Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Metal-Free Visible-light Synthesis of Quaternary α-Perfluoroalkyl Aldehydes via an Enamine Intermediate

Haruna Matsui, Mao Murase, Tomoko Yajima

Department of Chemistry, Ochanomizu University, 2-1-1, Otsuka, Bunkyo-ku, Tokyo 112-8610, Japan

Contents

1. Materials and instrumentation

All reactions were carried out under a nitrogen atomosphere. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a JEOL JNM-ECS400 (399.78 MHz for ^{1}H, 100.5 MHz for ^{13}C, and 376.2 MHz for ^{19}F) or BRUKER AVANCE 600 (600 MHz for ^{1}H, 150 MHz for ^{13}C) spectrometer with $CDCl_3$ as the solvent and tetramethylsilane (δ 0 ppm for ^{1}H), chloroform-*d* ($CDCl_3$: δ 76.9 ppm for ^{13}C) and trichlorofluoromethane ($CFCl_3$: 0 ppm for ^{19}F) as an internal standard unless otherwise noted. IR and UV-vis spectra were taken on JASCO FTIR-4100 and V-670 respectively. HRMS were obtaind with a JEOL JMS-T100GCv (FD) or JEOL JMS-700 (FAB, EI). Precoated Merck Kieselgel 60 F254 and Kanto silica gel 60 (spherical neutral) were used for thin layer chromatography and flash chromatography, respectively. All chemicals were used without further purification.

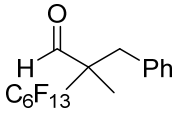
Optical absorption spectra was recorded in CH_2Cl_2 in 1 mm path quartz cuvettes using a JASCO V-650 UV-visible Spectrophotometer.

2. General procedure for perfluoroalkylation.

To an oven-dried 20 ml two-necked flask equipped with a magnetic stir bar was added aldehyde (0.26 mmol). The flask was fitted with a septum and degassed through alternating vacuum evacuation/argon backfill (×3) before dry CH_2Cl_2 (2.5 ml) was added. Then amine (2.0 equiv) and perfluoroalkyl iodide (1.1 equiv) was added. The mixture was stirred for corresponding time at room temperature under 23 W CFL lamp irradiation. The resulting mixture was extracted with ether and washed with brine. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to get product.

3. Characterization data of products.

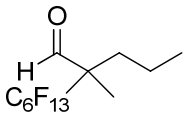
2-Benzyl-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-2-methyloctanal (**3a**)



3a

Colorless crystal; mp 64 ºC; $[\alpha]^{25}_{D}$ -8.4 (*c* 0.7, $CHCl_3$, 86% ee);^{1}H NMR (400 MHz, $CDCl_3$) δ 9.75 (1H, s), 7.27 (3H, m), 7.04 (2H, d, *J* = 12.0 Hz), 3.46 (1H, d, *J* = 14.0 Hz), 2.98 (1H, d, *J* = 14.0 Hz), 1.21 (3H, s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 196.3, 132.8, 130.9 (2C), 128.4 (2C), 127.5, 120.0-108.3 (m), 56.4 (t, *J* = 18.6 Hz), 35.1 (t, *J* = 5.5 Hz), 12.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -81.3 (3F), -114.0 (1F, d, *J* = 288.8 Hz), -116.7 (1F, d, *J* = 288.8 Hz), -117.7 (1F, d, *J* = 288.8 Hz), -119.3 (1F, d, *J* = 288.8 Hz), -121.63 (1F, d, *J* = 300.4 Hz), -123.0 (1F, d, *J* = 300.4 Hz), -122.5 (1F, d, *J* = 200.4 Hz), -123.8 (1F, d, *J* = 300.4 Hz), -125.9 (1F, d, *J* = 288.8 Hz), -127.2 (1F, d, *J* = 288.8 Hz); IR (neat, cm^{-1}) 1735, 1240, 1045, 746, 696, 663, 572, 513; HRMS (EI^+) calcd for $C_{16}H_{11}F_{13}O$ $[M]^+$: 466.0602. Found: 466.0592.

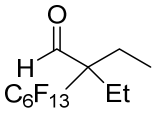
3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluoro-2-methy-2-propyloctanal (**3b**)



3b

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.63 (1H, s), 1.91 (1H, dt, *J* = 4.4 Hz, 12.6 Hz), 1.74 (1H, dt, *J* = 5.2 Hz, 12.8 Hz), 1.38 (1H, m), 1.32 (3H, s), 1.15 (1H, m), 0.95 (3H, t, *J* = 7.2 Hz); ^{13}C NMR (151 MHz, $CDCl_3$) δ 196.7, 120.5-108.3 (m), 55.8 (t, *J* = 18.1 Hz), 31.4, 16.3, 14.5, 12.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -80.7 (3F), -114.2 (1F, d, *J* = 288.8 Hz), -115.7 (1F, d, *J* = 288.8 Hz), -117.7 (1F, d, *J* = 300.4 Hz), -119.2 (1F, d, *J* = 300.4 Hz), -121.2 (1F, d, *J* = 300.4 Hz), -122.1 (1F, d, *J* = 300.4 Hz), -122.3 (1F, d, *J* = 300.4 Hz), -123.2 (1F, d, *J* = 300.4 Hz), -125.5 (1F, d, *J* = 288.8 Hz), -126.6 (1F, d, *J* = 288.8 Hz); IR (neat, cm^{-1}) 2970, 2882, 1740, 1228, 734, 696, 656, 527; HRMS (FD^+) calcd for $C_{12}H_{11}OF_{13}$ $[M]^+$: 418.0602. Found: 418.0641.

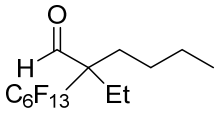
2,2-Diethyl 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctanal (**3c**)



3c

Colorless oil ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.58 (1H, s), 1.93 (4H, m), 0.89 (6H, t, *J* = 7.2 Hz); ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.8, 121.5-108.3 (m), 58.4 (t, *J* = 18.1 Hz), 18.1 (2C), 7.0 (2C); ^{19}F NMR (376 MHz, $CDCl_3$) δ -81.3 (3F), -111.9 (2F), -120.3 (2F), -122.3 (2F), -123.2 (2F), -126.6 (2F); IR (neat, cm^{-1}) 2982, 2738, 1230, 696, 654; HRMS (FD^+) calcd for $C_{12}H_{11}OF_{13}$ $[M]^+$: 418.0602. Found: 418.0565.

2-Ethyl 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-2-propyloctanal (**3d**)

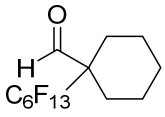


3d

Colorless oil ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.58 (1H, s), 1.96 (2H, m), 1.83 (2H, m), 1.45 (2H, m), 1.31 (1H, m), 1.13 (1H, m), 0.92 (3H, t, *J* = 7.2 Hz), 0.88 (3H, t, *J* = 7.2 Hz); ^{13}C NMR (151 MHz, $CDCl_3$) δ 197.1, 120.8-107.9 (m), 57.9 (t, *J* = 18.1 Hz), 24.2, 23.1, 17.9, 13.9 (2C), 6.9; ^{19}F NMR (376 MHz,

$CDCl_3$) δ -81.3 (3F), -111.9 (2F), -120.2 (2F), -122.3 (2F), -123.2 (2F), -126.6 (2F); IR (neat, cm^{-1}) 2965, 1737, 1230, 696, 656; HRMS (FD^+) calcd for $C_{14}H_{15}OF_{13}$ $[M]^+$: 446.0915. Found: 446.0867.

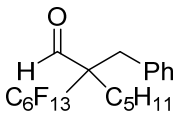
1-(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)cycrohexanecarboaldehyde (**3e**)



3e

Colorless oil ; ^1H NMR (400 MHz, $CDCl_3$) δ 9.61 (1H, s), 2.45 (2H, m), 1.71 (5H, m), 1.42 (2H, m), 1.18 (1H, m); ^{13}C NMR (151 MHz, $CDCl_3$) δ 197.7, 120.1-108.1 (m), 55.6 (t, *J* = 18.1 Hz), 24.6 (2C), 24.2, 21.3 (2C); ^{19}F NMR (376 MHz, $CDCl_3$) δ -81.3 (3F), -116.9 (2F), -118.8 (2F),-122.3 (2F), -123.3 (2F), -126.6 (2F); IR (neat, cm^{-1}) 2945, 2864, 1740, 1234, 1192, 1171, 1121, 694, 656, 564, 530; HRMS (EI^+) calcd for $C_{12}H_{10}F_{13}$ $[M\text{-}CHO]^+$: 401.0575. Found: 401.0599.

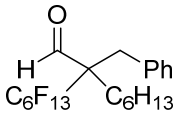
2-Benzyl-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-2-penthyloctanal (**3f**)



3f

Colorless oil ; ^1H NMR (400 MHz, $CDCl_3$) δ 9.70 (1H, s), 7.27 (3H, m), 7.09 (2H, d, *J* = 6.0 Hz), 3.43 (1H, d, *J* = 14.8 Hz), 3.13 (1H, d, *J* = 14.8 Hz), 1.77 (1H, m), 1.63 (1H, m), 1.48 (1H, m), 1.37 (1H, m), 1.29 (2H, m), 1.21 (2H, m), 0.88 (3H, t, *J* = 7.2 Hz); ^{13}C NMR (151 MHz, $CDCl_3$) δ 197.0, 133.4, 130.7 (2C), 128.5 (2C), 127.4, 120.9-108.1 (m), 59.2 (t, *J* = 18.1 Hz), 32.7, 32.3, 27.1, 22.8, 22.3, 14.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -81.3 (3F, s), -109.1 (1F, d, *J* = 288.8 Hz), -112.7 (1F, d, *J* = 288.8 Hz), -119.5(2F, s), -121.5 (1F, d, *J* = 300.4 Hz), -122.8 (1F, d, *J* = 300.4 Hz), -122.5 (1F, d, *J* = 300.4 Hz), -123.8 (1F, d, *J* = 300.4 Hz), -126.0 (1F, d, *J* = 300.4 Hz), -127.2 (1F, d, *J* = 300.4 Hz); IR (neat, cm^{-1}) 2959, 2932, 1736, 1456, 1225, 698, 658, 511; HRMS (EI^+) calcd for $C_{20}H_{19}OF_{13}$ $[M]^+$: 522.1228 Found: 522.1244.

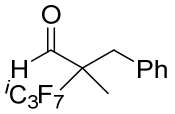
2-Benzyl-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-2-hexyloctanal (**3g**)



3g

Colorless oil ; ^1H NMR (400 MHz, $CDCl_3$) δ 9.70 (1H, s), 7.30 (3H, m), 7.09 (2H, m), 3.43 (1H, d, *J* = 14.8 Hz), 3.13 (1H, d, *J* = 14.4 Hz), 1.78 (1H, m), 1.65 (1H, m), 1.49 (1H, m), 1.33 (1H, m), 1.26 (6H, m), 0.88 (3H, t, *J* = 7.2 Hz); ^{13}C NMR (151 MHz, $CDCl_3$) δ 197.0, 133.4, 130.7 (2C), 128.5 (2C), 127.4, 120.6-108.3 (m), 59.2 (t, *J* = 18.1 Hz), 32.7, 31.5, 29.8, 27.1, 23.1, 22.6, 14.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -81.3 (3F, s), -109.1 (1F, d, *J* = 288.8 Hz), -112.6 (1F, d, *J* = 288.8 Hz), -119.4 (2F, s), -121.5 (1F, d, *J* = 300.4 Hz), -122.8 (1F, d, *J* = 300.4 Hz), -122.5 (1F, d, *J* = 300.4 Hz), -123.8 (1F, d, *J* = 300.4 Hz), -126.0 (1F, d, *J* = 300.4 Hz), -127.2 (1F, d, *J* = 300.4 Hz); IR (neat, cm^{-1}) 2958, 2930, 1740, 1456, 1363, 1226, 734, 698, 658, 511; HRMS (EI^+) calcd for $C_{21}H_{21}OF_{13}$ $[M]^+$: 536.1385. Found: 536.1387.

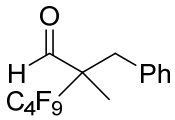
2-Benzyl-3,4,4,4-tetrafluoro-3-trifluoromethyl-2-methylbutanal (**5**)



5

Colorless oil ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.78 (1H, s), 7.29 (3H, m), 7.03 (2H, m), 3.57 (1H, d, *J* = 1.4 Hz), 2.97 (1H, d, *J* =13.6 Hz), 1.24 (3H, s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 196.0 (d, *J* = 7.5 Hz), 133.2, 131.0 (2C), 128.6 (2C), 127.3, 121.0 (dq, *J* = 289.5, 30.0 Hz), 95.1 (dsep, *J* = 211.3, 30.0 Hz), 53.7 (d, *J* = 16.5 Hz), 36.0, 13.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -69.0 (3F, s), -70.0 (3F, s), -181.7 (1F, s); IR (neat, cm^{-1}) 1741, 1456, 1290, 993, 977, 744, 702; HRMS (EI^+) calcd for $C_{13}H_{11}F_7O$ $[M]^+$: 316.0698. Found: 316.0691.

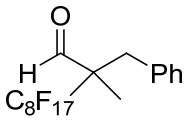
2-Benzyl-3,3,4,4,5,5,6,6,6-nonafluoro-2-methylhexanal (**6**)



6

Colorless crystal; mp 64 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.75 (1H, s), 7.31 (3H, m), 7.05 (2H, m), 3.46 (1H, d, *J* = 14.4 Hz), 2.98 (1H, d, *J* = 14.4 Hz), 1.21 (3H, s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 196.1, 133.1, 130.9 (2C), 128.5 (2C), 127.5, 120.3-106.3 (m), 56.6 (t, *J* = 18.1 Hz), 35.5, 12.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -81.3 (3F), -114.3 (1F, d, *J* = 288.8 Hz), -116.7 (1F, d, *J* = 288.8 Hz), -118.4 (1F, d, *J* = 300.4 Hz), -120.6 (1F, d, *J* = 300.4 Hz), -125.4 (1F, d, *J* = 300.4 Hz), -127.4 (1F, d, *J* = 300.4 Hz); IR (neat, cm^{-1}) 1735, 1460, 1356, 1150, 889, 756, 738, 702; HRMS (EI^+) calcd for $C_{14}H_{11}F_9O$ $[M]^+$: 366.0666. Found: 366.0664.

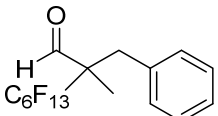
2-Benzyl-3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-2-methyldecanal (**7**)



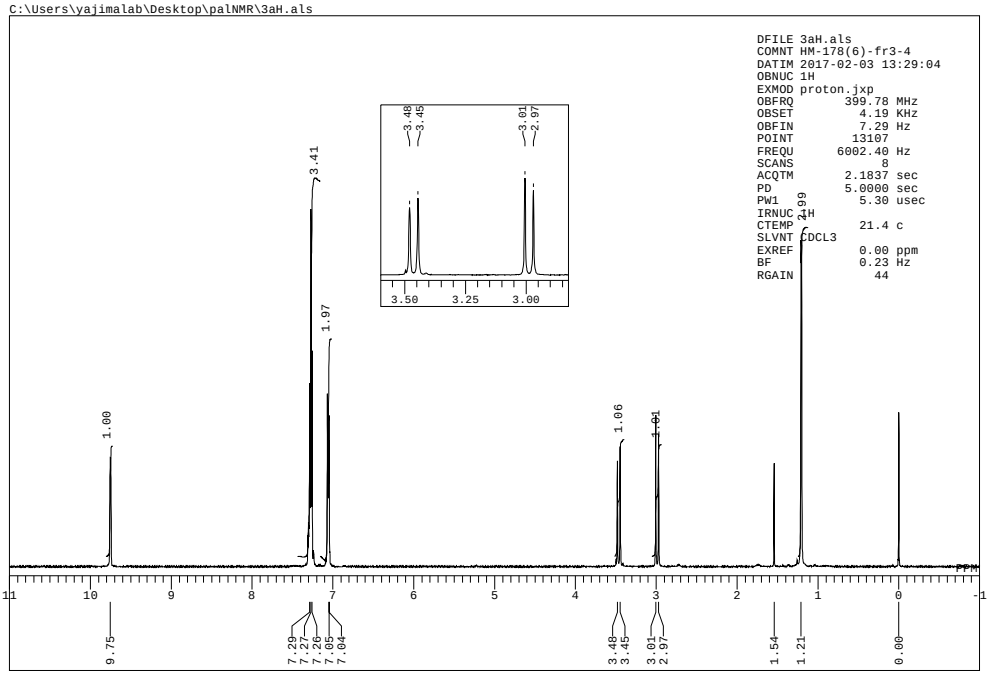
7

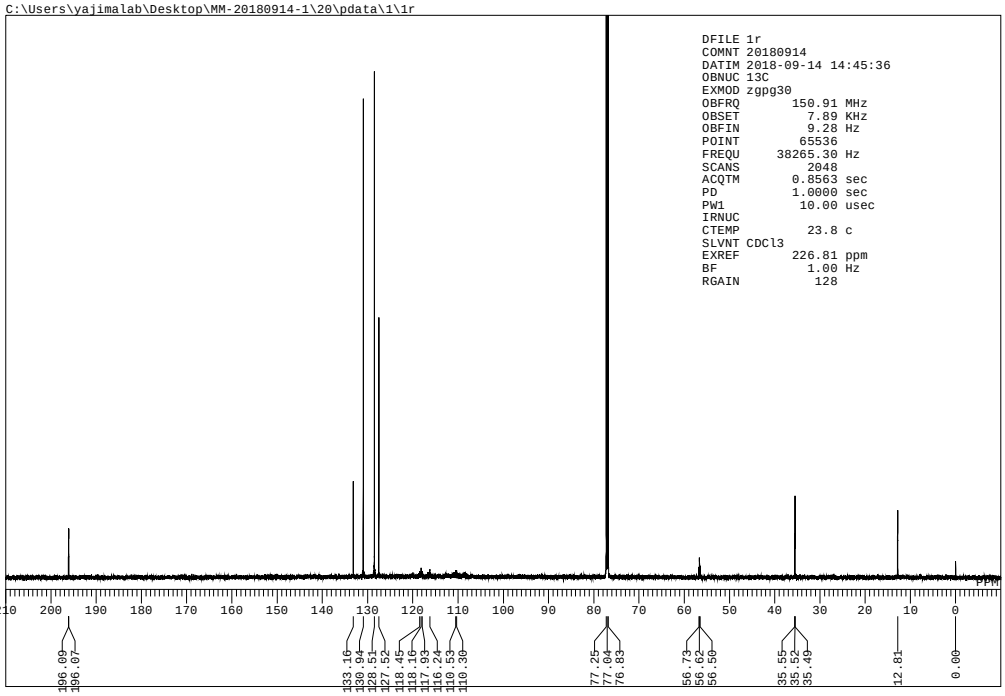
Colorless crystal; mp 96 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.75 (1H, s), 7.30 (3H, m), 7.06 (2H, m), 3.46 (1H, d, *J* = 14.4 Hz), 2.99 (1H, d, *J* = 14.4 Hz), 1.21 (3H, s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 196.1, 133.1, 130.1 (2C), 128.5 (2C), 127.5, 120.2-106.4 (m), 56.6 (t, *J* = 18.1 Hz), 35.8, 12.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -81.3 (3F, s), -114.1 (1F, d, *J* = 289.1 Hz), -116.7 (1F, d, *J* = 289.1 Hz), -117.7 (1F, d, *J* = 300.4 Hz), -119.2 (1F, d, *J* = 300.4 Hz), -122.3 (8F, m), -126.1 (1F, d, *J* = 300.4 Hz), -127.1 (1F, d, *J* = 300.4 Hz); IR (neat, cm^{-1}) 2367, 1735, 1560, 1500, 1150, 958, 738, 696, 651, 559, 513; HRMS (EI^+) calcd for $C_{18}H_{11}F_{17}O$ $[M]^+$: 566.0538. Found: 566.05274.

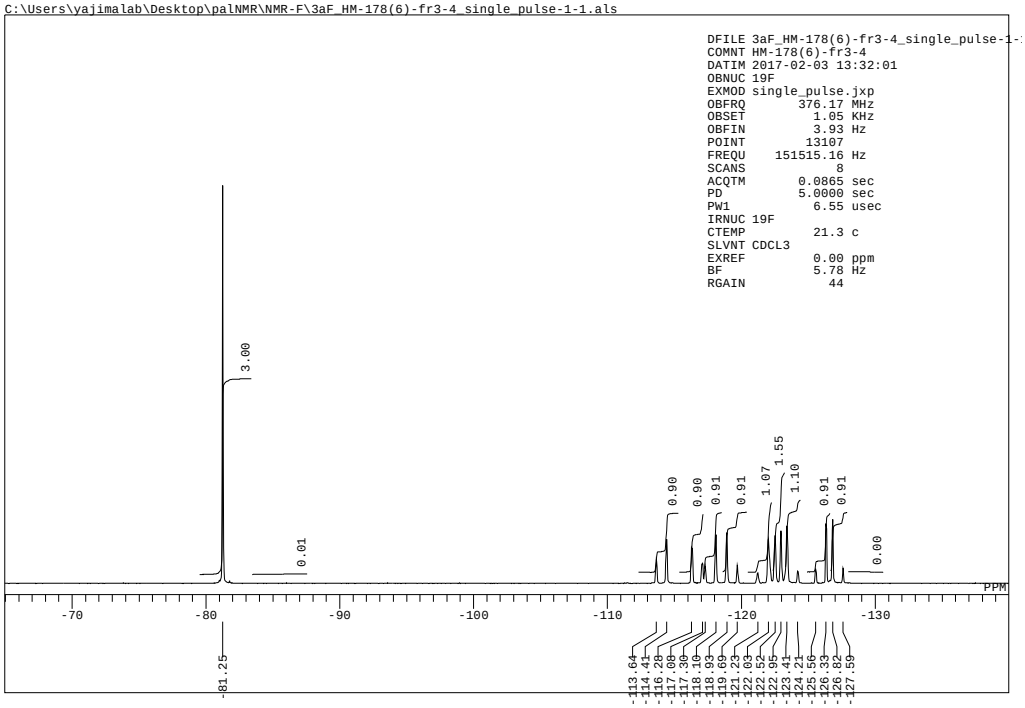
4. ^{1}H and ^{13}C NMR spectra

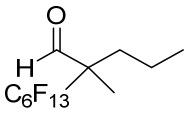


3a

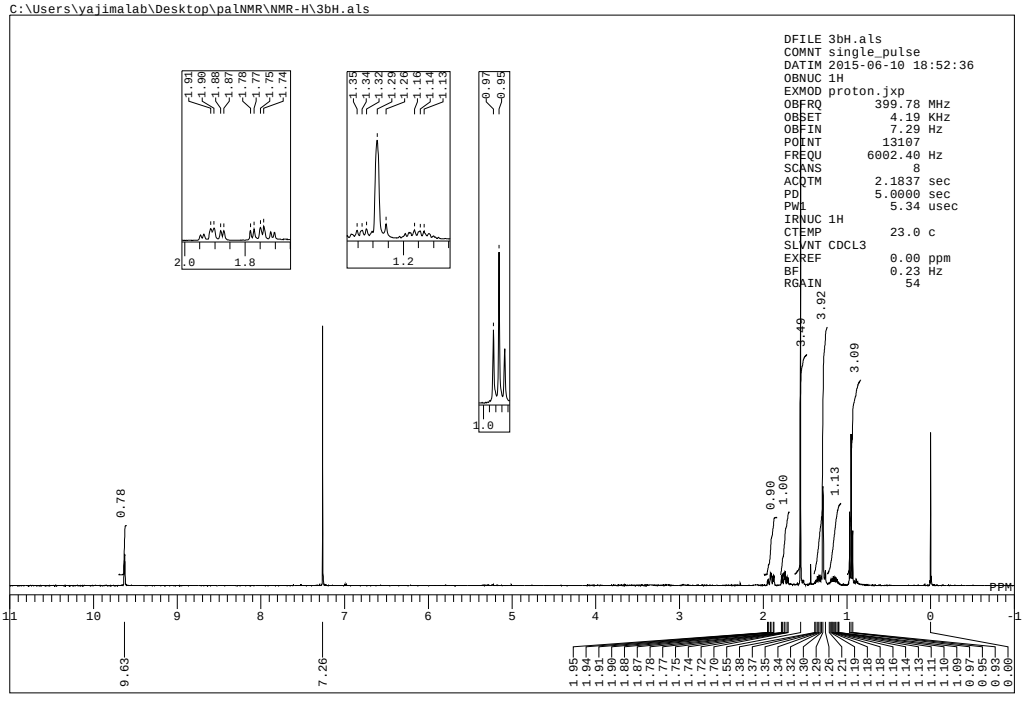


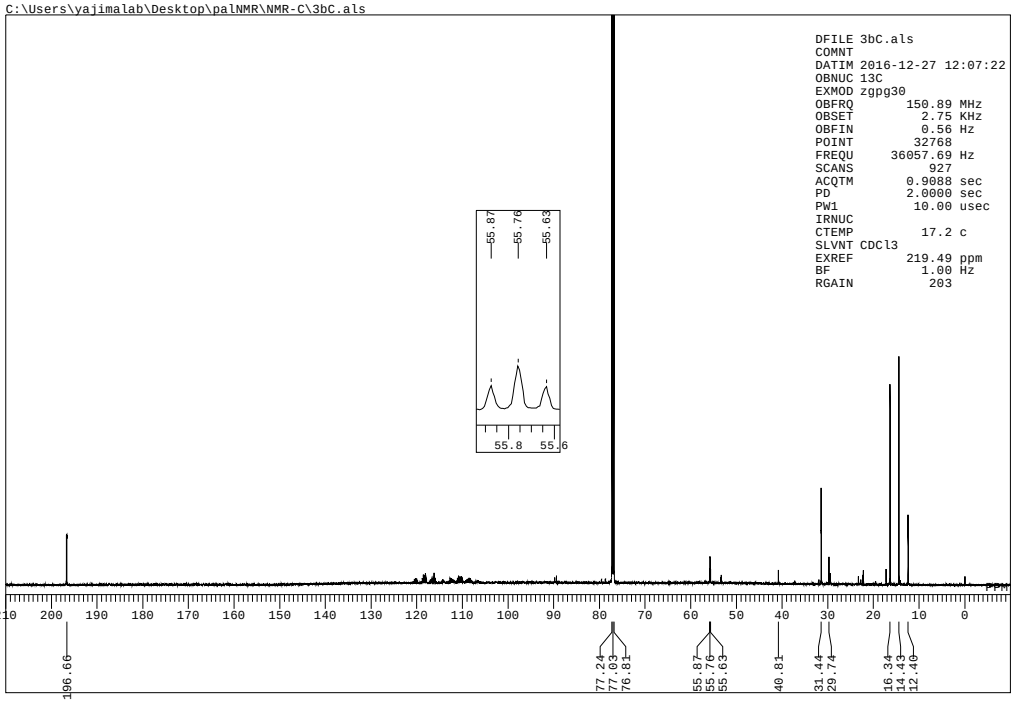


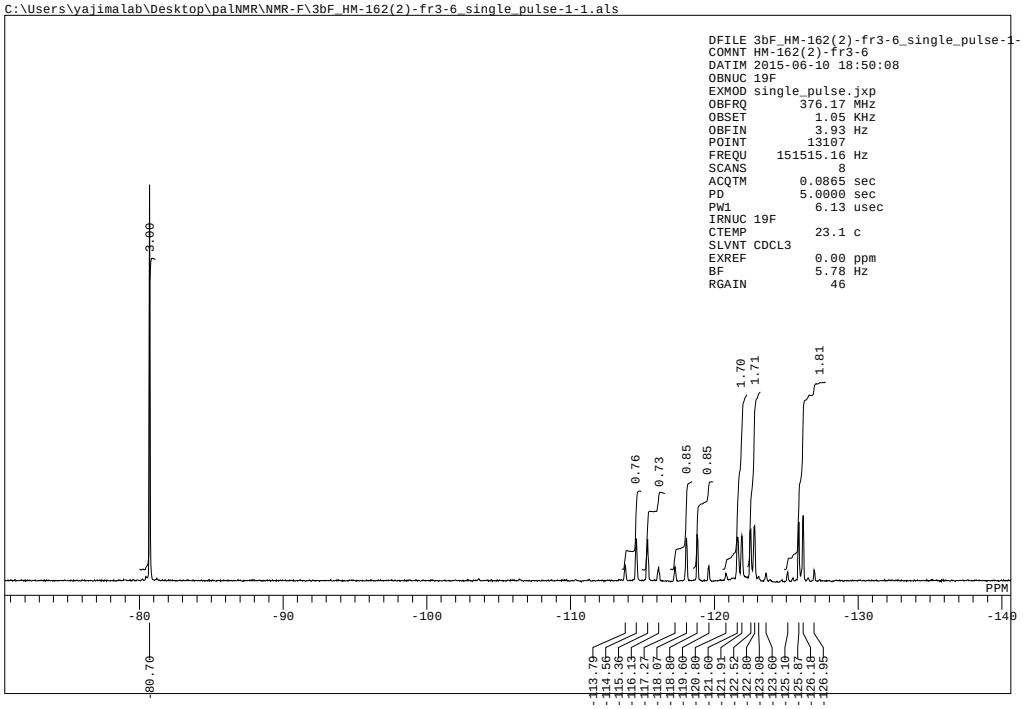

C:\Users\yajimalab\Desktop\palNMR\NMR-F\3aF_HM-178(6)-fr3-4_single_pulse-1-1.als
DFILE 3aF_HM-178(6)-fr3-4_single_pulse-1-
COMNT HM-178(6)-fr3-4
DATIM 2017-02-03 13:32:01
OBNUC 19F
EXMOD single_pulse.jxp
OBFRQ 376.17 MHz
OBSET 1.05 KHz
OBFIN 3.93 Hz
POINT 13107
FREQU 151515.16 Hz
SCANS 8
ACQTM 0.0865 sec
PD 5.0000 sec
PW1 6.55 usec
IRNUC 19F
CTEMP 21.3 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 5.78 Hz
RGAIN 44
3.00
0.01
0.90
0.90
0.91
0.91
1.07
1.55
1.10
0.91
0.91
0.00
PPM
-70
-80
-90
-100
-110
-120
-130
-81.25
-113.64
-114.41
-116.28
-117.08
-117.30
-118.10
-118.93
-119.84
-121.23
-122.03
-122.52
-122.95
-123.41
-124.21
-125.56
-126.33
-126.82
-127.59

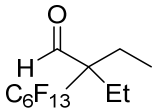

O
H
C6F13

3b


C:\Users\yajimalab\Desktop\palNMR\NMR-H\3bH.als
DFILE 3bH.als
COMNT single_pulse
DATIM 2015-06-10 18:52:36
OBNUC 1H
EXMOD proton.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.40 Hz
SCANS 8
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 5.34 usec
IRNUC 1H
CTEMP 23.0 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.23 Hz
RGAIN 54
3.92
3.49
3.09
1.13
1.00
0.90
0.78
PPM
9.63
7.26

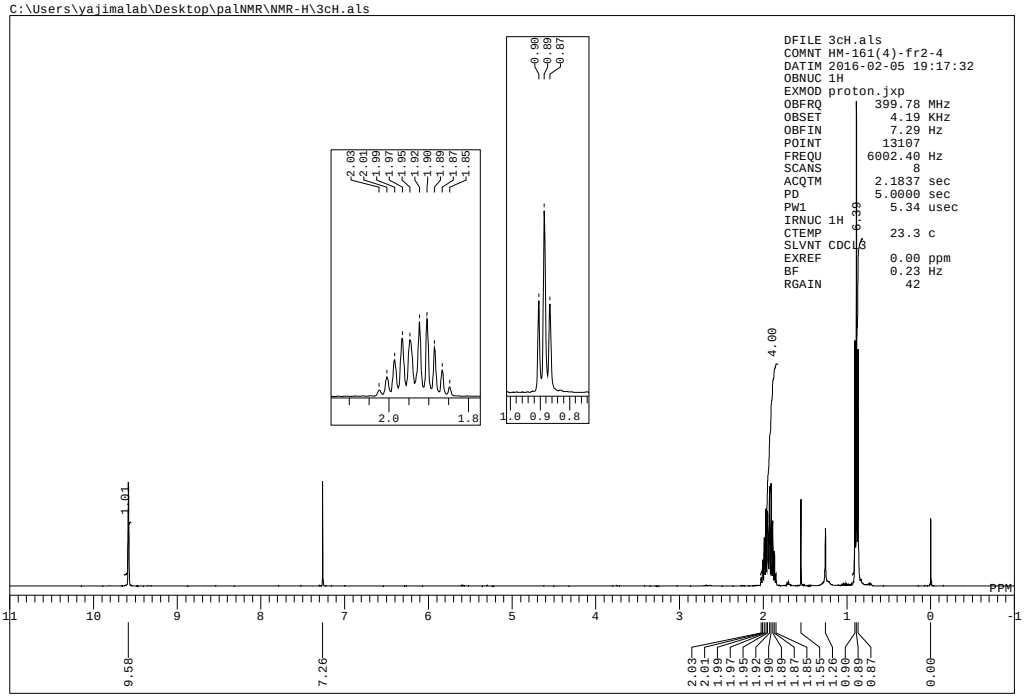

C:\Users\yajimalab\Desktop\palNMR\NMR-C\3bC.als
DFILE 3bC.als
COMNT
DATIM 2016-12-27 12:07:22
OBNUC 13C
EXMOD zgpg30
OBFRQ 150.89 MHz
OBSET 2.75 KHz
OBFIN 0.56 Hz
POINT 32768
FREQU 36057.69 Hz
SCANS 927
ACQTM 0.9088 sec
PD 2.0000 sec
PW1 10.00 usec
IRNUC
CTEMP 17.2 c
SLVNT CDCl3
EXREF 219.49 ppm
BF 1.00 Hz
RGAIN 203
55.87
55.76
55.63
55.8
55.6
PPM
196.66
77.24
77.03
76.81
55.87
55.76
55.63
40.81
31.44
29.74
16.34
14.43
12.40


C:\Users\yajimalab\Desktop\palNMR\NMR-F\3bF_HM-162(2)-fr3-6_single_pulse-1-1.als
DFILE 3bF_HM-162(2)-fr3-6_single_pulse-1-
COMNT HM-162(2)-fr3-6
DATIM 2015-06-10 18:50:08
OBNUC 19F
EXMOD single_pulse.jxp
OBFRQ 376.17 MHz
OBSET 1.05 KHz
OBFIN 3.93 Hz
POINT 13107
FREQU 151515.16 Hz
SCANS 8
ACQTM 0.0865 sec
PD 5.0000 sec
PW1 6.13 usec
IRNUC 19F
CTEMP 23.1 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 5.78 Hz
RGAIN 46
-9.00
0.76
0.73
0.85
0.85
1.70
1.71
1.81
PPM
-80.70
-113.79
-114.56
-115.36
-116.13
-117.27
-118.07
-118.80
-119.60
-120.80
-121.91
-122.52
-122.80
-123.08
-123.60
-125.10
-125.87
-126.18
-126.95

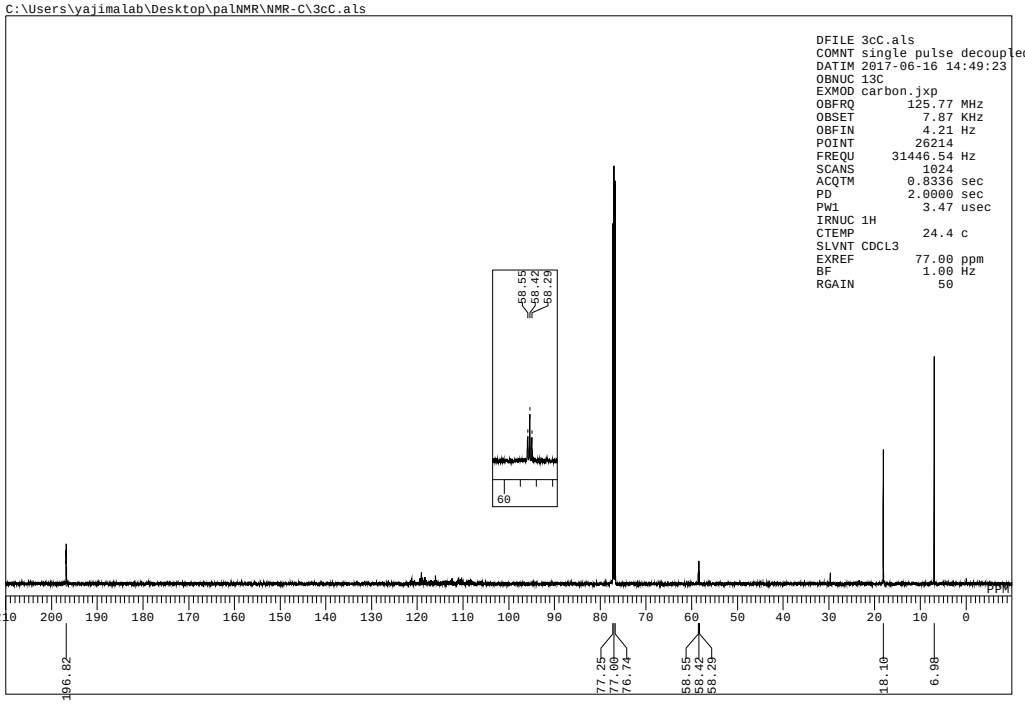


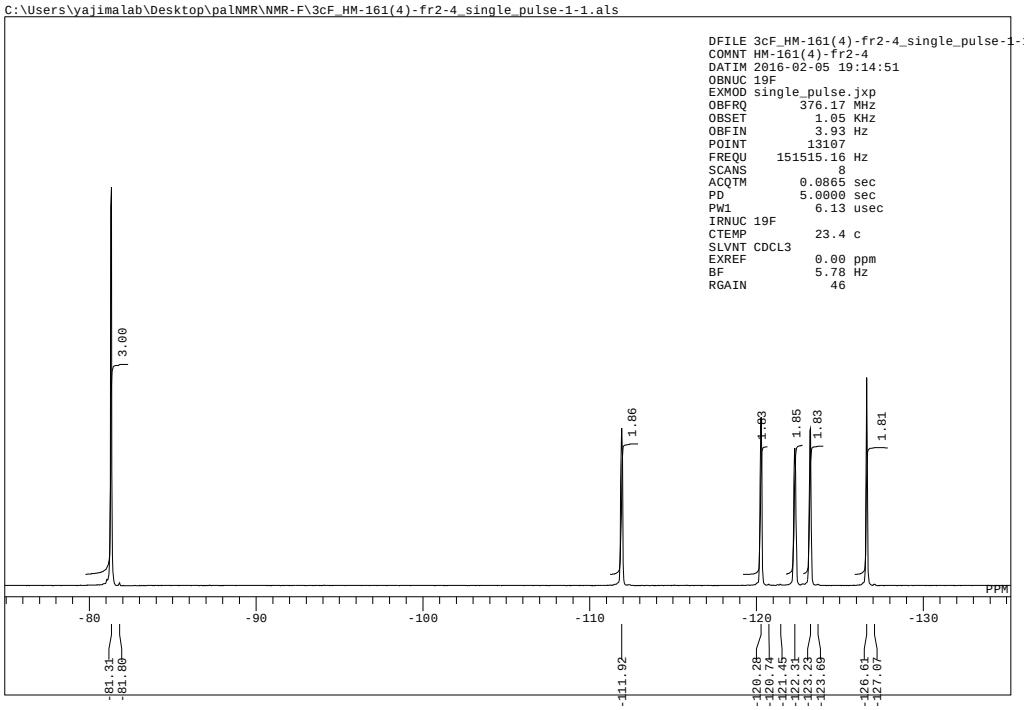
3c

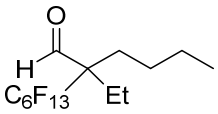
C:\Users\yajimalab\Desktop\palNMR\NMR-H\3cH.als



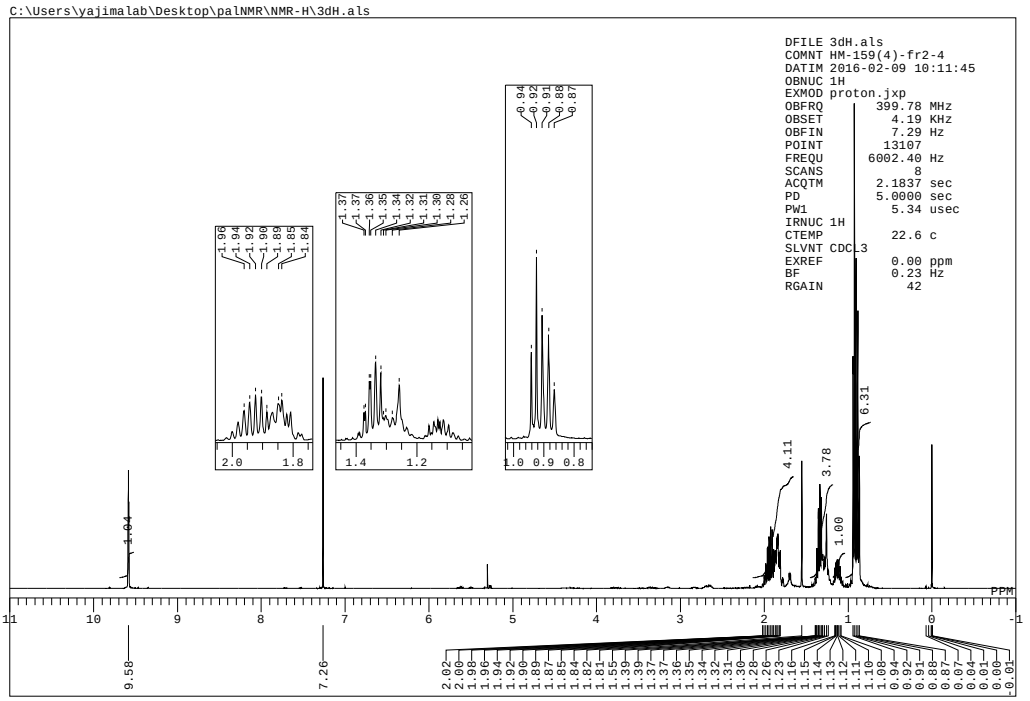
C:\Users\yajimalab\Desktop\palNMR\NMR-C\3cC.als



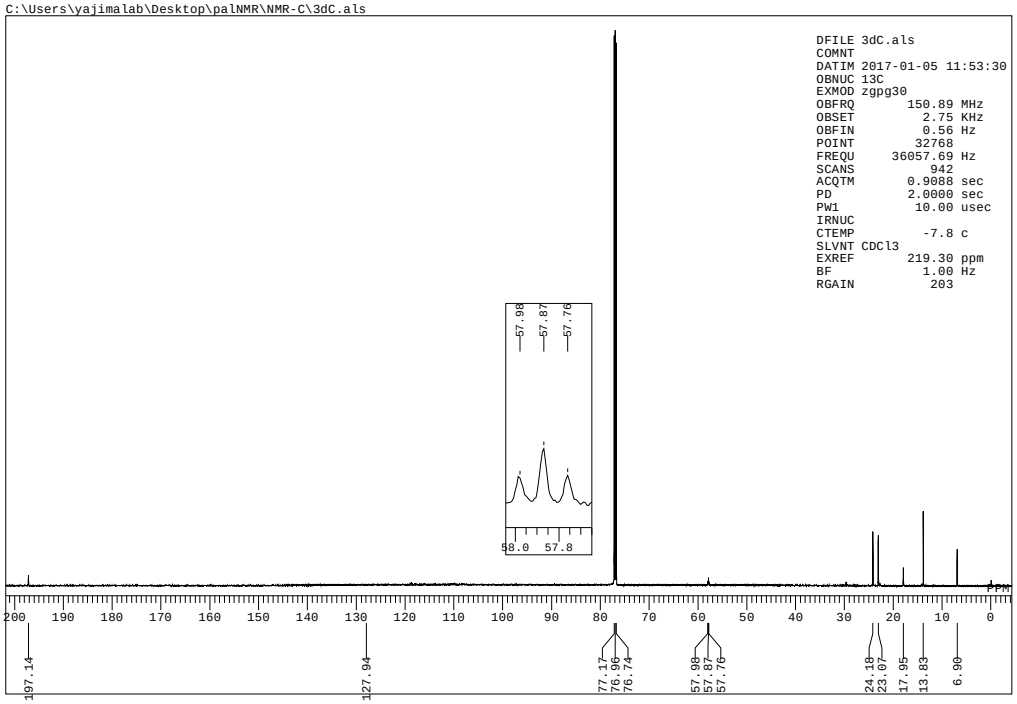

C:\Users\yajimalab\Desktop\palNMR\NMR-F\3cF_HM-161(4)-fr2-4_single_pulse-1-1.als
DFILE 3cF_HM-161(4)-fr2-4_single_pulse-1-
COMNT HM-161(4)-fr2-4
DATIM 2016-02-05 19:14:51
OBNUC 19F
EXMOD single_pulse.jxp
OBFRQ 376.17 MHz
OBSET 1.05 KHz
OBFIN 3.93 Hz
POINT 13107
FREQU 151515.16 Hz
SCANS 8
ACQTM 0.0865 sec
PD 5.0000 sec
PW1 6.13 usec
IRNUC 19F
CTEMP 23.4 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 5.78 Hz
RGAIN 46
3.00
1.86
1.83
1.85
1.83
1.81
PPM
-80
-90
-100
-110
-120
-130
-81.31
-81.80
-111.92
-120.28
-120.74
-121.45
-122.31
-123.23
-123.69
-126.61
-127.07


O
H
C6F13
Et

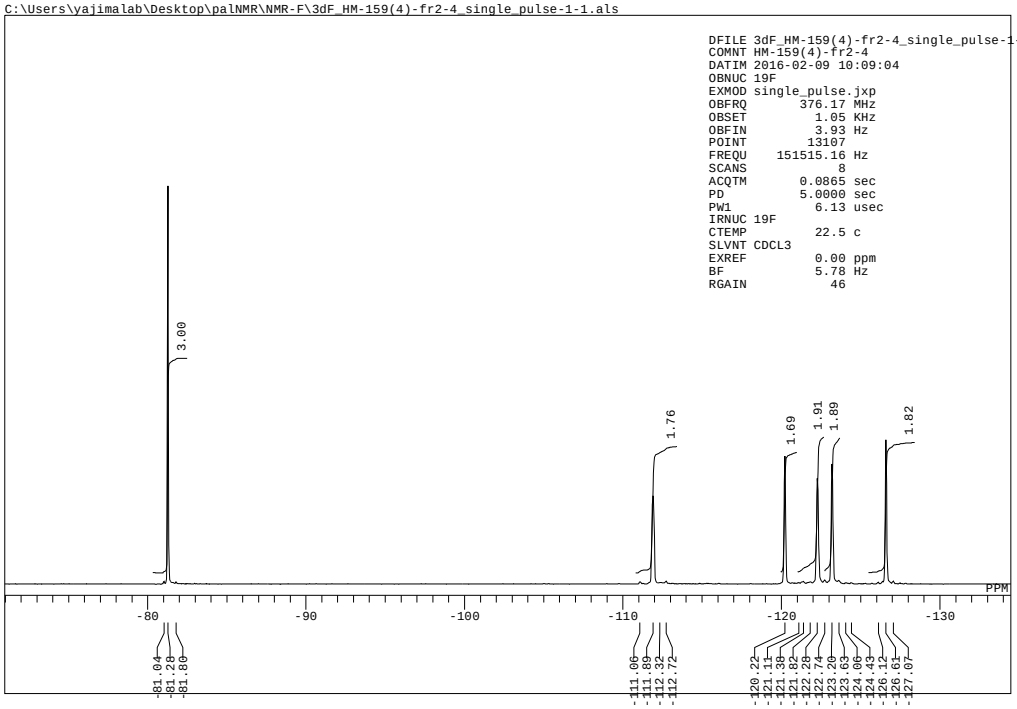
3d

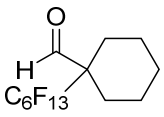

C:\Users\yajimalab\Desktop\palNMR\NMR-H\3dH.als
DFILE 3dH.als
COMNT HM-159(4)-fr2-4
DATIM 2016-02-09 10:11:45
OBNUC 1H
EXMOD proton.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.40 Hz
SCANS 8
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 5.34 usec
IRNUC 1H
CTEMP 22.6 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.23 Hz
RGAIN 42
1.04
9.58
7.26
4.11
3.78
6.31
1.00
PPM

C:\Users\yajimalab\Desktop\palNMR\NMR-C\3dC.als



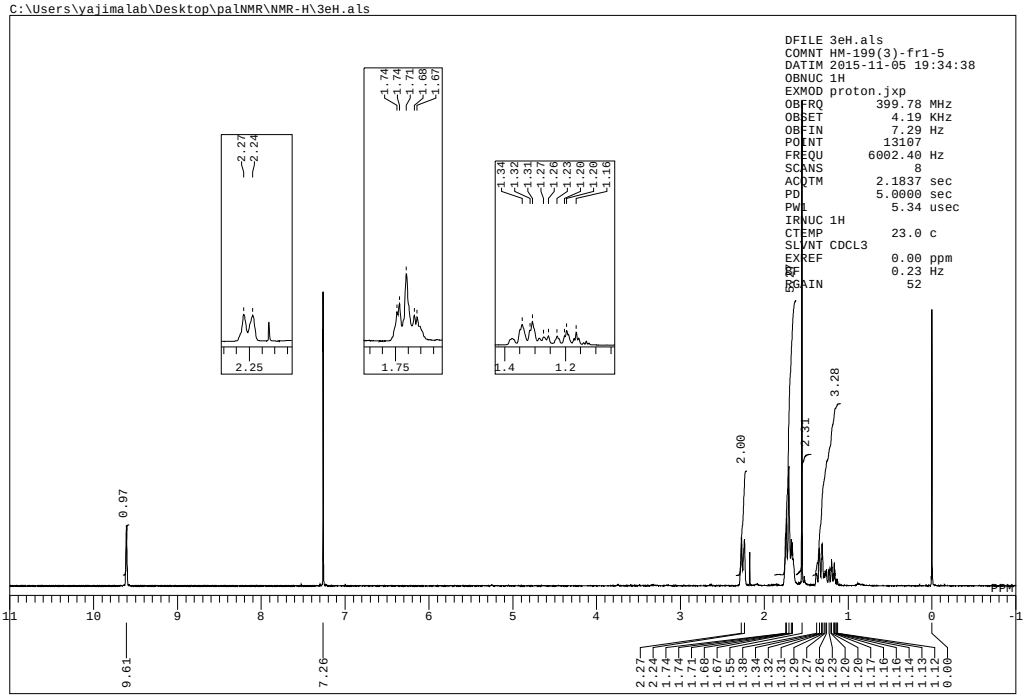
C:\Users\yajimalab\Desktop\palNMR\NMR-F\3dF_HM-159(4)-fr2-4_single_pulse-1-1.als



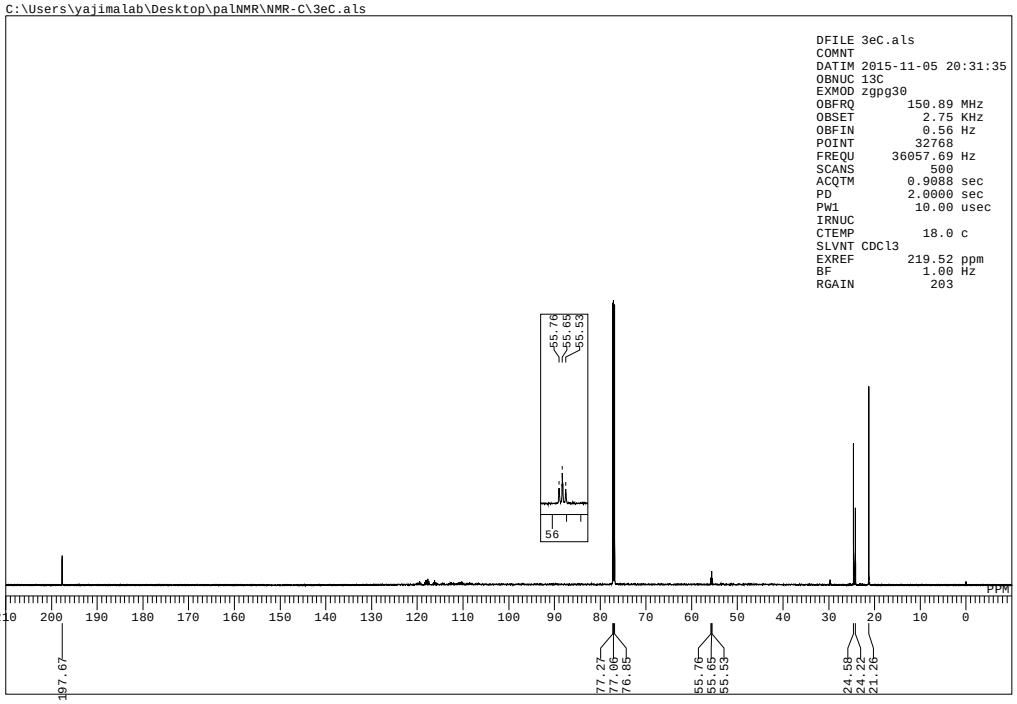


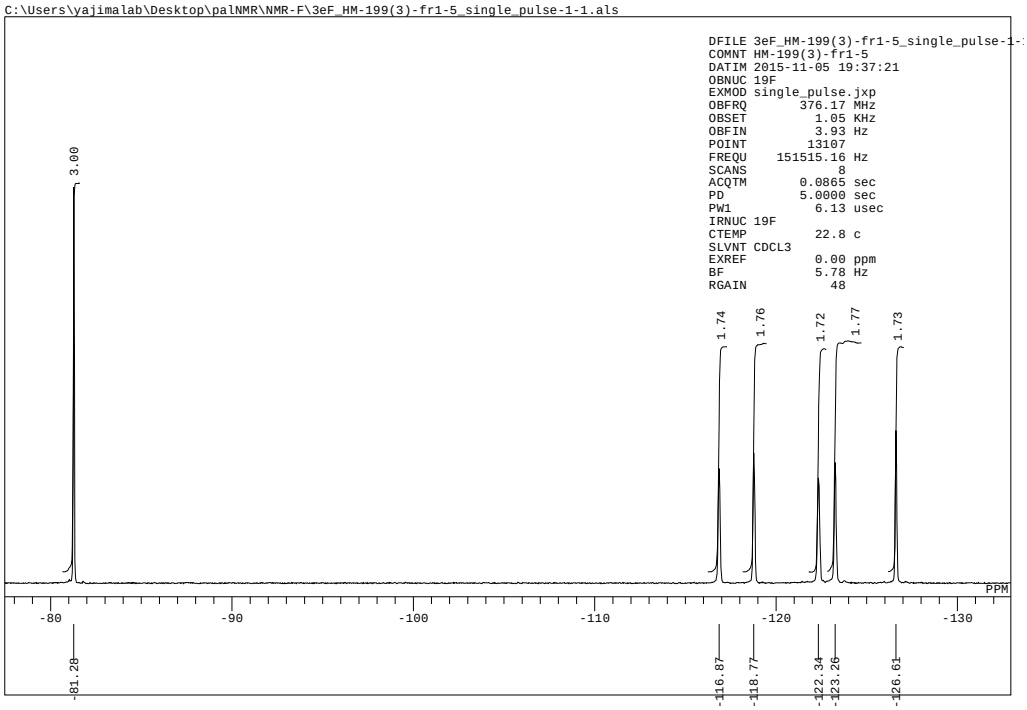
3e

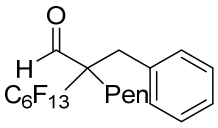
C:\Users\yajimalab\Desktop\palNMR\NMR-H\3eH.als



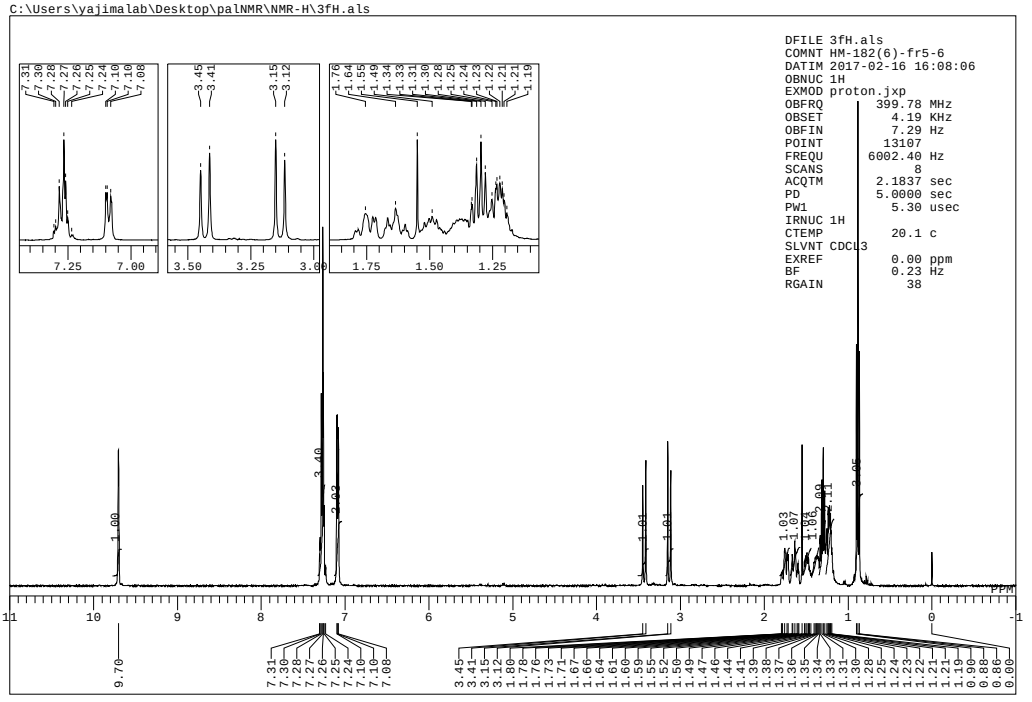
C:\Users\yajimalab\Desktop\palNMR\NMR-C\3eC.als



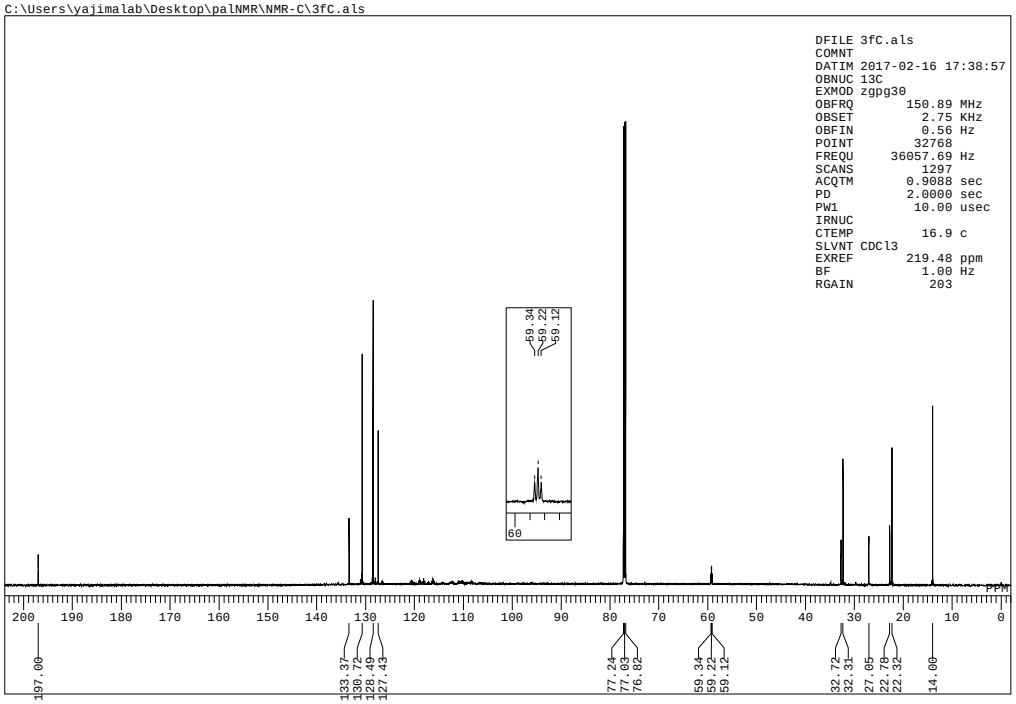

C:\Users\yajimalab\Desktop\palNMR\NMR-F\3eF_HM-199(3)-fr1-5_single_pulse-1-1.als
DFILE 3eF_HM-199(3)-fr1-5_single_pulse-1-
COMNT HM-199(3)-fr1-5
DATIM 2015-11-05 19:37:21
OBNUC 19F
EXMOD single_pulse.jxp
OBFRQ 376.17 MHz
OBSET 1.05 KHz
OBFIN 3.93 Hz
POINT 13107
FREQU 151515.16 Hz
SCANS 8
ACQTM 0.0865 sec
PD 5.0000 sec
PW1 6.13 usec
IRNUC 19F
CTEMP 22.8 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 5.78 Hz
RGAIN 48
3.00
1.74
1.76
1.72
1.77
1.73
PPM
-80
-90
-100
-110
-120
-130
-81.28
-116.87
-118.77
-122.34
-123.26
-126.61


O
H
C6F13
Pen

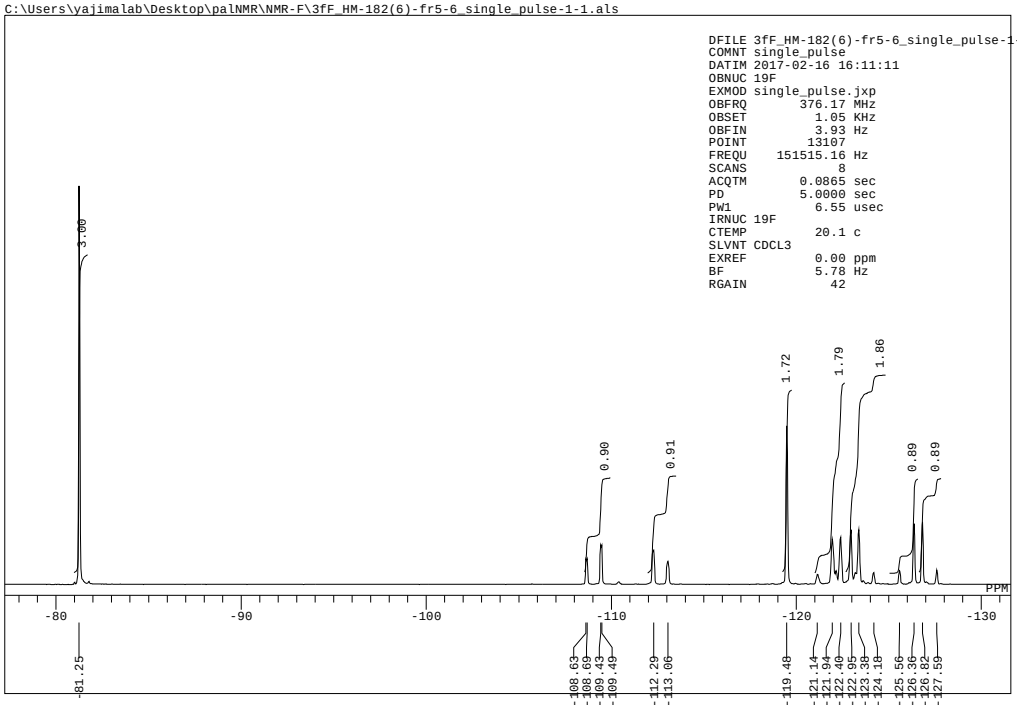
3f

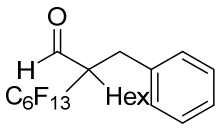

C:\Users\yajimalab\Desktop\palNMR\NMR-H\3fH.als
DFILE 3fH.als
COMNT HM-182(6)-fr5-6
DATIM 2017-02-16 16:08:06
OBNUC 1H
EXMOD proton.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.40 Hz
SCANS 8
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 5.30 usec
IRNUC 1H
CTEMP 20.1 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.23 Hz
RGAIN 38
7.31
7.30
7.28
7.27
7.26
7.25
7.24
7.10
7.10
7.08
3.45
3.41
3.15
3.12
1.76
1.64
1.55
1.49
1.34
1.33
1.31
1.30
1.28
1.25
1.24
1.23
1.22
1.21
1.21
1.19
1.00
3.40
2.03
1.01
1.01
1.03
1.07
1.02
1.00
2.11
3.05
PPM
9.70

C:\Users\yajimalab\Desktop\palNMR\NMR-C\3fC.als



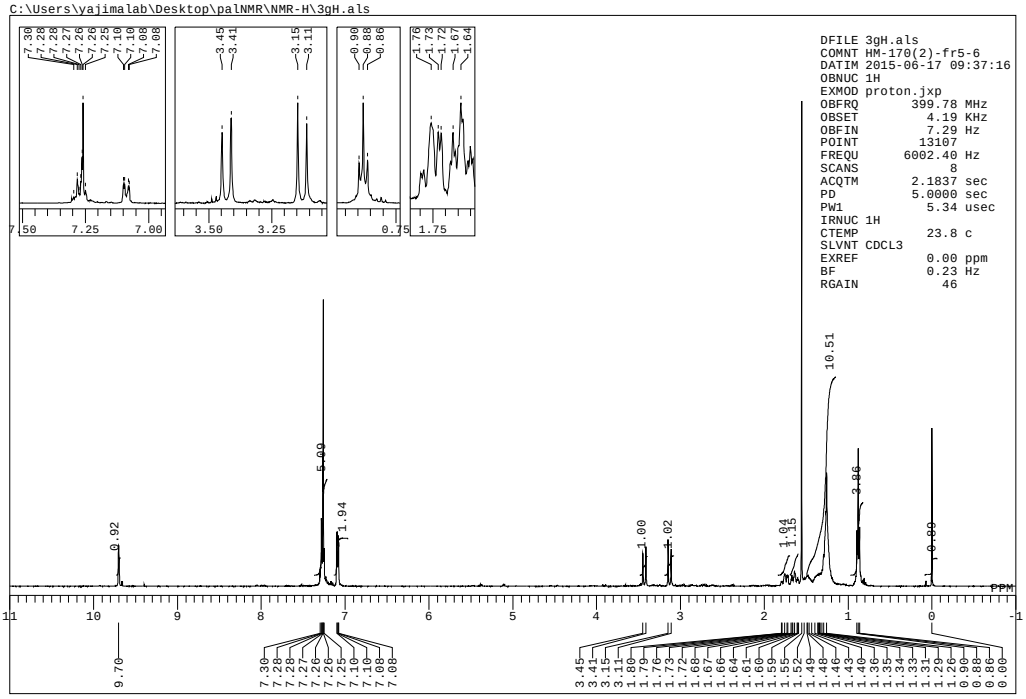
C:\Users\yajimalab\Desktop\palNMR\NMR-F\3fF_HM-182(6)-fr5-6_single_pulse-1-1.als



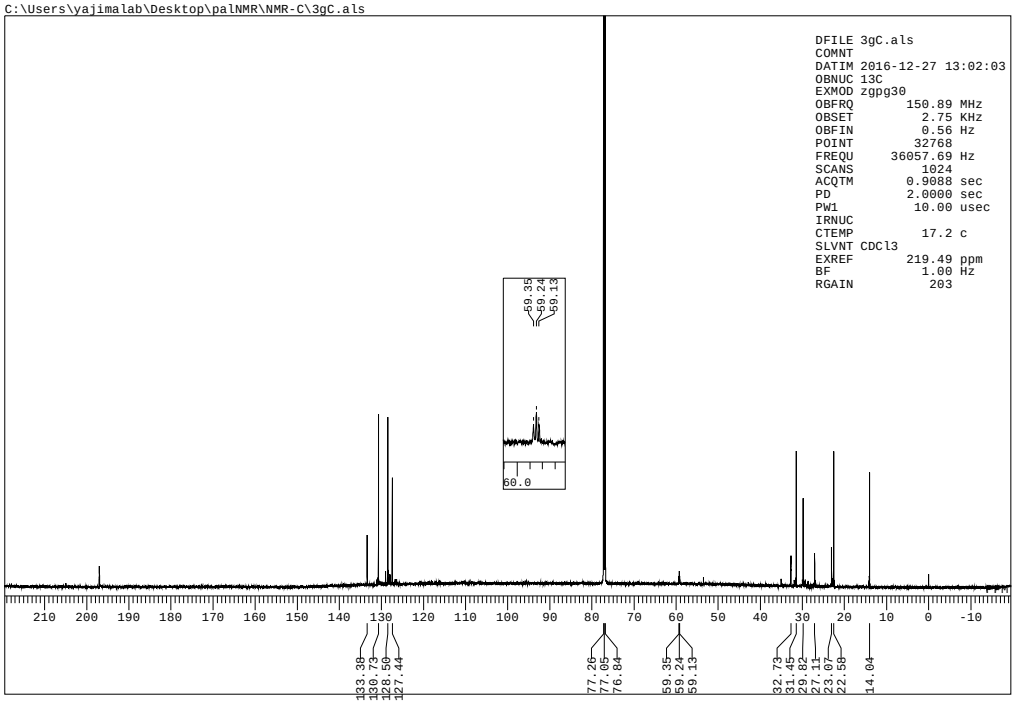


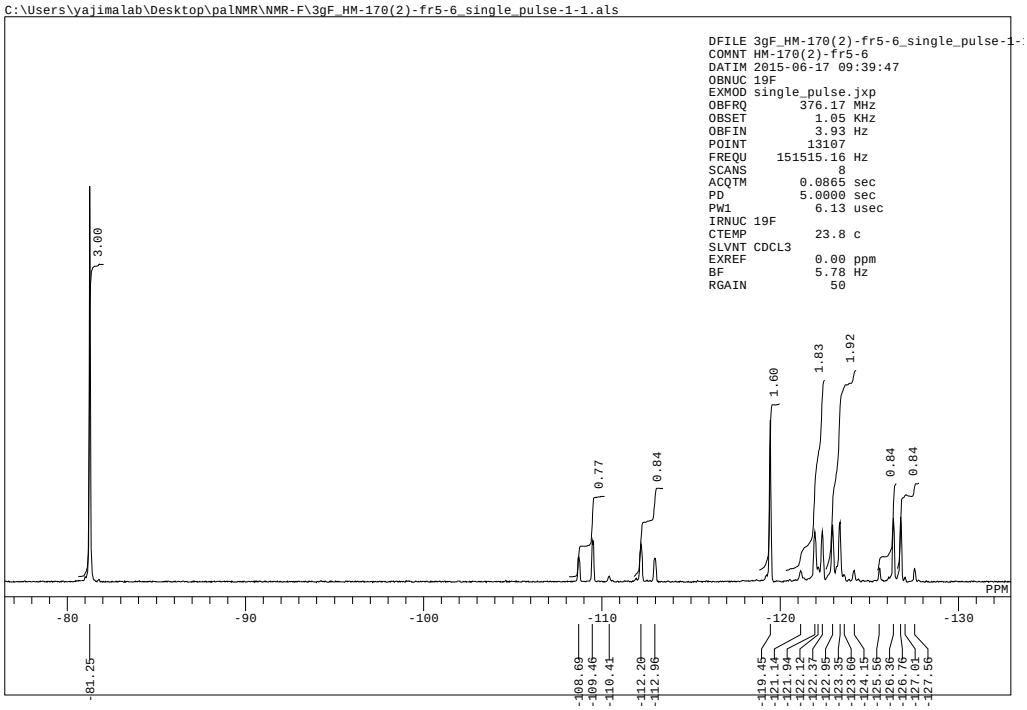
3g

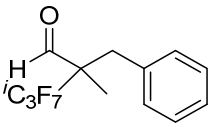
C:\Users\yajimalab\Desktop\palNMR\NMR-H\3gH.als



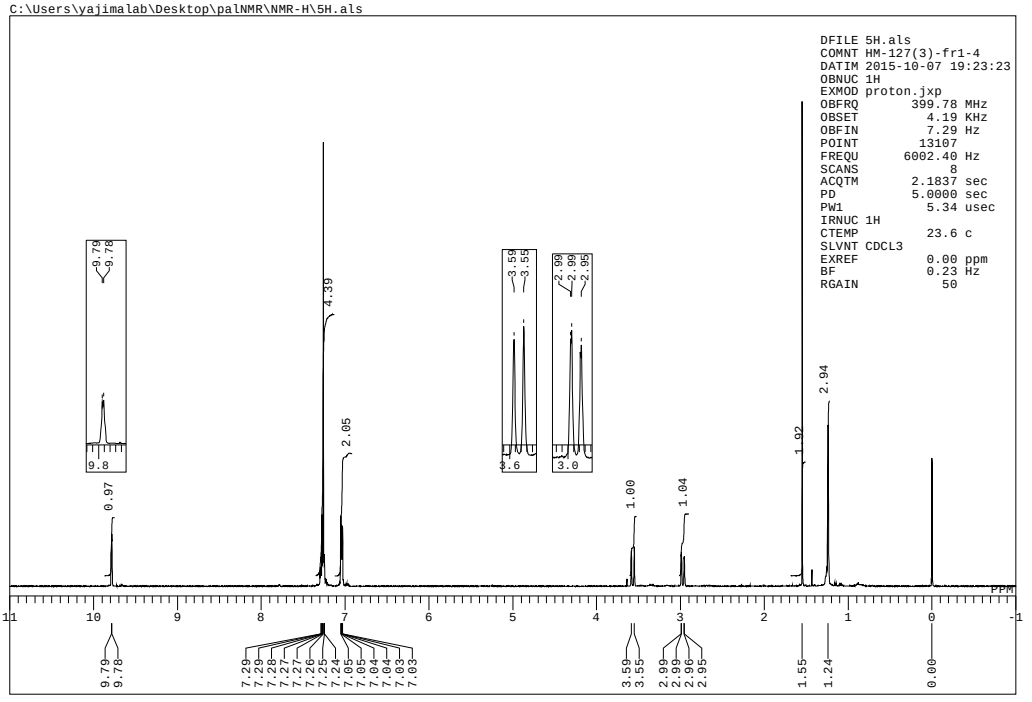
C:\Users\yajimalab\Desktop\palNMR\NMR-C\3gC.als



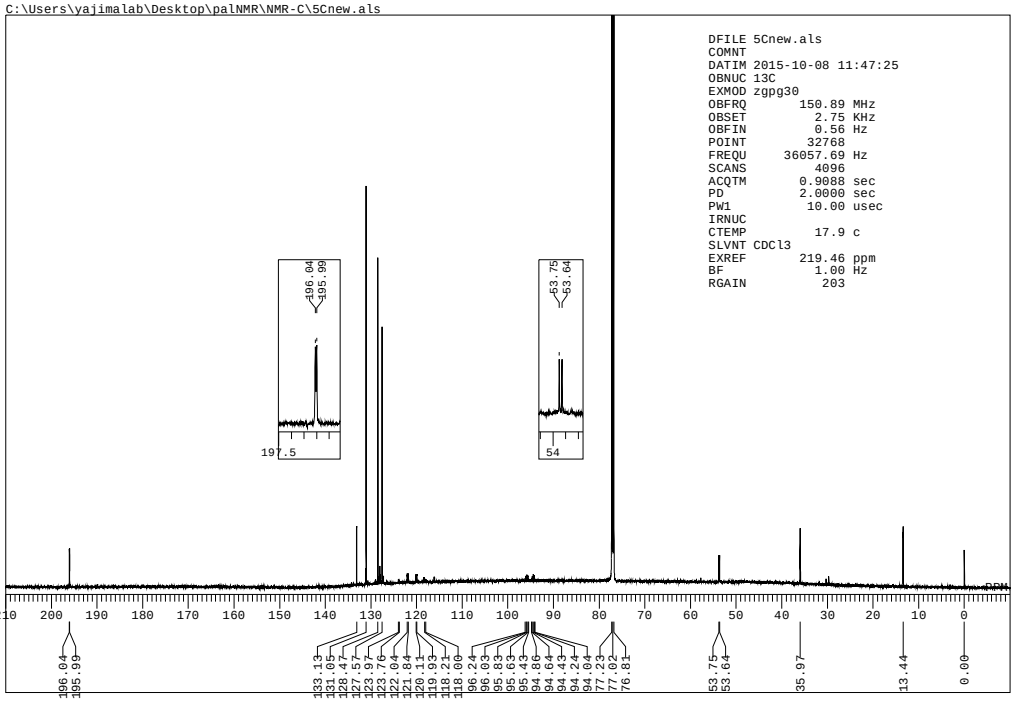

C:\Users\yajimalab\Desktop\palNMR\NMR-F\3gF_HM-170(2)-fr5-6_single_pulse-1-1.als
DFILE 3gF_HM-170(2)-fr5-6_single_pulse-1-
COMNT HM-170(2)-fr5-6
DATIM 2015-06-17 09:39:47
OBNUC 19F
EXMOD single_pulse.jxp
OBFRQ 376.17 MHz
OBSET 1.05 KHz
OBFIN 3.93 Hz
POINT 13107
FREQU 151515.16 Hz
SCANS 8
ACQTM 0.0865 sec
PD 5.0000 sec
PW1 6.13 usec
IRNUC 19F
CTEMP 23.8 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 5.78 Hz
RGAIN 50
3.00
0.77
0.84
1.60
1.83
1.92
0.84
0.84
PPM
-80
-90
-100
-110
-120
-130
-81.25
-108.69
-109.46
-110.41
-112.20
-112.96
-119.45
-121.14
-121.94
-122.12
-122.37
-122.95
-123.35
-123.60
-124.15
-125.36
-126.76
-127.01
-127.56



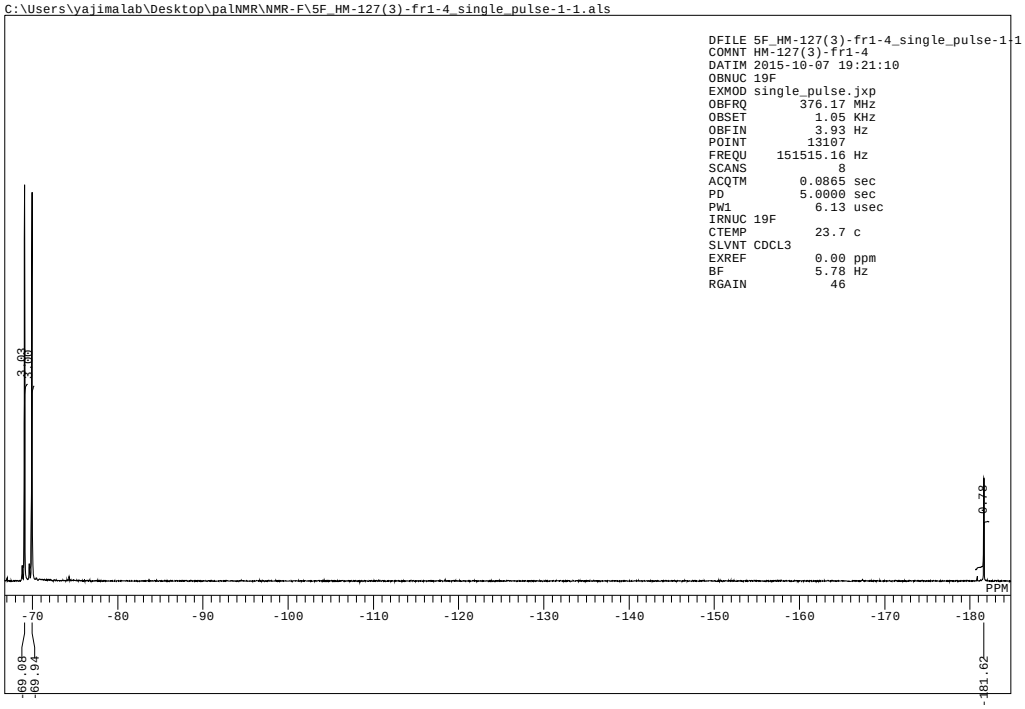
5

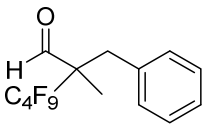

C:\Users\yajimalab\Desktop\palNMR\NMR-H\5H.als
DFILE 5H.als
COMNT HM-127(3)-fr1-4
DATIM 2015-10-07 19:23:23
OBNUC 1H
EXMOD proton.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.40 Hz
SCANS 8
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 5.34 usec
IRNUC 1H
CTEMP 23.6 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.23 Hz
RGAIN 50
9.79
9.78
4.39
2.05
3.59
3.55
2.99
2.96
2.95
0.97
1.00
1.04
1.92
2.94
9.8
4.6
3.0
PPM
11
10
9
8
7
6
5
4
3
2
1
0
-1
9.79
9.78
7.29
7.29
7.28
7.27
7.27
7.26
7.25
7.24
7.05
7.05
7.04
7.04
7.03
7.03
3.59
3.55
2.99
2.99
2.96
2.95
1.55
1.24
0.00

C:\Users\yajimalab\Desktop\palNMR\NMR-C\5Cnew.als



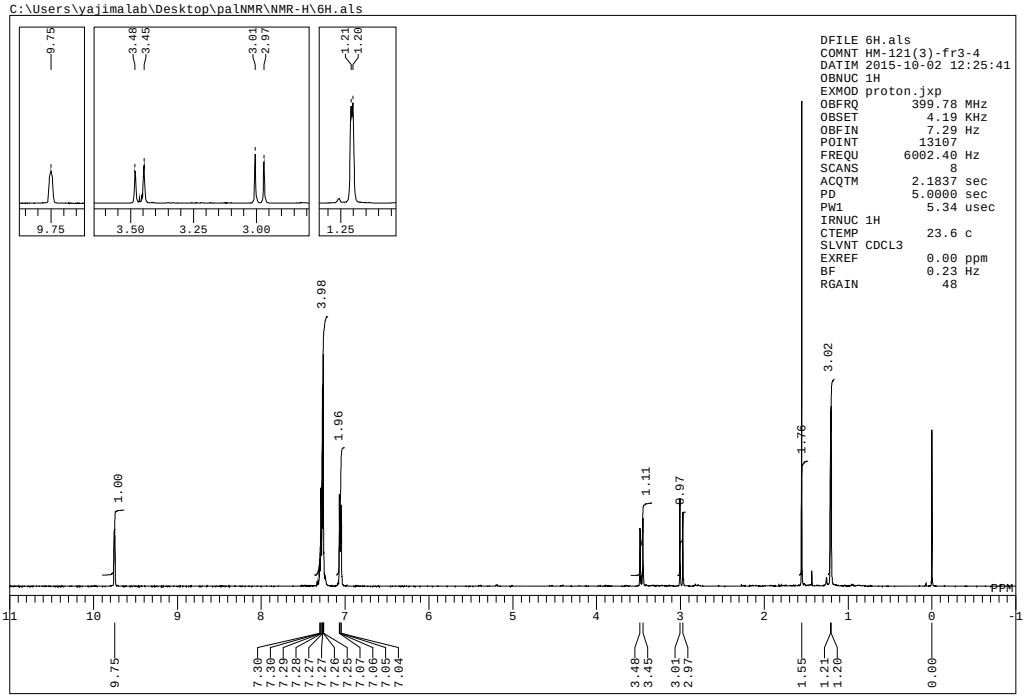
C:\Users\yajimalab\Desktop\palNMR\NMR-F\5F_HM-127(3)-fr1-4_single_pulse-1-1.als



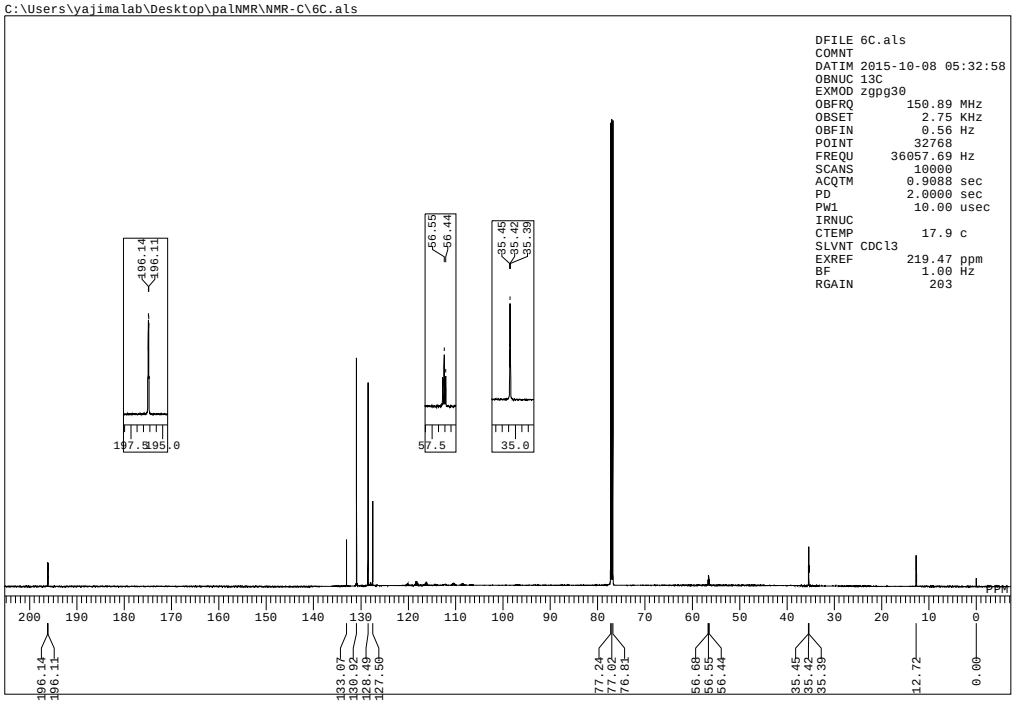


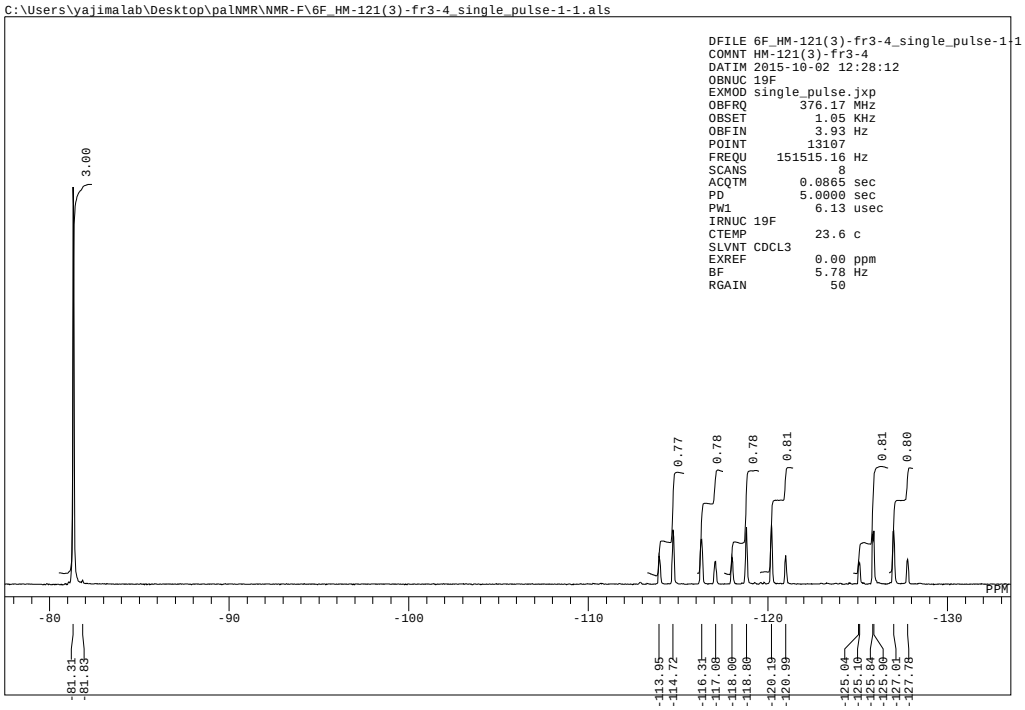
6

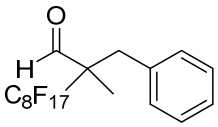
C:\Users\yajimalab\Desktop\palNMR\NMR-H\6H.als



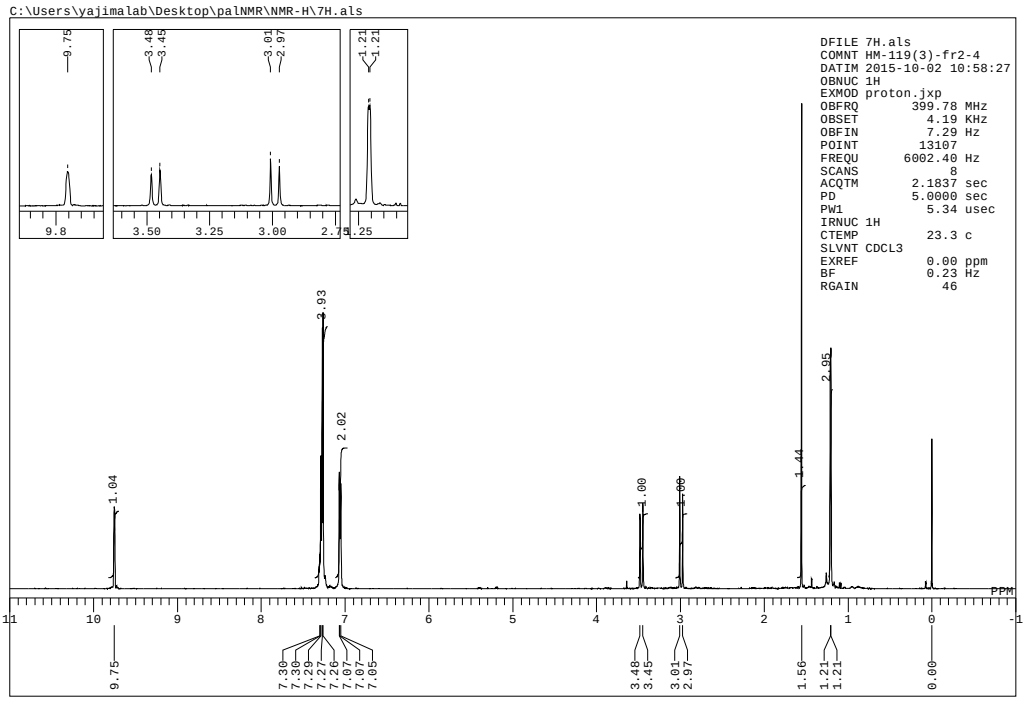
C:\Users\yajimalab\Desktop\palNMR\NMR-C\6C.als

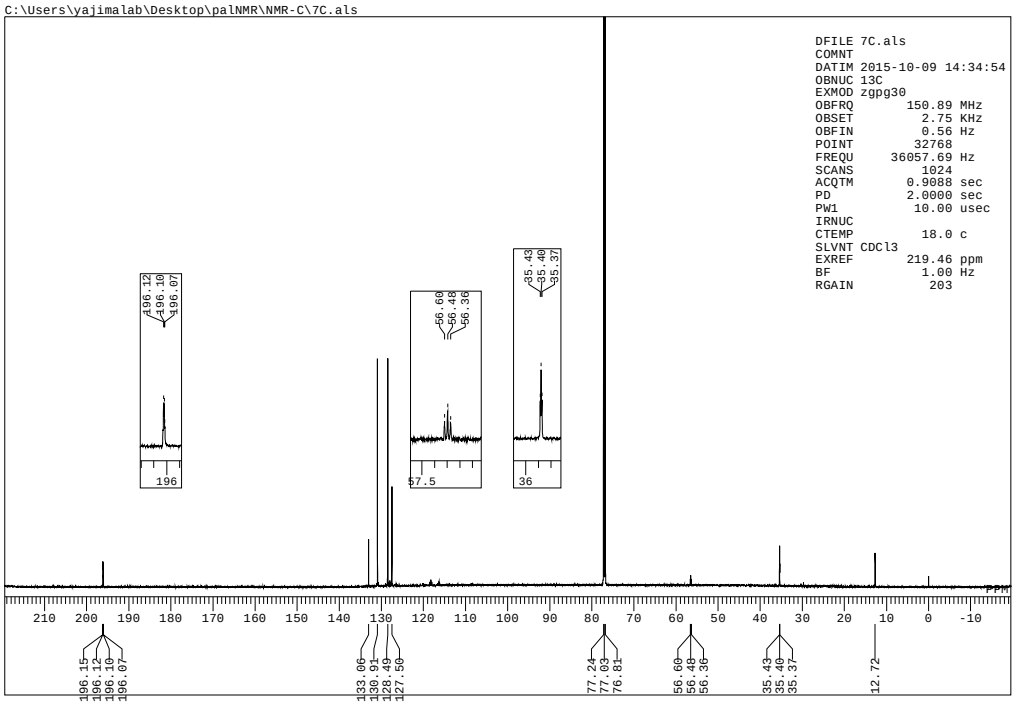


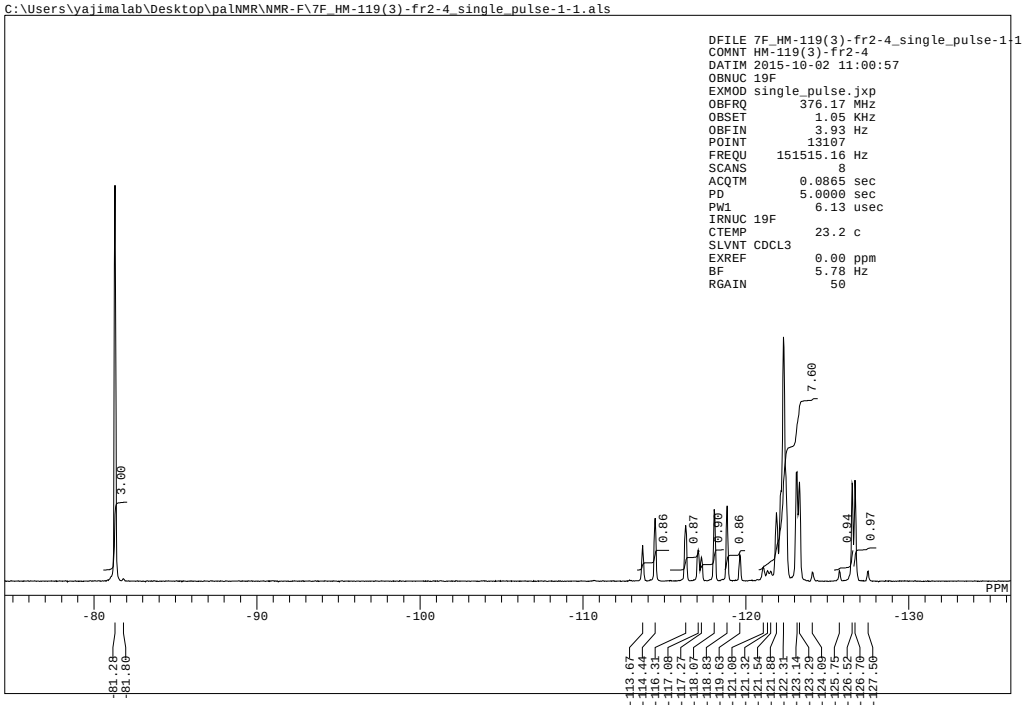

C:\Users\yajimalab\Desktop\palNMR\NMR-F\6F_HM-121(3)-fr3-4_single_pulse-1-1.als
DFILE 6F_HM-121(3)-fr3-4_single_pulse-1-1
COMNT HM-121(3)-fr3-4
DATIM 2015-10-02 12:28:12
OBNUC 19F
EXMOD single_pulse.jxp
OBFRQ 376.17 MHz
OBSET 1.05 KHz
OBFIN 3.93 Hz
POINT 13107
FREQU 151515.16 Hz
SCANS 8
ACQTM 0.0865 sec
PD 5.0000 sec
PW1 6.13 usec
IRNUC 19F
CTEMP 23.6 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 5.78 Hz
RGAIN 50
3.00
0.77
0.78
0.78
0.81
0.81
0.80
PPM
-80
-90
-100
-110
-120
-130
-81.31
-81.83
-113.95
-114.72
-116.31
-117.00
-118.00
-118.80
-120.19
-120.99
-125.04
-125.10
-125.84
-125.90
-127.01
-127.78


O
H
C8F17

7


C:\Users\yajimalab\Desktop\palNMR\NMR-H\7H.als
DFILE 7H.als
COMNT HM-119(3)-fr2-4
DATIM 2015-10-02 10:58:27
OBNUC 1H
EXMOD proton.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.40 Hz
SCANS 8
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 5.34 usec
IRNUC 1H
CTEMP 23.3 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.23 Hz
RGAIN 46
9.75
3.48
3.45
3.01
2.97
1.21
1.21
3.93
2.02
1.04
1.00
1.00
1.44
2.95
PPM
9.75
7.30
7.30
7.29
7.27
7.26
7.07
7.07
7.05
3.48
3.45
3.01
2.97
1.56
1.21
1.21
0.00

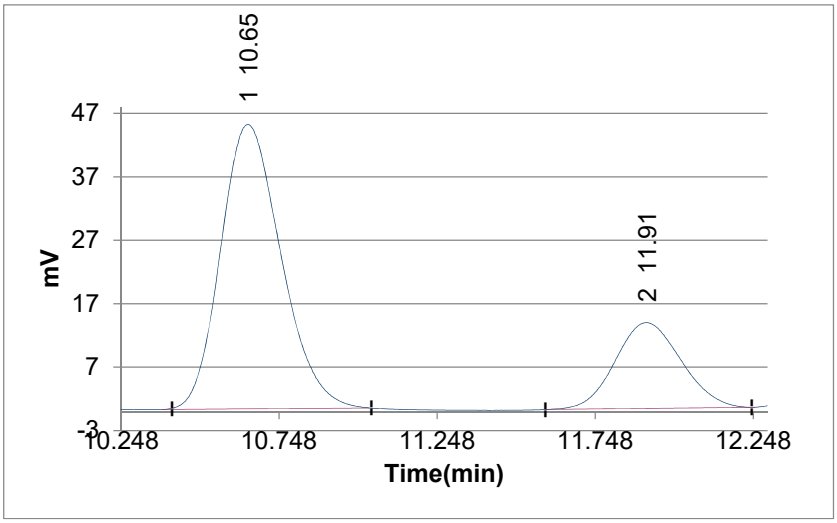

C:\Users\yajimalab\Desktop\palNMR\NMR-C\7C.als
DFILE 7C.als
COMNT
DATIM 2015-10-09 14:34:54
OBNUC 13C
EXMOD zgpg30
OBFRQ 150.89 MHz
OBSET 2.75 KHz
OBFIN 0.56 Hz
POINT 32768
FREQU 36057.69 Hz
SCANS 1024
ACQTM 0.9088 sec
PD 2.0000 sec
PW1 10.00 usec
IRNUC
CTEMP 18.0 c
SLVNT CDCl3
EXREF 219.46 ppm
BF 1.00 Hz
RGAIN 203
196.12
196.10
196.07
56.60
56.48
56.36
35.43
35.40
35.37
196
57.5
36
PPM
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
196.15
196.12
196.10
196.07
133.06
130.91
130.46
127.50
77.24
77.03
76.81
56.60
56.48
56.36
35.43
35.40
35.37
12.72


C:\Users\yajimalab\Desktop\palNMR\NMR-F\7F_HM-119(3)-fr2-4_single_pulse-1-1.als
DFILE 7F_HM-119(3)-fr2-4_single_pulse-1-1
COMNT HM-119(3)-fr2-4
DATIM 2015-10-02 11:00:57
OBNUC 19F
EXMOD single_pulse.jxp
OBFRQ 376.17 MHz
OBSET 1.05 KHz
OBFIN 3.93 Hz
POINT 13107
FREQU 151515.16 Hz
SCANS 8
ACQTM 0.0865 sec
PD 5.0000 sec
PW1 6.13 usec
IRNUC 19F
CTEMP 23.2 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 5.78 Hz
RGAIN 50
3.00
0.86
0.87
0.90
0.86
7.60
0.94
0.97
PPM
-80 -90 -100 -110 -120 -130
-81.28
-81.80
-113.67
-114.44
-116.31
-117.09
-117.27
-118.07
-118.83
-119.63
-121.08
-121.32
-121.54
-121.88
-122.31
-123.14
-123.29
-124.09
-125.52
-126.52
-126.70
-127.50

5. HPLC Charts

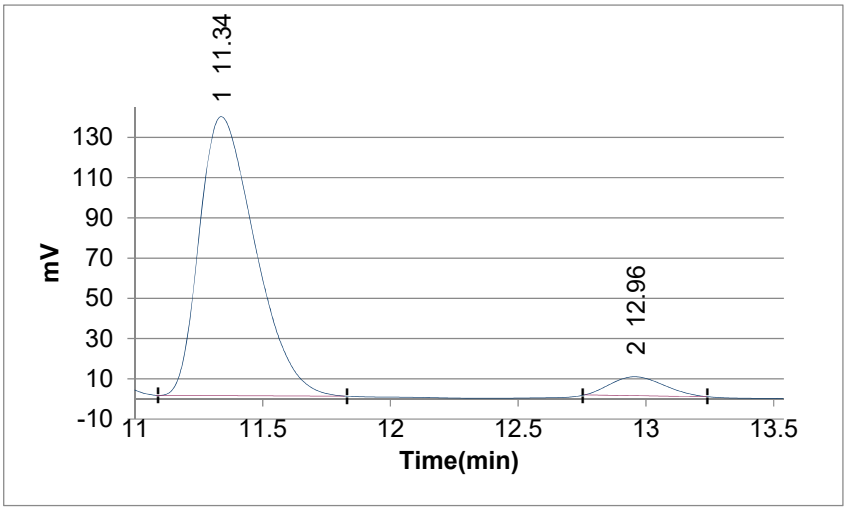
DAICEL Chiralpak OD, IPA/hexane = 10:90, flow late = 0.5 mL/min.

Table 3. entry 3



No.	Rt	Peak Name	Area	Area(%)	Height	Amount	NTP	Tf	Resolution
1	10.65		593411.8	75.2498	44811	----	14247.5	1.205	3.387
2	11.91		195177.7	24.7502	13512	----	15119.3	1.093	----
			788589.4	100	58323				

Table 3. entry 6



No.	Rt	Peak Name	Area	Area(%)	Height	Amount	NTP	Tf	Resolution
1	11.34		2101483	93.9395	138643	----	12412.7	1.449	4.112
2	12.96		135577.2	6.0605	9364	----	18502	1.181	----
			2237060	100	148007				