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Supporting Information

Synthesis of fluorinated allylic alcohols via photoinduced decarboxylative cross-coupling of α-fluoroacrylic acids and alcohols

Xiao-Yu Lu,* Meng-Ting Gao, Li-Juan Yu, Hong-Ye Pan, Xiang Zhang, Rui Huang, Kang Yang, Fu-Yi Shui, Yi-Wei Song and Gui-Xiang Yang

E-mail: xiaoyulu@mail.ustc.edu.cn

[†]School of Materials and Chemical Engineering, ChuZhou University, Chu Zhou, 239000, China.

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I. General Information

a. Materials

All the reactions were carried out in oven-dried schlenk tubes under argon atmosphere (purity ≥99.999%). *fac*-Ir(ppy)$_3$ (CAS: 94928-86-6) and Ru(bpy)$_3$Cl$_2$·6H$_2$O (CAS: 50525-27-4) was purchased from Adamas. Ir(*d*FCF$_3$ppy)$_2$(dtbpy)PF$_6$ (CAS: 870987-63-6) and Ir(dFCF$_3$ppy)$_2$(bpy)PF$_6$ (CAS: 1092775-62-6) was purchased from Bidepharm. The following chemicals were purchased and used as received: DABCO (Adamas), MeOH (Adamas), ^{i}PrOH (Adamas), EtOH (Adamas) were stored over 4 Å molecular sieves under an argon atmosphere in a septum-capped bottle. All the other reagents and solvents mentioned in this text were purchased from commercial sources and used without purification.

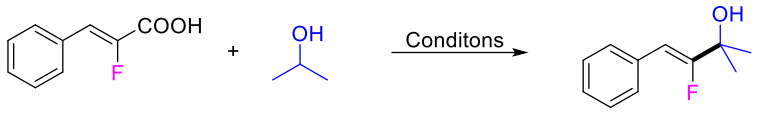
b. Analytical Methods

^{1}H-NMR, ^{13}C-NMR and ^{19}F-NMR spectra were recorded on a Bruker Avance 400 spectrometer at ambient temperature in Chloroform-d unless otherwise noted; Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity, integration, and coupling constant (Hz). Data for ^{13}C NMR are reported in terms of chemical shift (δ ppm), multiplicity, and coupling constant (Hz). Gas chromatographic (GC) analysis was acquired on a Shimadzu GC-2014 Series GC System equipped with a flame-ionization detector. GC-MS analysis was performed on Thermo Scientific AS 3000 Series GC-MS System. HRMS analysis was performed on Finnigan LCQ advantage Max Series MS System. Organic solutions were concentrated under reduced pressure on a Buchi rotary evaporator. Flash column chromatographic purification of products was accomplished using forced-flow chromatography on Silica Gel **(200-300 mesh)**.

II. General Experimental Procedures

a. Optimization of the reaction conditions

Under thermal conditions:

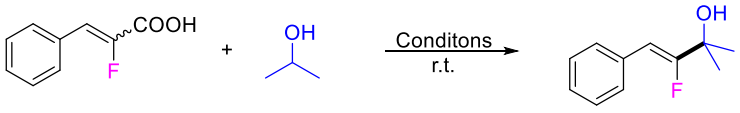


1a, 0.2 mmol **2a** **3a**

Entry	Catalyst (10 mol%)	Peroxide (3 eq)	Temperature (°C)	Yield%
1	CuBr	DTBP	100	Trace
2	$CuBr_2$	DTBP	100	Trace
3	CuBr	TBHP	100	Trace
4	CuI	DTBP	100	Trace
5	Ag_2CO_3	DTBP	100	< 3
6	$CuBr_2$	TBPB	100	Trace
7	CuBr	TBPB	100	Trace
8	$Fe(OAc)_2$	TBPB	100	Trace
9	Ag_2CO_3	TBPB	100	Trace

Reaction conditions: 1a (0.2 mmol), 2a (1 mL), catalyst (10 mol%), and peroxide (3 equiv) under an Ar atmosphere at 100 °C for 24 h.

Under photocatalytic conditions:



1a, 0.2 mmol
Z/E mixture

2a

3a

Entry	Catalyst	Peroxide (3 eq)	Base (1 eq)	Co-solvent	Yield%
1[a]	*fac*-Ir(ppy)$_3$	DTBP	-	-	Trace
2[b]	$Ru(bpy)_3Cl_2 \cdot 6H_2O$	DTBP	-	-	Trace
3[a]	*fac*-Ir(ppy)$_3$	TBHP	-	-	Trace
4[a]	*fac*-Ir(ppy)$_3$	TBPB	-	-	21
5[b]	$Ru(bpy)_3Cl_2 \cdot 6H_2O$	TBPB	-	-	Trace
6[b]	Eosin Y	TBPB	-	-	Trace
7[c]	***fac*-Ir(ppy)$_3$**	**TBPB**	**DABCO**	**-**	**45**
8[c]	*fac*-Ir(ppy)$_3$	TBPB	Et_3N	-	2
9[c]	*fac*-Ir(ppy)$_3$	TBPB	DIPEA	-	Trace
10[c]	*fac*-Ir(ppy)$_3$	TBPB	Cy_2NMe	-	Trace
11[c]	*fac*-Ir(ppy)$_3$	TBPB	TMEDA	-	Trace

12[c]	*fac*-Ir(ppy)$_3$	TBPB	Na_2CO_3	-	Trace
13[c]	*fac*-Ir(ppy)$_3$	TBPB	K_2CO_3	-	13
14[c]	*fac*-Ir(ppy)$_3$	TBPB	NaOAc	-	Trace
15[c]	*fac*-Ir(ppy)$_3$	TBPB	KOAc	-	Trace
16[c]	*fac*-Ir(ppy)$_3$	TBPB	K_3PO_4	-	12
17[c]	*fac*-Ir(ppy)$_3$	TBPB	Cs_2CO_3	-	23
18[d]	***fac*-Ir(ppy)$_3$**	**TBPB**	**DABCO**	**-**	**63**
19[d]	4-CzIPN	TBPB	DABCO	-	58
20[d]	Ir(*d*FCF$_3$ppy)$_2$(dtbpy)PF_6	TBPB	DABCO	-	8
21[d]	Ir(*d*FCF$_3$ppy)$_2$(bpy)PF_6	TBPB	DABCO	-	5
22[e]	*fac*-Ir(ppy)$_3$	TBPB	DABCO	$PhCF_3$	60
23[e]	*fac*-Ir(ppy)$_3$	TBPB	DABCO	DMAc	46
24[e]	*fac*-Ir(ppy)$_3$	TBPB	DABCO	DMF	38
25[e]	*fac*-Ir(ppy)$_3$	TBPB	DABCO	PhCl	64
26[e]	*fac*-Ir(ppy)$_3$	TBPB	DABCO	DCE	68
27[e]	*fac*-Ir(ppy)$_3$	TBPB	DABCO	$CHCl_3$	29
28[e]	*fac*-Ir(ppy)$_3$	TBPB	DABCO	Acetone	71
29[e]	***fac*-Ir(ppy)$_3$**	**TBPB**	**DABCO**	**CH_3CN**	**77(71[h])**
30[e]	*fac*-Ir(ppy)$_3$	TBPB	DABCO	EtOAc	65
31[e]	*fac*-Ir(ppy)$_3$	TBPB	DABCO	THF	26
32[e]	*fac*-Ir(ppy)$_3$	TBPB	DABCO	Dioxane	51
33[f]	*fac*-Ir(ppy)$_3$	TBPB	DABCO	CH_3CN	27
34[g]	-	TBPB	DABCO	CH_3CN	Trace
35	*The reaction was carried out under air*				Trace

Reaction conditions: [a]1a (0.2 mmol), 2a (1 mL), 1 mol % photocatalyst irradiated by 20 W blue LEDs for 24 h under Ar. [b]1a (0.2 mmol), 2a (1 mL), 5 mol % $Ru(bpy)_3Cl_2 \cdot 6H_2O$ irradiated by 20 W blue LEDs for 24 h under Ar. [c]1a (0.2 mmol), 2a (1 mL), 1 mol % photocatalyst and base (1 equiv) irradiated by 20 W blue LEDs for 24 h under Ar. [d]1a (0.2 mmol), 2a (1 mL), 1 mol % photocatalyst and base (1 equiv) irradiated by 20 W blue LEDs for 48 h under Ar. [e]1a (0.2 mmol), 2a (0.5 mL), 1 mol % photocatalyst, base (1 equiv) and co-solvent (0.5 mL) irradiated by 20 W blue LEDs for 48 h under Ar. [f]1a (0.2 mmol), 2a (5 equiv), 1 mol % photocatalyst, base (1 equiv) and co-solvent (1 mL) irradiated by 20 W blue LEDs for 48 h under Ar. [g]no photocatalyst. [h]Isolated yield.

b. Experimental Procedures for Examples Described (General Procedure).

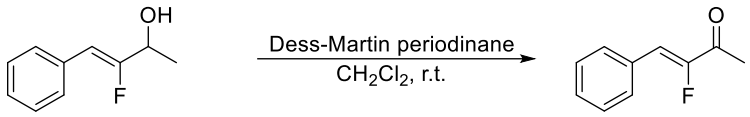
In air, and fluoro acrylic acids (0.2 mmol), *fac*-Ir(ppy)$_3$ (1 mol%), and DABCO (1 equiv) were added to a schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (three cycles). Alcohol (0.5 mL), CH_3CN (0.5 mL), and TBPB (115 μL, 3 equiv) were added in turn by syringe. The resulting reaction mixture was irradiated by 20 W blue

LEDs for 24 to 48 h under Ar. The crude product was purified on a silica gel **(200-300 mesh)** column using a mixture of petroleum ether (PE) and ethyl acetate (EtOAc) as eluent. The *E/Z* ratios were determined by ^{1}H NMR and ^{19}F NMR analyses.

c. Experimental Procedures for gram-scale reaction

In air, and fluoro acrylic acids (**1a**, 2 mmol), *fac*-Ir(ppy)$_3$ (1 mol%), and DABCO (1 equiv) were added to a schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (three cycles). ^{i}Pr-OH (4 mL), CH_3CN (4 mL), and TBPB (3 equiv) were added in turn by syringe. The resulting reaction mixture was irradiated by 20 W blue LEDs for 48 h under Ar. The crude product was purified on a silica gel (200-300 mesh) column using a mixture of petroleum ether and ethyl acetate (10:1) as eluent.

III. Synthetic transformation of products

(1) 

0.2 mmol
compound 29

compound 52
(27.1 mg, 83% yield)

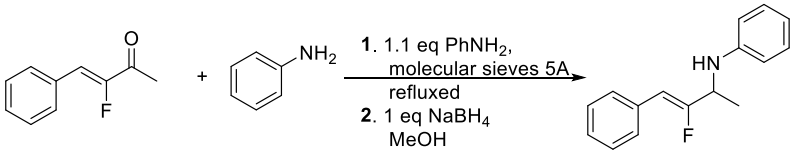
The alcohol (compound **29**, 0.2 mmol, 33 mg) was dissolved in CH_2Cl_2 (2 mL) and 3-oxo-1l5-benzo[d][1,2]iodaoxole-1,1,1(3H)-triyl triacetate (Dess-Martin periodinane, CAS: 87413-09-0, 1.3 equiv, 110 mg) was added. The mixture was stirred at room temperature until TLC showed complete disappearance of the starting alcohol. The solvent was removed under reduced pressure. The crude product was purified on a silica gel (200-300 mesh) column using a mixture of petroleum ether (PE) and ethyl acetate (EtOAc) as eluent (PE: EtOAc = 30:1) to give compound **52** (27 mg, 83% yield).[1]

(2) 

0.2 mmol
compound 29

compound 55
(32.9 mg, 72% yield)

To a solution of alcohol (compound **29**, 0.2 mmol, 33 mg, 1.0 equiv) in anhydrous CH_2Cl_2 (2 mL), under an atmosphere of argon at 0 °C was slowly added PBr_3 (19 μL, 1 equiv). The mixture was stirred for 10 min before being allowed to warm to room temperature. When full conversion was observed by TLC the mixture was poured into a separating funnel, diluted with CH_2Cl_2 (10 mL), and quenched with saturated aqueous solution of $NaHCO_3$ (10 mL). After phase separation, the aqueous phase was washed twice with CH_2Cl_2. The combined organic phases were washed with water, brine, dried over Na_2SO_4, filtered, and the solvent evaporated *in vacuo*. The crude product was purified on a silica gel (200-300 mesh) column using petroleum ether (PE) as eluent) to give compound **55** (33 mg, 72% yield).[2]

(3) 

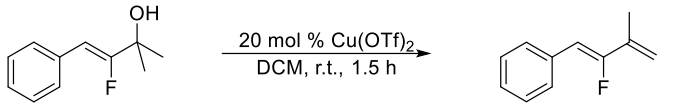
0.2 mmol
compound 52

compound 53
(38.6 mg, 80% yield)

Step1: A mixture of ketone (compound **52**, 32.8 mg, 0.2 mmol) and aniline (20 μL, 0.22 mmol)

in 2 mL of hexane (freshly distilled from calcium hydride) was refluxed for 15 h over molecular sieves 5A (0.1 g).

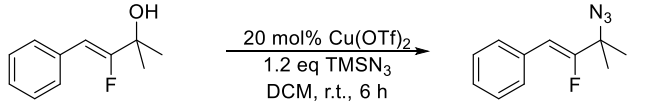
Step2: The solvent evaporated in vacuo. The residue was dissolved in MeOH (2 mL), and $NaBH_4$ (8 mg, 0.2 mmol) was added. The mixture was stirred for 1 h at room temperature. The crude product was purified on a silica gel (200-300 mesh) column using a mixture of petroleum ether (PE) and ethyl acetate (EtOAc) as eluent (PE: EtOAc = 15:1) to give compound **53** (38.5 mg, 80% yield).

(4) 

0.2 mmol
compound 3

compound 54
(24.1 mg, 75% yield)

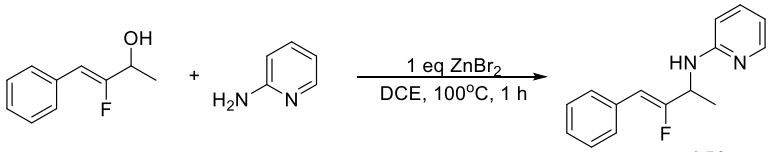
$Cu(OTf)_2$ (3.8 mg, 20 mol %) was added to a well-stirred solution of alcohol (compound **3**, 36 mg, 0.2 mmol, 1 equiv) in CH_2Cl_2 (3 mL). The mixture was stirred for 1.5 h and the volatiles were removed under reduced pressure. The residue was then purified by flash chromatography (silica gel column) with petroleum ether (PE) as eluent to give compound **54** (24 mg, 75% yield).[3]

(5) 

0.2 mmol
compound 3

compound 57
(31.0 mg, 76% yield)

$TMSN_3$ (31.5 μL, 1.2 equiv) was added to a well-stirred solution of alcohol (compound **3**, 36 mg, 0.2 mmol, 1 equiv) and $Cu(OTf)_2$ (7.6mg, 20 mol %) in 3 mL CH_2Cl_2 for 6 h and the volatiles were removed undetr reduced pressure. The crude product was purified on a silica gel (200-300 mesh) column using a mixture of petroleum ether (PE) and ethyl acetate (EtOAc) as eluent (PE: EtOAc = 30:1) to give compound **57** (31.0 mg, 76% yield).

(6) 

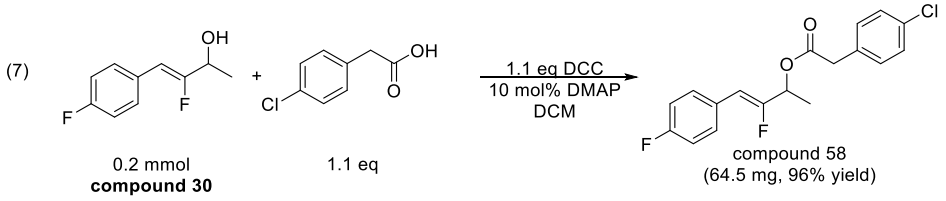
0.2 mmol
compound 29

1.2 eq

compound 56
(46.0 mg, 95% yield)

Alcohol (compound **29**, 0.2 mmol, 33 mg, 1.0 equiv), 2-amino pyridine (22 μL, 0.24 mmol, 1.2 equiv) were added in DCE (1 mL) in an 10 mL screw-cap reaction vial, and the reaction mixture was stirred at rt for 5 min. or until the reaction mixture becomes homogeneous, followed by $ZnBr_2$

(45 mg, 0.2 mmol, 1.0 equiv) addition and the reaction mixture was heated at 100 °C for 1 h. After completion of the reaction, added water (5 mL) and extracted with DCM (3 × 10 mL). The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified on a silica gel (200-300 mesh) column using petroleum ether/EtOAc (3:1) to give compound **56** (46.0 mg, 95% yield).[4]

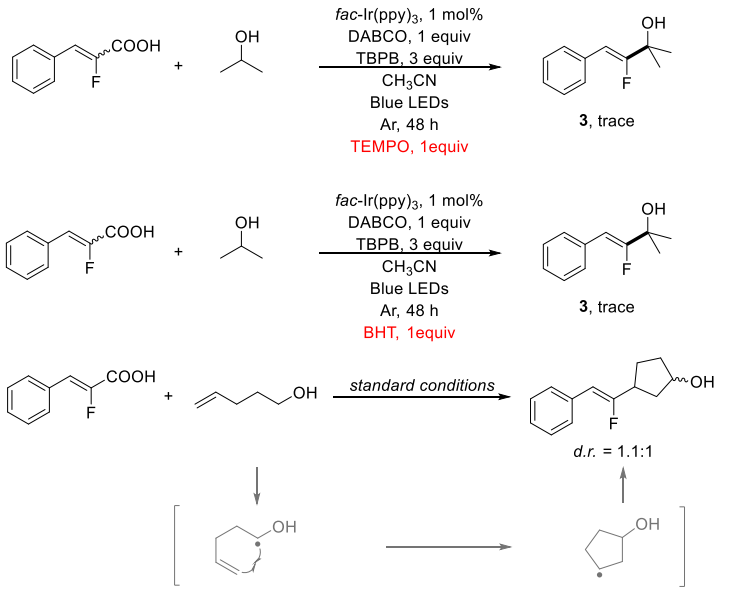


DCC (46 mg, 1.1 equiv) was added to a well-stirred solution of alcohol (compound **30**, 36.8 mg, 0.2 mmol, 1 equiv), 2-(4-chlorophenyl)acetic acid (37.5 mg, 1.1 equiv), and DMAP (2.5 mg, 10 mol%) in CH_2Cl_2 (5 mL). The mixture was stirred for 5 h and the volatiles were removed under reduced pressure. The crude product was purified on a silica gel (200-300 mesh) column using petroleum ether/EtOAc (20:1) to give compound **58** (64.5 mg, 96% yield).

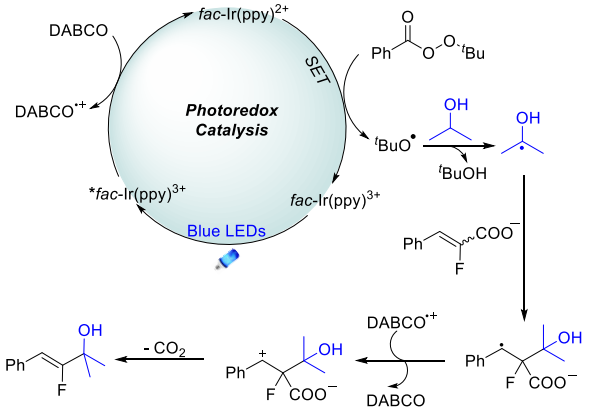
References

1. Yu, B.; Mohamed, S.; Ardisson, J.; Lannou, M.-I.; Sorin, G. Silver oxide(i) promoted Conia-ene/radical cyclization for a straightforward access to furan derivatives. *Chem. Commun.* **2022**, *58*, 1374-1377.
2. McCourt, R. O.; Dénès, F.; Sanchez-Sanz, G.; Scanlan, E. M. Rapid Access to Thiolactone Derivatives through Radical-Mediated Acyl Thiol–Ene and Acyl Thiol–Yne Cyclization. *Org. Lett.* **2018**, *20*, 2948-2951.
3. Yang, L.; Ji, W.-W.; Lin, E.; Li, J.-L.; Fan, W.-X.; Li, Q.; Wang, H. Synthesis of Alkylated Monofluoroalkenes via Fe-Catalyzed Defluorinative Cross-Coupling of Donor Alkenes with gem-Difluoroalkenes. *Org. Lett.* **2018**, *20*, 1924-1927.
4. Panigrahi, A.; Sharanappa Sherikar, M.; Ramaiah Prabhu, K. ZnBr2 Mediated C−N Bond Formation using Cinnamyl Alcohol and 2-Amino Pyridines. *Eur. J. Org. Chem.* **2021**, *2021*, 3054-3058.

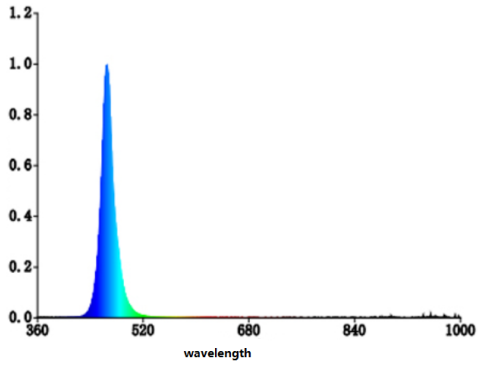
IV. Mechanism experiments and proposed catalytic cycle

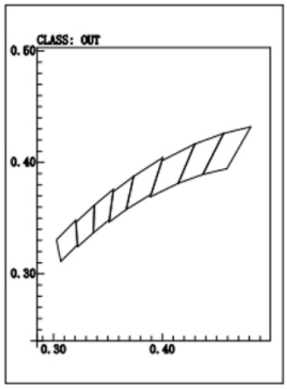


Proposed mechanism



V. Experimental apparatus and pictures





Manufacturers：Jia-deng;

Model: HCB-SKDS-1000 (China);

Wavelength of peak intensity：465.4 nm;

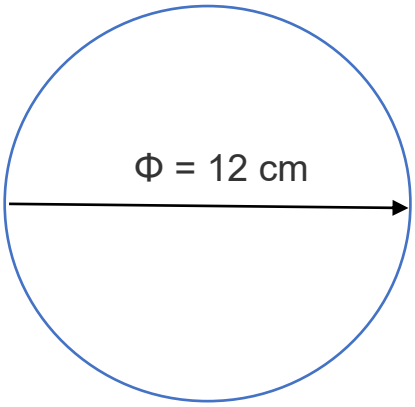
Luminous flux: 1.854 lm; Photosynthetic efficiency: 32.39 lm/W;

Chromaticity coordinates: x = 0.1328; y = 0.0623/u' =0.1526; v' = 0.1610; duv = 1.610e-001;

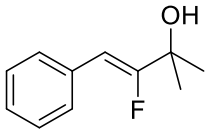
Color rendering index: Ra = -50.5;

The material of the irradiation vessel: ordinary glass.

Experimental apparatus and pictures:



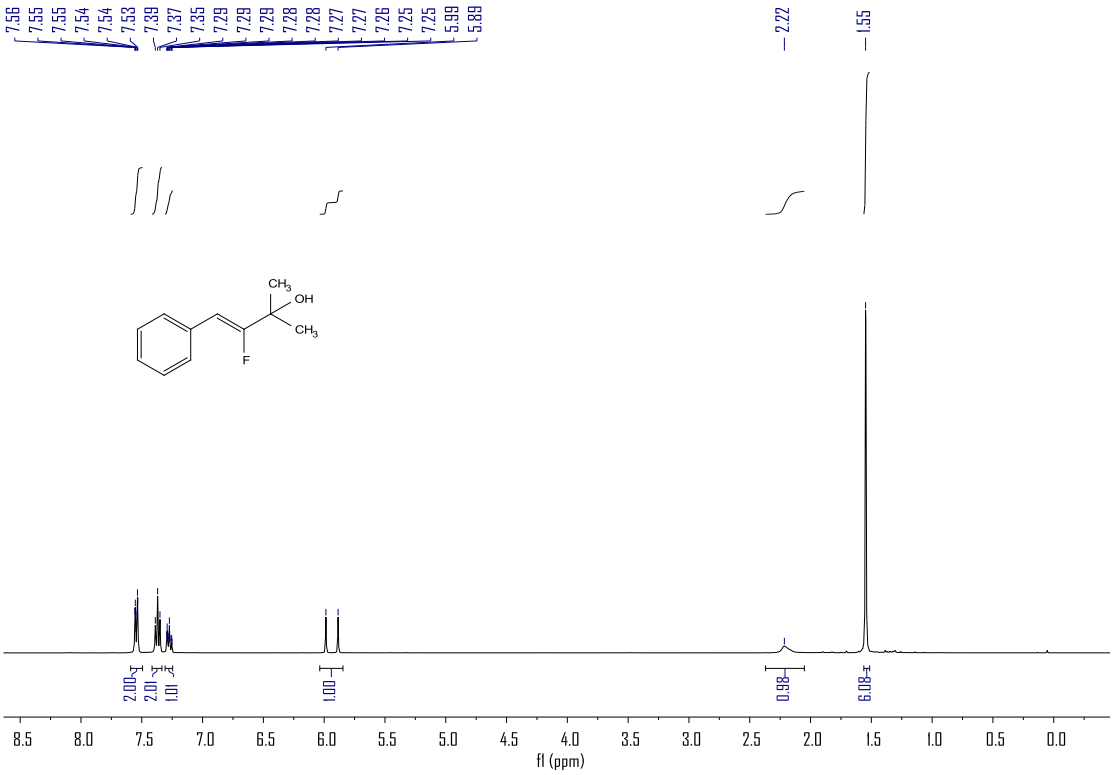
VI. Substrate Scope, Spectral Data and NMR Spectra

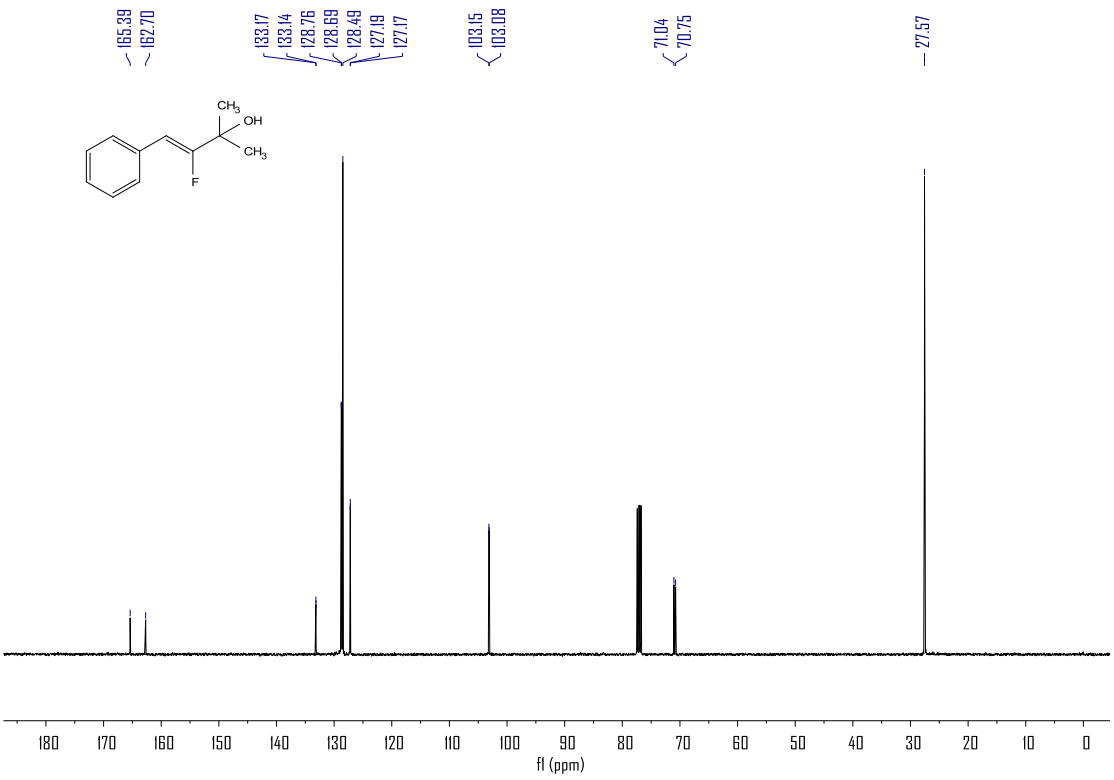


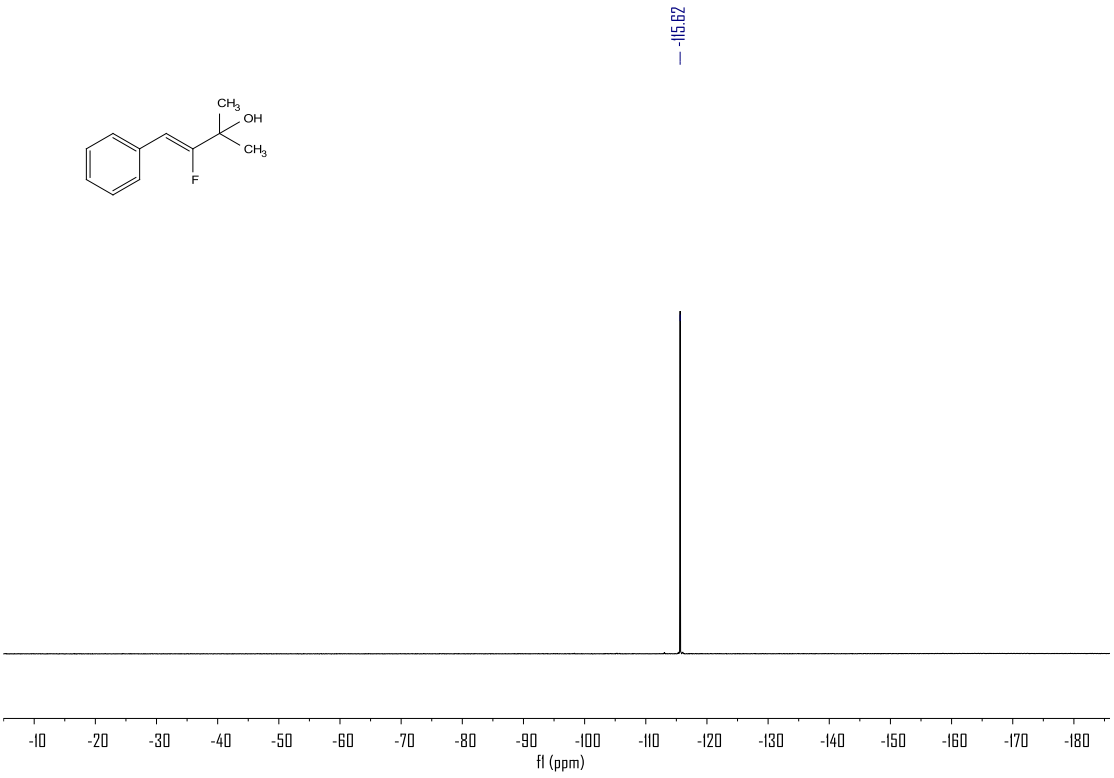
(Z)-3-fluoro-2-methyl-4-phenylbut-3-en-2-ol

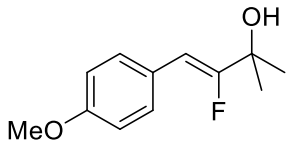
Following the general procedure (**product 3**, **pale-yellow liquid, 25.5 mg, 71%,** Z/E > 30:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (10:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.59 – 7.50 (m, 2H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.31 – 7.24 (m, 1H), 5.94 (d, *J* = 40.1 Hz, 1H), 2.22 (s, 1H), 1.55 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 164.05 (d, *J* = 270.4 Hz), 133.15 (d, *J* = 2.3 Hz), 128.73 (d, *J* = 7.4 Hz), 128.49, 127.18 (d, *J* = 2.2 Hz), 103.12 (d, *J* = 7.4 Hz), 70.90 (d, *J* = 29.0 Hz), 27.57. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -115.62.

HRMS (ESI) calcd for $C_{11}H_{13}FNaO$ ($M+Na^{+}$): 203.0843; found: 203.0851.





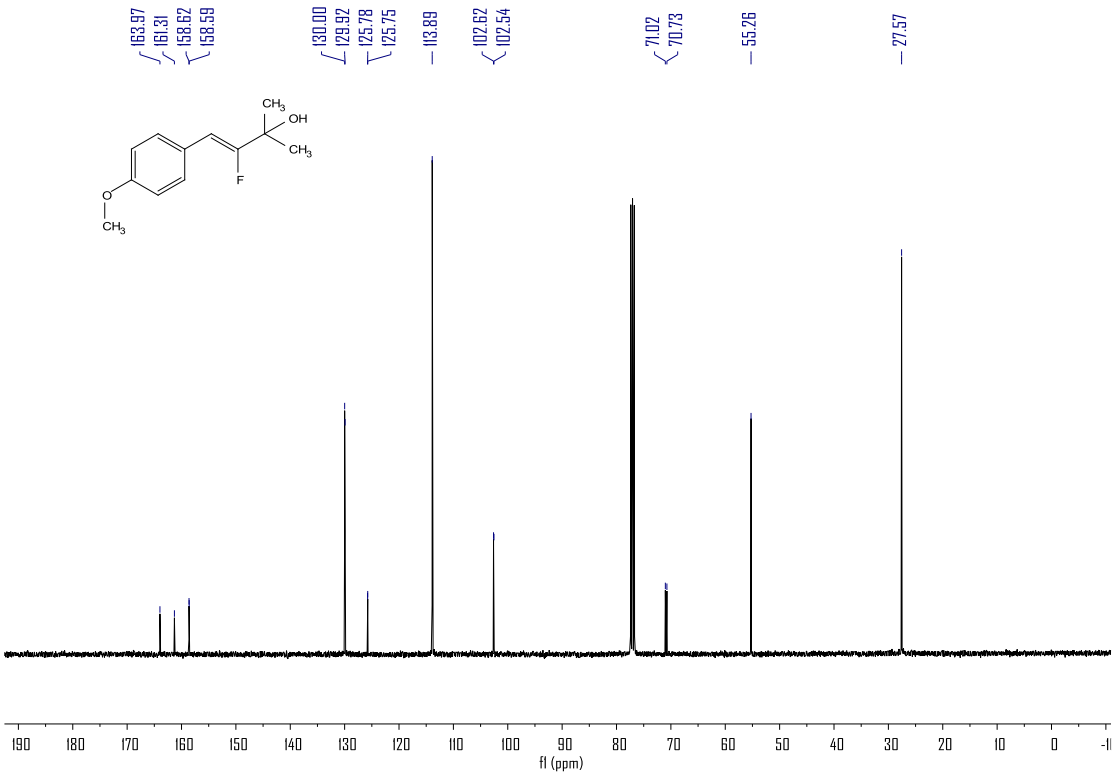


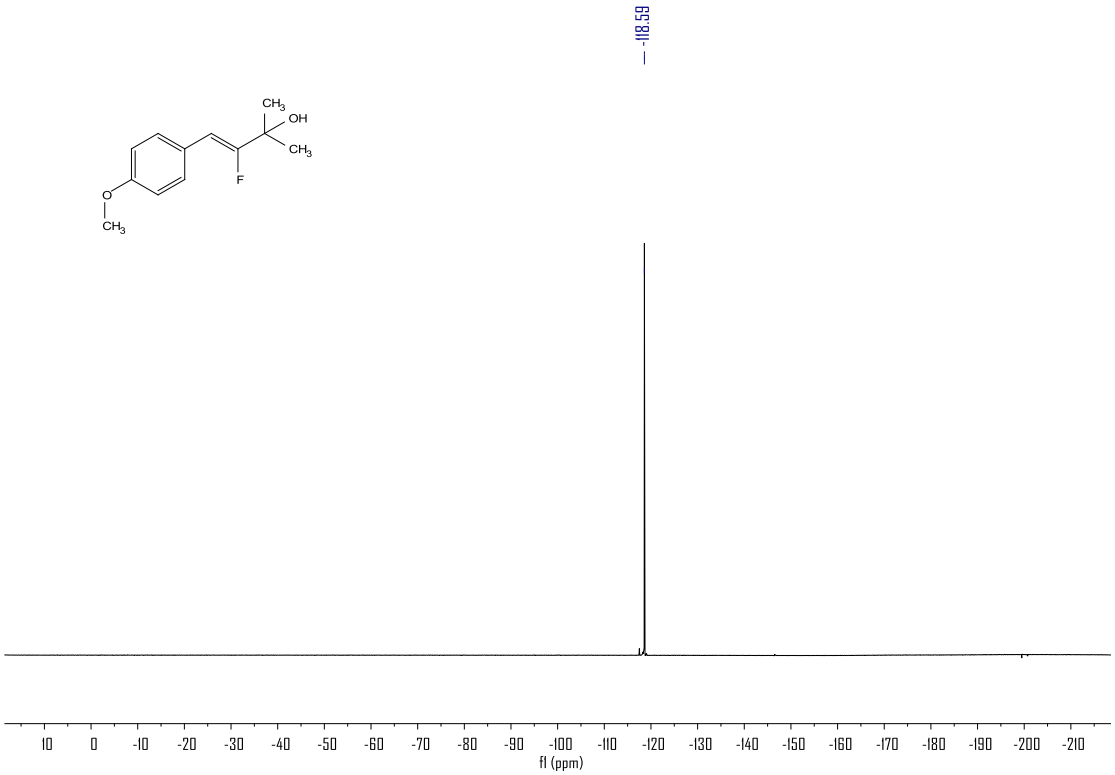


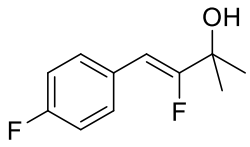
(Z)-3-fluoro-4-(4-methoxyphenyl)-2-methylbut-3-en-2-ol

Following the general procedure (**product 4**, **pale-yellow liquid, 30.2 mg, 72%,** Z/E > 30:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (10:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.44 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 5.82 (d, *J* = 40.4 Hz, 1H), 3.81 (s, 3H), 2.01 (s, 1H), 1.50 (d, *J* = 1.1 Hz, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 162.64 (d, *J* = 267.6 Hz), 158.61 (d, *J* = 2.9 Hz), 129.96 (d, *J* = 7.5 Hz), 125.77 (d, *J* = 2.3 Hz), 113.89, 102.58 (d, *J* = 7.8 Hz), 70.88 (d, *J* = 29.0 Hz), 55.26, 27.57. **^{19} F NMR** (376 MHz, $CDCl_3$) δ -118.59.

HRMS (ESI) calcd for $C_{12}H_{15}FNaO_2$ ($M+Na^+$): 233.0948; found: 233.0942.



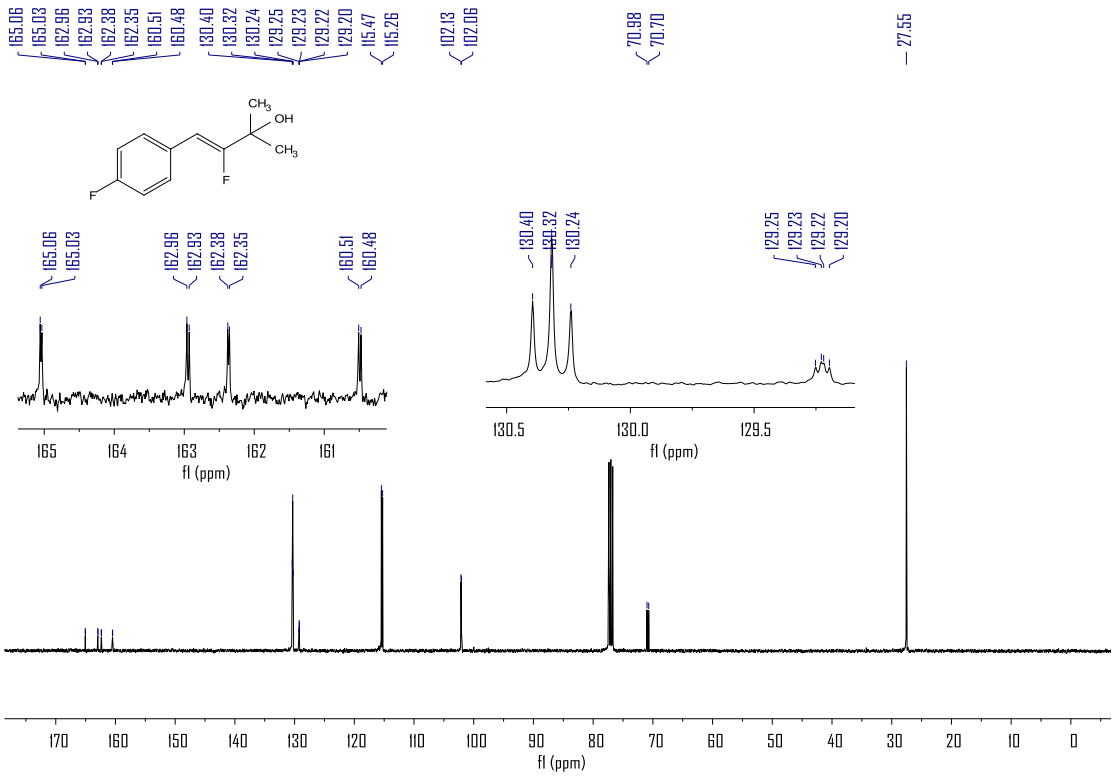


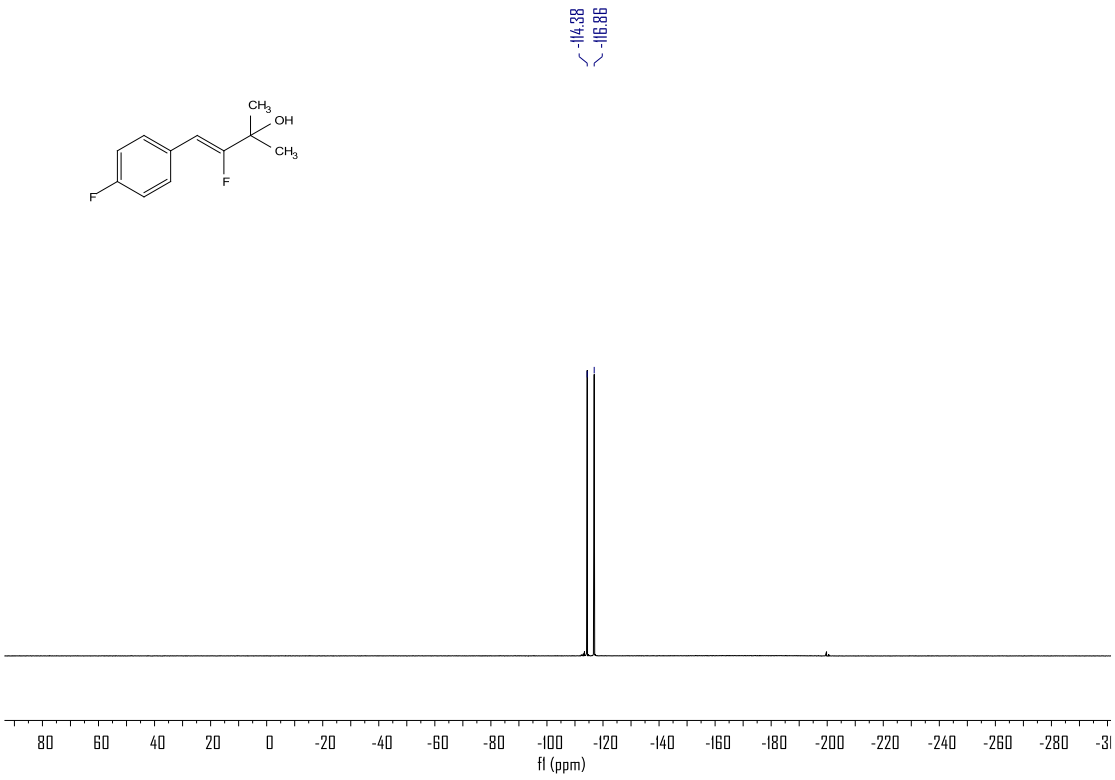


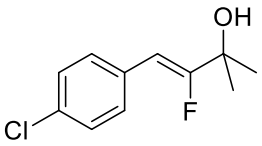
(Z)-3-fluoro-4-(4-fluorophenyl)-2-methylbut-3-en-2-ol

Following the general procedure (**product 5**, **pale-yellow liquid, 28.1 mg, 71%,** Z/E > 30:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (10:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.49 (dd, *J* = 8.6, 5.6 Hz, 2H), 7.04 (t, *J* = 8.7 Hz, 2H), 5.89 (d, *J* = 39.7 Hz, 1H), 2.07 (s, 1H), 1.53 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 163.71 (dd, *J* = 269.7, 2.4 Hz), 161.72 (dd, J = 246.9, 3.4 Hz), 130.32 (t, *J* = 7.8 Hz), 129.22(dd, *J* = 3.2 Hz, *J* = 2.3 Hz), 115.37 (d, *J* = 21.3 Hz), 102.10 (d, *J* = 7.5 Hz), 70.84 (d, *J* = 29.0 Hz), 27.55. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -114.38, -116.86.

HRMS (ESI) calcd for $C_{11}H_{12}F_2NaO$ ($M+Na^+$): 221.0748; found: 221.0746.



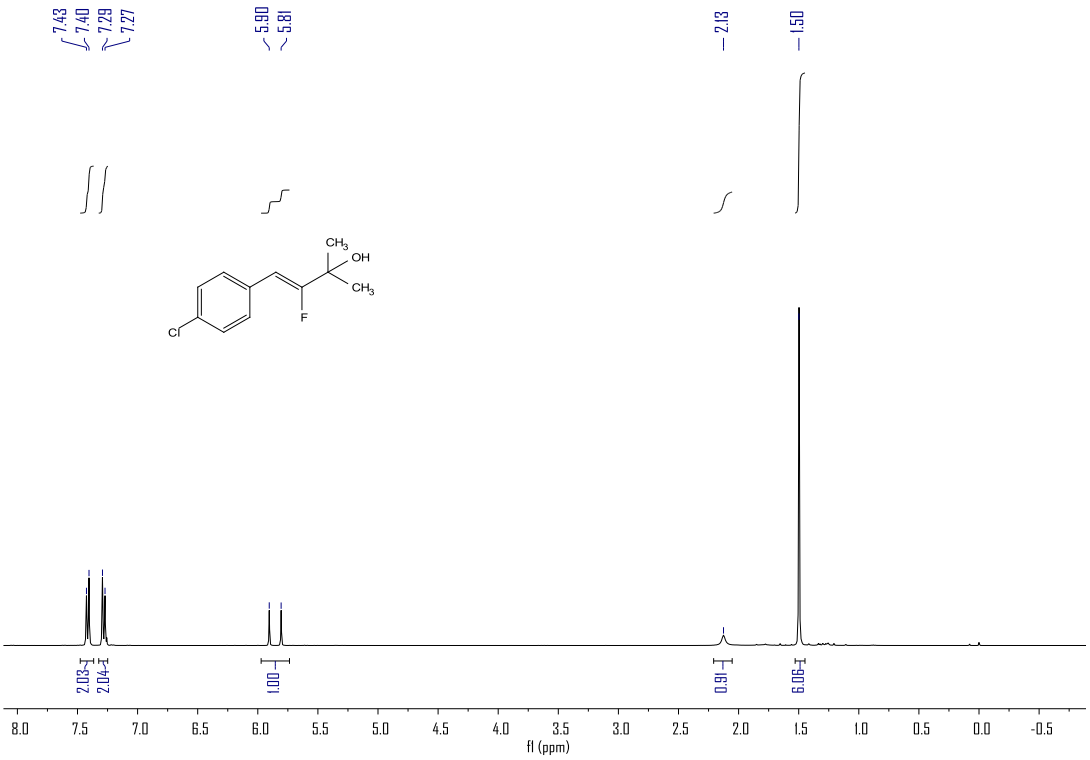


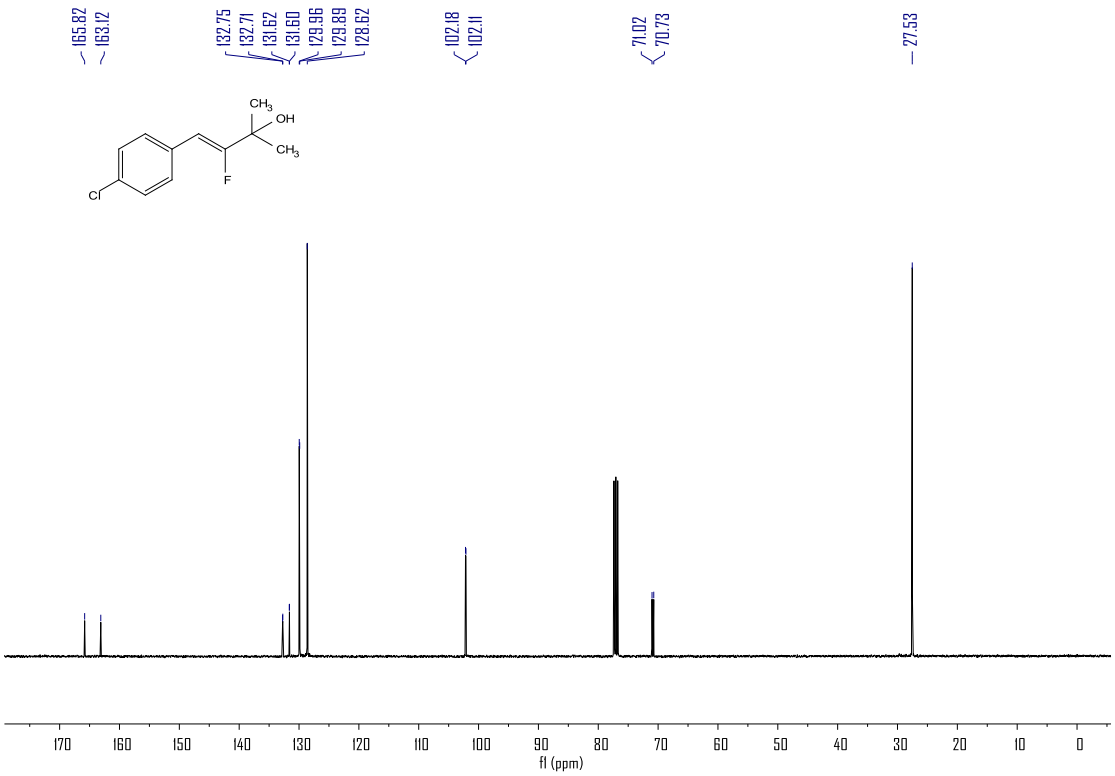


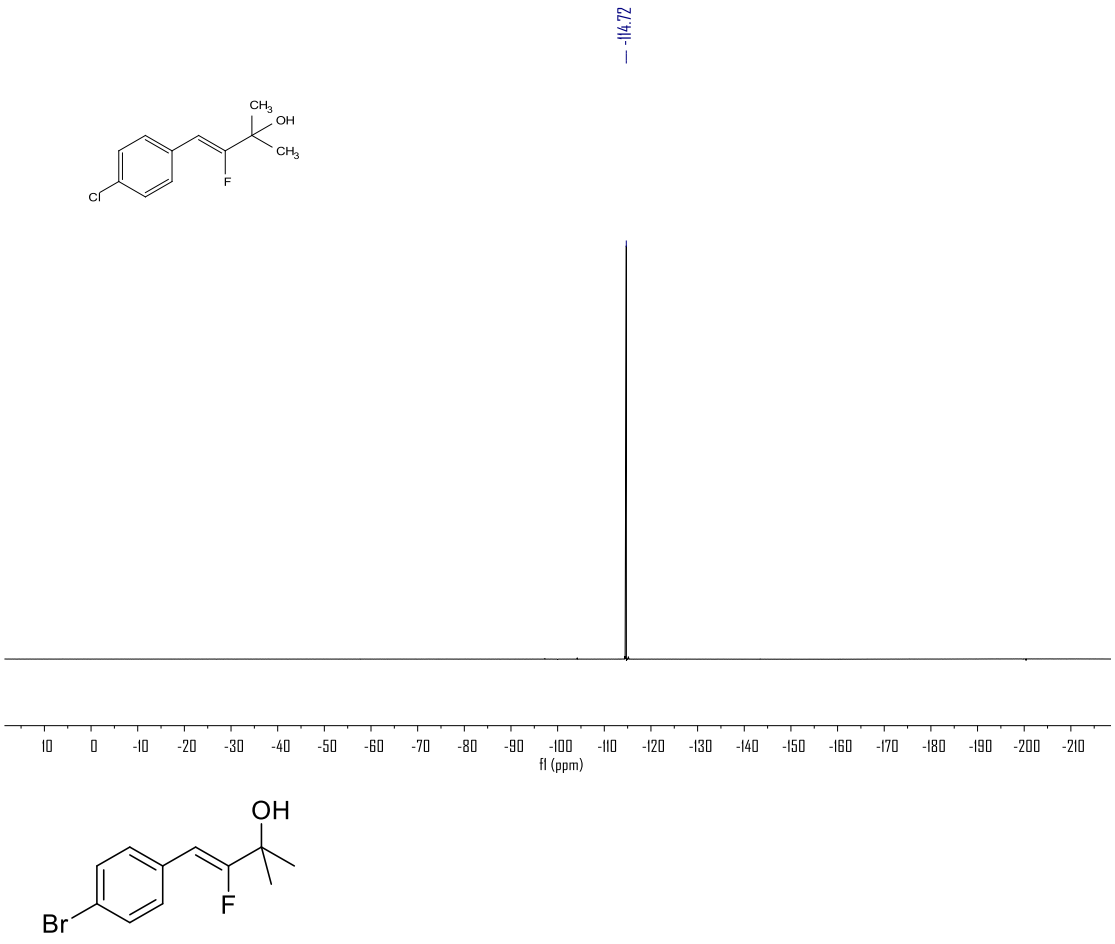
(Z)-4-(4-chlorophenyl)-3-fluoro-2-methylbut-3-en-2-ol

Following the general procedure (**product 6**, **pale-yellow liquid, 29.3 mg, 69%,** Z/E > 30:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (10:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.41 (d, *J* = 8.5 Hz, 2H), 7.28 (d, *J* = 8.5 Hz, 2H), 5.86 (d, *J* = 39.6 Hz, 1H), 2.13 (s, 1H), 1.50 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 164.47 (d, *J* = 271.3 Hz), 132.73 (d, *J* = 3.5 Hz), 131.61 (d, *J* = 2.3 Hz), 129.93 (d, *J* = 7.7 Hz), 128.62, 102.14 (d, *J* = 7.3 Hz), 70.87 (d, *J* = 29.0 Hz), 27.53. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -114.72.

HRMS (ESI) calcd for $C_{11}H_{12}ClFNaO$ ($M+Na^+$): 237.0453; found: 237.0460.



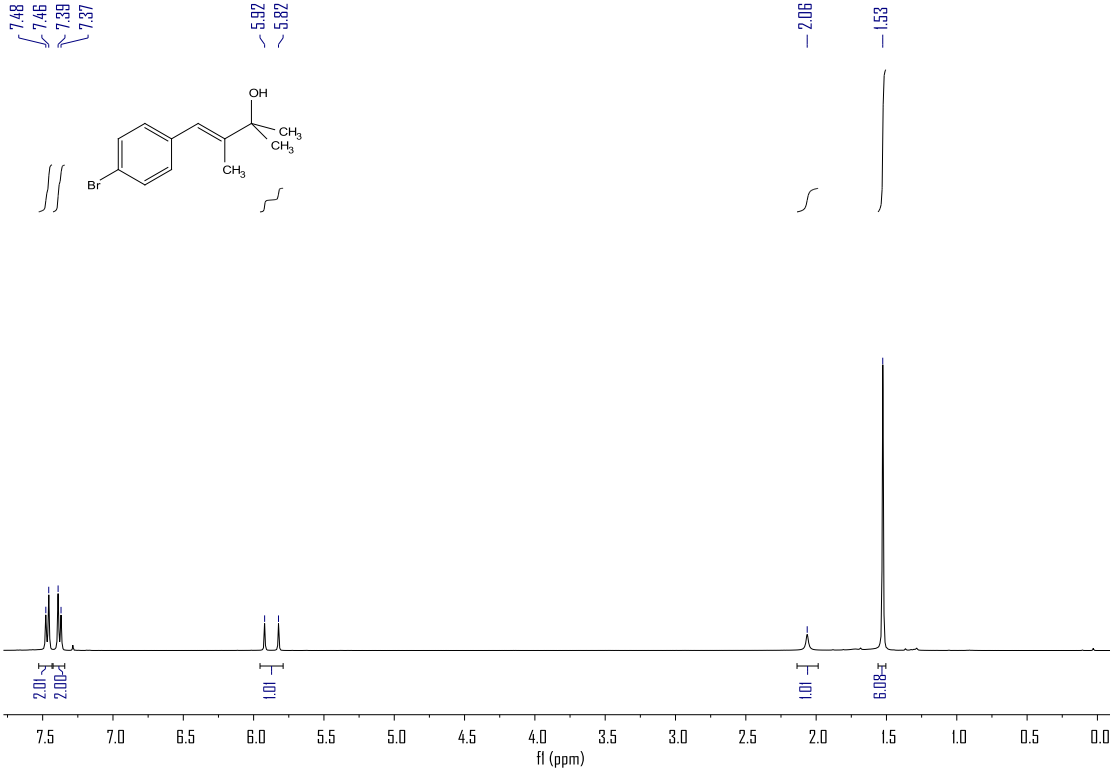


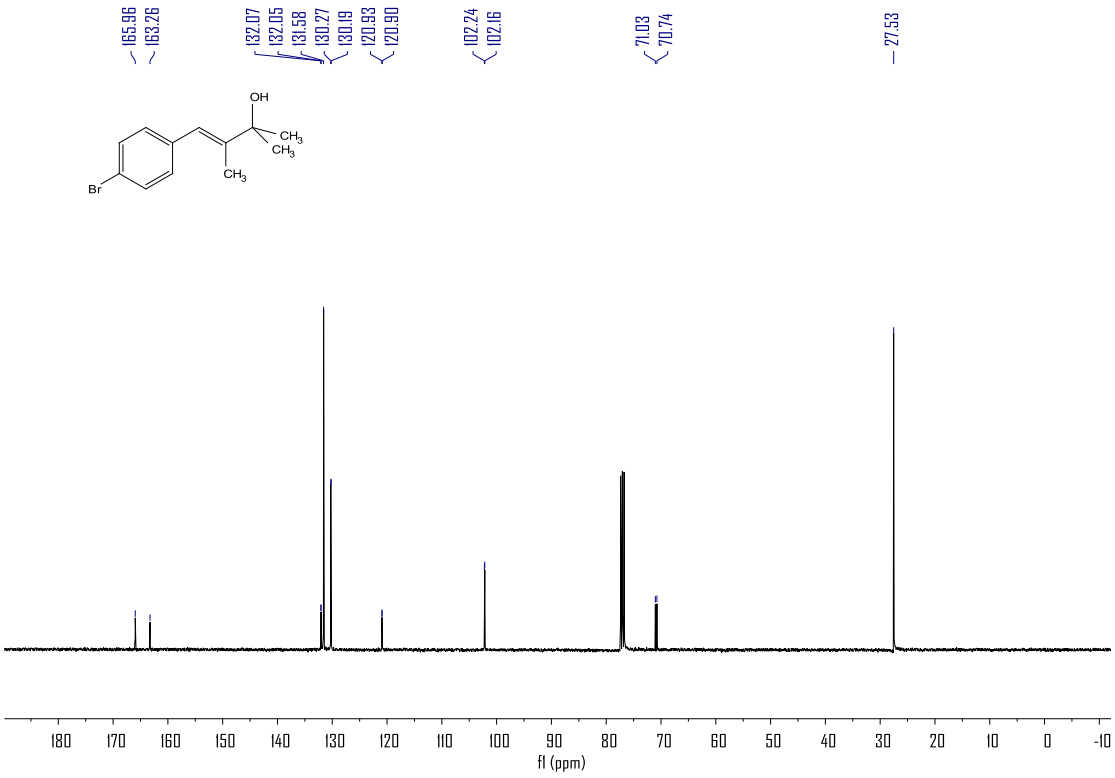


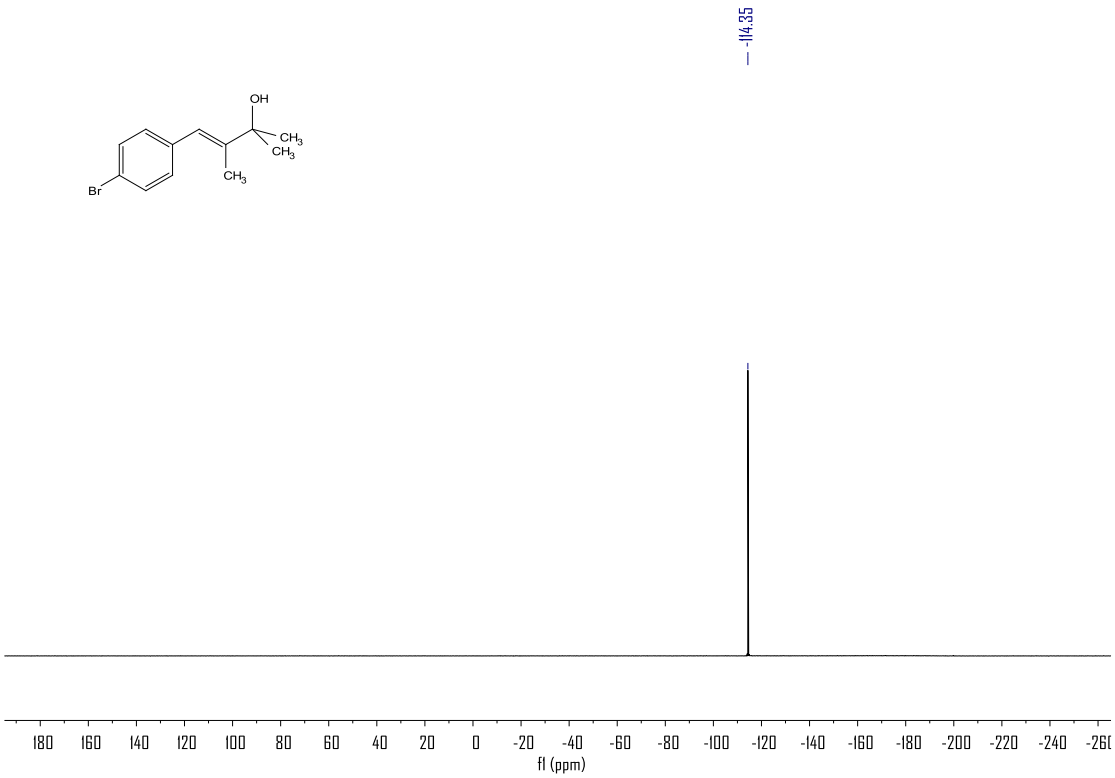
(Z)-4-(4-bromophenyl)-3-fluoro-2-methylbut-3-en-2-ol

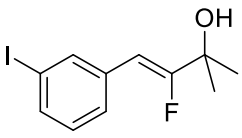
Following the general procedure (**product 7**, **pale-yellow liquid, 36.5 mg, 71%,** Z/E > 30:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (10:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.47 (d, *J* = 8.3 Hz, 2H), 7.38 (d, *J* = 8.3 Hz, 2H), 5.87 (d, *J* = 39.5 Hz, 1H), 2.06 (s, 1H), 1.53 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 164.61 (d, *J* = 271.5 Hz), 132.06 (d, *J* = 2.2 Hz), 131.58, 130.23 (d, *J* = 7.6 Hz), 120.91 (d, *J* = 3.4 Hz), 102.20 (d, *J* = 7.3 Hz), 70.89 (d, *J* = 29.0 Hz), 27.53. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -114.35.

HRMS (ESI) calcd for $C_{11}H_{12}BrFNaO$ ($M+Na^{+}$): 280.9948; found: 280.9953.





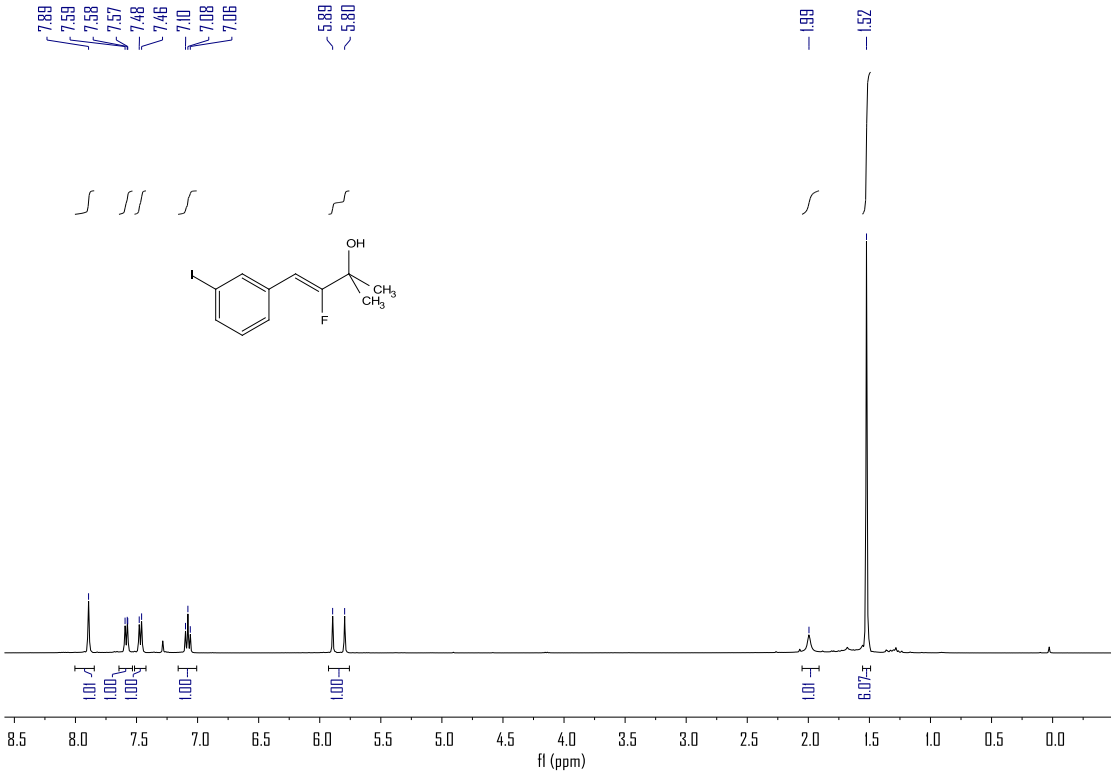


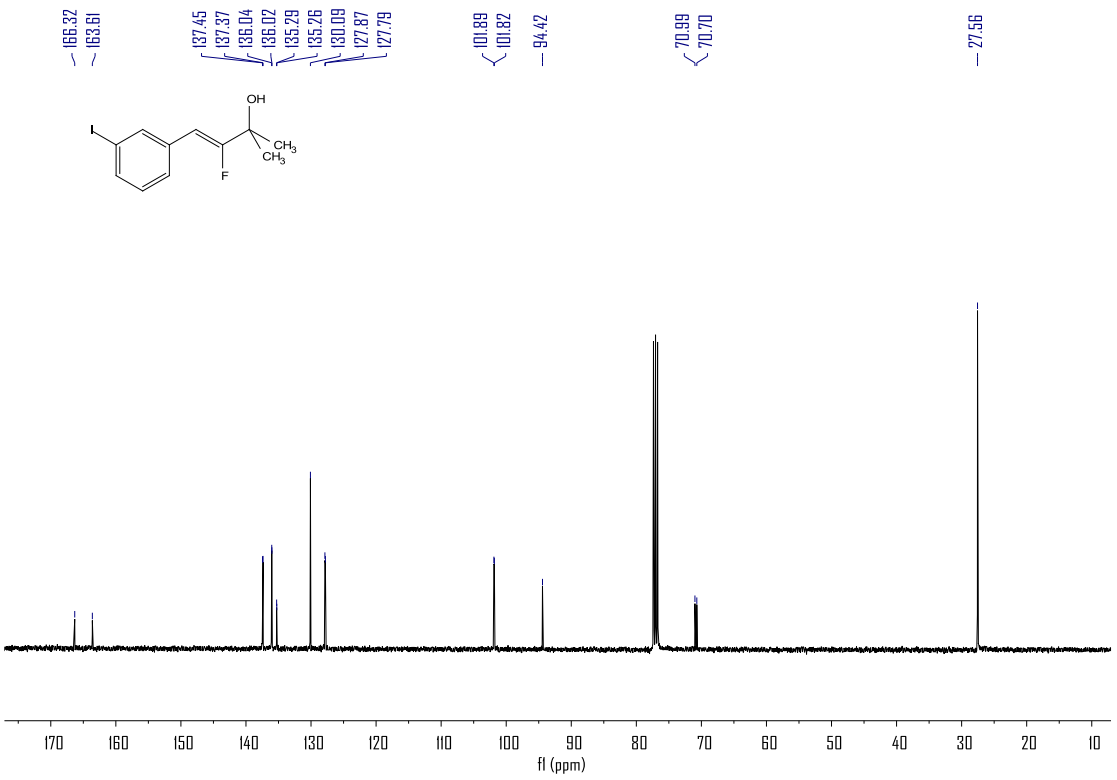


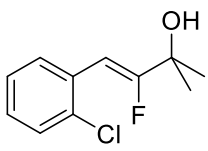
(Z)-3-fluoro-4-(3-iodophenyl)-2-methylbut-3-en-2-ol

Following the general procedure (**product 8**, **pale-yellow liquid, 41.5 mg, 68%,** Z/E > 30:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (10:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.89 (s, 1H), 7.67 – 7.54 (m, 1H), 7.47 (d, *J* = 7.8 Hz, 1H), 7.08 (t, *J* = 7.9 Hz, 1H), 5.85 (d, *J* = 39.3 Hz, 1H), 1.99 (s, 1H), 1.52 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 164.96 (d, *J* = 272.5 Hz), 137.41 (d, *J* = 8.2 Hz), 136.03 (d, *J* = 2.2 Hz), 135.28 (d, *J* = 2.3 Hz), 130.09, 127.83 (d, *J* = 7.4 Hz), 101.86 (d, *J* = 7.2 Hz), 94.42, 70.85 (d, *J* = 29.1 Hz), 27.56. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -113.47.

HRMS (ESI) calcd for $C_{11}H_{12}FINaO$ ($M+Na^{+}$): 328.9809; found: 328.9816.



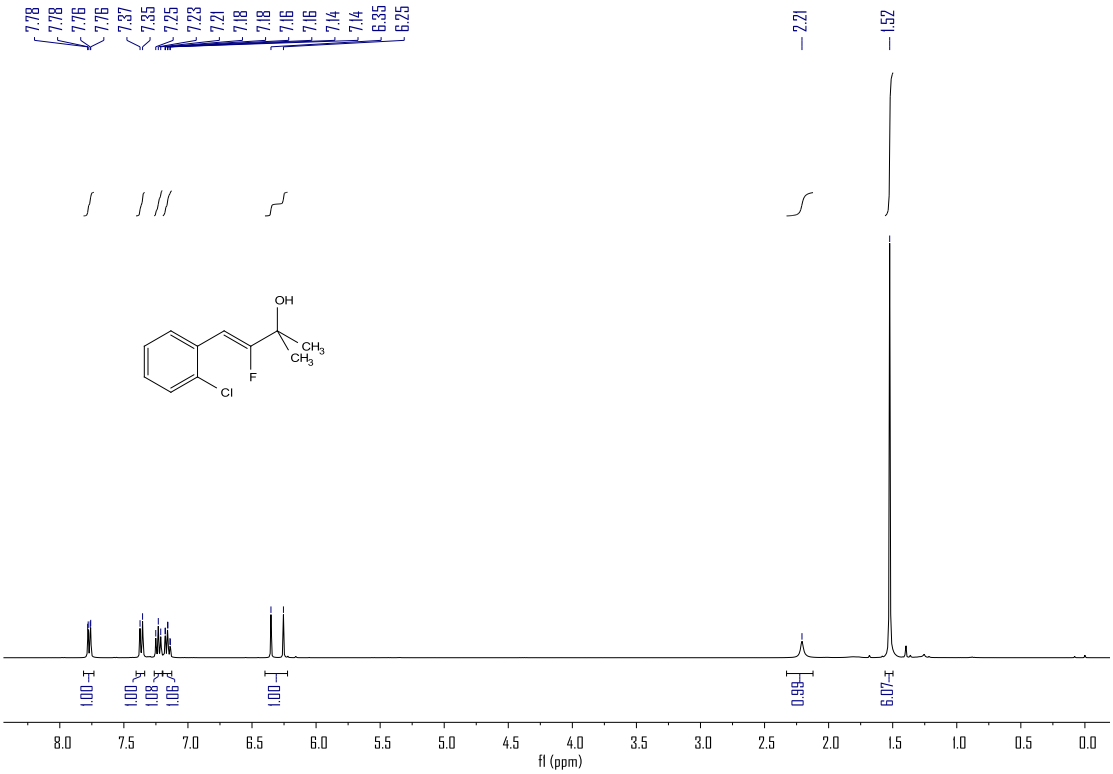


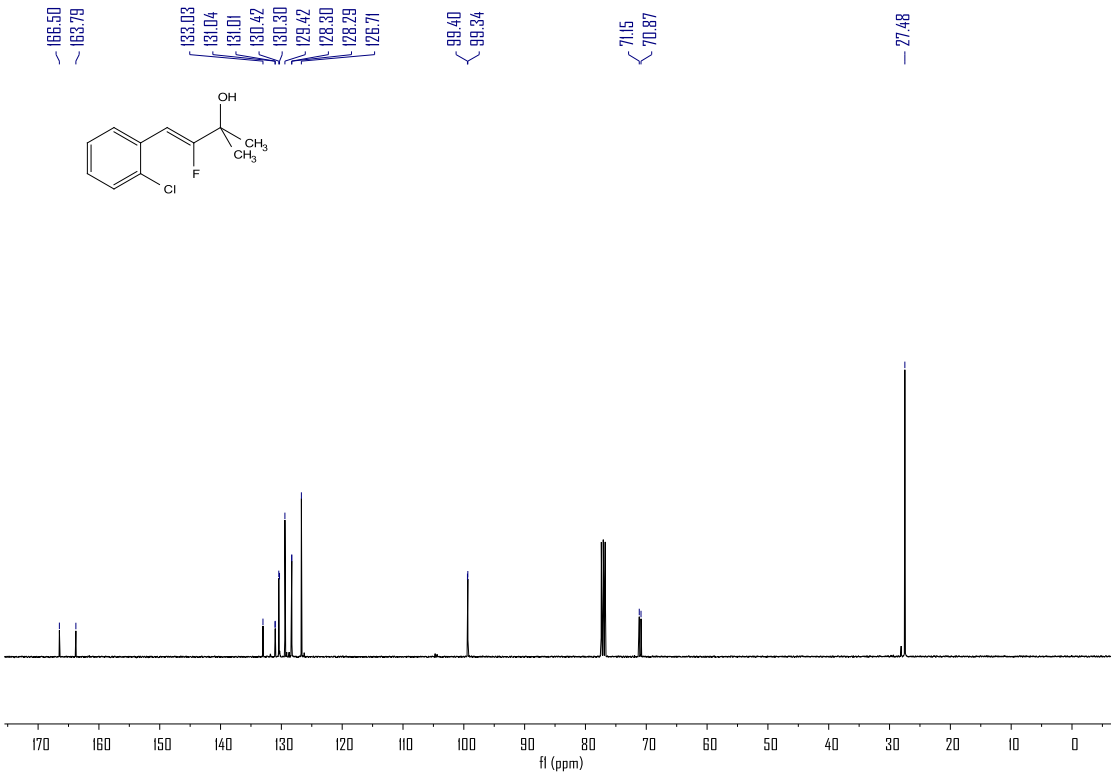


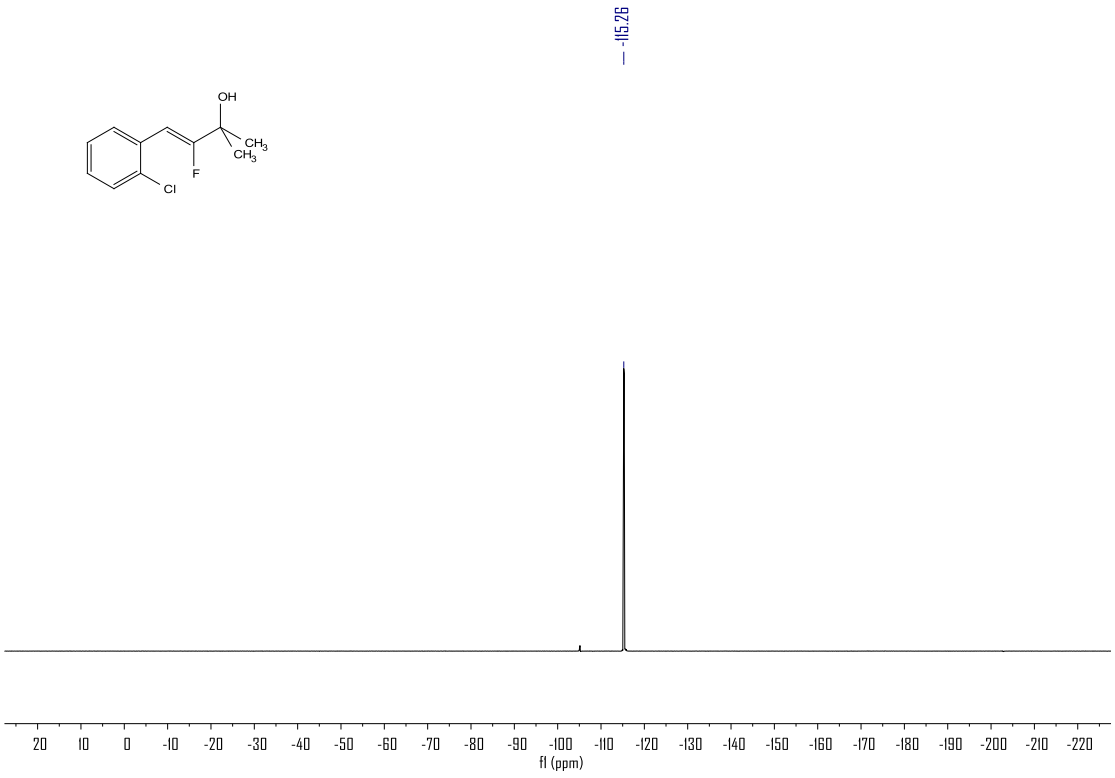
(Z)-4-(2-chlorophenyl)-3-fluoro-2-methylbut-3-en-2-ol

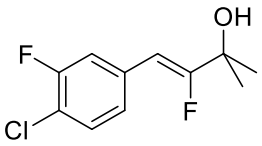
Following the general procedure (**product 9**, **pale-yellow liquid, 28.7 mg, 67%,** Z/E > 30:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (10:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.77 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.36 (d, *J* = 7.9 Hz, 1H), 7.23 (t, *J* = 7.8 Hz, 1H), 7.16 (td, *J* = 7.7, 1.3 Hz, 1H), 6.30 (d, *J* = 39.0 Hz, 1H), 2.21 (s, 1H), 1.52 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.14 (d, *J* = 272.9 Hz), 133.03, 131.02 (d, *J* = 2.5 Hz), 130.36 (d, *J* = 12.0 Hz), 129.42, 128.29 (d, *J* = 1.5 Hz), 126.71, 99.37 (d, *J* = 6.2 Hz), 71.01 (d, *J* = 28.8 Hz), 27.48. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -115.26.

HRMS (ESI) calcd for $C_{11}H_{12}ClFNaO$ ($M+Na^+$): 237.0453; found: 237.0451.





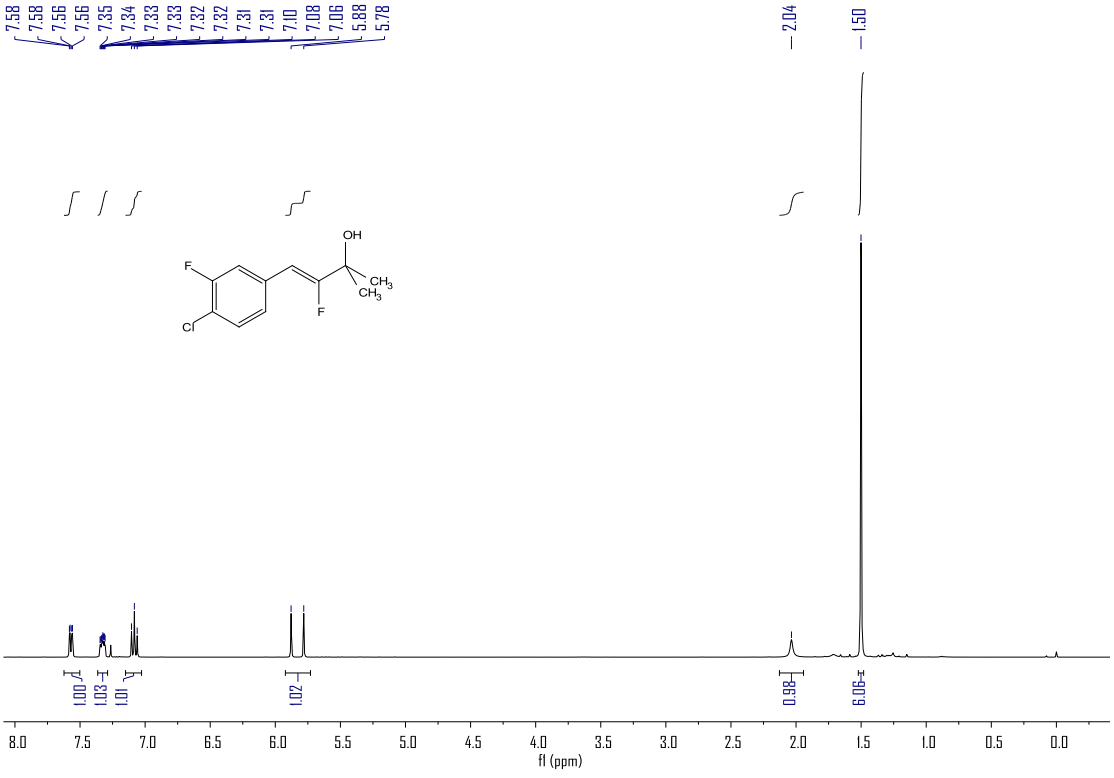


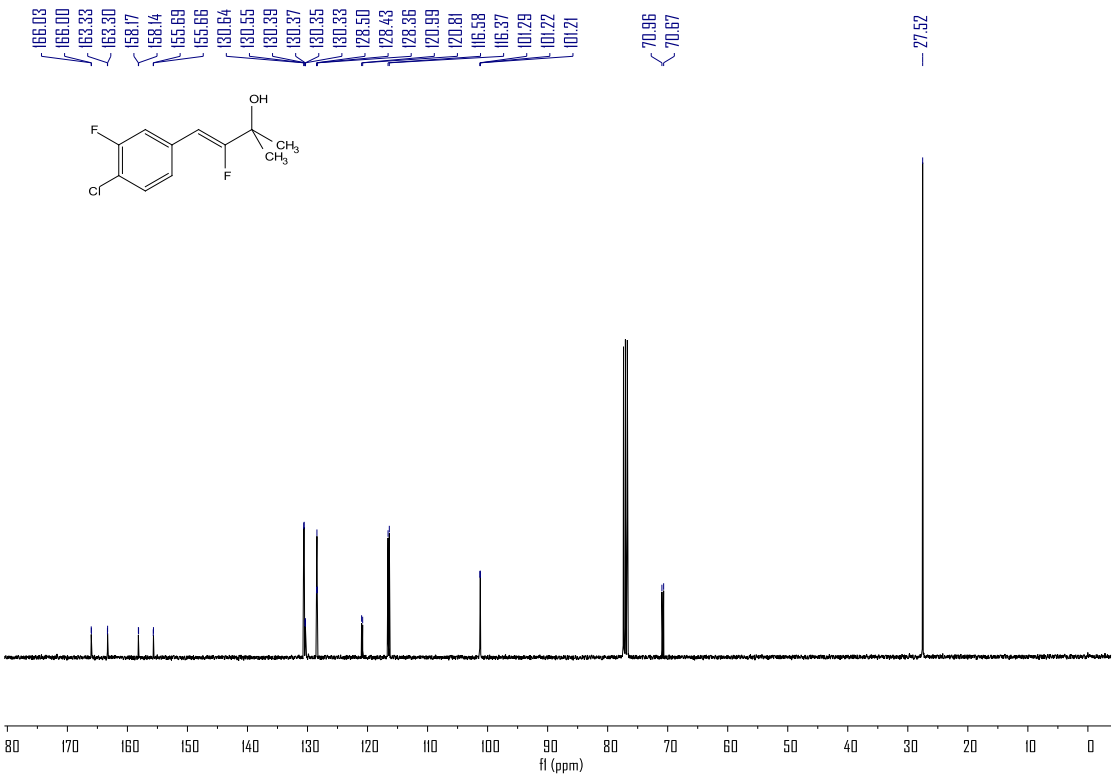


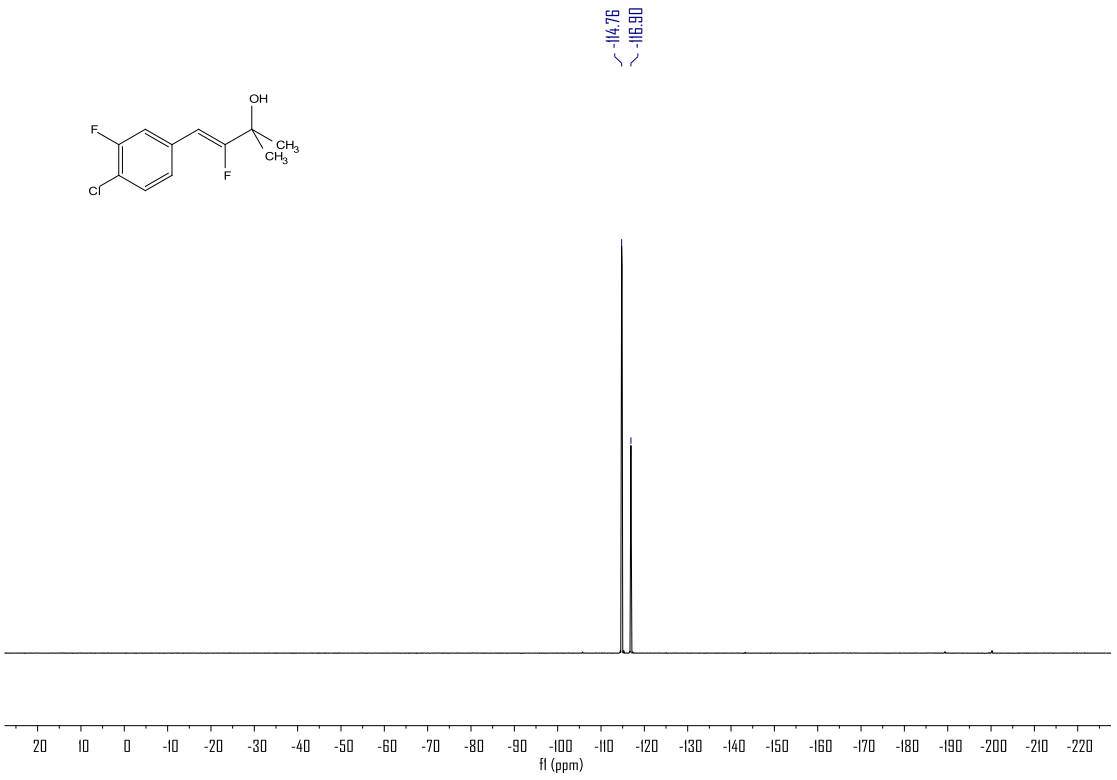
(Z)-4-(4-chloro-3-fluorophenyl)-3-fluoro-2-methylbut-3-en-2-ol

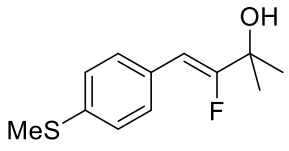
Following the general procedure (**product 10**, **pale-yellow liquid, 32.1 mg, 69%,** Z/E > 30:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (10:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.57 (dd, *J* = 7.1, 2.1 Hz, 1H), 7.33 (ddd, *J* = 8.7, 4.6, 2.2 Hz, 1H), 7.08 (t, *J* = 8.7 Hz, 1H), 5.83 (d, *J* = 39.0 Hz, 1H), 2.04 (s, 1H), 1.50 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 164.67 (dd, *J* = 271.6, 2.5 Hz), 156.92 (dd, *J* = 249.6, 3.2 Hz), 130.59 (d, *J* = 8.6 Hz), 130.36 (dd, *J* = 4.2, 2.1 Hz), 128.43 (t, *J* = 7.2 Hz), 120.90 (d, *J* = 17.7 Hz), 116.48 (d, *J* = 21.1 Hz), 102.20 – 100.08 (m), 70.82 (d, *J* = 29.0 Hz), 27.52. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -114.76, -116.90.

HRMS (ESI) calcd for $C_{11}H_{11}ClF_2NaO$ ($M+Na^+$): 255.0359; found: 255.0351.





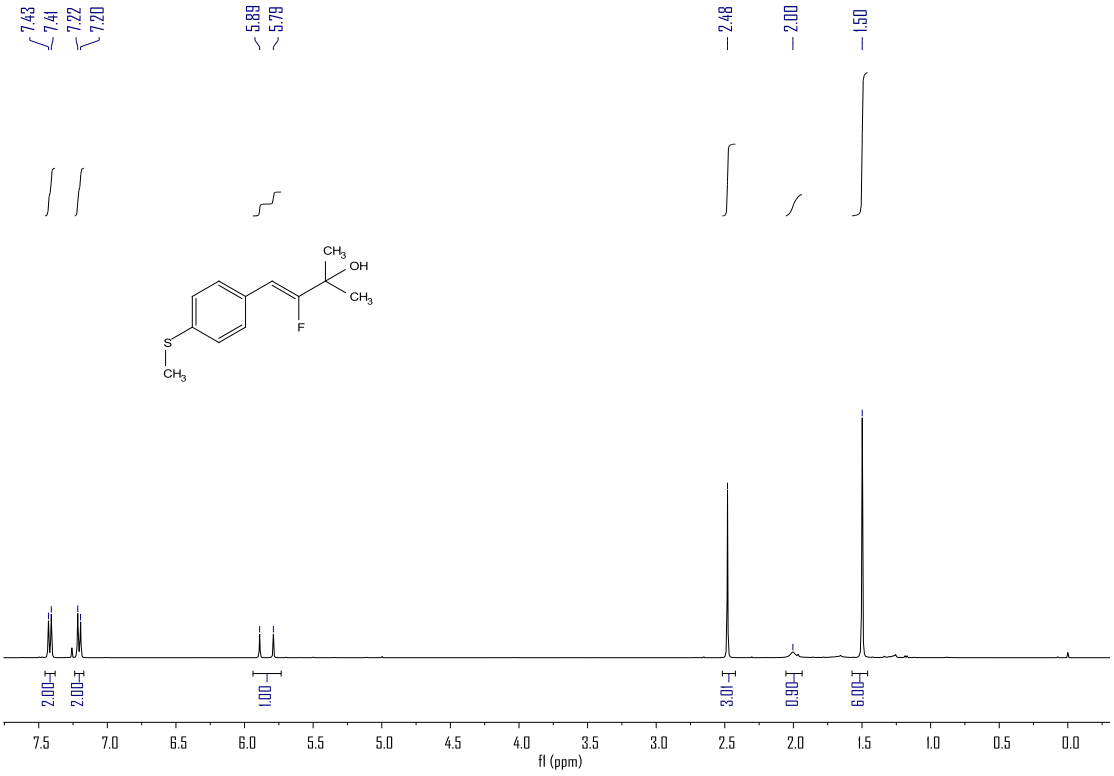


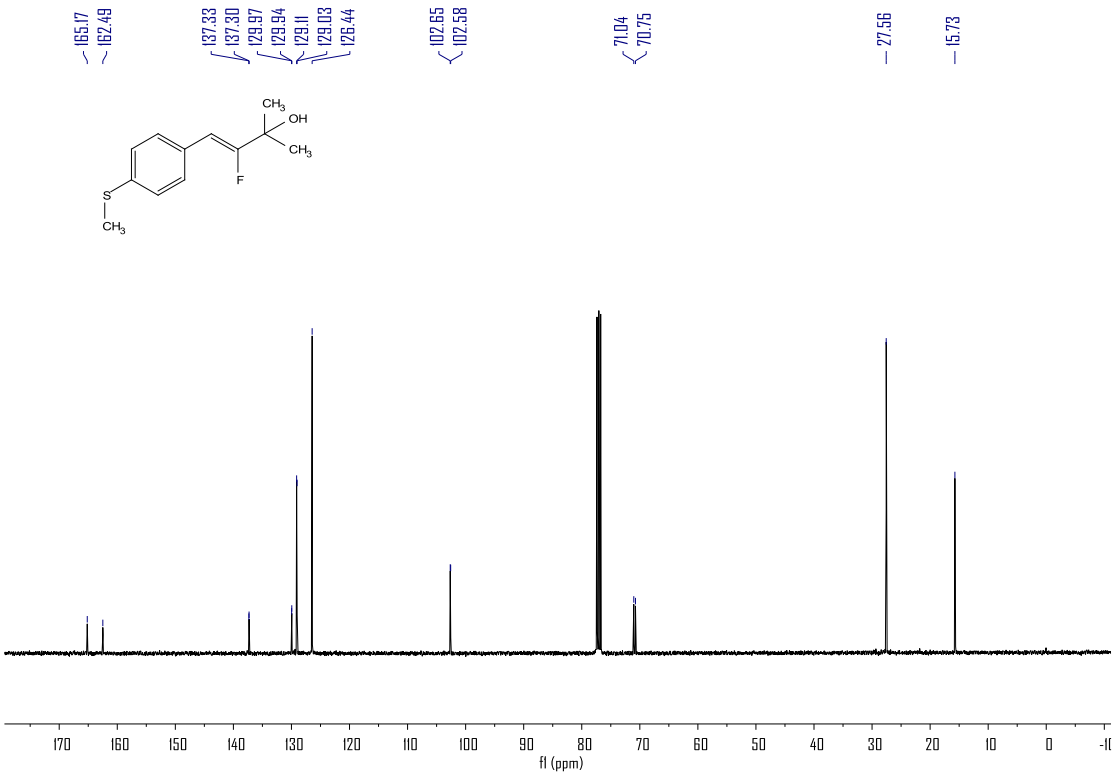


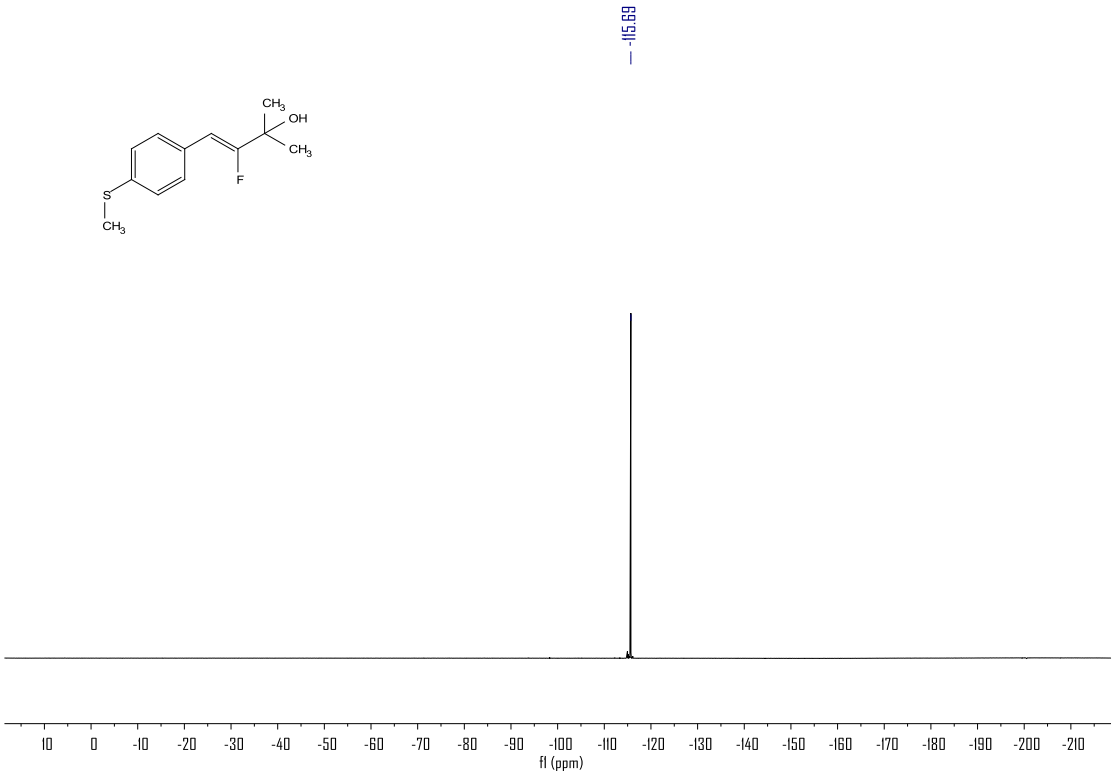
(Z)-3-fluoro-2-methyl-4-(4-(methylthio)phenyl)but-3-en-2-ol

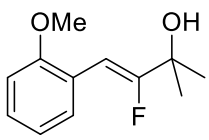
Following the general procedure (**product 11**, **pale-yellow liquid, 25.2 mg, 56%,** Z/E > 30:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (10:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.42 (d, *J* = 8.2 Hz, 2H), 7.21 (d, *J* = 8.2 Hz, 2H), 5.84 (d, *J* = 40.1 Hz, 1H), 2.48 (s, 3H), 2.00 (s, 1H), 1.50 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 163.83 (d, *J* = 270.0 Hz), 137.32 (d, *J* = 2.7 Hz), 129.95 (d, *J* = 2.4 Hz), 129.07 (d, *J* = 7.5 Hz), 126.44, 102.62 (d, *J* = 7.5 Hz), 70.89 (d, *J* = 29.0 Hz), 27.56, 15.73. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -115.69.

HRMS (ESI) calcd for $C_{12}H_{15}FNaOS$ ($M+Na^+$): 249.0720; found: 249.0727.





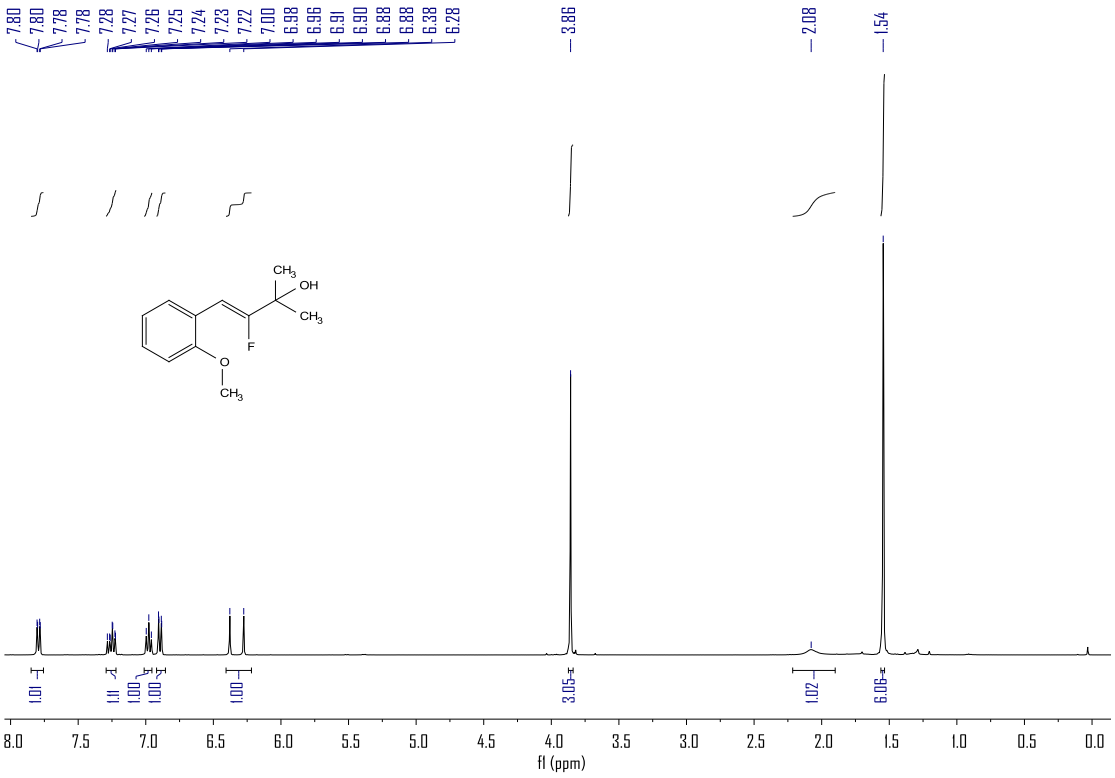


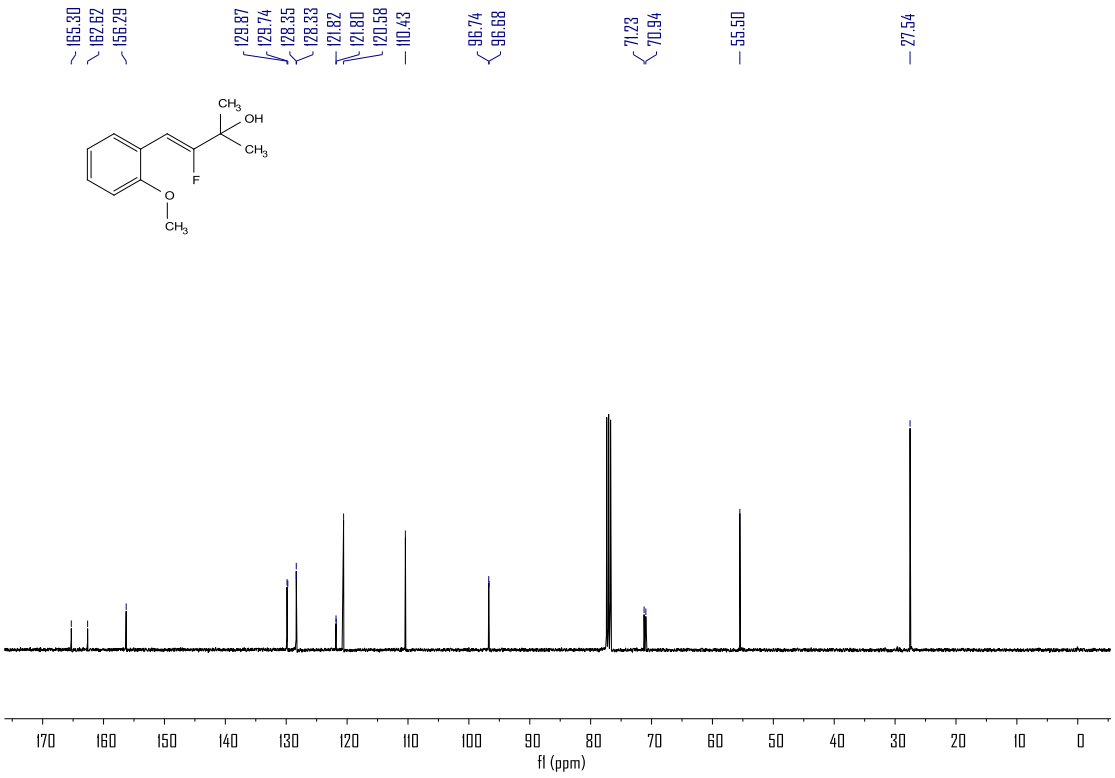


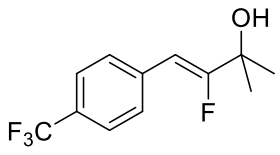
(Z)-3-fluoro-4-(2-methoxyphenyl)-2-methylbut-3-en-2-ol

Following the general procedure (**product 12**, **pale-yellow liquid, 31.5 mg, 75%,** Z/E > 30:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (10:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.79 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.31 – 7.18 (m, 1H), 6.98 (t, *J* = 7.6 Hz, 1H), 6.89 (dd, *J* = 8.3, 1.1 Hz, 1H), 6.33 (d, *J* = 41.2 Hz, 1H), 3.86 (s, 3H), 2.08 (s, 1H), 1.54 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 163.96 (d, *J* = 269.8 Hz), 156.29, 129.80 (d, *J* = 12.8 Hz), 128.34 (d, *J* = 1.8 Hz), 121.81 (d, *J* = 2.6 Hz), 120.58, 110.43, 96.71 (d, *J* = 6.0 Hz), 71.08 (d, *J* = 29.0 Hz), 55.50, 27.54. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -117.50.

HRMS (ESI) calcd for $C_{12}H_{15}FNaO_2$ ($M+Na^+$): 233.0948; found: 233.0956.



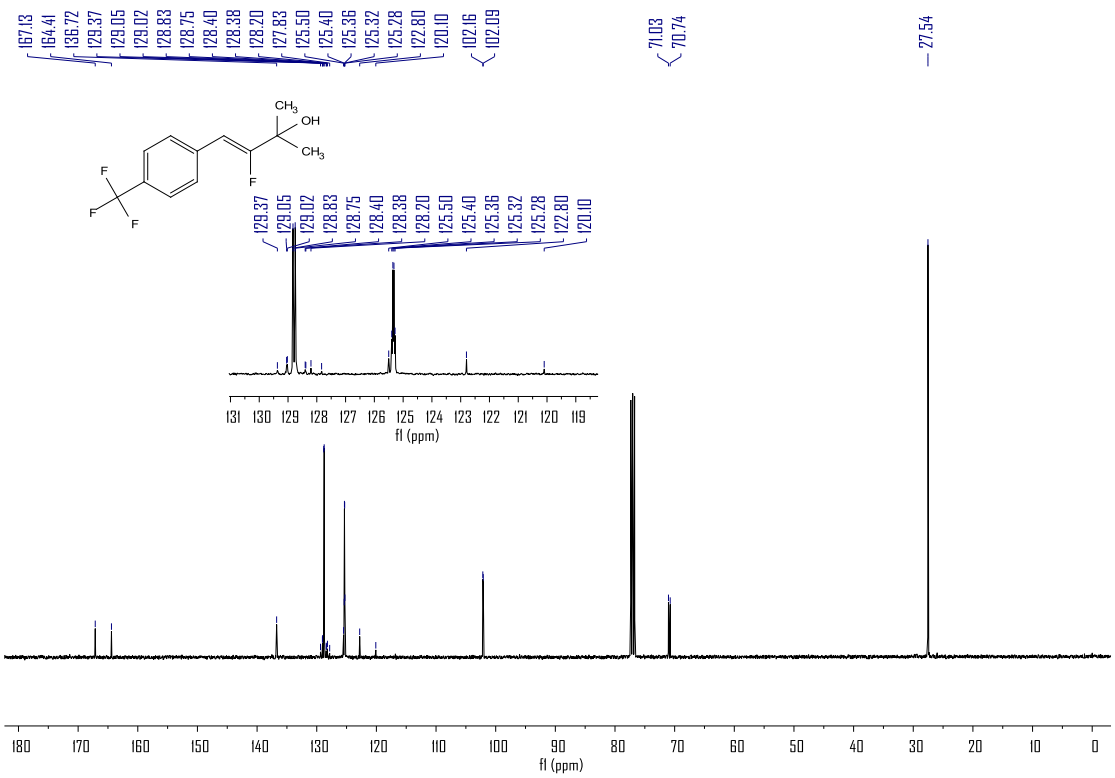


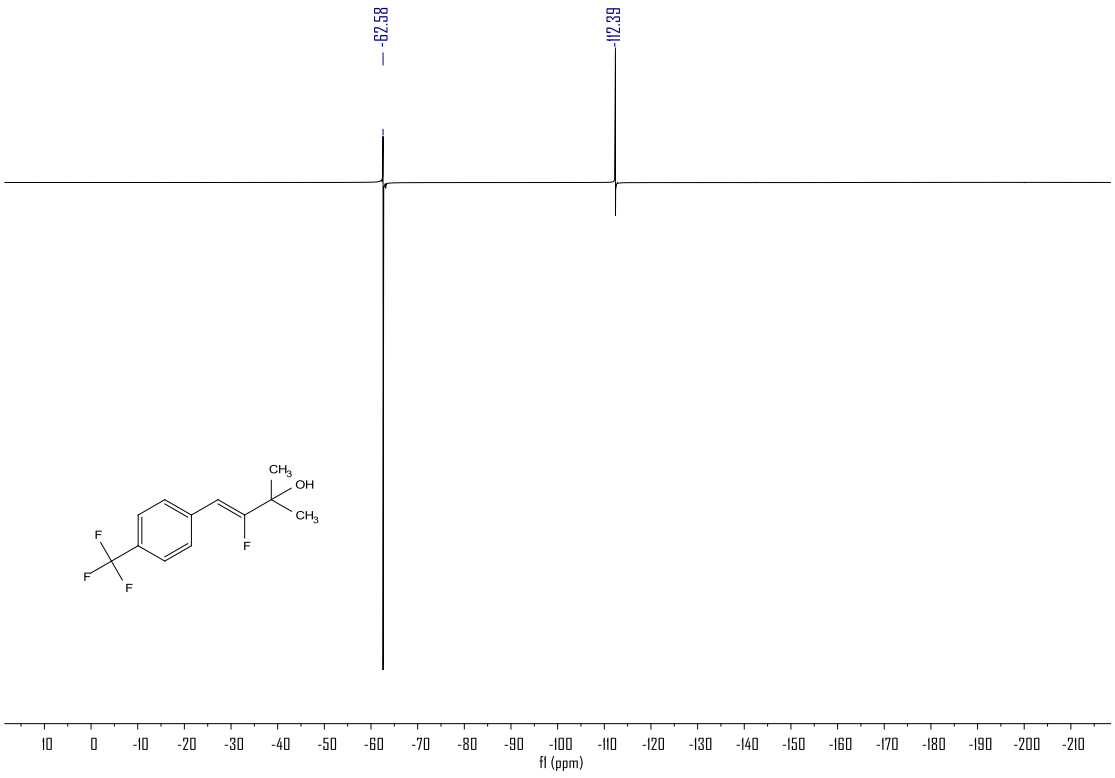


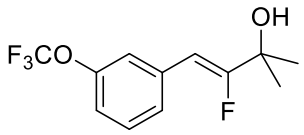
(Z)-3-fluoro-2-methyl-4-(4-(trifluoromethyl)phenyl)but-3-en-2-ol

Following the general procedure (**product 13**, **pale-yellow liquid, 33.2 mg, 67%,** Z/E > 30:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (10:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.61 – 7.54 (m, 4H), 5.97 (d, *J* = 39.2 Hz, 1H), 2.06 (s, 1H), 1.52 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.77 (d, *J* = 273.7 Hz), 136.72, 128.79 (d, *J* = 7.7 Hz), 128.71 (qd, J = 64.7, 2.4 Hz) 125.34 (q, *J* = 3.9 Hz), 124.15 (q, J = 271.9 Hz), 102.12 (d, *J* = 6.9 Hz), 70.89 (d, *J* = 29.2 Hz), 27.54. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.58, -112.39.

HRMS (ESI) calcd for $C_{12}H_{12}F_4NaO$ ($M+Na^+$): 271.0716; found: 271.0725.



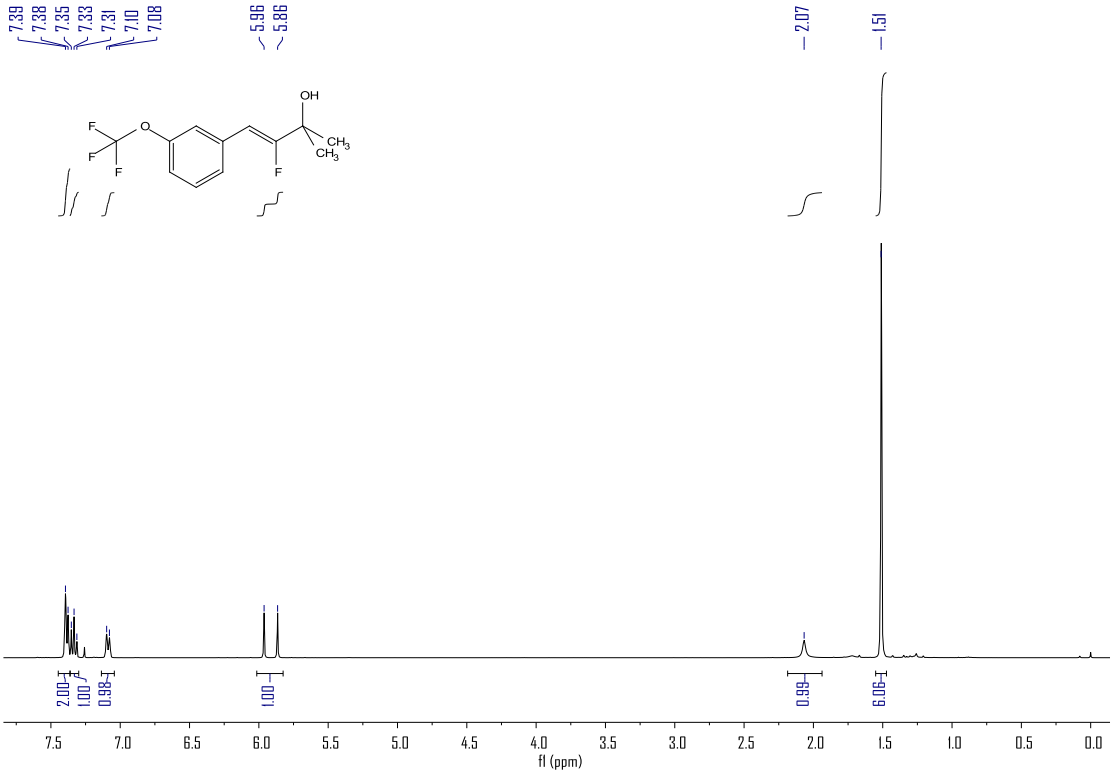


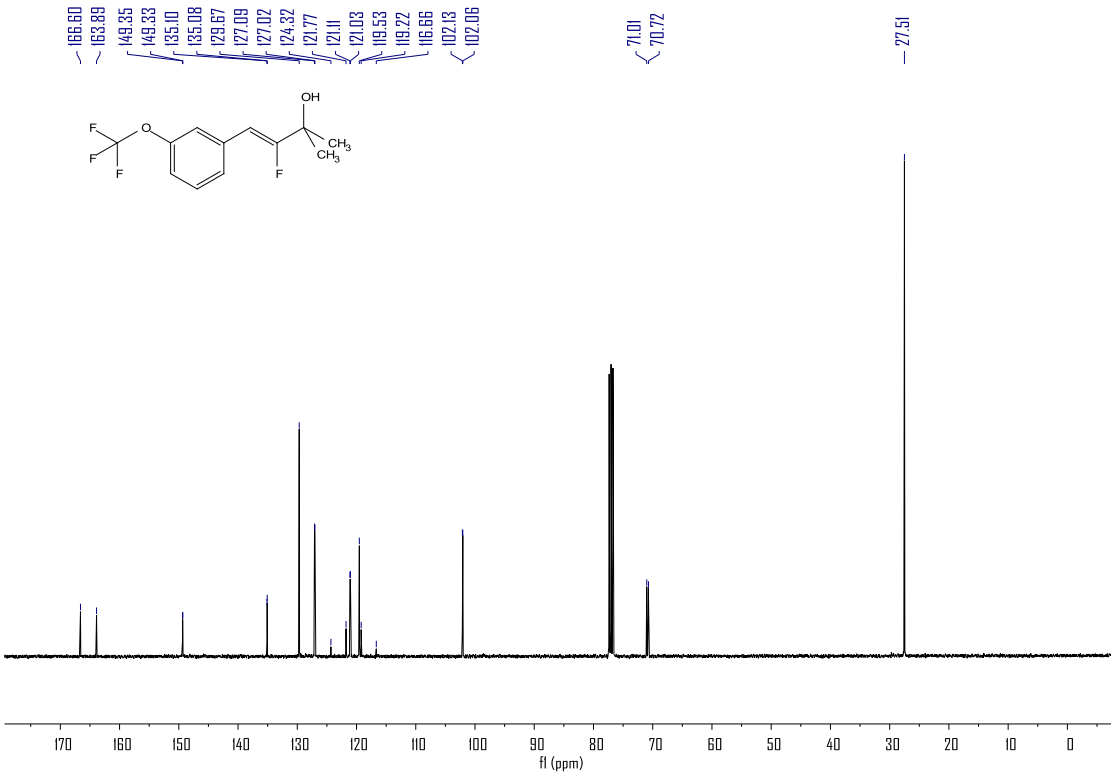


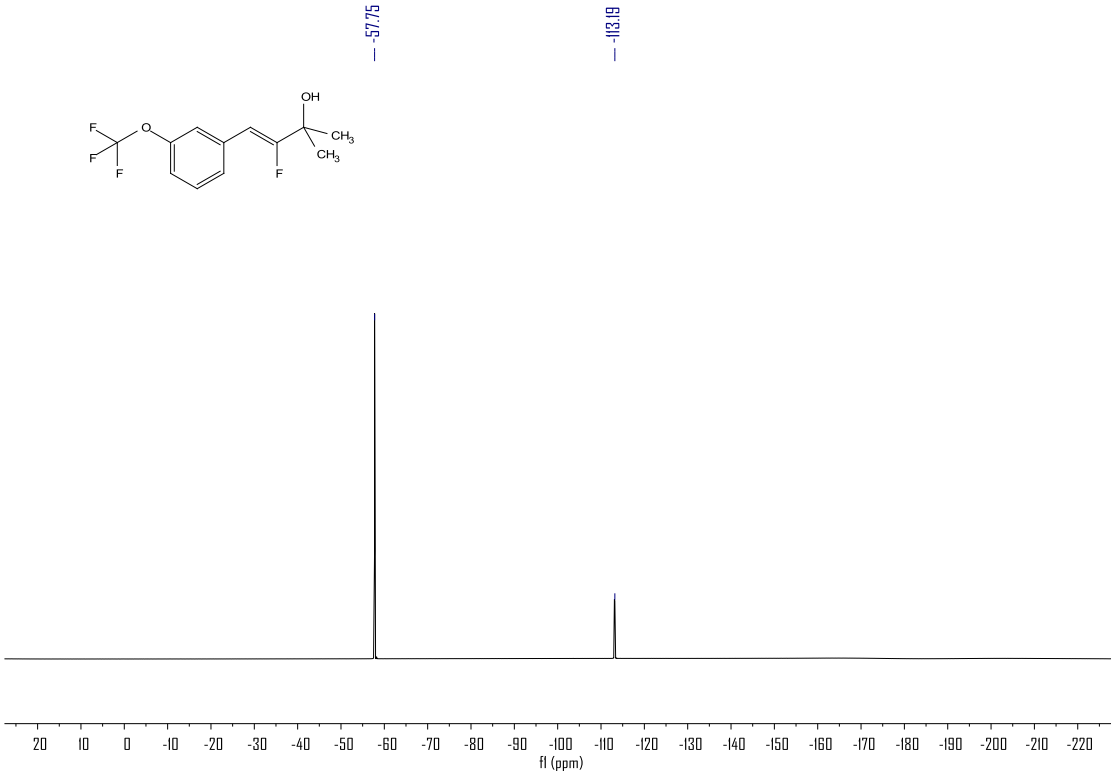
(Z)-3-fluoro-2-methyl-4-(3-(trifluoromethoxy)phenyl)but-3-en-2-ol

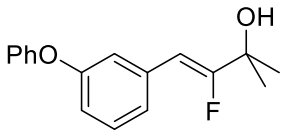
Following the general procedure (**product 14**, **pale-yellow liquid, 36.0 mg, 68%,** Z/E > 30:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (10:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.39 (d, *J* = 7.5 Hz, 2H), 7.33 (t, *J* = 8.0 Hz, 1H), 7.09 (d, *J* = 8.0 Hz, 1H), 5.91 (d, *J* = 39.0 Hz, 1H), 2.07 (s, 1H), 1.51 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.24 (d, *J* = 272.8 Hz), 149.34 (d, *J* = 2.0 Hz), 135.09 (d, *J* = 2.1 Hz), 129.67, 127.06 (d, *J* = 7.0 Hz), 120.49 (q, *J* = 257.0 Hz), 121.07 (d, *J* = 8.6 Hz), 119.53, 102.09 (d, *J* = 6.9 Hz), 70.86 (d, *J* = 29.0 Hz), 27.51. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -57.75, -113.19.

HRMS (ESI) calcd for $C_{12}H_{12}F_4NaO_2$ ($M+Na^+$): 287.0666; found: 287.0661.





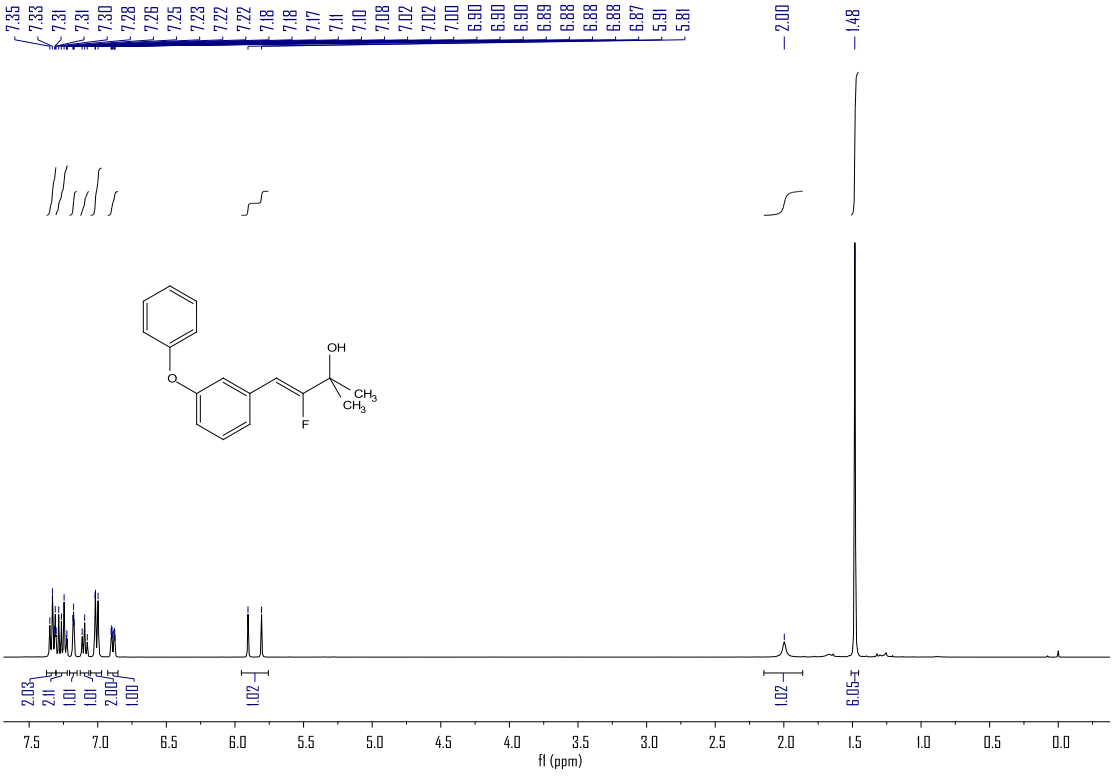


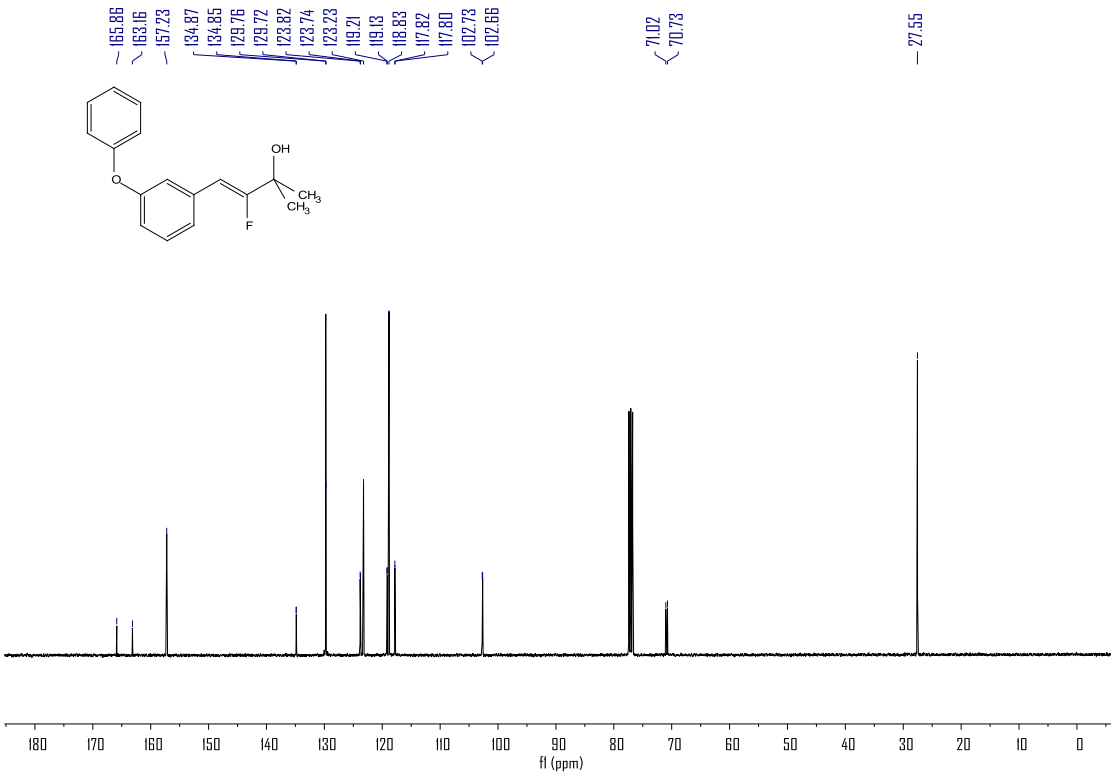


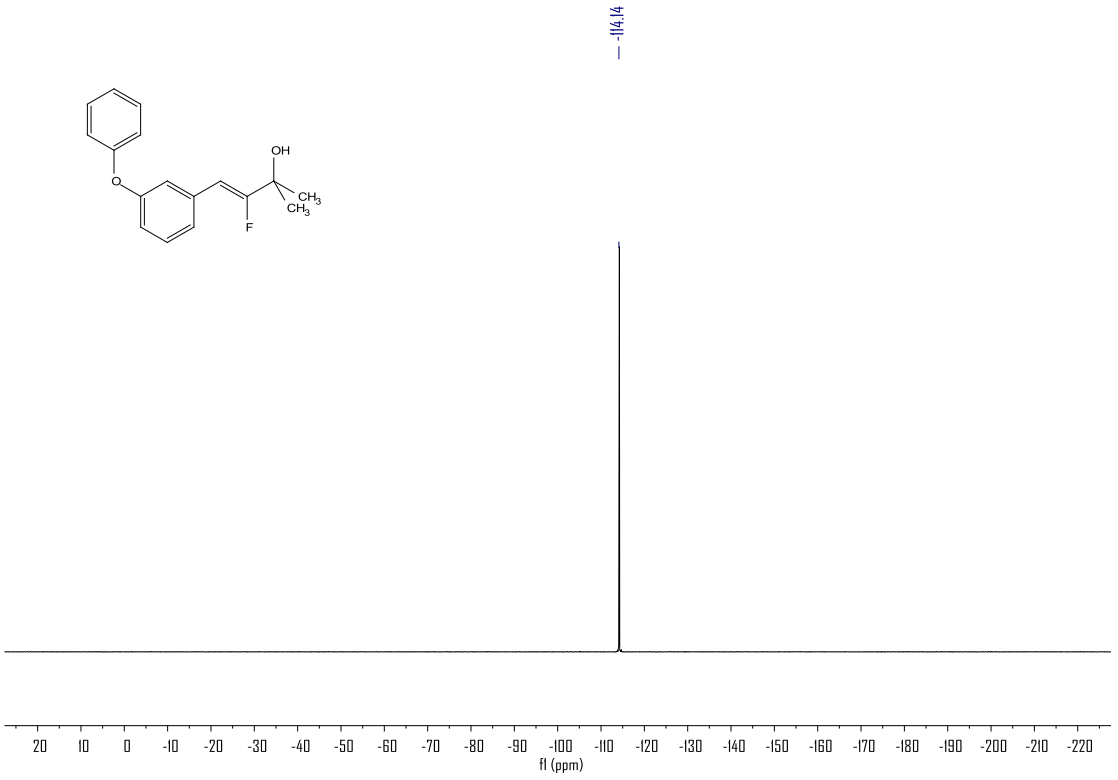
(Z)-3-fluoro-2-methyl-4-(3-phenoxyphenyl)but-3-en-2-ol

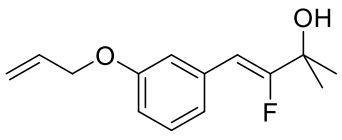
Following the general procedure (**product 15**, **pale-yellow liquid, 35.1 mg, 65%,** Z/E > 30:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (10:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.36 – 7.30 (m, 2H), 7.29 – 7.22 (m, 2H), 7.18 (t, *J* = 1.9 Hz, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 7.01 (d, *J* = 7.9 Hz, 2H), 6.89 (ddd, *J* = 8.0, 2.5, 1.3 Hz, 1H), 5.86 (d, *J* = 39.5 Hz, 1H), 2.00 (s, 1H), 1.48 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 164.51 (d, *J* = 271.7 Hz), 157.23, 134.86 (d, *J* = 2.3 Hz), 129.76, 129.72, 123.78 (d, *J* = 7.4 Hz), 123.23, 119.17 (d, *J* = 7.7 Hz), 118.83, 117.81 (d, *J* = 2.2 Hz), 102.69 (d, *J* = 7.1 Hz), 70.87 (d, *J* = 29.0 Hz), 27.55. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -114.14.

HRMS (ESI) calcd for $C_{17}H_{17}FNaO_2$ ($M+Na^+$): 295.1105; found: 295.1112.





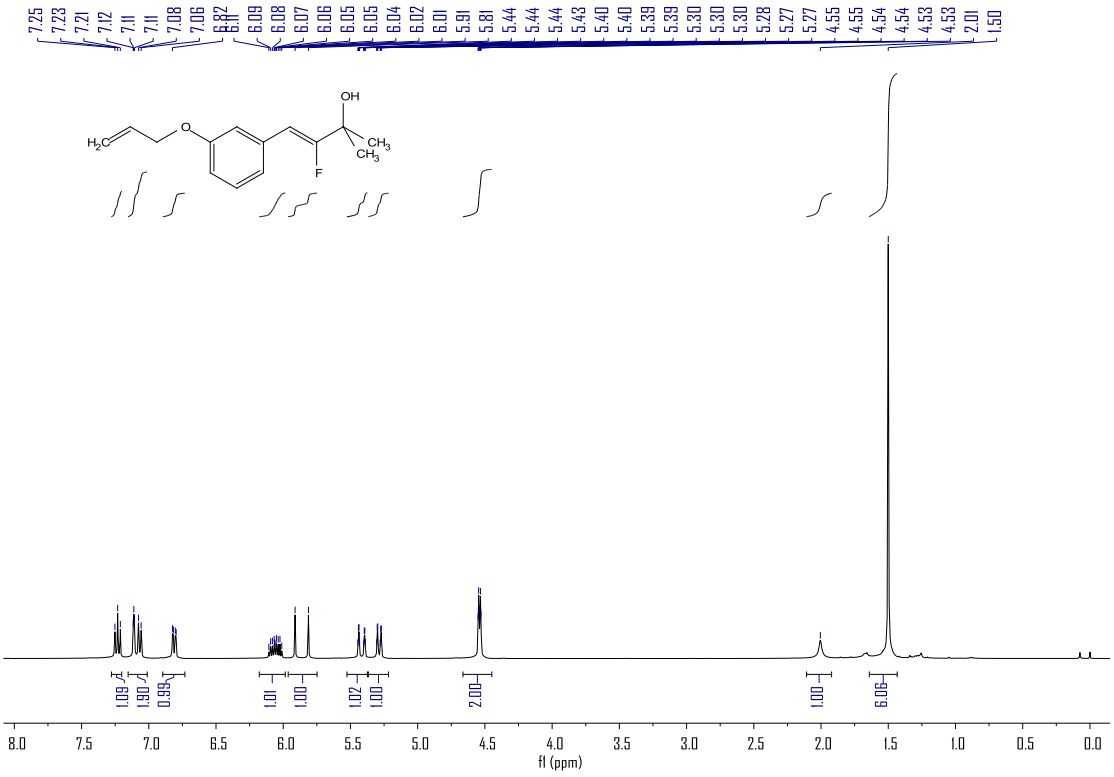


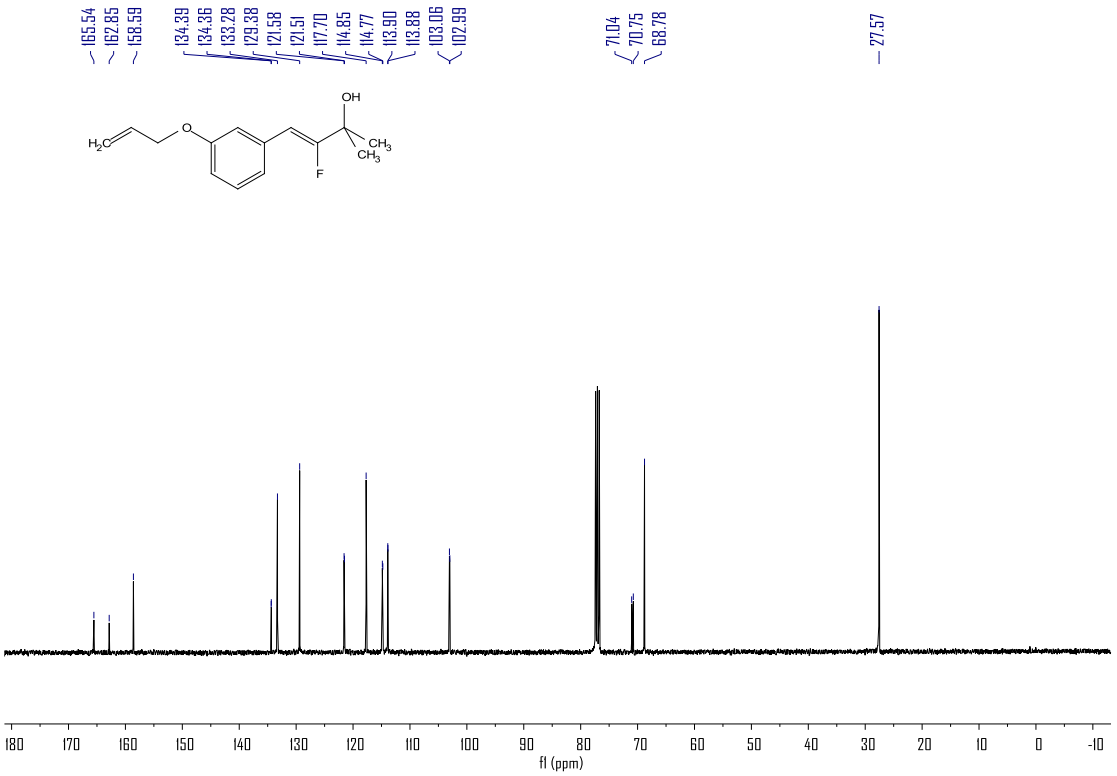


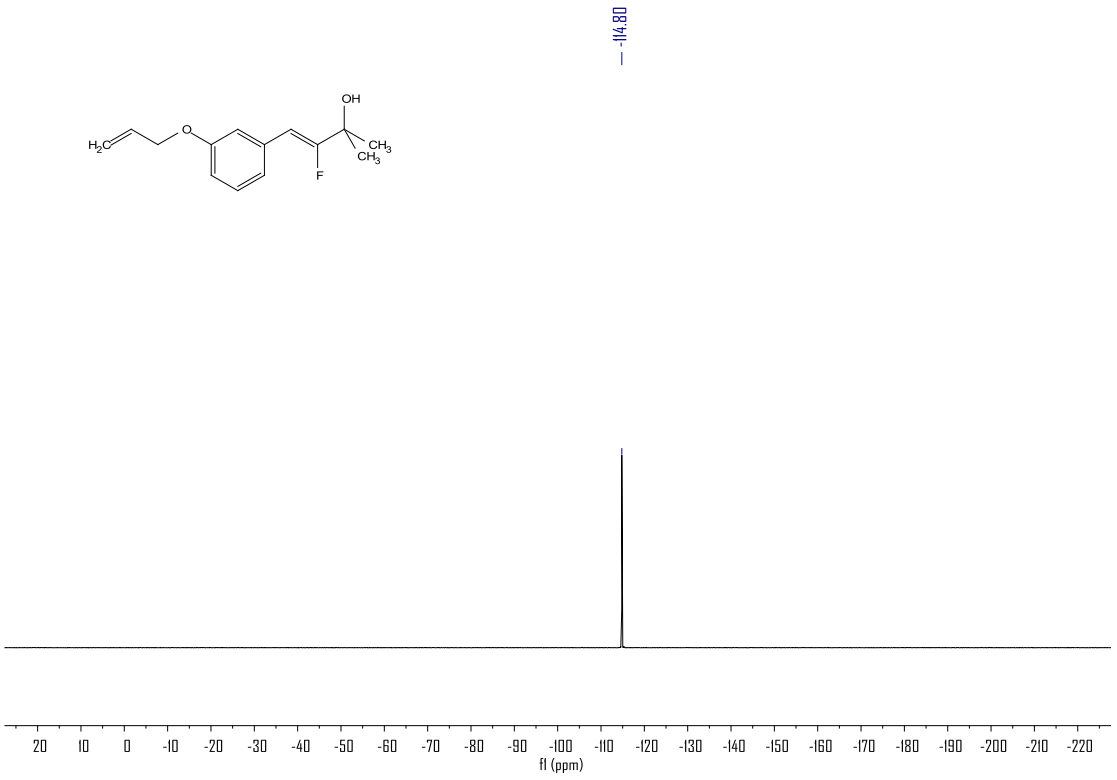
(Z)-4-(3-(allyloxy)phenyl)-3-fluoro-2-methylbut-3-en-2-ol

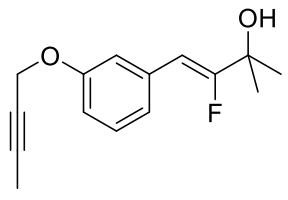
Following the general procedure (**product 16**, **pale-yellow liquid, 27.5 mg, 58%,** Z/E > 30:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (10:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.23 (t, *J* = 8.1 Hz, 1H), 7.15 – 6.97 (m, 2H), 6.81 (dd, *J* = 8.2, 2.6 Hz, 1H), 6.06 (ddt, *J* = 17.4, 10.5, 5.3 Hz, 1H), 5.86 (d, *J* = 39.8 Hz, 1H), 5.42 (dq, *J* = 17.2, 1.6 Hz, 1H), 5.29 (dd, *J* = 10.5, 1.6 Hz, 1H), 4.54 (dd, *J* = 5.4, 1.6 Hz, 2H), 2.01 (s, 1H), 1.50 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 164.20 (d, *J* = 270.9 Hz), 158.59, 134.38 (d, *J* = 2.3 Hz), 133.28, 129.38, 121.54 (d, *J* = 6.9 Hz), 117.70, 114.81 (d, *J* = 8.2 Hz), 113.89 (d, *J* = 2.1 Hz), 103.03 (d, *J* = 7.0 Hz), 70.90 (d, *J* = 29.1 Hz), 68.78, 27.57. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -114.80.

HRMS (ESI) calcd for $C_{14}H_{17}FNaO_2$ ($M+Na^+$): 259.1105; found: 259.1101.





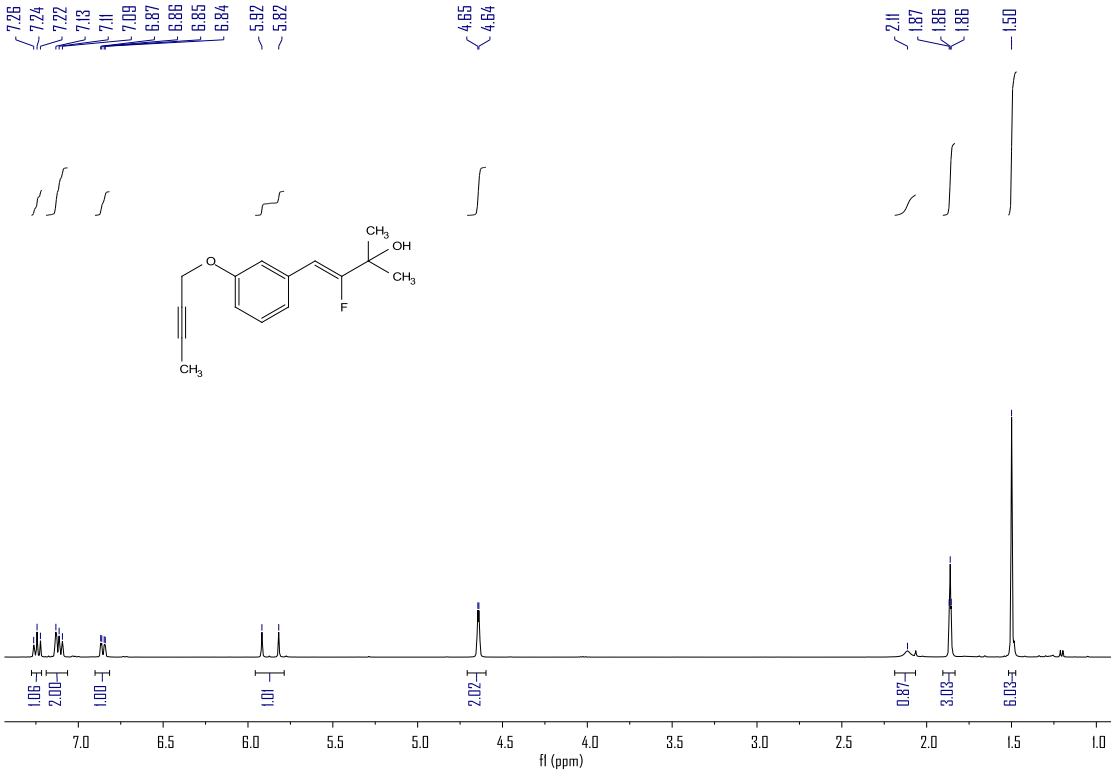


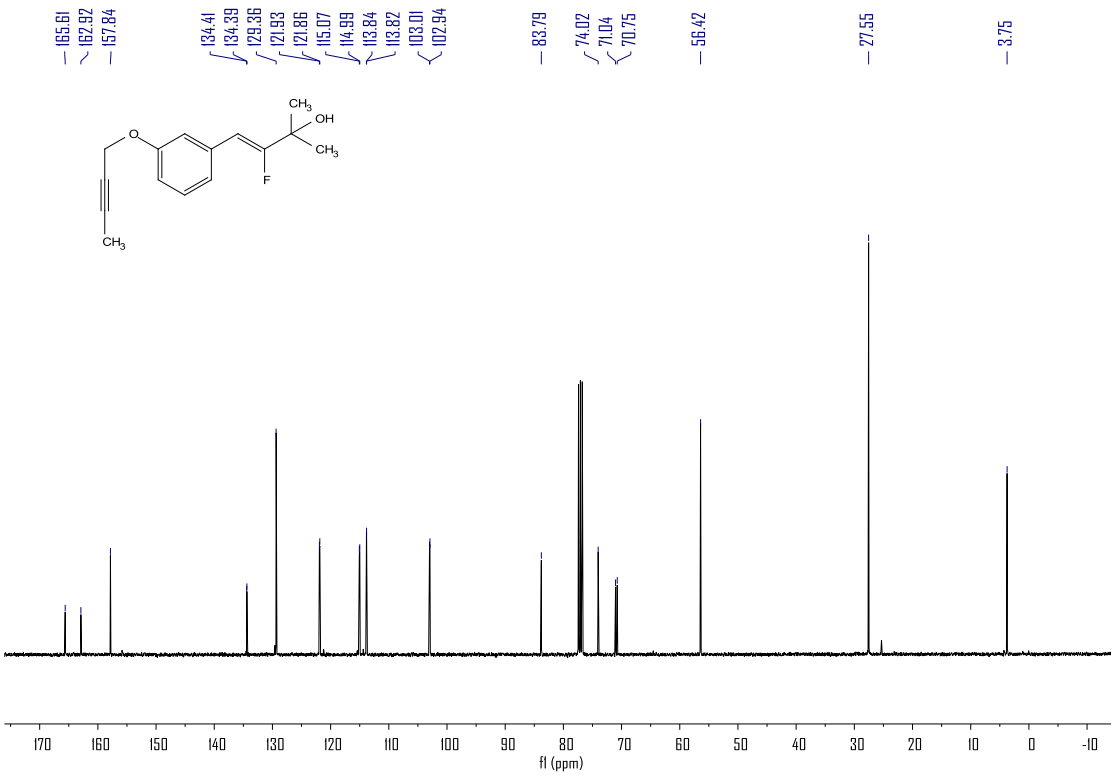


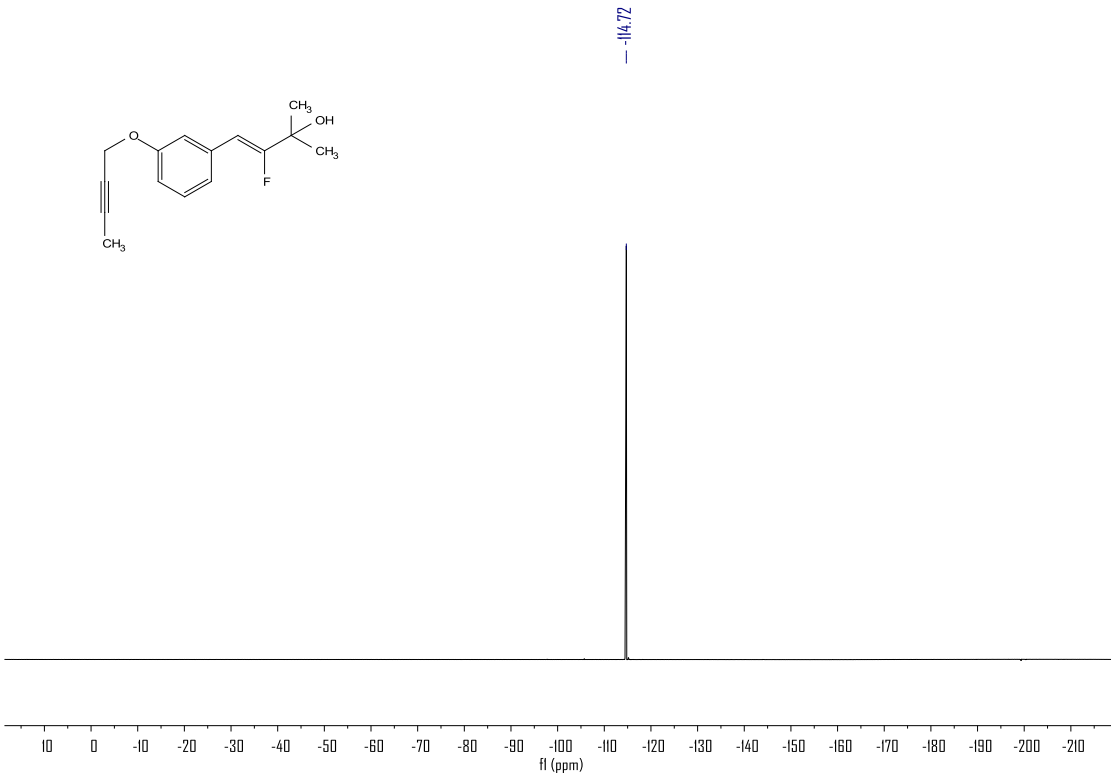
(Z)-4-(3-(but-2-yn-1-yloxy)phenyl)-3-fluoro-2-methylbut-3-en-2-ol

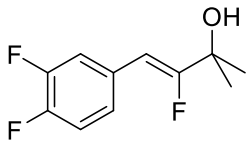
Following the general procedure (**product 17**, **pale-yellow liquid, 32.0 mg, 65%,** Z/E > 30:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (10:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.24 (t, *J* = 7.9 Hz, 1H), 7.14 – 7.07 (m, 2H), 6.85 (dd, *J* = 8.3, 2.5 Hz, 1H), 5.87 (d, *J* = 39.7 Hz, 1H), 4.64 (d, *J* = 2.4 Hz, 2H), 2.11 (s, 1H), 1.86 (s, 3H), 1.50 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 164.27 (d, *J* = 271.1 Hz), 157.84, 134.40 (d, *J* = 2.2 Hz), 129.36, 121.89 (d, *J* = 7.2 Hz), 115.03 (d, *J* = 7.9 Hz), 113.83 (d, *J* = 2.1 Hz), 102.97 (d, *J* = 7.1 Hz), 83.79, 74.02, 70.89 (d, *J* = 29.1 Hz), 56.42, 27.55, 3.75. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -114.72.

HRMS (ESI) calcd for $C_{15}H_{17}FNaO_2$ ($M+Na^+$): 271.1105; found: 271.1109.





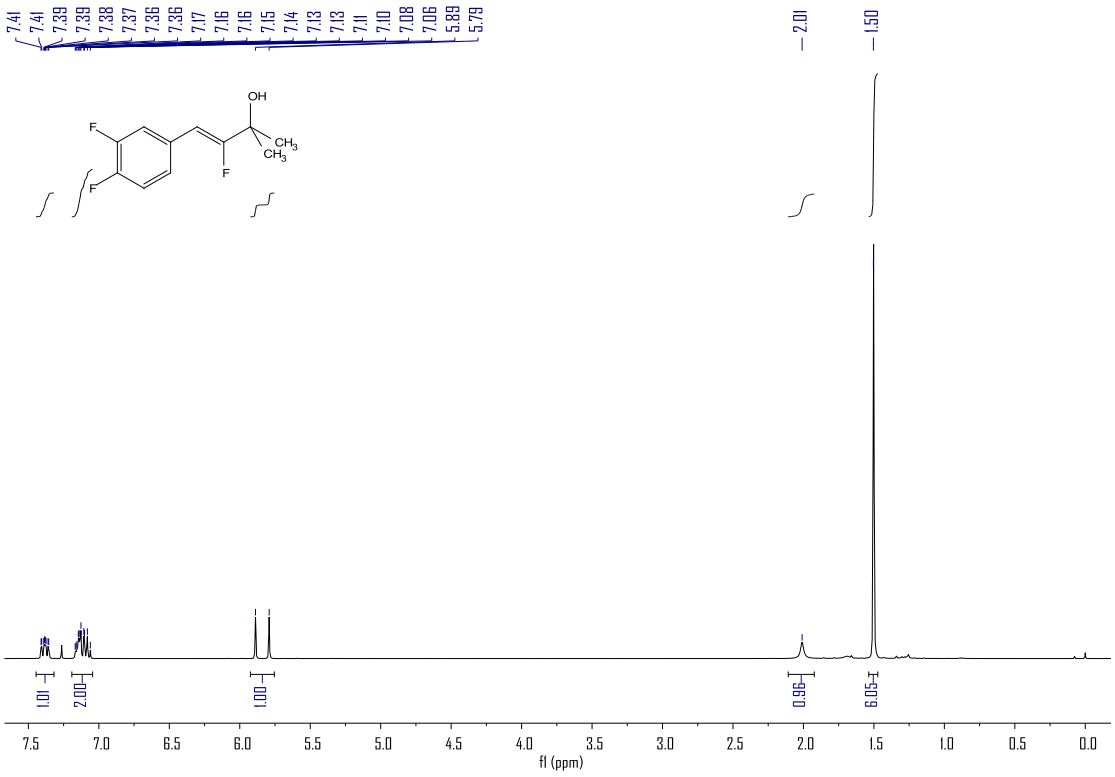


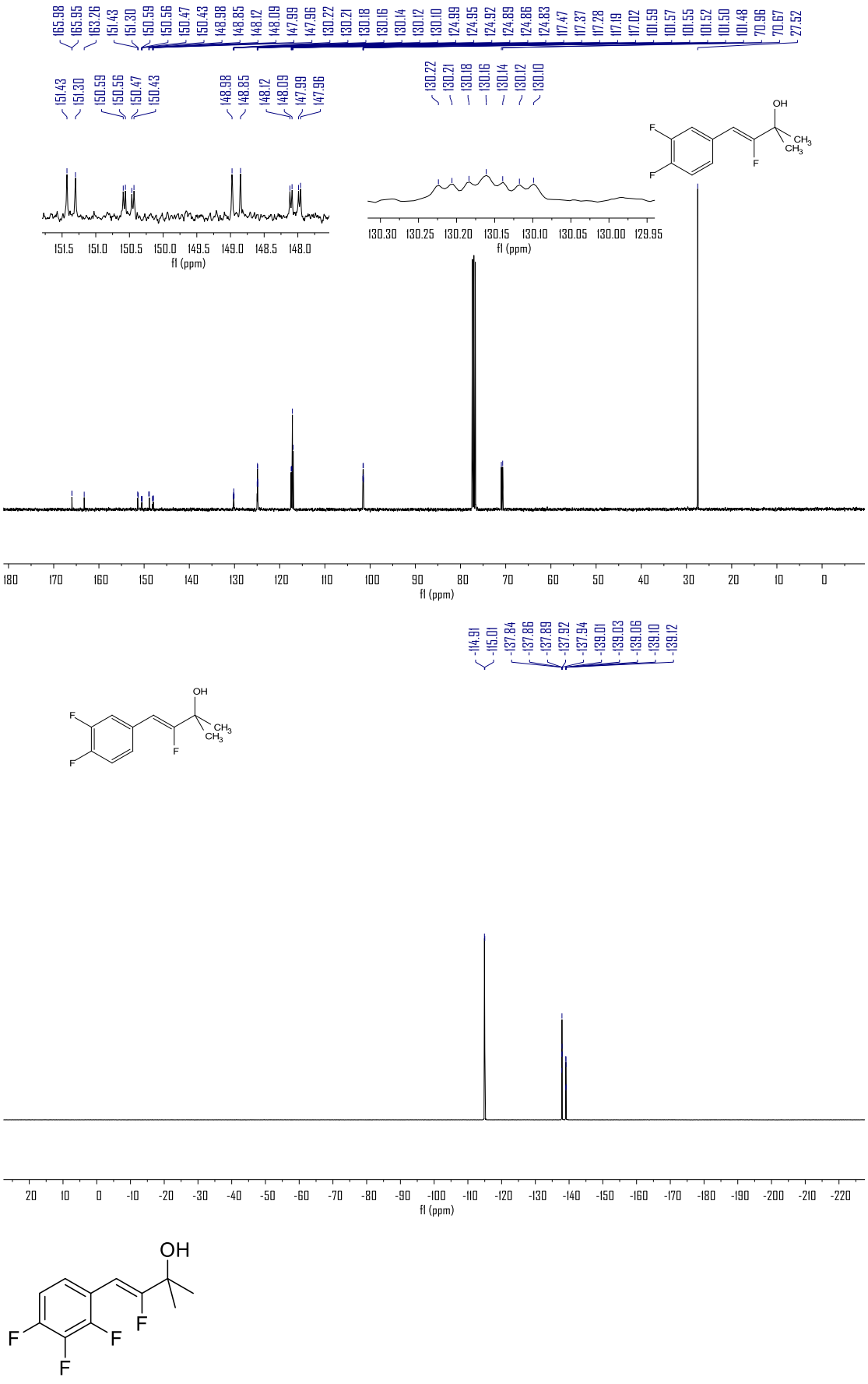


(Z)-4-(3,4-difluorophenyl)-3-fluoro-2-methylbut-3-en-2-ol

Following the general procedure (**product 18**, **pale-yellow liquid, 28.0 mg, 65%,** Z/E > 30:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (10:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.38 (ddd, *J* = 12.1, 7.7, 2.0 Hz, 1H), 7.18 – 7.01 (m, 2H), 5.84 (d, *J* = 38.8 Hz, 1H), 2.01 (s, 1H), 1.50 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 164.61 (dd, *J* = 271.5, 2.3 Hz), 150.14 (dd, *J* = 246.6, 12.7 Hz), 149.28 (ddd, J = 248.8, 12.7, 3.2 Hz), 130.16 (ddd, *J* = 6.2, 4.1, 1.8 Hz), 124.91 (td, *J* = 6.4, 3.5 Hz), 117.32 (dd, *J* = 18.3, 18.2 Hz), 117.11 (d, *J* = 17.3 Hz), 101.53 (d, *J* = 7.2 Hz), 70.81 (d, *J* = 29.1 Hz), 27.52. **^{19}F NMR** (No decoupling) (376 MHz, Chloroform-*d*) δ -114.96 (d, *J* = 38.4 Hz), -137.89 (dt, *J* = 20.5, 9.6 Hz), -139.06 (dt, *J* = 20.7, 9.2 Hz).

HRMS (ESI) calcd for $C_{11}H_{11}F_3NaO$ ($M+Na^+$): 239.0654; found: 239.0656.

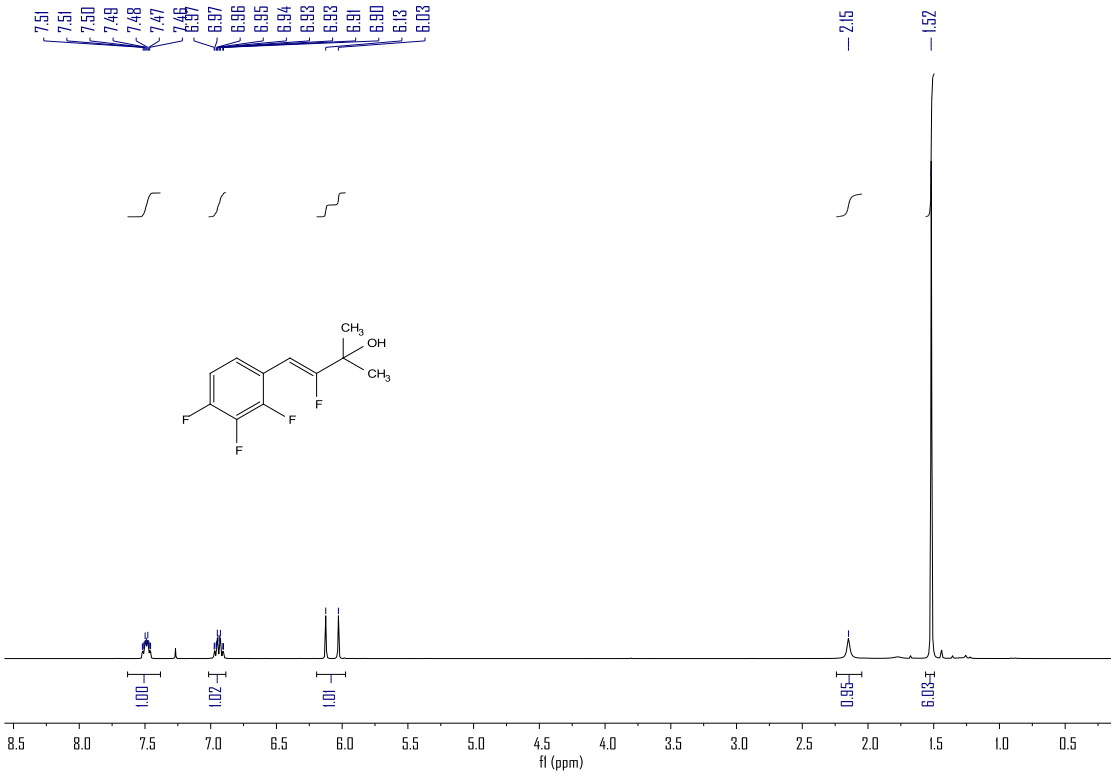


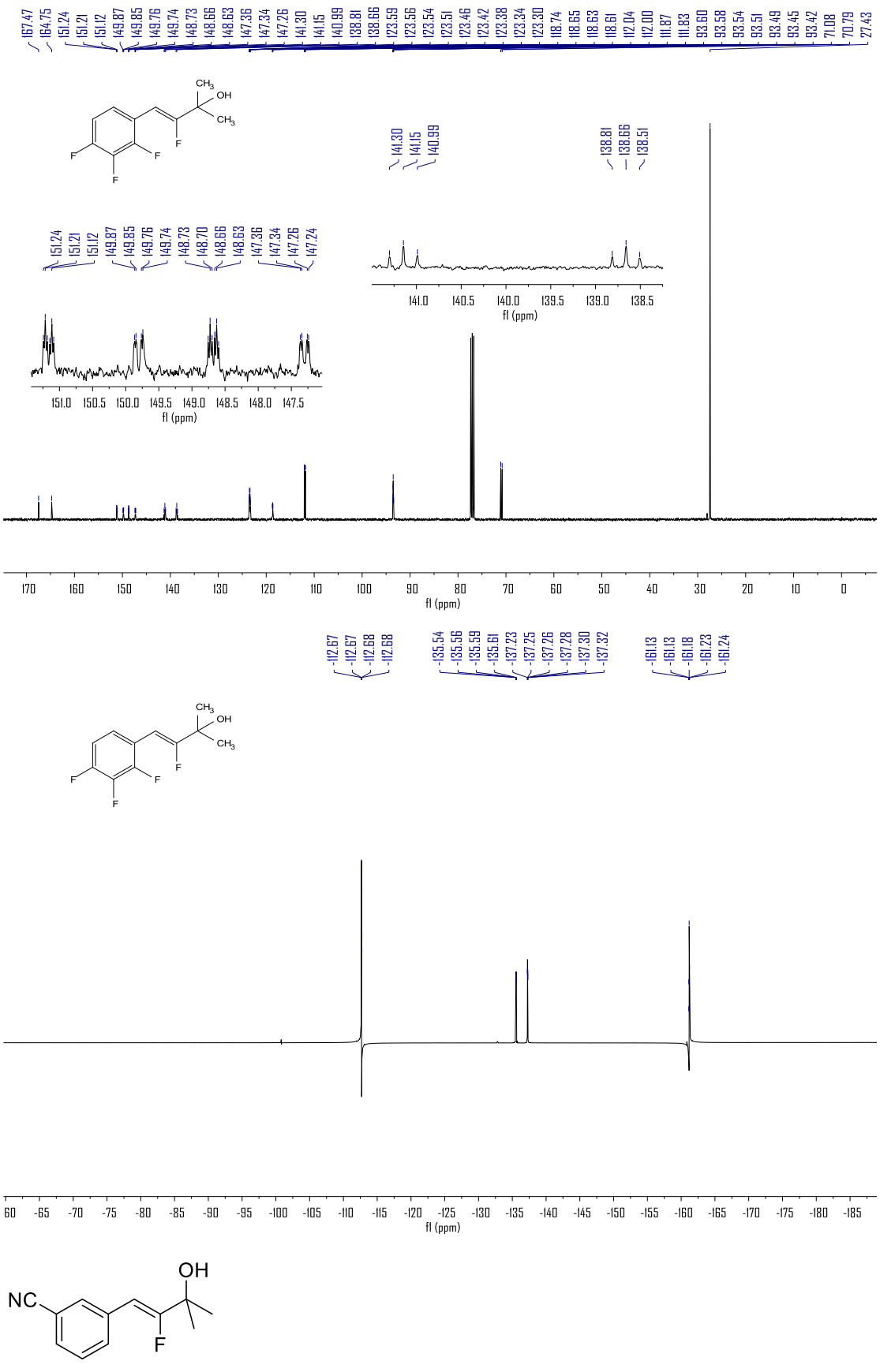


(Z)-3-fluoro-2-methyl-4-(2,3,4-trifluorophenyl)but-3-en-2-ol

Following the general procedure (**product 19**, **pale-yellow liquid, 24.7 mg, 53%,** Z/E > 30:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (10:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.57 – 7.41 (m, 1H), 7.01 – 6.84 (m, 1H), 6.08 (d, *J* = 38.6 Hz, 1H), 2.15 (s, 1H), 1.52 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 166.11 (d, *J* = 273.6 Hz), 149.92 (ddt, *J* = 250.6, 9.9, 2.9 Hz), 148.55 (ddd, J = 252.0, 10.3, 2.1 Hz), 139.90 (dt, *J* = 249.8, 15.5 Hz), 123.46 (ddt, *J* = 15.9, 7.7, 3.6 Hz), 118.69 (ddd, *J* = 9.8, 3.9, 2.4 Hz), 111.94 (dd, *J* = 17.3, 4.0 Hz), 93.51 (ddd, *J* = 9.2, 6.3, 2.6 Hz), 70.94 (d, *J* = 28.6 Hz), 27.43. **^{19}F NMR** (No decoupling) (376 MHz, Chloroform-*d*) δ -111.03 – -113.50 (m), -135.58 (dd, *J* = 20.5, 6.9 Hz), -137.27 (dt, *J* = 19.5, 5.7 Hz), -158.82 – -163.92 (m).

HRMS (ESI) calcd for $C_{11}H_{10}F_4NaO$ ($M+Na^+$): 257.0560; found: 257.0565.

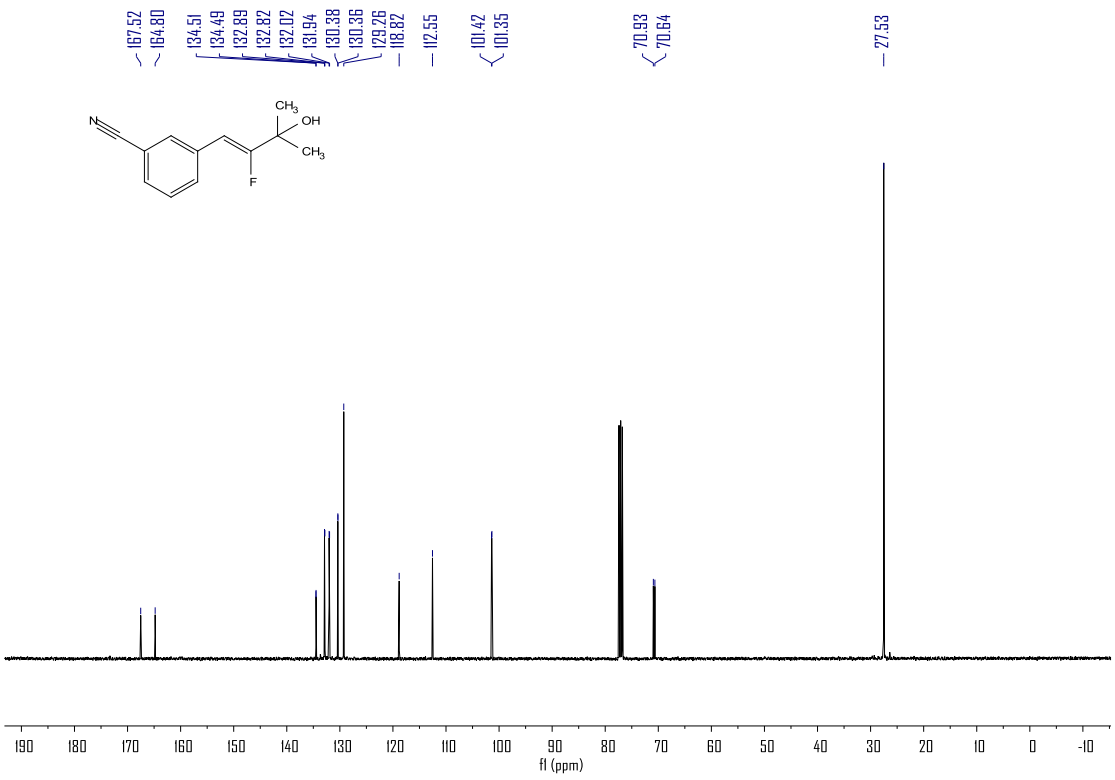


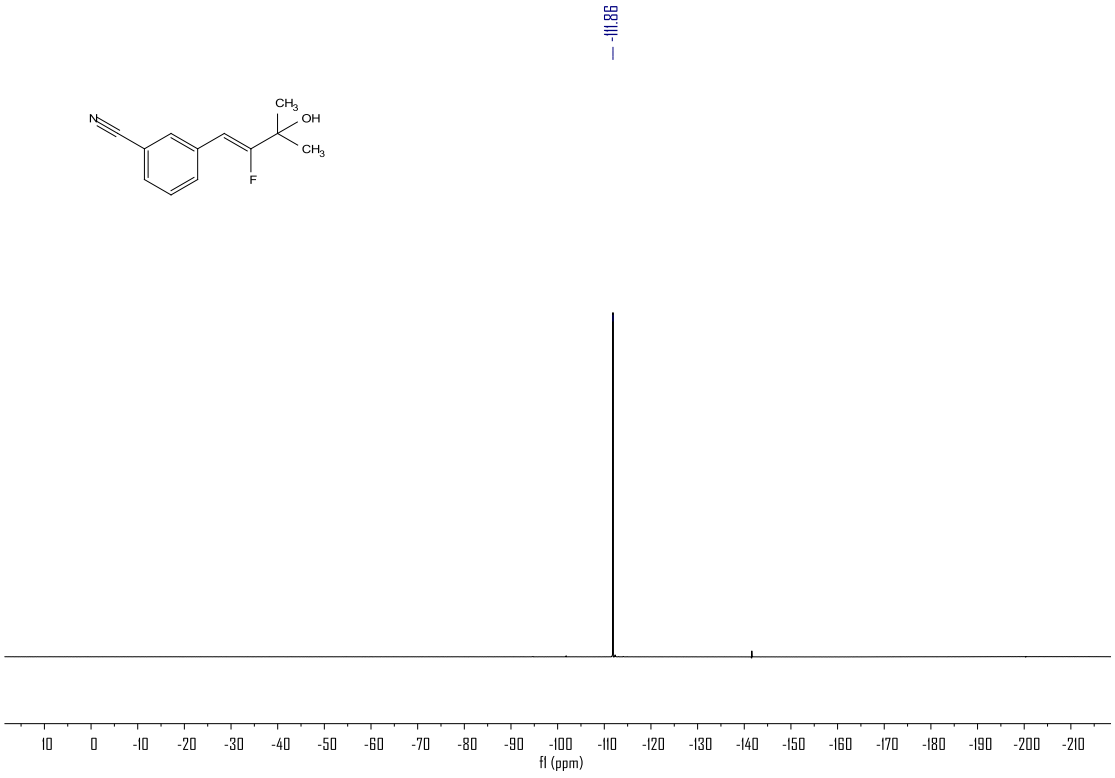


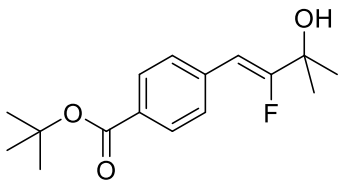
(Z)-3-(2-fluoro-3-hydroxy-3-methylbut-1-en-1-yl)benzonitrile

Following the general procedure (**product 20**, **pale-yellow liquid, 24.5 mg, 60%,** Z/E > 30:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (10:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.80 (s, 1H), 7.68 (dt, *J* = 7.9, 1.5 Hz, 1H), 7.50 (dt, *J* = 7.8, 1.4 Hz, 1H), 7.42 (t, *J* = 7.8 Hz, 1H), 5.94 (d, *J* = 38.7 Hz, 1H), 2.32 (s, 1H), 1.52 (d, *J* = 1.2 Hz, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 166.16 (d, *J* = 274.2 Hz), 134.50 (d, *J* = 2.0 Hz), 132.86 (d, *J* = 7.1 Hz), 131.98 (d, *J* = 8.4 Hz), 130.37 (d, *J* = 2.2 Hz), 129.26, 118.82, 112.55, 101.38 (d, *J* = 6.7 Hz), 70.79 (d, *J* = 29.1 Hz), 27.53. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -111.86.

HRMS (ESI) calcd for $C_{12}H_{12}FNNaO$ ($M+Na^+$): 228.0795; found: 228.0799.



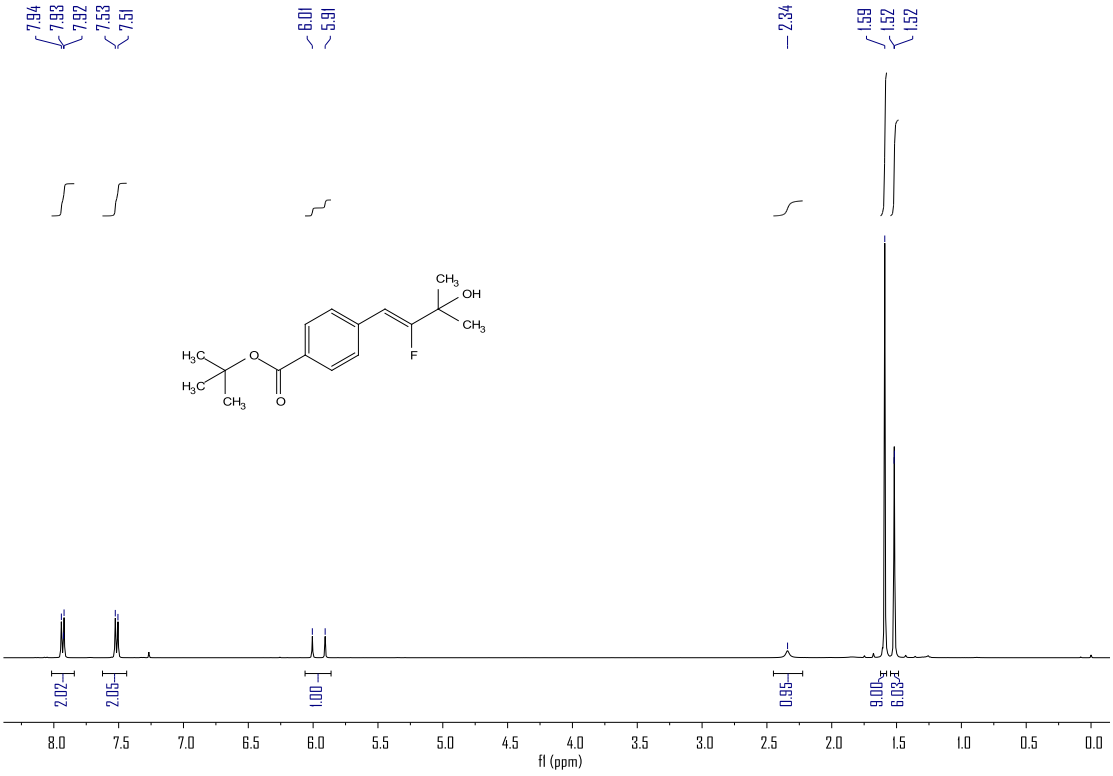


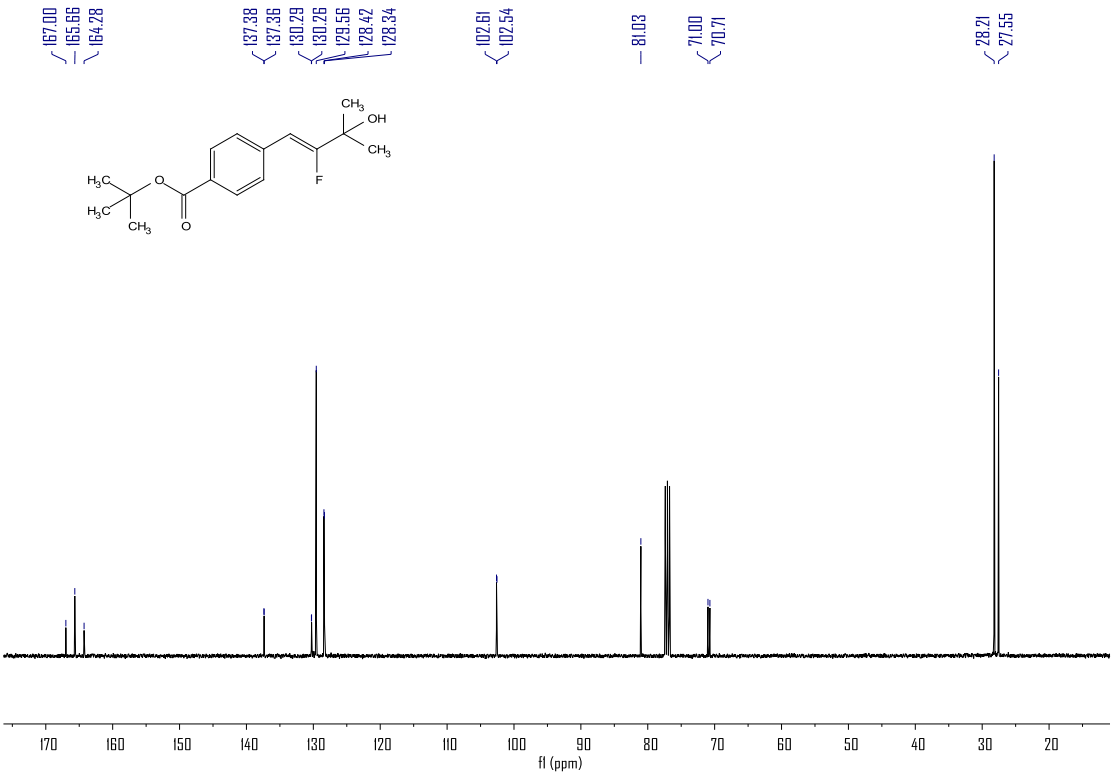


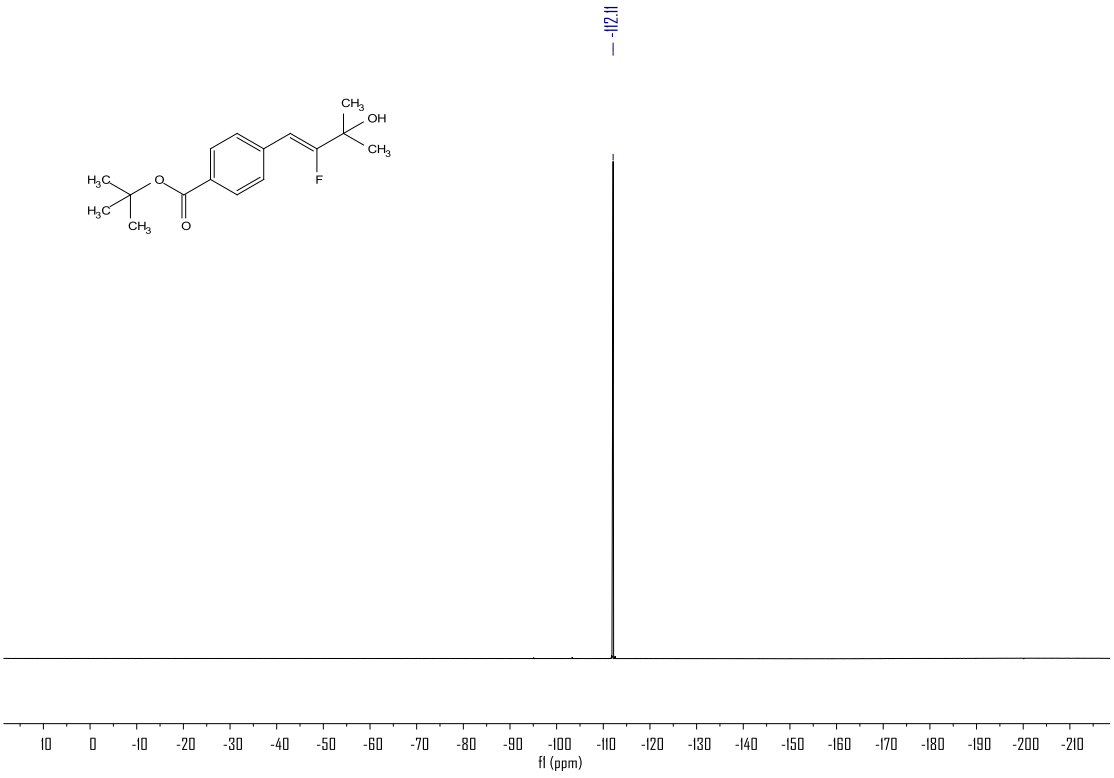
Tert-butyl-(Z)-4-(2-fluoro-3-hydroxy-3-methylbut-1-en-1-yl)benzoate

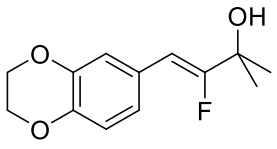
Following the general procedure (**product 21**, **pale-yellow liquid, 39.1 mg, 70%,** Z/E > 30:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (10:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 8.3 Hz, 2H), 7.52 (d, *J* = 8.2 Hz, 2H), 5.96 (d, *J* = 39.6 Hz, 1H), 2.34 (s, 1H), 1.59 (s, 9H), 1.52 (d, *J* = 1.1 Hz, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.66, 165.64 (d, *J* = 274.0 Hz), 137.37 (d, *J* = 2.5 Hz), 130.27 (d, *J* = 2.3 Hz), 129.56, 128.38 (d, *J* = 7.6 Hz), 102.58 (d, *J* = 6.9 Hz), 81.03, 70.85 (d, *J* = 29.0 Hz), 28.21, 27.55. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -112.11.

HRMS (ESI) calcd for $C_{16}H_{21}FNaO_3$ ($M+Na^+$): 303.1367; found: 303.1375.





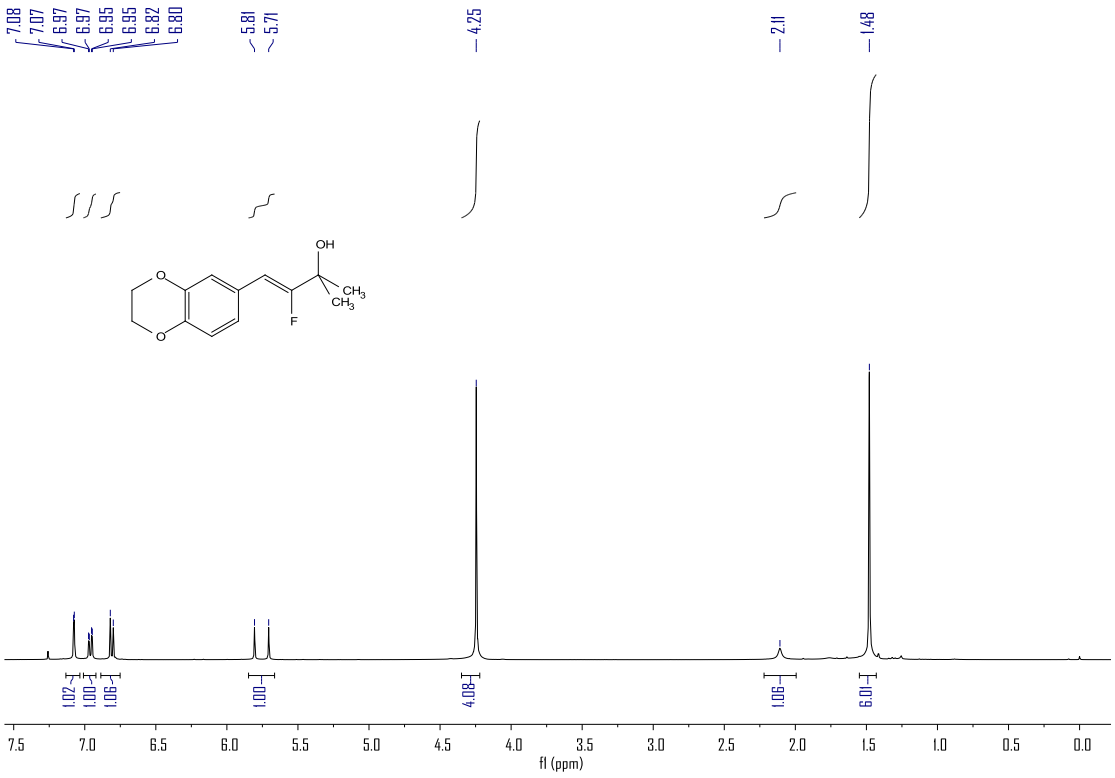


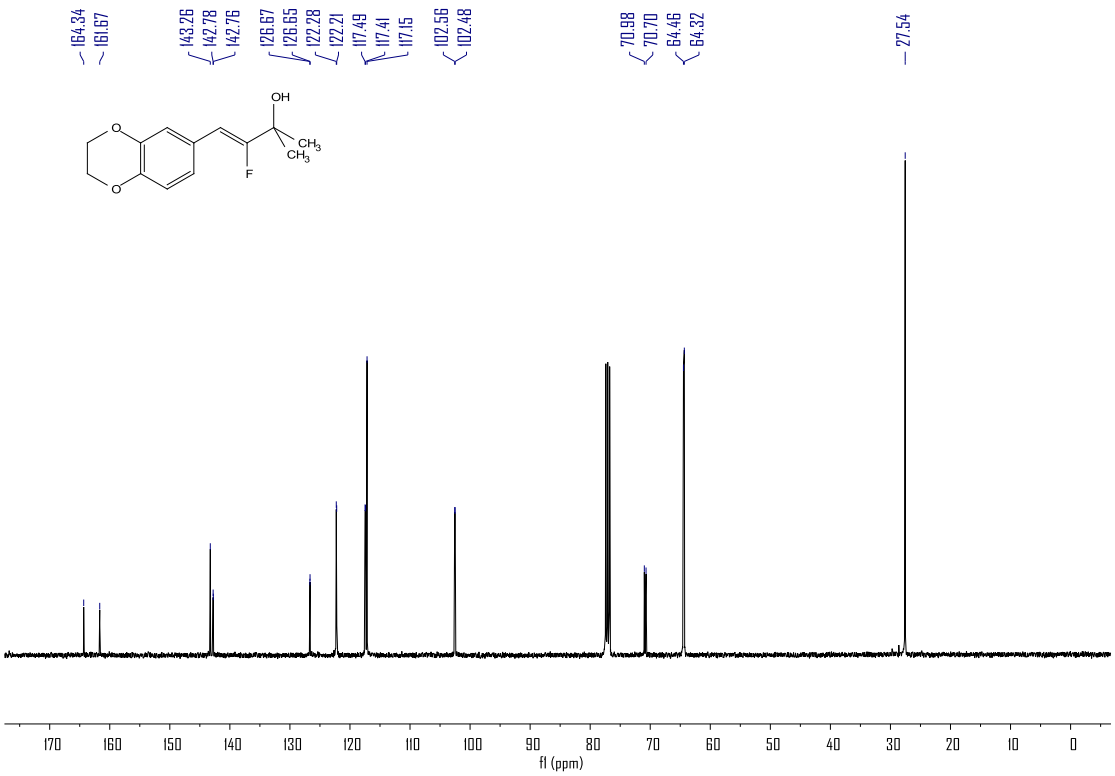


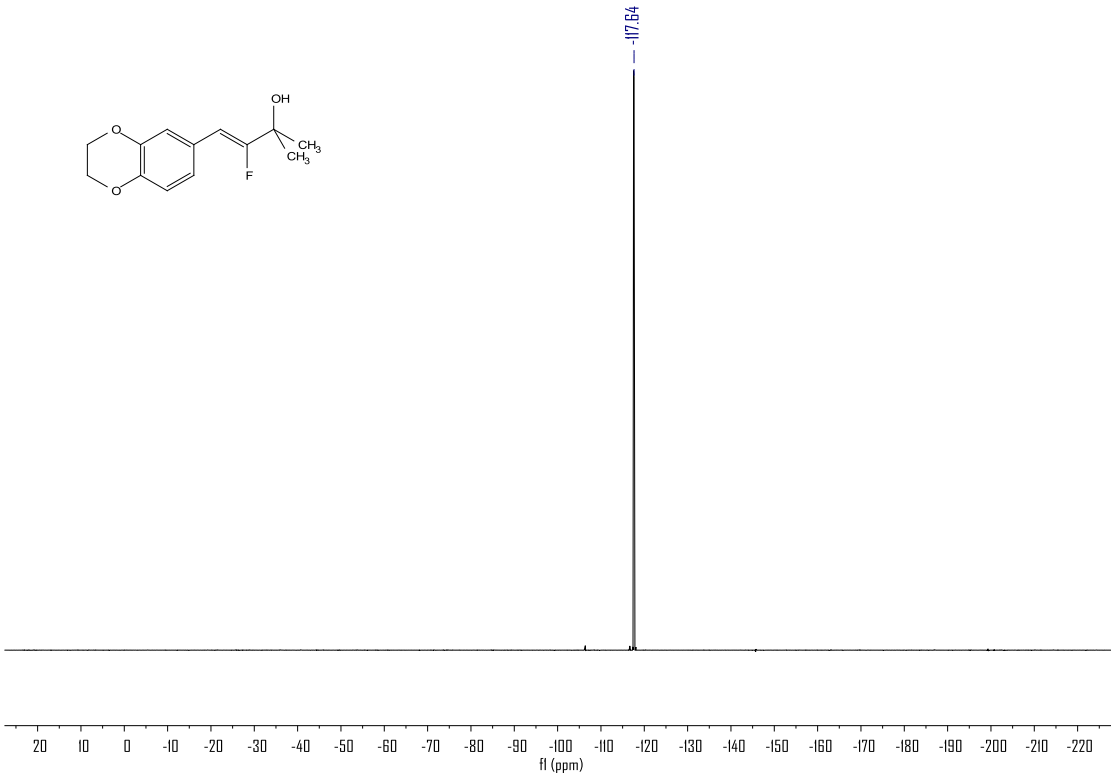
(Z)-4-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)-3-fluoro-2-methylbut-3-en-2-ol

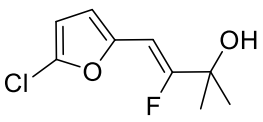
Following the general procedure (**product 22**, **pale-yellow liquid, 28.0 mg, 59%,** Z/E > 30:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (8:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.08 (d, *J* = 2.1 Hz, 1H), 6.96 (dd, *J* = 8.4, 2.1 Hz, 1H), 6.81 (d, *J* = 8.4 Hz, 1H), 5.76 (d, *J* = 39.9 Hz, 1H), 4.25 (s, 4H), 2.11 (s, 1H), 1.48 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 163.00 (d, *J* = 268.6 Hz), 143.26, 142.77 (d, *J* = 2.8 Hz), 126.66 (d, *J* = 2.1 Hz), 122.25 (d, *J* = 6.9 Hz), 117.45 (d, *J* = 8.2 Hz), 117.15, 102.52 (d, *J* = 7.6 Hz), 70.84 (d, *J* = 29.0 Hz), 64.46, 64.32, 27.54. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -117.64.

HRMS (ESI) calcd for $C_{13}H_{15}FNaO_3$ ($M+Na^+$): 261.0897; found: 261.0891.





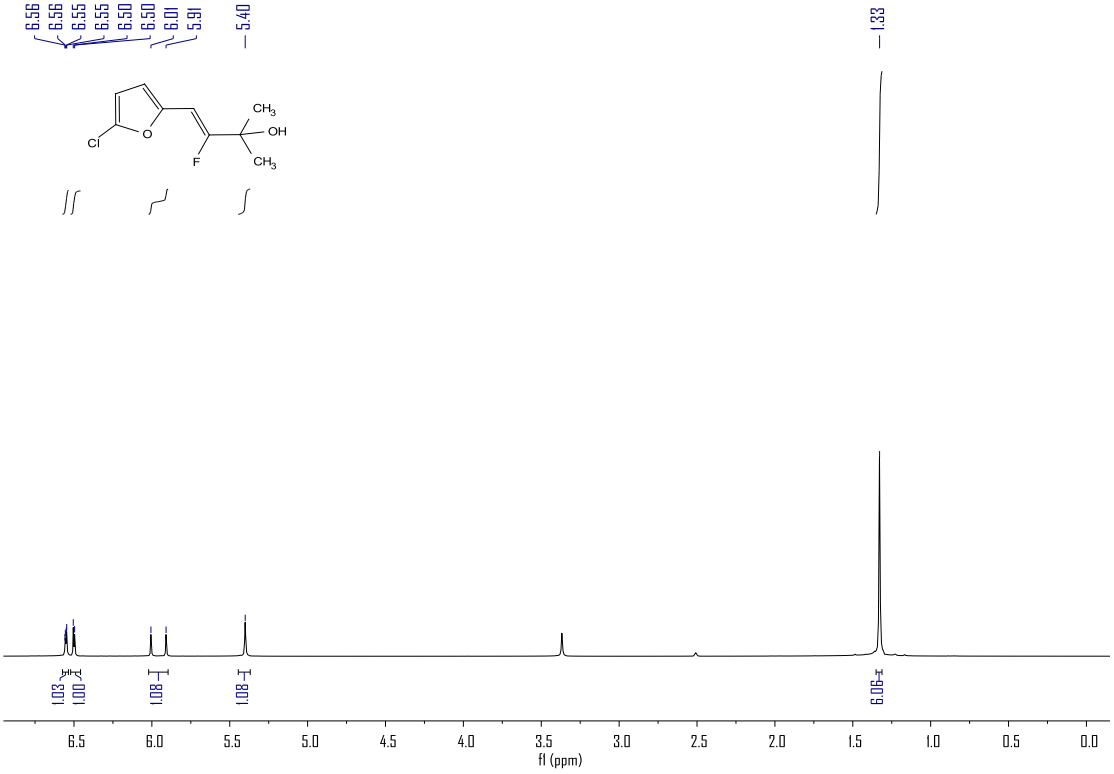


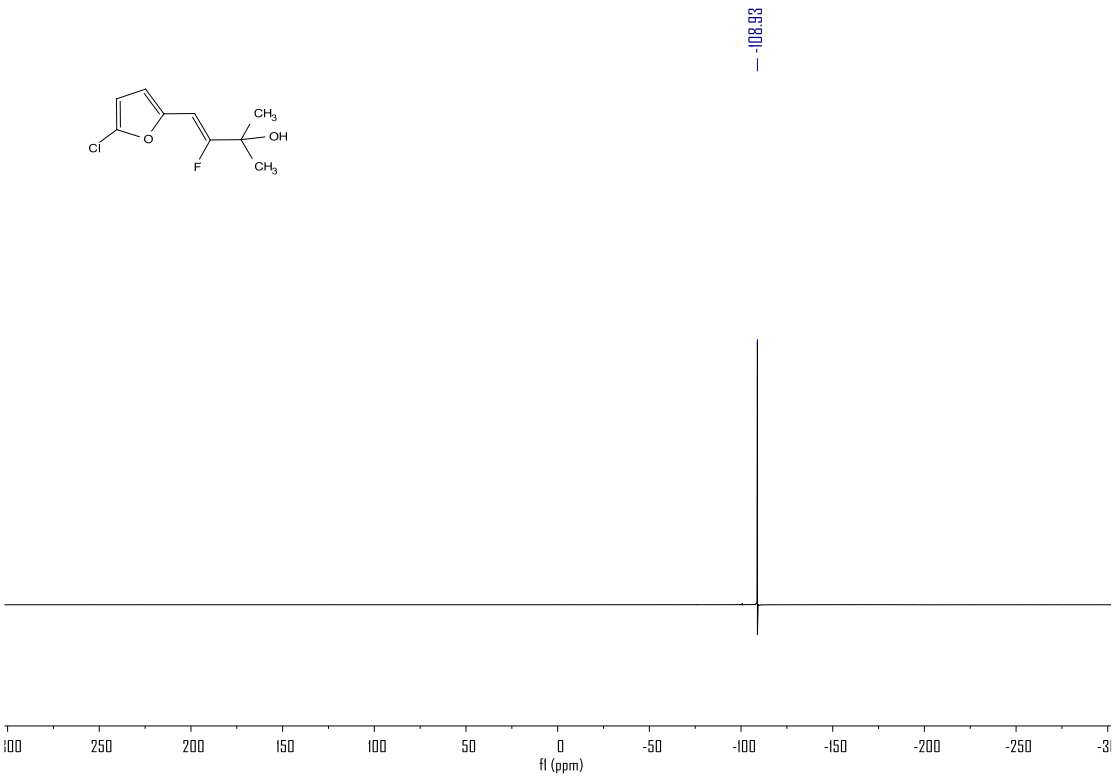


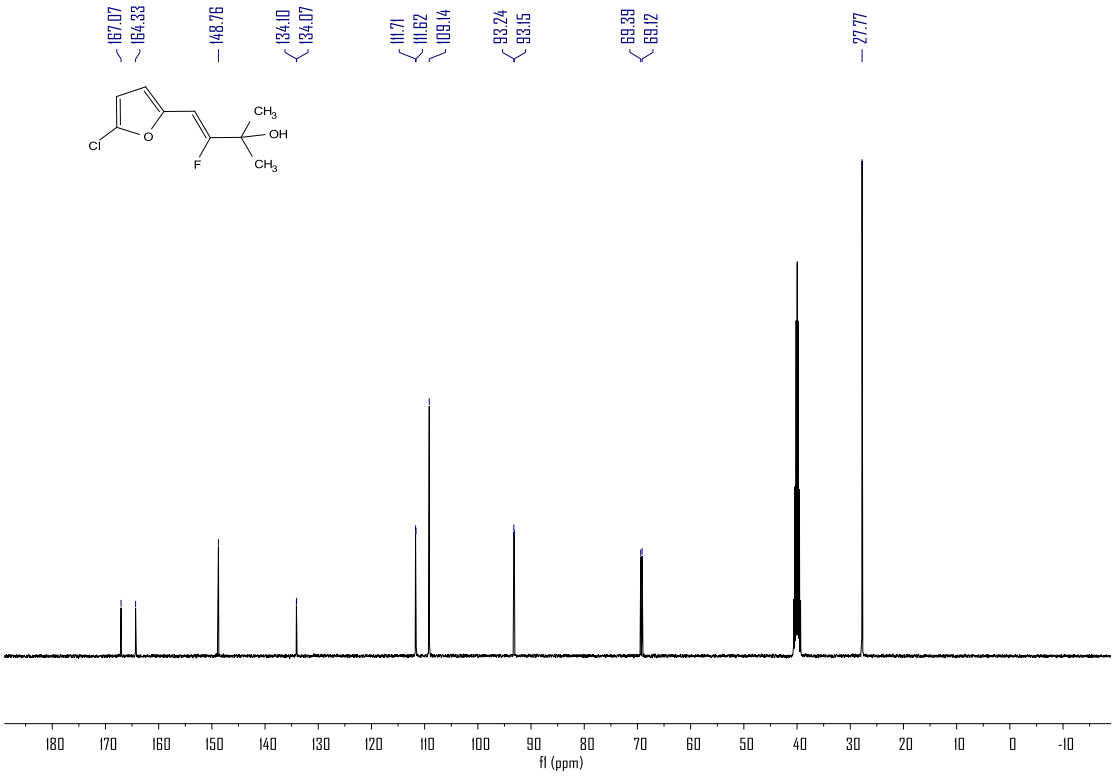
(Z)-4-(5-chlorofuran-2-yl)-3-fluoro-2-methylbut-3-en-2-ol

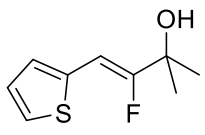
Following the general procedure (**product 23**, **pale-yellow liquid, 26.8 mg, 66%,** Z/E > 30:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (10:1) as an eluent. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 6.55 (dd, J = 3.5, 1.1 Hz, 1H), 6.50 (d, J = 3.5 Hz, 1H), 5.96 (d, J = 38.9 Hz, 1H), 5.40 (s, 1H), 1.33 (s, 6H). **^{19}F NMR** (376 MHz, DMSO-d_6) δ -108.93. **^{13}C NMR** (101 MHz, DMSO-d_6) δ 165.70 (d, J = 274.9 Hz), 148.76, 134.08 (d, J = 3.6 Hz), 111.66 (d, J = 9.2 Hz), 109.14, 93.19 (d, J = 9.1 Hz), 69.25 (d, J = 26.9 Hz), 27.77.

HRMS (ESI) calcd for $C_9H_{10}ClFNaO_2$ ($M+Na^+$): 227.0246; found: 227.0253.





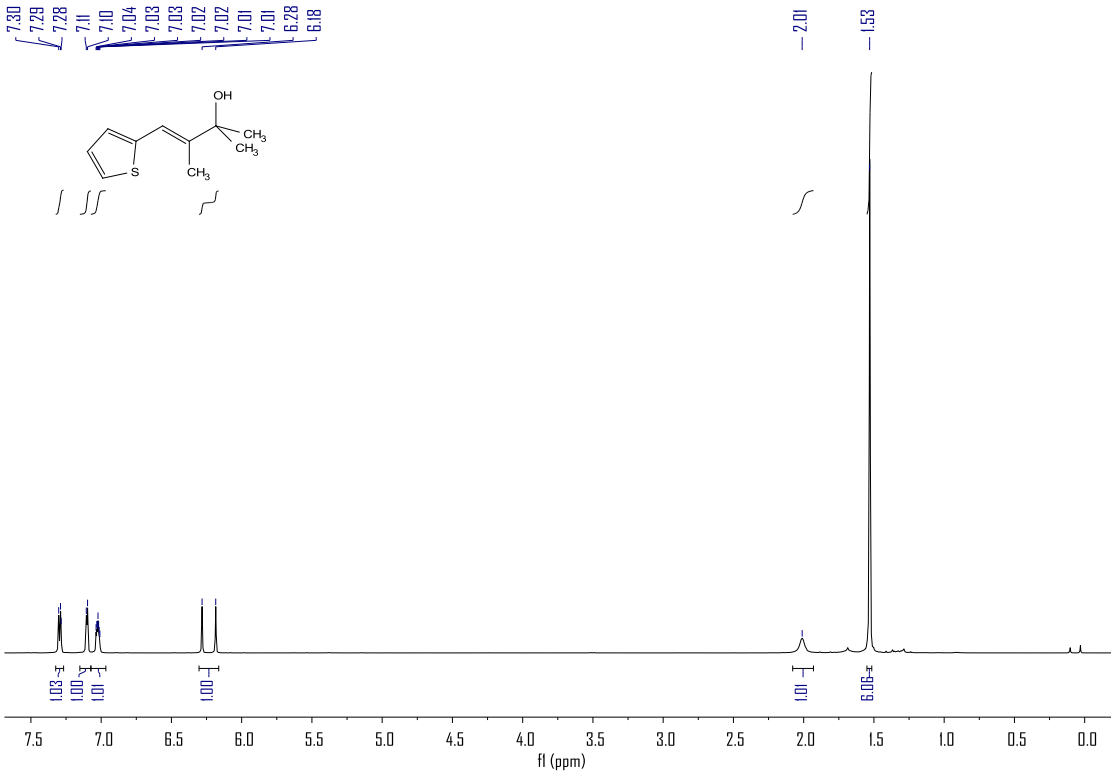


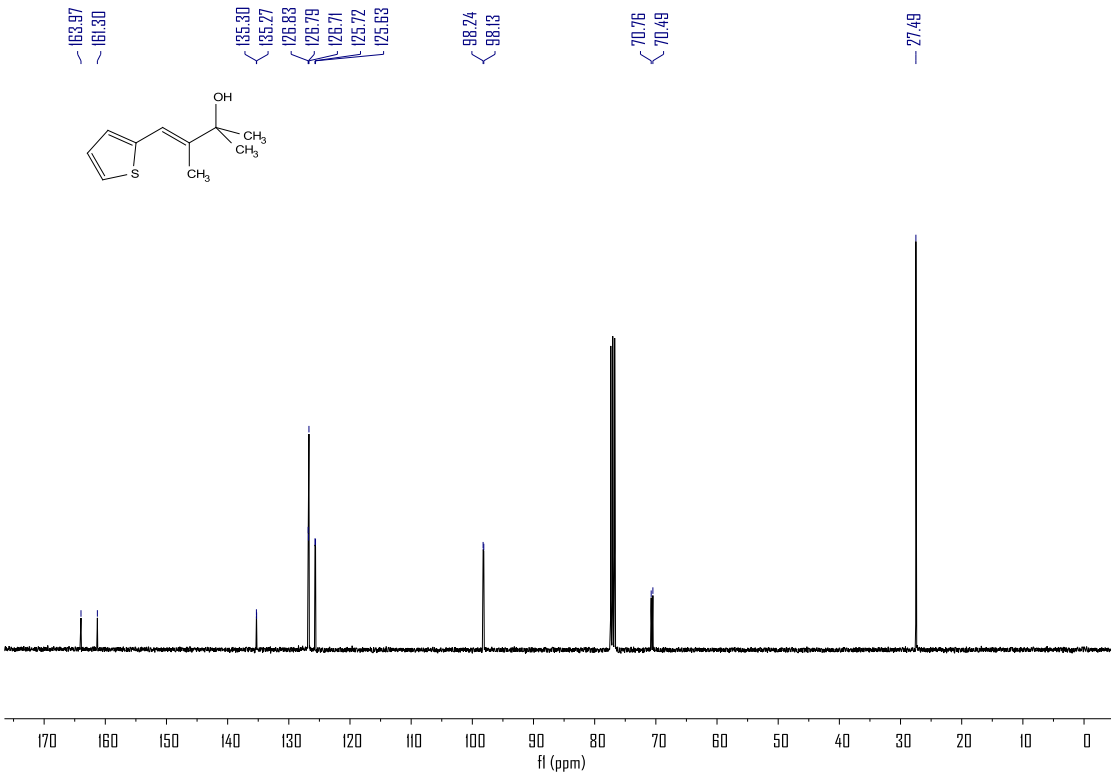


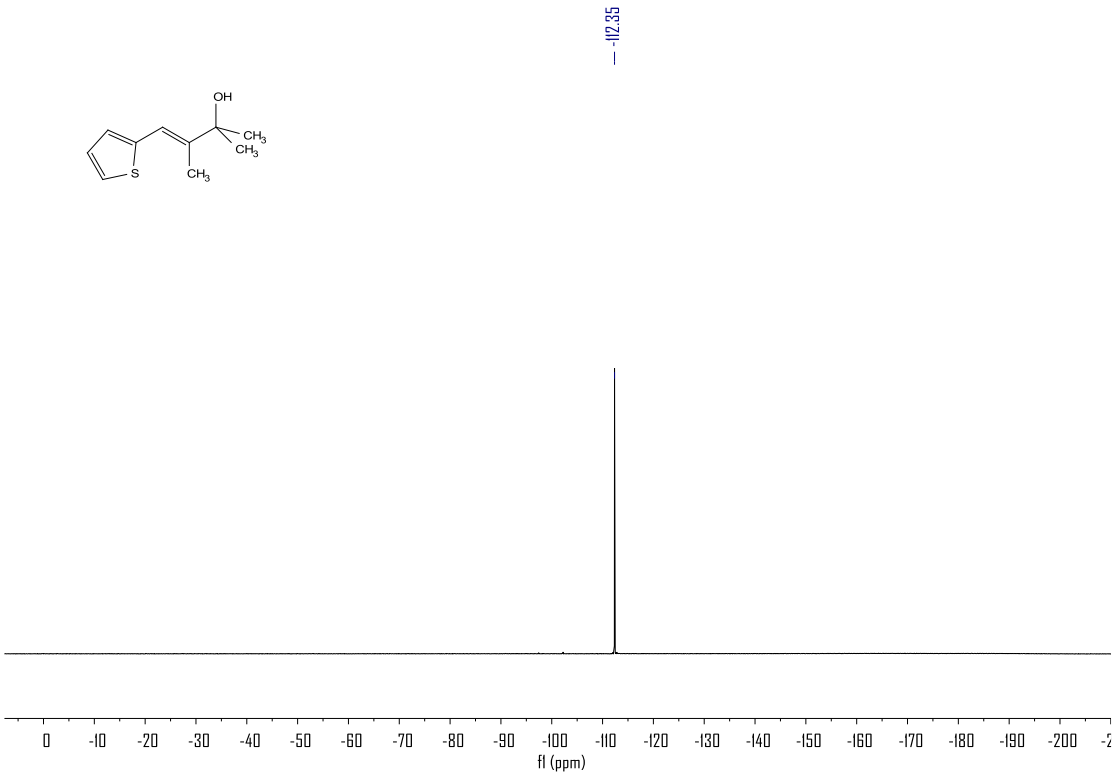
(Z)-3-fluoro-2-methyl-4-(thiophen-2-yl)but-3-en-2-ol

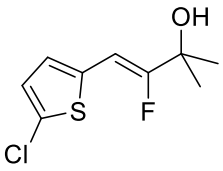
Following the general procedure (**product 24**, **pale-yellow liquid, 24.7 mg, 67%,** Z/E > 30:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (10:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.36 – 7.24 (m, 1H), 7.10 (d, *J* = 3.6 Hz, 1H), 7.02 (td, *J* = 3.6, 1.8 Hz, 1H), 6.23 (d, *J* = 38.9 Hz, 1H), 2.01 (s, 1H), 1.53 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 162.64 (d, *J* = 269.6 Hz), 135.28 (d, *J* = 3.4 Hz), 126.81 (d, *J* = 3.8 Hz), 126.71, 125.68 (d, *J* = 9.1 Hz), 98.18 (d, *J* = 11.2 Hz), 70.62 (d, *J* = 27.9 Hz), 27.49. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -112.35.

HRMS (ESI) calcd for $C_9H_{11}FNaOS$ ($M+Na^+$): 209.0407; found: 209.0410.





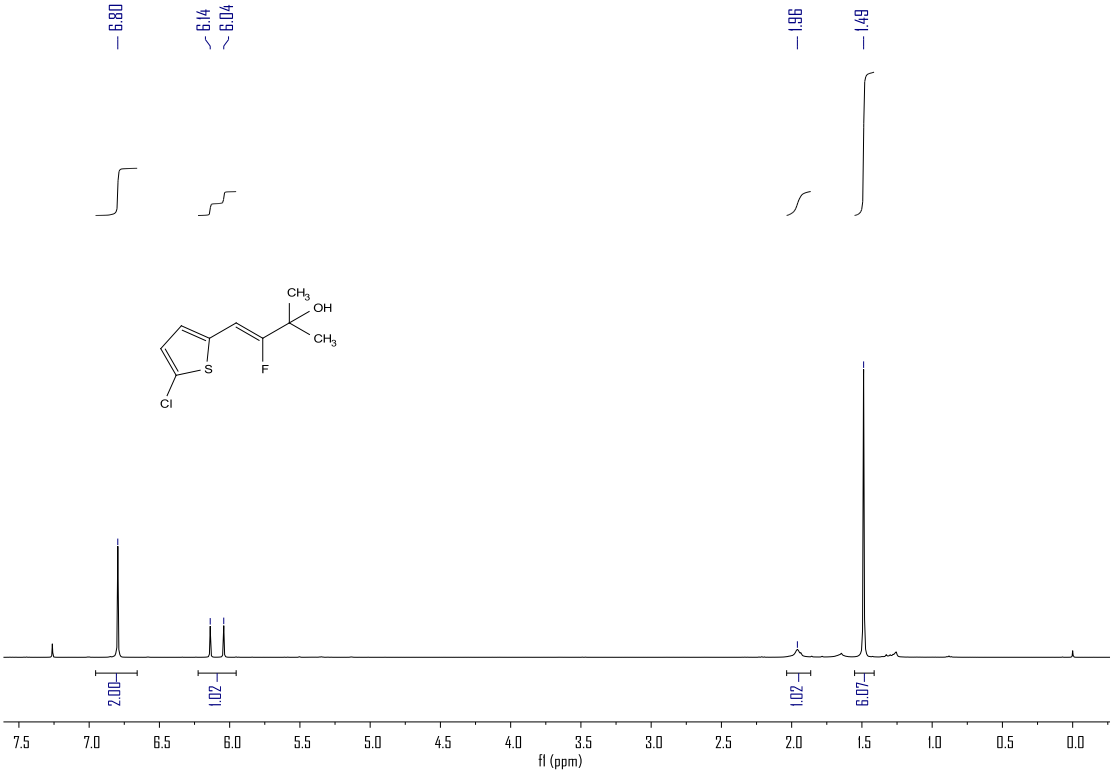


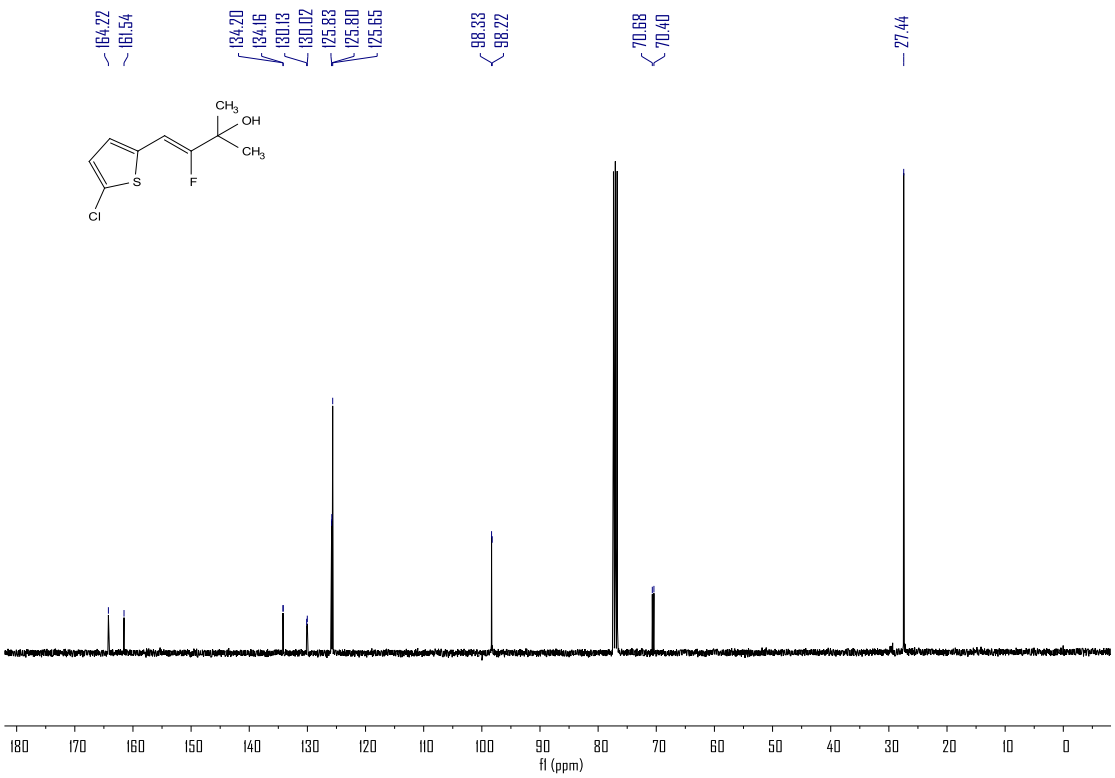


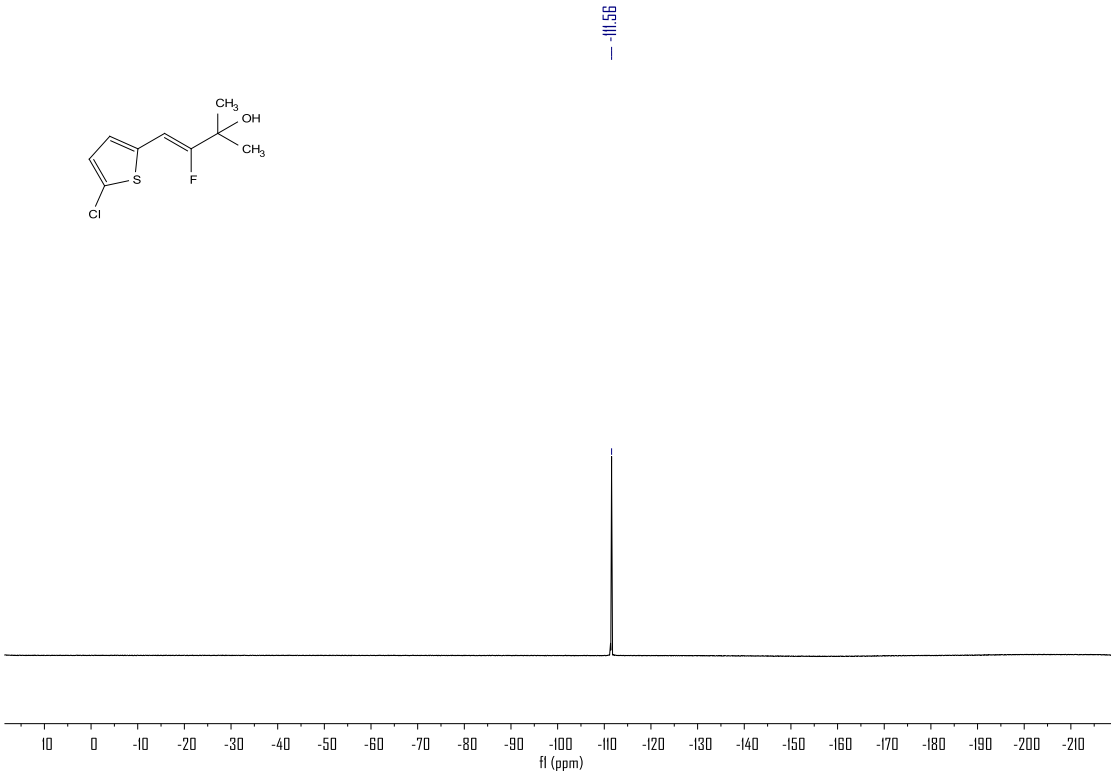
(Z)-4-(5-chlorothiophen-2-yl)-3-fluoro-2-methylbut-3-en-2-ol

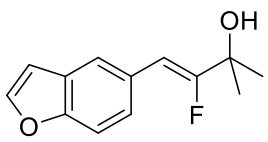
Following the general procedure (**product 25**, **pale-yellow liquid, 30.0 mg, 68%,** Z/E > 30:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (10:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 6.80 (s, 2H), 6.09 (d, *J* = 38.5 Hz, 1H), 1.96 (s, 1H), 1.49 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 162.88 (d, *J* = 270.1 Hz), 134.18 (d, *J* = 3.3 Hz), 130.07 (d, *J* = 11.5 Hz), 125.82 (d, *J* = 3.2 Hz), 125.65, 98.27 (d, *J* = 11.3 Hz), 70.54 (d, *J* = 27.9 Hz), 27.44. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -111.56.

HRMS (ESI) calcd for $C_9H_{10}ClFNaOS$ ($M+Na^+$): 243.0017; found: 243.0018.





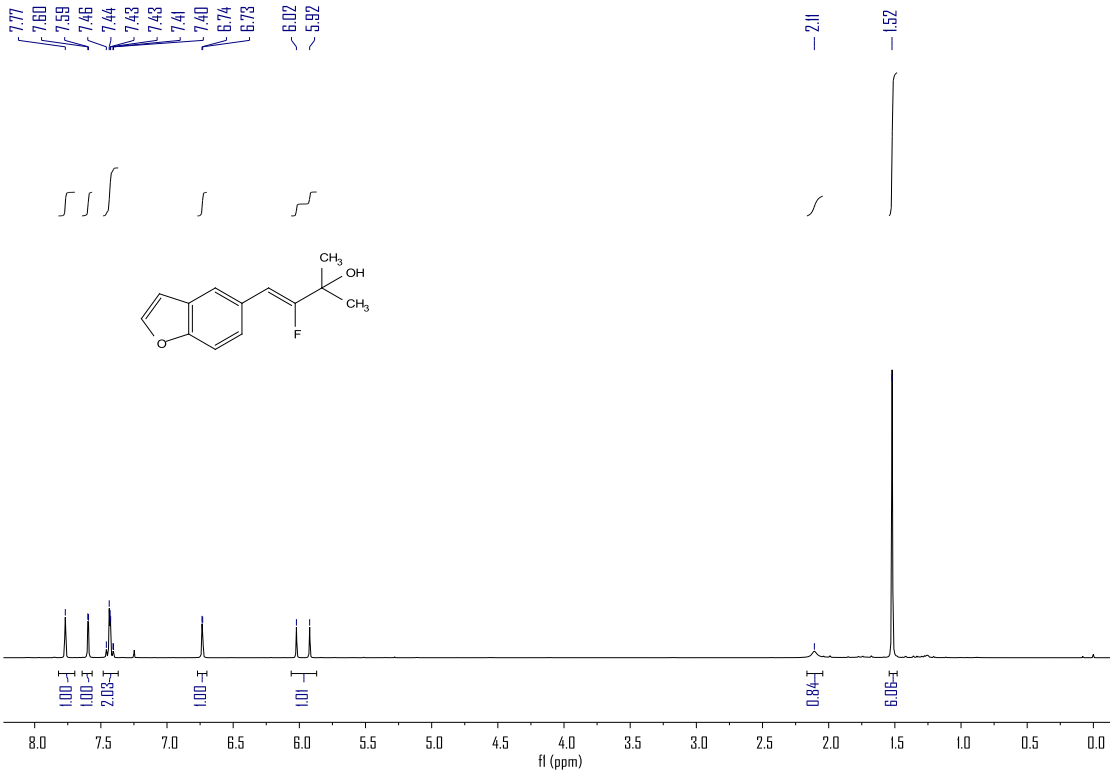


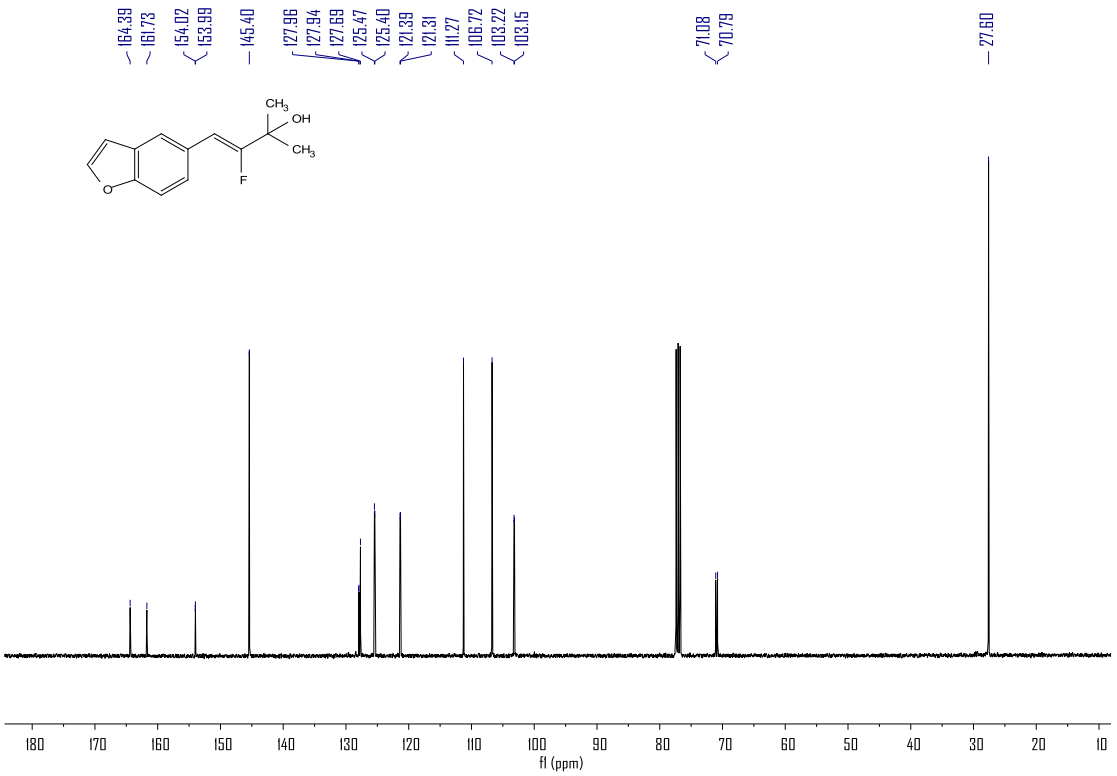


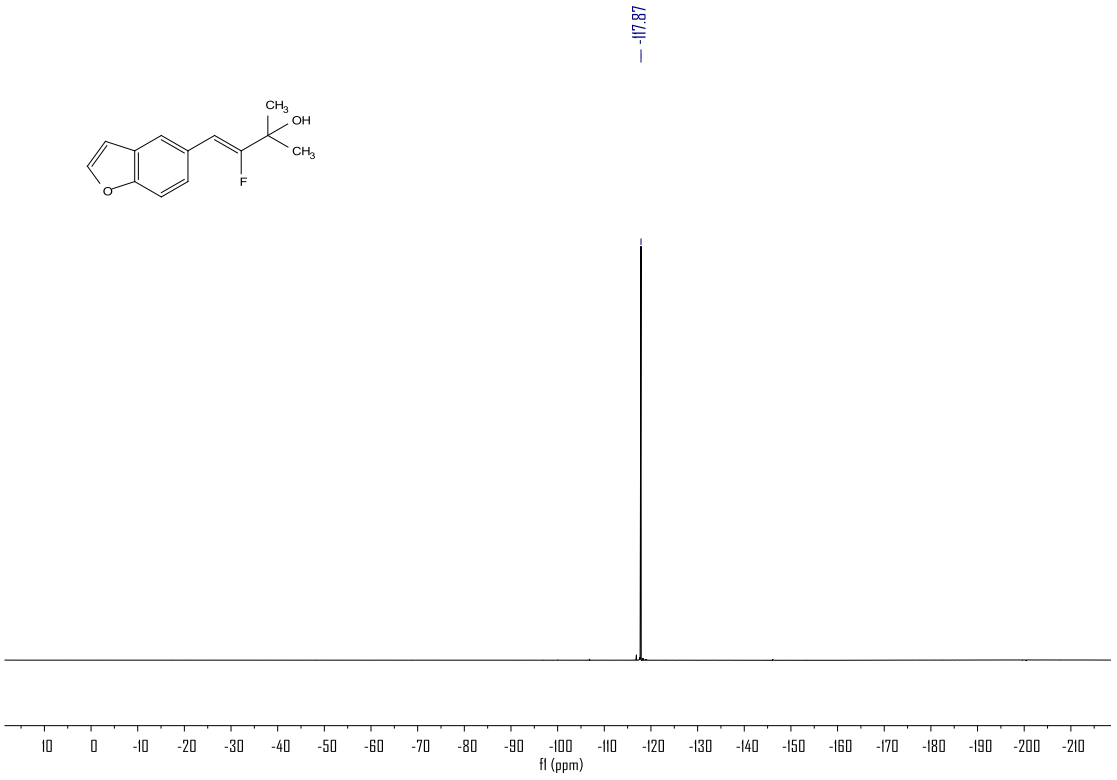
(Z)-4-(benzofuran-5-yl)-3-fluoro-2-methylbut-3-en-2-ol

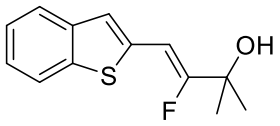
Following the general procedure (**product 26**, **pale-yellow liquid, 32.1 mg, 73%,** Z/E > 30:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (10:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.77 (s, 1H), 7.60 (d, *J* = 2.2 Hz, 1H), 7.47 – 7.39 (m, 2H), 6.73 (d, *J* = 2.1 Hz, 1H), 5.97 (d, *J* = 40.0 Hz, 1H), 2.11 (s, 1H), 1.52 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 163.06 (d, *J* = 268.3 Hz), 154.00 (d, *J* = 2.8 Hz), 145.40, 127.95 (d, *J* = 2.3 Hz), 127.69, 125.43 (d, *J* = 6.7 Hz), 121.35 (d, *J* = 8.4 Hz), 111.27, 106.72, 103.18 (d, *J* = 7.5 Hz), 70.94 (d, *J* = 29.3 Hz), 27.60. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -117.87.

HRMS (ESI) calcd for $C_{13}H_{13}FNaO_2$ ($M+Na^+$): 243.0792; found: 243.0797.





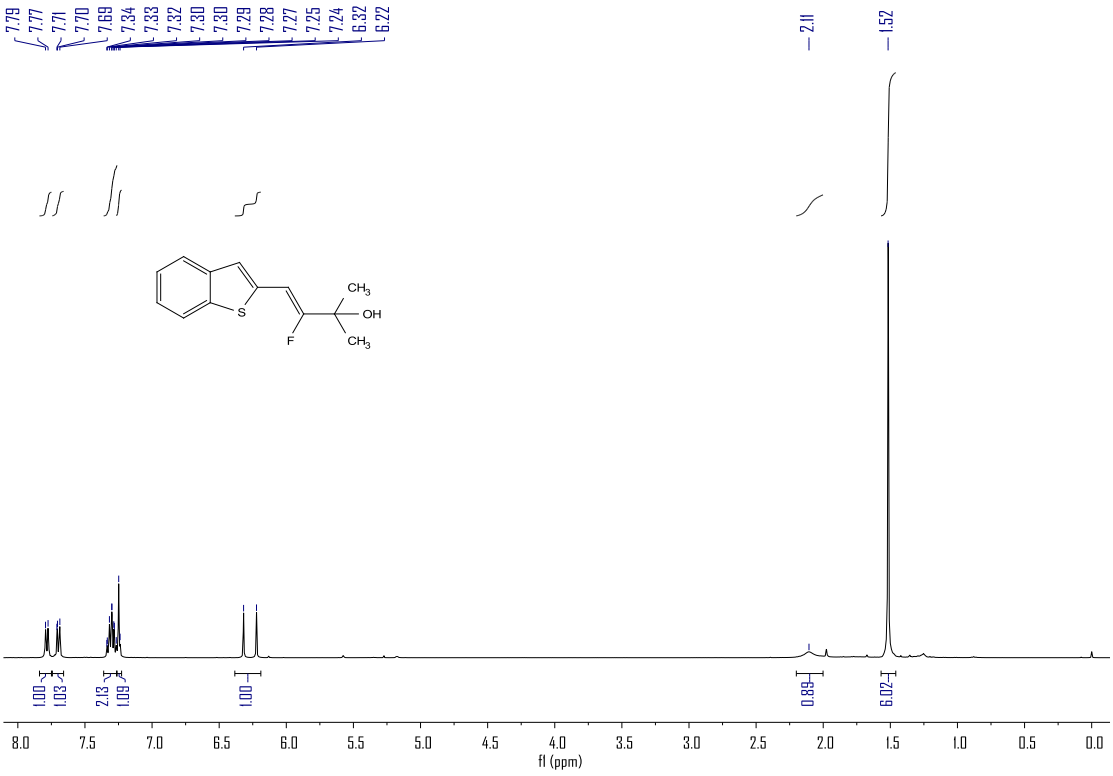


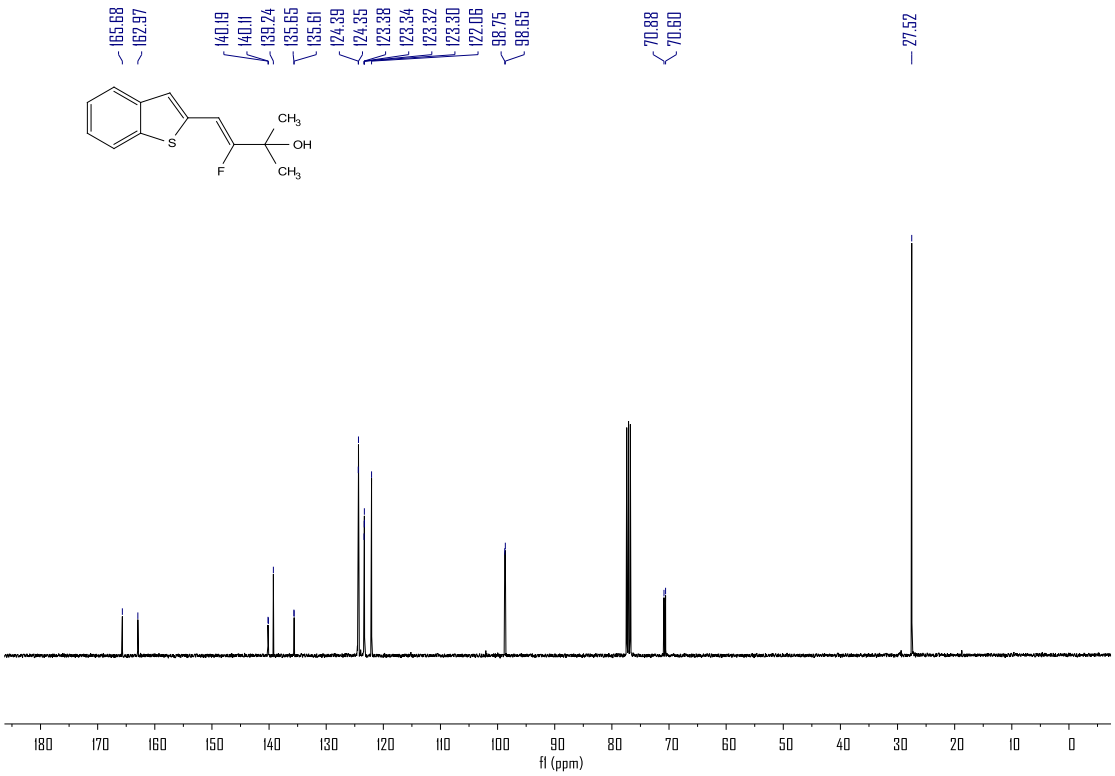


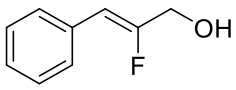
(Z)-4-(benzo[b]thiophen-2-yl)-3-fluoro-2-methylbut-3-en-2-ol

Following the general procedure (**product 27**, **pale-yellow liquid, 34.0 mg, 72%,** Z/E > 30:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (10:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 7.5 Hz, 1H), 7.75 – 7.64 (m, 1H), 7.35 – 7.26 (m, 2H), 7.25 (s, 1H), 6.27 (d, *J* = 38.5 Hz, 1H), 2.11 (s, 1H), 1.52 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 164.32 (d, *J* = 272.8 Hz), 140.15 (d, *J* = 7.7 Hz), 139.24, 135.63 (d, *J* = 3.9 Hz), 124.39, 124.35, 123.36 (d, *J* = 4.1 Hz), 123.31 (d, *J* = 1.8 Hz), 122.06, 98.70 (d, *J* = 10.4 Hz), 70.74 (d, *J* = 28.0 Hz), 27.52. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -110.26.

HRMS (ESI) calcd for $C_{13}H_{13}FNaOS$ ($M+Na^+$): 259.0563; found: 259.0557.



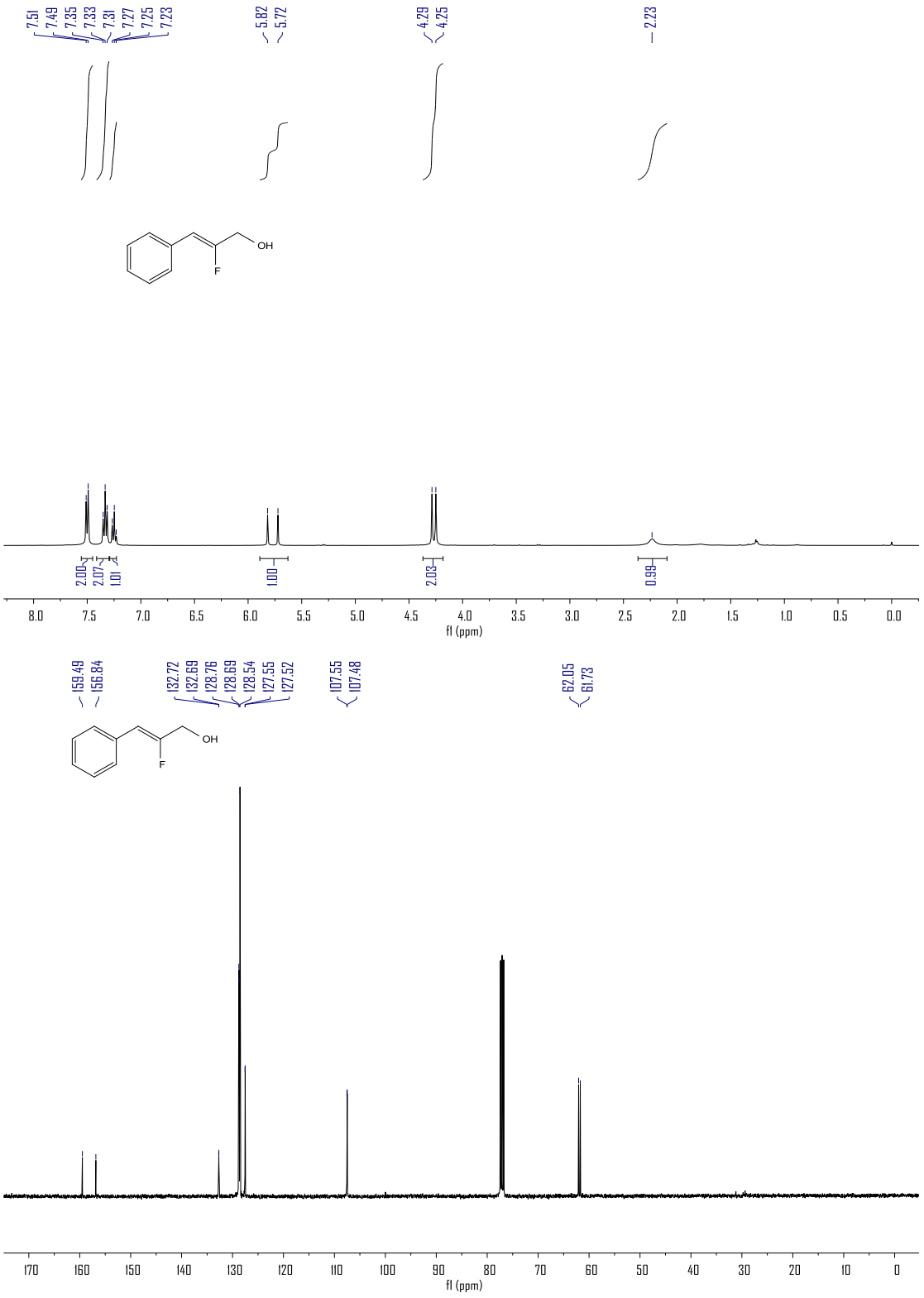


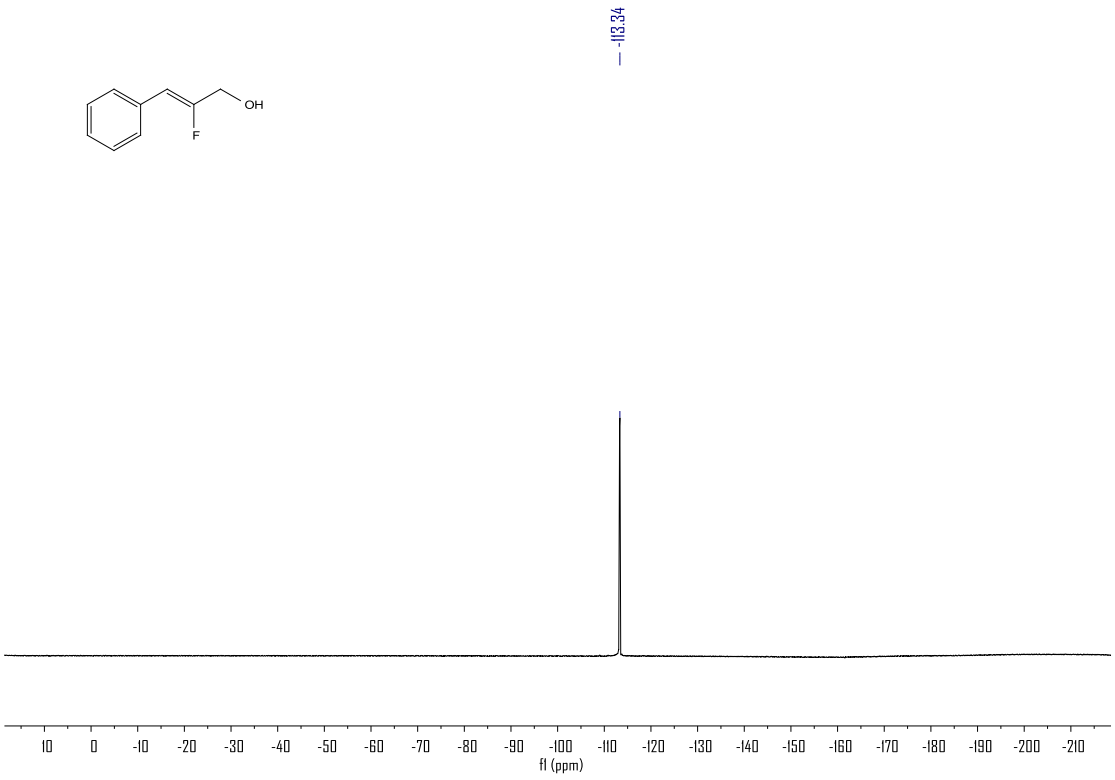


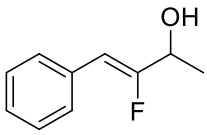
(Z)-2-fluoro-3-phenylprop-2-en-1-ol

Following the general procedure (**product 28**, **pale-yellow liquid, 19.0 mg, 63%,** Z/E > 20:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (10:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.50 (d, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.25 (t, *J* = 7.3 Hz, 1H), 5.77 (d, *J* = 38.8 Hz, 1H), 4.27 (d, *J* = 14.4 Hz, 2H), 2.23 (s, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 158.16 (d, *J* = 266.7 Hz), 132.70 (d, *J* = 2.9 Hz), 128.73 (d, *J* = 7.2 Hz), 128.54, 127.53 (d, *J* = 2.4 Hz), 107.51 (d, *J* = 6.6 Hz), 61.89 (d, *J* = 32.5 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -113.34. The characterization data is in agreement with the reported data.

HRMS (ESI) calcd for C_9H_9FNaO ($M+Na^+$): 175.0530; found: 175.0538.


7.51
7.49
7.35
7.33
7.31
7.27
7.25
7.23
5.82
5.72
4.29
4.25
2.23
OH
F
2.00
2.07
1.01
1.00
2.03
0.99
f1 (ppm)
159.49
156.84
132.72
132.69
128.76
128.69
128.54
127.55
127.52
107.55
107.48
62.05
61.73
OH
F
f1 (ppm)

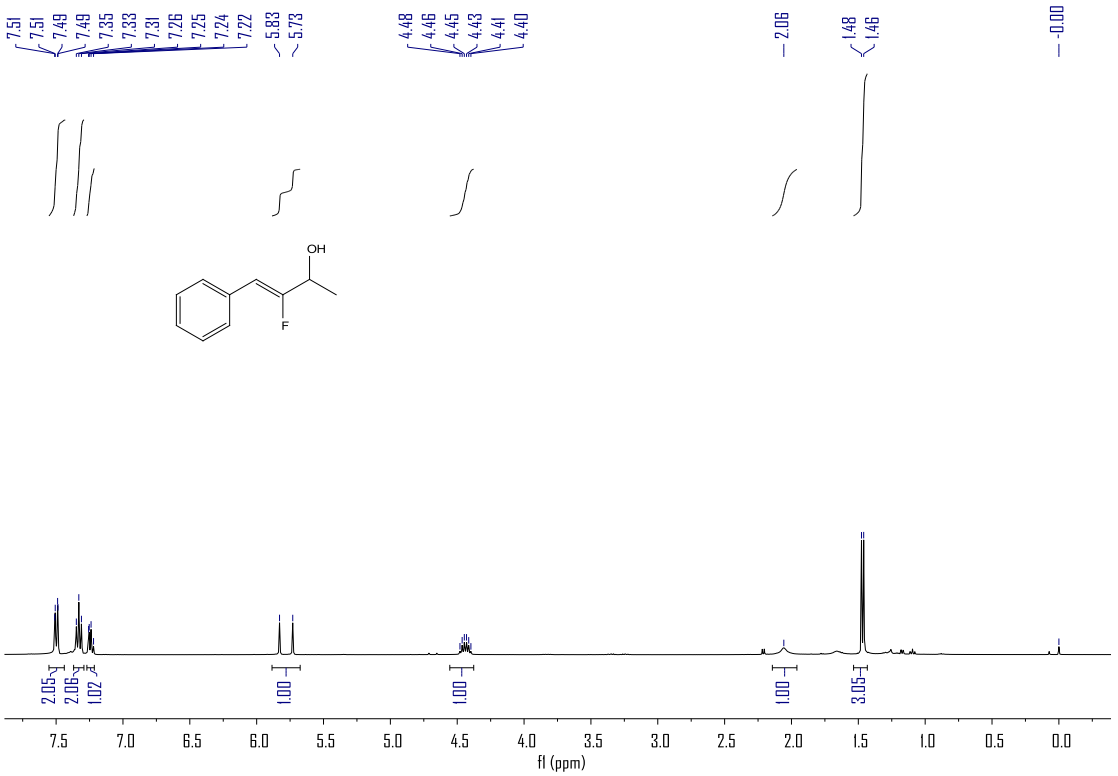


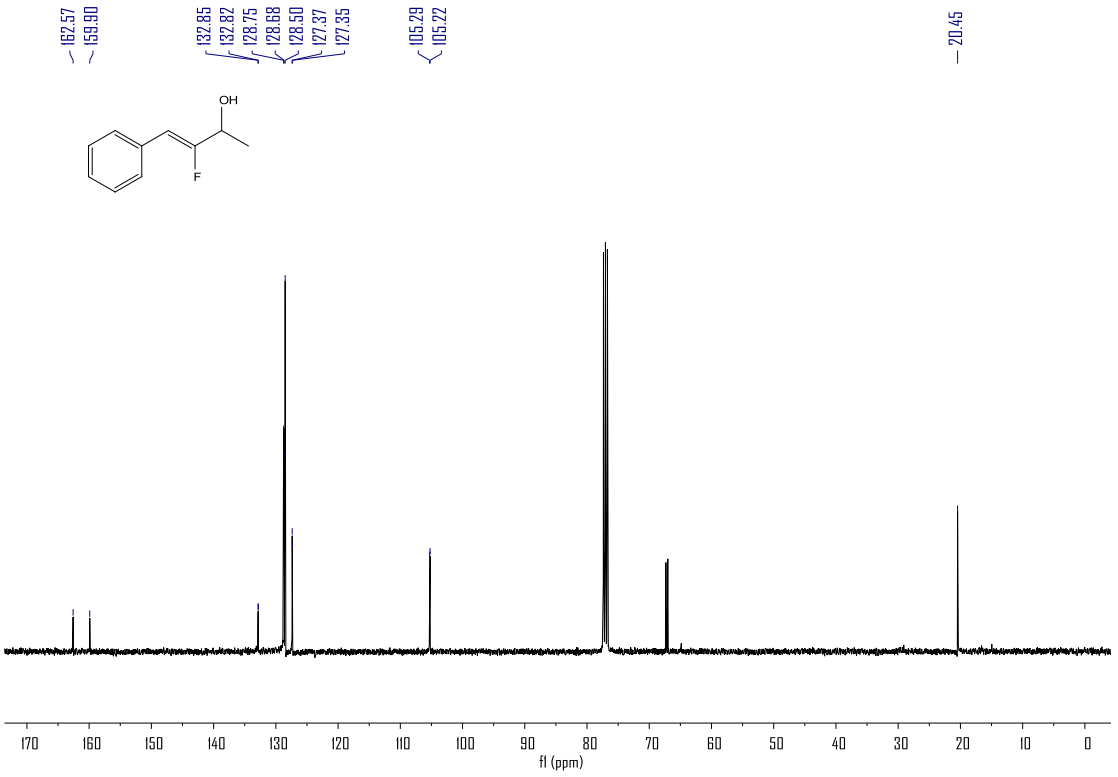


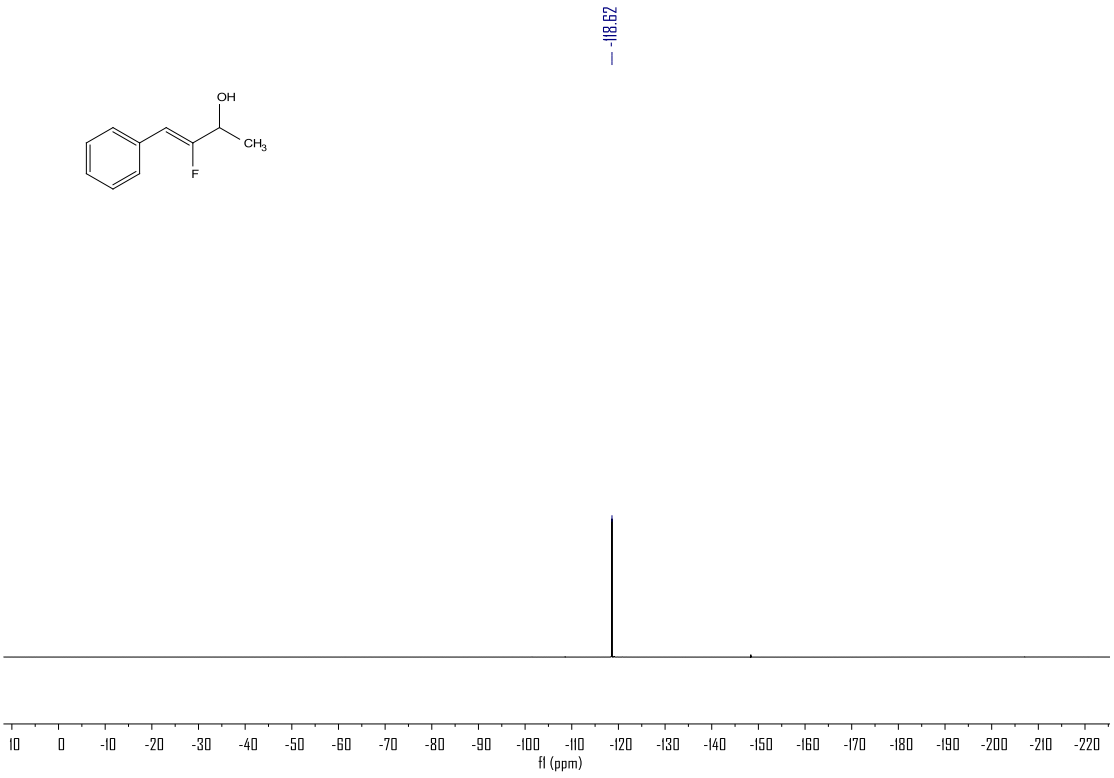
(Z)-3-fluoro-4-phenylbut-3-en-2-ol

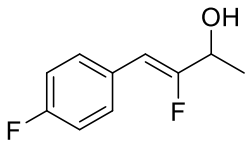
Following the general procedure (**product 29**, **pale-yellow liquid, 23.3 mg, 71%,** Z/E > 20:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (10:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.56 – 7.46 (m, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.27 – 7.21 (m, 1H), 5.78 (d, *J* = 39.5 Hz, 1H), 4.44 (dq, *J* = 13.1, 6.5 Hz, 1H), 2.06 (s, 1H), 1.47 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 161.24 (d, *J* = 268.9 Hz), 132.84 (d, *J* = 2.6 Hz), 128.71 (d, *J* = 7.2 Hz), 128.50, 127.36 (d, *J* = 2.4 Hz), 105.25 (d, *J* = 6.8 Hz), 67.17 (d, *J* = 31.1 Hz), 20.45. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -118.62.

HRMS (ESI) calcd for $C_{10}H_{11}FNaO$ ($M+Na^+$): 189.0686; found: 189.0693.


7.51
7.51
7.49
7.49
7.35
7.33
7.31
7.26
7.25
7.24
7.22
5.83
5.73
4.48
4.46
4.45
4.43
4.41
4.40
2.06
1.48
1.46
0.00
OH
F
2.05
2.06
1.02
1.00
1.00
1.00
3.05
f1 (ppm)


162.57
159.90
132.85
132.82
128.75
128.68
128.50
127.37
127.35
105.29
105.22
20.45
OH
F
f1 (ppm)

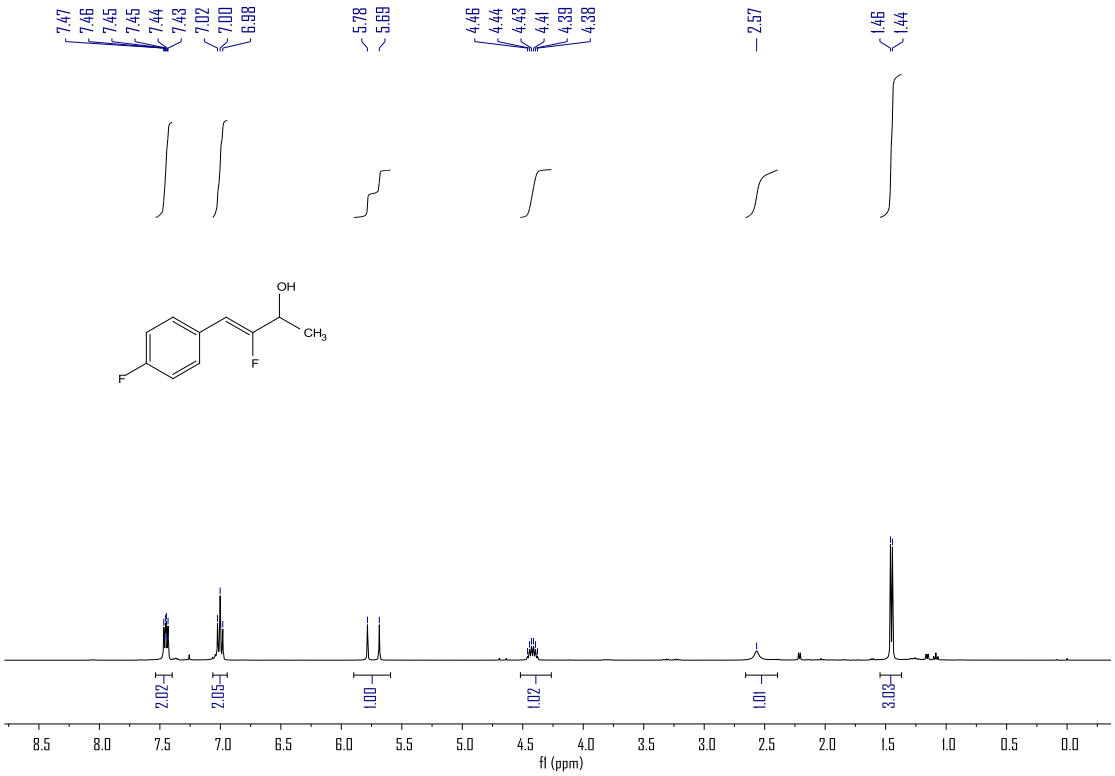


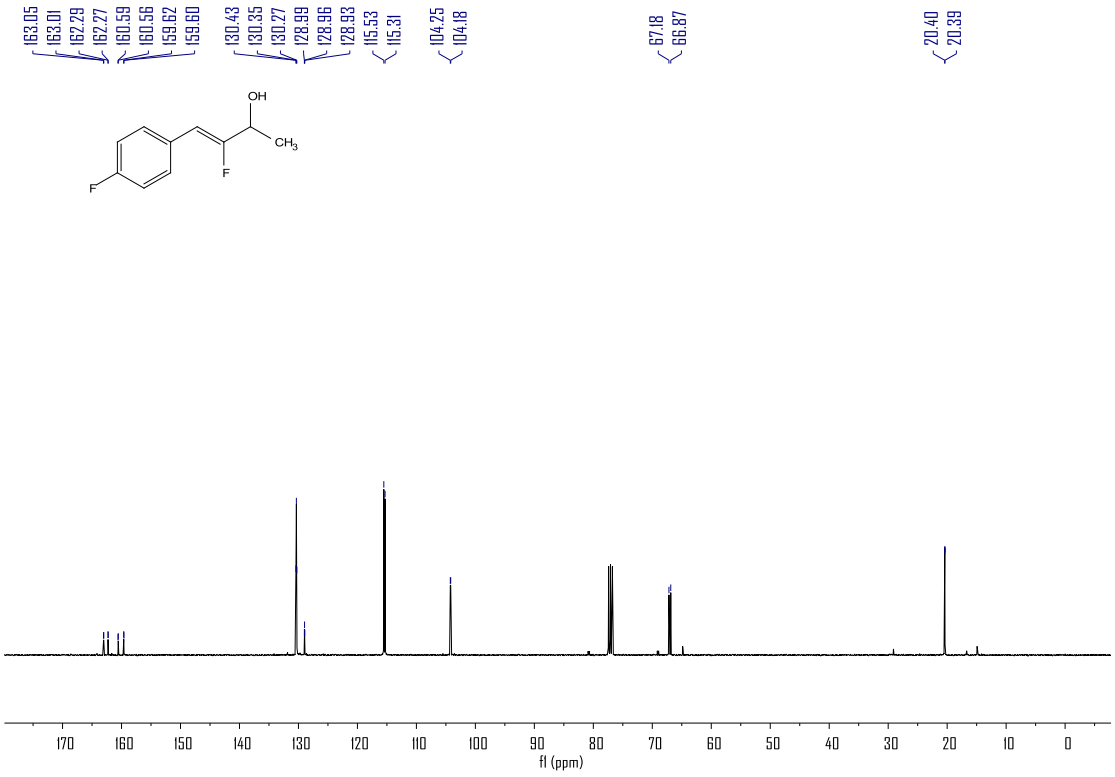


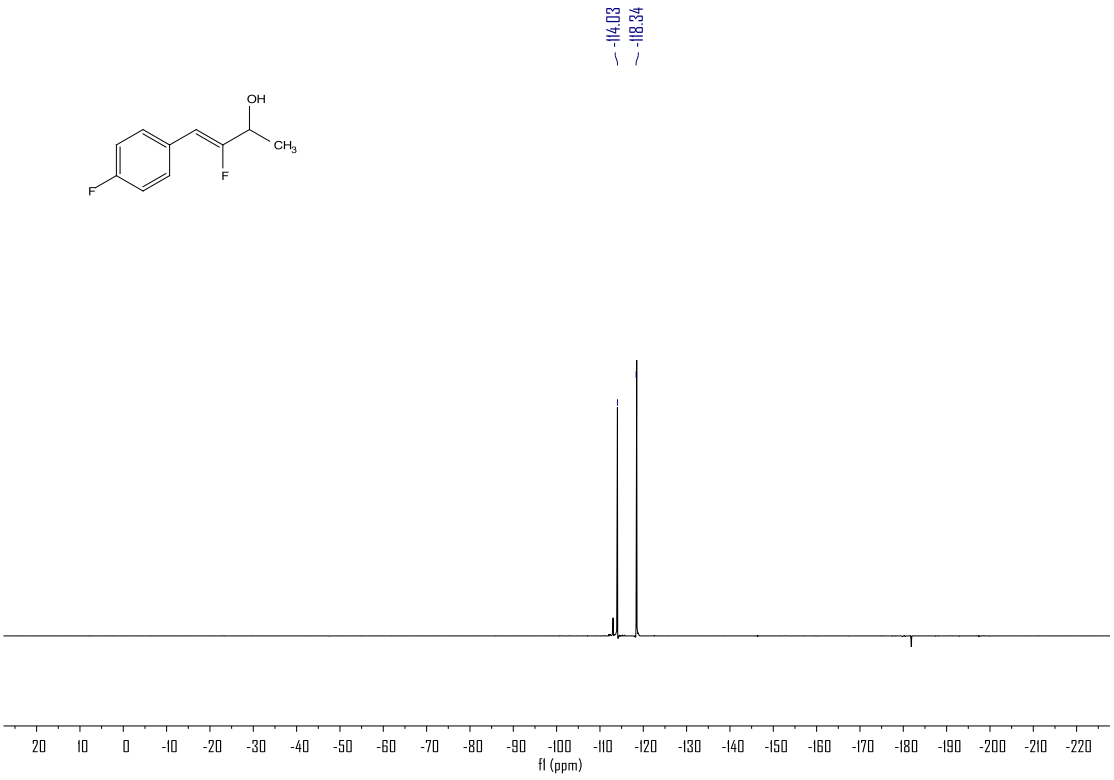
(Z)-3-fluoro-4-(4-fluorophenyl)but-3-en-2-ol

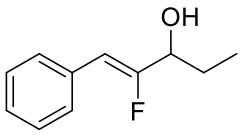
Following the general procedure (**product 30**, **pale-yellow liquid, 25.0 mg, 68%,** Z/E > 20:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.45 (dd, *J* = 8.7, 5.6 Hz, 2H), 7.00 (t, *J* = 8.7 Hz, 2H), 5.73 (d, *J* = 39.2 Hz, 1H), 4.49 – 4.35 (m, 1H), 2.57 (s, 1H), 1.45 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ161.80 (dd, J = 247.2, 3.4 Hz), 160.94 (dd, J = 268.4, 2.4 Hz), 130.35 (t, *J* = 7.8 Hz), 128.96 (t, *J* = 3.0 Hz), 115.42 (d, *J* = 21.4 Hz), 104.22 (d, *J* = 6.9 Hz), 67.02 (d, *J* = 31.2 Hz), 20.39 (d, *J* = 1.4 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -114.03, -118.34.

HRMS (ESI) calcd for $C_{10}H_{10}F_2NaO$ ($M+Na^+$): 207.0592; found: 207.0599.


7.47
7.46
7.45
7.45
7.44
7.43
7.02
7.00
6.98
5.78
5.69
4.46
4.44
4.43
4.41
4.39
4.38
2.57
1.46
1.44
OH
CH3
F
F
2.02
2.05
1.00
1.02
1.01
3.03
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


163.05
163.01
162.29
162.27
160.59
160.56
159.62
159.60
130.43
130.35
130.27
128.99
128.96
128.93
115.53
115.31
104.25
104.18
67.18
66.87
20.40
20.39
OH
CH3
F
F
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



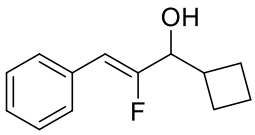


(Z)-2-fluoro-1-phenylpent-1-en-3-ol

Following the general procedure (**product 31**, **pale-yellow liquid, 22.0 mg, 61%,** Z/E > 20:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (10:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.50 (d, *J* = 7.2 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.25 (d, *J* = 7.2 Hz, 1H), 5.77 (d, *J* = 39.6 Hz, 1H), 4.16 (dt, *J* = 15.5, 6.6 Hz, 1H), 2.04 (s, 1H), 1.78 (ddt, *J* = 28.8, 14.0, 7.1 Hz, 2H), 1.01 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 160.12 (d, *J* = 269.6 Hz), 132.88 (d, *J* = 2.6 Hz), 128.71 (d, *J* = 7.2 Hz), 128.51, 127.35 (d, *J* = 2.3 Hz), 106.46 (d, *J* = 6.7 Hz), 72.72 (d, *J* = 30.0 Hz), 27.26, 9.67. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -118.18.

HRMS (ESI) calcd for $C_{11}H_{13}FNaO$ ($M+Na^+$): 203.0843; found: 203.0851.

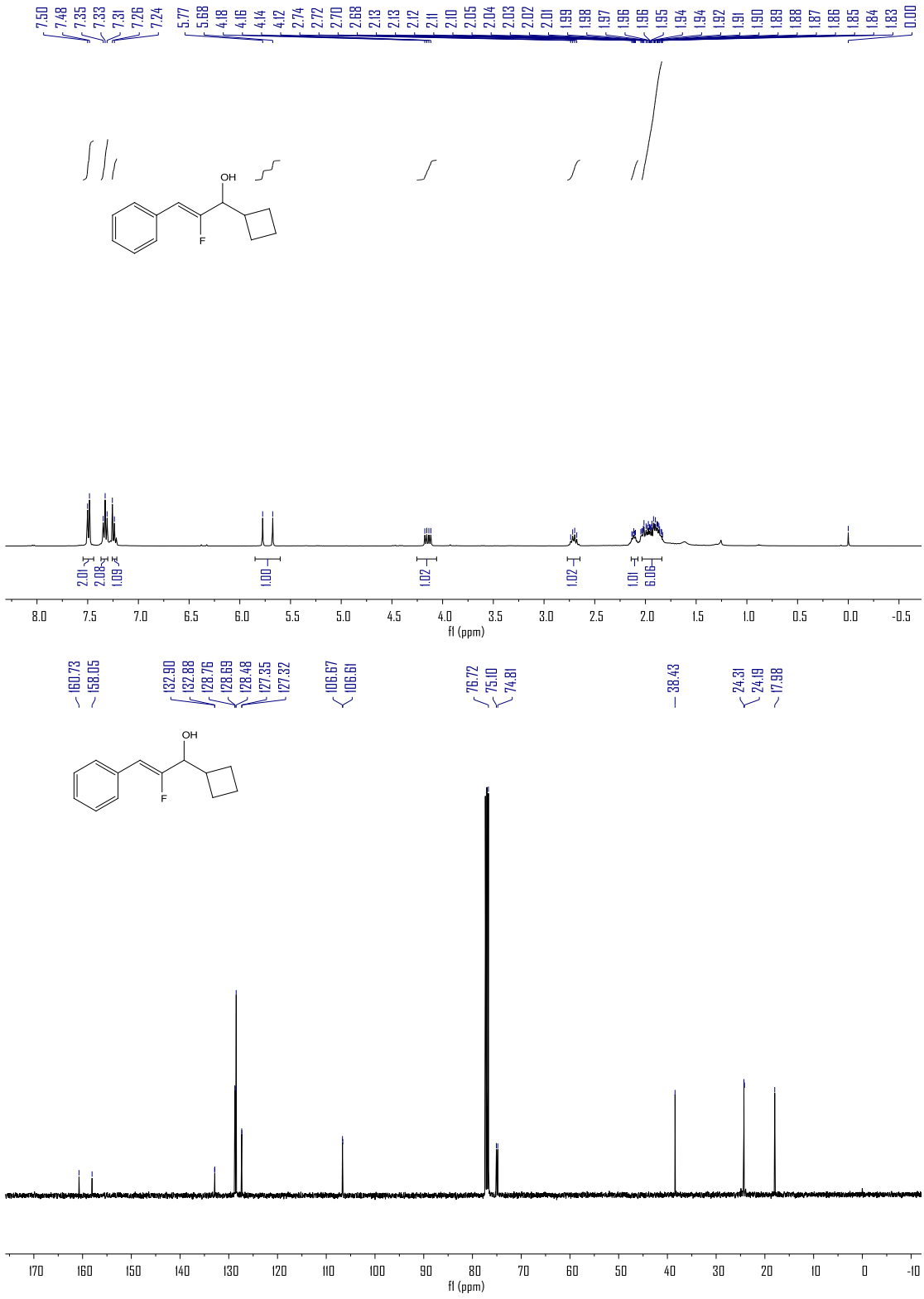

7.51
7.49
7.35
7.33
7.31
7.26
7.24
5.81
5.72
4.20
4.18
4.16
4.16
4.14
4.12
2.04
1.95
1.84
1.82
1.80
1.78
1.76
1.74
1.73
1.71
1.02
1.01
0.99
OH
CH3
F
2.00
2.05
1.23
1.00
1.00
0.96
2.06
3.01
f1 (ppm)
161.46
158.78
132.89
132.87
128.74
128.67
128.58
128.51
127.36
127.34
106.50
106.43
72.87
72.57
27.26
9.67
OH
CH3
F
f1 (ppm)

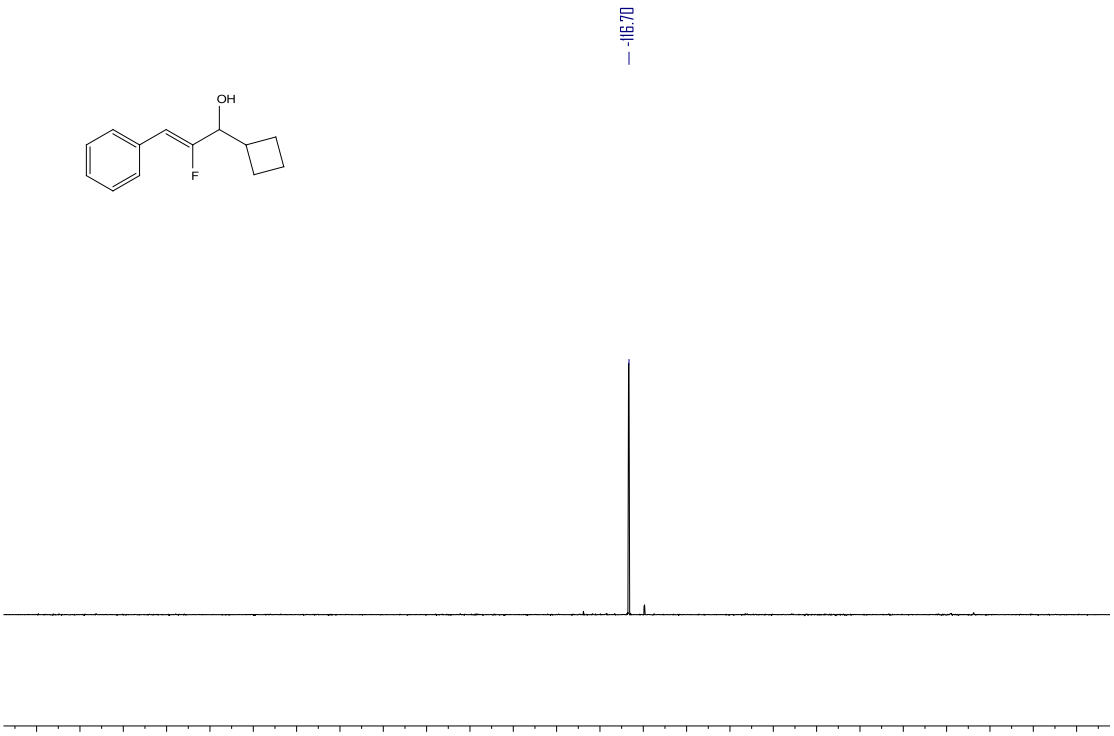


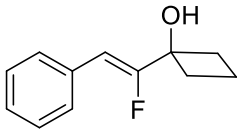
(Z)-1-cyclobutyl-2-fluoro-3-phenylprop-2-en-1-ol

Following the general procedure (**product 32**, **pale-yellow liquid, 17.5 mg, 42%,** Z/E = 20:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (10:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.49 (d, *J* = 7.7 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.25 (d, *J* = 8.1 Hz, 1H), 5.73 (d, *J* = 39.6 Hz, 1H), 4.15 (dd, *J* = 16.0, 7.9 Hz, 1H), 2.71 (q, *J* = 8.0 Hz, 1H), 2.17 – 2.09 (m, 1H), 2.06 – 1.77 (m, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 159.39 (d, *J* = 269.7 Hz), 132.89 (d, *J* = 2.5 Hz), 128.72 (d, *J* = 7.3 Hz), 128.48, 127.34 (d, *J* = 2.4 Hz), 106.64 (d, *J* = 6.6 Hz), 74.95 (d, *J* = 28.6 Hz), 38.43, 24.31, 24.19, 17.98. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -116.70.

HRMS (ESI) calcd for $C_{13}H_{15}FNaO$ ($M+Na^+$): 229.0999; found: 229.0995.


7.50
7.48
7.35
7.33
7.31
7.26
7.24
5.77
5.68
4.18
4.16
4.14
4.12
2.74
2.72
2.70
2.68
2.13
2.13
2.12
2.11
2.10
2.05
2.04
2.03
2.02
2.01
1.99
1.98
1.97
1.96
1.96
1.95
1.94
1.94
1.92
1.91
1.90
1.89
1.88
1.87
1.86
1.85
1.84
1.83
0.00
OH
F
2.01
2.08
1.09
1.00
1.02
1.02
1.01
6.06
f1 (ppm)
160.73
158.05
132.90
132.88
128.76
128.69
128.48
127.35
127.32
106.67
106.61
76.72
75.10
74.81
38.43
24.31
24.19
17.98
OH
F
f1 (ppm)

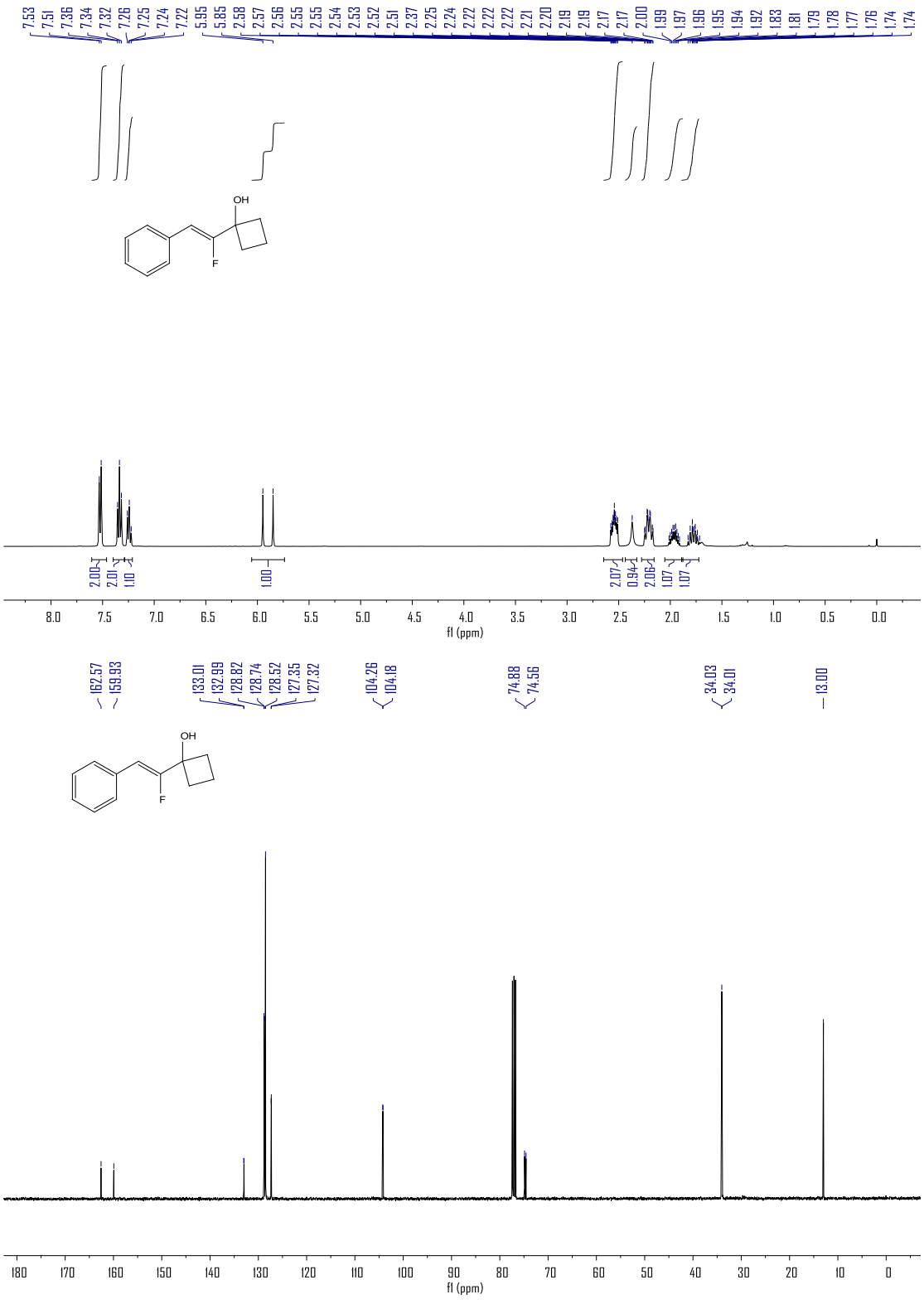


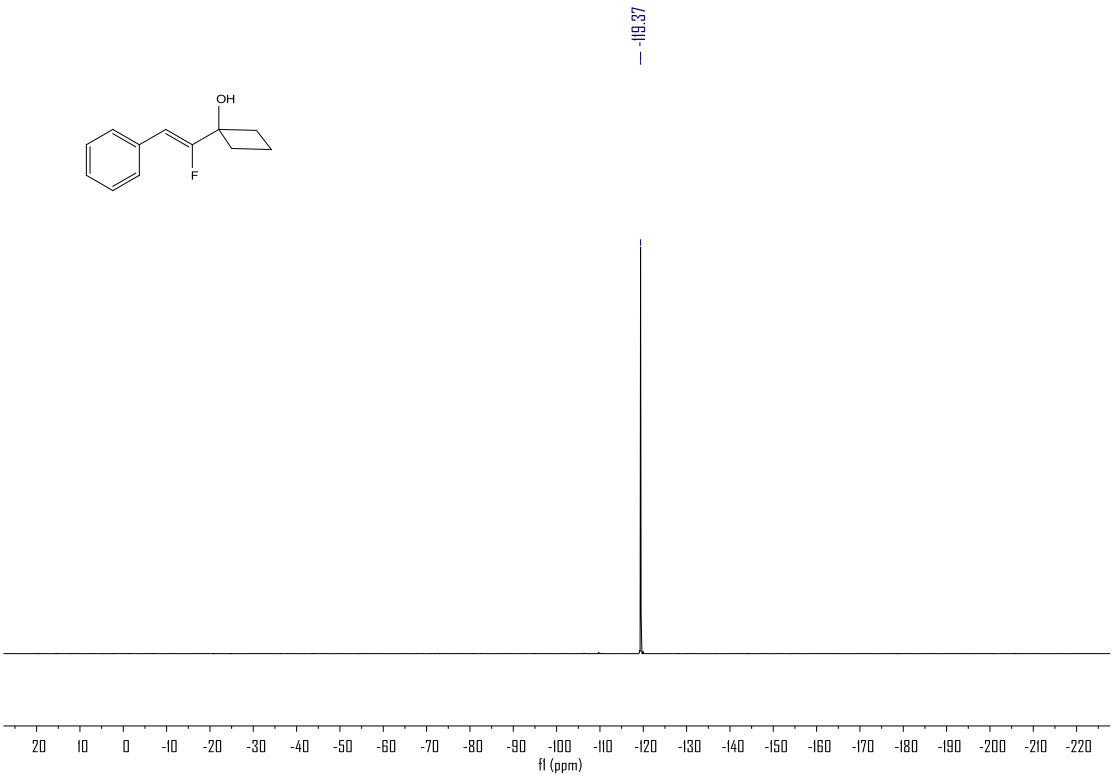


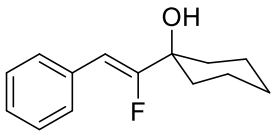
(Z)-1-(1-fluoro-2-phenylvinyl)cyclobutan-1-ol

Following the general procedure (**product 33**, **pale-yellow liquid, 21.5 mg, 56%,** Z/E > 20:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (10:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.52 (d, *J* = 7.3 Hz, 2H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.27 – 7.21 (m, 1H), 5.90 (d, *J* = 39.5 Hz, 1H), 2.54 (ddd, *J* = 15.8, 8.8, 4.9 Hz, 2H), 2.37 (s, 1H), 2.21 (dtd, *J* = 12.7, 9.8, 2.1 Hz, 2H), 1.96 (ddq, *J* = 14.8, 9.9, 4.9 Hz, 1H), 1.83 – 1.71 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 161.25 (d, *J* = 266.3 Hz), 133.00 (d, *J* = 2.6 Hz), 128.78 (d, *J* = 7.5 Hz), 128.52, 127.33 (d, *J* = 2.5 Hz), 104.22 (d, *J* = 8.1 Hz), 74.72 (d, *J* = 31.7 Hz), 34.02 (d, *J* = 2.5 Hz), 13.00. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -119.37.

HRMS (ESI) calcd for $C_{12}H_{13}FNaO$ ($M+Na^+$): 215.0843; found: 215.0851.


7.53
7.51
7.36
7.34
7.32
7.26
7.25
7.24
7.22
5.95
5.85
2.58
2.57
2.56
2.55
2.55
2.54
2.53
2.52
2.51
2.37
2.25
2.24
2.22
2.22
2.22
2.21
2.20
2.19
2.19
2.17
2.17
2.00
1.99
1.97
1.96
1.95
1.94
1.92
1.83
1.81
1.79
1.78
1.77
1.76
1.74
1.74
OH
F
2.00
2.01
1.10
1.00
2.07
0.94
2.06
1.07
1.07
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
162.57
159.93
133.01
132.99
128.82
128.74
128.52
127.35
127.32
104.26
104.18
74.88
74.56
34.03
34.01
13.00
OH
F
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

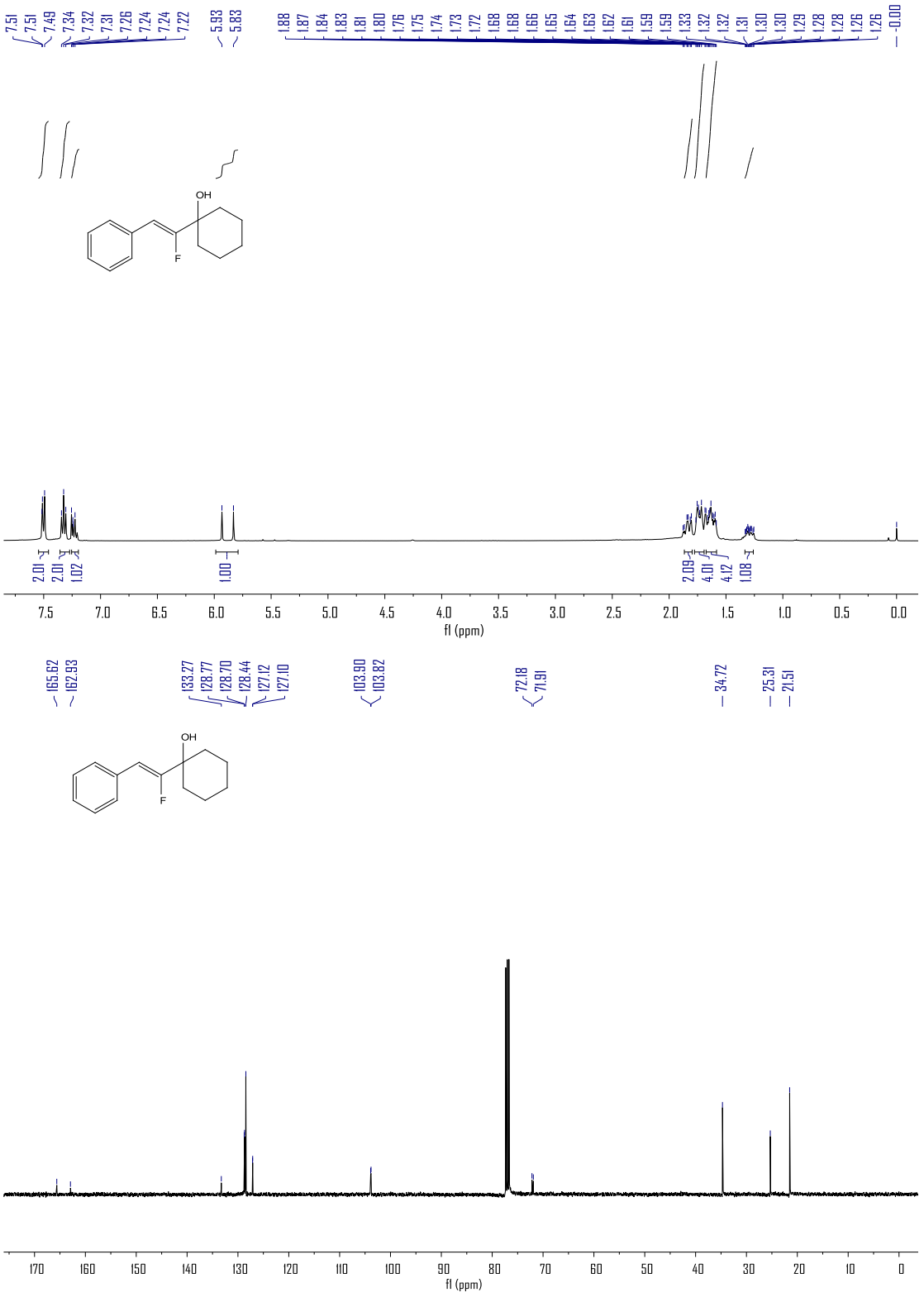


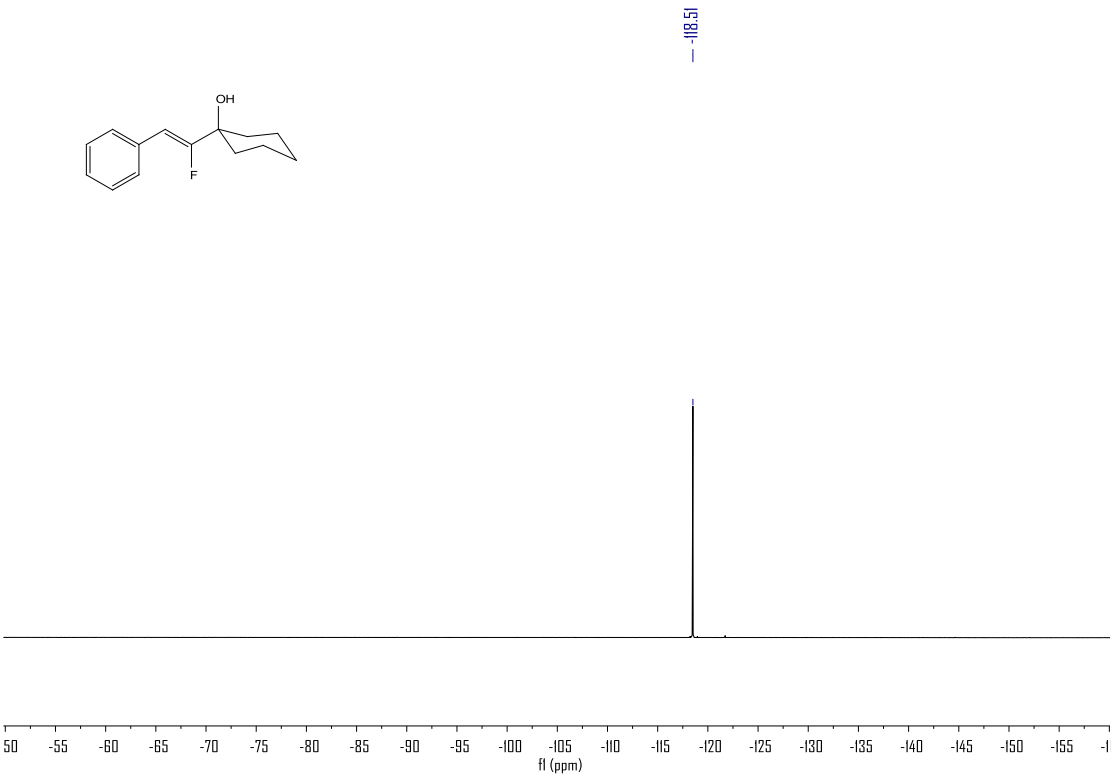


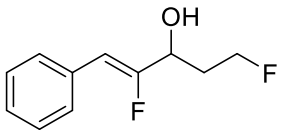
(Z)-1-(1-fluoro-2-phenylvinyl)cyclohexan-1-ol

Following the general procedure (**product 34**, **pale-yellow liquid, 17.0 mg, 40%,** Z/E > 20:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (10:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.50 (d, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.24 (d, *J* = 12.3 Hz, 1H), 5.88 (d, *J* = 40.6 Hz, 1H), 1.84 (td, *J* = 12.5, 11.5, 4.1 Hz, 2H), 1.77 – 1.71 (m, 4H), 1.69 – 1.58 (m, 4H), 1.33 – 1.25 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 164.28 (d, *J* = 270.4 Hz), 133.27, 128.73 (d, *J* = 7.4 Hz), 128.44, 127.11 (d, *J* = 2.4 Hz), 103.86 (d, *J* = 7.6 Hz), 72.05 (d, *J* = 27.1 Hz), 34.72, 25.31, 21.51. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -118.51.

HRMS (ESI) calcd for $C_{14}H_{17}FO$ ($M+Na^+$): 243.1156; found: 243.1163.


7.51
7.51
7.49
7.34
7.32
7.31
7.26
7.24
7.24
7.22
5.83
5.83
1.88
1.87
1.84
1.83
1.81
1.80
1.76
1.75
1.74
1.73
1.72
1.68
1.68
1.66
1.65
1.64
1.63
1.62
1.61
1.59
1.59
1.33
1.32
1.32
1.31
1.30
1.30
1.29
1.28
1.28
1.26
1.26
0.00
OH
F
2.01
2.01
1.02
1.00
2.09
4.01
4.12
1.08
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
165.62
162.93
133.27
128.77
128.70
128.44
127.12
127.10
103.90
103.82
72.18
71.91
34.72
25.31
21.51
OH
F
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

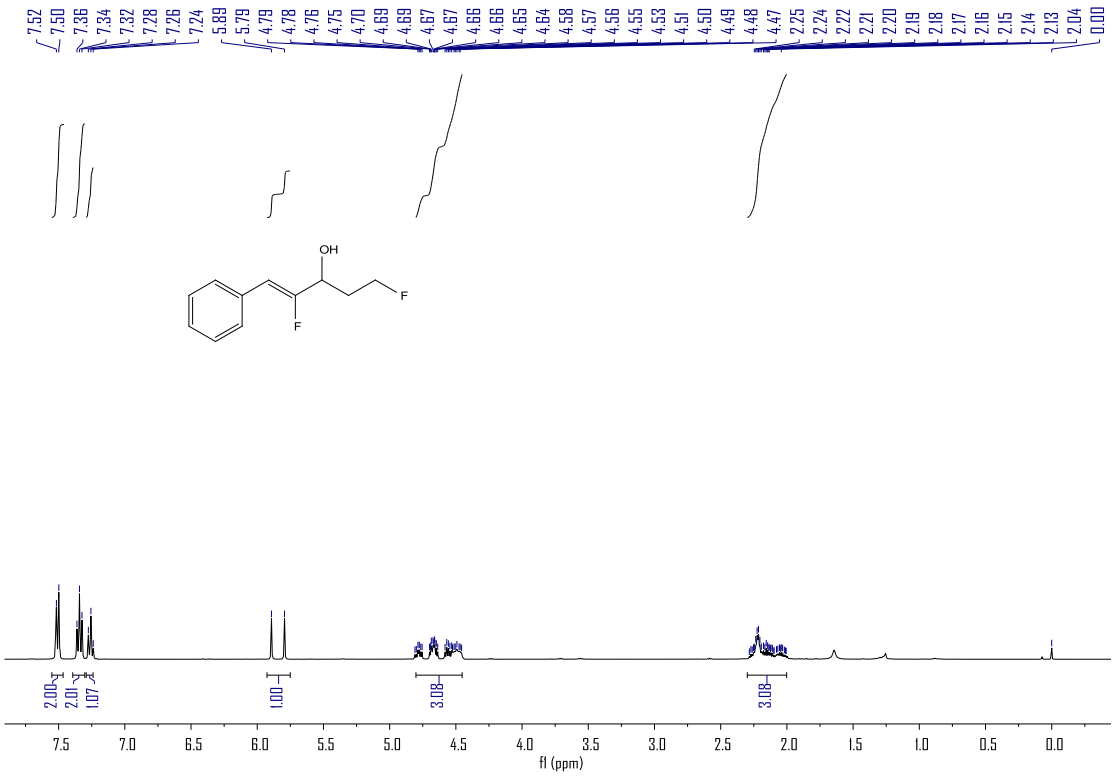


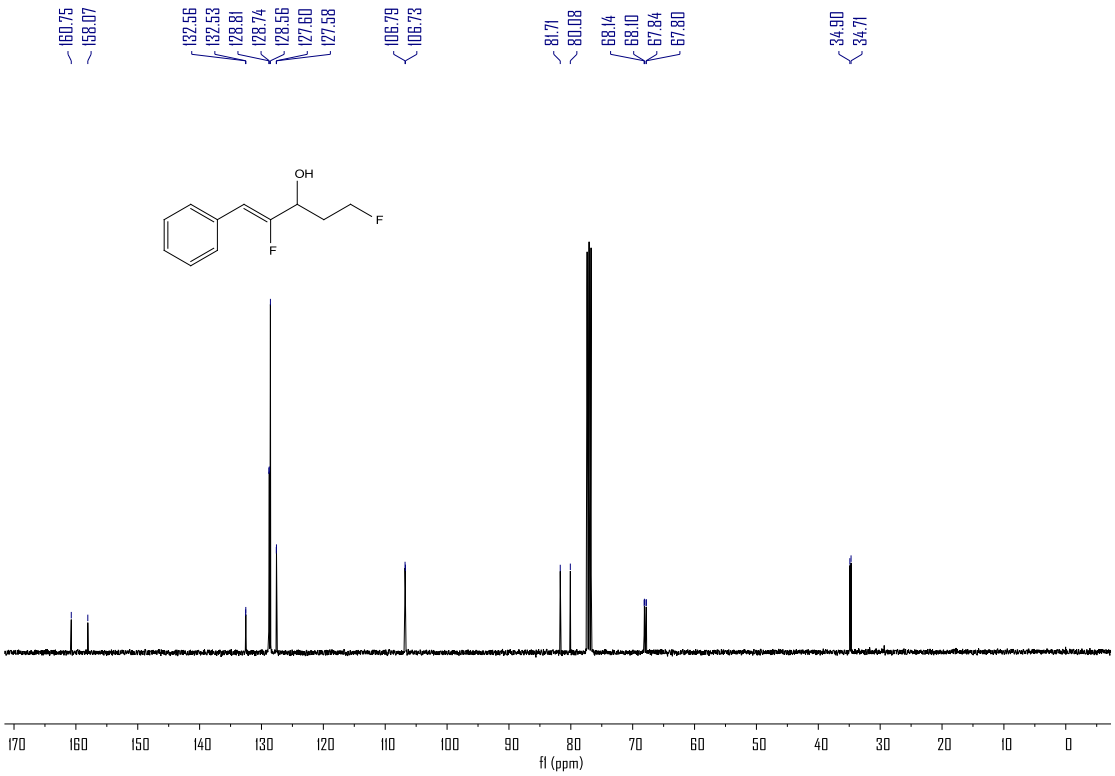


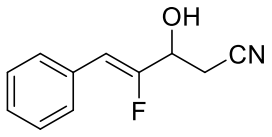
(Z)-2,5-difluoro-1-phenylpent-1-en-3-ol

Following the general procedure (**product 35**, **pale-yellow liquid, 17.8 mg, 45%,** Z/E > 20:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (10:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.51 (d, *J* = 7.2 Hz, 2H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.27 (d, *J* = 7.8 Hz, 1H), 5.84 (d, *J* = 39.5 Hz, 1H), 4.84 – 4.44 (m, 3H), 2.34 – 1.98 (m, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 159.41 (d, *J* = 268.9 Hz), 132.55 (d, *J* = 2.6 Hz), 128.77 (d, *J* = 7.3 Hz), 128.56, 127.59 (d, *J* = 2.4 Hz), 106.76 (d, *J* = 6.4 Hz), 80.89 (d, *J* = 163.9 Hz), 67.97 (dd, *J* = 30.8, 4.2 Hz), 34.80 (d, *J* = 19.4 Hz). **^{19}F NMR** (No decoupling) (376 MHz, Chloroform-*d*) δ -118.68 (dd, *J* = 39.4, 14.9 Hz), -221.44 (tdd, *J* = 47.0, 30.6, 23.2 Hz).

HRMS (ESI) calcd for $C_{11}H_{12}F_2NaO$ ($M+Na^+$): 221.0748; found: 221.0756.


7.52
7.50
7.36
7.34
7.32
7.28
7.26
7.24
5.89
5.79
4.79
4.78
4.76
4.75
4.70
4.69
4.69
4.67
4.67
4.66
4.66
4.65
4.64
4.58
4.57
4.56
4.55
4.53
4.51
4.50
4.49
4.48
4.47
2.25
2.24
2.22
2.21
2.20
2.19
2.18
2.17
2.16
2.15
2.14
2.13
2.04
0.00
OH
F
F
2.00
2.01
1.07
1.00
3.08
3.08
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

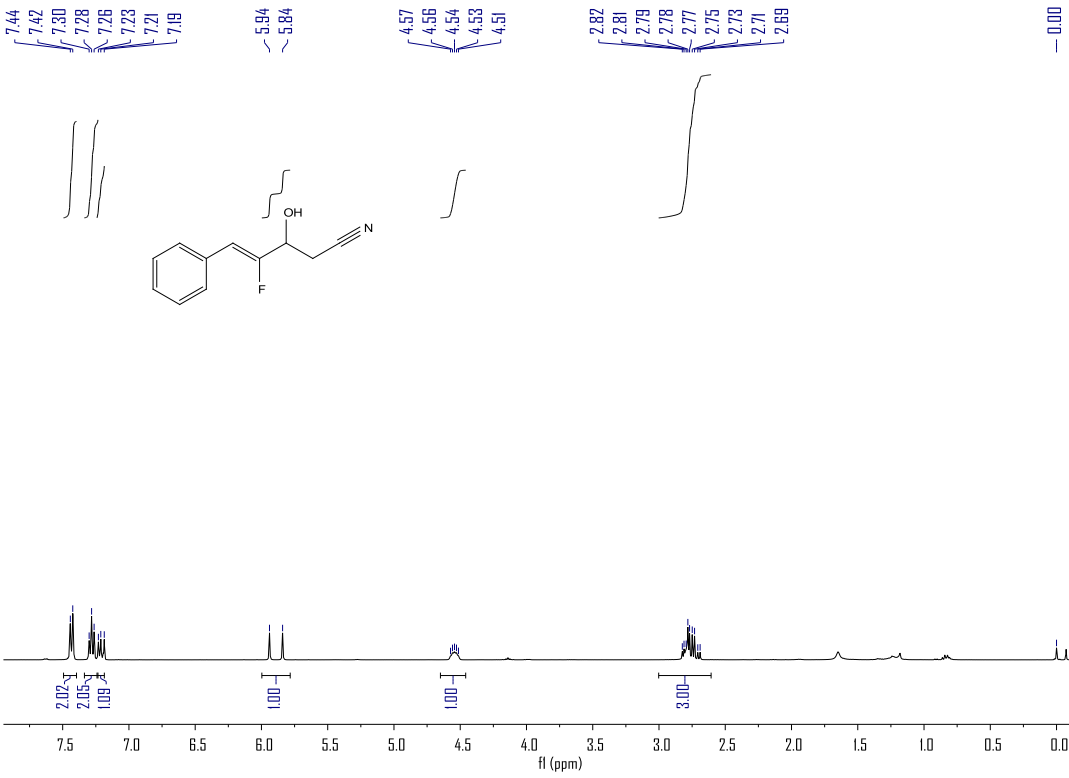


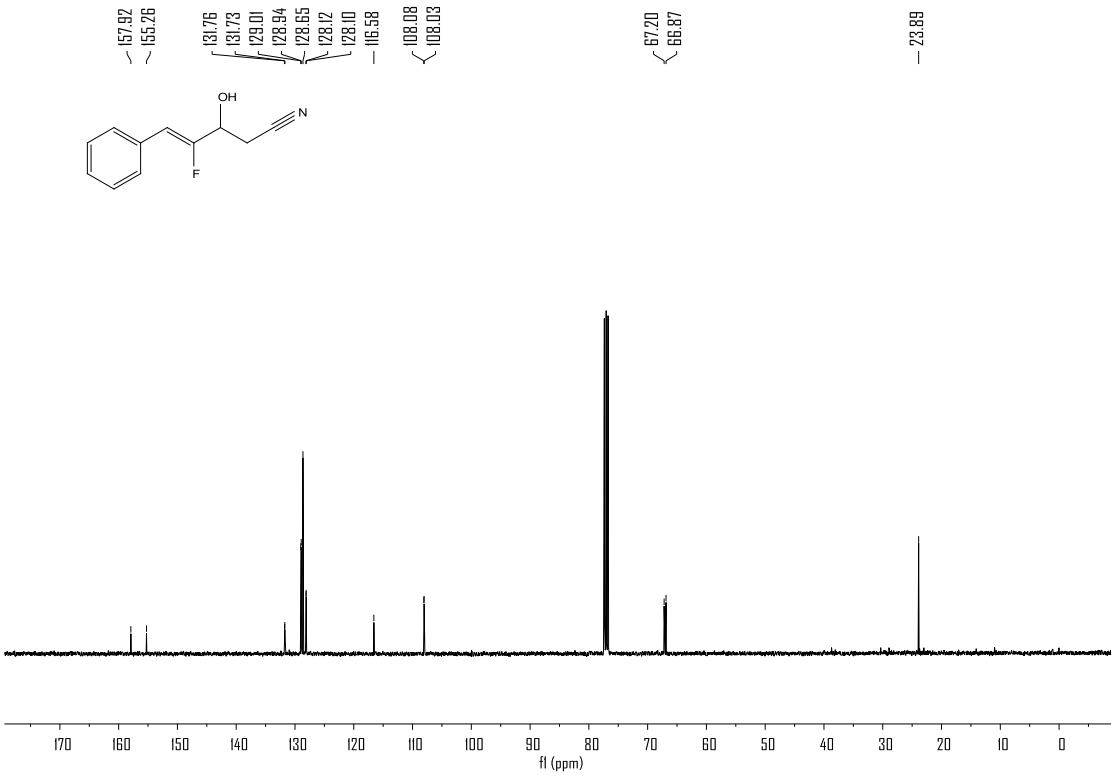


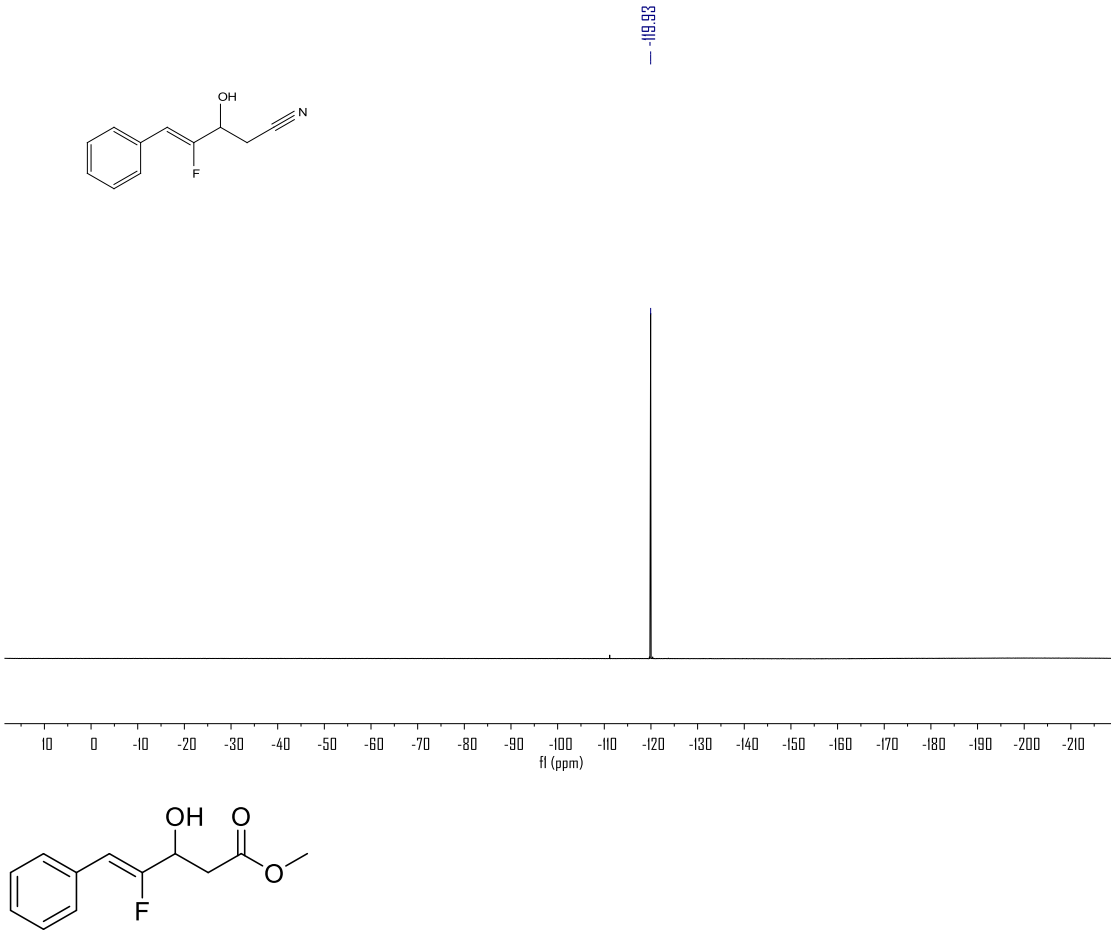
(Z)-4-fluoro-3-hydroxy-5-phenylpent-4-enenitrile

Following the general procedure (**product 36**, **pale-yellow liquid, 16.3 mg, 43%,** Z/E > 20:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (10:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.43 (d, *J* = 7.3 Hz, 2H), 7.28 (t, *J* = 7.5 Hz, 2H), 7.24 – 7.18 (m, 1H), 5.89 (d, *J* = 39.5 Hz, 1H), 4.54 (dt, *J* = 12.0, 5.9 Hz, 1H), 2.88 – 2.69 (m, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 156.59 (d, *J* = 267.9 Hz), 131.75 (d, *J* = 2.7 Hz), 128.98 (d, *J* = 7.2 Hz), 128.65, 128.11 (d, *J* = 2.4 Hz), 116.58, 108.05 (d, *J* = 5.4 Hz), 67.03 (d, *J* = 32.6 Hz), 23.89. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -119.93.

HRMS (ESI) calcd for $C_{11}H_{10}FNNaO$ ($M+Na^+$): 214.0639; found: 214.0645.



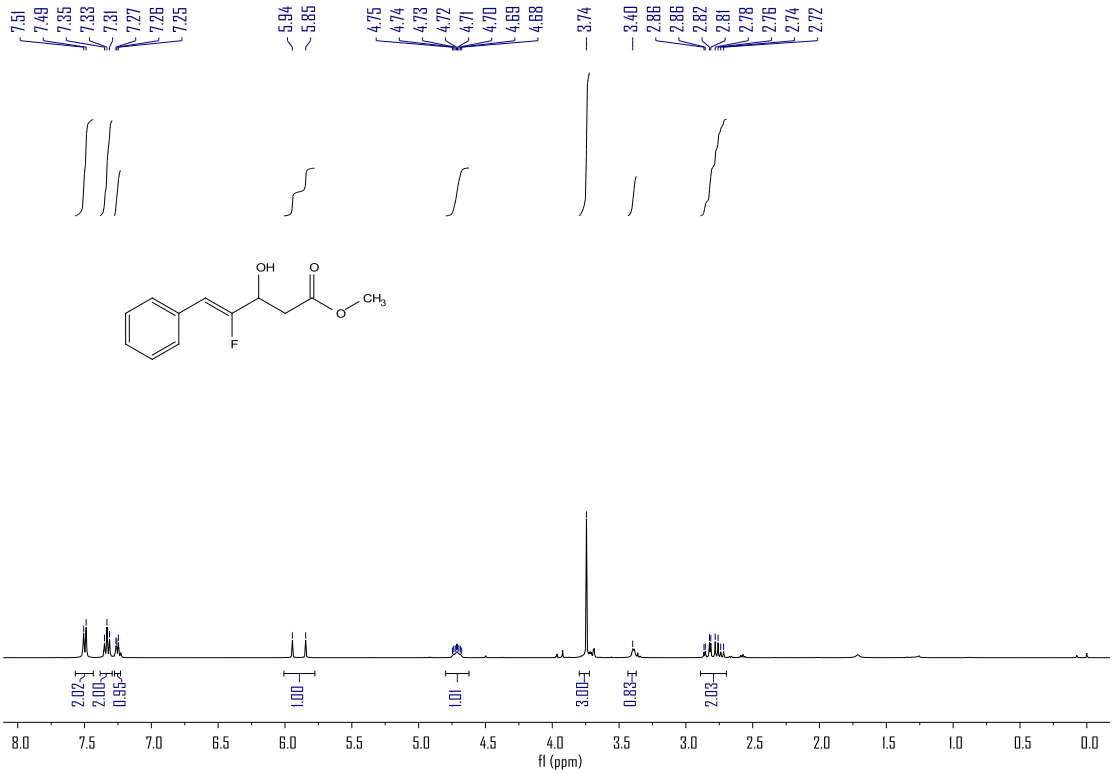


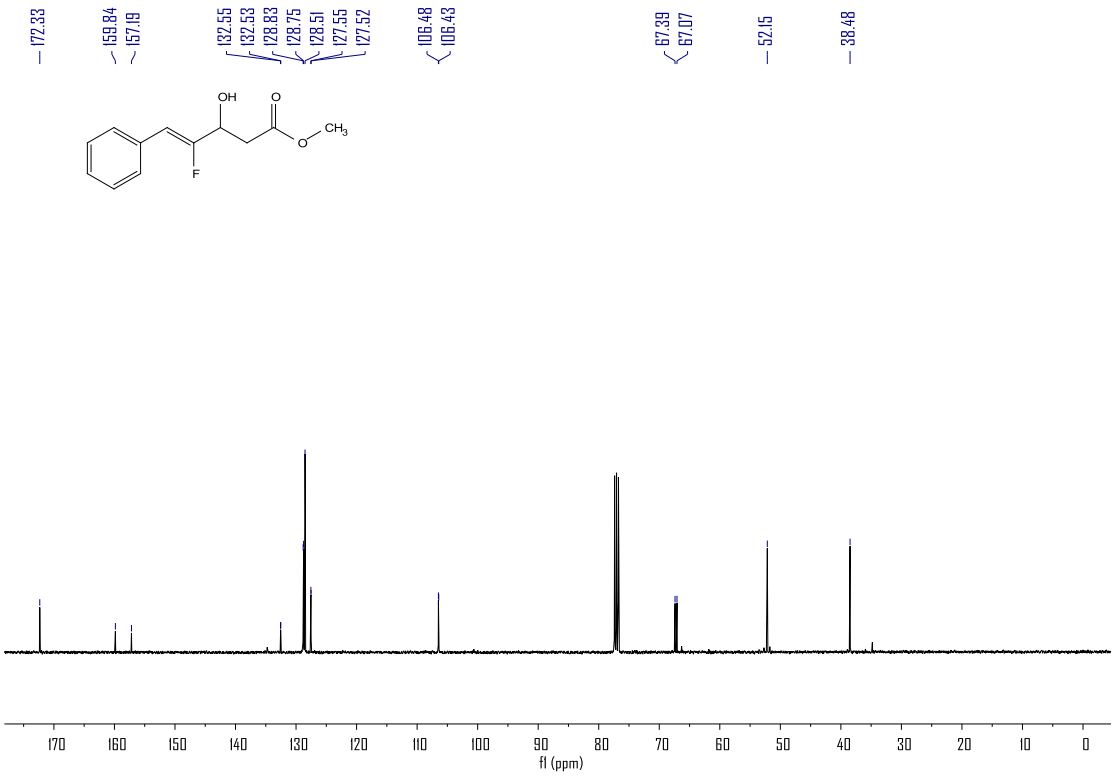


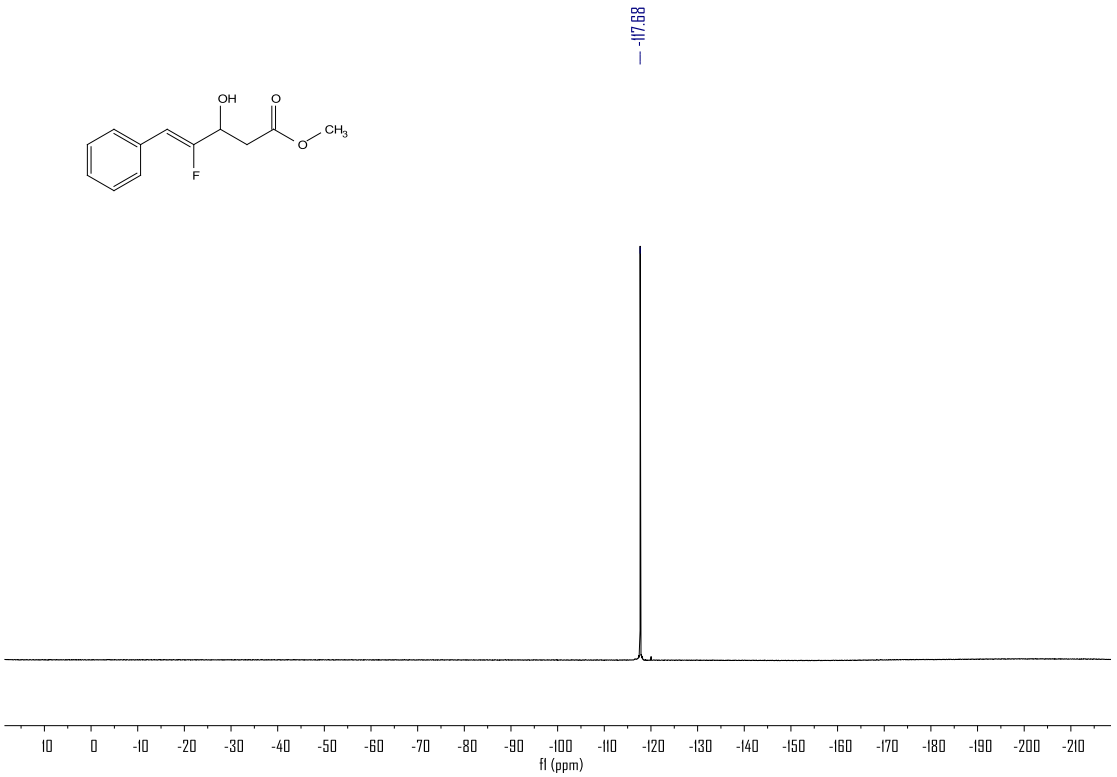
Methyl (Z)-4-fluoro-3-hydroxy-5-phenylpent-4-enoate

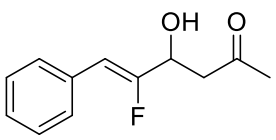
Following the general procedure (**product 37**, **pale-yellow liquid, 21.1 mg, 47%,** Z/E > 20:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (7:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.50 (d, *J* = 7.3 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.28 – 7.22 (m, 1H), 5.89 (d, *J* = 39.9 Hz, 1H), 4.71 (td, *J* = 8.4, 4.5 Hz, 1H), 3.74 (s, 3H), 3.40 (s, 1H), 2.89 – 2.70 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 172.33, 158.52 (d, *J* = 267.4 Hz), 132.54 (d, *J* = 2.6 Hz), 128.79 (d, *J* = 7.2 Hz), 128.51, 127.54 (d, *J* = 2.3 Hz), 106.45 (d, *J* = 5.6 Hz), 67.23 (d, *J* = 32.7 Hz), 52.15, 38.48. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -117.68.

HRMS (ESI) calcd for $C_{12}H_{13}FNaO_3$ ($M+Na^+$): 247.0741; found: 247.0745.





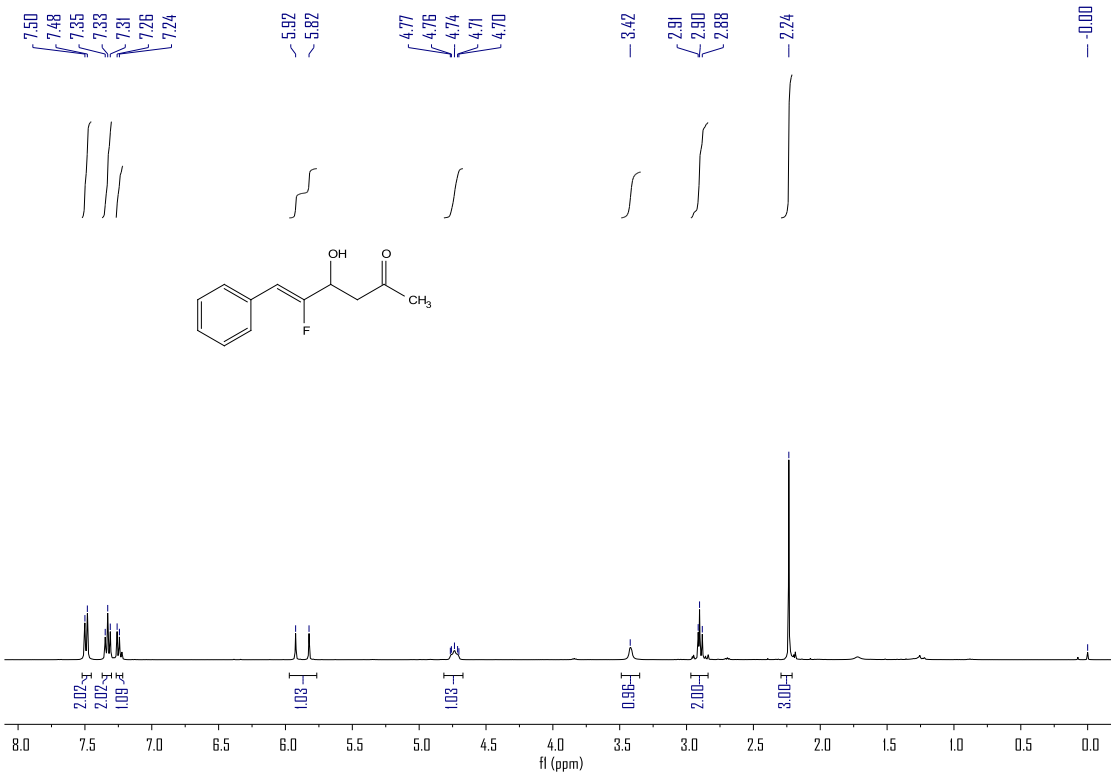


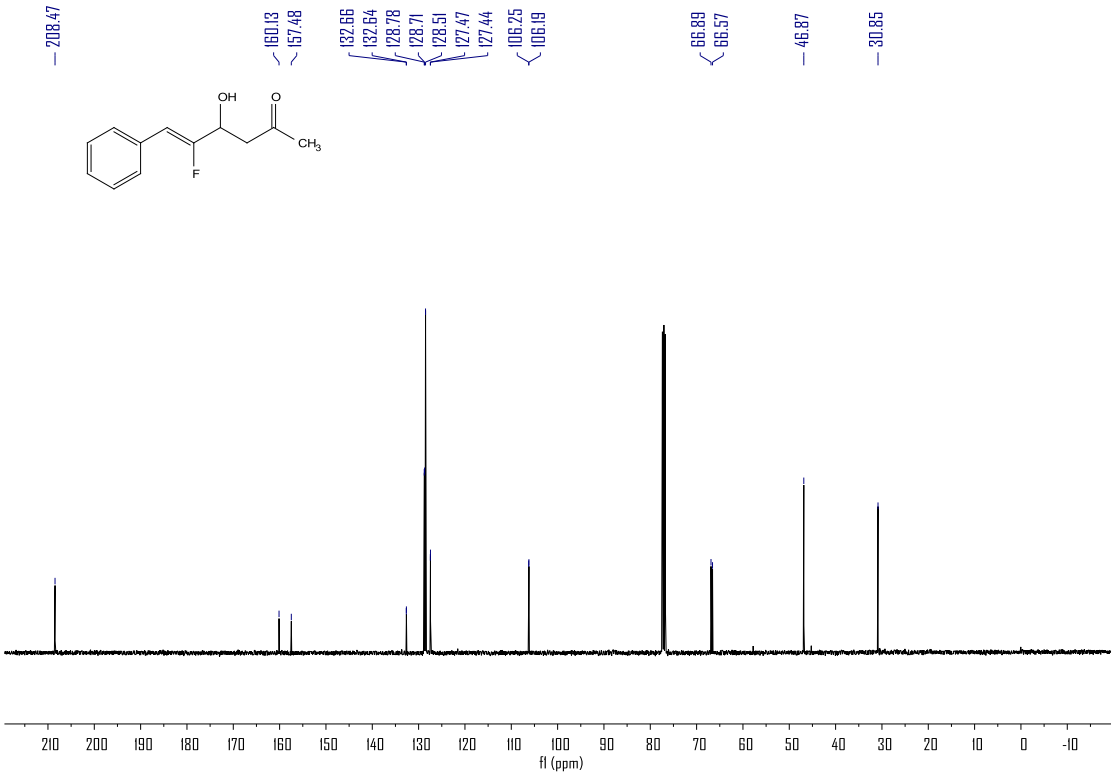


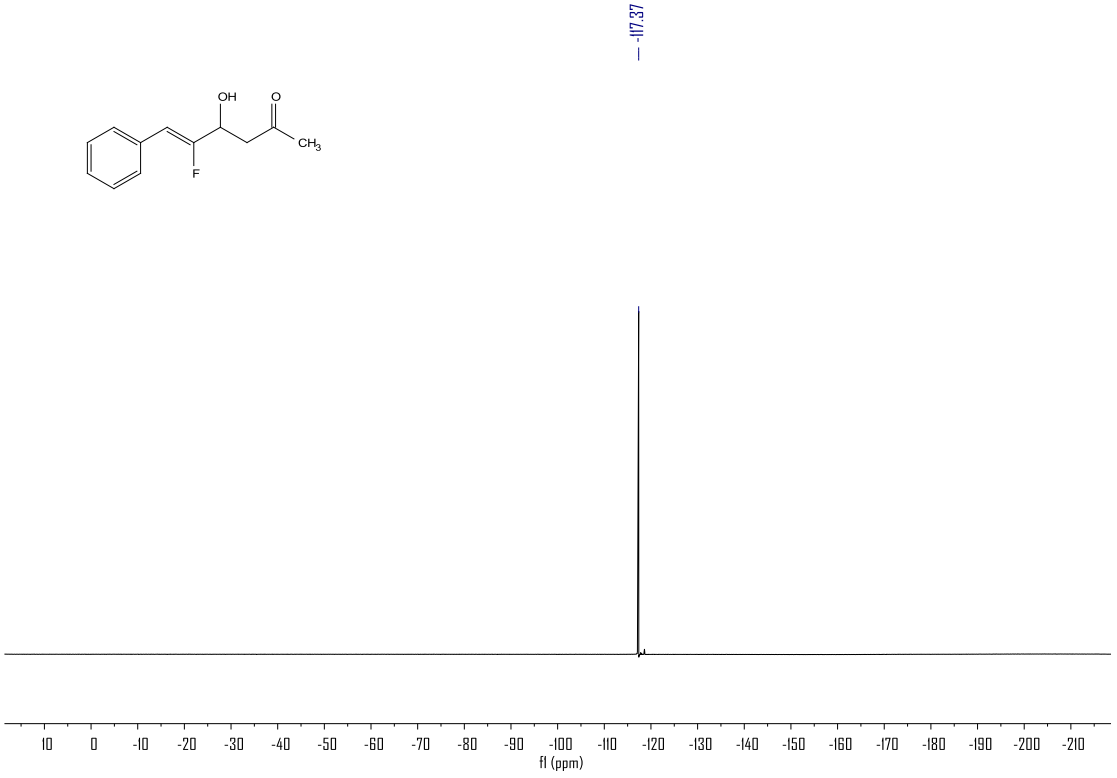
(Z)-5-fluoro-4-hydroxy-6-phenylhex-5-en-2-one

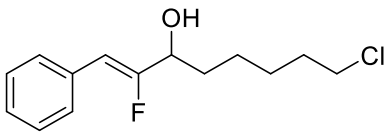
Following the general procedure (**product 38**, **pale-yellow liquid, 24.2 mg, 58%,** Z/E > 20:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (7:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.49 (d, *J* = 7.3 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.25 (d, *J* = 6.9 Hz, 1H), 5.87 (d, *J* = 40.1 Hz, 1H), 4.80 – 4.68 (m, 1H), 3.42 (s, 1H), 3.05 – 2.77 (m, 2H), 2.24 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 208.47, 158.80 (d, *J* = 266.6 Hz), 132.65 (d, *J* = 2.5 Hz), 128.75 (d, *J* = 7.1 Hz), 128.51, 127.45 (d, *J* = 2.4 Hz), 106.22 (d, *J* = 5.6 Hz), 66.73 (d, *J* = 32.8 Hz), 46.87, 30.85. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -117.37.

HRMS (ESI) calcd for $C_{12}H_{13}FNaO_2$ ($M+Na^+$): 231.0792; found: 231.0785.





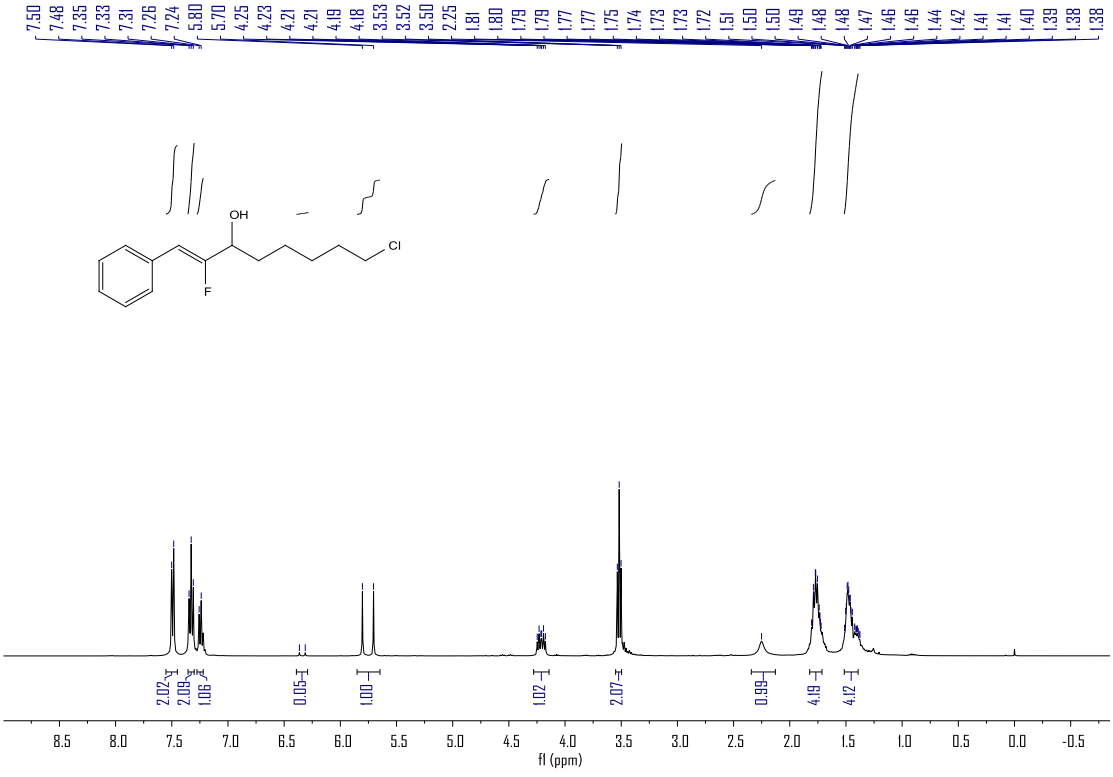


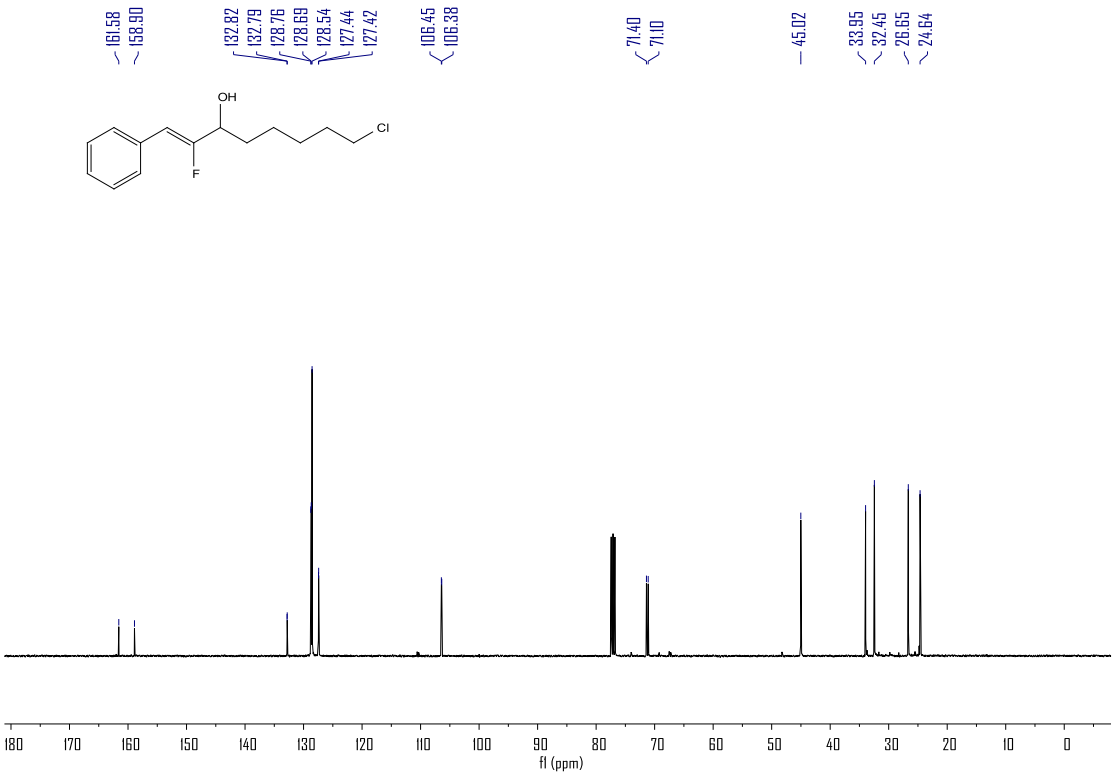


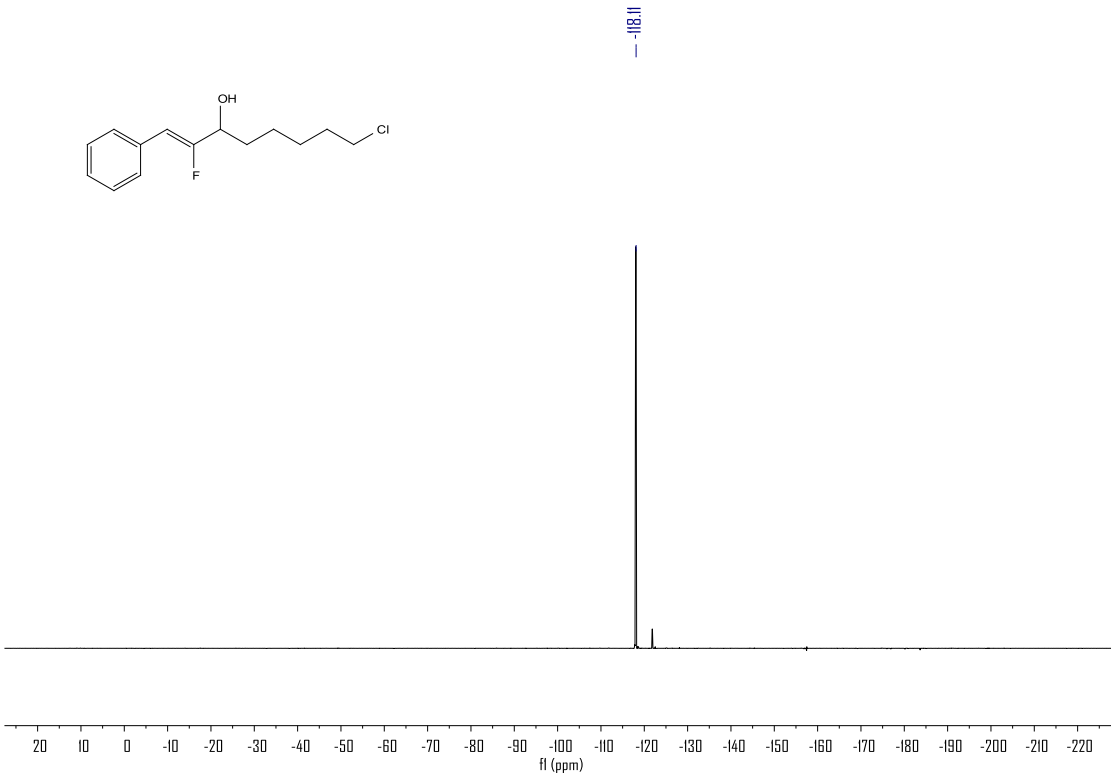
(Z)-8-chloro-2-fluoro-1-phenyloct-1-en-3-ol

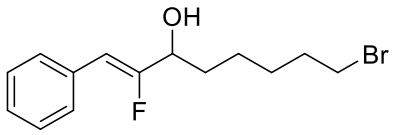
Following the general procedure (**product 39**, **pale-yellow liquid, 21.0 mg, 41%,** Z/E = 20:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (10:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.49 (d, *J* = 7.4 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.25 (d, *J* = 7.4 Hz, 1H), 5.75 (d, *J* = 39.7 Hz, 1H), 4.21 (dt, *J* = 15.9, 6.6 Hz, 1H), 3.52 (t, *J* = 6.6 Hz, 2H), 2.25 (s, 1H), 1.77 (ddt, *J* = 15.2, 9.0, 4.5 Hz, 4H), 1.54 – 1.37 (m, 4H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 160.24 (d, *J* = 269.7 Hz), 132.80 (d, *J* = 2.5 Hz), 128.72 (d, *J* = 7.3 Hz), 128.54, 127.43 (d, *J* = 2.5 Hz), 106.41 (d, *J* = 6.6 Hz), 71.25 (d, *J* = 30.1 Hz), 45.02, 33.95, 32.45, 26.65, 24.64. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -118.11.

HRMS (ESI) calcd for $C_{14}H_{18}ClFNaO$ ($M+Na^+$): 279.0922; found: 279.0925.





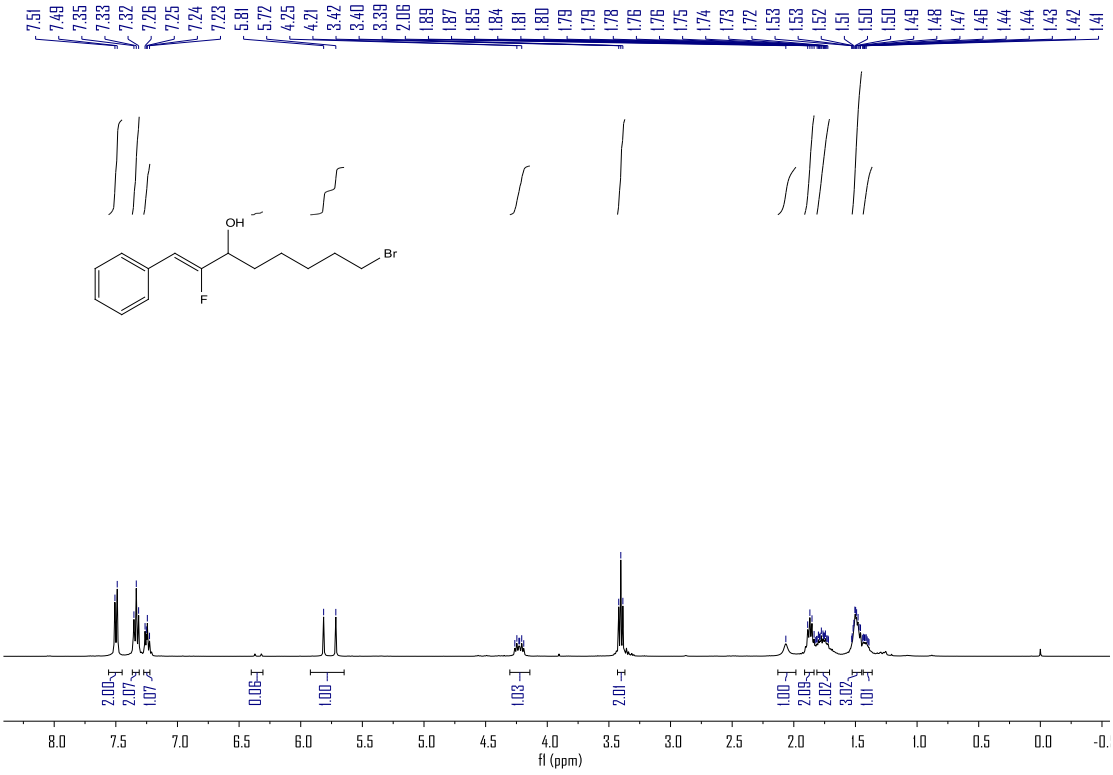


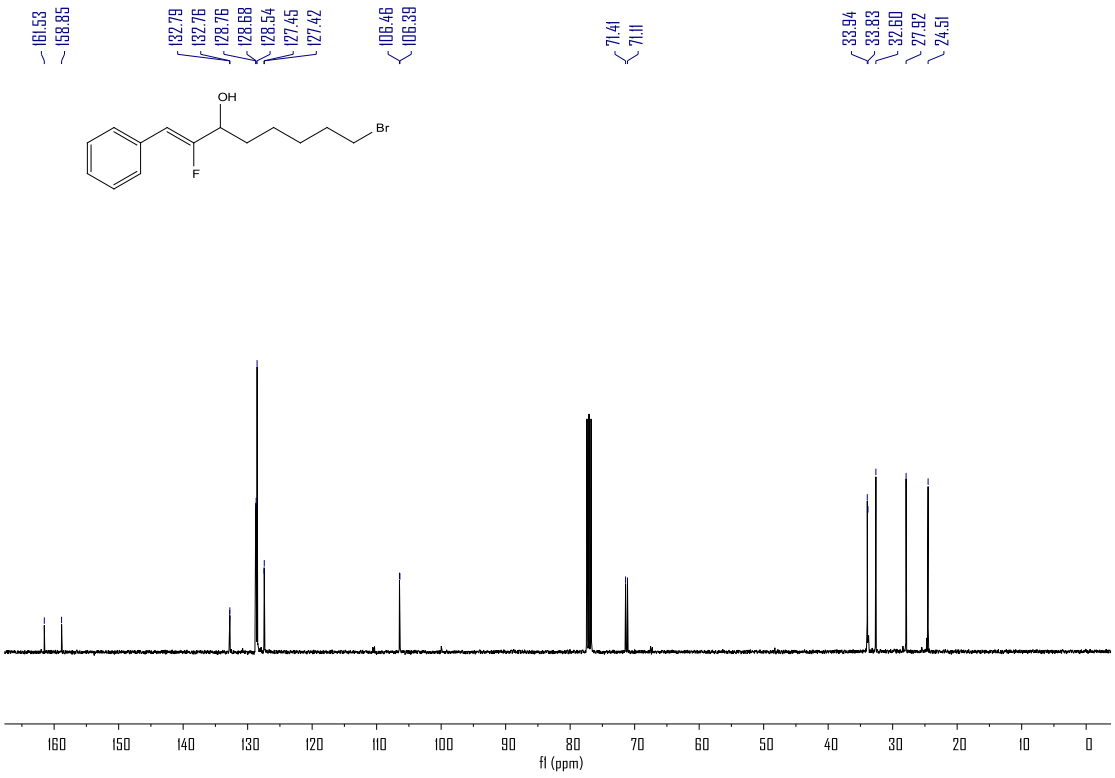


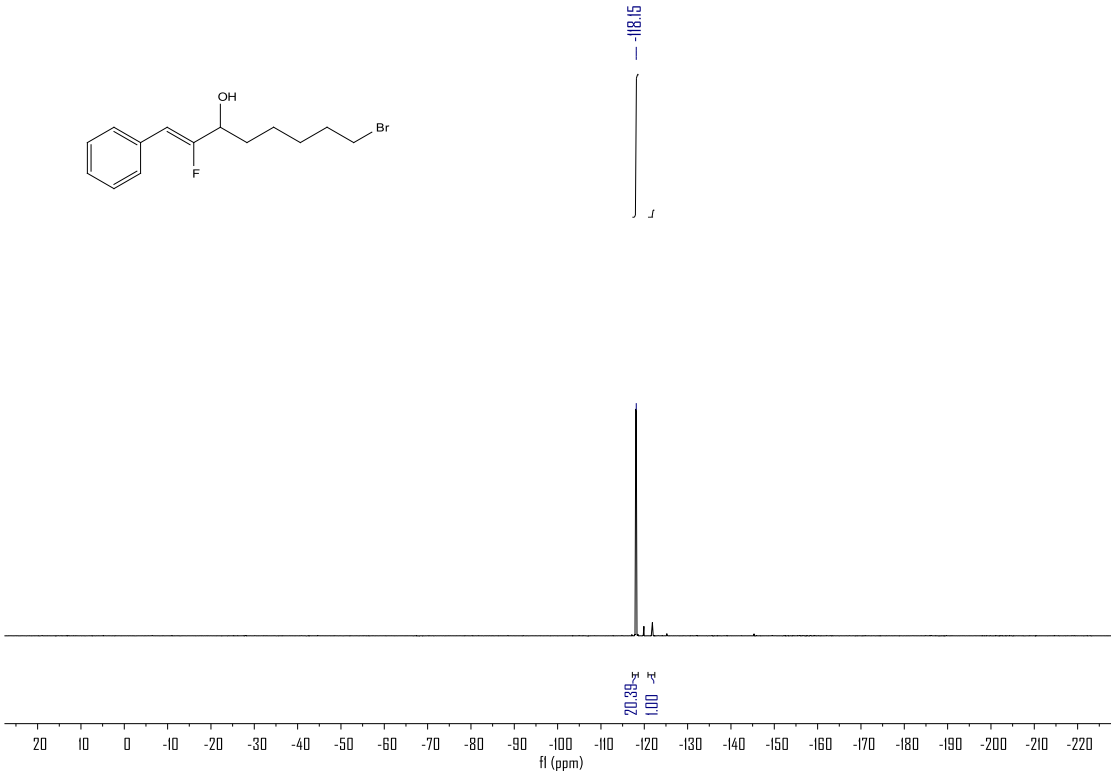
(Z)-8-bromo-2-fluoro-1-phenyloct-1-en-3-ol

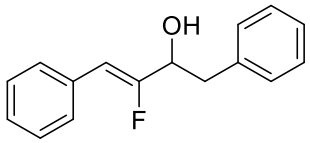
Following the general procedure (**product 40**, **pale-yellow liquid, 22.9 mg, 38%,** Z/E = 17:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (10:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.50 (d, *J* = 7.4 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.25 (dd, *J* = 8.9, 5.6 Hz, 1H), 5.76 (d, *J* = 39.6 Hz, 1H), 4.23 (dt, *J* = 15.8, 6.6 Hz, 1H), 3.40 (t, *J* = 6.7 Hz, 2H), 2.06 (s, 1H), 1.86 (q, *J* = 7.0 Hz, 2H), 1.82 – 1.68 (m, 2H), 1.50 (pd, *J* = 7.9, 6.2, 3.1 Hz, 3H), 1.42 (ddt, *J* = 9.0, 6.0, 2.5 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 160.19 (d, *J* = 269.6 Hz), 132.77 (d, *J* = 2.6 Hz), 128.72 (d, *J* = 7.2 Hz), 128.54, 127.44 (d, *J* = 2.5 Hz), 106.43 (d, *J* = 6.6 Hz), 71.26 (d, *J* = 30.1 Hz), 33.94, 33.83, 32.60, 27.92, 24.51. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -118.15.

HRMS (ESI) calcd for $C_{14}H_{18}BrFNaO$ ($M+Na^+$): 323.0417; found: 323.0425.





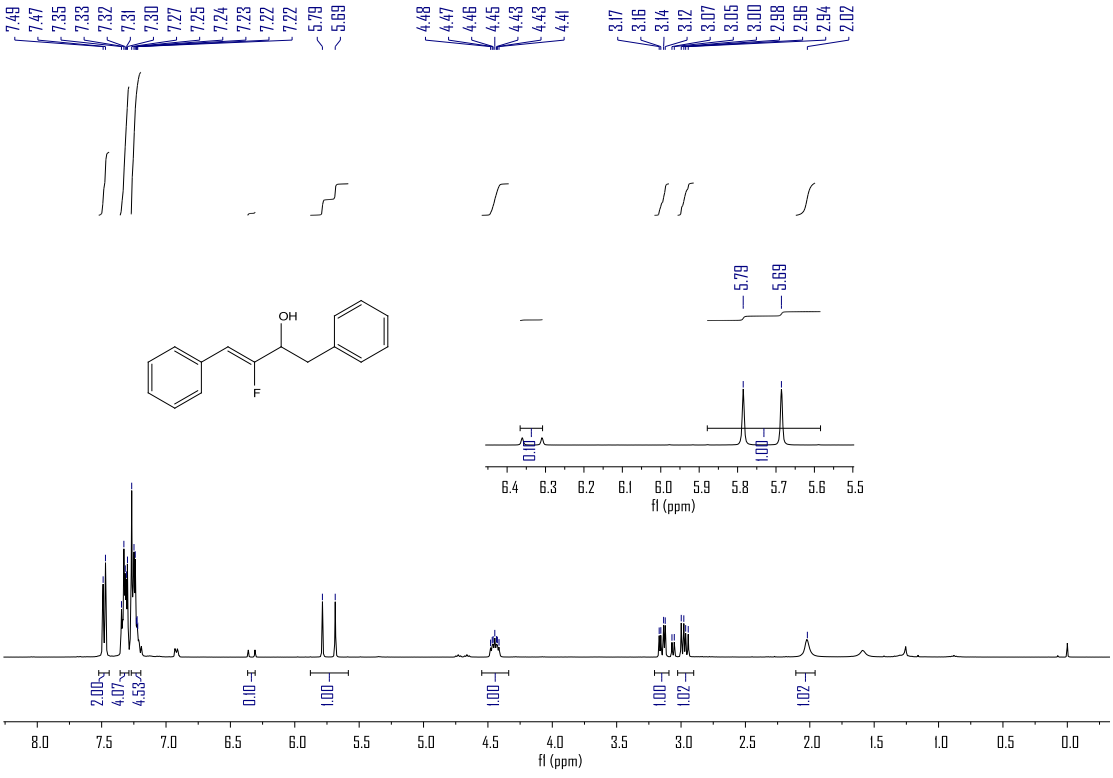


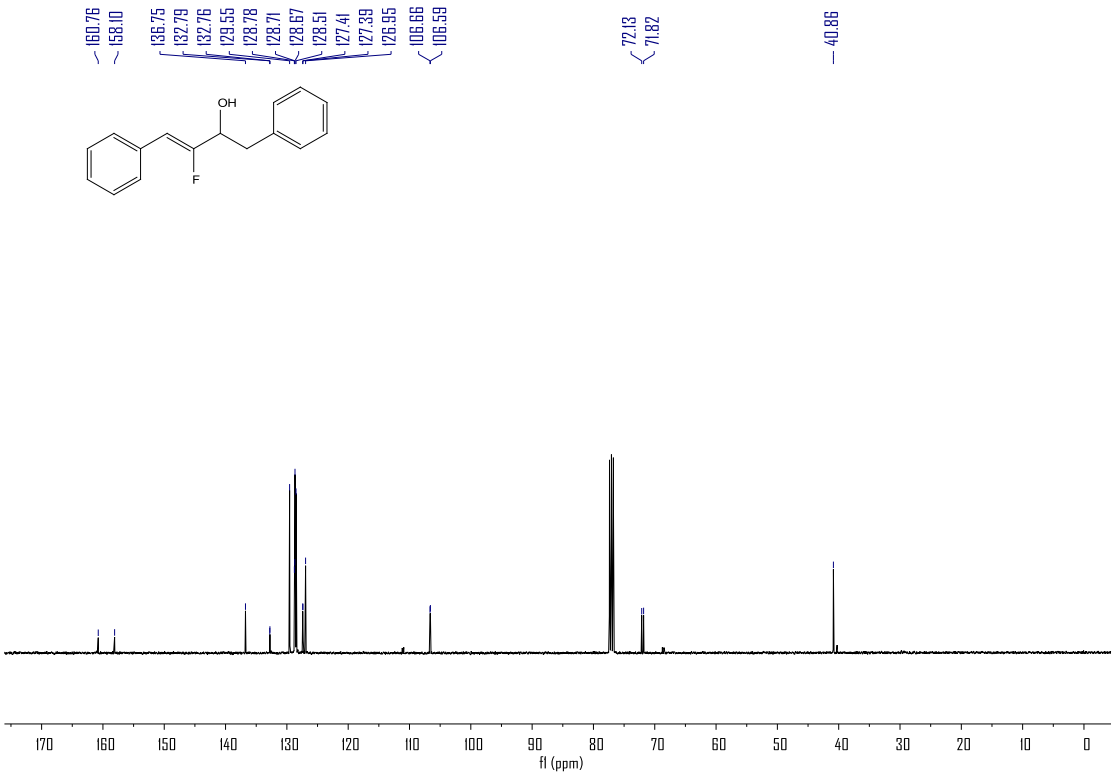


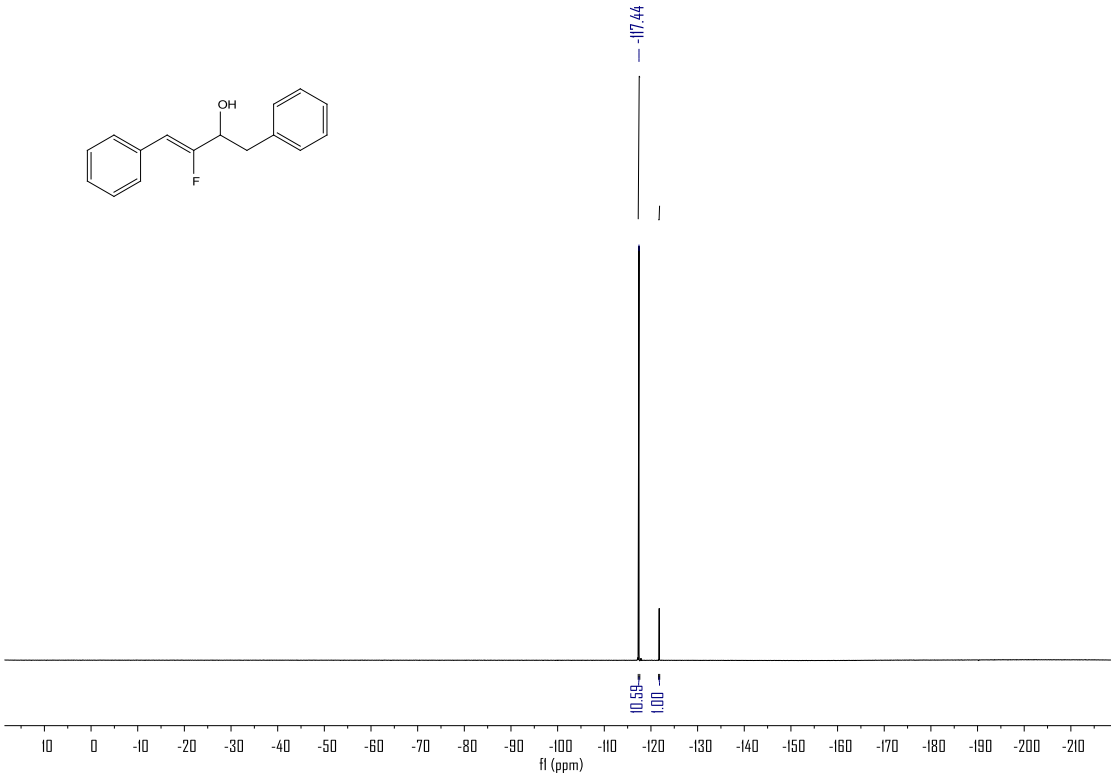
(Z)-3-fluoro-1,4-diphenylbut-3-en-2-ol

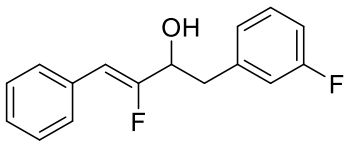
Following the general procedure (**product 41**, **pale-yellow liquid, 32.0 mg, 66%,** Z/E = 10:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (10:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.48 (d, *J* = 7.3 Hz, 2H), 7.36 – 7.29 (m, 4H), 7.28 – 7.20 (m, 4H), 5.74 (d, *J* = 39.8 Hz, 1H), 4.45 (ddd, *J* = 13.1, 7.9, 5.0 Hz, 1H), 3.15 (dd, *J* = 13.7, 5.1 Hz, 1H), 2.97 (dd, *J* = 13.7, 8.0 Hz, 1H), 2.02 (s, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 159.43 (d, *J* = 268.5 Hz), 136.75, 132.78 (d, *J* = 2.5 Hz), 129.55, 128.74 (d, *J* = 7.1 Hz), 128.67, 128.51, 127.40 (d, *J* = 2.3 Hz), 126.95, 106.62 (d, *J* = 6.2 Hz), 71.97 (d, *J* = 31.3 Hz), 40.86. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -117.44.

HRMS (ESI) calcd for $C_{16}H_{15}FNaO$ ($M+Na^+$): 265.0999; found: 265.0992.





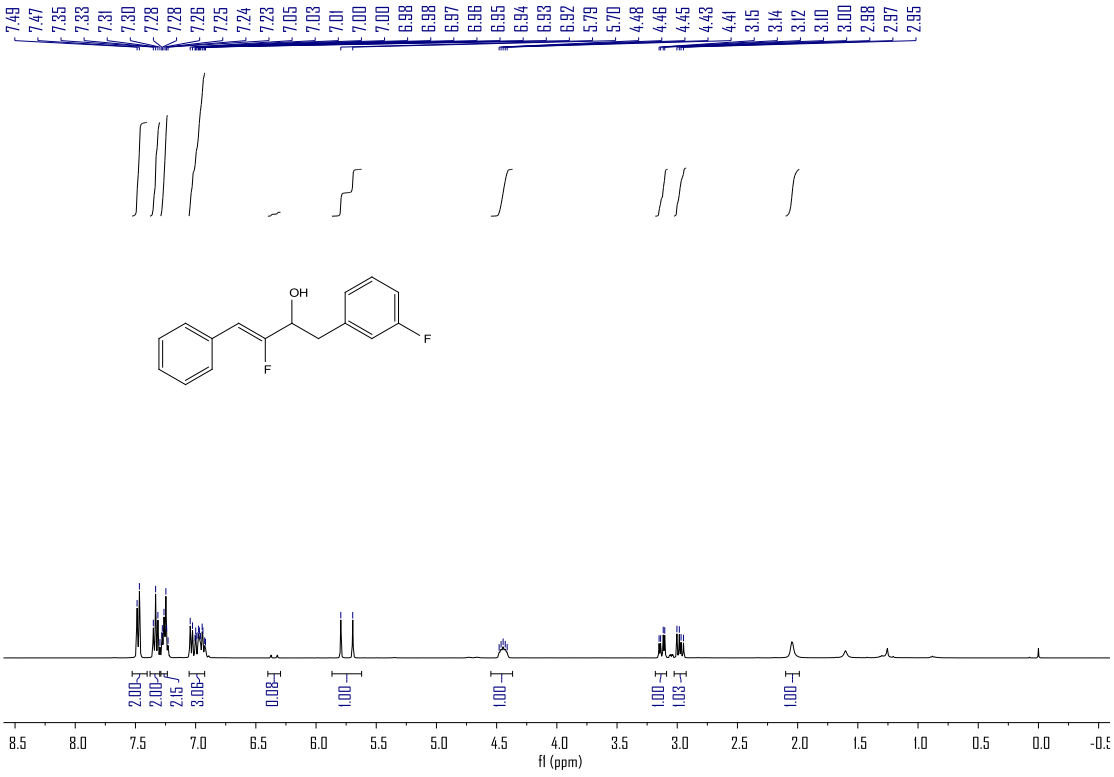


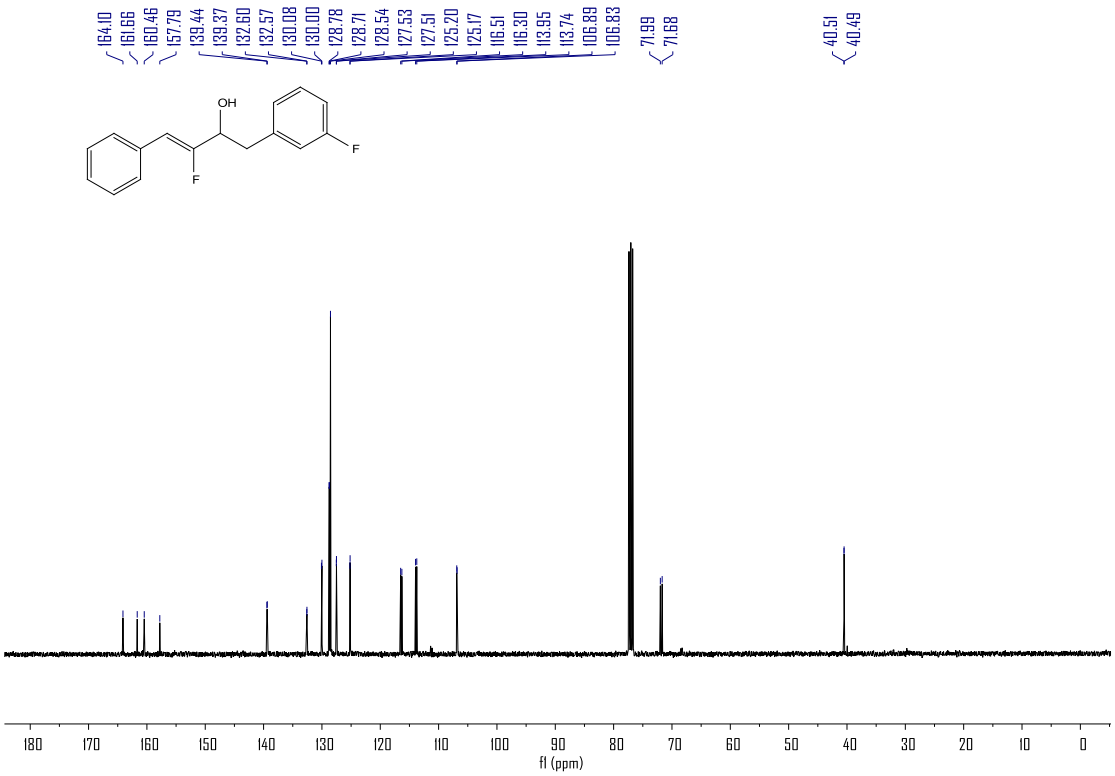


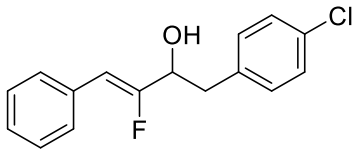
(Z)-3-fluoro-1-(3-fluorophenyl)-4-phenylbut-3-en-2-ol

Following the general procedure (**product 42**, **pale-yellow liquid, 32.1 mg, 62%,** Z/E = 13:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (10:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.48 (d, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.25 (q, *J* = 7.2, 6.4 Hz, 2H), 7.05 – 6.94 (m, 3H), 5.74 (d, *J* = 39.7 Hz, 1H), 4.45 (dt, *J* = 13.4, 6.5 Hz, 1H), 3.13 (dd, *J* = 13.8, 5.1 Hz, 1H), 2.98 (dd, *J* = 13.8, 8.0 Hz, 1H), 2.05 (s, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 162.88 (d, *J* = 246.0 Hz), 159.12 (d, *J* = 268.5 Hz), 139.40 (d, *J* = 7.4 Hz), 132.58 (d, *J* = 2.6 Hz), 130.04 (d, *J* = 8.3 Hz), 128.75 (d, *J* = 7.2 Hz), 128.54 , 127.52 (d, *J* = 2.3 Hz), 125.19 (d, *J* = 2.9 Hz), 116.40 (d, *J* = 21.1 Hz), 113.85 (d, *J* = 20.9 Hz), 106.86 (d, *J* = 6.1 Hz), 71.84 (d, *J* = 31.2 Hz), 40.50 (d, *J* = 1.8 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -113.15, -117.84.

HRMS (ESI) calcd for $C_{16}H_{14}F_2NaO$ ($M+Na^+$): 283.0905; found: 283.0911.



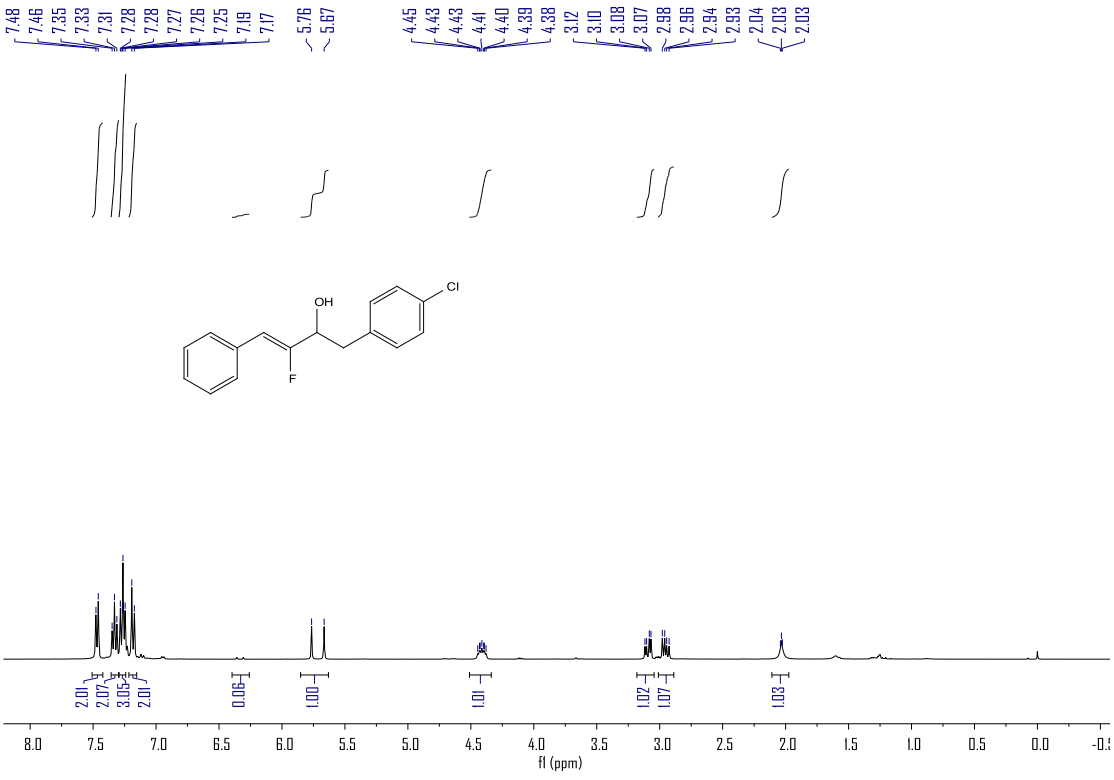


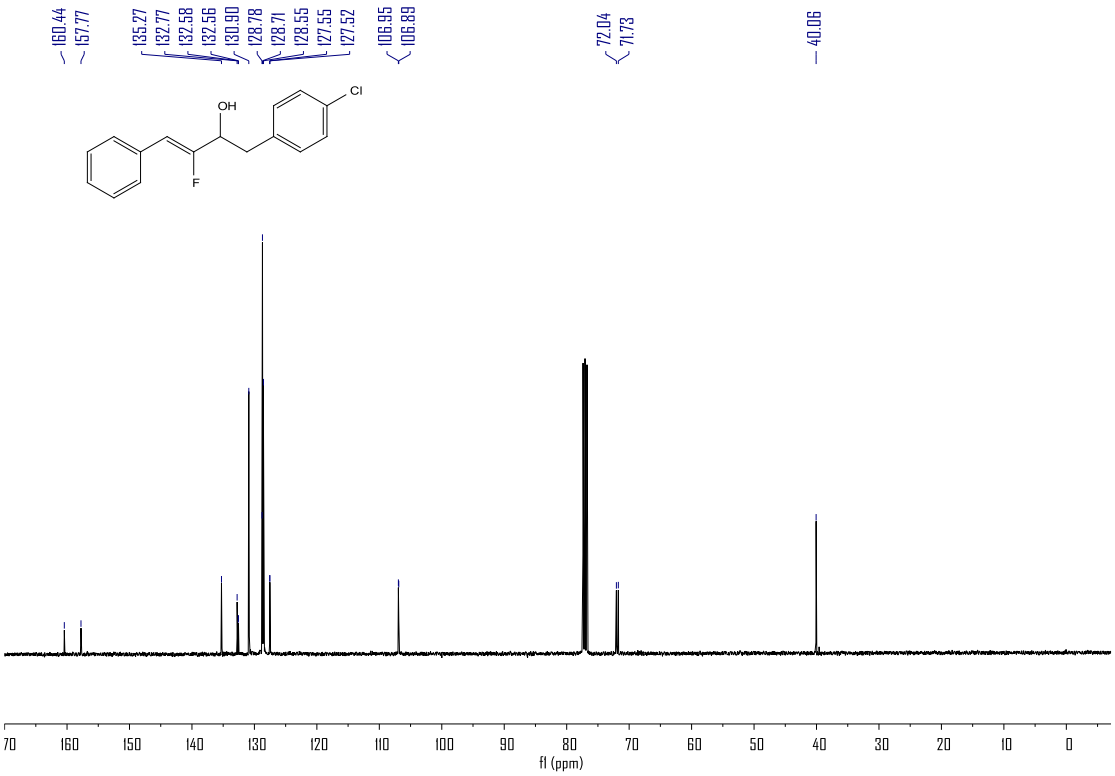


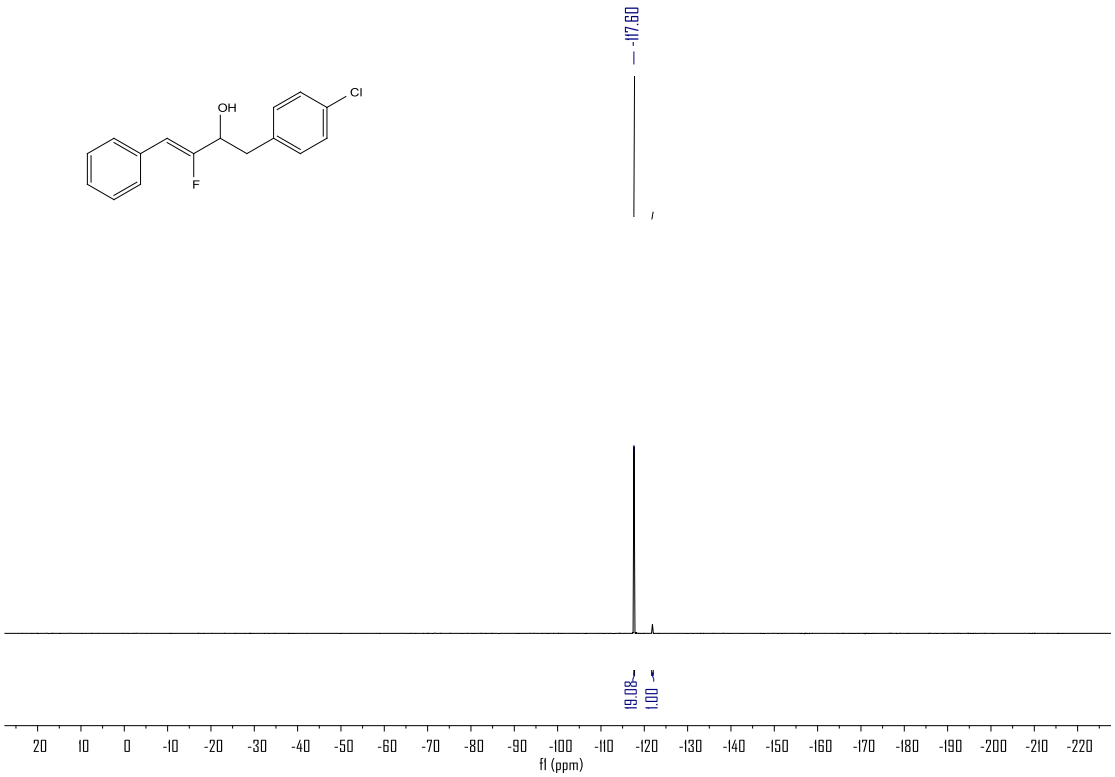
(Z)-1-(4-chlorophenyl)-3-fluoro-4-phenylbut-3-en-2-ol

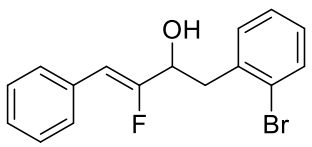
Following the general procedure (**product 43**, **pale-yellow liquid, 32.5 mg, 59%,** Z/E = 15:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (10:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.47 (d, *J* = 7.4 Hz, 2H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.26 (t, *J* = 7.6 Hz, 3H), 7.18 (d, *J* = 8.2 Hz, 2H), 5.72 (d, *J* = 39.8 Hz, 1H), 4.41 (ddd, *J* = 13.2, 7.6, 5.3 Hz, 1H), 3.09 (dd, *J* = 13.8, 5.3 Hz, 1H), 2.95 (dd, *J* = 13.8, 7.7 Hz, 1H), 2.07 – 1.95 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 159.10 (d, *J* = 268.5 Hz), 135.27, 132.77, 132.57 (d, *J* = 2.5 Hz), 130.90, 128.78, 128.71, 128.55, 127.54 (d, *J* = 2.3 Hz), 106.92 (d, *J* = 6.2 Hz), 71.89 (d, *J* = 31.2 Hz), 40.06. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -117.60.

HRMS (ESI) calcd for $C_{16}H_{14}ClFNaO$ ($M+Na^+$): 299.0609; found: 299.0607.





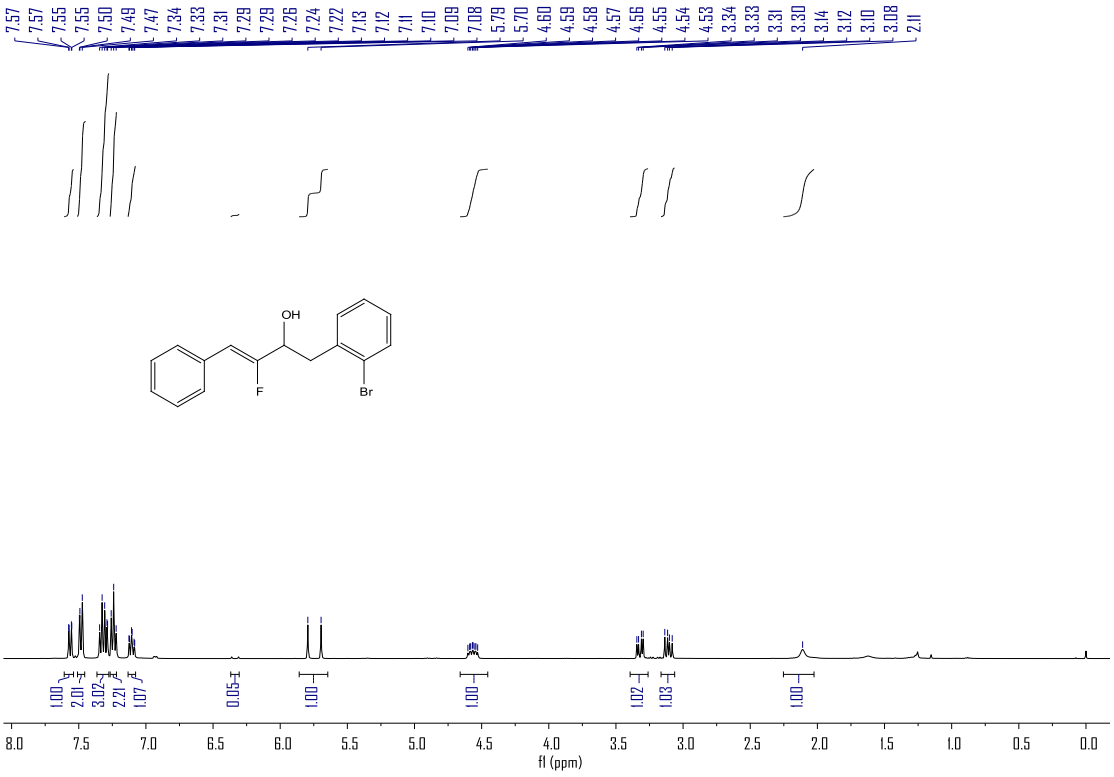


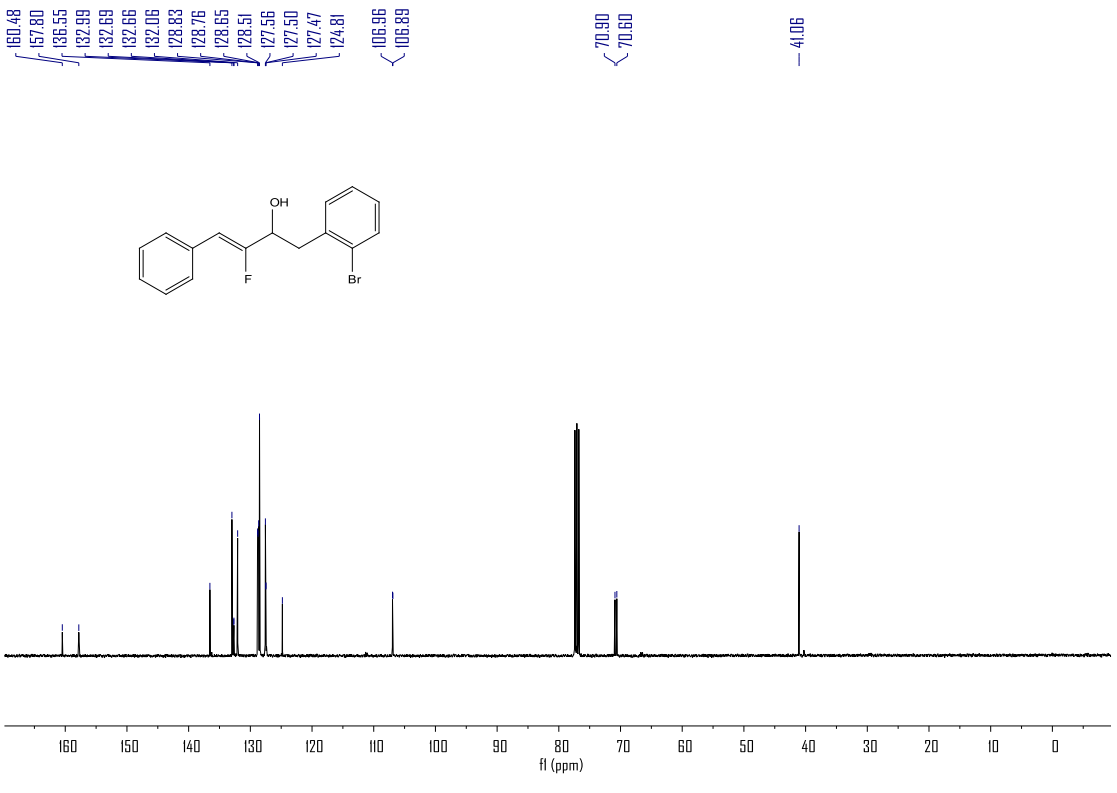


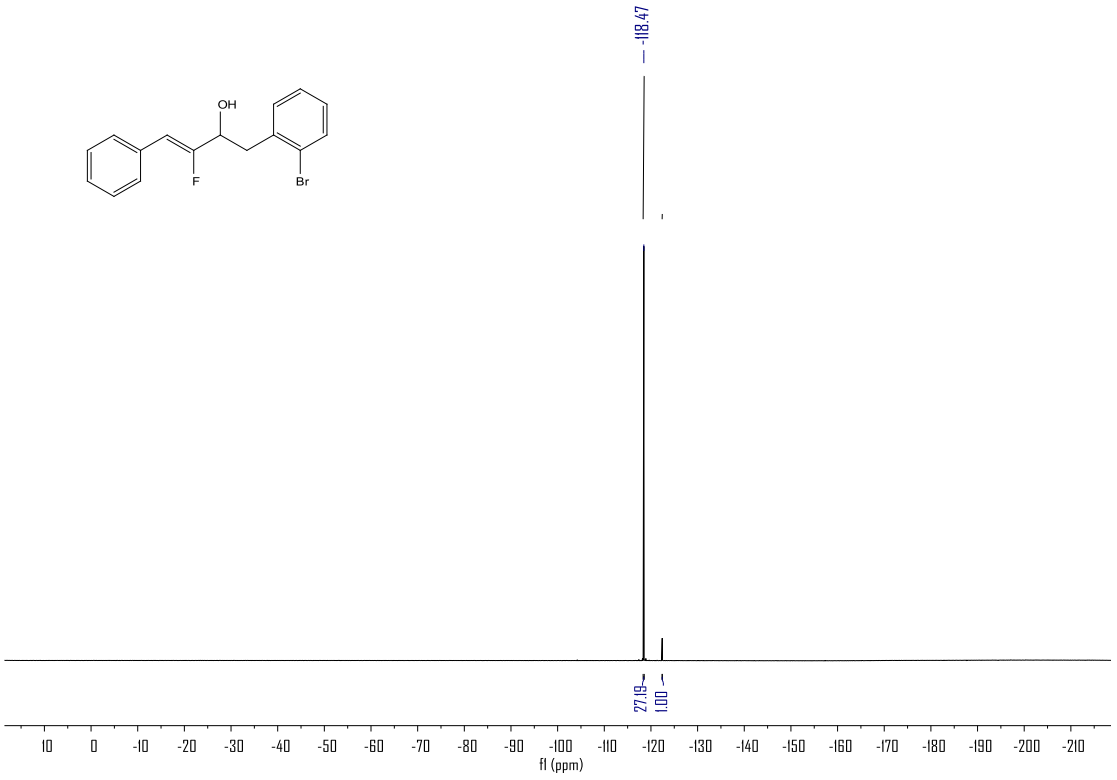
(Z)-1-(2-bromophenyl)-3-fluoro-4-phenylbut-3-en-2-ol

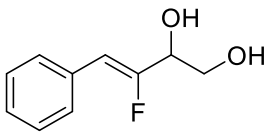
Following the general procedure (**product 44**, **pale-yellow liquid, 31.5 mg, 57%,** Z/E > 20:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (10:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.56 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.51 – 7.46 (m, 2H), 7.36 – 7.28 (m, 3H), 7.24 (t, *J* = 7.4 Hz, 2H), 7.10 (td, *J* = 7.7, 1.8 Hz, 1H), 5.75 (d, *J* = 39.5 Hz, 1H), 4.57 (ddd, *J* = 15.6, 8.3, 5.2 Hz, 1H), 3.32 (dd, *J* = 13.7, 5.2 Hz, 1H), 3.11 (dd, *J* = 13.7, 8.3 Hz, 1H), 2.11 (s, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 159.14 (d, *J* = 269.2 Hz), 136.55, 132.99, 132.68 (d, *J* = 2.6 Hz), 132.06, 128.79 (d, *J* = 7.1 Hz), 128.65, 128.51, 127.56, 127.49 (d, *J* = 2.3 Hz), 124.81, 106.93 (d, *J* = 6.3 Hz), 70.75 (d, *J* = 30.2 Hz), 41.06. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -118.47.

HRMS (ESI) calcd for $C_{16}H_{14}BrFNaO$ ($M+Na^+$): 343.0104; found: 343.0107.





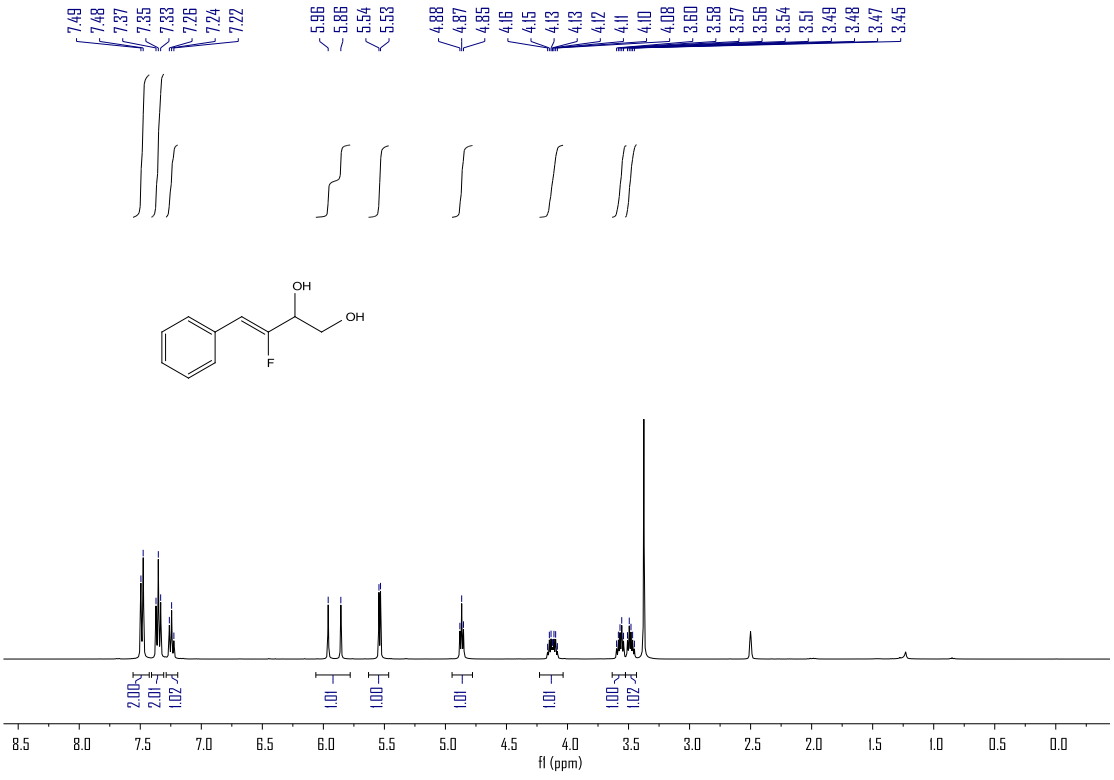


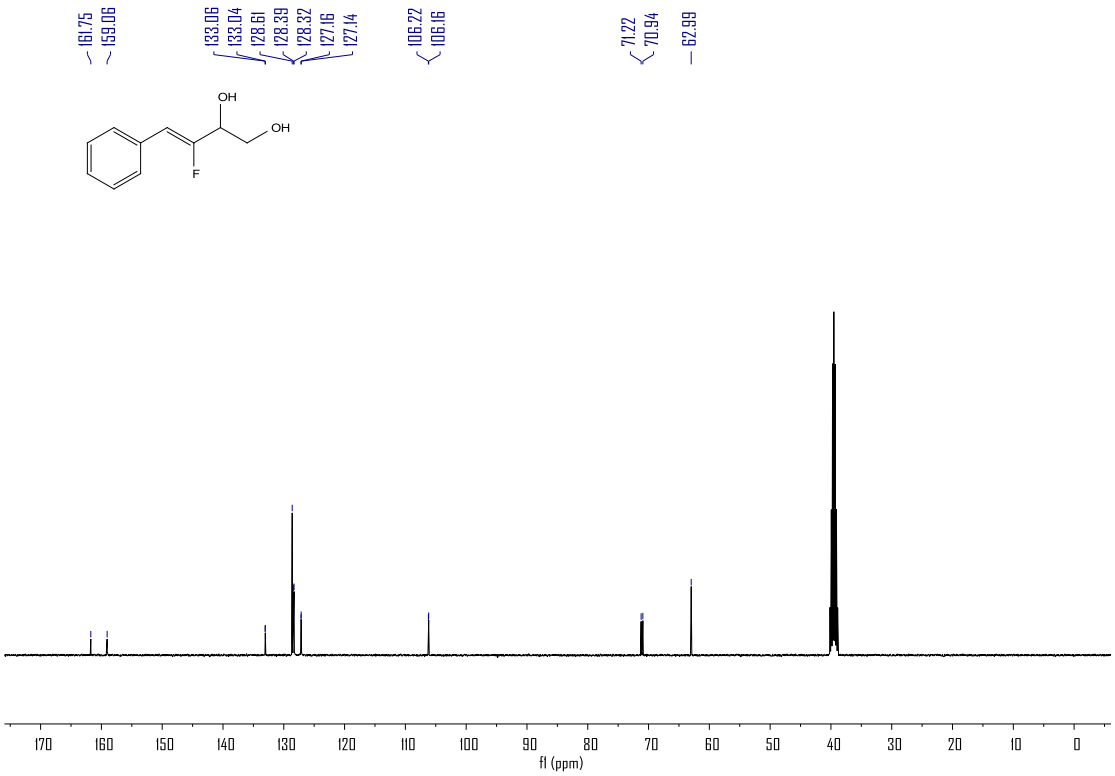


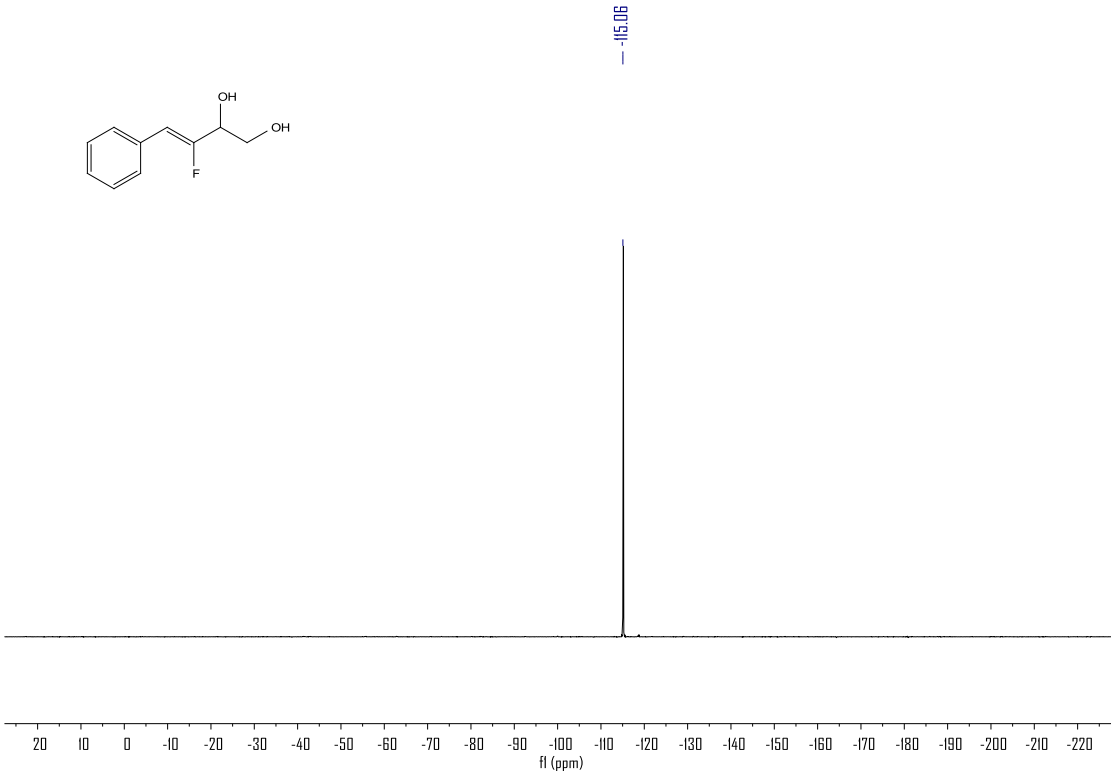
(Z)-3-fluoro-4-phenylbut-3-ene-1,2-diol

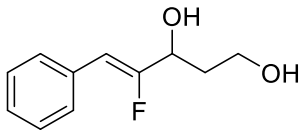
Following the general procedure (**product 45**, **pale-yellow liquid, 23.0 mg, 63%,** Z/E > 20:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (10:1) as an eluent. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.49 (d, J = 7.3 Hz, 2H), 7.35 (t, J = 7.6 Hz, 2H), 7.24 (t, J = 7.3 Hz, 1H), 5.91 (d, J = 41.5 Hz, 1H), 5.54 (d, J = 5.2 Hz, 1H), 4.87 (t, J = 5.9 Hz, 1H), 4.12 (dq, J = 15.2, 5.7 Hz, 1H), 3.57 (dt, J = 11.6, 5.9 Hz, 1H), 3.48 (dt, J = 11.2, 5.8 Hz, 1H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 160.40 (d, J = 270.3 Hz), 133.05 (d, J = 2.0 Hz), 128.61, 128.35 (d, J = 7.2 Hz), 127.15 (d, J = 2.2 Hz), 106.19 (d, J = 5.3 Hz), 71.08 (d, J = 28.8 Hz), 62.99. **^{19}F NMR** (376 MHz, DMSO-d_6) δ -115.06.

HRMS (ESI) calcd for $C_{10}H_{11}FNaO_2$ ($M+Na^+$): 205.0635; found: 205.0637.





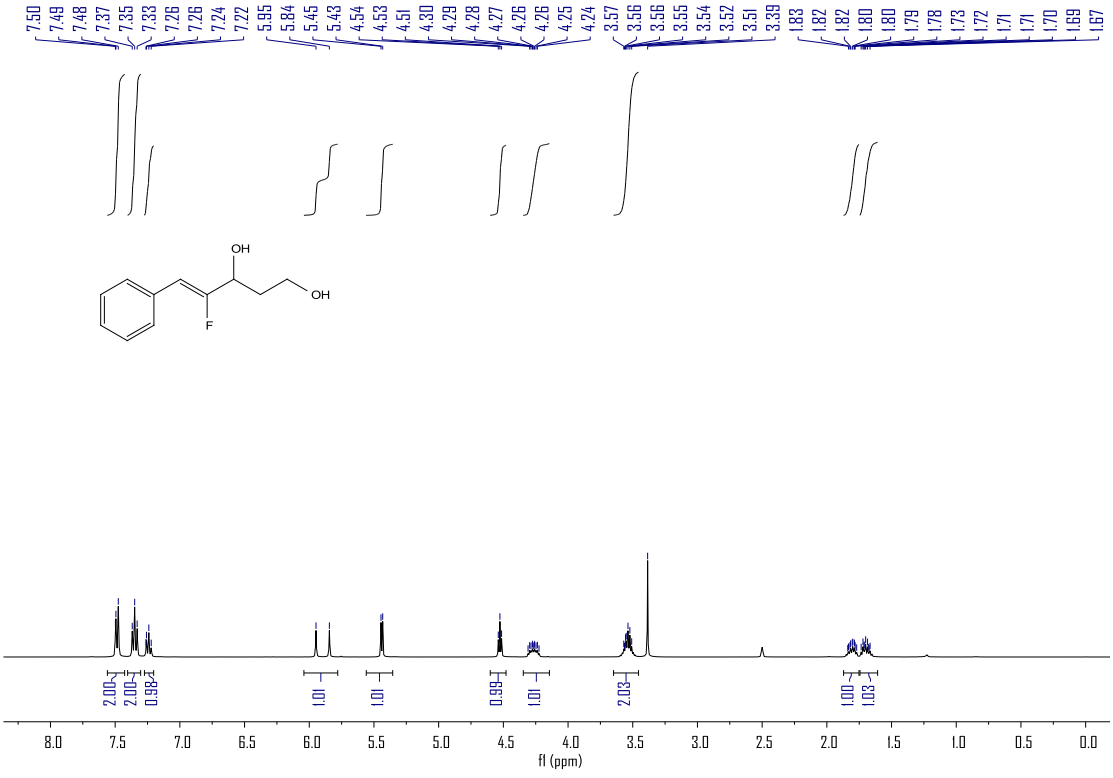


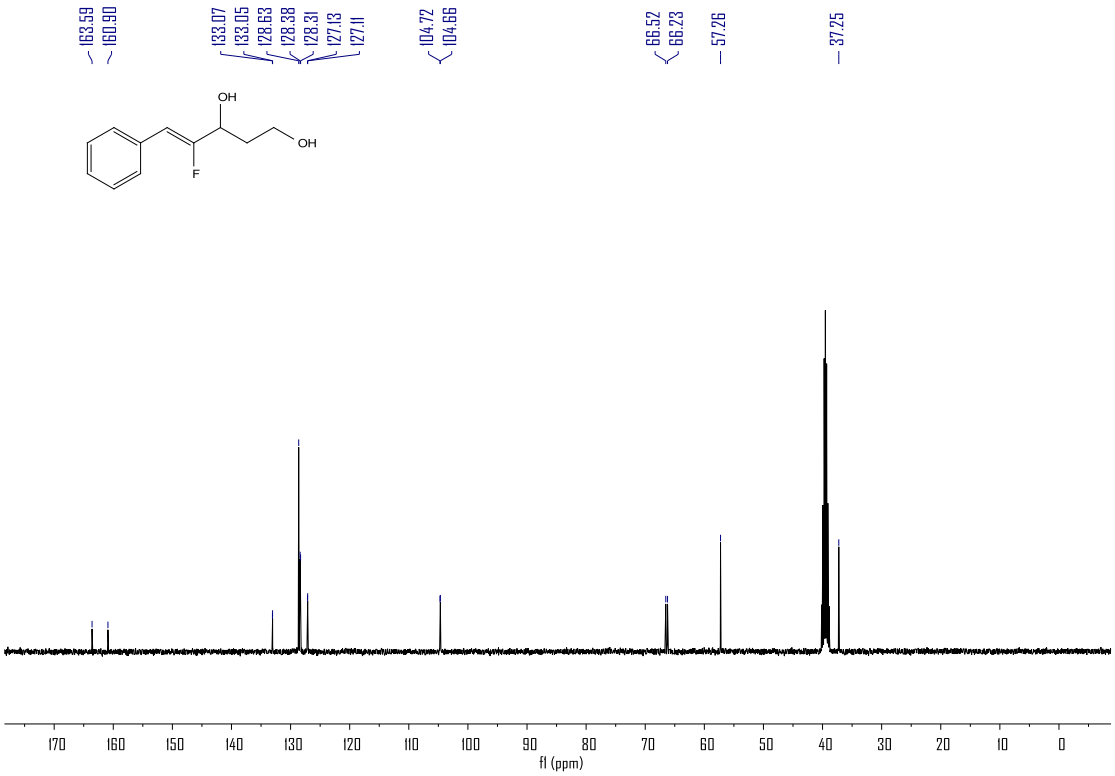


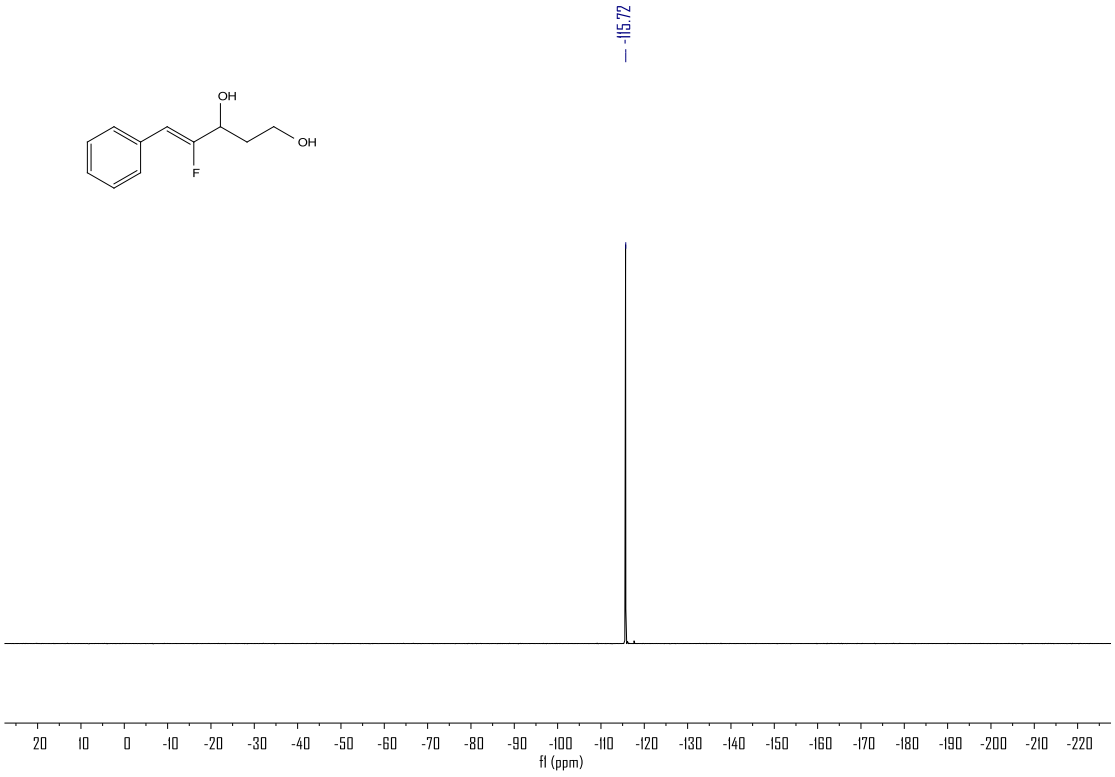
(Z)-4-fluoro-5-phenylpent-4-ene-1,3-diol

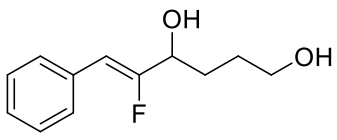
Following the general procedure (**product 46**, **pale-yellow solid, 23.4 mg, 60%,** Z/E > 20:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (10:1) as an eluent. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.49 (d, J = 7.3 Hz, 2H), 7.35 (t, J = 7.6 Hz, 2H), 7.24 (t, J = 7.3 Hz, 1H), 5.90 (d, J = 41.3 Hz, 1H), 5.44 (d, J = 5.3 Hz, 1H), 4.53 (t, J = 5.1 Hz, 1H), 4.36 – 4.20 (m, 1H), 3.54 (dq, J = 11.4, 5.6 Hz, 2H), 1.81 (ddt, J = 13.7, 7.0, 3.5 Hz, 1H), 1.74 – 1.63 (m, 1H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 162.25 (d, J = 270.8 Hz), 133.06 (d, J = 2.2 Hz), 128.63, 128.35 (d, J = 7.2 Hz), 127.12 (d, J = 2.1 Hz), 104.69 (d, J = 5.6 Hz), 66.37 (d, J = 29.7 Hz), 57.26, 37.25. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -115.72.

HRMS (ESI) calcd for $C_{11}H_{13}FNaO_2$ ($M+Na^+$): 219.0792; found: 219.0787.





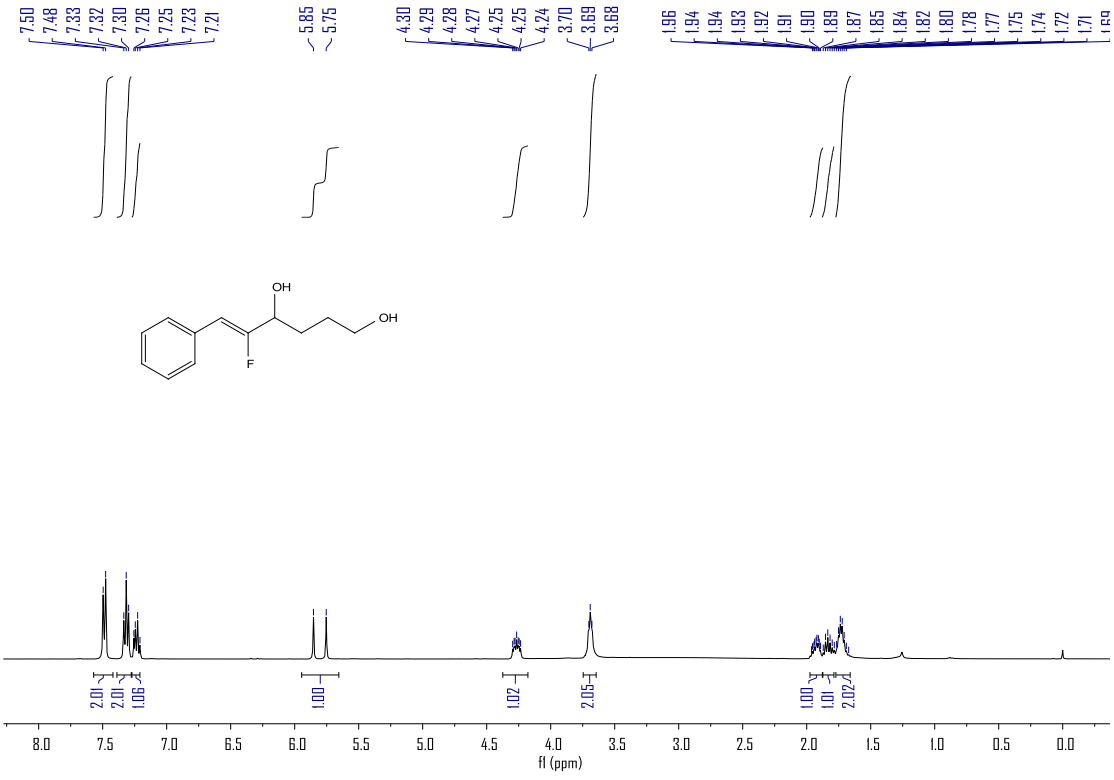


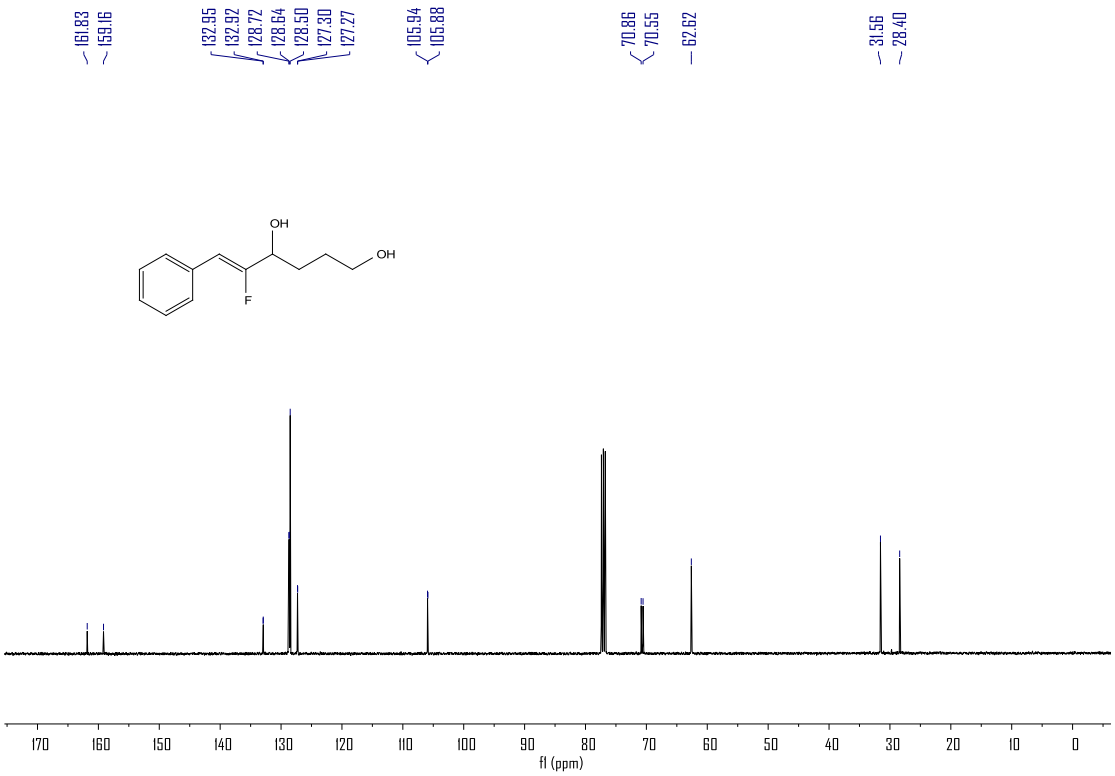


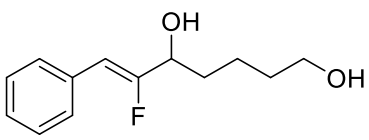
(Z)-5-fluoro-6-phenylhex-5-ene-1,4-diol

Following the general procedure (**product 47**, **pale-yellow liquid, 23.0 mg, 55%,** Z/E > 20:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (10:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.49 (d, *J* = 7.7 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.28 – 7.21 (m, 1H), 5.80 (d, *J* = 39.9 Hz, 1H), 4.27 (ddd, *J* = 12.4, 7.5, 4.4 Hz, 1H), 3.76 – 3.49 (m, 2H), 1.93 (ddt, *J* = 13.9, 6.8, 3.4 Hz, 1H), 1.82 (dt, *J* = 13.3, 6.8 Hz, 1H), 1.73 (h, *J* = 6.8, 6.3 Hz, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 160.50 (d, *J* = 269.2 Hz), 132.93 (d, *J* = 2.5 Hz), 128.68 (d, *J* = 7.2 Hz), 128.50, 127.28 (d, *J* = 2.2 Hz), 105.91 (d, *J* = 6.2 Hz), 70.70 (d, *J* = 31.2 Hz), 62.62, 31.56, 28.40. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -116.76.

HRMS (ESI) calcd for $C_{12}H_{15}FNaO_2$ ($M+Na^+$): 233.0948; found: 233.0953.



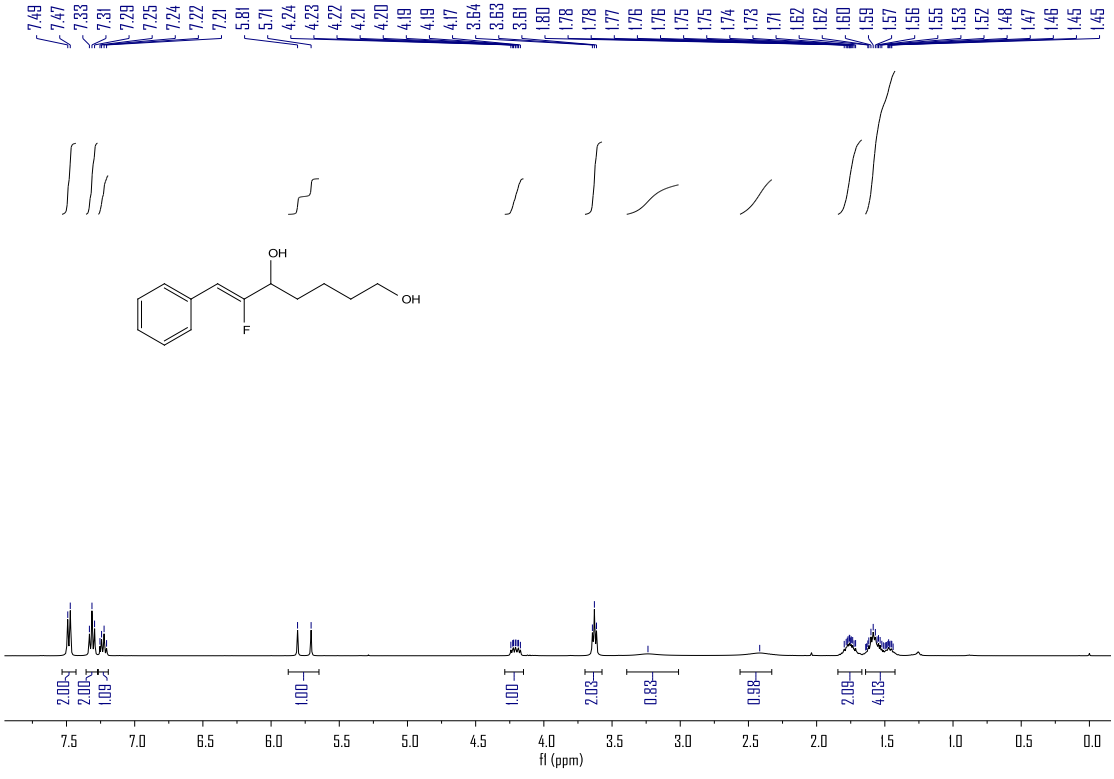


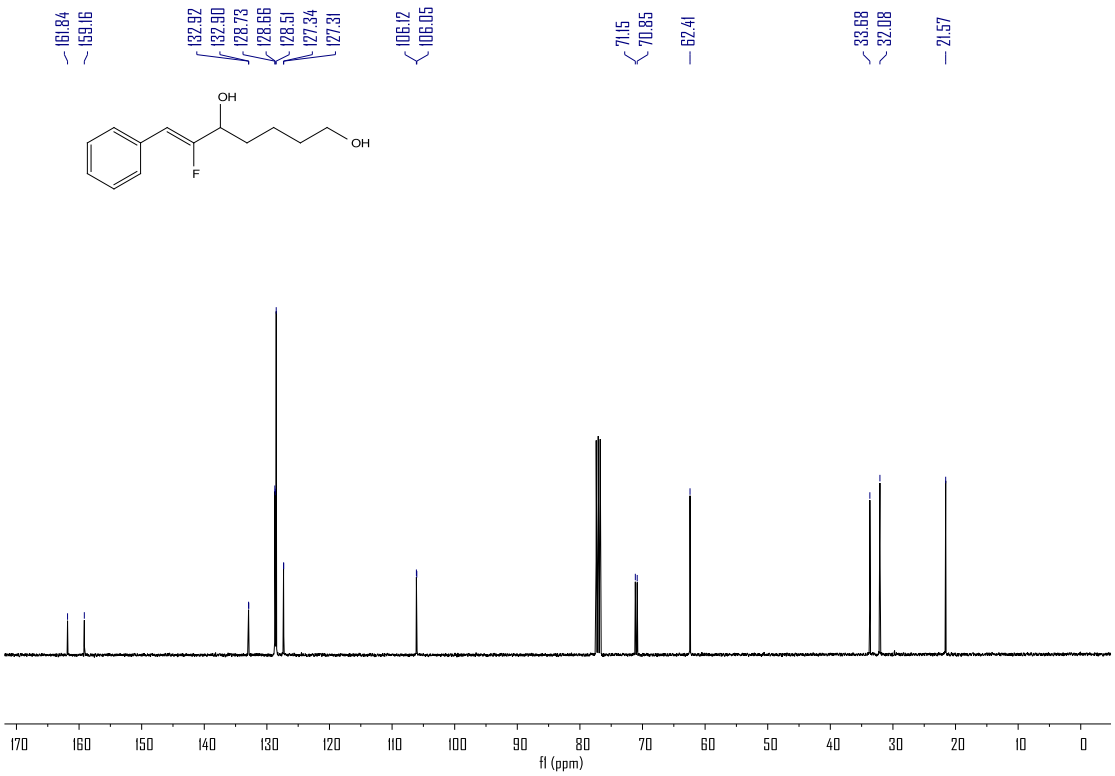


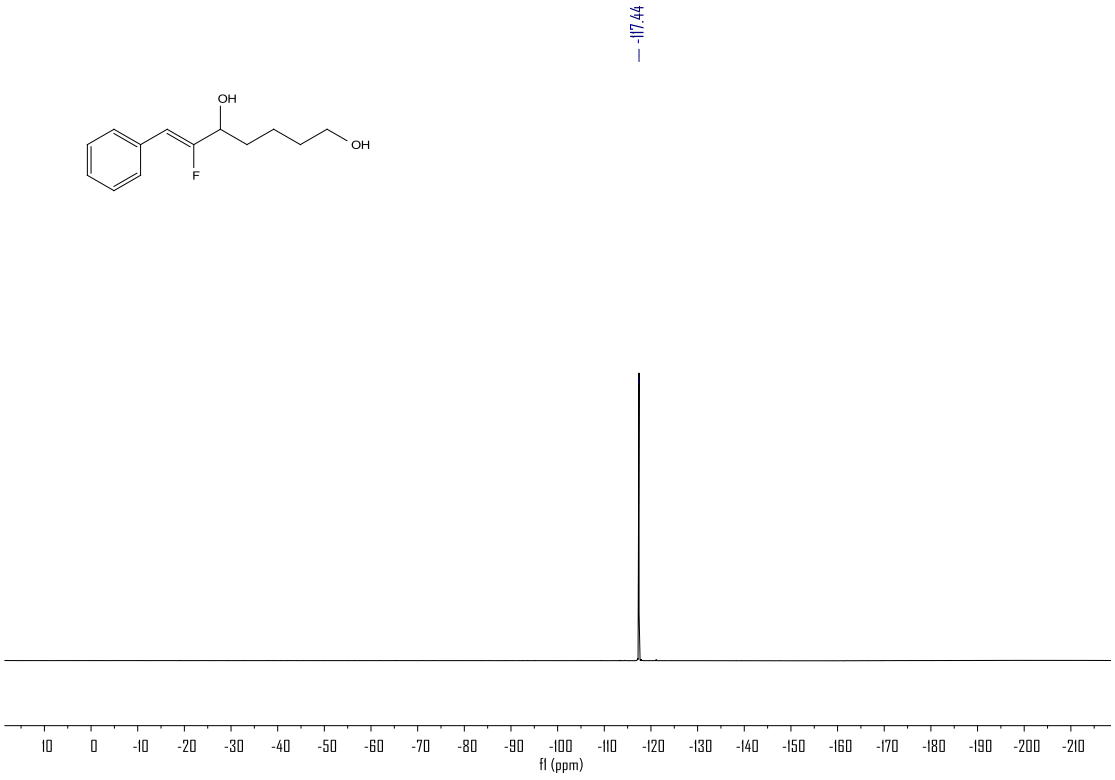
(Z)-6-fluoro-7-phenylhept-6-ene-1,5-diol

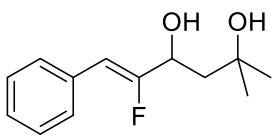
Following the general procedure (**product 48**, **pale-yellow liquid, 25.0 mg, 56%,** Z/E > 20:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (2:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.48 (d, *J* = 7.3 Hz, 2H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.23 (q, *J* = 7.3, 6.0 Hz, 1H), 5.76 (d, *J* = 39.7 Hz, 1H), 4.21 (ddd, *J* = 15.1, 7.6, 5.4 Hz, 1H), 3.63 (t, *J* = 6.0 Hz, 2H), 3.24 (s, 1H), 2.42 (s, 1H), 1.76 (dtd, *J* = 17.1, 8.8, 5.1 Hz, 2H), 1.65 – 1.44 (m, 4H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 160.50 (d, *J* = 269.7 Hz), 132.91 (d, *J* = 2.5 Hz), 128.69 (d, *J* = 7.2 Hz), 128.51, 127.33 (d, *J* = 2.3 Hz), 106.09 (d, *J* = 6.4 Hz), 71.00 (d, *J* = 30.4 Hz), 62.41, 33.68, 32.08, 21.57. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -117.44.

HRMS (ESI) calcd for $C_{13}H_{17}FNaO_2$ ($M+Na^+$): 247.1105; found: 247.1101.





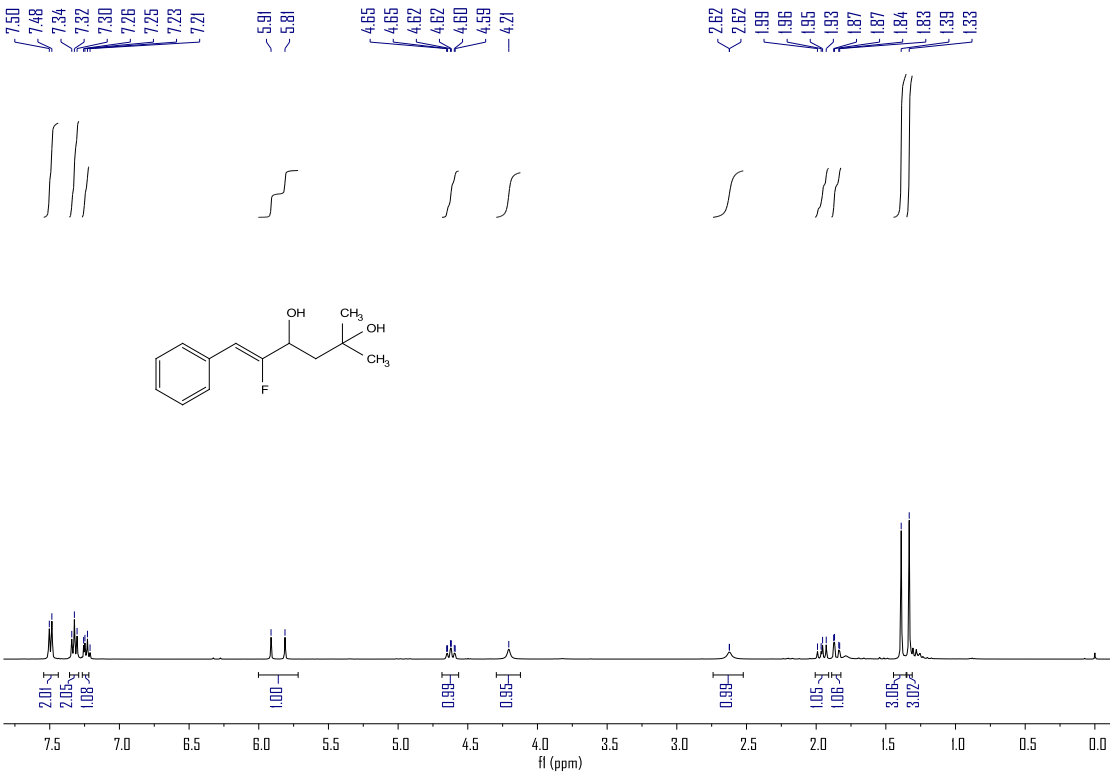


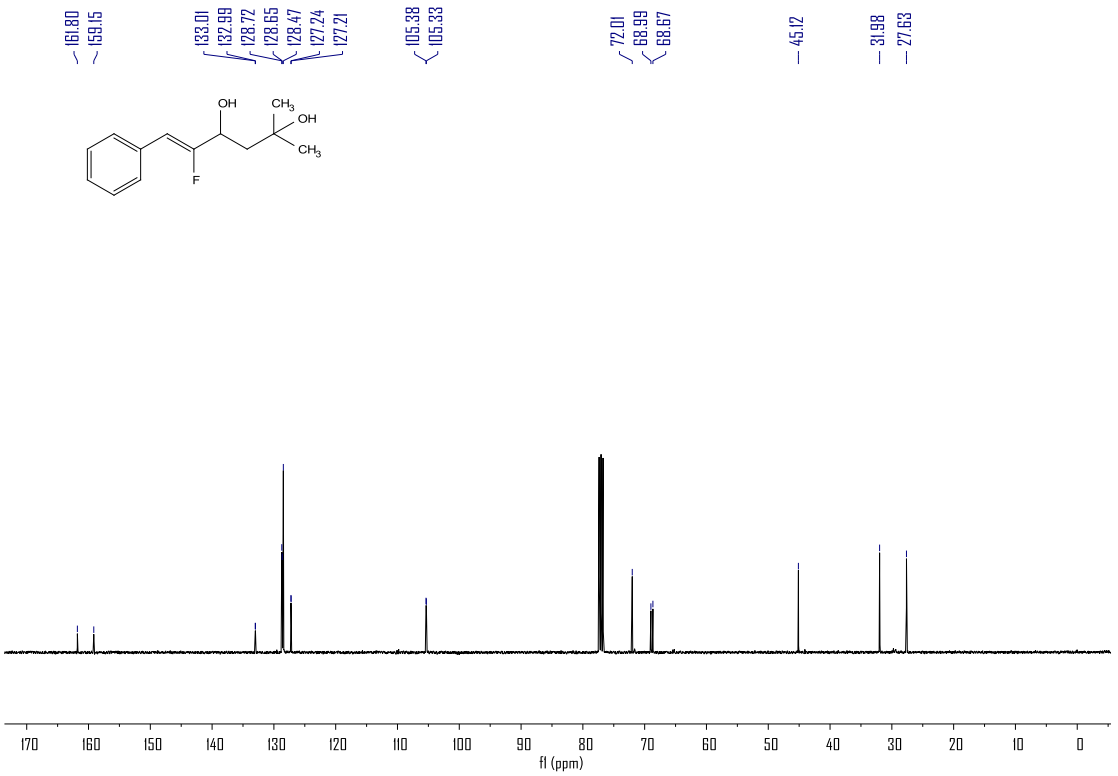


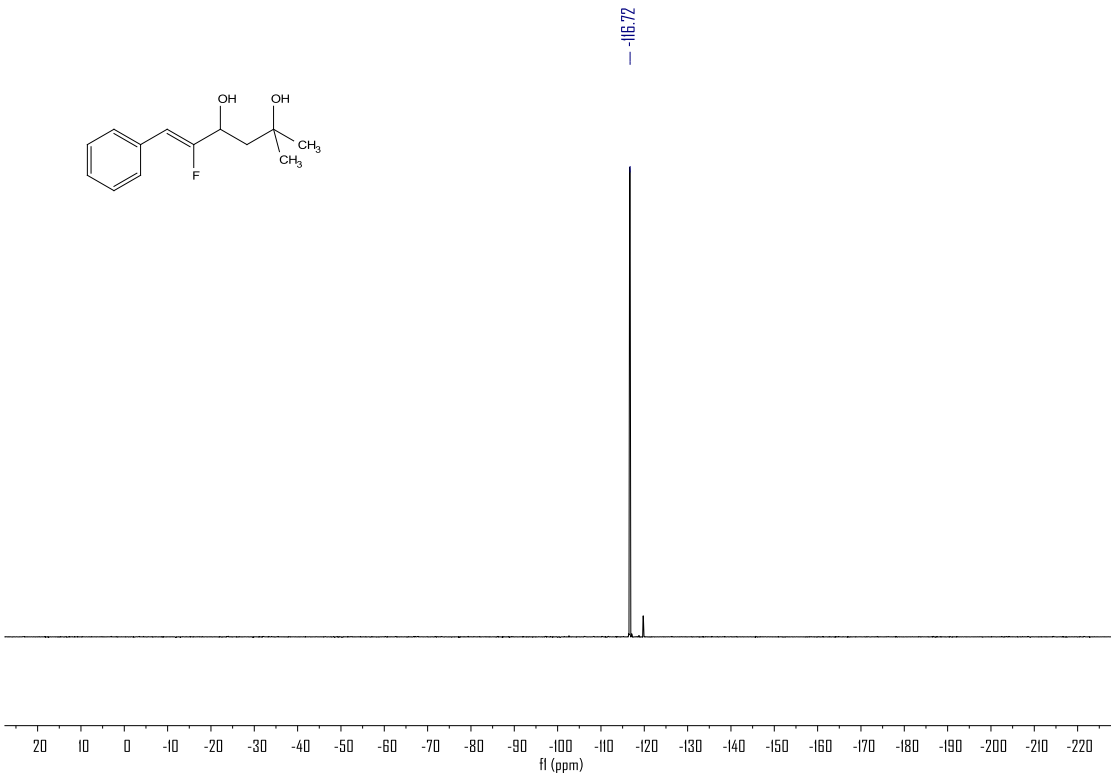
(Z)-5-fluoro-2-methyl-6-phenylhex-5-ene-2,4-diol

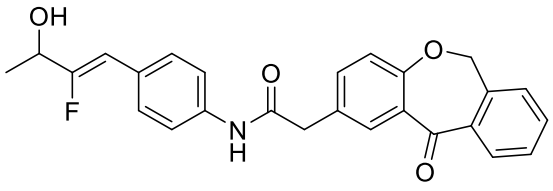
Following the general procedure (**product 49**, **pale-yellow liquid, 22.3 mg, 50%,** Z/E > 20:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (2:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.49 (d, *J* = 7.3 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.26 – 7.21 (m, 1H), 5.86 (d, *J* = 40.1 Hz, 1H), 4.62 (td, *J* = 11.0, 2.5 Hz, 1H), 4.21 (s, 1H), 2.64 – 2.57 (m, 1H), 1.96 (dd, *J* = 14.6, 10.5 Hz, 1H), 1.85 (dd, *J* = 14.7, 2.5 Hz, 1H), 1.39 (s, 3H), 1.33 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 160.47 (d, *J* = 267.2 Hz), 133.00 (d, *J* = 2.5 Hz), 128.69 (d, *J* = 7.1 Hz), 128.47, 127.23 (d, *J* = 2.3 Hz), 105.35 (d, *J* = 5.9 Hz), 72.01, 68.83 (d, *J* = 32.8 Hz), 45.12, 31.98, 27.63. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -116.72.

HRMS (ESI) calcd for $C_{13}H_{17}FNaO_2$ ($M+Na^+$): 247.1105; found: 247.1112.




161.80
159.15
133.01
132.99
128.72
128.65
128.47
127.24
127.21
105.38
105.33
72.01
68.99
68.67
45.12
31.98
27.63
OH
CH3
OH
CH3
F
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

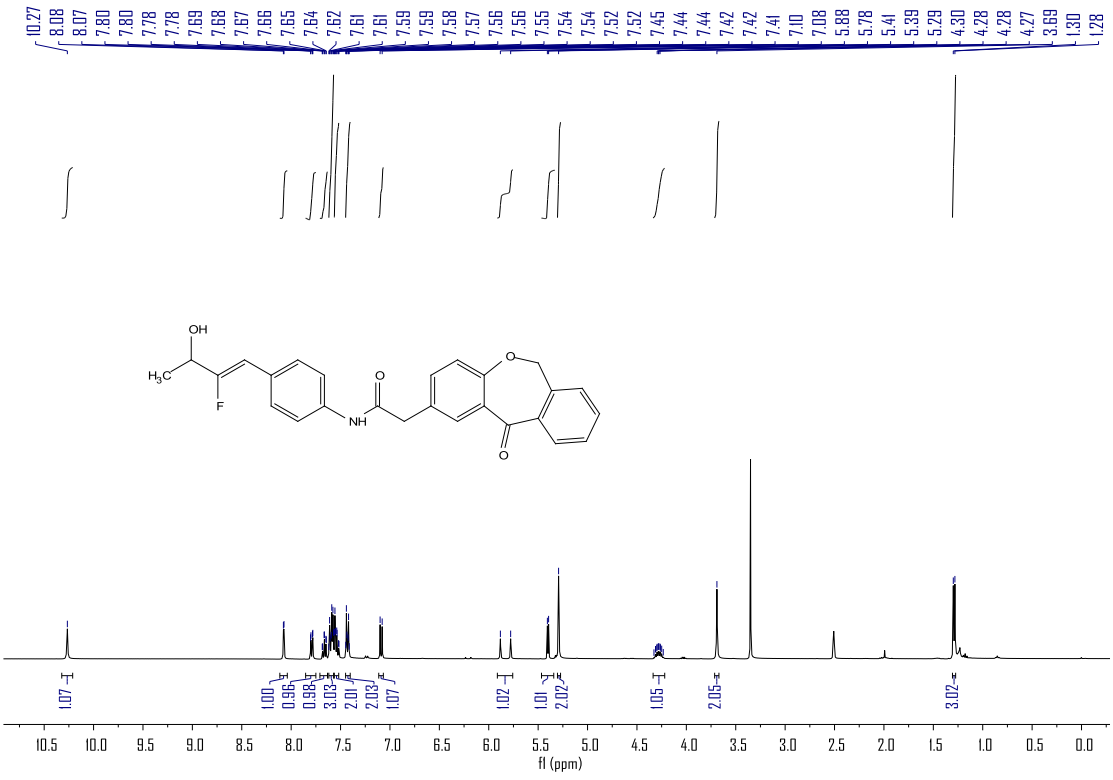

-116.72
OH
OH
CH3
CH3
F
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
f1 (ppm)


OH
F
N
H
O
O
O

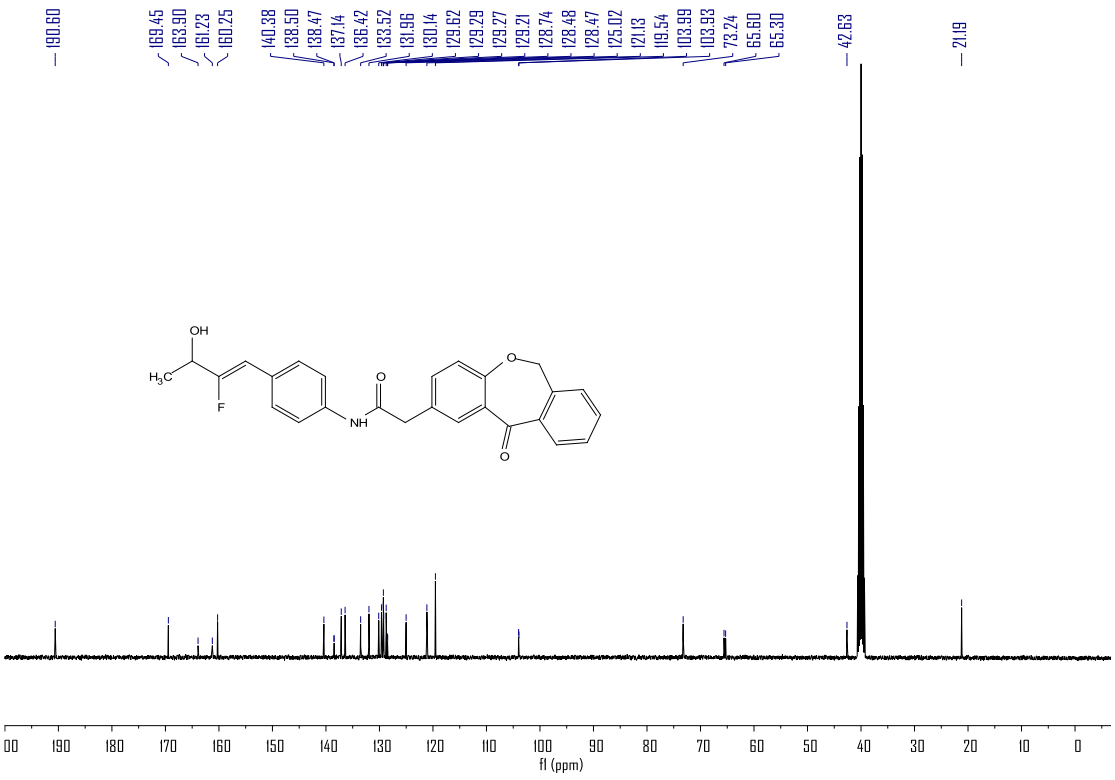
(Z)-N-(4-(2-fluoro-3-hydroxybut-1-en-1-yl)phenyl)-2-(11-oxo-6,11-dihydrodibenzo[b,e]oxepin-2-yl)acetamide

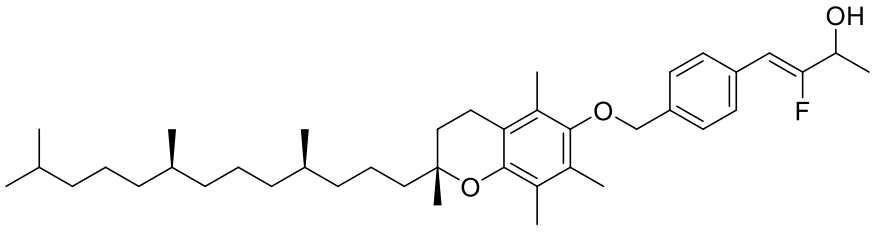
Following the general procedure (**product 50**, **pale-yellow liquid, 31.0 mg, 35%,** Z/E = 6:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (1:1) as an eluent. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 10.27 (s, 1H), 8.08 (d, J = 2.4 Hz, 1H), 7.79 (dd, J = 7.7, 1.4 Hz, 1H), 7.66 (td, J = 7.4, 1.4 Hz, 1H), 7.62 – 7.57 (m, 3H), 7.56 – 7.51 (m, 2H), 7.46 – 7.41 (m, 2H), 7.09 (d, J = 8.4 Hz, 1H), 5.83 (d, J = 41.6 Hz, 1H), 5.40 (d, J = 4.9 Hz, 1H), 5.29 (s, 2H), 4.28 (ddd, J = 13.3, 6.7, 5.2 Hz, 1H), 3.69 (s, 2H), 1.29 (d, J = 6.5 Hz, 3H). **^{19}F NMR** (376 MHz, DMSO-d_6) δ -116.79. **^{13}C NMR** (101 MHz, DMSO-d_6) δ 190.60, 169.45, 162.57 (d, J = 268.8 Hz), 160.25, 140.38, 138.48 (d, J = 2.5 Hz), 137.14, 136.42, 133.52, 131.96, 130.14, 129.62, 129.28 (d, J = 2.0 Hz), 129.21, 128.74, 128.48 (d, J = 1.6 Hz), 125.02, 121.13, 119.54, 103.96 (d, J = 5.9 Hz), 73.24, 65.45 (d, J = 30.5 Hz), 42.63 , 21.19 .

HRMS (APCI) calcd for $C_{26}H_{22}FNNaO_4$ ($M+Na^+$): 454.1425; found: 454.1433.




-116.79
OH
H3C
F
NH
O
O
O
f1 (ppm)

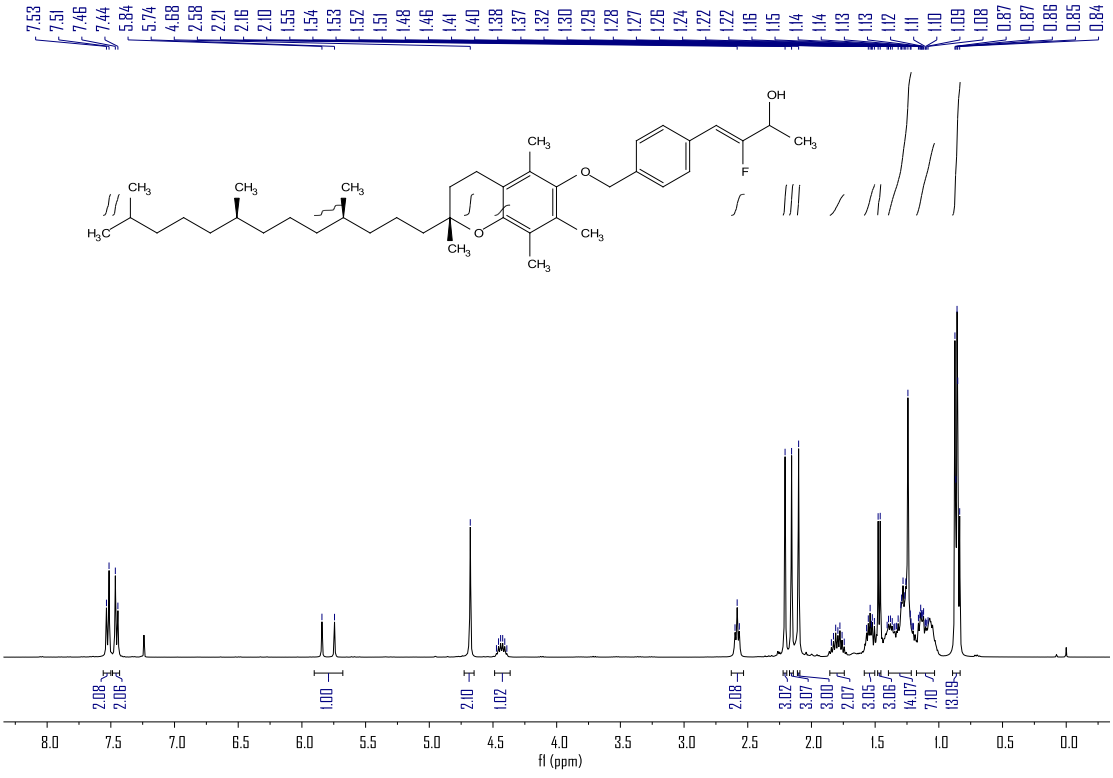

190.60
169.45
163.90
161.23
160.25
140.38
138.50
138.47
137.14
136.42
133.52
131.96
130.14
129.62
129.29
129.27
129.21
128.74
128.48
128.47
125.02
121.13
119.54
103.99
103.93
73.24
65.60
65.30
42.63
21.19
OH
H3C
F
NH
O
O
O
f1 (ppm)

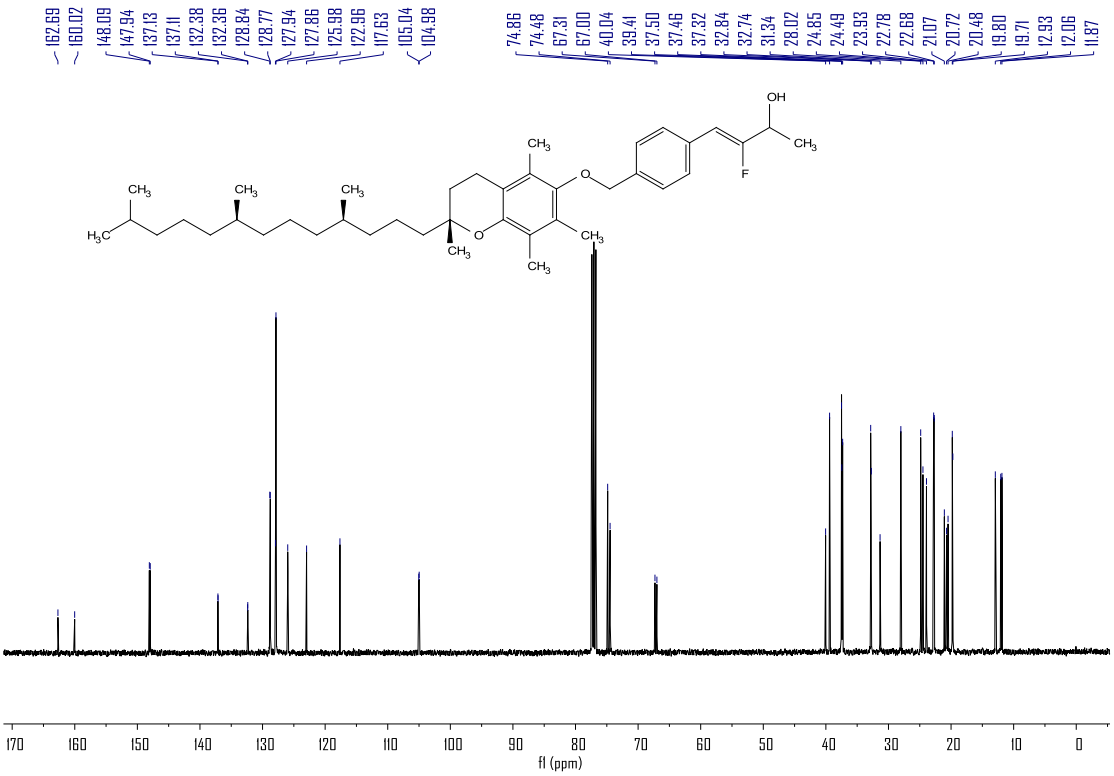

OH
F
O
O

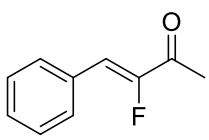
(Z)-3-fluoro-4-(4-((((R)-2,5,7,8-tetramethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chroman-6-yl)oxy)methyl)phenyl)but-3-en-2-ol

Following the general procedure (**product 51**, **pale-yellow liquid, 70.5 mg, 58%,** Z/E > 15:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (8:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.52 (d, *J* = 8.1 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 5.79 (d, *J* = 39.5 Hz, 1H), 4.68 (s, 2H), 4.43 (dq, *J* = 13.1, 6.5 Hz, 1H), 2.58 (t, *J* = 6.8 Hz, 2H), 2.21 (s, 3H), 2.16 (s, 3H), 2.10 (s, 3H), 1.85 – 1.74 (m, 2H), 1.58 – 1.50 (m, 3H), 1.47 (d, *J* = 6.5 Hz, 3H), 1.41 – 1.22 (m, 14H), 1.18 – 1.03 (m, 7H), 0.89 – 0.82 (m, 13H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 161.35 (d, *J* = 269.0 Hz), 148.09, 147.94, 137.12 (d, *J* = 2.2 Hz), 132.37 (d, *J* = 2.5 Hz), 128.80 (d, *J* = 7.2 Hz), 127.94, 127.86, 125.98, 122.96, 117.63, 105.01 (d, *J* = 6.7 Hz), 74.86, 74.48, 67.15 (d, *J* = 31.1 Hz), 40.04, 39.41, 37.50, 37.46, 37.32, 32.84, 32.74, 31.34, 28.02, 24.85, 24.49, 23.93, 22.78, 22.68, 21.07, 20.72, 20.48, 19.80, 19.71, 12.93, 12.06, 11.87. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -117.16.

HRMS (APCI) calcd for $C_{40}H_{61}FNaO_3$ ($M+Na^+$): 631.4497; found: 631.4491.

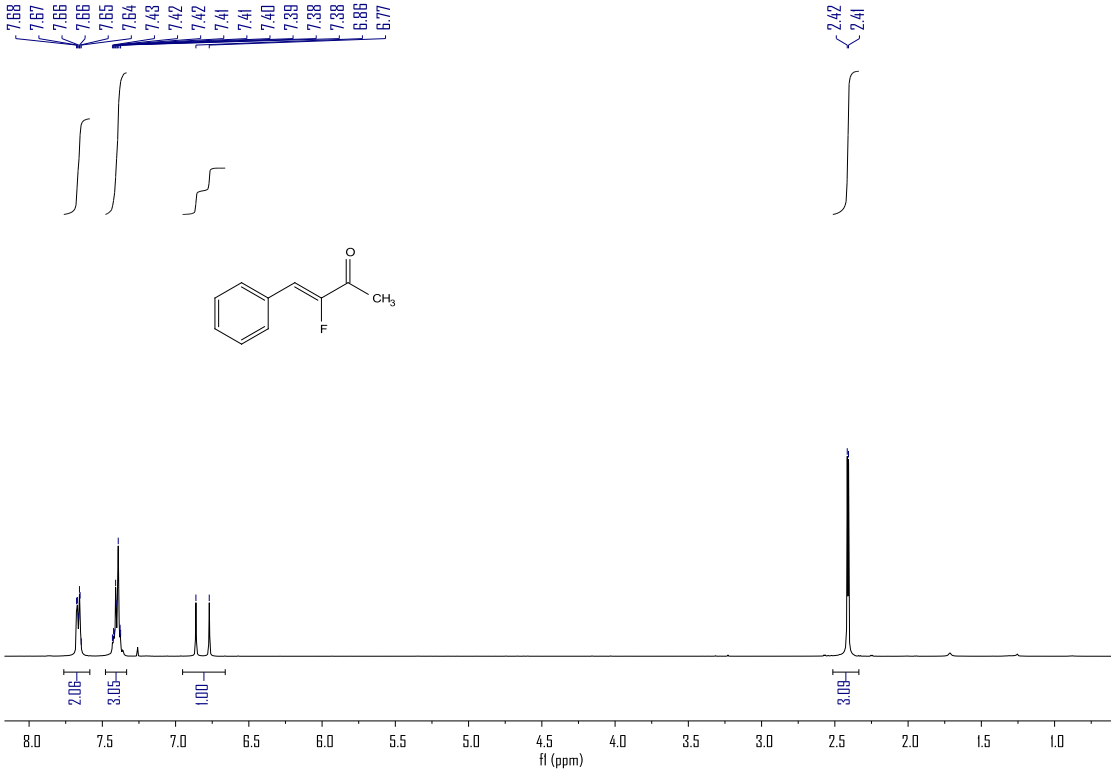


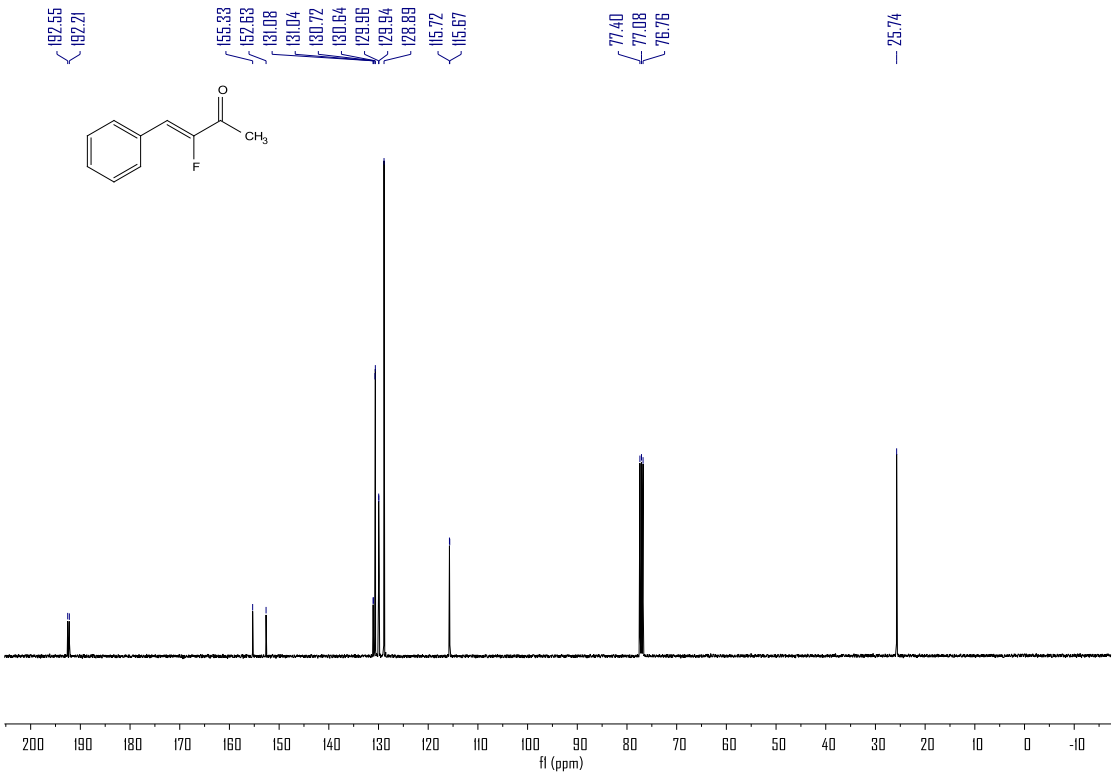


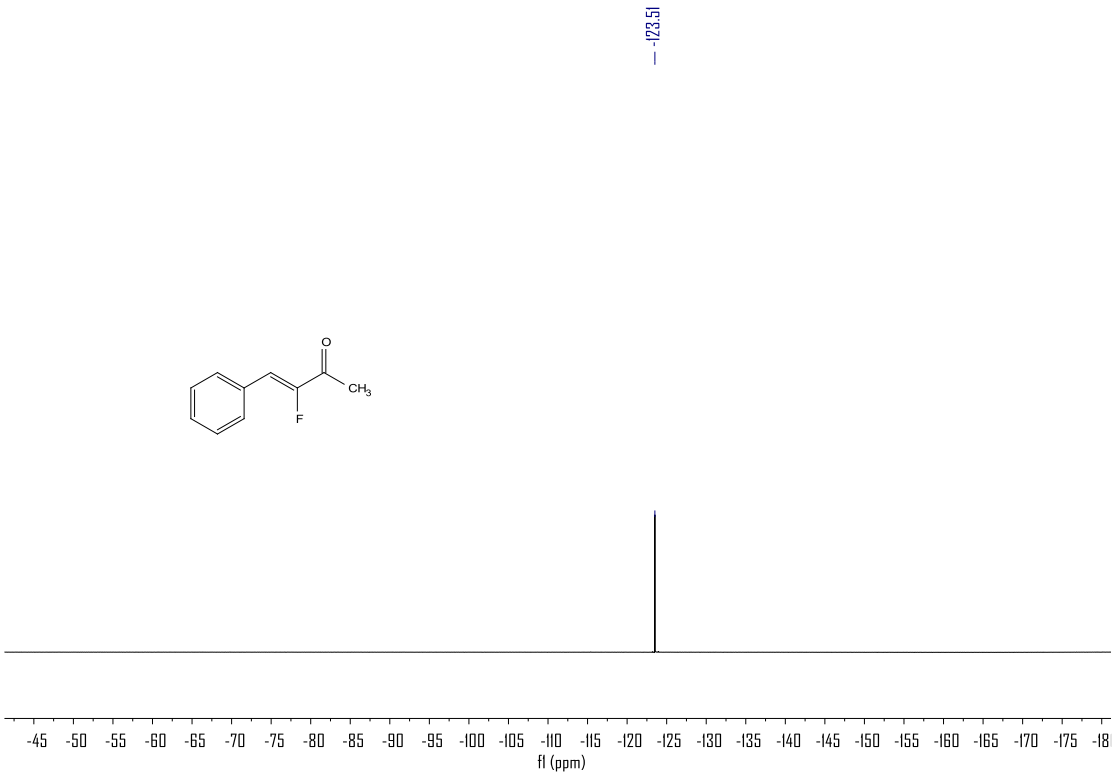


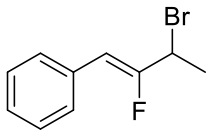
(Z)-3-fluoro-4-phenylbut-3-en-2-one

The residue was purified by silica gel-column chromatography using PE/EtOAc (30:1) as an eluent. **(product 52**, **pale-yellow liquid, 27mg, 83%)**. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.66 (dd, *J* = 7.7, 2.0 Hz, 2H), 7.49 – 7.31 (m, 3H), 6.82 (d, *J* = 36.4 Hz, 1H), 2.41 (d, *J* = 3.4 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 192.38 (d, *J* = 33.3 Hz), 153.98 (d, *J* = 271.7 Hz), 131.06 (d, *J* = 4.1 Hz), 130.68 (d, *J* = 8.3 Hz), 129.95 (d, *J* = 2.9 Hz), 128.89, 115.69 (d, *J* = 5.5 Hz), 25.74. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -123.51. The characterization data is in agreement with the reported data (*J. Fluorine Chem.* **2008**, 129, 983-985).





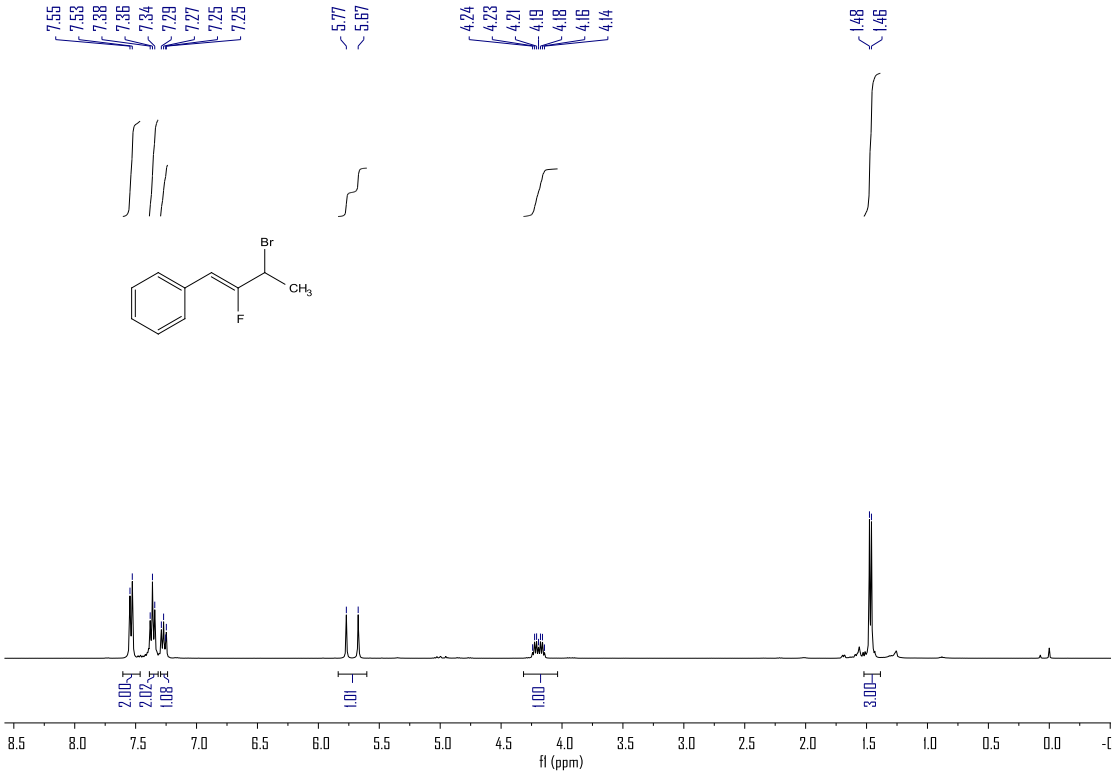


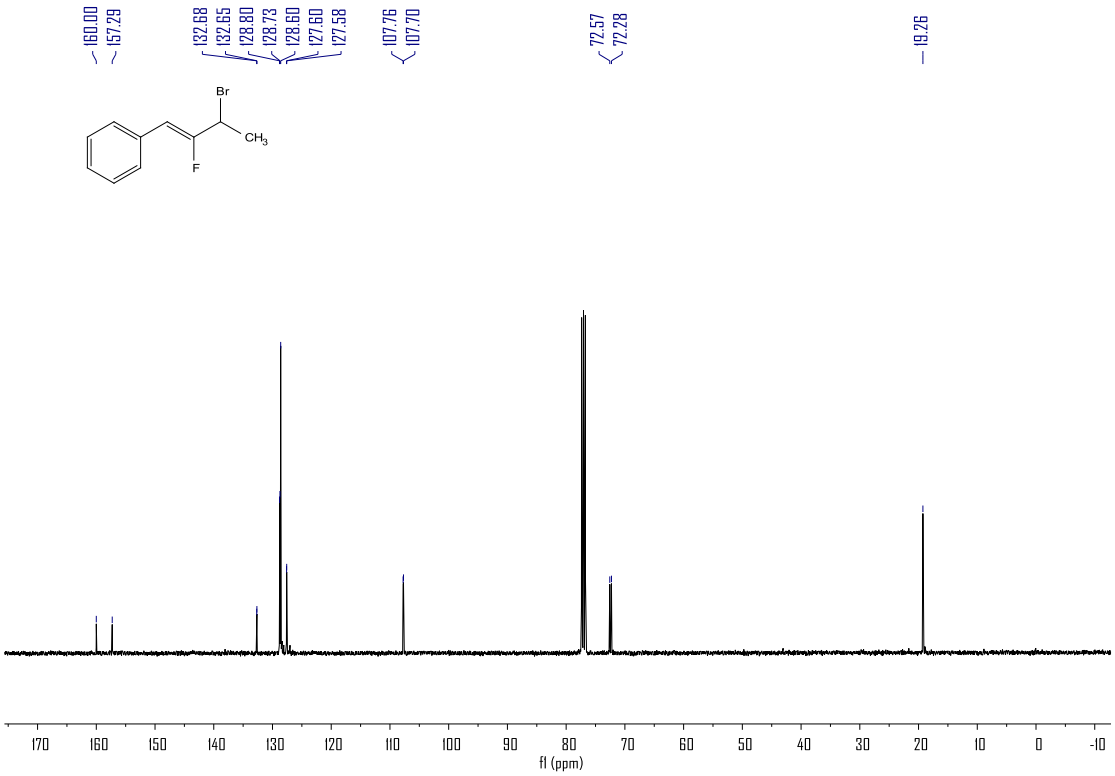


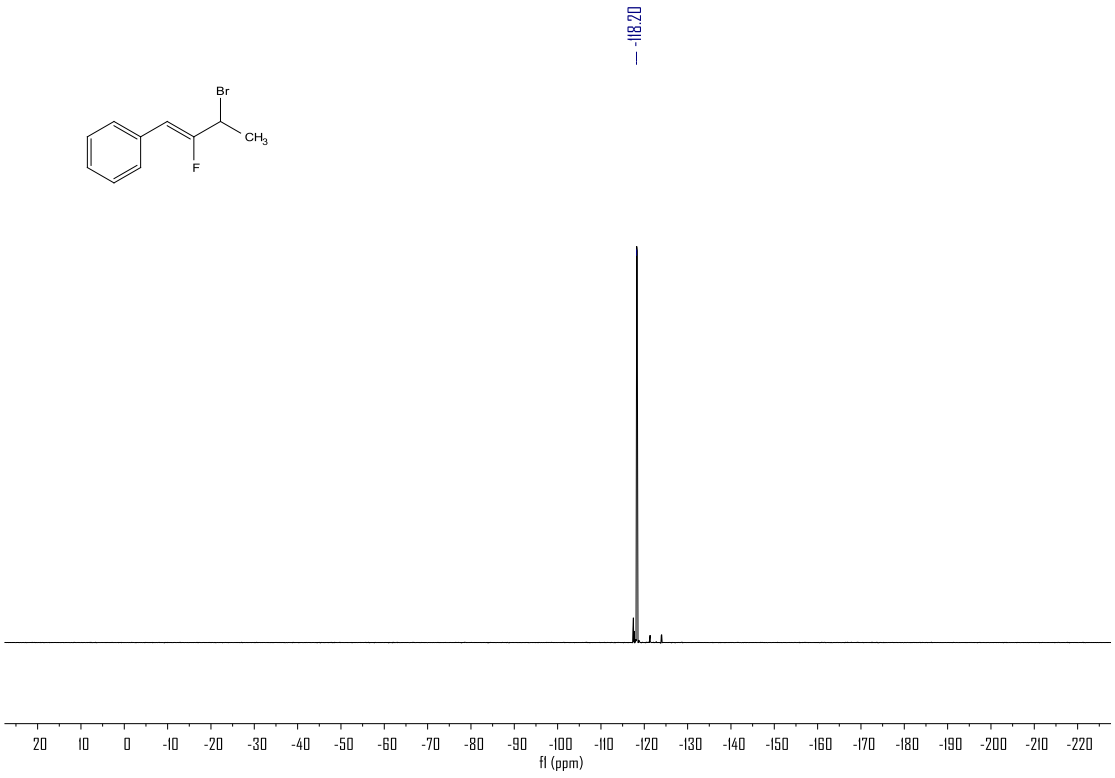
(Z)-(3-bromo-2-fluorobut-1-en-1-yl)benzene

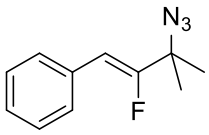
The residue was purified by silica gel-column chromatography using PE as an eluent. **(product 55**, **pale-yellow liquid, 33 mg, 72%)**. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.54 (d, *J* = 7.6 Hz, 2H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.26 (d, *J* = 9.0 Hz, 1H), 5.72 (d, *J* = 38.9 Hz, 1H), 4.26 – 4.13 (m, 1H), 1.47 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 158.64 (d, *J* = 273.0 Hz), 132.67 (d, *J* = 2.8 Hz), 128.77 (d, *J* = 7.5 Hz), 128.60, 127.59 (d, *J* = 2.4 Hz), 107.73 (d, *J* = 6.5 Hz), 72.43 (d, *J* = 28.6 Hz), 19.26. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -118.20.

HRMS (ESI) calcd for $C_{10}H_{11}BrF$ ($M+H^+$): 229.0023; found: 229.0026.





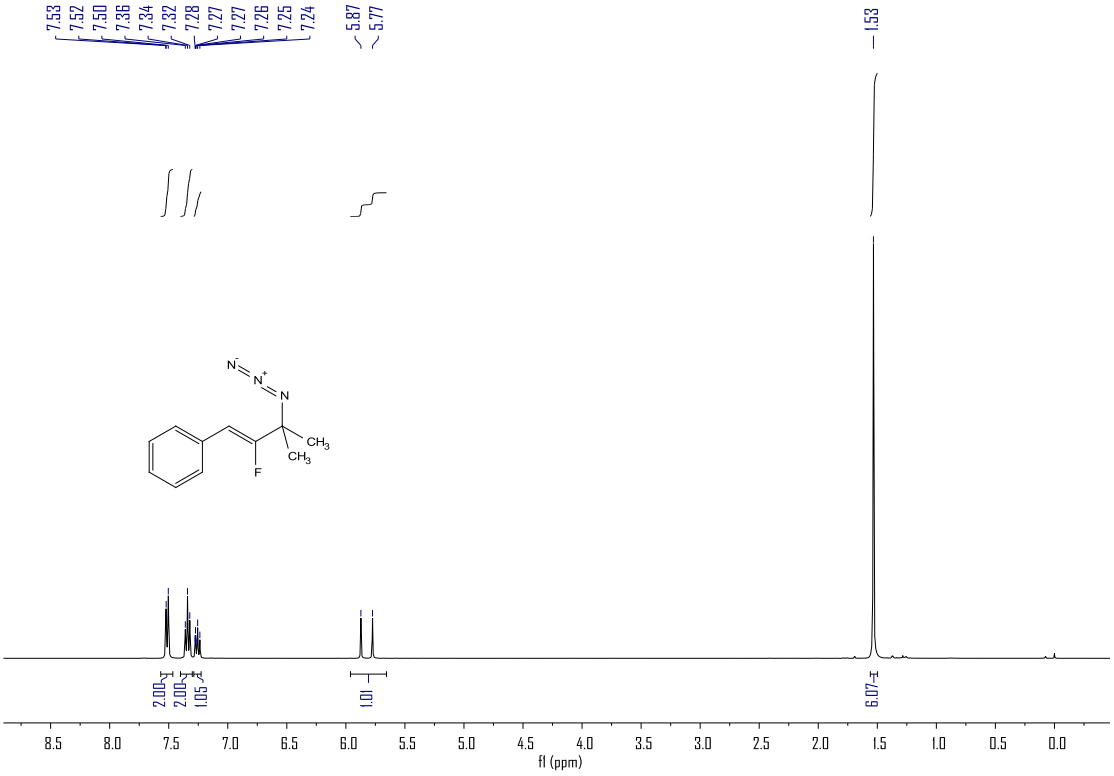


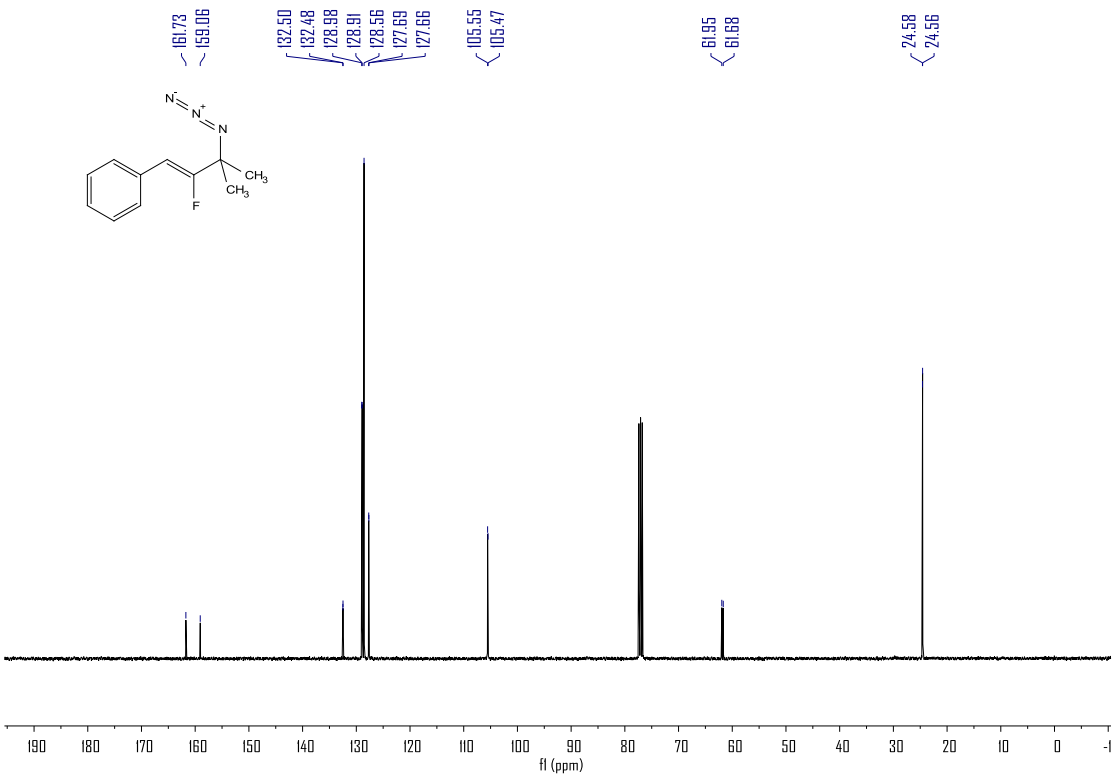


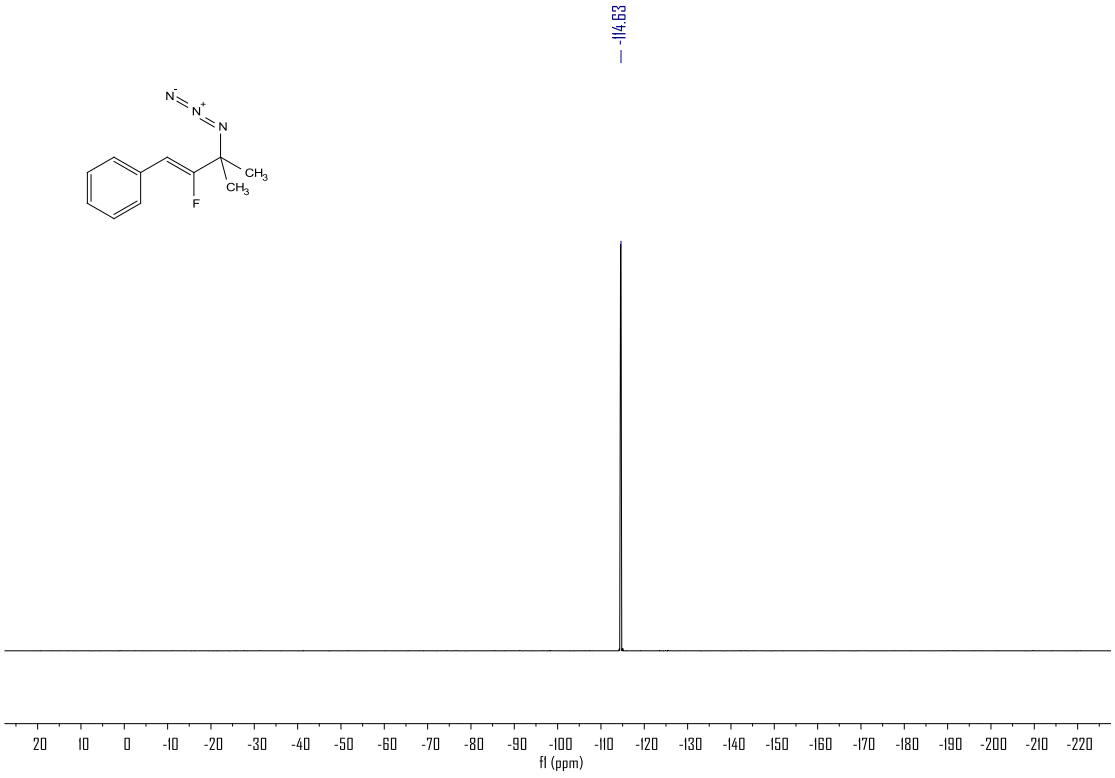
(Z)-(3-azido-2-fluoro-3-methylbut-1-en-1-yl)benzene

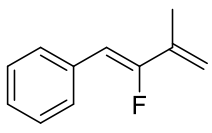
The residue was purified by silica gel-column chromatography using PE/EtOAc (30:1) as an eluent. **(product 57**, **pale-yellow liquid, 31 mg, 76%)**. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.58 – 7.46 (m, 2H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.29 – 7.15 (m, 1H), 5.82 (d, *J* = 39.4 Hz, 1H), 1.53 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 160.40 (d, *J* = 269.2 Hz), 132.49 (d, *J* = 2.5 Hz), 128.95 (d, *J* = 7.5 Hz), 128.56, 127.67 (d, *J* = 2.4 Hz), 105.51 (d, *J* = 7.9 Hz), 61.81 (d, *J* = 27.1 Hz), 24.57 (d, *J* = 2.1 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -114.63.

HRMS (ESI) calcd for $C_{11}H_{13}FN_3$ ($M+H^+$): 206.1088; found: 206.1092.





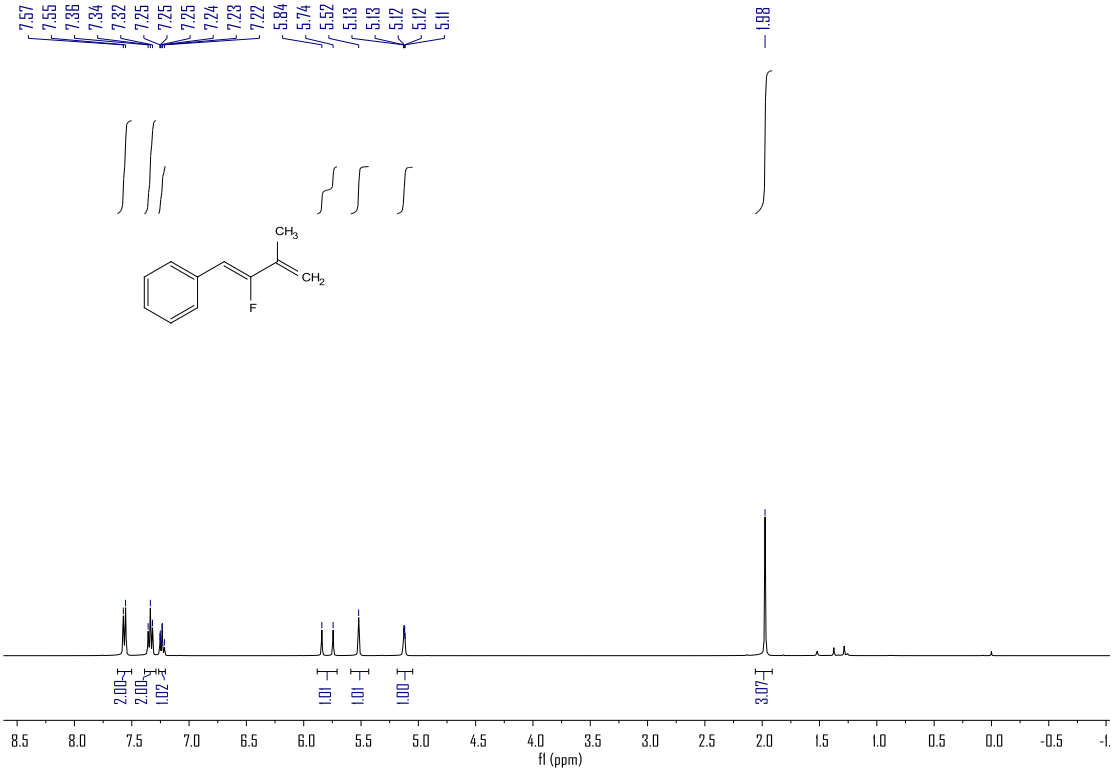


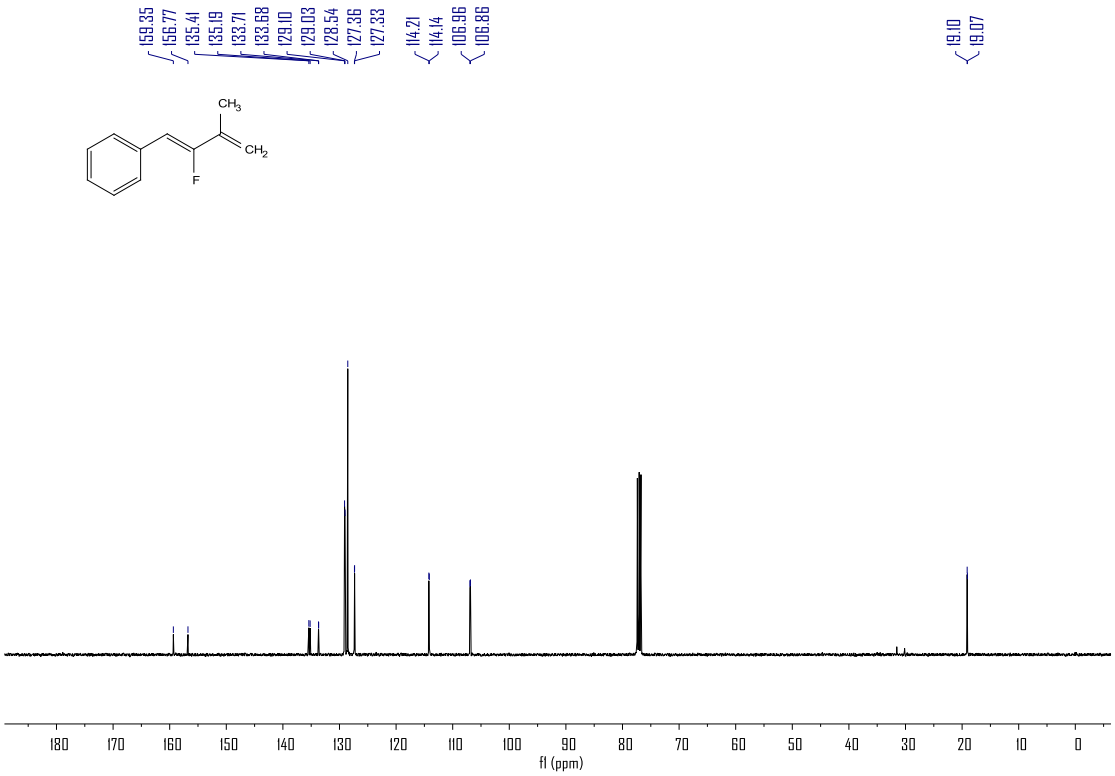


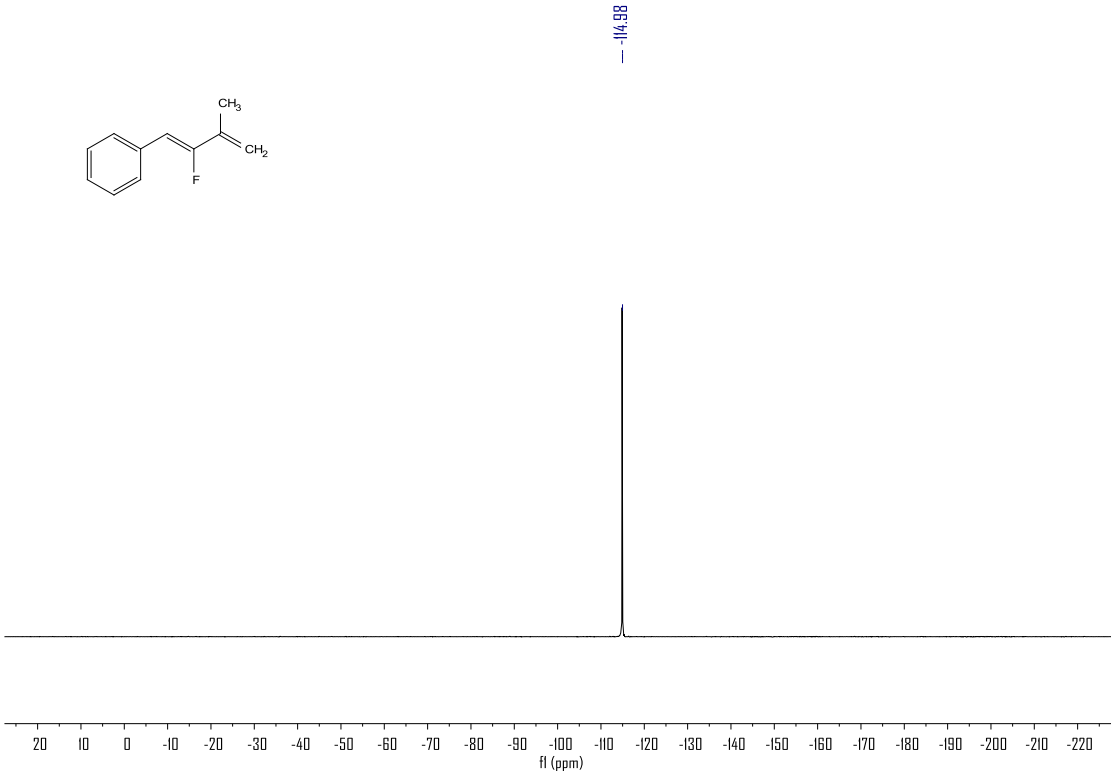
(Z)-(2-fluoro-3-methylbuta-1,3-dien-1-yl)benzene

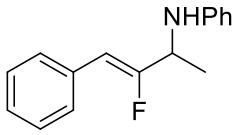
The residue was purified by silica gel-column chromatography using PE as an eluent. **(product 54**, **pale-yellow liquid, 24.0 mg, 75%)**. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.56 (d, *J* = 7.7 Hz, 2H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.27 – 7.14 (m, 1H), 5.79 (d, *J* = 39.3 Hz, 1H), 5.52 (s, 1H), 5.17 – 5.00 (m, 1H), 1.98 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 158.06 (d, *J* = 259.7 Hz), 135.30 (d, *J* = 22.7 Hz), 133.70 (d, *J* = 2.7 Hz), 129.06 (d, *J* = 7.9 Hz), 128.54, 127.34 (d, *J* = 2.5 Hz), 114.17 (d, *J* = 7.7 Hz), 106.91 (d, *J* = 10.5 Hz), 19.08 (d, *J* = 3.9 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -114.98.

HRMS (ESI) calcd for $C_{11}H_{12}F$ ($M+H^+$): 163.0918; found: 163.0920.





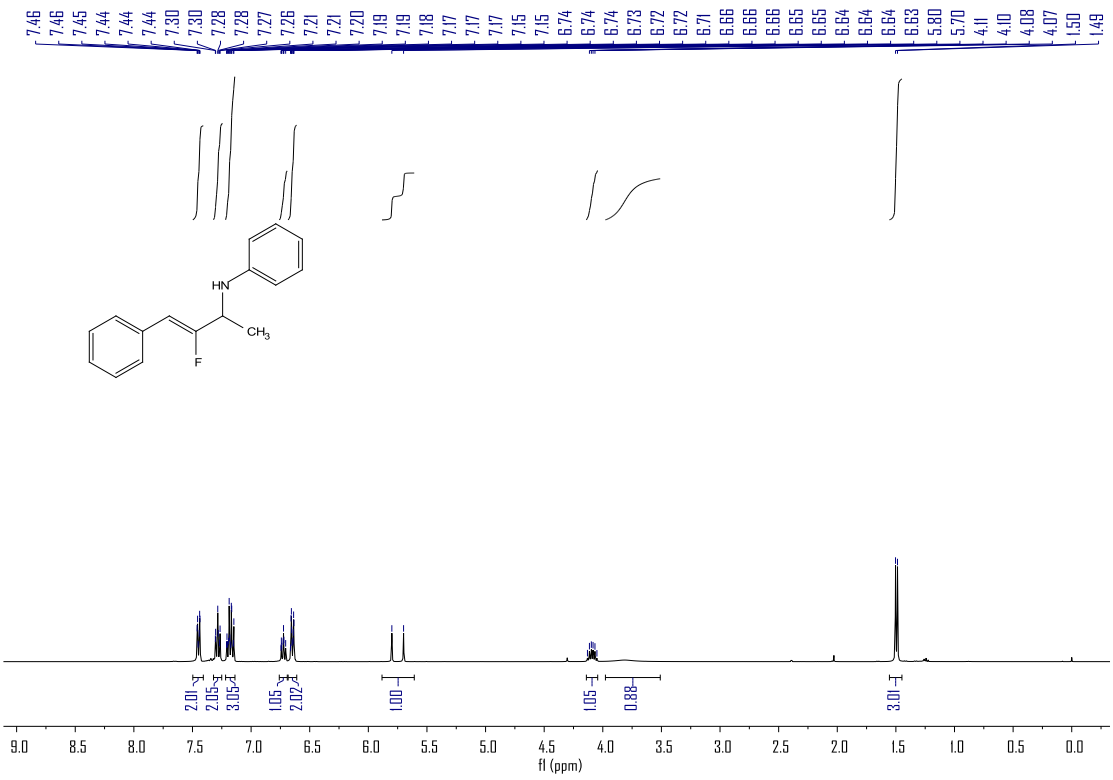


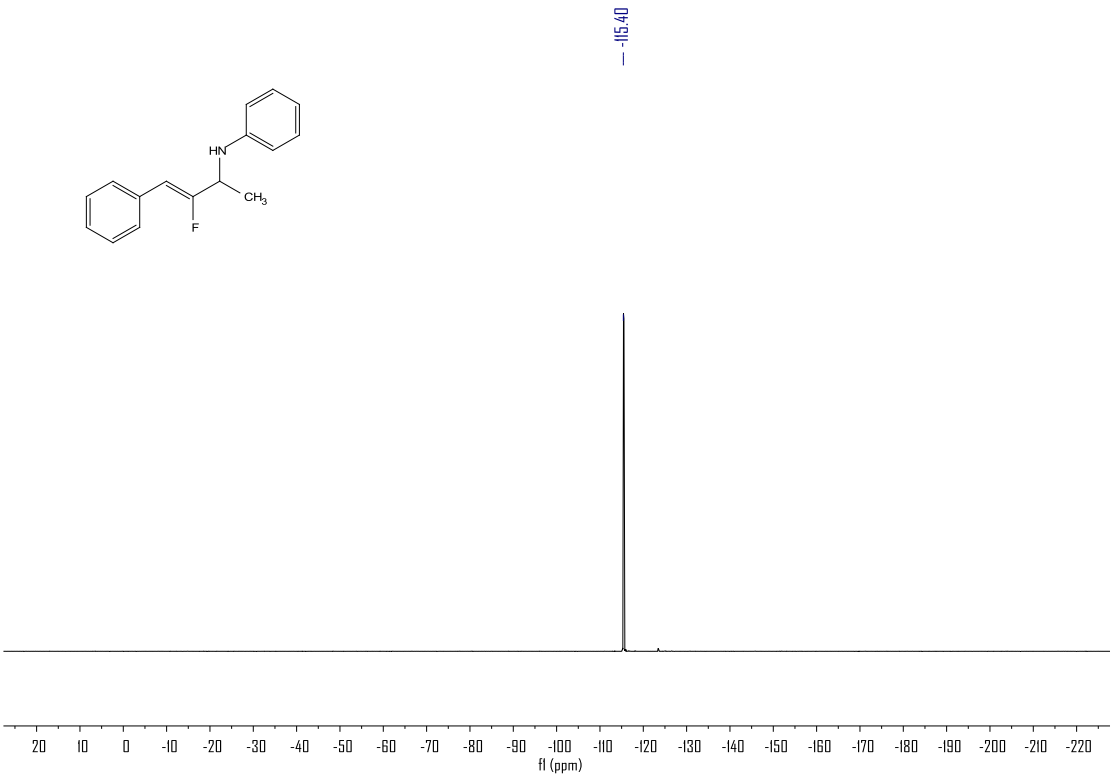


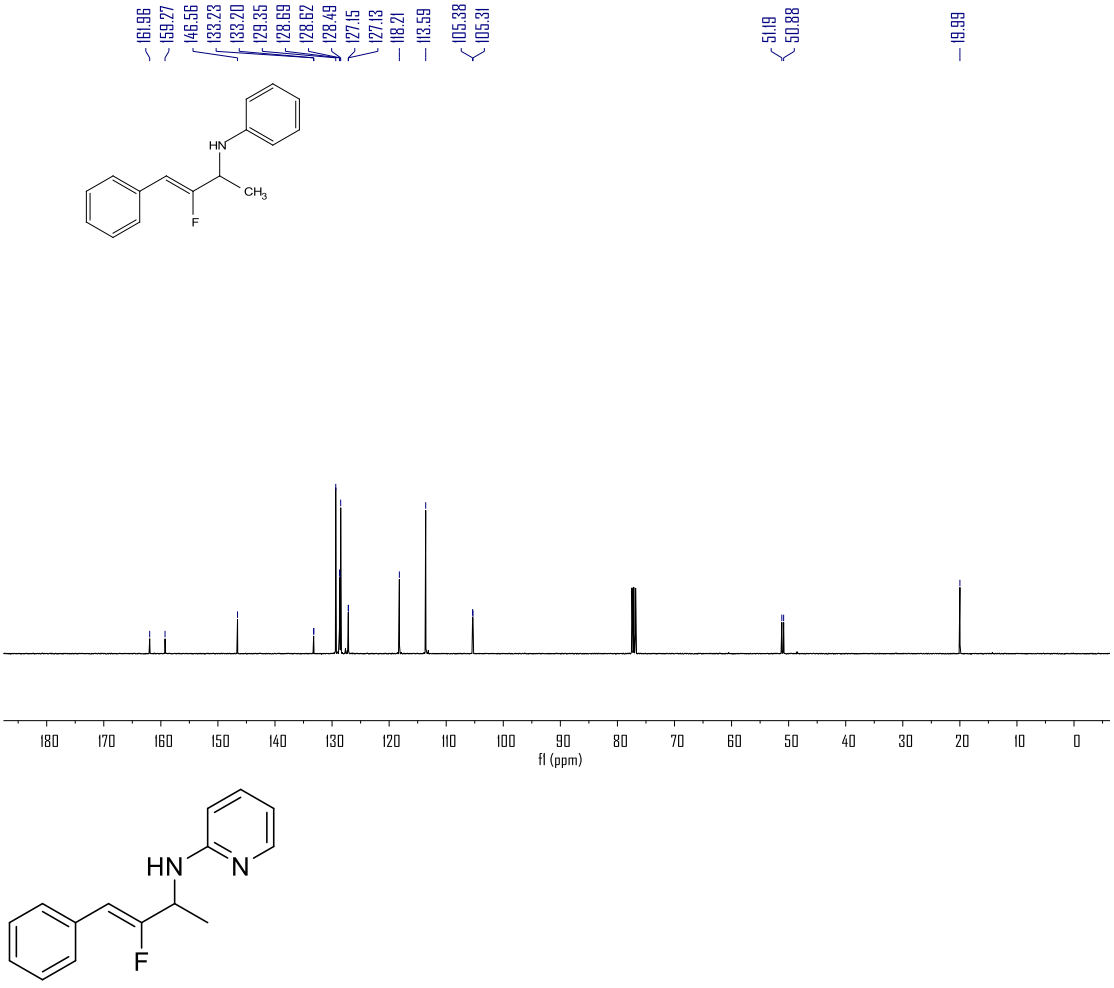
(Z)-N-(3-fluoro-4-phenylbut-3-en-2-yl)aniline

The residue was purified by silica gel-column chromatography using PE/EtOAc (30:1) as an eluent. **(product 53**, **yellow liquid, 38.5 mg, 80%)**. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.50 – 7.41 (m, 2H), 7.32 – 7.26 (m, 2H), 7.21 – 7.13 (m, 3H), 6.76 – 6.70 (m, 1H), 6.67 – 6.62 (m, 2H), 5.75 (d, *J* = 40.0 Hz, 1H), 4.13 – 4.02 (m, 1H), 3.81 (s, 1H), 1.49 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 160.61 (d, *J* = 270.7 Hz), 146.56, 133.22 (d, *J* = 2.5 Hz), 129.35, 128.66 (d, *J* = 7.3 Hz), 128.49, 127.14 (d, *J* = 2.3 Hz), 118.21, 113.59, 105.34 (d, *J* = 6.9 Hz), 51.04 (d, *J* = 31.9 Hz), 19.99. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -115.40.

HRMS (ESI) calcd for $C_{16}H_{17}FN$ ($M+H^+$): 242.1340; found: 242.1345.



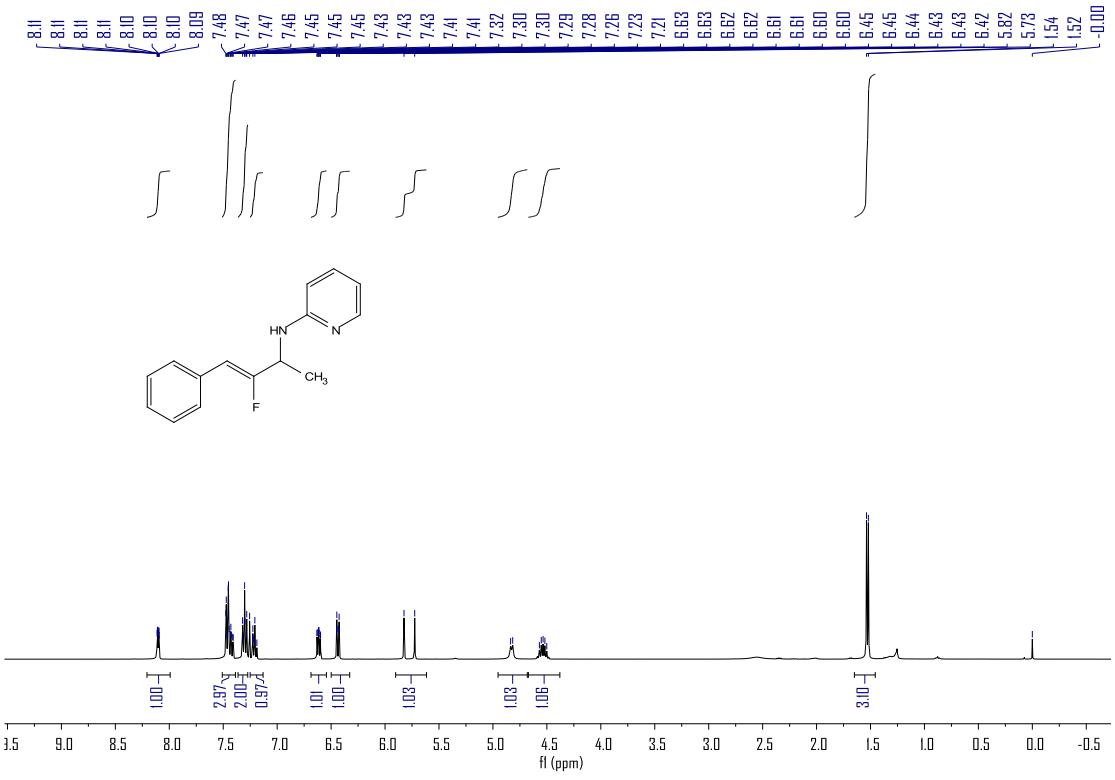


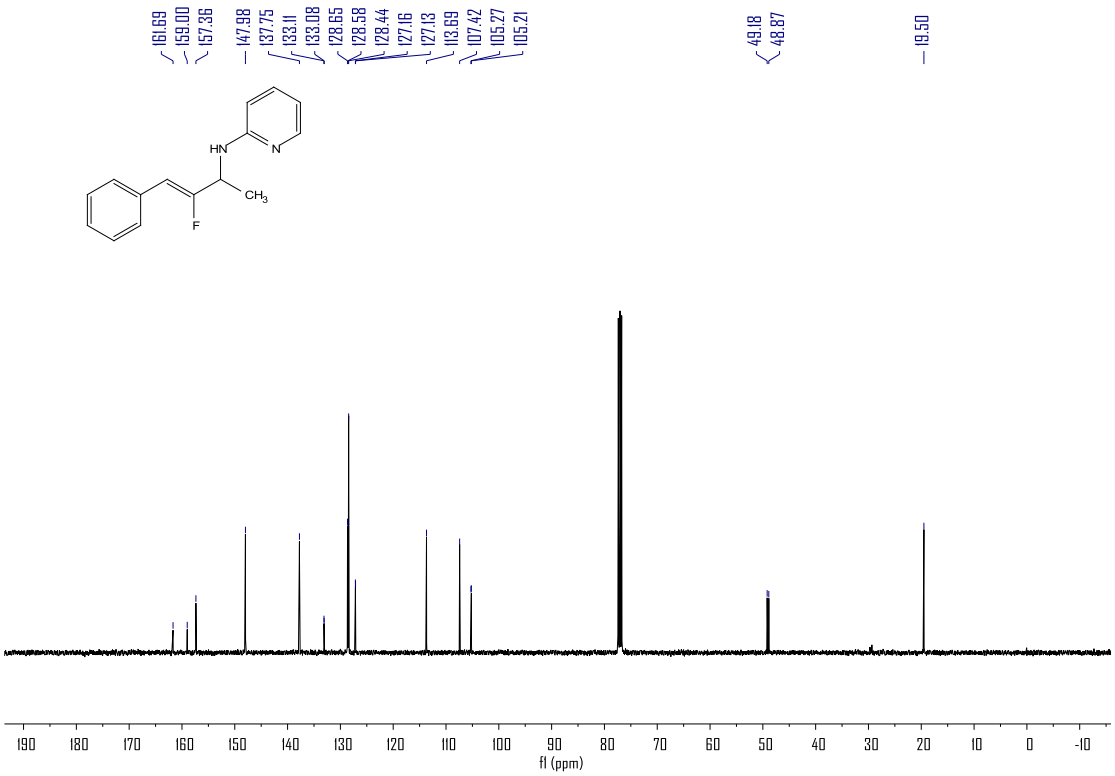


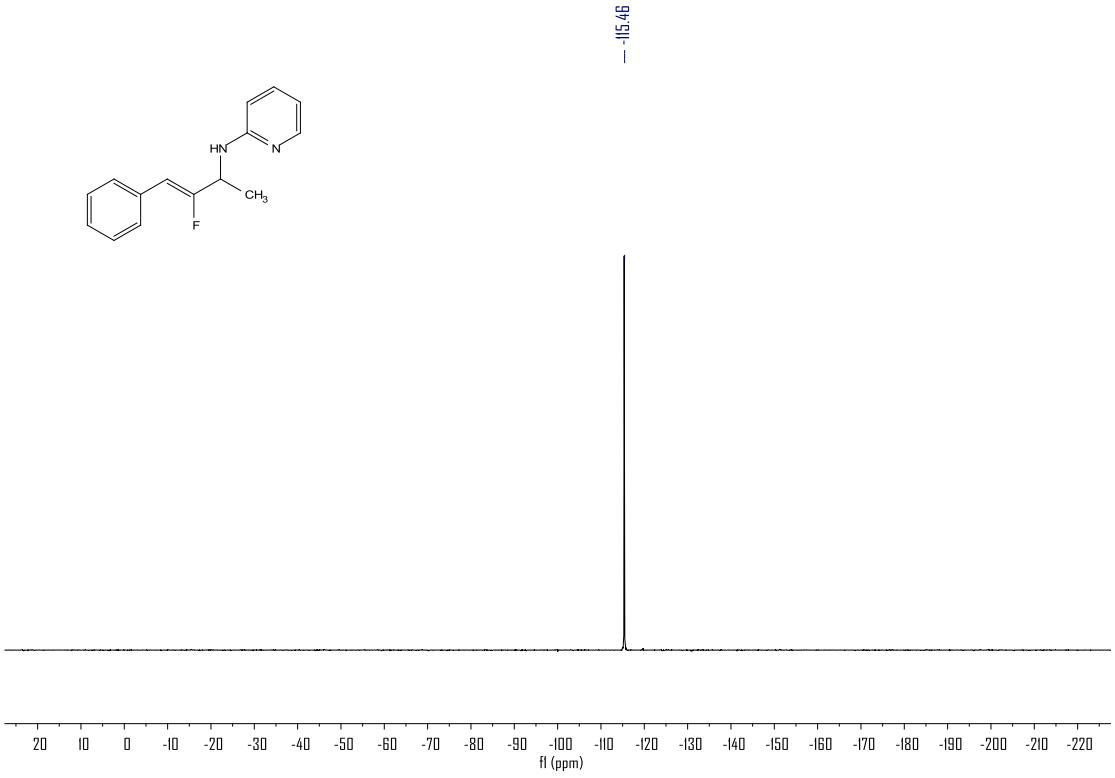
(Z)-N-(3-fluoro-4-phenylbut-3-en-2-yl)pyridin-2-amine

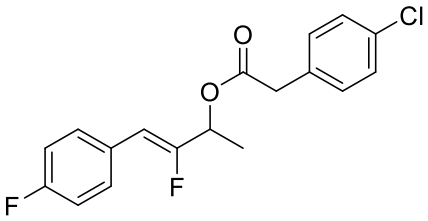
The residue was purified by silica gel-column chromatography using PE/EtOAc (3:1) as an eluent. **(product 56, yellow liquid, 46 mg, 95%)**. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.10 (ddd, *J* = 5.0, 1.9, 0.9 Hz, 1H), 7.50 – 7.40 (m, 3H), 7.30 (dd, *J* = 8.4, 6.9 Hz, 2H), 7.24 – 7.17 (m, 1H), 6.61 (ddd, *J* = 7.1, 5.1, 0.9 Hz, 1H), 6.44 (dd, *J* = 8.4, 0.9 Hz, 1H), 5.77 (d, *J* = 39.7 Hz, 1H), 4.83 (d, *J* = 7.8 Hz, 1H), 4.54 (dt, *J* = 13.7, 7.0 Hz, 1H), 1.53 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 160.35 (d, *J* = 270.5 Hz), 157.36, 147.98, 137.75, 133.11, 128.61 (d, *J* = 7.3 Hz), 128.44, 127.14 (d, *J* = 2.5 Hz), 113.69, 107.42, 105.24 (d, *J* = 7.0 Hz), 49.03 (d, *J* = 31.4 Hz), 19.50. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -115.46.

HRMS (ESI) calcd for $C_{15}H_{16}FN_2$ ($M+H^+$): 243.1292; found: 243.1296.




161.69
159.00
157.36
147.98
137.75
133.11
133.08
128.65
128.58
128.44
127.16
127.13
113.69
107.42
105.27
105.21
49.18
48.87
19.50
HN
N
CH3
F
f1 (ppm)

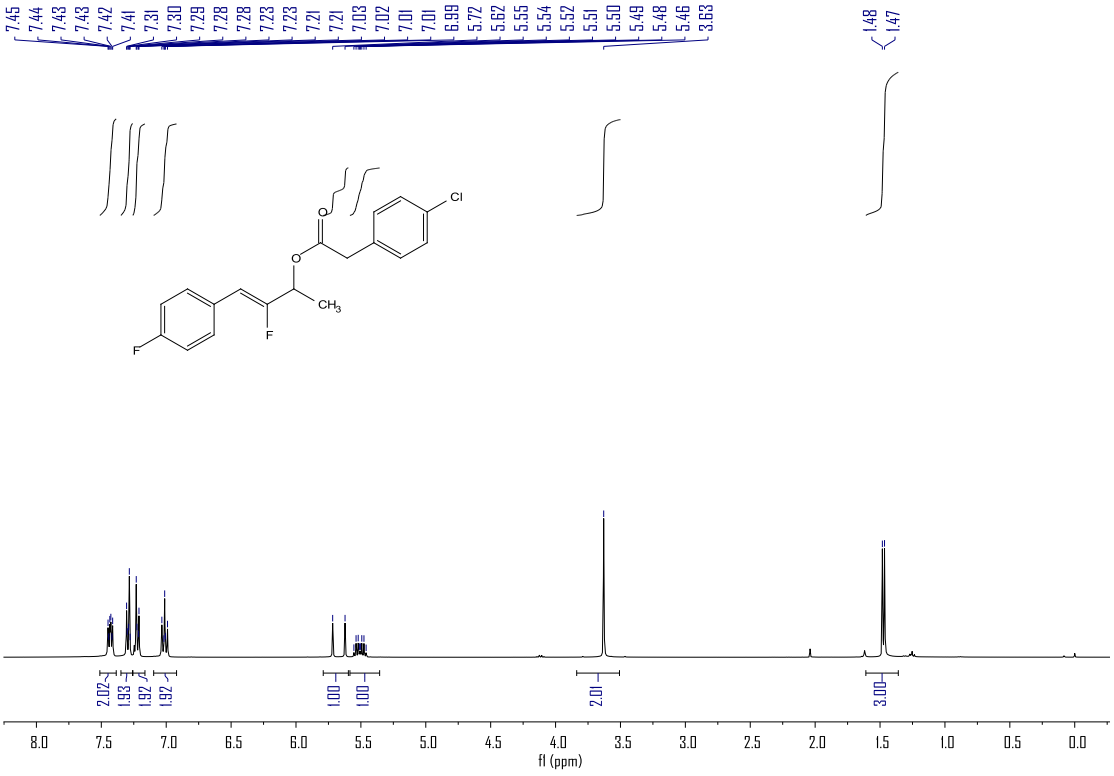

-115.46
HN
N
CH3
F
f1 (ppm)

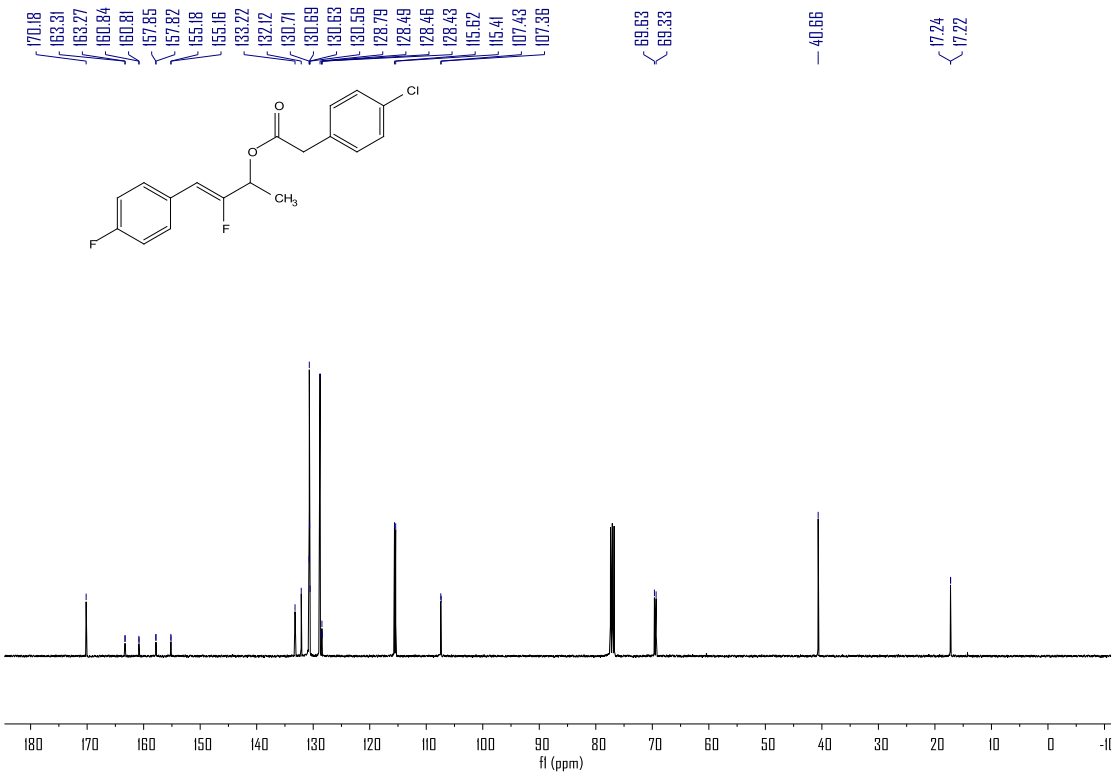


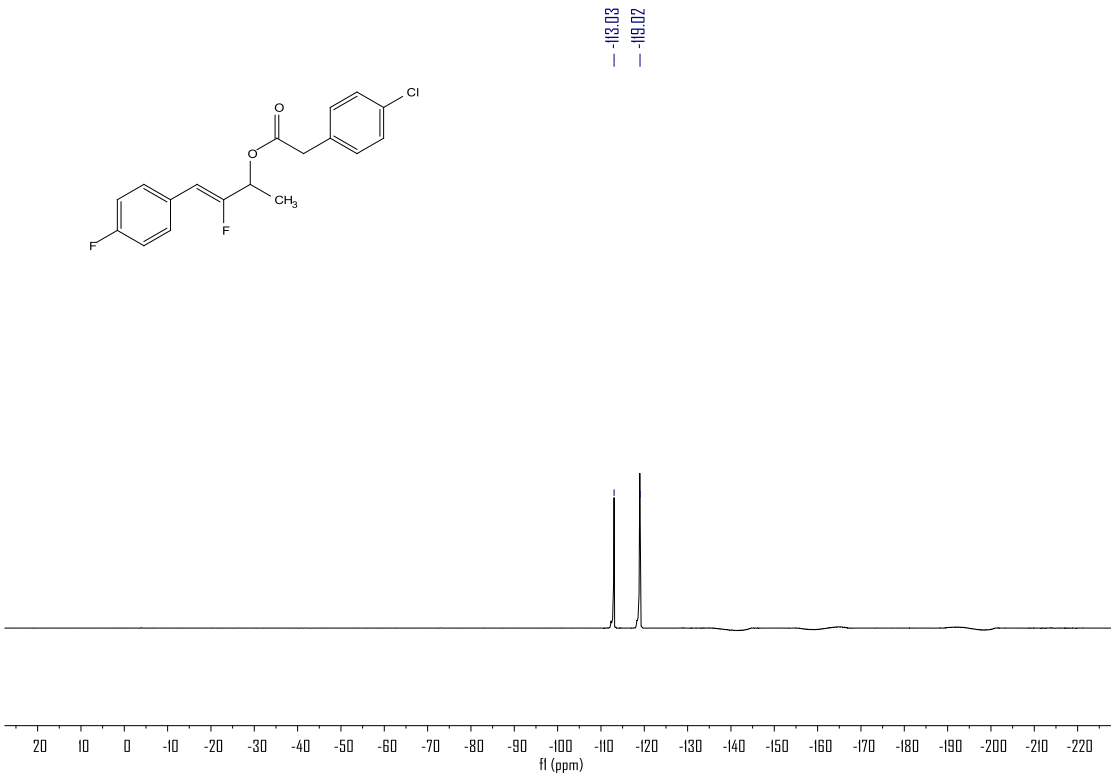
(Z)-3-fluoro-4-(4-fluorophenyl)but-3-en-2-yl 2-(4-chlorophenyl)acetate

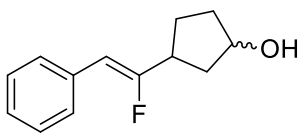
The residue was purified by silica gel-column chromatography using PE/EtOAc (30:1) as an eluent. **(product 58**, **pale-yellow liquid, 64.5 mg, 96%)**. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.49 – 7.37 (m, 2H), 7.33 – 7.28 (m, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.01 (t, *J* = 8.7 Hz, 2H), 5.67 (d, *J* = 38.1 Hz, 1H), 5.51 (dq, *J* = 17.7, 6.7 Hz, 1H), 3.63 (s, 2H), 1.47 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 170.18, 162.06 (dd, *J* = 248.1, 3.5 Hz), 156.50 (dd, *J* = 268.1, 2.5 Hz), 133.22, 132.12, 130.69, 130.63 (t, *J* = 7.8 Hz), 128.79, 128.46 (t, *J* = 3.2 Hz), 115.51 (d, *J* = 21.5 Hz), 107.39 (d, *J* = 6.9 Hz), 69.48 (d, *J* = 30.0 Hz), 40.66 , 17.23 (d, *J* = 2.2 Hz). **^{9}F NMR** (376 MHz, $CDCl_3$) δ -113.03, -119.02.

HRMS (ESI) calcd for $C_{18}H_{16}ClF_2O_2$ ($M+H^+$): 337.0801; found: 337.0807.





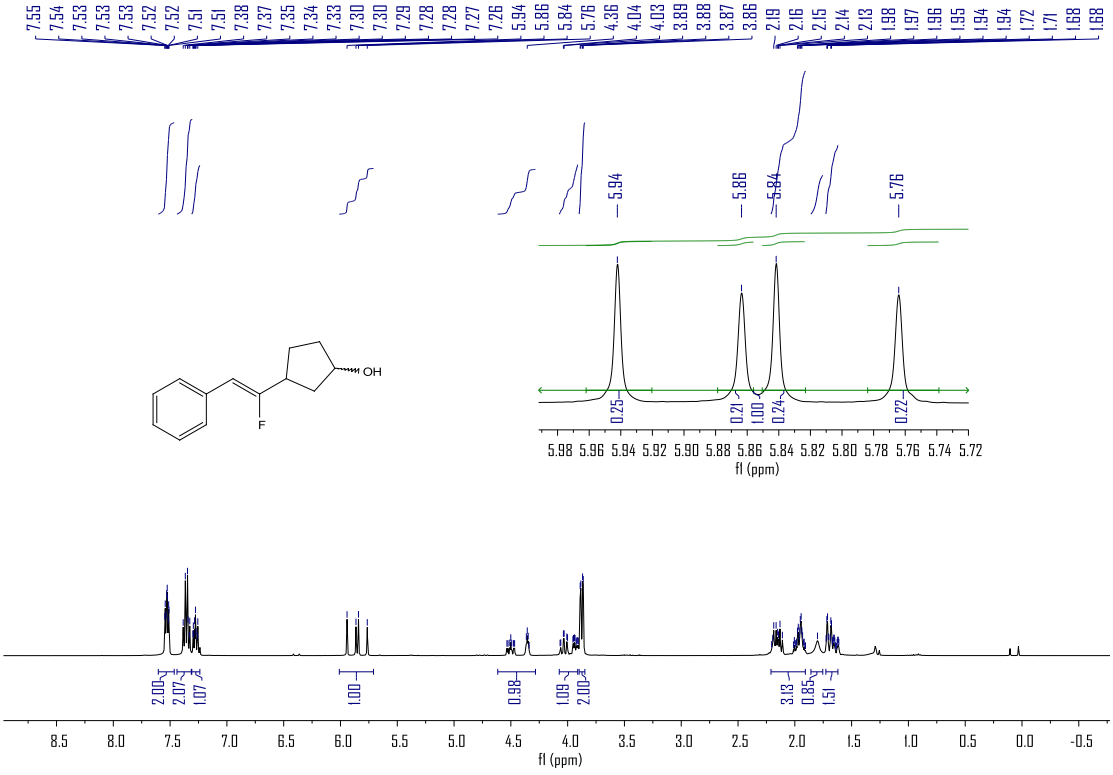


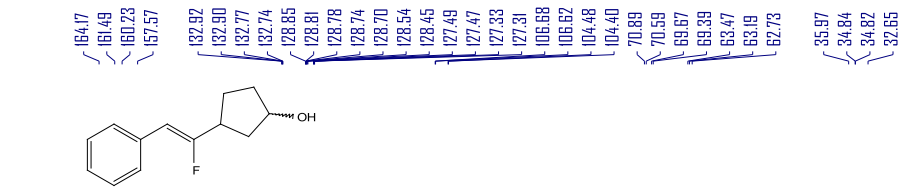


3-((Z)-1-fluoro-2-phenylvinyl)cyclopentan-1-ol

Following the general procedure (**59**, **pale-yellow liquid, 13.1 mg, *d.r.* = 1.1:1, 32%,** Z/E > 20:1). The residue was purified by silica gel-column chromatography using PE/EtOAc (10:1) as an eluent. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.57 – 7.48 (m, 2H), 7.40 – 7.32 (m, 2H), 7.28 (ddd, *J* = 8.3, 5.9, 1.7 Hz, 1H), 5.85 (dd, *J* = 40.0, 31.2 Hz, 1H), 4.55 – 4.30 (m, 1H), 4.07 – 3.91 (m, 1H), 3.88 (dd, *J* = 8.4, 2.3 Hz, 2H), 2.21 – 1.89 (m, 3H), 1.80 (s, 1H), 1.67 (ddq, *J* = 23.1, 14.1, 2.3 Hz, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 162.83 (d, *J* = 269.6 Hz), 158.90 (d, *J* = 267.1 Hz), 132.91 (d, *J* = 2.5 Hz), 132.76 (d, *J* = 2.5 Hz), 128.81 (d, *J* = 7.4 Hz), 128.77 (d, J = 7.3 Hz), 128.54, 128.45, 127.48 (d, *J* = 2.4 Hz), 127.32 (d, *J* = 2.3 Hz), 106.65 (d, *J* = 6.3 Hz), 104.44 (d, *J* = 7.7 Hz), 70.74 (d, *J* = 30.9 Hz), 69.53 (d, *J* = 28.0 Hz), 63.47, 63.19, 62.73, 35.97, 34.83 (d, *J* = 1.3 Hz), 32.65. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -116.38, -118.66.

HRMS (ESI) calcd for $C_{13}H_{15}FNaO$ ($M+Na^+$): 229.0999; found: 229.0991.

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157.57
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132.90
132.77
132.74
128.85
128.81
128.78
128.74
128.70
128.54
128.45
127.49
127.47
127.33
127.31
106.68
106.62
104.48
104.40
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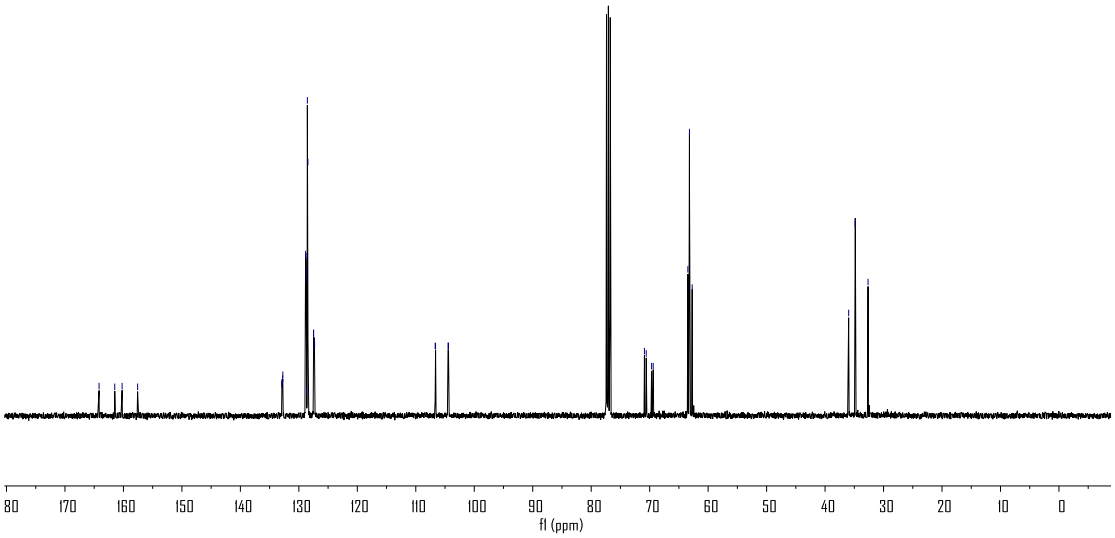
63.47
63.19
62.73
35.97
34.84
34.82
32.65
OH
F


80
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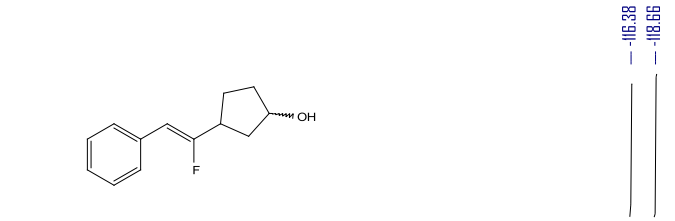
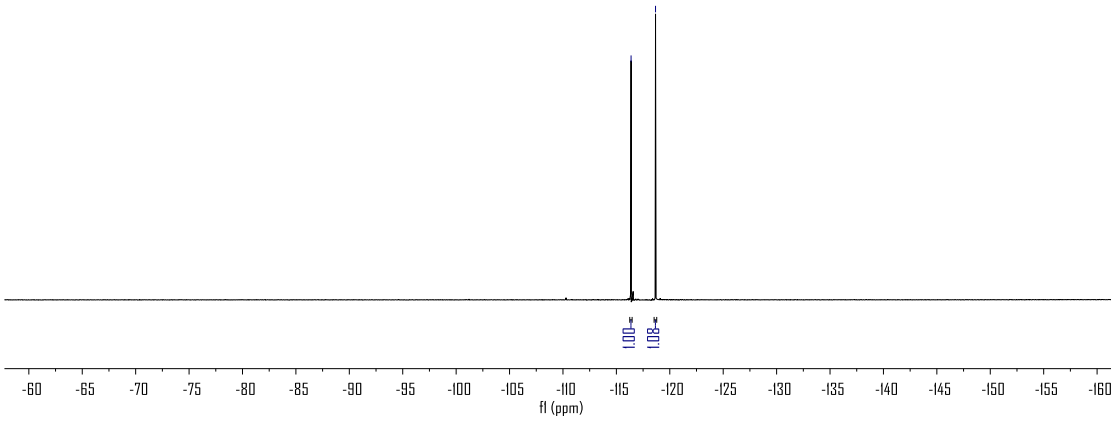
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-116.38
-118.66
OH
F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-130
-135
-140
-145
-150
-155
-160
f1 (ppm)