Supporting Information

Synthesis of Di/Trifluoromethyl Bis(1,2,4-triazoline)spiranes and 1,2,4-Triazoles via 1,3-Dipolar Cycloaddition of Nitrilimines and Carbodiimides

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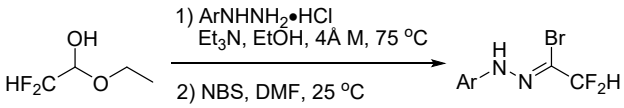
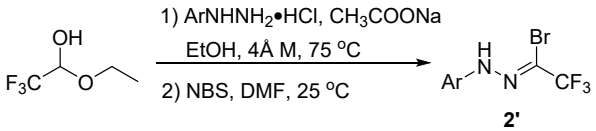
Synthesis of Difluoroacetohydrazonoyl Bromides 2[1]



Step 1: A mixture of hydrazine hydrochlorides (1.0 mmol, 1.0 equiv.), triethylamine (1.0 mmol, 1.0 equiv.), difluoroacetaldehyde ethyl hemiacetal (1.5 mmol, 1.5 equiv.), and freshly activated 4Å molecular sieves in EtOH (8 mL) was stirred at 75 °C in a round-bottom in an oil bath, and the reaction was monitored by TLC. After the reaction was completed, the solvent was removed in vacuo to afford intermediate products, which was used directly for the next step.

Step 2: To a solution of crude mixture from step 1 in DMF (8 mL) was added NBS. The resulting solution was stirred at room temperature, and the reaction was monitored by TLC. After the reaction was completed, the reaction was quenched with sat. NaCl aq., and the mixture was extracted with ethyl acetate (3 × 15 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo. The resulting products was purified by column chromatography on silica gel (EA)/petroleum ether (PE) (1:10−1:20) to afford difluoroacetohydrazonoyl bromides **2**.

Synthesis of Trifluoroacetohydrazonoyl Bromides 2′[2]



Step 1: A mixture of hydrazine hydrochlorides (2.0 mmol, 1.0 equiv.), triethylamine (1.0 mmol, 1.0 equiv.), trifluoroacetaldehyde ethyl hemiacetal (1.5 mmol, 1.5 equiv.), and freshly activated molecular sieves 4Å in EtOH (8 mL) was stirred at 75 °C in a round-bottom in an oil bath, and the reaction was monitored by TLC. After the reaction was completed, the solvent was removed in vacuo to afford intermediate products, which was used directly for the next step.

Step 2: To a solution of crude mixture from step 1 in DMF (8 mL) was added NBS (2.2 mmol, 1.1 equiv.). The resulting solution was stirred at room temperature, and the reaction was monitored by TLC. After the reaction was completed, the reaction was

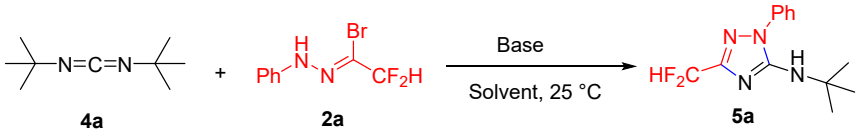
quenched with sat. NaCl aq., and the mixture was extracted with ethyl acetate (3 × 15 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo. The resulting products was purified by column chromatography on silica gel (EA)/petroleum ether (PE) (1:8−1:20) to afford trifluoroacetohydrazonoyl bromides **2′**.

References

[1] Tanaka, K.; Maeno, S.; Mitsuhashi, K. Cycloadditions of N-Aryl-C (Trifluoromethyl)nitrilimines with Dimethyl Fumarate and Maleate. *J. Heterocyclic Chem.* **1985**, *22*, 565.

[2] Mlostoń, G.; Urbaniak, K.; Utecht, G.; Lentz, D.; Jasinski, M. Trifluoromethylated 2,3-dihydro-1,3,4-thiadiazoles via the regioselective (3+2)-cycloadditions of fluorinated nitrile imines with aryl, hetaryl, and ferrocenyl thioketones. *J. Fluorine Chem*. **2016**, *192*, 147.

Table S1 Optimization of reaction conditions for synthesis of **5a**[a].

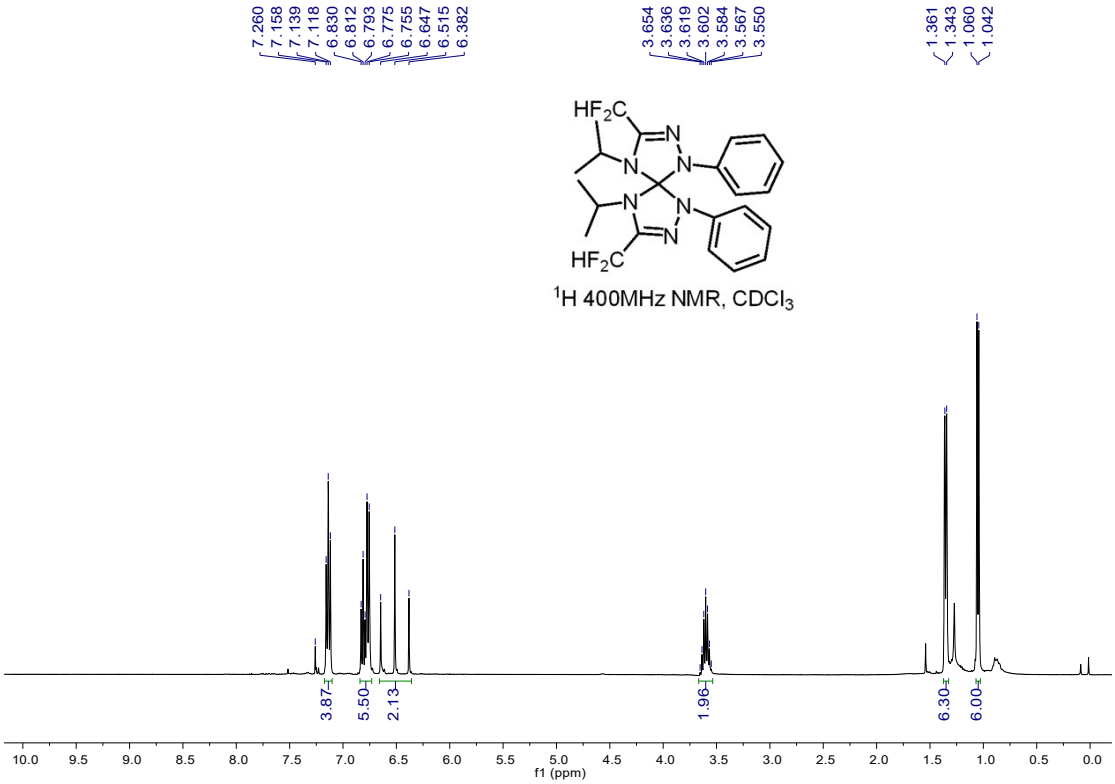


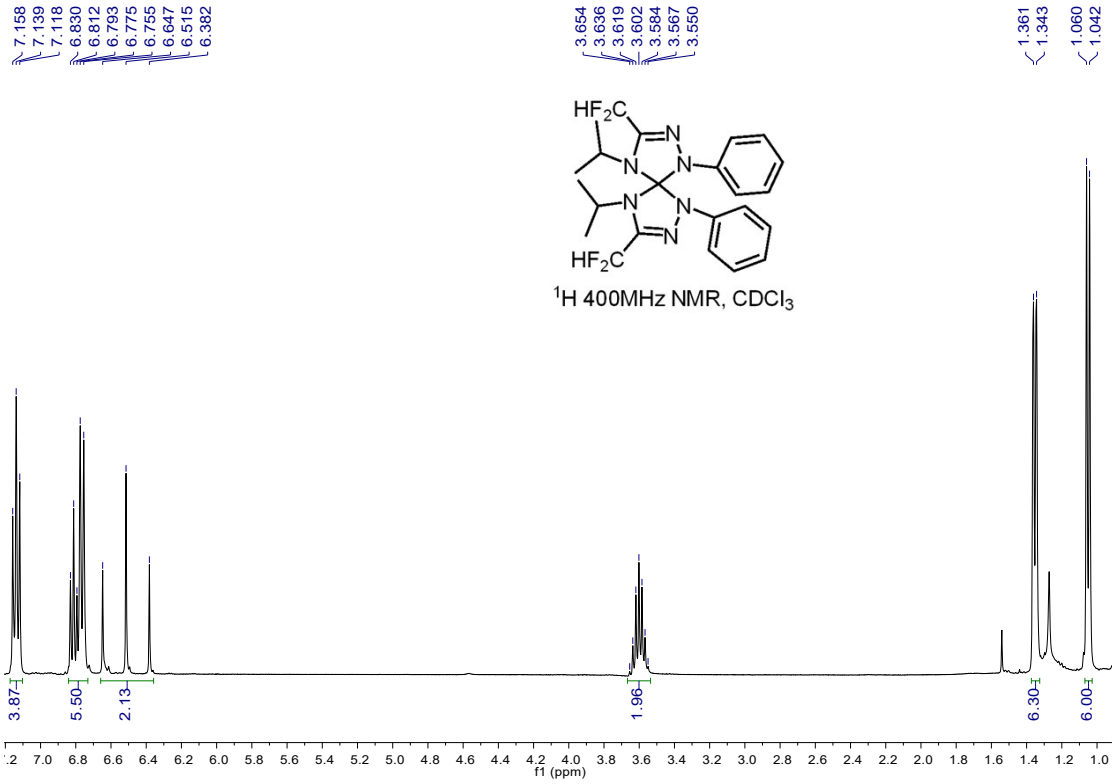
Entry	Mole ratio of **4a**/**2a**/base	Base	Solvent	Time (h)	Yield[b] (%) **5a**
1	1/2.5/2.5	K_2CO_3	DCM	18	45
2	1/1.2/1.2	K_2CO_3	DCM	10	65
3	1/1.0/1.0	K_2CO_3	DCM	10	49
4	1/1.2/1.2	Na_2CO_3	DCM	10	52
5	1/1.2/1.2	Cs_2CO_3	DCM	7	46
6	1/1.2/1.2	$NaHCO_3$	DCM	10	58
7	1/1.2/1.2	Et_3N	DCM	10	31
8	1/1.2/1.2	K_2CO_3	THF	10	trace
9	1/1.2/1.2	K_2CO_3	1,4-dioxane	10	80
10	1/1.2/1.2	K_2CO_3	MeCN	10	45

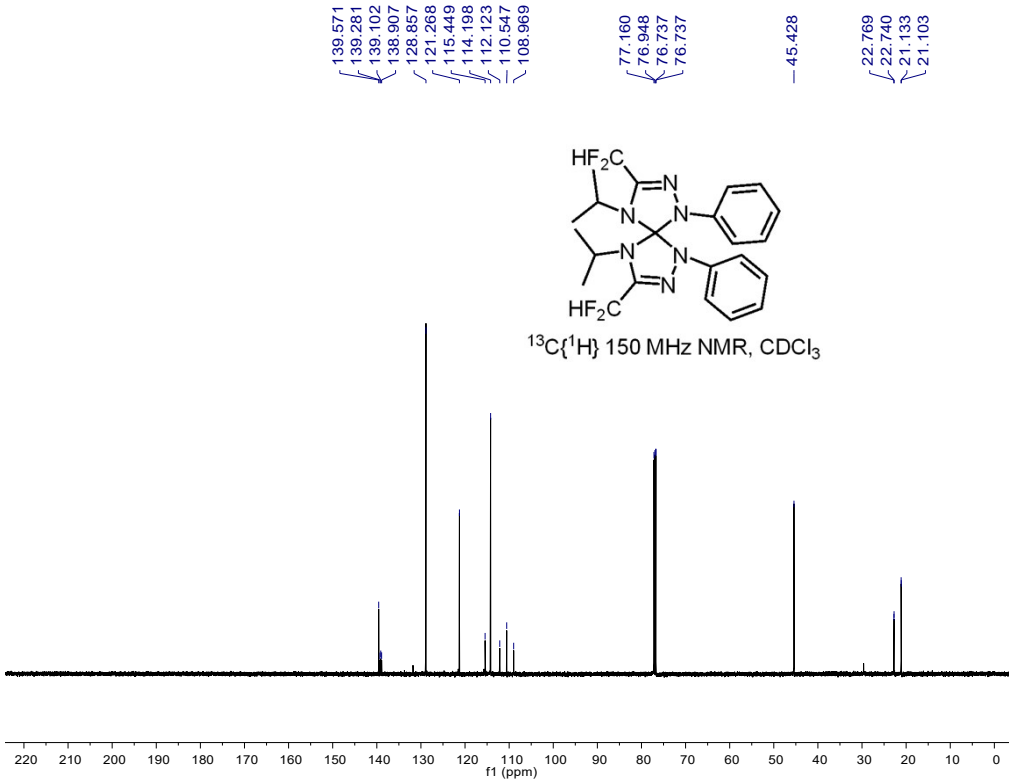
[a]Reaction conditions: **4a** (0.2 mmol, 1.0 equiv.), **2a** (0.2−0.5 mmol), base (0.2−0.5 mmol), solvent (3 mL), 25 °C, air atmosphere. [b]Isolated yields after chromatographic purification.

Copies of NMR and HRMS Spectra for Compounds **3**

NMR copies of compound **3a**:



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76.948
76.737
76.737
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22.740
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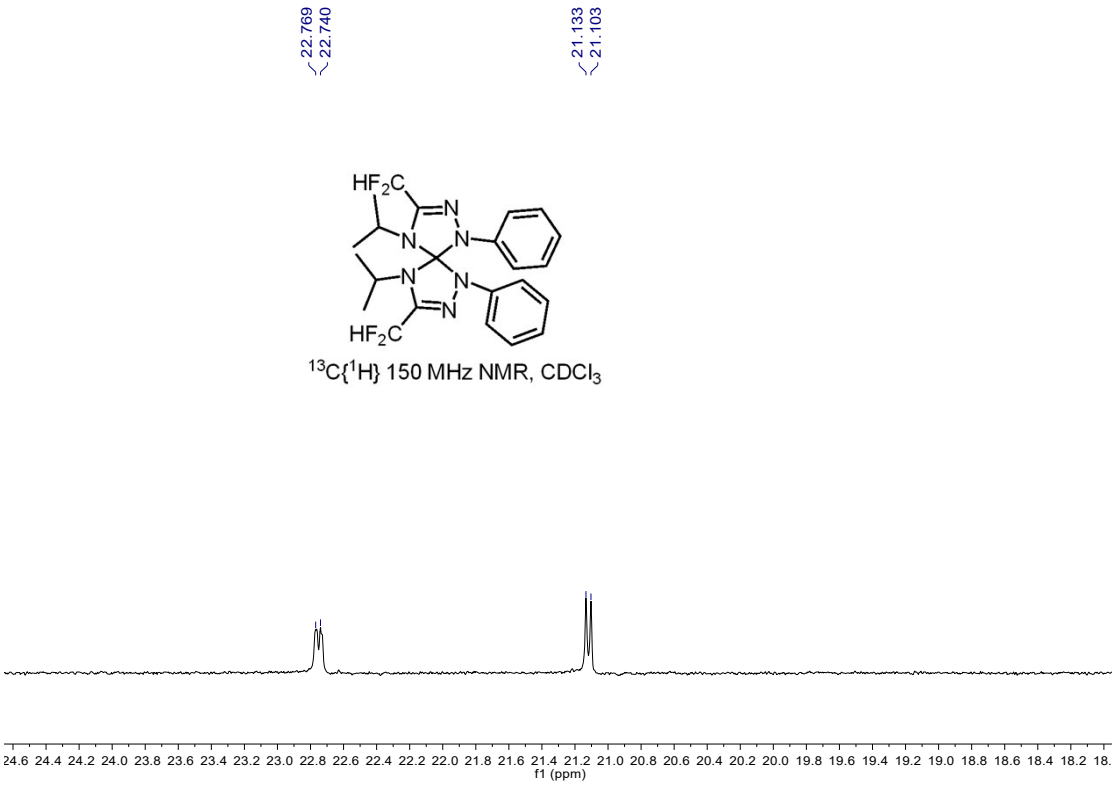
HF2C
13C{1H} 150 MHz NMR, CDCl3
f1 (ppm)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22.740
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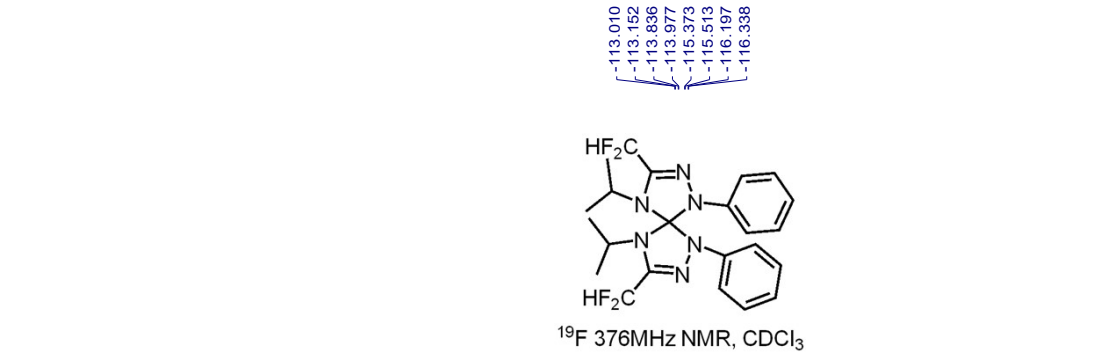
HF2C
HF2C
13C{1H} 150 MHz NMR, CDCl3
f1 (ppm)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-113.977
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-116.197
-116.338
HF2C
N
N
N
N
N
HF2C
19F 376MHz NMR, CDCl3
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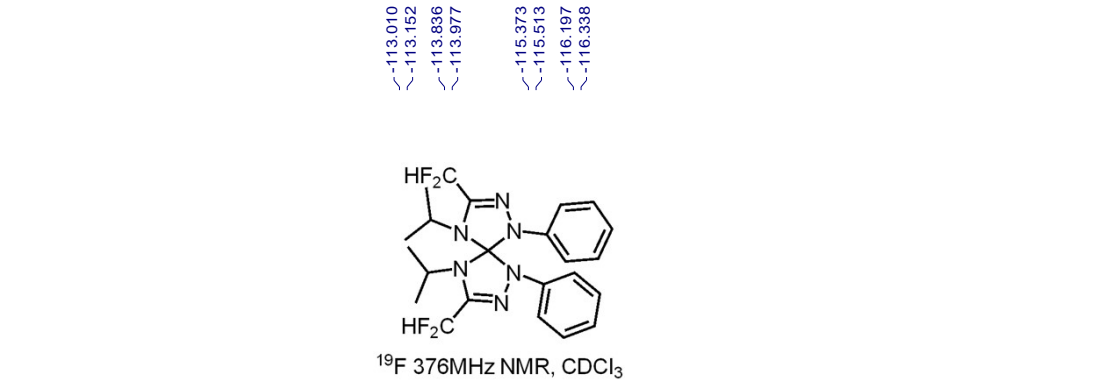
f1 (ppm)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-113.152
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-116.338
HF2C
N
N
N
N
N
HF2C
19F 376MHz NMR, CDCl3
-106 -107 -108 -109 -110 -111 -112 -113 -114 -115 -116 -117 -118 -119 -120 -121 -122 -123 -124 -125
f1 (ppm)

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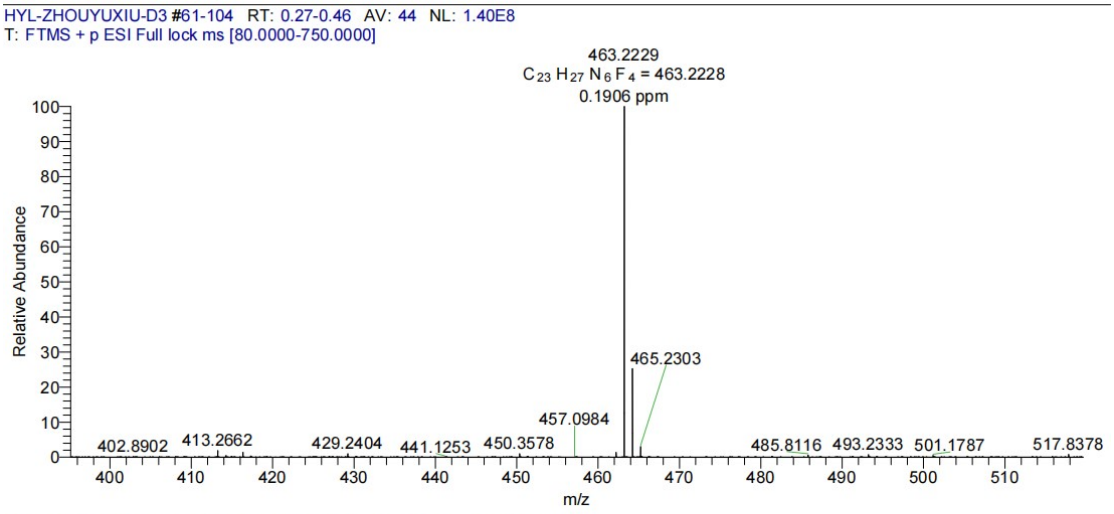

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m/z= 395.1615-519.6030

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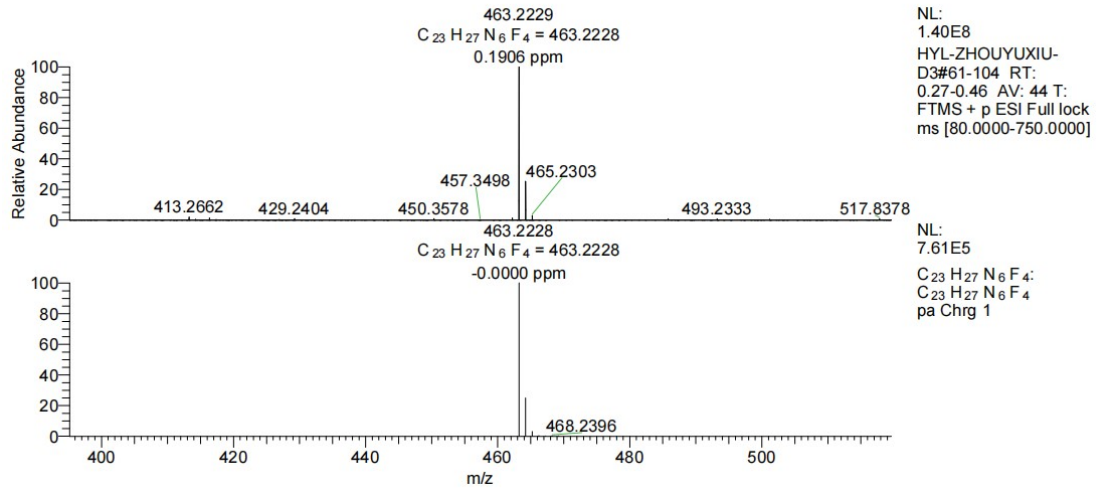
463.2229	143089616.0	100.00	463.2228	0.09	$C_{23}H_{27}N_6F_4$
464.2264	35608896.0	24.89			
465.2303	4204837.0	2.94			



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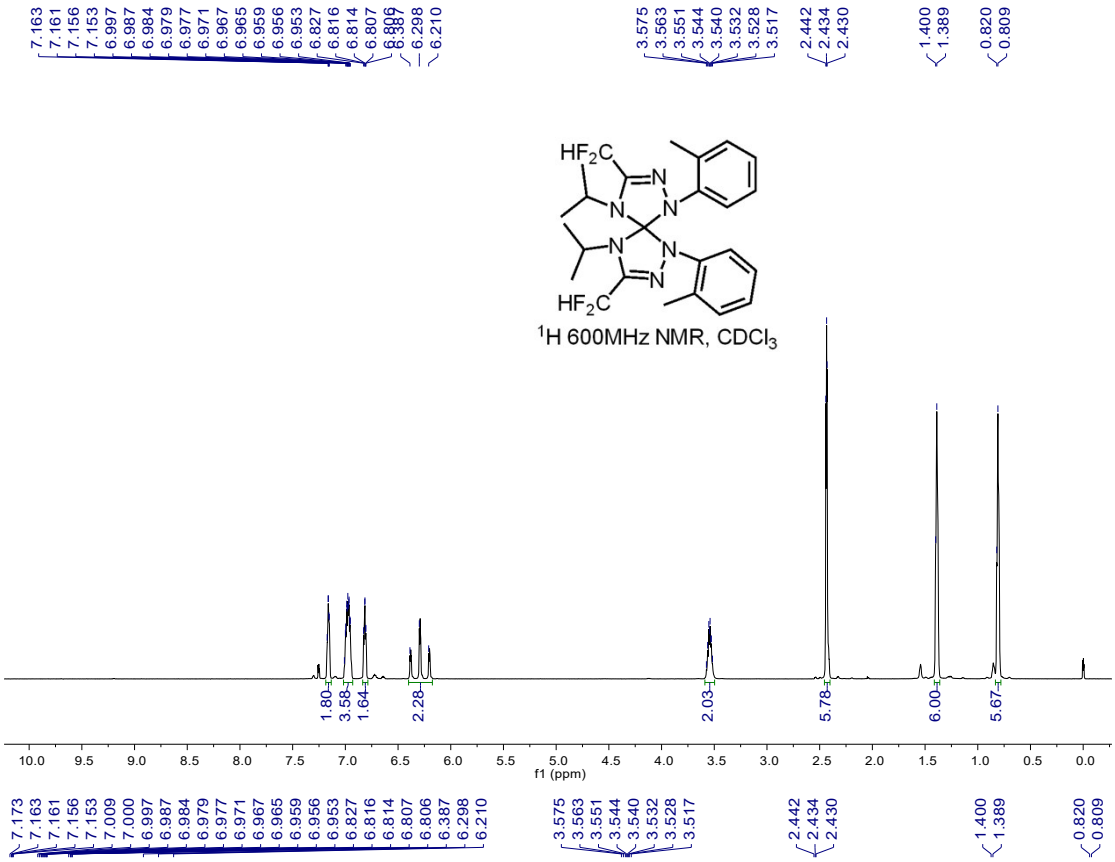

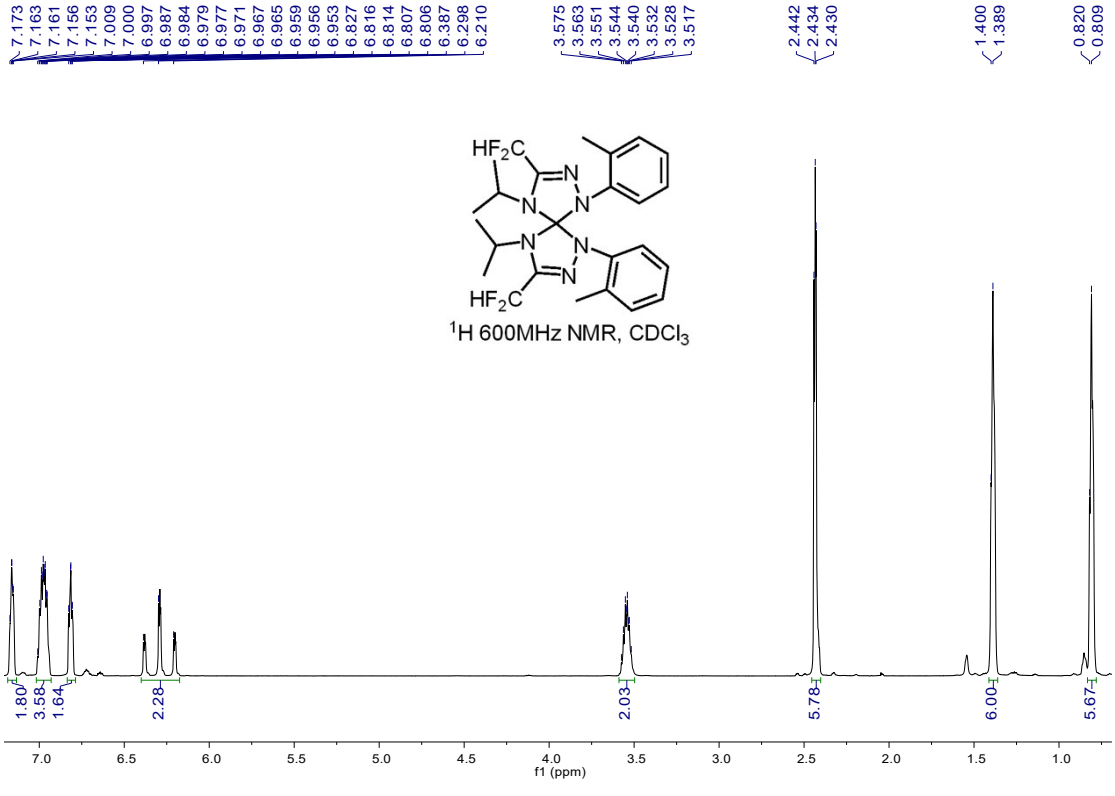

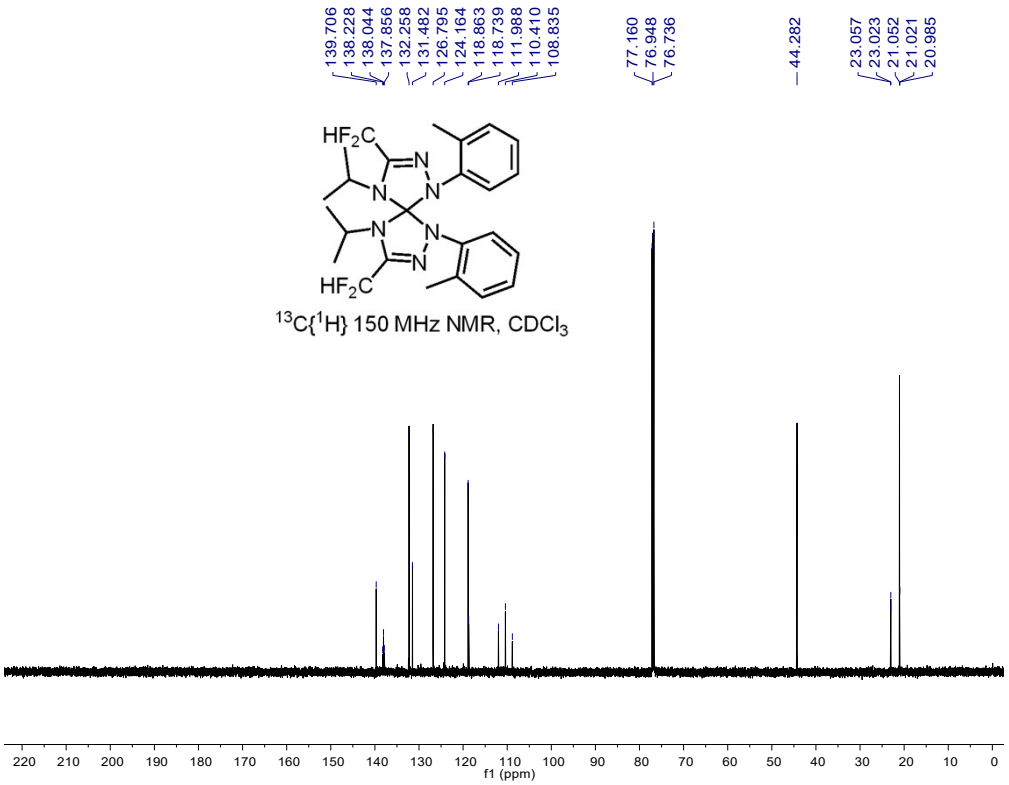
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131.482
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124.164
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118.739
111.988
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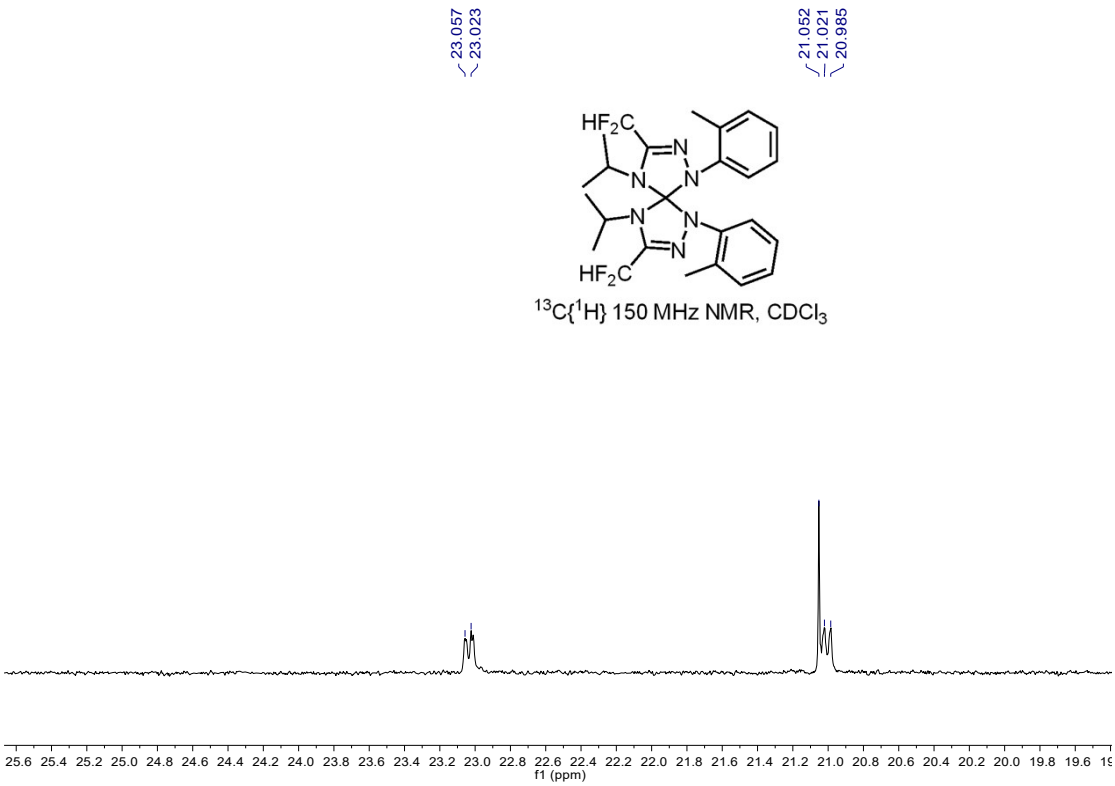
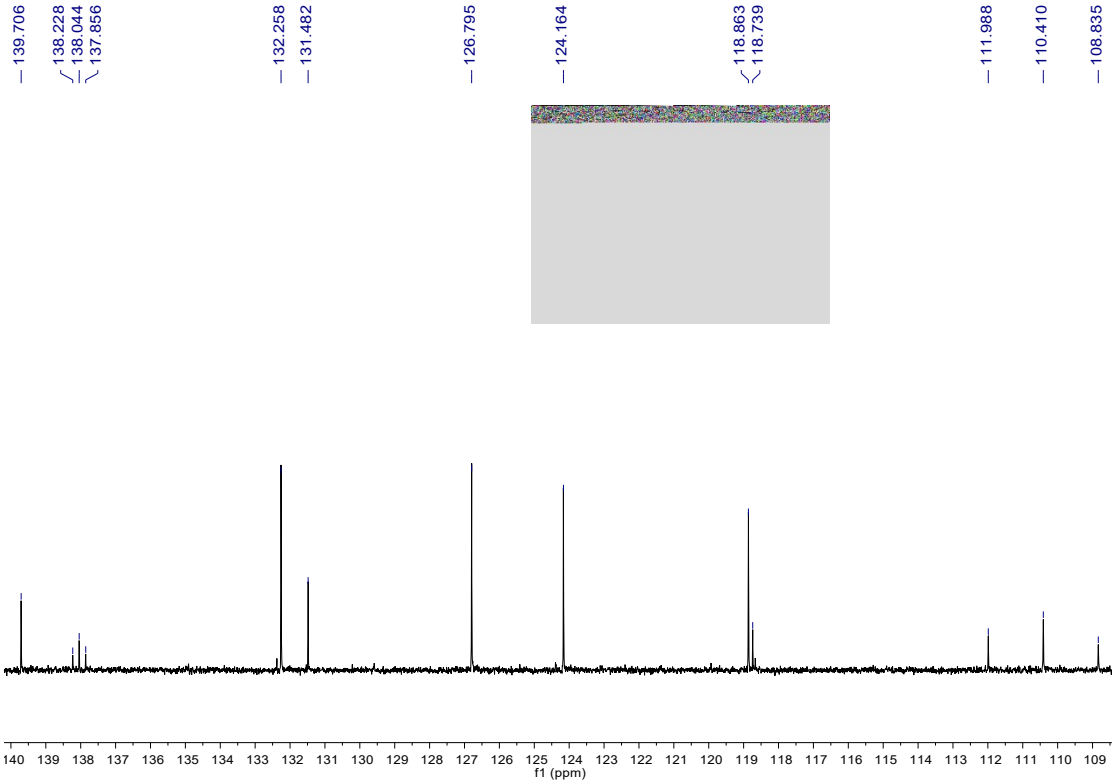
77.160
76.948
76.736
44.282
23.057
23.023
21.052
21.021
20.985
HF2C
HF2C
13C{1H} 150 MHz NMR, CDCl3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


23.057
23.023
21.052
21.021
20.985
HF2C
HF2C
13C{1H} 150 MHz NMR, CDCl3
25.6 25.4 25.2 25.0 24.8 24.6 24.4 24.2 24.0 23.8 23.6 23.4 23.2 23.0 22.8 22.6 22.4 22.2 22.0 21.8 21.6 21.4 21.2 21.0 20.8 20.6 20.4 20.2 20.0 19.8 19.6
f1 (ppm)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118.739
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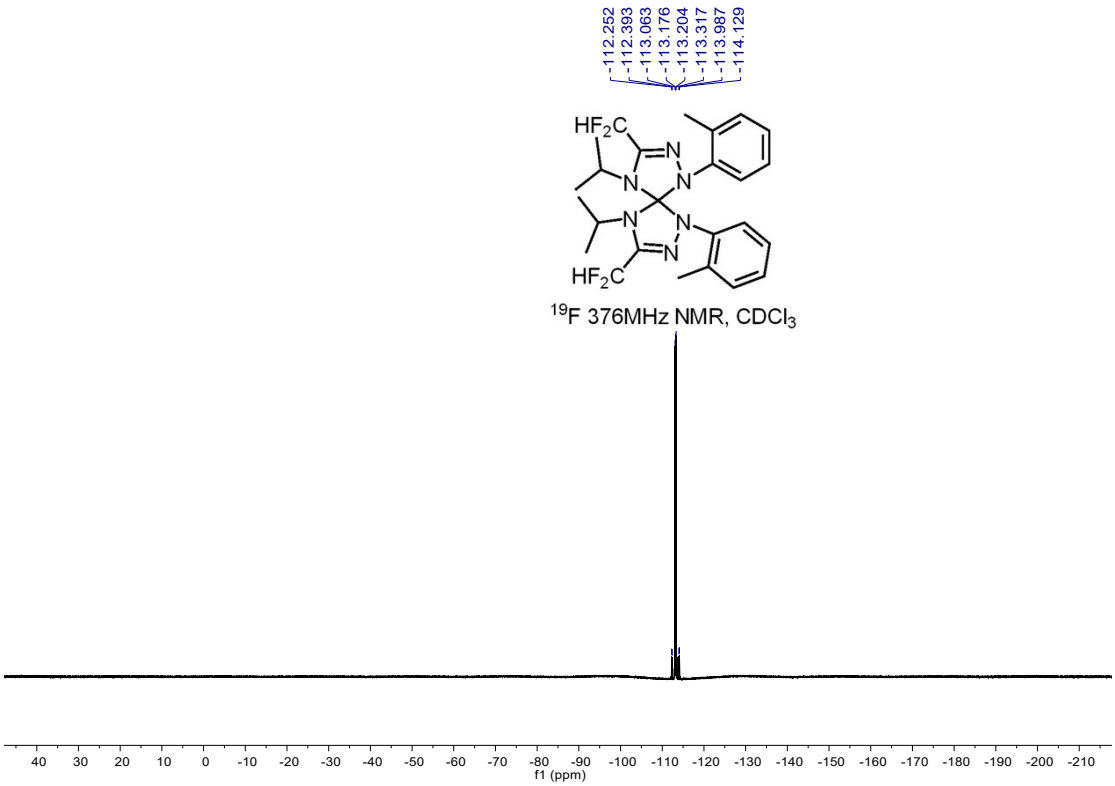
f1 (ppm)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N
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N
N
N
N
HF2C
19F 376MHz NMR, CDCl3
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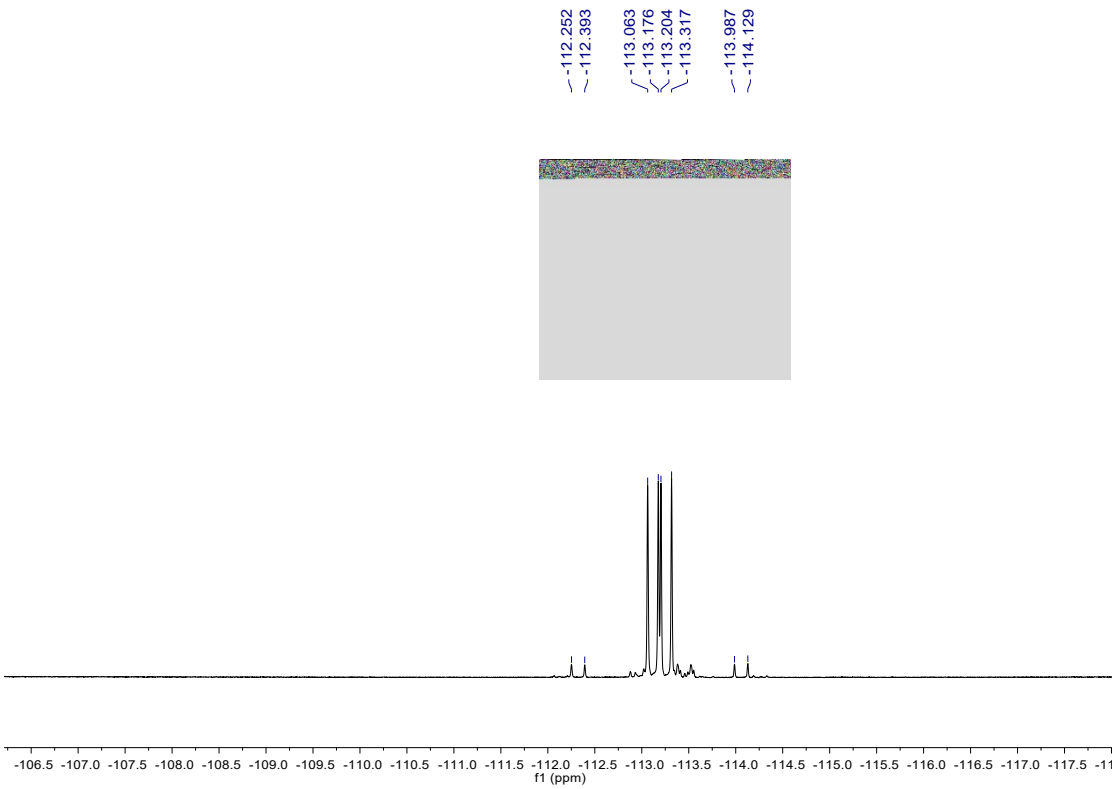
f1 (ppm)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-114.129
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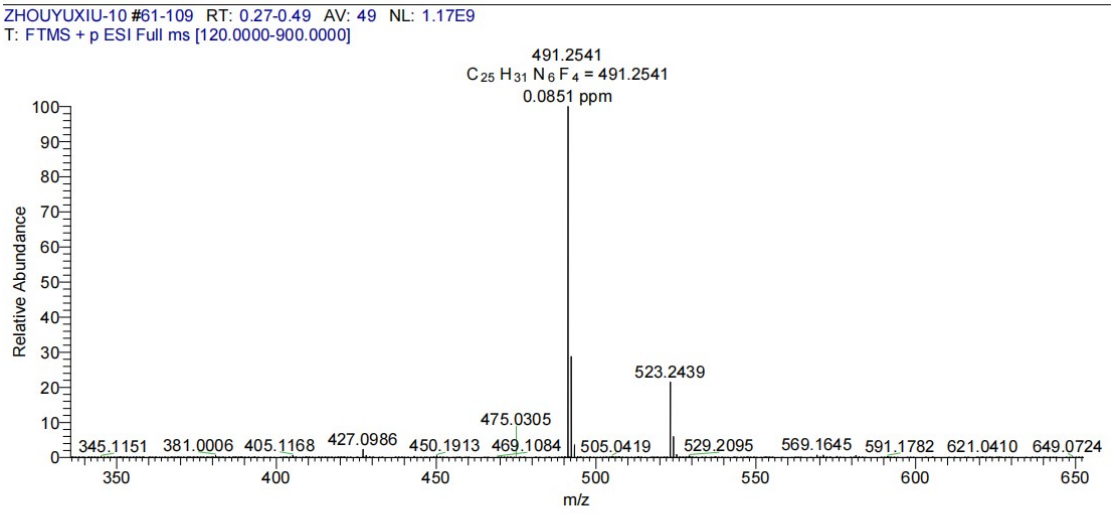
f1 (ppm)

HRMS (ESI) copy of compound **3b**:



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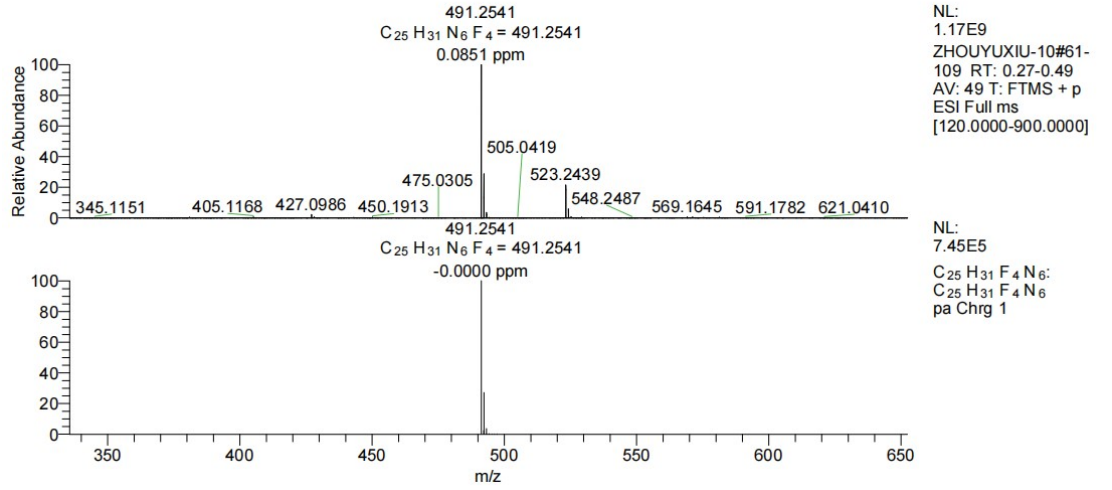

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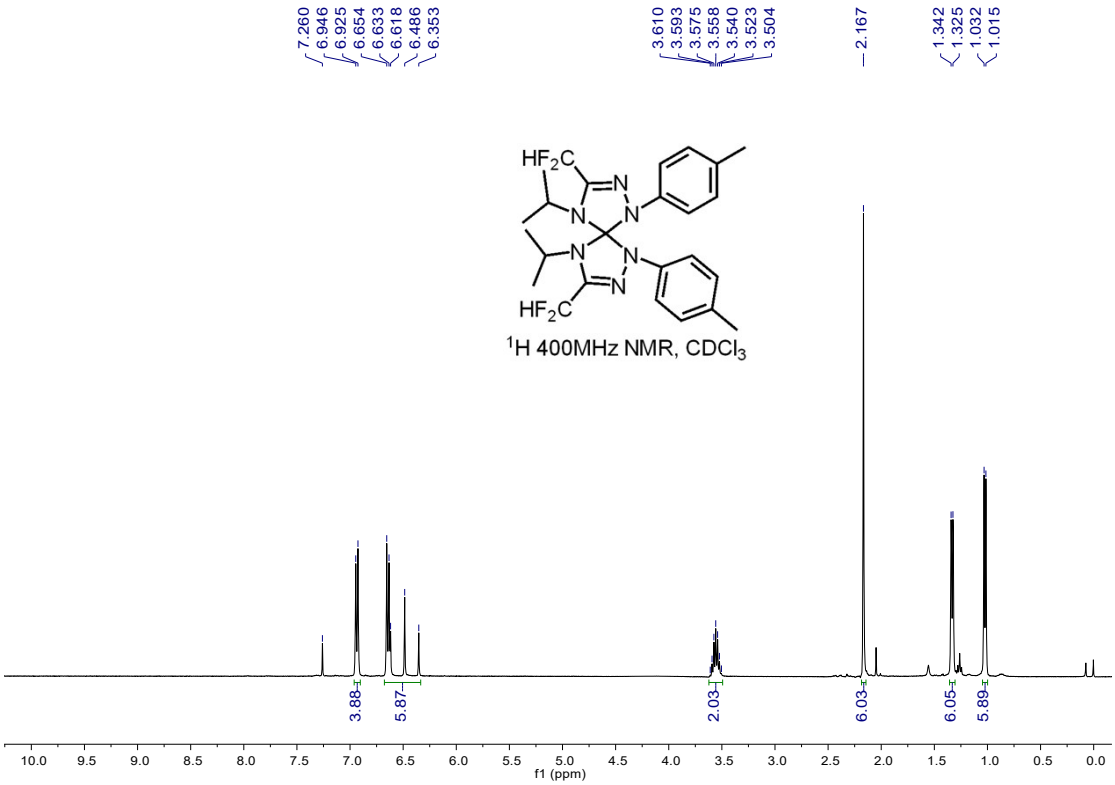

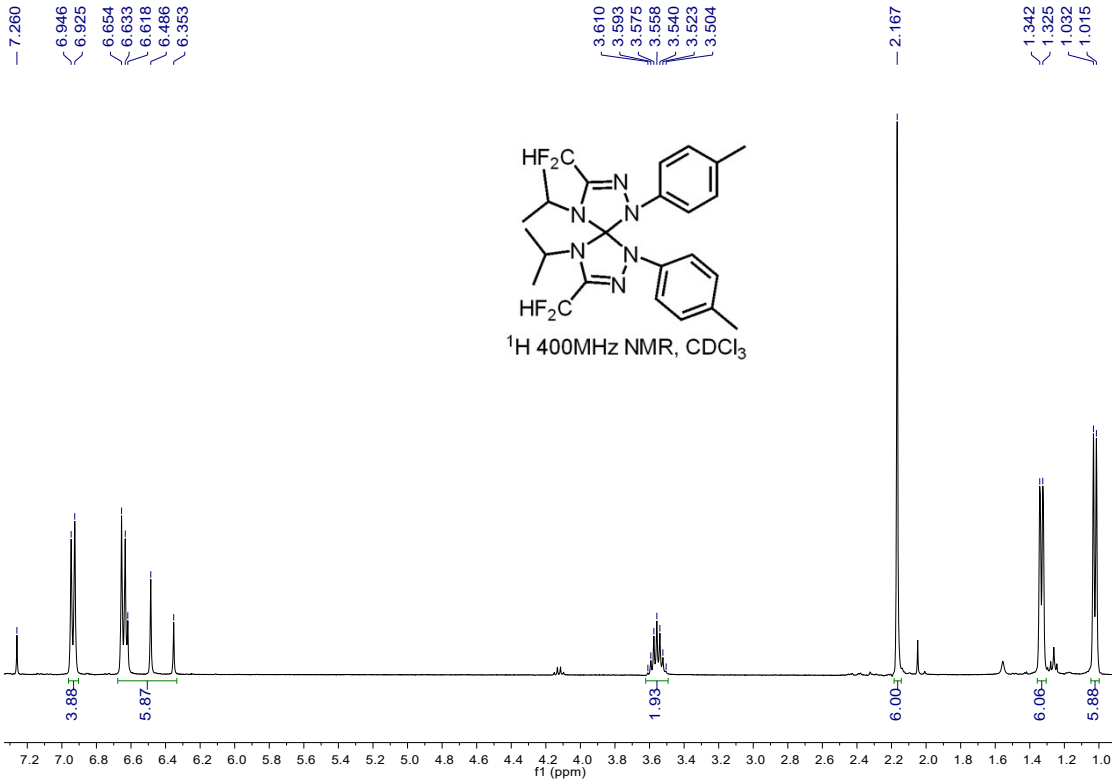

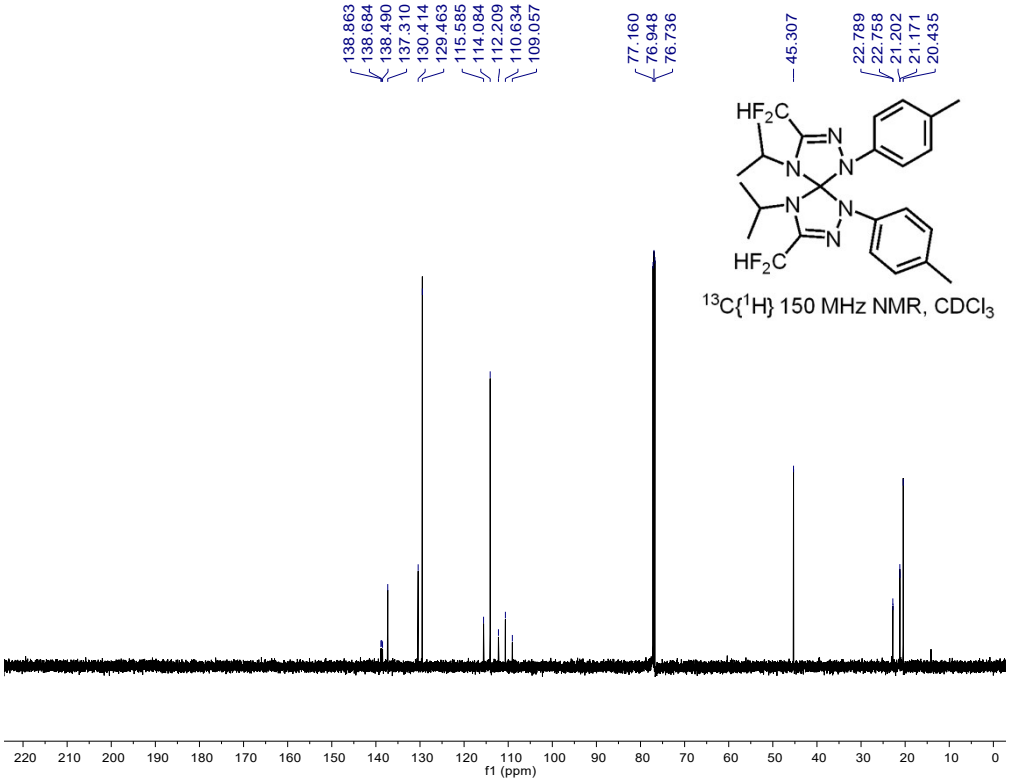
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129.463
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76.948
76.736
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HF2C
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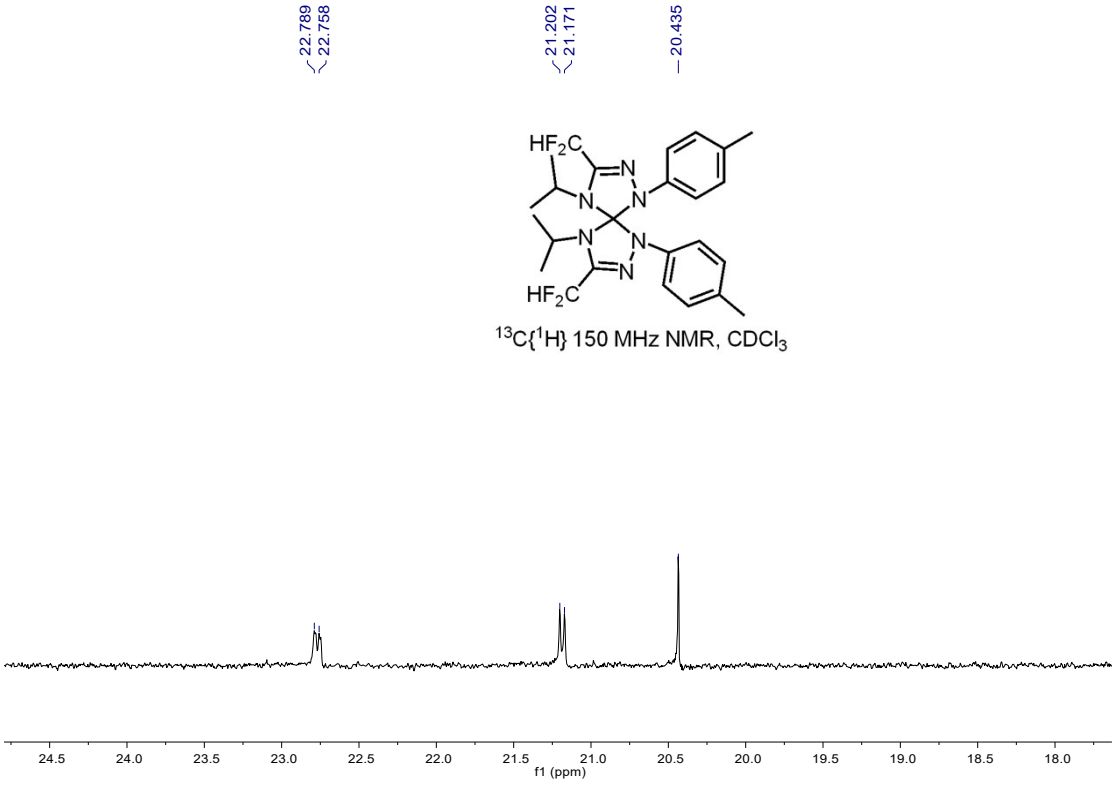
f1 (ppm)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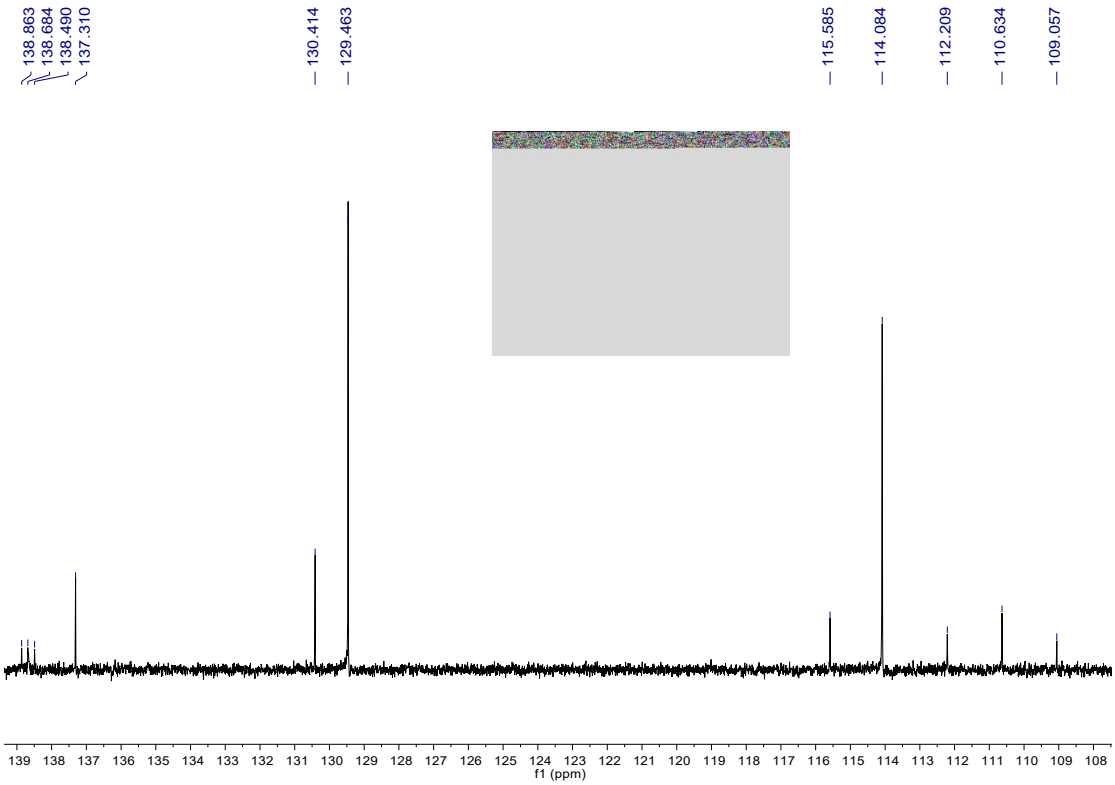
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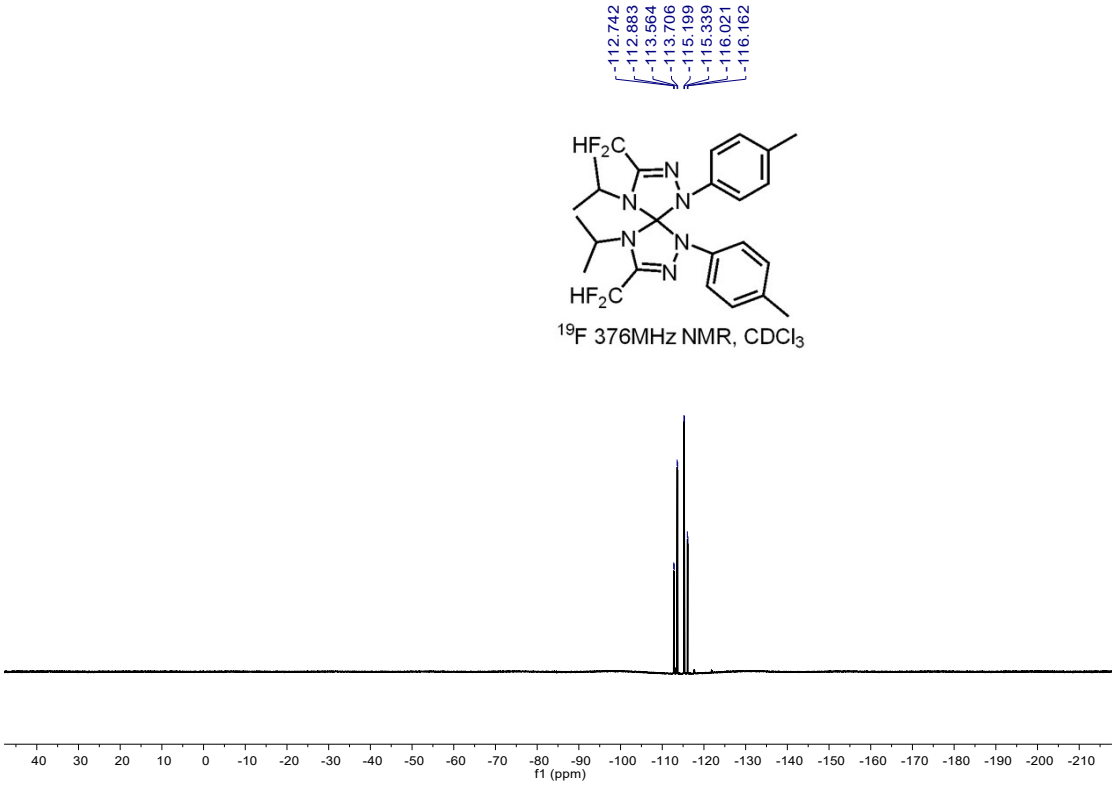
f1 (ppm)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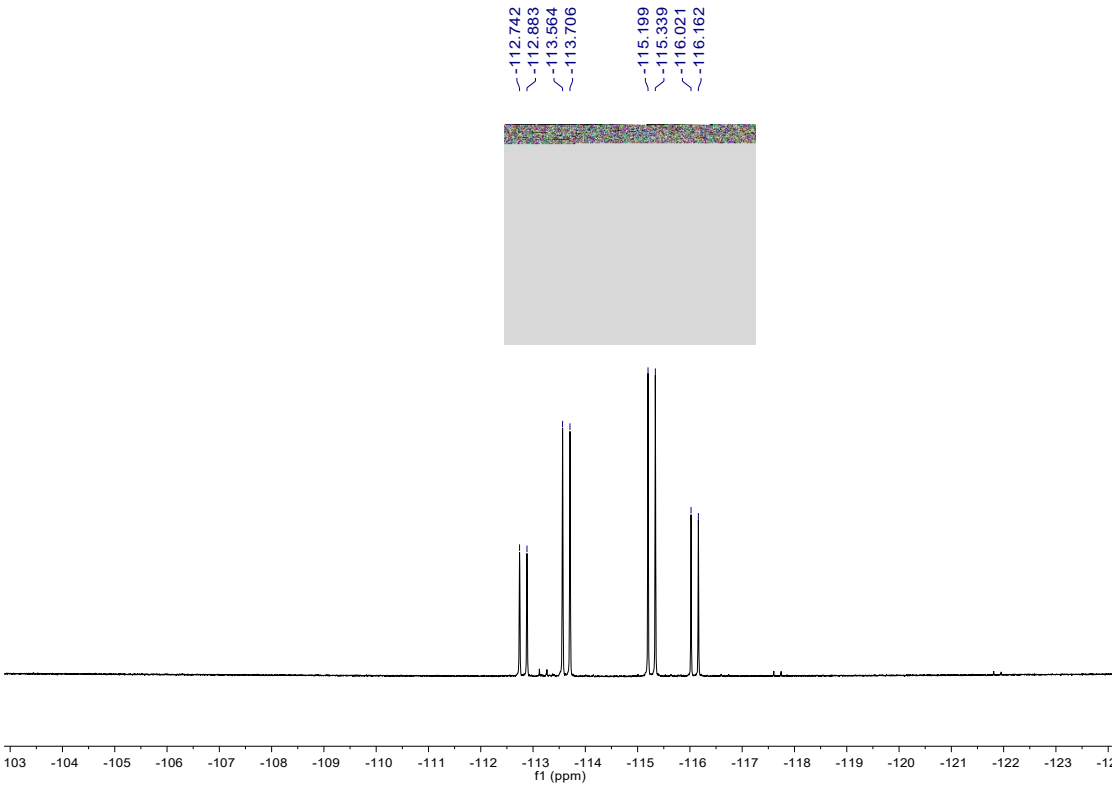
f1 (ppm)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-116.162
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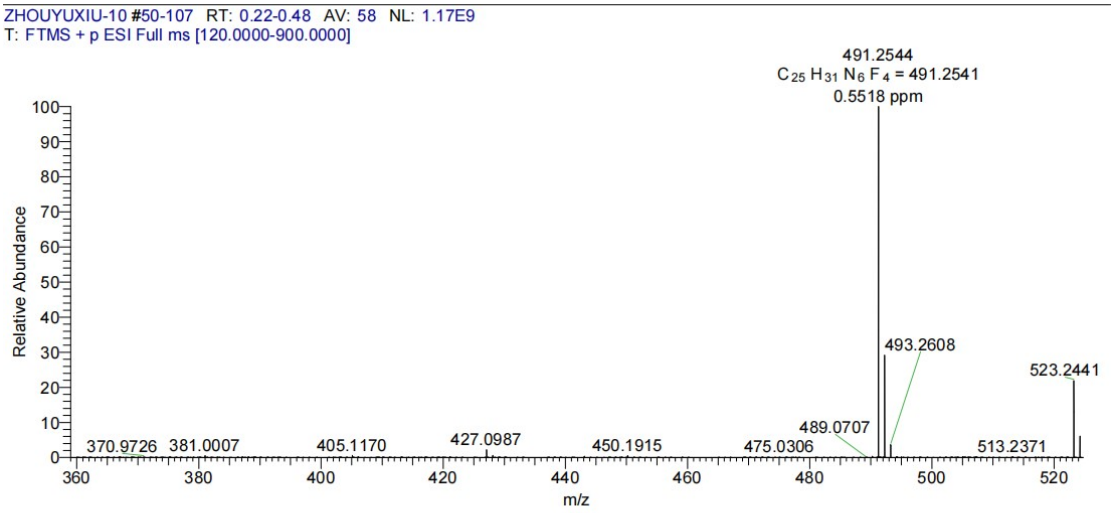
f1 (ppm)

HRMS (ESI) copy of compound **3c**:



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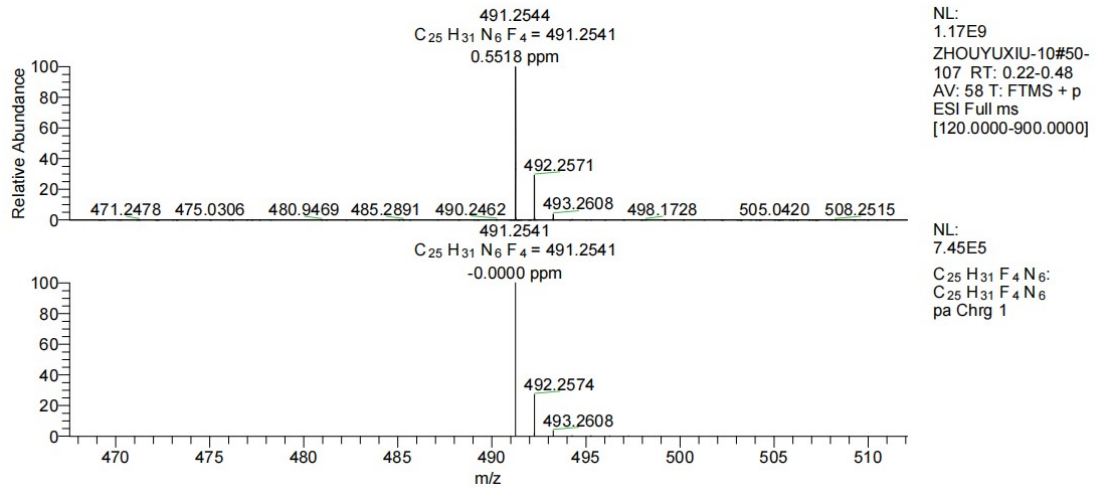
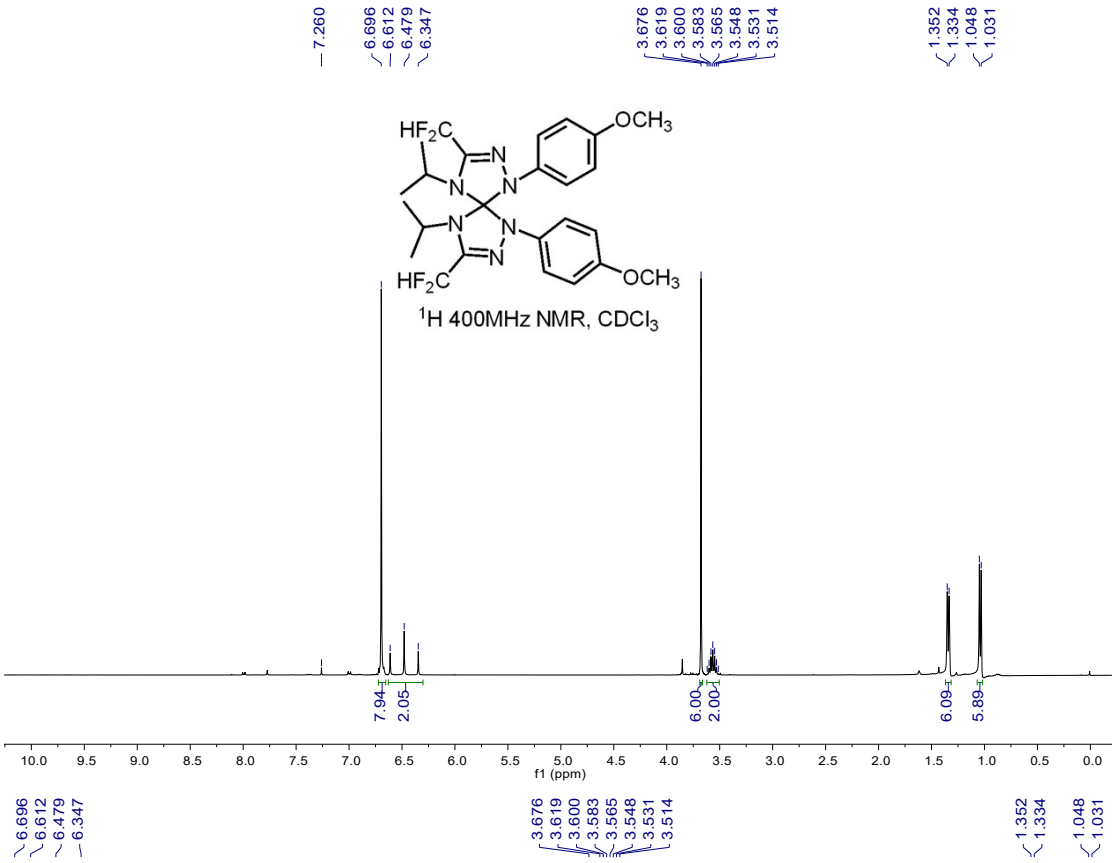
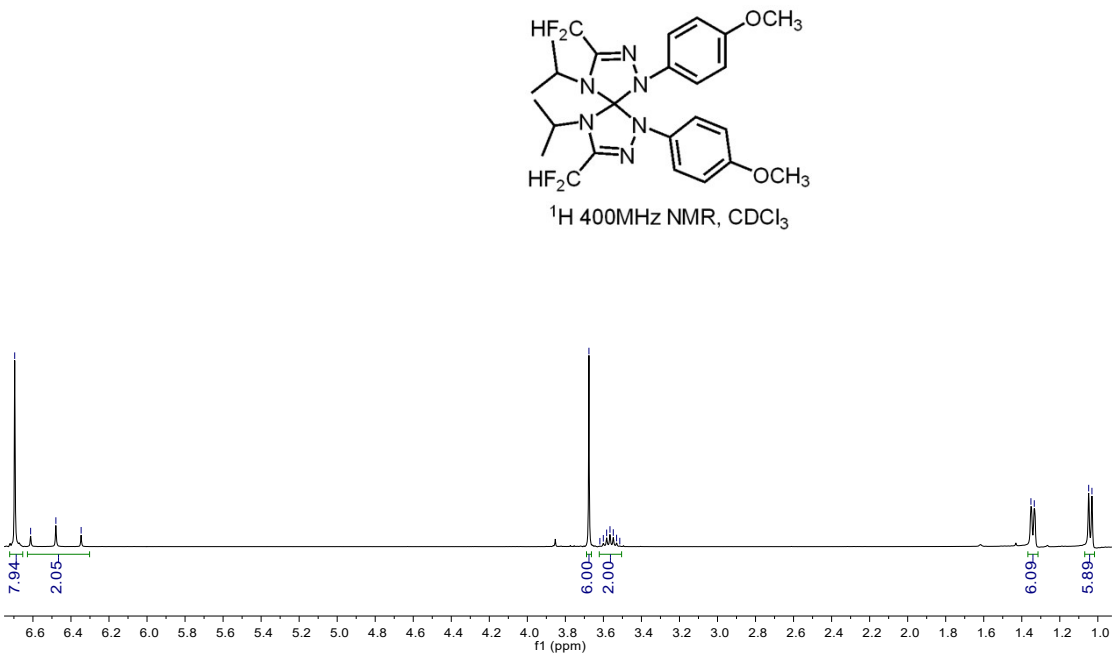
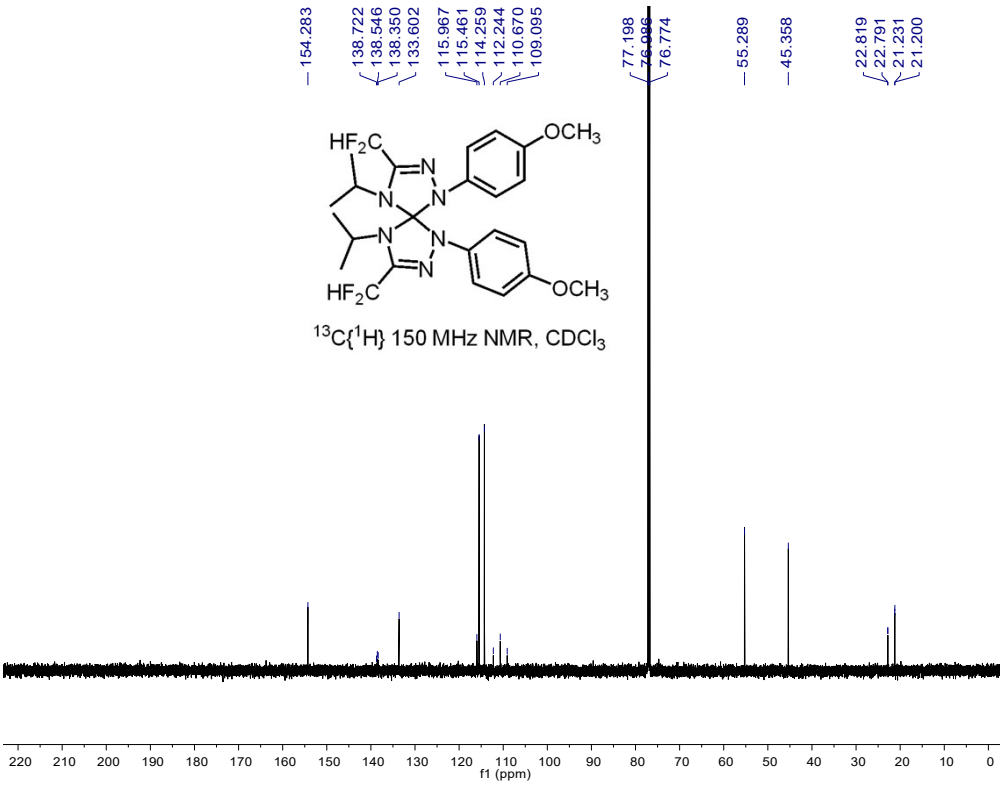
524.2473	71900512.0	5.96			



NMR copies of compound **3d**:







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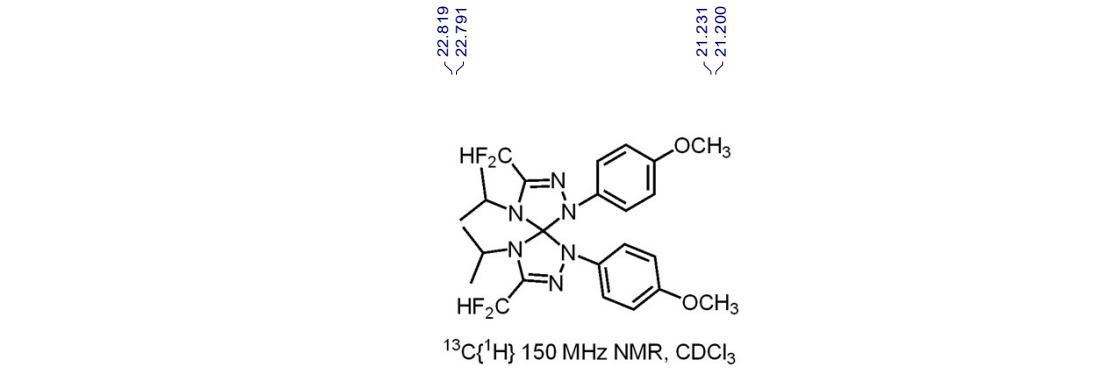
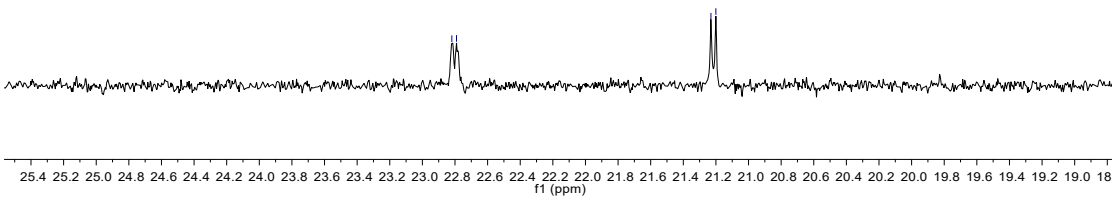
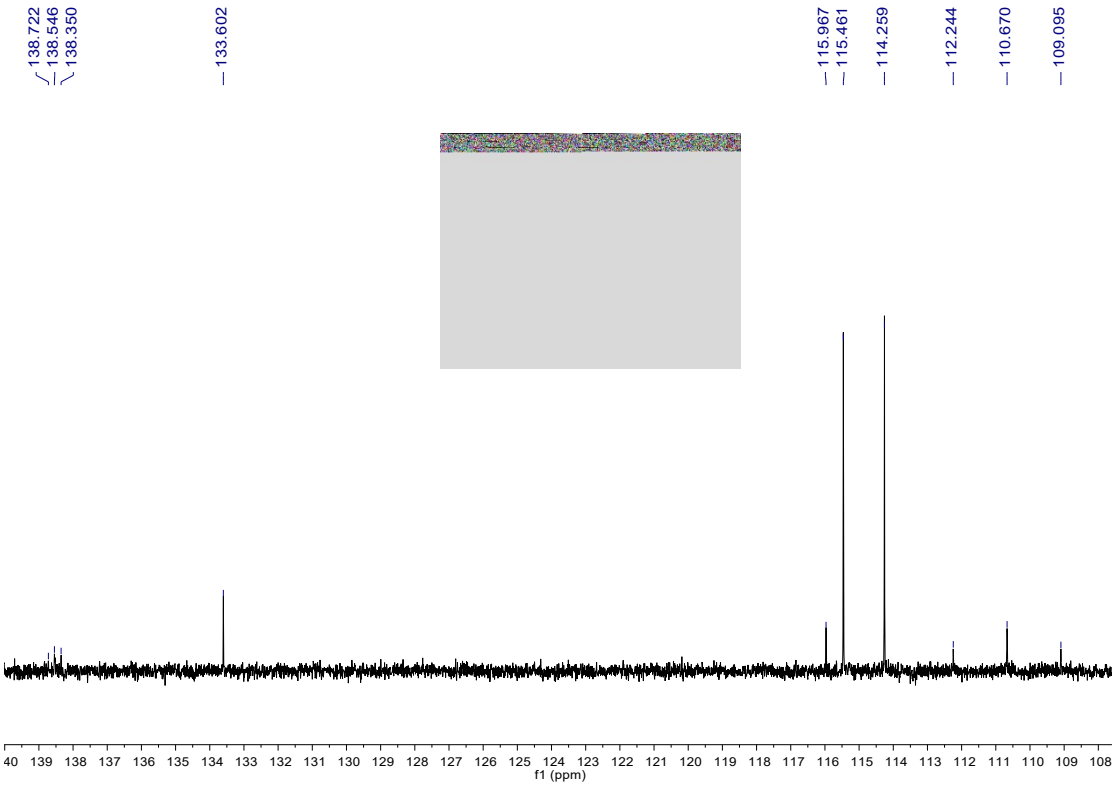
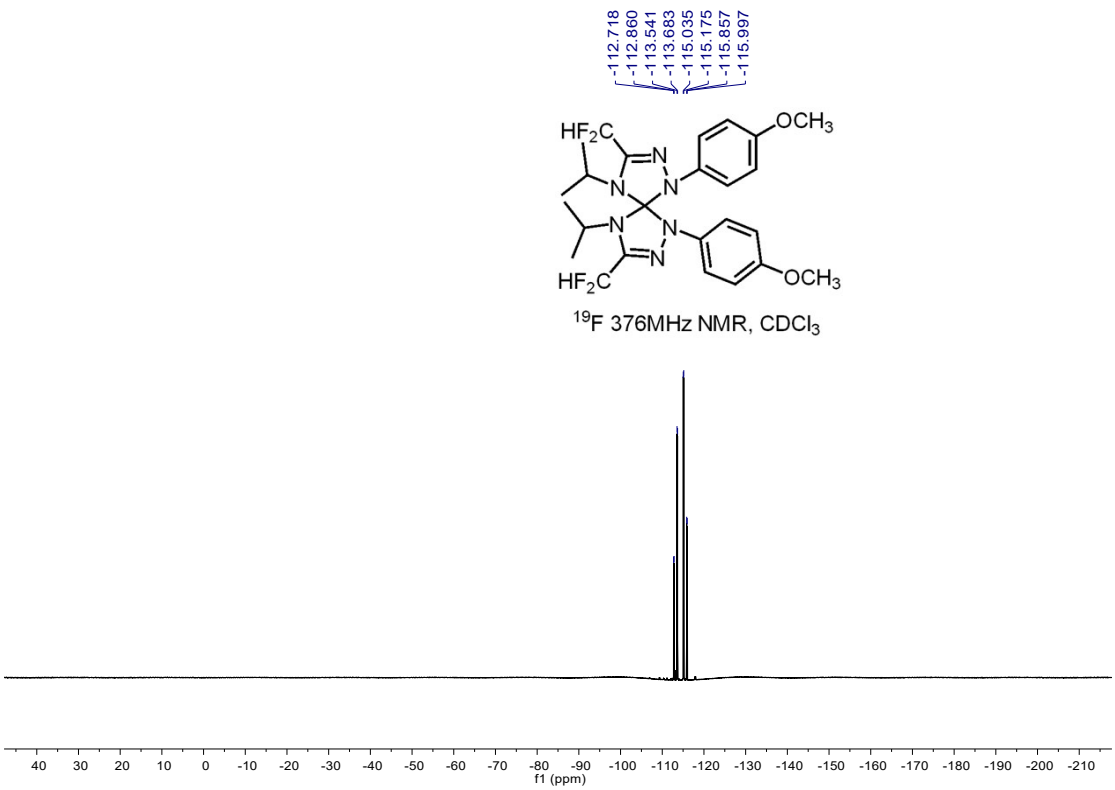
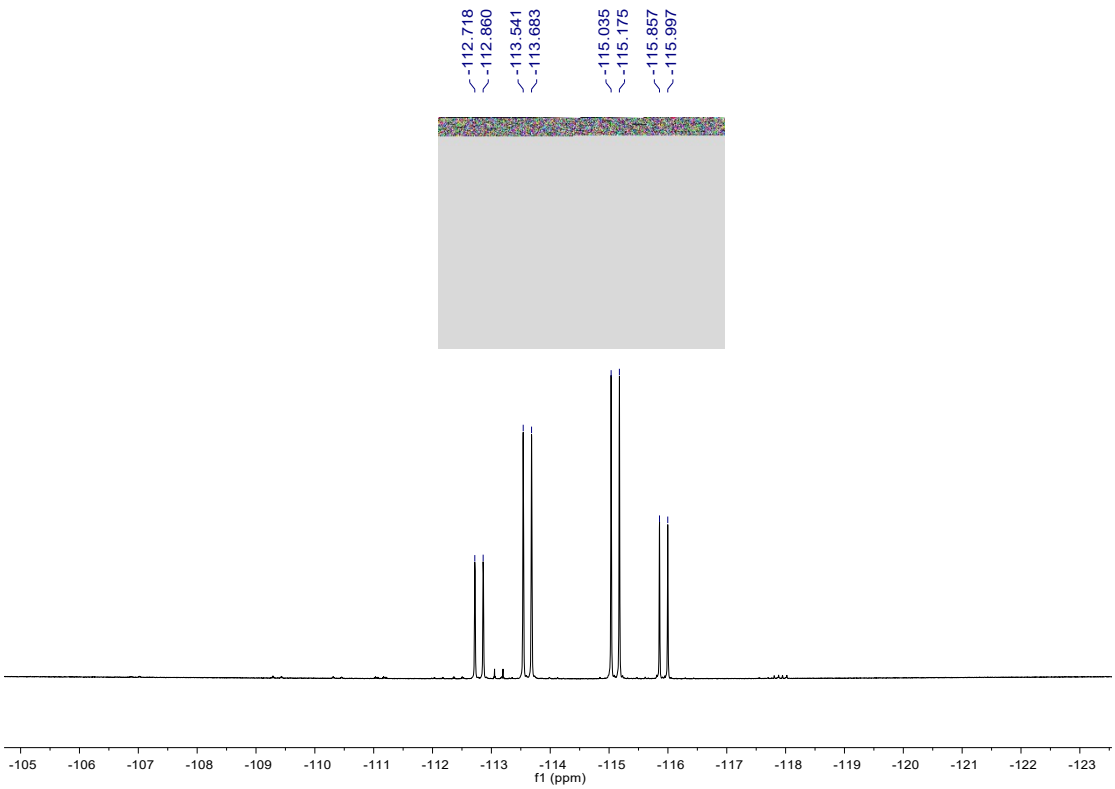


$^{13}C\{^{1}H\}$ 150 MHz NMR, $CDCl_3$

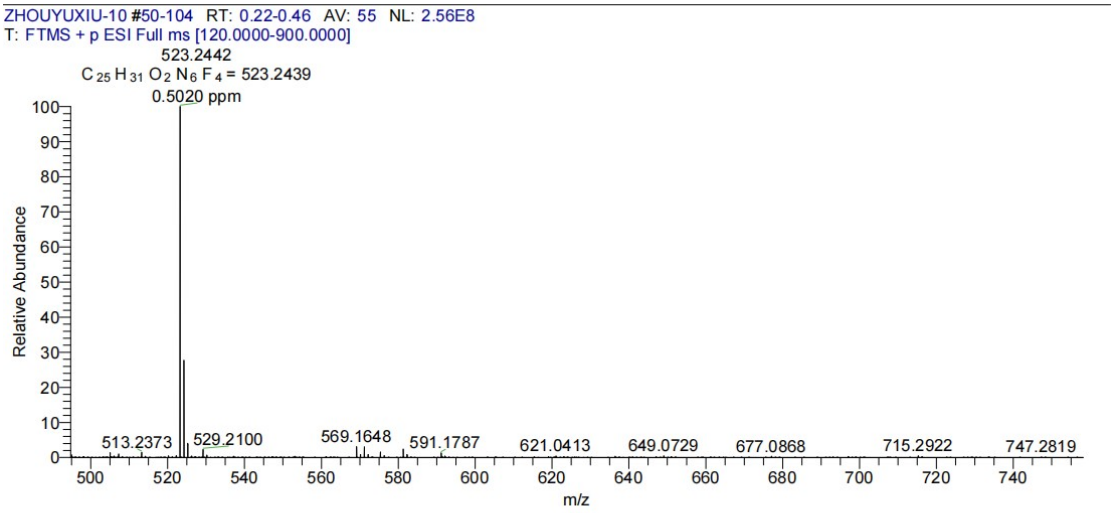



138.722
138.546
138.350
133.602
115.967
115.461
114.259
112.244
110.670
109.095
f1 (ppm)


-112.718
-112.860
-113.541
-113.683
-115.035
-115.175
-115.857
-115.997
HF2C
OCH3
HF2C
OCH3
19F 376MHz NMR, CDCl3
f1 (ppm)

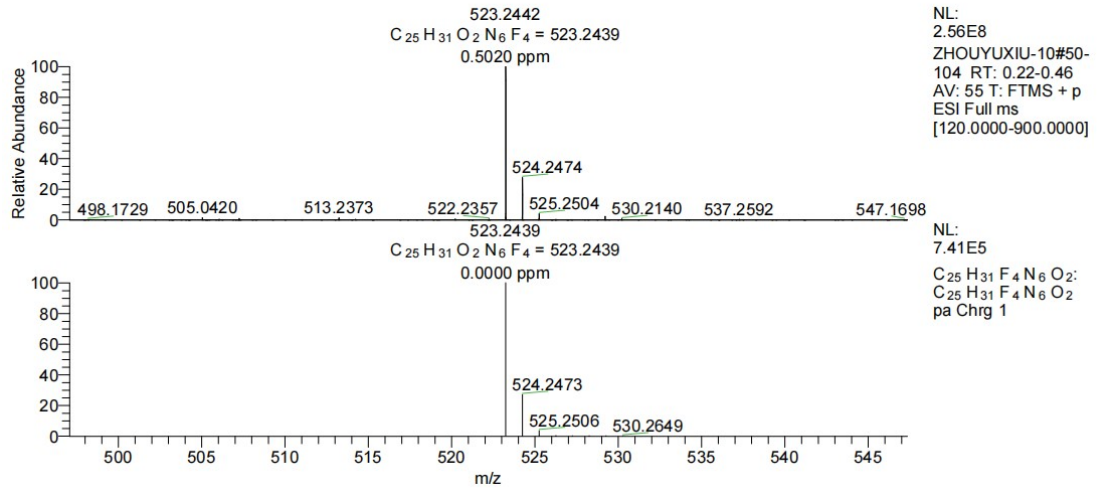

-112.718
-112.860
-113.541
-113.683
-115.035
-115.175
-115.857
-115.997
-105
-106
-107
-108
-109
-110
-111
-112
-113
-114
-115
-116
-117
-118
-119
-120
-121
-122
-123
f1 (ppm)

HRMS (ESI) copy of compound **3d**:

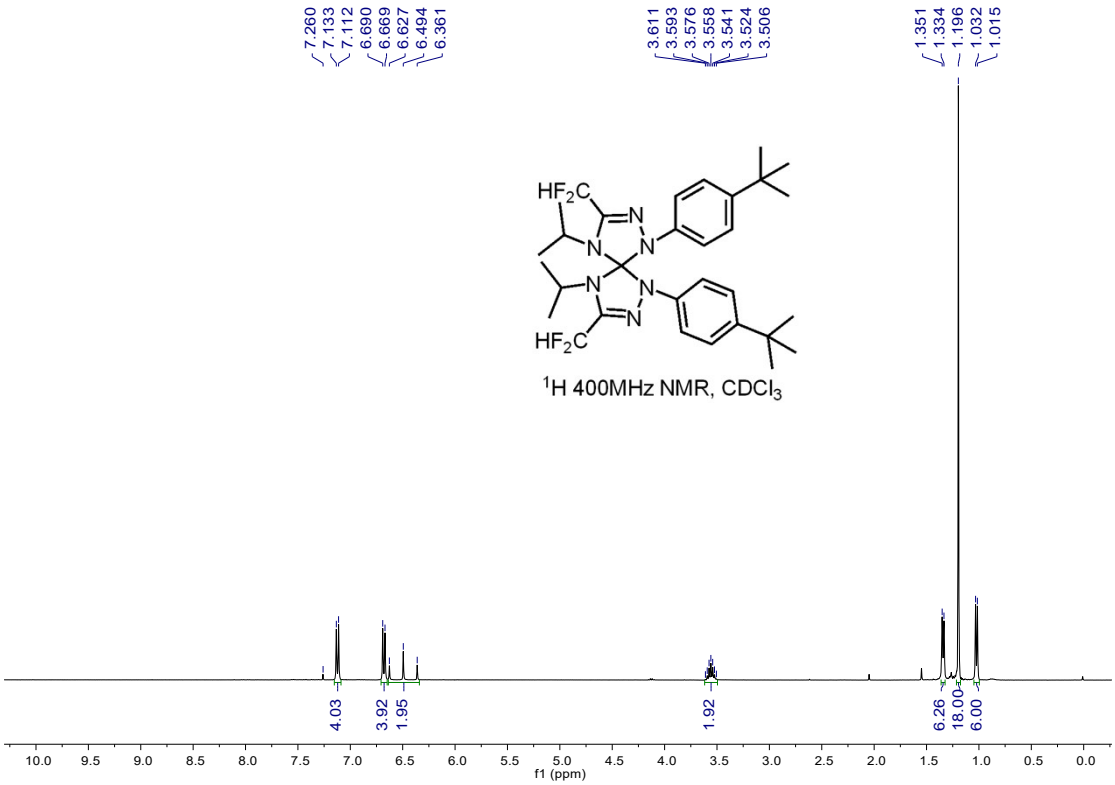


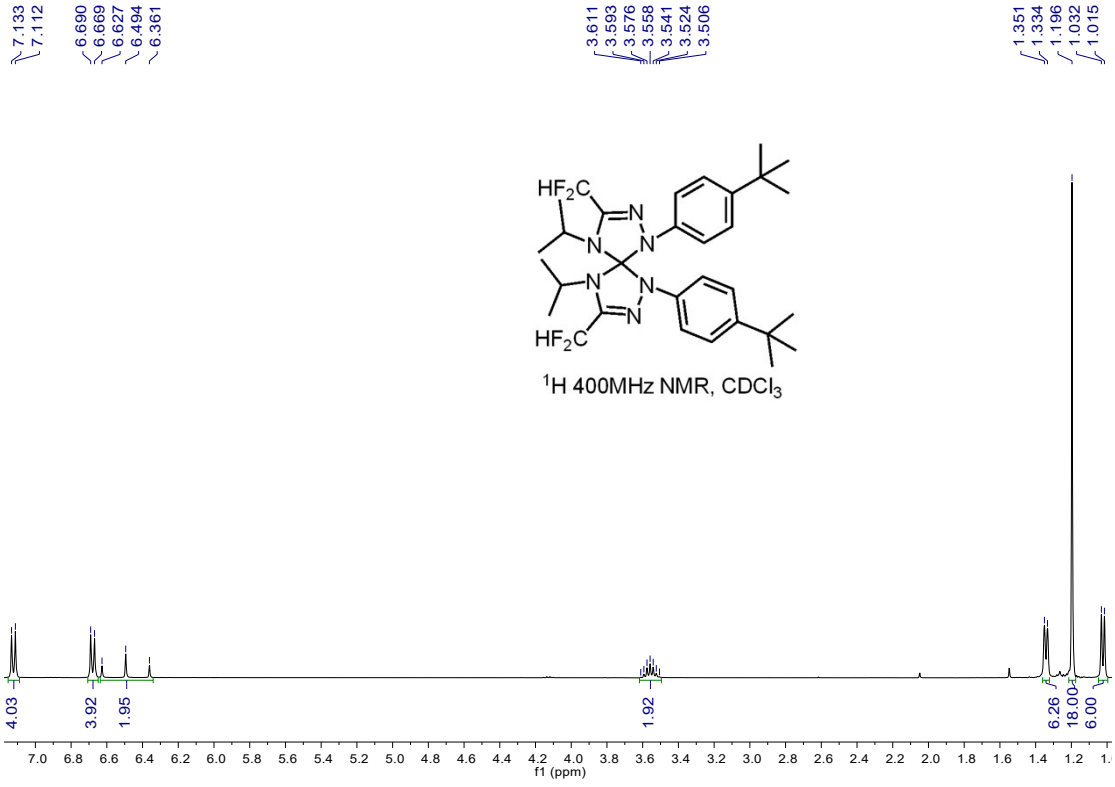
ZHOUYUXIU-10#50-104 RT: 0.22-0.46 AV: 55
T: FTMS + p ESI Full ms [120.0000-900.0000]
m/z= 494.7458-758.1356

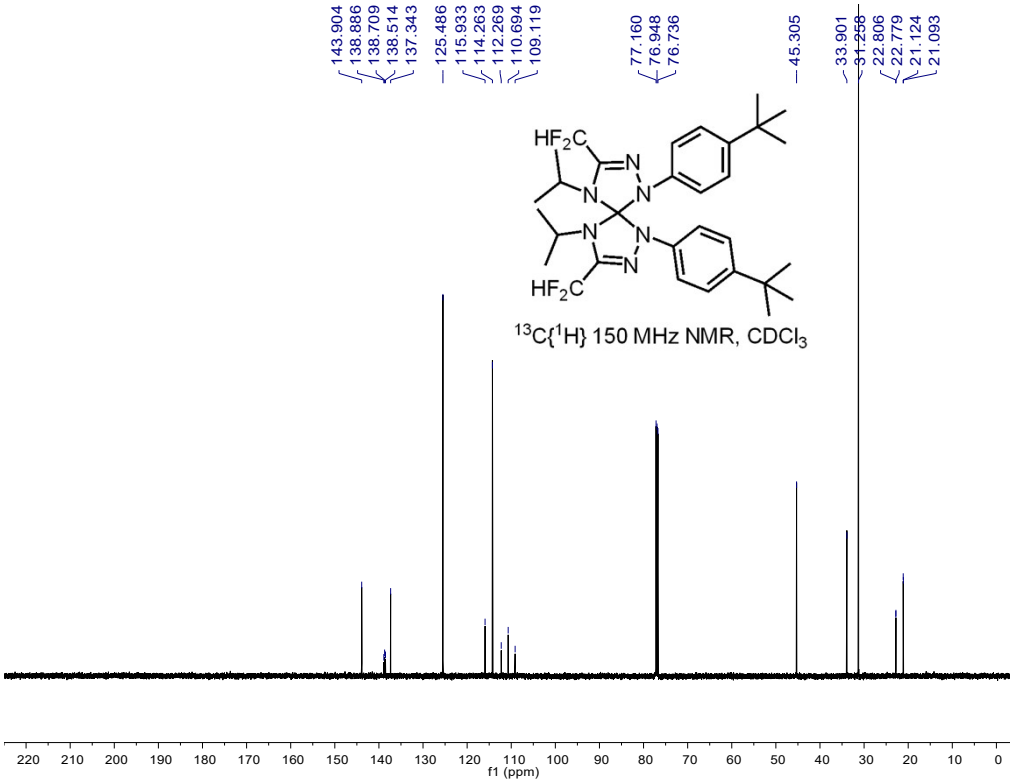
m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
523.2442	258230816.0	100.00	523.2439	0.26	$C_{25}H_{31}O_2N_6F_4$
524.2474	71567296.0	27.71			
525.2504	10382575.0	4.02			
569.1648	8233455.0	3.19			

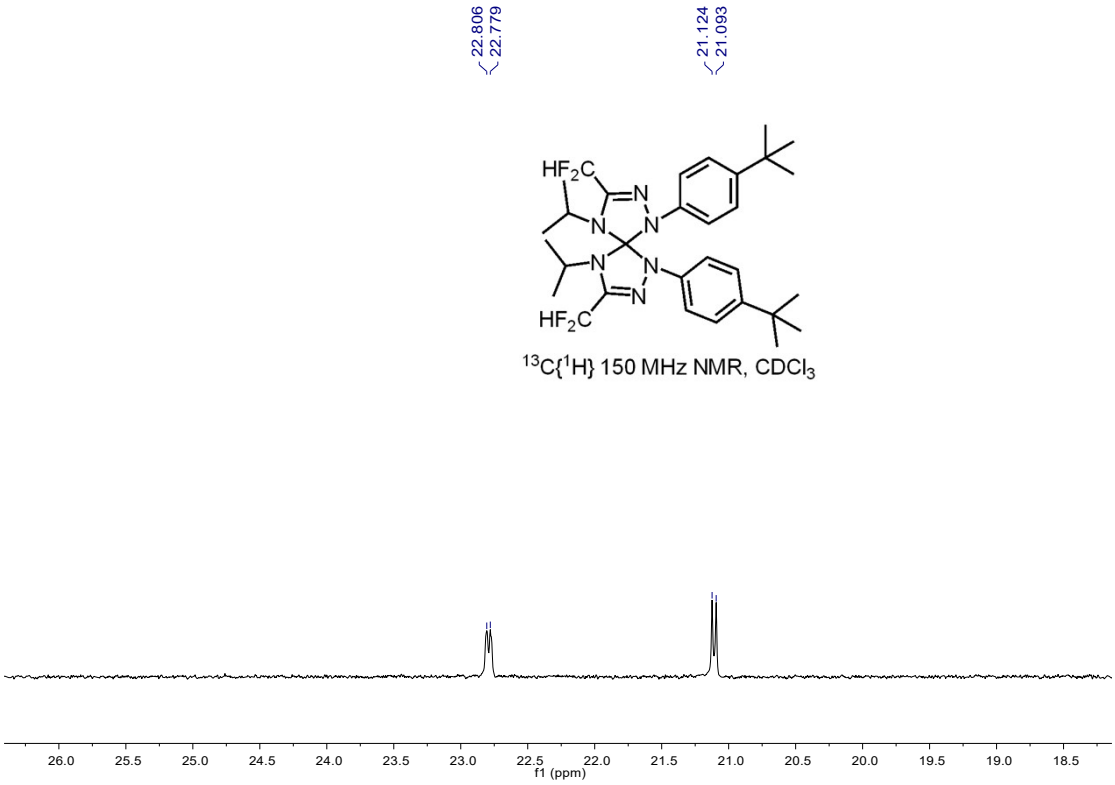


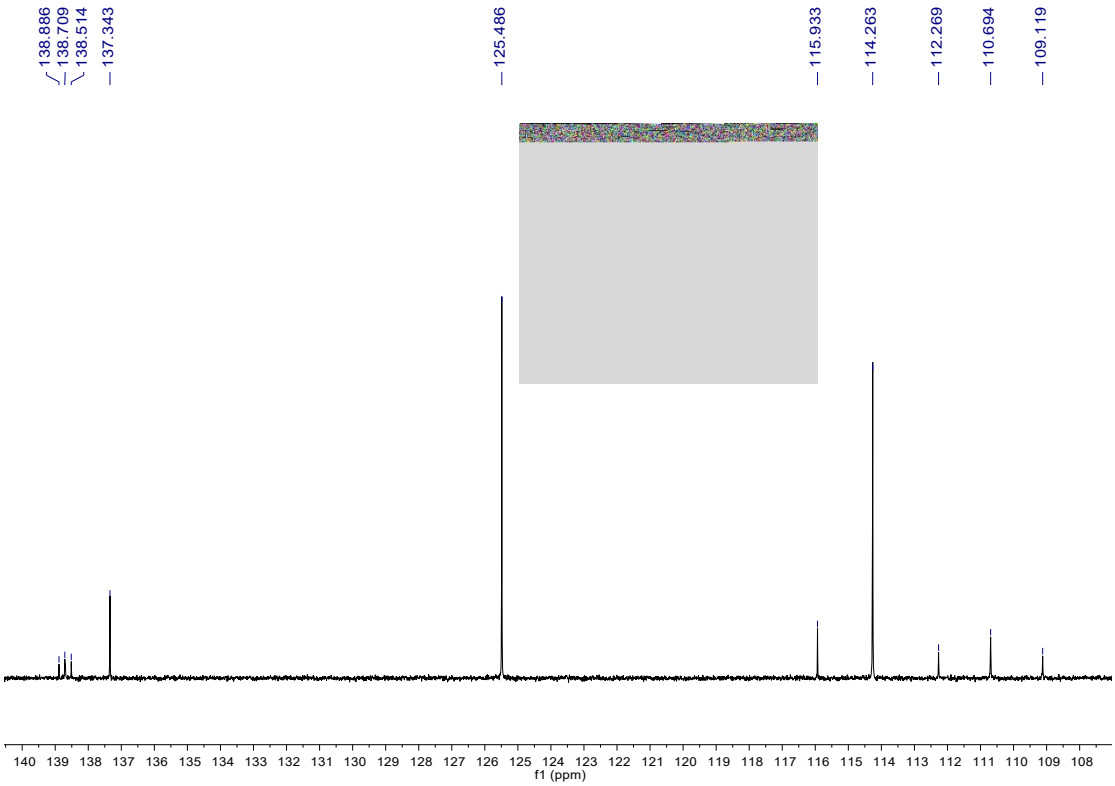
NMR copies of compound **3e**:

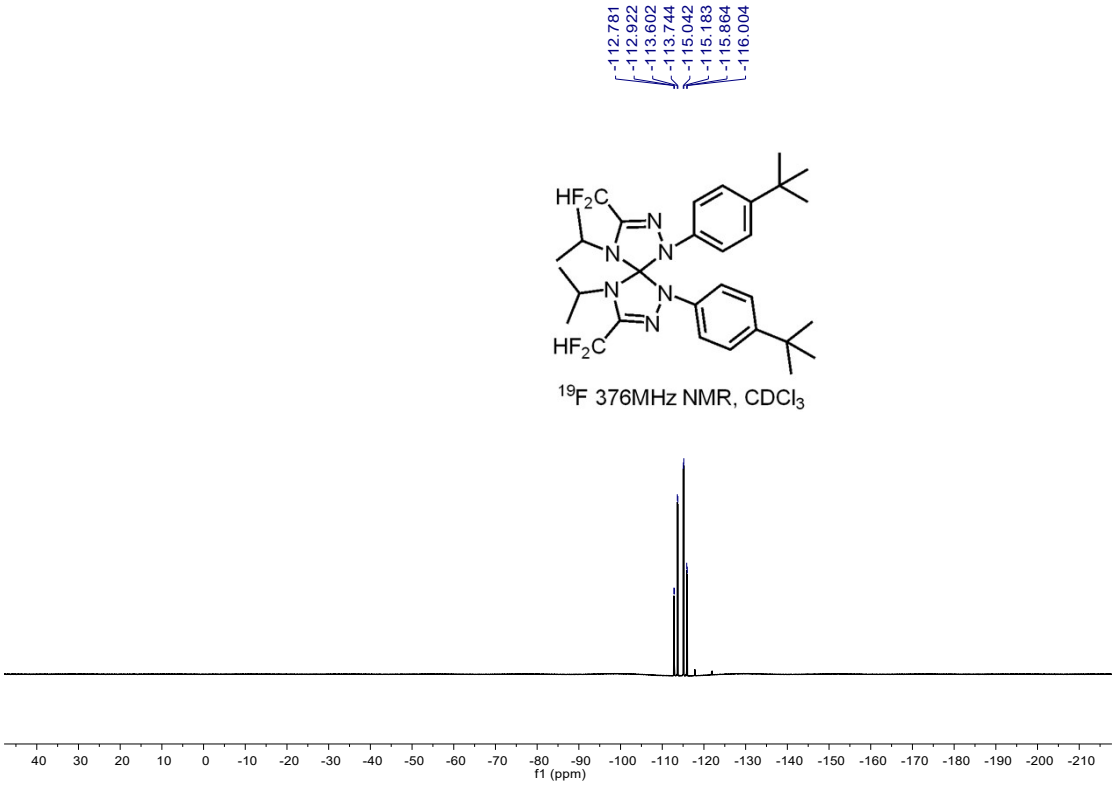




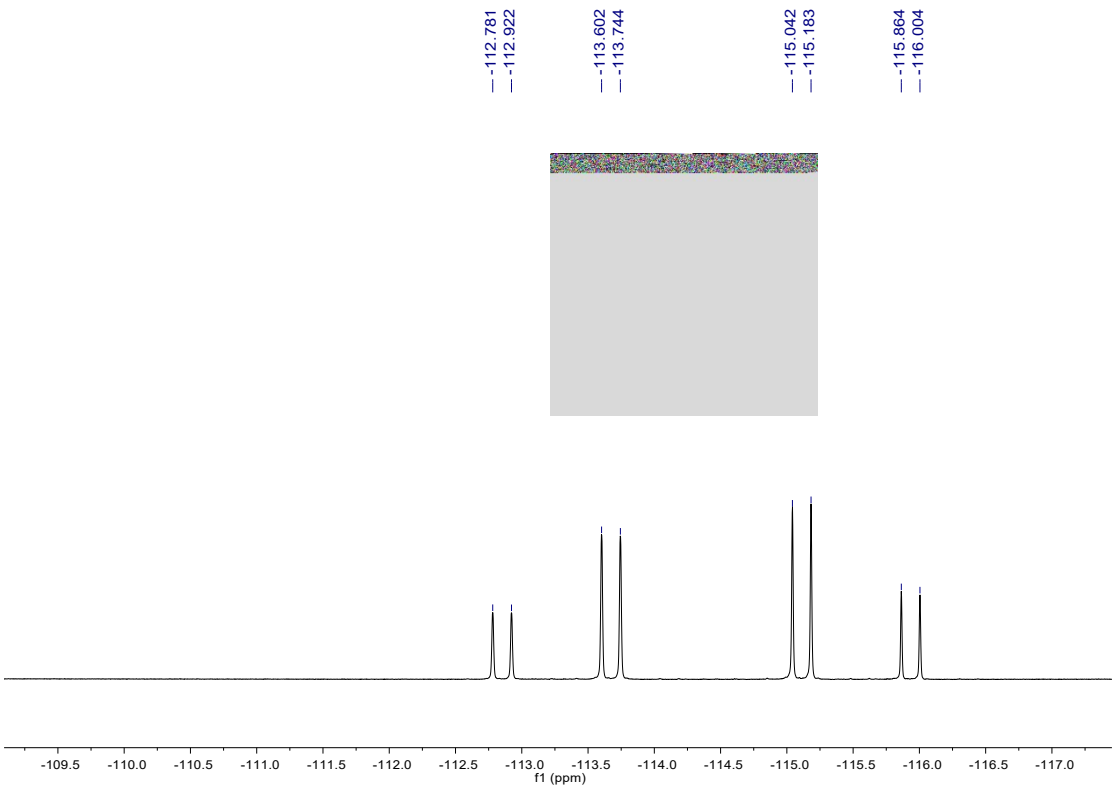

143.904
138.886
138.709
138.514
137.343
125.486
115.933
114.263
112.269
110.694
109.119
77.160
76.948
76.736
45.305
33.901
31.258
22.806
22.779
21.124
21.093
HF2C
HF2C
13C{1H} 150 MHz NMR, CDCl3
f1 (ppm)


22.806
22.779
21.124
21.093
HF2C
HF2C
13C{1H} 150 MHz NMR, CDCl3
f1 (ppm)

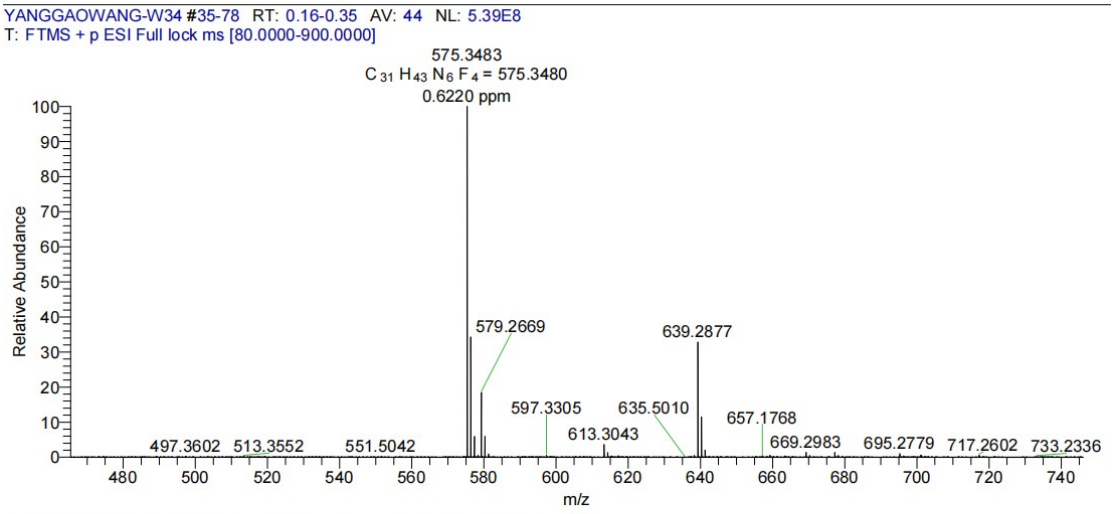




^{19}F 376MHz NMR, $CDCl_3$

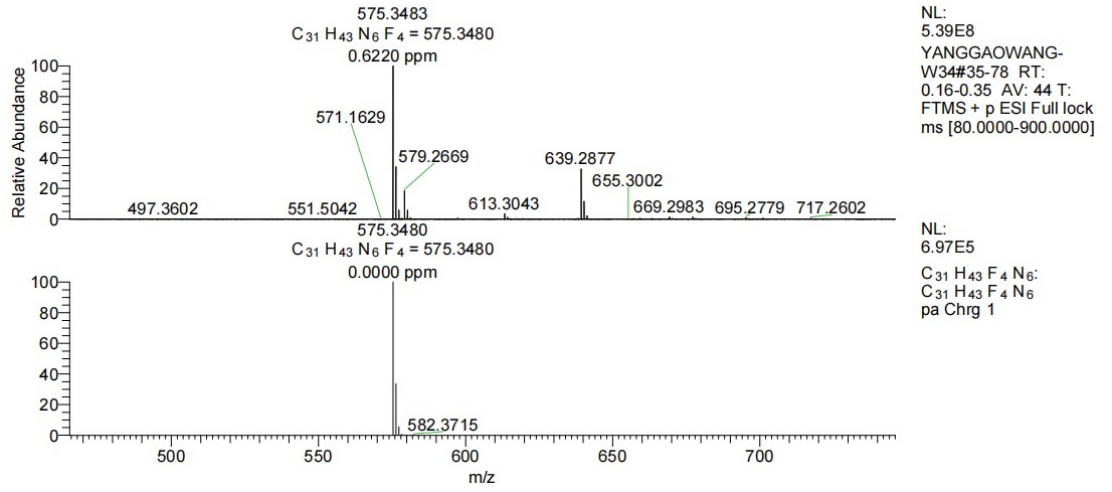

-112.781
-112.922
-113.602
-113.744
-115.042
-115.183
-115.864
-116.004
-109.5
-110.0
-110.5
-111.0
-111.5
-112.0
-112.5
-113.0
-113.5
-114.0
-114.5
-115.0
-115.5
-116.0
-116.5
-117.0
f1 (ppm)

HRMS (ESI) copy of compound **3e**:

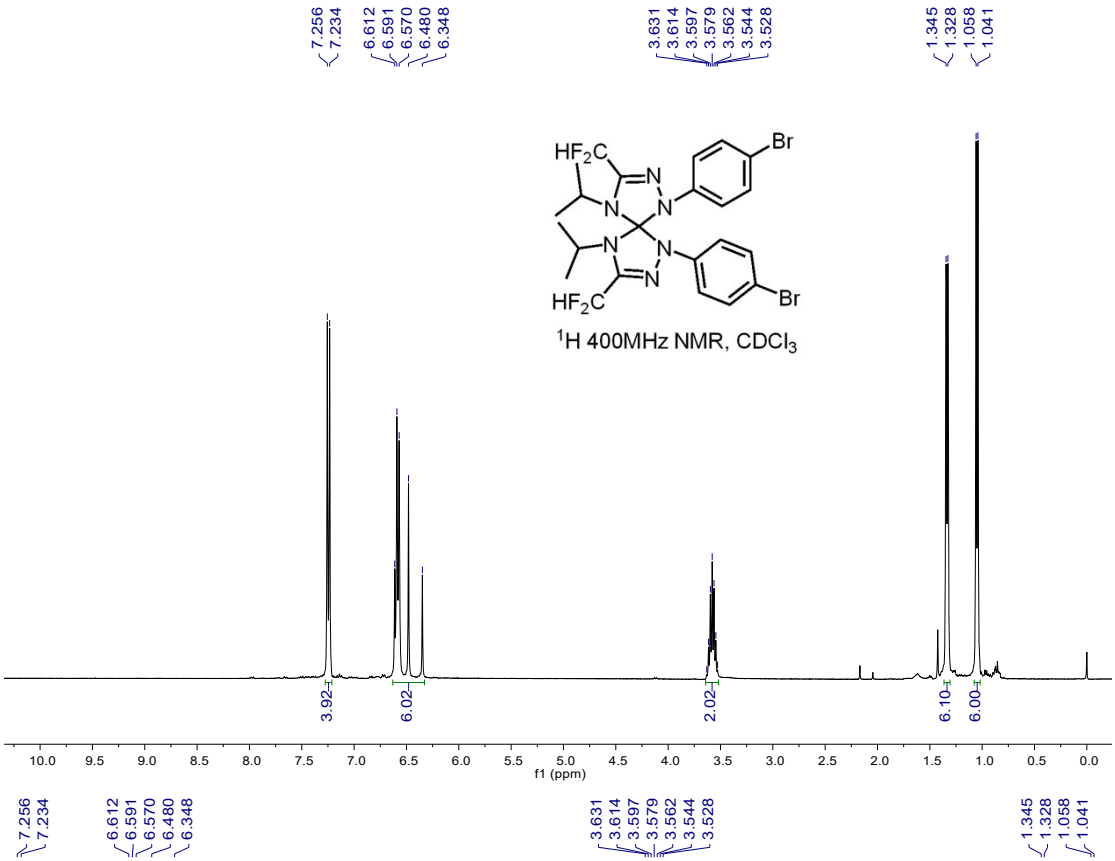


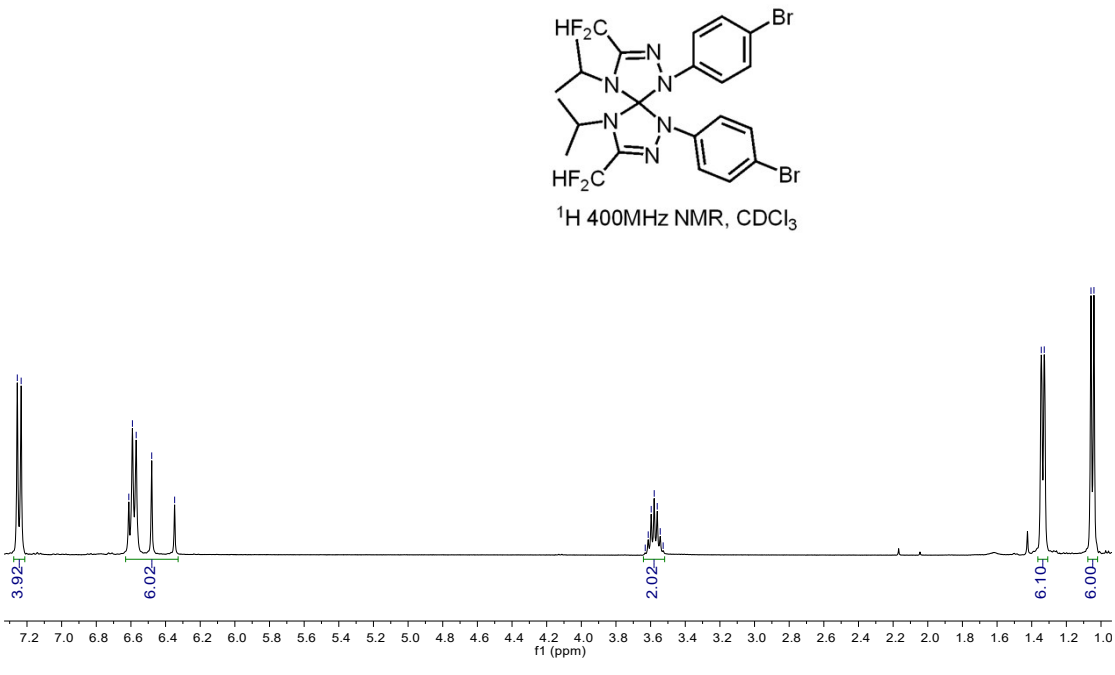
YANGGAOWANG-W34#35-78 RT: 0.16-0.35 AV: 44
T: FTMS + p ESI Full lock ms [80.0000-900.0000]
m/z= 465.4107-746.0495

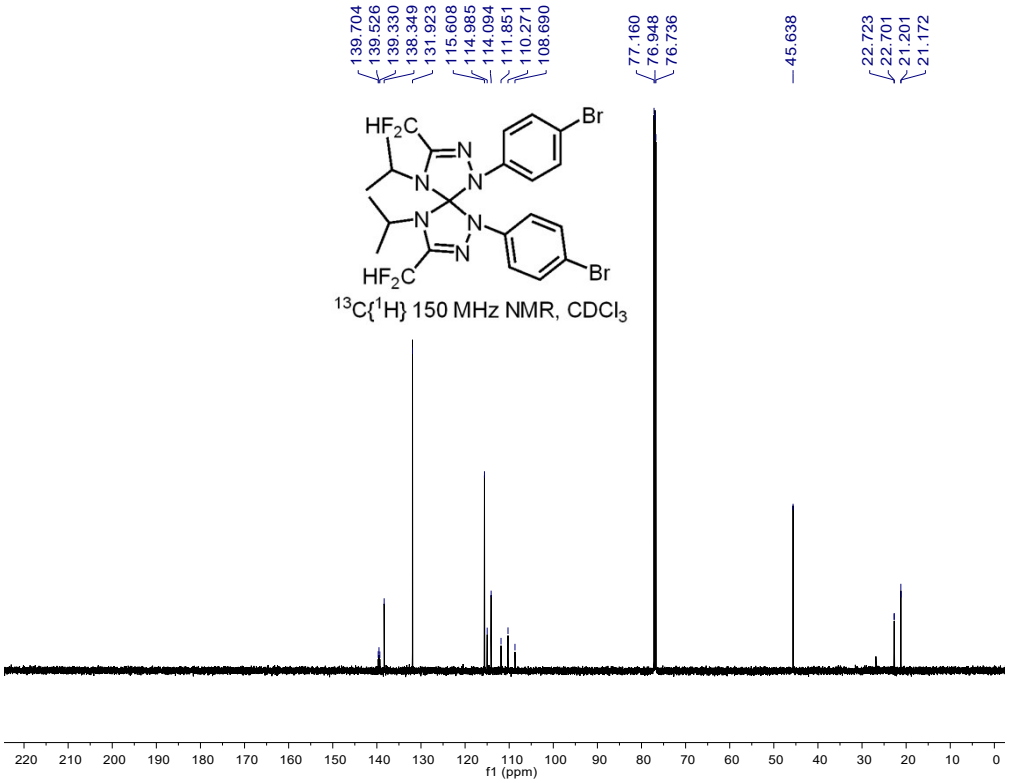
m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
575.3483	547655040.0	100.00	575.3480	0.36	$C_{31}H_{43}N_6F_4$
576.3514	190475440.0	34.78			
579.2669	100620240.0	18.37			
639.2877	180036304.0	32.87			

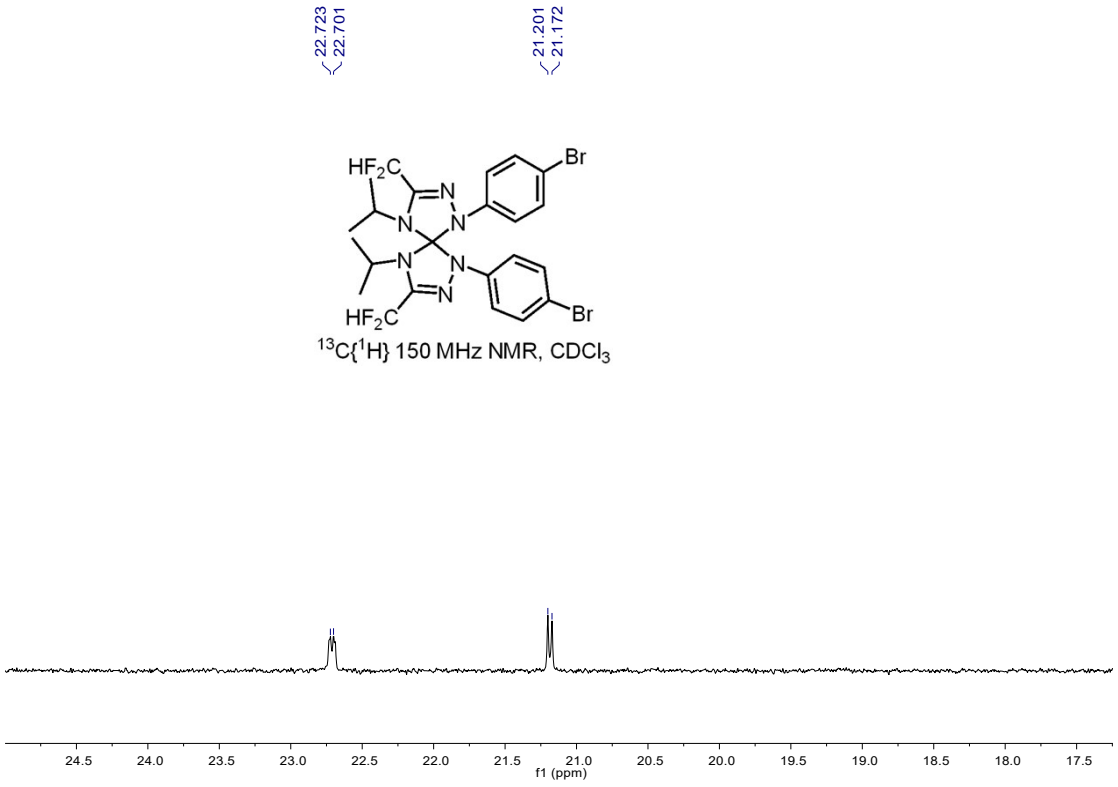


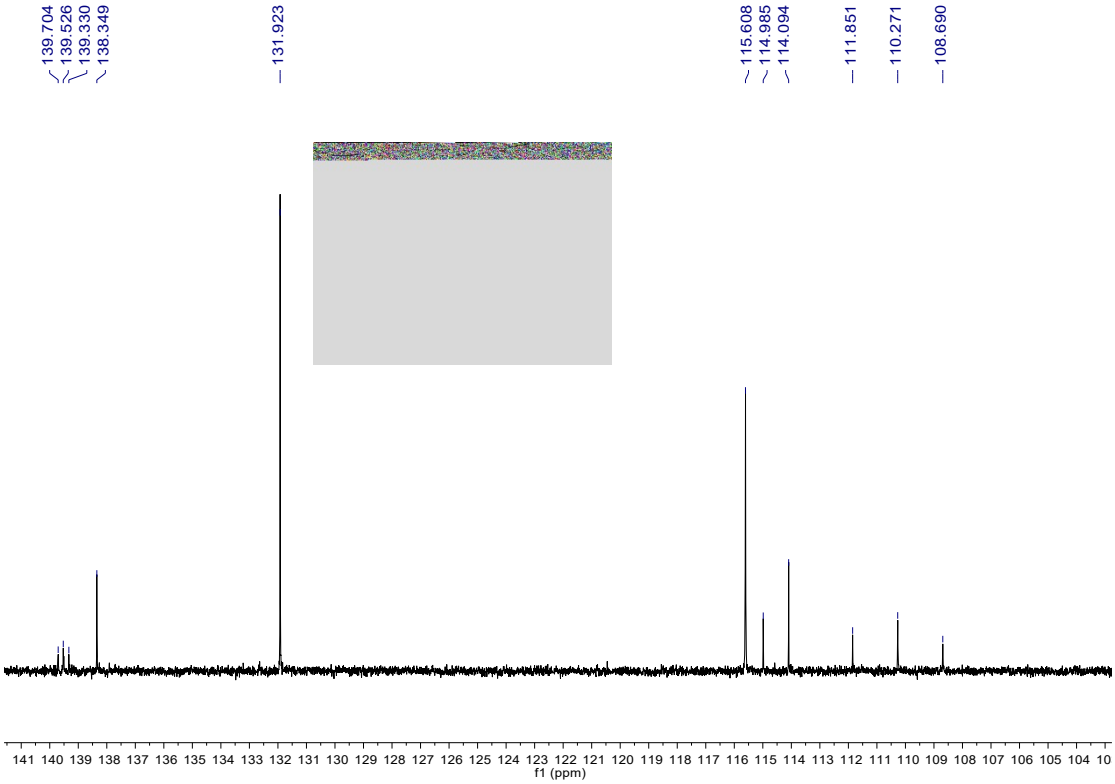
NMR copies of compound **3f**:

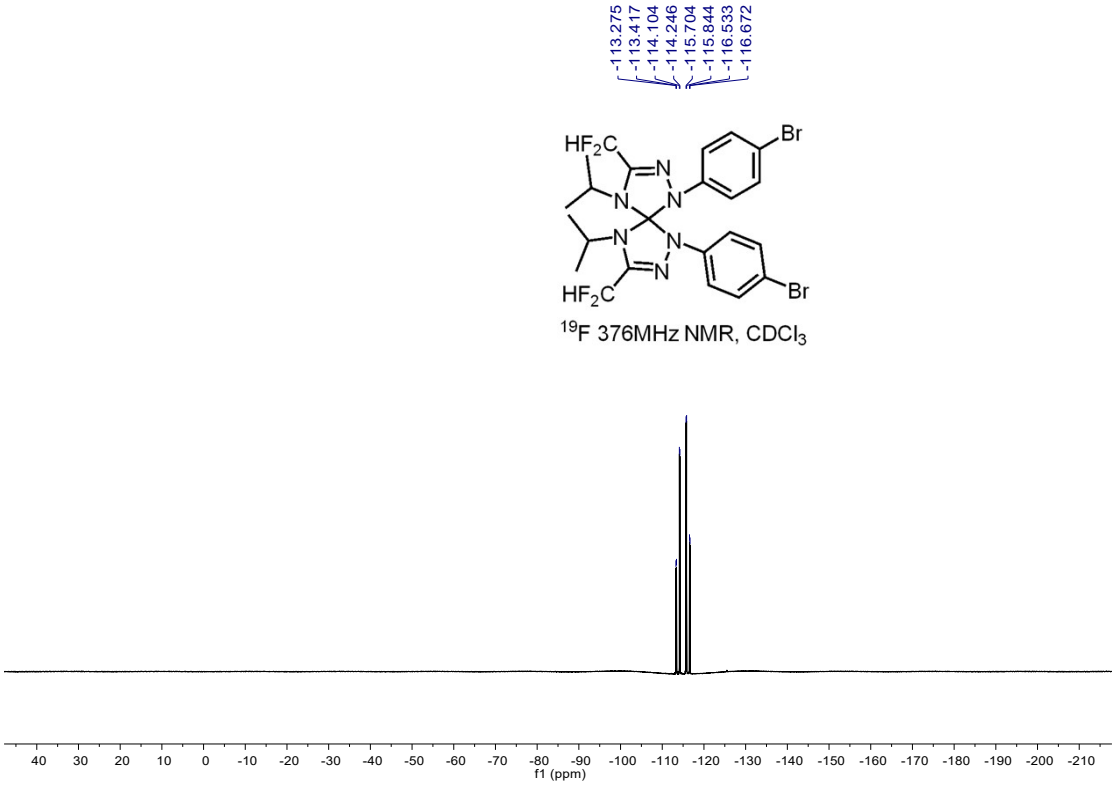


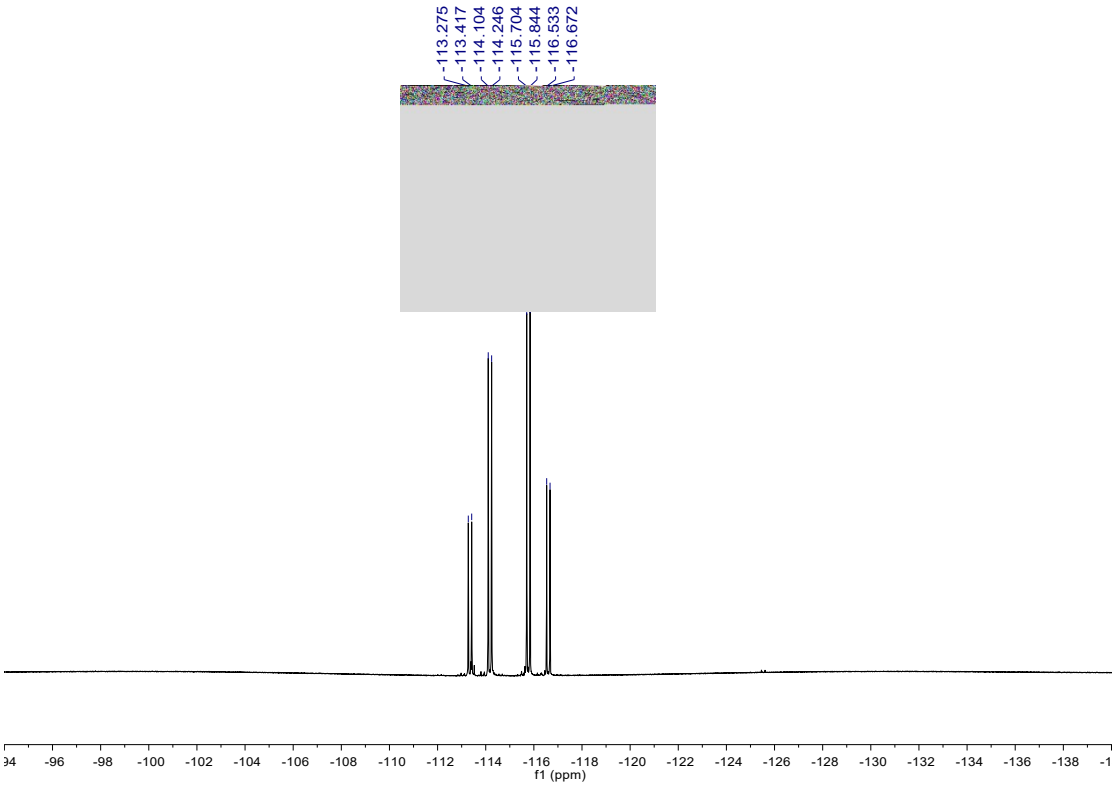



139.704
139.526
139.330
138.349
131.923
115.608
114.985
114.094
111.851
110.271
108.690
77.160
76.948
76.736
45.638
22.723
22.701
21.201
21.172
HF2C
Br
HF2C
Br
13C{1H} 150 MHz NMR, CDCl3
f1 (ppm)

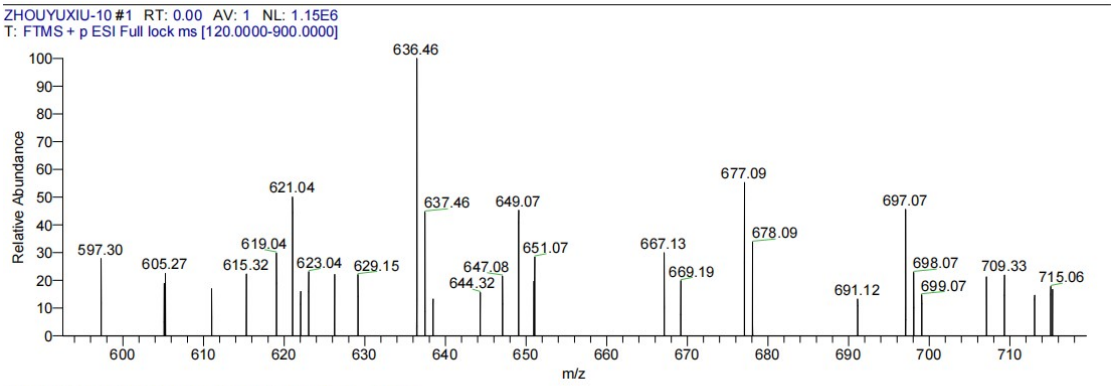

22.723
22.701
21.201
21.172
HF2C
Br
HF2C
Br
13C{1H} 150 MHz NMR, CDCl3
f1 (ppm)

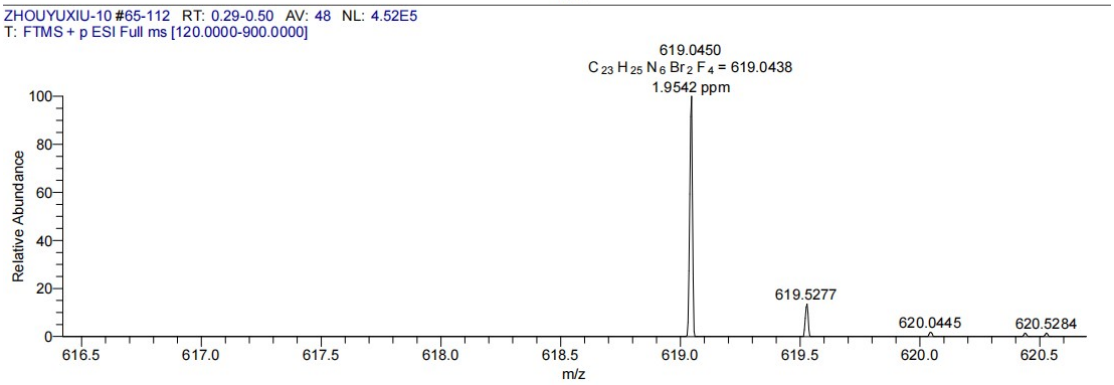

139.704
139.526
139.330
138.349
131.923
115.608
114.985
114.094
111.851
110.271
108.690
141 140 139 138 137 136 135 134 133 132 131 130 129 128 127 126 125 124 123 122 121 120 119 118 117 116 115 114 113 112 111 110 109 108 107 106 105 104 10
f1 (ppm)


-113.275
-113.417
-114.104
-114.246
-115.704
-115.844
-116.533
-116.672
HF2C
Br
HF2C
Br
19F 376MHz NMR, CDCl3
40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


-113.275
-113.417
-114.104
-114.246
-115.704
-115.844
-116.533
-116.672
-94
-96
-98
-100
-102
-104
-106
-108
-110
-112
-114
-116
-118
-120
-122
-124
-126
-128
-130
-132
-134
-136
-138
f1 (ppm)

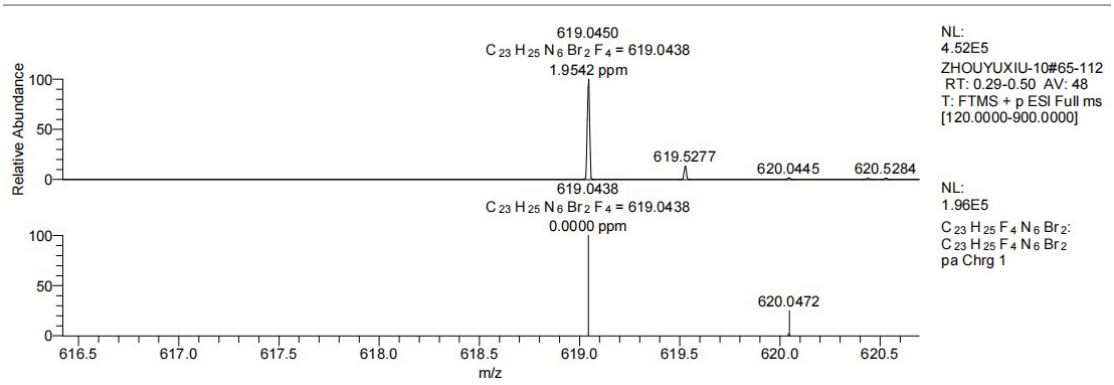
HRMS (ESI) copy of compound **3f**:



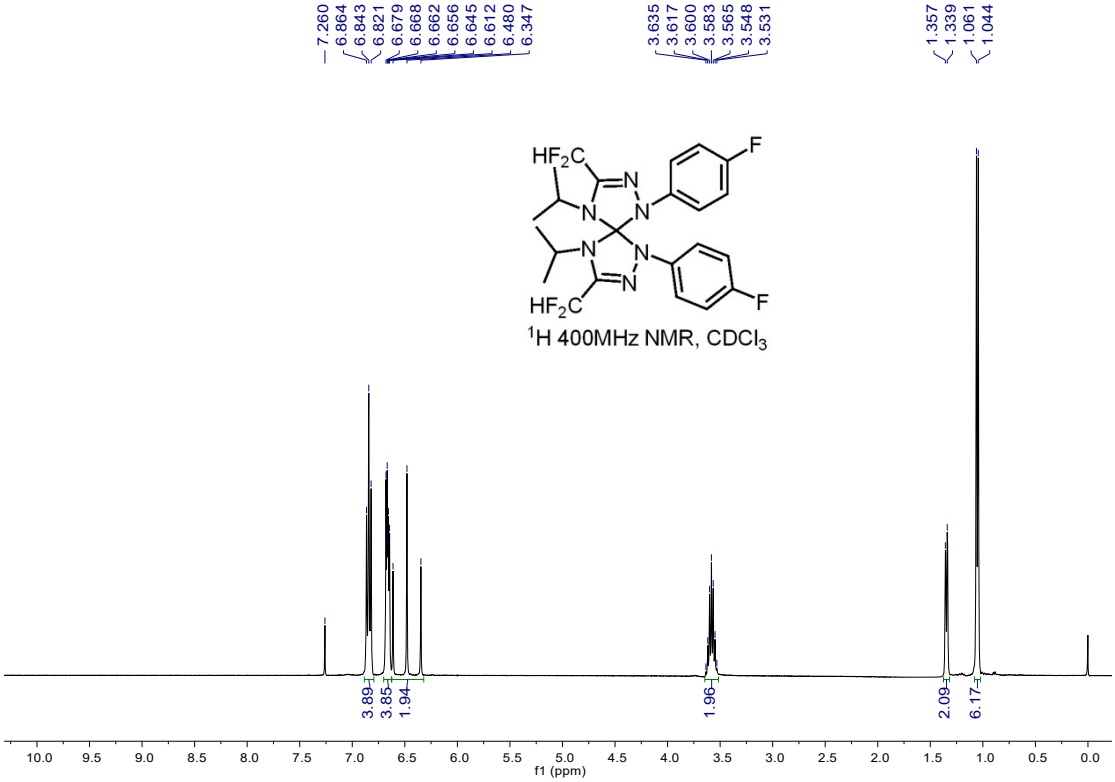


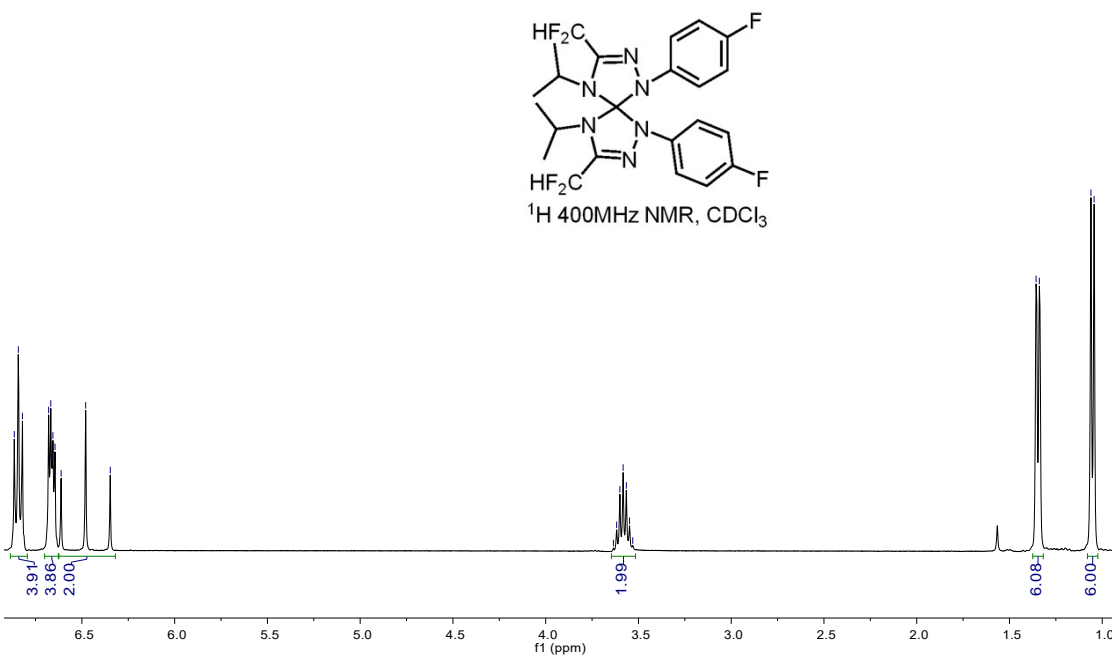
ZHOUYUXIU-10#65-112 RT: 0.29-0.50 AV: 48
T: FTMS + p ESI Full ms [120.0000-900.0000]
m/z= 616.4210-620.6939

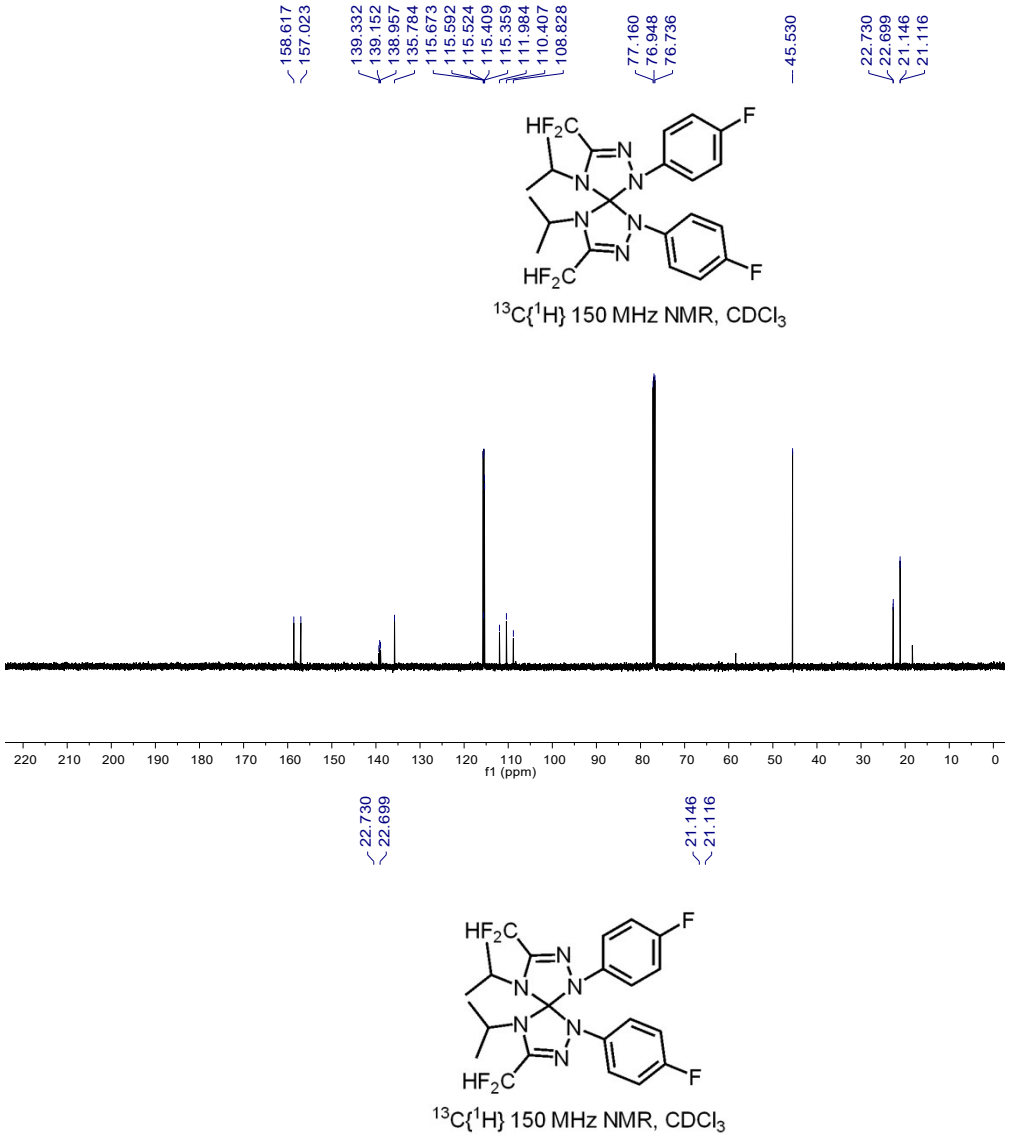
m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
619.0450	462111.3	100.00	619.0438	1.21	$C_{23}H_{25}N_6Br_2F_4$
619.5277	62064.2	13.43			
620.0445	8054.9	1.74			
620.5284	6714.8	1.45			

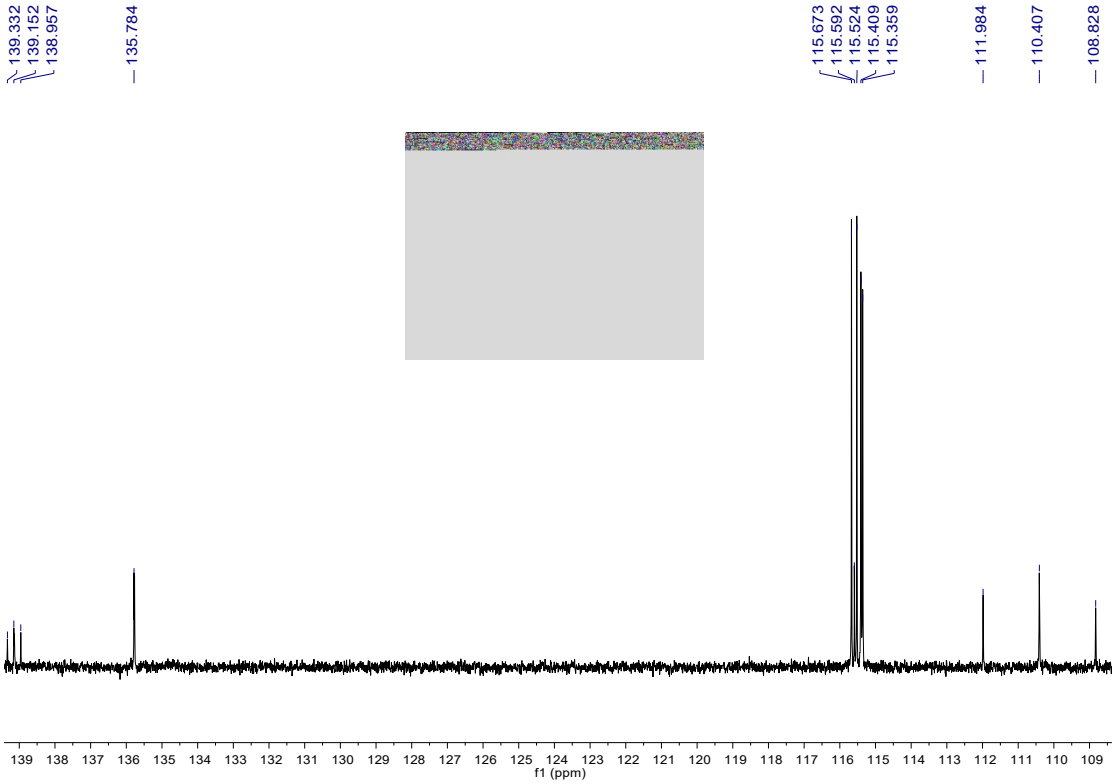


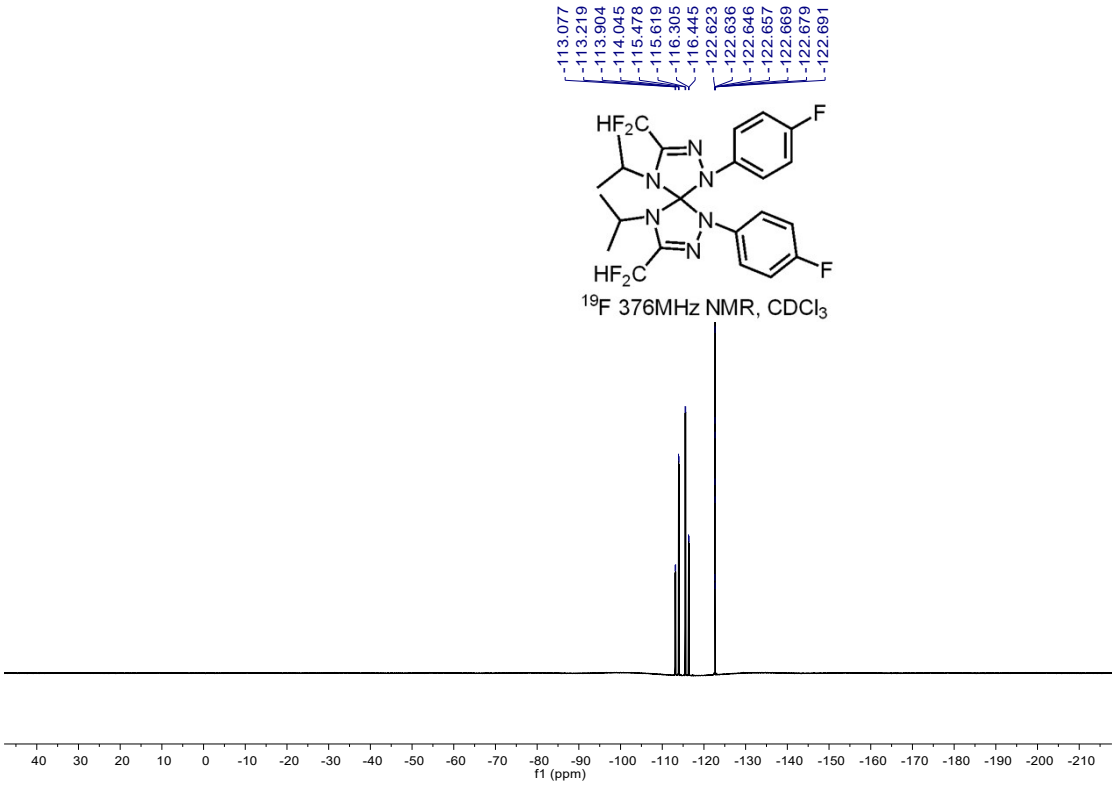
NMR copies of compound **3g**:

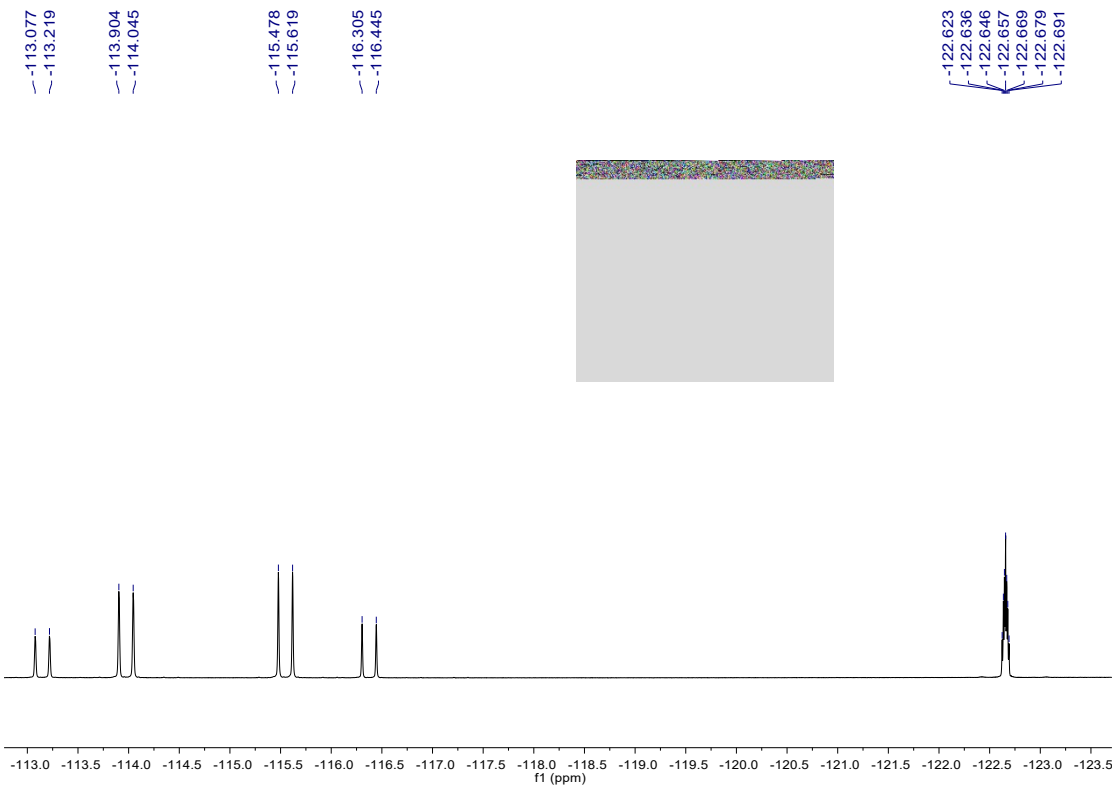




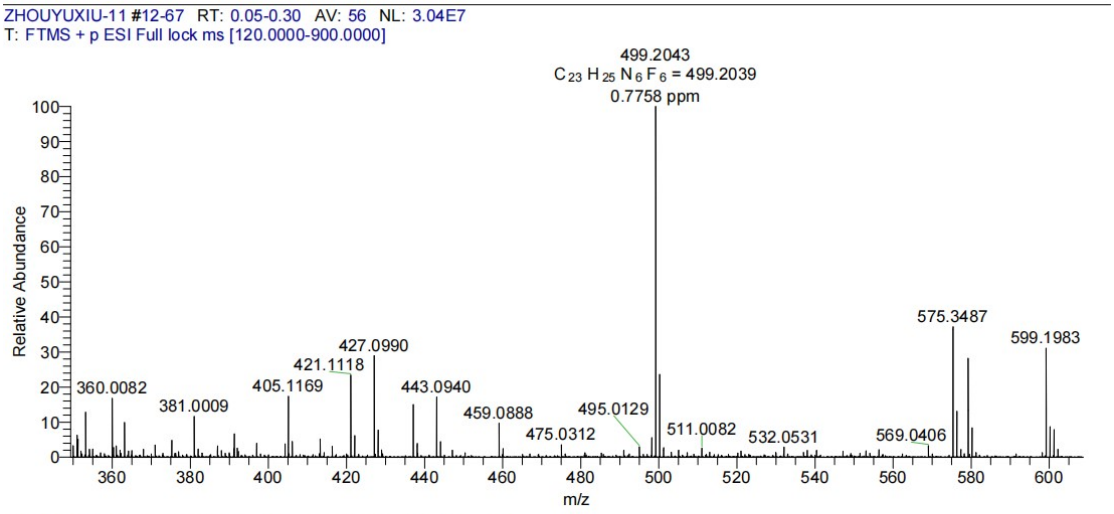

158.617
157.023
139.332
139.152
138.957
135.784
115.673
115.592
115.524
115.409
115.359
111.984
110.407
108.828
77.160
76.948
76.736
45.530
22.730
22.699
21.146
21.116
HF2C
F
N
HF2C
F
13C{1H} 150 MHz NMR, CDCl3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
22.730
22.699
21.146
21.116
HF2C
F
N
HF2C
F
13C{1H} 150 MHz NMR, CDCl3
24.6 24.4 24.2 24.0 23.8 23.6 23.4 23.2 23.0 22.8 22.6 22.4 22.2 22.0 21.8 21.6 21.4 21.2 21.0 20.8 20.6 20.4 20.2 20.0 19.8 19.6
f1 (ppm)


139.332
139.152
138.957
135.784
115.673
115.592
115.524
115.409
115.359
111.984
110.407
108.828
f1 (ppm)


-113.077
-113.219
-113.904
-114.045
-115.478
-115.619
-116.305
-116.445
-122.623
-122.636
-122.646
-122.657
-122.669
-122.679
-122.691
HF2C
F
HF2C
F
19F 376MHz NMR, CDCl3
f1 (ppm)

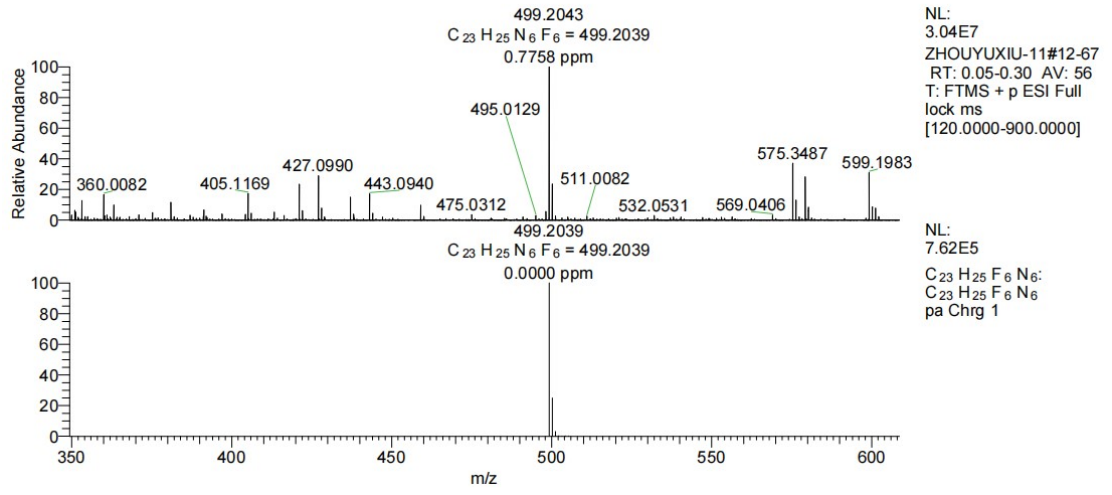

-113.077
-113.219
-113.904
-114.045
-115.478
-115.619
-116.305
-116.445
-122.623
-122.636
-122.646
-122.657
-122.669
-122.679
-122.691
-113.0 -113.5 -114.0 -114.5 -115.0 -115.5 -116.0 -116.5 -117.0 -117.5 -118.0 -118.5 -119.0 -119.5 -120.0 -120.5 -121.0 -121.5 -122.0 -122.5 -123.0 -123.5
f1 (ppm)

HRMS (ESI) copy of compound **3g**:

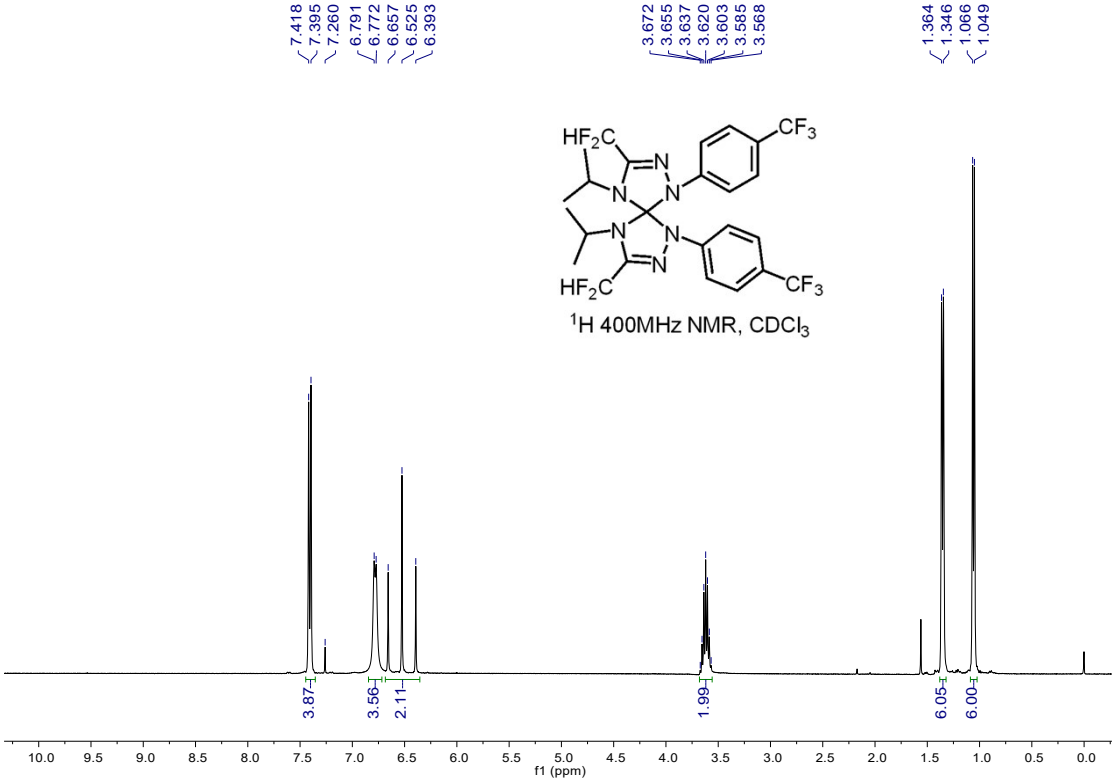


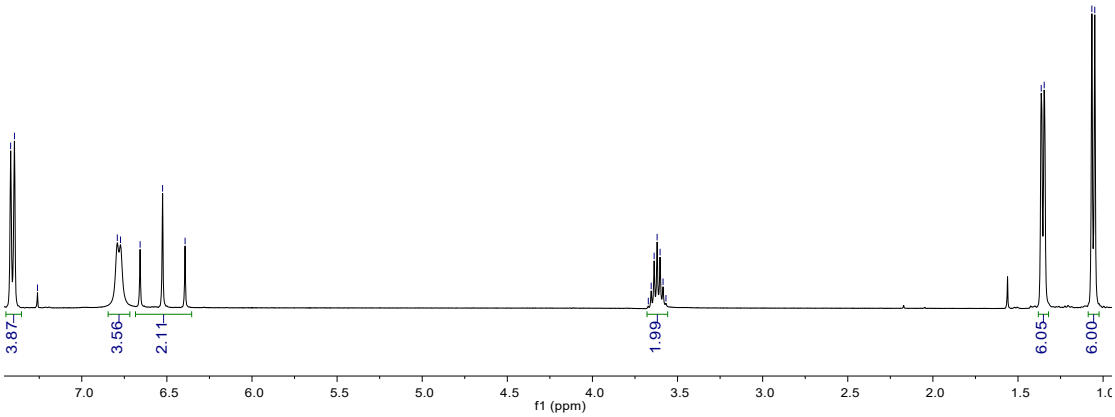
ZHOUYUXIU-11#12-67 RT: 0.05-0.30 AV: 56
T: FTMS + p ESI Full lock ms [120.0000-900.0000]
m/z= 349.3220-608.6441

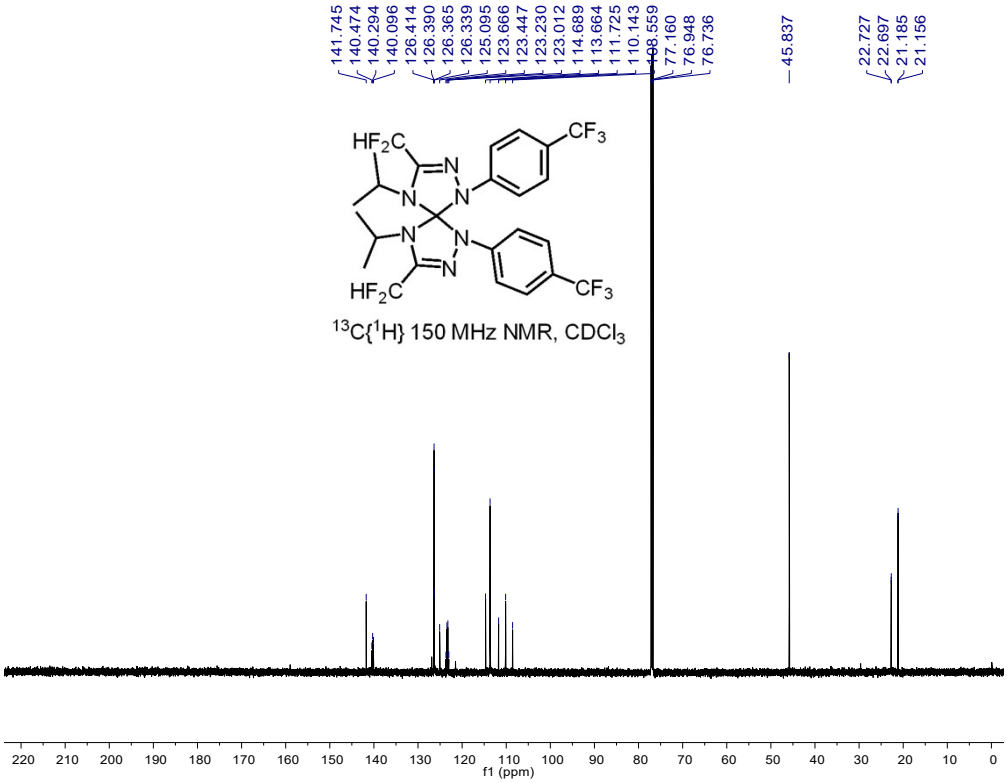
m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
427.0990	8979011.0	29.35			
499.2043	30591456.0	100.00	499.2039	0.39	$C_{23}H_{25}N_6F_6$
575.3487	11712624.0	38.29			
599.1983	9448322.0	30.89			

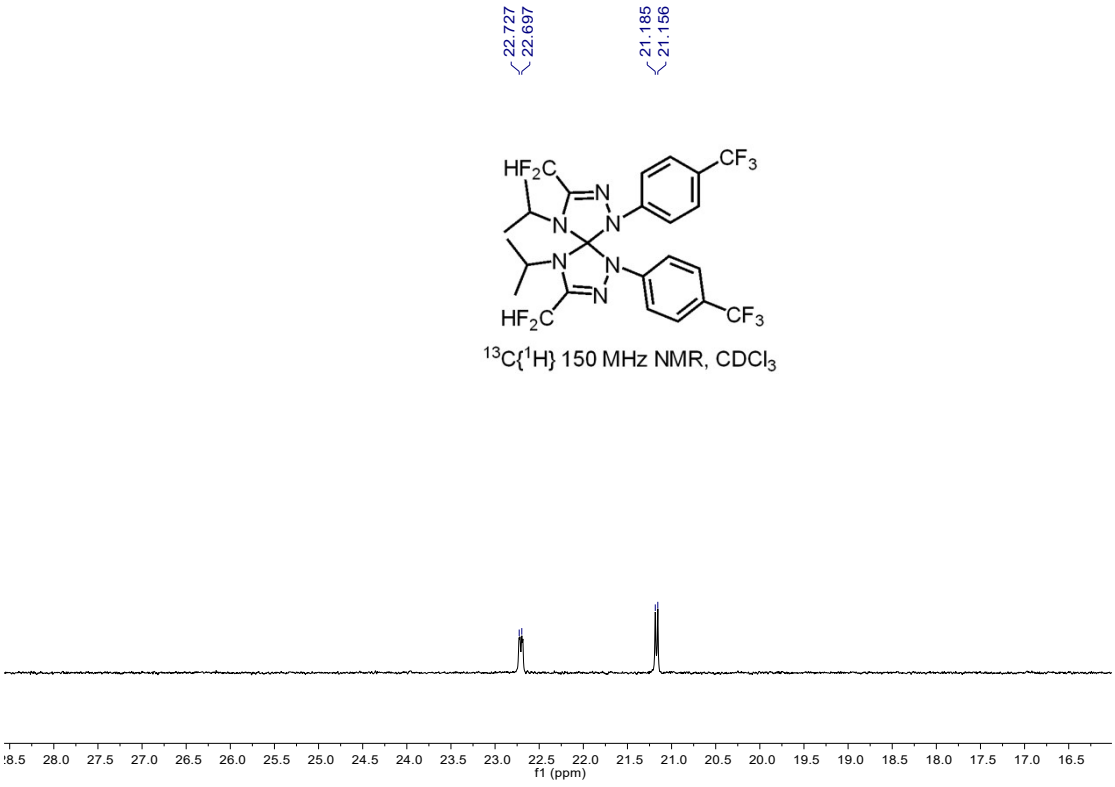


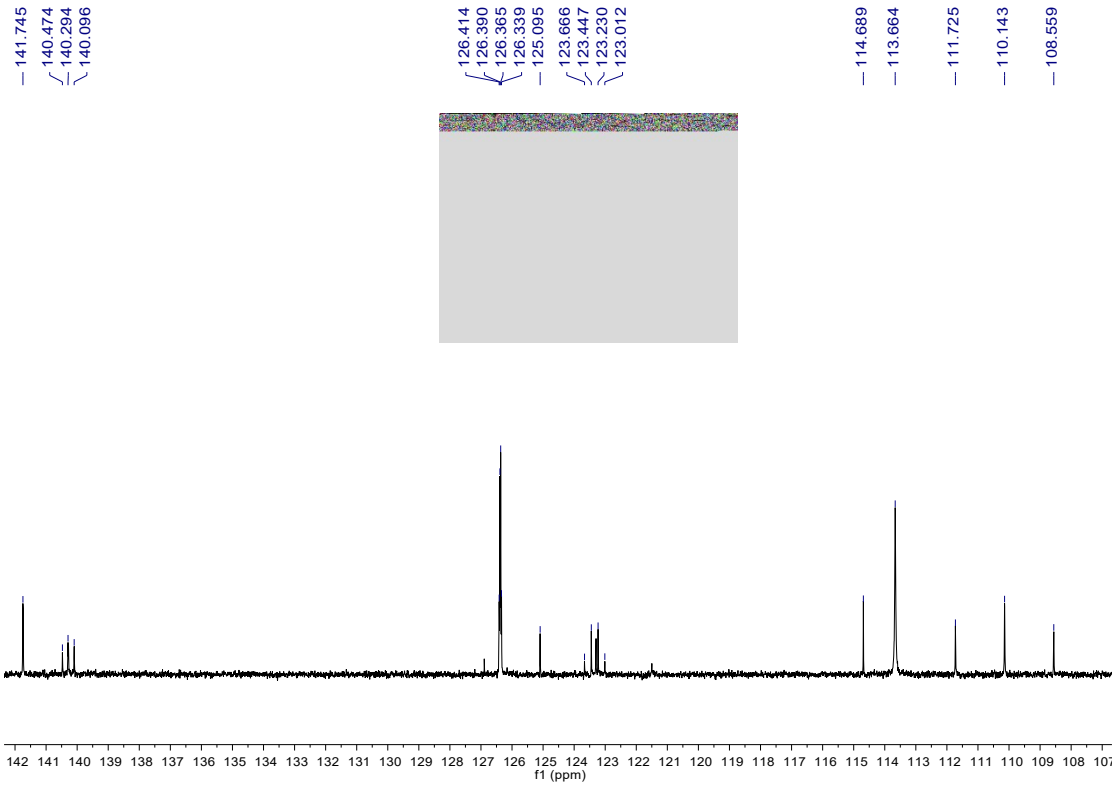
NMR copies of compound **3h**:

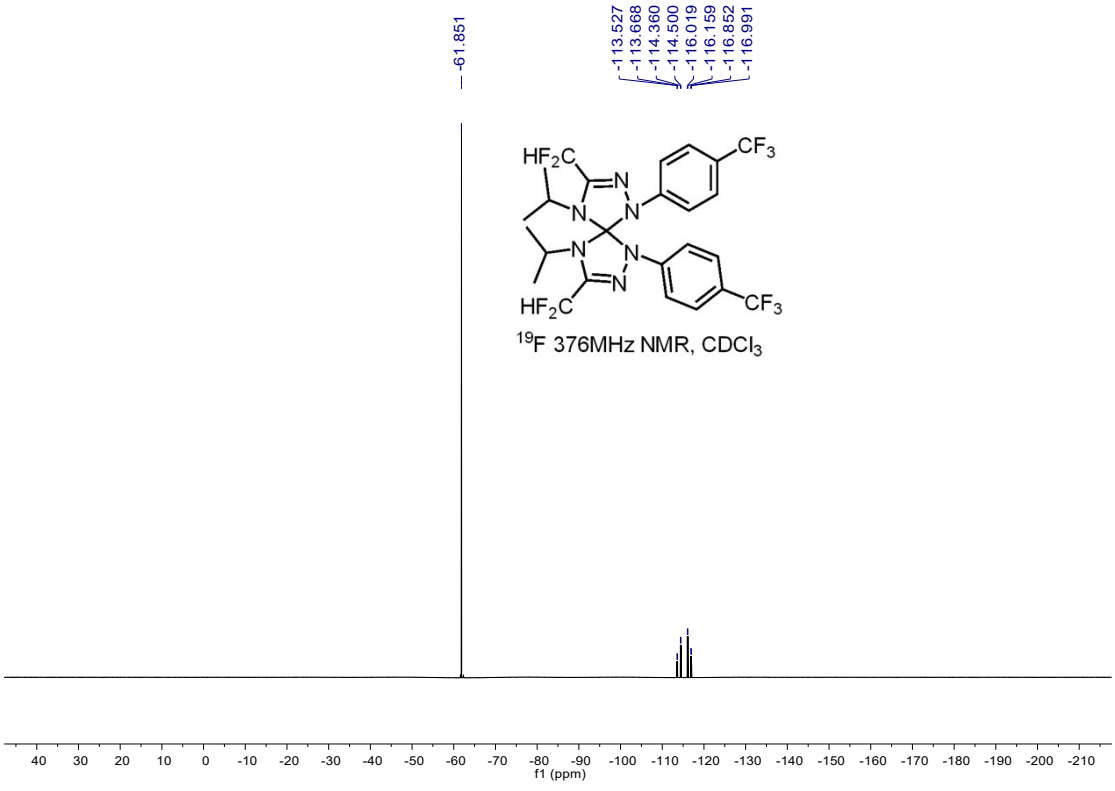


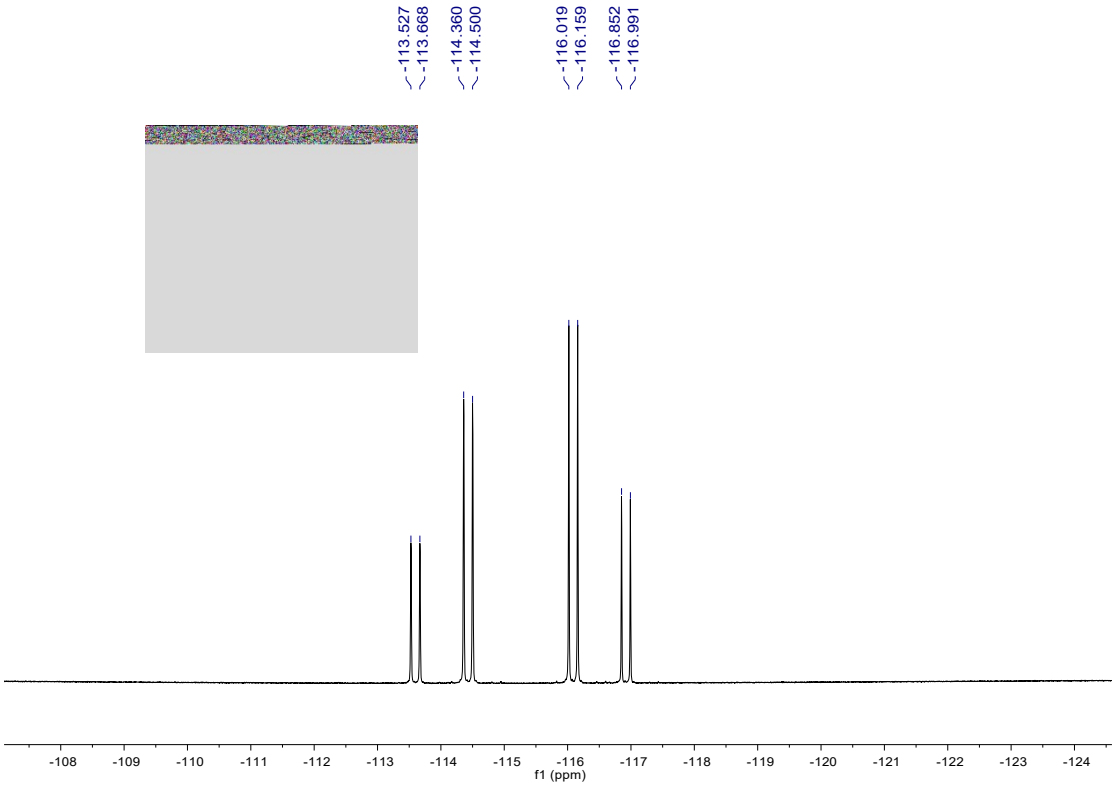



141.745
140.474
140.294
140.096
126.414
126.390
126.365
126.339
125.095
123.666
123.447
123.230
123.012
114.689
113.664
111.725
110.143
77.160
76.948
76.736
45.837
22.727
22.697
21.185
21.156
HF2C
CF3
HF2C
CF3
13C{1H} 150 MHz NMR, CDCl3
f1 (ppm)

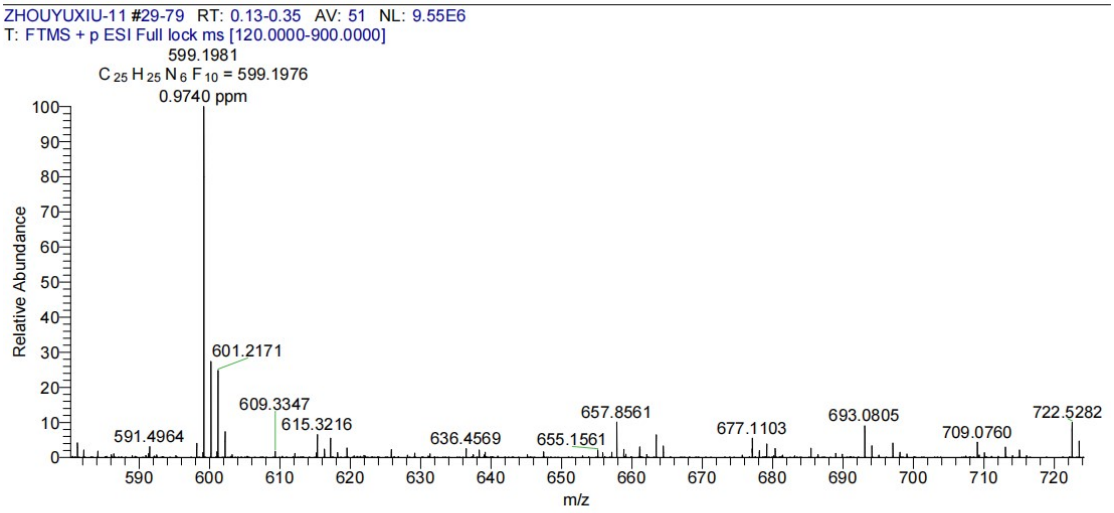

22.727
22.697
21.185
21.156
HF2C
CF3
HF2C
CF3
13C{1H} 150 MHz NMR, CDCl3
f1 (ppm)


141.745
140.474
140.294
140.096
126.414
126.390
126.365
126.339
125.095
123.666
123.447
123.230
123.012
114.689
113.664
111.725
110.143
108.559
f1 (ppm)


-61.851
-113.527
-113.668
-114.360
-114.500
-116.019
-116.159
-116.852
-116.991
HF2C
CF3
HF2C
CF3
19F 376MHz NMR, CDCl3
f1 (ppm)

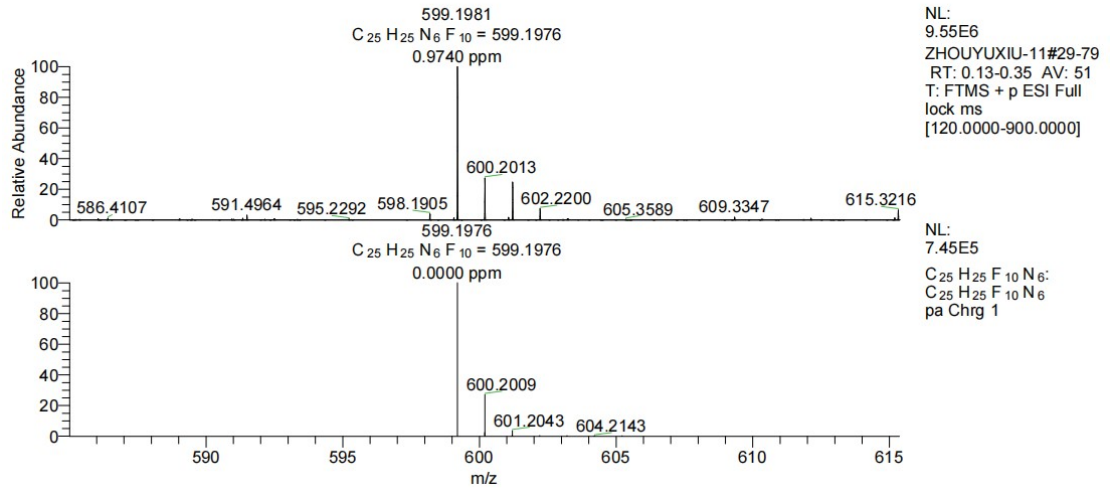

-113.527
-113.668
-114.360
-114.500
-116.019
-116.159
-116.852
-116.991
-108
-109
-110
-111
-112
-113
-114
-115
-116
-117
-118
-119
-120
-121
-122
-123
-124
f1 (ppm)

HRMS (ESI) copy of compound **3h**:

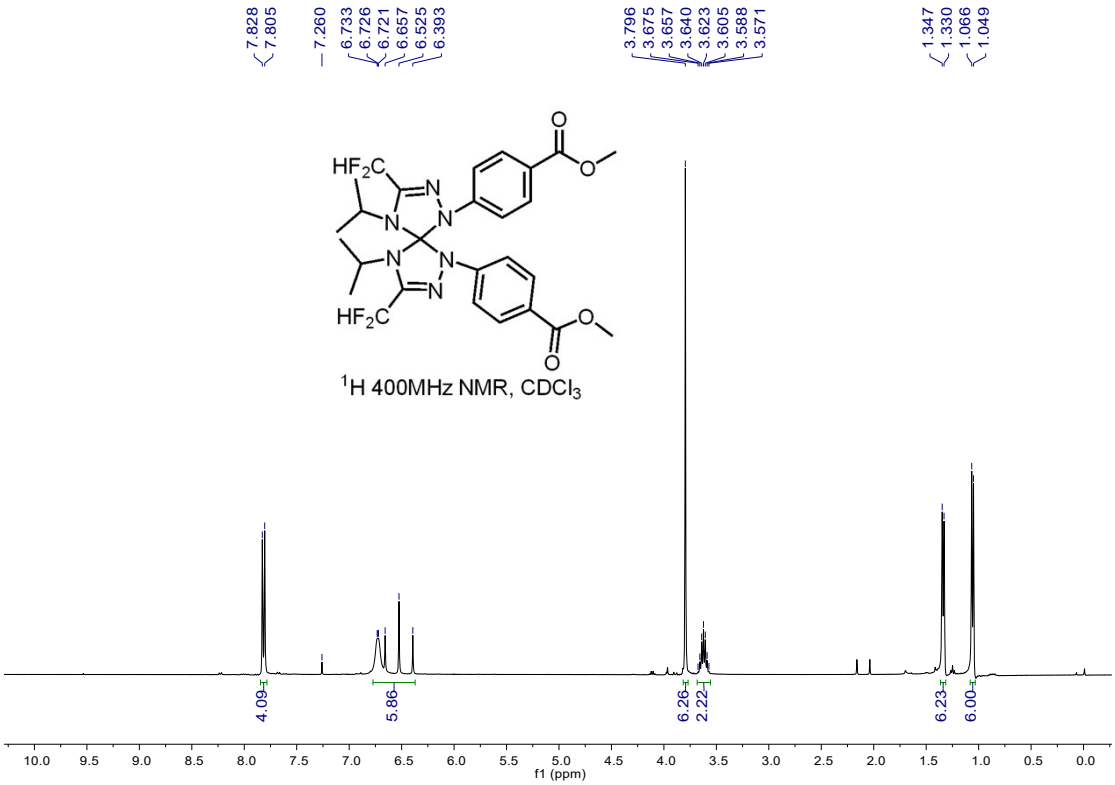


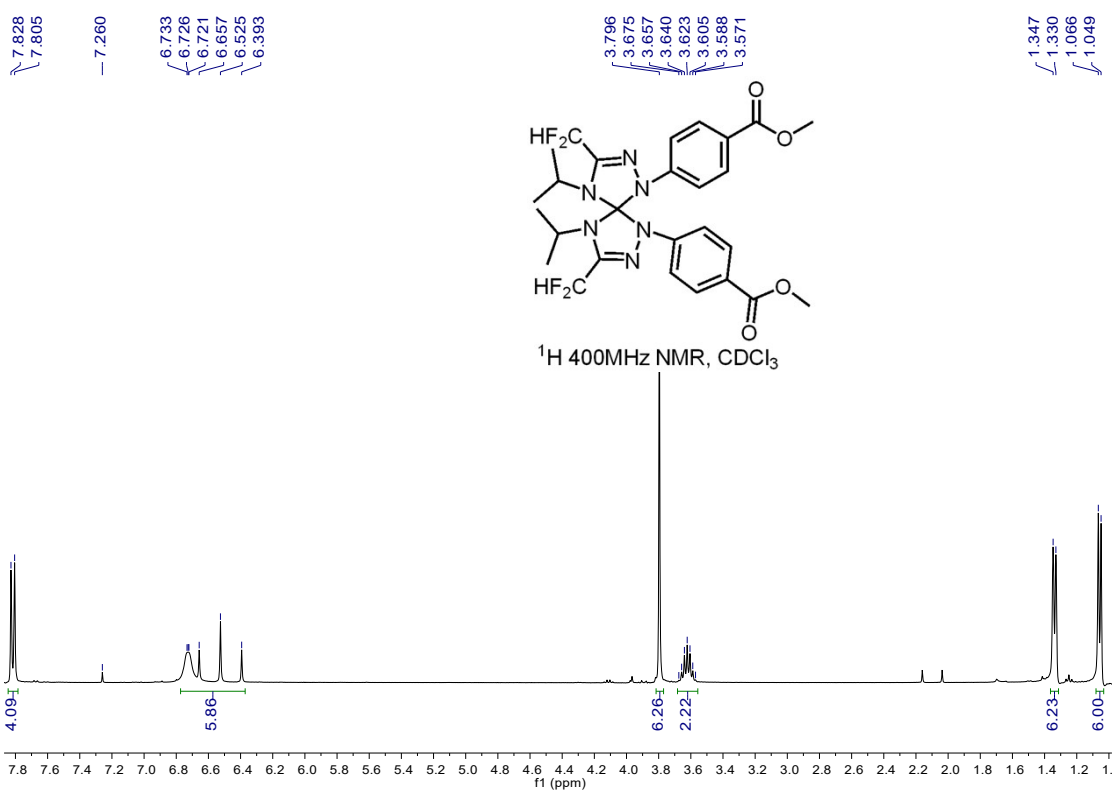
ZHOUYUXIU-11#29-79 RT: 0.13-0.35 AV: 51
T: FTMS + p ESI Full lock ms [120.0000-900.0000]
m/z= 580.2589-724.0815

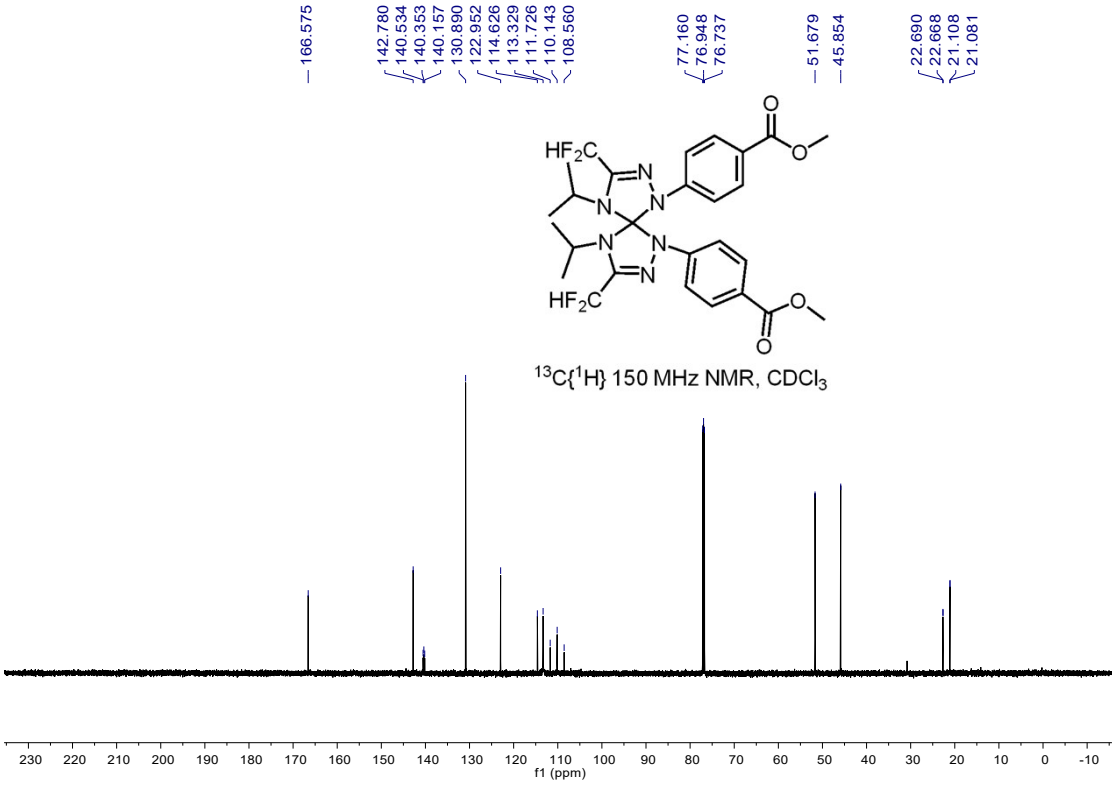
m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
599.1981	9554245.0	100.00	599.1976	0.58	$C_{25}H_{25}N_6F_{10}$
600.2013	2620759.0	27.43			
601.2171	2374653.3	24.85			
657.8561	967915.4	10.13			

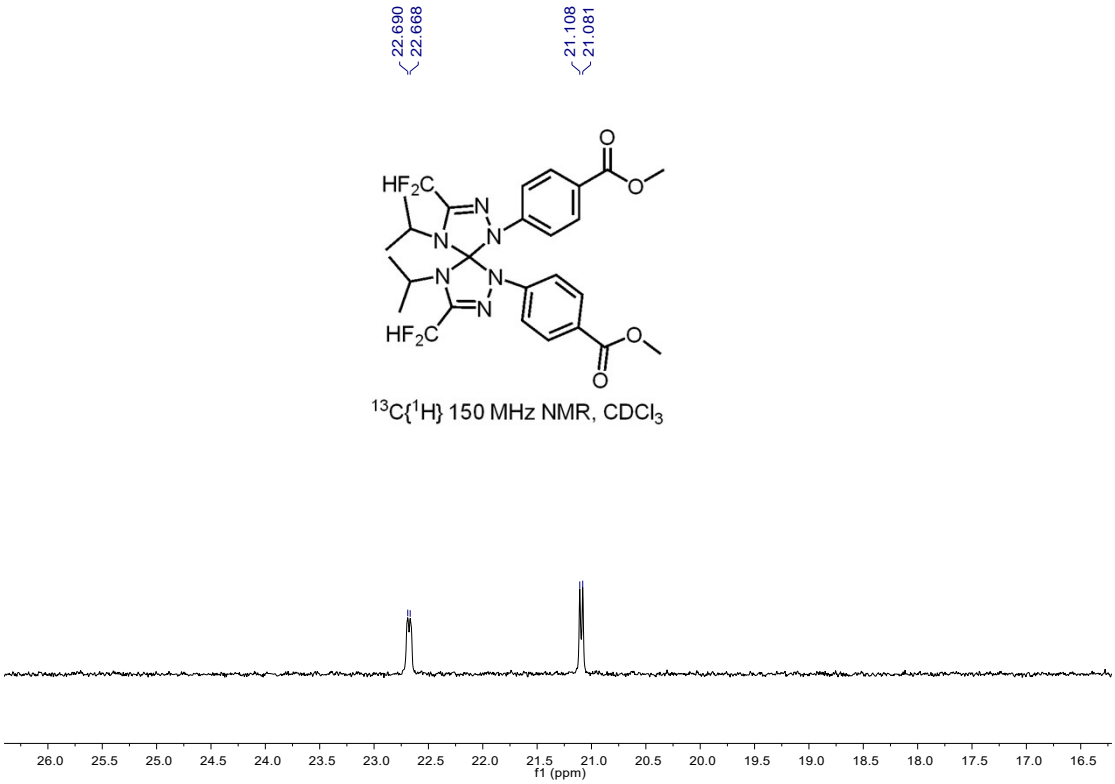


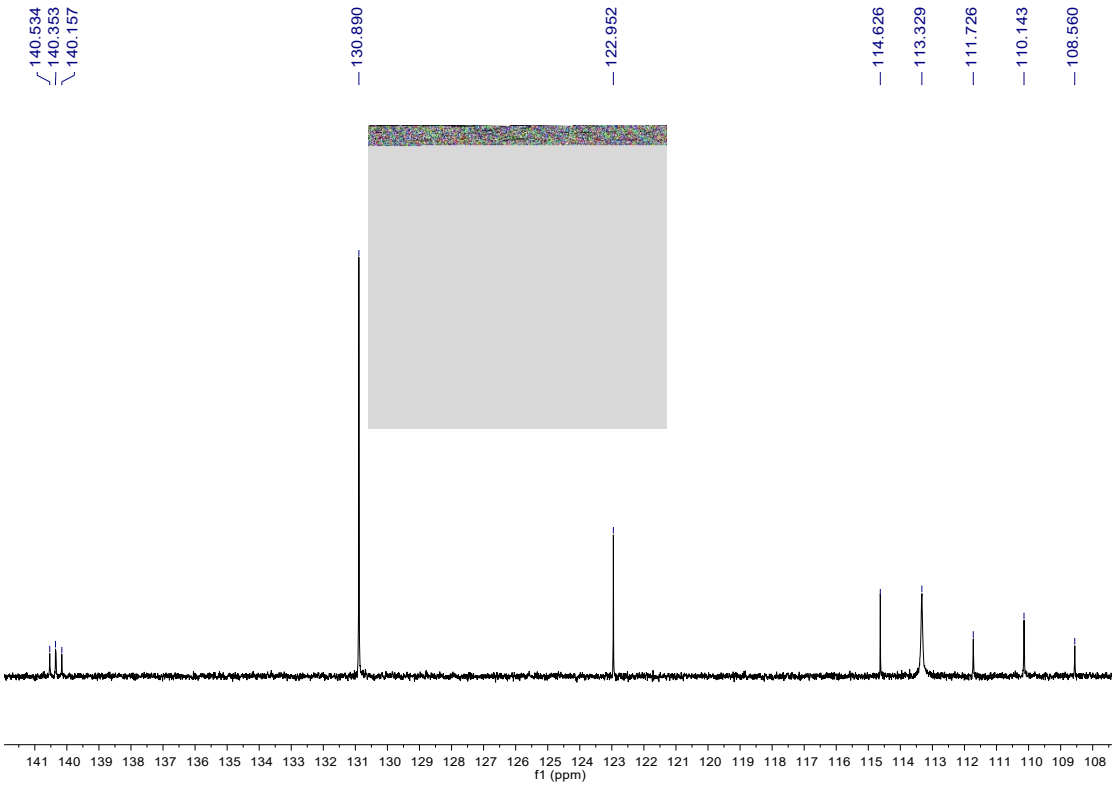
NMR copies of compound **3i**:

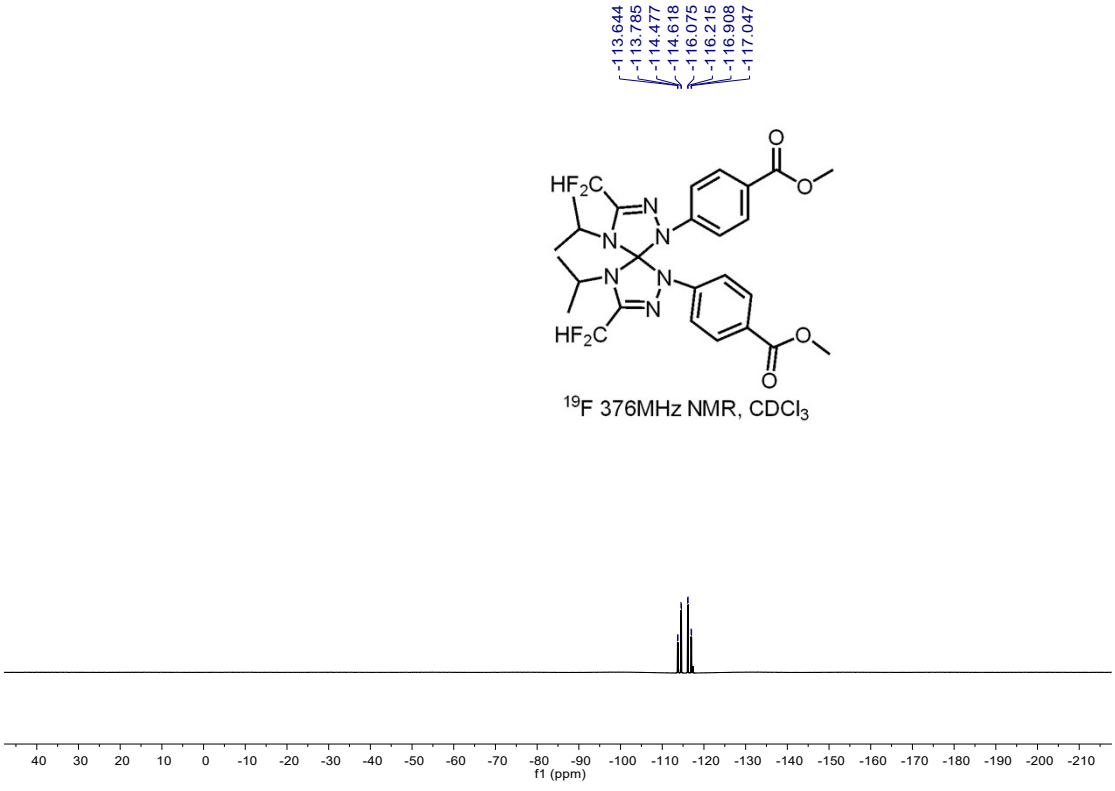




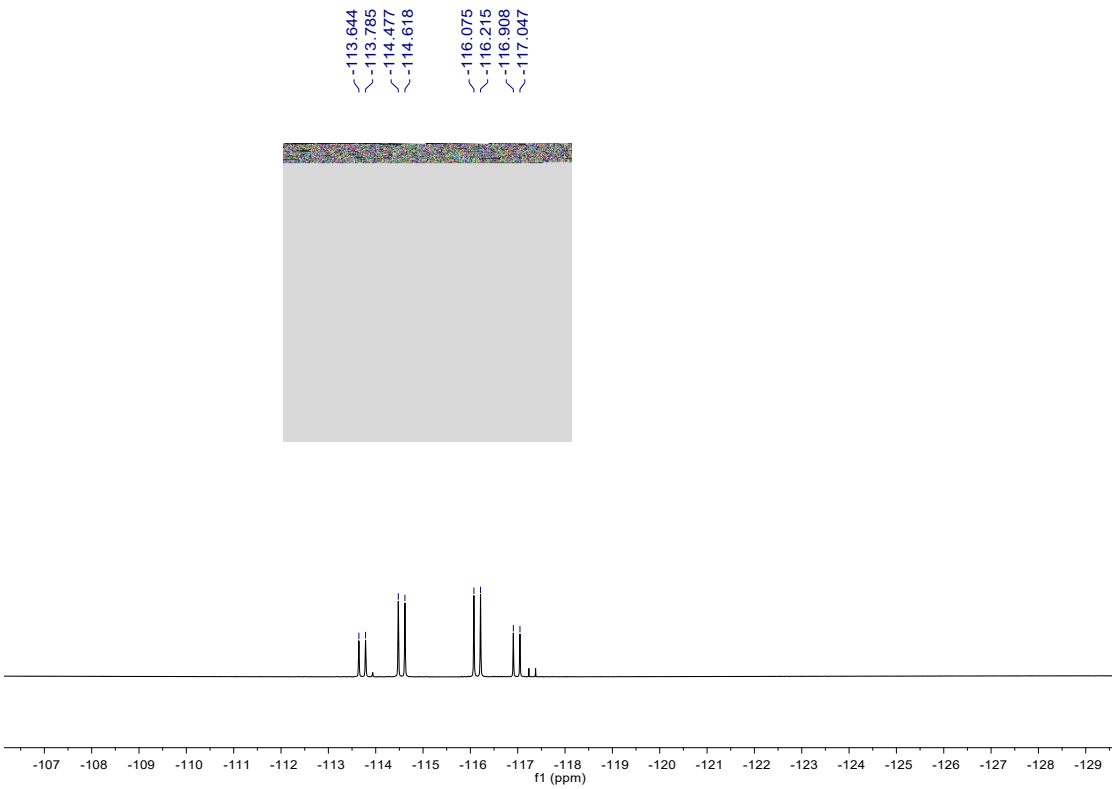

166.575
142.780
140.534
140.353
140.157
130.890
122.952
114.626
113.329
111.726
110.143
108.560
77.160
76.948
76.737
51.679
45.854
22.690
22.668
21.108
21.081
HF2C
HF2C
O
O
O
O
13C{1H} 150 MHz NMR, CDCl3
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


22.690
22.668
21.108
21.081
HF2C
HF2C
O
O
O
O
13C{1H} 150 MHz NMR, CDCl3
26.0 25.5 25.0 24.5 24.0 23.5 23.0 22.5 22.0 21.5 21.0 20.5 20.0 19.5 19.0 18.5 18.0 17.5 17.0 16.5
f1 (ppm)

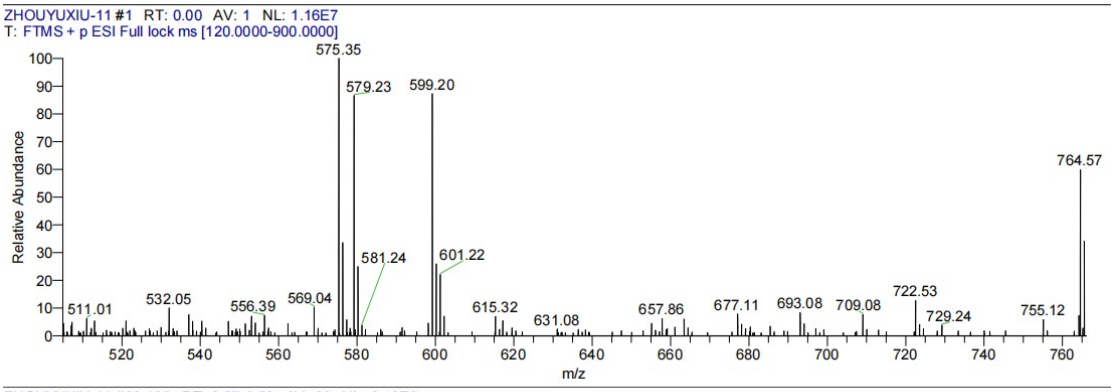


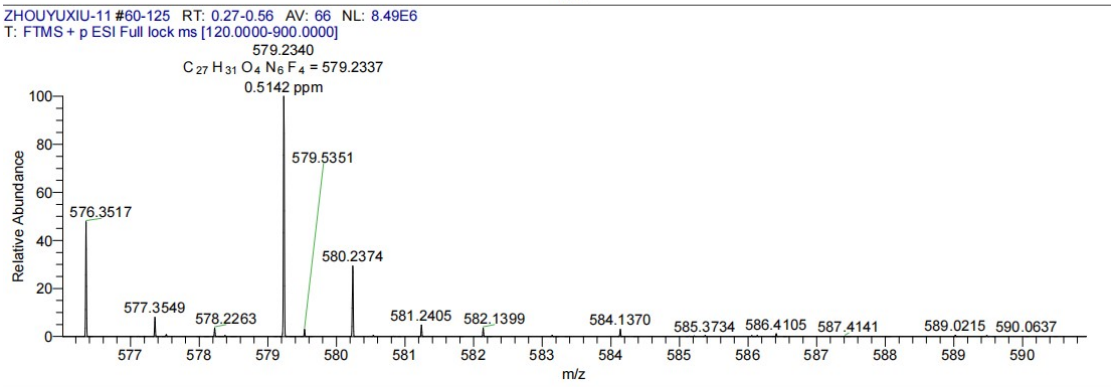


^{19}F 376MHz NMR, $CDCl_3$


-113.644
-113.785
-114.477
-114.618
-116.075
-116.215
-116.908
-117.047
-107 -108 -109 -110 -111 -112 -113 -114 -115 -116 -117 -118 -119 -120 -121 -122 -123 -124 -125 -126 -127 -128 -129
f1 (ppm)

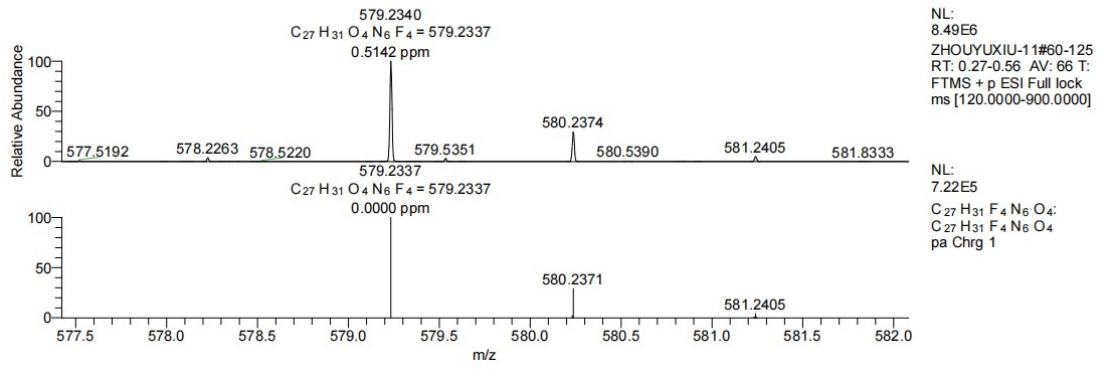
HRMS (ESI) copy of compound **3i**:



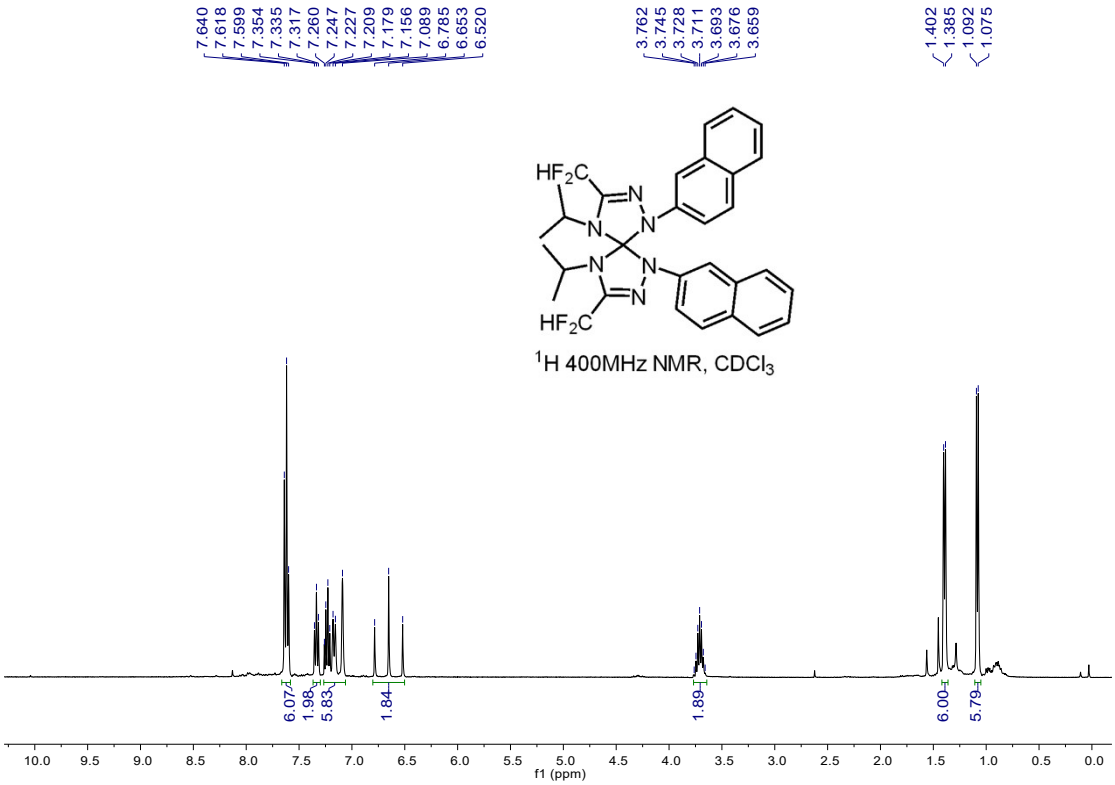


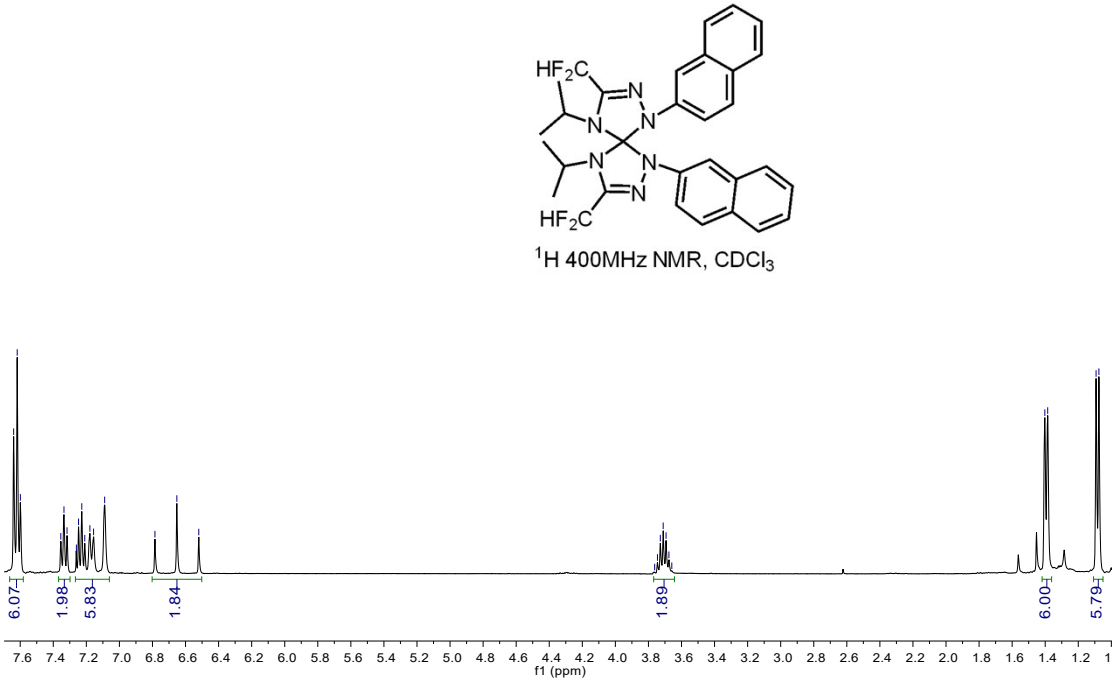
ZHOUYUXIU-11#60-125 RT: 0.27-0.56 AV: 66
T: FTMS + p ESI Full lock ms [120.0000-900.0000]
m/z= 576.0107-590.9278

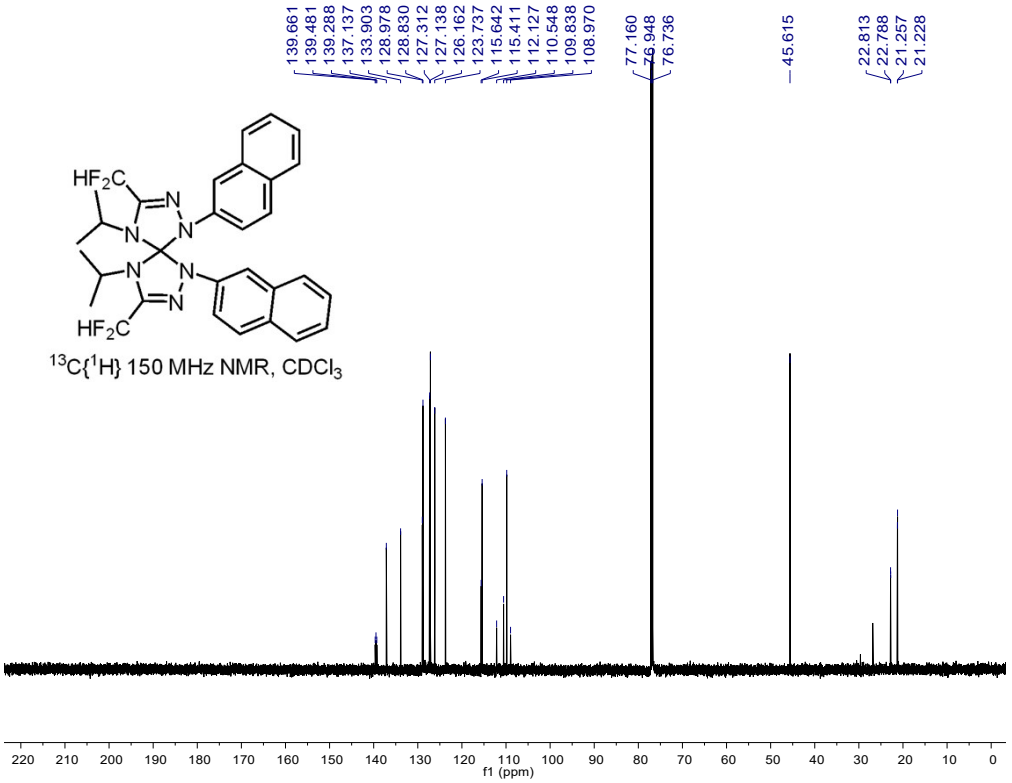
m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
576.3517	4077658.8	47.90			
577.3549	691967.3	8.13			
579.2340	8513683.0	100.00	579.2337	0.30	$C_{27}H_{31}O_4N_6F_4$
580.2374	2525476.3	29.66			

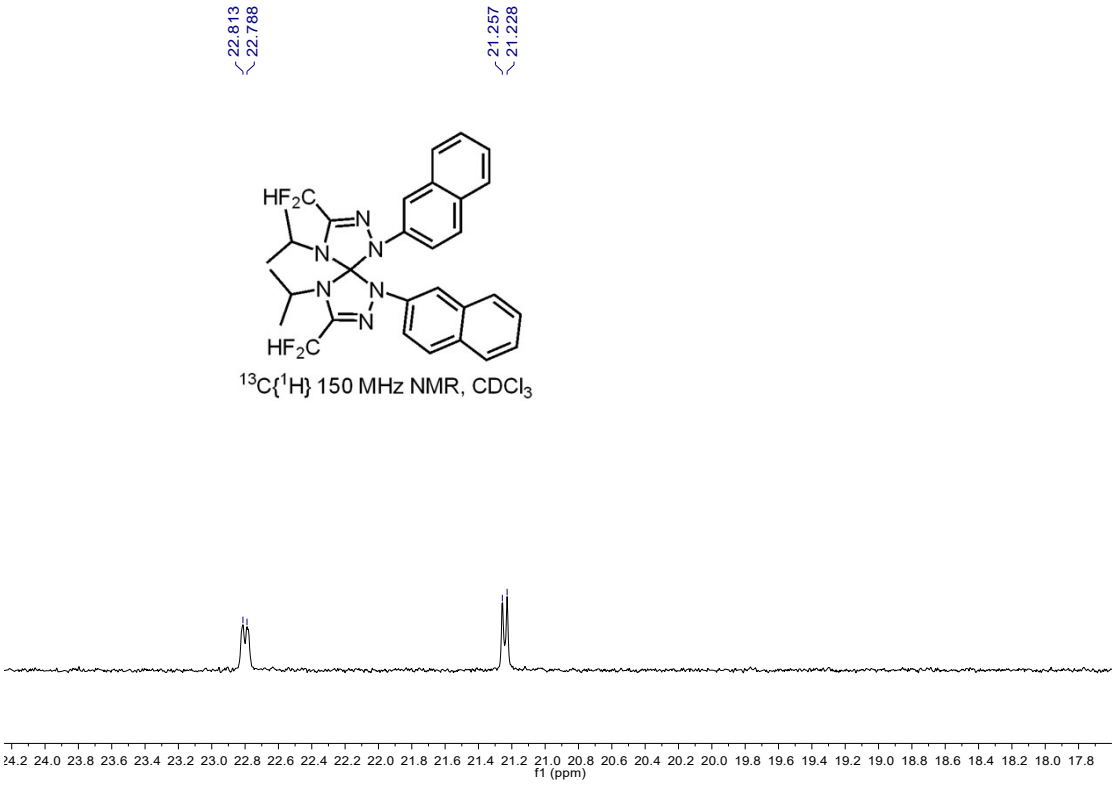


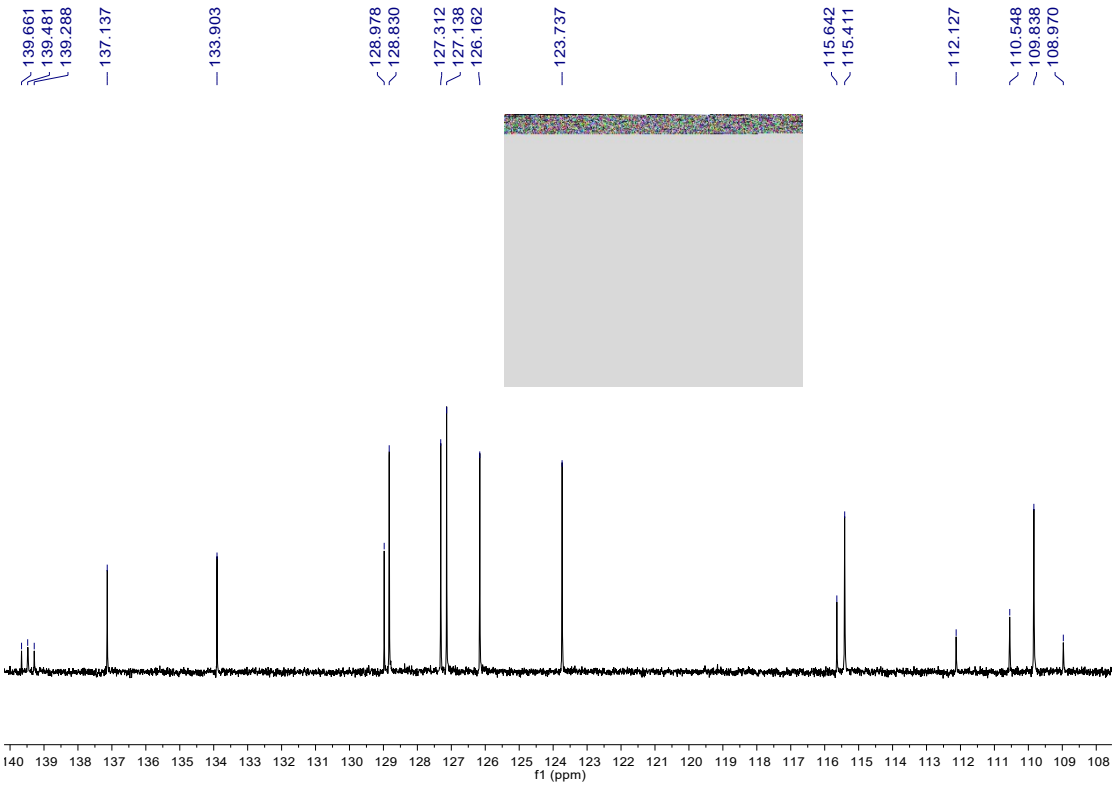
NMR copies of compound **3j**:

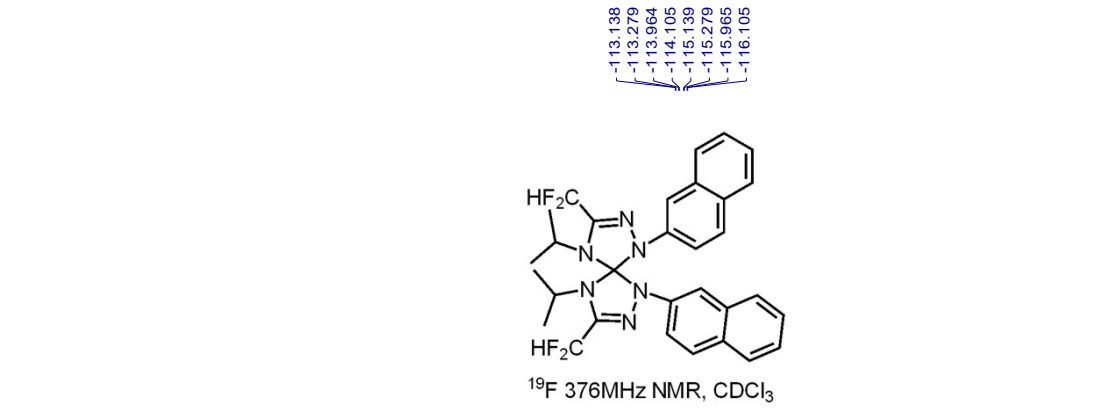




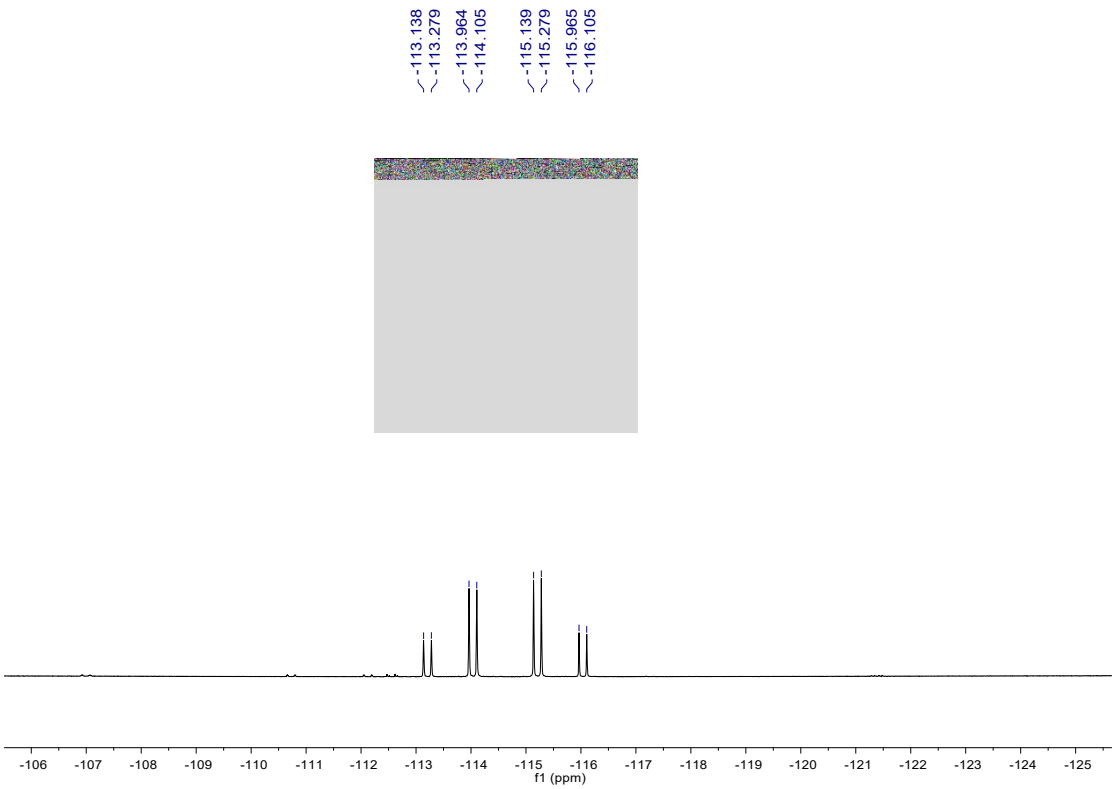

139.661
139.481
139.288
137.137
133.903
128.978
128.830
127.312
127.138
126.162
123.737
115.642
115.411
112.127
110.548
109.838
108.970
77.160
76.948
76.736
45.615
22.813
22.788
21.257
21.228
HF2C
HF2C
13C{1H} 150 MHz NMR, CDCl3
f1 (ppm)


22.813
22.788
21.257
21.228
HF2C
HF2C
13C{1H} 150 MHz NMR, CDCl3
f1 (ppm)

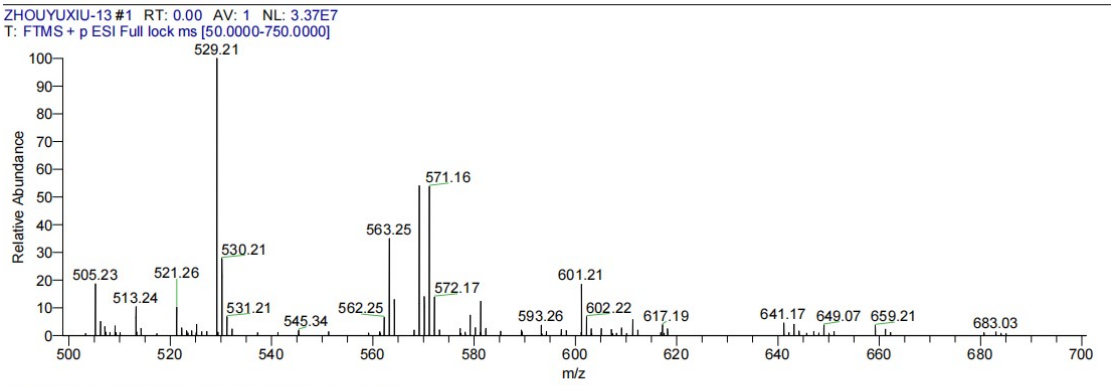


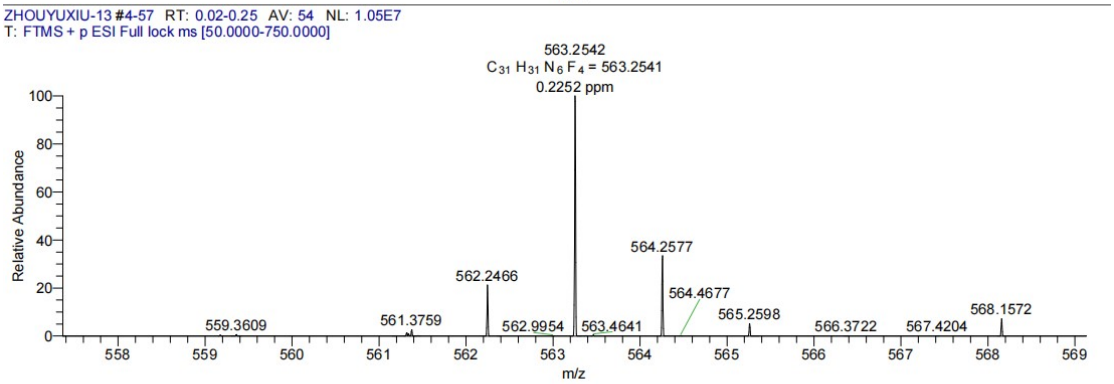


^{19}F 376MHz NMR, $CDCl_3$


-113.138
-113.279
-113.964
-114.105
-115.139
-115.279
-115.965
-116.105
-106
-107
-108
-109
-110
-111
-112
-113
-114
-115
-116
-117
-118
-119
-120
-121
-122
-123
-124
-125
f1 (ppm)

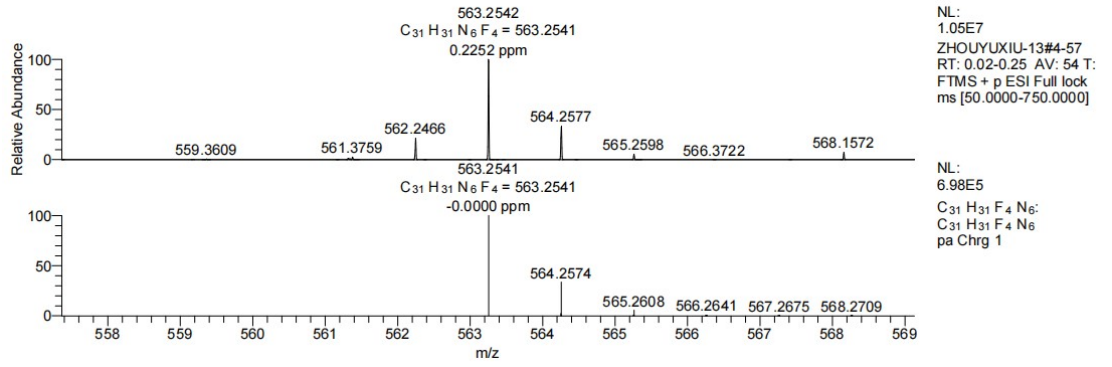
HRMS (ESI) copy of compound **3j**:



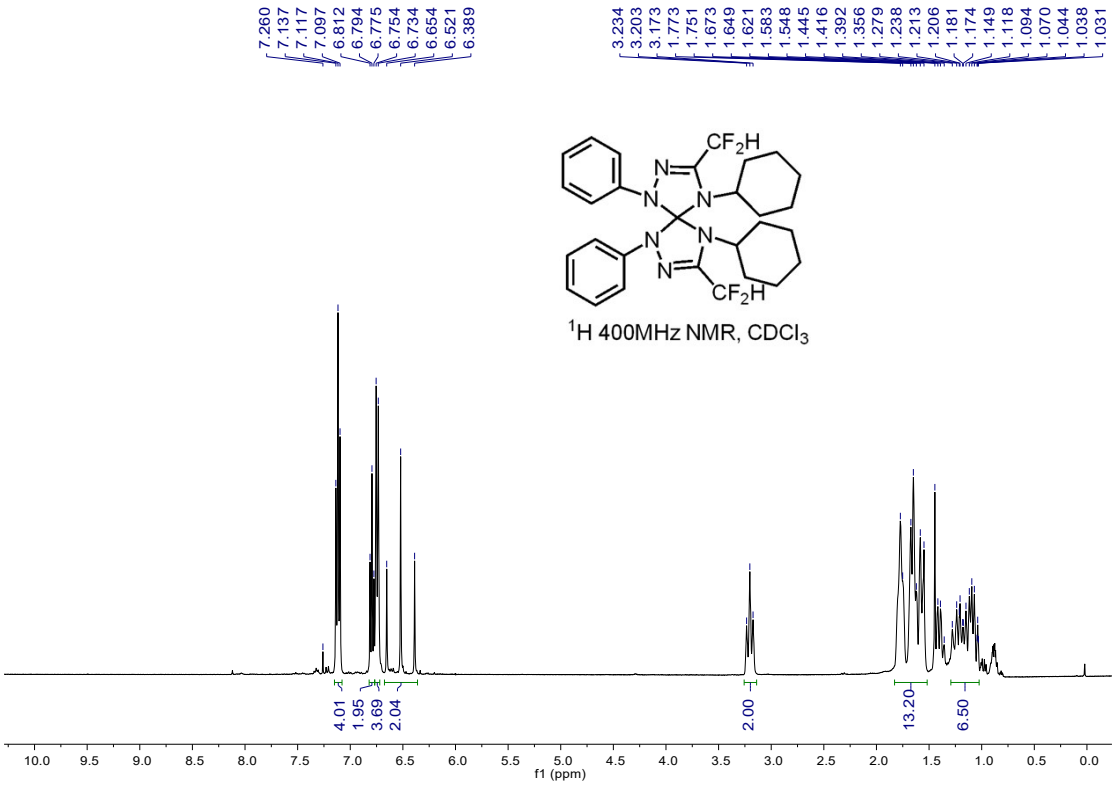


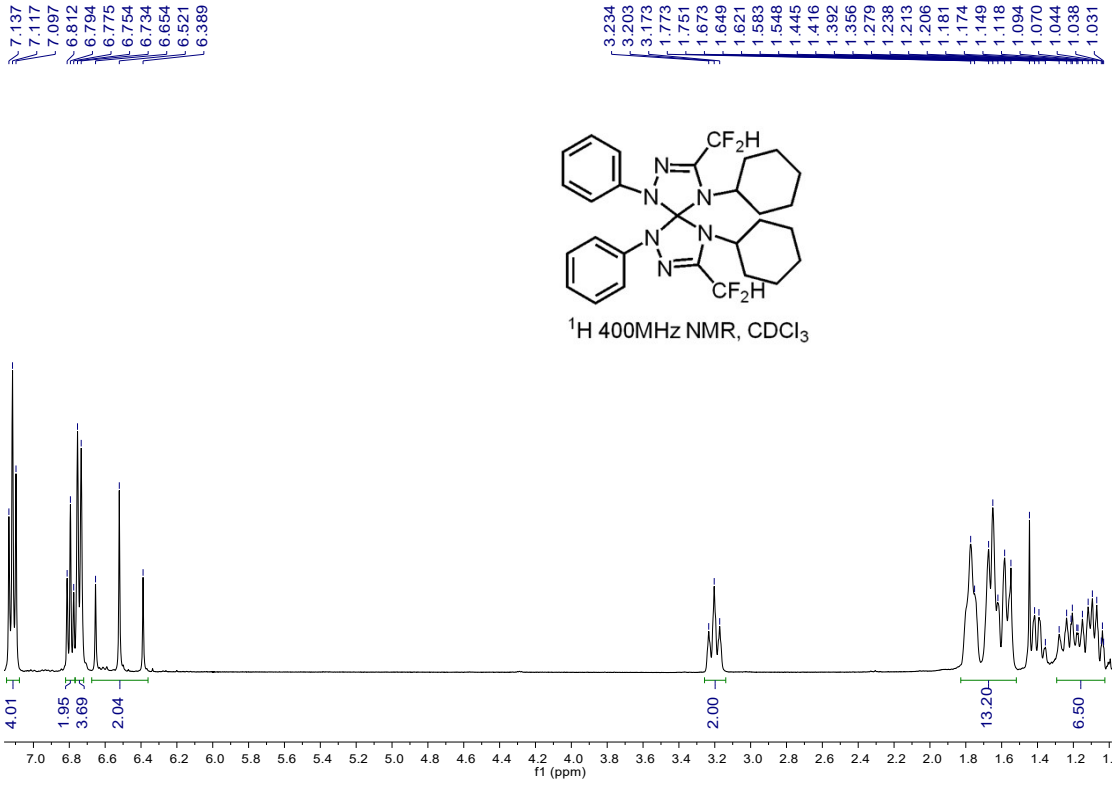
ZHOUYUXIU-13#4-57 RT: 0.02-0.25 AV: 54
T: FTMS + p ESI Full lock ms [50.0000-750.0000]
m/z= 557.3638-569.1287

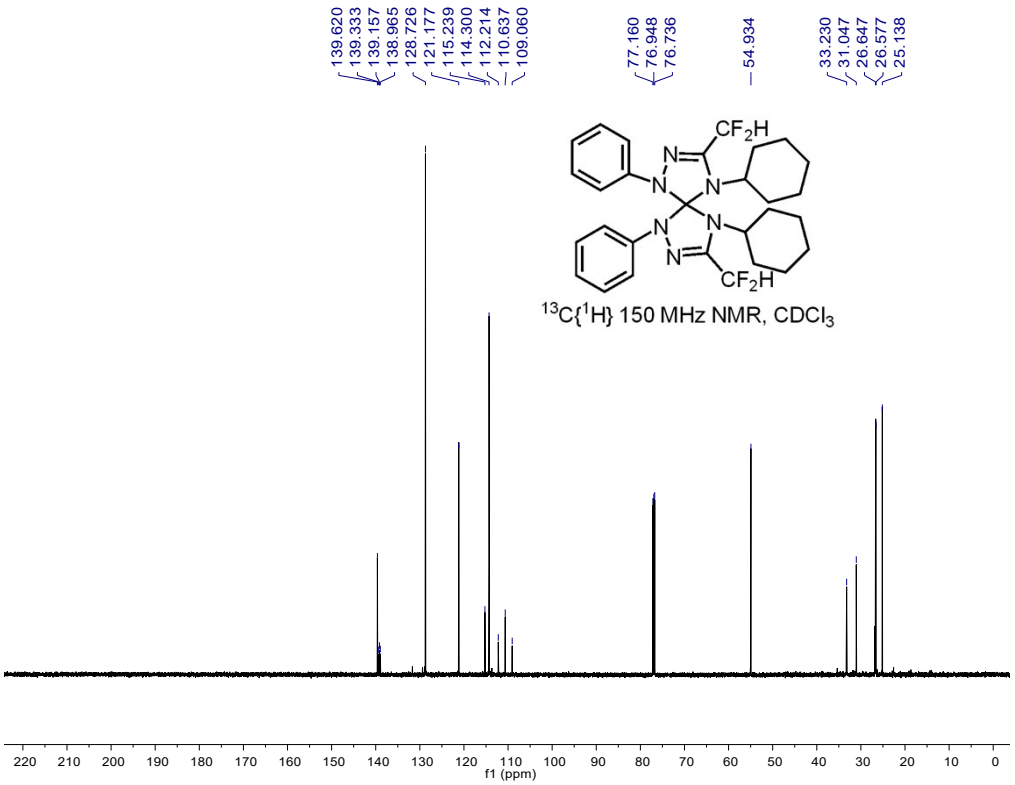
m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
562.2466	2235130.0	20.69			
563.2542	10801967.0	100.00	563.2541	0.13	$C_{31}H_{31}N_6F_4$
564.2577	3595902.3	33.29			
568.1572	768963.6	7.12			

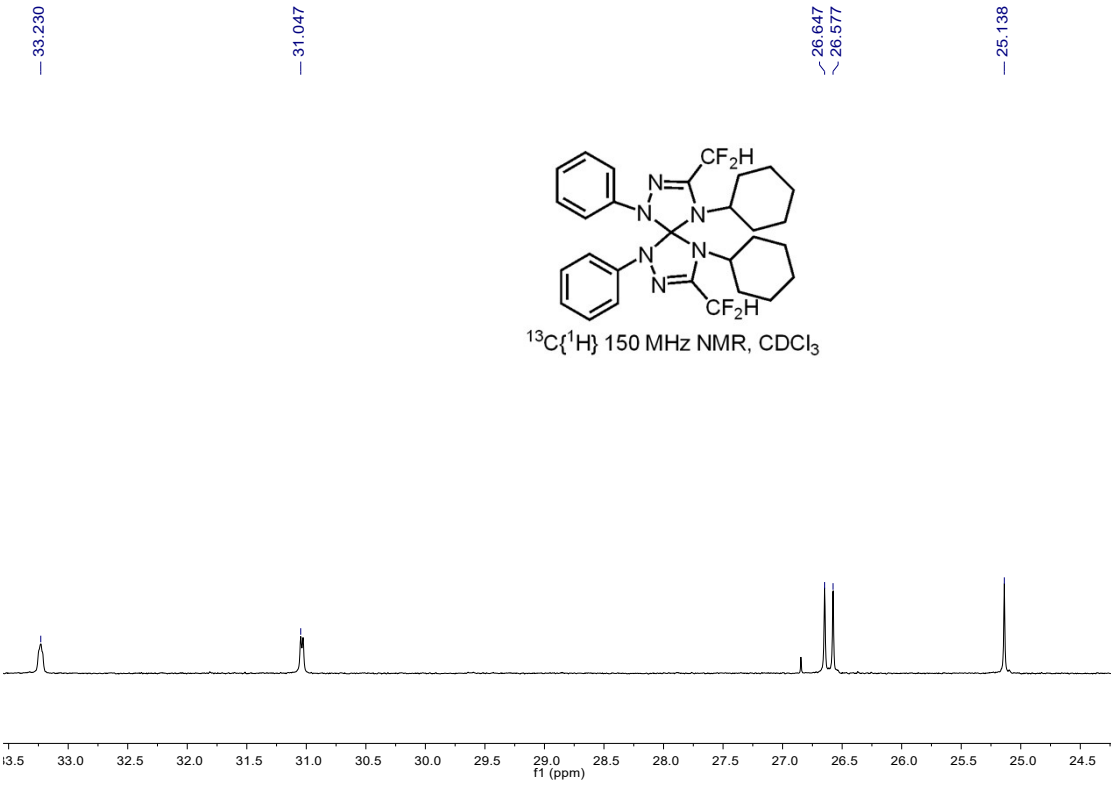


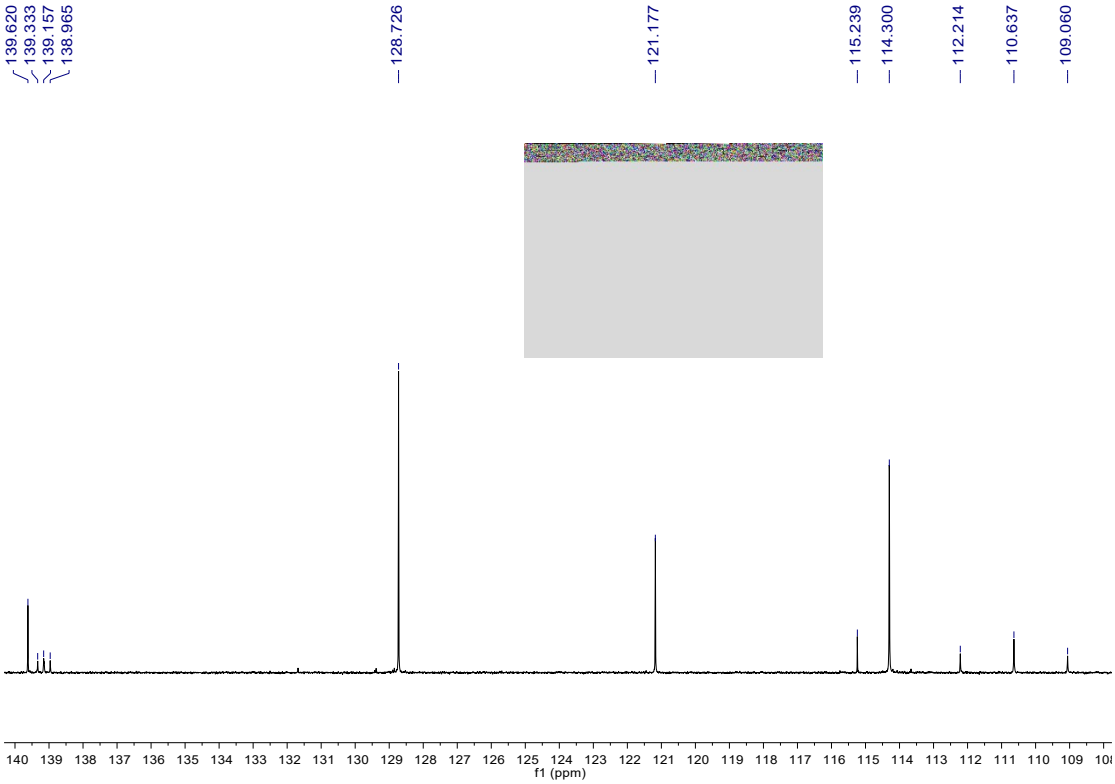
NMR copies of compound **3k**:

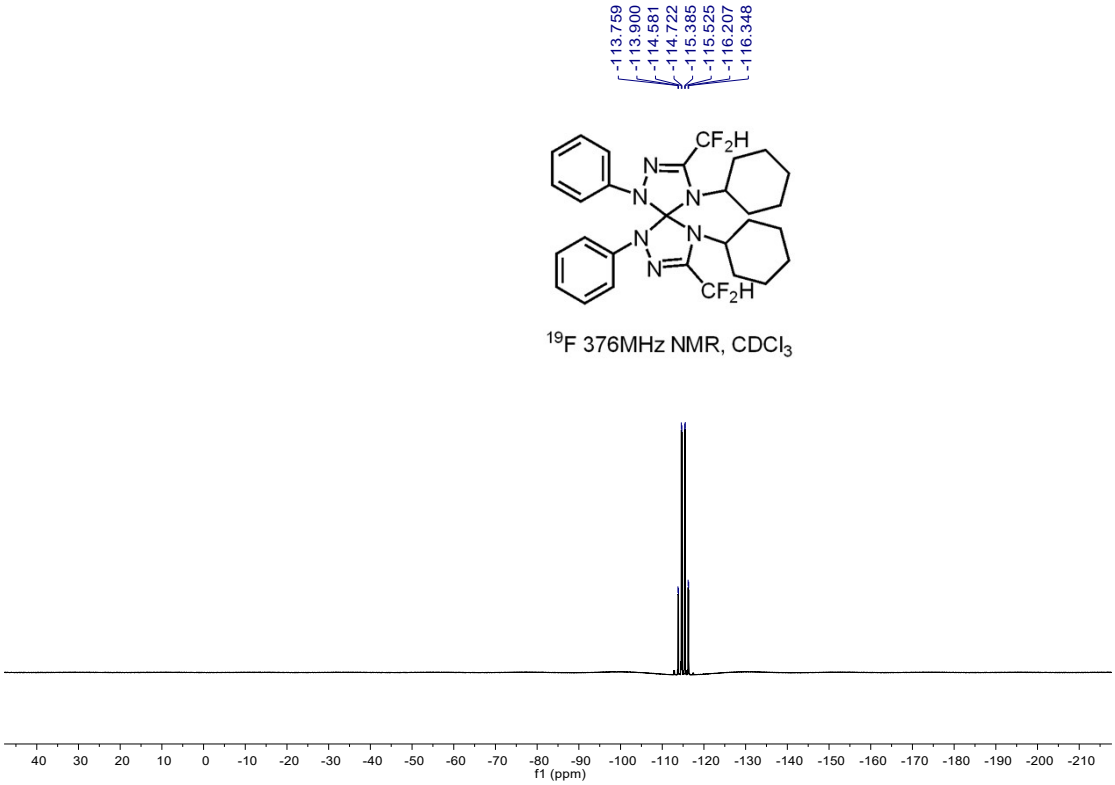





139.620
139.333
139.157
138.965
128.726
121.177
115.239
114.300
112.214
110.637
109.060
77.160
76.948
76.736
54.934
33.230
31.047
26.647
26.577
25.138
CF2H
CF2H
13C{1H} 150 MHz NMR, CDCl3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

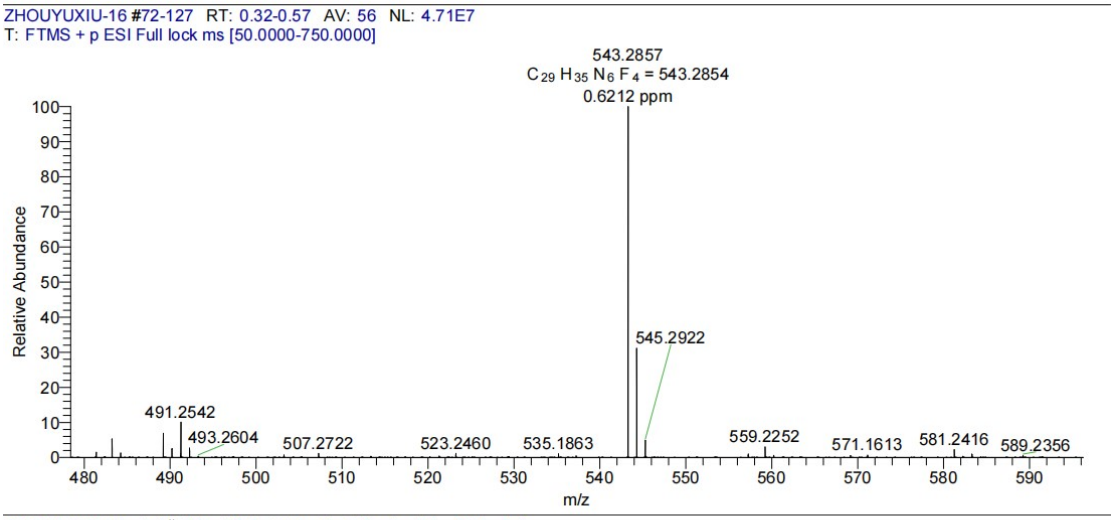

33.230
31.047
26.647
26.577
25.138
CF2H
CF2H
13C{1H} 150 MHz NMR, CDCl3
33.5 33.0 32.5 32.0 31.5 31.0 30.5 30.0 29.5 29.0 28.5 28.0 27.5 27.0 26.5 26.0 25.5 25.0 24.5
f1 (ppm)





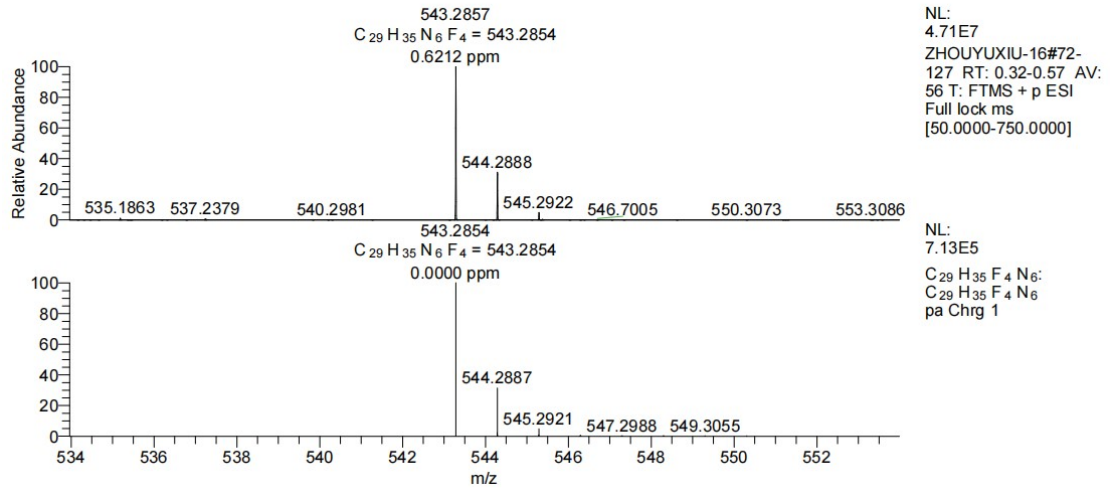
^{19}F 376MHz NMR, $CDCl_3$

HRMS (ESI) copy of compound **3k**:

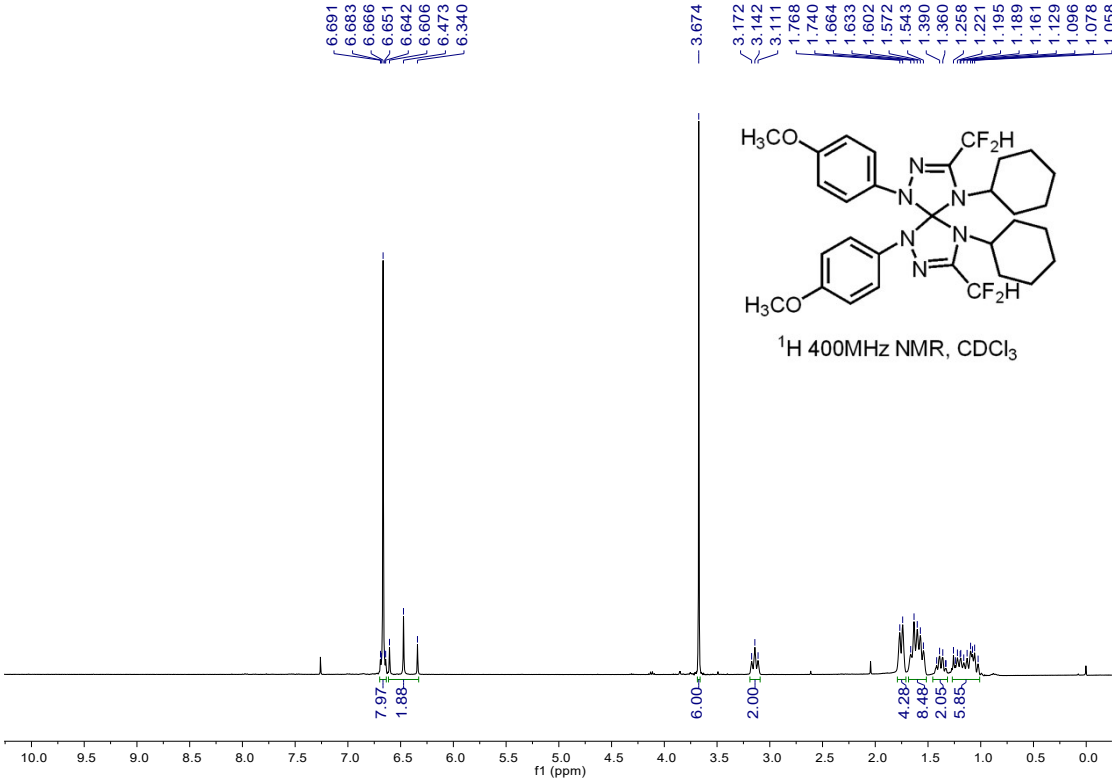


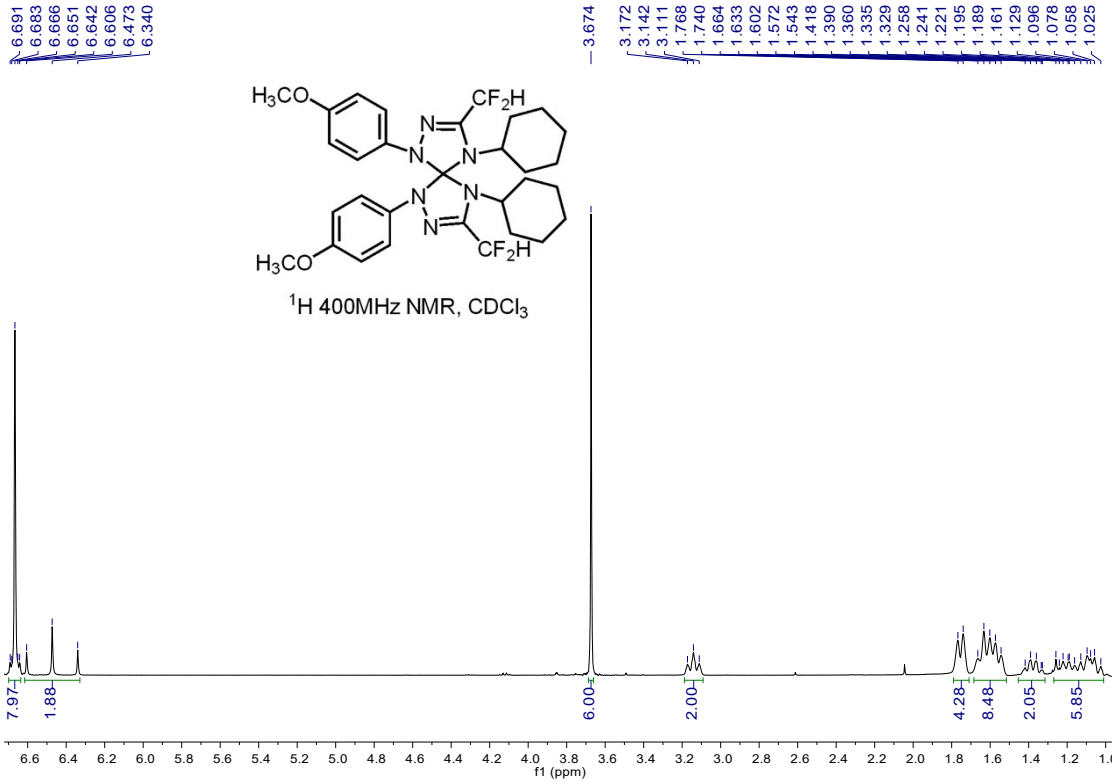
ZHOUYUXIU-16#72-127 RT: 0.32-0.57 AV: 56
T: FTMS + p ESI Full lock ms [50.0000-750.0000]
m/z= 478.4091-596.2190

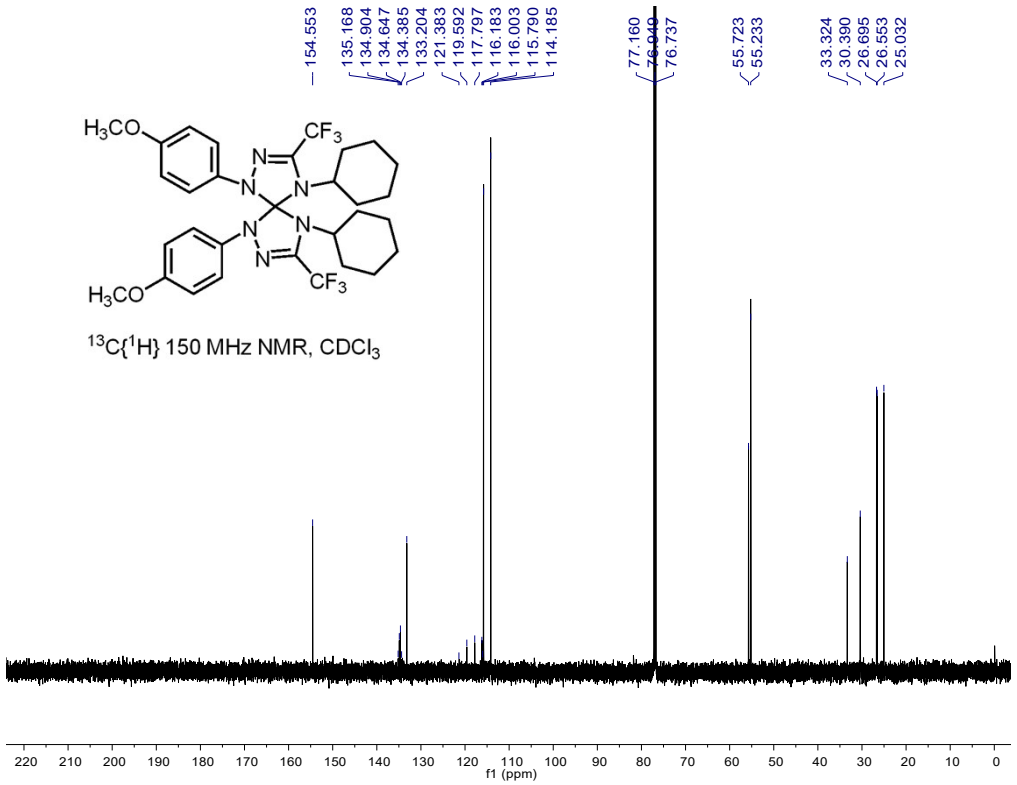
m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
489.2071	3256523.0	6.83			
491.2542	4897277.5	10.27			
543.2857	47707308.0	100.00	543.2854	0.34	$C_{29}H_{35}N_6F_4$
544.2888	14979149.0	31.40			

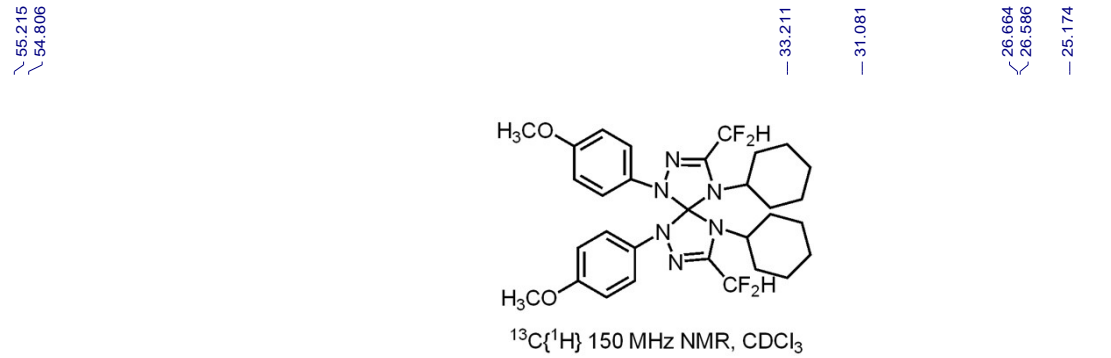


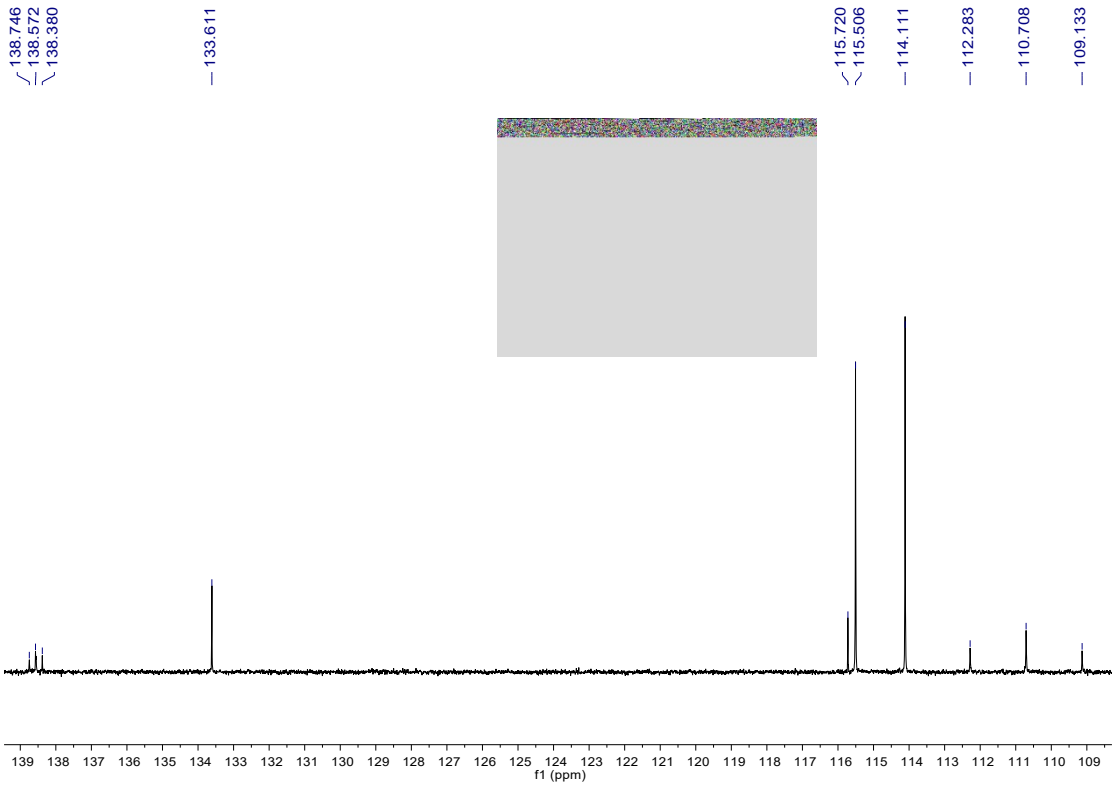
NMR copies of compound **3l**:

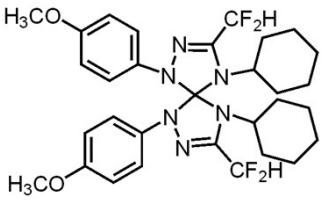




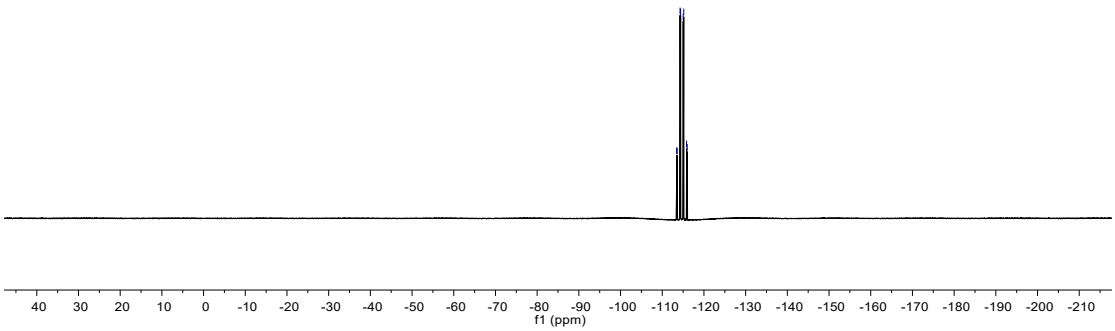

154.553
135.168
134.904
134.647
134.385
133.204
121.383
119.592
117.797
116.183
116.003
115.790
114.185
77.160
76.940
76.737
55.723
55.233
33.324
30.390
26.695
26.553
25.032
H3CO
CF3
CF3
H3CO
13C{1H} 150 MHz NMR, CDCl3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

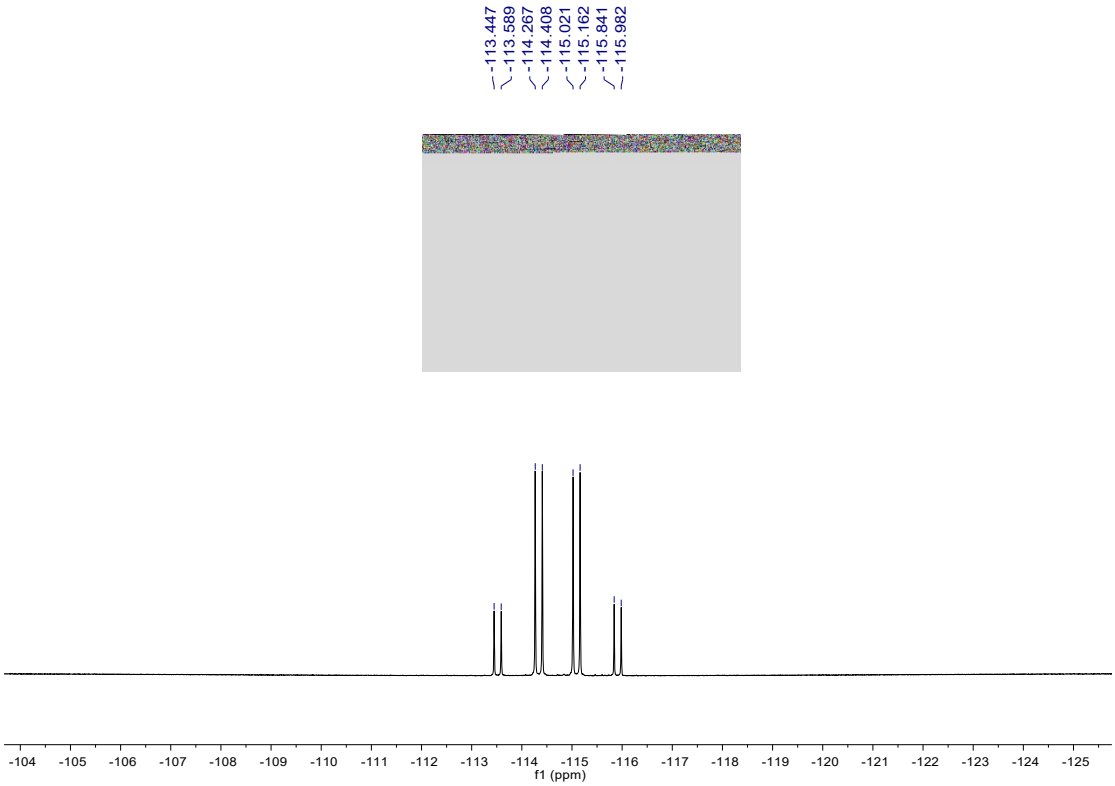

55.215
54.806
33.211
31.081
26.664
26.586
25.174
H3CO
CF2H
CF2H
H3CO
13C{1H} 150 MHz NMR, CDCl3
55 54 53 52 51 50 49 48 47 46 45 44 43 42 41 40 39 38 37 36 35 34 33 32 31 30 29 28 27 26 25
f1 (ppm)



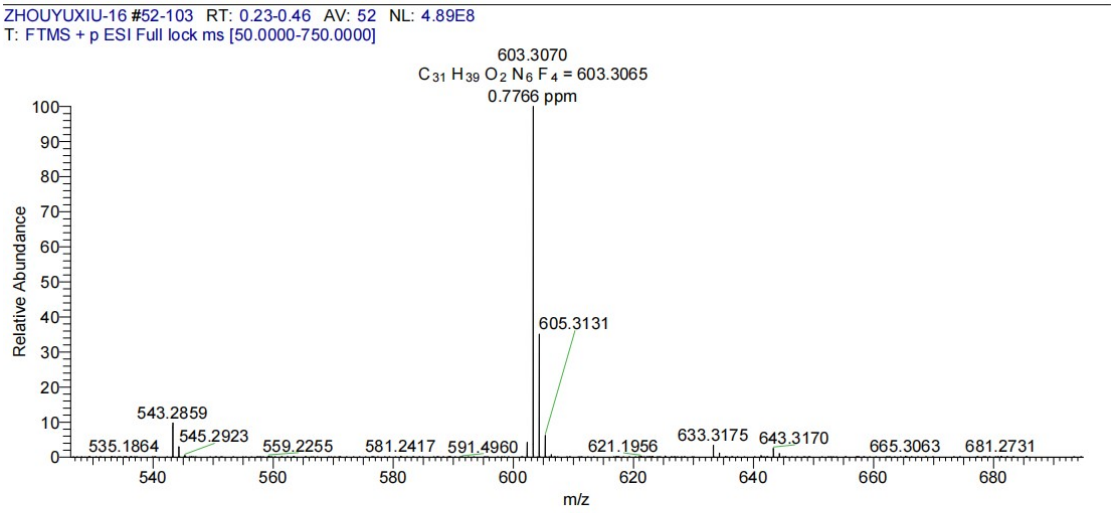


^{19}F 376MHz NMR, $CDCl_3$



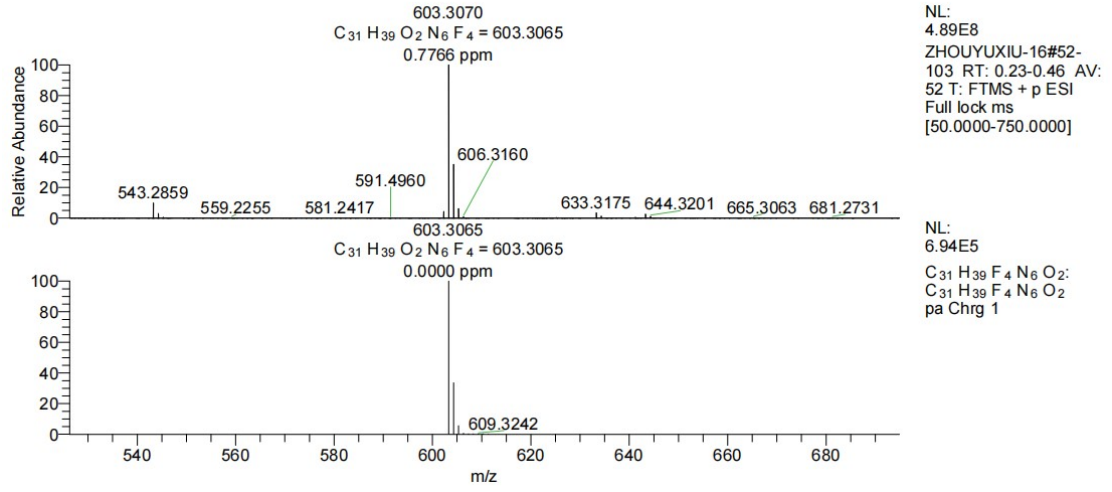

-113.447
-113.589
-114.267
-114.408
-115.021
-115.162
-115.841
-115.982
-104 -105 -106 -107 -108 -109 -110 -111 -112 -113 -114 -115 -116 -117 -118 -119 -120 -121 -122 -123 -124 -125
f1 (ppm)

HRMS (ESI) copy of compound **3l**:

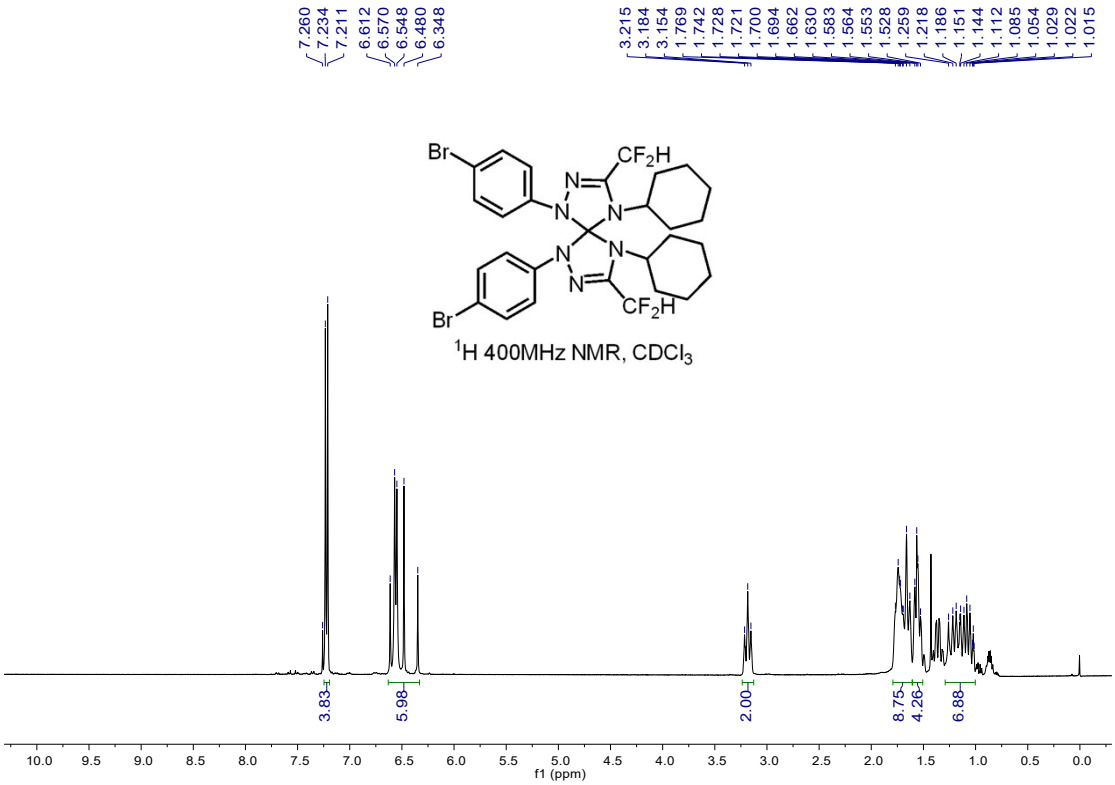


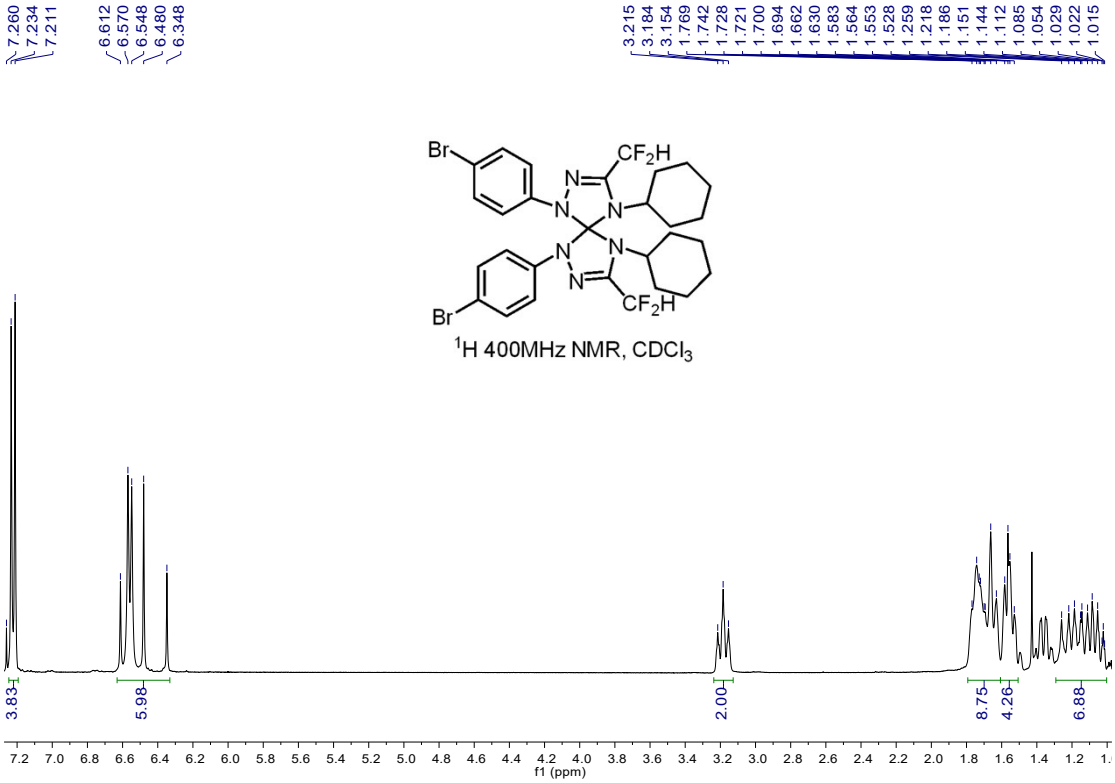
ZHOUYUXIU-16#52-103 RT: 0.23-0.46 AV: 52
T: FTMS + p ESI Full lock ms [50.0000-750.0000]
m/z= 526.2450-694.8856

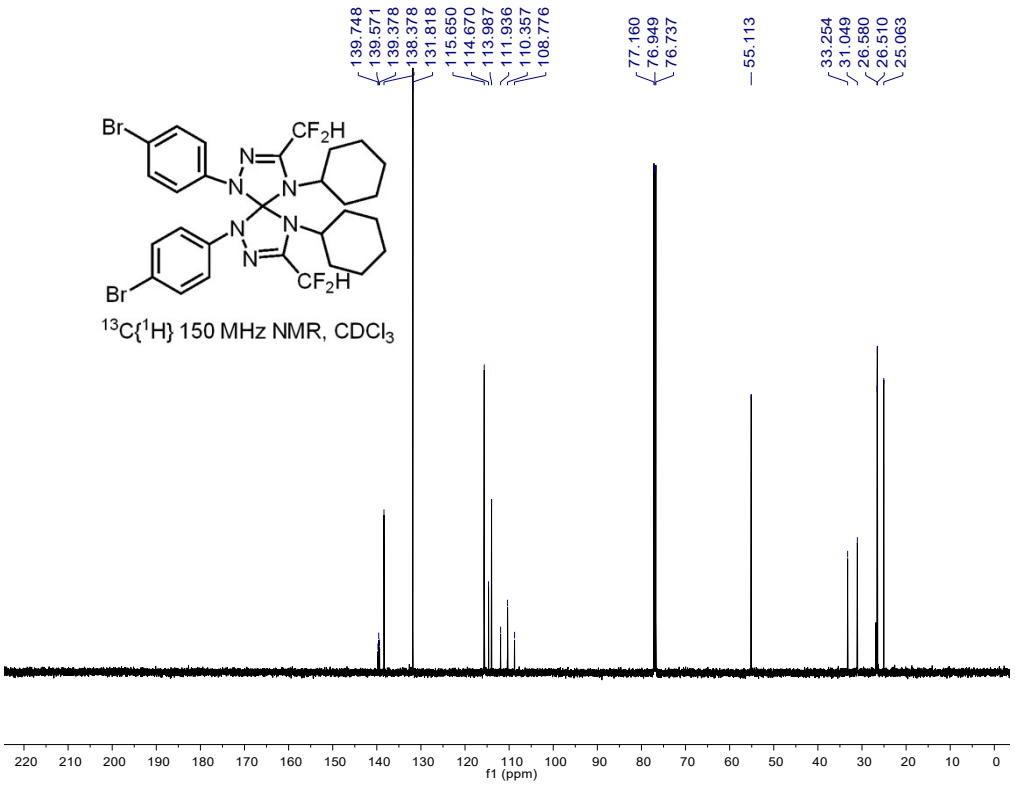
m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
543.2859	48126172.0	9.59			
603.3070	501911616.0	100.00	603.3065	0.47	$C_{31}H_{39}O_2N_6F_4$
604.3101	173514080.0	34.57			
605.3131	30503212.0	6.08			

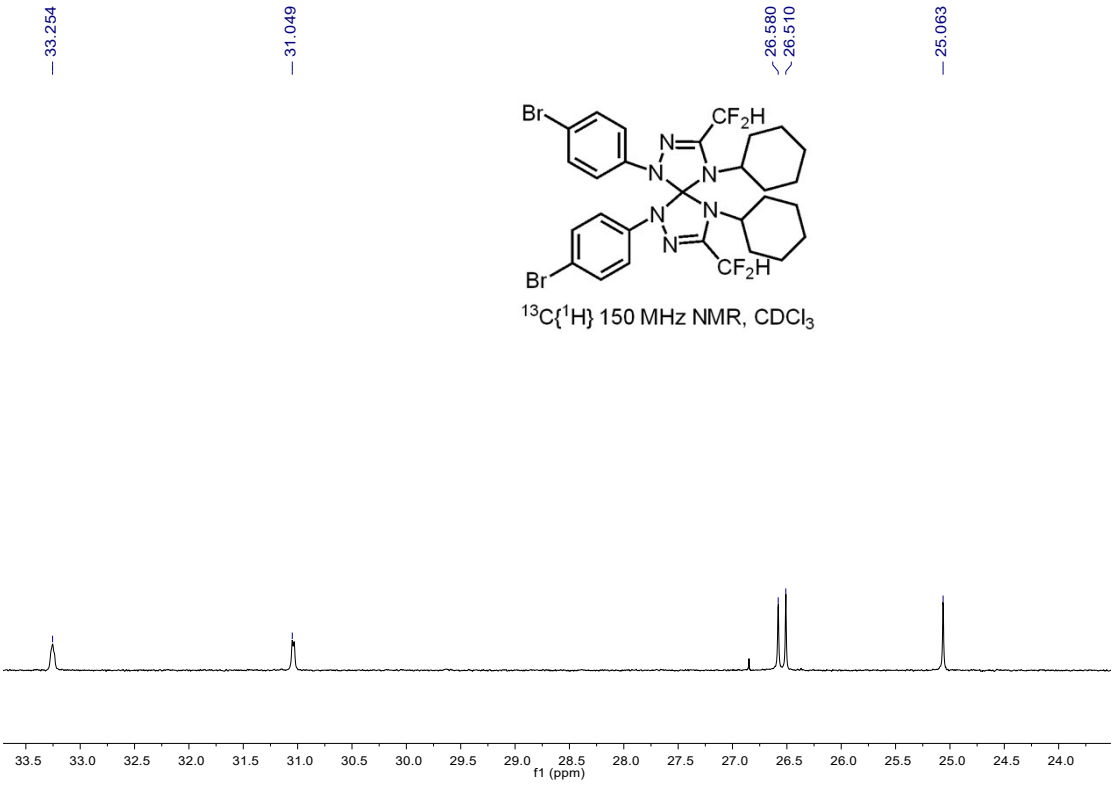


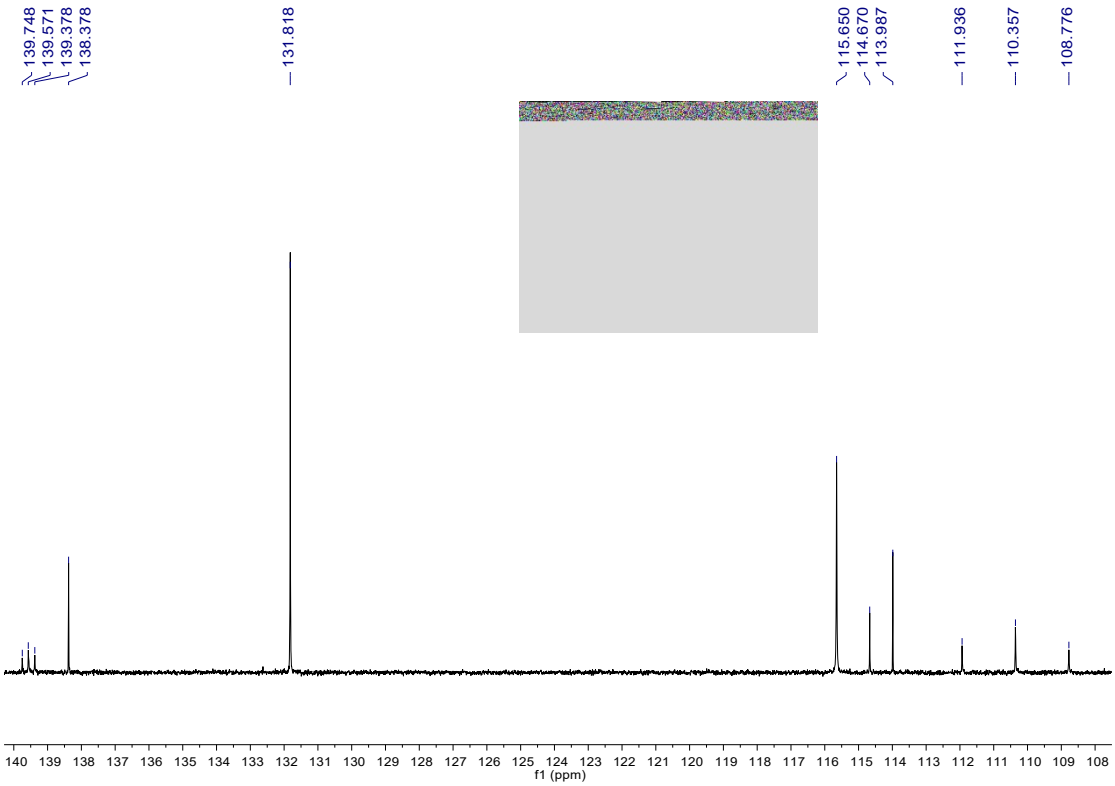
NMR copies of compound **3m**:

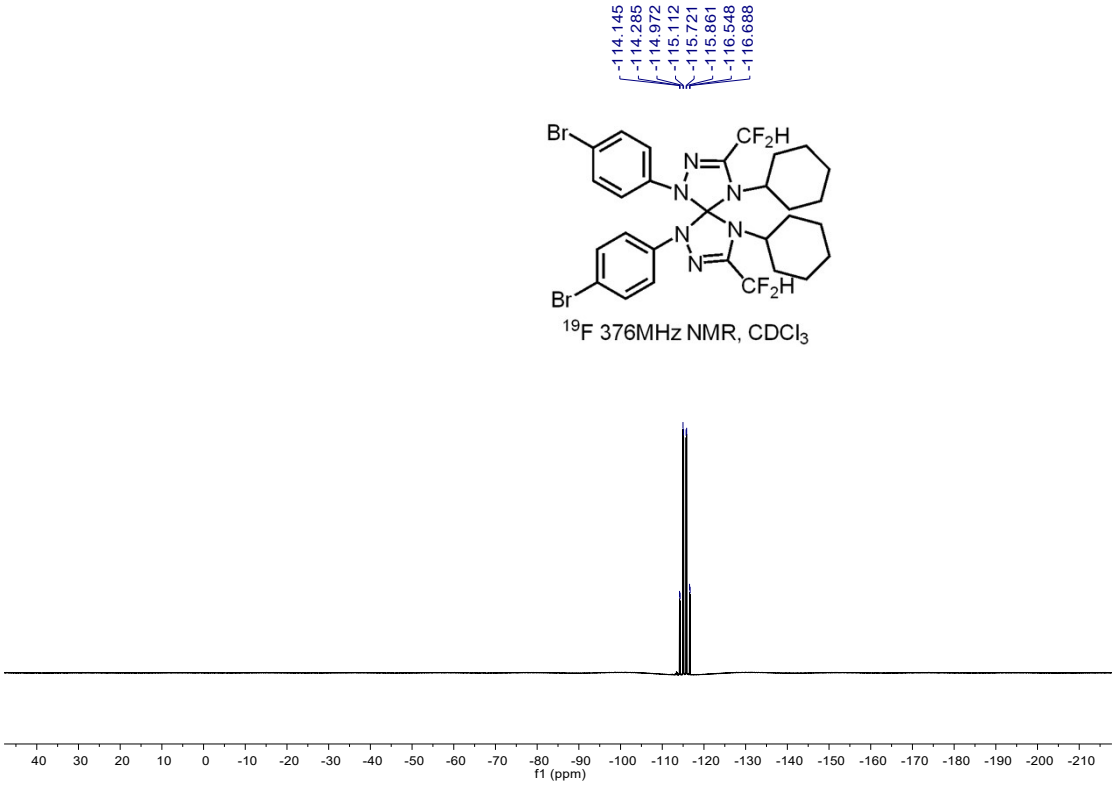


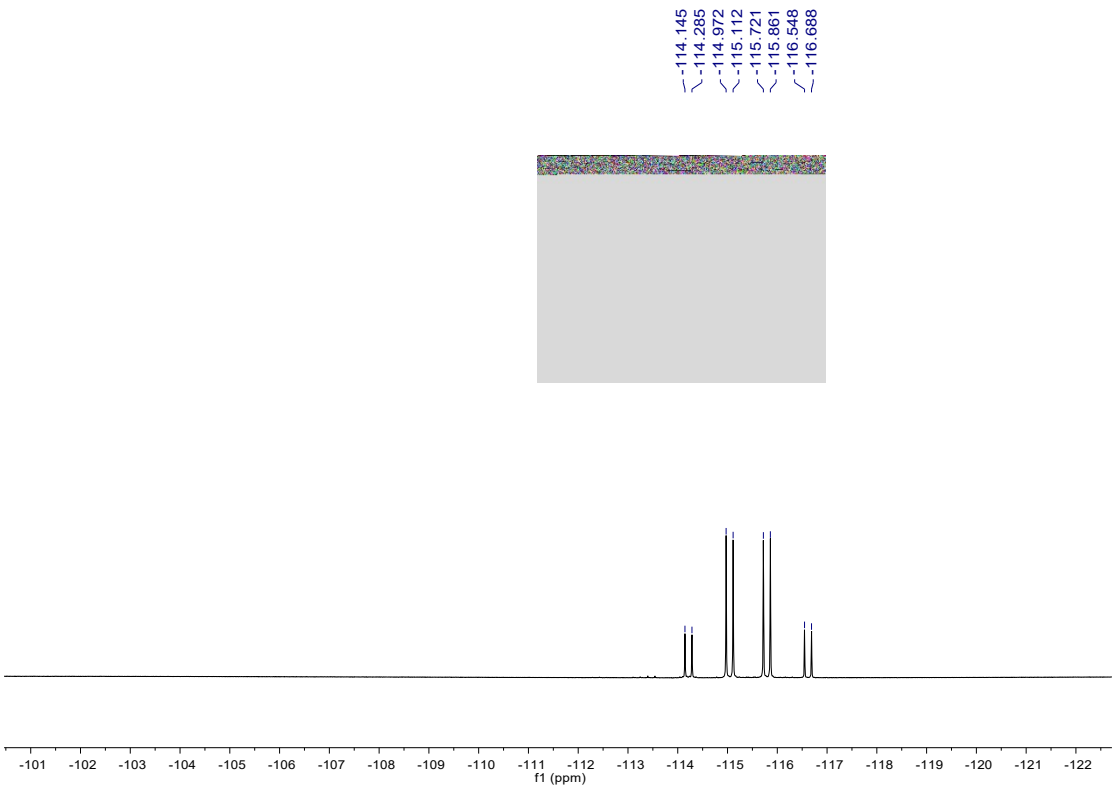



139.748
139.571
139.378
138.378
131.818
115.650
114.670
113.987
111.936
110.357
108.776
77.160
76.949
76.737
55.113
33.254
31.049
26.580
26.510
25.063
Br
CF2H
N
Br
CF2H
13C{1H} 150 MHz NMR, CDCl3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

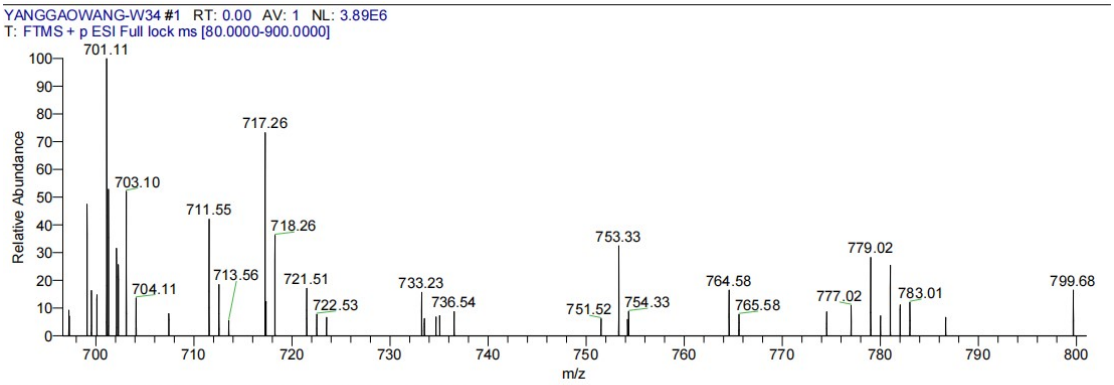

33.254
31.049
26.580
26.510
25.063
Br
CF2H
N
Br
CF2H
13C{1H} 150 MHz NMR, CDCl3
33.5 33.0 32.5 32.0 31.5 31.0 30.5 30.0 29.5 29.0 28.5 28.0 27.5 27.0 26.5 26.0 25.5 25.0 24.5 24.0
f1 (ppm)

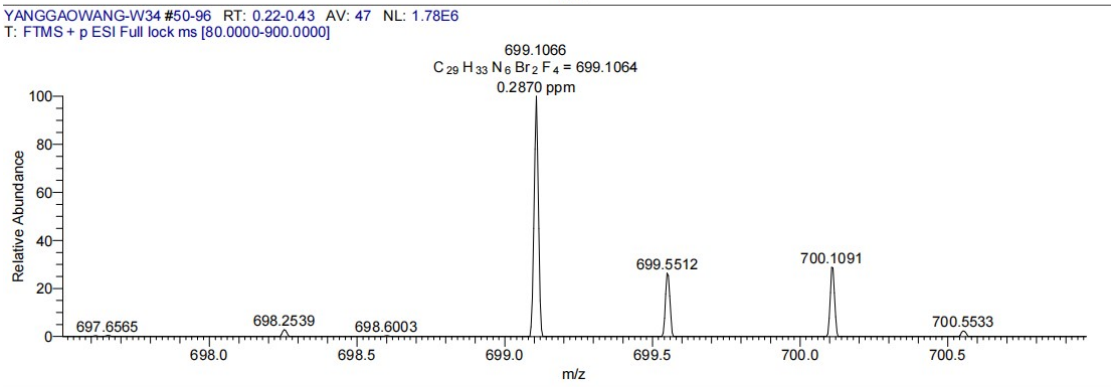

139.748
139.571
139.378
138.378
131.818
115.650
114.670
113.987
111.936
110.357
108.776
140 139 138 137 136 135 134 133 132 131 130 129 128 127 126 125 124 123 122 121 120 119 118 117 116 115 114 113 112 111 110 109 108
f1 (ppm)


-114.145
-114.285
-114.972
-115.112
-115.721
-115.861
-116.548
-116.688
Br
CF2H
N
N
N
N
N
N
Br
CF2H
19F 376MHz NMR, CDCl3
40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


-114.145
-114.285
-114.972
-115.112
-115.721
-115.861
-116.548
-116.688
-101
-102
-103
-104
-105
-106
-107
-108
-109
-110
-111
-112
-113
-114
-115
-116
-117
-118
-119
-120
-121
-122
f1 (ppm)

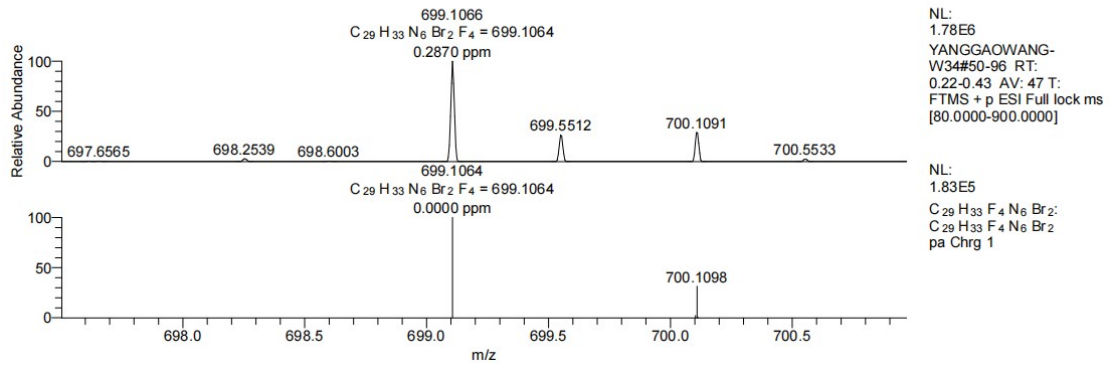
HRMS (ESI) copy of compound **3m**:



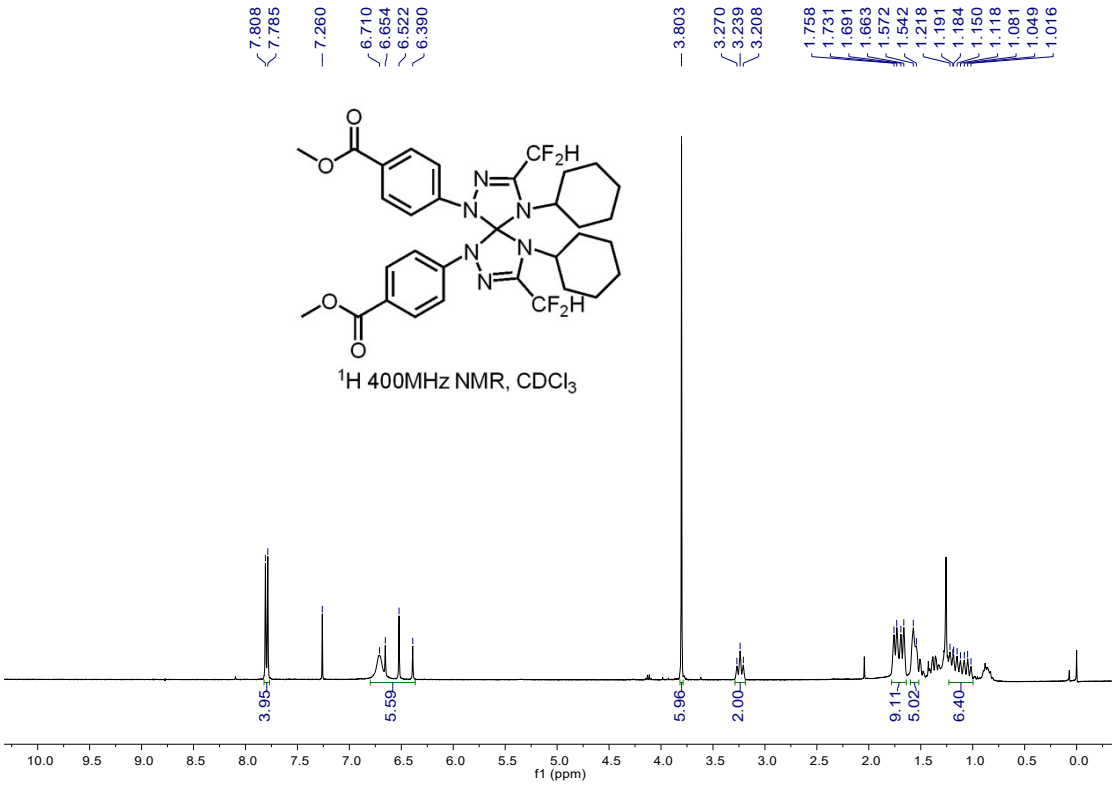


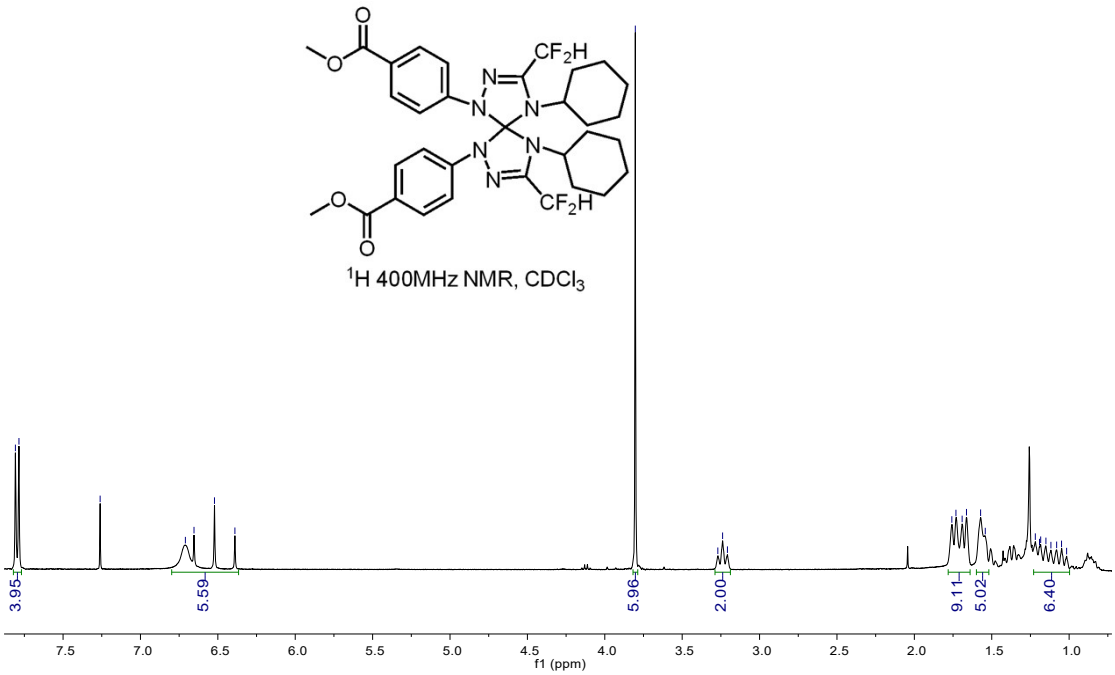
YANGGAOWANG-W34#50-96 RT: 0.22-0.43 AV: 47
T: FTMS + p ESI Full lock ms [80.0000-900.0000]
m/z= 697.5033-700.9684

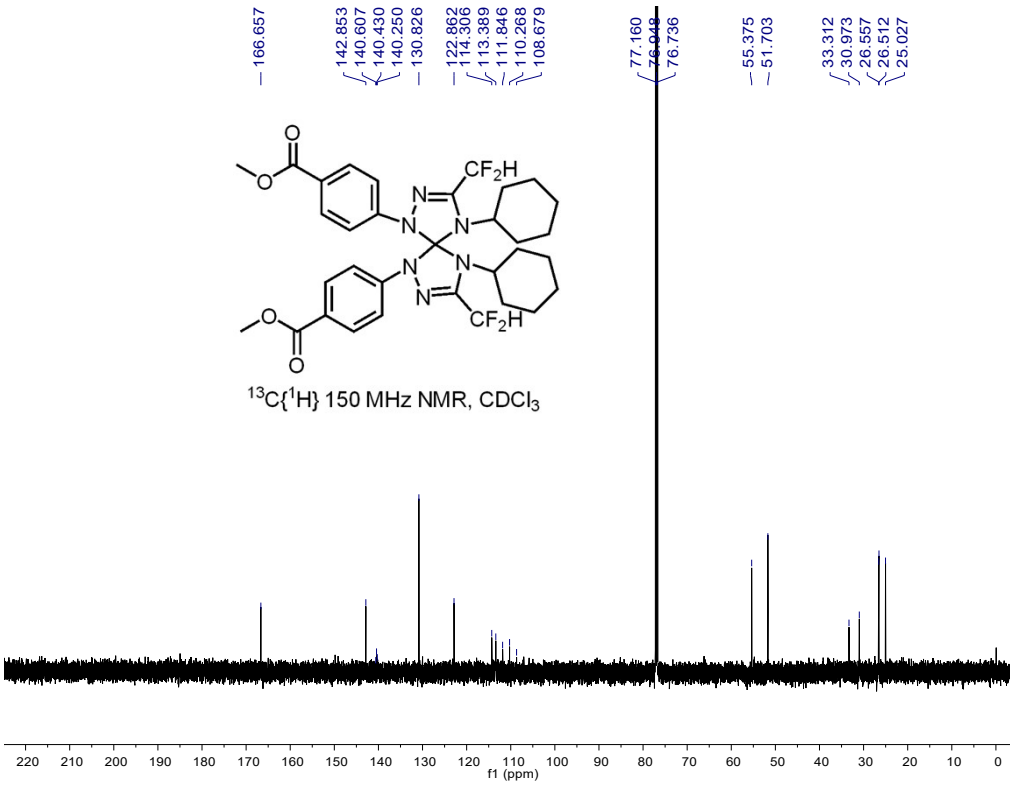
m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
698.2539	51232.7	2.88			
699.1066	1778049.3	100.00	699.1064	0.20	$C_{29}H_{33}N_6Br_2F_4$
699.5512	482922.5	27.16			
700.1091	534910.8	30.08			



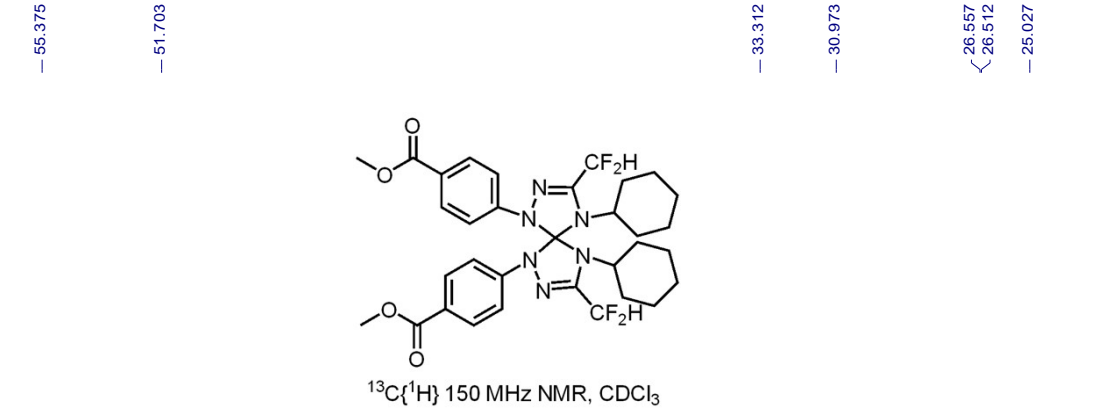
NMR copies of compound **3n**:



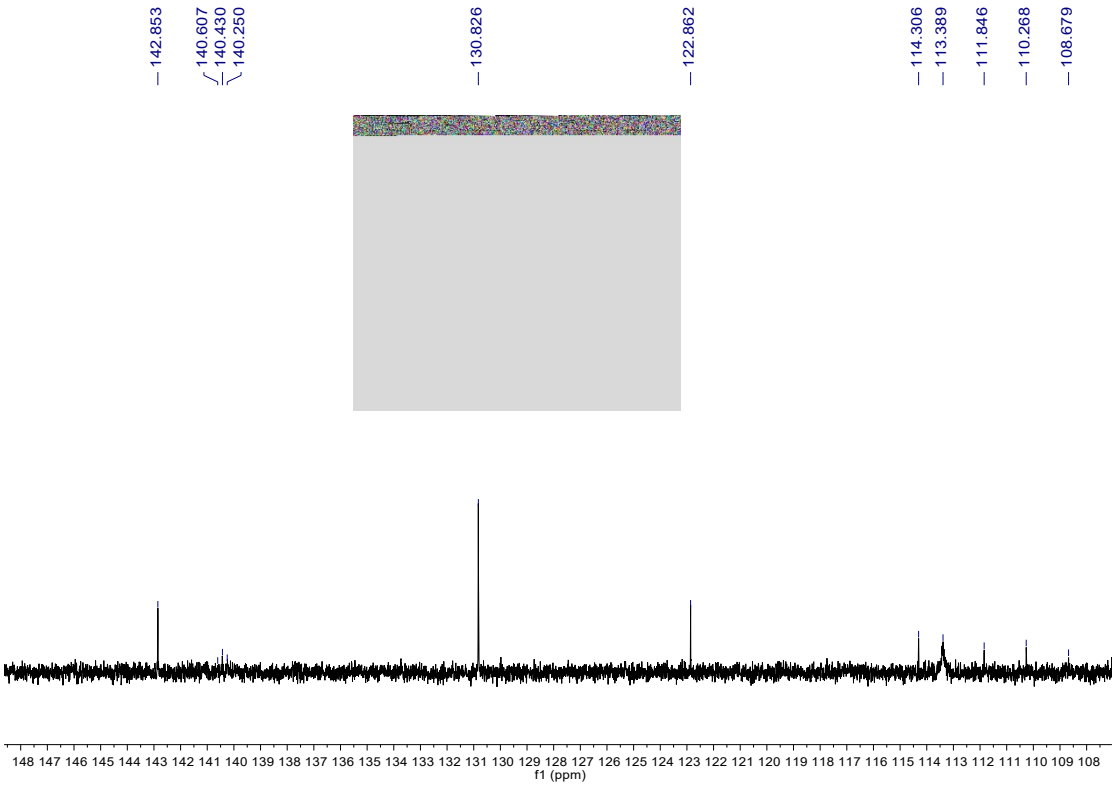


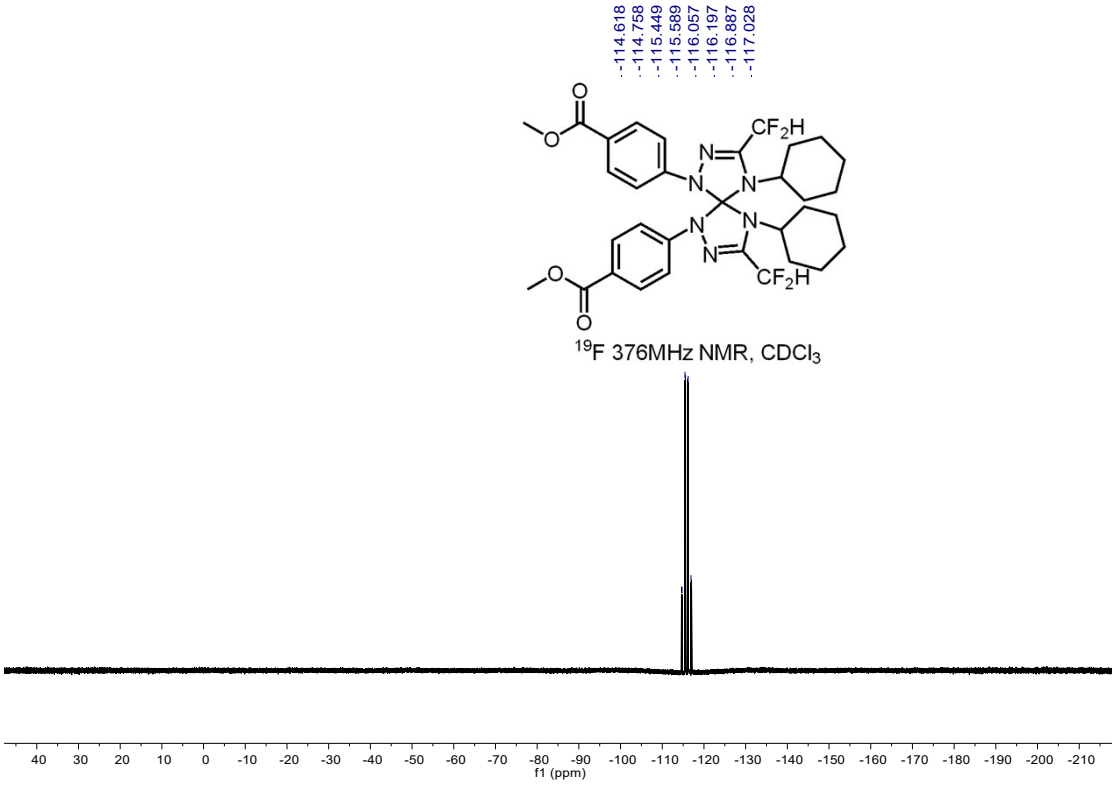


$^{13}C\{^{1}H\}$ 150 MHz NMR, $CDCl_3$

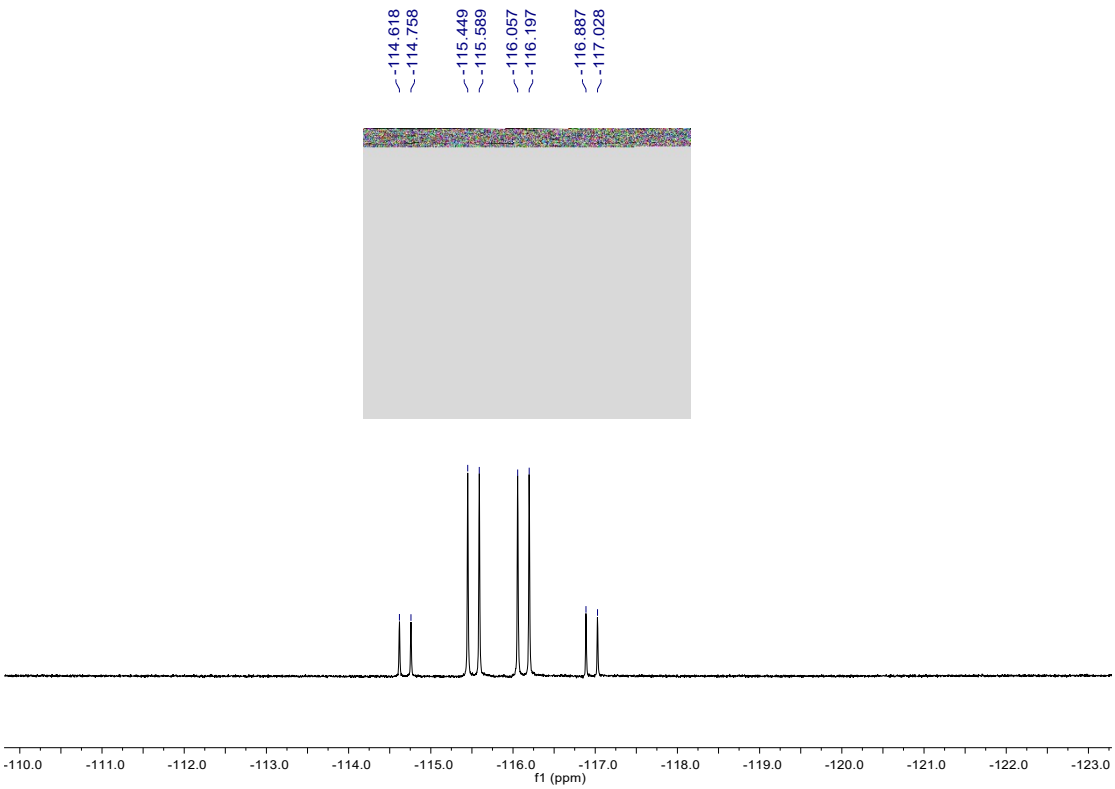


$^{13}C\{^{1}H\}$ 150 MHz NMR, $CDCl_3$

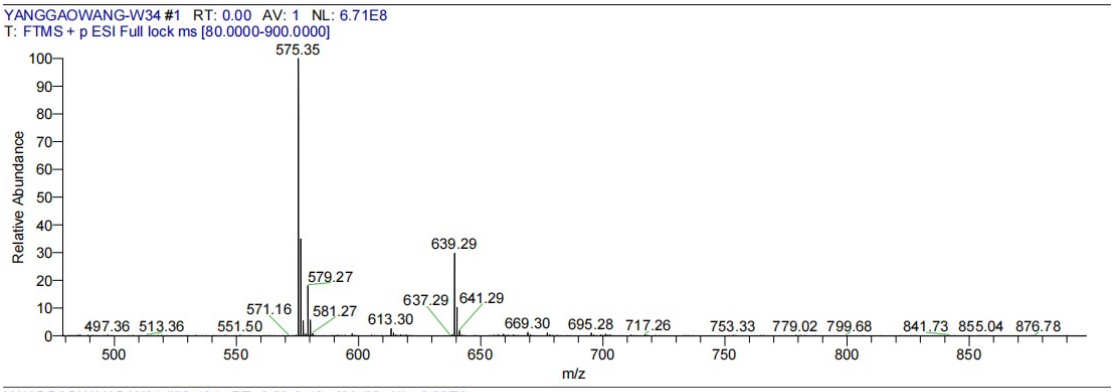


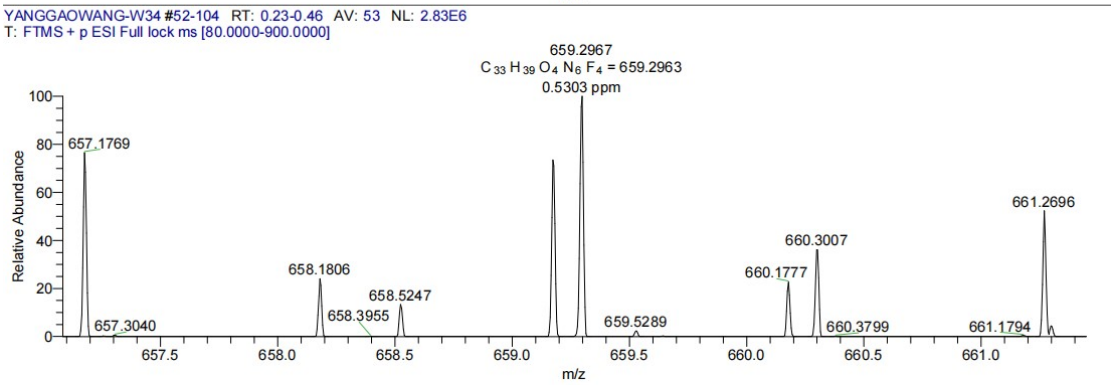


^{19}F 376MHz NMR, $CDCl_3$


-114.618
-114.758
-115.449
-115.589
-116.057
-116.197
-116.887
-117.028
-110.0
-111.0
-112.0
-113.0
-114.0
-115.0
-116.0
-117.0
-118.0
-119.0
-120.0
-121.0
-122.0
-123.0
f1 (ppm)

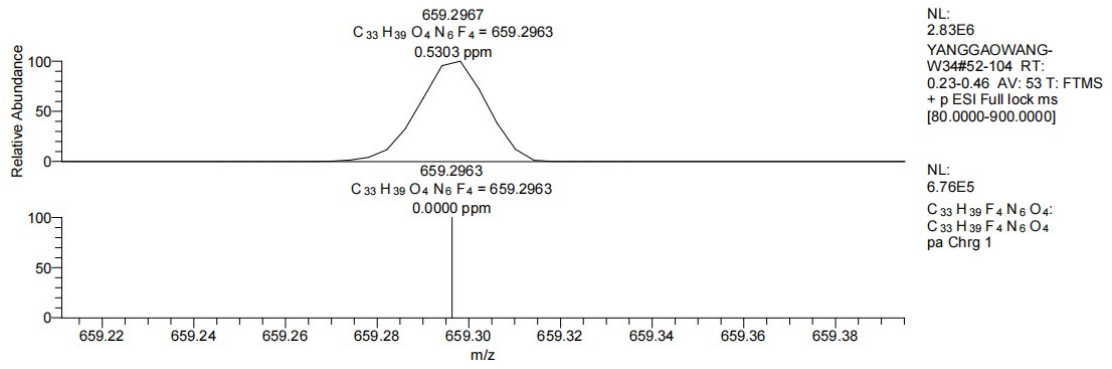
HRMS (ESI) copy of compound **3n**:



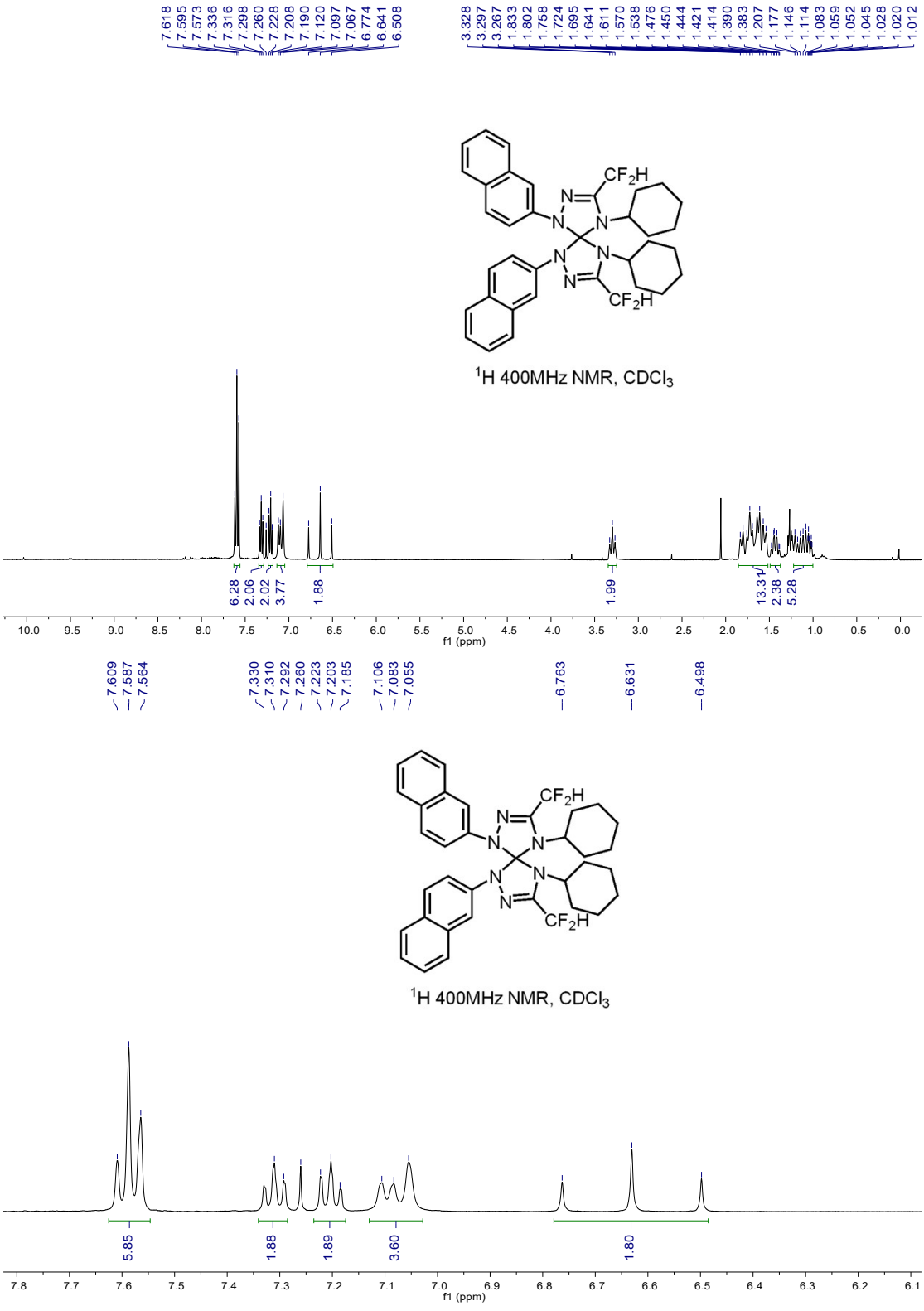


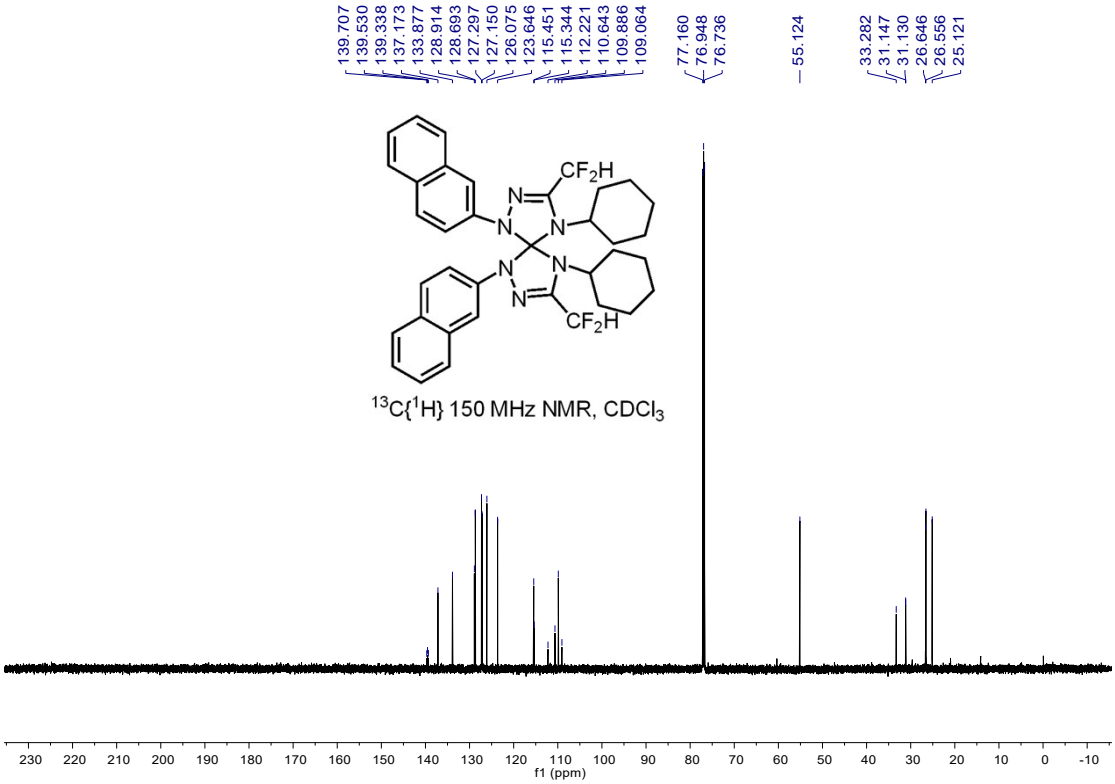
YANGGAOWANG-W34#52-104 RT: 0.23-0.46 AV: 53
T: FTMS + p ESI Full lock ms [80.0000-900.0000]
m/z= 657.0829-661.4480

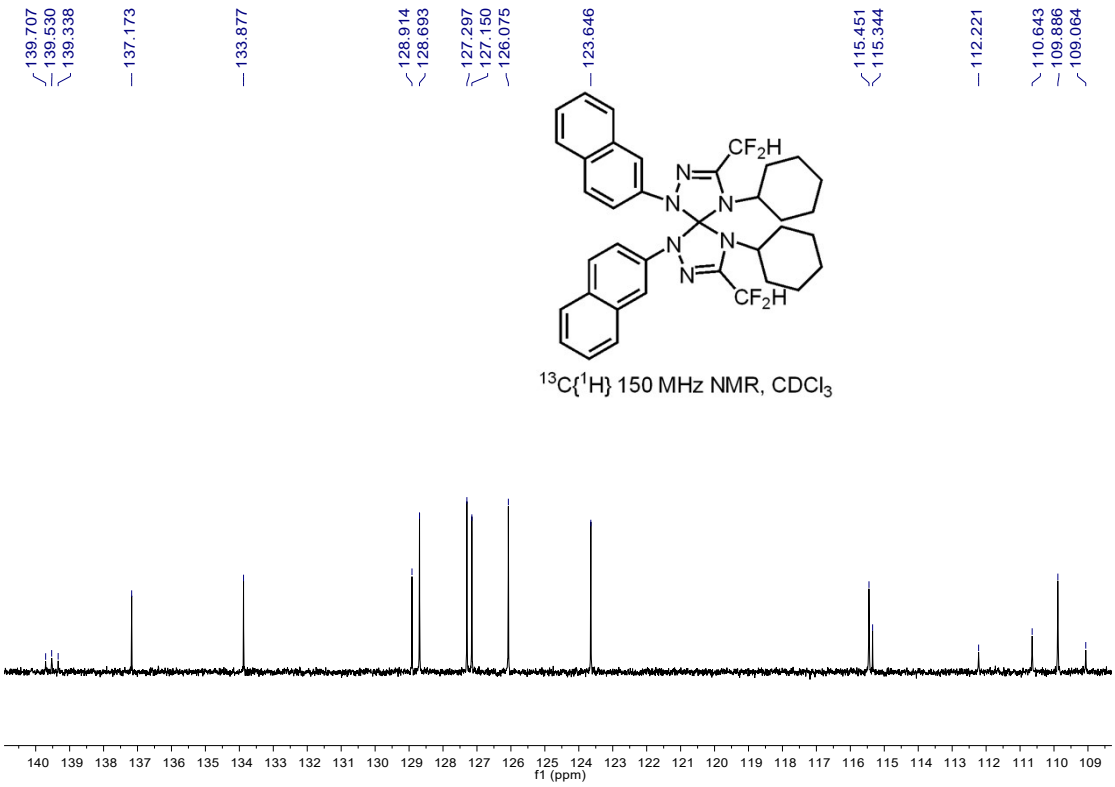
m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
657.1769	2186879.8	75.79			
659.1754	2140261.3	74.17	659.2963	-120.97	$C_{33}H_{39}O_4N_6F_4$
659.2967	2885512.5	100.00	659.2963	0.35	$C_{33}H_{39}O_4N_6F_4$
661.2696	1480612.1	51.31			

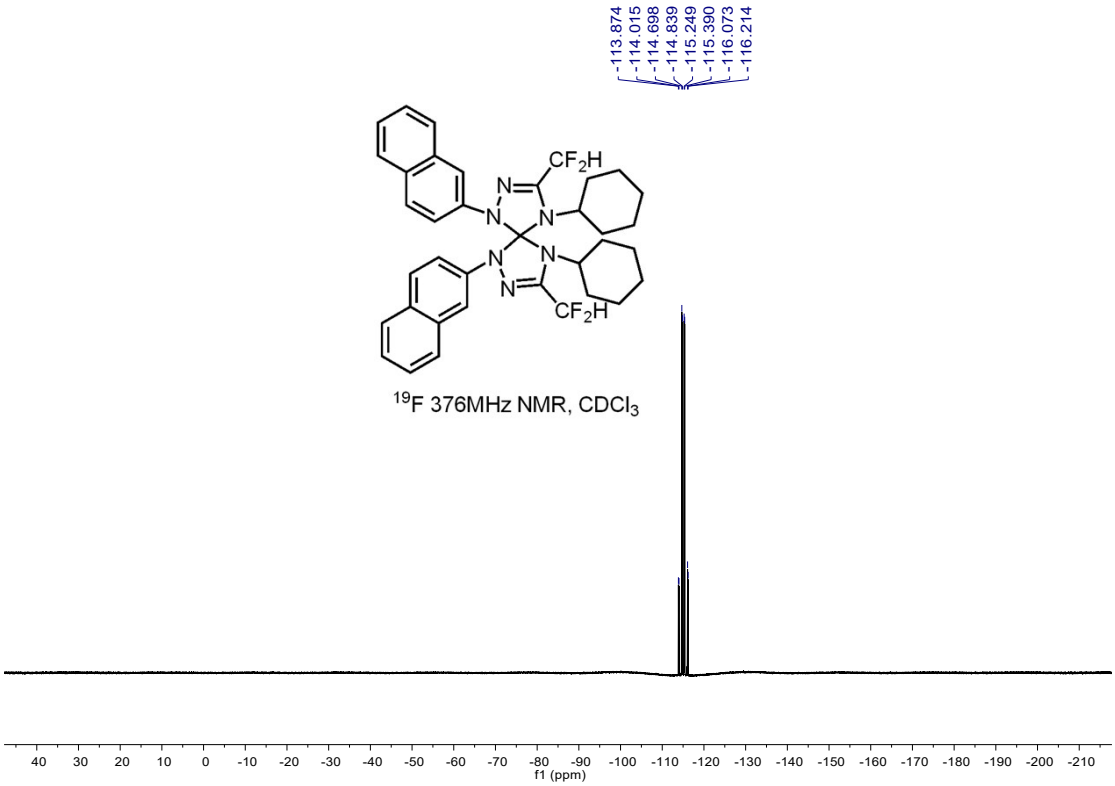


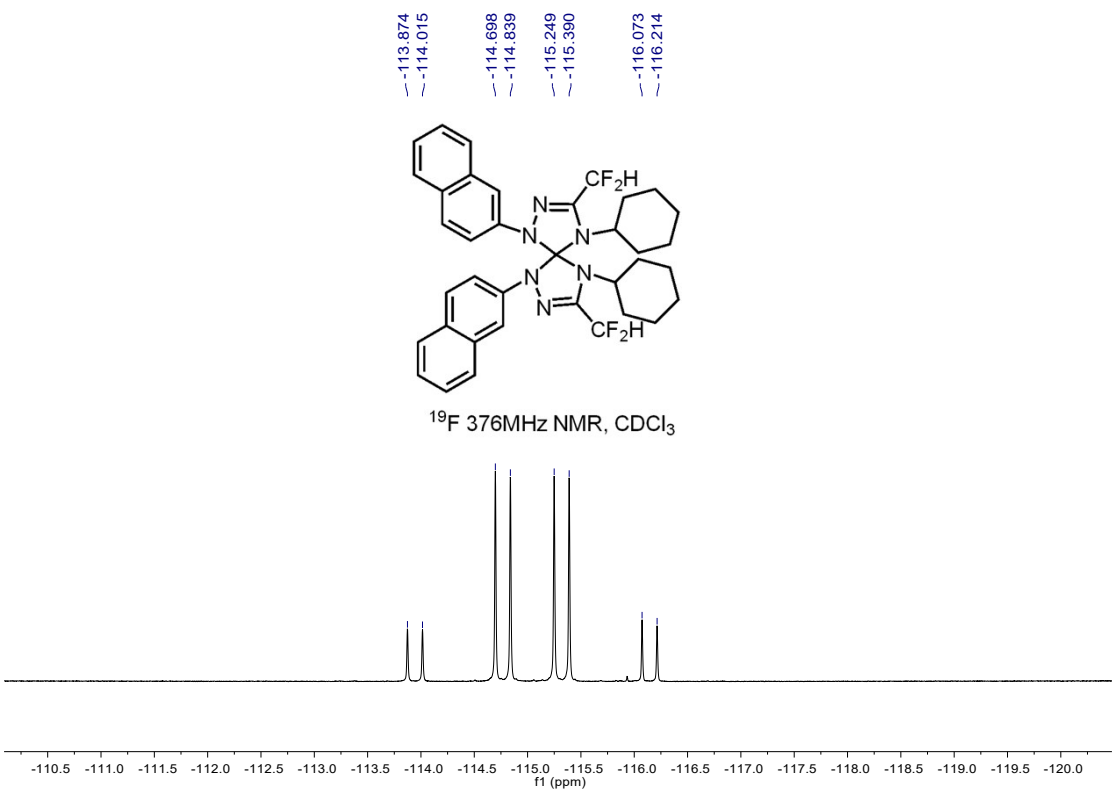
NMR copies of compound **3o**:




139.707
139.530
139.338
137.173
133.877
128.914
128.693
127.297
127.150
126.075
123.646
115.451
115.344
112.221
110.643
109.886
109.064
77.160
76.948
76.736
55.124
33.282
31.147
31.130
26.646
26.556
25.121
CF2H
CF2H
13C{1H} 150 MHz NMR, CDCl3
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

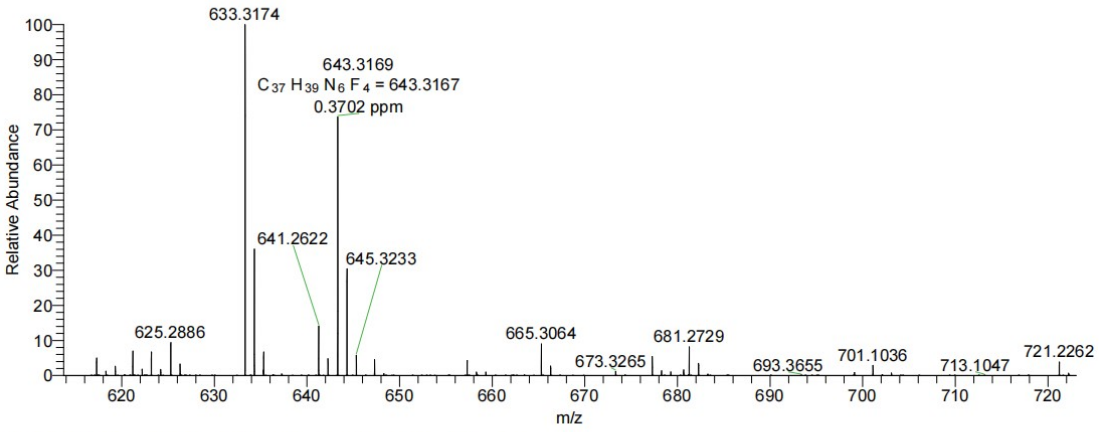

139.707
139.530
139.338
137.173
133.877
128.914
128.693
127.297
127.150
126.075
123.646
115.451
115.344
112.221
110.643
109.886
109.064
CF2H
CF2H
13C{1H} 150 MHz NMR, CDCl3
140 139 138 137 136 135 134 133 132 131 130 129 128 127 126 125 124 123 122 121 120 119 118 117 116 115 114 113 112 111 110 109
f1 (ppm)


-113.874
-114.015
-114.698
-114.839
-115.249
-115.390
-116.073
-116.214
CF2H
CF2H
19F 376MHz NMR, CDCl3
40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


-113.874
-114.015
-114.698
-114.839
-115.249
-115.390
-116.073
-116.214
CF2H
CF2H
19F 376MHz NMR, CDCl3
-110.5 -111.0 -111.5 -112.0 -112.5 -113.0 -113.5 -114.0 -114.5 -115.0 -115.5 -116.0 -116.5 -117.0 -117.5 -118.0 -118.5 -119.0 -119.5 -120.0
f1 (ppm)

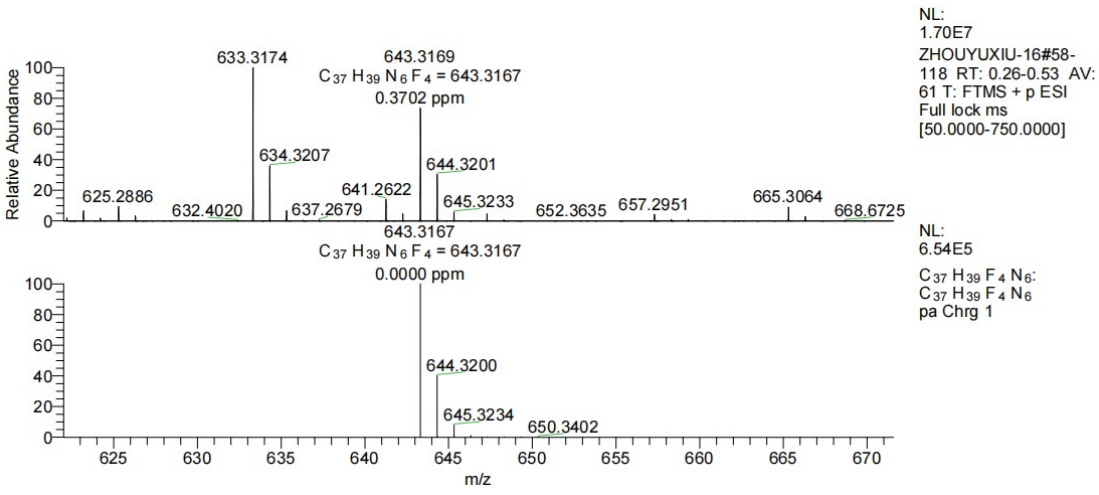
HRMS (ESI) copy of compound **3o**:

ZHOUYUXIU-16 #58-118 RT: 0.26-0.53 AV: 61 NL: 1.70E7
T: FTMS + p ESI Full lock ms [50.0000-750.0000]



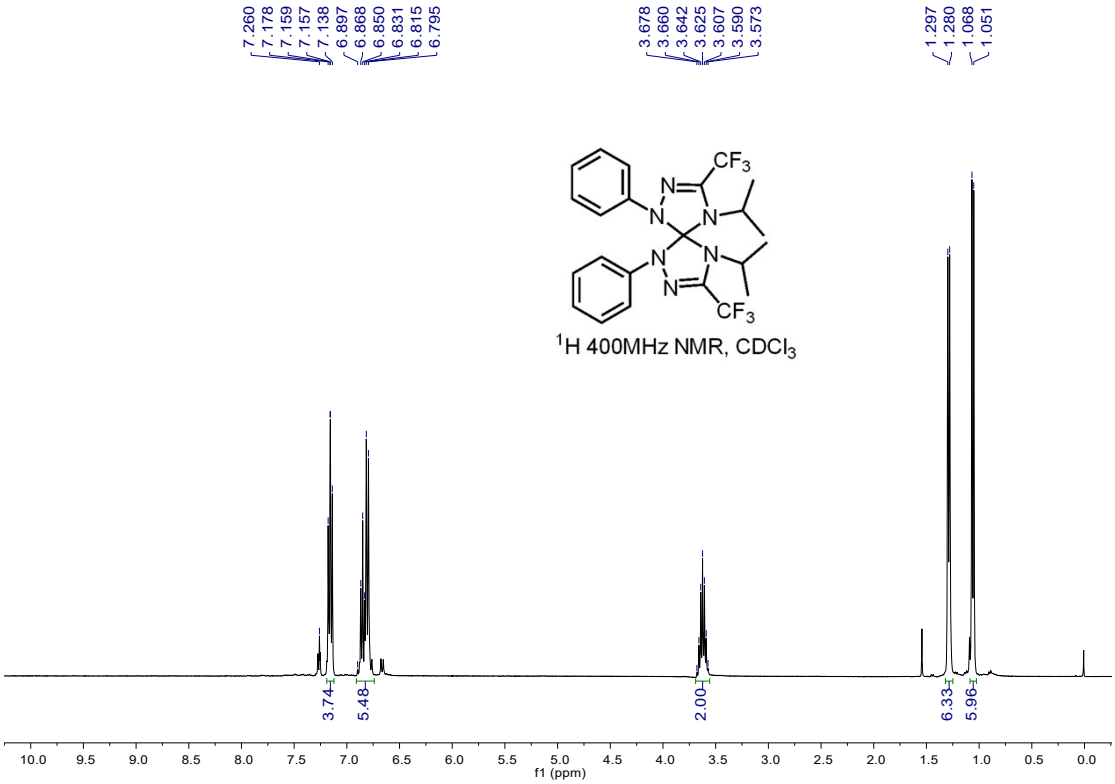
ZHOUYUXIU-16#58-118 RT: 0.26-0.53 AV: 61
T: FTMS + p ESI Full lock ms [50.0000-750.0000]
m/z= 613.7128-723.0341

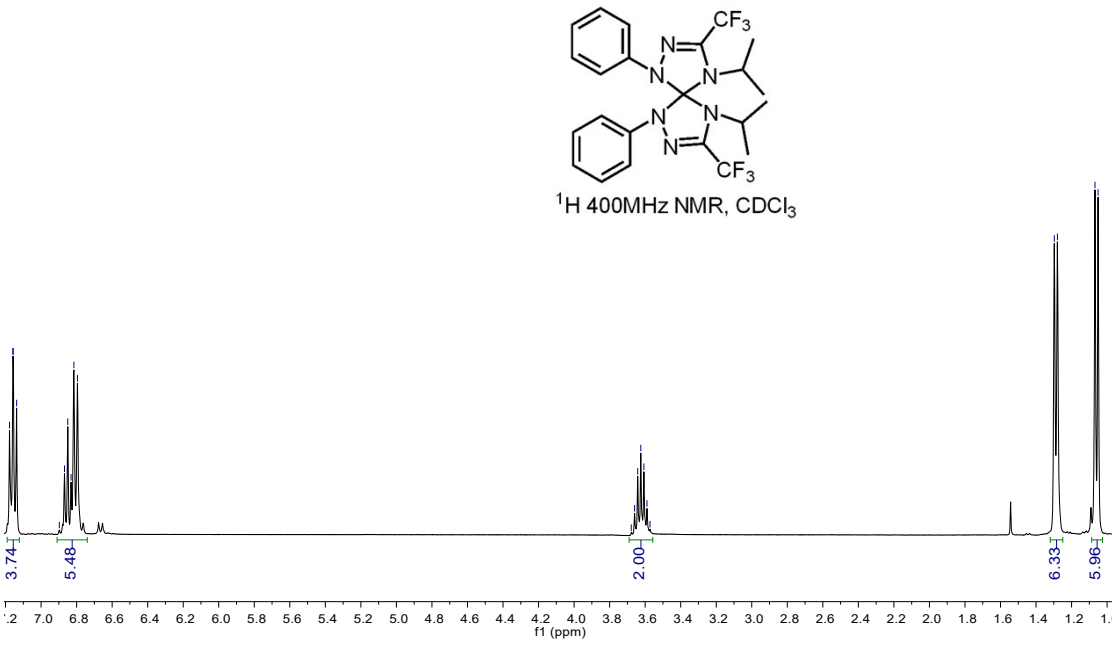
m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
633.3174	17195970.0	100.00			
634.3207	6132686.5	35.66			
643.3169	12565983.0	73.08	643.3167	0.24	C37 H39 N6 F4
644.3201	5188929.0	30.18			

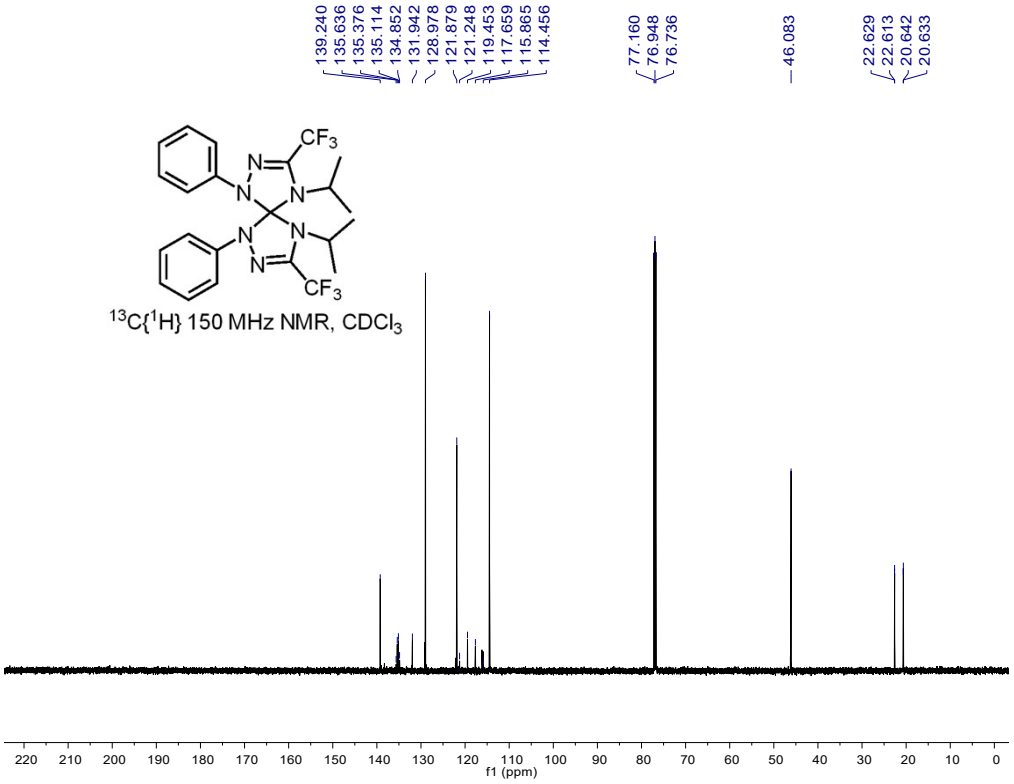


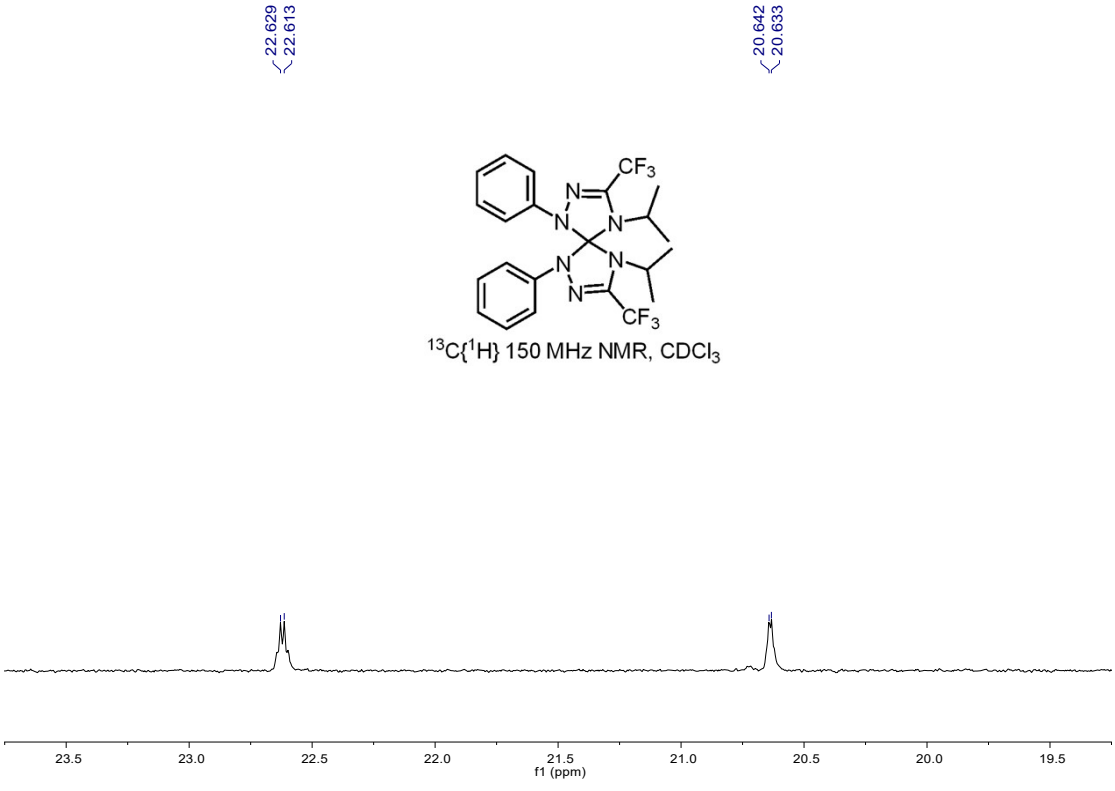
Copies of NMR and HRMS Spectra for Compounds **3′**

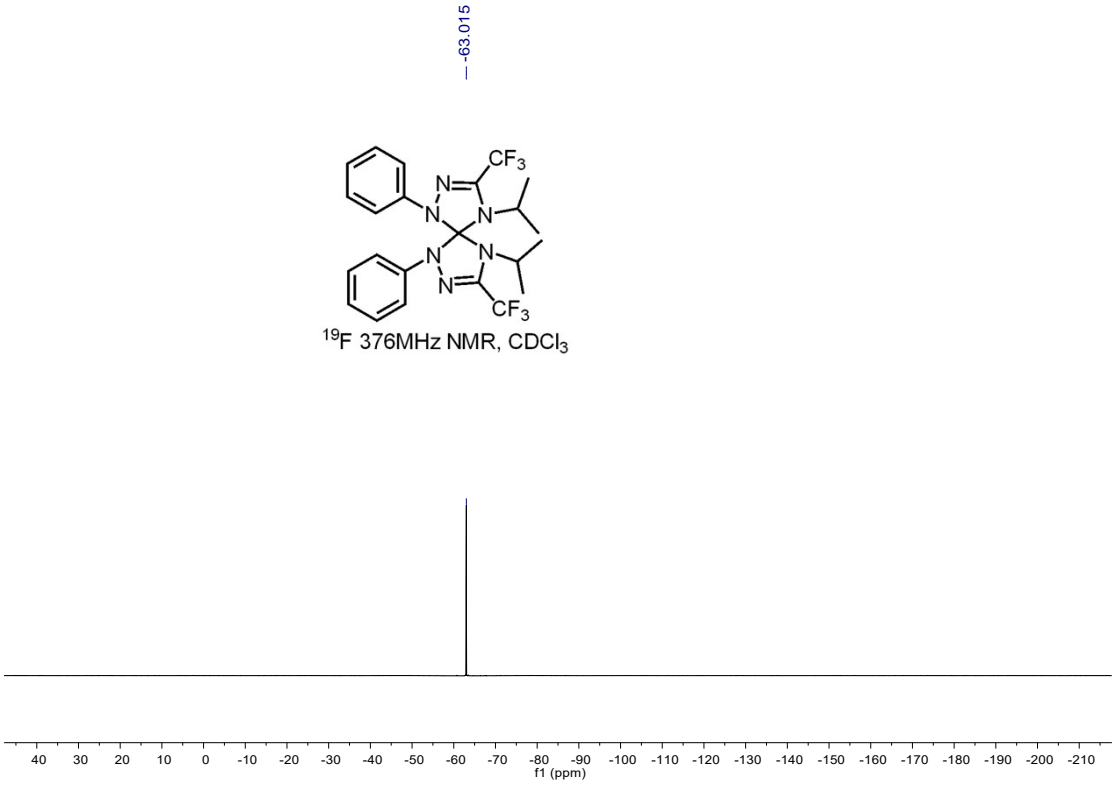
NMR copies of compound **3′a**:



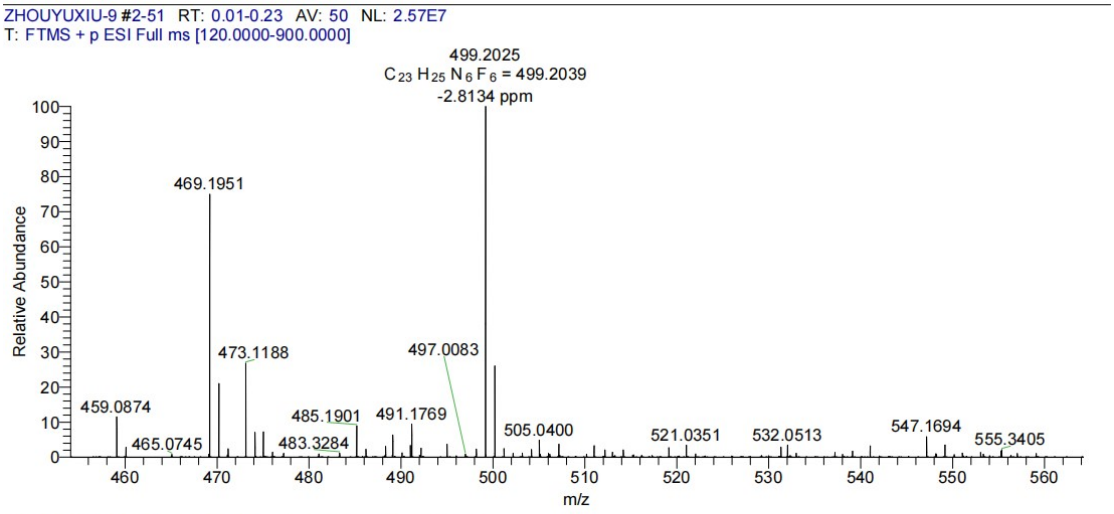



139.240
135.636
135.376
135.114
134.852
131.942
128.978
121.879
121.248
119.453
117.659
115.865
114.456
77.160
76.948
76.736
46.083
22.629
22.613
20.642
20.633
CF3
CF3
13C{1H} 150 MHz NMR, CDCl3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


22.629
22.613
20.642
20.633
CF3
CF3
13C{1H} 150 MHz NMR, CDCl3
23.5 23.0 22.5 22.0 21.5 21.0 20.5 20.0 19.5
f1 (ppm)

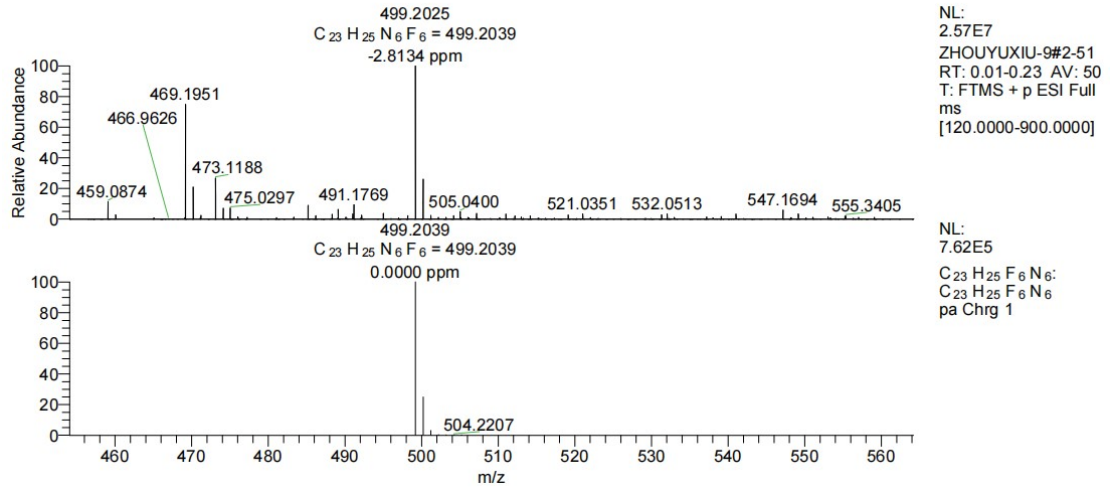

-63.015
CF3
N
N
N
N
N
CF3
19F 376MHz NMR, CDCl3
40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

HRMS (ESI) copy of compound **3′a**:

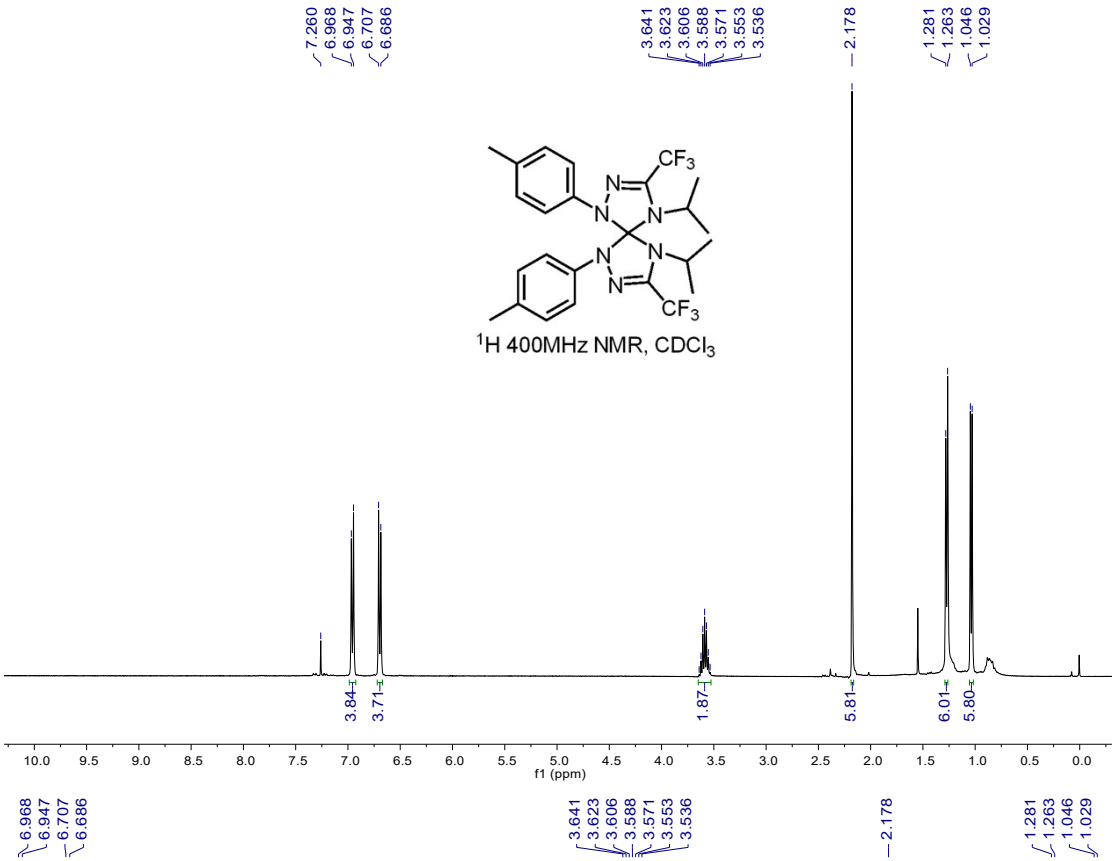


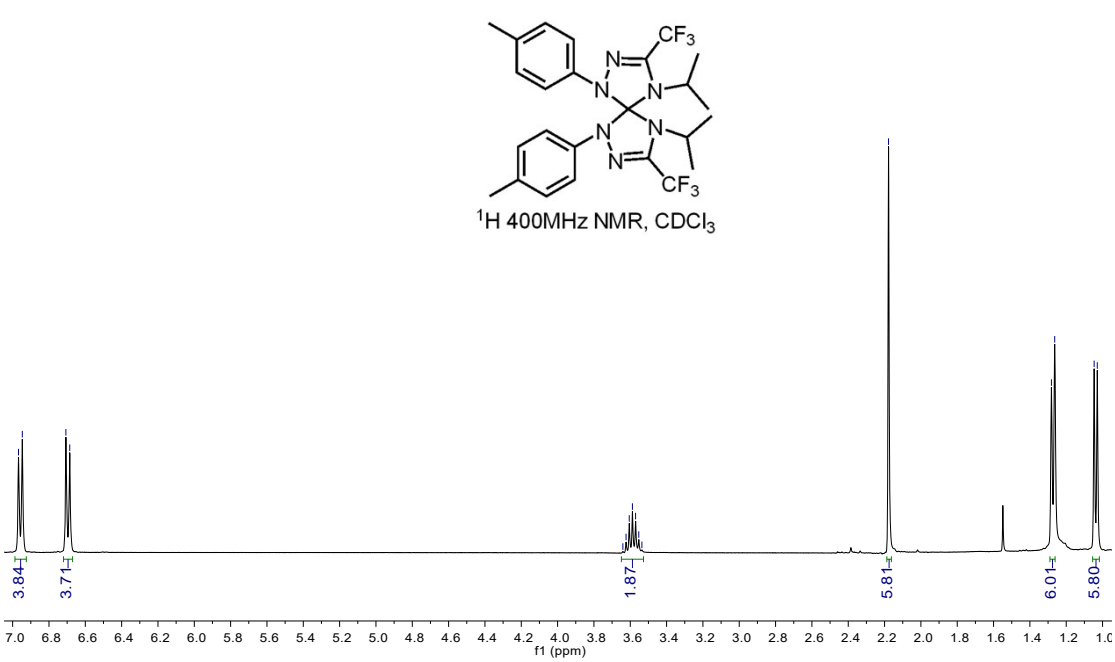
ZHOUYUXIU-9#2-51 RT: 0.01-0.23 AV: 50
T: FTMS + p ESI Full ms [120.0000-900.0000]
m/z= 454.0597-564.1806

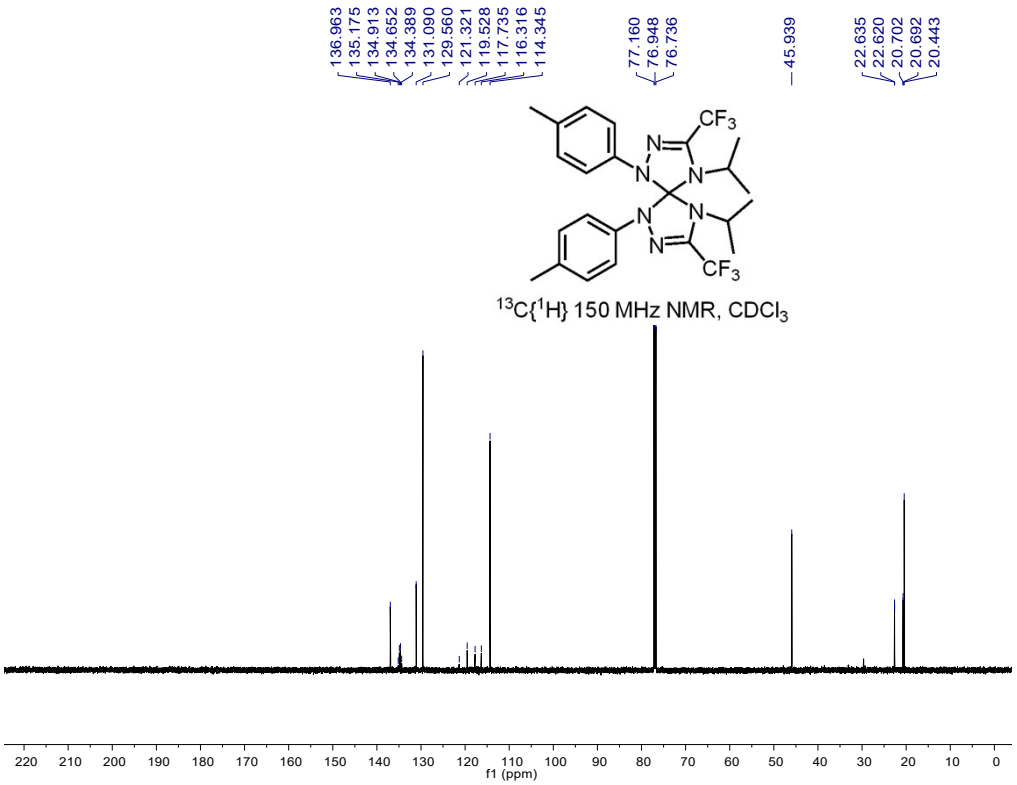
m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
469.1951	19420410.0	74.19			
473.1188	6978433.0	26.66			
499.2025	26175528.0	100.00	499.2039	-1.40	C23 H25 N6 F6
500.2061	6759371.0	25.82			

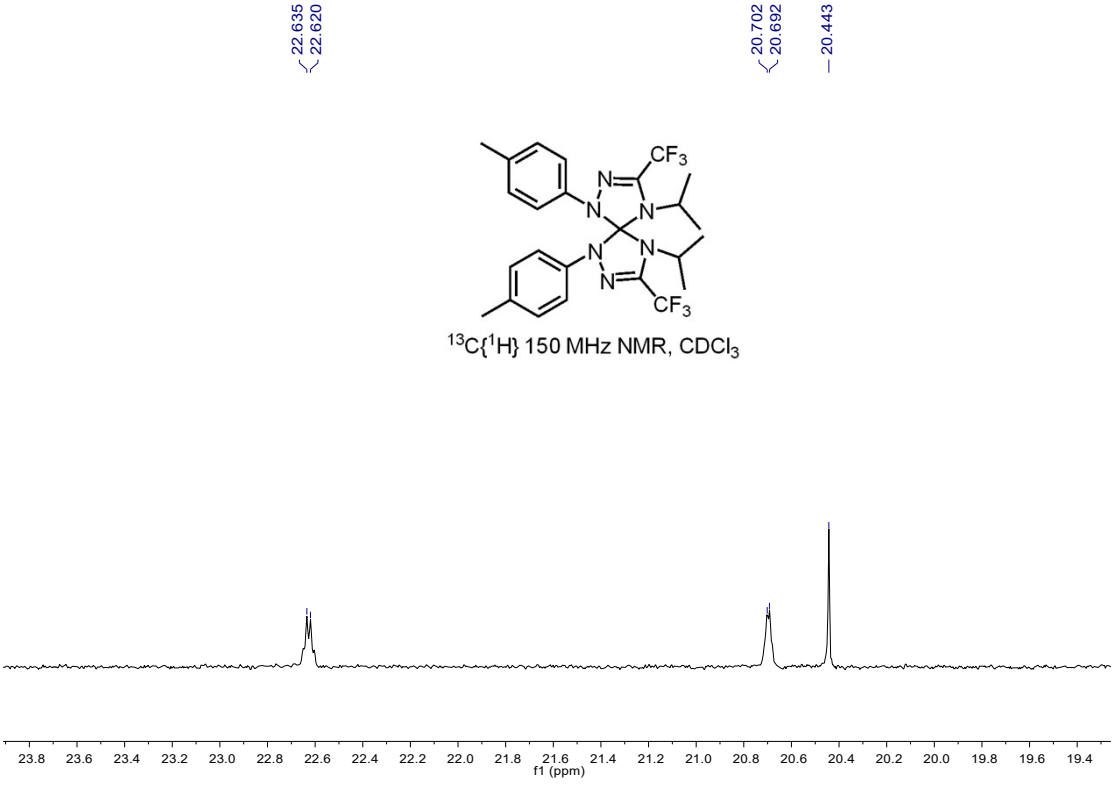


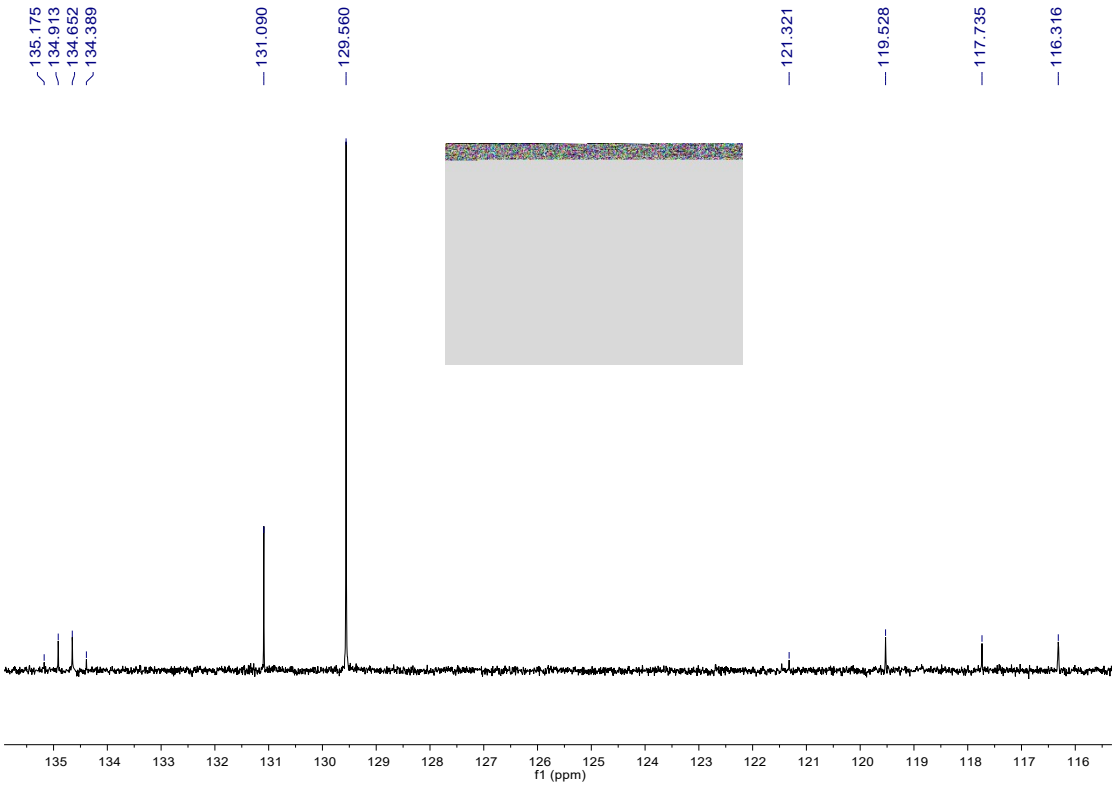
NMR copies of compound **3′c**:

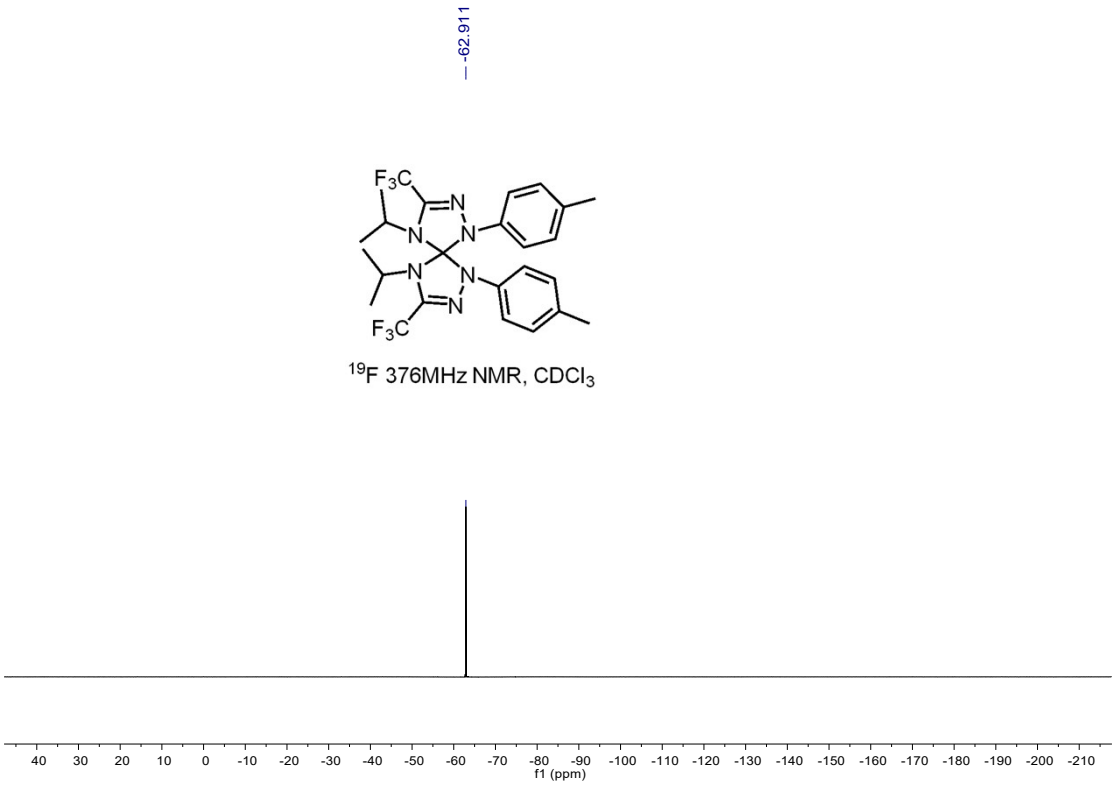





136.963
135.175
134.913
134.652
134.389
131.090
129.560
121.321
119.528
117.735
116.316
114.345
77.160
76.948
76.736
45.939
22.635
22.620
20.702
20.692
20.443
CF3
CF3
13C{1H} 150 MHz NMR, CDCl3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

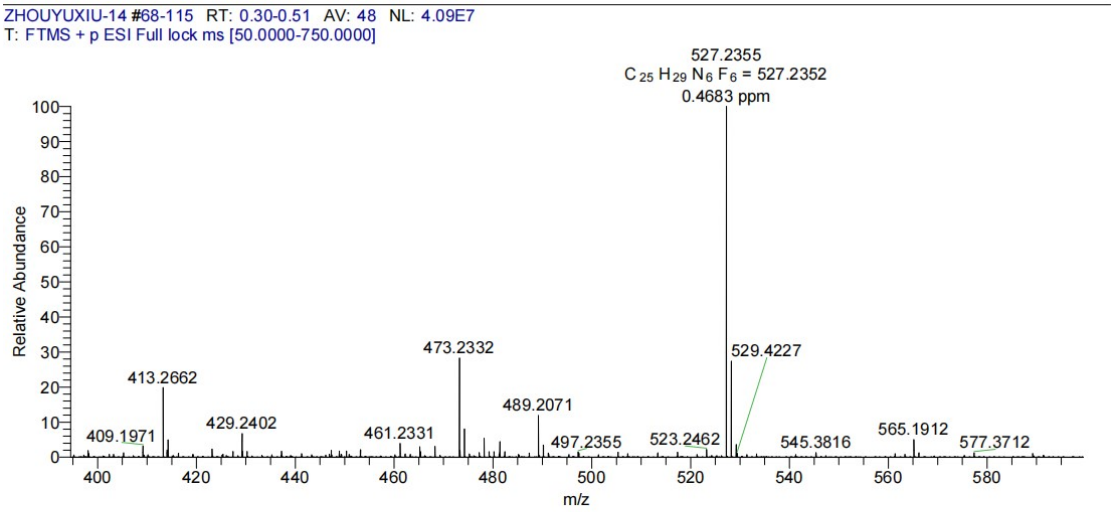

22.635
22.620
20.702
20.692
20.443
CF3
CF3
13C{1H} 150 MHz NMR, CDCl3
23.8 23.6 23.4 23.2 23.0 22.8 22.6 22.4 22.2 22.0 21.8 21.6 21.4 21.2 21.0 20.8 20.6 20.4 20.2 20.0 19.8 19.6 19.4
f1 (ppm)





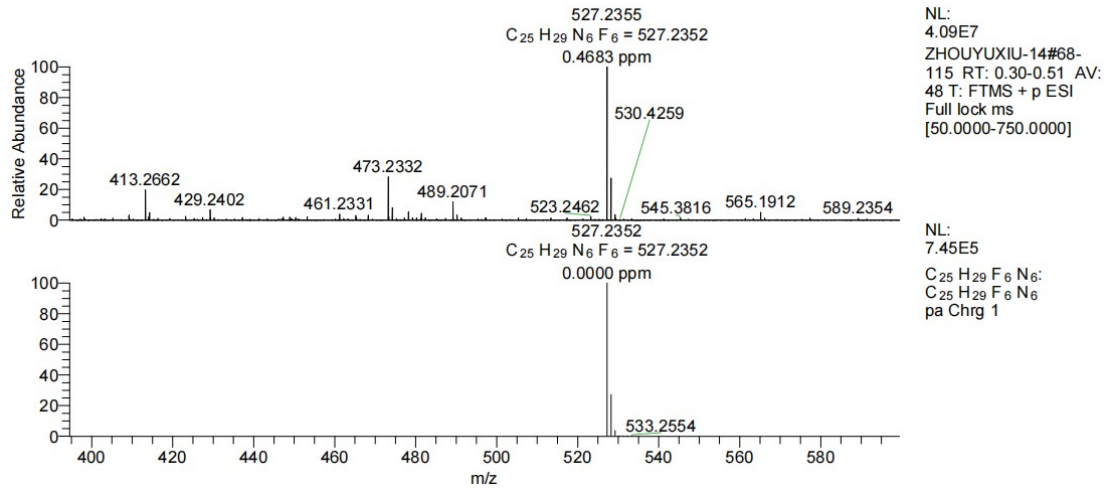
^{19}F 376MHz NMR, $CDCl_3$

HRMS (ESI) copy of compound **3′c**:

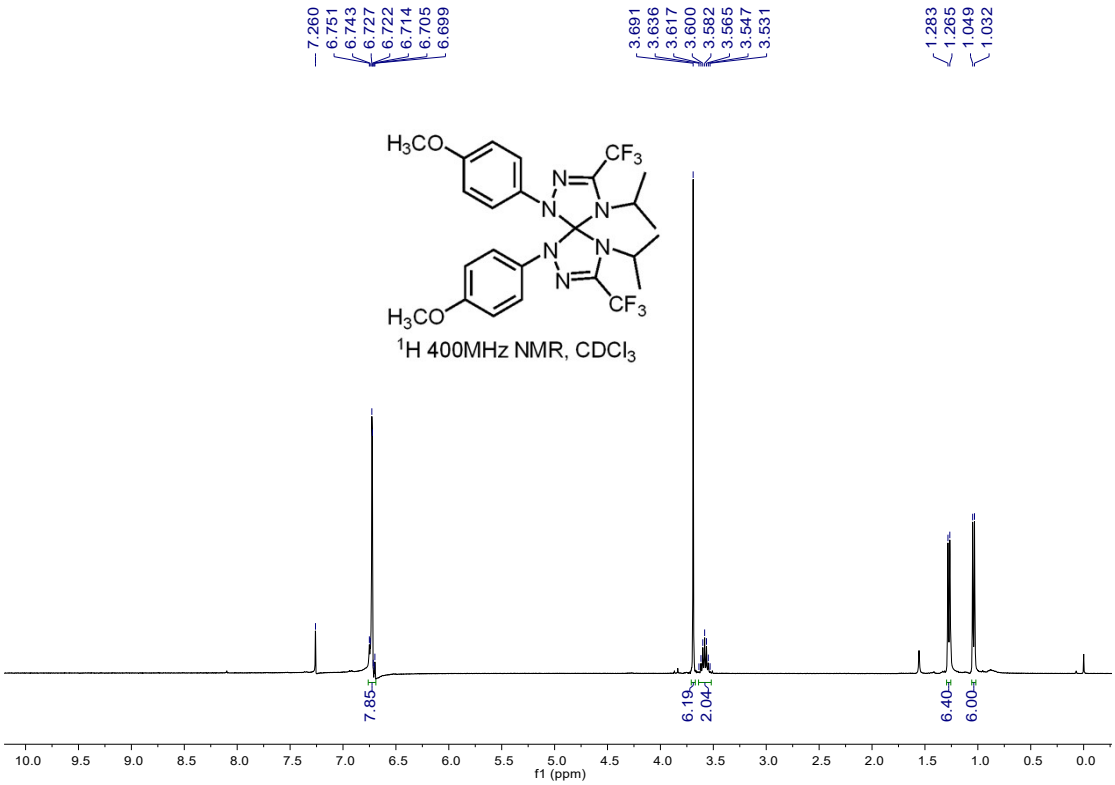


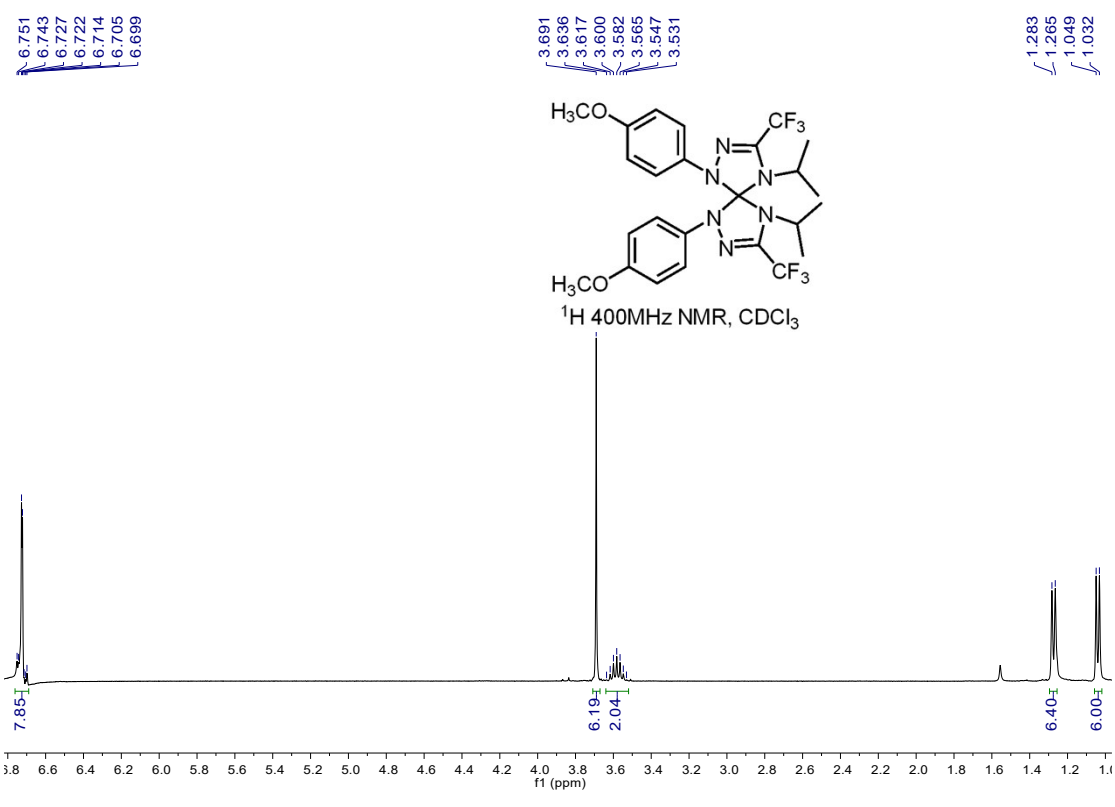
ZHOUYUXIU-14#68-115 RT: 0.30-0.51 AV: 48
T: FTMS + p ESI Full lock ms [50.0000-750.0000]
m/z= 394.5241-599.4133

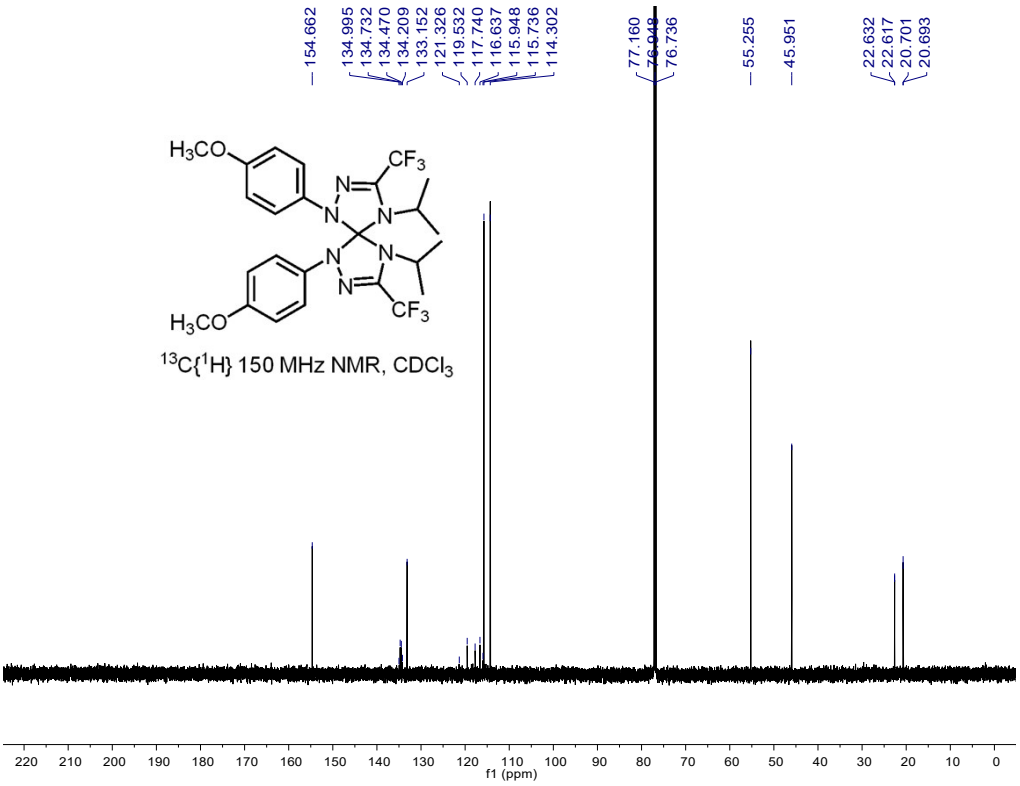
m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
413.2662	8214149.0	19.72			
473.2332	11547784.0	27.72			
527.2355	41660288.0	100.00	527.2352	0.25	C25 H29 N6 F6
528.2389	11317670.0	27.17			

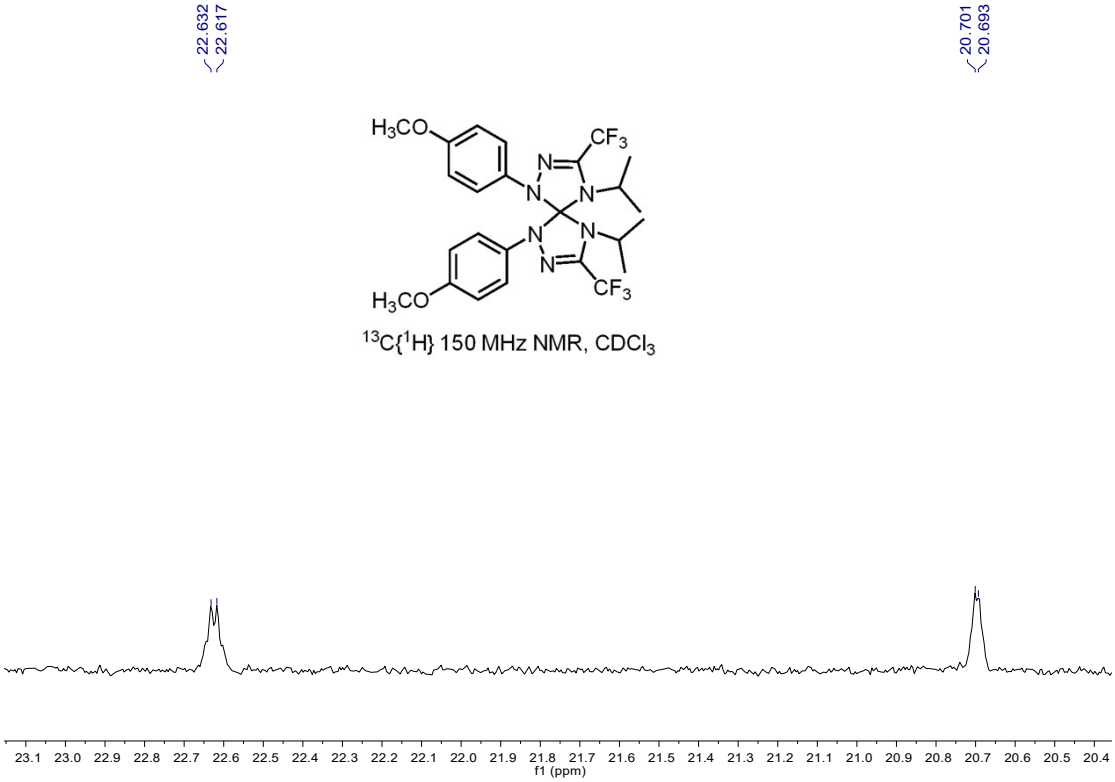


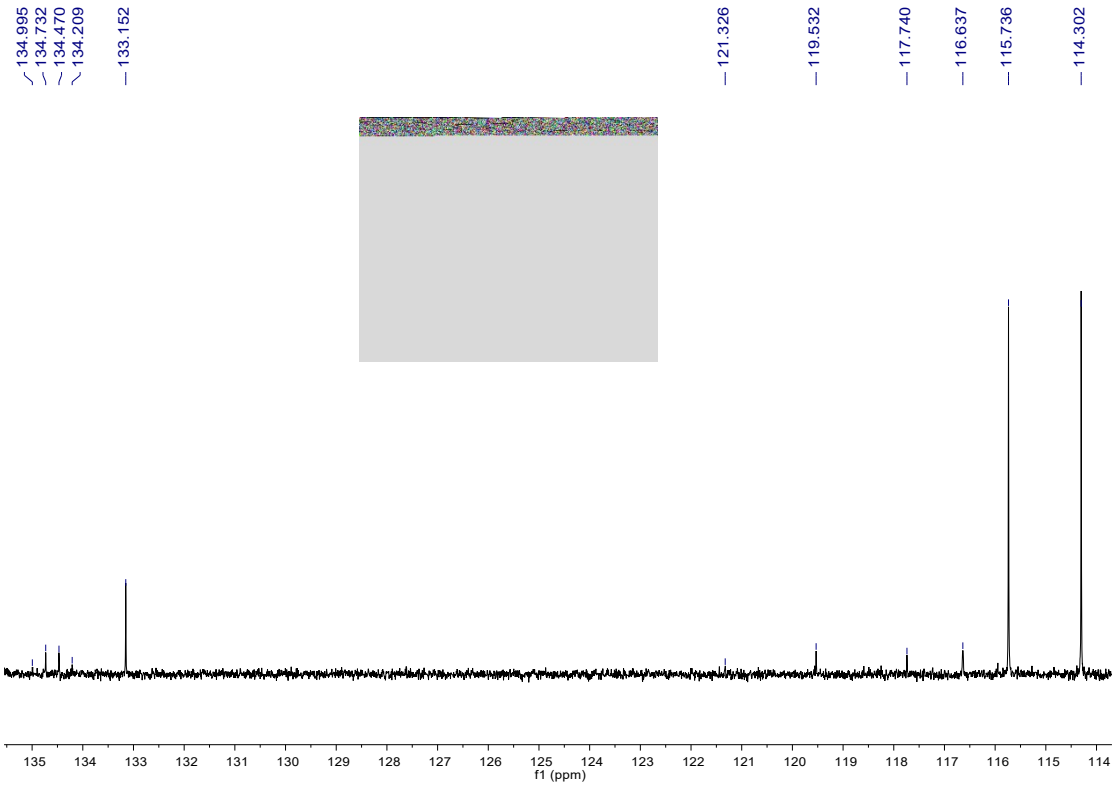
NMR copies of compound **3′d**:

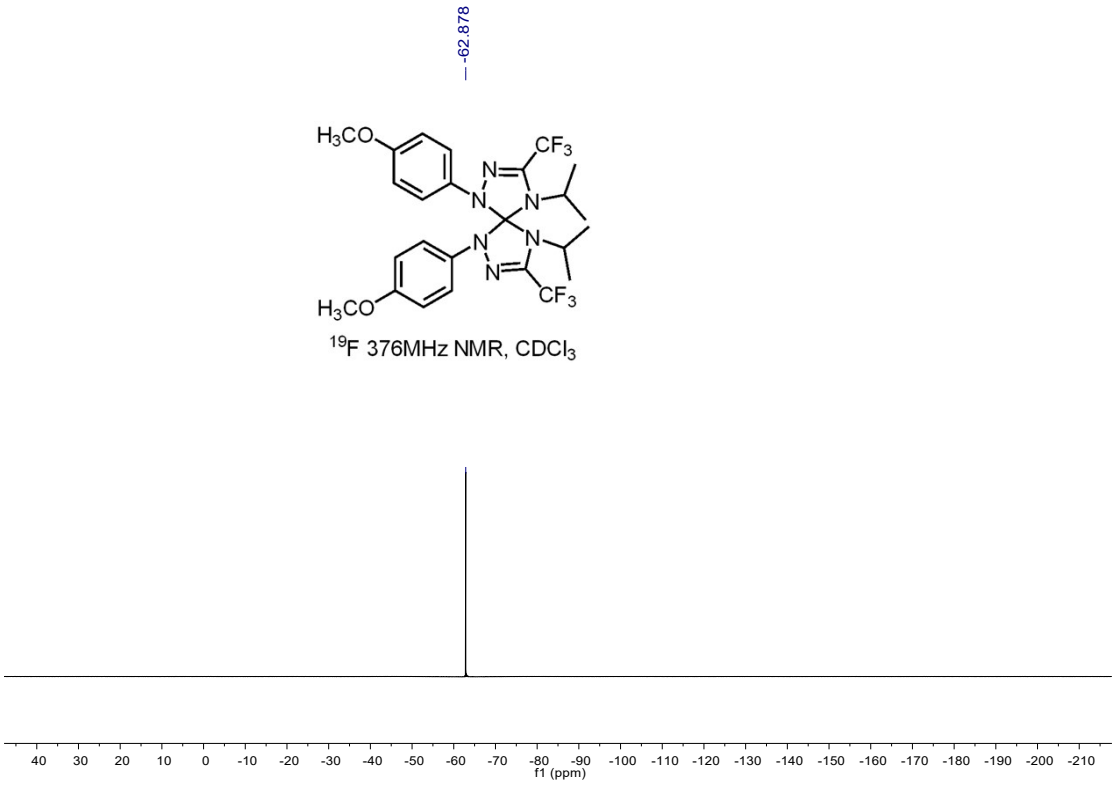





154.662
134.995
134.732
134.470
134.209
133.152
121.326
119.532
117.740
116.637
115.948
115.736
114.302
77.160
76.948
76.736
55.255
45.951
22.632
22.617
20.701
20.693
H3CO
CF3
N
N
N
N
N
N
H3CO
CF3
13C{1H} 150 MHz NMR, CDCl3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

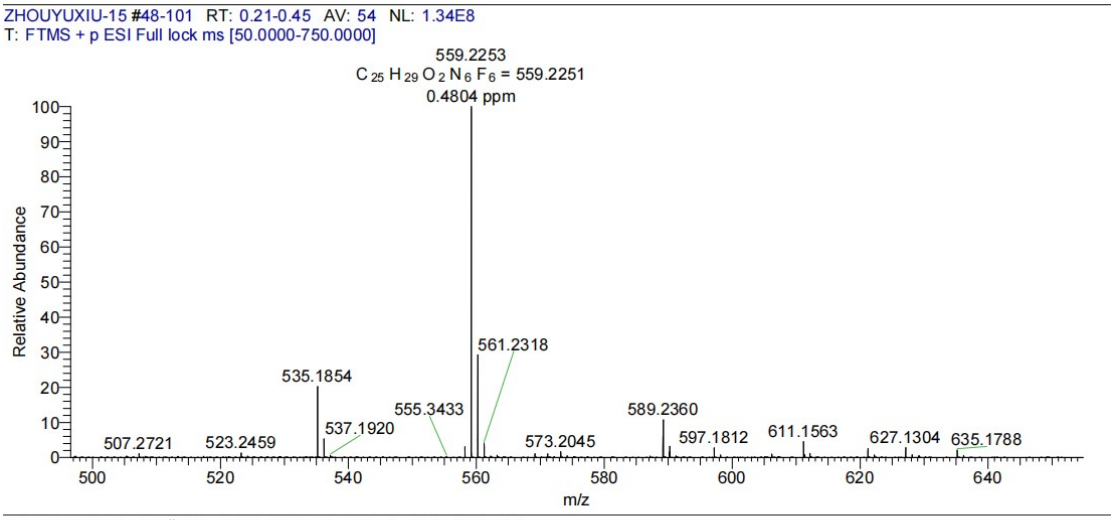

22.632
22.617
20.701
20.693
H3CO
CF3
N
N
N
N
N
N
H3CO
CF3
13C{1H} 150 MHz NMR, CDCl3
23.1 23.0 22.9 22.8 22.7 22.6 22.5 22.4 22.3 22.2 22.1 22.0 21.9 21.8 21.7 21.6 21.5 21.4 21.3 21.2 21.1 21.0 20.9 20.8 20.7 20.6 20.5 20.4
f1 (ppm)





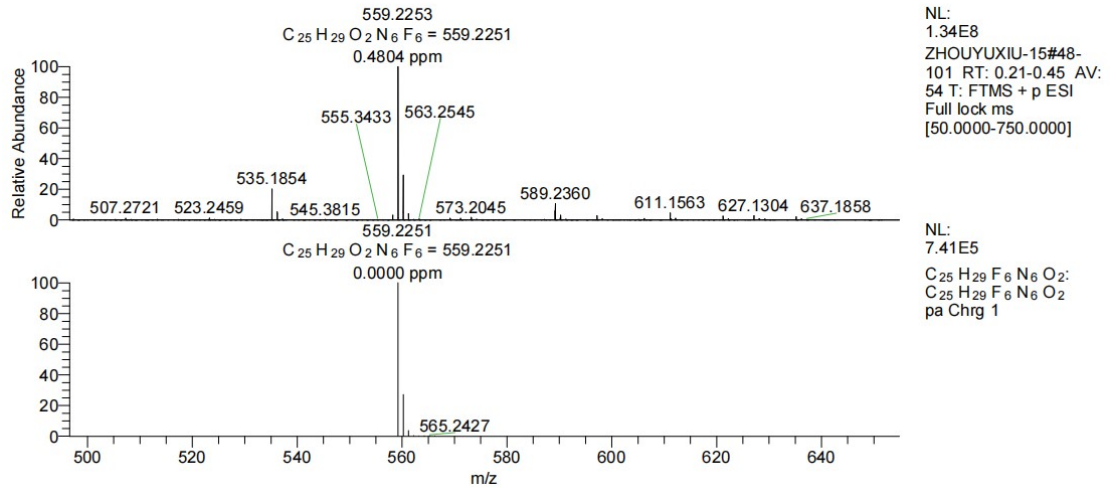
^{19}F 376MHz NMR, $CDCl_3$

HRMS (ESI) copy of compound **3′d**:

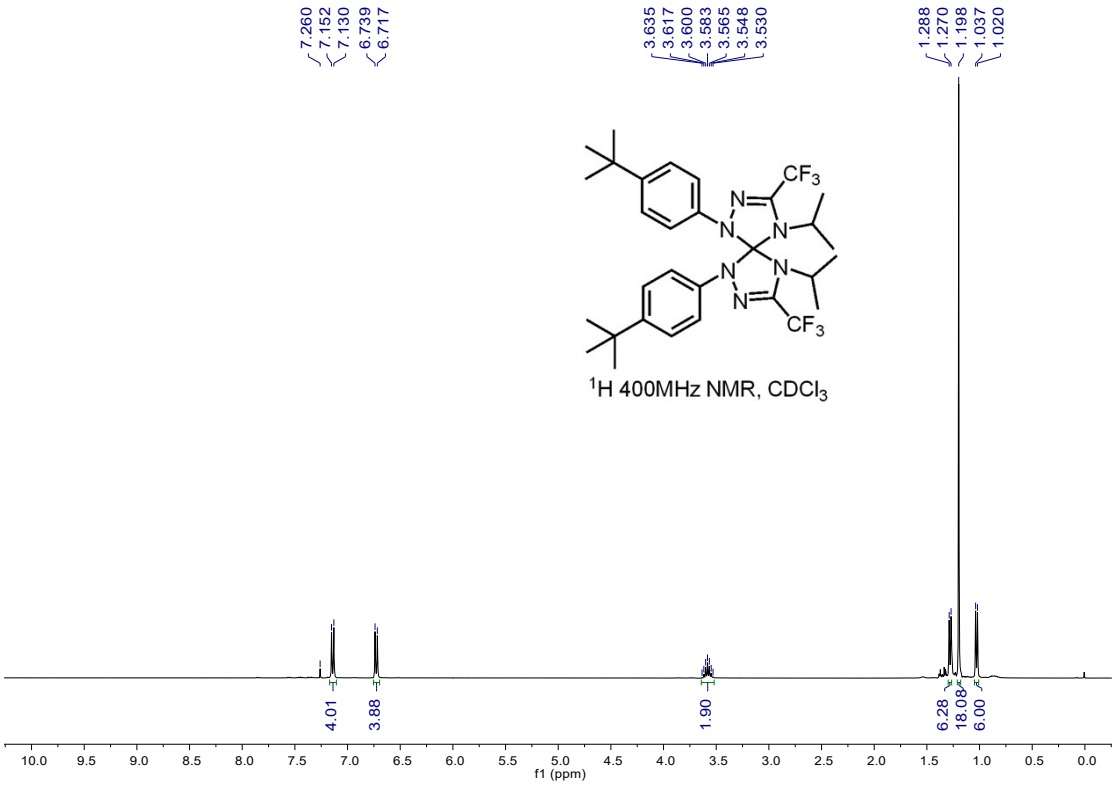


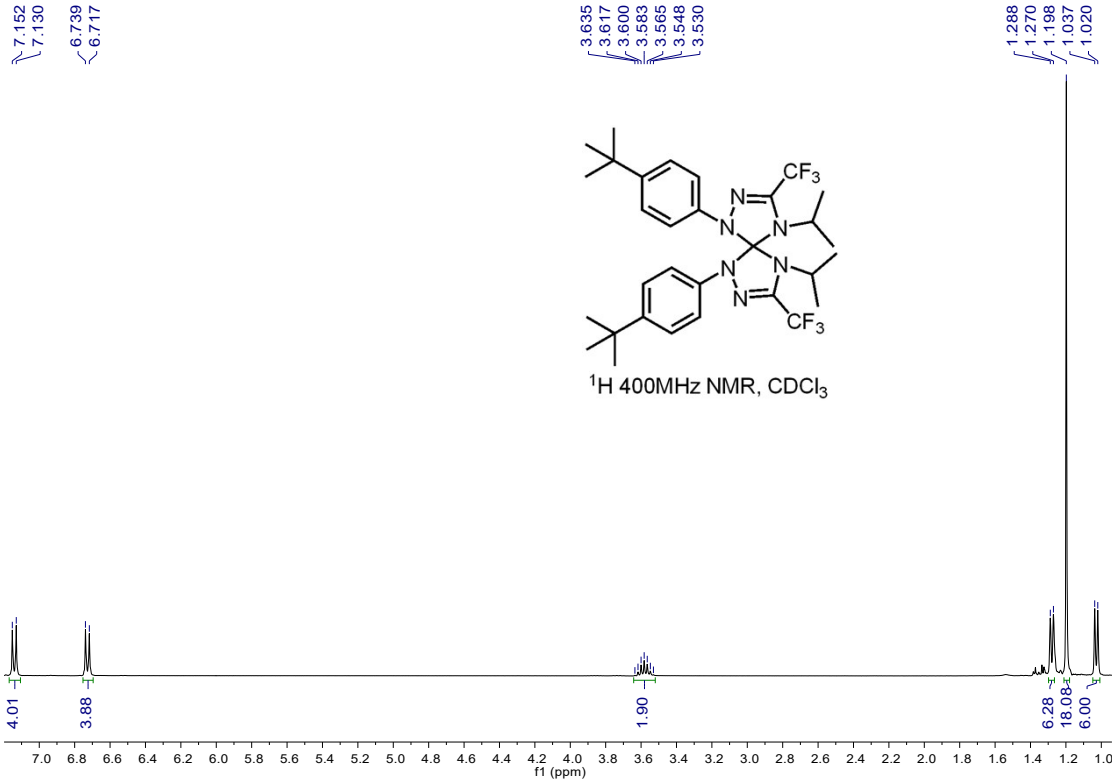
ZHOUYUXIU-15#48-101 RT: 0.21-0.45 AV: 54
T: FTMS + p ESI Full lock ms [50.0000-750.0000]
m/z= 496.5680-654.8452

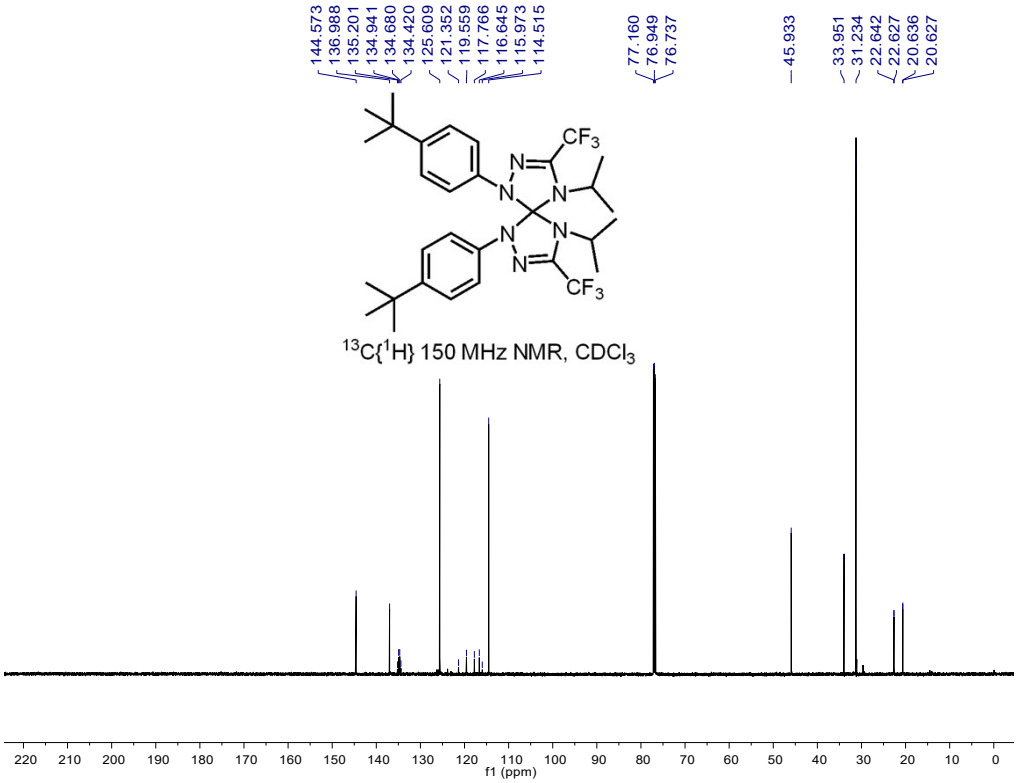
m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
535.1854	28185416.0	20.28			
559.2253	138948384.0	100.00	559.2251	0.27	$C_{25}H_{29}O_2N_6F_6$
560.2286	39299060.0	28.28			
589.2360	14891453.0	10.72			

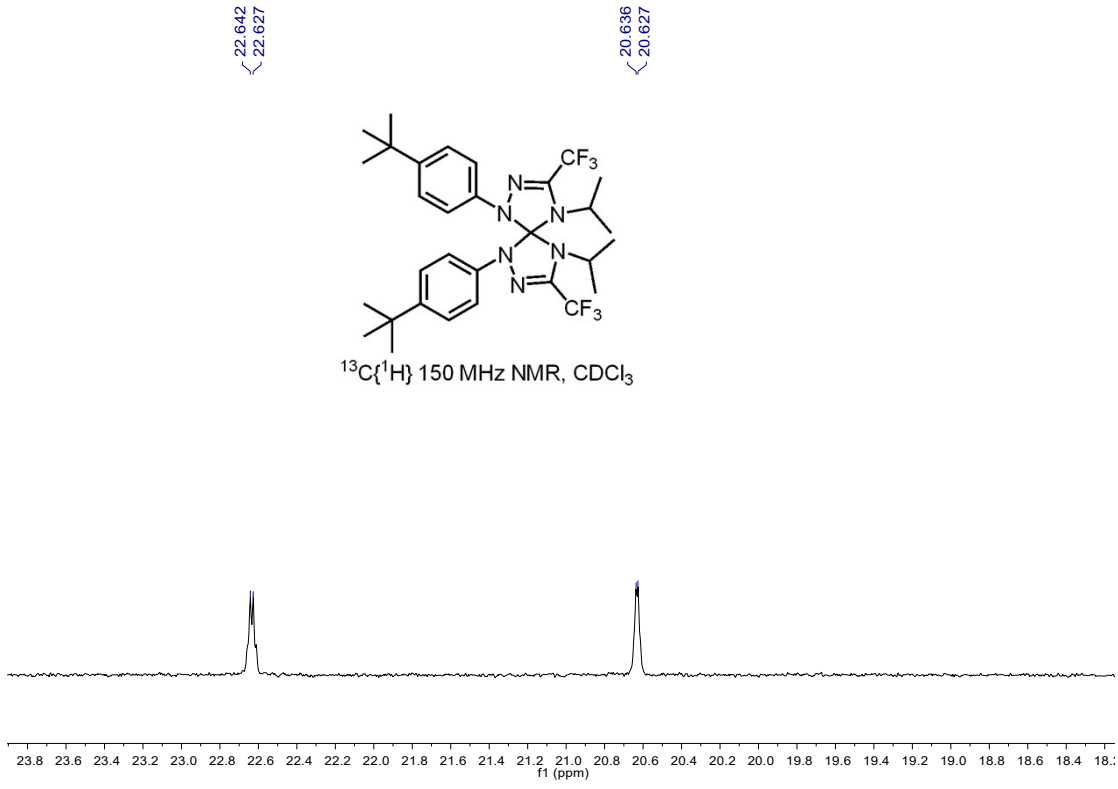


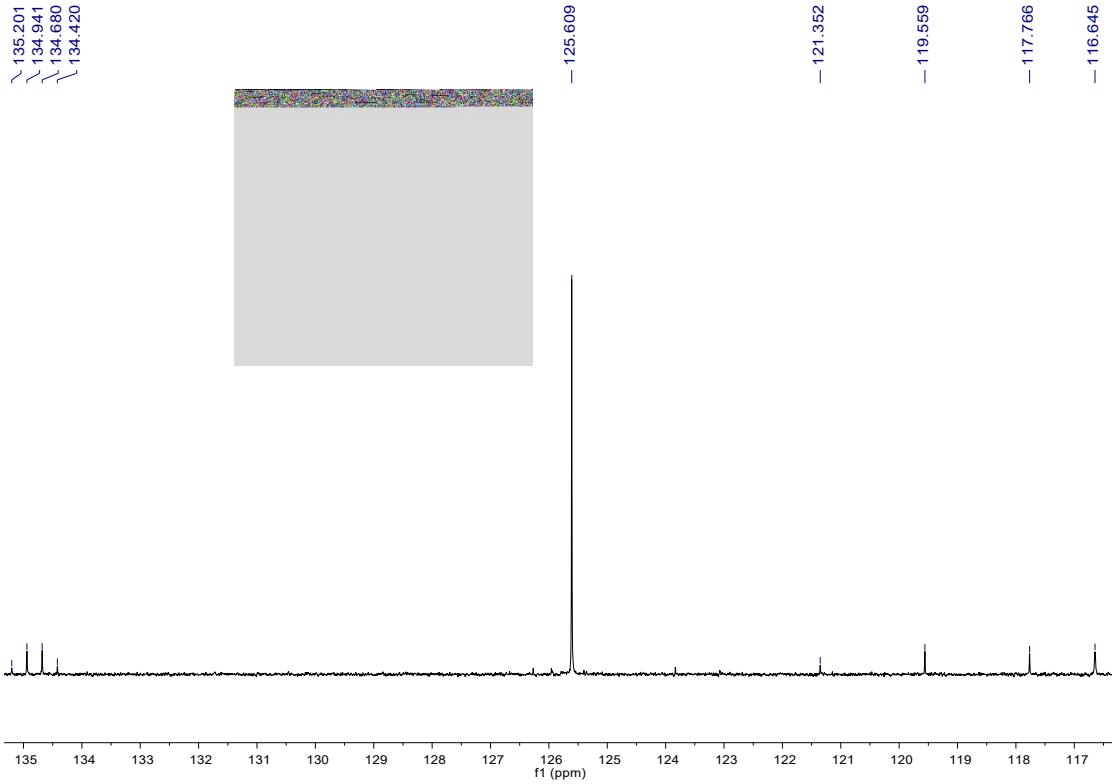
NMR copies of compound **3′e**:

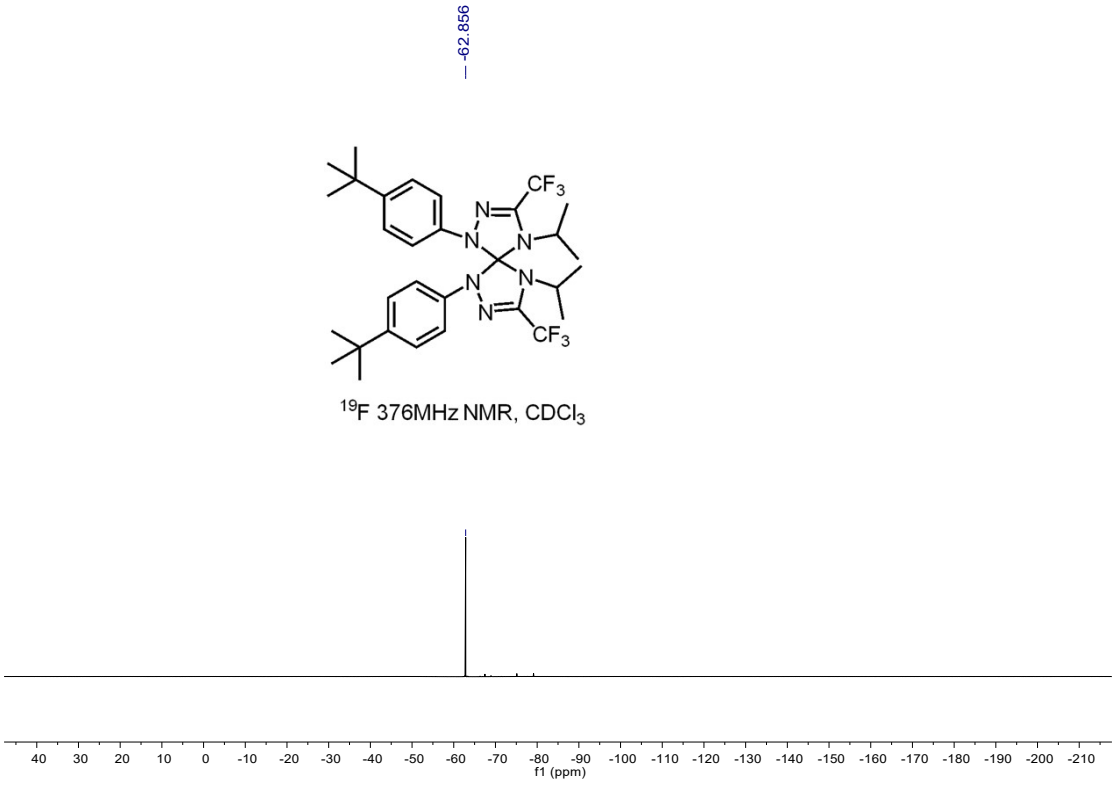





144.573
136.988
135.201
134.941
134.680
134.420
125.609
121.352
119.559
117.766
116.645
115.973
114.515
77.160
76.949
76.737
45.933
33.951
31.234
22.642
22.627
20.636
20.627
CF3
CF3
13C{1H} 150 MHz NMR, CDCl3
f1 (ppm)

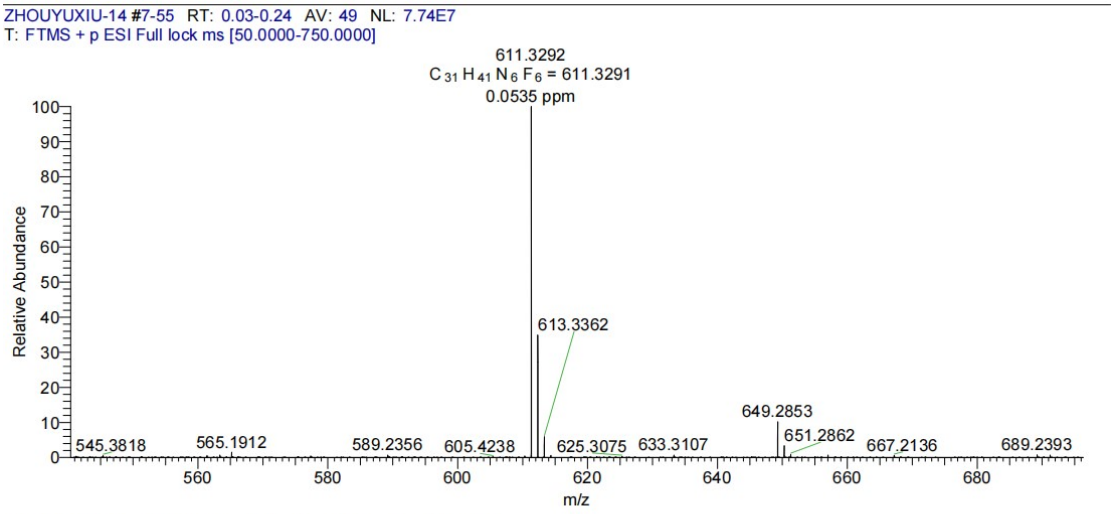

22.642
22.627
20.636
20.627
CF3
CF3
13C{1H} 150 MHz NMR, CDCl3
f1 (ppm)





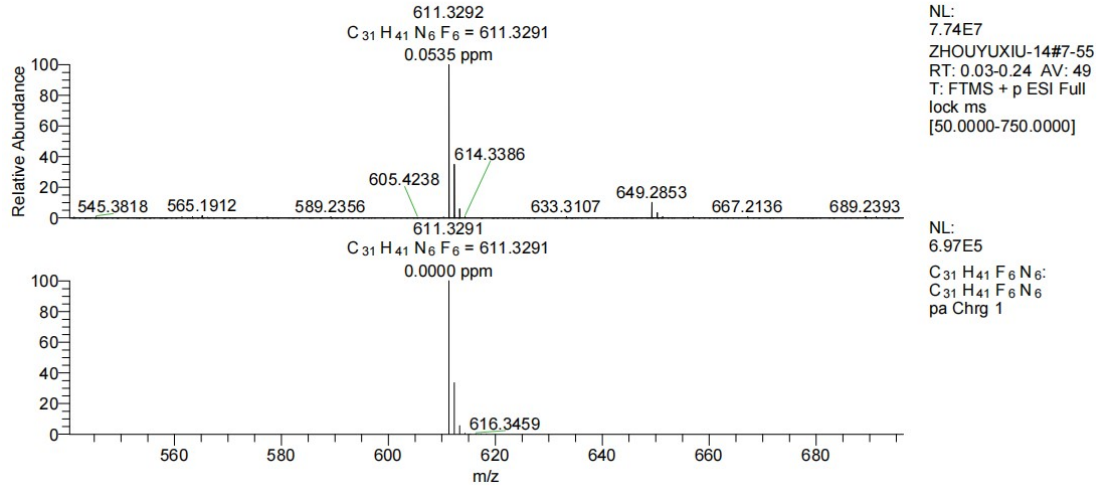
^{19}F 376MHz NMR, $CDCl_3$

HRMS (ESI) copy of compound **3′e**:

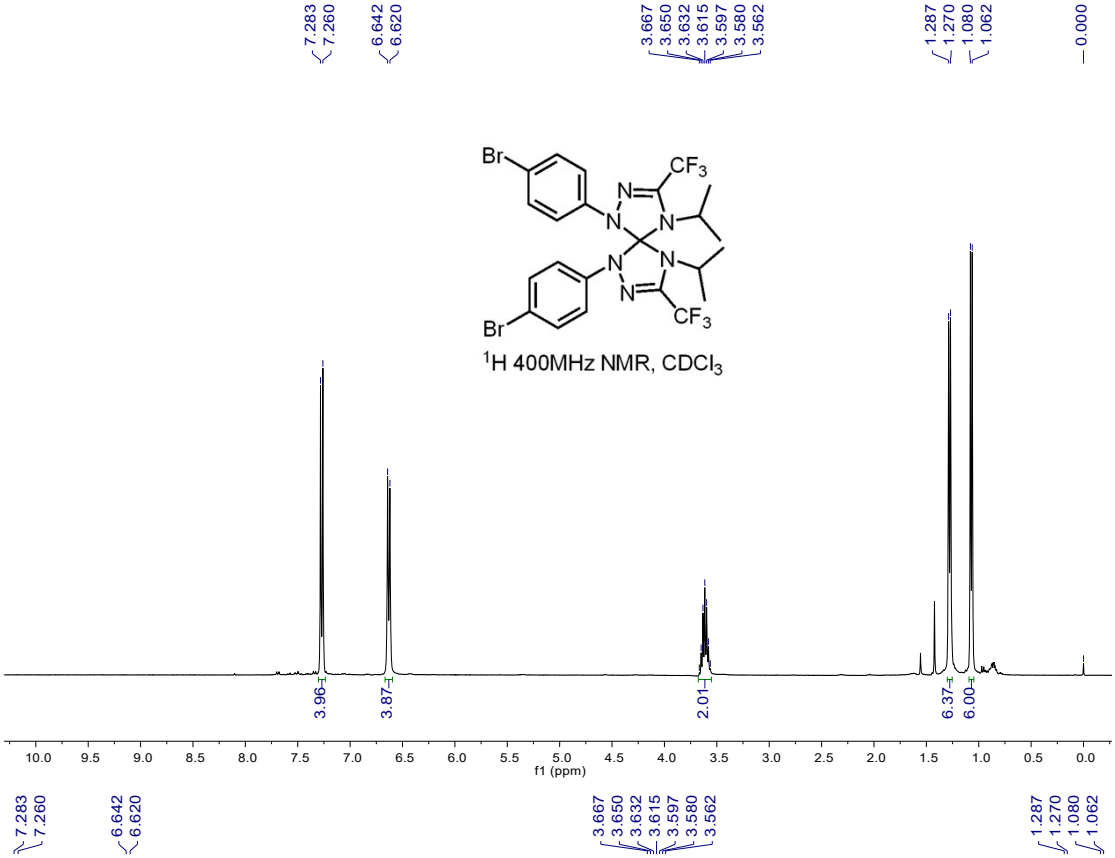


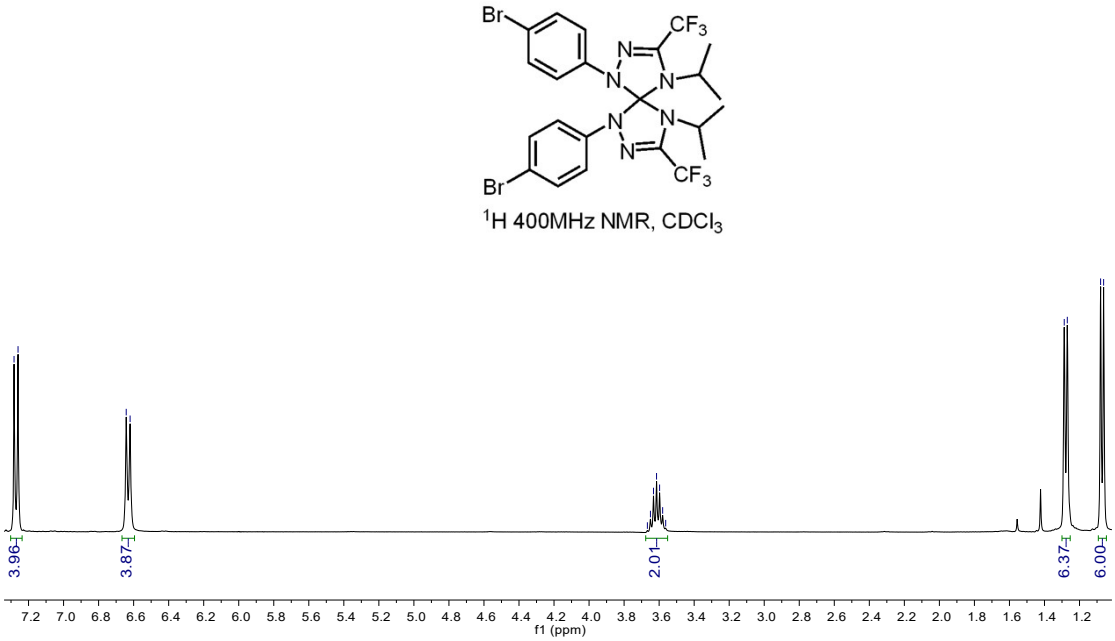
ZHOUYUXIU-14#7-55 RT: 0.03-0.24 AV: 49
T: FTMS + p ESI Full lock ms [50.0000-750.0000]
m/z= 540.3769-696.2988

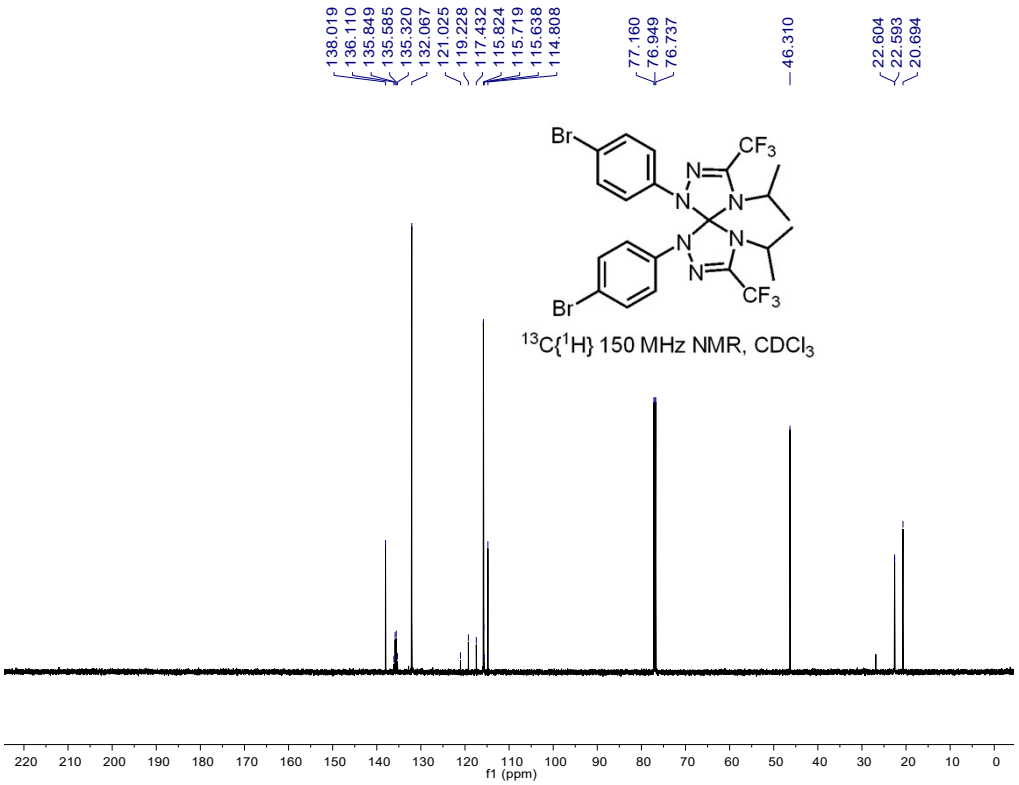
m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
611.3292	77968592.0	100.00	611.3291	0.03	C31 H41 N6 F6
612.3328	27083076.0	34.74			
613.3362	4587971.5	5.88			
649.2853	7904784.0	10.14			

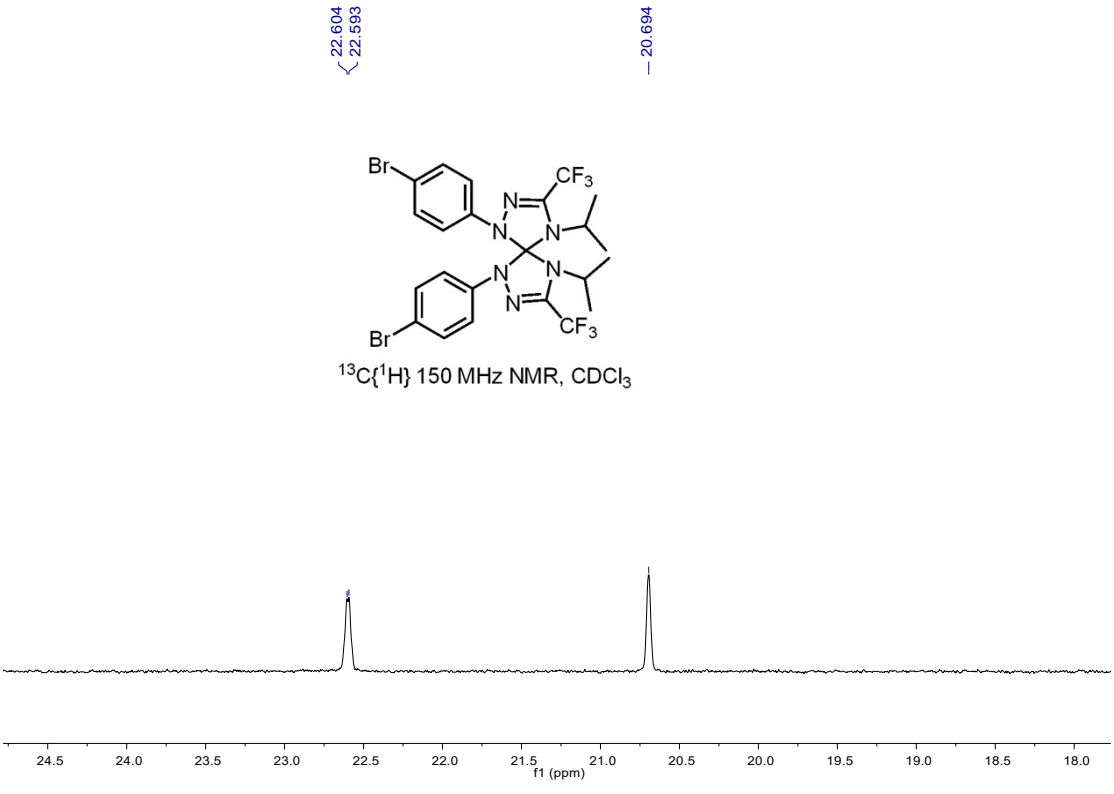


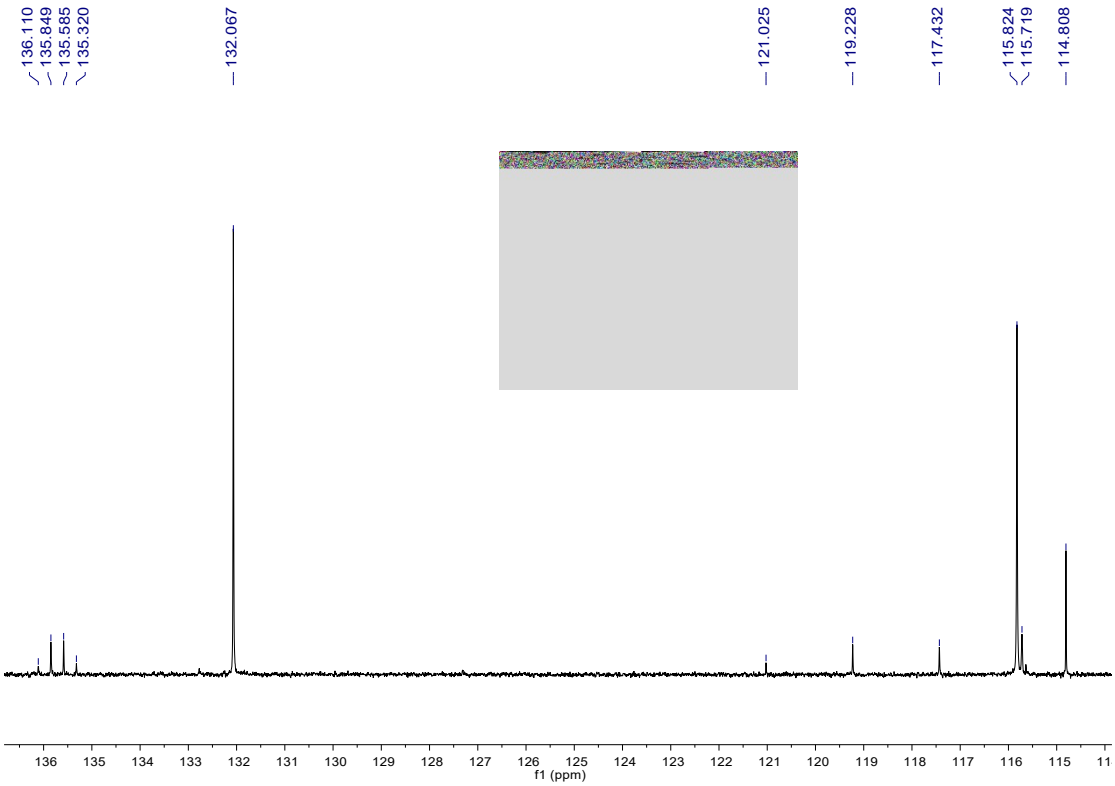
NMR copies of compound **3′f**:

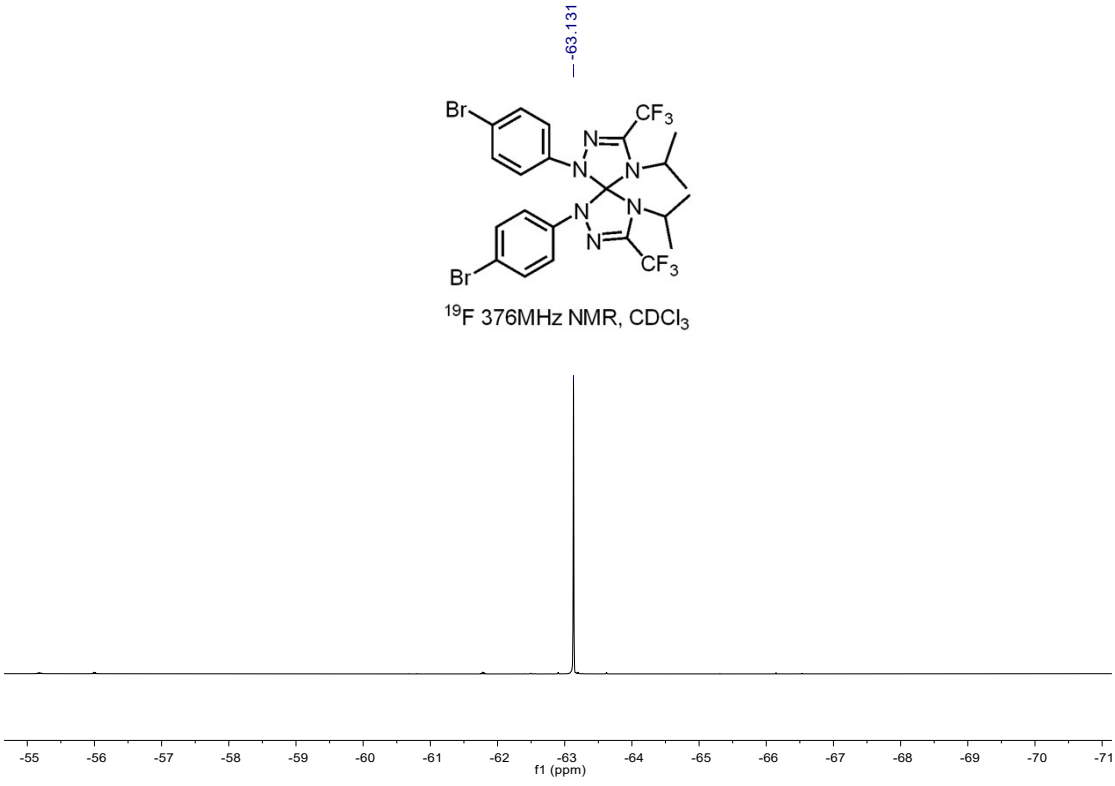





138.019
136.110
135.849
135.585
135.320
132.067
121.025
119.228
117.432
115.824
115.719
115.638
114.808
77.160
76.949
76.737
46.310
22.604
22.593
20.694
Br
CF3
N
N
N
N
N
N
Br
CF3
13C{1H} 150 MHz NMR, CDCl3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

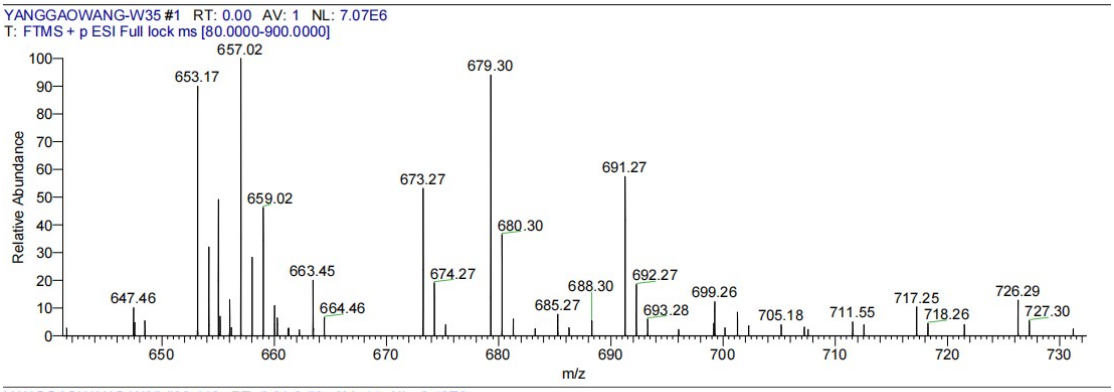

22.604
22.593
20.694
Br
CF3
N
N
N
N
N
N
Br
CF3
13C{1H} 150 MHz NMR, CDCl3
24.5 24.0 23.5 23.0 22.5 22.0 21.5 21.0 20.5 20.0 19.5 19.0 18.5 18.0
f1 (ppm)

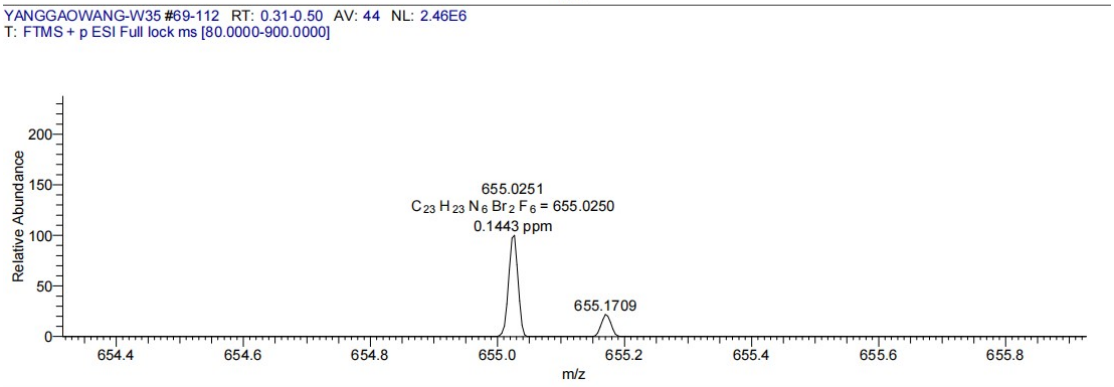




^{19}F 376MHz NMR, $CDCl_3$

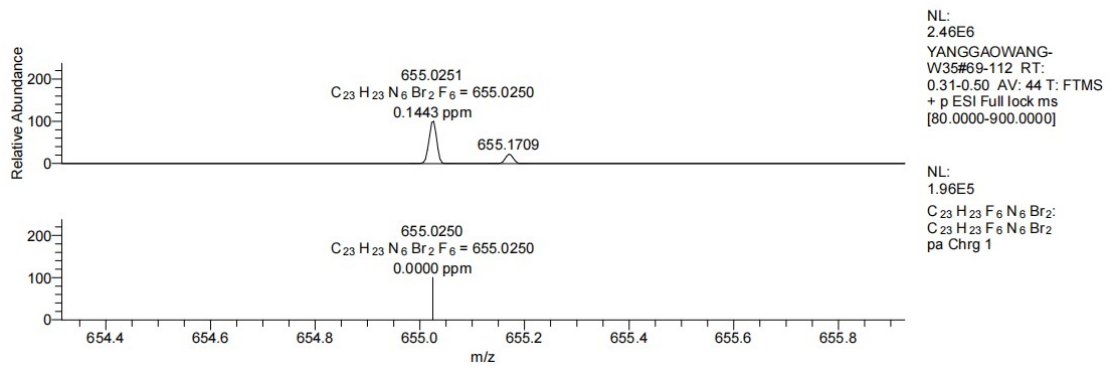
HRMS (ESI) copy of compound **3′f**:



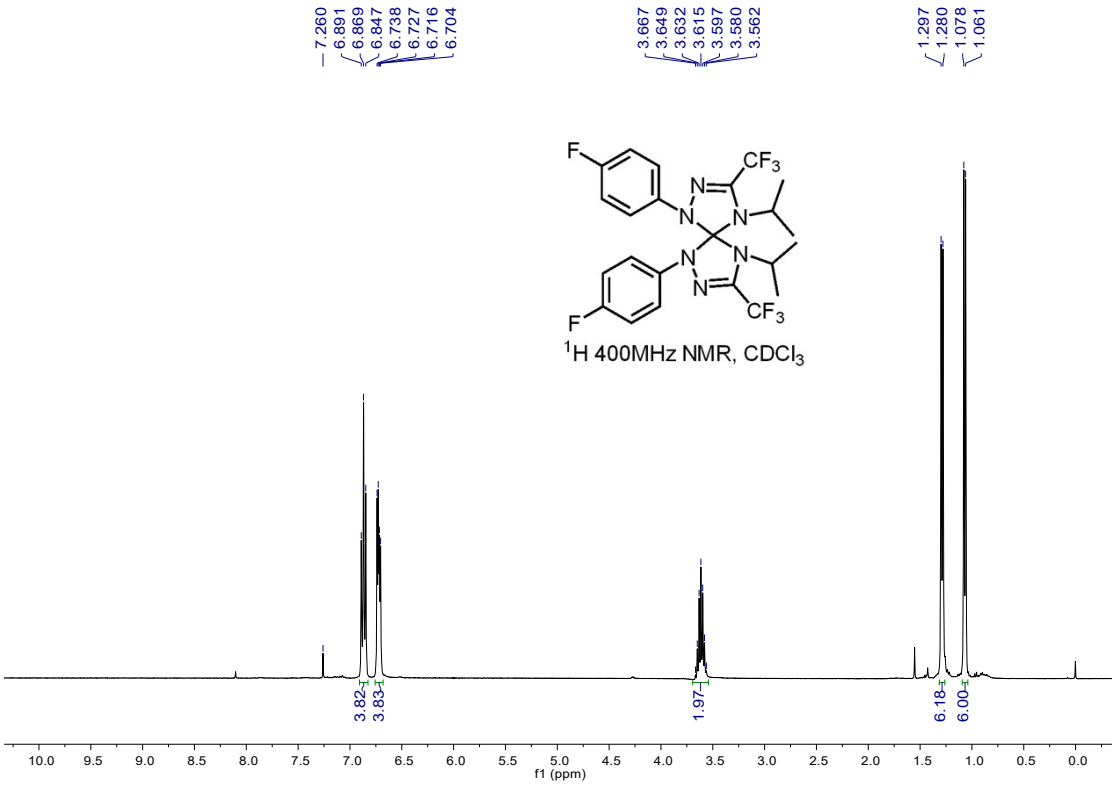


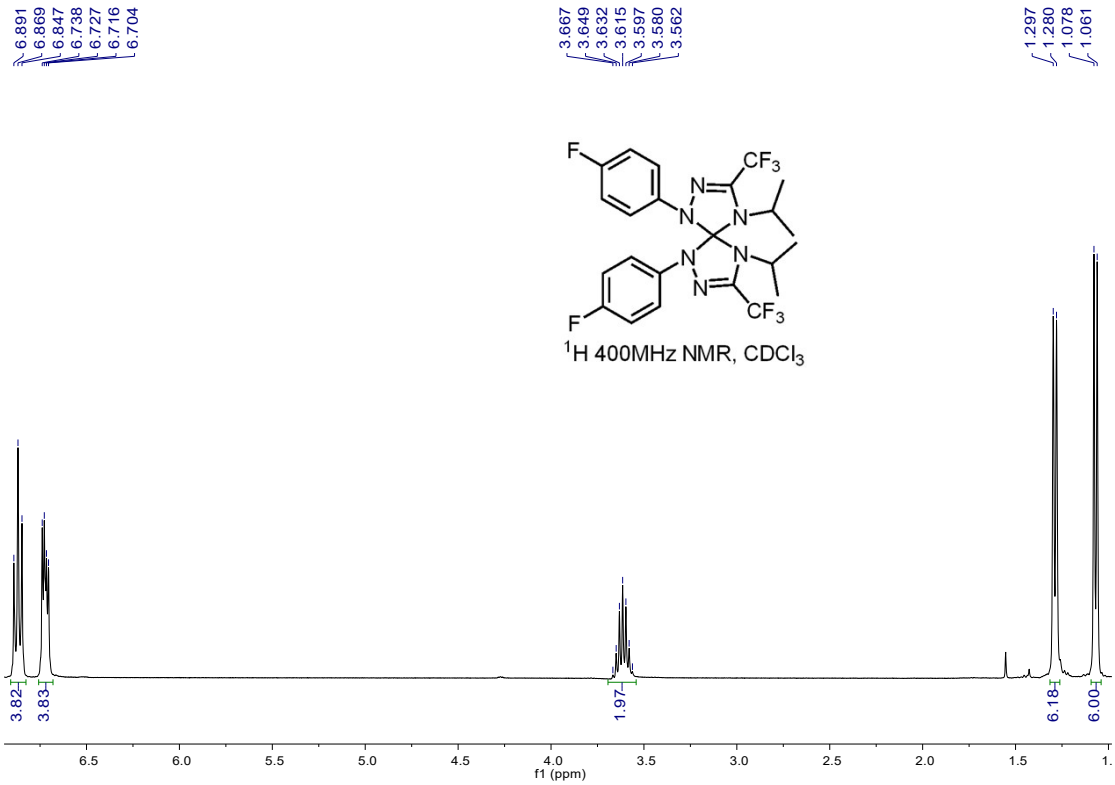
YANGGAOWANG-W35#69-112 RT: 0.31-0.50 AV: 44
T: FTMS + p ESI Full lock ms [80.0000-900.0000]
m/z= 654.3157-655.9266

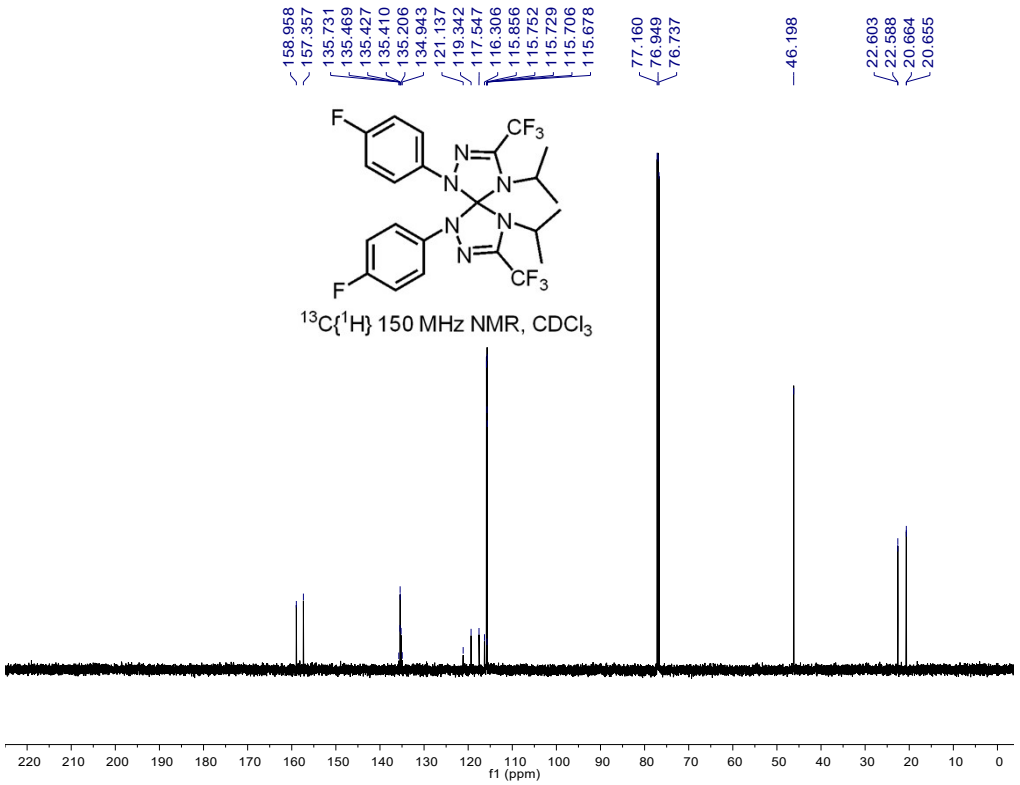
m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
655.0251	2528773.3	100.00	655.0250	0.09	$C_{23}H_{23}N_6Br_2F_6$
655.1709	542978.8	21.47	655.0250	145.96	$C_{23}H_{23}N_6Br_2F_6$

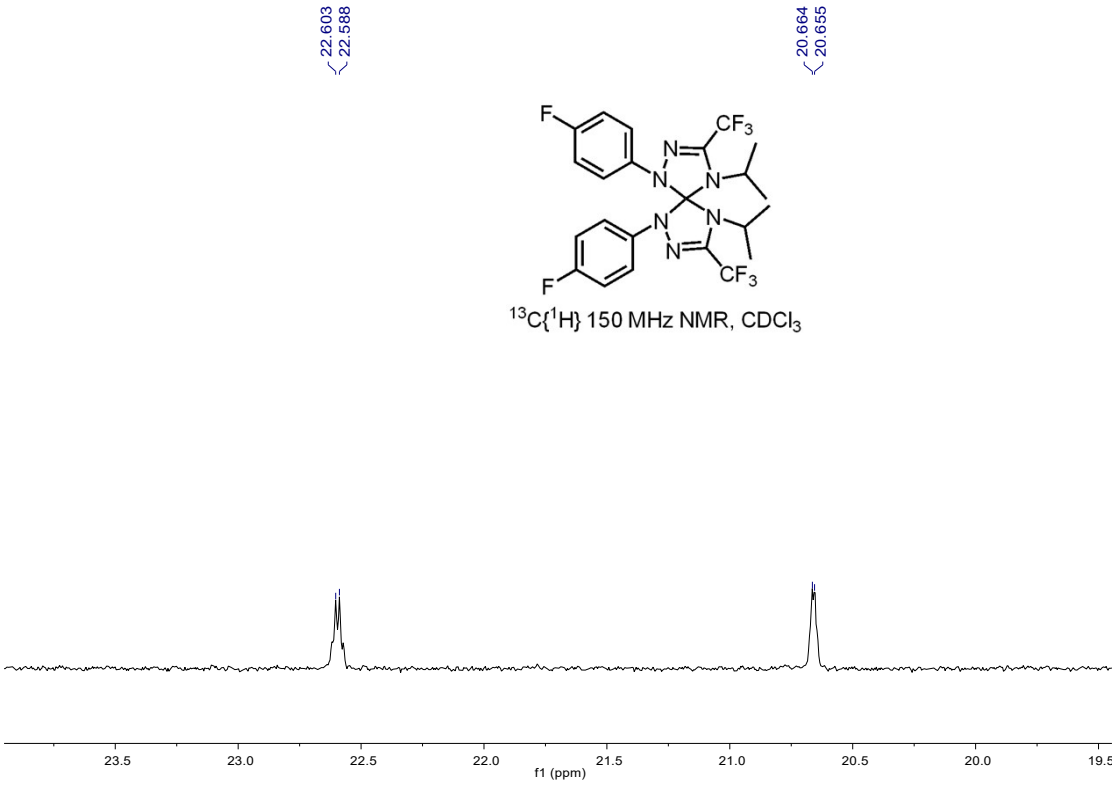


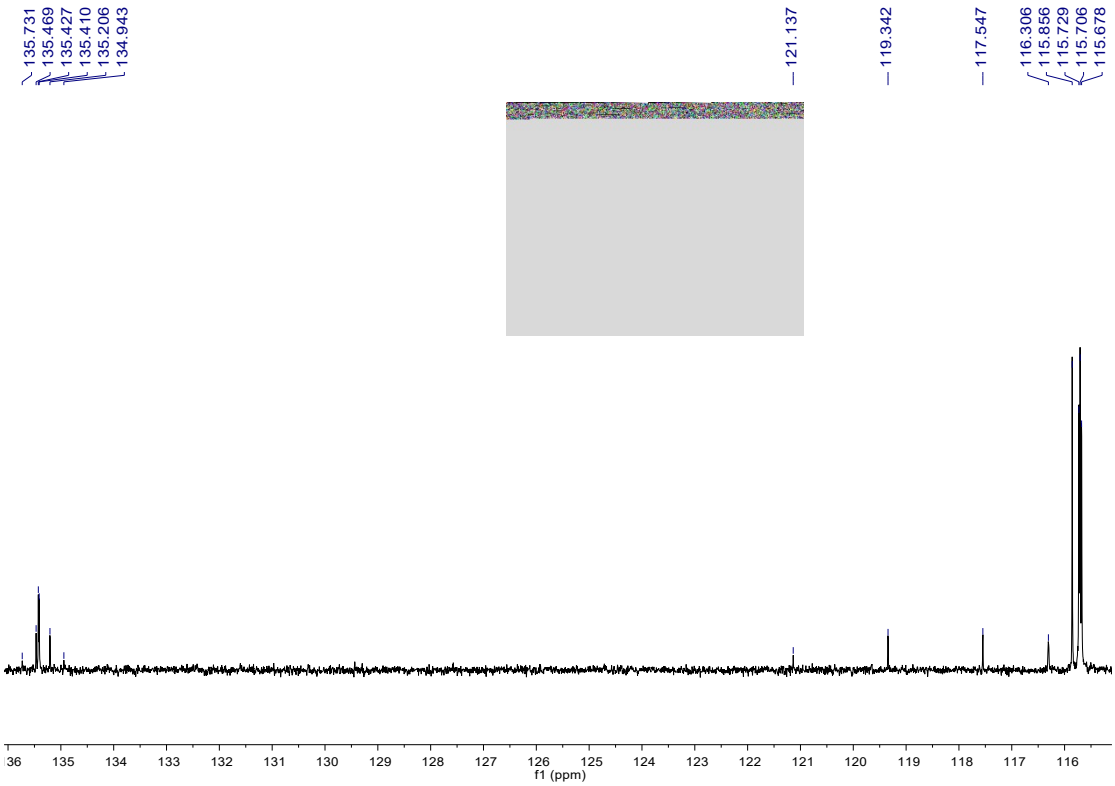
NMR copies of compound **3′g**:

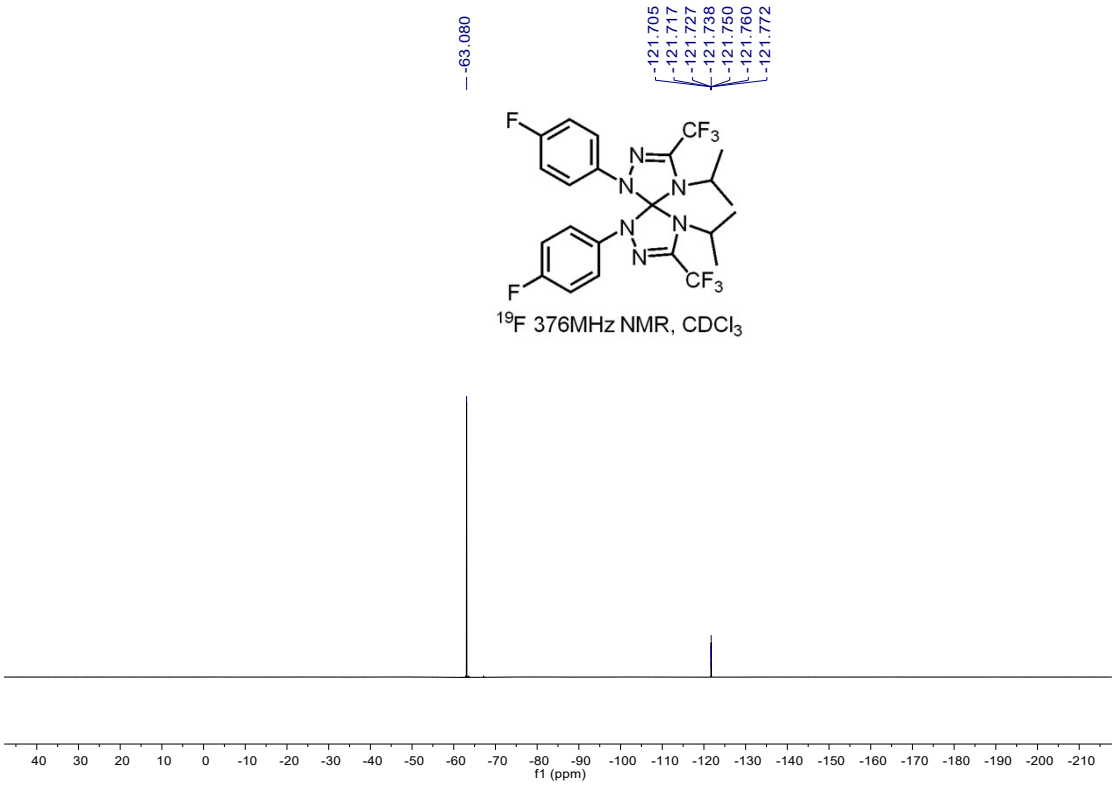




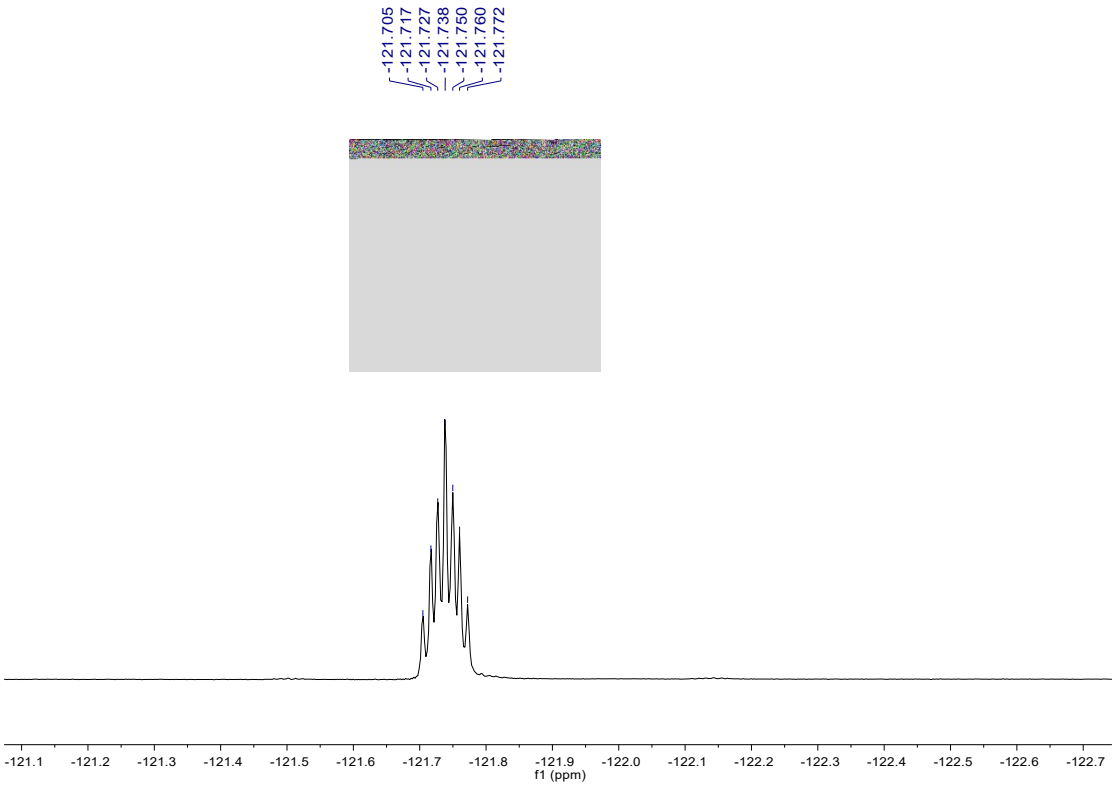

158.958
157.357
135.731
135.469
135.427
135.410
135.206
134.943
121.137
119.342
117.547
116.306
115.856
115.752
115.729
115.706
115.678
77.160
76.949
76.737
46.198
22.603
22.588
20.664
20.655
F
CF3
N
N
N
N
N
F
CF3
13C{1H} 150 MHz NMR, CDCl3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


22.603
22.588
20.664
20.655
F
CF3
N
N
N
N
N
F
CF3
13C{1H} 150 MHz NMR, CDCl3
23.5 23.0 22.5 22.0 21.5 21.0 20.5 20.0 19.5
f1 (ppm)

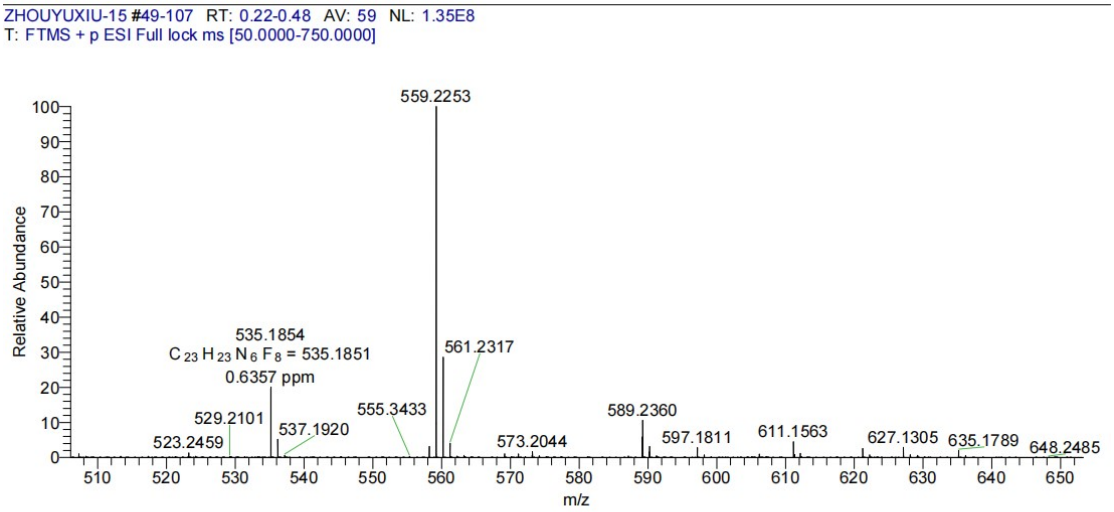




^{19}F 376MHz NMR, $CDCl_3$

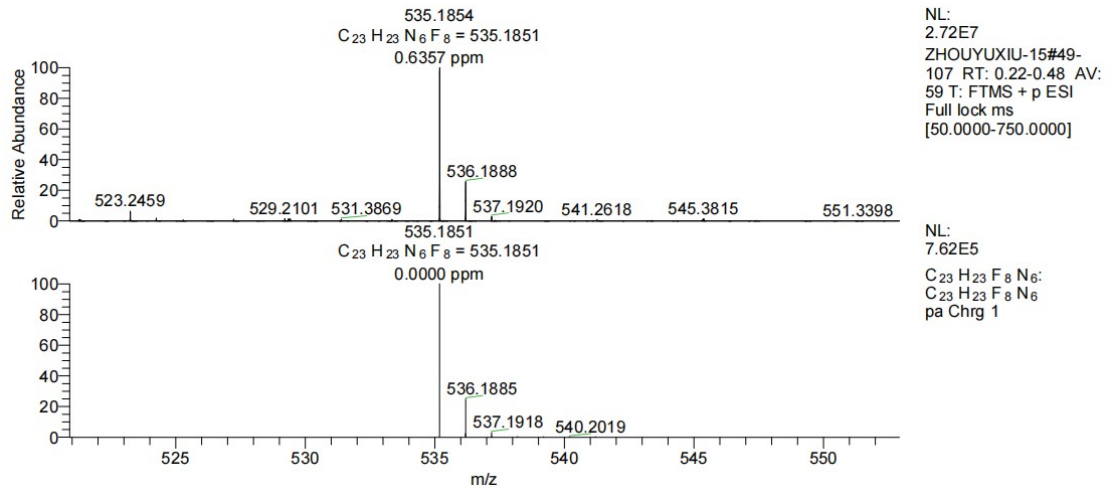

-121.705
-121.717
-121.727
-121.738
-121.750
-121.760
-121.772
-121.1
-121.2
-121.3
-121.4
-121.5
-121.6
-121.7
-121.8
-121.9
-122.0
-122.1
-122.2
-122.3
-122.4
-122.5
-122.6
-122.7
f1 (ppm)

HRMS (ESI) copy of compound **3′g**:

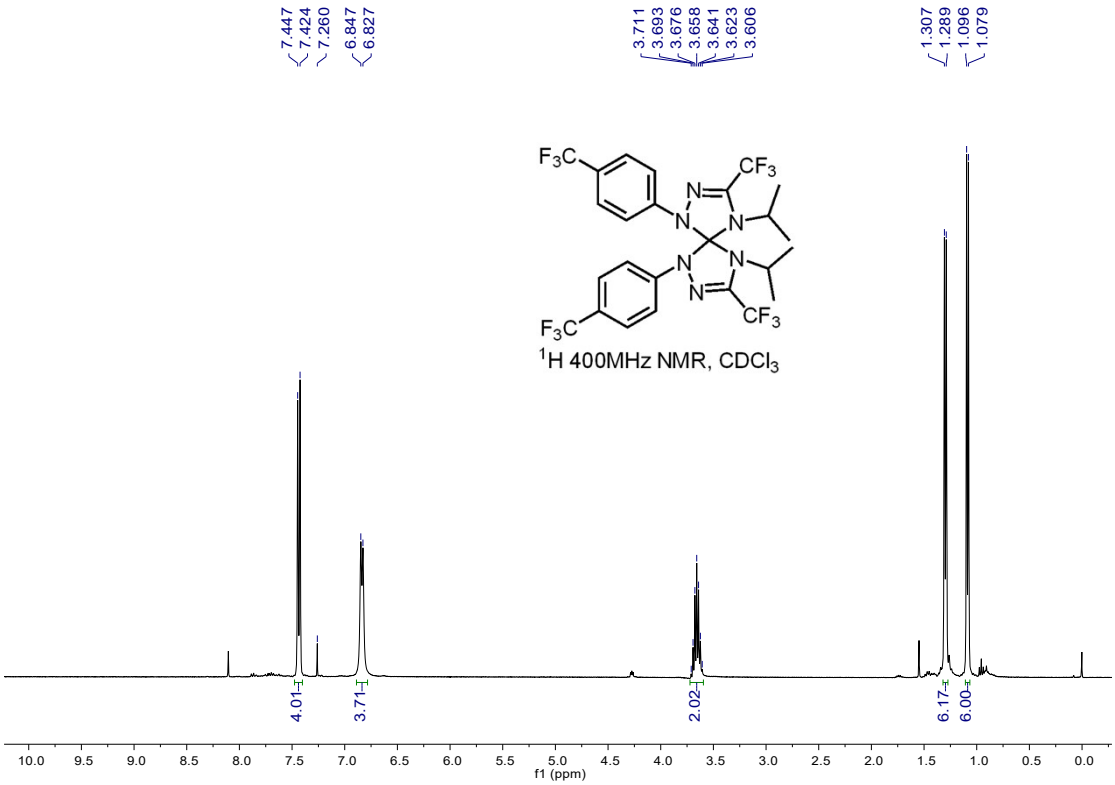


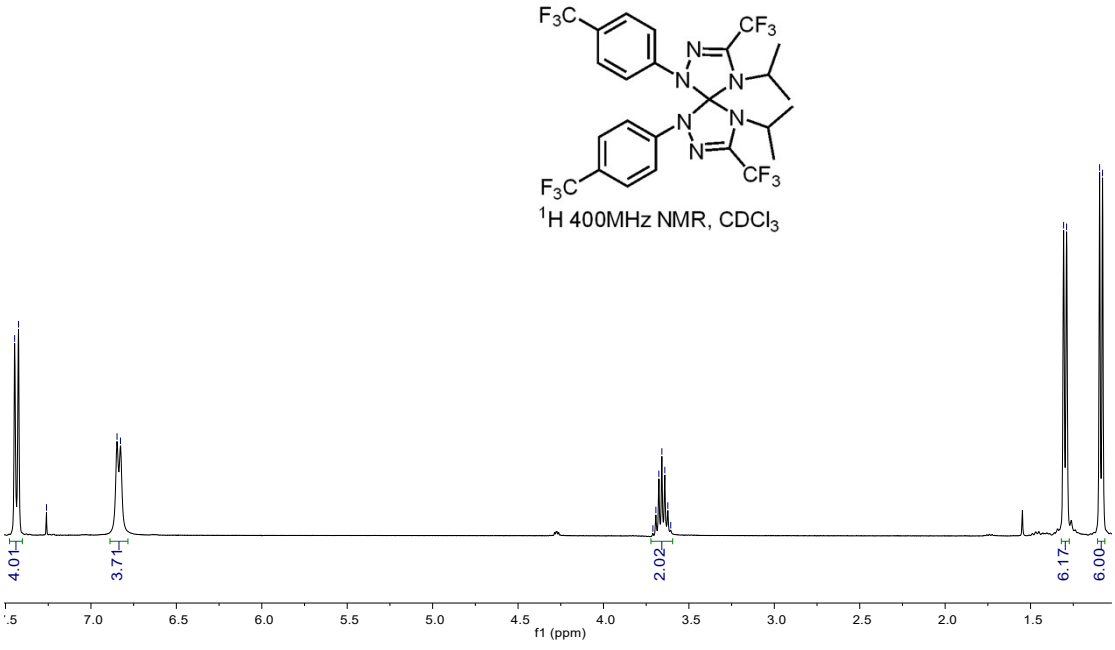
ZHOUYUXIU-15#49-107 RT: 0.22-0.48 AV: 59
T: FTMS + p ESI Full lock ms [50.0000-750.0000]
m/z= 506.0589-653.2508

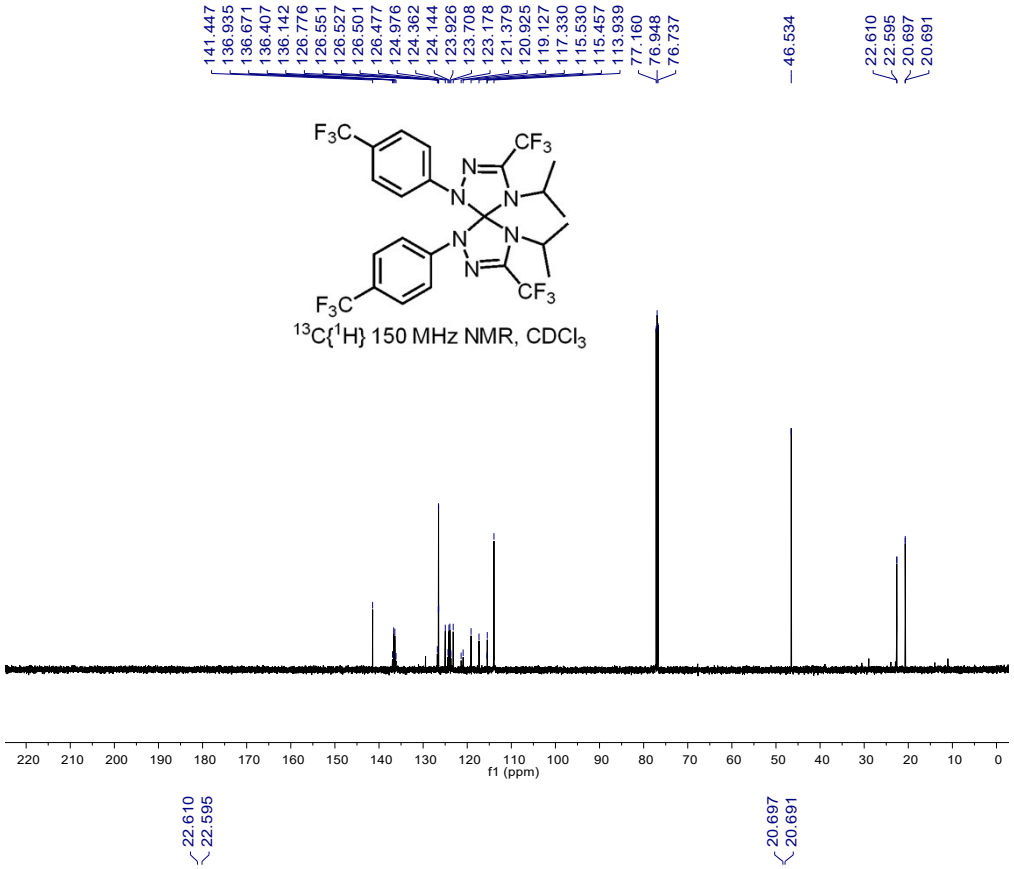
m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
535.1854	28006438.0	20.18	535.1851	0.34	C 23 H 23 N 6 F 8
559.2253	138809392.0	100.00			
560.2285	38714608.0	27.89			
589.2360	14659855.0	10.56			

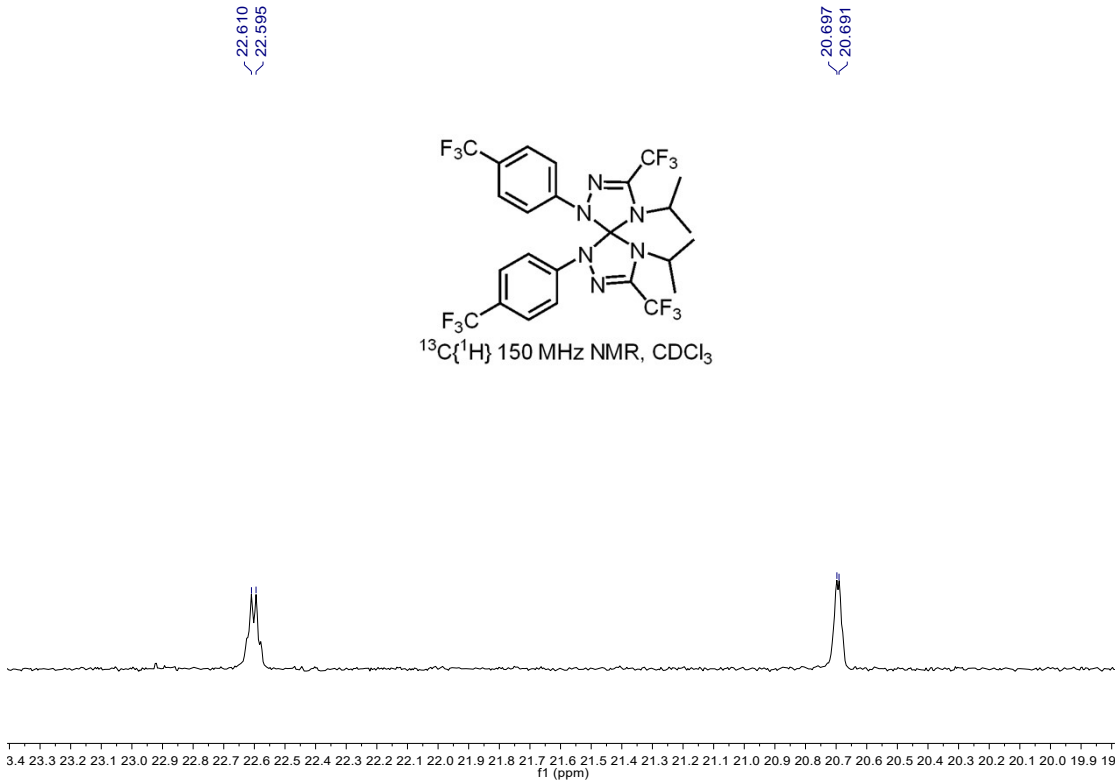


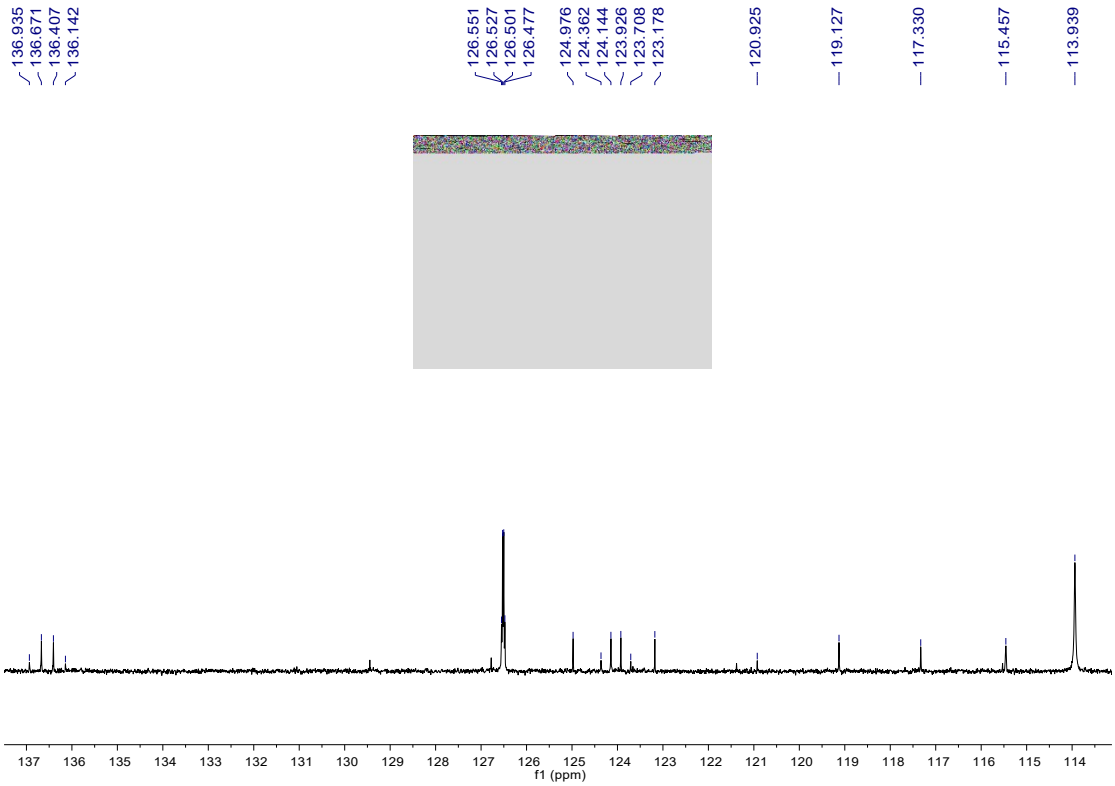
NMR copies of compound **3′h**:

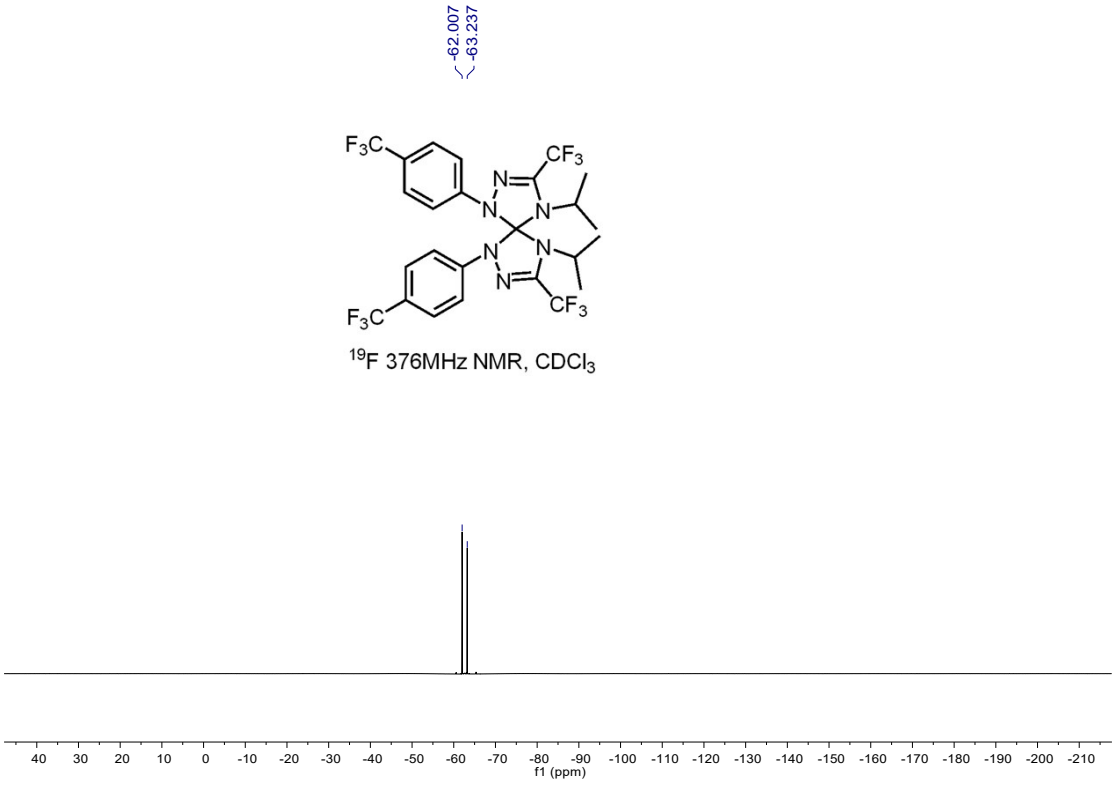





141.447
136.935
136.671
136.407
136.142
126.776
126.551
126.527
126.501
126.477
124.976
124.362
124.144
123.926
123.708
123.178
121.379
120.925
119.127
117.330
115.530
115.457
113.939
77.160
76.948
76.737
46.534
22.610
22.595
20.697
20.691
F3C
CF3
N
N
N
N
N
F3C
CF3
13C{1H} 150 MHz NMR, CDCl3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

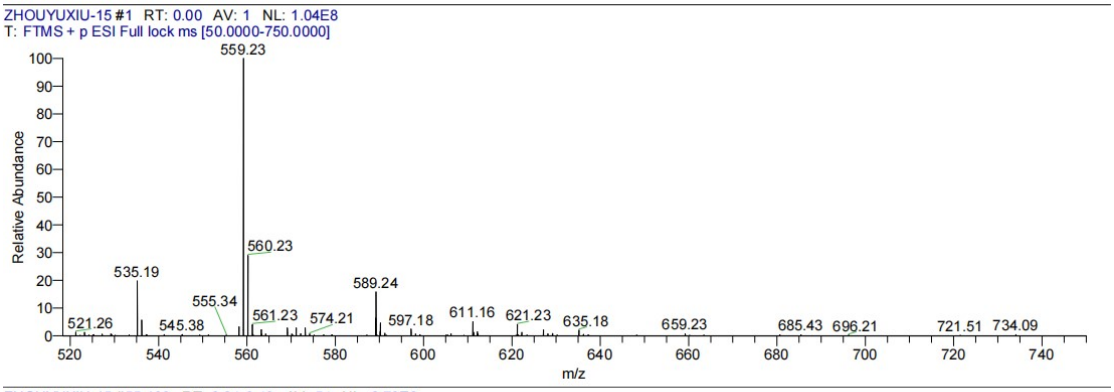

22.610
22.595
20.697
20.691
F3C
CF3
N
N
N
N
N
F3C
CF3
13C{1H} 150 MHz NMR, CDCl3
3.4 23.3 23.2 23.1 23.0 22.9 22.8 22.7 22.6 22.5 22.4 22.3 22.2 22.1 22.0 21.9 21.8 21.7 21.6 21.5 21.4 21.3 21.2 21.1 21.0 20.9 20.8 20.7 20.6 20.5 20.4 20.3 20.2 20.1 20.0 19.9 19
f1 (ppm)

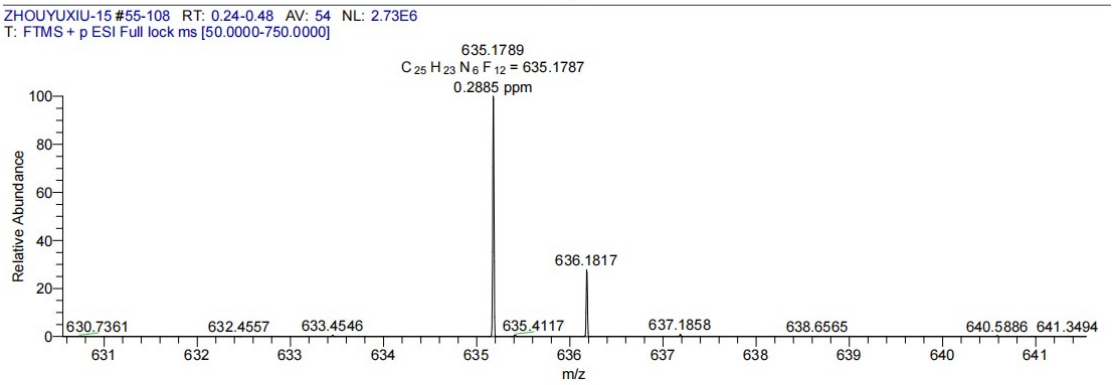




^{19}F 376MHz NMR, $CDCl_3$

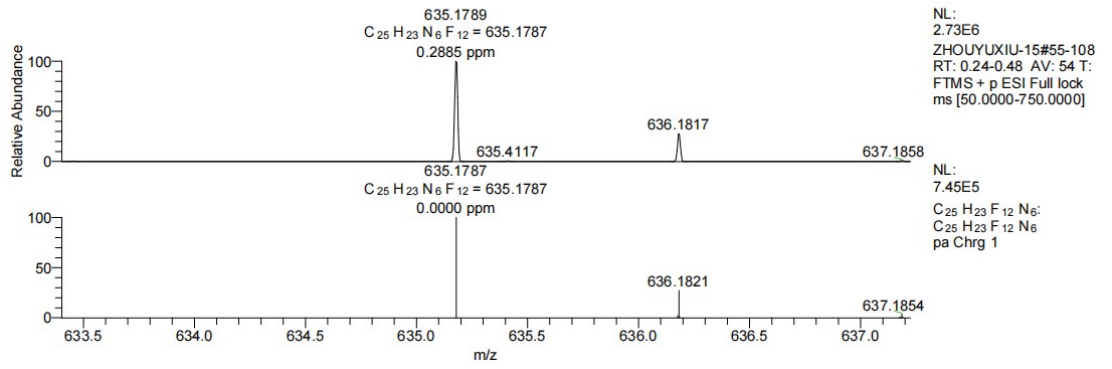
HRMS (ESI) copy of compound **3′h**:



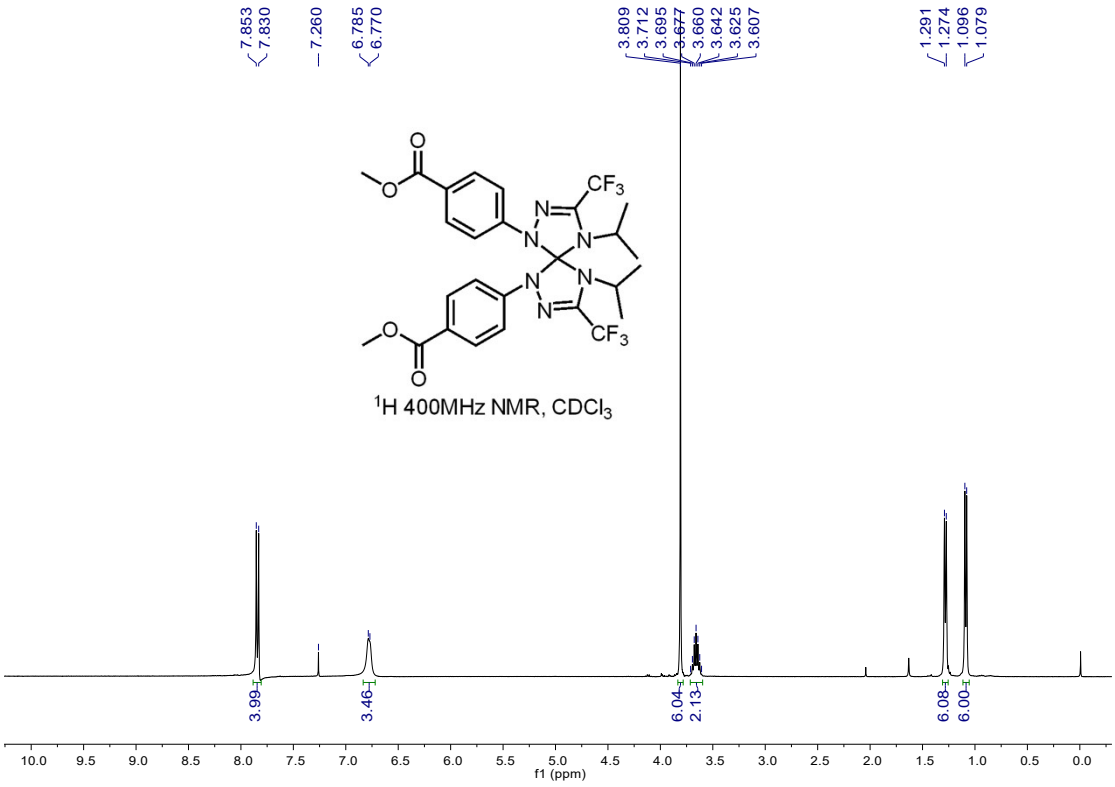


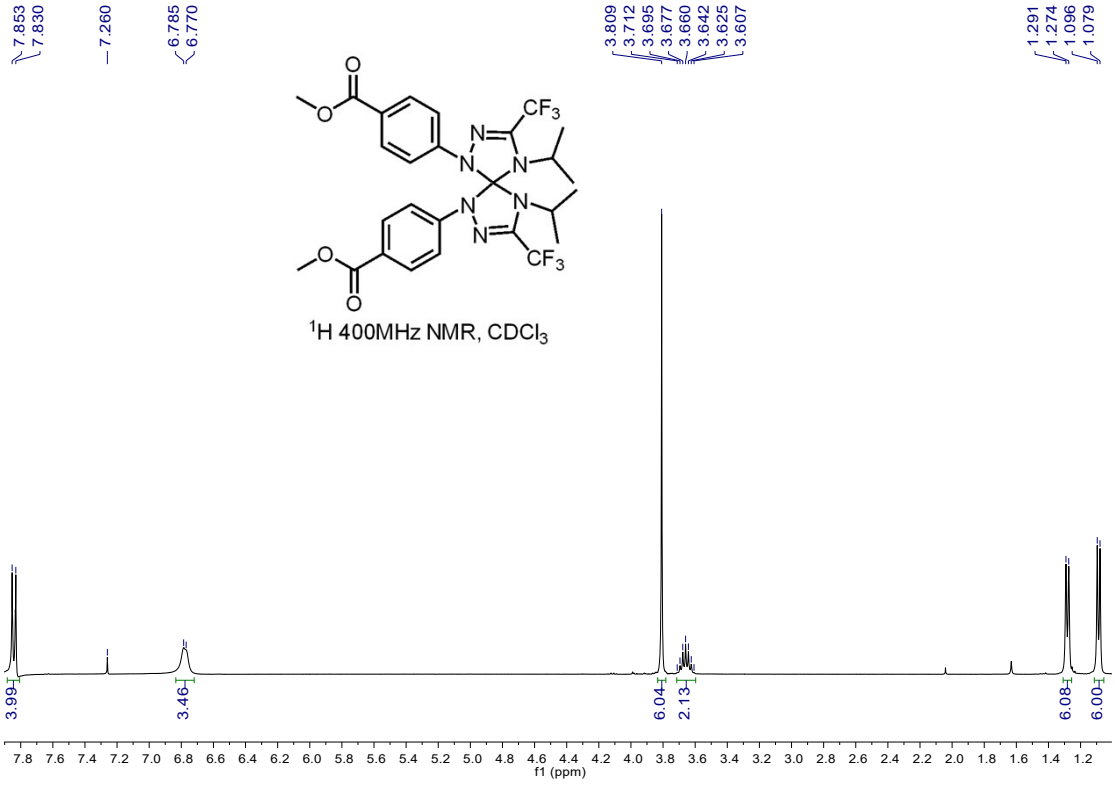
ZHOUYUXIU-15#55-108 RT: 0.24-0.48 AV: 54
T: FTMS + p ESI Full lock ms [50.0000-750.0000]
m/z= 630.5565-641.5412

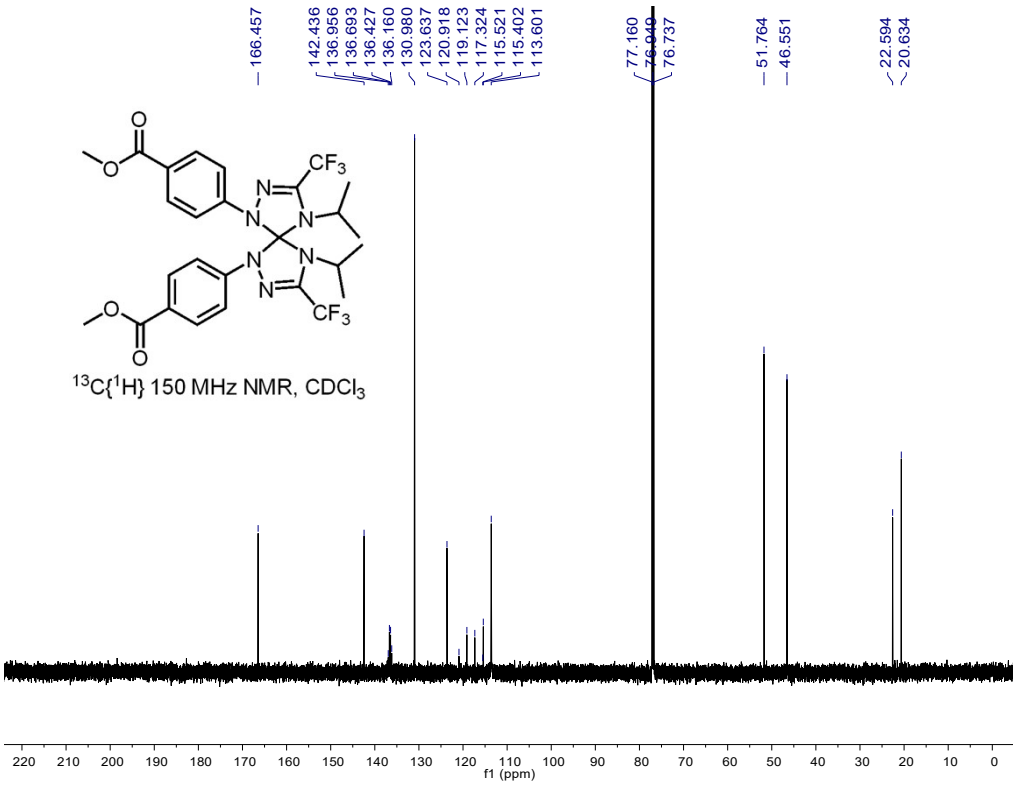
m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
635.1789	2815636.5	100.00	635.1787	0.18	$C_{25}H_{23}N_6F_{12}$
635.4117	16948.7	0.60			
636.1817	772847.8	27.45			
637.1858	23563.2	0.84			

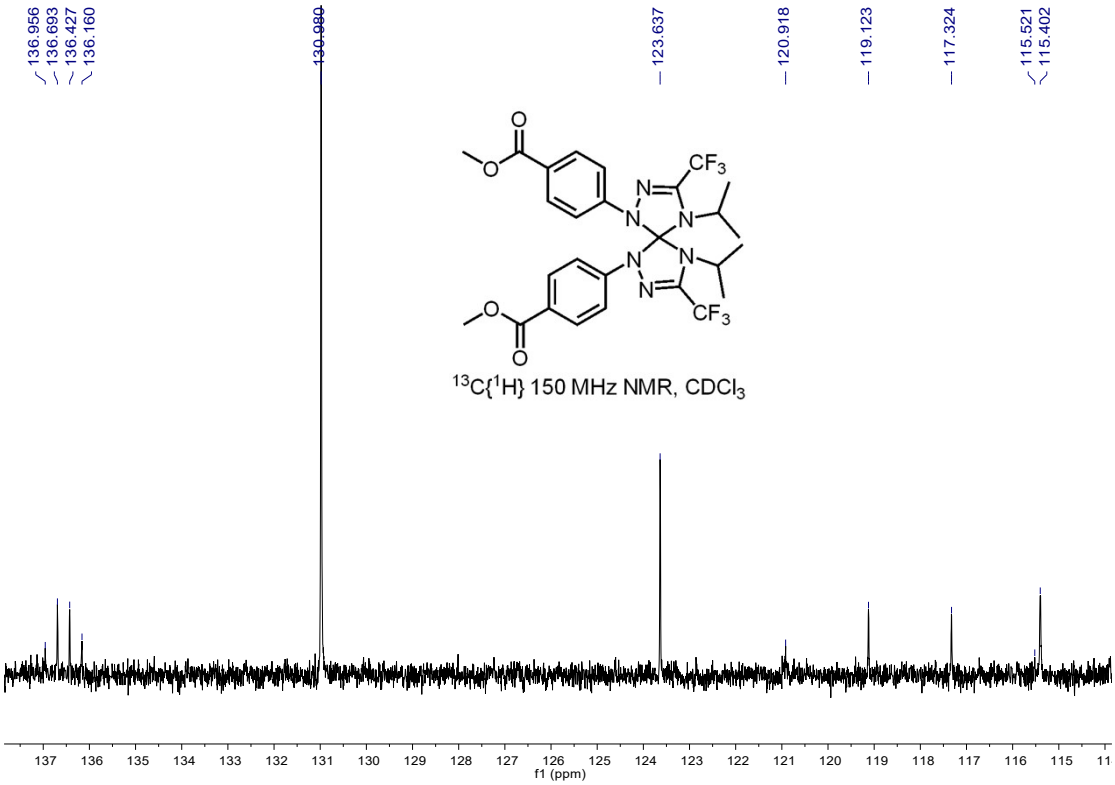


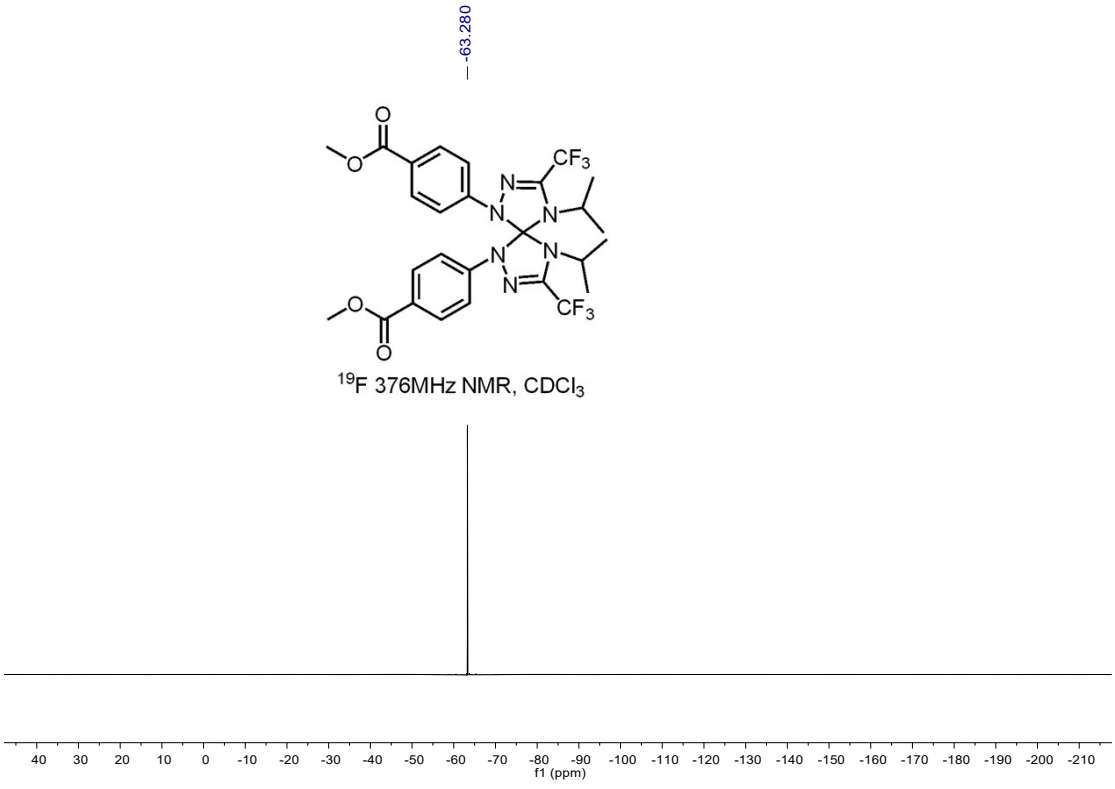
NMR copies of compound **3′i**:



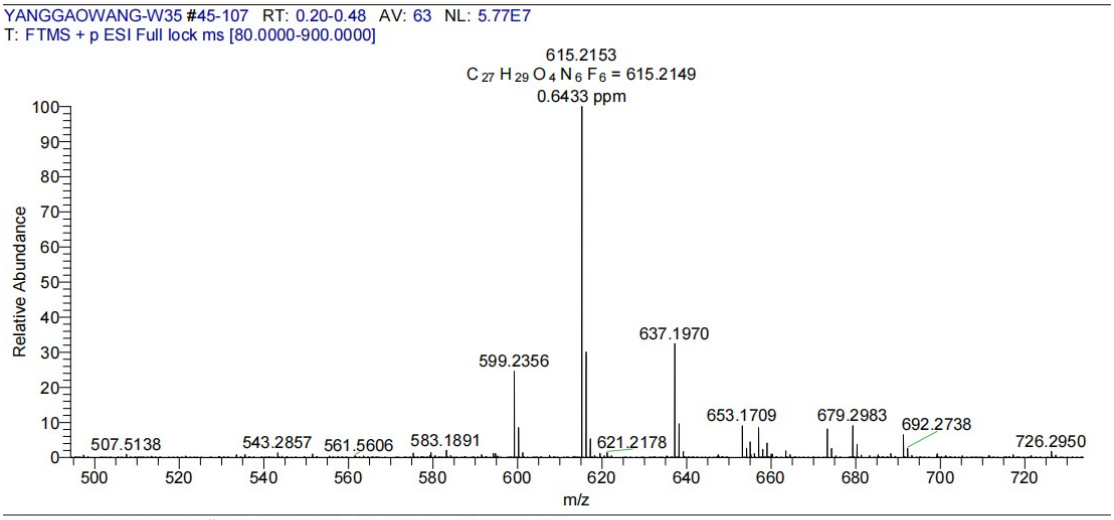



166.457
142.436
136.956
136.693
136.427
136.160
130.980
123.637
120.918
119.123
117.324
115.521
115.402
113.601
77.160
76.949
76.737
51.764
46.551
22.594
20.634
CF3
CF3
13C{1H} 150 MHz NMR, CDCl3
f1 (ppm)


136.956
136.693
136.427
136.160
130.980
123.637
120.918
119.123
117.324
115.521
115.402
CF3
CF3
13C{1H} 150 MHz NMR, CDCl3
f1 (ppm)

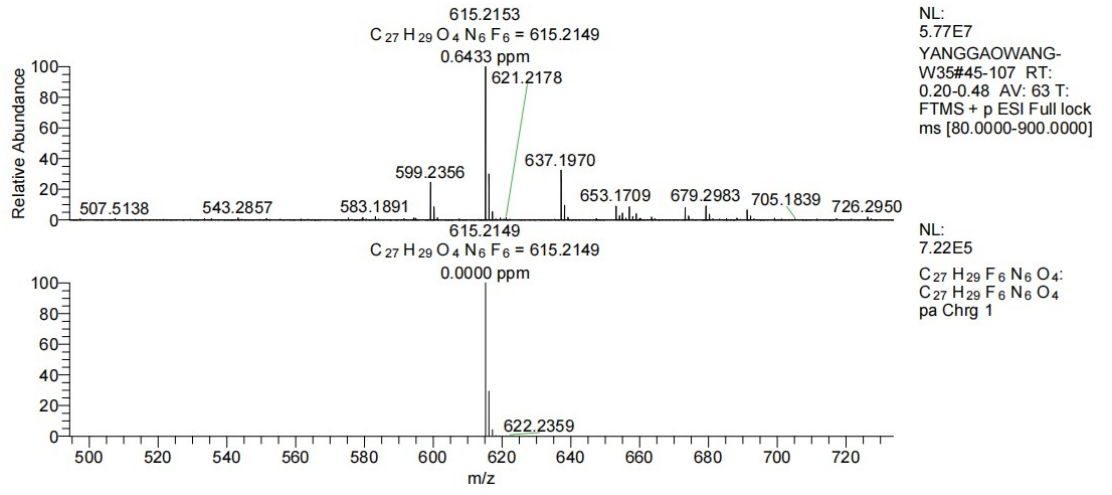

-63.280
CF3
CF3
19F 376MHz NMR, CDCl3
40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

HRMS (ESI) copy of compound **3′i**:

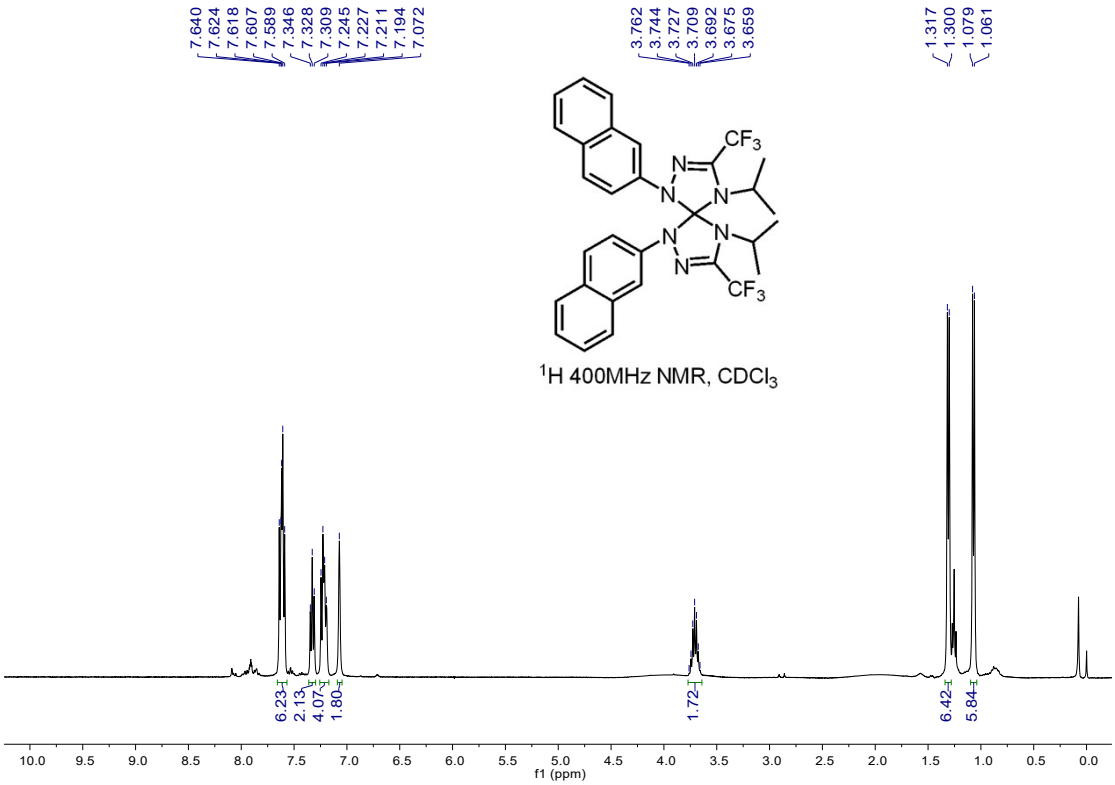


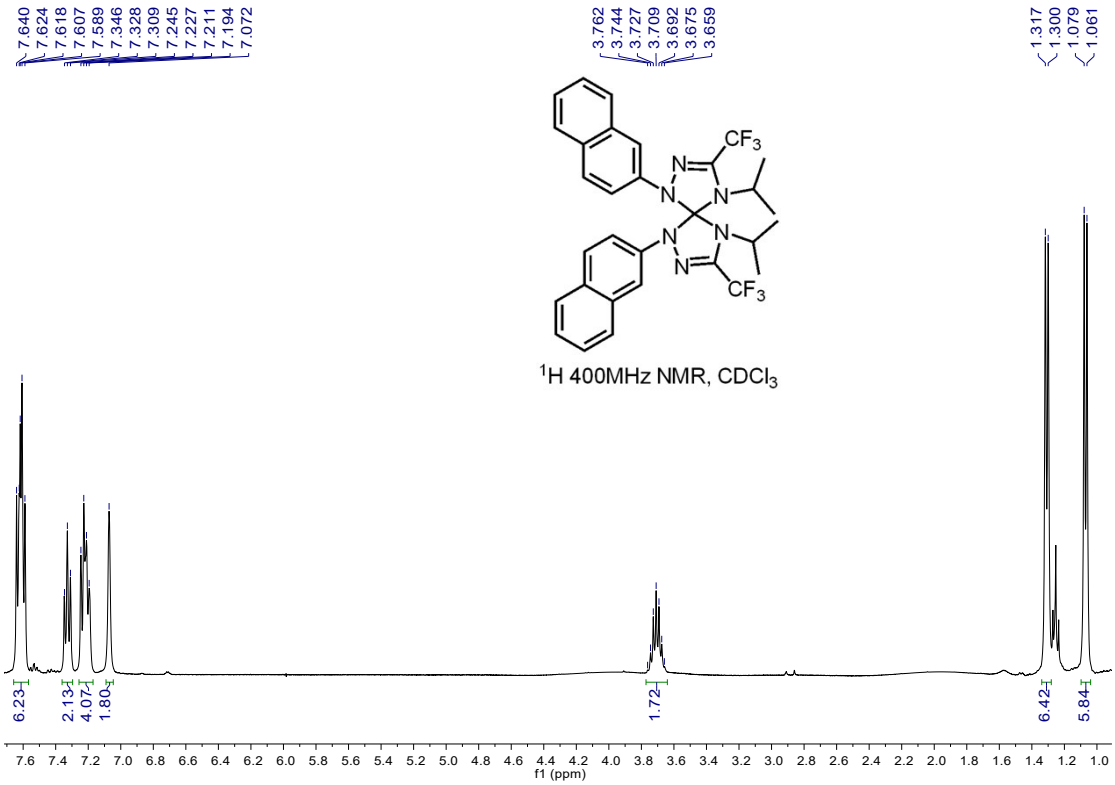
YANGGAOWANG-W35#45-107 RT: 0.20-0.48 AV: 63
T: FTMS + p ESI Full lock ms [80.0000-900.0000]
m/z= 494.2764-733.7549

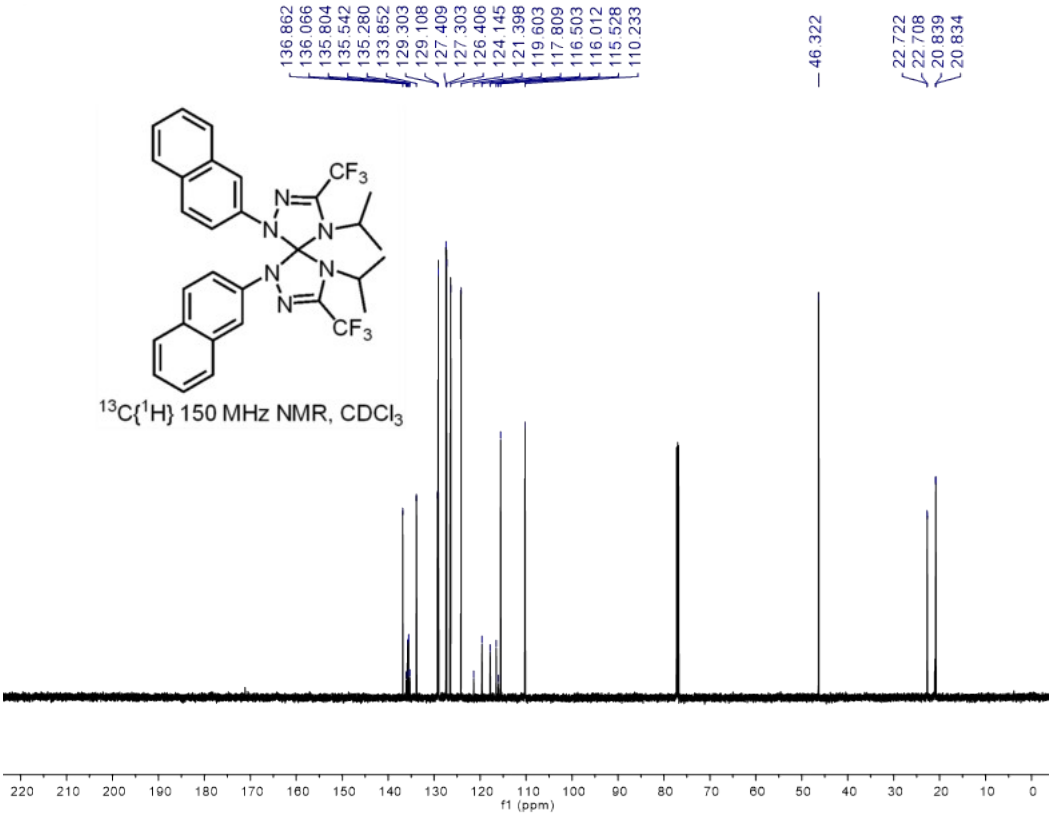
m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
599.2356	14215544.0	24.08			
615.2153	59033916.0	100.00	615.2149	0.40	$C_{27}H_{29}O_4N_6F_6$
616.2185	17902728.0	30.33			
637.1970	18733928.0	31.73			

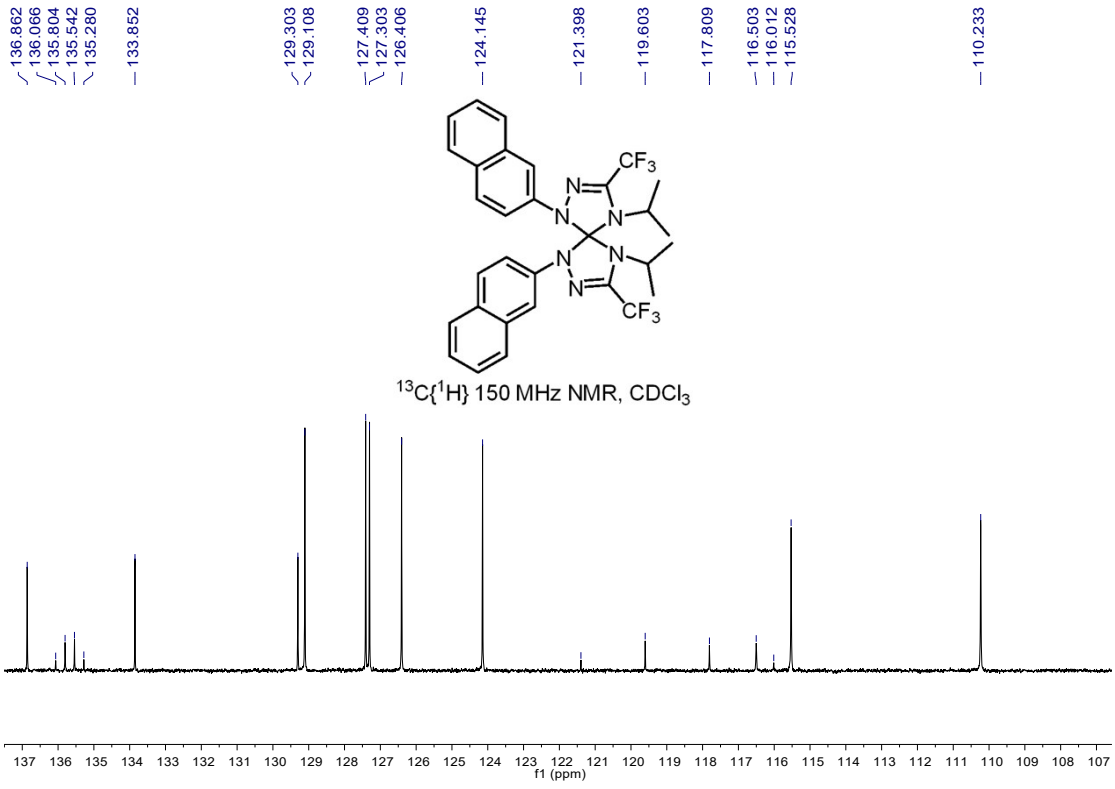


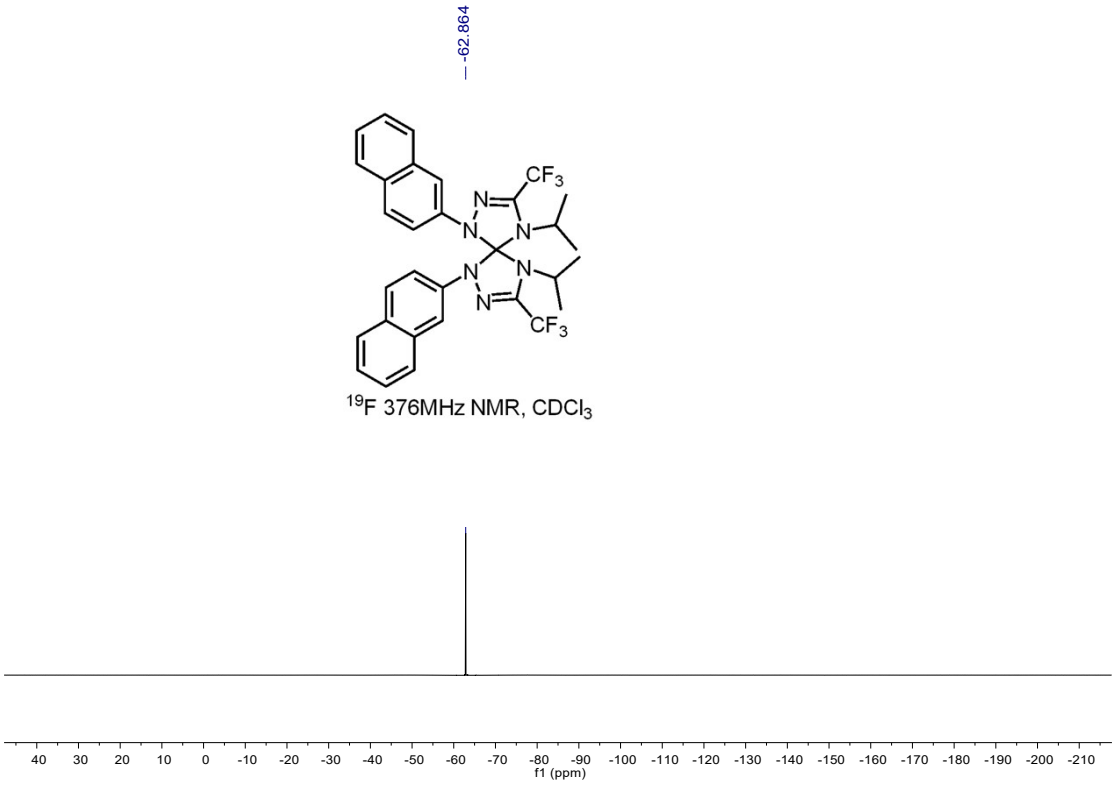
NMR copies of compound **3′j**:



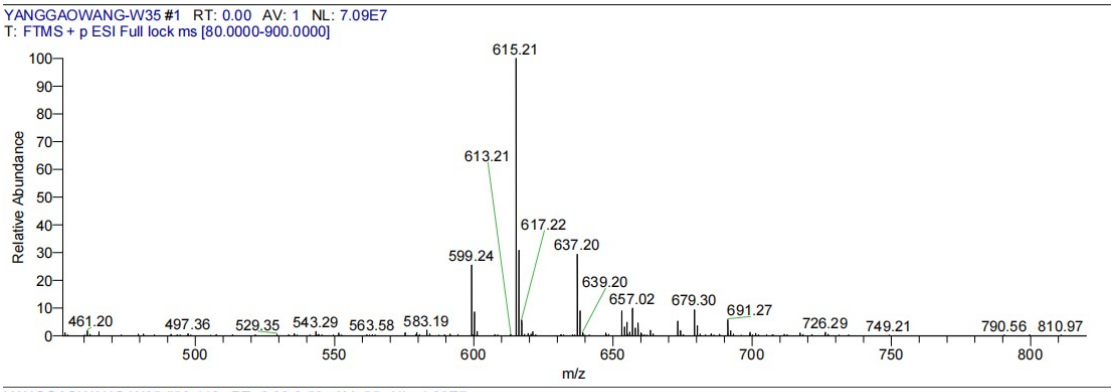


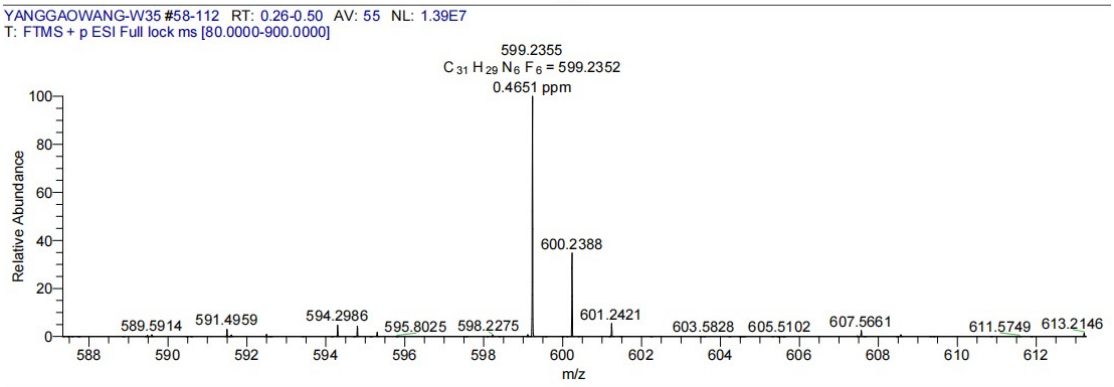

136.862
136.066
135.804
135.542
135.280
133.852
129.303
129.108
127.409
127.303
126.406
124.145
121.398
119.603
117.809
116.503
116.012
115.528
110.233
46.322
22.722
22.708
20.839
20.834
CF3
CF3
13C{1H} 150 MHz NMR, CDCl3
f1 (ppm)


136.862
136.066
135.804
135.542
135.280
133.852
129.303
129.108
127.409
127.303
126.406
124.145
121.398
119.603
117.809
116.503
116.012
115.528
110.233
CF3
CF3
13C{1H} 150 MHz NMR, CDCl3
f1 (ppm)


-62.864
CF3
N
N
N
N
N
CF3
19F 376MHz NMR, CDCl3
40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

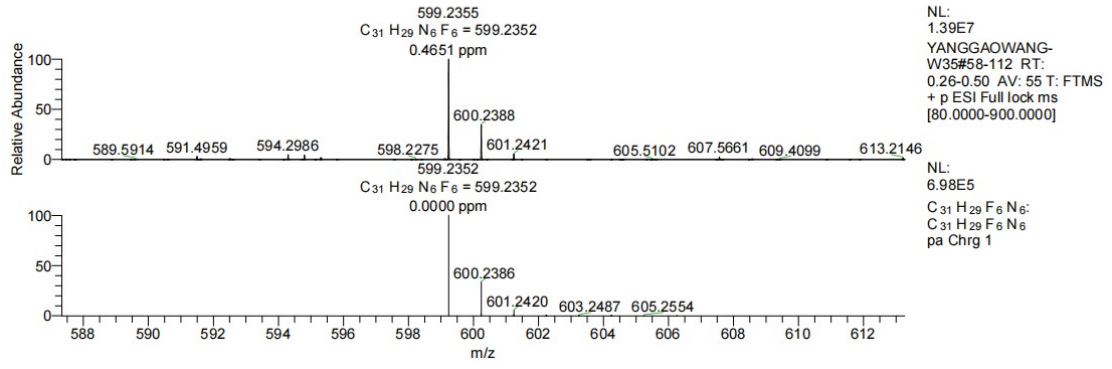
HRMS (ESI) copy of compound **3′j**:



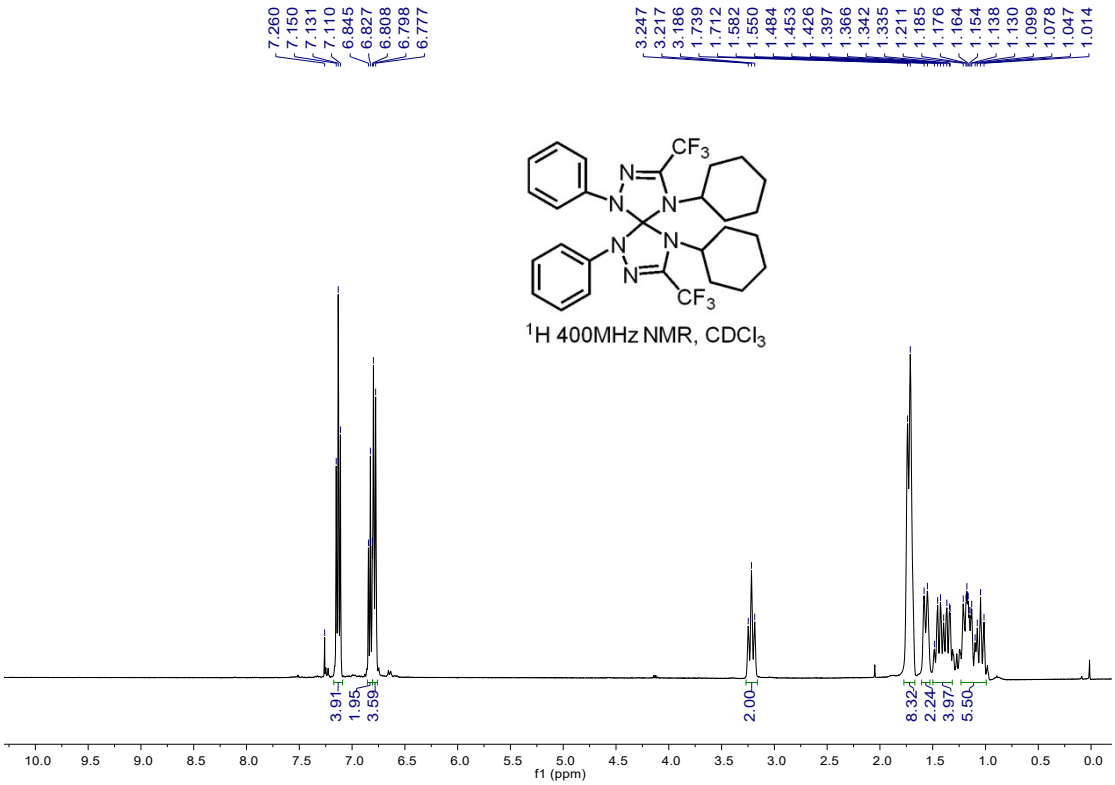


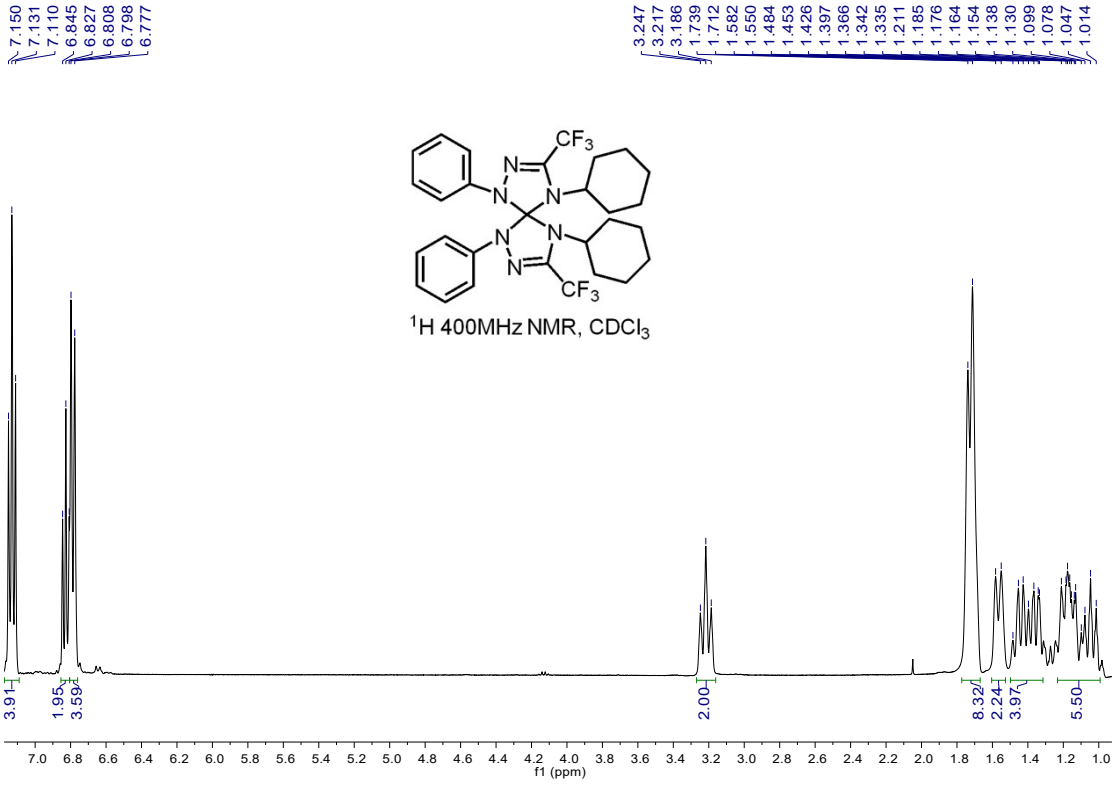
YANGGAOWANG-W35#58-112 RT: 0.26-0.50 AV: 55
T: FTMS + p ESI Full lock ms [80.0000-900.0000]
m/z= 587.3342-613.2647

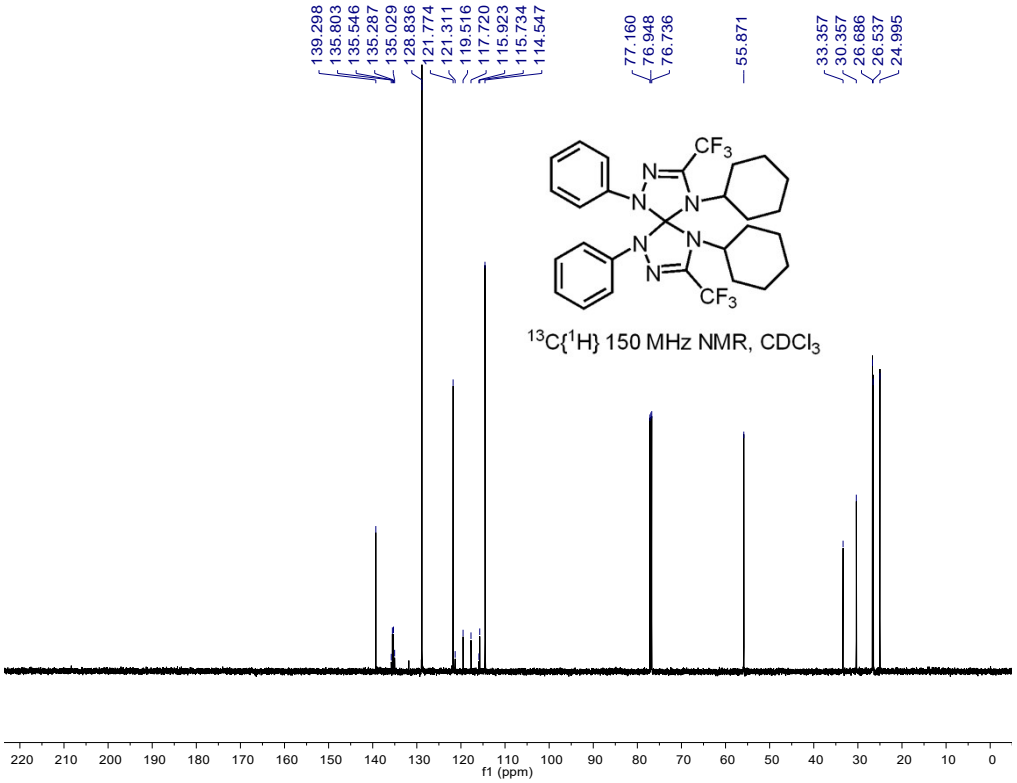
m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
594.2986	671100.4	4.83			
599.2355	13891422.0	100.00	599.2352	0.28	$C_{31}H_{29}N_6F_6$
600.2388	4825719.5	34.74			
601.2421	780103.4	5.62			

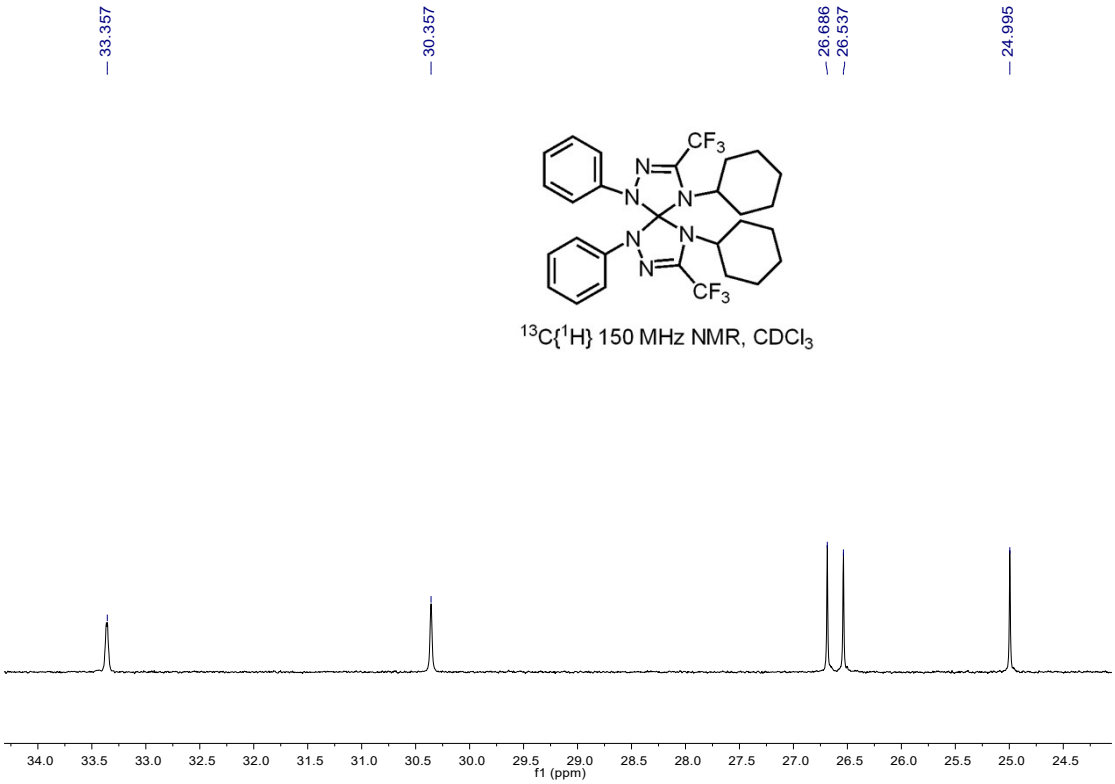


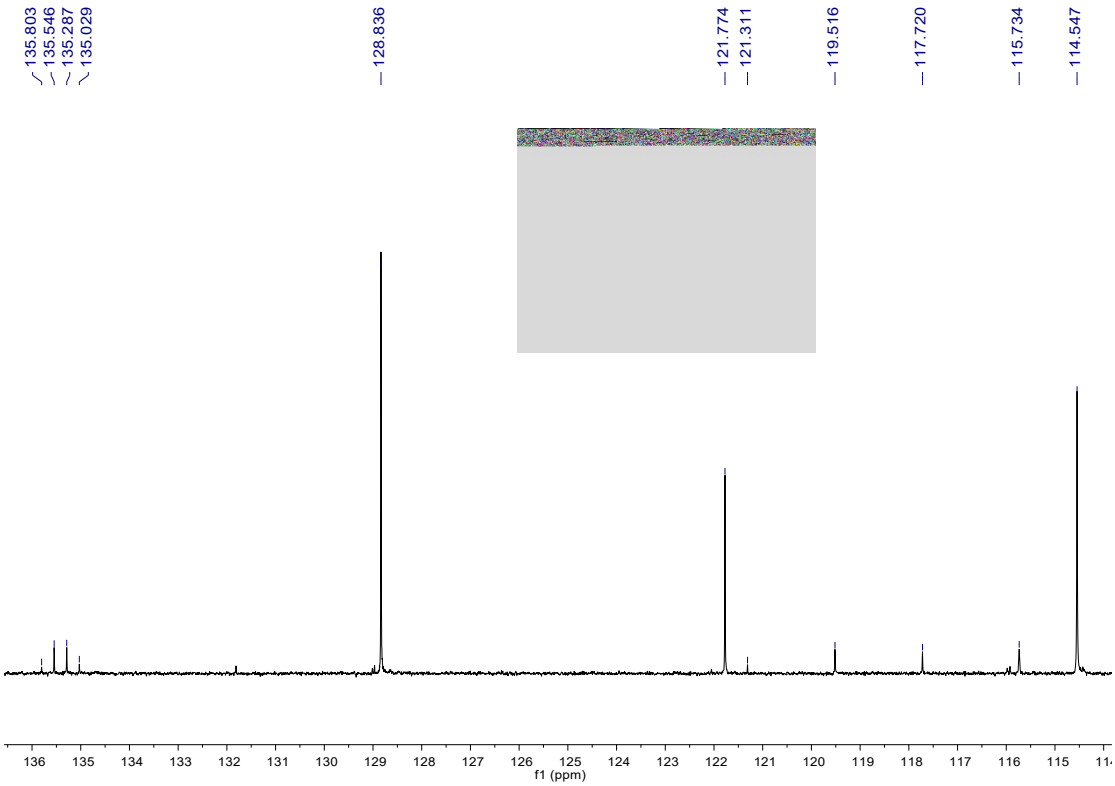
NMR copies of compound **3′k**:

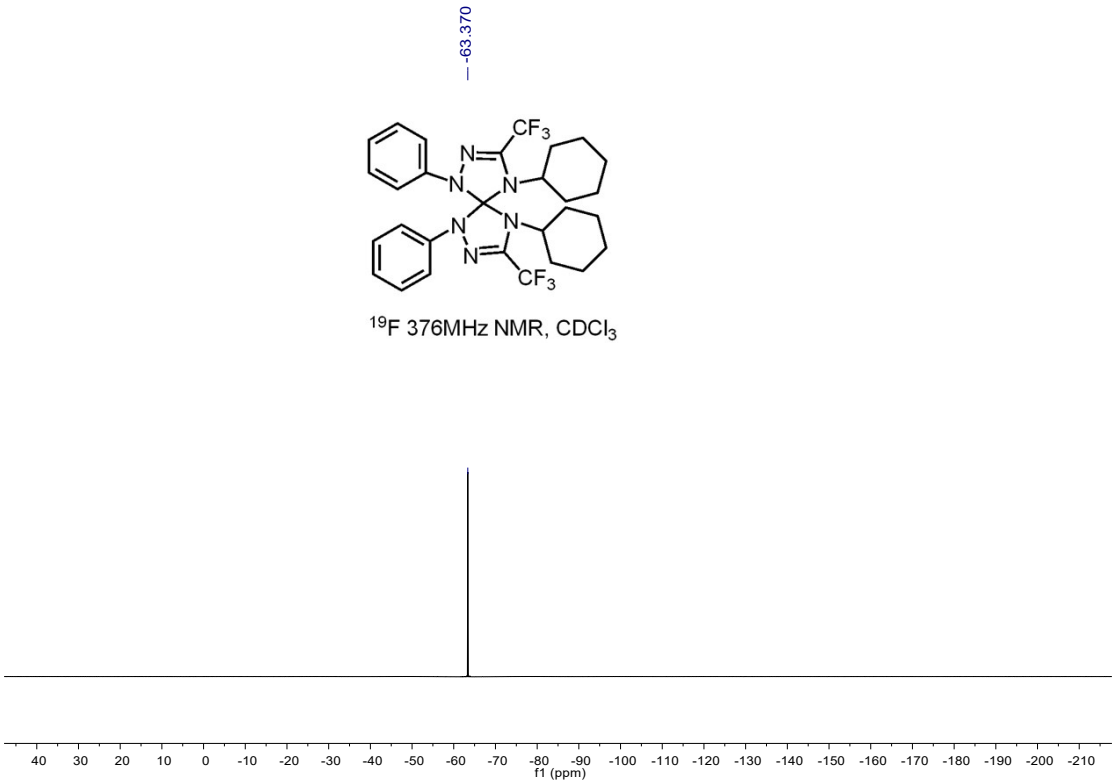





139.298
135.803
135.546
135.287
135.029
128.836
121.774
121.311
119.516
117.720
115.923
115.734
114.547
77.160
76.948
76.736
55.871
33.357
30.357
26.686
26.537
24.995
CF3
CF3
13C{1H} 150 MHz NMR, CDCl3
f1 (ppm)

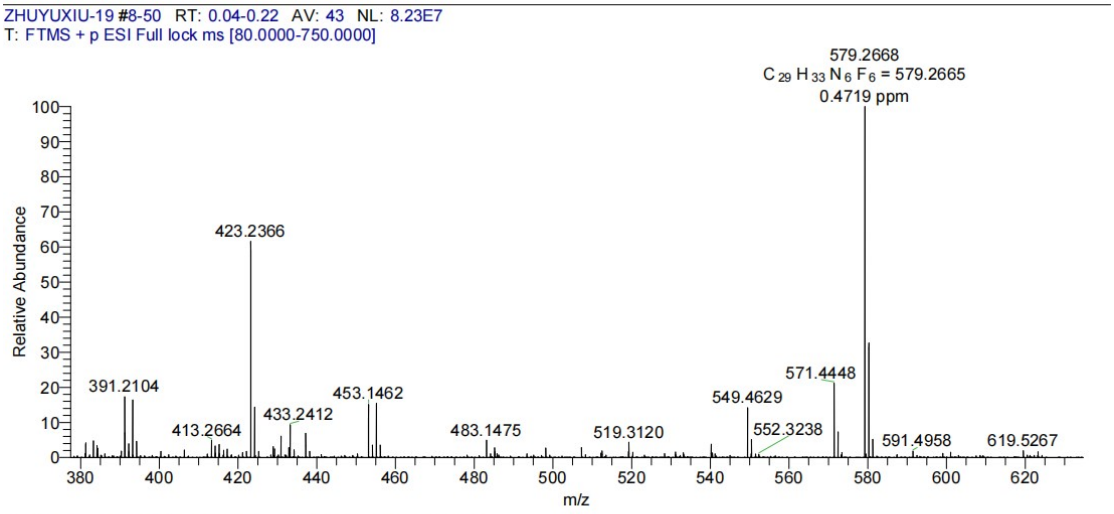

33.357
30.357
26.686
26.537
24.995
CF3
CF3
13C{1H} 150 MHz NMR, CDCl3
f1 (ppm)





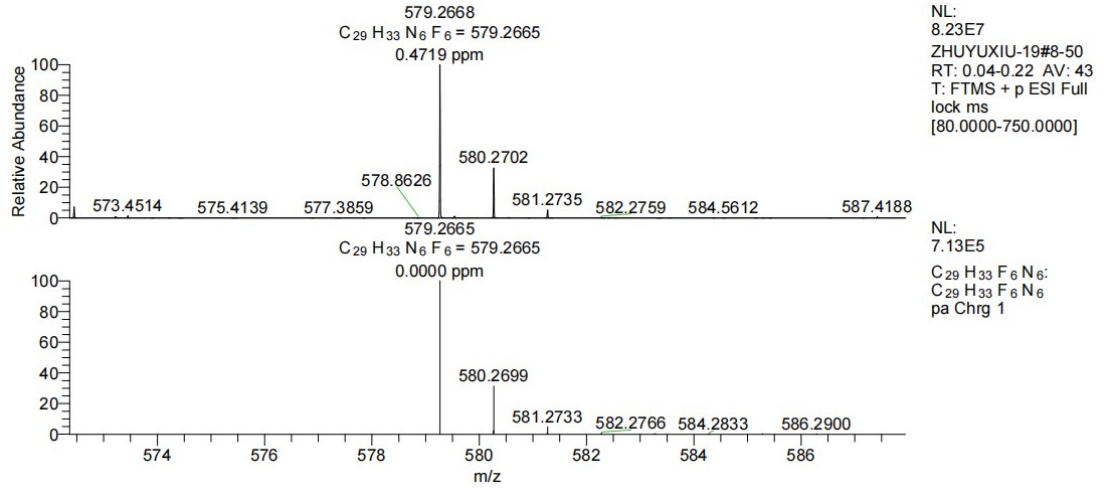
^{19}F 376MHz NMR, $CDCl_3$

HRMS (ESI) copy of compound **3′k**:

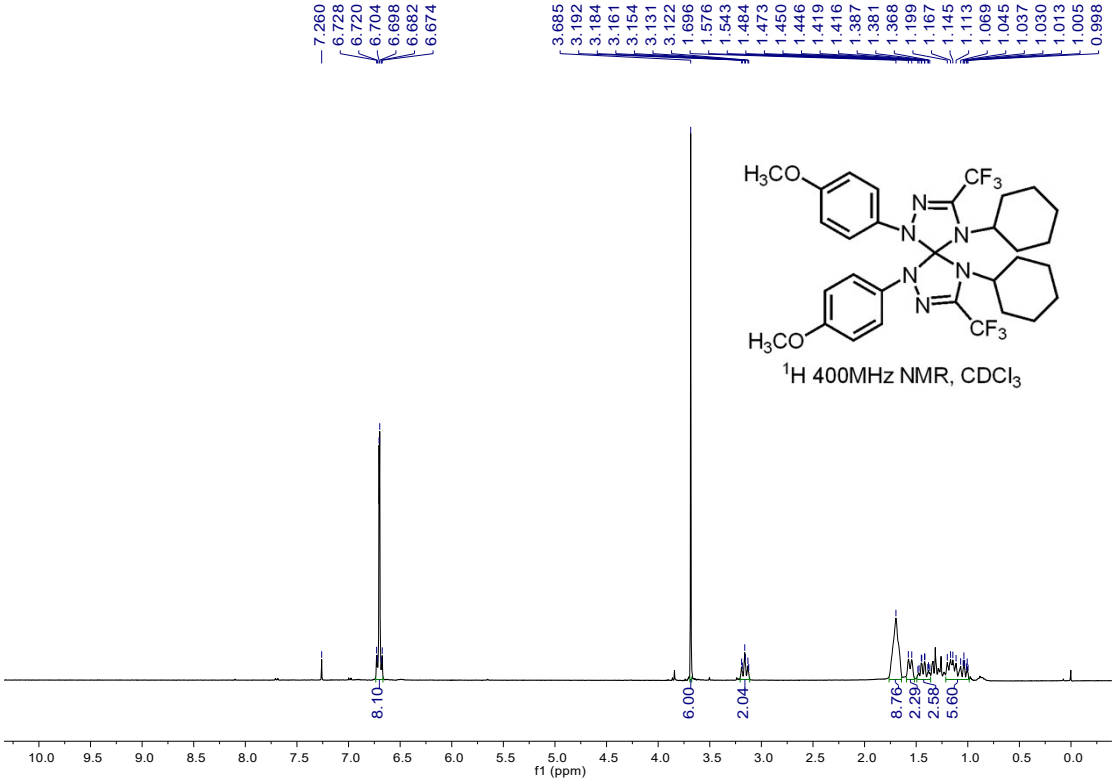


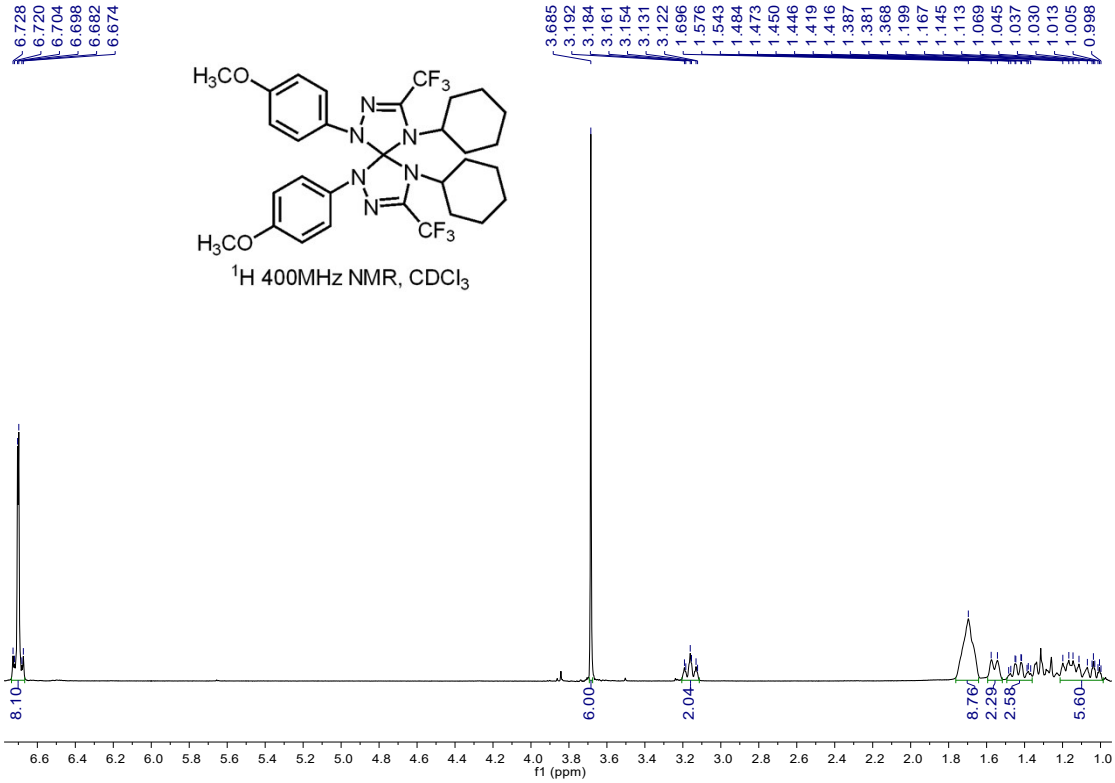
ZHUYUXIU-19#8-50 RT: 0.04-0.22 AV: 43
T: FTMS + p ESI Full lock ms [80.0000-750.0000]
m/z= 377.4381-634.6936

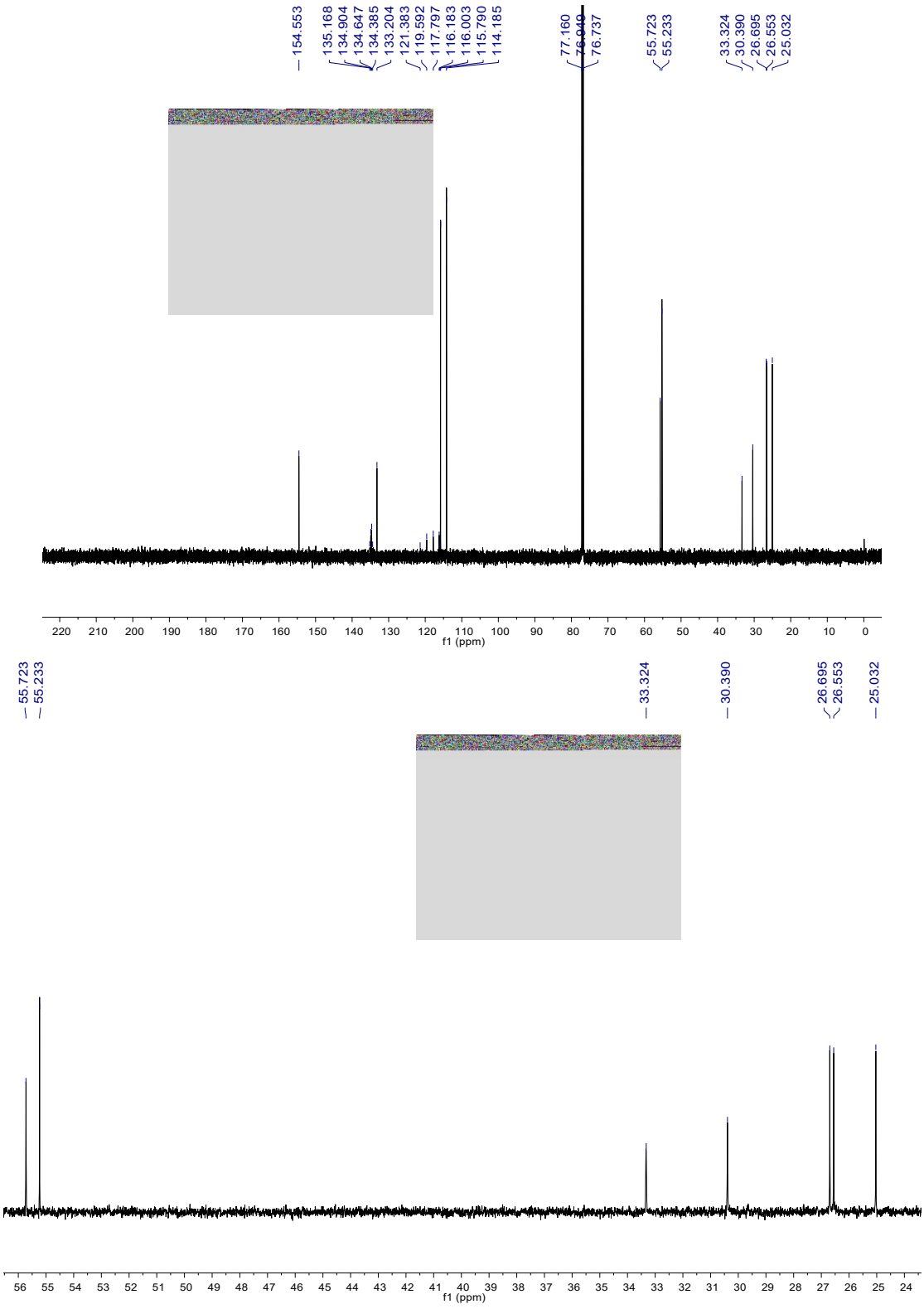
m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
423.2366	51725780.0	60.37			
571.4448	17449384.0	20.37			
579.2668	85677992.0	100.00	579.2665	0.27	C29 H33 N6 F6
580.2702	27402642.0	31.98			

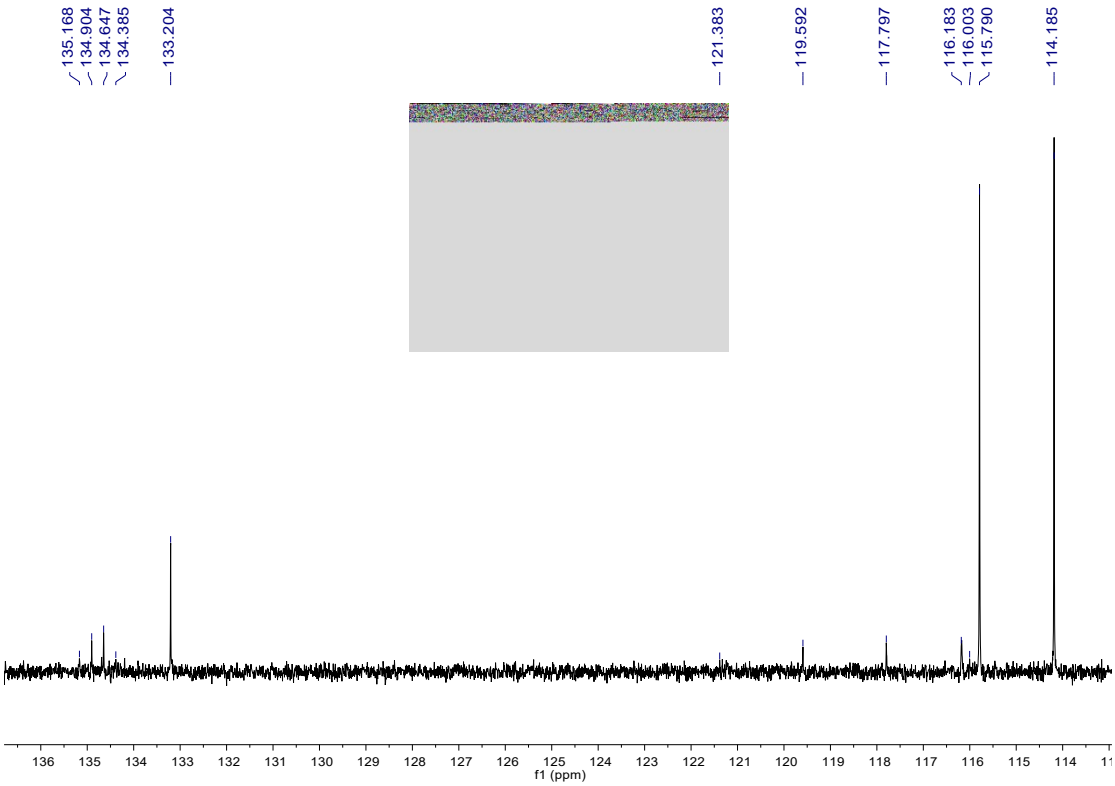


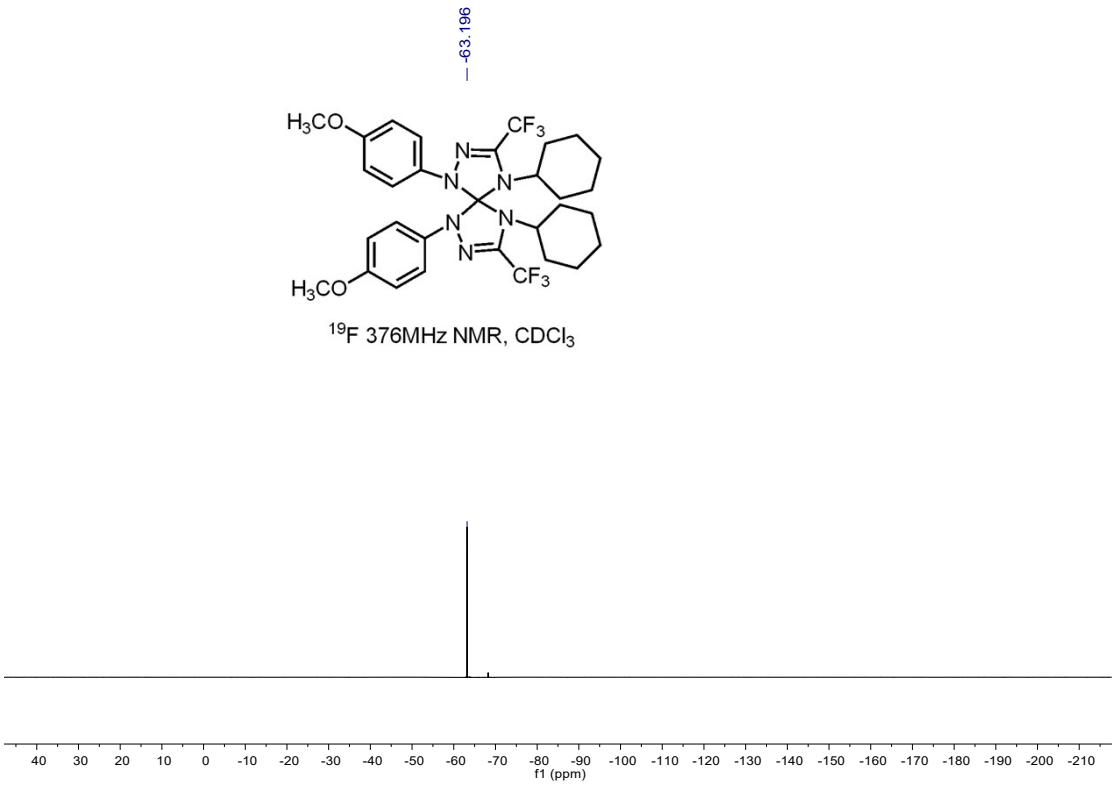
NMR copies of compound **3′l**:





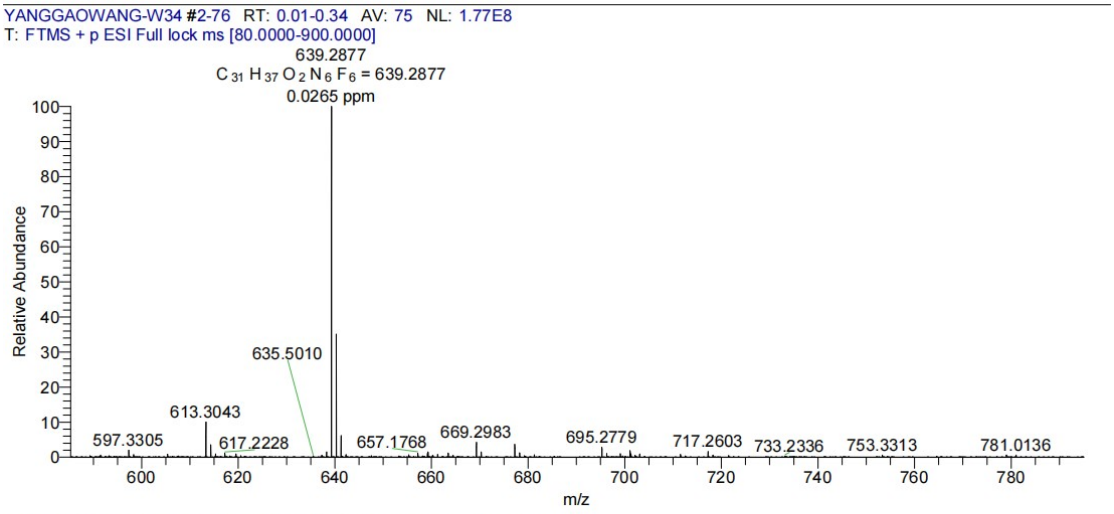

154.553
135.168
134.904
134.647
134.385
133.204
121.383
119.592
117.797
116.183
116.003
115.790
114.185
77.160
76.949
76.737
55.723
55.233
33.324
30.390
26.695
26.553
25.032
f1 (ppm)





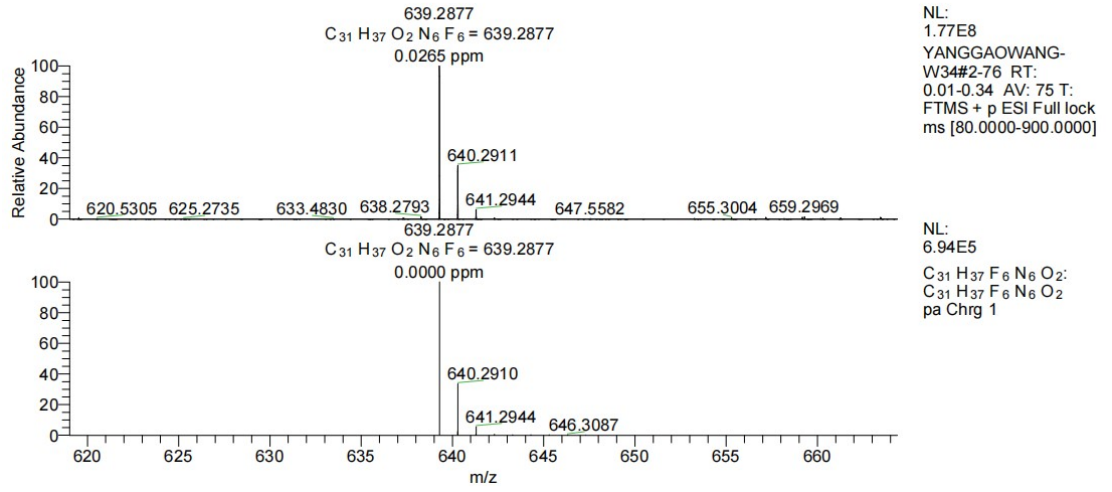
^{19}F 376MHz NMR, $CDCl_3$

HRMS (ESI) copy of compound **3′l**:

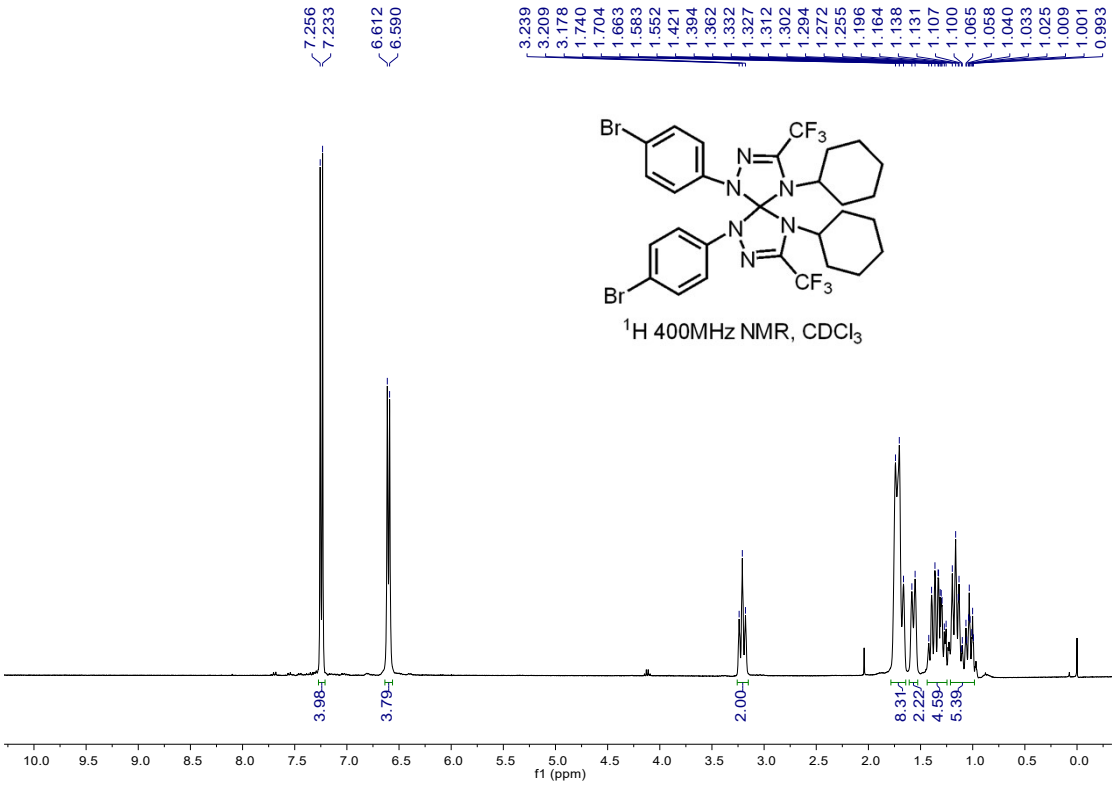


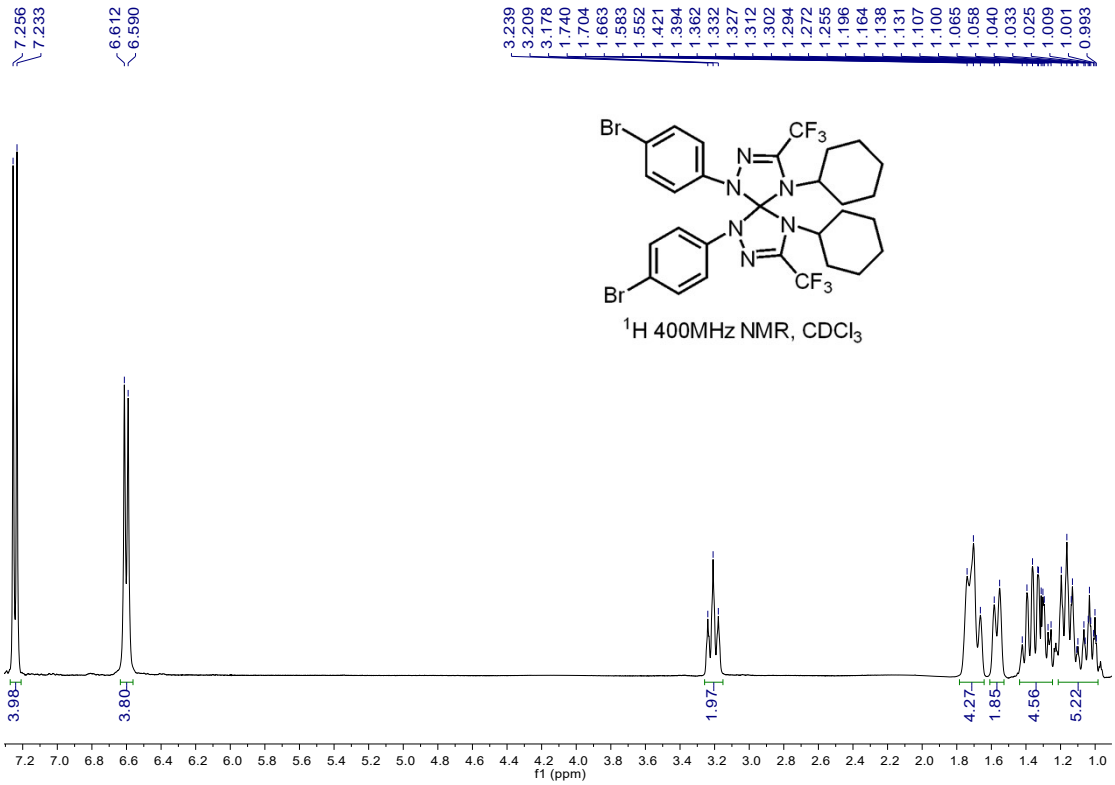
YANGGAOWANG-W34#2-76 RT: 0.01-0.34 AV: 75
T: FTMS + p ESI Full lock ms [80.0000-900.0000]
m/z= 585.2802-794.8773

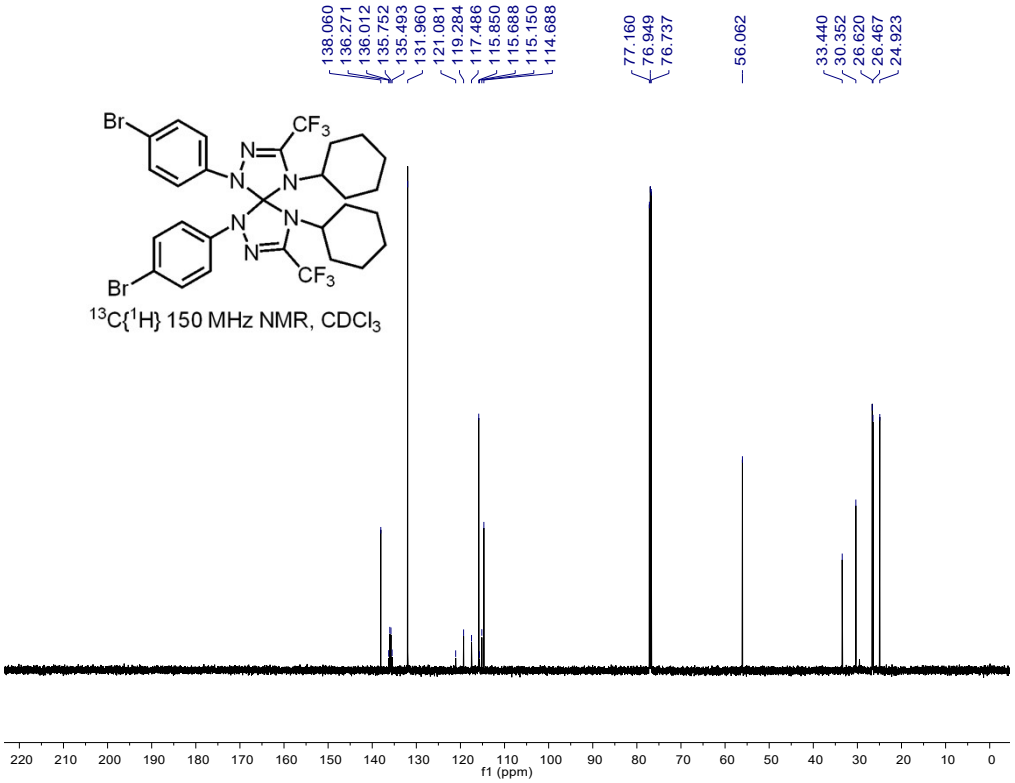
m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
613.3043	17953196.0	9.94			
639.2877	180591120.0	100.00	639.2877	0.02	$C_{31}H_{37}O_2N_6F_6$
640.2911	62633360.0	34.68			
641.2944	11060461.0	6.12			

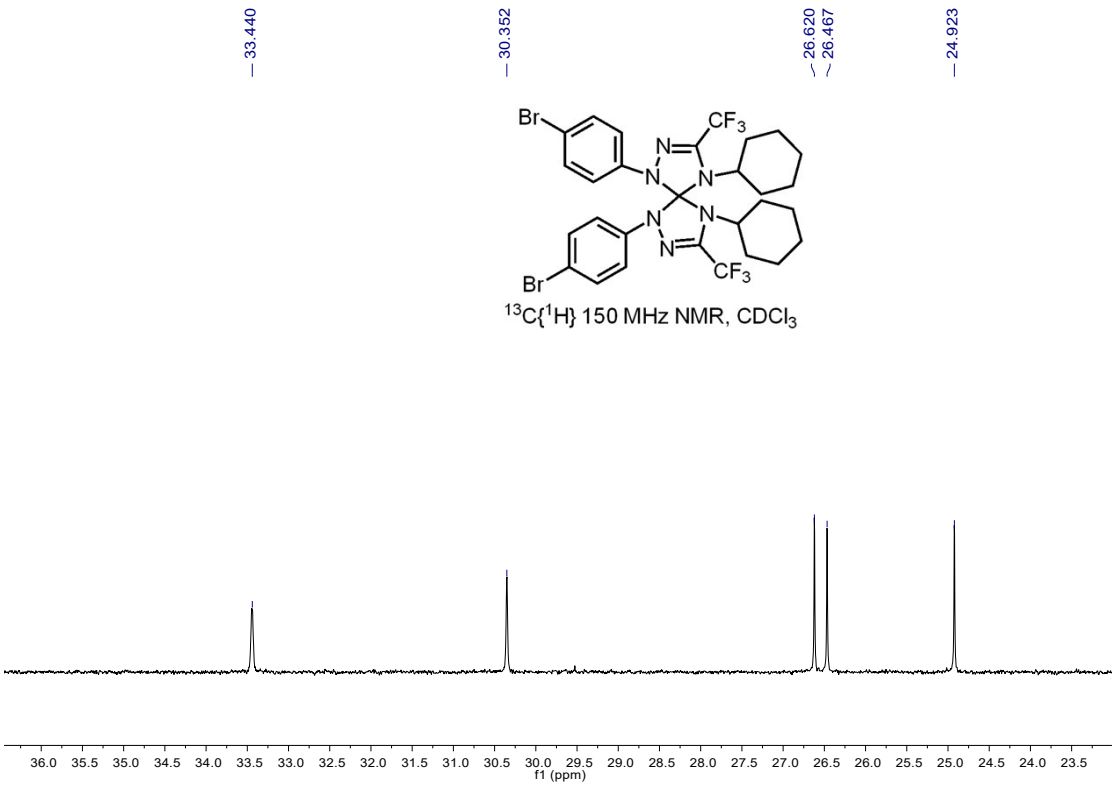


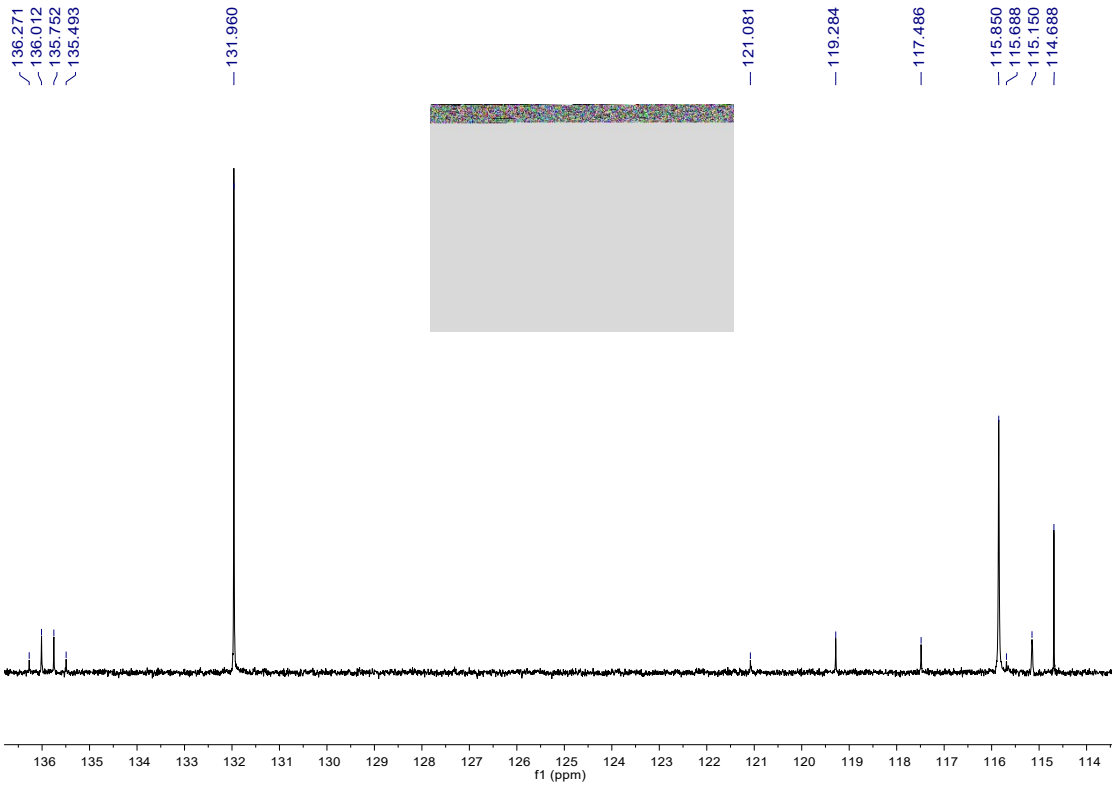
NMR copies of compound **3′m**:

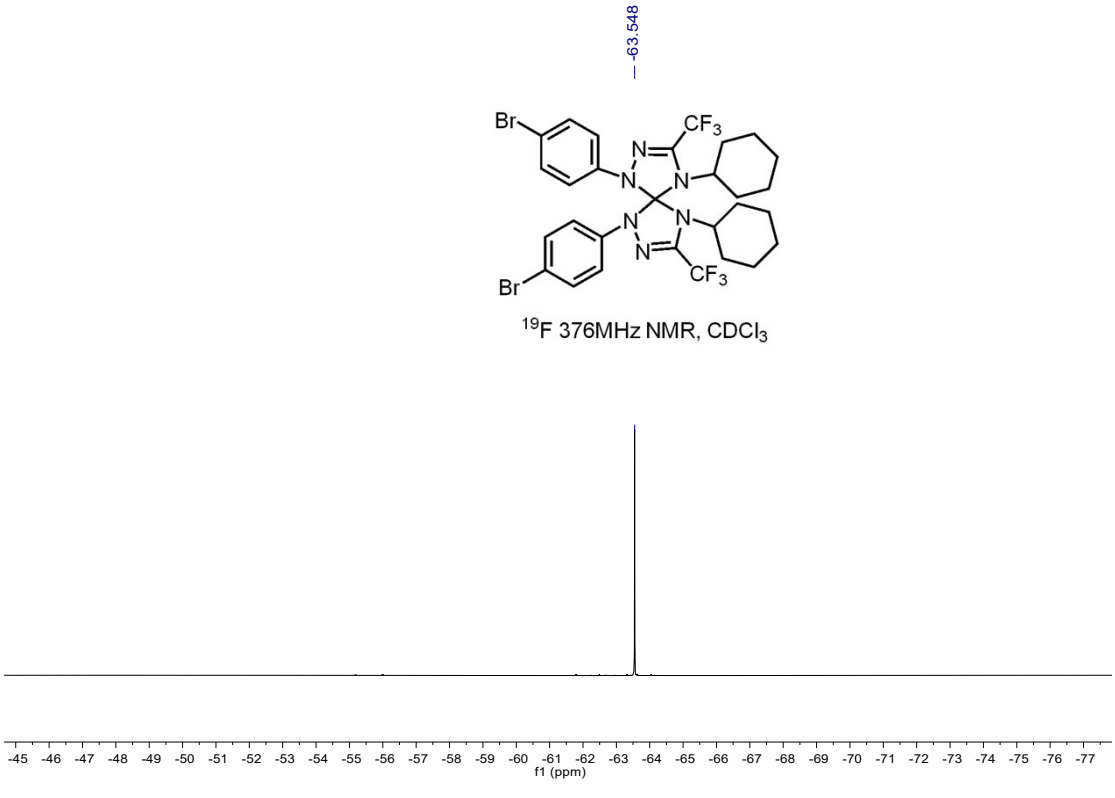





138.060
136.271
136.012
135.752
135.493
131.960
121.081
119.284
117.486
115.850
115.688
115.150
114.688
77.160
76.949
76.737
56.062
33.440
30.352
26.620
26.467
24.923
Br
CF3
N
Br
CF3
13C{1H} 150 MHz NMR, CDCl3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

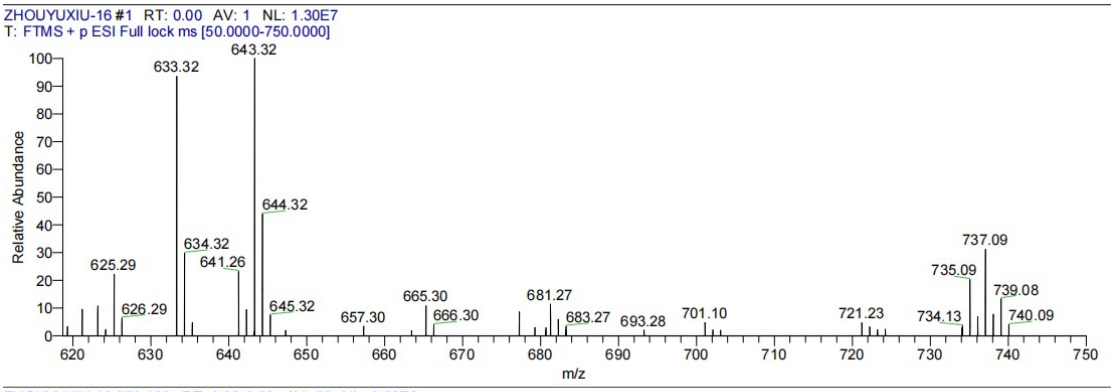

33.440
30.352
26.620
26.467
24.923
Br
CF3
N
Br
CF3
13C{1H} 150 MHz NMR, CDCl3
36.0 35.5 35.0 34.5 34.0 33.5 33.0 32.5 32.0 31.5 31.0 30.5 30.0 29.5 29.0 28.5 28.0 27.5 27.0 26.5 26.0 25.5 25.0 24.5 24.0 23.5
f1 (ppm)

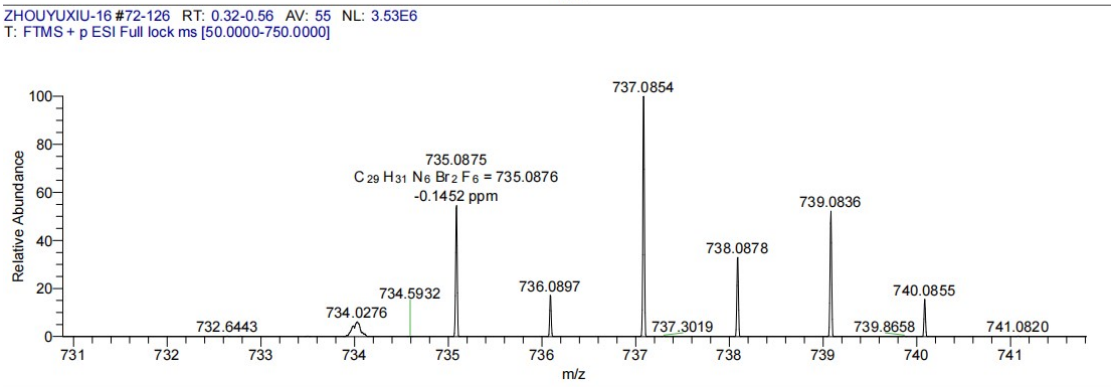




^{19}F 376MHz NMR, $CDCl_3$

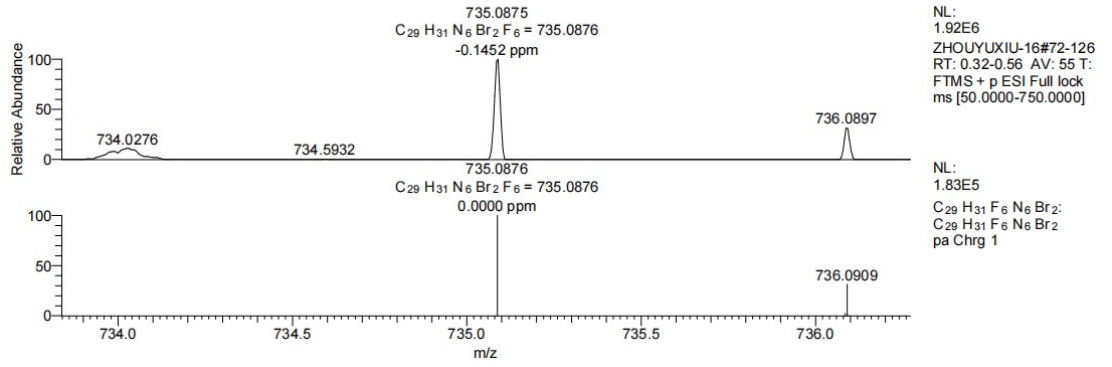
HRMS (ESI) copy of compound **3′m**:



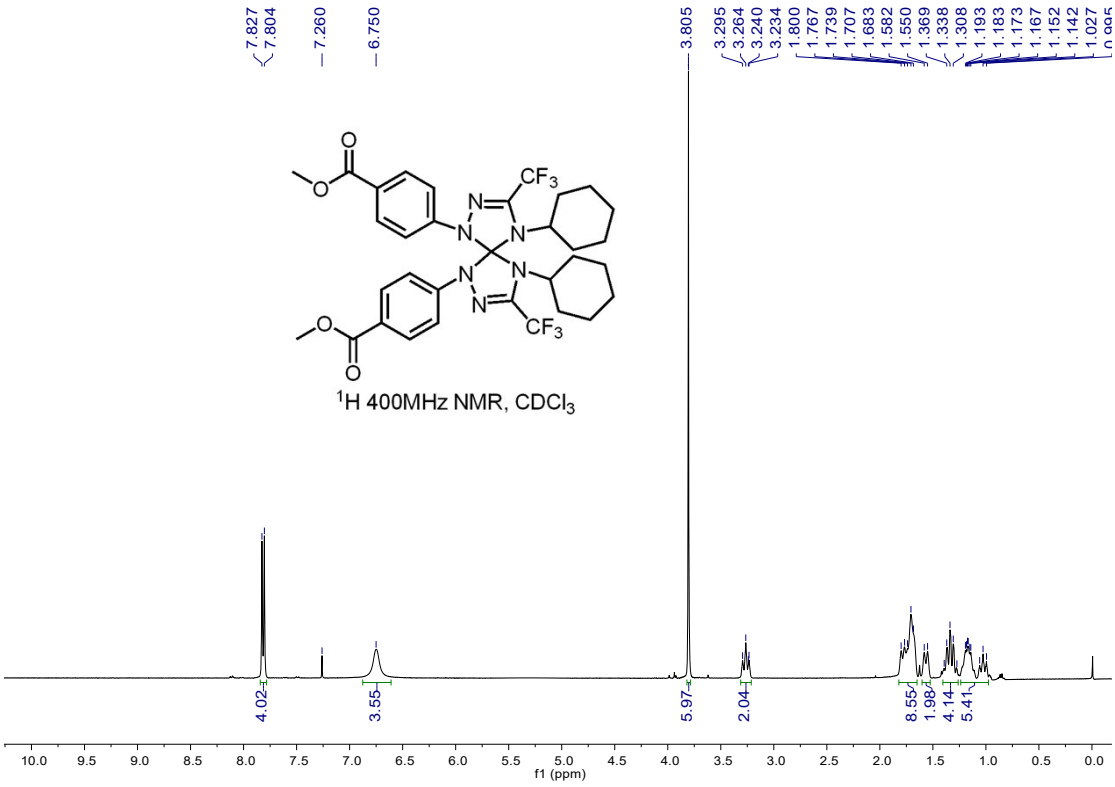


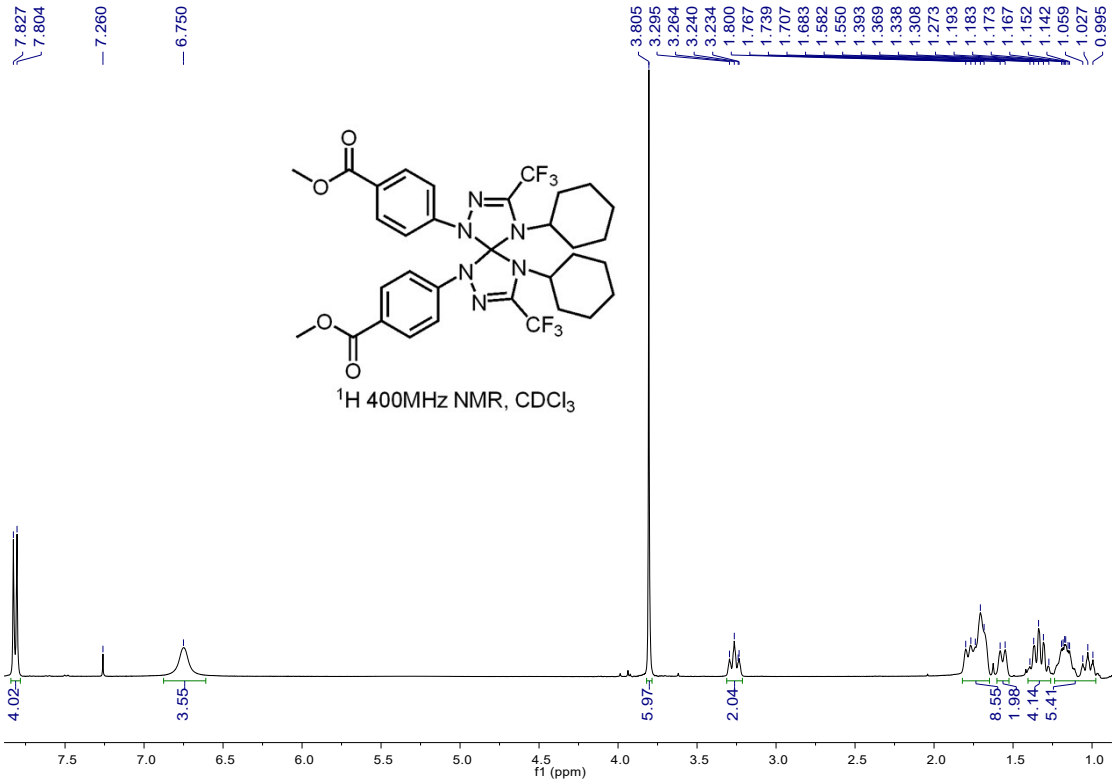
ZHOUYUXIU-16#72-126 RT: 0.32-0.56 AV: 55
T: FTMS + p ESI Full lock ms [50.0000-750.0000]
m/z= 730.8851-741.8079

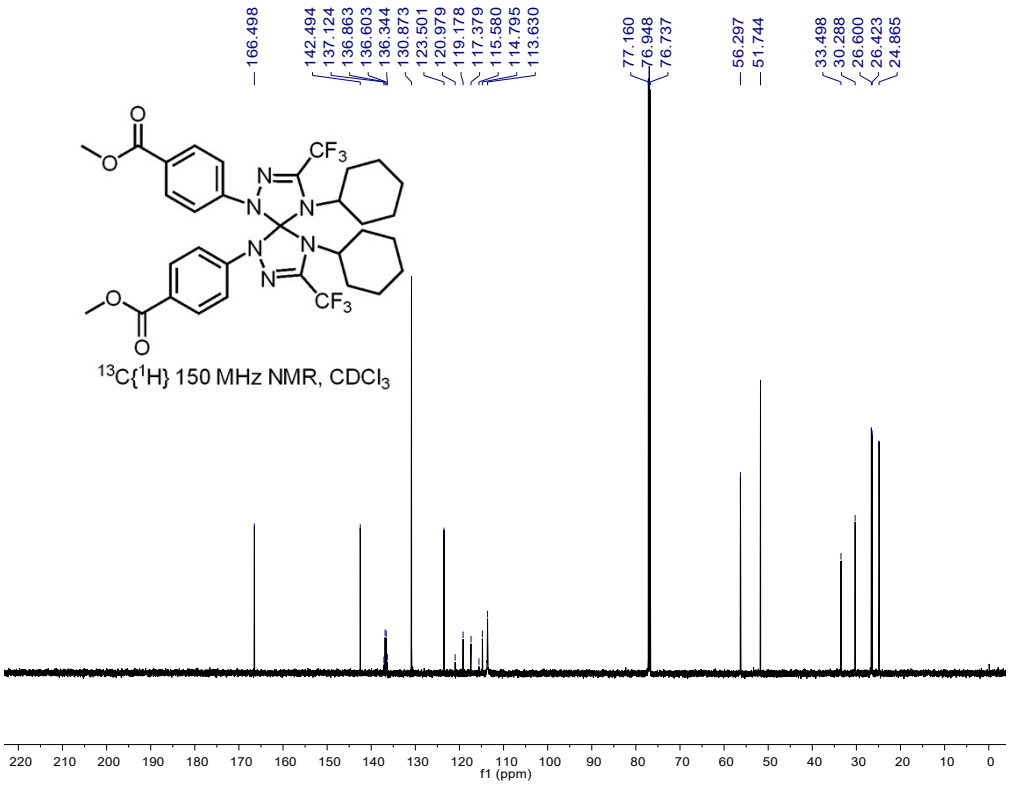
m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
735.0875	1981205.5	54.12	735.0876	-0.11	$C_{29}H_{31}N_6Br_2F_6$
737.0854	3661035.3	100.00			
738.0878	1200922.6	32.80			
739.0836	1858036.0	50.75			

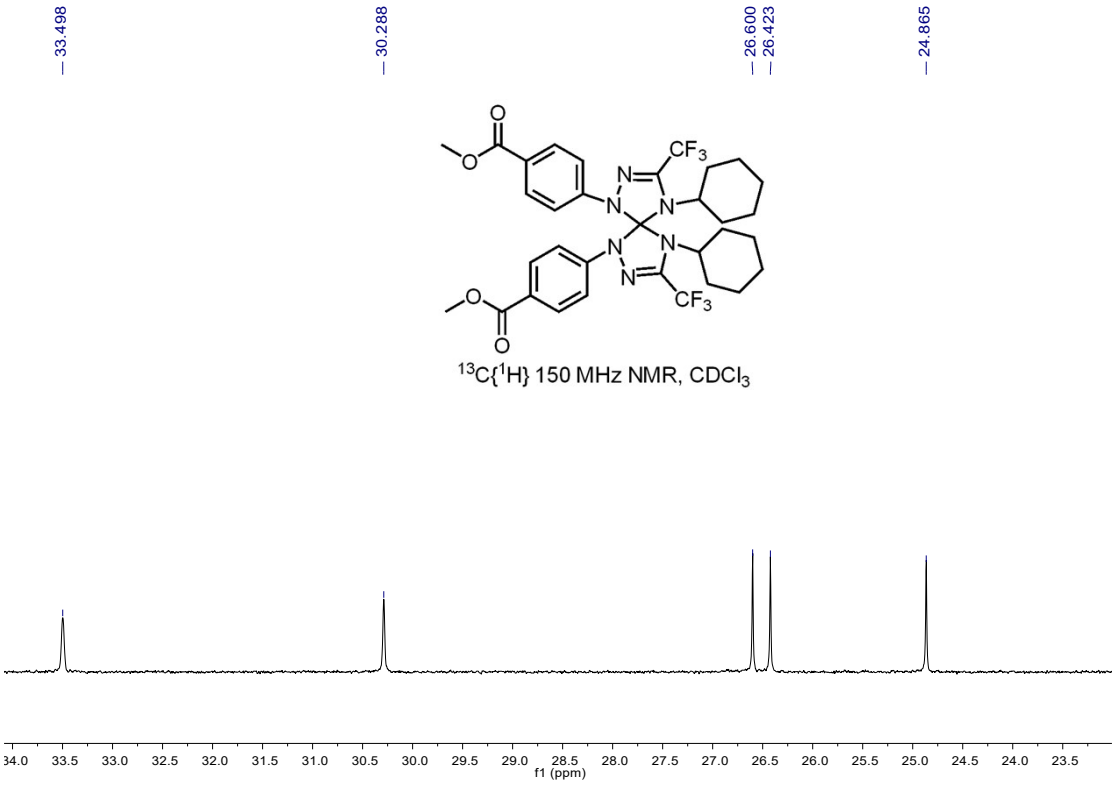


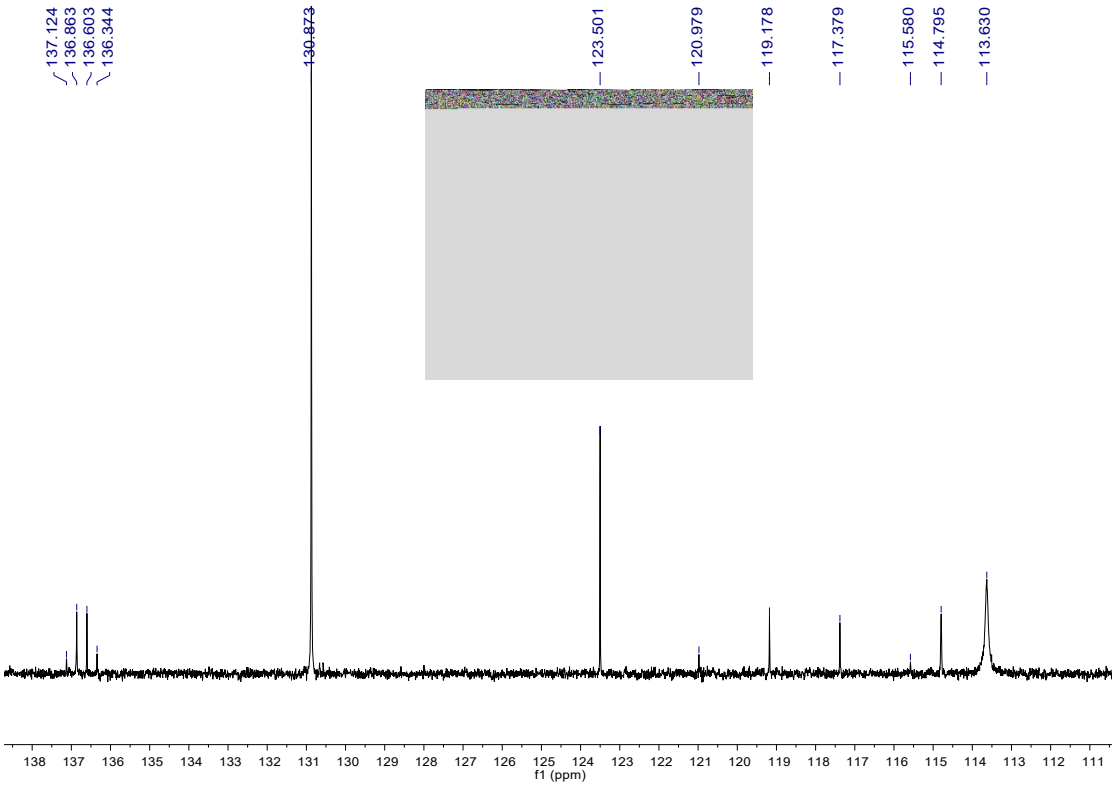
NMR copies of compound **3′n**:

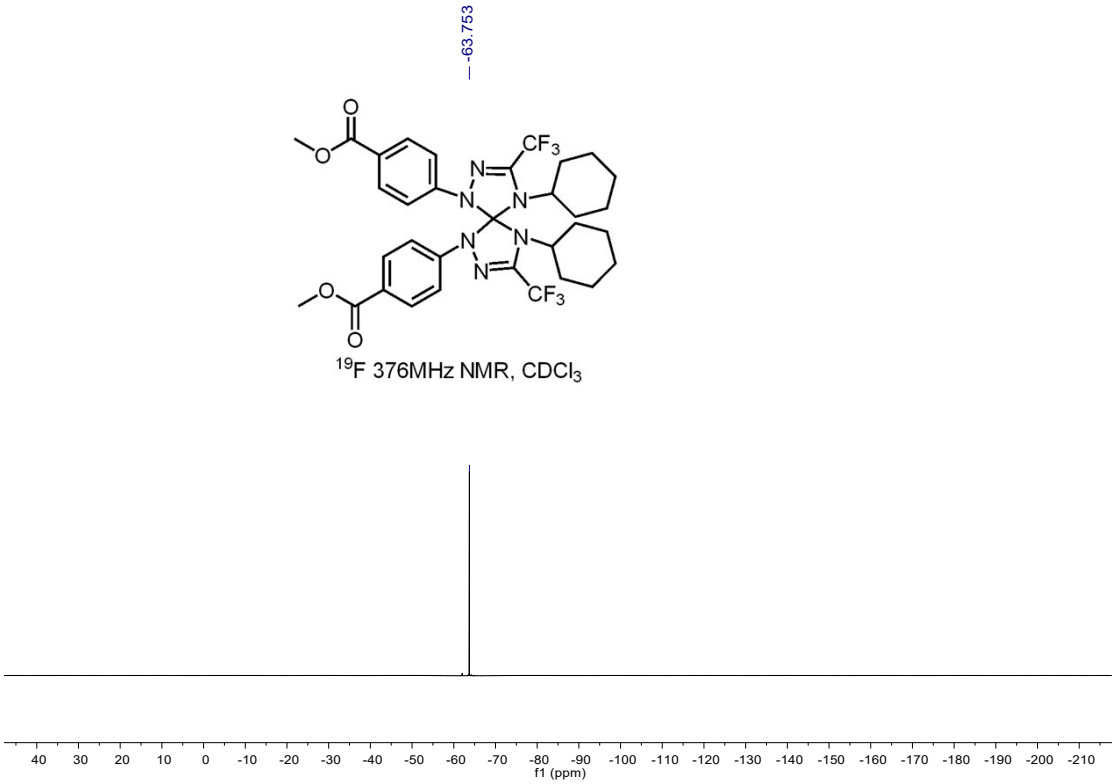





166.498
142.494
137.124
136.863
136.603
136.344
130.873
123.501
120.979
119.178
117.379
115.580
114.795
113.630
77.160
76.948
76.737
56.297
51.744
33.498
30.288
26.600
26.423
24.865
CF3
CF3
13C{1H} 150 MHz NMR, CDCl3
f1 (ppm)

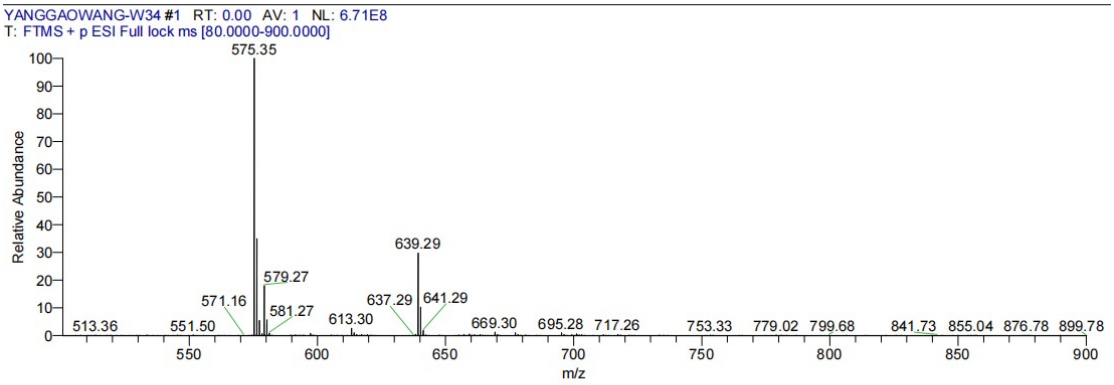

33.498
30.288
26.600
26.423
24.865
CF3
CF3
13C{1H} 150 MHz NMR, CDCl3
f1 (ppm)

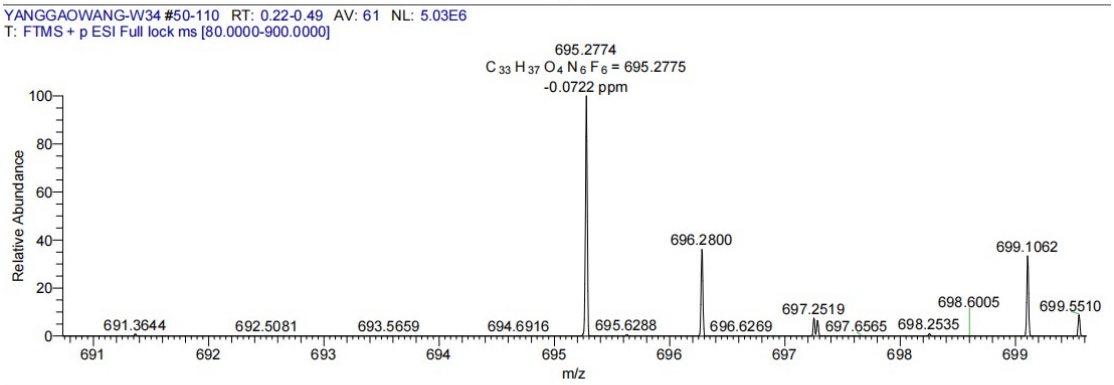




^{19}F 376MHz NMR, $CDCl_3$

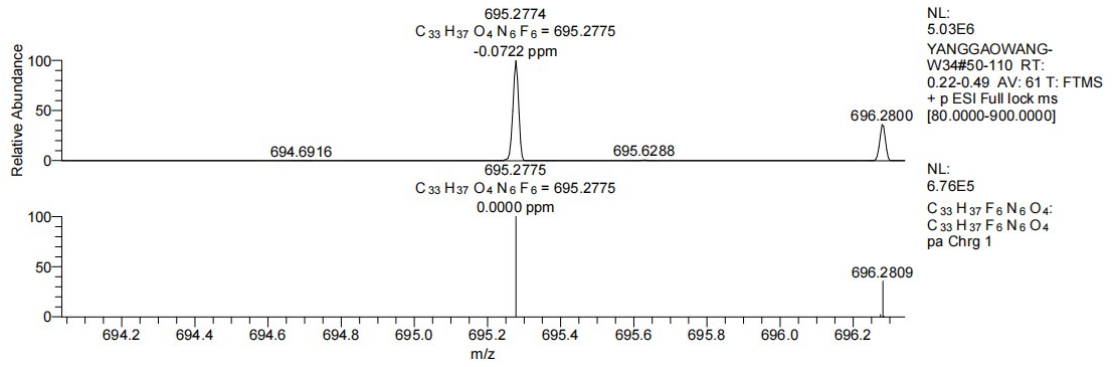
HRMS (ESI) copy of compound **3′n**:



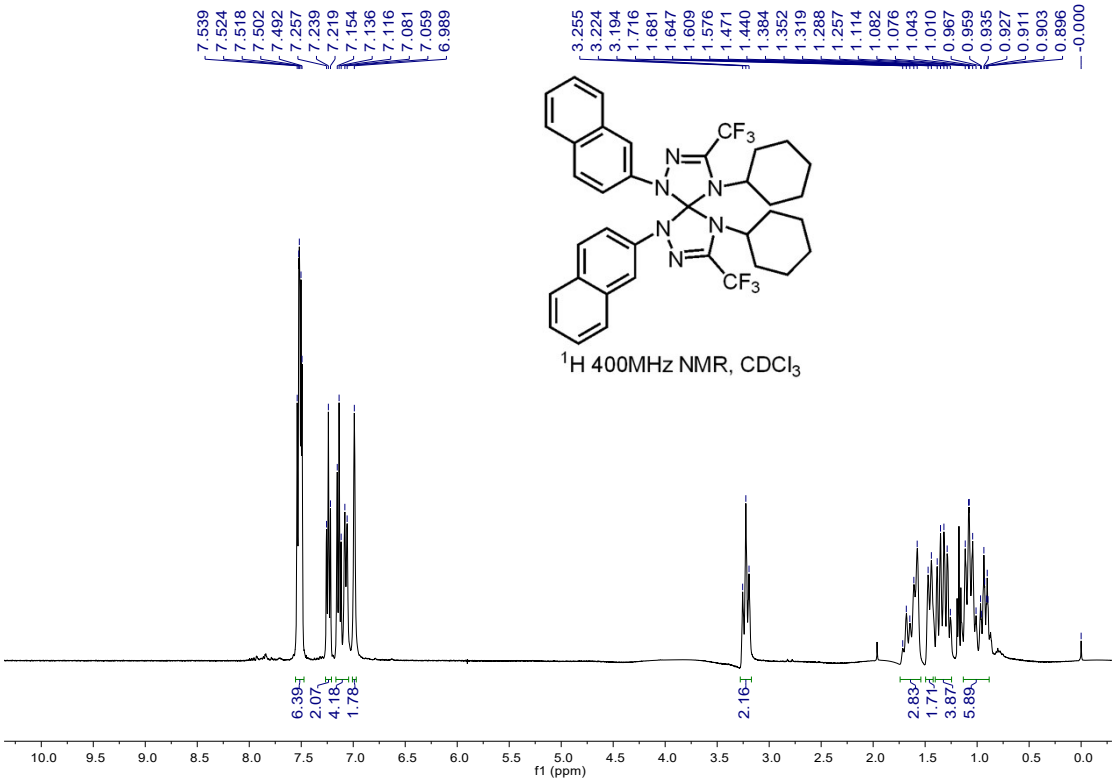


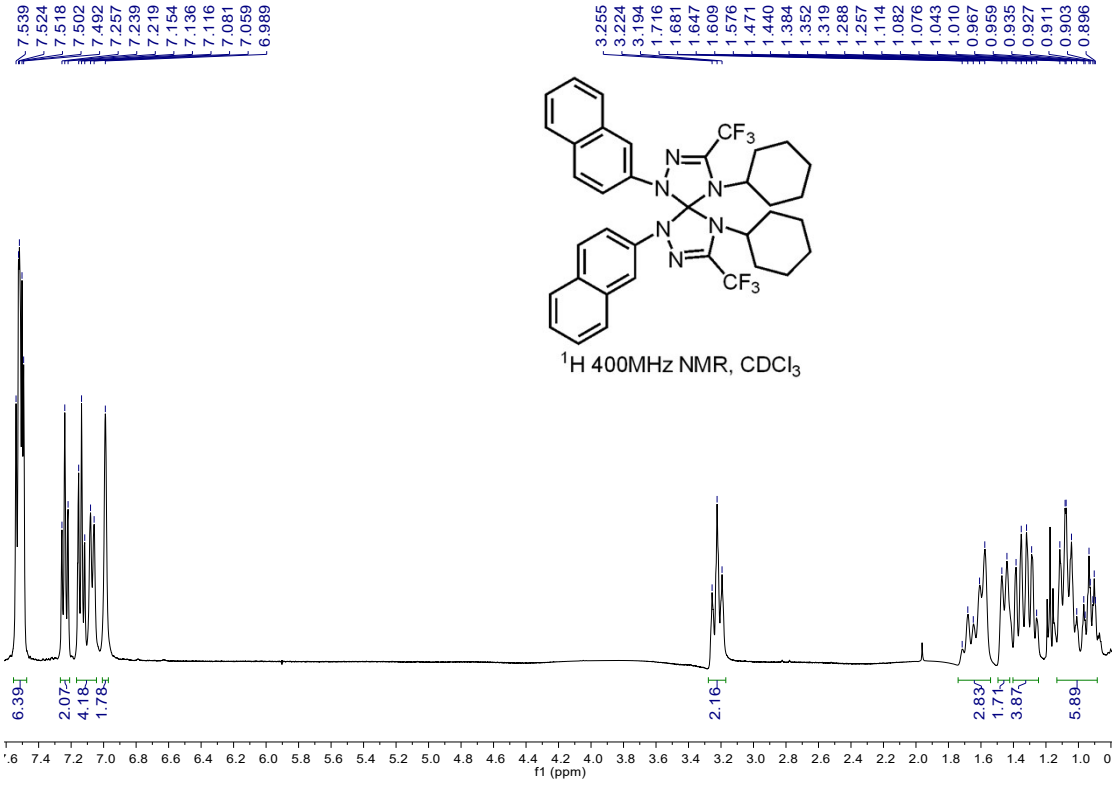
YANGGAOWANG-W34#50-110 RT: 0.22-0.49 AV: 61
T: FTMS + p ESI Full lock ms [80.0000-900.0000]
m/z= 690.7342-699.6133

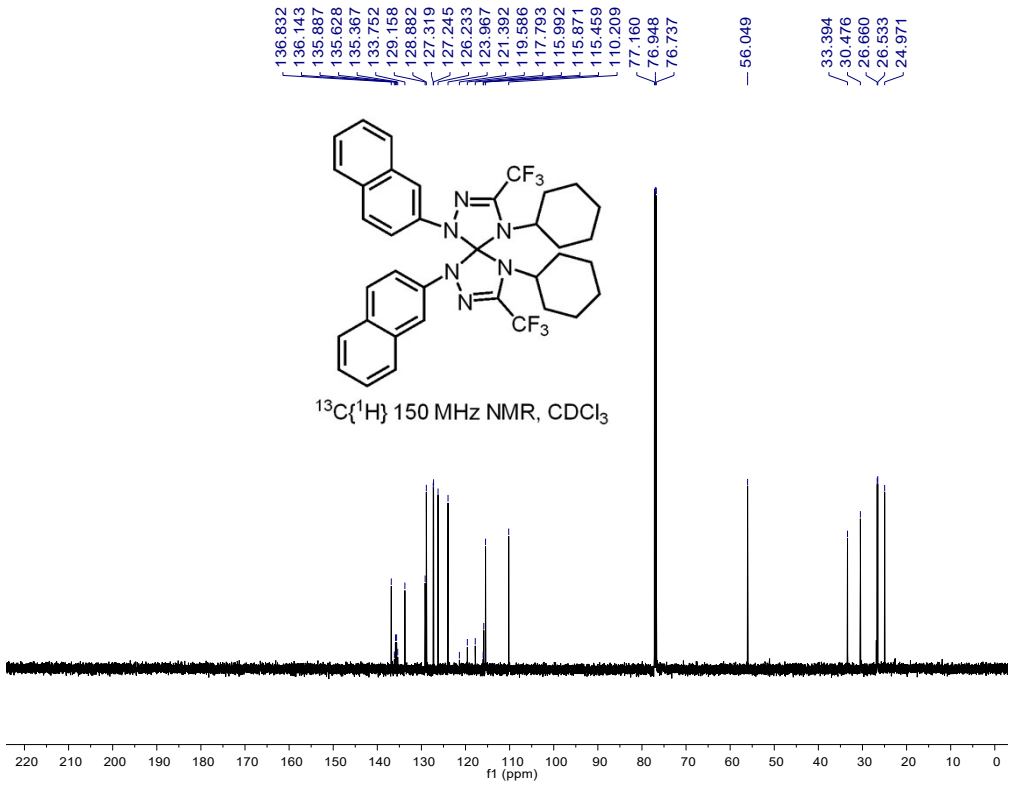
m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
695.2774	5033655.0	100.00	695.2775	-0.05	$C_{33}H_{37}O_4N_6F_6$
696.2800	1854653.4	36.85			
699.1062	1686791.0	33.51			
699.5510	453353.7	9.01			

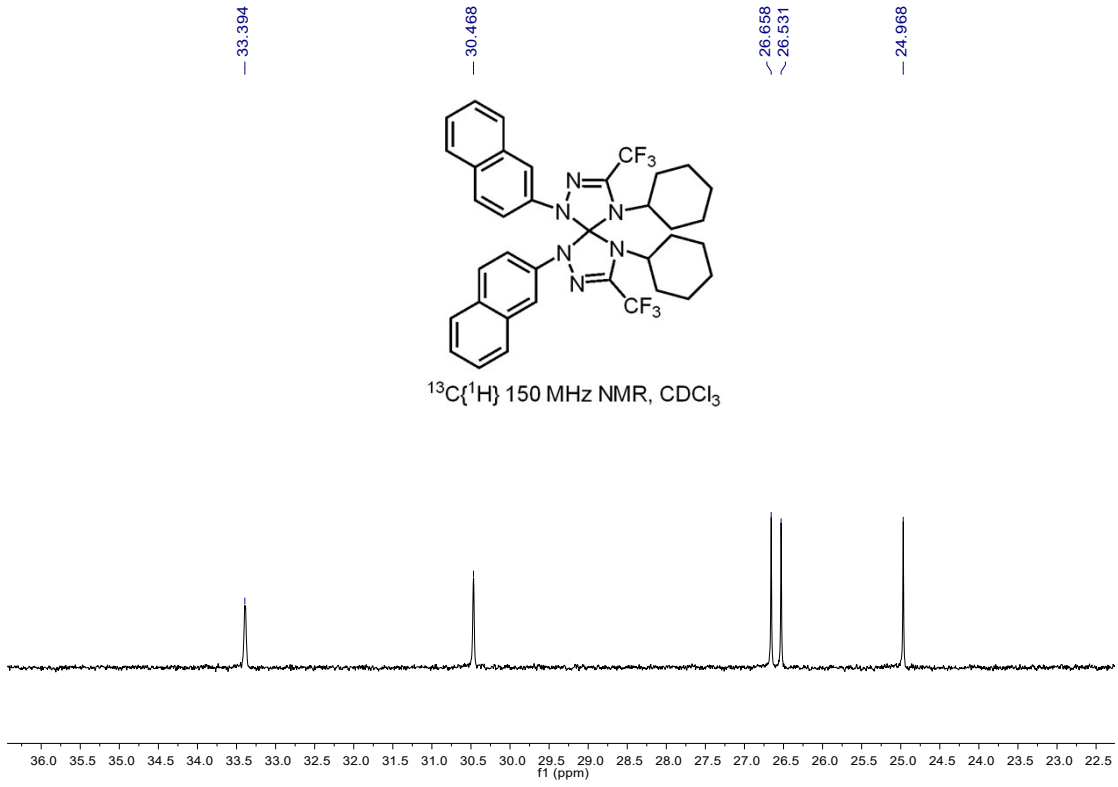


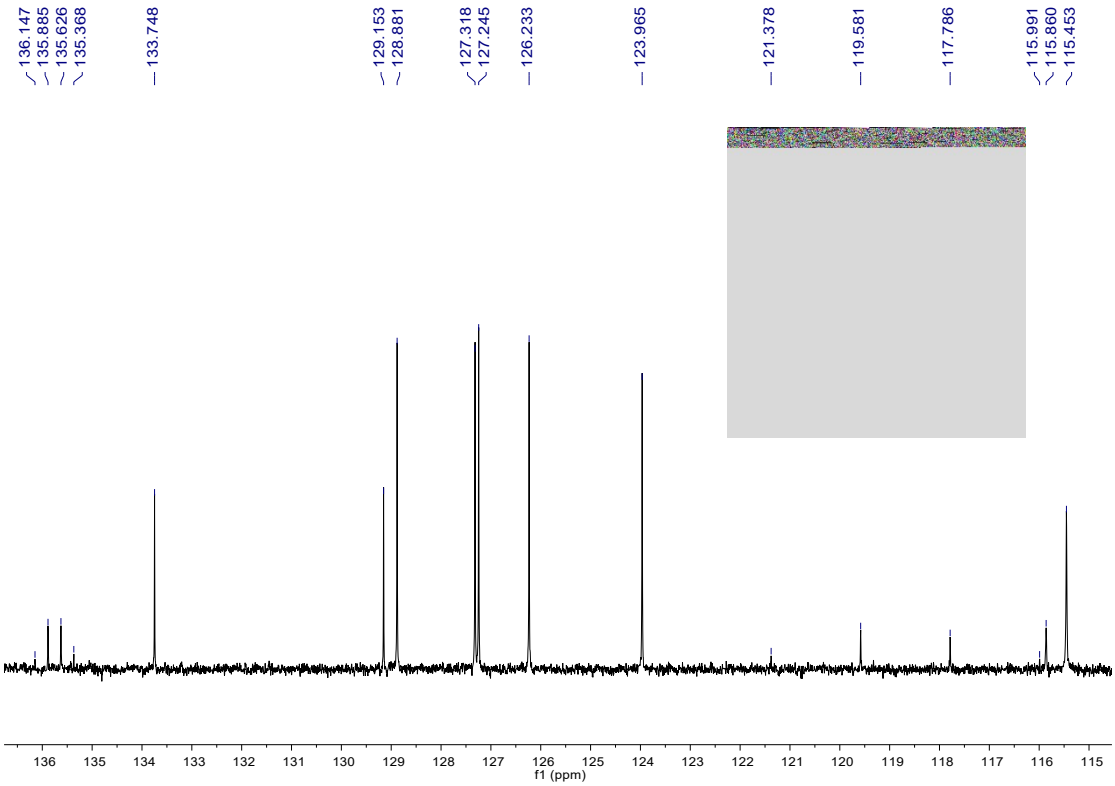
NMR copies of compound **3′o**:

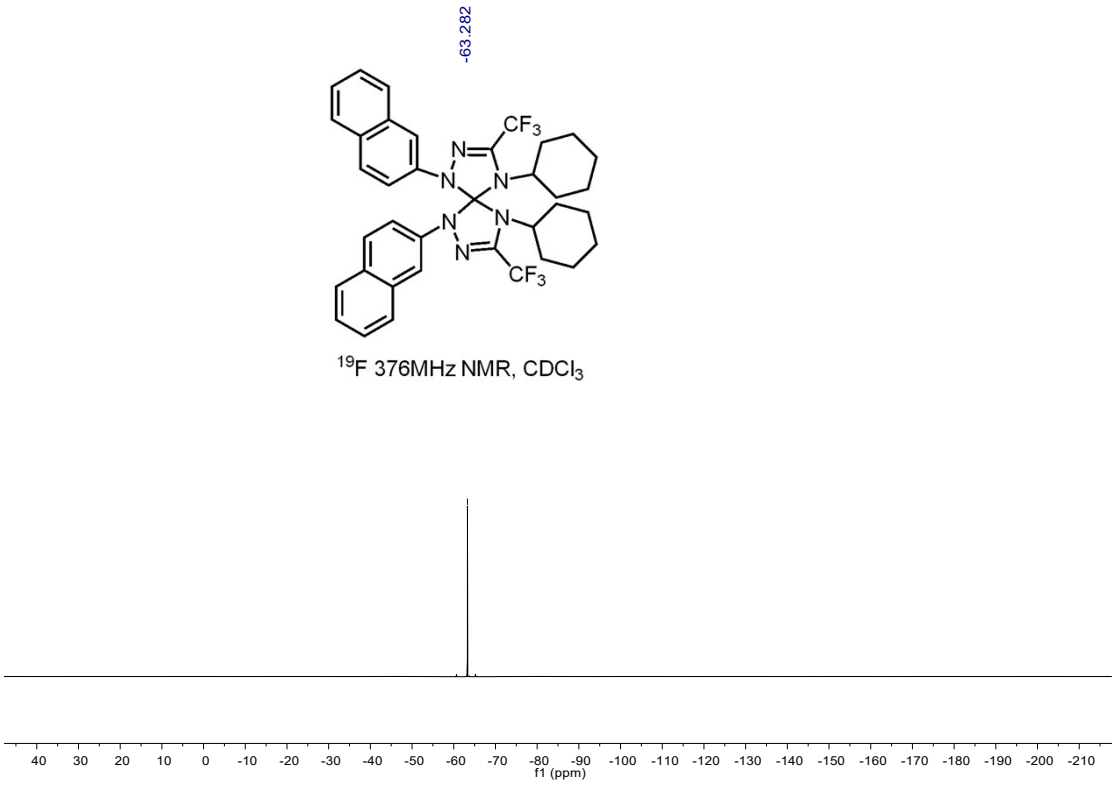





136.832
136.143
135.887
135.628
135.367
133.752
129.158
128.882
127.319
127.245
126.233
123.967
121.392
119.586
117.793
115.992
115.871
115.459
110.209
77.160
76.948
76.737
56.049
33.394
30.476
26.660
26.533
24.971
CF3
CF3
13C{1H} 150 MHz NMR, CDCl3
f1 (ppm)

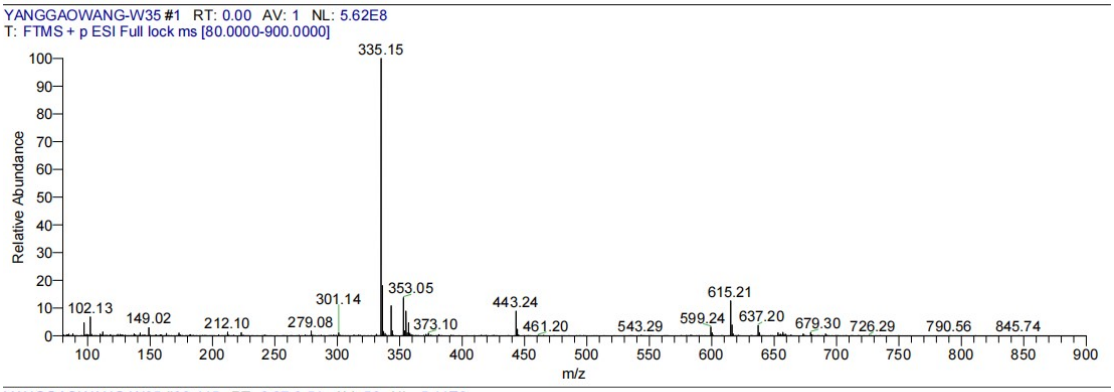

33.394
30.468
26.658
26.531
24.968
CF3
CF3
13C{1H} 150 MHz NMR, CDCl3
f1 (ppm)

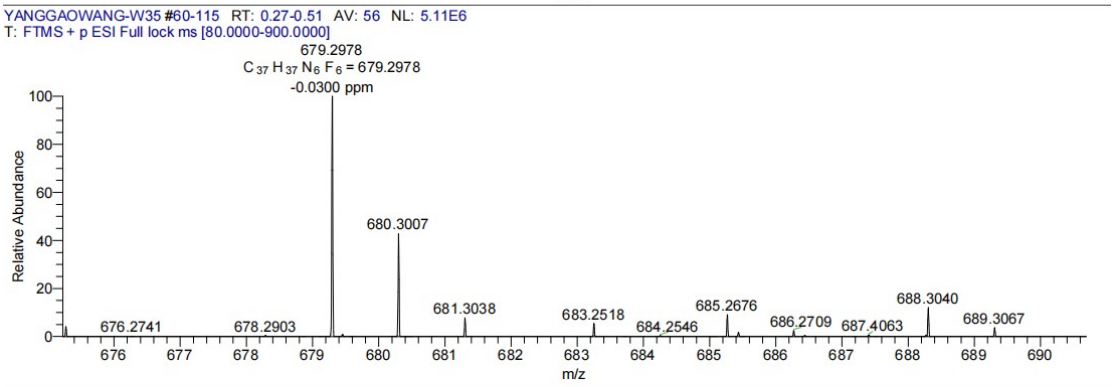




^{19}F 376MHz NMR, $CDCl_3$

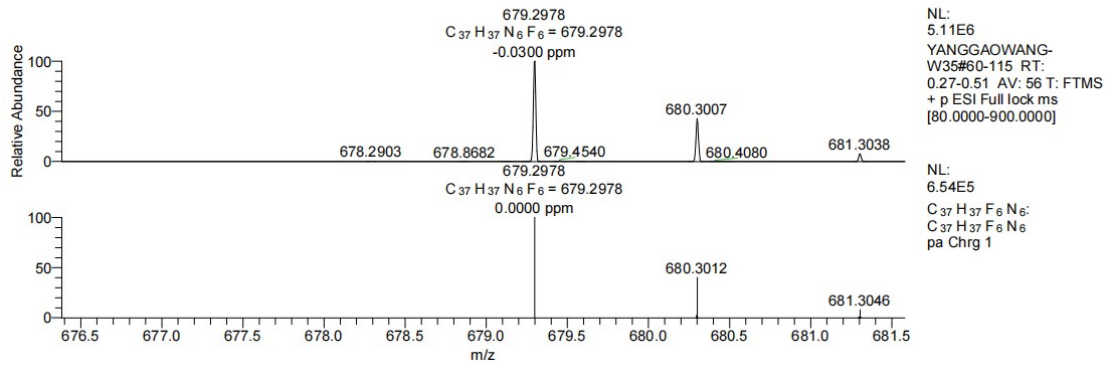
HRMS (ESI) copy of compound **3′o**:





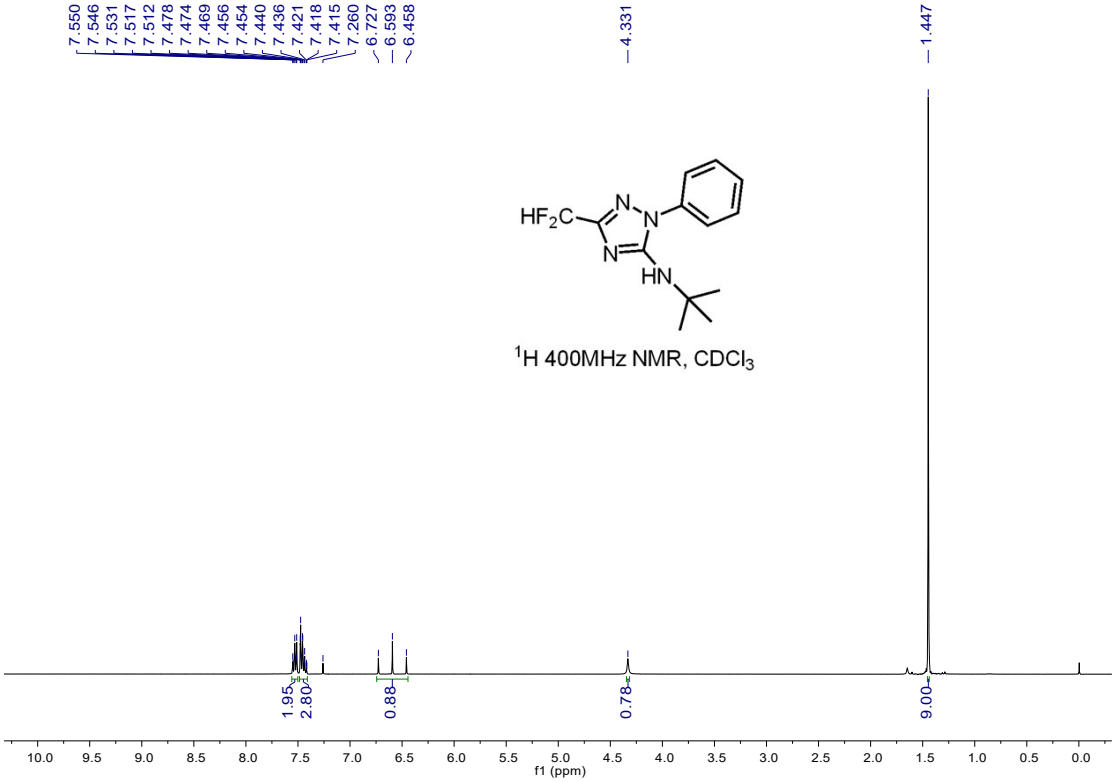
YANGGAOWANG-W35#60-115 RT: 0.27-0.51 AV: 56
T: FTMS + p ESI Full lock ms [80.0000-900.0000]
m/z= 675.2251-690.6894

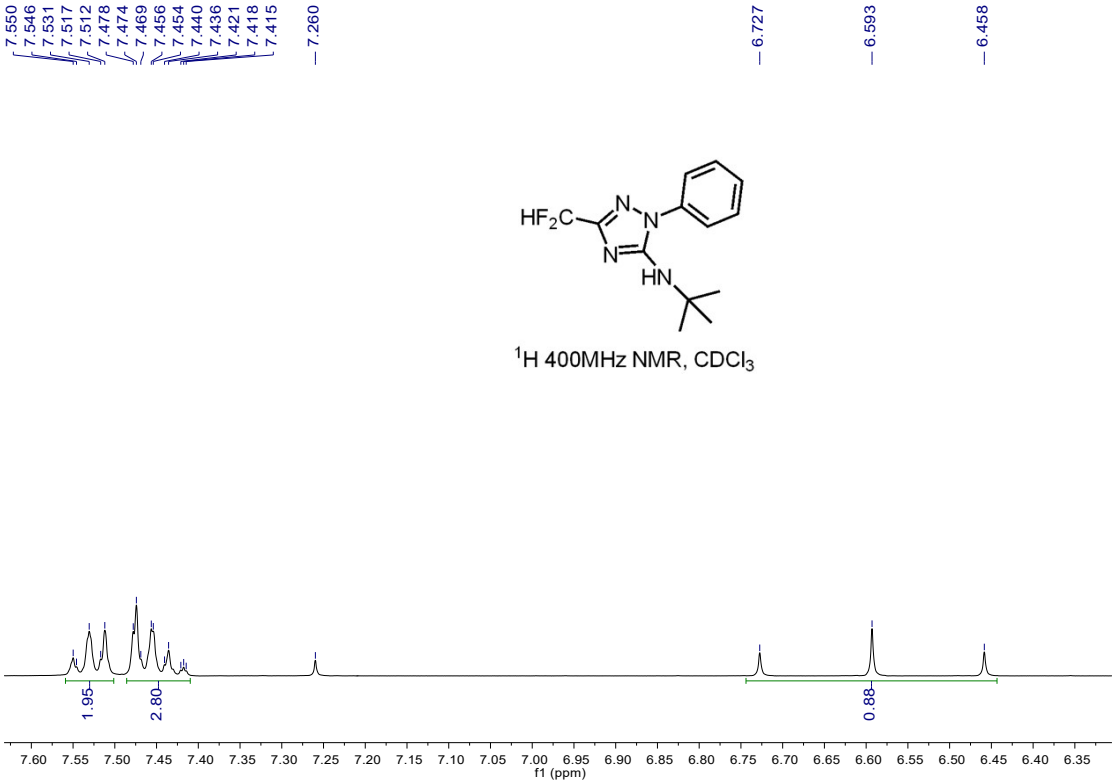
m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
679.2978	5297176.5	100.00	679.2978	-0.02	$C_{37}H_{37}N_6F_6$
680.3007	2194986.3	41.44			
685.2676	469928.4	8.87			
688.3040	619967.7	11.70			

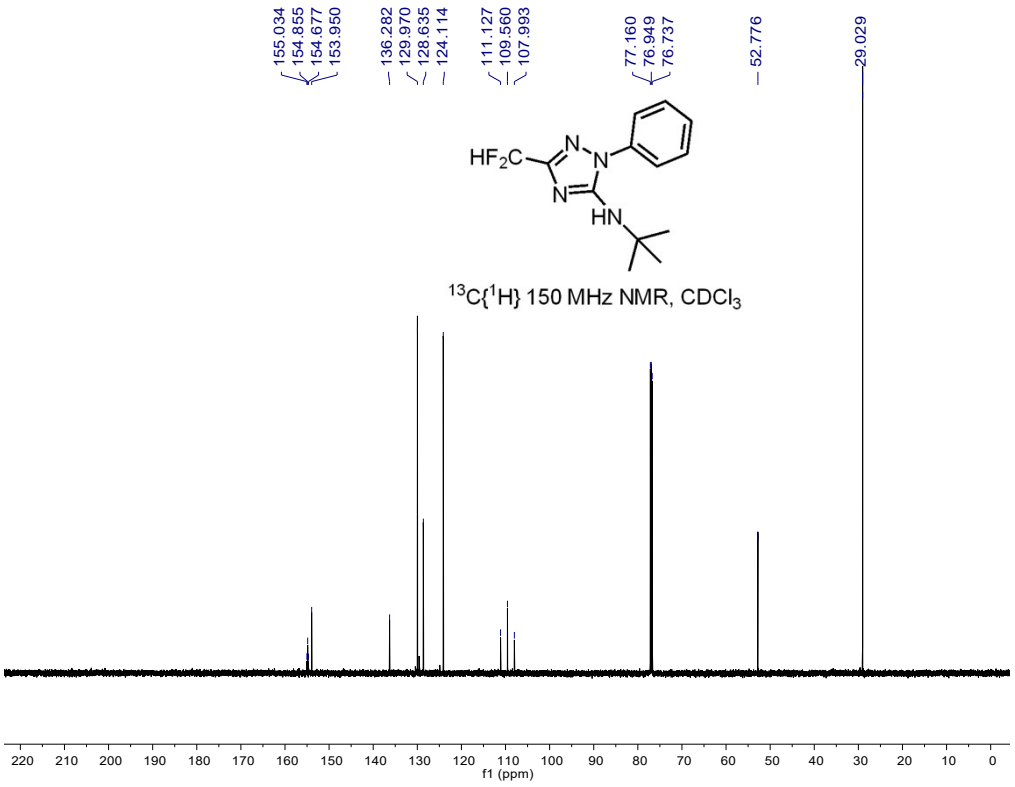


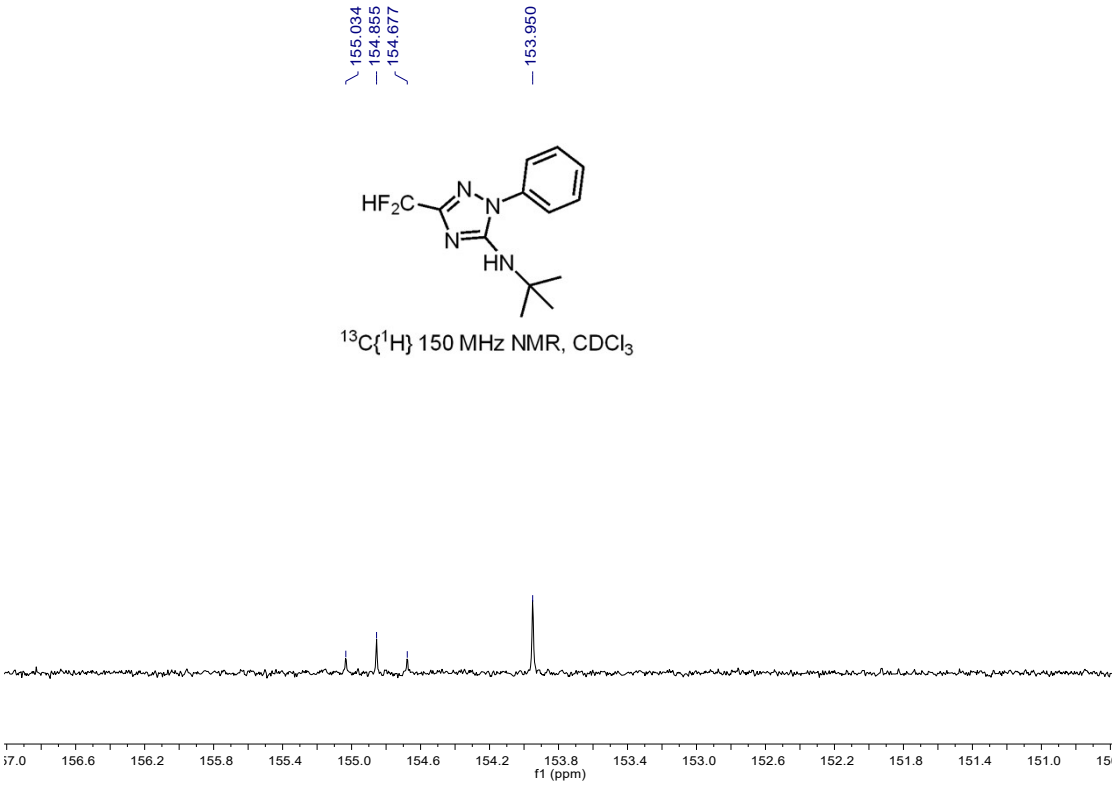
Copies of NMR and HRMS Spectra for Compounds **5**

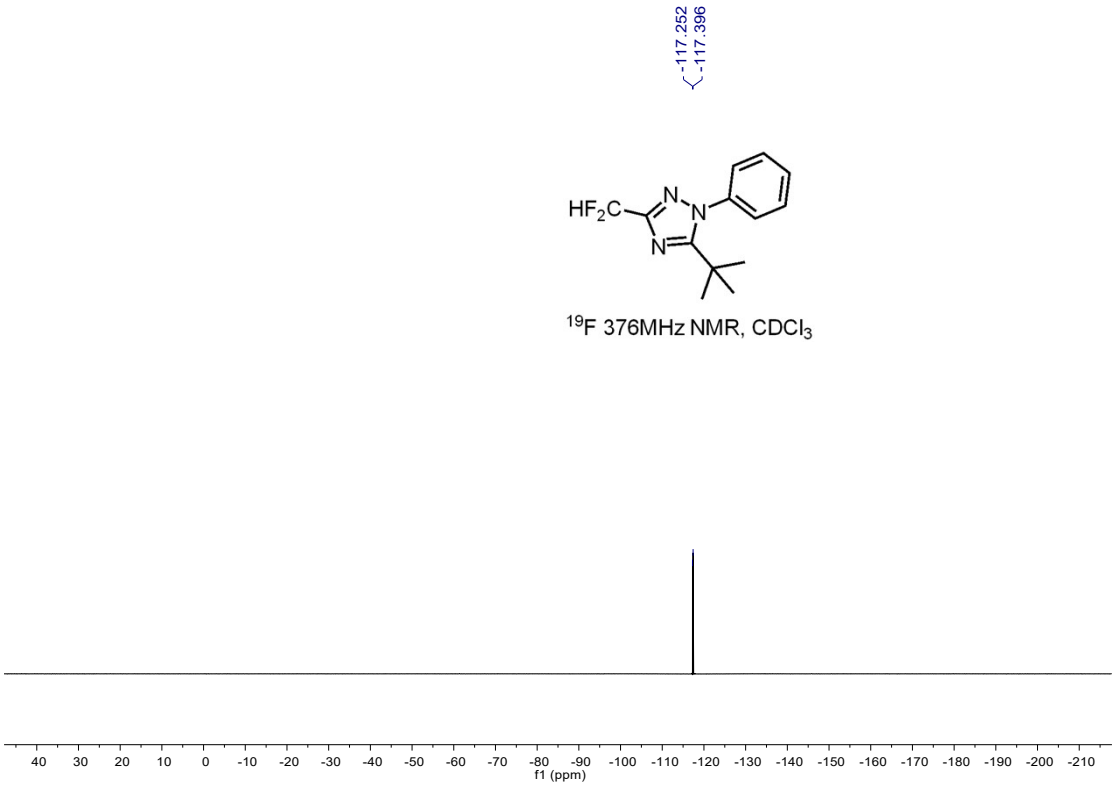
NMR copies of compound **5a**:



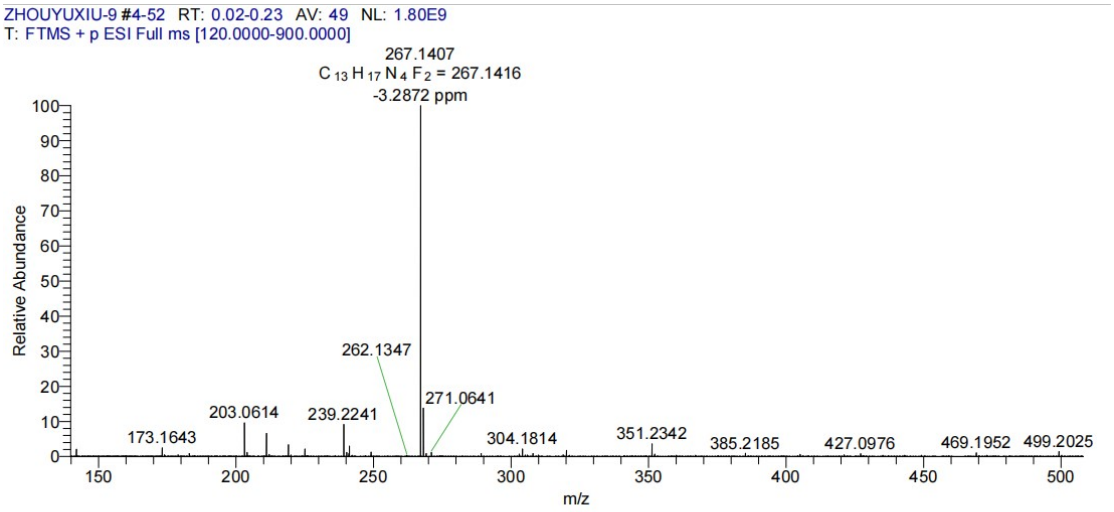



155.034
154.855
154.677
153.950
136.282
129.970
128.635
124.114
111.127
109.560
107.993
77.160
76.949
76.737
52.776
29.029
HF2C
N
N
N
HN
13C{1H} 150 MHz NMR, CDCl3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


155.034
154.855
154.677
153.950
HF2C
N
N
N
HN
13C{1H} 150 MHz NMR, CDCl3
156.6 156.2 155.8 155.4 155.0 154.6 154.2 153.8 153.4 153.0 152.6 152.2 151.8 151.4 151.0
f1 (ppm)

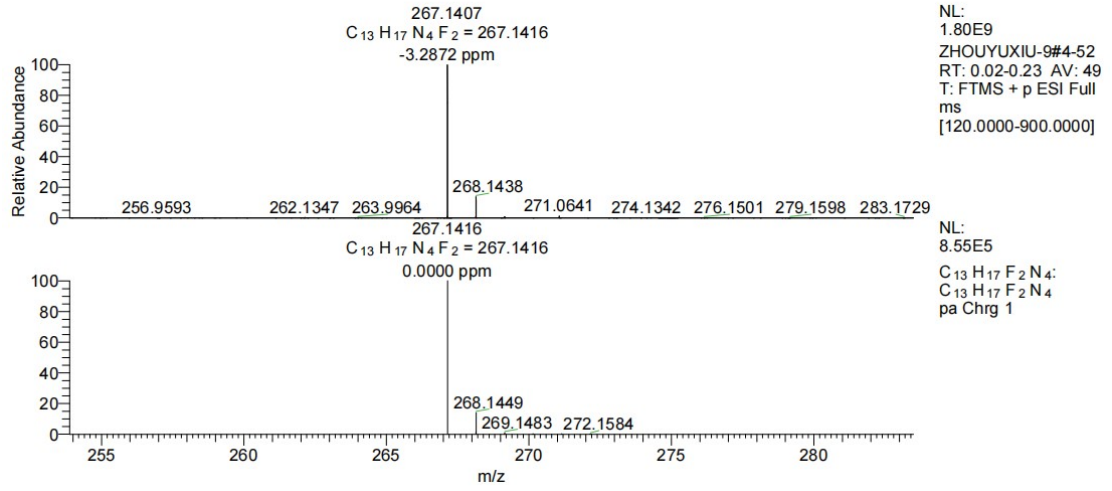

-117.252
-117.396
HF2C
N
N
N
19F 376MHz NMR, CDCl3
40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

HRMS (ESI) copy of compound **5a**:

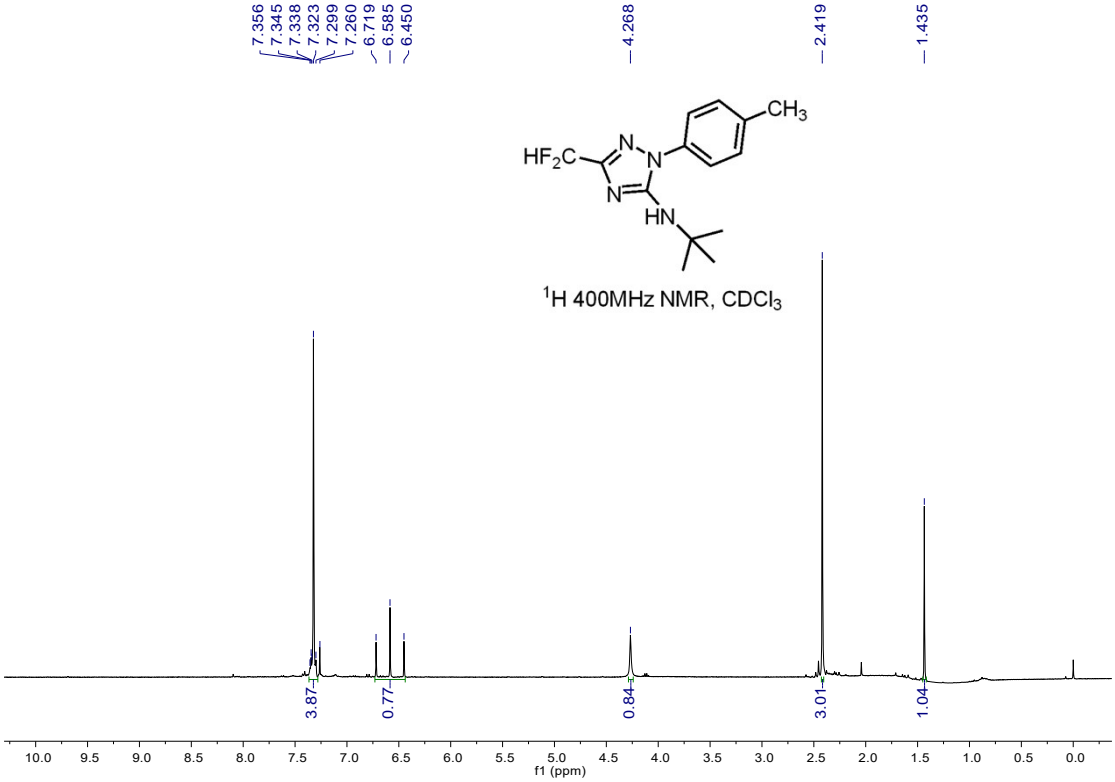


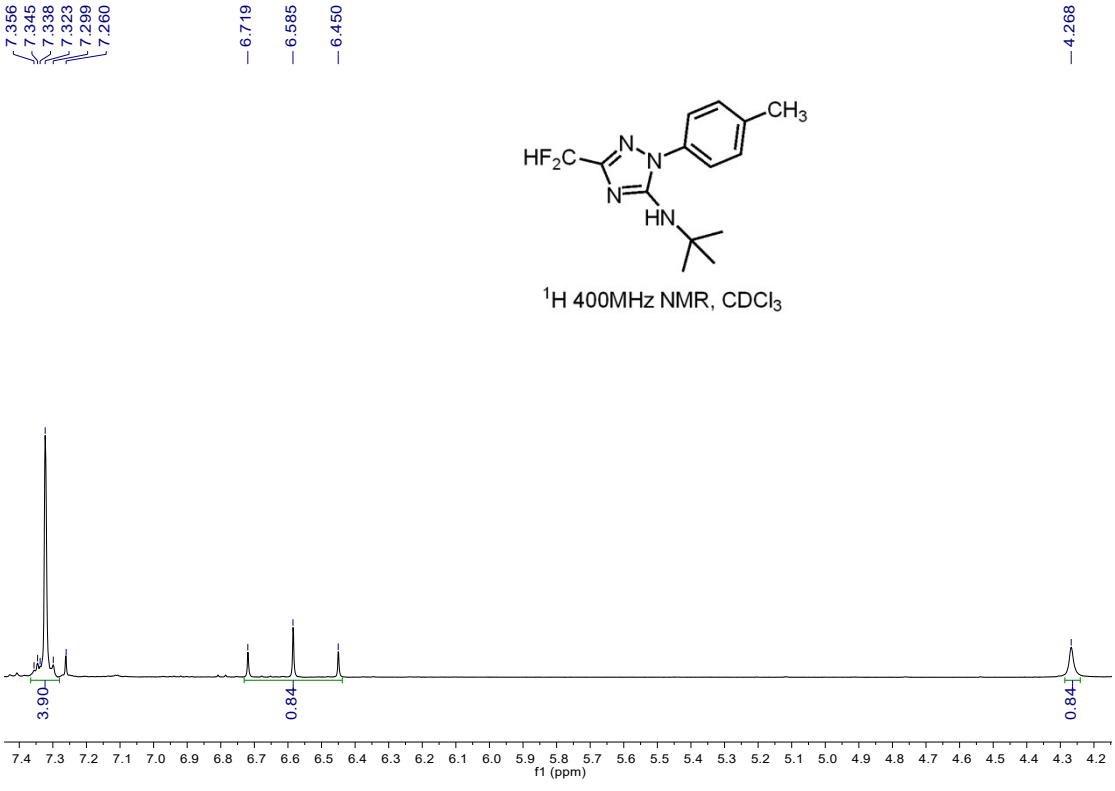
ZHOUYUXIU-9#4-52 RT: 0.02-0.23 AV: 49
T: FTMS + p ESI Full ms [120.0000-900.0000]
m/z= 139.8305-507.9661

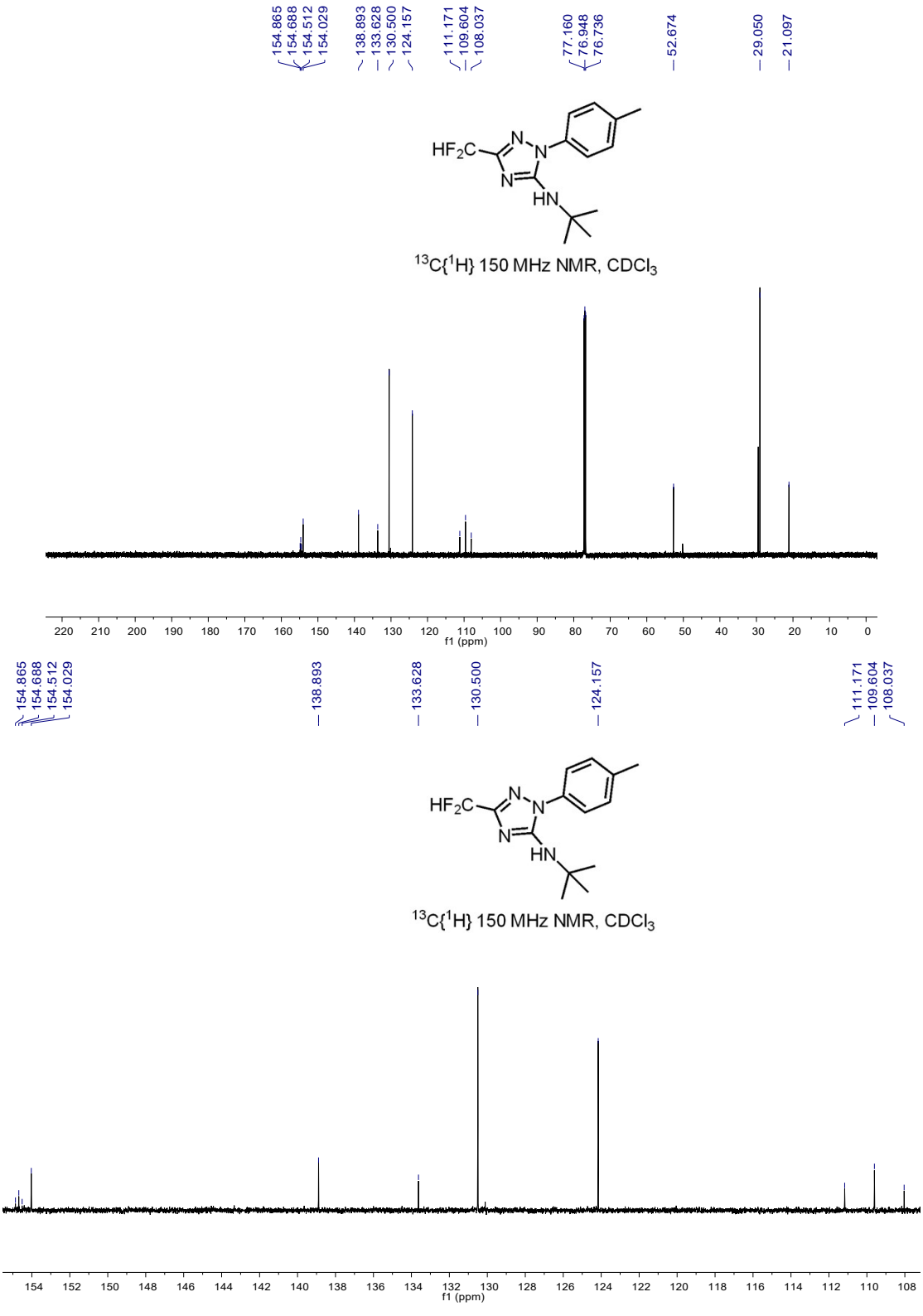
m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
203.0614	174248832.0	9.60			
239.2241	169754336.0	9.35			
267.1407	1814824576.0	100.00	267.1416	-0.88	$C_{13}H_{17}N_4F_2$
268.1438	248694576.0	13.70			

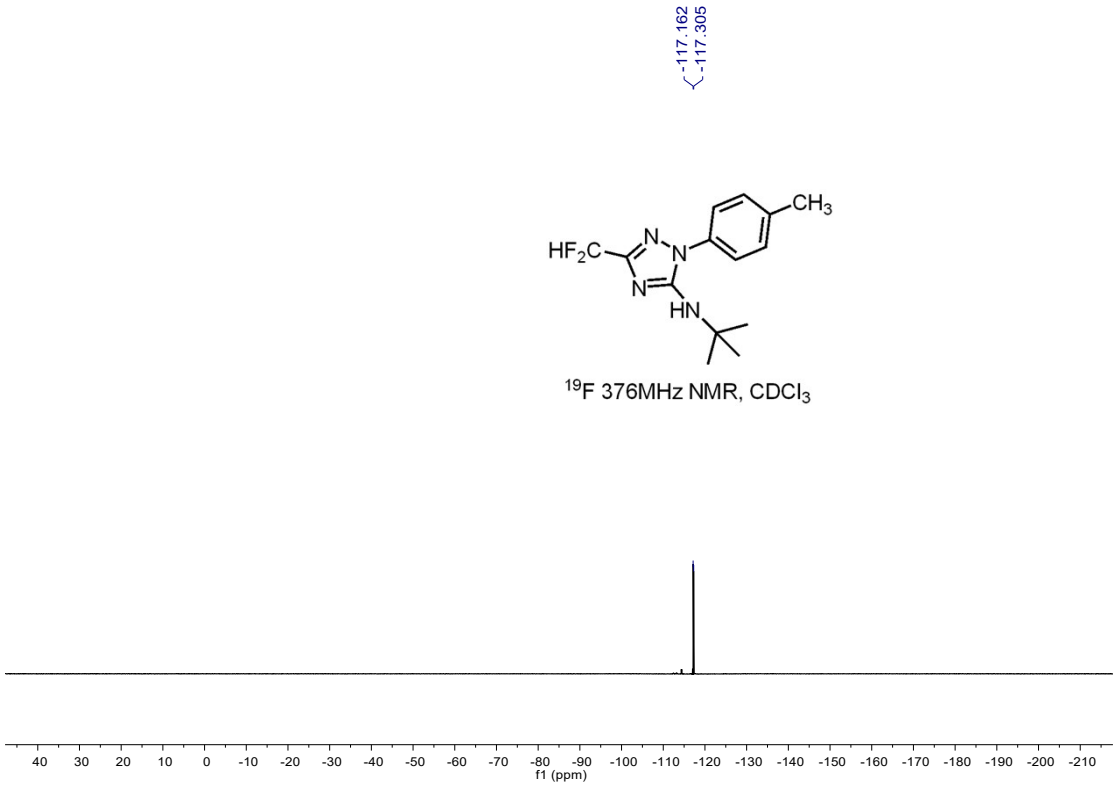


NMR copies of compound **5b**:

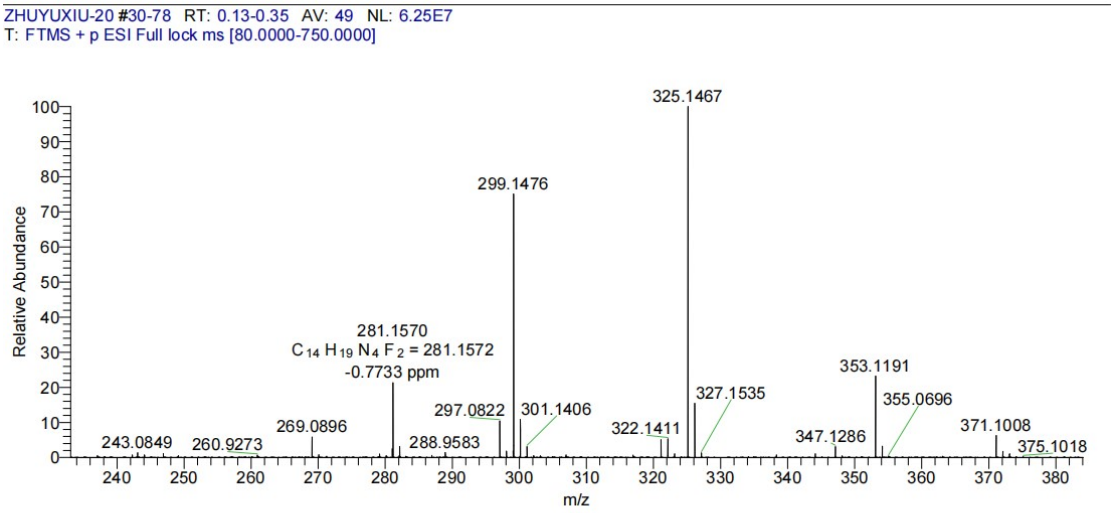





154.865
154.688
154.512
154.029
138.893
133.628
130.500
124.157
111.171
109.604
108.037
77.160
76.948
76.736
52.674
29.050
21.097
HF2C
N
N
N
HN
13C{1H} 150 MHz NMR, CDCl3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
154.865
154.688
154.512
154.029
138.893
133.628
130.500
124.157
111.171
109.604
108.037
HF2C
N
N
N
HN
13C{1H} 150 MHz NMR, CDCl3
154 152 150 148 146 144 142 140 138 136 134 132 130 128 126 124 122 120 118 116 114 112 110 108
f1 (ppm)

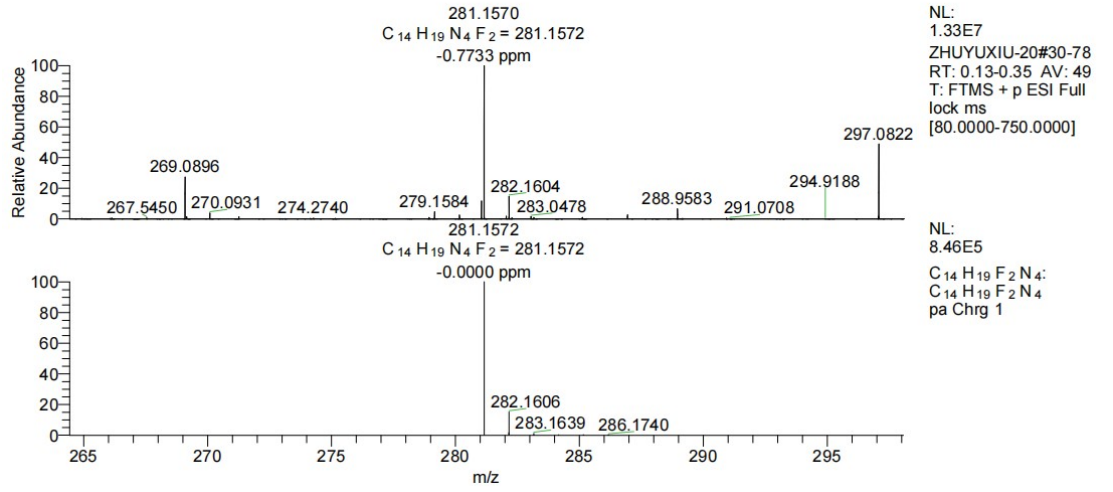

-117.162
-117.305
CH3
HF2C
N
N
N
HN
19F 376MHz NMR, CDCl3
40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

HRMS (ESI) copy of compound **5b**:

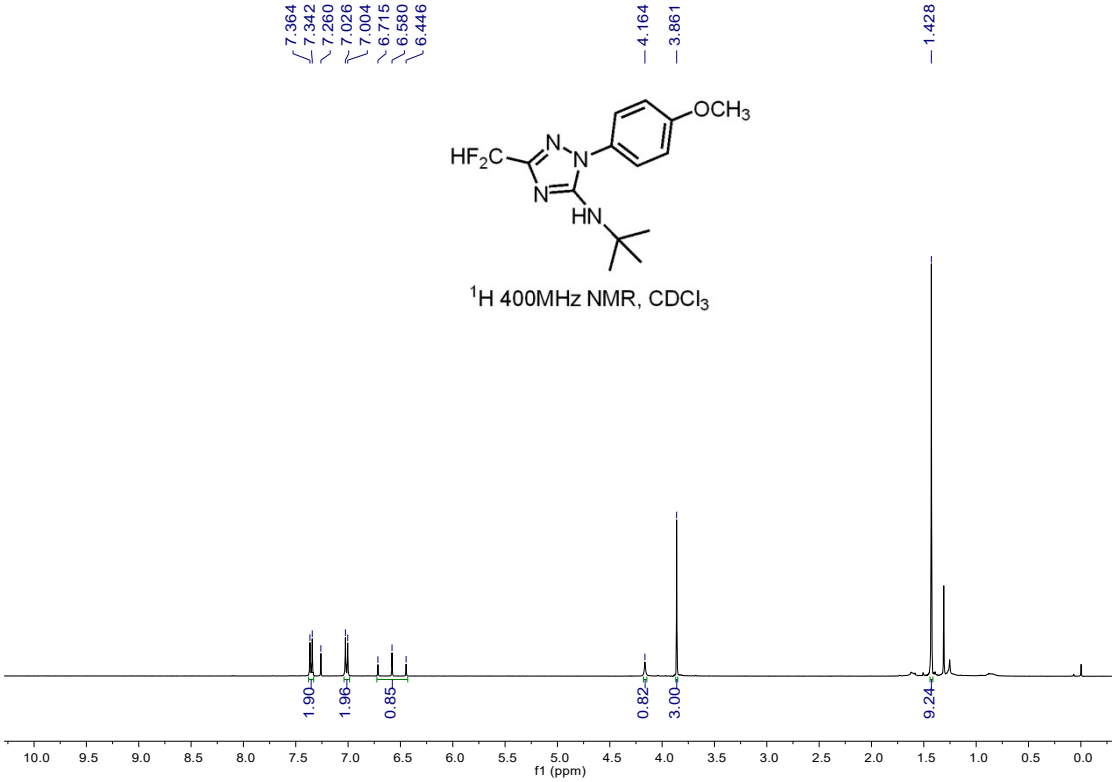


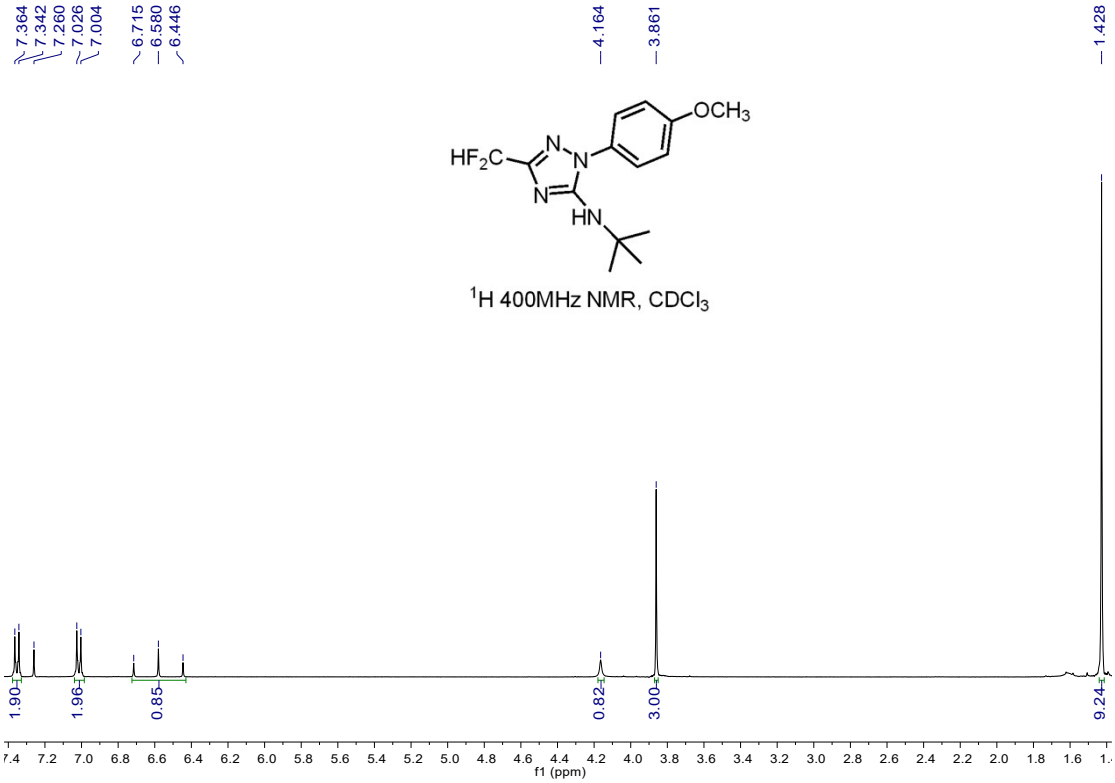
ZHUYUXIU-20#30-78 RT: 0.13-0.35 AV: 49
T: FTMS + p ESI Full lock ms [80.0000-750.0000]
m/z= 233.0696-384.0545

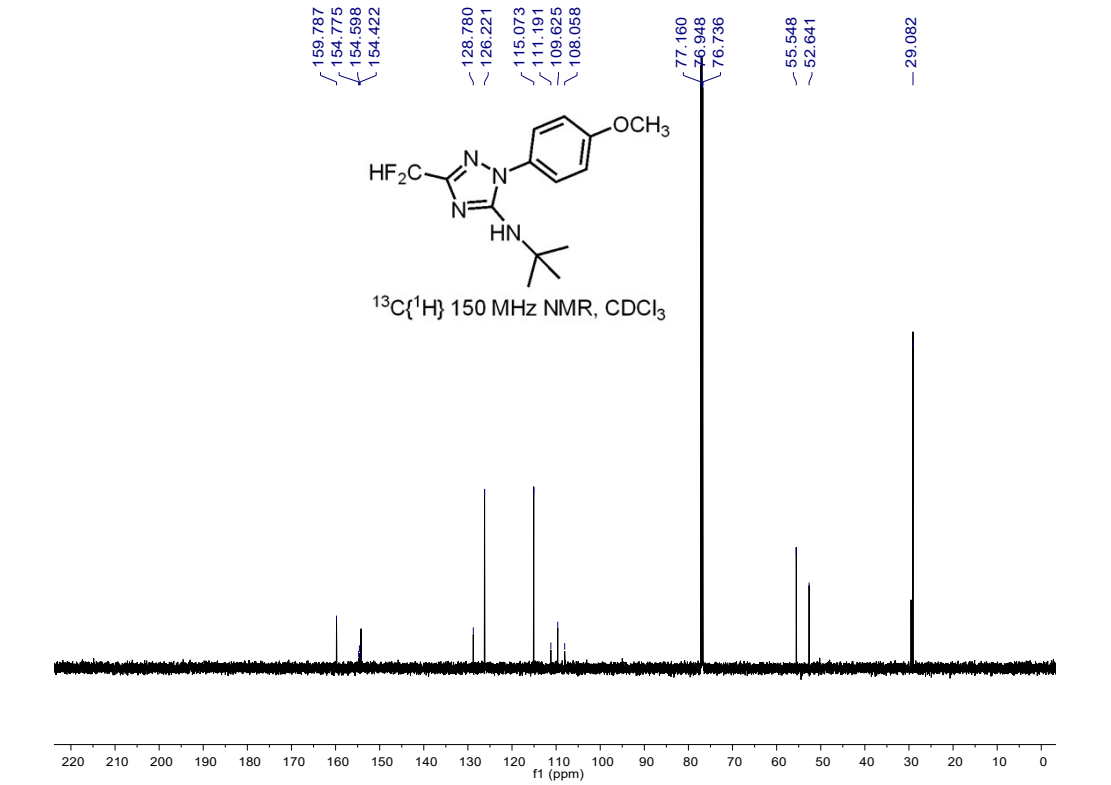
m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
281.1570	13509615.0	21.61	281.1572	-0.22	$C_{14}H_{19}N_4F_2$
299.1476	47333944.0	75.73			
325.1467	62504164.0	100.00			
353.1191	14537687.0	23.26			

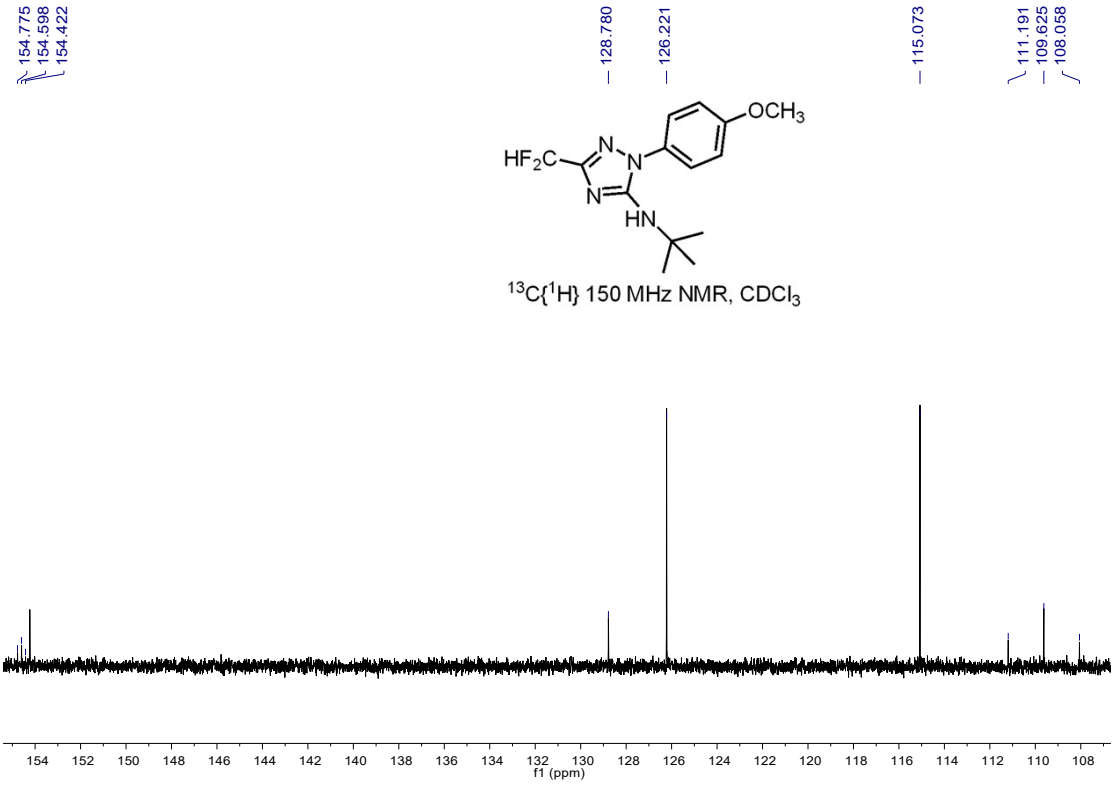


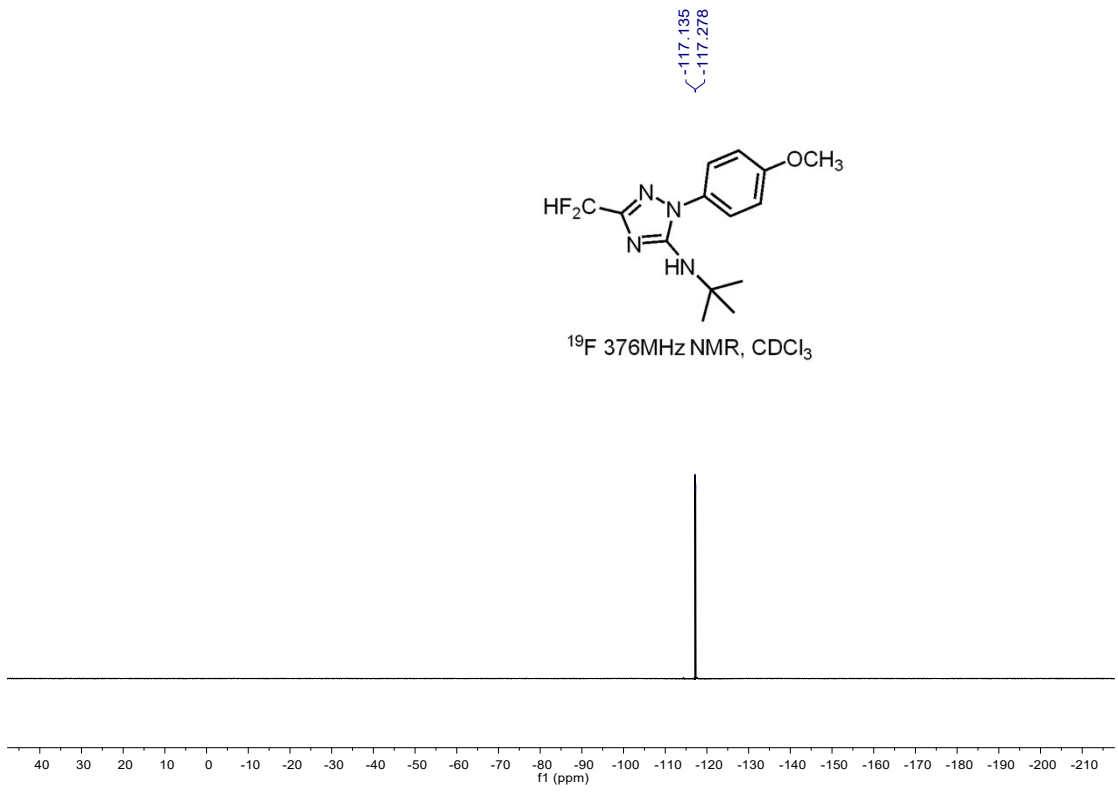
NMR copies of compound **5c**:



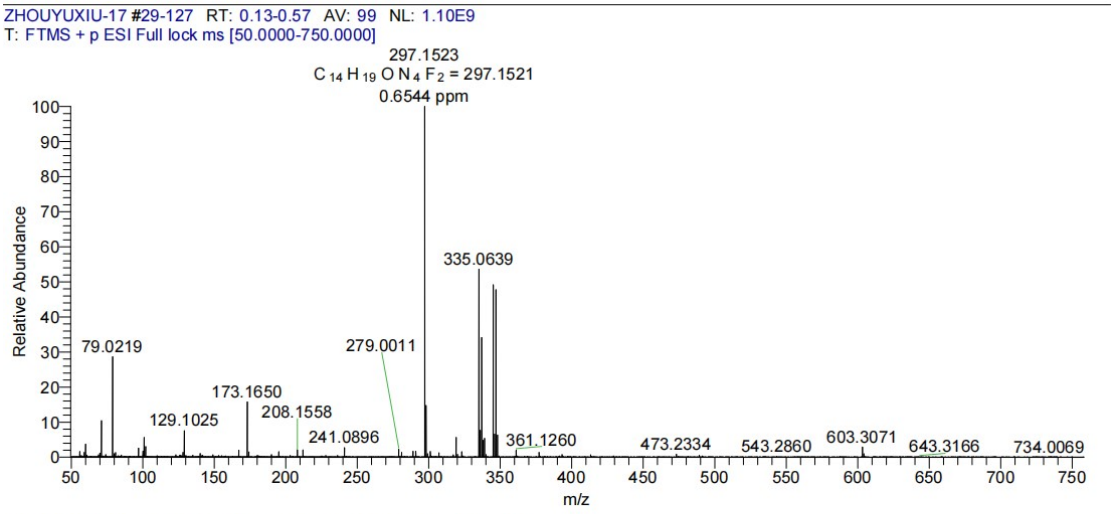



159.787
154.775
154.598
154.422
128.780
126.221
115.073
111.191
109.625
108.058
77.160
76.948
76.736
55.548
52.641
29.082
OCH3
HF2C
N
N
N
HN
13C{1H} 150 MHz NMR, CDCl3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


154.775
154.598
154.422
128.780
126.221
115.073
111.191
109.625
108.058
OCH3
HF2C
N
N
N
HN
13C{1H} 150 MHz NMR, CDCl3
154 152 150 148 146 144 142 140 138 136 134 132 130 128 126 124 122 120 118 116 114 112 110 108
f1 (ppm)

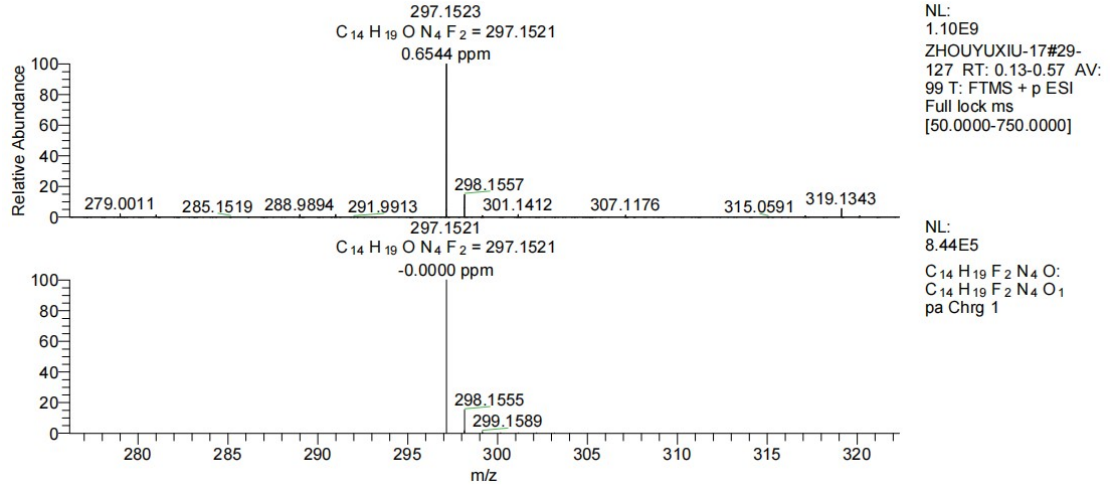

-117.135
-117.278
OCH3
HF2C
N
N
N
HN
19F 376MHz NMR, CDCl3
40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

HRMS (ESI) copy of compound **5c**:

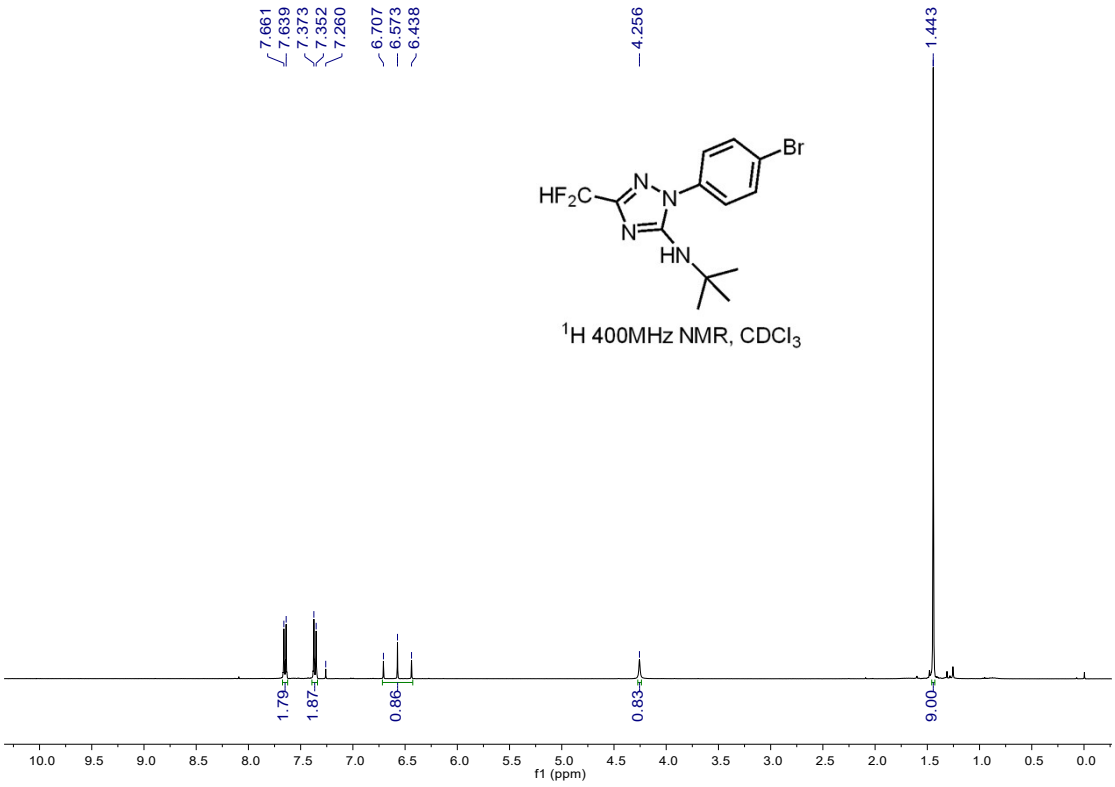


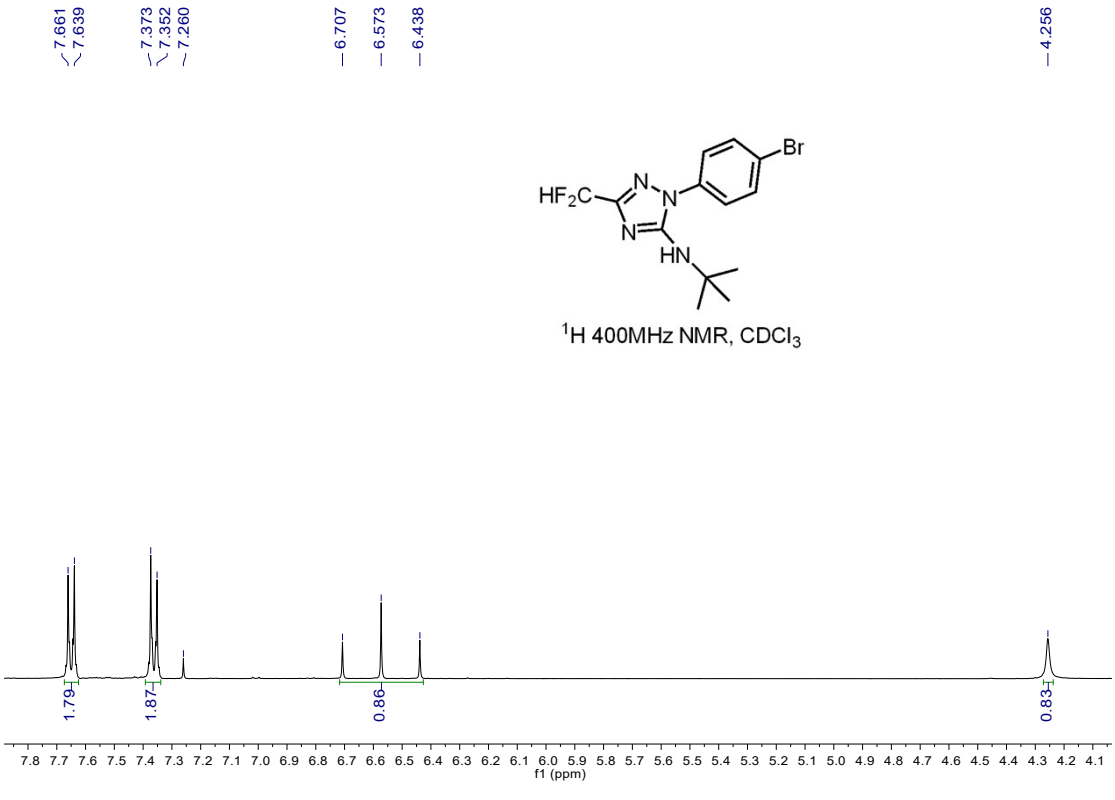
ZHOUYUXIU-17#29-127 RT: 0.13-0.57 AV: 99
T: FTMS + p ESI Full lock ms [50.0000-750.0000]

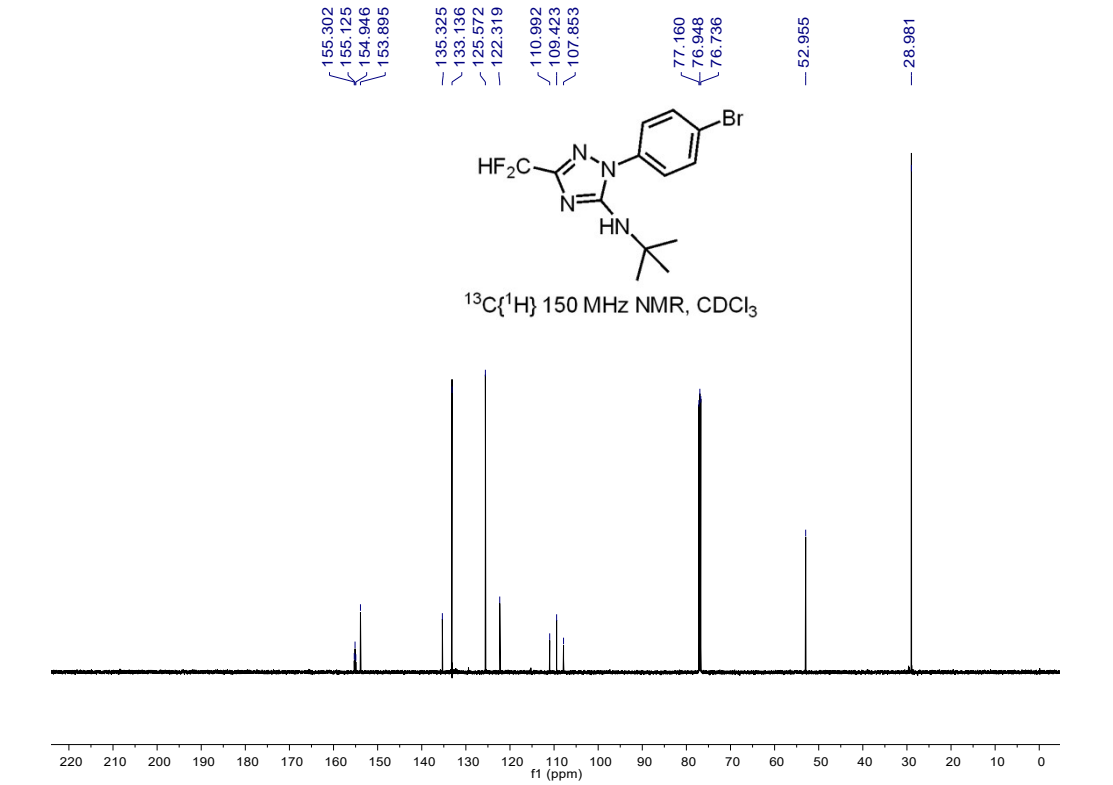
m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
297.1523	1098244480.0	100.00	297.1521	0.19	$C_{14}H_{19}ON_4F_2$
335.0639	606753024.0	55.25			
345.0524	541057216.0	49.27			
347.0503	524785376.0	47.78			

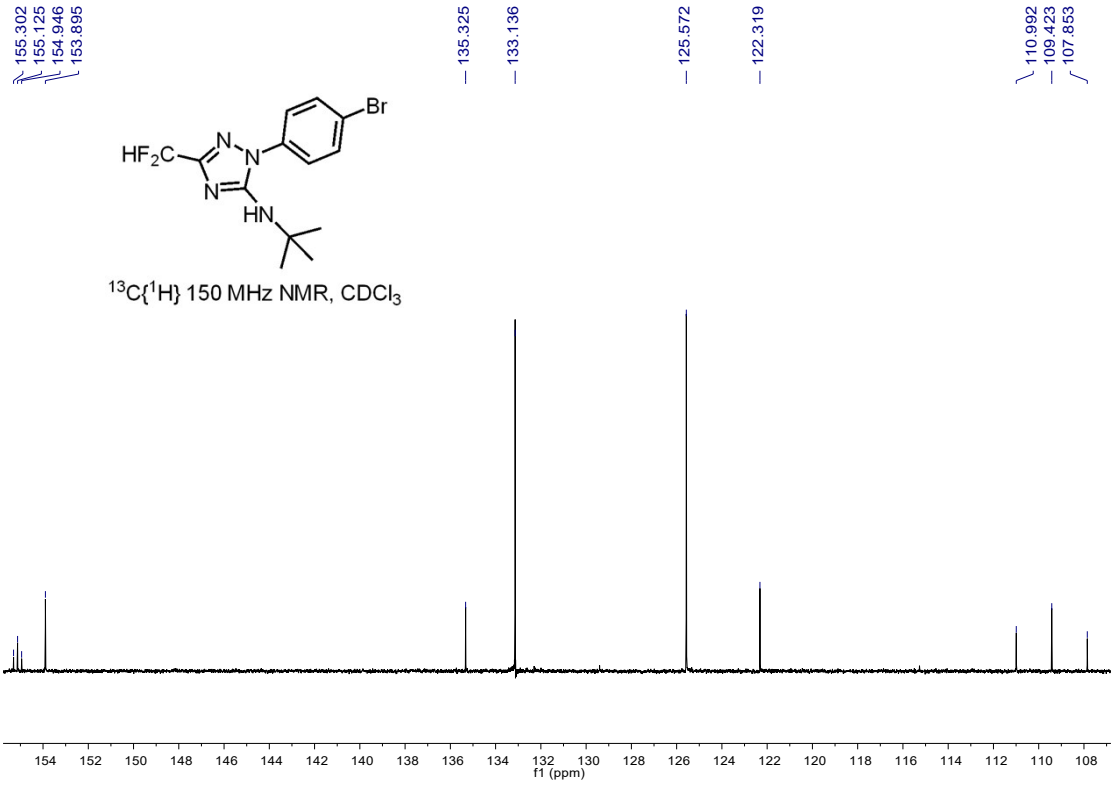


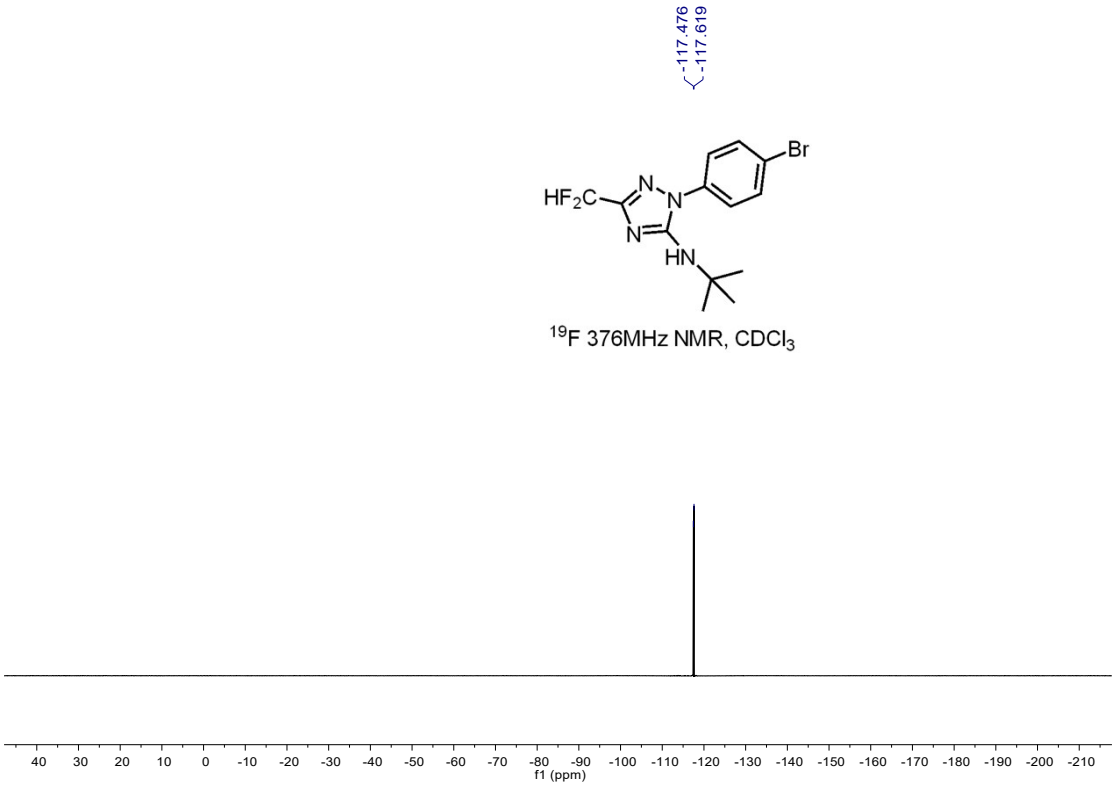
NMR copies of compound **5d**:





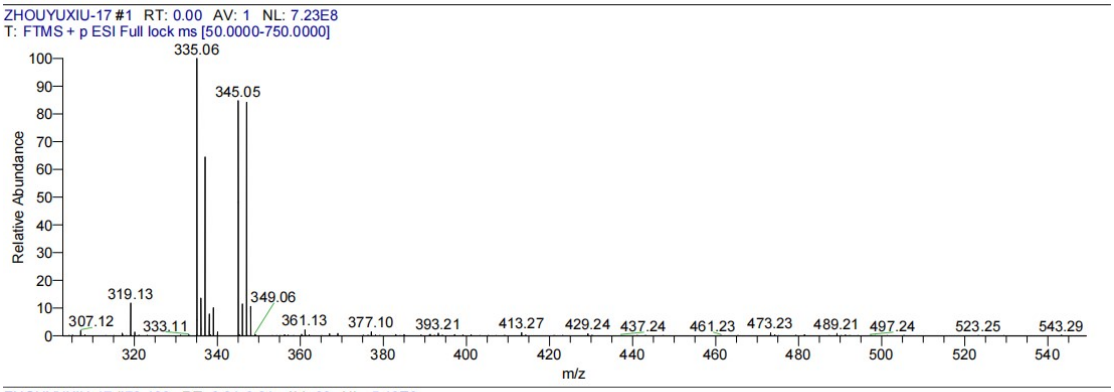

155.302
155.125
154.946
153.895
135.325
133.136
125.572
122.319
110.992
109.423
107.853
77.160
76.948
76.736
52.955
28.981
Br
HF2C
N
N
N
HN
13C{1H} 150 MHz NMR, CDCl3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

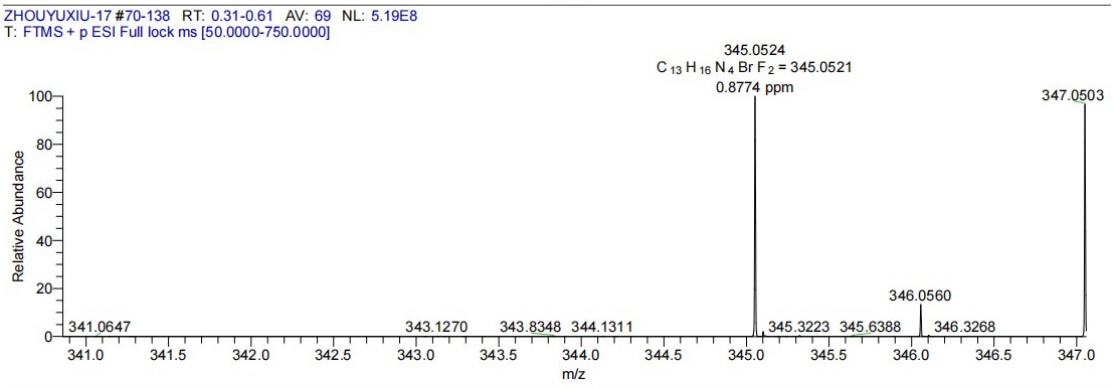

155.302
155.125
154.946
153.895
135.325
133.136
125.572
122.319
110.992
109.423
107.853
Br
HF2C
N
N
N
HN
13C{1H} 150 MHz NMR, CDCl3
154 152 150 148 146 144 142 140 138 136 134 132 130 128 126 124 122 120 118 116 114 112 110 108
f1 (ppm)



^{19}F 376MHz NMR, $CDCl_3$

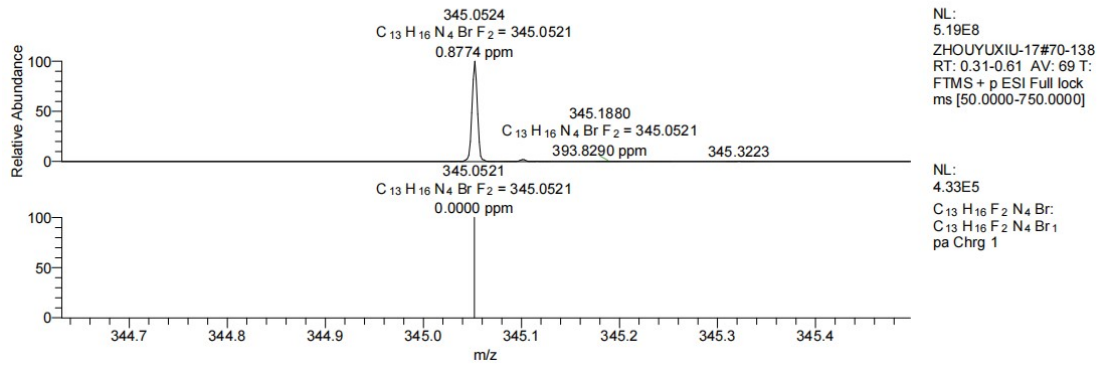
HRMS (ESI) copy of compound **5d**:



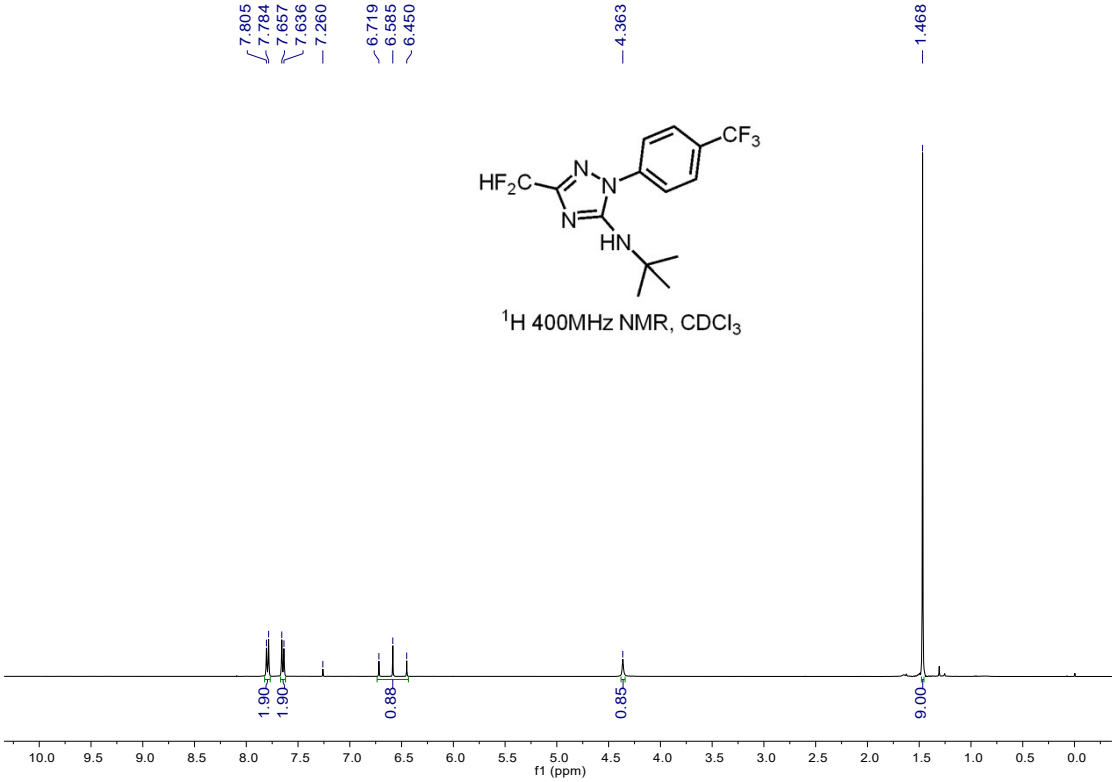


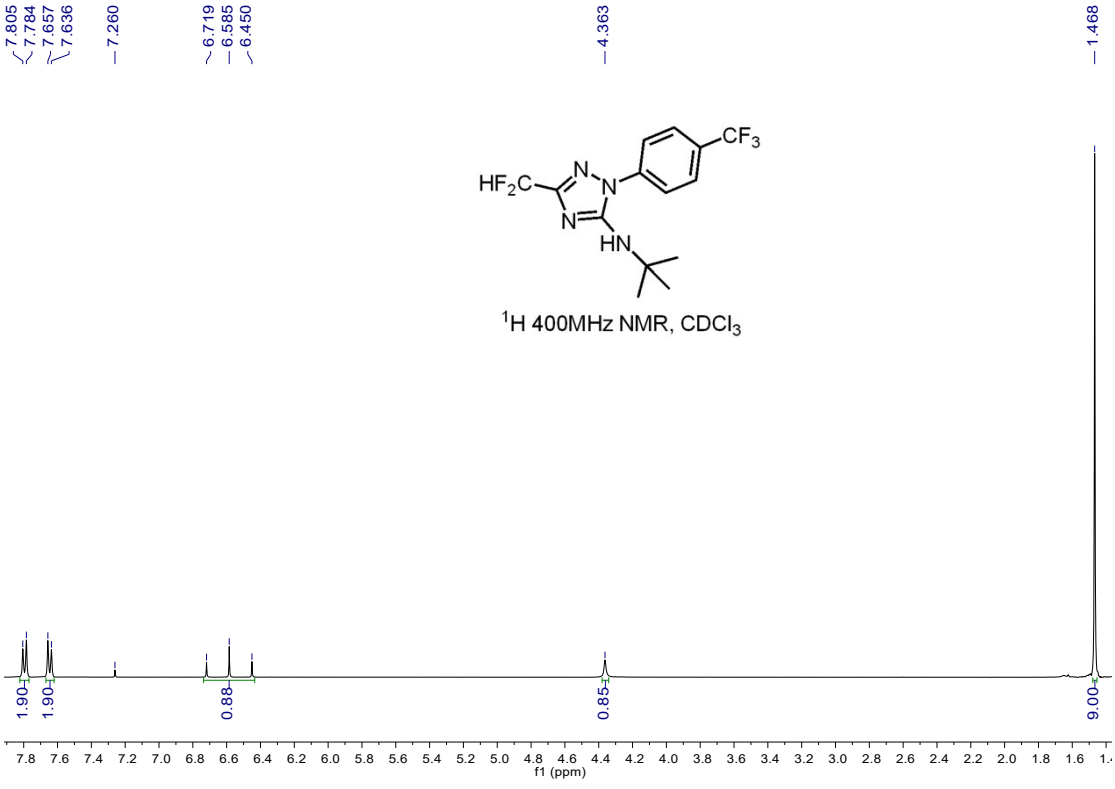
ZHOUYUXIU-17#70-138 RT: 0.31-0.61 AV: 69
T: FTMS + p ESI Full lock ms [50.0000-750.0000]
m/z= 340.8593-347.0574

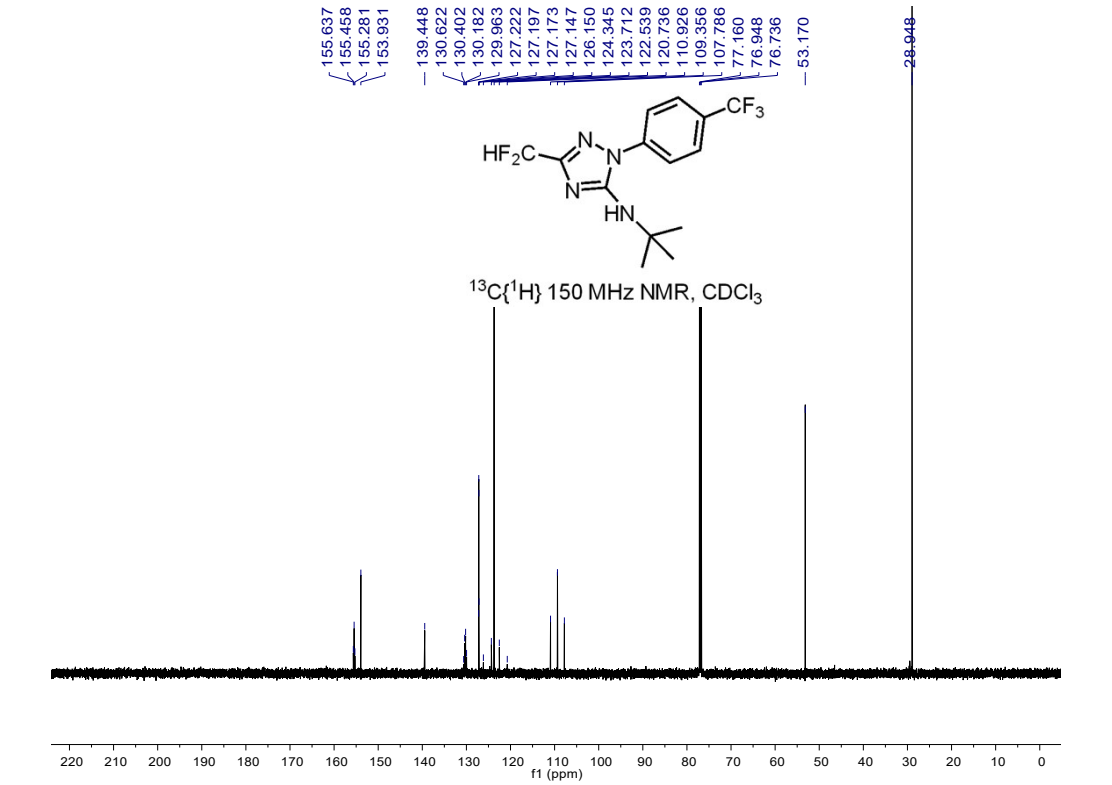
m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
345.0524	518549632.0	100.00	345.0521	0.30	$C_{13}H_{16}N_4BrF_2$
345.1015	10421096.0	2.01	345.0521	49.45	$C_{13}H_{16}N_4BrF_2$
346.0560	69466792.0	13.40			
347.0503	501657216.0	96.74			

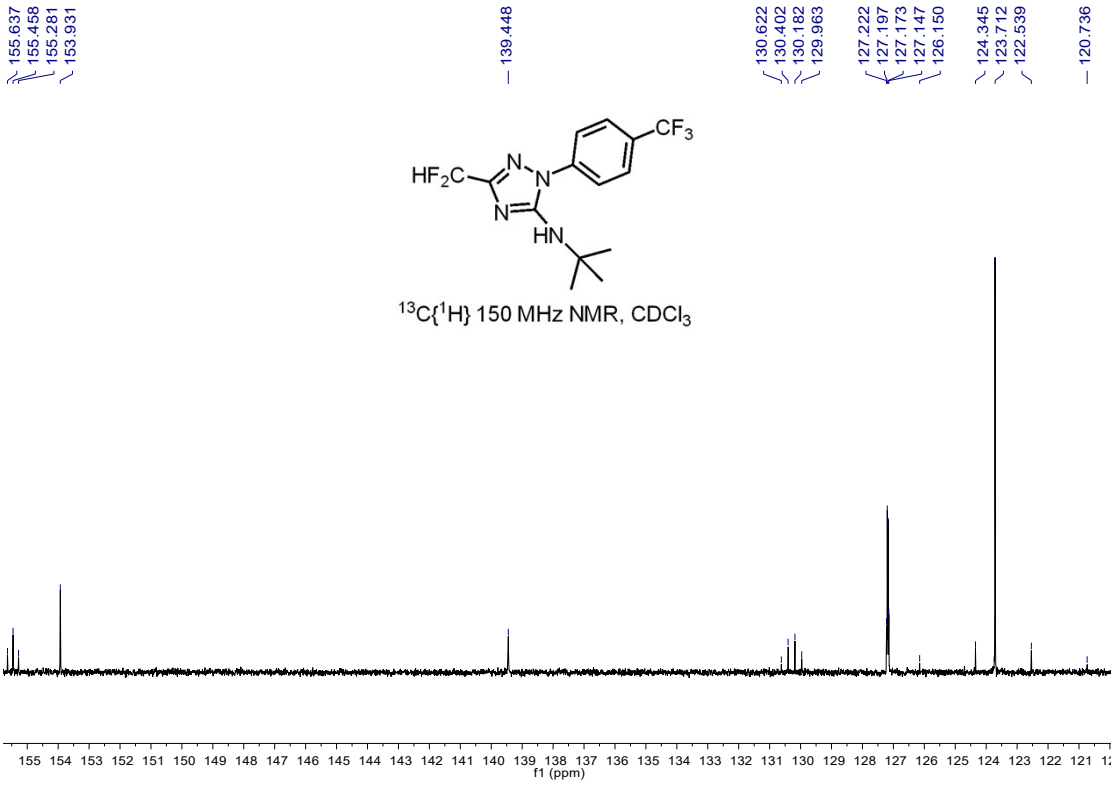


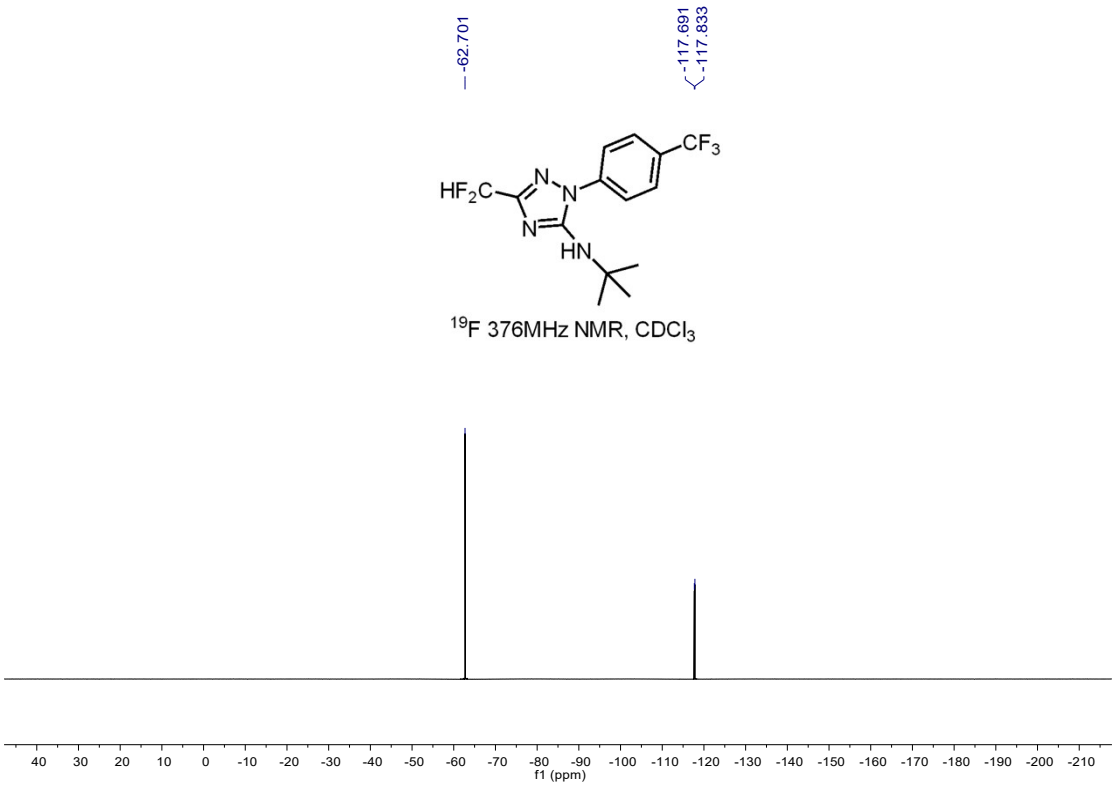
NMR copies of compound **5e**:



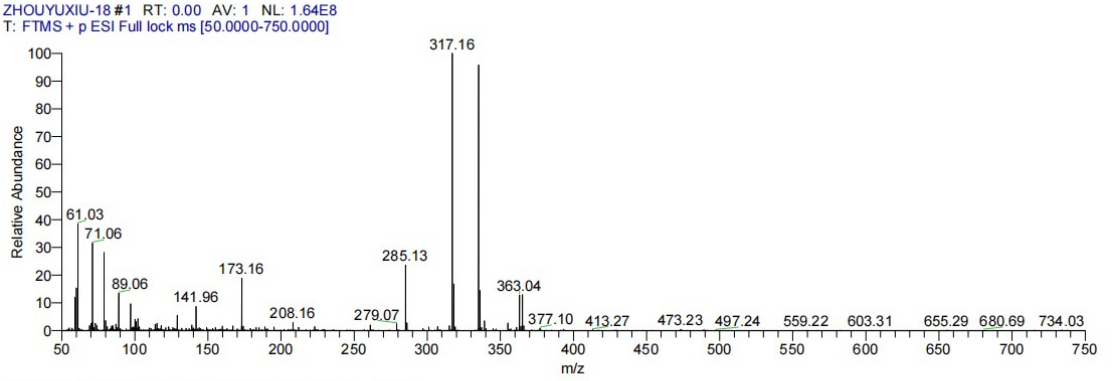


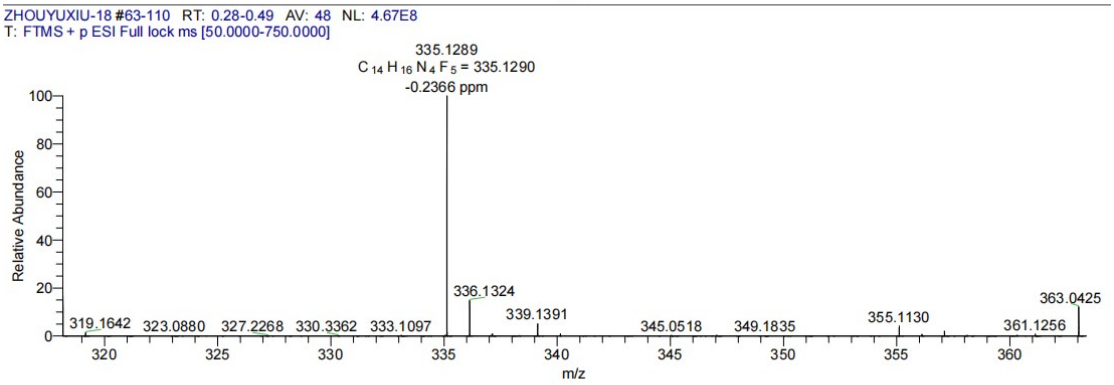

155.637
155.458
155.281
153.931
139.448
130.622
130.402
130.182
129.963
127.222
127.197
127.173
127.147
126.150
124.345
123.712
122.539
120.736
110.926
109.356
107.786
77.160
76.948
76.736
53.170
28.948
CF3
HF2C
N
N
N
HN
13C{1H} 150 MHz NMR, CDCl3
f1 (ppm)


155.637
155.458
155.281
153.931
139.448
130.622
130.402
130.182
129.963
127.222
127.197
127.173
127.147
126.150
124.345
123.712
122.539
120.736
CF3
HF2C
N
N
N
HN
13C{1H} 150 MHz NMR, CDCl3
f1 (ppm)


-62.701
-117.691
-117.833
CF3
HF2C
N
N
N
HN
19F 376MHz NMR, CDCl3
40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

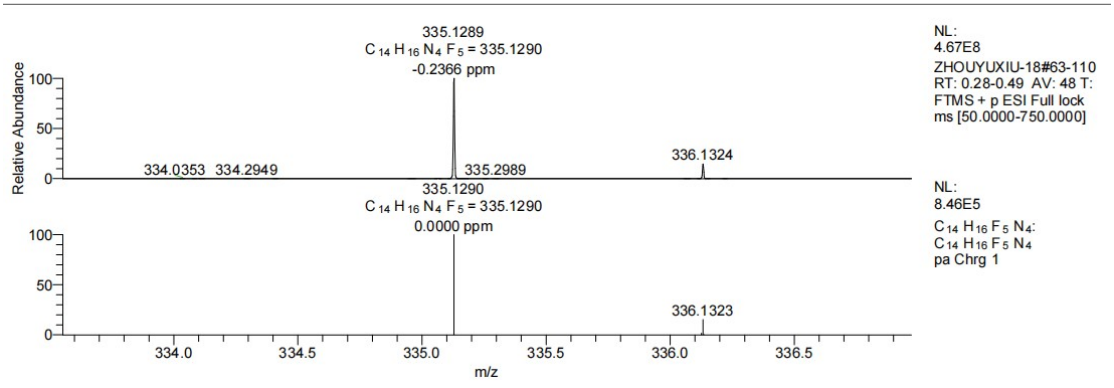
HRMS (ESI) copy of compound **5e**:



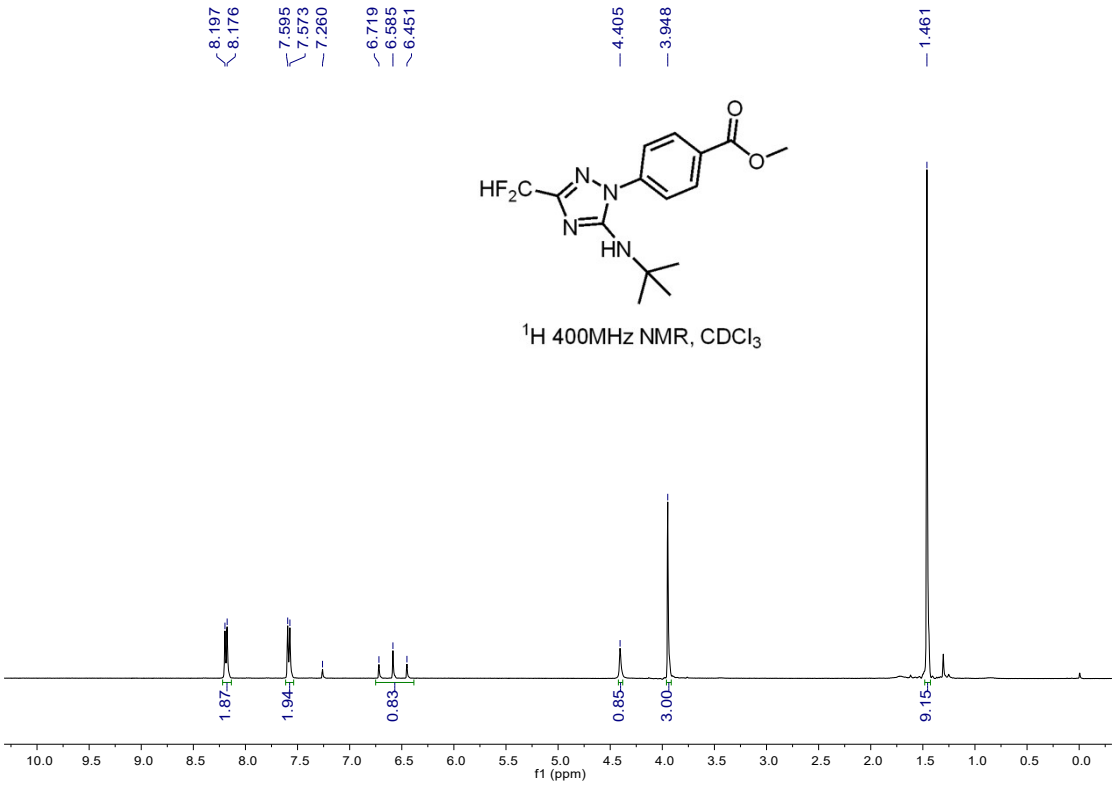


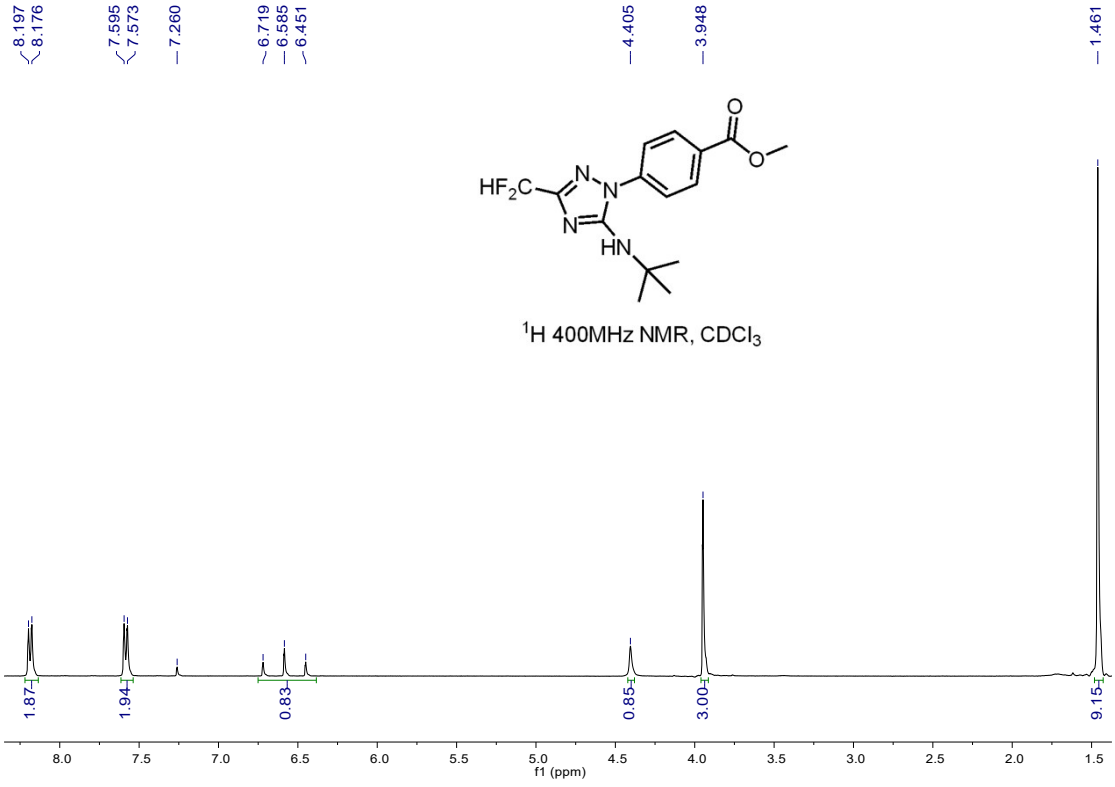
ZHOUYUXIU-18#63-110 RT: 0.28-0.49 AV: 48
T: FTMS + p ESI Full lock ms [50.0000-750.0000]
m/z= 318.1525-363.3721

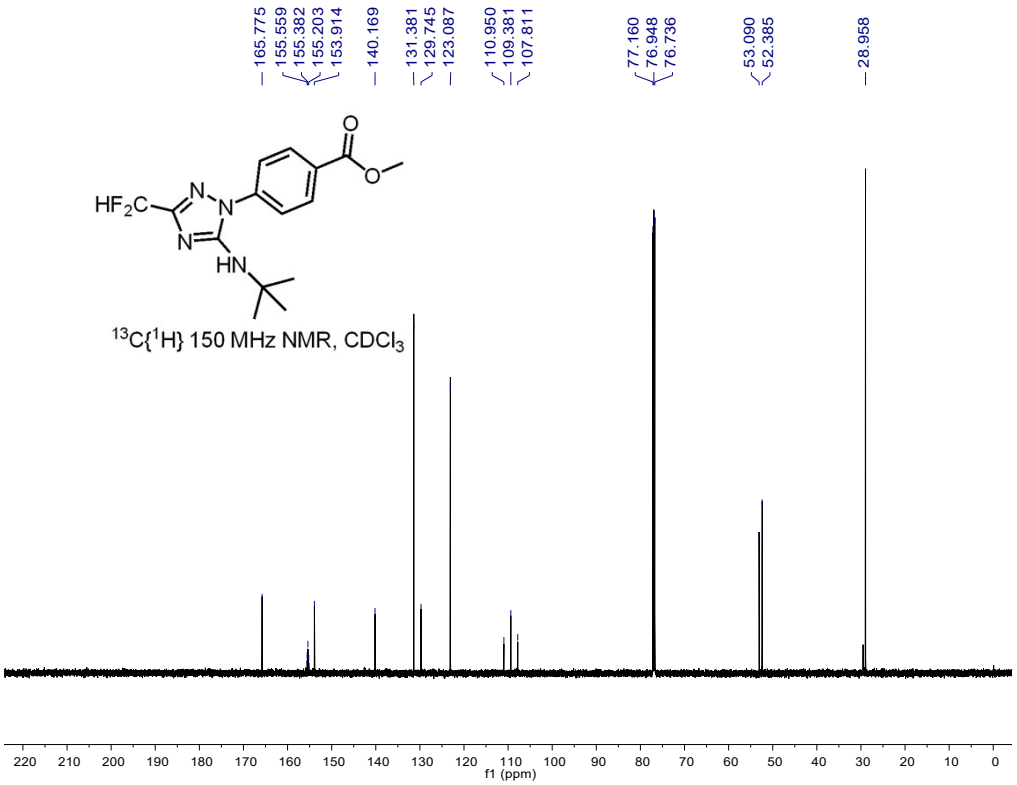
m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
318.1606	81946816.0	17.06			
335.1289	480246944.0	100.00	335.1290	-0.08	$C_{14}H_{16}N_4F_5$
336.1324	68875624.0	14.34			
363.0425	58229916.0	12.12			

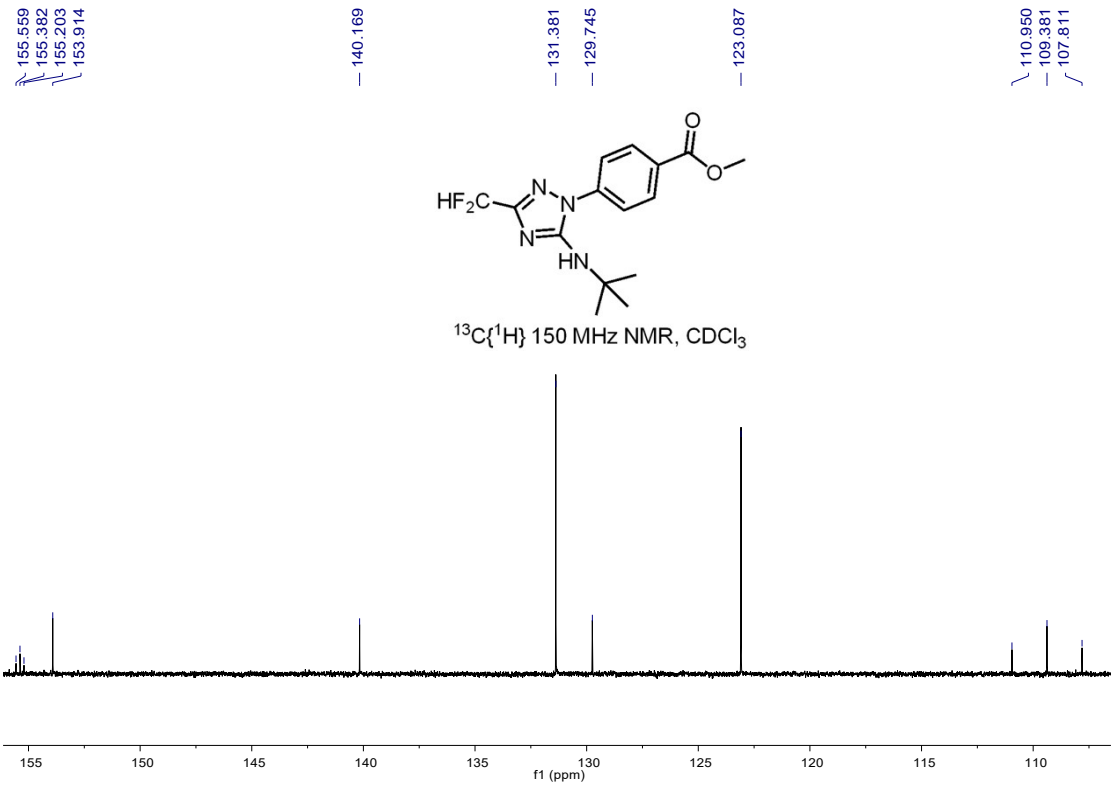


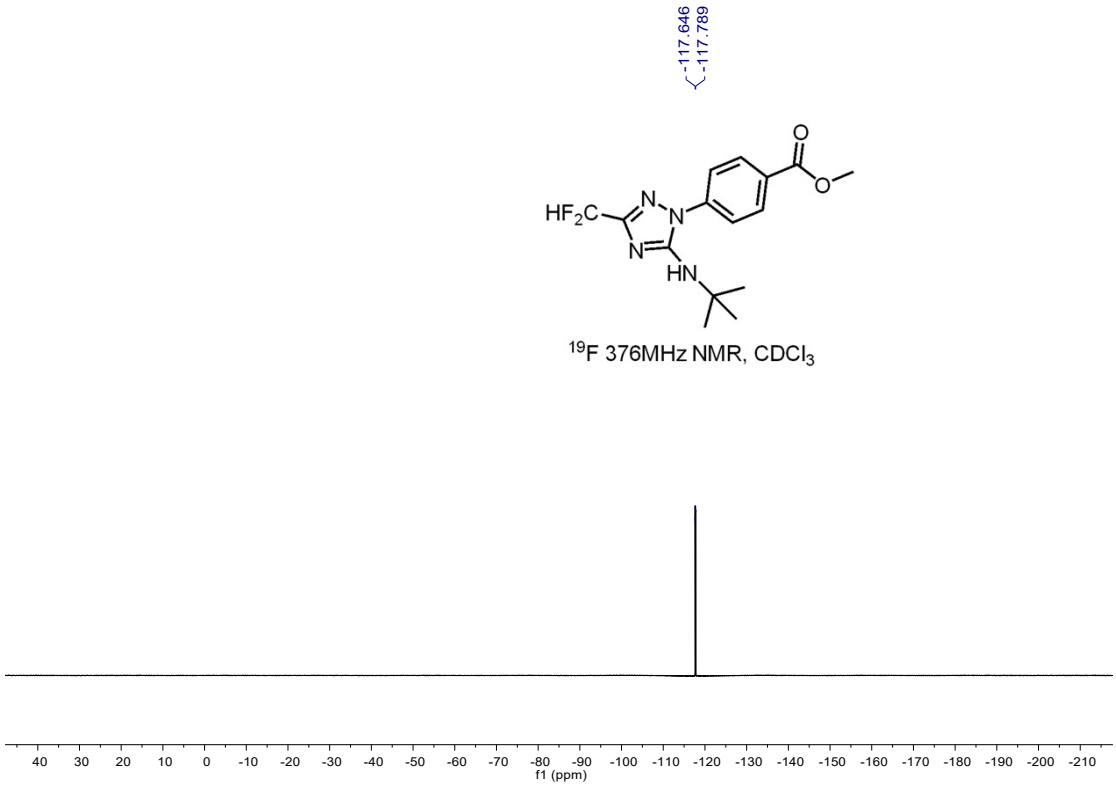
NMR copies of compound **5f**:



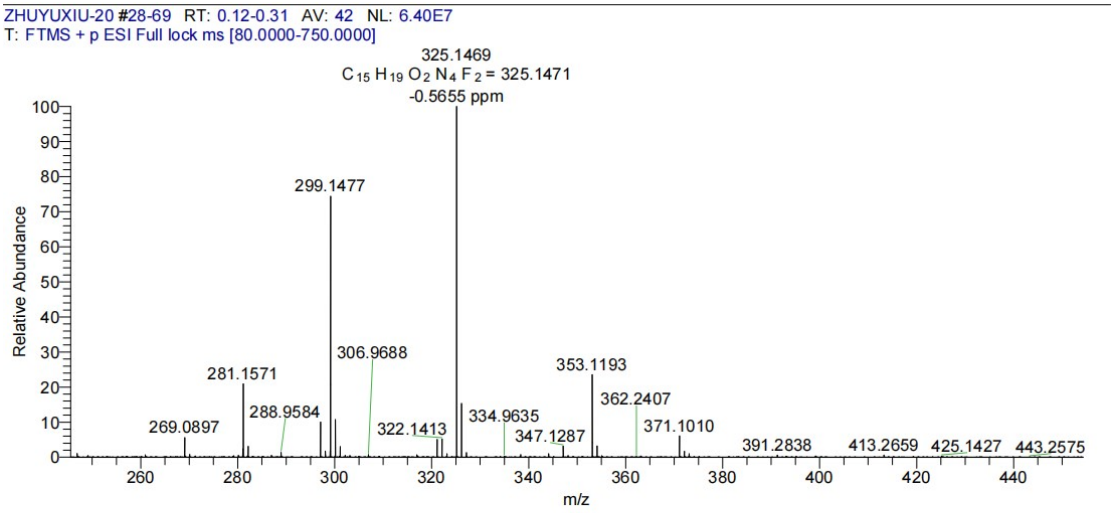



165.775
155.559
155.382
155.203
153.914
140.169
131.381
129.745
123.087
110.950
109.381
107.811
77.160
76.948
76.736
53.090
52.385
28.958
HF2C
N
N
N
HN
O
O
13C{1H} 150 MHz NMR, CDCl3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


155.559
155.382
155.203
153.914
140.169
131.381
129.745
123.087
110.950
109.381
107.811
HF2C
N
N
N
HN
O
O
13C{1H} 150 MHz NMR, CDCl3
155 150 145 140 135 130 125 120 115 110
f1 (ppm)

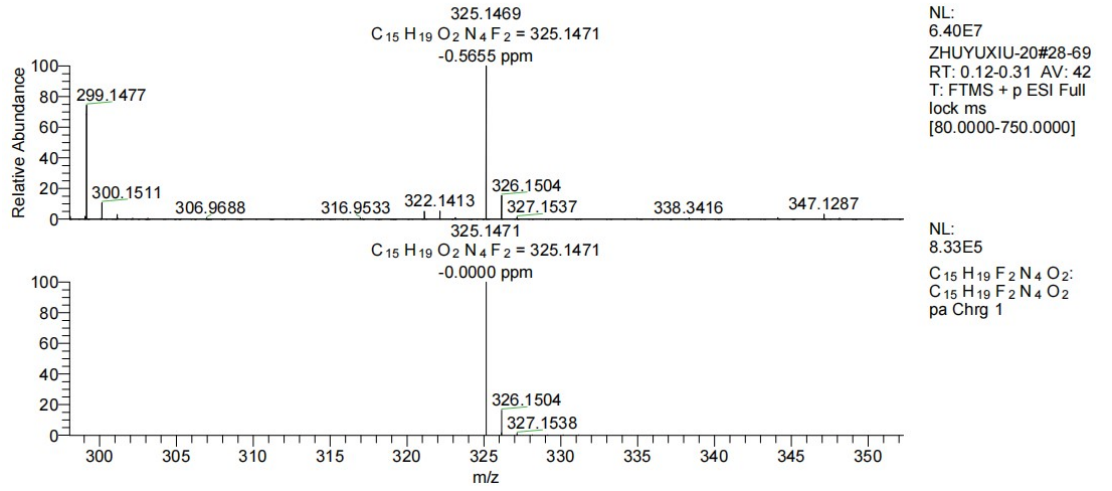

-117.646
-117.789
O
O
N
N
N
HF2C
HN
19F 376MHz NMR, CDCl3
40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

HRMS (ESI) copy of compound **5f**:

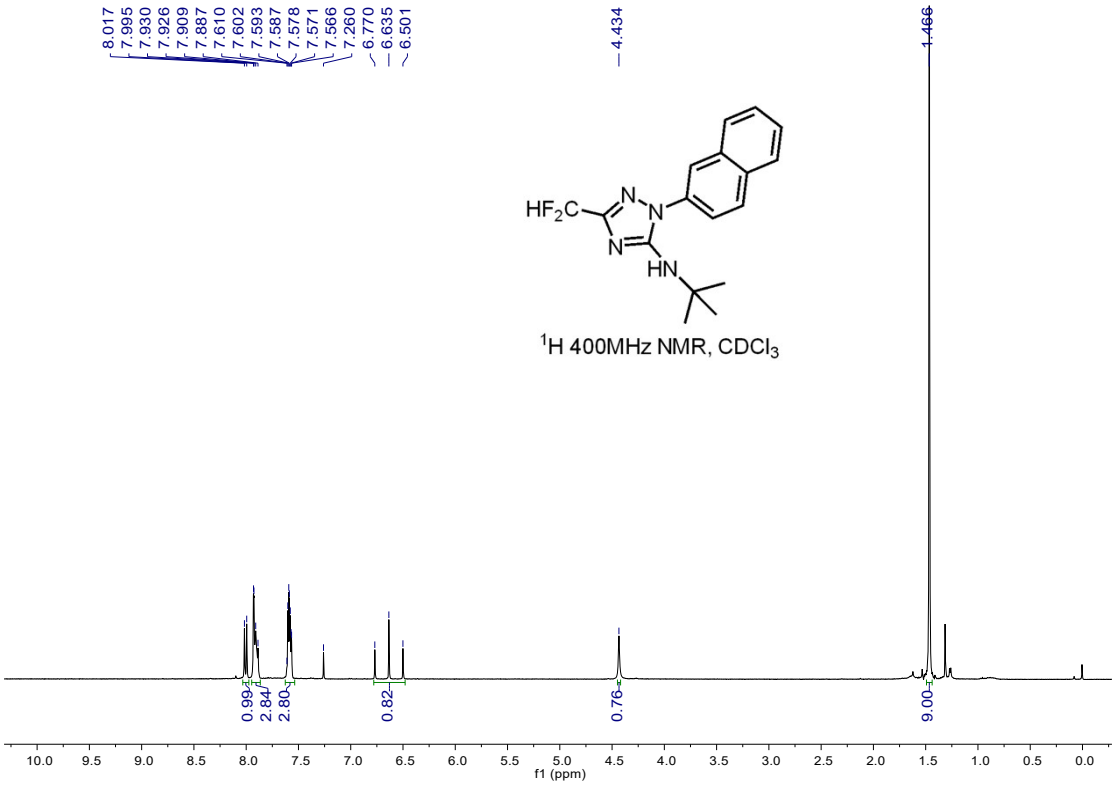


ZHUYUXIU-20#28-69 RT: 0.12-0.31 AV: 42
T: FTMS + p ESI Full lock ms [80.0000-750.0000]
m/z= 245.5346-454.3090

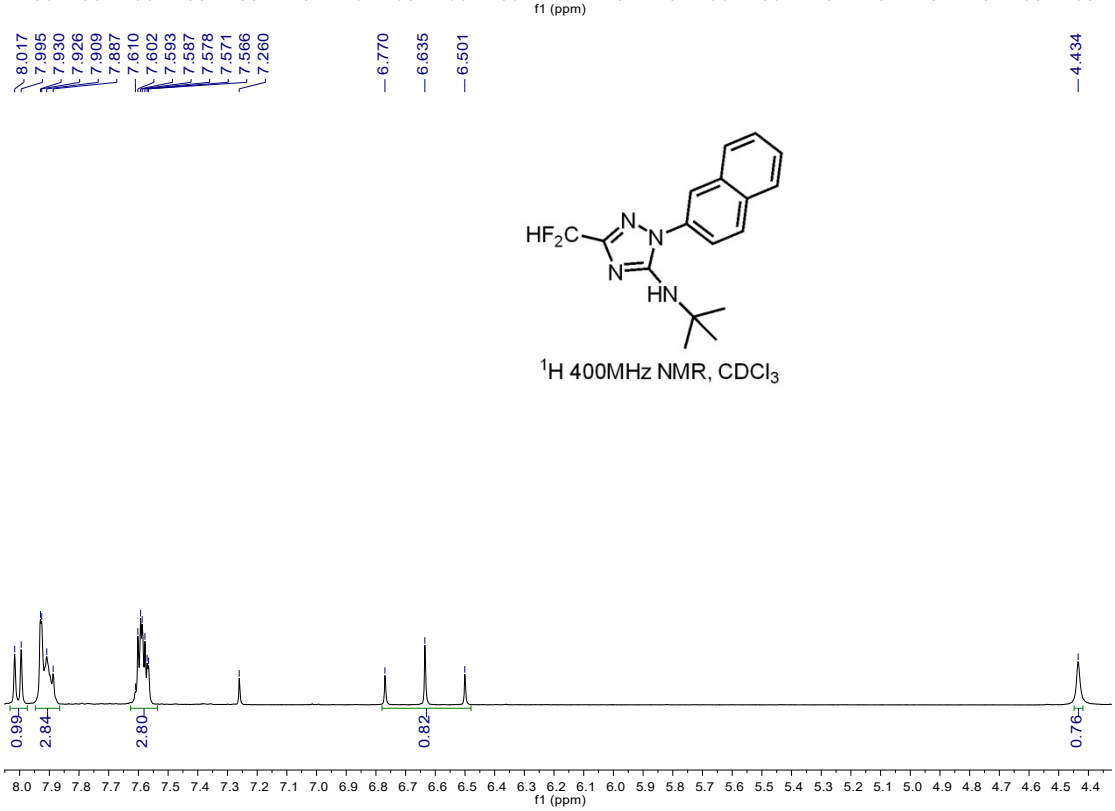
m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
281.1571	13642548.0	21.32			
299.1477	48133296.0	75.22			
325.1469	63993288.0	100.00	325.1471	-0.18	C15 H19 O2 N4 F2
353.1193	15075819.0	23.56			



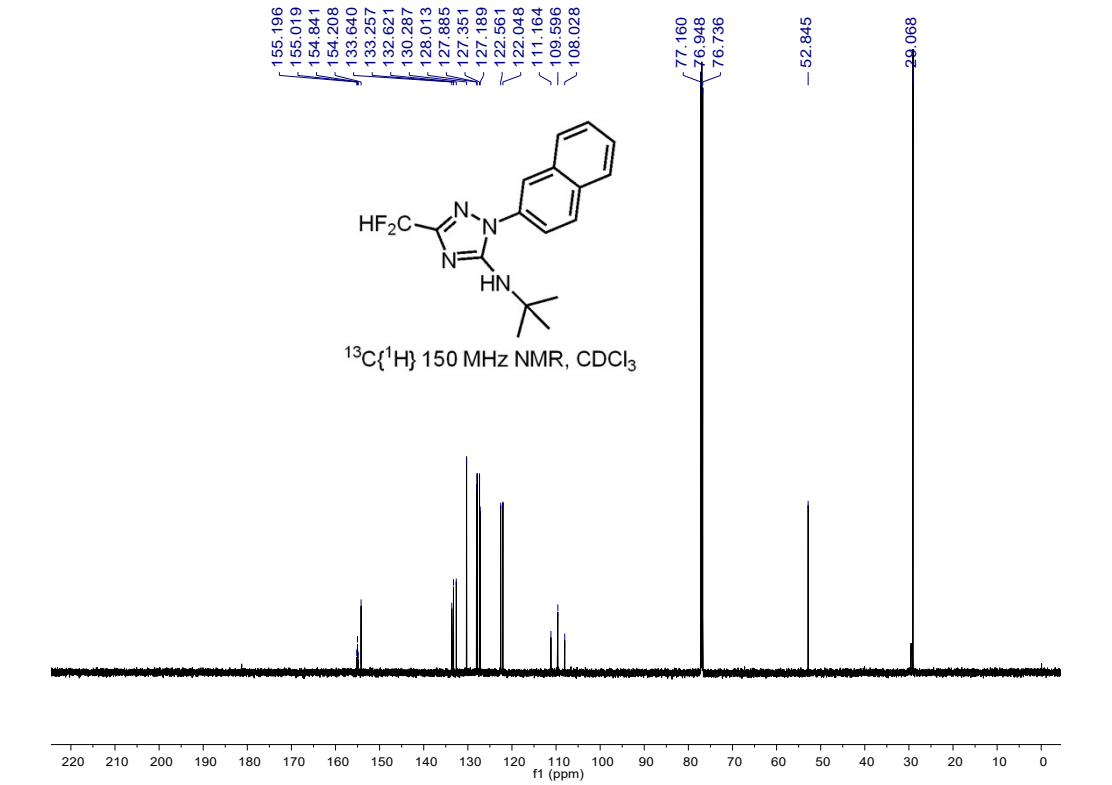
NMR copies of compound **5g**:

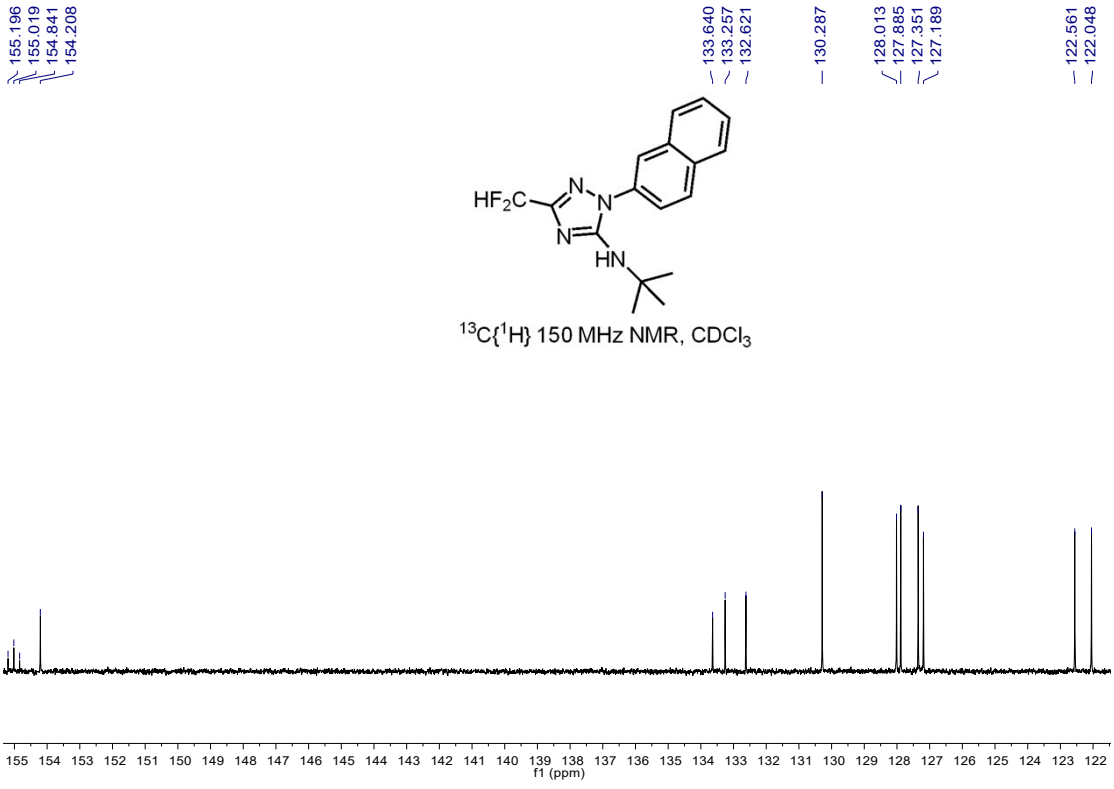


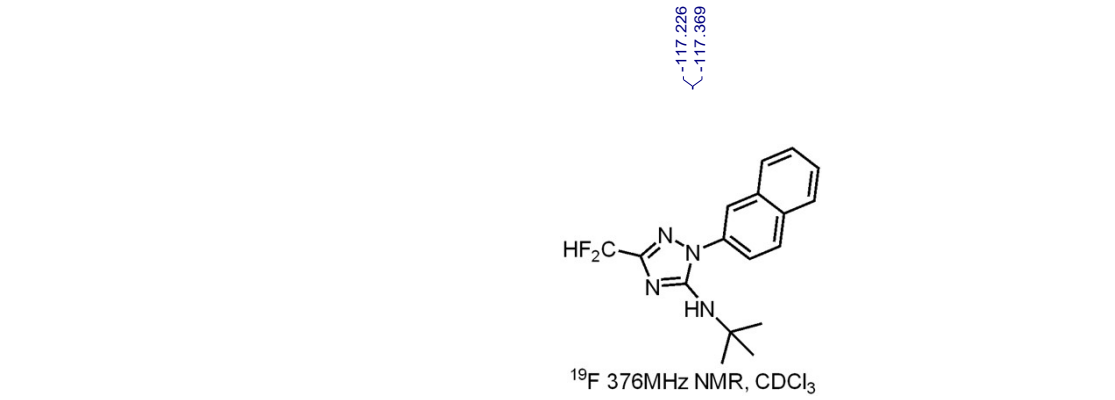
^{1}H 400MHz NMR, $CDCl_3$

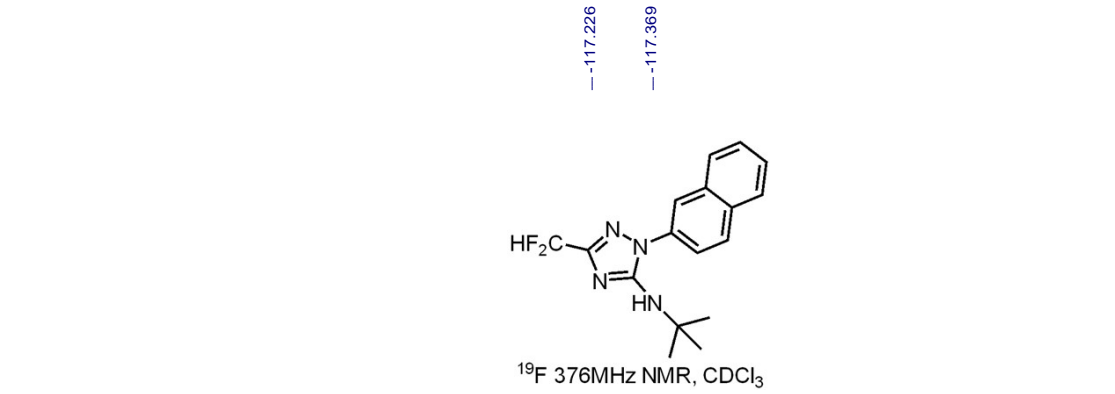


^{1}H 400MHz NMR, $CDCl_3$

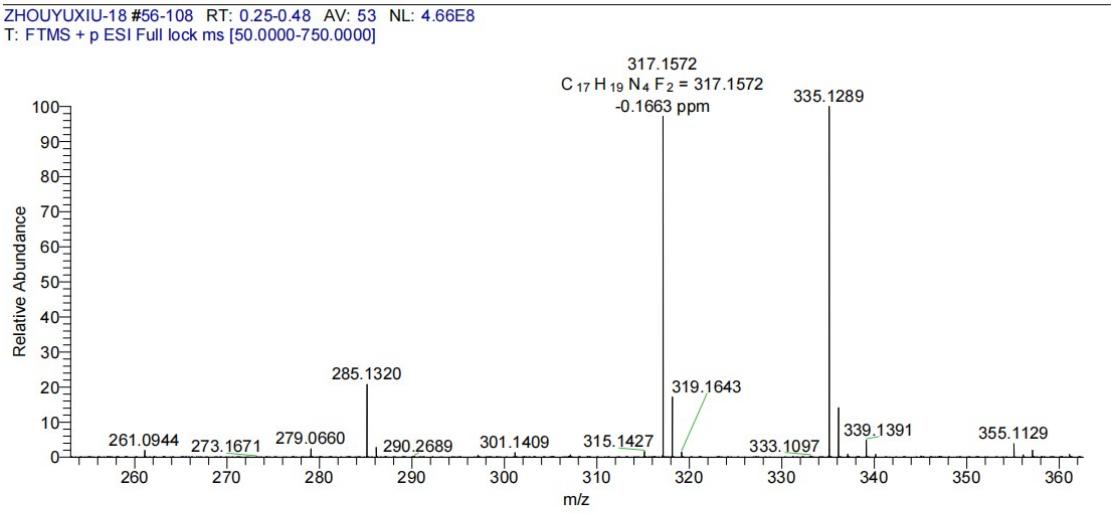

155.196
155.019
154.841
154.208
133.640
133.257
132.621
130.287
128.013
127.885
127.351
127.189
122.561
122.048
111.164
109.596
108.028
77.160
76.948
76.736
52.845
29.068
HF2C
N
N
N
HN
13C{1H} 150 MHz NMR, CDCl3
f1 (ppm)


155.196
155.019
154.841
154.208
133.640
133.257
132.621
130.287
128.013
127.885
127.351
127.189
122.561
122.048
HF2C
N
N
N
HN
13C{1H} 150 MHz NMR, CDCl3
f1 (ppm)


-117.226
-117.369
HF2C
N
N
N
HN
19F 376MHz NMR, CDCl3
40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

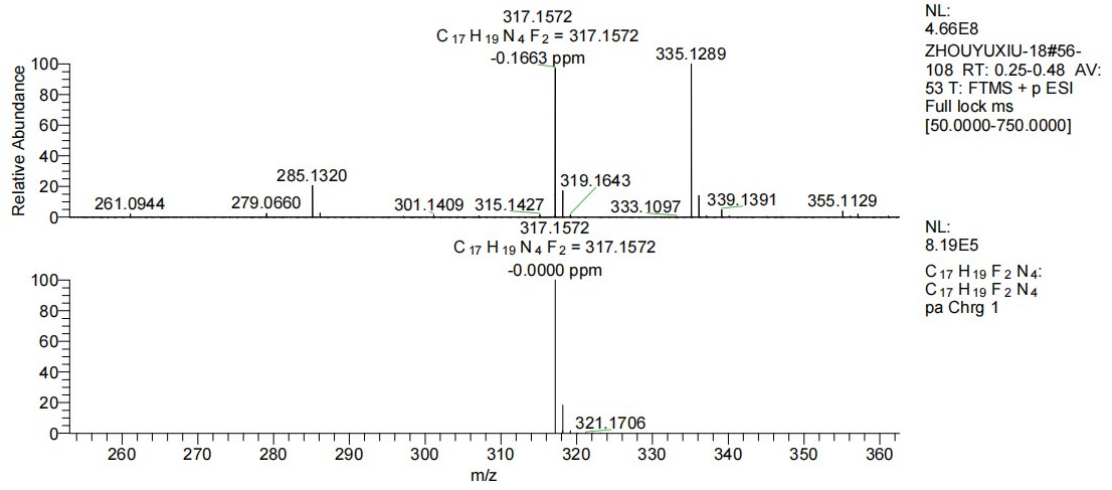

-117.226
-117.369
HF2C
N
N
N
HN
19F 376MHz NMR, CDCl3
-115.9 -116.0 -116.1 -116.2 -116.3 -116.4 -116.5 -116.6 -116.7 -116.8 -116.9 -117.0 -117.1 -117.2 -117.3 -117.4 -117.5 -117.6 -117.7 -117.8 -117.9 -118.0 -118.1 -118.2 -118.3
f1 (ppm)

HRMS (ESI) copy of compound **5g**:

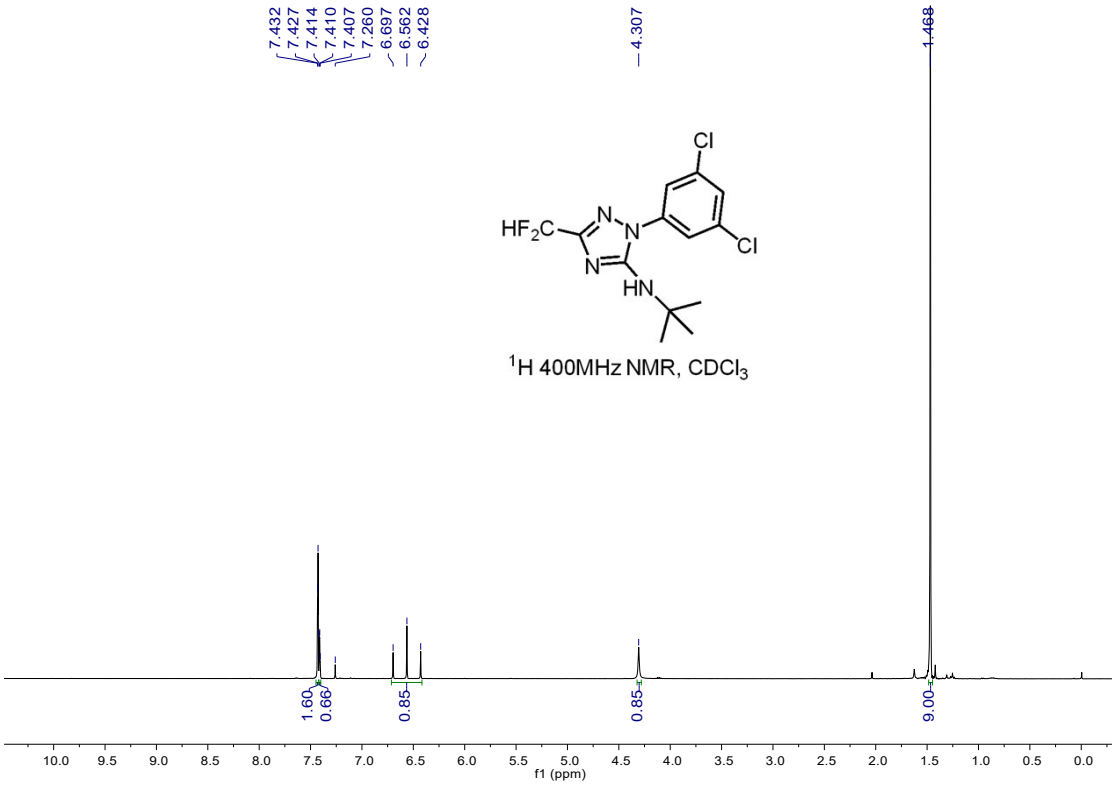


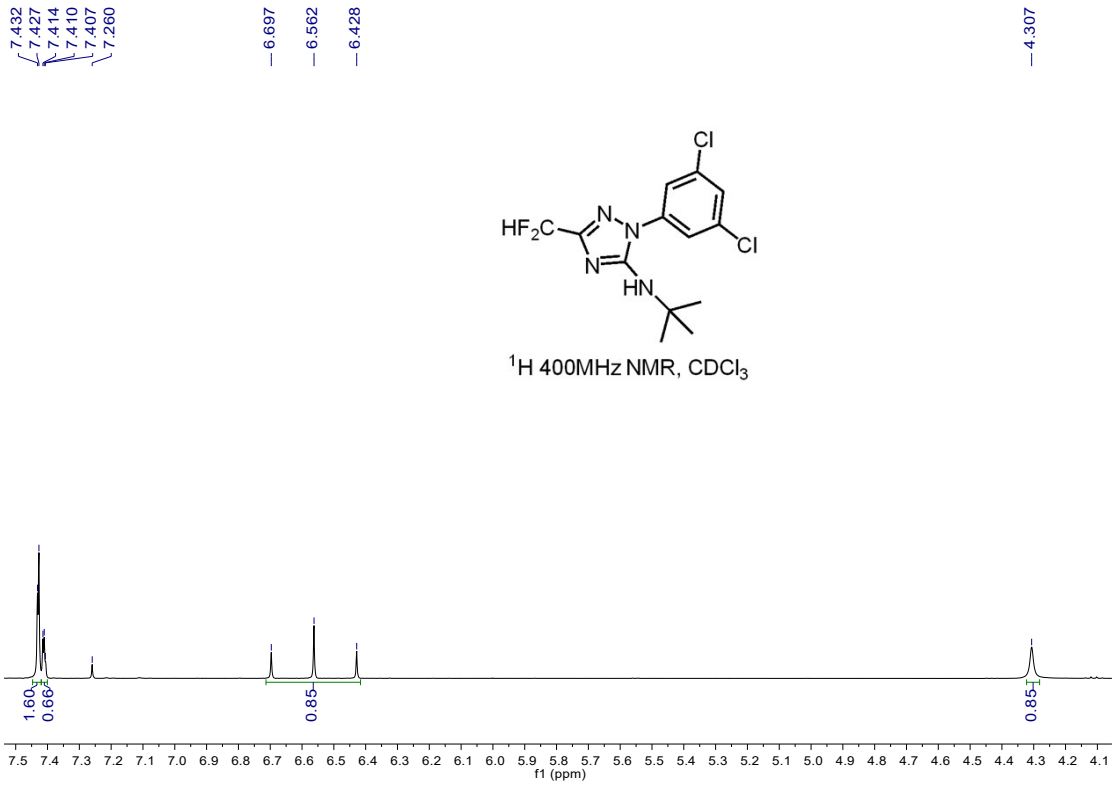
ZHOUYUXIU-18#56-108 RT: 0.25-0.48 AV: 53
T: FTMS + p ESI Full lock ms [50.0000-750.0000]
m/z= 253.0639-362.5815

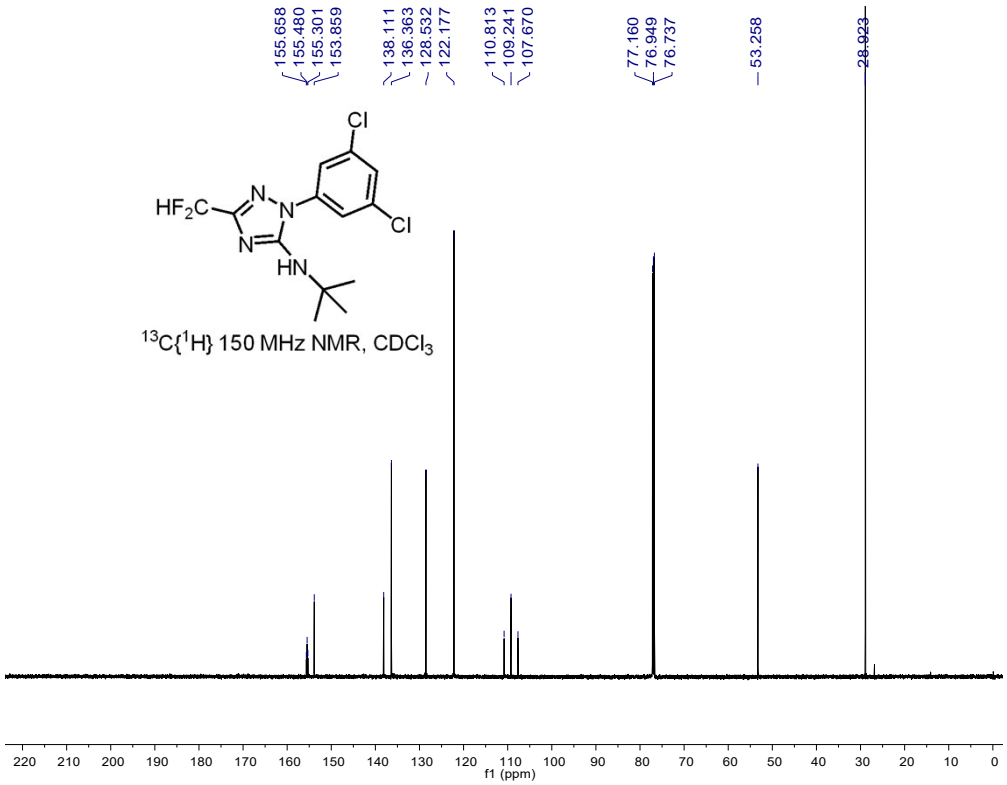
m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
285.1320	96624424.0	20.67			
317.1572	455982752.0	97.56	317.1572	-0.05	$C_{17}H_{19}N_4F_2$
318.1608	80517016.0	17.23			
335.1289	467372608.0	100.00			

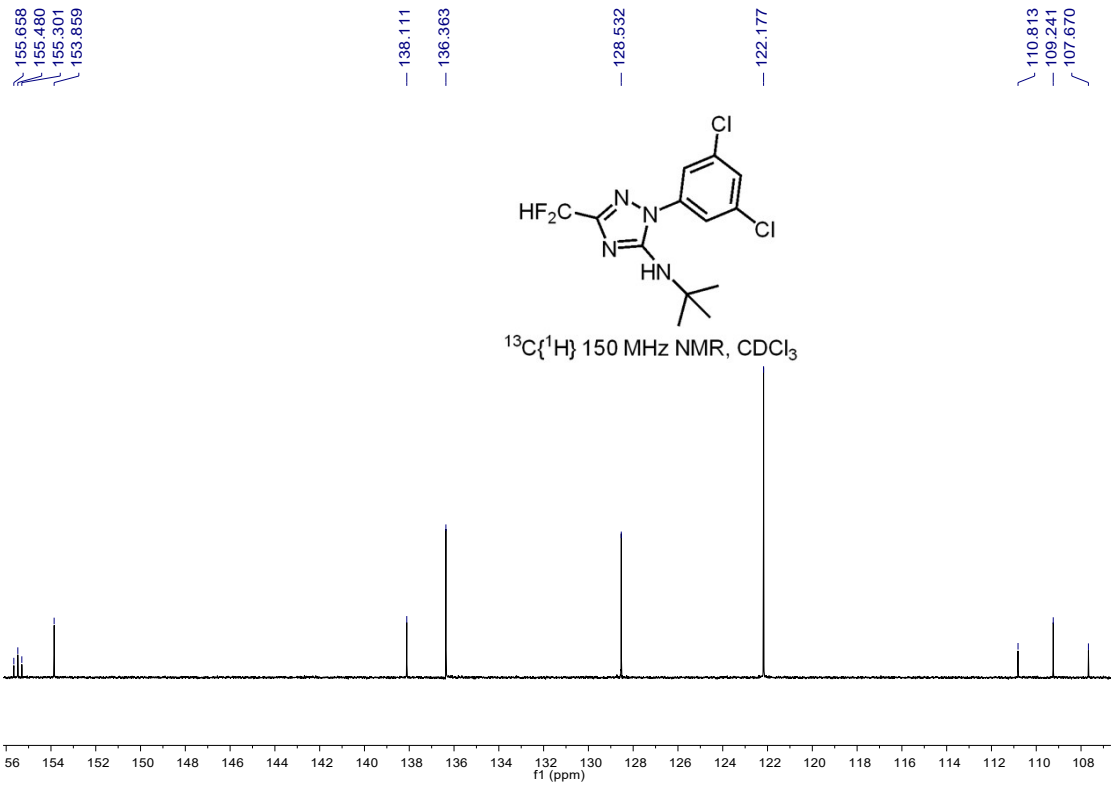


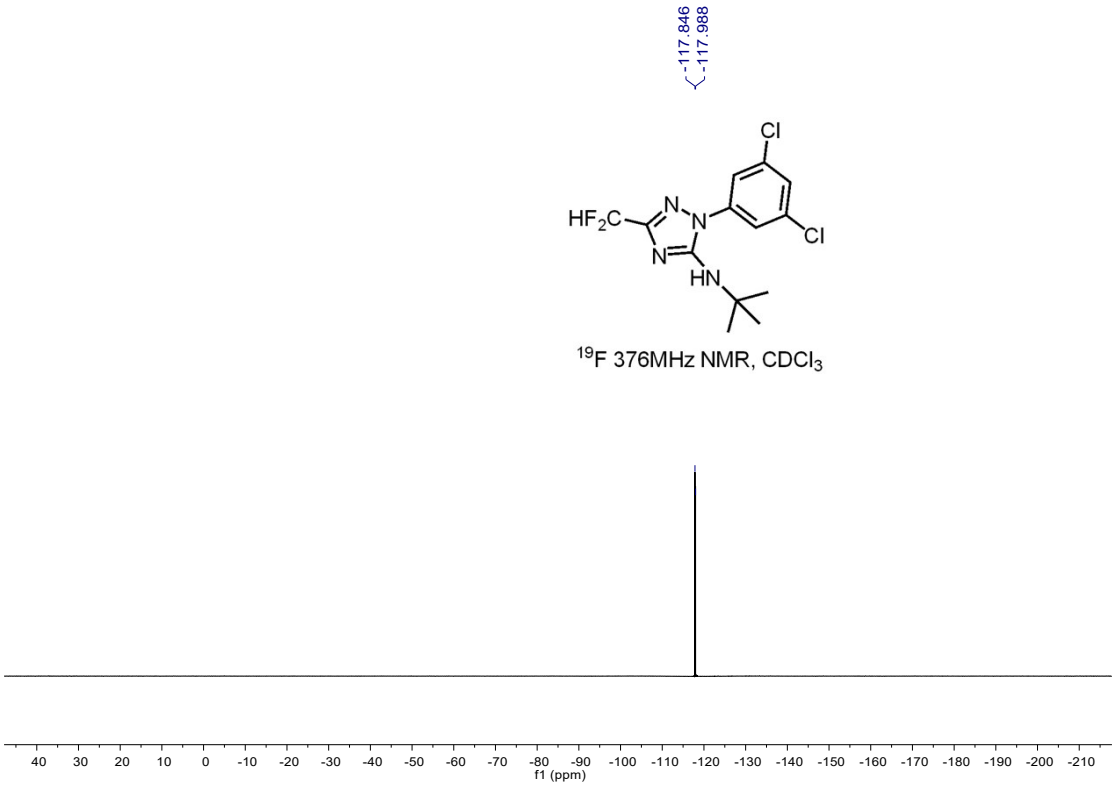
NMR copies of compound **5h**:



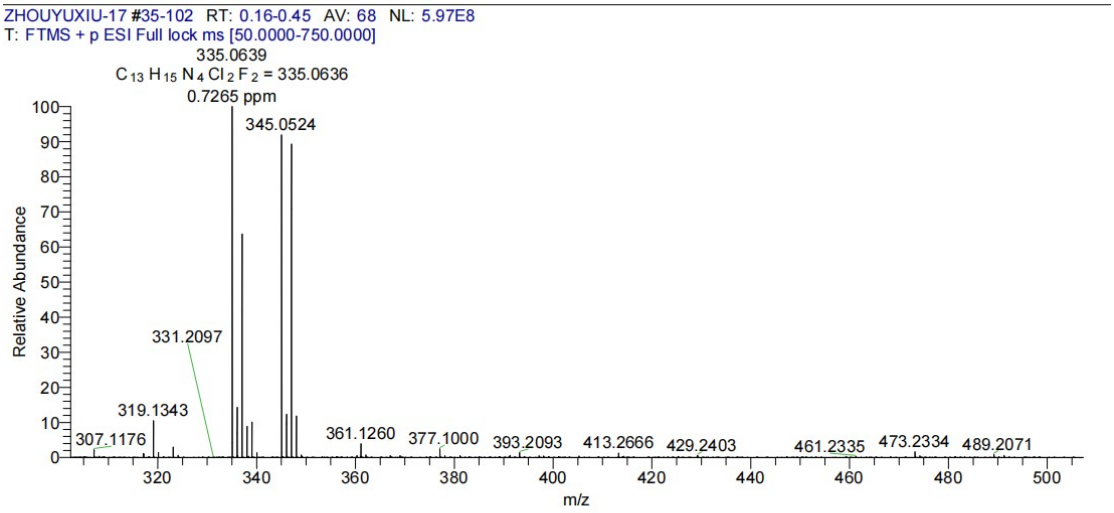



155.658
155.480
155.301
153.859
138.111
136.363
128.532
122.177
110.813
109.241
107.670
77.160
76.949
76.737
53.258
28.923
Cl
HF2C
N
N
N
HN
Cl
13C{1H} 150 MHz NMR, CDCl3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


155.658
155.480
155.301
153.859
138.111
136.363
128.532
122.177
110.813
109.241
107.670
Cl
HF2C
N
N
N
HN
Cl
13C{1H} 150 MHz NMR, CDCl3
56 154 152 150 148 146 144 142 140 138 136 134 132 130 128 126 124 122 120 118 116 114 112 110 108
f1 (ppm)

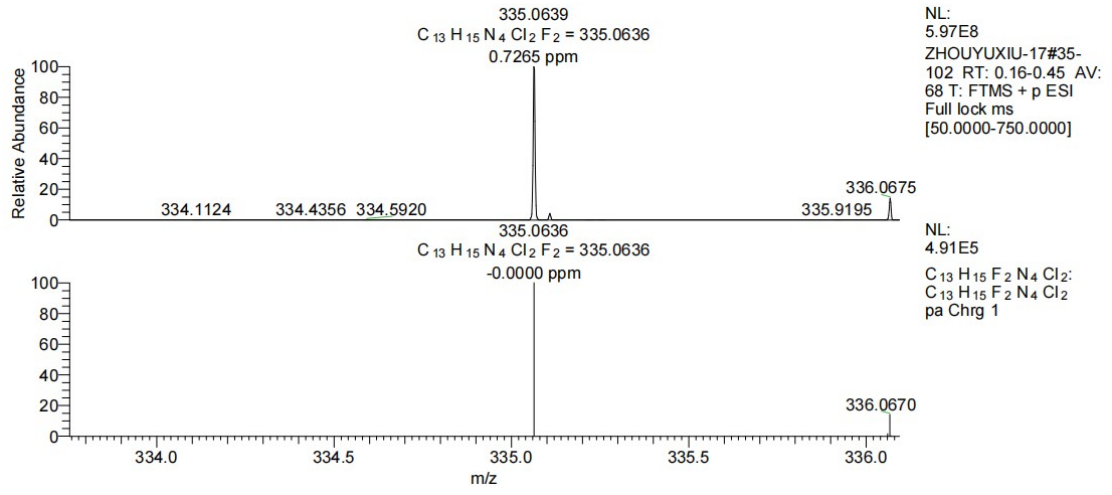

-117.846
-117.988
Cl
Cl
HF2C
N
N
N
HN
19F 376MHz NMR, CDCl3
40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

HRMS (ESI) copy of compound **5h**:



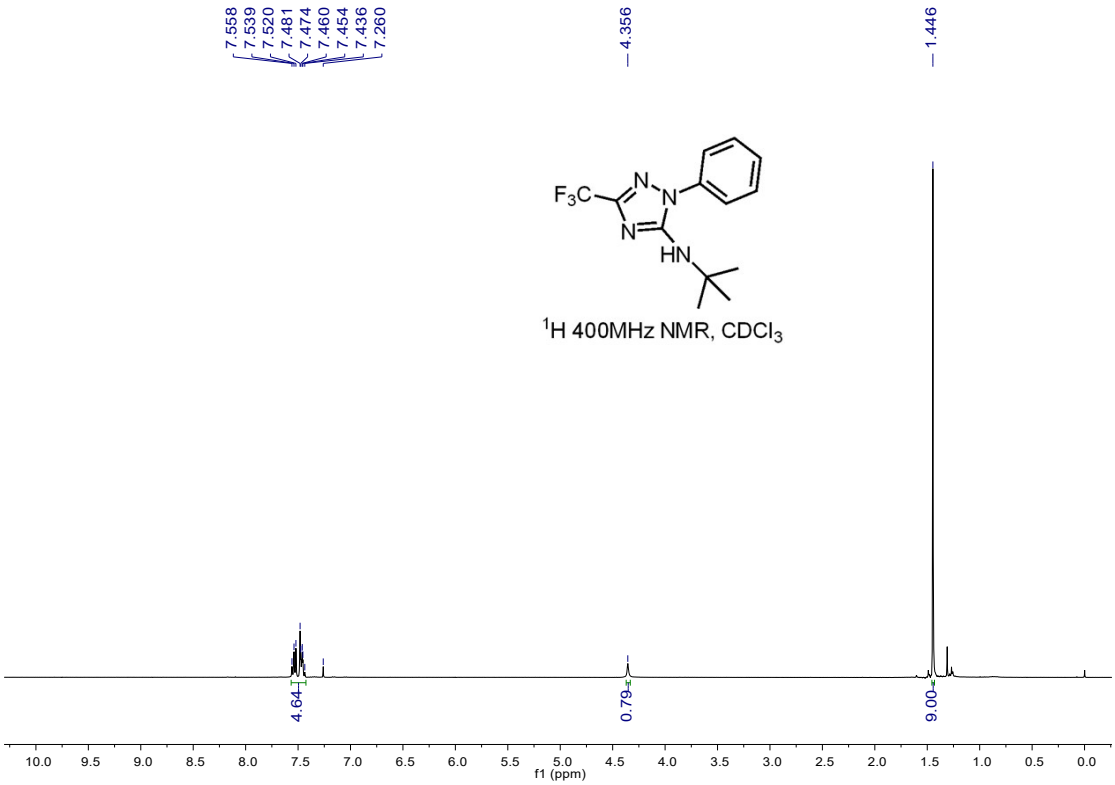
ZHOUYUXIU-17#35-102 RT: 0.16-0.45 AV: 68
T: FTMS + p ESI Full lock ms [50.0000-750.0000]
m/z= 302.3468-507.2360

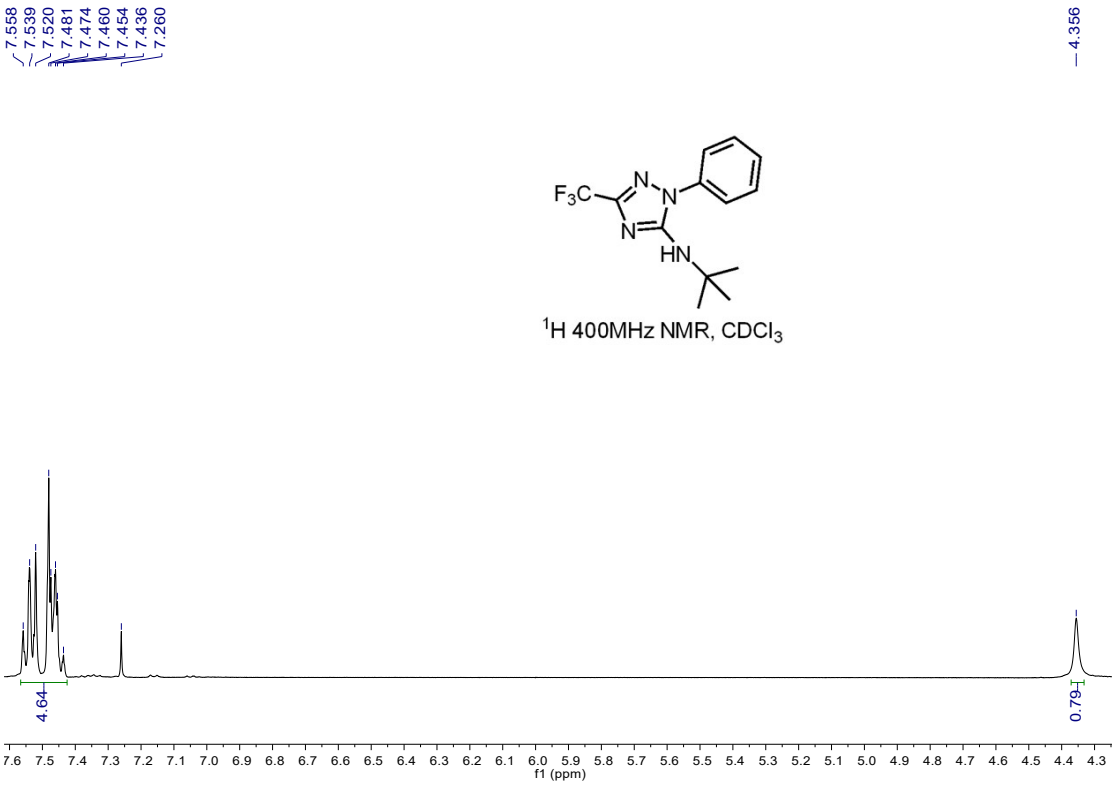
m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
335.0639	615462592.0	100.00	335.0636	0.24	$C_{13}H_{15}N_4Cl_2F_2$
337.0610	390467424.0	63.44			
345.0524	549966208.0	89.36			
347.0503	533407008.0	86.67			

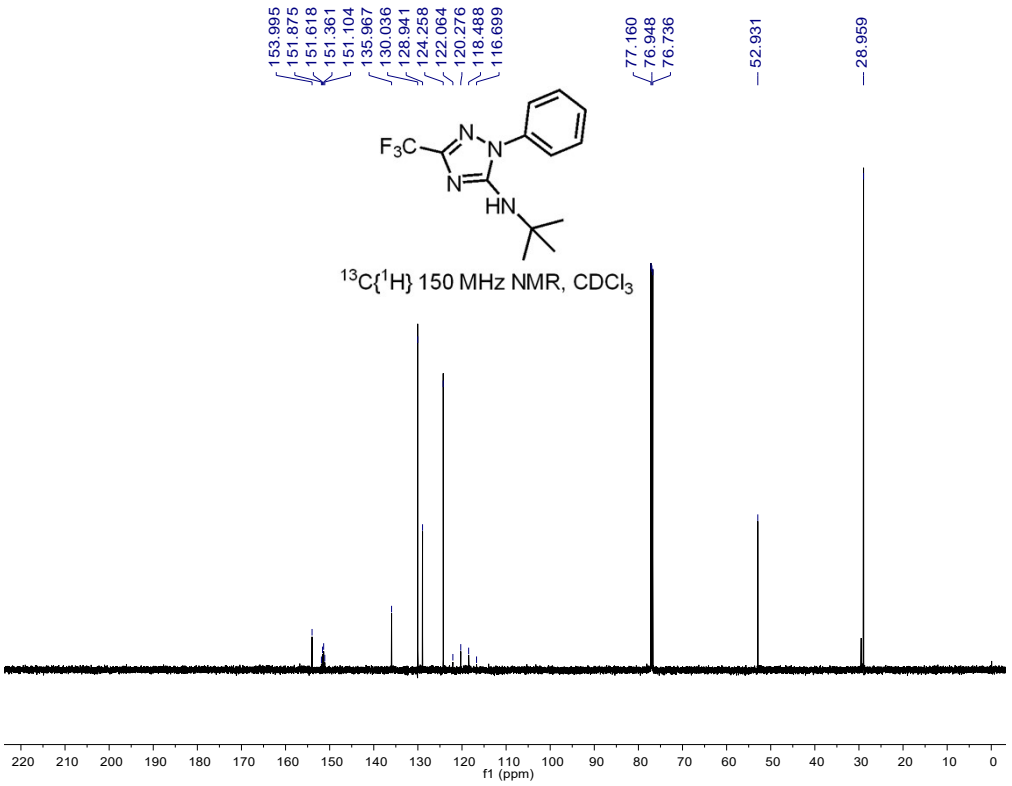


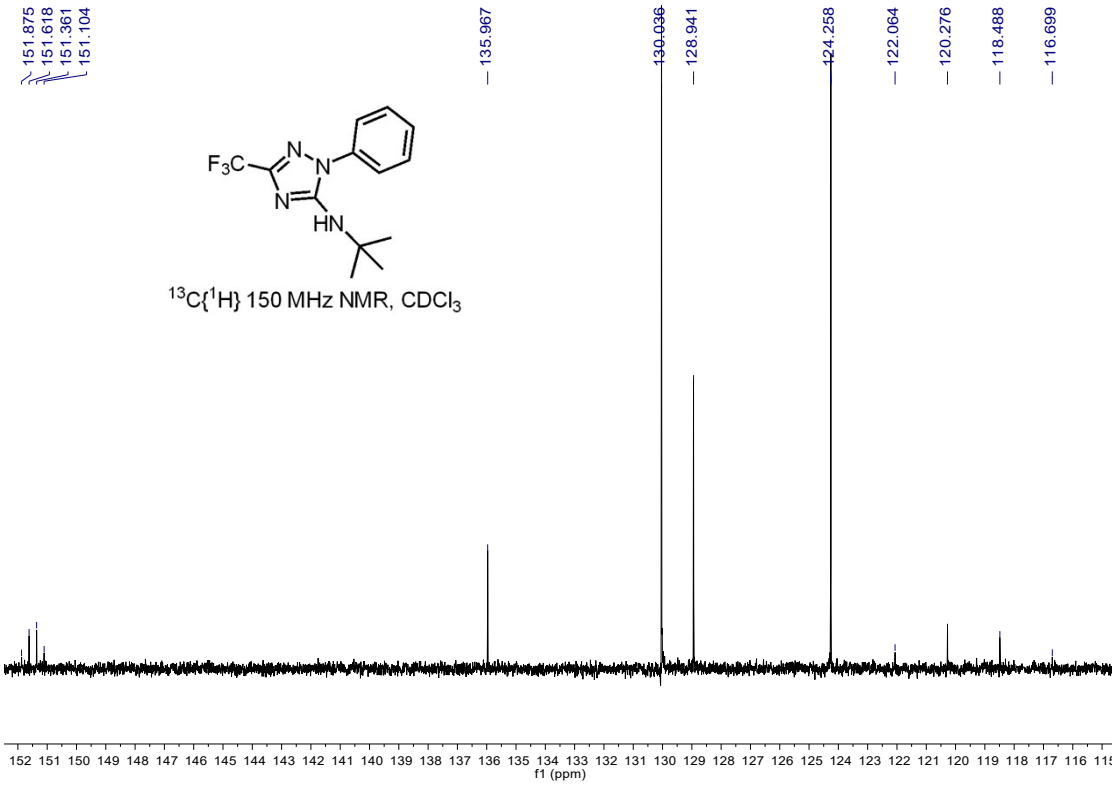
Copies of NMR and HRMS Spectra for Compound **5′**

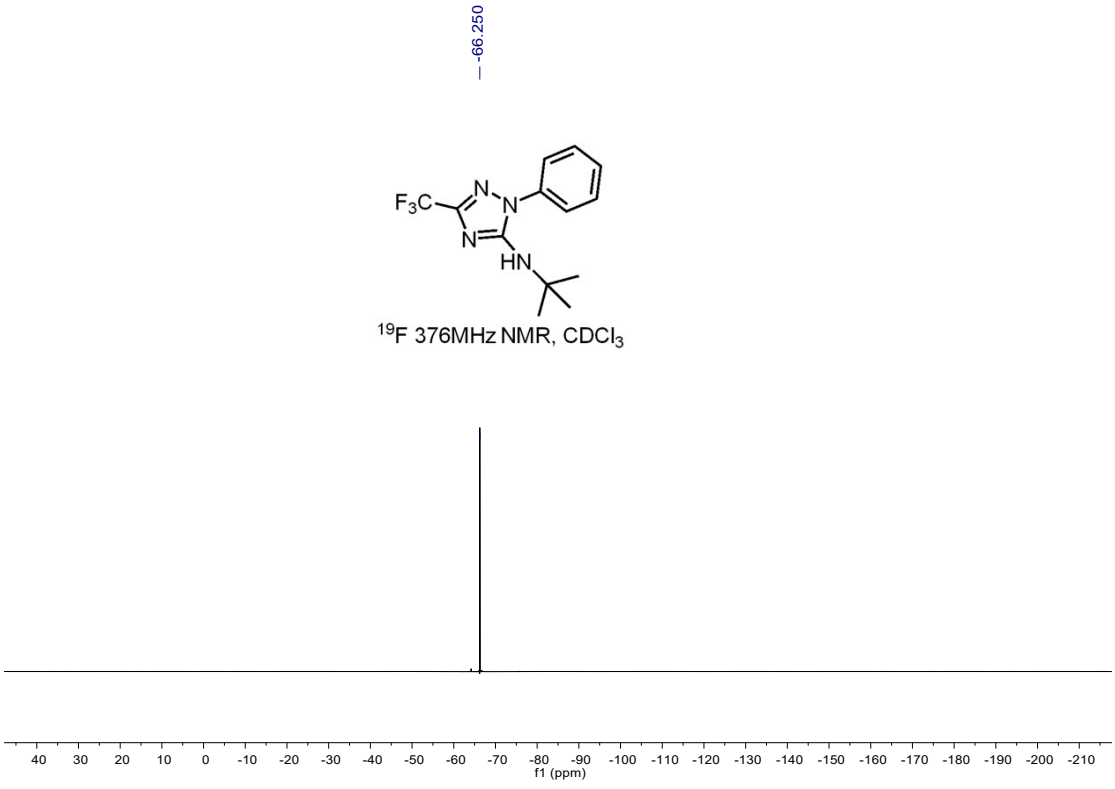
NMR copies of compound **5′a**:





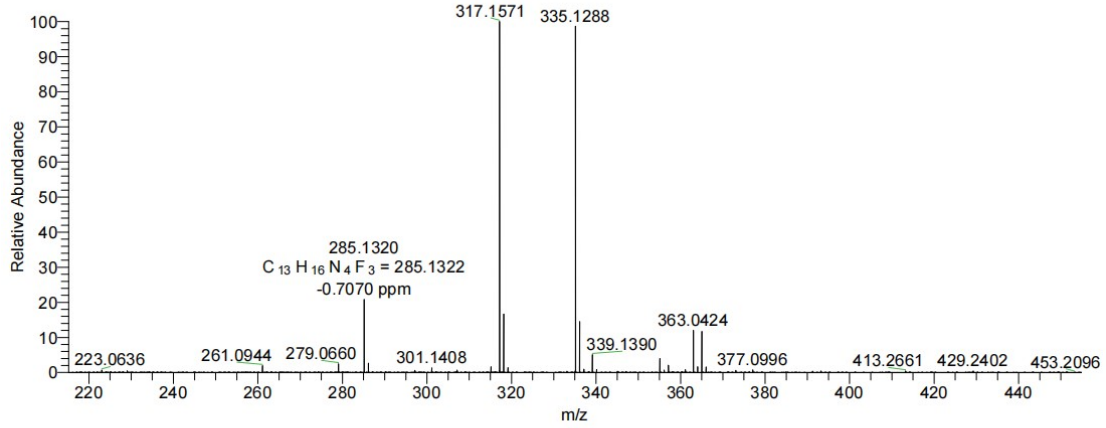

153.995
151.875
151.618
151.361
151.104
135.967
130.036
128.941
124.258
122.064
120.276
118.488
116.699
77.160
76.948
76.736
52.931
28.959
F3C
N
N
N
HN
13C{1H} 150 MHz NMR, CDCl3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


151.875
151.618
151.361
151.104
135.967
130.036
128.941
124.258
122.064
120.276
118.488
116.699
F3C
N
N
N
HN
13C{1H} 150 MHz NMR, CDCl3
152 151 150 149 148 147 146 145 144 143 142 141 140 139 138 137 136 135 134 133 132 131 130 129 128 127 126 125 124 123 122 121 120 119 118 117 116 115
f1 (ppm)


-66.250
F3C
N
N
N
HN
19F 376MHz NMR, CDCl3
40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

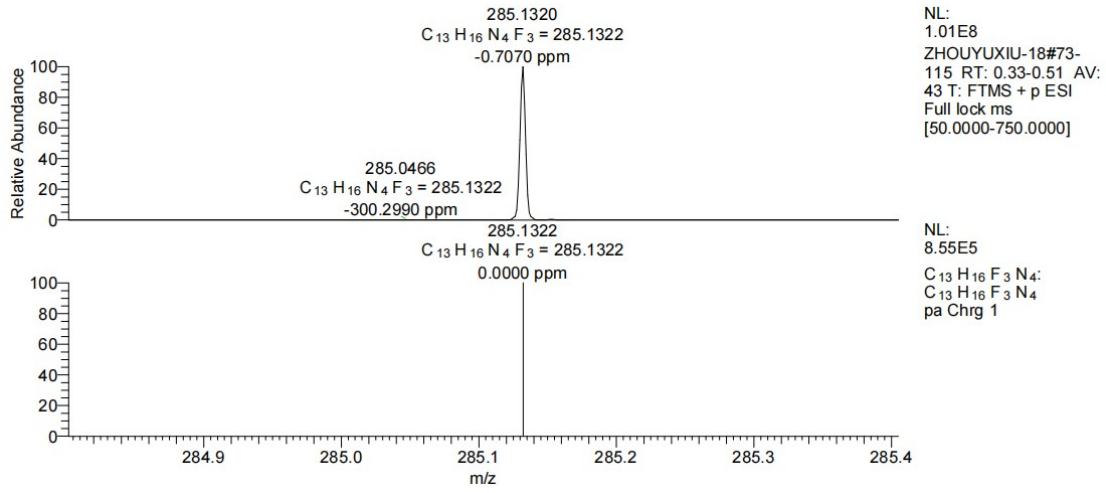
HRMS (ESI) copy of compound **5′a**:

ZHOUYUXIU-18 #73-115 RT: 0.33-0.51 AV: 43 NL: 4.85E8
T: FTMS + p ESI Full lock ms [50.0000-750.0000]

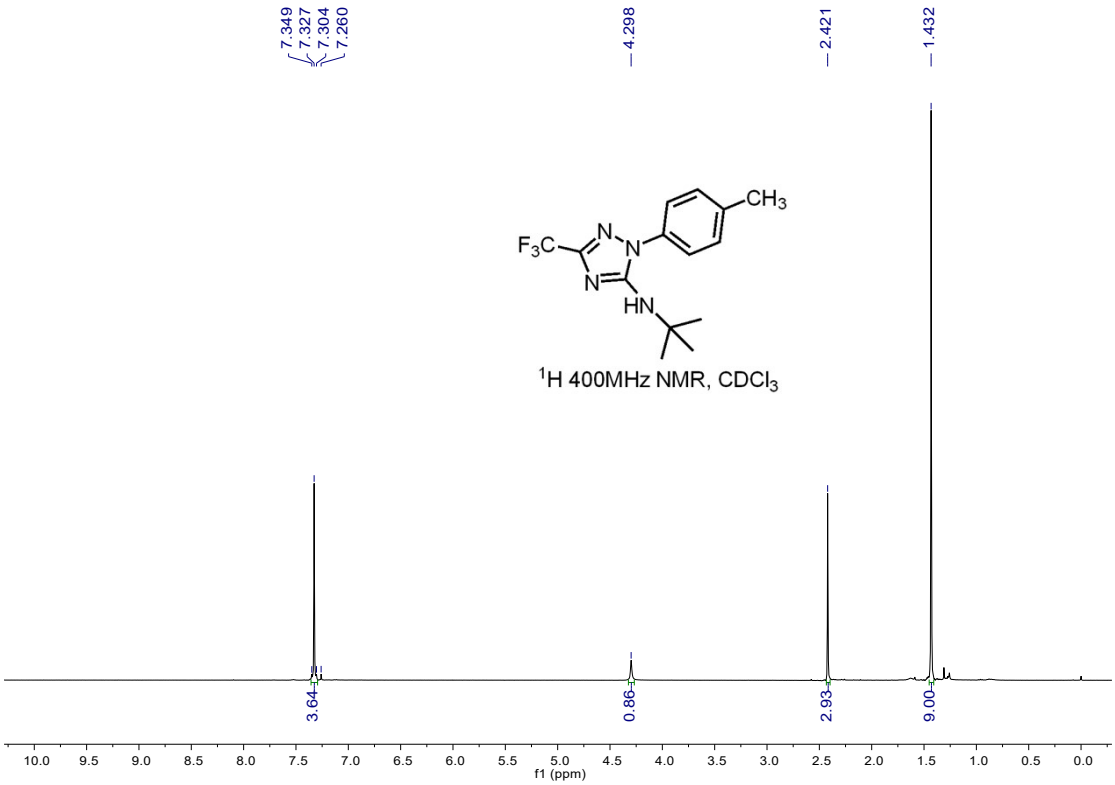


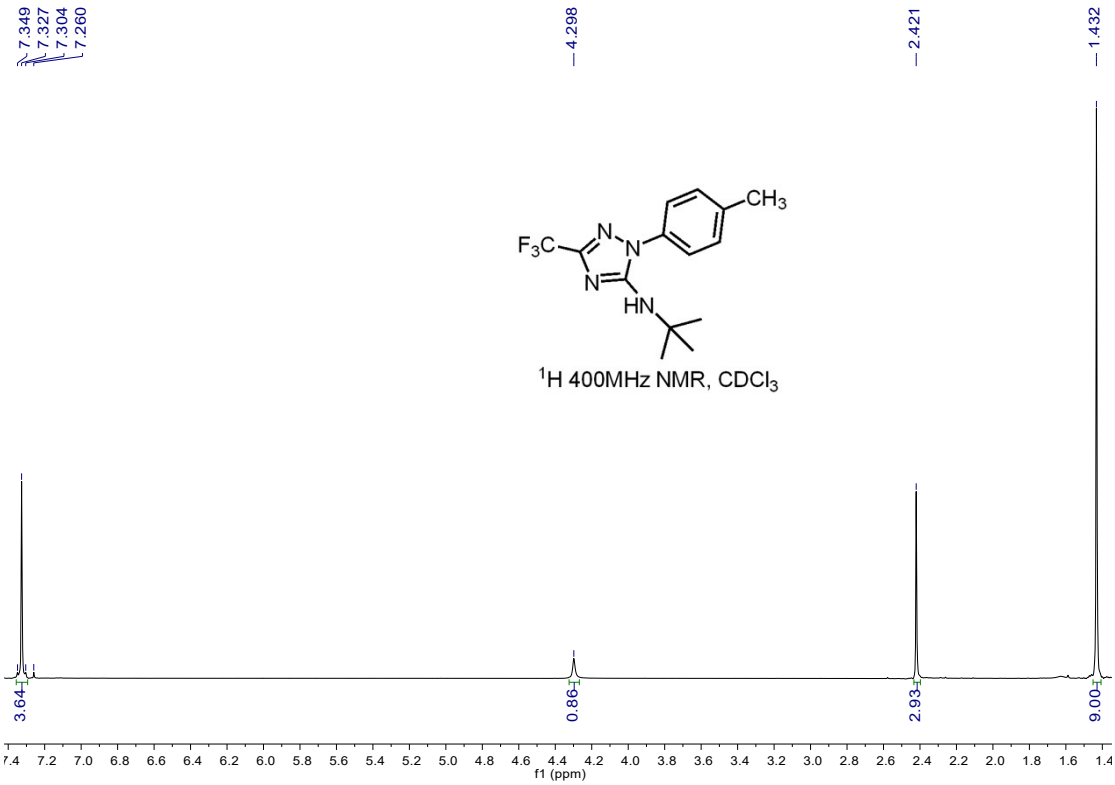
ZHOUYUXIU-18#73-115 RT: 0.33-0.51 AV: 43
T: FTMS + p ESI Full lock ms [50.0000-750.0000]
m/z= 215.1890-454.7588

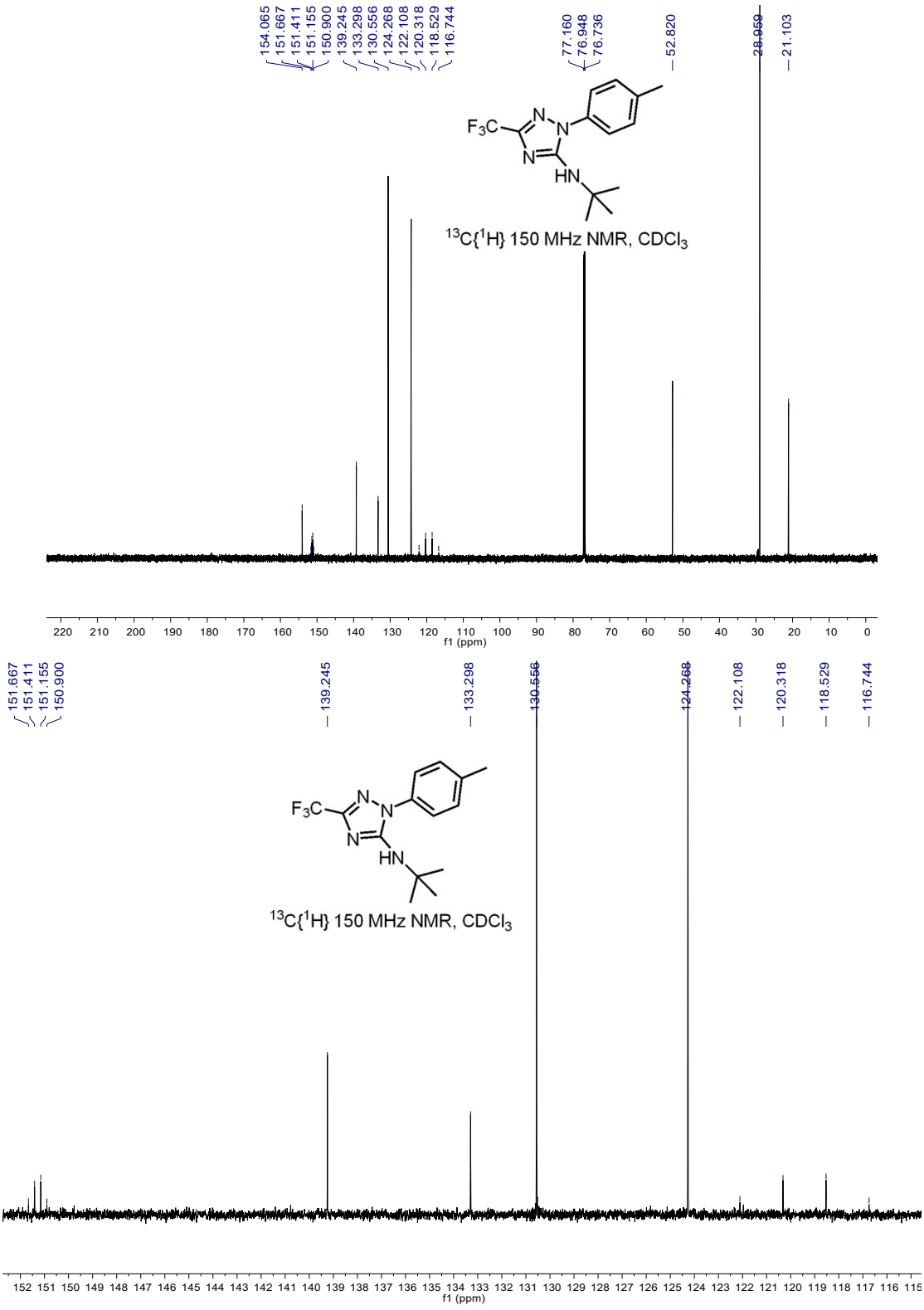
m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
285.1320	101237632.0	20.62	285.1322	-0.20	C 13 H 16 N 4 F 3
317.1571	485311392.0	98.83			
318.1606	83889992.0	17.08			
335.1288	491081568.0	100.00			

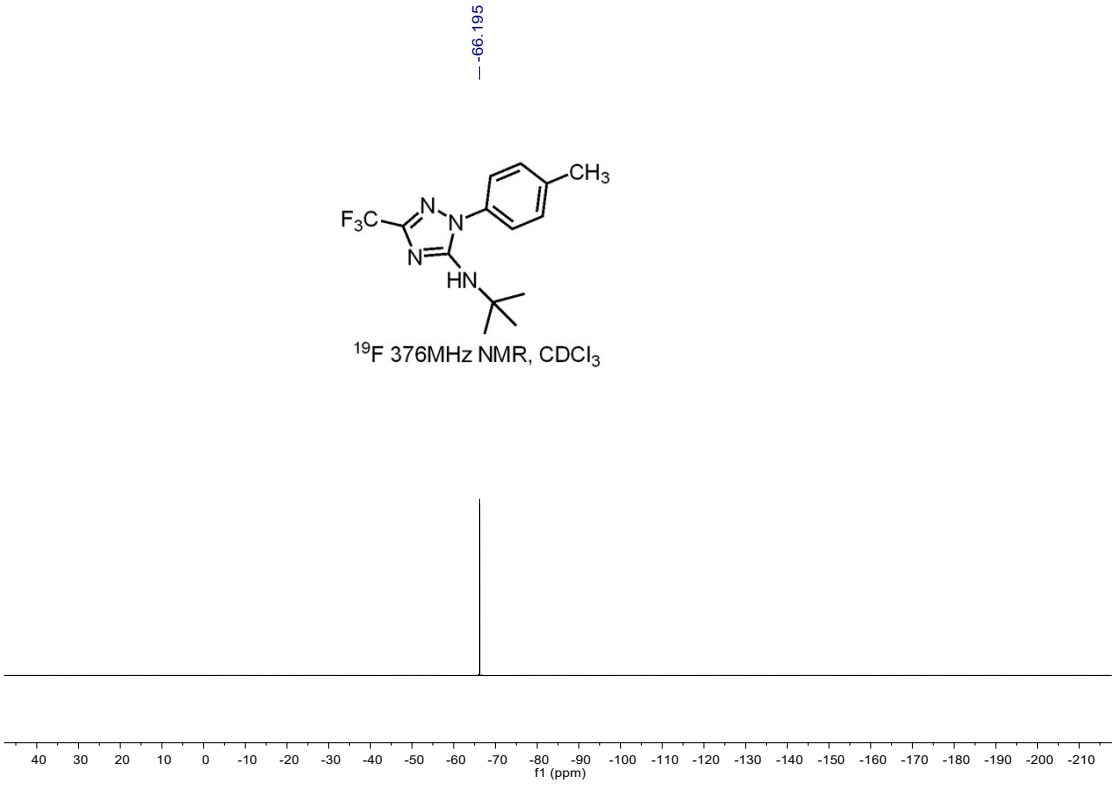


NMR copies of compound **5′b**:



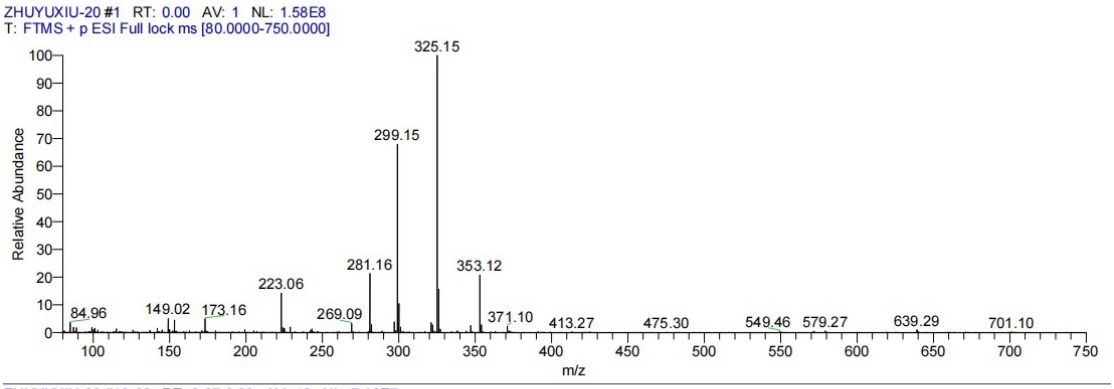


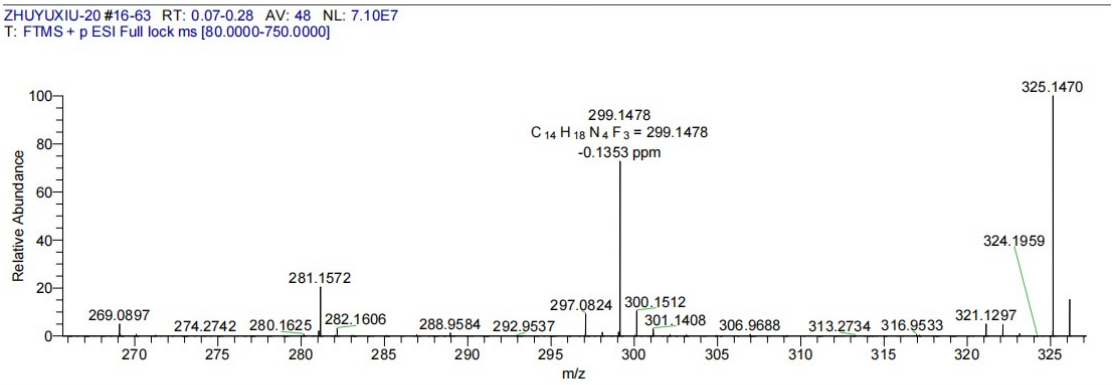

154.065
151.667
151.411
151.155
150.900
139.245
133.298
130.556
124.268
122.108
120.318
118.529
116.744
77.160
76.948
76.736
52.820
28.959
21.103
F3C
N
N
N
HN
13C{1H} 150 MHz NMR, CDCl3
f1 (ppm)
151.667
151.411
151.155
150.900
139.245
133.298
130.556
124.268
122.108
120.318
118.529
116.744
F3C
N
N
N
HN
13C{1H} 150 MHz NMR, CDCl3
f1 (ppm)



^{19}F 376MHz NMR, $CDCl_3$

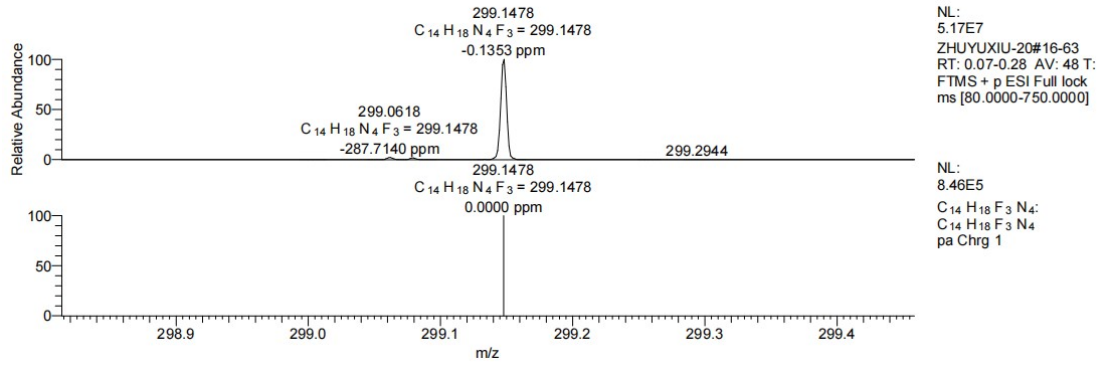
HRMS (ESI) copy of compound **5′b**:



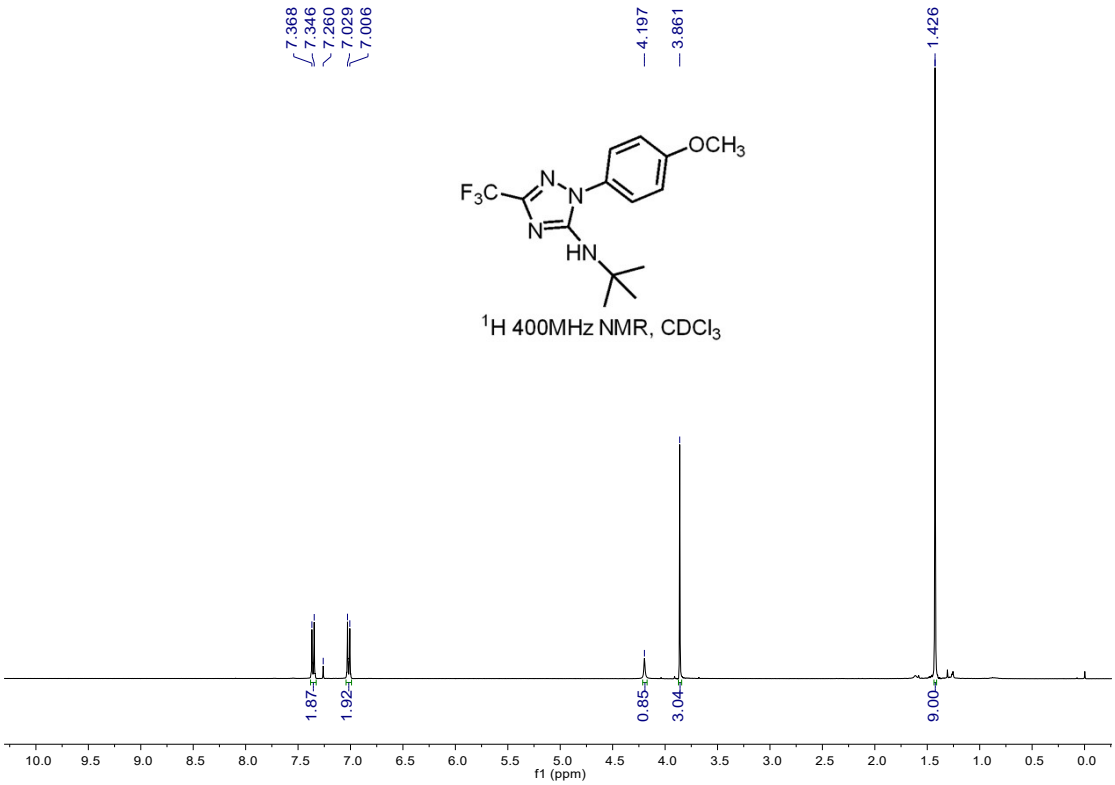


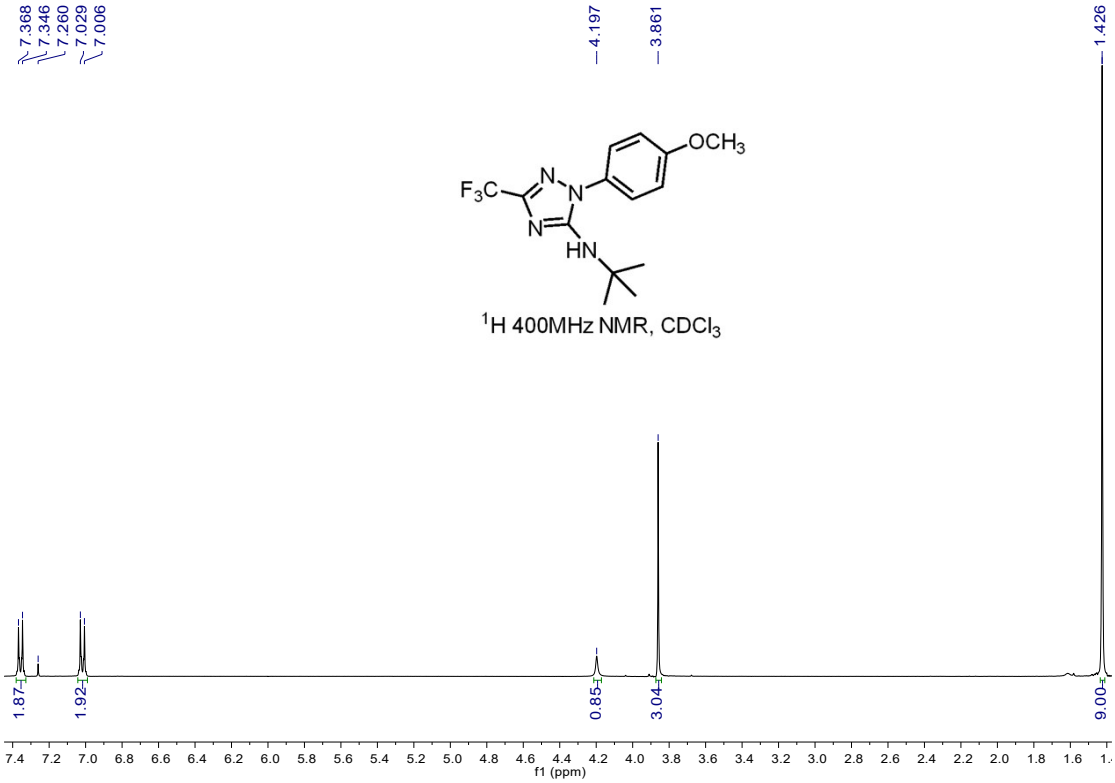
ZHUYUXIU-20#16-63 RT: 0.07-0.28 AV: 48
T: FTMS + p ESI Full lock ms [80.0000-750.0000]
m/z= 265.6783-327.1382

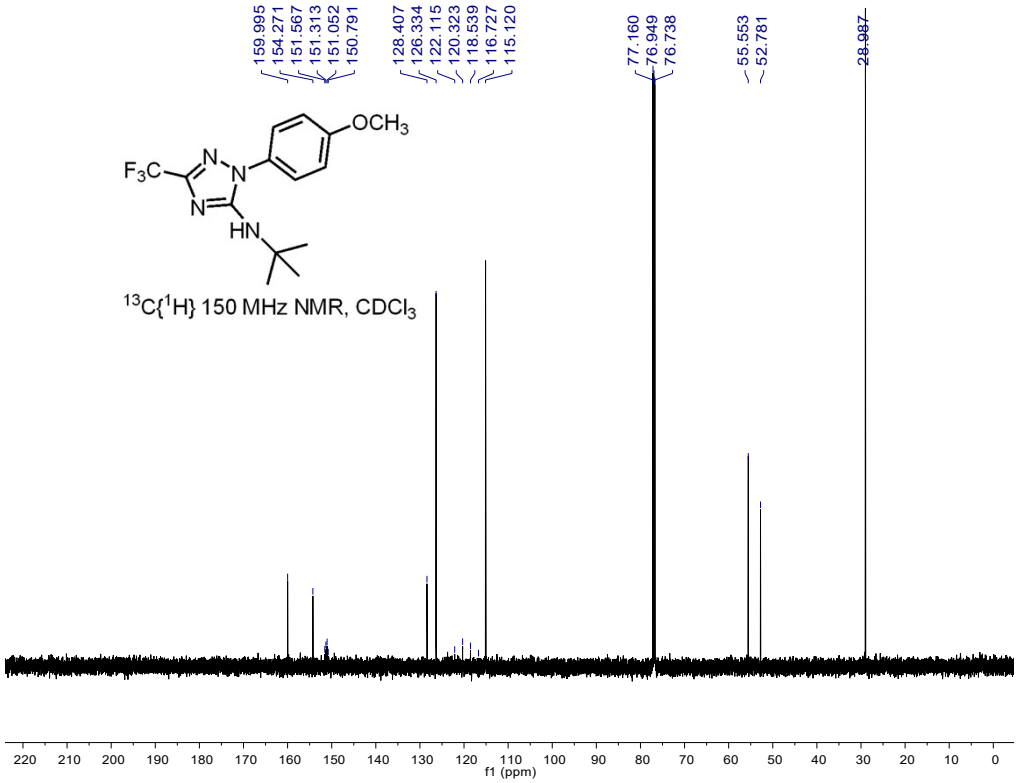
m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
281.1572	14918277.0	20.99			
299.1478	52653728.0	74.08	299.1478	-0.04	$C_{14}H_{18}N_4F_3$
325.1470	71080240.0	100.00			
326.1505	10869526.0	15.29			

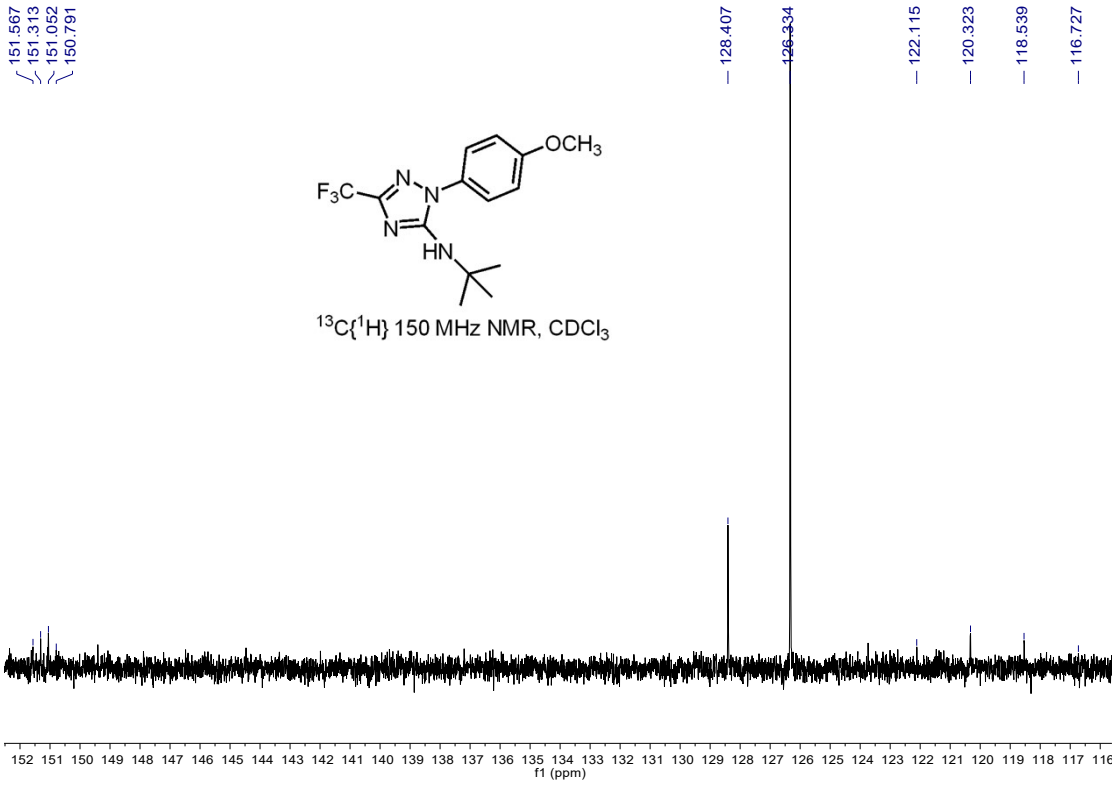


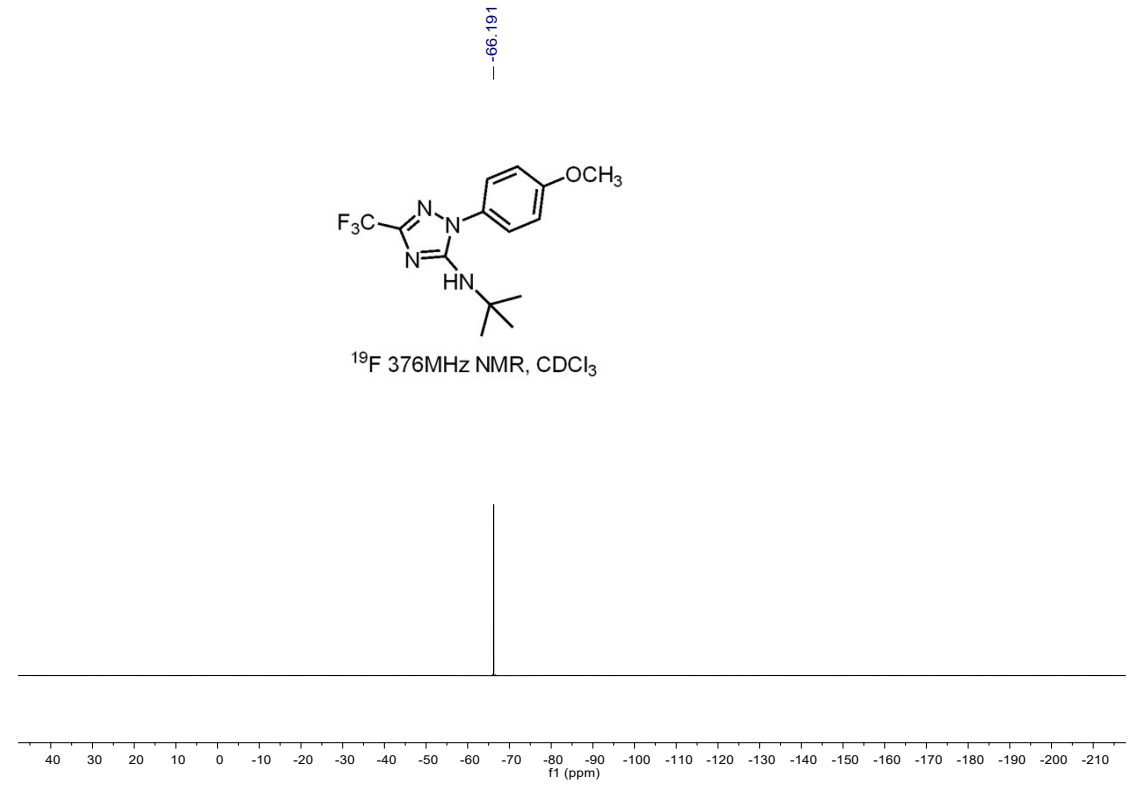
NMR copies of compound **5′c**:



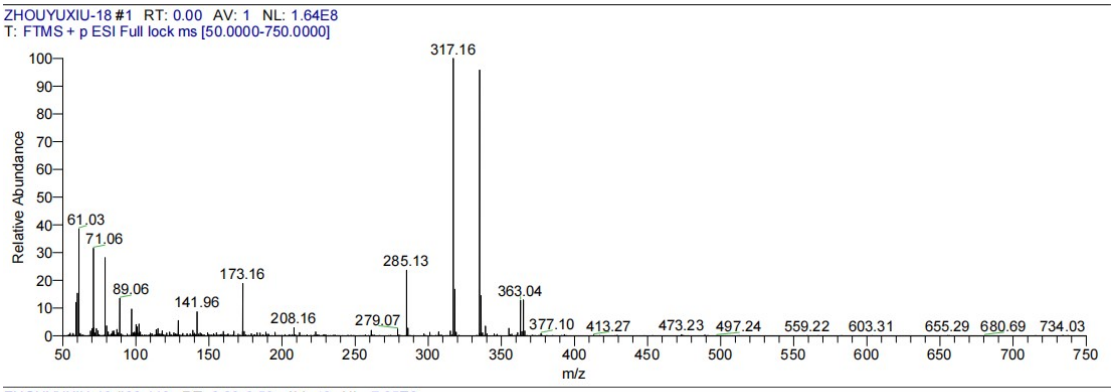


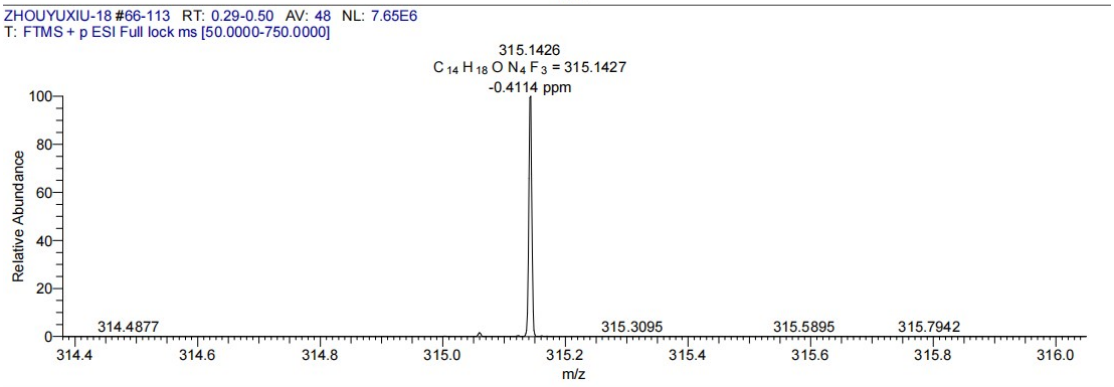

159.995
154.271
151.567
151.313
151.052
150.791
128.407
126.334
122.115
120.323
118.539
116.727
115.120
77.160
76.949
76.738
55.553
52.781
28.987
OCH3
F3C
N
N
N
HN
13C{1H} 150 MHz NMR, CDCl3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


151.567
151.313
151.052
150.791
128.407
126.334
122.115
120.323
118.539
116.727
OCH3
F3C
N
N
N
HN
13C{1H} 150 MHz NMR, CDCl3
152 151 150 149 148 147 146 145 144 143 142 141 140 139 138 137 136 135 134 133 132 131 130 129 128 127 126 125 124 123 122 121 120 119 118 117 116
f1 (ppm)


-66.191
OCH3
F3C
N
N
N
HN
19F 376MHz NMR, CDCl3
40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

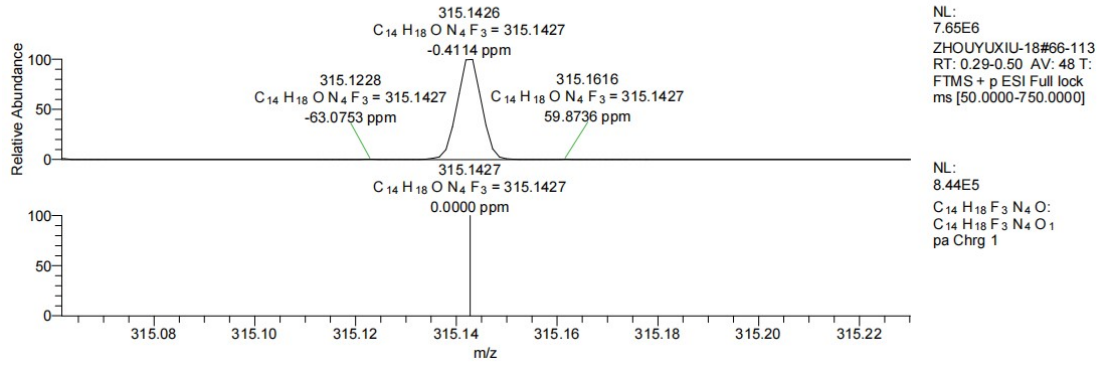
HRMS (ESI) copy of compound **5′c**:



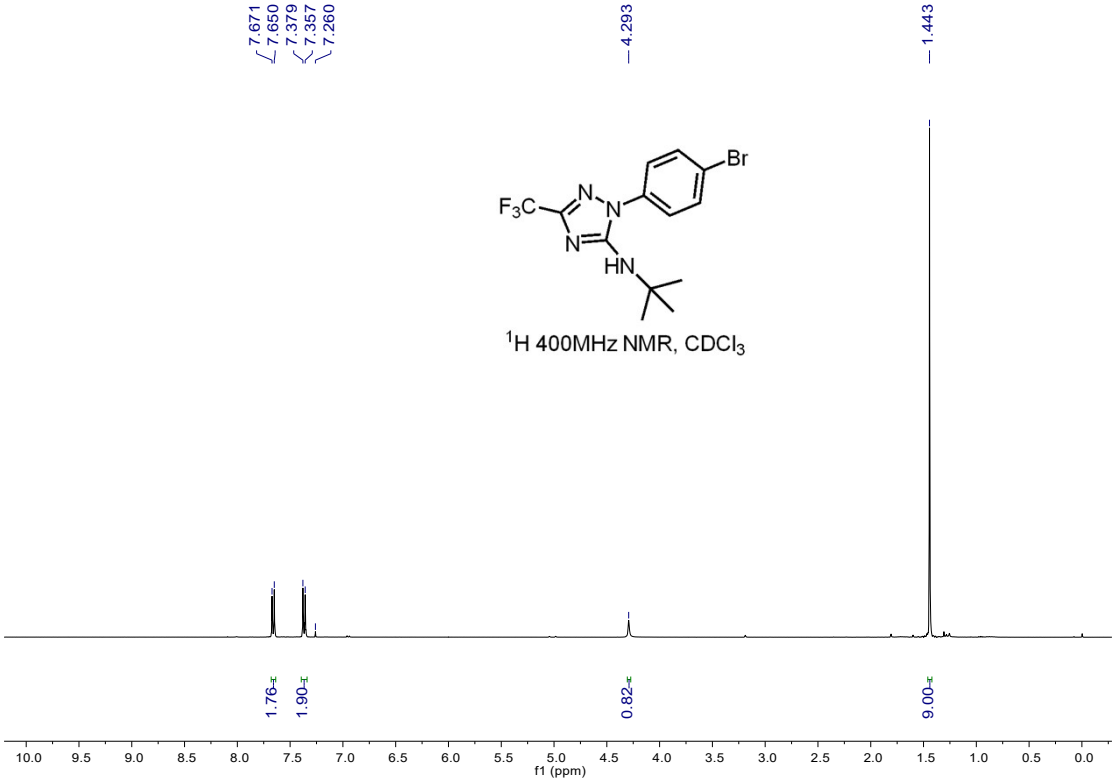


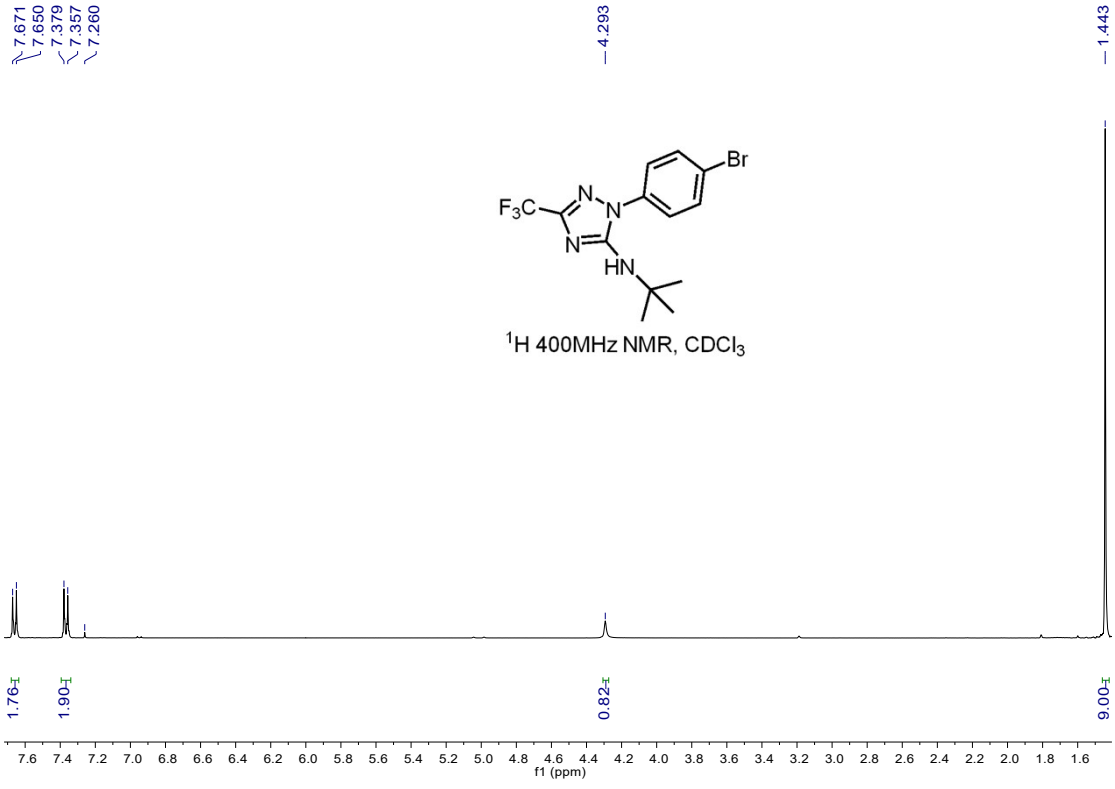
ZHOUYUXIU-18#66-113 RT: 0.29-0.50 AV: 48
T: FTMS + p ESI Full lock ms [50.0000-750.0000]
m/z= 314.3799-316.0493

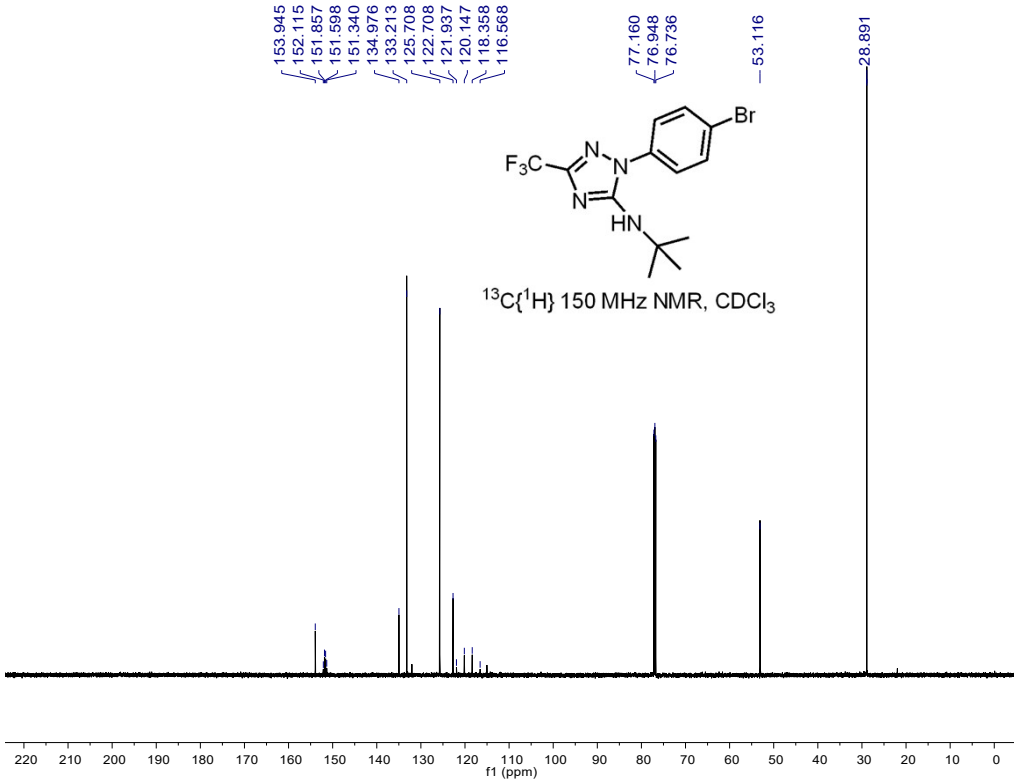
m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
315.0598	123794.5	1.56	315.1427	-82.88	$C_{14}H_{18}ON_4F_3$
315.1228	22014.6	0.28	315.1427	-19.88	$C_{14}H_{18}ON_4F_3$
315.1426	7946150.5	100.00	315.1427	-0.13	$C_{14}H_{18}ON_4F_3$
315.1616	18021.4	0.23	315.1427	18.87	$C_{14}H_{18}ON_4F_3$

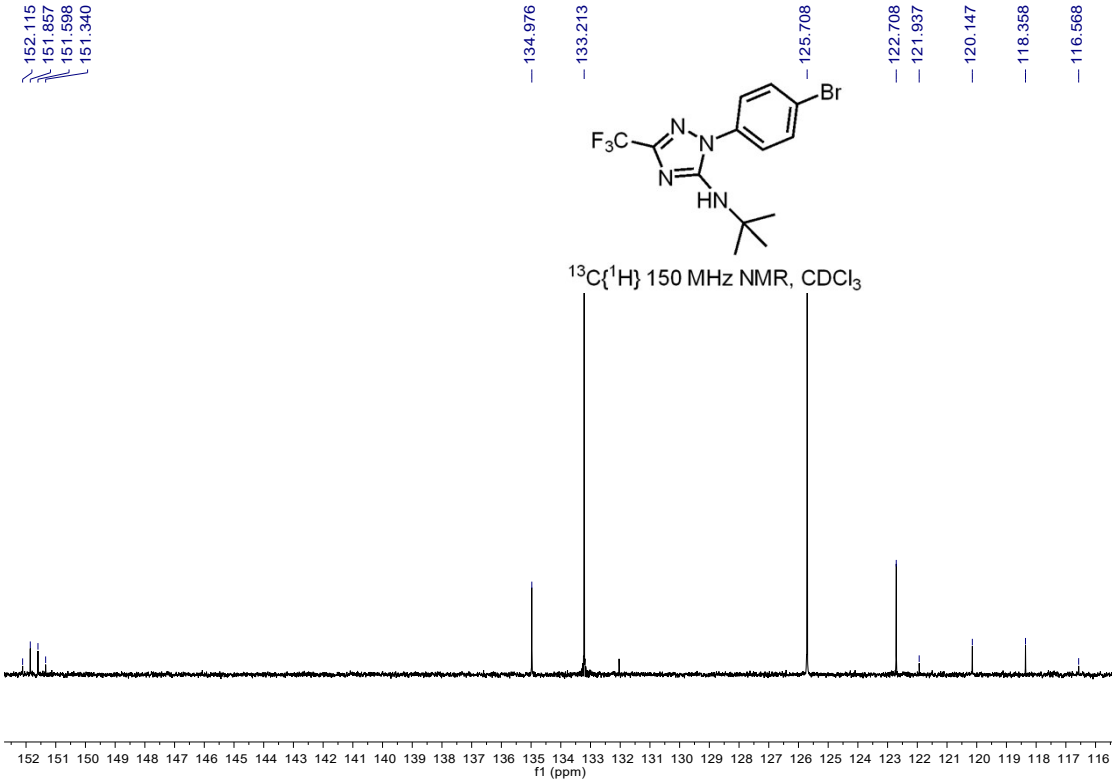


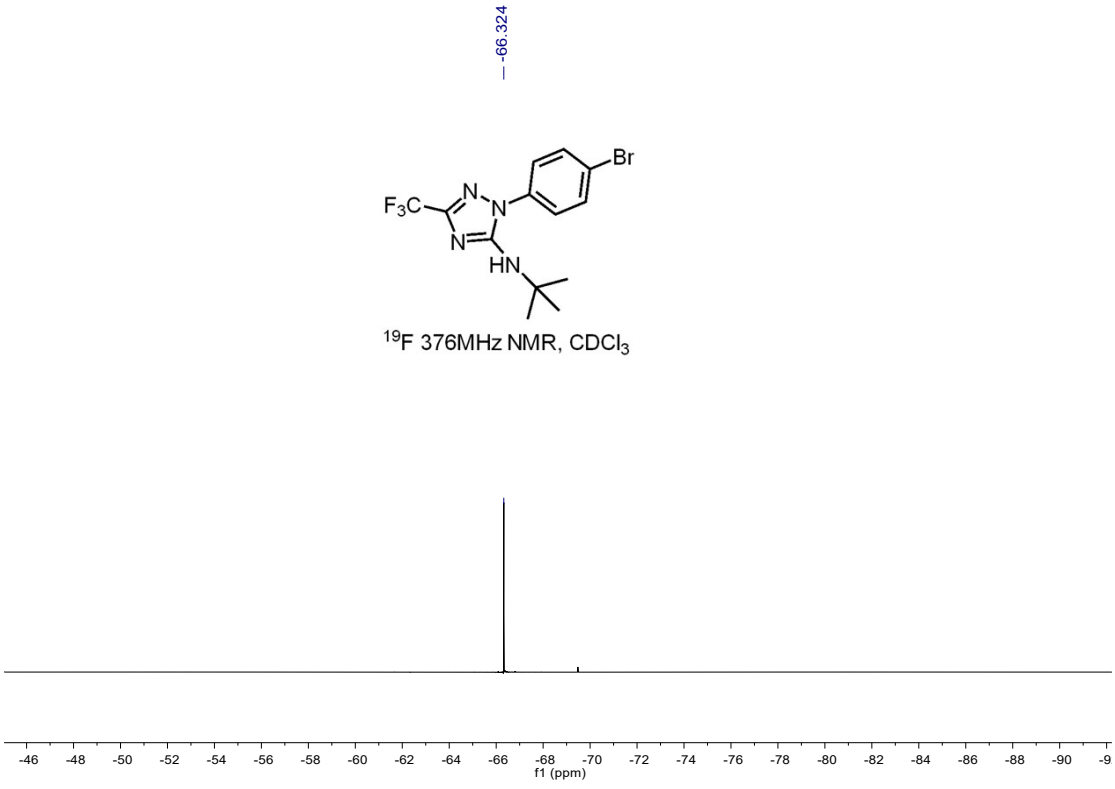
NMR copies of compound **5′d**:



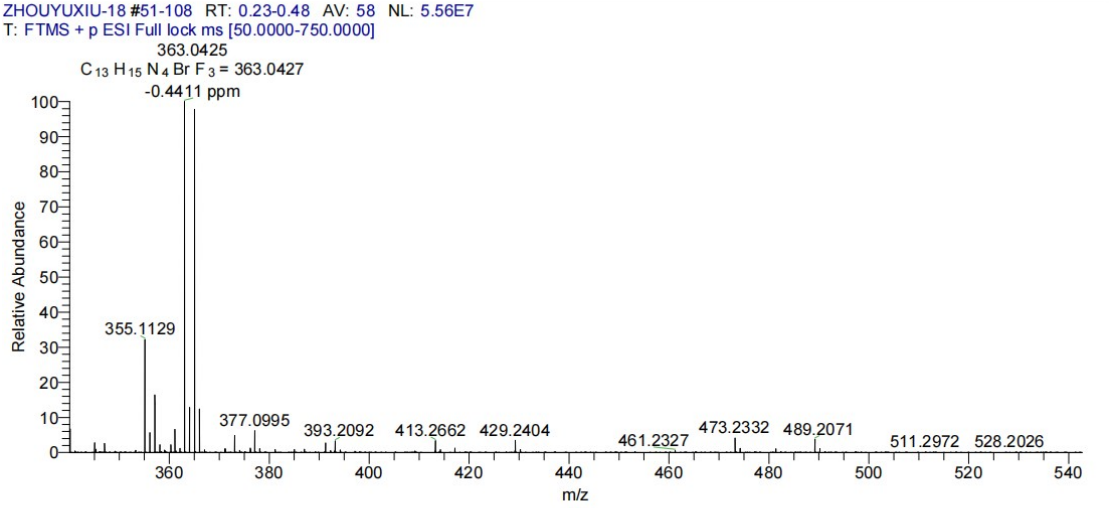



153.945
152.115
151.857
151.598
151.340
134.976
133.213
125.708
122.708
121.937
120.147
118.358
116.568
77.160
76.948
76.736
53.116
28.891
Br
F3C
N
N
N
HN
13C{1H} 150 MHz NMR, CDCl3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


152.115
151.857
151.598
151.340
134.976
133.213
125.708
122.708
121.937
120.147
118.358
116.568
Br
F3C
N
N
N
HN
13C{1H} 150 MHz NMR, CDCl3
152 151 150 149 148 147 146 145 144 143 142 141 140 139 138 137 136 135 134 133 132 131 130 129 128 127 126 125 124 123 122 121 120 119 118 117 116
f1 (ppm)

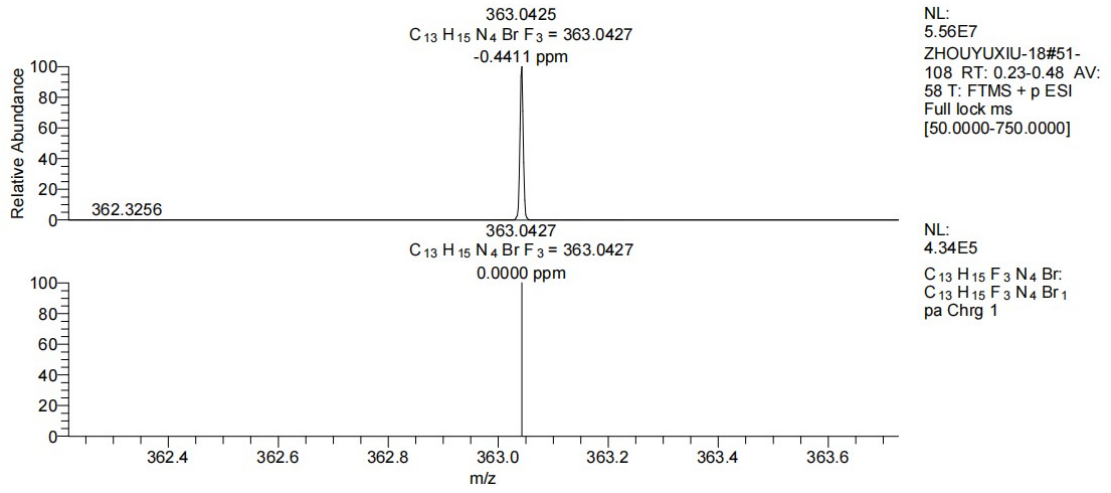

-66.324
Br
F3C
N
N
N
HN
19F 376MHz NMR, CDCl3
-46
-48
-50
-52
-54
-56
-58
-60
-62
-64
-66
-68
-70
-72
-74
-76
-78
-80
-82
-84
-86
-88
-90
-9
f1 (ppm)

HRMS (ESI) copy of compound **5′d**:

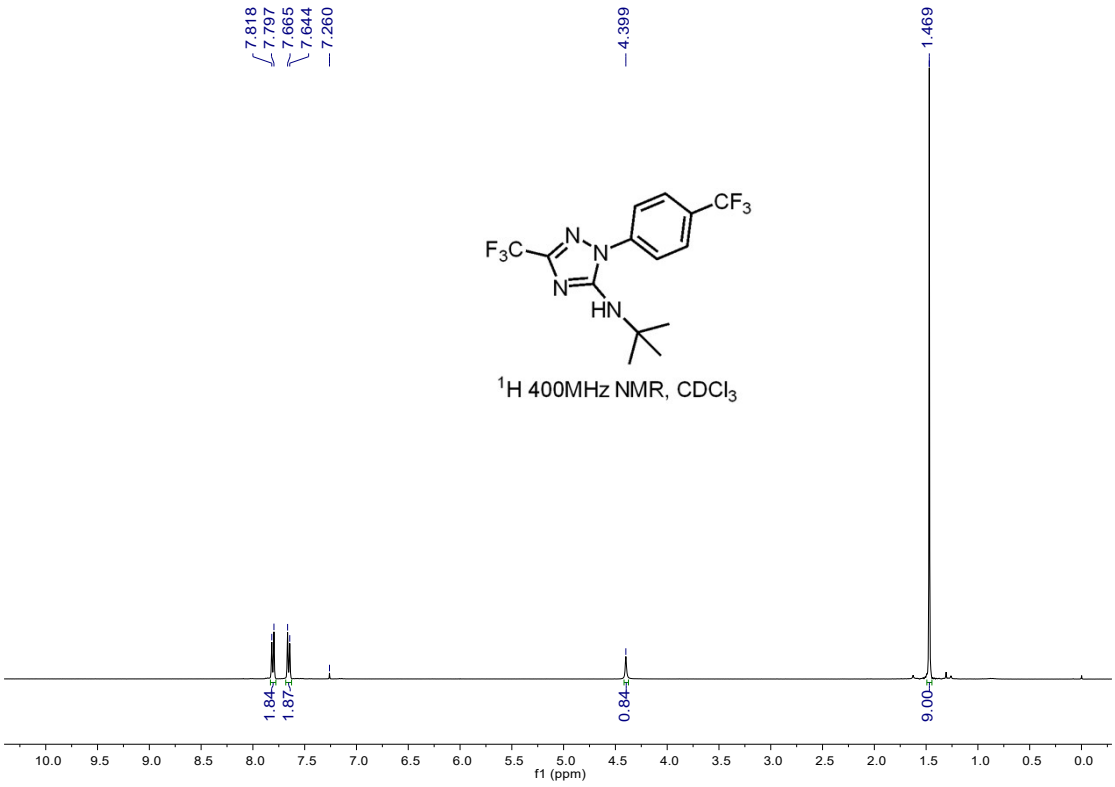


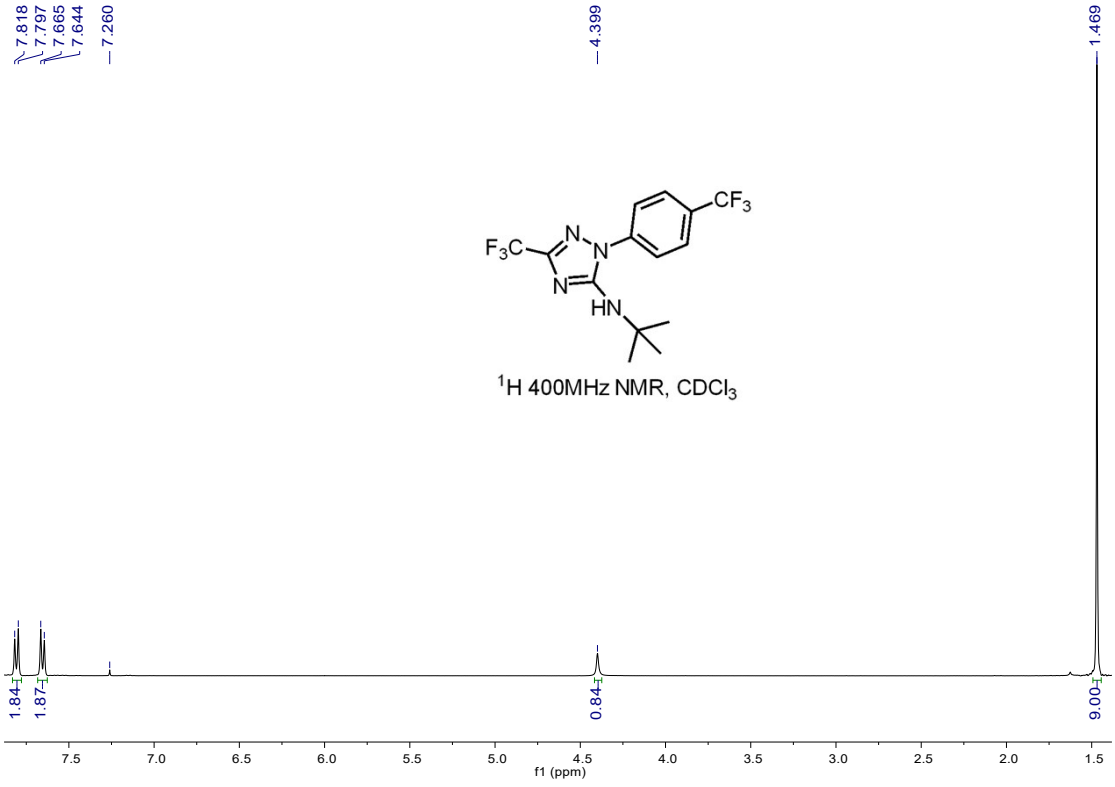
ZHOUYUXIU-18#51-108 RT: 0.23-0.48 AV: 58
T: FTMS + p ESI Full lock ms [50.0000-750.0000]
m/z= 340.0348-542.6638

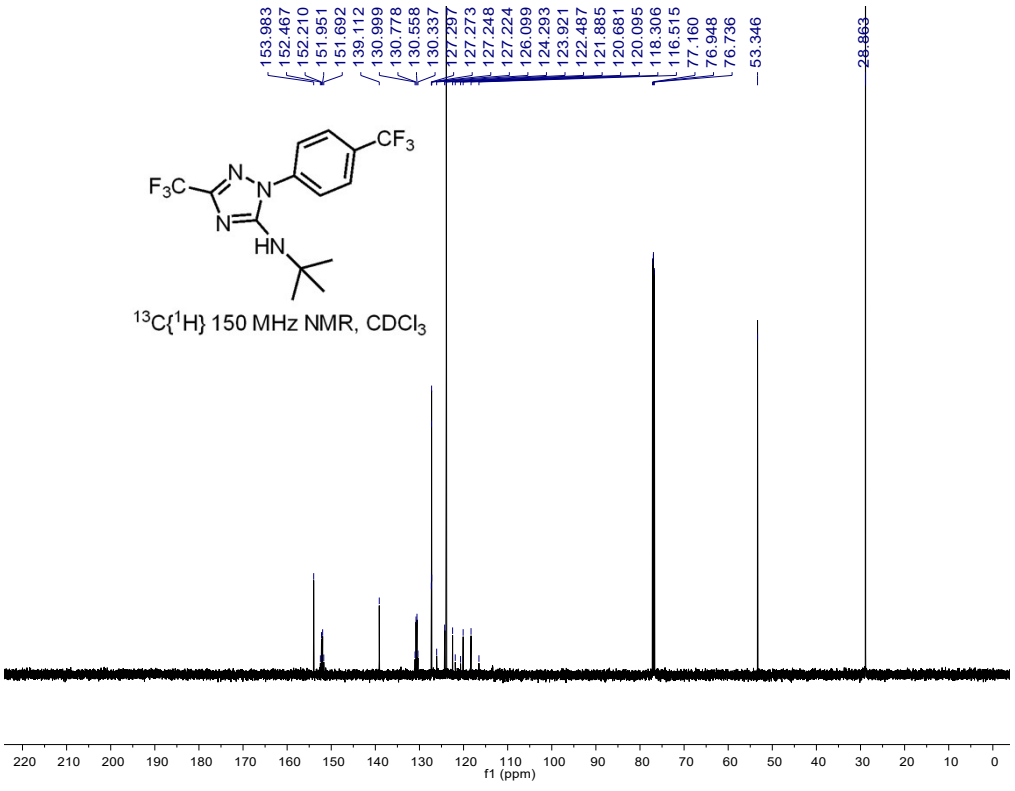
m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
355.1129	18300882.0	32.33			
357.1107	9136968.0	16.14			
363.0425	56600944.0	100.00	363.0427	-0.16	$C_{13}H_{15}N_4BrF_3$
365.0405	54581792.0	96.43			

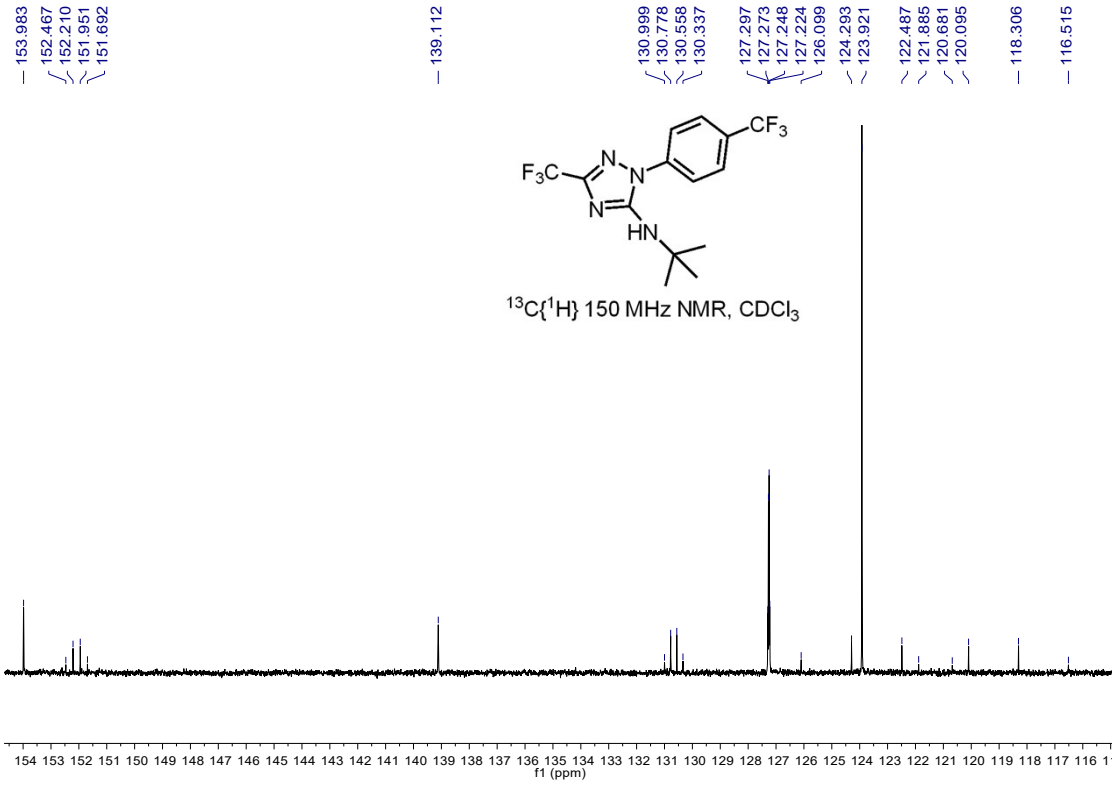


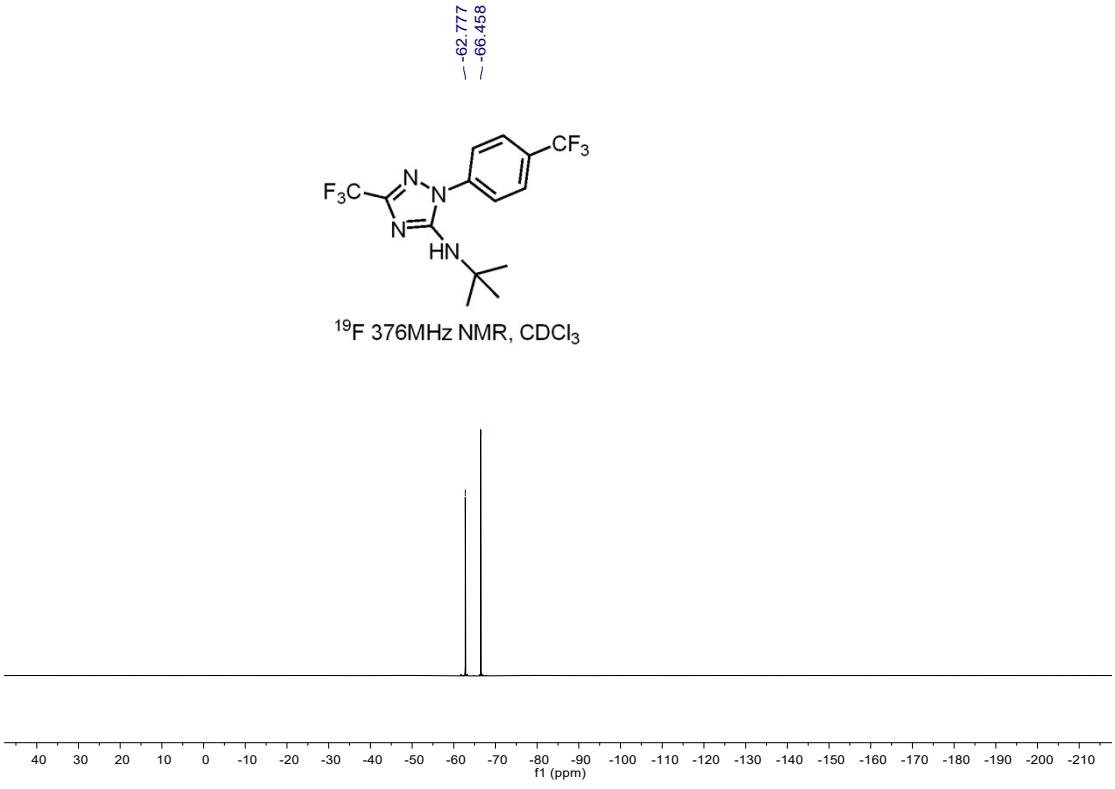
NMR copies of compound **5′e**:



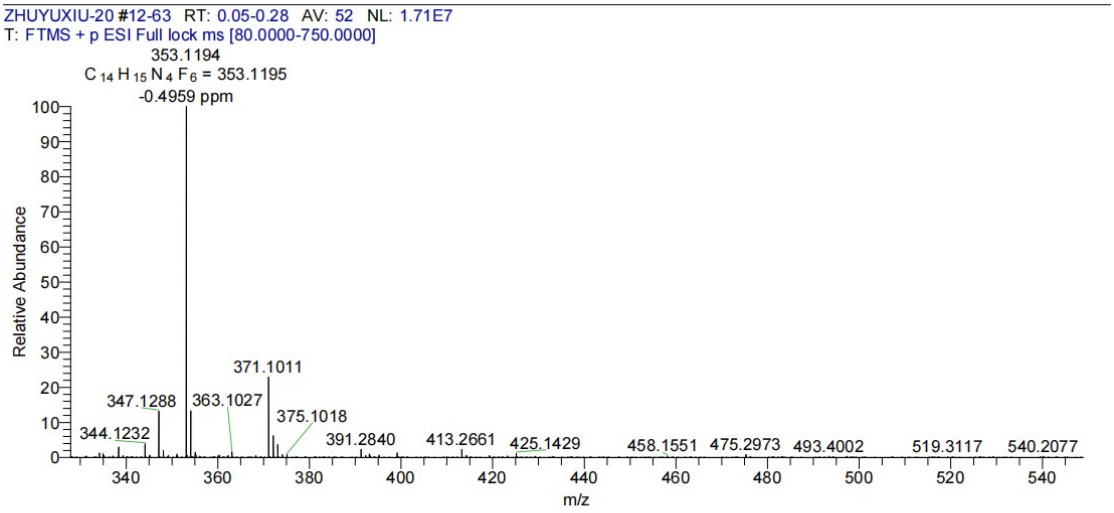



153.983
152.467
152.210
151.951
151.692
139.112
130.999
130.778
130.558
130.337
127.297
127.273
127.248
127.224
126.099
124.293
123.921
122.487
121.885
120.681
120.095
118.306
116.515
77.160
76.948
76.736
53.346
28.863
CF3
F3C
N
N
N
HN
13C{1H} 150 MHz NMR, CDCl3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


153.983
152.467
152.210
151.951
151.692
139.112
130.999
130.778
130.558
130.337
127.297
127.273
127.248
127.224
126.099
124.293
123.921
122.487
121.885
120.681
120.095
118.306
116.515
CF3
F3C
N
N
N
HN
13C{1H} 150 MHz NMR, CDCl3
154 153 152 151 150 149 148 147 146 145 144 143 142 141 140 139 138 137 136 135 134 133 132 131 130 129 128 127 126 125 124 123 122 121 120 119 118 117 116 1
f1 (ppm)

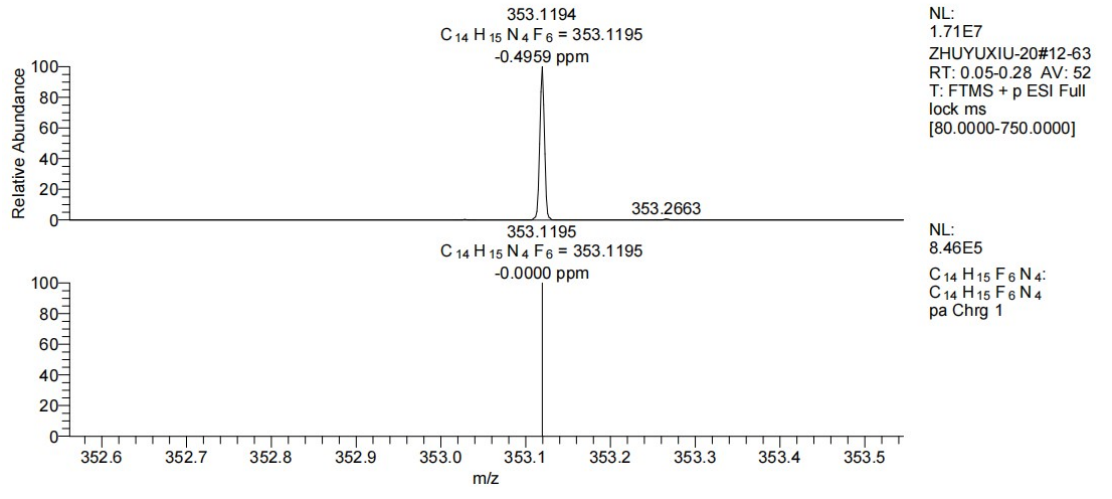

-62.777
-66.458
CF3
F3C
N
N
N
HN
19F 376MHz NMR, CDCl3
40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

HRMS (ESI) copy of compound **5′e**:

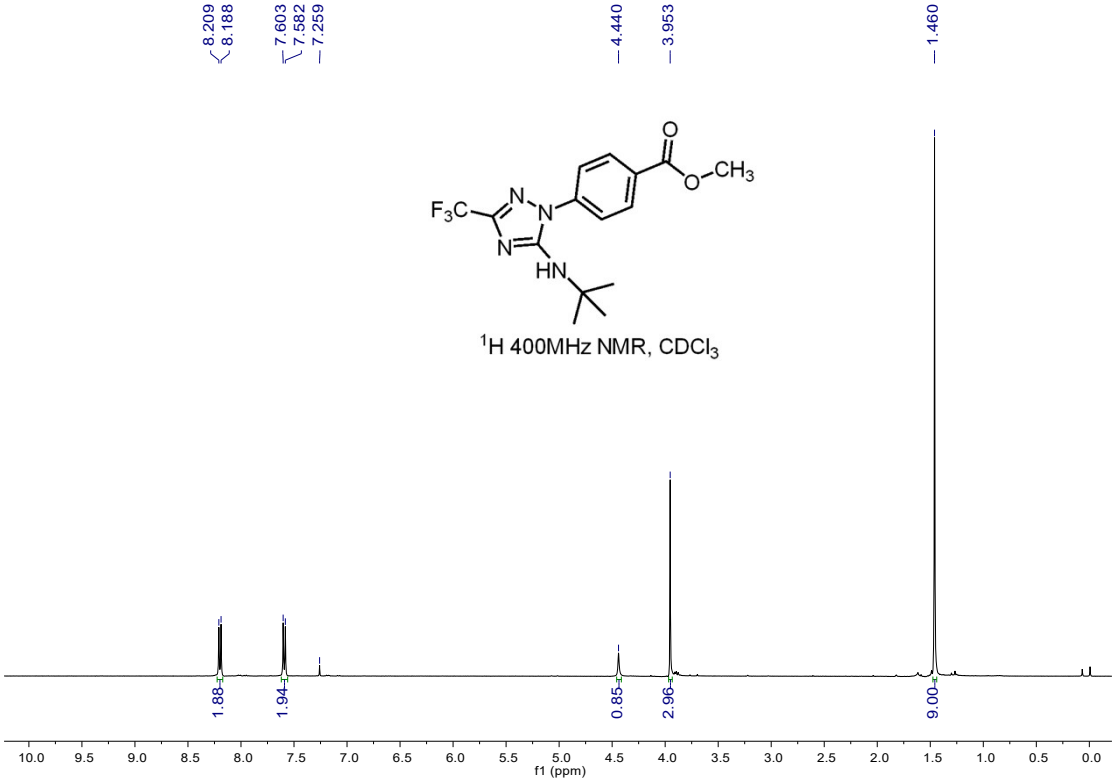


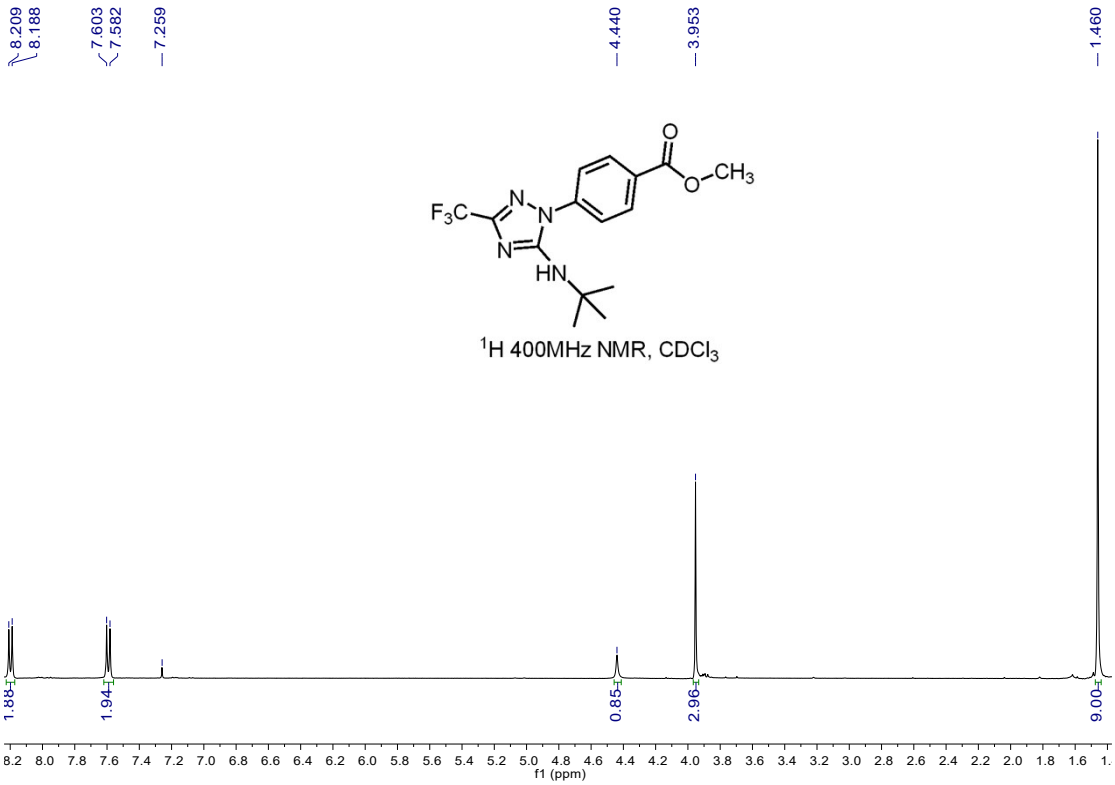
ZHUYUXIU-20#12-63 RT: 0.05-0.28 AV: 52
T: FTMS + p ESI Full lock ms [80.0000-750.0000]
m/z= 327.8557-548.8727

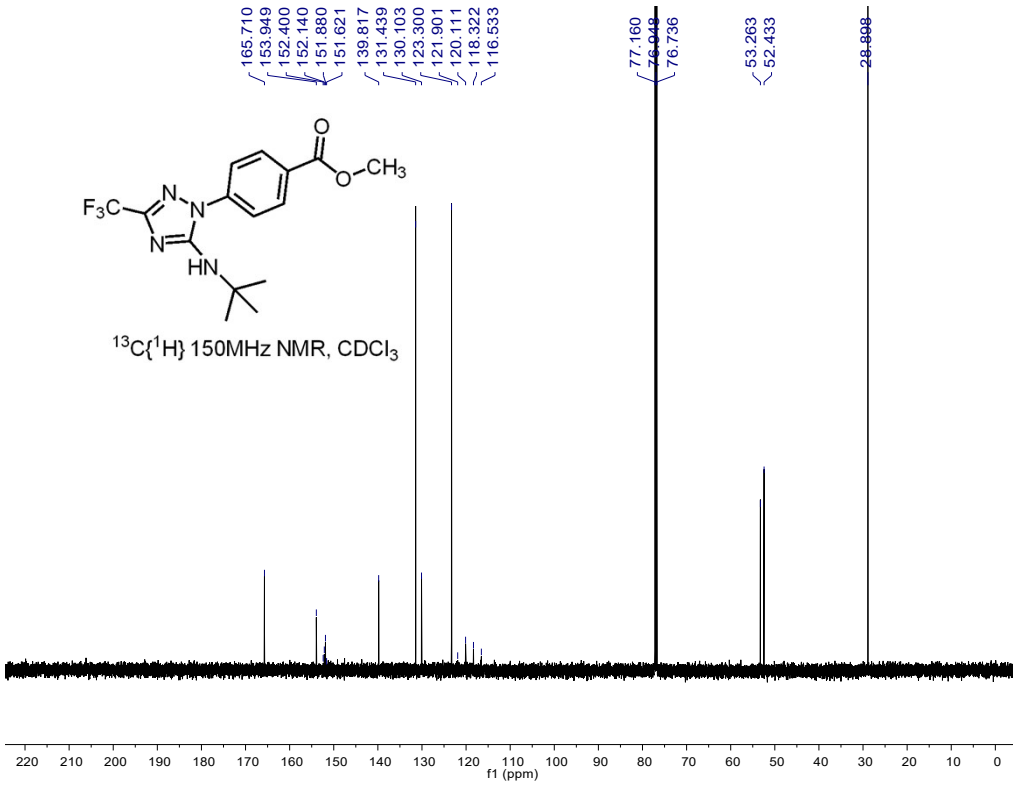
m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
347.1288	2274891.5	13.31			
353.1194	17095402.0	100.00	353.1195	-0.18	$C_{14}H_{15}N_4F_6$
354.1230	2341058.5	13.69			
371.1011	3912925.0	22.89			

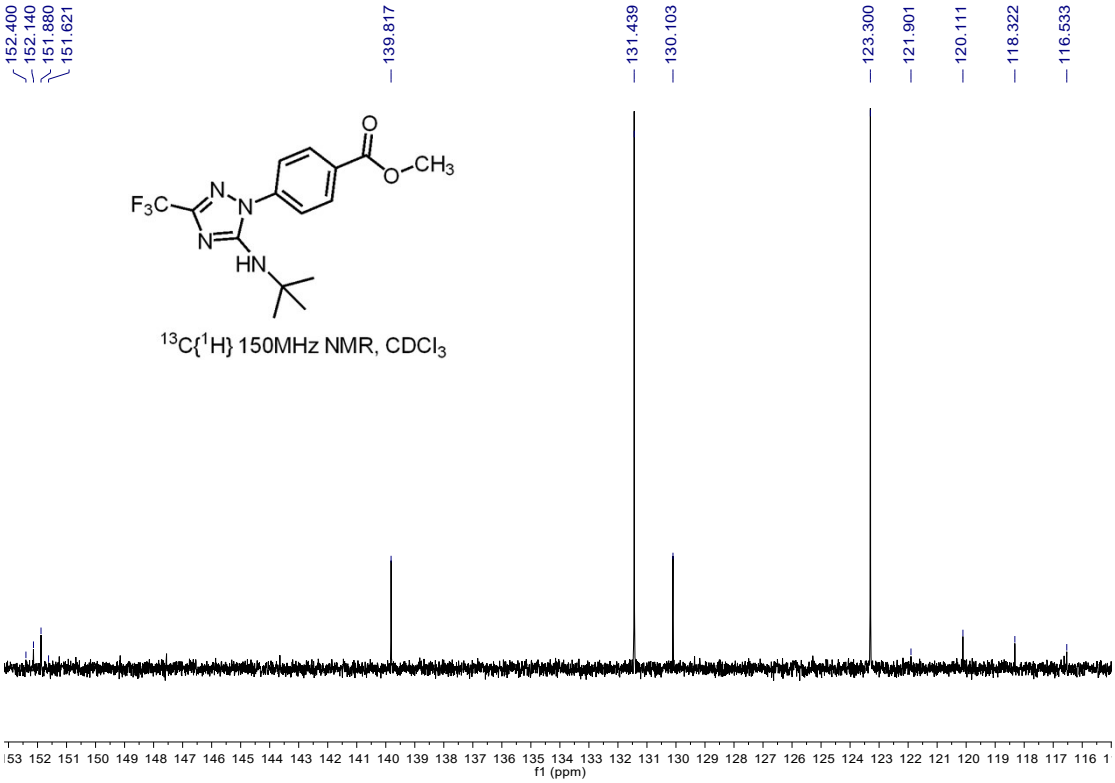


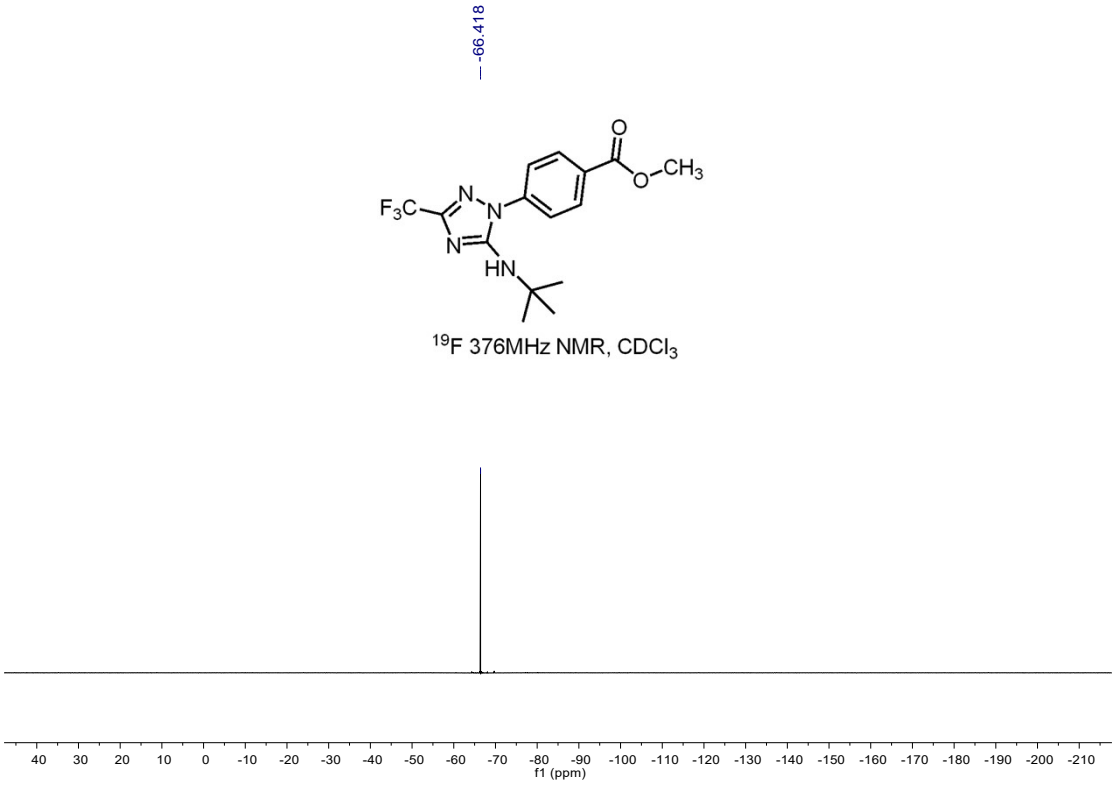
NMR copies of compound **5′f**:





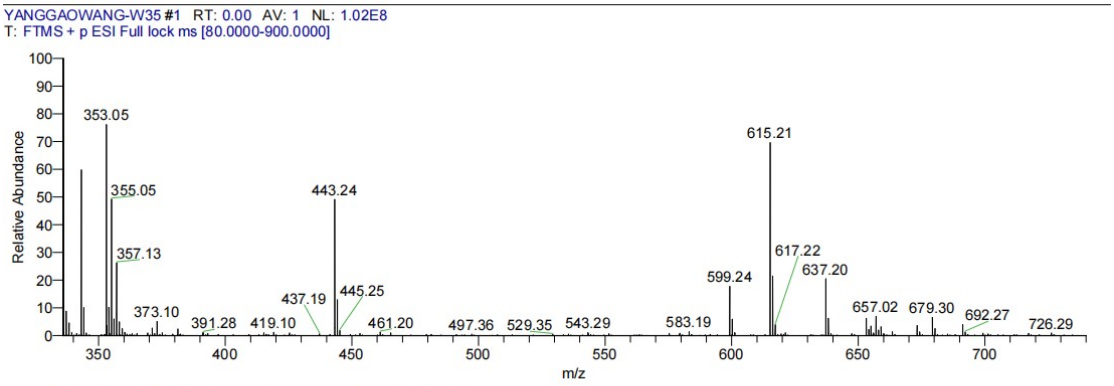

165.710
153.949
152.400
152.140
151.880
151.621
139.817
131.439
130.103
123.300
121.901
120.111
118.322
116.533
77.160
76.736
53.263
52.433
28.898
O
O
CH3
F3C
N
N
N
HN
13C{1H} 150MHz NMR, CDCl3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

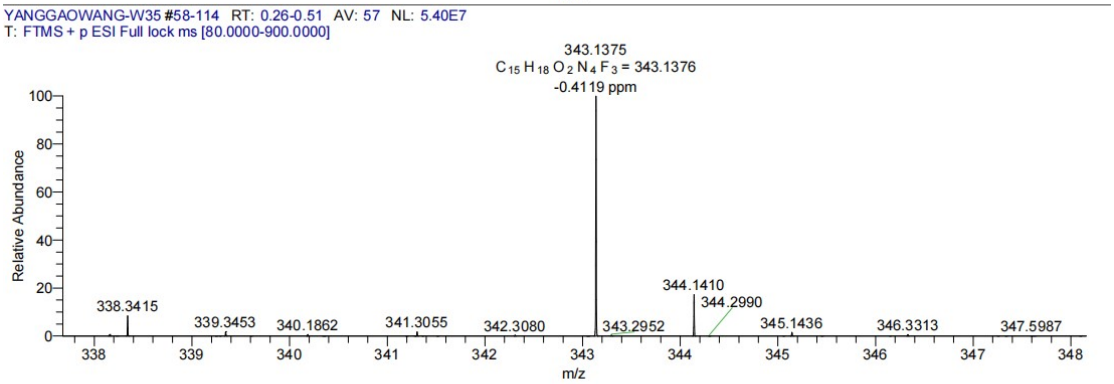

152.400
152.140
151.880
151.621
139.817
131.439
130.103
123.300
121.901
120.111
118.322
116.533
O
O
CH3
F3C
N
N
N
HN
13C{1H} 150MHz NMR, CDCl3
53 152 151 150 149 148 147 146 145 144 143 142 141 140 139 138 137 136 135 134 133 132 131 130 129 128 127 126 125 124 123 122 121 120 119 118 117 116 1
f1 (ppm)



^{19}F 376MHz NMR, $CDCl_3$

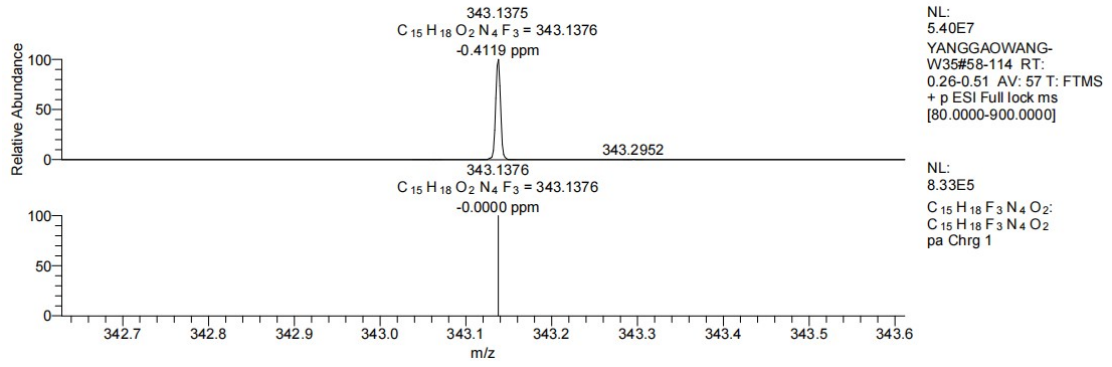
HRMS (ESI) copy of compound **5′f**:



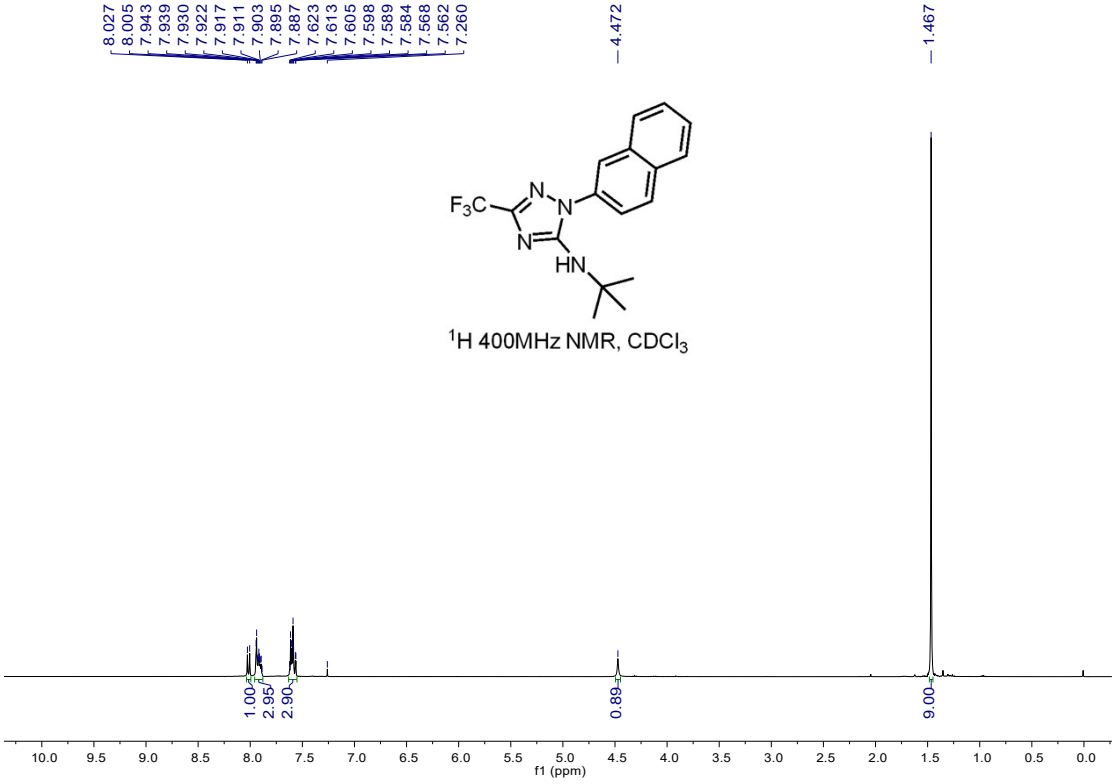


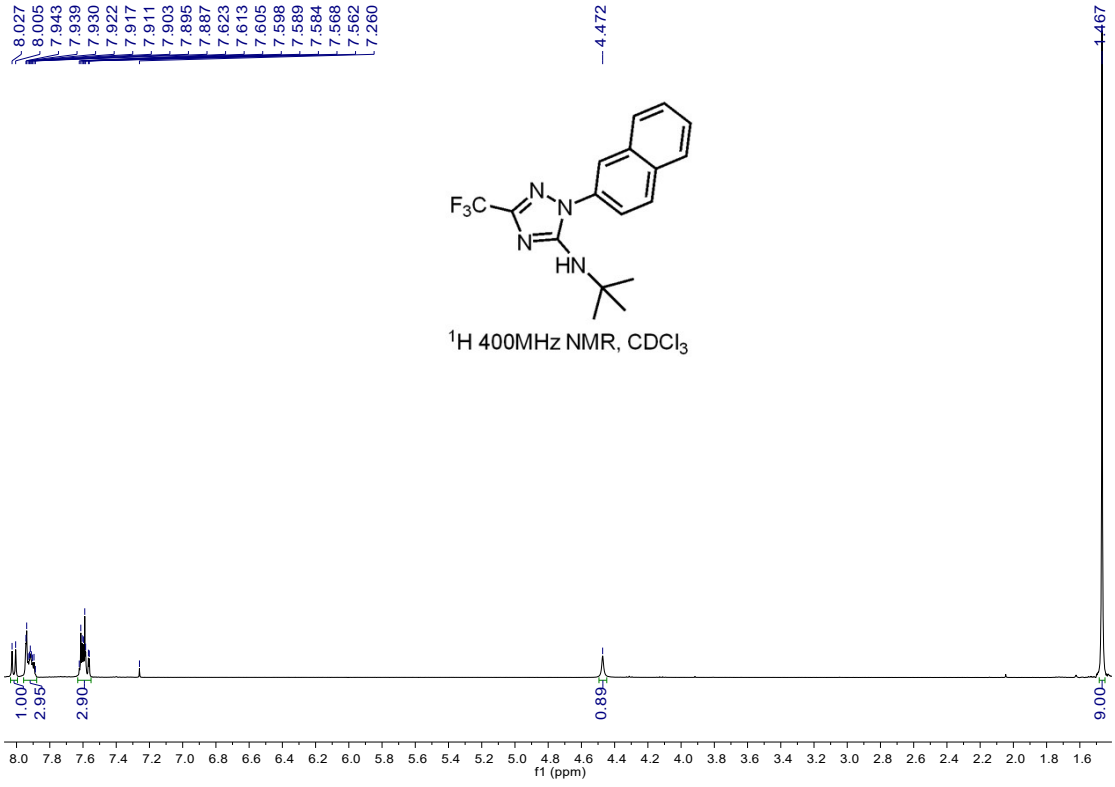
YANGGAOWANG-W35#58-114 RT: 0.26-0.51 AV: 57
T: FTMS + p ESI Full lock ms [80.0000-900.0000]
m/z= 337.6766-348.1563

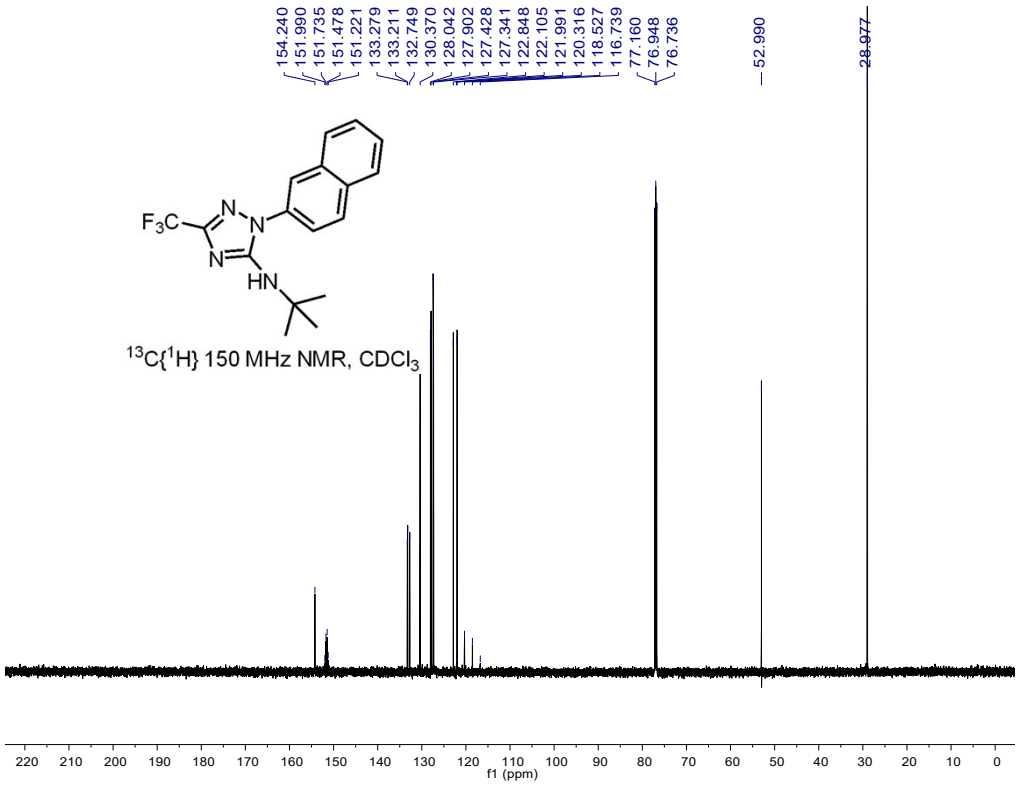
m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
338.3415	4615302.5	8.42			
339.3453	1026776.1	1.87			
343.1375	54840876.0	100.00	343.1376	-0.14	$C_{15}H_{18}O_2N_4F_3$
344.1410	9318529.0	16.99			

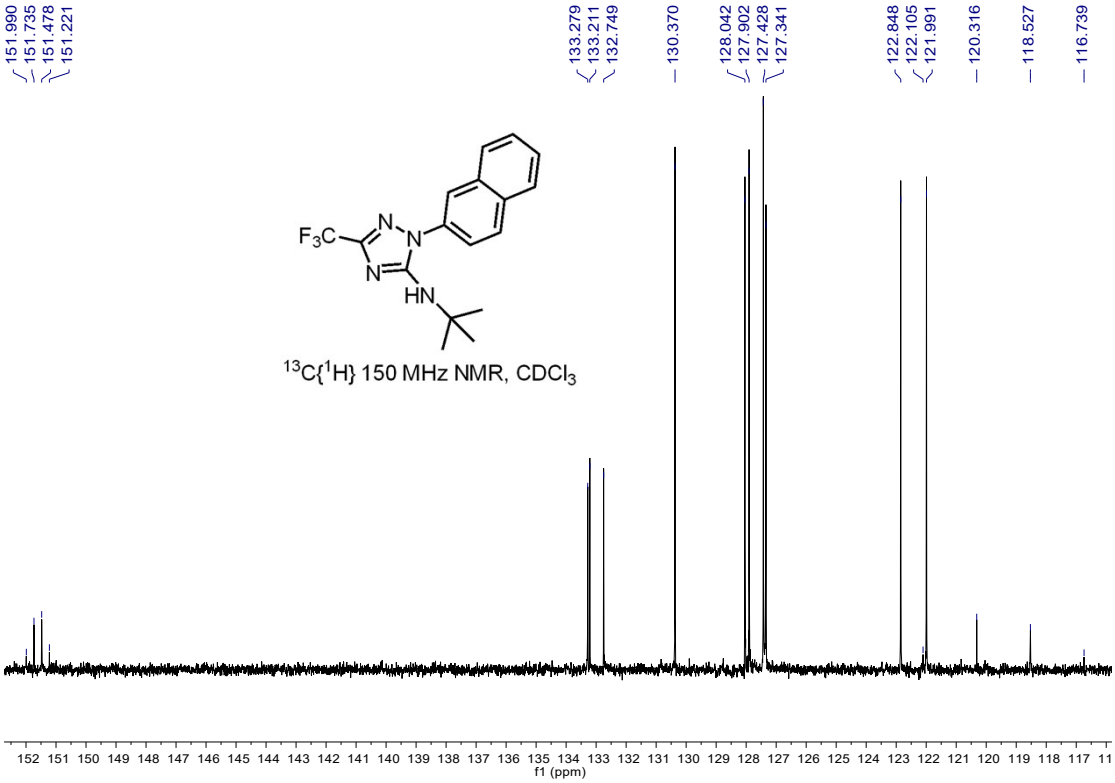


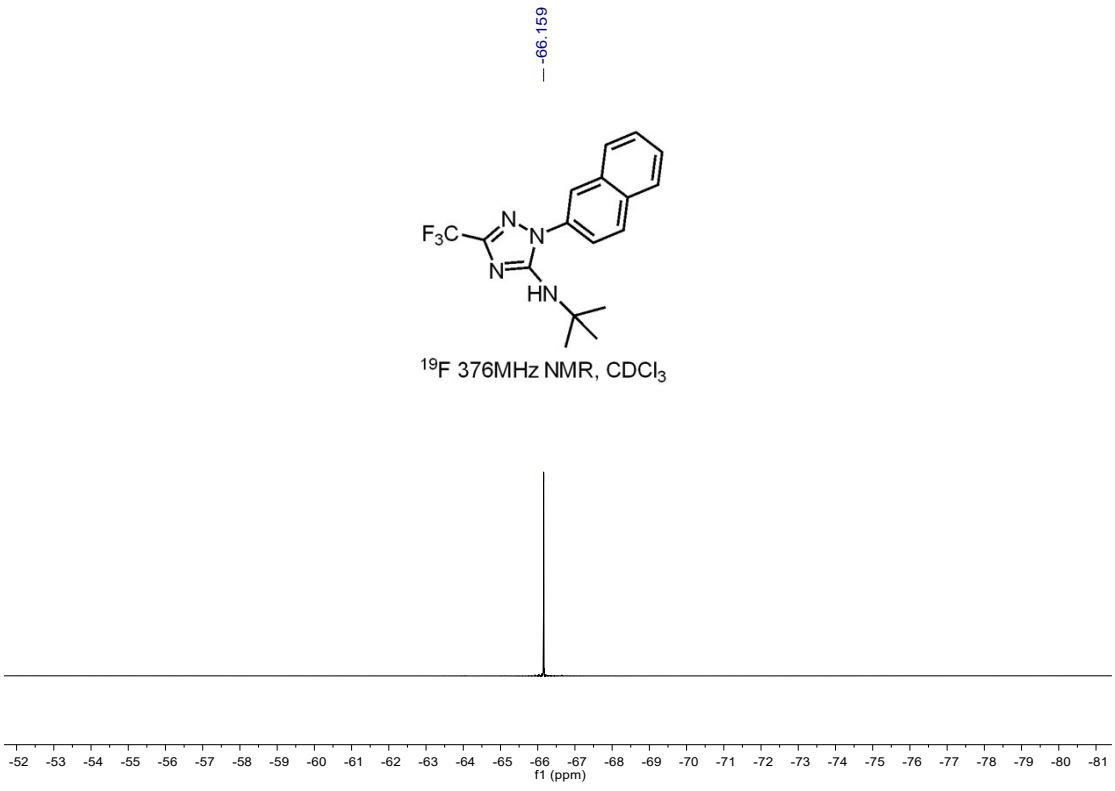
NMR copies of compound **5′g**:



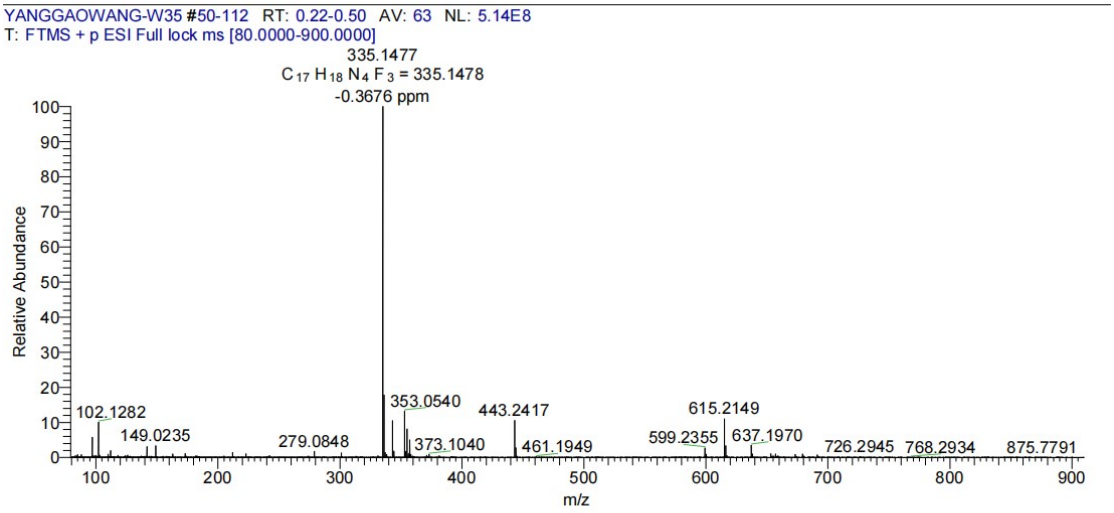



154.240
151.990
151.735
151.478
151.221
133.279
133.211
132.749
130.370
128.042
127.902
127.428
127.341
122.848
122.105
121.991
120.316
118.527
116.739
77.160
76.948
76.736
52.990
28.977
F3C
N
N
N
HN
13C{1H} 150 MHz NMR, CDCl3
f1 (ppm)


151.990
151.735
151.478
151.221
133.279
133.211
132.749
130.370
128.042
127.902
127.428
127.341
122.848
122.105
121.991
120.316
118.527
116.739
F3C
N
N
N
HN
13C{1H} 150 MHz NMR, CDCl3
f1 (ppm)

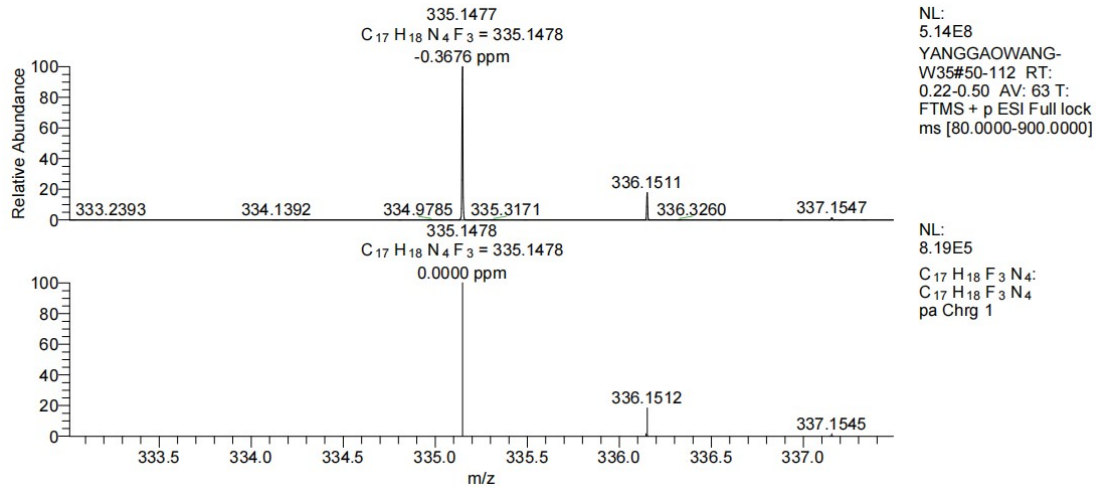

-66.159
F3C
N
N
N
HN
19F 376MHz NMR, CDCl3
-52 -53 -54 -55 -56 -57 -58 -59 -60 -61 -62 -63 -64 -65 -66 -67 -68 -69 -70 -71 -72 -73 -74 -75 -76 -77 -78 -79 -80 -81
f1 (ppm)

HRMS (ESI) copy of compound **5′g**:

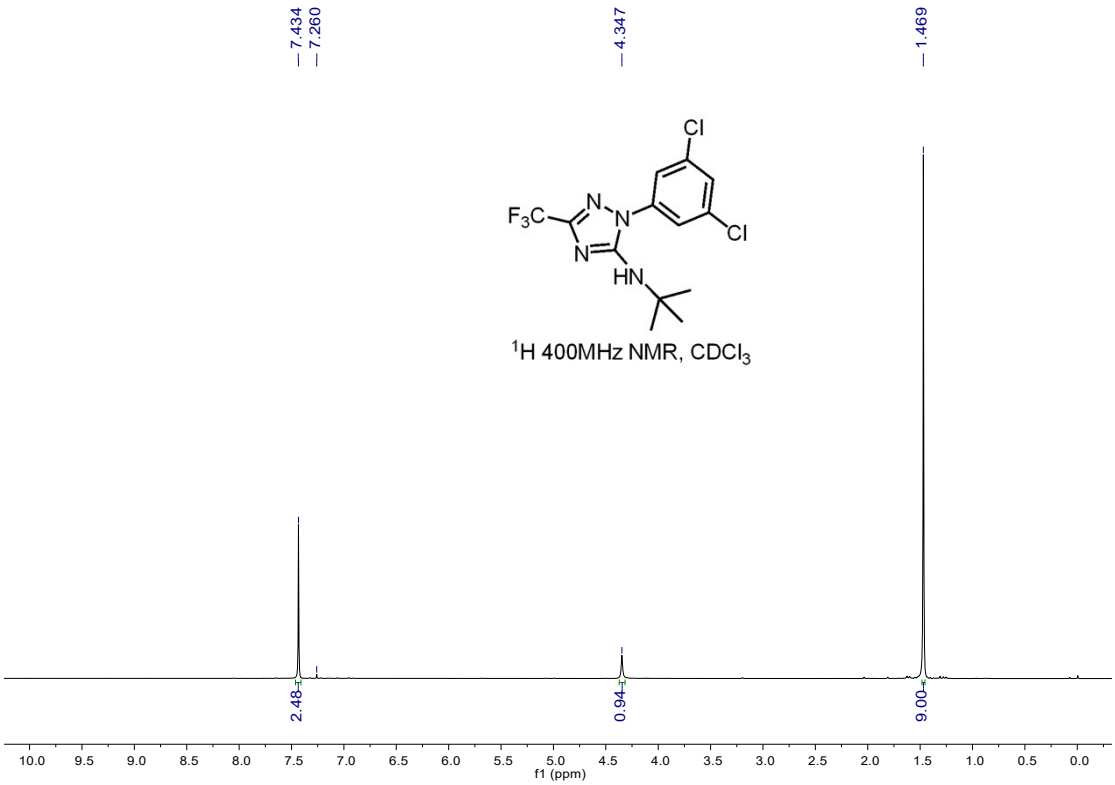


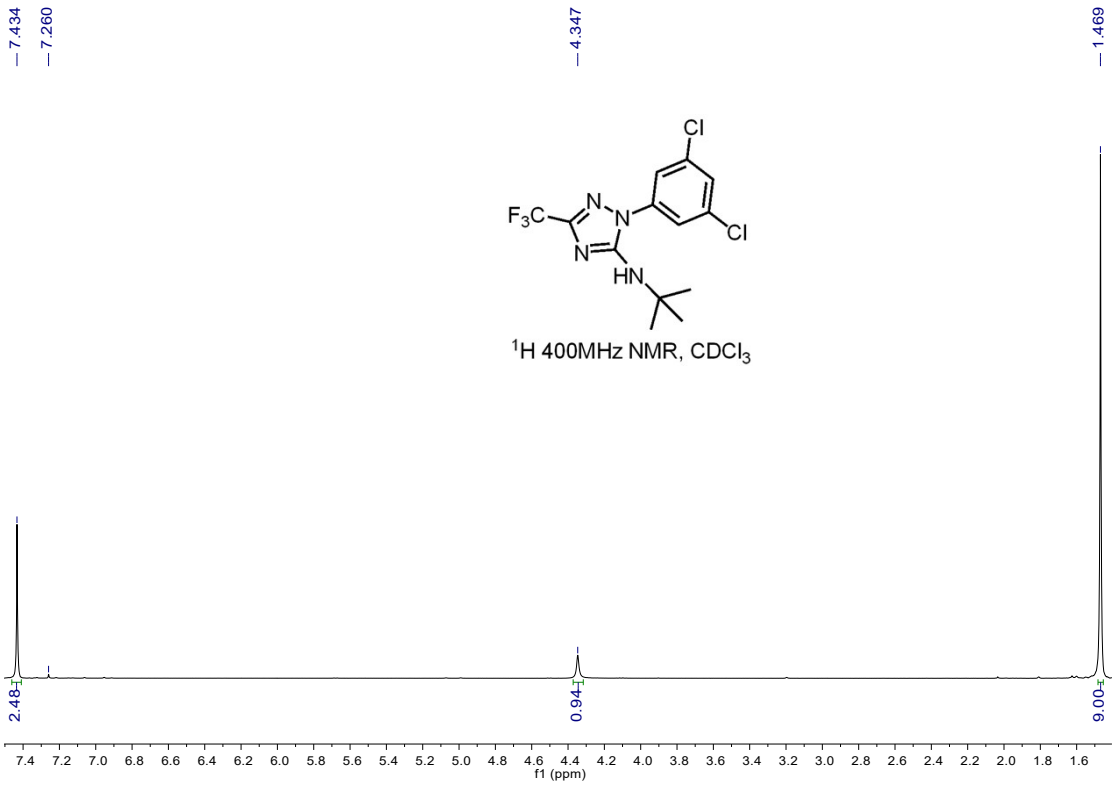
YANGGAOWANG-W35#50-112 RT: 0.22-0.50 AV: 63
T: FTMS + p ESI Full lock ms [80.0000-900.0000]

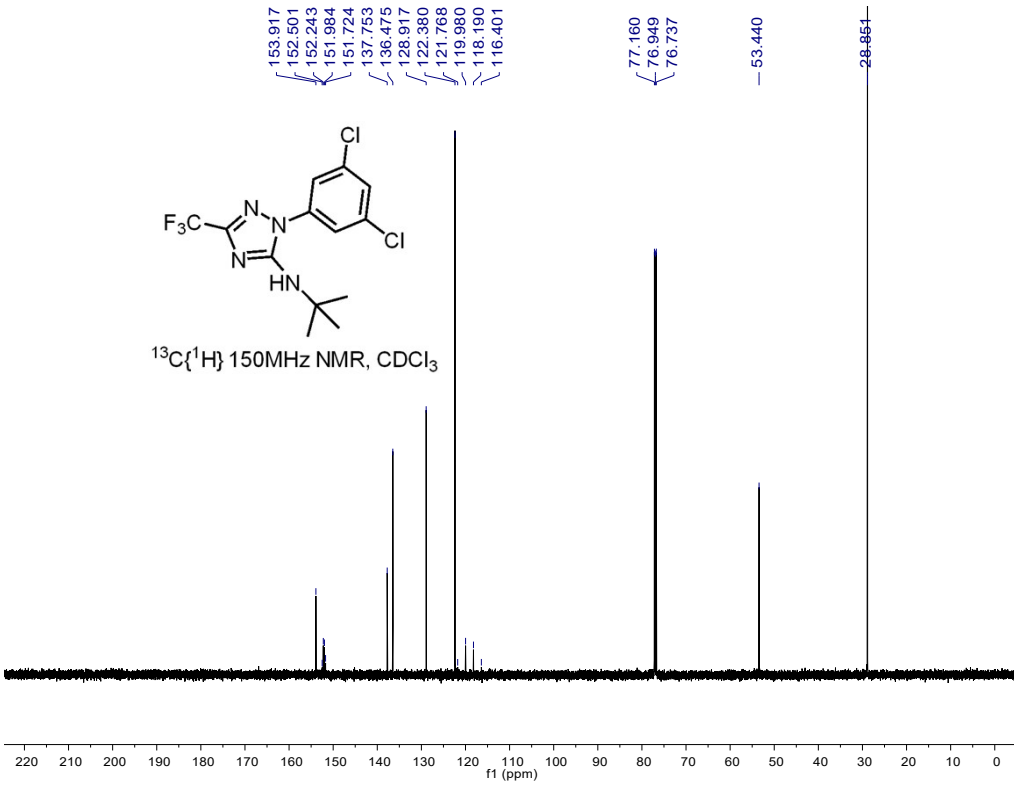
m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
335.1477	519770016.0	100.00	335.1478	-0.12	$C_{17}H_{18}N_4F_3$
336.1511	91708112.0	17.64			
353.0540	67989520.0	13.08			
615.2149	57655716.0	11.09			

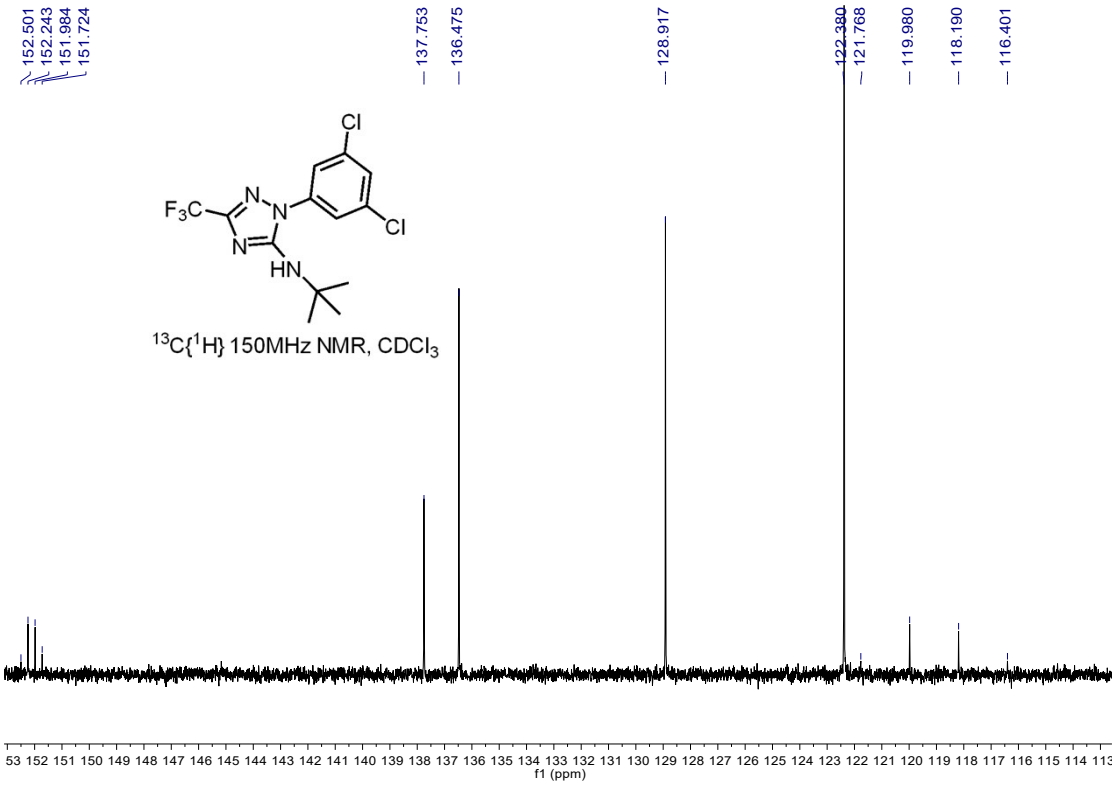


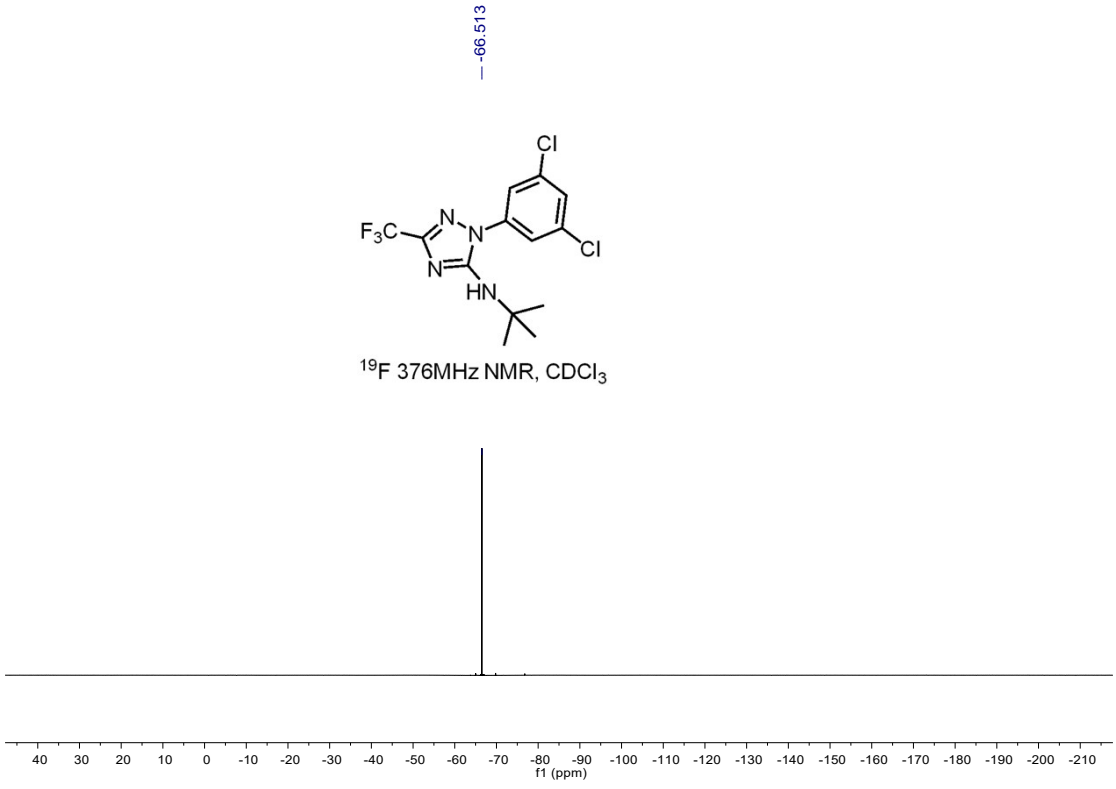
NMR copies of compound **5′h**:



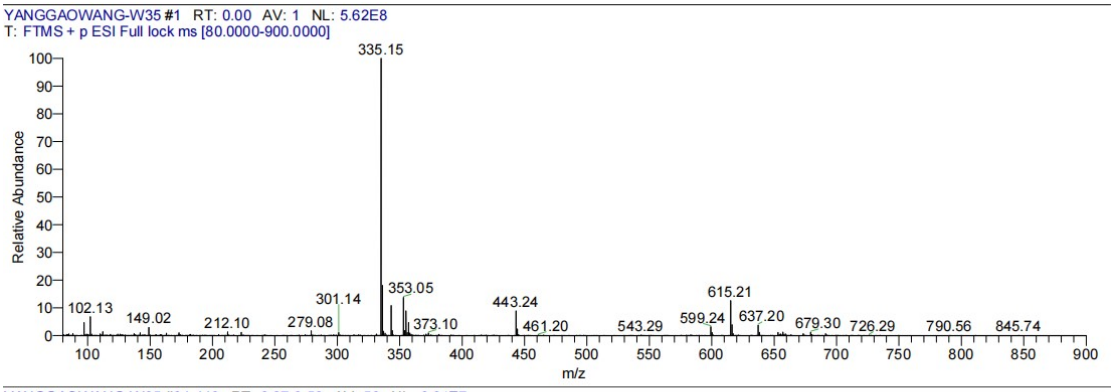


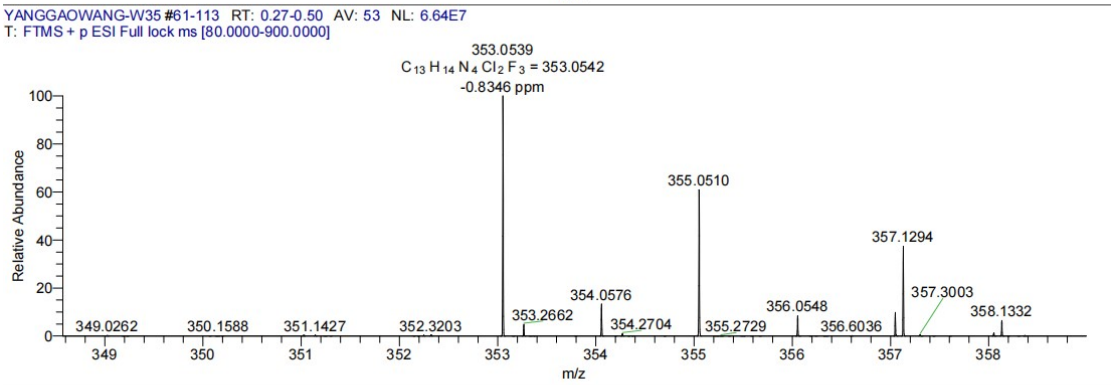

153.917
152.501
152.243
151.984
151.724
137.753
136.475
128.917
122.380
121.768
119.980
118.190
116.401
77.160
76.949
76.737
53.440
28.851
Cl
Cl
F3C
N
N
N
HN
13C{1H} 150MHz NMR, CDCl3
f1 (ppm)


152.501
152.243
151.984
151.724
137.753
136.475
128.917
122.380
121.768
119.980
118.190
116.401
Cl
Cl
F3C
N
N
N
HN
13C{1H} 150MHz NMR, CDCl3
f1 (ppm)


-66.513
Cl
F3C
N
N
N
Cl
HN
19F 376MHz NMR, CDCl3
40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

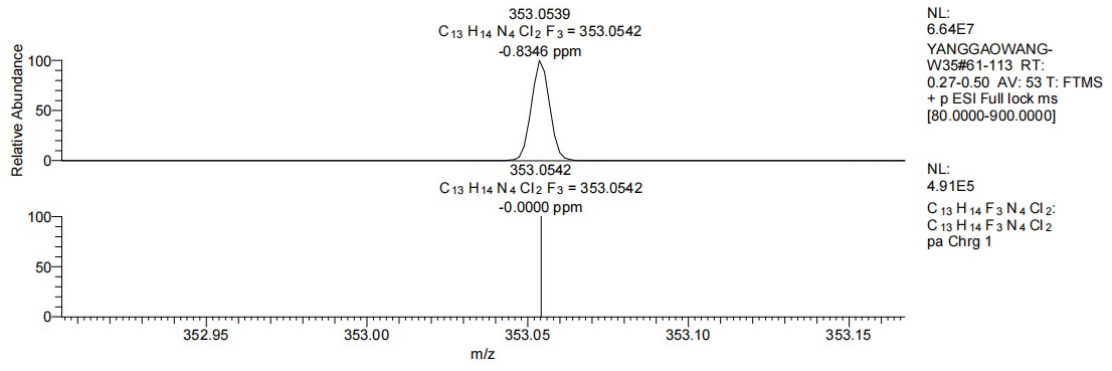
HRMS (ESI) copy of compound **5′h**:





YANGGAOWANG-W35#61-113 RT: 0.27-0.50 AV: 53
T: FTMS + p ESI Full lock ms [80.0000-900.0000]
m/z= 348.5721-358.9918

m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
353.0539	66774868.0	100.00	353.0542	-0.29	$C_{13}H_{14}N_4Cl_2F_3$
354.0576	8849748.0	13.25			
355.0510	42015820.0	62.92			
357.1294	24804566.0	37.15			



X-Ray Crystallographic Data of Compound **3a**

Thermal ellipsoids are set at a 50% probability level. Crystal data have been deposited to CCDC, number 2250252.

Crystallization Details

The obtained compound **3a** (15 mg) was dissolved in THF (0.3 mL) in a NMR tube at room temperature. Then petroleum ether (2 mL) was added to the solution slowly along the tube wall, resulting in a two-phase mixture. The colorless crystal of **3a** was formed after the two-phase mixture has diffused.

Experimental

A suitable crystal was selected on a ROD, Synergy Custom system, HyPix diffractometer. The crystal was kept at 150.00(10) K during data collection. Using Olex2, the structure was solved with the SHELXT structure solution program using Intrinsic Phasing and refined with the SHELXL refinement package using Least Squares minimisation.

Crystal structure determination

Crystal Data for $C_{23}H_{26}F_4N_6$ (M = 462.50 g/mol): triclinic, space group P-1 (no. 2), a = 9.52305(17) Å, b = 13.1270(2) Å, c = 18.3358(3) Å, α = 84.4953(15)°, β = 88.2625(15)°, γ = 89.6565(15)°, V = 2280.51(7) Å^3, Z = 4, T = 150.00(10) K, μ(Cu Kα) = 0.897 mm^{-1}, *Dcalc* = 1.347 g/cm^3, 26437 reflections measured (4.844° ≤ 2Θ ≤ 152.698°), 9012 unique (R_{int} = 0.0307, R_{sigma} = 0.0310) which were used in all calculations. The final R_1 was 0.0406 (I > 2σ(I)) and wR_2 was 0.1091 (all data).

Refinement model description

Number of restraints - 0, number of constraints - unknown.

Details:

1. Fixed Uiso

 At 1.2 times of:

 All C(H) groups

 At 1.5 times of:

 All C(H,H,H) groups

2.a Ternary CH refined with riding coordinates:

 C3(H3), C5(H5), C12(H12), C21(H21), C26(H26), C28(H28), C29(H29), C32(H32)

2.b Aromatic/amide H refined with riding coordinates:

 C7(H7), C8(H8), C9(H9), C10(H10), C11(H11), C16(H16), C17(H17), C18(H18), C19(H19), C20(H20), C36(H36), C37(H37), C38(H38), C39(H39), C40(H40), C42(H42), C43(H43), C44(H44), C45(H45), C46(H46)

2.c Idealised Me refined as rotating group:

 C13(H13A,H13B,H13C), C14(H14A,H14B,H14C), C22(H22A,H22B,H22C), C23(H23A,H23B,H23C), C30(H30A,H30B,H30C), C31(H31A,H31B,H31C), C33(H33A,H33B,H33C), C34(H34A,H34B,H34C)

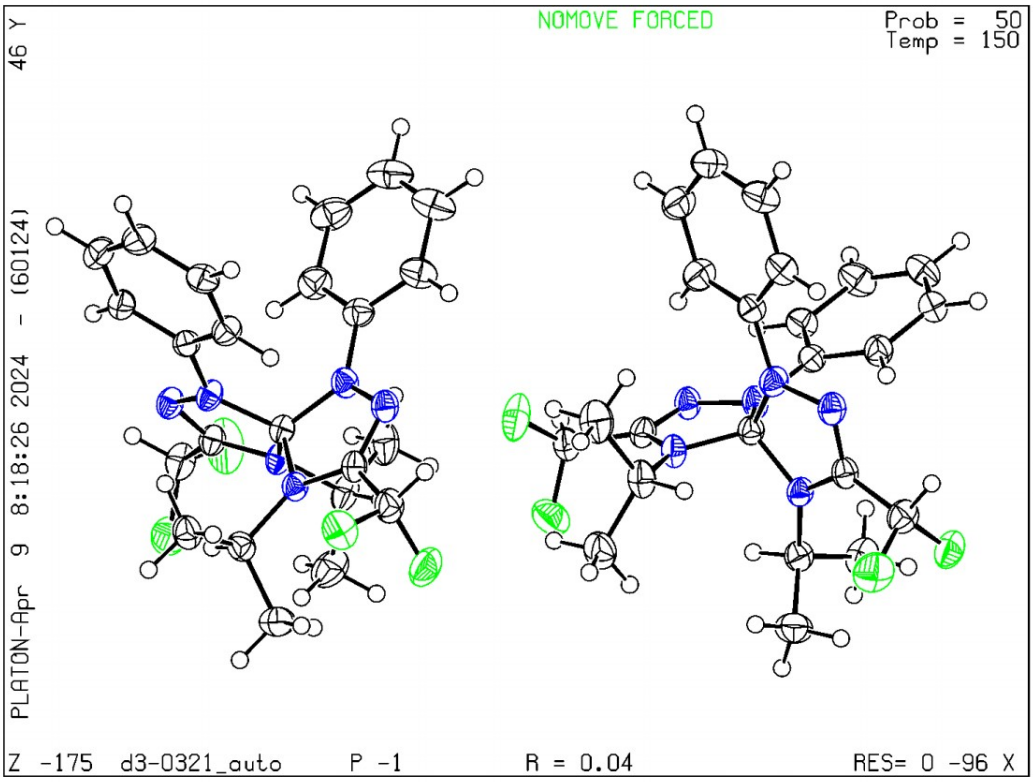

NOMOVE FORCED
Prob = 50
Temp = 150
46 Y
PLATON-Apr 9 8:18:26 2024 - (60124)
Z -175 d3-0321_auto P -1 R = 0.04 RES= 0 -96 X

Table S1 Crystal data and structure refinement for compound 3a

Empirical formula	$C_{23}H_{26}F_4N_6$
Formula weight	462.50
Temperature/K	150.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	9.52305(17)
b/Å	13.1270(2)
c/Å	18.3358(3)
α/°	84.4953(15)
β/°	88.2625(15)
γ/°	89.6565(15)
Volume/Å^3	2280.51(7)
Z	4
ρcalcg/cm^3	1.347
μ/mm^{-1}	0.897
F(000)	968.0
Crystal size/mm^3	0.05 × 0.03 × 0.02
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection	4.844 to 152.698
Index ranges	$-11 \le h \le 11$, $-16 \le k \le 16$, $-22 \le l \le 22$
Reflections collected	26437
Independent reflections	9012 [R_{int} = 0.0307, R_{sigma} = 0.0310]
Data/restraints/parameters	9012/0/604
Goodness-of-fit on F^2	1.047
Final R indexes [I>=2σ (I)]	R_1 = 0.0406, wR_2 = 0.1054
Final R indexes [all data]	R_1 = 0.0466, wR_2 = 0.1091
Largest diff. peak/hole / e Å^{-3}	0.56/-0.22

Table S2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for compound 3a. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
F1	5159.1(11)	3980.2(8)	751.7(6)	51.2(3)
F2	2936.5(10)	3876.5(7)	1044.0(5)	42.8(2)
F3	7283.8(11)	-1615.9(8)	2392.7(7)	53.3(3)
F4	6037.5(12)	-1704.3(7)	1438.7(5)	48.2(2)
N1	5308.7(13)	1943.1(9)	2705.6(7)	30.0(3)
N2	5087.0(13)	2942.9(9)	2412.0(7)	30.6(3)
N3	4298.4(12)	1875.1(8)	1637.3(6)	26.4(2)
N4	3690.4(12)	483.4(9)	2584.1(7)	29.2(3)
N5	4091.9(12)	-538.5(8)	2594.0(7)	29.4(3)
N6	5809.4(12)	436.0(9)	2040.3(7)	28.3(2)
C1	4773.5(14)	1187.8(10)	2255.6(8)	26.1(3)
C2	4506.6(14)	2863.9(10)	1791.6(8)	28.0(3)
C3	4231.1(16)	3838.5(11)	1337.6(9)	35.4(3)
C4	5313.1(14)	-523.1(10)	2267.8(8)	27.7(3)
C5	5952.4(15)	-1539.8(11)	2161.2(8)	31.8(3)
C6	5789.3(15)	1766.6(12)	3424.1(8)	31.3(3)
C7	5878.5(17)	784.0(13)	3782.3(9)	39.8(4)
C8	6375.0(18)	647.6(15)	4488.3(9)	46.3(4)
C9	6776(2)	1474.3(17)	4847.4(10)	51.5(5)
C10	6694(2)	2451.4(16)	4487.6(10)	52.9(5)
C11	6215.0(18)	2603.1(14)	3780.9(9)	42.1(4)
C12	3608.8(15)	1443.4(11)	1029.1(8)	30.3(3)
C13	2017.9(17)	1559.4(12)	1065.3(10)	40.4(4)
C14	4225(2)	1853.4(14)	283.1(9)	44.1(4)
C15	2560.1(14)	745.2(10)	3046.9(7)	27.0(3)
C16	1782.9(15)	-29.7(11)	3444.5(8)	31.5(3)
C17	676.4(17)	220.6(13)	3899.4(9)	40.4(4)
C18	317.0(17)	1232.2(13)	3966.9(9)	38.9(4)
C19	1081.8(16)	1996.1(12)	3568.0(8)	33.7(3)
C20	2191.7(15)	1765.6(11)	3106.5(8)	31.7(3)
C21	7177.6(15)	802.1(11)	1713.8(9)	34.5(3)
C22	8362.6(17)	688.5(14)	2252.9(11)	46.5(4)
C23	7548.9(18)	333.2(14)	1004.9(10)	44.1(4)
F5	10555.5(11)	-925.7(8)	790.8(6)	50.3(3)

F6	12727.0(10)	-1112.5(7)	1102.8(5)	42.0(2)
F7	9604.6(12)	-6568.9(8)	1287.3(6)	54.7(3)
F8	8166.9(10)	-6595.5(8)	2223.5(8)	60.1(3)
N7	10047.3(12)	-3042.2(9)	2698.8(7)	28.2(2)
N8	10342.5(12)	-2038.7(9)	2428.5(7)	29.6(3)
N9	11202.7(12)	-3086.9(8)	1633.2(6)	25.3(2)
N10	11672.4(12)	-4510.9(8)	2568.4(7)	27.0(2)
N11	11295.4(12)	-5526.0(8)	2531.9(7)	28.4(2)
N12	9640.4(11)	-4516.9(8)	1998.8(7)	27.4(2)
C24	10644.3(13)	-3787.5(10)	2239.3(7)	24.8(3)
C25	11004.3(14)	-2104.2(10)	1811.4(8)	27.7(3)
C26	11387.3(17)	-1118.2(11)	1382.3(9)	36.4(3)
C27	10121.2(14)	-5487.1(10)	2194.2(8)	27.4(3)
C28	9535.5(16)	-6483.9(11)	2025.8(9)	35.6(3)
C29	8307.0(15)	-4124.9(11)	1684.2(9)	35.4(3)
C30	7057.1(16)	-4302.3(14)	2217.2(11)	45.8(4)
C31	8039.4(19)	-4518.7(15)	947.2(10)	48.5(4)
C32	11997.5(15)	-3506.3(11)	1026.0(8)	29.1(3)
C33	11578.9(18)	-3019.0(13)	277.1(9)	40.6(4)
C34	13577.9(15)	-3467.8(12)	1121.5(9)	34.5(3)
C35	9492.3(14)	-3242.3(11)	3417.3(8)	30.2(3)
C36	9318.5(16)	-4237.4(12)	3746.8(9)	37.5(3)
C37	8748.2(18)	-4396.6(15)	4452.4(9)	45.0(4)
C38	8349(2)	-3581.1(17)	4836.8(9)	50.9(4)
C39	8513(2)	-2594.4(16)	4505.4(10)	51.8(5)
C40	9078.2(18)	-2417.0(13)	3800.7(9)	40.3(4)
C41	12729.7(13)	-4282.0(10)	3049.0(7)	25.4(3)
C42	13085.6(15)	-3271.2(11)	3136.9(8)	30.3(3)
C43	14120.8(15)	-3069.2(12)	3620.5(8)	32.3(3)
C44	14825.5(16)	-3855.4(13)	4010.8(9)	38.3(3)
C45	14478.7(17)	-4858.4(13)	3915.0(9)	39.8(4)
C46	13446.5(15)	-5077.8(11)	3437.7(8)	30.9(3)

Table S3 Anisotropic Displacement Parameters ($Å^2×10^3$) for compound 3a. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U11	U22	U33	U23	U13	U12
F1	55.7(6)	42.7(5)	51.1(6)	13.6(4)	8.8(5)	-8.9(4)
F2	45.5(5)	32.3(5)	50.1(6)	1.1(4)	-9.7(4)	8.1(4)
F3	42.5(5)	38.0(5)	80.6(8)	-8.7(5)	-17.7(5)	15.2(4)
F4	64.3(6)	38.8(5)	42.1(5)	-11.1(4)	8.1(5)	0.1(4)
N1	33.9(6)	24.1(6)	31.8(6)	-1.3(5)	-3.4(5)	0.7(5)
N2	32.6(6)	21.9(5)	36.8(7)	-1.0(5)	0.2(5)	0.4(4)
N3	42.5(5)	38.0(5)	80.6(8)	-8.7(5)	-17.7(5)	15.2(4)
N4	29.0(6)	20.6(5)	36.6(6)	0.9(5)	7.1(5)	1.6(4)
N5	31.1(6)	20.0(5)	36.0(6)	0.6(5)	3.1(5)	2.0(4)
N6	24.7(5)	22.3(5)	37.1(6)	0.2(5)	4.1(5)	2.1(4)
C1	25.6(6)	23.6(6)	28.5(7)	-0.6(5)	1.6(5)	0.8(5)
C2	27.4(6)	22.4(6)	33.9(7)	-2.3(5)	2.0(5)	-0.2(5)
C3	40.1(8)	26.0(7)	39.6(8)	0.5(6)	-2.9(6)	-1.4(6)
C4	28.6(7)	22.0(6)	31.9(7)	0.9(5)	-0.7(5)	1.4(5)
C5	31.4(7)	25.9(7)	37.7(8)	-3.0(6)	2.0(6)	4.0(5)
C6	28.8(7)	37.3(8)	27.6(7)	-2.8(6)	1.2(5)	5.0(6)
C7	40.6(8)	41.9(9)	35.7(8)	1.8(7)	-1.6(6)	4.6(7)
C8	42.3(9)	57.5(11)	36.6(9)	6.6(8)	2.5(7)	12.0(8)
C9	50.7(10)	75.1(13)	28.9(8)	-7.1(8)	-2.5(7)	17.1(9)
C10	62.4(11)	62.5(12)	36.5(9)	-17.9(9)	-5.7(8)	12.3(9)
C11	48.1(9)	42.4(9)	37.0(9)	-10.8(7)	-1.8(7)	7.9(7)
C12	35.1(7)	23.4(6)	32.9(7)	-4.1(5)	-2.5(6)	-0.3(5)
C13	36.0(8)	35.1(8)	50.5(10)	-3.5(7)	-9.6(7)	-2.0(6)
C14	58.4(10)	43.4(9)	30.2(8)	-1.9(7)	1.6(7)	0.9(8)
C15	25.6(6)	28.9(7)	25.9(7)	-1.2(5)	0.1(5)	1.2(5)
C16	34.4(7)	29.1(7)	30.8(7)	-2.6(6)	2.4(6)	-3.5(6)
C17	41.8(8)	40.8(9)	38.2(8)	-4.6(7)	11.7(7)	-10.0(7)
C18	35.6(8)	45.4(9)	36.2(8)	-10.6(7)	9.7(6)	-1.2(6)
C19	34.4(7)	34.2(8)	33.0(8)	-6.1(6)	-0.1(6)	5.5(6)
C20	32.6(7)	28.4(7)	33.1(7)	0.5(6)	2.6(6)	1.9(6)
C21	26.1(7)	26.7(7)	49.1(9)	1.1(6)	8.4(6)	-0.8(5)
C22	28.6(8)	46.8(10)	64.5(12)	-8.7(8)	0.8(7)	-2.2(7)
C23	39.8(9)	44.4(9)	45.9(10)	1.8(7)	13.5(7)	4.7(7)
F5	53.9(6)	43.0(5)	50.1(6)	14.6(4)	-1.2(5)	13.6(4)
F6	43.5(5)	30.5(5)	50.9(6)	-1.4(4)	9.5(4)	-7.7(4)
F7	66.8(7)	46.6(6)	55.3(6)	-21.7(5)	-23.7(5)	10.2(5)
F8	37.3(5)	36.4(5)	107.2(10)	-10.9(6)	3.4(6)	-12.5(4)

N7	31.2(6)	21.9(5)	31.1(6)	-2.1(5)	1.9(5)	0.7(4)
N8	31.2(6)	22.0(5)	35.5(7)	-2.0(5)	0.2(5)	0.8(4)
N9	27.6(5)	19.9(5)	28.0(6)	-1.0(4)	0.7(4)	0.8(4)
N10	27.4(6)	19.7(5)	33.8(6)	0.0(4)	-7.2(5)	-0.2(4)
N11	29.6(6)	20.8(5)	34.8(6)	-1.6(5)	-4.7(5)	-0.3(4)
N12	23.1(5)	22.3(5)	36.8(6)	-1.2(5)	-6.5(5)	-0.1(4)
C24	24.0(6)	22.0(6)	28.4(7)	-1.2(5)	-2.5(5)	0.9(5)
C25	28.0(6)	20.7(6)	34.1(7)	-2.0(5)	-0.9(5)	2.1(5)
C26	41.8(8)	25.0(7)	41.2(8)	1.3(6)	4.0(7)	3.5(6)
C27	27.1(6)	22.4(6)	32.8(7)	-1.8(5)	-2.4(5)	-0.1(5)
C28	31.7(7)	26.5(7)	49.6(9)	-5.9(6)	-9.4(6)	-1.6(6)
C29	28.4(7)	27.8(7)	50.4(9)	-1.9(6)	-13.8(6)	2.9(5)
C30	26.0(7)	44.7(9)	68.0(12)	-11.4(8)	-5.7(7)	3.5(6)
C31	44.6(9)	50.7(10)	51.0(10)	-2.8(8)	-20.7(8)	0.4(8)
C32	32.4(7)	24.9(7)	30.2(7)	-5.1(5)	1.0(5)	0.4(5)
C33	48.0(9)	44.3(9)	29.5(8)	-3.5(7)	-3.0(7)	1.0(7)
C34	30.2(7)	33.2(8)	39.3(8)	-2.2(6)	5.6(6)	2.8(6)
C35	26.6(6)	35.3(7)	28.7(7)	-2.8(6)	-2.7(5)	-2.8(5)
C36	36.2(8)	38.4(8)	36.9(8)	1.4(6)	0.8(6)	-2.7(6)
C37	39.1(8)	56.6(10)	37.3(9)	7.0(8)	-2.9(7)	-9.9(7)
C38	49.5(10)	74.8(13)	28.0(8)	-4.0(8)	1.7(7)	-13.0(9)
C39	61.0(11)	62.3(12)	34.2(9)	-16.7(8)	3.8(8)	-6.6(9)
C40	46.7(9)	42.4(9)	33.1(8)	-10.1(7)	-1.0(7)	-4.7(7)
C41	23.5(6)	28.8(7)	23.7(6)	-1.9(5)	-0.6(5)	0.4(5)
C42	31.5(7)	27.7(7)	31.6(7)	-0.8(6)	-3.3(6)	-1.3(5)
C43	31.9(7)	35.3(8)	30.4(7)	-7.1(6)	-0.4(6)	-4.9(6)
C44	35.0(8)	47.6(9)	34.0(8)	-9.8(7)	-9.9(6)	2.0(7)
C45	41.7(8)	41.2(9)	36.9(8)	-3.4(7)	-13.3(7)	10.0(7)
C46	33.5(7)	28.1(7)	31.3(7)	-3.0(6)	-3.6(6)	4.5(6)

Table S4 Bond Lengths for compound 3a.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
F1	C3	1.3697(19)	F5	C26	1.3654(19)
F2	C3	1.3589(18)	F6	C26	1.3602(18)
F3	C5	1.3493(18)	F7	C28	1.369(2)
F4	C5	1.3624(18)	F8	C28	1.3472(18)
N1	N2	1.3874(16)	N7	N8	1.3894(16)
N1	C1	1.4534(17)	N7	C24	1.4535(17)
N1	C6	1.4055(19)	N7	C35	1.4061(19)
N2	C2	1.2929(19)	N8	C25	1.2883(19)
N3	C1	1.4608(17)	N9	C24	1.4621(17)
N3	C2	1.3716(17)	N9	C25	1.3714(17)
N3	C12	1.4717(18)	N9	C32	1.4754(17)
N4	N5	1.3913(16)	N10	N11	1.3904(16)
N4	C1	1.4658(17)	N10	C24	1.4625(17)
N4	C15	1.4117(17)	N10	C41	1.4104(17)
N5	C4	1.2908(18)	N11	C27	1.2930(18)
N6	C1	1.4636(17)	N12	C24	1.4637(17)
N6	C4	1.3701(18)	N12	C27	1.3695(17)
N6	C21	1.4805(18)	N12	C29	1.4797(17)
C2	C3	1.484(2)	C25	C26	1.490(2)
C4	C5	1.4910(18)	C27	C28	1.4884(19)
C6	C7	1.393(2)	C29	C30	1.522(2)
C6	C11	1.399(2)	C29	C31	1.521(2)
C7	C8	1.387(2)	C32	C33	1.522(2)
C8	C9	1.384(3)	C32	C34	1.522(2)
C9	C10	1.388(3)	C35	C36	1.394(2)
C10	C11	1.383(2)	C35	C40	1.396(2)
C12	C13	1.522(2)	C36	C37	1.386(2)
C12	C14	1.523(2)	C37	C38	1.382(3)
C15	C16	1.396(2)	C38	C39	1.385(3)
C15	C20	1.396(2)	C39	C40	1.384(2)
C16	C17	1.382(2)	C41	C42	1.3968(19)
C17	C18	1.385(2)	C41	C46	1.3941(19)
C18	C19	1.381(2)	C42	C43	1.389(2)
C19	C20	1.384(2)	C43	C44	1.381(2)
C21	C22	1.520(2)	C44	C45	1.388(2)
C21	C23	1.522(2)	C45	C46	1.385(2)

Table S5 Bond Angles for compound 3a.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N2	N1	C1	113.11(11)	N8	N7	C24	112.85(11)
N2	N1	C6	118.96(12)	N8	N7	C35	119.23(11)
C6	N1	C1	127.07(12)	C35	N7	C24	126.56(12)
C2	N2	N1	105.10(11)	C25	N8	N7	105.27(11)
C1	N3	C12	119.27(11)	C24	N9	C32	119.22(10)
C2	N3	C1	108.35(11)	C25	N9	C24	108.27(11)
C2	N3	C12	132.11(12)	C25	N9	C32	131.92(12)
N5	N4	C1	112.80(10)	N11	N10	C24	112.80(10)
N5	N4	C15	118.83(11)	N11	N10	C41	119.16(11)
C15	N4	C1	125.65(11)	C41	N10	C24	125.92(11)
C4	N5	N4	105.11(11)	C27	N11	N10	105.21(11)
C1	N6	C21	118.91(11)	C24	N12	C29	118.84(11)
C4	N6	C1	108.41(11)	C27	N12	C24	108.41(10)
C4	N6	C21	132.30(11)	C27	N12	C29	132.38(12)
N1	C1	N3	99.12(10)	N7	C24	N9	99.10(10)
N1	C1	N4	117.59(11)	N7	C24	N10	117.26(11)
N1	C1	N6	114.90(11)	N7	C24	N12	115.10(11)
N3	C1	N4	114.08(11)	N9	C24	N10	114.58(11)
N3	C1	N6	113.03(11)	N9	C24	N12	112.50(11)
N6	C1	N4	98.96(10)	N10	C24	N12	99.11(10)
N2	C2	N3	114.18(12)	N8	C25	N9	114.22(12)
N2	C2	C3	116.19(12)	N8	C25	C26	116.35(12)
N3	C2	C3	129.55(13)	N9	C25	C26	129.37(13)
F1	C3	C2	111.54(12)	F5	C26	C25	111.30(13)
F2	C3	F1	105.33(12)	F6	C26	F5	105.42(13)
F2	C3	C2	113.09(12)	F6	C26	C25	112.88(12)
N5	C4	N6	114.63(12)	N11	C27	N12	114.47(12)
N5	C4	C5	116.11(12)	N11	C27	C28	116.34(12)
N6	C4	C5	129.20(12)	N12	C27	C28	129.04(12)
F3	C5	F4	105.32(12)	F7	C28	C27	110.77(13)
F3	C5	C4	112.18(12)	F8	C28	F7	105.41(13)
F4	C5	C4	111.48(12)	F8	C28	C27	112.97(12)
C7	C6	N1	121.88(14)	N12	C29	C30	112.74(13)
C7	C6	C11	119.38(15)	N12	C29	C31	112.43(13)
C11	C6	N1	118.73(14)	C31	C29	C30	112.07(14)
C8	C7	C6	119.76(16)	N9	C32	C33	112.67(12)
C9	C8	C7	121.04(17)	N9	C32	C34	112.25(11)
C8	C9	C10	119.08(16)	C33	C32	C34	111.88(13)
C11	C10	C9	120.79(18)	C36	C35	N7	121.84(13)
C10	C11	C6	119.95(17)	C36	C35	C40	119.54(14)

N3	C12	C13	112.84(12)	C40	C35	N7	118.60(14)
N3	C12	C14	112.42(12)	C37	C36	C35	119.74(16)
C13	C12	C14	111.66(14)	C38	C37	C36	120.91(17)
C16	C15	N4	119.46(12)	C37	C38	C39	119.15(16)
C16	C15	C20	119.32(13)	C40	C39	C38	120.94(17)
C20	C15	N4	121.20(12)	C39	C40	C35	119.71(17)
C17	C16	C15	119.80(14)	C42	C41	N10	121.23(12)
C16	C17	C18	121.09(15)	C46	C41	N10	119.52(12)
C19	C18	C17	118.91(14)	C46	C41	C42	119.25(13)
C18	C19	C20	121.13(14)	C43	C42	C41	119.93(13)
C19	C20	C15	119.75(14)	C44	C43	C42	120.97(14)
N6	C21	C22	113.06(13)	C43	C44	C45	118.85(14)
N6	C21	C23	112.36(13)	C46	C45	C44	121.17(14)
C22	C21	C23	112.15(13)	C45	C46	C41	119.82(14)

Table S6 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for compound 3a.

Atom	*x*	*y*	*z*	U(eq)
F1	5159.1(11)	3980.2(8)	751.7(6)	51.2(3)
F2	2936.5(10)	3876.5(7)	1044.0(5)	42.8(2)
F3	7283.8(11)	-1615.9(8)	2392.7(7)	53.3(3)
F4	6037.5(12)	-1704.3(7)	1438.7(5)	48.2(2)
N1	5308.7(13)	1943.1(9)	2705.6(7)	30.0(3)
N2	5087.0(13)	2942.9(9)	2412.0(7)	30.6(3)
N3	4298.4(12)	1875.1(8)	1637.3(6)	26.4(2)
N4	3690.4(12)	483.4(9)	2584.1(7)	29.2(3)
N5	4091.9(12)	-538.5(8)	2594.0(7)	29.4(3)
N6	5809.4(12)	436.0(9)	2040.3(7)	28.3(2)
C1	4773.5(14)	1187.8(10)	2255.6(8)	26.1(3)
C2	4506.6(14)	2863.9(10)	1791.6(8)	28.0(3)
C3	4231.1(16)	3838.5(11)	1337.6(9)	35.4(3)
C4	5313.1(14)	-523.1(10)	2267.8(8)	27.7(3)
C5	5952.4(15)	-1539.8(11)	2161.2(8)	31.8(3)
C6	5789.3(15)	1766.6(12)	3424.1(8)	31.3(3)
C7	5878.5(17)	784.0(13)	3782.3(9)	39.8(4)
C8	6375.0(18)	647.6(15)	4488.3(9)	46.3(4)
C9	6776(2)	1474.3(17)	4847.4(10)	51.5(5)
C10	6694(2)	2451.4(16)	4487.6(10)	52.9(5)
C11	6215.0(18)	2603.1(14)	3780.9(9)	42.1(4)
C12	3608.8(15)	1443.4(11)	1029.1(8)	30.3(3)
C13	2017.9(17)	1559.4(12)	1065.3(10)	40.4(4)
C14	4225(2)	1853.4(14)	283.1(9)	44.1(4)
H3	4322.56	4419.67	1647.79	43
H5	5370.05	-2090.04	2435.19	38
H7	5600.19	209.77	3543.81	48
H8	6441.07	-23.96	4729.06	56
H9	7102.34	1374.46	5333.64	62
H10	6970.7	3022.9	4729.64	64
H11	6174.83	3274.67	3537.95	50
H12	3808.25	691.62	1084.05	36

H13A	1662.37	1322.24	1559.23	61
H13B	1601	1149.77	708.55	61
H13C	1765.95	2280.79	951.37	61
H14A	3926.35	2565.14	169.5	66
H14B	3893.66	1437.64	-92.88	66
H14C	5253.24	1821.37	292.53	66
H16	2013.89	-727.07	3402.37	38
H17	153.45	-309.81	4170.49	48
H18	-443.13	1397.57	4282.36	47
H19	842.09	2691.81	3611.01	40
H20	2700.87	2299.66	2831.33	38
H21	7063.57	1553.4	1577.54	41
H22A	8101.6	1032.94	2688.63	70
H22B	9218.69	998.79	2021.5	70
H22C	8531.56	-39.34	2396.18	70
H23A	7805.32	-387.71	1117.02	66
H23B	8343.44	702.98	753.89	66
H23C	6737.05	382.41	687.36	66
H26	11272.43	-549.97	1705.67	44
H28	10086.13	-7053.93	2283.17	43
H29	8415.91	-3366.28	1588.05	42
H30A	6888	-5038.83	2317.25	69
H30B	6222.2	-3970.01	2001.74	69
H30C	7256.15	-4012.32	2676.01	69
H31A	8893.68	-4442.47	635.51	73
H31B	7274.36	-4124.47	709.26	73
H31C	7777.63	-5242.9	1022.19	73
H32	11742.82	-4246.56	1045.33	35
H33A	10553.23	-3022.18	247.01	61
H33B	11994.94	-3408.76	-105.51	61
H33C	11918.87	-2312.17	207.32	61
H34A	13888.3	-2753.43	1071.1	52
H34B	14057.27	-3837.65	746.01	52
H34C	13805.76	-3787.64	1608.79	52

H36	9590.04	-4804.12	3488.4	45
H37	8630.08	-5075.62	4675.24	54
H38	7966.26	-3696.25	5322.08	61
H39	8234.34	-2031.05	4765.57	62
H40	9183.65	-1736.5	3578.89	48
H42	12620.2	-2722.51	2866.23	36
H43	14347.35	-2379.93	3683.64	39
H44	15535.27	-3712.35	4339.12	46
H45	14957.8	-5404.11	4181.48	48
H46	13227.75	-5768.69	3375.48	37

X-Ray Crystallographic Data of Compound **5a**

Thermal ellipsoids are set at a 50% probability level. Crystal data have been deposited to CCDC, number 2264556.

Crystallization Details

The obtained compound **5a** (15 mg) was dissolved in THF (0.3 mL) in a NMR tube at room temperature. Then petroleum ether (2 mL) was added to the solution slowly along the tube wall, resulting in a two-phase mixture. The colorless crystal of compound **5a** was formed after the two-phase mixture has diffused.

Experimental

A suitable crystal was selected on a ROD, Synergy Custom system, HyPix diffractometer. The crystal was kept at 301.22(10) K during data collection. Using Olex2, the structure was solved with the SHELXT structure solution program using Intrinsic Phasing and refined with the SHELXL refinement package using Least Squares minimisation.

Crystal structure determination

Crystal Data for $C_{13}H_{16}F_2N_4$ (M =266.30 g/mol): monoclinic, space group P21 (no. 4), a = 6.1731(3) Å, b = 9.5526(5) Å, c = 11.6141(5) Å, β = 96.315(4), V = 680.72(6) $Å^3$, Z = 2, T = 301.22(10) K, μ(Cu Kα) = 0.842 mm-1, Dcalc = 1.299 g/cm3, 8813 reflections measured (7.658° ≤ 2Θ ≤ 155.834°), 2592 unique (Rint = 0.0614, Rsigma = 0.0413) which were used in all calculations. The final R1 was 0.0686 (I > 2σ(I)) and wR_2 was 0.1899 (all data).

Refinement model description

Number of restraints - 1, number of constraints - unknown.

Details:

1. Fixed Uiso
  At 1.2 times of:
  All C(H) groups, All N(H) groups
  At 1.5 times of:
  All C(H,H,H) groups
2. a Ternary CH refined with riding coordinates:
  C2(H2A)

2.b Aromatic/amide H refined with riding coordinates:
  N2(H2), C5(H5), C8(H8), C10(H10), C11(H11), C13(H13)

2.c Idealised Me refined as rotating group:
  C3(H3A,H3B,H3C), C7(H7A,H7B,H7C), C9(H9A,H9B,H9C)

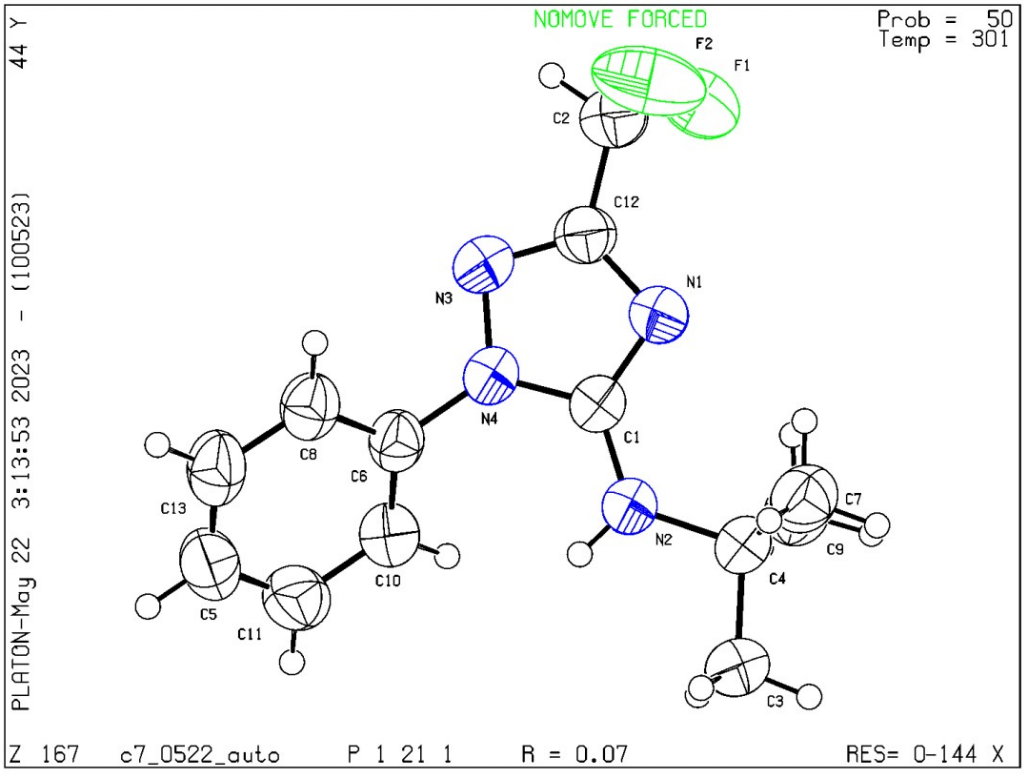

NOMOVE FORCED
Prob = 50
Temp = 301
F2
F1
C2
C12
N3
N1
N4
C1
C8
C6
C13
C7
N2
C9
C10
C4
C5
C11
C3
PLATON-May 22 3:13:53 2023 - (100523)
44 Y
Z 167 c7_0522_auto P 1 21 1 R = 0.07 RES= 0-144 X

Table S7 Crystal data and structure refinement for compound 5a

Empirical formula	$C_{13}H_{16}F_2N_4$
Formula weight	266.30
Temperature/K	301.22(10)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	6.1731(3)
b/Å	9.5526(5)
c/Å	11.6141(5)
α/°	90
β/°	96.315(4)
γ/°	90
Volume/Å^3	680.72(6)
Z	2
ρcalcg/cm^3	1.299
μ/mm^{-1}	0.842
F(000)	280.0
Crystal size/mm^3	0.13 × 0.06 × 0.05
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection	7.658 to 155.834
Index ranges	$-7 \le h \le 7$, $-11 \le k \le 10$, $-14 \le l \le 14$
Reflections collected	8813
Independent reflections	2592 [R_{int} = 0.0614, R_{sigma} = 0.0413]
Data/restraints/parameters	2592/1/175
Goodness-of-fit on F^2	1.044
Final R indexes [I>=2σ (I)]	R_1 = 0.0686, wR_2 = 0.1831
Final R indexes [all data]	R_1 = 0.0723, wR_2 = 0.1899
Largest diff. peak/hole / e Å^{-3}	0.40/-0.36
Flack parameter	-0.12(9)

Table S8 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for compound 5a. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
F1	676(6)	7833(4)	8213(3)	104.9(10)
F2	3458(8)	8824(4)	7675(4)	131.5(16)
N1	2855(5)	5771(3)	6972(3)	57.6(7)
N2	3952(5)	3602(4)	6170(3)	63.9(8)
N3	5251(5)	5763(4)	8595(3)	63.5(8)
N4	5504(5)	4572(3)	7950(2)	57.5(7)
C1	4056(5)	4611(4)	6971(3)	53.3(7)
C2	2881(8)	7786(5)	8352(4)	73.8(11)
C3	2721(8)	2104(5)	4581(4)	79.6(13)
C4	2274(6)	3477(4)	5163(3)	58.4(8)
C5	10449(7)	1715(6)	9022(3)	76.0(12)
C6	7157(5)	3585(4)	8311(3)	55.8(8)
C7	2419(8)	4687(5)	4344(3)	75.4(11)
C8	9229(6)	4081(5)	8704(3)	63.3(9)
C9	27(6)	3424(5)	5590(4)	73.3(11)
C10	6721(6)	2172(5)	8288(3)	64.6(9)
C11	8376(8)	1225(5)	8633(4)	74.8(11)
C12	3657(6)	6408(4)	7966(3)	59.1(8)
C13	10858(6)	3135(6)	9074(4)	74.4(12)

Table S9 Anisotropic Displacement Parameters ($Å^2×10^3$) for compound 5a. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U11	U22	U33	U23	U13	U12
F1	97(2)	98(2)	119(2)	-16.2(19)	12.4(15)	31.2(17)
F2	174(4)	59.0(19)	173(4)	0(2)	68(3)	1(2)
N1	60.1(14)	55.1(17)	57.2(15)	-2.4(12)	4.6(11)	5.3(12)
N2	62.0(15)	65(2)	61.3(16)	-14.3(14)	-8.6(12)	13.5(13)
N3	67.3(16)	63.1(19)	58.4(16)	-12.4(14)	-0.9(12)	1.9(14)
N4	56.6(14)	60.3(18)	53.7(14)	-6.7(12)	-2.8(10)	2.2(12)
C1	53.1(14)	53.6(18)	52.3(15)	-2.8(13)	1.8(11)	-0.8(13)
C2	86(3)	66(3)	68(2)	-9.4(18)	4.3(18)	8(2)
C3	81(2)	74(3)	80(3)	-25(2)	-10(2)	12(2)
C4	60.0(16)	59(2)	53.7(17)	-7.3(14)	-4.2(12)	0.6(14)
C5	73(2)	92(3)	63(2)	6(2)	5.1(16)	24(2)
C6	51.3(15)	68(2)	47.6(15)	-0.5(13)	4.4(11)	3.5(14)
C7	87(3)	73(3)	65(2)	0(2)	1.3(18)	-6(2)
C8	54.7(16)	77(2)	58.4(18)	0.2(16)	5.3(13)	-0.9(15)
C9	58.6(19)	75(3)	85(3)	-9(2)	2.8(16)	-6.6(17)
C10	64.7(19)	65(2)	63(2)	1.3(15)	1.6(14)	3.3(16)
C11	90(3)	67(3)	67(2)	2.9(18)	6.4(18)	9(2)
C12	65.3(17)	55.2(19)	56.8(17)	-3.3(14)	6.8(13)	1.3(15)
C13	53.4(17)	103(4)	66(2)	0(2)	2.5(14)	8.1(18)

Table S10 Bond Lengths for compound 5a.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
F1	C2	1.354(6)	C2	C12	1.487(6)
F2	C2	1.338(7)	C3	C4	1.514(6)
N1	C1	1.334(5)	C4	C7	1.505(6)
N1	C12	1.350(5)	C4	C9	1.525(5)
N2	C1	1.336(4)	C5	C11	1.391(7)
N2	C4	1.480(4)	C5	C13	1.380(8)
N3	N4	1.381(4)	C6	C8	1.393(5)
N3	C12	1.313(5)	C6	C10	1.376(6)
N4	C1	1.367(4)	C8	C13	1.385(6)
N4	C6	1.418(5)	C10	C11	1.390(6)

Table S11 Bond Angles for compound 5a.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	N1	C12	102.9(3)	C3	C4	C9	109.5(4)
C1	N2	C4	125.8(3)	C7	C4	C3	110.9(3)
C12	N3	N4	102.0(3)	C7	C4	C9	110.5(4)
N3	N4	C6	120.5(3)	C13	C5	C11	120.2(4)
C1	N4	N3	109.0(3)	C8	C6	N4	118.4(4)
C1	N4	C6	130.3(3)	C10	C6	N4	120.9(3)
N1	C1	N2	128.0(3)	C10	C6	C8	120.7(4)
N1	C1	N4	109.6(3)	C13	C8	C6	119.3(4)
N2	C1	N4	122.4(3)	C6	C10	C11	119.8(4)
F1	C2	C12	110.3(4)	C10	C11	C5	119.7(5)
F2	C2	F1	103.6(4)	N1	C12	C2	123.8(4)
F2	C2	C12	111.3(4)	N3	C12	N1	116.5(3)
N2	C4	C3	106.0(3)	N3	C12	C2	119.6(4)
N2	C4	C7	110.6(3)	C5	C13	C8	120.3(4)
N2	C4	C9	109.1(3)				

Table S12 Torsion Angles for compound 5a.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
F1	C2	C12	N1	45.1(6)	C1	N4	C6	C8	132.0(4)
F1	C2	C12	N3	-136.6(4)	C1	N4	C6	C10	-48.9(5)
F2	C2	C12	N1	-69.2(5)	C4	N2	C1	N1	-7.8(6)
F2	C2	C12	N3	109.0(5)	C4	N2	C1	N4	172.3(3)
N3	N4	C1	N1	-1.0(4)	C6	N4	C1	N1	-177.3(3)
N3	N4	C1	N2	178.9(3)	C6	N4	C1	N2	2.6(6)
N3	N4	C6	C8	-43.9(4)	C6	C8	C13	C5	1.9(6)
N3	N4	C6	C10	135.2(4)	C6	C10	C11	C5	1.3(6)
N4	N3	C12	N1	-0.6(5)	C8	C6	C10	C11	-1.6(6)
N4	N3	C12	C2	-179.0(3)	C10	C6	C8	C13	0.1(5)
N4	C6	C8	C13	179.2(3)	C11	C5	C13	C8	-2.2(6)
N4	C6	C10	C11	179.3(3)	C12	N1	C1	N2	-179.3(4)
C1	N1	C12	N3	0.0(5)	C12	N1	C1	N4	0.6(4)
C1	N1	C12	C2	178.3(4)	C12	N3	N4	C1	0.9(4)
C1	N2	C4	C3	-174.7(4)	C12	N3	N4	C6	177.6(3)
C1	N2	C4	C7	65.0(5)	C13	C5	C11	C10	0.6(6)
C1	N2	C4	C9	-56.9(5)					

Table S13 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 5a.

Atom	x	y	z	U(eq)
H2	4949.11	2969.39	6246.63	77
H2A	3437.03	7961.31	9162.82	89
H3A	4155.32	2125.48	4335.76	119
H3B	1663.85	1967.36	3920.65	119
H3C	2626.26	1349.63	5119.42	119
H5	11563.11	1084.19	9246.89	91
H7A	2178.81	5547.11	4738.1	113
H7B	1332.11	4582.39	3692.47	113
H7C	3839.05	4702.26	4080.31	113
H8	9514.84	5036.77	8718.26	76
H9A	-81.27	2603.19	6057.03	110
H9B	-1072.18	3393.28	4938.15	110
H9C	-180.99	4243.02	6044.69	110
H10	5323.42	1852	8042.47	78
H11	8097.39	268.4	8604.99	90
H13	12234.41	3458.59	9359.13	89