Supporting Information

Consecutive Iridium Catalyzed C-C and C-H Bond Forming Hydrogenations for the Diastereo- and Enantioselective Synthesis of syn-3-Fluoro-1-Alcohols: C-H (2-Fluoro)allylation of Primary Alcohols

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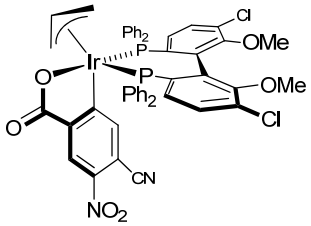
I. General Information: All reactions were run under an atmosphere of argon. Sealed tubes (13x100m^2) were purchased from Fischer Scientific (catalog number 14-959-35C) and were flame dried followed by cooling in a desiccator. Tetrahydrofuran was dried over sodium metal, benzophenone, and distilled immediately prior to use. Dichloromethane was dried over $CaCl_2$ and distilled immediately prior to use. Anhydrous solvents were transferred by oven-dried syringes. All ligands and $[Ir(cod)Cl]_2$ were used as received from Strem Chemical Inc. Alcohols were distilled or recrystallized prior to use. Both allyl acetate and 3-chloro-2-fluoroprop-1-ene were distilled prior to use. Analytical thin-layer chromatography (TLC) was carried out using 0.25 mm commercial silica gel plates (Dynanmic Absorbents F_{254}). Visualization was accomplished with UV light followed by dipping in p-anisaldehyde solution then heating. Purification of reactions was carried out by flash chromatography using Silacycle silica gel (40-63 μm).

II. Spectroscopy, Spectrometry, and Data Collection: Infrared spectra were recorded on a Perkin-Elmer 1600 spectrometer. High-resolution mass spectra (HRMS) were obtained on a Karatos MS9 and are reported as m/z (relative intensity). Accurate masses are reported for the molecular ion (M, M+H, M-H, or M-F) or a suitable fragment ion. ^{1}H Nuclear magnetic resonance spectra were recorded using a 400 MHz spectrometer. Coupling constants are reported in Hertz (Hz). For $CDCl_3$ solutions and chemical shifts are reported as parts per million (ppm) relative to residual $CHCl_3$ δ_H (7.26 ppm). ^{13}C Nuclear magnetic resonance spectra were recorded using a 100 MHz spectrometer. For CDCl3 solutions and chemical shifts are reported as parts per million (ppm) relative to residual $CDCl_3$ δ_C (77.0 ppm). ^{19}F Nuclear magnetic resonance spectra were recorded using a 400 MHz spectrometer. Chemical shifts are reported as parts per million (ppm). Optical rotations were performed on an Automatic Polarimeter AP-300 using dichloromethane as solvent. Melting points were taken on a Stuart SMP3 melting point apparatus.

III. Experimental Details and Spectral Data

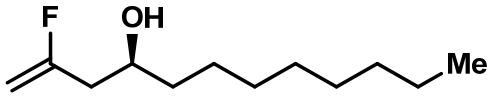
III.a. Synthesis of Catalyst Ir-Cat-I:



To a mixture of $[Ir(cod)Cl]_2$ (134.3 mg, 0.20 mmol, 100 mol%), (*R*)-Cl,MeO-BIPHEP (260.6 mg, 0.40 mmol, 200 mol%), Cs_2CO_3 (260.6 mg, 0.80 mmol, 400 mol%), and 4-CN-3-NO_2BzOH (153.7 mg, 0.89 mmol, 400 mol%) in a sealed tube under an atmosphere of argon was added THF (4.0 mL, 0.05 M) and allyl acetate (100.1 mg, 1.0 mmol, 500 mol%). The reaction mixture was stirred for 30 min at ambient temperature and heated for 1.5 h at 80 °C, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was filtered with the aid of THF (10 mL). The filtrate was concentrated *in vacuo*, and the residue was subjected to flash column chromatography (dichloromethane:ether, 3:1). The residue obtained upon chromatographic isolation was dissolved in THF (2 mL) and hexane (50 mL) was added. The resulting yellow precipitate was collected by filtration and dried under vacuum to provide **Ir-Cat-I** (344.0 mg, 0.320 mmol) in 80% yield.

III.b. Experimental Procedures and Spectroscopic Data for Adducts 3a-3i from the Alcohol Oxidation Level

(4S)-2-Fluoro-dodec-1-ene-4-ol (4a)



To a resealable pressure tube (13x100 mm) equipped with a magnetic stir bar was added **Ir-Cat-I** (10.7 mg, 0.01 mmol, 5 mol%) and K_3PO_4 (42.4 mg, 0.2 mmol, 100 mol%). The tube was sealed with a rubber septum and purged with argon. THF (0.2 mL), 3-chloro-2-fluoroprop-1-ene (28.4 mg, 0.3 mmol, 150 mol%), alcohol **2a** (28.9 mg, 0.2 mmol, 100 mol%), and H_2O (18.0 mg, 1.0 mmol, 500 mol%) were added to the purged tube, and the rubber septum was quickly replaced with a screw cap. The reaction mixture was heated in an oil bath at 60 °C for 24 hours, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was concentrated *in vacuo* and purified by flash chromatography (SiO_2: ethyl acetate:hexanes, 1:19) to furnish the title compound **4a** (30.9 mg, 0.153 mmol) as a colorless oil in 76% yield and **5a** (3.5 mg, 0.019 mmol) as a colorless oil in 10% yield.

TLC (SiO_2): R_f=0.38 (ethyl acetate:hexanes, 1:9)

$[\alpha]_D^{23}$=-5.5°

^{1}H NMR (400 MHz, CDCl3): δ 4.65 (dd, *J*=17.6, 2.8 Hz, 1H), 4.35 (dd, *J*=50.4, 2.8 Hz, 1H), 3.88-3.82 (m, 1H), 2.44-2.22 (m, 2H), 1.50-1.44 (m, 2H), 1.28-1.21 (m, 12H), 0.88 (t, *J*=2.8 Hz, 3H).

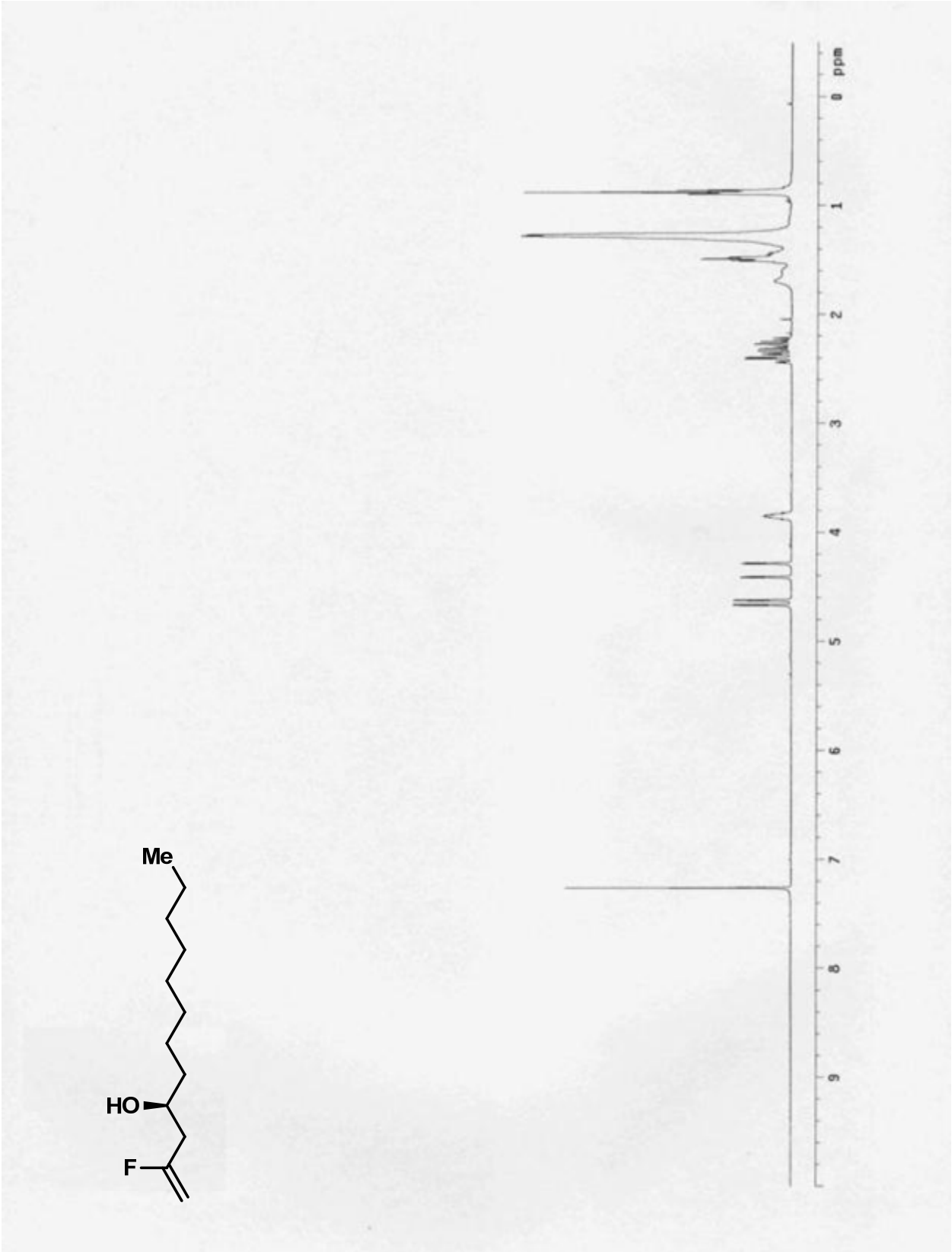
^{13}C NMR (100 MHz, CDCl3): δ 163.9 (d, *J*=256.0 Hz), 92.4 (d, *J*=19.3 Hz), 68.5, 40.3 (d, *J*=26.1), 36.8, 31.8, 29.5, 29.5, 29.2, 25.5, 22.6, 14.1

^{19}F NMR (400 MHz, CDCl3): δ -94.55 (ddt, *J*=53.2, 44.0, 18.0 Hz).

HRMS (CI) Calcd. for $C_{12}H_{23}0$ $[M-F]^+$: 183.1747, Found: 183.1749.

FTIR (neat): 3352, 2955, 2925, 2855, 1672, 1466, 1247, 1181, 1085, 939, 847 cm^{-1}.

HPLC Enantiomeric excess was determined by the analysis of the 3,5-dinitrobenzoate derivative of the product (Chiralcel AD-H column, hexanes:*i*-PrOH = 99:1, 1.0 mL/min, 254 nm), t_{minor} = N/A, t_{major} = 9.1 min; ee = 99%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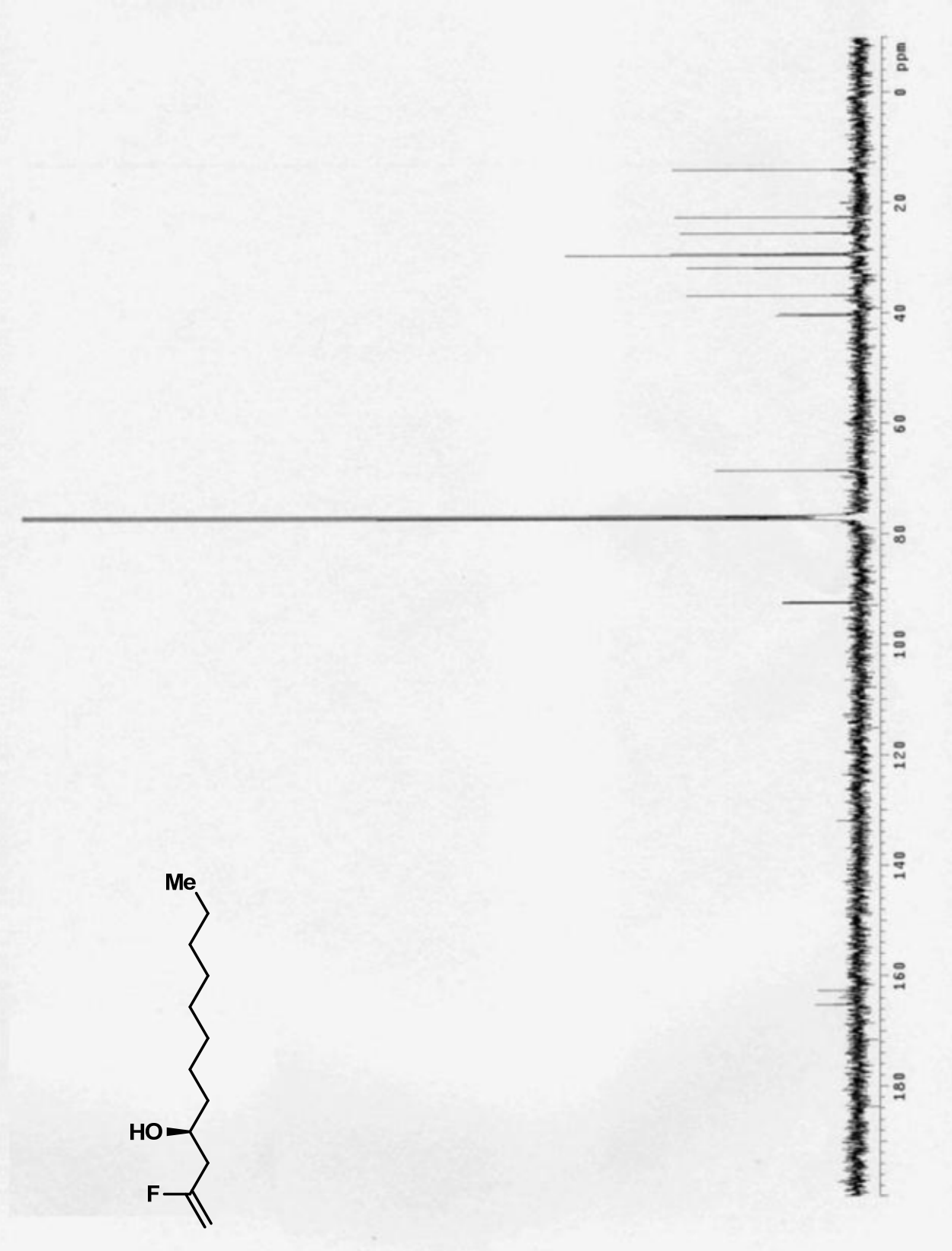
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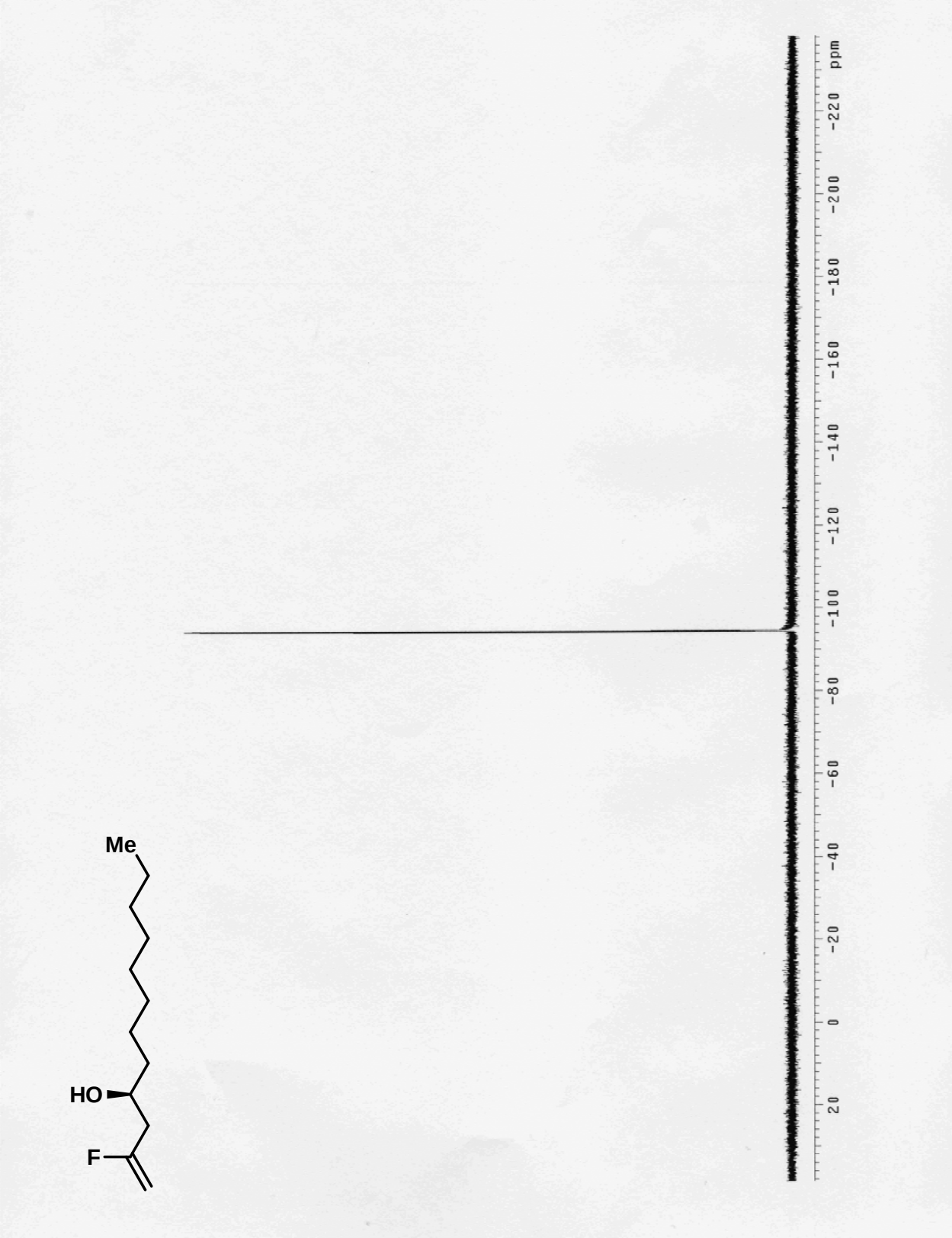
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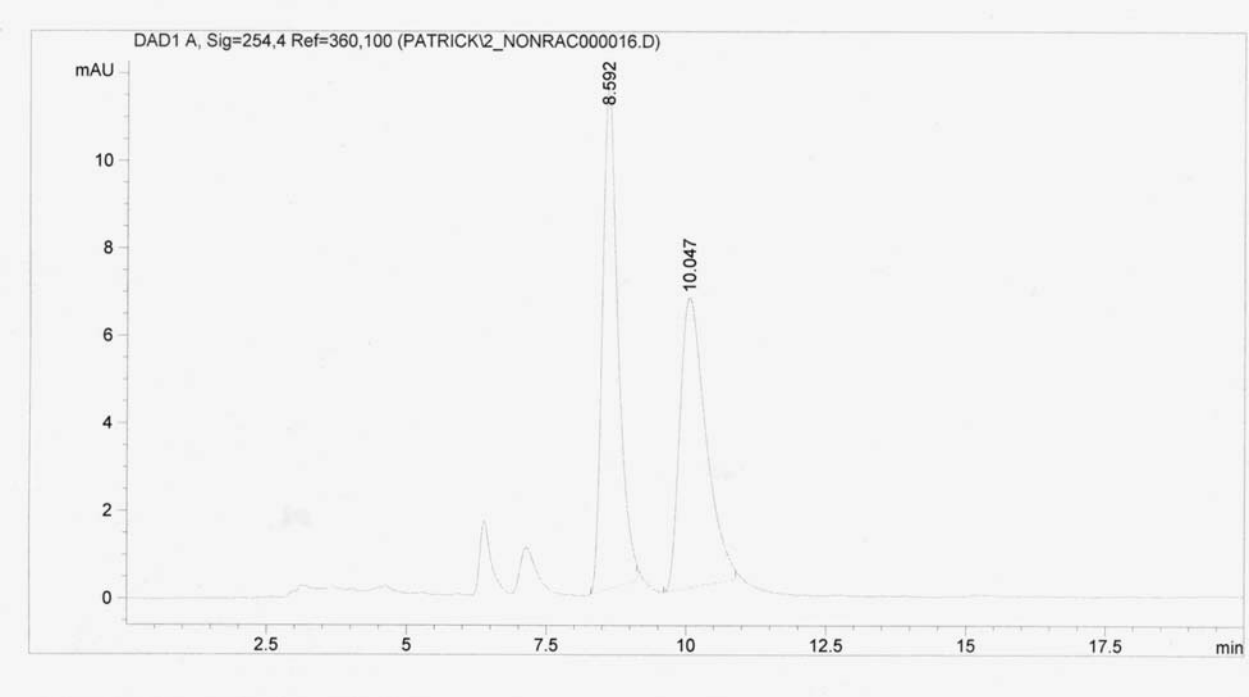

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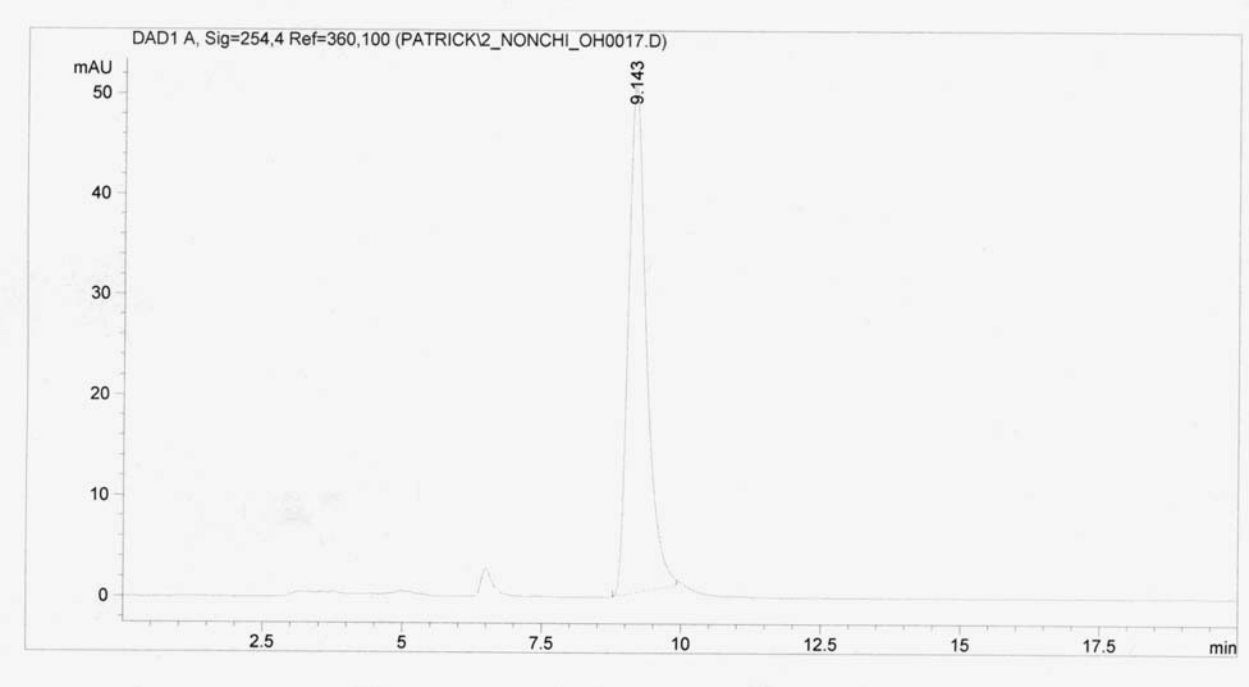

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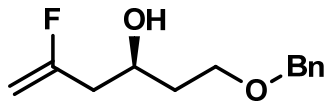
(4S)-6-Benzyloxy-2-fluorohexa-1-ene-4-ol (4b)



To a resealable pressure tube (13x100 mm) equipped with a magnetic stir bar was added **Ir-Cat-I** (10.7 mg, 0.01 mmol, 5 mol%) and K_3PO_4 (42.4 mg, 0.2 mmol, 100 mol%). The tube was sealed with a rubber septum and purged with argon. THF (0.2 mL), 3-chloro-2-fluoroprop-1-ene (28.4 mg, 0.3 mmol, 150 mol%), alcohol **2b** (33.2 mg, 0.2 mmol, 100 mol%), and H_2O (18.0 mg, 1.0 mmol, 500 mol%) were added to the purged tube, and the rubber septum was quickly replaced with a screw cap. The reaction mixture was heated in an oil bath at 60 °C for 24 hours, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was concentrated *in vacuo* and purified by flash chromatography (SiO_2: ethyl acetate:hexanes, 1:9) to furnish the title compound **4b** (29.3 mg, 0.131 mmol) as a colorless oil in 65% yield and **5b** (2.4 mg, 0.012 mmol) as a colorless oil in 6% yield.

TLC (SiO_2) : R_f=0.22 (ethyl acetate:hexanes, 1:9)

[α]$_D^{23}$=-39.3°

^{1}H NMR (400 MHz, CDCl3): δ 7.37-7.28 (m, 5H), 4.63 (dd, *J*=17.6, 2.8 Hz, 1H), 4.53 (s, 2H), 4.34 (dd, *J*=50.0, 2.8 Hz, 1H), 4.11-4.05 (m, 1H), 3.77-3.64 (m, 2H), 3.10 (br, 1H), 2.46-2.29 (m, 2H), 1.85-1.78 (m, 2H).

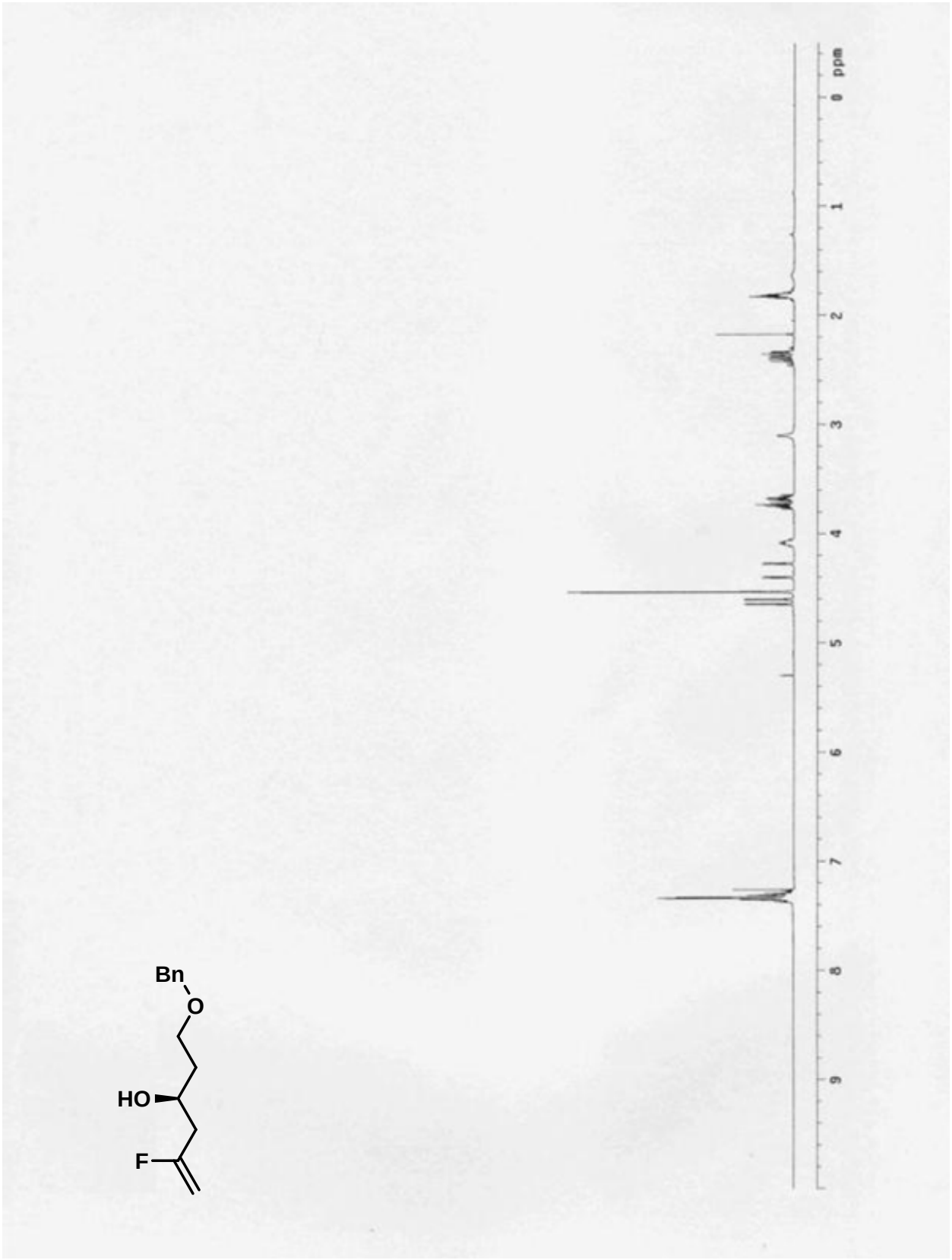
^{13}C NMR (100 MHz, CDCl3): δ 163.8 (d, *J*=255.0 Hz), 137.8, 128.5, 128.5, 127.8, 127.7, 127.7, 92.2 (d, *J*=20.1 Hz), 73.4, 68.9, 68.3, 40.1 (d, *J*=26.1 Hz), 35.8.

^{19}F NMR (400 MHz, CDCl3): δ -94.60 (ddt, *J*=53.2, 36.8, 4.6 Hz).

HRMS (CI) Calcd. for $C_{13}H_{17}FO_2$ $[M]^+$: 224.1210, Found: 224.1213.

FTIR (neat): 3444, 3063, 2954, 2865, 2359, 1674, 1636, 1452, 1275, 1176, 1113, 1072, 935, 852, 749, 714, 699 cm^{-1}.

HPLC (Chiralcel OD-H column, hexanes:*i*-PrOH = 98:2, 1.0 mL/min, 210 nm), t_{minor}=11.8 min, t_{major}=12.4 min; ee = 98%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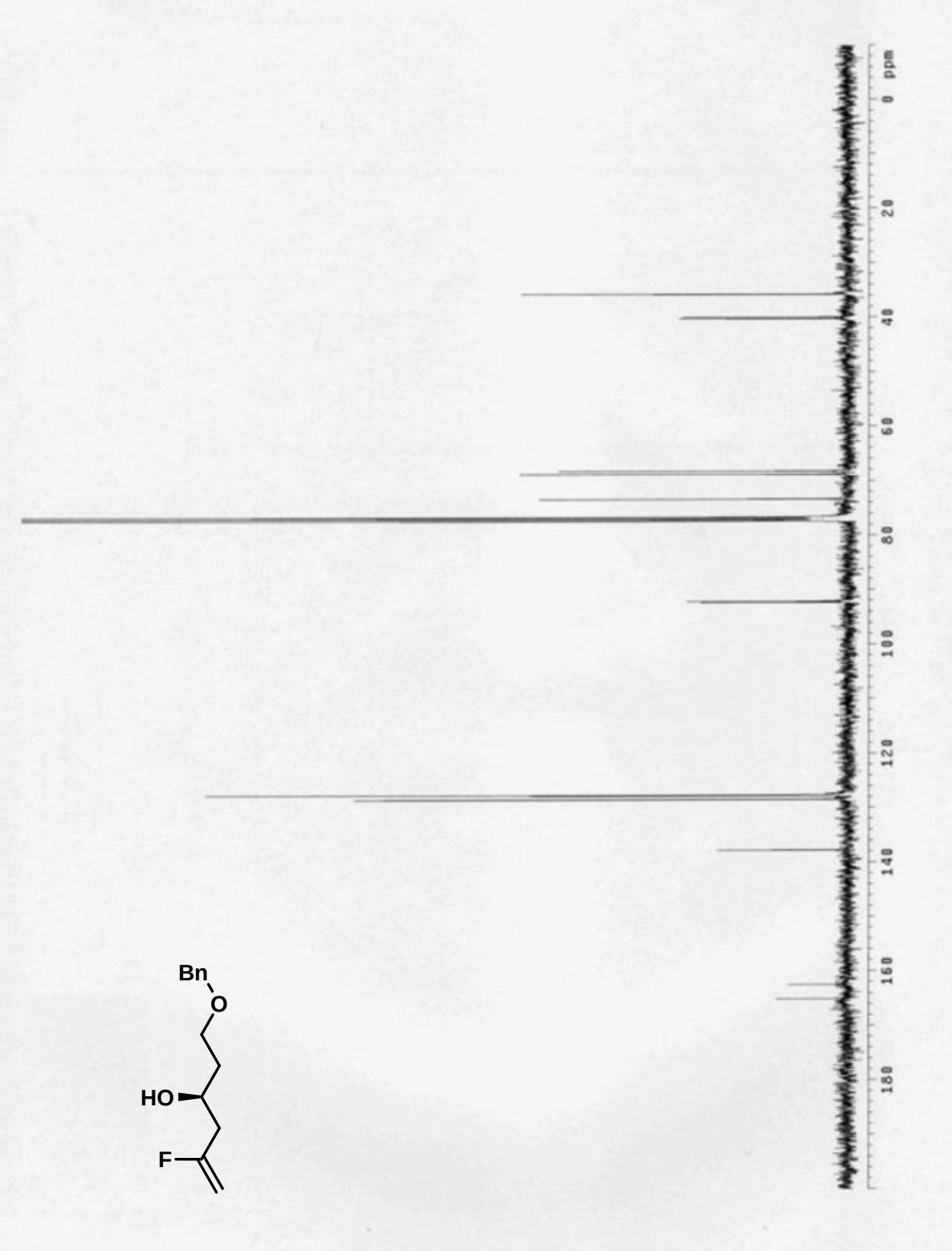
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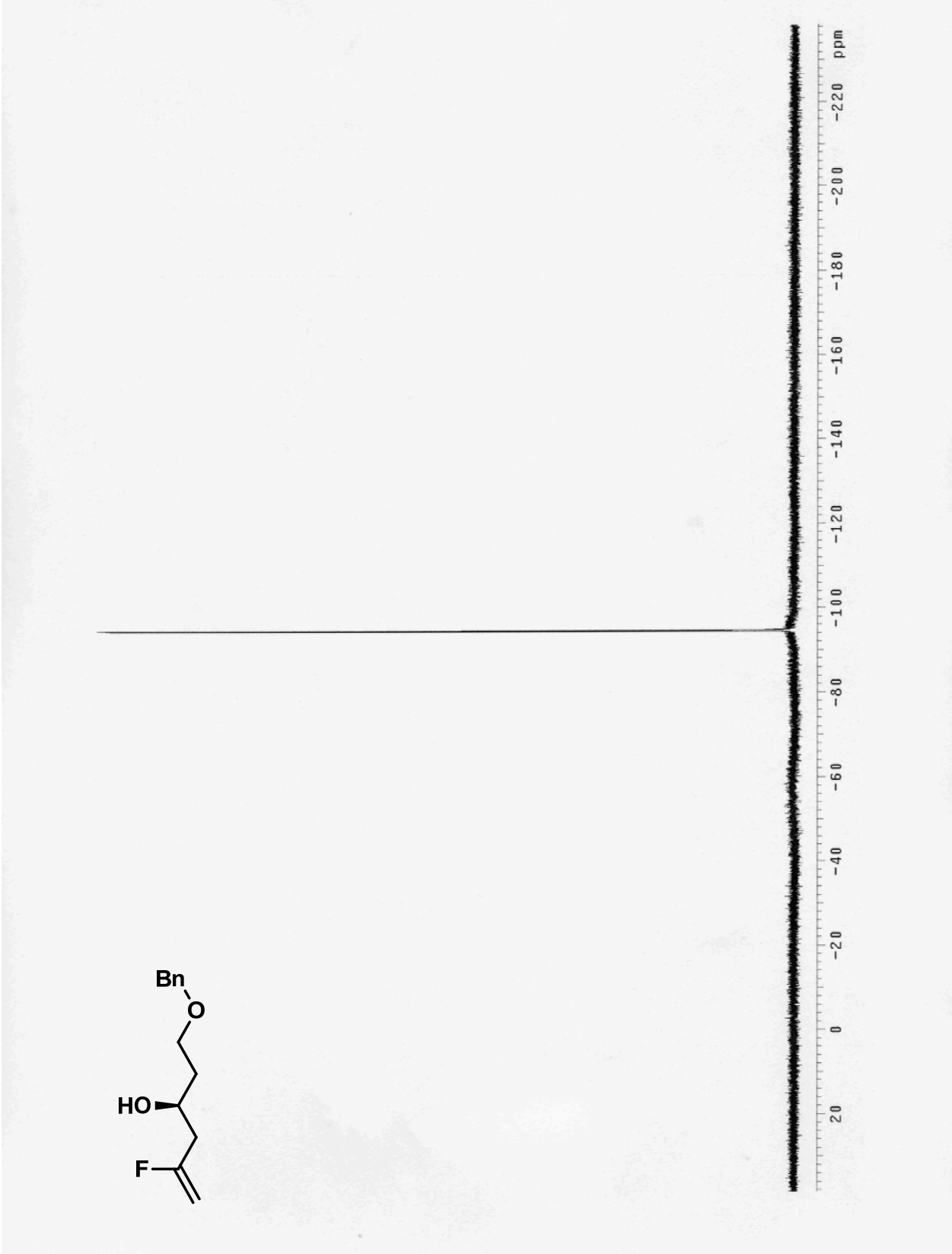
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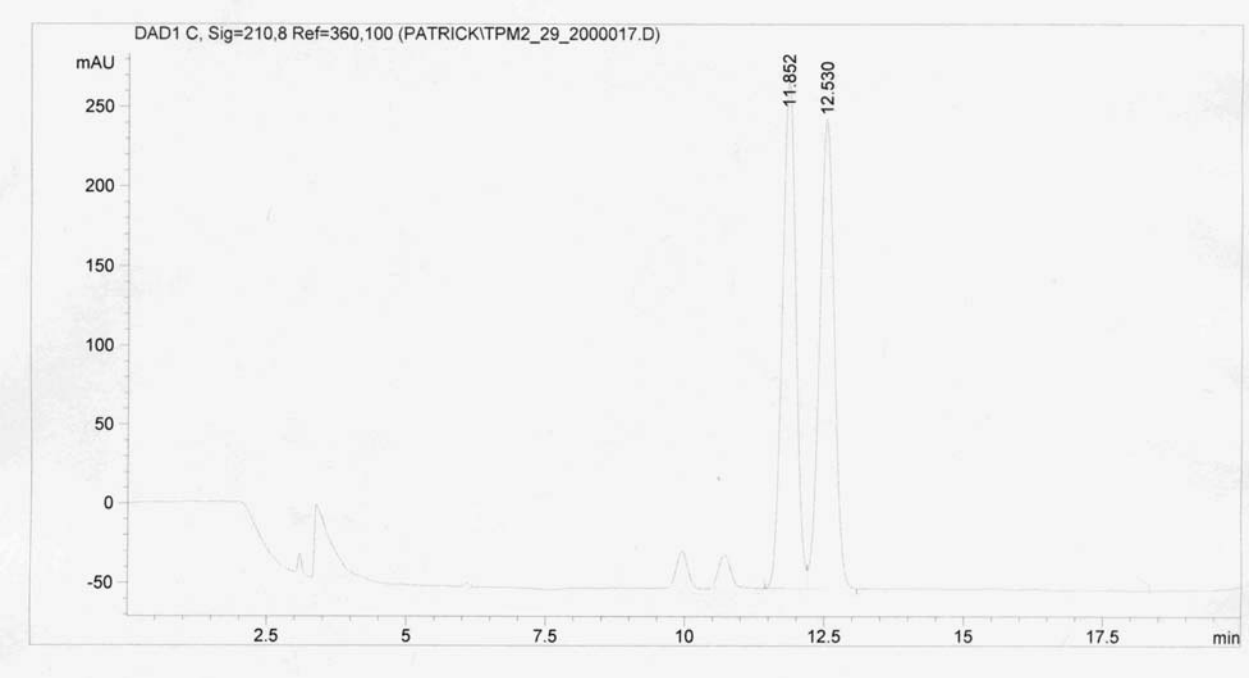

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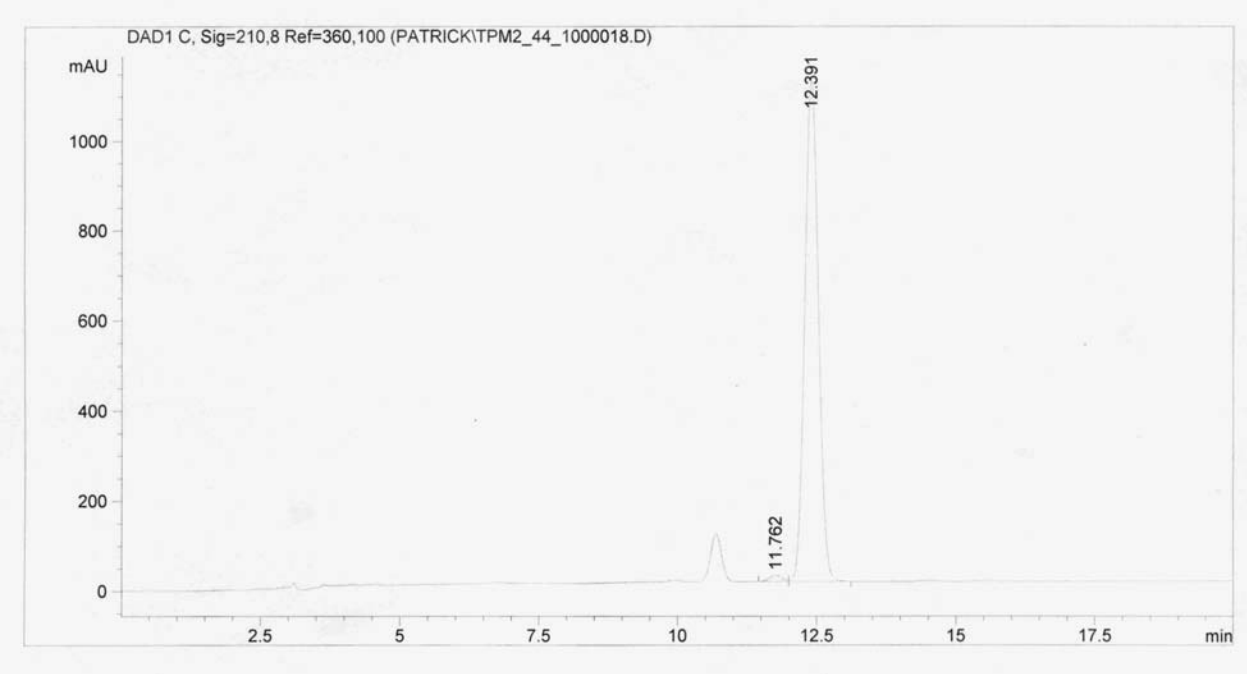

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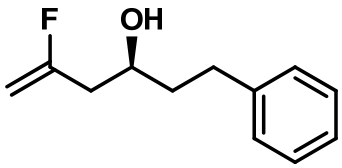
1	11.762	BV	0.2386	215.47427	14.07298	1.1183
2	12.391	VB	0.2677	1.90525e4	1113.05432	98.8817

(4S)-2-Fluoro-6-phenylhexa-1-en-4-ol (4c)



To a resealable pressure tube (13x100 mm) equipped with a magnetic stir bar was added **Ir-Cat-I** (10.7 mg, 0.01 mmol, 5 mol%) and K_3PO_4 (42.4 mg, 0.2 mmol, 100 mol%). The tube was sealed with a rubber septum and purged with argon. THF (0.2 mL), 3-chloro-2-fluoroprop-1-ene (28.4 mg, 0.3 mmol, 150 mol%), alcohol **2c** (27.2 mg, 0.2 mmol, 100 mol%), and H_2O (18.0 mg, 1.0 mmol, 500 mol%) were added to the purged tube, and the rubber septum was quickly replaced with a screw cap. The reaction mixture was heated in an oil bath at 60 °C for 24 hours, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was concentrated *in vacuo* and purified by flash chromatography (SiO_2: ethyl acetate:hexanes, 1:9) to furnish the title compound **4c** (34.6 mg, 0.178 mmol) as a yellow oil in 89% yield and **5c** (1.8 mg, 0.010 mmol) as a yellow oil in 5% yield.

TLC (SiO_2): R_f=0.2 (ethyl acetate:hexanes, 1:9)

[α]$_D^{23}$=-28.4°

^{1}H NMR (400 MHz, CDCl3): δ 7.32-7.22 (m, 5H), 4.66 (dd, *J*=17.6, 2.8 Hz, 1H), 4.35 (dd, *J*=50.0, 2.8 Hz, 1H), 3.92-3.86 (m, 1H), 2.87-2.80 (m, 2H), 2.47-2.27 (m, 2H), 1.86-1.80 (m, 3H).

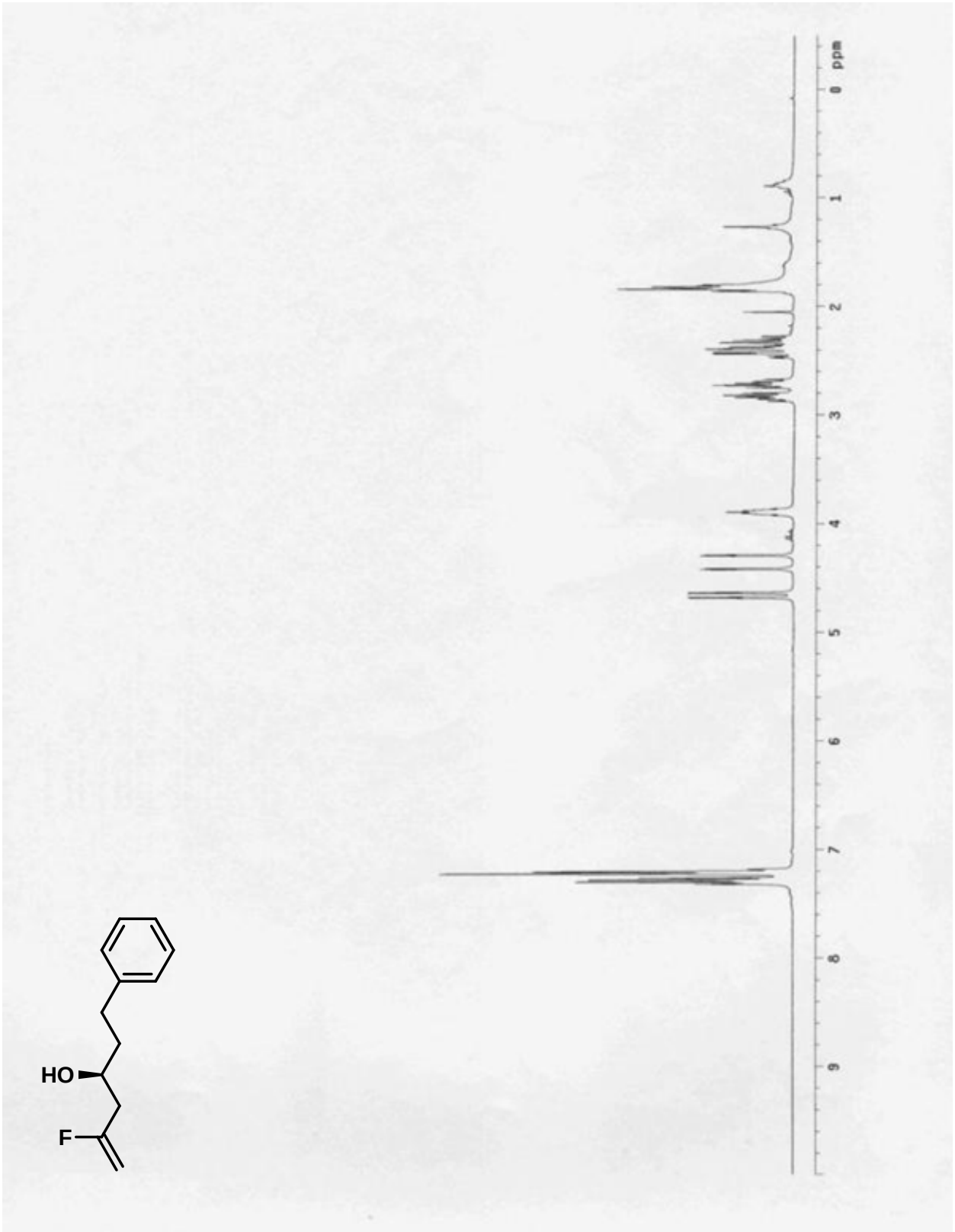
^{13}C NMR (100 MHz, CDCl3): δ 163.6 (d, *J*=255.2 Hz), 141.8, 128.4, 128.4, 125.9, 92.7 (d, *J*=19.3 Hz), 67.8, 40.4 (d, *J*=25.3 Hz), 38.4, 31.9.

^{19}F NMR (400 MHz, CDCl3): δ -94.50 (ddt, *J*=52.8, 42.8, 17.2 Hz).

HRMS (CI) Calcd. for $C_{12}H_{15}FO$ $[M]^+$: 194.1107, Found: 194.1107.

FTIR (neat): 3335, 2952, 2921, 2902, 2889, 1678, 1493, 1451, 1435, 1343, 1299, 1254, 1230, 1181, 1074, 1058, 1028, 1015, 941, 932, 854, 845, 749, 699 cm^{-1}.

HPLC (Chiralcel OD-H column, hexanes:*i*-PrOH = 95:5, 1.0 mL/min, 210 nm), t_{minor} = 9.8 min, t_{major} = 14.2 min; ee = 99%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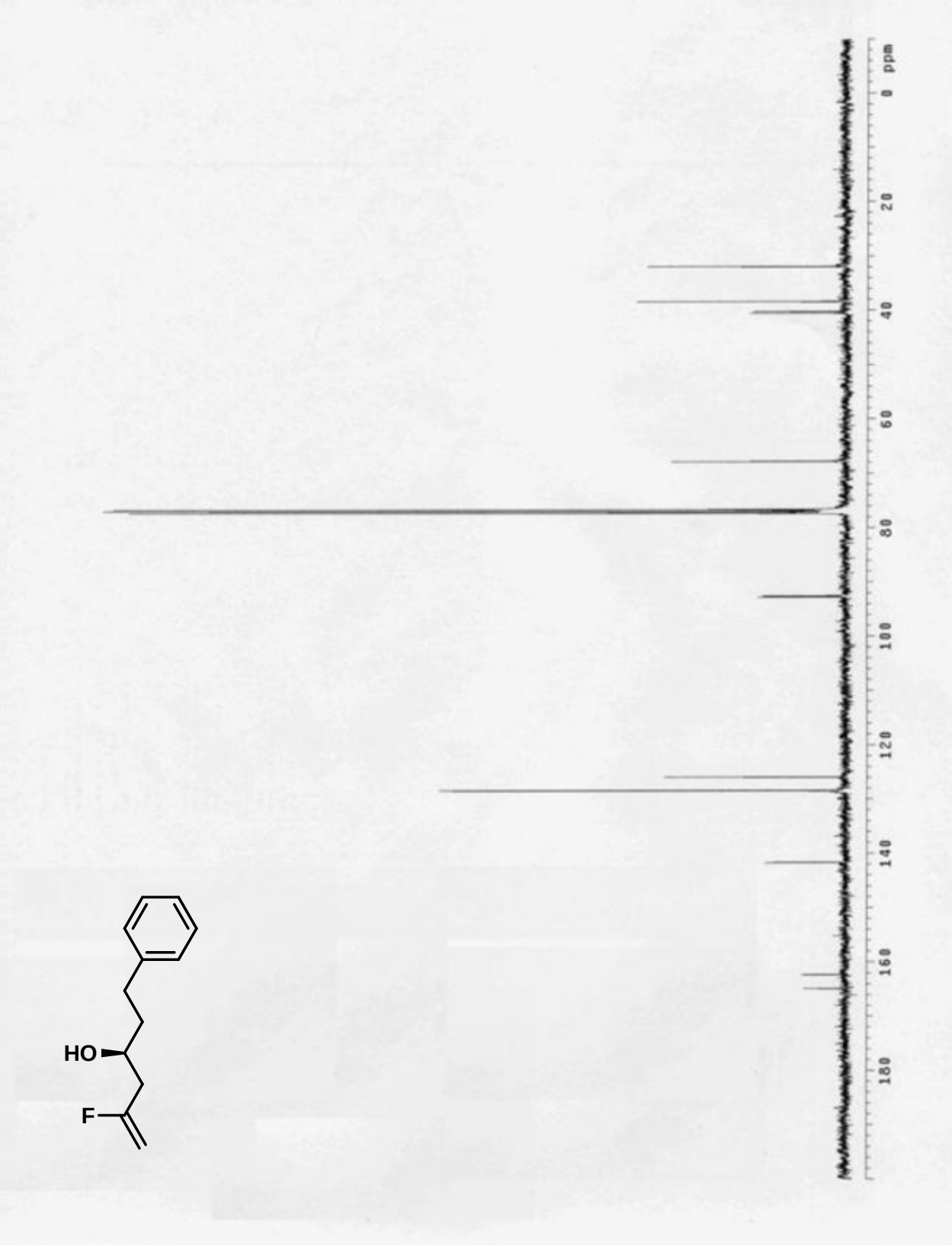
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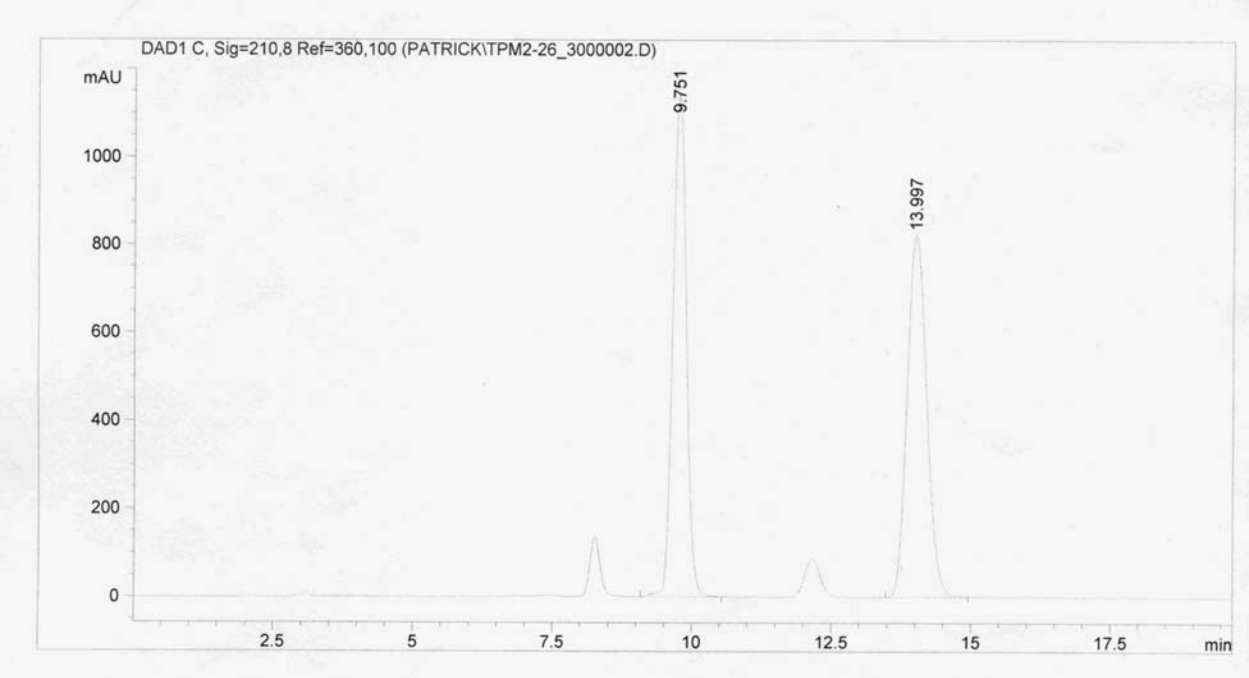

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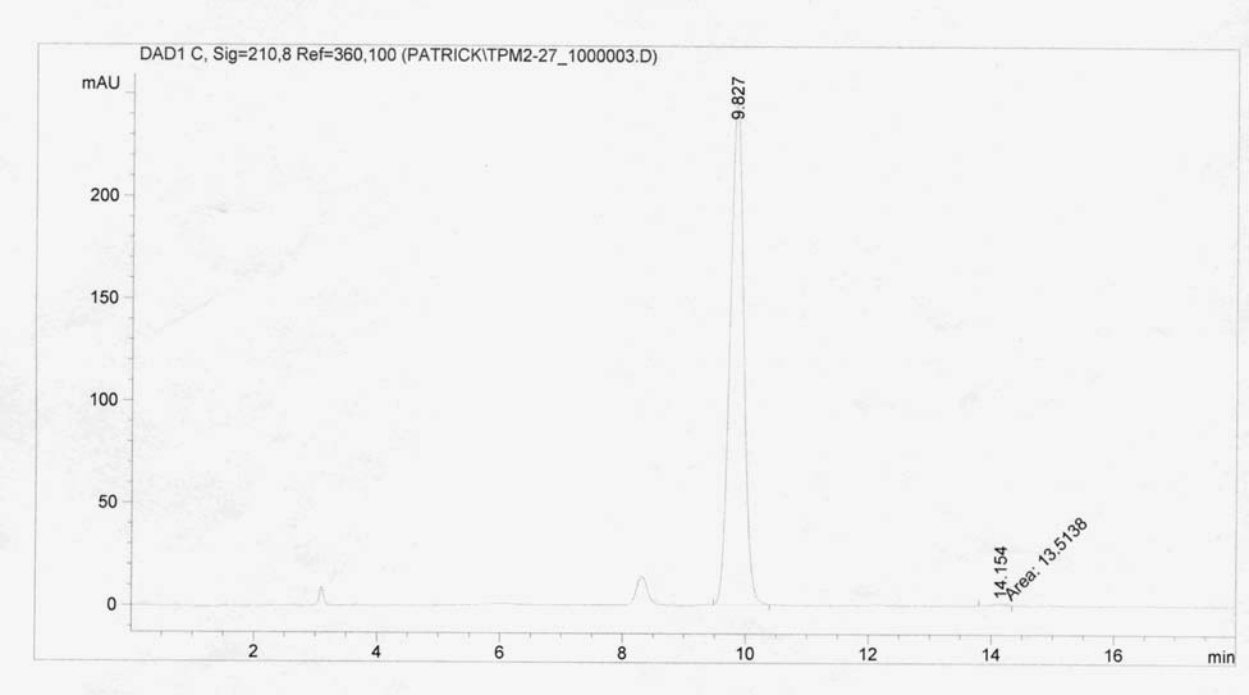

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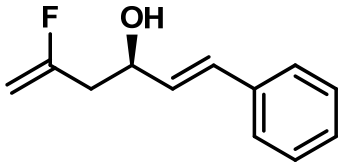
2	14.154	MM	0.2876	13.51383	7.83075e-1	0.3518

(3R)-5-Fluoro-1-phenylhexa-1,5-diene-3-ol (4d)



To a resealable pressure tube (13x100 mm) equipped with a magnetic stir bar was added **Ir-Cat-I** (10.7 mg, 0.01 mmol, 5 mol%) and K_3PO_4 (42.4 mg, 0.2 mmol, 100 mol%). The tube was sealed with a rubber septum and purged with argon. THF (0.2 mL), 3-chloro-2-fluoroprop-1-ene (28.4 mg, 0.3 mmol, 150 mol%), alcohol **2d** (26.8 mg, 0.2 mmol, 100 mol%), and H_2O (18.0 mg, 1.0 mmol, 500 mol%) were added to the purged tube, and the rubber septum was quickly replaced with a screw cap. The reaction mixture was heated in an oil bath at 40 °C for 24 hours, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was concentrated *in vacuo* and purified by flash chromatography (SiO_2: ethyl/hexanes, 1:9) to furnish the title compound **4d** (29.4 mg, 0.153 mmol) as a colorless oil in 76% yield and **5d** (1.3 mg, 0.007 mmol) as a colorless oil in 4% yield.

TLC (SiO_2): R_f= 0.2 (ethyl acetate:hexanes, 1:9)

$[\alpha]_D^{23}$=+25.8°

^{1}H NMR (400 MHz, CDCl3): δ 7.33-7.16 (m, 5H), 6.59 (d, *J*=16.0 Hz, 1H), 6.17 (dd, *J*=16.0, 8.0 Hz, 1H), 4.61 (dd, *J*=17.2, 2.8 Hz, 1H), 4.52-4.48 (m, 1H), 4.33 (dd, *J*=50.0, 2.8 Hz, 1H), 2.49-2.42 (m, 1H), 1.84 (br, 1H).

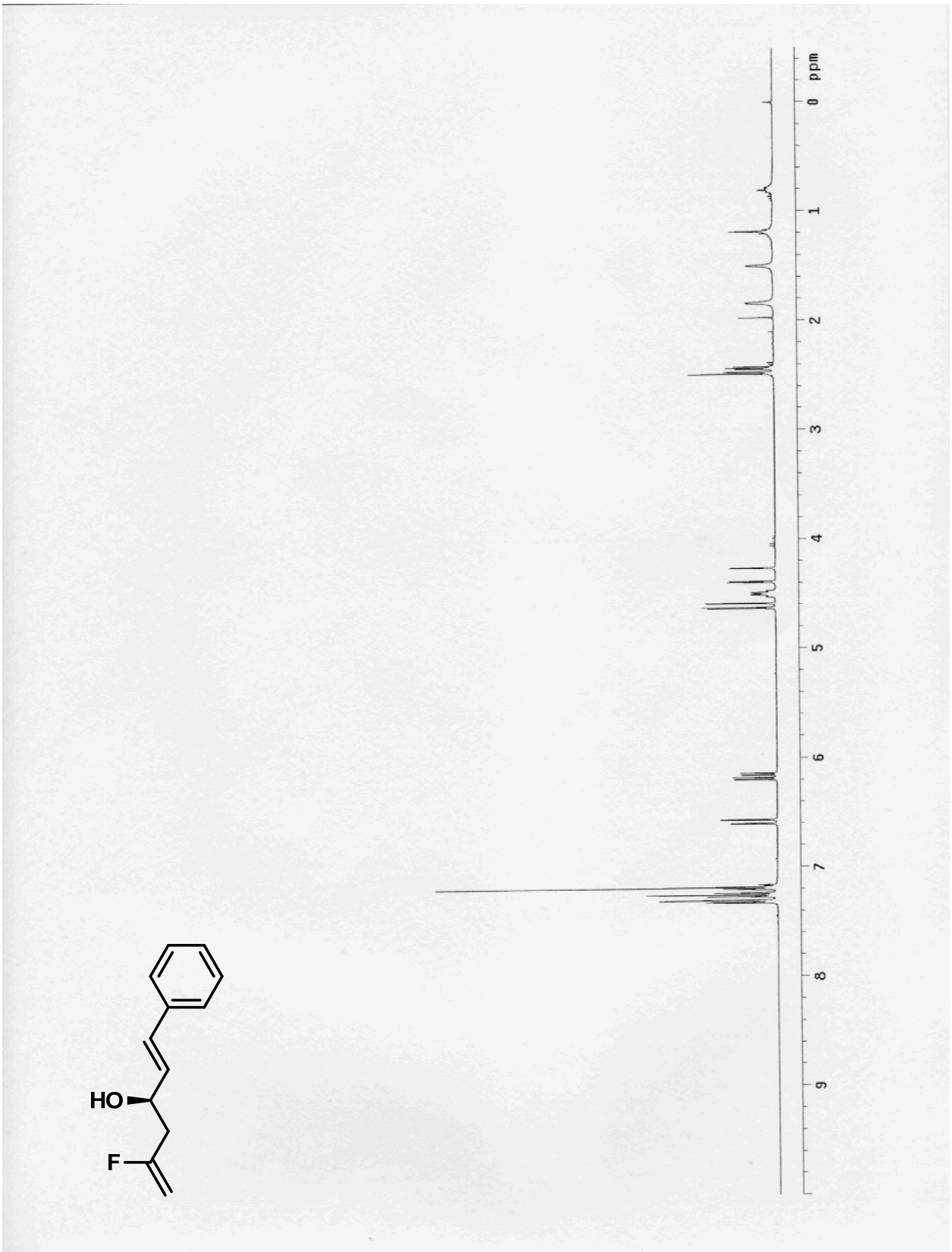
^{13}C NMR (100 MHz, CDCl3): δ 156.0 (d, *J*=256.0 Hz), 129.3, 124.0, 123.5, 121.6, 120.9, 119.5, 85.9 (d, *J*=19.4 Hz), 62.5, 33.4 (d, *J*=26.0 Hz).

^{19}F NMR (400 MHz, CDCl3): δ -94.97 (ddt, *J*=52.8, 40.0, 18.0 Hz).

HRMS (CI) Calcd. for $C_{12}H_{12}FO$ $[M-H]^+$: 191.0871, Found: 191.0872.

FTIR (neat): 3400, 3028, 2926, 1674, 1601, 1495, 1453, 1422, 1243, 1178, 1070, 1029, 968, 938, 854, 749, 699, 659 cm^{-1}.

HPLC (Chiralcel OJ-H column, hexanes:*i*-PrOH = 95:5, 1.0 mL/min, 254 nm), t_{minor} = 14.6 min, t_{major} = 16.0 min; ee = 98%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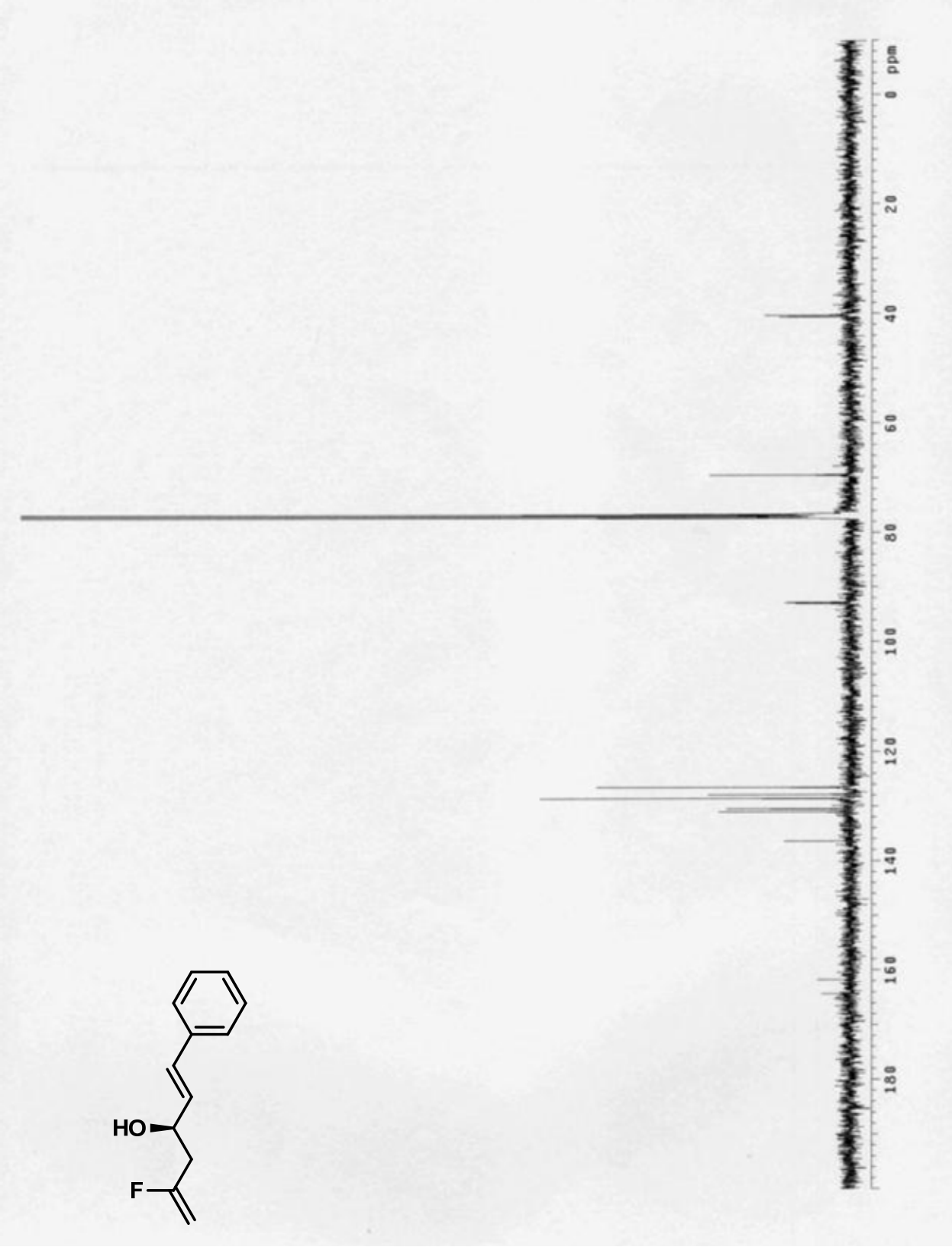
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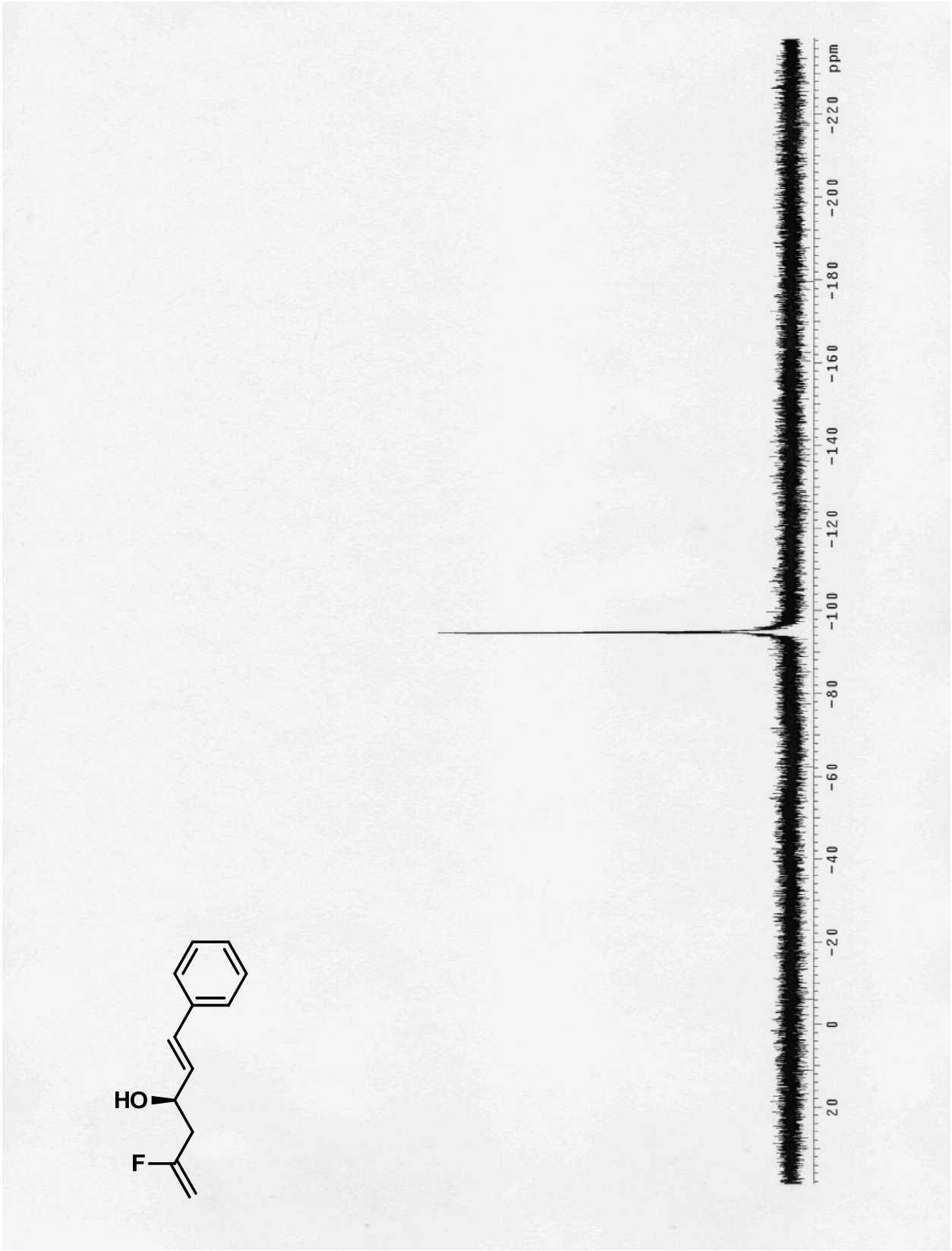
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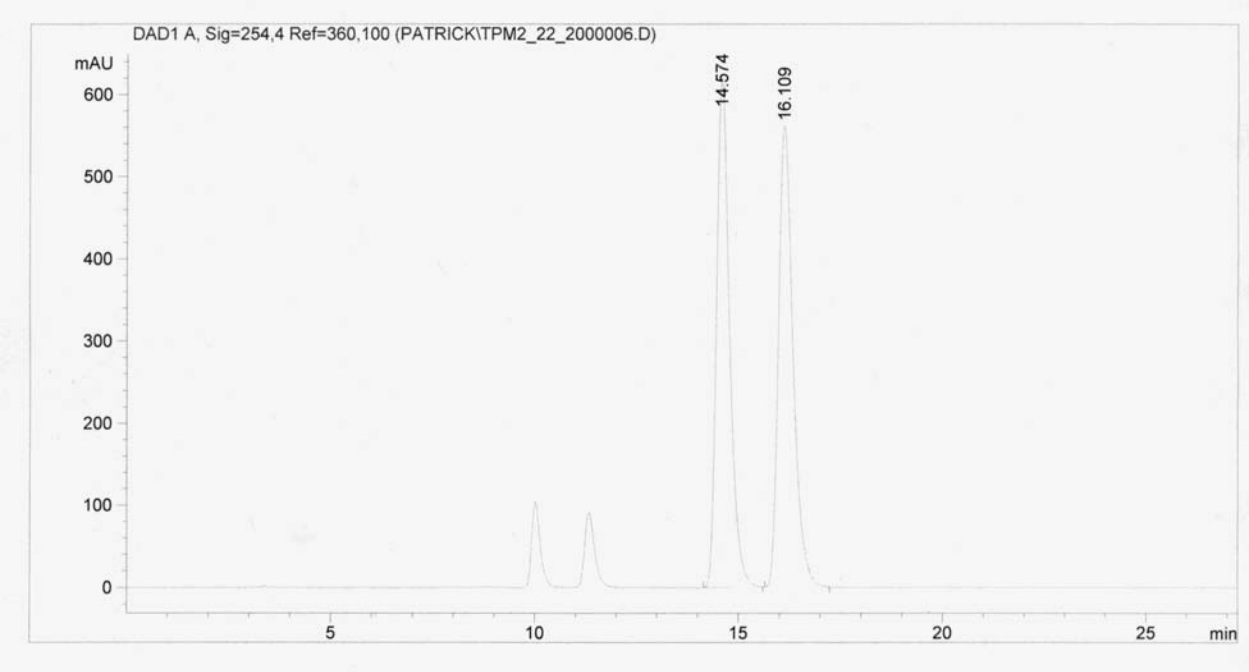
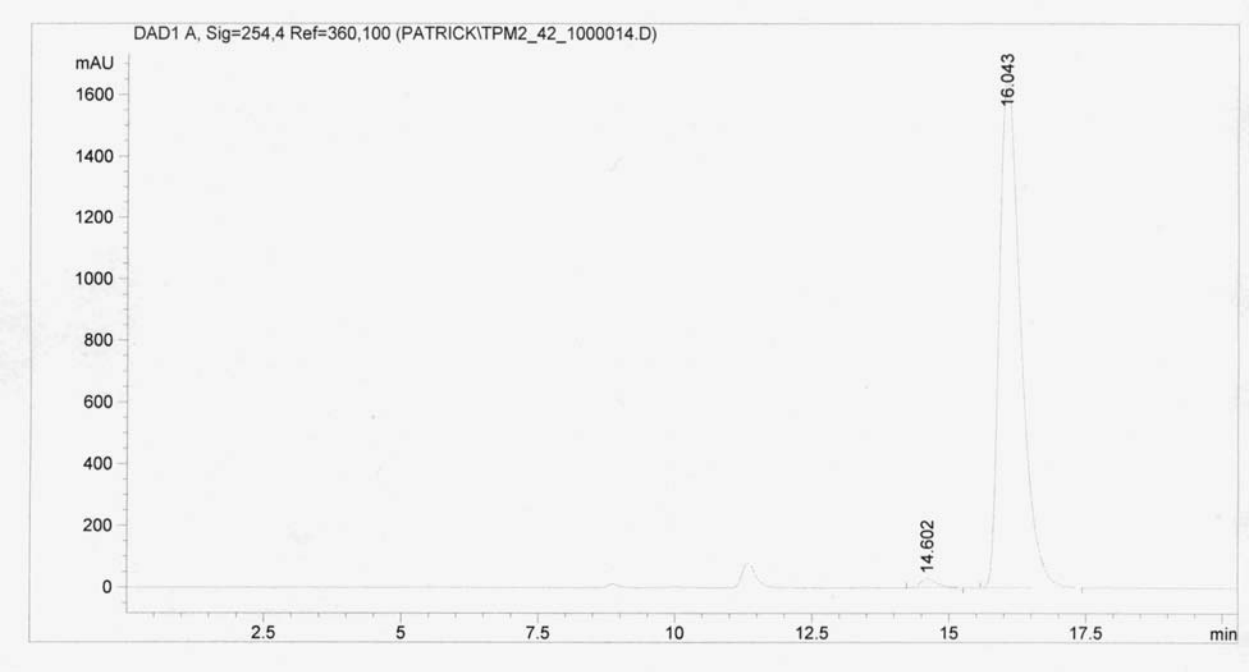
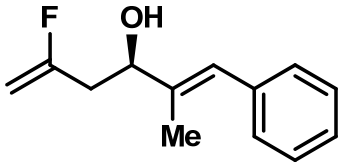


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.574	BB	0.3386	1.38242e4	618.85553	49.7717
2	16.109	BB	0.3756	1.39510e4	561.95593	50.2283



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.602	BB	0.3285	634.24323	29.07792	1.3910
2	16.043	BB	0.4178	4.49604e4	1650.49707	98.6090

(3R)-5-Fluoro-2-methyl-1phenylhexa-1,5-diene-3-ol (4e)



To a resealable pressure tube (13x100 mm) equipped with a magnetic stir bar was added **Ir-Cat-I** (10.7 mg, 0.01 mmol, 5 mol%) and K_3PO_4 (42.4 mg, 0.2 mmol, 100 mol%). The tube was sealed with a rubber septum and purged with argon. THF (0.2 mL), 3-chloro-2-fluoroprop-1-ene (28.4 mg, 0.3 mmol, 150 mol%), alcohol **2e** (29.2 mg, 0.2 mmol, 100 mol%), and H_2O (18.0 mg, 1.0 mmol, 500 mol%) were added to the purged tube, and the rubber septum was quickly replaced with a screw cap. The reaction mixture was heated in an oil bath at 40 °C for 24 hours, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was concentrated *in vacuo* and purified by flash chromatography (SiO_2: ethyl acetate/hexanes, 1:9) to furnish the title compound **4e** (32.8 mg, 0.159 mmol) as a colorless oil in 80% yield and **5e** (2.0 mg, 0.011 mmol) as a colorless oil in 5% yield.

TLC (SiO_2): R_f= 0.25 (ethyl acetate:hexanes, 1:9)

[α]$_D^{23}$=+1.5°

^{1}H NMR (400 MHz, CDCl3): δ 7.36-7.21 (m, 5H), 6.58 (br, 1H), 4.68 (dd, *J*=17.6, 2.8 Hz, 1H), 4.45-4.44 (m, 1H), 4.41 (dd, *J*=50, 2.8 Hz, 1H), 2.58-2.46 (m, 1H), 1.90 (br, 1H), 1.90 (d, *J*=1.6 Hz, 3H).

^{13}C NMR (100 MHz, CDCl3): δ 163.4 (d, *J*=256.0 Hz), 138.7, 137.2, 129.0, 128.1, 126.6, 126.3, 92.6 (d, *J*=19.3 Hz), 74.3, 38.7 (d, *J*=26.0 Hz), 13.4.

^{19}F NMR (400 MHz, CDCl3): δ -95.39 (ddt, *J*=52.8, 40.8, 17.6 Hz).

HRMS (CI) Calcd. for $C_{13}H_{15}FO$ $[M]^+$: 206.1109, Found: 206.1107.

FTIR (neat): 3390, 2920, 1674, 1491, 1445, 1380, 1333, 1242, 1178, 1015, 940, 920, 854, 749, 699 cm^{-1}.

HPLC (Chiralcel OJ-H column, hexanes:*i*-PrOH = 95:5, 1.0 mL/min, 254 nm), t_{minor} = 10.3 min, t_{major} = 12.3 min; ee = 98%


ppm
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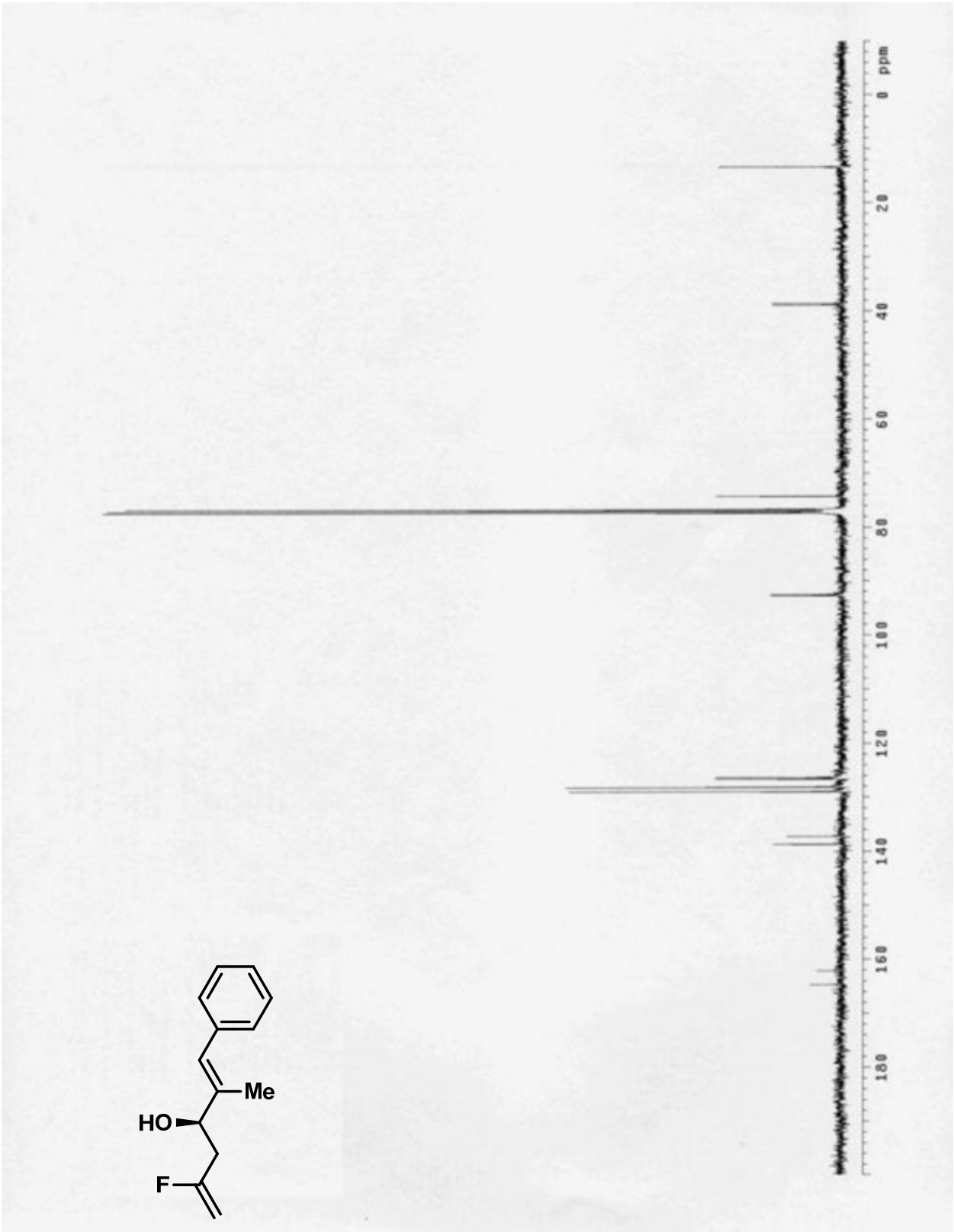
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HO
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ppm
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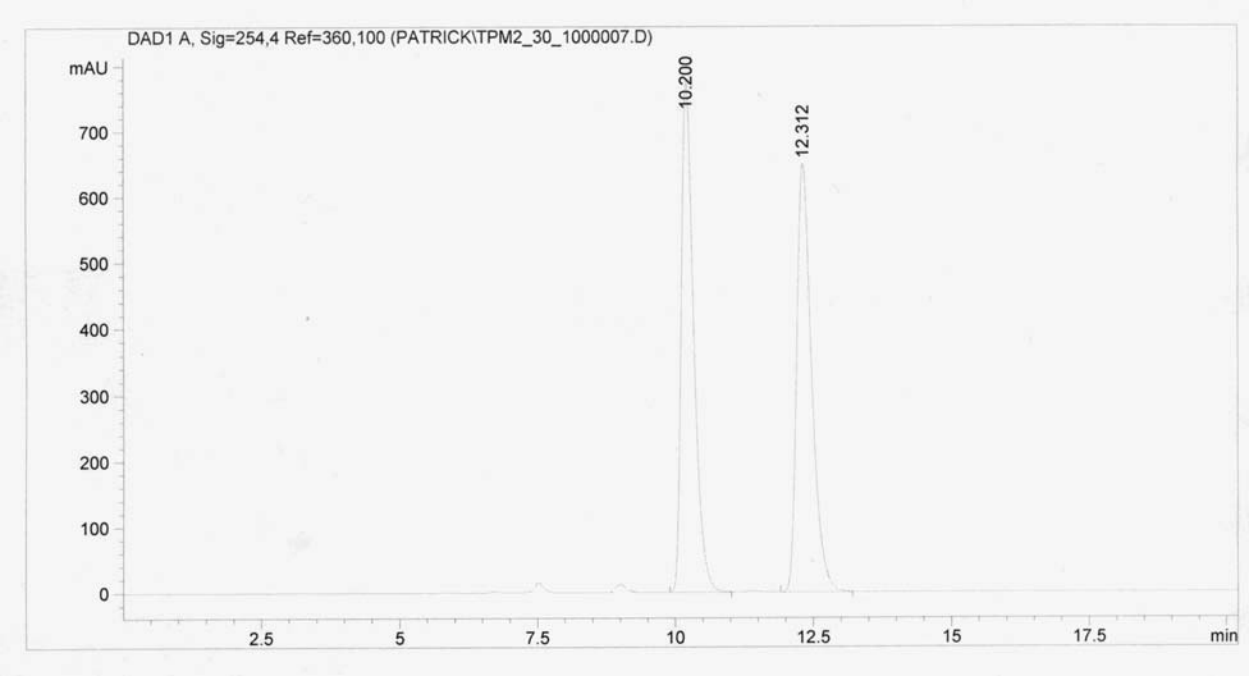
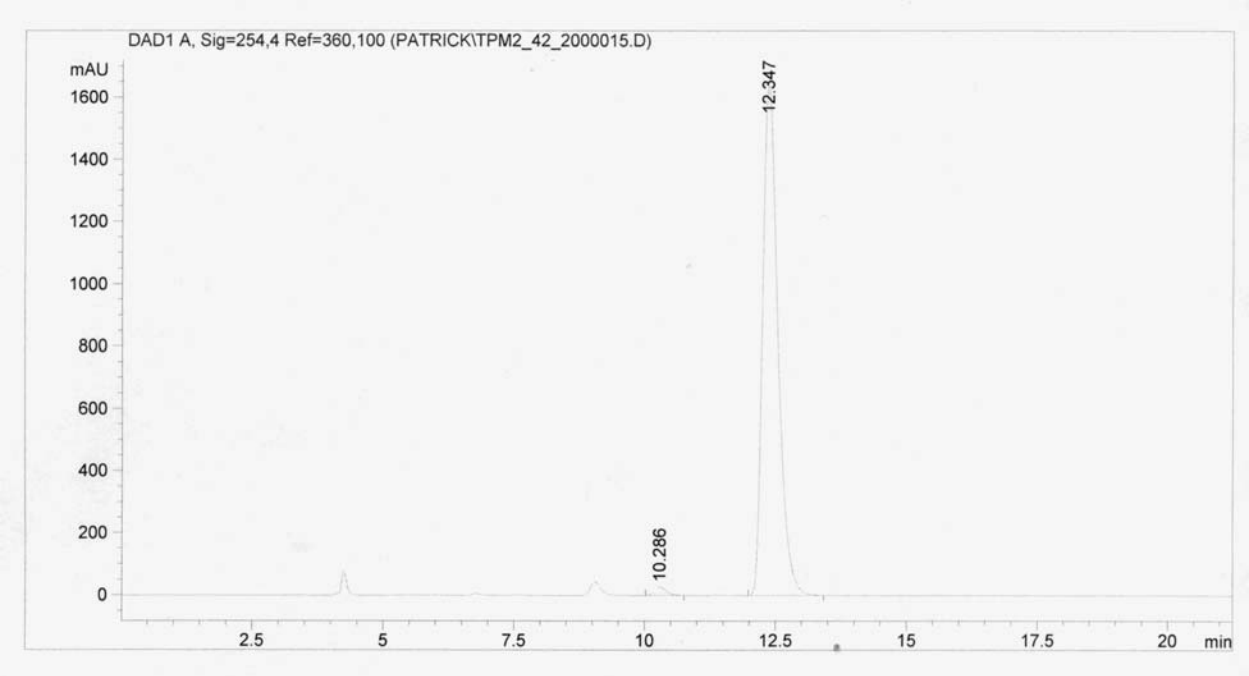
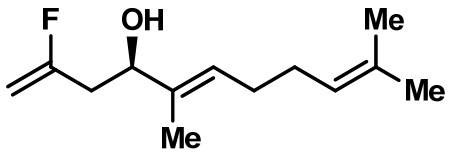


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.200	BB	0.2375	1.21983e4	775.59875	49.9786
2	12.312	VB	0.2833	1.22088e4	649.35803	50.0214



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.286	BB	0.2326	416.54034	27.21012	1.2367
2	12.347	BB	0.3128	3.32647e4	1638.81714	98.7633

(4R)-2-Fluoro-6,10-dimethylundeca-1,5,9-triene-4-ol (4f)



To a resealable pressure tube (13x100 mm) equipped with a magnetic stir bar was added **Ir-Cat-I** (10.7 mg, 0.01 mmol, 5 mol%) and K_3PO_4 (42.4 mg, 0.2 mmol, 100 mol%). The tube was sealed with a rubber septum and purged with argon. THF (0.2 mL), 3-chloro-2-fluoroprop-1-ene (28.4 mg, 0.3 mmol, 150 mol%), alcohol **2f** (30.9 mg, 0.2 mmol, 100 mol%), and H_2O (18.0 mg, 1.0 mmol, 500 mol%) were added to the purged tube, and the rubber septum was quickly replaced with a screw cap. The reaction mixture was heated in an oil bath at 40 °C for 24 hours, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was concentrated *in vacuo* and purified by flash chromatography (SiO_2: ethyl acetate:hexanes, 1:9) to furnish the title compound **4f** (31.8 mg, 0.150 mmol) as a yellow oil in 75% yield and **5f** (1.4 mg, 0.007 mmol) as a yellow oil in 4% yield.

TLC (SiO_2): R_f= 0.28 (ethyl acetate:hexanes, 1:9)

[α]$_D^{23}$=+7.9°

^{1}H NMR (400 MHz, CDCl3): δ 5.21 (d, *J*=8.4 Hz, 1H), 5.1-5.06 (m, 1H), 4.66-4.61 (m, 1H), 4.63 (dd, *J*=17.2, 2.8 Hz, 1H), 4.34 (dd, *J*=50.0, 2.4 Hz, 1H), 2.49-2.30 (m, 2H), 2.12-2.07 (m, 2H), 2.05-2.00 (m, 1H), 1.69 (dd, *J*=8.8, 1.2 Hz, 6H), 1.60 (s, 3H), 1.59 (br, 1H).

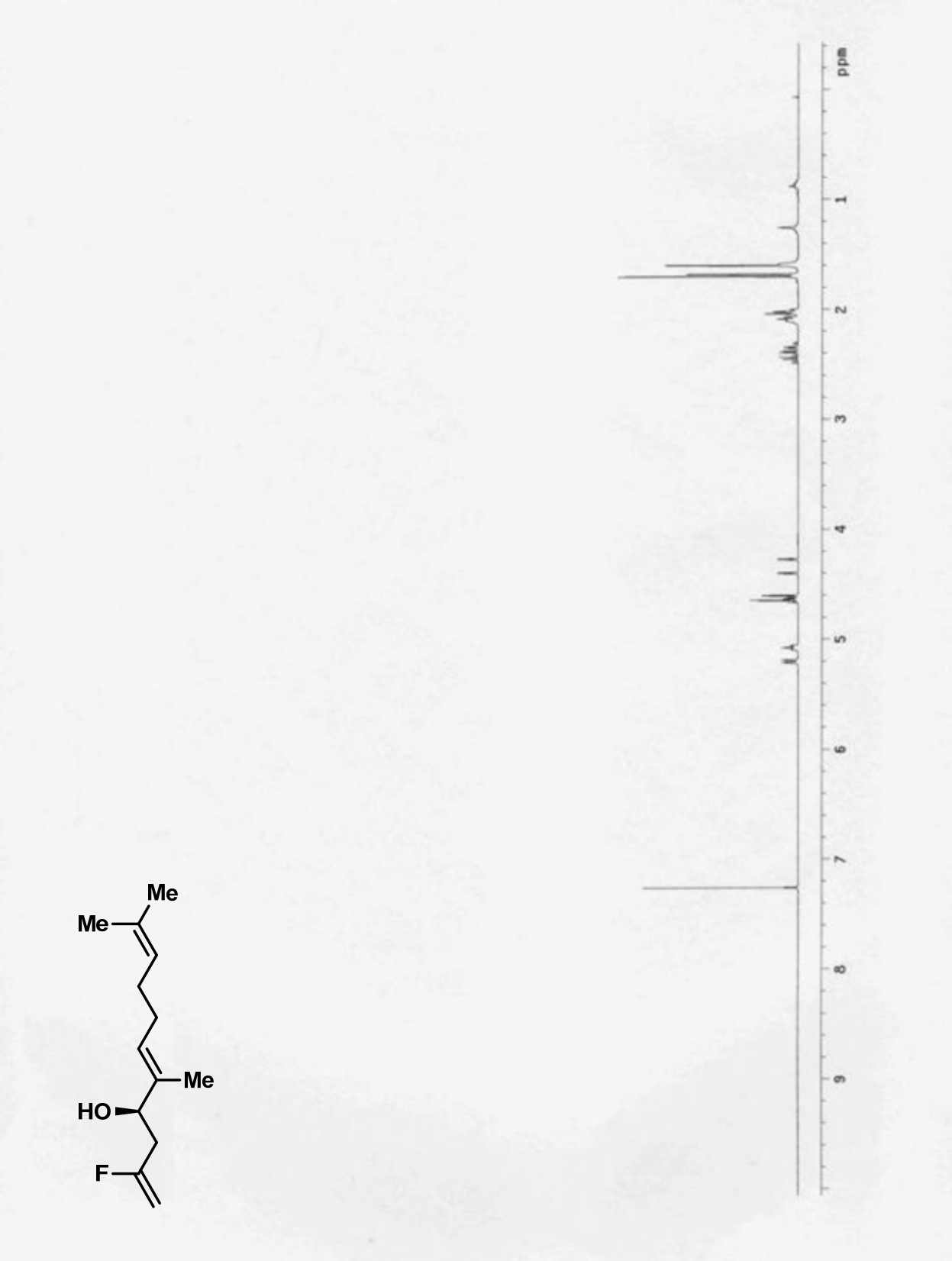
^{13}C NMR (100 MHz, CDCl3): δ 163.5 (d, *J*=256.0 Hz), 139.8, 131.8, 126.1, 123.8, 92.4 (d, *J*=19.3 Hz), 65.4, 40.4 (*J*=25.3 Hz), 39.5, 26.3, 25.7, 17.7, 16.6.

^{19}F NMR (400 MHz, CDCl3): δ -94.88 (ddt, *J*=53.2, 41.2, 18.0).

HRMS (CI) Calcd. for $C_{13}H_{20}FO$ $[M-H]^+$: 211.1501, Found: 211.1498.

FTIR (neat): 3382, 2964, 2916, 2857, 2361, 1672, 1442, 1377, 1261, 1241, 1192, 1108, 1037, 940, 847, 821, 810 cm^{-1}.

HPLC Enantiomeric excess was determined by the analysis of the 4-nitrobenzoate derivative of the product (Chiralcel OJ-H column, hexanes:*i*-PrOH = 98:2, 1.0 mL/min, 254 nm), t_{minor} = 5.8 min, t_{major} = 5.4 min; ee = 95%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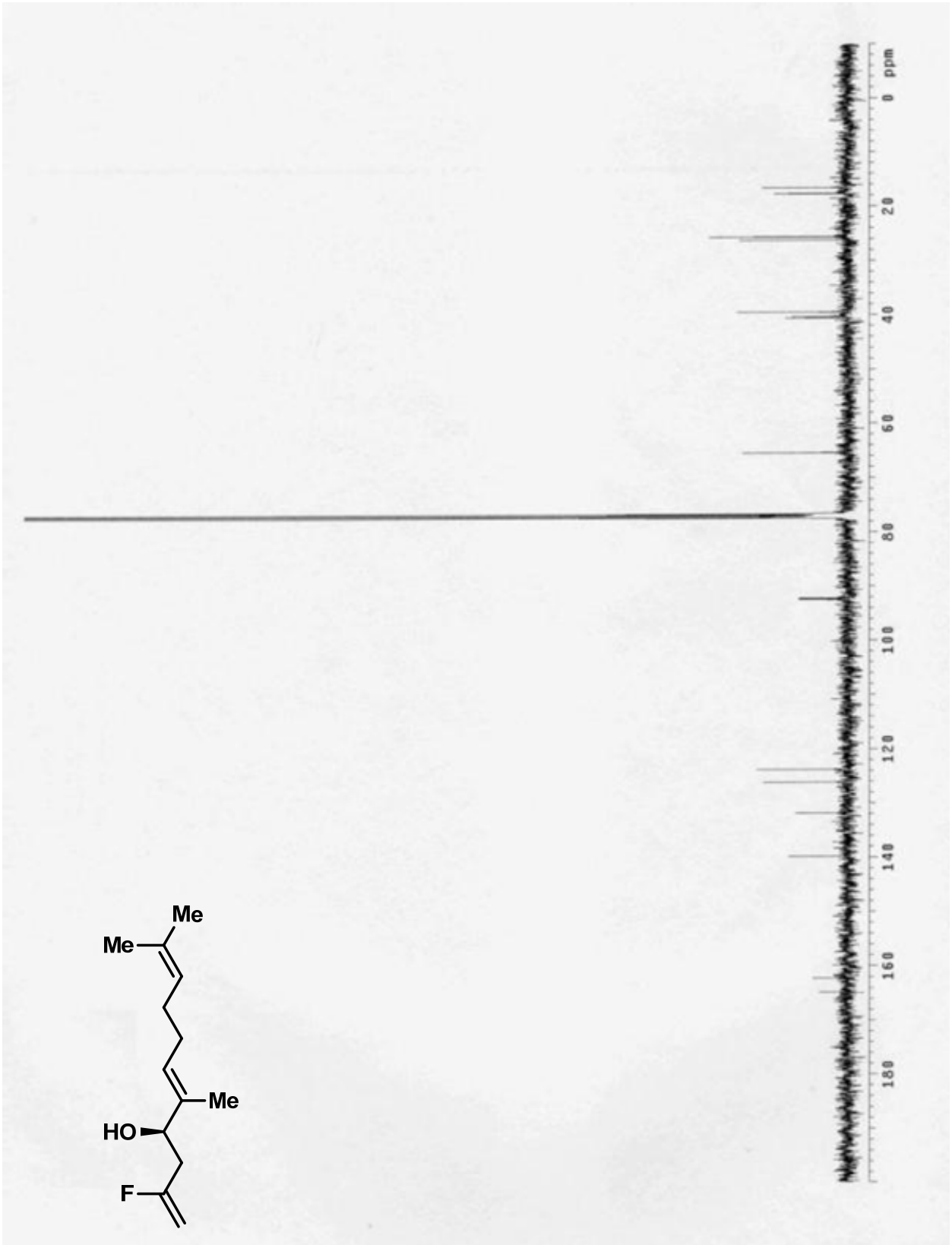
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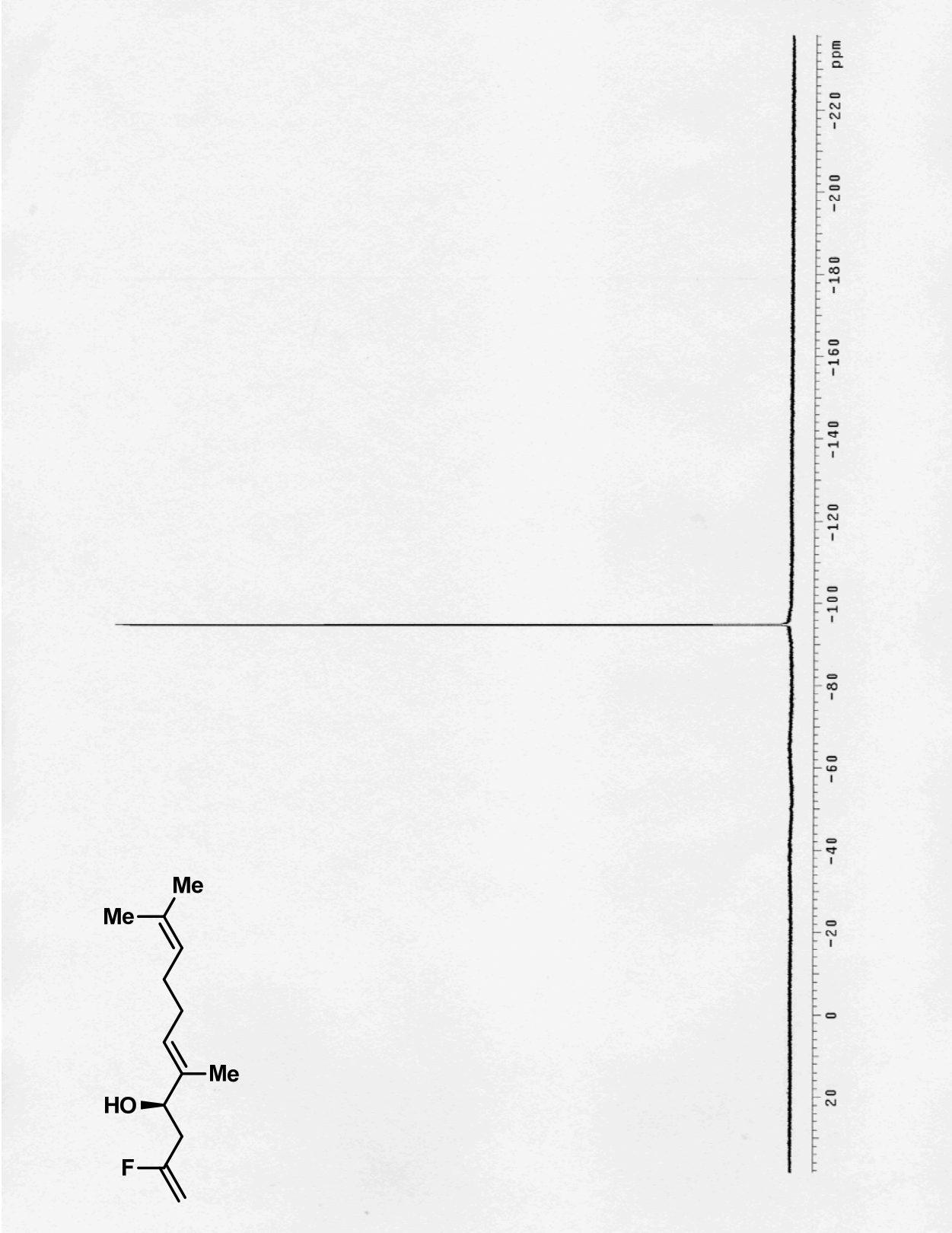
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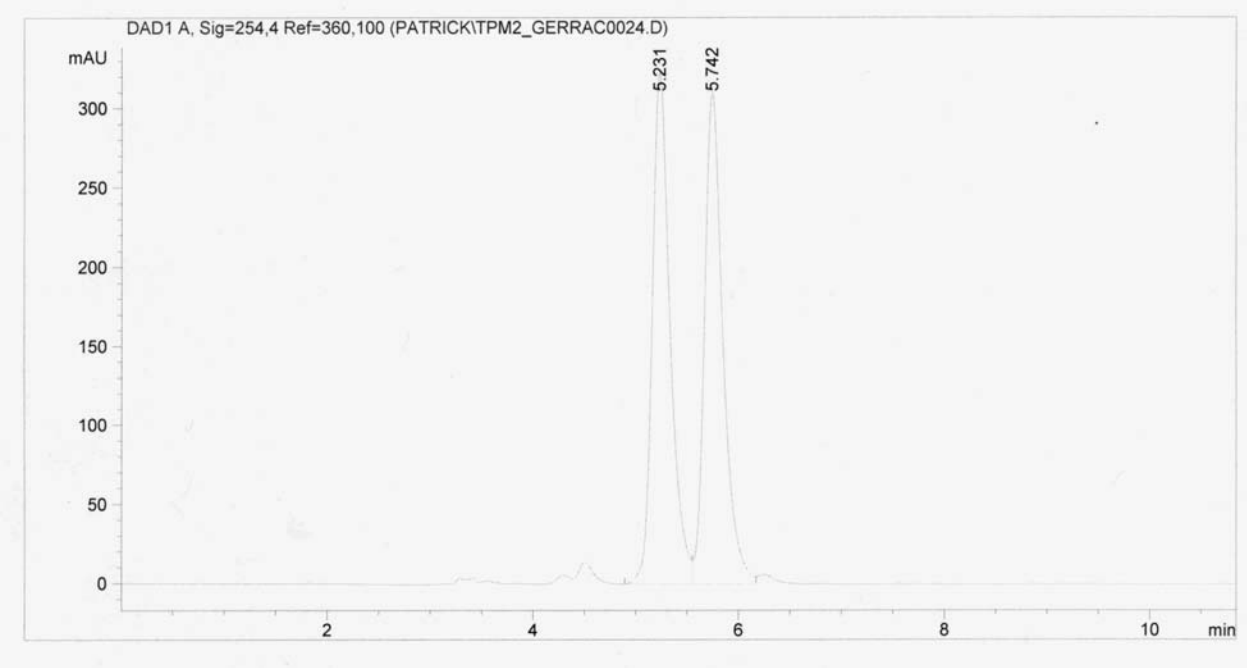
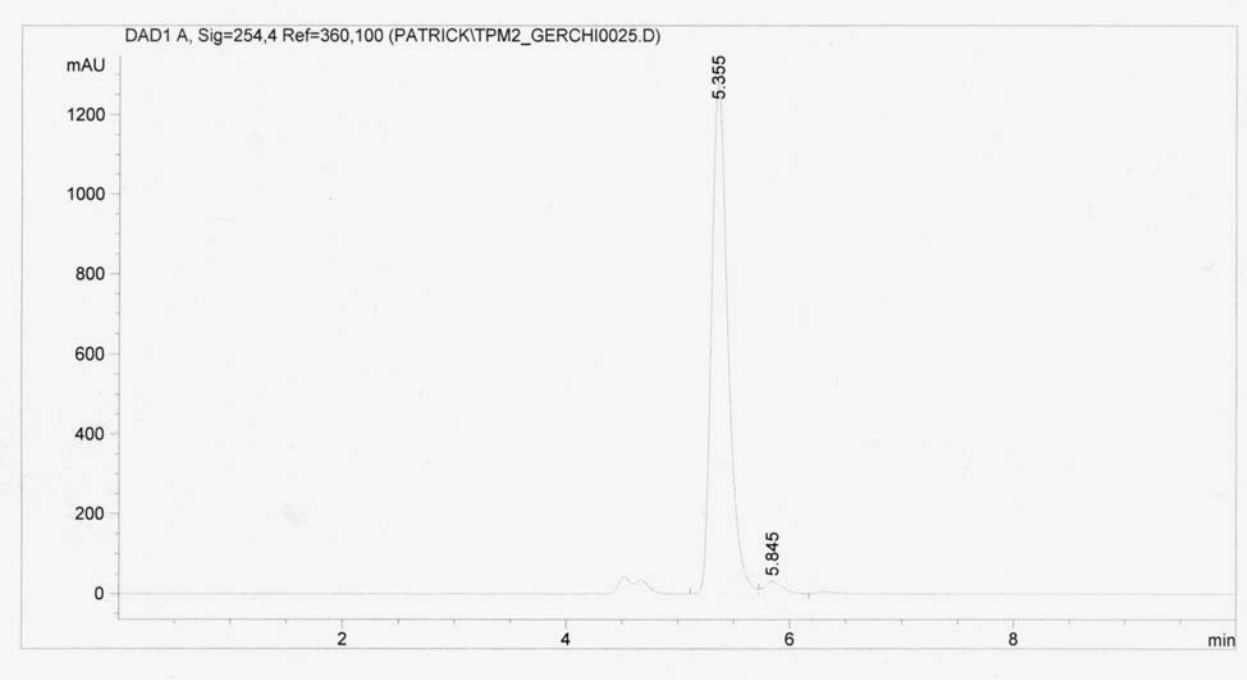
ppm

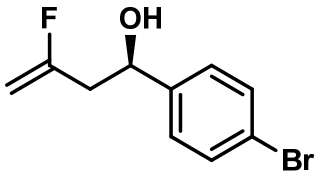


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.231	BV	0.1815	3916.59277	322.86990	50.1903
2	5.742	VV	0.1881	3886.88770	310.37445	49.8097



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.355	BV	0.1571	1.31098e4	1284.17468	97.3068
2	5.845	VV	0.1724	362.84540	31.49163	2.6932

(4R)-4-(4-Bromophenyl)-2-fluorobuta-1-ene-4-ol (4g)



To a resealable pressure tube (13x100 mm) equipped with a magnetic stir bar was added alcohol **2g** (37.4 mg, 0.2 mmol, 100 mol%), **Ir-Cat-I** (10.7 mg, 0.01 mmol, 5 mol%), and K_3PO_4 (42.4 mg, 0.2 mmol, 100 mol%). The tube was sealed with a rubber septum and purged with argon. THF (0.2 mL), 3-chloro-2-fluoroprop-1-ene (28.4 mg, 0.3 mmol, 150 mol%), and H_2O (18.0 mg, 1.0 mmol, 500 mol%) were added to the purged tube, and the rubber septum was quickly replaced with a screw cap. The reaction mixture was heated in an oil bath at 40 °C for 24 hours, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was concentrated *in vacuo* and purified by flash chromatography (SiO_2: ethyl acetate:hexanes, 1:9) to furnish the title compound **4g** (42.0 mg, 0.171 mmol) as a white solid in 86% yield and **5g** (3.1 mg, 0.014 mmol) as a white solid in 7% yield.

TLC (SiO_2): R_f= 0.24 (ethyl acetate:hexanes, 1:9)

[α]$_D^{23}$=+56.3°

^{1}H NMR (400 MHz, CDCl3): δ 7.51-7.47 (m, 2H), 7.27-7.24 (m, 2H), 4.95-4.91 (m, 1H), 4.67 (dd, *J*=17.2, 3.2 Hz, 1H), 4.34 (dd, *J*=50.0, 2.8 Hz, 1H), 2.62-2.54 (m, 2H), 2.16 (d, *J*=2.8 Hz, 1H).

^{13}C NMR (100 MHz, CDCl3): δ 162.8 (d, *J*=255.2 Hz), 142.0, 131.6, 131.6, 127.4, 127.4, 121.7, 93.2 (d, *J*=19.3 Hz), 70.3, 42.3 (d, *J*=26.1 Hz).

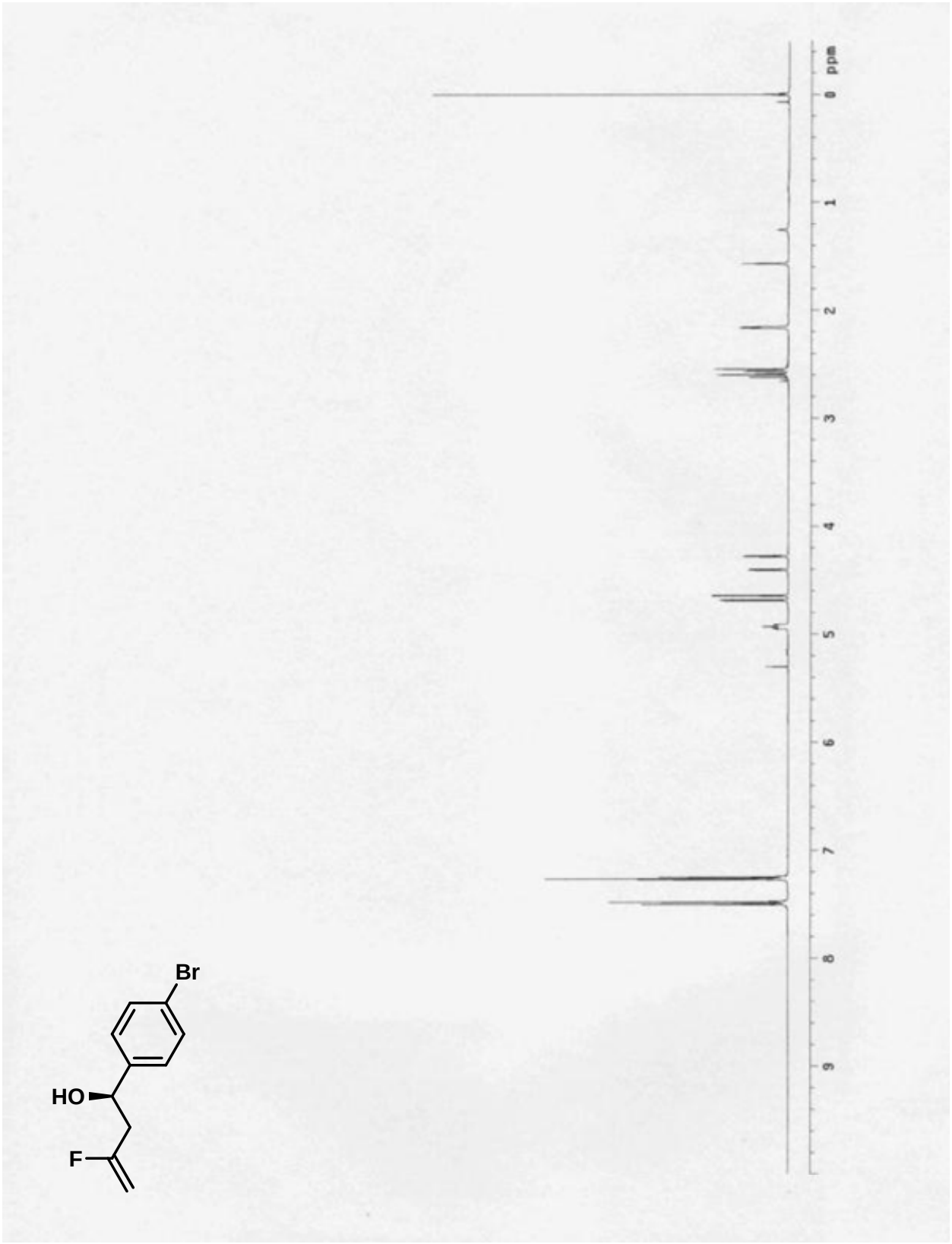
^{19}F NMR (400 MHz, CDCl3): δ -95.99 (ddt, *J*=52.8, 40.4, 17.6 Hz).

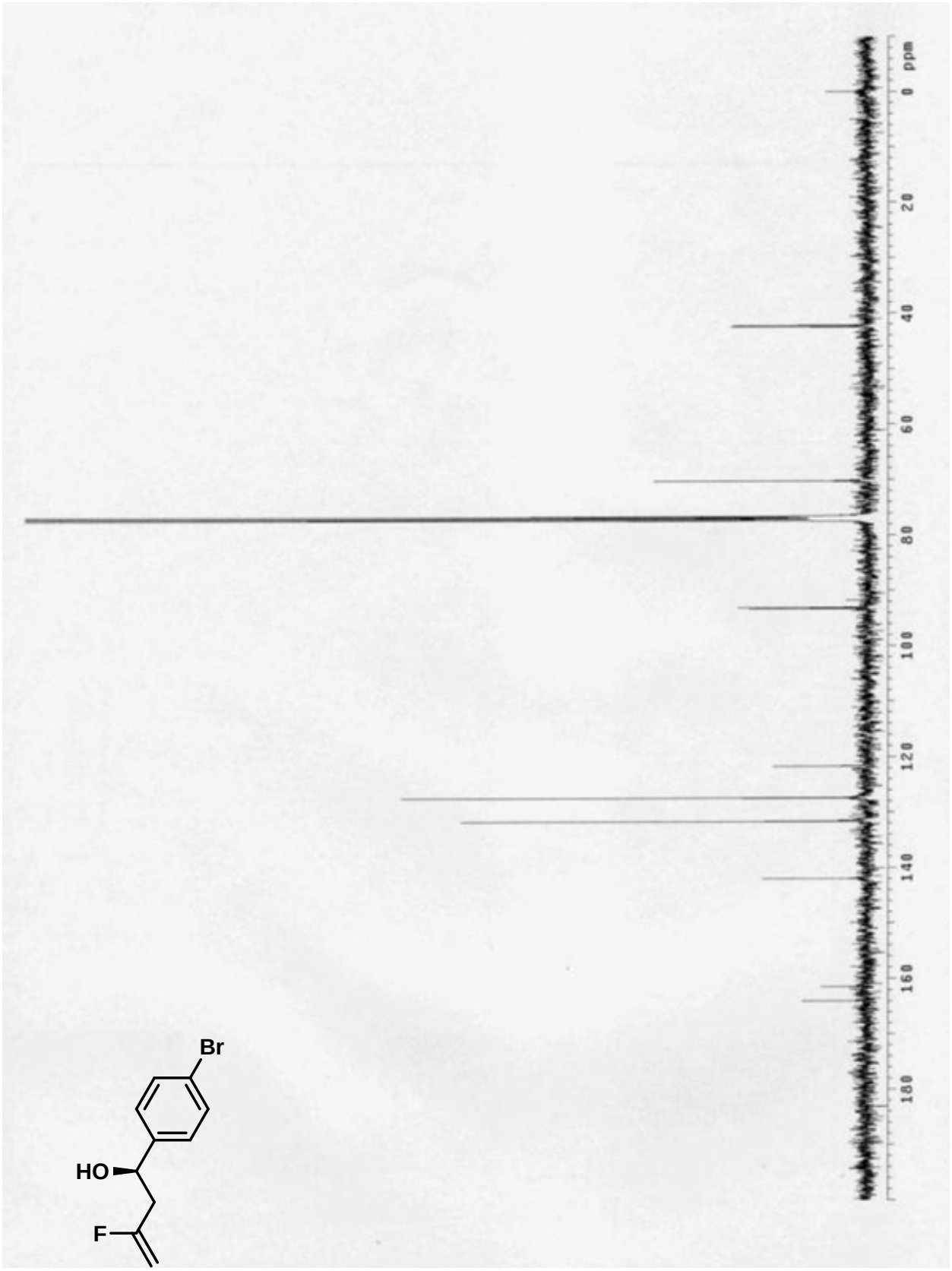
HRMS (CI) Calcd. for $C_{10}H_{11}BrFO$ $[M+H]^+$: 244.9977, Found: 244.9977.

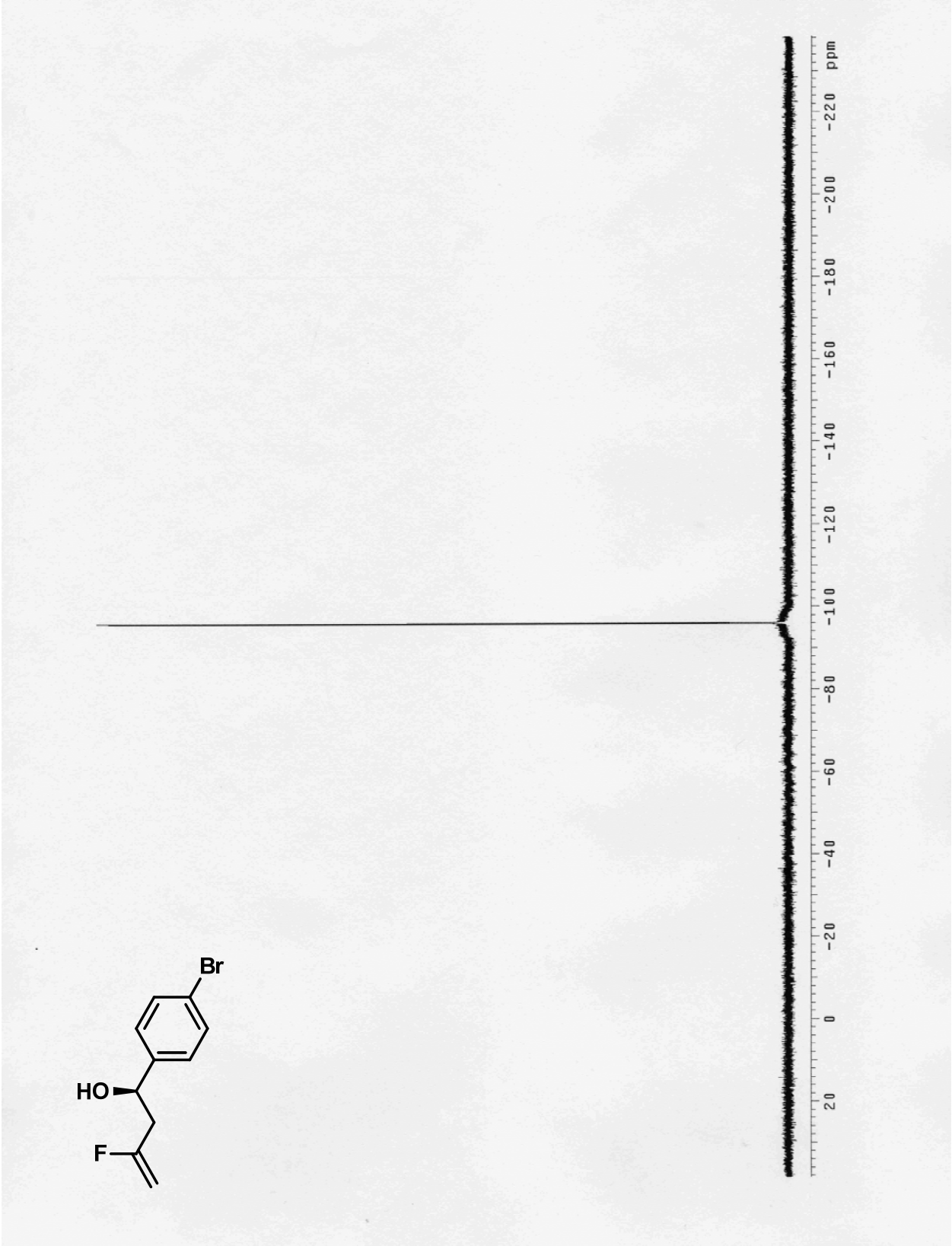
FTIR (neat): 3408, 2920, 1676, 1593, 1488, 1406, 1305, 1242, 1171, 1103, 1070, 1009, 937, 856, 816, 776, 672, 658 cm^{-1}.

HPLC (Chiralcel OJ-H column, hexanes:*i*-PrOH = 95:5, 1.0 mL/min, 230 nm), t_{minor} = 12.2 min, t_{major} = 13.1 min; ee = 99%

MP 67-69°C



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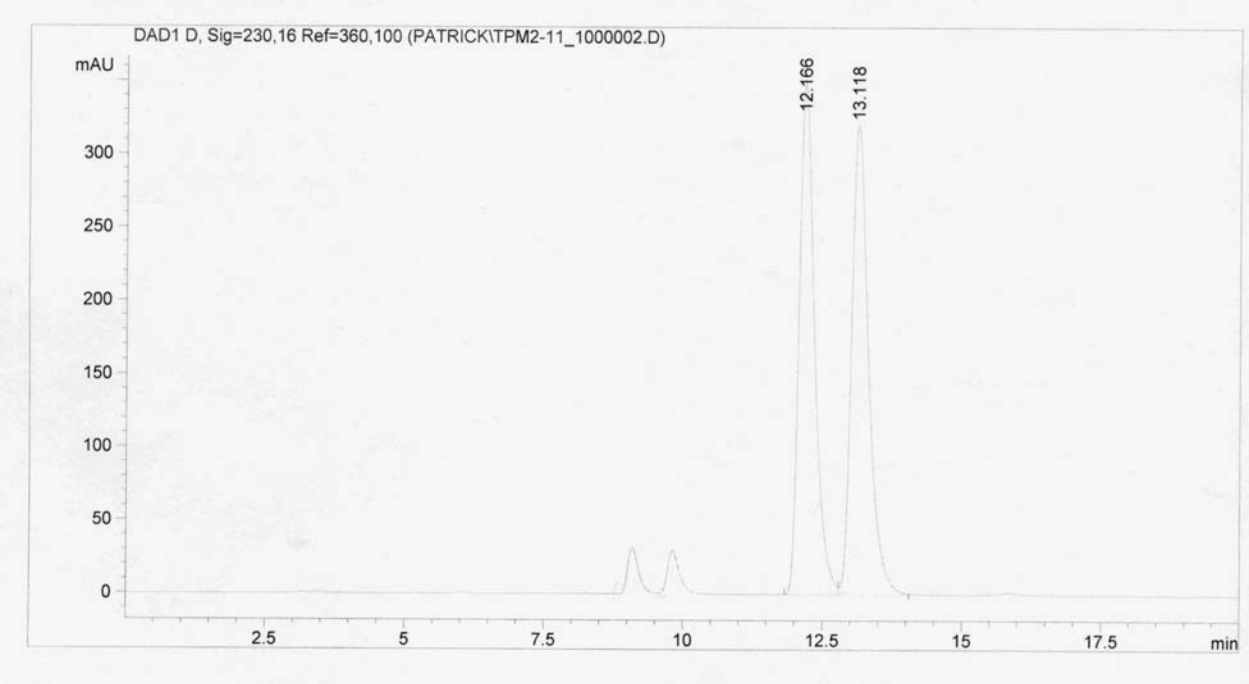
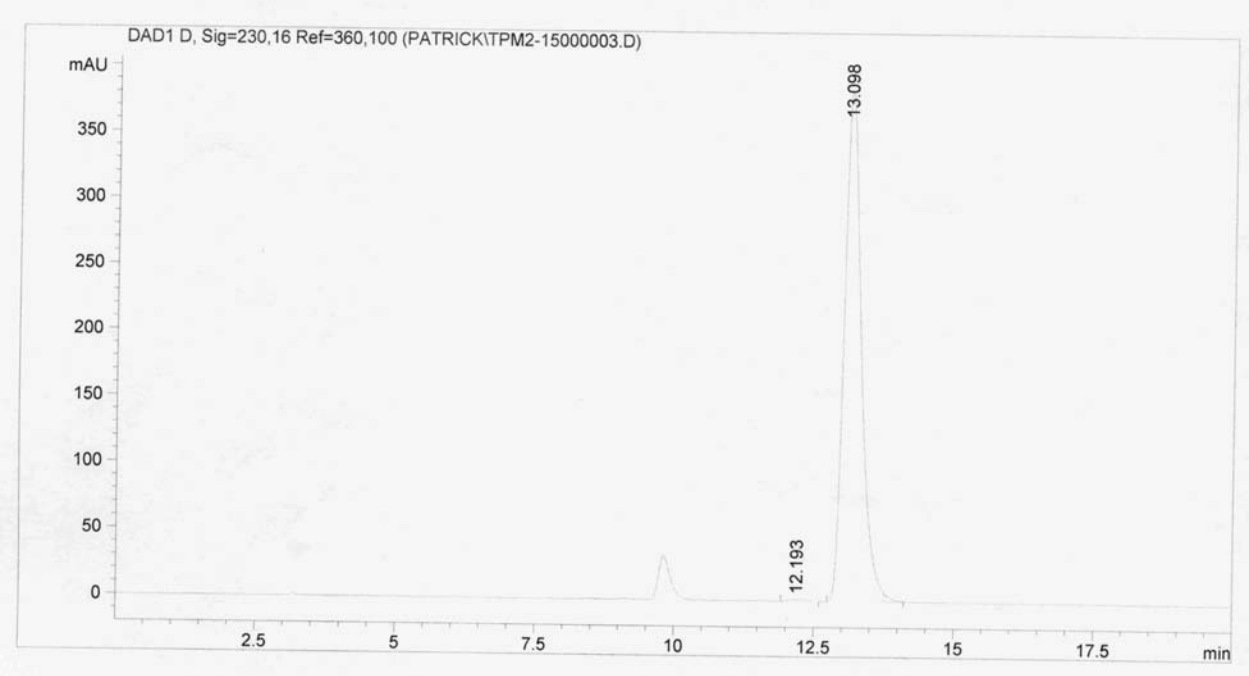
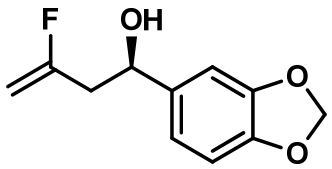


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.166	BV	0.2927	6725.58008	349.15466	49.8118
2	13.118	VB	0.3206	6776.39941	320.61572	50.1882



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.193	BB	0.2518	28.13190	1.62619	0.3413
2	13.098	BB	0.3219	8214.97168	386.67972	99.6587

(1R)-1-(Benzo[*d*][1,3]dioxo-5-yl)-3-fluorobuta-3-ene-1-ol (4h)



To a resealable pressure tube (13x100 mm) equipped with a magnetic stir bar was added alcohol **2h** (30.4 mg, 0.2 mmol, 100 mol%), **Ir-Cat-I** (10.7 mg, 0.01 mmol, 5 mol%), and K_3PO_4 (42.4 mg, 0.2 mmol, 100 mol%). The tube was sealed with a rubber septum and purged with argon. THF (0.2 mL), 3-chloro-2-fluoroprop-1-ene (28.4 mg, 0.3 mmol, 150 mol%), and H_2O (18.0 mg, 1.0 mmol, 500 mol%) were added to the purged tube, and the rubber septum was quickly replaced with a screw cap. The reaction mixture was heated in an oil bath at 40 °C for 24 hours, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was concentrated *in vacuo* and purified by flash chromatography (SiO_2: ethyl acetate:hexanes, 1:9) to furnish the title compound **4h** (34.2 mg, 0.163 mmol) as a colorless oil in 81% yield and **5h** (1.0 mg, 0.005 mmol) as a colorless oil in 3% yield.

TLC (SiO_2): R_f=0.18 (ethyl acetate:hexanes, 1:9)

$[\alpha]_D^{23}$=+119.2°

^{1}H NMR (400 MHz, CDCl3): δ 6.89 (d, *J*=2.0 Hz, 1H), 6.81 (dd, *J*=8.0, 2.0 Hz, 1H), 6.79 (t, *J*=8.0 Hz, 1H), 5.96 (s, 1H), 4.89-4.86 (m, 1H), 4.65 (dd, *J*=17.2, 2.8 Hz, 1H), 4.34 (dd, *J*=50.0, 2.8 Hz, 1H), 2.67-2.50 (m, 2H), 2.06 (br, 1H).

^{13}C NMR (100 MHz, CDCl3): δ 163.1 (d, *J*=255.2), 147.8, 147.2, 137.1, 119.2, 108.1, 106.2, 101.0, 92.7 (d, *J*=19.4), 70.8, 42.3 (d, *J*=26.0).

^{19}F NMR (400 MHz, CDCl3): δ -95.86 (ddt, *J*=53.2, 40.4, 18.0 Hz).

HRMS (CI) Calcd. for $C_{11}H_{11}FO_3$ $[M]^+$: 210.0693, Found: 210.0692.

FTIR (neat): 3402, 2897, 1675, 1503, 1488, 1443, 1238, 1188, 1123, 1095, 1037, 932, 900, 856, 811, 786, 728 cm^{-1}.

HPLC (Chiralcel OJ-H column, hexanes:*i*-PrOH = 95:5, 1.0 mL/min, 280 nm), t_{minor} = 19.8 min, t_{major} = 21.5 min; ee = 99%


0 ppm
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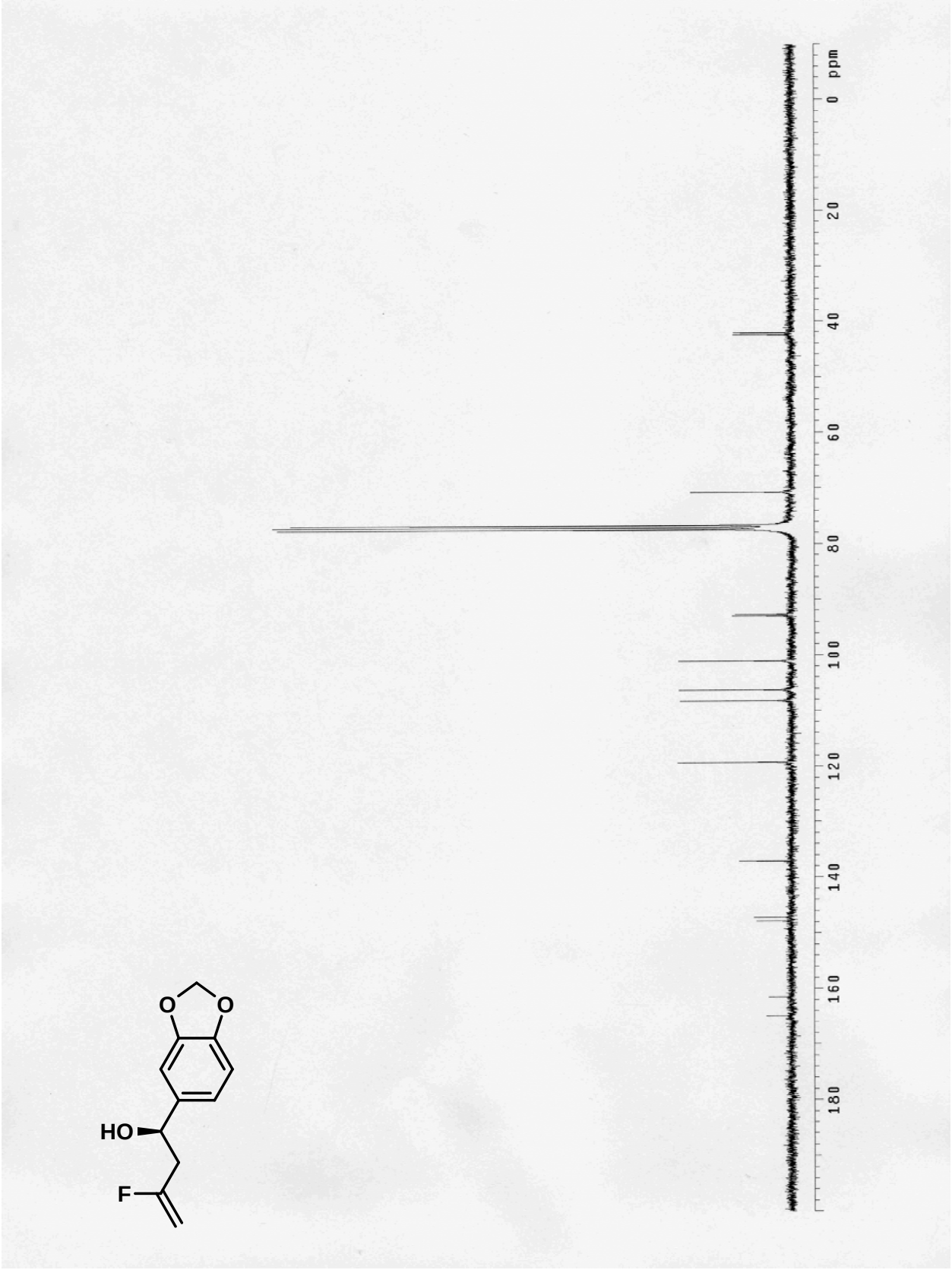
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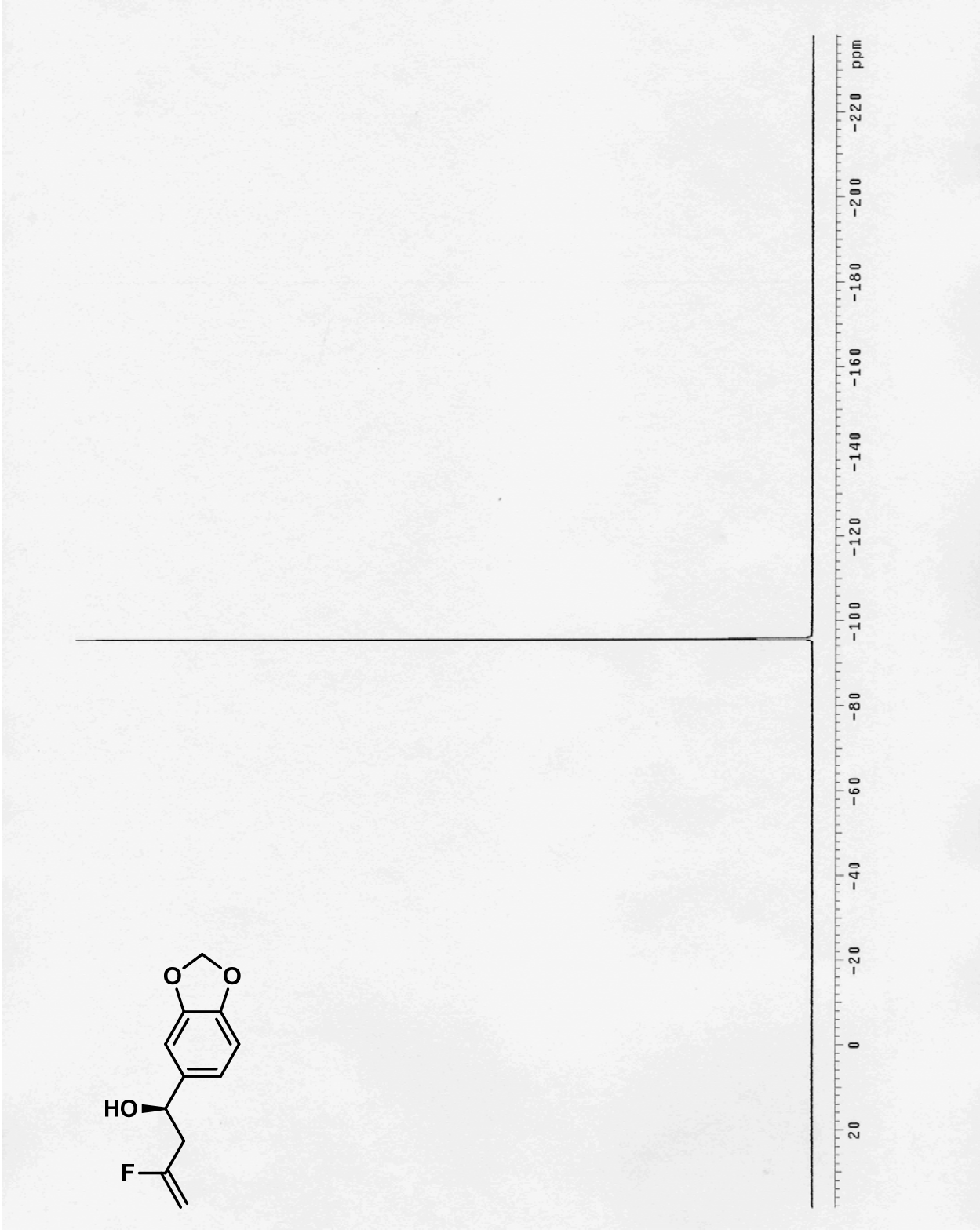
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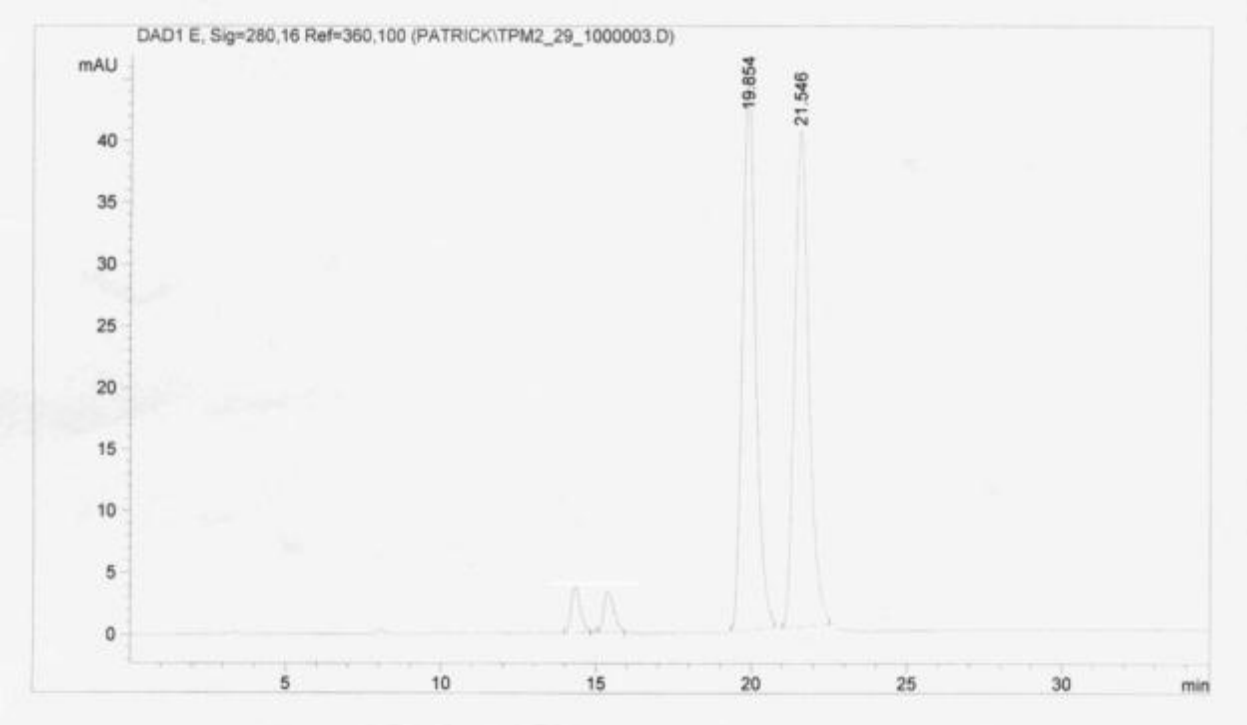
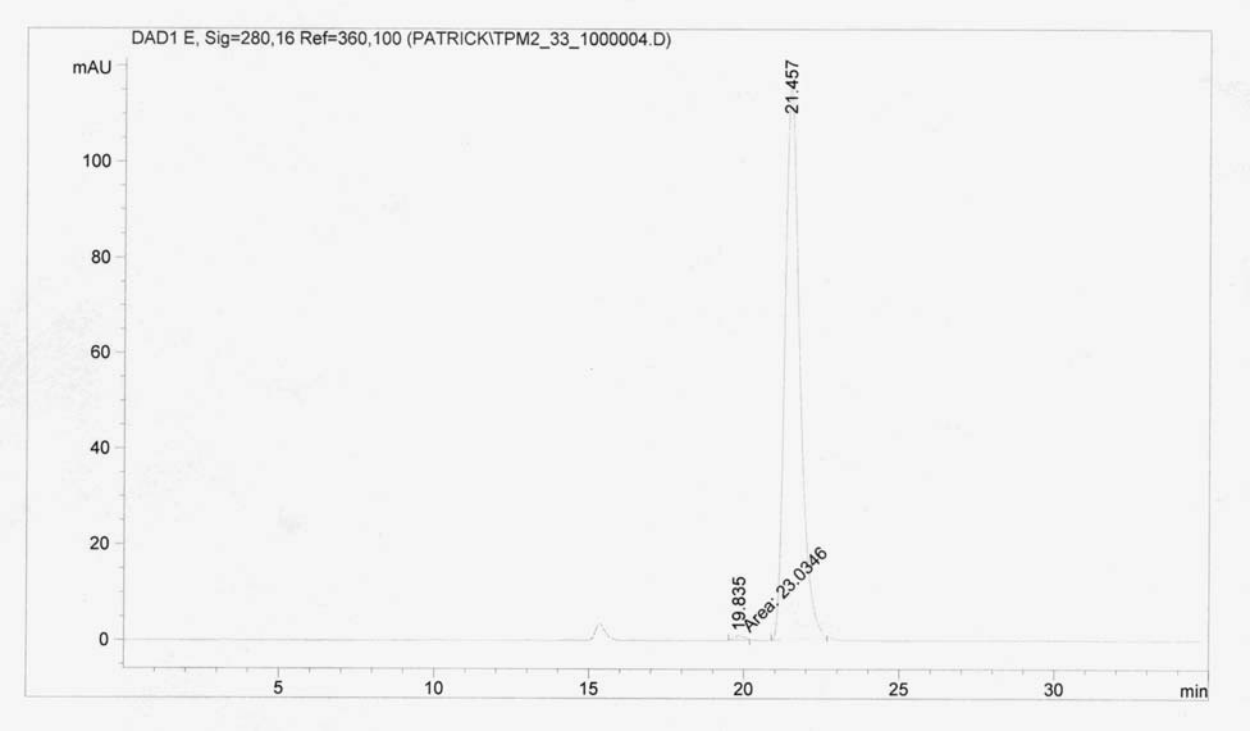
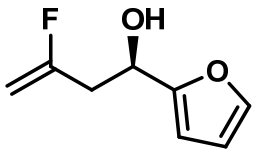


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.854	BB	0.4473	1310.93591	44.29390	47.6459
2	21.546	BB	0.4868	1290.00415	40.15759	46.8851



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.835	MM	0.4127	23.03462	9.30159e-1	0.5895
2	21.457	BB	0.5107	3884.46851	115.41161	99.4105

(1R)-3-Fluoro-1-furfurylbuta-3-ene-1-ol (4i)



To a resealable pressure tube (13x100 mm) equipped with a magnetic stir bar was added **Ir-Cat-I** (10.7 mg, 0.01 mmol, 5 mol%) and K_3PO_4 (42.4 mg, 0.2 mmol, 100 mol%). The tube was sealed with a rubber septum and purged with argon. THF (0.2 mL), 3-chloro-2-fluoroprop-1-ene (28.4 mg, 0.3 mmol, 150 mol%), alcohol **2i** (19.6 mg, 0.2 mmol, 100 mol%), and H_2O (18.0 mg, 1.0 mmol, 500 mol%) were added to the purged tube, and the rubber septum was quickly replaced with a screw cap. The reaction mixture was heated in an oil bath at 40 °C for 24 hours, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was concentrated *in vacuo* and purified by flash chromatography (SiO_2: ethyl acetate:hexanes, 1:9) to furnish the title compound **4i** (20.3 mg, 0.130 mmol) as a yellow oil in 65% yield and **5i** (1.4 mg, 0.01 mmol) as a yellow oil in 5% yield.

TLC (SiO_2): R_f= 0.19 (ethyl acetate:hexane, 1:9)

[α]$_D^{23}$=+23.4°

^{1}H NMR (400 MHz, CDCl3): δ 7.39 (dd,*J*=1.6, 0.4 Hz, 1H), 6.35 (dd, *J*=3.2, 2 Hz, 1H), 6.30 (d, *J*=3.2 Hz, 1H), 5.00-4.05 (m, 1H), 4.67 (dd, *J*=17.2, 2.8 Hz, 1H), 4.39 (dd, *J*=49.6, 2.8 Hz, 1H), 2.78 (d, *J*=6.8 Hz, 1H), 2.74-2.72 (m, 1H), 2.12 (br, 1H).

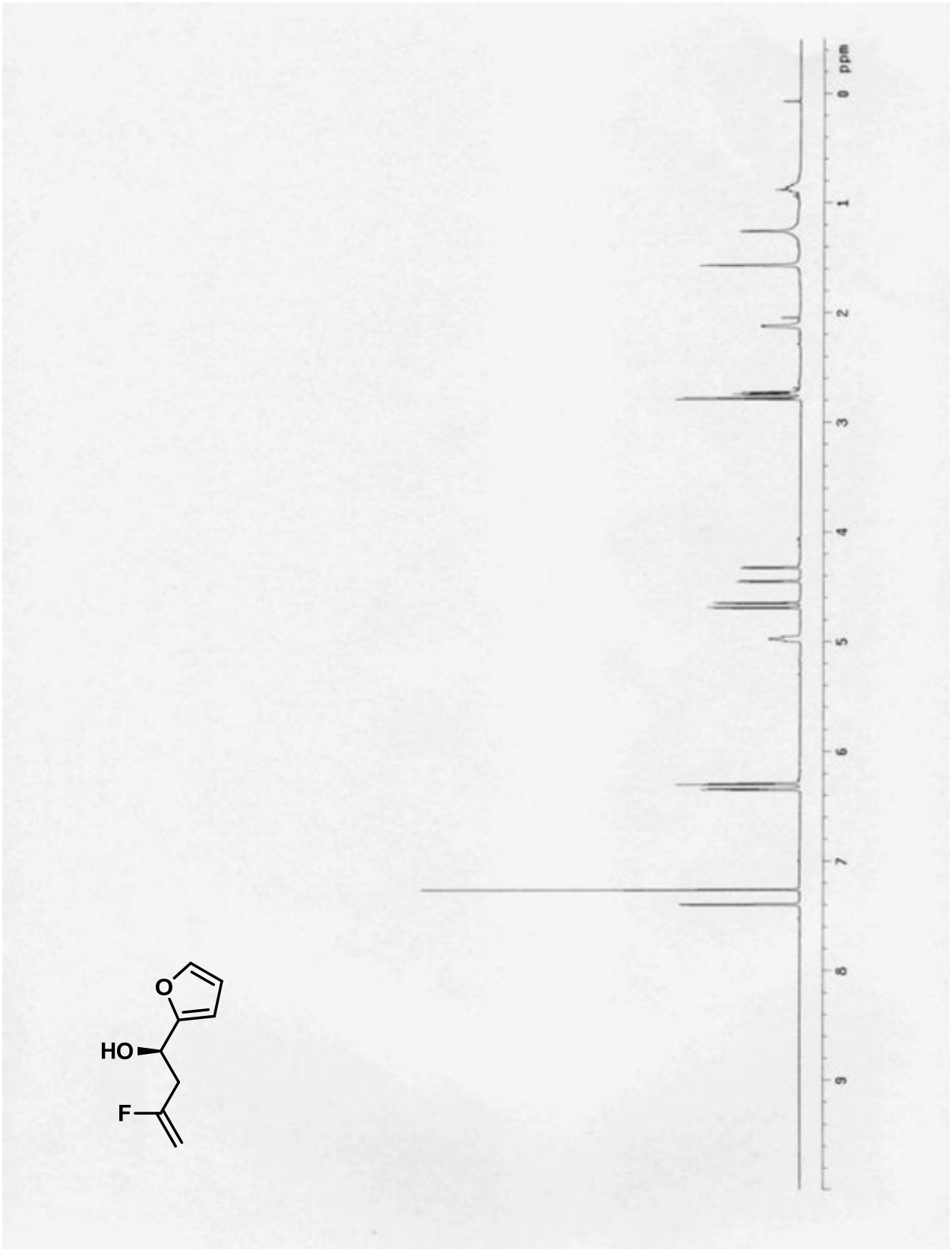
^{13}C NMR (100 MHz, CDCl3): δ 163.4 (d, *J*=255.2 Hz), 155.0, 142.3, 110.3, 106.5, 93.0 (d, *J*=19.3 Hz), 64.6, 38.6 (d, *J*=26.8 Hz).

^{19}F NMR (400 MHz, CDCl3): δ -96.15 (ddt, *J*=53.6, 39.6, 18.8 Hz).

HRMS (CI) Calcd. for $C_8H_9FO_2$ $[M]^+$: 156.0587, Found: 156.0587.

FTIR (neat): 3384, 2919, 1676, 1505, 1429, 1344, 1290, 1244, 1144, 1058, 1010, 937, 913, 884, 856 813, 739, 657 cm^{-1}.

HPLC (Chiralcel OJ-H column, hexanes:*i*-PrOH = 95:5, 1.0 mL/min, 210 nm), t_{minor} = 10.6 min, t_{major} = 11.3 min; ee = 99%


O
HO
F
ppm
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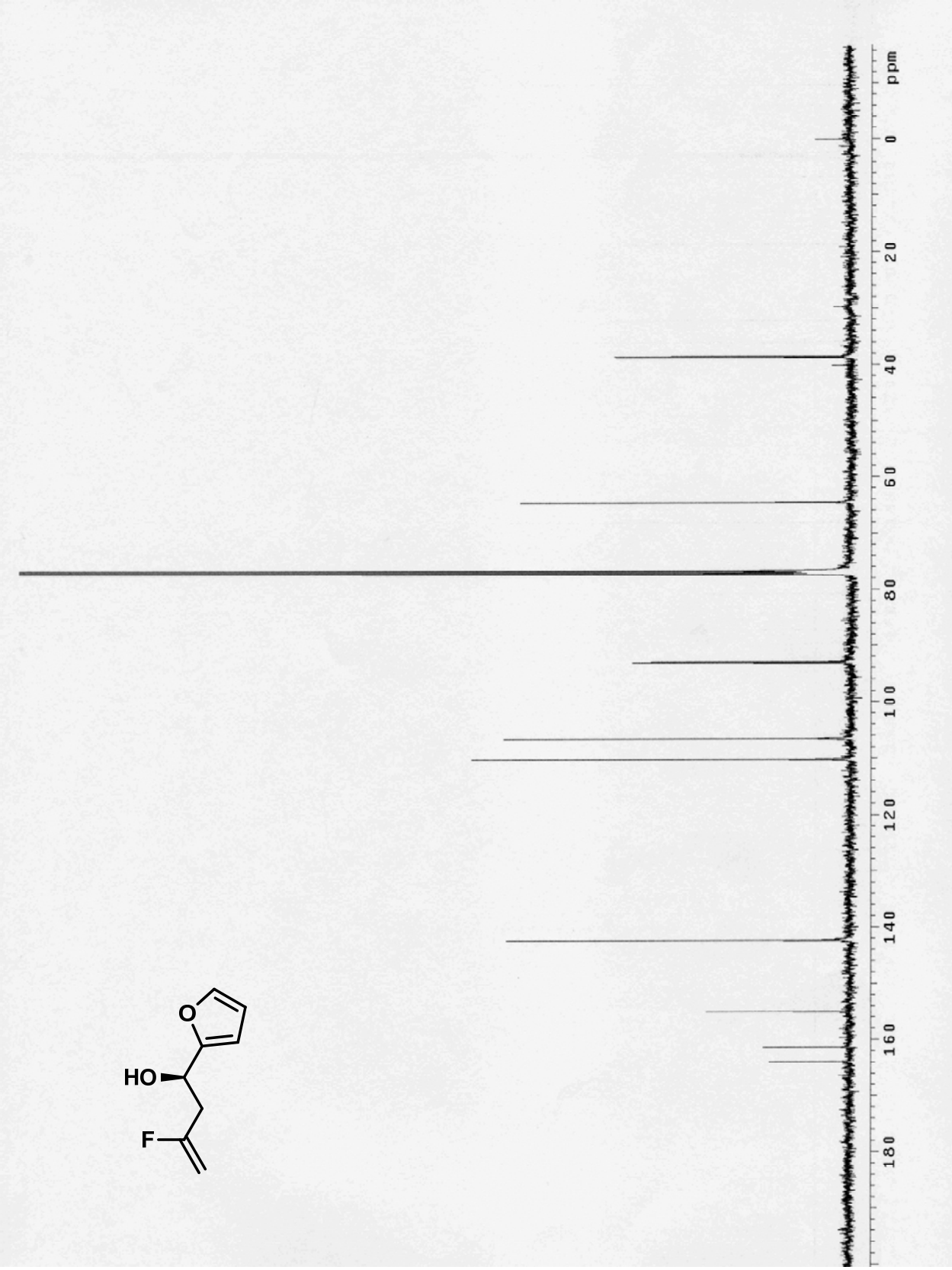
1
2
3
4
5
6
7
8
9


ppm
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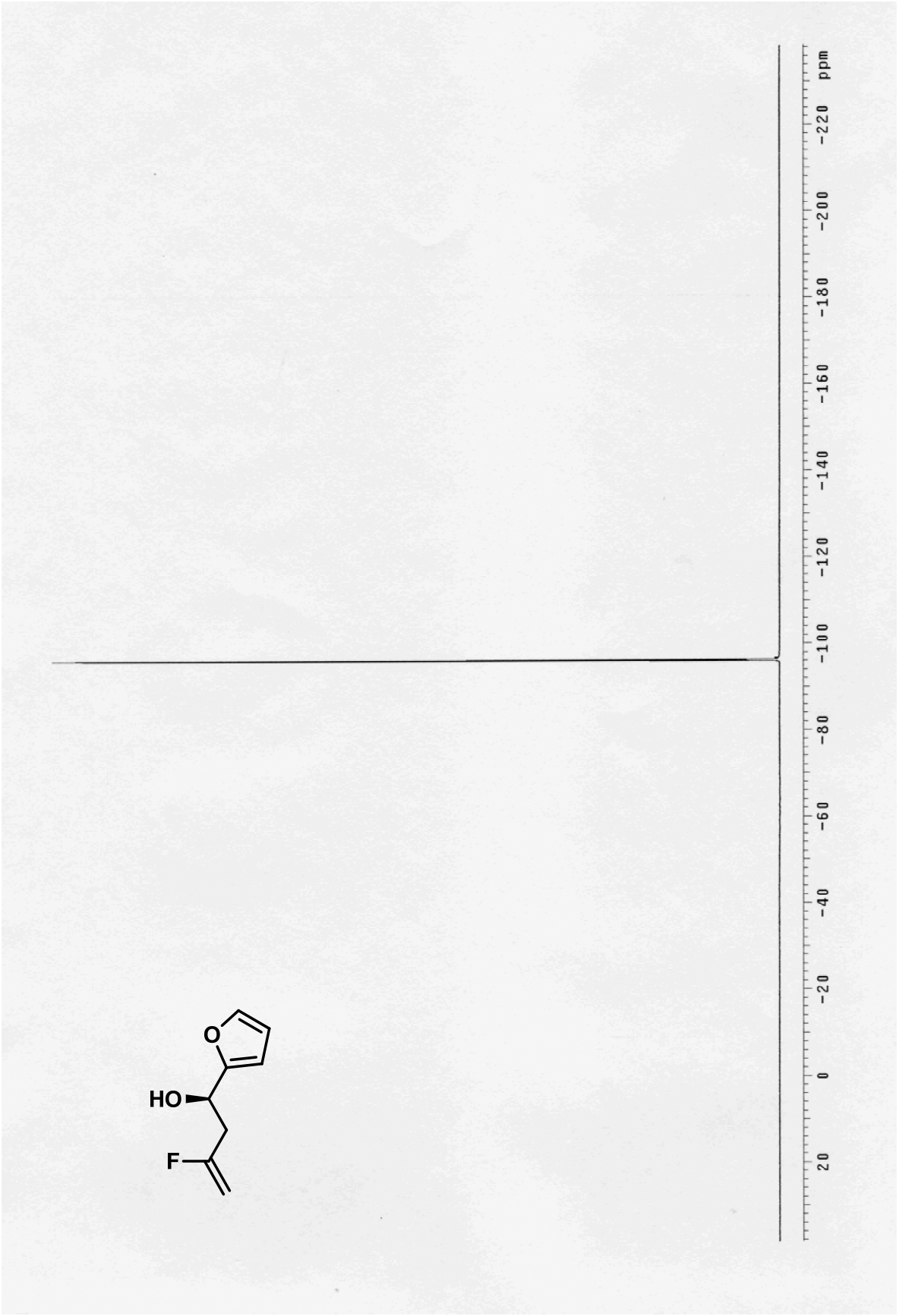
HO
F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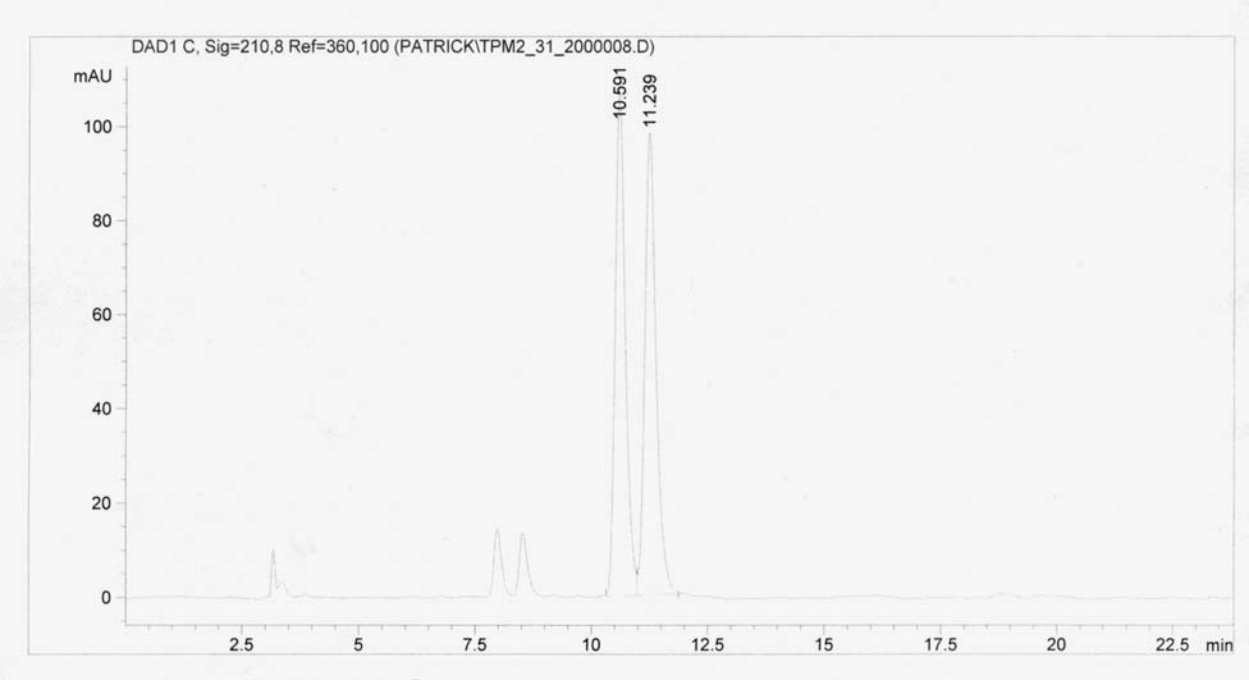
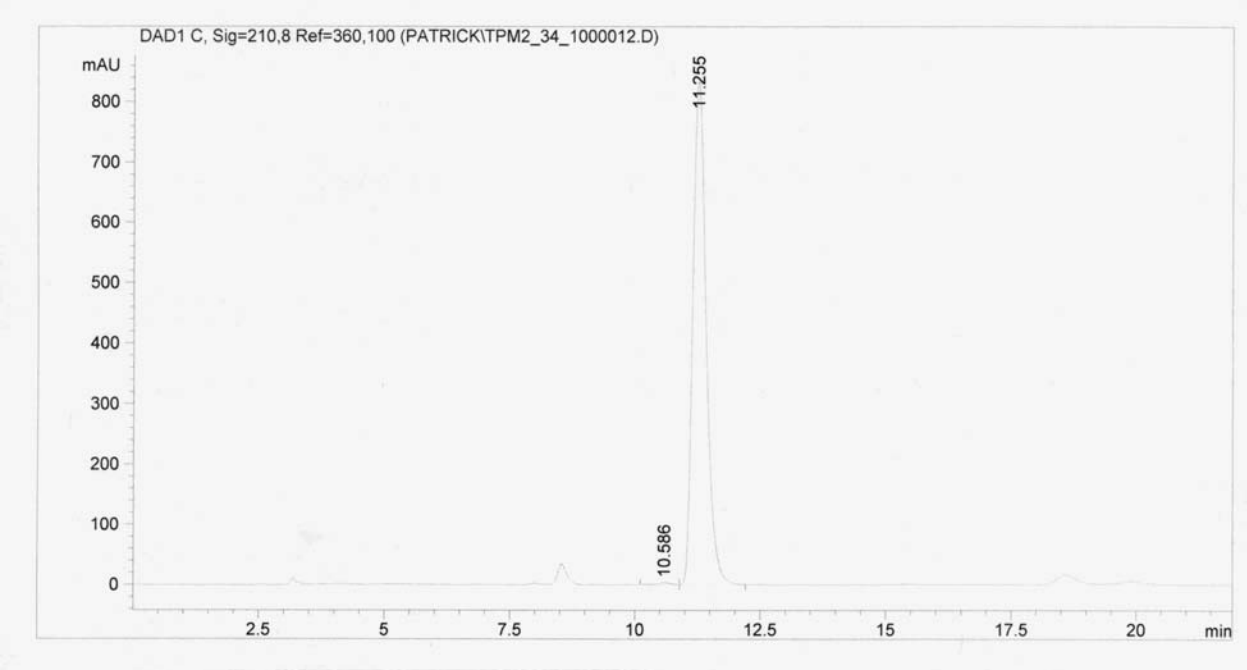
-140
-160
-180
-200
-220
ppm



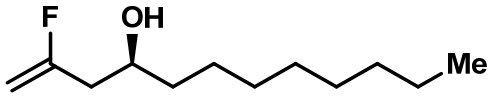
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.591	BV	0.2305	1639.01404	107.12891	49.6174
2	11.239	VB	0.2540	1664.29041	98.08391	50.3826



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.586	BV	0.2617	71.36349	3.93333	0.4595
2	11.255	VB	0.2881	1.54594e4	834.61639	99.5405

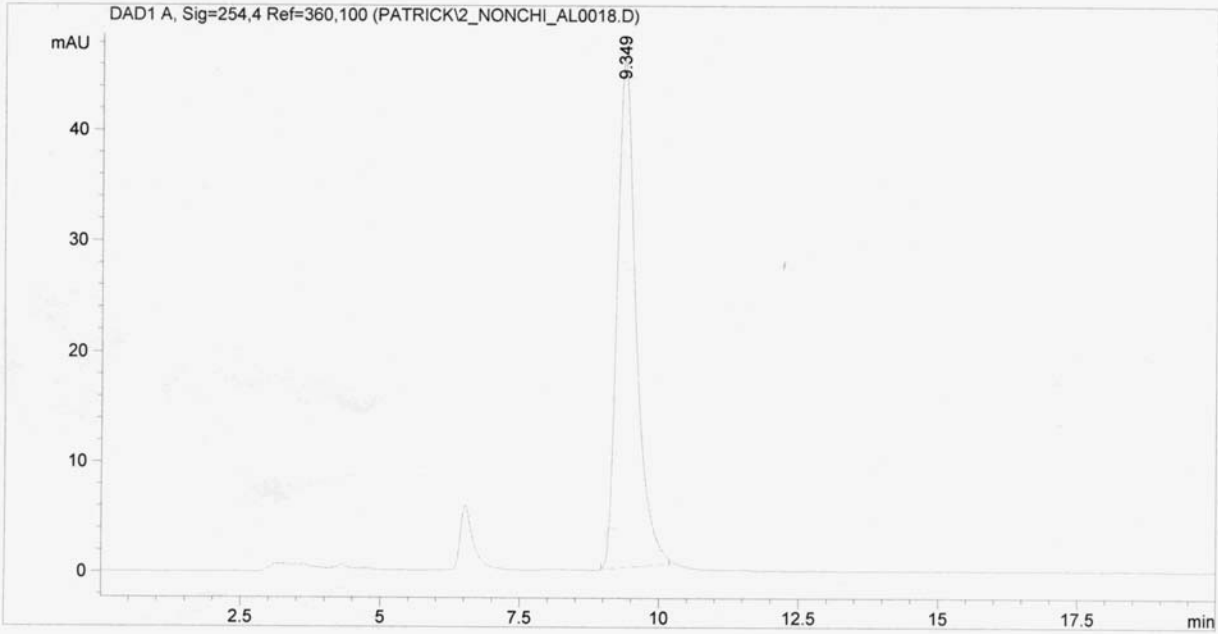
III.c. Experimental Procedures and Spectroscopic Data for Adducts 3a-3i from the Aldehyde Oxidation Level

(4S)-2-Fluoro-dodec-1-ene-4-ol (4a)



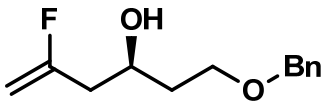
To a resealable pressure tube (13x100 mm) equipped with a magnetic stir bar was added **Ir-Cat-I** (10.7 mg, 0.01 mmol, 5 mol%) and K_3PO_4 (42.4 mg, 0.2 mmol, 100 mol%). The tube was sealed with a rubber septum and purged with argon. THF (0.2 mL), 3-chloro-2-fluoroprop-1-ene (28.4 mg, 0.3 mmol, 150 mol%), aldehyde **3a** (28.4 mg, 0.2 mmol, 100 mol%), isopropanol (24.0 mg, 0.4 mmol, 200 mol%), and H_2O (18.0 mg, 1.0 mmol, 500 mol%) were added to the purged tube, and the rubber septum was quickly replaced with a screw cap. The reaction mixture was heated in an oil bath at 60 °C for 24 hours, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was concentrated *in vacuo* and purified by flash chromatography (SiO_2: ethyl acetate:hexanes 1:19) to furnish the title compound **4a** (24.5 mg, 0.116 mmol) as a colorless oil in 61% yield and **5a** (1.9 mg, 0.010 mmol) as a colorless oil in 5% yield.

HPLC Enantiomeric excess was determined by the analysis of the 3,5-dintorbenzoate derivative of the product (Chiralcel AD-H column, hexanes:*i*-PrOH = 99:1, 1.0 mL/min, 254 nm), t_{minor} = N/A, t_{major} = 9.3 min; ee = 99%



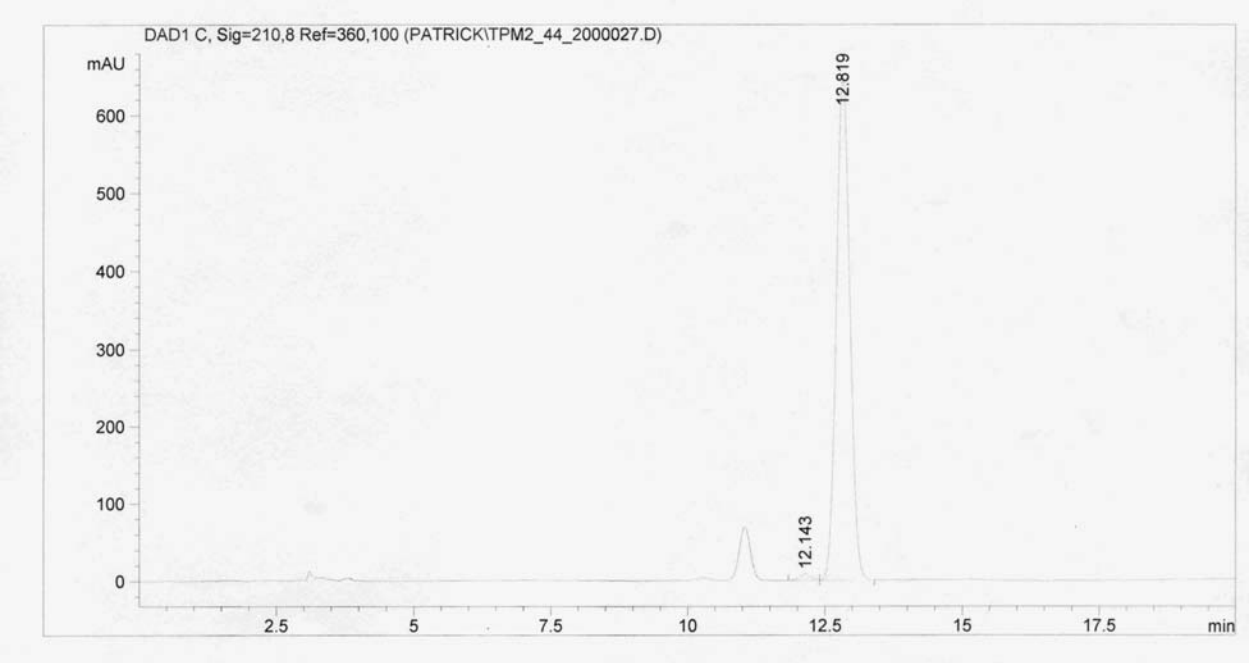
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.349	BB	0.3551	1091.71729	45.96155	100.0000

(4S)-6-Benzyloxy-2-fluorohexa-1-ene-4-ol (4b)



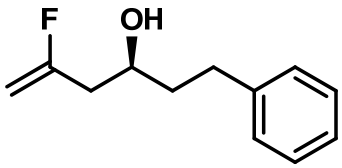
To a resealable pressure tube (13x100 mm) equipped with a magnetic stir bar was added **Ir-Cat-I** (10.7 mg, 0.01 mmol, 5 mol%) and K_3PO_4 (42.4 mg, 0.2 mmol, 100 mol%). The tube was sealed with a rubber septum and purged with argon. THF (0.2mL), 3-chloro-2-fluoroprop-1-ene (28.4 mg, 0.3 mmol, 150 mol%), aldehyde **3b** (32.8 mg, 0.2 mmol, 100 mol%), isopropanol (24.0 mg, 0.4 mmol, 200 mol%), and H_2O (18.0 mg, 1.0 mmol, 500 mol%) were added to the purged tube, and the rubber septum was quickly replaced with a screw cap. The reaction mixture was heated in an oil bath at 60 °C for 24 hours, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was concentrated *in vacuo* and purified by flash chromatography (SiO_2: ethyl acetate:hexanes, 1:9) to furnish the title compound **4b** (24.8 mg, 0.111 mmol) as a colorless oil in 55% yield and **5b** (2.3 mg, 0.011 mmol) as a colorless oil in 6% yield.

HPLC (Chiralcel OD-H column, hexanes:*i*-PrOH = 98:2, 1.0 mL/min, 210 nm), t_{minor} = 12.1 min, t_{major} = 12.8 min; ee = 98%



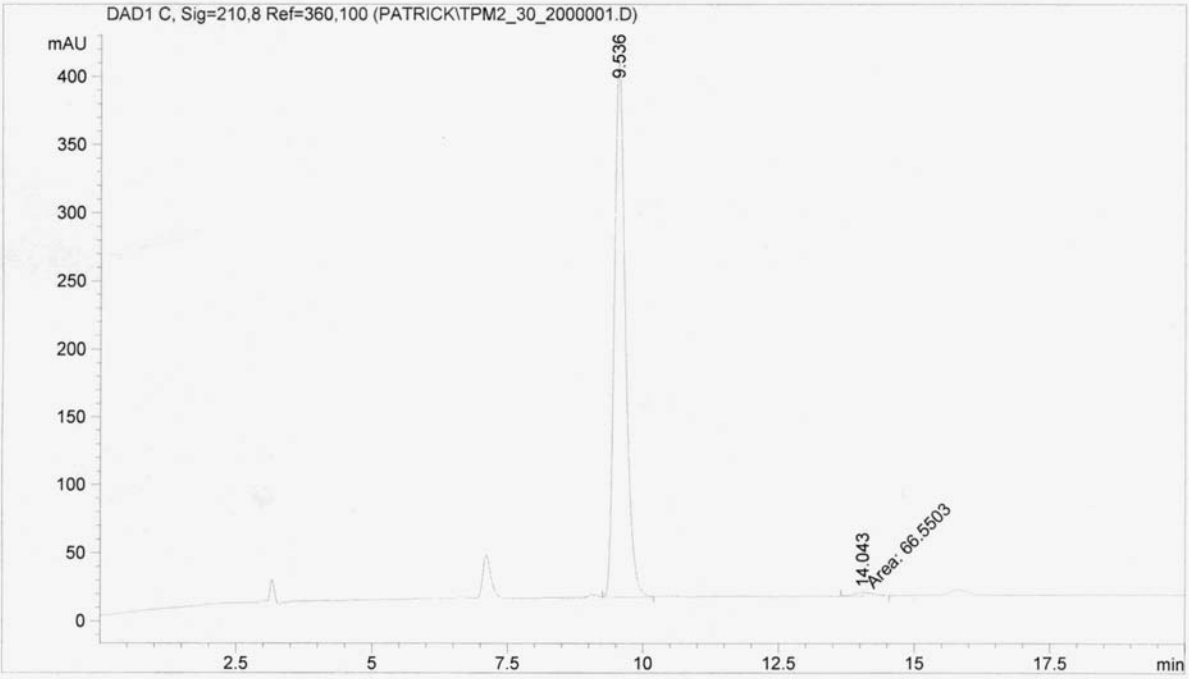
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.143	BV	0.2417	128.30276	8.32924	1.1385
2	12.819	VB	0.2691	1.11416e4	646.51965	98.8615

(4S)-2-Fluoro-6-phenylhexa-1-en-4-ol (4c)



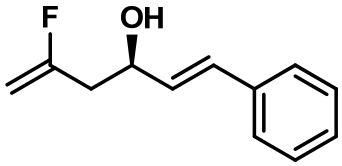
To a resealable pressure tube (13x100 mm) equipped with a magnetic stir bar was added **Ir-Cat-I** (10.7 mg, 0.01 mmol, 5 mol%) and K_3PO_4 (42.4 mg, 0.2 mmol, 100 mol%). The tube was sealed with a rubber septum and purged with argon. THF (0.2 mL), 3-chloro-2-fluoroprop-1-ene (28.4 mg, 0.3 mmol, 150 mol%), aldehyde **3c** (26.8 mg, 0.2 mmol, 100 mol%), isopropanol (24.0 mg, 0.4 mmol, 200 mol%), and H_2O (18.0 mg, 1.0 mmol, 500 mol%) were added to the purged tube, and the rubber septum was quickly replaced with a screw cap. The reaction mixture was heated in an oil bath at 60 °C for 24 hours, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was concentrated *in vacuo* and purified by flash chromatography (SiO_2: ethyl acetate:hexanes, 1:9) to furnish the title compound **4c** (25.2 mg, 0.0.130 mmol) as a yellow oil in 65% yield and **5c** (2.2 mg, 0.012 mmol) as a yellow oil in 6% yield.

HPLC (Chiralcel OD-H column, hexanes:*i*-PrOH = 95:5, 1.0 mL/min, 210 nm), t_{minor} = 9.5 min, t_{major} = 14.0 min; ee = 98%



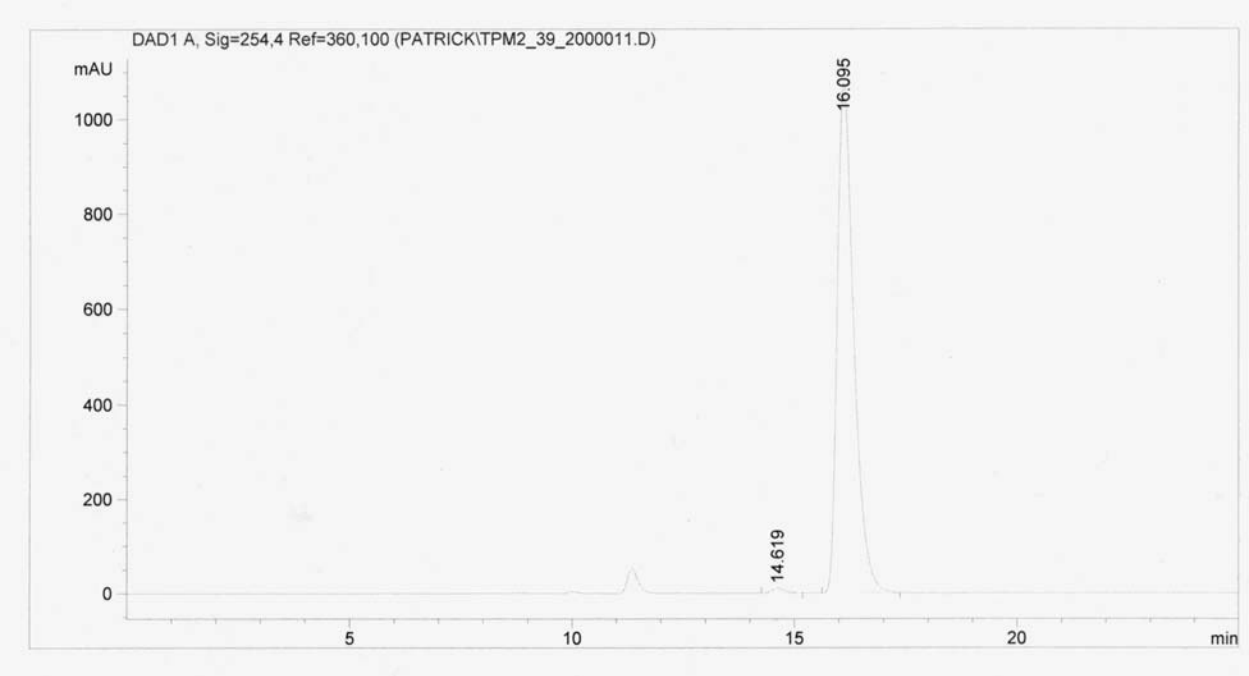
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.536	VB	0.2177	5653.99951	393.39713	98.8366
2	14.043	MM	0.4264	66.55029	2.60149	1.1634

(3R)-5-Fluoro-1-phenylhexa-1,5-diene-3-ol (4d)



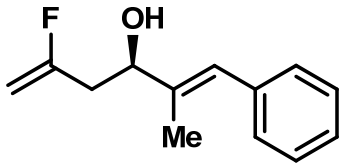
To a resealable pressure tube (13x100 mm) equipped with a magnetic stir bar was added **Ir-Cat-I** (10.7 mg, 0.01 mmol, 5 mol%) and K_3PO_4 (42.4 mg, 0.2 mmol, 100 mol%). The tube was sealed with a rubber septum and purged with argon. THF (0.2 mL), 3-chloro-2-fluoroprop-1-ene (28.4 mg, 0.3 mmol, 150 mol%), aldehyde **3d** (26.4 mg, 0.2 mmol, 100 mol%), isopropanol (24.0 mg, 0.4 mmol, 200 mol%), and H_2O (18.0 mg, 1.0 mmol, 500 mol%) were added to the purged tube, and the rubber septum was quickly replaced with a screw cap. The reaction mixture was heated in an oil bath at 40 °C for 24 hours, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was concentrated *in vacuo* and purified by flash chromatography (SiO_2: ethyl acetate:hexanes, 1:9) to furnish the title compound **4d** (28.5 mg, 0.148 mmol) as a colorless oil in 74% yield and **5d** (1 mg, 0.006 mmol) as a colorless oil in 3% yield.

HPLC (Chiralcel OJ-H column, hexanes:*i*-PrOH = 95:5, 1.0 mL/min, 254 nm), t_{minor} = 14.6 min, t_{major} = 16.1 min; ee = 98%



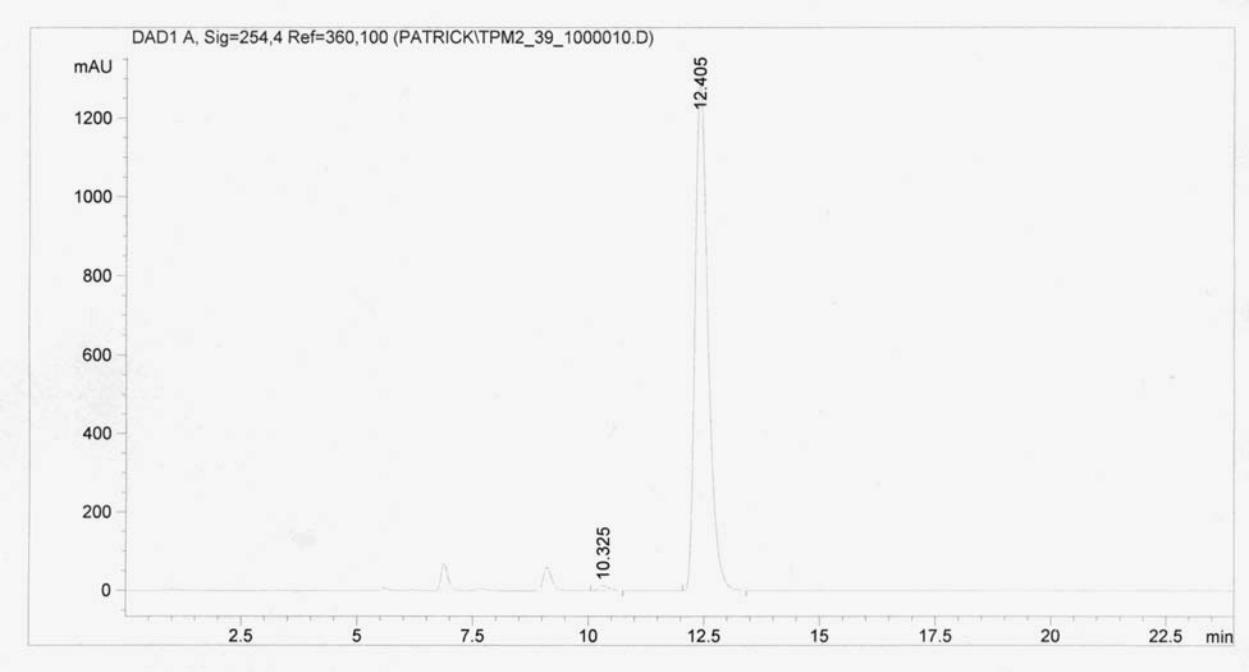
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.619	BB	0.3250	226.03453	10.50771	0.8050
2	16.095	BB	0.3943	2.78515e4	1074.86841	99.1950

(3R)-5-Fluoro-2-methyl-1phenylhexa-1,5-diene-3-ol (4e)



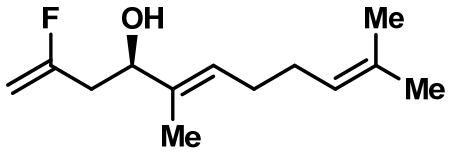
To a resealable pressure tube (13x100 mm) equipped with a magnetic stir bar was added **Ir-Cat-I** (10.7 mg, 0.01 mmol, 5 mol%) and K_3PO_4 (42.4 mg, 0.2 mmol, 100 mol%). The tube was sealed with a rubber septum and purged with argon. THF (0.2 mL), 3-chloro-2-fluoroprop-1-ene (28.4 mg, 0.3 mmol, 150 mol%), aldehyde **3e** (29.6 mg, 0.2 mmol, 100 mol%), isopropanol (24.0 mg, 0.4 mmol, 200 mol%), and H_2O (18.0 mg, 1.0 mmol, 500 mol%) were added to the purged tube, and the rubber septum was quickly replaced with a screw cap. The reaction mixture was heated in an oil bath at 40 °C for 24 hours, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was concentrated *in vacuo* and purified by flash chromatography (SiO_2: ethyl acetate:hexanes, 1:9) to furnish the title compound **4e** (38.5 mg, 0.187 mmol) as a colorless oil in 93% yield and **5e** (1.4 mg, 0.007 mmol) as a colorless oil in 4% yield.

HPLC (Chiralcel OJ-H column, hexanes:*i*-PrOH = 95:5, 1.0 mL/min, 254 nm), t_{minor} = 10.3 min, t_{major} = 12.4 min; ee = 98%



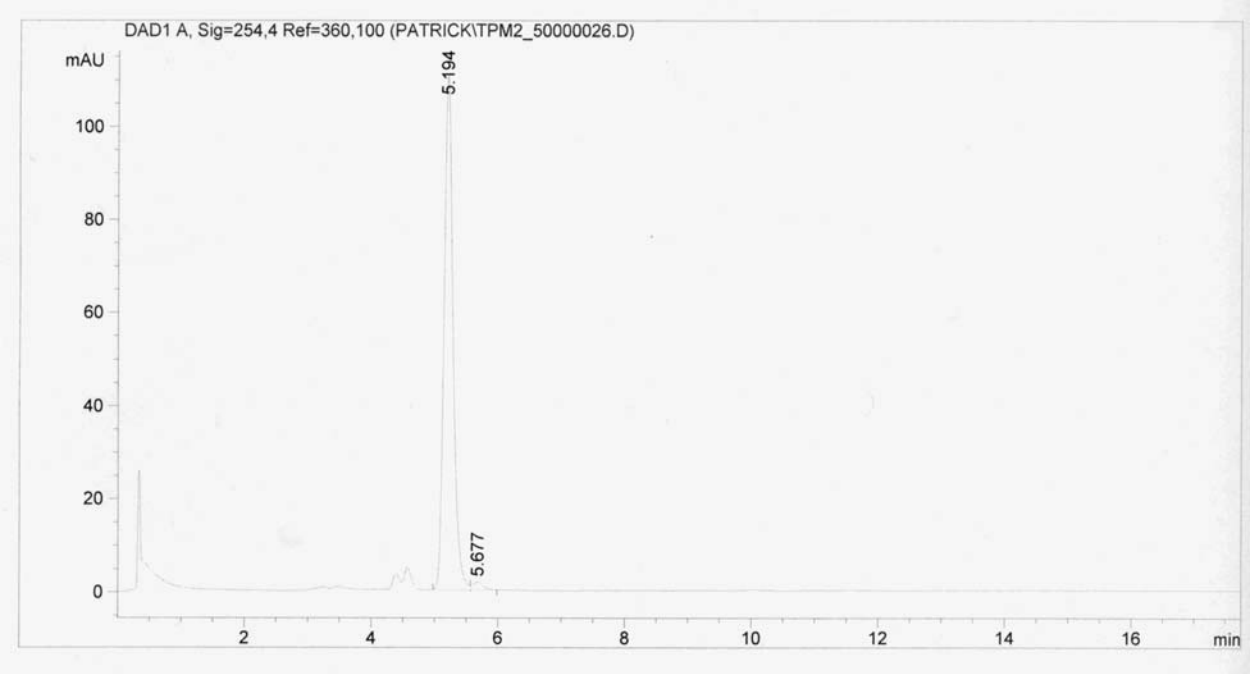
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.325	BB	0.2316	196.07742	12.87925	0.7695
2	12.405	BB	0.2983	2.52845e4	1291.81689	99.2305

(4R)-2-Fluoro-6,10-dimethylundeca-1,5,9-triene-4-ol (4f)



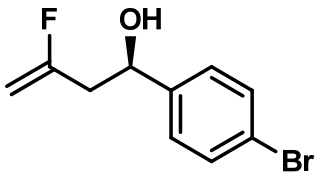
To a resealable pressure tube (13x100 mm) equipped with a magnetic stir bar was added **Ir-Cat-I** (10.7 mg, 0.01 mmol, 5 mol%) and K_3PO_4 (42.4 mg, 0.2 mmol, 100 mol%). The tube was sealed with a rubber septum and purged with argon. THF (0.2 mL), 3-chloro-2-fluoroprop-1-ene (28.4 mg, 0.3 mmol, 150 mol%), aldehyde **3f** (30.4 mg, 0.2 mmol, 100 mol%), isopropanol (24.0 mg, 0.4 mmol, 200 mol%), and H_2O (18.0 mg, 1.0 mmol, 500 mol%) were added to the purged tube, and the rubber septum was quickly replaced with a screw cap. The reaction mixture was heated in an oil bath at 40 °C for 24 hours, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was concentrated *in vacuo* and purified by flash chromatography (SiO_2: ethyl acetate:hexanes, 1:9) to furnish the title compound **4f** (31.6 mg, 0.149 mmol) as a yellow oil in 74% yield and **5f** (1.3 mg, 0.007 mmol) as a yellow oil in 3% yield.

HPLC Enantiomeric excess was determined by the analysis of the 4-nitrobenzoate derivative of the product (Chiralcel OJ-H column, hexanes:*i*-PrOH = 98:2, 1.0 mL/min, 254 nm), t_{minor} = 5.7 min, t_{major} = 5.2 min; ee = 96%



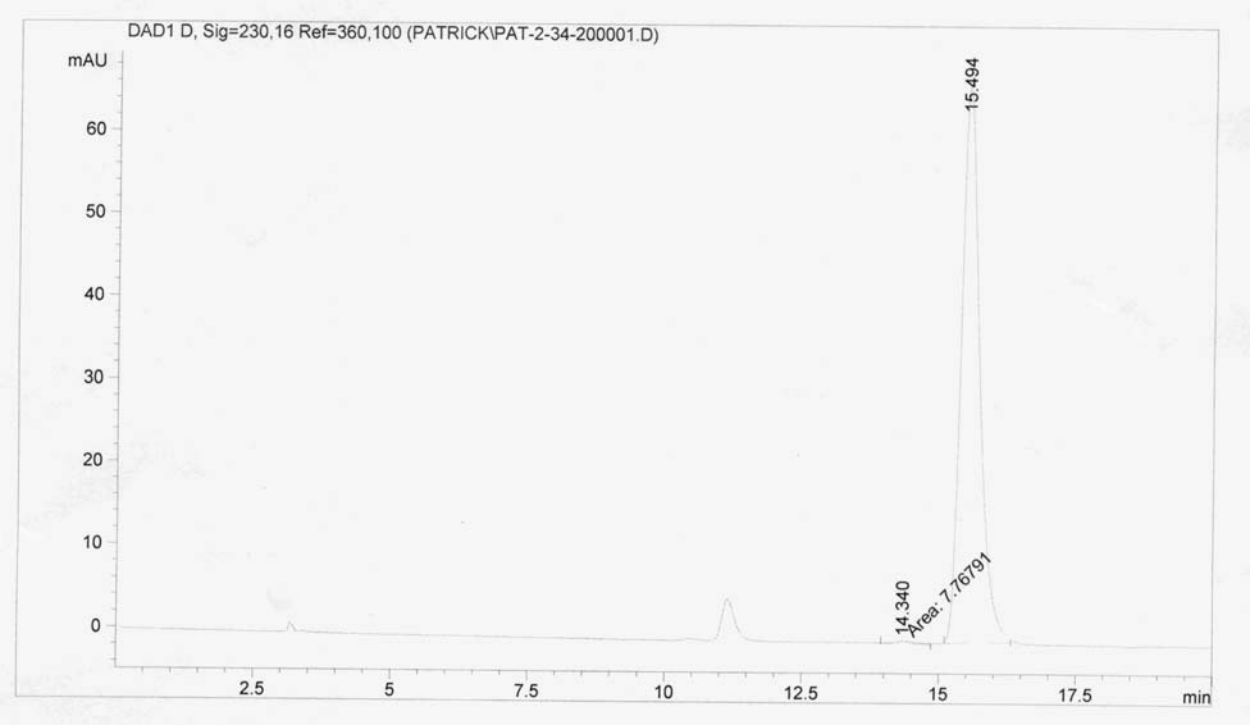
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.194	BV	0.1497	1093.51599	110.29647	98.2468
2	5.677	VB	0.1635	19.51354	1.75776	1.7532

(4R)-4-(4-Bromophenyl)-2-fluorobuta-1-ene-4-ol (4g)



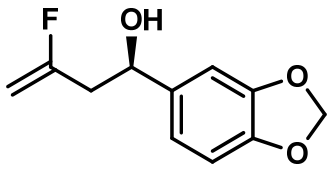
To a resealable pressure tube (13x100 mm) equipped with a magnetic stir bar was added aldehyde **3g** (37.0 mg, 0.2 mmol, 100 mol%), **Ir-Cat-I** (10.7 mg, 0.01 mmol, 5 mol%), and K_3PO_4 (42.4 mg, 0.2 mmol, 100 mol%). The tube was sealed with a rubber septum and purged with argon. THF (0.2 mL), 3-chloro-2-fluoroprop-1-ene (28.4 mg, 0.3 mmol, 150 mol%), isopropanol (24.0 mg, 0.4 mmol, 200 mol%), and H_2O (18.0 mg, 1.0 mmol, 500 mol%) were added to the purged tube, and the rubber septum was quickly replaced with a screw cap. The reaction mixture was heated in an oil bath at 40 °C for 24 hours, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was concentrated *in vacuo* and purified by flash chromatography (SiO_2: ethyl acetate:hexanes, 1:9) to furnish the title compound **4g** (43.6 mg, 0.178 mmol) as a white solid in 89% yield and **5g** (2.2 mg, 0.010 mmol) as a white solid in 5% yield.

HPLC (Chiralcel OJ-H column, hexanes:*i*-PrOH = 95:5, 1.0 mL/min, 230 nm), t_{minor} = 14.3 min, t_{major} = 15.5 min; ee = 99%



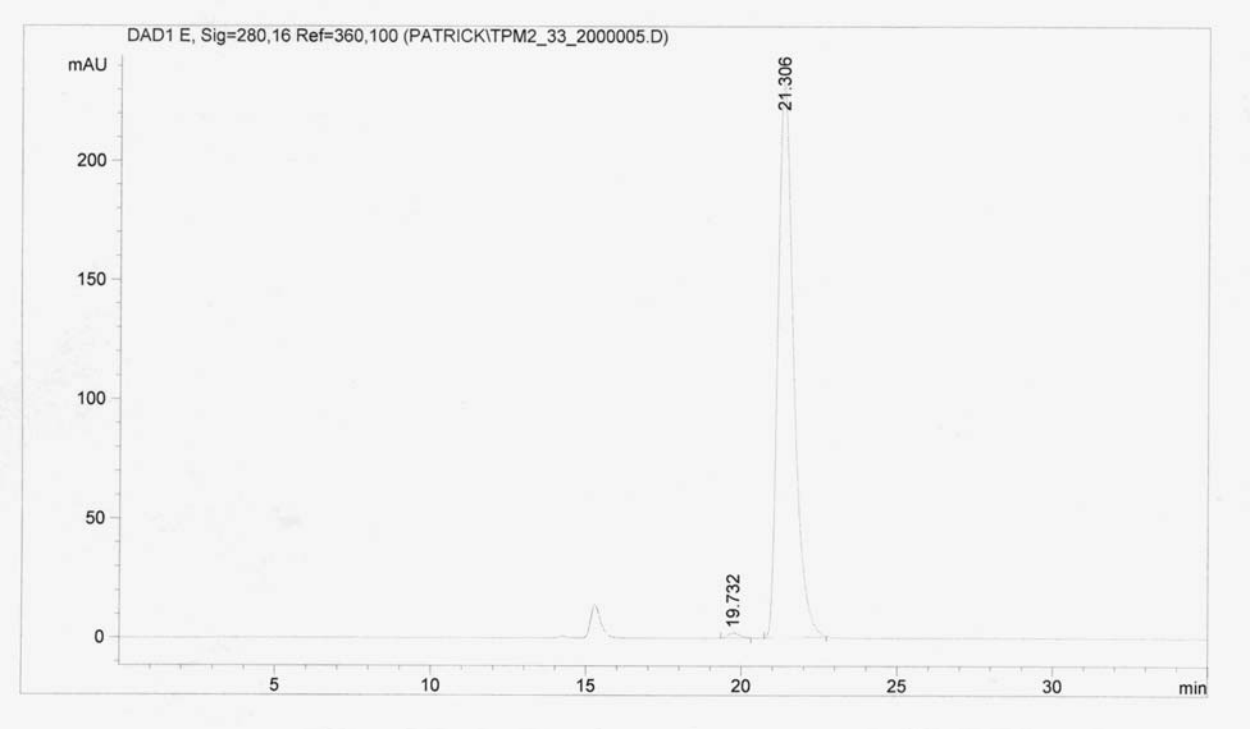
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.340	MM	0.4186	7.76791	3.09274e-1	0.4925
2	15.494	BB	0.3520	1569.31580	67.30836	99.5075

(1R)-1-(Benzo[*d*][1,3]dioxo-5-yl)-3-fluorobuta-3-ene-1-ol (4h)



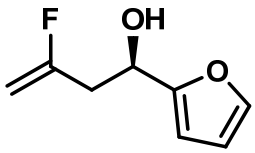
To a resealable pressure tube (13x100 mm) equipped with a magnetic stir bar was added aldehyde **3h** (30.3 mg, 0.2 mmol, 100 mol%), **Ir-Cat-I** (10.7 mg, 0.01 mmol, 5 mol%), and K_3PO_4 (42.4 mg, 0.2 mmol, 100 mol%). The tube was sealed with a rubber septum and purged with argon. THF (0.2 mL), 3-chloro-2-fluoroprop-1-ene (28.4 mg, 0.3 mmol, 150 mol%), isopropanol (24.0 mg, 0.4 mmol, 200 mol%), and H_2O (18.0 mg, 1.0 mmol, 500 mol%) were added to the purged tube, and the rubber septum was quickly replaced with a screw cap. The reaction mixture was heated in an oil bath at 40 °C for 24 hours, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was concentrated *in vacuo* and purified by flash chromatography (SiO_2: ethyl acetate:hexanes, 1:9) to furnish the title compound **4h** (36.8 mg, 0.175 mmol) as a colorless oil in 88% yield and **5h** (1.9 mg, 0.010 mmol) as a colorless oil in 5% yield.

HPLC (Chiralcel OJ-H column, hexanes:*i*-PrOH = 95:5, 1.0 mL/min, 280 nm), t_{minor} = 19.7 min, t_{major} = 21.3 min; ee = 99%



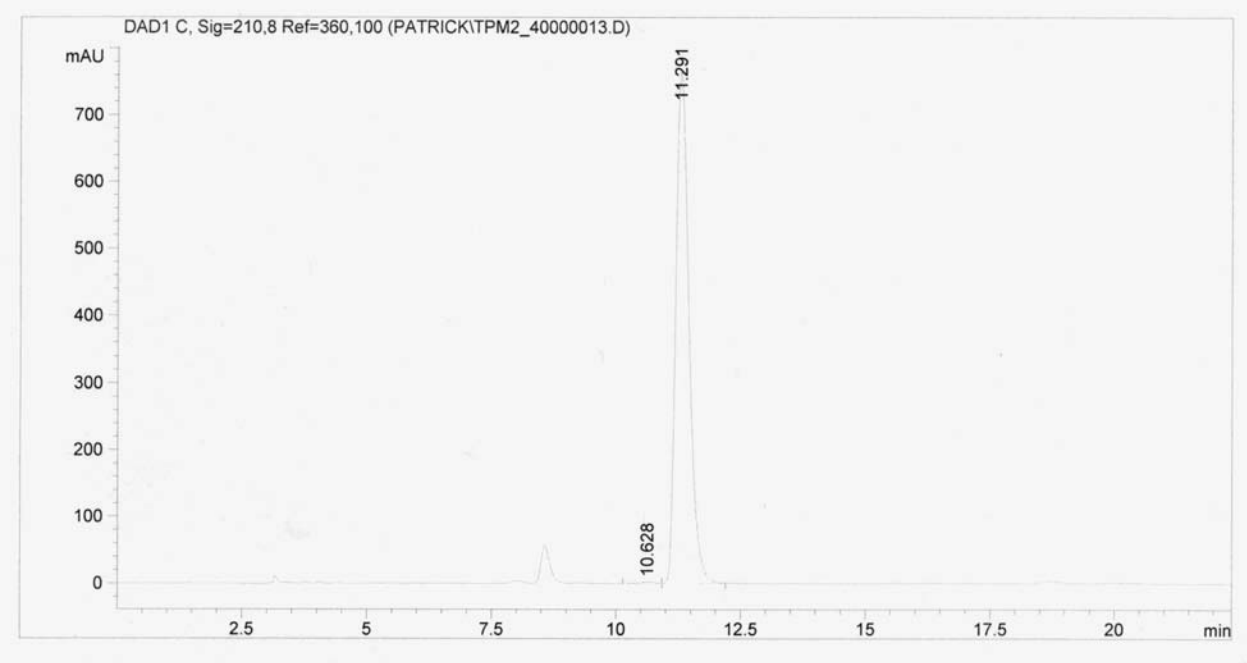
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.732	BB	0.4016	60.00493	2.20407	0.7261
2	21.306	BB	0.5356	8204.38965	232.52441	99.2739

(1R)-3-Fluoro-1-furfurylbuta-3-ene-1-ol (4i)



To a resealable pressure tube (13x100 mm) equipped with a magnetic stir bar was added **Ir-Cat-I** (10.7 mg, 0.01 mmol, 5 mol%) and K_3PO_4 (42.4 mg, 0.2 mmol, 100 mol%). The tube was sealed with a rubber septum and purged with argon. THF (0.2 mL), 3-chloro-2-fluoroprop-1-ene (28.4 mg, 0.3 mmol, 150 mol%), aldehyde **3i** (19.2 mg, 0.2 mmol, 100 mol%), isopropanol (24.0 mg, 0.4 mmol, 200 mol%), and H_2O (18.0 mg, 1.0 mmol, 500 mol%) were added to the purged tube, and the rubber septum was quickly replaced with a screw cap. The reaction mixture was heated in an oil bath at 40 °C for 24 hours, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was concentrated *in vacuo* and purified by flash chromatography (SiO_2: ethyl acetate:hexanes, 1:9) to furnish the title compound **4i** (22.8 mg, 0.146 mmol) as a yellow oil in 73% yield and **5i** (1.4 mg, 0.010 mmol) as a yellow oil in 5% yield.

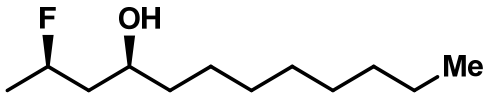
HPLC (Chiralcel OJ-H column, hexanes:*i*-PrOH = 95:5, 1.0 mL/min, 210 nm), t_{minor} = 10.6 min, t_{major} = 11.3 min; ee = 99%



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.628	BV	0.2707	49.70620	2.67561	0.3519
2	11.291	VB	0.2850	1.40742e4	763.77069	99.6481

III.d. Experimental Procedures and Spectroscopic Data for Hydrogenation Products:

(4*S*)-2-fluorododecan-4-ol (6a)



To a vial containing a magnetic stir bar was added Crabtree's catalyst (0.0025 mmol, 2 mg). The vial was charged with dichloromethane (0.05M, 2 mL) followed by alcohol **4a** (20.2 mg, 0.1 mmol). The vial was capped with a septum, and purged with H_2 (1 atm). The reaction was allowed to stir for 16 hours at 0 °C. The reaction mixture was allowed to warm to ambient temperature, then concentrated *in vacuo* and purified by flash chromatography (SiO_2: ethyl acetate:hexanes, 1:9) to furnish the title compound **6a** (16.8 mg, 0.082 mmol) as a colorless oil in 82% yield and 7:1 dr.

TLC (SiO_2): R_f= 0.19 (ethyl acetate:hexanes, 1:9)

[α]$_D^{23}$=-5.9°

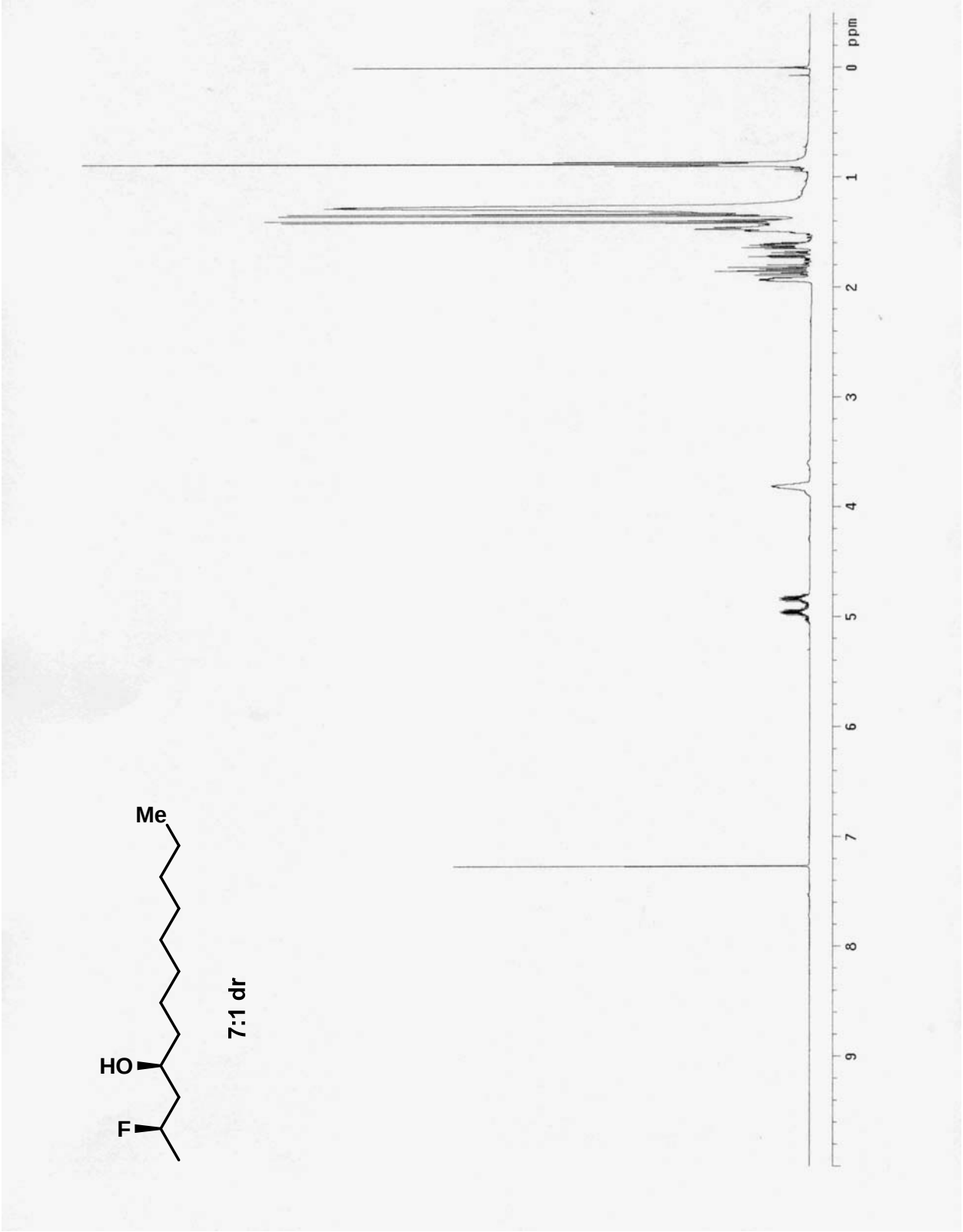
^{1}H NMR (400 MHz, CDCl3): δ 4.99-4.80 (m, 1H), 3.86-3.78 (m, 1H), 1.93 (br, 1H), 1.89-1.60 (m, 2H), 1.51-1.42 (m, 2H), 1.38 (dd, *J*=24.4, 6.4 Hz, 3H), *J*= 1.28-1.27 (m, 12H), 0.88 (t, *J*=6.8 Hz, 3H).

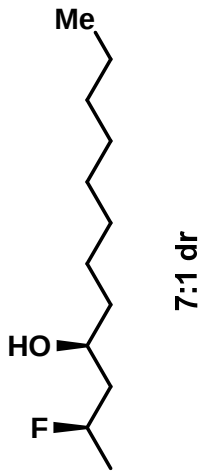
^{13}C NMR (100 MHz, CDCl3): δ 91.1 (d, *J*=160.7 Hz), 70.2, 44.1 (d, *J*=18.6 Hz), 37.5, 31.9, 29.6, 29.5, 29.2, 25.4, 22.7, 21.4 (d, *J*=22.3 Hz), 14.1.

^{19}F NMR (400 MHz, CDCl3): δ -172.24 - -172.71 (m), -175.37 - -175.70 (m).

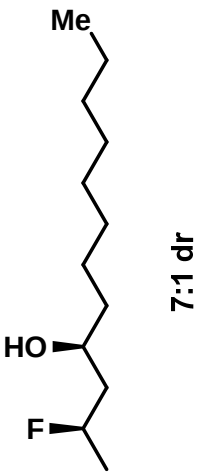
HRMS (CI) Calcd. for $C_{12}H_{24}FO$ $[M-H]^+$: 203.1810, Found: 203.1811.

FTIR (neat): 3374, 2925, 2854, 1463, 1385, 1129, 1082, 924, 819 cm^{-1}.


Me
HO
F
7:1 dr
0
1
2
3
4
5
6
7
8
9
ppm

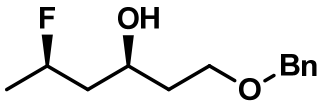


7:1 dr



7:1 dr

(3S)-1-(benzyloxy)-5-fluorohexan-3-ol (6b)



To a vial containing a magnetic stir bar was added Crabtree's catalyst (0.0025 mmol, 2 mg). The vial was charged with dichloromethane (0.05M, 2 mL) followed by alcohol **4b** (22.4 mg, 0.1 mmol). The vial was capped with a septum, and purged with H_2 (1 atm). The reaction was allowed to stir for 16 hours at room temperature. The reaction mixture was concentrated *in vacuo* and purified by flash chromatography (SiO_2: ethyl acetate:hexanes, 1:9) to furnish the title compound **6b** (19.9 mg, 0.087 mmol) as a colorless oil in 88% yield and 9:1 dr.

TLC (SiO_2): R_f= 0.19 (ethyl acetate:hexanes, 1:5)

$[\alpha]_D^{23}$=-13.0°

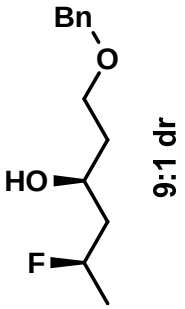
^{1}H NMR (400 MHz, CDCl3): δ 7.30-7.19 (m, 5H), 4.92-4.73 (m, 1H), 4.46 (s, 2H), 3.99-3.91 (m, 1H), 3.69-3.56 (m, 2H), 1.92-1.52 (m, 4H), 1.30 (dd, *J*=24.4, 6.0 Hz, 3H).

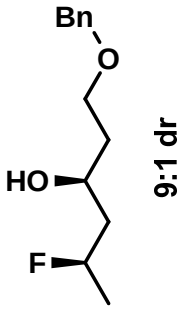
^{13}C NMR (100 MHz, CDCl3): δ 137.8, 128.5, 127.8, 127.7, 89.7 (d, *J*=85.96 Hz), 73. 4, 68.9, 44.0 (d, *J*=102 Hz), 36.4, 21.2 (d, *J*=119.2 Hz).

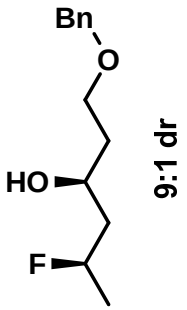
^{19}F NMR (400 MHz, CDCl3): δ -172.12 - -172.57 (m), -175.28 - -175.62 (m).

HRMS (CI) Calcd. for $C_{13}H_{20}FO_2$ $[M+H]^+$: 227.1445, Found: 227.1447.

FTIR (neat): 3430, 2923, 2866, 1454, 1385, 1206, 1094, 1027, 923, 822, 737, 697 cm^{-1}.

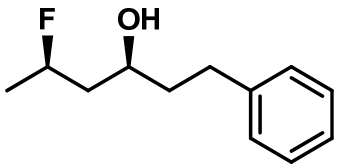






9:1 dr

(3*S*)-5-fluoro-1-phenylhexan-3-ol (6c)



To a vial containing a magnetic stir bar was added Crabtree's catalyst (0.0025 mmol, 2 mg). The vial was charged with dichloromethane (0.05M, 2 mL) followed by alcohol **4c** (19.6 mg, 0.1 mmol). The vial was capped with a septum, and purged with H_2 (1 atm).The reaction was allowed to stir for 16 hours at room temperature. The reaction mixture was concentrated *in vacuo* and purified by flash chromatography (SiO_2: ethyl acetate:hexanes, 1:9) to furnish the title compound **6c** (13.5 mg, 0.0688 mmol) as a yellow oil in 70% yield 5:1 dr.

TLC (SiO_2): R_f= 0.19 (ethyl acetate:hexanes, 1:9)

$[\alpha]_D^{23}$=-14.2°

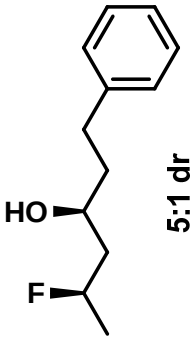
^{1}H NMR (400 MHz, CDCl3): δ 7.27 (t, *J*=6.4 Hz, 2H), 7.19 (dd, *J*=6.4, 2.4 Hz, 3H), 4.96-4.78 (m, 1H), 3.88-3.81 (m, 1H), 2.82-2.64 (m, 2H), 2.01-1.98 (m, 1H), 1.94-1.57 (m, 4H), 1.35 (dd, *J*=24.4, 6.0 Hz, 3H).

^{13}C NMR (100 MHz, CDCl3): δ 141.9, 128.4, 125.9, 91.2 (dd, *J*=160.7 Hz), 69.6, 44.1 (d, *J*=18.6 Hz), 39.1, 31.8, 21.4 (d, *J*=22.4 Hz).

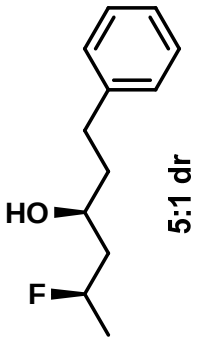
^{19}F NMR (400 MHz, CDCl3): δ -172.33 - -172.80 (m), -175.39 – 175.78 (m).

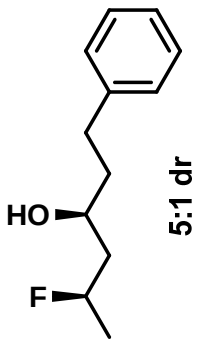
HRMS (CI) Calcd. for $C_{12}H_{16}FO$ $[M-H]^+$: 195.1184, Found: 195.1185.

FTIR (neat): 3363, 2976, 2935, 1652, 1539, 1515, 1506, 1455, 1435, 1417, 1386, 1136, 1091, 1053, 922, 864, 825, 813, 747, 699 cm^{-1}.

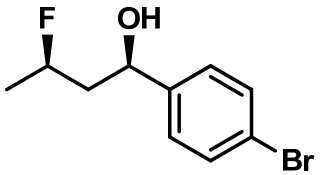


5:1 dr





(1*R*)-1-(4-bromophenyl)-3-fluorobutan-1-ol (6g)



To a vial containing a magnetic stir bar was added alcohol **4g** (0.125 mmol,30.6 mg) followed by Crabtree's catalyst (0.003 mmol, 2.5 mg). The vial was charged with dichloromethane (0.05M, 2.5 mL). The vial was capped with a septum, and purged with H_2 (1 atm) for five minutes. The reaction was allowed to stir for 16 hours at room temperature. The reaction mixture was then concentrated *in vacuo* and purified by flash chromatography (SiO_2: ethyl acetate:hexanes, 1:9) to furnish the title compound **6g** (49 mg, 0.2 mmol) as a white solid in >99% yield and 6:1 dr.

TLC (SiO_2): R_f= 0.19 (ethyl acetate:hexanes, 1:9)

$[\alpha]_D^{23}$=38.1°

^{1}H NMR (400 MHz, CDCl3): δ 7.49 (d, *J*=8.4 Hz, 2H), 7.27 (d, *J*=4.4 Hz, 2H), 4.89 (t, 6.0 Hz, 1H), 4.77-4.59 (m, 1H), 2.27 (dd, *J*=5.2, 2.4 Hz, 1H), 2.24-2.17 (m, 1H), 1.89-1.74 (m, 1H), 1.36 (dd, *J*=24.4, 6.0 Hz, 3H).

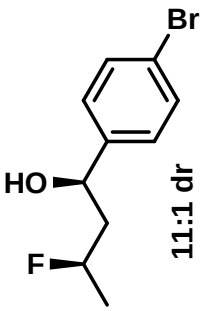
^{13}C NMR (100 MHz, CDCl3): δ 142.7, 131.7, 127.7, 121.6, 90.0 (d, *J*=162.2 Hz), 71.8, 46.1 (d, *J*=19.4 Hz), 21.3 (d, *J*=22.6 Hz).

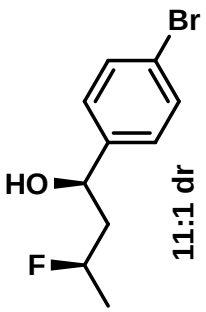
^{19}F NMR (400 MHz, CDCl3): δ -173.68 - -174.14 (m), -175.65 - -176.05 (m).

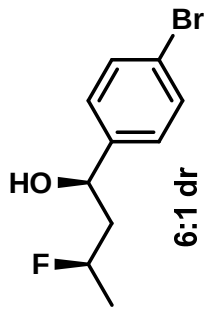
HRMS (CI) Calcd. for $C_{10}H_{12}FO$ $[M+]^+$: 246.0056, Found: 246.0056.

FTIR (neat): 3365.05, 2932.50, 1485.54, 1457.05, 1384.94, 1135.50, 1070.51, 1010.36, 829.09 cm^{-1}.

MP 54-56 °C







III.e. Absolute and relative Stereochemical determination:

The absolute and relative stereochemistry was determined by x-ray analysis of product 6g and was found to be *R,R*, see figure 1.

Figure 1. View of molecule showing the atom labeling scheme. Displacement ellipsoids are scaled to the 50% probability level. The configuration at C7 and C9 is *R, R*.