Electronic Supplementary Information

Ir-Catalysed Formation of C–F Bonds. From Allylic Alcohols to α-Fluoroketones.

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General

Air and moisture sensitive reactions were carried out under an atmosphere of dry nitrogen. Reagents were used as obtained from commercial suppliers without further purification. THF was used as obtained from supplier (puriss. p. a., stabilized with 2,6-di-tert-butyl-4-methylphenol ~250 mg/l). The undistilled THF used in the reactions tested negative for peroxides (0% by Quantofix peroxide). A potassium dihydrogen phosphate/disodium hydrogen phosphate buffer (pH 7; per litre: 3.54 g KH_2PO_4/14.7g Na_2HPO_4) was used as obtained from supplier. Flash chromatography was carried out on 60 Å (35-70 μm) silica gel. Spectra were recorded at 400 or 500 MHz for ^{1}H NMR, at 100 or 125 MHz for ^{13}C NMR, and at 376 MHz for ^{19}F NMR on a Bruker Advance spectrometer. ^{1}H and ^{13}C NMR chemical shifts (δ) are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard, ($CDCl_3$: δ_H 7.26 and δ_C 77.16). ^{19}F NMR chemical shifts (δ) (^{1}H-decuopled) are reported in ppm from $CFCl_3$ with C_6H_5F (δ -113.15) as internal standard. Coupling constants (J) are given in Hz. High resolution mass spectra (HRMS) were recorded on Bruker microTOF ESI-TOF mass spectrometer.

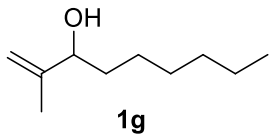
Preparation of allylic alcohols

Alcohols **1a** and **1e** were used as obtained from supplier. Allylic alcohols **1c**,[1] **1f,**[2] and **1h**[3] were prepared as described in the literature.

Allylic alcohols **1b-d** were prepared in a similar manner to **1h**:[3]

The corresponding aldehyde (1 equiv) was added to a solution of vinylmagnesium bromide (1M in THF, 1.1 equiv) at 0 °C, and then the reaction mixture was slowly warmed to room temperature. On consumption of the aldehyde (as monitored by TLC: EtOAc/Pentane 1:20), the reaction was quenched with NH_4Cl (aq), extracted with EtOAc (x 3) and washed with brine. The combined organic phases were dried over $MgSO_4$ and the solvent was removed under reduced pressure. Purification by column chromatography (EtOAc/Pentane 1:20 – 1:5) afforded the pure allylic alcohols.

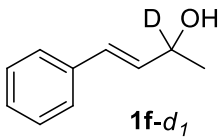
Synthesis of 2-Methylnon-1-en-3-ol (1g):



1g

A solution of hexylmagnesium bromide (2M, in diethylether, 20 mmol) was added to a suspension of methacrolein (20 mmol) and $CeCl_3$ (20 mmol) in dry THF (100 mL) at -78 °C. The reaction was left to slowly warm to room temperature overnight (15 h). The mixture was quenched with NH_4Cl (aq), extracted with Et_2O (x 3) and washed with brine. Purification by column chromatography (EtOAc/Pentane 1:30 – 1:10) afforded **1g** as a colourless oil.

Synthesis of (*E*)-4-Phenyl-3-buten-2-deuterium-2-ol (1f-d_1):



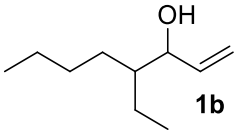
1f-d_1

$NaBD_4$ (172 mg, 4.1 mmol) was added in portions to a solution of benzylideneacetone (585 mg, 4 mmol) and $CeCl_3 \cdot 7H_2O$ (372 mg, 4.5 mmol) in MeOH (25 mL) at 0 °C. The reaction

mixture was stirred at room temperature for 2 h before the addition of HCl (aq, 1M). The methanol was removed under reduced pressure, and the product extracted repeatedly with Et_2O. The combined organic phases were dried over $MgSO_4$, and solvents were evaporated. Purification by column chromatography (Pentane/EtOAc 10:1) afforded **1f-*d*$_1$** as a white solid (540 mg, 92 %, 96 %[D] (D content determined by ^{1}H NMR and HRMS-ESI).

Characterization data of allylic alcohols (1b, 1d, 1g and 1f-*d*$_1$):

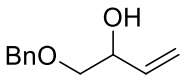
4-Ethyloct-1-en-3-ol (1b)



1b

Yellow oil, 73 % isolated yield as a mixture of 2 diastereomers (dr = 1:1): ^{1}H NMR ($CDCl_3$, 400 MHz, mixture of diastereomers): δ 4.87 (ddd, J_{HH} = 17.0 Hz, J_{HH} = 10.5 Hz, J_{HH} = 6.1 Hz, 2H), 5.25-5.20 (m, 2H), 5.16-5.13 (m, 2H), 4.14-4.10 (m, 2H), 1.65-1.16 (m, 16H), 0.92-0.87 (m, 12H); ^{13}C NMR ($CDCl_3$, 125 MHz, mixture of diastereomers): δ 139.9, 139.8, 115.2, 115.1, 74.8, 74.7, 45.1, 45.0, 29.6, 29.5, 23.0 (2C), 22.3, 21.8, 14.1 (2C), 11.7, 11.5.

1-(Benzyloxy)but-3-en-2-ol (1d)

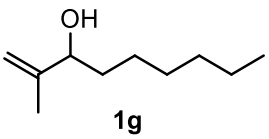


1d

Colourless oil, 76 % isolated yield: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.38-7.28 (m, 5H), 5.84 (ddd, J_{HH} = 17.2 Hz, J_{HH} = 10.5 Hz, J_{HH} = 5.5 Hz, 1H), 5.37 (dt, J_{HH} = 17.2 Hz, J_{HH} = 1.5 Hz,1H), 5.20 (dt, J_{HH} = 10.5 Hz, J_{HH} = 1.5 Hz,1H), 4.58 (s, 2H), 4.36 (m, 1H), 3.55 (dd, J_{HH} = 9.6 Hz, J_{HH} = 3.4 Hz,1H), 3.39 (dd, J_{HH} = 9.6 Hz, J_{HH} = 7.9 Hz,1H), 2.51 (br s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 137.9, 136.7, 128.6 (2C), 128.0, 127.9 (2C), 116.6, 74.1, 73.5, 71.6; HRMS-ESI: *m/z* 201.0884 ([M+Na]$^+$, calcd. for $C_{11}H_{14}O_2Na_1$: 201.0886)

The NMR data were identical to those previously reported for this compound.[4]

2-Methylnon-1-en-3-ol (1g)



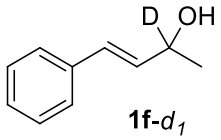
1g

Colourless oil, 53 % isolated yield: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.93 (m, 1H), 4.83 (m, 1H), 4.04 (t, J_{HH} = 6.5 Hz, 1H), 1.72 (m, 3H), 1.58-1.51 (m, 2H), 1.40-1.22 (m, 8H), 0.88 (t,

J_{HH} = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 147.8, 111.1, 76.2, 35.1, 31.9, 29.4, 25.7, 22.7, 17.6, 14.2.

The NMR data were identical to those previously reported for this compound.[5]

(*E*)-4-Phenyl-3-buten-2-deuterium-2-ol (1f-d_1):



1f-d_1

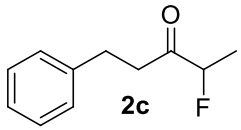
White solid, 92% isolated yield: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.40-7.36 (m, 2H), 7.34-7.29 (m, 2H), 7.26-7.22 (m, 1H), 6.56 (d, J_{HH} = 15.9 Hz, 1H), 6.26 (d, J_{HH} = 15.9 Hz, 1H), 1.97 (s, 1H), 1.37 (s, 3H) ; ^{13}C NMR ($CDCl_3$, 125 MHz): δ 136.8, 133.6, 129.4, 128.7 (2C), 127.7, 126.5 (2C), 66.6 (t, J_{CD} = 22 Hz), 23.4; HRMS-ESI: *m/z* 172.0840 ([M+Na]$^+$, calcd. for $C_{10}H_{11}D_1O_1Na_1$: 172.0843).

General procedure for the isomerization/fluorination of allylic alcohols

$[IrCp^*Cl_2]_2$ (4 mg, $5\cdot10^{-3}$ mmol, 1 mol%) was dissolved in a mixture of THF (2.5 mL) and H_2O (0.5 mL) at 30 °C. Selectfluor® (0.63 mmol, 1.25 eq) and the corresponding allylic alcohol (0.5 mmol) were added to the reaction mixture. The reaction was stirred at 30 °C for the time indicated in Table 3. On completion (as monitored by TLC) water (1 mL) was added and the reaction mixture was extracted with Et_2O (3x2 mL), and dried over $MgSO_4$. Evaporation of the solvent afforded a mixture of α-fluorinated ketone (**2a-h**) and non-fluorinated ketone (**3a-h**). The yield and F/H ratios were determined by ^{1}H NMR using 1,4-dimethoxybenzene (0.25 mmol) as an internal standard. Isolated products were purified by column chromatography (EtOAC/Pentane or Et_2O/Pentane 1:40 – 1:20). TLC plates were developed with $KMnO_4$ or Cerium Molybdate (Hanessian's stain).

Characterization data of isolated α-fluoroketones 2c, 2d, 2f and 2h:

4-Fluoro-1-phenylpentan-3-one (2c)

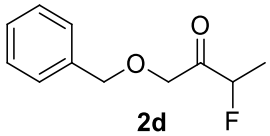


2c

Pale yellow oil, 77% isolated yield: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.31-7.26 (m, 2H), 7.22-7.20 (m, 3H), 4.87 (dq, J_{HH} = 6.9 Hz J_{HF} = 49.6 Hz, 1H), 2.99-2.89 (m, 4H), 1.44 (dd, J_{HH} = 6.9 Hz J_{HF} = 23.9 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 209.4 (d, J_{CF} = 24 Hz), 140.9,

128.7 (2C), 128.5 (2C), 126.4, 92.7 (d, J_{CF} = 181 Hz), 39.2, 28.9 (d, J_{CF} = 2 Hz), 17.6 (d, J_{CF} = 22 Hz); ^{19}F NMR ($CDCl_3$, 376.4 MHz): δ -184.5; HRMS-ESI: *m/z* 203.0837 ([M+Na]$^+$, calcd. for $C_{11}H_{13}O_1F_1Na_1$: 203.0843).

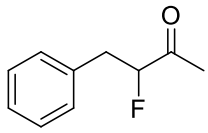
1-(Benzyloxy)-3-fluorobutan-2-one (2d)



2d

Pale yellow oil, 74 % isolated yield: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.37-7.28 (m, 5H), 5.05 (dq, J_{HH} = 6.9 Hz, J_{HF} = 48.8 Hz, 1H), 4.63 (s, 2H), 4.49-3.97 (m, 2H), 1.52 (dd, J_{HH} = 6.9 Hz, J_{HF} = 24.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 206.2 (d, J_{CF} = 23 Hz), 137.1, 128.7 (2C), 128.3, 128.2 (2C), 92.2 (d, J_{CF} = 179 Hz), 73.6, 71.9 (d, J_{CF} = 4 Hz), 17.7 (d, J_{CF} = 21 Hz); ^{19}F NMR ($CDCl_3$, 376.4 MHz): δ 191.3; HRMS-ESI: *m/z* 219.0782 ([M+Na]$^+$, calcd. for $C_{11}H_{13}O_2F_1Na_1$: 219.0792).

3-Fluoro-4-phenylbutan-2-one (2f)

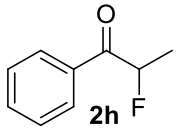


2f

Pale yellow oil, 67 % isolated yield: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.34-7.22 (m, 5H), 4.94 (ddd, J_{HH} = 3.8 Hz, J_{HH} = 7.5 Hz, J_{HF} = 49.9 Hz, 1H), 3.19 (ddd, J_{HH} = 3.8 Hz, J_{HH} = 14.7 Hz, J_{HF} = 28.9 Hz, 1H), 3.05 (ddd, J_{HH} = 7.5 Hz, J_{HH} = 14.7 Hz, J_{HF} = 26.2 Hz, 1H), 2.14 (d, J_{HF} = 4.9 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz: δ 208.1 (d, J_{CF} = 26 Hz), 135.4, 129.6 (2C), 128.7 (2C), 127.2 (2C), 96.0 (d, J_{CF} = 185 Hz), 38.2 (d, J_{CF} = 21 Hz), 26.5; ^{19}F NMR ($CDCl_3$, 376.4 MHz): δ 188.2; HRMS-ESI: *m/z* 189.0694 ([M+Na]$^+$, calcd. for $C_{10}H_{11}O_1F_1Na_1$: 189.0686).

The NMR data were identical to those previously reported for this compound.[6]

2-Fluoro-1-phenylpropan-1-one (2h)



2h

Colourless oil, 68 % (contaminated with ~4 % propiophenone): ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.01-7.99 (m, 2H), 7.65-7.61 (m, 1H), 7.53-7.49 (m, 2H), 5.73 (dq, J_{HH} = 6.8 Hz, J_{HF} = 48.6 Hz, 1H), 1.69 (dd, J_{HH} = 6.8 Hz, J_{HF} = 24 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 197.1 (d, J_{CF} = 19.3 Hz), 134.2, 133.9, 129.1 (J_{CF} = 3.7 Hz, 2C), 128.9 (2C), 90.4 (d, J_{CF} = 180 Hz), 18.4 (d, J_{CF} = 23 Hz); ^{19}F NMR ($CDCl_3$, 376.4 MHz): δ -181.4; HRMS-ESI: *m/z*175.0537([M+Na]$^{+}$, calcd. for $C_9H_9O_1F_1Na_1$: 175.0530)

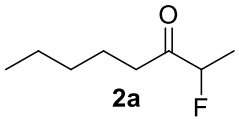
The ^{1}H NMR data were identical to those previously reported for this compound.[7]

Litt ^{19}F NMR: -180.6,7 -181.9 to -182.3[8] and -183.5[9]

Selected NMR data of α-fluoroketones 2a, 2b, 2g and 2f-d[1]:

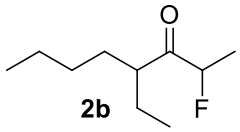
α-Fluoroketones **2c-d**, **2f** and **2h** were not isolated due to difficulty of separation, volatility and difficulty of detection by TLC. Yields were calculated using 1,4-dimethoxybenzene or fluorobenzene as internal standard and are shown in Table 3. Selected ^{1}H and ^{19}F NMR peaks are presented here:

2-Fluorooctan-3-one (2a)



^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.85 (dq, J_{HH} = 6.9 Hz, J_{HF} = 49.6 Hz, 1H), 2.59 (dt, J_{HH} = 3.7 Hz, J_{HF} = 2.9 Hz, 2H), 1.63-1.53 (m, 2H), 1.46 (dd, J_{HF} = 24 Hz, J_{HH} = 6.9 Hz, 3H), 1.37-1.20 (m, 4H), 0.89 (t, J_{HH} = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 210.7 (d, J_{CF} = 24 Hz), 92.7 (d, J_{CF} = 181 Hz), 37.5, 31.5, 22.54, 22.53, 17.8 (d, J_{CF} = 23 Hz), 14.0; ^{19}F NMR ($CDCl_3$, 376.4 MHz): δ -184.2

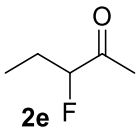
4-Ethyl-2-fluorooctan-3-one (2b)



Mixture of 2 diastereomers (dr = 1:1): ^{1}H NMR ($CDCl_3$, 400 MHz, two diastereomers): δ 4.88 (dq, J_{HH} = 6.9 Hz J_{HF} = 49.5 Hz, 1H), 4.87 (dq, J_{HH} = 6.9 Hz J_{HF} = 49.5 Hz, 1H), 2.93-2.87 (m, 2H), 1.72-1.53 (m, 4H), 1.55-1.34 (m, 4H), 1.46 (dd, J_{HH} = 6.9 Hz J_{HF} = 23.8 Hz, 6H), 1.33-1.14 (m, 8H), 0.89-0.81 (m, 12H); ^{13}C NMR ($CDCl_3$, 125 MHz, two diastereomers): δ 213.70 (d, J_{CF} = 22 Hz), 213.67 (d, J_{CF} = 23 Hz) 92.58 (d, J_{CF} = 182 Hz), 92.56 (d, J_{CF} = 182

Hz), 48.0, 47.9, 30.6, 30.2, 29.8, 29.7, 24.3, 23.9, 22.9 (2C), 17.6 (d, J_{CF} = 22 Hz), 17.5 (d, J_{CF} = 22 Hz), 14.0 (2C), 12.0, 11.8; ^{19}F NMR ($CDCl_3$, 376.4 MHz, 2 diastereomers): δ -184.56, -158.57

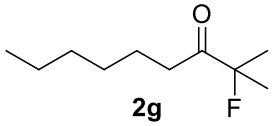
3-fluoropentan-2-one (2e)



2e

^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.67 (ddd, J_{HH} = 4.5 Hz, J_{HH} = 7.5 Hz, J_{HF} = 50.2 Hz, 1H), 2.25 (d, J_{HF} = 4.8 Hz, 3H), 1.93-1.74 (m, 2H), 1.01 (t, J_{HH} = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 208.5 (d, J_{CF} = 26 Hz), 97.0 (d, J_{CF} = 184 Hz), 26.2, 25.3 (d, J_{CF} = 21 Hz), 8.9 (d, J_{CF} = 4.3 Hz); ^{19}F NMR ($CDCl_3$, 376.4 MHz): δ -191.1

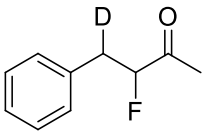
2-Fluoro-2-methylnonan-3-one (2g)



2g

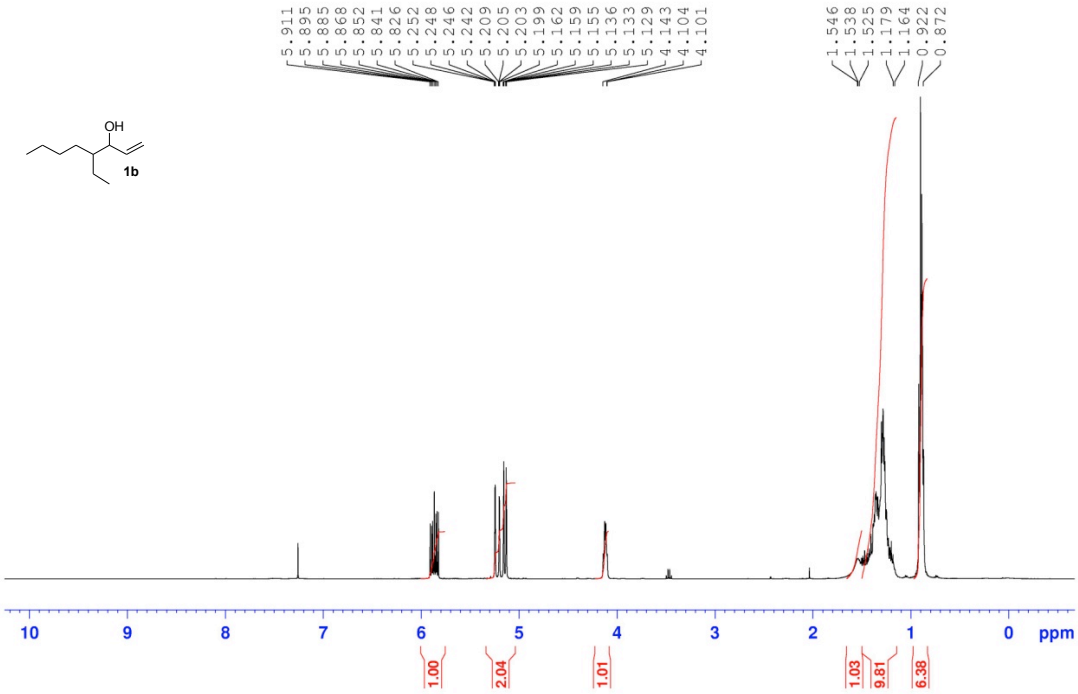
^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.64 (dt, J_{HH} = 7.4 Hz, J_{HF} = 3.2 Hz, 2H), 1.64-1.18 (m, 8H), 1.43 (d, J_{HF} = 23 Hz, 6H), 0.92-0.82 (m, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 212.8 (d, J_{CF} = 28 Hz), 99.1 (d, J_{CF} = 179 Hz), 36.6, 31.7, 29.0, 24.3 (d, J_{CF} = 24 Hz, 2C), 23.0 (d, J_{CF} = 2 Hz), 22.6, 14.2; ^{19}F NMR ($CDCl_3$, 376.4 MHz): δ -149.0

3-Fluoro-4-deuterium-4-phenylbutan-2-one (2f-d_1)



2f-d_1

Mixture of 2 diastereomers. Deuterium content was 95% as determined by ^{1}H NMR and ^{19}F NMR. ^{1}H NMR ($CDCl_3$, 400 MHz, two diastereomers): δ 7.34-7.22 (m, 10H), 5.01-4.85 (m, 2H), 3.25-2.98 (m, 2H), 2.138 (d, J_{HF} = 4.9 Hz, 3H), 2.136 (d, J_{HF} = 4.9 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 208.1 (d, J_{CF} = 26 Hz), 135.4, 129.6 (2C), 128.7 (2C), 127.3, 90.0 (d, J_{CF} = 187 Hz), 37.9 (dt, J_{CF} = 20 Hz, J_{CD} = 20 Hz), 26.5; ^{19}F NMR ($CDCl_3$, 376.4 MHz, two diastereomers): δ: -188.44 (t, J_{DF} = 4.4 Hz), -188, 47 (t, J_{DF} = 4.0 Hz). Minor peak (5%) from non deuturated **2f** at -188.2; HRMS-ESI: *m/z* 190.0749 ([M+Na]$^+$, calcd. for $C_{10}H_{10}D_1O_1F_1Na_1$: 190.0749)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4.101
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1.538
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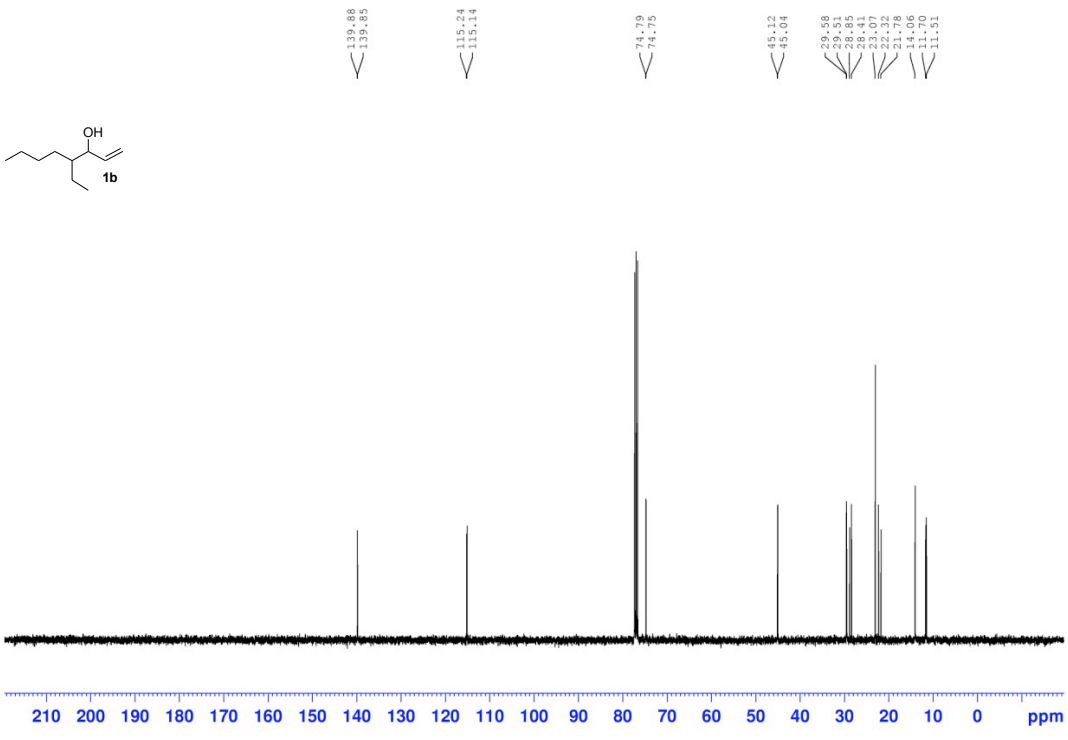
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140
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120
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100
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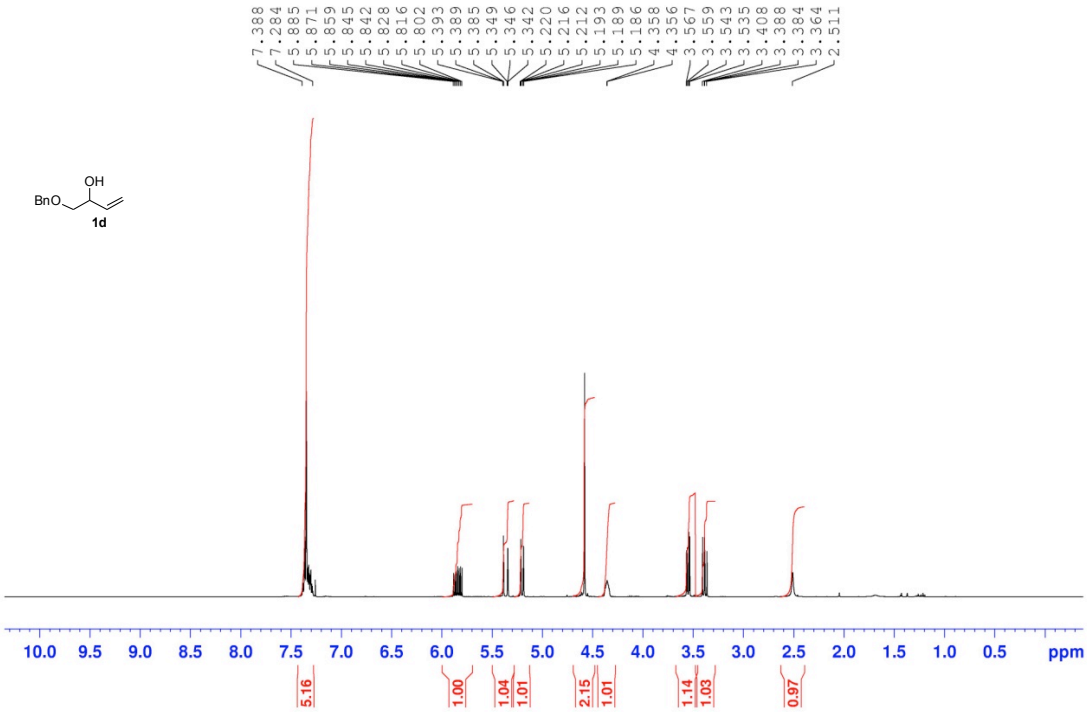
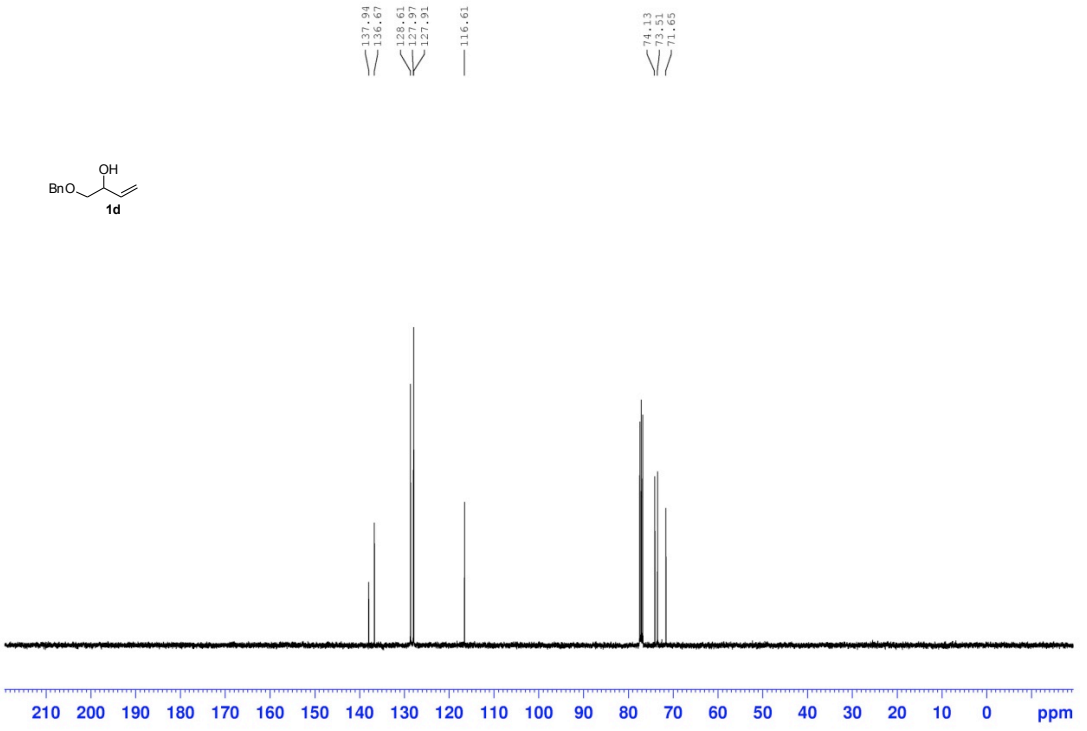
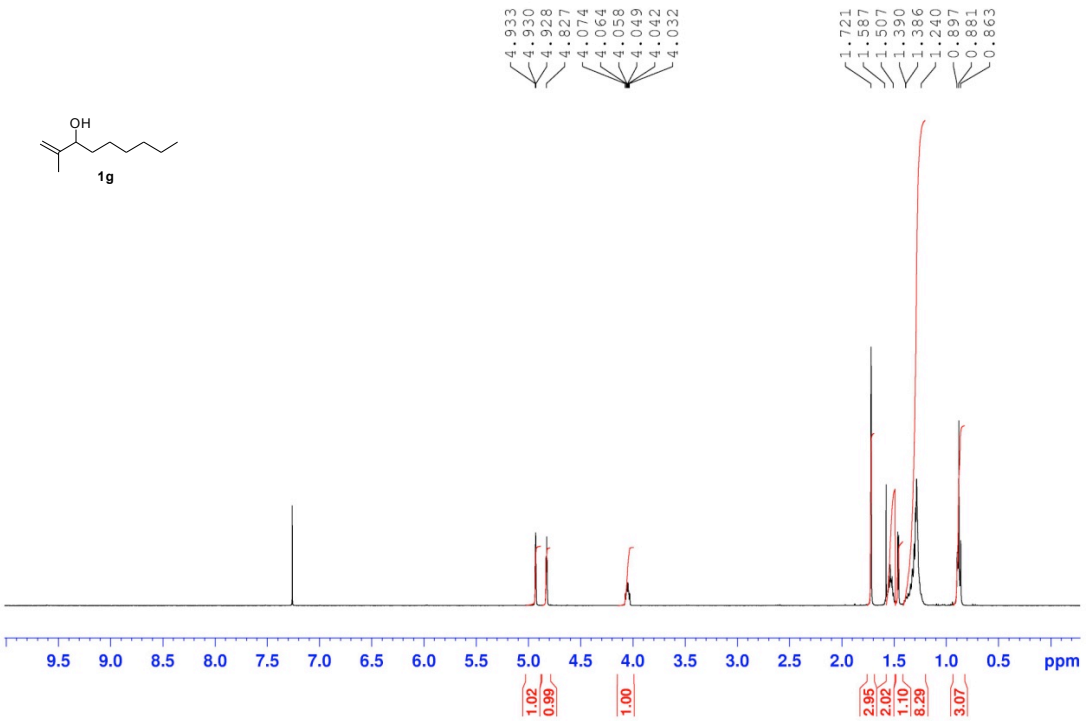
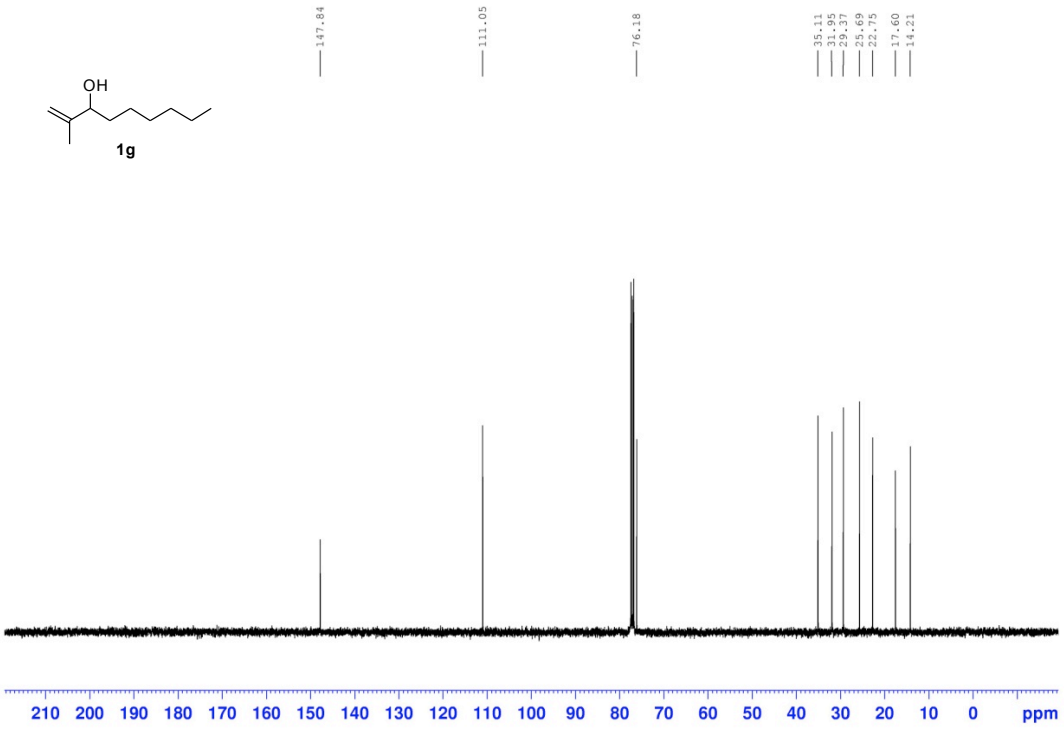
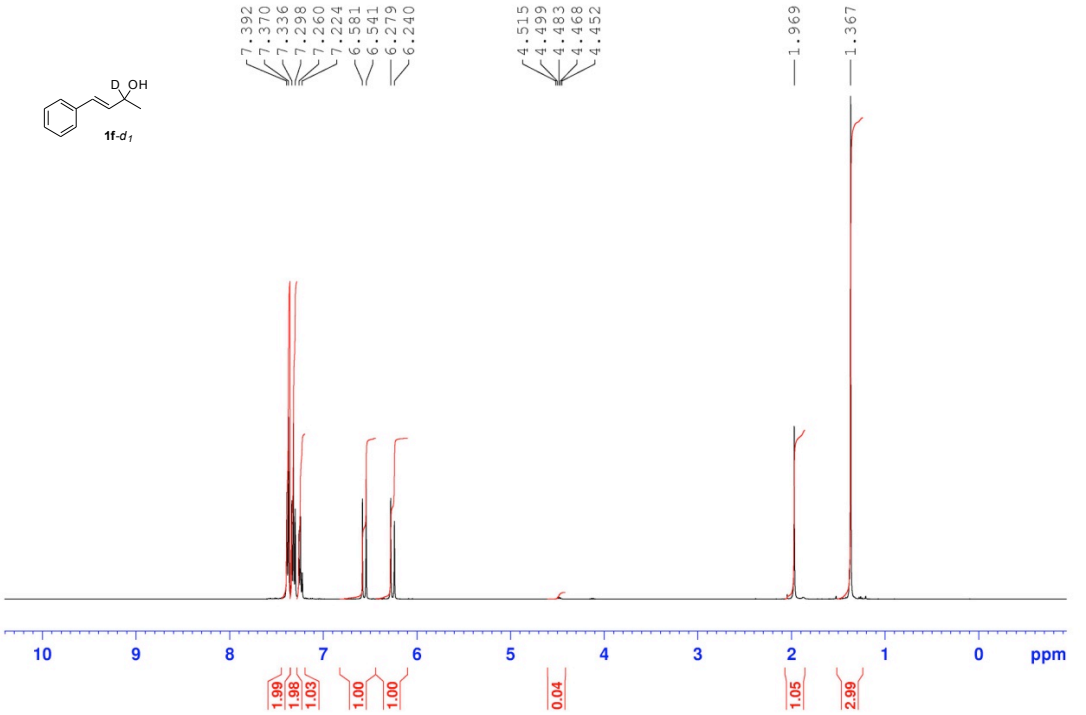
80
70
60
50
40
30
20
10
0
ppm

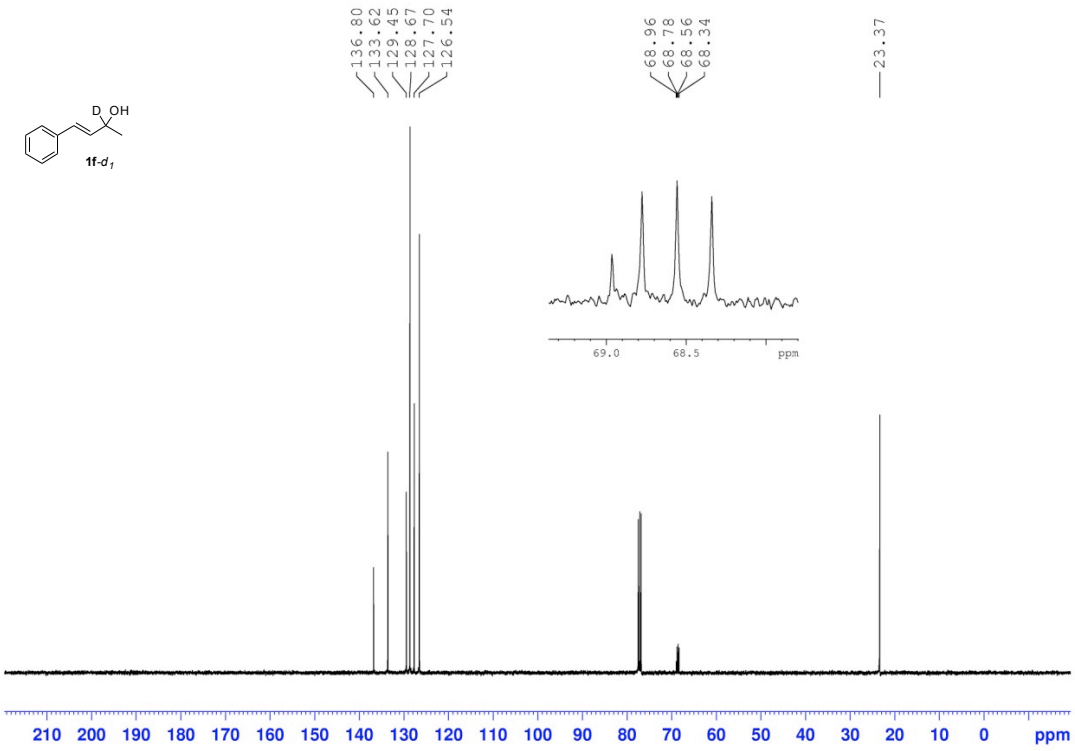

7.388
7.284
5.885
5.871
5.859
5.845
5.842
5.828
5.816
5.802
5.393
5.389
5.385
5.349
5.346
5.342
5.220
5.216
5.212
5.193
5.189
5.186
4.358
4.356
3.567
3.559
3.543
3.535
3.408
3.388
3.384
3.364
2.511
OH
BnO
1d
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
5.16
1.00
1.04
1.01
2.15
1.01
1.14
1.03
0.97

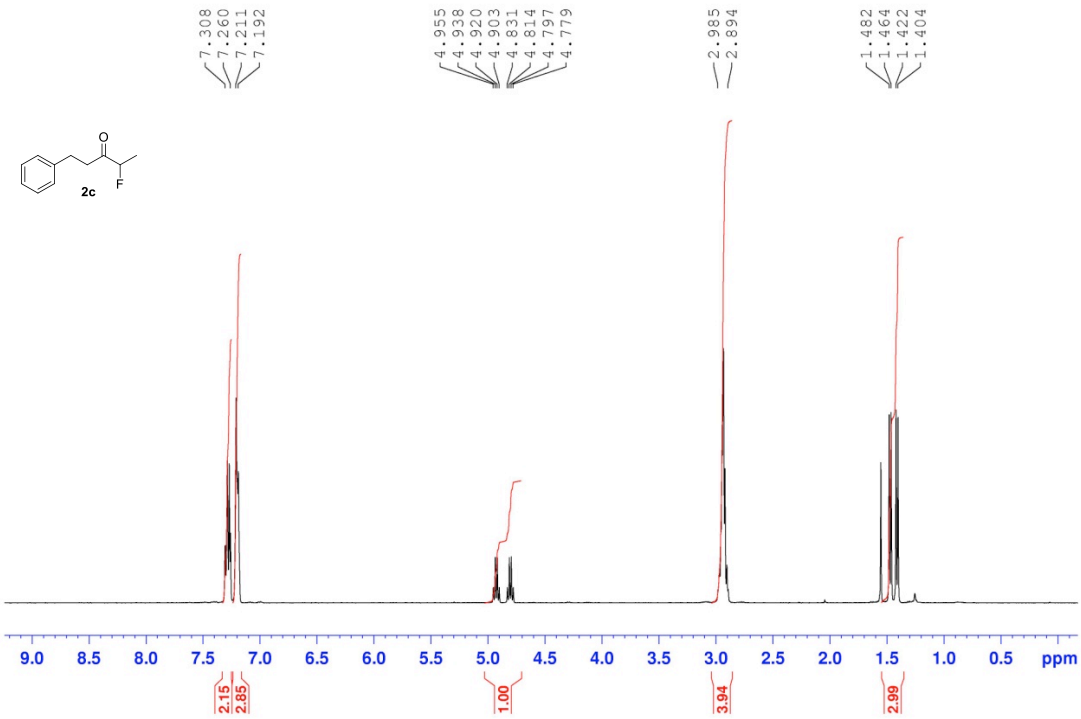

137.94
136.67
128.61
127.97
127.91
116.61
74.13
73.51
71.65
OH
BnO
1d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

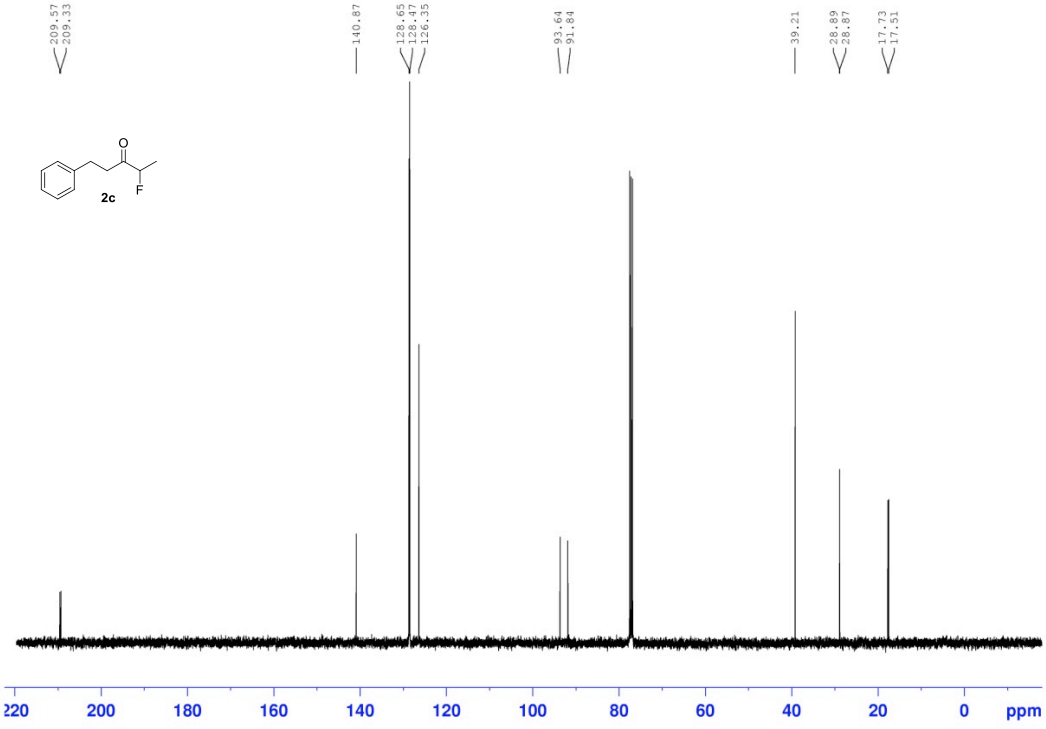

4.933
4.930
4.928
4.827
4.074
4.064
4.058
4.049
4.042
4.032
1.721
1.587
1.507
1.390
1.386
1.240
0.897
0.881
0.863
OH
1g
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.02
0.99
1.00
2.95
2.02
1.10
8.29
3.07

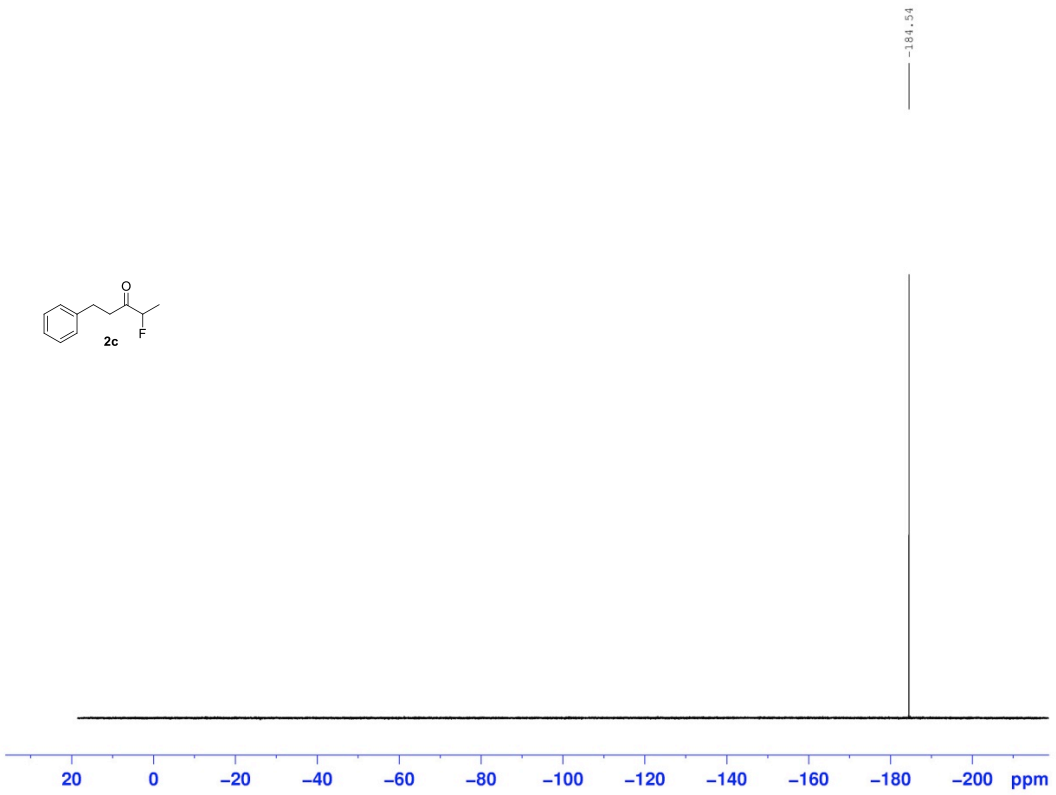

147.84
111.05
76.18
35.11
31.95
29.37
25.69
22.75
17.60
14.21
OH
1g
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

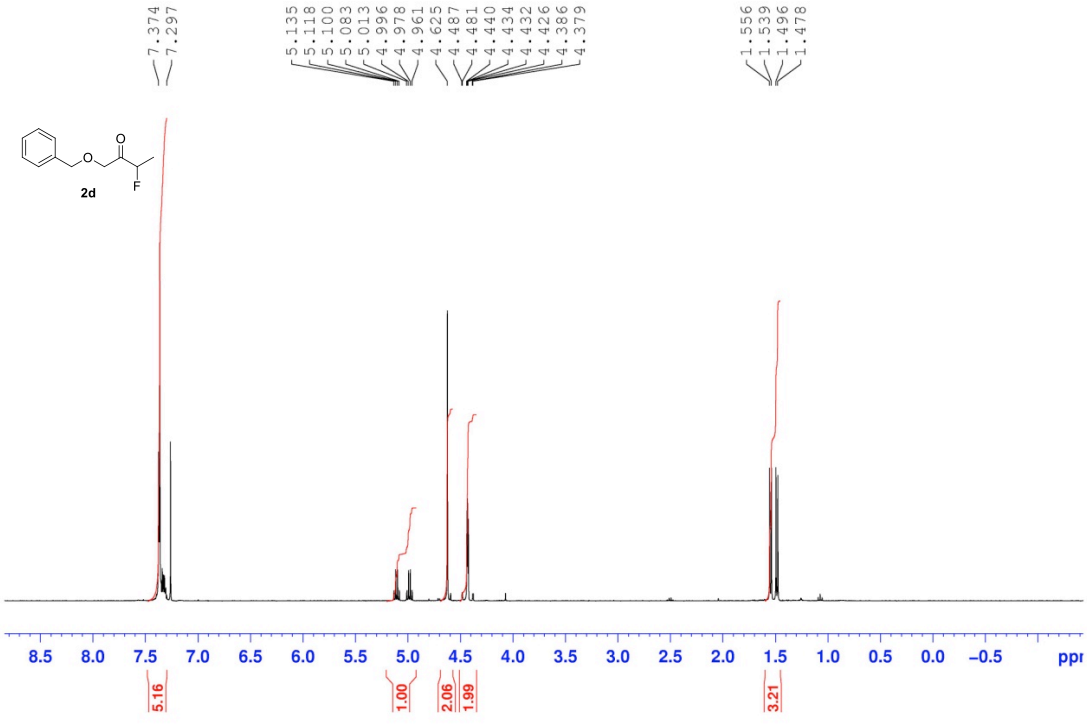

7.392
7.370
7.336
7.298
7.260
7.224
6.581
6.541
6.279
6.240
4.515
4.499
4.483
4.468
4.452
1.969
1.367
D OH
1f-d_1
10 9 8 7 6 5 4 3 2 1 0 ppm
1.99
1.98
1.03
1.00
1.00
0.04
1.05
2.99

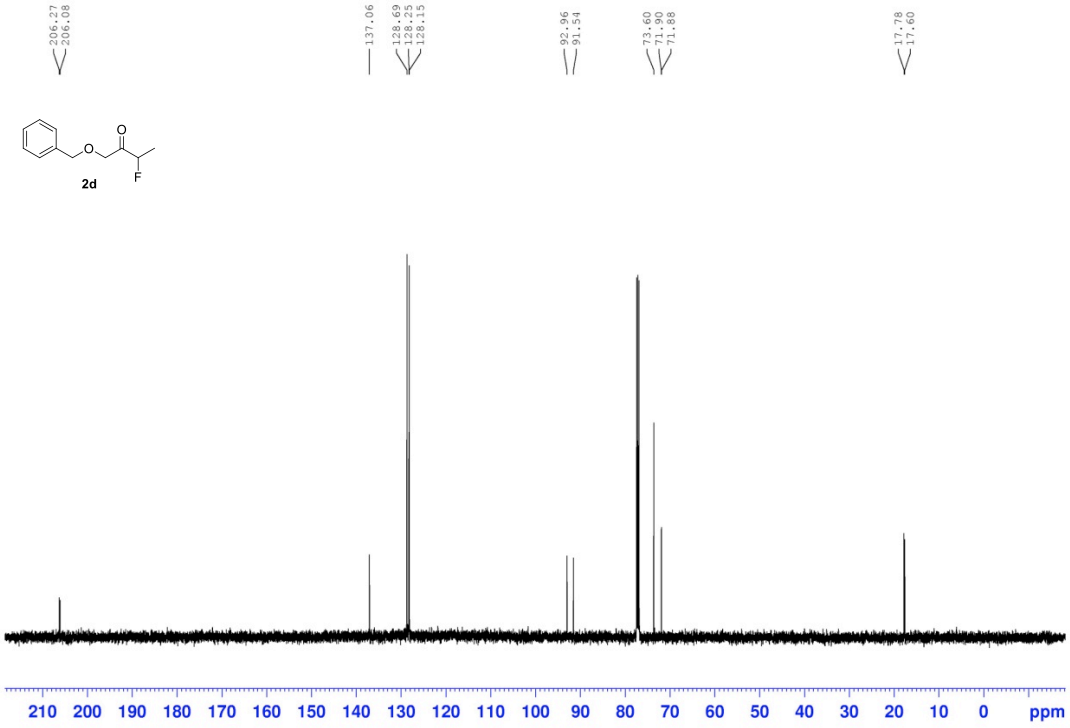

136.80
133.62
129.45
128.67
127.70
126.54
68.96
68.78
68.56
68.34
23.37
D OH
1f-d_1
69.0
68.5
ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

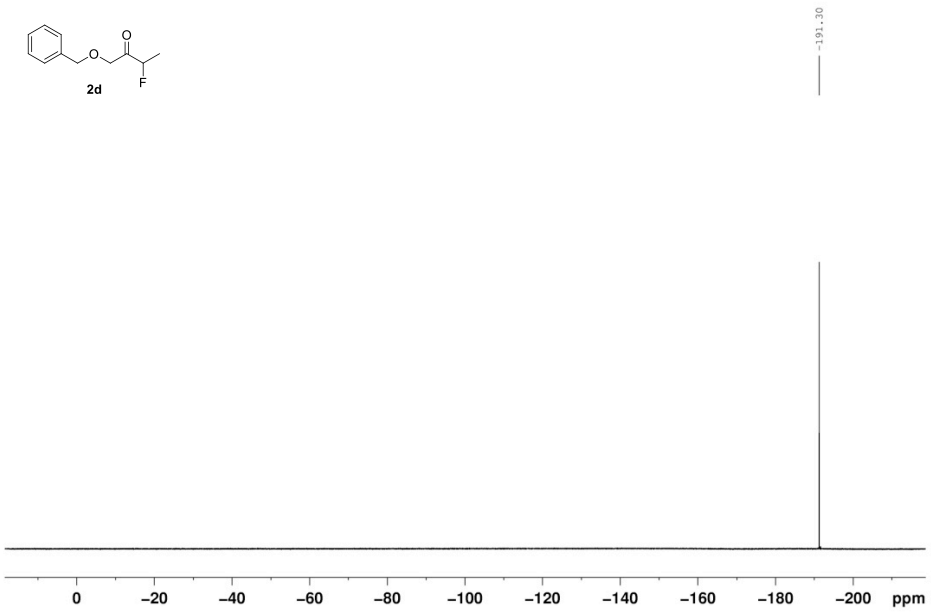

7.308
7.260
7.211
7.192
4.955
4.938
4.920
4.903
4.831
4.814
4.797
4.779
2.985
2.894
1.482
1.464
1.422
1.404
O
F
2c
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.15
2.85
1.00
3.94
2.99

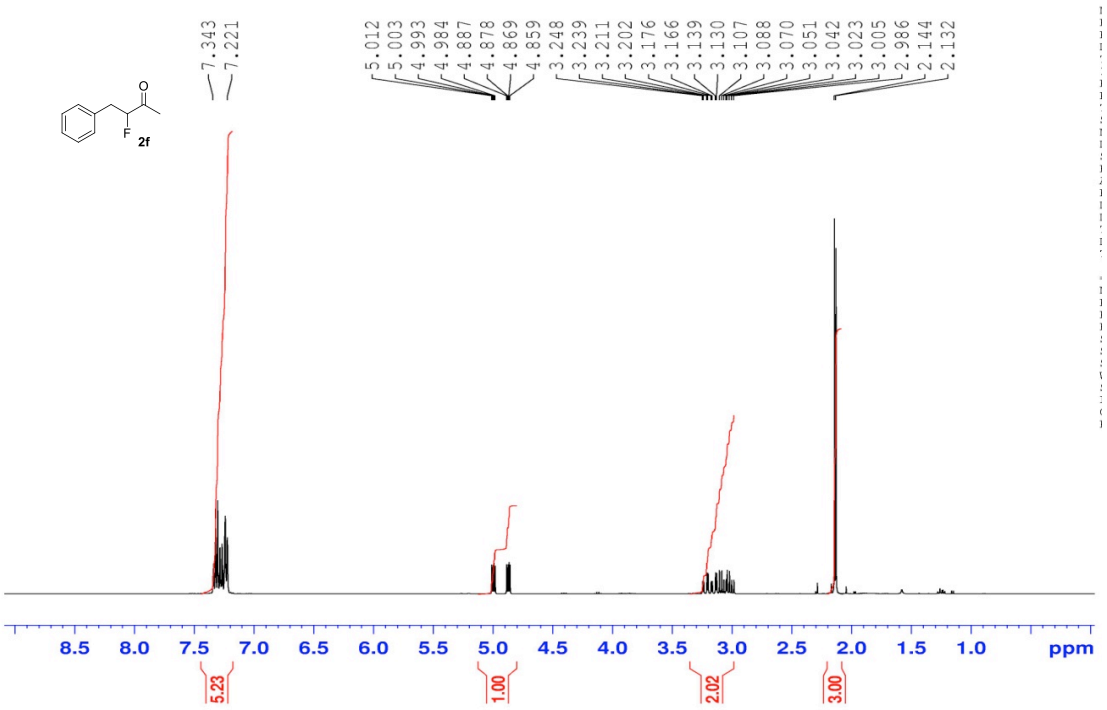

209.57
209.33
140.87
128.65
128.47
126.35
93.64
91.84
39.21
28.89
28.87
17.73
17.51
O
F
2c
220
200
180
160
140
120
100
80
60
40
20
0
ppm

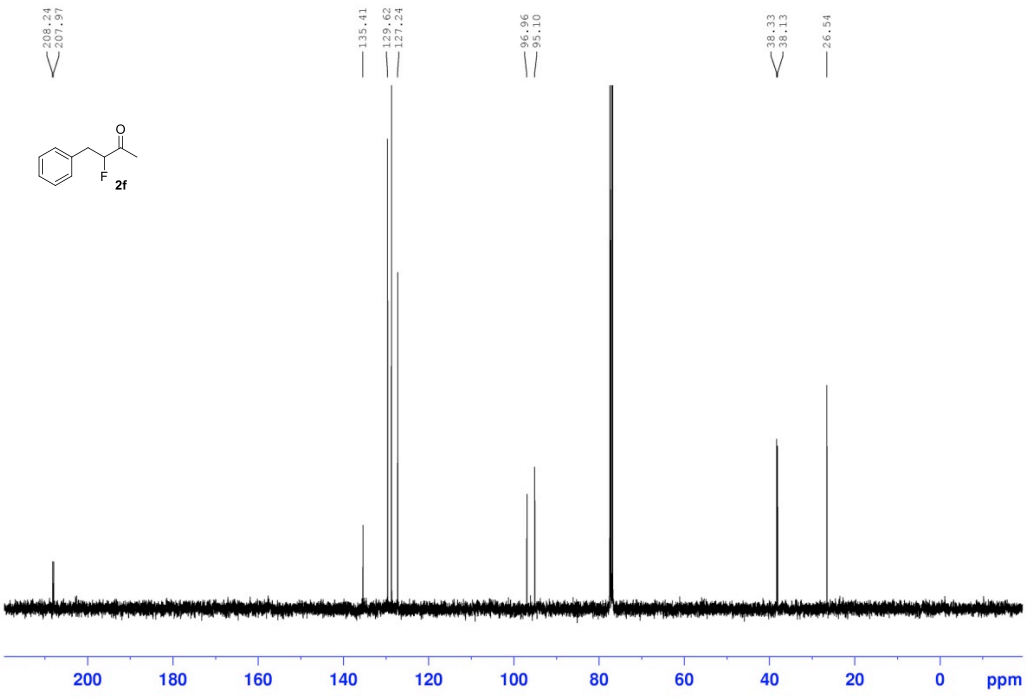

-184.54
2c
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm

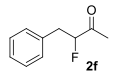

7.374
7.297
5.135
5.118
5.100
5.083
5.013
4.996
4.978
4.961
4.625
4.487
4.481
4.440
4.434
4.432
4.426
4.386
4.379
1.556
1.539
1.496
1.478
2d
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
ppm
5.16
1.00
2.06
1.99
3.21


206.27
206.08
137.06
128.69
128.25
128.15
92.96
91.54
73.60
71.90
71.88
17.78
17.60
O
O
F
2d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

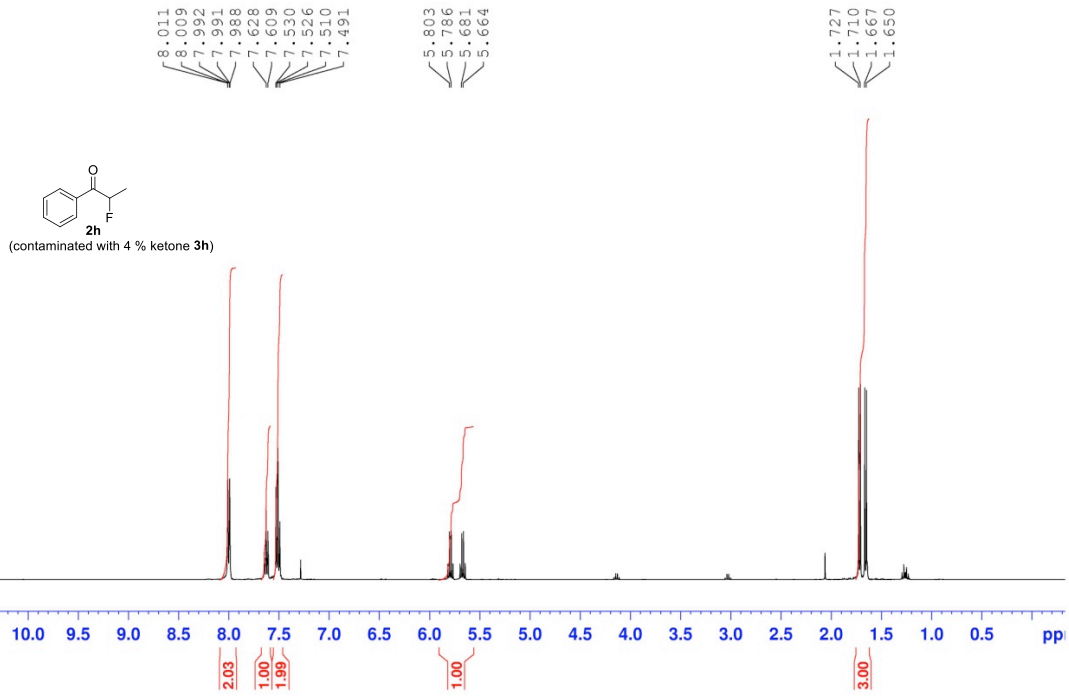

-191.30
O
O
F
2d
0 −20 −40 −60 −80 −100 −120 −140 −160 −180 −200 ppm


7.343
7.221
5.012
5.003
4.993
4.984
4.887
4.878
4.869
4.859
3.248
3.239
3.211
3.202
3.176
3.166
3.139
3.130
3.107
3.088
3.070
3.051
3.042
3.023
3.005
2.986
2.144
2.132
2f
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 ppm
5.23
1.00
2.02
3.00

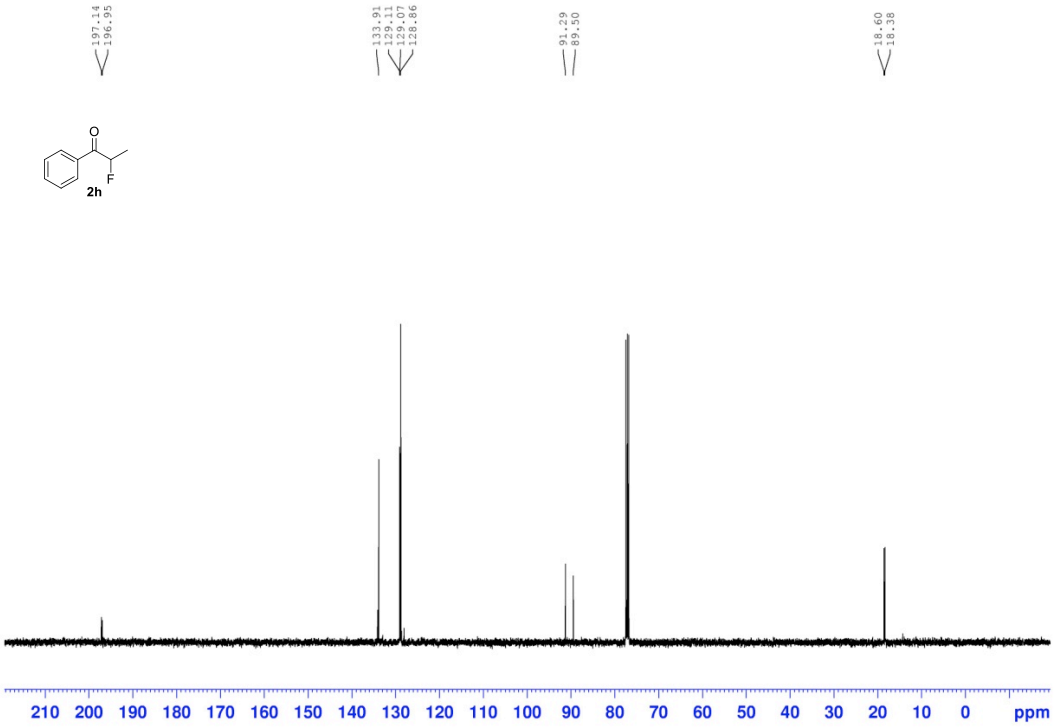

208.24
207.97
135.41
129.62
127.24
96.96
95.10
38.33
38.13
26.54
2f
200 180 160 140 120 100 80 60 40 20 0 ppm

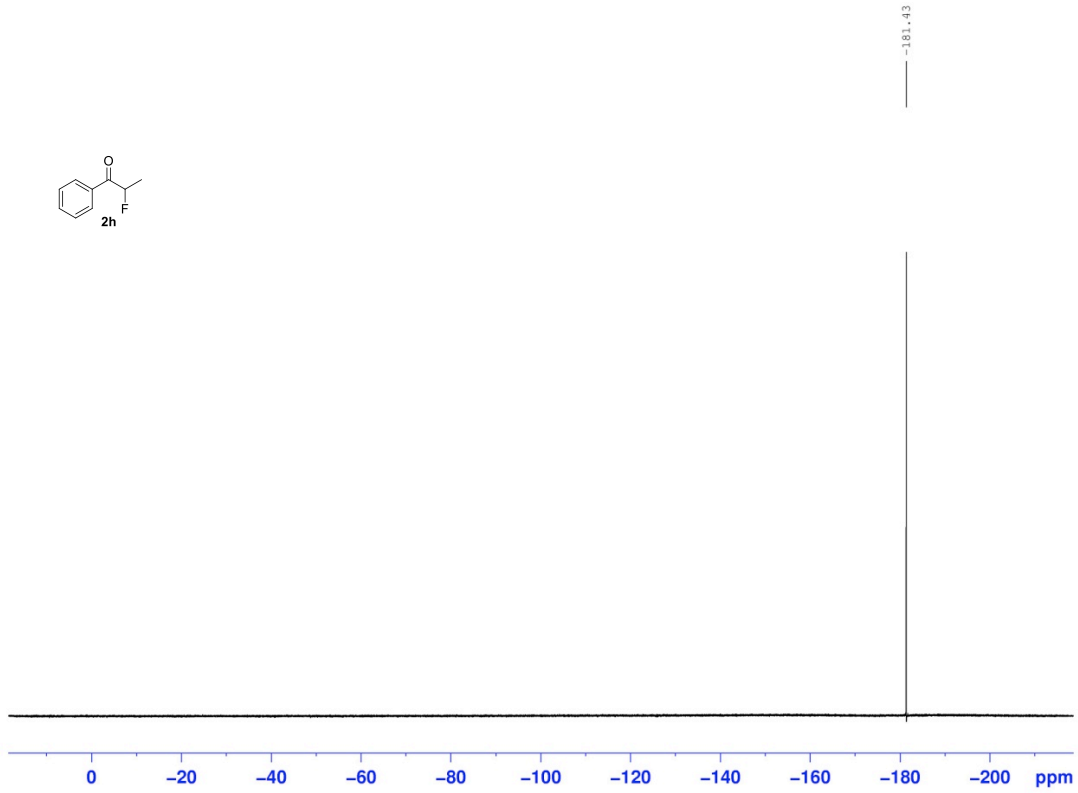


2f

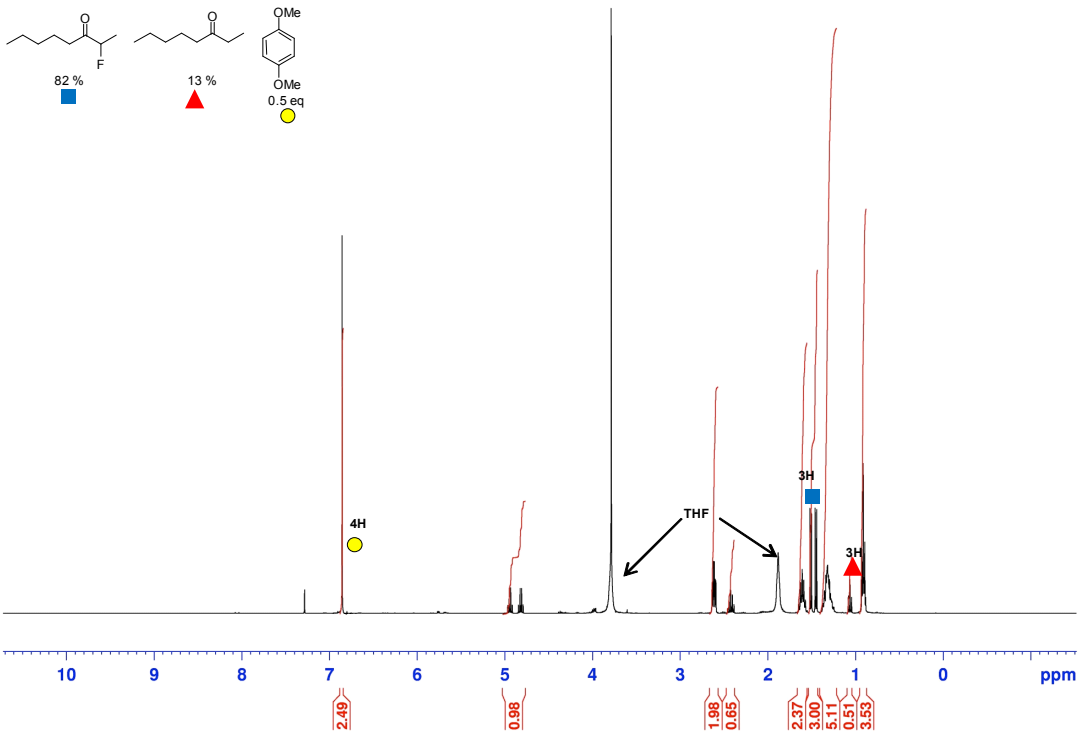


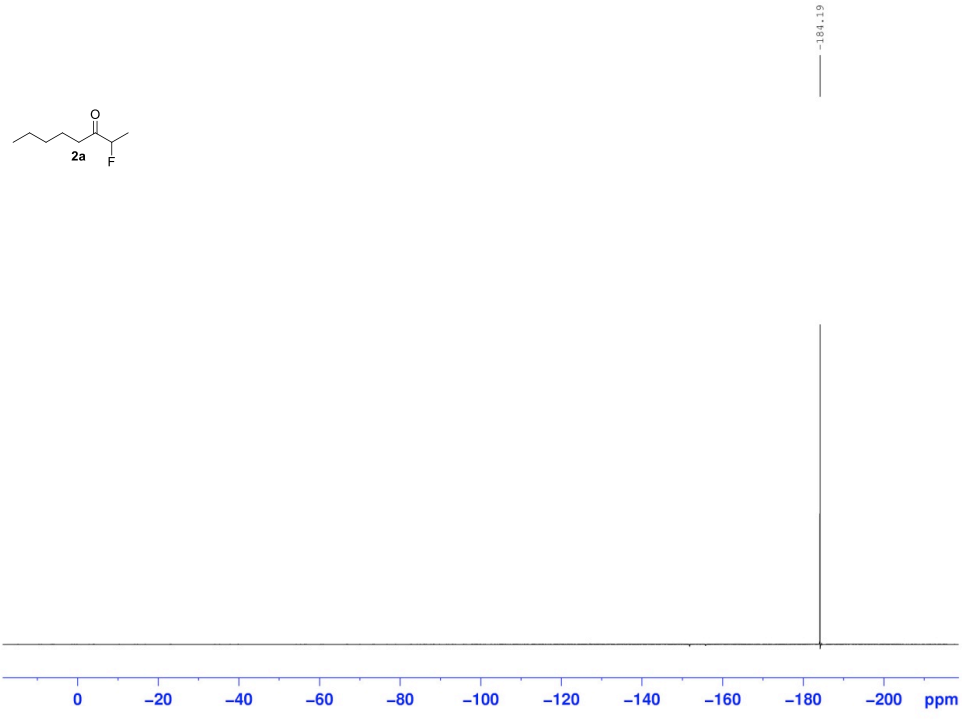
2h
(contaminated with 4 % ketone **3h**)


197.14
196.95
133.91
129.11
129.07
128.86
91.29
89.50
18.60
18.38
O
F
2h
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

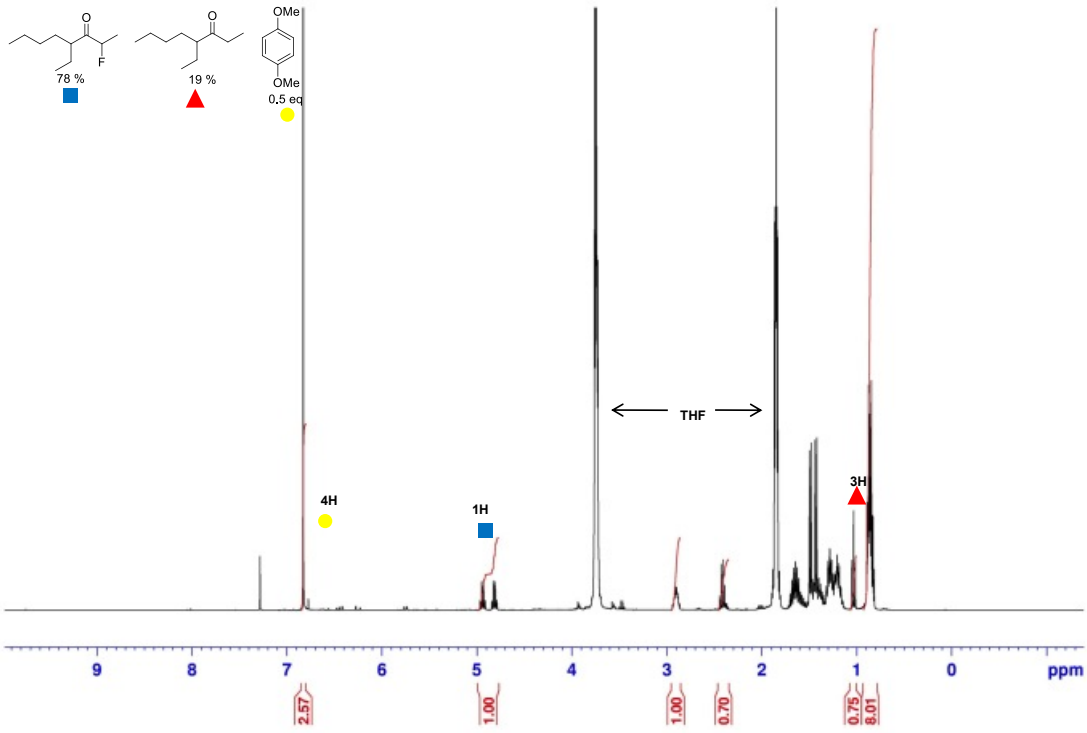

-181.43
O
F
2h
0 −20 −40 −60 −80 −100 −120 −140 −160 −180 −200 ppm

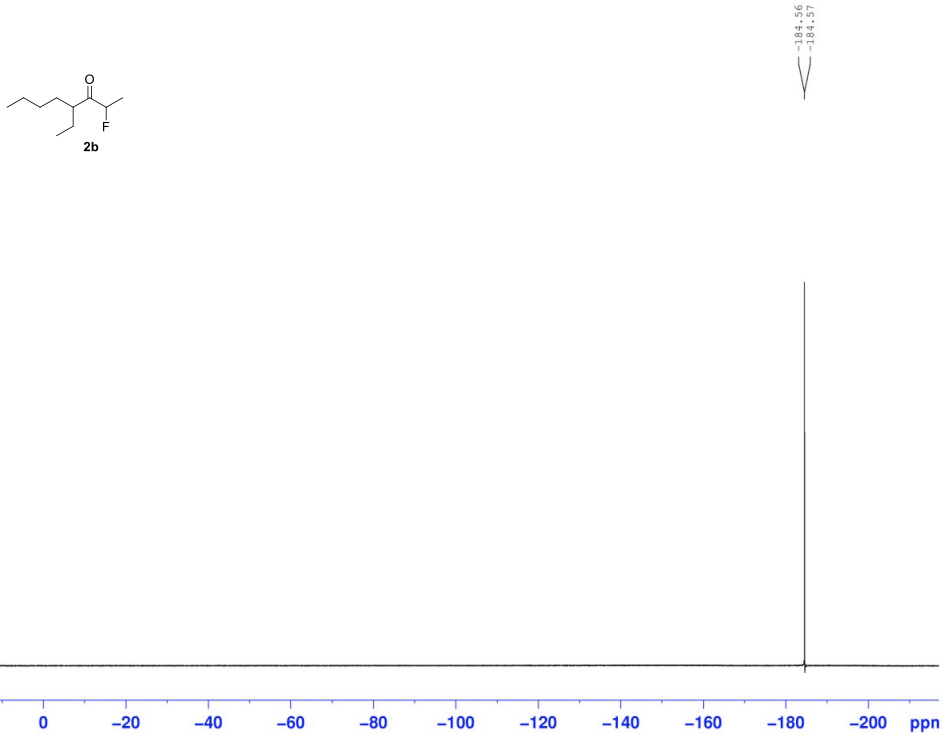
Crude NMR of **2a:**



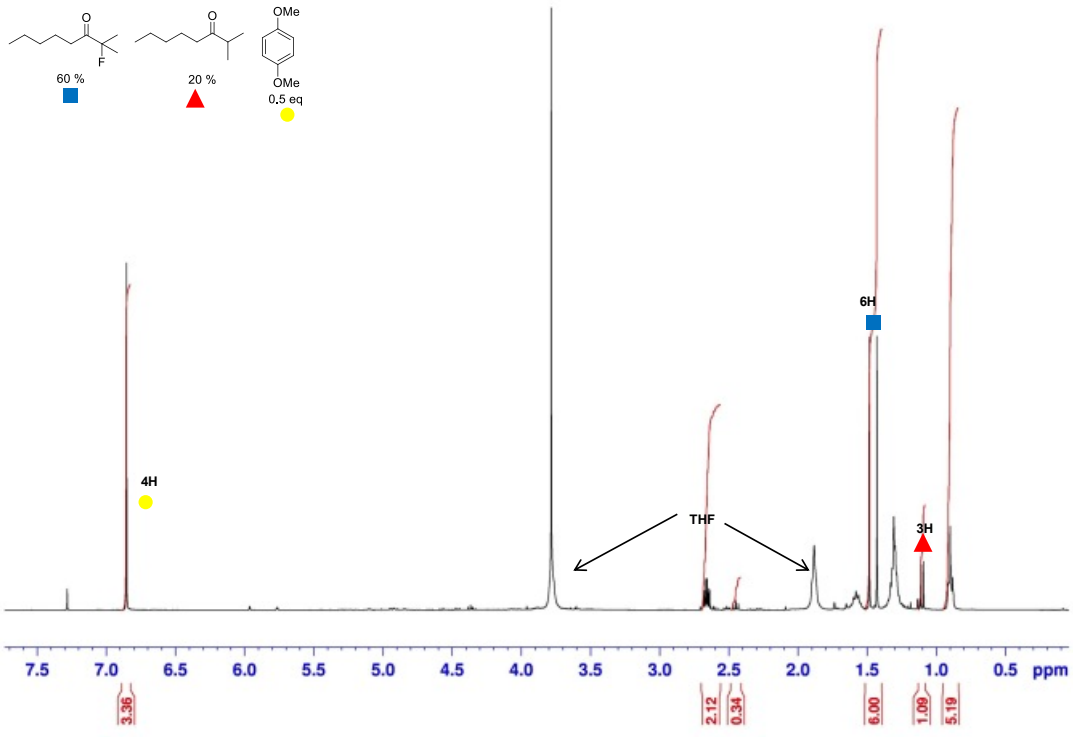


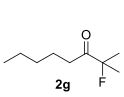
Crude NMR of **2b**

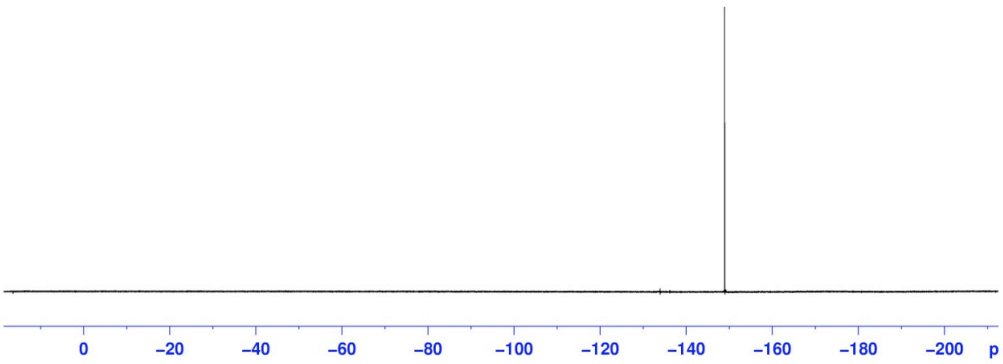




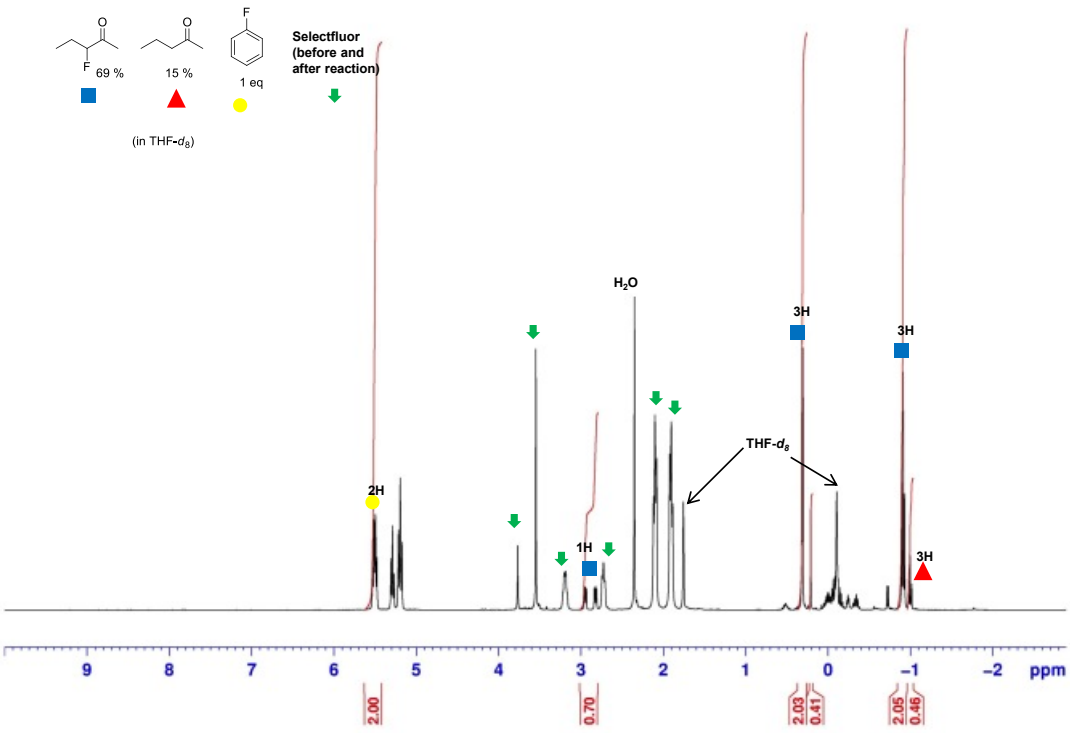
Crude NMR of **2g**

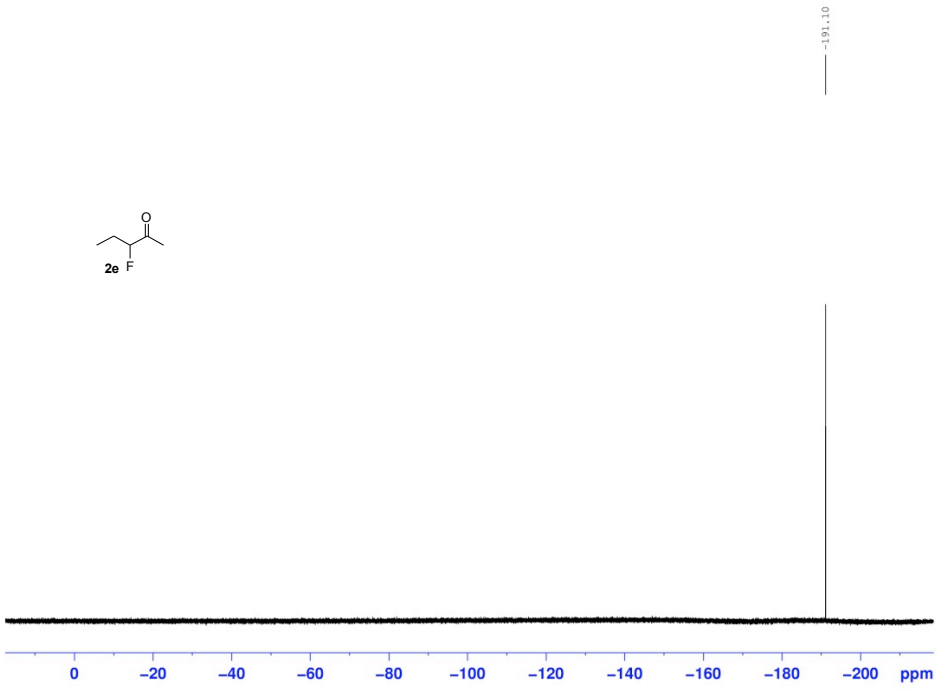




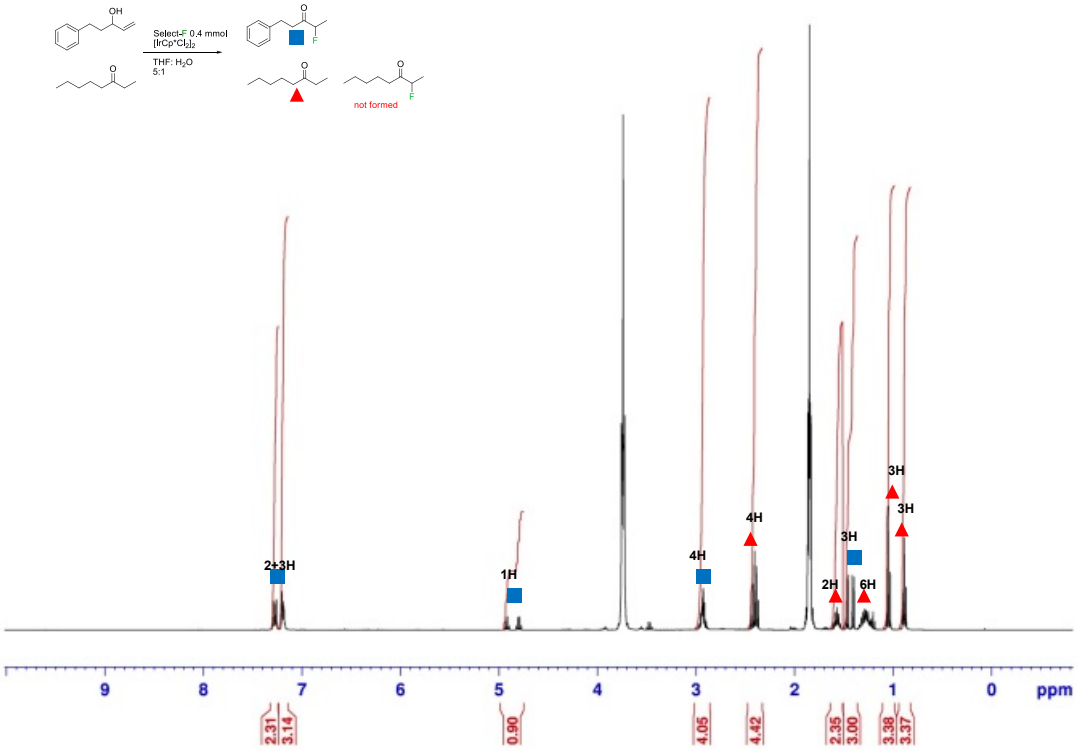


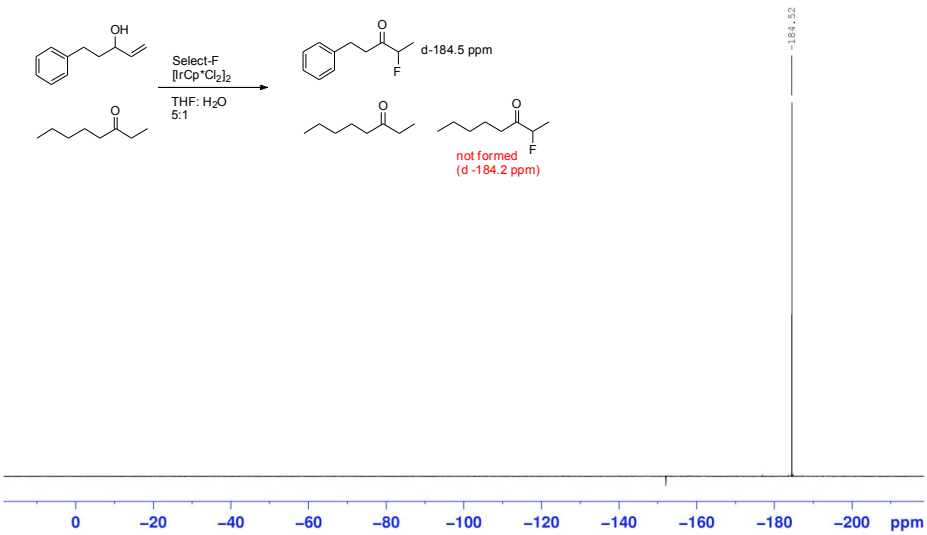
Crude NMR of **2e** in THF-d_8

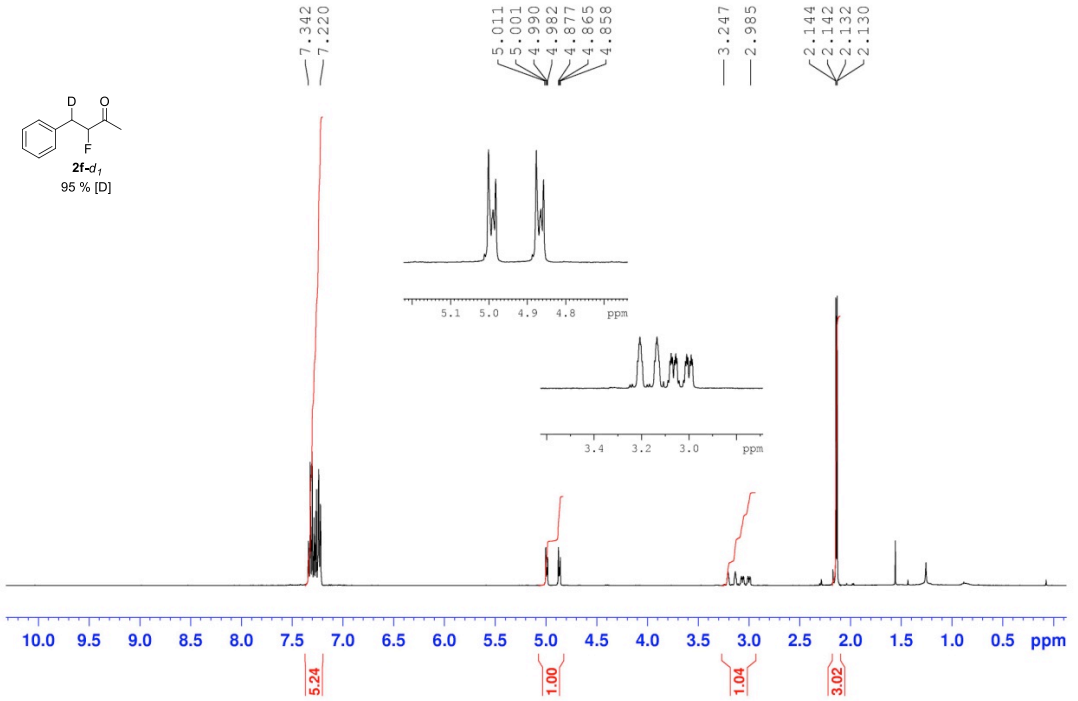


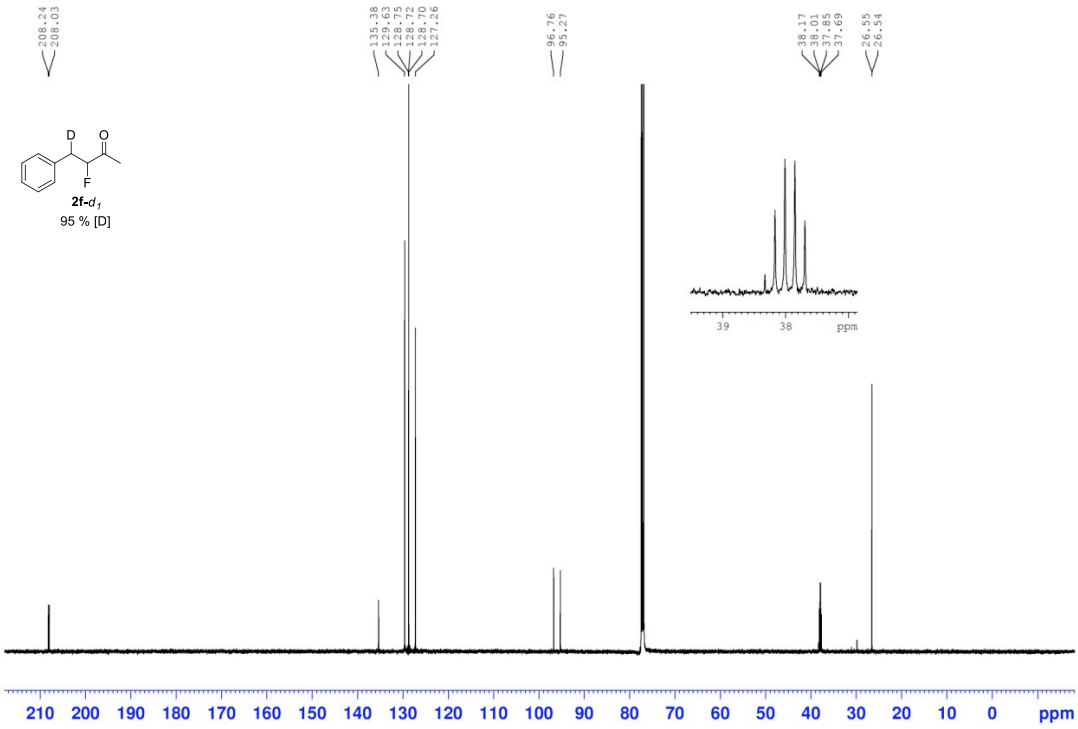


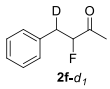
Control experiment: fluorination of allylic alcohol **1c** (1 equiv) in the presence of ketone **3a**





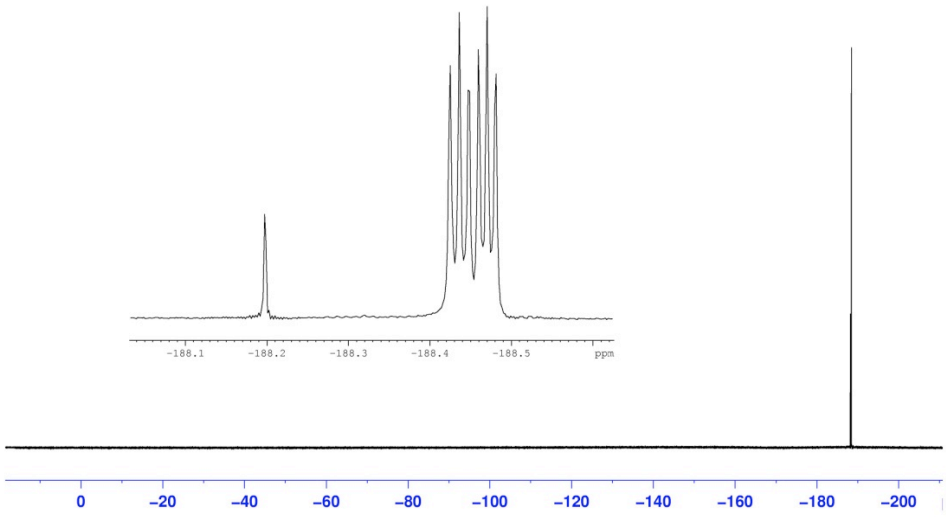

7.342
7.220
5.011
5.001
4.990
4.982
4.877
4.865
4.858
3.247
2.985
2.144
2.142
2.132
2.130
D
O
F
2f-d_1
95 % [D]
5.1 5.0 4.9 4.8 ppm
3.4 3.2 3.0 ppm
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
5.24
1.00
1.04
3.02


208.24
208.03
135.38
128.93
128.75
128.72
128.70
127.26
96.76
95.27
38.17
38.01
37.85
37.69
26.55
26.54
D
O
F
2f-d_1
95 % [D]
39 38 ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

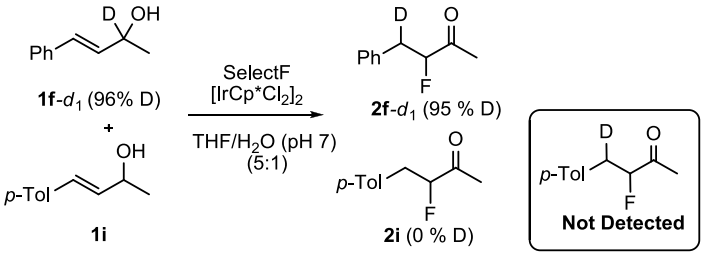


2f-d_1

95 % [D] (Two diastereomers, two 1:1:1 triplets δ 188.42 and 188.47)
5 % non-deuturated **2f** (singlet at δ 188.2)

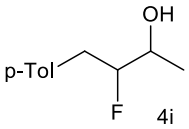


Crossover experiment of **1f**-d_1 and **1i**:



Analysis of the reaction mixture by ^{1}H , ^{19}F and ^{13}C NMR showed **2f**-d_1 and **2i** as only products. However, due to the difficulty of detecting minor amounts of deuturated **2i** by NMR (overlapping signals), the ketones were reduced to the corresponding alcohols (**4f, 4i**) with $NaBH_4$ in THF/H_2O, and analysed by HRMS-ESI (unreduced **2i** and **2f**-d_1 did not give sufficient intensities accurate detection of small amounts of deuterium).

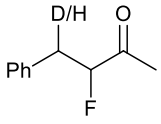
The height of m/z peaks were corrected for the natural ^{13}C content .



4i

HRMS-ESI: *m/z* 205.1009 ([M+Na]$^+$, calcd. for $C_{11}H_{15}F_1O_1Na_1$: 205.0999) 100 %

HRMS-ESI: *m/z* calcd. for $C_{11}D_1H_{14}F_1O_1Na_1$: 206.1062 0 %



4f

HRMS-ESI: *m/z* 192.0913 ([M+Na]$^+$, calcd. for $C_{10}H_{12}D_1F_1O_1Na_1$: 192.0905) 95 %

HRMS-ESI: *m/z* 191.0851 ([M+Na]$^+$, calcd. for $C_{10}H_{13}F_1O_1Na_1$: 191.0843) 5 %

1 Kim, J. W.; Koike, T.; Kotani, M.; Yamaguchi, K.; Mizuno, N. *Chemistry – A European Journal* **2008**, *14*, 4104-4109.
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3 L. J. Gazzard, W. B. Motherwell, D. A. Sandham, *J. Chem. Soc., Perkin Trans. 1* **1999**, 979.
4 Ghosh, A. K.; Leshchenko, S.; Noetzel, M. *The Journal of Organic Chemistry* **2004**, *69*, 7822-7829.
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