Supplementary Information

Synthesis of gem-difluoroalkenes via Nickel-Catalyzed Allylic Defluorinative Reductive Cross-Coupling of Trifluoromethyl Alkenes with Epoxides

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1. General Information

1.1 Materials

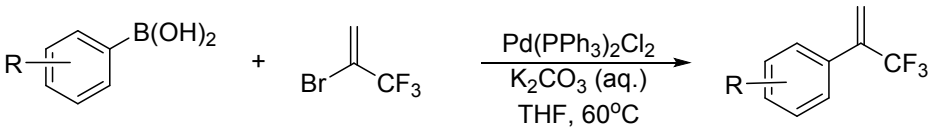
The following chemicals were purchased and used as received: $NiBr_2$·diglyme (Aldrich, CAS: 312696-09-6), 4,4'-Di-tert-butyl-2,2'-bipyridine (dtbpy, CAS: 72914-19-3, Energy-Chemical), $NiCl_2(PPh_3)_2$ (CAS: 14264-16-5, Adamas-beta), $Ni(acac)_2$ (CAS: 3264-82-2, Adamas-beta), Cyclohexene oxide (CAS: 286-20-4, Adamas-beta), Et_3N·HCl (CAS: 554-68-7, Adamas-beta), Isobutylene Oxide (CAS: 558-30-5, TCI), Cyclopentene oxide (CAS: 285-67-6, Adamas-beta), 3,6-dioxabicyclo[3.1.0]hexane (CAS: 285-69-8, Adamas-beta), NaI (dry, anhydrous, Sinopharm Chemical Reagent Co., Ltd.), DMAc (Hengyue Chemical Technology Co., Ltd., 4 Å molecular sieves). N-methylpyrrolidin-2-one (Hengyue Chemical Technology Co., Ltd., 4 Å molecular sieves). All the other reagents and solvents mentioned in this text were purchased from commercial sources and used without purification.

1.2 Analytical Methods

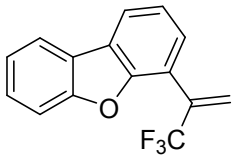
^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on a Bruker 400 MHz spectrometer at 295 K in $CDCl_3$ unless otherwise noted. ^{19}F NMR were reported as 19F exp. comp. pulse decoupling (F19CPD) unless otherwise noted. Data for ^{1}H-NMR are reported as follows: chemical shift (δ ppm), multiplicity, 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 ESI-mass data were acquired on Thermo LTQ Orbitrap XL instrument. Organic solutions were concentrated under reduced pressure on a Buchi rotary evaporator. Column chromatographic purification of products was accomplished using forced-flow chromatography on Silica Gel (200-300 mesh).

2. Preparation of Substrates

2.1 Preparation of Trifluoromethyl Alkenes

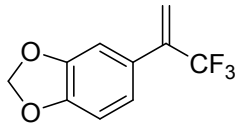


In a Schlenk tube equipped with stir bar, arylboronic acids (1.0 equiv., 10 mmol) and $Pd(PPh_3)_2Cl_2$ (3 mol%, 0.3 mmol, 210.6 mg) were added. The vessel was evacuated and filled with argon (three cycles), then aqueous K_2CO_3 (2.0 M, 20 mL) and THF (30 mL) were added. After the addition of 2-bromo-3,3,3-trifluoropropene (2.0 equiv., 20 mmol, 2.1 mL), the solution was stirred at 60 ℃ for over night. The mixture was purified by column chromatography to afford the corresponding trifluoromethyl alkenes.[1]



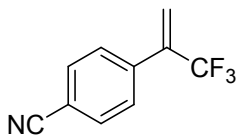
4-(3,3,3-trifluoroprop-1-en-2-yl)dibenzo[b,d]furan

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.92 (m, 2H), 7.62 – 7.57 (m, 1H), 7.56 – 7.46 (m, 2H), 7.41 – 7.34 (m, 2H), 6.41 – 6.35 (m, 2H).



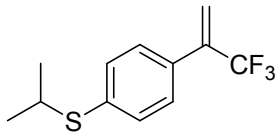
5-(3,3,3-trifluoroprop-1-en-2-yl)benzo[d][1,3]dioxole

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.95 – 6.90 (m, 2H), 6.81 – 6.73 (m, 1H), 5.98 (s, 2H), 5.86 (dd, *J* = 2.6, 1.4 Hz, 1H), 5.67 (dd, *J* = 3.5, 1.5 Hz, 1H).



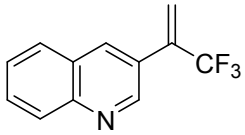
4-(3,3,3-trifluoroprop-1-en-2-yl)benzonitrile

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.66 (m, 2H), 7.57 (d, *J* = 8.2 Hz, 2H), 6.12 (q, *J* = 1.5 Hz, 1H), 5.91 (q, *J* = 1.7 Hz, 1H).



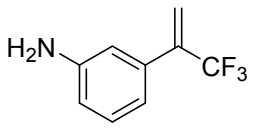
isopropyl(4-(3,3,3-trifluoroprop-1-en-2-yl)phenyl)sulfane

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.32 (m, 4H), 5.95 (q, *J* = 1.4 Hz, 1H), 5.78 (q, *J* = 1.7 Hz, 1H), 3.46 (p, *J* = 6.7 Hz, 1H), 1.33 (d, *J* = 6.7 Hz, 6H).



3-(3,3,3-trifluoroprop-1-en-2-yl)quinolone

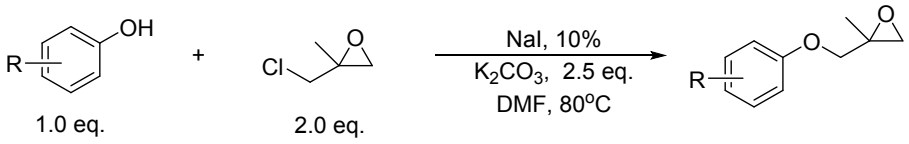
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.93 (d, *J* = 2.3 Hz, 1H), 8.24 (m, 1H), 8.10 (m, 1H), 7.82 (m, 1H), 7.72 (m, 1H), 7.59 (m, 1H), 6.13 (dd, *J* = 2.6, 1.2 Hz, 1H), 5.92 (dd, *J* = 3.1, 1.5 Hz, 1H).



3-(3,3,3-trifluoroprop-1-en-2-yl)aniline

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (t, *J* = 7.9 Hz, 1H), 6.85 (d, *J* = 7.7 Hz, 1H), 6.77 (s, 1H), 6.67 (dd, *J* = 8.0, 1.7 Hz, 1H), 5.91 (q, *J* = 1.4 Hz, 1H), 5.72 (q, *J* = 1.7 Hz, 1H), 3.63 (s, 2H).

2.2 Preparation of Epoxides



The respective phenol (1.0 eq) was dissolved in DMF (10 mL/mmol), K_2CO_3 (3.0 eq), NaI (10 mol%), and 2-(chloromethyl)-2-methyloxirane (2.5 eq) were added and the mixture was heated to 80 °C for 12 h. The crude product was purified by columnchromatography.[2]

Rferences

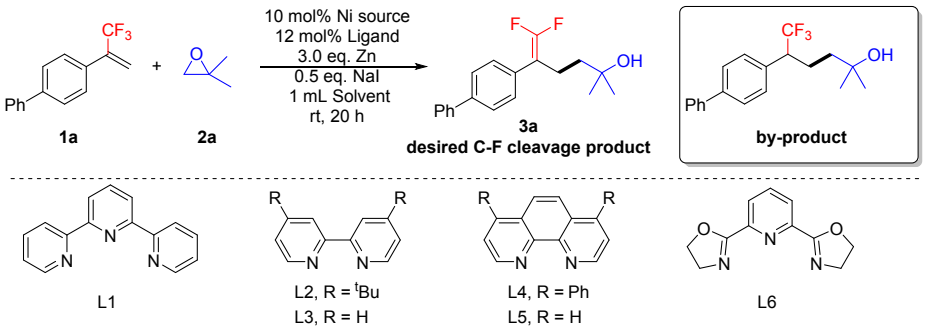
1. (a) X. Lu, X. X. Wang, T. J. Gong, J. J. Pi, S. J. He and Y. Fu, *Chem Sci*, **2019**, 10, 809-814; (b) Y. Lan, F. Yang and C. Wang, *ACS Catal.*, **2018**, 8, 9245-9251.
2. X.-Y. Lu, C.-T. Yang, J.-H. Liu, Z.-Q. Zhang, X. Lu, X. Lou, B. Xiao and Y. Fu, *Chem. Commun.*, **2015**, 51, 2388-2391.

3. General Experimental Procedures

3.1 General procedure for Table 1

In air, Nickel source (10 mol%), Ligand (12 mol%), reductant (3.0 equiv.), NaI (0.5 equiv.), and additive (1.2 equiv.) were added to a schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (three cycles). To these solids, **1a** (0.2 mmol), **2a** (3 equiv.) and Solvent (1.0 mL) were added in turn by syringe. The resulting reaction mixture was stirred vigorously at room temperature (about 25 °C to 30 °C) for 20 h. Triphenylmethane was added as internal standard. The product was yielded by GC.

Table S1. Optimization of the reaction conditions



Entry[a]	Ni source	Ligand	Addtive	Solvent	Yield%
1	$NiBr_2$·diglyme	L1	-	DMAc	trace
2	$NiBr_2$·diglyme	L2	-	DMAc	trace
3	$NiBr_2$·diglyme	L1	Et_3N·HCl	DMAc	52
4	**$NiBr_2$·diglyme**	**L2**	**Et_3N·HCl**	**DMAc**	**96**
5	$NiBr_2$·diglyme	L3	Et_3N·HCl	DMAc	43
6	$NiBr_2$·diglyme	L4	Et_3N·HCl	DMAc	61
7	$NiBr_2$·diglyme	L5	Et_3N·HCl	DMAc	66
8	**$NiBr_2$·diglyme**	**L6**	**Et_3N·HCl**	DMAc	**95**
9	$NiCl_2(PPh_3)_2$	L2	Et_3N·HCl	DMAc	57
10	$Ni(acac)_2$	L2	Et_3N·HCl	DMAc	26
11	$Ni(cod)_2$	L2	Et_3N·HCl	DMAc	92
12	$NiBr_2$·diglyme	L2	Et_3N·HCl	MeCN	51
13	$NiBr_2$·diglyme	L2	Et_3N·HCl	NMP	73
14[b]	$NiBr_2$·diglyme	L2	Et_3N·HCl	DMAc	2
15	$NiBr_2$·diglyme	L2	H_2O	DMAc	5
16[c]	$NiBr_2$·diglyme	L2	MeOH	DMAc	80
17[c]	$NiBr_2$·diglyme	L2	EtOH	DMAc	66
18	$NiBr_2$·diglyme	L2	NH_4Cl	DMAc	31
19[d]	-	L2	Et_3N·HCl	DMAc	0
20[e]	$NiBr_2$·diglyme	L2	Et_3N·HCl	DMAc	0

21[f]	$NiBr_2$·diglyme	L2	Et_3N·HC	DMAc	0
22[g]	$NiBr_2$·diglyme	L2	Et_3N·HC	DMAc	trace

[a] **Reaction conditions**: 1a (0.2 mmol), 2a (3 eq.), Reductant (3 equiv.), NaI (0.5 equiv.) in 1.0 mL solvent at room temperature for 20 h. [b] Mn instead of Zn. [c] 5 equiv. alcohol instead of Et_3N·HCl. [d] no Ni source. [e] no NaI. [f] NaCl as additive. [g] NaBr as additive. The yield was determined by GC using Triphenylmethane as internal standard. NMP = 1-methyl-2-pyrrolidinone.

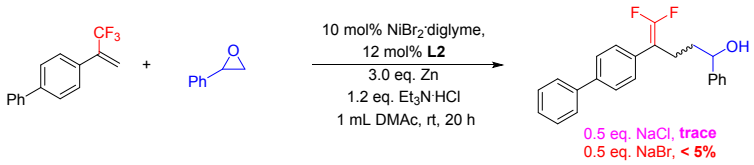
3.2 General procedure for Table 2

In air, $NiBr_2$·diglyme (10 mol%), dtbpy (**L2**, 12 mol%), Zn (3.0 equiv.), NaI (0.5 equiv.), and Et_3N·HCl (1.2 equiv.) were added to a schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (three cycles). To these solids, DMAc (1.0 mL) trifluoromethyl alkenes and epoxy (3 equiv.) were added in turn by syringe. The resulting reaction mixture was stirred vigorously at room temperature (about 25 °C to 30 °C) for 20 h. The mixture was purified by column chromatography to afford the desired products.

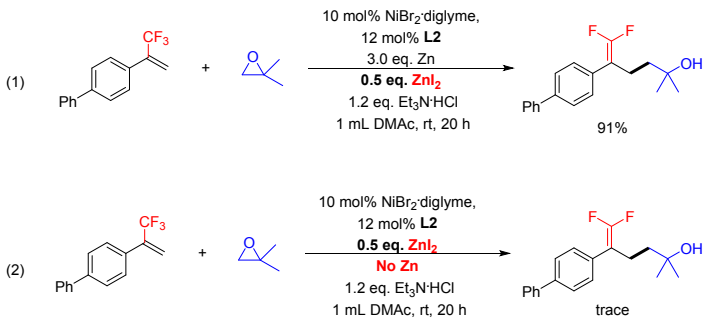
3.3 General procedure for Table 3

In air, $NiBr_2$·diglyme (10 mol%), **L2** (12 mol%), Zn (3.0 equiv.), NaI (0.5 equiv.), and Et_3N·HCl (1.2 equiv.) or MeOH (50 μL) were added to a schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (three cycles). To these solids, DMAc (1.0 mL) trifluoromethyl alkenes (0.2 mmol) and epoxy (3 equiv.) were added in turn by syringe. The resulting reaction mixture was stirred vigorously at room temperature (about 25 °C to 30 °C) for 20 h. The mixture was purified by column chromatography to afford the desired products.

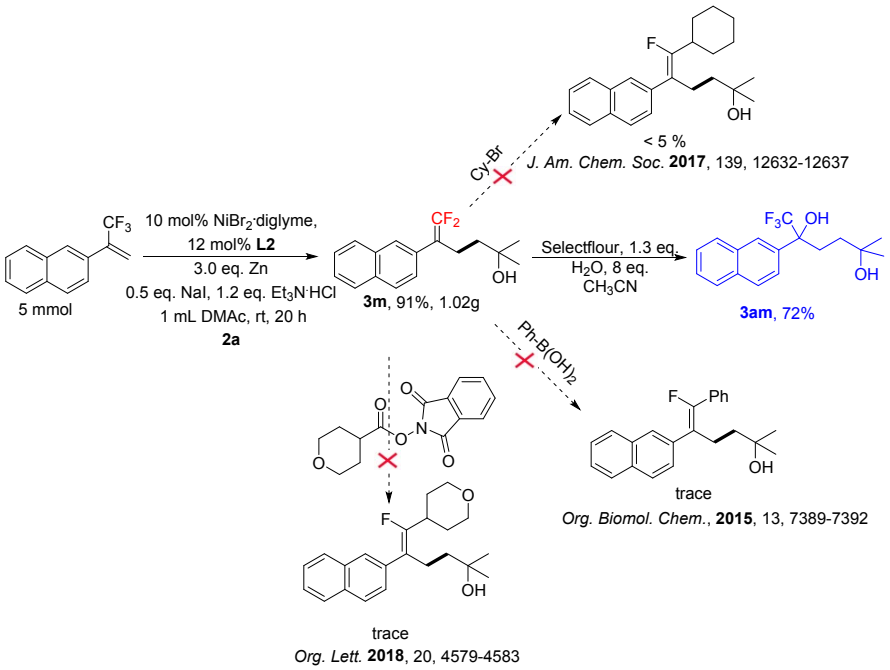
Experiment of Styrene oxide



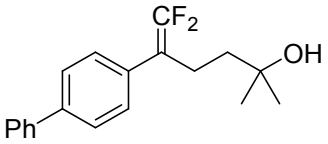
Experiment of ZnI_2



Gram-scale reaction and derivatization of product



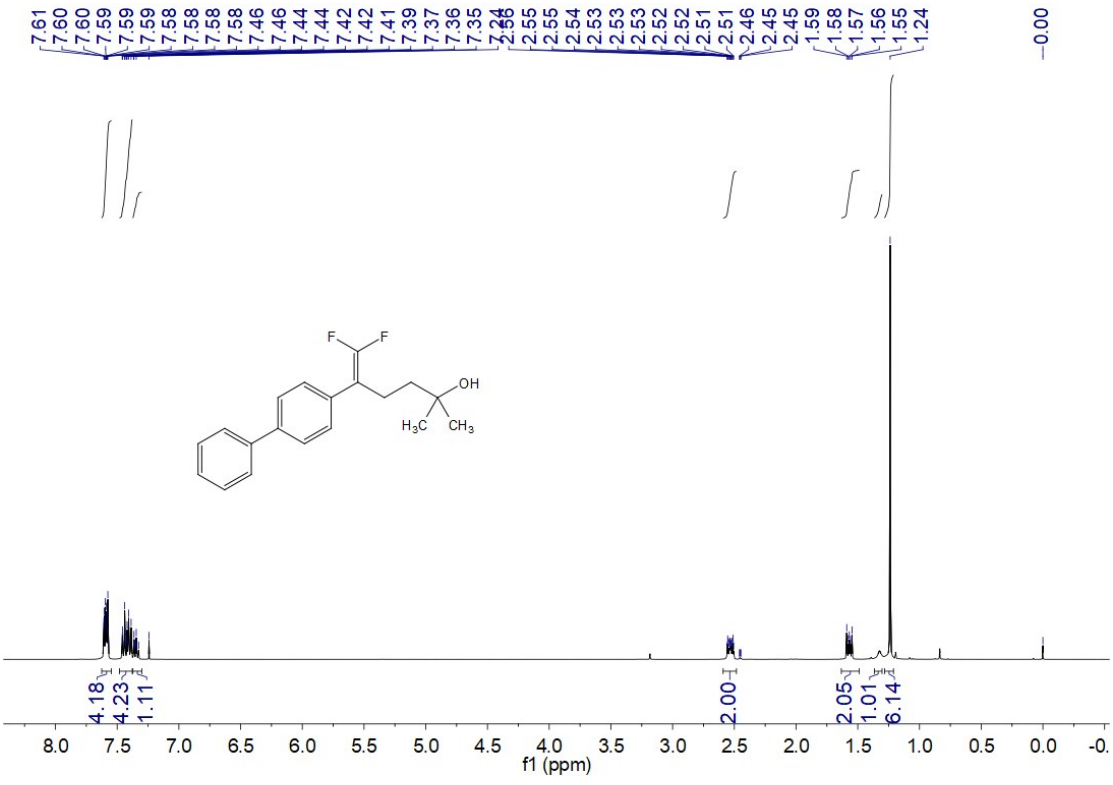
4. Substrate Scope and Spectral Data

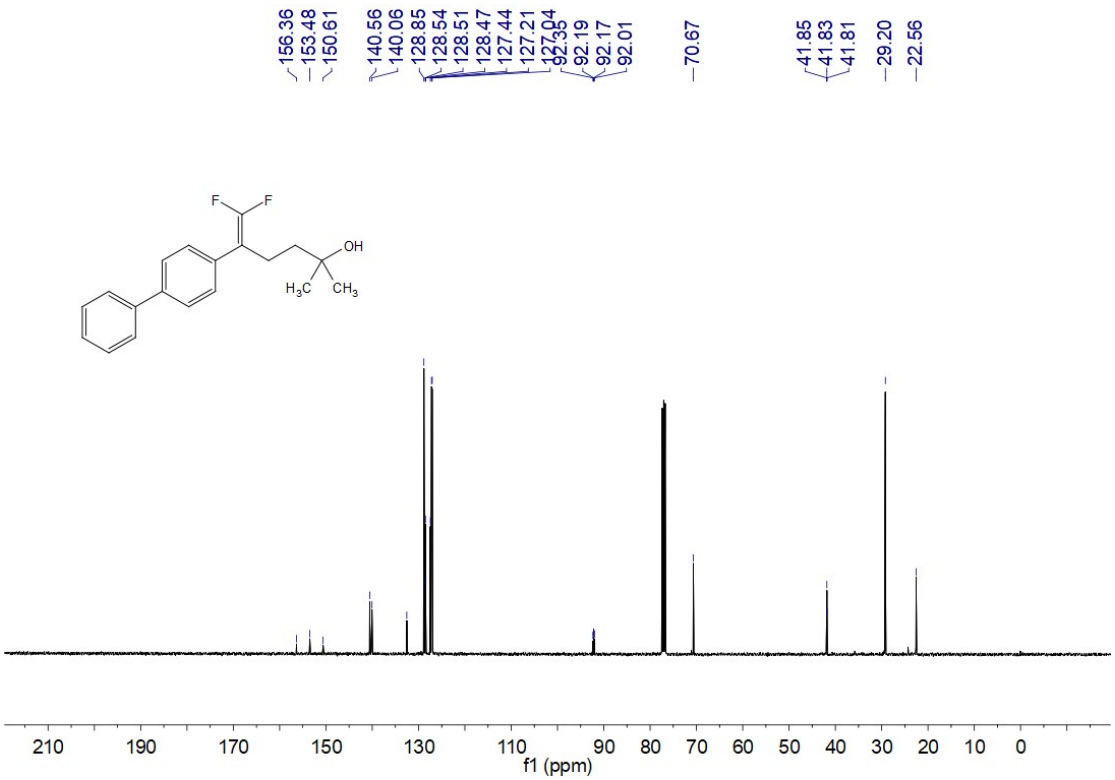


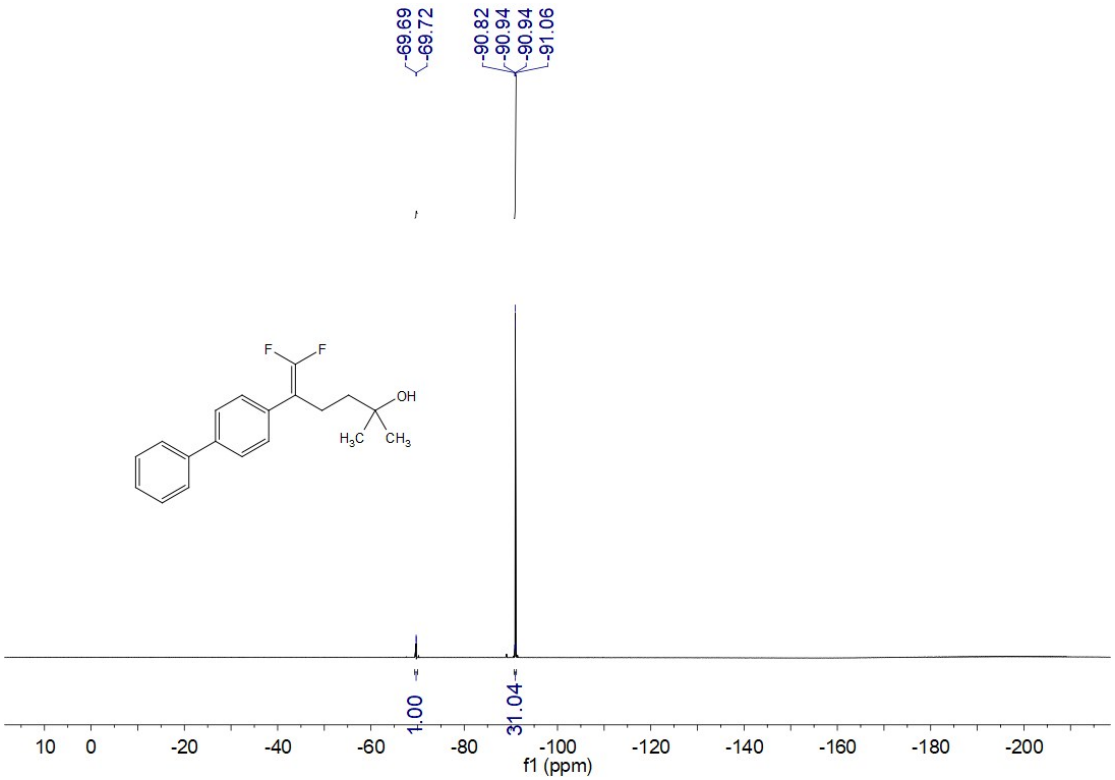
5-([1,1'-biphenyl]-4-yl)-6,6-difluoro-2-methylhex-5-en-2-ol (3a)

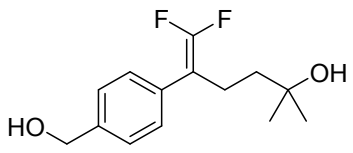
<u>Selectivity</u> (desired C-F cleavage product: addition by-product, determined by ^{1}H NMR and ^{19}F NMR) > 45:1.

Prepared according to the general procedure, as a sticky liquid. **^{1}H NMR** (400 MHz, CDCl3) δ 7.63 – 7.54 (m, 4H), 7.48 – 7.37 (m, 4H), 7.37 – 7.30 (m, 1H), 2.57 – 2.49 (m, 2H), 1.62 – 1.51 (m, 2H), 1.30 (br s, *J* = 15.9 Hz, 1H), 1.24 (s, 6H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -90.88 (d, *J* = 43.1 Hz), -91.00 (d, *J* = 43.2 Hz). **^{13}C NMR (101 MHz, CDCl3)** δ 153.49 (dd, *J* = 290.7, 286.3 Hz), 140.56, 140.06, 132.55 (dd, *J* = 0.9 Hz, *J* = 1.0 Hz), 128.85, 128.51 (dd, *J* = 3.4, 3.4 Hz), 127.44, 127.21, 127.04, 92.18 (t, *J* = 16.0 Hz), 70.67, 41.83 (t, *J* = 2.5 Hz), 29.20, 22.56. **HRMS** (APCI) calcd for $C_{19}H_{20}F_2NaO$ ($M+Na^+$): 325.1374; found: 325.1377. **IR** (KBr/cm-1) 3419, 2987, 1616, 1488, 1395, 1356, 1185, 1172, 1001, 787, 773, 612.







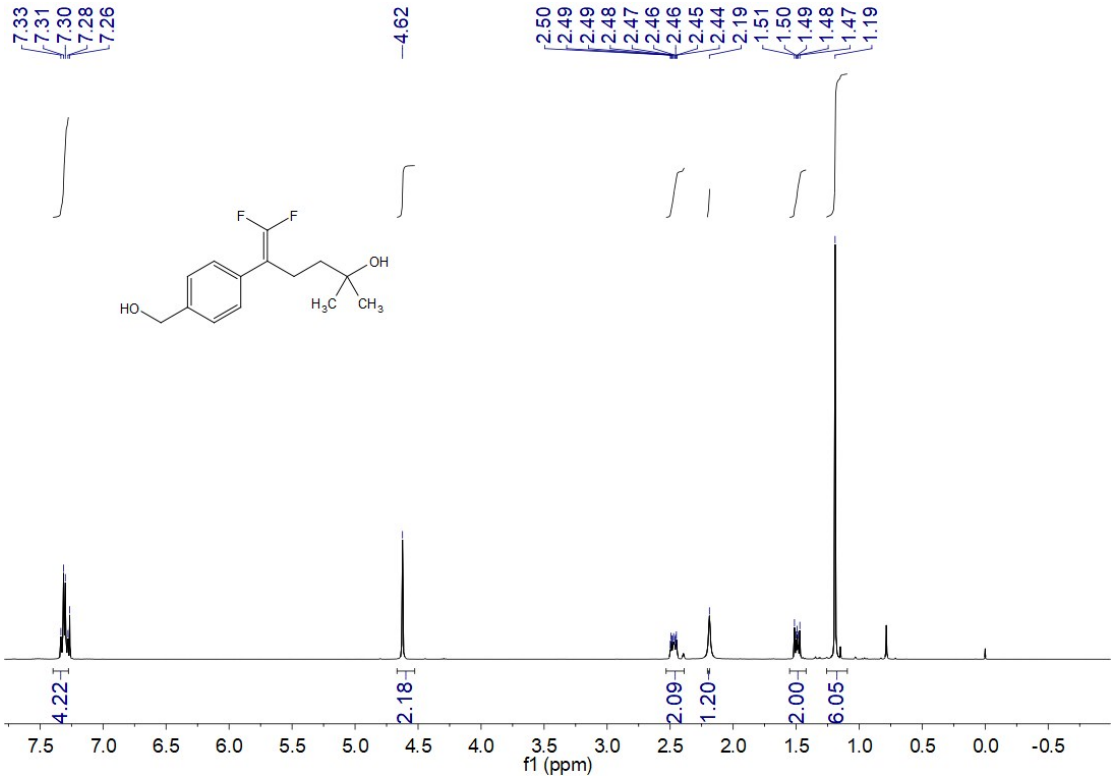


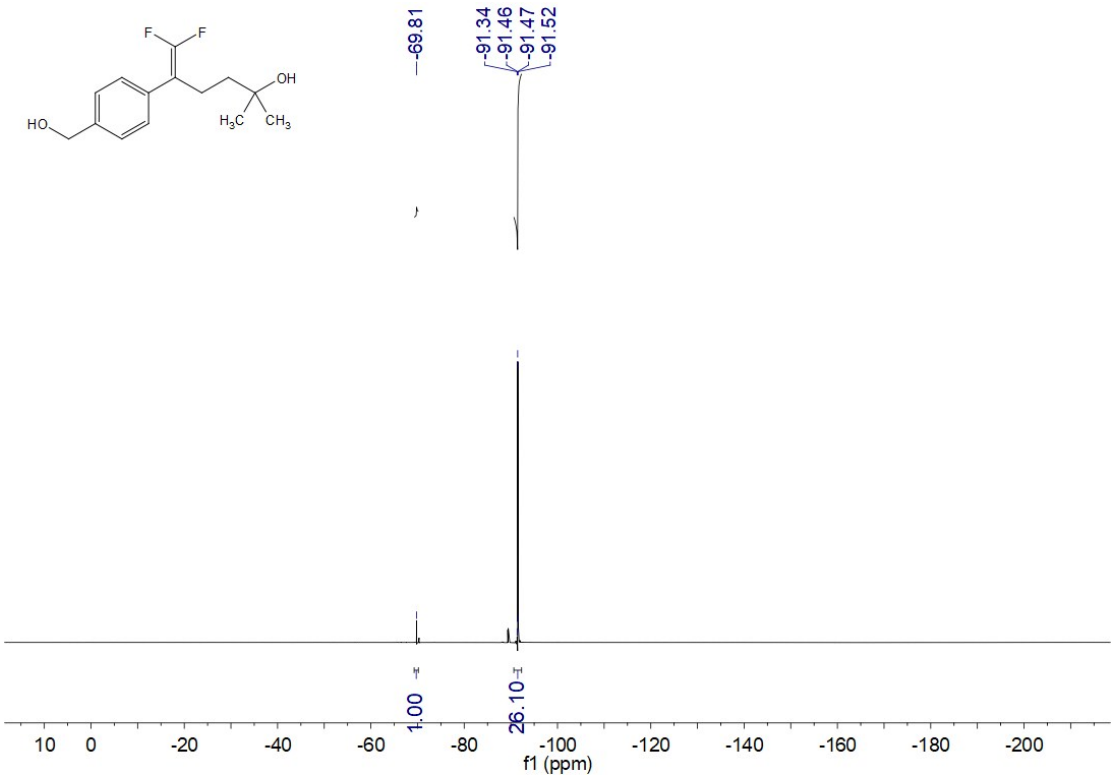
6,6-difluoro-5-(4-(hydroxymethyl)phenyl)-2-methylhex-5-en-2-ol (3l)

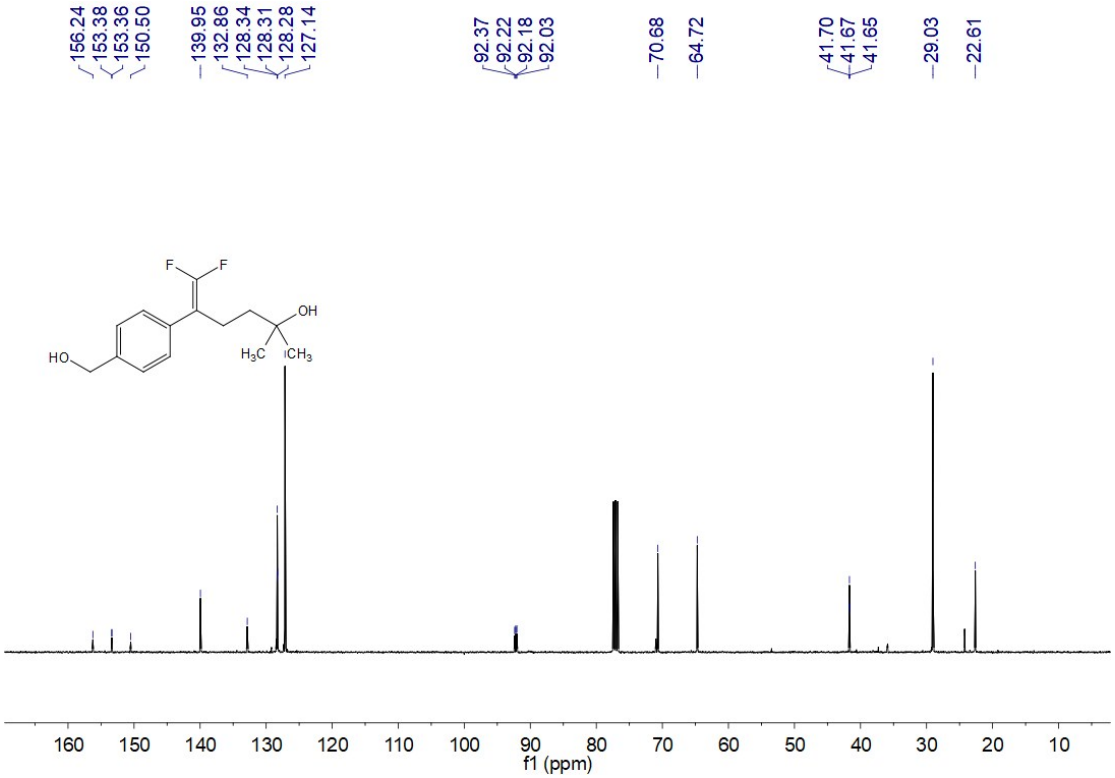
<u>Selectivity</u> (desired C-F cleavage product: addition by-product, determined

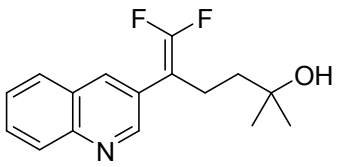
by ^{1}H NMR and ^{19}F NMR) = 35:1.

Prepared according to the general procedure, as a sticky liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 – 7.28 (m, 4H), 4.62 (s, 2H), 2.52 – 2.41 (m, 2H), 2.19 (br s, 1H), 1.53 – 1.38 (m, 2H), 1.19 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.37 (dd, *J* = 289.3, 287.9 Hz), 139.95, 132.86, 128.31 (t, *J* = 3.3 Hz), 127.14, 92.20 (dd, *J* = 19.1, 15.5 Hz), 70.68, 64.72, 41.67 (t, *J* = 2.2 Hz), 29.03, 22.61.**^{19}F NMR** (376 MHz, $CDCl_3$) δ -91.40 (d, *J* = 43.8 Hz), -91.49 (d, *J* = 19.1 Hz). **HRMS** (APCI) calcd for $C_{14}H_{18}F_2NaO_2$ ($M+Na^+$): 279.1167; found: 279.1171. **IR** (KBr/cm^{-1}) 3422, 2981 2071, 1719, 1637, 1616, 1487, 1454, 1395, 1353, 1255, 1173, 750, 613.







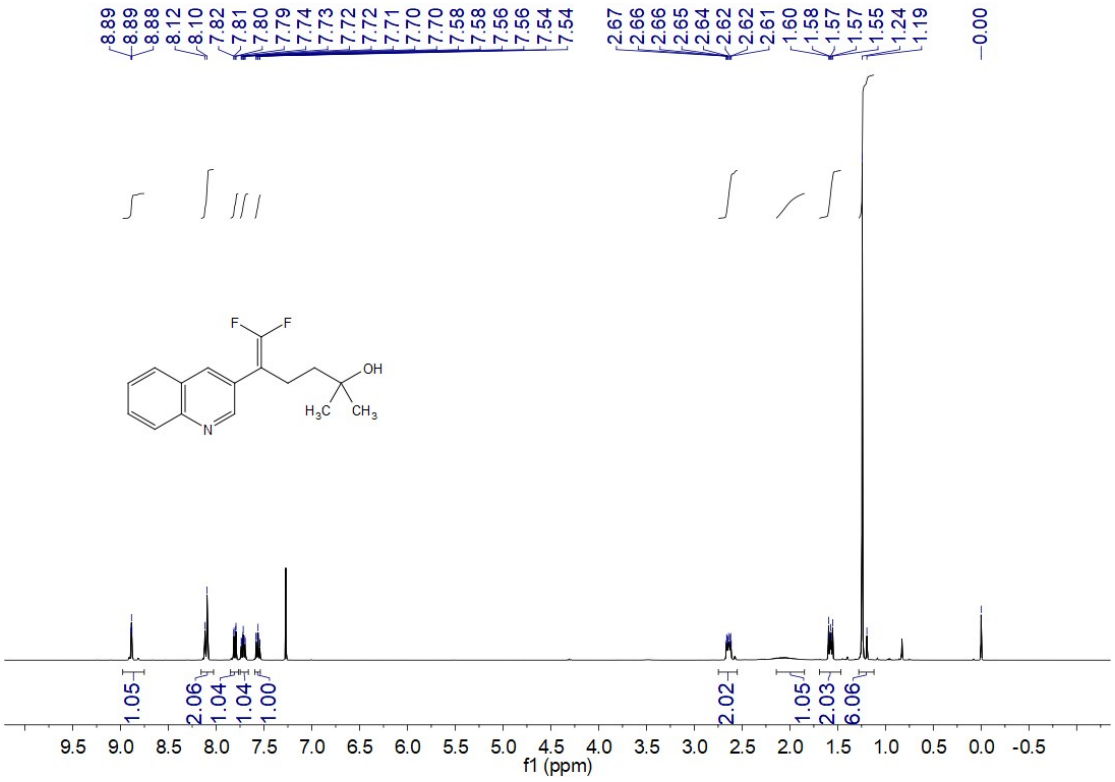


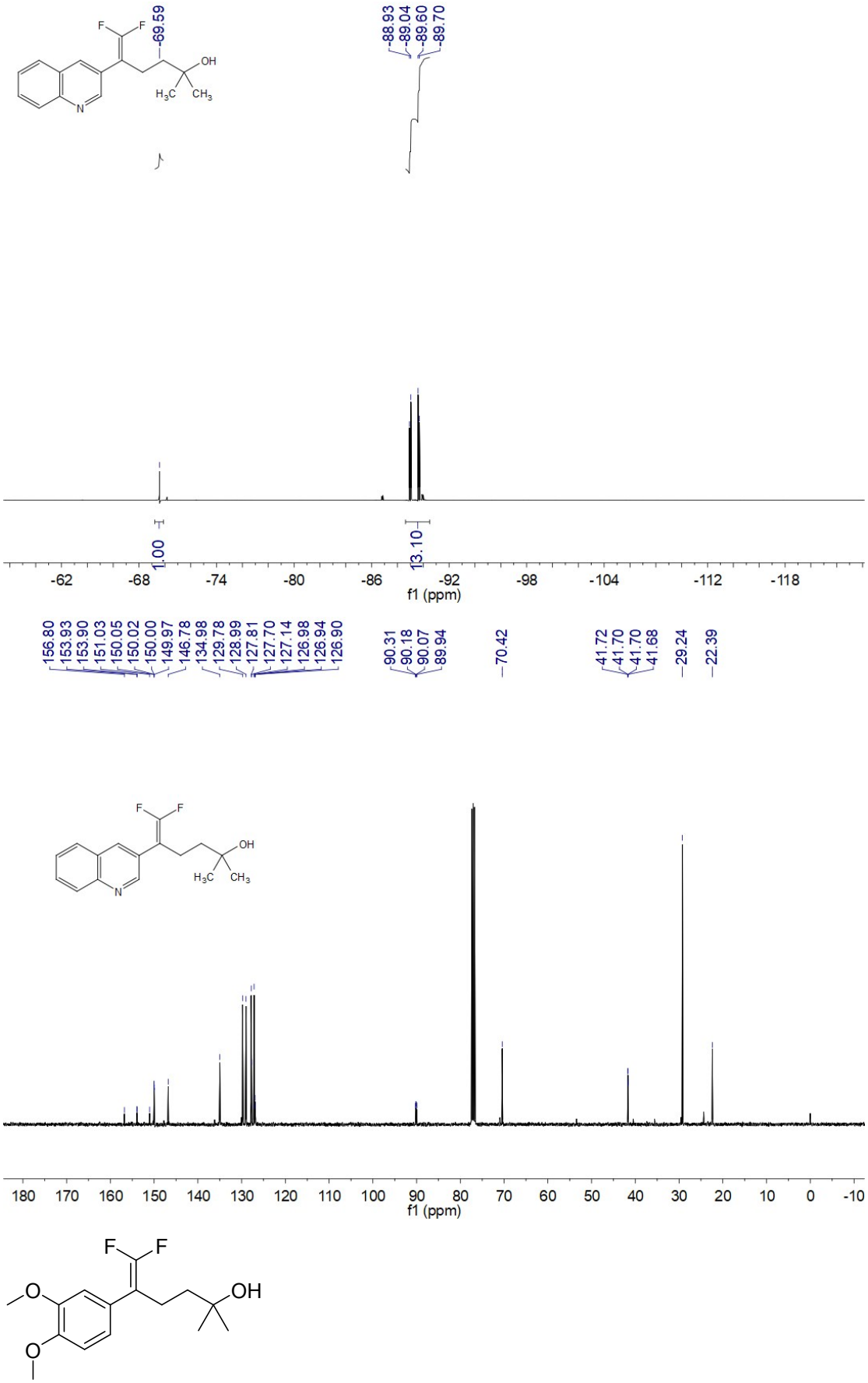
6,6-difluoro-2-methyl-5-(quinolin-3-yl)hex-5-en-2-ol (3n)

<u>Selectivity</u> (desired C-F cleavage product: addition by-product, determined

by ^{1}H NMR and ^{19}F NMR) = 35:1.

Prepared according to the general procedure, as a sticky liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.89 (t, *J* = 1.9 Hz, 1H), 8.11 (d, *J* = 8.6 Hz, 2H), 7.80 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.72 (ddd, *J* = 8.4, 7.0, 1.4 Hz, 1H), 7.58 – 7.44 (m, 1H), 2.64 (ddd, *J* = 11.0, 4.6, 2.3 Hz, 2H), 2.09 (brs, 1H), 1.69 – 1.51 (m, 2H), 1.24 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.92 (dd, *J* = 292.0, 288.9 Hz), 150.01 (dd, *J* = 4.6, 2.8 Hz), 146.78, 134.98, 129.78, 128.99, 127.81, 127.70, 127.14, 126.94 (t, *J* = 4.3 Hz), 90.12 (dd, *J* = 23.4, 13.0 Hz), 70.42, 41.70 (dd, *J* = 2.5, 1.9 Hz), 29.24, 22.39.**^{19}F NMR** (376 MHz, $CDCl_3$) δ -88.98 (d, *J* = 39.4 Hz), -89.65 (d, *J* = 39.4 Hz). **HRMS** (APCI) calcd for $C_{16}H_{17}F_2NNaO$ ($M+Na^+$): 300.1170; found: 300.1173. **IR** (KBr/cm^{-1}) 3419, 2980, 1637, 1616, 1488, 1396, 1350, 1173, 751, 615.

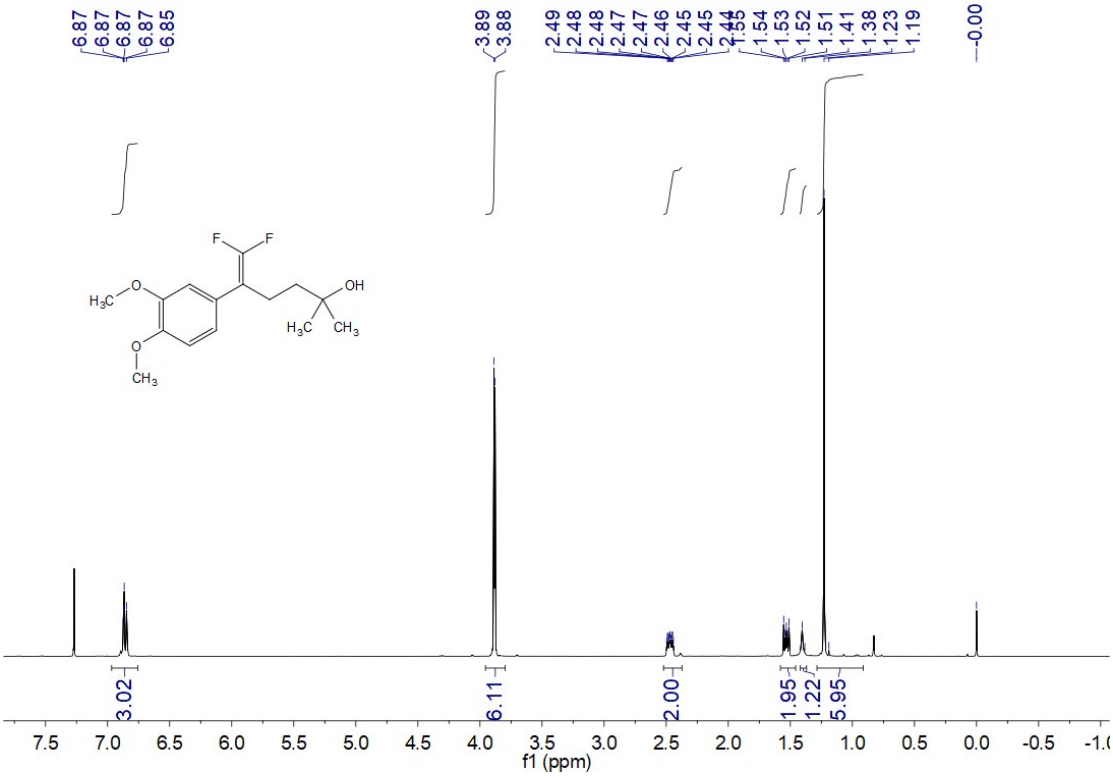


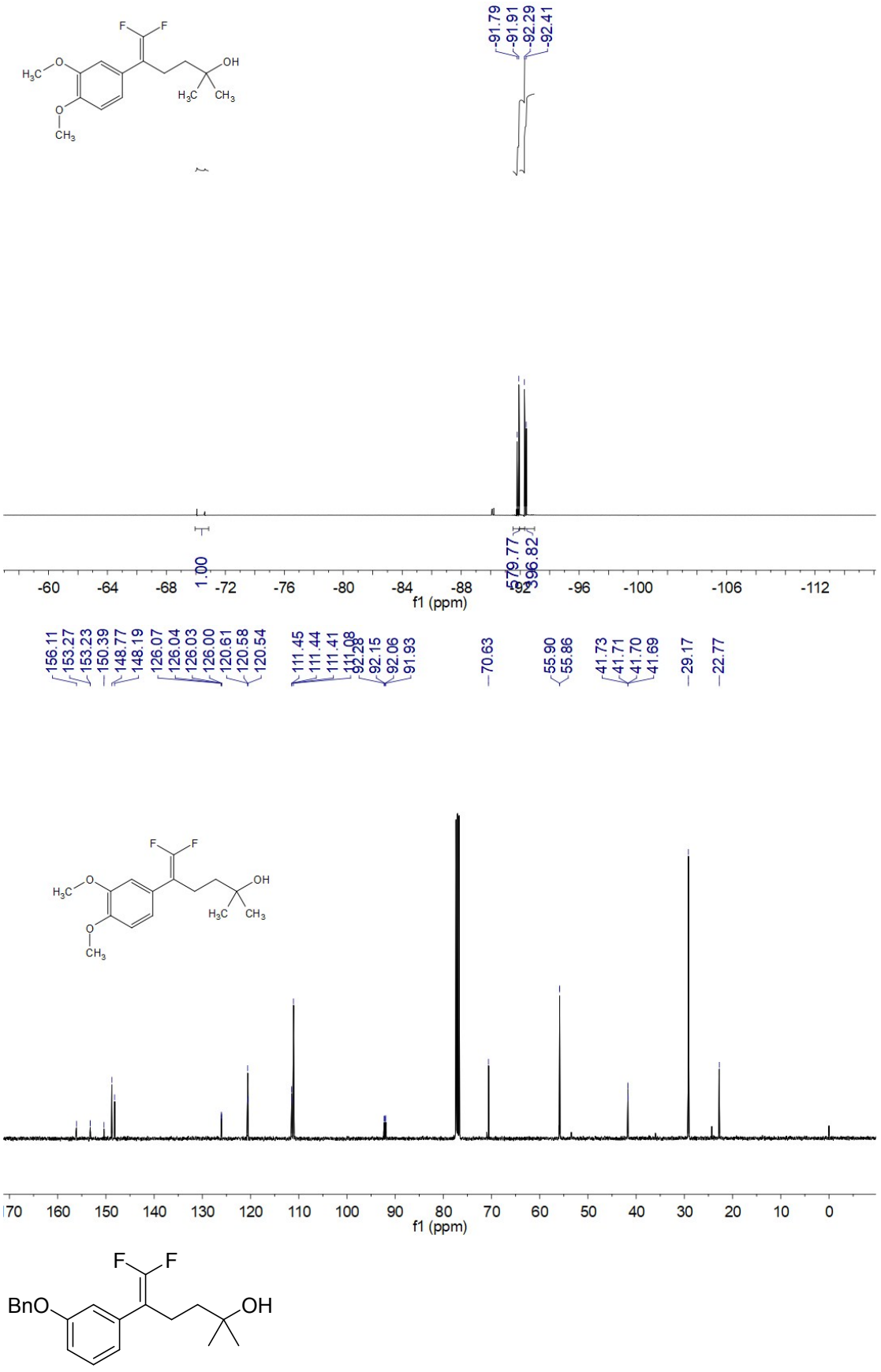


5-(3,4-dimethoxyphenyl)-6,6-difluoro-2-methylhex-5-en-2-ol (3b)

<u>Selectivity</u> (desired C-F cleavage product: addition by-product, determined by ^{1}H NMR and ^{19}F NMR) = 40:1.

Prepared according to the general procedure, as a sticky liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.94 – 6.68 (m, 3H), 3.89 (s, 3H), 3.88 (s, 3H), 2.57 – 2.40 (m, 2H), 1.62 – 1.48 (m, 2H), 1.41 (br s, 1H), 1.23 (s, 6H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -91.85 (d, *J* = 46.0 Hz), -92.35 (d, *J* = 46.1 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.25 (dd, *J* = 289.6, 286.0 Hz), 148.77, 148.19, 126.04 (dd, *J* = 4.2, 3.4 Hz), 120.58 (t, *J* = 3.4 Hz), 111.45 (dd, *J* = 3.9, 3.1 Hz), 111.08, 92.11 (dd, *J* = 21.8, 13.0 Hz), 70.63, 55.90, 55.86, 41.71 (dd, *J* = 2.5, 1.9 Hz), 29.17, 22.77. **HRMS** (APCI) calcd for $C_{15}H_{20}F_2NaO_3$ ($M+Na^+$): 309.1273; found: 309.1271. **IR** (KBr/cm^{-1}) 3419, 2985, 1632, 1616, 1485, 1244, 1174, 1027, 1001, 787, 696, 612.



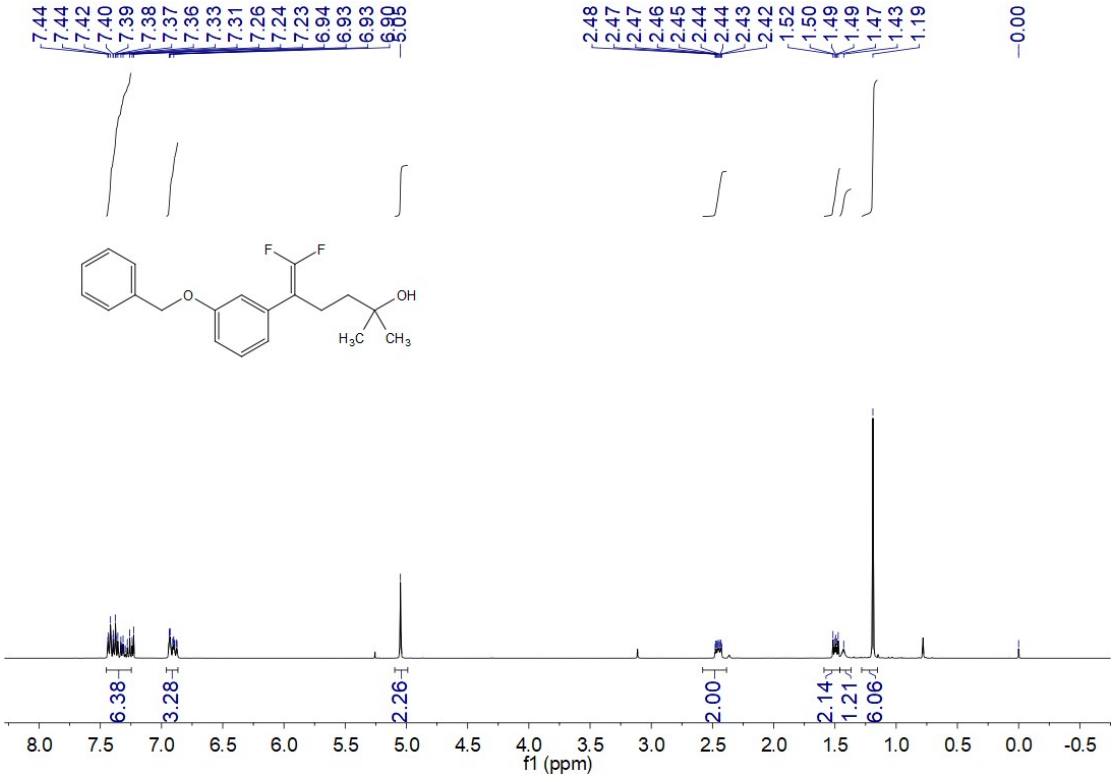


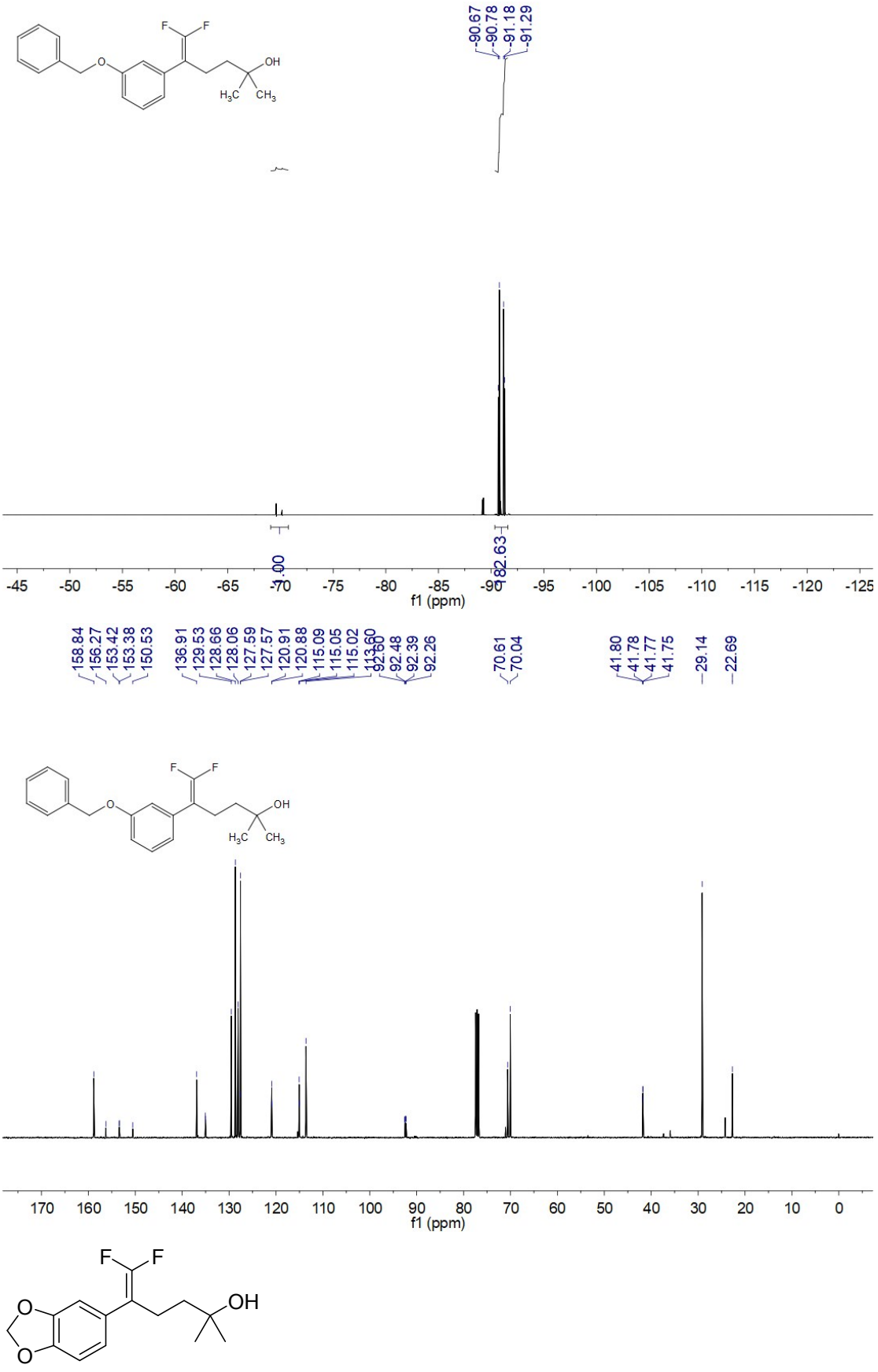
5-(3-(benzyloxy)phenyl)-6,6-difluoro-2-methylhex-5-en-2-ol (3e)

<u>Selectivity</u> (desired C-F cleavage product: addition by-product, determined

by ^{1}H NMR and ^{19}F NMR) > 50:1.

Prepared according to the general procedure, as a sticky liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 – 7.16 (m, 6H), 7.02 – 6.68 (m, 3H), 5.05 (s, 2H), 2.51 – 2.34 (m, 2H), 1.56 – 1.45 (m, 2H), 1.43 (br s, 1H), 1.19 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.84, 153.40 (dd, *J* = 290.9, 286.5 Hz), 136.91, 135.06 (dd, *J* = 4.5, 3.4 Hz), 129.53, 128.66, 128.06, 127.57, 120.91 (t, *J* = 3.3 Hz), 115.05 (t, *J* = 3.4 Hz), 113.60, 92.43 (dd, *J* = 21.8, 12.7 Hz), 70.61, 70.04, 41.78 (dd, *J* = 2.6, 1.9 Hz), 29.14, 22.69.**^{19}F NMR** (376 MHz, $CDCl_3$) δ -90.73 (d, *J* = 43.1 Hz), -91.24 (d, *J* = 43.0 Hz). **HRMS** (APCI) calcd for $C_{20}H_{22}F_2NaO_2$ ($M+Na^+$): 355.1480; found: 355.1487. **IR** (KBr/cm^{-1}) 3414, 2978, 1727, 1637, 1616, 1488, 1455, 1395, 1244, 1174, 1027, 1002, 786, 695, 618.



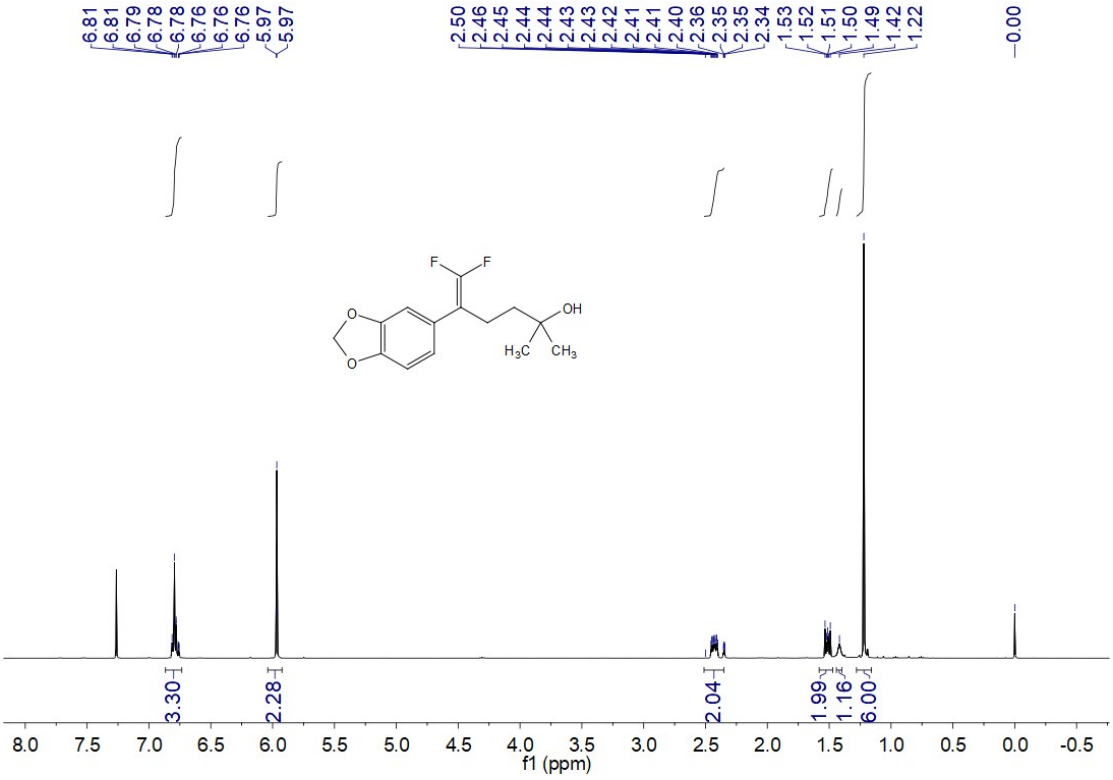


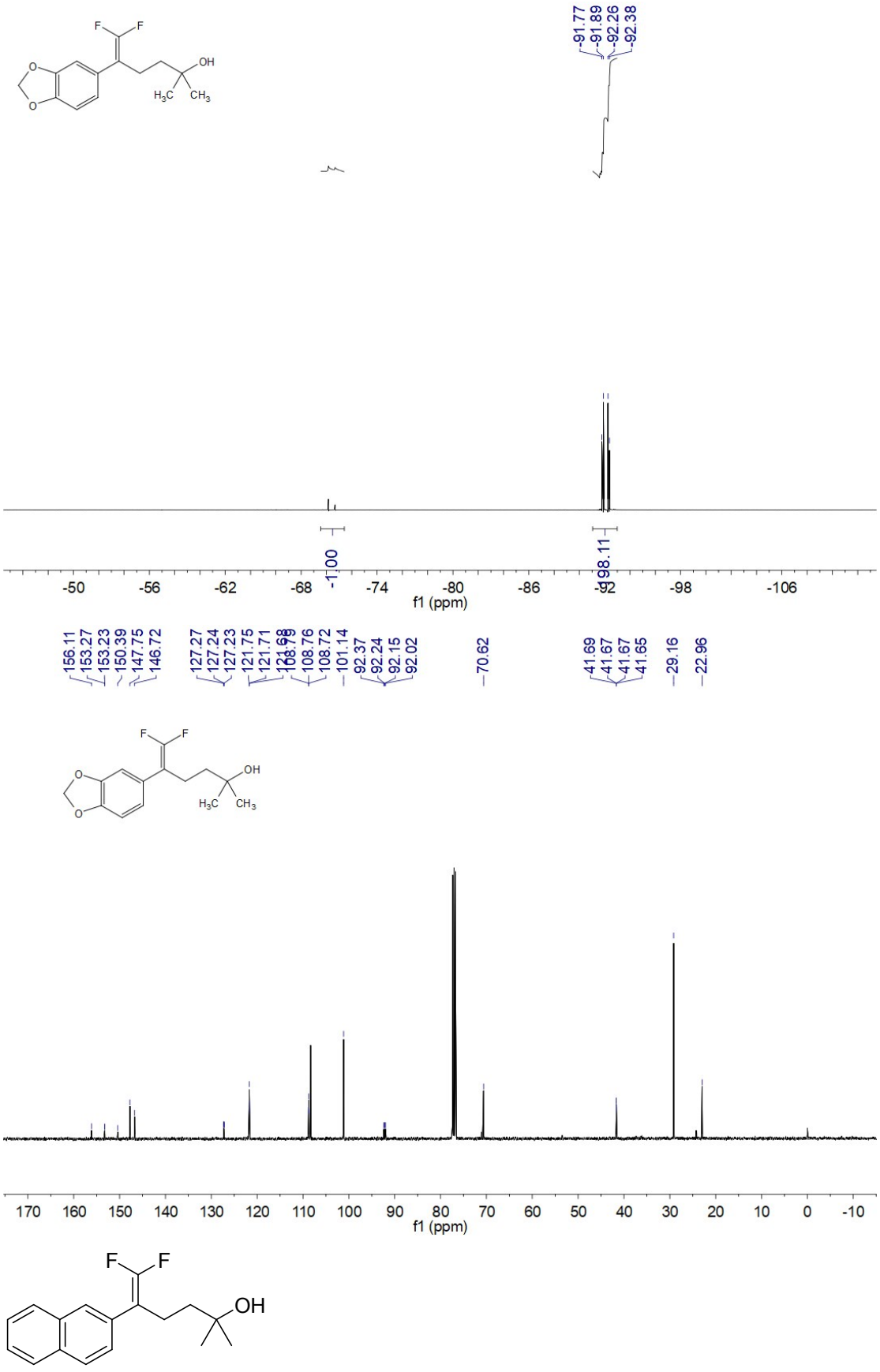
5-(benzo[d][1,3]dioxol-5-yl)-6,6-difluoro-2-methylhex-5-en-2-ol (3f)

<u>Selectivity</u> (desired C-F cleavage product: addition by-product, determined

by ^{1}H NMR and ^{19}F NMR) > 50:1.

Prepared according to the general procedure, as a sticky liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.93 – 6.55 (m, 3H), 5.97 (s, 2H), 2.47 – 2.37 (m, 2H), 1.59 – 1.44 (m, 2H), 1.42 (br s, 1H), 1.22 (s, 6H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -91.83 (d, *J* = 45.6 Hz), -92.32 (d, *J* = 45.5 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.25 (dd, *J* = 289.5, 286.2 Hz), 147.75, 146.72, 127.24 (dd, *J* = 4.5, 3.1 Hz), 121.71 (t, *J* = 3.3 Hz), 108.76 (t, *J* = 3.5 Hz), 108.35, 101.14, 92.20 (dd, *J* = 22.2, 13.2 Hz), 70.62, 41.67 (dd, *J* = 2.7, 1.8 Hz), 29.16, 22.96. **HRMS** (APCI) calcd for $C_{14}H_{16}F_2NaO_3$ (M+Na$^+$): 293.0960; found: 293.0965. **IR** (KBr/cm^{-1}) 3418, 2980, 1637, 1616, 1487, 1453, 1352, 1172, 751, 617.



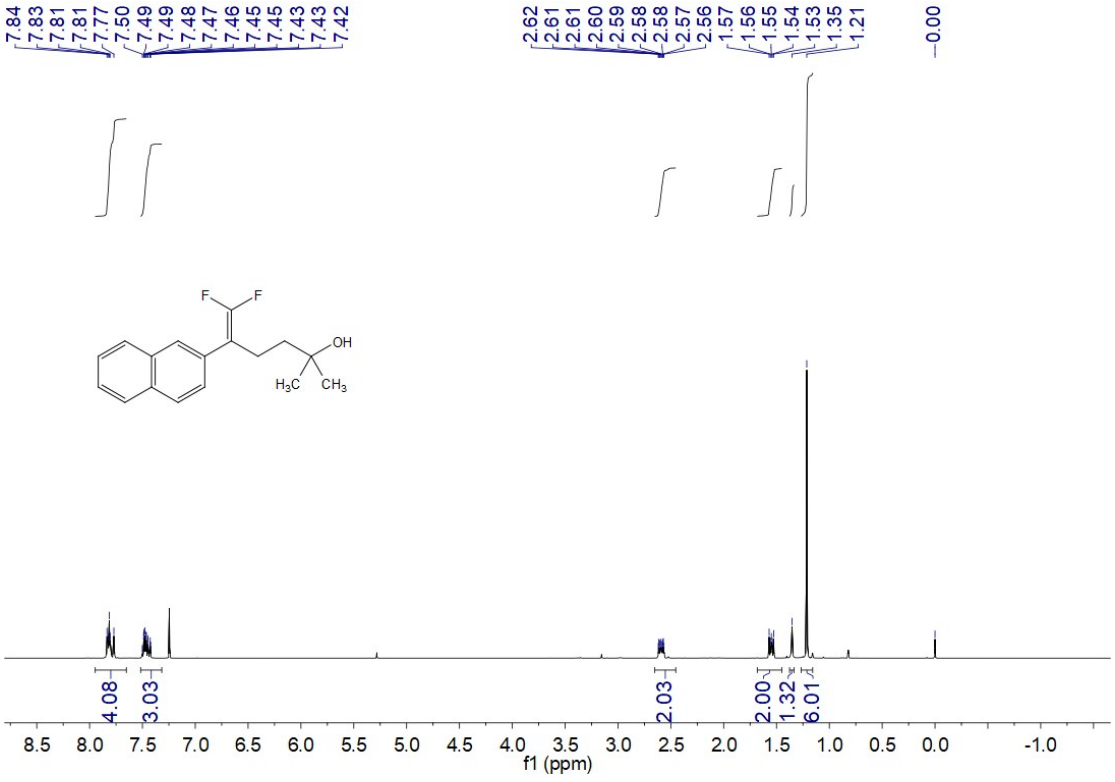


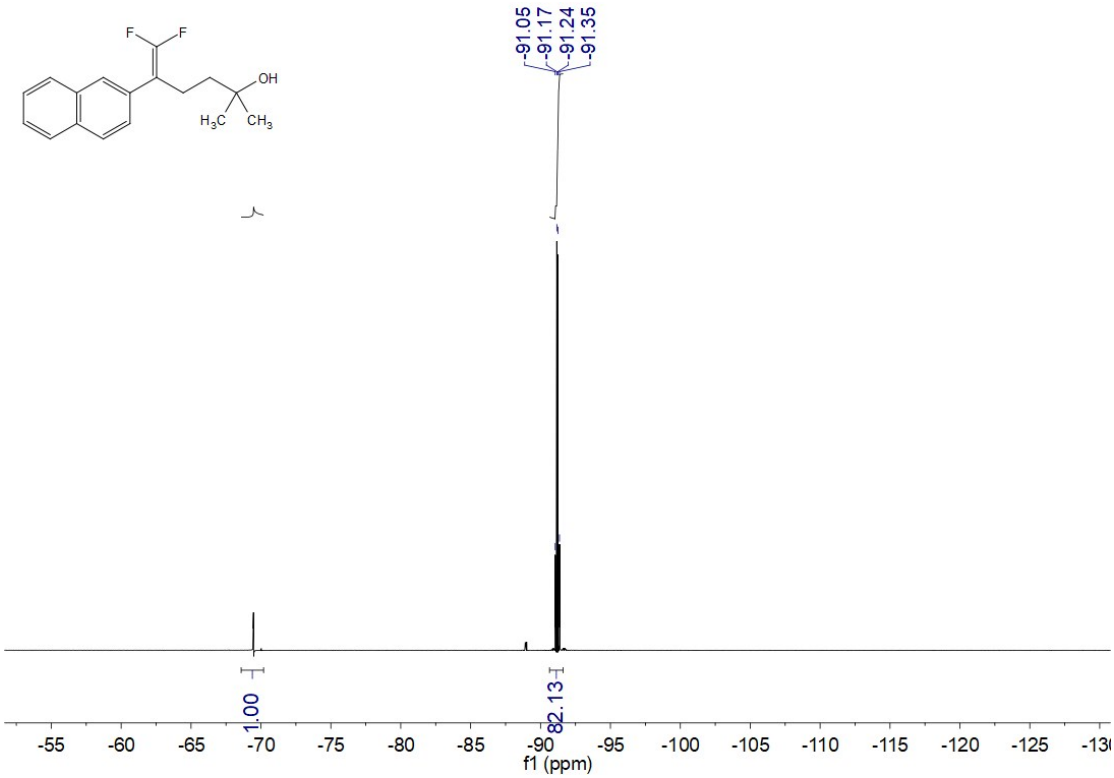
6,6-difluoro-2-methyl-5-(naphthalen-2-yl)hex-5-en-2-ol (3m)

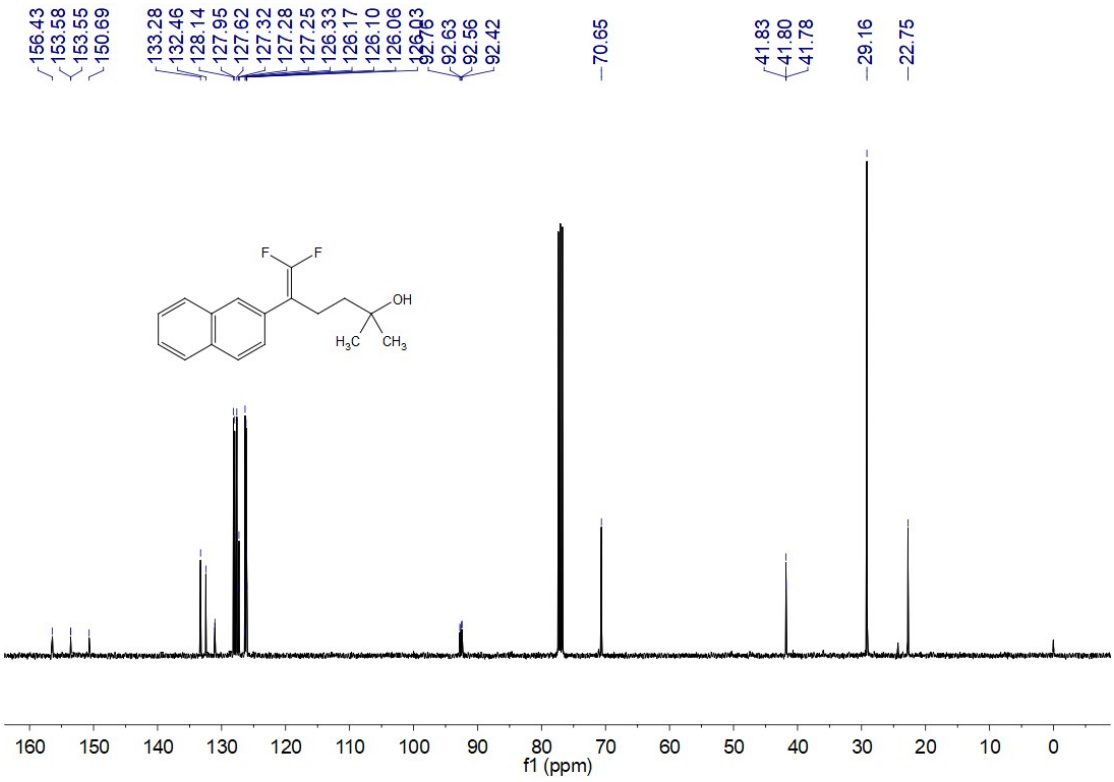
<u>Selectivity</u> (desired C-F cleavage product: addition by-product, determined

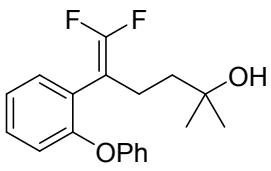
by ^{1}H NMR and ^{19}F NMR) > 50:1.

Prepared according to the general procedure, as a sticky liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 – 7.73 (m, 4H), 7.62 – 7.37 (m, 3H), 2.75 – 2.46 (m, 2H), 1.63 – 1.46 (m, 2H), 1.35 (br s, 1H), 1.21 (s, 6H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -91.11 (d, J = 43.3 Hz), -91.30 (d, J = 43.3 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.56 (dd, J = 290.3, 287.3 Hz), 133.28, 132.46, 131.03 (dd, J = 3.6, 2.5 Hz), 128.14, 127.95, 127.62, 127.28 (t, J = 3.4 Hz), 126.33, 126.17, 126.06 (t, J = 3.2 Hz), 92.59 (dd, J = 20.9, 13.9 Hz), 70.65, 41.79 (t, J = 2.3 Hz), 29.16, 22.75. **HRMS** (APCI) calcd for $C_{17}H_{18}F_2NaO$ (M+Na$^+$): 299.1218; found: 299.1216. **IR** (KBr/cm^{-1}) 3412, 2983, 2829, 1717, 1617, 1489, 1457, 1396, 1369, 1356, 1244, 1173, 1103, 1002, 787, 773, 610.







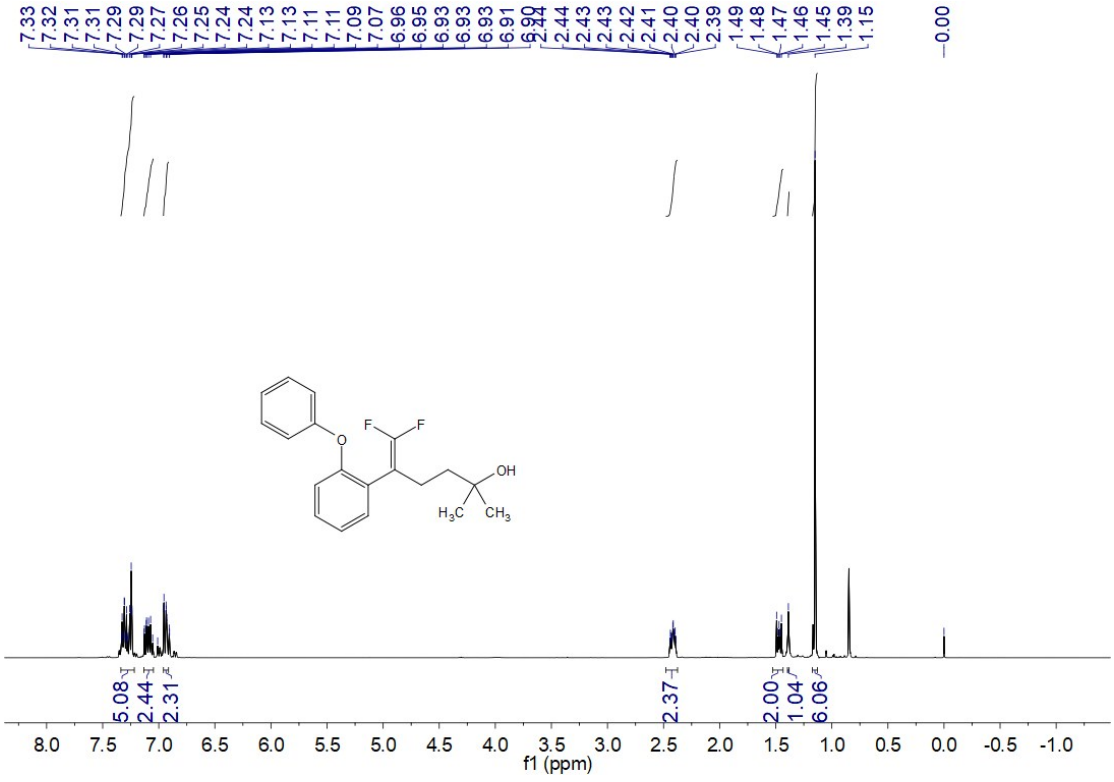


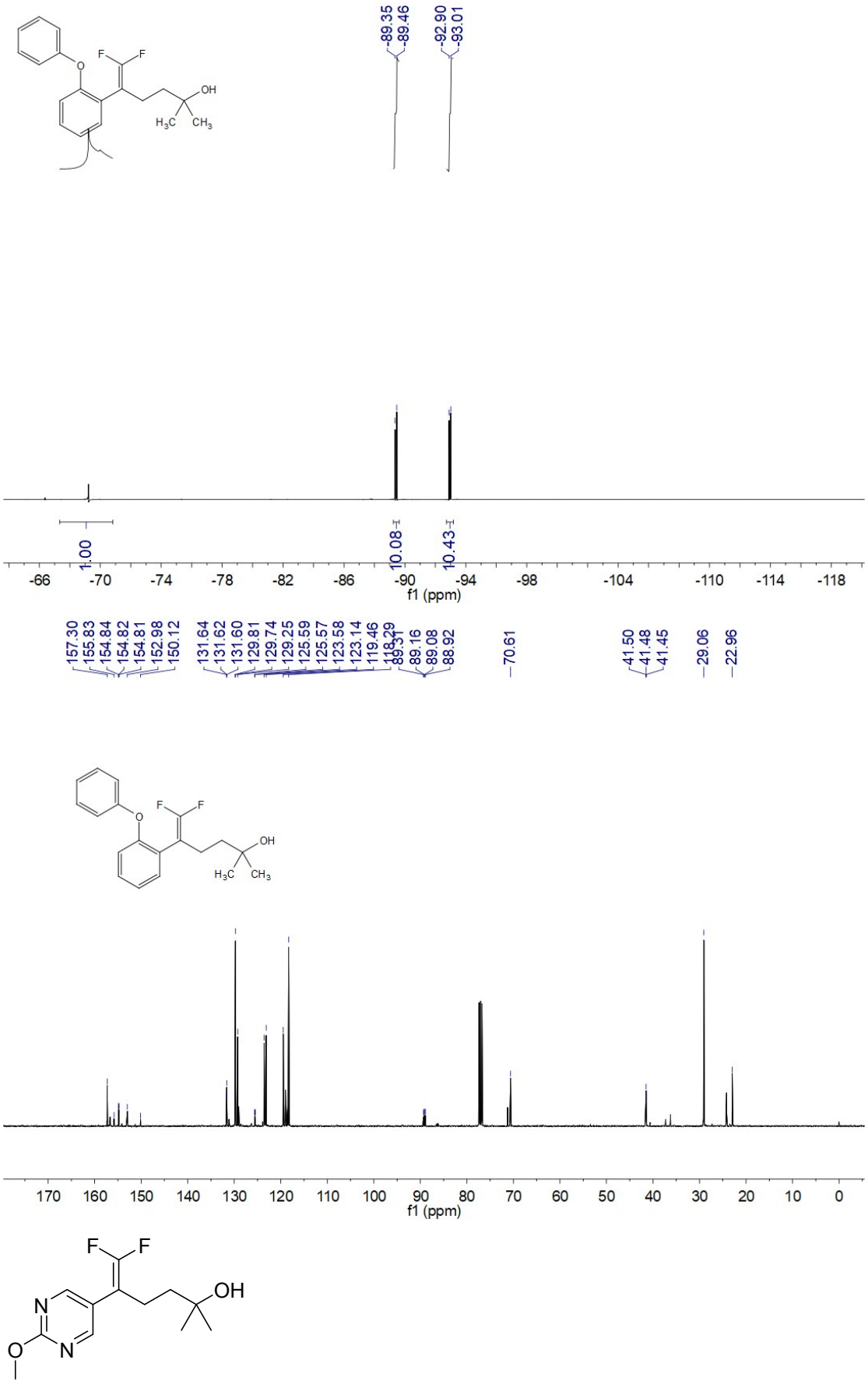
6,6-difluoro-2-methyl-5-(2-phenoxyphenyl)hex-5-en-2-ol (3t)

<u>Selectivity</u> (desired C-F cleavage product: addition by-product, determined

by ^{1}H NMR and ^{19}F NMR) = 15:1.

Prepared according to the general procedure, as a sticky liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.21 (m, 5H), 7.12 – 7.01 (m, 2H), 6.99 – 6.84 (m, 2H), 2.48 – 2.00 (m, 2H), 1.47 (dd, *J* = 7.9, 4.4 Hz, 2H), 1.39 (br s, 1H), 1.15 (s, 6H).**^{19}F NMR** (376 MHz, $CDCl_3$) δ -89.41 (d, *J* = 42.6 Hz), -92.96 (d, *J* = 42.7 Hz).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.30, 154.82 (dd, *J* = 2.3, 1.0 Hz), 152.98 (dd, *J* = 288.1, 287.3 Hz), 131.62 (t, *J* = 2.3 Hz), 129.74, 129.25, 125.55 (dd, *J* = 5.1, 1.9 Hz), 123.58, 123.14, 119.46, 118.29, 89.12 (dd, *J* = 23.9, 16.0 Hz), 70.61, 41.46 (d, *J* = 2.4 Hz), 29.06, 22.96. **HRMS** (APCI) calcd for $C_{19}H_{20}F_2NaO_2$ ($M+Na^+$): 341.1324; found: 341.1331. **IR** (KBr/cm^{-1}) 3419, 2976, 2830, 2359, 2064, 1738, 1600, 1488, 1447, 1396, 1368, 1356, 1241, 1186, 1173, 798, 787, 752, 691, 613.

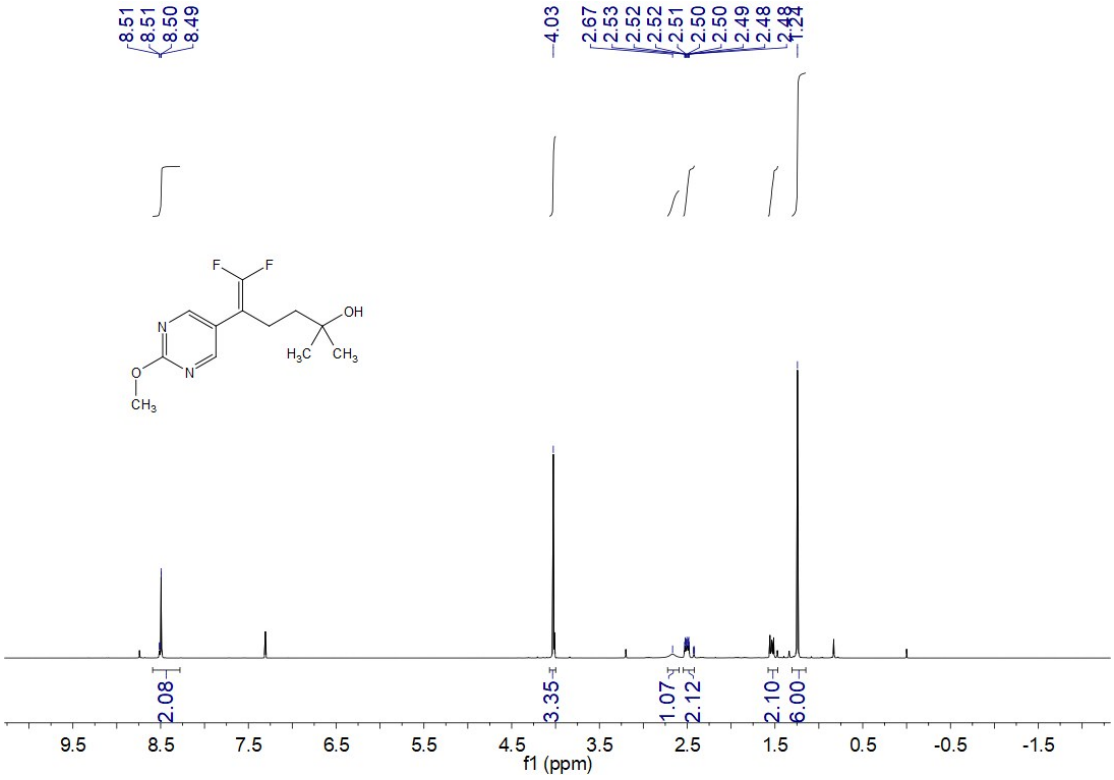


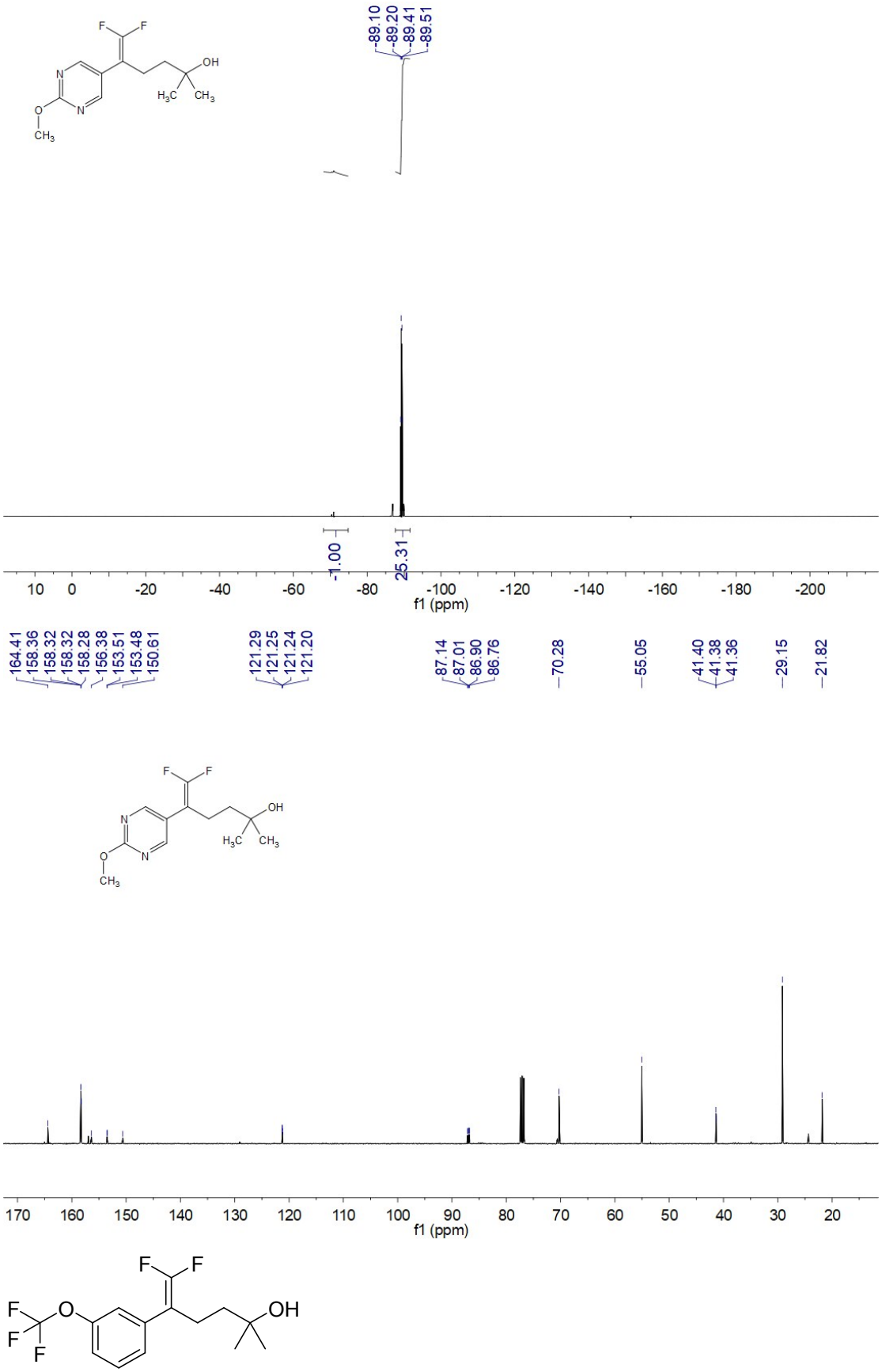


6,6-difluoro-5-(2-methoxypyrimidin-5-yl)-2-methylhex-5-en-2-ol (3p)

<u>Selectivity</u> (desired C-F cleavage product: addition by-product, determined by ^{1}H NMR and ^{19}F NMR) > 35:1.

Prepared according to the general procedure, as a sticky liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.53 – 8.36 (m, 2H), 4.03 (s, 3H), 2.67 (br s, 1H), 2.54 – 2.42 (m, 2H), 1.59 – 1.43 (m, 2H), 1.24 (s, 6H).**^{19}F NMR** (376 MHz, $CDCl_3$) δ -89.15 (d, *J* = 40.2 Hz), -89.46 (d, *J* = 40.2 Hz).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.41, 158.32 (dd, *J* = 4.1, 3.6 Hz), 153.50 (dd, *J* = 291.5, 289.0 Hz), 121.22 (dd, *J* =4.0, 3.9 Hz), 86.95 (dd, *J* = 24.7, 13.6 Hz), 70.28, 55.05, 41.37 (t, *J* = 2.2 Hz), 29.15, 21.82. **HRMS** (APCI) calcd for $C_{12}H_{16}F_2N_2NaO_2$ ($M+Na^+$): 281.1072; found: 281.1078. **IR** (KBr/cm^{-1}) 3419, 2981, 2830, 1727, 1598, 1478, 1415, 1368, 1355, 1245, 1033, 611



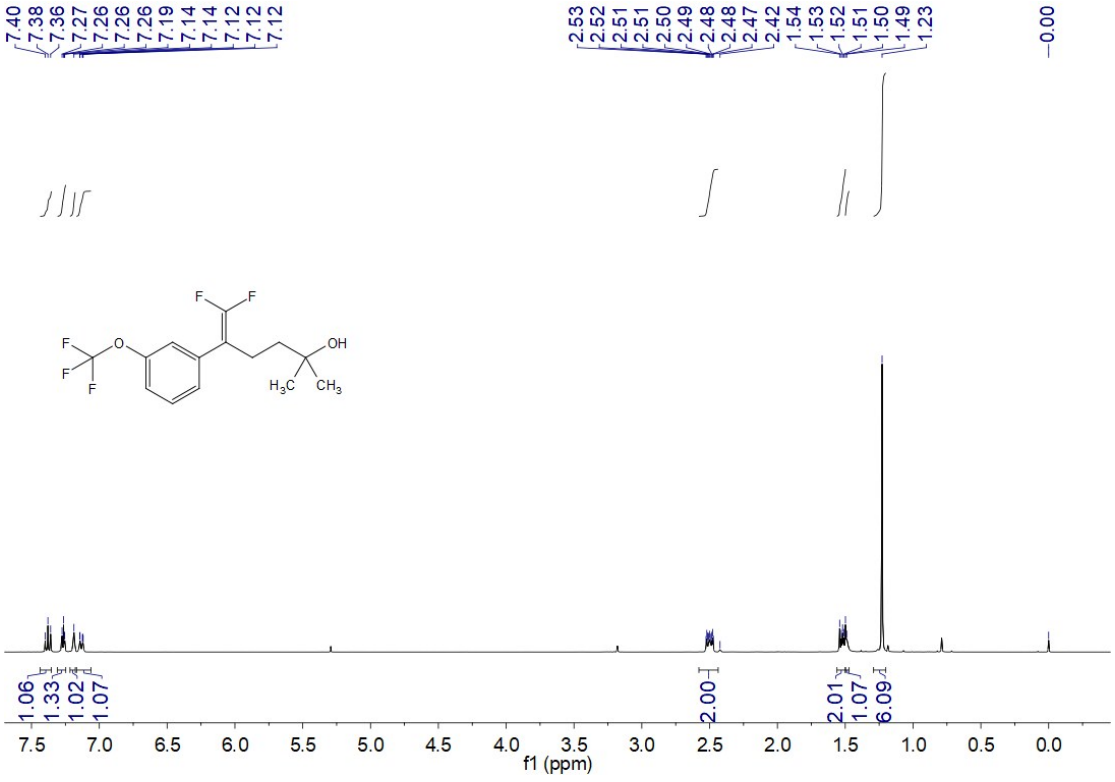


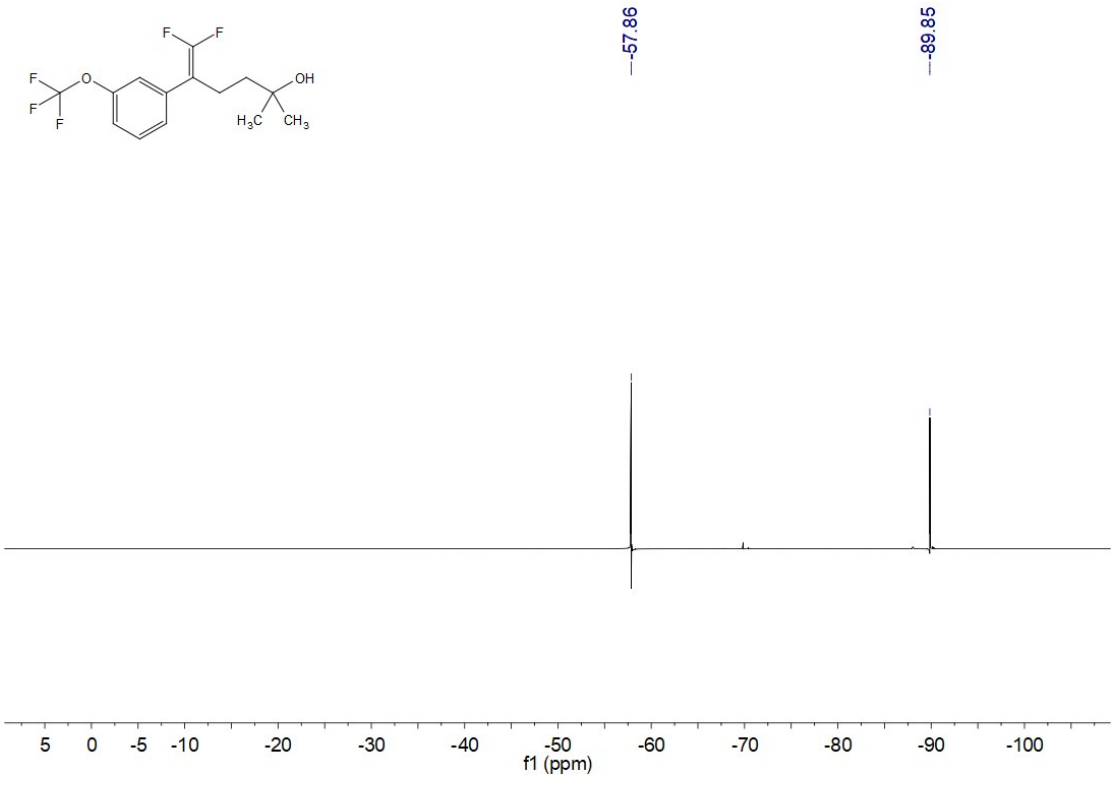
6,6-difluoro-2-methyl-5-(3-(trifluoromethoxy)phenyl)hex-5-en-2-ol (3d)

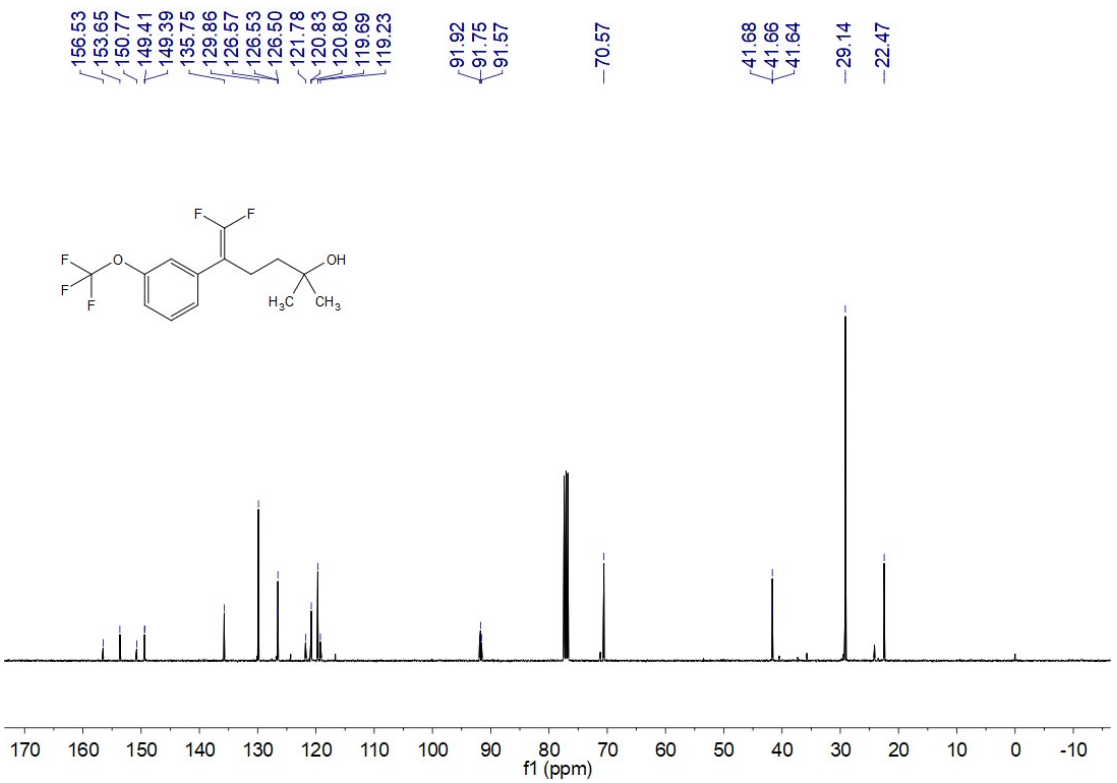
<u>Selectivity</u> (desired C-F cleavage product: addition by-product, determined

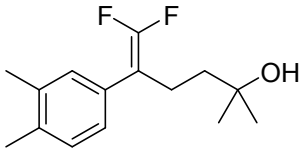
by ^{1}H NMR and ^{19}F NMR) > 50:1.

Prepared according to the general procedure, as a sticky liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 (t, *J* = 8.0 Hz, 1H), 7.26 (dd, *J* = 5.3, 2.5 Hz, 1H), 7.19 (s, 1H), 7.16 – 7.10 (m, 1H), 2.55 – 2.47 (m, 2H), 1.59 – 1.36 (m, 2H), 1.44 (br s, 1H), 1.23 (s, 6H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -57.86, -89.85. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.65 (dd, *J* = 289.9, 289.1 Hz), 149.40 (dd, *J* = 3.3, 1.6 Hz), 135.75, 129.86, 126.53 (t, *J* = 3.5 Hz), 120.80 (t, *J* = 3.4 Hz), 120.51 (q, *J* = 257.2 Hz), 119.69, 91.75 (t, *J* = 17.6 Hz), 70.57, 41.66 (t, *J* = 2.3 Hz), 29.14, 22.47. **HRMS** (APCI) calcd for $C_{14}H_{15}F_5NaO_2$ (M+Na+): 333.0884; found: 333.0886. **IR** (KBr/cm^{-1}) 3421, 2981, 1726, 1616, 1488, 1395, 1353, 1255, 1218, 1173, 788, 619.







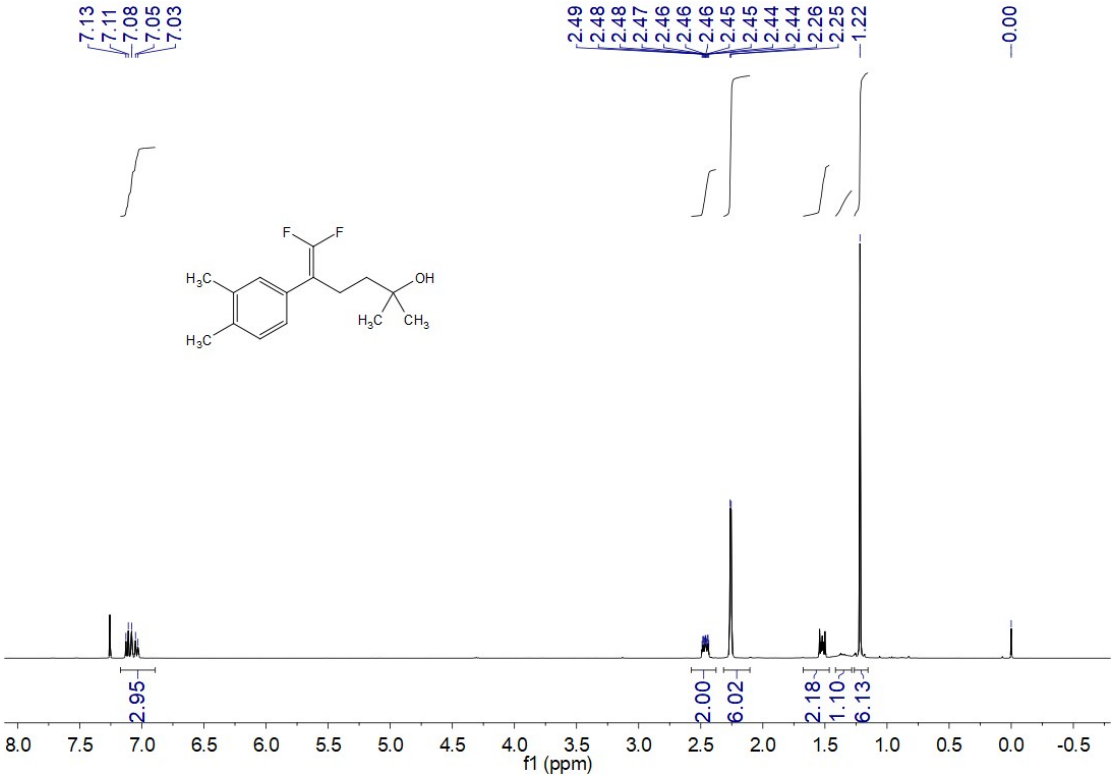


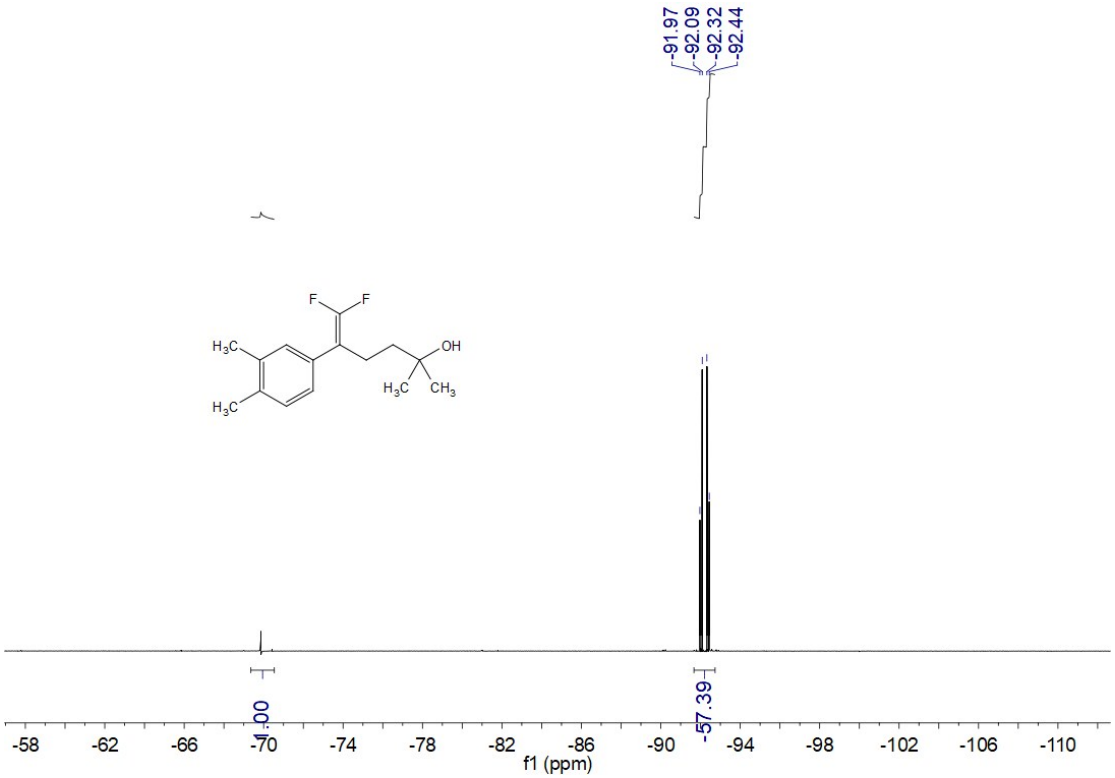
5-(3,4-dimethylphenyl)-6,6-difluoro-2-methylhex-5-en-2-ol (3c)

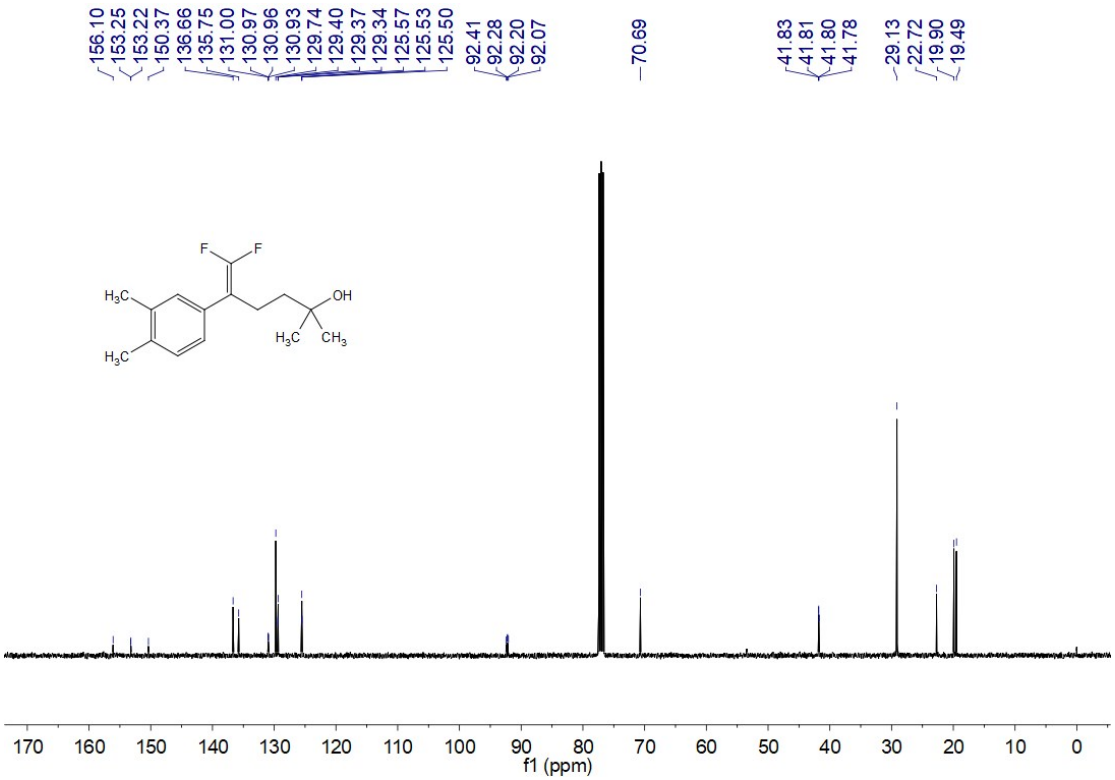
<u>Selectivity</u> (desired C-F cleavage product: addition by-product, determined

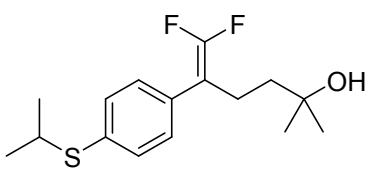
by ^{1}H NMR and ^{19}F NMR) > 50:1.

Prepared according to the general procedure, as a sticky liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.20 – 6.89 (m, 3H), 2.55 – 2.35 (m, 2H), 2.26 (s, 3H), 2.25 (s, 3H), 1.62 – 1.48 (m, 2H), 1.35 (br s, 1H), 1.22 (s, 6H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -92.03 (d, *J* = 45.6 Hz), -92.38 (d, *J* = 45.6 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.23 (dd, *J* = 289.6, 286.1 Hz), 136.66, 135.75, 130.96 (dd, *J* = 4.1, 3.2 Hz), 129.74, 129.37 (t, *J* = 3.2 Hz), 125.53 (t, *J* = 3.2 Hz), 92.24 (dd, *J* = 21.2, 13.3 Hz), 70.69, 41.80 (dd, *J* = 2.7, 1.9 Hz), 29.13, 22.72, 19.90, 19.49. **HRMS** (APCI) calcd for $C_{15}H_{20}F_2NaO$ ($M+Na^+$): 277.1374; found: 277.1375. **IR** (KBr/cm^{-1}) 3429, 2986, 2829, 1616, 1488, 1457, 1396, 1368, 1356, 1185, 1174, 1002, 787, 773, 598.







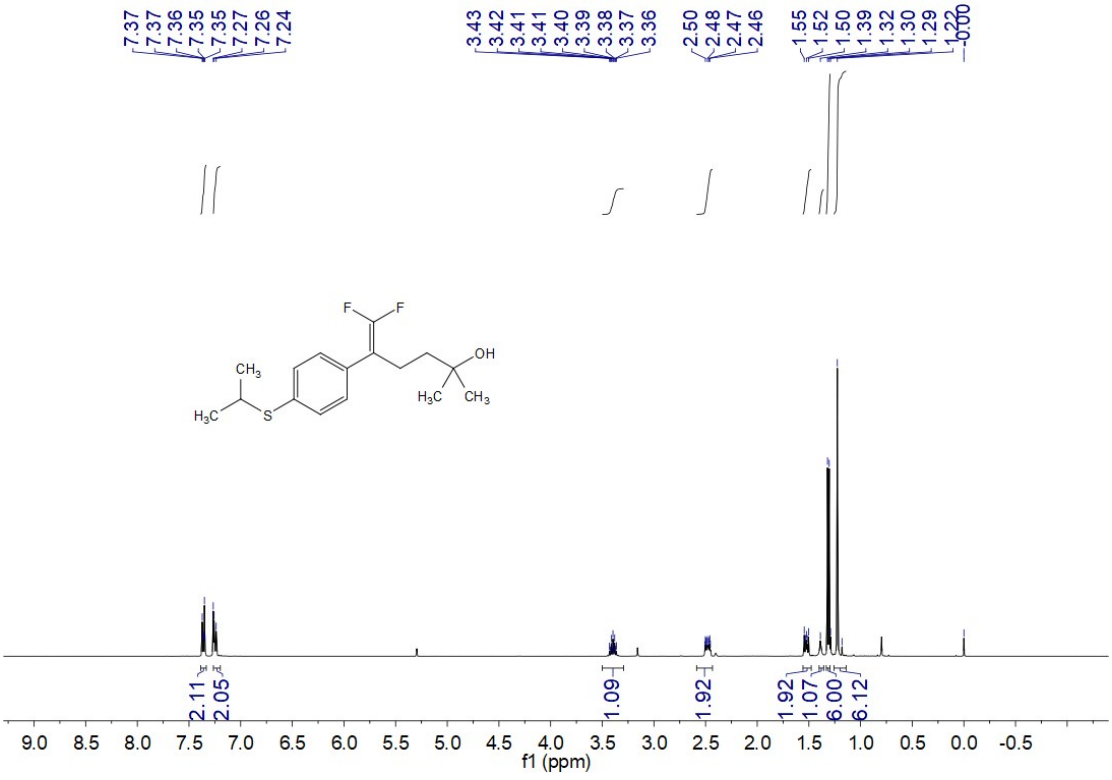


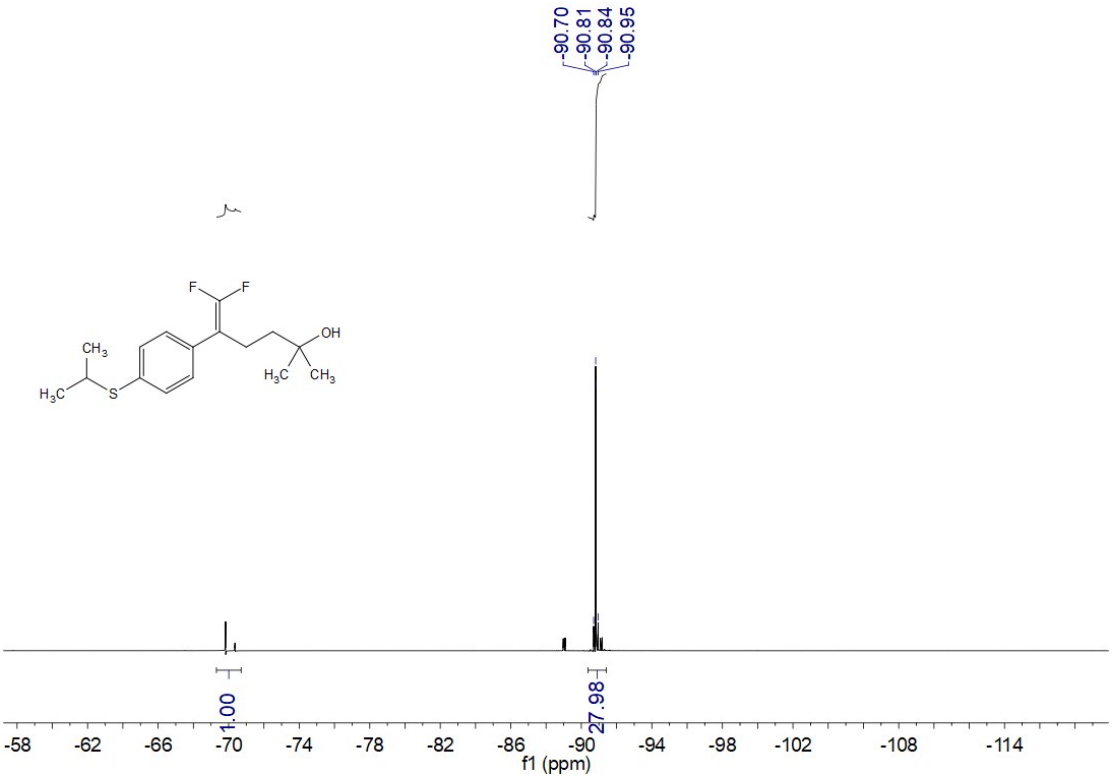
6,6-difluoro-5-(4-(isopropylthio)phenyl)-2-methylhex-5-en-2-ol (3g)

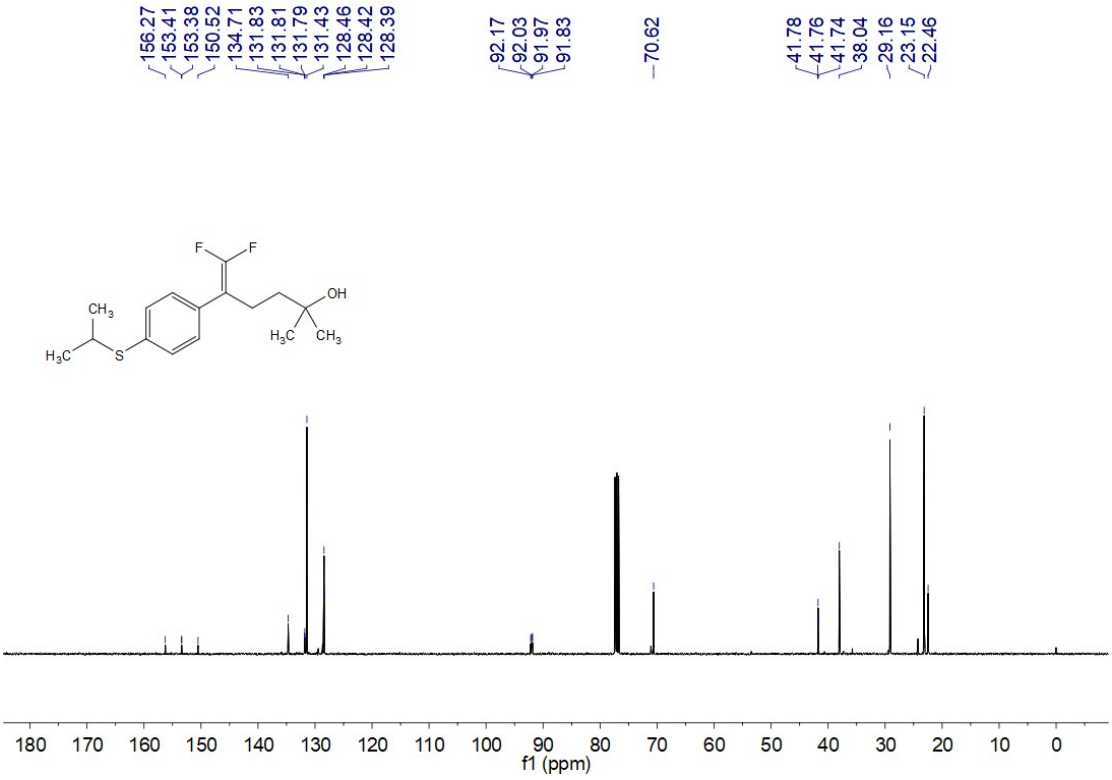
<u>Selectivity</u> (desired C-F cleavage product: addition by-product, determined

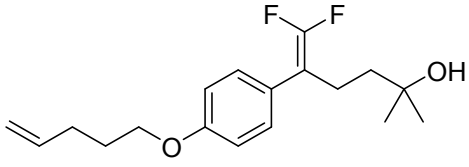
by ^{1}H NMR and ^{19}F NMR) > 40:1.

Prepared according to the general procedure, as a sticky liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 – 7.31 (m, 2H), 7.30 – 7.18 (m, 2H), 3.47 – 3.24 (m, 1H), 2.63 – 2.43 (m, 2H), 1.64 – 1.46 (m, 2H), 1.39 (br s, 1H), 1.31 (d, *J* = 6.7 Hz, 6H), 1.22 (s, 6H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -90.76 (d, *J* = 42.8 Hz), -90.90 (d, *J* = 42.6 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.39 (dd, *J* = 290.4, 287.8 Hz), 134.71, 131.80 (t, *J* = 2.1 Hz), 131.43, 128.42 (t, *J* = 3.5 Hz), 92.00 (dd, *J* = 20.1, 14.3 Hz), 70.62, 41.76 (t, *J* = 2.2 Hz), 38.04, 29.16, 23.15, 22.46. **HRMS** (APCI) calcd for $C_{16}H_{22}F_2NaOS$ ($M+Na^+$): 323.1252; found: 323.1250. **IR** (KBr/cm^{-1}) 3420, 2982, 1616, 1488, 1396, 1355, 1235, 1174, 1091, 1002, 786, 619.





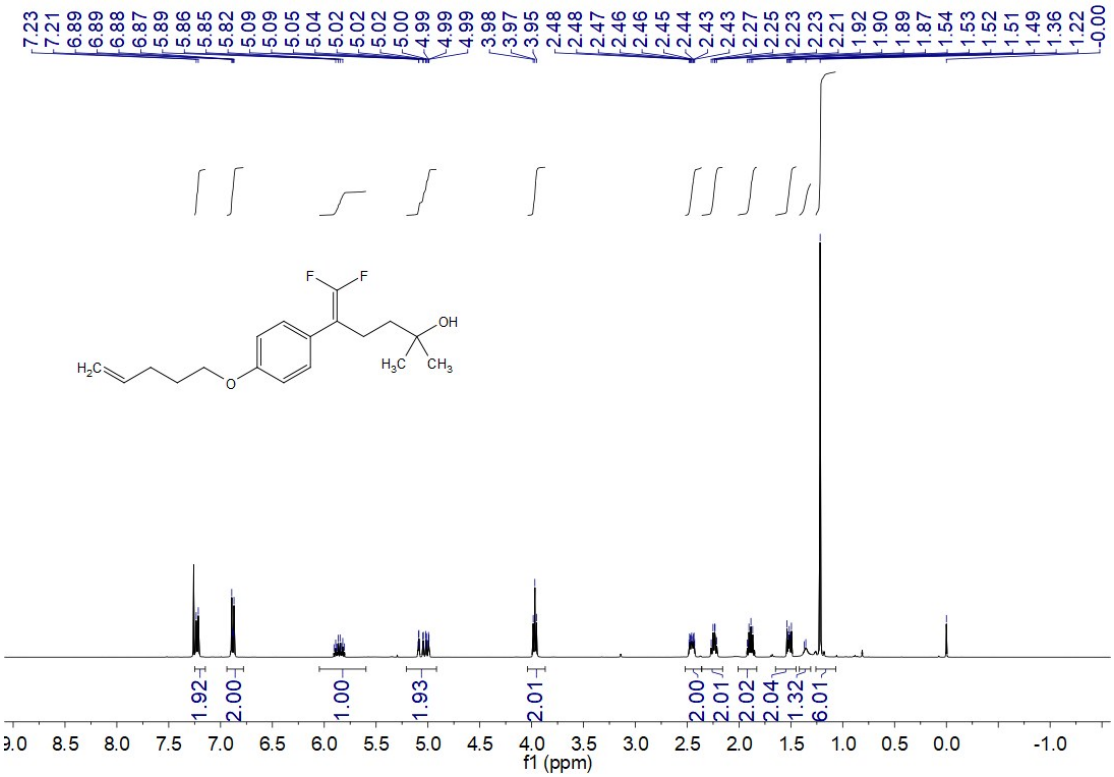


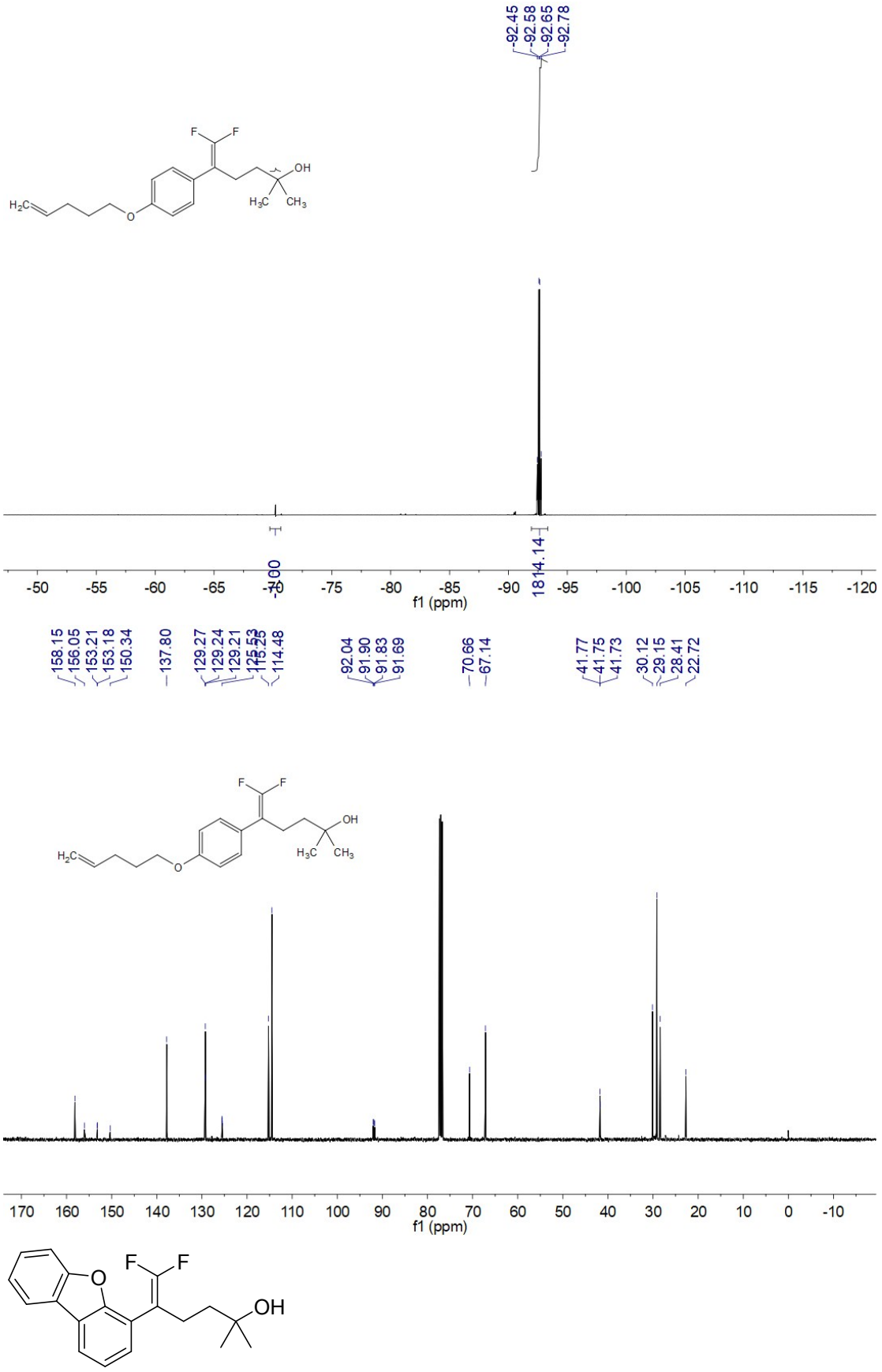


6,6-difluoro-2-methyl-5-(4-(pent-4-en-1-yloxy)phenyl)hex-5-en-2-ol (3h)

<u>Selectivity</u> (desired C-F cleavage product: addition by-product, determined by ^{1}H NMR and ^{19}F NMR) > 50:1.

Prepared according to the general procedure, as a sticky liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.1 Hz, 2H), 6.93 – 6.79 (m, 2H), 5.99 – 5.68 (m, 1H), 5.29 – 4.80 (m, 2H), 3.97 (t, *J* = 6.4 Hz, 2H), 2.53 – 2.37 (m, 2H), 2.31 – 2.09 (m, 2H), 1.89 (dd, *J* = 14.4, 6.7 Hz, 2H), 1.57 – 1.45 (m, 2H), 1.36 (br s, 1H), 1.22 (s, 6H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -92.52 (d, *J* = 46.7 Hz), -92.71 (d, *J* = 46.5 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.15, 153.19 (dd, *J* = 289.0, 286.0 Hz), 137.80, 129.24 (t, *J* = 3.4 Hz), 125.53 (dd, *J* = 3.4, 2.6 Hz), 115.25, 114.48, 91.87 (dd, *J* = 20.9, 14.0 Hz), 70.66, 67.14, 41.74 (t, *J* = 2.2 Hz), 30.12, 29.15, 28.41, 22.72. **HRMS** (APCI) calcd for $C_{18}H_{24}F_2NaO_2$ ($M+Na^+$): 333.1637; found: 333.1639. **IR** (KBr/cm^{-1}) 3417, 2981, 2830, 1727, 1611, 1514, 1488, 1441, 1396, 1356, 1248, 1233, 1174, 1090, 757, 661, 609.



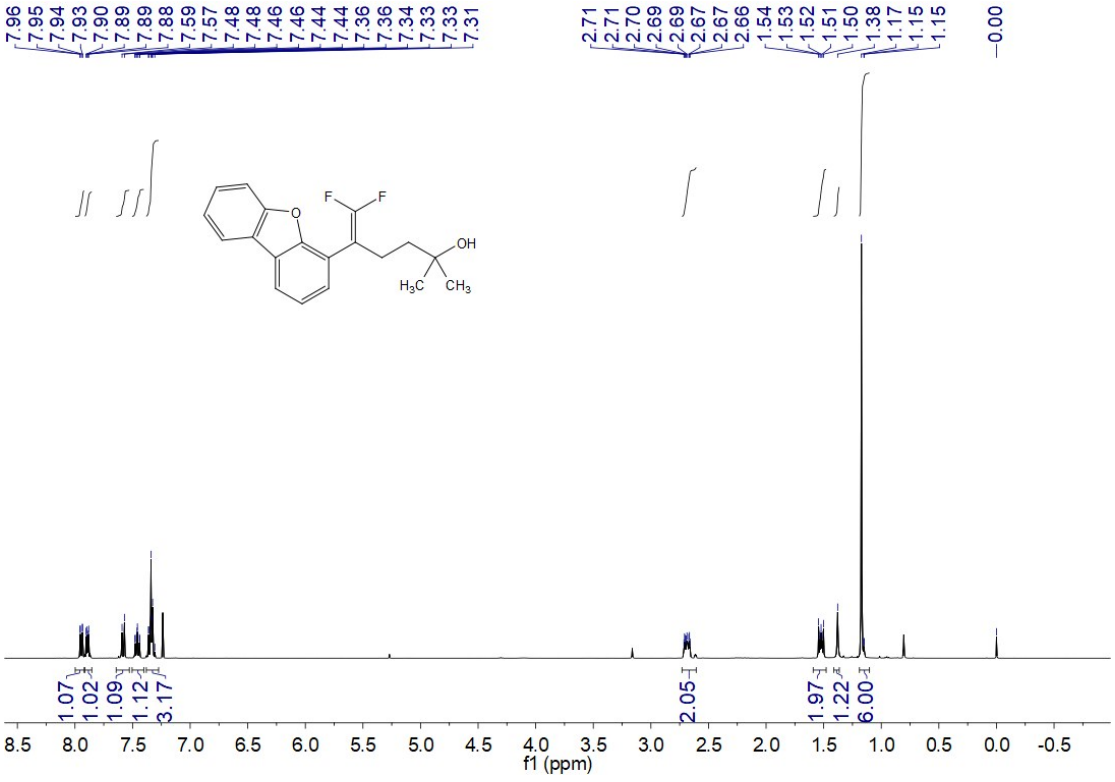


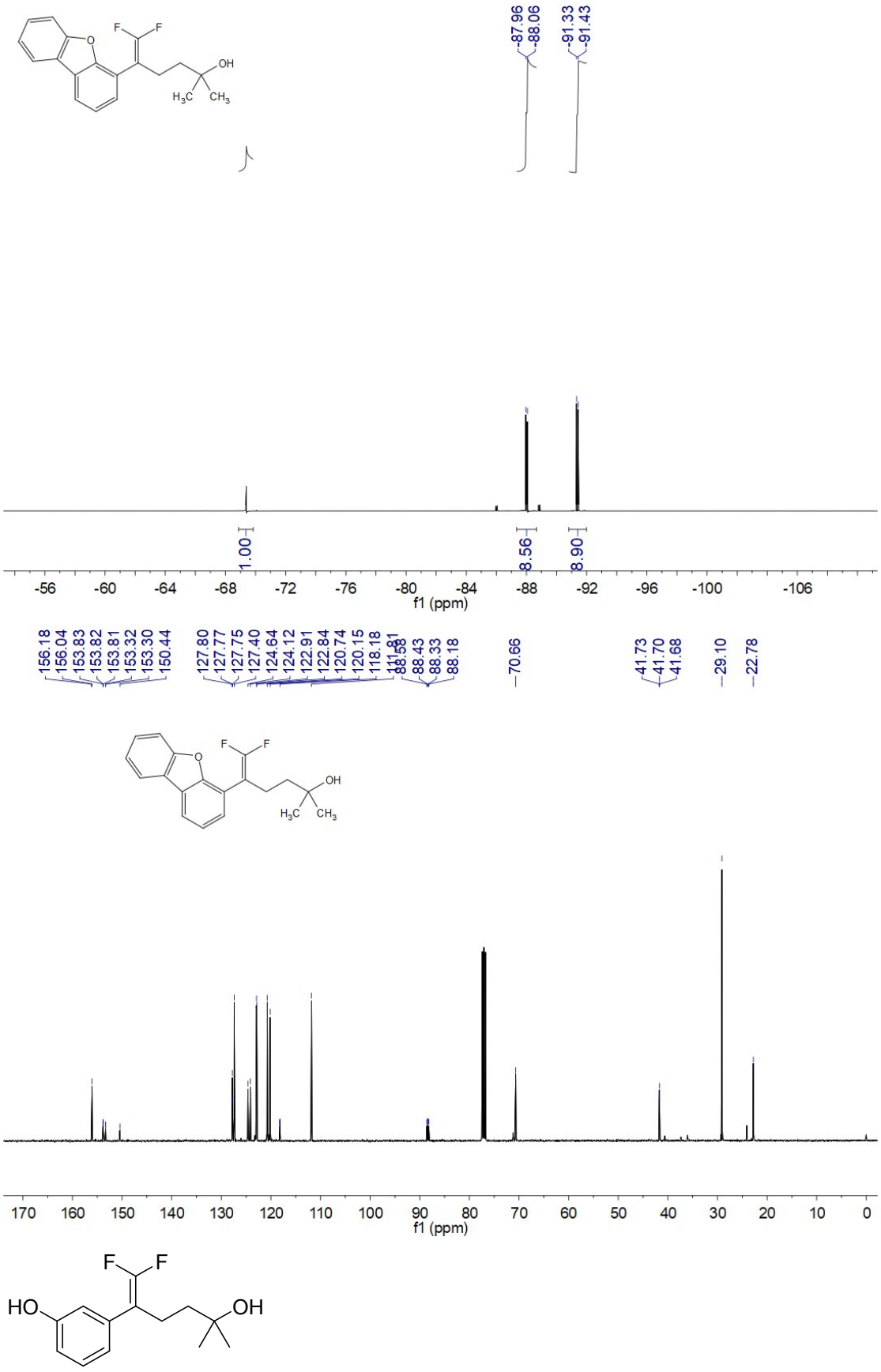
5-(dibenzo[b,d]furan-4-yl)-6,6-difluoro-2-methylhex-5-en-2-ol (3o)

<u>Selectivity</u> (desired C-F cleavage product: addition by-product, determined

by ^{1}H NMR and ^{19}F NMR) = 16:1.

Prepared according to the general procedure, as a sticky liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 7.7, 0.6 Hz, 1H), 7.89 (dd, *J* = 5.4, 3.5 Hz, 1H), 7.58 (d, *J* = 8.2 Hz, 1H), 7.49 – 7.41 (m, 1H), 7.40 – 7.32 (m, 3H), 2.73 – 2.66 (m, 2H), 1.55 – 1.49 (m, 2H), 1.38 (br s, 1H), 1.17 (s, 6H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -88.01 (d, *J* = 39.2 Hz), -91.38 (d, *J* = 39.4 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.04, 153.83 (d, *J* = 1.6 Hz), 153.31 (dd, *J* = 290.0, 287.7 Hz), 127.77 (t, *J* = 2.6 Hz), 127.40, 124.64, 124.12, 122.91, 122.84, 120.74, 120.15, 118.19 (dd, *J* = 5.1, 2.3 Hz), 111.81, 88.38 (dd, *J* = 24.7, 15.2 Hz), 70.66, 41.69 (t, *J* = 2.2 Hz), 29.10, 22.78. **HRMS** (APCI) calcd for $C_{19}H_{18}F_2NaO_2$ ($M+Na^+$): 339.1167; found: 339.1163. **IR** (KBr/cm^{-1}) 3418, 2360, 1733, 1616, 1487, 1451, 1396, 1353, 1246, 1190, 1112, 1002, 787, 752, 616.



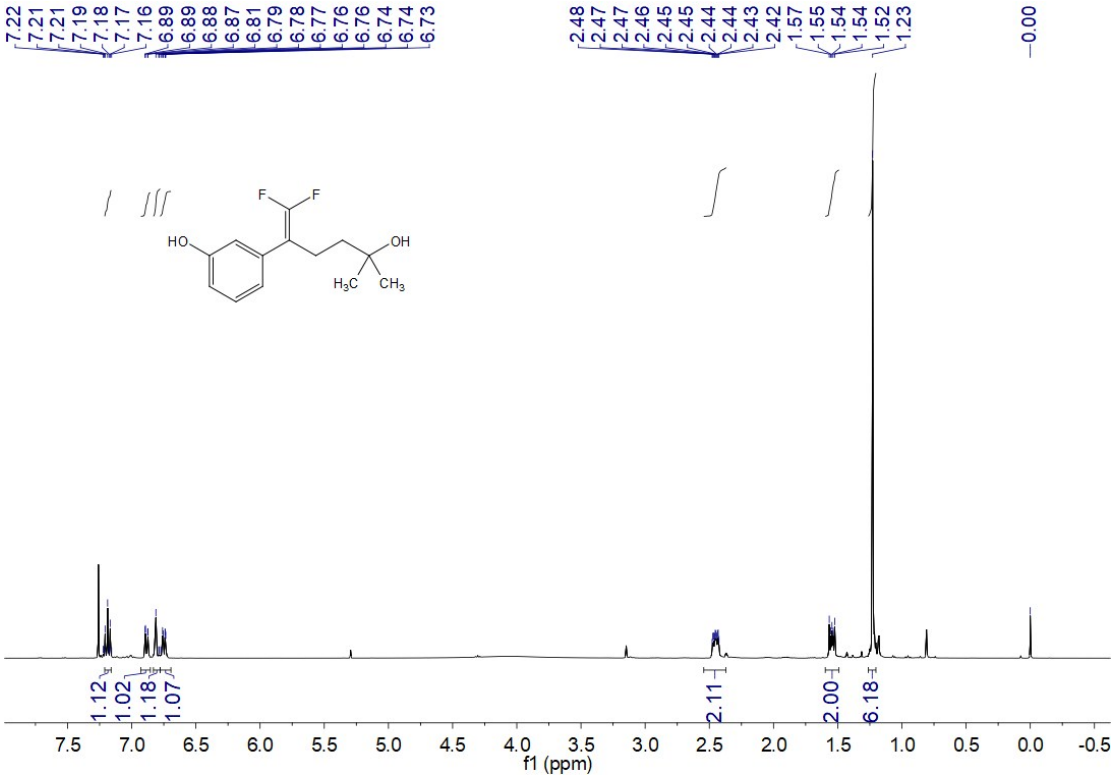


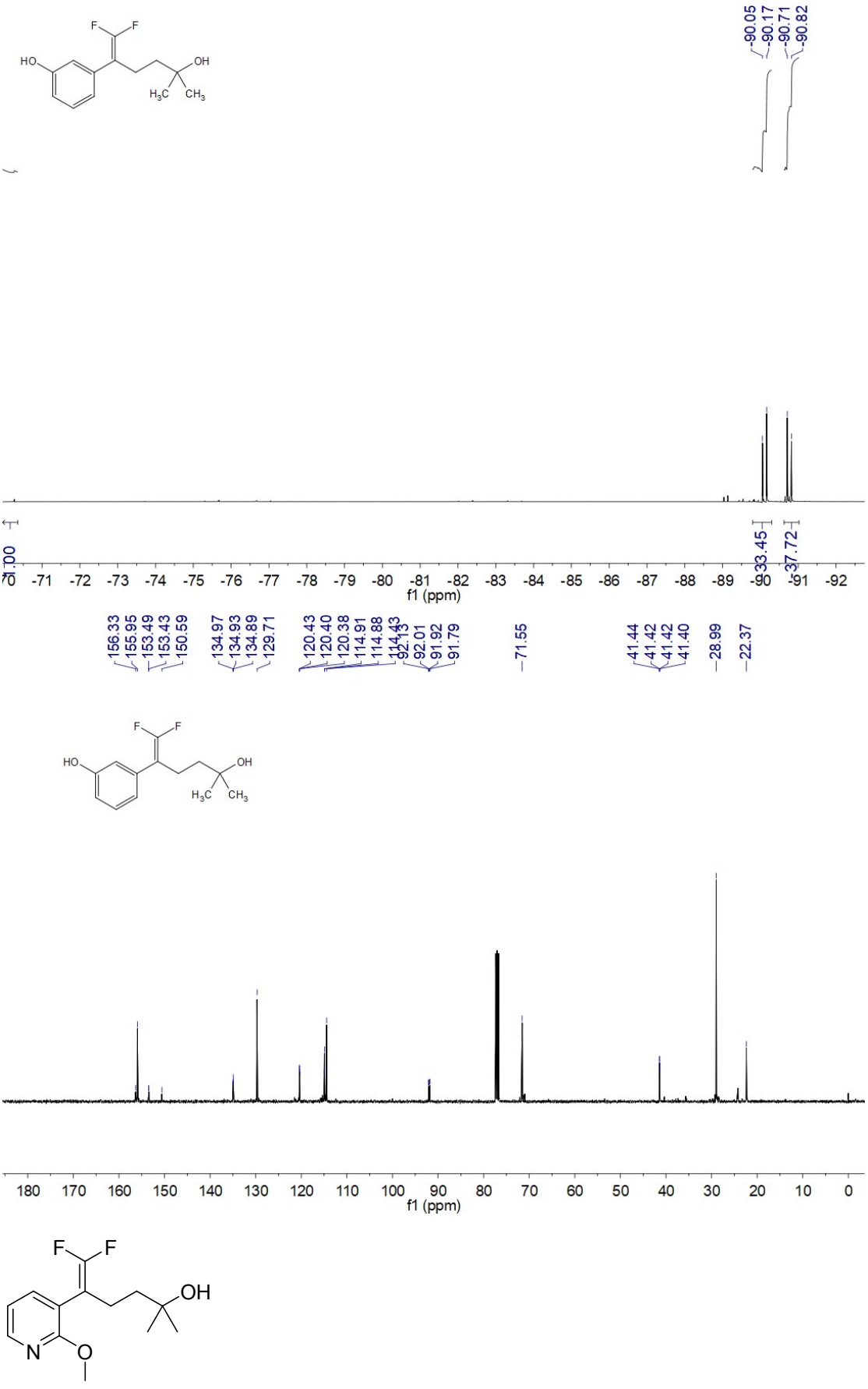
3-(1,1-difluoro-5-hydroxy-5-methylhex-1-en-2-yl)phenol (3k)

<u>Selectivity</u> (desired C-F cleavage product: addition by-product, determined

by ^{1}H NMR and ^{19}F NMR) > 40:1.

Prepared according to the general procedure, as a sticky liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25 – 7.14 (m, 1H), 6.88 (dd, *J* = 7.7, 0.8 Hz, 1H), 6.81 (s, 1H), 6.77 – 6.71 (m, 1H), 2.51 – 2.39 (m, 2H), 1.63 – 1.49 (m, 2H), 1.23 (s, 6H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -90.11 (d, *J* = 42.4 Hz), -90.77 (d, *J* = 42.4 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.95, 153.46 (dd, *J* = 291.8, 286.3 Hz), 134.91 (t, *J* = 3.9 Hz), 129.71, 120.39 (dd, *J* = 5.0, 2.8 Hz), 114.91 (t, *J* = 3.3 Hz), 114.43, 91.96 (dd, *J* = 21.9, 12.4 Hz), 71.55, 41.42 (dd, *J* = 2.2, 1.7 Hz), 28.99, 22.37. **HRMS** (APCI) calcd for $C_{13}H_{16}F_2NaO_2$ ($M+Na^+$): 265.1011; found: 265.1016. **IR** (KBr/cm^{-1}) 3422, 2982, 1617, 1485, 1452, 1396, 1355, 1243, 1103, 1001, 787, 773, 619.

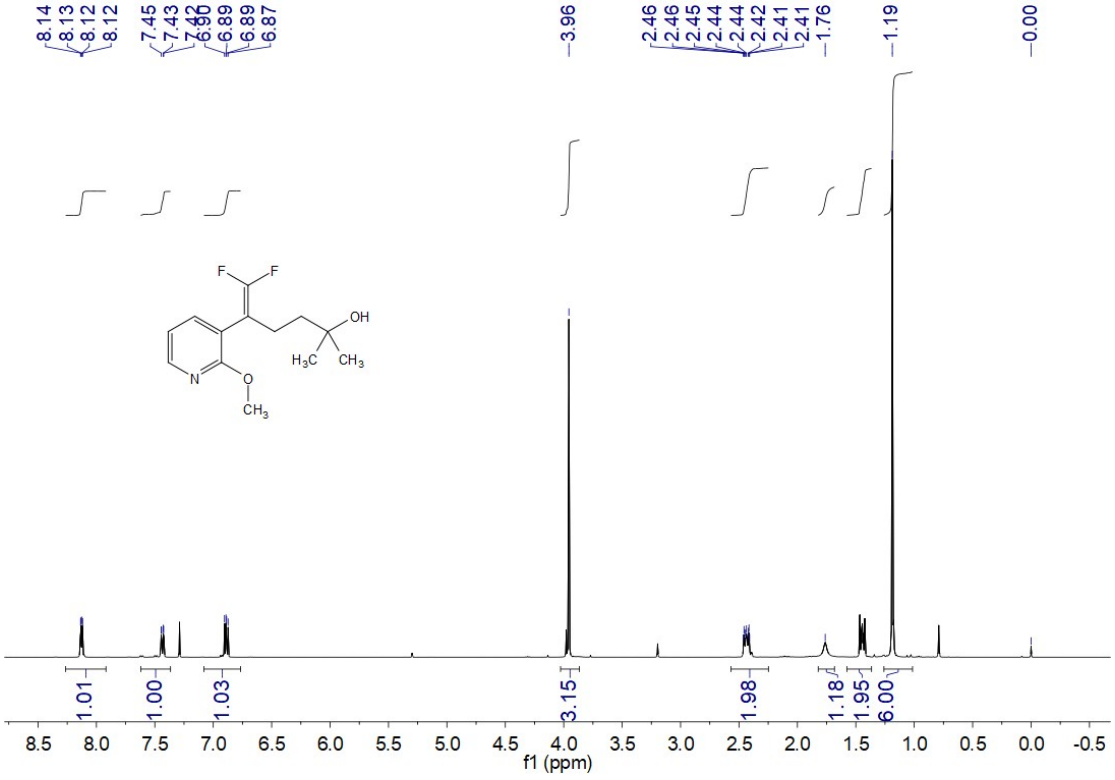


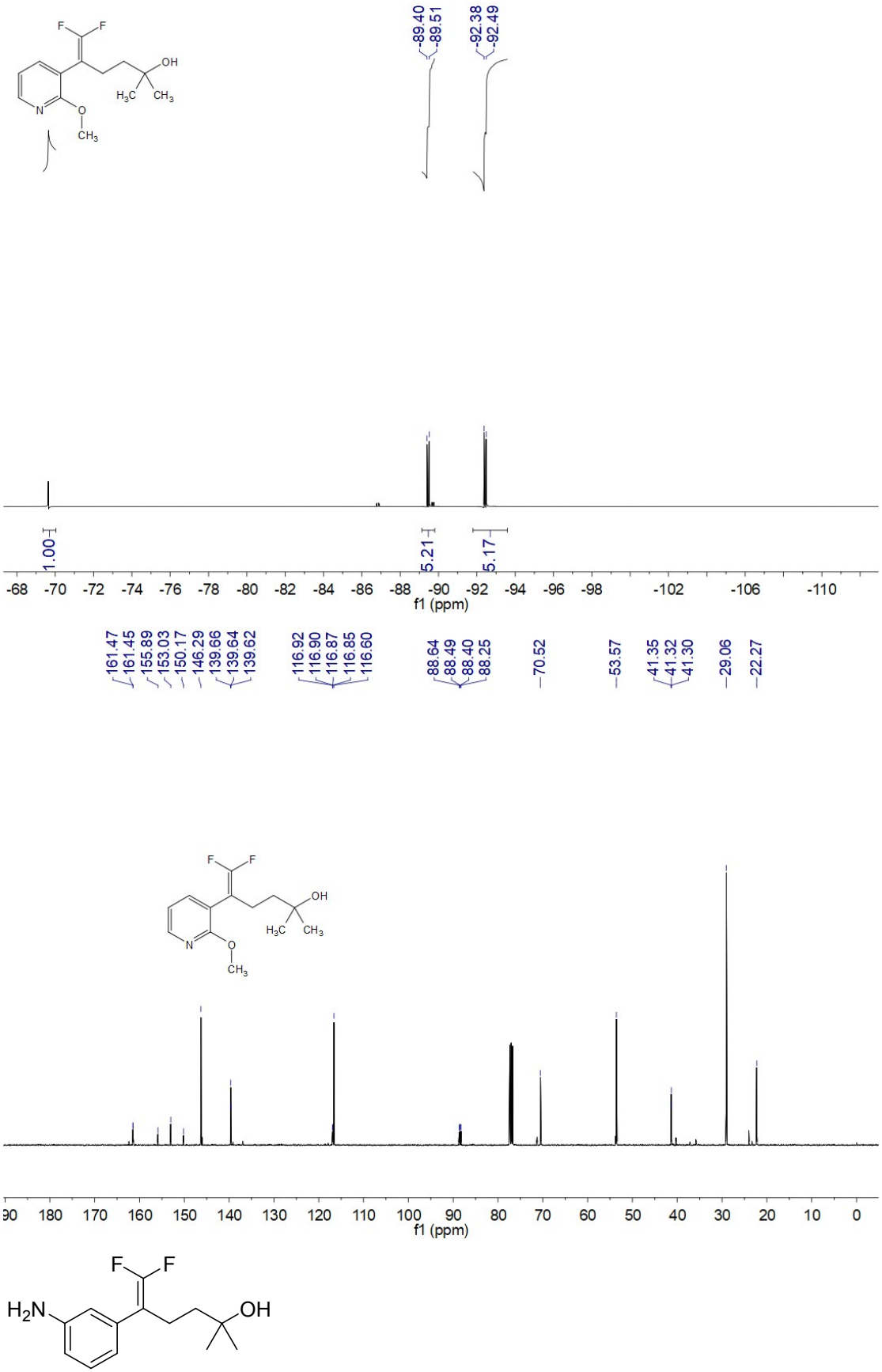


6,6-difluoro-5-(2-methoxypyridin-3-yl)-2-methylhex-5-en-2-ol (3q)

<u>Selectivity</u> (desired C-F cleavage product: addition by-product, determined by ^{1}H NMR and ^{19}F NMR) = 12:1.

Prepared according to the general procedure, as a sticky liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13 (dd, *J* = 5.0, 1.9 Hz, 1H), 7.43 (dd, *J* = 7.2, 1.3 Hz, 1H), 6.89 (dd, *J* = 7.3, 5.0 Hz, 1H), 3.96 (s, 3H), 2.50 – 2.37 (m, 2H), 1.76 (br s, 1H), 1.52 – 1.34 (m, 2H), 1.19 (s, 6H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -89.46 (d, *J* = 41.8 Hz), -92.43 (d, *J* = 41.7 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.46 (t, *J* = 2.4 Hz), 153.03 (dd, *J* = 288.1, 287.9 Hz), 146.29, 139.64 (t, *J* = 2.3 Hz), 116.89 (dd, *J* = 5.2, 1.9 Hz), 116.60, 88.45 (dd, *J* = 24.3, 15.5 Hz), 70.52, 53.57, 41.31 (t, *J* = 2.2 Hz), 29.06, 22.27. **HRMS** (APCI) calcd for $C_{13}H_{17}F_2NNaO_2$ ($M+Na^+$): 280.1120; found: 280.1123. **IR** (KBr/cm^{-1}) 3417, 2976, 1743, 1590, 1465, 1404, 1368, 1249, 1173, 1096, 1020, 775, 600.



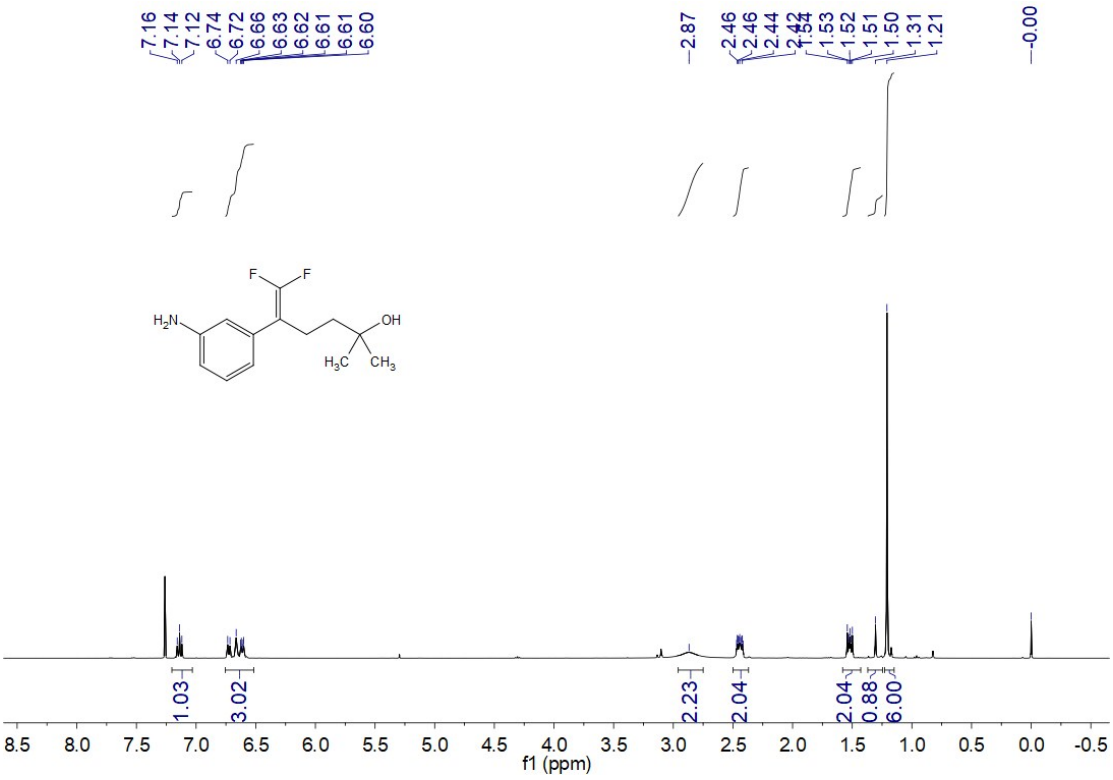


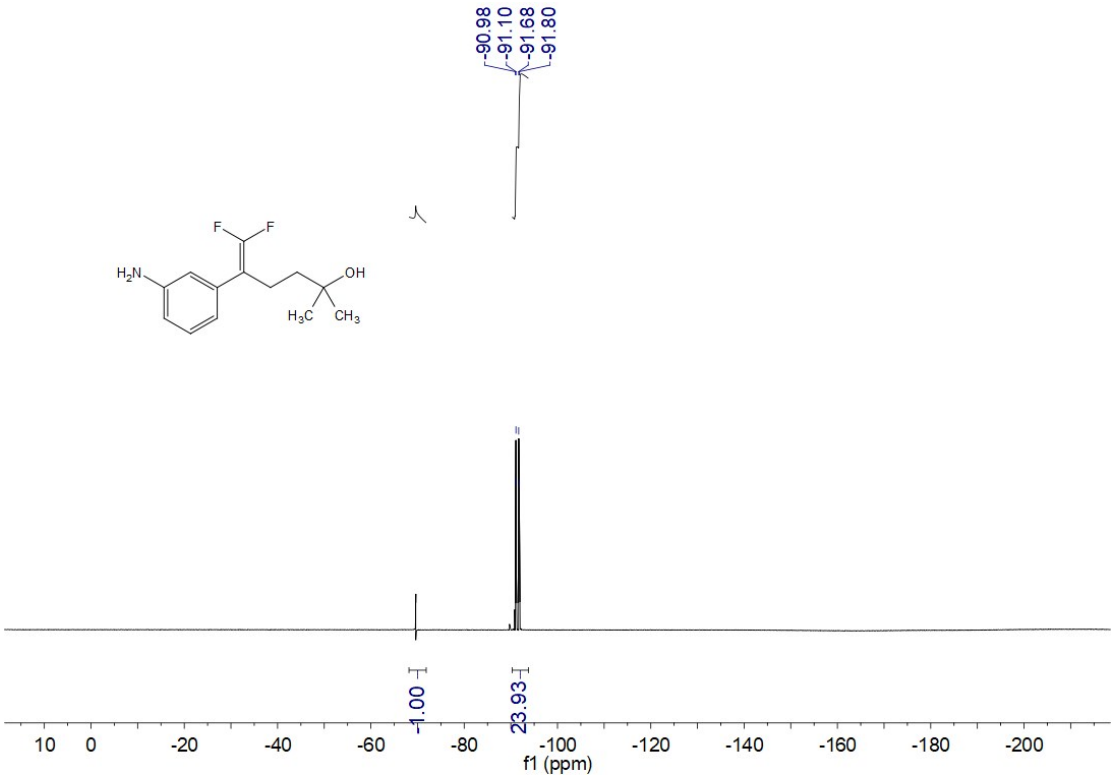
5-(3-aminophenyl)-6,6-difluoro-2-methylhex-5-en-2-ol (3u)

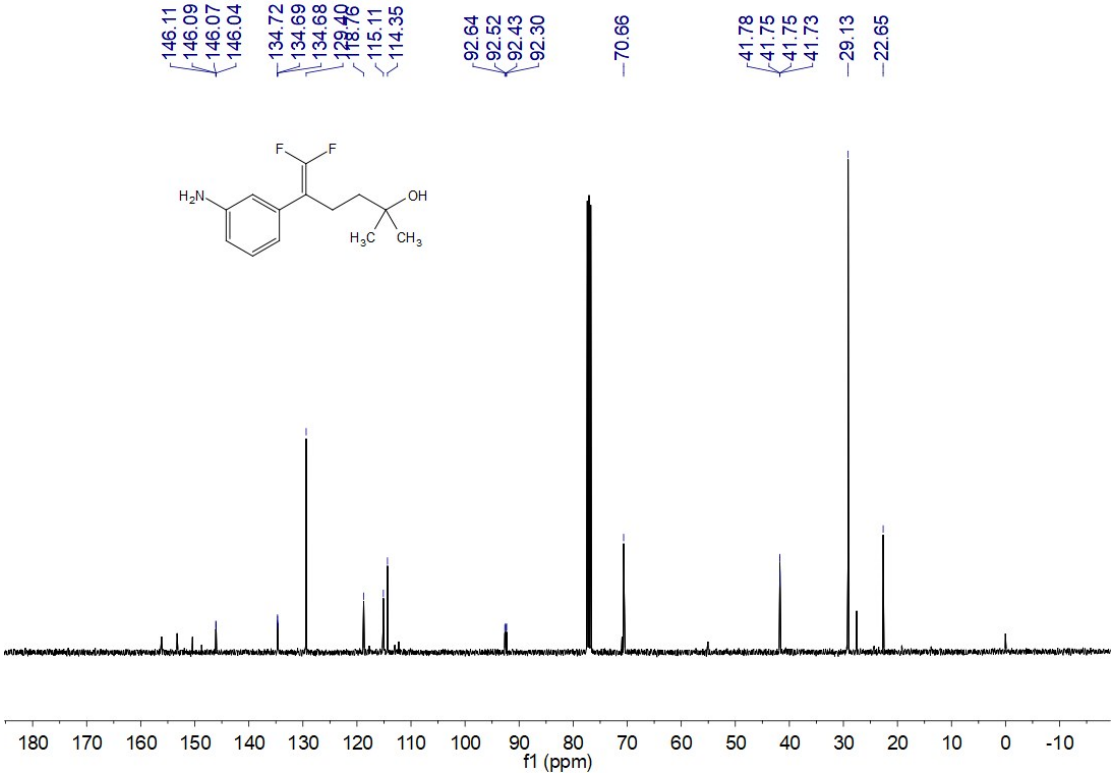
<u>Selectivity</u> (desired C-F cleavage product: addition by-product, determined

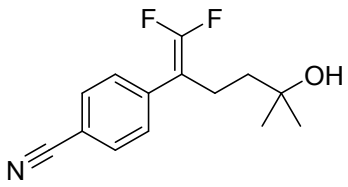
by ^{1}H NMR and ^{19}F NMR) >35:1.

Prepared according to the general procedure, as a sticky liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.14 (t, *J* = 7.8 Hz, 1H), 6.82 – 6.51 (m, 3H), 2.87 (br s, 2H), 2.55 – 2.31 (m, 2H), 1.65 – 1.44 (m, 2H), 1.31 (br s, 1H), 1.21 (s, 6H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -91.04 (d, *J* = 44.1 Hz), -91.74 (d, *J* = 44.1 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.28 (dd, *J* = 290.5, 286.0 Hz), 146.08 (dd, *J* = 4.9, 2.6 Hz), 134.69 (dd, *J* = 4.4, 3.3 Hz), 129.40, 118.76, 115.11, 114.35, 92.47 (dd, *J* = 21.6, 12.9 Hz), 70.66, 41.75 (dd, *J* = 2.5, 2.0 Hz), 29.13, 22.65. **HRMS** (APCI) calcd for $C_{13}H_{17}F_2NNaO$ ($M+Na^+$): 264.1170; found: 264.1172. **IR** (KBr/cm^{-1}) 3423, 2981, 1637, 1617, 1487, 1456, 1396, 1356, 1172, 1101, 1001, 787, 775, 618.





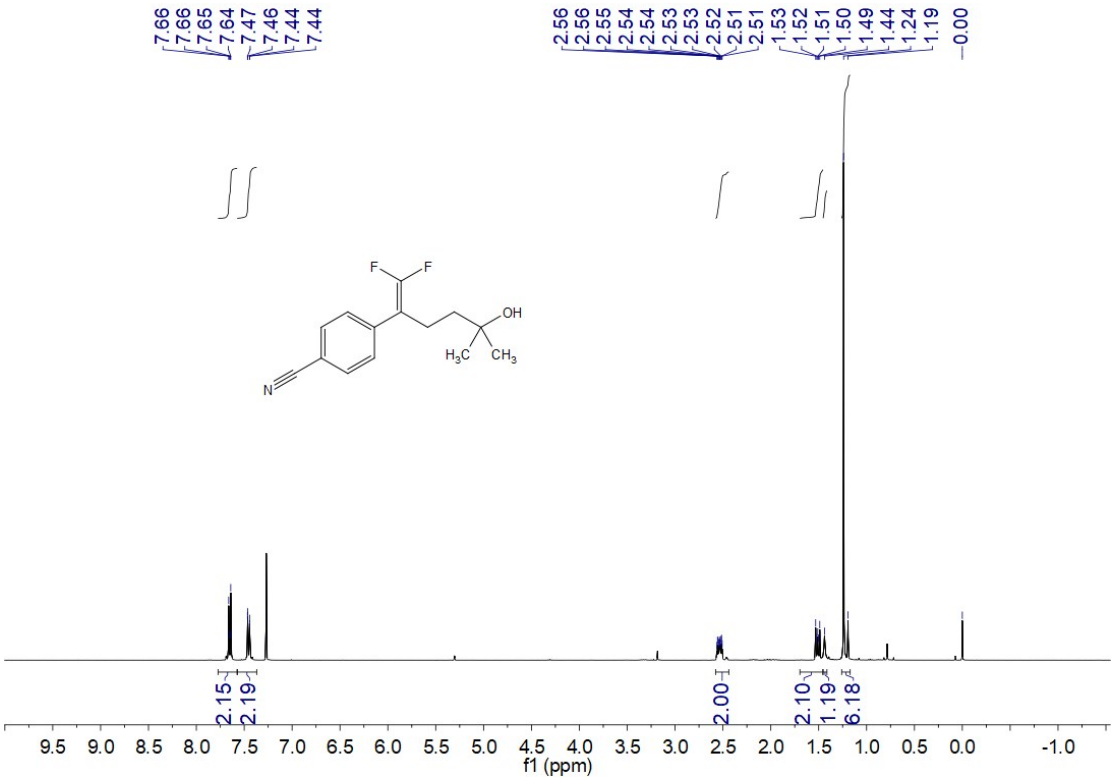


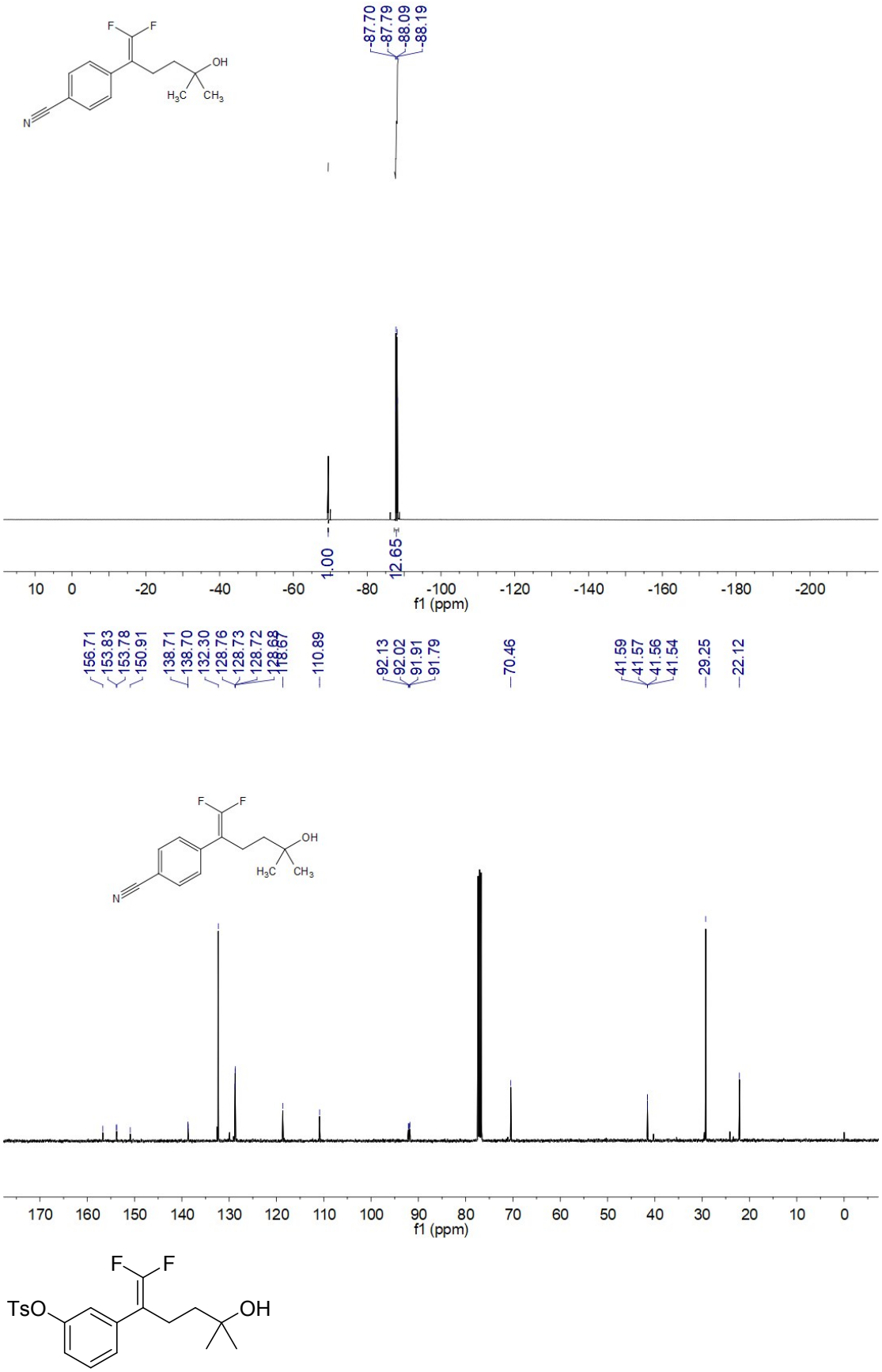


4-(1,1-difluoro-5-hydroxy-5-methylhex-1-en-2-yl)benzonitrile (3j)

<u>Selectivity</u> (desired C-F cleavage product: addition by-product, determined by ^{1}H NMR and ^{19}F NMR) = 18:1.

Prepared according to the general procedure, as a sticky liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 – 7.57 (m, 2H), 7.45 (dd, *J* = 8.7, 1.0 Hz, 2H), 2.71 – 2.49 (m, 2H), 1.65 – 1.45 (m, 2H), 1.44 (br s, 1H), 1.24 (s, 6H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -87.74 (d, *J* = 36.0 Hz), -88.14 (d, *J* = 36.0 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.81 (dd, *J* = 294.0, 289.2 Hz), 138.70 (dd, *J* = 4.8, 4.0 Hz), 132.30, 128.72 (dd, *J* = 4.2, 3.4 Hz), 118.67, 110.89, 91.96 (dd, *J* = 23.0, 11.7 Hz), 70.46, 41.57 (dd, *J* = 2.4, 1.9 Hz), 29.25, 22.12. **HRMS** (APCI) calcd for $C_{14}H_{15}F_2NNaO$ ($M+Na^+$): 274.1014; found: 274.1018. **IR** (KBr/cm^{-1}) 3416, 2981, 2229, 1637, 1616, 1487, 1395, 1242, 1174, 1002, 786, 620.



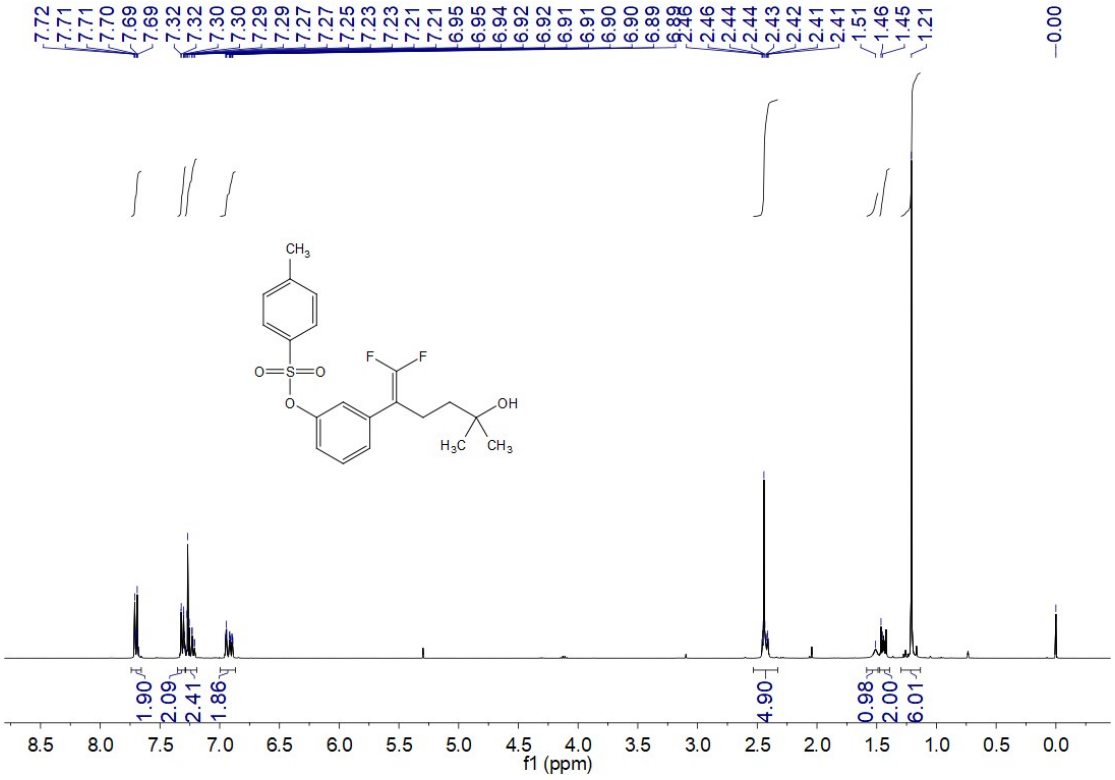


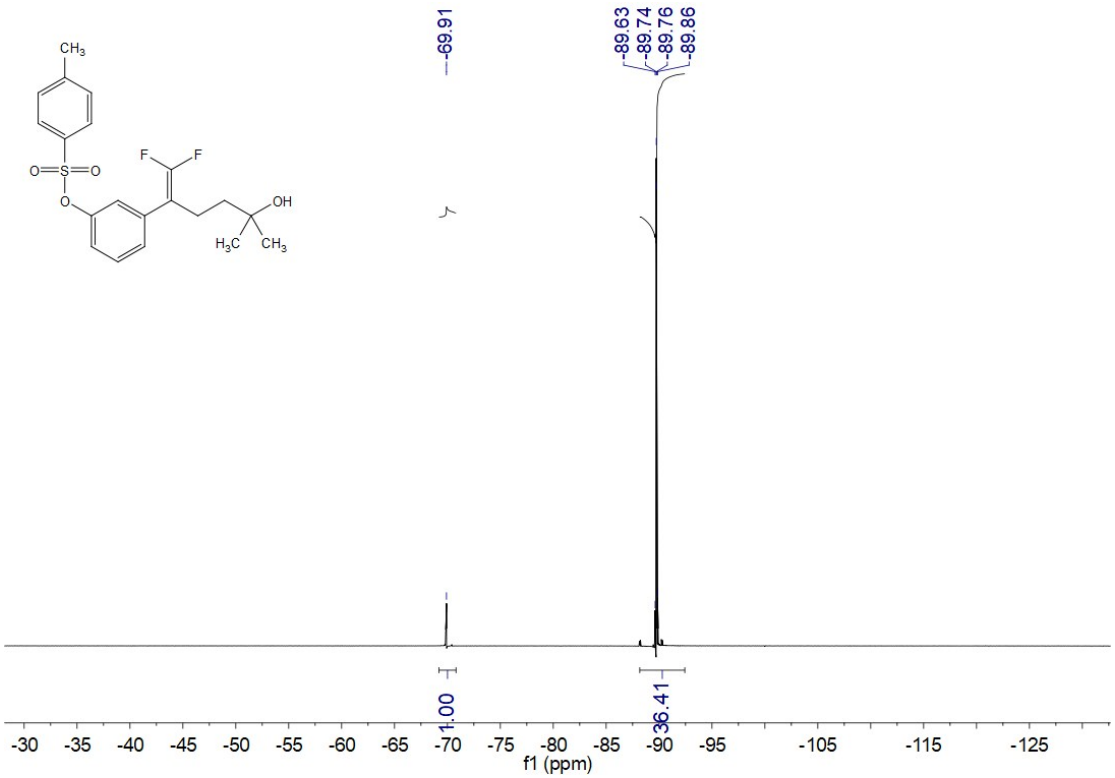
3-(1,1-difluoro-5-hydroxy-5-methylhex-1-en-2-yl)phenyl 4-methylbenzenesulfonate (3i)

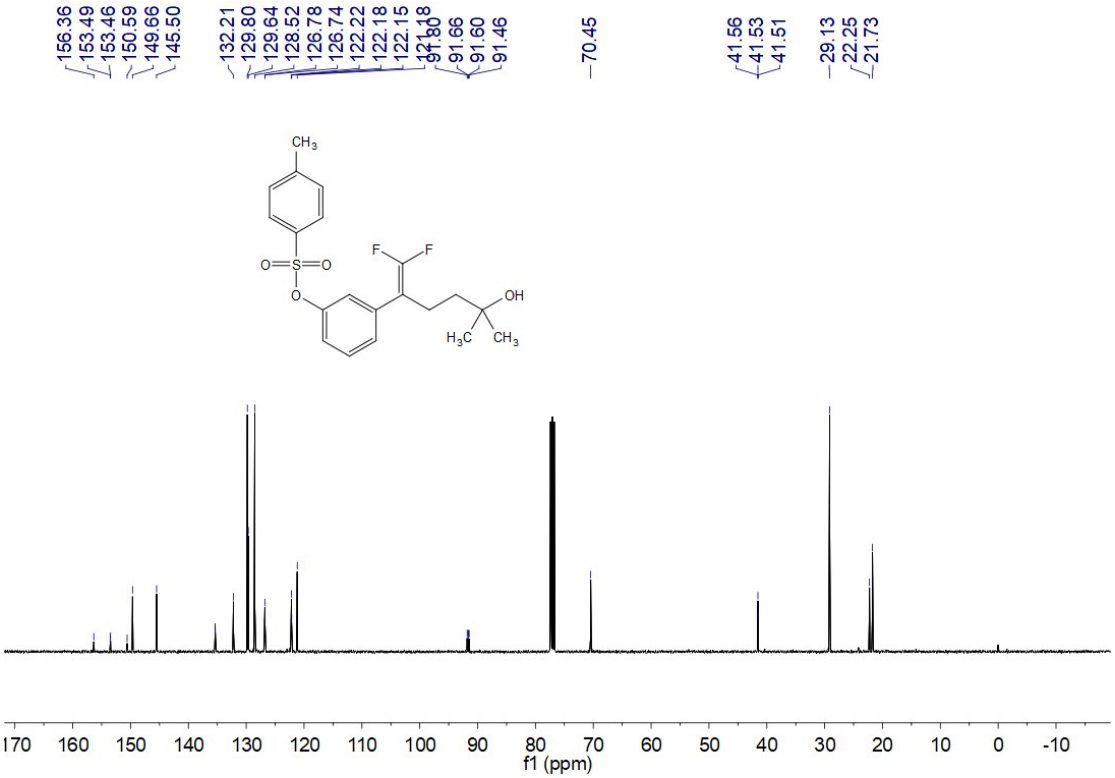
<u>Selectivity</u> (desired C-F cleavage product: addition by-product, determined

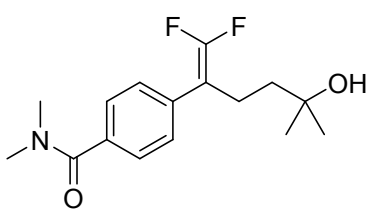
by ^{1}H NMR and ^{19}F NMR) > 50:1.

Prepared according to the general procedure, as a sticky liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 – 7.54 (m, 2H), 7.36 – 7.29 (m, 2H), 7.28 – 7.19 (m, 2H), 6.98 – 6.87 (m, 2H), 2.53 – 2.38 (m, 5H), 1.51 (br s, 1H), 1.47 – 1.39 (m, 2H), 1.21 (s, 6H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -89.68 (d, *J* = 39.8 Hz), -89.81 (d, *J* = 39.9 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.48 (dd, *J* = 291.4, 288.6 Hz), 149.66, 145.50, 135.36 (dd, *J* = 2.8, 1.8 Hz), 132.21, 129.80, 129.64, 128.52, 126.78 (t, *J* = 3.7 Hz), 122.18 (t, *J* = 3.6 Hz), 121.18, 91.63 (dd, *J* = 20.5, 14.4 Hz), 70.45, 41.53 (t, *J* = 2.2 Hz), 29.13, 22.25, 21.73. **HRMS** (APCI) calcd for $C_{20}H_{22}F_2NaO_4S$ ($M+Na^+$): 419.1099; found: 419.1103. **IR** (KBr/cm^{-1}) 3419, 2981, 2829, 2361, 1721, 1608, 1488, 1456, 1396, 1370, 1240, 1193, 1179, 1150, 1093, 800, 772, 759, 662, 609.





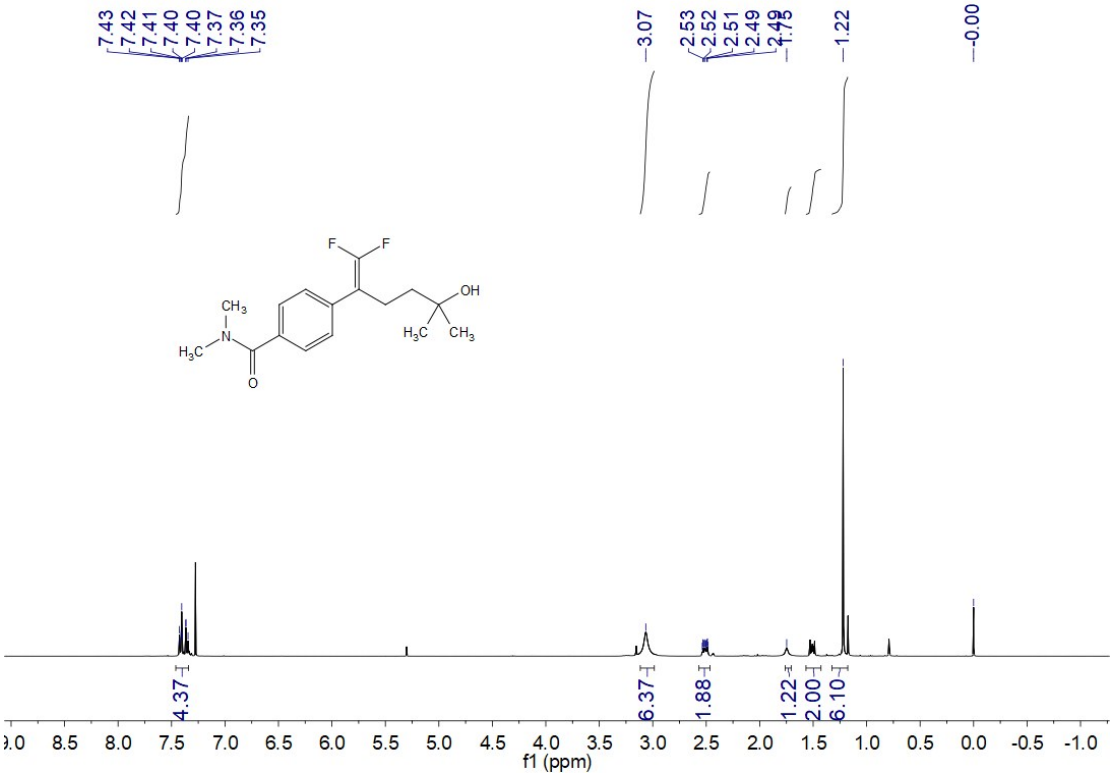


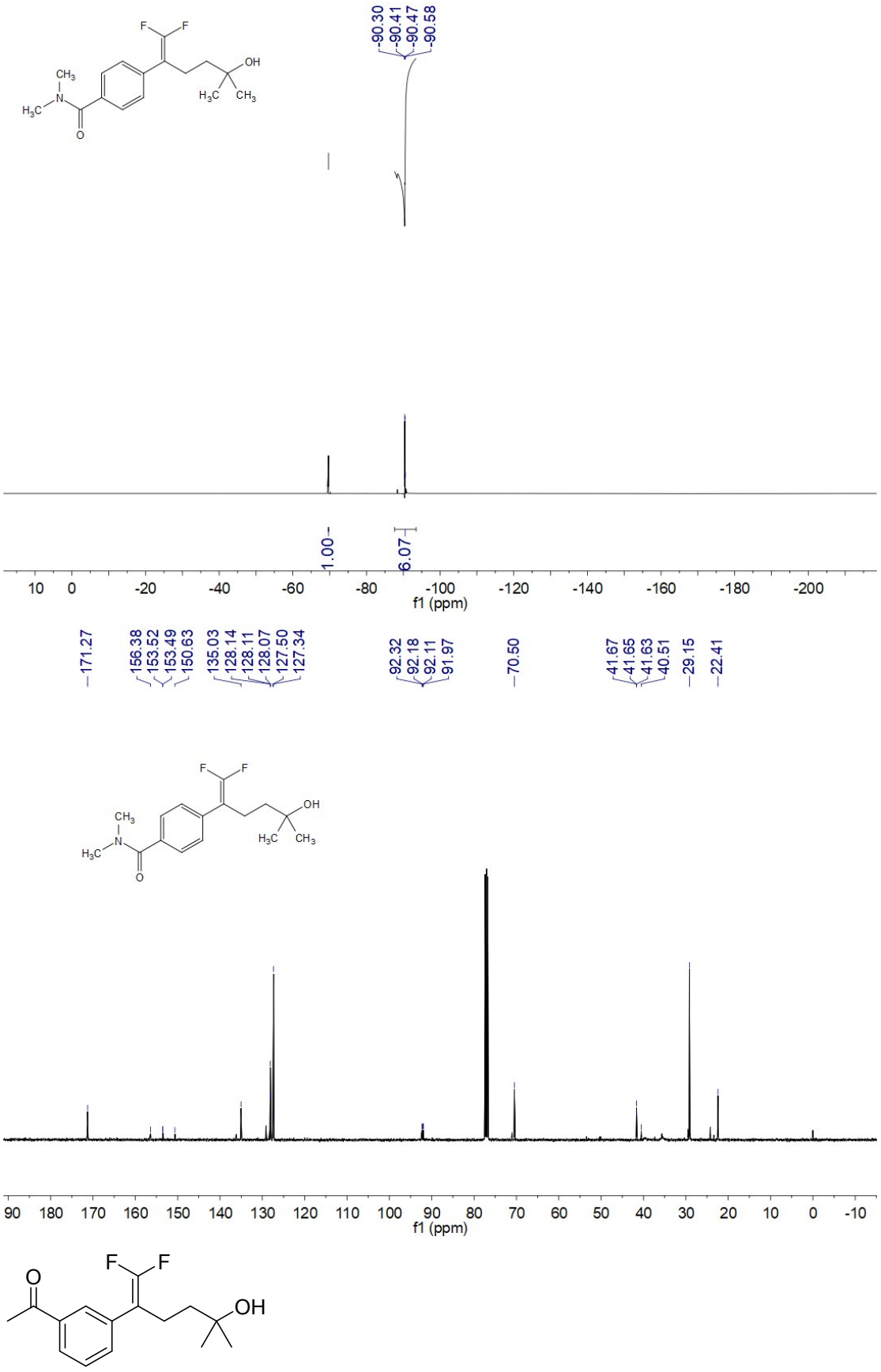


4-(1,1-difluoro-5-hydroxy-5-methylhex-1-en-2-yl)-N,N-dimethylbenzamide (3s)

<u>Selectivity</u> (desired C-F cleavage product: addition by-product, determined by ^{1}H NMR and ^{19}F NMR) = 10:1.

Prepared according to the general procedure, as a sticky liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 – 7.30 (m, 4H), 3.07 (br s, 6H), 2.58 – 2.43 (m, 2H), 1.75 (br s, 1H), 1.57 – 1.48 (m, 2H), 1.22 (s, 6H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -90.35 (d, *J* = 41.4 Hz), -90.52 (d, *J* = 41.3 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.27, 153.50 (dd, *J* = 291.0, 287.9 Hz), 135.03, 128.11 (t, *J* = 3.5 Hz), 127.50, 127.34, 92.14 (dd, *J* = 20.9, 13.7 Hz), 70.50, 41.64 (d, *J* = 2.2 Hz), 40.51, 29.15, 22.41. **HRMS** (APCI) calcd for $C_{16}H_{21}F_2NNaO_2$ ($M+Na^+$): 320.1433; found: 320.1437. **IR** (KBr/cm^{-1}) 3410, 2983, 2068, 1714, 1637, 1617, 1488, 1396, 1353, 1235, 1173, 615.



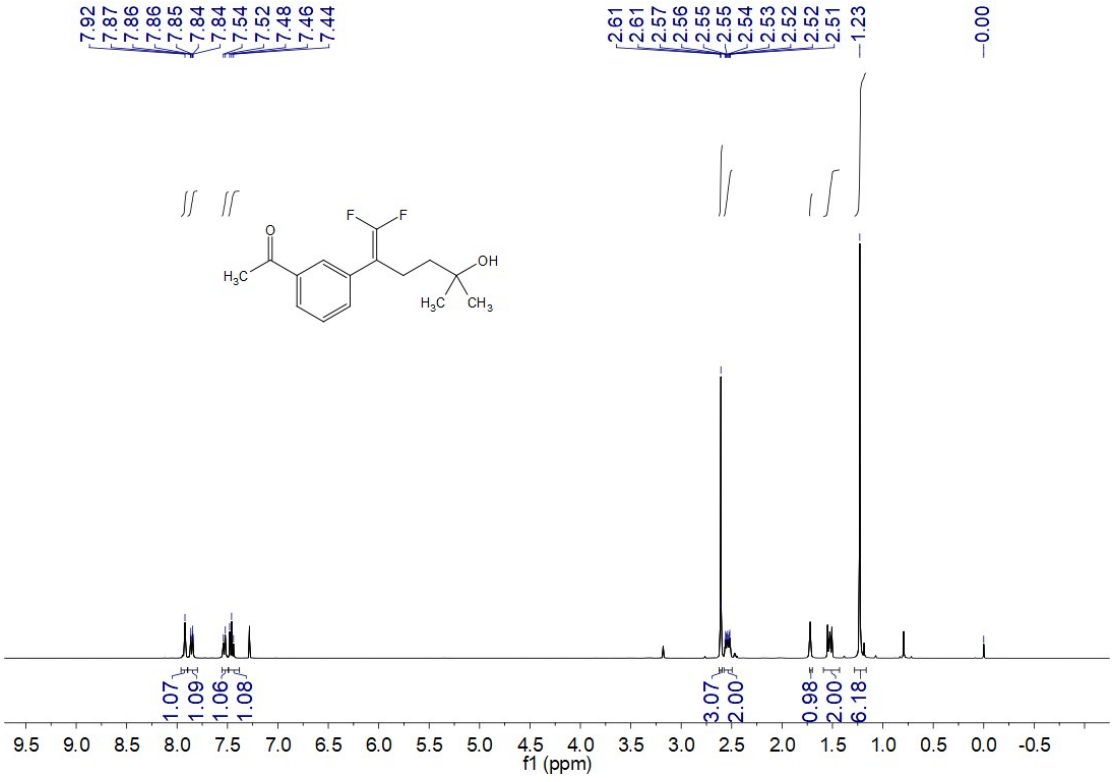


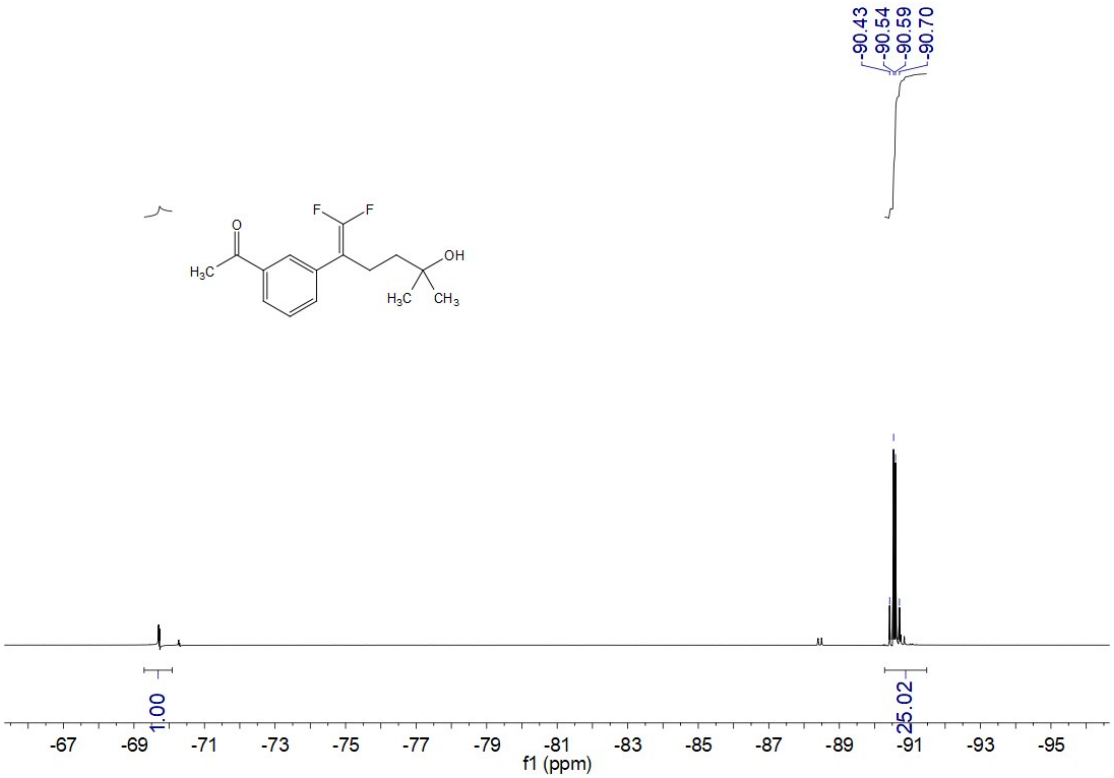
1-(3-(1,1-difluoro-5-hydroxy-5-methylhex-1-en-2-yl)phenyl)ethan-1-one (3r)

<u>Selectivity</u> (desired C-F cleavage product: addition by-product, determined by

^{1}H NMR and ^{19}F NMR) > 35:1.

Prepared according to the general procedure, as a sticky liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.90 – 7.80 (m, 1H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 1H), 2.61 (s, 3H), 2.57 – 2.49 (m, 2H), 1.72 (br s, 1H), 1.57 – 1.47 (m, 2H), 1.23 (s, 6H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -90.48 (d, *J* = 41.9 Hz), -90.65 (d, *J* = 41.9 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 198.01, 153.54 (dd, *J* = 290.7, 288.0 Hz), 137.33, 134.29 (dd, *J* = 3.7, 2.4 Hz), 132.83 (t, *J* = 3.4 Hz), 128.82, 127.94 (t, *J* = 3.4 Hz), 127.28, 92.04 (dd, *J* = 21.2, 13.8 Hz), 70.45, 41.62 (t, *J* = 2.3 Hz), 29.14, 26.67, 22.57. **HRMS** (APCI) calcd for $C_{15}H_{18}F_2NaO_2$ ($M+Na^+$): 291.1167; found: 291.1171. **IR** (KBr/cm^{-1}) 3413, 2986, 1637, 1616, 1488, 1461, 1396, 1355, 1173, 1011, 792, 779, 620.

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-90.70
F
F
O
H3C
OH
H3C
CH3
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25.02
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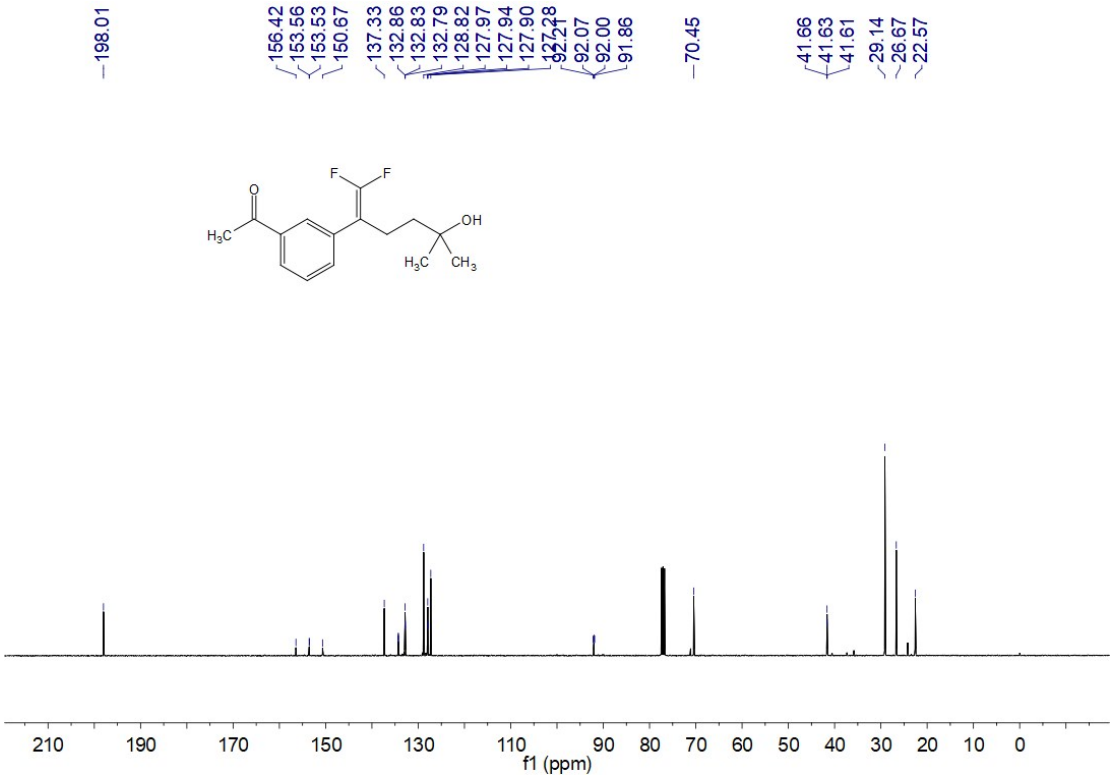
-87
-89
-91
-93
-95
f1 (ppm)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150.67
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132.86
132.83
132.79
128.82
127.97
127.94
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127.28
92.21
92.07
92.00
91.86
70.45
41.66
41.63
41.61
29.14
26.67
22.57
F
F
O
H3C
OH
H3C
CH3
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170
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130
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90
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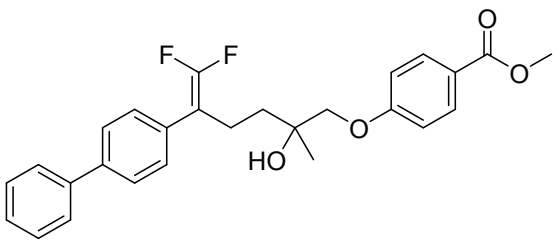
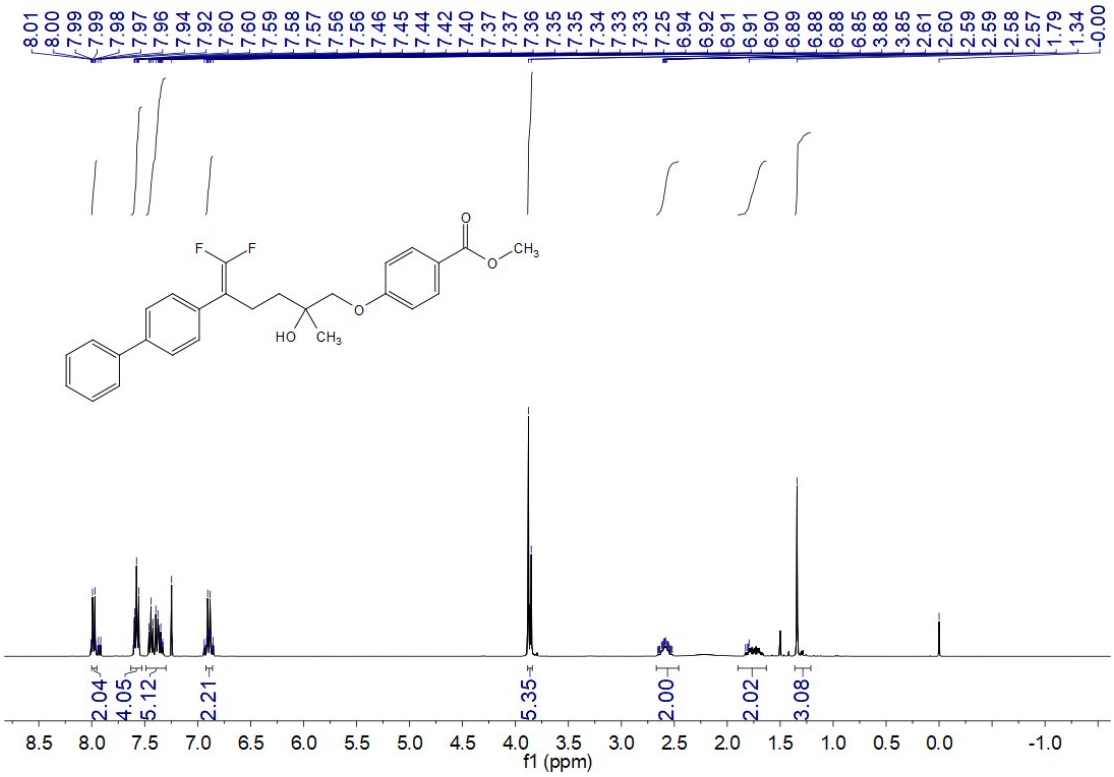
70
60
50
40
30
20
10
0
f1 (ppm)

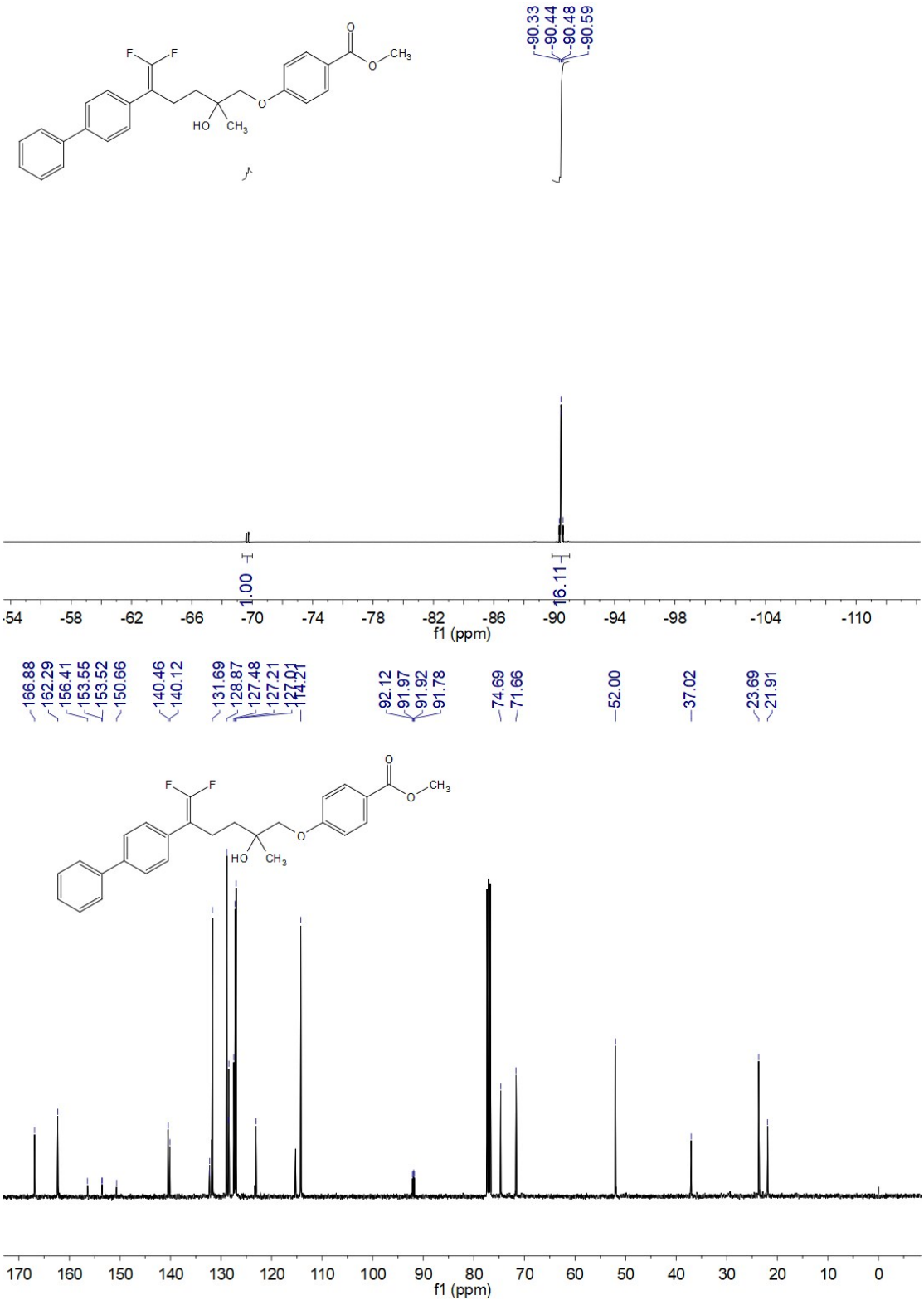

F
F
O
O
HO
O

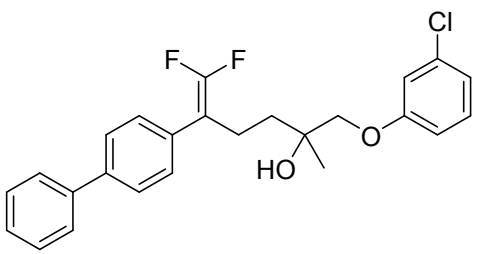
methyl-4-((5-([1,1'-biphenyl]-4-yl)-6,6-difluoro-2-hydroxy-2-methylhex-5-en-1-yl)oxy)benzoate (4b)

<u>Selectivity</u> (desired C-F cleavage product: addition by-product, determined by ^{1}H NMR and ^{19}F NMR) = 25:1.

Prepared according to the general procedure, as a sticky liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 – 7.94 (m, 2H), 7.60 – 7.53 (m, 4H), 7.47 – 7.32 (m, 5H), 6.93 – 6.82 (m, 2H), 3.94 – 3.76 (m, 5H), 2.68 – 2.43 (m, 2H), 1.81 (dd, *J* = 9.4, 4.4 Hz, 2H), 1.34 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -90.39 (d, *J* = 42.2 Hz), -90.53 (d, *J* = 42.1 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.88, 162.29, 153.53 (dd, *J* = 290.6, 288.0 Hz), 140.46, 140.12, 132.25 (t, *J* = 2.2 Hz), 131.69, 128.87, 128.46 (t, *J* = 3.5 Hz), 127.48, 127.21, 127.01, 123.07, 114.21, 91.95 (dd, *J* = 19.9, 14.6 Hz), 74.69, 71.66, 52.00, 37.02, 23.69, 21.91. **HRMS** (APCI) calcd for $C_{27}H_{26}F_2NaO_4$ ($M+Na^+$): 475.1691; found: 475.1685. **IR** (KBr/cm^{-1}) 3421, 2982, 2068, 1716, 1637, 1616, 1487, 1395, 1368, 1277, 1184, 1108, 705, 619.



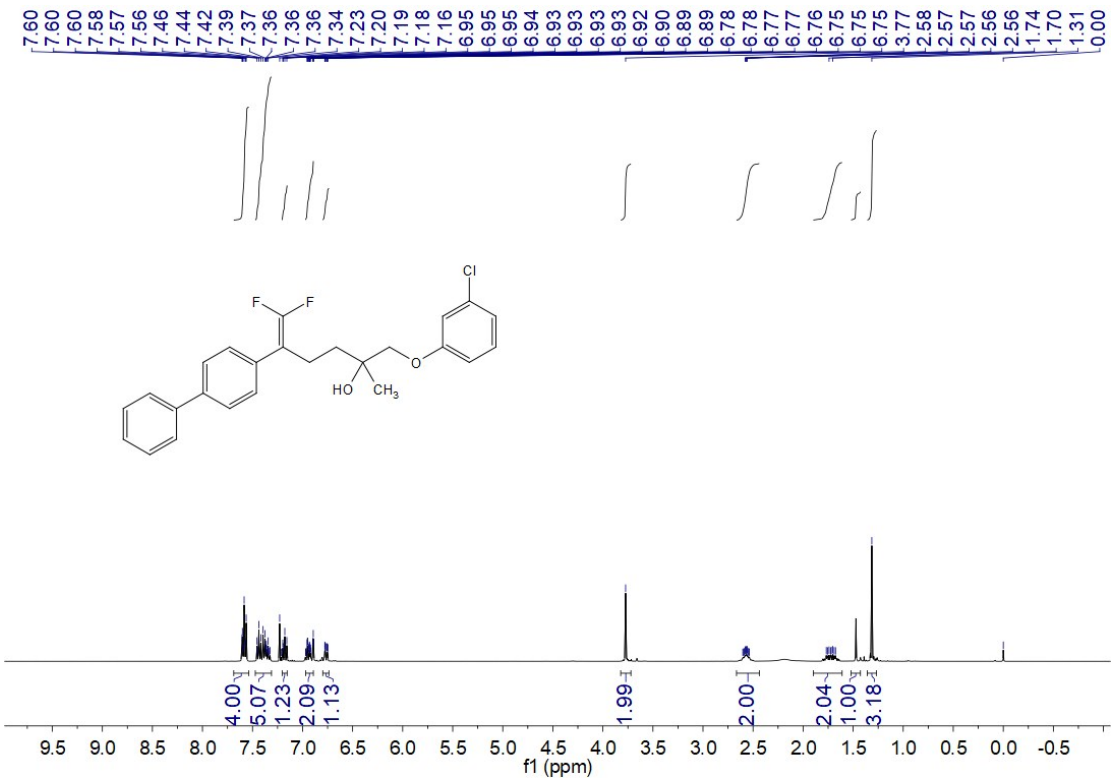

-90.33
-90.44
-90.48
-90.59
1.00
16.11
f1 (ppm)
166.88
162.29
156.41
153.55
153.52
150.66
140.46
140.12
131.69
128.87
127.48
127.21
127.01
114.21
92.12
91.97
91.92
91.78
74.69
71.66
52.00
37.02
23.69
21.91
f1 (ppm)



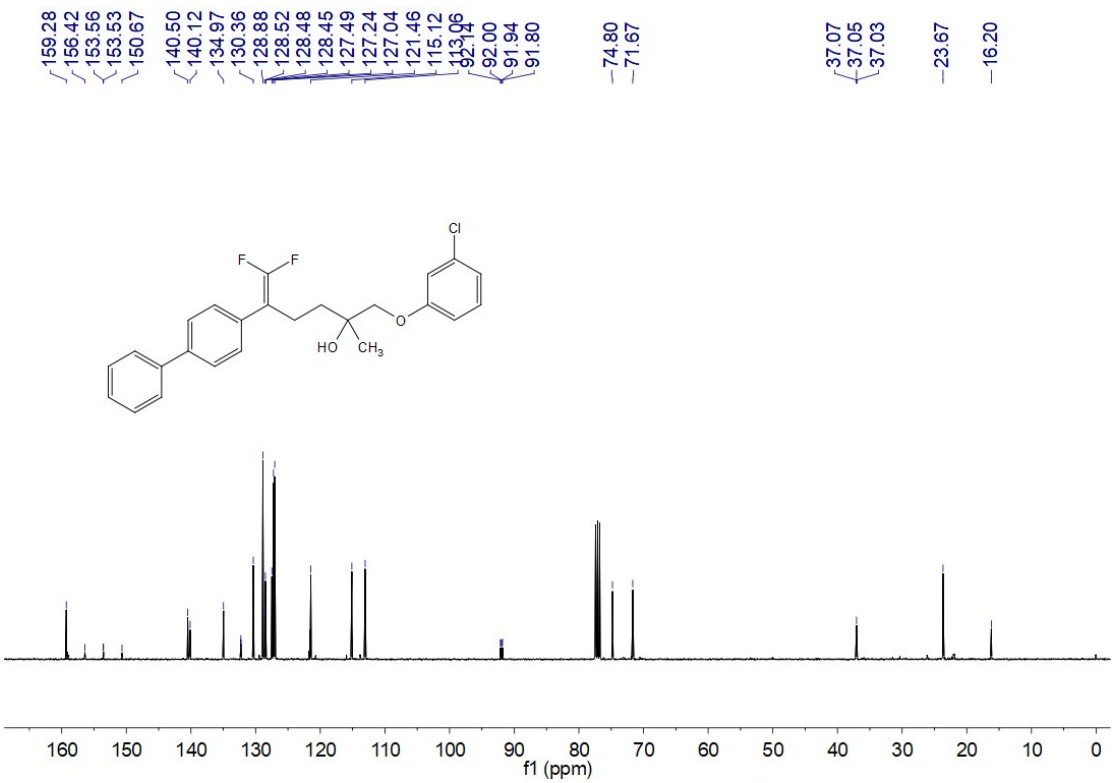
5-([1,1'-biphenyl]-4-yl)-1-(3-chlorophenoxy)-6,6-difluoro-2-methylhex-5-en-2-ol (4e)

Selectivity (desired C-F cleavage product: addition by-product, determined by ^{1}H NMR and ^{19}F NMR) > 45:1.

Prepared according to the general procedure, as a sticky liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 – 7.54 (m, 4H), 7.49 – 7.31 (m, 5H), 7.22 – 7.11 (m, 1H), 6.99 – 6.85 (m, 2H), 6.80 – 6.71 (m, 1H), 3.77 (s, 2H), 2.63 – 2.49 (m, 2H), 1.84 – 1.63 (m, 2H), 1.47 (br s, 1H), 1.31 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -90.36 (d, *J* = 42.1 Hz), -90.51 (d, *J* = 42.2 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.28, 153.54 (dd, *J* = 290.7, 287.8 Hz), 140.50, 140.12, 134.97, 132.27 (d, *J* = 2.5 Hz), 130.36, 128.88, 128.48 (t, *J* = 3.5 Hz), 127.49, 127.24, 127.04, 121.46, 115.12, 113.06, 91.97 (dd, *J* = 20.2, 14.3 Hz), 74.80, 71.67, 37.05 (t, *J* = 2.2 Hz), 23.67, 16.20. **HRMS** (APCI) calcd for $C_{25}H_{23}ClF_2NaO_2$ ($M+Na^+$): 451.1247; found: 451.1251. **IR** (KBr/cm^{-1}) 3417, 2983, 2830, 1719, 1595, 1487, 1461, 1369, 1356, 1233, 1173, 1044, 1005, 772, 680, 602.




-90.30
-90.42
-90.46
-90.57
F
F
Cl
O
HO
CH3
1.00
33.43
f1 (ppm)


159.28
156.42
153.56
153.53
150.67
140.50
140.12
134.97
130.36
128.88
128.52
128.48
128.45
127.49
127.24
127.04
121.46
115.12
113.06
92.14
92.00
91.94
91.80
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37.03
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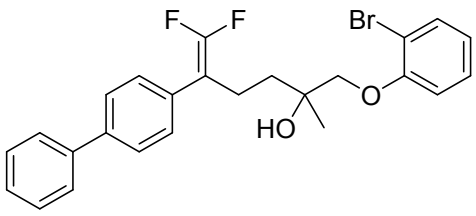
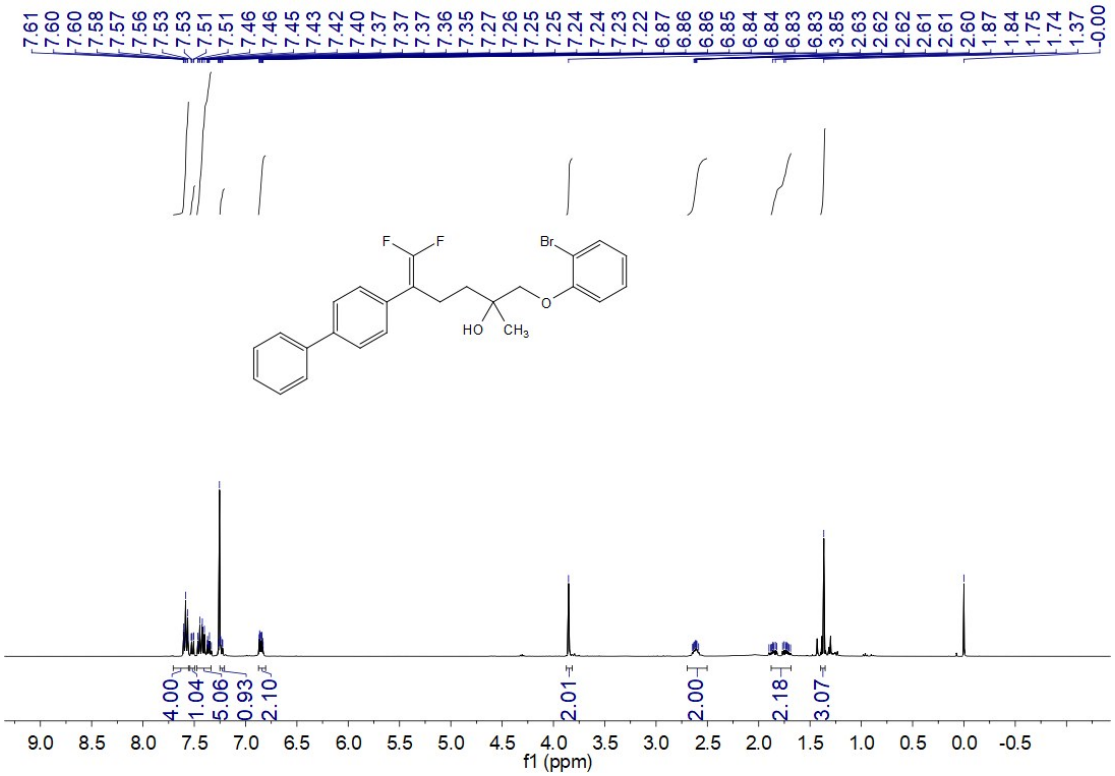
16.20
F
F
Cl
O
HO
CH3
f1 (ppm)


F
F
Br
O
HO

5-([1,1'-biphenyl]-4-yl)-1-(2-bromophenoxy)-6,6-difluoro-2-methylhex-5-en-2-ol (4f)

Selectivity (desired C-F cleavage product: addition by-product, determined by ^{1}H NMR and ^{19}F NMR) = 30:1.

Prepared according to the general procedure, as a sticky liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 – 7.55 (m, 4H), 7.52 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.47 – 7.35 (m, 5H), 7.26 – 7.21 (m, 1H), 6.85 (ddd, *J* = 8.1, 3.7, 1.6 Hz, 2H), 3.85 (s, 2H), 2.68 – 2.52 (m, 2H), 1.96 – 1.60 (m, 2H), 1.37 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -90.51 (d, *J* = 42.5 Hz), -90.65 (d, *J* = 42.5 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.79, 153.50 (dd, *J* = 291.5, 289.2 Hz), 140.58, 140.08, 133.30, 132.31 (t, *J* = 2.1 Hz), 128.82, 128.56, 128.50 (t, *J* = 3.5 Hz), 127.41, 127.23, 127.05, 122.41, 113.44, 112.47, 92.01 (dd, *J* = 19.7, 14.7 Hz), 75.84, 71.73, 36.97 (t, *J* = 2.1 Hz), 23.53, 21.91. **HRMS** (APCI) calcd for $C_{25}H_{23}BrF_2NaO_2$ ($M+Na^+$): 495.0742; found: 495.0748. **IR** (KBr/cm^{-1}) 3415, 2986, 1637, 1616, 1396, 1353, 1174, 1003, 786, 619.




F
F
Br
O
HO
CH3
-90.46
-90.57
-90.60
-90.71
1.00
20.97
-52
-56
-60
-64
-68
-72
-76
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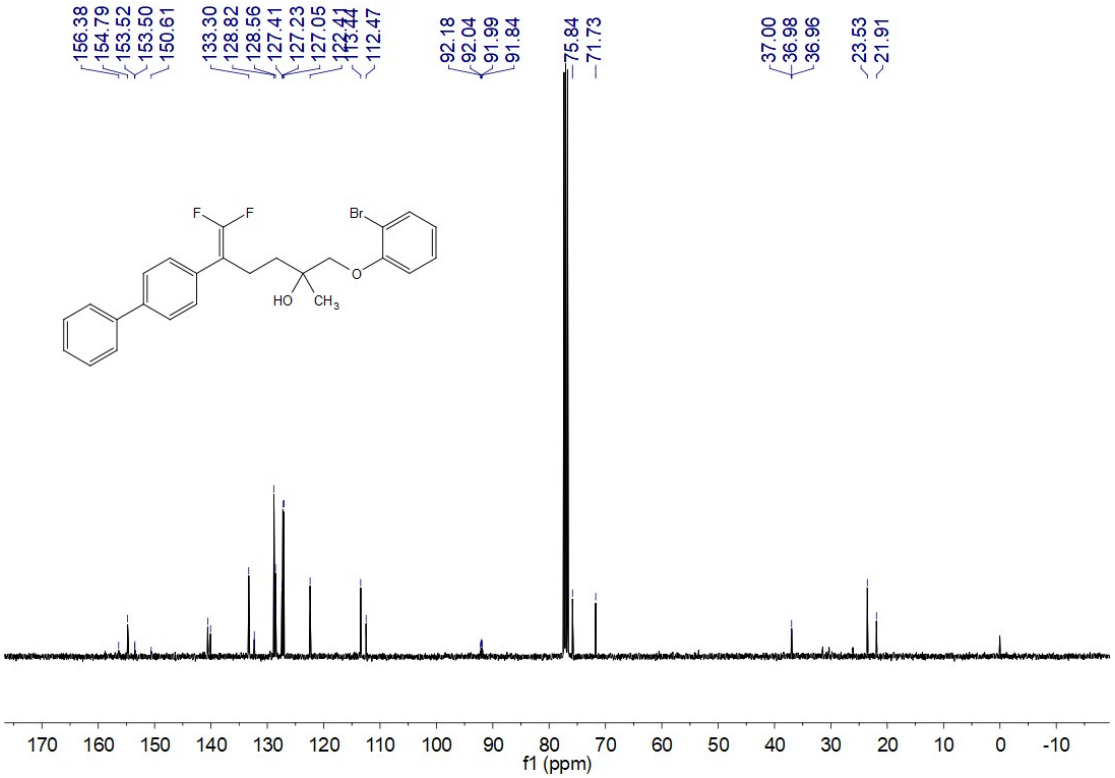
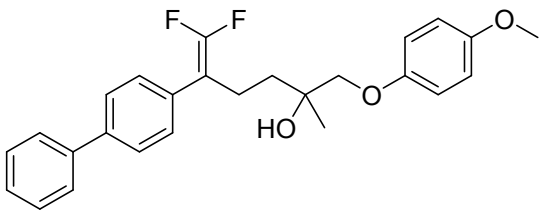
-84
-88
-92
-96
-100
-106
f1 (ppm)

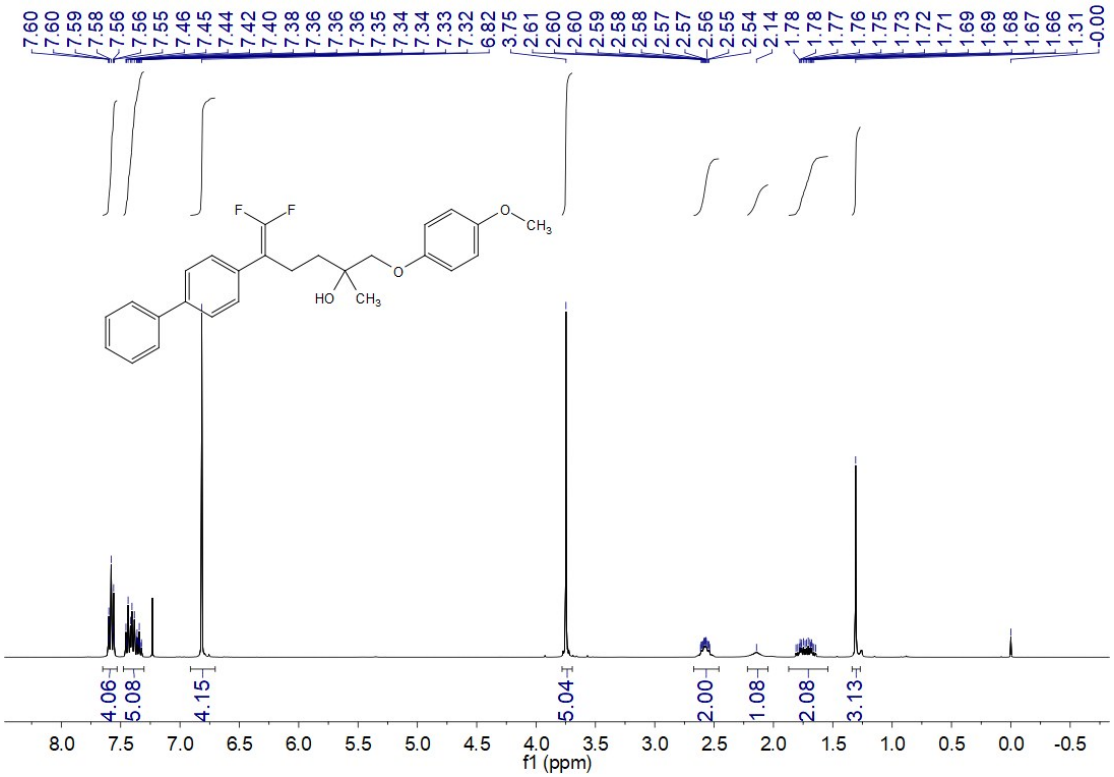

156.38
154.79
153.52
153.50
150.61
133.30
128.82
128.56
127.41
127.23
127.05
112.47
92.18
92.04
91.99
91.84
75.84
71.73
37.00
36.98
36.96
23.53
21.91
F
F
Br
O
HO
CH3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

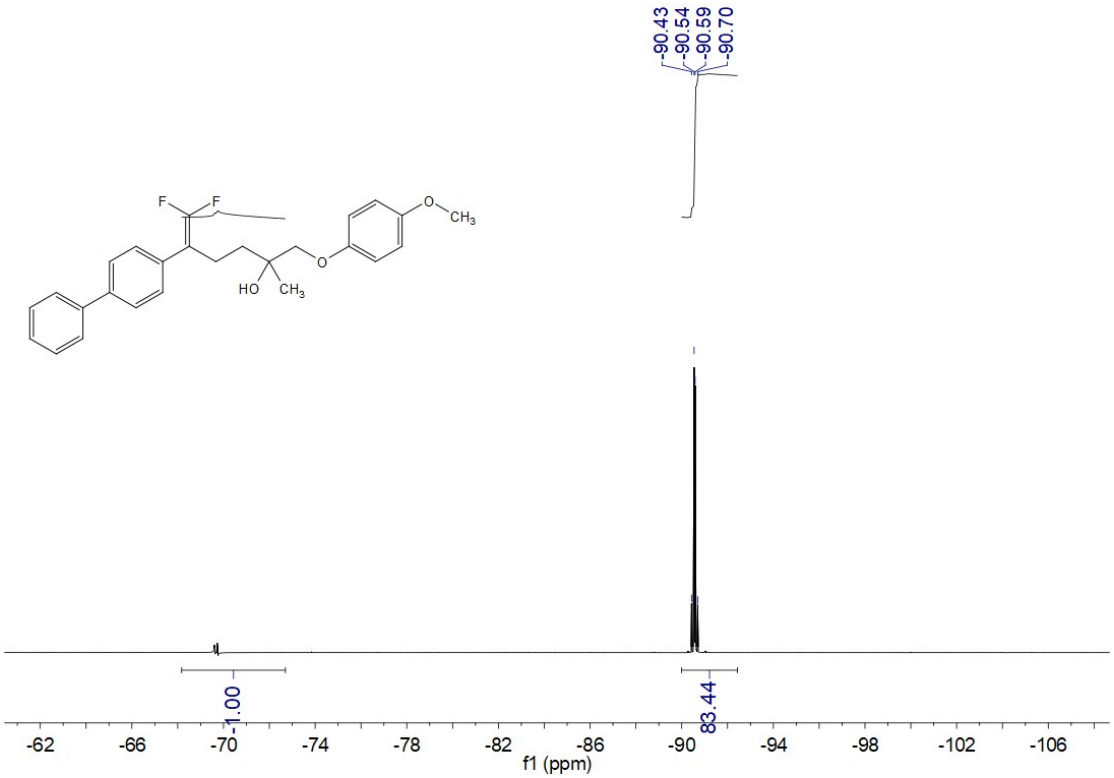

F
F
O
O
HO

5-([1,1'-biphenyl]-4-yl)-6,6-difluoro-1-(4-methoxyphenoxy)-2-methylhex-5-en-2-ol (4d)

<u>Selectivity</u> (desired C-F cleavage product: addition by-product, determined by ^{1}H NMR and ^{19}F NMR) > 50:1.

Prepared according to the general procedure, as a sticky liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 – 7.53 (m, 4H), 7.50 – 7.30 (m, 5H), 6.82 (s, 4H), 3.75 (s, 5H), 2.65 – 2.47 (m, 2H), 2.14 (br s, 1H), 1.83 – 1.61 (m, 2H), 1.31 (s, 3H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -90.48 (d, *J* = 42.4 Hz), -90.64 (d, *J* = 42.4 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.17, 153.54 (dd, *J* = 290.8, 287.6 Hz), 152.79, 140.56, 140.07, 132.38 (d, *J* = 2.8 Hz), 128.86, 128.50 (t, *J* = 3.5 Hz), 127.46, 127.21, 127.04, 115.63, 114.70 (s), 92.08 (dd, *J* = 20.5, 13.9 Hz), 75.43, 71.72, 55.75, 37.14 (t, *J* = 2.2 Hz), 23.66, 22.00. **HRMS** (APCI) calcd for $C_{26}H_{26}F_2NaO_3$ ($M+Na^+$): 447.1742; found: 447.1748. **IR** (KBr/cm^{-1}) 3417, 2978, 1616, 1486, 1456, 1245, 1174, 1028, 1001, 786, 695, 619.




-90.43
-90.54
-90.59
-90.70
F
F
O
CH3
HO
CH3
O
1.00
83.44
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-66
-70
-74
-78
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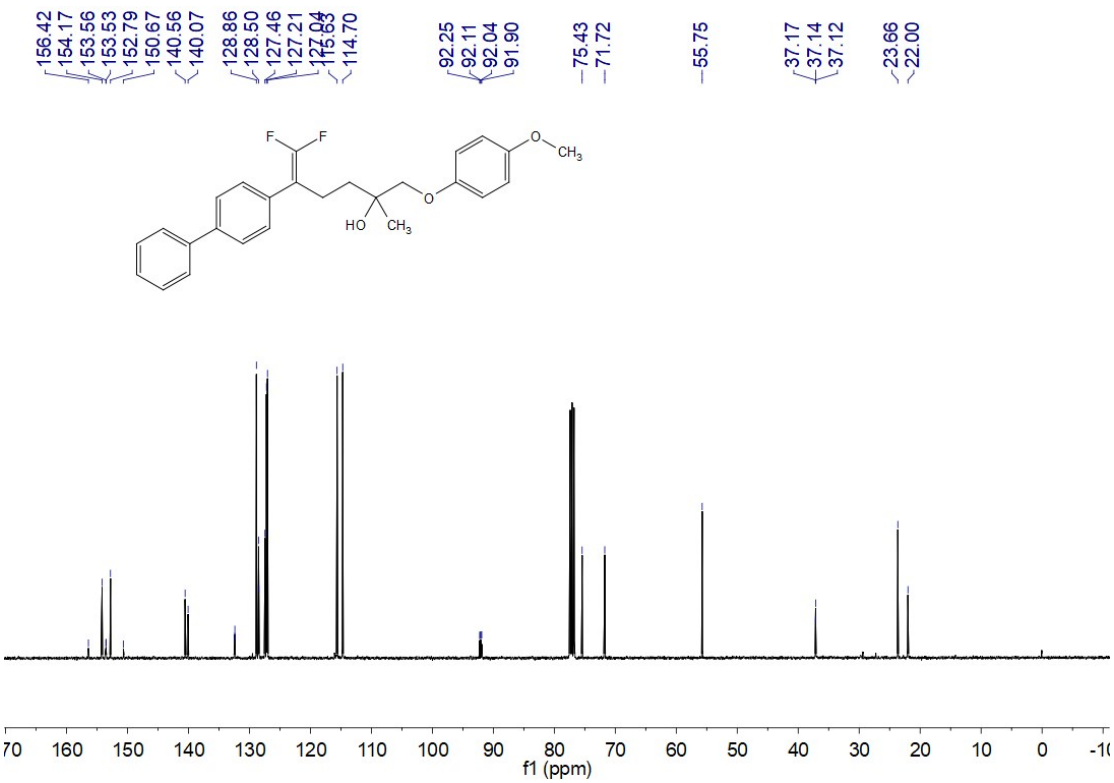
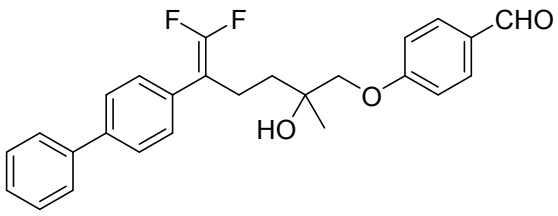
-86
-90
-94
-98
-102
-106
f1 (ppm)

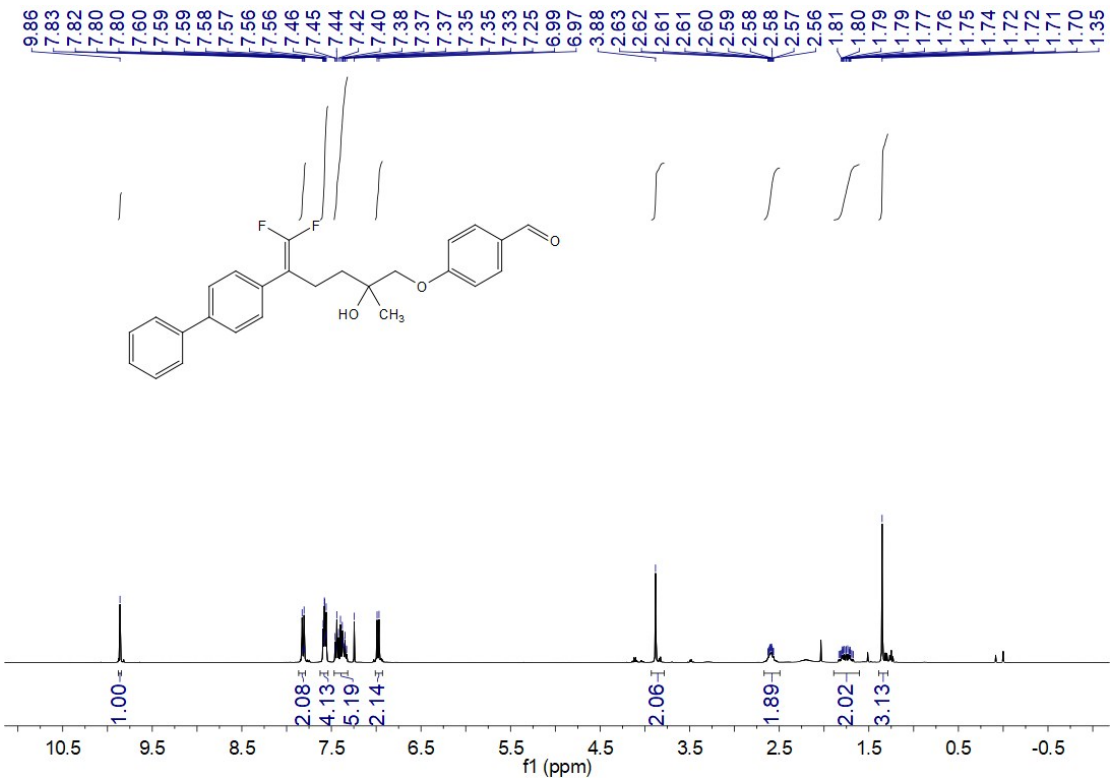

156.42
154.17
153.56
153.53
152.79
150.67
140.56
140.07
128.86
128.50
127.46
127.21
115.83
114.70
92.25
92.11
92.04
91.90
75.43
71.72
55.75
37.17
37.14
37.12
23.66
22.00
F
F
O
CH3
HO
CH3
O
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

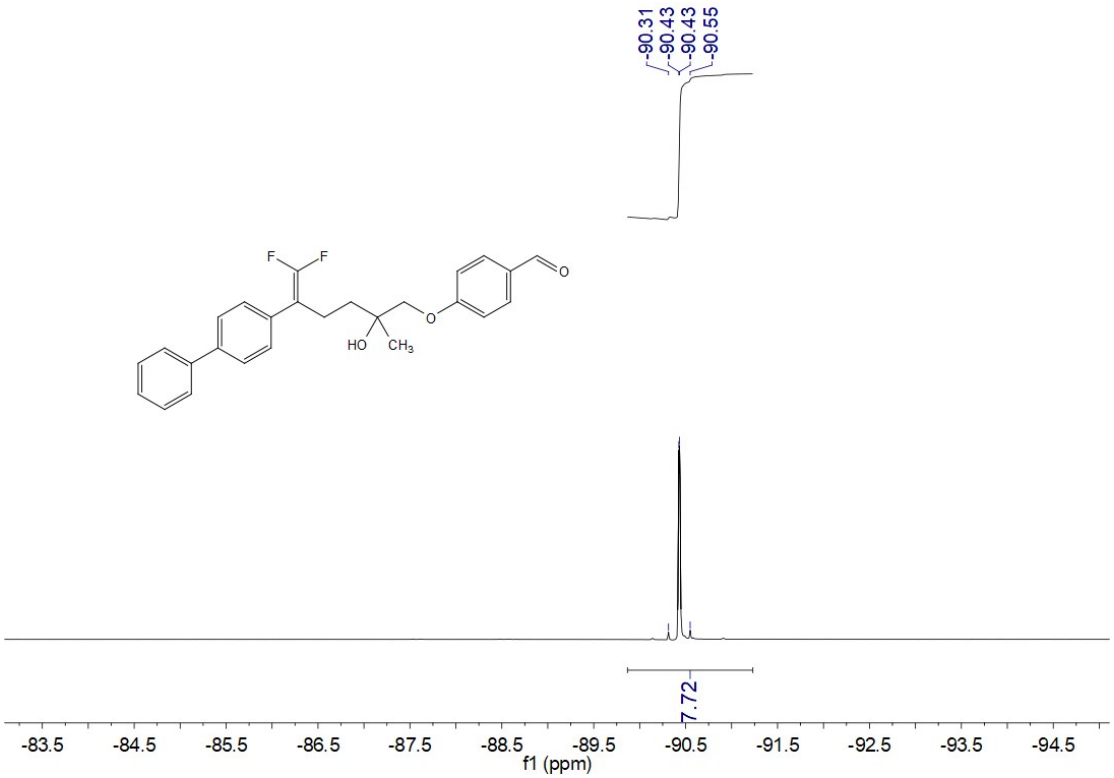

F
F
CHO
O
HO

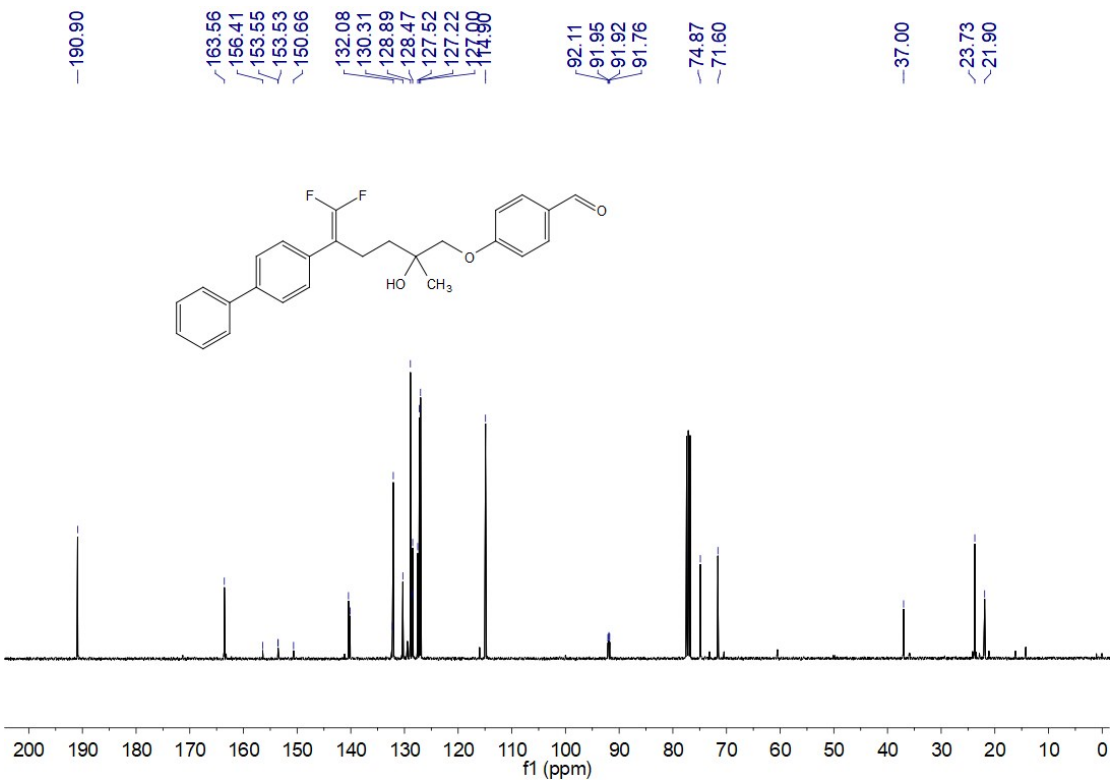
4-((5-([1,1'-biphenyl]-4-yl)-6,6-difluoro-2-hydroxy-2-methylhex-5-en-1-yl)oxy)benzaldehyde (4c)

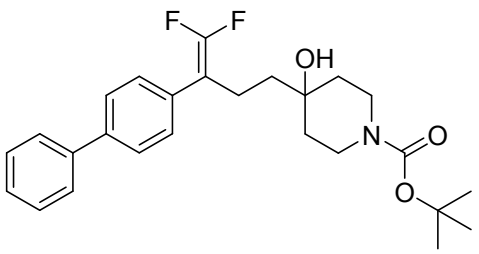
<u>Selectivity</u> (desired C-F cleavage product: addition by-product, determined by ^{1}H NMR and ^{19}F NMR) > 30:1.

Prepared according to the general procedure, as a sticky liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.86 (s, 1H), 7.81 (dd, *J* = 8.1, 3.2 Hz, 2H), 7.63 – 7.53 (m, 4H), 7.49 – 7.33 (m, 5H), 6.98 (d, *J* = 8.7 Hz, 2H), 3.88 (s, 2H), 2.65 – 2.50 (m, 2H), 1.87 – 1.65 (m, 2H), 1.35 (s, 3H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -90.37 (d, *J* = 42.3 Hz), -90.49 (d, *J* = 43.6 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 190.90, 163.56, 153.54 (dd, *J* = 290.3, 288.4 Hz), 140.43, 140.14, 132.24, 132.08, 130.31, 128.89, 128.47 (t, *J* = 3.5 Hz), 127.52, 127.22, 127.00, 114.90, 91.93 (dd, *J* = 19.2, 15.3 Hz), 74.87, 71.60, 37.00, 23.73, 21.90. **HRMS** (APCI) calcd for $C_{26}H_{24}F_2NaO_3$ ($M+Na^+$): 445.1586; found: 445.1592. **IR** (KBr/cm^{-1}) 3418, 2986, 1614, 1487, 1461, 1441, 1395, 1354, 1173, 1002, 786, 695, 618.




-90.31
-90.43
-90.43
-90.55
F
F
O
O
HO
CH3
7.72
-83.5
-84.5
-85.5
-86.5
-87.5
-88.5
-89.5
-90.5
-91.5
-92.5
-93.5
-94.5
f1 (ppm)

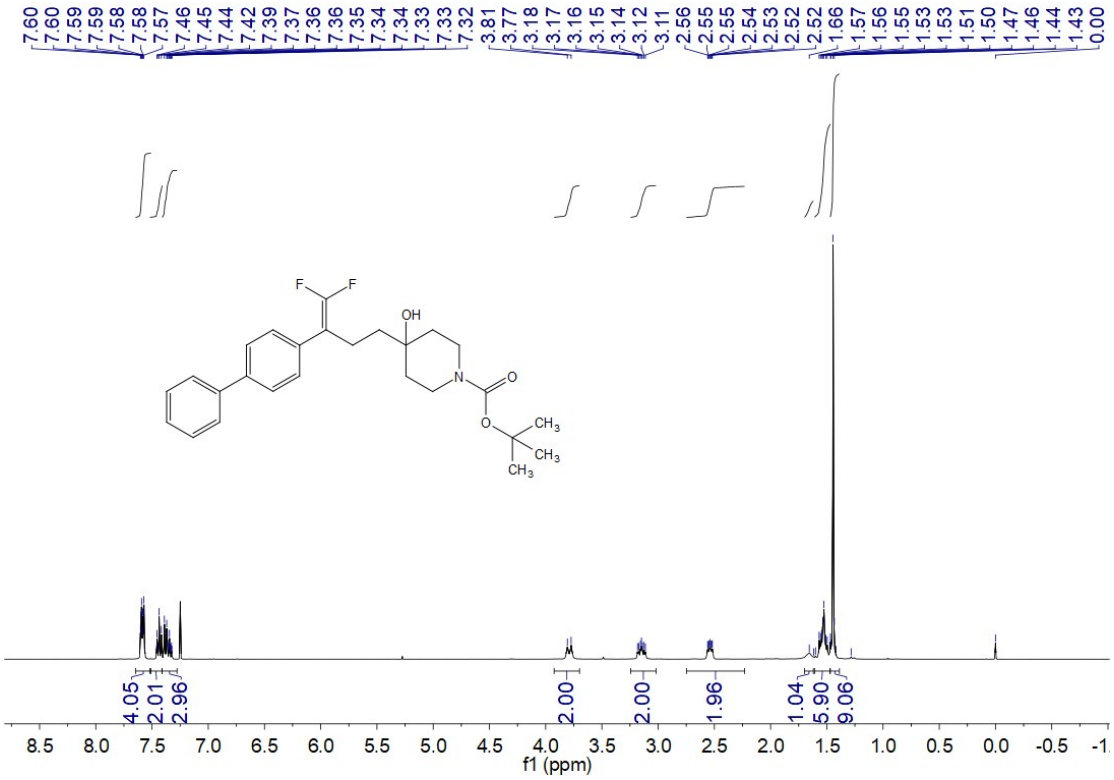

190.90
163.56
156.41
153.55
153.53
150.66
132.08
130.31
128.89
128.47
127.52
127.22
92.11
91.95
91.92
91.76
74.87
71.60
37.00
23.73
21.90
F
F
O
O
HO
CH3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

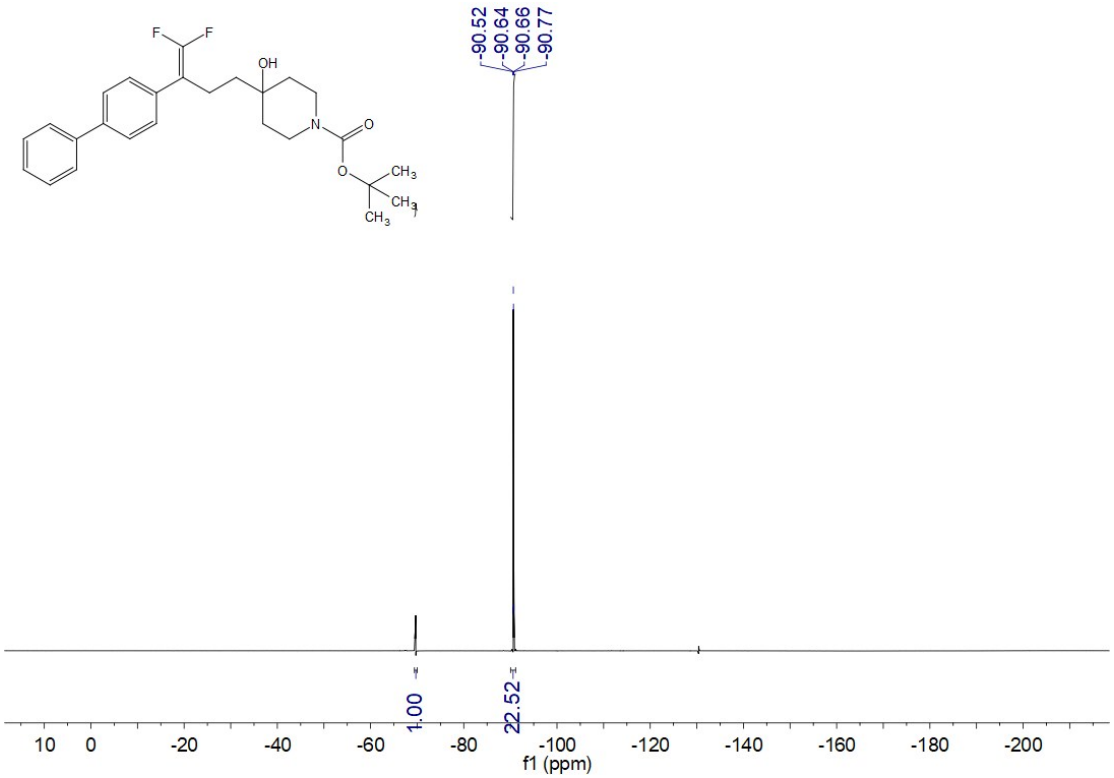

F
F
OH
N
O
O

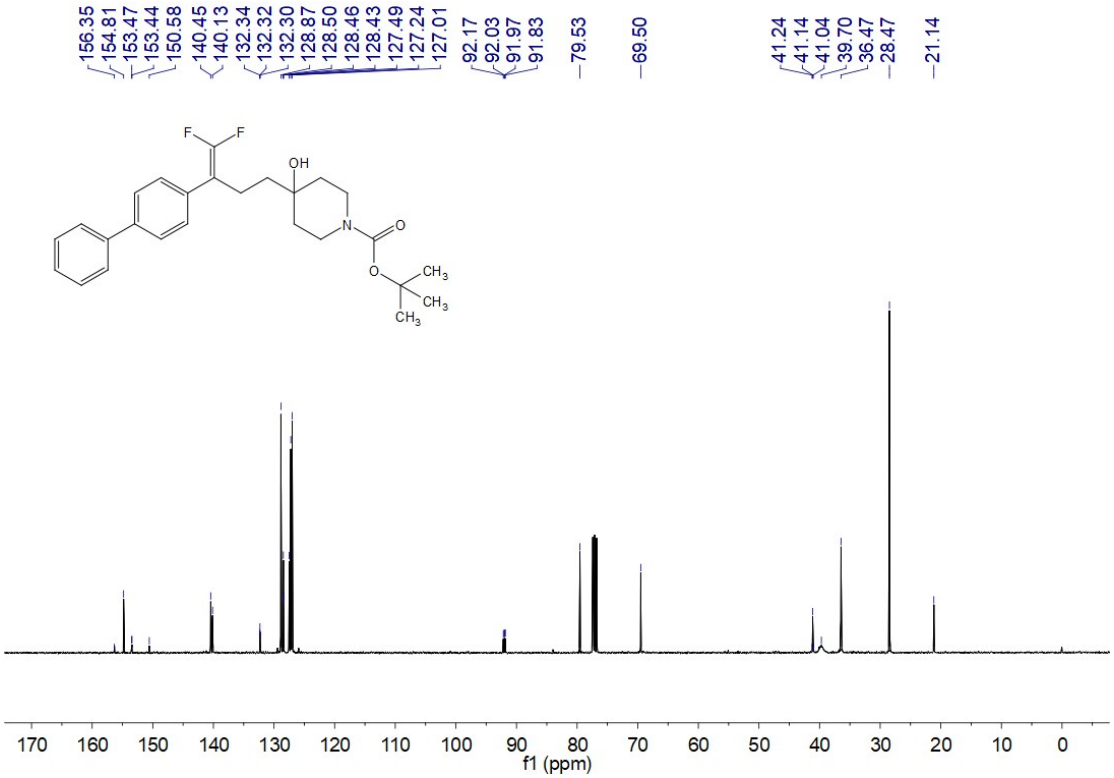
tert-butyl-4-(3-([1,1'-biphenyl]-4-yl)-4,4-difluorobut-3-en-1-yl)-4-hydroxypiperidine-1-carboxylate (4h)

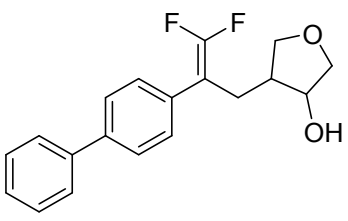
<u>Selectivity</u> (desired C-F cleavage product: addition by-product, determined by ^{1}H NMR and ^{19}F NMR) > 35:1.

Prepared according to the general procedure, as a sticky liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.55 (m, 4H), 7.48 – 7.40 (m, 2H), 7.41 – 7.31 (m, 3H), 3.79 (d, *J* = 13.4 Hz, 2H), 3.25 – 2.98 (m, 2H), 2.64 – 2.32 (m, 2H), 1.66 (br s, 1H), 1.58 – 1.49 (m, 6H), 1.44 (s, 9H) . **^{19}F NMR** (376 MHz, $CDCl_3$) δ -90.58 (d, *J* = 42.5 Hz), -90.72 (d, *J* = 42.5 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.81, 153.45 (dd, *J* = 290.6, 287.8 Hz), 140.45, 140.13, 132.32 (t, *J* = 2.4 Hz), 128.87, 128.46 (t, *J* = 3.4 Hz), 127.49, 127.24, 127.01, 92.00 (dd, *J* = 20.1, 14.4 Hz), 79.53, 69.50, 41.14 (t, *J* = 2.3 Hz), 39.70, 36.47, 28.47, 21.14. **HRMS** (APCI) calcd for $C_{26}H_{31}F_2NNaO_3$ ($M+Na^+$): 466.2164; found: 466.2167. **IR** (KBr/cm^{-1}) 3418, 2989, 2351, 1636, 1615, 1557, 1511, 1487, 1462, 1396, 1356, 1268, 1241, 1173, 1110, 1002, 786, 735, 607.




-90.52
-90.64
-90.66
-90.77
1.00
22.52
f1 (ppm)

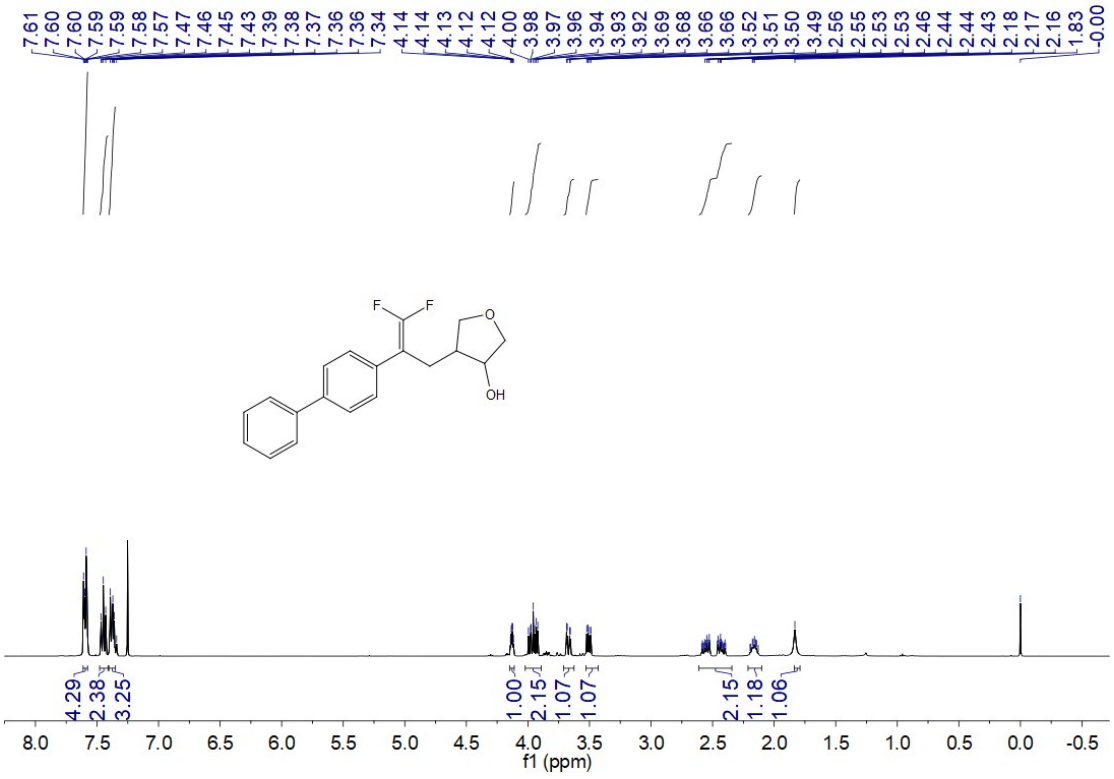

156.35
154.81
153.47
153.44
150.58
140.45
140.13
132.34
132.32
132.30
128.87
128.50
128.46
128.43
127.49
127.24
127.01
92.17
92.03
91.97
91.83
79.53
69.50
41.24
41.14
41.04
39.70
36.47
28.47
21.14
f1 (ppm)

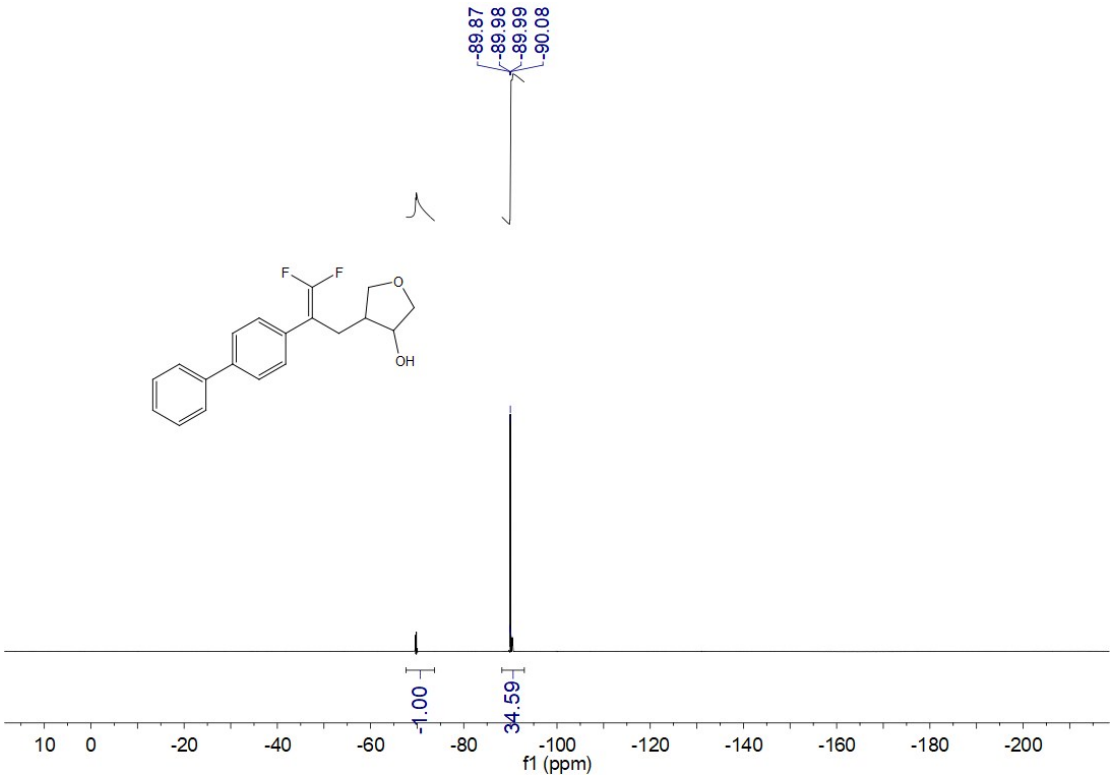


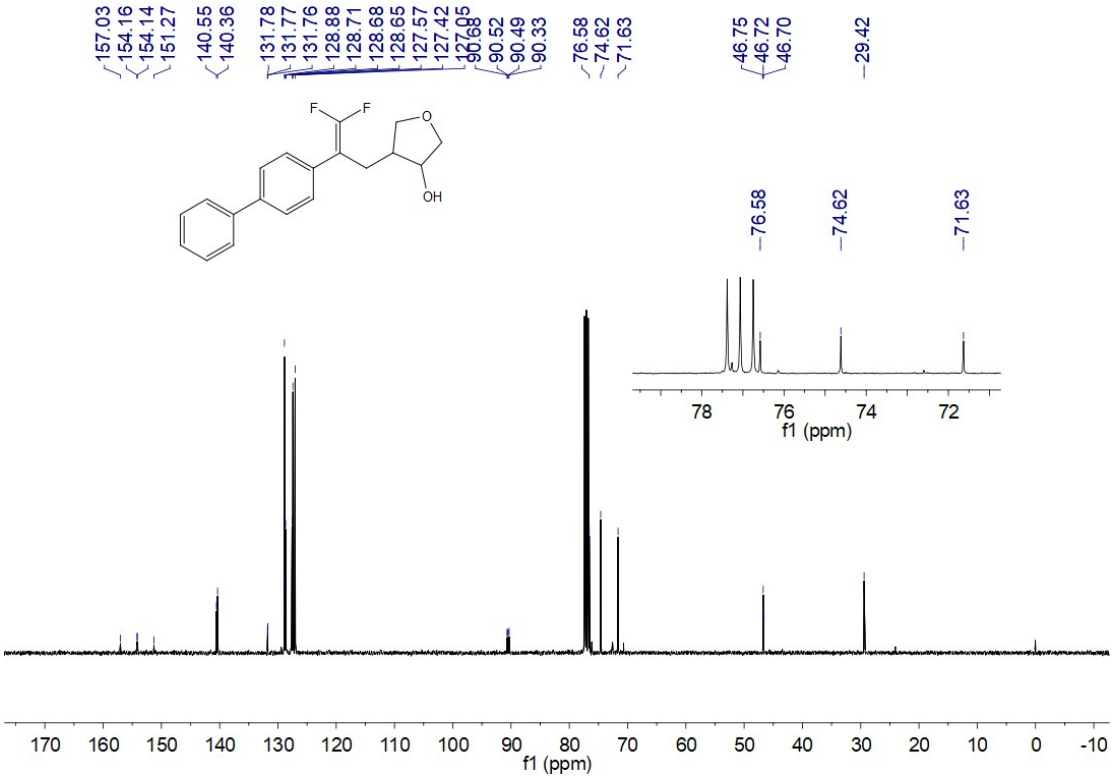
4-(2-([1,1'-biphenyl]-4-yl)-3,3-difluoroallyl)tetrahydrofuran-3-ol (4k)

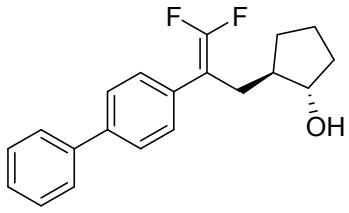
Selectivity (desired C-F cleavage product: addition by-product, determined by ^{1}H NMR and ^{19}F NMR) > 35:1, d.r. = 9:1.

Prepared according to the general procedure, as a sticky liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 – 7.55 (m, 4H), 7.45 (dd, *J* = 10.3, 4.8 Hz, 2H), 7.41 – 7.32 (m, 3H), 4.13 (dt, *J* = 4.7, 2.4 Hz, 1H), 4.03 – 3.91 (m, 2H), 3.67 (dd, *J* = 9.9, 2.4 Hz, 1H), 3.51 (dd, *J* = 8.8, 4.5 Hz, 1H), 2.60 – 2.33 (m, 2H), 2.16 (qd, *J* = 7.9, 3.9 Hz, 1H), 1.83 (br s, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -89.92 (d, *J* = 41.1 Hz), -90.04 (d, *J* = 33.5 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.15 (dd, *J* = 290.4, 288.6 Hz), 140.55, 140.36, 131.76 (dd, *J* = 2.1, 0.9 Hz), 128.88, 128.68 (t, *J* = 3.1 Hz), 127.57, 127.42, 127.05, 90.51 (dd, *J* = 19.6, 16.1 Hz), 76.58, 74.62, 71.63, 46.72 (t, *J* = 2.3 Hz), 29.42. **HRMS** (APCI) calcd for $C_{19}H_{18}F_2NaO_2$ ($M+Na^+$): 339.1167; found: 339.1171. **IR** (KBr/cm^{-1}) 3417, 2988, 2069, 1726, 1637, 1616, 1487, 1456, 1396, 1353, 1238, 1184, 1107, 1002, 786, 763, 697, 620.




-89.87
-89.98
-89.99
-90.08
F
F
O
OH
-1.00
34.59
10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200
f1 (ppm)


157.03
154.16
154.14
151.27
140.55
140.36
131.78
131.77
131.76
128.88
128.71
128.68
128.65
127.57
127.42
127.05
90.52
90.49
90.33
76.58
74.62
71.63
46.75
46.72
46.70
29.42
F
F
O
OH
78 76 74 72
f1 (ppm)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

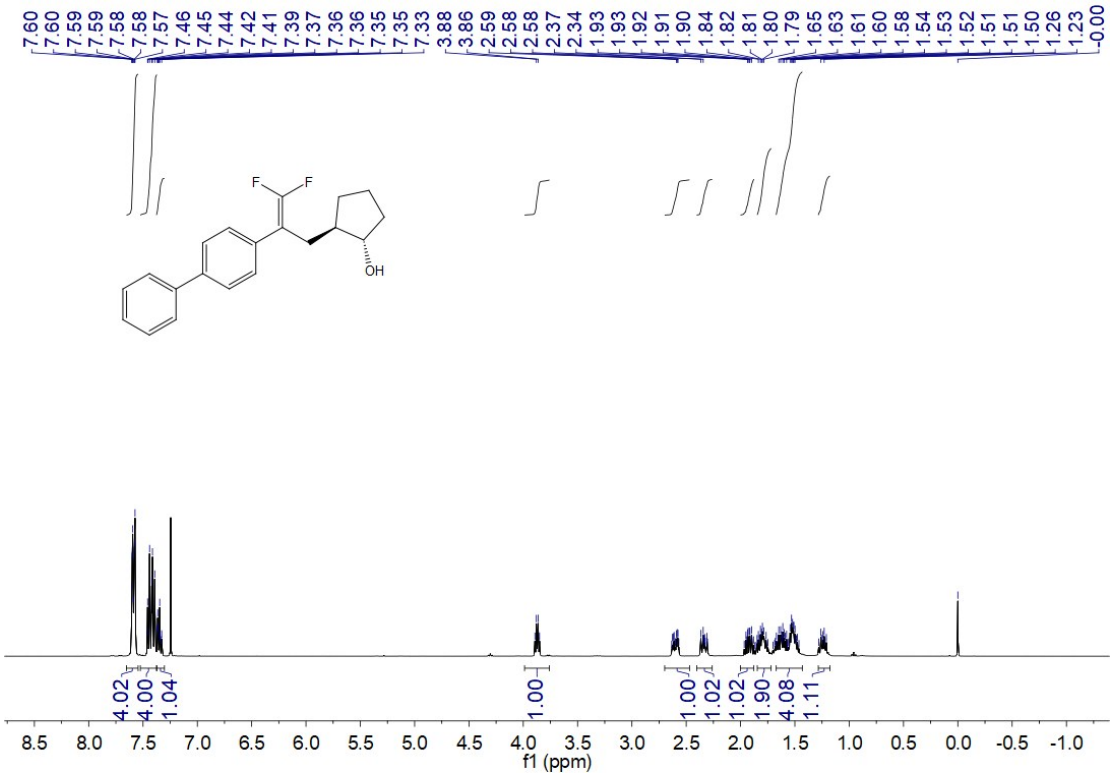

F
F
OH

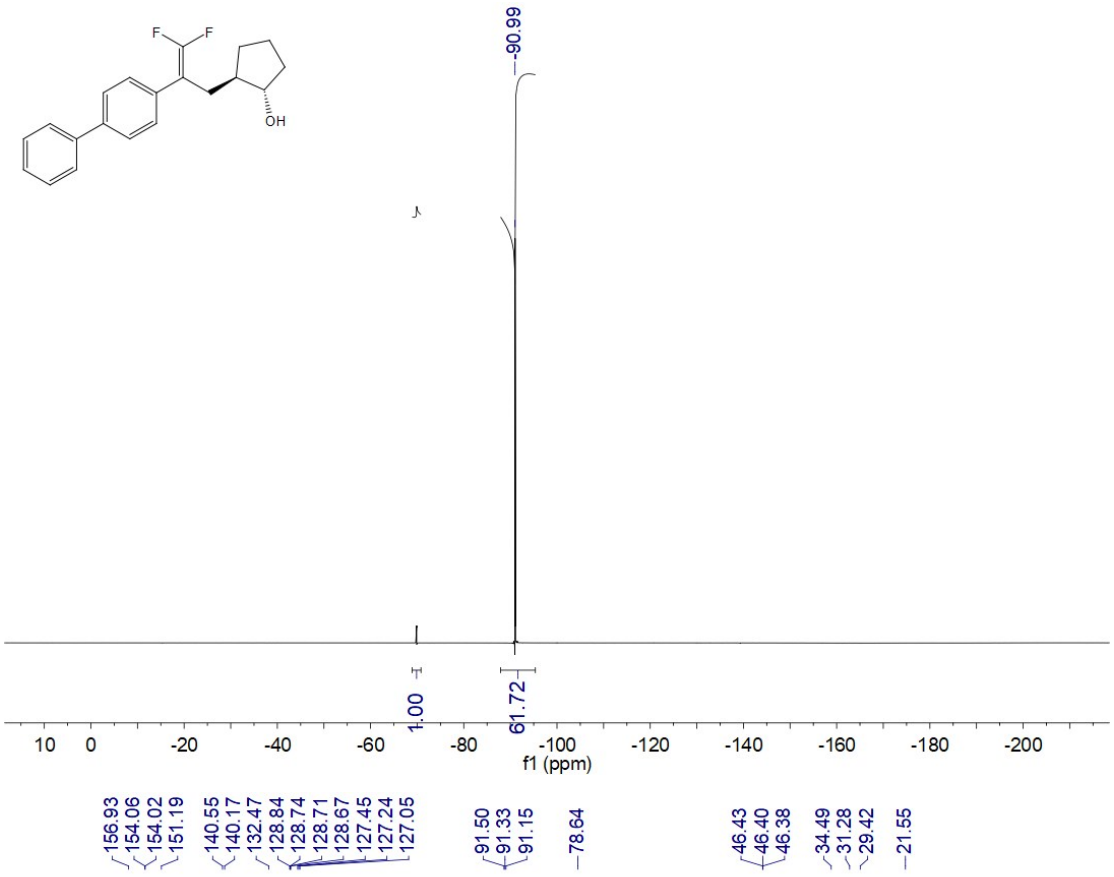
(Major)

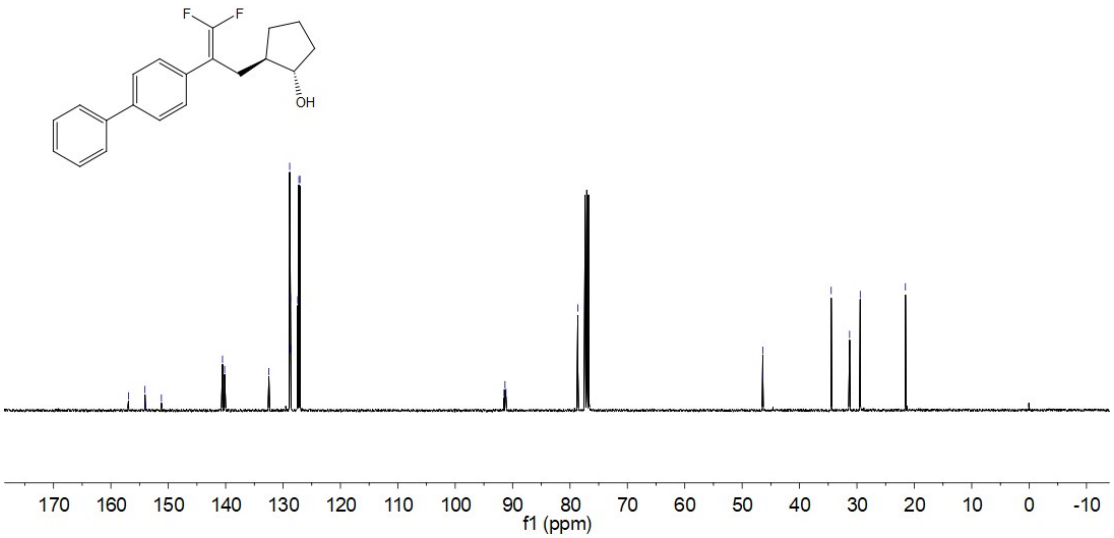
2-(2-([1,1'-biphenyl]-4-yl)-3,3-difluoroallyl)cyclopentan-1-ol (4i)

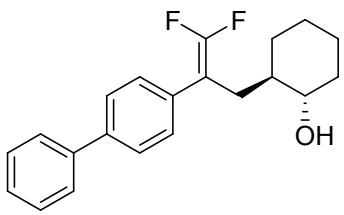
<u>Selectivity</u> (desired C-F cleavage product: addition by-product, determined by ^{1}H NMR and ^{19}F NMR) > 35:1, <u>d.r. > 10:1.</u>

Prepared according to the general procedure, as a sticky liquid. The assignment of the major *<u>trans</u>* configuration was based on the large coupling constant at 3.87 ppm. **^{31}H NMR** (400 MHz, $CDCl_3$) δ 7.62 – 7.52 (m, 4H), 7.49 – 7.38 (m, 4H), 7.35 (ddd, *J* = 7.4, 3.9, 1.2 Hz, 1H), 3.87 (dd, *J* = 11.7, 5.3 Hz, 1H), 2.60 (ddt, *J* = 14.2, 6.0, 2.9 Hz, 1H), 2.43 – 2.25 (m, 1H), 2.03 – 1.88 (m, 1H), 1.90 – 1.71 (m, 2H), 1.71 – 1.40 (m, 4H), 1.32 – 1.16 (m, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -90.99. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.06 (t, *J* = 288.5 Hz), 140.55, 140.17, 132.47, 128.84, 128.71 (t, *J* = 3.2 Hz), 127.45, 127.24, 127.05, 91.33 (t, *J* = 17.4 Hz), 78.64, 46.40 (t, *J* = 2.2 Hz), 34.49, 31.28, 29.42, 21.55. **HRMS** (APCI) calcd for $C_{20}H_{20}F_2NaO$ ($M+Na^+$): 337.1374; found: 337.1379. **IR** (KBr/cm^{-1}) 3416, 2988, 2829, 1617, 1489, 1396, 1357, 1173, 1003, 787, 610




F
F
OH
-90.99
1.00
61.72
10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200
f1 (ppm)
156.93
154.06
154.02
151.19
140.55
140.17
132.47
128.84
128.74
128.71
128.67
127.45
127.24
127.05
91.50
91.33
91.15
78.64
46.43
46.40
46.38
34.49
31.28
29.42
21.55


F
F
OH
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

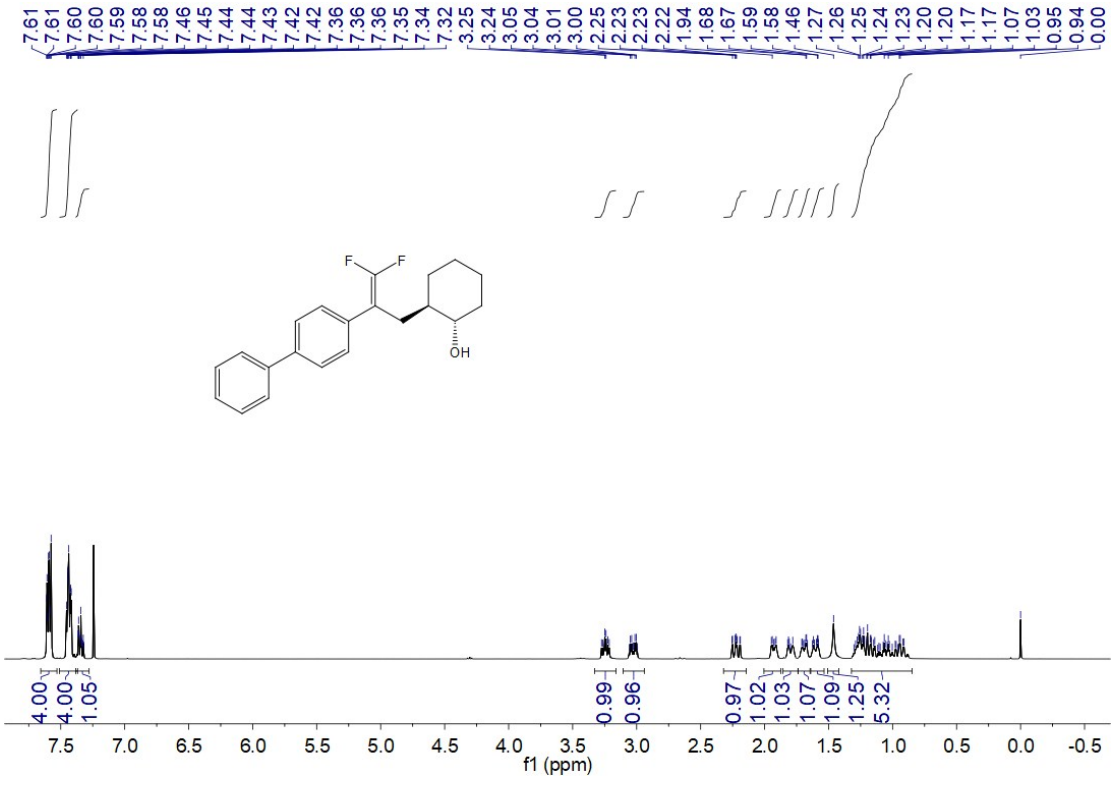

F
F
OH

(Trans, Major)

(trans)-2-(2-([1,1'-biphenyl]-4-yl)-3,3-difluoroallyl)cyclohexan-1-ol (4j, Trans)

<u>Selectivity</u> (desired C-F cleavage product: addition by-product, determined by ^{1}H NMR and ^{19}F NMR) > 50:1, <u>d.r. = 2.5:1.</u>

Prepared according to the general procedure, as a sticky liquid. The assignment of the major *<u>trans</u>* configuration was based on the large coupling constant at 3.24 and 3.03 ppm. **^{1}H NMR (**400 MHz, $CDCl_3$) δ 7.65 – 7.50 (m, 4H), 7.50 – 7.41 (m, 4H), 7.39 – 7.31 (m, 1H), 3.24 (td, *J* = 10.0, 4.3 Hz, 1H), 3.03 (ddd, *J* = 14.3, 8.0, 3.8 Hz, 1H), 2.22 (ddd, *J* = 14.3, 10.1, 2.0 Hz, 1H), 1.99 – 1.87 (m, 1H), 1.85 – 1.75 (m, 1H), 1.73 – 1.65 (m, 1H), 1.64 – 1.54 (m, 1H), 1.46 (br s, 1H), 1.31 – 0.86 (m, 5H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -90.32 (d, *J* = 42.9 Hz), -90.54 (d, *J* = 42.9 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.17 (dd, *J* = 290.6, 286.5 Hz), 140.51, 139.90, 132.65 (t, *J* = 3.1 Hz), 128.80, 128.60 (t, *J* = 3.4 Hz), 127.38, 127.13, 126.98, 90.56 (dd, *J* = 21.4, 13.2 Hz), 74.62, 43.37 (t, *J* = 2.0 Hz), 35.80, 30.30, 29.80, 25.22, 24.83. **HRMS** (APCI) calcd for $C_{21}H_{22}F_2NaO$ ($M+Na^+$): 351.1531; found: 351.1536. **IR** (KBr/cm^{-1}) 3418, 2988, 2931, 2856, 1715, 1616, 1488, 1448, 1368, 1356, 788, 751, 610.



157.04
154.19
154.15
151.30
140.51
139.90
132.70
132.66
132.63
128.80
128.63
128.60
128.56
127.38
127.13
126.98
90.73
90.60
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74.62
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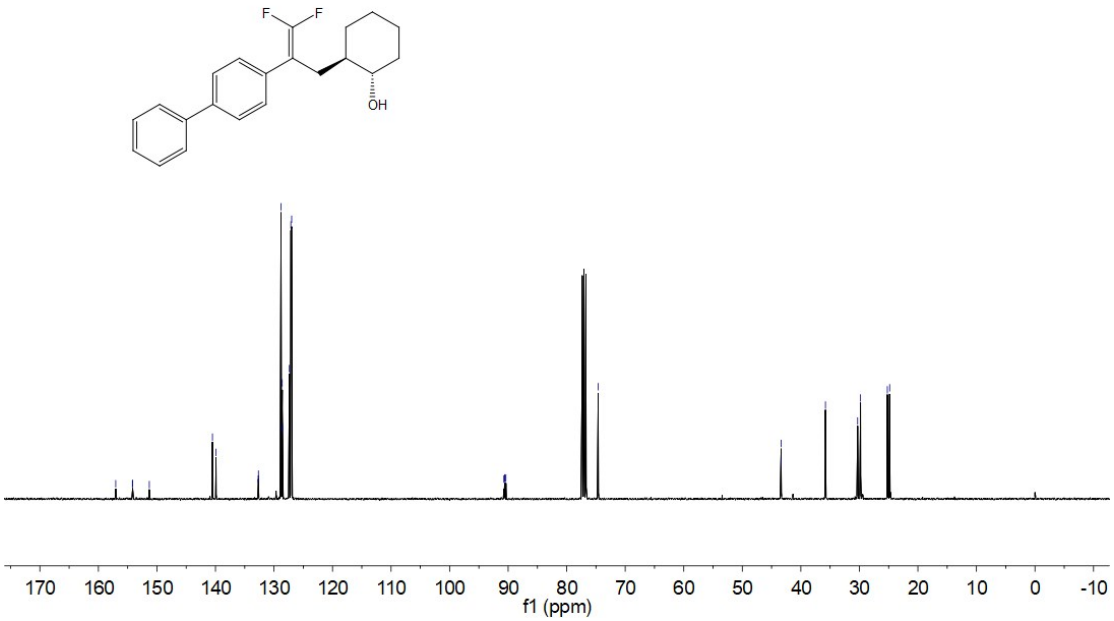
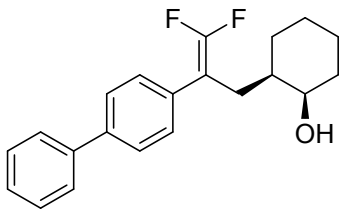
43.37
43.35
35.80
30.30
29.80
25.22
24.83

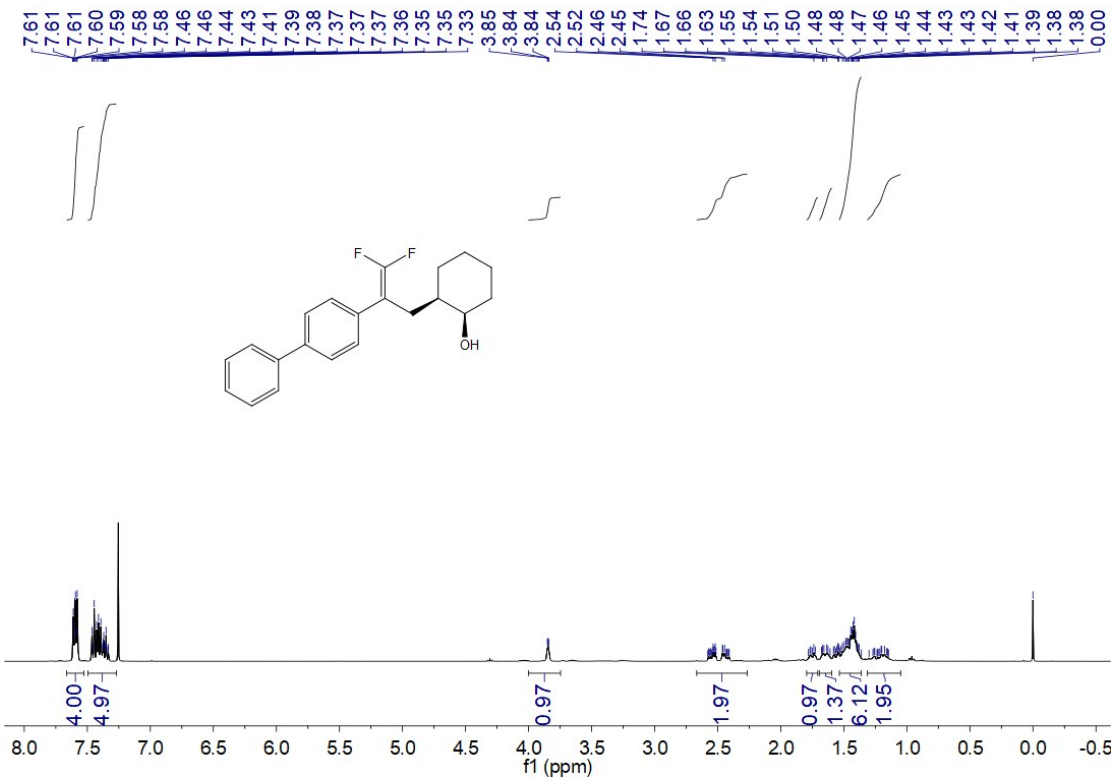


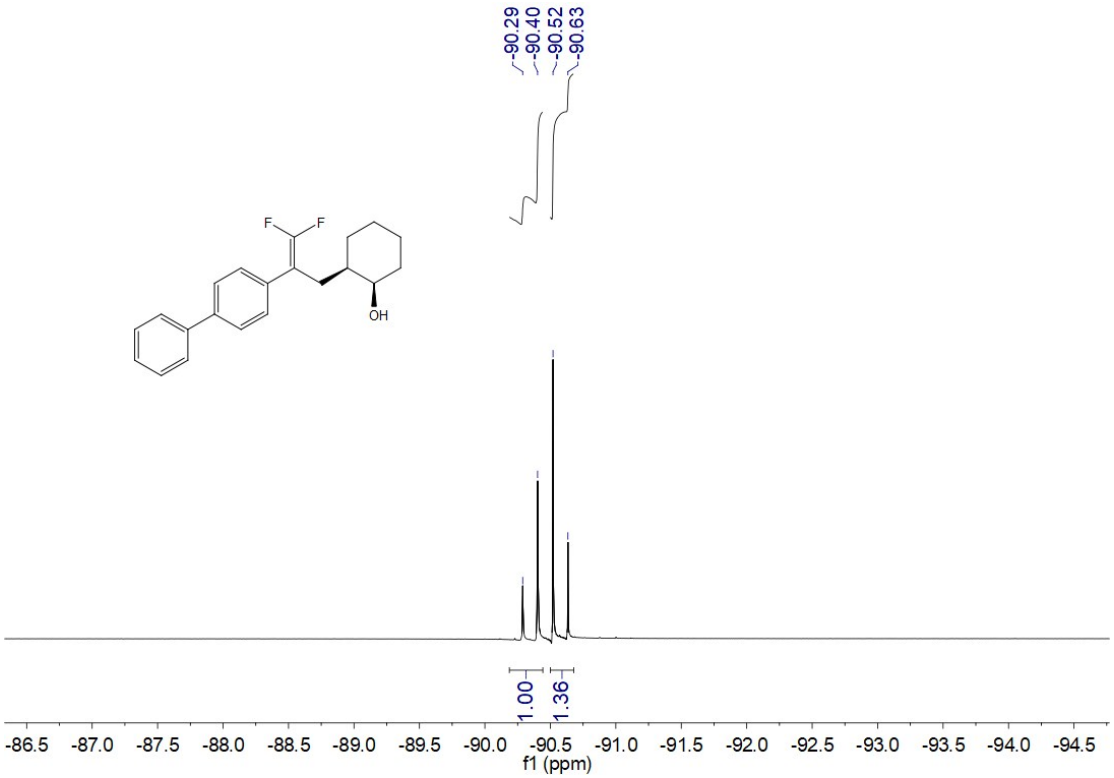


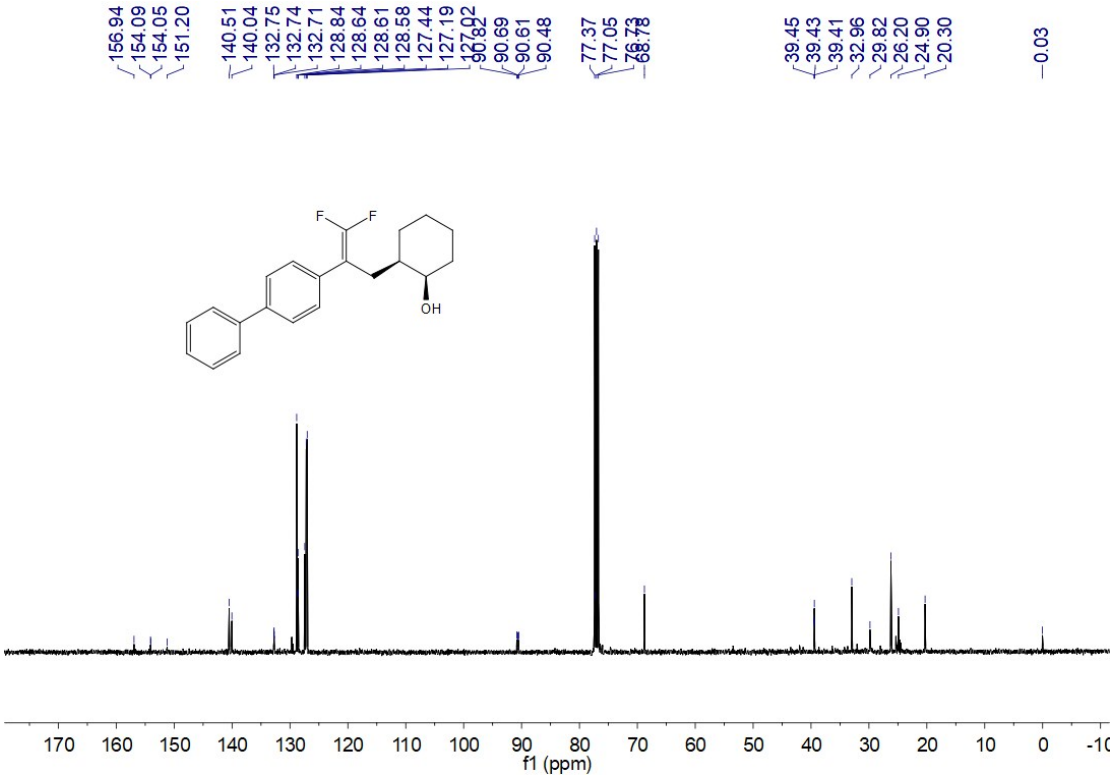
(cis)-2-(2-([1,1'-biphenyl]-4-yl)-3,3-difluoroallyl)cyclohexan-1-ol (4j, cis)

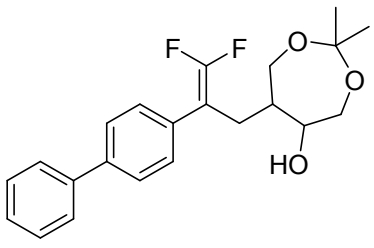
Selectivity (desired C-F cleavage product: addition by-product, determined by ^{1}H NMR and ^{19}F NMR) > 50:1

Prepared according to the general procedure, as a sticky liquid. The assignment of the major *cis* configuration was based on the large coupling constant at 3.85 ppm. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 – 7.53 (m, 4H), 7.52 – 7.34 (m, 5H), 3.85 (t, *J* = 2.3 Hz, 1H), 2.61 – 2.36 (m, 2H), 1.80 – 1.73 (m, 1H), 1.69 – 1.60 (m, 1H), 1.59 – 1.36 (m, 6H), 1.31 – 1.08 (m, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -90.35 (d, *J* = 42.9 Hz), -90.58 (d, *J* = 42.9 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.07 (dd, *J* = 290.9, 286.9 Hz), 140.51, 140.04, 132.75 (dd, *J* = 4.0, 2.8 Hz), 128.84, 128.61 (t, *J* = 3.3 Hz), 127.44, 127.19, 127.02, 90.65 (dd, *J* = 21.6, 13.2 Hz), 68.78, 39.43 (t, *J* = 2.2 Hz), 32.96, 29.82, 26.20, 24.90, 20.30. **HRMS** (APCI) calcd for $C_{21}H_{22}F_2NaO$ ($M+Na^+$): 351.1531; found: 351.1537. **IR** (KBr/cm^{-1}) 3419, 2987, 1616, 1483, 1368, 1353, 788, 750, 609.




-90.29
-90.40
-90.52
-90.63
F
F
OH
1.00
1.36
-86.5 -87.0 -87.5 -88.0 -88.5 -89.0 -89.5 -90.0 -90.5 -91.0 -91.5 -92.0 -92.5 -93.0 -93.5 -94.0 -94.5
f1 (ppm)

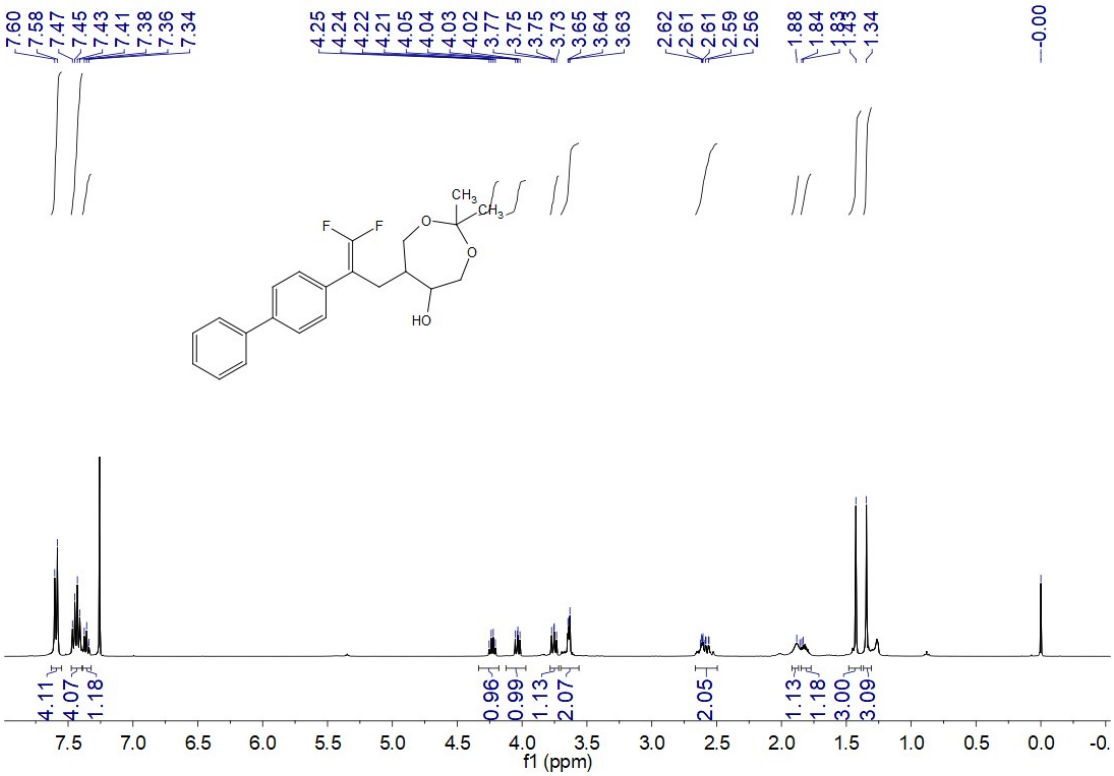

156.94
154.09
154.05
151.20
140.51
140.04
132.75
132.74
132.71
128.84
128.64
128.61
128.58
127.44
127.19
127.02
90.82
90.69
90.61
90.48
77.37
77.05
76.73
68.78
39.45
39.43
39.41
32.96
29.82
26.20
24.90
20.30
0.03
F
F
OH
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


F
F
O
O
HO

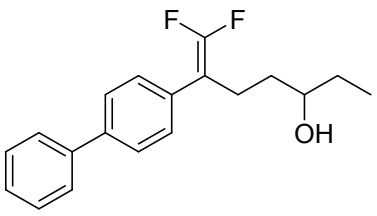
6-(2-([1,1'-biphenyl]-4-yl)-3,3-difluoroallyl)-2,2-dimethyl-1,3-dioxepan-5-ol (4l)

Selectivity (desired C-F cleavage product: addition by-product, determined by ^{1}H NMR and ^{19}F NMR) > 50:1, d. r. = 7:1

Prepared according to the general procedure, as a sticky liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.4 Hz, 4H), 7.44 (dd, *J* = 15.3, 7.5 Hz, 4H), 7.36 (t, *J* = 7.3 Hz, 1H), 4.23 (dd, *J* = 12.8, 6.5 Hz, 1H), 4.03 (dd, *J* = 8.4, 6.5 Hz, 1H), 3.75 (dd, *J* = 8.2, 7.2 Hz, 1H), 3.69 – 3.60 (m, 2H), 2.67 – 2.49 (m, 2H), 1.88 (br s, 1H), 1.85 – 1.78 (m, 1H), 1.43 (s, 3H), 1.34 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -89.66 (d, *J* = 41.3 Hz), -89.83 (d, *J* = 41.2 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.93 (dd, *J* = 291.4, 287.7 Hz), 140.42, 140.36, 131.90 (t, *J* = 2.9 Hz), 128.86, 128.58 (dd, *J* = 7.2, 3.9 Hz), 127.52, 127.36, 127.31, 127.03, 108.83, 90.29 (dd, *J* = 20.7, 14.4 Hz), 73.63, 66.95, 62.61, 41.19 (t, *J* = 2.0 Hz), 30.98, 26.46, 25.14. **HRMS** (APCI) calcd for $C_{22}H_{24}F_2NaO_3$ ($M+Na^+$): 397.1586; found: 397.1589. **IR** (KBr/cm^{-1}) 3417, 2989, 2829, 1617, 1498, 1441, 1396, 1369, 1356, 1245, 1032, 610.



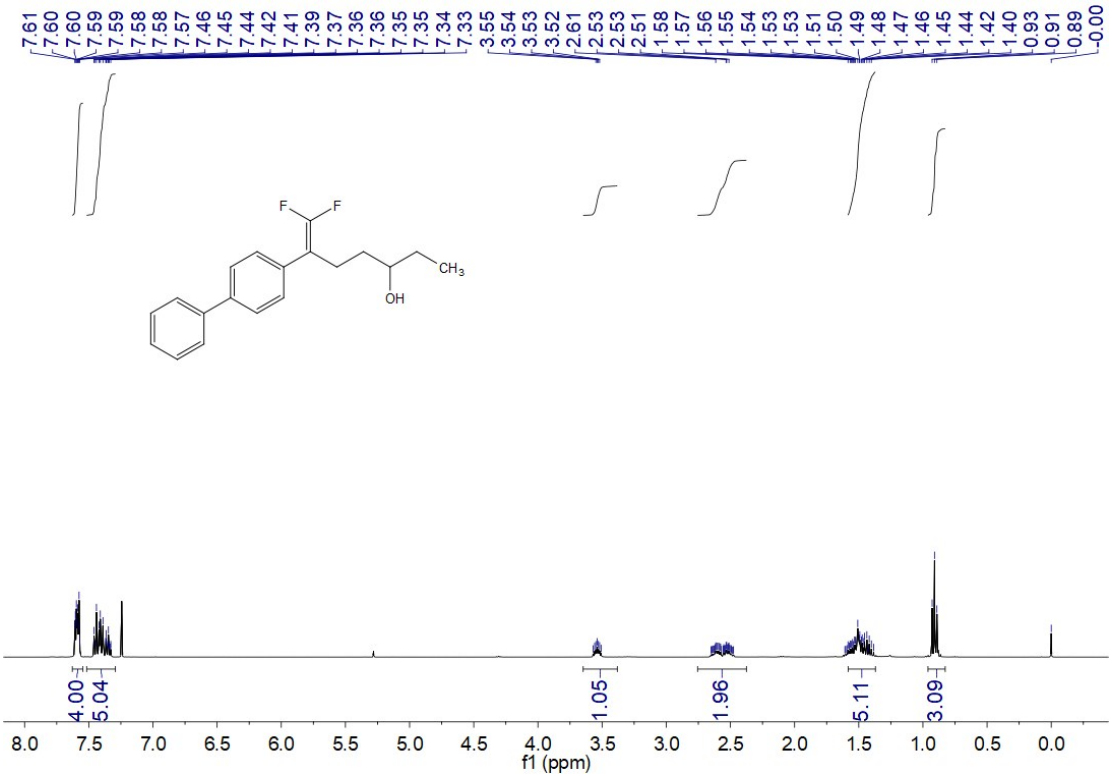

F
F
CH3
CH3
O
O
HO
-89.61
-89.72
-89.78
-89.89
1.00
97.60
f1 (ppm)
156.81
153.95
153.91
151.05
140.42
140.36
128.86
128.59
128.56
127.52
127.36
127.31
127.03
90.46
90.32
90.26
90.11
73.63
66.95
62.61
41.21
41.19
41.17
30.98
26.46
25.14
f1 (ppm)

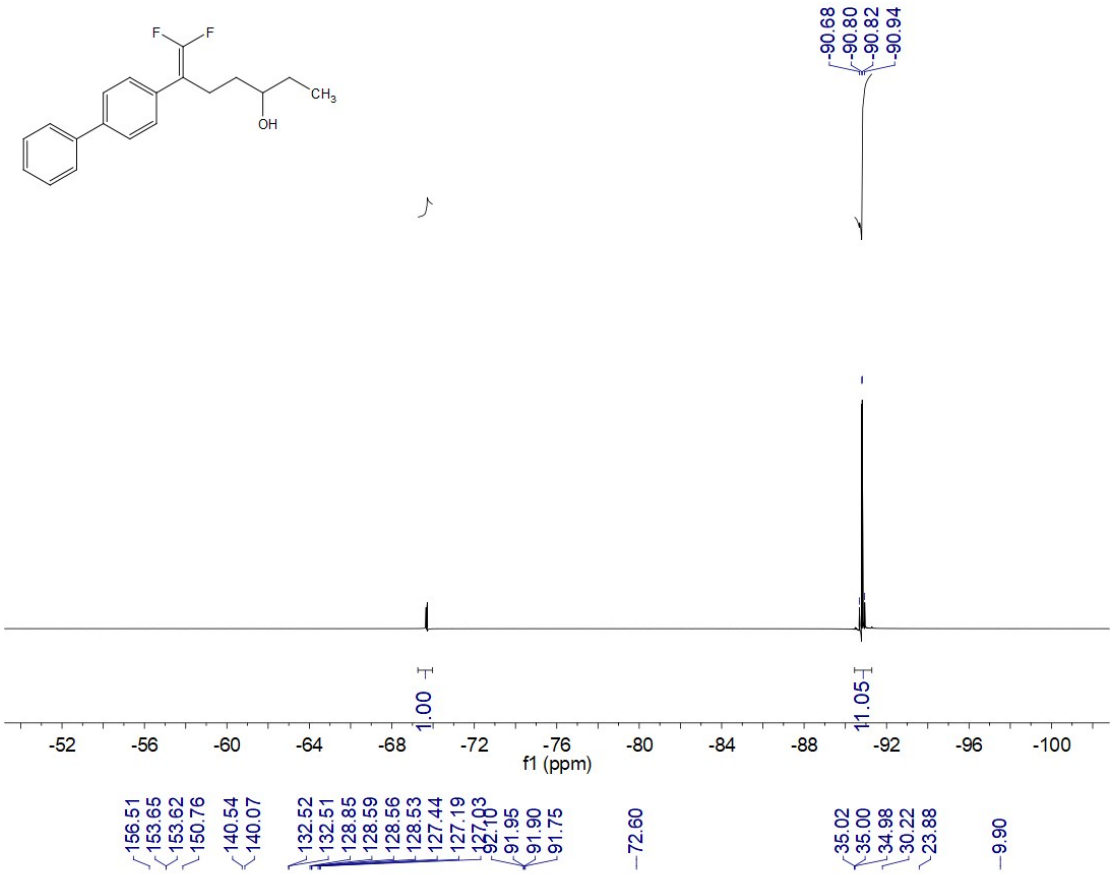

F
F
OH

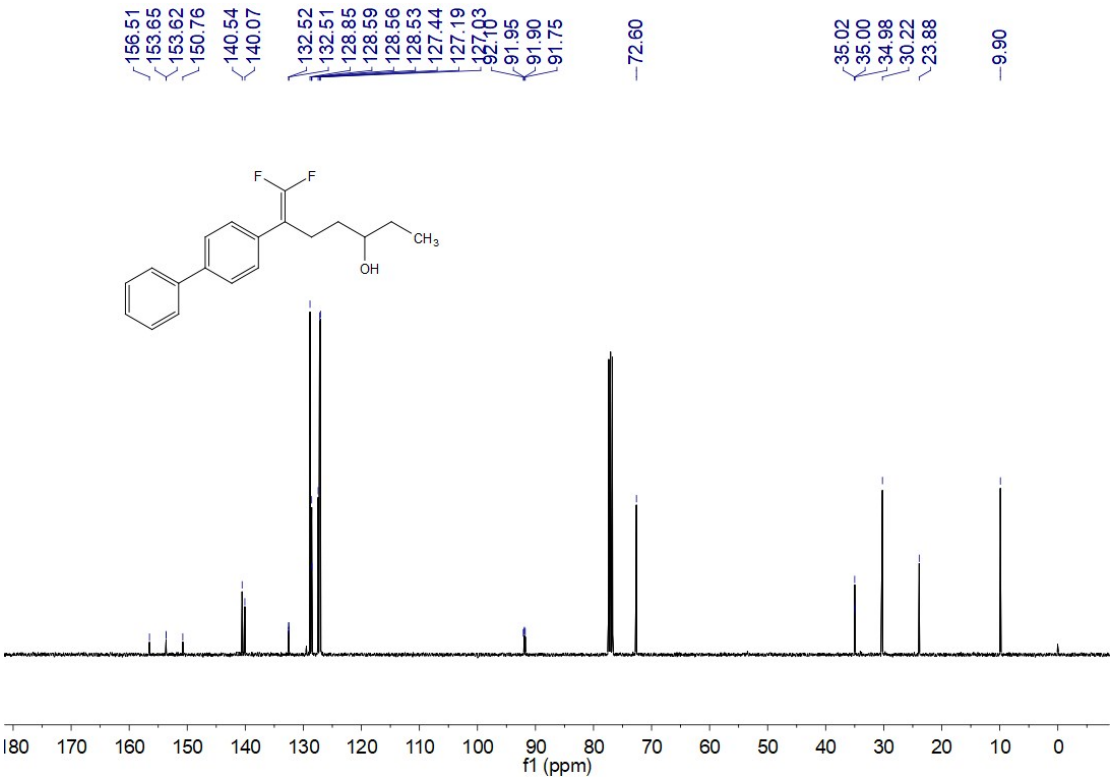
6-([1,1'-biphenyl]-4-yl)-7,7-difluorohept-6-en-3-ol (4m)

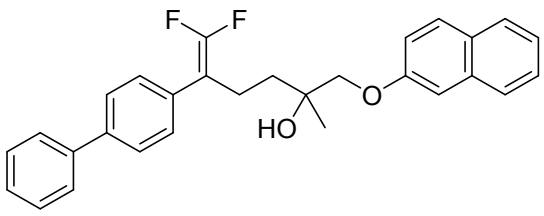
<u>Selectivity</u> (desired C-F cleavage product: addition by-product, Determined by ^{1}H NMR and ^{19}F NMR) > 35:1, L: B = 14:1.

Prepared according to the general procedure, as a sticky liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 – 7.54 (m, 4H), 7.50 – 7.30 (m, 5H), 3.59 – 3.42 (m, 1H), 2.72 – 2.32 (m, 2H), 1.68 – 1.33 (m, 5H), 0.91 (t, *J* = 7.4 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -90.74 (d, *J* = 42.9 Hz), -90.88 (d, *J* = 42.9 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.64 (dd, *J* = 290.1, 287.8 Hz), 140.54, 140.07, 132.52 (dd, *J* = 2.6, 1.7 Hz), 128.85, 128.56 (t, *J* = 3.4 Hz), 127.44, 127.19, 127.03, 91.93 (dd, *J* = 19.9, 14.7 Hz), 72.60, 35.00 (t, *J* = 2.3 Hz), 30.22, 23.88, 9.90. **HRMS** (APCI) calcd for $C_{19}H_{20}F_2NaO$ ($M+Na^+$): 325.1374; found: 325.1378. **IR** (KBr/cm^{-1}) 3417, 2988, 2829, 1615, 1487, 1460, 1396, 1355, 1186, 1173, 1001, 787, 773, 613.




F
F
CH3
OH
-90.68
-90.80
-90.82
-90.94
1.00
11.05
-52
-56
-60
-64
-68
-72
-76
-80
-84
-88
-92
-96
-100
f1 (ppm)

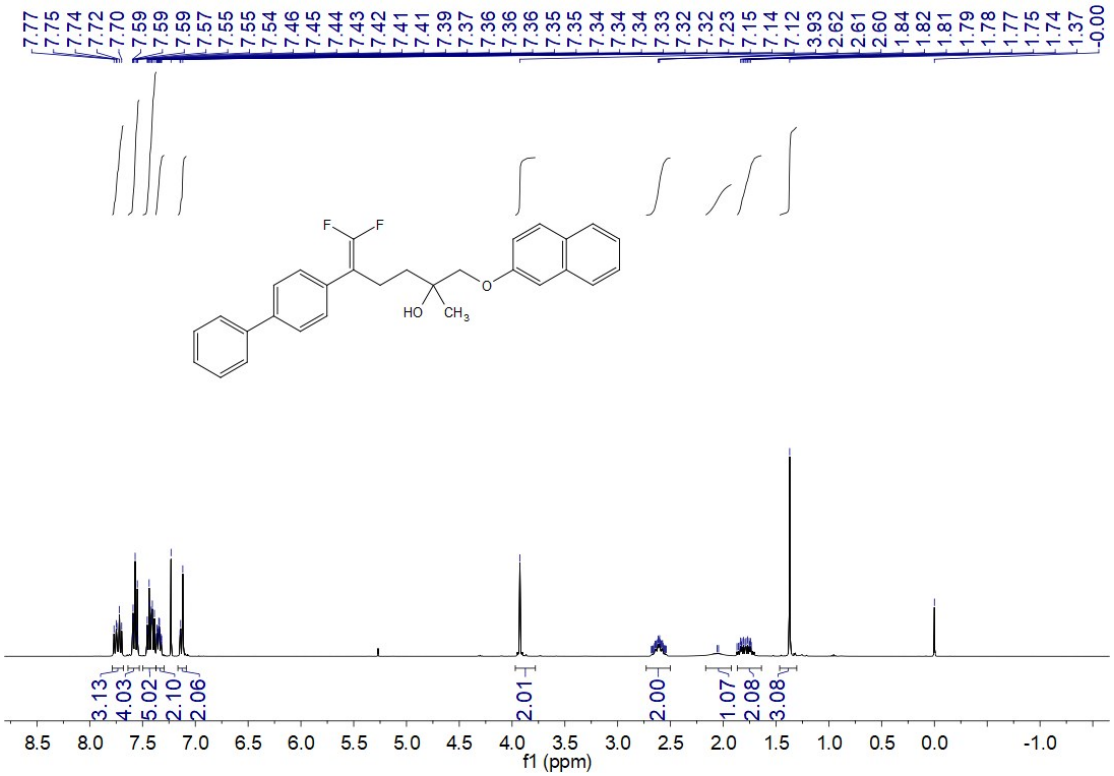

156.51
153.65
153.62
150.76
140.54
140.07
132.52
132.51
128.85
128.59
128.56
128.53
127.44
127.19
127.03
127.00
92.10
91.95
91.90
91.75
72.60
35.02
35.00
34.98
30.22
23.88
9.90
F
F
CH3
OH
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

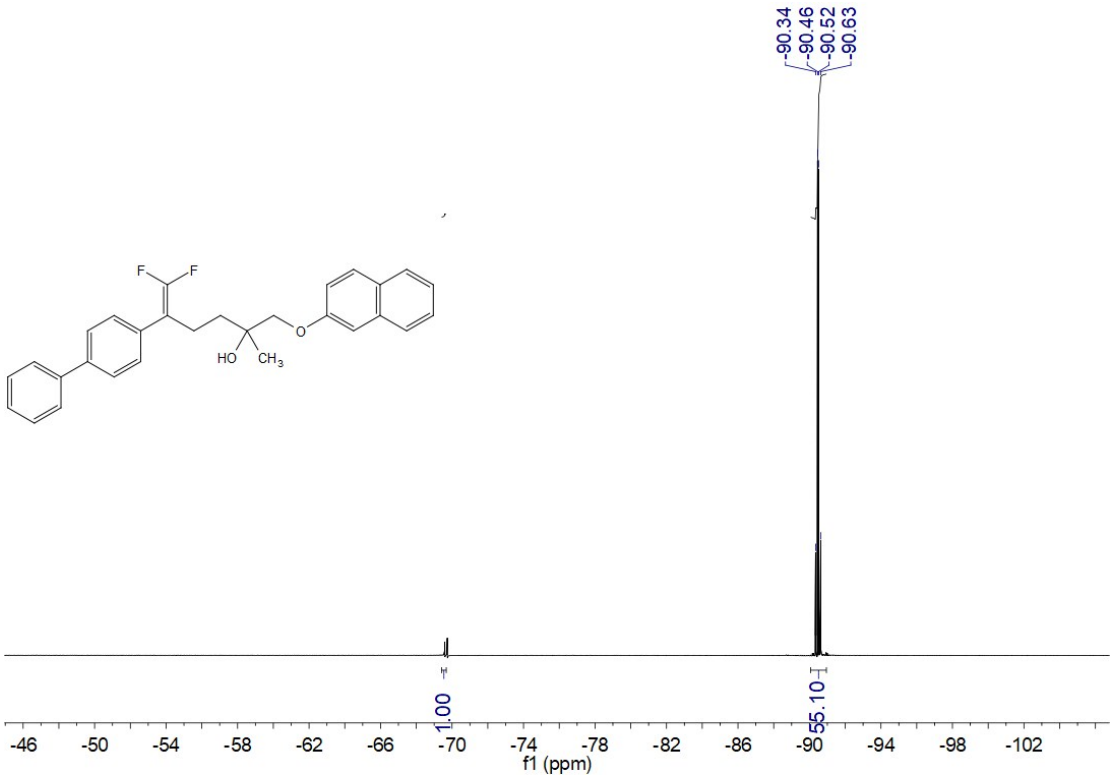

F
F
O
HO

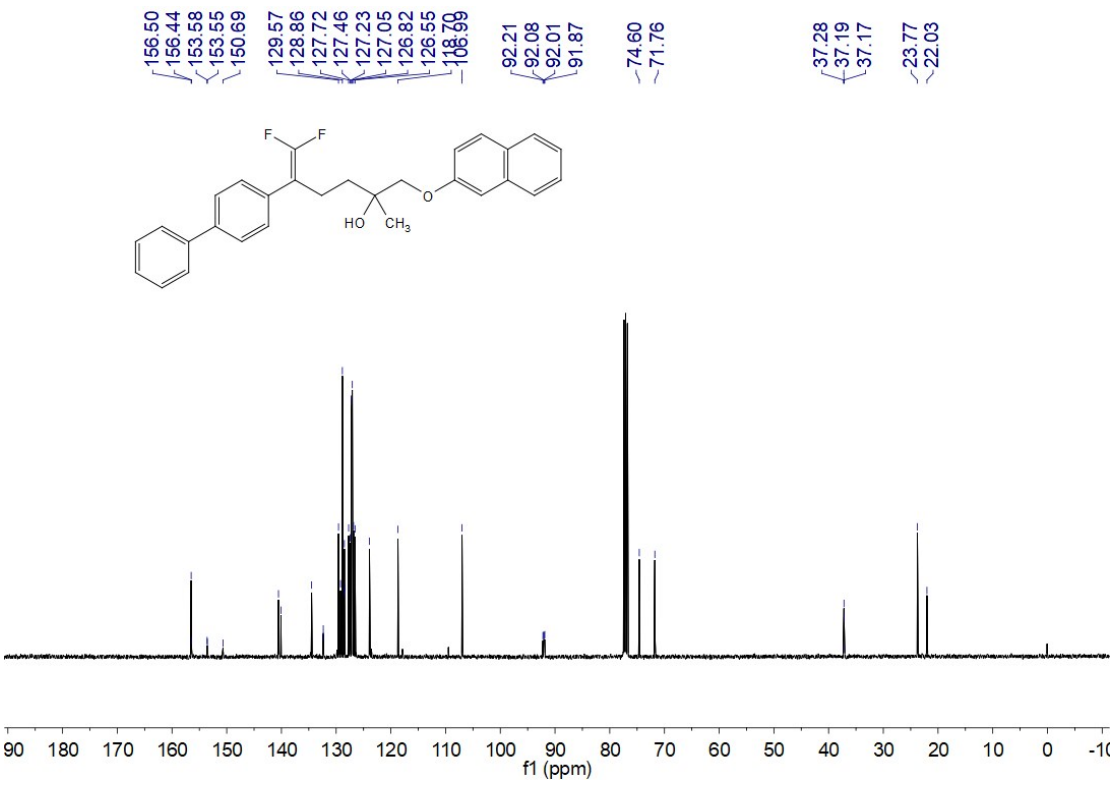
5-([1,1'-biphenyl]-4-yl)-6,6-difluoro-2-methyl-1-(naphthalen-2-yloxy)hex-5-en-2-ol (4a)

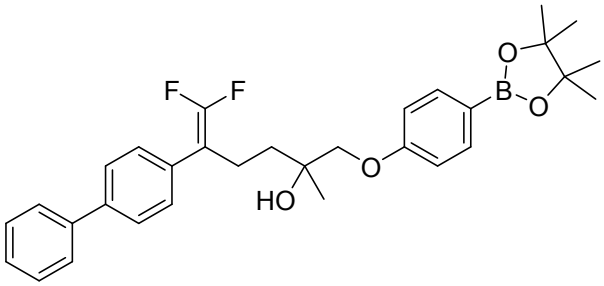
Selectivity (desired C-F cleavage product: addition by-product, Determined by ^{1}H NMR and ^{19}F NMR) > 50:1

Prepared according to the general procedure, as a sticky liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 – 7.65 (m, 3H), 7.63 – 7.55 (m, 4H), 7.52 – 7.39 (m, 5H), 7.37 – 7.28 (m, 2H), 7.17 – 7.06 (m, 2H), 3.93 (s, 2H), 2.80 – 2.51 (m, 2H), 2.06 (br s, 1H), 1.93 – 1.73 (m, 2H), 1.37 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -90.40 (d, *J* = 42.3 Hz), -90.57 (d, *J* = 42.3 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.50, 153.56 (dd, *J* = 291.0, 287.6 Hz), 140.54, 140.09, 134.49, 132.36 (t, *J* = 2.9 Hz), 129.57, 129.20, 128.86, 128.50 (t, *J* = 3.5 Hz), 127.72, 127.46, 127.23, 127.05, 126.82, 126.55, 123.91, 118.70, 106.99, 92.04 (dd, *J* = 20.5, 13.9 Hz), 74.60, 71.76, 37.18 (d, *J* = 2.3 Hz), 23.77, 22.03. **HRMS** (APCI) calcd for $C_{29}H_{26}F_2NaO_2$ ($M+Na^+$): 467.1793; found: 467.1796. **IR** (KBr/cm^{-1}) 3418, 2985, 1617, 1488, 1457, 1370, 1355, 1172, 1101, 1001, 788, 615.




-90.34
-90.46
-90.52
-90.63
F
F
HO
CH3
O
1.00
55.10
-46 -50 -54 -58 -62 -66 -70 -74 -78 -82 -86 -90 -94 -98 -102
f1 (ppm)

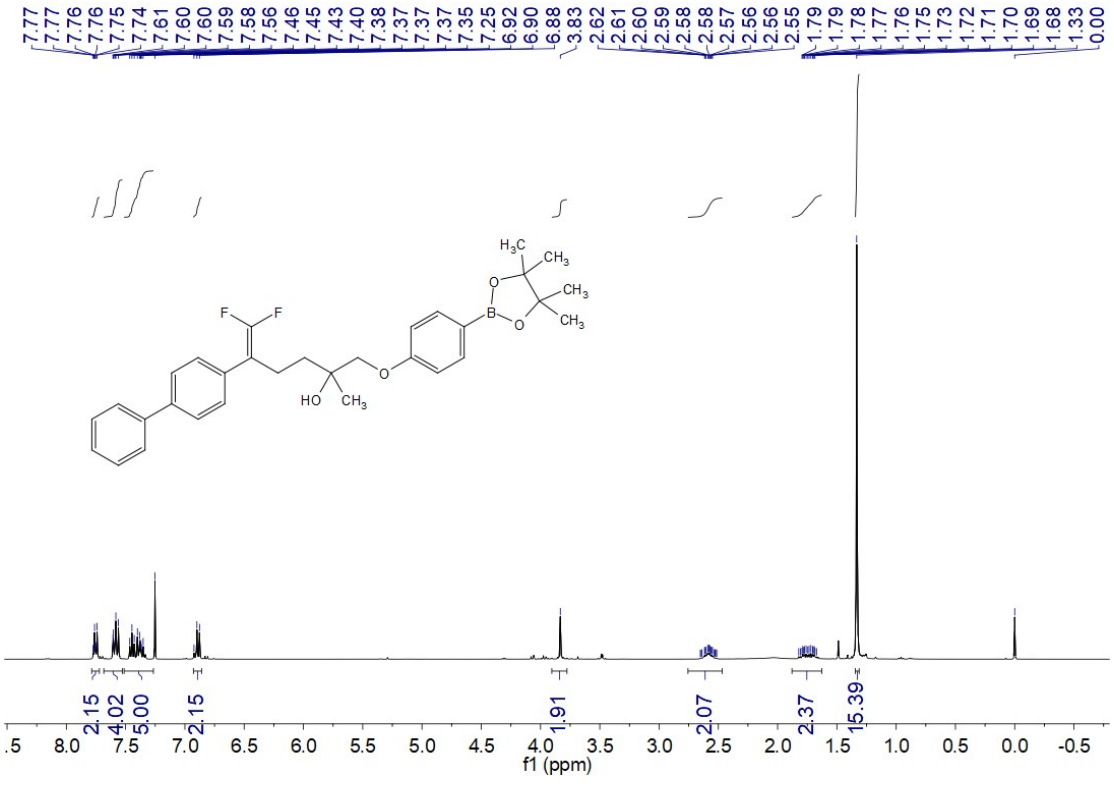

156.50
156.44
153.58
153.55
150.69
129.57
128.86
127.72
127.46
127.23
127.05
126.82
126.55
92.21
92.08
92.01
91.87
74.60
71.76
37.28
37.19
37.17
23.77
22.03
F
F
HO
CH3
O
90 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

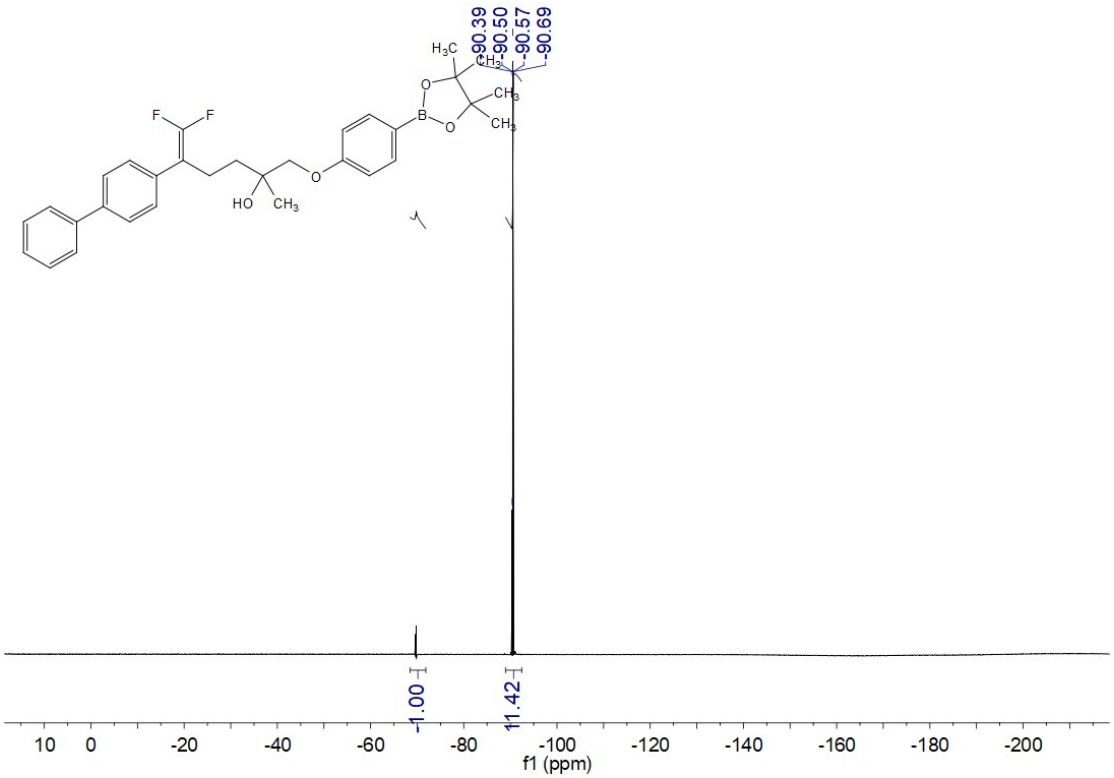


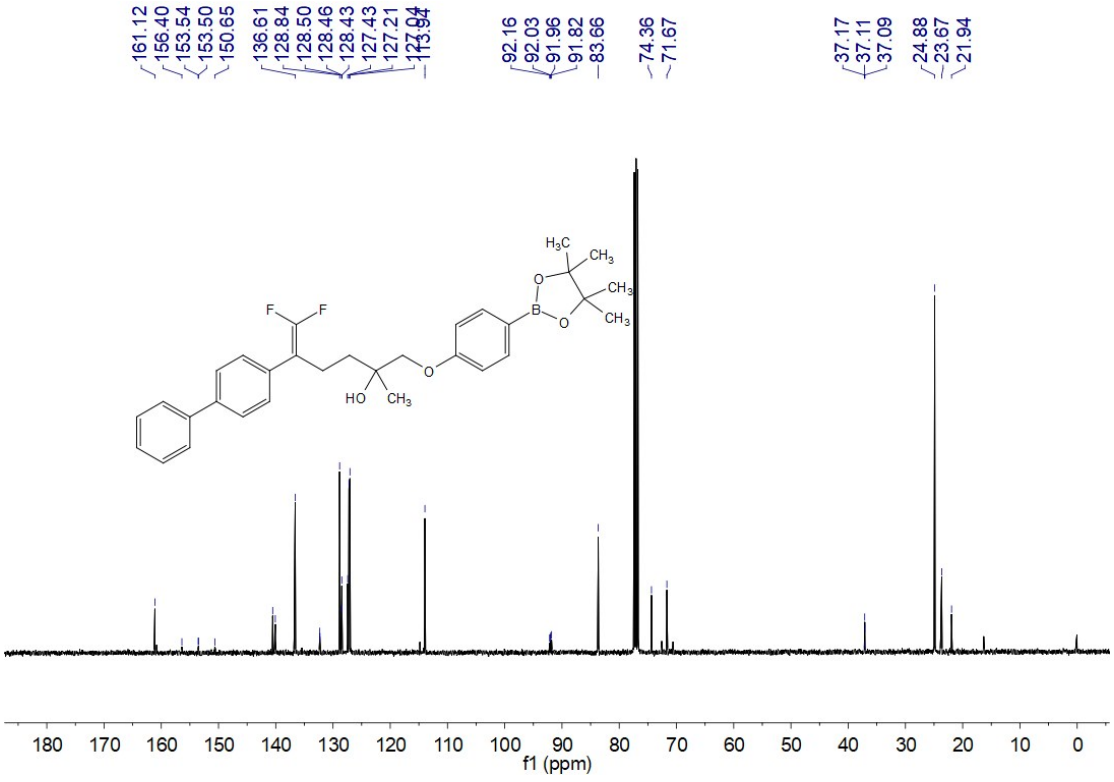
5-([1,1'-biphenyl]-4-yl)-6,6-difluoro-2-methyl-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenoxy)hex-5-en-2-ol (4g)

<u>Selectivity</u> (desired C-F cleavage product: addition by-product, Determined by ^{1}H NMR and ^{19}F NMR) = 18:1

Prepared according to the general procedure, as a sticky liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 – 7.67 (m, 2H), 7.67 – 7.52 (m, 4H), 7.45 – 7.28 (m, 5H), 6.90 (t, *J* = 9.3 Hz, 2H), 3.83 (s, 2H), 2.63 – 2.47 (m, 2H), 1.86 – 1.66 (m, 2H), 1.33 (s, 15H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -90.45 (d, *J* = 42.3 Hz), -90.63 (d, *J* = 42.3 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.12, 153.52 (dd, *J* = 291.1, 287.5 Hz), 140.54, 140.08, 136.61, 132.31 (t, *J* = 3.1 Hz), 128.84, 128.46 (t, *J* = 3.5 Hz), 127.43, 127.21, 127.04, 113.94, 91.99 (dd, *J* = 20.7, 13.8 Hz), 83.66, 74.36, 71.67, 37.10 (t, *J* = 2.3 Hz), 24.88, 23.67, 21.94. **HRMS** (APCI) calcd for $C_{31}H_{35}BF_2NaO_4$ ($M+Na^+$): 543.2489; found: 543.2496. **IR** (KBr/cm^{-1}) 3419, 2984, 2829, 1604, 1490, 1458, 1396, 1358, 1173, 1143, 772, 607.




-90.39
-90.50
-90.57
-90.69
1.00
11.42
f1 (ppm)


161.12
156.40
153.54
153.50
150.65
136.61
128.84
128.50
128.46
128.43
127.43
127.21
92.16
92.03
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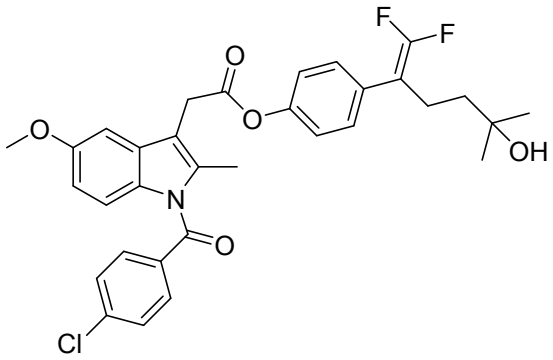
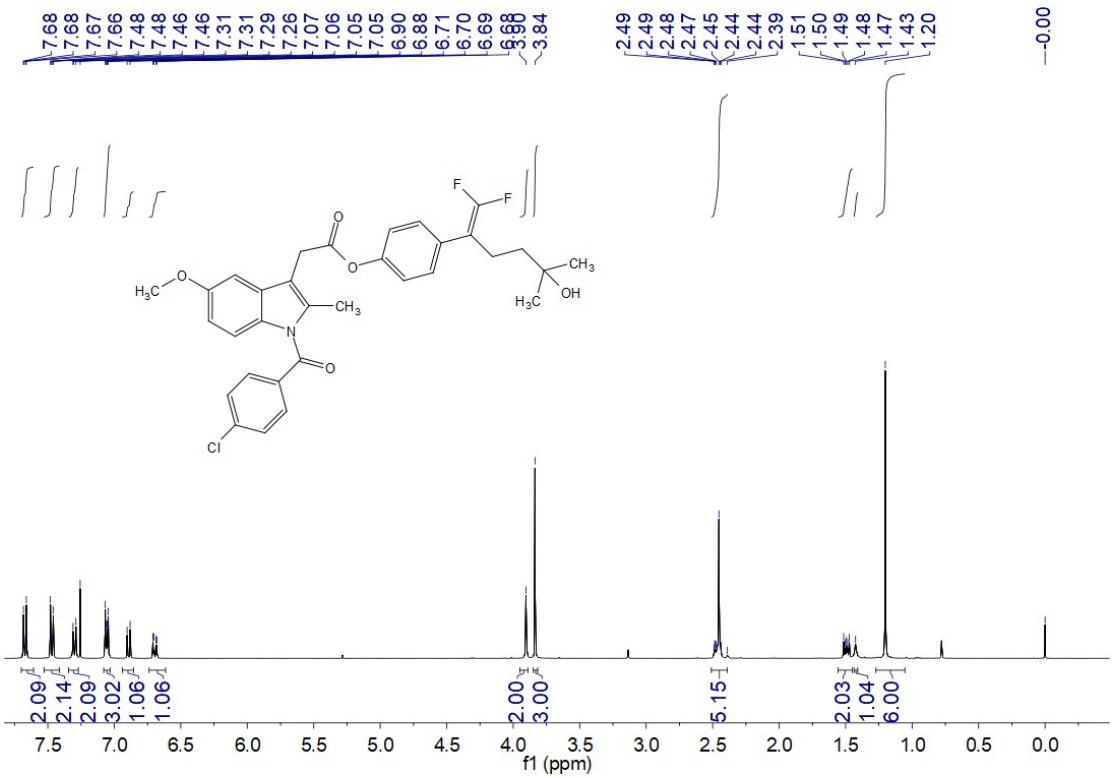
74.36
71.67
37.17
37.11
37.09
24.88
23.67
21.94
f1 (ppm)

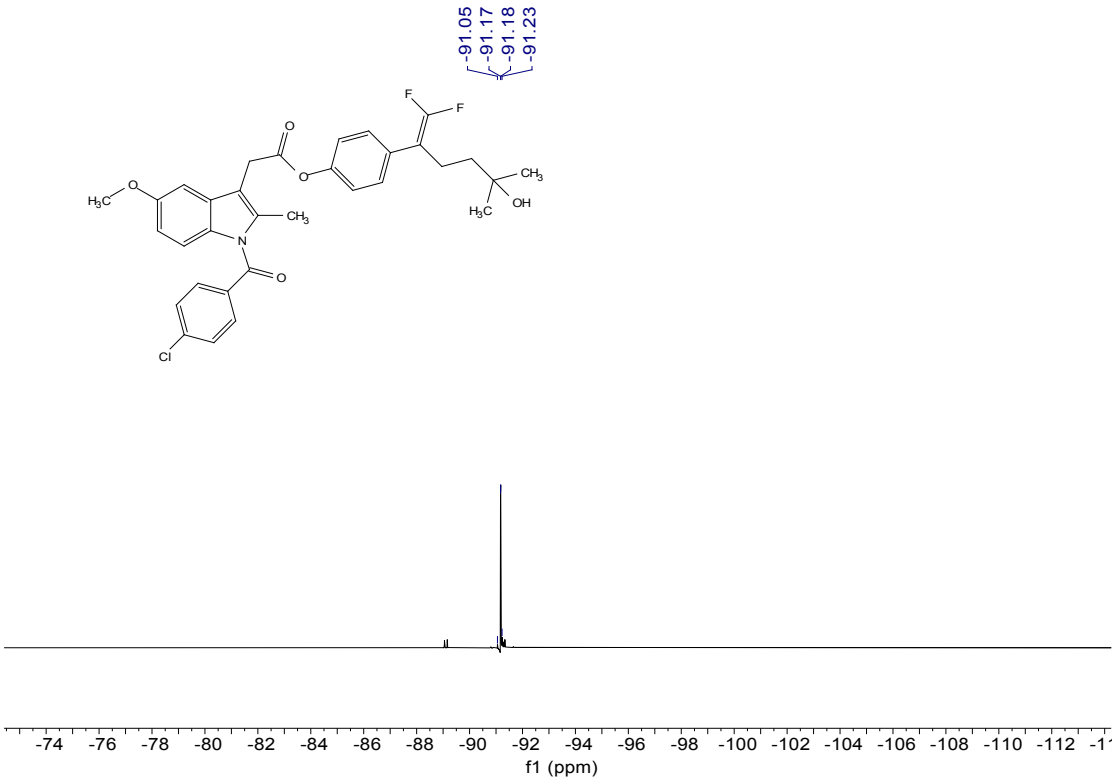


4-(1,1-difluoro-5-hydroxy-5-methylhex-1-en-2-yl)phenyl-2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetate (5a)

<u>Selectivity</u> (desired C-F cleavage product: addition by-product, Determined by ^{1}H NMR and ^{19}F NMR) > 50:1

Prepared according to the general procedure, as a sticky solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 – 7.63 (m, 2H), 7.52 – 7.38 (m, 2H), 7.37 – 7.27 (m, 2H), 7.06 (dd, *J* = 5.7, 3.0 Hz, 3H), 6.89 (d, *J* = 9.0 Hz, 1H), 6.69 (dd, *J* = 9.0, 2.5 Hz, 1H), 3.90 (s, 2H), 3.84 (s, 3H), 2.51 – 2.40 (m, 5H), 1.55 – 1.46 (m, 2H), 1.43 (br s, 1H), 1.20 (s, 6H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -91.11 (d, *J* = 45.1 Hz), -91.20 (d, *J* = 45.1 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.29, 168.35, 156.13, 153.40 (t, *J* = 288.7 Hz), 149.66, 139.39, 136.27, 133.80, 131.34, 131.24, 130.85, 130.49, 129.22, 129.18, 121.48, 115.07, 111.94, 111.81, 101.21, 91.79 (t, *J* = 17.6 Hz), 70.53, 55.75, 41.65 (t, *J* = 2.1 Hz), 30.59, 29.16, 22.61, 13.47. **HRMS** (APCI) calcd for $C_{32}H_{30}ClF_2NNaO_5$ ($M+Na^+$): 604.1673; found: 604.1681. **IR** (KBr/cm^{-1}) 3417, 2989, 1637, 1616, 1485, 1451, 1395, 1246, 1172, 1026, 1002, 619.


7.68
7.68
7.67
7.66
7.48
7.48
7.46
7.46
7.31
7.29
7.26
7.07
7.06
7.05
7.05
6.90
6.88
6.71
6.70
6.69
6.68
3.90
3.84
2.49
2.49
2.48
2.47
2.45
2.44
2.44
2.39
1.51
1.50
1.49
1.48
1.47
1.43
1.20
0.00
F
F
O
O
CH3
H3C
OH
H3C
O
CH3
N
O
Cl
2.09
2.14
2.09
3.02
1.06
1.06
2.00
3.00
5.15
2.03
1.04
6.00
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)


-91.05
-91.17
-91.18
-91.23
F
F
O
O
CH3
H3C
OH
H3C
O
CH3
N
O
Cl
-74
-76
-78
-80
-82
-84
-86
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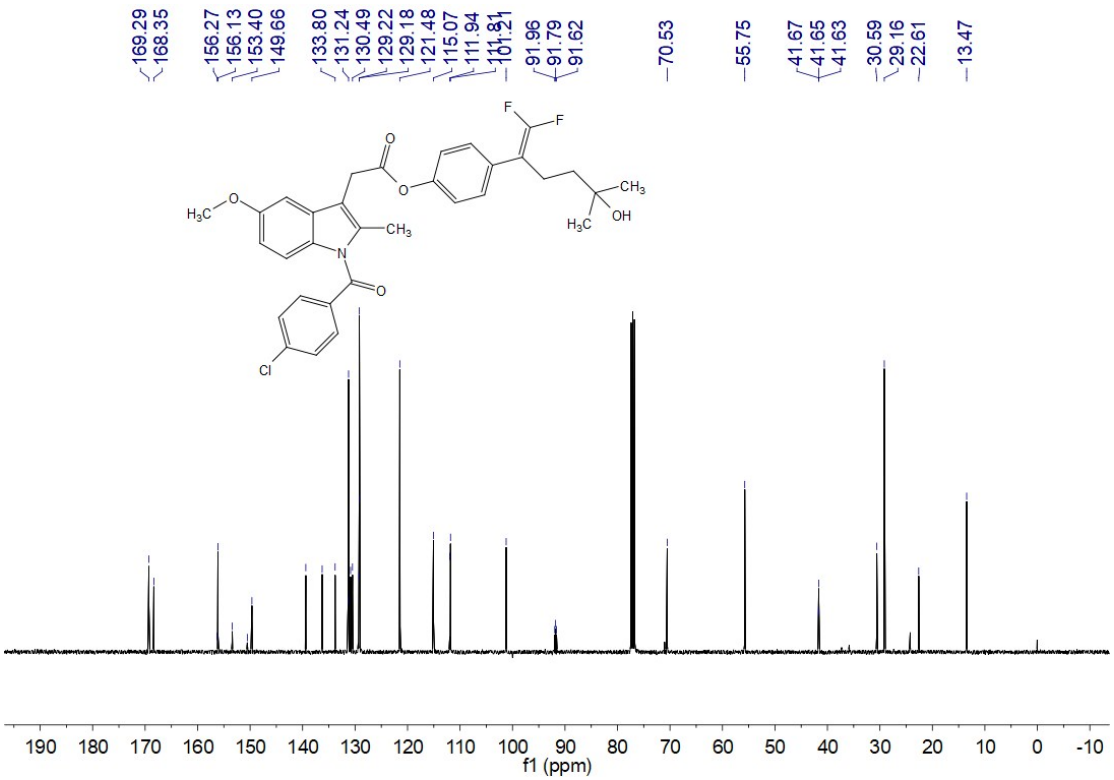
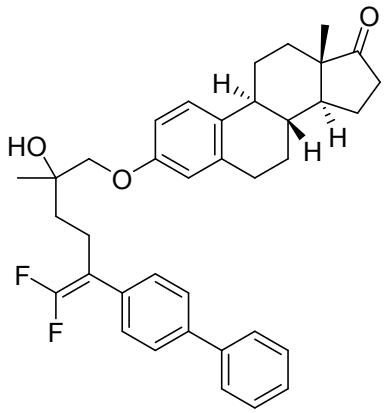
-102
-104
-106
-108
-110
-112
f1 (ppm)



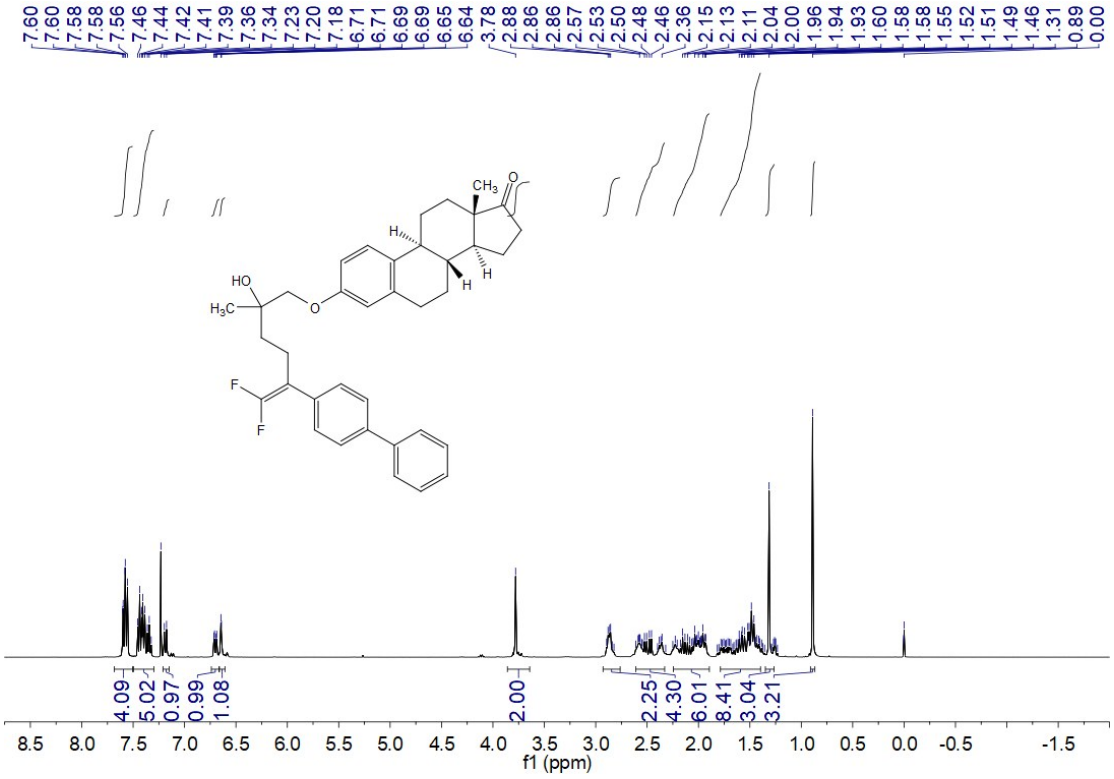


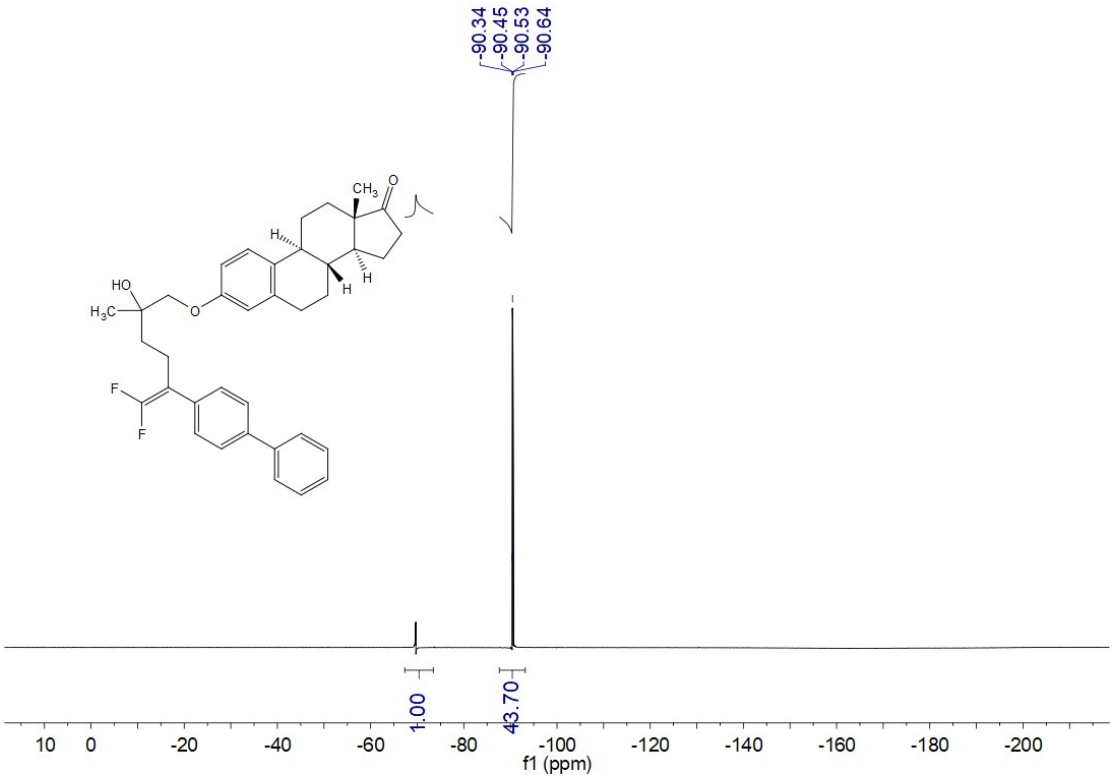
(8R,9S,13S,14S)-3-((5-([1,1'-biphenyl]-4-yl)-6,6-difluoro-2-hydroxy-2-methylhex-5-en-1-yl)oxy)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (5b)

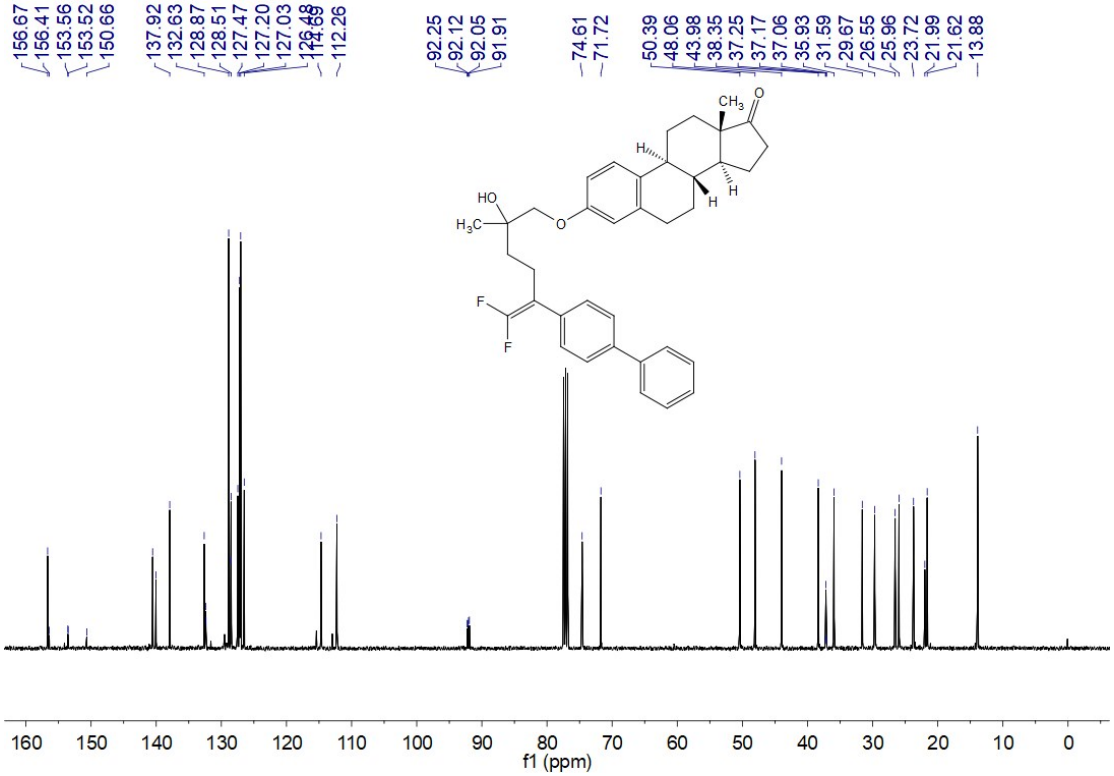
<u>Selectivity</u> (desired C-F cleavage product: addition by-product, Determined by ^{1}H NMR and ^{19}F NMR) > 50:1

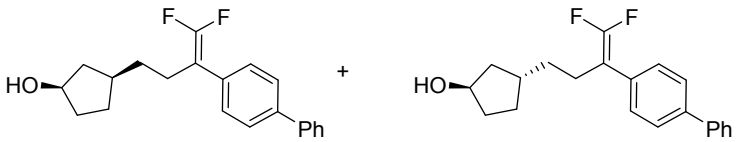
Prepared according to the general procedure, as a sticky solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 – 7.50 (m, 4H), 7.49 – 7.29 (m, 5H), 7.19 (d, *J* = 8.6 Hz, 1H), 6.70 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.64 (d, *J* = 2.2 Hz, 1H), 3.78 (s, 2H), 2.95 – 2.78 (m, 2H), 2.68 – 2.34 (m, 4H), 2.24 – 1.86 (m, 6H), 1.83 – 1.39 (m, 8H), 1.30 (s, 3H), 0.89 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -90.40 (d, *J* = 42.3 Hz), -90.59 (d, *J* = 42.3 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$) δ156.67, 153.54 (dd, *J* = 291.1, 287.4 Hz), 140.55, 140.03,

137.92, 132.63, 132.39 (t, J = 3.3 Hz), 128.87, 128.51 (t, J = 3.5 Hz), 127.47, 127.20, 127.03, 126.48, 114.69, 112.26, 92.08 (dd, J = 20.9, 13.4 Hz), 74.61, 71.72, 50.39, 48.06, 43.98, 38.35, 37.12 (t, J = 2.5 Hz), 35.93, 31.59, 29.67, 26.55, 25.96, 23.72, 21.99, 21.62, 13.88. **HRMS** (APCI) calcd for $C_{37}H_{40}F_2NaO_3$ ($M+Na^+$): 593.2838; found: 593.2843. **IR** (KBr/cm^{-1}) 3418, 2981, 2932, 2868, 2831, 2248, 1732, 1611, 1488, 1455, 1396, 1370, 1356, 1235, 1173, 1006, 766, 732, 581.







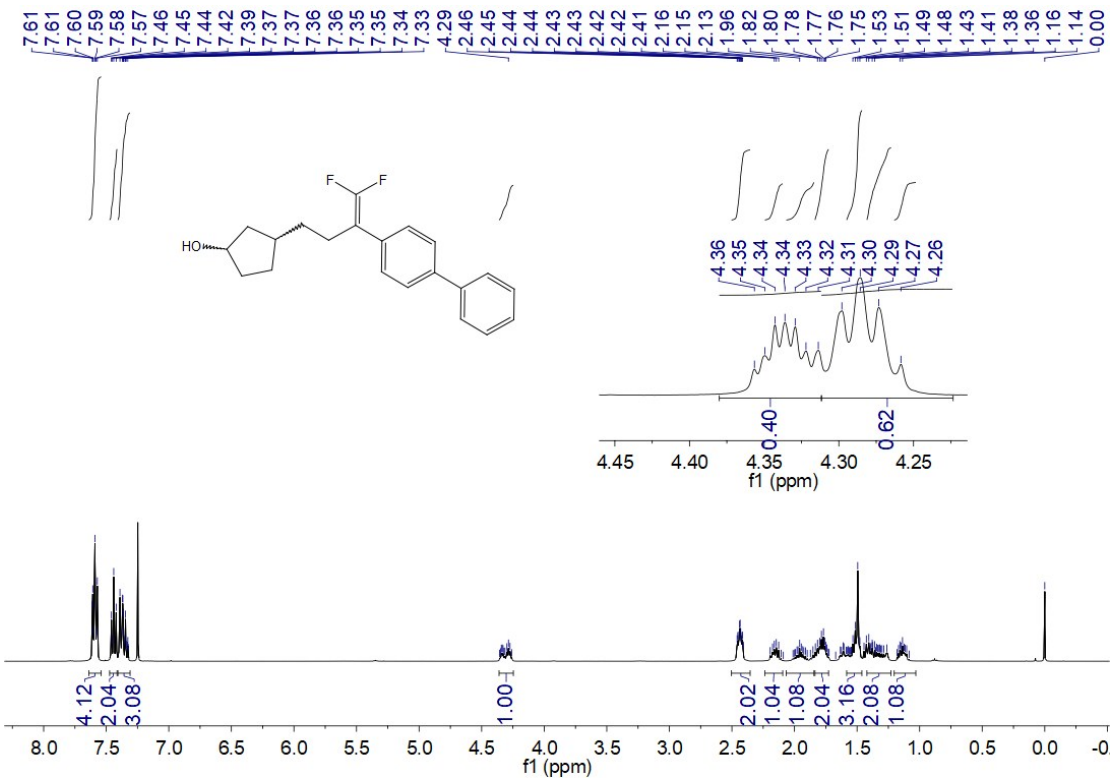


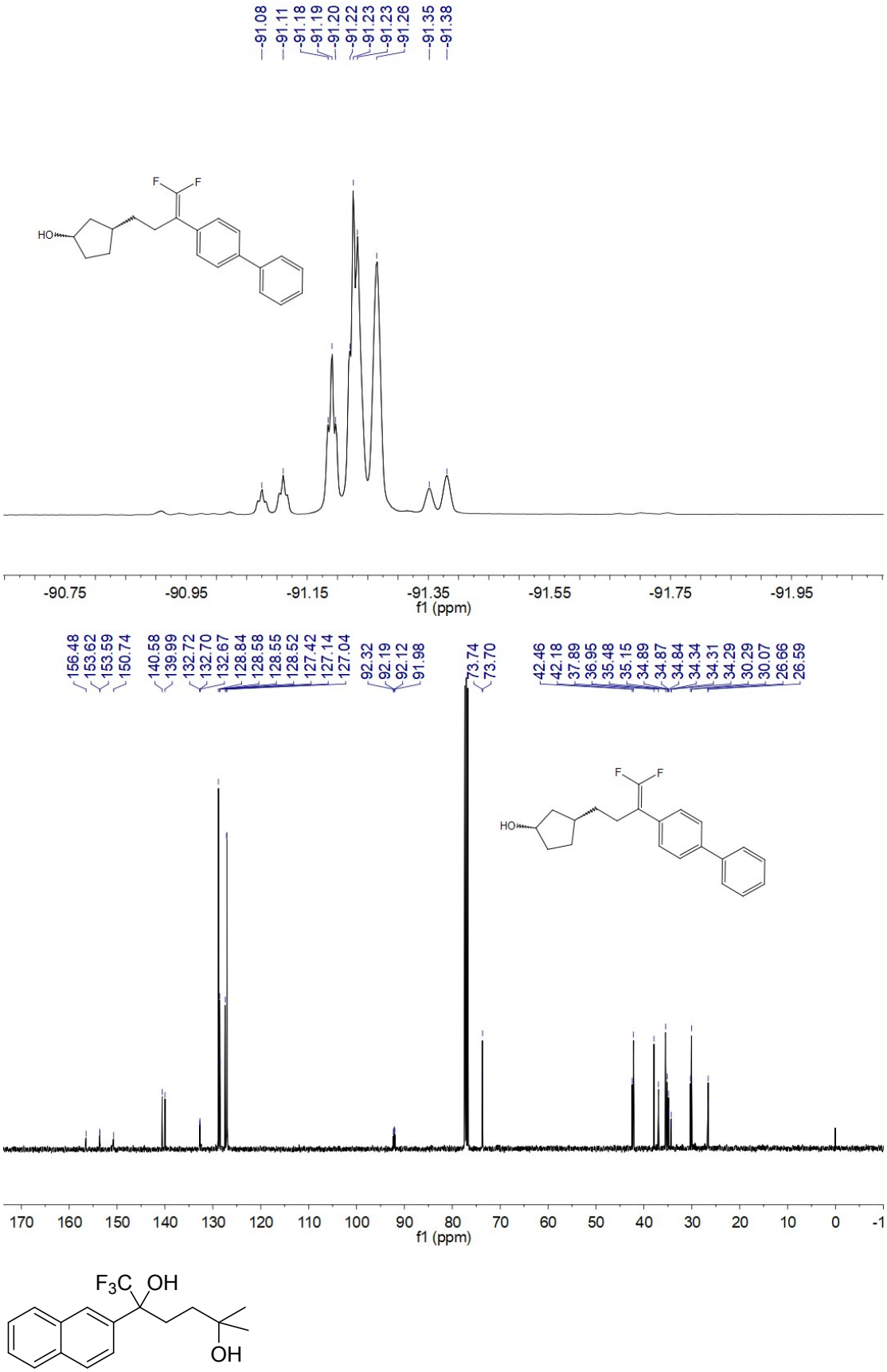
(d.r. = 1.5:1, Mixture, cis+trans)

3-(3-([1,1'-biphenyl]-4-yl)-4,4-difluorobut-3-en-1-yl)cyclopentan-1-ol (6a)

<u>Selectivity</u> (desired C-F cleavage product: addition by-product, Determined by ^{1}H NMR and ^{19}F NMR) > 30:1, d.r. = 1.5:1

Prepared according to the general procedure, as a sticky solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 – 7.53 (m, 4H), 7.52 – 7.41 (m, 2H), 7.41 – 7.30 (m, 3H), 4.38 – 4.21 (m, 1H), 2.50 – 2.36 (m, 2H), 2.14 (tt, *J* = 14.9, 7.5 Hz, 1H), 2.03 – 1.87 (m, 1H), 1.83 – 1.71 (m, 2H), 1.57 – 1.45 (m, 3H), 1.43 – 1.22 (m, 2H), 1.19 – 1.02 (m, 1H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -91.08, -91.11, -91.18, -91.19, -91.20, -91.22, -91.23, -91.23, -91.26, -91.35, -91.38. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.61 (dd, *J* = 290.2, 287.5 Hz), 140.58, 139.99, 132.71 (t, *J* = 2.3 Hz), 128.84, 128.55 (t, *J* = 3.3 Hz), 127.42, 127.14, 127.04, 92.15 (dd, *J* = 20.4, 13.9 Hz), 73.74, 73.70, 42.46, 42.18, 37.89, 36.95, 35.48, 35.15, 34.87 (t, *J* = 2.2 Hz), 34.31 (t, *J* = 2.3 Hz), 30.29, 30.07, 26.66, 26.59. **HRMS** (APCI) calcd for $C_{21}H_{22}F_2NaO$ ($M+Na^+$): 351.1531; found: 351.1536. **IR** (KBr/cm^{-1}) 3419, 2986, 1616, 1488, 1461, 1396, 1187, 1173, 1002, 773, 615.

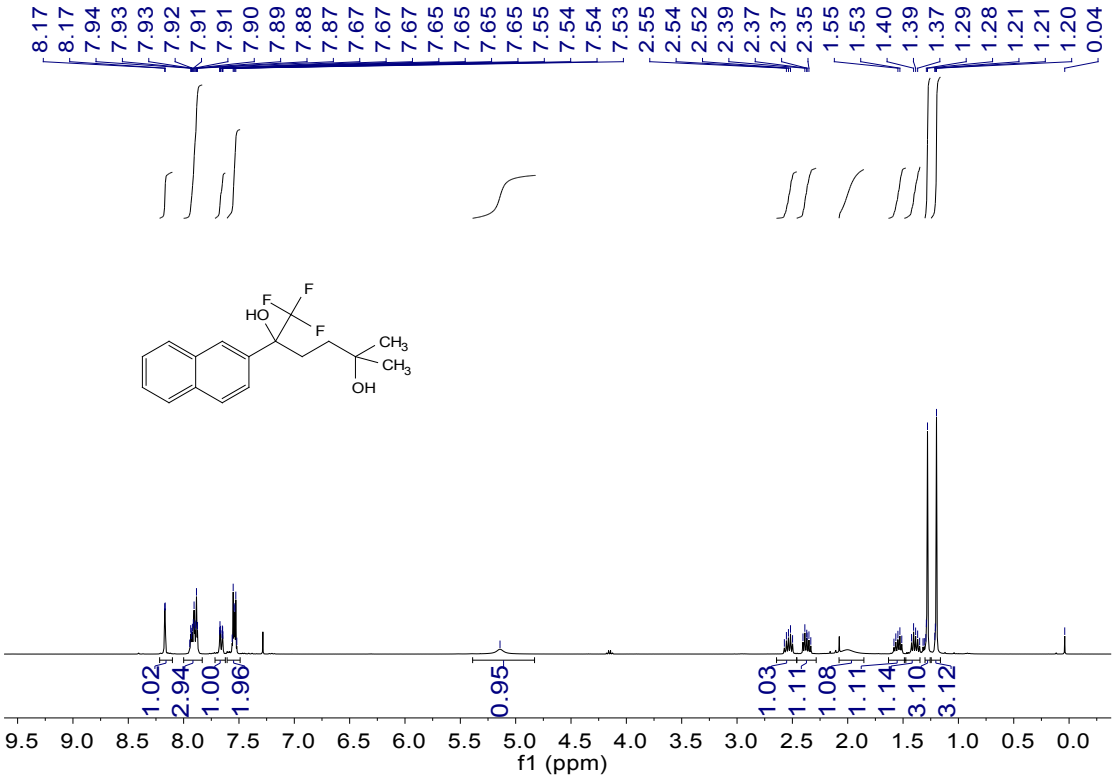


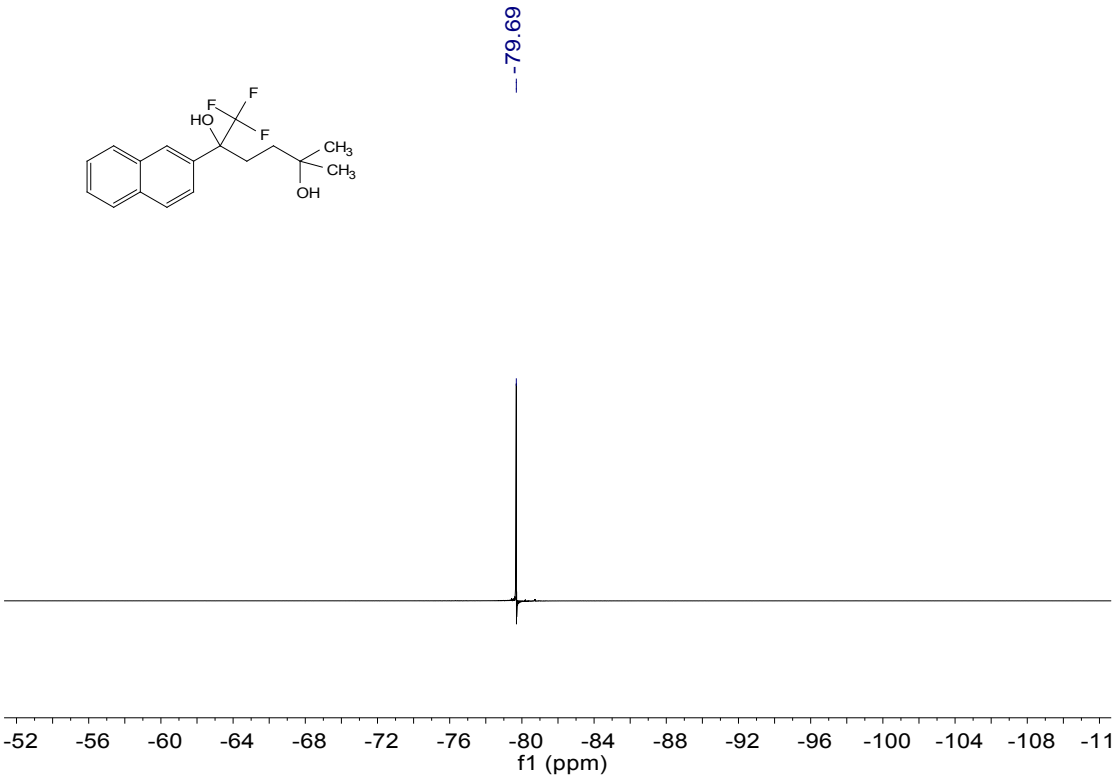


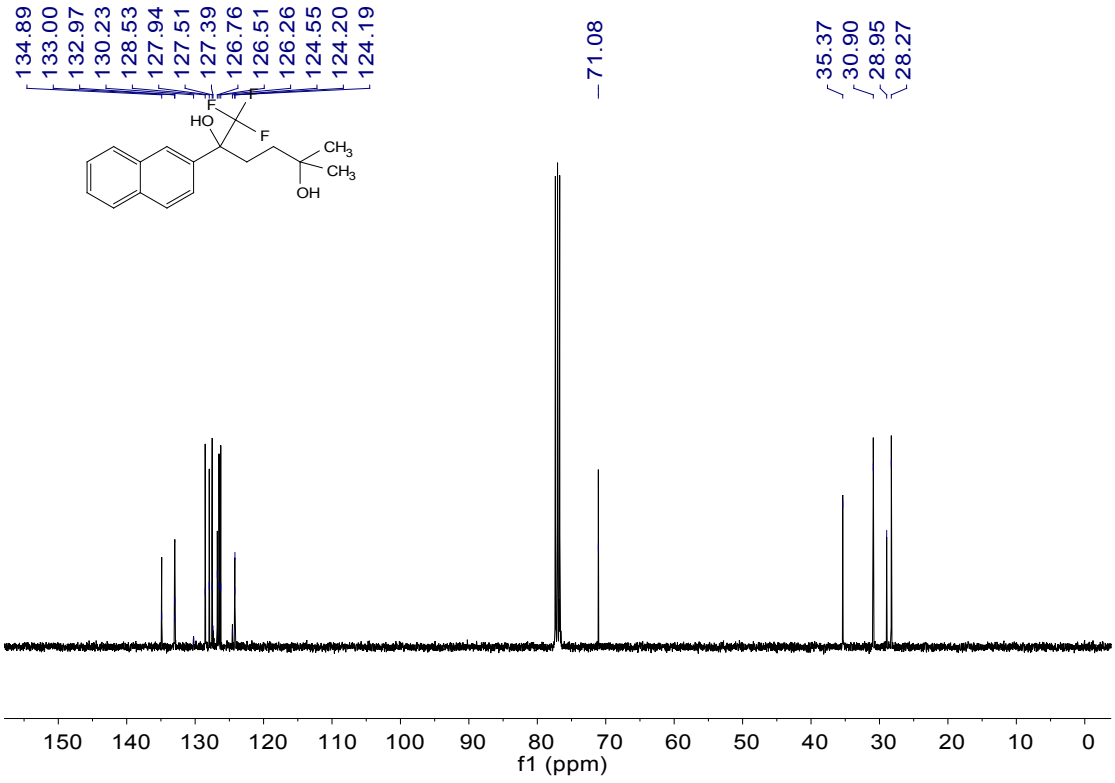
1,1,1-trifluoro-5-methyl-2-(naphthalen-2-yl)hexane-2,5-diol (3am)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 1.8 Hz, 1H), 7.99 – 7.83 (m, 3H), 7.75 – 7.63 (m, 1H), 7.54

(dt, J = 6.3, 3.5 Hz, 2H), 5.14 (s, 1H), 2.61 – 2.47 (m, 1H), 2.45 – 2.32 (m, 1H), 2.00 (s, 1H), 1.55 (dt, J = 14.0, 6.8 Hz, 1H), 1.39 (dt, J = 14.6, 7.3 Hz, 1H), 1.28 (s, 3H), 1.20 (s, 3H). **^{19}F NMR (**376 MHz, $CDCl_3$) δ -79.69. ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.89, 133.00, 132.97, 128.53, 127.94, 127.51, 126.76, 126.26, 125.97 (q, J = 285.7 Hz), 125.51, 124.19, 71.08, 35.37, 30.90, 28.95, 28.27. **HRMS** (APCI) calcd for $C_{17}H_{20}F_3O_2$ ($M+H^+$): 313.1410; found: 313.1413.




-79.69
F
F
HO
F
CH3
CH3
OH
-52 -56 -60 -64 -68 -72 -76 -80 -84 -88 -92 -96 -100 -104 -108 -11
f1 (ppm)


134.89
133.00
132.97
130.23
128.53
127.94
127.51
127.39
126.76
126.51
126.26
124.55
124.20
124.19
71.08
35.37
30.90
28.95
28.27
F
HO
F
CH3
CH3
OH
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)