Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.
This journal is © The Royal Society of Chemistry 2014

Supporting Information

Generalized access to fluorinated β-keto amino compounds through asymmetric additions of α,α-difluoroenolates to CF_3-sulfinylimine

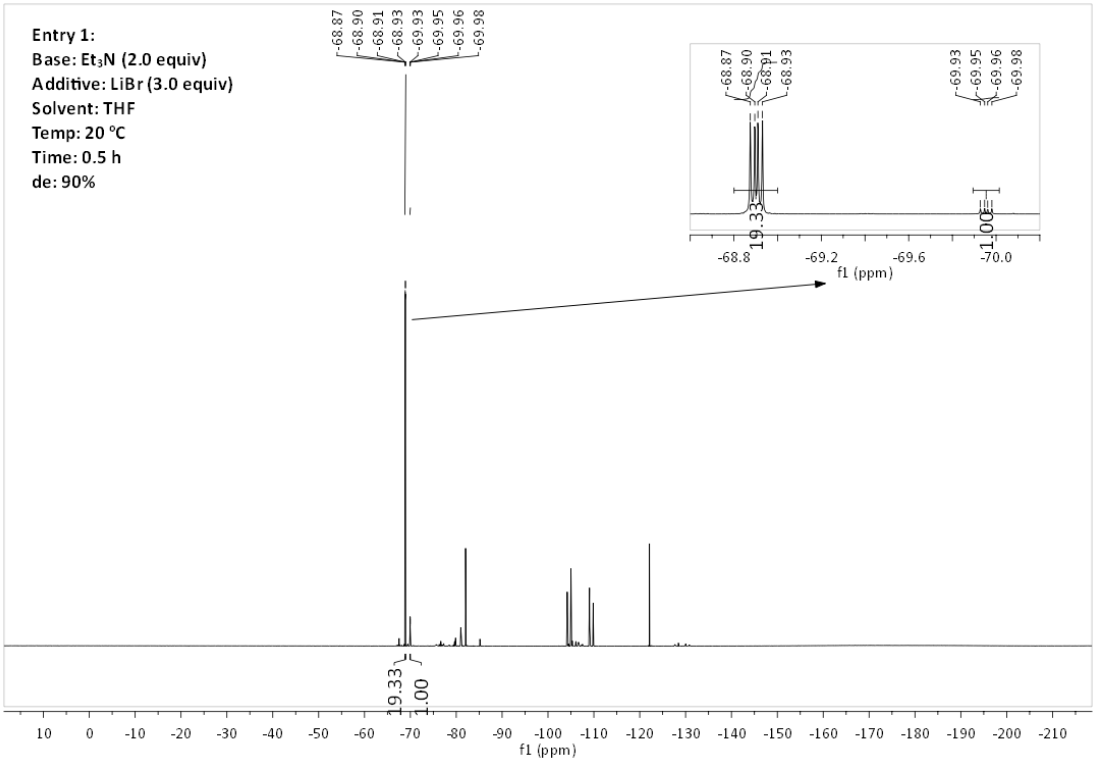
Chen Xie, Lingmin Wu, Haibo Mei, Vadim A. Soloshonok, Jianlin Han* and Yi Pan

Page Number

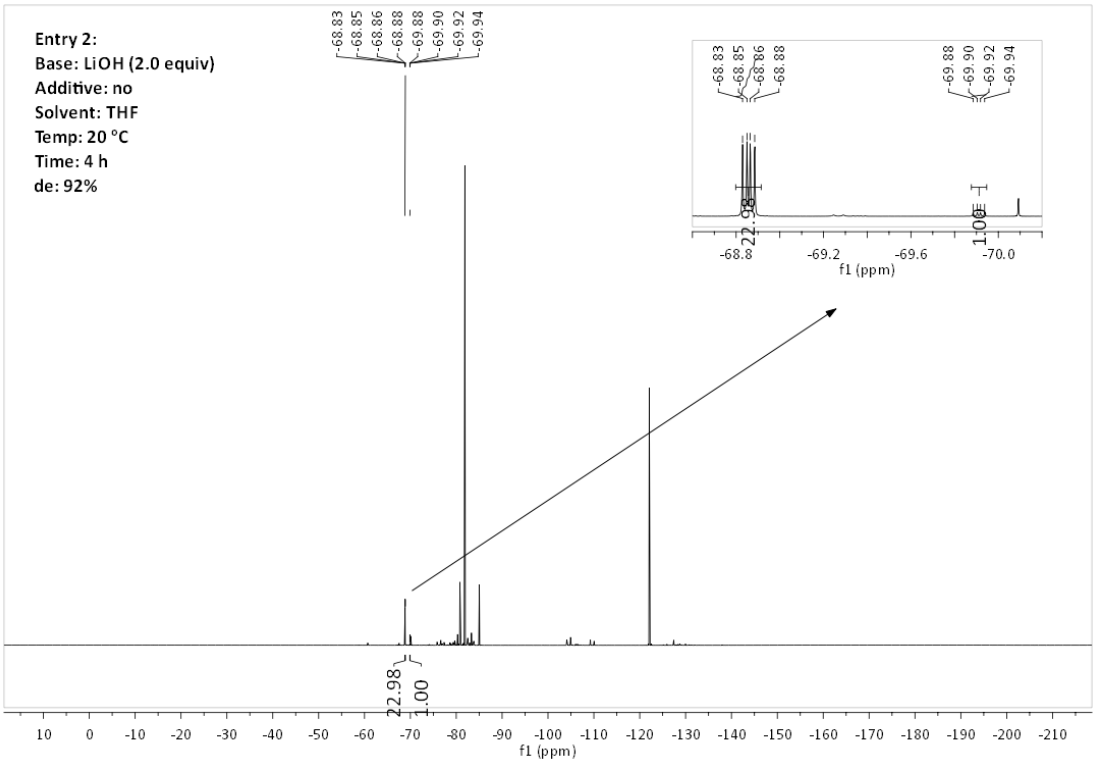
1. **19F-NMR spectra of crude reaction mixture for optimization of the reaction conditions (Table 1)…….S2**
2. **NMR spectra of compounds 10-13…….S12**
3. **19F NMR spectra for the study of the configurational stability……..S49**

1. ^{19}F-NMR spectra of crude reaction mixture for optimization of the reaction conditions (Table 1)

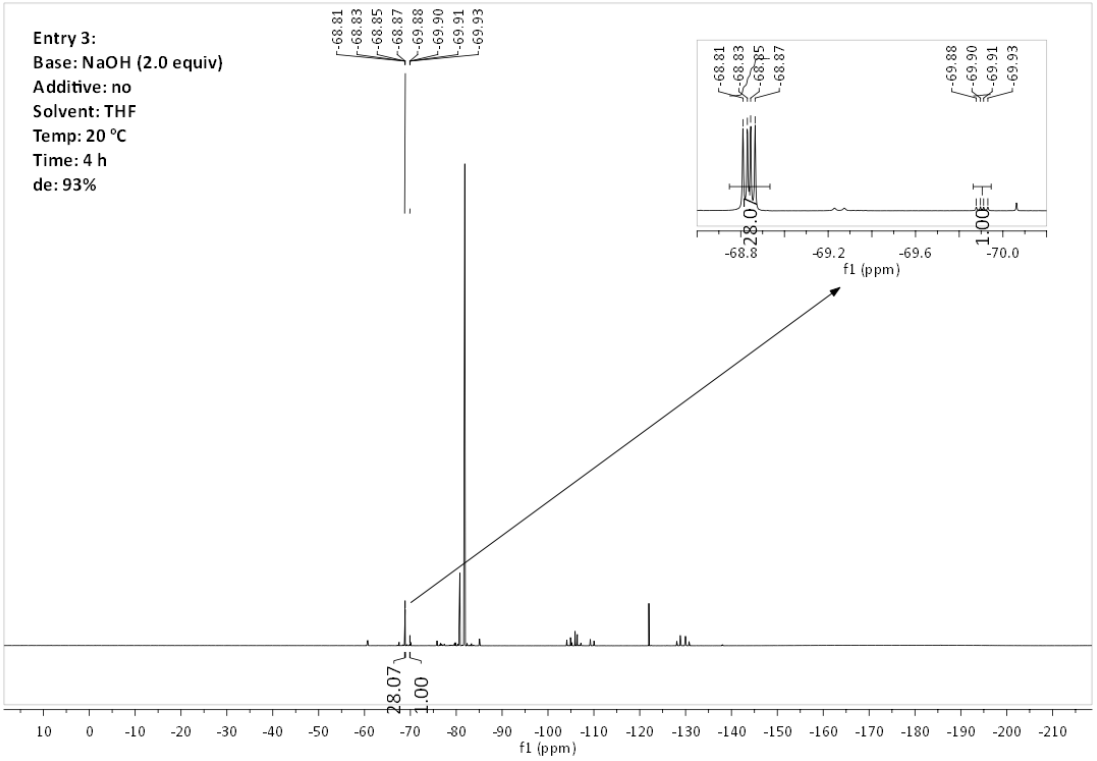
^{19}F-NMR spectra of crude reaction mixture for Entry 1 of Table 1



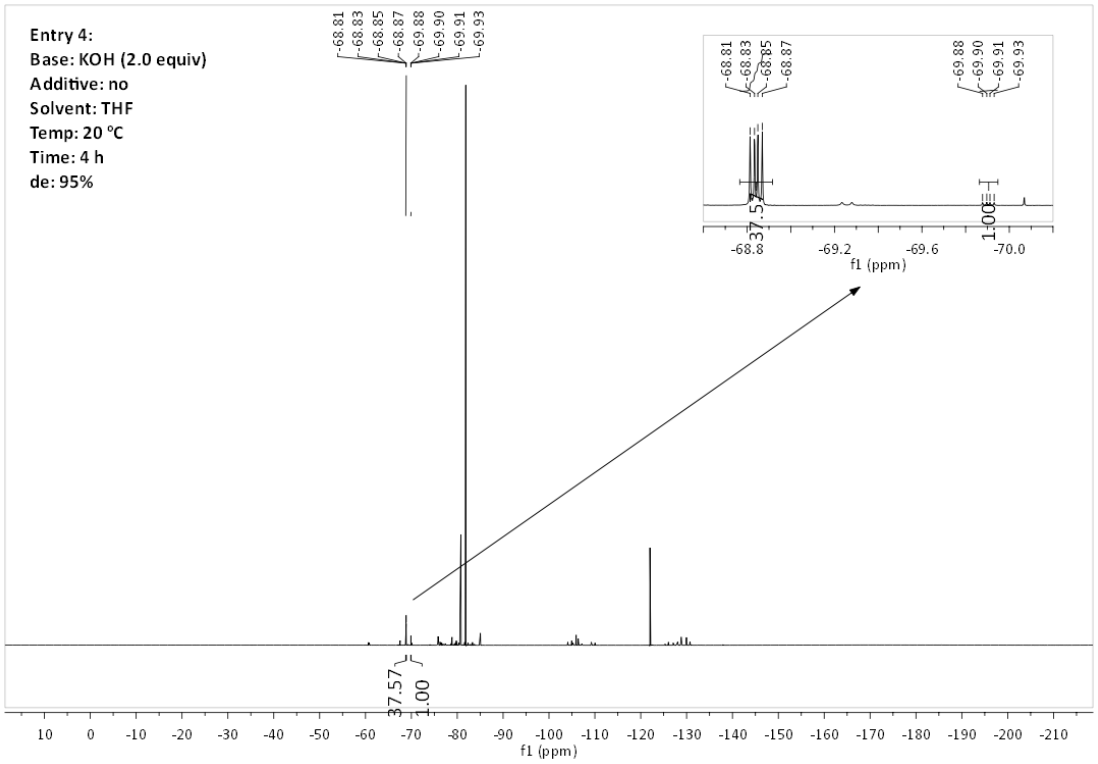
^{19}F-NMR spectra of crude reaction mixture for Entry 2 of Table 1



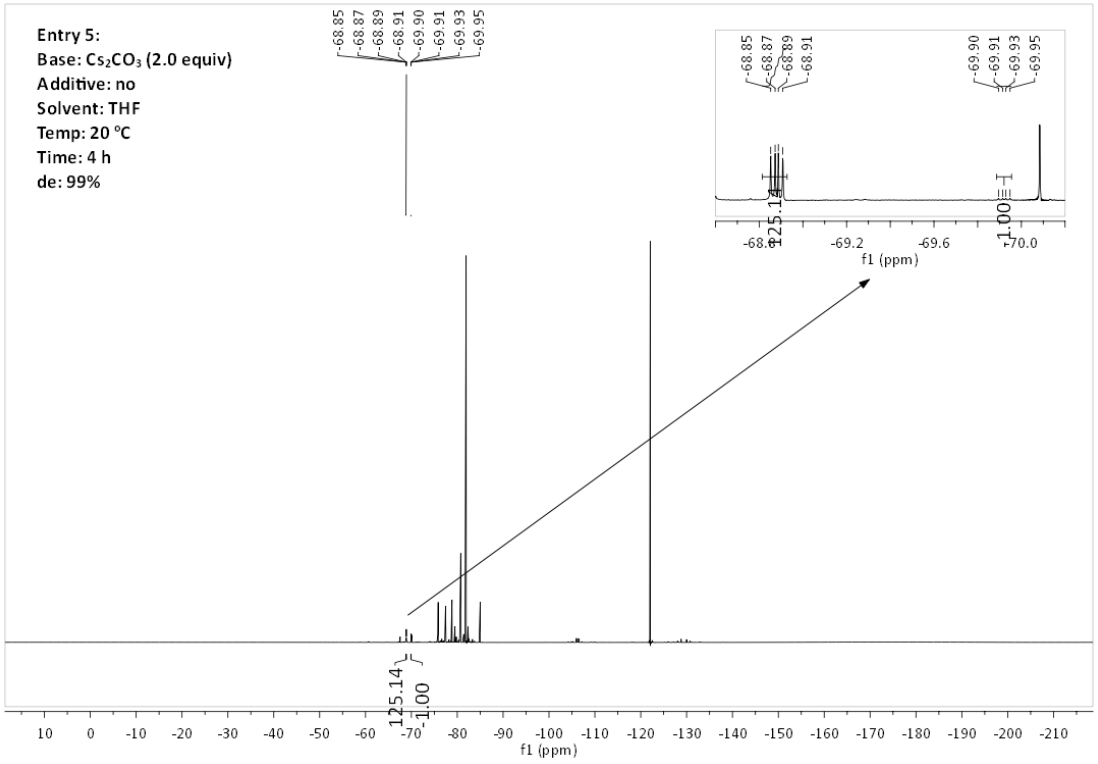
^{19}F-NMR spectra of crude reaction mixture for Entry 3 of Table 1



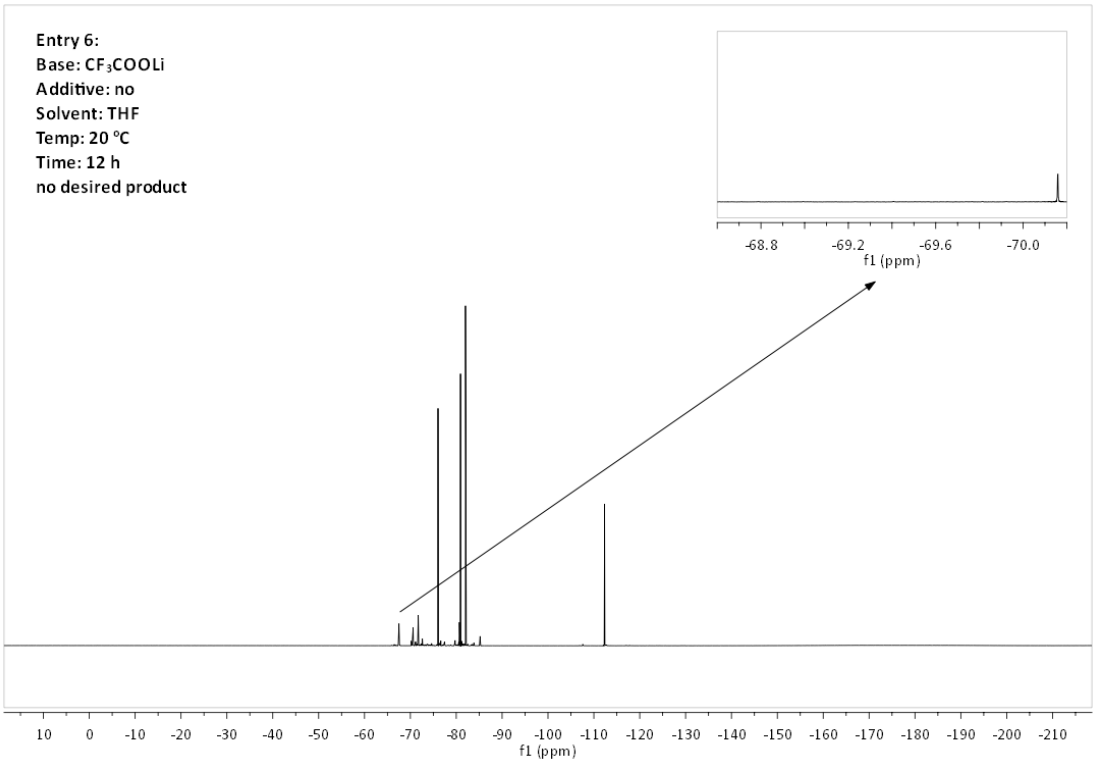
^{19}F-NMR spectra of crude reaction mixture for Entry 4 of Table 1



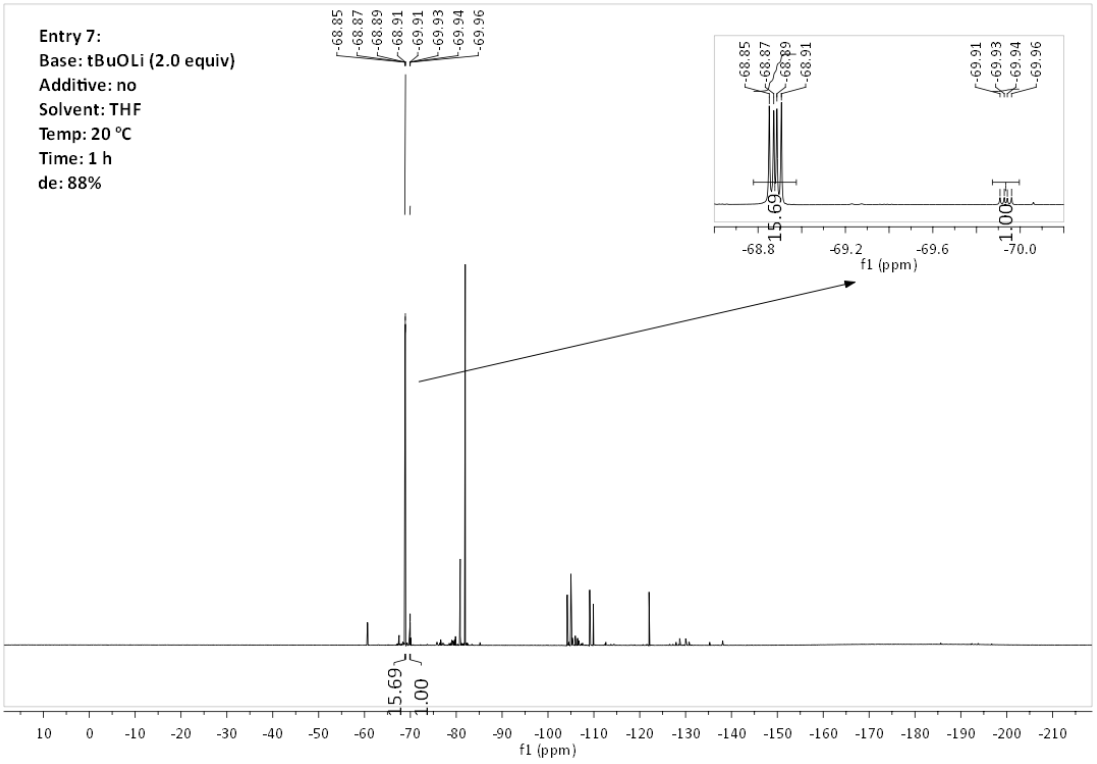
^{19}F-NMR spectra of crude reaction mixture for Entry 5 of Table 1



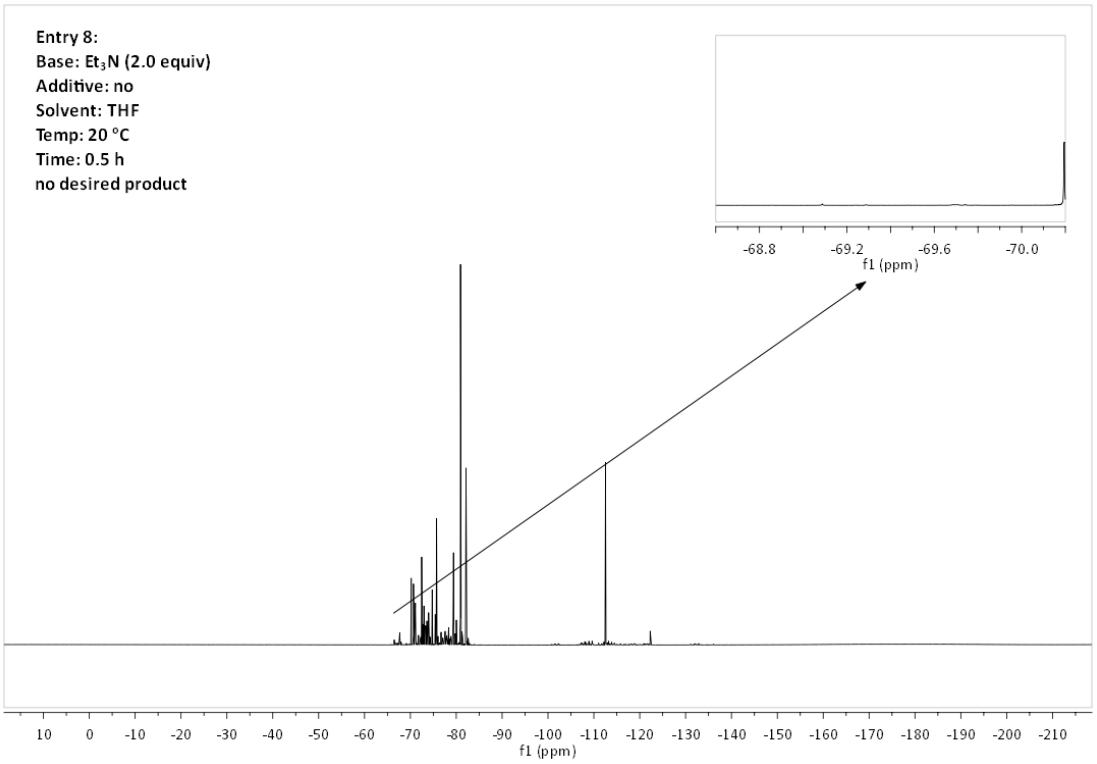
^{19}F-NMR spectra of crude reaction mixture for Entry 6 of Table 1



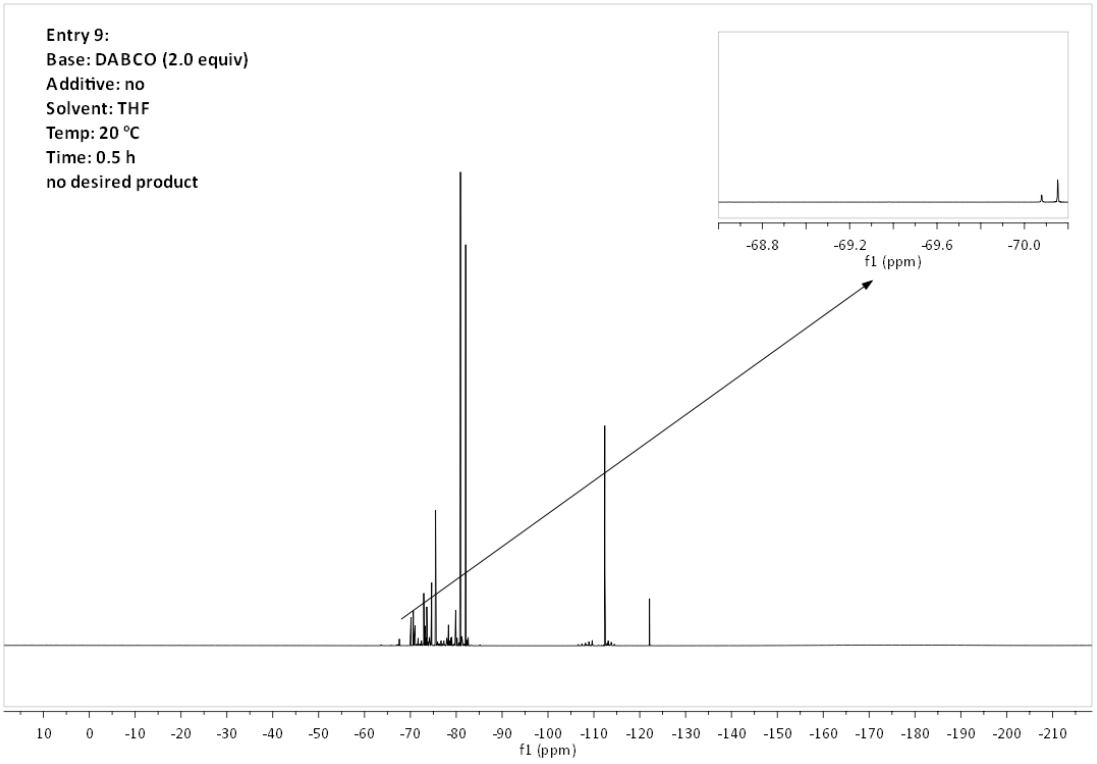
^{19}F-NMR spectra of crude reaction mixture for Entry 7 of Table 1



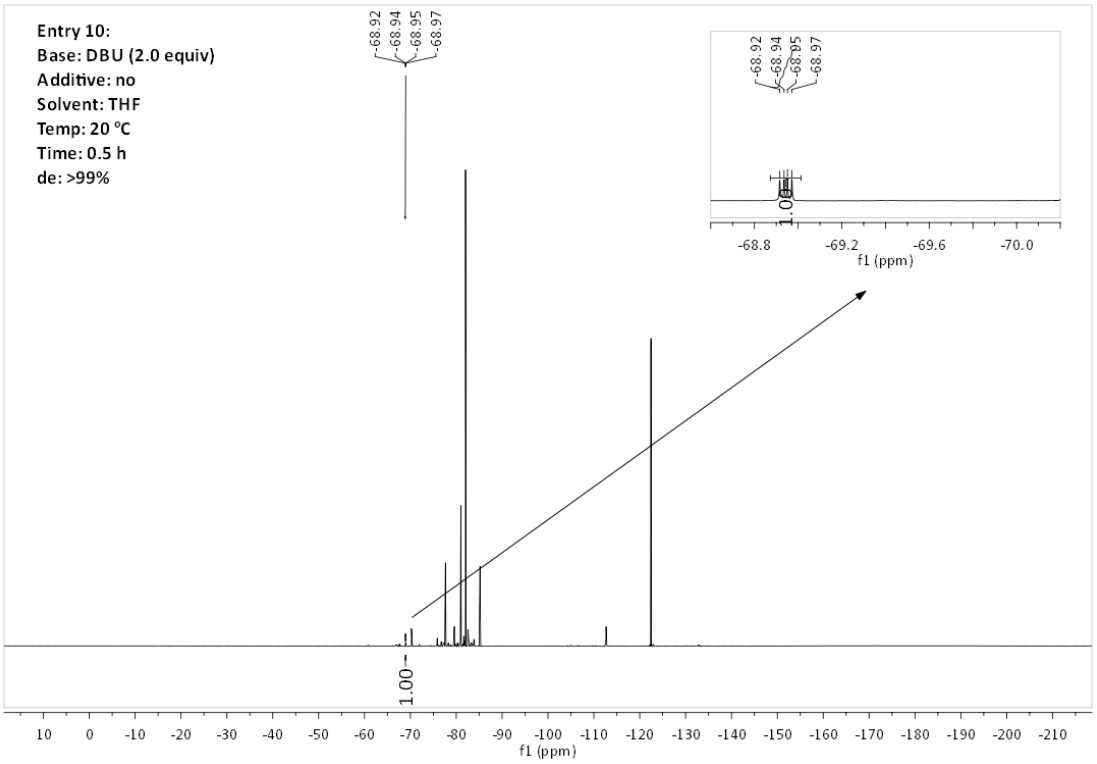
^{19}F-NMR spectra of crude reaction mixture for Entry 8 of Table 1



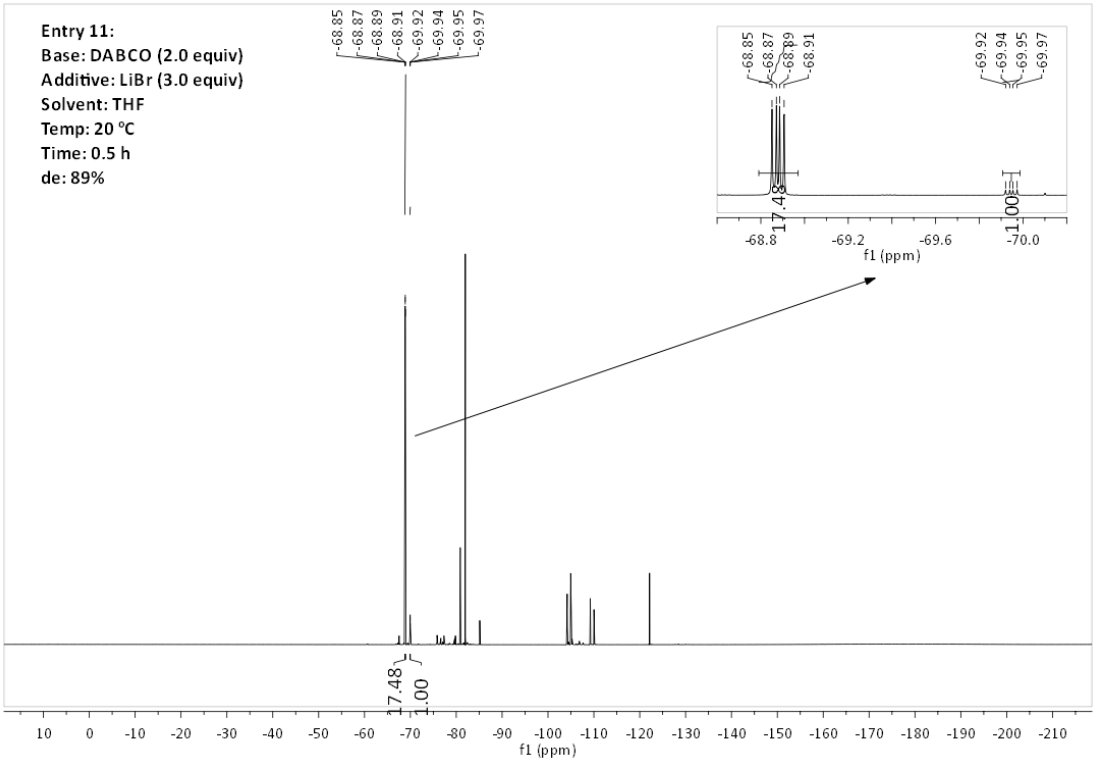
^{19}F-NMR spectra of crude reaction mixture for Entry 9 of Table 1



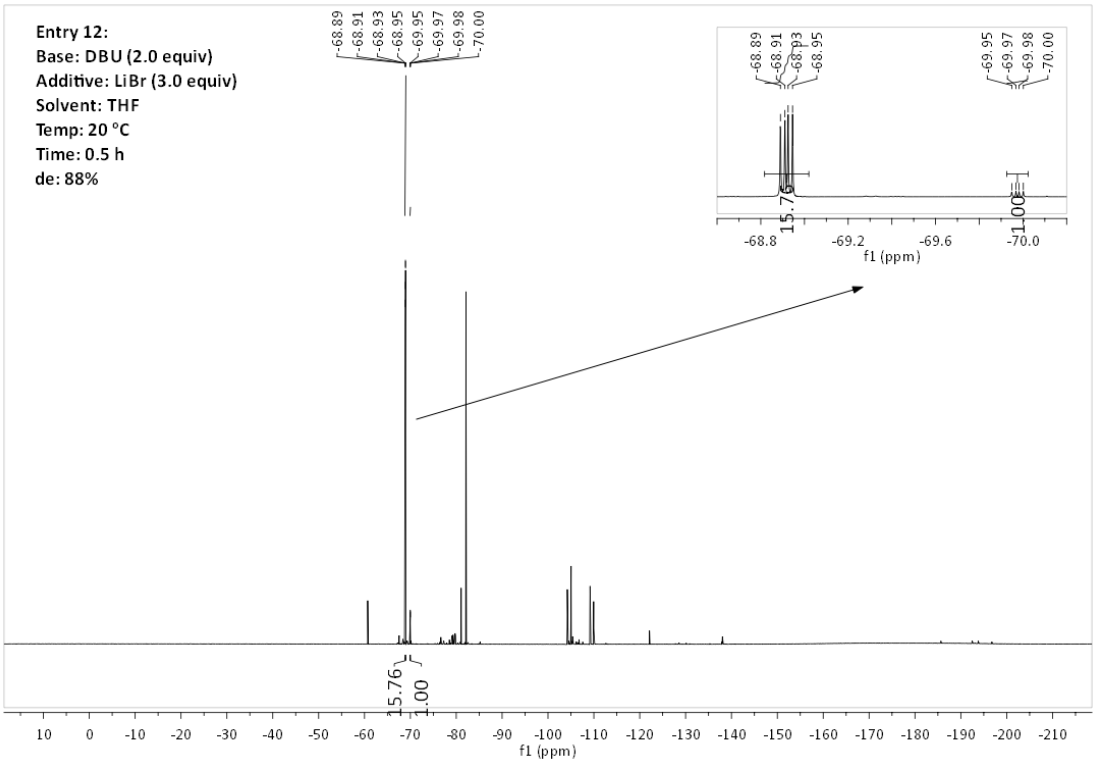
^{19}F-NMR spectra of crude reaction mixture for Entry 10 of Table 1



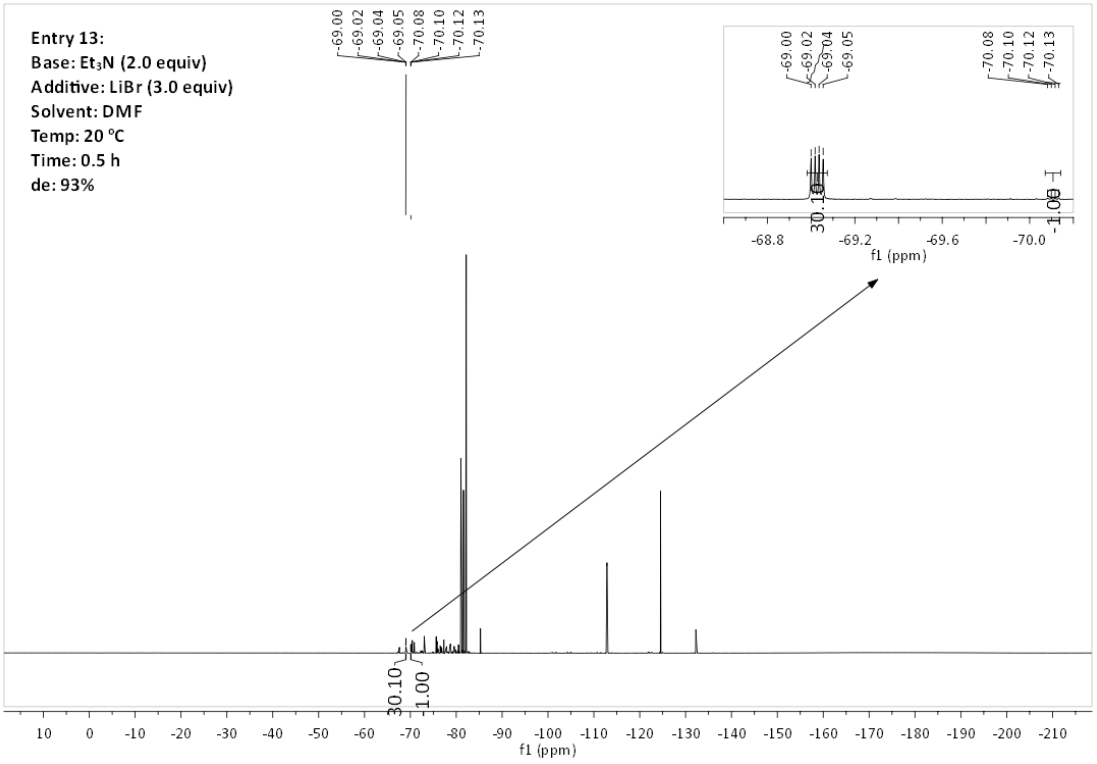
^{19}F-NMR spectra of crude reaction mixture for Entry 11 of Table 1



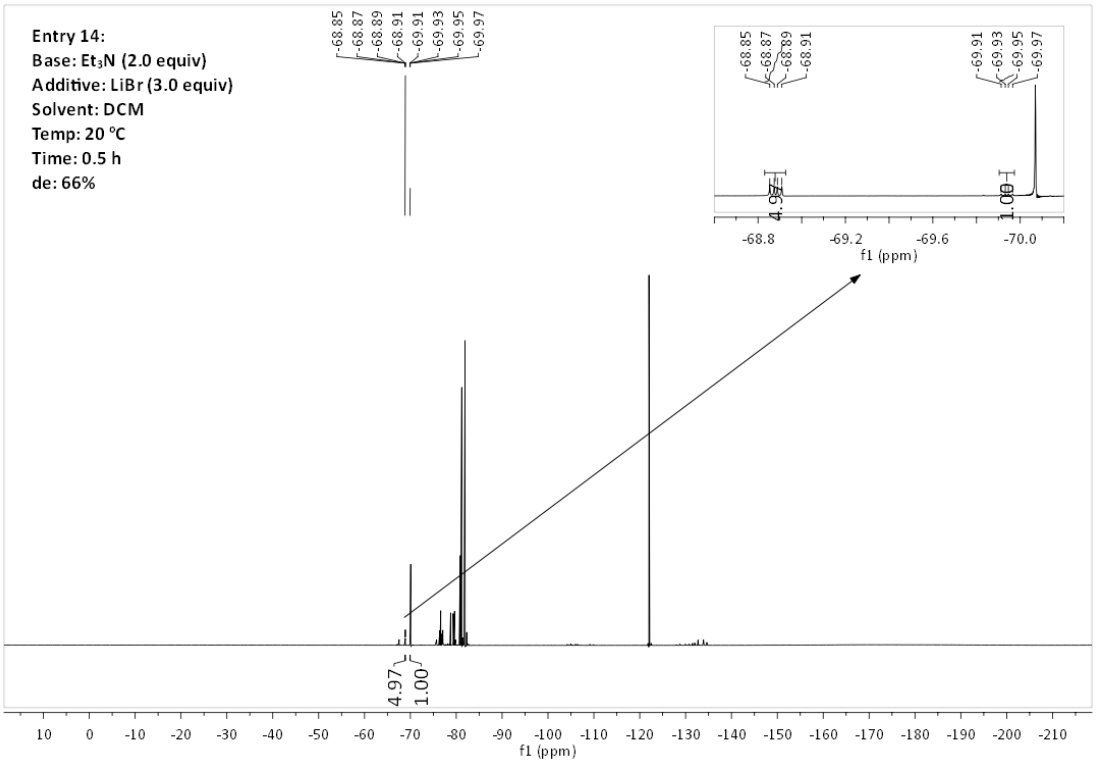
^{19}F-NMR spectra of crude reaction mixture for Entry 12 of Table 1



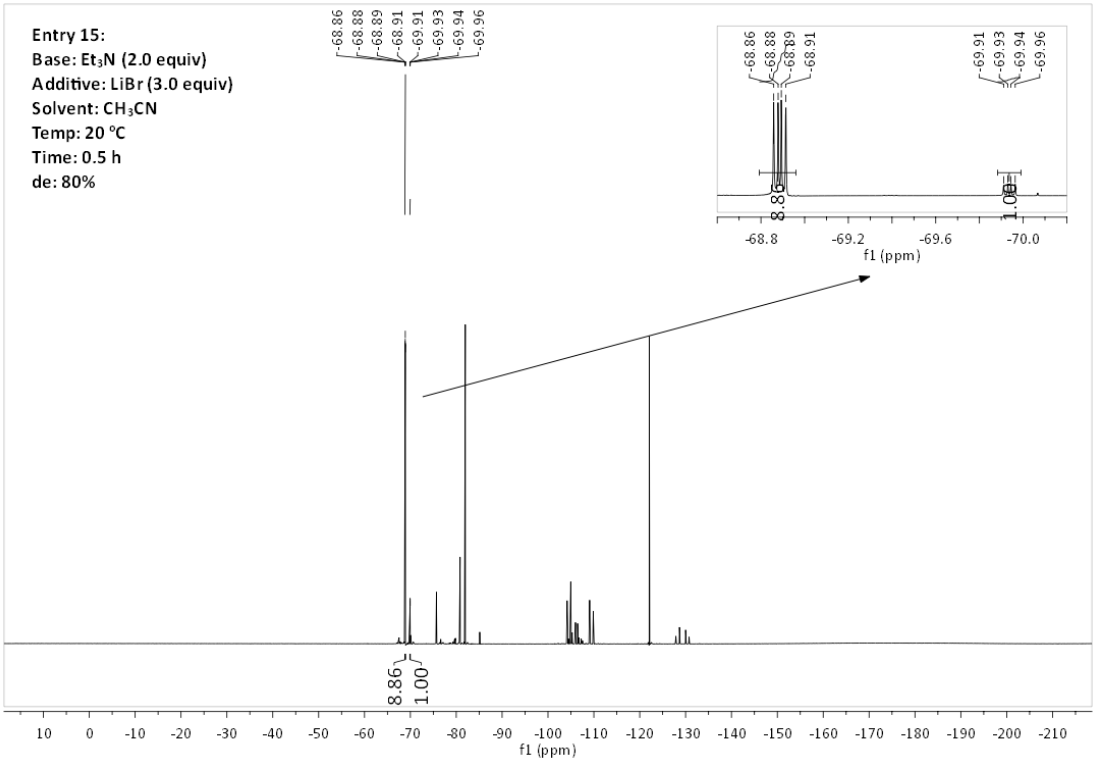
^{19}F-NMR spectra of crude reaction mixture for Entry 13 of Table 1



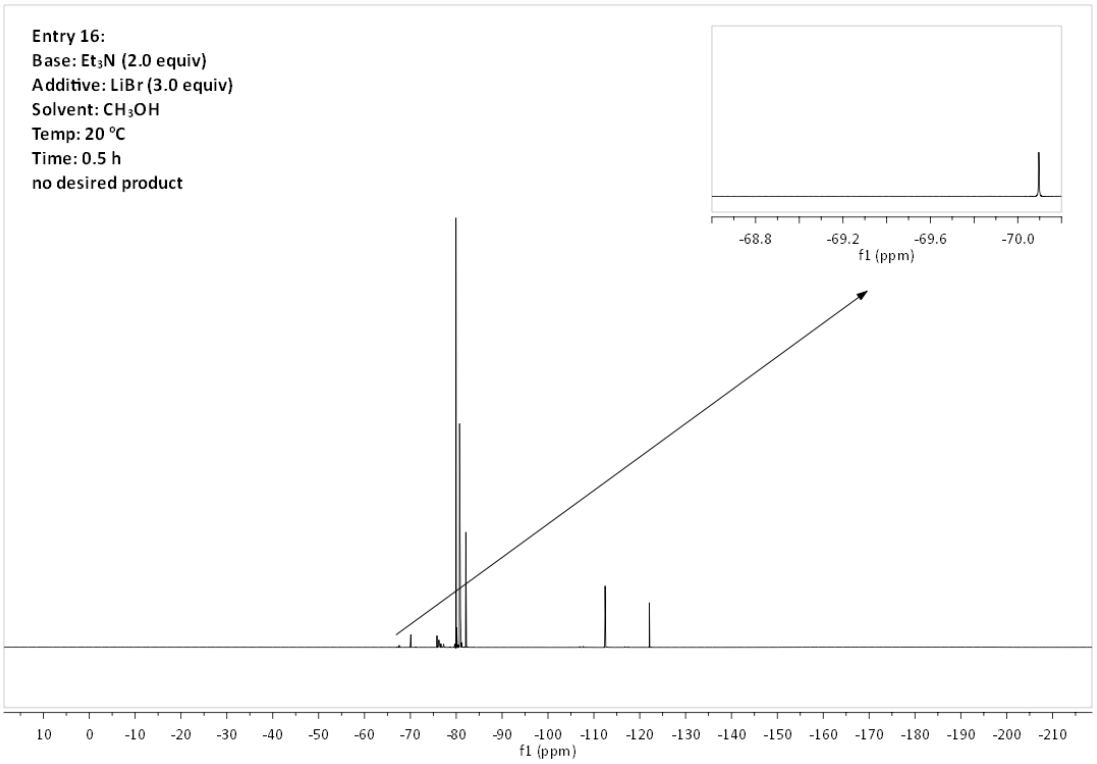
^{19}F-NMR spectra of crude reaction mixture for Entry 14 of Table 1



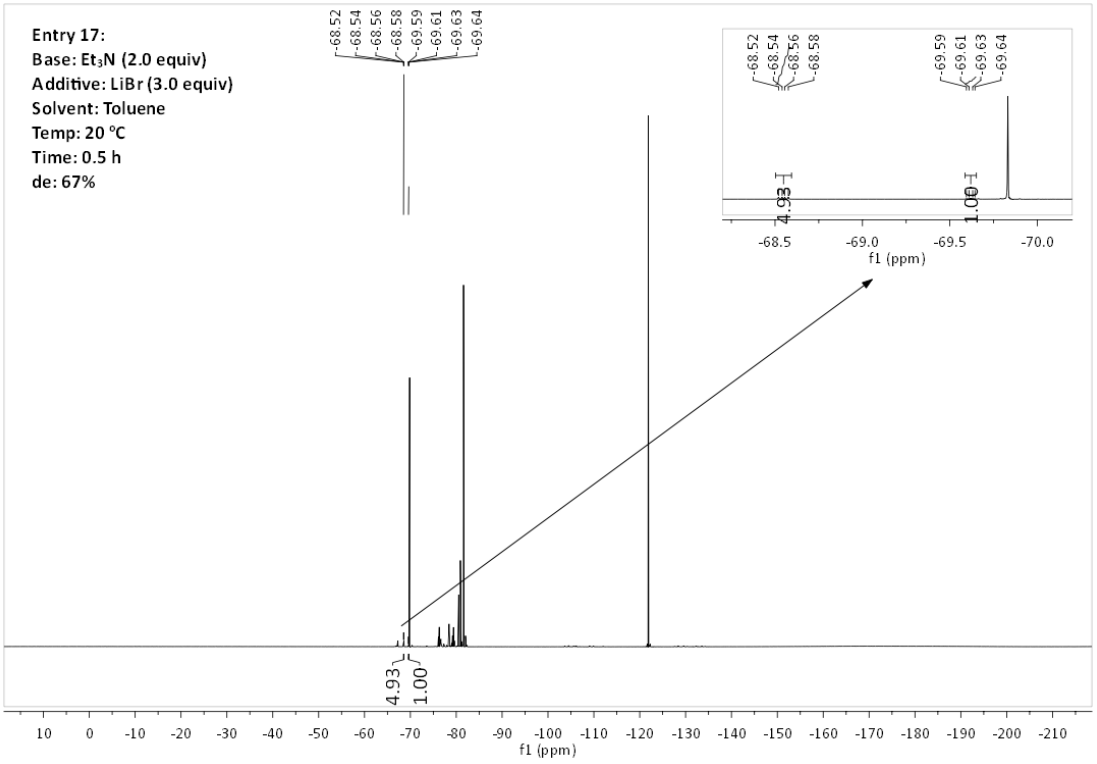
^{19}F-NMR spectra of crude reaction mixture for Entry 15 of Table 1



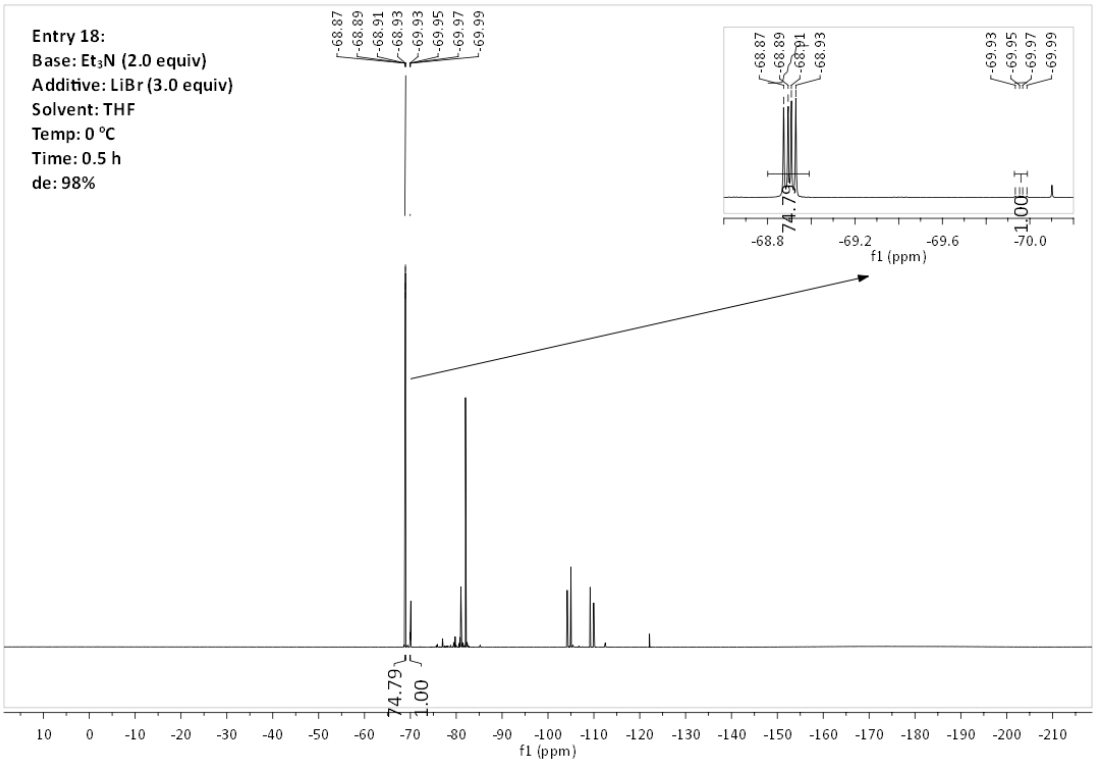
^{19}F-NMR spectra of crude reaction mixture for Entry 16 of Table 1



^{19}F-NMR spectra of crude reaction mixture for Entry 17 of Table 1

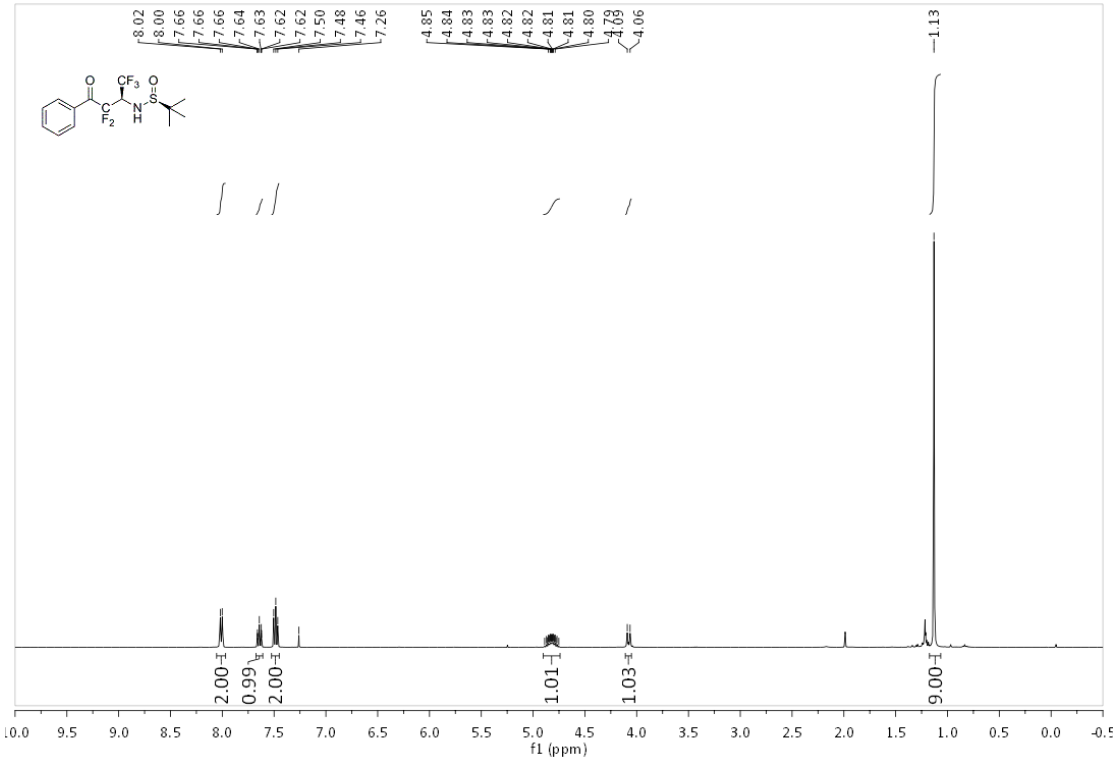


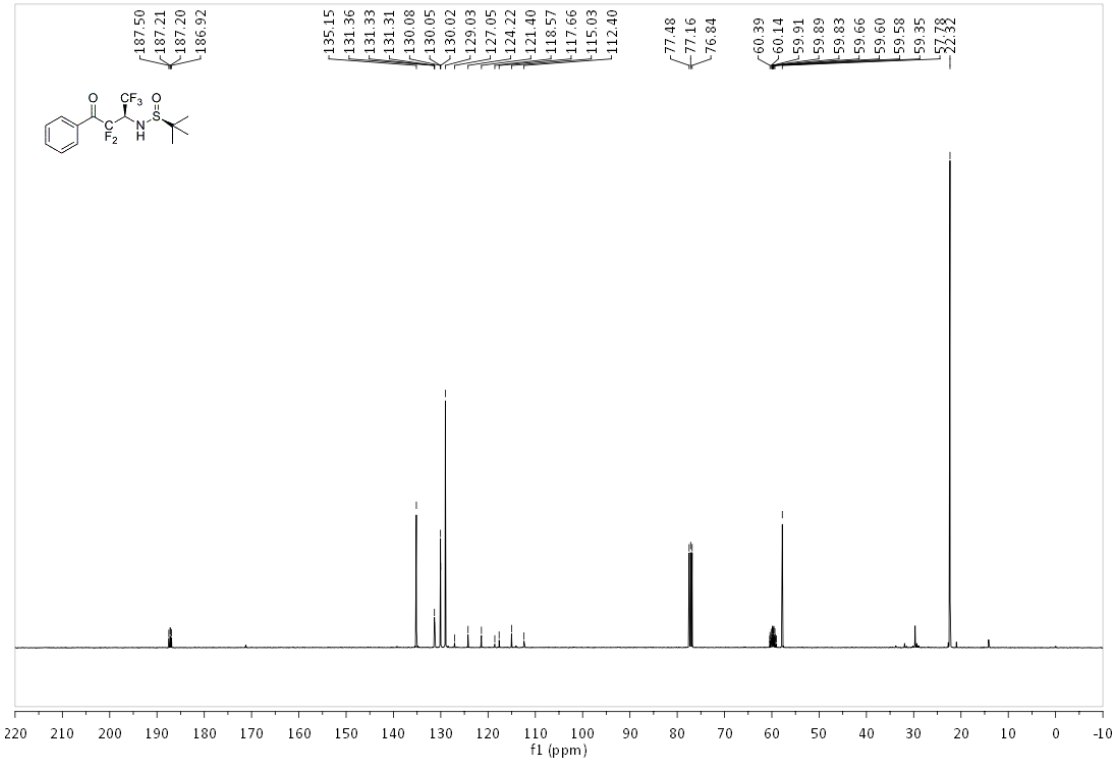
^{19}F-NMR spectra of crude reaction mixture for Entry 18 of Table 1

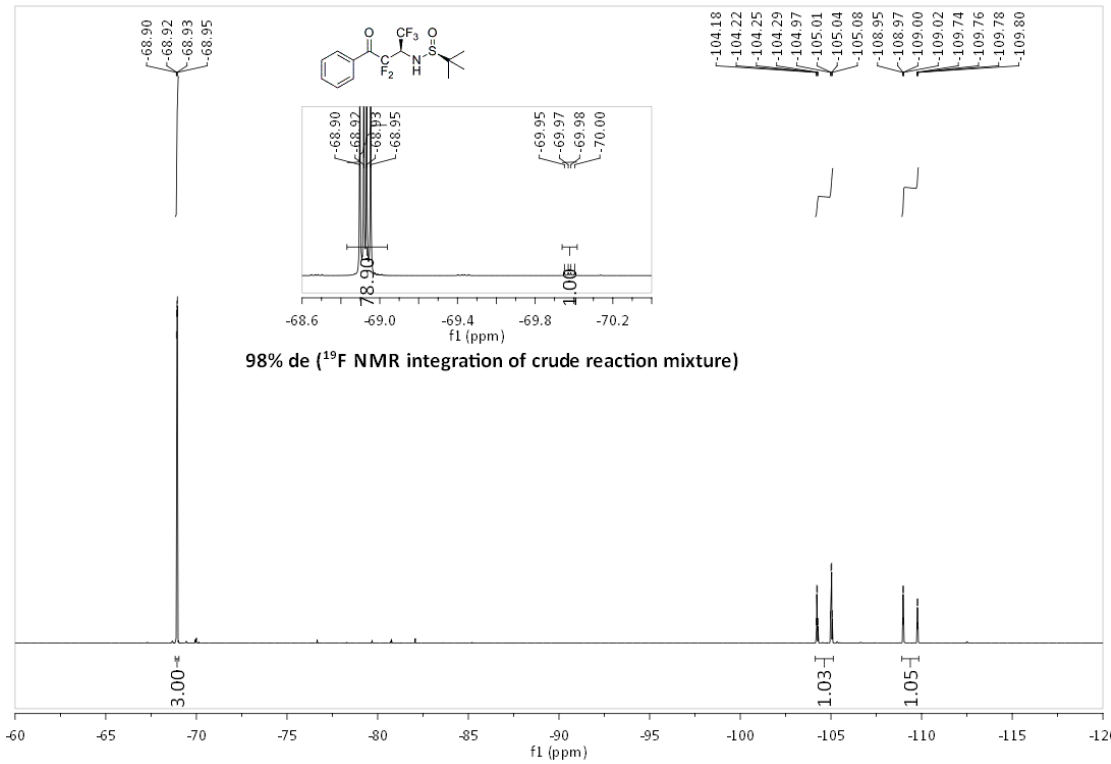


2. NMR spectra of compounds 10-13

^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra of **10a**

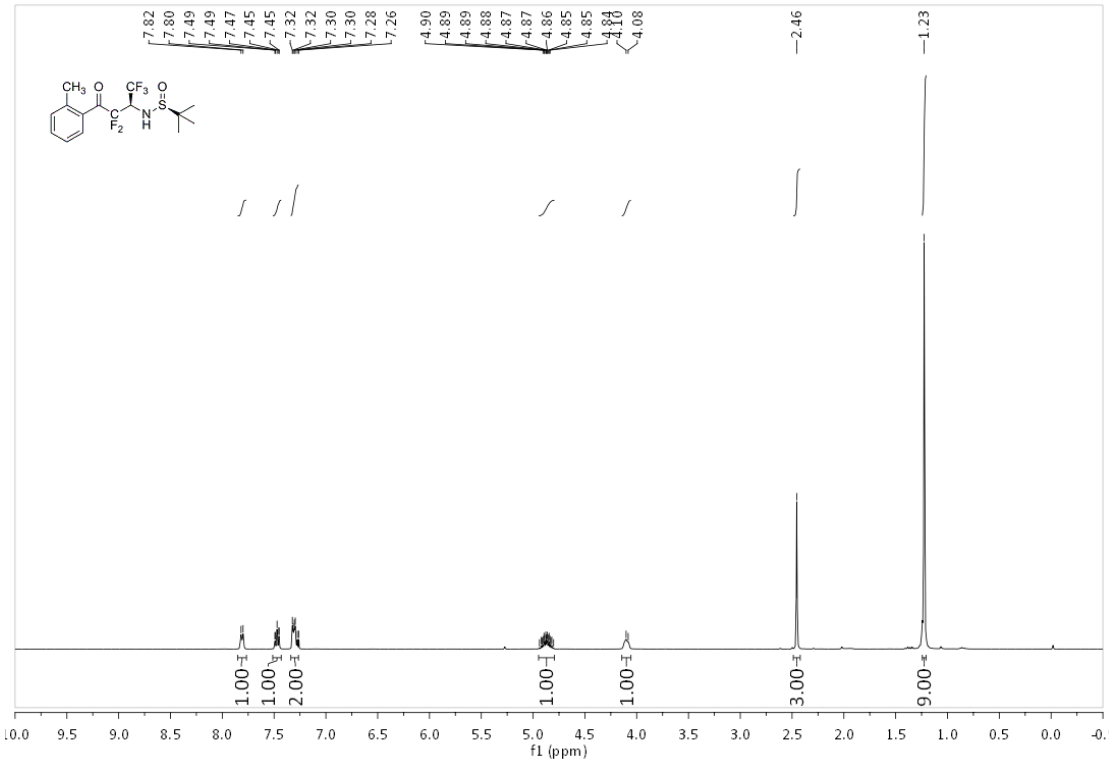


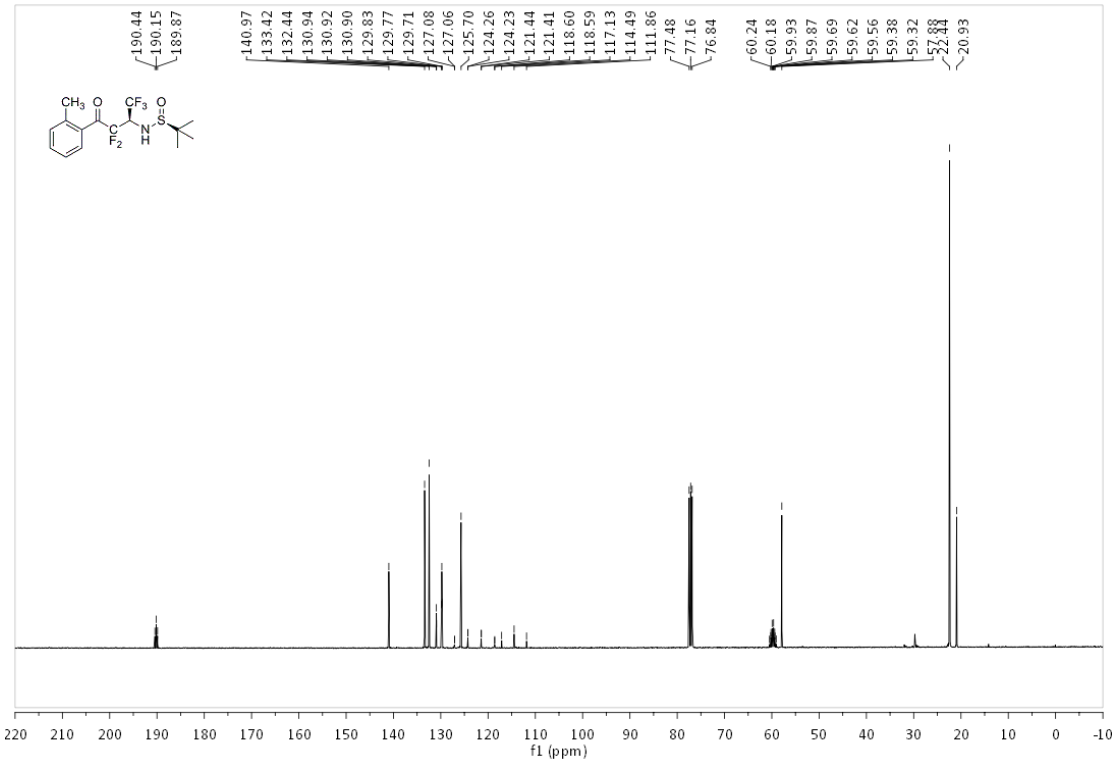


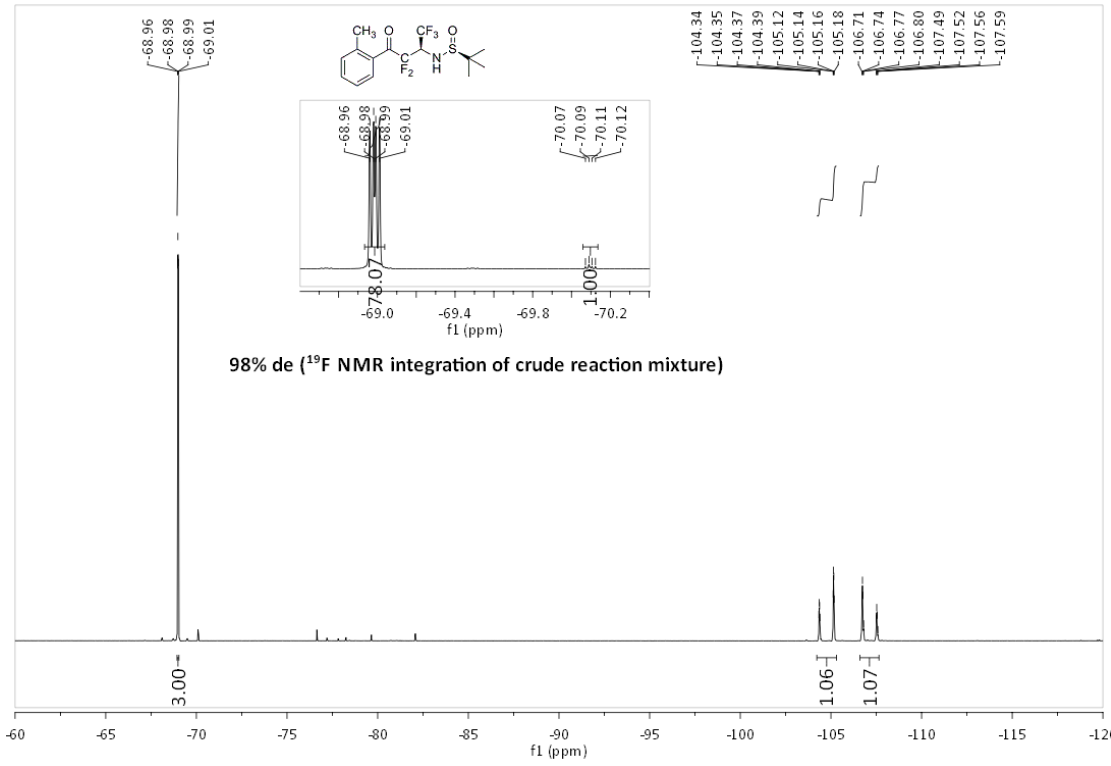


98% de (^{19}F NMR integration of crude reaction mixture)

^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra of **10b**

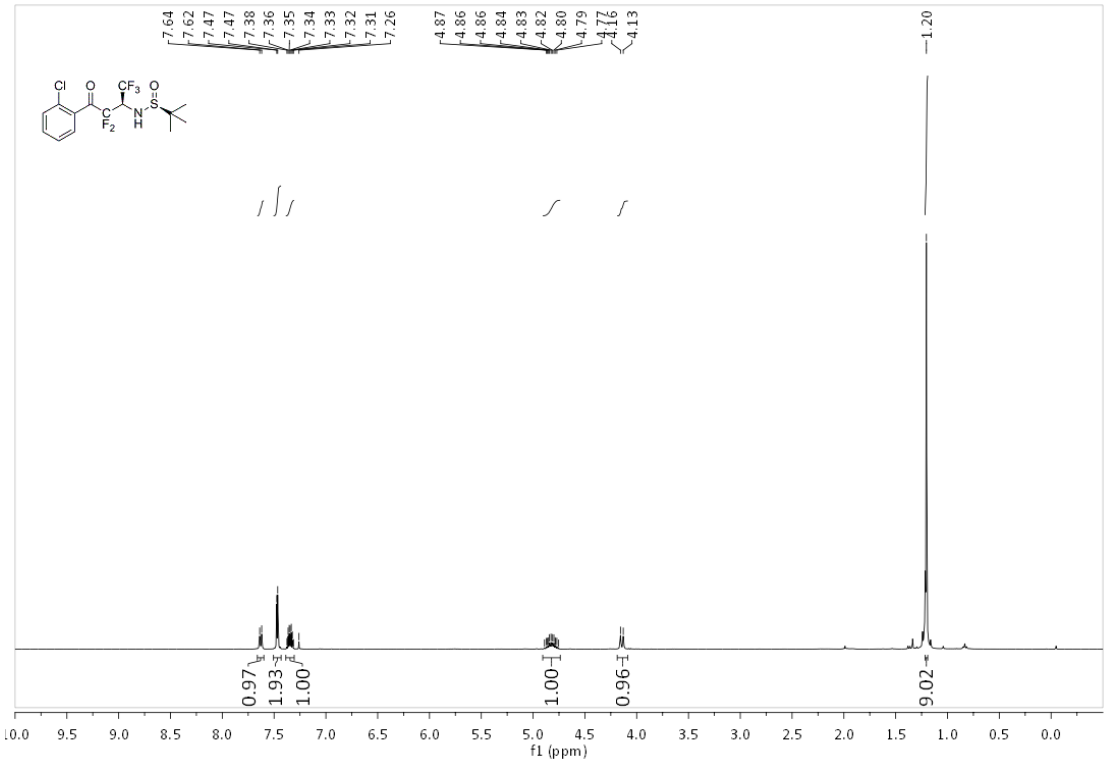


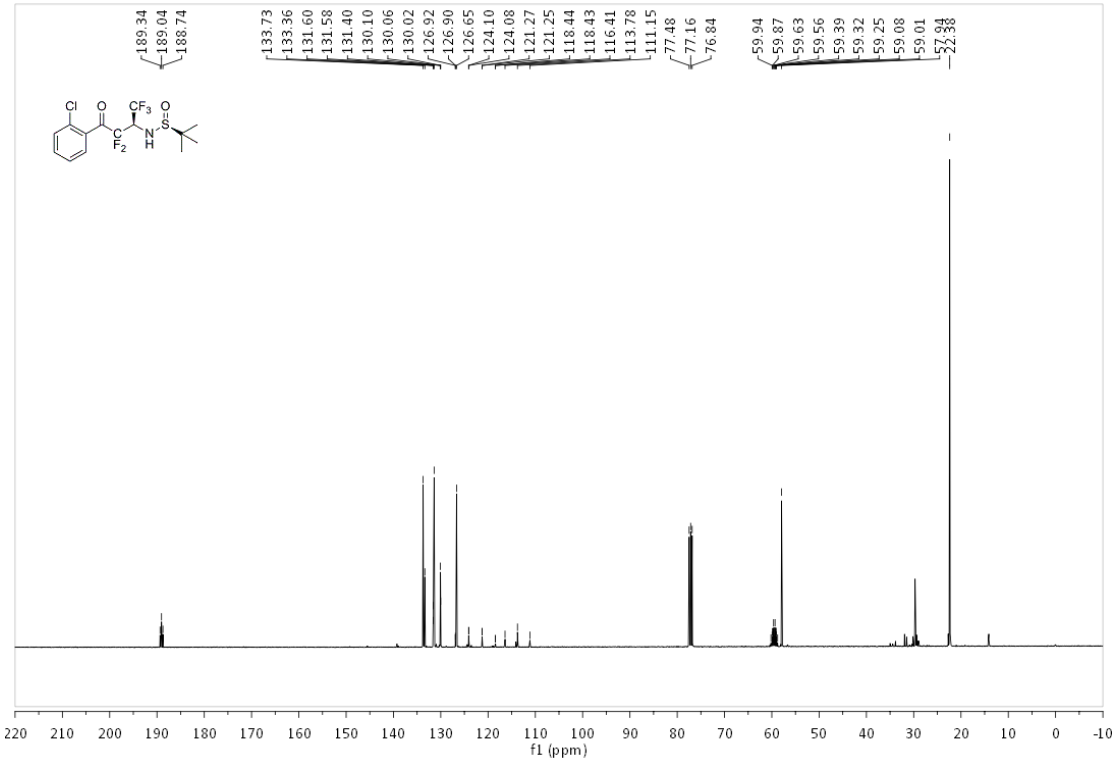


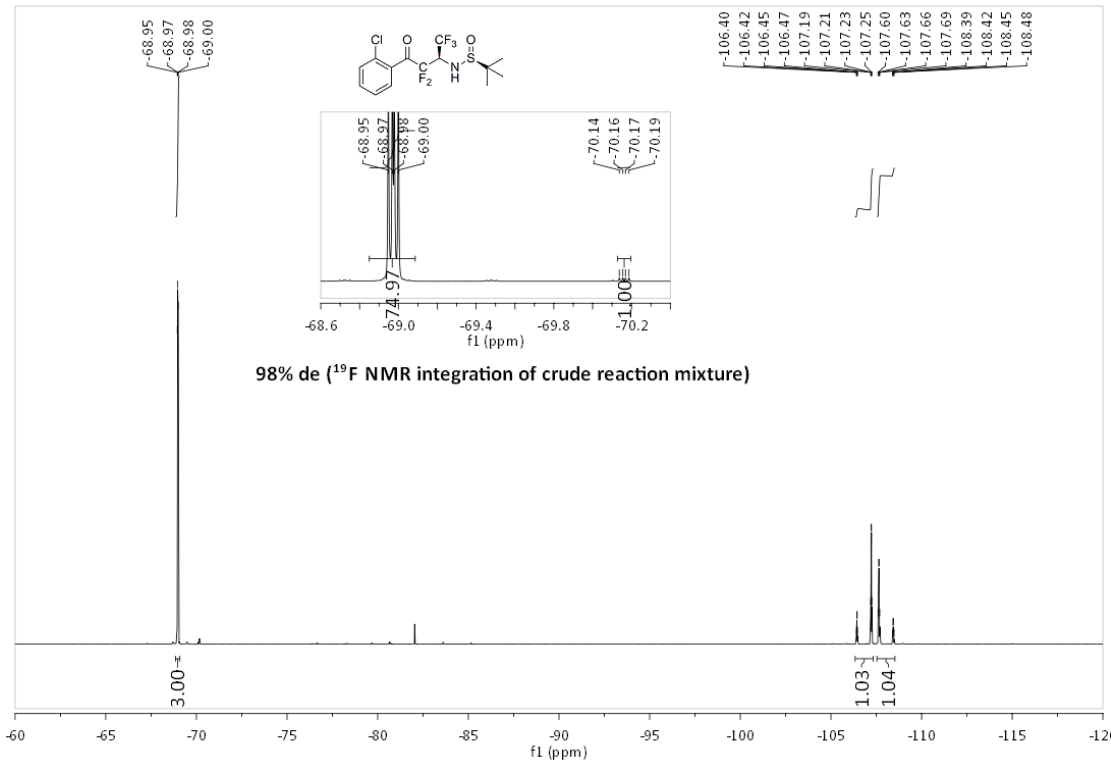


98% de (^{19}F NMR integration of crude reaction mixture)

^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra of **10c**

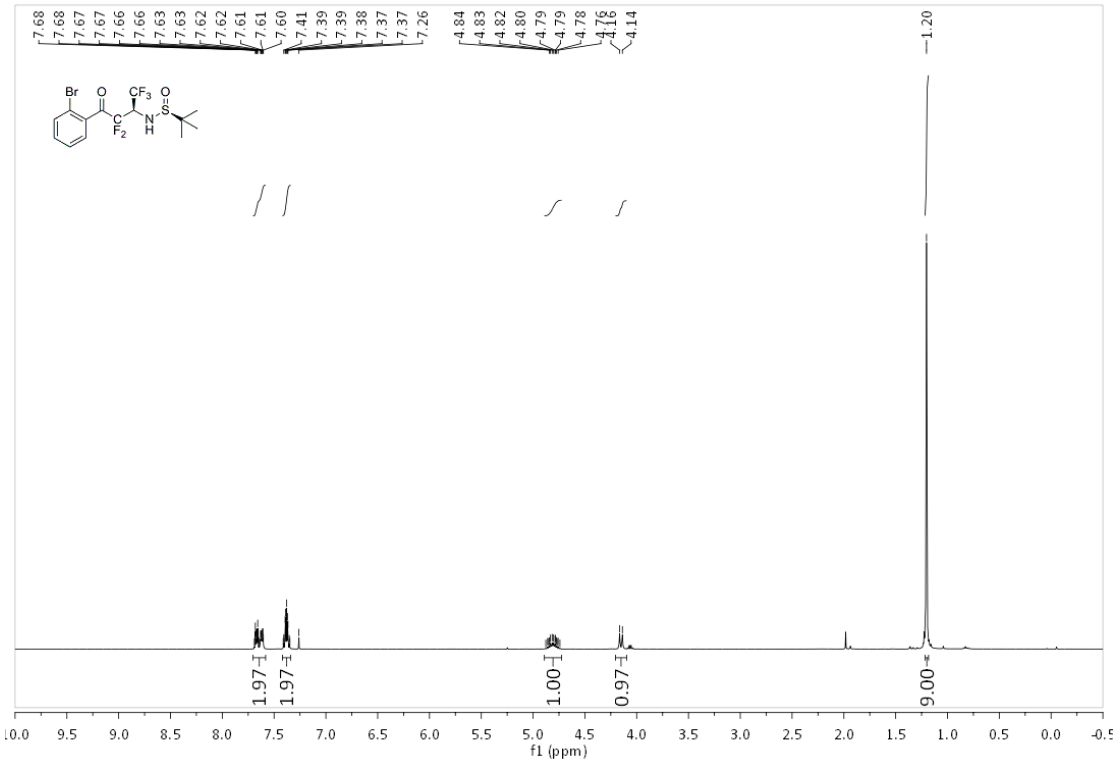


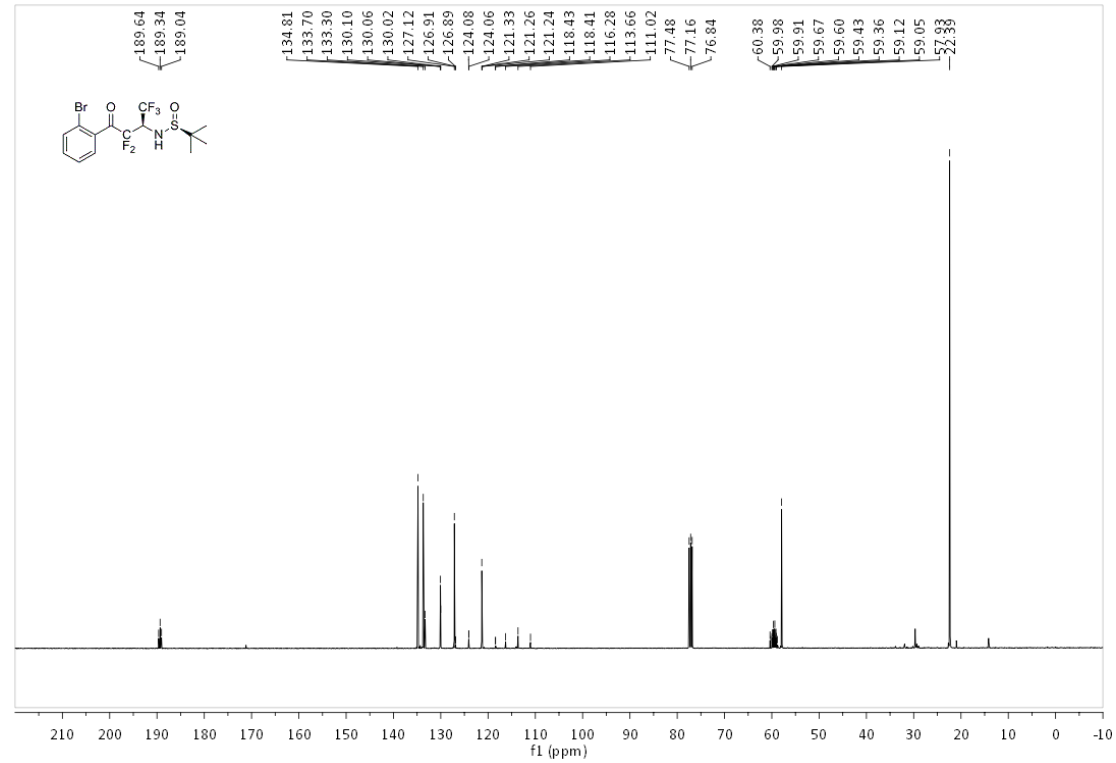


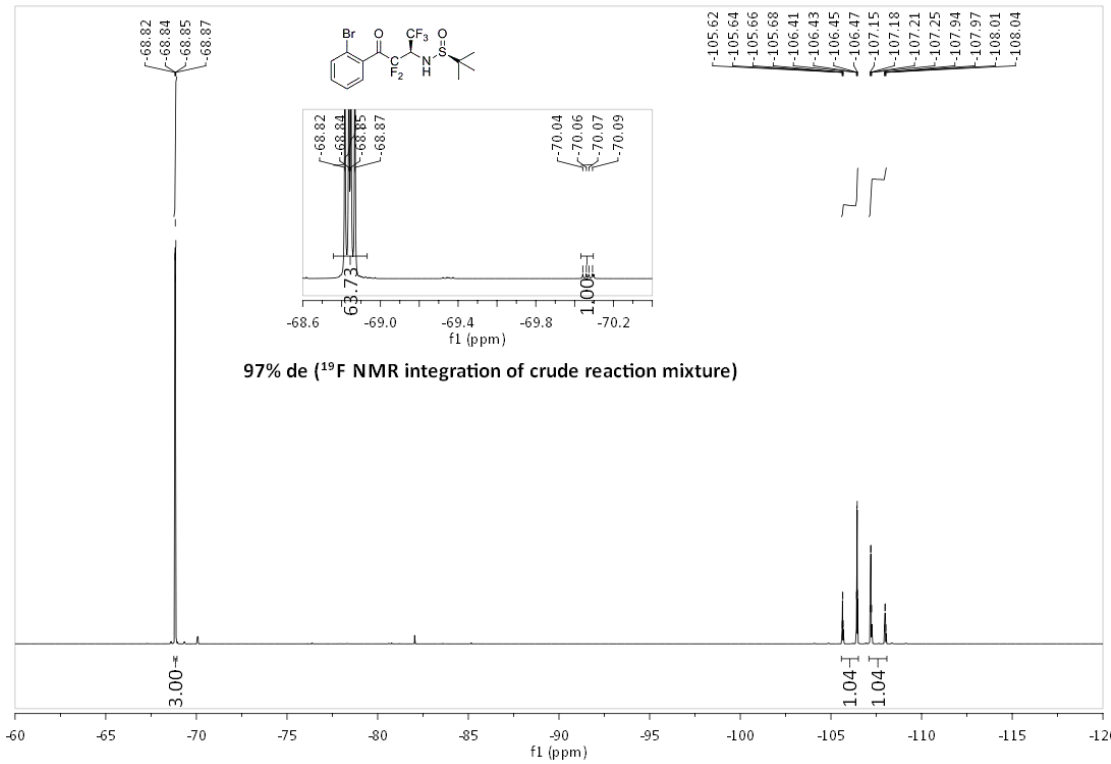


98% de (^{19}F NMR integration of crude reaction mixture)

^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra of **10d**

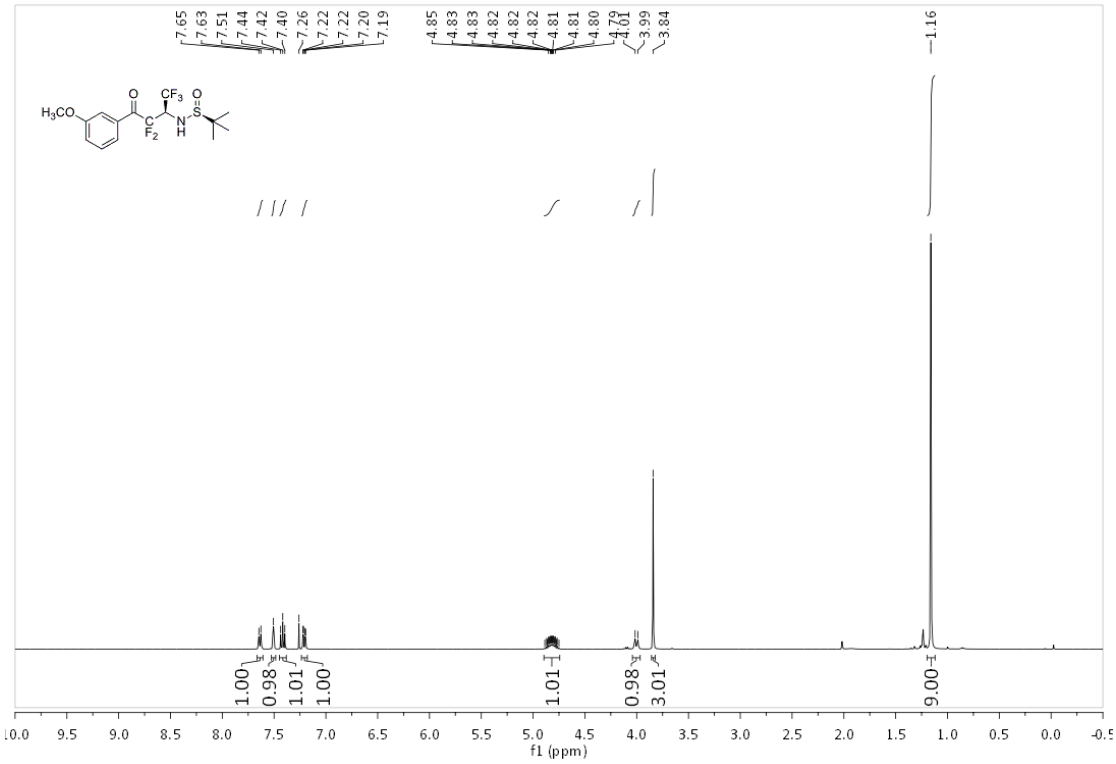


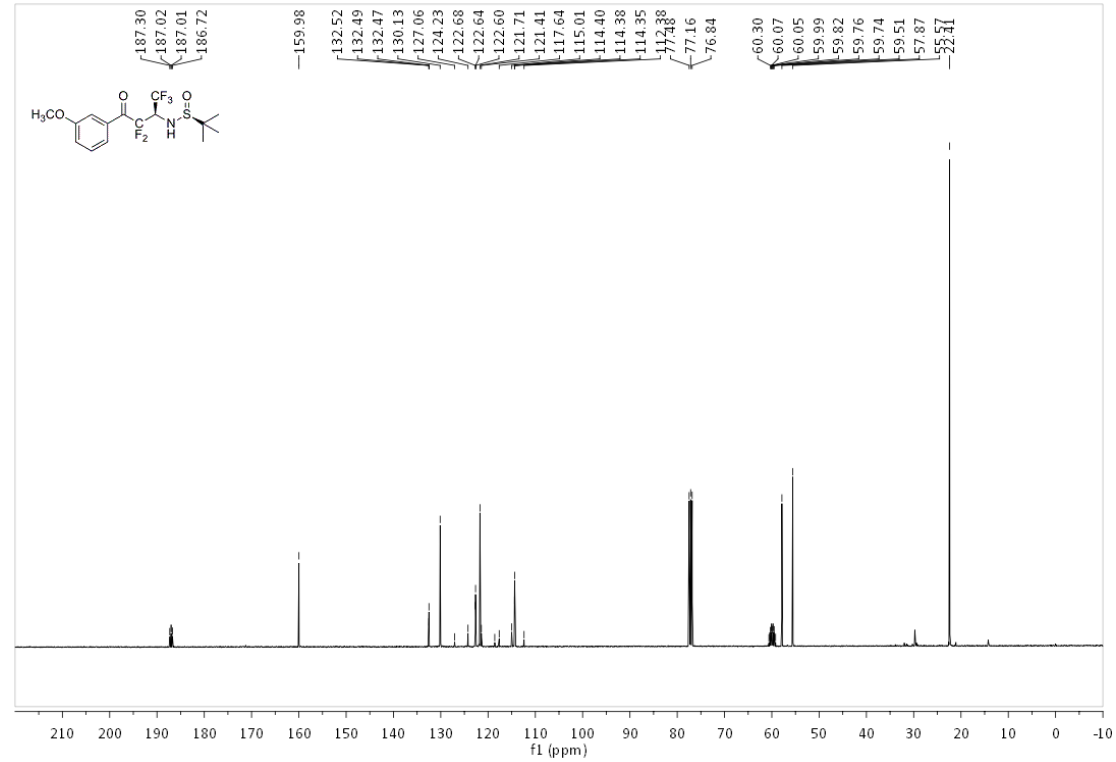


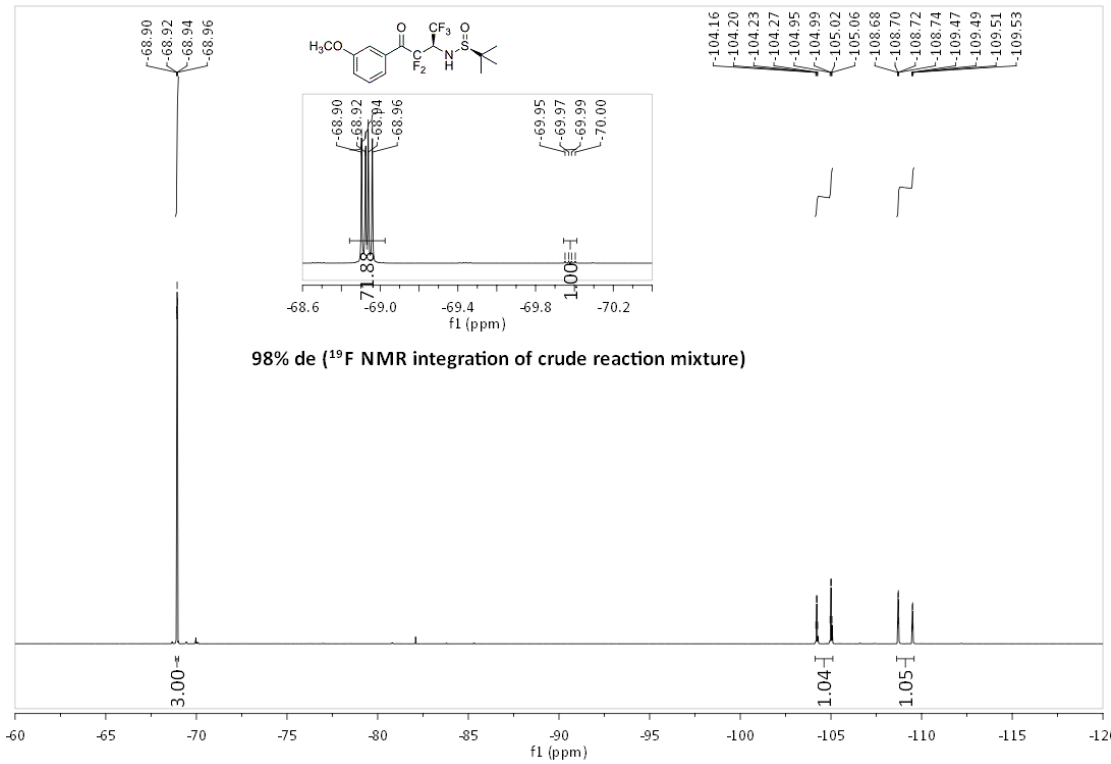


97% de (^{19}F NMR integration of crude reaction mixture)

^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra of **10e**

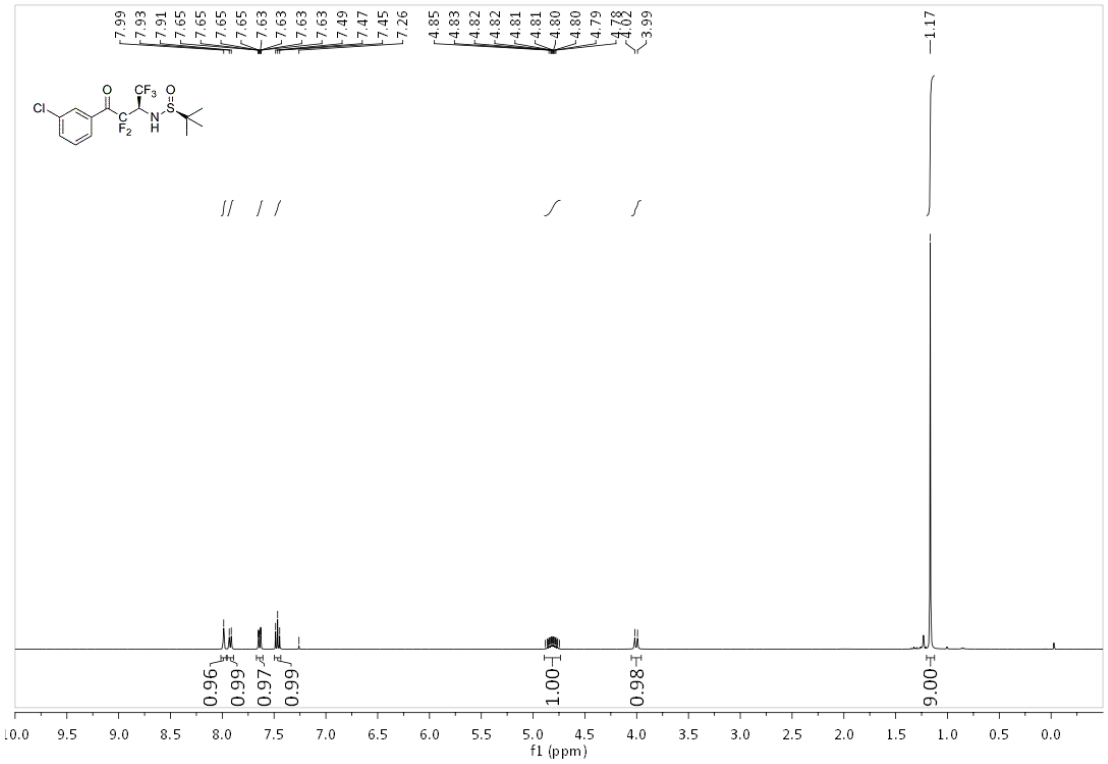


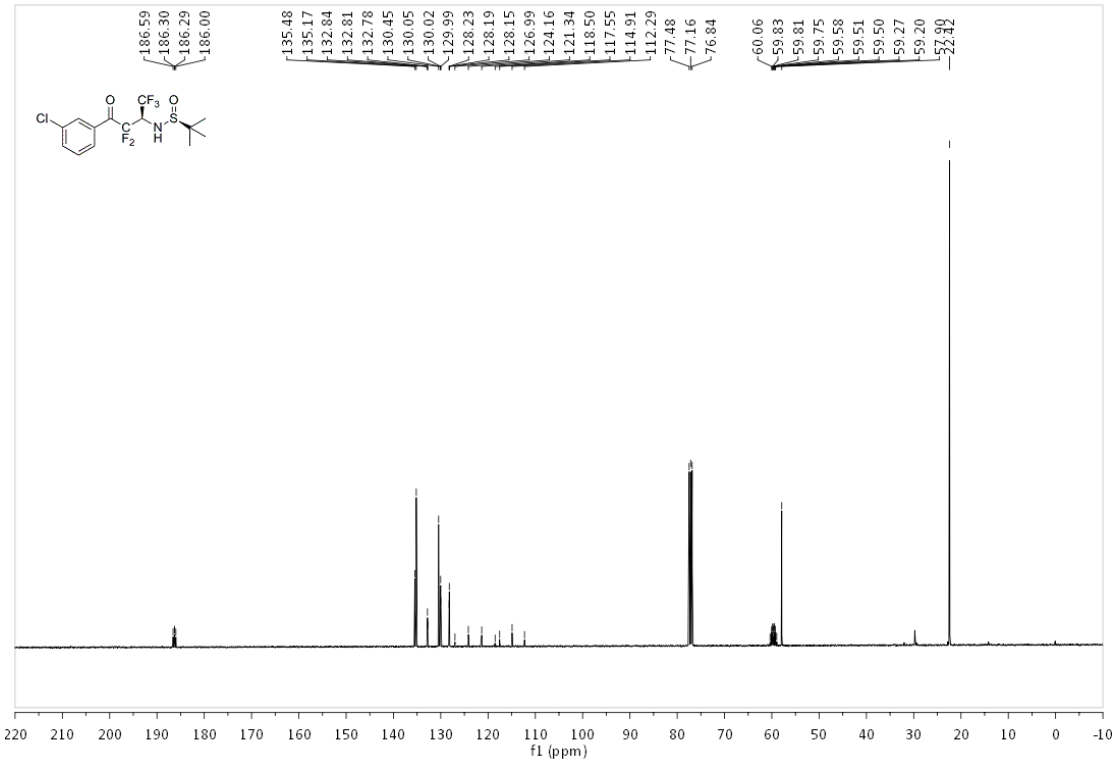


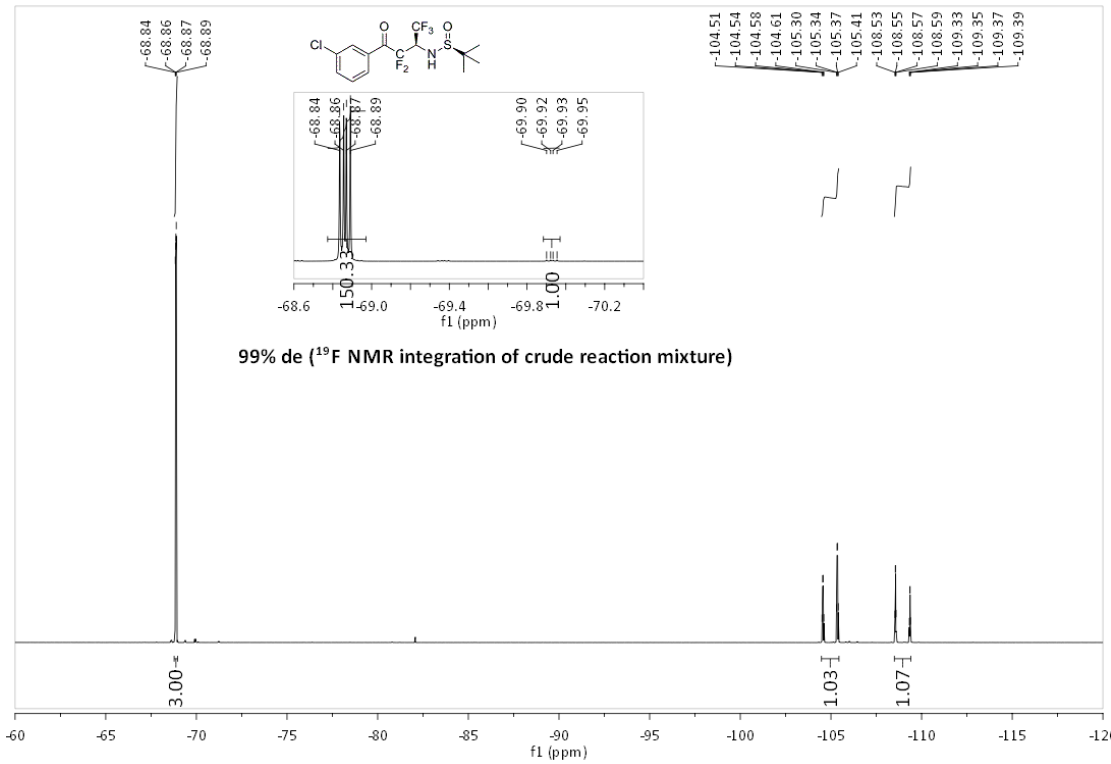


98% de (^{19}F NMR integration of crude reaction mixture)

^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra of **10f**

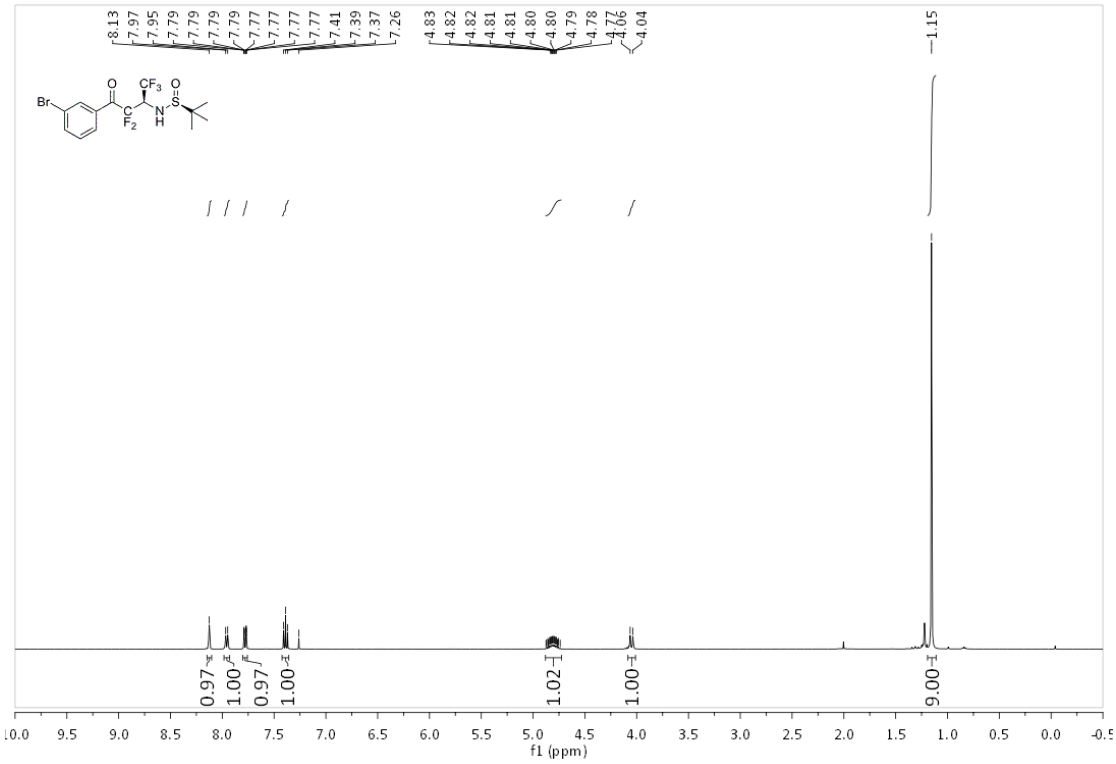


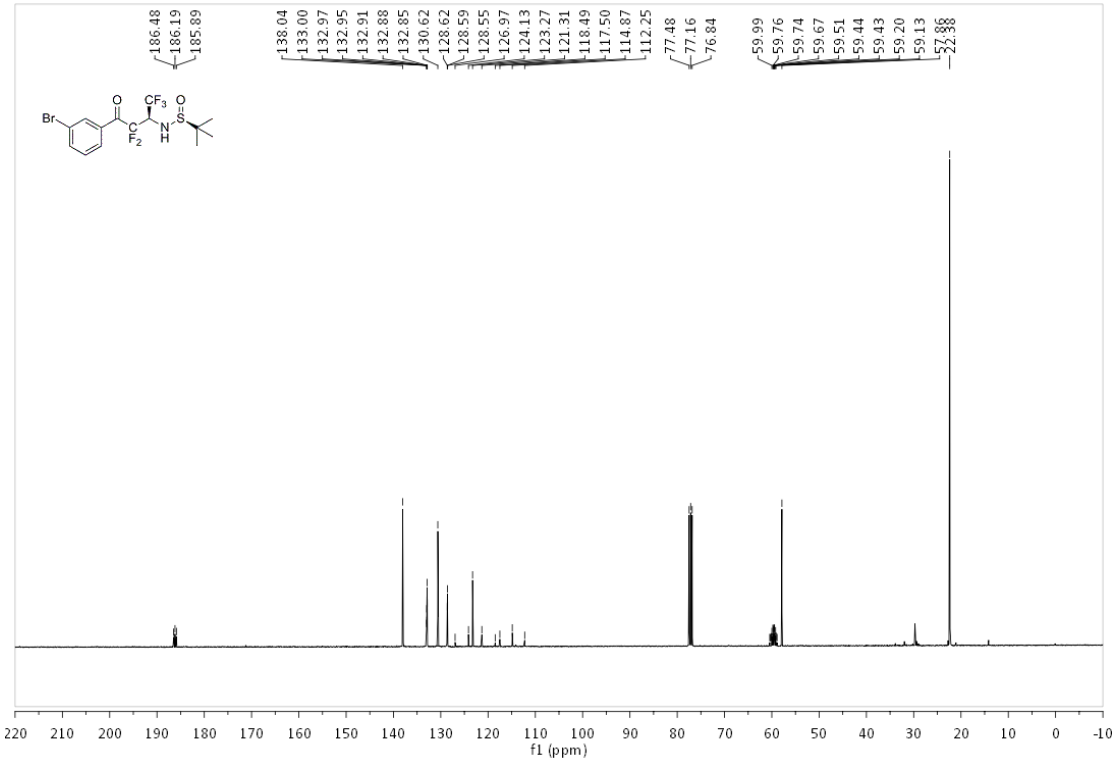


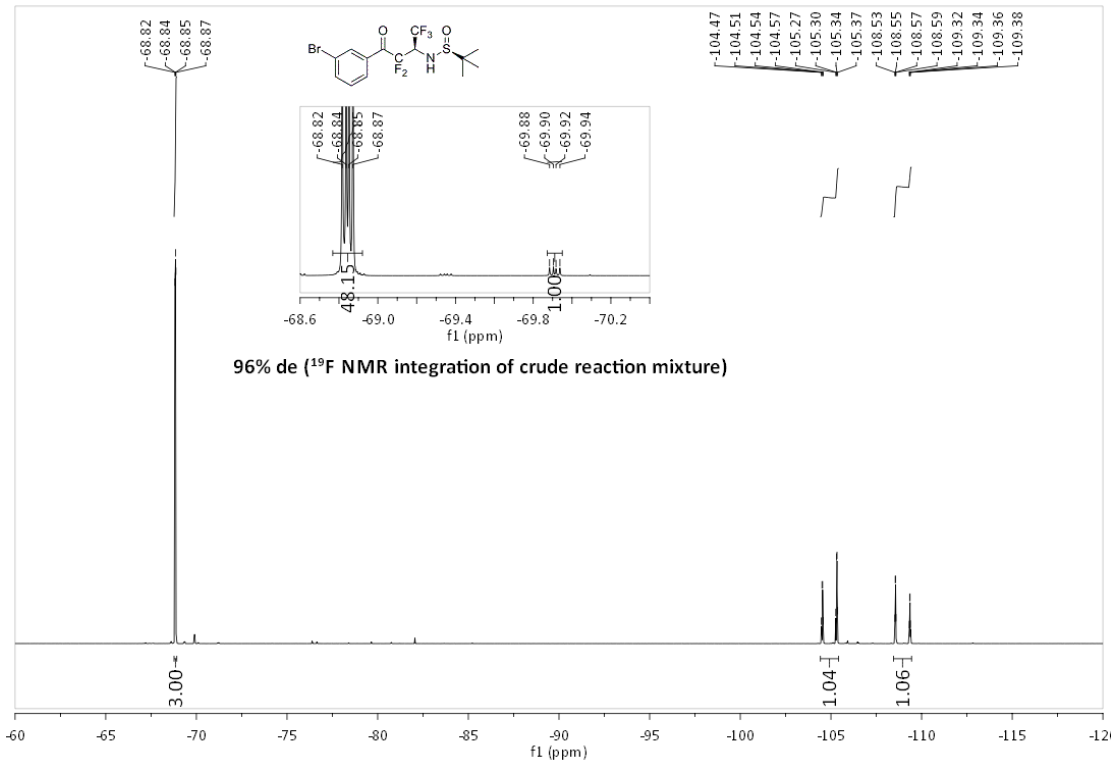


99% de (^{19}F NMR integration of crude reaction mixture)

^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra of **10g**

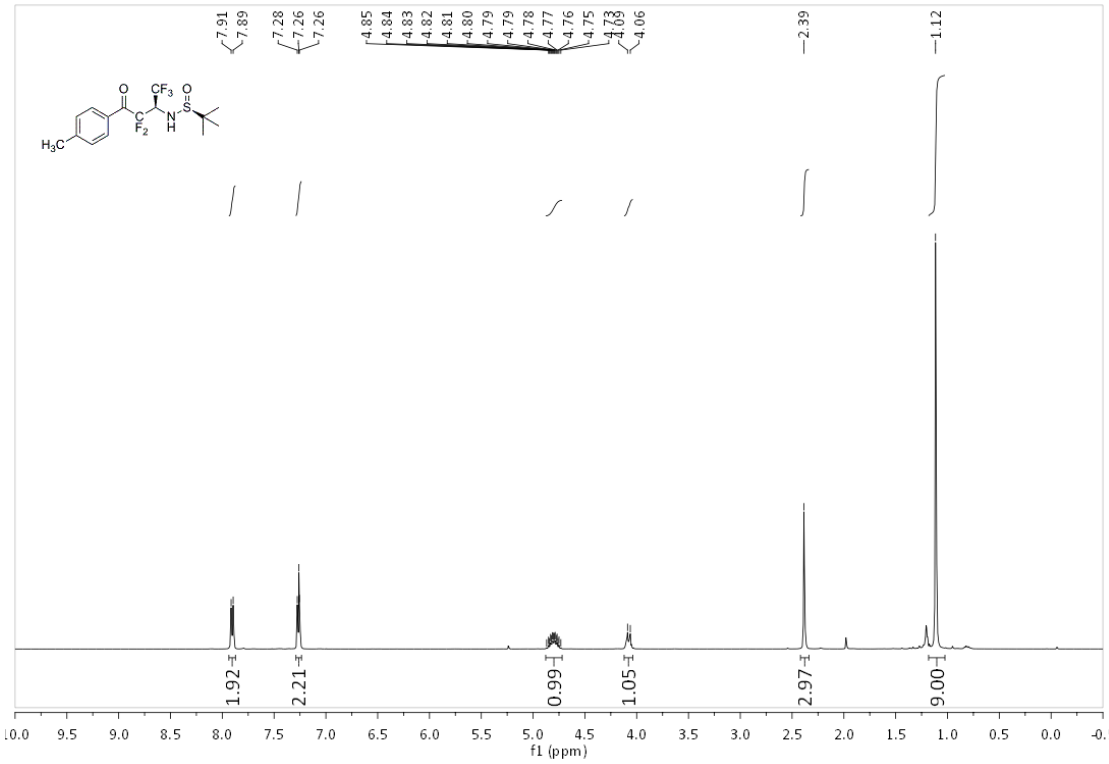


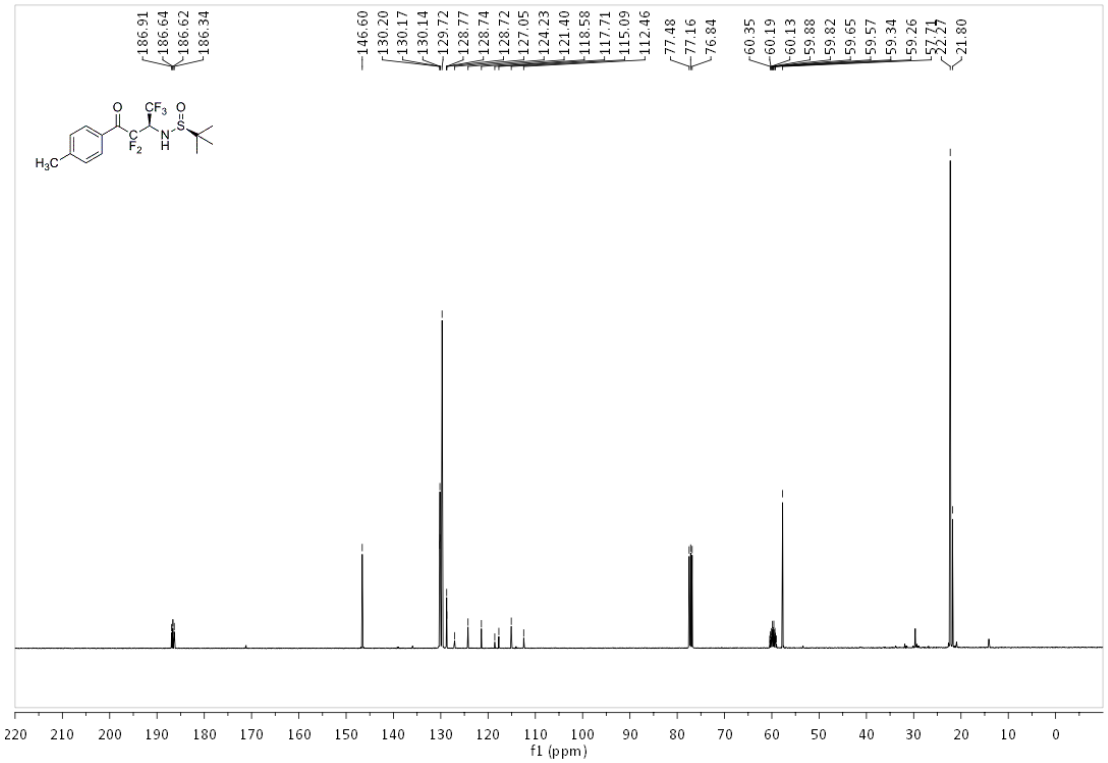


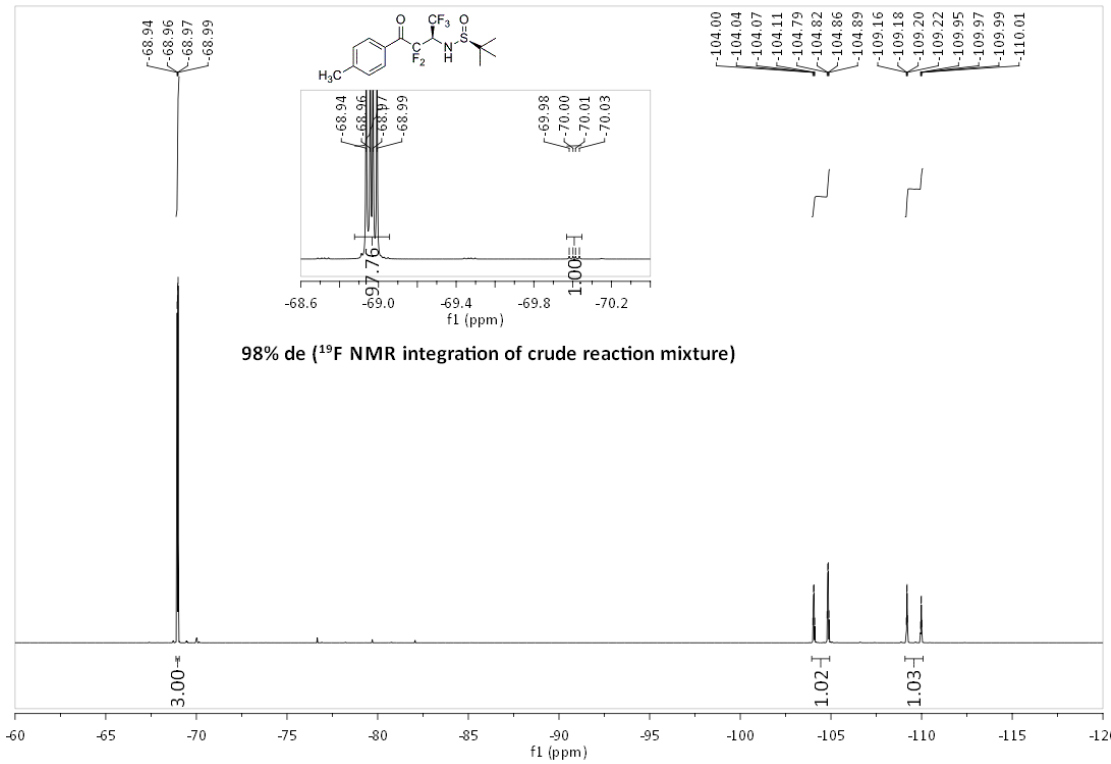


96% de (^{19}F NMR integration of crude reaction mixture)

^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra of **10h**

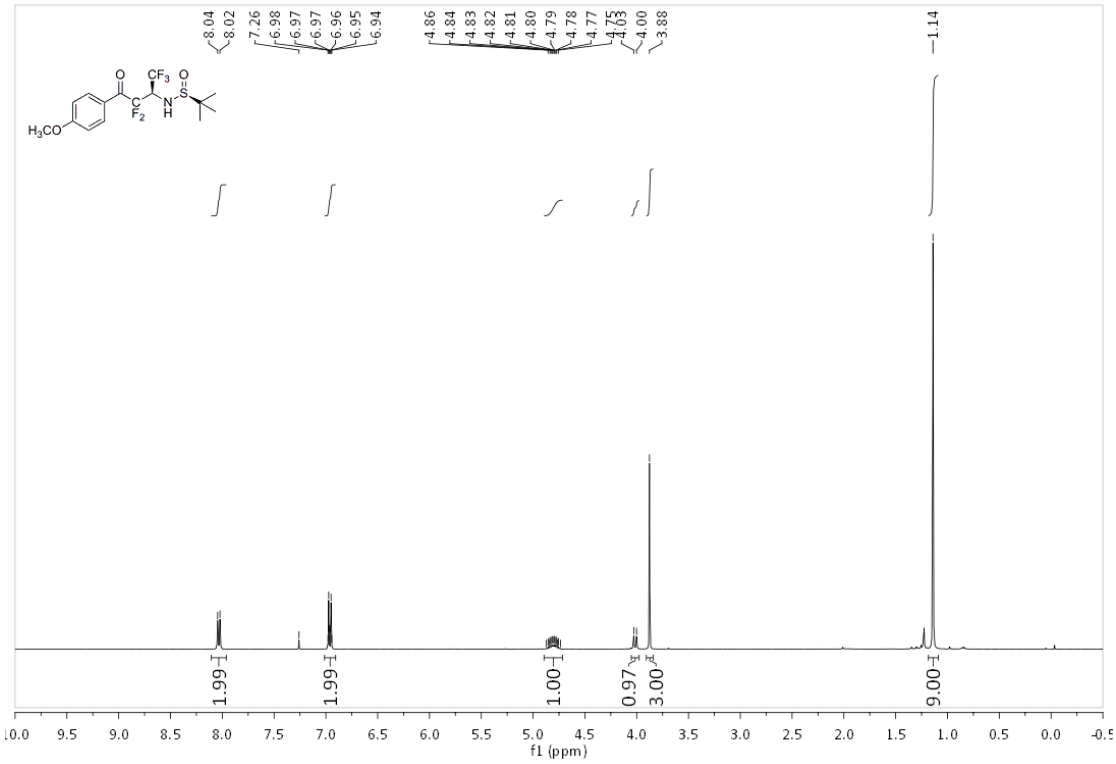


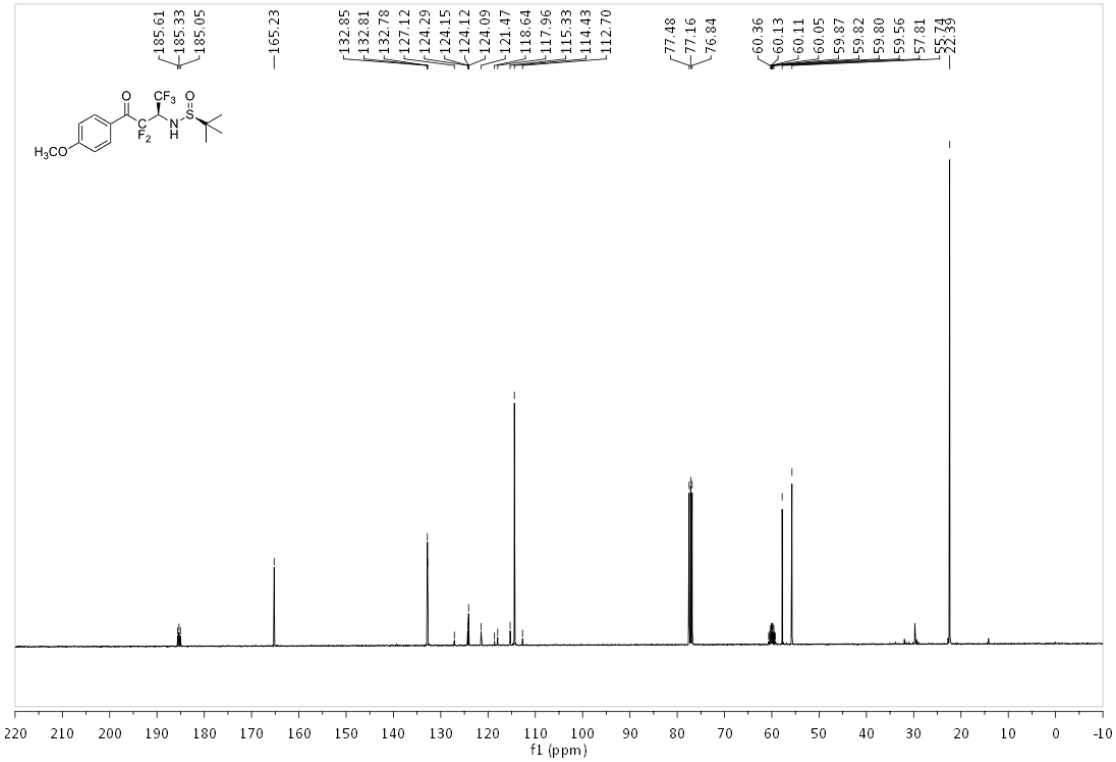


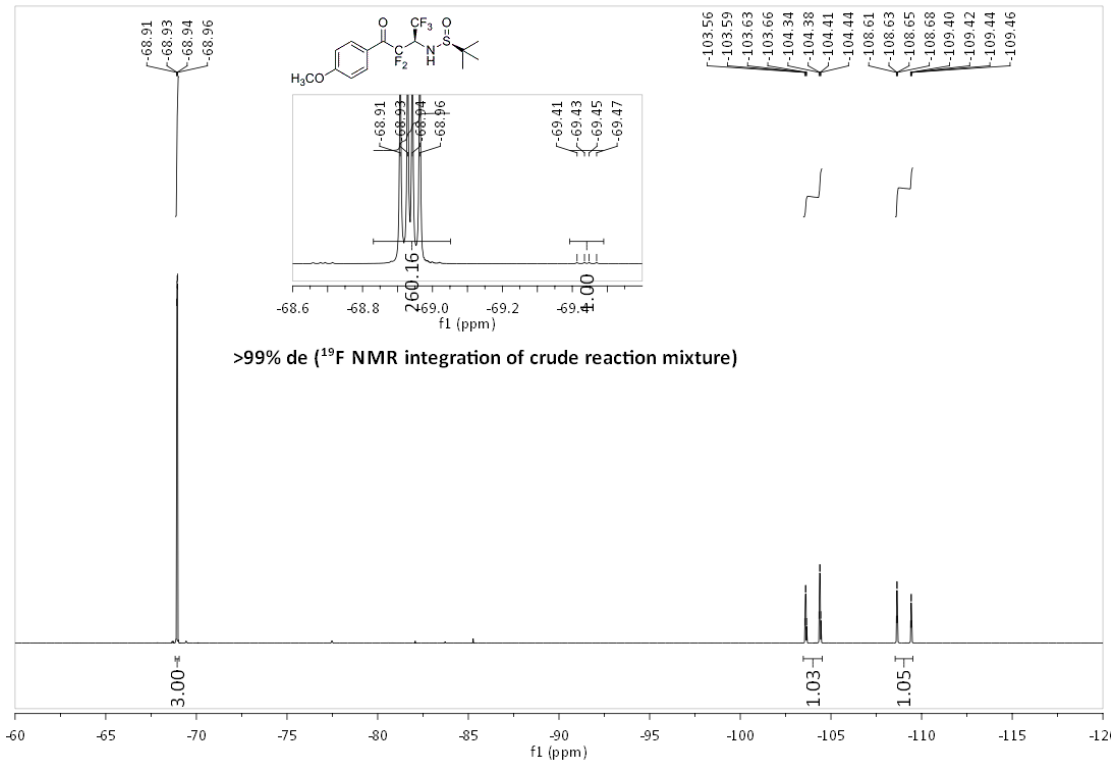


98% de (^{19}F NMR integration of crude reaction mixture)

^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra of **10i**

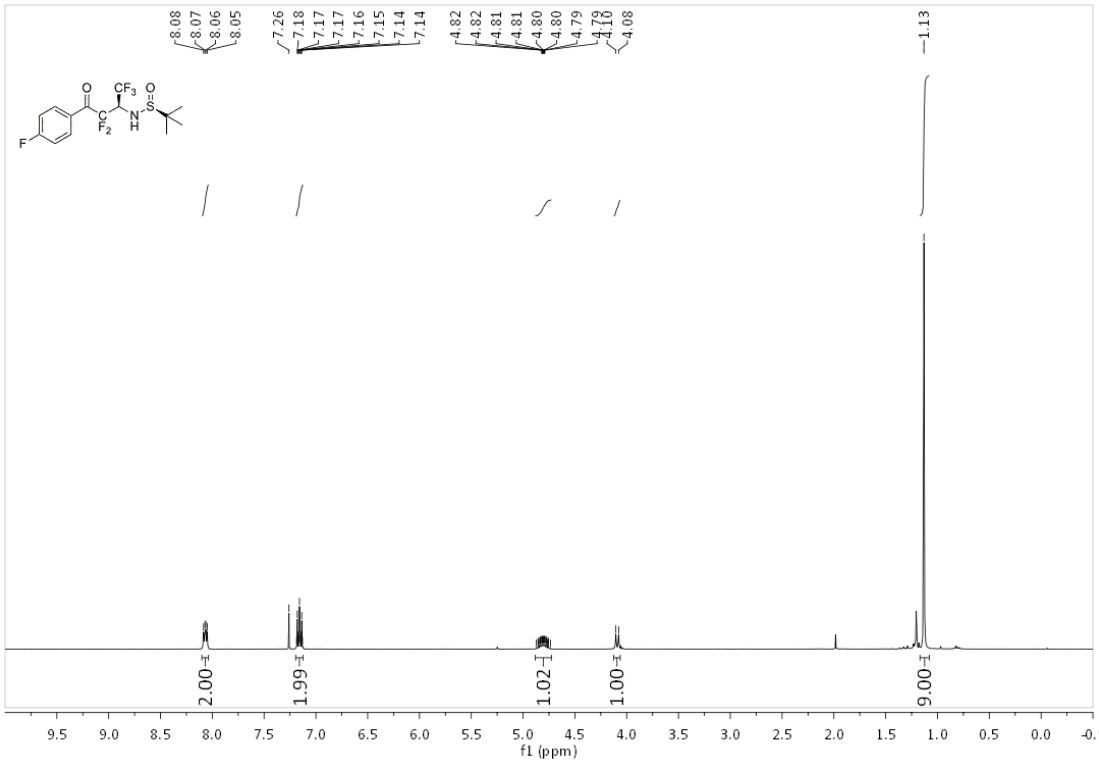


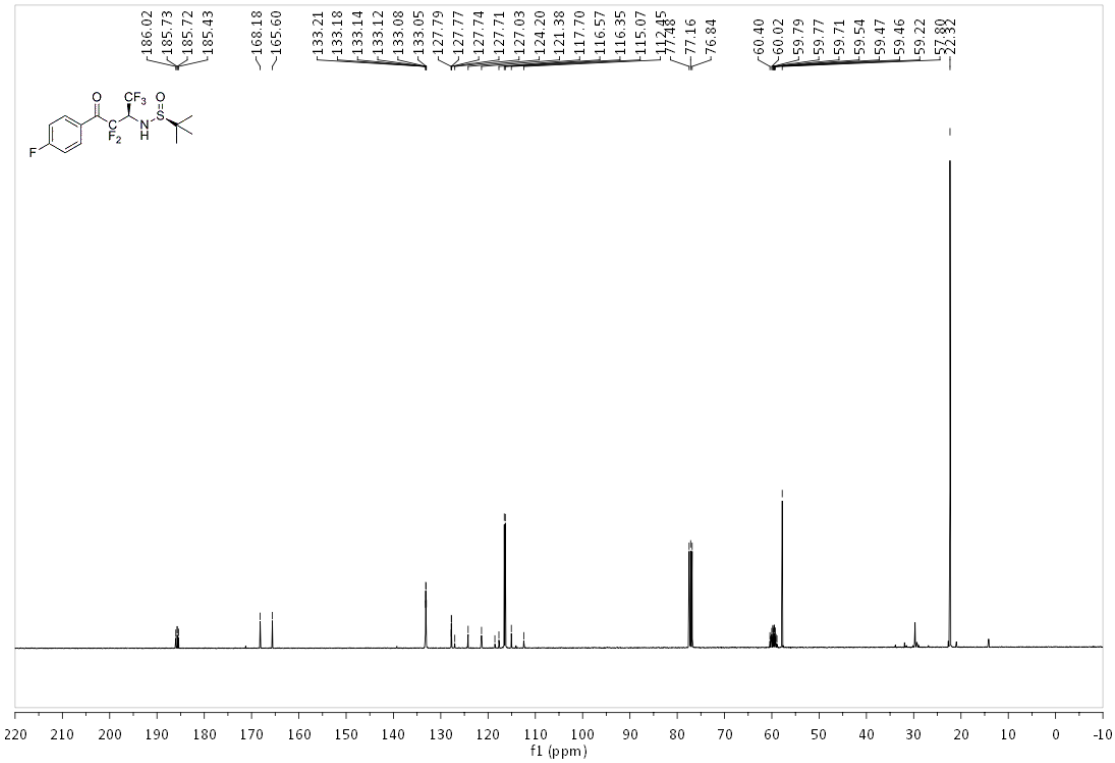


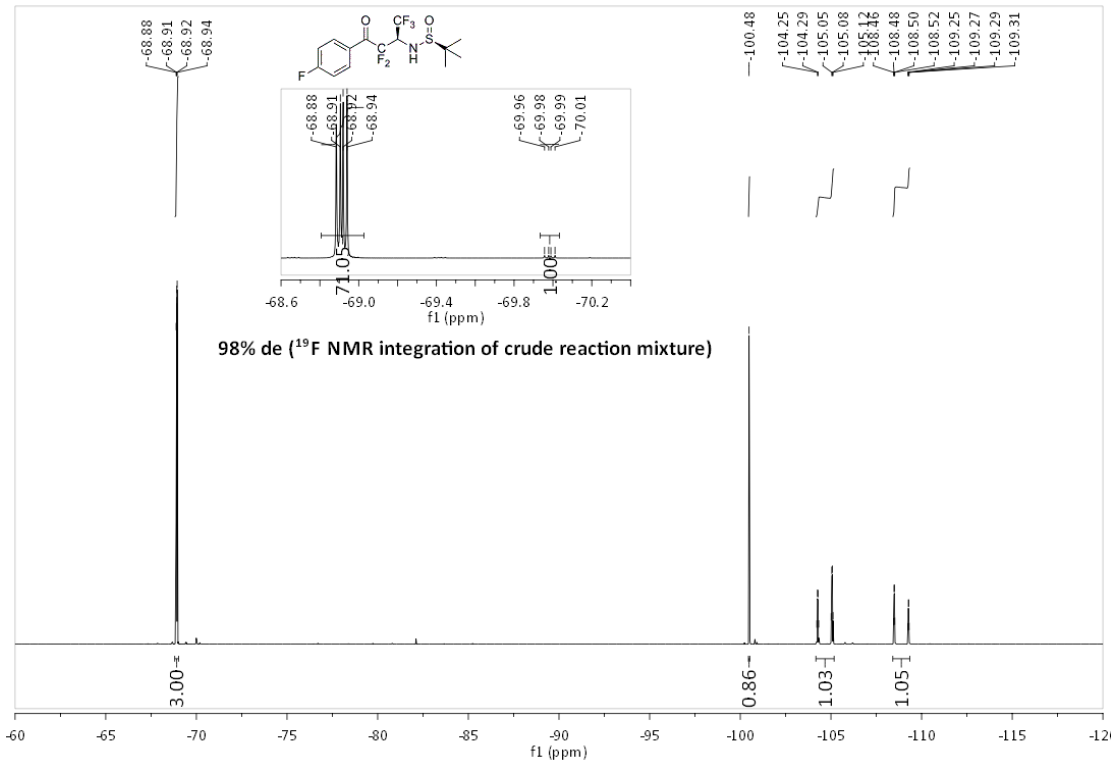


>99% de (^{19}F NMR integration of crude reaction mixture)

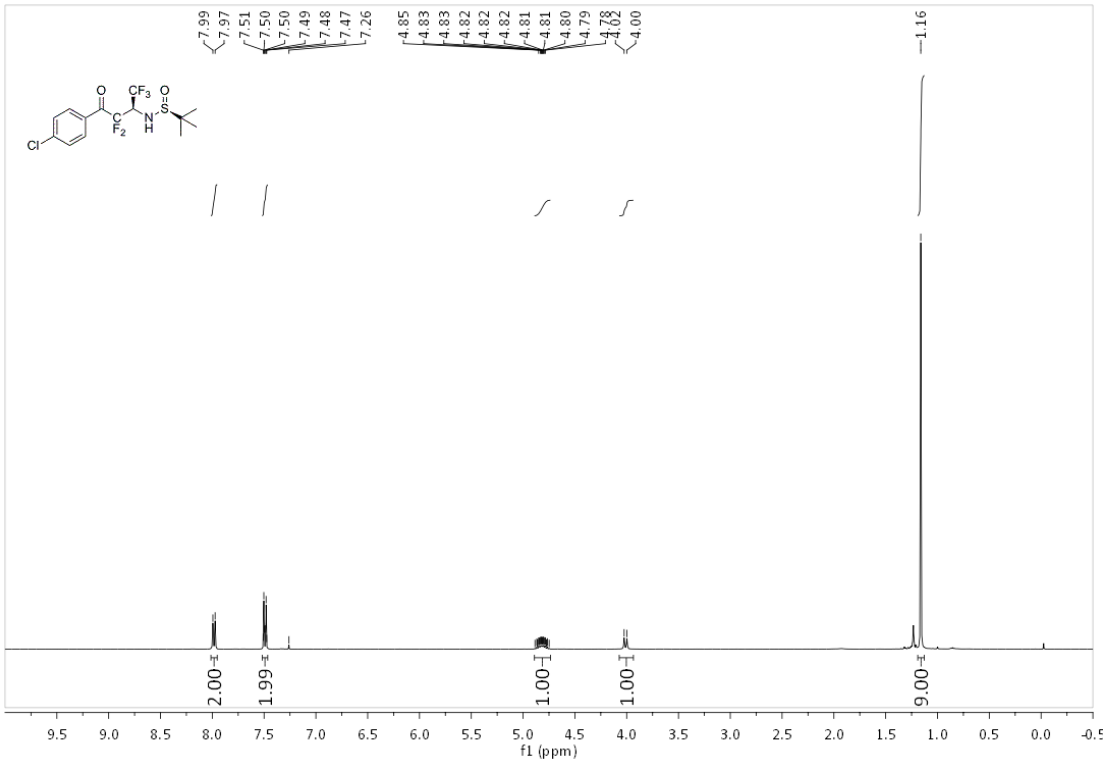
^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra of **10j**

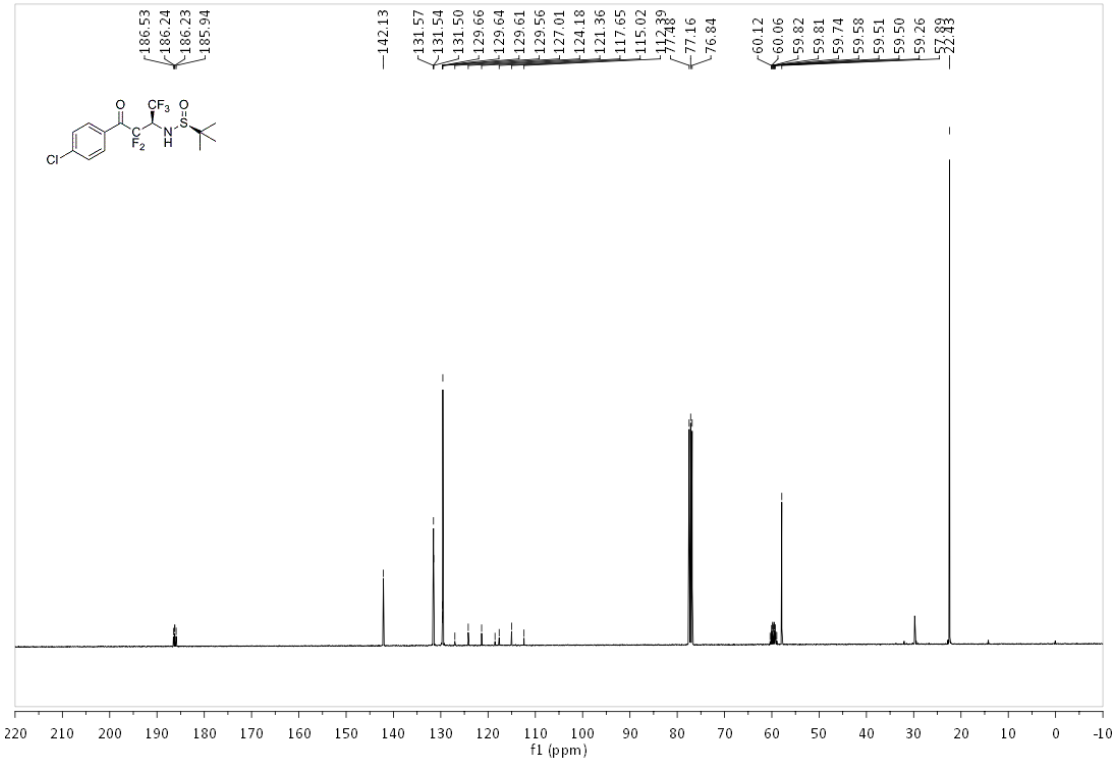


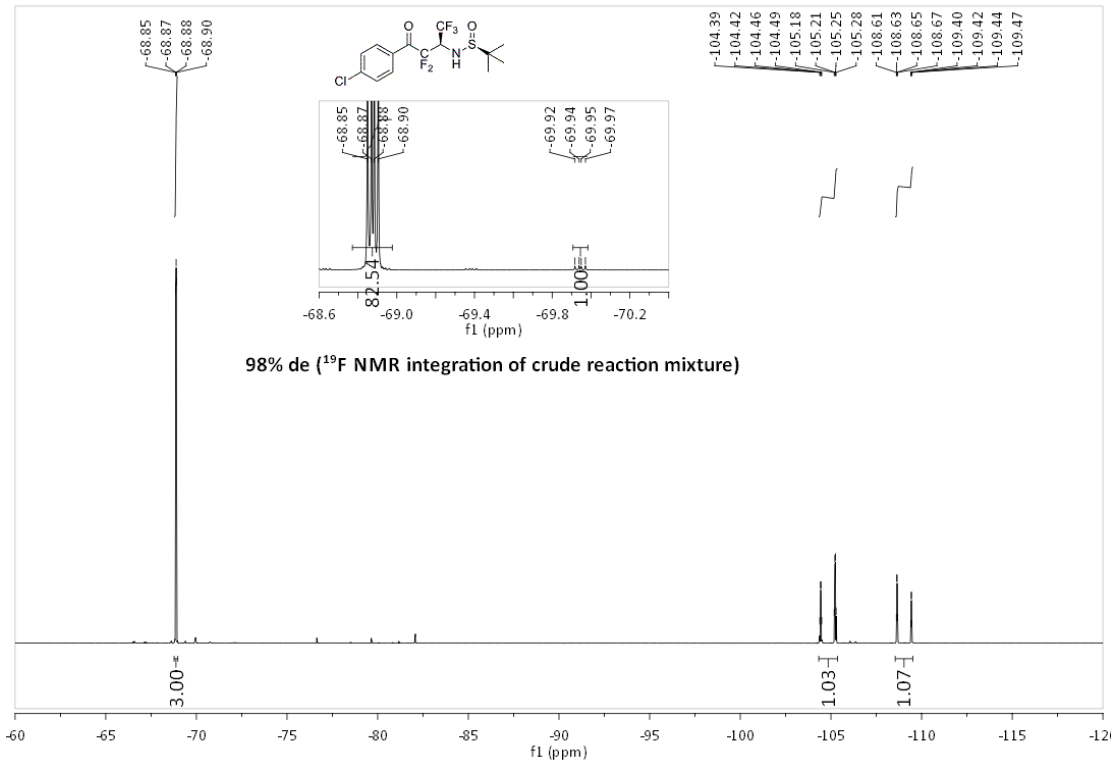



-68.88
-68.91
-68.92
-68.94
-100.48
-104.25
-104.29
-105.05
-105.08
-108.48
-108.50
-108.52
-109.25
-109.27
-109.29
-109.31
-68.88
-68.91
-68.92
-68.94
-69.96
-69.98
-69.99
-70.01
71.05
1.00
-68.6
-69.0
-69.4
-69.8
-70.2
f1 (ppm)
98% de (19F NMR integration of crude reaction mixture)
3.00
0.86
1.03
1.05
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
f1 (ppm)

^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra of **10k**

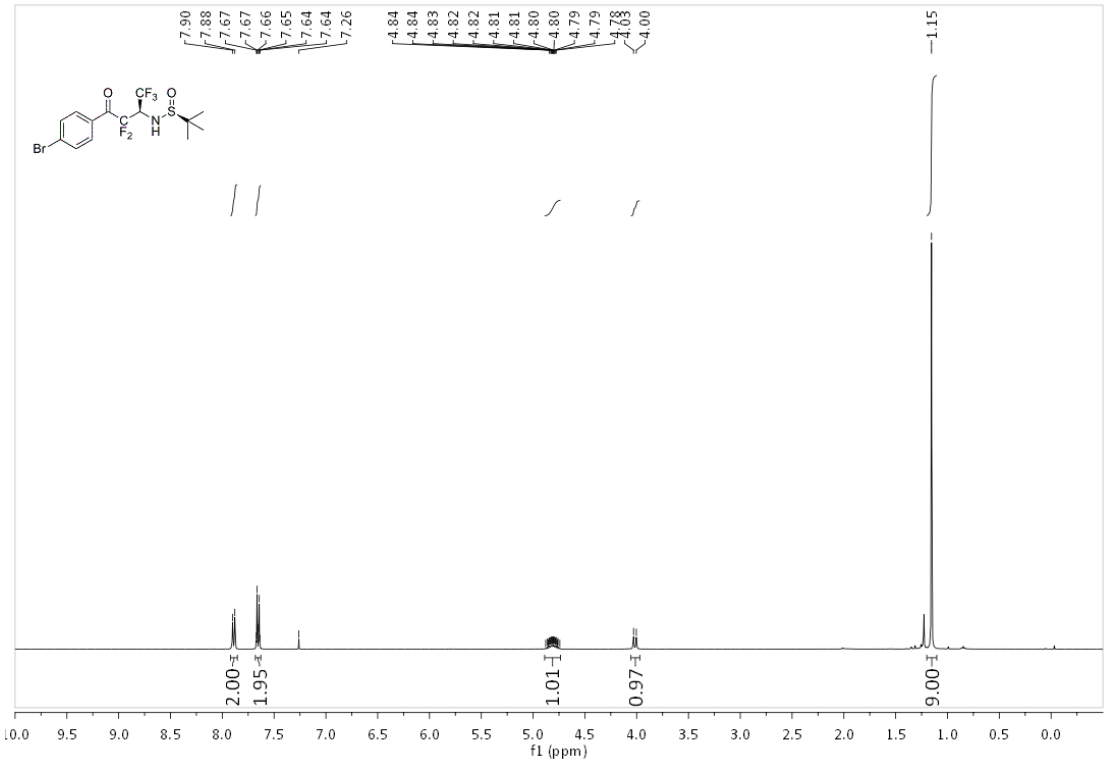


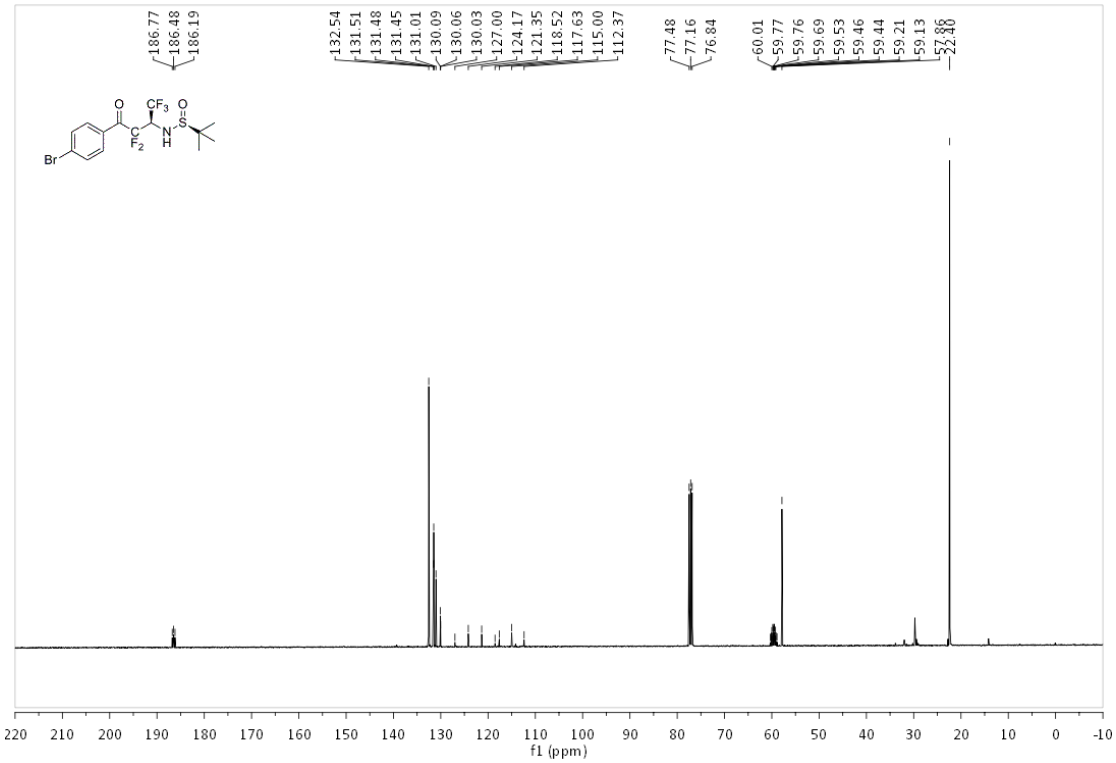


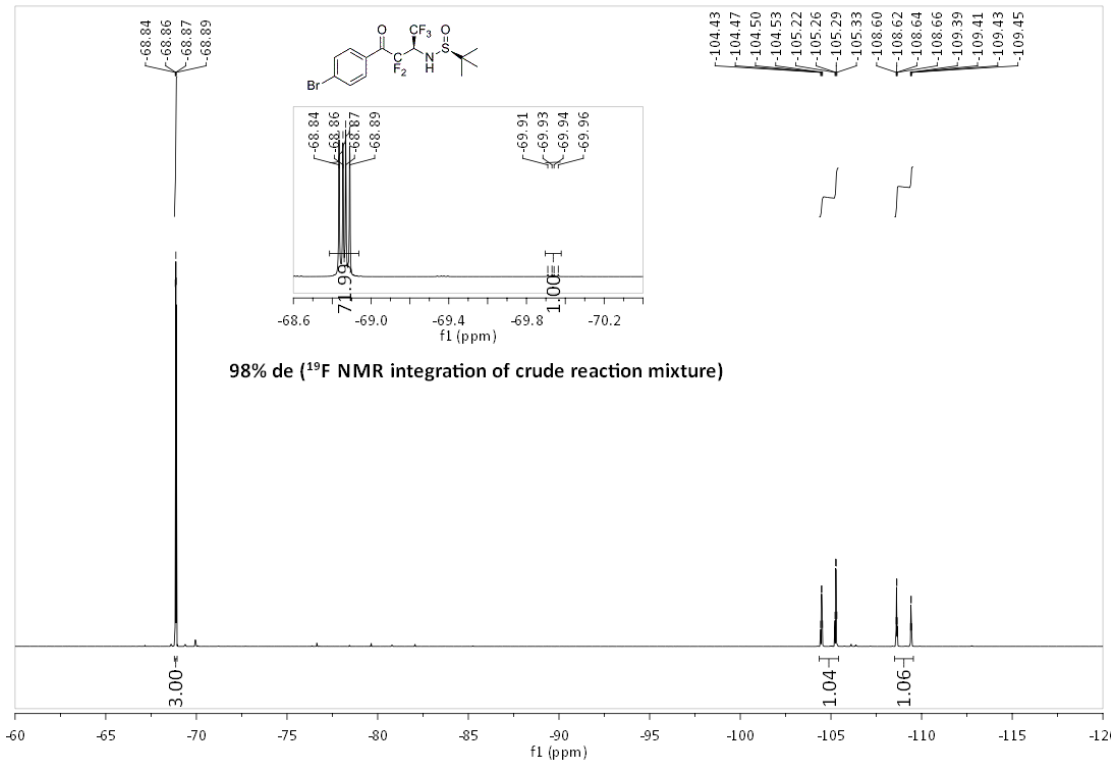


98% de (^{19}F NMR integration of crude reaction mixture)

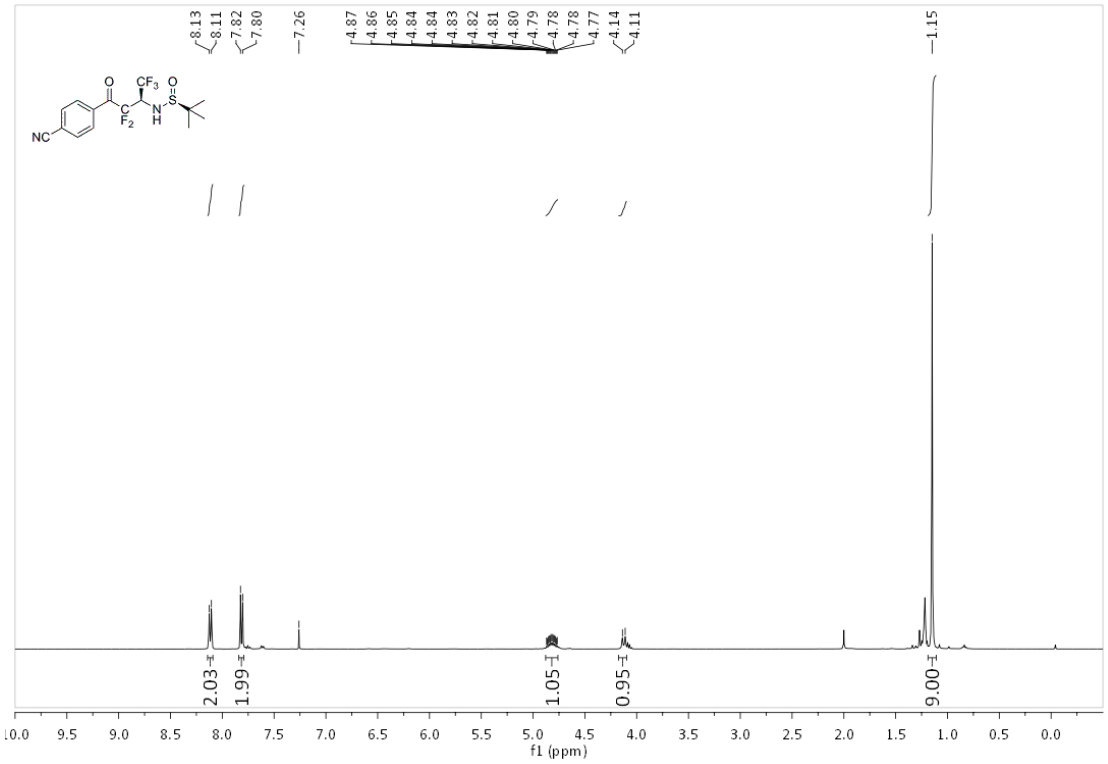
^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra of **10l**

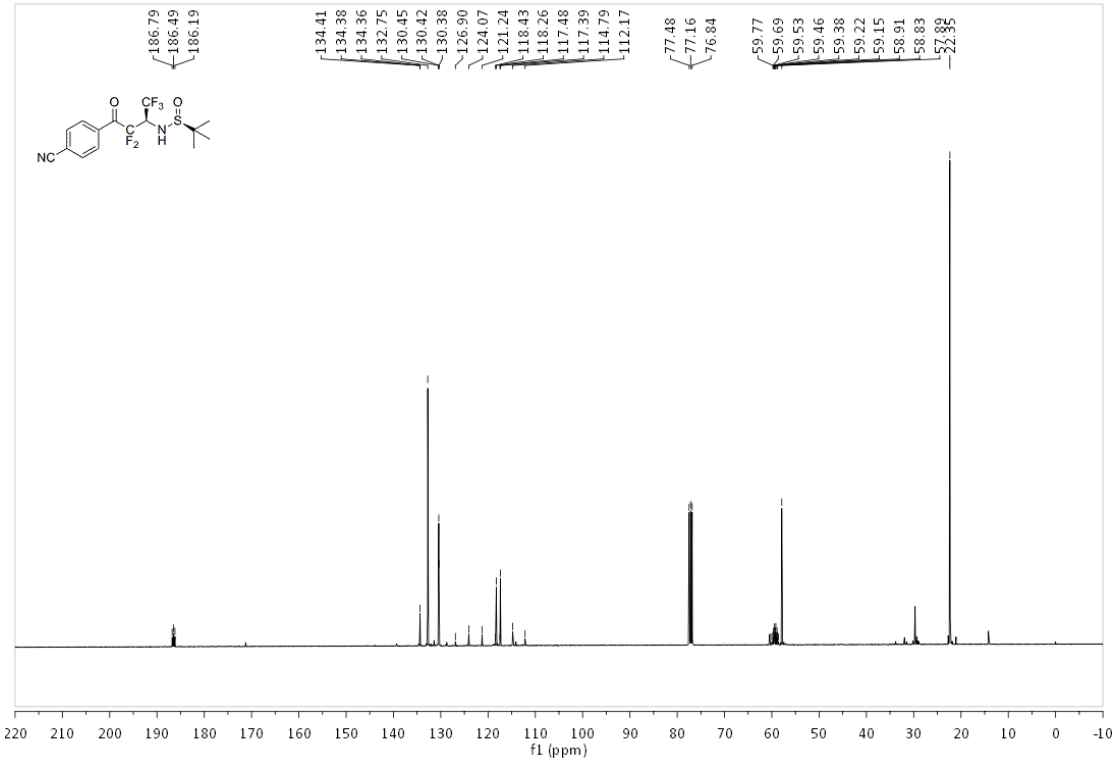


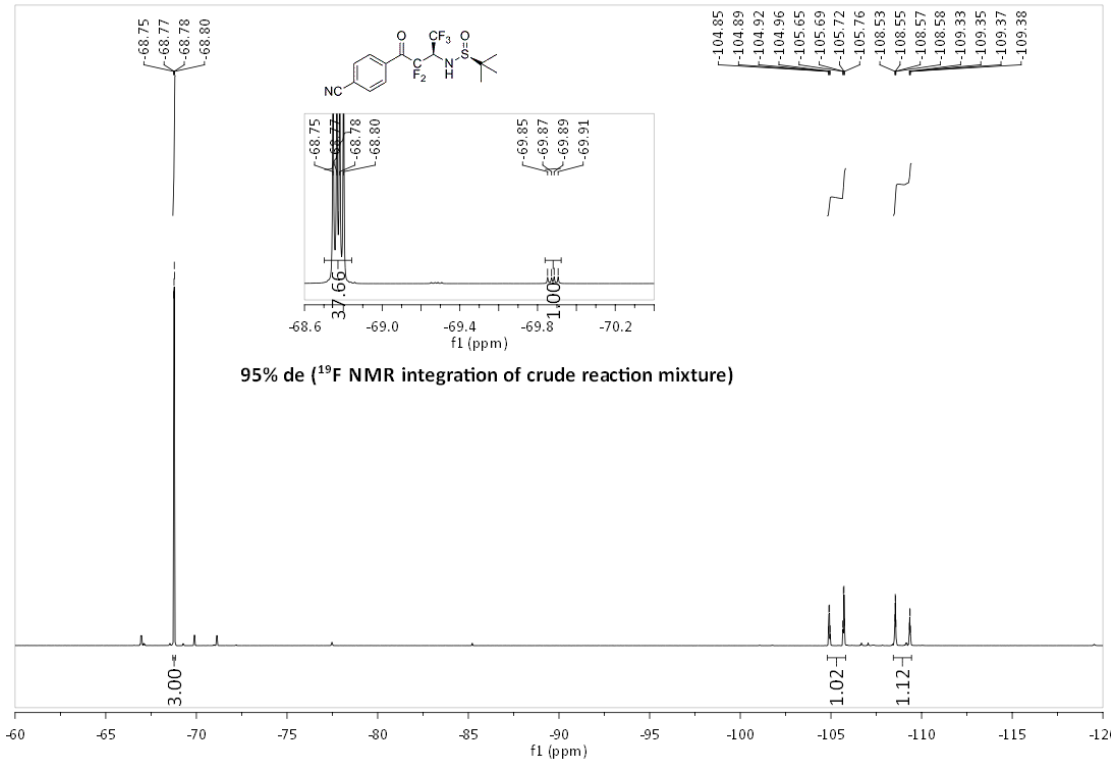



-68.84
-68.86
-68.87
-68.89
-104.43
-104.47
-104.50
-104.53
-105.22
-105.26
-105.29
-105.33
-108.60
-108.62
-108.64
-108.66
-109.39
-109.41
-109.43
-109.45
Br
-68.84
-68.86
-68.87
-68.89
-69.91
-69.93
-69.94
-69.96
71.99
1.00
-68.6
-69.0
-69.4
-69.8
-70.2
f1 (ppm)
98% de (19F NMR integration of crude reaction mixture)
3.00
1.04
1.06
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
f1 (ppm)

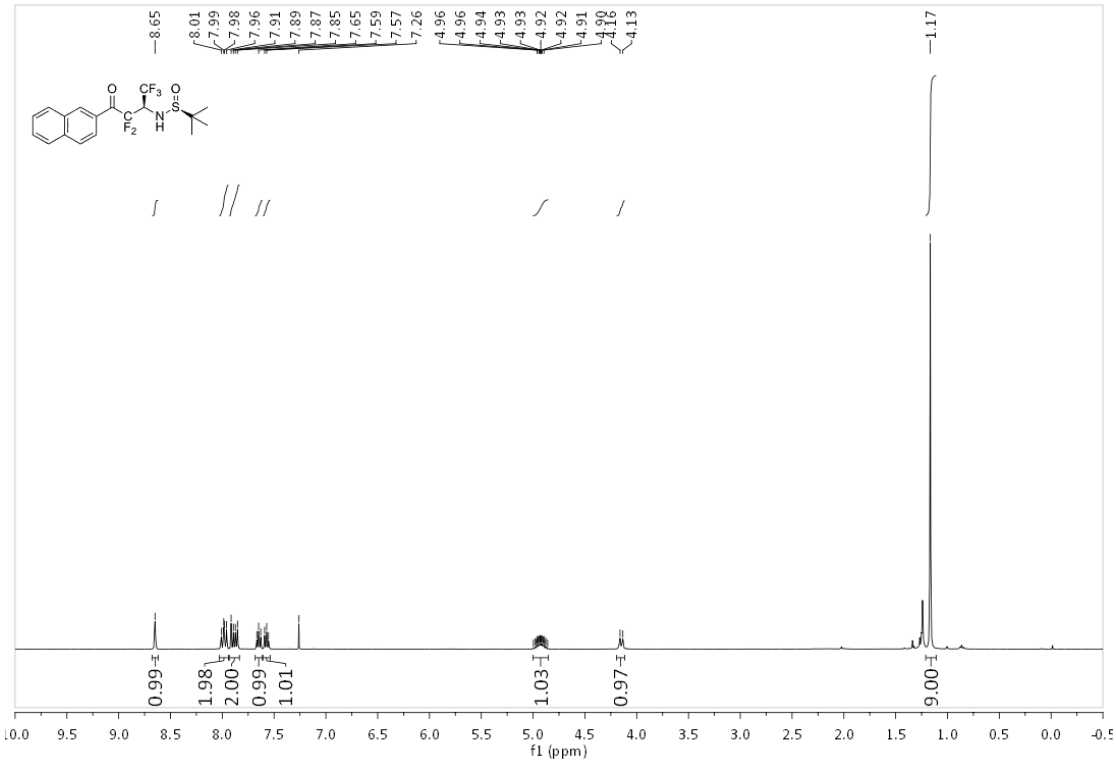
^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra of **10m**

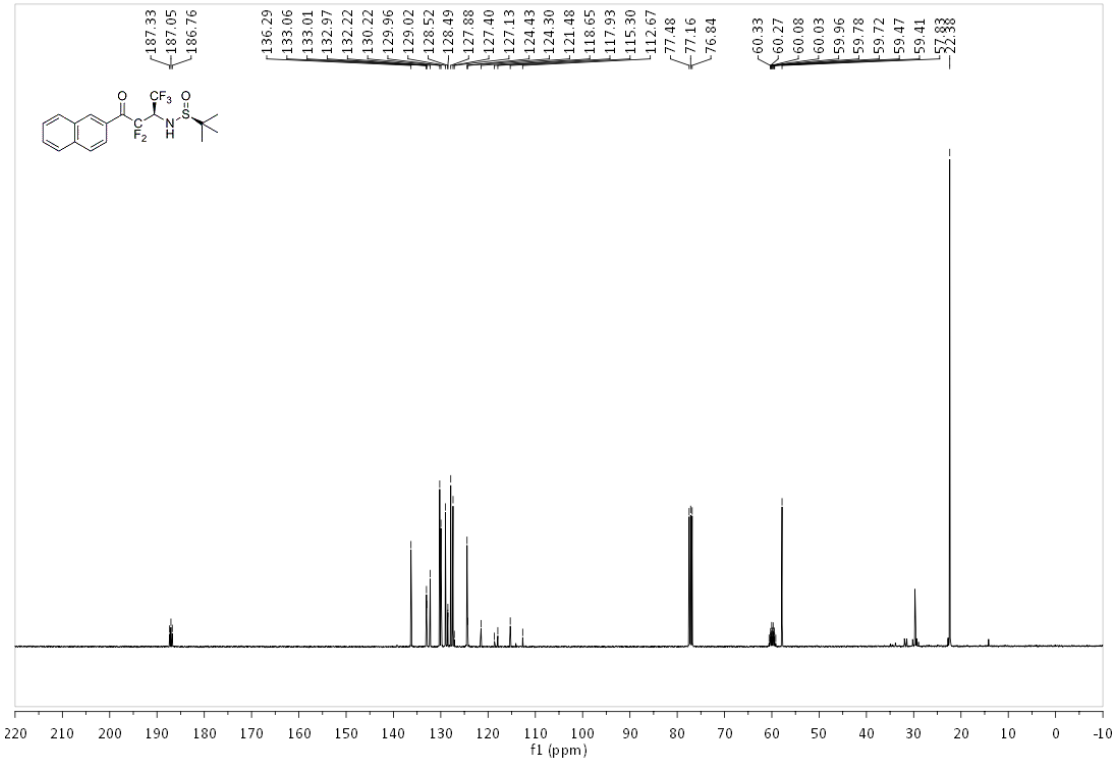


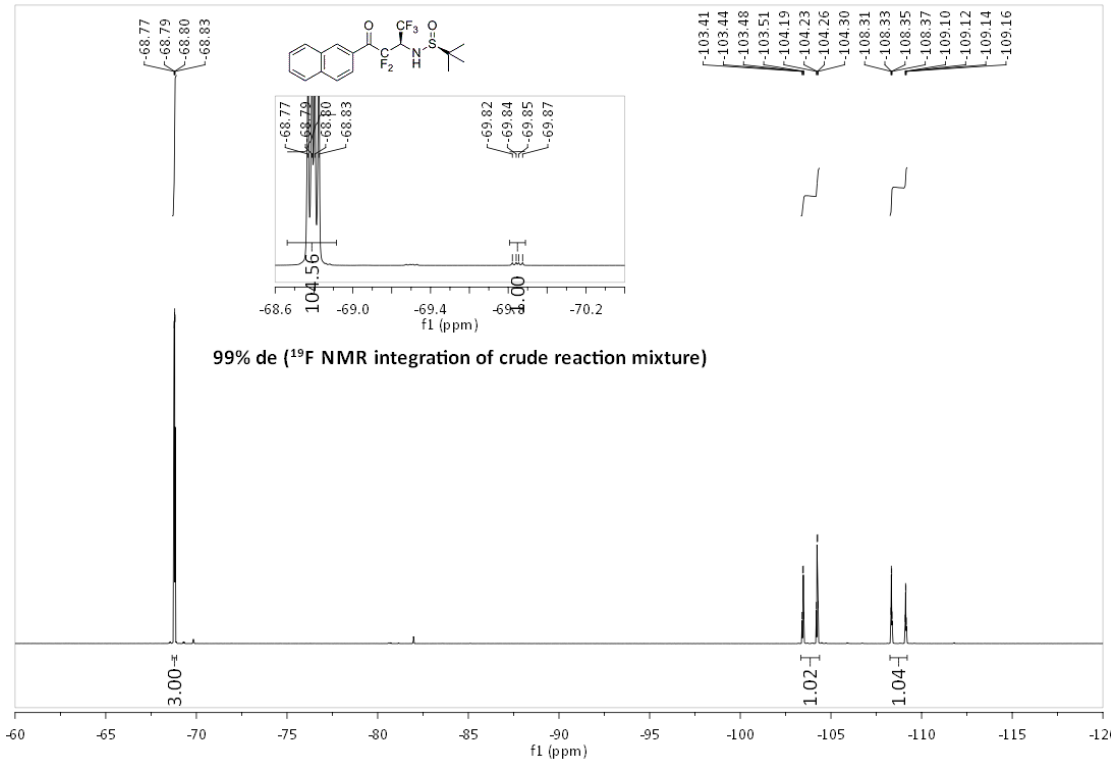



-68.75
-68.77
-68.78
-68.80
-104.85
-104.89
-104.92
-104.96
-105.65
-105.69
-105.72
-105.76
-108.53
-108.55
-108.57
-108.58
-109.33
-109.35
-109.37
-109.38
NC
-69.85
-69.87
-69.89
-69.91
37.66
1.00
-68.6
-69.0
-69.4
-69.8
-70.2
f1 (ppm)
95% de (19F NMR integration of crude reaction mixture)
3.00
1.02
1.12
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
f1 (ppm)

^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra of **10n**

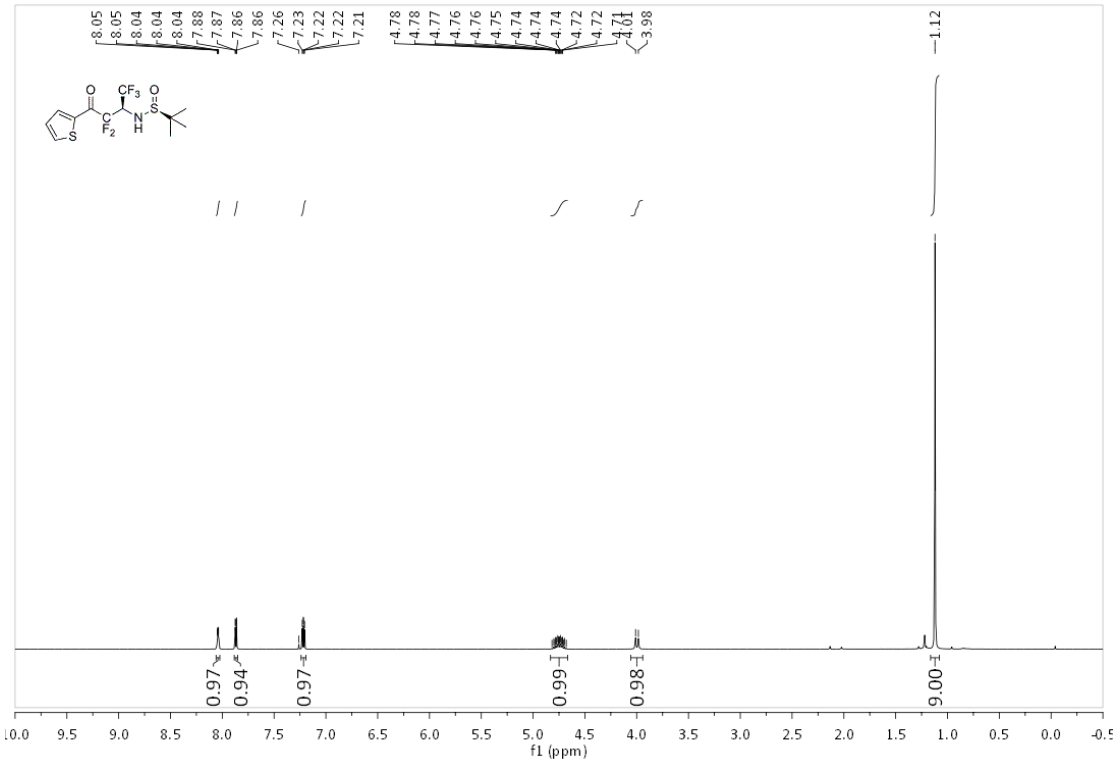


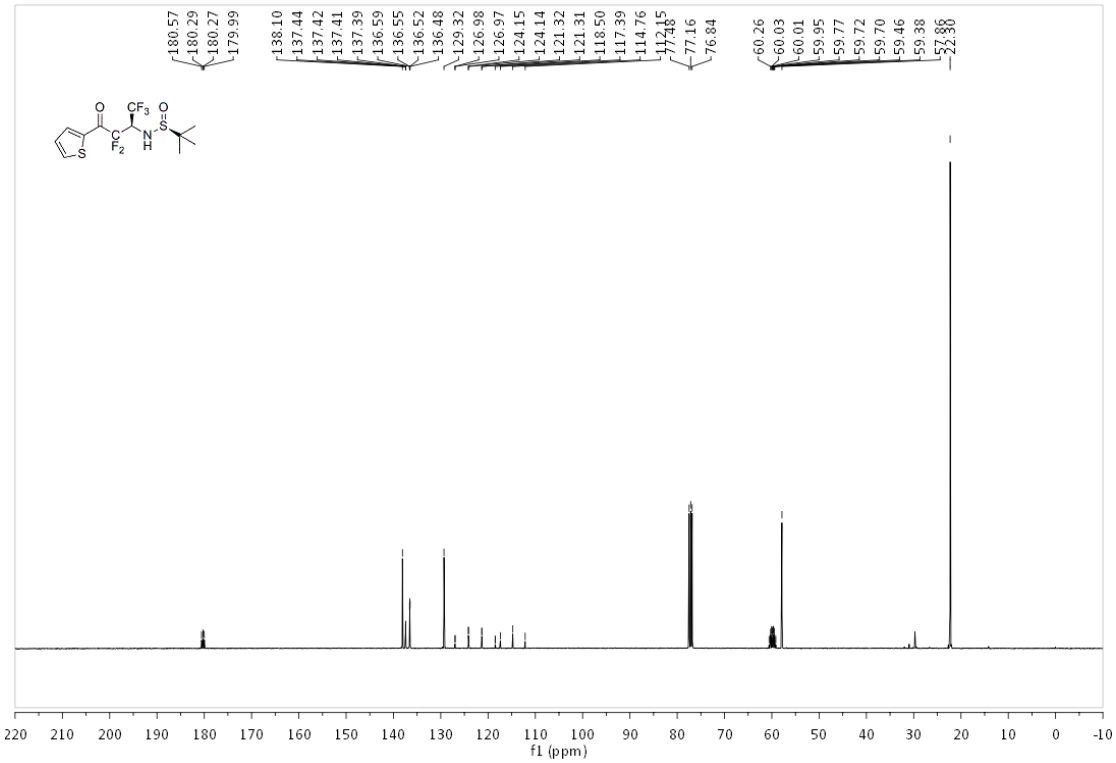


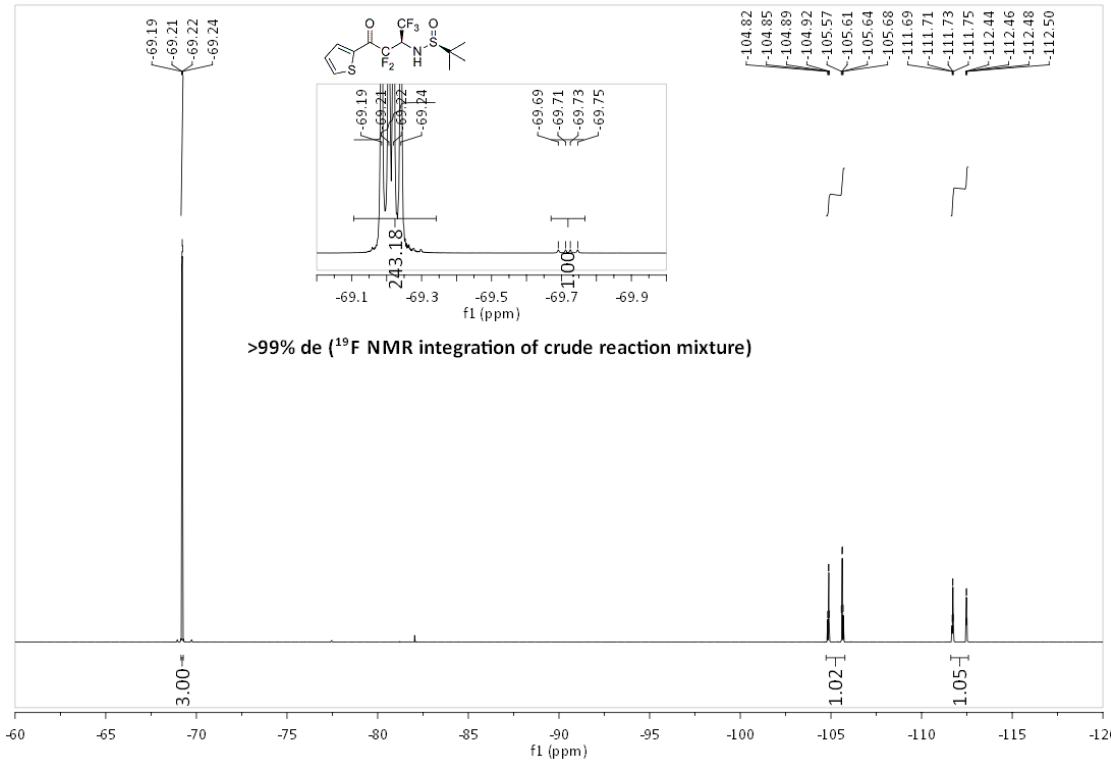


99% de (^{19}F NMR integration of crude reaction mixture)

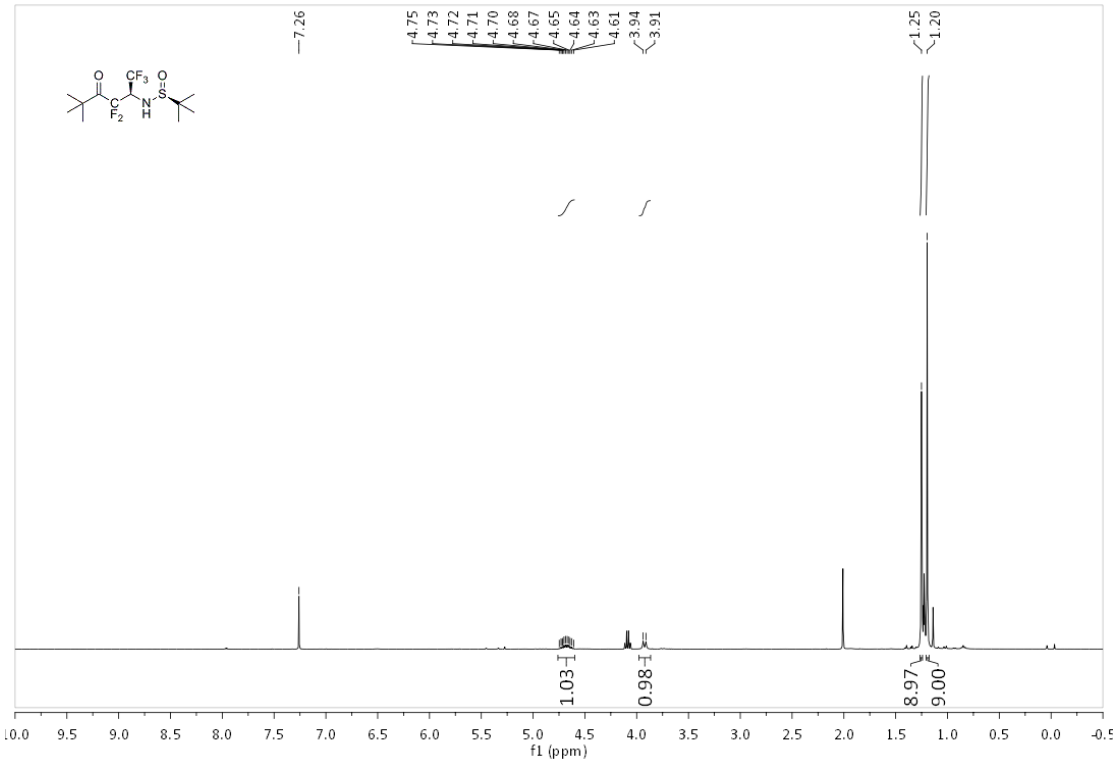
^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra of **10o**

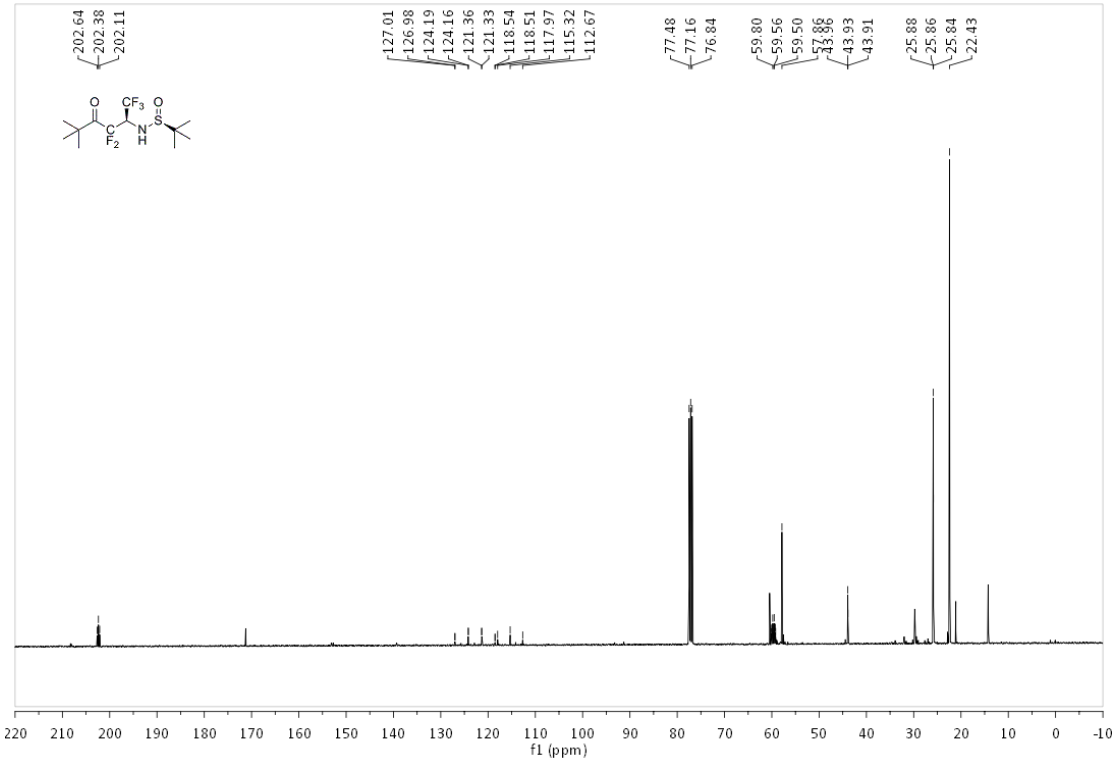


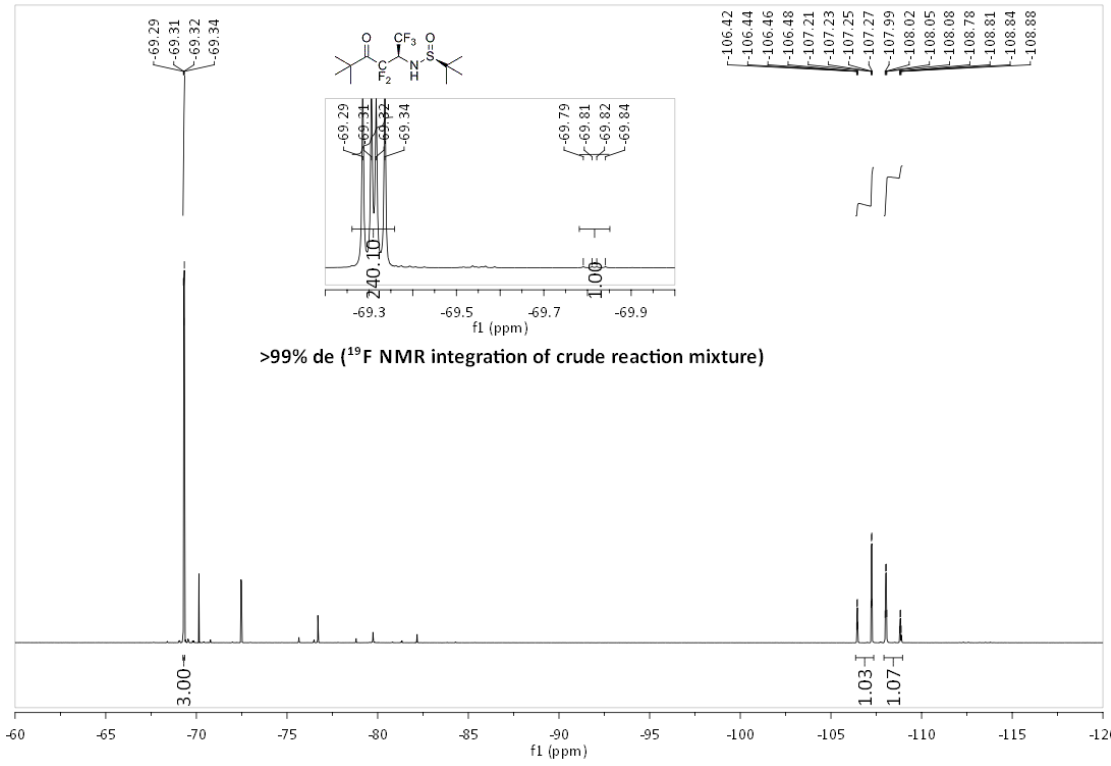



-69.19
-69.21
-69.22
-69.24
-104.82
-104.85
-104.89
-104.92
-105.57
-105.61
-105.64
-105.68
-111.69
-111.71
-111.73
-111.75
-112.44
-112.46
-112.48
-112.50
-69.69
-69.71
-69.73
-69.75
243.18
1.00
f1 (ppm)
>99% de (^{19}F NMR integration of crude reaction mixture)
3.00
1.02
1.05
f1 (ppm)

^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra of **10p**

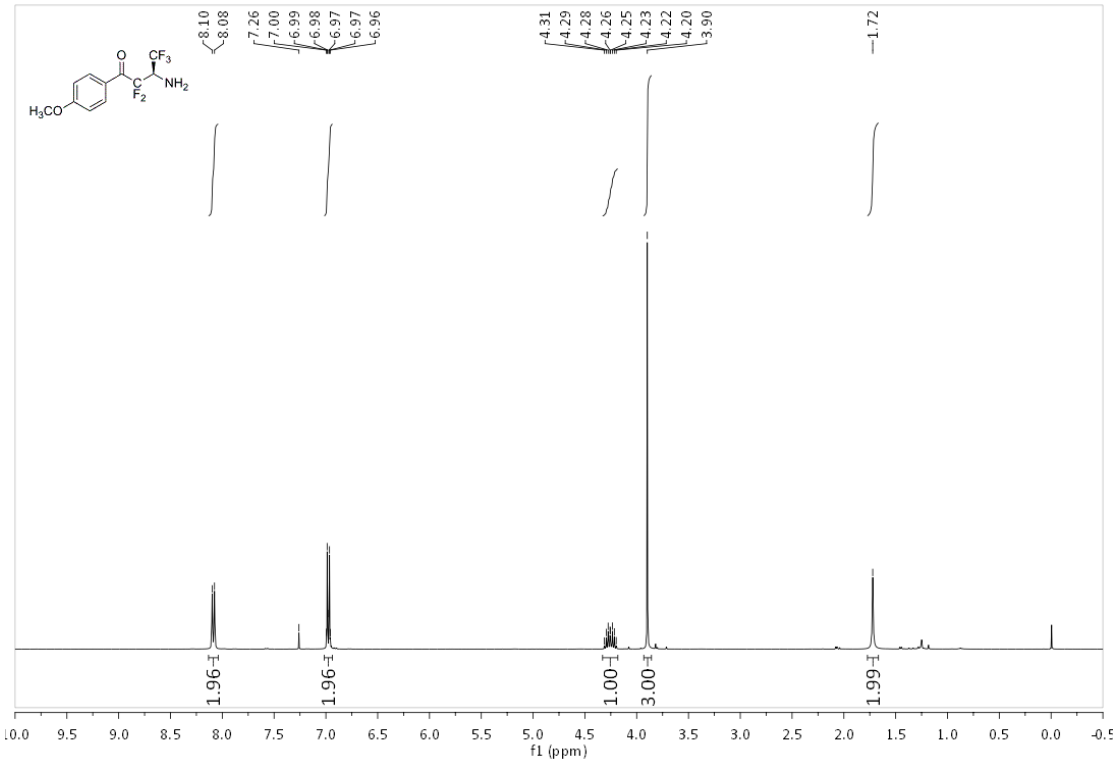


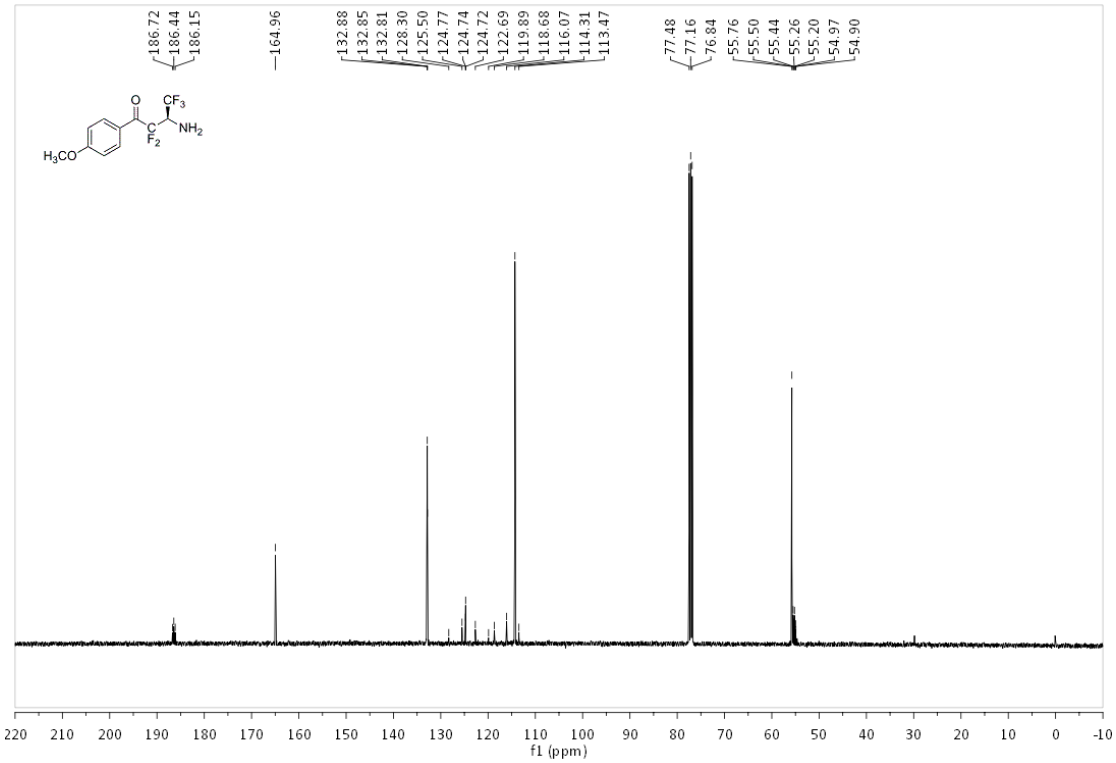


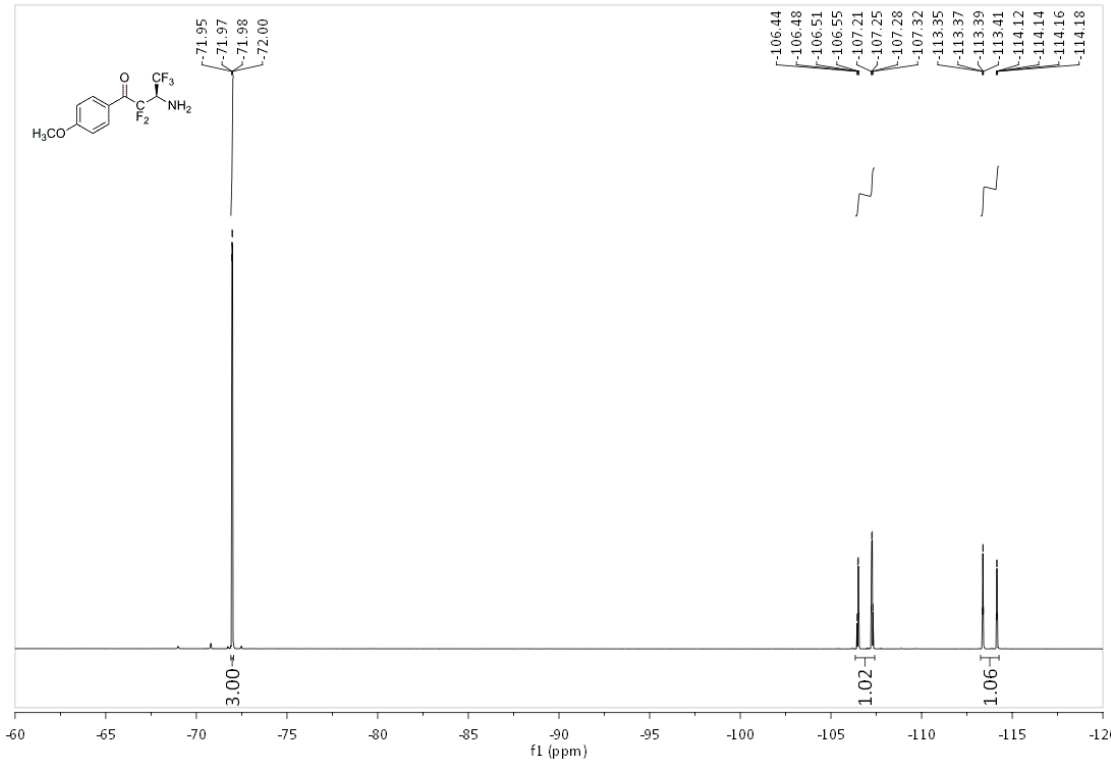


>99% de (^{19}F NMR integration of crude reaction mixture)

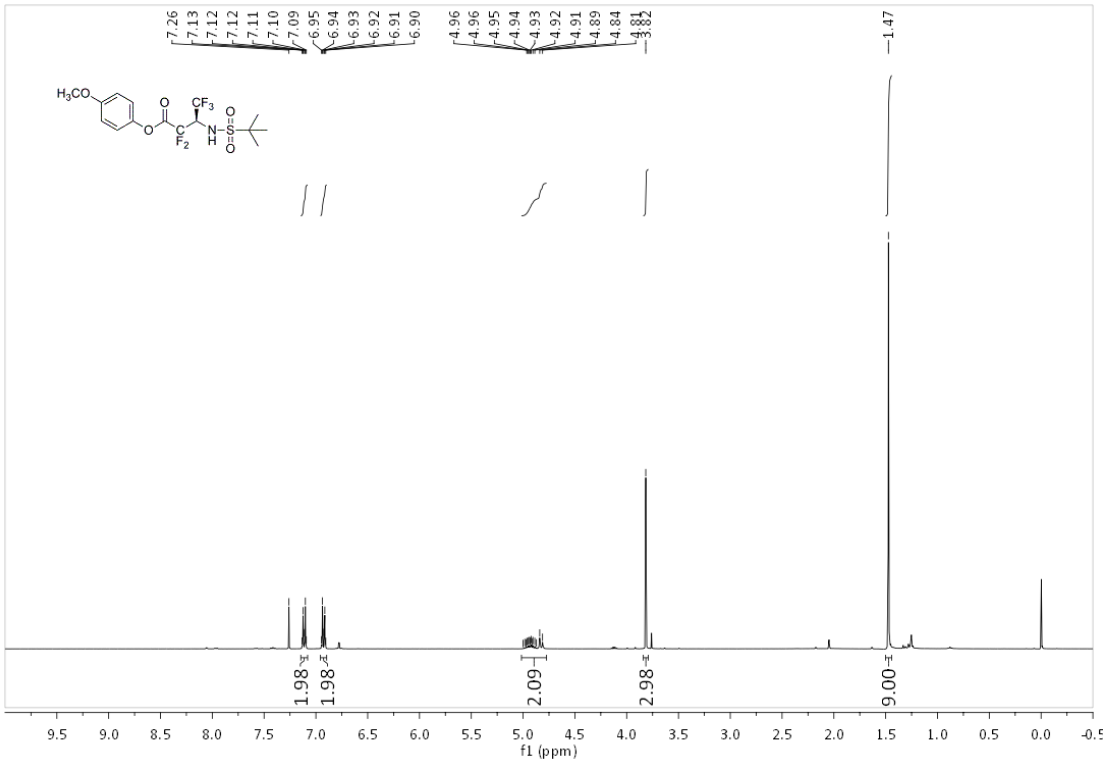
^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra of **11**

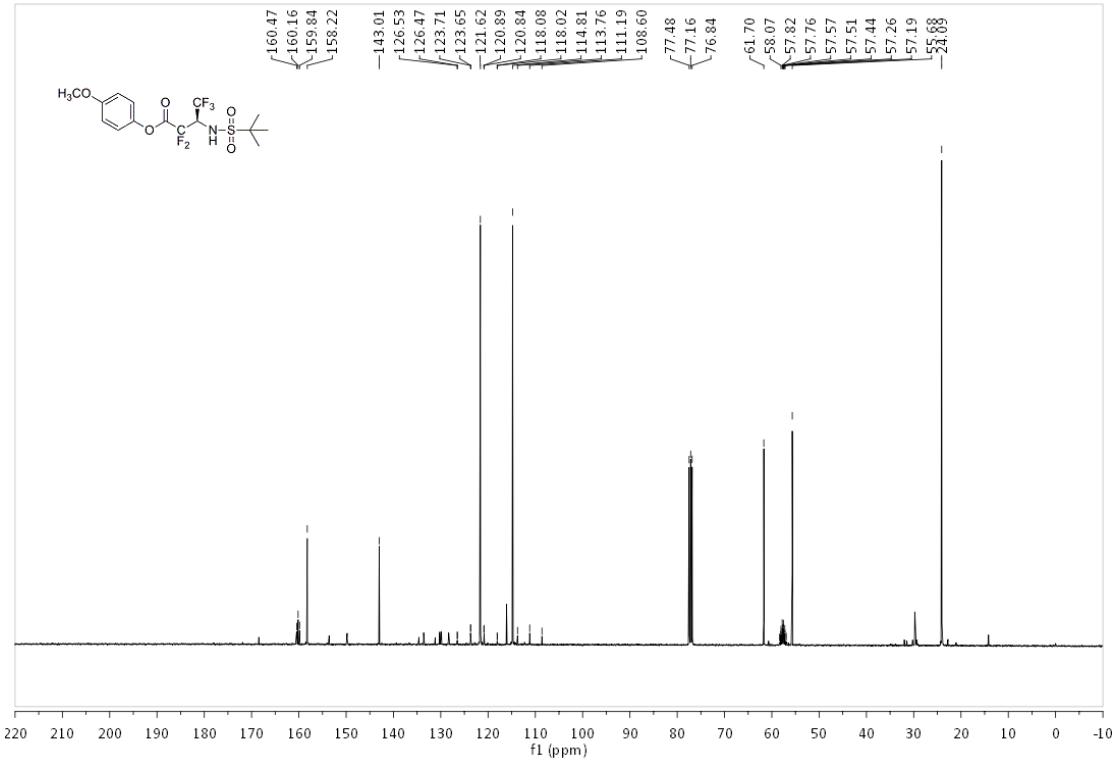


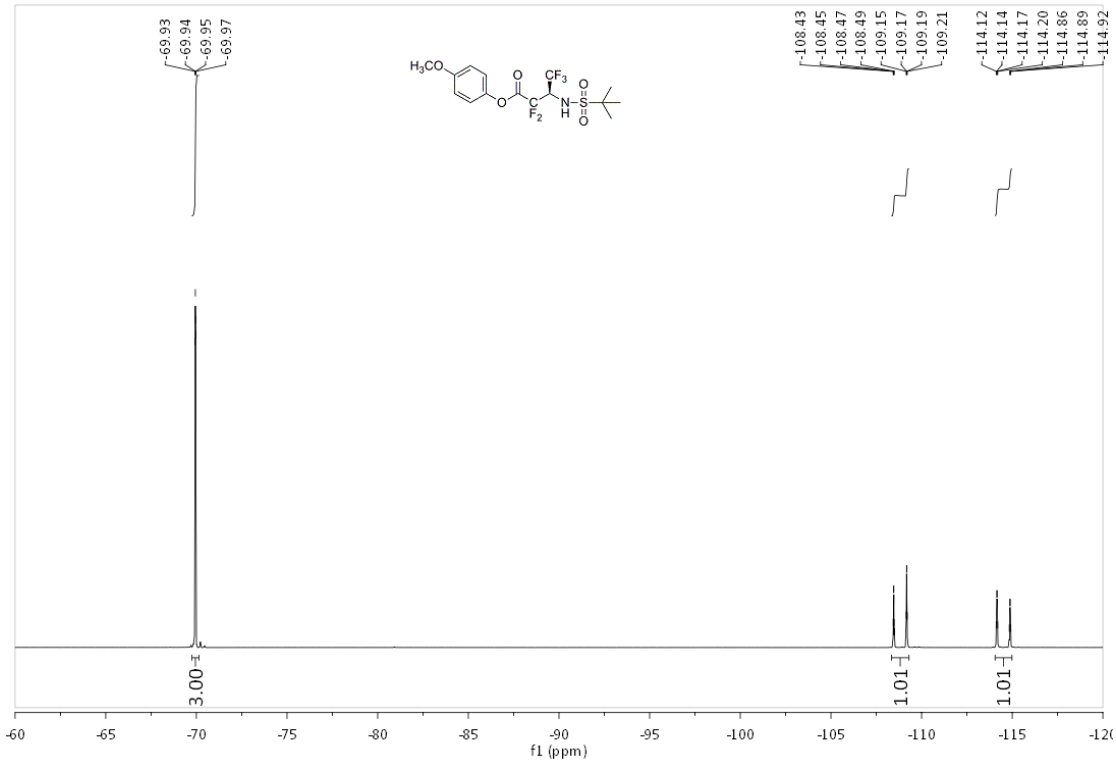



-71.95
-71.97
-71.98
-72.00
-106.44
-106.48
-106.51
-106.55
-107.21
-107.25
-107.28
-107.32
-113.35
-113.37
-113.39
-113.41
-114.12
-114.14
-114.16
-114.18
O
CF3
NH2
F2
H3CO
3.00
1.02
1.06
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
f1 (ppm)

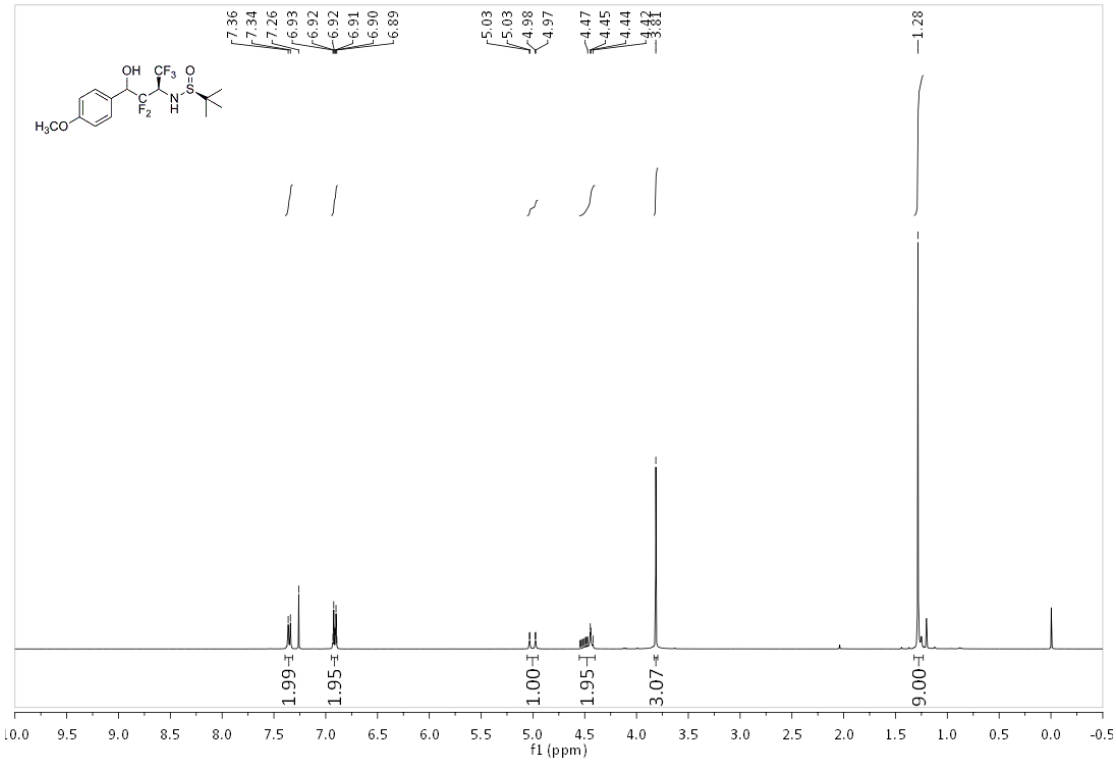
^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra of **12**

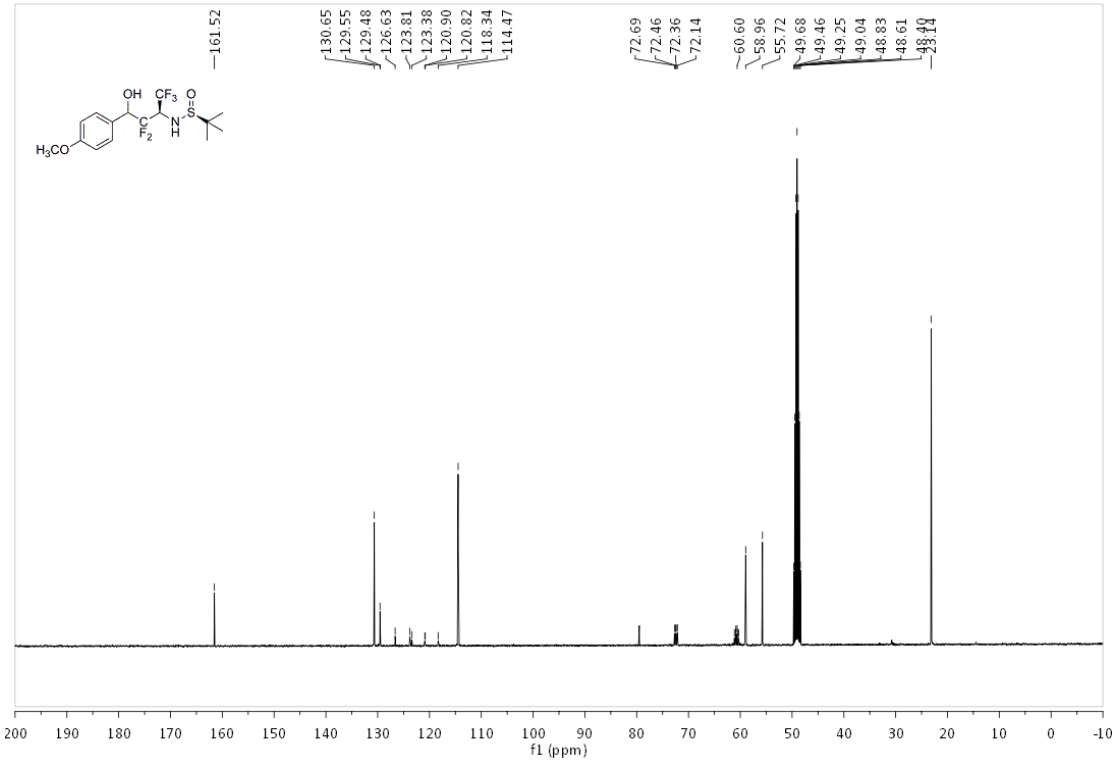


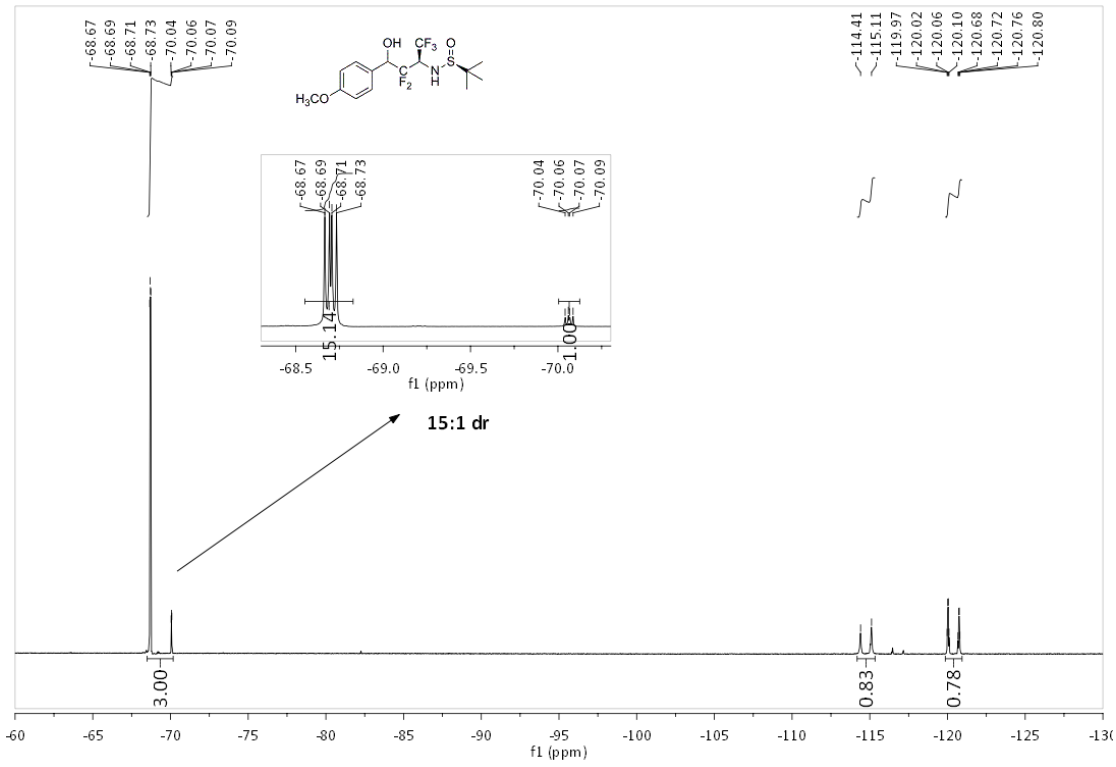




^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectrum of **13**

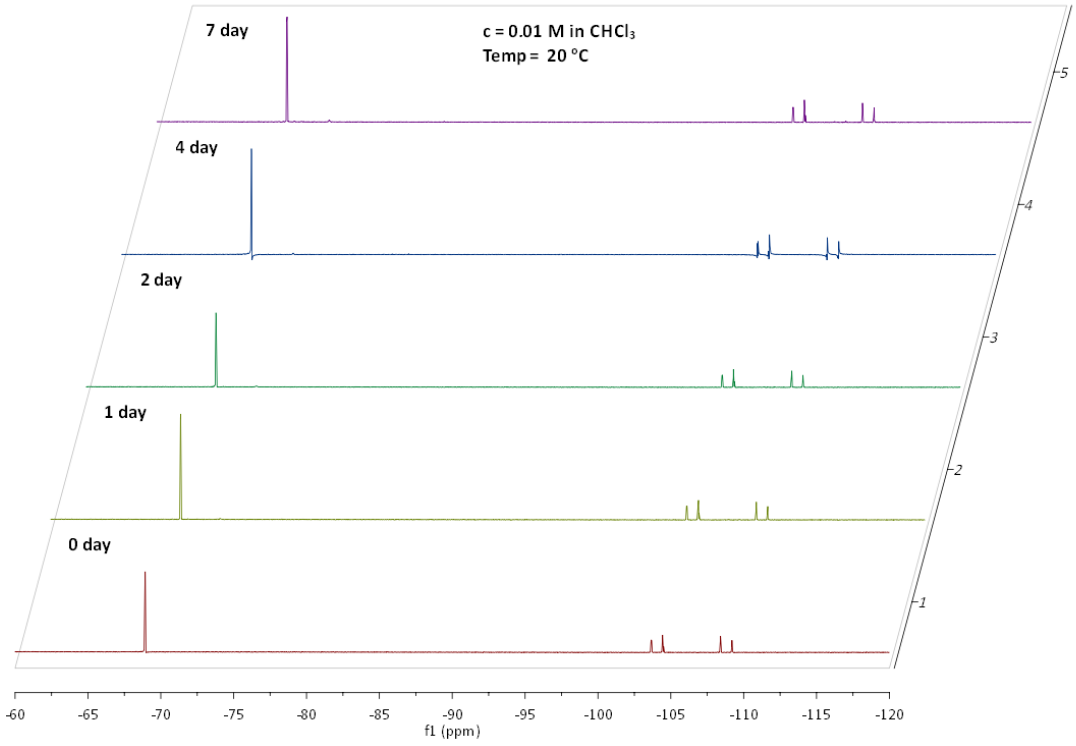


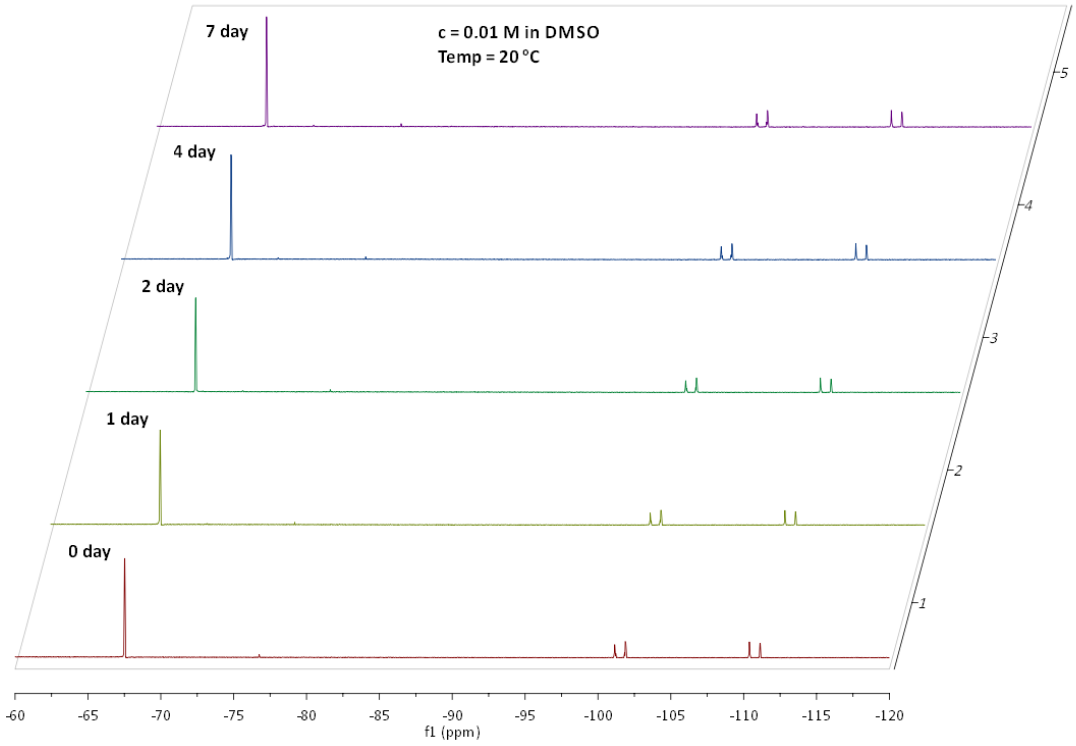

161.52
130.65
129.55
129.48
126.63
123.81
123.38
120.90
120.82
118.34
114.47
72.69
72.46
72.36
72.14
60.60
58.96
55.72
49.68
49.46
49.25
49.04
48.83
48.61
48.40
23.14
OH
CF3
O
S
N
H
F2
H3CO
f1 (ppm)

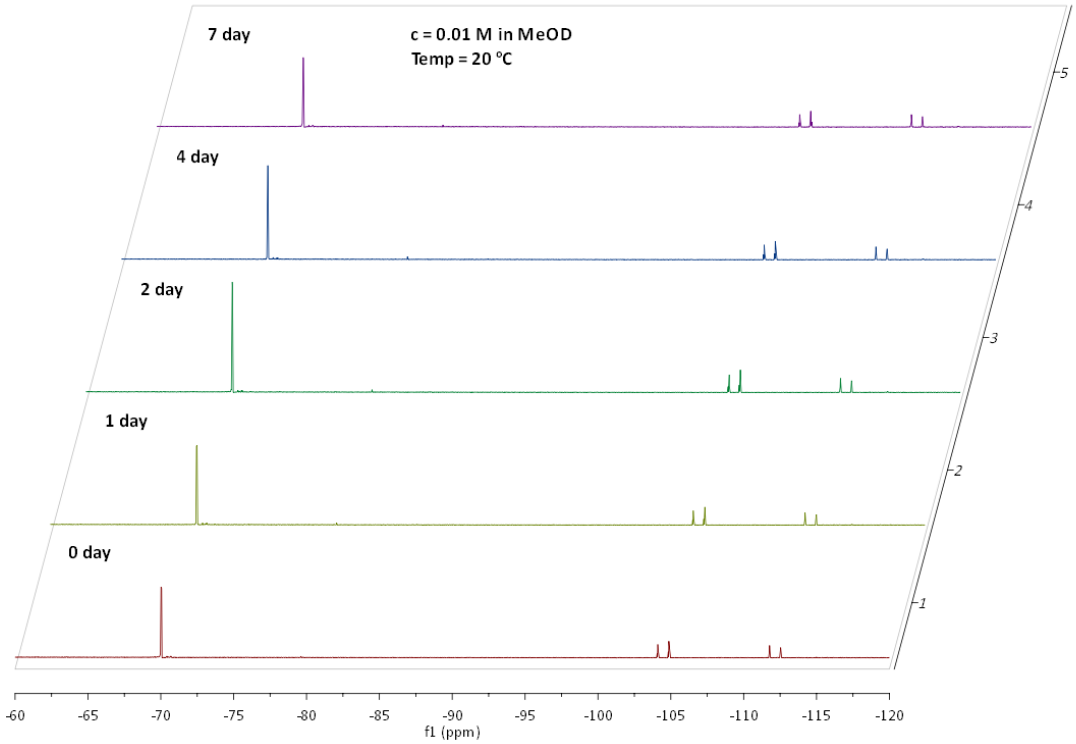

68.67
68.69
68.71
68.73
70.04
70.06
70.07
70.09
114.41
115.11
119.97
120.02
120.06
120.10
120.68
120.72
120.76
120.80
15.14
1.00
3.00
0.83
0.78
15:1 dr
f1 (ppm)

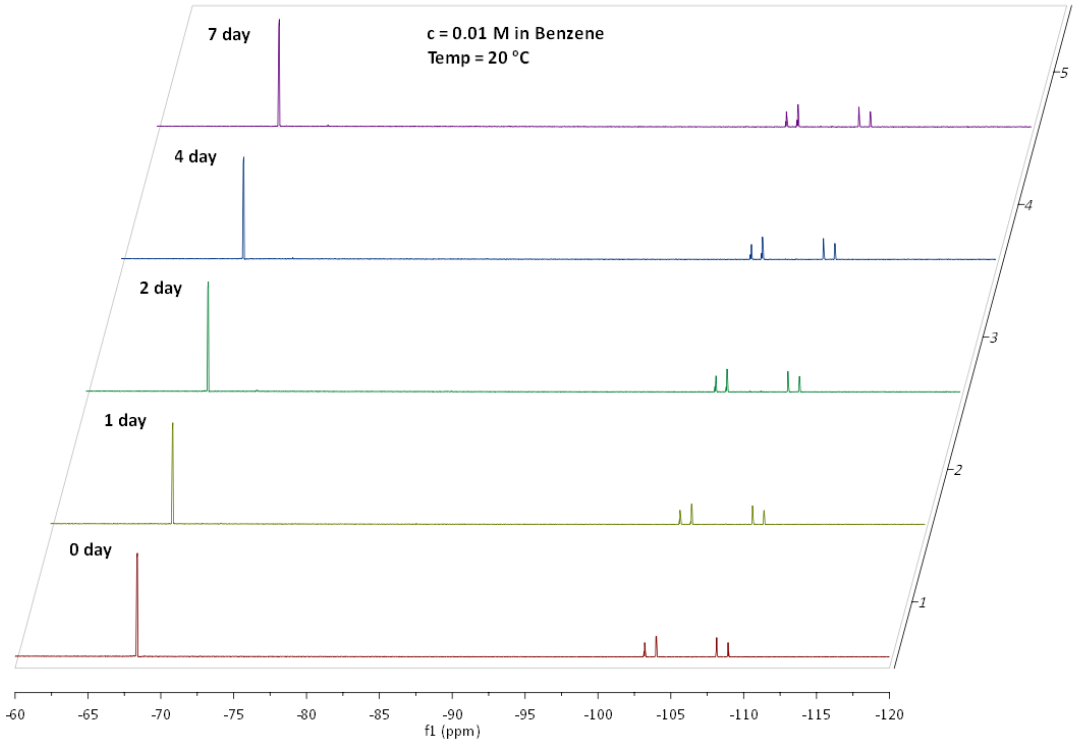
3. ^{19}F NMR spectra for the study of the configurational stability

The product (**10i**) is quite stable in $CHCl_3$, DMSO, Benzene and CH_3OH. (c = 0.01 mol/L)



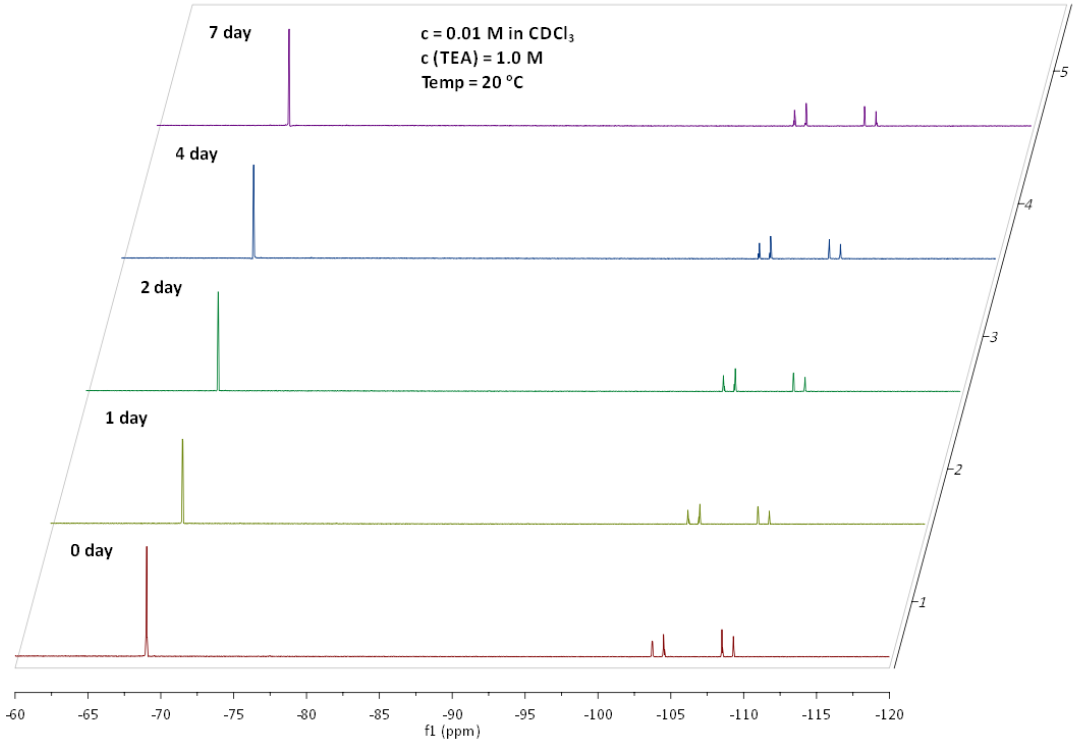


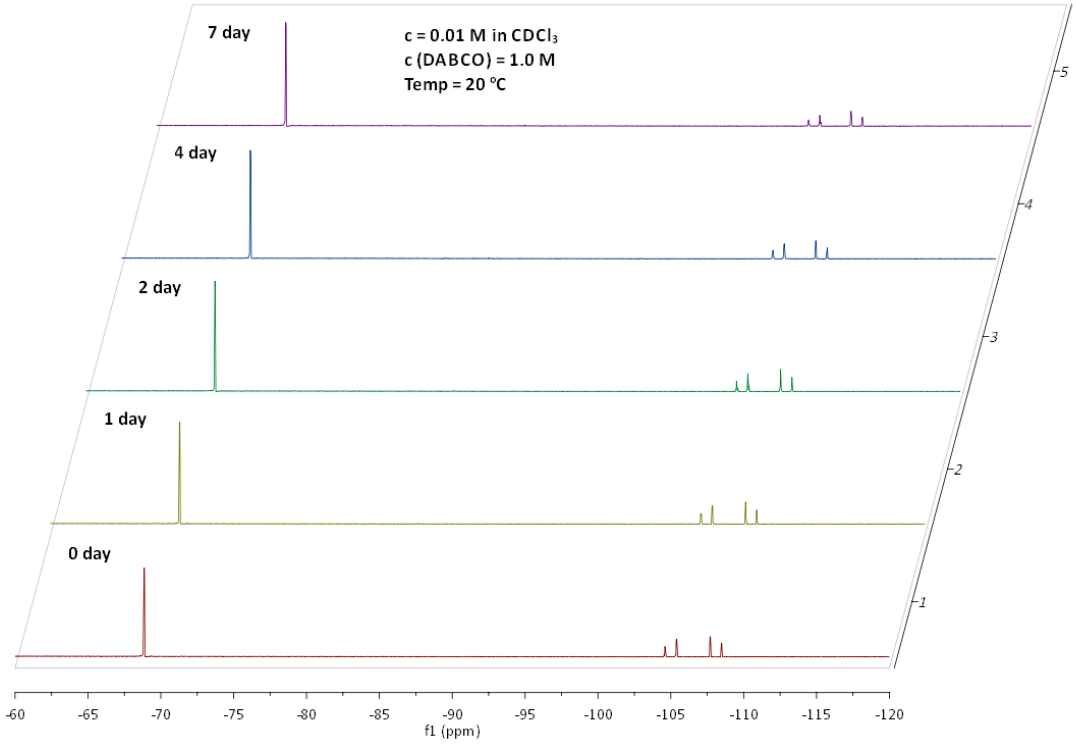

7 day
c = 0.01 M in MeOD
Temp = 20 °C
4 day
2 day
1 day
0 day
5
4
3
2
1
-60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120
f1 (ppm)

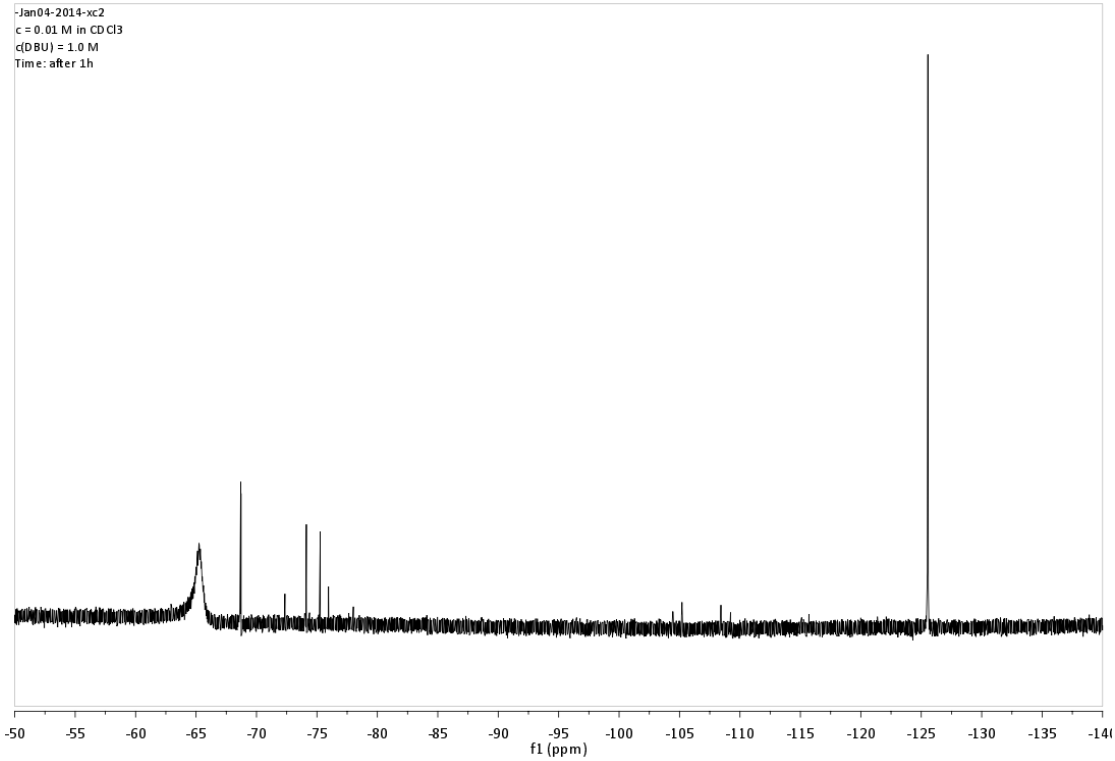

7 day
c = 0.01 M in Benzene
Temp = 20 °C
4 day
2 day
1 day
0 day
5
4
3
2
1
-60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120
f1 (ppm)

The product (**10i**) is also stable with TEA and DABCO in $CHCl_3$.

(c (product) = 0.01 mol/L, c (TEA or DABCO) = 1.0 mol/L)





The product (**10i**) is unstable with DBU in $CHCl_3$, the solution turned from colorless to light yellow immediately when DBU was added, and the product changed shown by TLC.

(c (product) = 0.01 mol/L, c (DBU) = 1.0 mol/L)