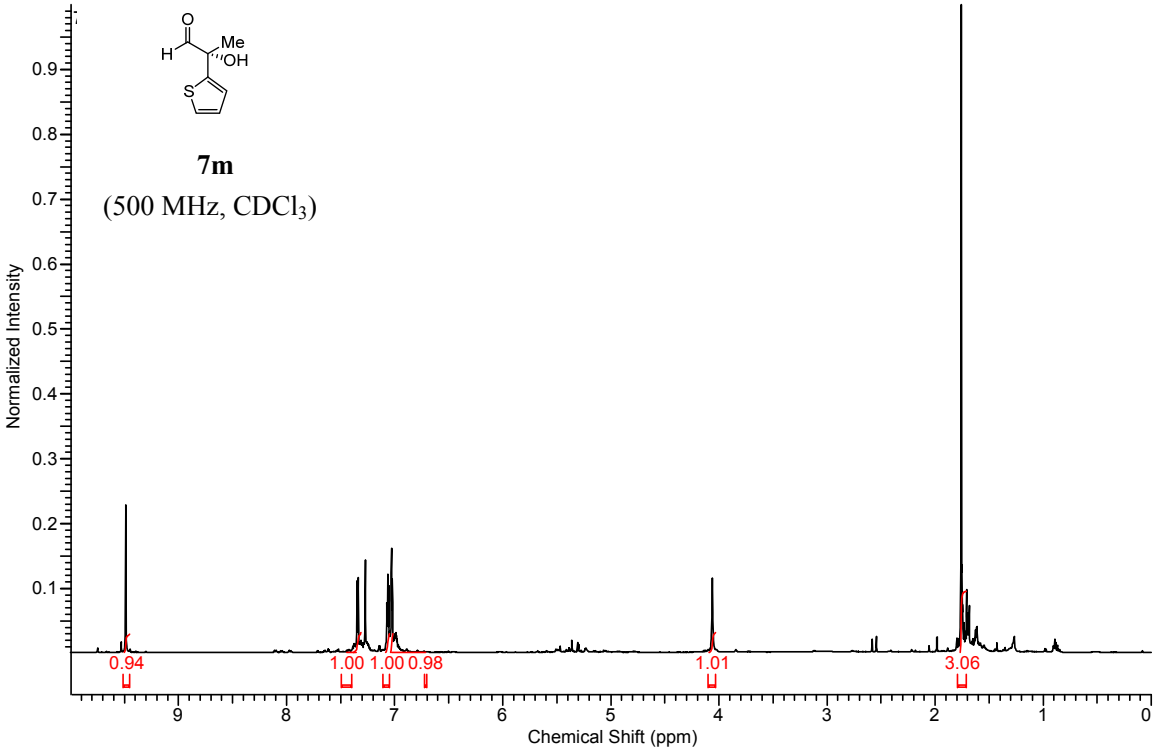

O
H
Me
OH
Br
7j
(126 MHz, CDCl3)
Normalized Intensity
199.16
138.28
132.00
127.55
122.50
78.86
23.70
Chemical Shift (ppm)

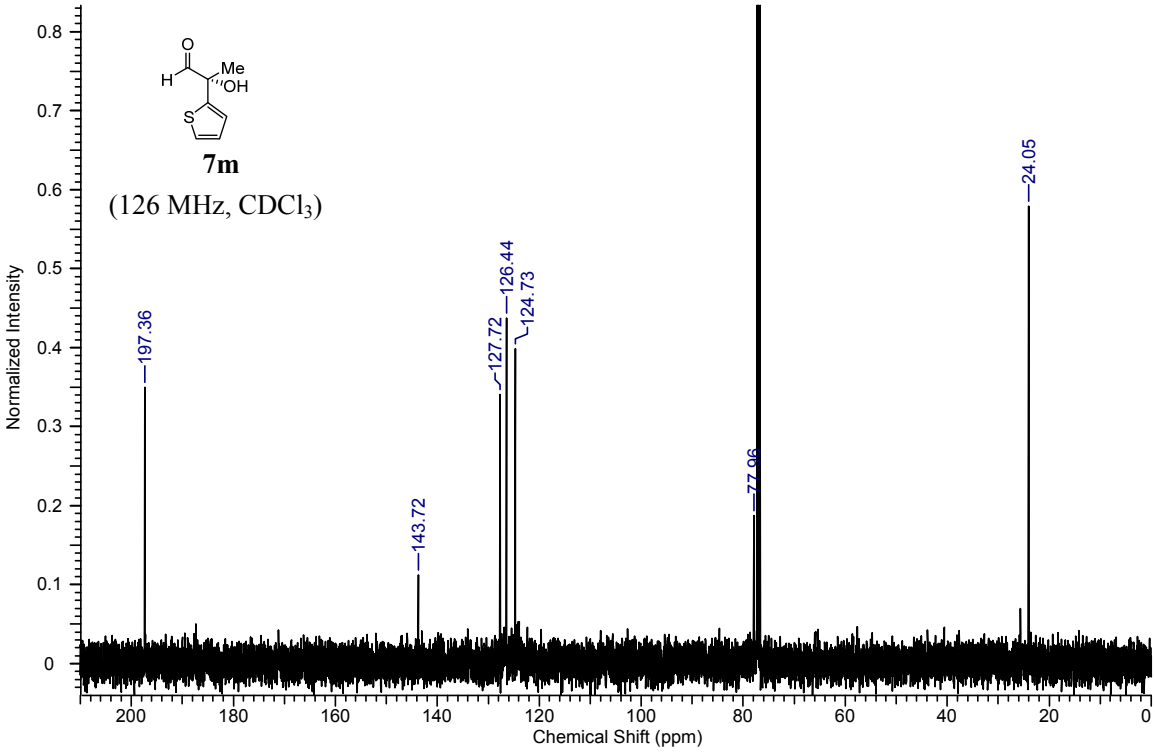

O
H
Me
OH
Br
7k
(500 MHz, CDCl3)
Normalized Intensity
1.00
1.00 1.04 1.03 0.99
0.98
3.01
Chemical Shift (ppm)

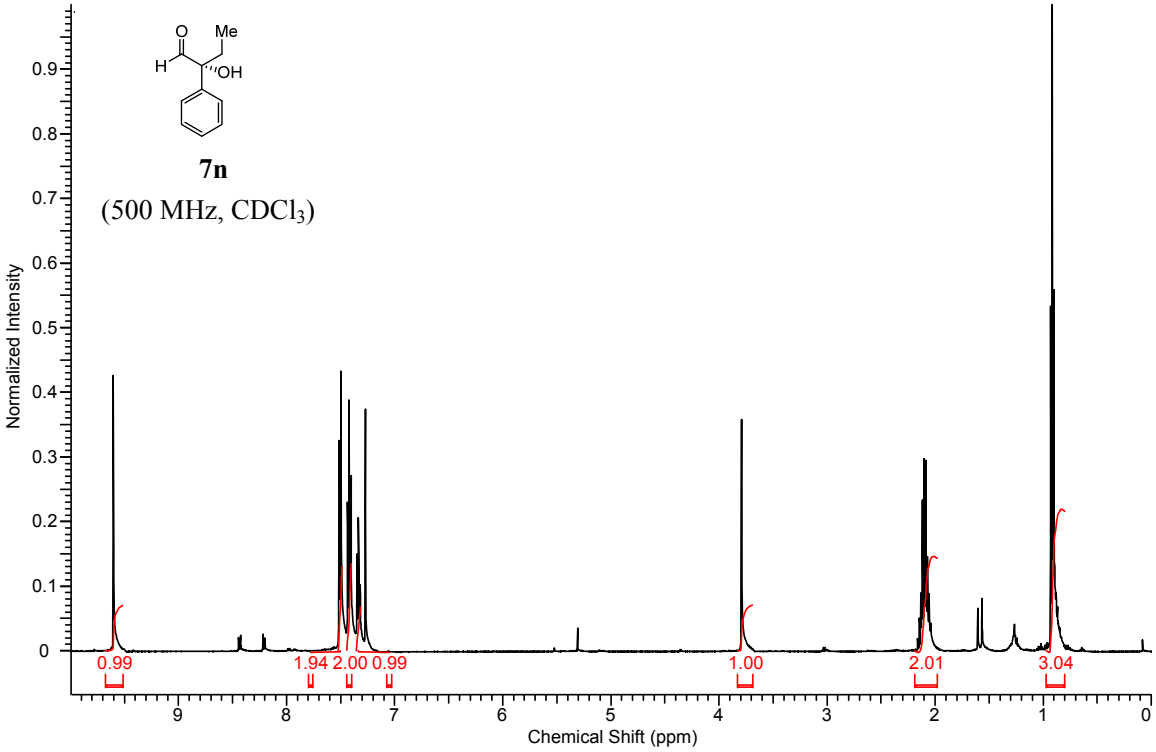

O
H
Me
OH
Br
7k
(126 MHz, CDCl3)
Normalized Intensity
199.12
141.56
131.31
130.38
124.40
123.18
78.77
23.81
Chemical Shift (ppm)

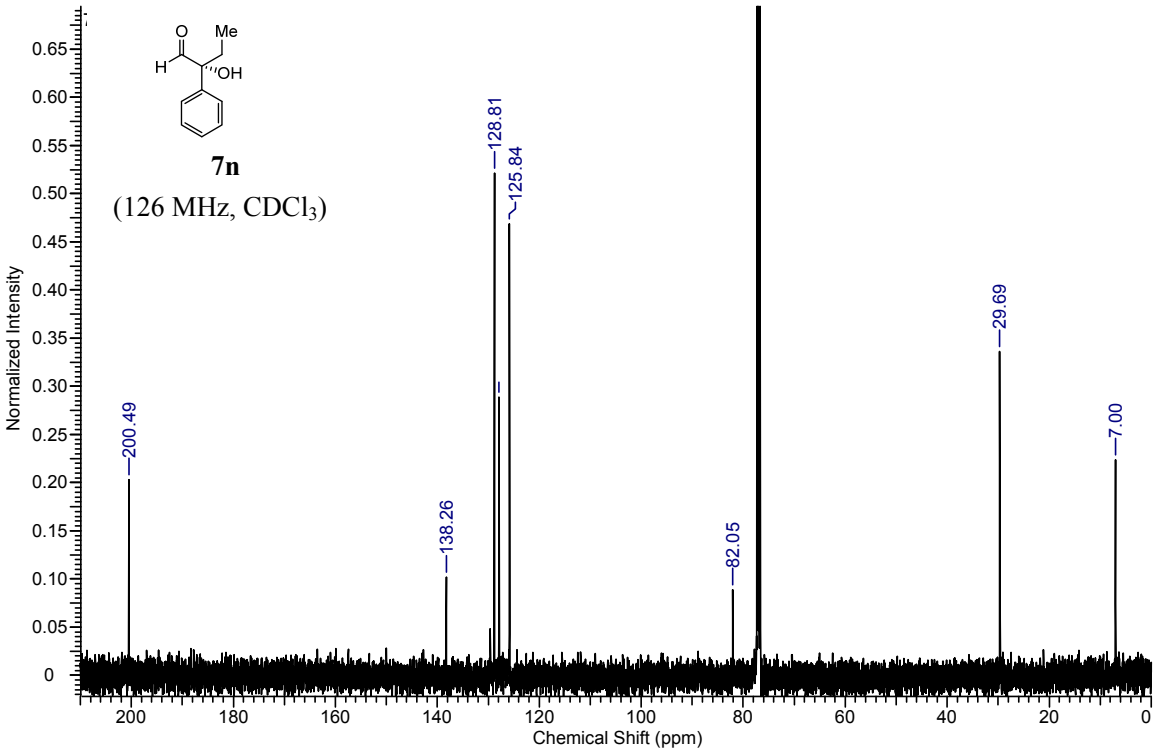

7l
(500 MHz, CDCl3)
Normalized Intensity
Chemical Shift (ppm)
1.00
4.05
1.01
3.03

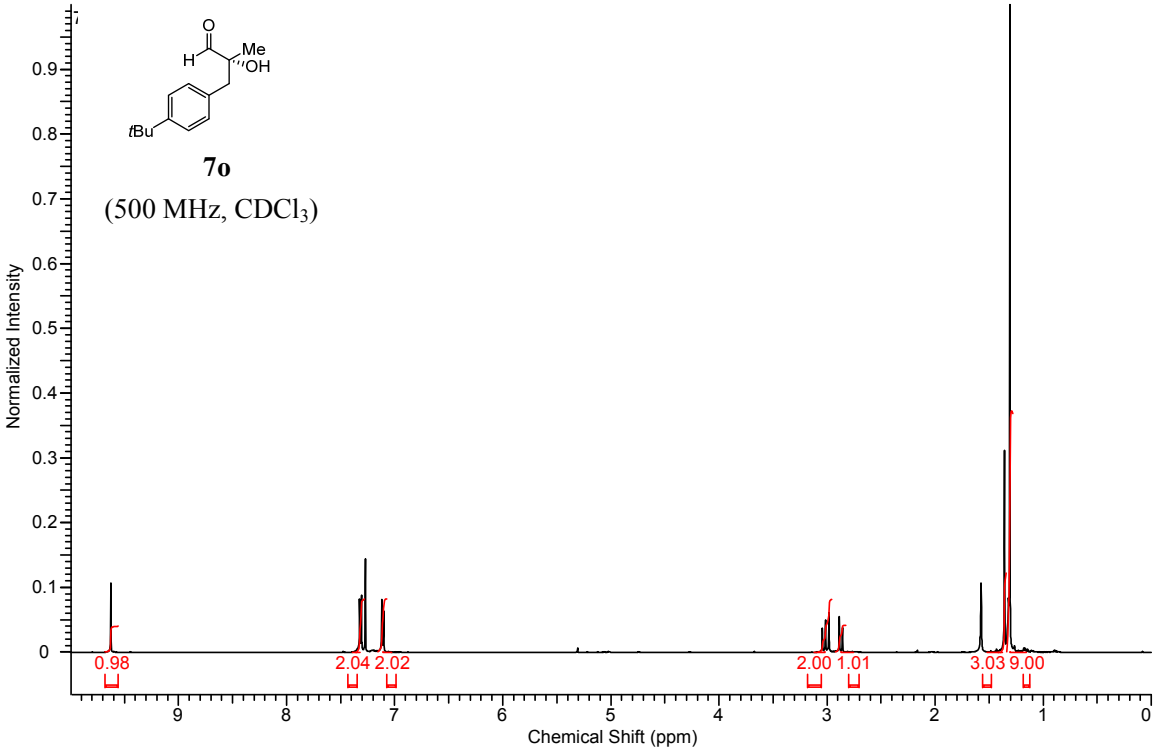

7l
(126 MHz, CDCl3)
Normalized Intensity
Chemical Shift (ppm)
199.23
137.71
134.32
129.03
127.22
78.79
23.71

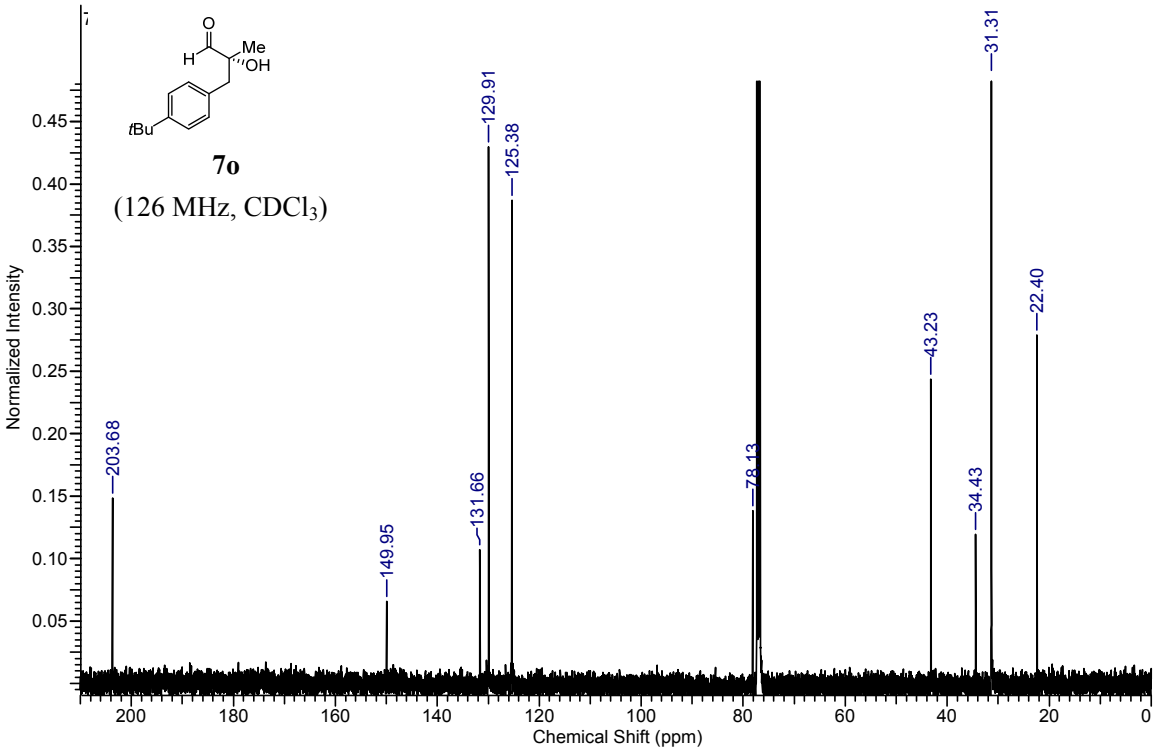

7m
(500 MHz, CDCl3)
Normalized Intensity
Chemical Shift (ppm)
0.94
1.00
1.00
0.98
1.01
3.06

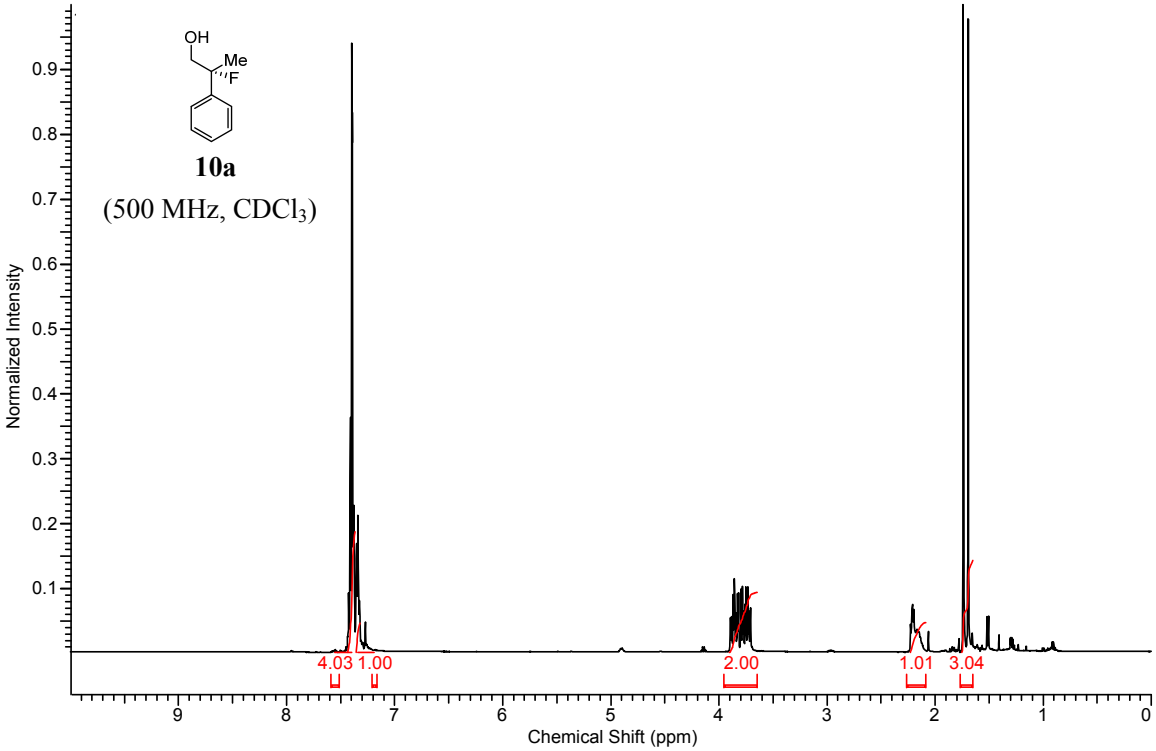

7m
(126 MHz, CDCl3)
Normalized Intensity
Chemical Shift (ppm)
197.36
143.72
127.72
126.44
124.73
77.06
24.05

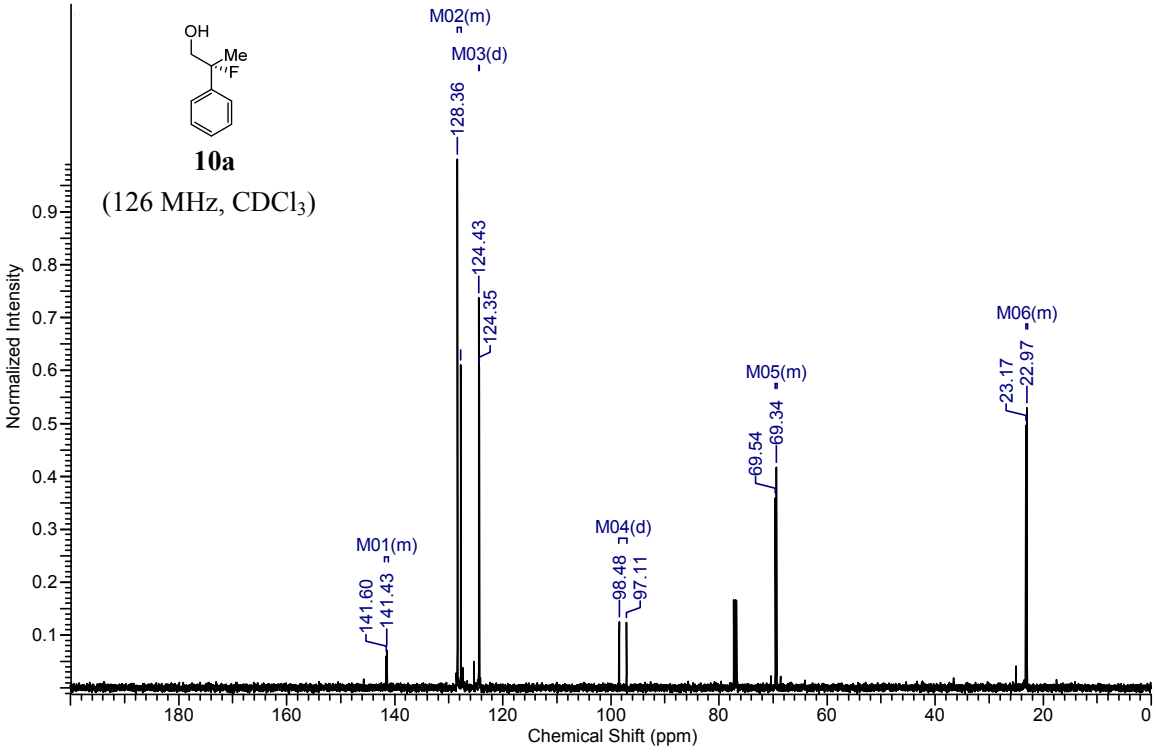

O
Me
H
OH
7n
(500 MHz, CDCl3)
Normalized Intensity
0.99
1.94
2.00
0.99
1.00
2.01
3.04
Chemical Shift (ppm)

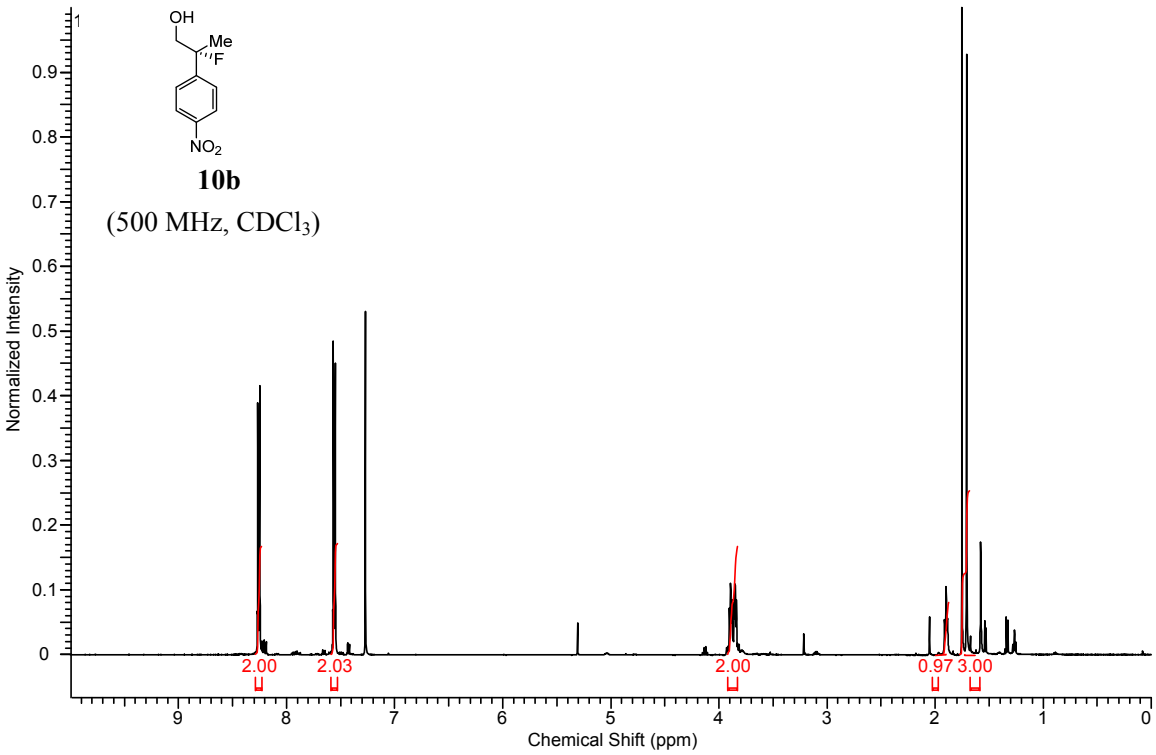

O
Me
H
OH
7n
(126 MHz, CDCl3)
Normalized Intensity
200.49
138.26
128.81
125.84
82.05
29.69
7.00
Chemical Shift (ppm)

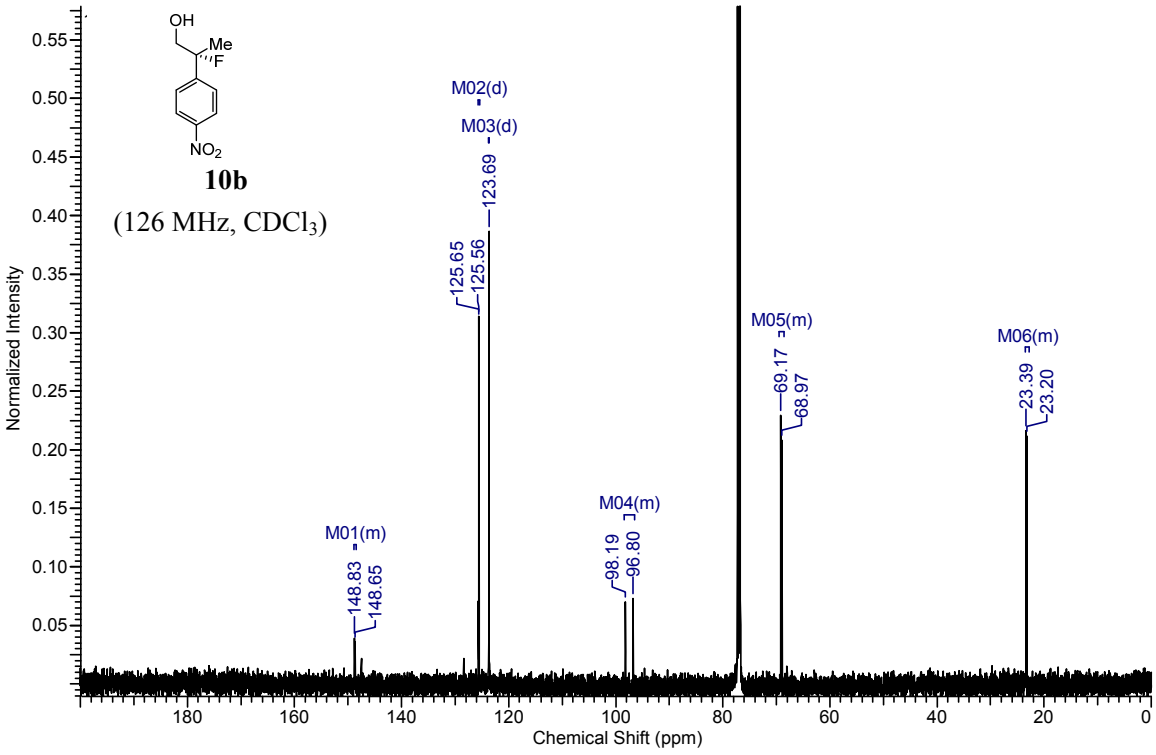

O
H
Me
OH
tBu
7o
(500 MHz, CDCl3)
Normalized Intensity
0.98
2.04
2.02
2.00
1.01
3.03
9.00
Chemical Shift (ppm)

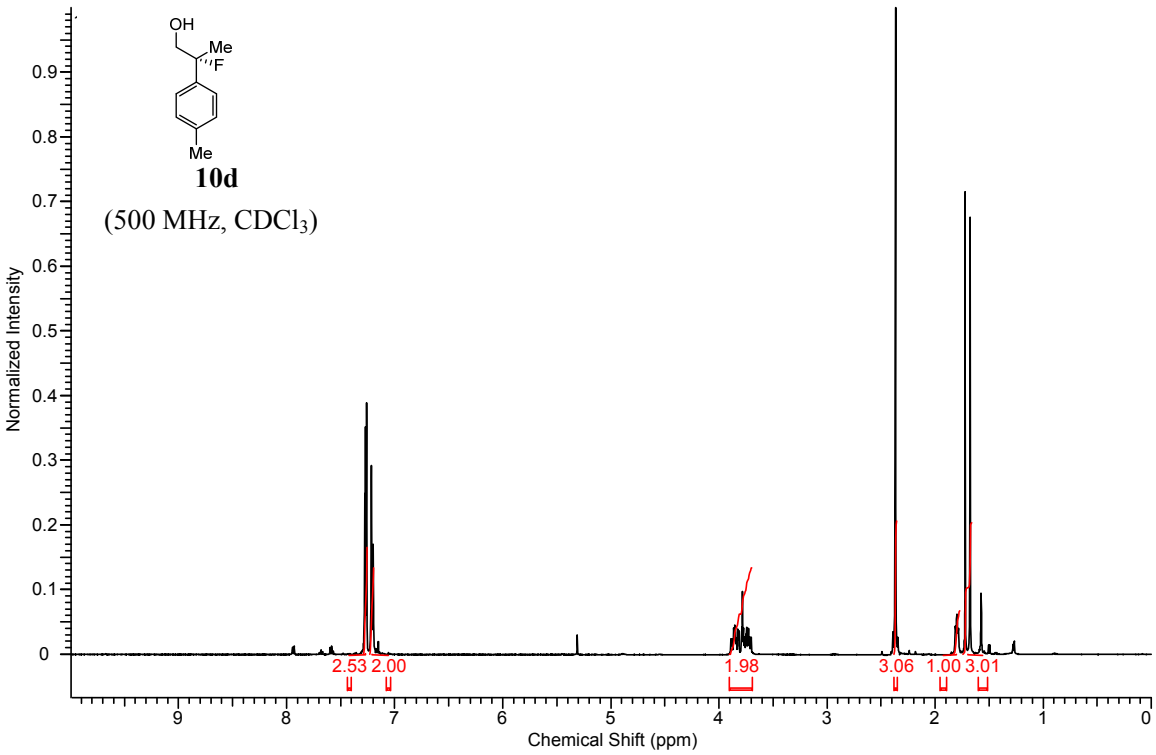

O
H
Me
OH
tBu
7o
(126 MHz, CDCl3)
Normalized Intensity
203.68
149.95
131.66
129.91
125.38
78.13
43.23
34.43
31.31
22.40
Chemical Shift (ppm)

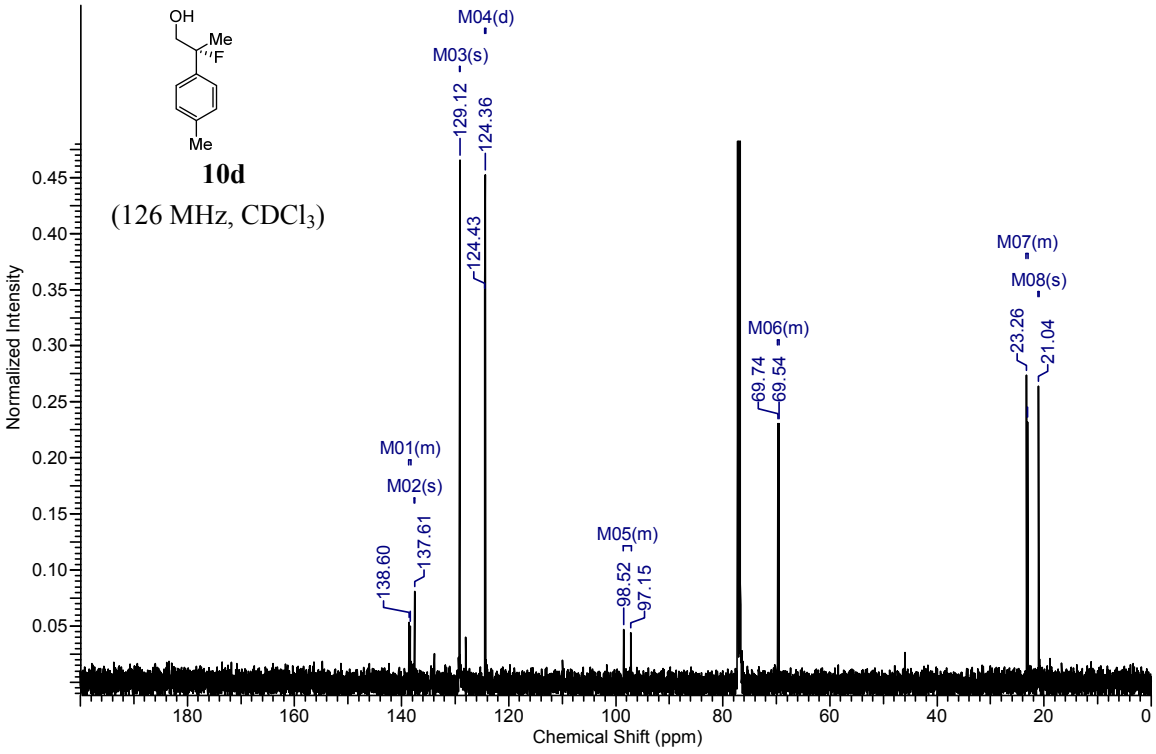

OH
Me
F
10a
(500 MHz, CDCl3)
Normalized Intensity
4.03
1.00
2.00
1.01
3.04
Chemical Shift (ppm)

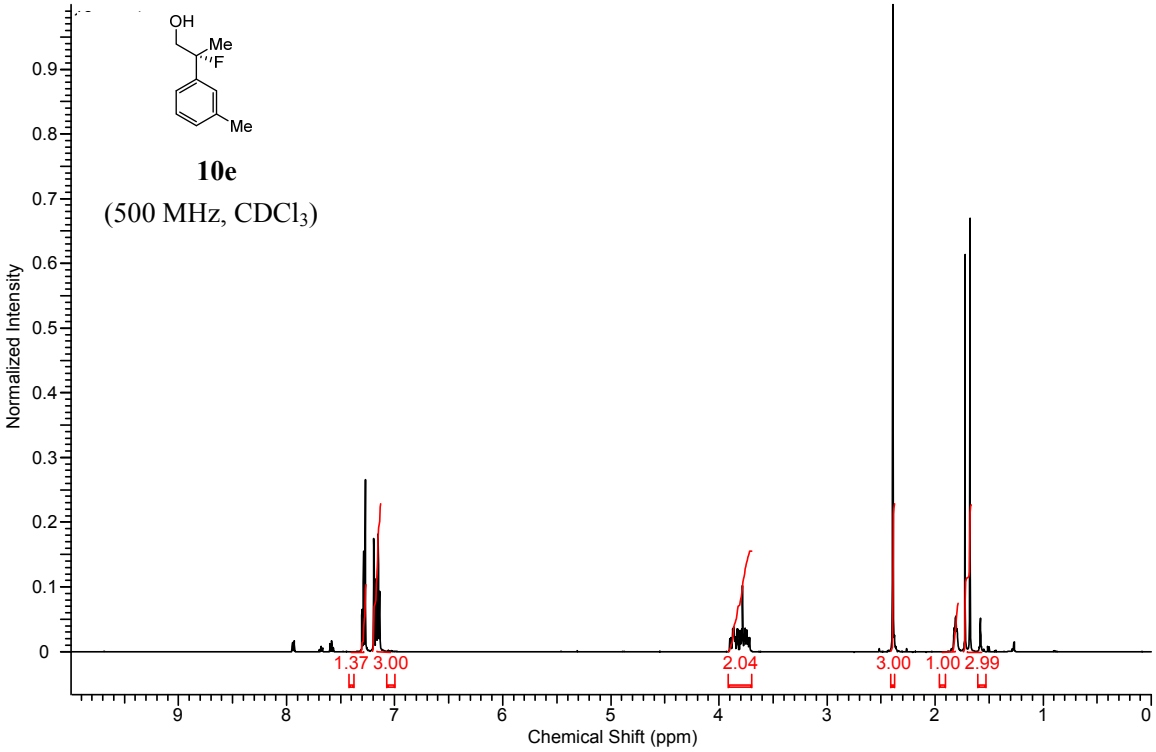

OH
Me
F
10a
(126 MHz, CDCl3)
Normalized Intensity
M01(m)
141.60
141.43
M02(m)
M03(d)
128.36
124.43
124.35
M04(d)
98.48
97.11
M05(m)
69.54
69.34
M06(m)
23.17
22.97
Chemical Shift (ppm)

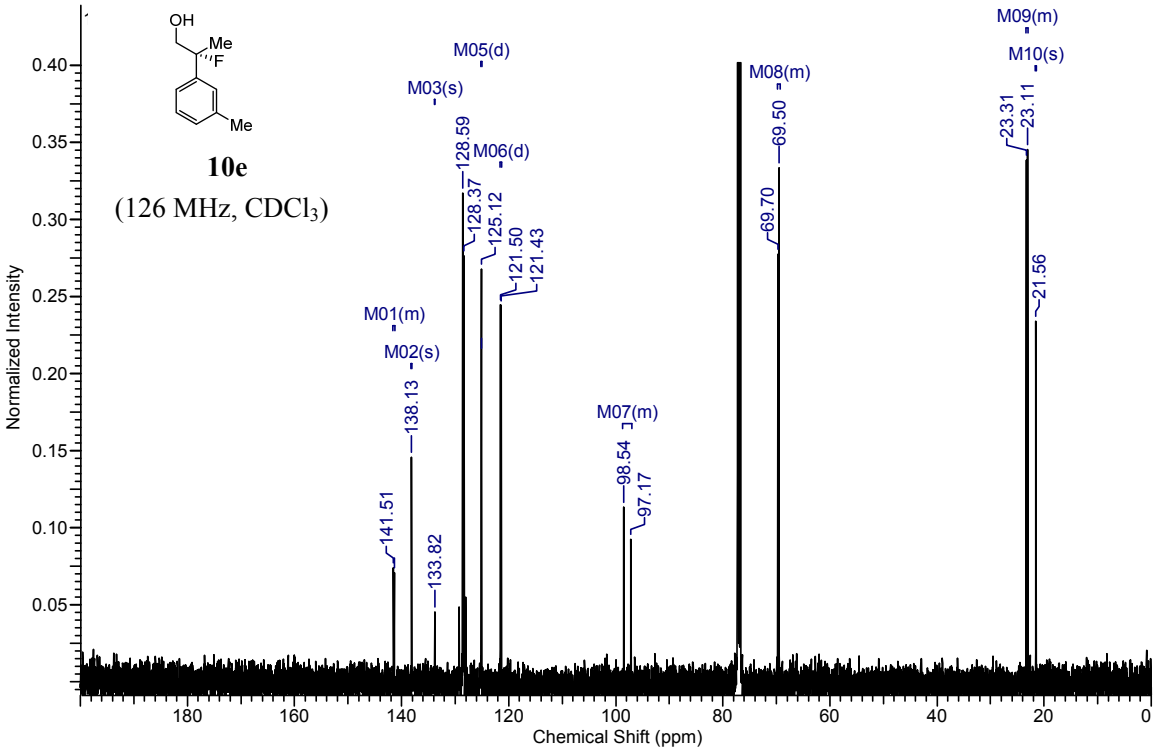

OH
Me
F
NO2
10b
(500 MHz, CDCl3)
Normalized Intensity
2.00
2.03
2.00
0.97
3.00
Chemical Shift (ppm)

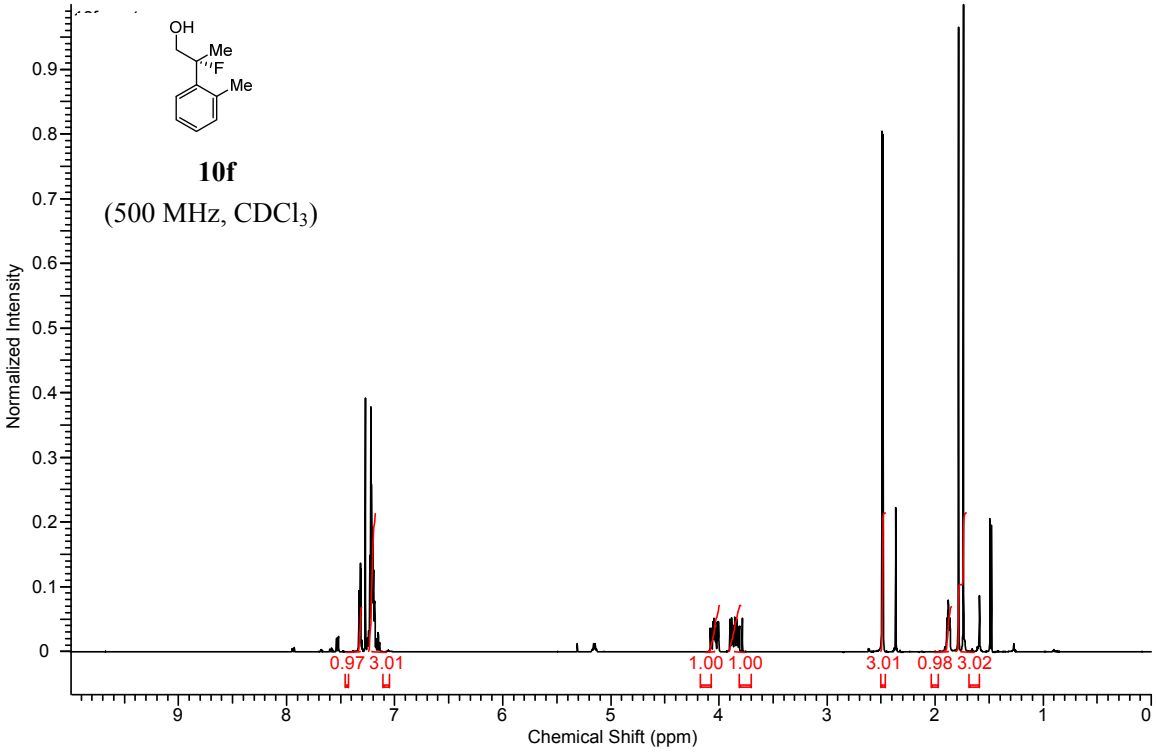

OH
Me
F
NO2
10b
(126 MHz, CDCl3)
Normalized Intensity
M01(m)
148.83
148.65
M02(d)
M03(d)
125.65
125.56
123.69
M04(m)
98.19
96.80
M05(m)
69.17
68.97
M06(m)
23.39
23.20
Chemical Shift (ppm)

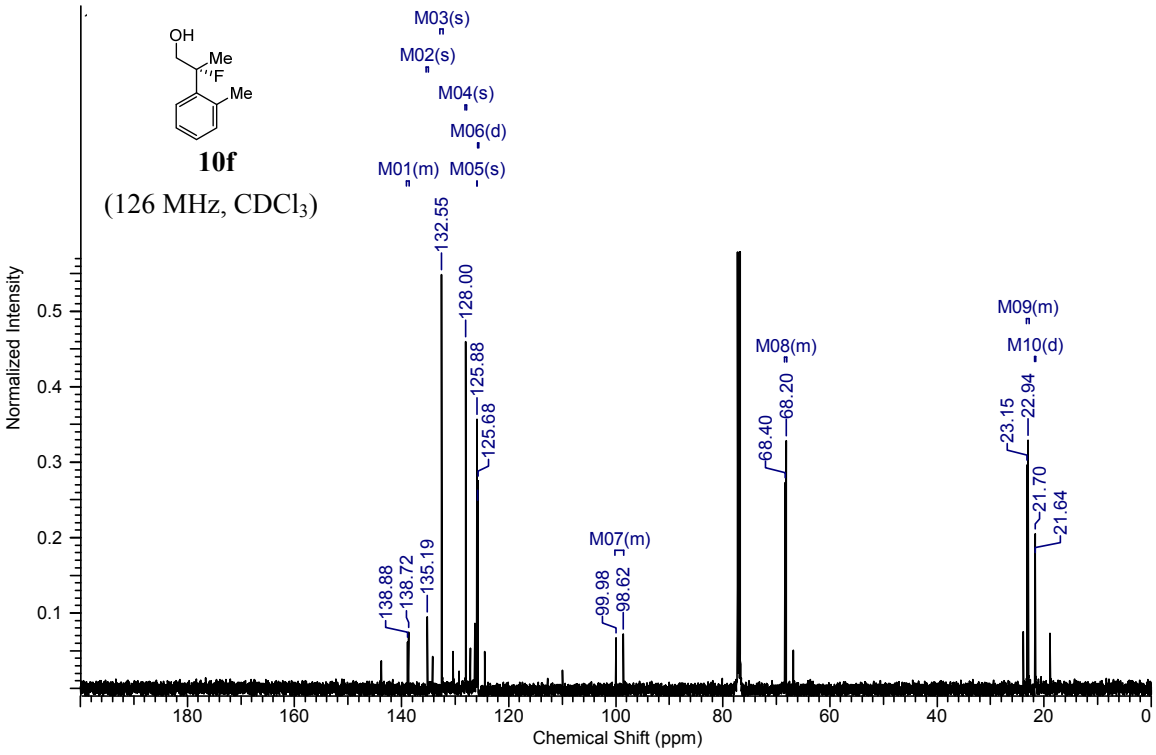

OH
Me
F
Me
10d
(500 MHz, CDCl3)
Normalized Intensity
2.53 2.00
1.98
3.06 1.00 3.01
Chemical Shift (ppm)

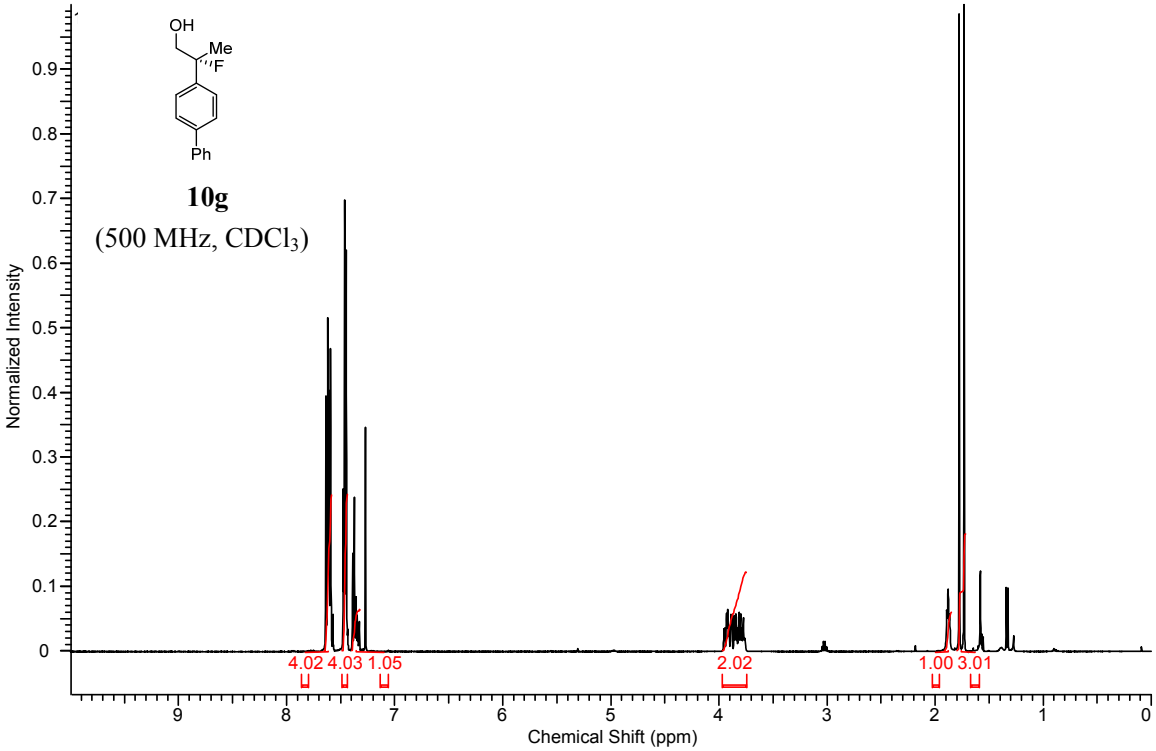

OH
Me
F
Me
10d
(126 MHz, CDCl3)
Normalized Intensity
M04(d)
M03(s)
129.12
124.36
124.43
M07(m)
M08(s)
M06(m)
23.26
21.04
69.74
69.54
M01(m)
M02(s)
138.60
137.61
M05(m)
98.52
97.15
Chemical Shift (ppm)

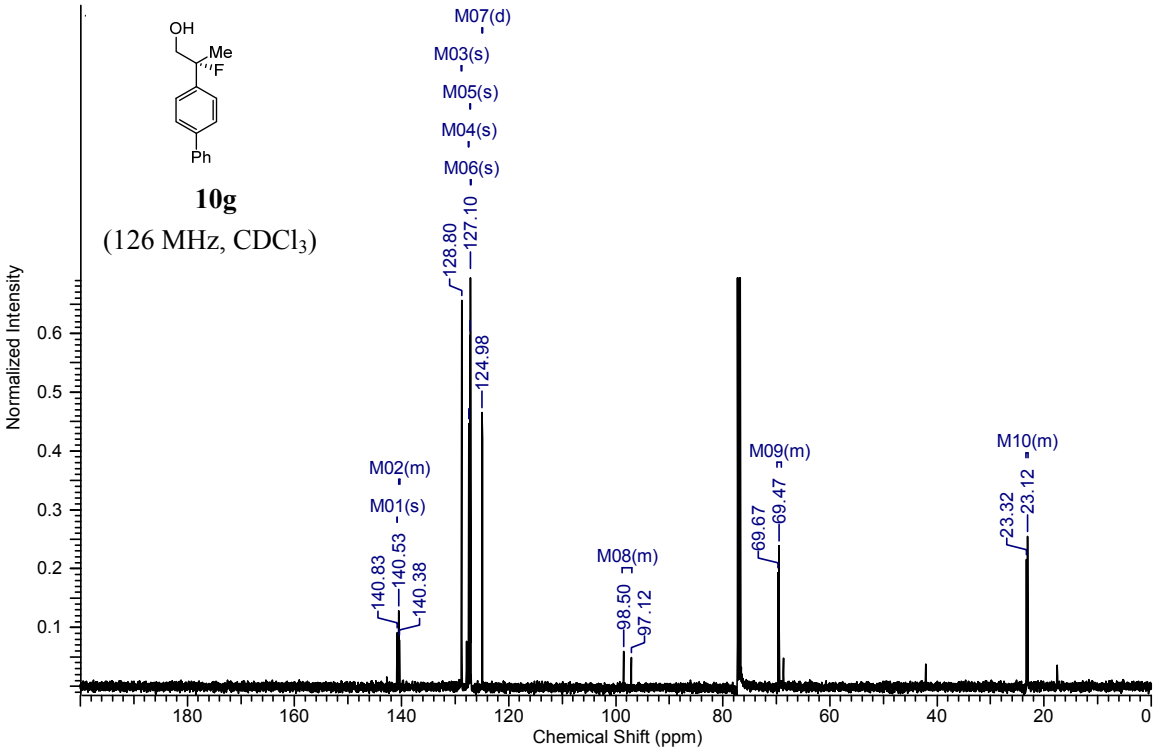

OH
Me
F
Me
10e
(500 MHz, CDCl3)
Normalized Intensity
1.37 3.00
2.04
3.00 1.00 2.99
Chemical Shift (ppm)

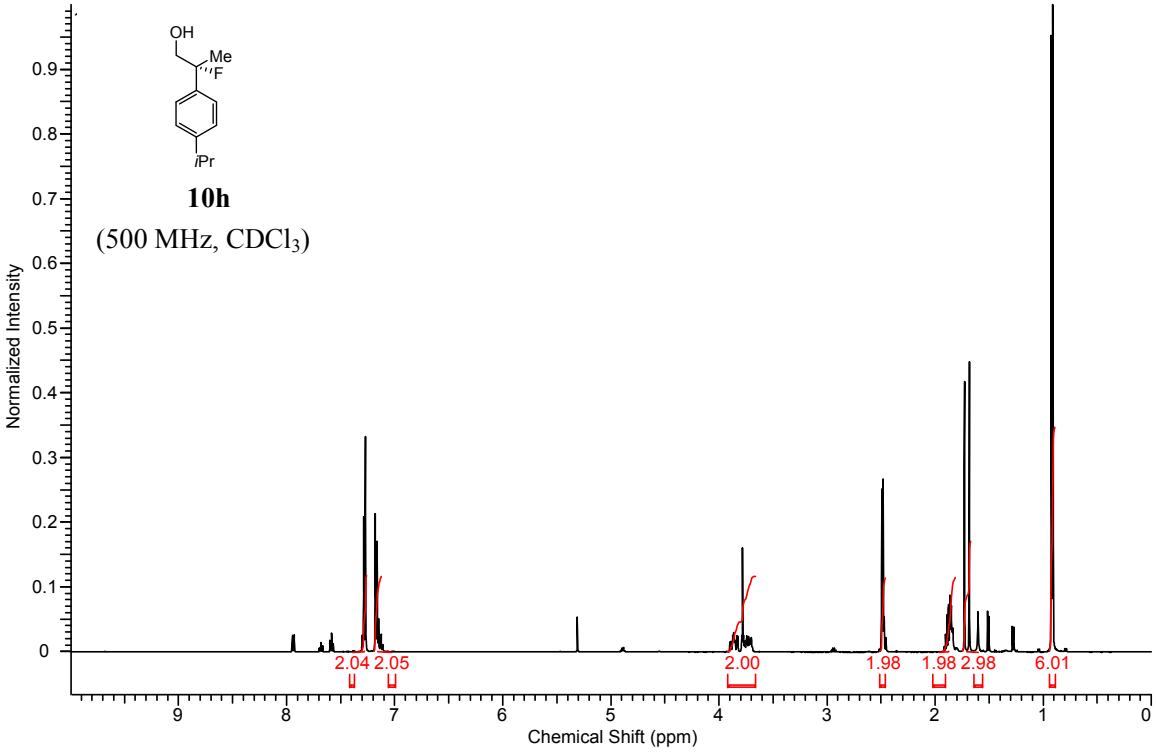

OH
Me
F
Me
10e
(126 MHz, CDCl3)
Normalized Intensity
M01(m)
M02(s)
M03(s)
M05(d)
M06(d)
M07(m)
M08(m)
M09(m)
M10(s)
141.51
138.13
133.82
128.59
128.37
125.12
121.50
121.43
98.54
97.17
69.70
69.50
23.31
23.11
21.56
Chemical Shift (ppm)

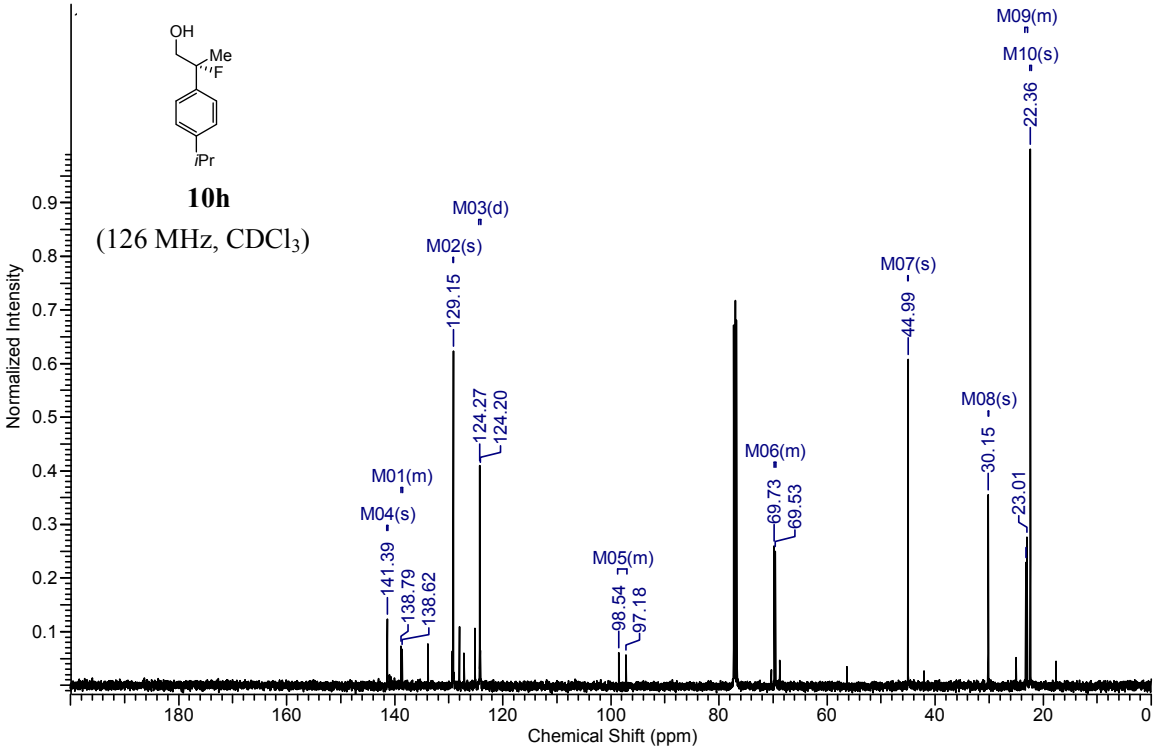

OH
Me
F
Me
10f
(500 MHz, CDCl3)
Normalized Intensity
0.97 3.01
1.00 1.00
3.01
0.98 3.02
Chemical Shift (ppm)

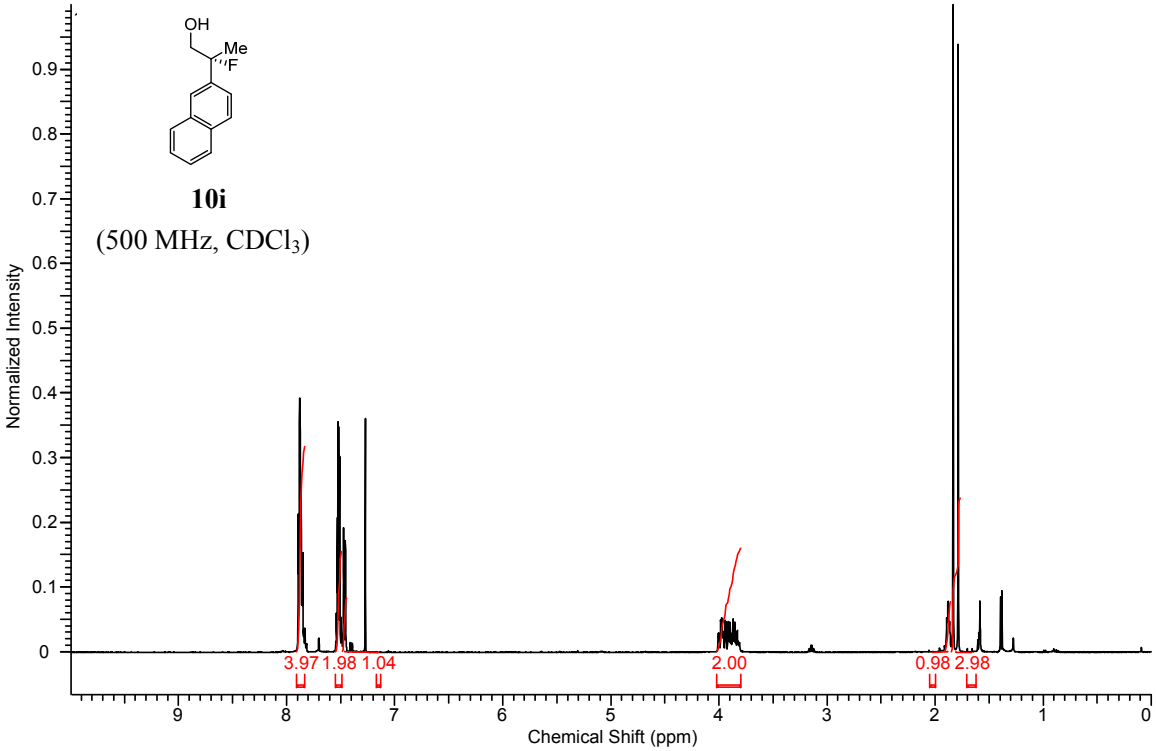

OH
Me
F
Me
10f
(126 MHz, CDCl3)
M03(s)
M02(s)
M04(s)
M06(d)
M01(m)
M05(s)
132.55
128.00
125.88
125.68
138.88
138.72
135.19
M07(m)
99.98
98.62
M08(m)
68.40
68.20
M09(m)
M10(d)
23.15
22.94
21.70
21.64
Normalized Intensity
Chemical Shift (ppm)

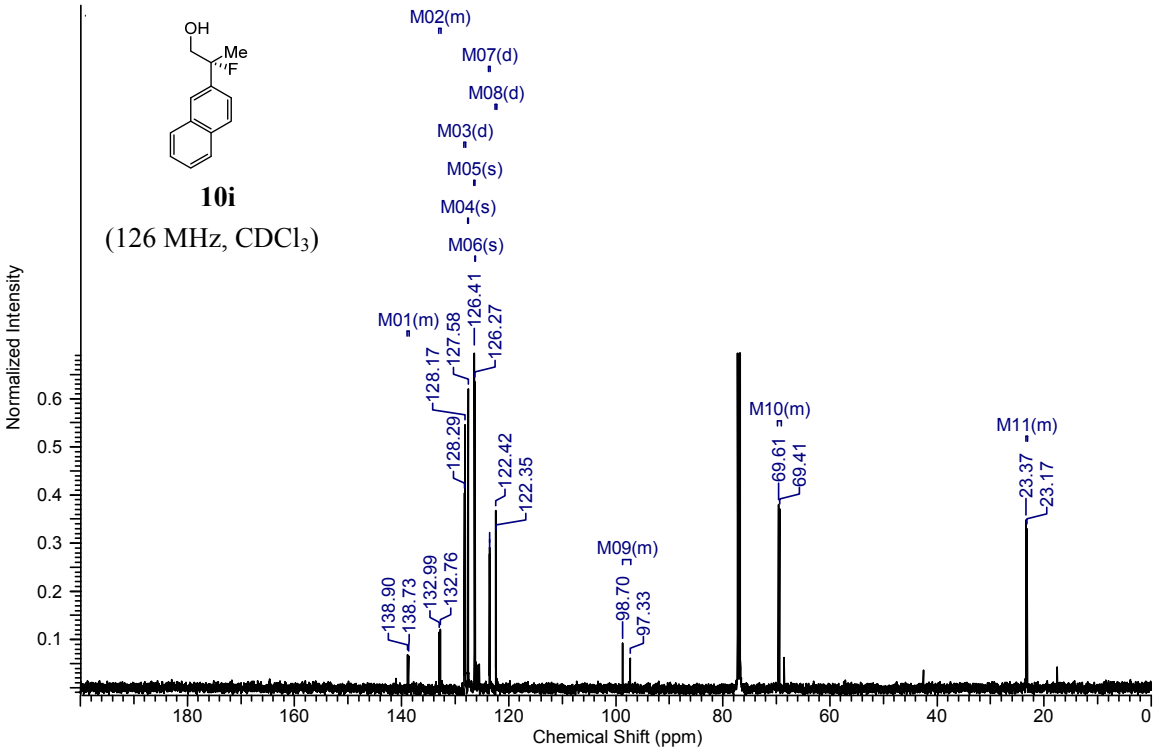

OH
Me
F
Ph
10g
(500 MHz, CDCl3)
Normalized Intensity
4.02 4.03 1.05
2.02
1.00 3.01
Chemical Shift (ppm)

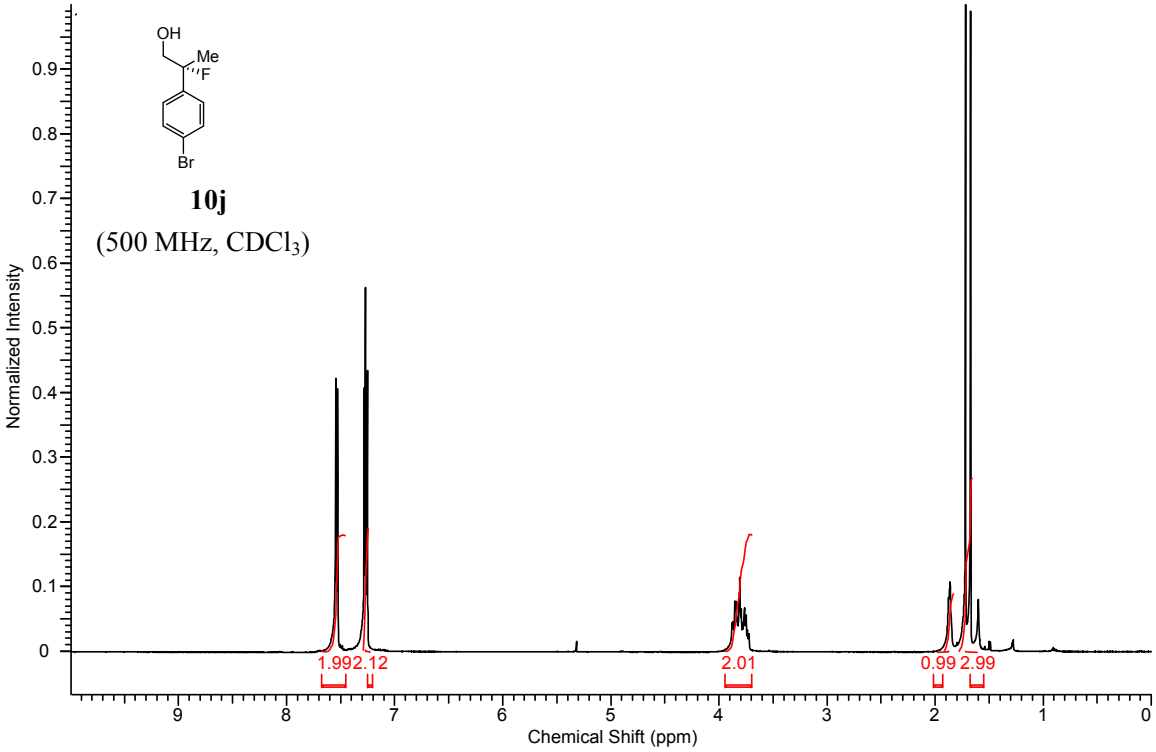

OH
Me
F
Ph
10g
(126 MHz, CDCl3)
Normalized Intensity
M07(d)
M03(s)
M05(s)
M04(s)
M06(s)
128.80
127.10
124.98
M02(m)
M01(s)
140.83
140.53
140.38
M08(m)
98.50
97.12
M09(m)
69.67
69.47
M10(m)
23.32
23.12
Chemical Shift (ppm)

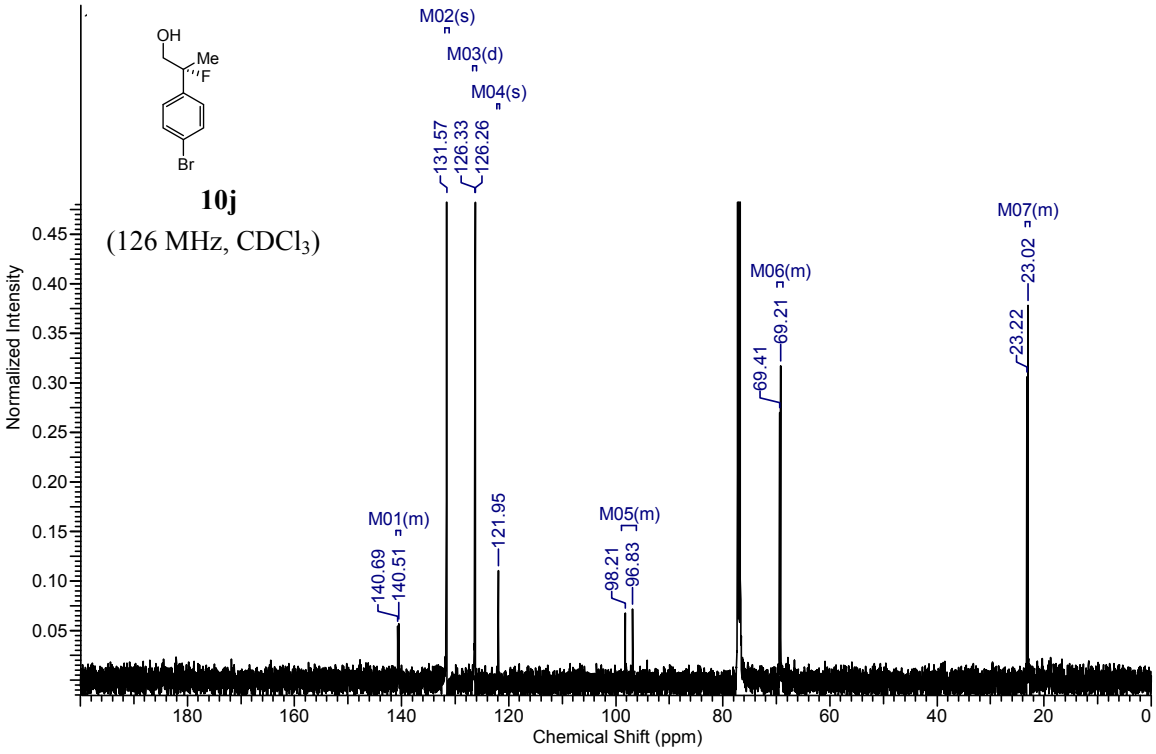

OH
Me
F
iPr
10h
(500 MHz, CDCl3)
Normalized Intensity
2.04 2.05
2.00
1.98
1.98 2.98
6.01
Chemical Shift (ppm)

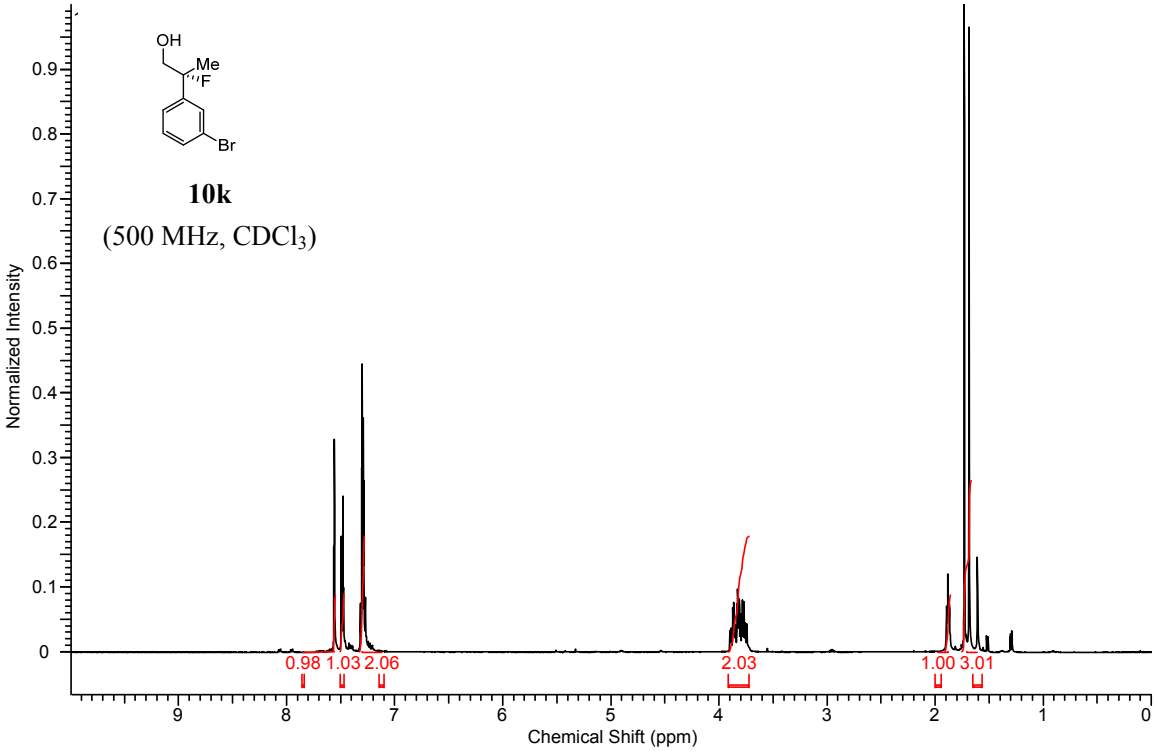

OH
Me
F
iPr
10h
(126 MHz, CDCl3)
Normalized Intensity
M09(m)
M10(s)
22.36
M03(d)
M02(s)
129.15
M07(s)
44.99
124.27
124.20
M08(s)
30.15
M01(m)
M04(s)
M06(m)
69.73
69.53
23.01
141.39
138.79
138.62
M05(m)
98.54
97.18
Chemical Shift (ppm)

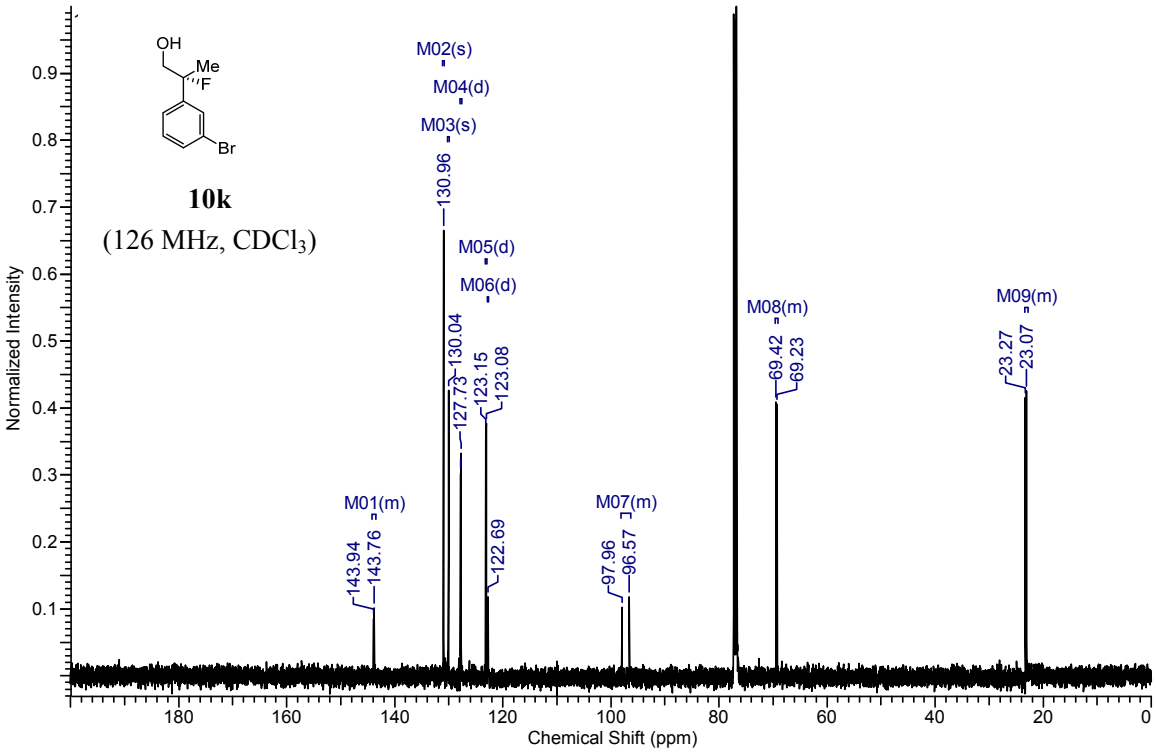

OH
Me
F
10i
(500 MHz, CDCl3)
Normalized Intensity
3.97 1.98 1.04
2.00
0.98 2.98
Chemical Shift (ppm)

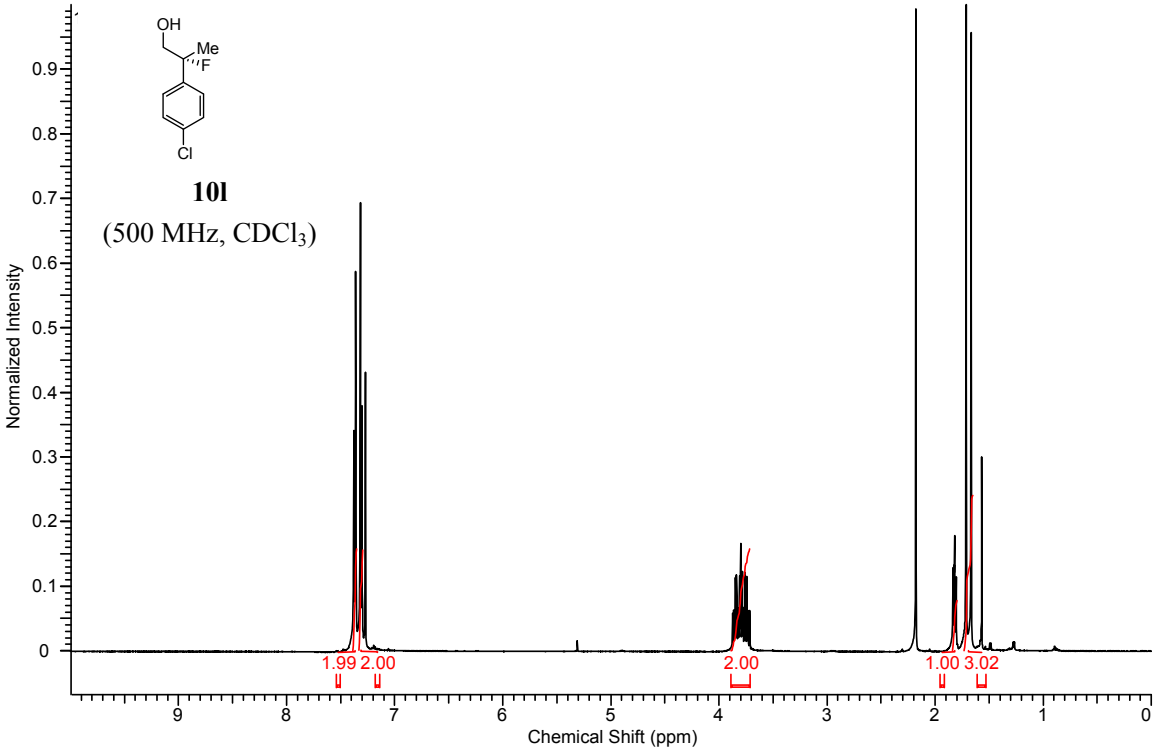

OH
Me
F
10i
(126 MHz, CDCl3)
Normalized Intensity
M02(m)
M07(d)
M08(d)
M03(d)
M05(s)
M04(s)
M06(s)
M01(m)
126.41
126.27
127.58
128.17
128.29
122.42
122.35
138.90
138.73
132.99
132.76
M09(m)
98.70
97.33
M10(m)
69.61
69.41
M11(m)
23.37
23.17
Chemical Shift (ppm)

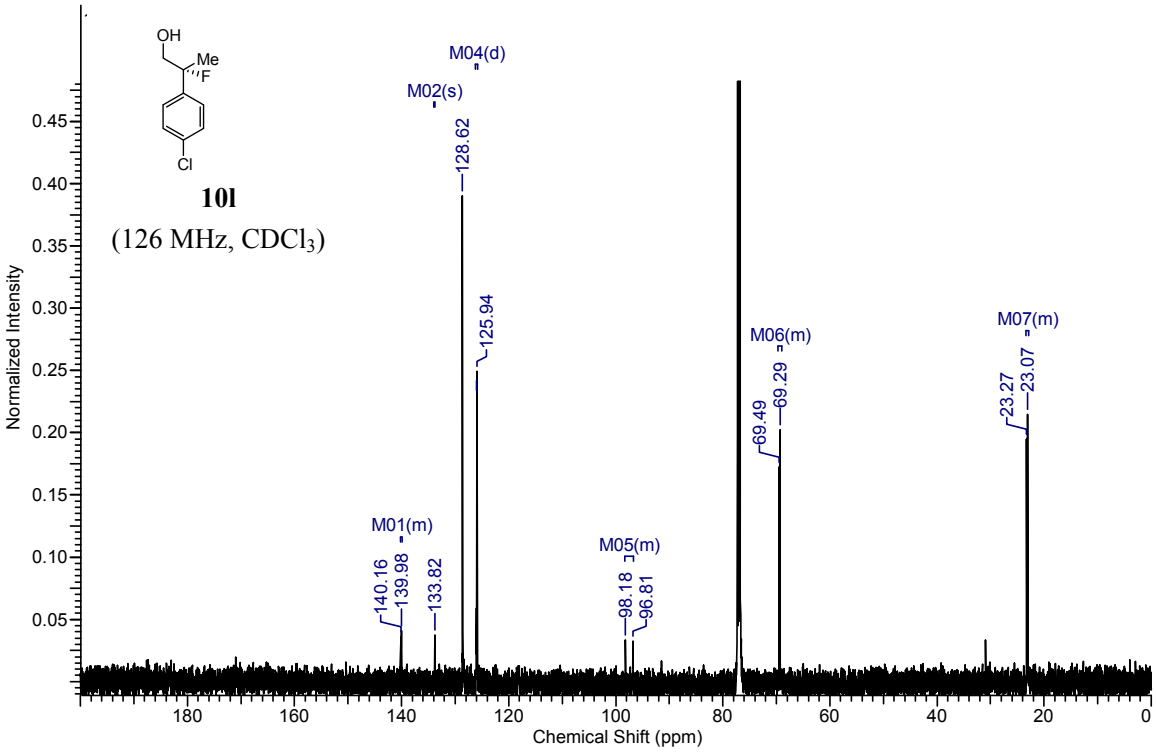

OH
Me
F
Br
10j
(500 MHz, CDCl3)
Normalized Intensity
1.99
2.12
2.01
0.99
2.99
Chemical Shift (ppm)

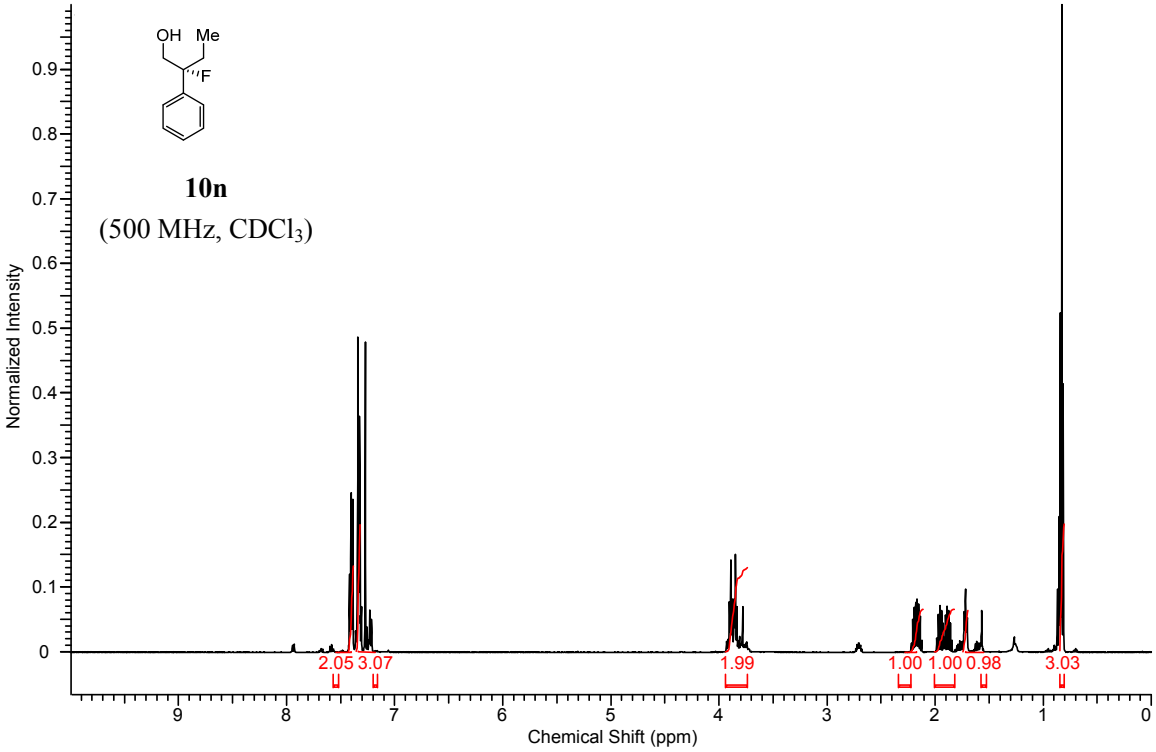

OH
Me
F
Br
10j
(126 MHz, CDCl3)
M02(s)
M03(d)
M04(s)
131.57
126.33
126.26
M01(m)
140.69
140.51
121.95
M05(m)
98.21
96.83
69.41
M06(m)
69.21
M07(m)
23.22
23.02
Normalized Intensity
Chemical Shift (ppm)

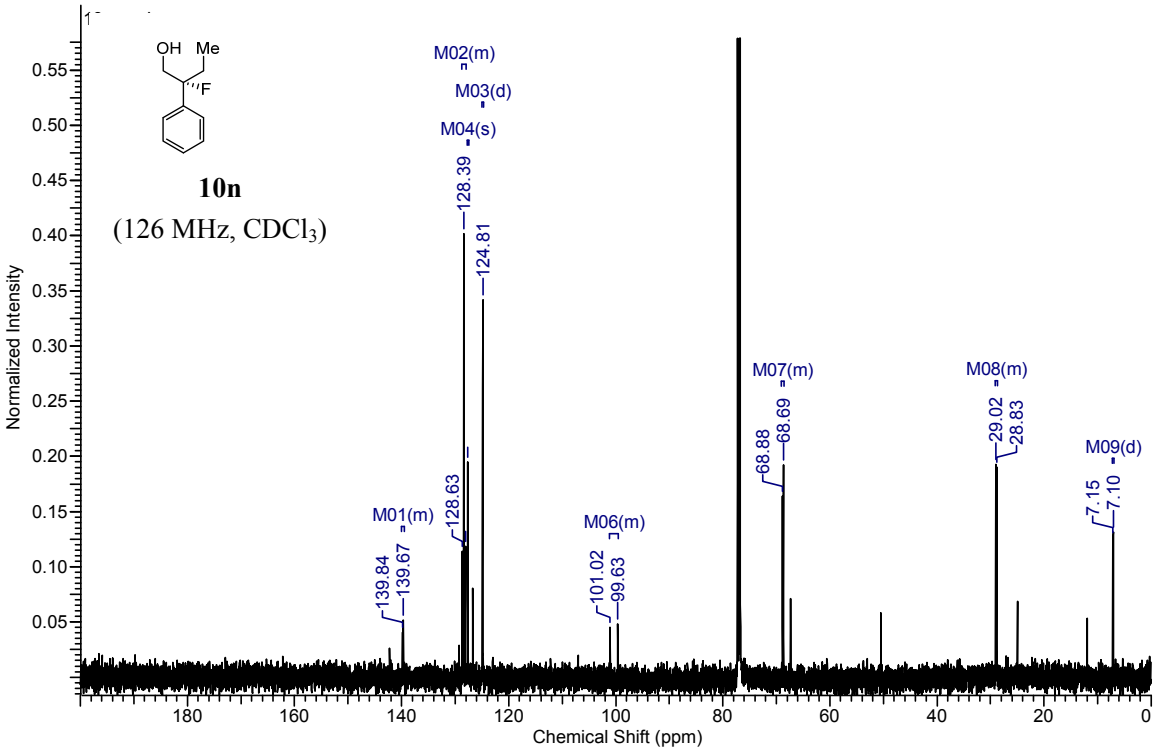

OH
Me
F
Br
10k
(500 MHz, CDCl3)
Normalized Intensity
0.98 1.03 2.06
2.03
1.00 3.01
Chemical Shift (ppm)

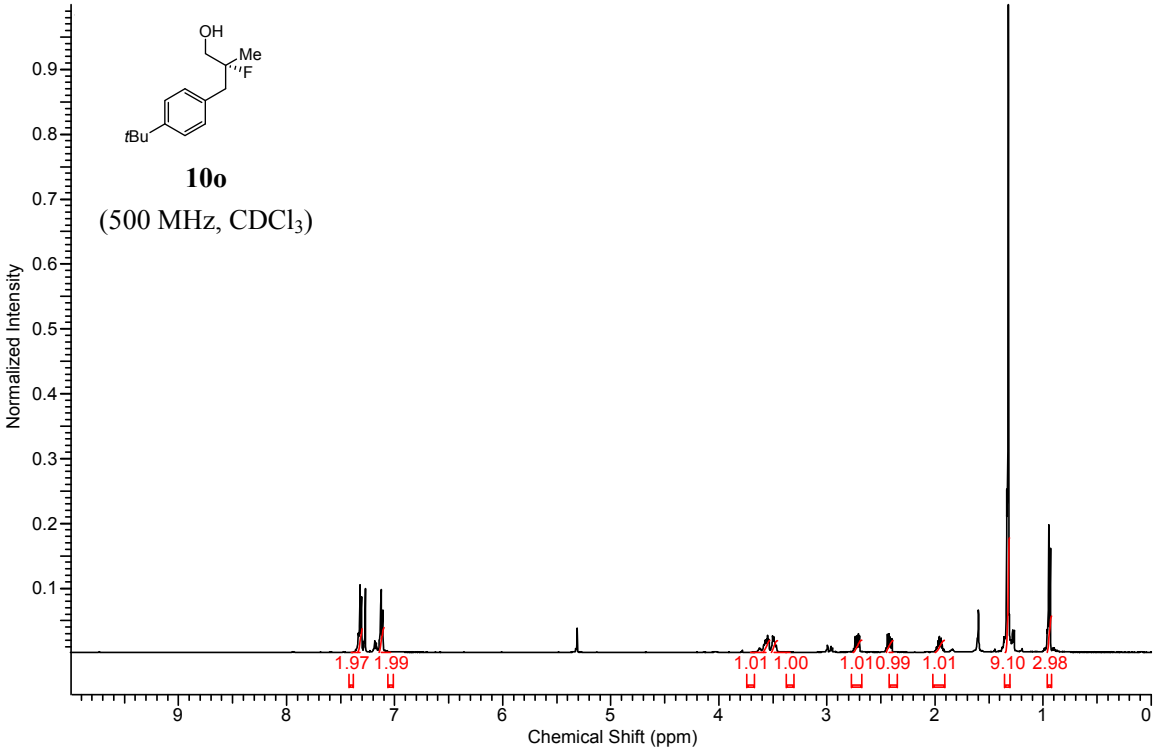

OH
Me
F
Br
10k
(126 MHz, CDCl3)
Normalized Intensity
M02(s)
M04(d)
M03(s)
130.96
M05(d)
M06(d)
130.04
127.73
123.15
123.08
122.69
M01(m)
143.94
143.76
M07(m)
97.96
96.57
M08(m)
69.42
69.23
M09(m)
23.27
23.07
Chemical Shift (ppm)

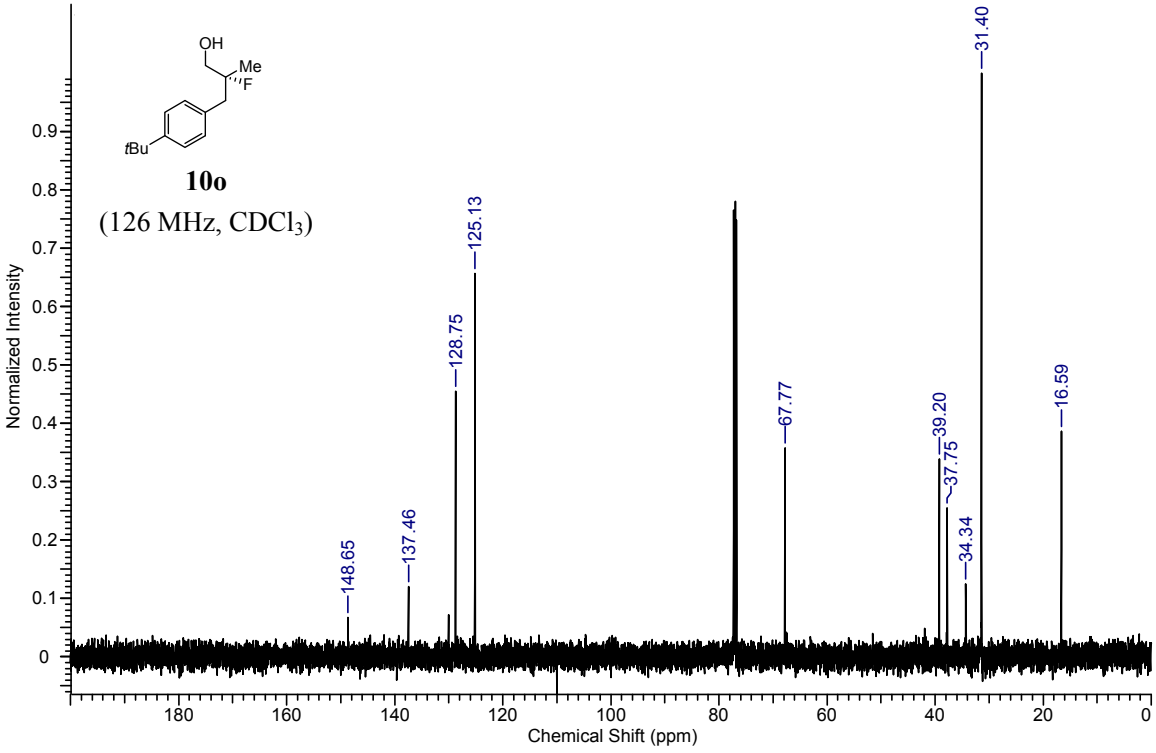

OH
Me
F
Cl
10l
(500 MHz, CDCl3)
Normalized Intensity
1.99 2.00
2.00
1.00 3.02
Chemical Shift (ppm)

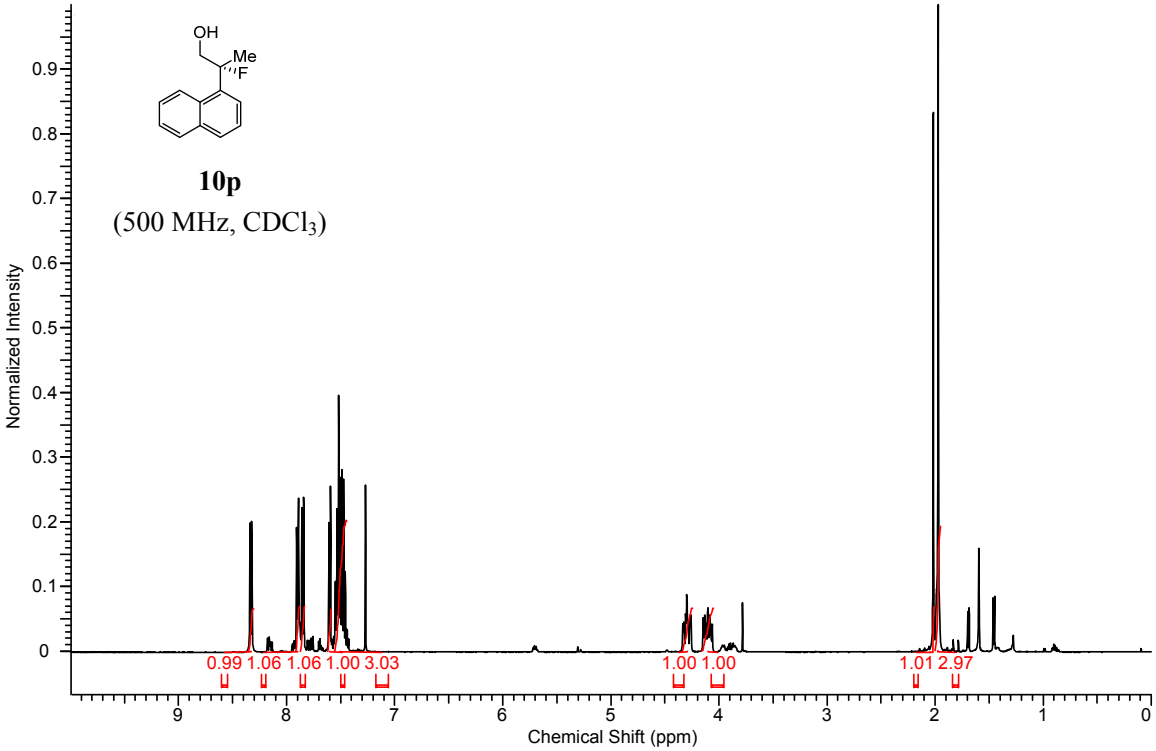

OH
Me
F
Cl
10l
(126 MHz, CDCl3)
Normalized Intensity
M04(d)
M02(s)
128.62
125.94
M01(m)
140.16
139.98
133.82
M05(m)
98.18
96.81
M06(m)
69.49
69.29
M07(m)
23.27
23.07
Chemical Shift (ppm)

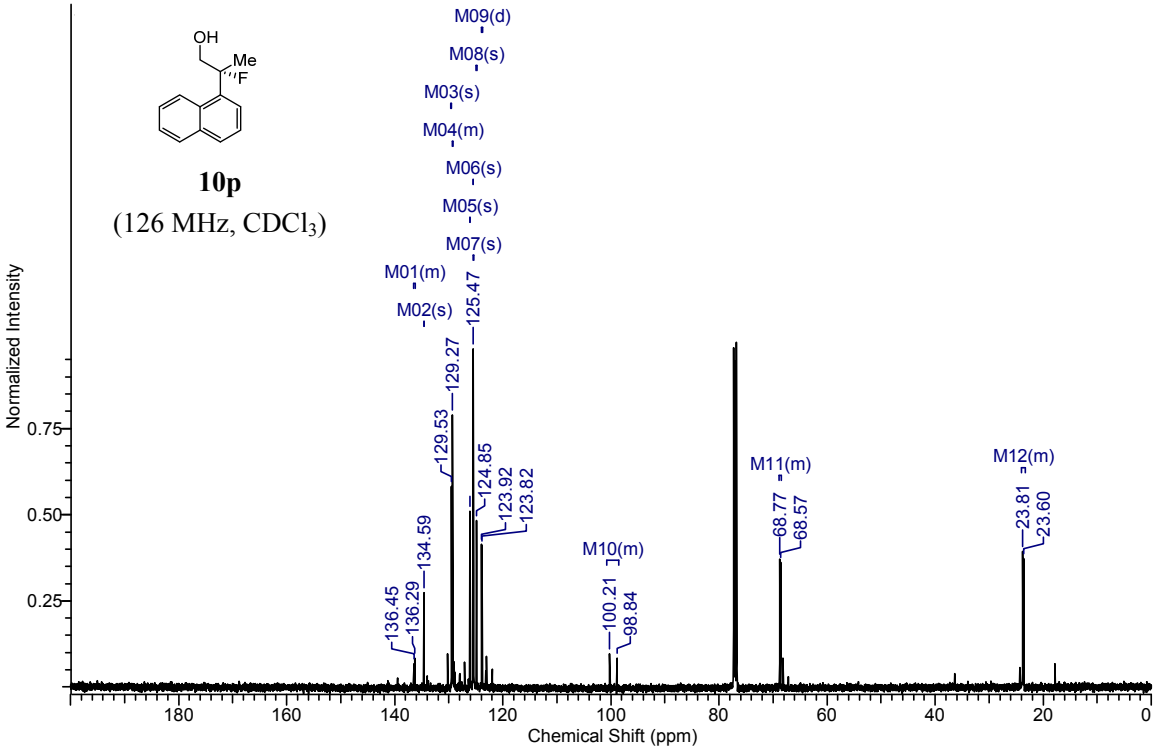

OH Me
F
10n
(500 MHz, CDCl3)
Normalized Intensity
Chemical Shift (ppm)
2.05 3.07
1.99
1.00 1.00 0.98
3.03


OH Me
F
10n
(126 MHz, CDCl3)
Normalized Intensity
Chemical Shift (ppm)
M01(m)
M02(m)
M03(d)
M04(s)
M06(m)
M07(m)
M08(m)
M09(d)
139.84
139.67
128.63
128.39
124.81
101.02
99.63
68.88
68.69
29.02
28.83
7.15
7.10


OH
Me
F
tBu
10o
(500 MHz, CDCl3)
Normalized Intensity
1.97 1.99
1.01 1.00
1.01 0.99
1.01
9.10 2.98
Chemical Shift (ppm)


OH
Me
F
tBu
10o
(126 MHz, CDCl3)
Normalized Intensity
148.65
137.46
128.75
125.13
67.77
39.20
37.75
34.34
31.40
16.59
Chemical Shift (ppm)

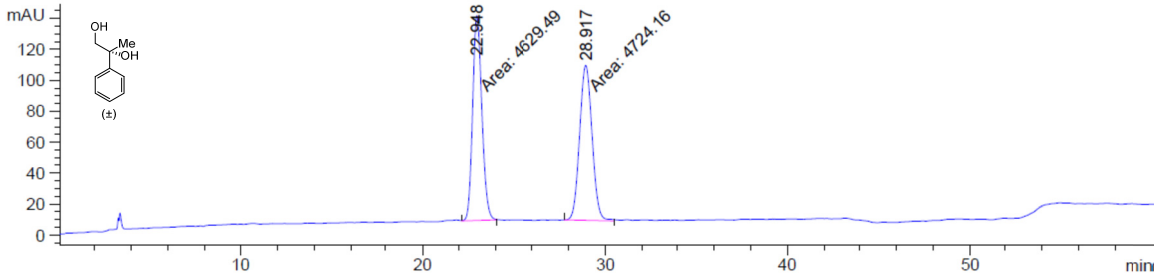

OH
Me
F
10p
(500 MHz, CDCl3)
Normalized Intensity
0.99 1.06 1.06 1.00 3.03
1.00 1.00
1.01 2.97
Chemical Shift (ppm)


OH
Me
F
10p
(126 MHz, CDCl3)
Normalized Intensity
M09(d)
M08(s)
M03(s)
M04(m)
M06(s)
M05(s)
M07(s)
M01(m)
M02(s)
125.47
129.27
129.53
124.85
123.92
123.82
134.59
136.45
136.29
M10(m)
100.21
98.84
M11(m)
68.77
68.57
M12(m)
23.81
23.60
Chemical Shift (ppm)

## 6. Chiral HPLC Traces of Enantioenriched α-Functionalization Products

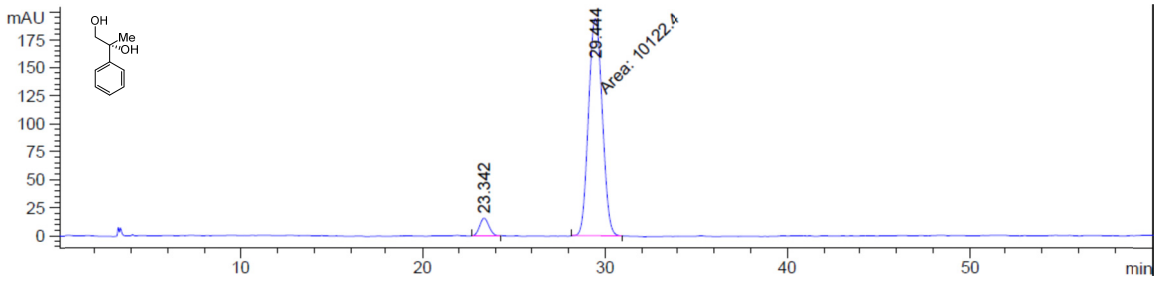
### Product 7ad:

**Racemic Sample:** HPLC (ChiralPak AS-H, 5% *i*PrOH in hexanes, 1 mL/min, 210 nm)



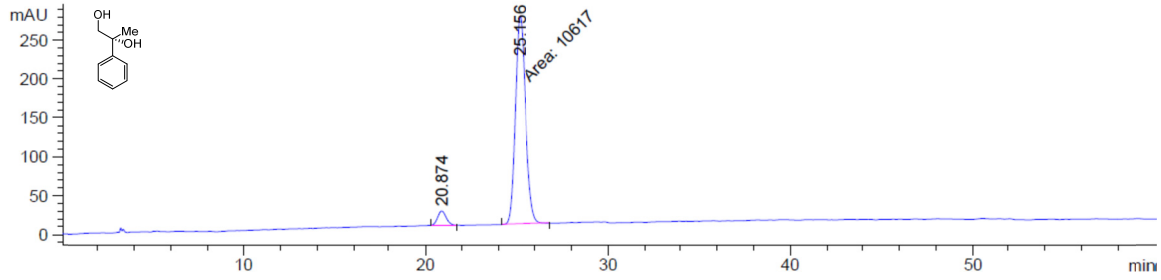

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 22.948 | MM | 0.5834 | 4629.48730 | 132.25562 | 49.4939 |
| 2 | 28.917 | MM | 0.7862 | 4724.16260 | 100.15047 | 50.5061 |

**Enantioenriched Sample:** HPLC (ChiralPak AS-H, 5% *i*PrOH in hexanes, 1 mL/min, 210 nm)



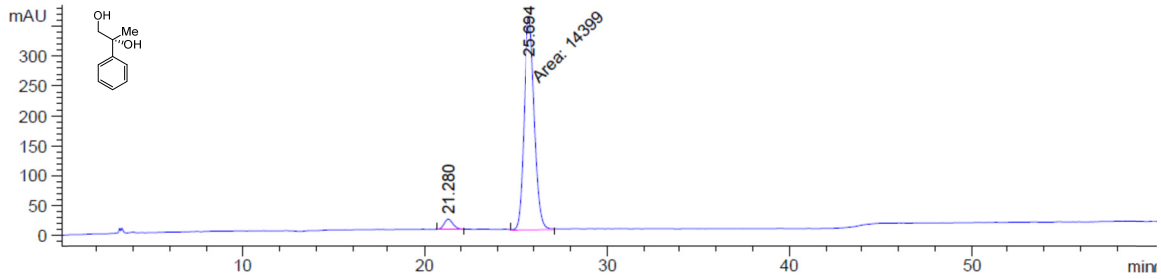

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 23.342 | BB | 0.5380 | 549.86890 | 15.64543 | 5.1523 |
| 2 | 29.444 | MM | 0.8668 | 1.01224e4 | 194.62679 | 94.8477 |

**Gram-Scale (Scheme 2a):** HPLC (ChiralPak AS-H, 5% *i*PrOH in hexanes, 1 mL/min, 210 nm)




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 20.874 | BB | 0.4989 | 600.76764 | 18.49823 | 5.3555 |
| 2 | 25.156 | MM | 0.6612 | 1.06170e4 | 267.62454 | 94.6445 |

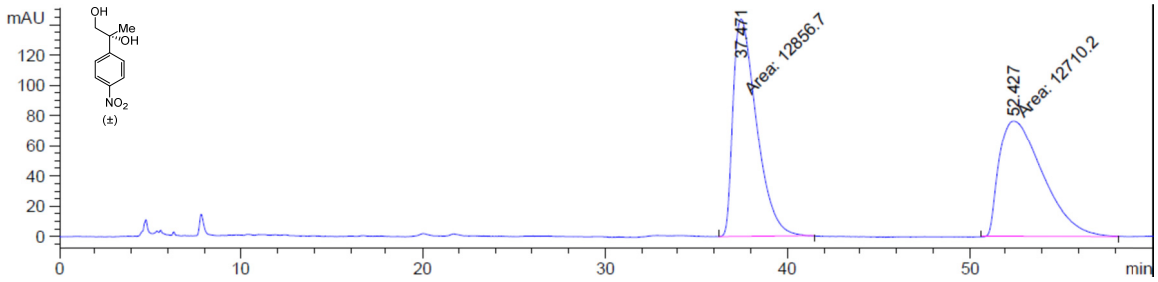
**Low Temperature (Scheme 2c):** HPLC (ChiralPak AS-H, 5% *i*PrOH in hexanes, 1 mL/min, 210 nm)




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 21.280 | BB | 0.5111 | 555.89697 | 16.84314 | 3.7172 |
| 2 | 25.694 | MM | 0.6720 | 1.43990e4 | 357.10974 | 96.2828 |

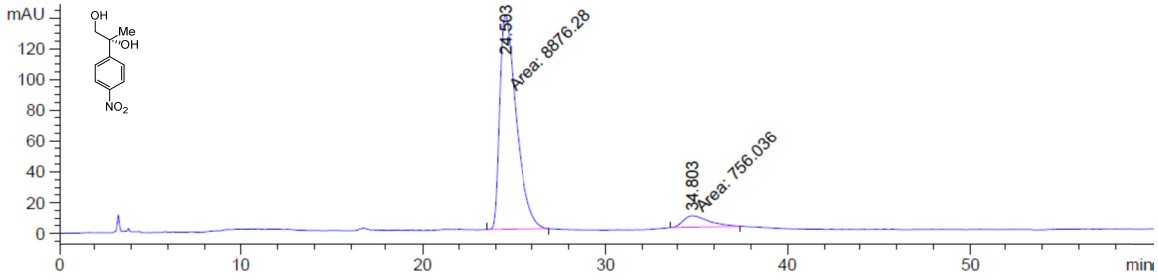
**Product 7bd:**

**Racemic Sample:** HPLC (ChiralPak AS-H, 10% *i*PrOH in hexanes, 1 mL/min, 210 nm)




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 37.471 | MM | 1.4876 | 1.28567e4 | 144.04404 | 50.2866 |
| 2 | 52.427 | MM | 2.7616 | 1.27102e4 | 76.70787 | 49.7134 |

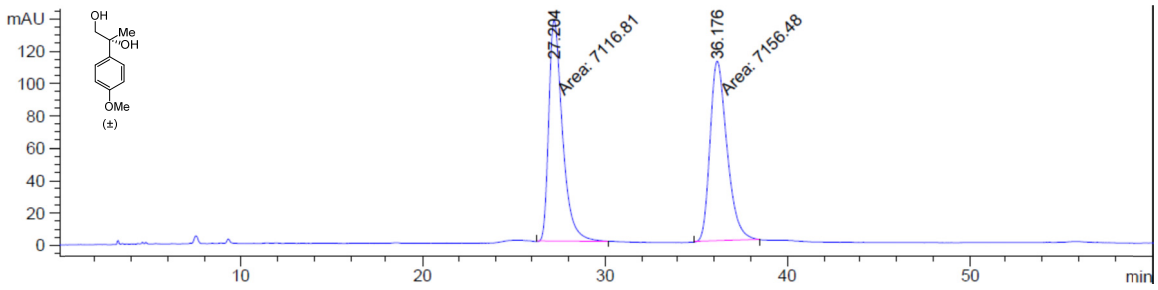
**Enantioenriched Sample:** HPLC (ChiralPak AS-H, 10% *i*PrOH in hexanes, 1 mL/min, 210 nm)




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 24.503 | MM | 1.0600 | 8876.27832 | 139.56398 | 92.1510 |
| 2 | 34.803 | MM | 1.6718 | 756.03601 | 7.53709 | 7.8490 |

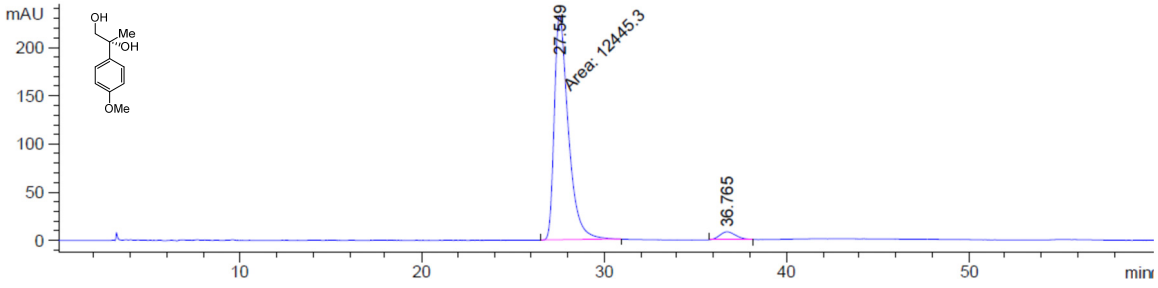
**Product 7cd:**

**Racemic Sample:** HPLC (ChiralCel OD-H, 5% *i*PrOH in hexanes, 1 mL/min, 224 nm)




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 27.204 | MM | 0.8667 | 7116.81445 | 136.85446 | 49.8610 |
| 2 | 36.176 | MM | 1.0714 | 7156.48242 | 111.32085 | 50.1390 |

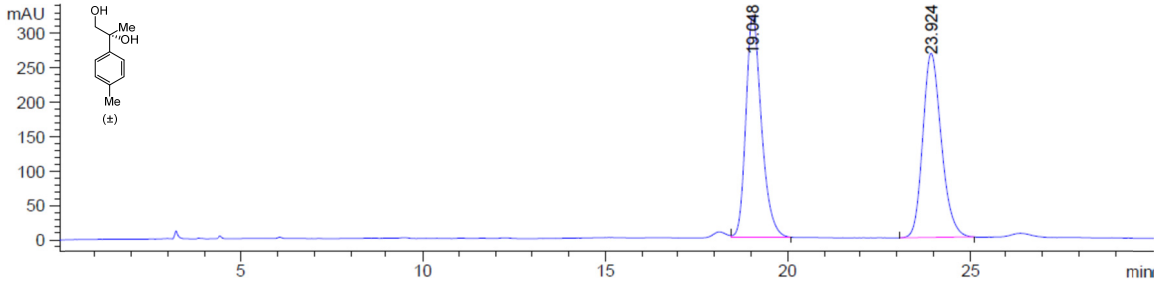
**Enantioenriched Sample:** HPLC (ChiralCel OD-H, 5% *i*PrOH in hexanes, 1 mL/min, 224 nm)




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 27.549 | MM | 0.8905 | 1.24453e4 | 232.93216 | 96.1652 |
| 2 | 36.765 | BB | 0.7204 | 496.28830 | 8.19603 | 3.8348 |

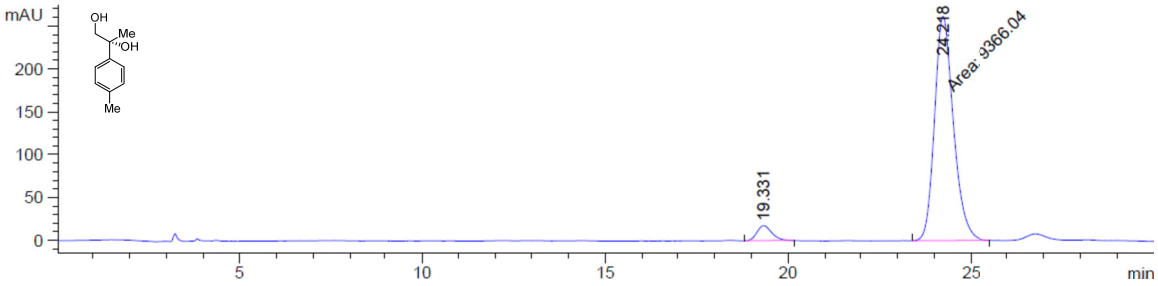
**Product 7dd:**

**Racemic Sample:** HPLC (ChiralPak AD-H, 5% *i*PrOH in hexanes, 1 mL/min, 212 nm)




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 19.048 | VB | 0.4492 | 9496.76172 | 322.87686 | 50.2783 |
| 2 | 23.924 | BB | 0.5352 | 9391.64062 | 267.75479 | 49.7217 |

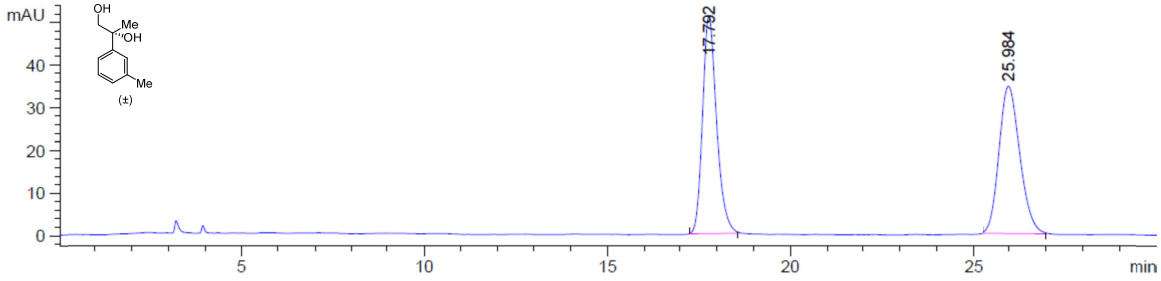
**Enantioenriched Sample:** HPLC (ChiralPak AD-H, 5% *i*PrOH in hexanes, 1 mL/min, 212 nm)




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 19.331 | BB | 0.4171 | 501.17303 | 17.55530 | 5.0792 |
| 2 | 24.218 | MM | 0.5958 | 9366.04102 | 262.02197 | 94.9208 |

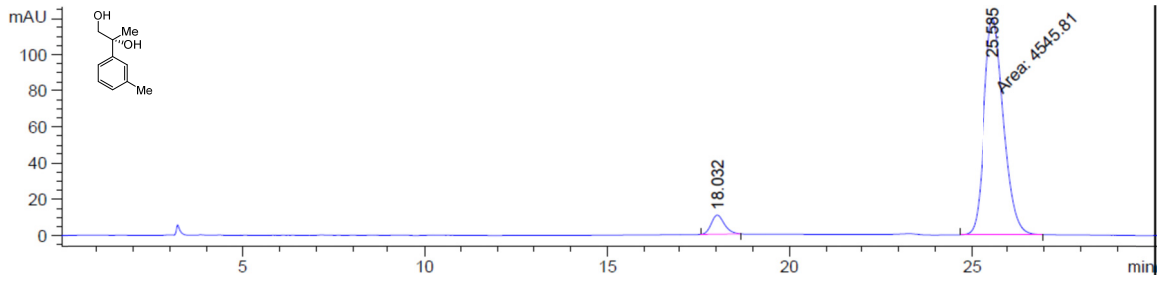
**Product 7ed:**

**Racemic Sample:** HPLC (ChiralPak AD-H, 5% *i*PrOH in hexanes, 1 mL/min, 220 nm)




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 17.792 | BB | 0.4037 | 1349.03931 | 51.15623 | 49.8849 |
| 2 | 25.984 | BB | 0.5997 | 1355.26624 | 34.69785 | 50.1151 |

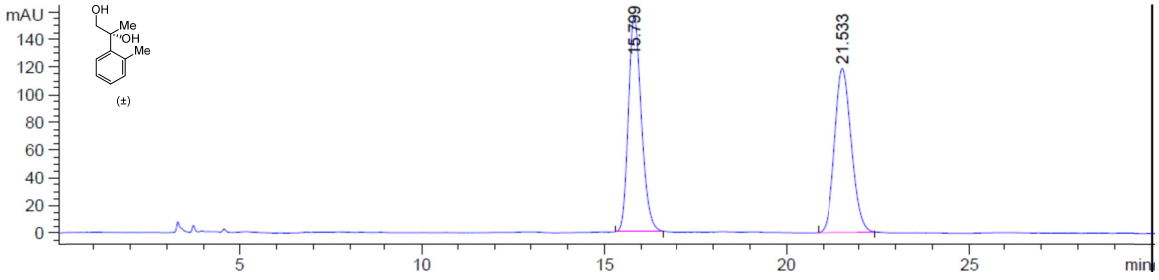
**Enantioenriched Sample:** HPLC (ChiralPak AD-H, 5% *i*PrOH in hexanes, 1 mL/min, 220 nm)




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 18.032 | BB | 0.3816 | 269.30273 | 10.70263 | 5.5929 |
| 2 | 25.585 | MM | 0.6306 | 4545.80664 | 120.14509 | 94.4071 |

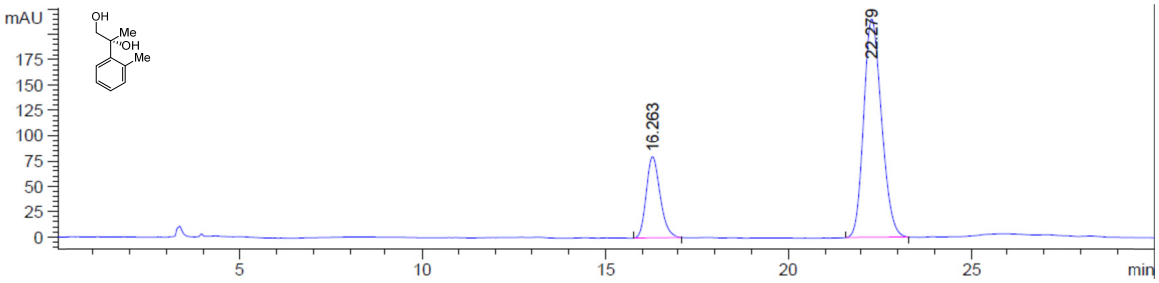
**Product 7fd:**

**Racemic Sample:** HPLC (ChiralPak AS-H, 5% *i*PrOH in hexanes, 1 mL/min, 210 nm)




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 15.799 | BB | 0.3791 | 3843.57886 | 156.17709 | 50.2877 |
| 2 | 21.533 | BB | 0.4951 | 3799.60693 | 118.81152 | 49.7123 |

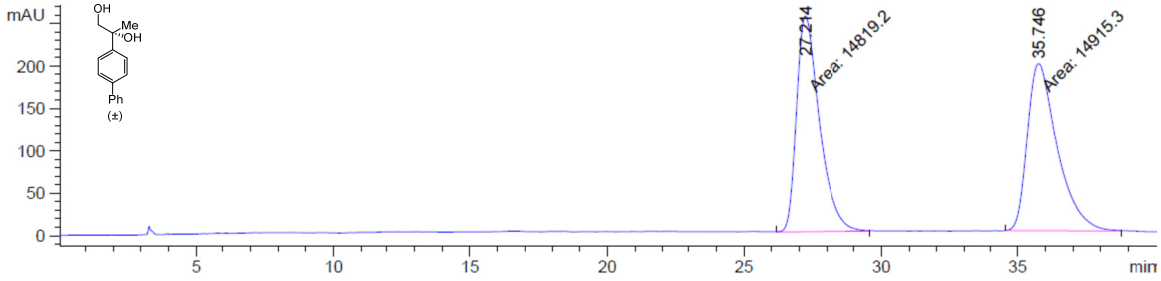
**Enantioenriched Sample:** HPLC (ChiralPak AS-H, 5% *i*PrOH in hexanes, 1 mL/min, 210 nm)




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 16.263 | BB | 0.3983 | 2101.78052 | 80.04806 | 22.4087 |
| 2 | 22.279 | BB | 0.5232 | 7277.53223 | 215.93819 | 77.5913 |

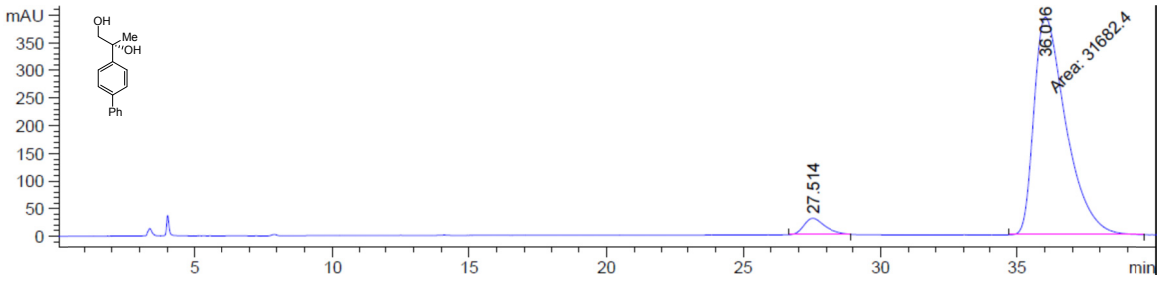
**Product 7gd:**

**Racemic Sample:** HPLC (ChiralPak AS-H, 5% *i*PrOH in hexanes, 1 mL/min, 210 nm)




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 27.214 | MM | 0.9693 | 1.48192e4 | 254.81523 | 49.8383 |
| 2 | 35.746 | MM | 1.2583 | 1.49153e4 | 197.55556 | 50.1617 |

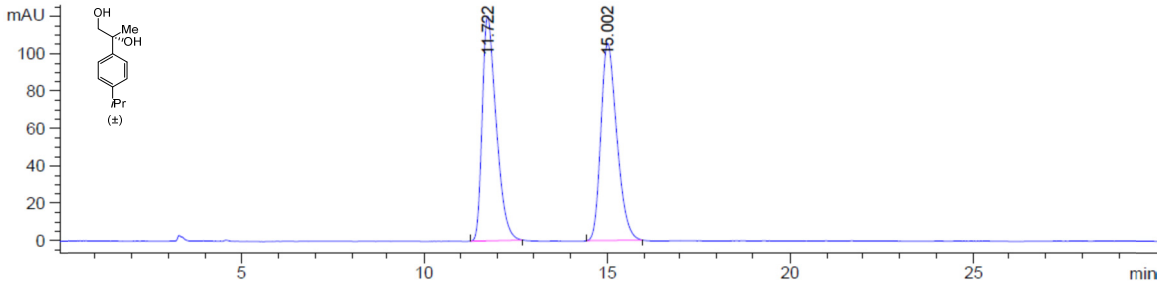
**Enantioenriched Sample:** HPLC (ChiralPak AS-H, 5% *i*PrOH in hexanes, 1 mL/min, 210 nm)




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 27.514 | BB | 0.7392 | 1623.30151 | 29.71992 | 4.8739 |
| 2 | 36.016 | MM | 1.3391 | 3.16824e4 | 394.31262 | 95.1261 |

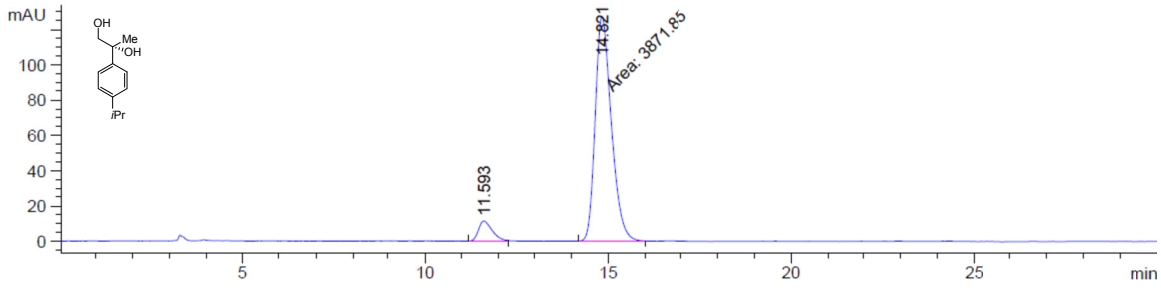
**Product 7hd:**

**Racemic Sample:** HPLC (ChiralPak AS-H, 5% *i*PrOH in hexanes, 1 mL/min, 218 nm)




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 11.722 | BB | 0.3953 | 3174.47681 | 120.51311 | 49.8491 |
| 2 | 15.002 | BB | 0.4577 | 3193.69727 | 105.92864 | 50.1509 |

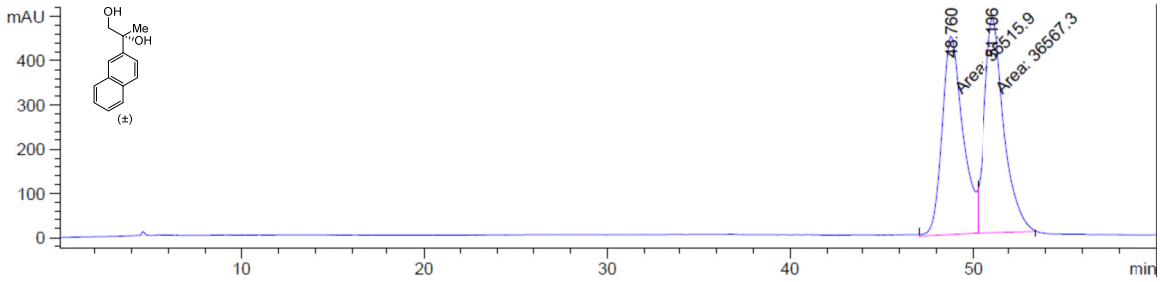
**Enantioenriched Sample:** HPLC (ChiralPak AS-H, 5% *i*PrOH in hexanes, 1 mL/min, 218 nm)




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 11.593 | BB | 0.3660 | 291.42462 | 11.33432 | 6.9999 |
| 2 | 14.821 | MM | 0.5063 | 3871.85376 | 127.46449 | 93.0001 |

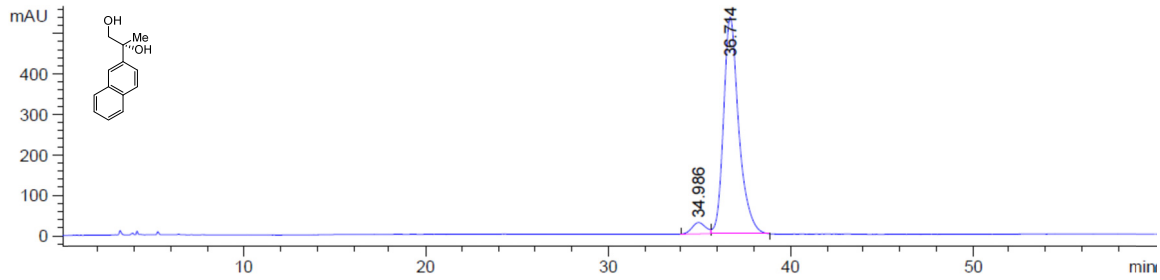
**Product 7id:**

**Racemic Sample:** HPLC (ChiralPak AD-H, 5% *i*PrOH in hexanes, 1 mL/min, 210 nm)




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 48.760 | MM | 1.3189 | 3.55159e4 | 448.79260 | 49.2707 |
| 2 | 51.106 | MM | 1.2546 | 3.65673e4 | 485.77567 | 50.7293 |

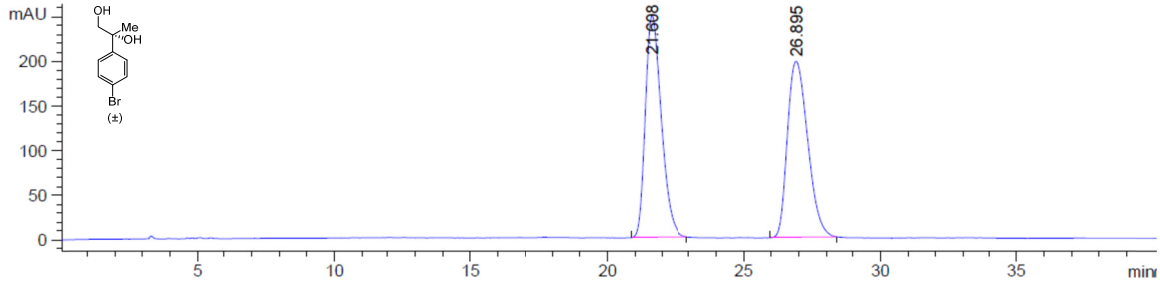
**Enantioenriched Sample:** HPLC (ChiralPak AD-H, 5% *i*PrOH in hexanes, 1 mL/min, 210 nm)




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 34.986 | BV | 0.7044 | 1484.58203 | 28.65477 | 4.5839 |
| 2 | 36.714 | VB | 0.8484 | 3.09022e4 | 536.14972 | 95.4161 |

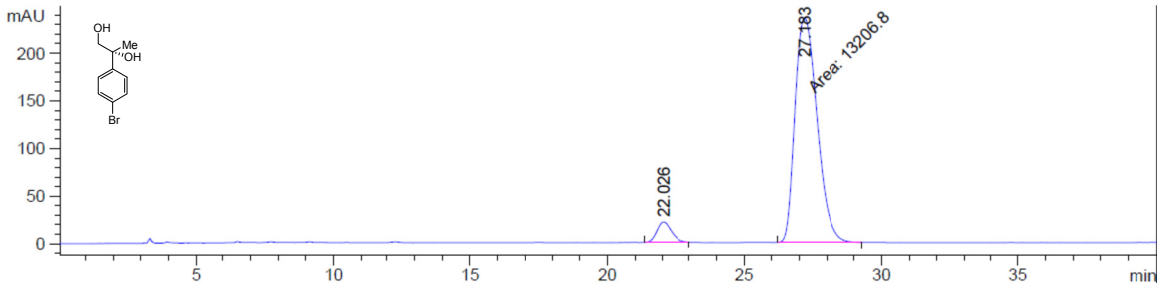
**Product 7jd:**

**Racemic Sample:** HPLC (ChiralPak AS-H, 5% *i*PrOH in hexanes, 1 mL/min, 220 nm)




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 21.608 | BB | 0.6232 | 1.01024e4 | 249.06339 | 49.9351 |
| 2 | 26.895 | BB | 0.8053 | 1.01286e4 | 197.83139 | 50.0649 |

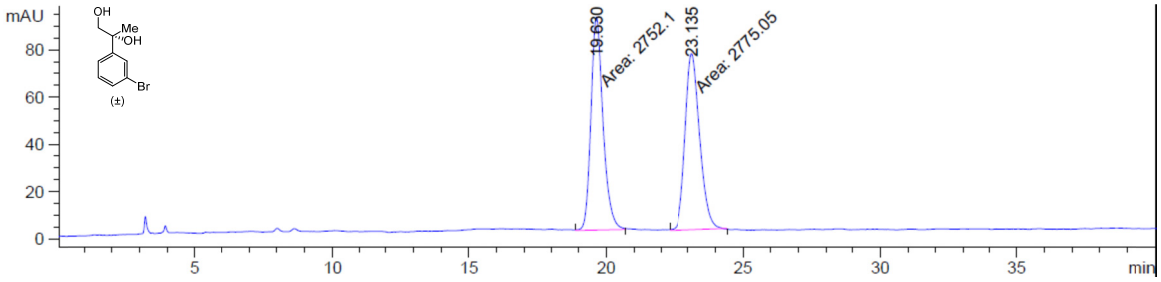
**Enantioenriched Sample:** HPLC (ChiralPak AS-H, 5% *i*PrOH in hexanes, 1 mL/min, 220 nm)




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 22.026 | BB | 0.5617 | 809.48267 | 21.57646 | 5.7753 |
| 2 | 27.183 | MM | 0.9312 | 1.32068e4 | 236.38676 | 94.2247 |

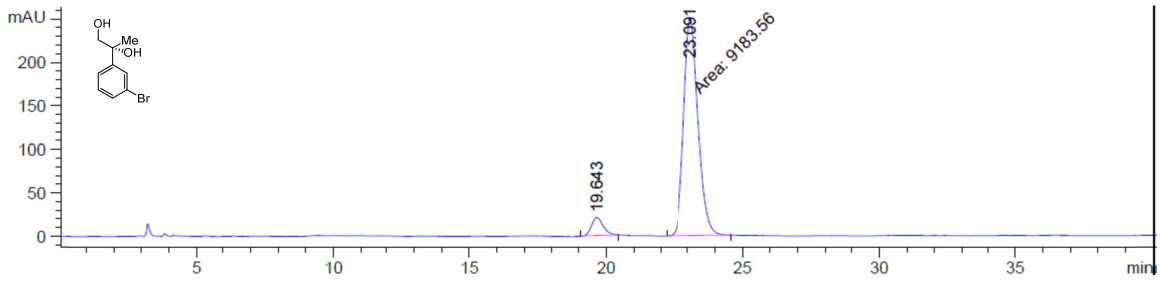
**Product 7kd:**

**Racemic Sample:** HPLC (ChiralPak AD-H, 5% *i*PrOH in hexanes, 1 mL/min, 210 nm)




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 19.630 | MM | 0.5080 | 2752.10181 | 90.29829 | 49.7924 |
| 2 | 23.135 | MM | 0.6189 | 2775.04761 | 74.72766 | 50.2076 |

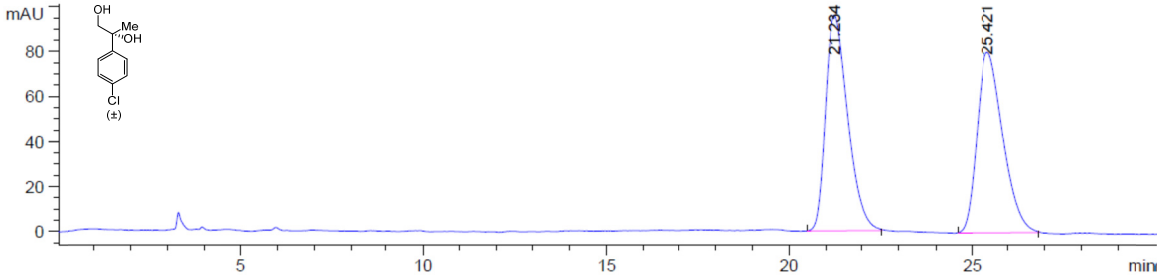
**Enantioenriched Sample:** HPLC (ChiralPak AD-H, 5% *i*PrOH in hexanes, 1 mL/min, 210 nm)




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 19.643 | BB | 0.4483 | 641.67133 | 21.24650 | 6.5309 |
| 2 | 23.091 | MM | 0.6121 | 9183.55566 | 250.07281 | 93.4691 |

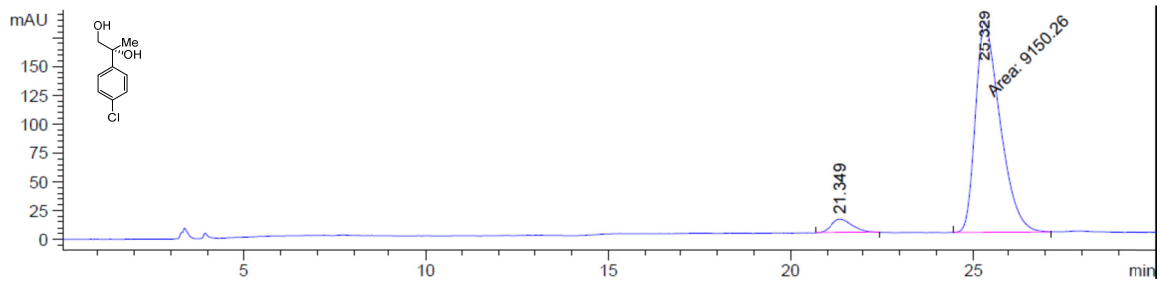
**Product 7ld:**

**Racemic Sample:** HPLC (ChiralPak AS-H, 5% *i*PrOH in hexanes, 1 mL/min, 210 nm)




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 21.234 | BB | 0.6400 | 4096.82520 | 95.98598 | 50.1173 |
| 2 | 25.421 | BB | 0.7469 | 4077.65015 | 80.50800 | 49.8827 |

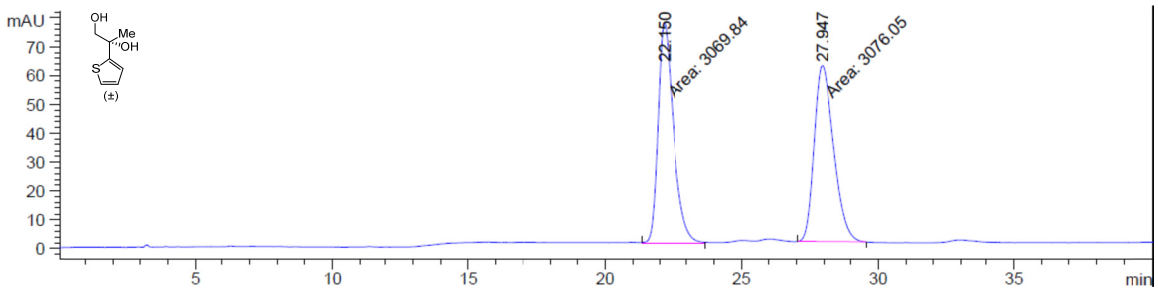
**Enantioenriched Sample:** HPLC (ChiralPak AS-H, 5% *i*PrOH in hexanes, 1 mL/min, 210 nm)




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 21.349 | BB | 0.4957 | 486.57935 | 11.78452 | 5.0492 |
| 2 | 25.329 | MM | 0.8293 | 9150.25879 | 183.88464 | 94.9508 |

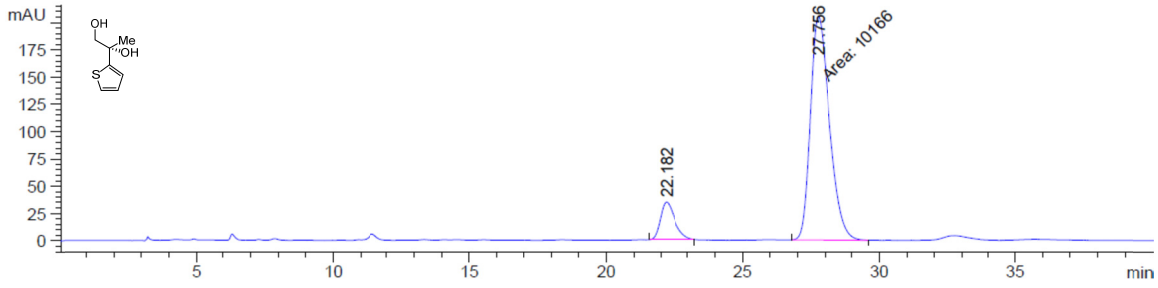
**Product 7md:**

**Racemic Sample:** HPLC (ChiralPak AD-H, 5% *i*PrOH in hexanes, 1 mL/min, 234 nm)




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 22.150 | MM | 0.6685 | 3069.84424 | 76.53101 | 49.9495 |
| 2 | 27.947 | MM | 0.8374 | 3076.05347 | 61.22161 | 50.0505 |

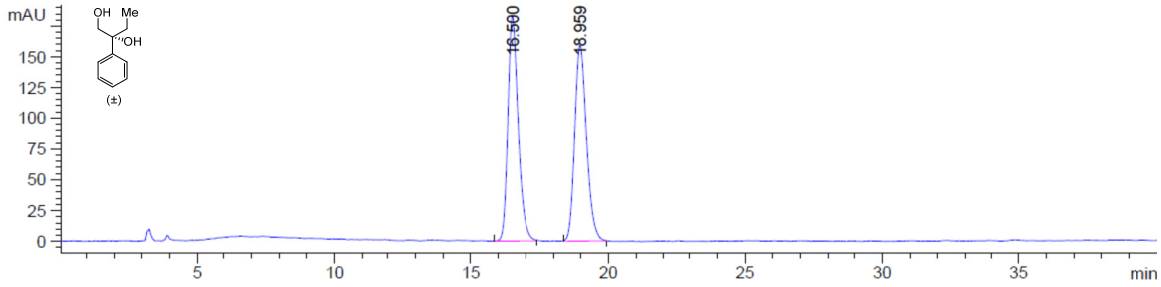
**Enantioenriched Sample:** HPLC (ChiralPak AD-H, 5% *i*PrOH in hexanes, 1 mL/min, 234 nm)




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 22.182 | BB | 0.5688 | 1314.20642 | 34.31496 | 11.4476 |
| 2 | 27.756 | MM | 0.8227 | 1.01660e4 | 205.95561 | 88.5524 |

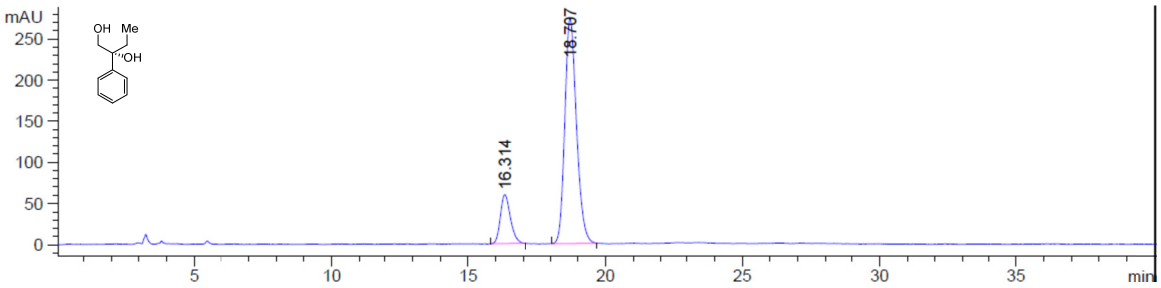
**Product 7nd:**

**Racemic Sample:** HPLC (ChiralPak AD-H, 5% *i*PrOH in hexanes, 1 mL/min, 208 nm)




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 16.500 | VB | 0.4001 | 4763.32520 | 182.72224 | 50.0482 |
| 2 | 18.959 | BB | 0.4562 | 4754.14258 | 159.31174 | 49.9518 |

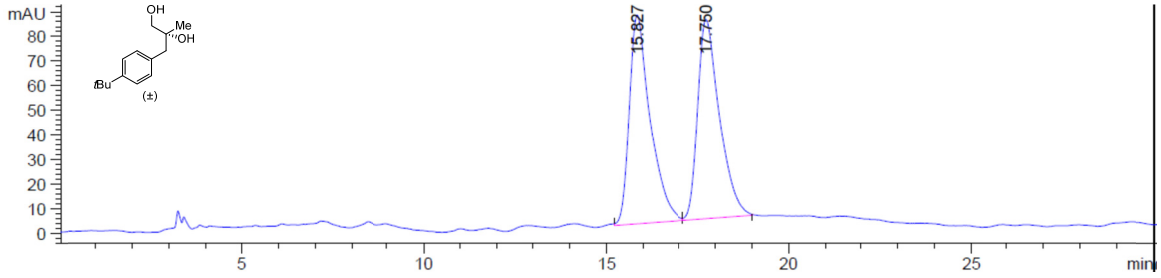
**Enantioenriched Sample:** HPLC (ChiralPak AD-H, 5% *i*PrOH in hexanes, 1 mL/min, 208 nm)




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 16.314 | BB | 0.3887 | 1507.73120 | 59.29536 | 15.8020 |
| 2 | 18.707 | BB | 0.4481 | 8033.67334 | 273.98355 | 84.1980 |

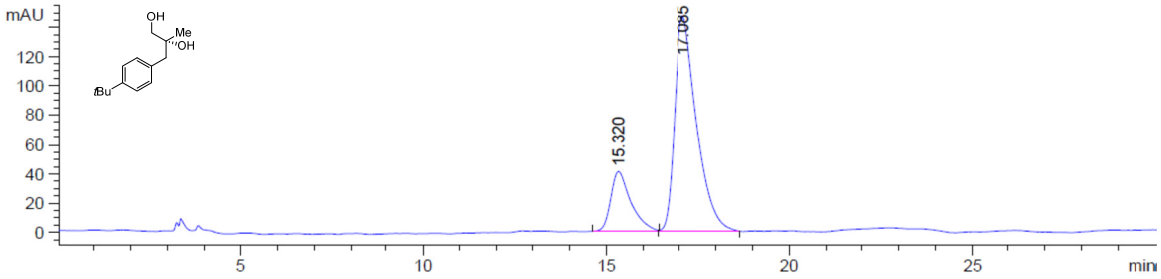
**Product 7od:**

**Racemic Sample:** HPLC (ChiralCel OD-H, 4% *i*PrOH in hexanes, 1 mL/min, 210 nm)




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 15.827 | BB | 0.5671 | 3372.89795 | 84.96974 | 50.1576 |
| 2 | 17.750 | BB | 0.5980 | 3351.69873 | 81.12016 | 49.8424 |

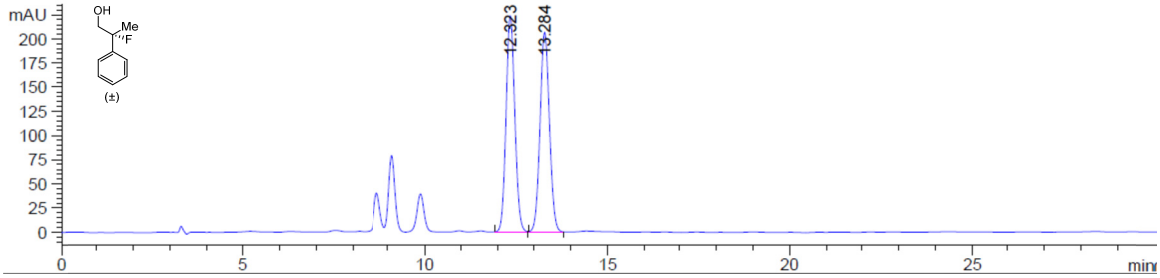
**Enantioenriched Sample:** HPLC (ChiralCel OD-H, 4% *i*PrOH in hexanes, 1 mL/min, 210 nm)




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 15.320 | BB | 0.5437 | 1558.59888 | 40.79943 | 19.9638 |
| 2 | 17.085 | BB | 0.6218 | 6248.50977 | 147.03355 | 80.0362 |

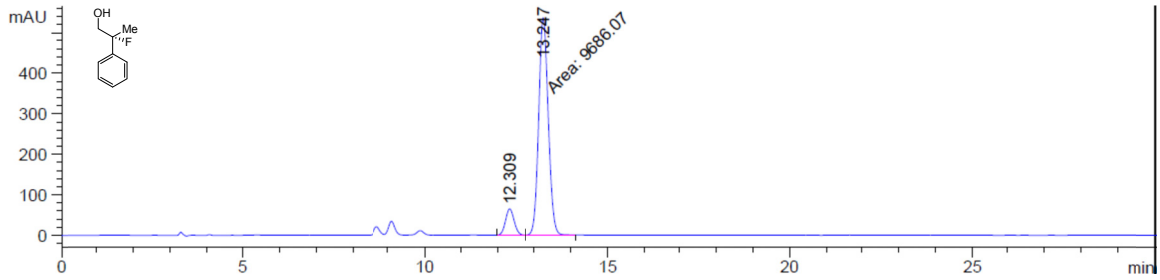
**Product 10a:**

**Racemic Sample:** HPLC (ChiralPak AS-H, 5% *i*PrOH in hexanes, 1 mL/min, 210 nm)



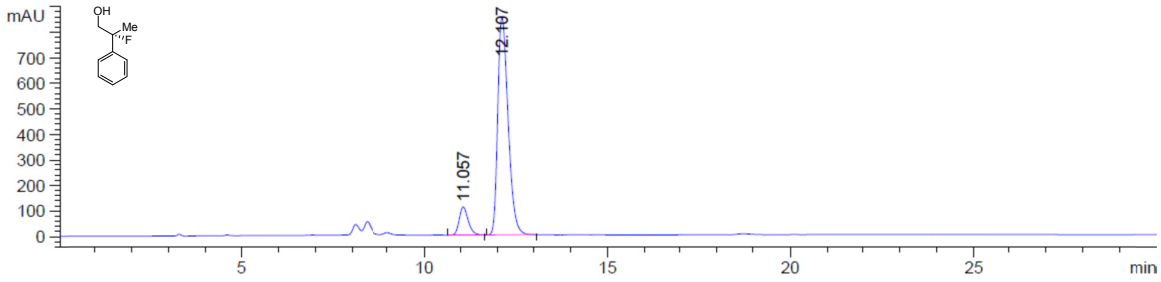

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 12.323 | BB | 0.2573 | 3712.61206 | 224.09485 | 50.1804 |
| 2 | 13.284 | BB | 0.2778 | 3685.92456 | 206.96823 | 49.8196 |

**Enantioenriched Sample:** HPLC (ChiralPak AS-H, 5% *i*PrOH in hexanes, 1 mL/min, 210 nm)



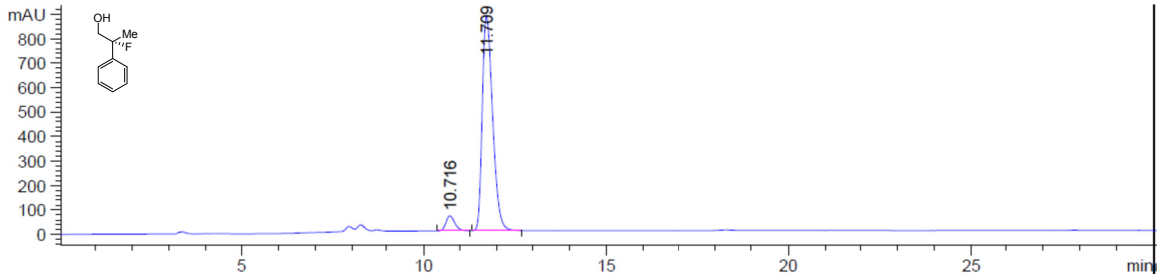

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 12.309 | BV | 0.2543 | 1054.68774 | 64.66357 | 9.8195 |
| 2 | 13.247 | MM | 0.3009 | 9686.07031 | 536.57977 | 90.1805 |

**Gram-Scale (Scheme 2b):** HPLC (ChiralPak AS-H, 5% *i*PrOH in hexanes, 1 mL/min, 210 nm)




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 11.057 | VB | 0.2607 | 1870.87598 | 109.83036 | 10.0671 |
| 2 | 12.107 | BB | 0.3041 | 1.67131e4 | 854.76379 | 89.9329 |

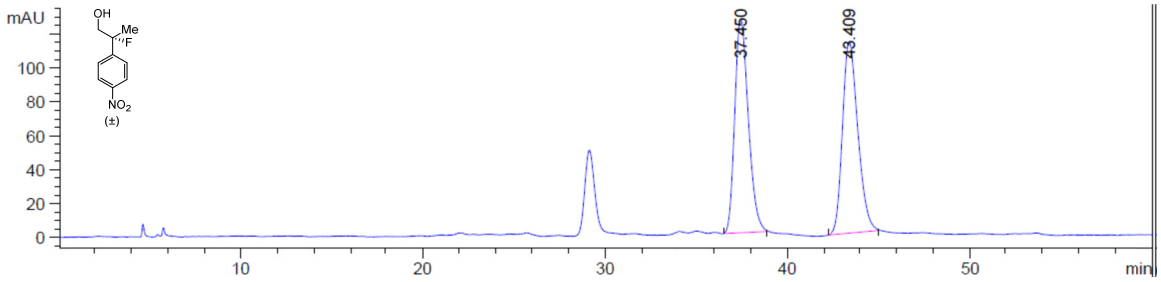
**Recrystallized (Scheme 2b):** HPLC (ChiralPak AS-H, 5% *i*PrOH in hexanes, 1 mL/min, 210 nm)




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 10.716 | BB | 0.2573 | 1023.85791 | 61.15664 | 5.6230 |
| 2 | 11.709 | BB | 0.3044 | 1.71846e4 | 877.97858 | 94.3770 |

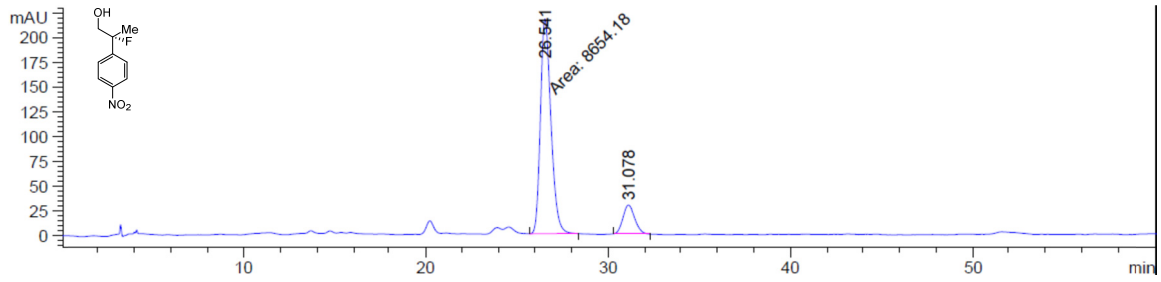
**Product 10b:**

**Racemic Sample:** HPLC (ChiralCel OD-H, 5% *i*PrOH in hexanes, 1 mL/min, 210 nm)




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 37.450 | BB | 0.7598 | 6494.49512 | 126.33352 | 49.6472 |
| 2 | 43.409 | BB | 0.8197 | 6586.80859 | 113.39614 | 50.3528 |

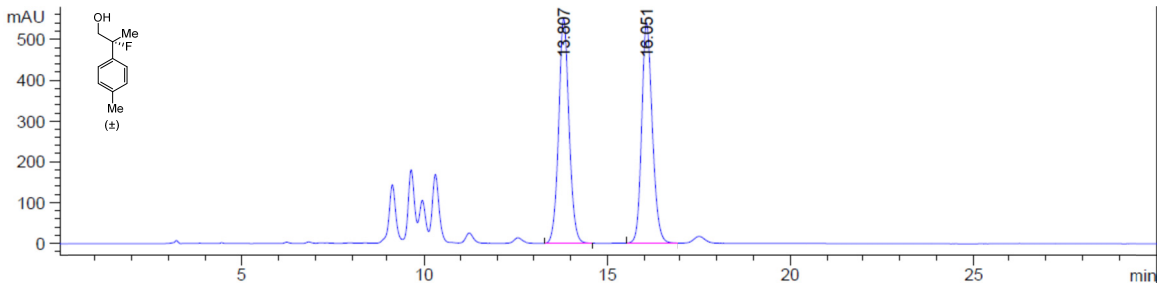
**Enantioenriched Sample:** HPLC (ChiralCel OD-H, 5% *i*PrOH in hexanes, 1 mL/min, 210 nm)




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 26.541 | MM | 0.6629 | 8654.17871 | 217.57680 | 86.7795 |
| 2 | 31.078 | BB | 0.6751 | 1318.43201 | 29.18034 | 13.2205 |

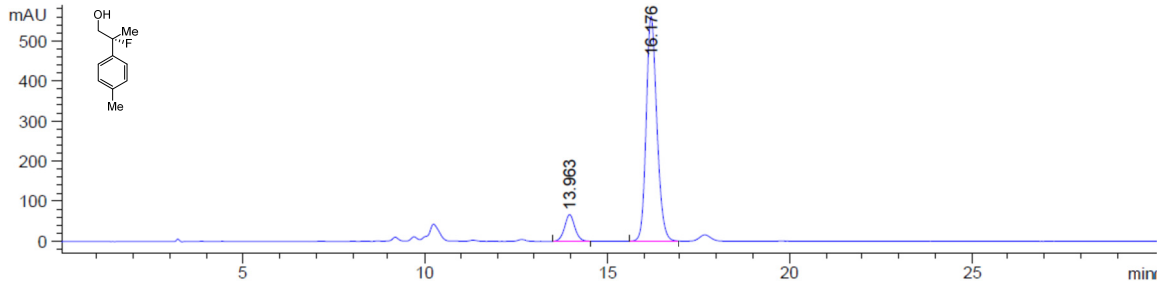
**Product 10d:**

**Racemic Sample:** HPLC (ChiralPak AD-H, 5% *i*PrOH in hexanes, 1 mL/min, 212 nm)




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 13.807 | BB | 0.2965 | 1.07791e4 | 550.35449 | 49.9519 |
| 2 | 16.051 | BB | 0.3078 | 1.07999e4 | 538.82233 | 50.0481 |

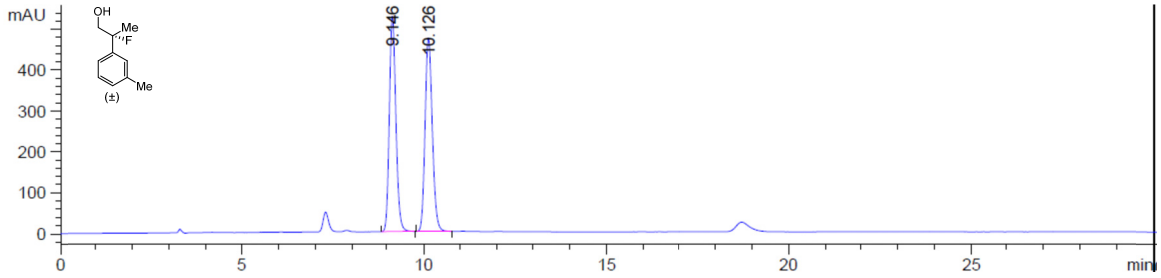
**Enantioenriched Sample:** HPLC (ChiralPak AD-H, 5% *i*PrOH in hexanes, 1 mL/min, 212 nm)




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 13.963 | BB | 0.2972 | 1299.29260 | 66.71931 | 10.2985 |
| 2 | 16.176 | BB | 0.3093 | 1.13170e4 | 561.03461 | 89.7015 |

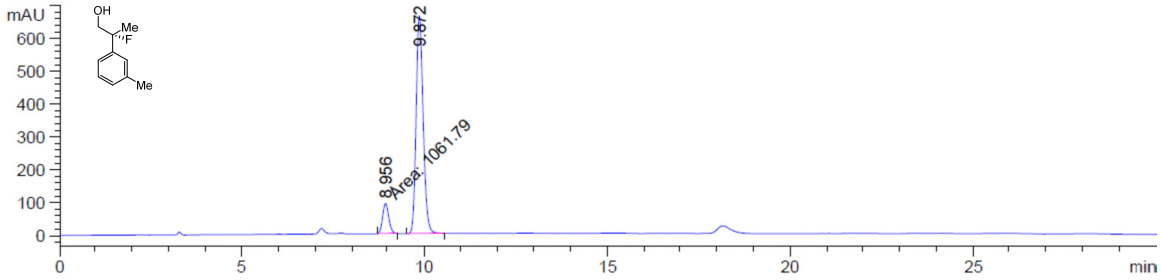
**Product 10e:**

**Racemic Sample:** HPLC (ChiralPak AS-H, 5% *i*PrOH in hexanes, 1 mL/min, 210 nm)




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 9.146 | BB | 0.1903 | 6521.90479 | 527.40594 | 50.1677 |
| 2 | 10.126 | BB | 0.2135 | 6478.29199 | 473.99240 | 49.8323 |

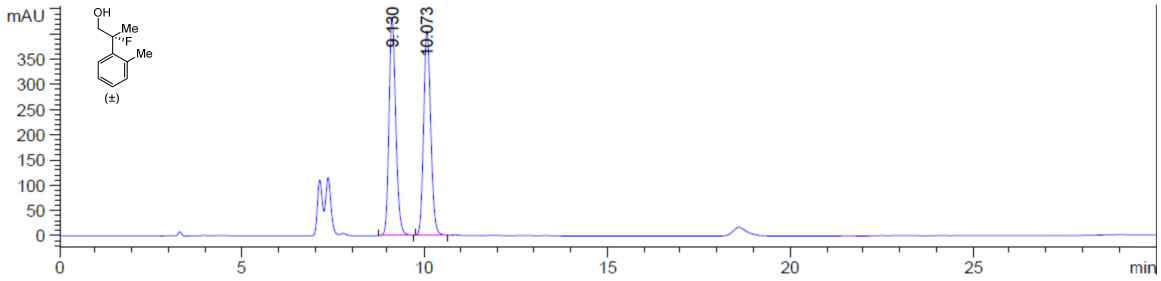
**Enantioenriched Sample:** HPLC (ChiralPak AS-H, 5% *i*PrOH in hexanes, 1 mL/min, 210 nm)




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 8.956 | MM | 0.1936 | 1061.78845 | 91.38493 | 10.7597 |
| 2 | 9.872 | BB | 0.2052 | 8806.43848 | 662.00531 | 89.2403 |

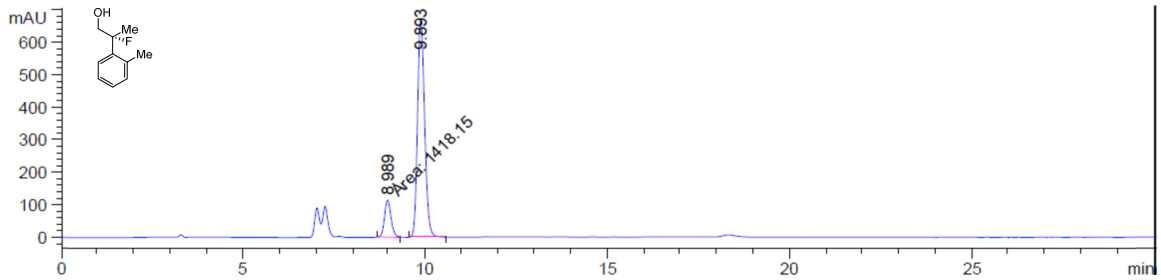
**Product 10f:**

**Racemic Sample:** HPLC (ChiralPak AS-H, 5% *i*PrOH in hexanes, 1 mL/min, 210 nm)



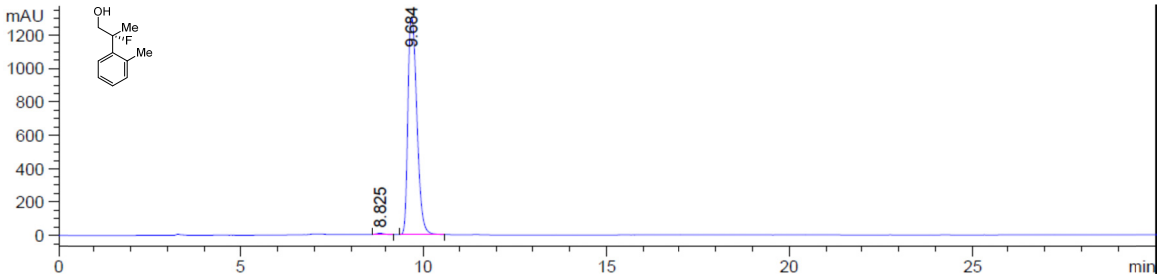

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 9.130 | BB | 0.1970 | 5541.72803 | 433.89447 | 50.3980 |
| 2 | 10.073 | BB | 0.2082 | 5454.19385 | 407.25186 | 49.6020 |

**Enantioenriched Sample:** HPLC (ChiralPak AS-H, 5% *i*PrOH in hexanes, 1 mL/min, 210 nm)




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 8.989 | MM | 0.2087 | 1418.15430 | 113.26067 | 13.6222 |
| 2 | 9.893 | BB | 0.2086 | 8992.43164 | 669.88745 | 86.3778 |

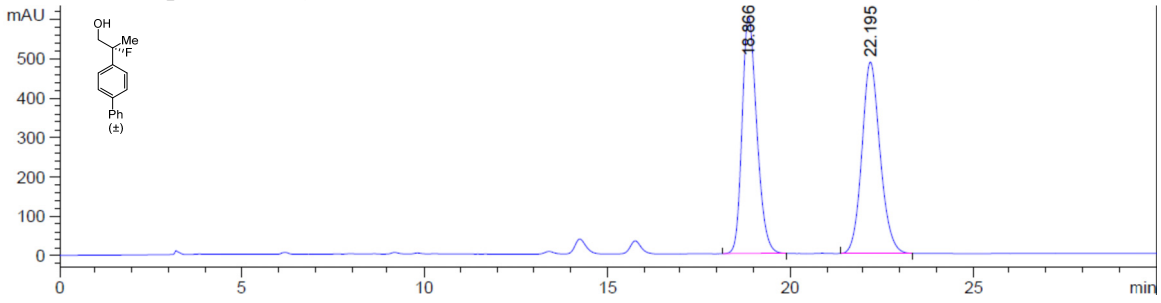
**Recrystallized Sample:** HPLC (ChiralPak AS-H, 5% *i*PrOH in hexanes, 1 mL/min, 210 nm)




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 8.825 | BB | 0.2100 | 118.13734 | 8.30518 | 0.5336 |
| 2 | 9.684 | BB | 0.2669 | 2.20209e4 | 1304.55188 | 99.4664 |

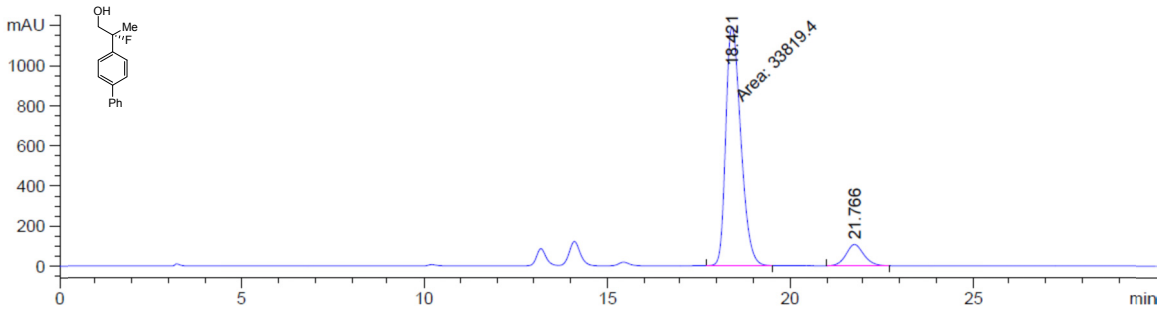
**Product 10g:**

**Racemic Sample:** HPLC (ChiralPak AD-H, 5% *i*PrOH in hexanes, 1 mL/min, 210 nm)



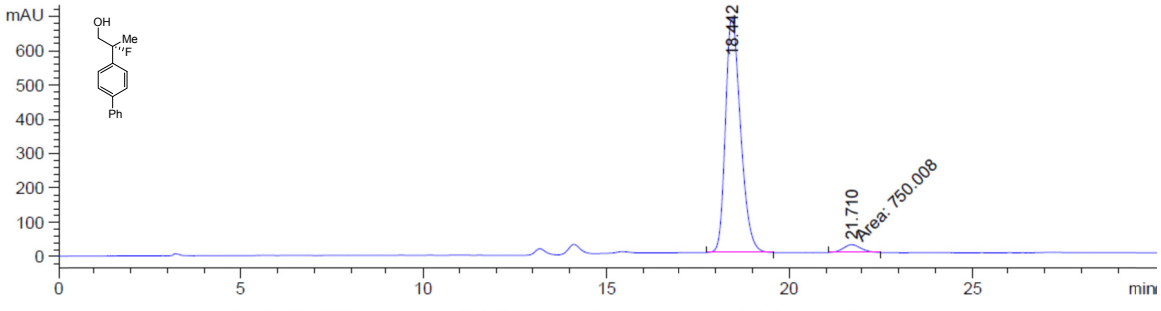

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 18.866 | BB | 0.4285 | 1.67205e4 | 601.09253 | 49.9386 |
| 2 | 22.195 | BB | 0.5254 | 1.67616e4 | 487.22552 | 50.0614 |

**Enantioenriched Sample:** HPLC (ChiralPak AD-H, 5% *i*PrOH in hexanes, 1 mL/min, 210 nm)




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 18.421 | MM | 0.4720 | 3.38194e4 | 1194.30237 | 90.4176 |
| 2 | 21.766 | BB | 0.5098 | 3584.16431 | 106.18194 | 9.5824 |

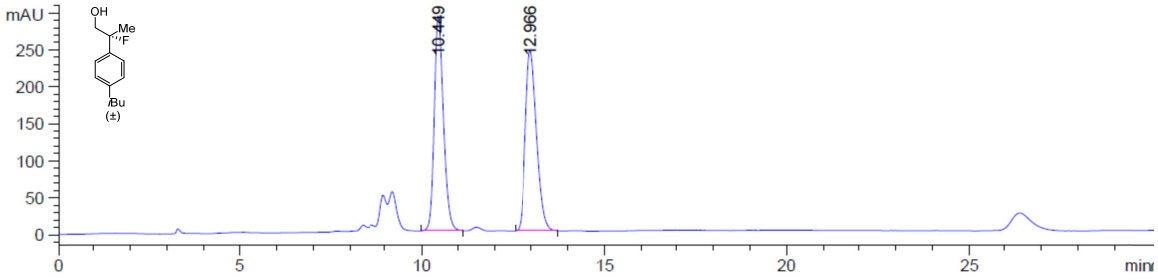
**Recrystallized Sample:** HPLC (ChiralPak AD-H, 5% *i*PrOH in hexanes, 1 mL/min, 210 nm)




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 18.442 | BB | 0.4396 | 1.95212e4 | 686.76831 | 96.3001 |
| 2 | 21.710 | MM | 0.5544 | 750.00812 | 22.54724 | 3.6999 |

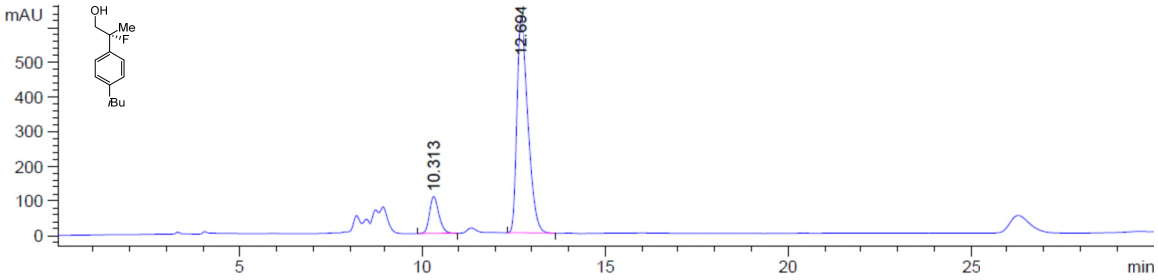
**Product 10h:**

**Racemic Sample:** HPLC (ChiralPak AS-H, 3% *i*PrOH in hexanes, 1 mL/min, 210 nm)



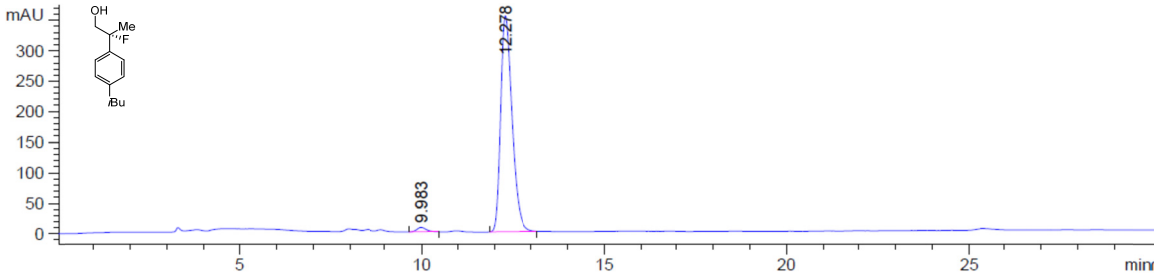

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 10.449 | BB | 0.2653 | 5062.55518 | 290.47849 | 49.0648 |
| 2 | 12.966 | BB | 0.3330 | 5255.54590 | 244.31799 | 50.9352 |

**Enantioenriched Sample:** HPLC (ChiralPak AS-H, 3% *i*PrOH in hexanes, 1 mL/min, 210 nm)




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 10.313 | BB | 0.2692 | 1877.69031 | 105.73077 | 12.0001 |
| 2 | 12.694 | BB | 0.3429 | 1.37696e4 | 625.43268 | 87.9999 |

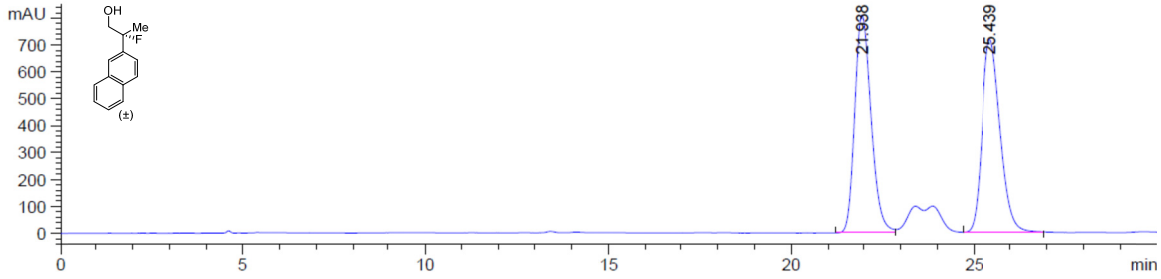
**Recrystallized Sample:** HPLC (ChiralPak AS-H, 3% *i*PrOH in hexanes, 1 mL/min, 210 nm)




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 9.983 | BB | 0.2658 | 131.80803 | 7.40172 | 1.6837 |
| 2 | 12.278 | BB | 0.3335 | 7696.77881 | 354.28949 | 98.3163 |

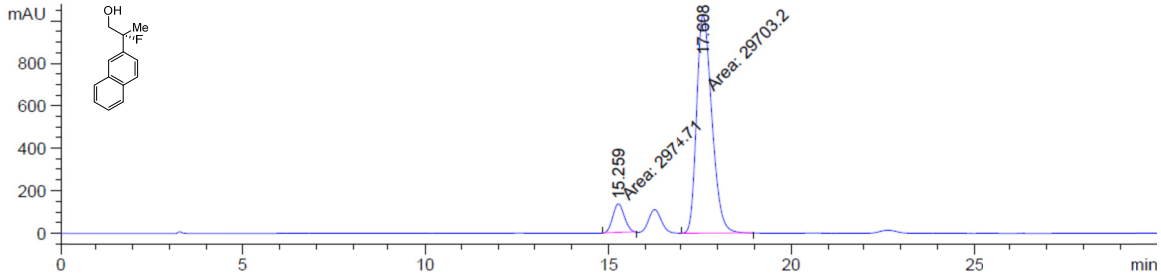
**Product 10i:**

**Racemic Sample:** HPLC (ChiralCel OD-H, 5% *i*PrOH in hexanes, 1 mL/min, 210 nm)



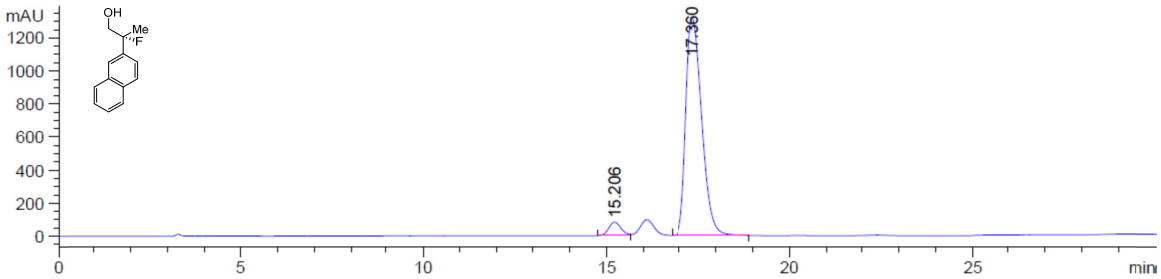

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 21.938 | BV | 0.4794 | 2.49490e4 | 809.93427 | 49.6321 |
| 2 | 25.439 | BB | 0.5472 | 2.53189e4 | 718.35339 | 50.3679 |

**Enantioenriched Sample:** HPLC (ChiralCel OD-H, 5% *i*PrOH in hexanes, 1 mL/min, 210 nm)




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 15.259 | MM | 0.3665 | 2974.70850 | 135.27261 | 9.1031 |
| 2 | 17.608 | MM | 0.4817 | 2.97032e4 | 1027.73291 | 90.8969 |

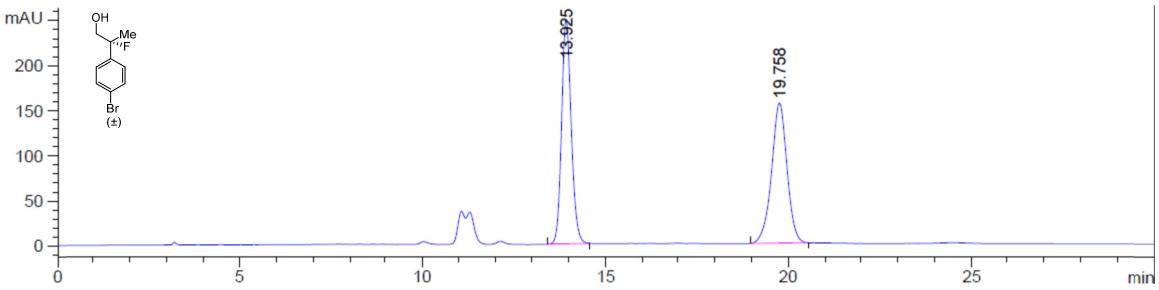
**Recrystallized Sample:** HPLC (ChiralCel OD-H, 5% *i*PrOH in hexanes, 1 mL/min, 210 nm)




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 15.206 | BV | 0.3635 | 1916.15930 | 81.72425 | 4.5950 |
| 2 | 17.360 | BB | 0.4725 | 3.97844e4 | 1324.08276 | 95.4050 |

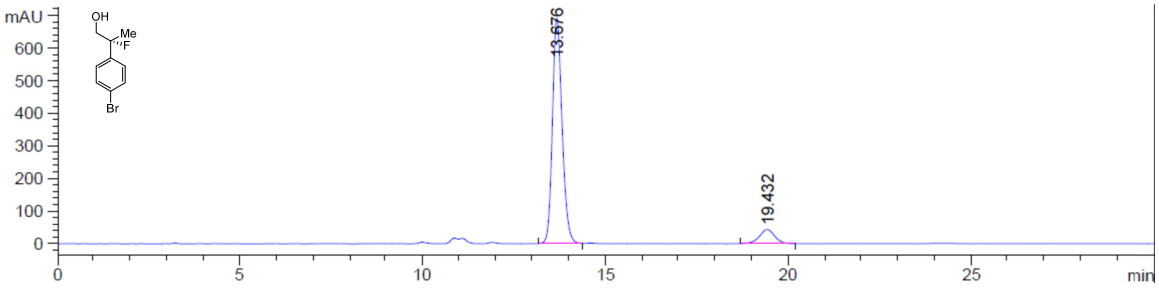
**Product 10j:**

**Racemic Sample:** HPLC (ChiralPak AD-H, 5% *i*PrOH in hexanes, 1 mL/min, 220 nm)



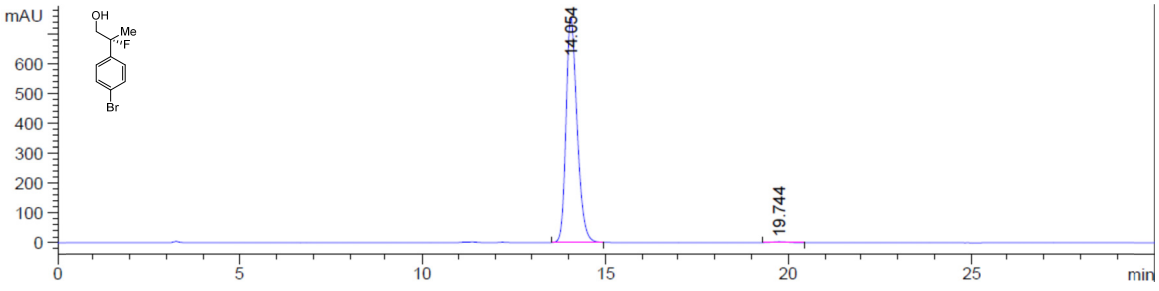

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 13.925 | BB | 0.2775 | 4519.63330 | 249.33534 | 49.9294 |
| 2 | 19.758 | BB | 0.4410 | 4532.40576 | 155.99428 | 50.0706 |

**Enantioenriched Sample:** HPLC (ChiralPak AD-H, 5% *i*PrOH in hexanes, 1 mL/min, 220 nm)




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 13.676 | BB | 0.2807 | 1.26003e4 | 691.08923 | 91.0264 |
| 2 | 19.432 | BB | 0.4286 | 1242.16907 | 43.30905 | 8.9736 |

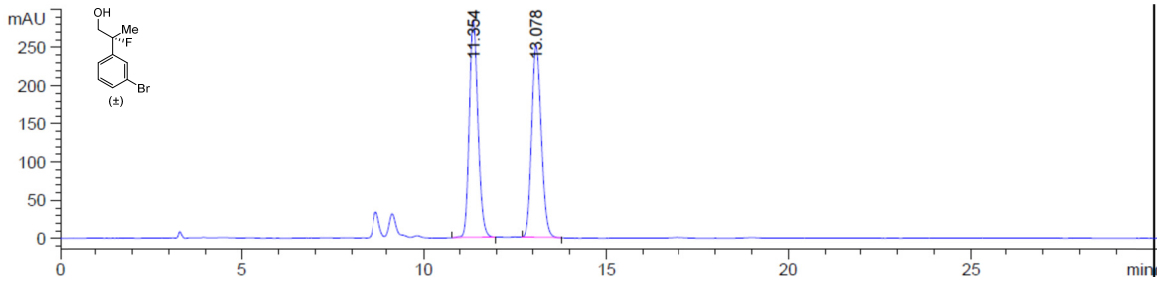
**Recrystallized Sample:** HPLC (ChiralPak AD-H, 5% *i*PrOH in hexanes, 1 mL/min, 220 nm)




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 14.054 | BB | 0.3188 | 1.57277e4 | 755.73529 | 99.5113 |
| 2 | 19.744 | BB | 0.3305 | 77.23315 | 2.82886 | 0.4887 |

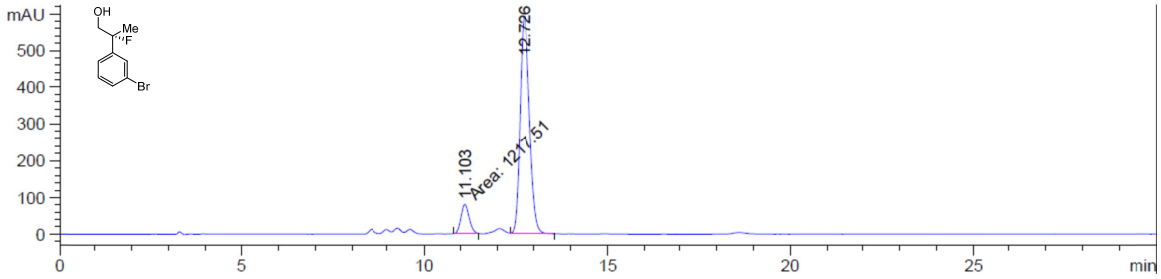
**Product 10k:**

**Racemic Sample:** HPLC (ChiralPak AS-H, 5% *i*PrOH in hexanes, 1 mL/min, 210 nm)




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 11.354 | BB | 0.2545 | 4700.10889 | 284.83240 | 50.2724 |
| 2 | 13.078 | BB | 0.2854 | 4649.18018 | 251.79150 | 49.7276 |

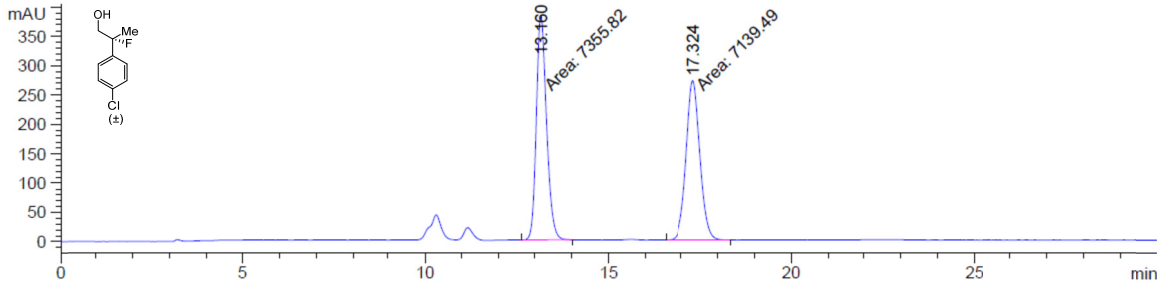
**Enantioenriched Sample:** HPLC (ChiralPak AS-H, 5% *i*PrOH in hexanes, 1 mL/min, 210 nm)




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 11.103 | MM | 0.2584 | 1217.50769 | 78.51477 | 9.9902 |
| 2 | 12.726 | VB | 0.2879 | 1.09695e4 | 592.88409 | 90.0098 |

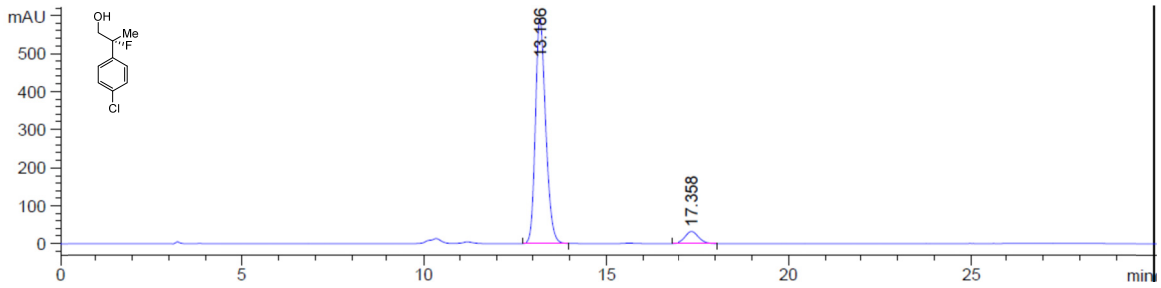
**Product 10l:**

**Racemic Sample:** HPLC (ChiralPak AD-H, 5% *i*PrOH in hexanes, 1 mL/min, 220 nm)



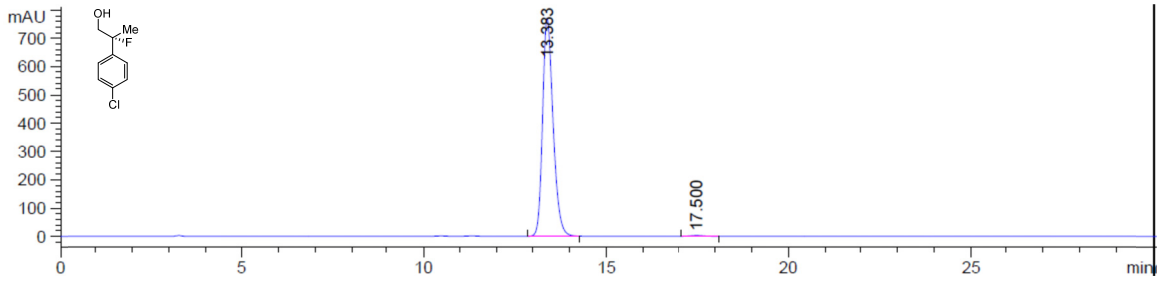

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 13.160 | MM | 0.3193 | 7355.82471 | 383.96832 | 50.7462 |
| 2 | 17.324 | MM | 0.4361 | 7139.49219 | 272.83130 | 49.2538 |

**Enantioenriched Sample:** HPLC (ChiralPak AD-H, 5% *i*PrOH in hexanes, 1 mL/min, 220 nm)




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 13.186 | BB | 0.2985 | 1.15024e4 | 592.57880 | 93.1856 |
| 2 | 17.358 | BB | 0.3975 | 841.14270 | 32.12370 | 6.8144 |

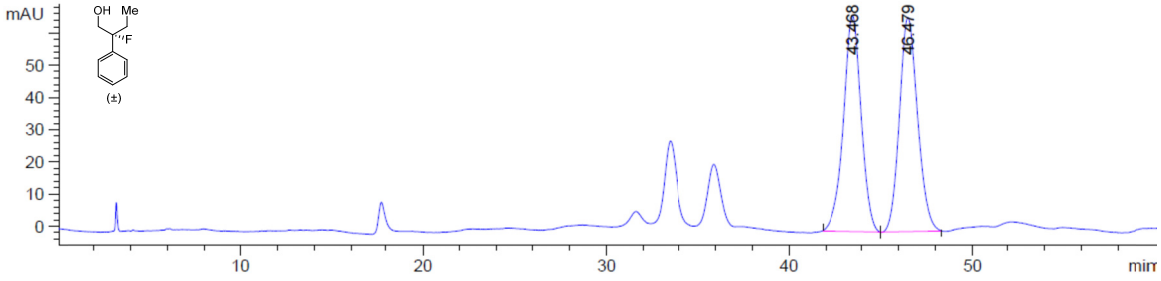
**Recrystallized Sample:** HPLC (ChiralPak AD-H, 5% *i*PrOH in hexanes, 1 mL/min, 220 nm)




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 13.383 | BB | 0.3064 | 1.53830e4 | 772.29919 | 99.5039 |
| 2 | 17.500 | BB | 0.3465 | 76.68895 | 3.03772 | 0.4961 |

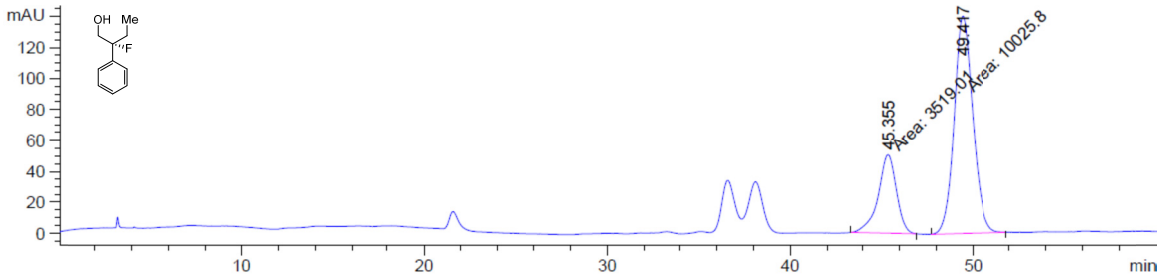
**Product 10n:**

**Racemic Sample:** HPLC (ChiralPak AD-H, 2% *i*PrOH in hexanes, 1 mL/min, 210 nm)




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 43.468 | BV | 0.8969 | 4504.08496 | 67.28899 | 49.6757 |
| 2 | 46.479 | VB | 0.9903 | 4562.88770 | 66.51547 | 50.3243 |

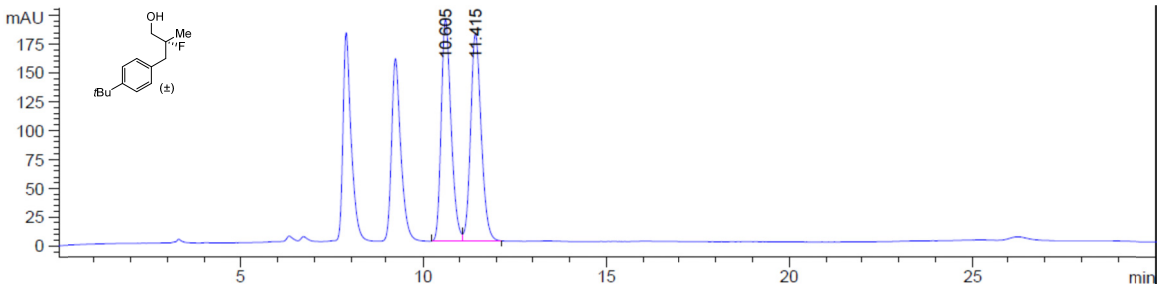
**Enantioenriched Sample:** HPLC (ChiralPak AD-H, 2% *i*PrOH in hexanes, 1 mL/min, 210 nm)




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 45.355 | MM | 1.1519 | 3519.00732 | 50.91728 | 25.9804 |
| 2 | 49.417 | MM | 1.1881 | 1.00258e4 | 140.64679 | 74.0196 |

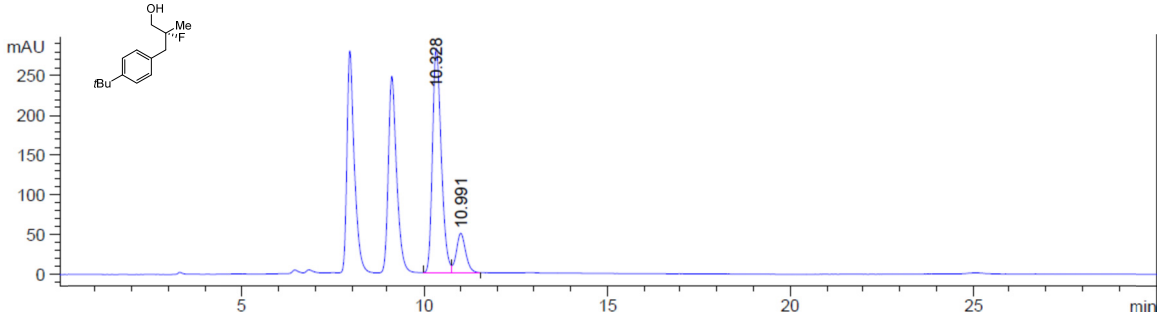
**Product 10o:**

**Racemic Sample:** HPLC (ChiralPak AS-H, 3% *i*PrOH in hexanes, 1 mL/min, 218 nm)




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 10.605 | BV | 0.2866 | 3573.31885 | 192.47142 | 49.7920 |
| 2 | 11.415 | VB | 0.3052 | 3603.17480 | 180.27177 | 50.2080 |

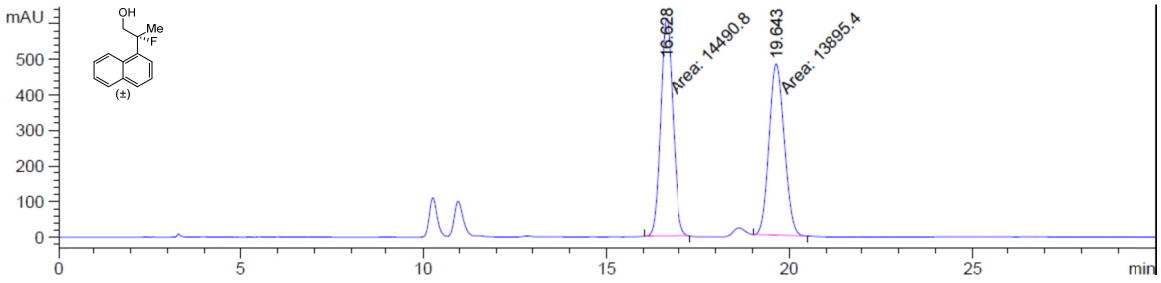
**Enantioenriched Sample:** HPLC (ChiralPak AS-H, 3% *i*PrOH in hexanes, 1 mL/min, 218 nm)




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 10.328 | BV | 0.2551 | 4674.09326 | 282.44897 | 84.3507 |
| 2 | 10.991 | VB | 0.2671 | 867.17065 | 49.32686 | 15.6493 |

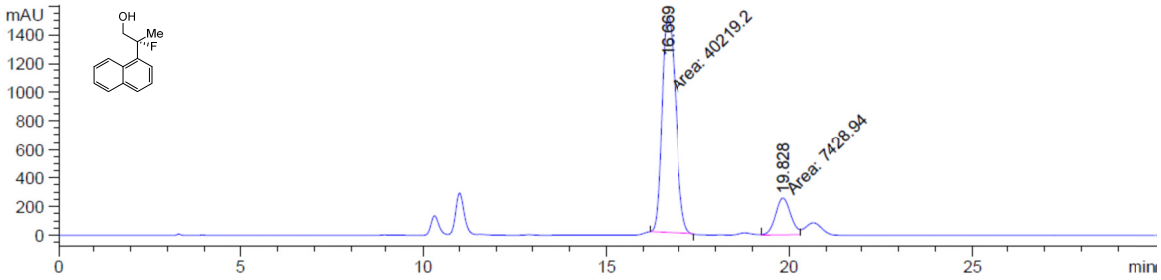
**Product 10p:**

**Racemic Sample:** HPLC (ChiralPak AS-H, 5% *i*PrOH in hexanes, 1 mL/min, 210 nm)



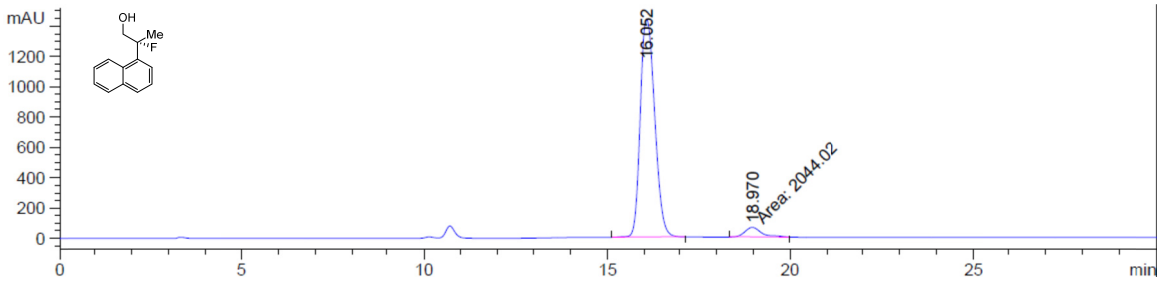

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 16.628 | MM | 0.3937 | 1.44908e4 | 613.41718 | 51.0488 |
| 2 | 19.643 | MM | 0.4797 | 1.38954e4 | 482.75018 | 48.9512 |

**Enantioenriched Sample:** HPLC (ChiralPak AS-H, 5% *i*PrOH in hexanes, 1 mL/min, 210 nm)




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 16.669 | MM | 0.4430 | 4.02192e4 | 1513.08484 | 84.4088 |
| 2 | 19.828 | MM | 0.4829 | 7428.93896 | 256.37814 | 15.5912 |

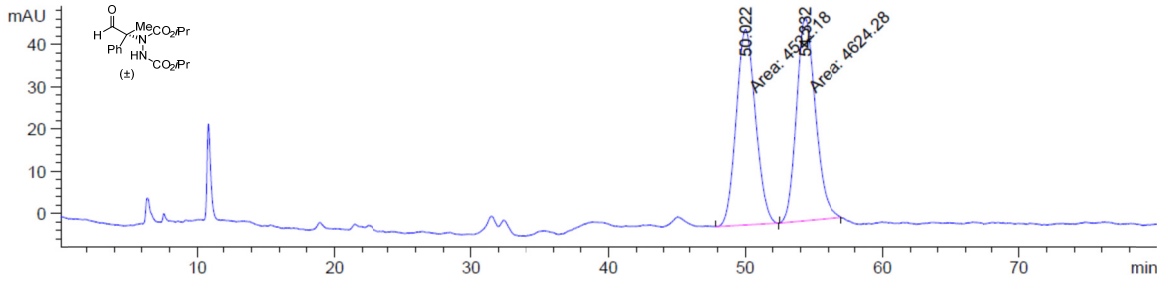
**Recrystallized Sample:** HPLC (ChiralPak AS-H, 5% *i*PrOH in hexanes, 1 mL/min, 210 nm)




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 16.052 | BB | 0.4297 | 3.91904e4 | 1439.15405 | 95.0429 |
| 2 | 18.970 | MM | 0.5347 | 2044.01855 | 63.70945 | 4.9571 |

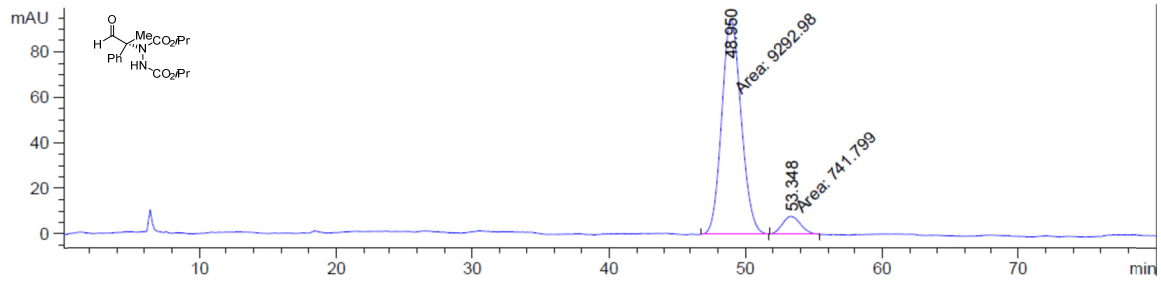
**Product 13:**

**Racemic Sample:** HPLC (ChiralPak AD-H, 5% *i*PrOH in hexanes, 0.5 mL/min, 210 nm)




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 50.022 | MM | 1.6258 | 4522.17822 | 46.35797 | 49.4418 |
| 2 | 54.332 | MM | 1.5978 | 4624.28418 | 48.23573 | 50.5582 |

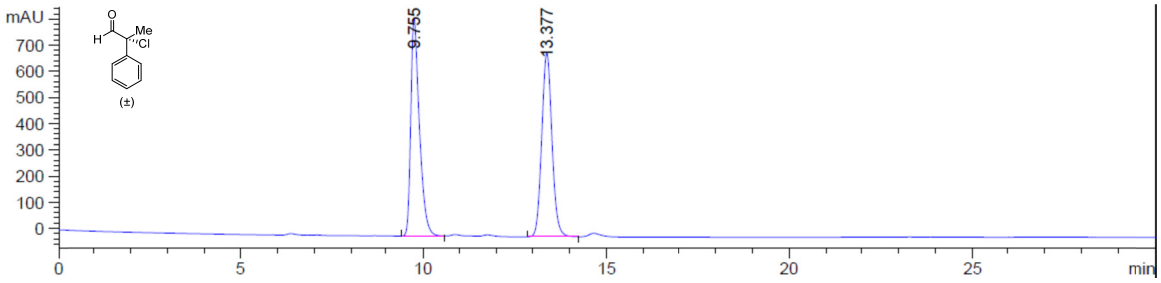
**Enantioenriched Sample:** HPLC (ChiralPak AD-H, 5% *i*PrOH in hexanes, 0.5 mL/min, 210 nm)




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 48.950 | MM | 1.6318 | 9292.97949 | 94.91341 | 92.6077 |
| 2 | 53.348 | MM | 1.5616 | 741.79852 | 7.91699 | 7.3923 |

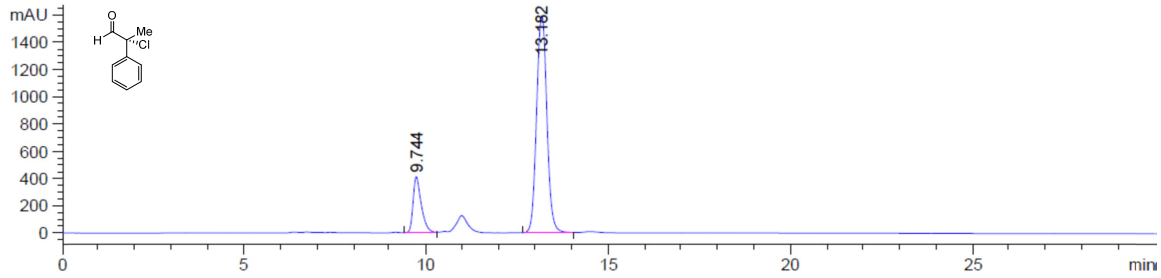
**Product 15:**

**Racemic Sample:** HPLC (ChiralPak AD-H, 2% *i*PrOH in hexanes, 0.5 mL/min, 210 nm)




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 9.755 | BB | 0.2424 | 1.36122e4 | 834.01392 | 49.9881 |
| 2 | 13.377 | BB | 0.2999 | 1.36187e4 | 703.23041 | 50.0119 |

**Enantioenriched Sample:** HPLC (ChiralPak AD-H, 5% *i*PrOH in hexanes, 0.5 mL/min, 210 nm)

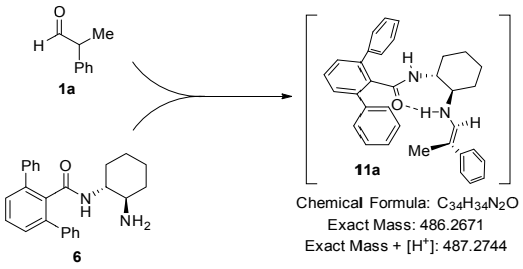


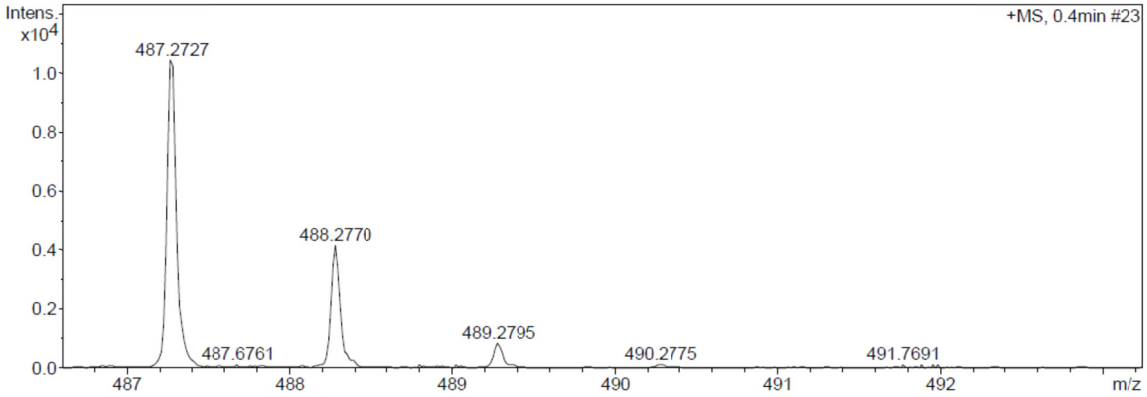

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 9.744 | VV | 0.2281 | 6421.30713 | 411.38879 | 17.0662 |
| 2 | 13.182 | BB | 0.3083 | 3.12046e4 | 1594.92261 | 82.9338 |

## 7. Mass Spectrometry and Computational Procedures and Results

A 1-dram vial was charged with aldehyde substrate **1a** (20 μL, 20 mg, 0.15 mmol). No precautions were taken to ensure dryness of vial or to exclude air or moisture. The aldehyde was then dissolved in THF (0.5 mL, 0.3 M). Solid catalyst **6** (11.1 mg, 0.03 mmol, 20 mol%) was added, followed by TFA (2.3 μL, 3.4 mg, 0.03 mmol, 20 mol%) by syringe. $NaHCO_3$ (12.6 mg, 0.15 mmol, 1.0 equiv) was added to the vial, which was then sealed. The mixture was allowed to stir for 10 min, then an aliquot of this mixture was submitted to mass spectrometry (ESI-TOF).

**Scheme S17.**




Calculations were performed at Harvard University using Gaussian 09[22] at the B3LYP[23] level of density functional theory with the 6-31G(d)[24] basis set. Relative energies are for uncorrected electronic energy differences. Figures were generated using CYLview.[25]

---

[22] Gaussian 09, Revision A.1, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg,

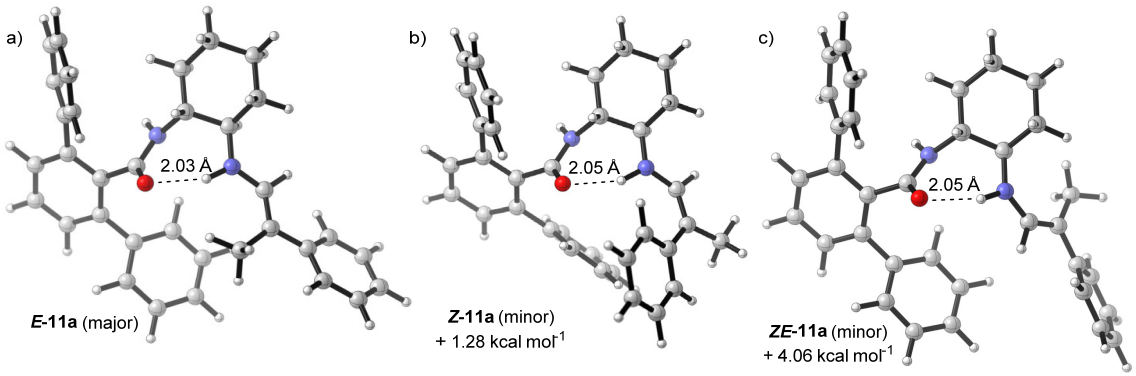



**Figure S1.** Lowest energy structures for various geometries of putative enamine **11a**.

The lowest energy structure for proposed enamine intermediate **11a** was located computationally (Figure S1), revealing a key intramolecular hydrogen bond between the benzamide carbonyl and the enamine NH. This stabilizing interaction appears to rigidify the catalyst backbone and cause the terphenyl moiety to project one of its aryl rings directly behind one face of the reactive nucleophile. Although the origin of stereoselectivity in these α-functionalization reactions is not fully understood, we speculate that it is primarily determined by the *E*/Z ratio of intermediate **11a**, with the electrophilic component of the reaction approaching the enamine almost exclusively from the exposed front face. The lowest energy calculated structures for ***E*-11a** (Figure S1a) and ***Z*-11a** (Figure S1b) are separated by a difference of 1.28 kcal $mol^{-1}$, owing to a steric clash between substrate and catalyst phenyl rings in ***Z*-11a**. At room temperature, this would correspond to an 8.8:1 ratio of ***E*-11a** to ***Z*-11a**, or approximately 90% *ee*, which is precisely what we observe in the α-hydroxylation of substrate **1a** to product **7a**.

However, it should be considered that these calculations represent enamine ground states. Although the steric destabilization of ***Z*-11a** almost certainly still exists in the subsequent transition state for nucleophilic attack, the identity of the electrophile must also play a role in the location of this saddle point along a reaction coordinate. Different electrophiles, much like different acids, bases, and solvents, may also influence the partitioning of enamine **11a** between *E* and *Z* isomers. Therefore, enantioselectivities do not remain constant with different classes of electrophiles, although they are generally high.

---

J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

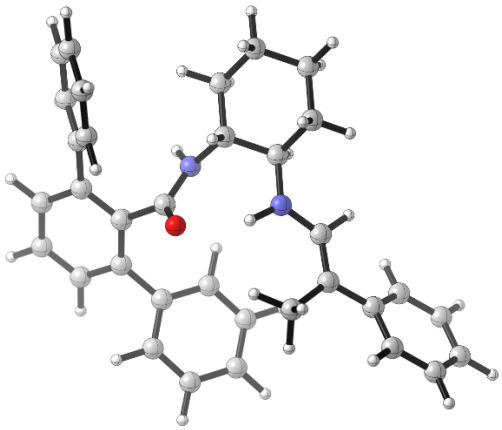
[23] B3LYP = Becke-3-Lee-Yang-Parr density functional theory: (a) Becke, A. D. *J. Chem. Phys.* **1993***, 98*, 1372–1377. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785–789.

[24] (a) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971***, 54*, 724–728. (b) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys*. **1972,** *56*, 2257–2261. (c) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta.* **1973***, 28*, 213–223.

[25] Legault, C. Y., *CYLview*, version 1.0b; Université de Sherbrooke, 2009; http://www.cylview.org.

Finally, we have located a third enamine **11a** structure by rotating the C–N bond between catalyst **6** and substrate **1a** in ***E*-11a** (Figure S1c). This intermediate (***ZE*-11a**), which would also provide the minor enantiomers of products **7a** and **9a**, maintains an *E*-geometry on the enamine bond, but has *Z*-geometry on the C–N bond. This stationary point lies 4.06 kcal $mol^{-1}$ above ***E*-11a**, and is therefore not considered a significant component in the overall mechanism.

***E*-11a**:



E(RB3LYP): –1500.85238008
Zero-point correction: 0.601051 (Hartree/Particle)
Thermal correction to Energy: 0.633405
Thermal correction to Enthalpy: 0.634349
Thermal correction to Gibbs Free Energy: 0.534510

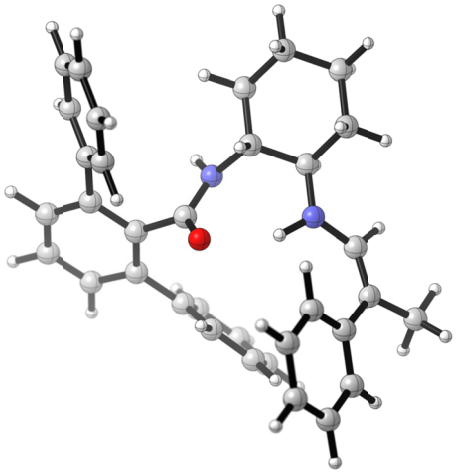
Cartesian coordinates:

| | | | |
|---|---|---|---|
| C | 2.19453 | 3.5984 | -0.75084 |
| C | 1.37754 | 2.40942 | -1.29783 |
| C | -0.12724 | 2.6163 | -0.99775 |
| C | -0.6114 | 3.95419 | -1.58536 |
| C | 0.21864 | 5.14309 | -1.08072 |
| C | 1.71497 | 4.93127 | -1.34339 |
| H | 1.49228 | 2.35883 | -2.39044 |
| H | 2.08752 | 3.61474 | 0.34232 |
| H | 3.26063 | 3.4473 | -0.95966 |
| H | -0.55171 | 3.90812 | -2.68412 |
| H | -1.66839 | 4.08476 | -1.32827 |
| H | -0.1282 | 6.06391 | -1.56215 |
| H | 0.05051 | 5.27094 | -0.00271 |
| H | 1.90502 | 4.94193 | -2.42636 |
| H | 2.29859 | 5.75474 | -0.91739 |

| | | | |
|---|---|---|---|
| H | -0.25941 | 2.62845 | 0.08924 |
| N | -0.95721 | 1.52475 | -1.5054 |
| C | -1.50661 | 0.52438 | -0.75417 |
| C | -2.55706 | -0.16485 | -1.32505 |
| C | -3.82166 | 0.45336 | -1.32 |
| C | -2.34627 | -1.40966 | -1.9495 |
| C | -4.8985 | -0.21465 | -1.91496 |
| C | -3.45493 | -2.0485 | -2.52542 |
| C | -4.7181 | -1.46363 | -2.50433 |
| H | -5.87587 | 0.2585 | -1.91633 |
| H | -3.30844 | -3.00263 | -3.02246 |
| H | -5.55862 | -1.97288 | -2.96667 |
| H | -1.32073 | 1.65028 | -2.44411 |
| N | 1.81878 | 1.129 | -0.72349 |
| C | 2.95007 | 0.48151 | -1.03976 |
| H | 1.15288 | 0.69272 | -0.07017 |
| C | -4.02684 | 1.79426 | -0.69398 |
| C | -3.48941 | 2.94947 | -1.28516 |
| C | -4.7816 | 1.92609 | 0.48004 |
| C | -3.69598 | 4.20553 | -0.71258 |
| H | -2.94232 | 2.86667 | -2.22285 |
| C | -4.98838 | 3.18257 | 1.05218 |
| H | -5.19895 | 1.03814 | 0.94614 |
| C | -4.44499 | 4.32402 | 0.45994 |
| H | -3.28719 | 5.09148 | -1.19105 |
| H | -5.57764 | 3.26899 | 1.96096 |
| H | -4.61283 | 5.3015 | 0.90334 |
| C | -1.01163 | -2.0652 | -2.03587 |
| C | 0.11253 | -1.38324 | -2.52978 |
| C | -0.8709 | -3.42007 | -1.69391 |
| C | 1.33775 | -2.03335 | -2.67357 |
| H | 0.01687 | -0.34523 | -2.83346 |
| C | 0.35427 | -4.07219 | -1.83998 |
| H | -1.73034 | -3.96104 | -1.30804 |
| C | 1.46452 | -3.38068 | -2.32815 |
| H | 2.18948 | -1.49215 | -3.07743 |
| H | 0.43669 | -5.12552 | -1.58407 |
| H | 2.41536 | -3.89108 | -2.45577 |
| O | -1.03038 | 0.18617 | 0.5511 |
| H | 3.61783 | 0.8949 | -1.76647 |
| C | 3.25059 | -0.70914 | -0.43235 |

| | | | |
|---|---|---|---|
| C | 2.28765 | -1.30174 | 0.6132 |
| H | 2.28896 | -0.68636 | 1.48853 |
| H | 1.29894 | -1.34052 | 0.20596 |
| H | 2.606 | -2.29007 | 0.87156 |
| C | 4.54911 | -1.45365 | -0.79449 |
| C | 4.85358 | -2.66606 | -0.17494 |
| C | 5.41971 | -0.9169 | -1.74274 |
| C | 6.02911 | -3.34119 | -0.50338 |
| H | 4.16683 | -3.08929 | 0.57232 |
| C | 6.596 | -1.59204 | -2.07096 |
| H | 5.17948 | 0.03841 | -2.23157 |
| C | 6.90057 | -2.80392 | -1.45118 |
| H | 6.26932 | -4.29667 | -0.01504 |
| H | 7.28232 | -1.16861 | -2.81861 |
| H | 7.82755 | -3.33625 | -1.70963 |

***Z*-11a**:



E(RB3LYP): –1500.85033821
Zero-point correction: 0.601824 (Hartree/Particle)
Thermal correction to Energy: 0.633869
Thermal correction to Enthalpy: 0.634813
Thermal correction to Gibbs Free Energy: 0.535909

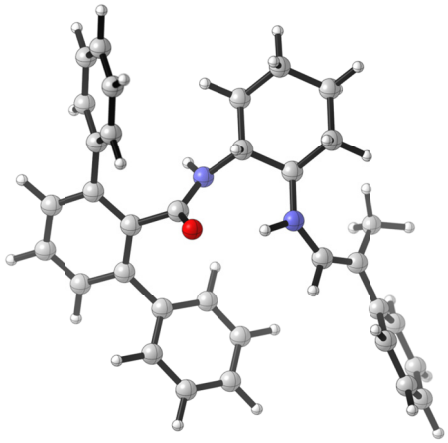
Cartesian coordinates:

| | | | |
|---|---|---|---|
| C | 2.19453 | 3.5984 | -0.75084 |
| C | 1.37754 | 2.40942 | -1.29783 |
| C | -0.12724 | 2.6163 | -0.99775 |
| C | -0.6114 | 3.95419 | -1.58536 |

| | | | |
|---|---|---|---|
| C | 0.21864 | 5.14309 | -1.08072 |
| C | 1.71497 | 4.93127 | -1.34339 |
| H | 1.49228 | 2.35883 | -2.39044 |
| H | 2.08752 | 3.61474 | 0.34232 |
| H | 3.26063 | 3.4473 | -0.95966 |
| H | -0.55171 | 3.90812 | -2.68412 |
| H | -1.66839 | 4.08476 | -1.32827 |
| H | -0.1282 | 6.06391 | -1.56215 |
| H | 0.05051 | 5.27094 | -0.00271 |
| H | 1.90502 | 4.94193 | -2.42636 |
| H | 2.29859 | 5.75474 | -0.91739 |
| H | -0.25941 | 2.62845 | 0.08924 |
| N | -0.95721 | 1.52475 | -1.5054 |
| C | -1.50661 | 0.52438 | -0.75417 |
| C | -2.55706 | -0.16485 | -1.32505 |
| C | -3.82166 | 0.45336 | -1.32 |
| C | -2.34627 | -1.40966 | -1.9495 |
| C | -4.8985 | -0.21465 | -1.91496 |
| C | -3.45493 | -2.0485 | -2.52542 |
| C | -4.7181 | -1.46363 | -2.50433 |
| H | -5.87587 | 0.2585 | -1.91633 |
| H | -3.30844 | -3.00263 | -3.02246 |
| H | -5.55862 | -1.97288 | -2.96667 |
| H | -1.32073 | 1.65028 | -2.44411 |
| N | 1.81878 | 1.129 | -0.72349 |
| C | 2.95007 | 0.48151 | -1.03976 |
| H | 1.15288 | 0.69272 | -0.07017 |
| C | -4.02684 | 1.79426 | -0.69398 |
| C | -3.48941 | 2.94947 | -1.28516 |
| C | -4.7816 | 1.92609 | 0.48004 |
| C | -3.69598 | 4.20553 | -0.71258 |
| H | -2.94232 | 2.86667 | -2.22285 |
| C | -4.98838 | 3.18257 | 1.05218 |
| H | -5.19895 | 1.03814 | 0.94614 |
| C | -4.44499 | 4.32402 | 0.45994 |
| H | -3.28719 | 5.09148 | -1.19105 |
| H | -5.57764 | 3.26899 | 1.96096 |
| H | -4.61283 | 5.3015 | 0.90334 |
| C | -1.01163 | -2.0652 | -2.03587 |
| C | 0.11253 | -1.38324 | -2.52978 |
| C | -0.8709 | -3.42007 | -1.69391 |

| | | | |
|---|---|---|---|
| C | 1.33775 | -2.03335 | -2.67357 |
| H | 0.01687 | -0.34523 | -2.83346 |
| C | 0.35427 | -4.07219 | -1.83998 |
| H | -1.73034 | -3.96104 | -1.30804 |
| C | 1.46452 | -3.38068 | -2.32815 |
| H | 2.18948 | -1.49215 | -3.07743 |
| H | 0.43669 | -5.12552 | -1.58407 |
| H | 2.41536 | -3.89108 | -2.45577 |
| O | -1.03038 | 0.18617 | 0.5511 |
| H | 3.61783 | 0.8949 | -1.76647 |
| C | 3.25059 | -0.70914 | -0.43235 |
| C | 4.55018 | -1.45033 | -0.79745 |
| H | 4.48462 | -1.81119 | -1.80263 |
| H | 5.37932 | -0.77933 | -0.71274 |
| H | 4.68955 | -2.27548 | -0.13066 |
| C | 2.29046 | -1.30531 | 0.61375 |
| C | 2.59806 | -2.51792 | 1.23134 |
| C | 1.11454 | -0.6324 | 0.94489 |
| C | 1.72917 | -3.05775 | 2.17959 |
| H | 3.52543 | -3.04807 | 0.97045 |
| C | 0.24502 | -1.17269 | 1.89317 |
| H | 0.87233 | 0.32371 | 0.4586 |
| C | 0.55238 | -2.38525 | 2.51022 |
| H | 1.97137 | -4.01355 | 2.66632 |
| H | -0.68212 | -0.64198 | 2.15405 |
| H | -0.13271 | -2.81132 | 3.25761 |

***ZE*-11a**:



E(RB3LYP): –1500.84591639
Zero-point correction: 0.602142 (Hartree/Particle)
Thermal correction to Energy: 0.634163
Thermal correction to Enthalpy: 0.635107
Thermal correction to Gibbs Free Energy: 0.536151

Cartesian coordinates:

| | | | |
|---|---|---|---|
| C | 6.15171 | 0.40262 | -1.41019 |
| C | 5.01241 | 0.35631 | -2.44952 |
| C | 5.46033 | 1.04917 | -3.75968 |
| C | 6.74556 | 0.39551 | -4.29872 |
| C | 7.87661 | 0.39829 | -3.26054 |
| C | 7.43066 | -0.2561 | -1.94685 |
| H | 4.78146 | -0.69116 | -2.69239 |
| H | 6.34817 | 1.45466 | -1.16254 |
| H | 5.83051 | -0.08387 | -0.48113 |
| H | 6.52541 | -0.64208 | -4.59521 |
| H | 7.05278 | 0.92826 | -5.20545 |
| H | 8.75128 | -0.11959 | -3.66887 |
| H | 8.18809 | 1.43372 | -3.06667 |
| H | 7.25118 | -1.32849 | -2.11068 |
| H | 8.22453 | -0.18522 | -1.19523 |
| H | 5.65508 | 2.10374 | -3.53809 |
| N | 4.42416 | 1.02544 | -4.79111 |
| C | 3.63152 | 2.07891 | -5.15009 |
| C | 3.00903 | 1.98723 | -6.3783 |
| C | 3.78308 | 2.25562 | -7.52295 |
| C | 1.6669 | 1.57111 | -6.47551 |
| C | 3.1812 | 2.14536 | -8.78207 |
| C | 1.10071 | 1.48278 | -7.75635 |

| | | | |
|---|---|---|---|
| C | 1.84435 | 1.77195 | -8.89718 |
| H | 3.77409 | 2.34872 | -9.66878 |
| H | 0.07119 | 1.15112 | -7.85097 |
| H | 1.38679 | 1.68555 | -9.87837 |
| H | 4.45257 | 0.23244 | -5.42309 |
| N | 3.78714 | 0.99972 | -1.95073 |
| C | 2.95007 | 0.48151 | -1.03976 |
| H | 3.55166 | 1.89533 | -2.40133 |
| C | 5.21882 | 2.65367 | -7.41237 |
| C | 6.18903 | 1.72479 | -7.00164 |
| C | 5.62663 | 3.95383 | -7.74197 |
| C | 7.53373 | 2.08901 | -6.91604 |
| H | 5.89273 | 0.69885 | -6.78929 |
| C | 6.9717 | 4.31761 | -7.65667 |
| H | 4.88322 | 4.68002 | -8.05798 |
| C | 7.9275 | 3.38852 | -7.24173 |
| H | 8.27444 | 1.35416 | -6.61221 |
| H | 7.27275 | 5.32844 | -7.91778 |
| H | 8.97457 | 3.67203 | -7.18251 |
| C | 0.83463 | 1.21259 | -5.29346 |
| C | 1.27828 | 0.28707 | -4.33464 |
| C | -0.45902 | 1.74233 | -5.15834 |
| C | 0.45711 | -0.09345 | -3.27381 |
| H | 2.26143 | -0.16145 | -4.43993 |
| C | -1.2825 | 1.36007 | -4.09843 |
| H | -0.81614 | 2.46129 | -5.89029 |
| C | -0.82677 | 0.4423 | -3.15019 |
| H | 0.81274 | -0.82698 | -2.55485 |
| H | -2.28616 | 1.77069 | -4.02205 |
| H | -1.47224 | 0.1331 | -2.33247 |
| O | 3.43561 | 3.22075 | -4.31181 |
| H | 2.04761 | 0.99803 | -0.78746 |
| C | 3.25059 | -0.70914 | -0.43235 |
| C | 4.55018 | -1.45033 | -0.79745 |
| H | 4.48462 | -1.81119 | -1.80263 |
| H | 5.37932 | -0.77933 | -0.71274 |
| H | 4.68955 | -2.27548 | -0.13066 |
| C | 2.29046 | -1.30531 | 0.61375 |
| C | 2.59806 | -2.51792 | 1.23134 |
| C | 1.11454 | -0.6324 | 0.94489 |
| C | 1.72917 | -3.05775 | 2.17959 |

| | | | |
|---|---|---|---|
| H | 3.52543 | -3.04807 | 0.97045 |
| C | 0.24502 | -1.17269 | 1.89317 |
| H | 0.87233 | 0.32371 | 0.4586 |
| C | 0.55238 | -2.38525 | 2.51022 |
| H | 1.97137 | -4.01355 | 2.66632 |
| H | -0.68212 | -0.64198 | 2.15405 |
| H | -0.13271 | -2.81132 | 3.25761 |

**8. Supplementary Optimization Tables**

**Table S1.** α-Hydroxylation Catalyst Screen.

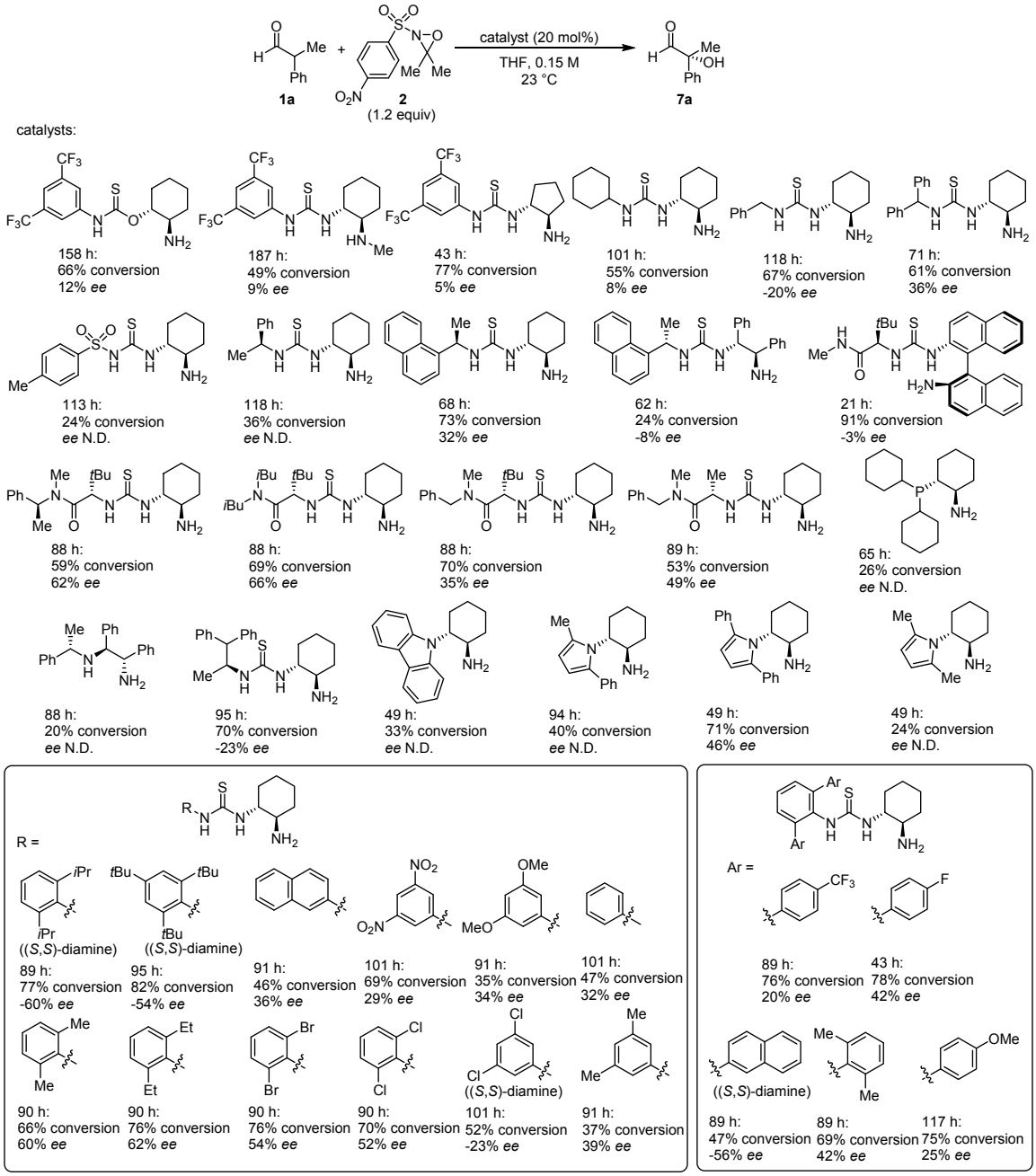



**Table S2.** α-Fluorination Catalyst Screen.

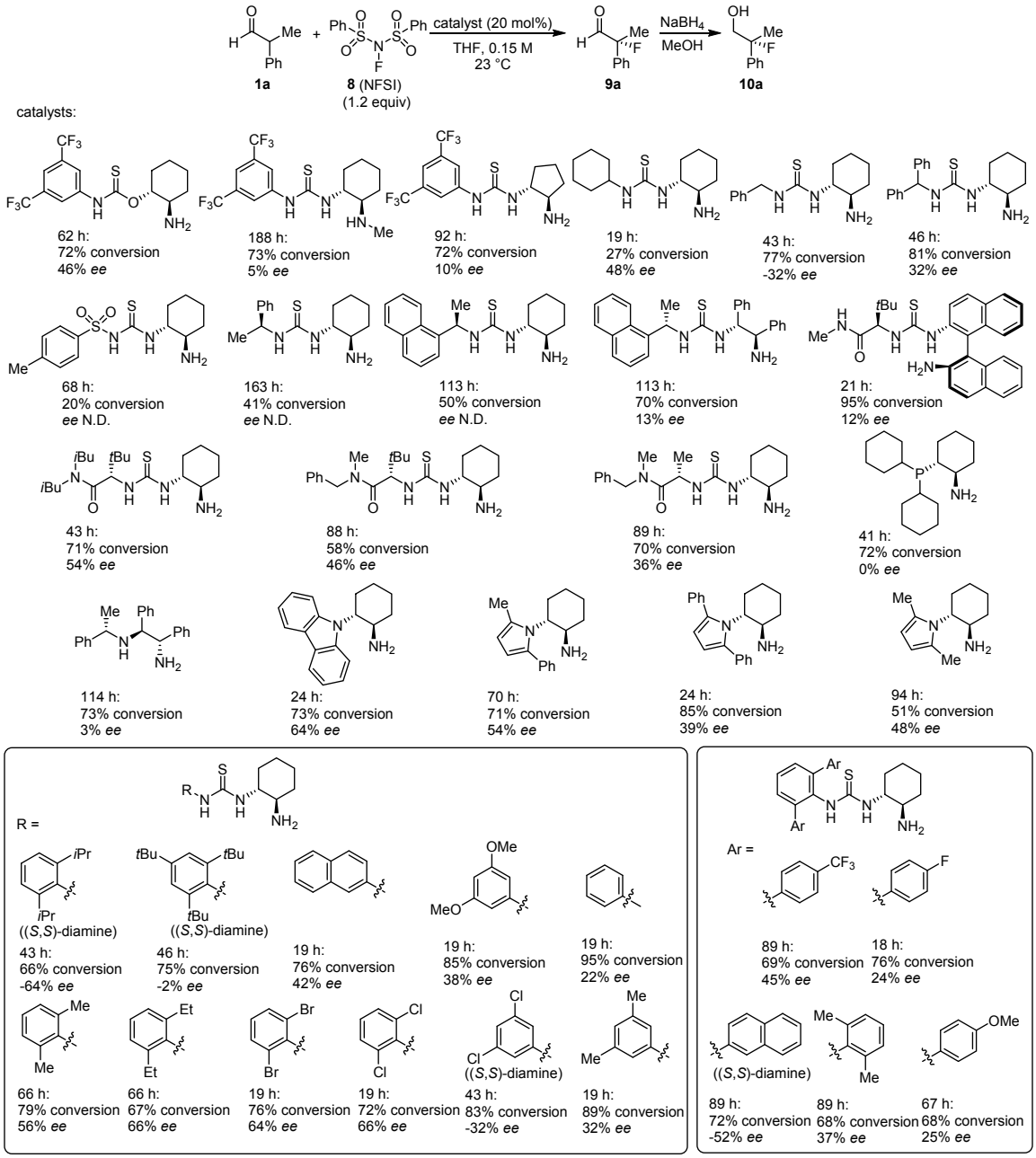



**Table S3.** α-Hydroxylation Amide Catalyst Screen.

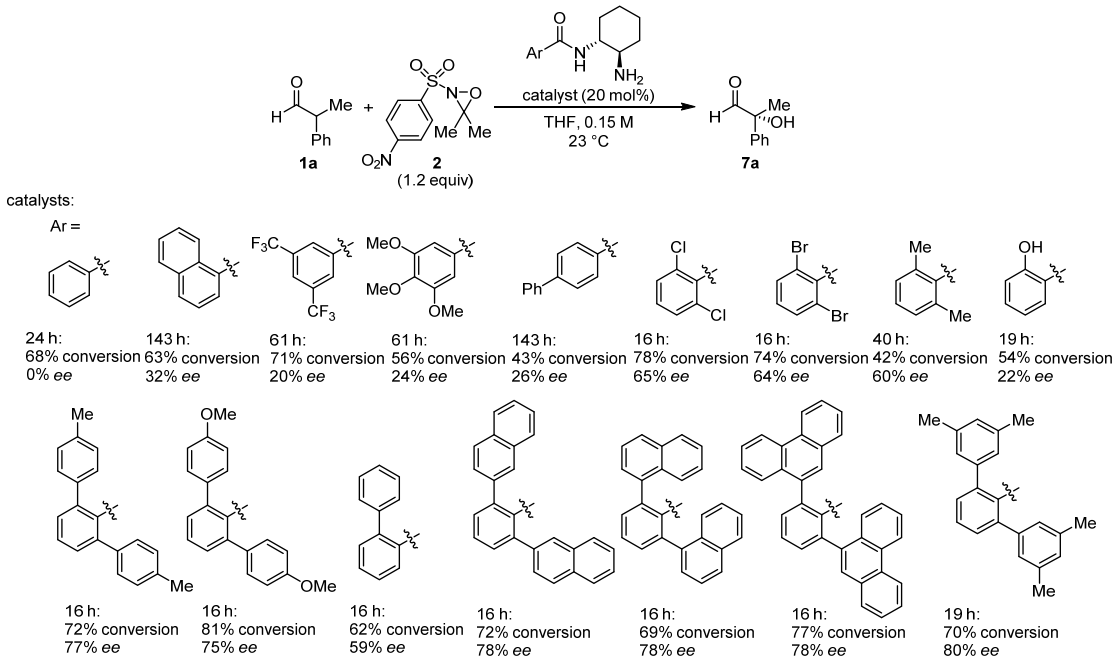



**Table S4.** α-Fluorination Amide Catalyst Screen.

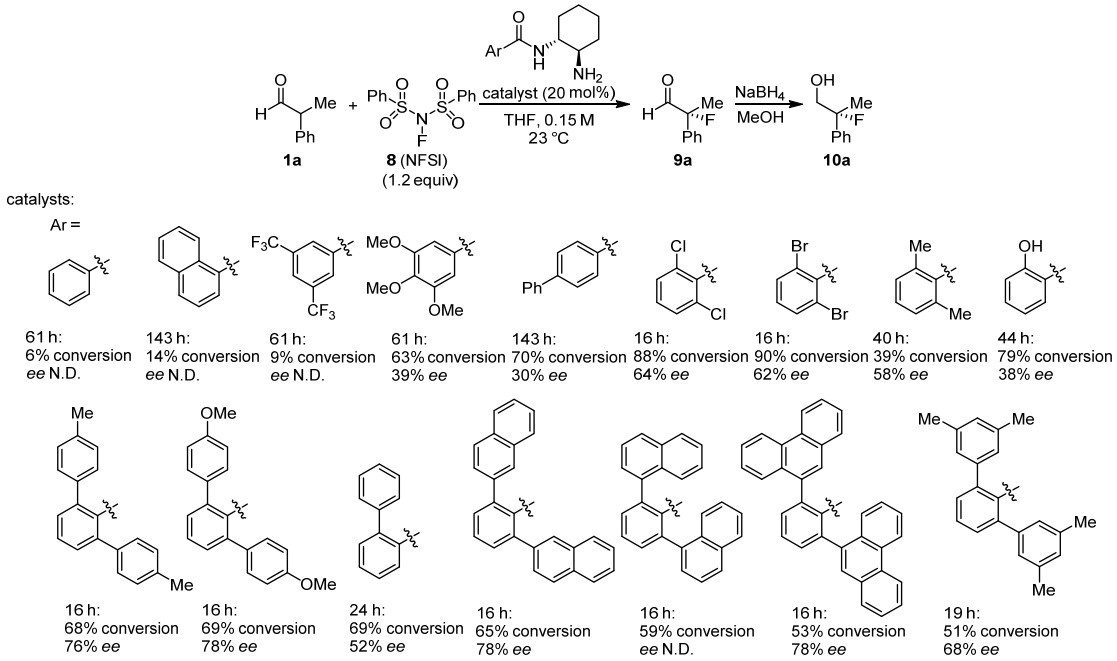
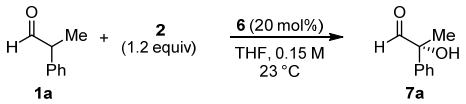



**Table S5.** α-Hydroxylation Additive Screen.

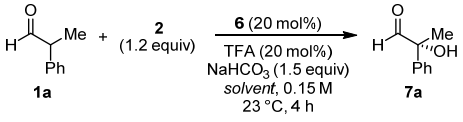
**Table S6.** α-Fluorination Additive Screen.




| Entry | Additive(s) | Time | Conversion[a] | ee[b] |
|---|---|---|---|---|
| 1 | None | 16 h | 73% | 75% |
| 2 | 1 equiv $H_2O$ | 19 h | 77% | 72% |
| 3 | 20 mol% AcOH | 19 h | 72% | 79% |
| 4 | 20 mol% BzOH | 17 h | 61% | 81% |
| 5 | 20 mol% DCA | 2 h | 91% | 80% |
| 6 | 20 mol% TCA | 2 h | 64% | 70% |
| 7 | 20 mol% TFA | 2 h | 87% | 73% |
| 8 | 0.5 equiv NaOAc | 160 h | 54% | 42% |
| 9 | 0.5 equiv NaOBz | 160 h | 66% | 42% |
| 10 | 1.5 equiv $Na_2CO_3$ | 92 h | 52% | 57% |
| 11 | 1.5 equiv $NaHCO_3$ | 48 h | 72% | 71% |
| 12 | 20 mol% TFA + 1.5 equiv $NaHCO_3$ | 4 h | 85% | 87% |
| 13 | 20 mol% TCA +1.5 equiv $NaHCO_3$ | 4 h | 66% | 87% |
| 14 | 20 mol% DCA +1.5 equiv $NaHCO_3$ | 4 h | 85% | 84% |
| 15 | 20 mol% TFA + 1.5 equiv $Na_2CO_3$ | 4 h | 87% | 88% |
| 16 | 20 mol% TCA +1.5 equiv $Na_2CO_3$ | 4 h | 67% | 86% |
| 17 | 20 mol% DCA +1.5 equiv $Na_2CO_3$ | 4 h | 75% | 85% |
| 18 | 20 mol% TFA +1.0 equiv $NEt_3$ | 19 h | 56% | 16% |
| 19 | 20 mol% TCA +1.0 equiv $NEt_3$ | 19 h | 56% | 18% |

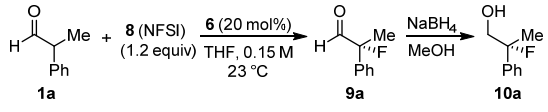
[a]Determined by GC. [b]Determined by HPLC.

**Table S7.** α-Hydroxylation Solvent Screen.




| Entry | Solvent | Conversion[a] | ee[b] |
|---|---|---|---|
| 1 | THF | 88% | 87% |
| 2 | 2-MeTHF | 87% | 87% |
| 3 | THP | 83% | 87% |
| 4 | Dioxane | 88% | 81% |
| 5 | CPME | 34% | 84% |
| 6 | tBME | 20% | 84% |
| 7 | $Et_2O$ | 14% | 83% |
| 8 | toluene | 62% | 71% |
| 9 | benzene | 61% | 70% |
| 10 | EtOAc | 62% | 84% |
| 11 | MeCN | 38% | 79% |
| 12 | MeOH | 9% | 33% |
| 13 | DMF | 8% | N.D. |
| 14 | DCM | 6% | 72% |
| 15 | hexanes | 7% | 59% |

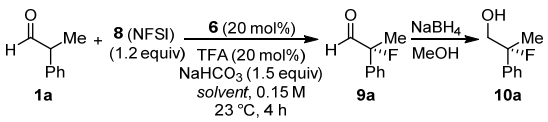
[a]Determined by GC. [b]Determined by HPLC.




| Entry | Additive(s) | Time | Conversion[a] | ee[b] |
|---|---|---|---|---|
| 1 | None | 16 h | 74% | 78% |
| 2 | 1 equiv $H_2O$ | 19 h | 71% | 77% |
| 3 | 20 mol% AcOH | 19 h | 80% | 77% |
| 4 | 20 mol% BzOH | 17 h | 79% | 81% |
| 5 | 20 mol% DCA | 2 h | 63% | 80% |
| 6 | 20 mol% TCA | 2 h | 68% | 80% |
| 7 | 20 mol% TFA | 2 h | 64% | 80% |
| 8 | 0.5 equiv NaOAc | 16 h | 89% | 78% |
| 9 | 0.5 equiv NaOBz | 16 h | 95% | 78% |
| 10 | 1.5 equiv $Na_2CO_3$ | 19 h | 87% | 79% |
| 11 | 1.5 equiv $NaHCO_3$ | 4 h | 82% | 79% |
| 12 | 20 mol% TFA + 1.5 equiv $NaHCO_3$ | 4 h | 83% | 83% |
| 13 | 20 mol% TCA +1.5 equiv $NaHCO_3$ | 4 h | 73% | 82% |
| 14 | 20 mol% DCA +1.5 equiv $NaHCO_3$ | 4 h | 67% | 79% |
| 15 | 20 mol% TFA + 1.5 equiv $Na_2CO_3$ | 4 h | 79% | 81% |
| 16 | 20 mol% TCA +1.5 equiv $Na_2CO_3$ | 4 h | 73% | 82% |
| 17 | 20 mol% DCA +1.5 equiv $Na_2CO_3$ | 4 h | 81% | 81% |
| 18 | 20 mol% TFA +1.0 equiv $NEt_3$ | 19 h | 78% | 70% |
| 19 | 20 mol% TCA +1.0 equiv $NEt_3$ | 19 h | 81% | 70% |

[a]Determined by GC. [b]Determined by HPLC.

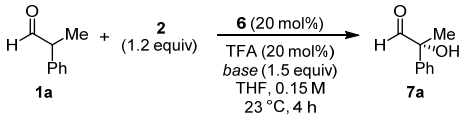
**Table S8.** α-Fluorination Solvent Screen.




| Entry | Solvent | Conversion[a] | ee[b] |
|---|---|---|---|
| 1 | THF | 71% | 83% |
| 2 | 2-MeTHF | 59% | 76% |
| 3 | THP | 66% | 76% |
| 4 | Dioxane | 69% | 75% |
| 5 | CPME | 47% | 63% |
| 6 | tBME | 27% | 58% |
| 7 | $Et_2O$ | 31% | 58% |
| 8 | toluene | 30% | 40% |
| 9 | benzene | 31% | 40% |
| 10 | EtOAc | 69% | 74% |
| 11 | MeCN | 48% | 71% |
| 12 | MeOH | 24% | 54% |
| 13 | DMF | 58% | 58% |
| 14 | DCM | 22% | 45% |
| 15 | hexanes | 8% | 34% |

[a]Determined by GC. [b]Determined by HPLC.

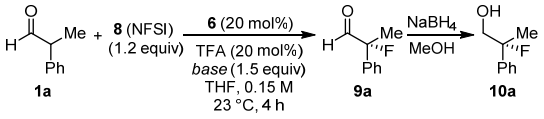
**Table S9.** α-Hydroxylation Base Screen.




| Entry | Base | Conversion[a] | ee[b] |
|---|---|---|---|
| 1 | $NaHCO_3$ | 88% | 87% |
| 2 | $Na_2CO_3$ | 87% | 88% |
| 3 | $K_2CO_3$ | 29% | 60% |
| 4 | $Li_2CO_3$ | 82% | 80% |
| 5 | $Cs_2CO_3$ | 31% | 47% |
| 6 | $BaCO_3$ | 87% | 83% |
| 7 | $CaCO_3$ | 86% | 79% |
| 8 | $NaH_2PO_4$ | 86% | 83% |
| 9 | $Na_2HPO_4$ | 86% | 86% |
| 10 | NaOAc | 71% | 79% |
| 11 | NaOBz | 82% | 76% |
| 12 | $NaClO_4$ | 35% | 84% |
| 13 | $LiClO_4$ | 11% | 80% |
| 14 | $NEt_3$ | 33% | 16% |

[a]Determined by GC. [b]Determined by HPLC.

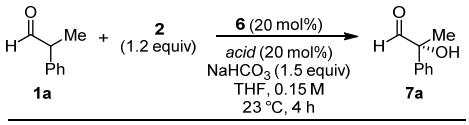
**Table S10.** α-Fluorination Base Screen.




| Entry | Base | Conversion[a] | ee[b] |
|---|---|---|---|
| 1 | $NaHCO_3$ | 83% | 83% |
| 2 | $Na_2CO_3$ | 79% | 81% |
| 3 | $K_2CO_3$ | 74% | 73% |
| 4 | $Li_2CO_3$ | 78% | 73% |
| 5 | $Cs_2CO_3$ | 56% | 74% |
| 6 | $BaCO_3$ | 80% | 82% |
| 7 | $CaCO_3$ | 80% | 82% |
| 8 | $NaH_2PO_4$ | 82% | 82% |
| 9 | $Na_2HPO_4$ | 82% | 80% |
| 10 | NaOAc | 86% | 75% |
| 11 | NaOBz | 88% | 75% |
| 12 | $NaClO_4$ | 26% | 76% |
| 13 | $LiClO_4$ | 9% | 72% |
| 14 | $NEt_3$ | 56% | 70% |

[a]Determined by GC. [b]Determined by HPLC.

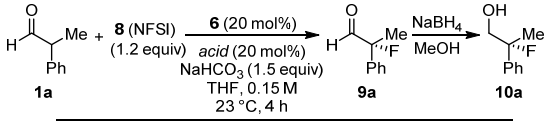
**Table S11.** α-Hydroxylation Acid Screen.




| Entry | Acid | Conversion[a] | ee[b] |
|---|---|---|---|
| 1 | TFA | 88% | 87% |
| 2 | TCA | 73% | 83% |
| 3 | DCA | 83% | 83% |
| 4 | AcOH | 73% | 75% |
| 5 | BzOH | 58% | 75% |
| 6 | 2-$NO_2$-BzOH | 84% | 81% |
| 7 | 3-$NO_2$-BzOH | 81% | 81% |
| 8 | 4-$NO_2$-BzOH | 83% | 84% |
| 9 | $MeSO_2OH$ | 15% | 78% |
| 10 | $PhSO_2OH$ | 41% | 70% |
| 11 | 2-NBSA | 28% | 69% |
| 12 | 4-NBSA | 29% | 73% |
| 13 | 2,4-diNBSA | 33% | 72% |
| 14 | $(PhO)_2PO_2H$ | 71% | 81% |
| 15 | $(BnO)_2PO_2H$ | 80% | 78% |
| 16 | $H_2SO_4$ | 23% | 80% |
| 17 | HCl | 33% | 70% |
| 18 | HFIP | 34% | 73% |
| 19 | phenol | 30% | 73% |
| 20 | 4-$NO_2$-phenol | 35% | 72% |
| 21 | L-tartaric acid | 94% | 84% |
| 22 | D-tartaric acid | 90% | 83% |

[a]Determined by GC. [b]Determined by HPLC.

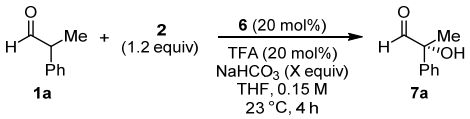
**Table S12.** α-Fluorination Acid Screen.




| Entry | Acid | Conversion[a] | ee[b] |
|---|---|---|---|
| 1 | TFA | 83% | 83% |
| 2 | TCA | 74% | 78% |
| 3 | DCA | 83% | 82% |
| 4 | AcOH | 59% | 80% |
| 5 | BzOH | 61% | 79% |
| 6 | 2-$NO_2$-BzOH | 73% | 82% |
| 7 | 3-$NO_2$-BzOH | 73% | 82% |
| 8 | 4-$NO_2$-BzOH | 77% | 80% |
| 9 | $MeSO_2OH$ | 15% | 78% |
| 10 | $PhSO_2OH$ | 33% | 75% |
| 11 | 2-NBSA | 41% | 76% |
| 12 | 4-NBSA | 27% | 78% |
| 13 | 2,4-diNBSA | 26% | 75% |
| 14 | $(PhO)_2PO_2H$ | 61% | 82% |
| 15 | $(BnO)_2PO_2H$ | 76% | 80% |
| 16 | $H_2SO_4$ | 22% | 76% |
| 17 | HCl | 29% | 74% |
| 18 | HFIP | 50% | 78% |
| 19 | phenol | 54% | 78% |
| 20 | 4-$NO_2$-phenol | 58% | 78% |
| 21 | L-tartaric acid | 75% | 82% |
| 22 | D-tartarc acid | 74% | 79% |

[a]Determined by GC. [b]Determined by HPLC.

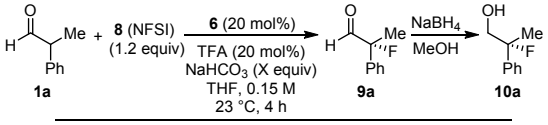
**Table S13.** α-Hydroxylation $NaHCO_3$ Loading.




| Entry | X | Conversion[a] | ee[b] |
|---|---|---|---|
| 1 | 0.0 | 87% | 73% |
| 2 | 0.5 | 85% | 84% |
| 3 | 1.0 | 85% | 84% |
| 4 | 1.5 | 85% | 84% |
| 5 | 2.0 | 85% | 84% |
| 6 | 5.0 | 85% | 84% |

[a]Determined by GC. [b]Determined by HPLC.

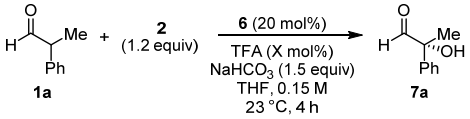
**Table S14.** α-Fluorination $NaHCO_3$ Loading.




| Entry | X | Conversion[a] | ee[b] |
|---|---|---|---|
| 1 | 0.0 | 64% | 80% |
| 2 | 0.5 | 83% | 83% |
| 3 | 1.0 | 83% | 82% |
| 4 | 1.5 | 83% | 83% |
| 5 | 2.0 | 83% | 82% |
| 6 | 5.0 | 83% | 81% |

[a]Determined by GC. [b]Determined by HPLC.

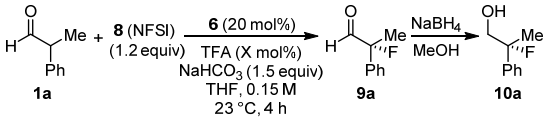
**Table S15.** α-Hydroxylation TFA Loading.




| Entry | X | Conversion[a] | ee[b] |
|---|---|---|---|
| 1 | 10 | 84% | 83% |
| 2 | 20 | 85% | 84% |
| 3 | 50 | 82% | 85% |

[a]Determined by GC. [b]Determined by HPLC.

**Table S16.** α-Fluorination TFA Loading.




| Entry | X | Conversion[a] | ee[b] |
|---|---|---|---|
| 1 | 10 | 84% | 83% |
| 2 | 20 | 83% | 83% |
| 3 | 50 | 85% | 84% |

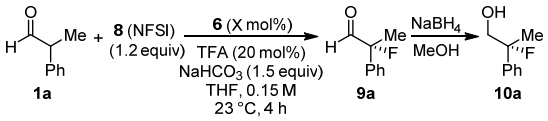
[a]Determined by GC. [b]Determined by HPLC.

**Table S17.** α-Hydroxylation Catalyst Loading.


| Entry | X | Conversion[a] | ee[b] |
|---|---|---|---|
| 1 | 5 | 37% | 77% |
| 2 | 10 | 63% | 83% |
| 3 | 20 | 85% | 84% |

[a]Determined by GC. [b]Determined by HPLC.

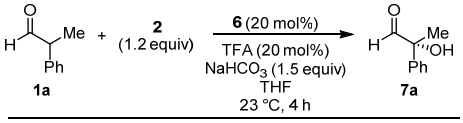
**Table S18.** α-Fluorination Catalyst Loading.




| Entry | X | Conversion[a] | ee[b] |
|---|---|---|---|
| 1 | 5 | 60% | 78% |
| 2 | 10 | 65% | 81% |
| 3 | 20 | 83% | 83% |

[a]Determined by GC. [b]Determined by HPLC.

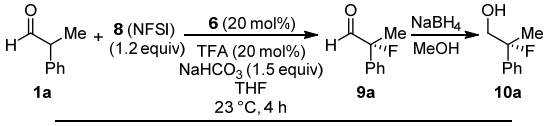
**Table S19.** α-Hydroxylation Concentration.




| Entry | Concentration | Conversion[a] | ee[b] |
|---|---|---|---|
| 1 | 0.075 M | 82% | 85% |
| 2 | 0.15 M | 85% | 84% |
| 3 | 0.3 M | 78% | 85% |

[a]Determined by GC. [b]Determined by HPLC.

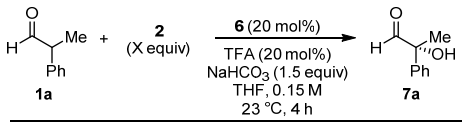
**Table S20.** α-Fluorination Concentration.




| Entry | Concentration | Conversion[a] | ee[b] |
|---|---|---|---|
| 1 | 0.075 M | 72% | 81% |
| 2 | 0.15 M | 83% | 83% |
| 3 | 0.3 M | 85% | 82% |

[a]Determined by GC. [b]Determined by HPLC.

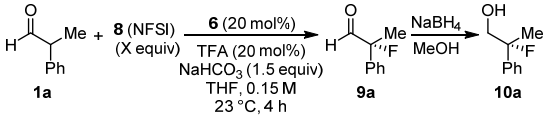
**Table S21.** α-Hydroxylation Electrophile Loading.




| Entry | X | Conversion[a] | ee[b] |
|---|---|---|---|
| 1 | 0.8 | 84% | 84% |
| 2 | 1.0 | 84% | 84% |
| 3 | 1.2 | 85% | 84% |
| 4 | 2.0 | 84% | 84% |

[a]Determined by GC. [b]Determined by HPLC.

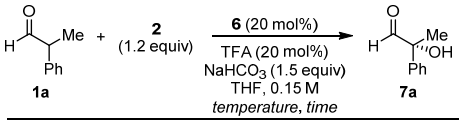
**Table S22.** α-Fluorination Electrophile Loading.




| Entry | X | Conversion[a] | ee[b] |
|---|---|---|---|
| 1 | 0.8 | 78% | 83% |
| 2 | 1.0 | 78% | 80% |
| 3 | 1.2 | 83% | 83% |
| 4 | 2.0 | 77% | 80% |

[a]Determined by GC. [b]Determined by HPLC.

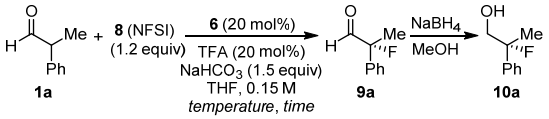
**Table S23.** α-Hydroxylation Temperature Screen.




| Entry | Temperature | Time | Conversion[a] | ee[b] |
|---|---|---|---|---|
| 1 | 23 °C | 4 h | 88% | 87% |
| 2 | 3 °C | 4 h | 73% | 86% |
| 3 | –10 °C | 21 h | 61% | 88% |
| 4 | –25 °C | 46 h | >65% | 93% |

[a]Determined by GC. [b]Determined by HPLC.

**Table S24.** α-Fluorination Temperature Screen.

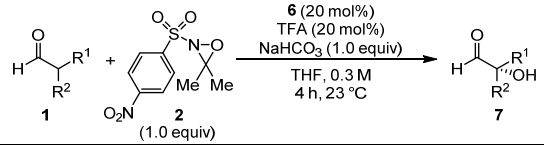



| Entry | Temperature | Time | Conversion[a] | ee[b] |
|---|---|---|---|---|
| 1 | 23 °C | 4 h | 83% | 83% |
| 2 | 3 °C | 4 h | 71% | 80% |

[a]Determined by GC. [b]Determined by HPLC.

## 9. Results with Additional Substrates

**Table S25.** Additional α-Hydroxylation Reactions.



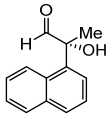
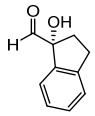
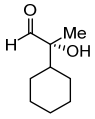
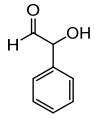
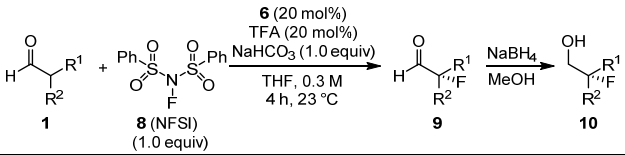
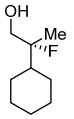
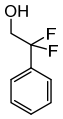

| | | | |
|---|---|---|---|
|  |  |  |  |
| **20 h:**<br>59% yield<br>56% *ee* | 94% yield<br>83% *ee* | **20 h:**<br>23% yield<br>39% *ee* | 80% conversion<br>20% *ee* |

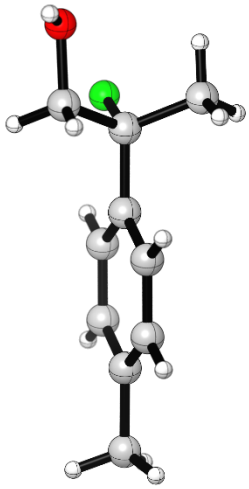
**Table S26.** Additional α-Fluorination Reactions.



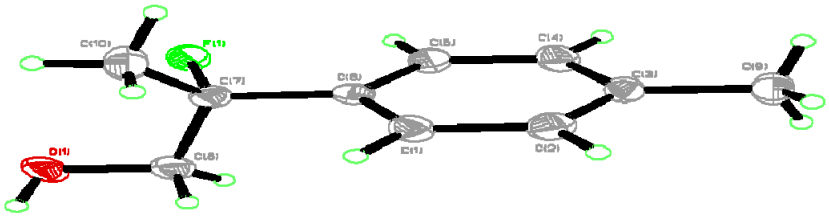

| | |
|---|---|
|  |  |
| **20 h:**<br>56% yield<br>20% *ee* | 48% conversion |

## 10. X-Ray Crystallography Information

**Fluorohydrin 10d:**



Fluorohydrin **10d** was crystallized from hexanes/$Et_2O$. A crystal was mounted on a diffractometer and data was collected at 100 K. The intensities of the reflections were collected by means of a Bruker APEX II DUO CCD diffractometer ($Cu_{K\alpha}$ radiation, λ=1.54178 Å), equipped with an Oxford Cryosystems nitrogen flow apparatus. The collection method involved 1.0° scans in $\omega$ at 30°, 55°, 80° and 115° in $2\theta$. Data integration down to 0.84 Å resolution was carried out using SAINT V8.34 C[26] with reflection spot size optimization. Absorption corrections were made with the program SADABS.[26] The structure was solved by the Intrinsic Phasing methods and refined by least-squares methods again $F^2$ using SHELXT-2014 and SHELXL-2014[27] with OLEX 2 interface.[28] Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were allowed to ride on the respective atoms. The ORTEP plot was produced with SHELXL-2014 program.



[26] Bruker AXS APEX II, Bruker AXS, Madison, Wisconsin, 2014.

[27] Sheldrick, G. M. *Acta Cryst.* **2008**, *A64*, 112–122.

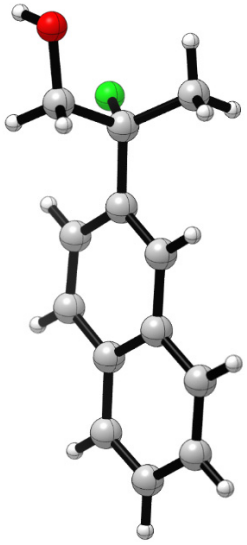
[28] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Cryst.* **2009**, *42*, 339–341.

**Figure S2.** View of crystal structure depicting 50% probability displacement.

| | |
|---|---|
| Crystal data | |
| Chemical formula | $C_{10}H_{13}FO$ |
| $M_r$ | 168.20 |
| Crystal system, space group | Orthorhombic, $P2_12_12_1$ |
| Temperature (K) | 100 |
| $a$, $b$, $c$ (Å) | 5.5342 (2), 11.1421 (4), 14.6505 (6) |
| $V$ (Å$^3$) | 903.39 (6) |
| $Z$ | 4 |
| Radiation type | Cu $K\alpha$ |
| $\mu$ (mm$^{-1}$) | 0.76 |
| Crystal size (mm) | 0.18 × 0.14 × 0.10 |
| | |
| Data collection | |
| Diffractometer | Bruker D8 goniometer with CCD area detector diffractometer |
| Absorption correction | Multi-scan<br>*SADABS* |
| $T_{min}$, $T_{max}$ | 0.687, 0.753 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 22169, 1597, 1534 |
| $R_{int}$ | 0.036 |
| $(\sin \theta/\lambda)_{max}$ (Å$^{-1}$) | 0.596 |
| | |
| Refinement | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.026, 0.068, 1.06 |
| No. of reflections | 1597 |
| No. of parameters | 115 |
| H-atom treatment | H atoms treated by a mixture of independent and constrained refinement |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.13, -0.13 |

| | |
|---|---|
| Absolute structure | Flack x determined using 596 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons, S.; Flack, H. D.; Wagner, T. *Acta Cryst.*, **2013**, *B69*, 249–259.) |
| Absolute structure parameter | 0.05 (5) |

**Fluorohydrin 10i:**



Fluorohydrin **10i** was crystallized from hexanes/$Et_2O$. A crystal was mounted on a diffractometer and data was collected at 100 K. The intensities of the reflections were collected by means of a Bruker APEX II DUO CCD diffractometer ($Cu_{K\alpha}$ radiation, $\lambda$=1.54178 Å), equipped with an Oxford Cryosystems nitrogen flow apparatus. The collection method involved 1.0° scans in $\omega$ at 30°, 55°, 80° and 115° in $2\theta$. Data integration down to 0.84 Å resolution was carried out using SAINT V8.34 C[26] with reflection spot size optimization. Absorption corrections were made with the program SADABS.[26] The structure was solved by the Intrinsic Phasing methods and refined by least-squares methods again $F^2$ using SHELXT-2014 and SHELXL-2014[27] with OLEX 2 interface.[28] Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were allowed to ride on the respective atoms. The ORTEP plot was produced with SHELXL-2014 program.

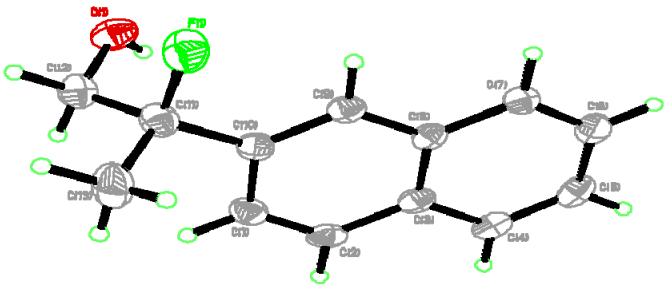
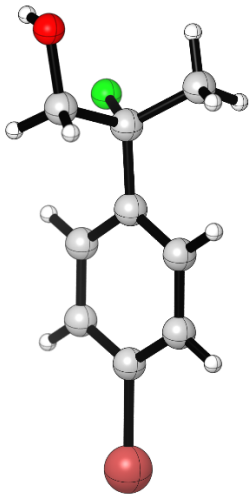


**Figure S3.** View of crystal structure depicting 50% probability displacement.

| | |
|---|---|
| Crystal data | |
| Chemical formula | $C_{39}H_{39}F_3O_3$ |
| $M_r$ | 612.70 |
| Crystal system, space group | Orthorhombic, $P2_12_12_1$ |
| Temperature (K) | 100 |
| $a$, $b$, $c$ (Å) | 6.1061 (2), 18.8064 (5), 27.8827 (7) |
| $V$ (Å$^3$) | 3201.88 (16) |
| $Z$ | 4 |
| Radiation type | Cu $K\alpha$ |
| μ (mm$^{-1}$) | 0.74 |
| Crystal size (mm) | 0.16 × 0.08 × 0.06 |
| | |
| Data collection | |
| Diffractometer | Bruker D8 goniometer with CCD area detector diffractometer |
| Absorption correction | Multi-scan<br>*SADABS* |
| $T_{min}$, $T_{max}$ | 0.773, 0.864 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 56690, 5672, 5034 |
| $R_{int}$ | 0.069 |

| | |
|---|---|
| $(\sin\theta/\lambda)_{max}$ (Å$^{-1}$) | 0.596 |
| | |
| Refinement | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.042, 0.111, 1.07 |
| No. of reflections | 5672 |
| No. of parameters | 416 |
| No. of restraints | 37 |
| H-atom treatment | H atoms treated by a mixture of independent and constrained refinement |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.34, -0.25 |
| Absolute structure | Flack x determined using 1993 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons, S.; Flack, H. D.; Wagner, T. *Acta Cryst.*, **2013**, *B69*, 249–259.) |
| Absolute structure parameter | 0.05 (7) |

**Fluorohydrin 10j:**



Fluorohydrin **10j** was crystallized from hexanes/$Et_2O$. A crystal was mounted on a diffractometer and data was collected at 100 K. The intensities of the reflections were collected by means of a Bruker APEX II DUO CCD diffractometer ($Mo_{K\alpha}$ radiation, λ=0.71073 Å), equipped with an Oxford Cryosystems nitrogen flow apparatus. The collection method involved 0.5° scans in $\omega$ at 28° in $2\theta$. Data integration down to 0.78 Å resolution was carried out using SAINT V8.34 C[26] with reflection spot size optimization. Absorption corrections were made with the program SADABS.[26] The structure was solved by the direct methods procedure and refined by least-squares methods again $F^2$ using SHELXT-2014 and SHELXL-2014[27] with OLEX 2 interface.[28] Non-hydrogen atoms were refined

anisotropically, and hydrogen atoms were allowed to ride on the respective atoms. The ORTEP plot was produced with SHELXL-2014 program.

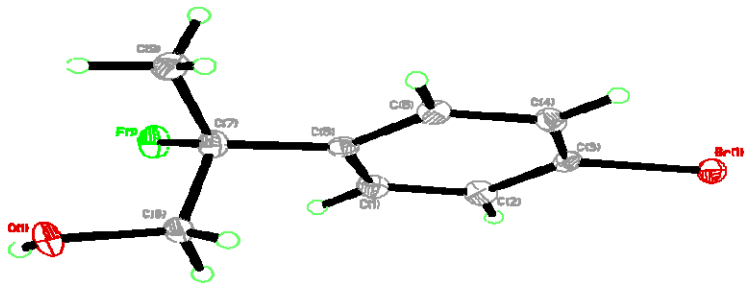


**Figure S4.** View of crystal structure depicting 50% probability displacement.

| | |
|---|---|
| Crystal data | |
| Chemical formula | $C_9H_{10}BrFO$ |
| $M_r$ | 233.08 |
| Crystal system, space group | Monoclinic, $P2_1$ |
| Temperature (K) | 100 |
| $a$, $b$, $c$ (Å) | 8.013 (3), 5.1662 (18), 10.972 (4) |
| β (°) | 93.376 (5) |
| $V$ (Å$^3$) | 453.4 (3) |
| $Z$ | 2 |
| Radiation type | Mo $K\alpha$ |
| μ (mm$^{-1}$) | 4.50 |
| Crystal size (mm) | 0.14 × 0.12 × 0.10 |
| | |
| Data collection | |
| Diffractometer | Bruker D8 goniometer with CCD area detector diffractometer |
| Absorption correction | Multi-scan<br>*SADABS* |
| $T_{min}$, $T_{max}$ | 0.508, 0.746 |

| | |
|---|---|
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 10136, 2018, 1898 |
| $R_{int}$ | 0.037 |
| $(\sin \theta/\lambda)_{max}$ ($Å^{-1}$) | 0.646 |
| | |
| Refinement | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.019, 0.047, 1.04 |
| No. of reflections | 2018 |
| No. of parameters | 114 |
| No. of restraints | 1 |
| H-atom treatment | H atoms treated by a mixture of independent and constrained refinement |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e $Å^{-3}$) | 0.32, -0.20 |
| Absolute structure | Flack x determined using 805 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons, S.; Flack, H. D.; Wagner, T. *Acta Cryst.*, **2013**, *B69*, 249–259.) |
| Absolute structure parameter | -0.008 (9) |