Supplementary Materials

Asymmetric Electrophilic Difluoromethylthiolation of Indanone-Based β-Keto Esters using Difluoromethanesulfonyl Hypervalent Iodonium Ylides

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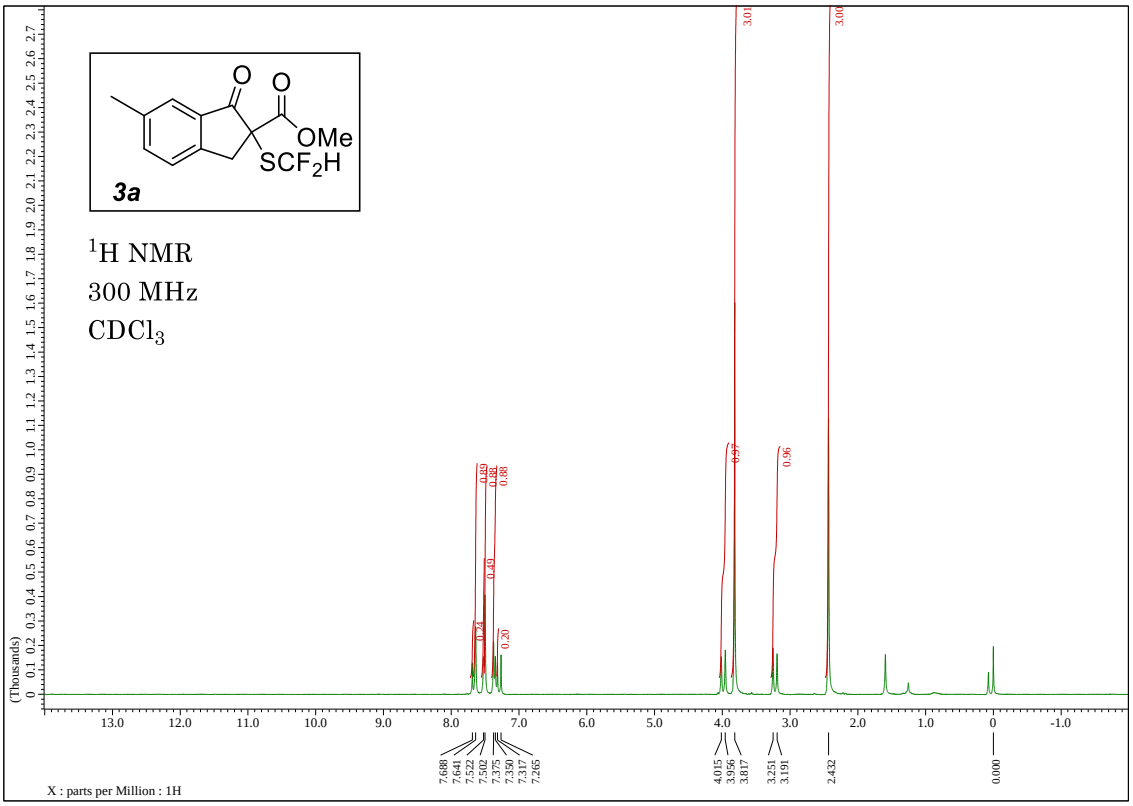
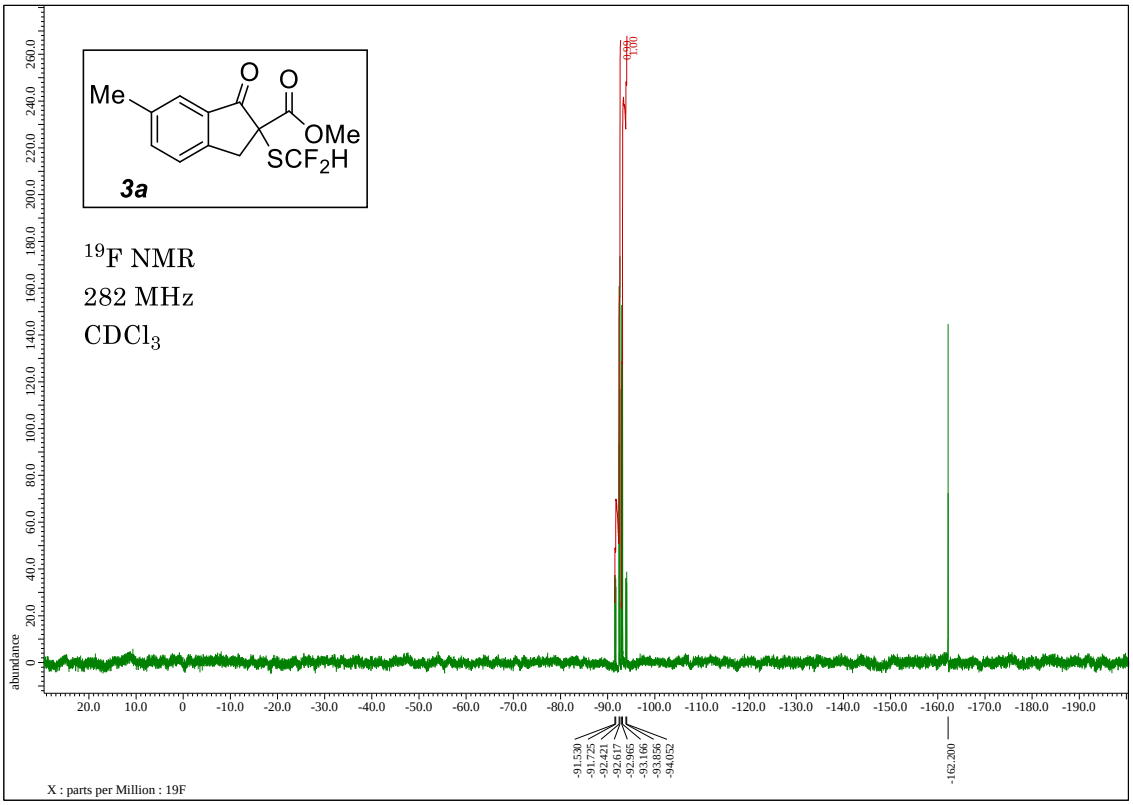
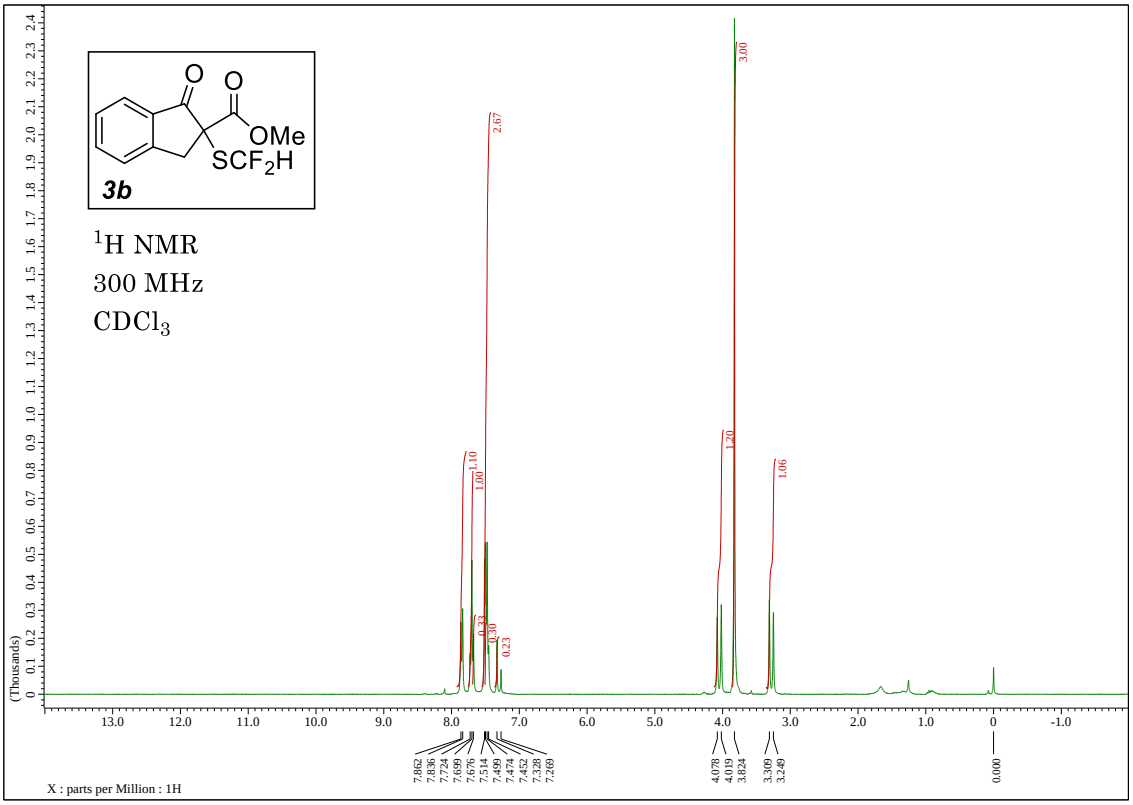
^{1}H, ^{13}C and ^{19}F NMR spectra of compound 3



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$CDCl_3$
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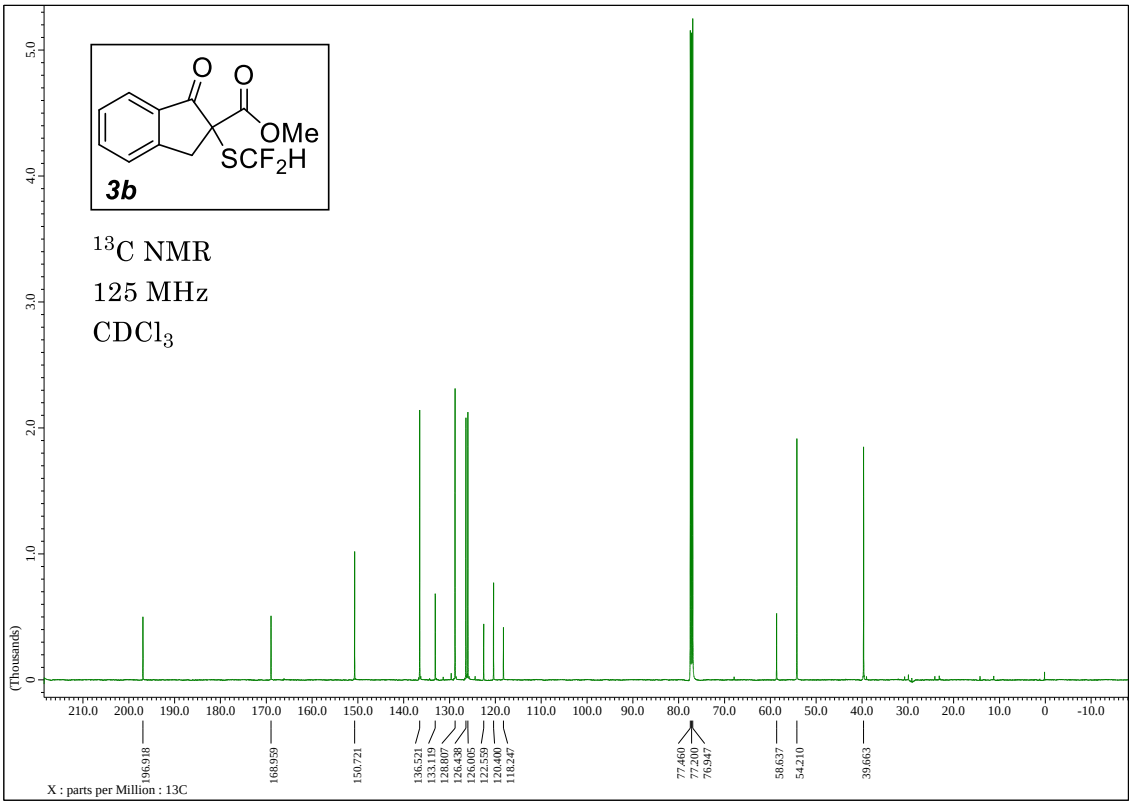
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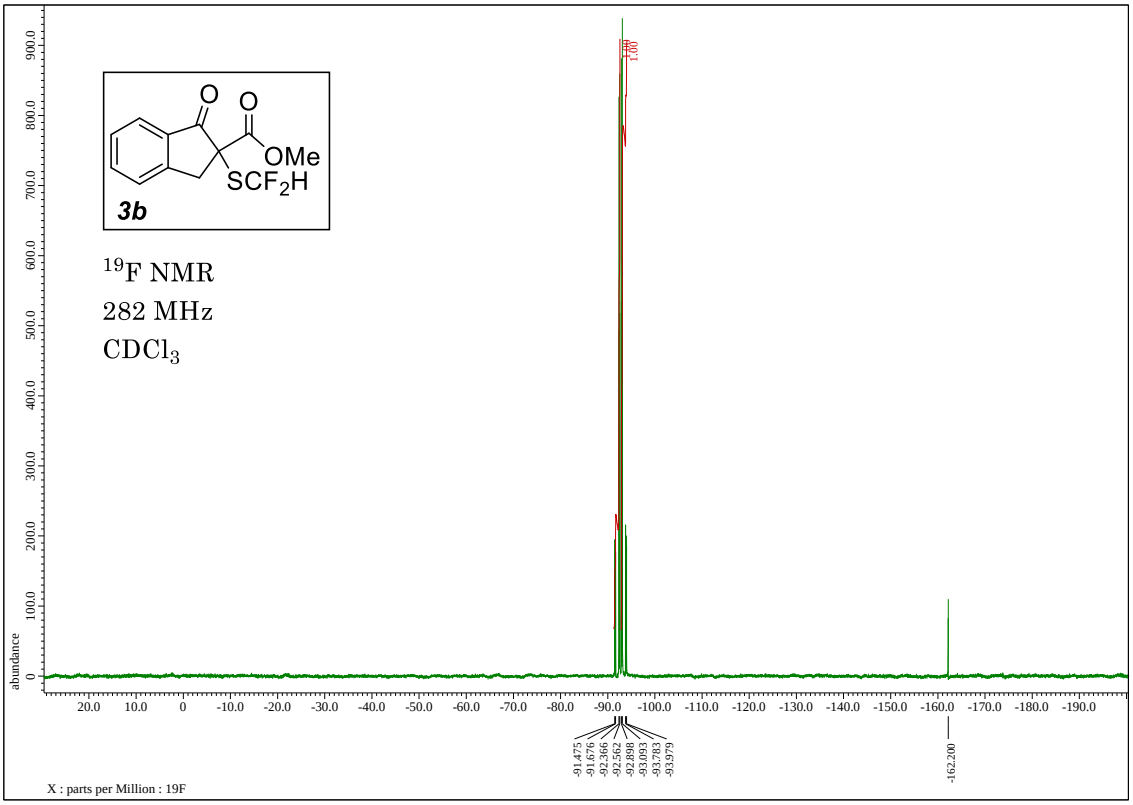
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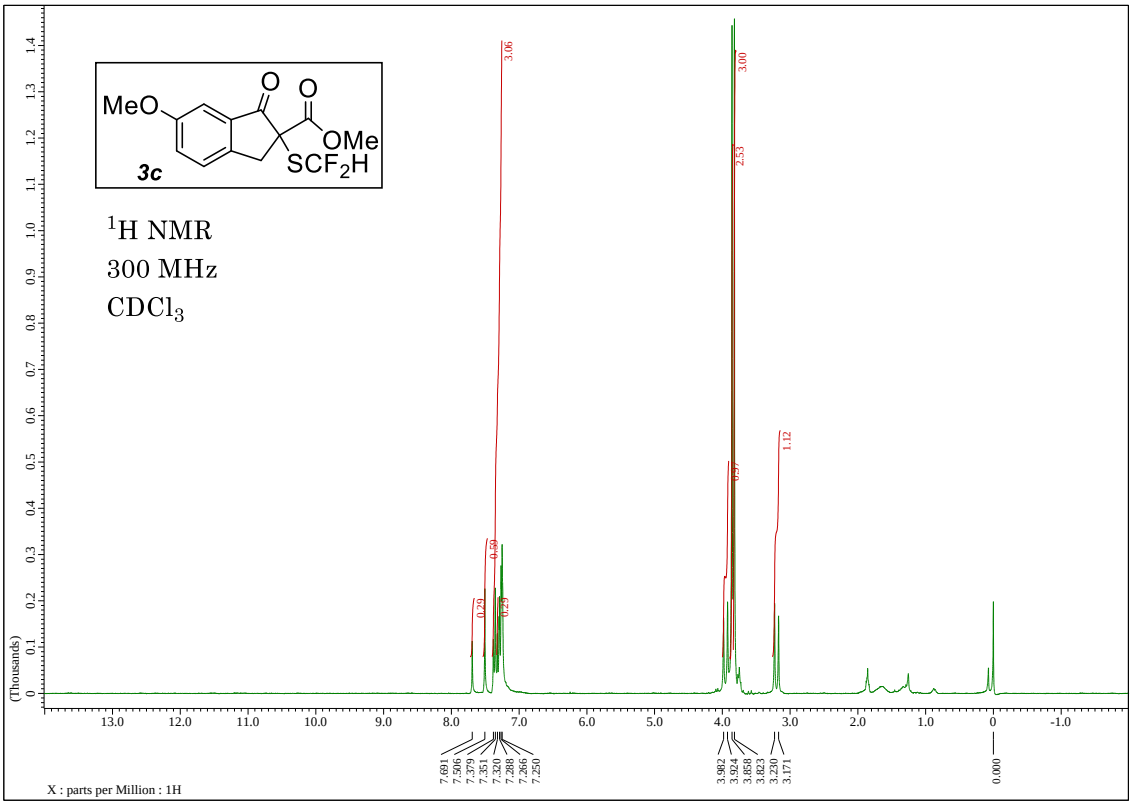
282 MHz
$CDCl_3$
abundance
X : parts per Million : 19F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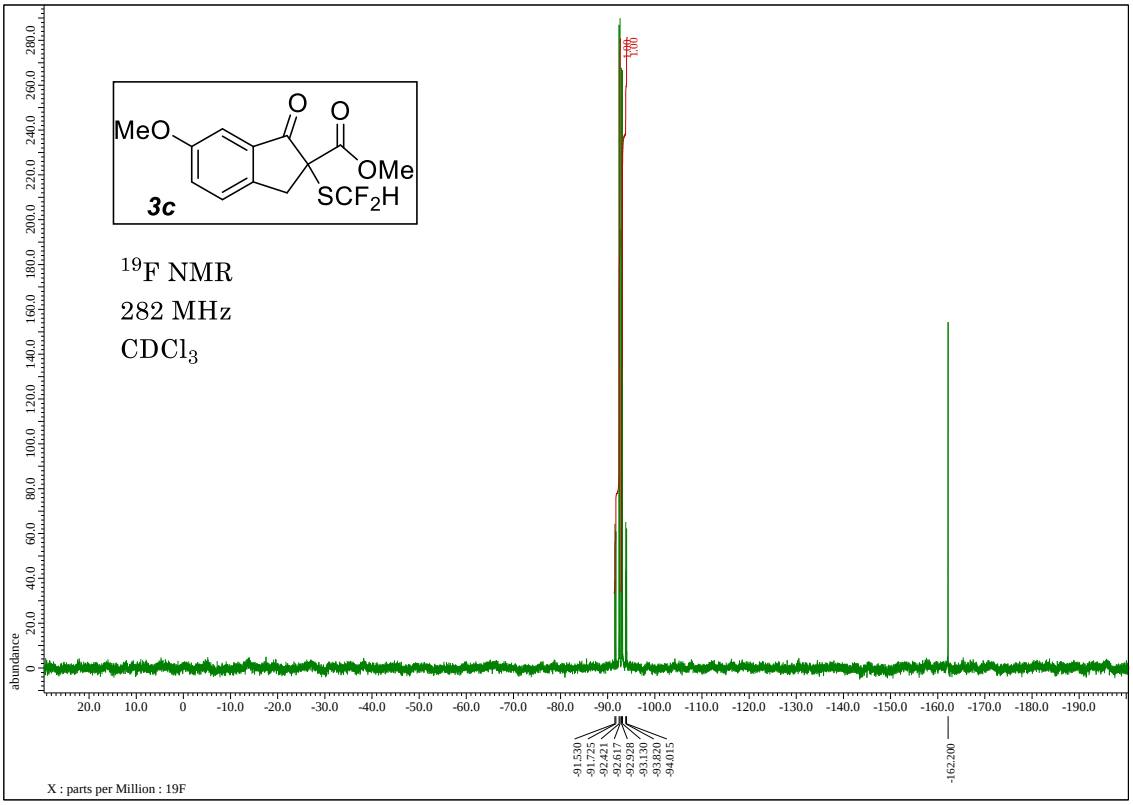
^{1}H NMR
300 MHz
$CDCl_3$
(Thousands)
X : parts per Million : 1H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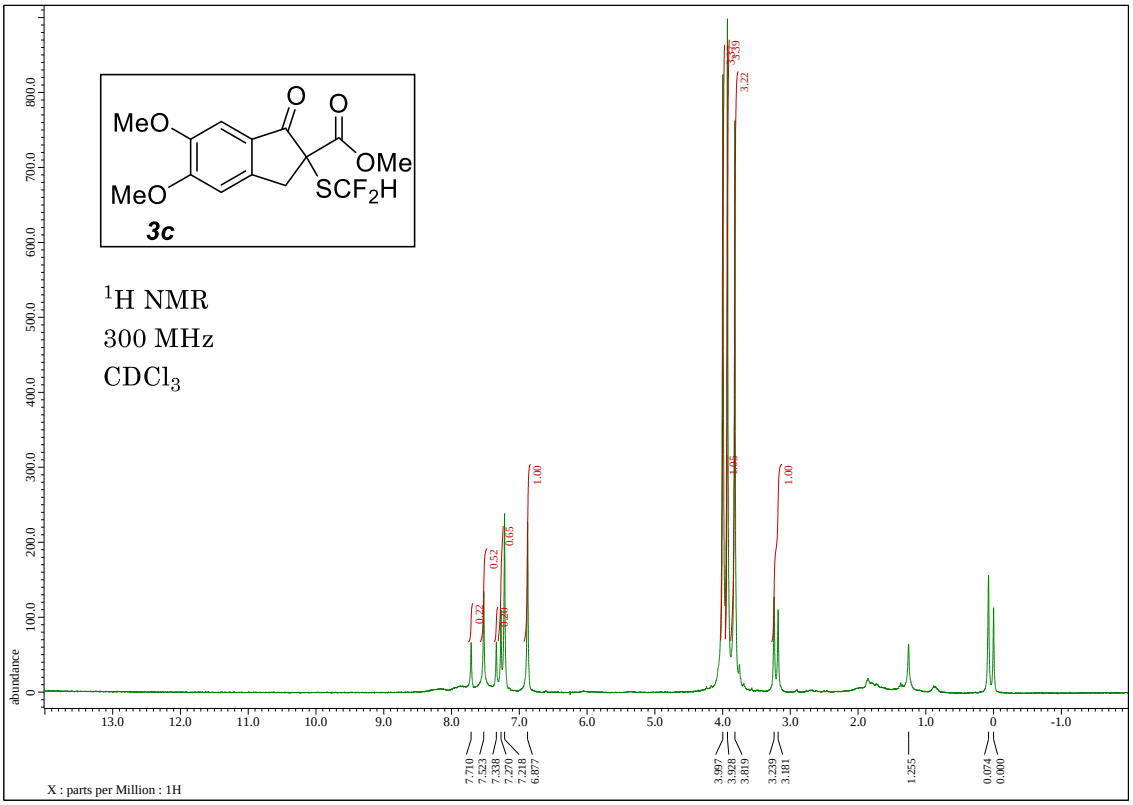
O
O
OMe
SCF2H
3c
19F NMR
282 MHz
CDCl3
abundance
X : parts per Million : 19F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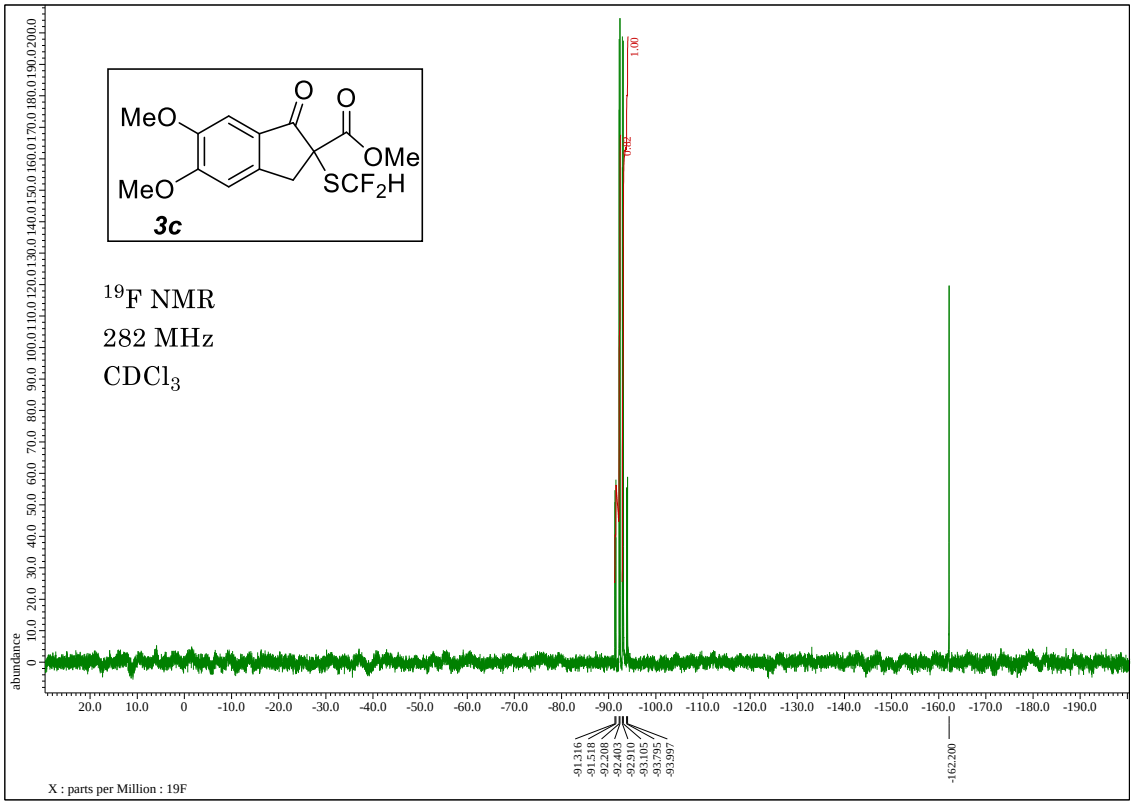
3c
1H NMR
300 MHz
CDCl3
abundance
X : parts per Million : 1H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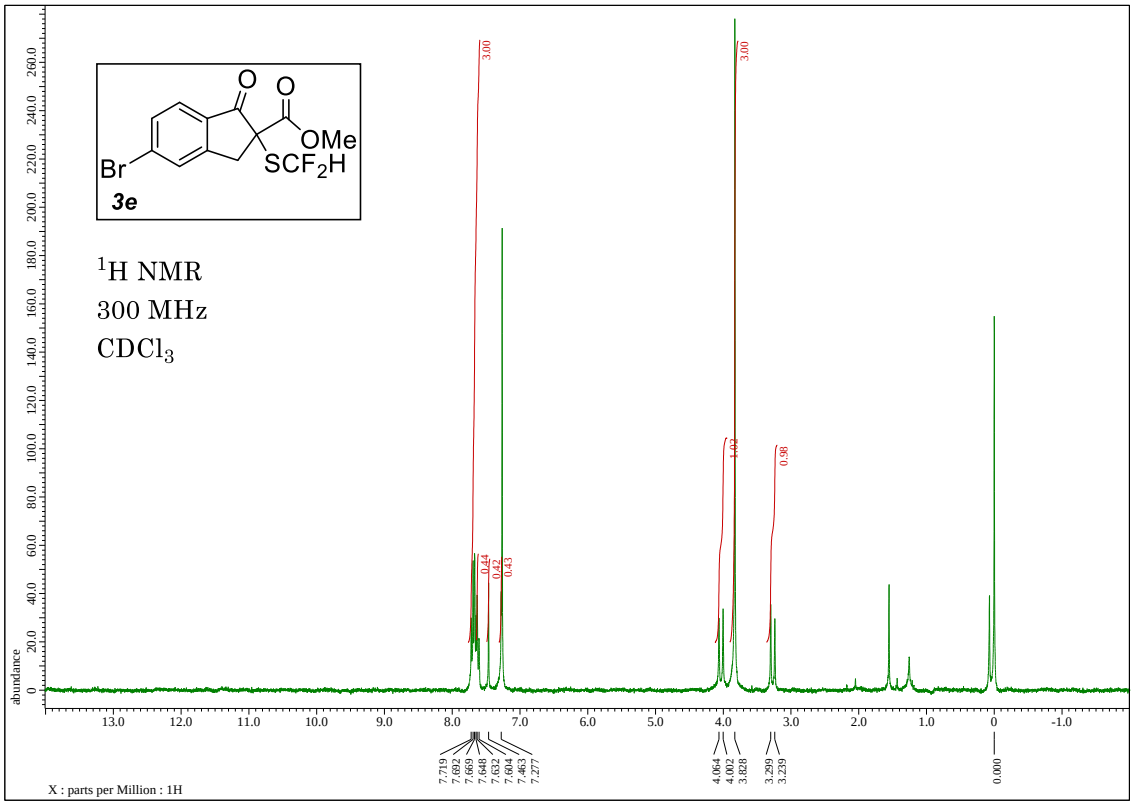
SCF2H
3c
19F NMR
282 MHz
CDCl3
abundance
X : parts per Million : 19F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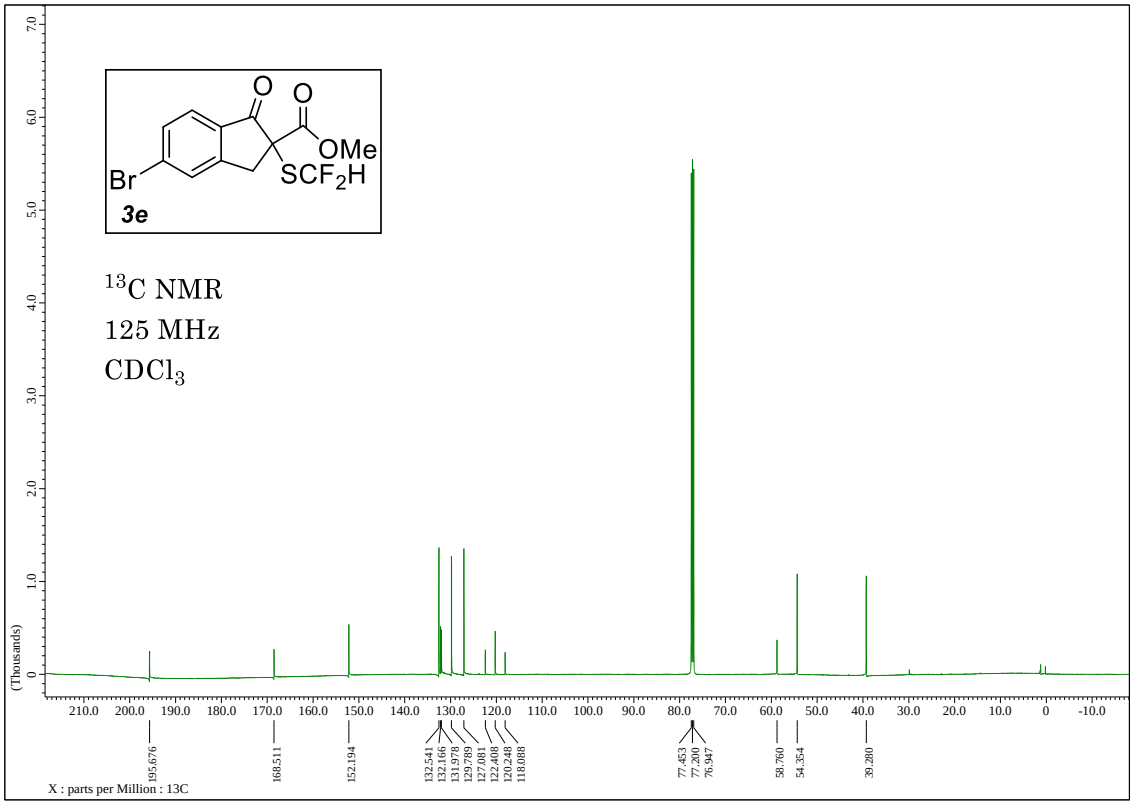
O
O
OMe
SCF2H
3e
1H NMR
300 MHz
CDCl3
abundance
X : parts per Million : 1H


Br
OMe
SCF2H
3e
13C NMR
125 MHz
CDCl3
(Thousands)
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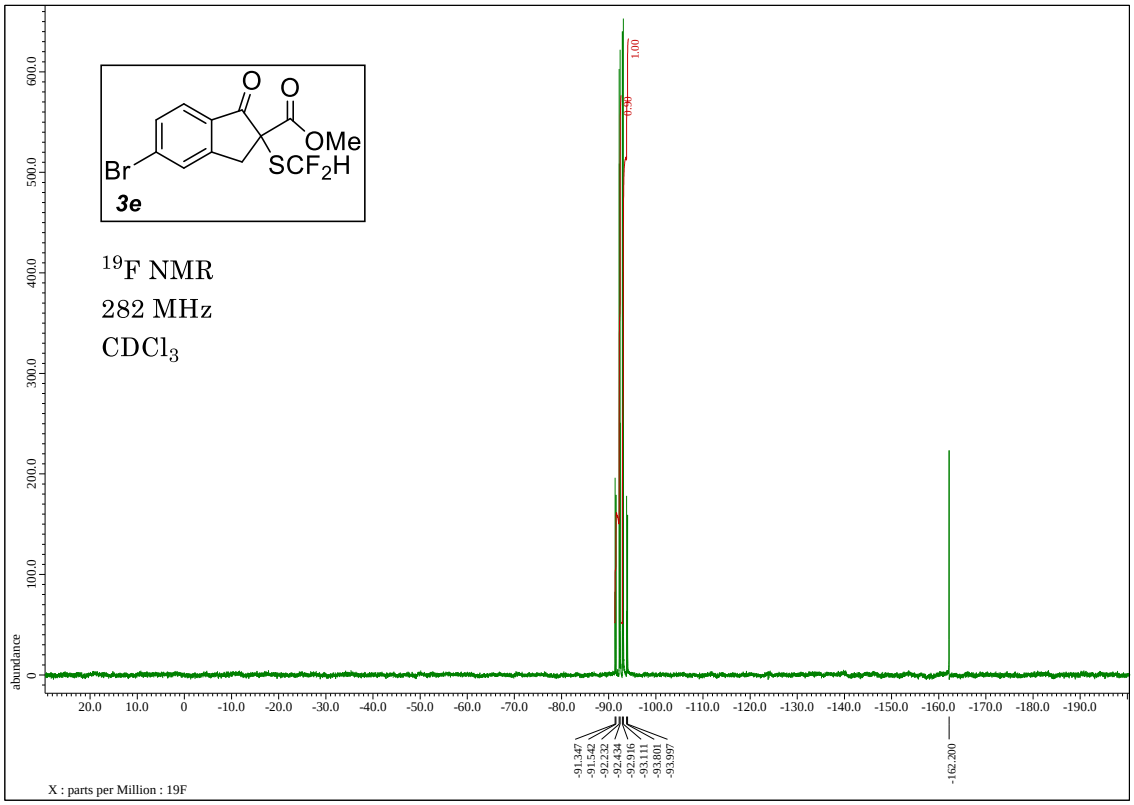
152.194
132.541
132.166
131.978
129.789
127.081
122.408
120.248
118.088
77.453
77.200
76.947
58.760
54.354
39.280
X : parts per Million : 13C


Br
OMe
SCF2H
3e
19F NMR
282 MHz
CDCl3
1.00
0.98
abundance
-91.347
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-92.434
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-93.111
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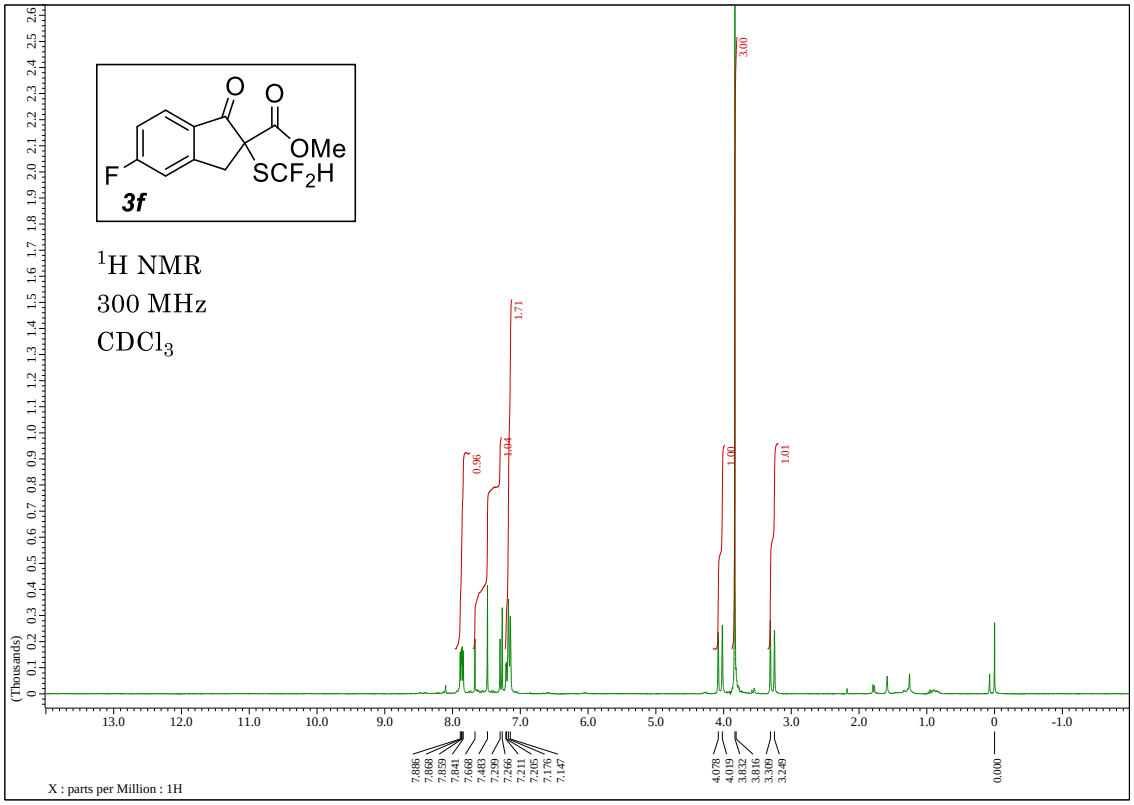
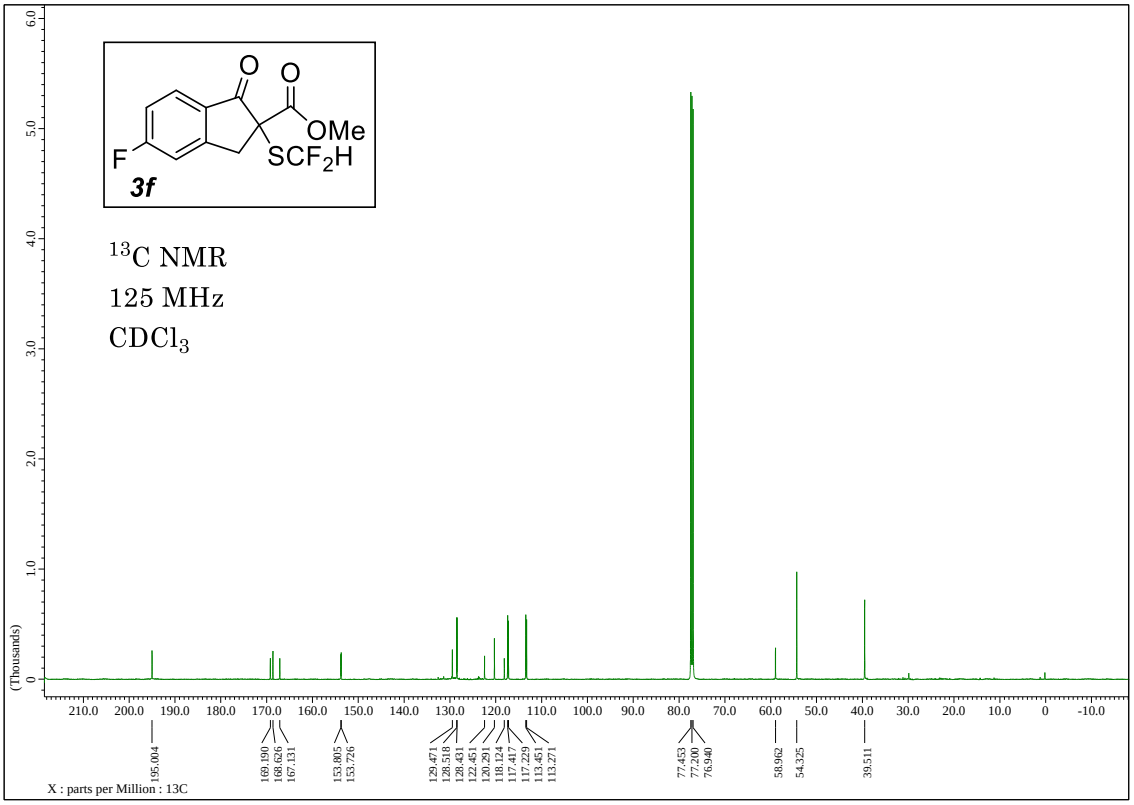
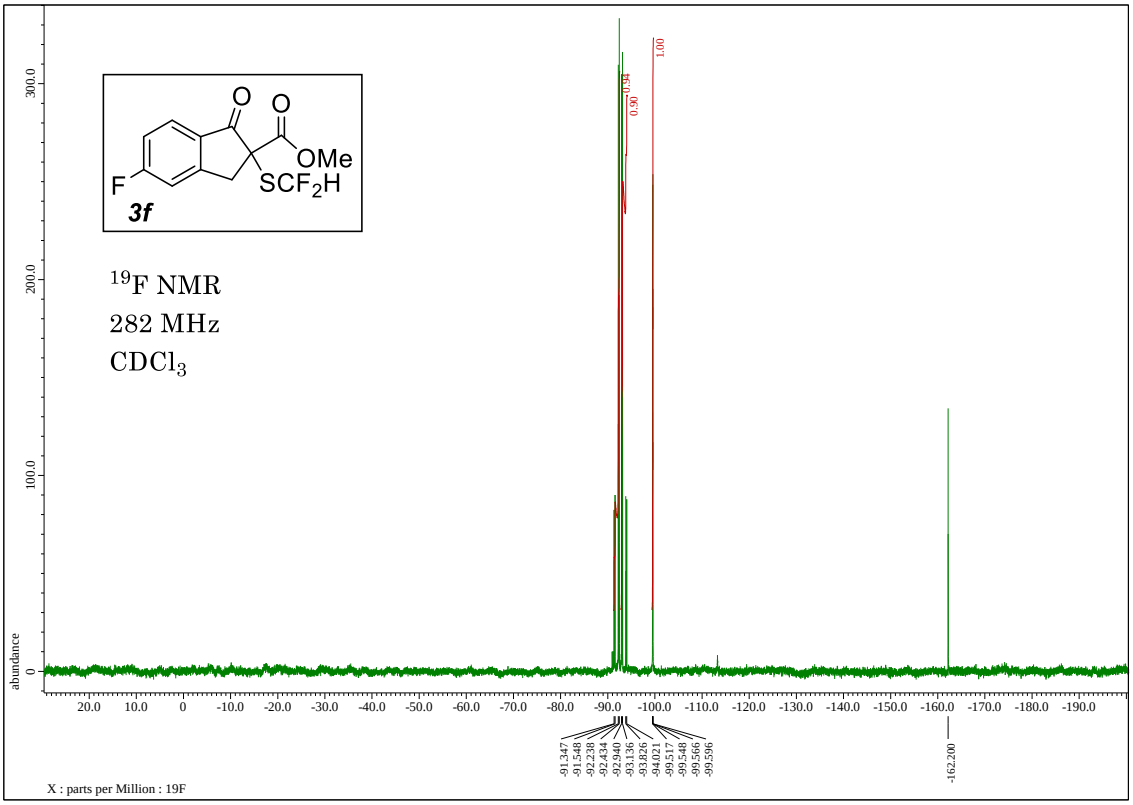
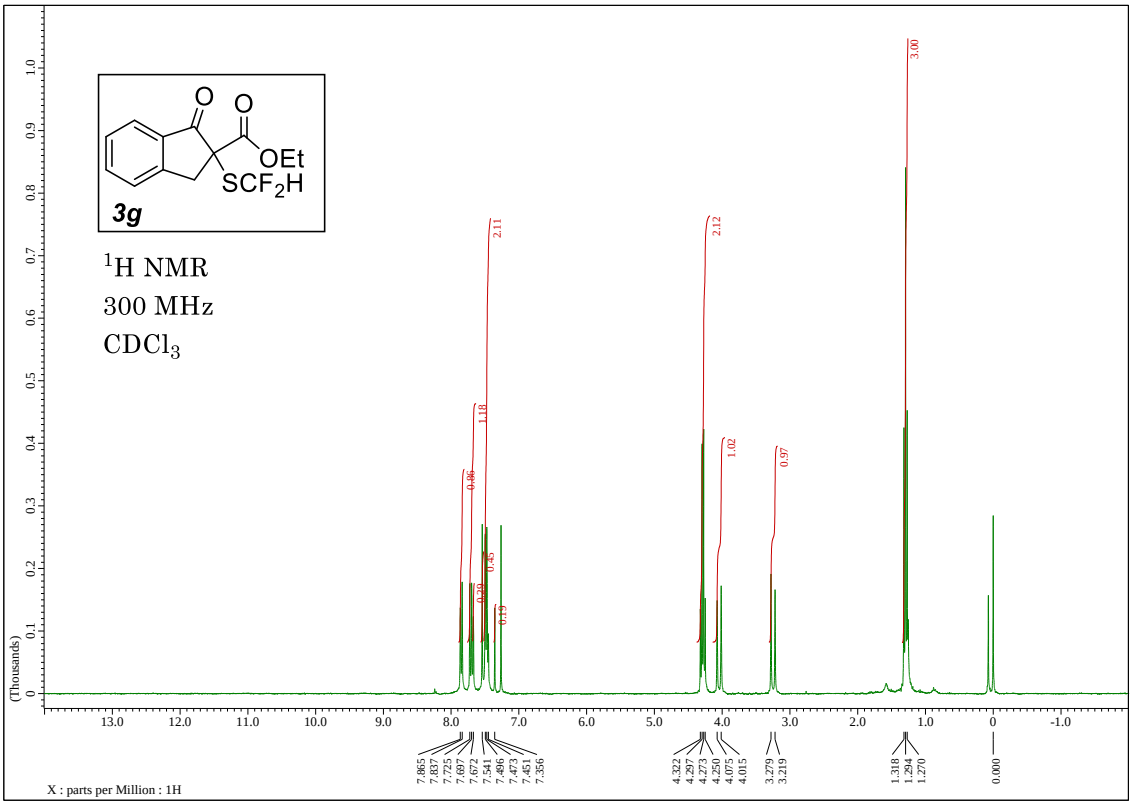
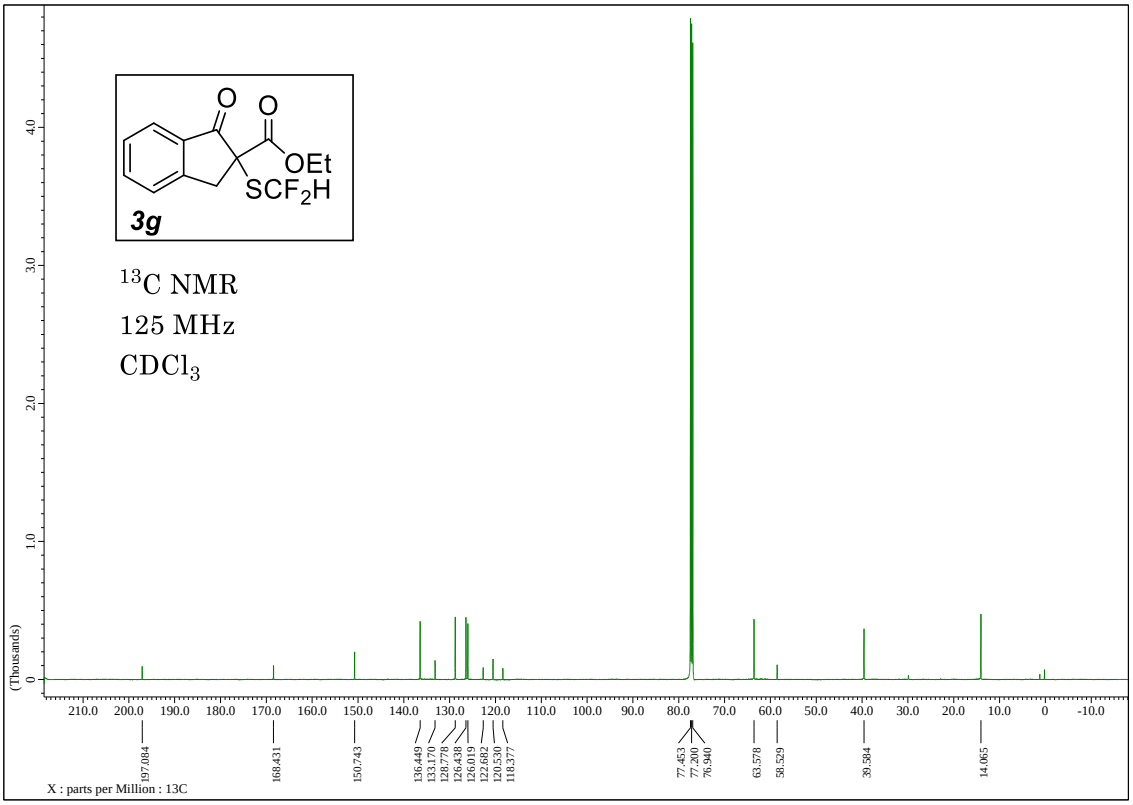
-93.997
-162.200
X : parts per Million : 19F

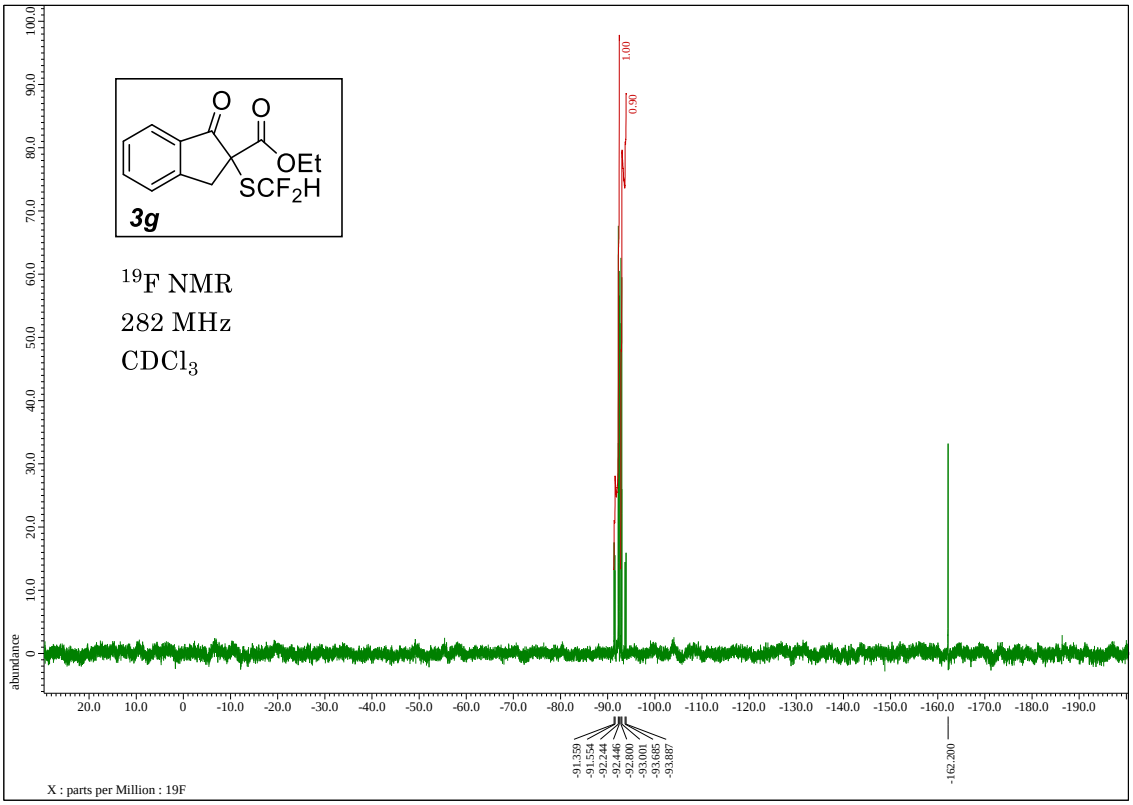

3f
1H NMR
300 MHz
CDCl3
X : parts per Million : 1H


3f
13C NMR
125 MHz
CDCl3
X : parts per Million : 13C


3f
^{19}F NMR
282 MHz
$CDCl_3$
abundance
X : parts per Million : 19F


3g
^{1}H NMR
300 MHz
$CDCl_3$
(Thousands)
X : parts per Million : 1H


3g
^{13}C NMR
125 MHz
$CDCl_3$
(Thousands)
197.084
168.431
150.743
136.449
133.170
128.778
126.438
126.019
122.682
120.530
118.377
77.453
77.200
76.940
63.578
58.529
39.584
14.065
X : parts per Million : 13C


3g
^{19}F NMR
282 MHz
$CDCl_3$
abundance
1.00
0.90
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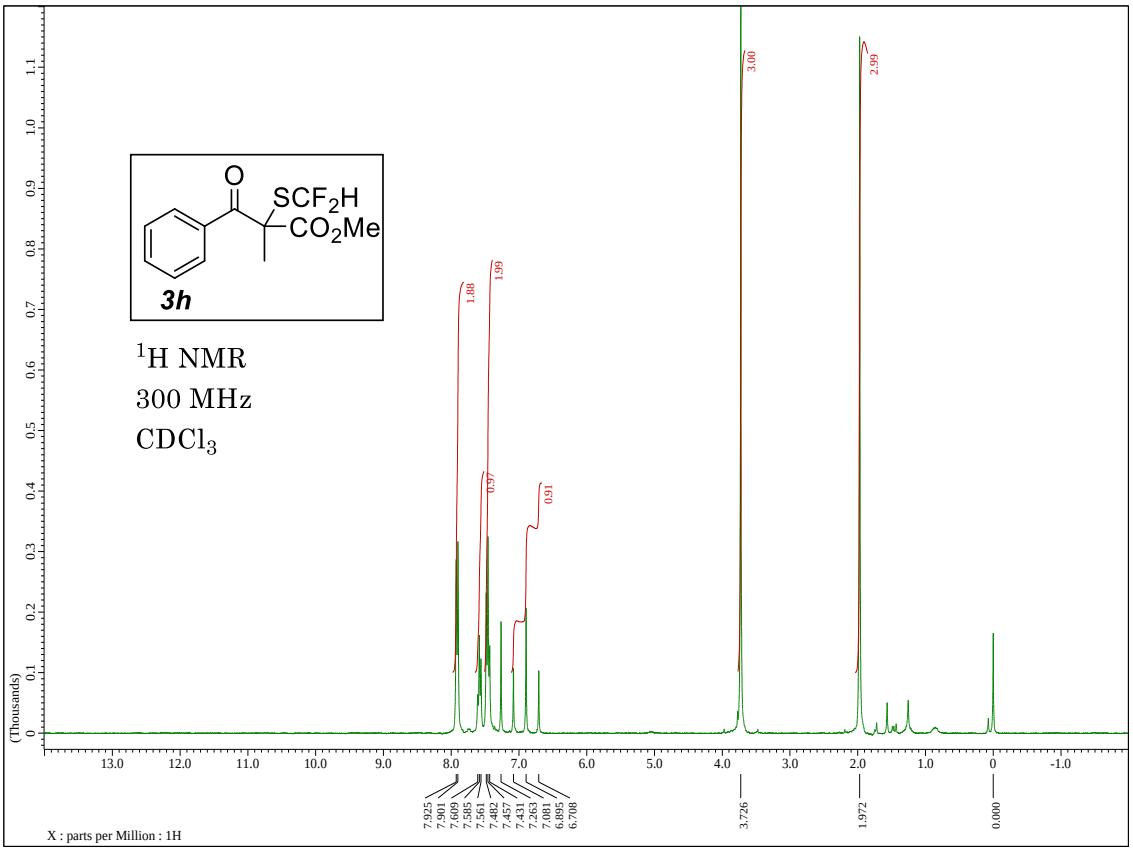
-91.554
-92.244
-92.446
-92.800
-93.001
-93.685
-93.887
-162.200
X : parts per Million : 19F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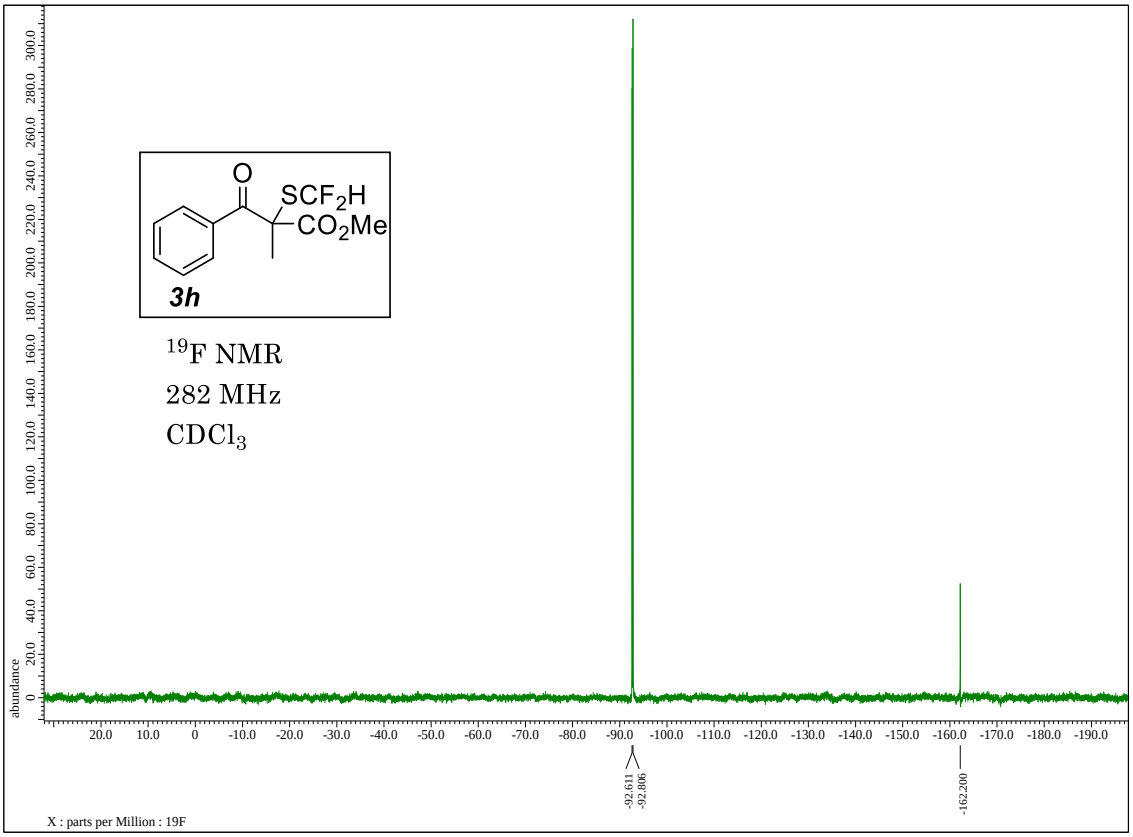
SCF2H
CO2Me
3h
1H NMR
300 MHz
CDCl3
3.00
2.99
1.88
1.99
0.97
0.91
(Thousands)
7.925
7.901
7.609
7.585
7.561
7.482
7.457
7.431
7.263
7.001
6.895
6.708
3.726
1.972
0.000
X : parts per Million : 1H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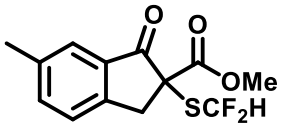
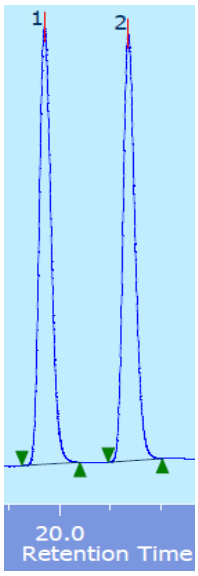
SCF2H
CO2Me
3h
19F NMR
282 MHz
CDCl3
abundance
-92.611
-92.806
-162.200
X : parts per Million : 19F

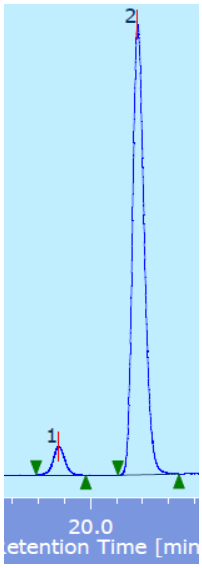
HPLC data of compound 3

Methyl 2-((difluoromethyl)thio)-6-methyl-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (3a)



chiral pack IB3, Hexane/*i*PrOH = 98:2, 0.5 mL/min

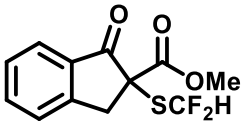




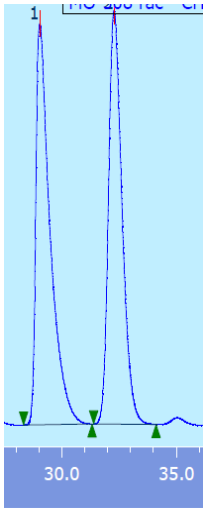
No.	tR (min)	Area (%)	High (%)
1	19.392	50.257	50.610
2	22.692	49.743	49.390

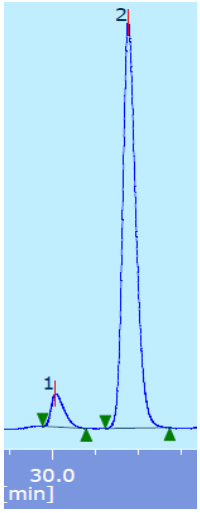
No.	tR (min)	Area (%)	High (%)
1	18.775	5.917	5.955
2	21.800	94.083	94.045

Methyl 2-((difluoromethyl)thio)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (3b)



chiral pack IB3, Hexane/*i*PrOH = 98:2, 0.5 mL/min

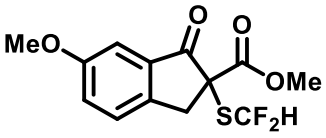




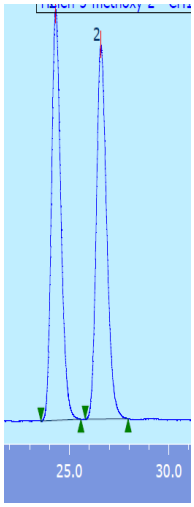
No.	tR (min)	Area (%)	High (%)
1	29.025	50.081	49.253
2	32.258	49.919	50.747

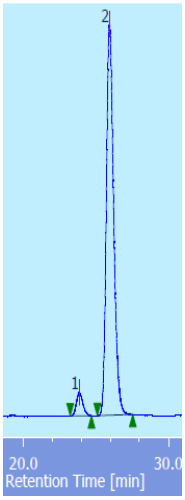
No.	tR (min)	Area (%)	High (%)
1	30.150	7.479	7.578
2	33.533	92.251	92.422

Methyl 2-((difluoromethyl)thio)-6-methoxy-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (3c)



chiral pack IB3, Hexane/*i*PrOH = 95:5, 0.5 mL/min

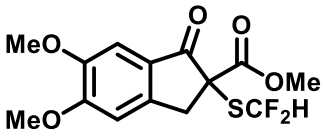




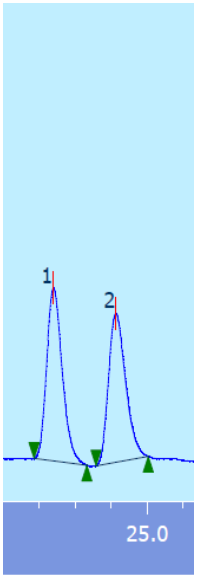
No.	tR (min)	Area (%)	High (%)
1	24.308	49.845	52.304
2	26.575	50.155	47.696

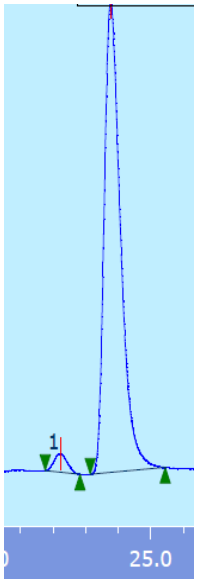
No.	tR (min)	Area (%)	High (%)
1	23.850	5.064	5.588
2	25.933	94.936	94.412

Methyl 2-((difluoromethyl)thio)-5,6-dimethoxy-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (3d)



chiral pack OD-3, Hexane/*i*PrOH = 95:5, 1.0 mL/min

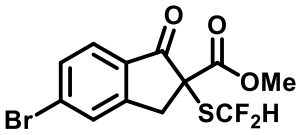




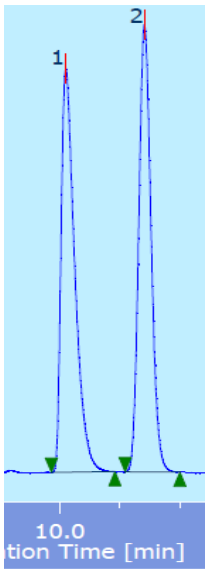
No.	tR (min)	Area (%)	High (%)
1	22.392	51.293	53.710
2	24.133	48.707	46.290

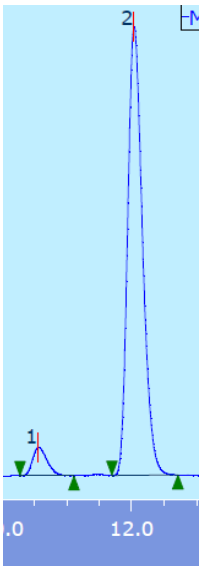
No.	tR (min)	Area (%)	High (%)
1	22.208	3.074	3.827
2	23.767	96.926	96.173

Methyl 5-bromo-2-((difluoromethyl)thio)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (3e)



chiral pack OD-3, Hexane/*i*PrOH = 95:5, 1.0 mL/min

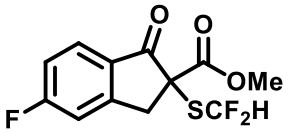




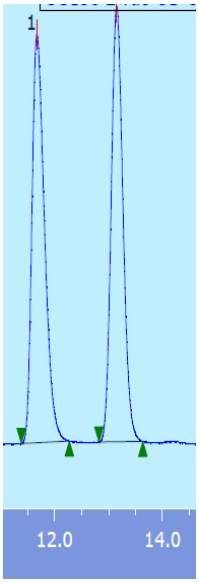
No.	tR (min)	Area (%)	High (%)
1	10.092	50.065	47.444
2	11.408	49.935	52.556

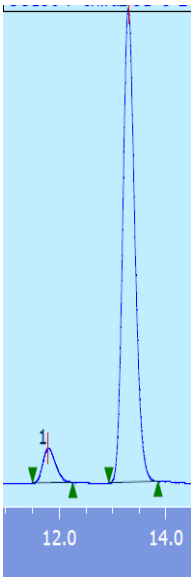
No.	tR (min)	Area (%)	High (%)
1	10.558	5.916	5.965
2	12.033	94.084	94.035

Methyl 2-((difluoromethyl)thio)-5-fluoro-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (3f)



chiral pack OD-3, Hexane/*i*PrOH = 95:5, 1.0 mL/min

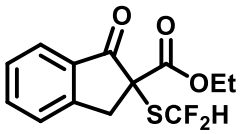




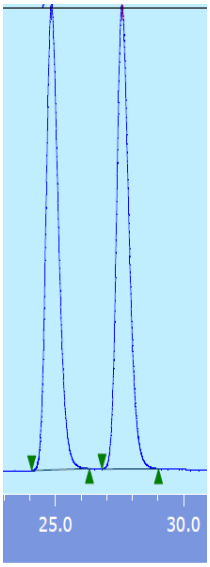
No.	tR (min)	Area (%)	High (%)
1	11.675	50.039	48.403
2	13.142	49.961	51.597

No.	tR (min)	Area (%)	High (%)
1	11.792	7.175	6.770
2	13.292	92.825	93.230

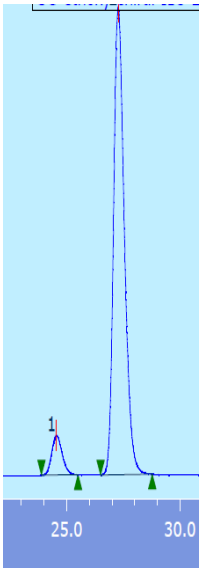
Ethyl 2-((difluoromethyl)thio)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (3g)



chiral pack IB3, Hexane/*i*PrOH = 99:1, 1.0 mL/min

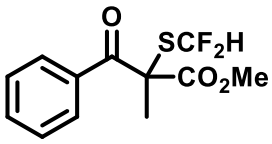


No.	tR (min)	Area (%)	High (%)
1	24.833	50.018	50.086
2	27.583	49.982	49.914

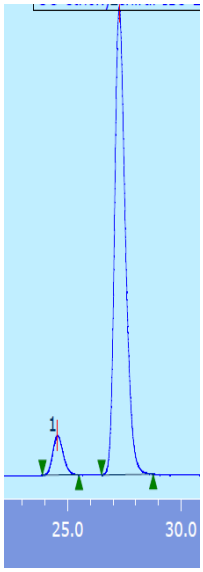


No.	tR (min)	Area (%)	High (%)
1	24.542	7.634	7.805
2	27.258	92.366	92.195

Methyl 2-((difluoromethyl)thio)-2-methyl-3-oxo-3-phenylpropanoate (3h)



chiral pack OD3, Hexane/*i*PrOH = 99:1, 0.53 mL/min



No.	tR (min)	Area (%)	High (%)
1	40.200	43.763	47.481
2	45.317	56.237	52.519