Highly enantioselective addition of *N*-2,2,2-trifluoroethyl-isatin ketimines to ethylene sulfonyl fluoride

Jie Chen, Dong-yu Zhu, Xue-jing Zhang*, Ming Yan*

Guangdong Provincial Key Laboratory of Chiral Molecules and Drug Discovery, School of Pharmaceutical Sciences,

Sun Yat-sen University, Guangzhou 510006, China.

E-mail: yanming@mail.sysu.edu.cn; zhangxj33@mail.sysu.edu.cn

Supporting Information

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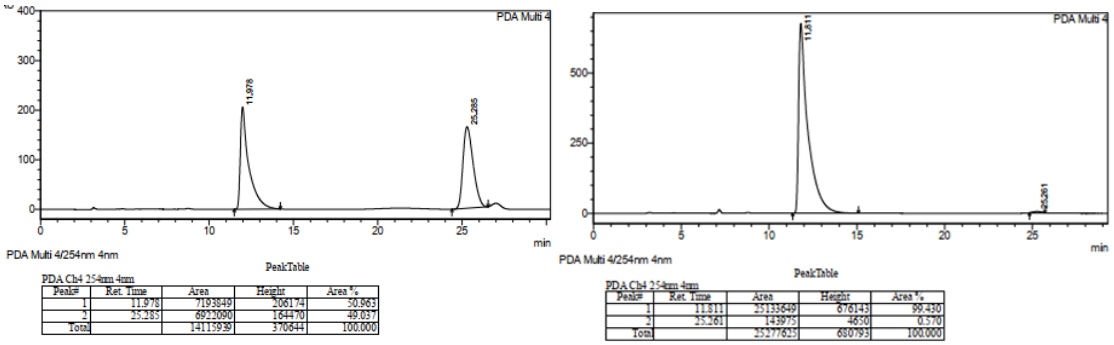
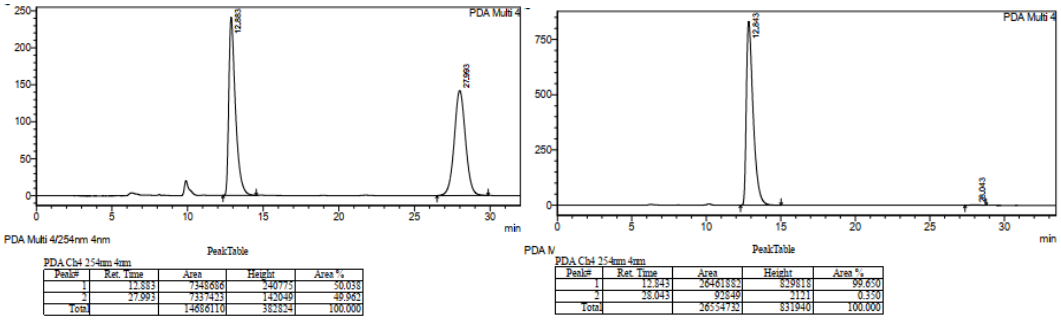
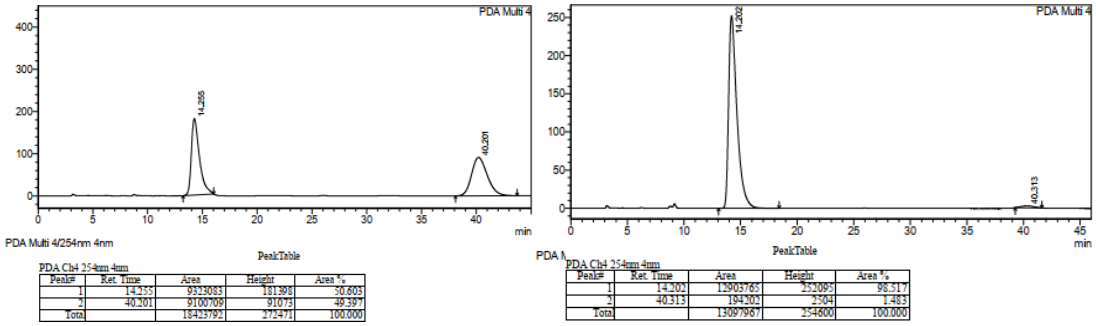
(R,E)-4,4,4-Trifluoro-3-((1-methyl-2-oxoindolin-3-ylidene)amino)butane-1-sulfonyl fluoride (3a)



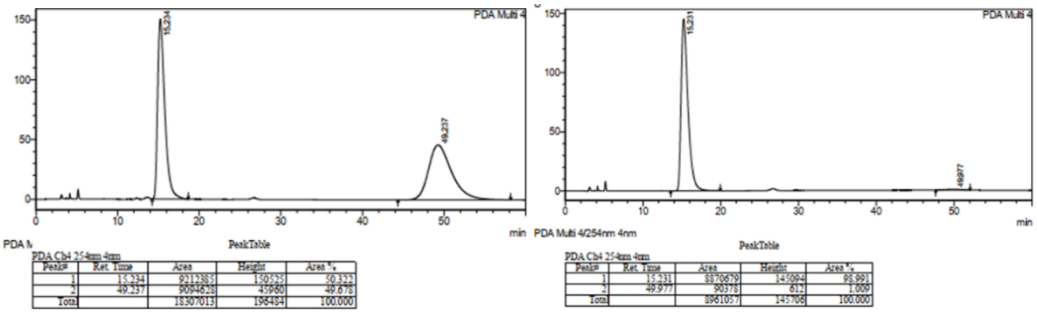
(R,E)-3-((1-Allyl-2-oxoindolin-3-ylidene)amino)-4,4,4-trifluorobutane-1-sulfonyl fluoride (3b)



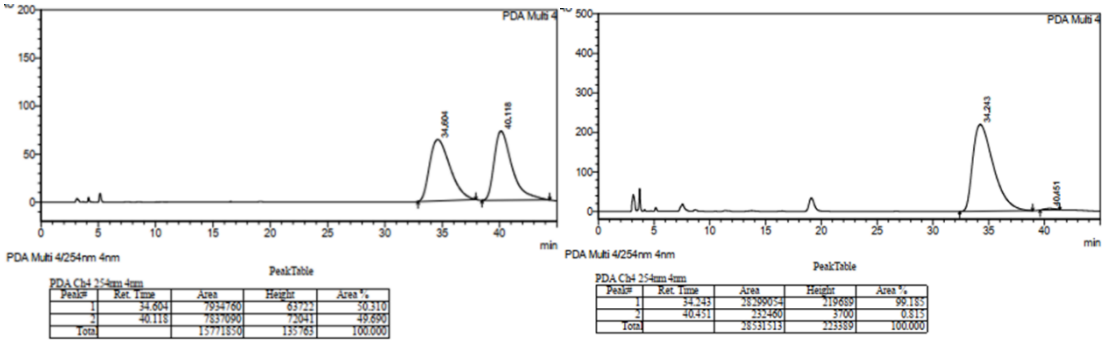
(R,E)-3-((1-Benzyl-2-oxoindolin-3-ylidene)amino)-4,4,4-trifluorobutane-1-sulfonyl fluoride (3c)



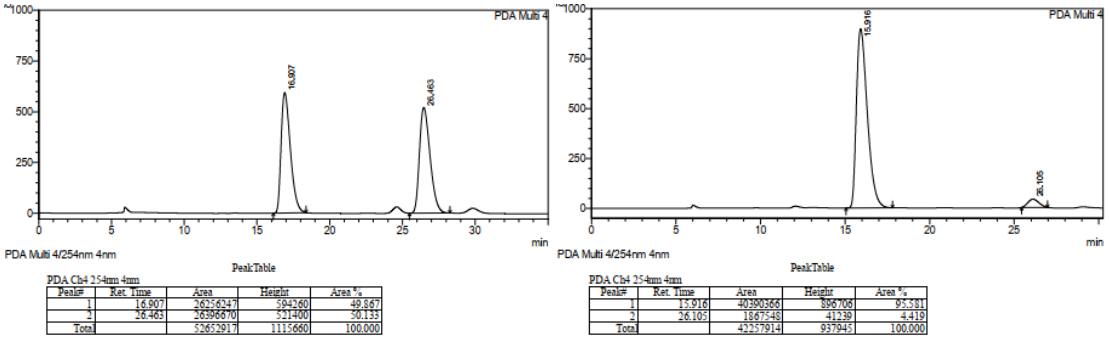
(R,E)-4,4,4-Trifluoro-3-((1-(4-methoxybenzyl)-2-oxoindolin-3-ylidene)amino)butane-1-sulfonyl fluoride (3d)



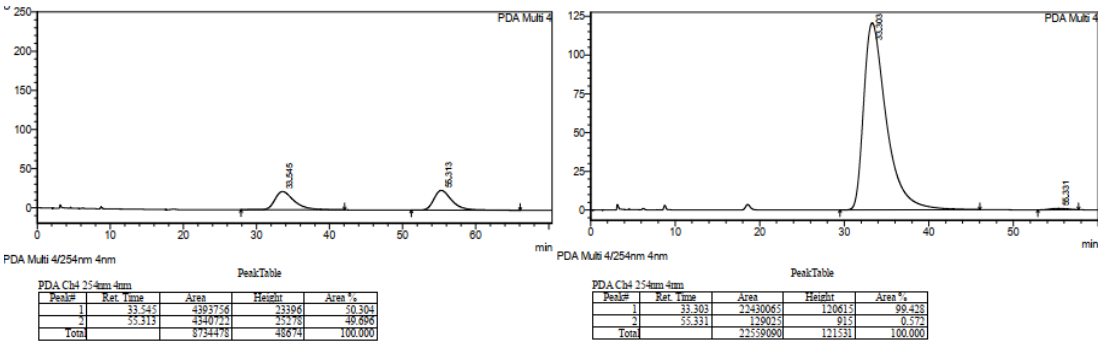
(R,E)-4,4,4-Trifluoro-3-((1-(4-nitrobenzyl)-2-oxoindolin-3-ylidene)amino)butane-1-sulfonyl fluoride (3e)



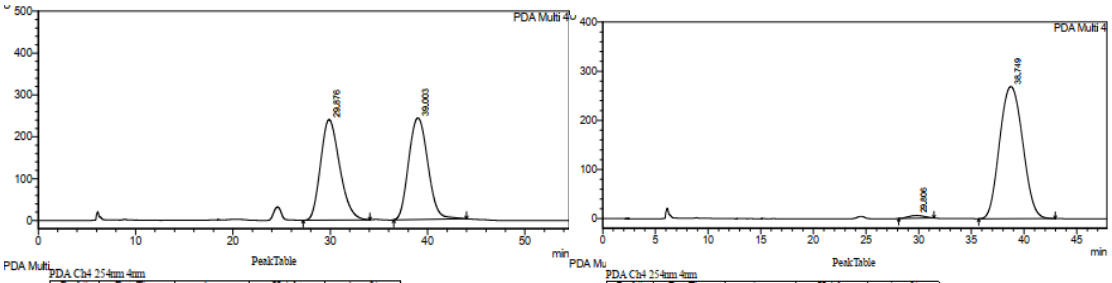
(R,E)-4,4,4-Trifluoro-3-((2-oxo-1-phenylindolin-3-ylidene)amino)butane-1-sulfonyl fluoride (3f)



(R,E)-4,4,4-Trifluoro-3-((1-(naphthalen-2-ylmethyl)-2-oxoindolin-3-ylidene)amino)butane-1-sulfonyl fluoride (3g)



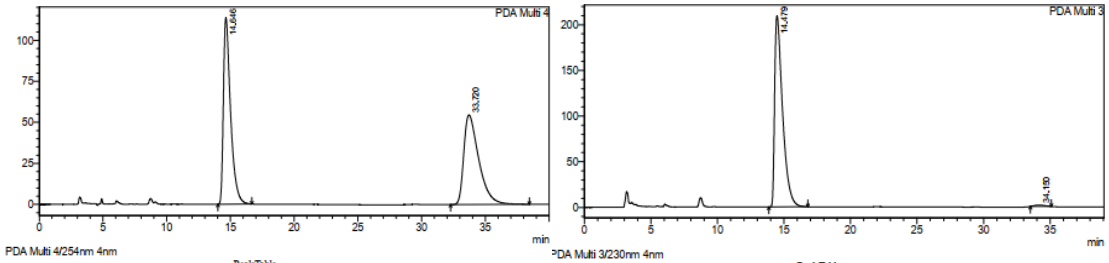
(R,E)-4,4,4-Trifluoro-3-((2-oxoindolin-3-ylidene)amino)butane-1-sulfonyl fluoride (3h)



Peak#	Ret. Time	Area	Height	Area %
1	29.876	32777202	240278	49.697
2	39.003	33177470	242591	50.303
Total		65954672	482869	100.000

Peak#	Ret. Time	Area	Height	Area %
1	29.806	598431	5567	1.439
2	38.749	41000387	269041	98.561
Total		41598818	274607	100.000

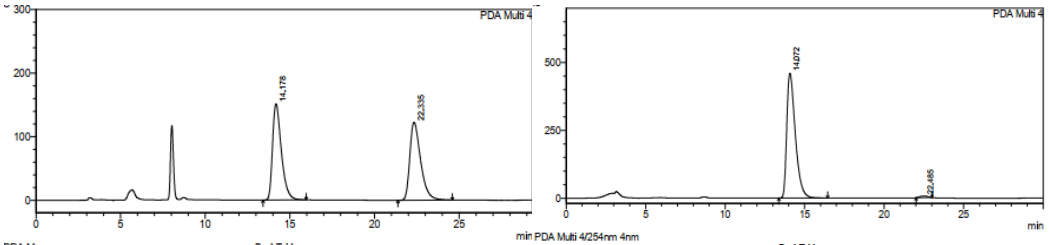
(R,E)-4,4,4-Trifluoro-3-((5-fluoro-1-methyl-2-oxoindolin-3-ylidene)amino)butane-1-sulfonyl fluoride (3i)



Peak#	Ret. Time	Area	Height	Area %
1	14.646	4450091	113653	49.944
2	33.720	4460045	54582	50.056
Total		8910136	168234	100.000

Peak#	Ret. Time	Area	Height	Area %
1	14.479	8667554	209203	99.073
2	34.150	81115	1492	0.927
Total		8748669	210695	100.000

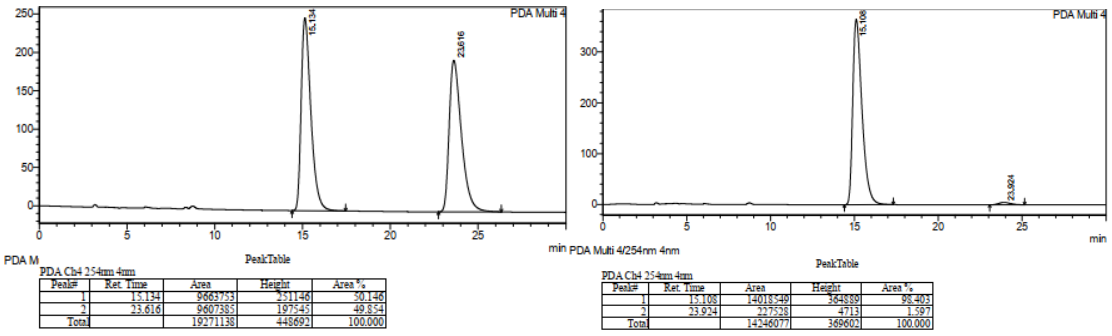
(R,E)-3-((5-Chloro-1-methyl-2-oxoindolin-3-ylidene)amino)-4,4,4-trifluorobutane-1-sulfonyl fluoride (3j)



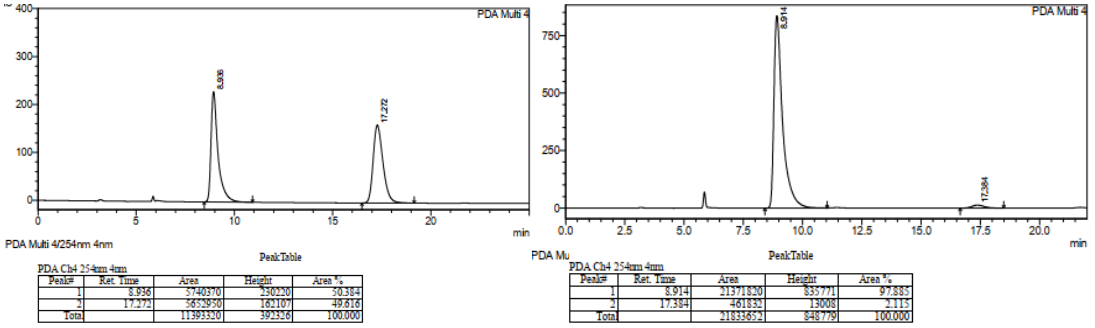
Peak#	Ret. Time	Area	Height	Area %
1	14.178	5503797	151531	50.165
2	22.335	5467583	122776	49.835
Total		10971380	274307	100.000

Peak#	Ret. Time	Area	Height	Area %
1	14.072	17218064	460868	98.809
2	22.485	207541	6065	1.191
Total		17425605	466933	100.000

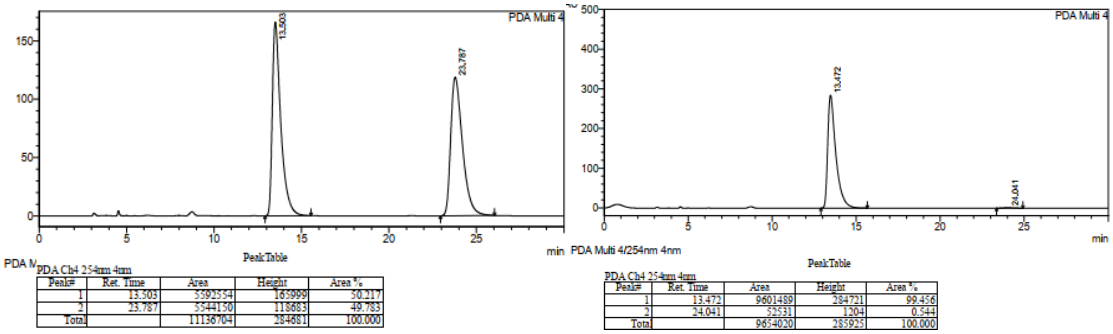
(R,E)-3-((5-Bromo-1-methyl-2-oxoindolin-3-ylidene)amino)-4,4,4-trifluorobutane-1-sulfonyl fluoride (3k)



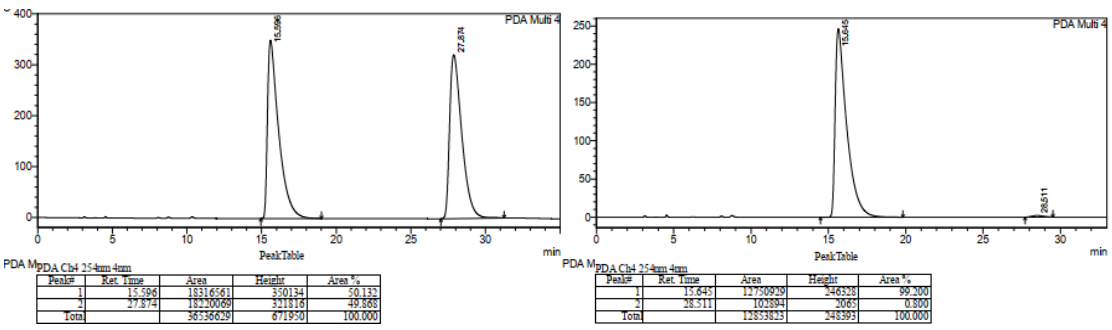
(R,E)-3-((1,5-Dimethyl-2-oxoindolin-3-ylidene)amino)-4,4,4-trifluorobutane-1-sulfonyl fluoride (3l)



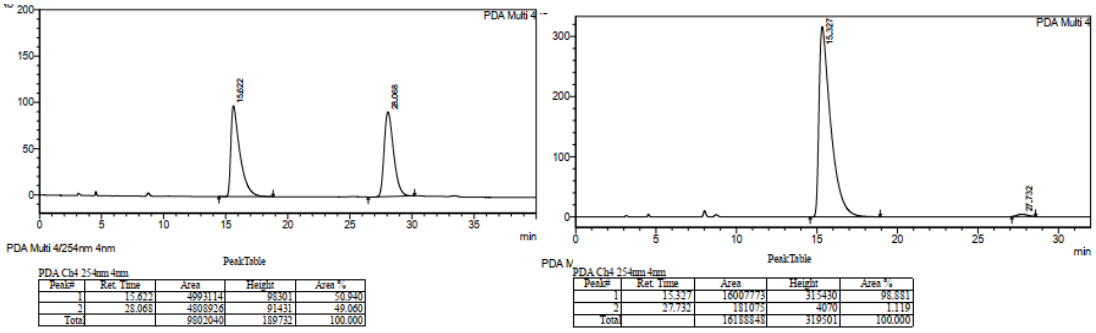
(R,E)-4,4,4-Trifluoro-3-((5-methoxy-1-methyl-2-oxoindolin-3-ylidene)amino)butane-1-sulfonyl fluoride (3m)



(R,E)-4,4,4-Trifluoro-3-((6-fluoro-1-methyl-2-oxoindolin-3-ylidene)amino)butane-1-sulfonyl fluoride (3n)



(R,E)-3-((6-Chloro-1-methyl-2-oxoindolin-3-ylidene)amino)-4,4,4-trifluorobutane-1-sulfonyl fluoride (3o)



PeakTable

PDA Ch4 254nm 4nm

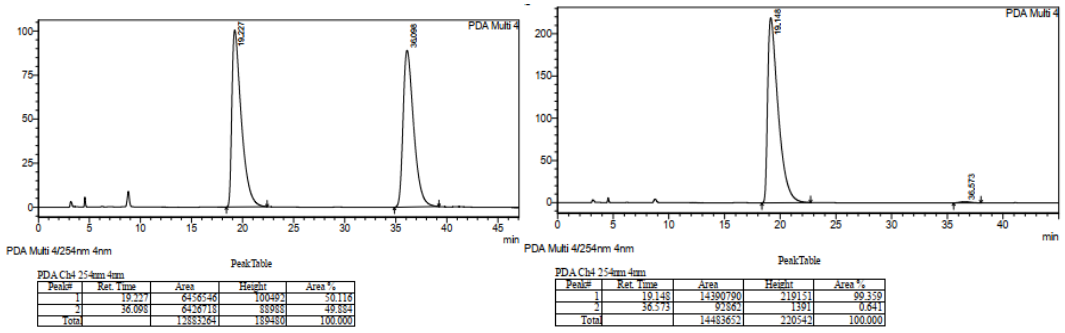
Peak#	Ret. Time	Area	Height	Area %
1	15.622	4993114	98301	50.940
2	28.068	4808926	91431	49.060
Total		9802040	189732	100.000

PeakTable

PDA Ch4 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	15.327	16007773	315430	98.881
2	27.732	181075	4070	1.119
Total		16188848	319501	100.000

(R,E)-3-((6-Bromo-1-methyl-2-oxoindolin-3-ylidene)amino)-4,4,4-trifluorobutane-1-sulfonyl fluoride (3p)



PeakTable

PDA Ch4 254nm 4nm

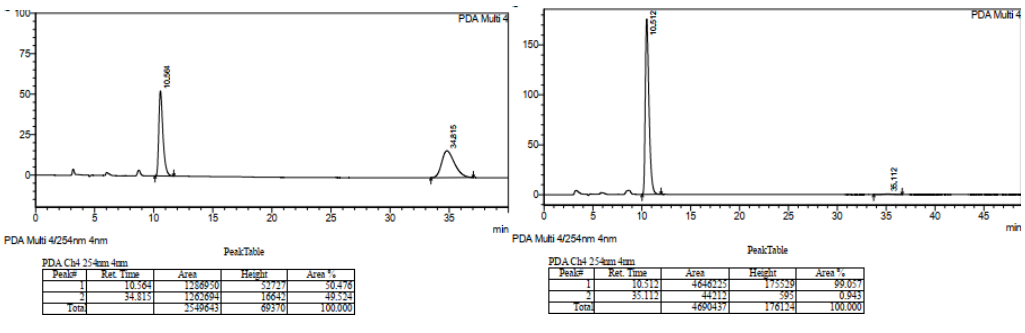
Peak#	Ret. Time	Area	Height	Area %
1	19.227	6456546	100492	50.116
2	36.098	6426718	88988	49.884
Total		12883264	189480	100.000

PeakTable

PDA Ch4 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	19.148	14390790	219151	99.359
2	36.573	92862	1391	0.641
Total		14483652	220542	100.000

(R,E)-4,4,4-Trifluoro-3-((7-fluoro-1-methyl-2-oxoindolin-3-ylidene)amino)butane-1-sulfonyl fluoride (3q)



PeakTable

PDA Ch4 254nm 4nm

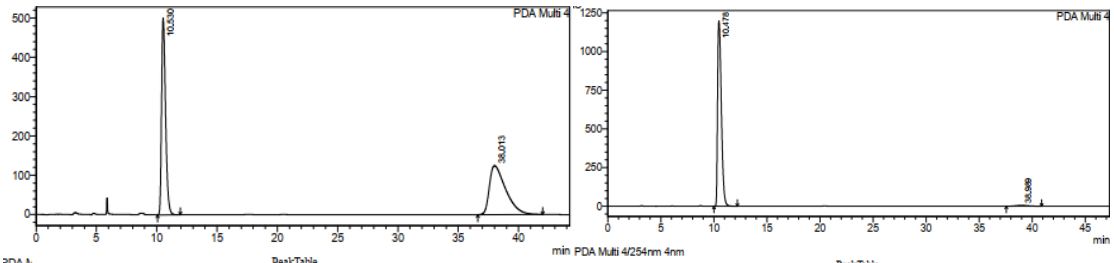
Peak#	Ret. Time	Area	Height	Area %
1	10.564	1286950	52737	50.476
2	34.815	1262694	16642	49.524
Total		2549643	69379	100.000

PeakTable

PDA Ch4 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	10.512	4646225	175529	99.057
2	35.112	44212	595	0.943
Total		4690437	176124	100.000

(R,E)-3-((7-Chloro-1-methyl-2-oxoindolin-3-ylidene)amino)-4,4,4-trifluorobutane-1-sulfonyl fluoride (3r)



PeakTable

PDA Ch4 254nm 4nm

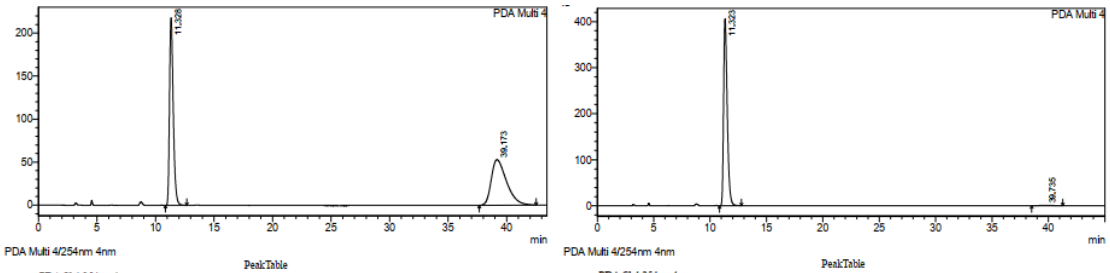
Peak#	Ret. Time	Area	Height	Area %
1	10.530	11545622	500414	49.720
2	38.013	11675433	124488	50.280
Total		23221055	624902	100.000

PeakTable

PDA Ch4 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	10.478	29337810	1196557	98.424
2	38.989	469845	3364	1.576
Total		29807655	1201921	100.000

(R,E)-3-((7-Bromo-1-methyl-2-oxoindolin-3-ylidene)amino)-4,4,4-trifluorobutane-1-sulfonyl fluoride (3s)



PeakTable

PDA Ch4 254nm 4nm

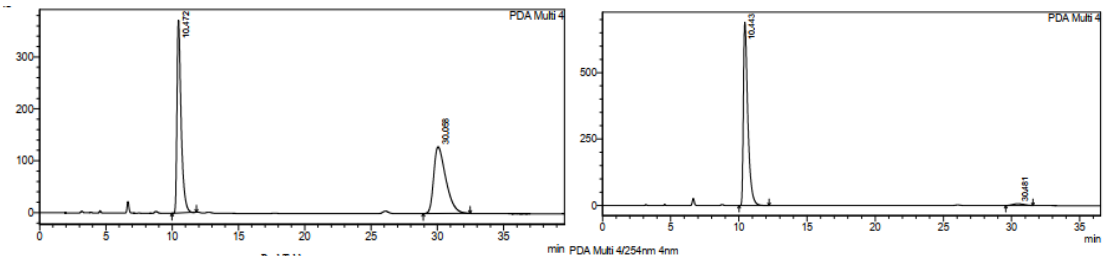
Peak#	Ret. Time	Area	Height	Area %
1	11.328	4867966	218131	50.342
2	39.173	4801855	53032	49.658
Total		9669821	271163	100.000

PeakTable

PDA Ch4 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	11.323	9126996	405402	99.122
2	39.735	80883	996	0.878
Total		9207879	406399	100.000

(R,E)-3-((1,7-Dimethyl-2-oxoindolin-3-ylidene)amino)-4,4,4-trifluorobutane-1-sulfonyl fluoride (3t)



PeakTable

PDA Ch4 254nm 4nm

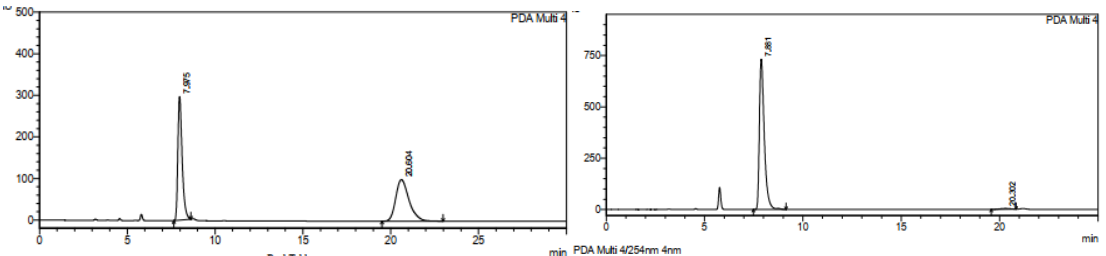
Peak#	Ret. Time	Area	Height	Area %
1	10.472	8073459	371008	49.731
2	30.058	8160783	128657	50.269
Total		16234242	489665	100.000

PeakTable

PDA Ch4 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	10.443	15649665	688596	97.678
2	30.481	372078	6530	2.322
Total		16021743	695126	100.000

(R,E)-4,4,4-Trifluoro-3-((1,5,7-trimethyl-2-oxoindolin-3-ylidene)amino)butane-1-sulfonyl fluoride (3u)



PeakTable

PDA Ch4 254nm 4nm

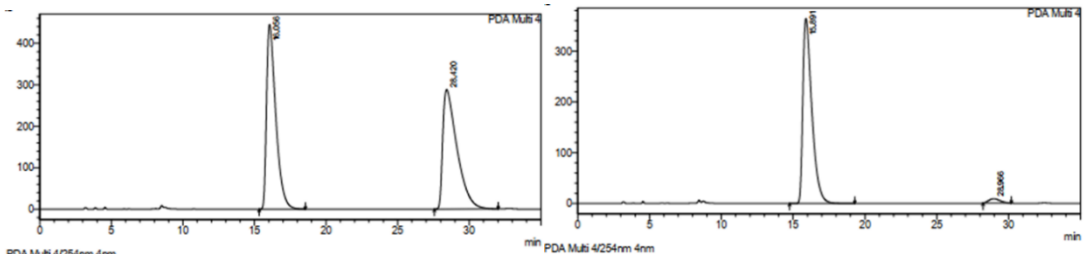
Peak#	Ret. Time	Area	Height	Area %
1	7.975	5062780	297564	49.012
2	20.604	5266972	100077	50.988
Total		10329752	397641	100.000

PeakTable

PDA Ch4 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	7.881	12691461	732445	98.746
2	20.302	161207	4194	1.254
Total		12852668	736639	100.000

(R,E)-3-((5,6-Difluoro-1-methyl-2-oxoindolin-3-ylidene)amino)-4,4,4-trifluorobutane-1-sulfonyl fluoride (3v)



PeakTable

PDA Ch4 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	16.056	19948221	445368	49.985
2	28.420	19960548	288519	50.015
Total		39908769	733905	100.000

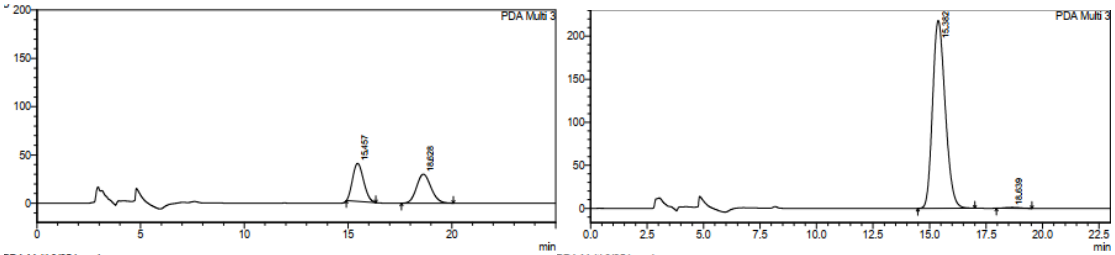
PeakTable

PDA Ch4 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	16.691	15879215	364170	97.082
2	28.966	477286	8387	2.918
Total		16356501	372757	100.000

2. HPLC spectra of products 4 and 5

(R)-3-(Trifluoromethyl)isothiazolidine 1,1-dioxide (4)



PeakTable

PDA Ch3 254nm 4nm

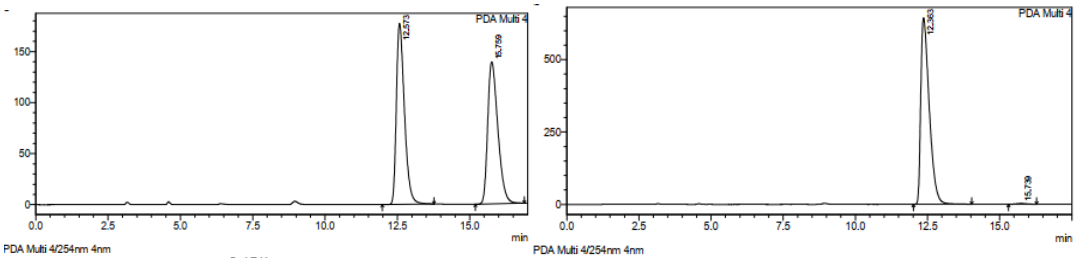
Peak#	Ret. Time	Area	Height	Area %
1	15.457	1442336	39104	49.845
2	18.628	1451281	30083	50.155
Total		2893617	69276	100.000

PeakTable

PDA Ch3 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	15.382	8510474	218157	99.432
2	18.639	48580	1072	0.568
Total		8559054	219229	100.000

(R)-4,4,4-Trifluoro-3-(((S)-1-methyl-2-oxoindolin-3-yl)amino)butane-1-sulfonyl fluoride (5)



PeakTable

PDA Ch4 254nm 4nm

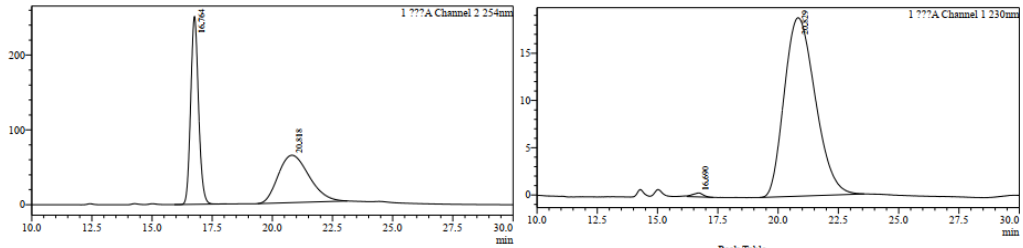
Peak#	Ret. Time	Area	Height	Area %
1	12.573	3442383	177209	50.341
2	15.759	3395794	139150	49.659
Total		6838177	316359	100.000

PeakTable

PDA Ch4 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	12.363	13190443	643908	99.546
2	15.739	60107	2579	0.454
Total		13250550	646487	100.000

(S)-3-((R)-1,1-dioxido-3-(trifluoromethyl)isothiazolidin-2-yl)-1-methylindolin-2-one (6)



Peak Table

???A Channel 1 230nm

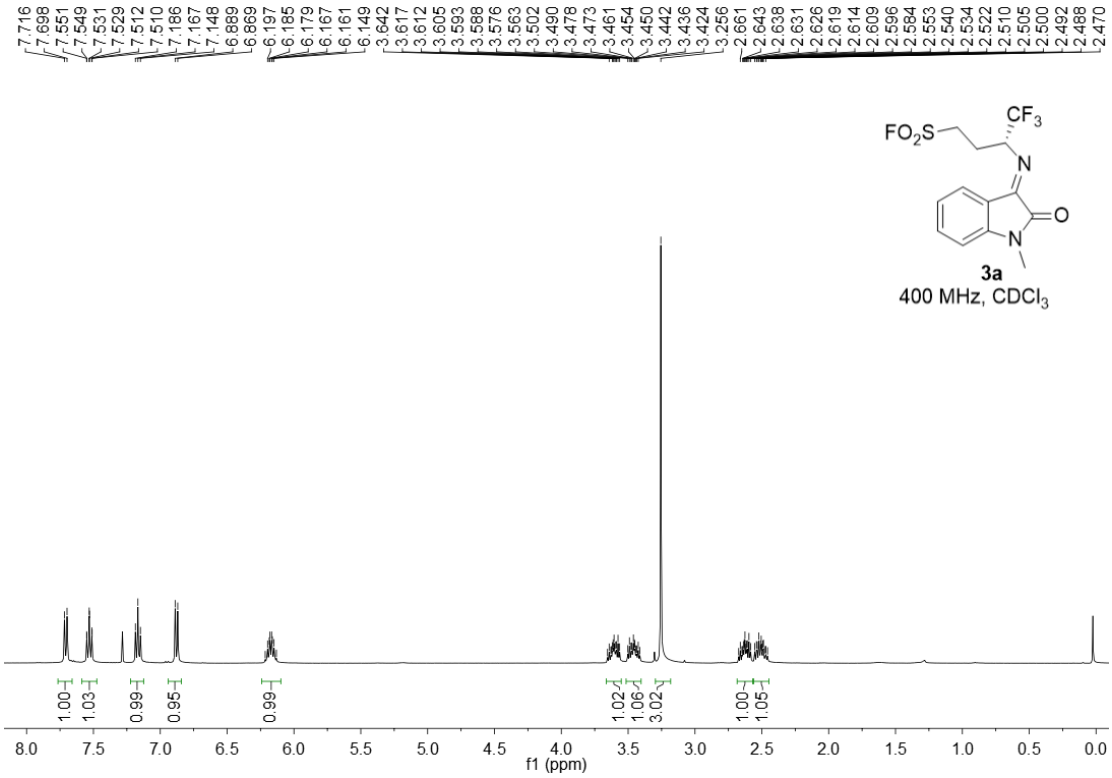
Peak#	Ret. Time	Area	Height	Area%
1	16.762	3840627	169166	49.846
2	20.814	3864403	43151	50.154
Total		7705030	212318	100.000

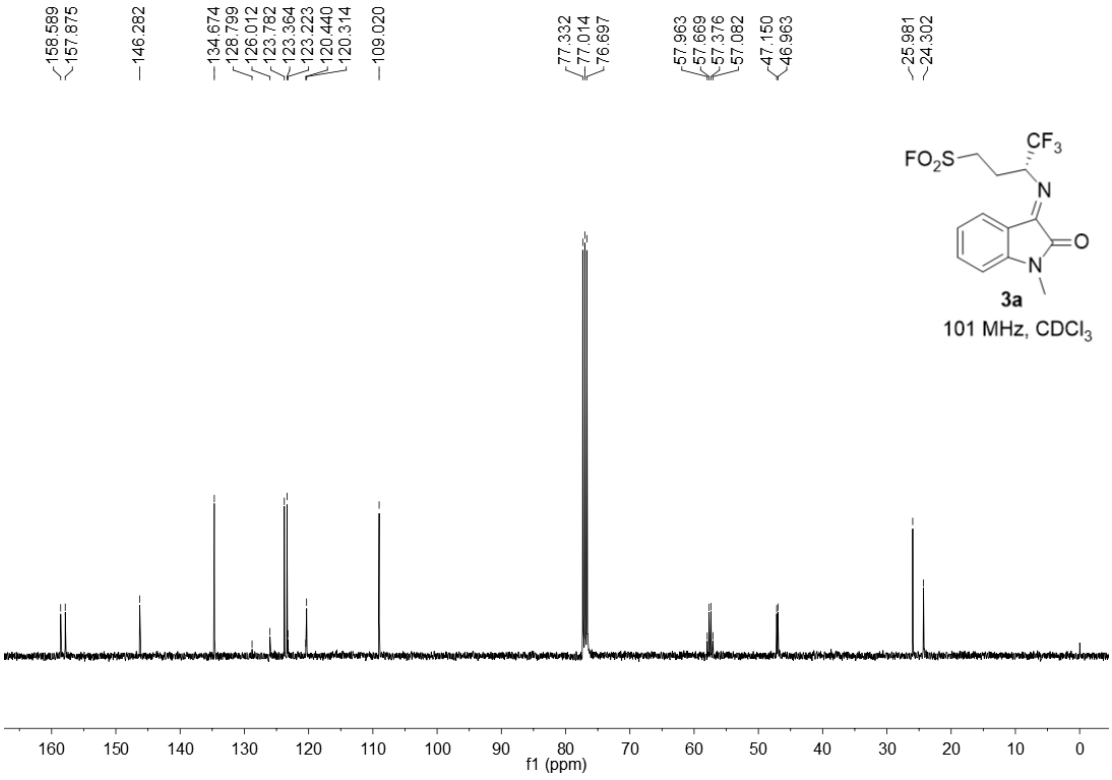
Peak Table

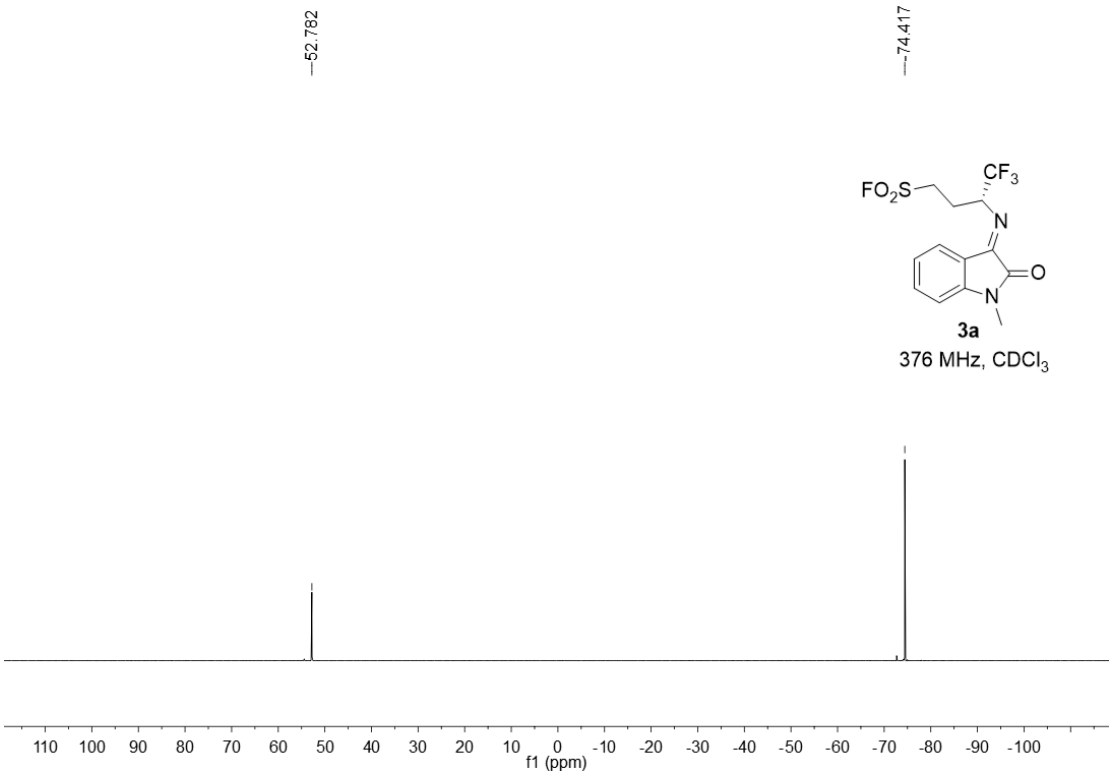
???A Channel 1 230nm

Peak#	Ret. Time	Area	Height	Area%
1	16.690	12731	422	0.747
2	20.829	1691155	18876	99.253
Total		1703887	19298	100.000

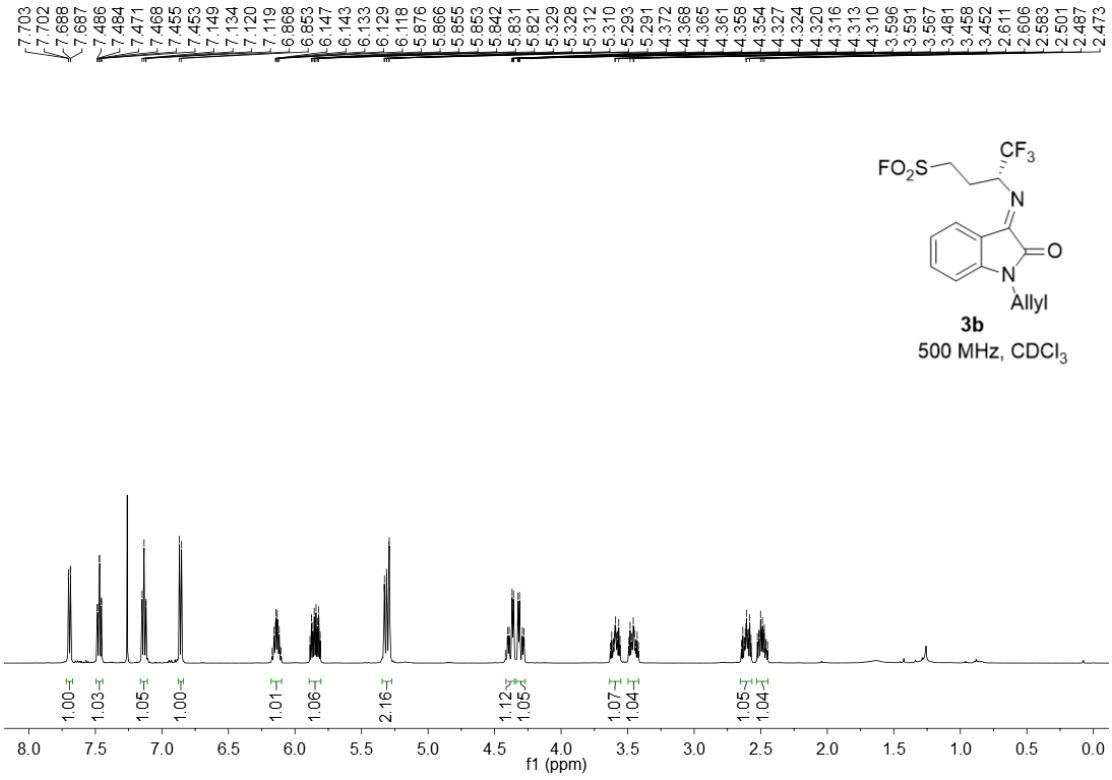
3. NMR spectra of products

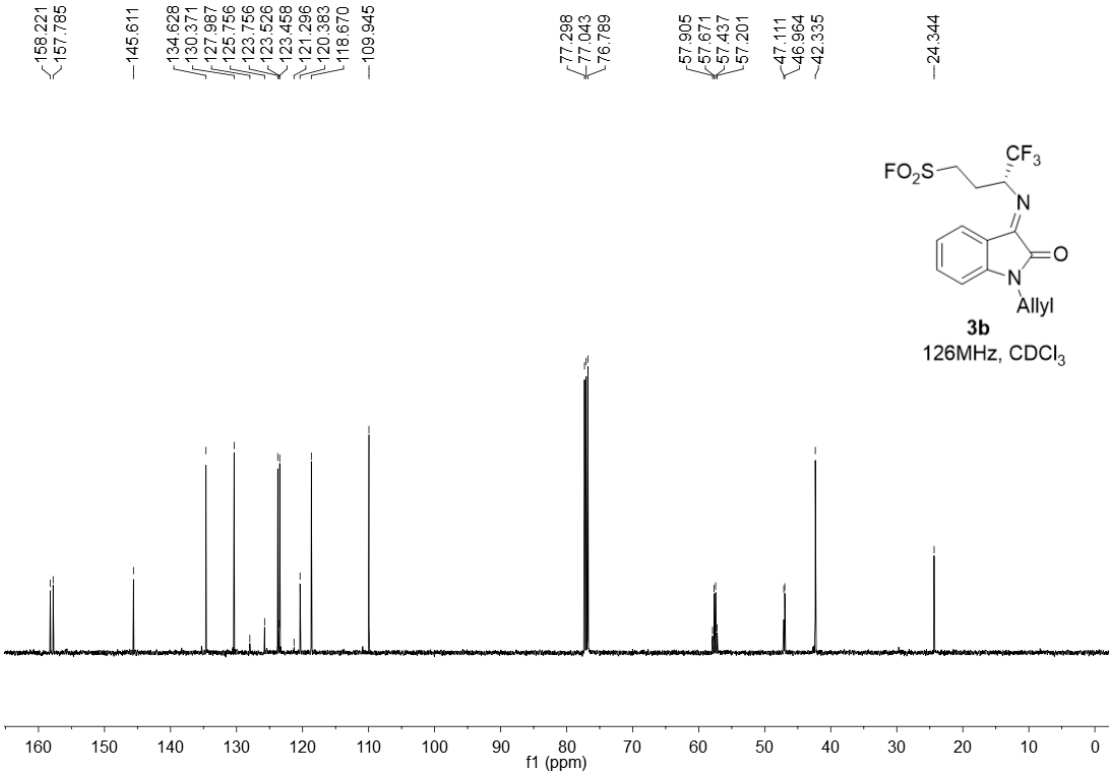


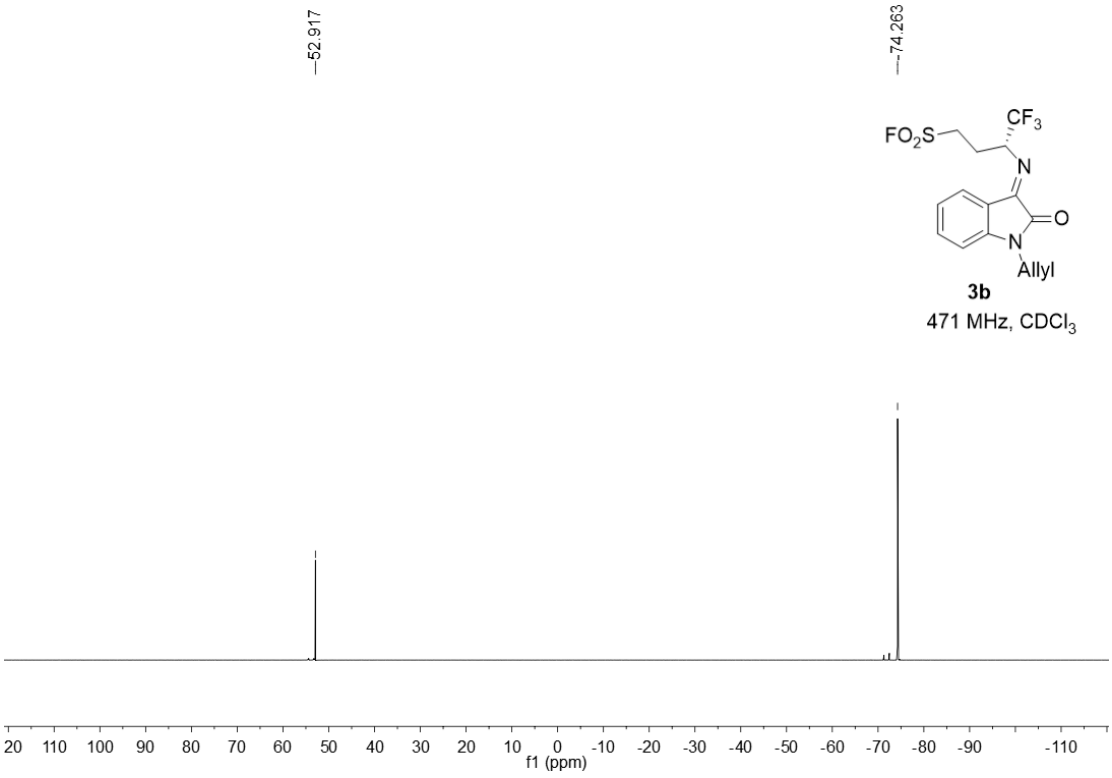




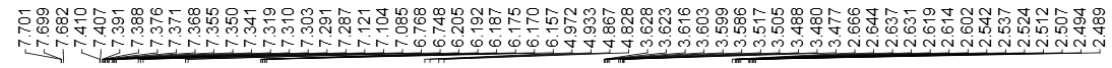
^{1}H, $^{13}C\{1H\}$ and $^{19}F\{^{1}H, ^{13}C\}$ NMR spectra of **3a**

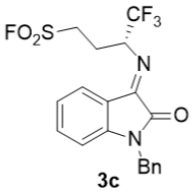






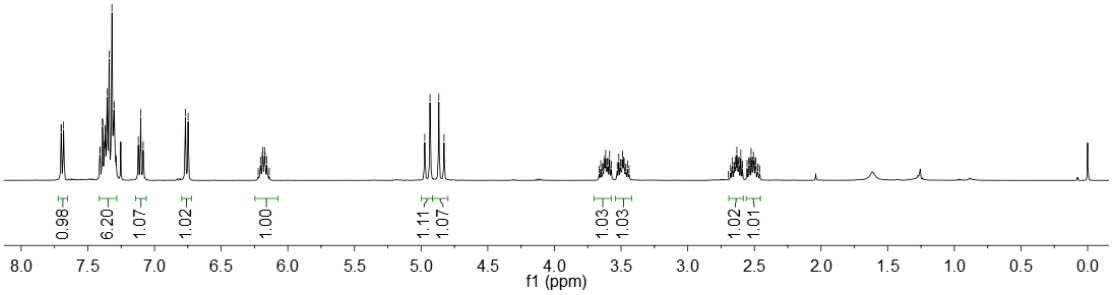
^{1}H, ^{13}C{1H} and ^{19}F{^{1}H, ^{13}C} NMR spectra of **3b**

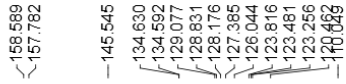


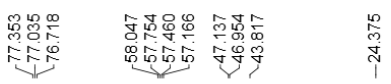


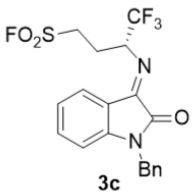
3c

400 MHz, $CDCl_3$



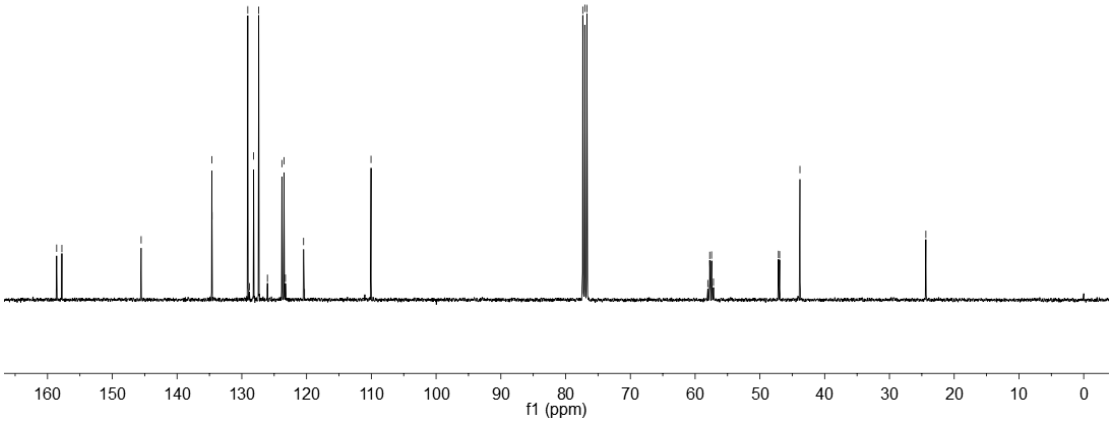


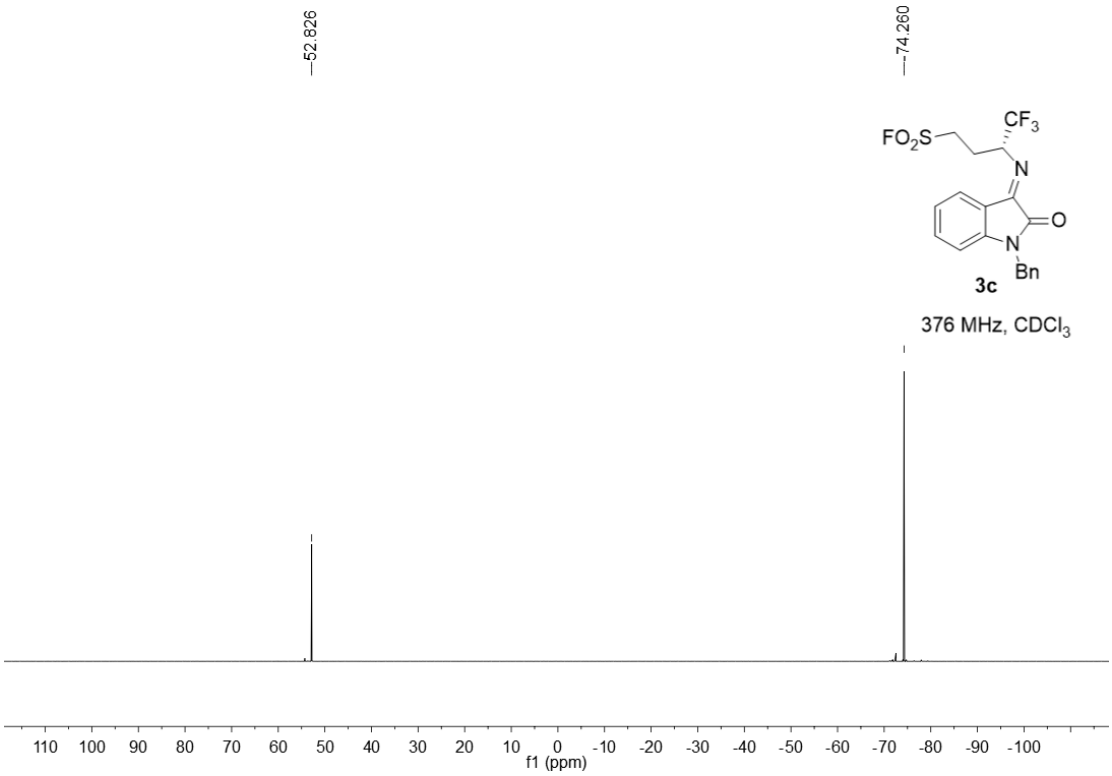




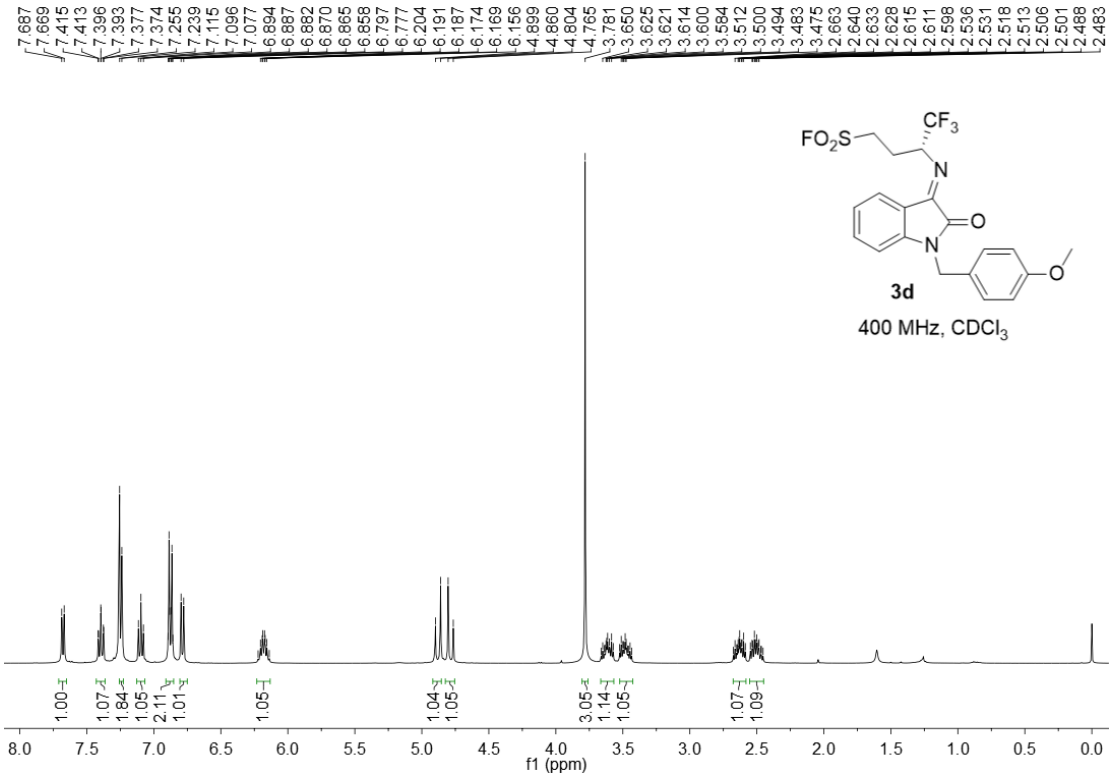
3c

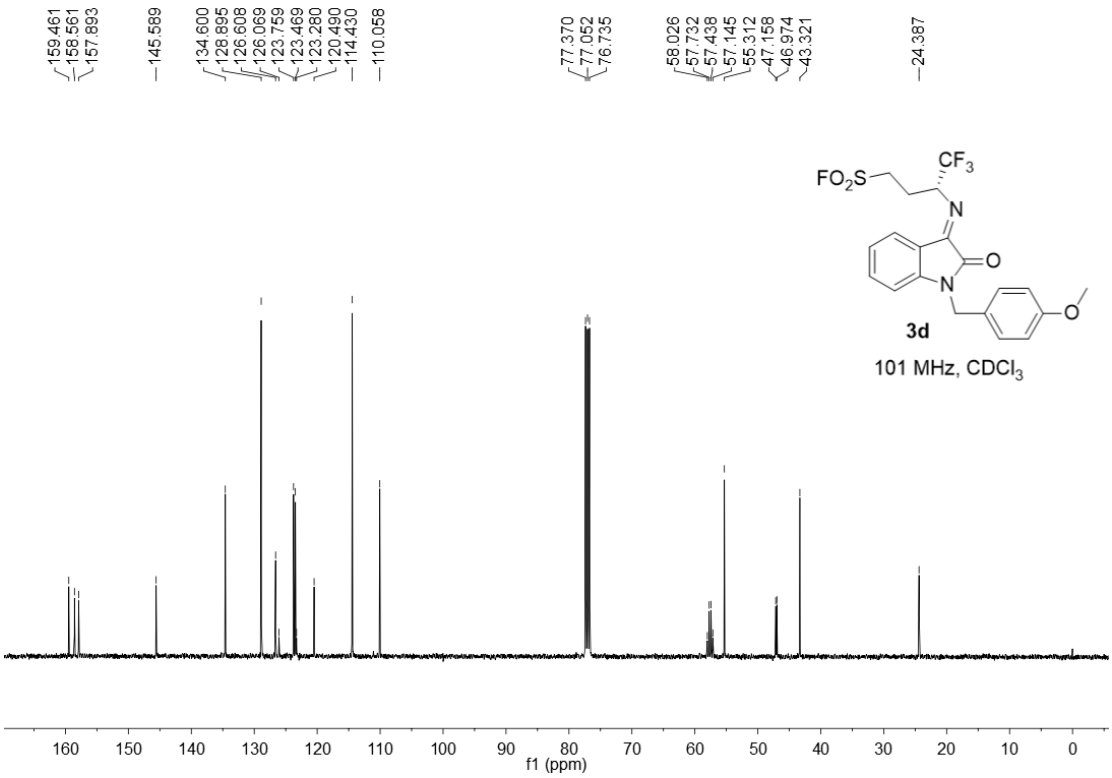
101 MHz, $CDCl_3$

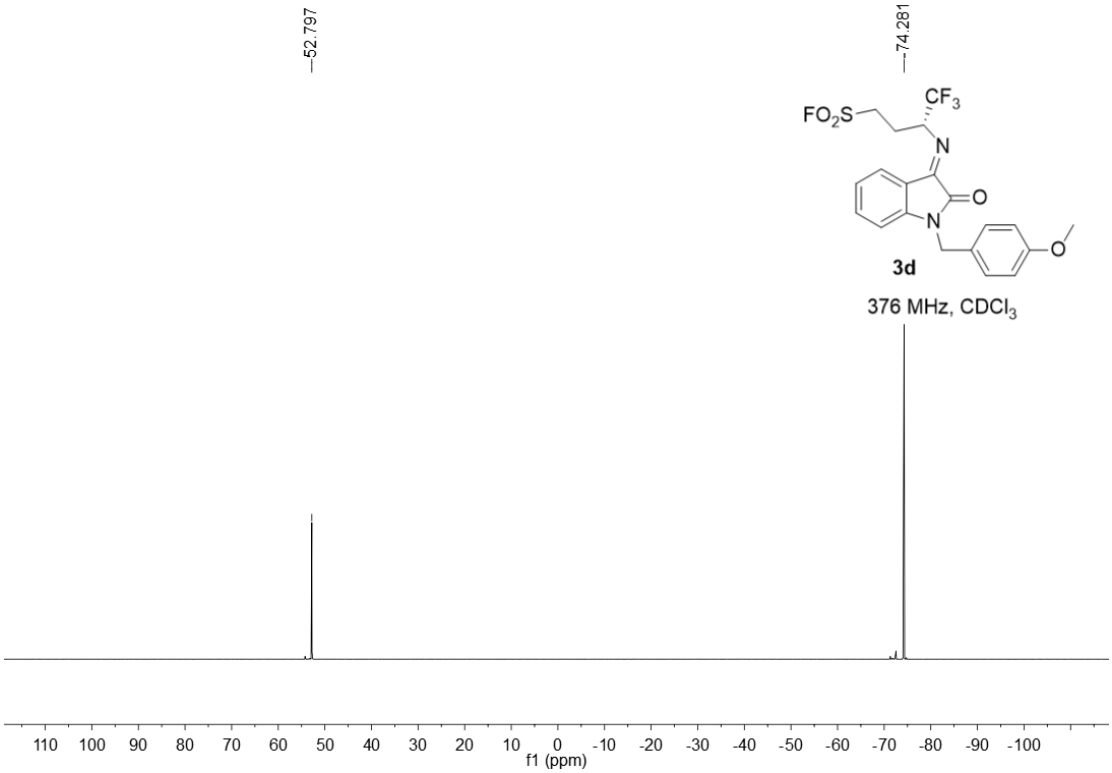




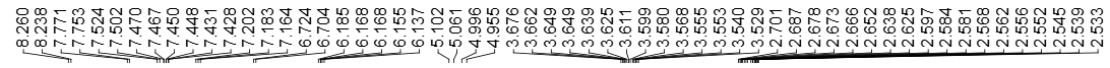
^{1}H, $^{13}C\{1H\}$ and $^{19}F\{^{1}H, ^{13}C\}$ NMR spectra of **3c**

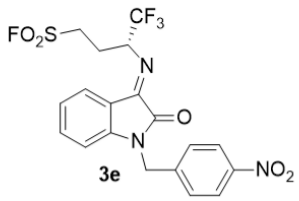




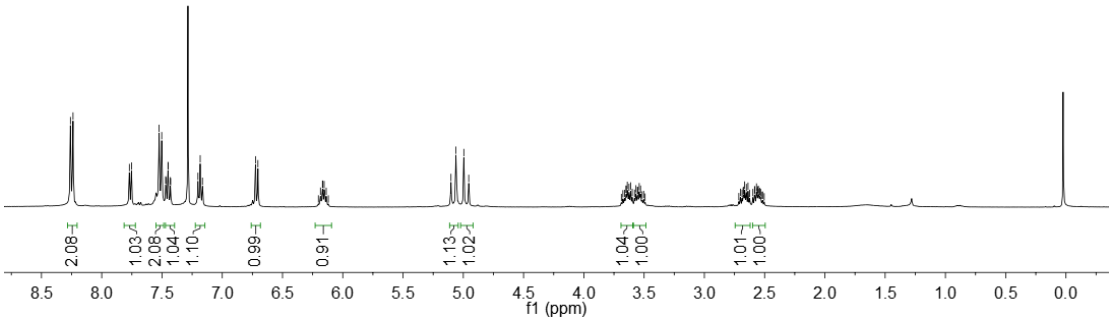


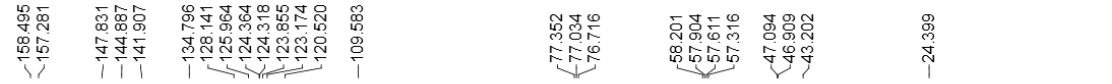
^{1}H, $^{13}C\{1H\}$ and $^{19}F\{^{1}H, ^{13}C\}$ NMR spectra of **3d**

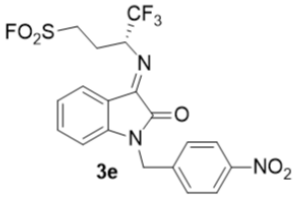




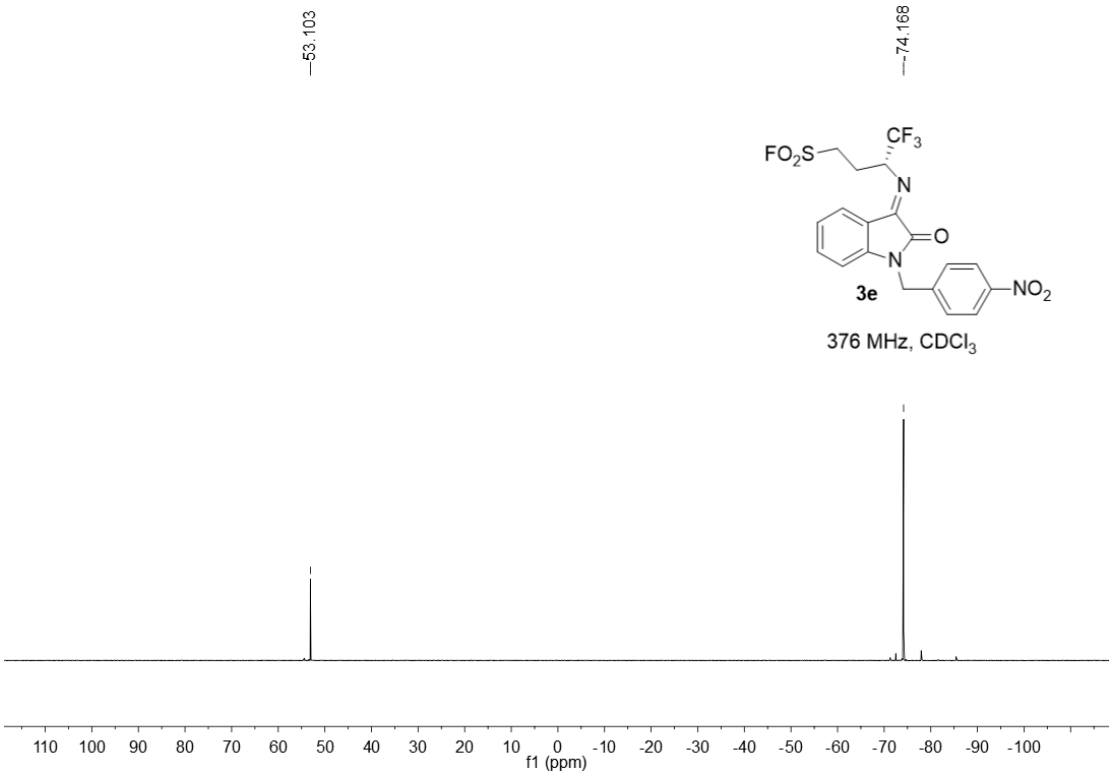
400 MHz, $CDCl_3$



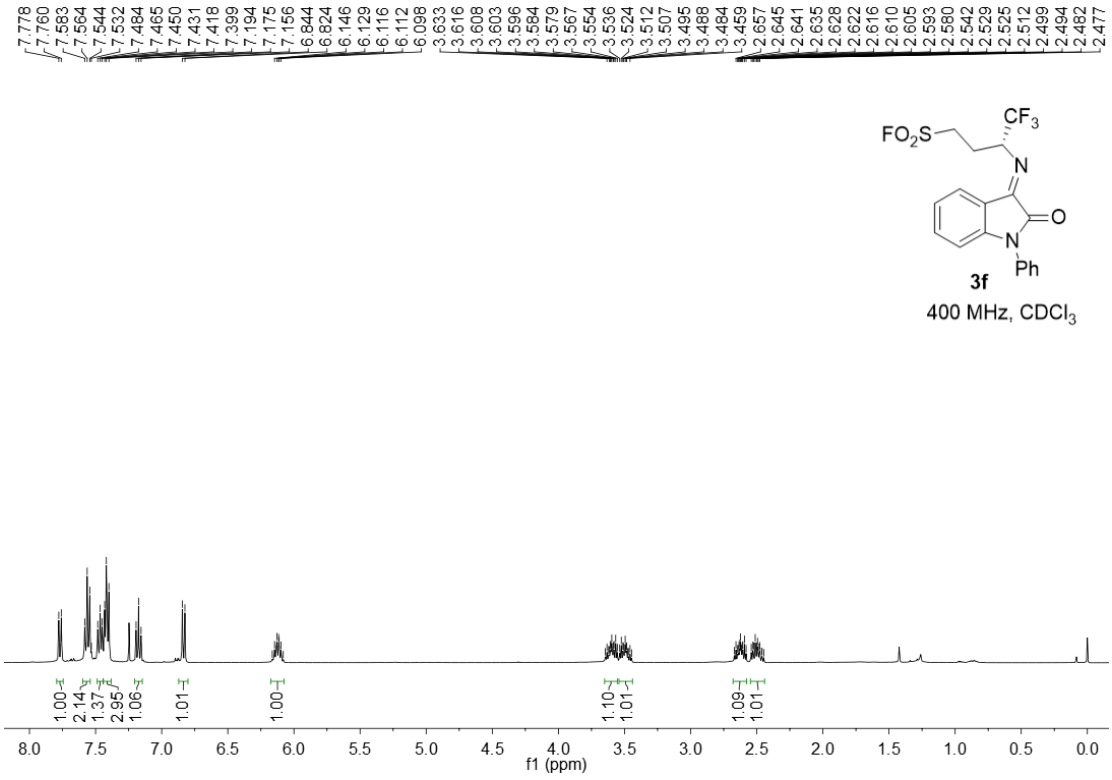


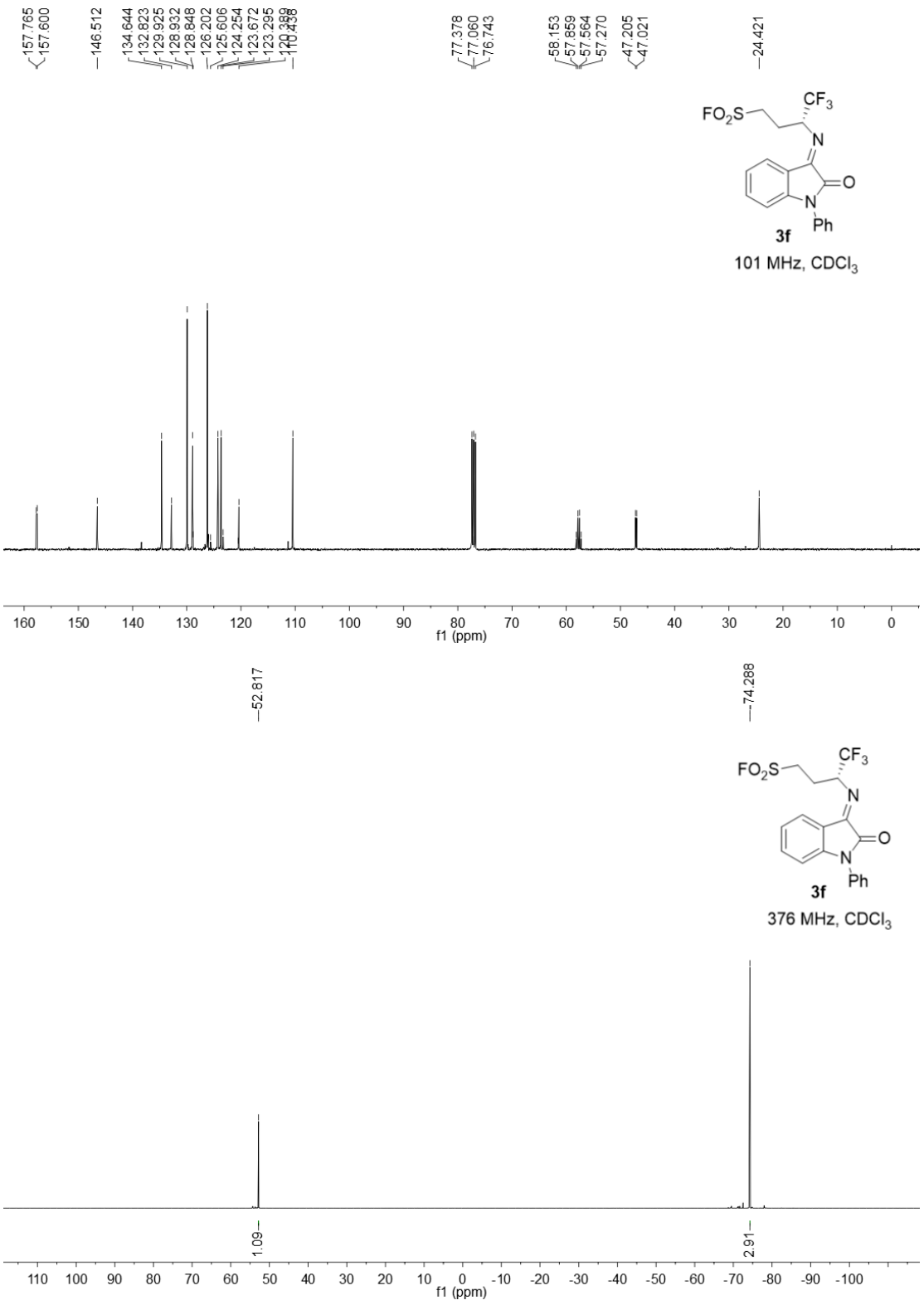


101 MHz, $CDCl_3$

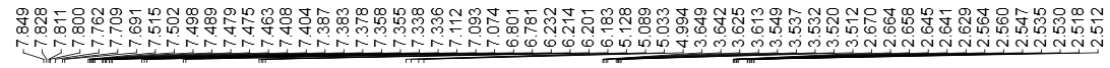


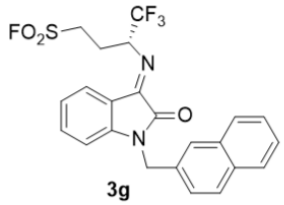
^{1}H, $^{13}C\{1H\}$ and $^{19}F\{^{1}H, ^{13}C\}$ NMR spectra of **3e**





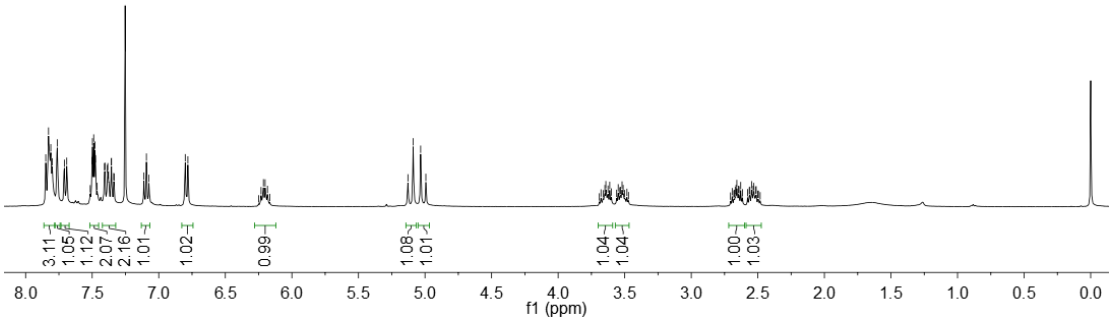
^{1}H, ^{13}C{1H} and ^{19}F{^{1}H, ^{13}C} NMR spectra of **3f**

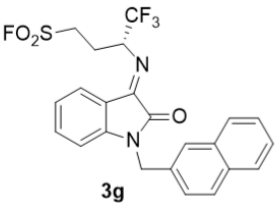




3g

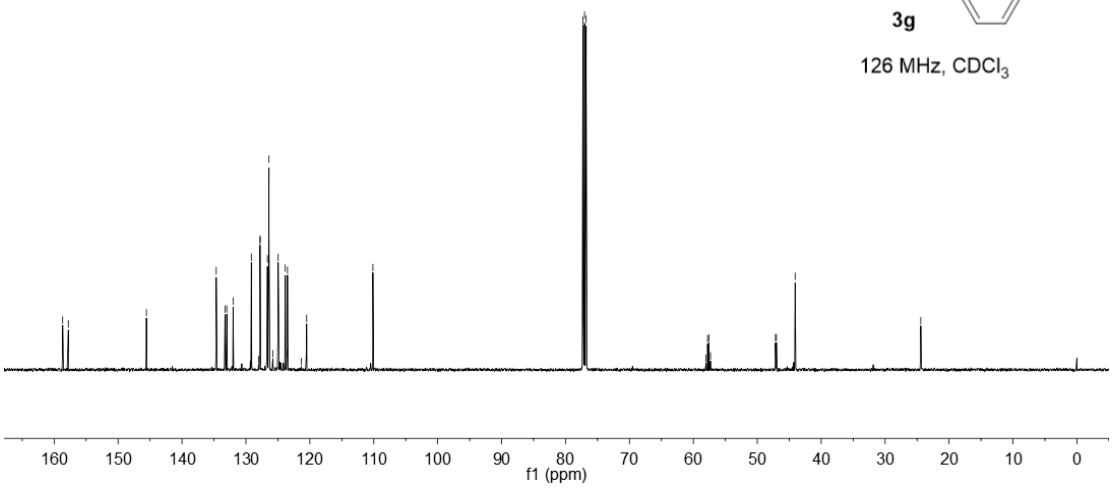
400 MHz, $CDCl_3$

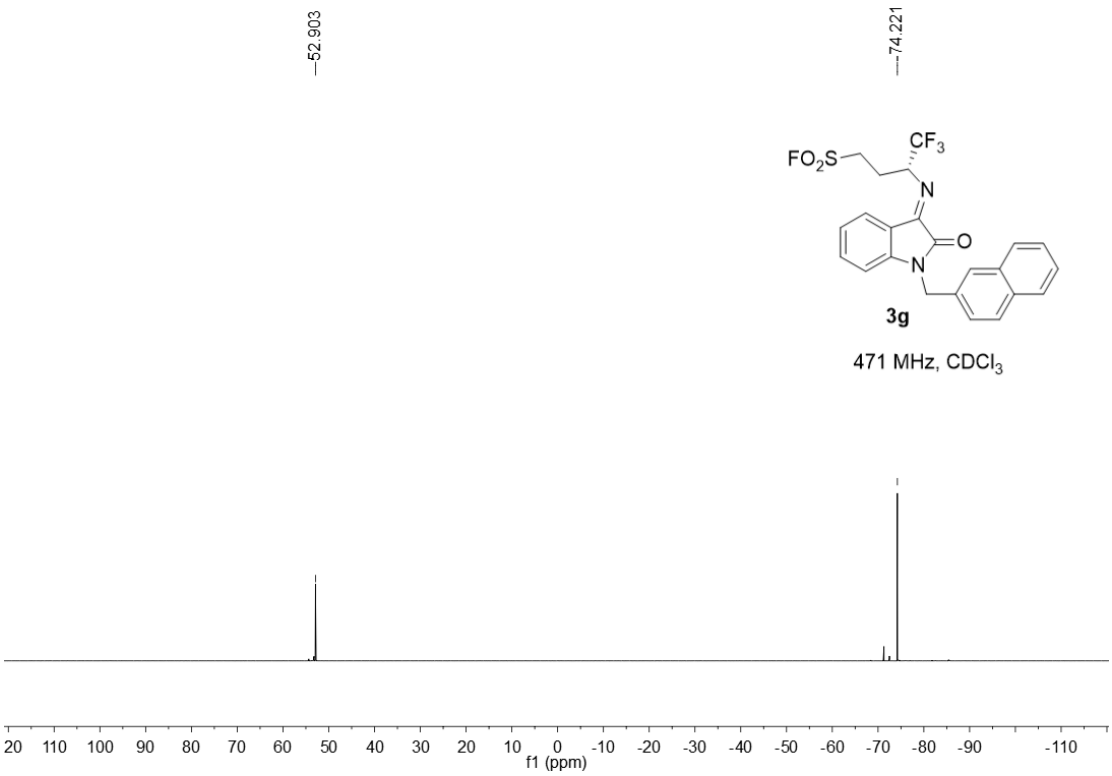




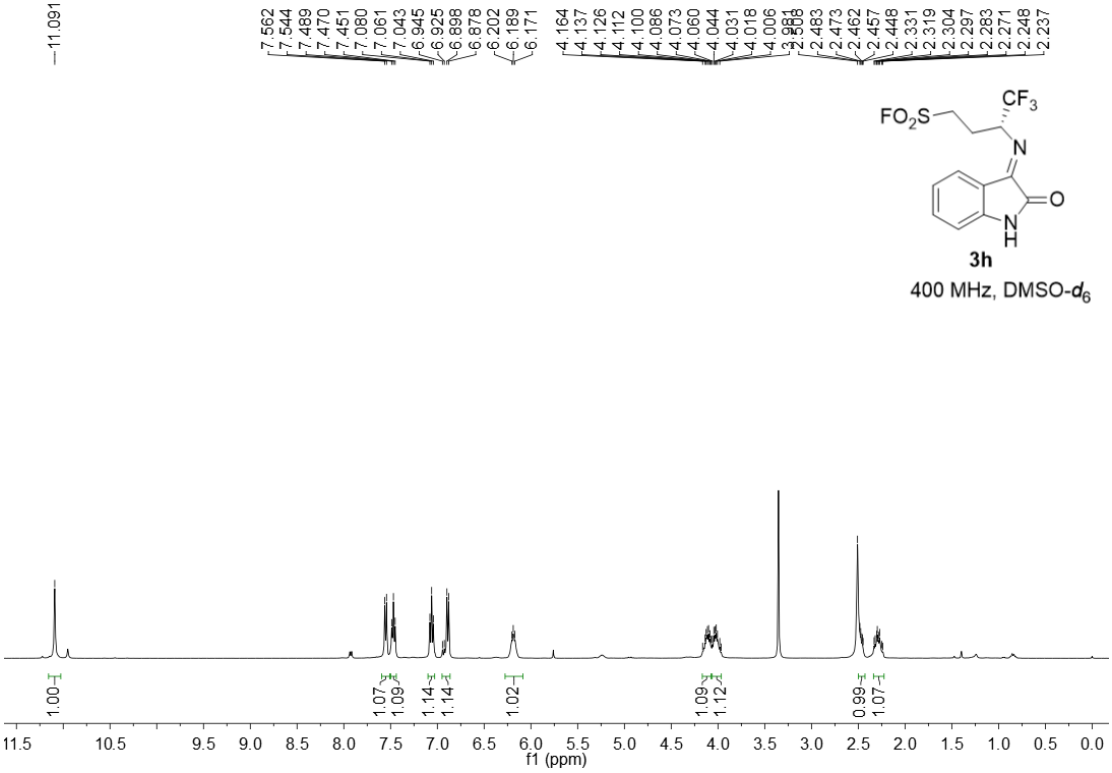
3g

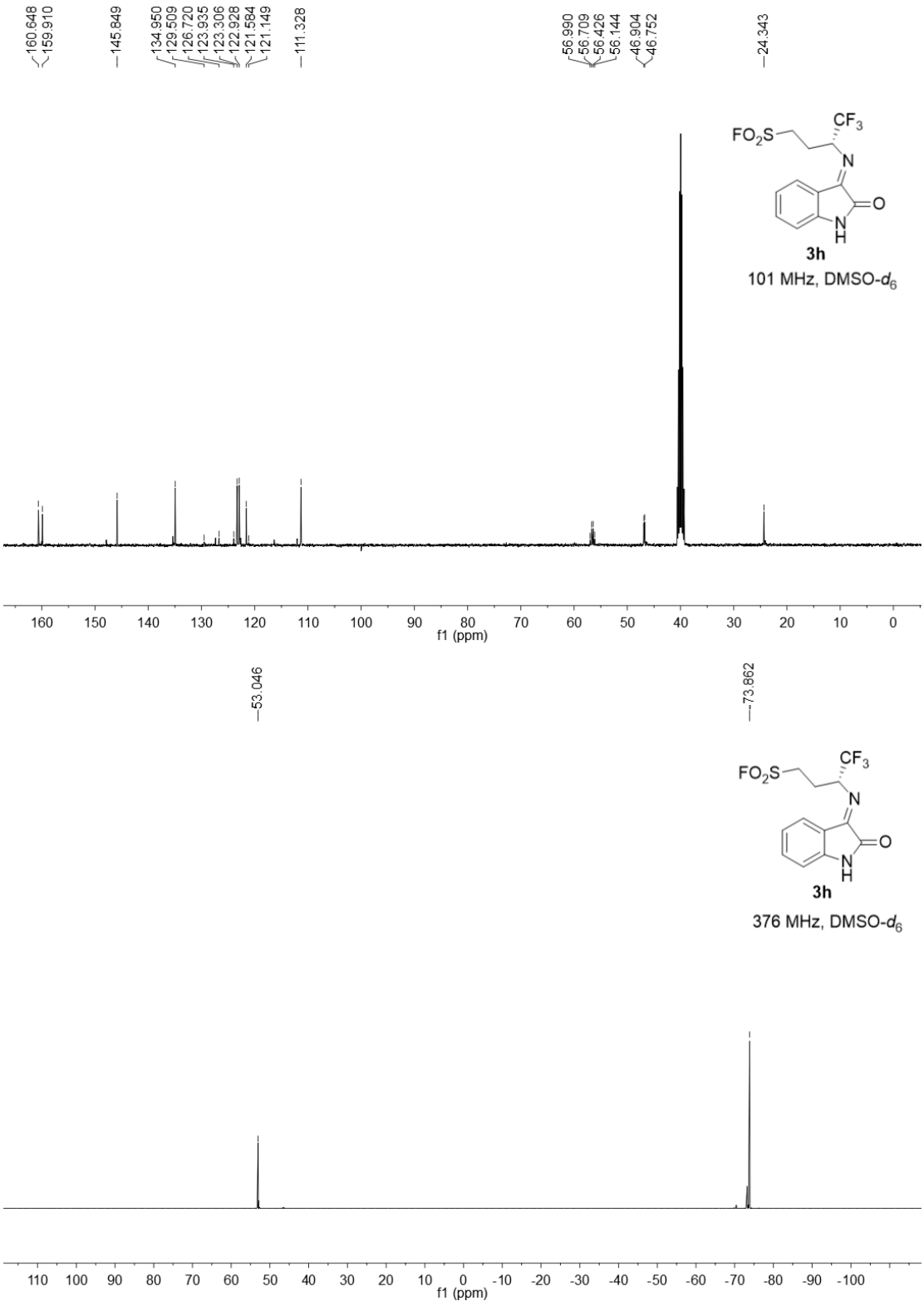
126 MHz, $CDCl_3$



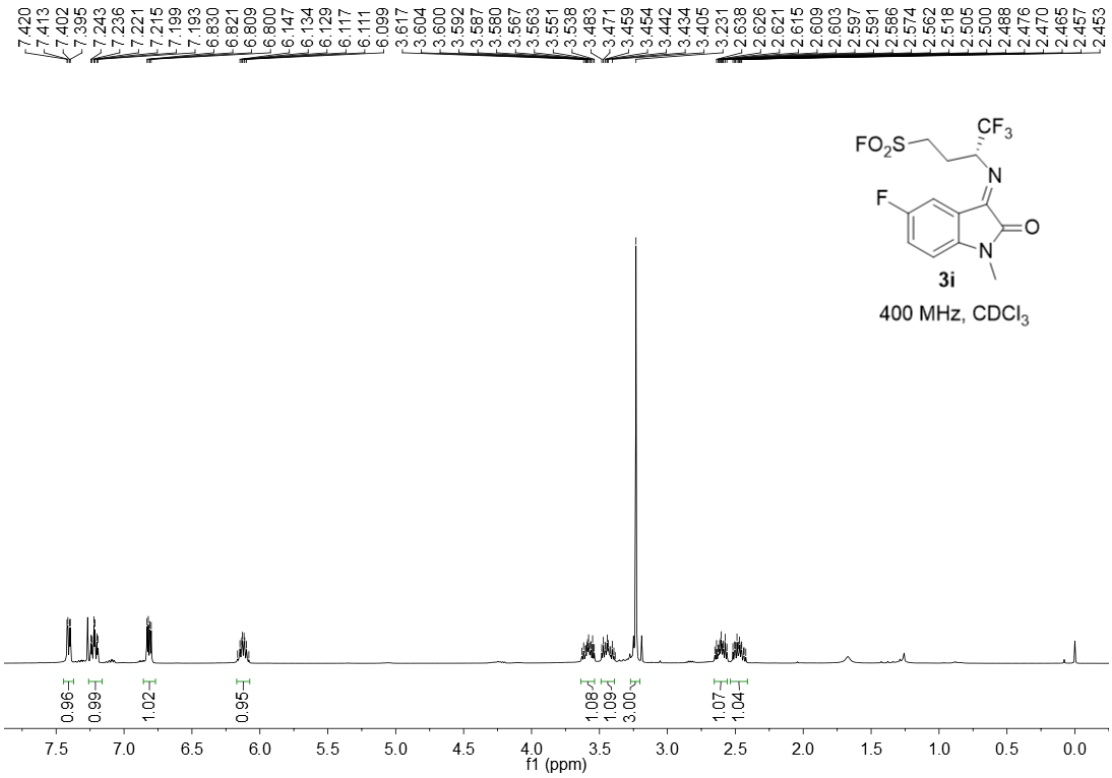


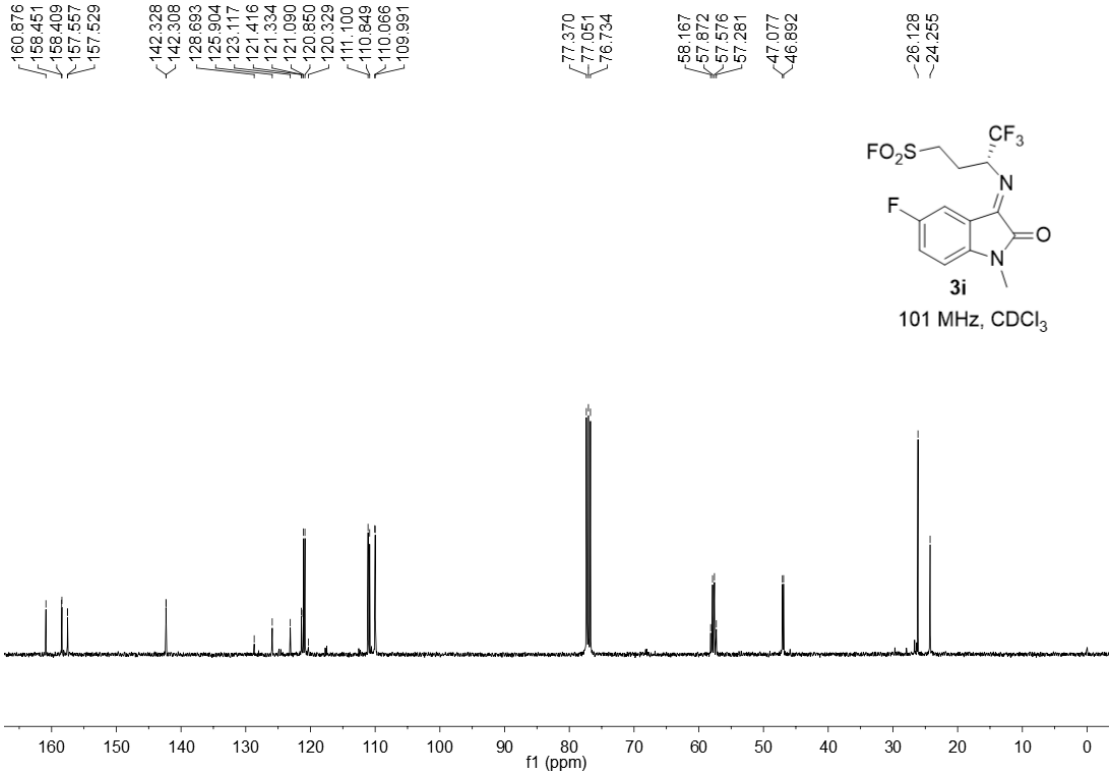
^{1}H, $^{13}C\{1H\}$ and $^{19}F\{^{1}H, ^{13}C\}$ NMR spectra of **3g**

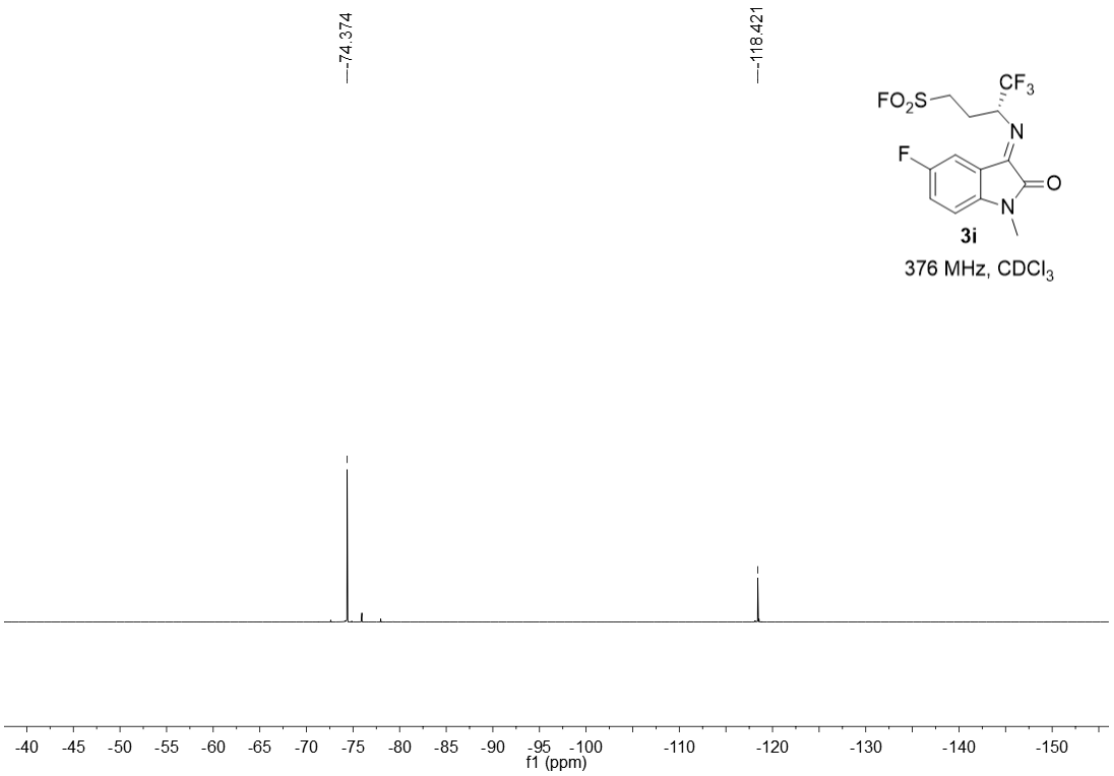


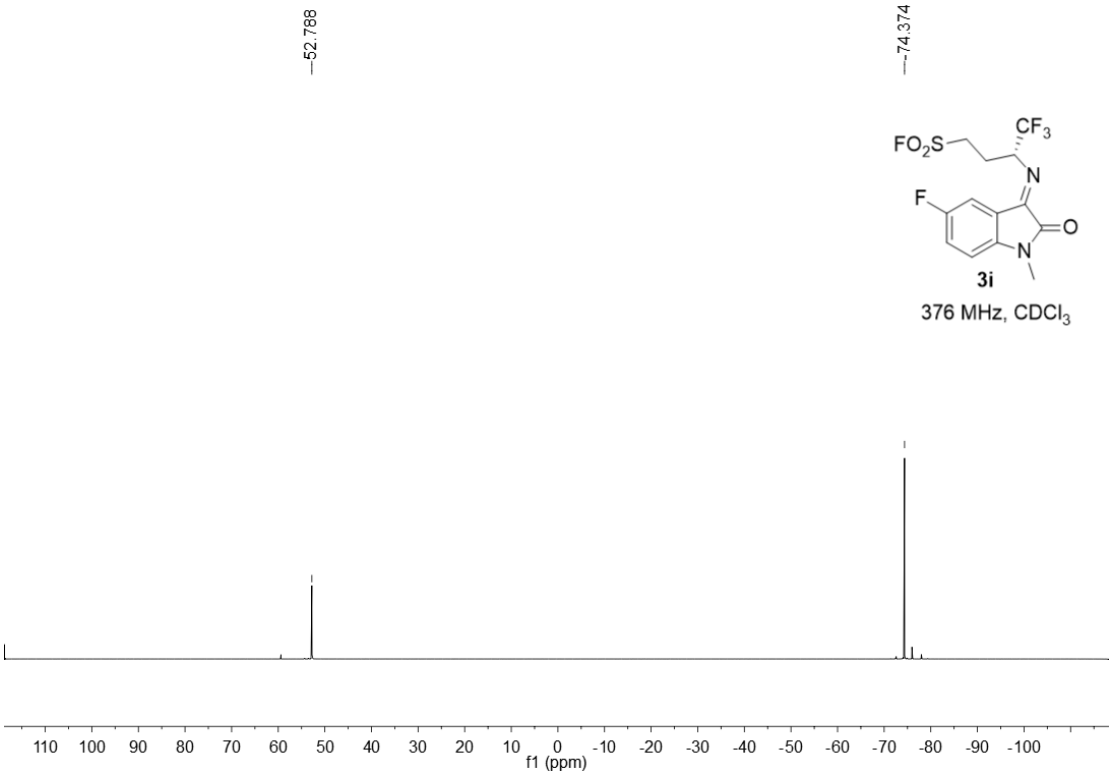


^{1}H, $^{13}C\{1H\}$ and $^{19}F\{^{1}H, ^{13}C\}$ NMR spectra of **3h**

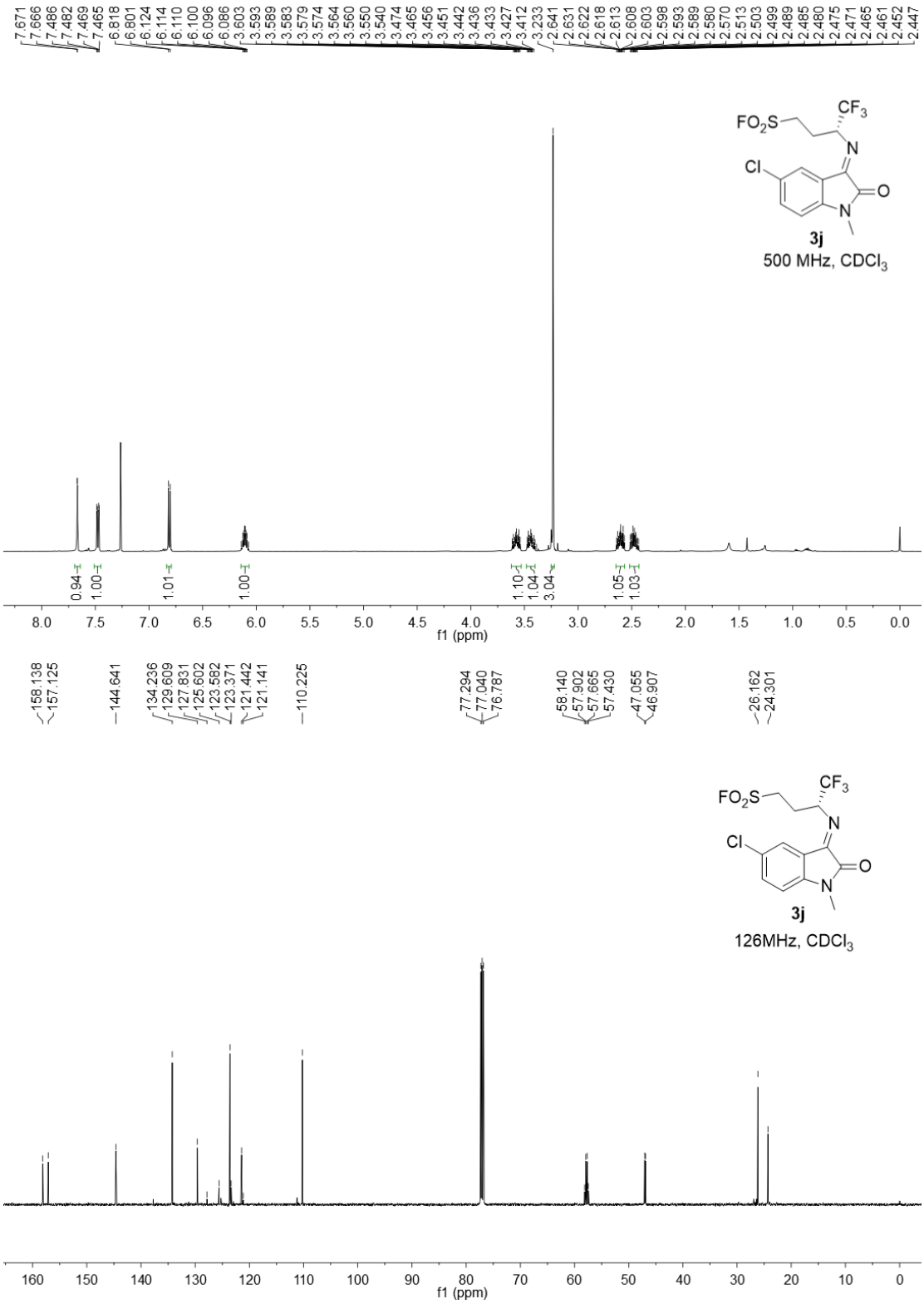

7.420
7.413
7.402
7.395
7.243
7.236
7.221
7.215
7.199
7.193
6.830
6.821
6.809
6.800
6.147
6.134
6.129
6.117
6.111
6.099
3.617
3.604
3.600
3.592
3.587
3.580
3.567
3.563
3.551
3.538
3.483
3.471
3.459
3.454
3.442
3.434
3.405
3.231
2.638
2.626
2.621
2.615
2.609
2.603
2.597
2.591
2.586
2.574
2.562
2.518
2.505
2.500
2.488
2.476
2.470
2.465
2.457
2.453
FO2S
CF3
N
F
O
N
3i
400 MHz, CDCl3
0.96
0.99
1.02
0.95
1.08
1.09
3.00
1.07
1.04
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

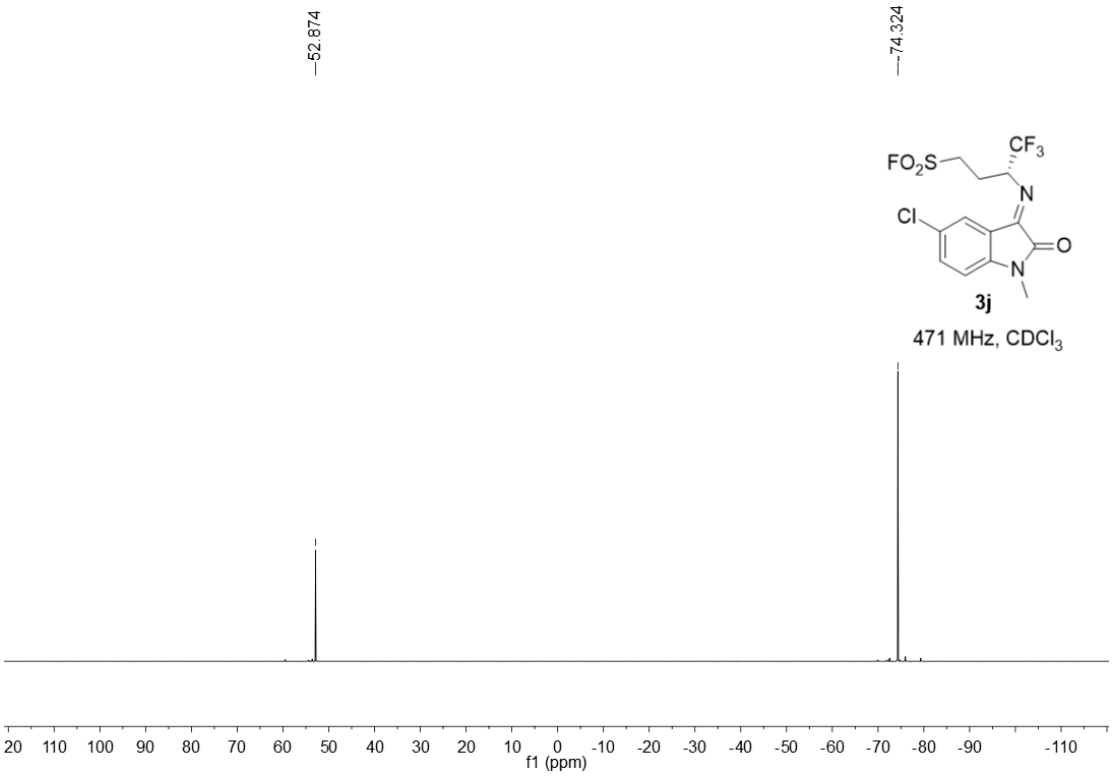

160.876
158.451
158.409
157.557
157.529
142.328
142.308
128.693
125.904
123.117
121.416
121.334
121.090
120.850
120.329
111.100
110.849
110.066
109.991
77.370
77.051
76.734
58.167
57.872
57.576
57.281
47.077
46.892
26.128
24.255
FO2S
CF3
N
F
O
N
3i
101 MHz, CDCl3
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



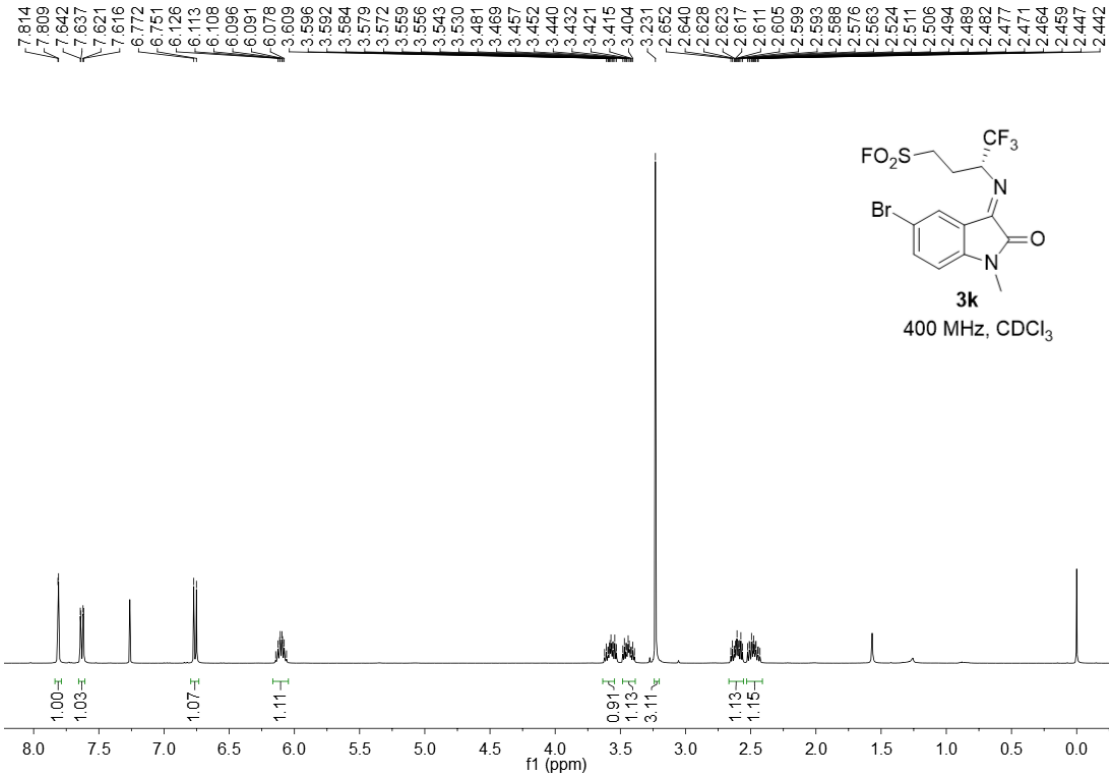


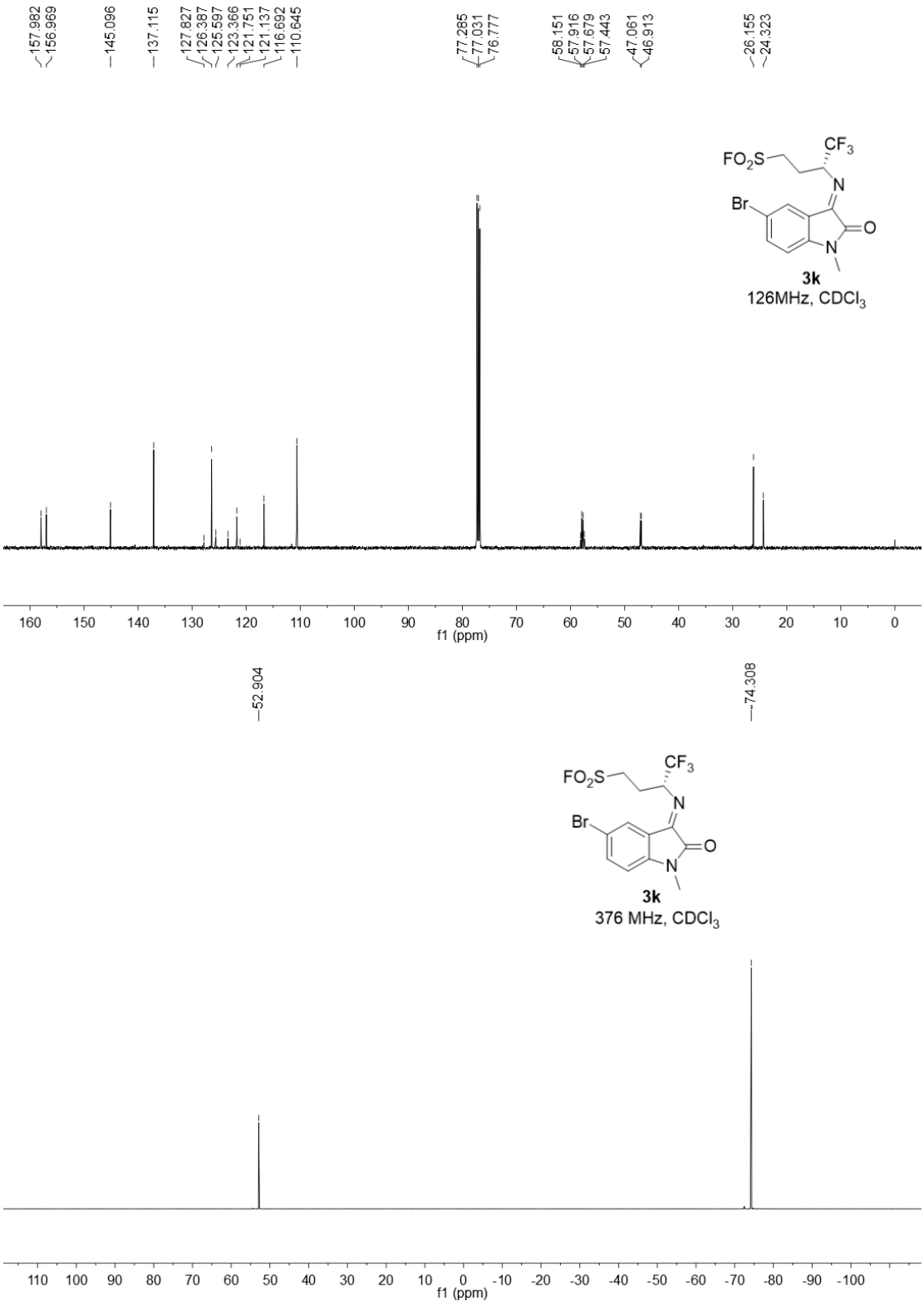
^{1}H, $^{13}C\{1H\}$ and $^{19}F\{^{1}H, ^{13}C\}$ NMR spectra of **3i**


7.671
7.666
7.486
7.482
7.469
7.465
6.818
6.801
6.124
6.114
6.110
6.100
6.096
6.086
3.603
3.593
3.589
3.583
3.579
3.574
3.564
3.560
3.550
3.540
3.474
3.465
3.456
3.451
3.442
3.436
3.433
3.427
3.412
3.233
2.641
2.631
2.622
2.618
2.613
2.608
2.603
2.598
2.593
2.589
2.580
2.570
2.513
2.503
2.499
2.489
2.485
2.480
2.475
2.471
2.465
2.461
2.452
2.447
FO2S
CF3
N
Cl
O
N
3j
500 MHz, CDCl3
0.94
1.00
1.01
1.00
1.10
1.04
3.04
1.05
1.03
f1 (ppm)
158.138
157.125
144.641
134.236
129.609
127.831
125.602
123.582
123.371
121.442
121.141
110.225
77.294
77.040
76.787
58.140
57.902
57.665
57.430
47.055
46.907
26.162
24.301
FO2S
CF3
N
Cl
O
N
3j
126MHz, CDCl3
f1 (ppm)

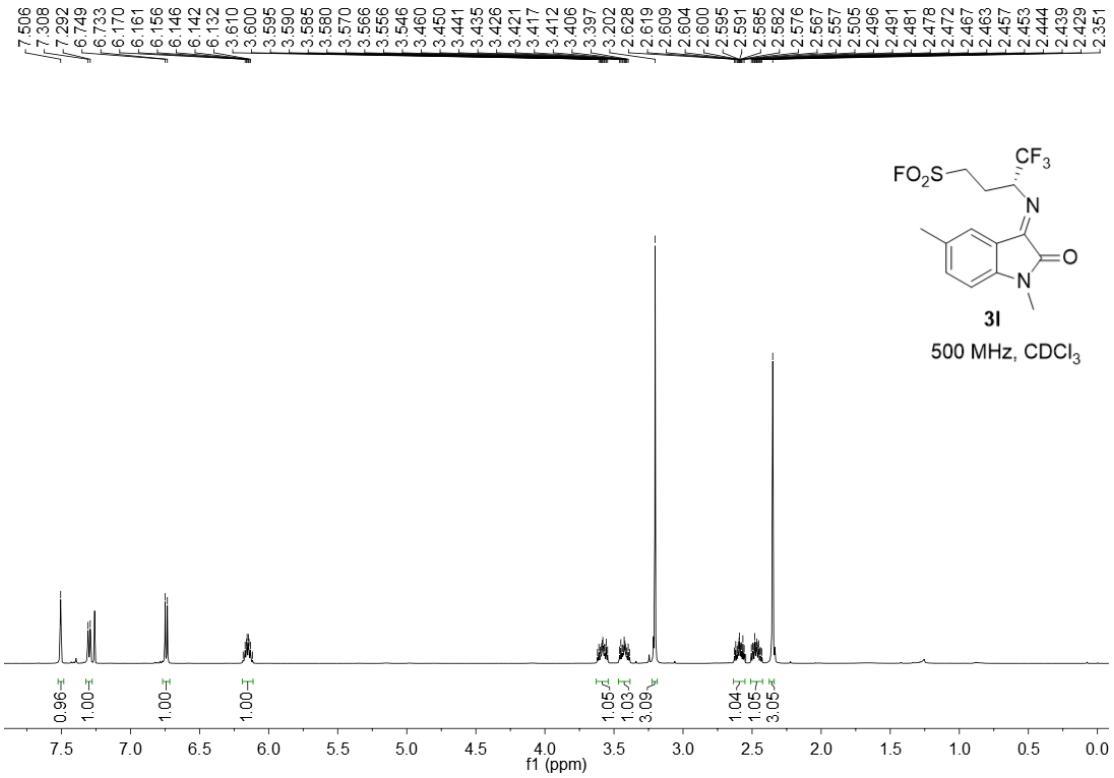


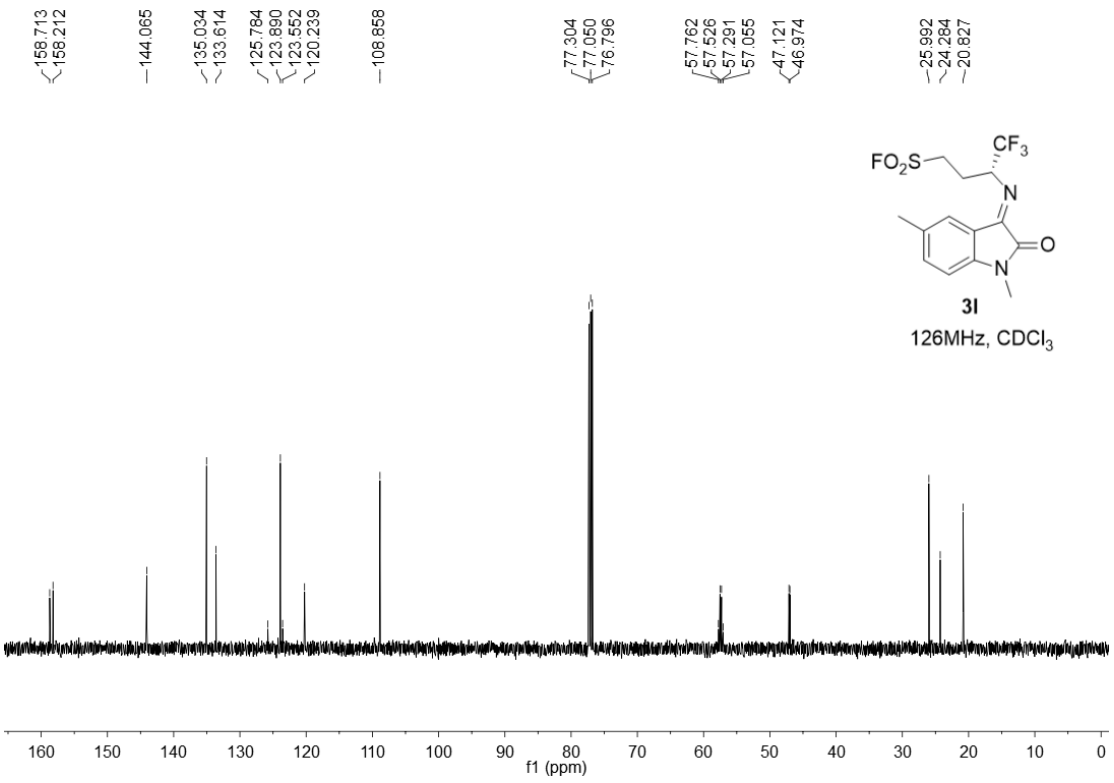
^{1}H, $^{13}C\{1H\}$ and $^{19}F\{^{1}H, ^{13}C\}$ NMR spectra of **3j**

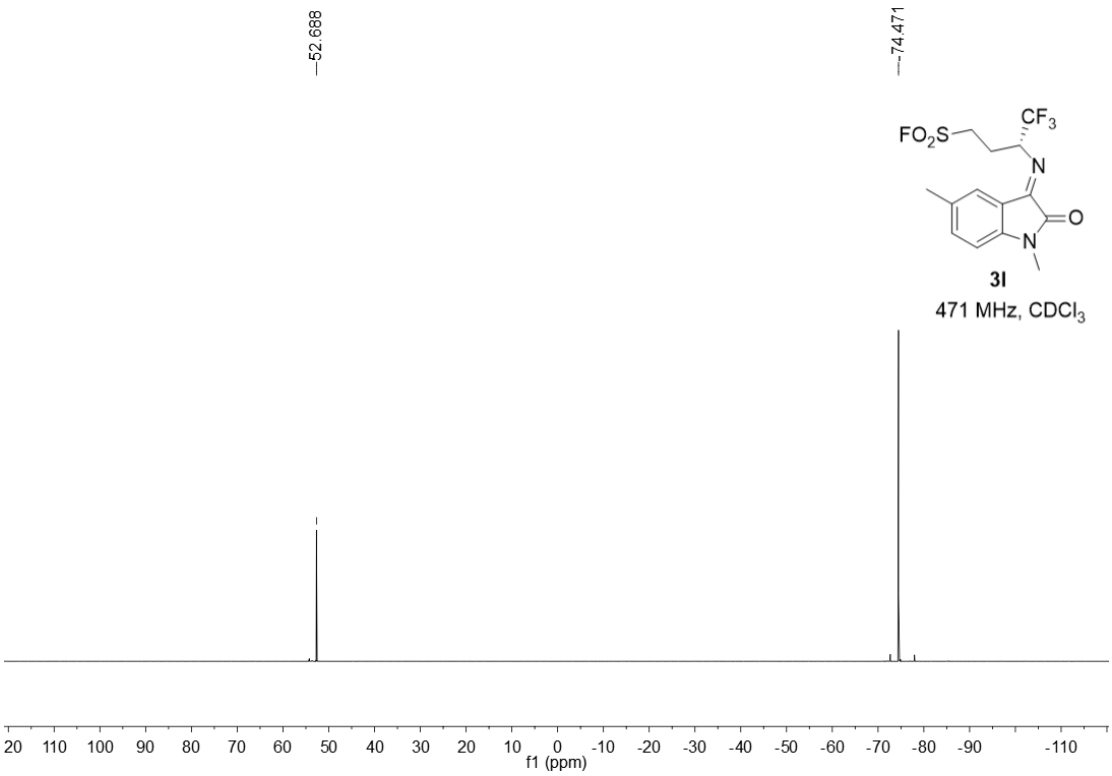




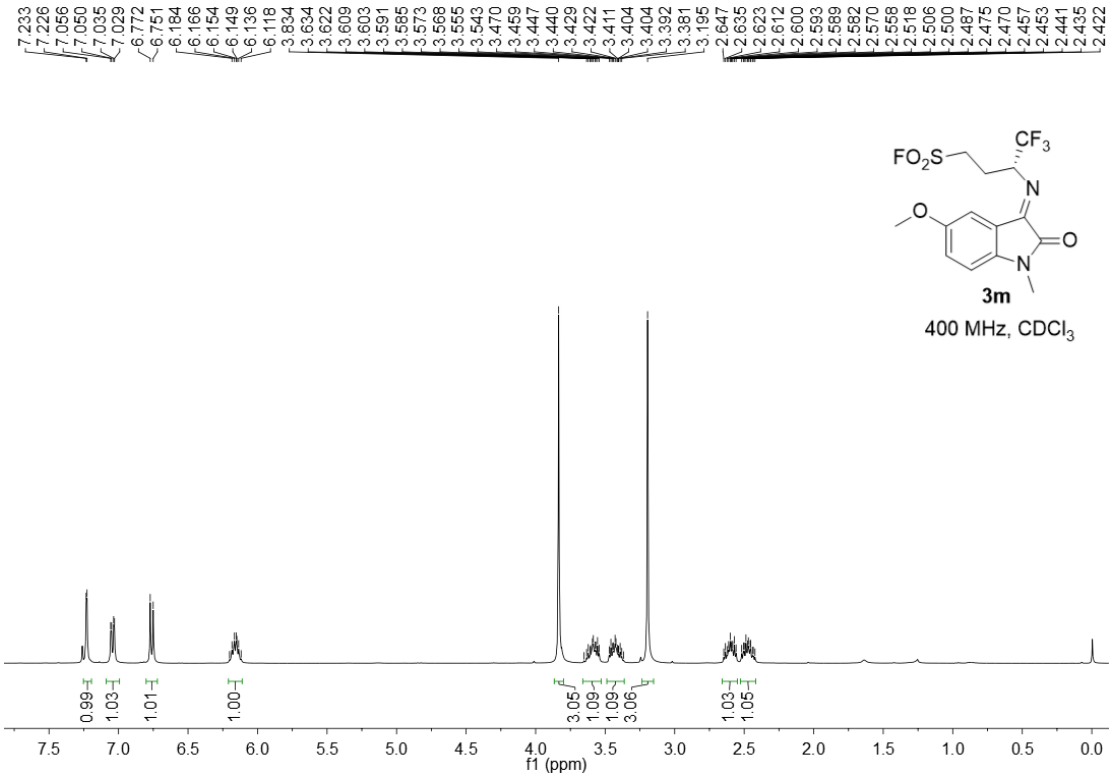
^{1}H,$^{13}C\{1H\}$ and $^{19}F\{^{1}H, ^{13}C\}$ NMR spectra of **3k**

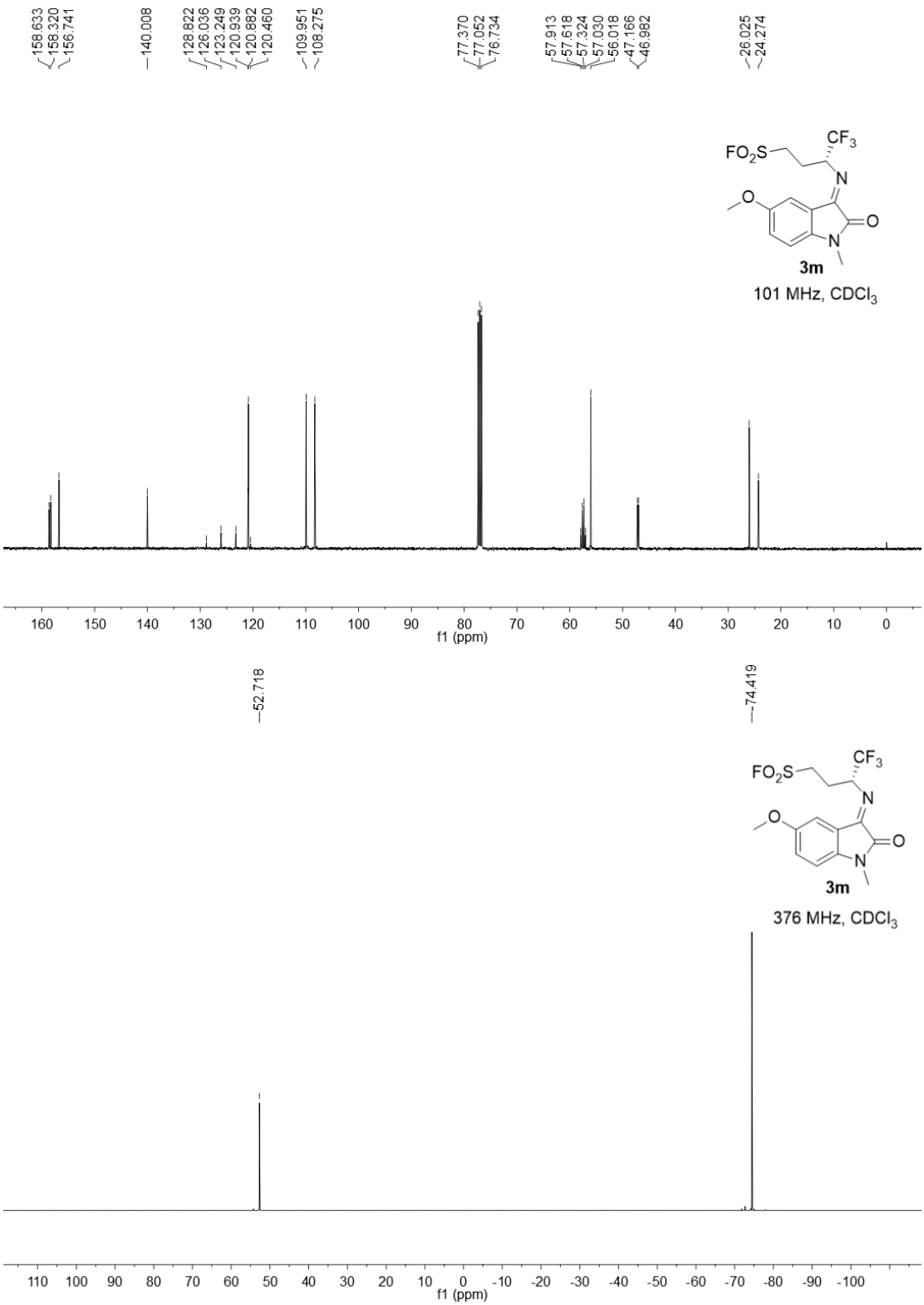

7.506
7.308
7.292
6.749
6.733
6.170
6.161
6.156
6.146
6.142
6.132
3.610
3.600
3.595
3.590
3.585
3.580
3.570
3.566
3.556
3.546
3.460
3.450
3.441
3.435
3.426
3.421
3.417
3.412
3.406
3.397
3.202
2.628
2.619
2.609
2.604
2.600
2.595
2.591
2.585
2.582
2.576
2.567
2.557
2.505
2.496
2.491
2.481
2.478
2.472
2.467
2.463
2.457
2.453
2.444
2.439
2.429
2.351
FO2S
CF3
N
O
N
3l
500 MHz, CDCl3
0.96
1.00
1.00
1.00
1.05
1.03
3.09
1.04
1.05
3.05
f1 (ppm)


158.713
158.212
144.065
135.034
133.614
125.784
123.890
123.552
120.239
108.858
77.304
77.050
76.796
57.762
57.526
57.291
57.055
47.121
46.974
25.992
24.284
20.827
FO2S
CF3
N
O
N
3l
126MHz, CDCl3
f1 (ppm)

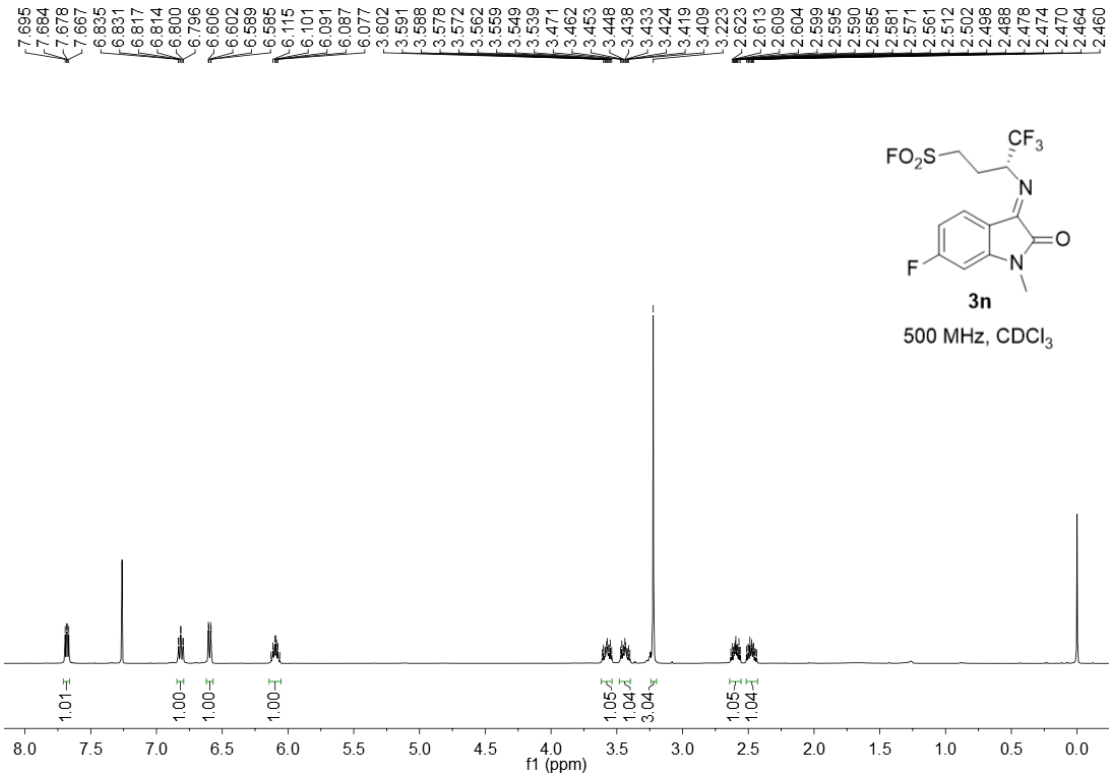


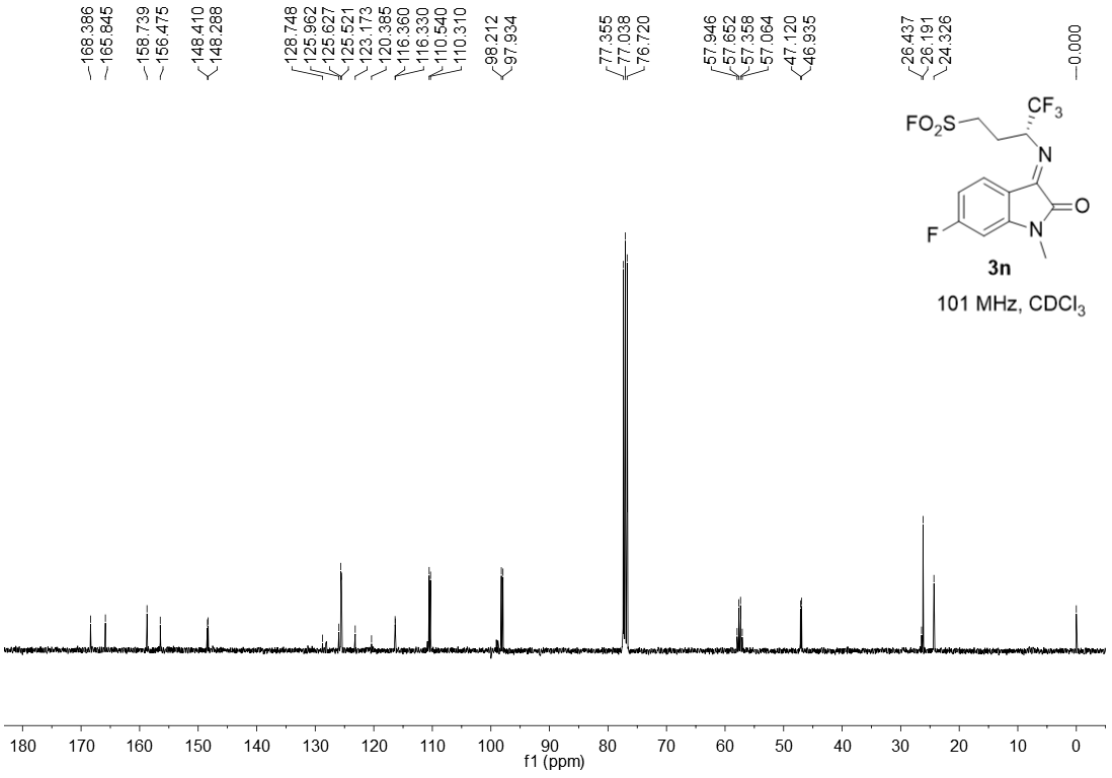
^{1}H, $^{13}C\{1H\}$ and ^{19}F $\{^{1}H, ^{13}C\}$NMR spectra of **3l**

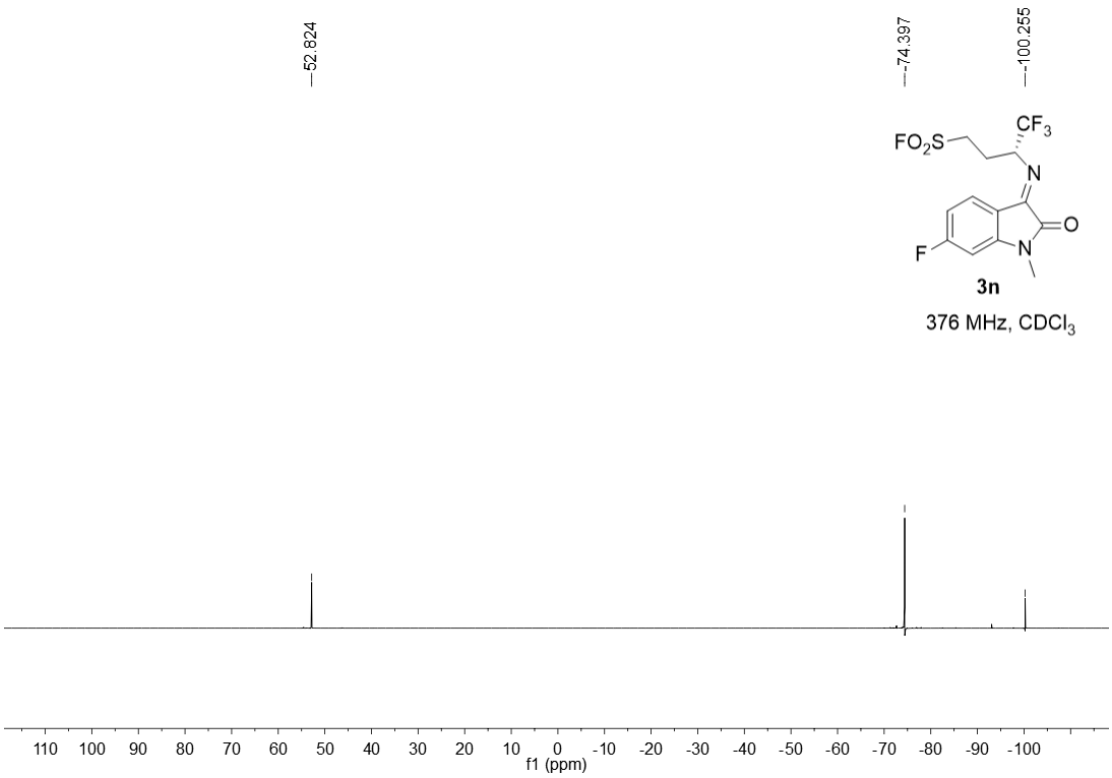




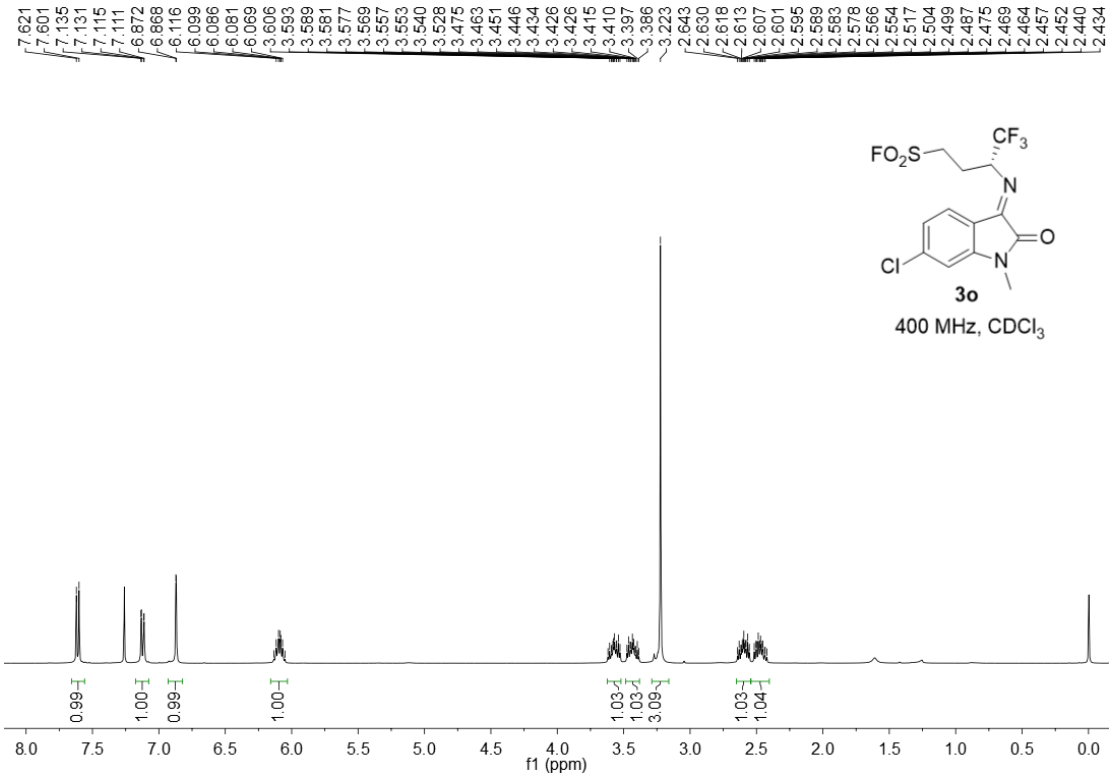
^{1}H, $^{13}C\{1H\}$ and ^{19}F $\{^{1}H, ^{13}C\}$NMR spectra of **3m**

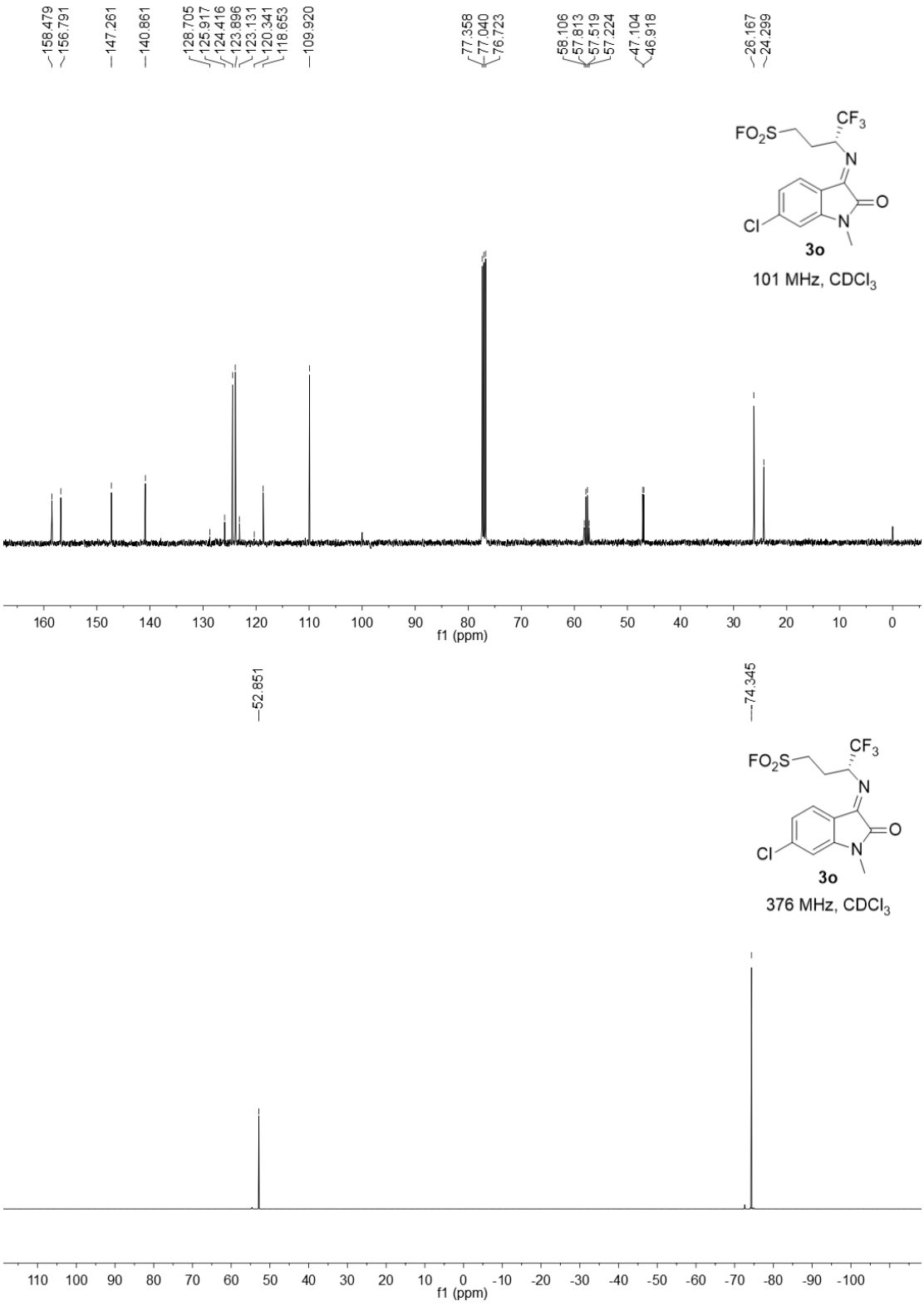

7.695
7.684
7.678
7.667
6.835
6.831
6.817
6.814
6.800
6.796
6.606
6.602
6.589
6.585
6.115
6.101
6.091
6.087
6.077
3.602
3.591
3.588
3.578
3.572
3.562
3.559
3.549
3.539
3.471
3.462
3.453
3.448
3.438
3.433
3.424
3.419
3.409
3.223
2.623
2.613
2.609
2.604
2.599
2.595
2.590
2.585
2.581
2.571
2.561
2.512
2.502
2.498
2.488
2.478
2.474
2.470
2.464
2.460
FO2S
CF3
N
O
F
N
3n
500 MHz, CDCl3
1.01
1.00
1.00
1.00
1.05
1.04
3.04
1.05
1.04
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
f1 (ppm)


168.386
165.845
158.739
156.475
148.410
148.288
128.748
125.962
125.627
125.521
123.173
120.385
116.360
116.330
110.540
110.310
98.212
97.934
77.355
77.038
76.720
57.946
57.652
57.358
57.064
47.120
46.935
26.437
26.191
24.326
0.000
FO2S
CF3
N
O
F
N
3n
101 MHz, CDCl3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

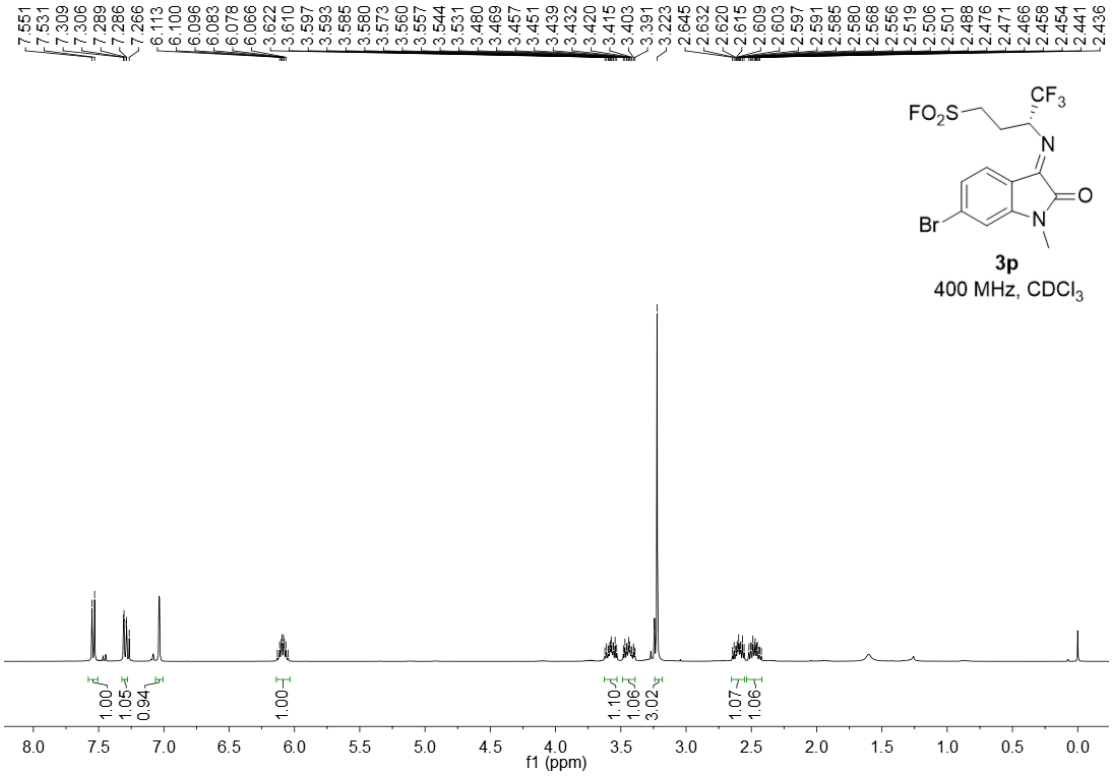


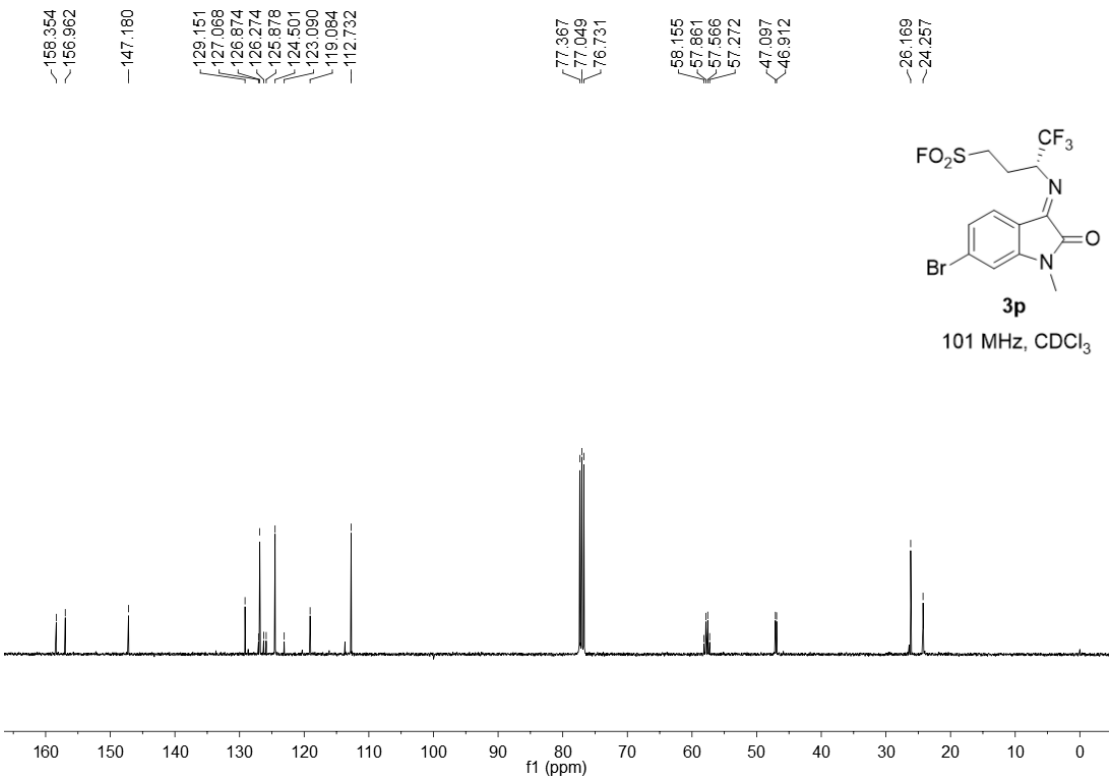
^{1}H, $^{13}C\{1H\}$ and $^{19}F\{^{1}H, ^{13}C\}$ NMR spectra of **3n**

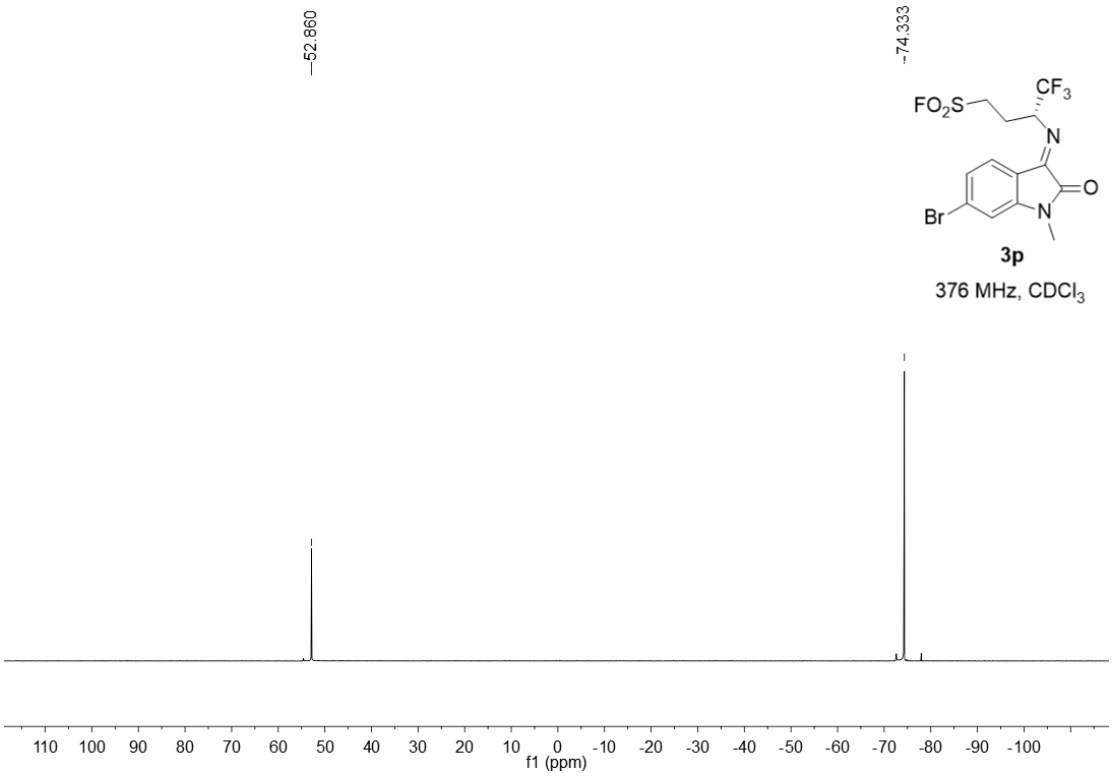




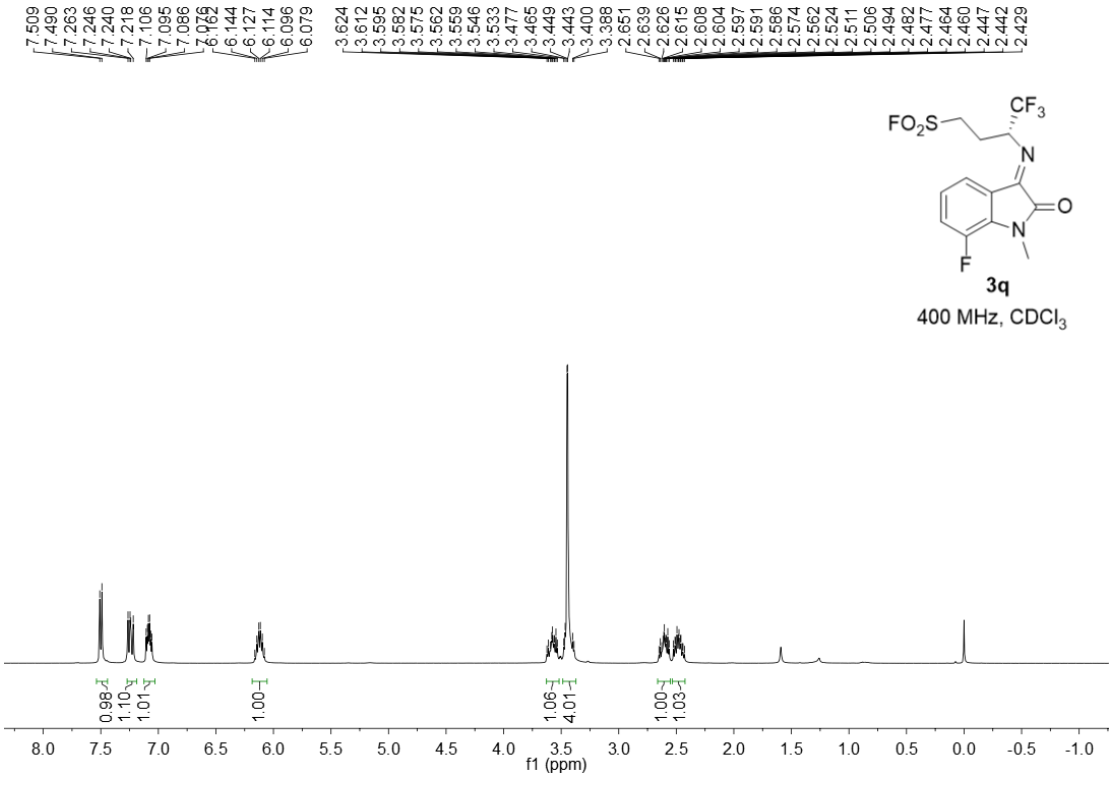
^{1}H, $^{13}C\{1H\}$ and $^{19}F\{^{1}H, ^{13}C\}$ NMR spectra of **3o**

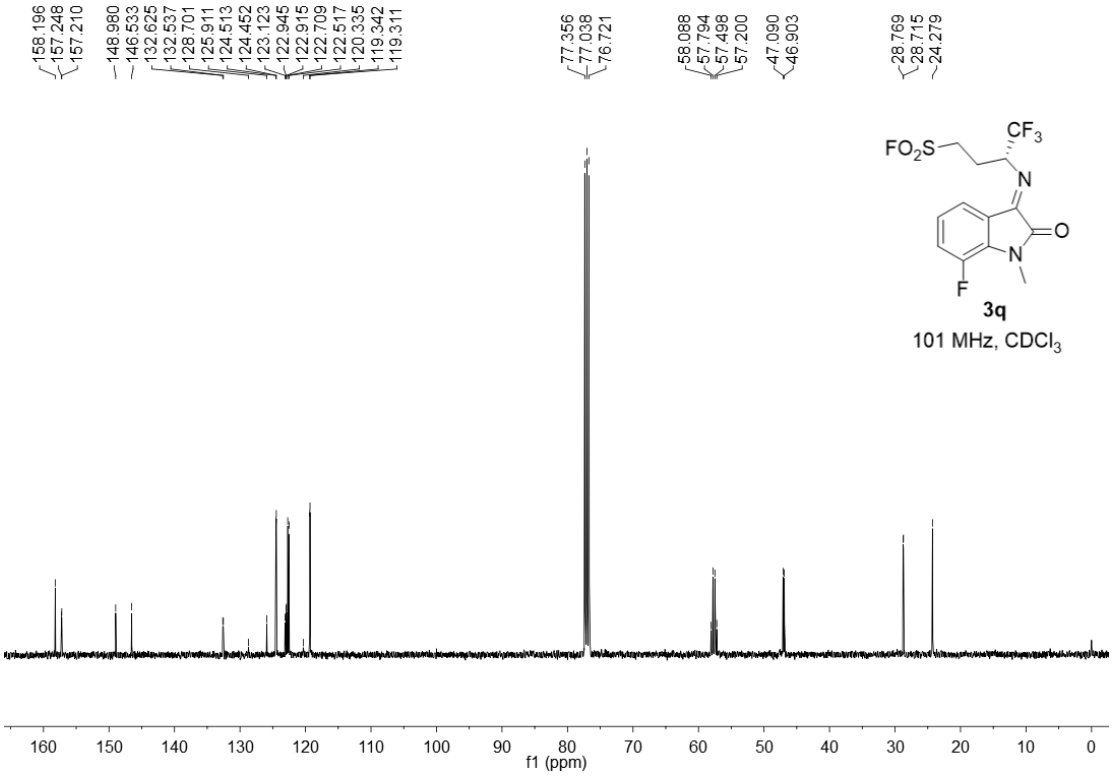

7.551
7.531
7.309
7.306
7.289
7.286
7.266
6.113
6.100
6.096
6.083
6.078
6.066
3.622
3.610
3.597
3.593
3.585
3.580
3.573
3.560
3.557
3.544
3.531
3.480
3.469
3.457
3.451
3.439
3.432
3.420
3.415
3.403
3.391
3.223
2.645
2.632
2.620
2.615
2.609
2.603
2.597
2.591
2.585
2.580
2.568
2.556
2.519
2.506
2.501
2.488
2.476
2.471
2.466
2.458
2.454
2.441
2.436
FO2S
CF3
N
O
Br
N
3p
400 MHz, CDCl3
1.00
1.05
0.94
1.00
1.10
1.06
3.02
1.07
1.06
f1 (ppm)

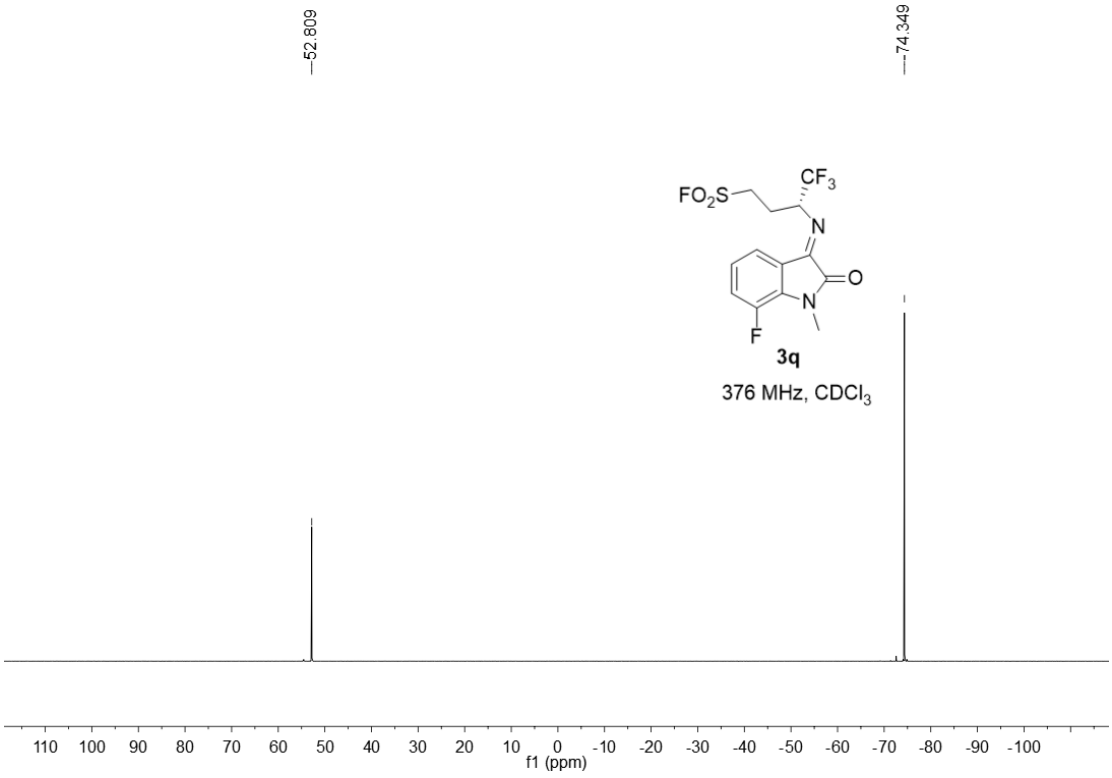

158.354
156.962
147.180
129.151
127.068
126.874
126.274
125.878
124.501
123.090
119.084
112.732
77.367
77.049
76.731
58.155
57.861
57.566
57.272
47.097
46.912
26.169
24.257
FO2S
CF3
N
O
Br
N
3p
101 MHz, CDCl3
f1 (ppm)

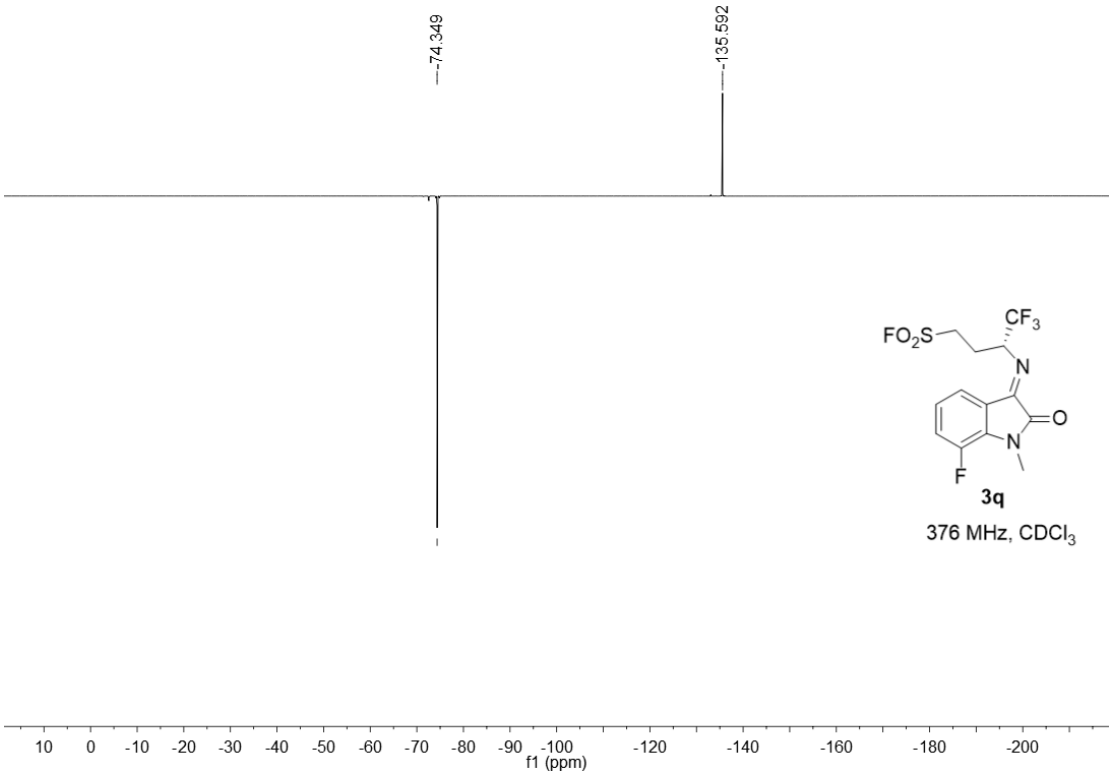


^{1}H,$^{13}C\{1H\}$ and $^{19}F\{^{1}H, ^{13}C\}$ NMR spectra of **3p**

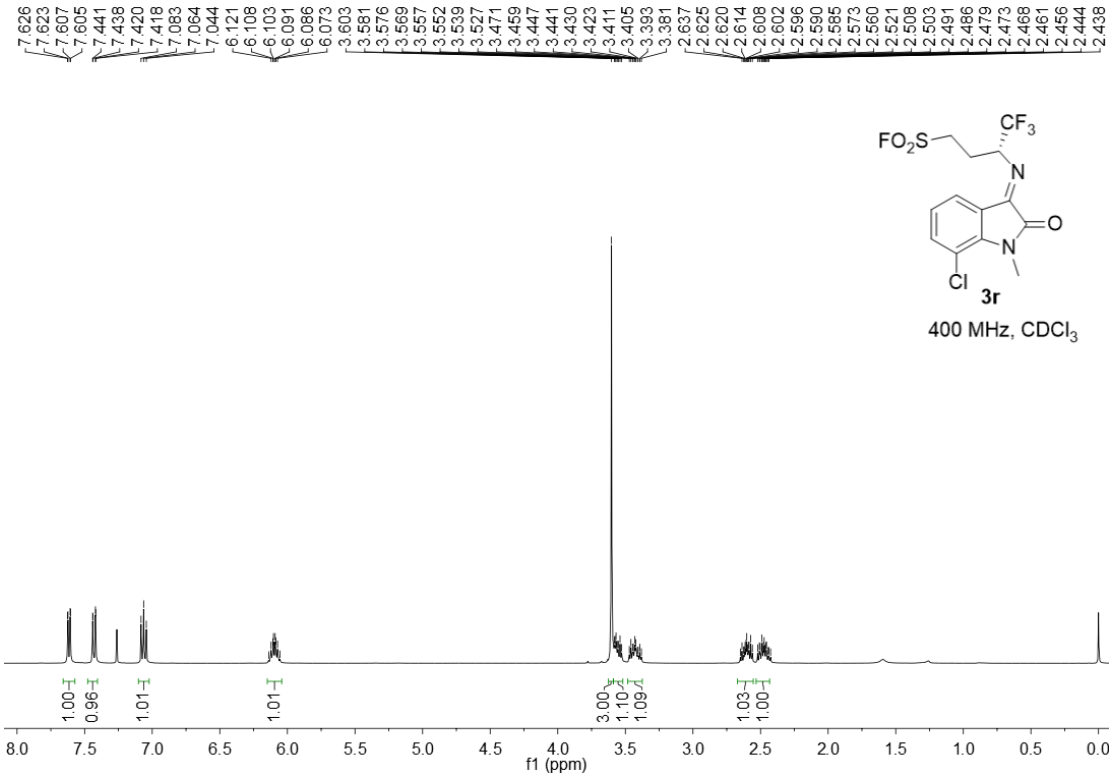


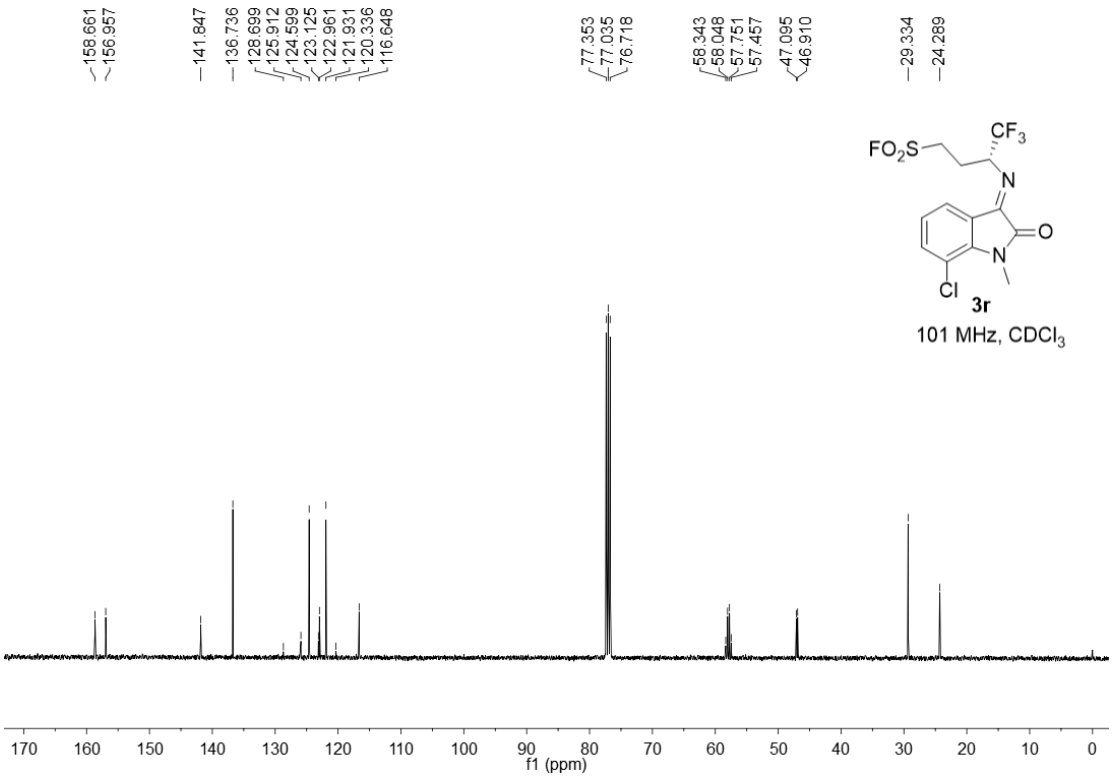

158.196
157.248
157.210
148.980
146.533
132.625
132.537
128.701
125.911
124.513
124.452
123.123
122.945
122.915
122.709
122.517
120.335
119.342
119.311
77.356
77.038
76.721
58.088
57.794
57.498
57.200
47.090
46.903
28.769
28.715
24.279
FO2S
CF3
N
O
N
F
3q
101 MHz, CDCl3
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

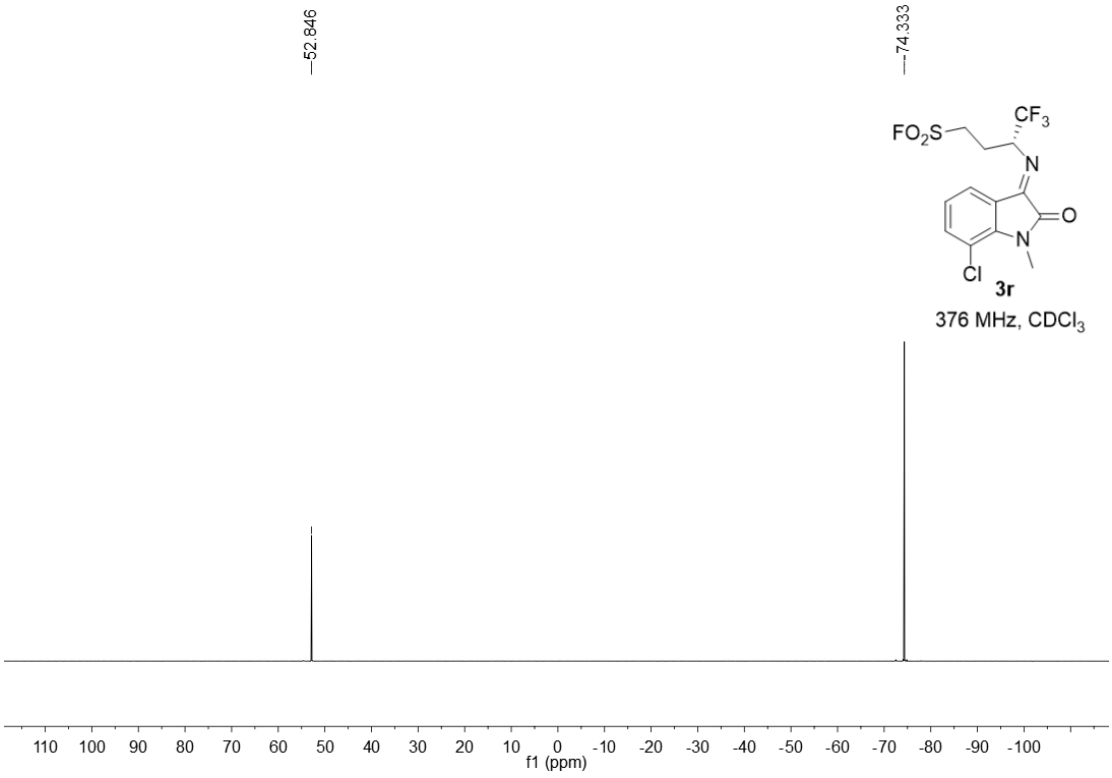

52.809
74.349
FO2S
CF3
N
O
N
F
3q
376 MHz, CDCl3
110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100
f1 (ppm)



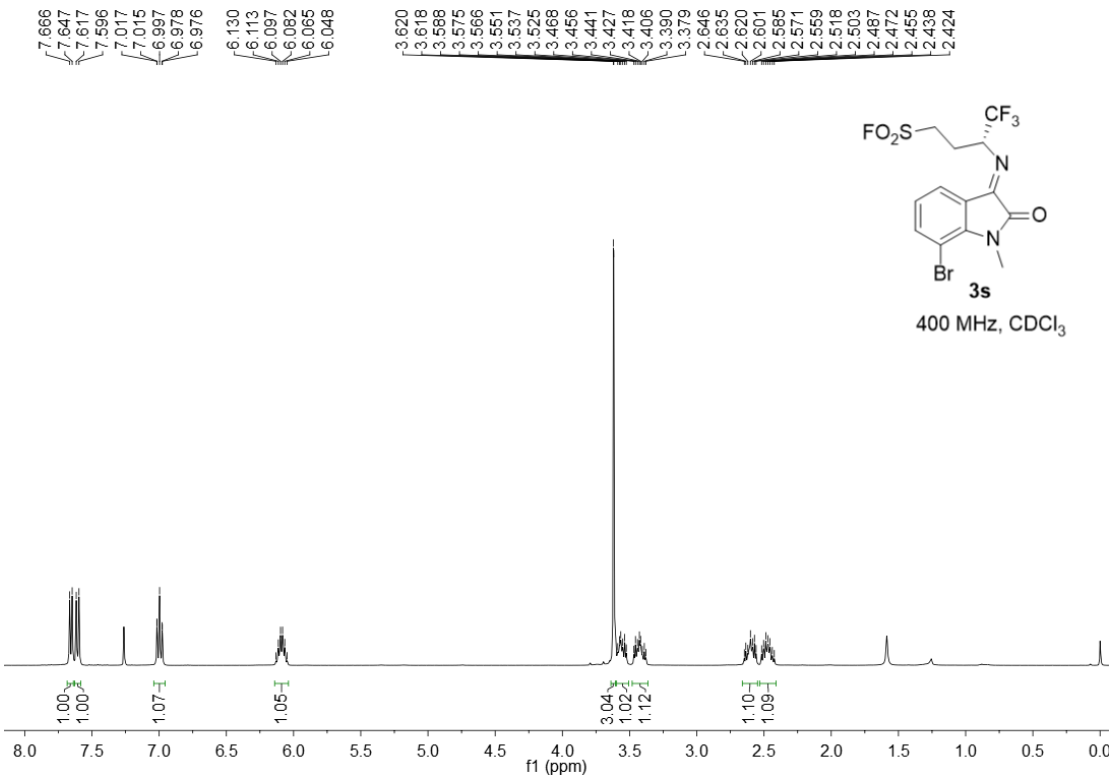
^{1}H, $^{13}C\{1H\}$ and ^{19}F $\{^{1}H, ^{13}C\}$NMR spectra of **3q**

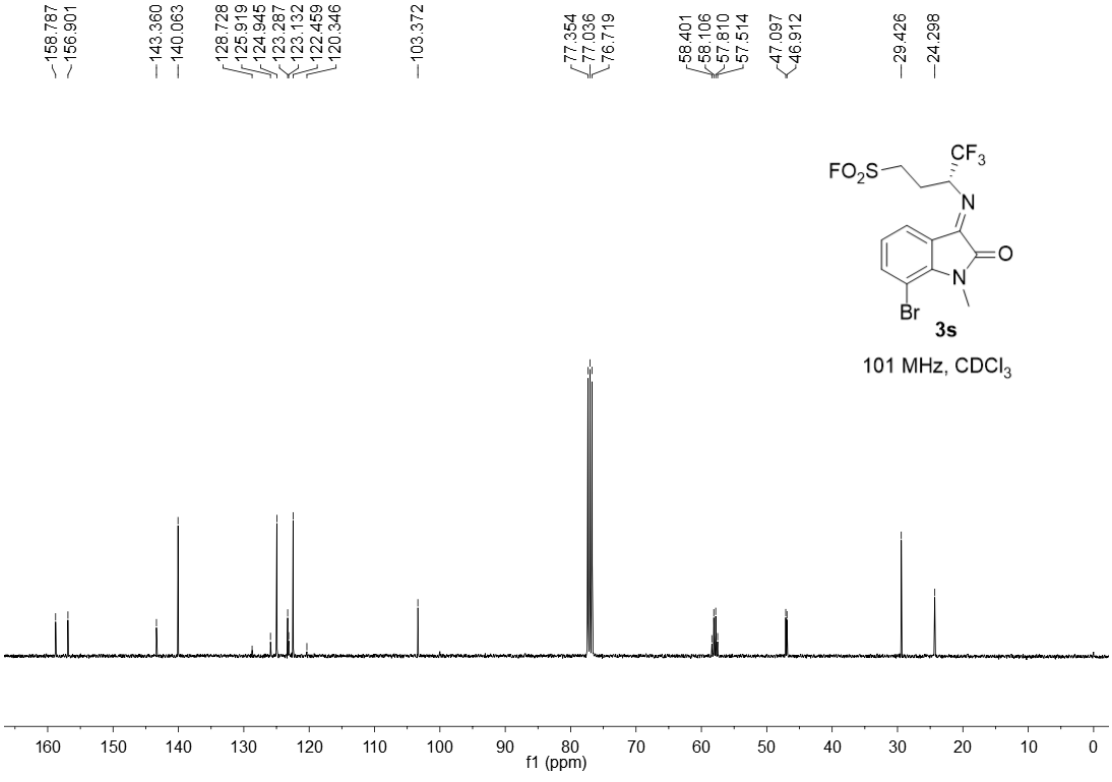


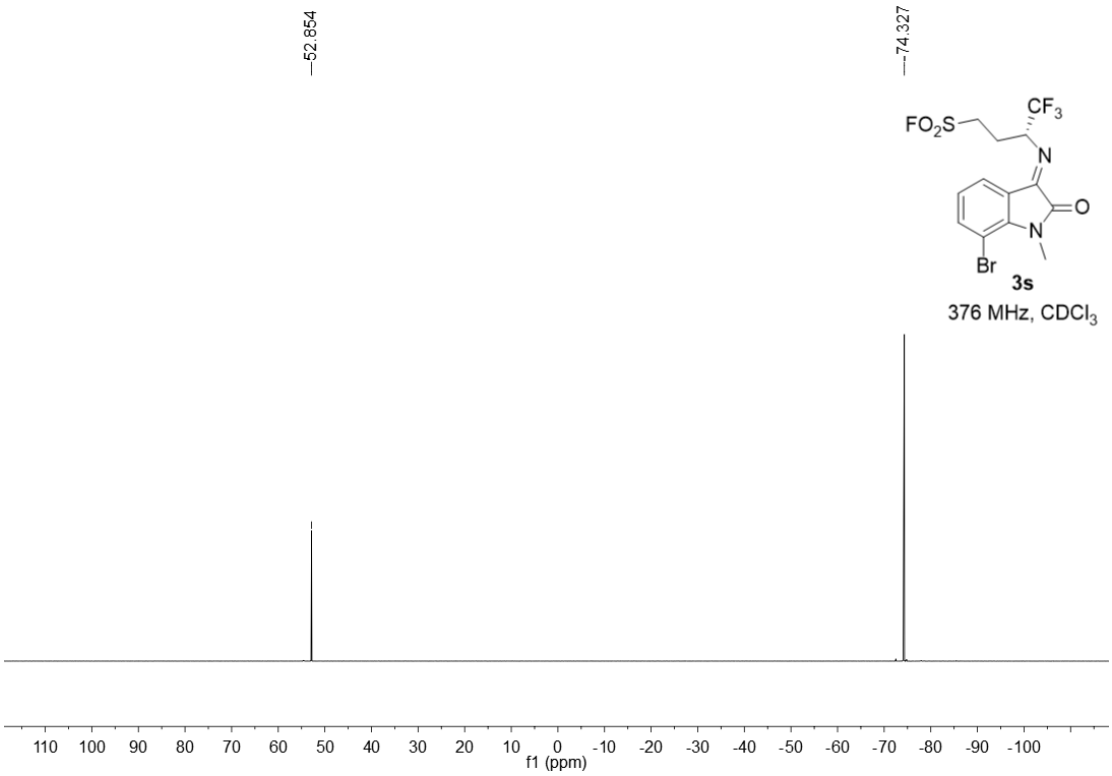




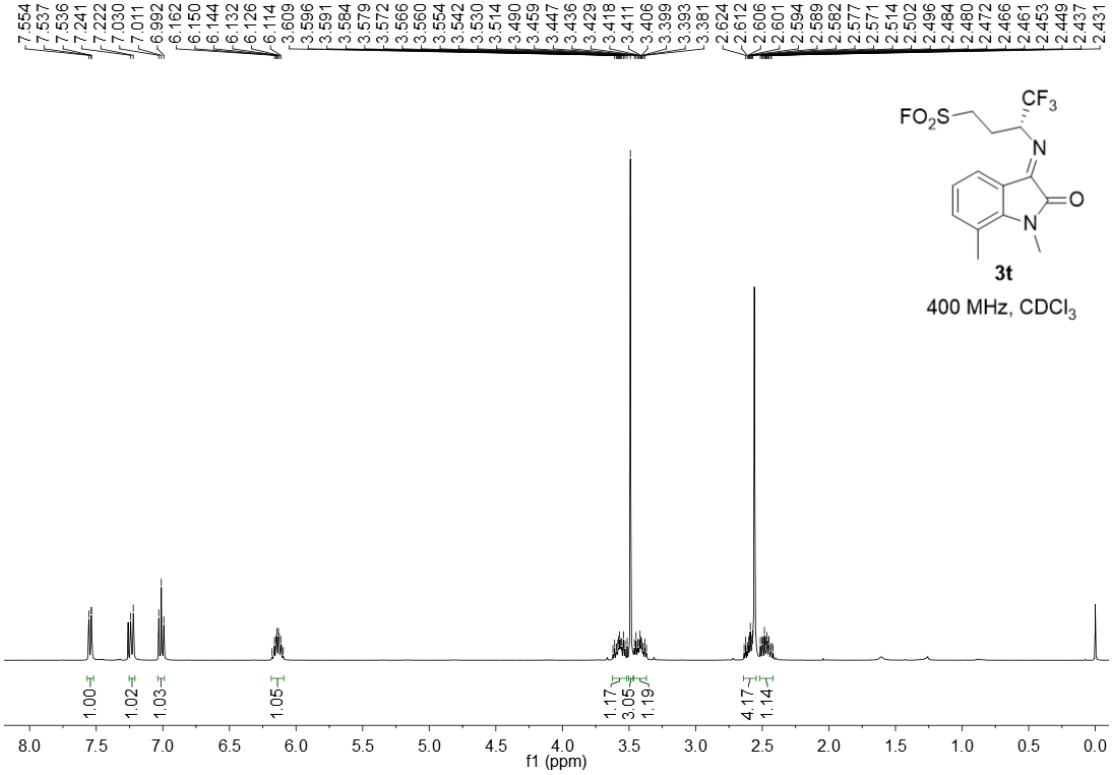
^{1}H, ^{13}C{1H} and ^{19}F {^{1}H, ^{13}C}NMR spectra of **3r**

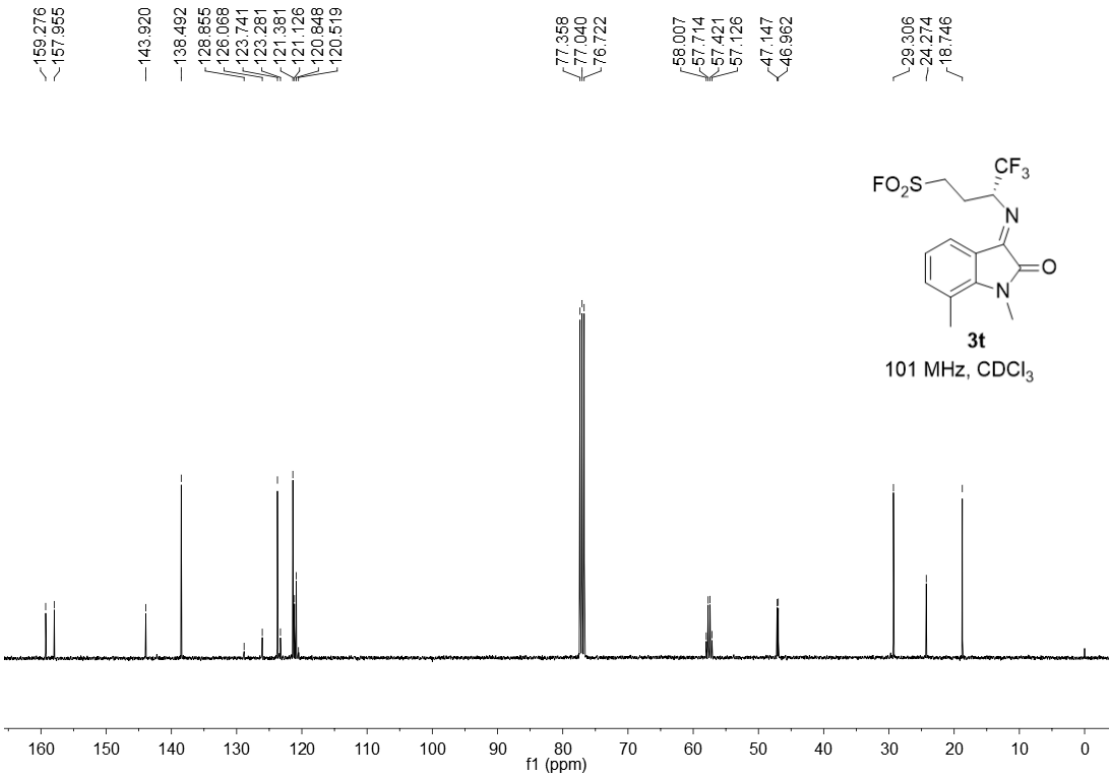

7.666
7.647
7.617
7.596
7.017
7.015
6.997
6.978
6.976
6.130
6.113
6.097
6.082
6.065
6.048
3.620
3.618
3.588
3.575
3.566
3.551
3.537
3.525
3.468
3.456
3.441
3.427
3.418
3.406
3.390
3.379
2.646
2.635
2.620
2.601
2.585
2.571
2.559
2.518
2.503
2.487
2.472
2.455
2.438
2.424
FO2S
CF3
N
O
N
Br
3s
400 MHz, CDCl3
1.00
1.00
1.07
1.05
3.04
1.02
1.12
1.10
1.09
f1 (ppm)

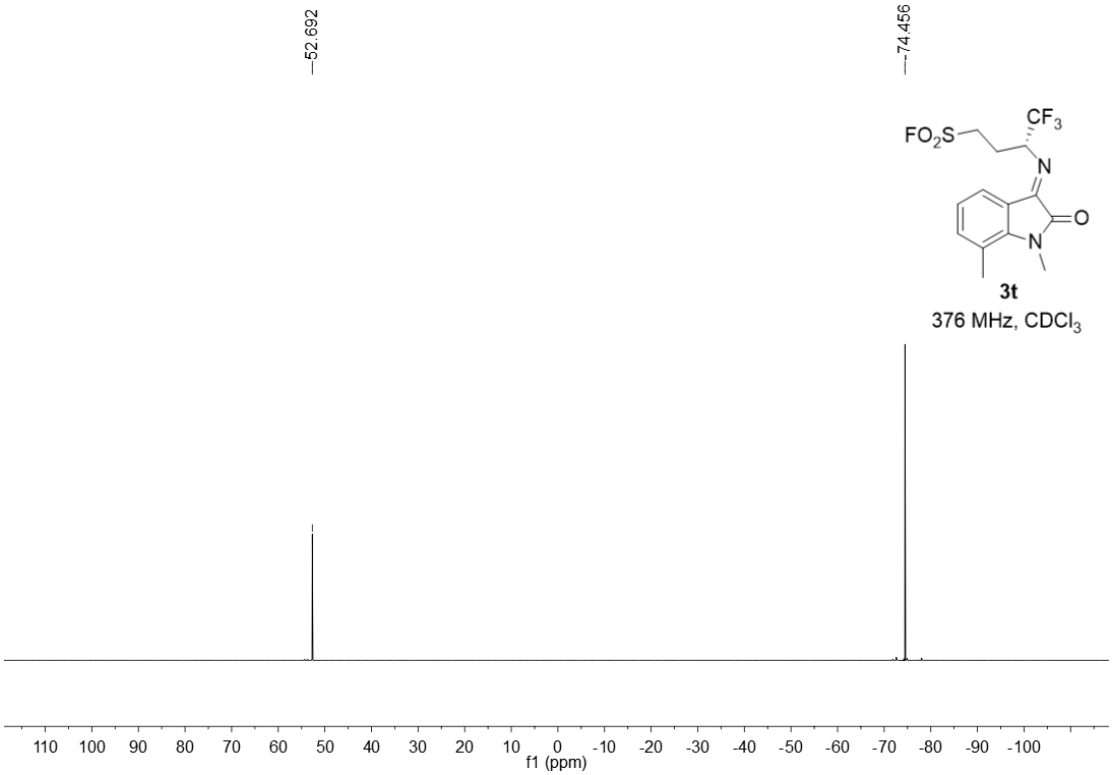

158.787
156.901
143.360
140.063
128.728
125.919
124.945
123.287
123.132
122.459
120.346
103.372
77.354
77.036
76.719
58.401
58.106
57.810
57.514
47.097
46.912
29.426
24.298
FO2S
CF3
N
O
N
Br
3s
101 MHz, CDCl3
f1 (ppm)



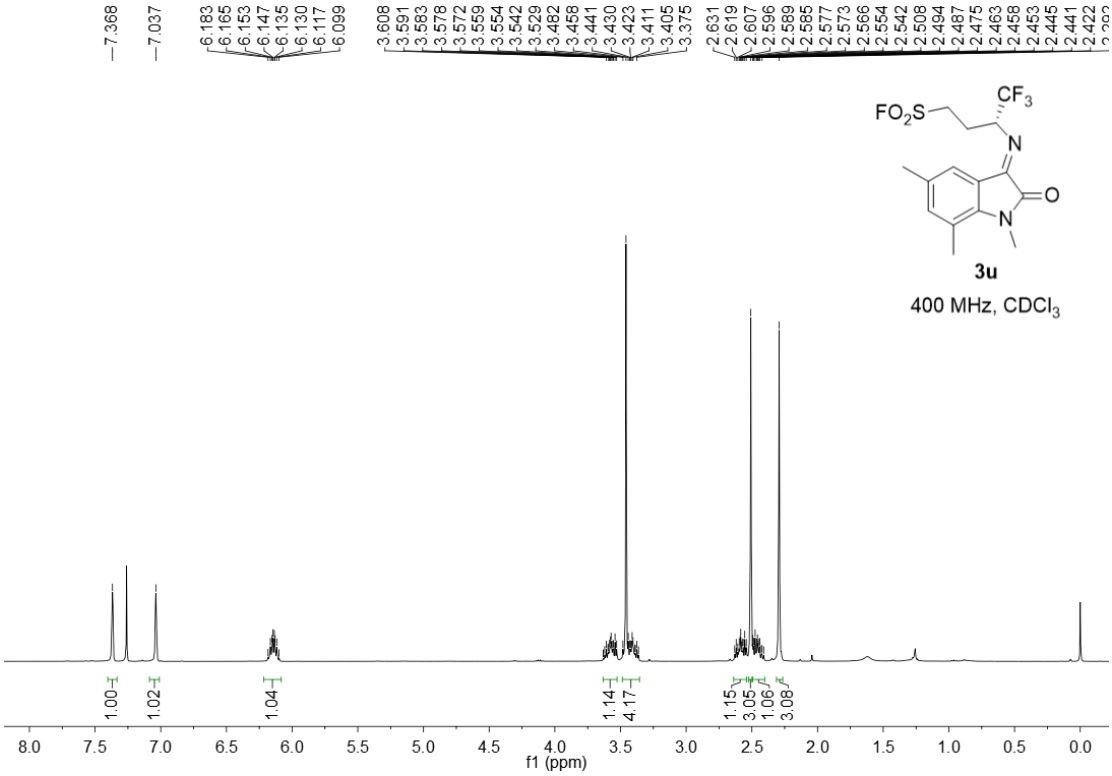
^{1}H, $^{13}C\{1H\}$ and $^{19}F\{^{1}H, ^{13}C\}$ NMR spectra of **3s**

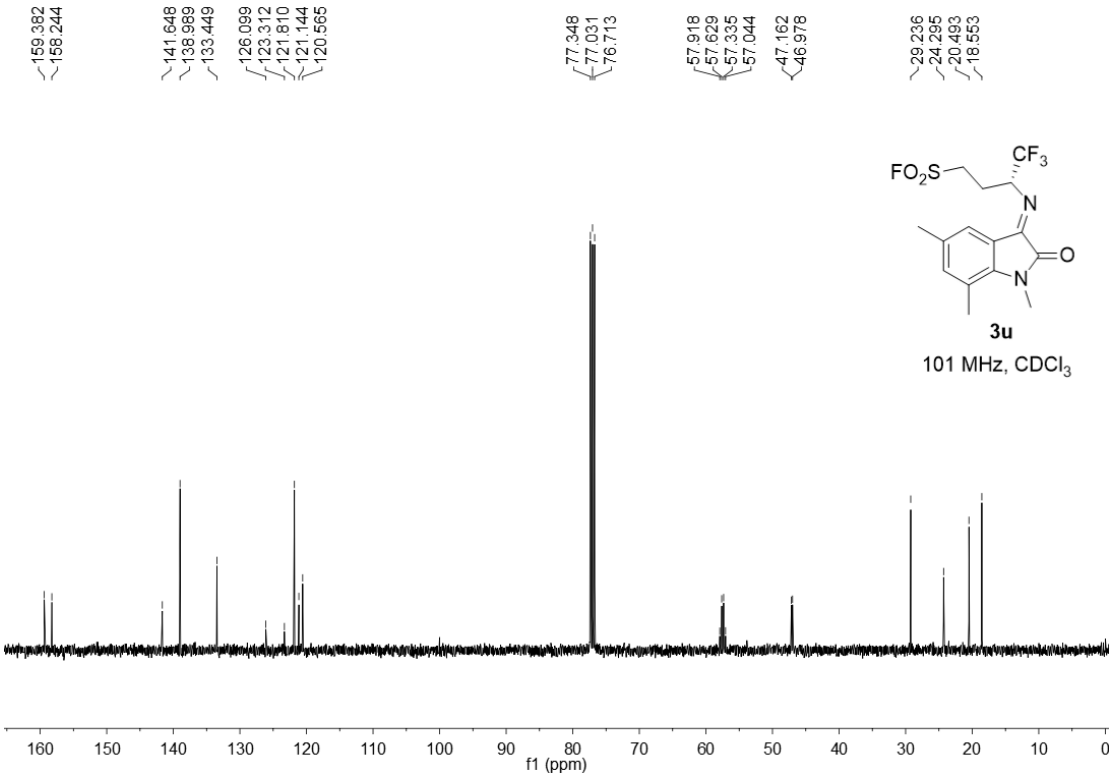


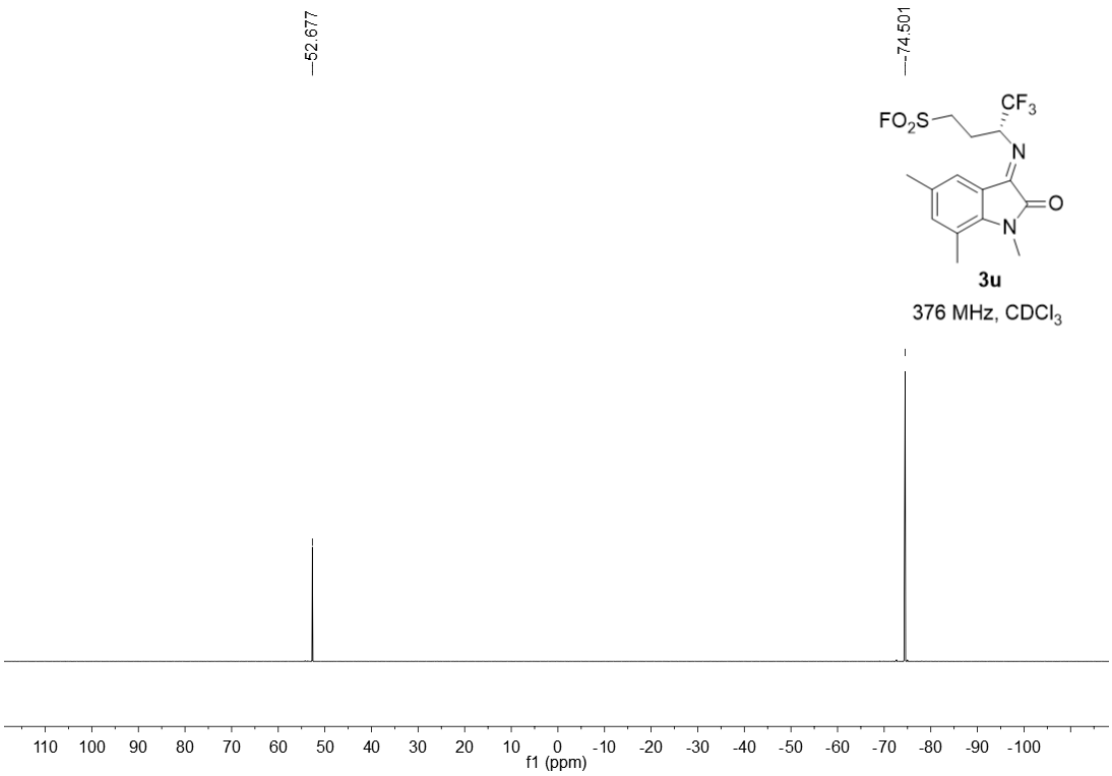




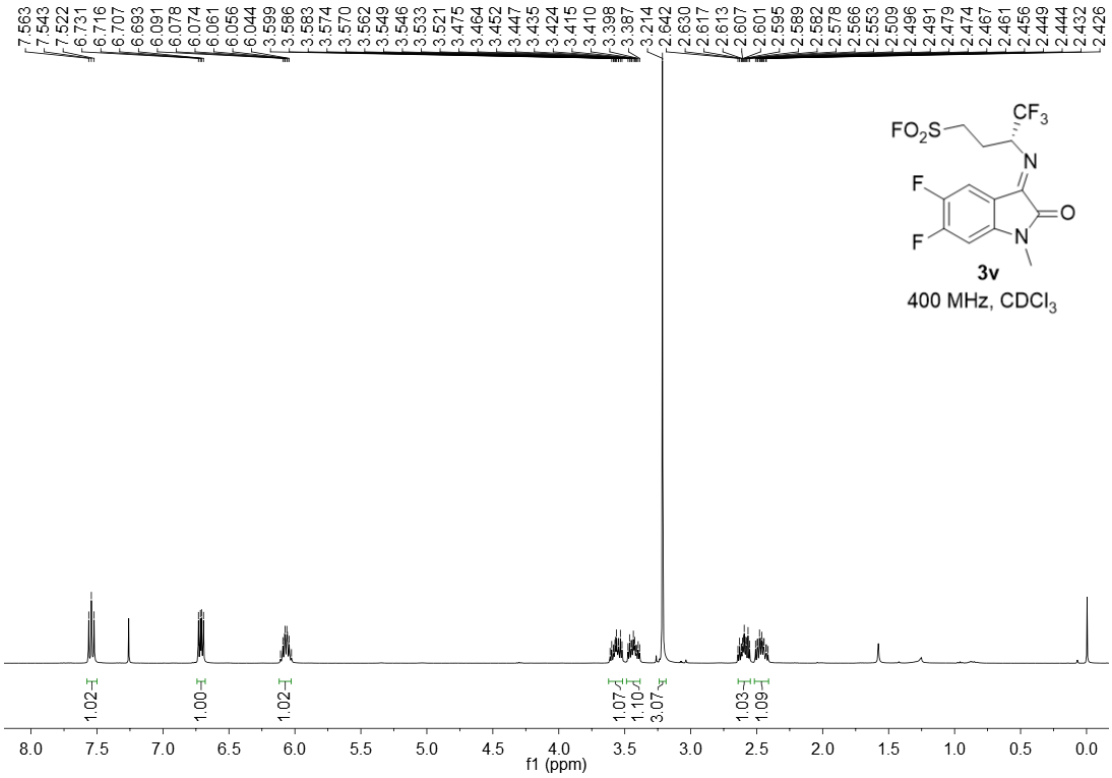
^{1}H, $^{13}C\{1H\}$ and $^{19}F\{^{1}H, ^{13}C\}$NMR spectra of **3t**

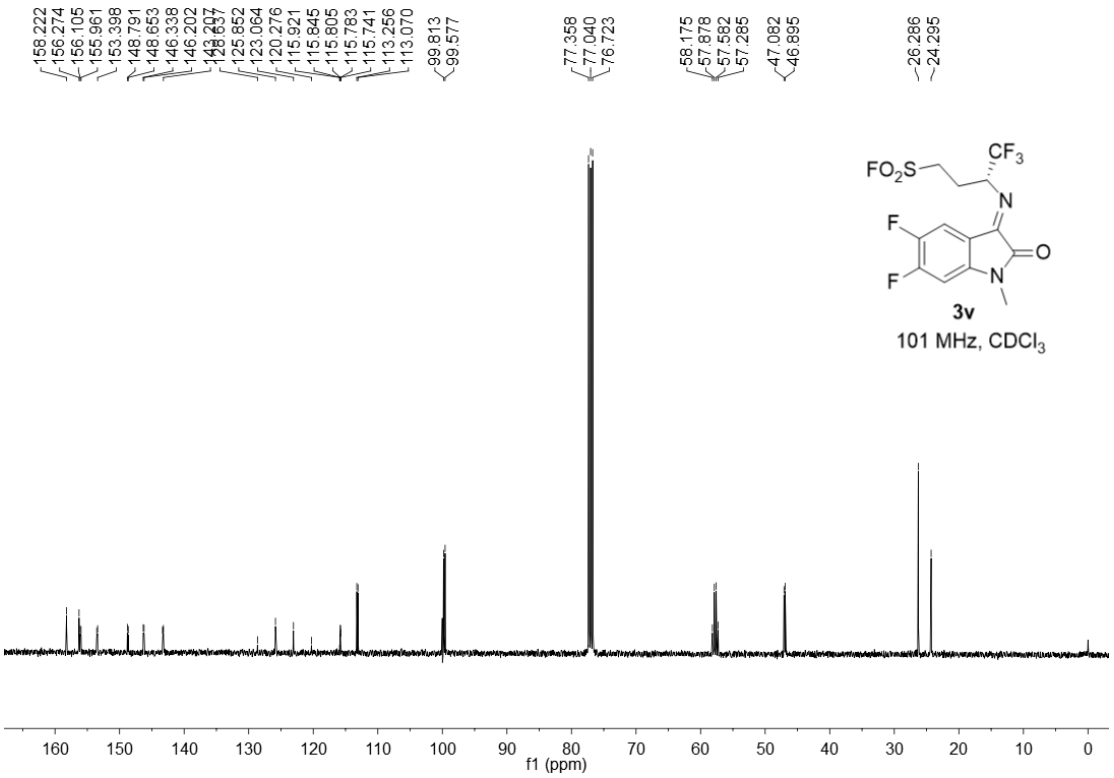

7.368
7.037
6.183
6.165
6.153
6.147
6.135
6.130
6.117
6.099
3.608
3.591
3.583
3.578
3.572
3.559
3.554
3.542
3.529
3.482
3.458
3.441
3.430
3.423
3.411
3.405
3.375
2.631
2.619
2.607
2.596
2.589
2.585
2.577
2.573
2.566
2.554
2.542
2.508
2.494
2.487
2.475
2.463
2.458
2.453
2.445
2.441
2.422
CF3
FO2S
N
O
N
3u
400 MHz, CDCl3
1.00
1.02
1.04
1.14
4.17
1.15
3.05
1.06
3.08
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
f1 (ppm)

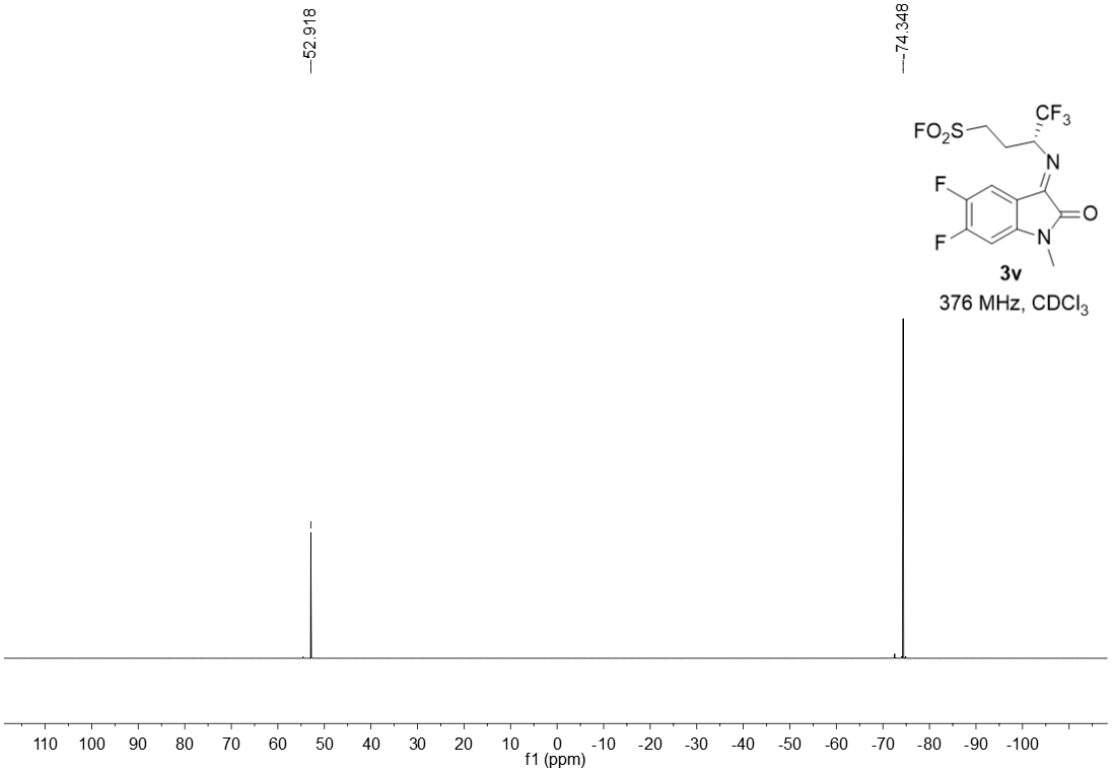

159.382
158.244
141.648
138.989
133.449
126.099
123.312
121.810
121.144
120.565
77.348
77.031
76.713
57.918
57.629
57.335
57.044
47.162
46.978
29.236
24.295
20.493
18.553
CF3
FO2S
N
O
N
3u
101 MHz, CDCl3
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

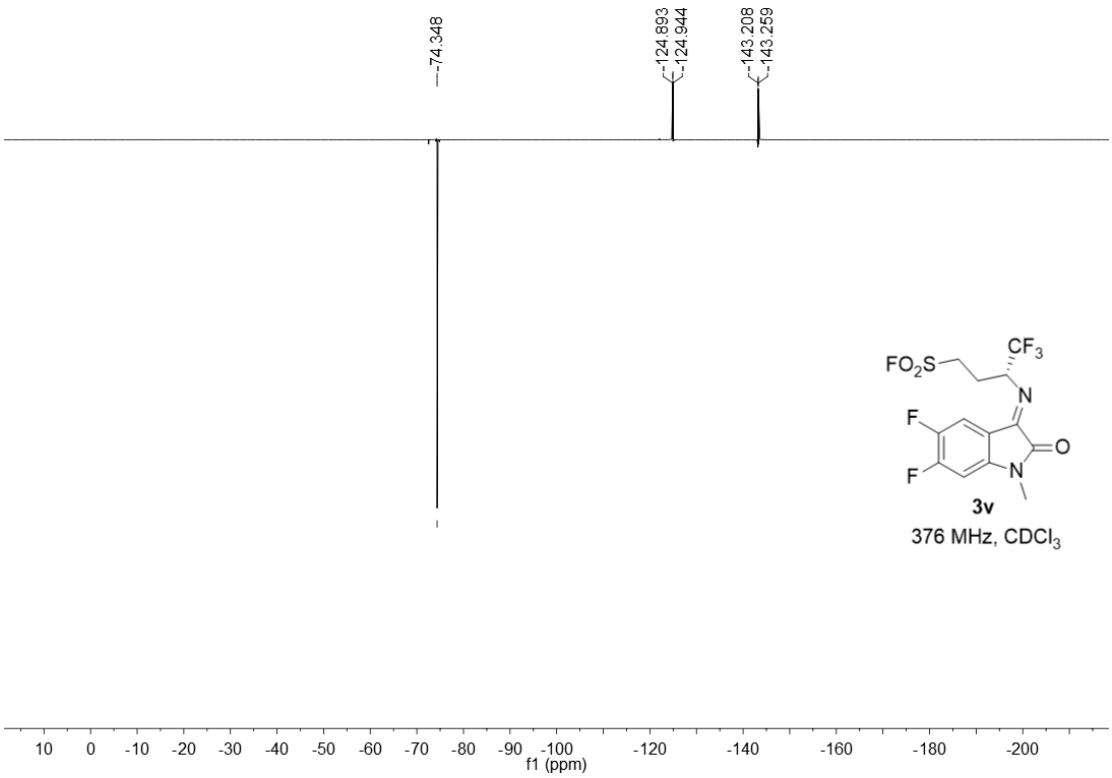


^{1}H, $^{13}C\{1H\}$ and ^{19}F $\{^{1}H, ^{13}C\}$NMR spectra of **3u**

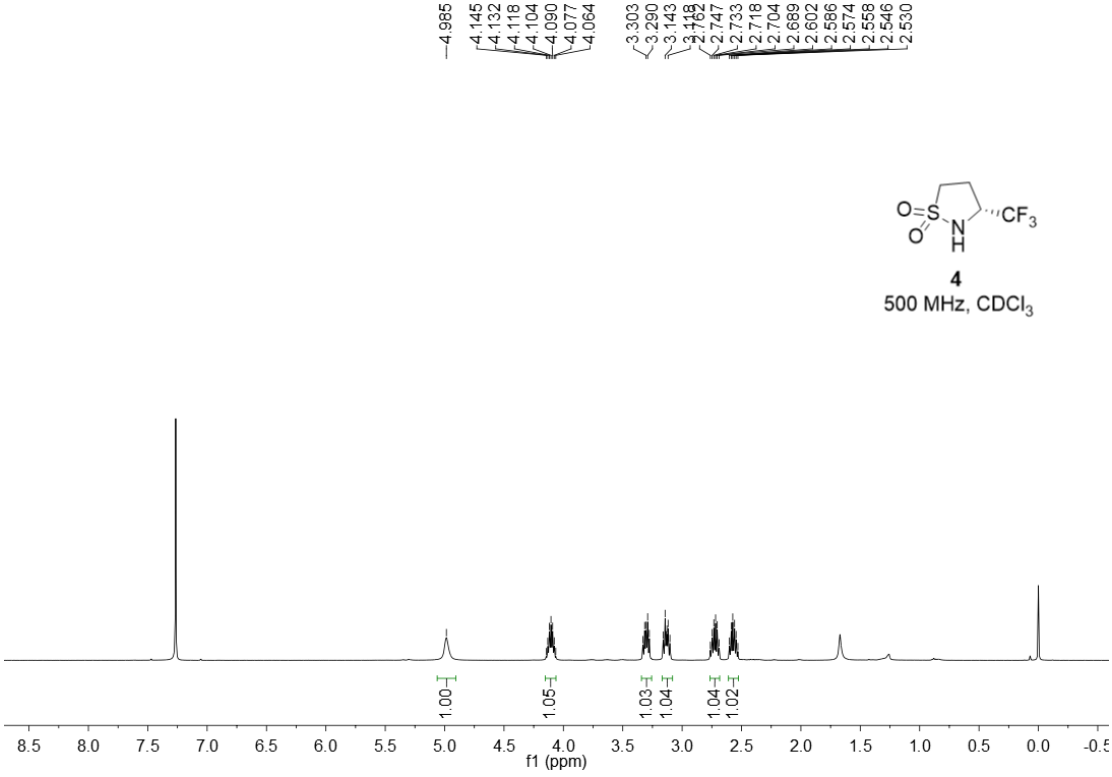


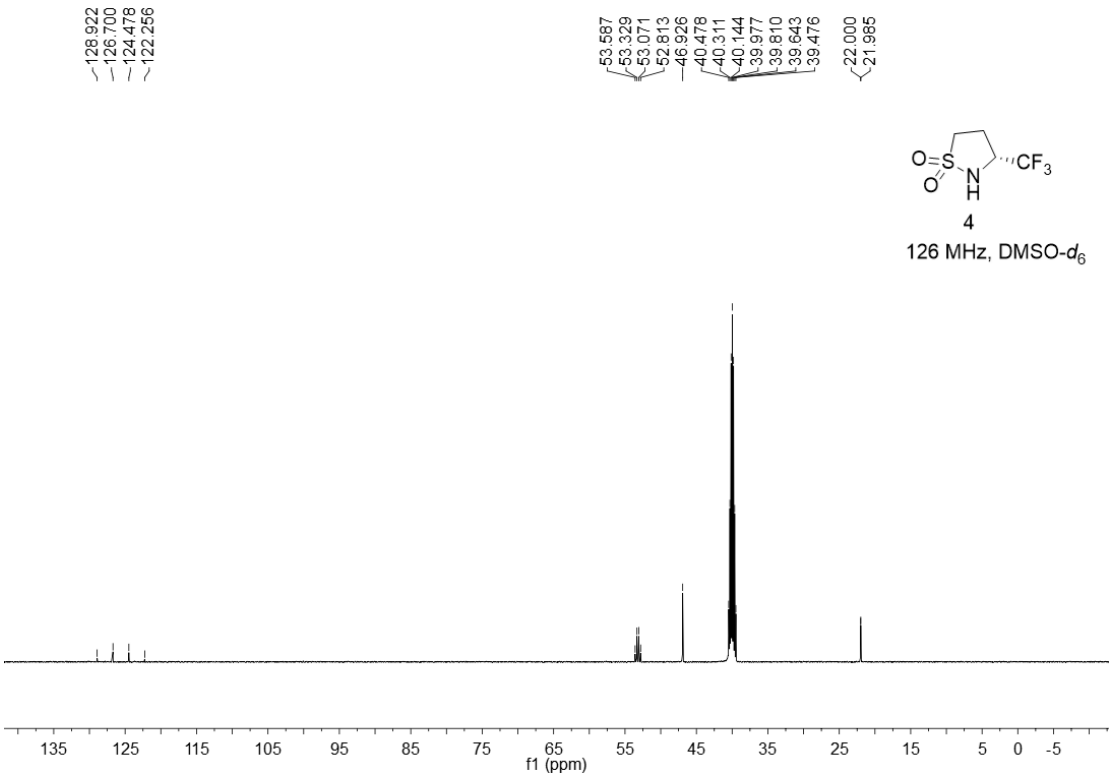

158.222
156.274
156.105
155.961
153.398
148.791
148.653
146.338
146.202
125.852
123.064
120.276
115.921
115.845
115.805
115.783
115.741
113.256
113.070
99.813
99.577
77.358
77.040
76.723
58.175
57.878
57.582
57.285
47.082
46.895
26.286
24.295
FO2S
CF3
N
F
F
O
N
3v
101 MHz, CDCl3
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

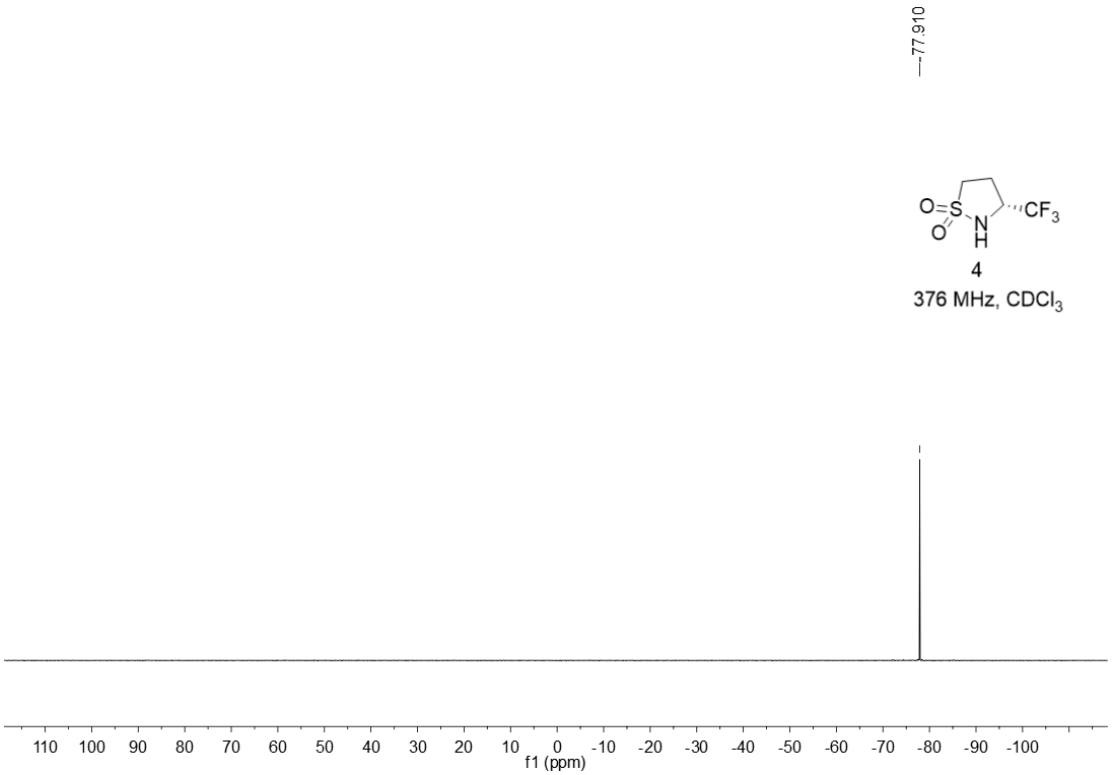

52.918
74.348
FO2S
CF3
N
F
F
O
N
3v
376 MHz, CDCl3
110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100
f1 (ppm)



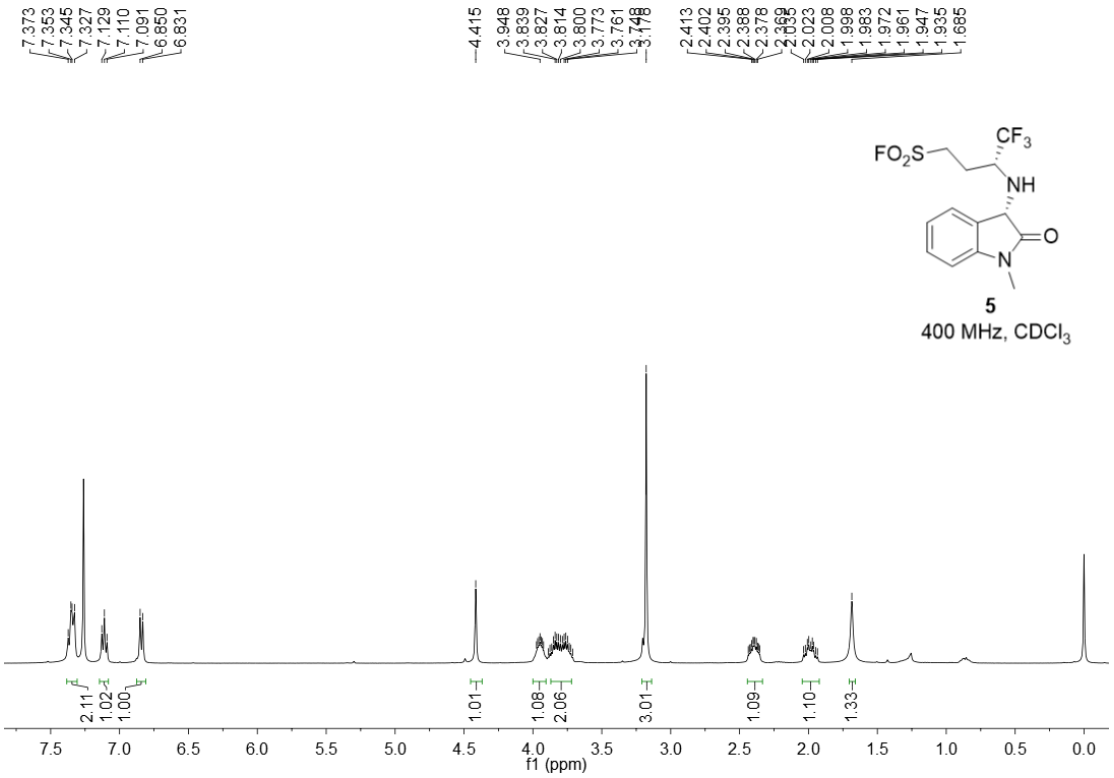
^{1}H,$^{13}C\{1H\}$ and ^{19}F $\{^{1}H, ^{13}C\}$NMR spectra of **3v**

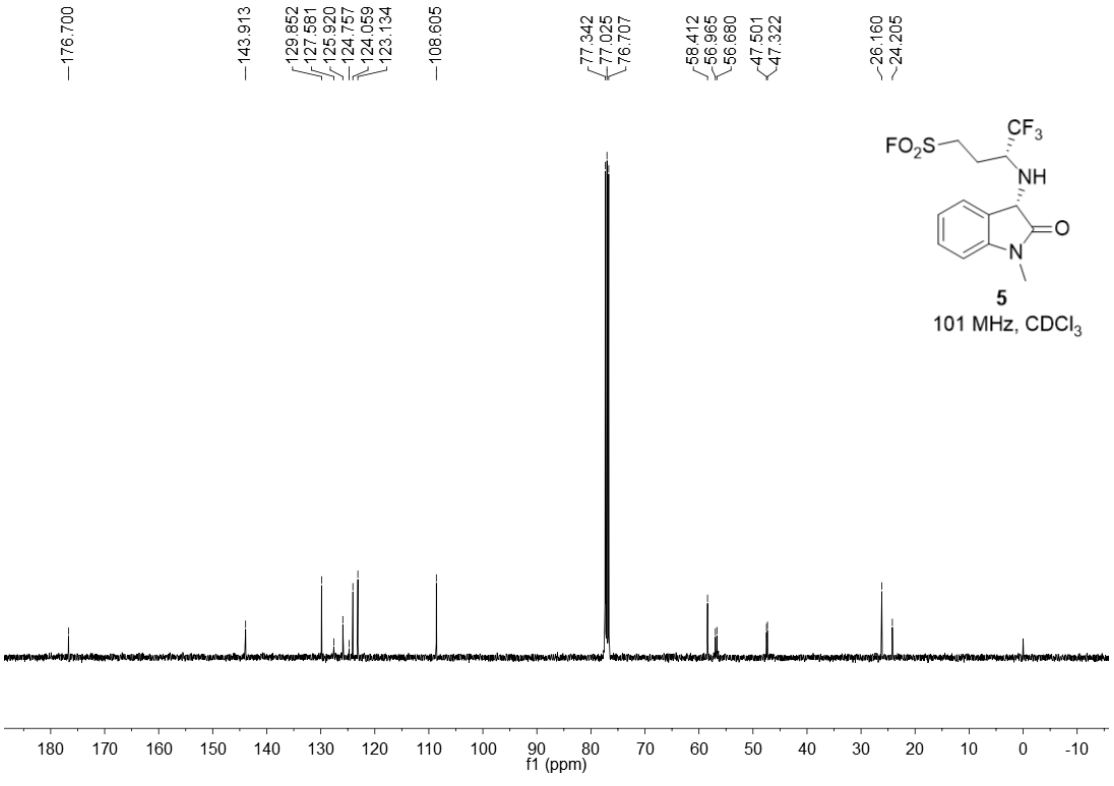


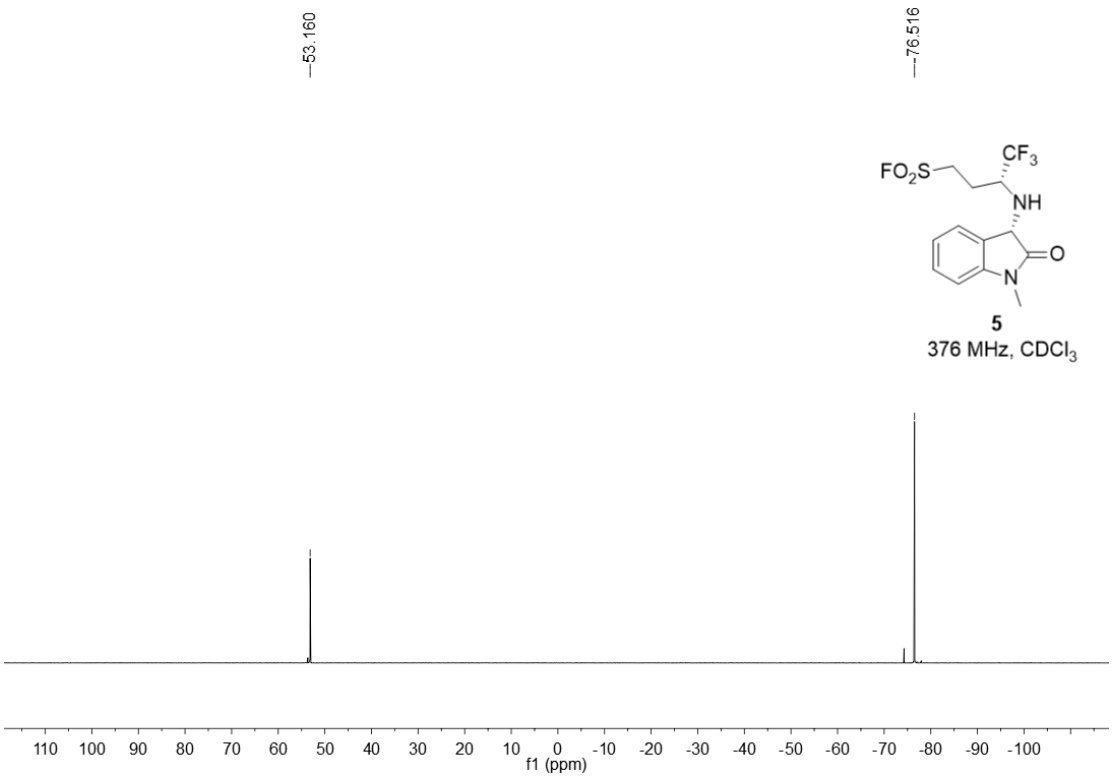




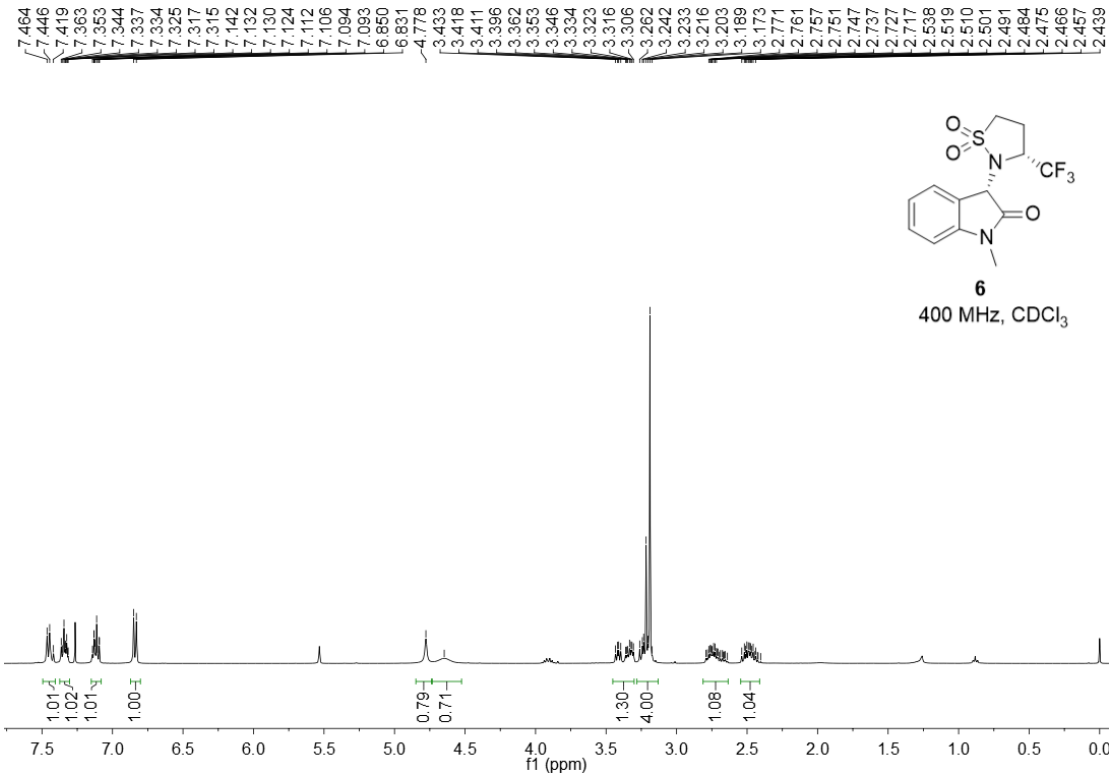
^{1}H, $^{13}C\{1H\}$ and $^{19}F\{^{1}H, ^{13}C\}$ NMR spectra of **4**

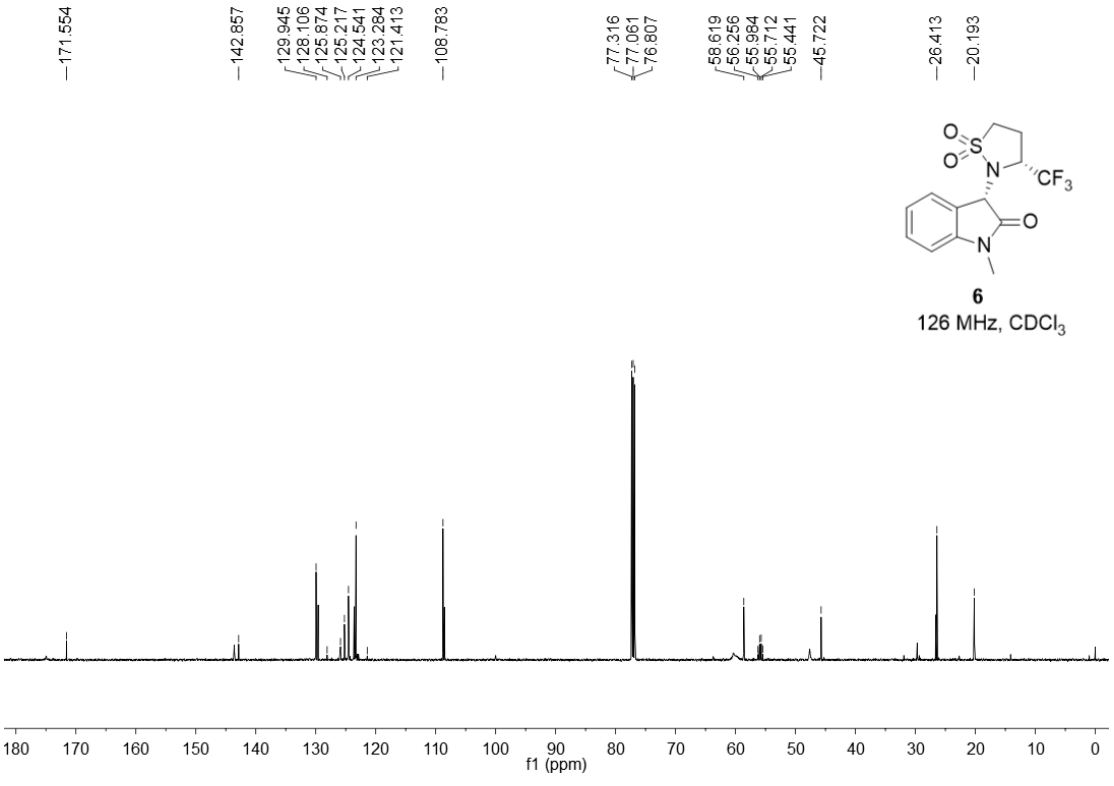

7.373
7.353
7.345
7.327
7.129
7.110
7.091
6.850
6.831
4.415
3.948
3.839
3.827
3.814
3.800
3.773
3.761
2.413
2.402
2.395
2.388
2.378
2.023
2.008
1.998
1.983
1.972
1.961
1.947
1.935
1.685
CF3
FO2S
NH
O
N
5
400 MHz, CDCl3
2.11
1.02
1.00
1.01
1.08
2.06
3.01
1.09
1.10
1.33
f1 (ppm)

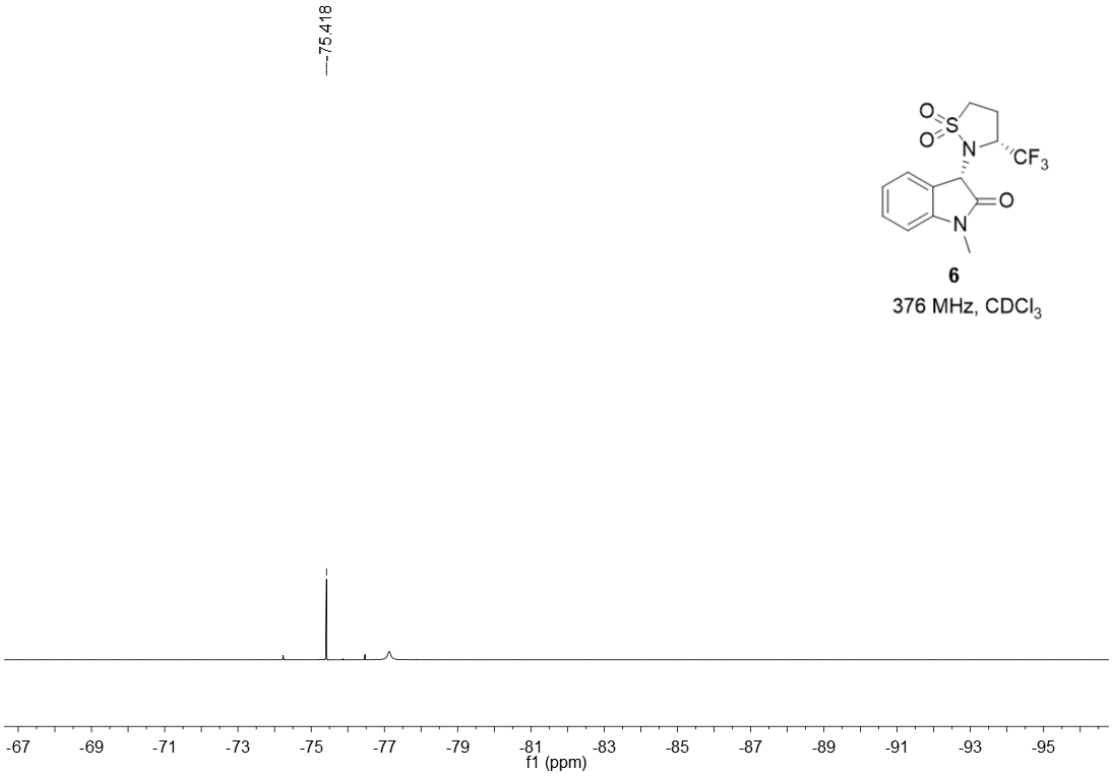

176.700
143.913
129.852
127.581
125.920
124.757
124.059
123.134
108.605
77.342
77.025
76.707
58.412
56.965
56.680
47.501
47.322
26.160
24.205
CF3
FO2S
NH
O
N
5
101 MHz, CDCl3
f1 (ppm)



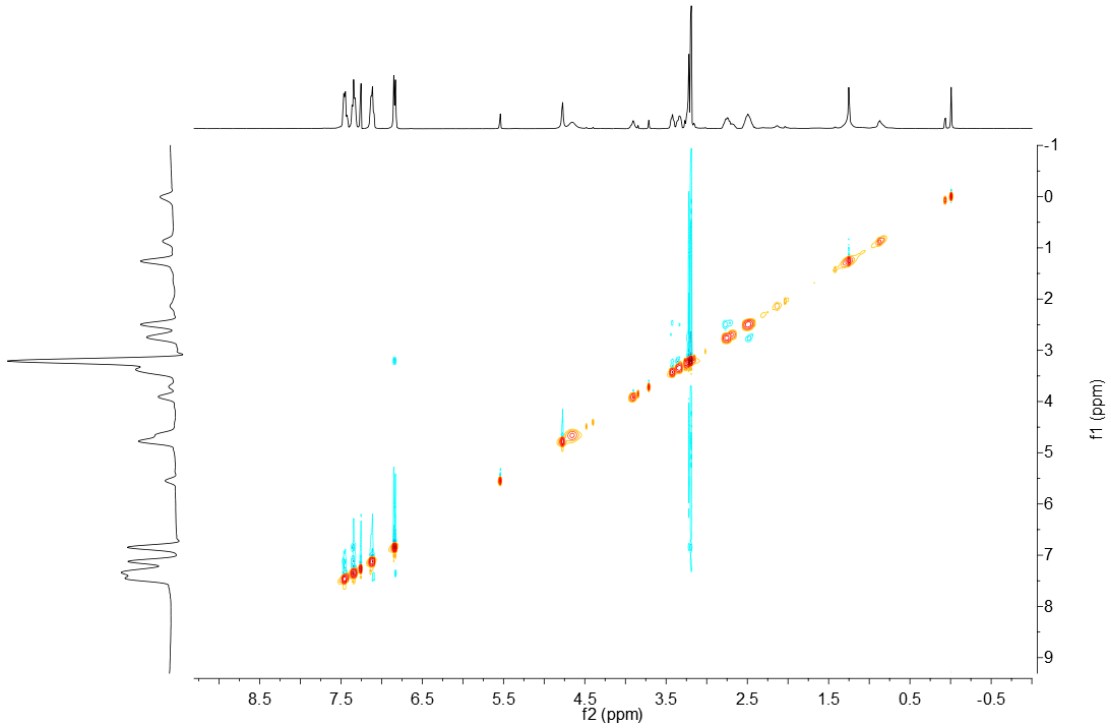
$^{1}H,^{13}C\{1H\}$ and ^{19}F $\{^{1}H, ^{13}C\}$NMR spectra of **5**

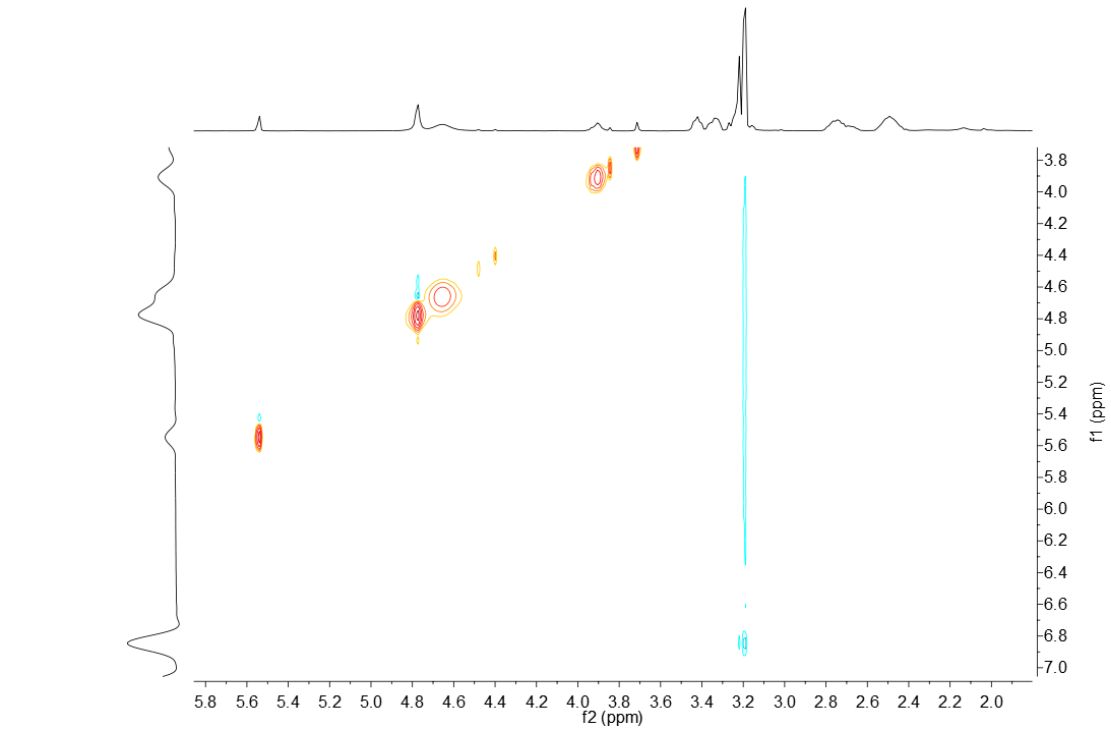

7.464
7.446
7.419
7.363
7.353
7.344
7.337
7.334
7.325
7.317
7.315
7.142
7.132
7.130
7.124
7.112
7.106
7.094
7.093
6.850
6.831
4.778
3.433
3.418
3.411
3.396
3.362
3.353
3.346
3.334
3.323
3.316
3.306
3.262
3.242
3.233
3.216
3.203
3.189
3.173
2.771
2.761
2.757
2.751
2.747
2.737
2.727
2.717
2.538
2.519
2.510
2.501
2.491
2.484
2.475
2.466
2.457
2.439
6
400 MHz, CDCl3
1.01
1.02
1.01
1.00
0.79
0.71
1.30
4.00
1.08
1.04
f1 (ppm)


171.554
142.857
129.945
128.106
125.874
125.217
124.541
123.284
121.413
108.783
77.316
77.061
76.807
58.619
56.256
55.984
55.712
55.441
45.722
26.413
20.193
6
126 MHz, CDCl3
f1 (ppm)



$^{1}H,^{13}C\{1H\}$ and ^{19}F $\{^{1}H, ^{13}C\}$NMR spectra of **6**





NOESY spetra of product **6**

4. The X-ray crystal data of product 3d

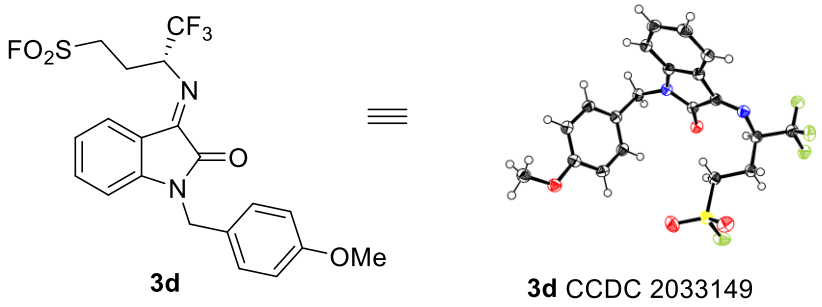
The absolute configuration of **3d** was determined by single crystal X-ray analysis. (CCDC 2033149 contains the supplementary crystallographic data for this structure. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre)
X-ray structure of product 3d (ellipsoid contour at 50% probability)

Experimental

Single crystals of **3d** ($C_{20}H_{18}F_4N_2O_4S$) were grown by slow evaporation in petroleum ether/CH_2Cl_2 = 8 /1 under air atmosphere. A suitable crystal was selected and mounted on a XtaLAB Synergy R, DW system, HyPix diffractometer. The crystal was kept at 100.00(10) K during data collection. Using Olex2, the structure was solved with the ShelXS structure solution program using Direct Methods and refined with the ShelXL refinement package using Least Squares minimisation.

Crystal structure determination of 3d

Crystal Data for $C_{20}H_{18}F_4N_2O_4S$ (M =458.42 g/mol): monoclinic, space group P21 (no. 4), a = 4.90510(10) Å, b = 18.8099(3) Å, c = 10.9514(2) Å, β = 95.3540(10)°, V = 1006.02(3) Å3, Z = 2, T = 100.00(10) K, μ(CuKα) = 2.054 mm-1, Dcalc = 1.513 g/cm3, 20562 reflections measured (8.108° ≤ 2Θ ≤ 153.936°), 4168 unique (Rint = 0.0479, Rsigma = 0.0328) which were used in all calculations. The final R1 was 0.0355 (I > 2σ(I)) and wR2 was 0.0982 (all data).



Crystal data and structure refinement for 3d.

Empirical formula	$C_{20}H_{18}F_4N_2O_4S$
Formula weight	458.42
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	4.90510(10)
b/Å	18.8099(3)

c/Å	10.9514(2)
α/°	90
β/°	95.3540(10)
γ/°	90
Volume/Å^3	1006.02(3)
Z	2
ρ_{calc}g/cm^3	1.513
μ/mm^{-1}	2.054
F(000)	472.0
Crystal size/mm^3	0.3 × 0.15 × 0.05
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.108 to 153.936
Index ranges	-6 ≤ h ≤ 6, -23 ≤ k ≤ 23, -13 ≤ l ≤ 12
Reflections collected	20562
Independent reflections	4168 [R_{int} = 0.0479, R_{sigma} = 0.0328]
Data/restraints/parameters	4168/1/281
Goodness-of-fit on F^2	1.073
Final R indexes [I>=2σ (I)]	R_1 = 0.0355, wR_2 = 0.0970
Final R indexes [all data]	R_1 = 0.0365, wR_2 = 0.0982
Largest diff. peak/hole / e Å^{-3}	0.30/-0.36
Flack parameter	-0.025(10)

5. The X-ray crystal data of product 5

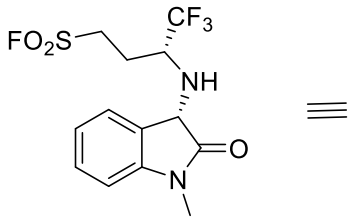
The absolute configuration of **5** was determined by single crystal X-ray analysis. (CCDC 2033148 contains the supplementary crystallographic data for this structure. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre)
X-ray structure of product **5** (ellipsoid contour at 50% probability)

Experimental

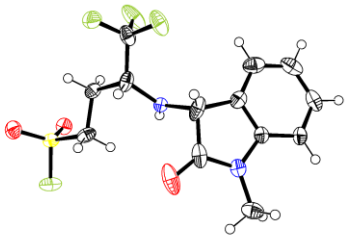
Single crystals of **5** ($C_{13}H_{14}F_4N_2O_3S$) were grown by slow evaporation in petroleum ether/CH_2Cl_2 = 8 /1 under air atmosphere. A suitable crystal was selected and mounted on a XtaLAB Synergy R, DW system, HyPix diffractometer. The crystal was kept at 100.00(10) K during data collection. Using Olex2, the structure was solved with the ShelXS structure solution program using Direct Methods and refined with the ShelXL refinement package using Least Squares minimisation.

Crystal structure determination of 5

Crystal Data for $C_{13}H_{14}F_4N_2O_3S$ (M =354.32 g/mol): orthorhombic, space group P212121 (no. 19), a = 5.25068(4) Å, b = 12.41283(9) Å, c = 22.58089(17) Å, V = 1471.729(19) Å3, Z = 4, T = 100.00(10) K, μ(CuKα) = 2.554 mm-1, Dcalc = 1.599 g/cm3, 15352 reflections measured (7.83° ≤ 2Θ ≤ 153.726°), 3066 unique (Rint = 0.0295, Rsigma = 0.0186) which were used in all calculations. The final R1 was 0.0319 (I > 2 σ (I)) and wR2 was 0.0835 (all data).



5



5 CCDC 2033148

Crystal data and structure refinement for 5.

Empirical formula	$C_{13}H_{14}F_4N_2O_3S$
Formula weight	354.32
Temperature/K	100.00(10)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	5.25068(4)
b/Å	12.41283(9)
c/Å	22.58089(17)
α /°	90

β /°	90
γ /°	90
Volume/Å^3	1471.729(19)
Z	4
ρ_{calc}g/cm^3	1.599
μ /mm^{-1}	2.554
F(000)	728.0
Crystal size/mm^3	0.2 × 0.05 × 0.05
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.83 to 153.726
Index ranges	-5 ≤ h ≤ 6, -15 ≤ k ≤ 15, -28 ≤ l ≤ 28
Reflections collected	15352
Independent reflections	3066 [R_{int} = 0.0295, R_{sigma} = 0.0186]
Data/restraints/parameters	3066/0/220
Goodness-of-fit on F^2	1.098
Final R indexes [I>=2σ (I)]	R_1 = 0.0319, wR_2 = 0.0818
Final R indexes [all data]	R_1 = 0.0333, wR_2 = 0.0835
Largest diff. peak/hole / e Å^{-3}	0.34/-0.34
Flack parameter	-0.012(8)