**Supporting Information**

# TfOH and $HBF_4$ Mediated Formal Cycloisomerizations and [4+3] Cycloadditions of Allene-Alkynylbenzenes

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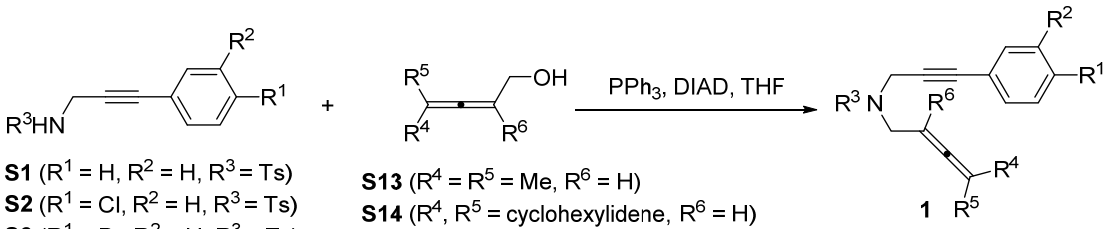
**Contents**

## 1. Scheme S1 for Synthesis of 1,6 allenye Substrates

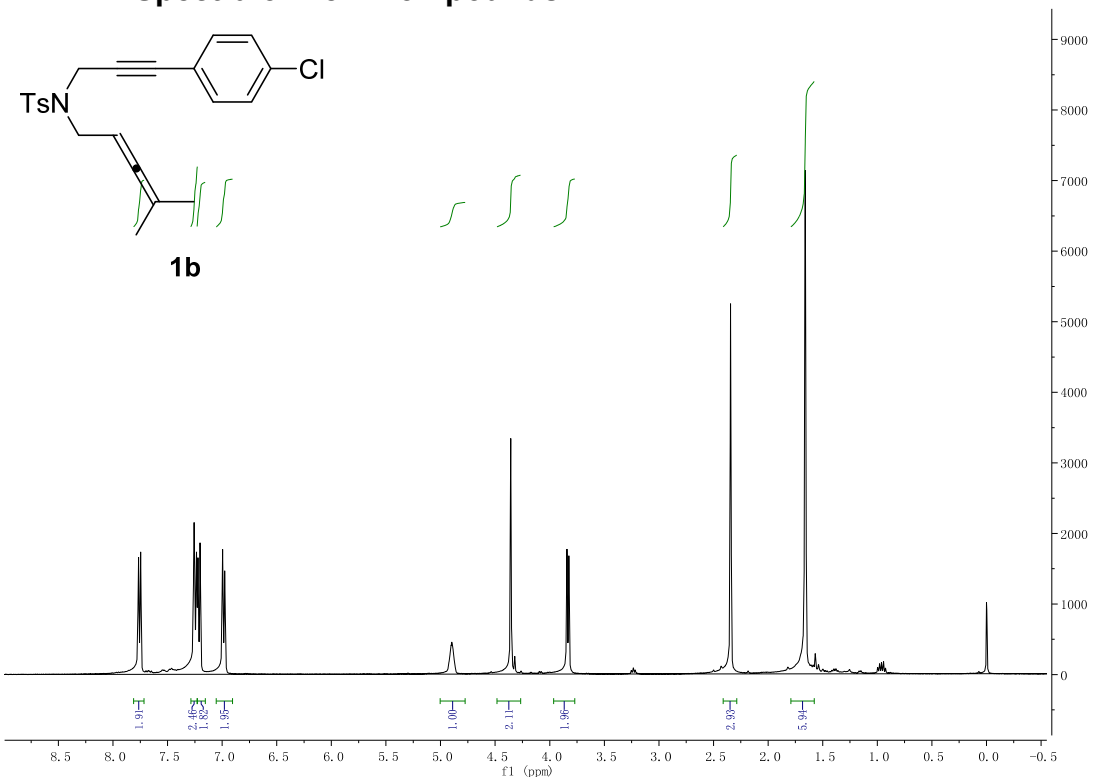
### Scheme S1

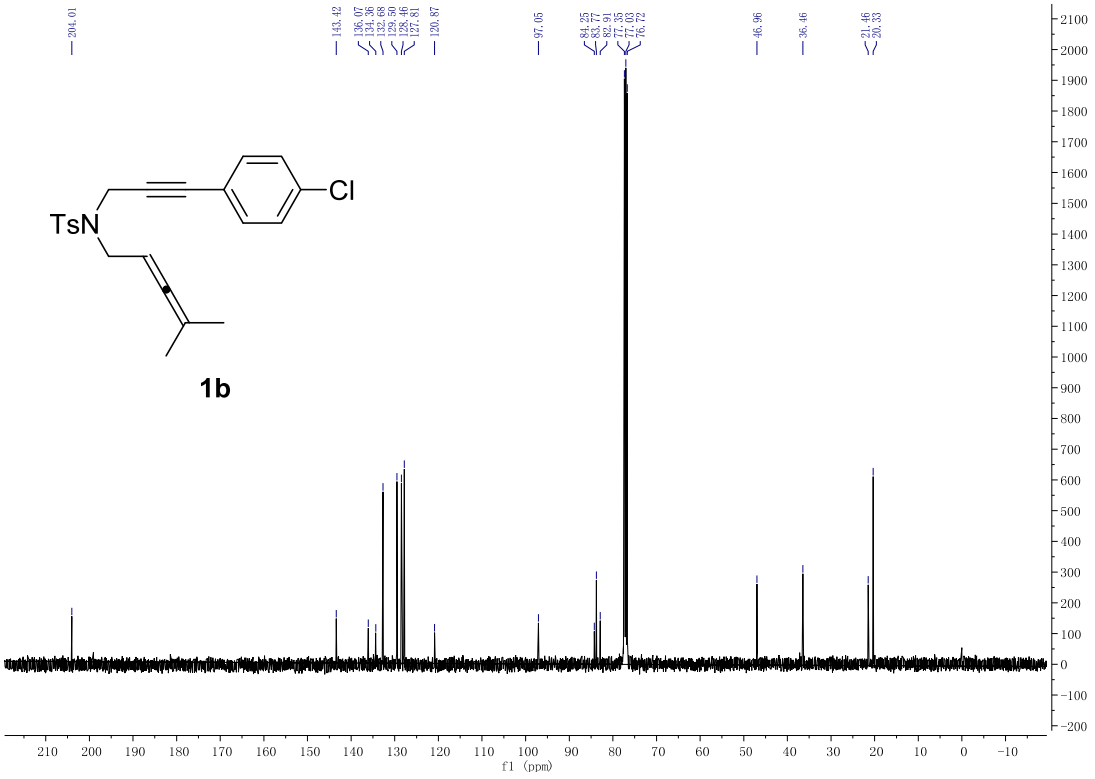


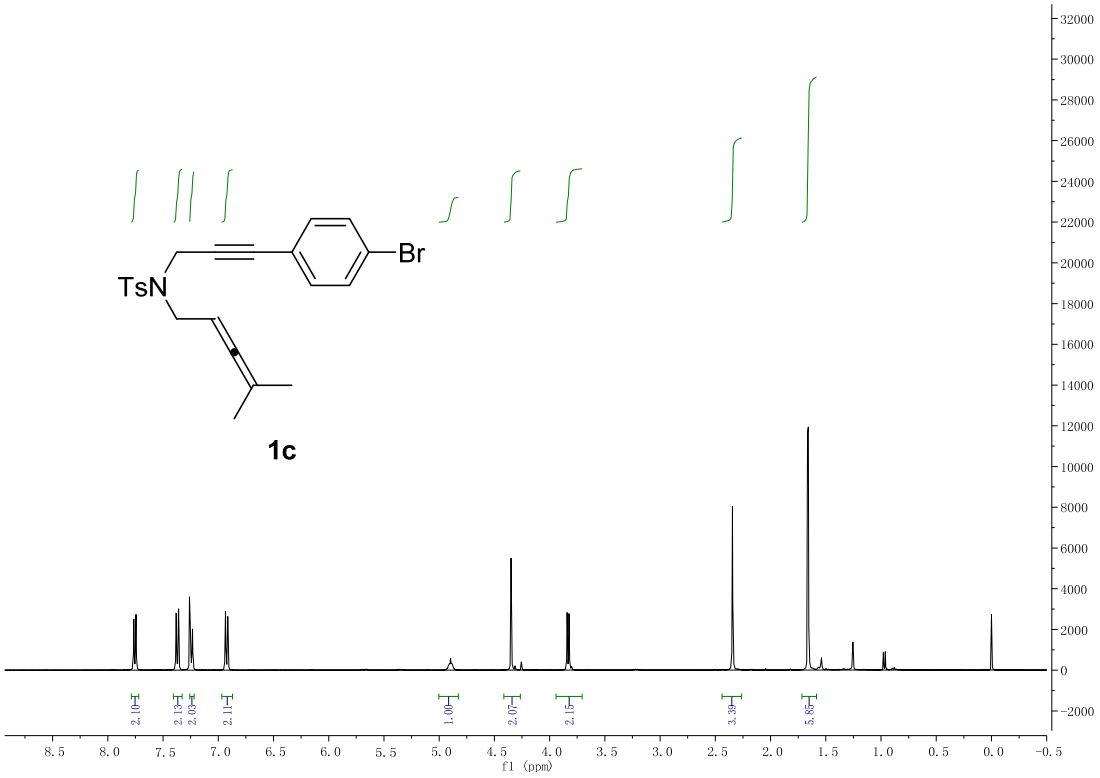

**S1** ($R^1$ = H, $R^2$ = H, $R^3$ = Ts)
**S2** ($R^1$ = Cl, $R^2$ = H, $R^3$ = Ts)
**S3** ($R^1$ = Br, $R^2$ = H, $R^3$ = Ts)
**S4** ($R^1$ = H, $R^2$ = Cl, $R^3$ = Ts)
**S5** ($R^1$ = H, $R^2$ = Br, $R^3$ = Ts)
**S6** ($R^1$ = $CF_3$, $R^2$ = H, $R^3$ = Ts)
**S7** ($R^1$ = H, $R^2$ = $CF_3$, $R^3$ = Ts)
**S8** ($R^1$ = COOEt, $R^2$ = H, $R^3$ = Ts)
**S9** ($R^1$ = F, $R^2$ = H, $R^3$ = Ts)
**S10** ($R^1$ = $R^2$ = Cl, $R^3$ = Ts)
**S11** ($R^1$ = H, $R^2$ = Me, $R^3$ = Ts)
**S12** ($R^1$ = H, $R^2$ = H, $R^3$ = Ns)

**S13** ($R^4$ = $R^5$ = Me, $R^6$ = H)
**S14** ($R^4$, $R^5$ = cyclohexylidene, $R^6$ = H)
**S15** ($R^4$ = $R^5$ = $R^6$ = Me)

## 2. NMR Spectra of New Compounds

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TsN
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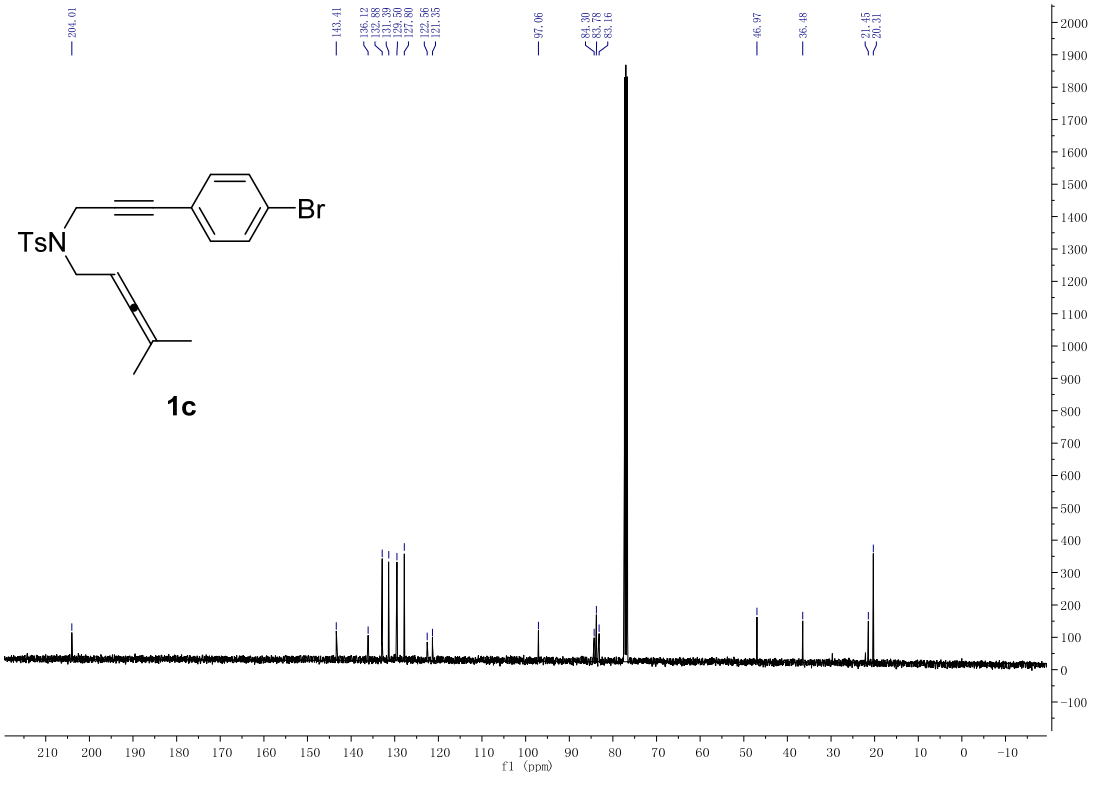
2.13
2.03
2.11
1.00
2.07
2.15
3.39
5.85
f1 (ppm)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143.41
136.12
132.88
131.39
129.50
127.80
122.56
121.35
97.06
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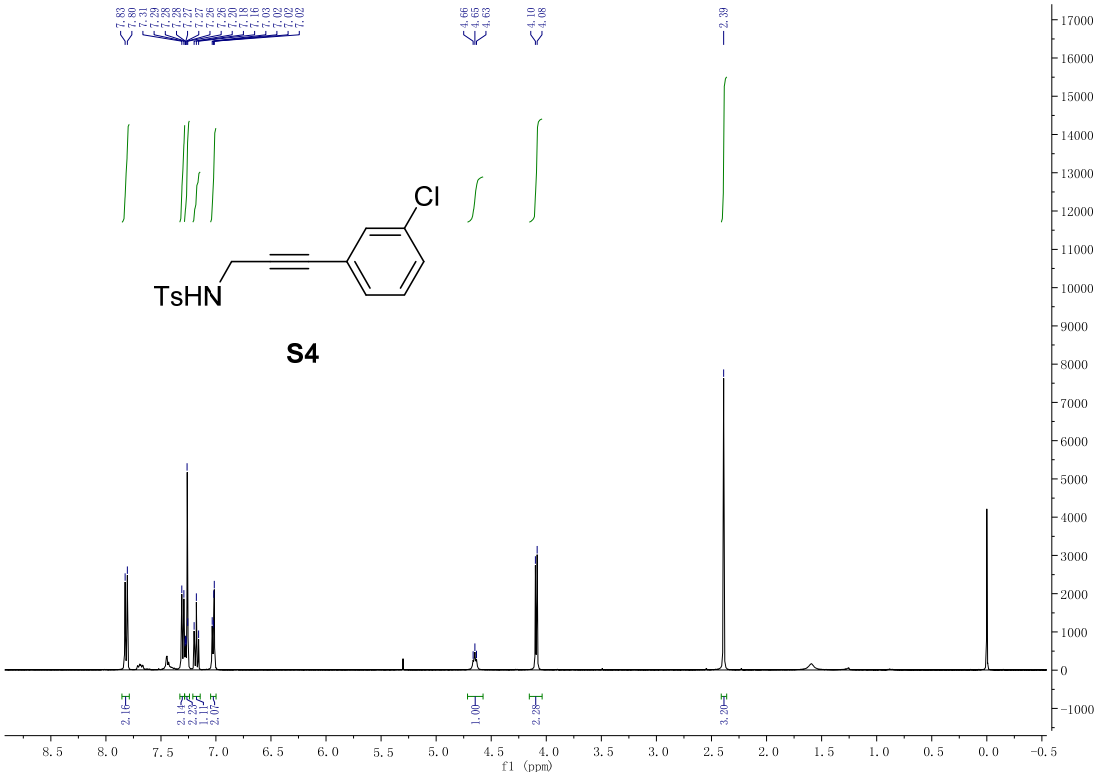
83.16
46.97
36.48
21.45
20.31
Br
TsN
1c
f1 (ppm)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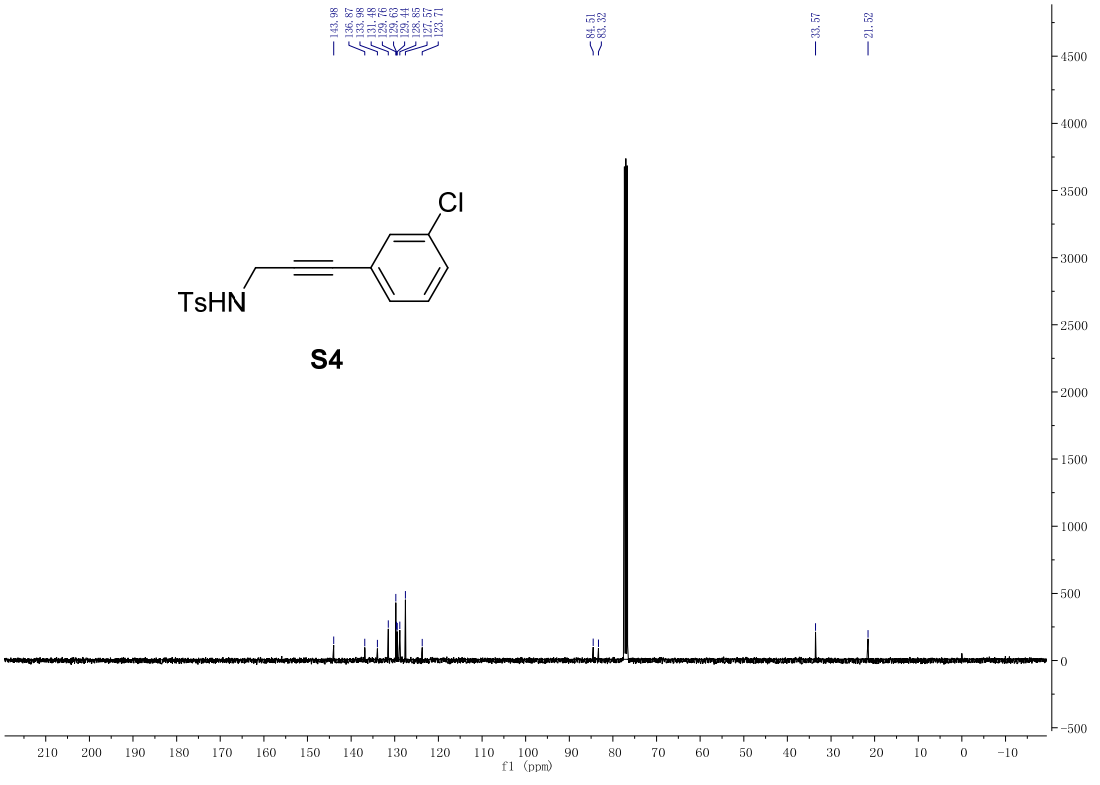
TsHN
S4
f1 (ppm)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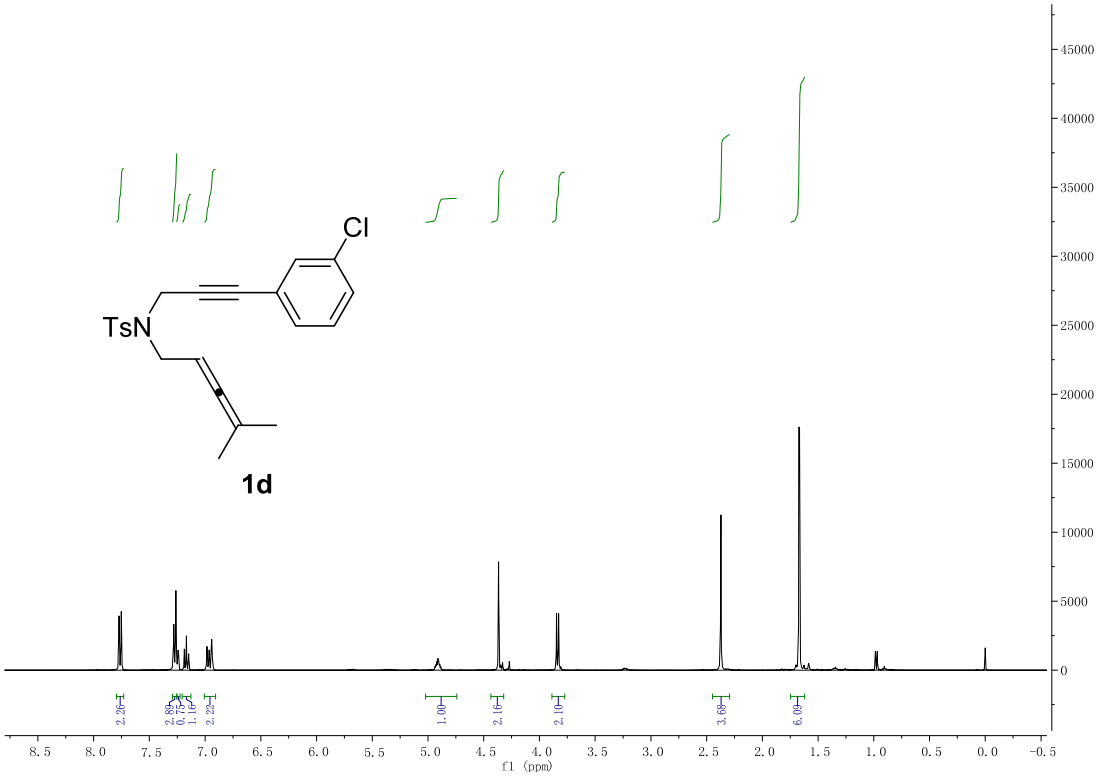
S4
f1 (ppm)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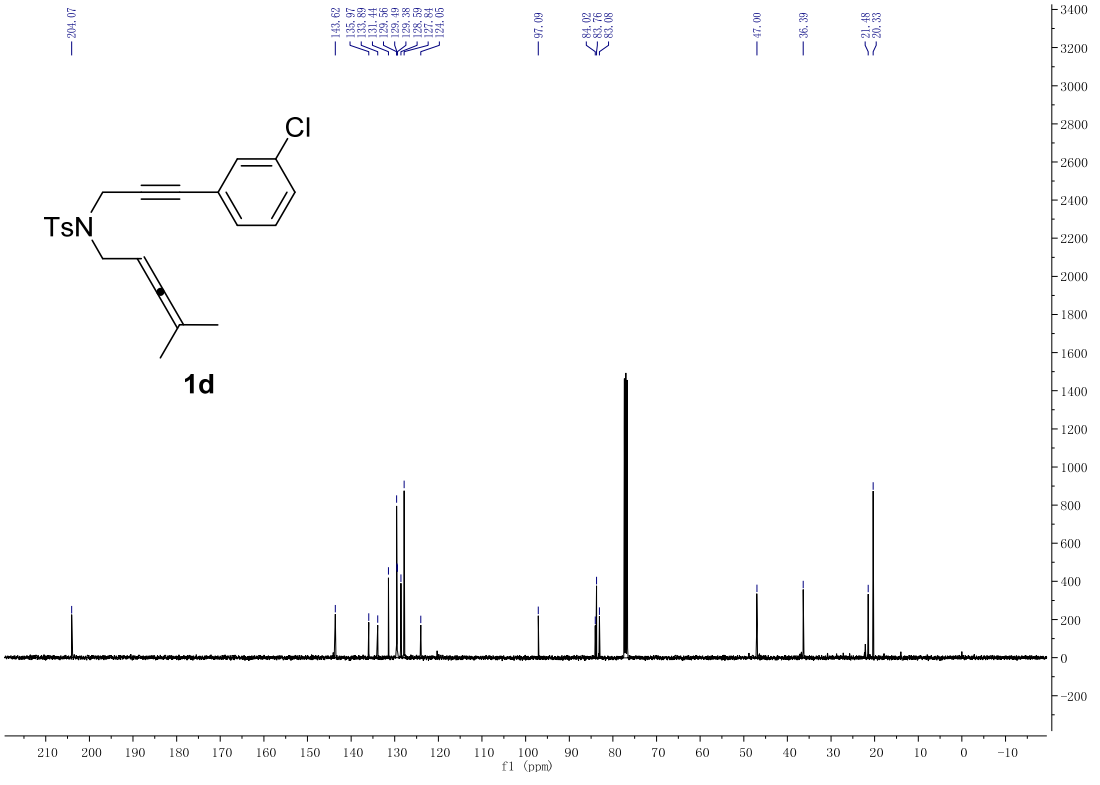
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129.49
128.38
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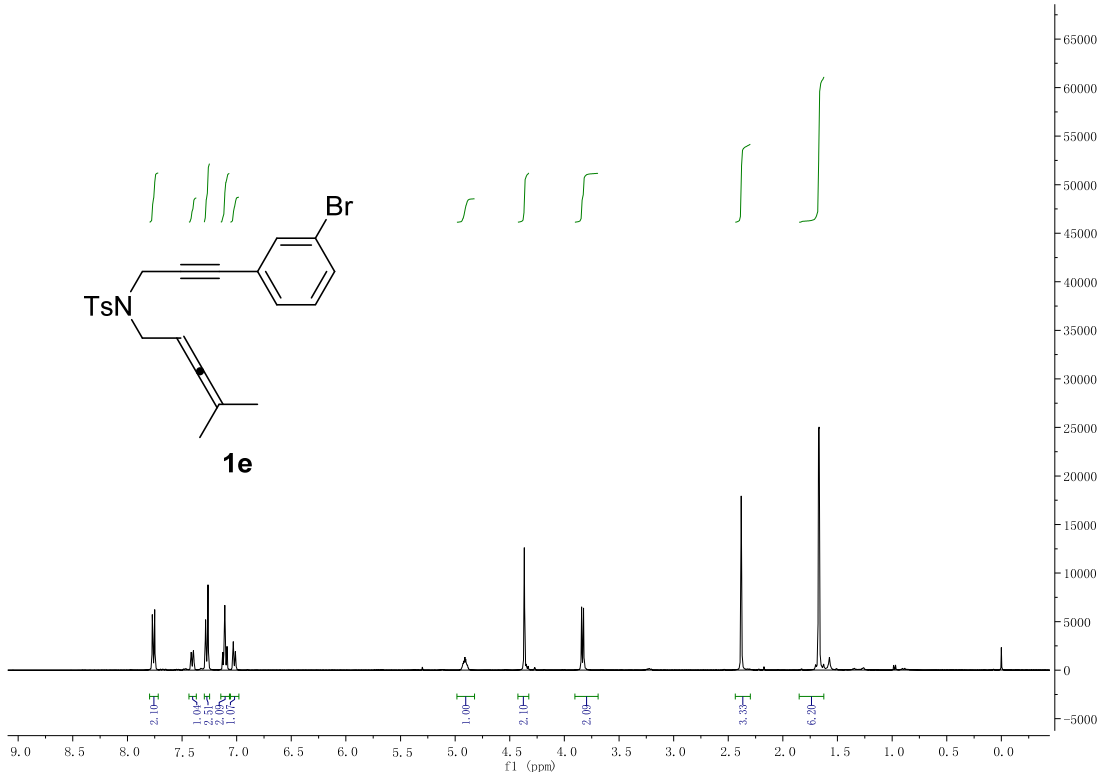
20.33
Cl
TsN
1d
f1 (ppm)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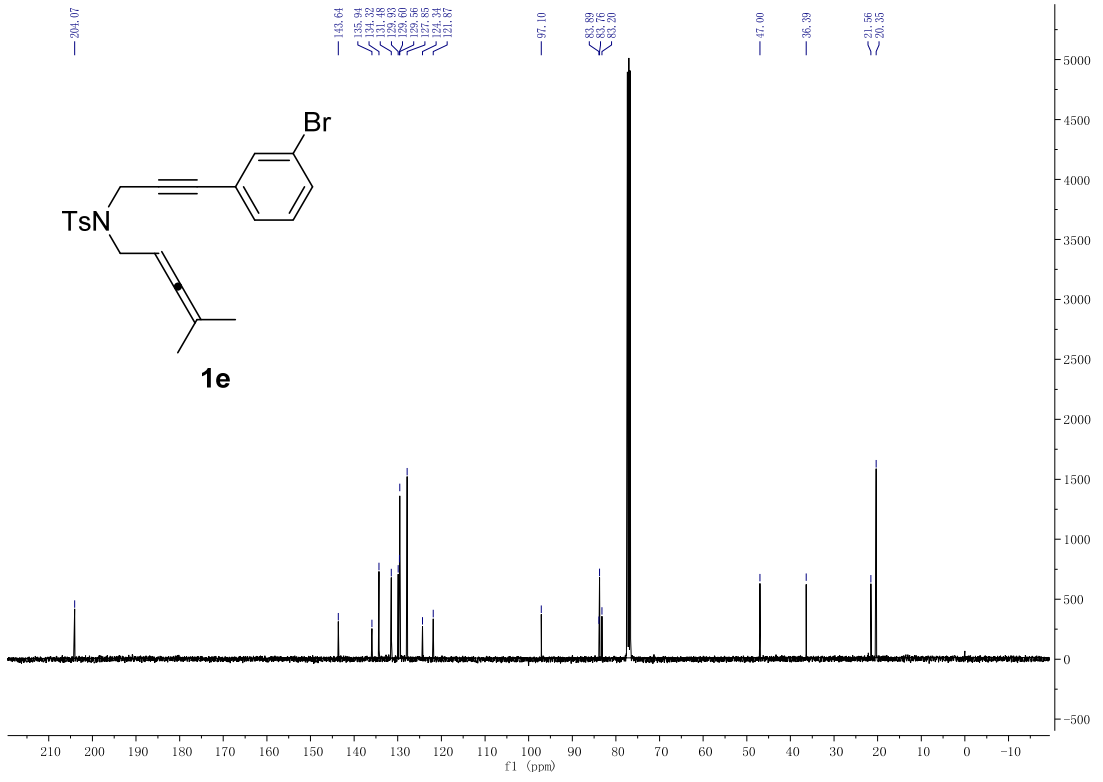
TsN
1e
f1 (ppm)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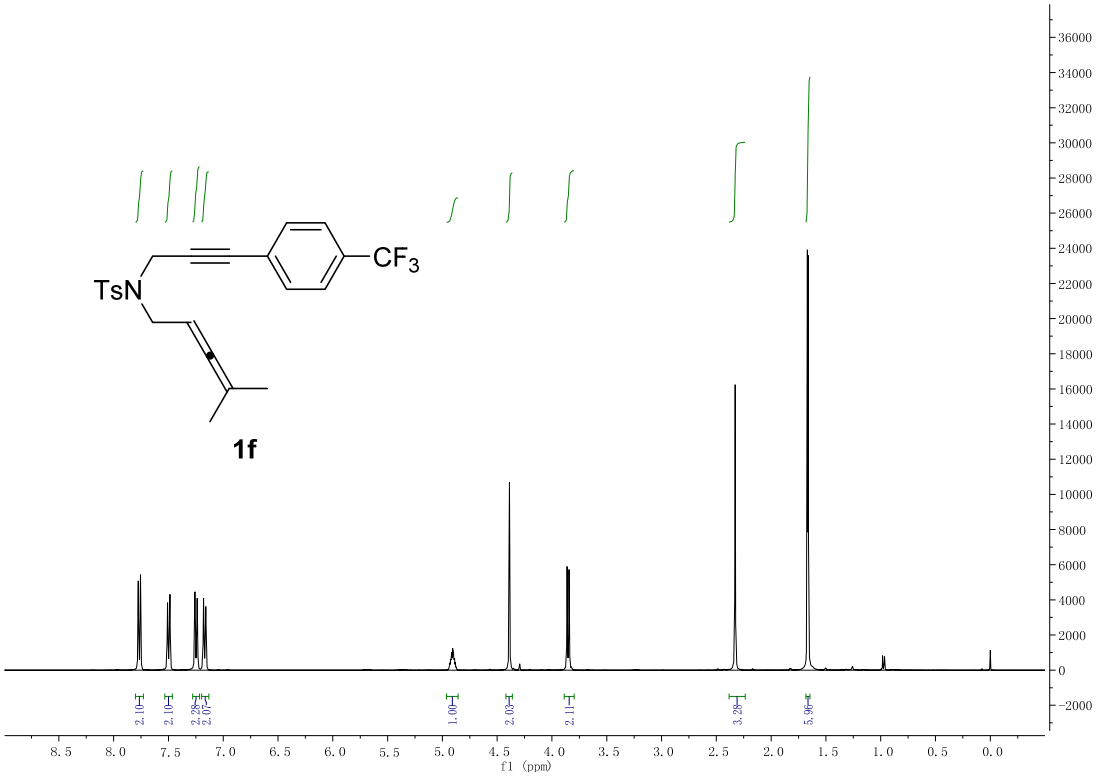
21.56
20.35
Br
TsN
1e
f1 (ppm)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2.11
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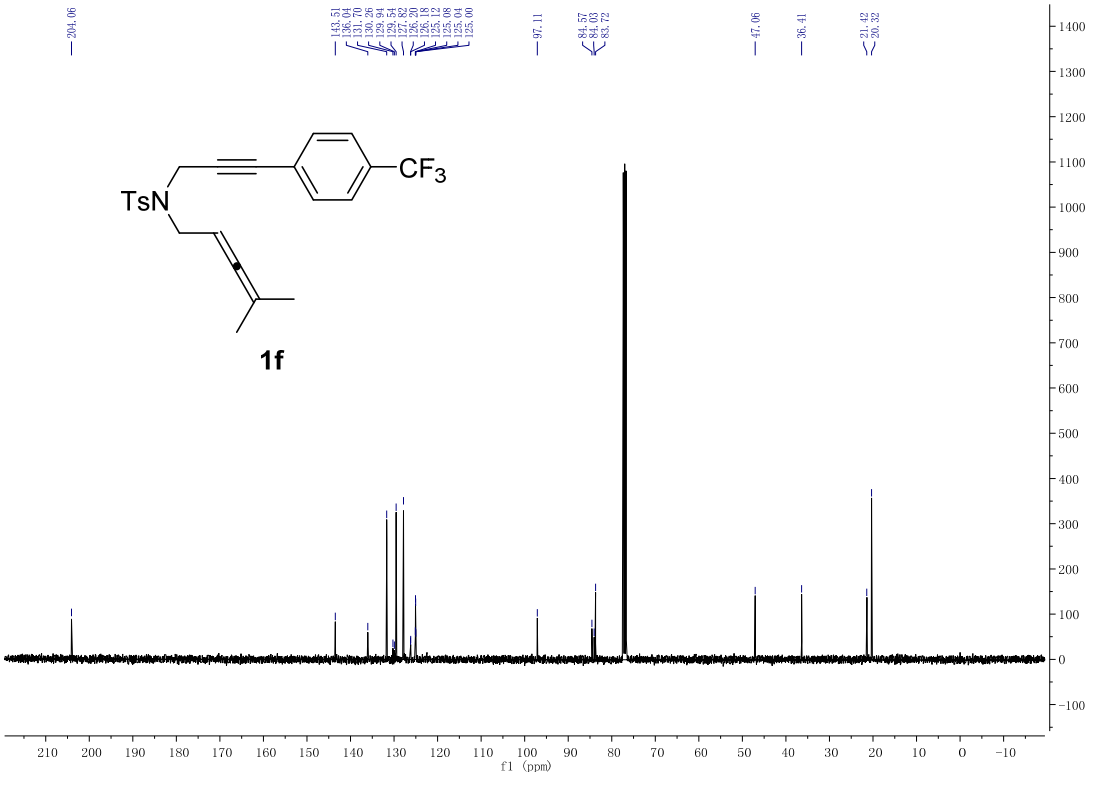
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125.04
125.00
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47.06
36.41
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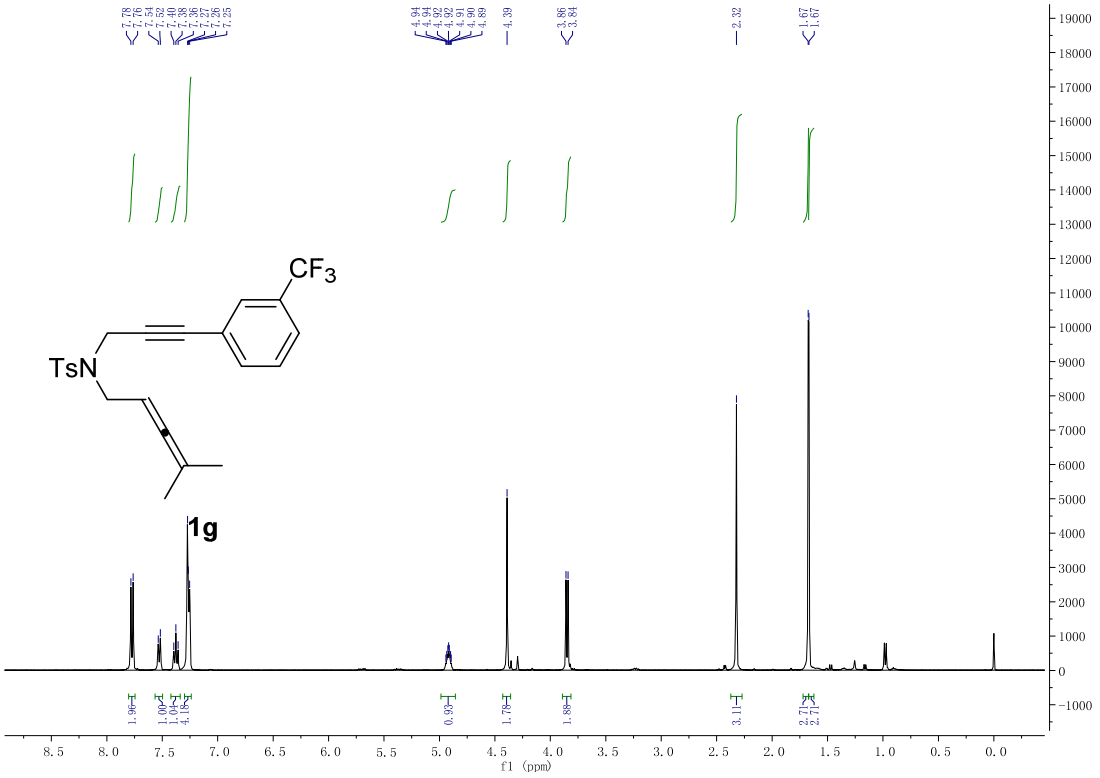
20.32
TsN
CF3
1f
f1 (ppm)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4.92
4.91
4.90
4.89
4.39
3.86
3.84
2.32
1.67
1.67
CF3
TsN
1g
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1.88
3.11
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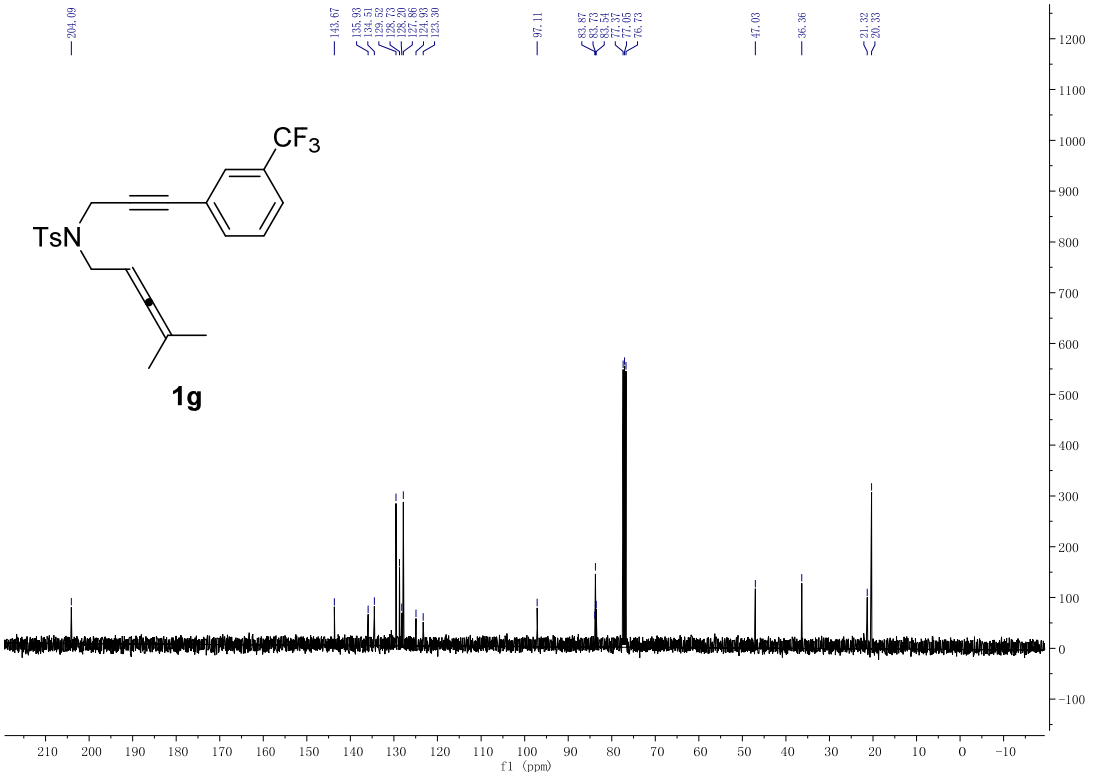
2.71
f1 (ppm)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128.20
127.86
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97.11
83.87
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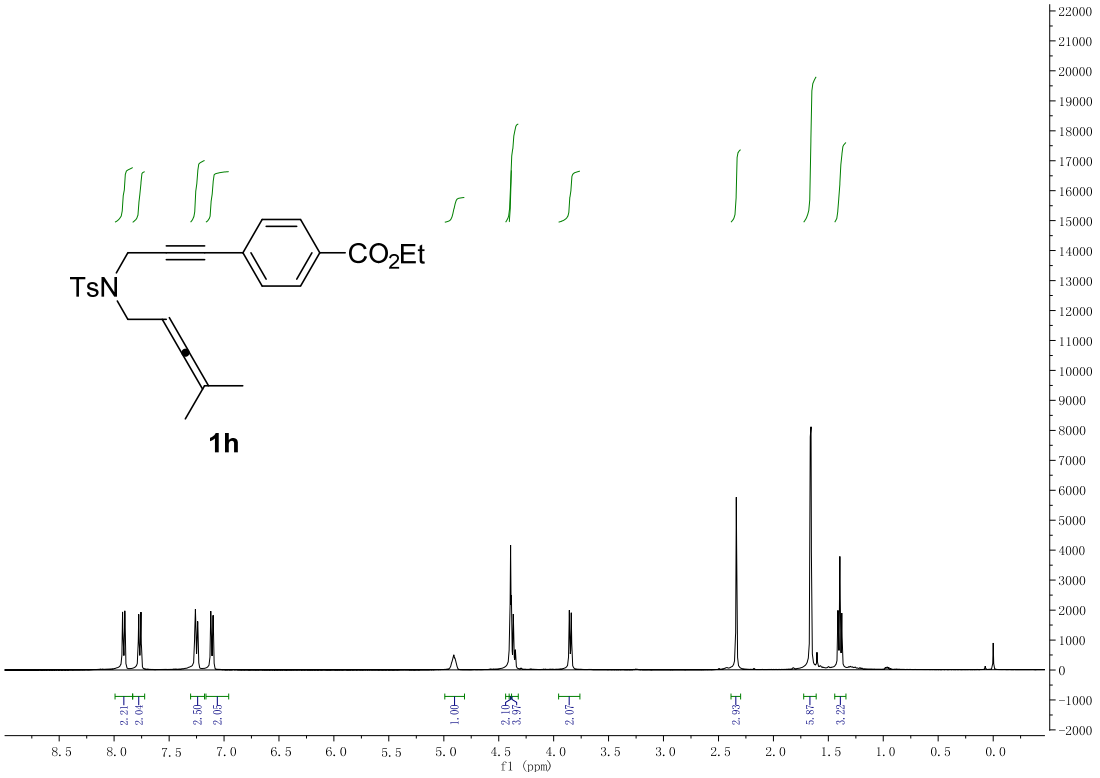
21.32
20.33
CF3
TsN
1g
f1 (ppm)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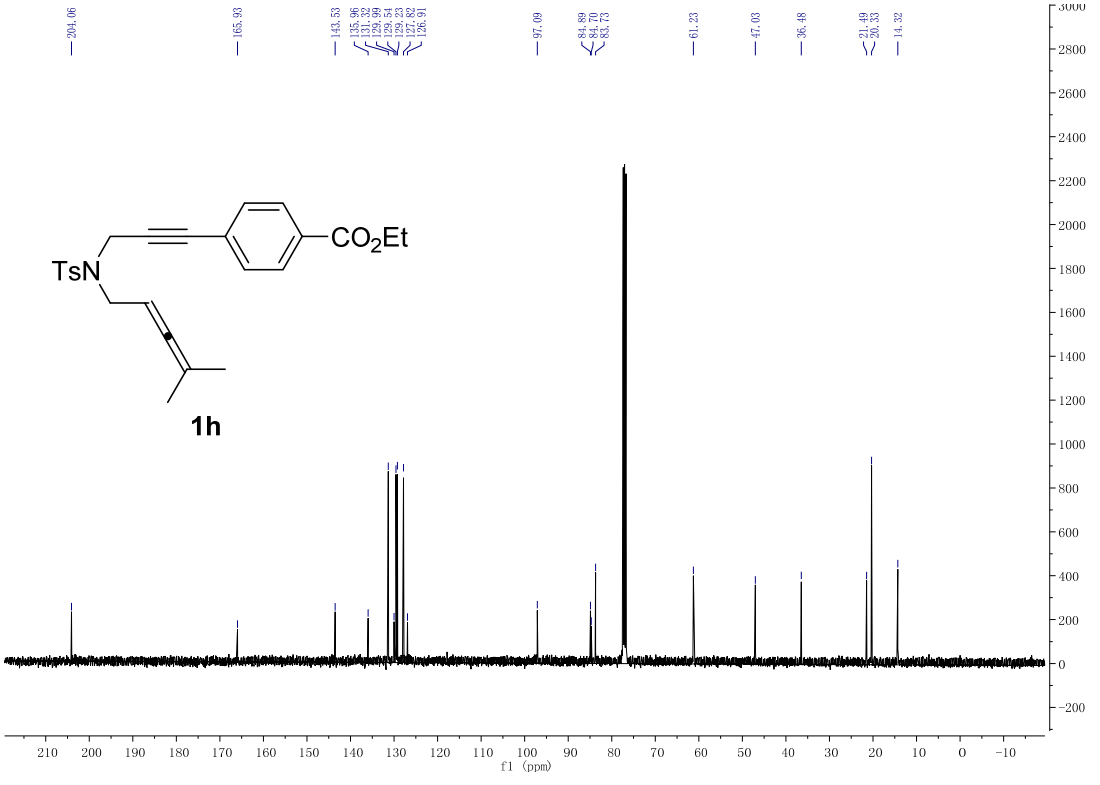
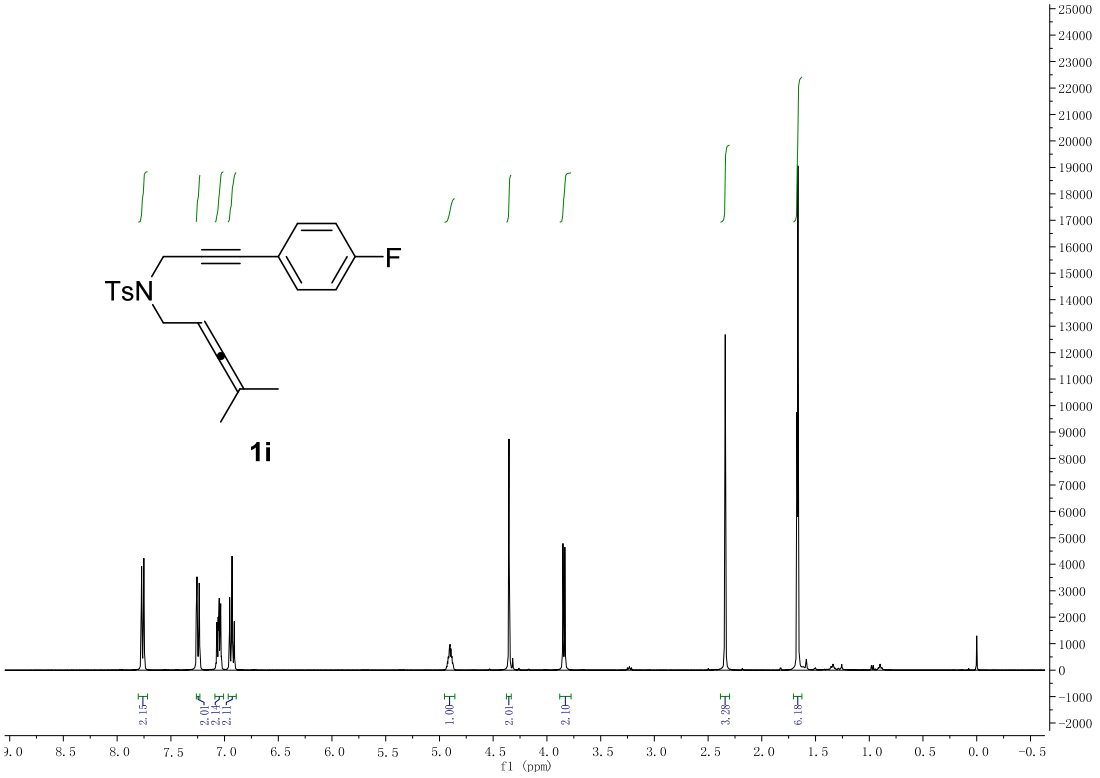
CO2Et
1h
f1 (ppm)


TsN
CO2Et
1h
f1 (ppm)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1.00
2.01
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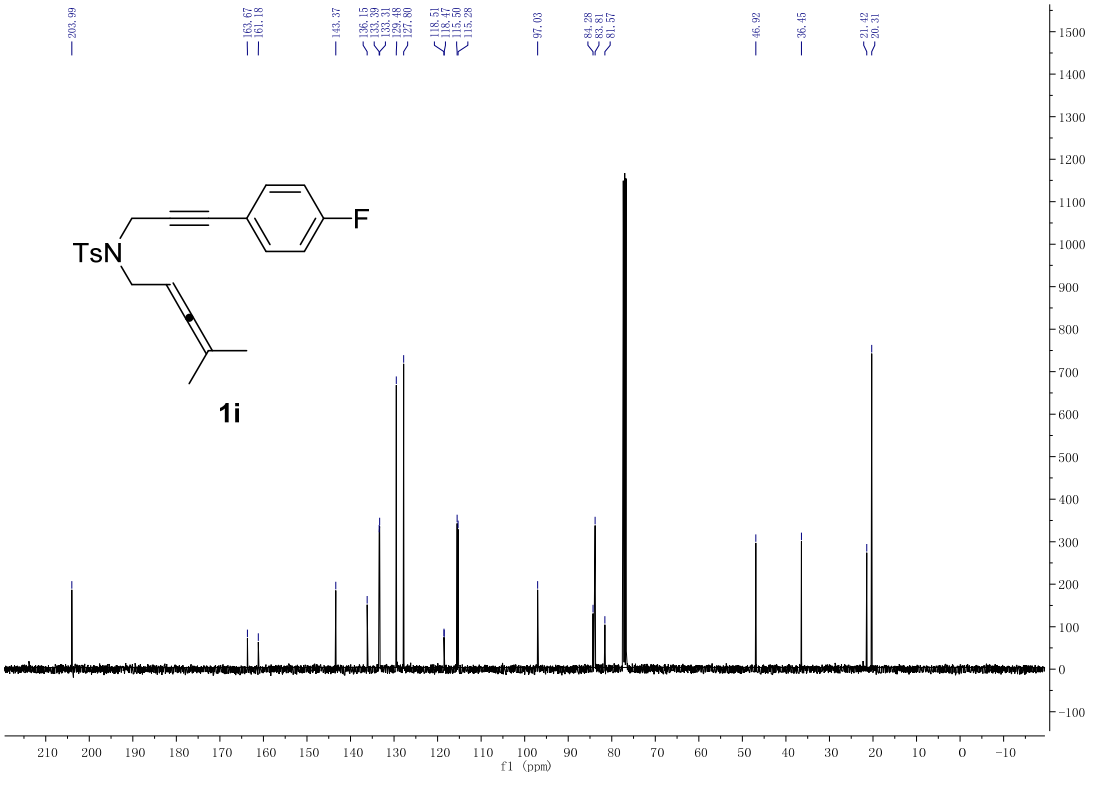
3.28
6.18
f1 (ppm)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115.50
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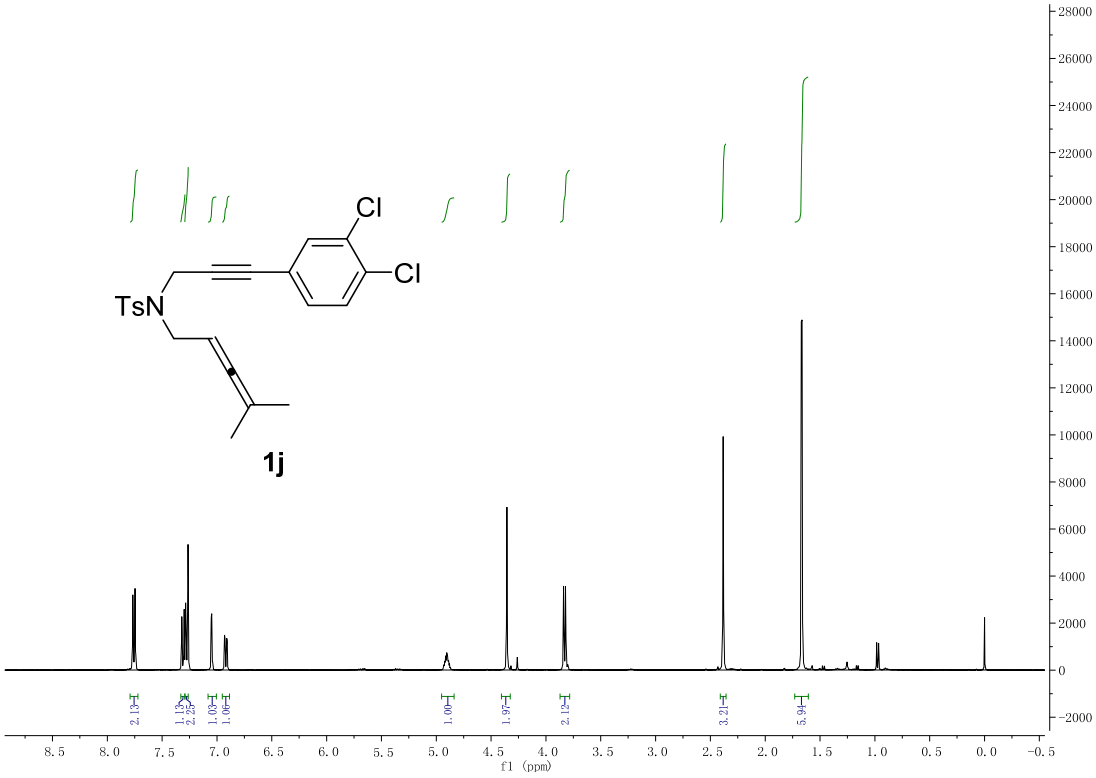
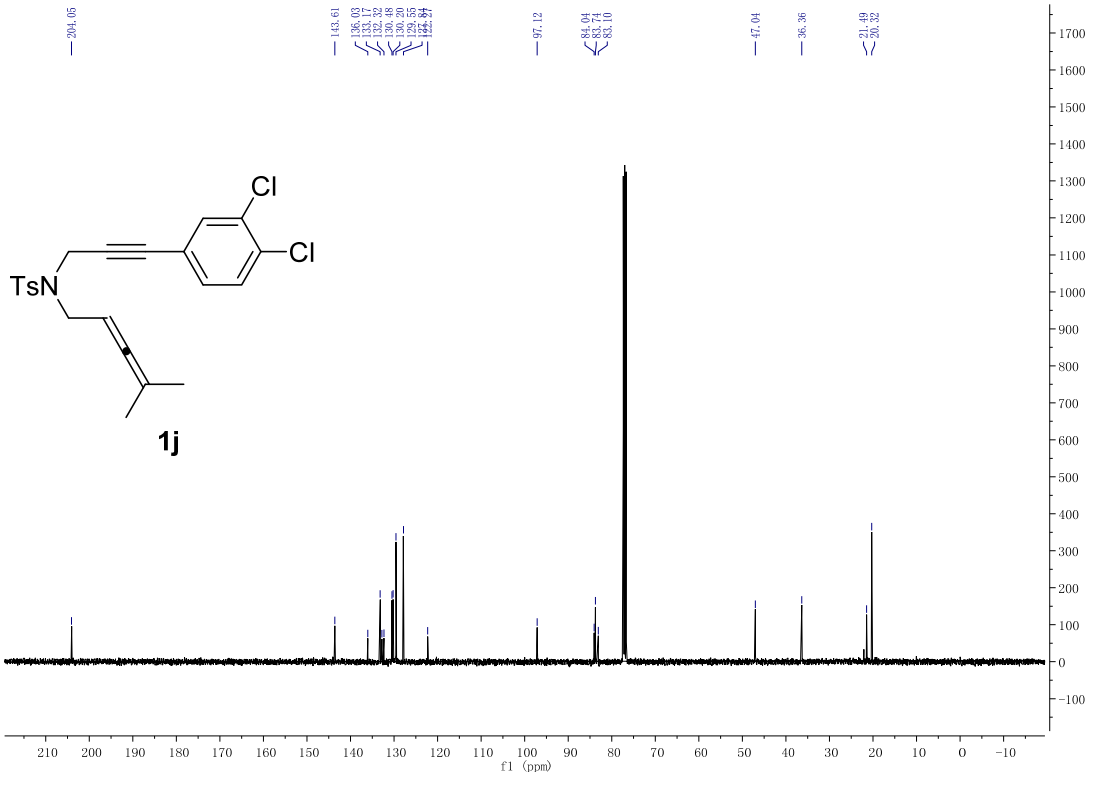
21.42
20.31
TsN
F
1i
f1 (ppm)


Cl
Cl
TsN
1j
f1 (ppm)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83.10
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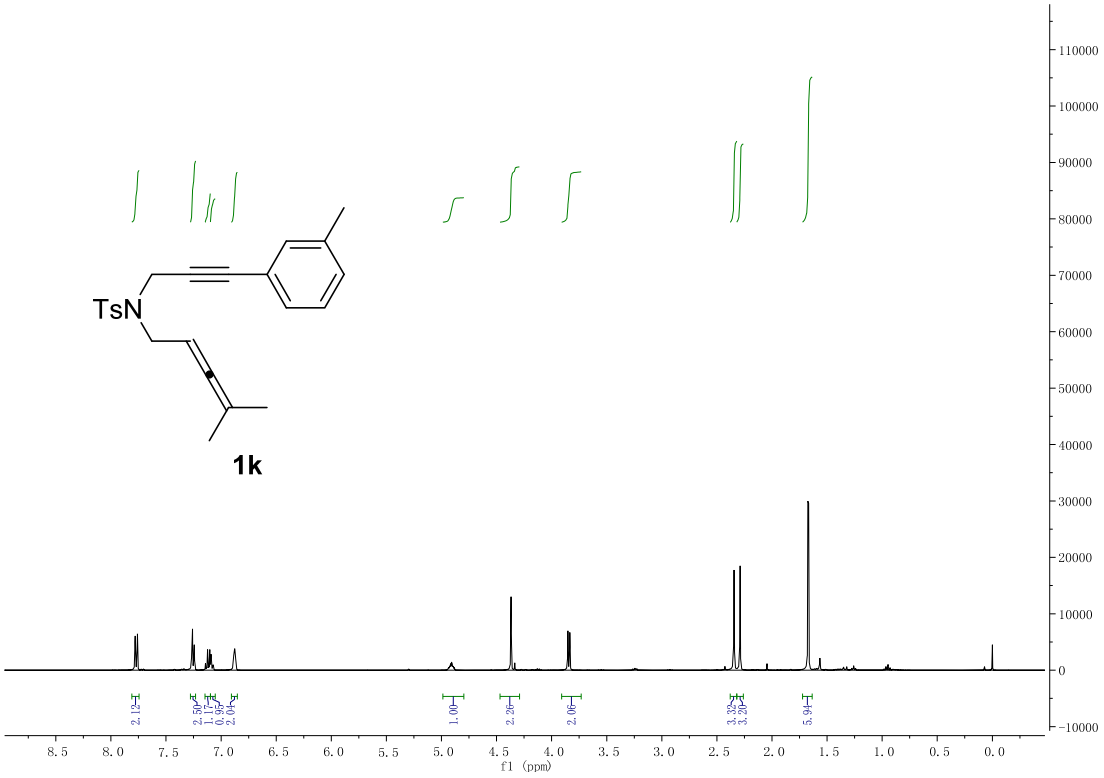
21.49
20.32
Cl
Cl
TsN
1j
f1 (ppm)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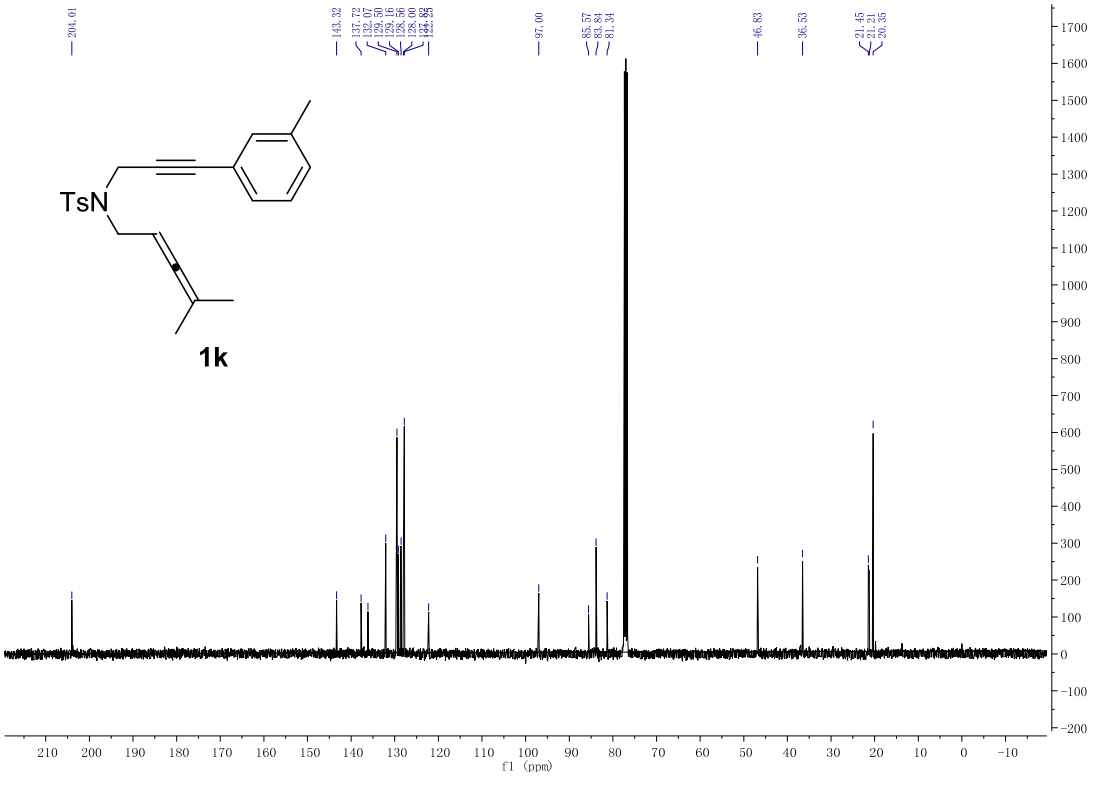
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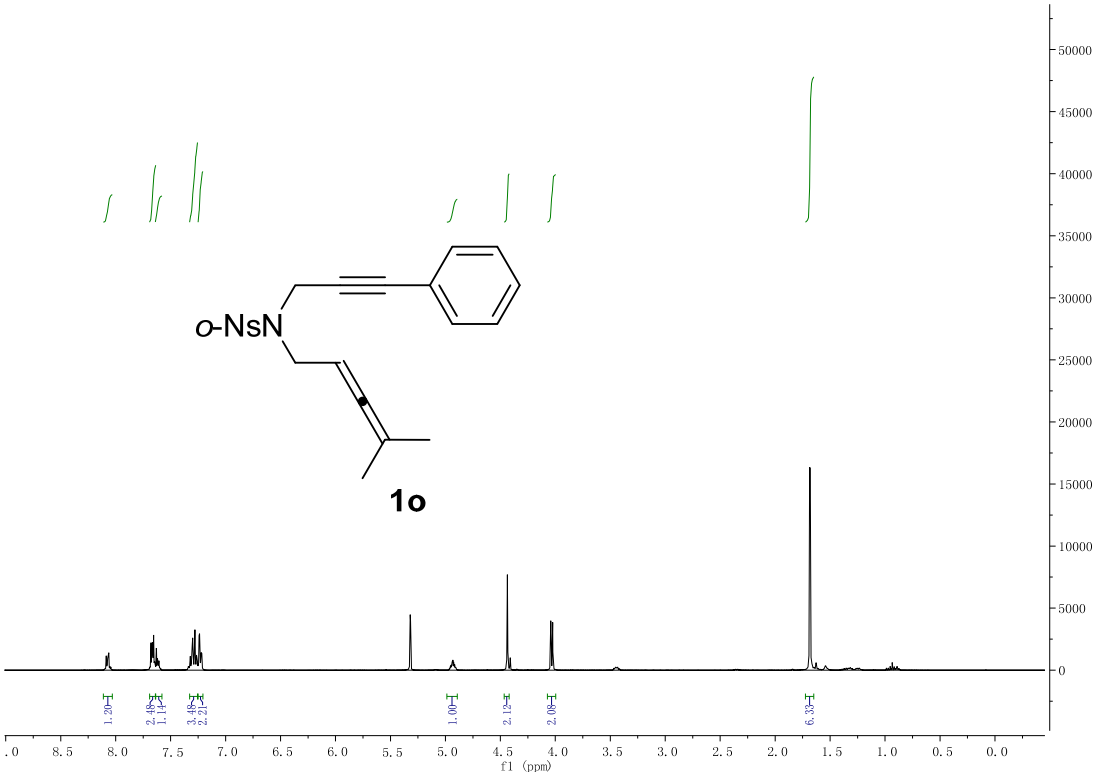
21.45
21.31
20.35
TsN
1k
f1 (ppm)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2.00
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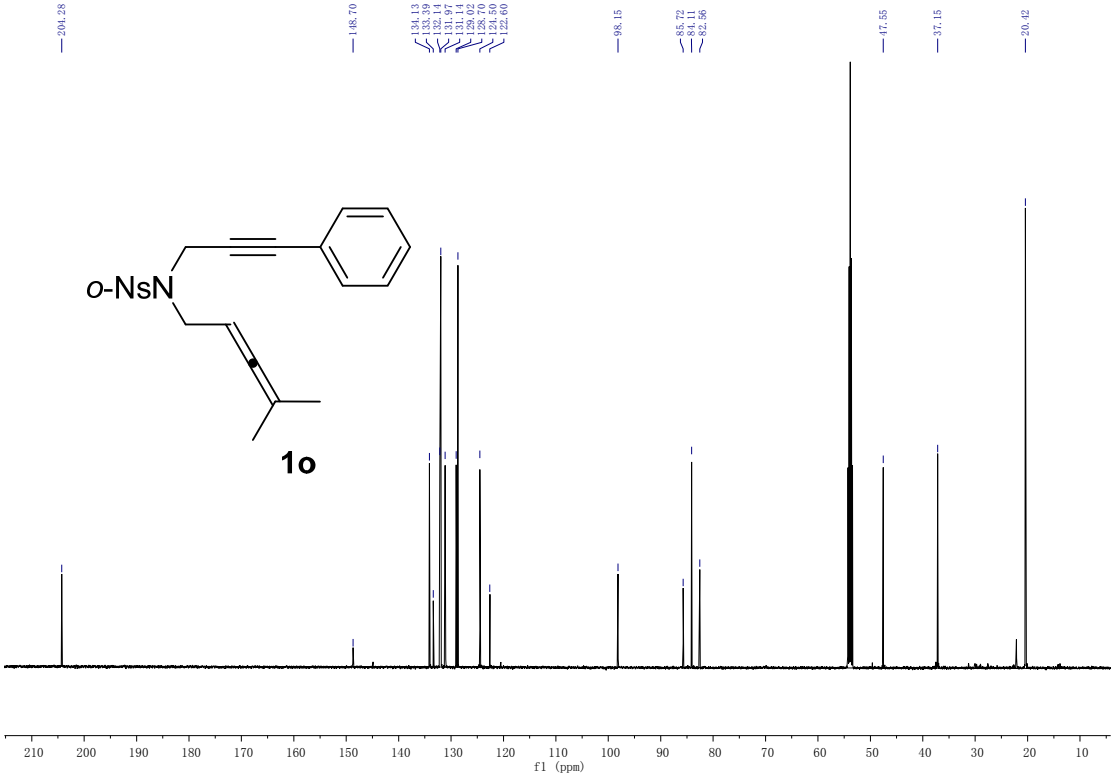
f1 (ppm)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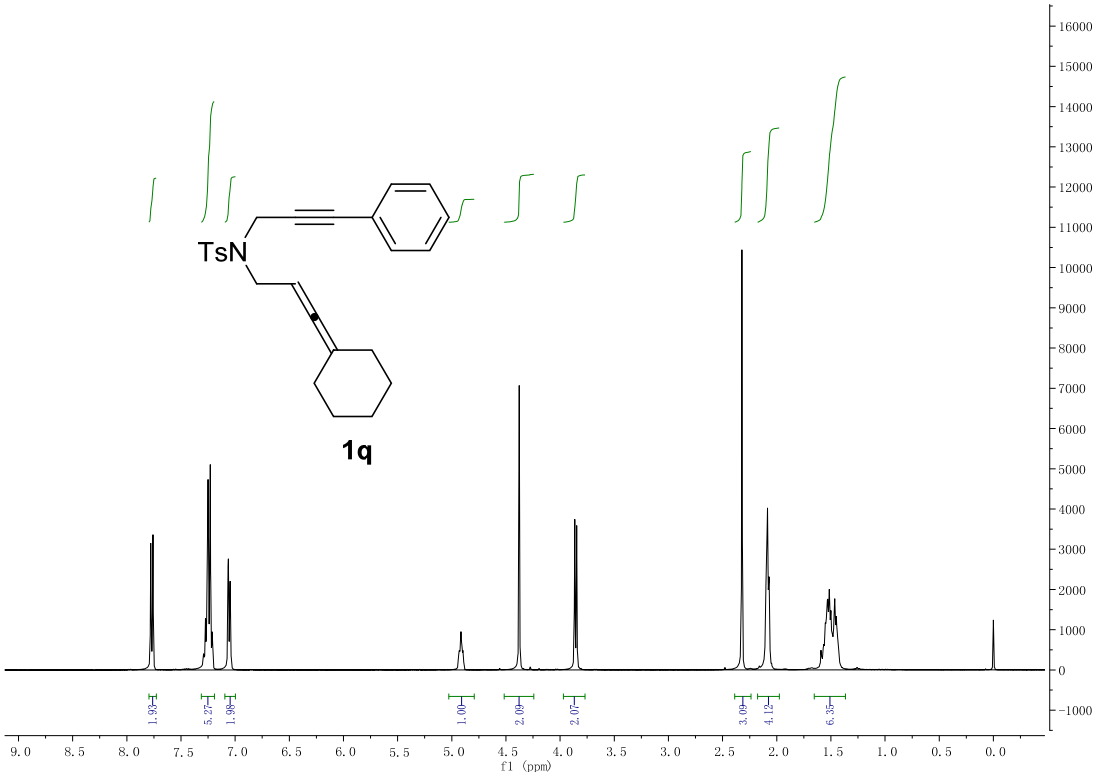
37.15
20.42
o-NsN
1o
f1 (ppm)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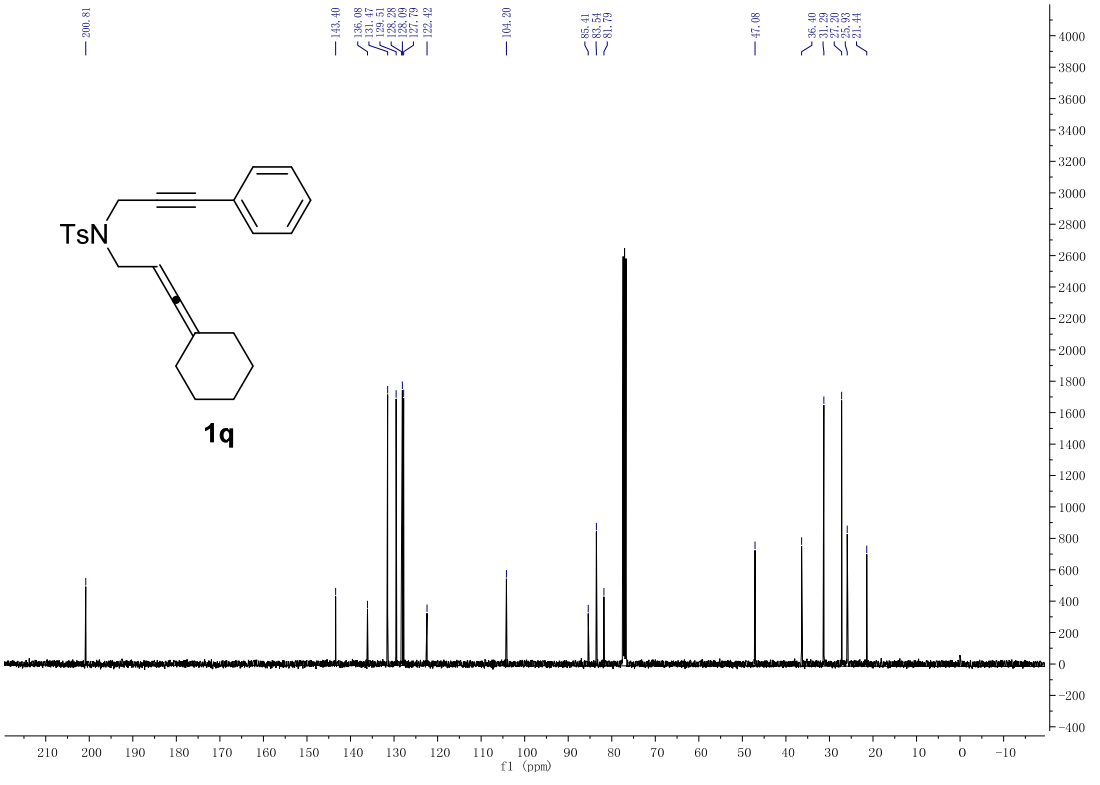
2.07
3.09
4.12
6.33
f1 (ppm)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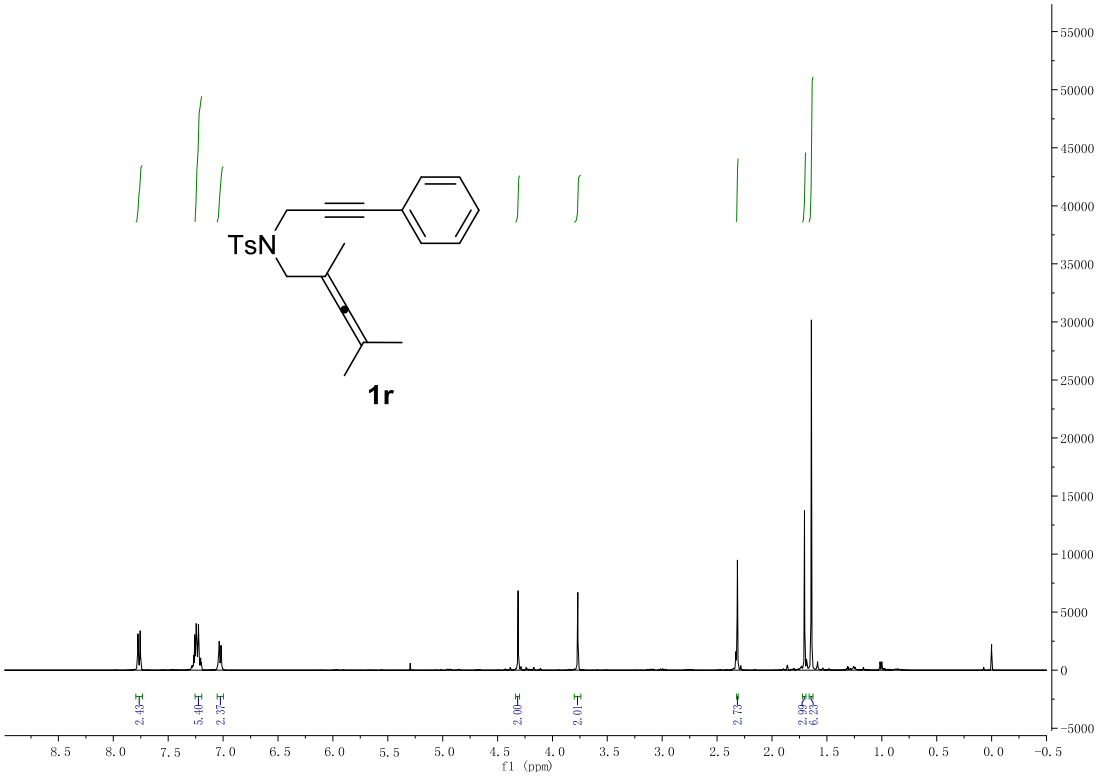
21.44
TsN
1q
f1 (ppm)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6.23
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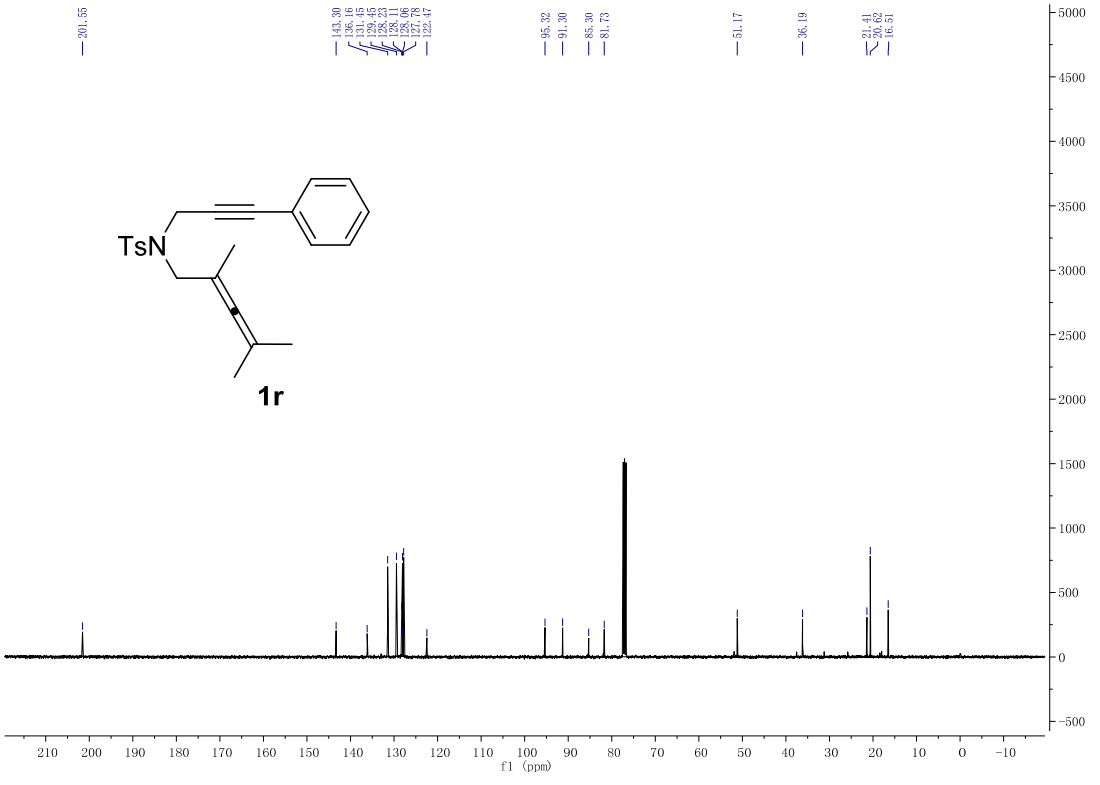
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122.47
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20.62
16.51
TsN
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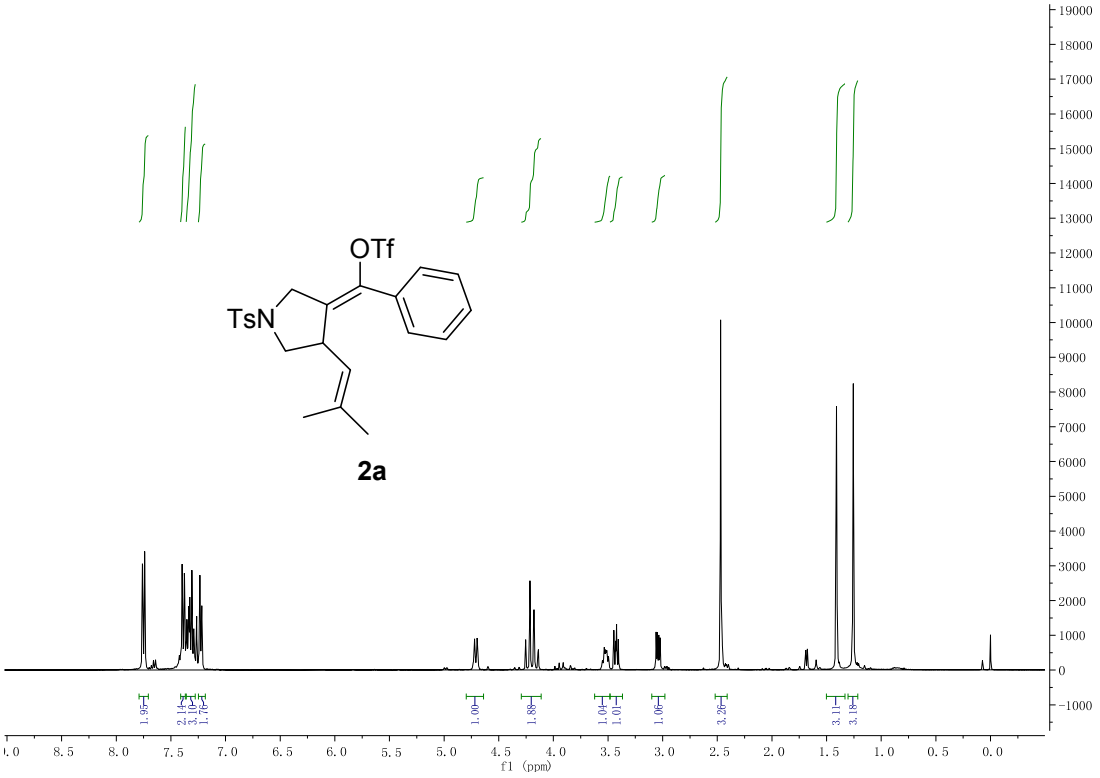
f1 (ppm)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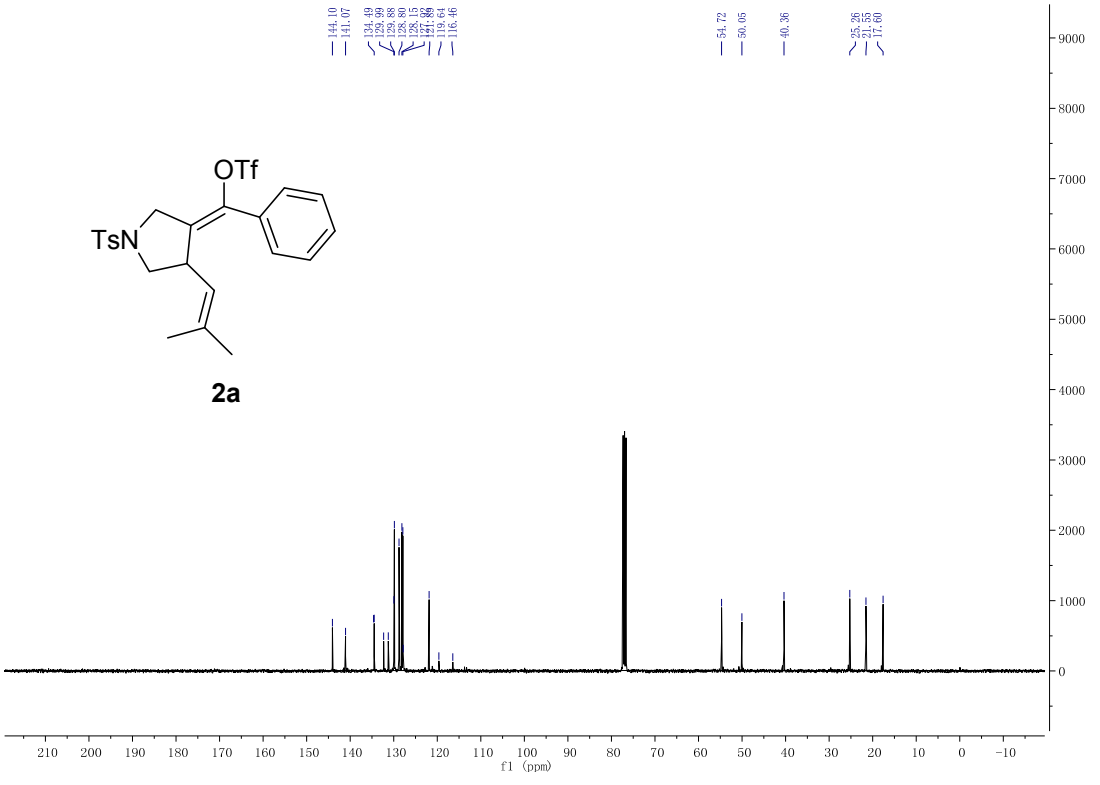
3.11
3.18
f1 (ppm)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129.88
128.80
128.15
119.64
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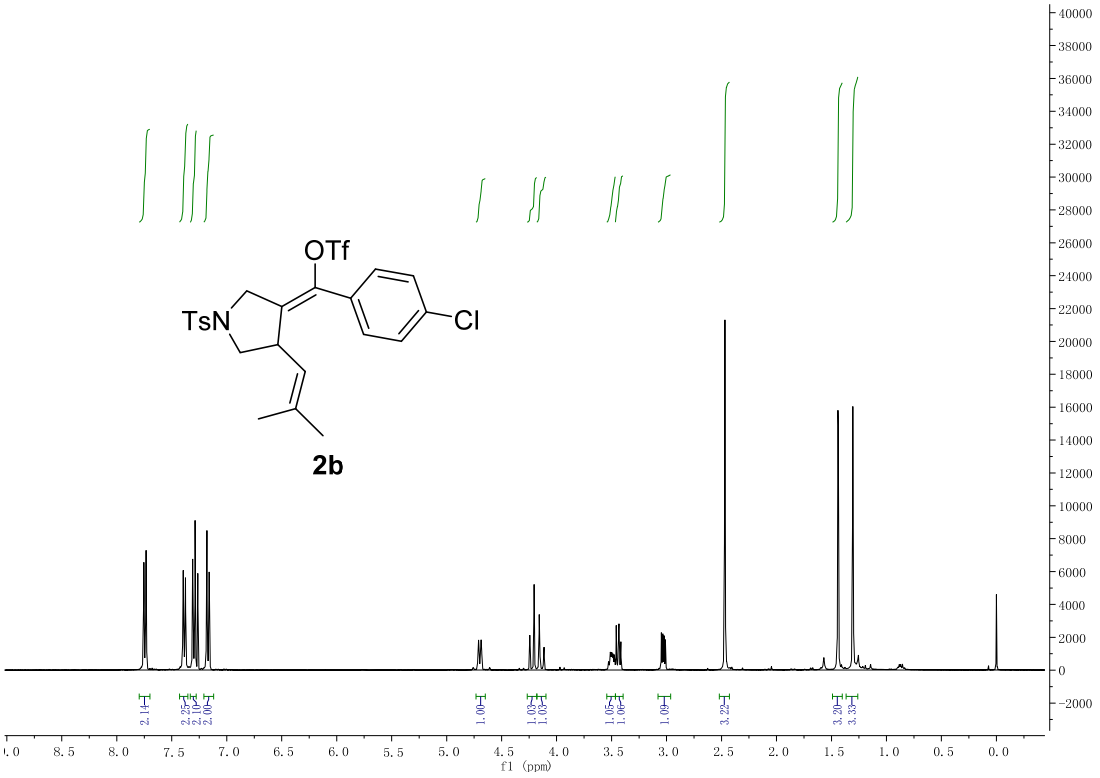
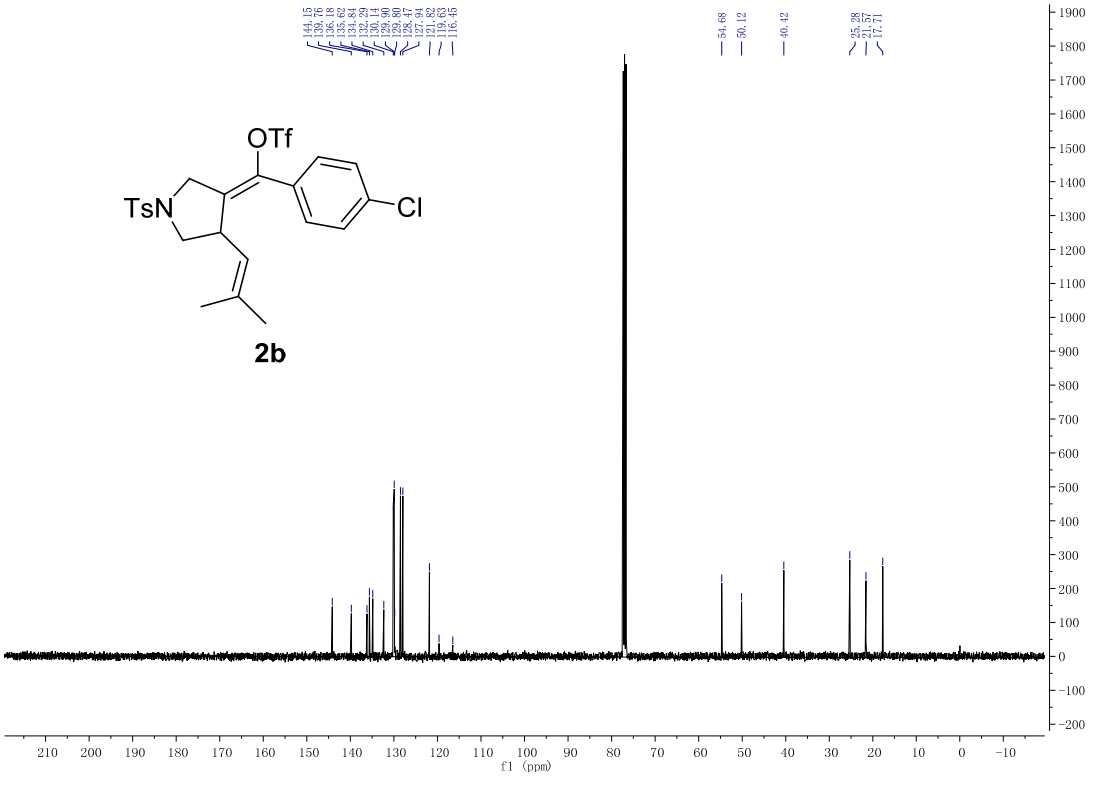
50.05
40.36
25.26
21.55
17.60
OTf
TsN
2a
f1 (ppm)


OTf
TsN
Cl
2b
f1 (ppm)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139.76
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134.84
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128.47
127.94
121.82
119.63
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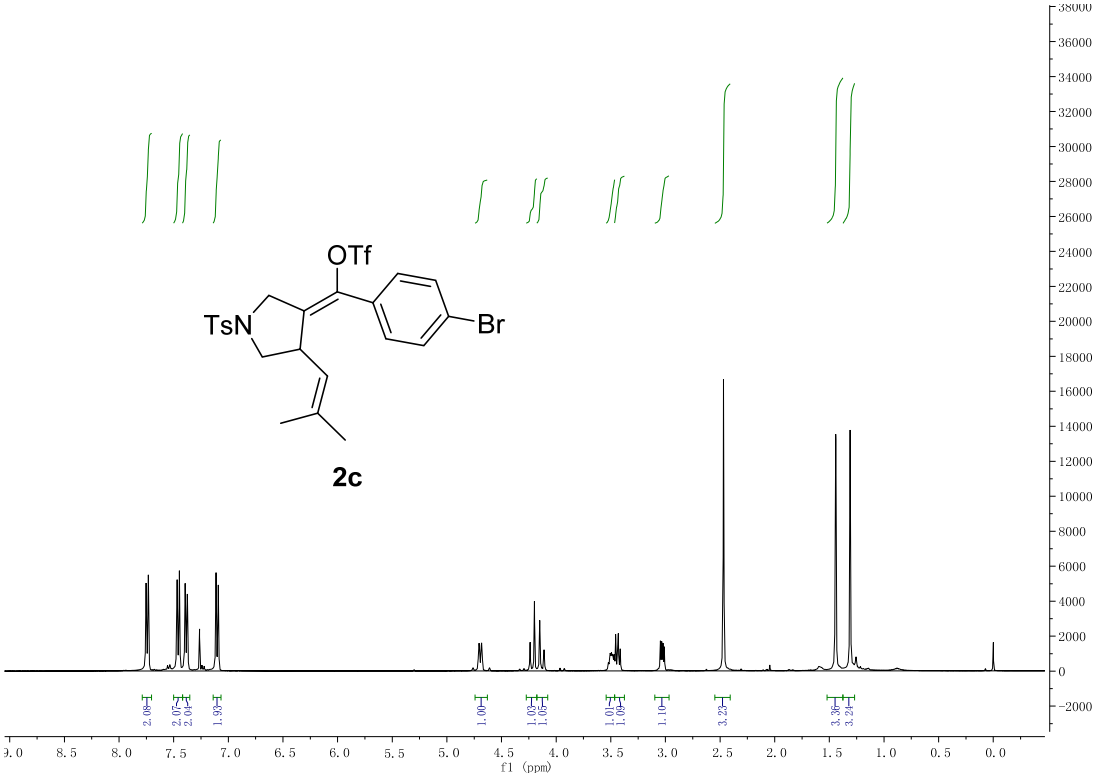
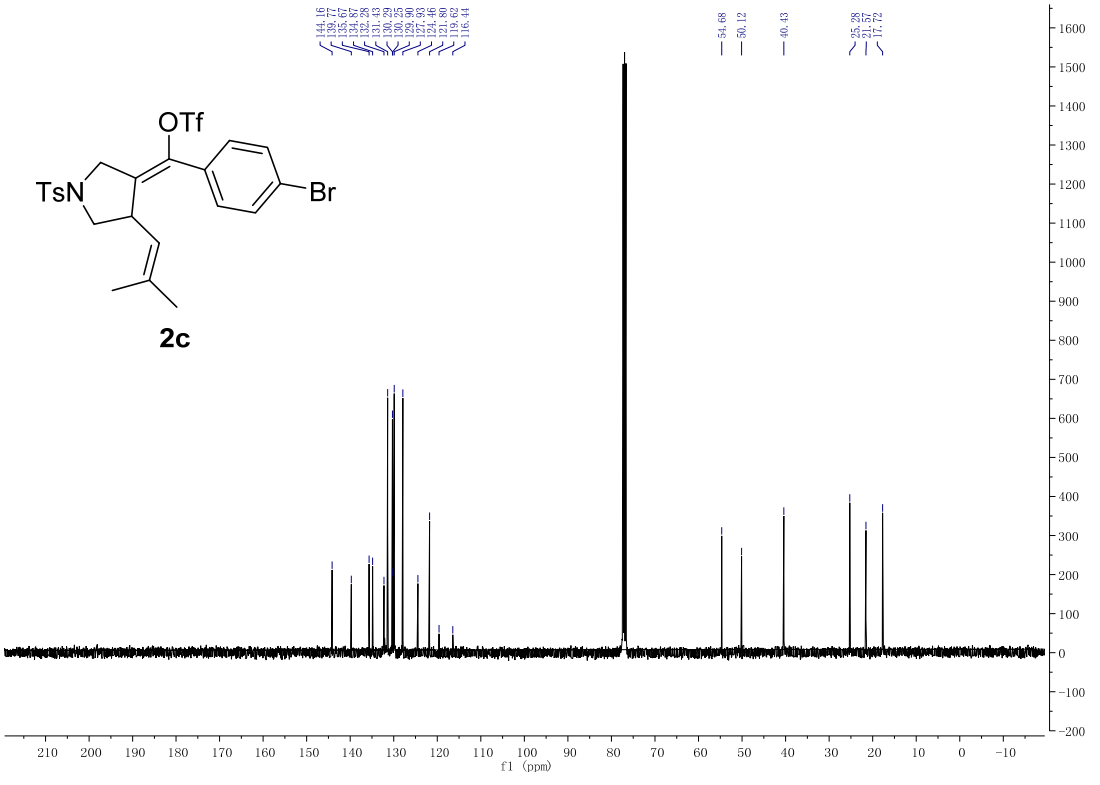
50.12
40.42
25.28
21.57
17.71
OTf
TsN
Cl
2b
f1 (ppm)


OTf
TsN
Br
2c
f1 (ppm)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124.46
121.80
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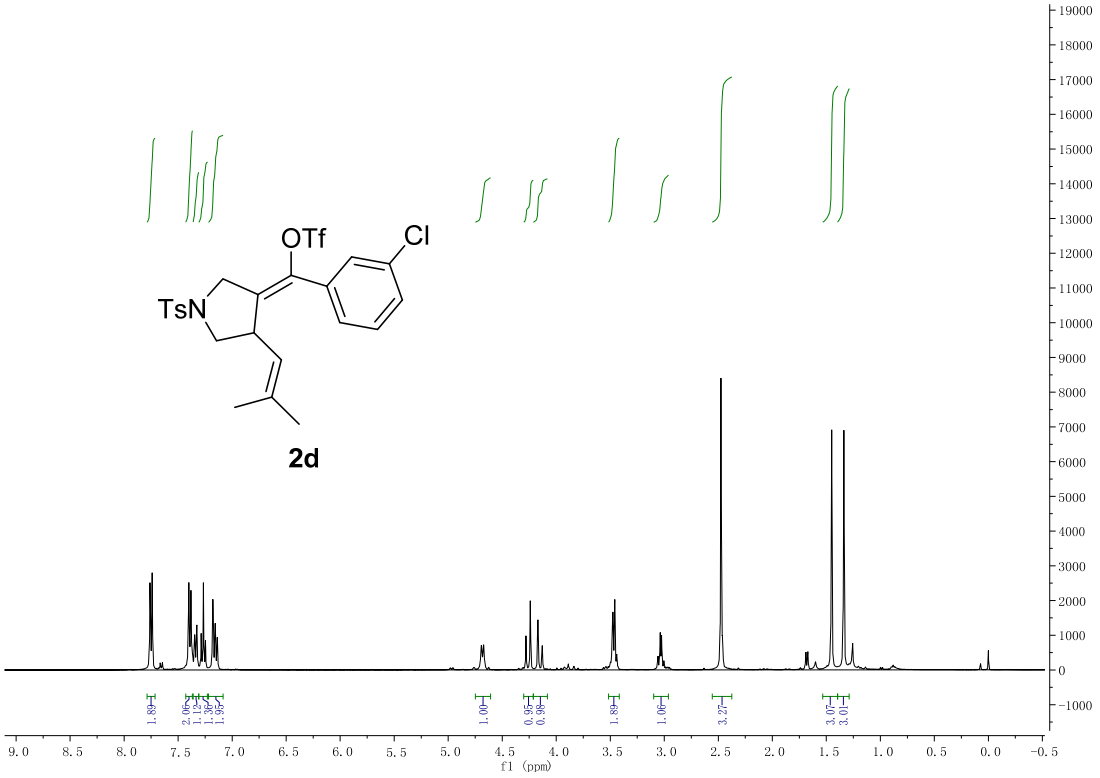
21.57
17.72
OTf
TsN
Br
2c
f1 (ppm)


OTf
Cl
TsN
2d
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2.05
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1.00
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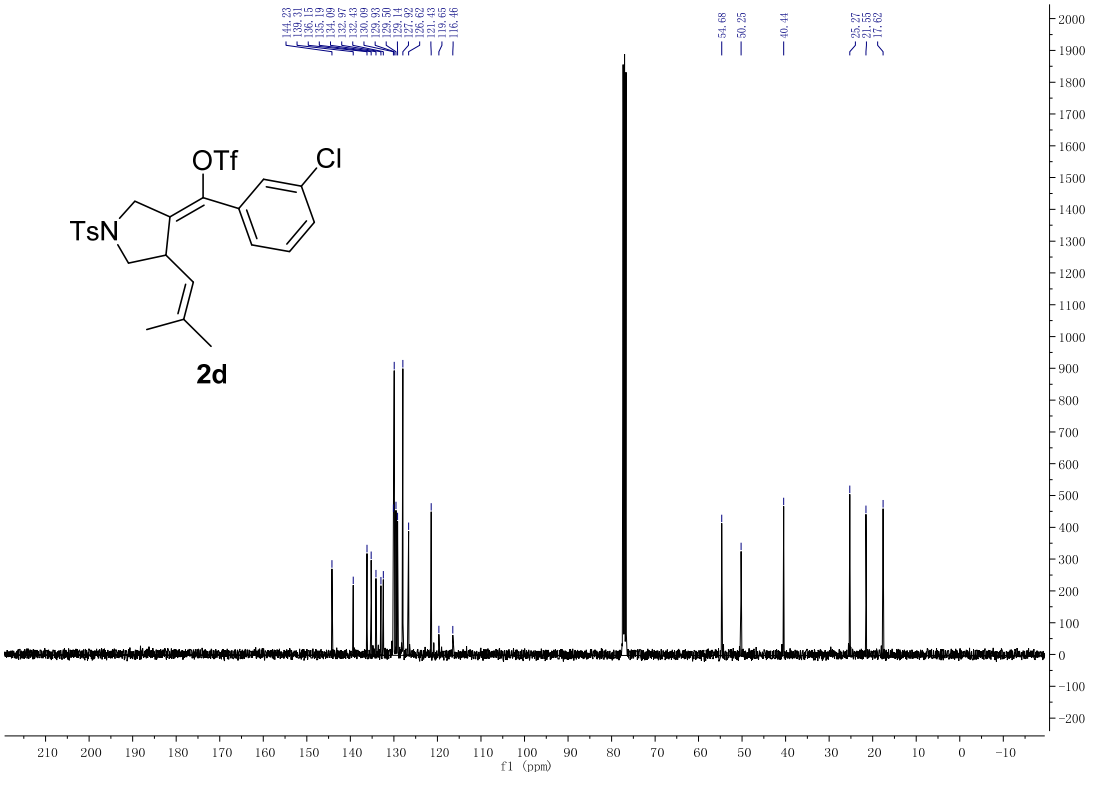
0.98
1.89
1.06
3.27
3.07
3.01
f1 (ppm)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136.15
135.19
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130.09
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129.50
129.14
127.69
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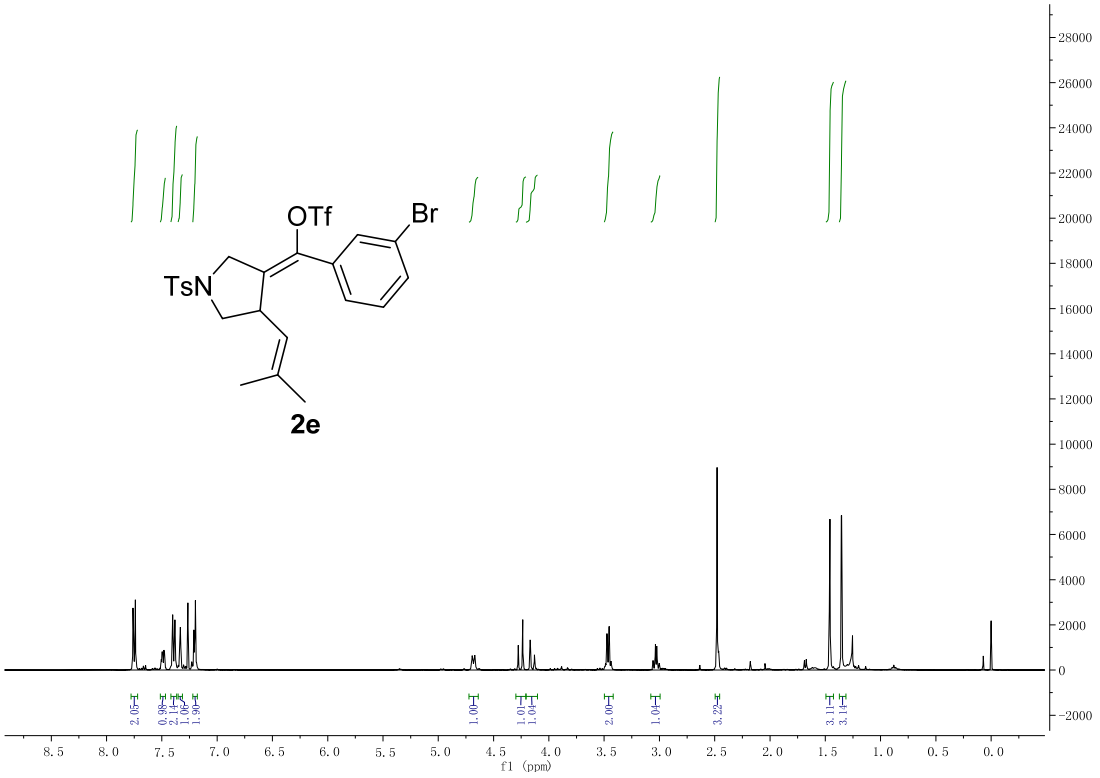
121.43
119.65
116.46
54.68
50.25
40.44
25.27
21.55
17.62
OTf
Cl
TsN
2d
f1 (ppm)


OTf
Br
TsN
2e
2.05
0.98
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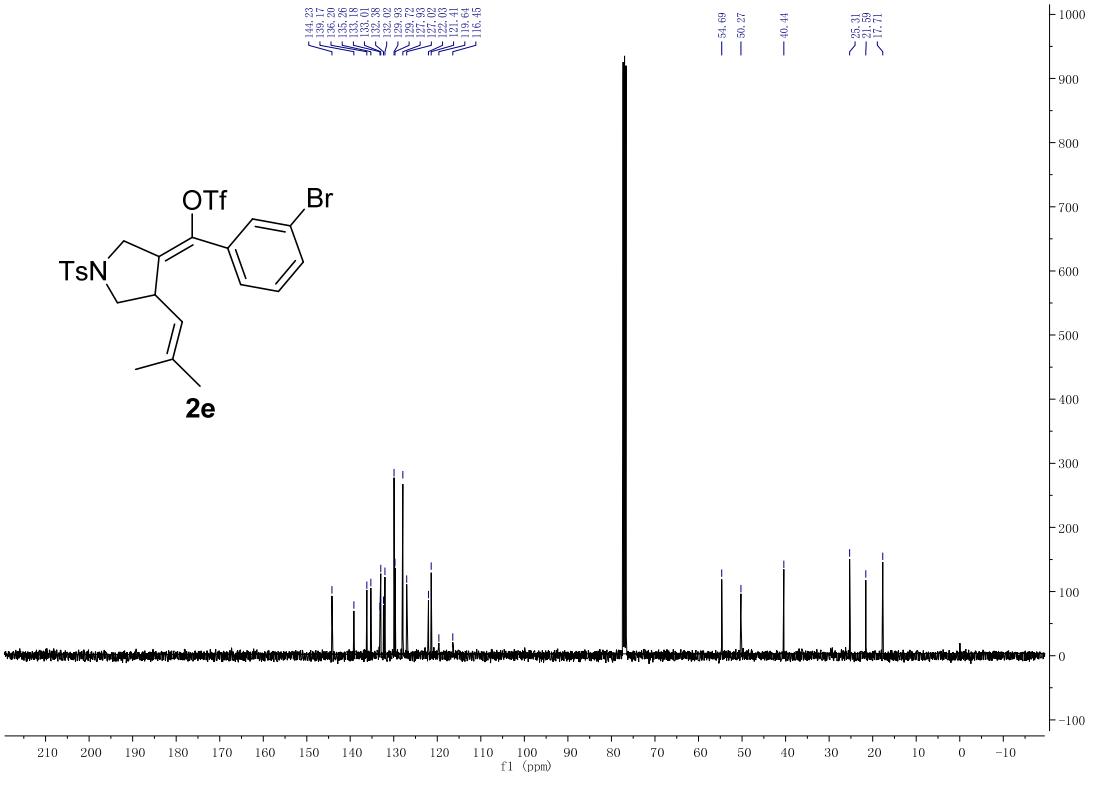
1.04
2.00
1.04
3.22
3.11
3.14
f1 (ppm)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127.93
127.02
122.03
121.41
119.64
116.45
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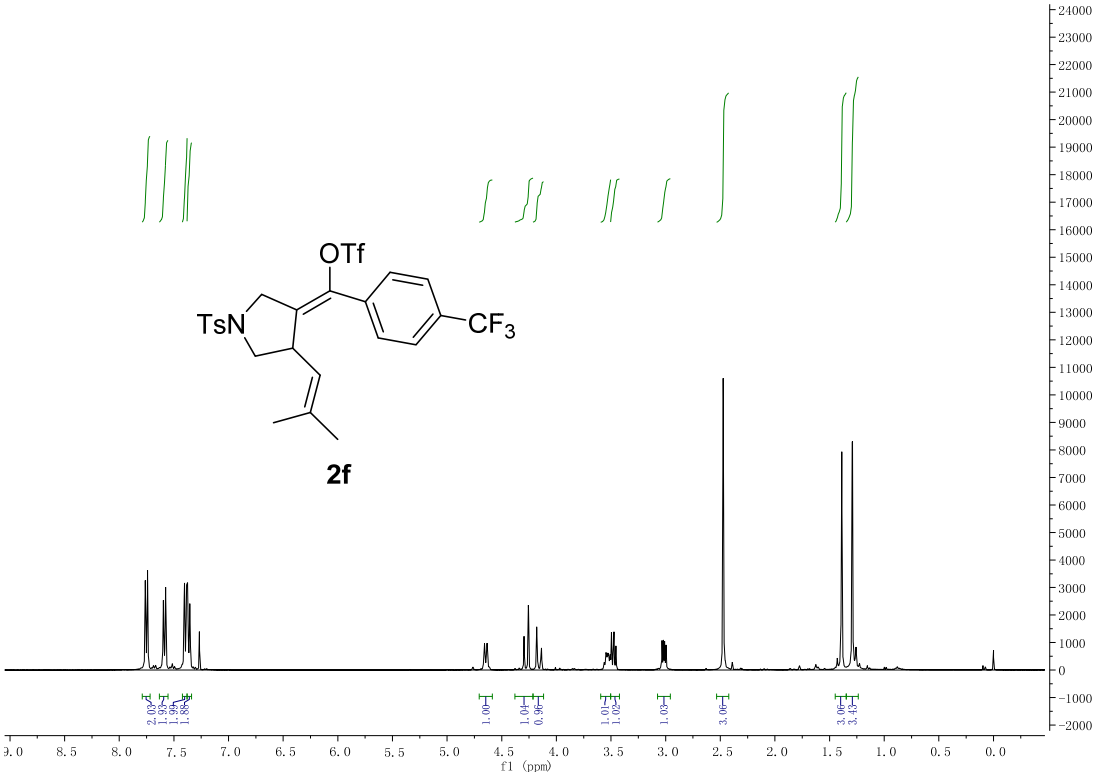
50.27
40.44
25.31
21.59
17.71
OTf
Br
TsN
2e
f1 (ppm)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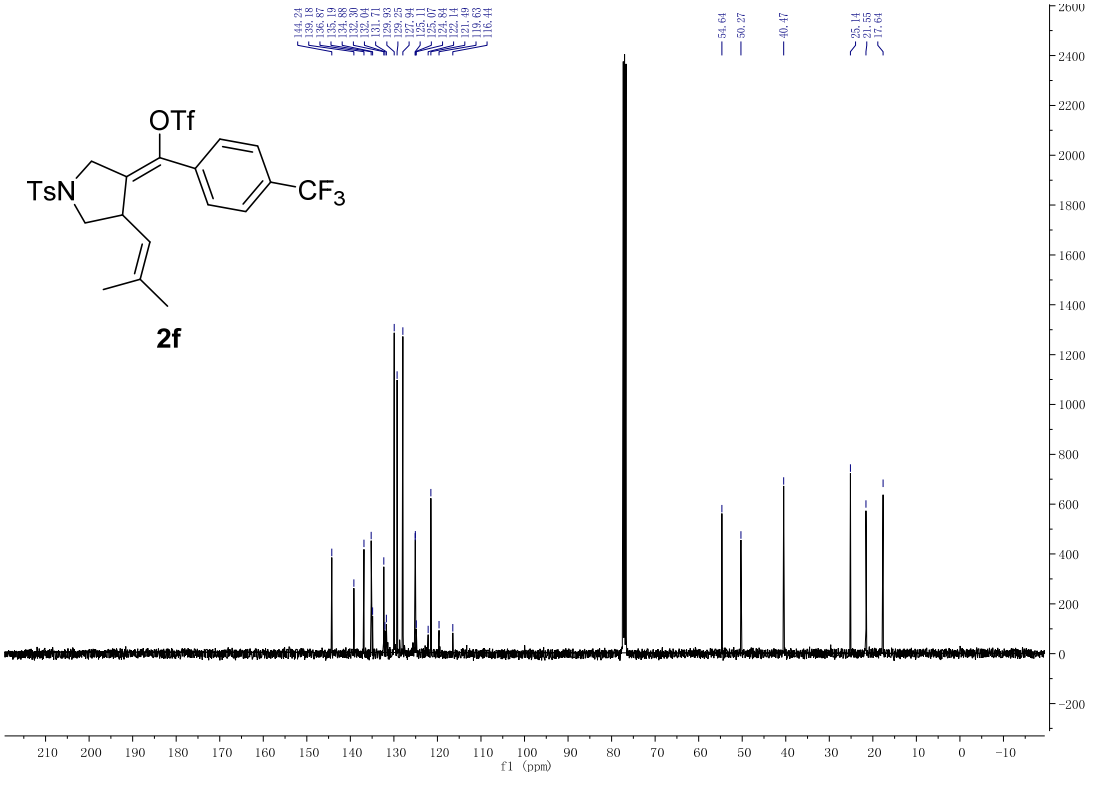
TsN
CF3
2f
f1 (ppm)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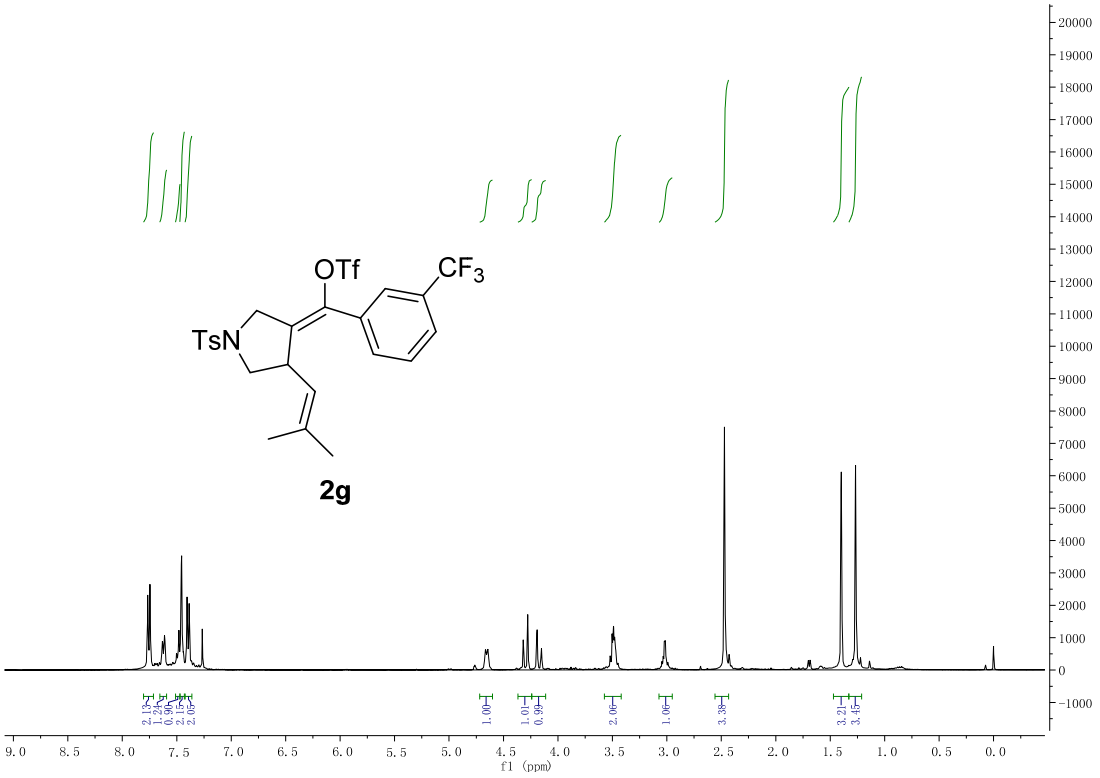
TsN
CF3
2f
f1 (ppm)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CF3
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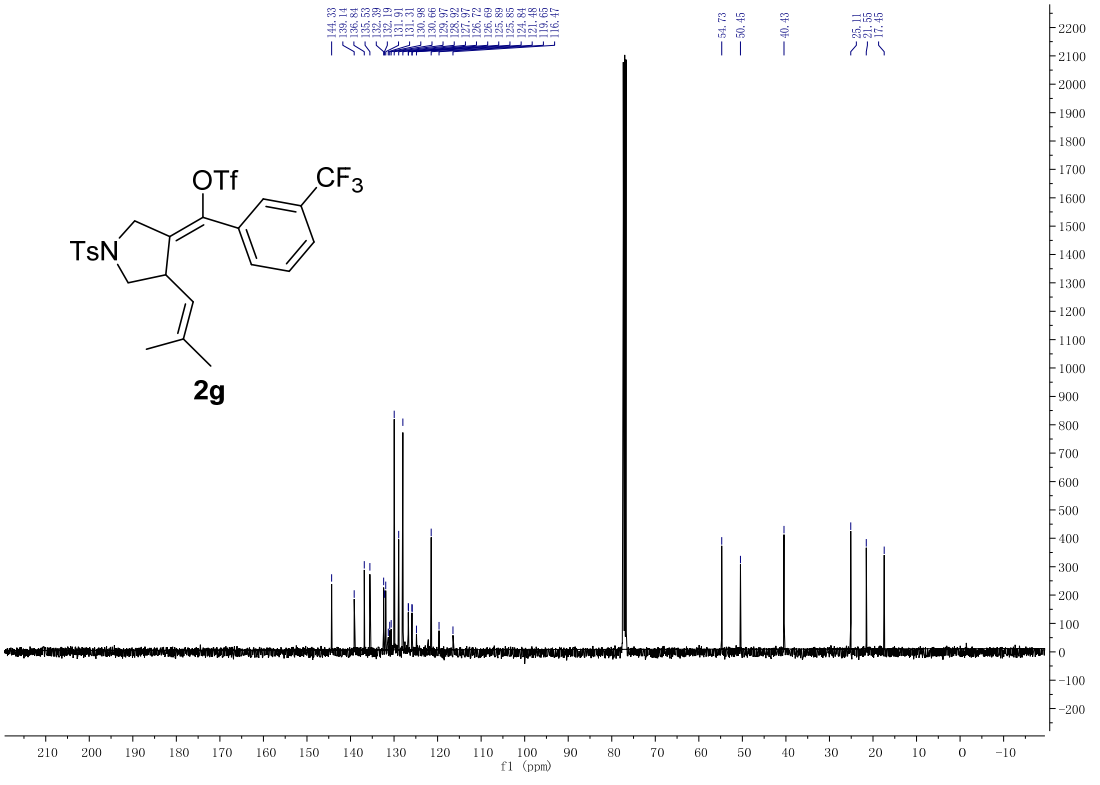
2g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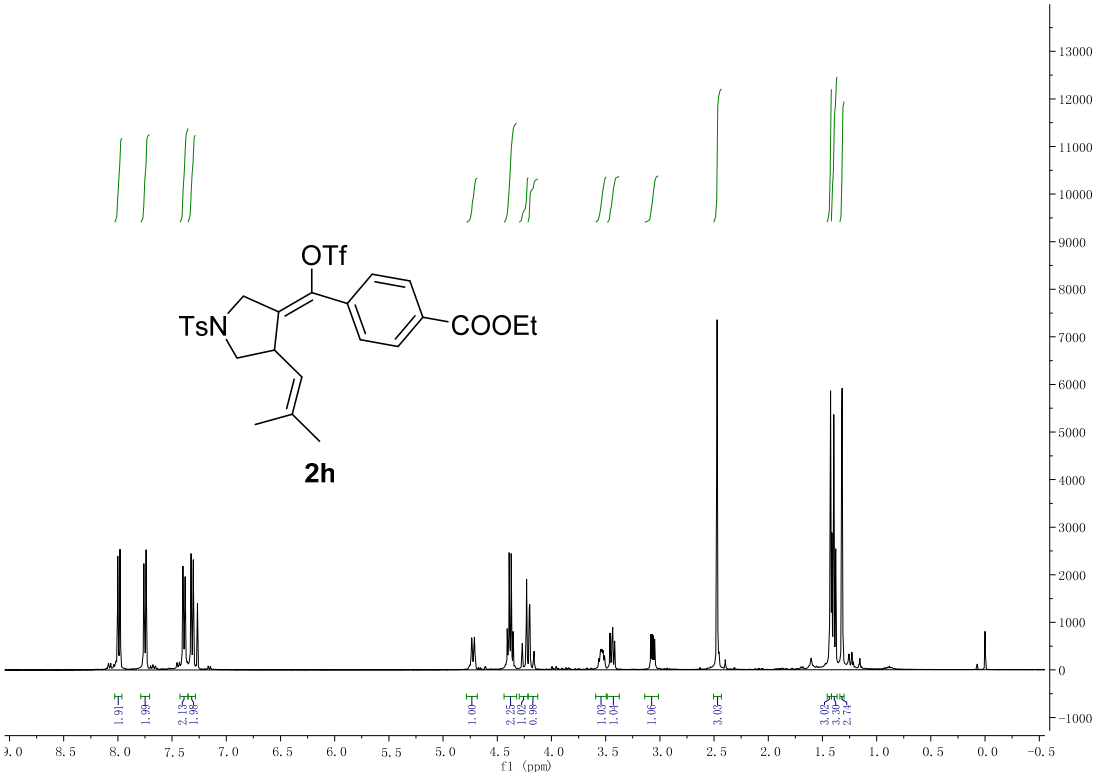
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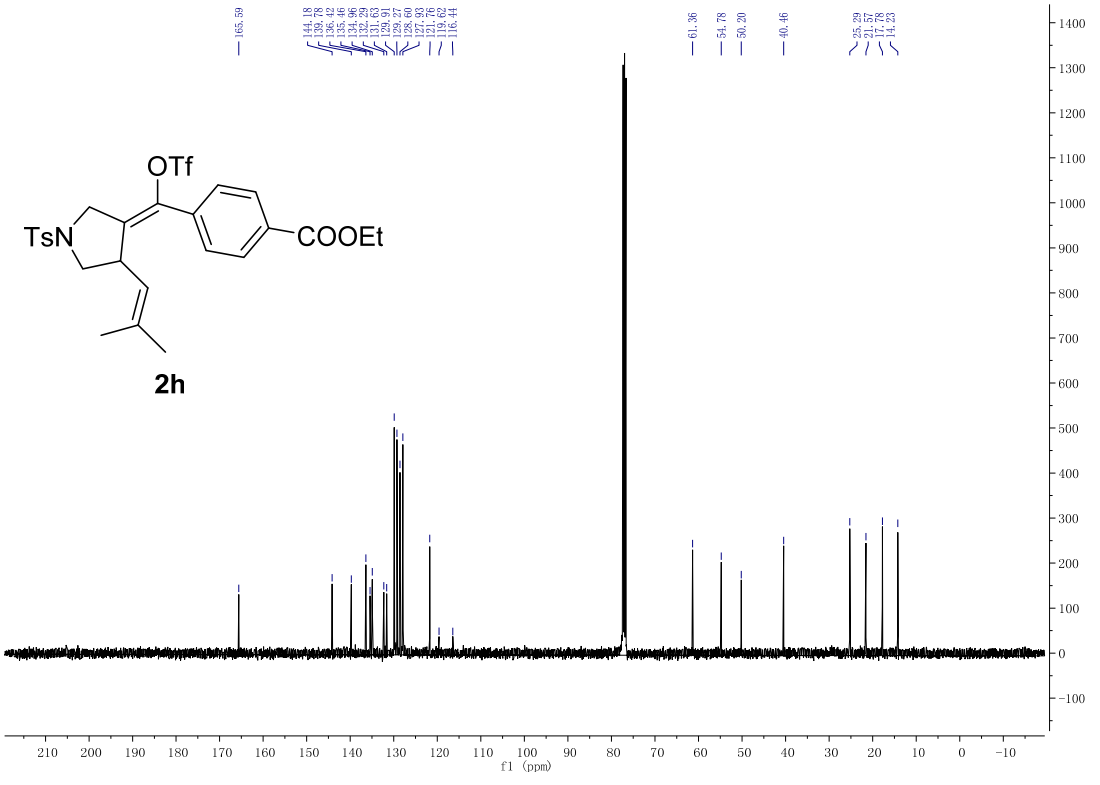
2h
f1 (ppm)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131.63
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128.66
127.95
121.76
119.62
116.44
61.36
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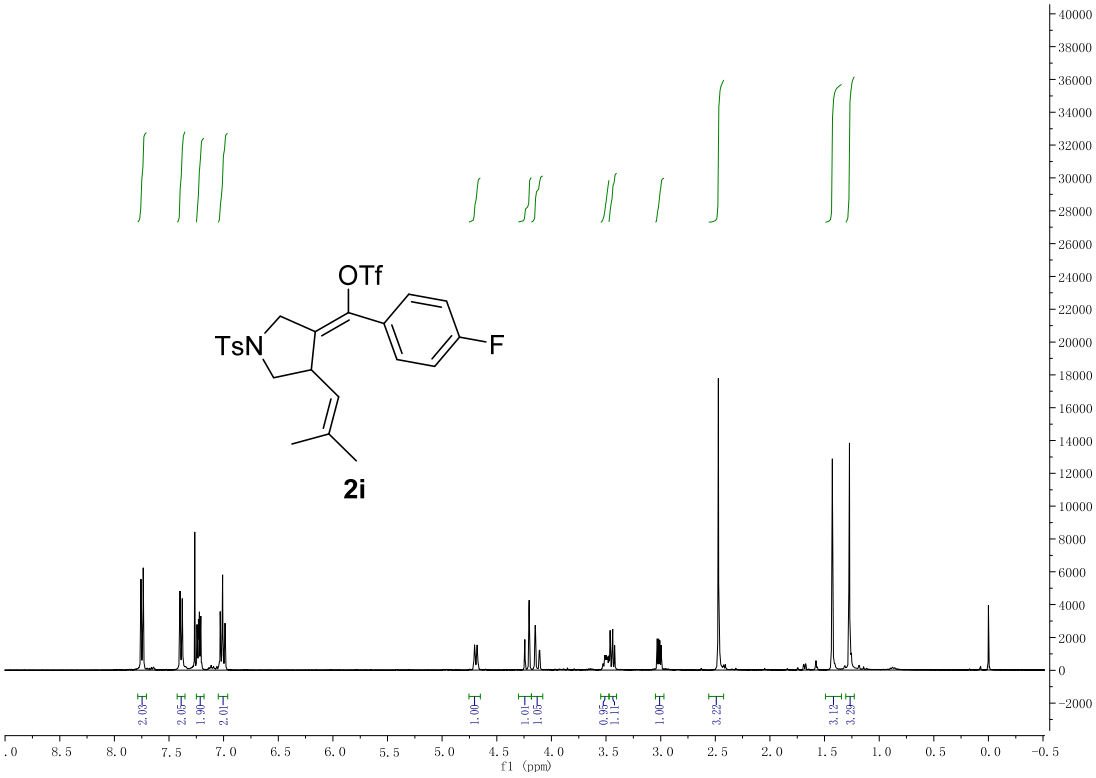
40.46
25.89
21.57
17.78
14.23
OTf
TsN
COOEt
2h
f1 (ppm)


OTf
TsN
F
2i
2.03
2.05
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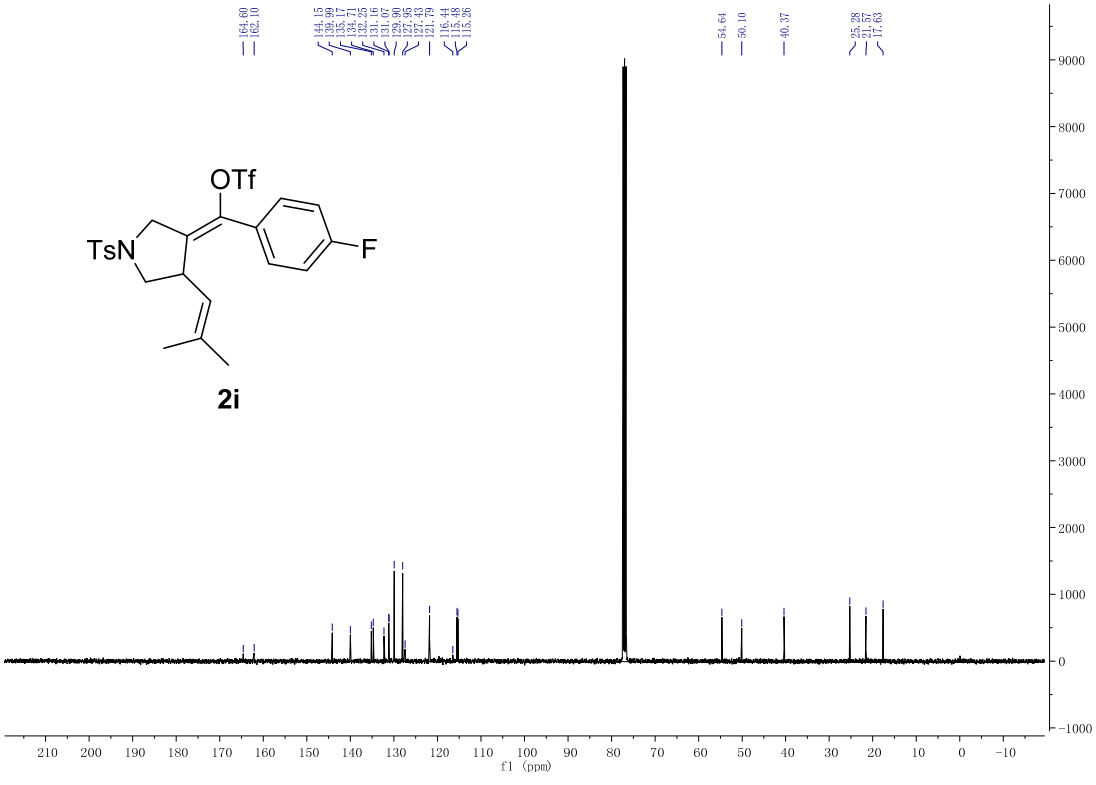
2.01
1.00
1.01
1.05
0.95
1.11
1.00
3.22
3.12
3.29
f1 (ppm)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134.71
132.25
131.16
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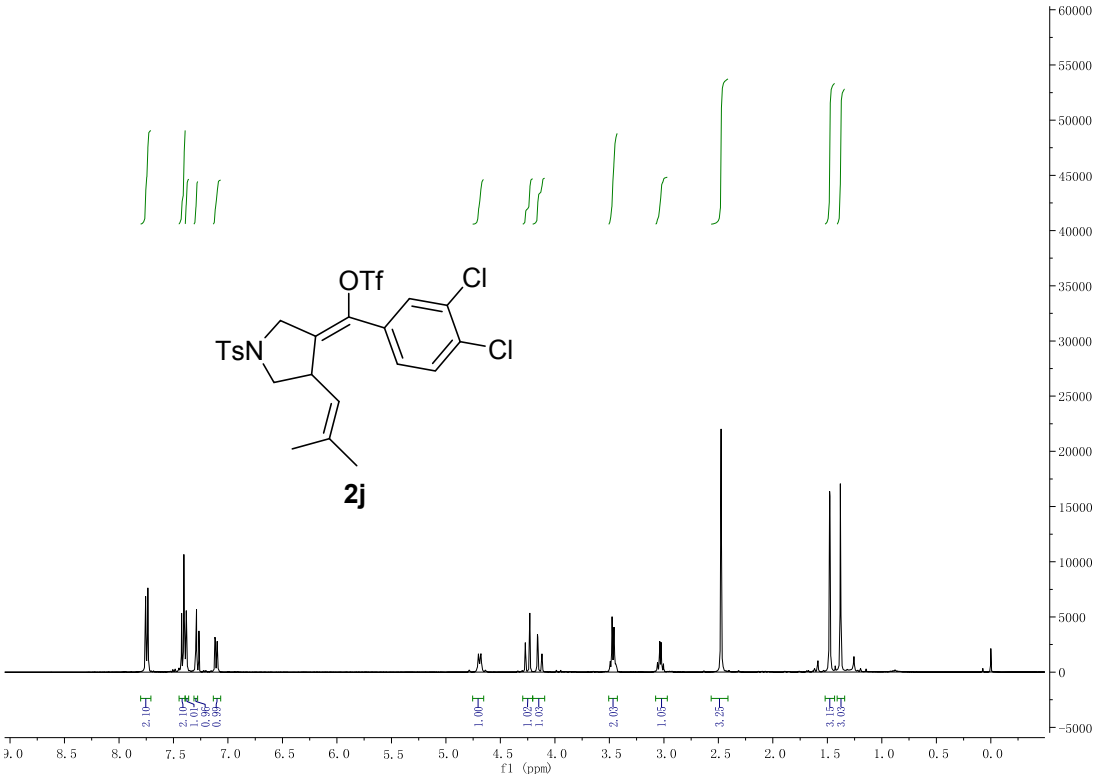
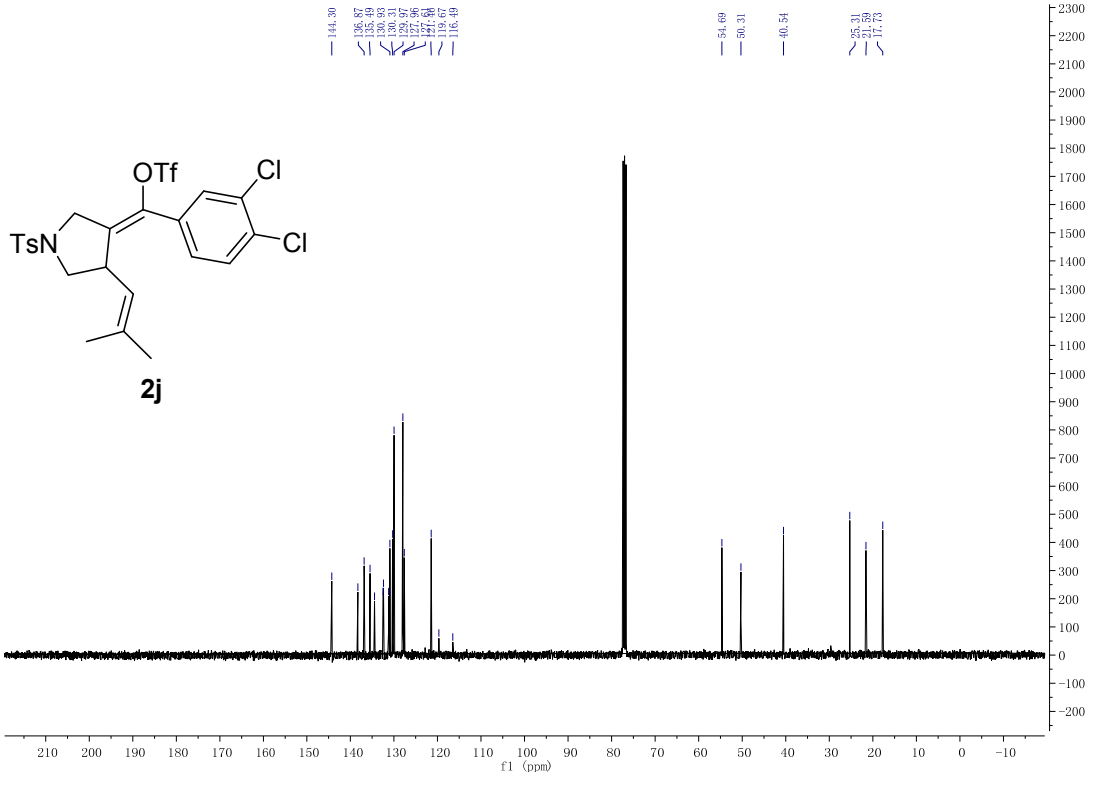
129.90
129.65
127.43
121.79
116.44
115.48
115.26
54.64
50.10
40.37
25.28
21.57
17.63
OTf
TsN
F
2i
f1 (ppm)


OTf
Cl
Cl
TsN
2j
f1 (ppm)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135.49
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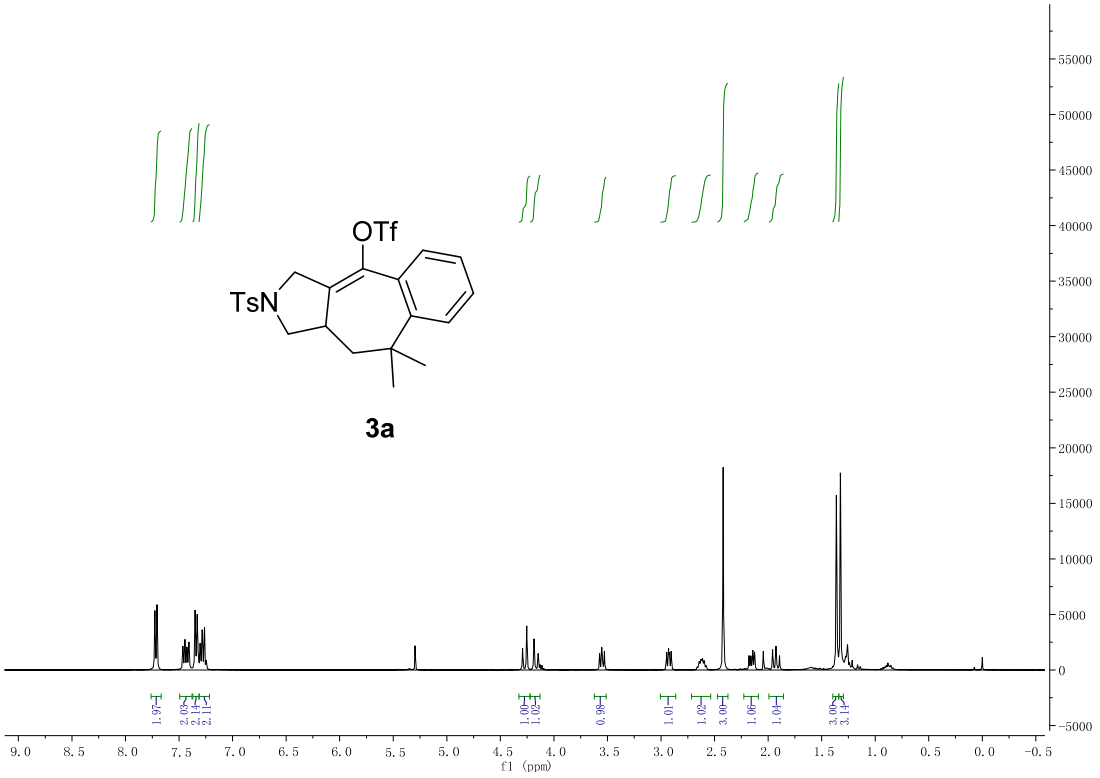
130.31
129.97
127.96
119.67
116.49
54.69
50.31
40.54
25.31
21.59
17.73
OTf
Cl
Cl
TsN
2j
f1 (ppm)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TsN
3a
1.97
2.09
2.14
2.11
1.00
1.02
0.90
1.01
1.02
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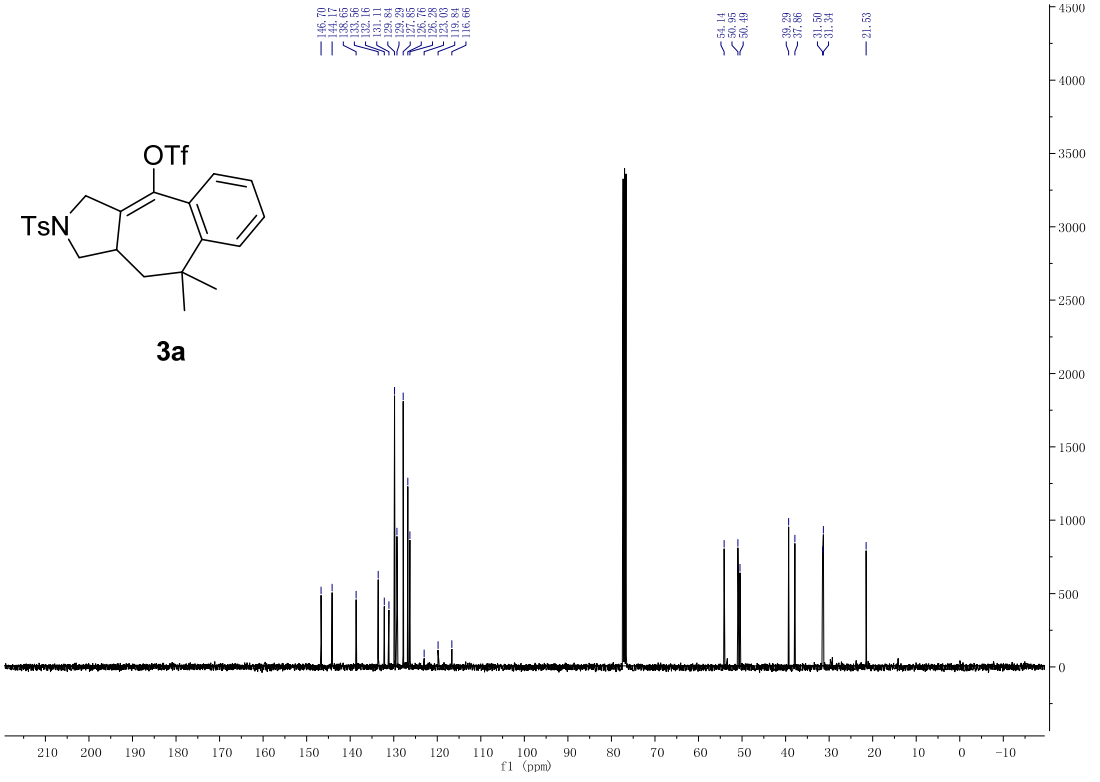
1.06
1.04
3.00
3.14
f1 (ppm)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116.66
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39.29
37.86
31.50
31.34
21.53
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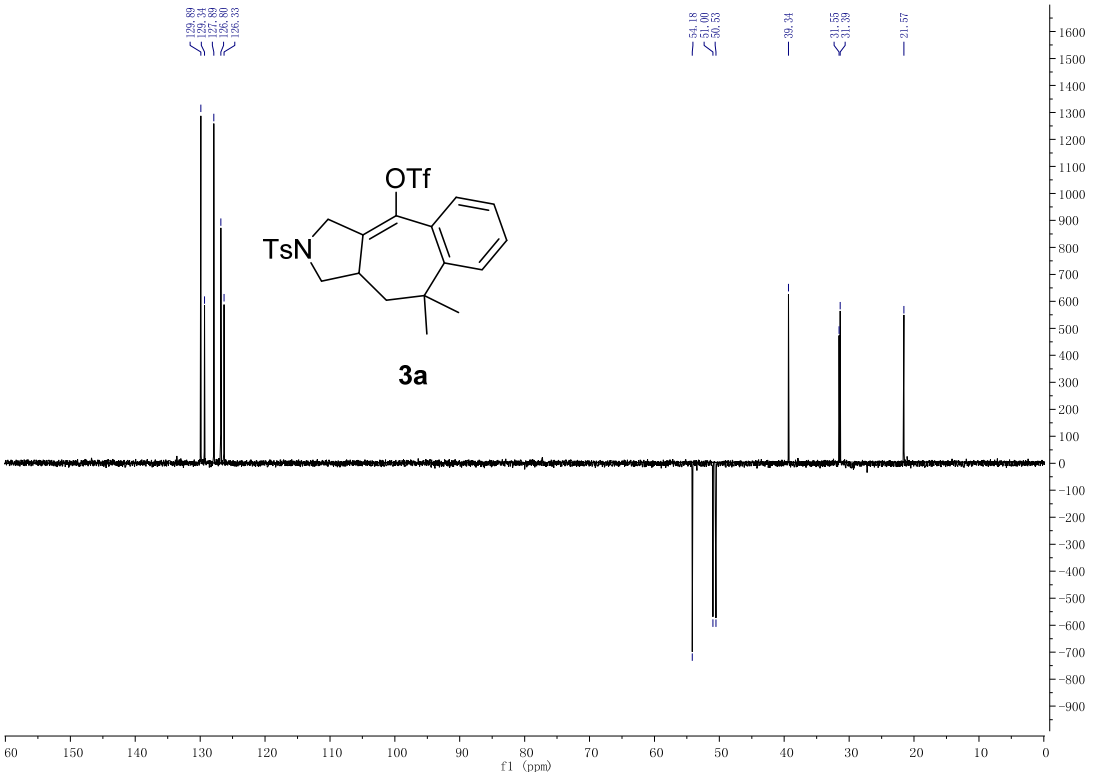
TsN
3a
f1 (ppm)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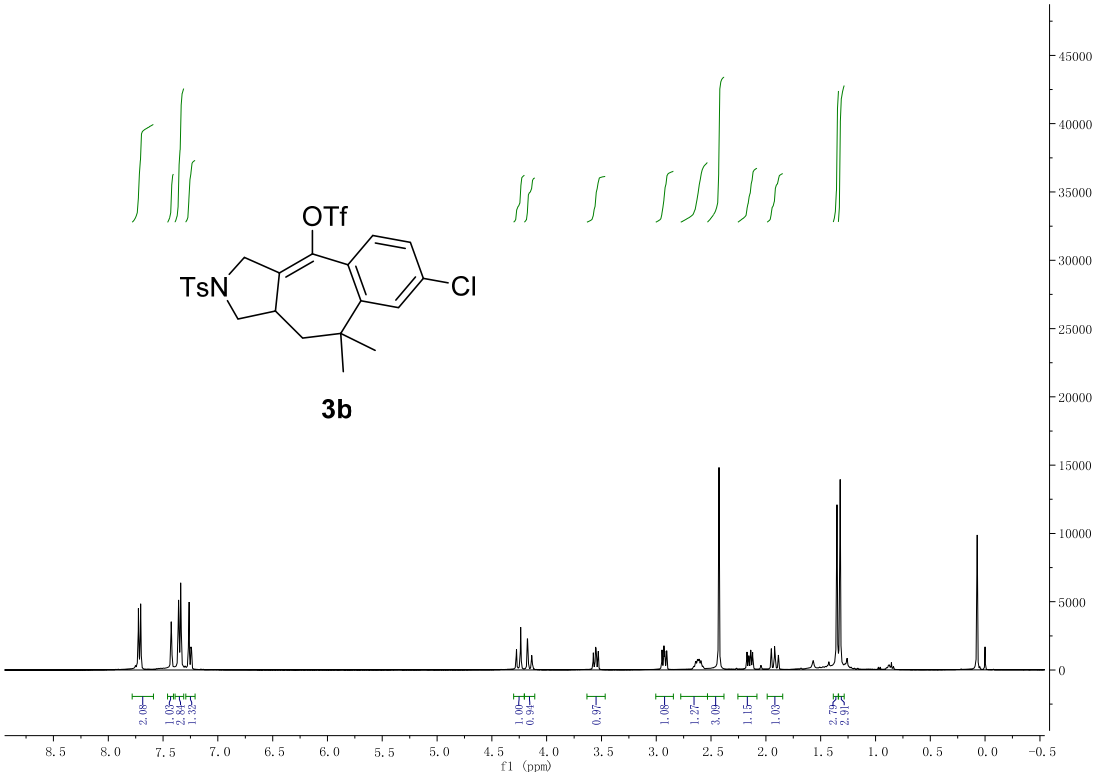
39.34
31.55
31.39
21.57
OTf
TsN
3a
f1 (ppm)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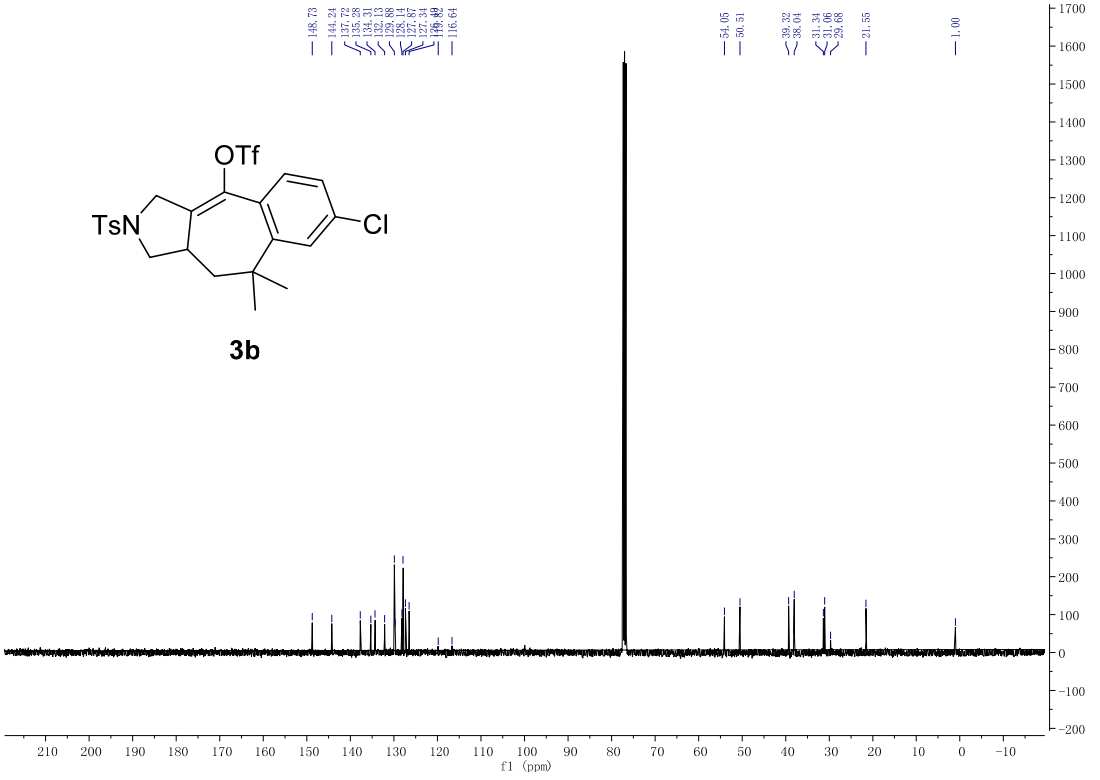
TsN
Cl
3b
f1 (ppm)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132.13
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128.14
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127.34
116.64
54.05
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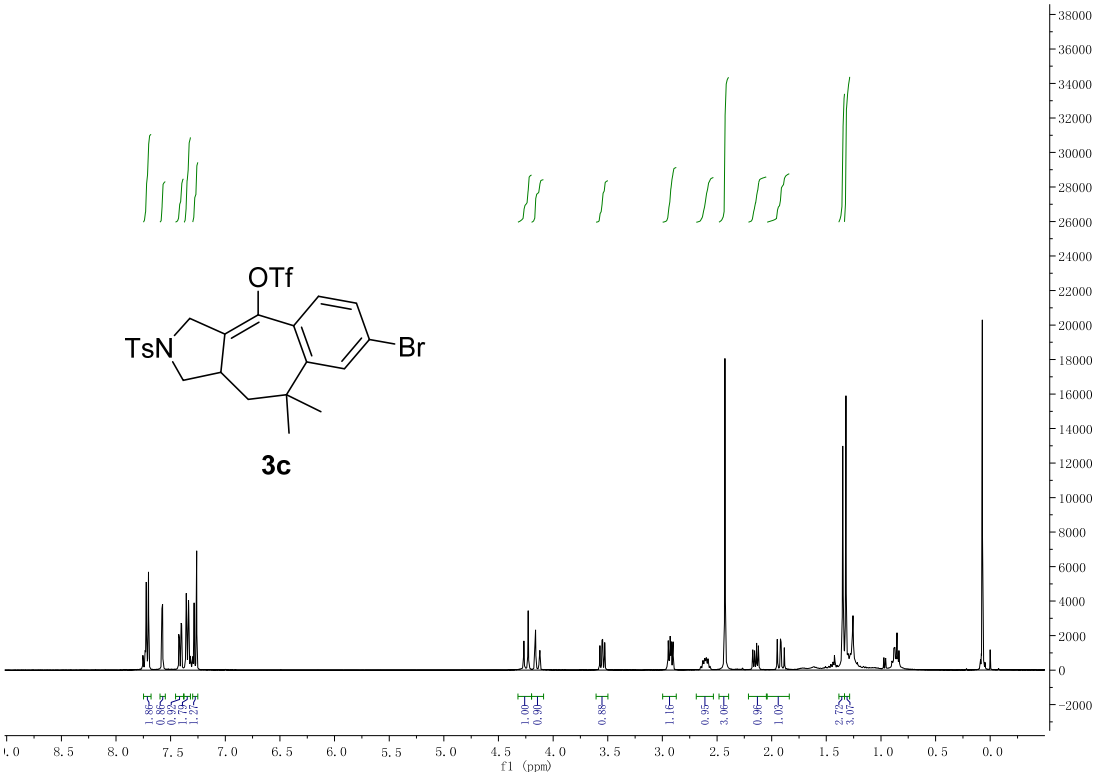
39.32
38.04
31.34
31.06
29.68
21.55
1.00
OTf
TsN
Cl
3b
f1 (ppm)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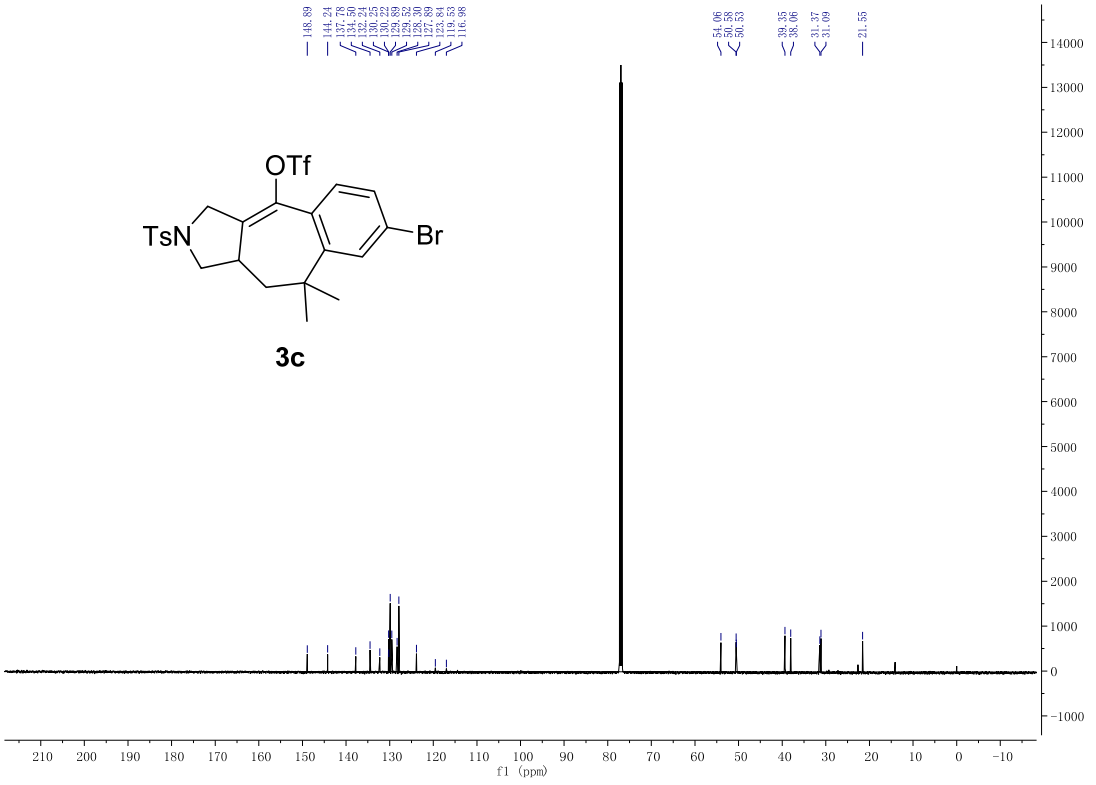
TsN
Br
3c
f1 (ppm)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127.89
123.84
119.53
116.98
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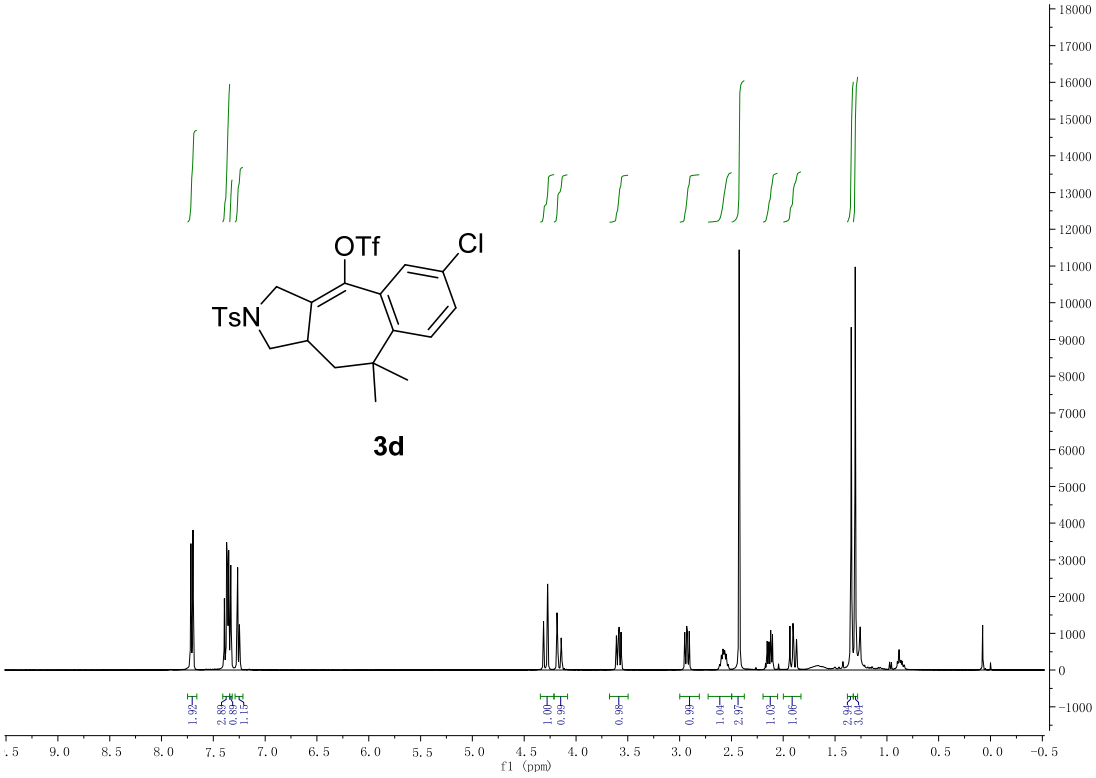
39.35
38.06
31.37
31.09
21.55
OTf
TsN
Br
3c
f1 (ppm)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TsN
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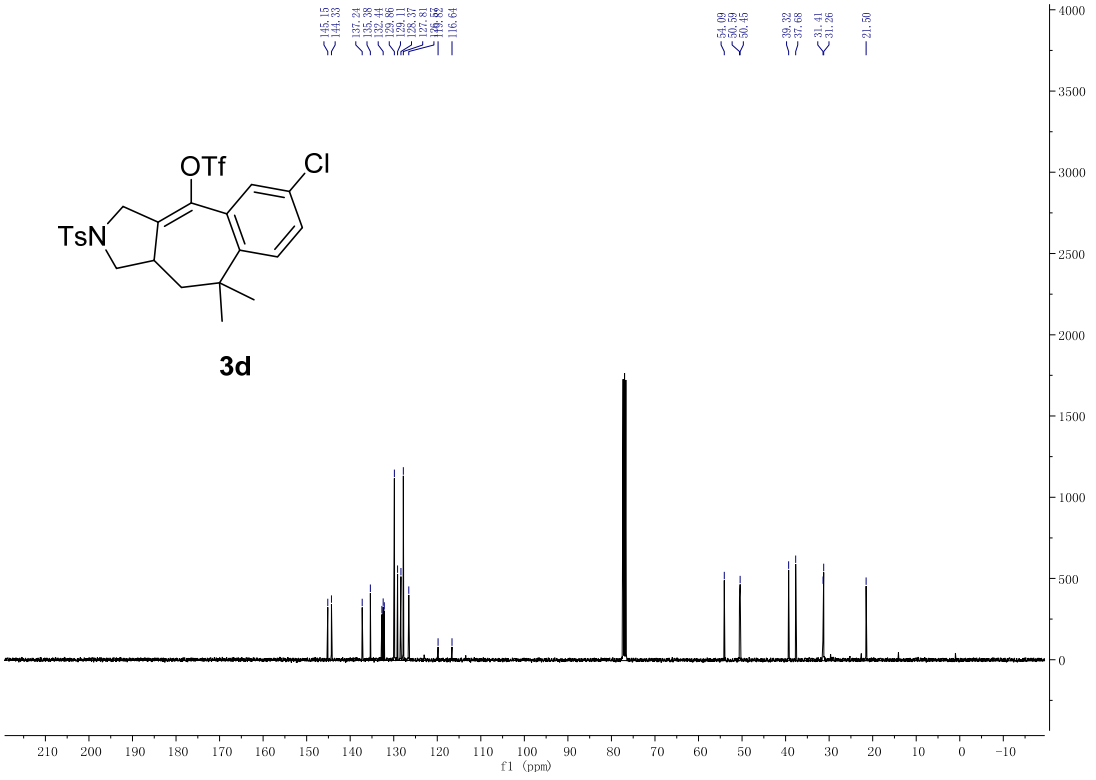
f1 (ppm)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39.32
37.68
31.41
31.26
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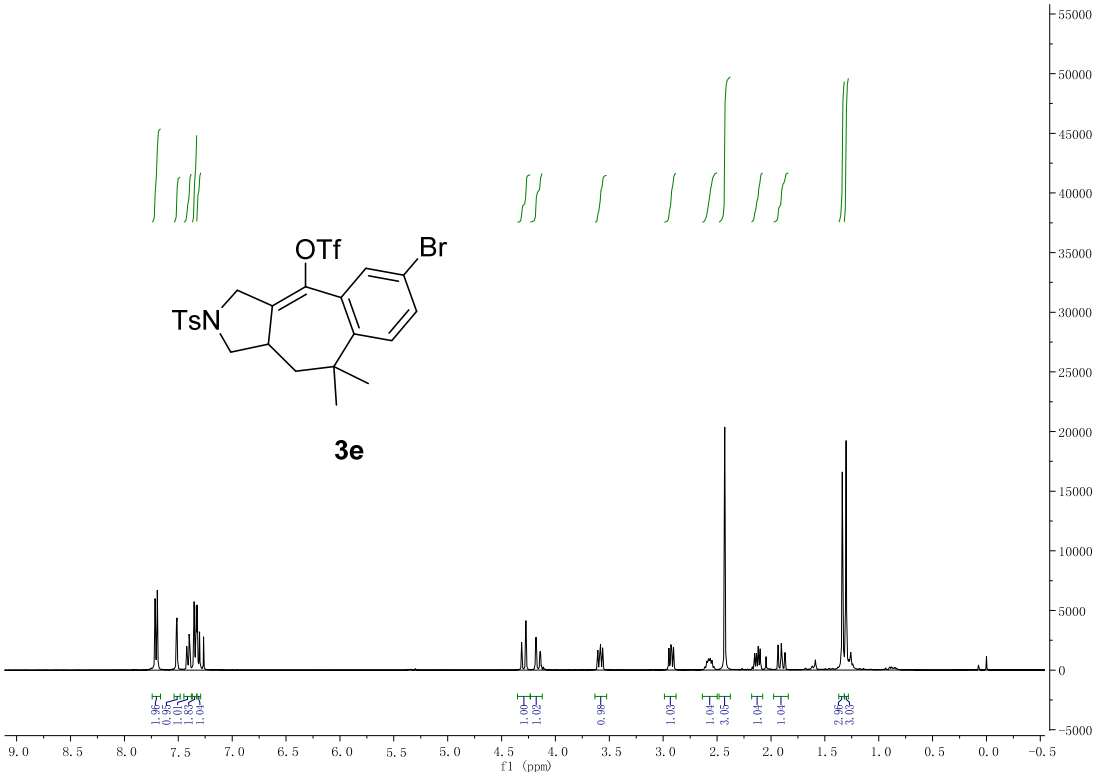
OTf
Cl
TsN
3d
f1 (ppm)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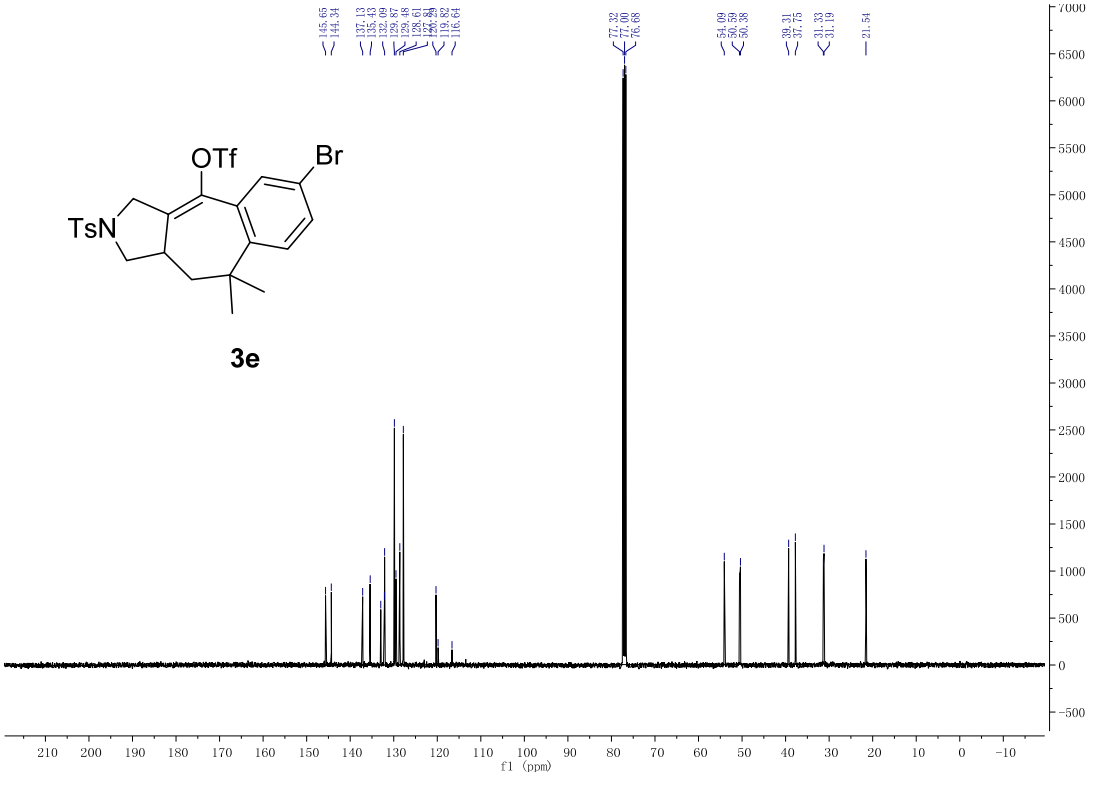
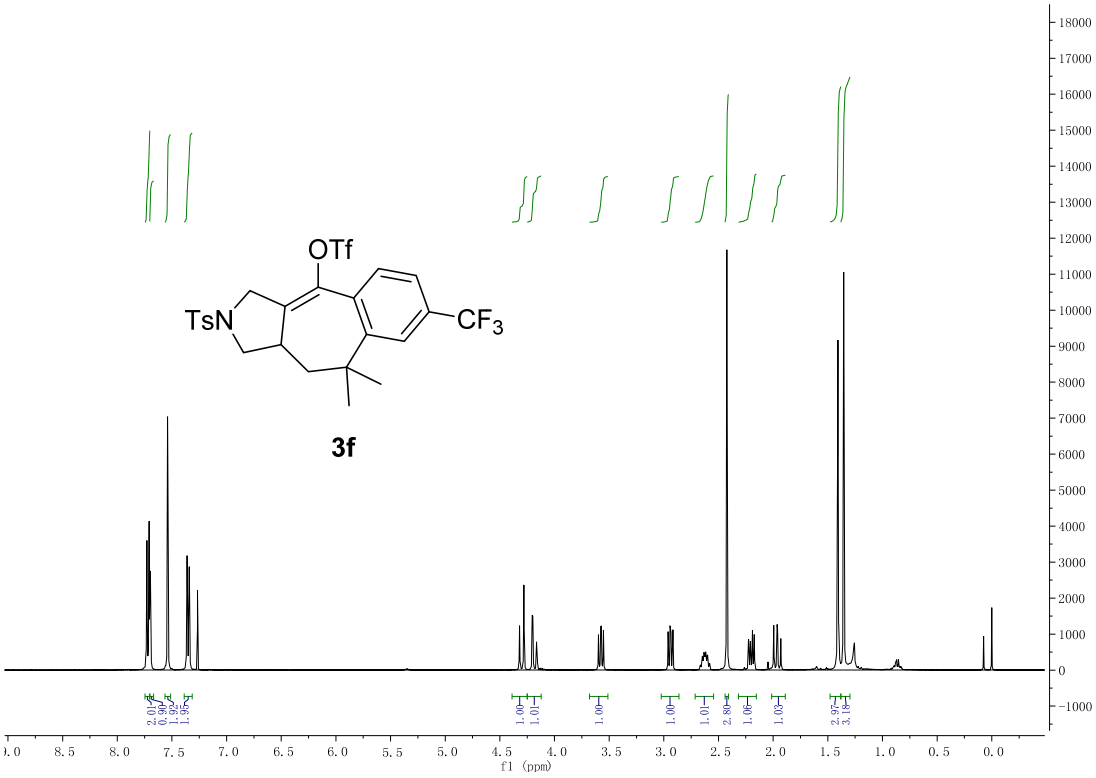
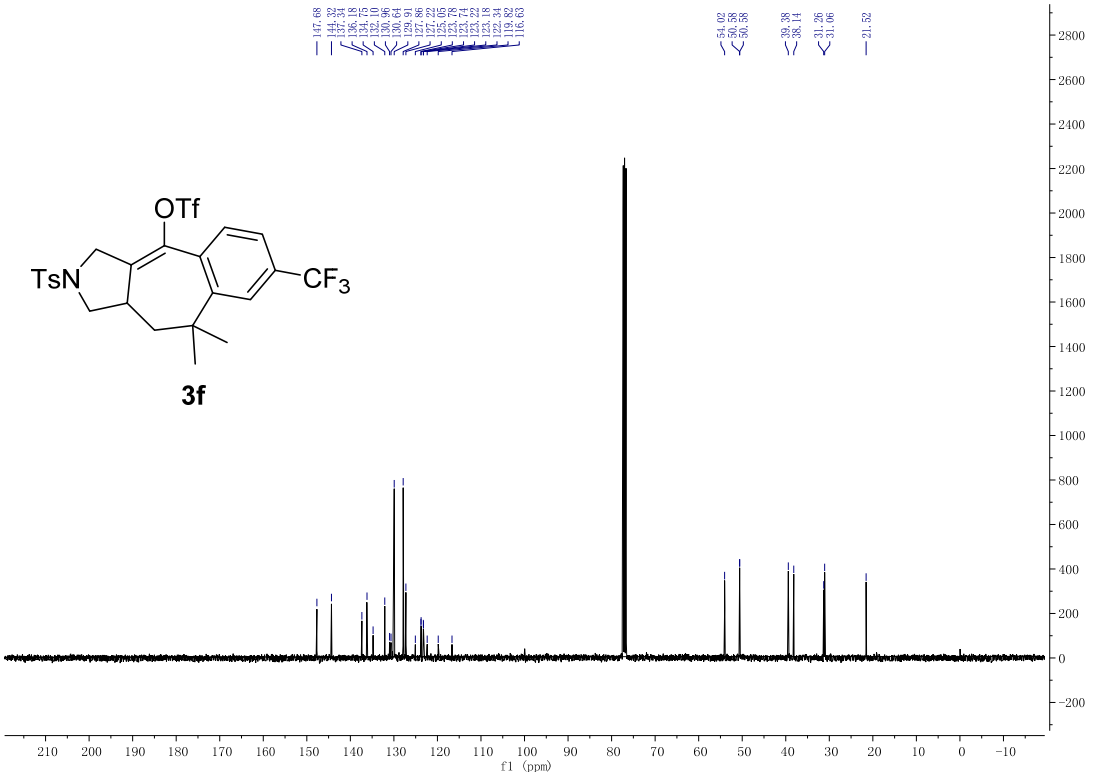

OTf
Br
TsN
3e


OTf
TsN
CF3
3f
f1 (ppm)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TsN
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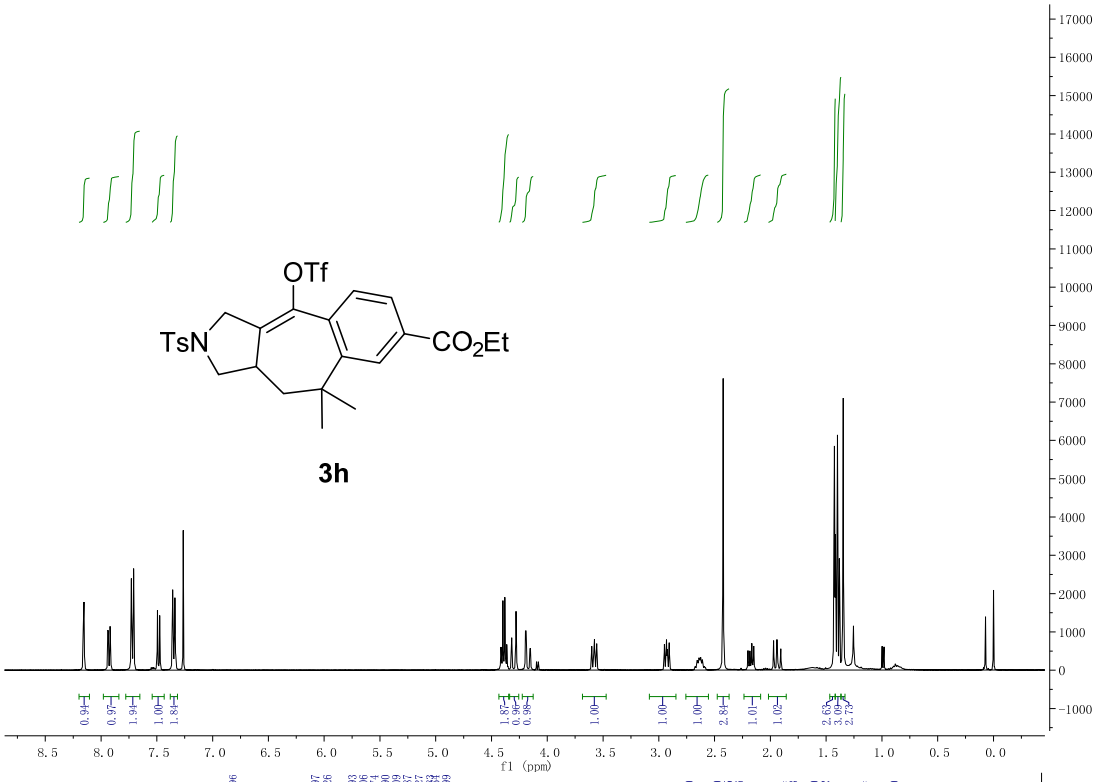
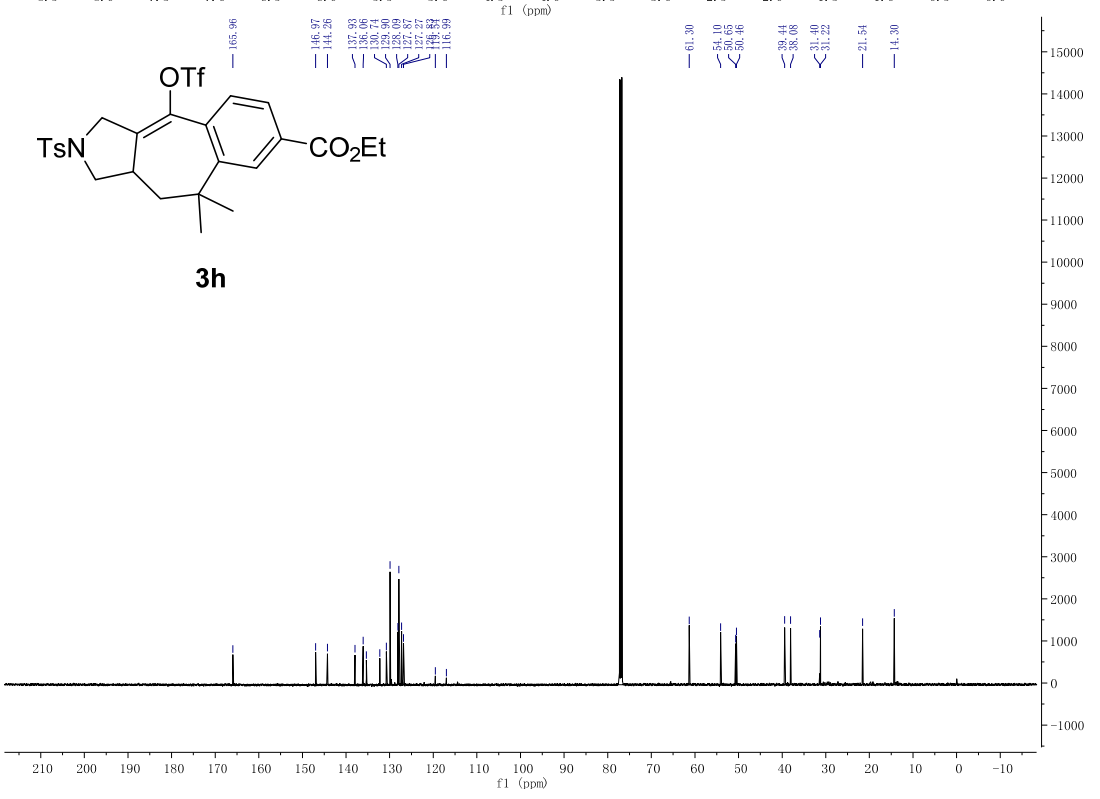
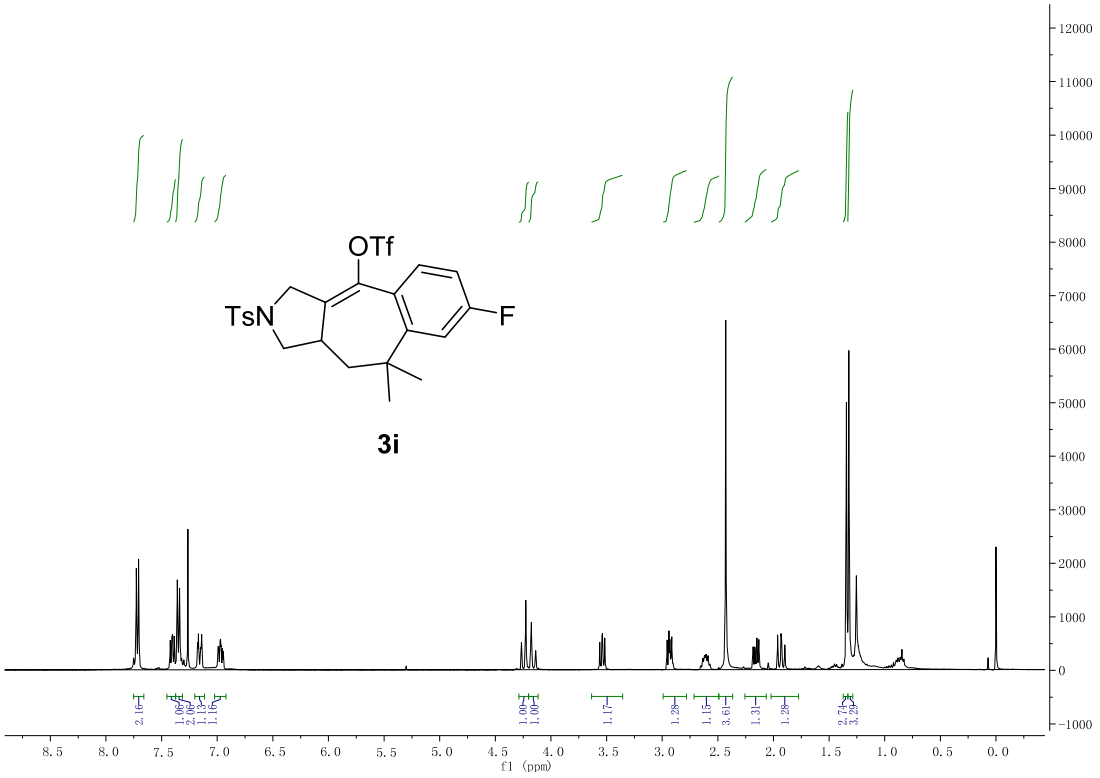
3f
f1 (ppm)

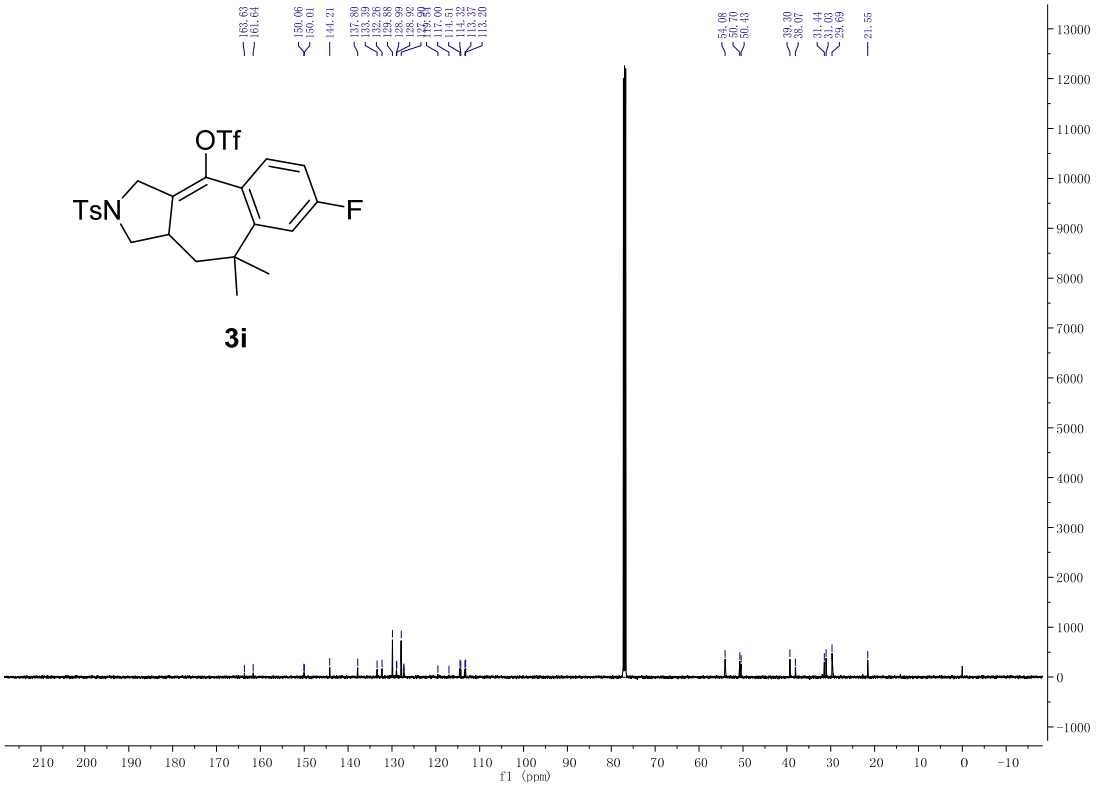



**3h**




**3h**


OTf
TsN
F
3i
f1 (ppm)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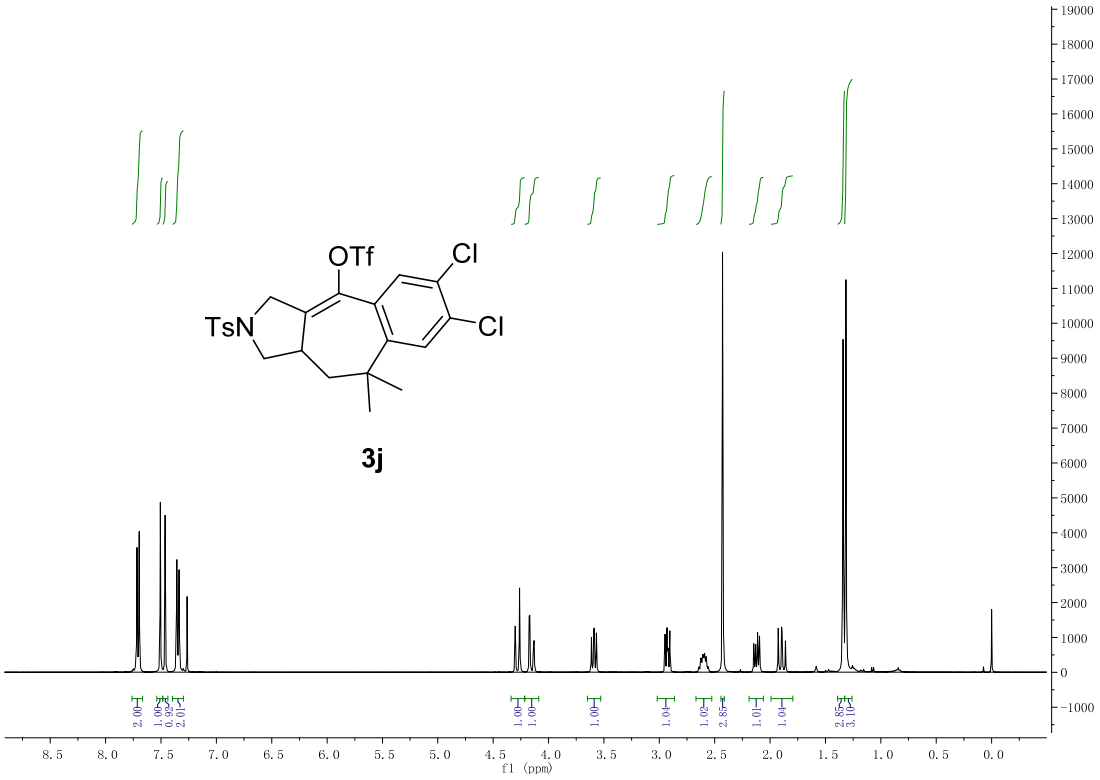
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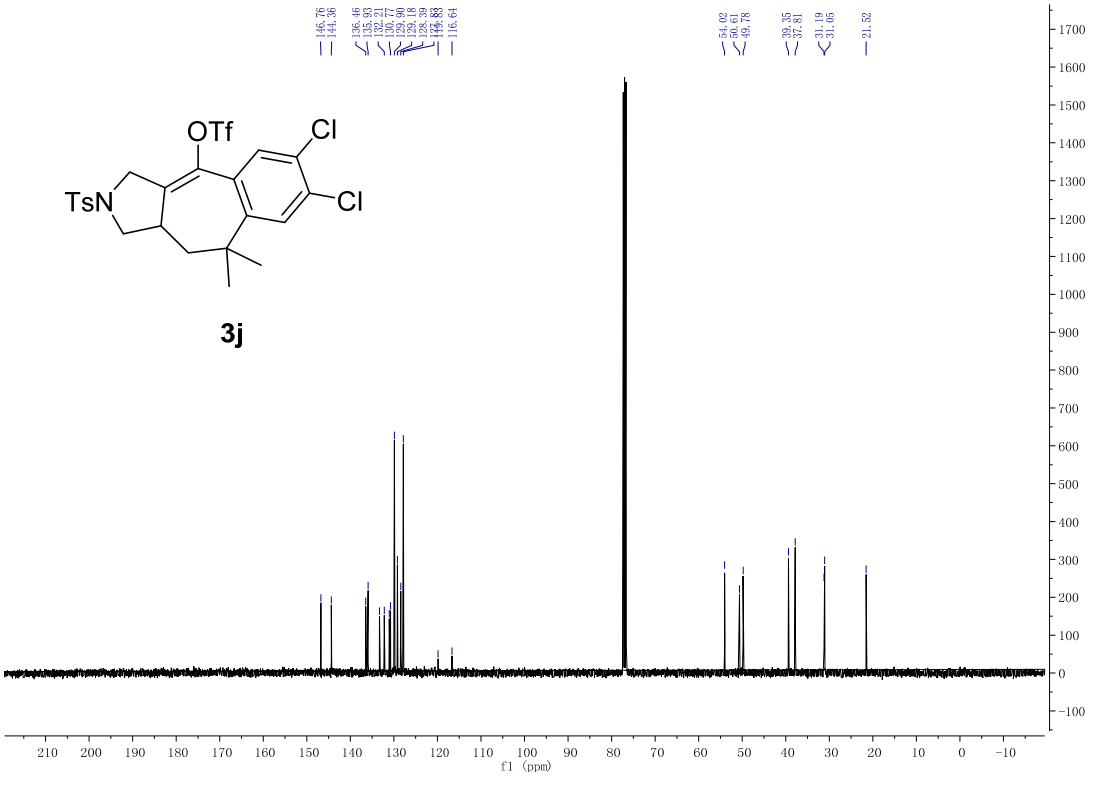
TsN
Cl

**3j**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54.02
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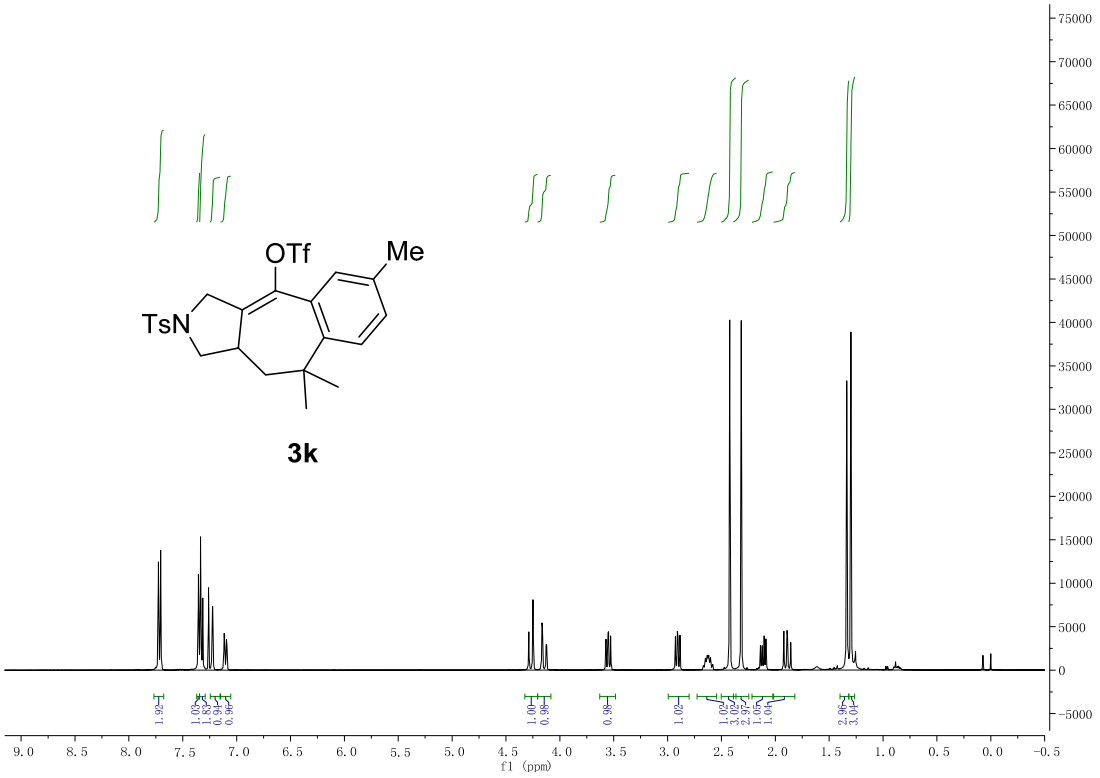
39.35
37.81
31.19
31.05
21.52
f1 (ppm)


OTf
Cl
TsN
Cl

**3j**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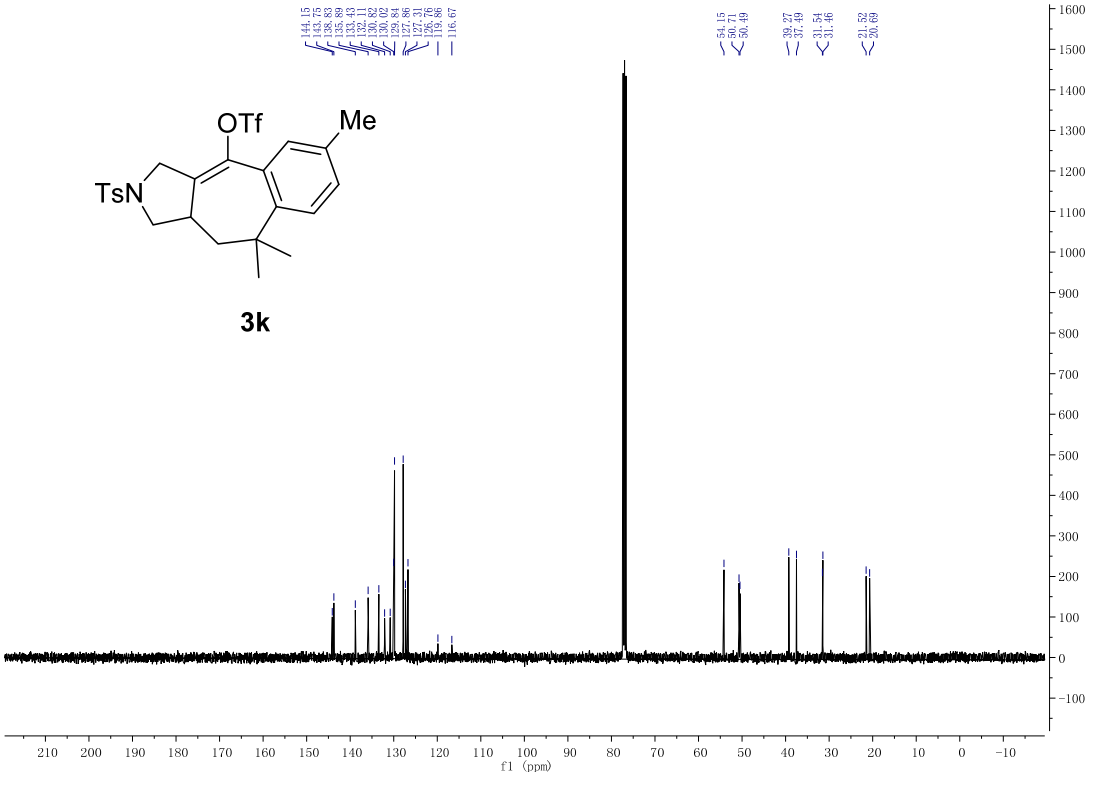
3k
f1 (ppm)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119.86
116.67
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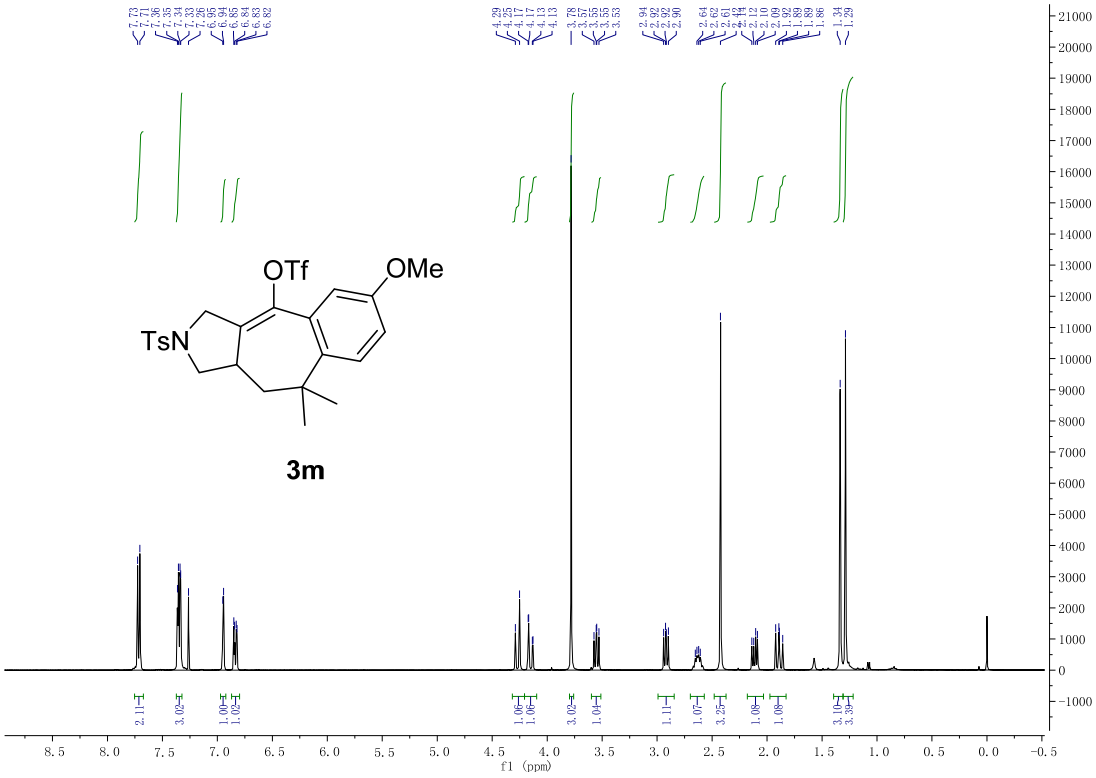
OTf
Me
TsN
3k
f1 (ppm)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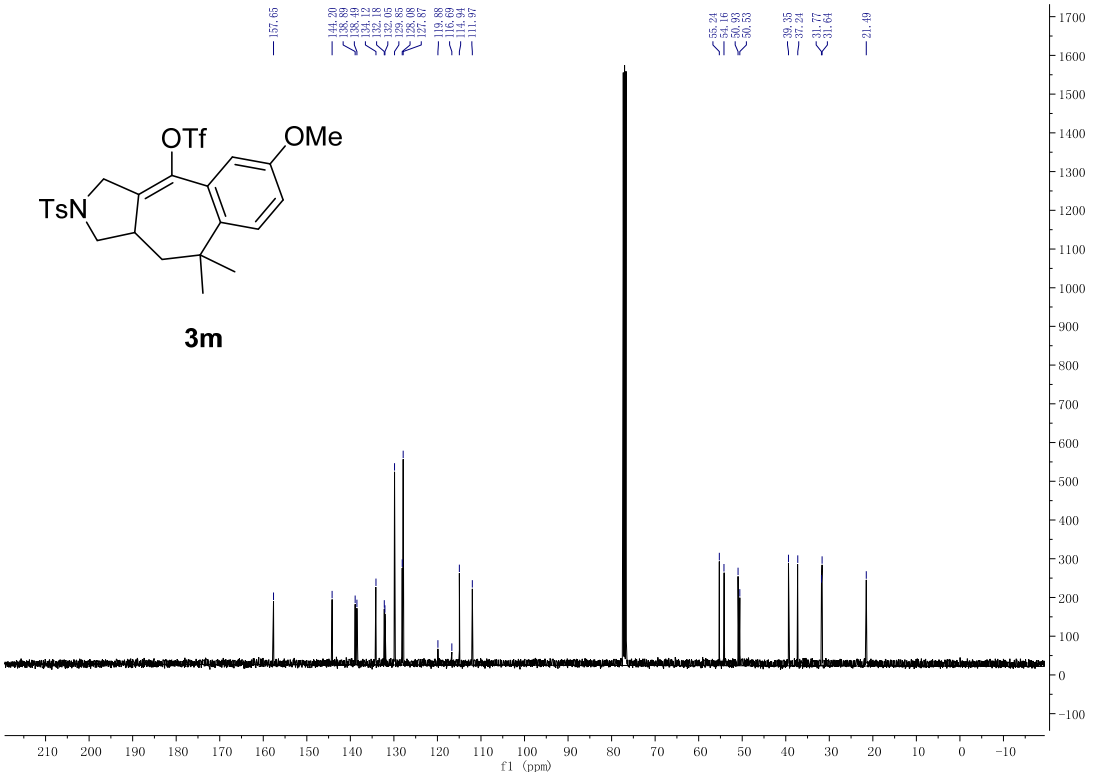
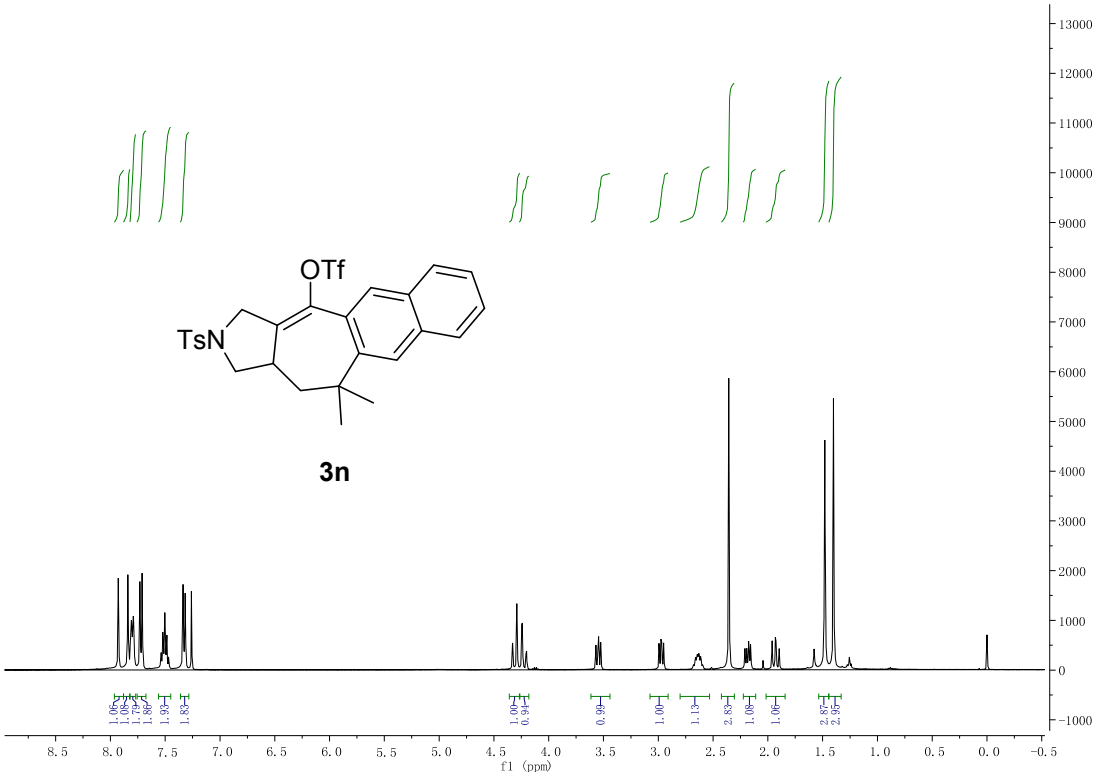
OMe
TsN
3m
f1 (ppm)


OTf
OMe
TsN
3m
f1 (ppm)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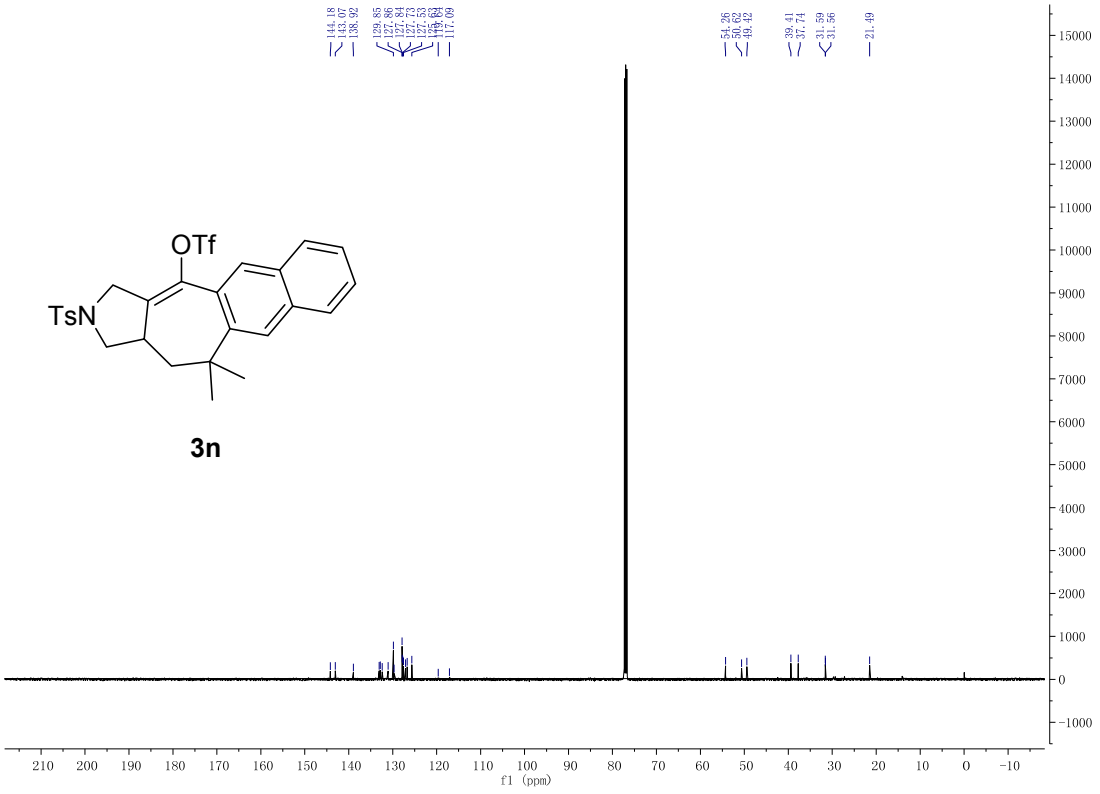
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119.64
117.09
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39.41
37.74
31.59
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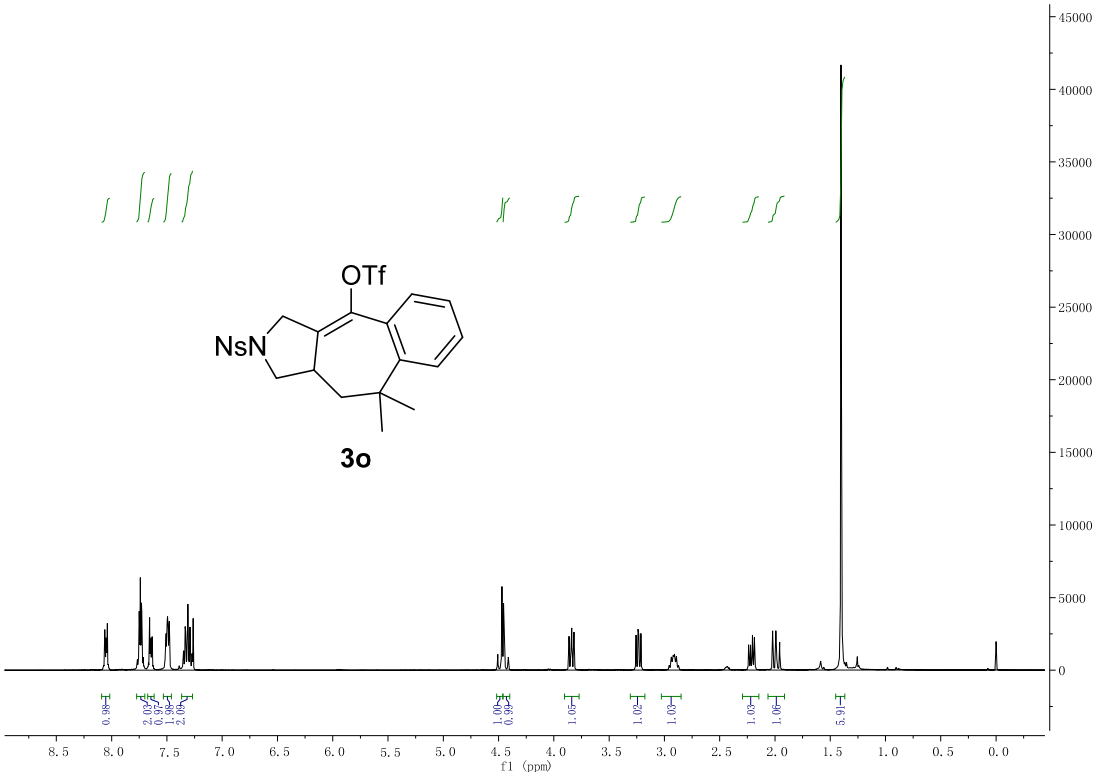
21.49
OTf
TsN
3n
f1 (ppm)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30000
25000
20000
15000
10000
5000
0
0.98
2.02
0.97
0.98
2.09
1.06
0.99
1.05
1.02
1.03
1.03
1.06
5.91
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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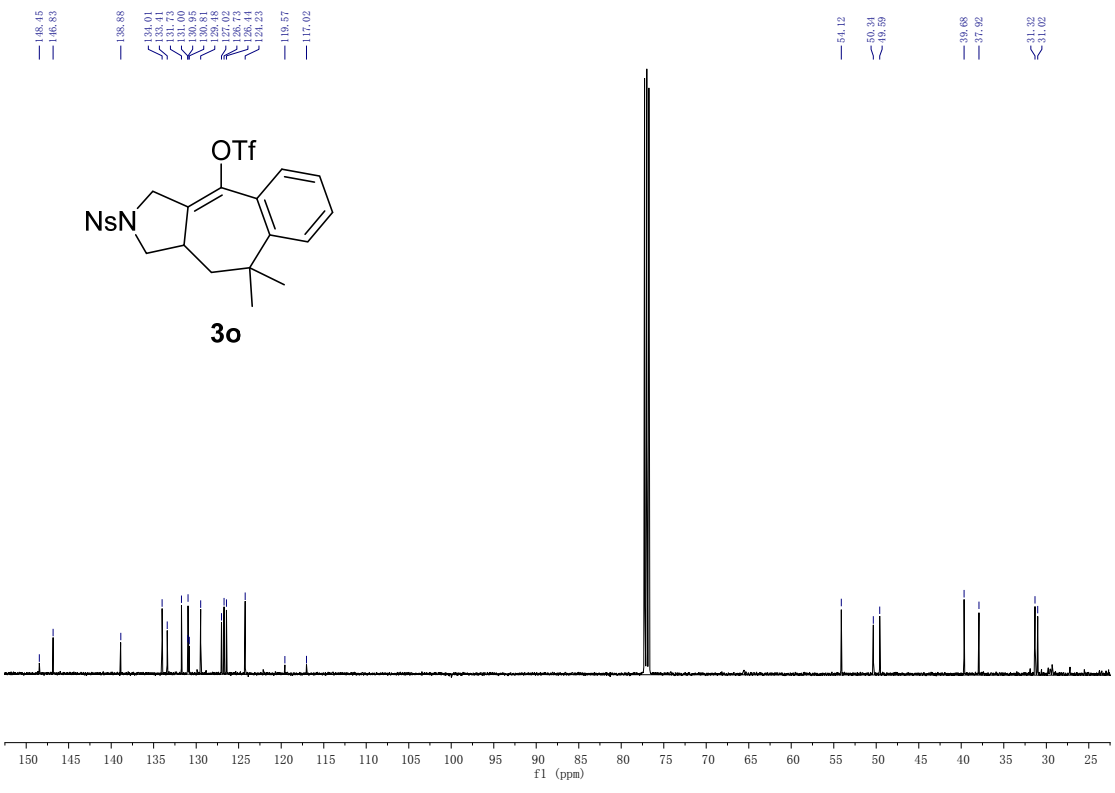
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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127.69
126.73
126.44
124.23
119.57
117.02
54.12
50.34
49.99
39.68
37.92
31.32
31.02
OTf
NsN
3o
150
145
140
135
130
125
120
115
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45
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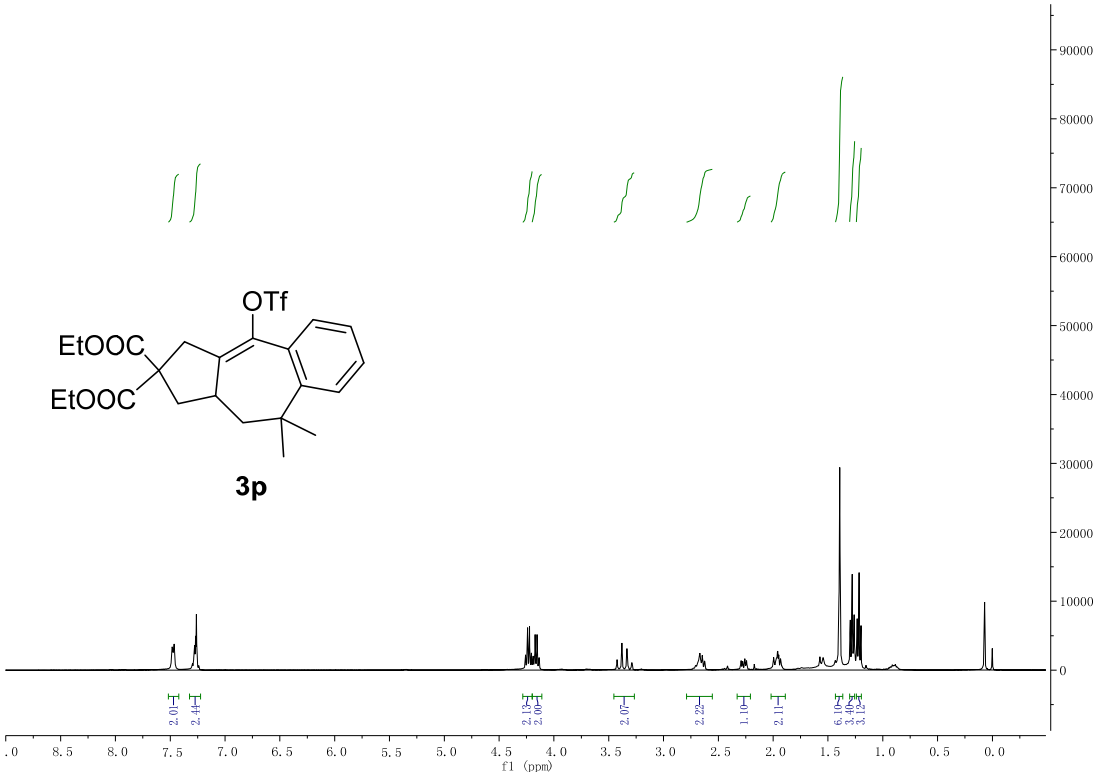
30
25
f1 (ppm)


OTf
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EtOOC
3p
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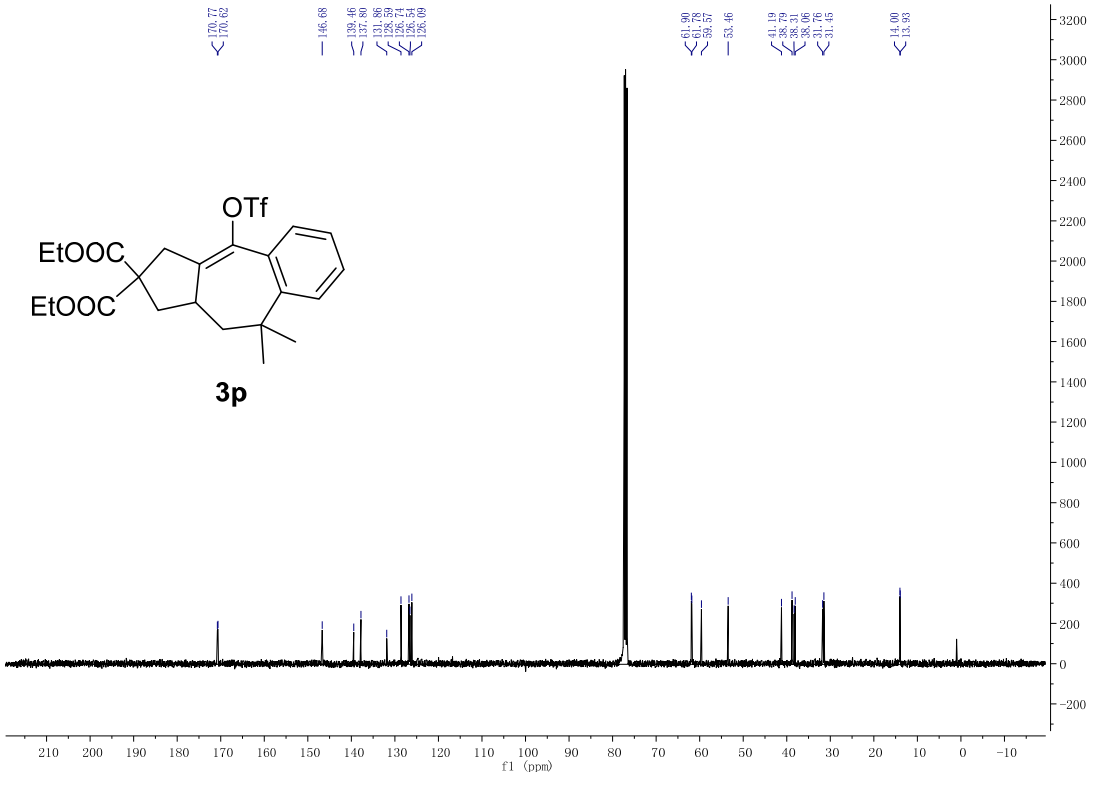
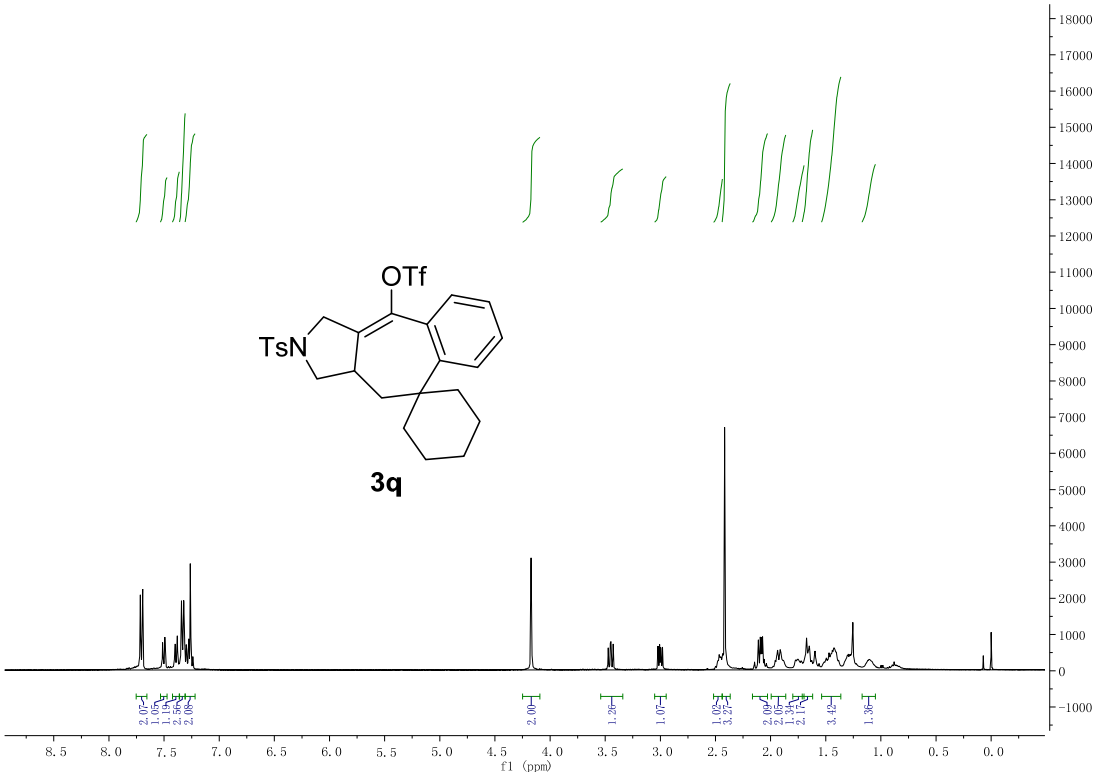
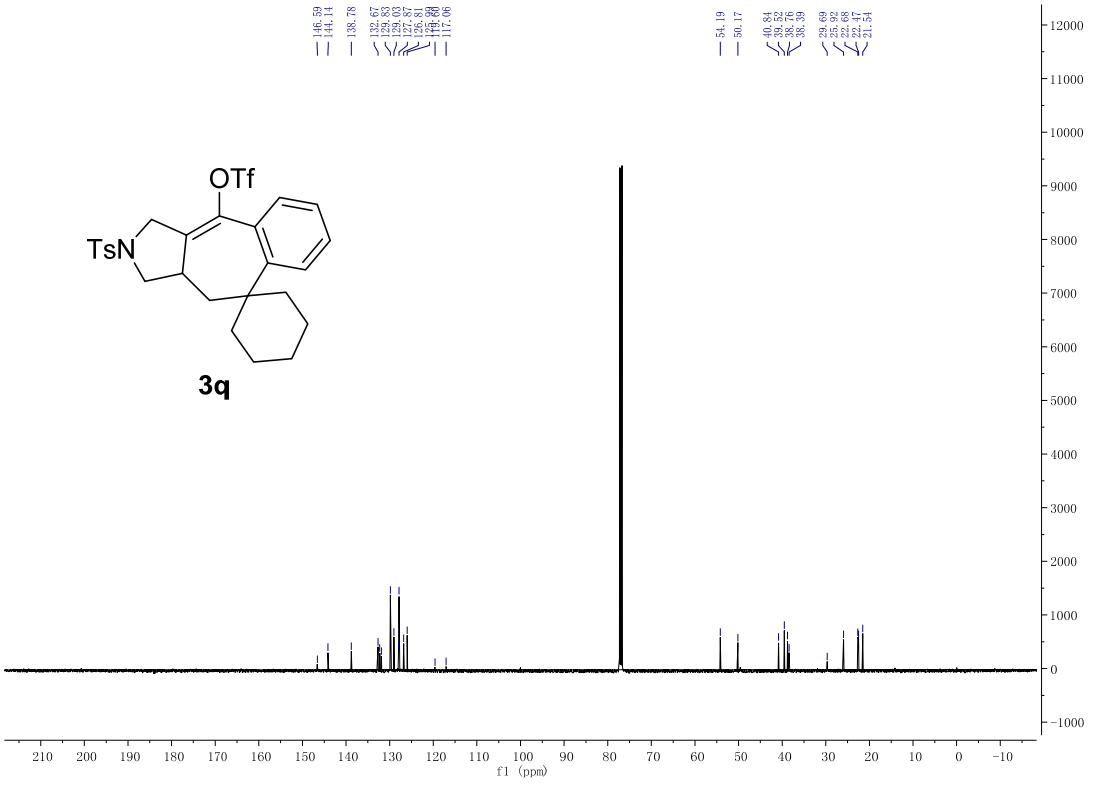
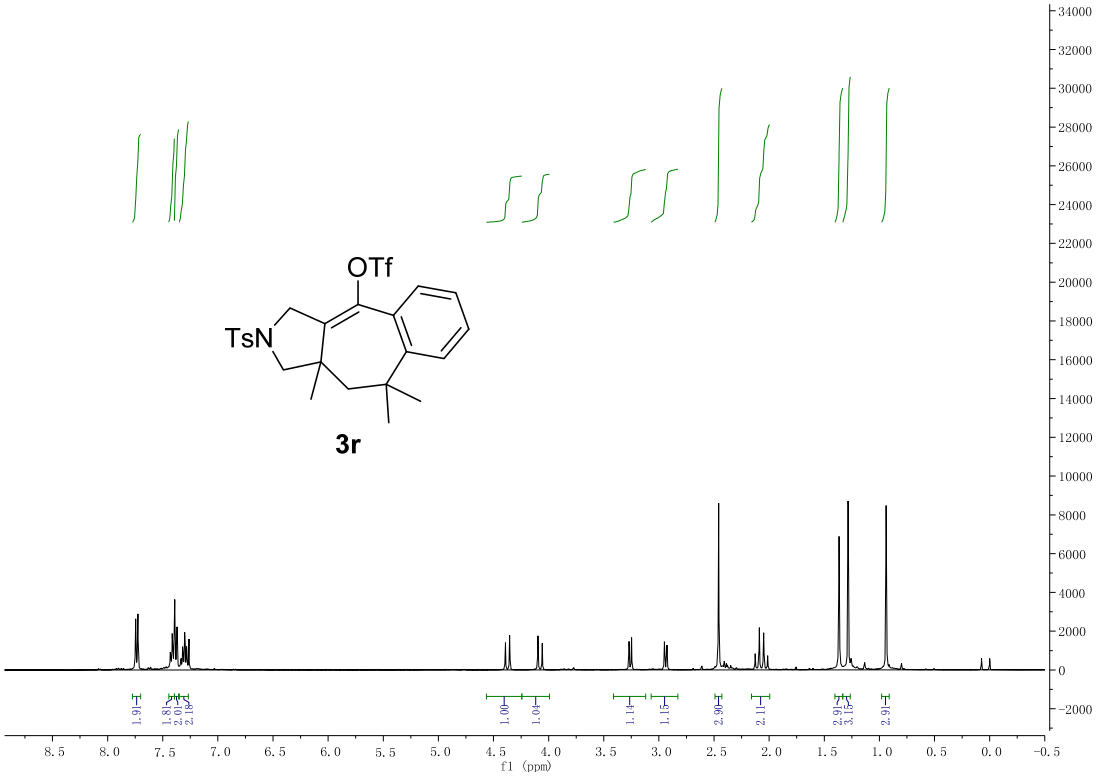
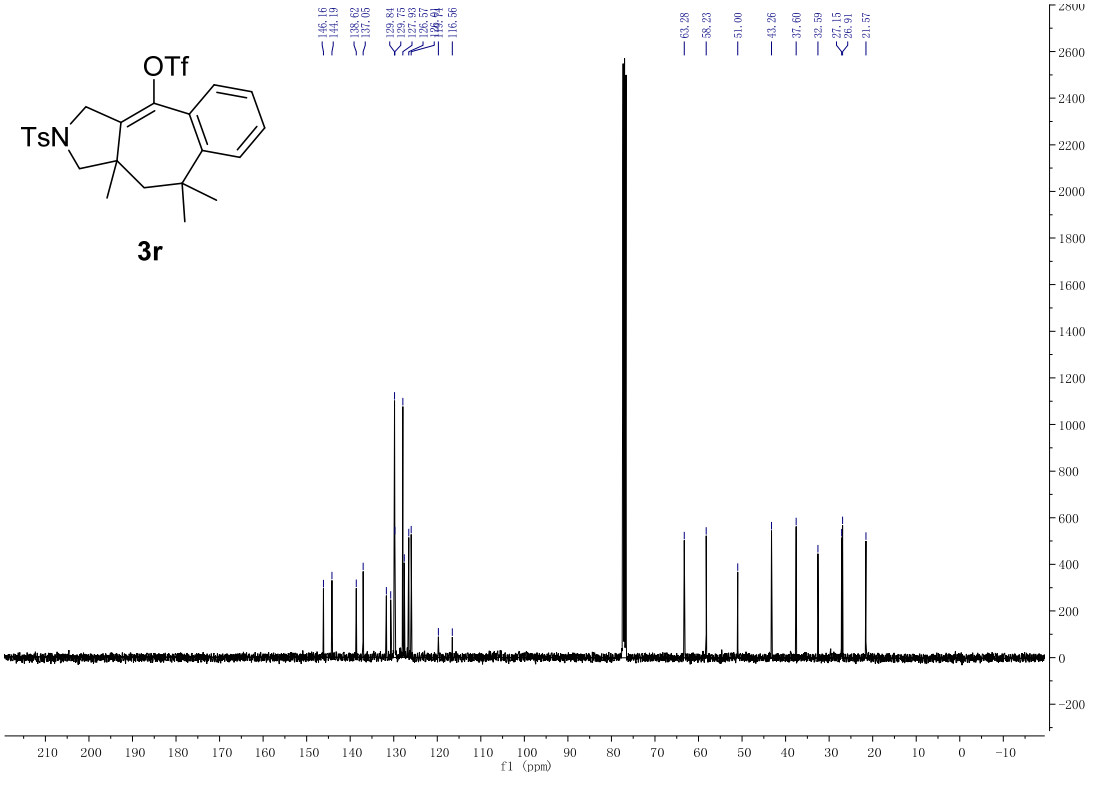

OTf
EtOOC
EtOOC
3p
f1 (ppm)


OTf
TsN
3q
f1 (ppm)


OTf
TsN
3q
f1 (ppm)


OTf
TsN
3r
f1 (ppm)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129.75
127.93
126.57
116.56
63.28
58.23
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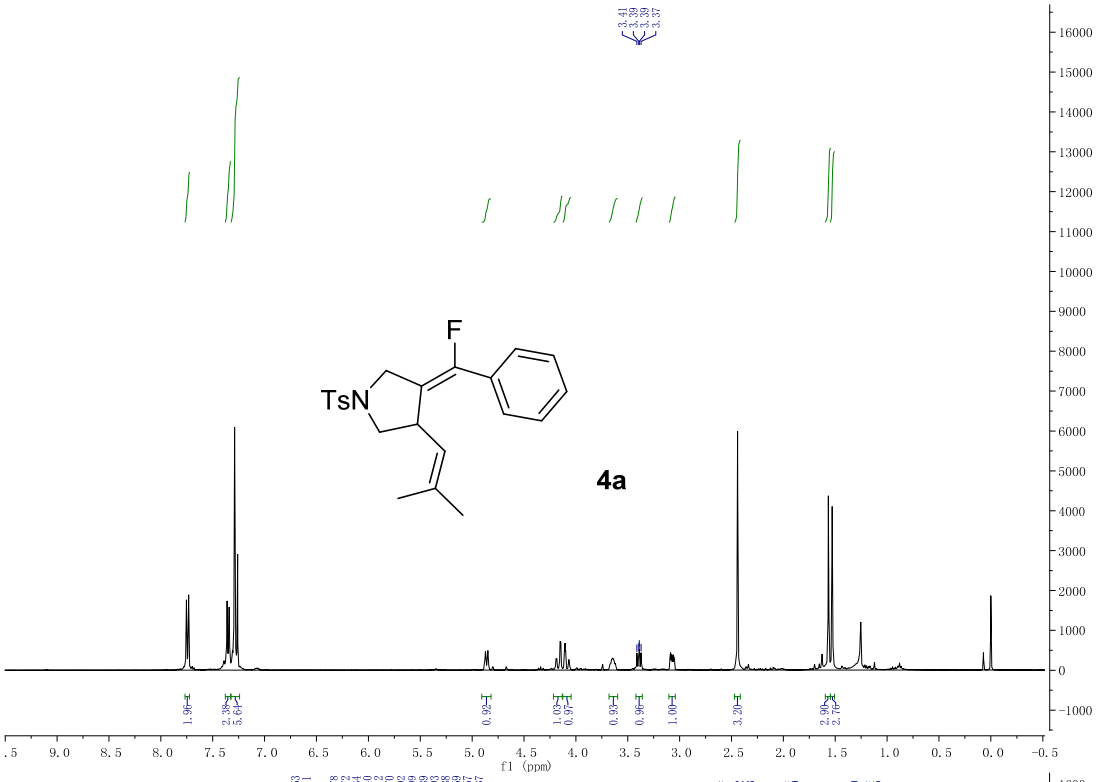
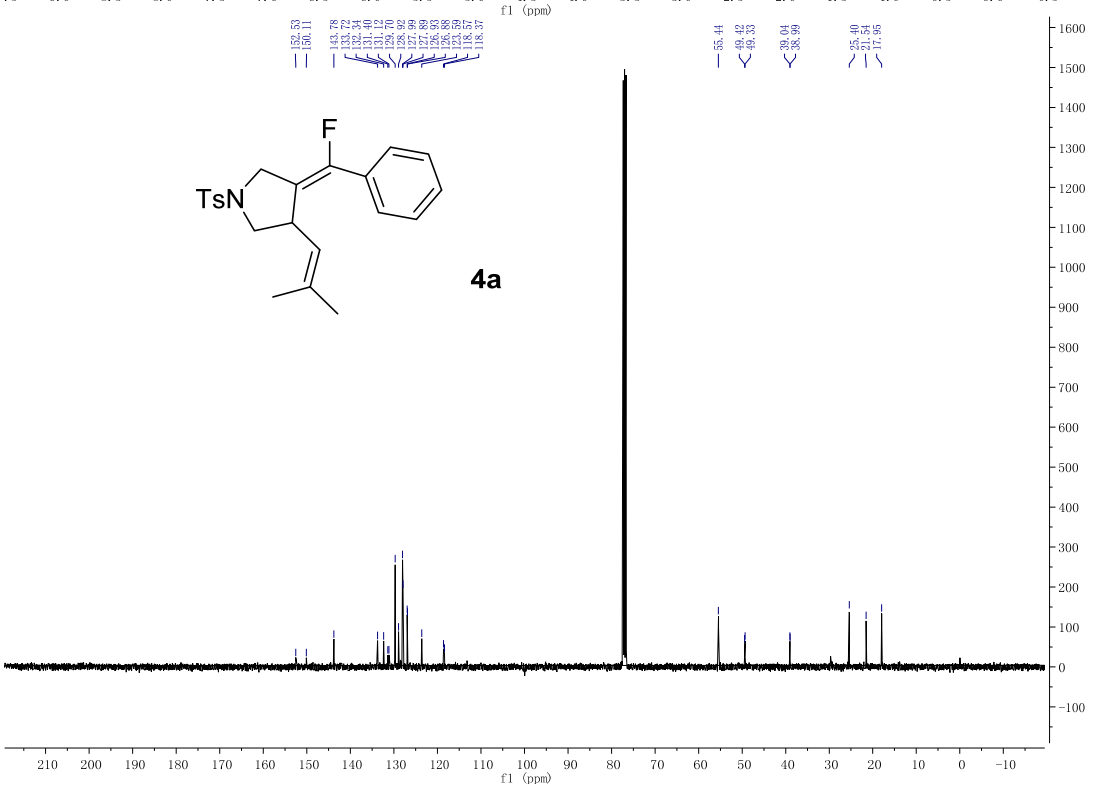
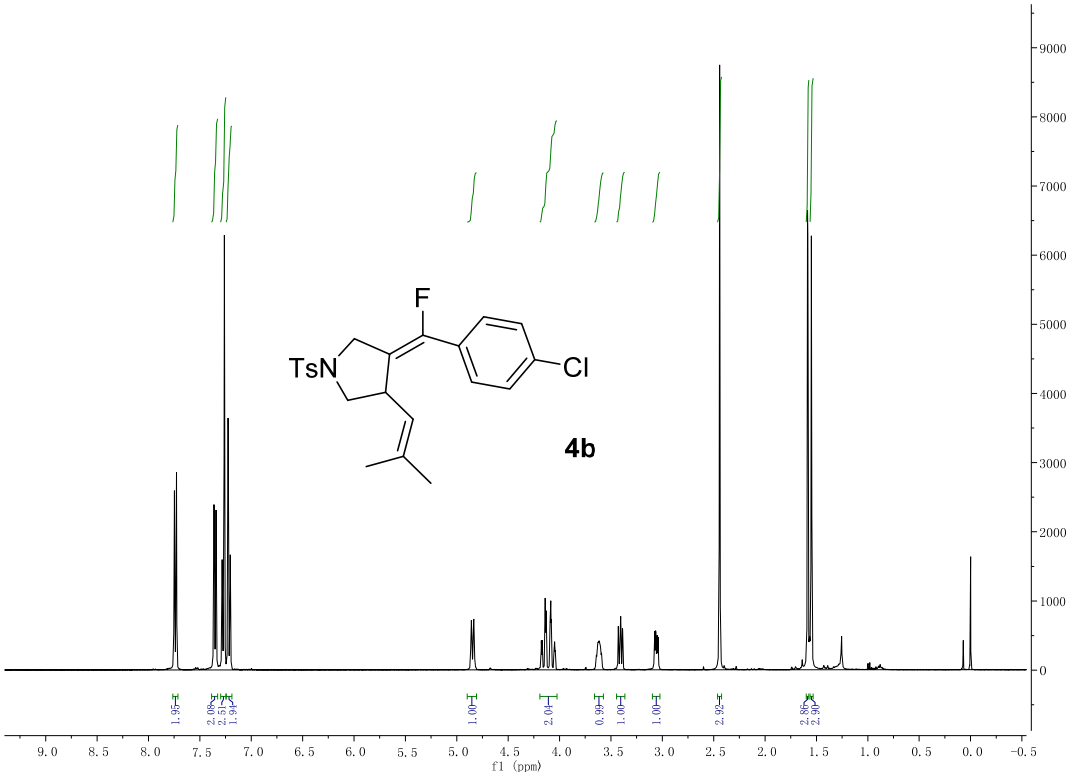
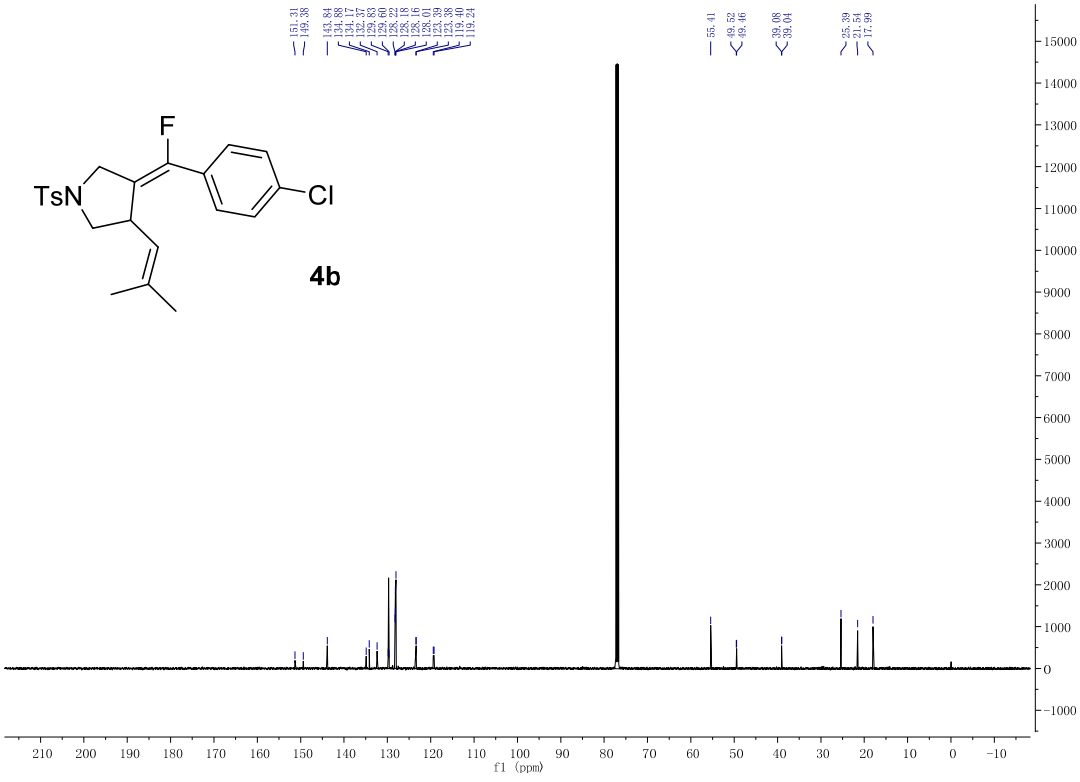
43.26
37.60
32.59
27.15
26.91
21.57
OTf
TsN
3r
f1 (ppm)


F
TsN
4a


F
TsN
4a


F
TsN
Cl
4b
f1 (ppm)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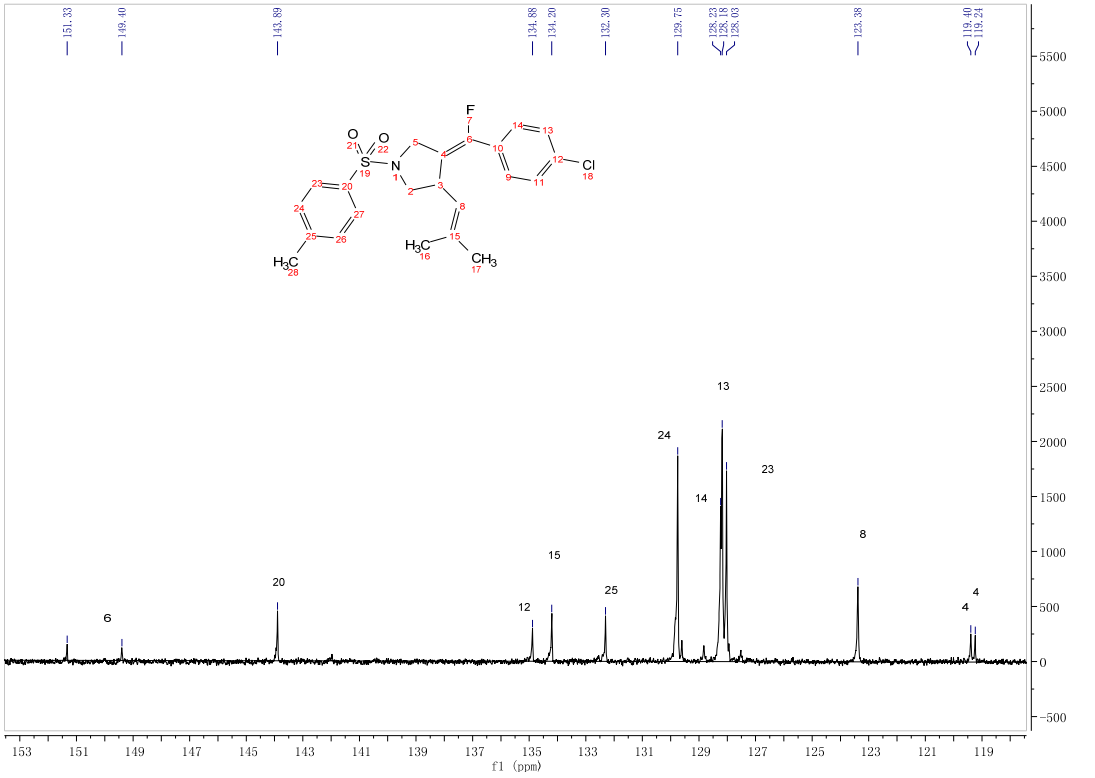
TsN
Cl
4b
f1 (ppm)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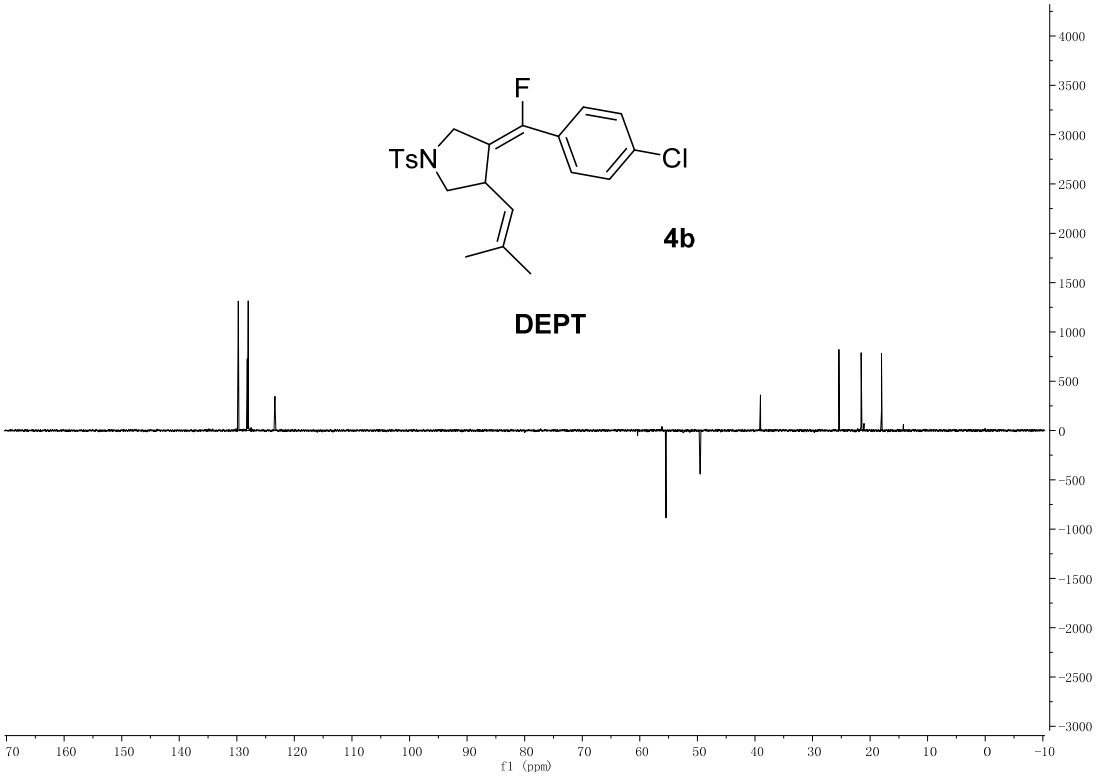
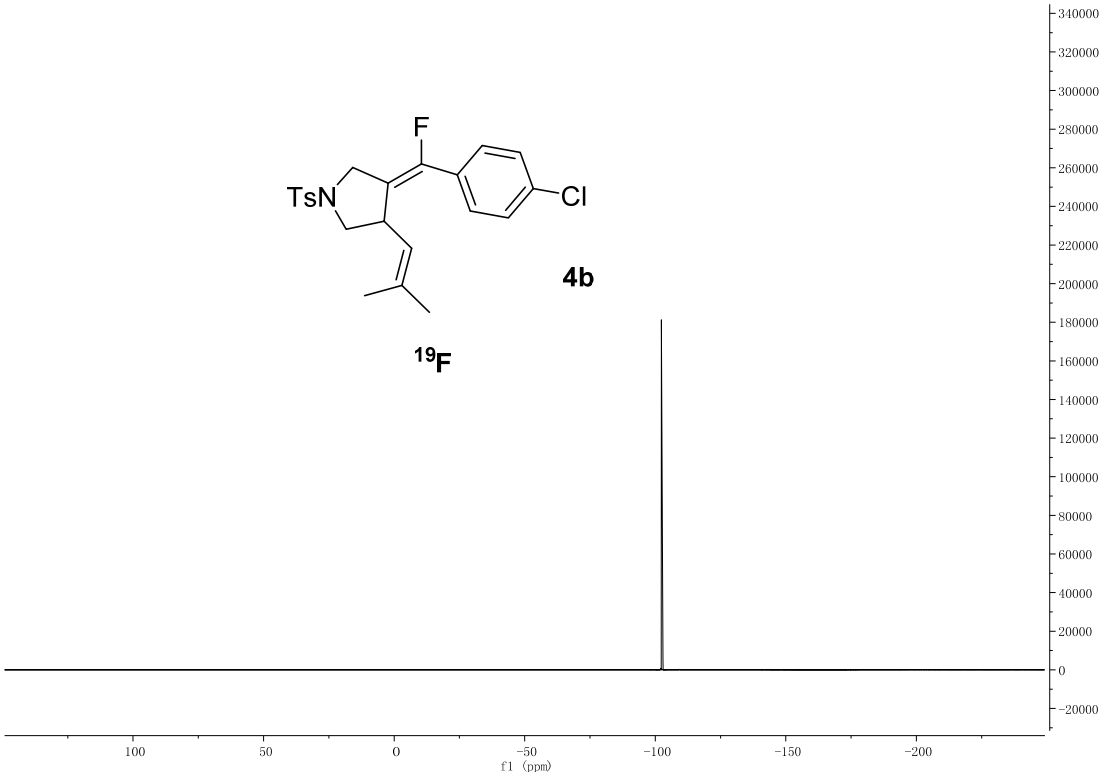
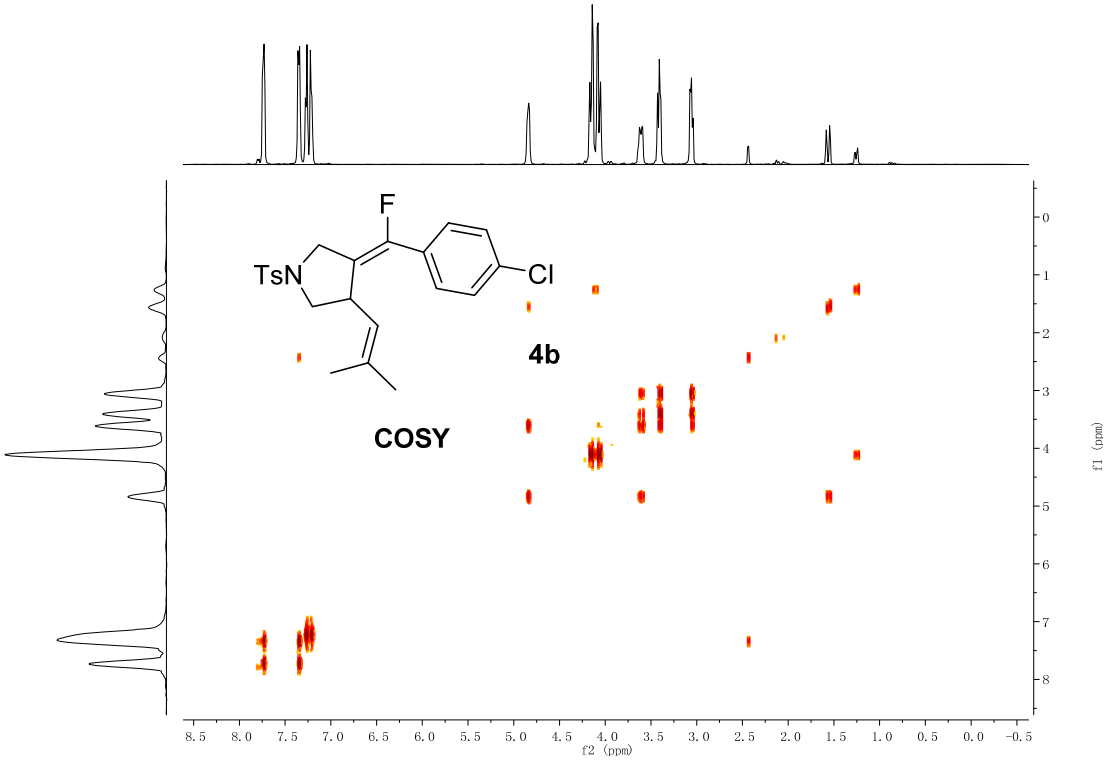
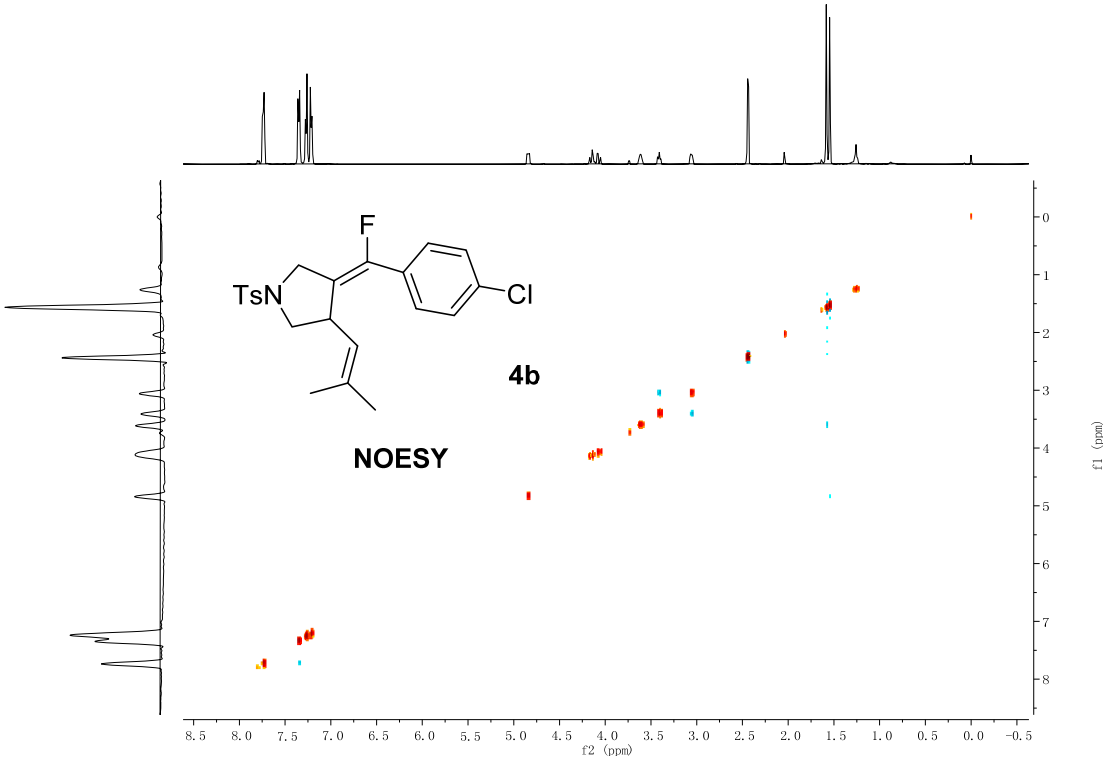
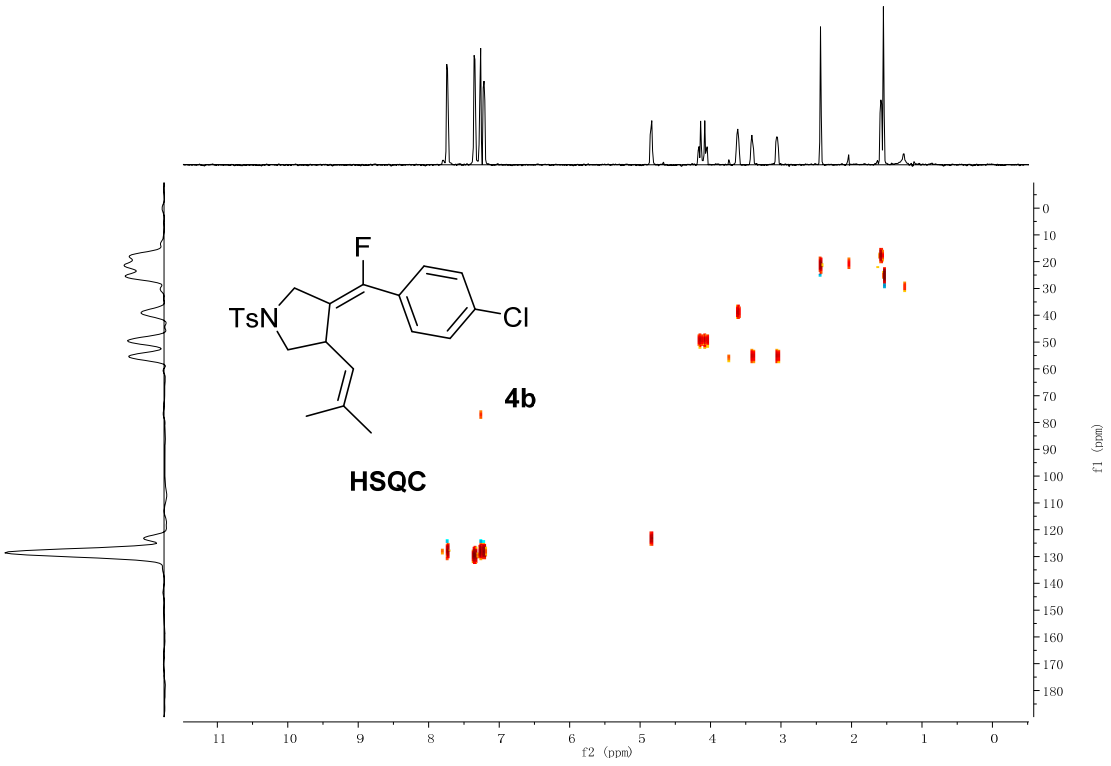
129.75
128.23
128.18
128.03
123.38
119.40
119.24
F
O
O
S
N
Cl
H3C
CH3
H3C
13
24
23
14
8
15
20
25
12
6
4
4
f1 (ppm)

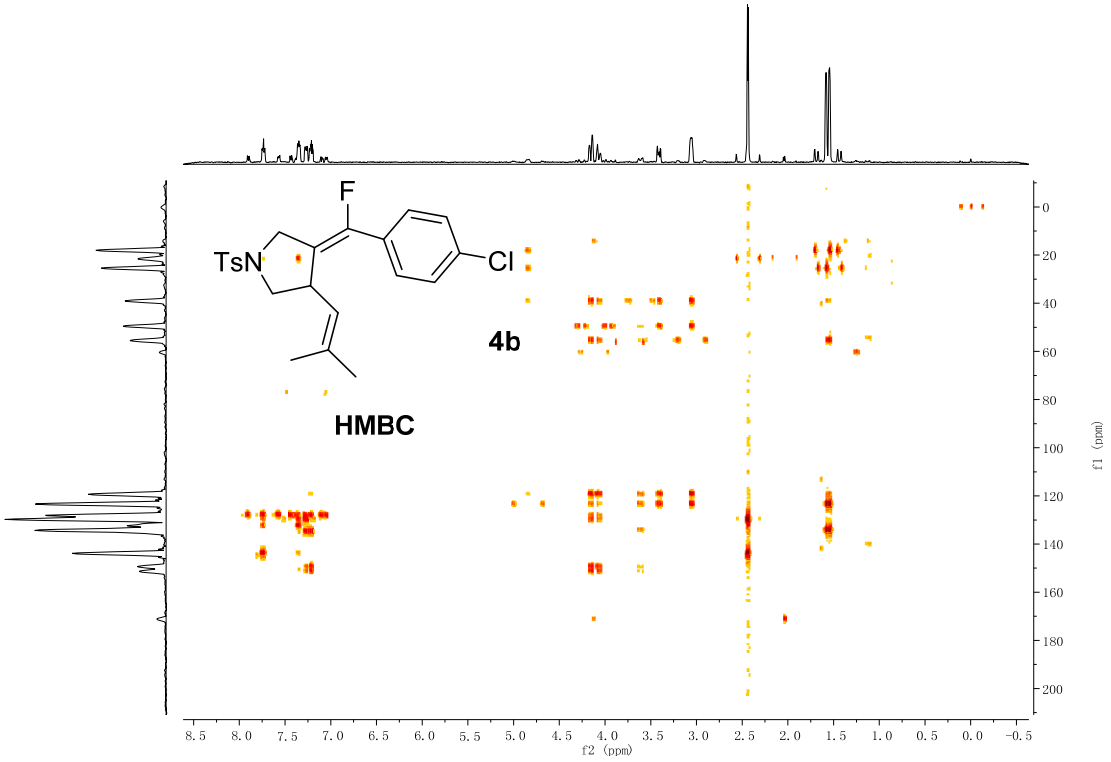

F
TsN
Cl
4b
DEPT
f1 (ppm)

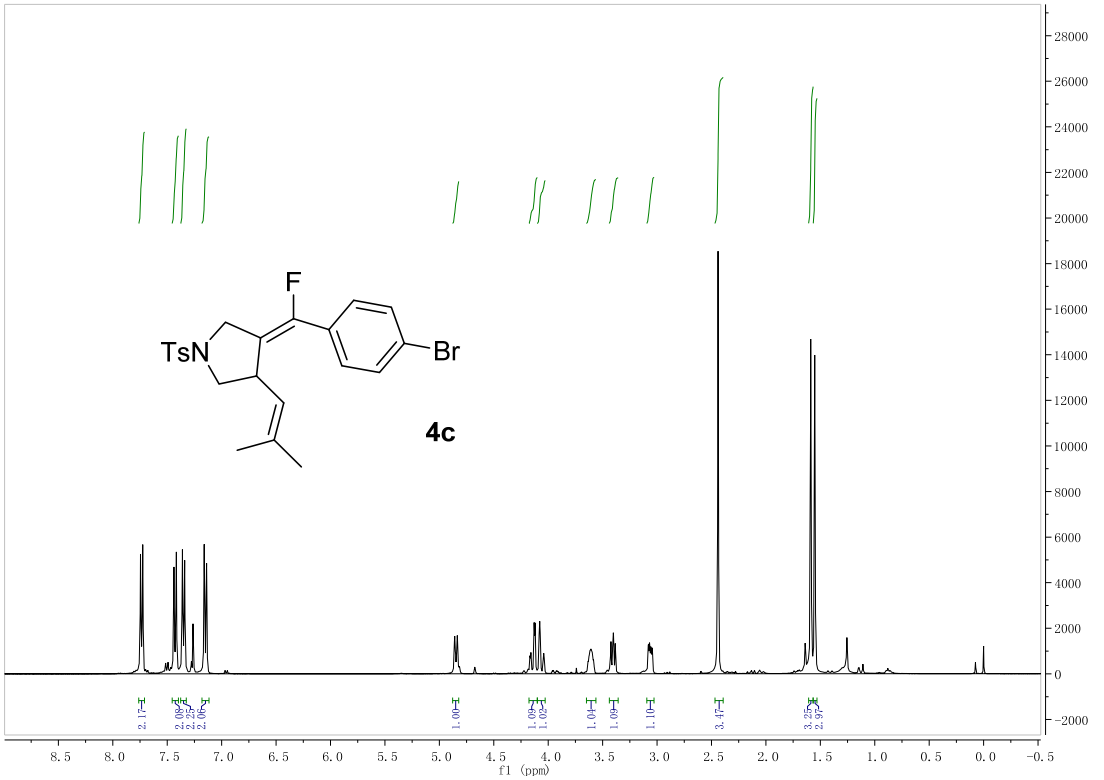

F
TsN
Cl
4b
19F
f1 (ppm)

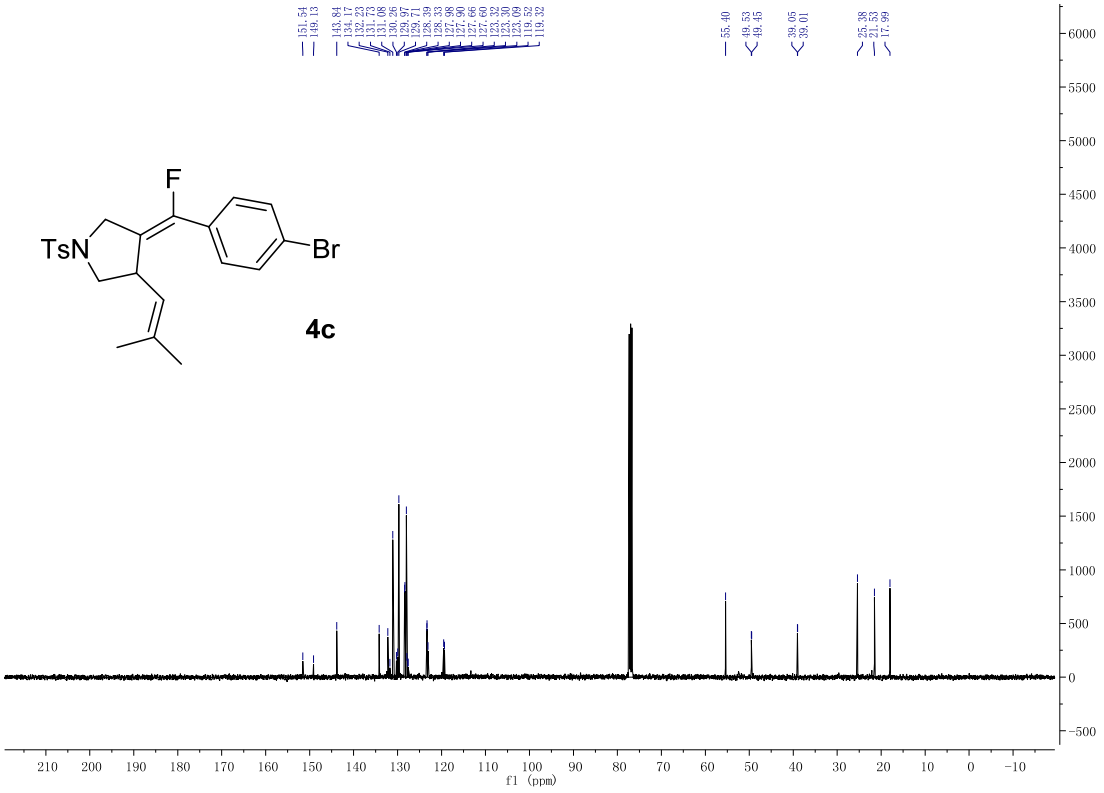

F
TsN
Cl
4b
COSY
f2 (ppm)
f1 (ppm)

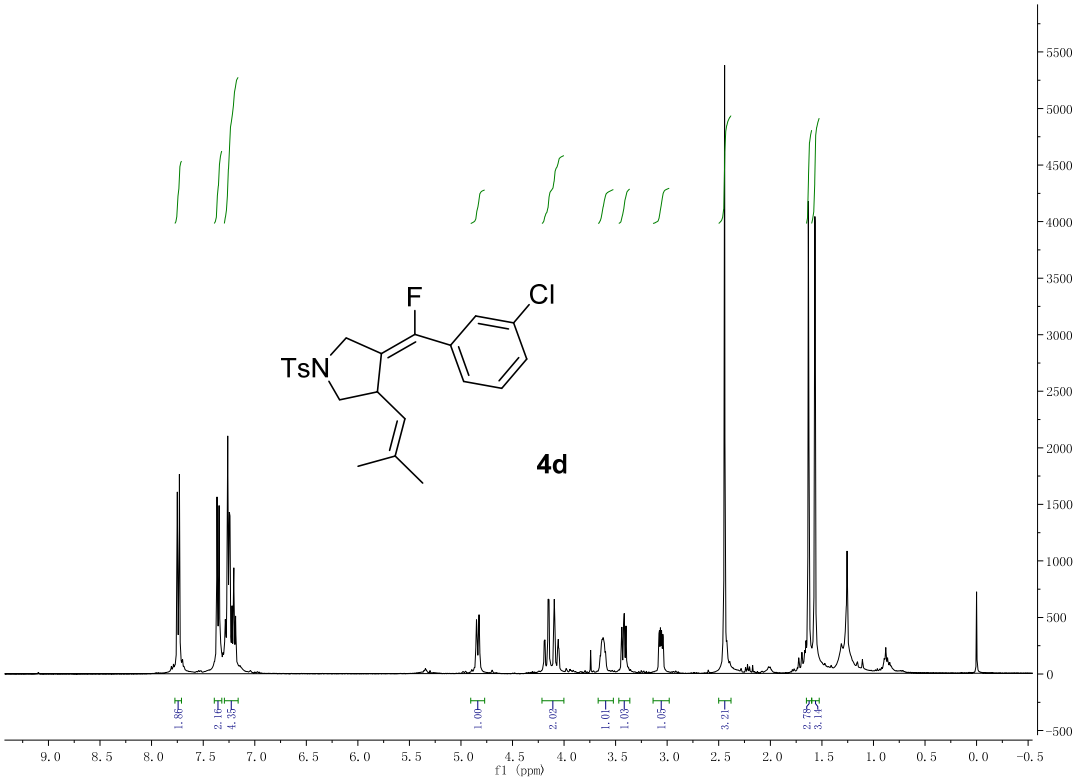

F
TsN
Cl
4b
NOESY
f2 (ppm)
f1 (ppm)

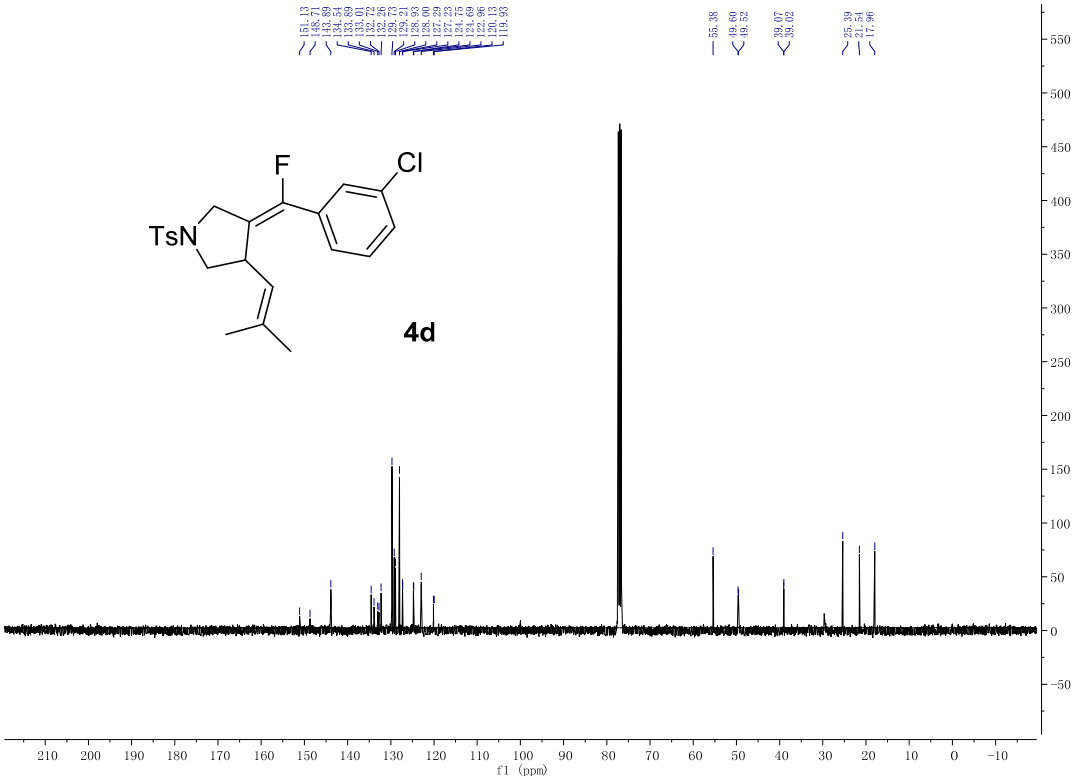

F
TsN
Cl
4b
HSQC
f2 (ppm)
f1 (ppm)


F
TsN
Cl
4b
HMBC
f1 (ppm)
f2 (ppm)


F
TsN
Br
4c
f1 (ppm)


F
TsN
Br
4c
f1 (ppm)


F
Cl
TsN
4d
1.88
2.10
4.35
1.00
2.02
1.01
1.03
1.05
3.21
2.78
3.14
f1 (ppm)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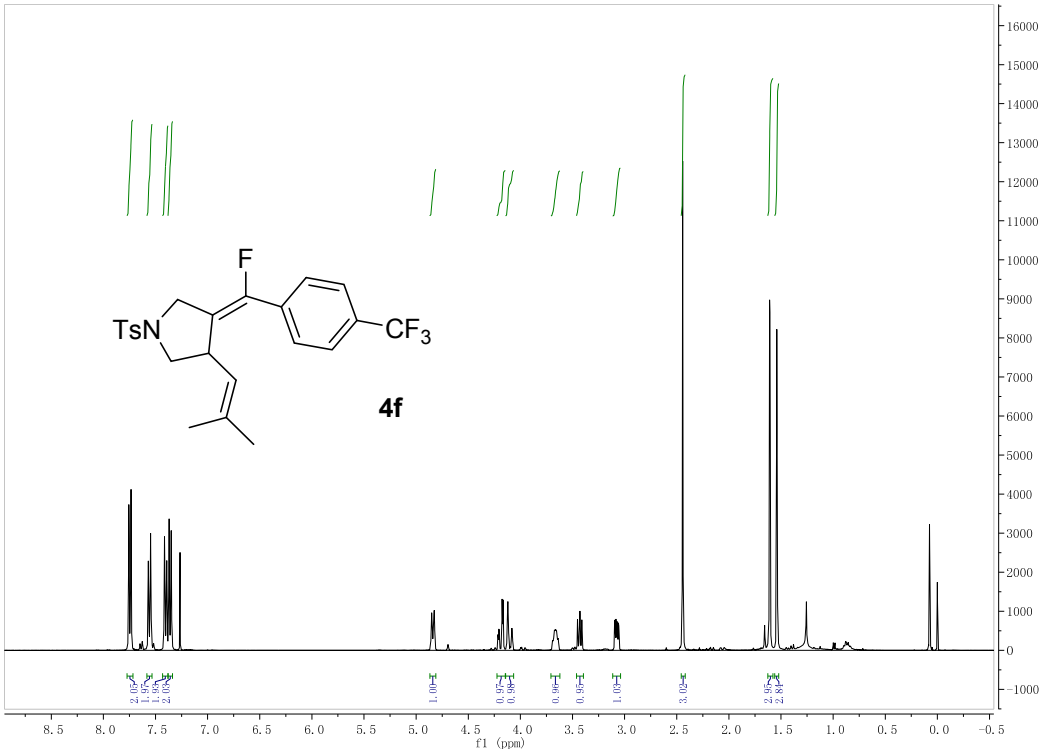
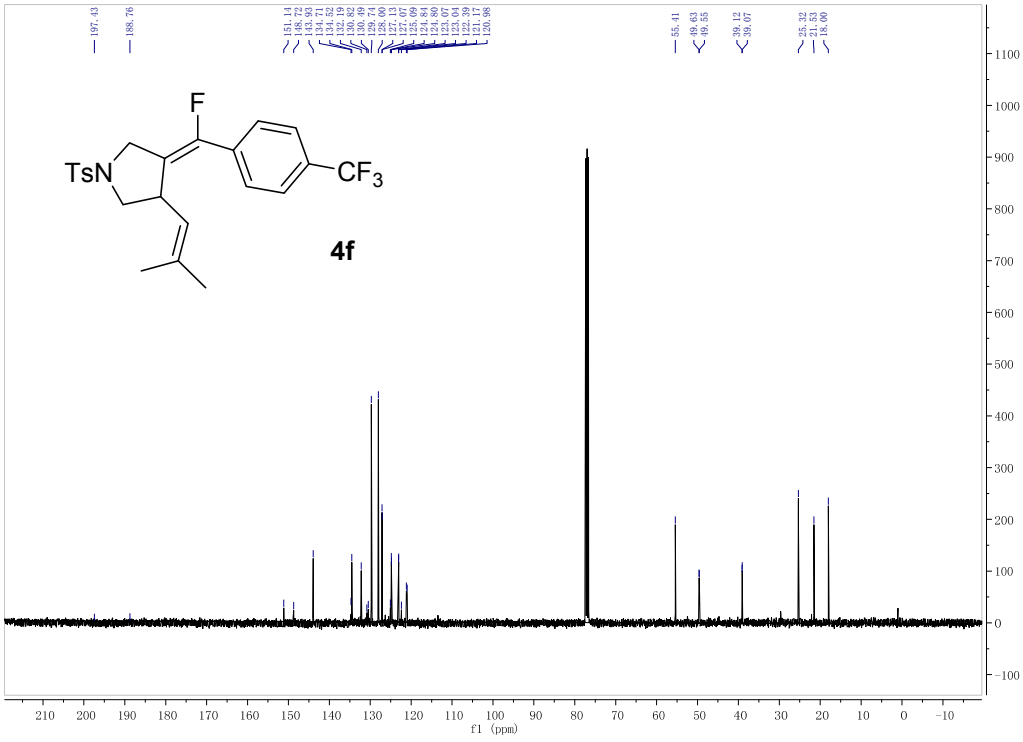
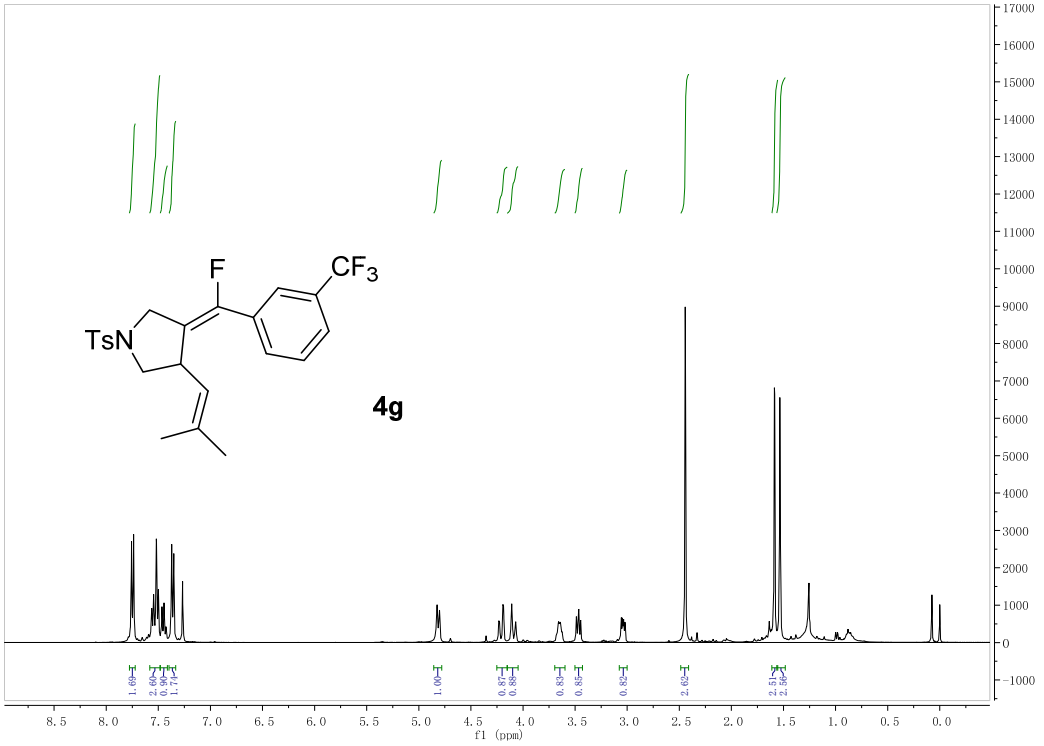
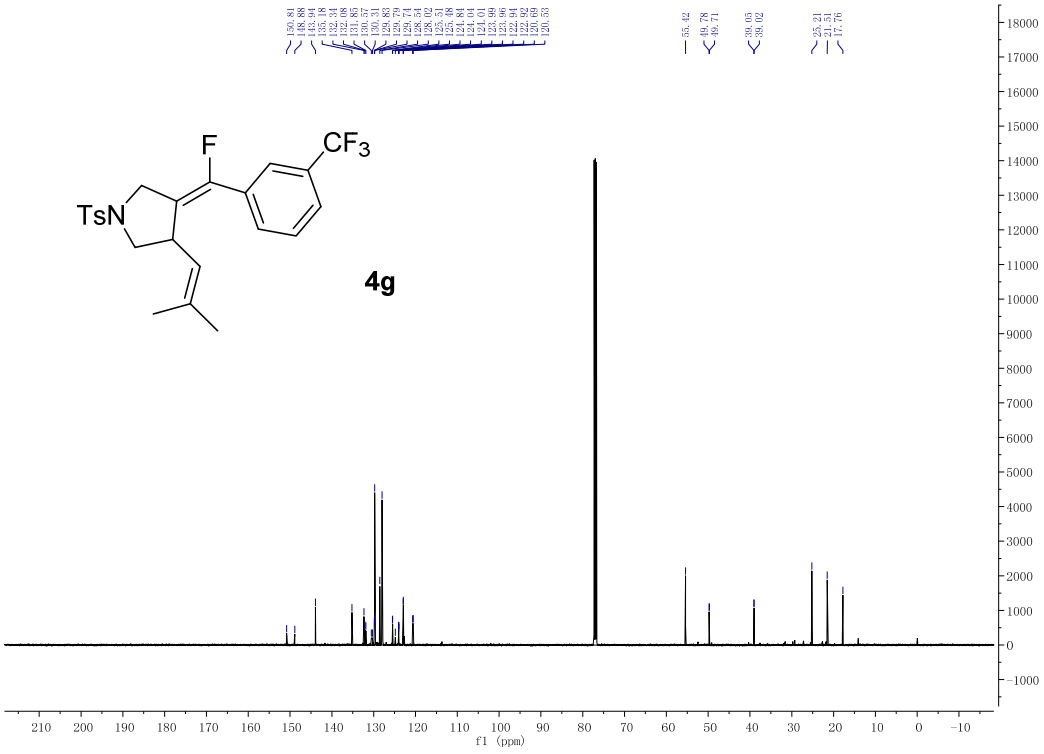
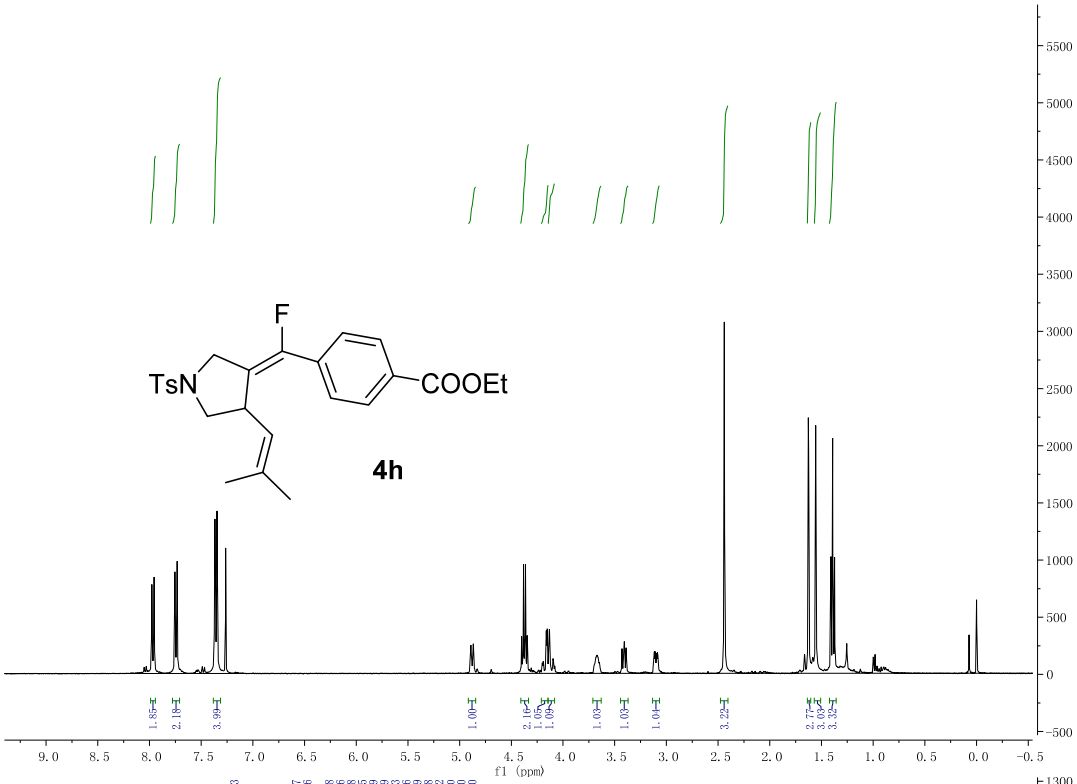
143.89
141.54
133.89
133.01
132.72
132.26
131.73
129.21
128.93
128.00
127.29
127.23
124.75
124.69
122.96
120.13
118.93
55.38
49.69
49.52
39.07
39.02
25.39
21.54
17.96
F
Cl
TsN
4d
f1 (ppm)

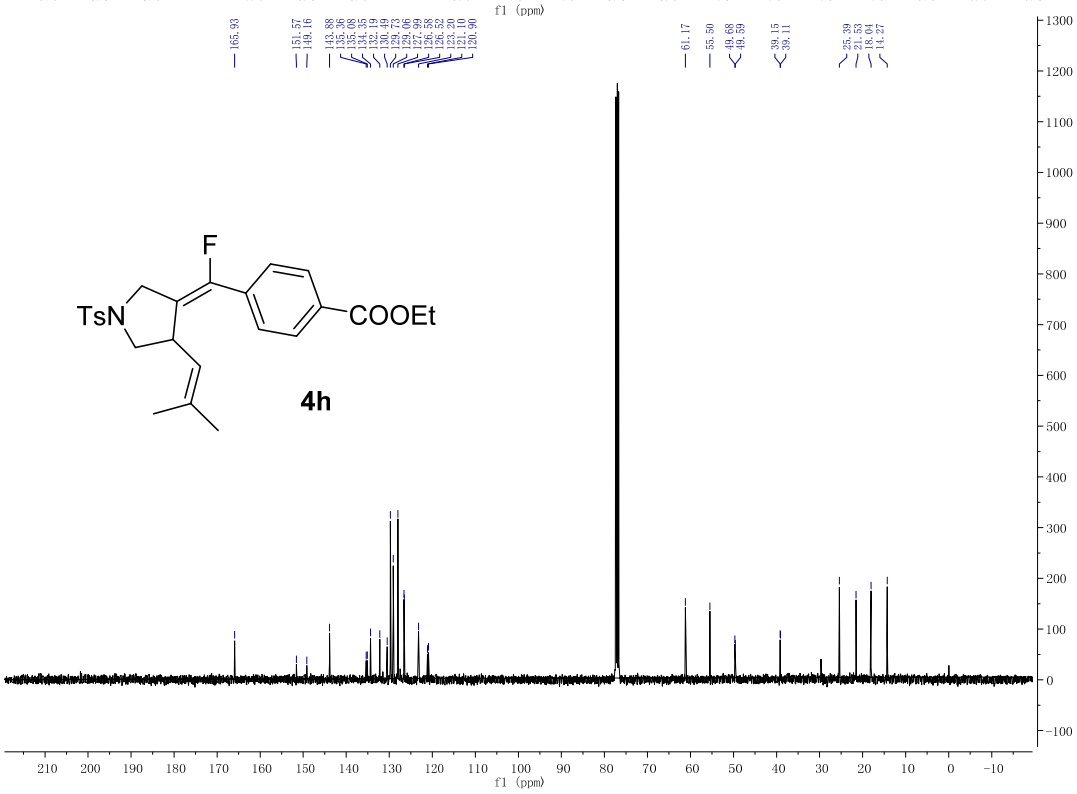

F
TsN
CF3
4f
f1 (ppm)


F
TsN
CF3
4f
f1 (ppm)


F
CF3
TsN
4g
f1 (ppm)


F
CF3
TsN
4g
f1 (ppm)


F
TsN
COOEt
4h
1.85
2.18
3.99
1.00
2.10
1.05
1.09
1.03
1.03
1.04
3.22
2.77
3.03
3.32
f1 (ppm)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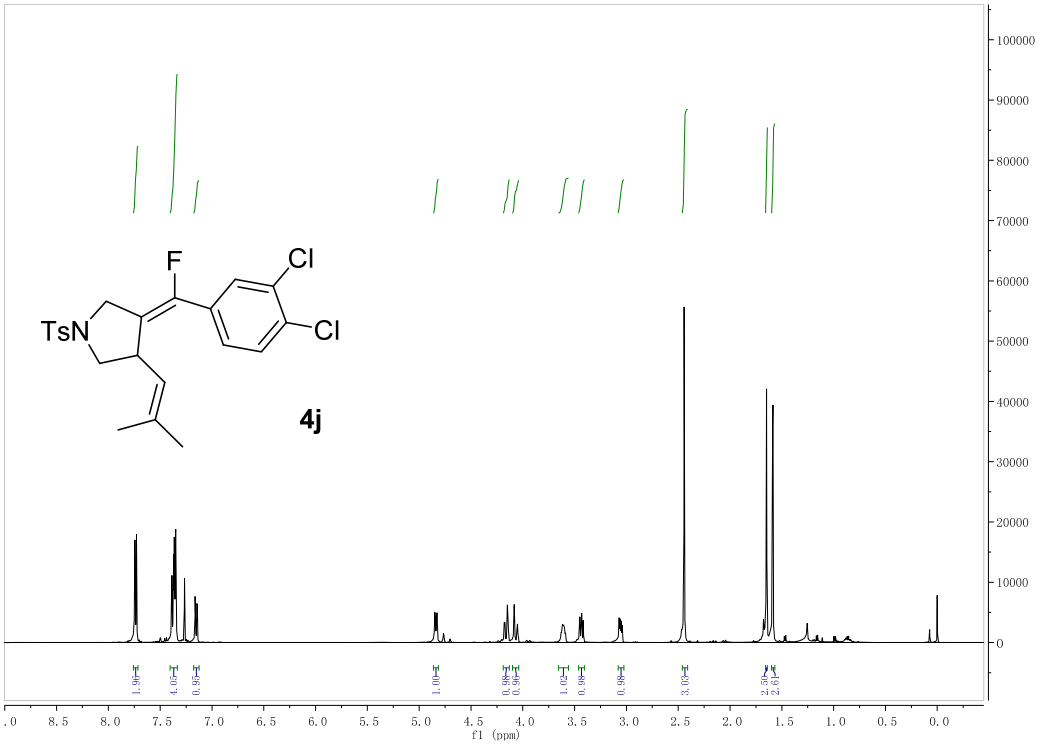
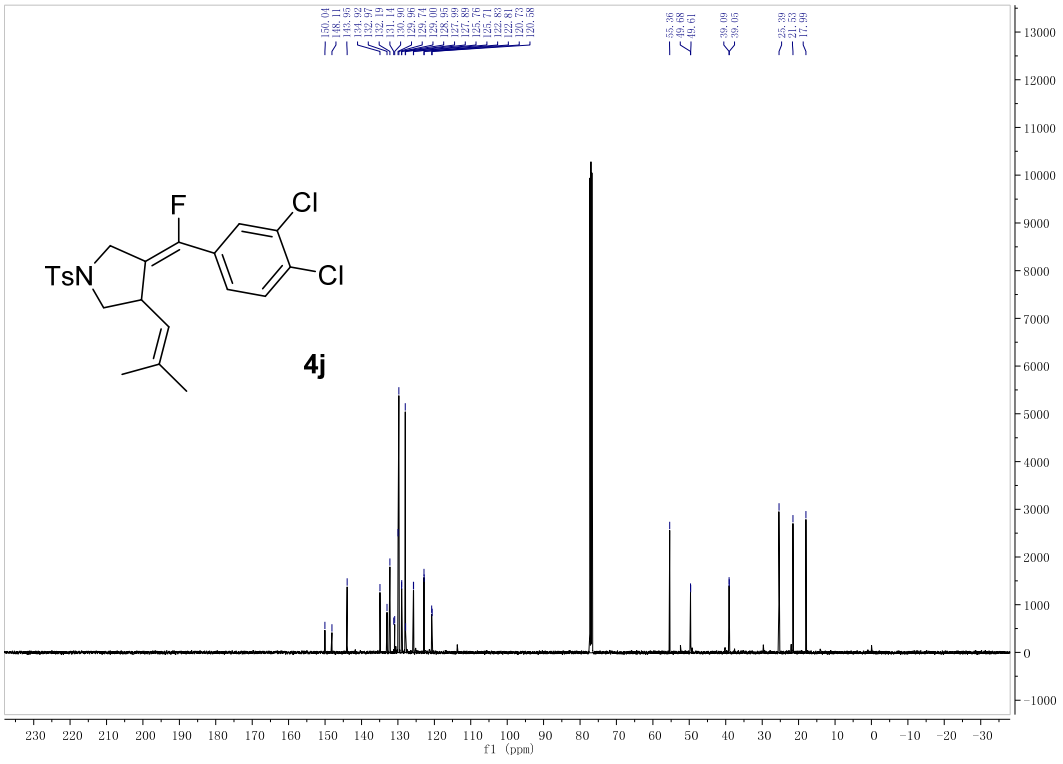
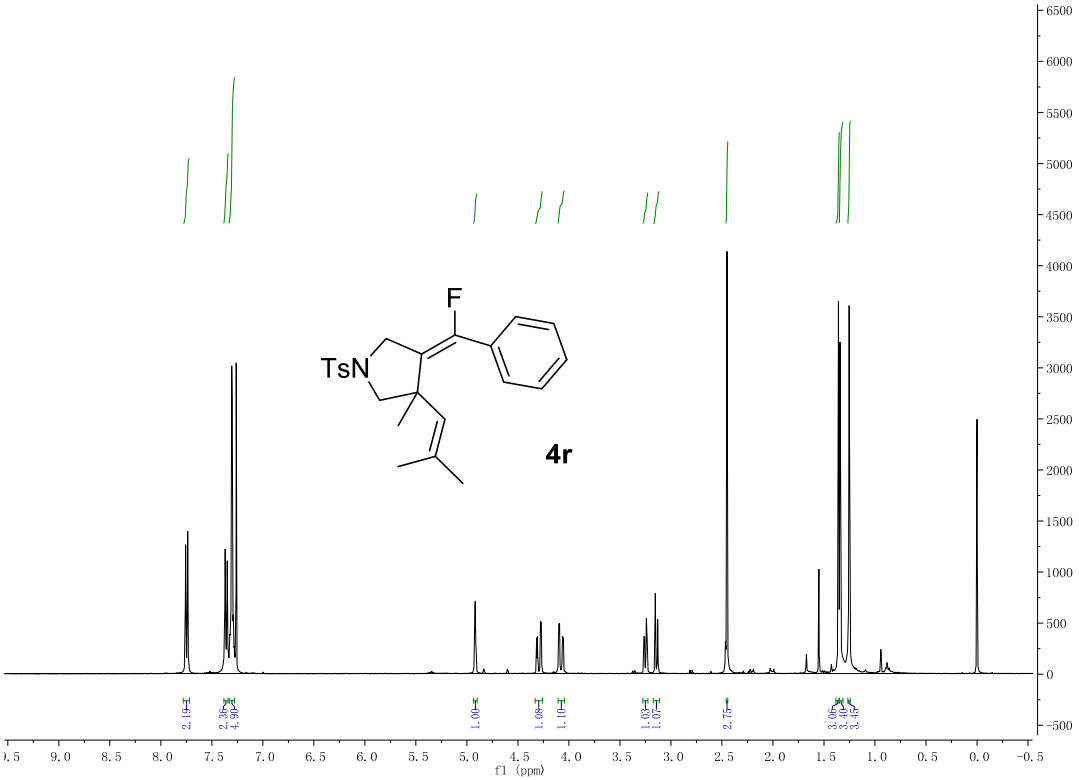
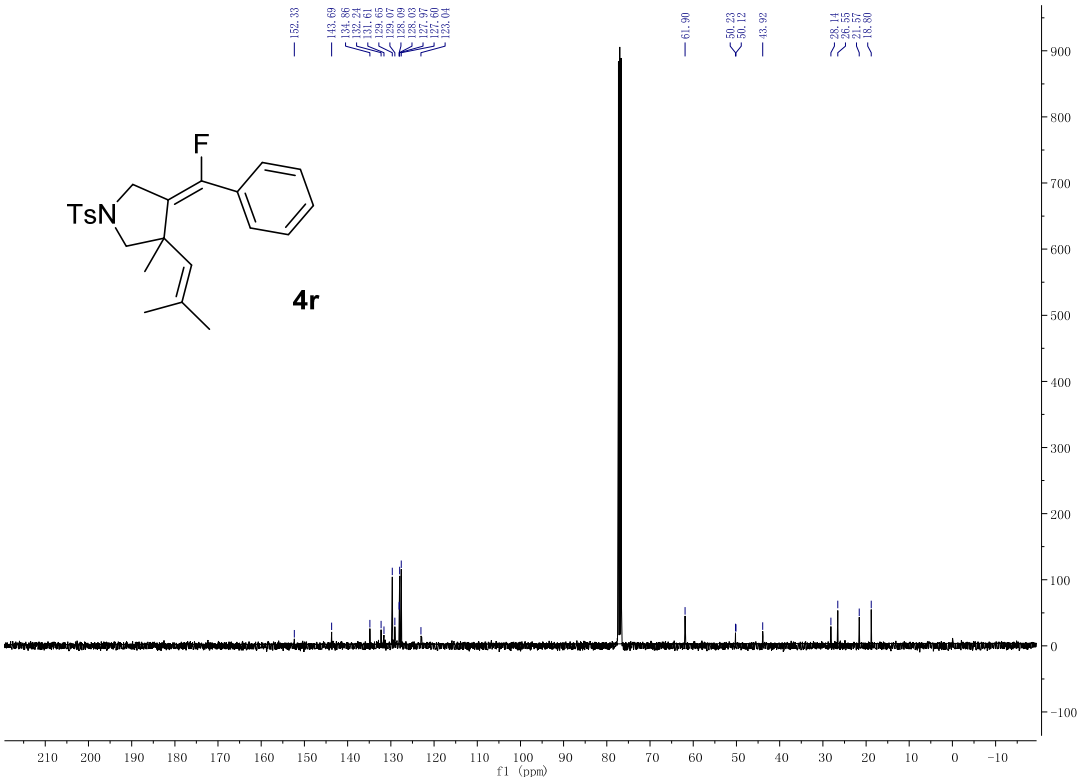
135.08
134.35
132.19
130.49
129.73
129.06
127.99
126.58
126.52
123.10
122.11
120.90
61.17
55.50
49.68
49.59
39.15
39.11
25.39
21.83
18.84
14.27
F
TsN
COOEt
4h
f1 (ppm)


F
Cl
TsN
Cl
4j
f1 (ppm)


F
Cl
TsN
Cl
4j
f1 (ppm)


F
TsN
4r
f1 (ppm)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132.24
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129.55
129.07
128.09
128.03
127.97
127.60
123.04
61.90
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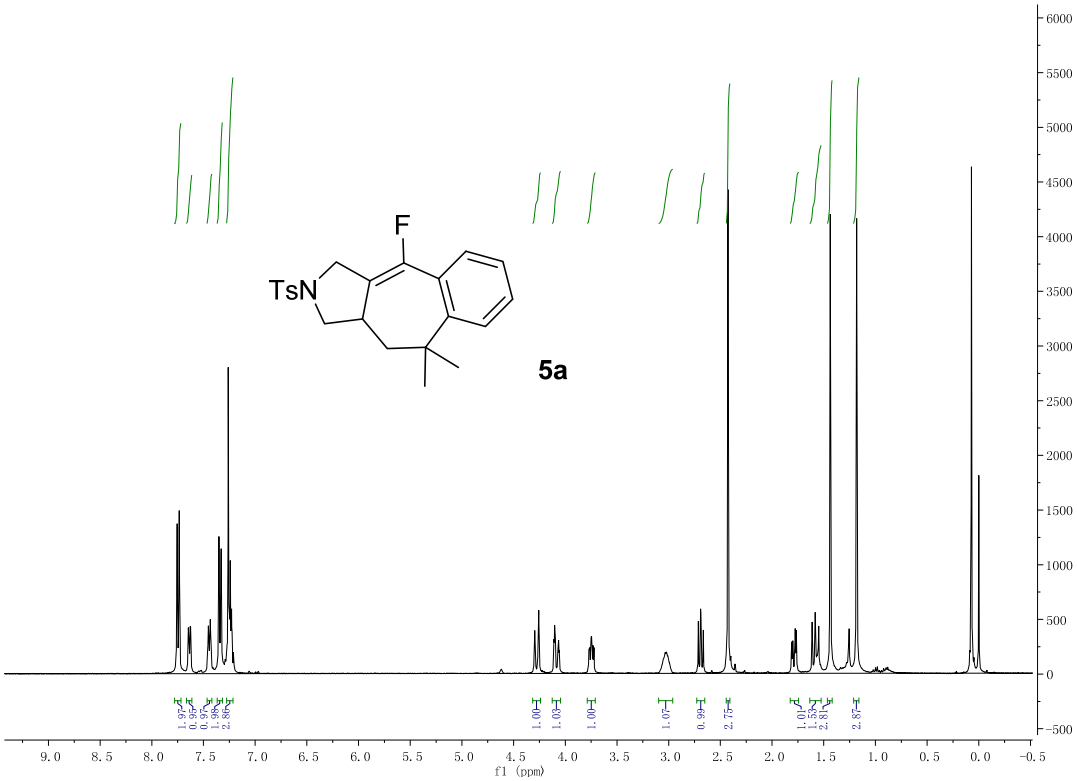
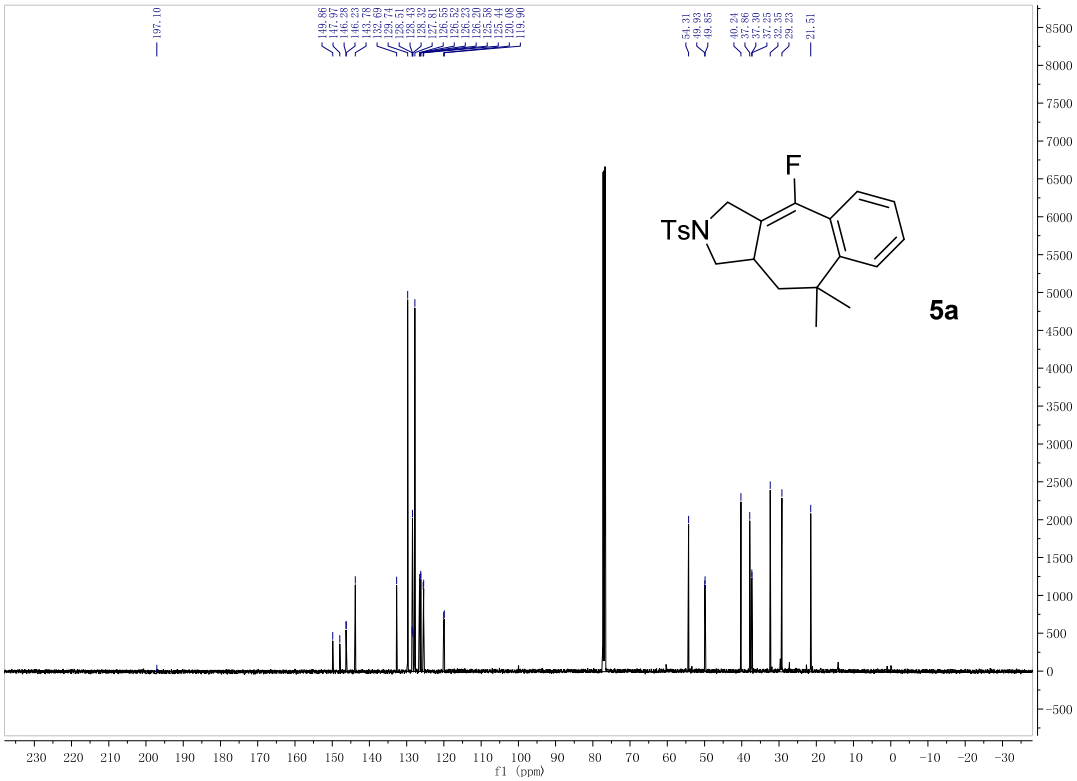
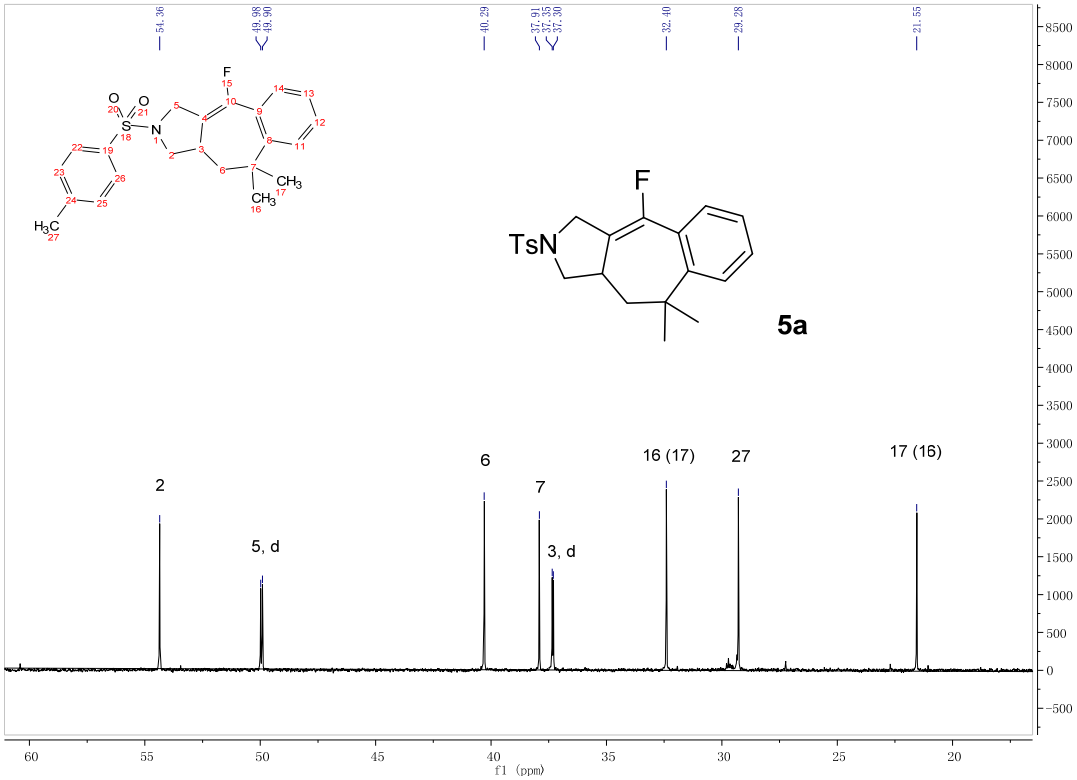
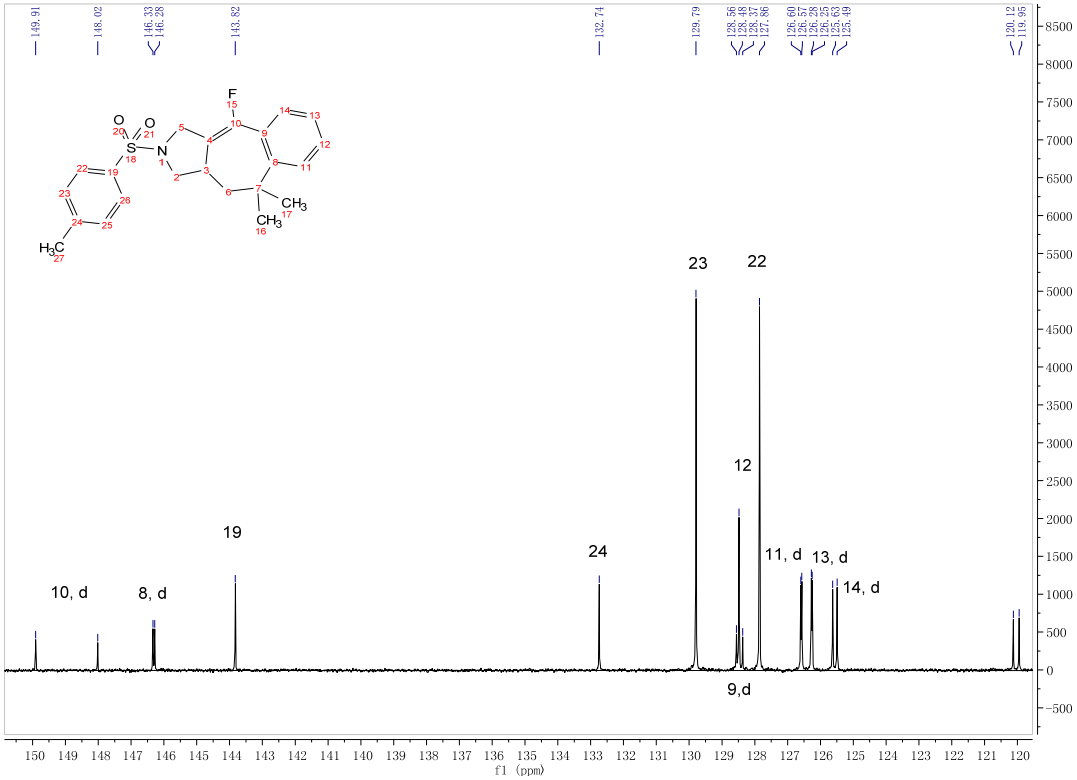
50.12
43.92
28.14
26.55
21.57
18.80
F
TsN
4r
f1 (ppm)


F
TsN
5a
f1 (ppm)


F
TsN
5a
f1 (ppm)


54.36
49.98
49.90
40.29
37.91
37.55
37.30
32.40
29.28
21.55
F
TsN
5a
2
5, d
6
7
3, d
16 (17)
27
17 (16)
f1 (ppm)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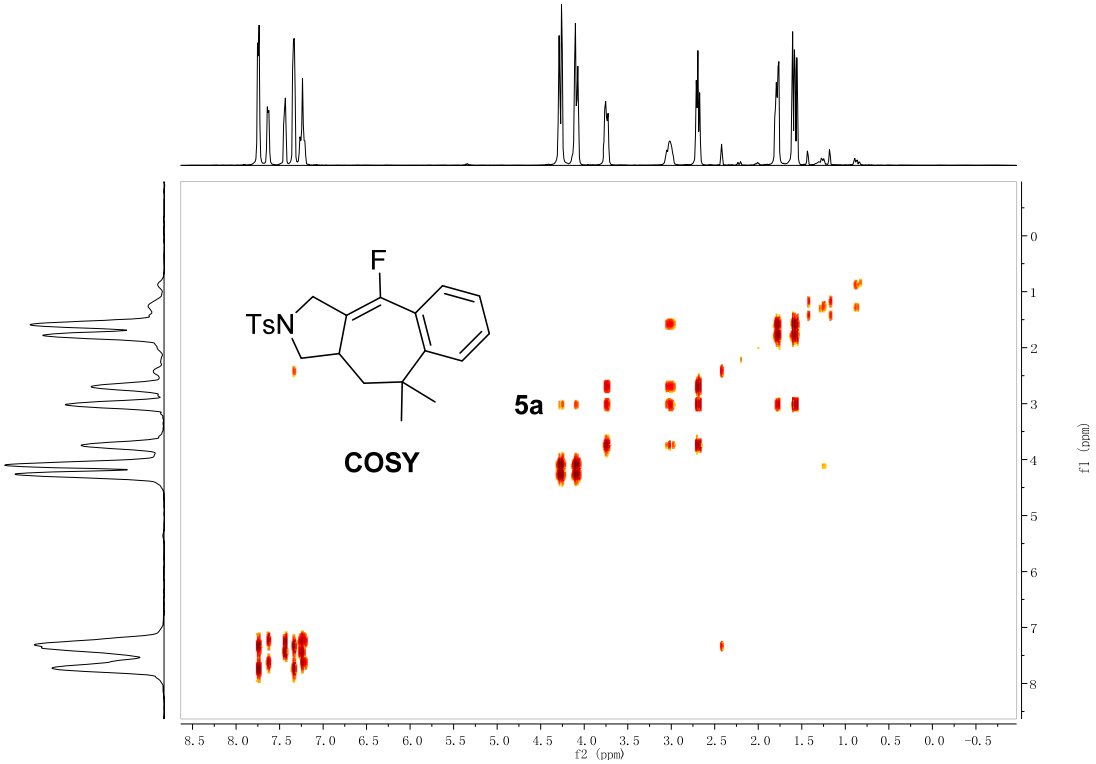
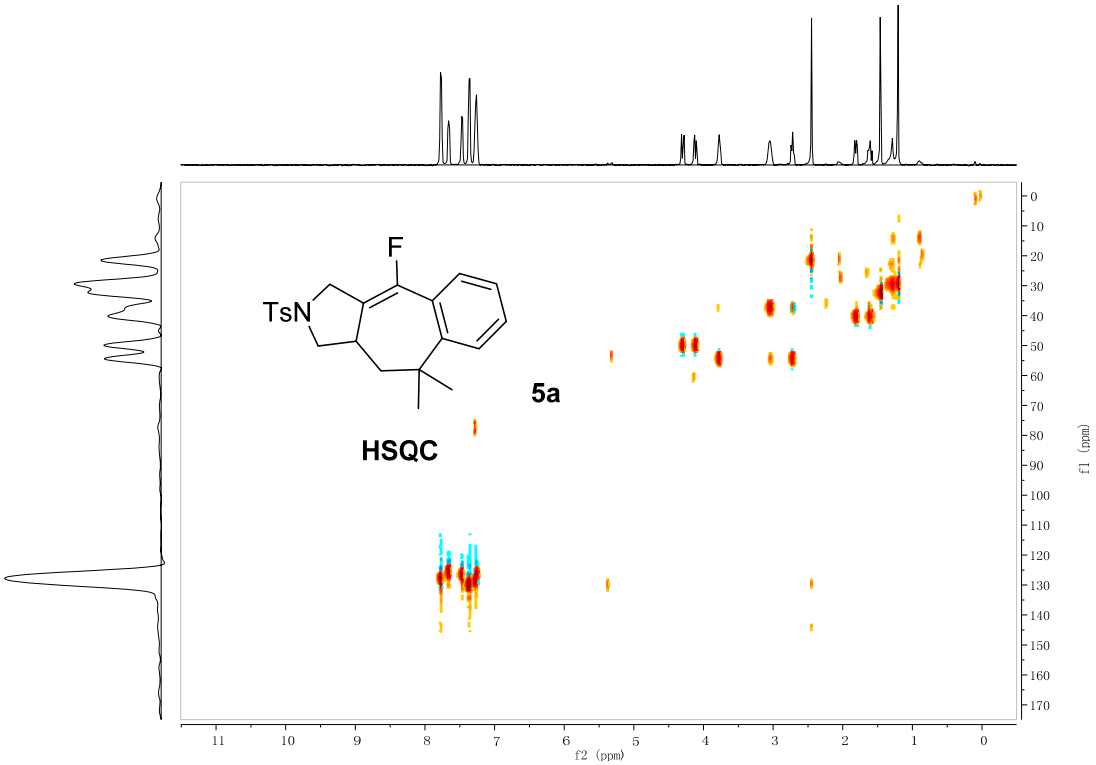
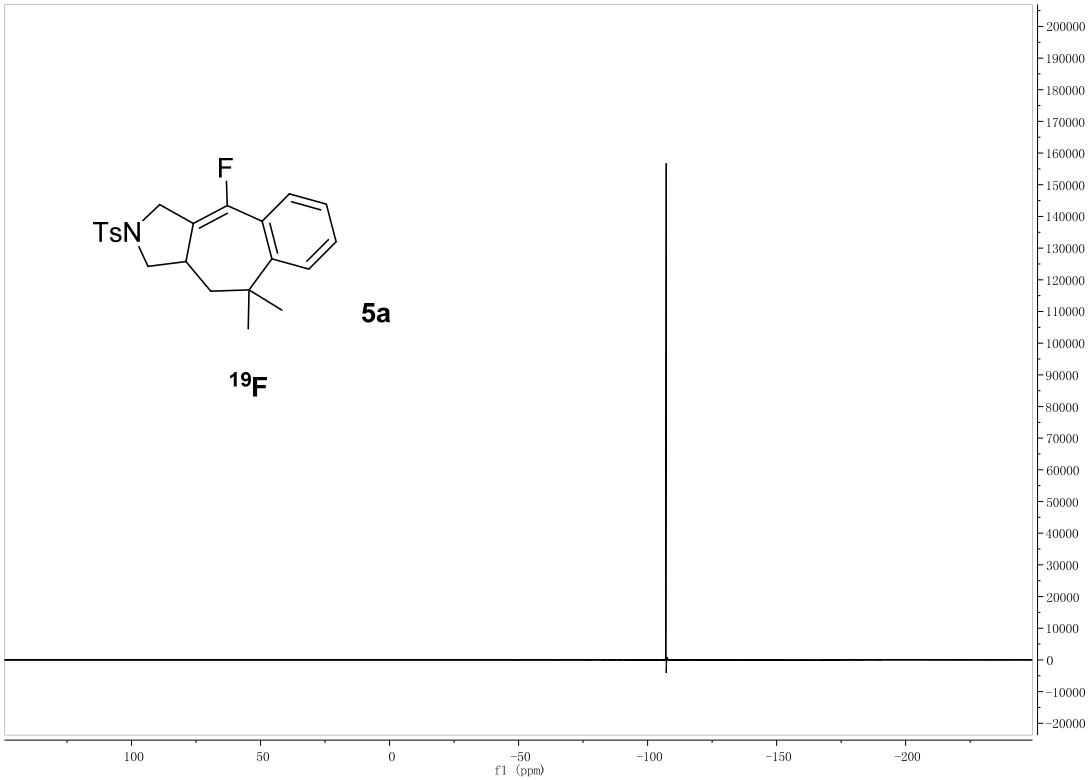
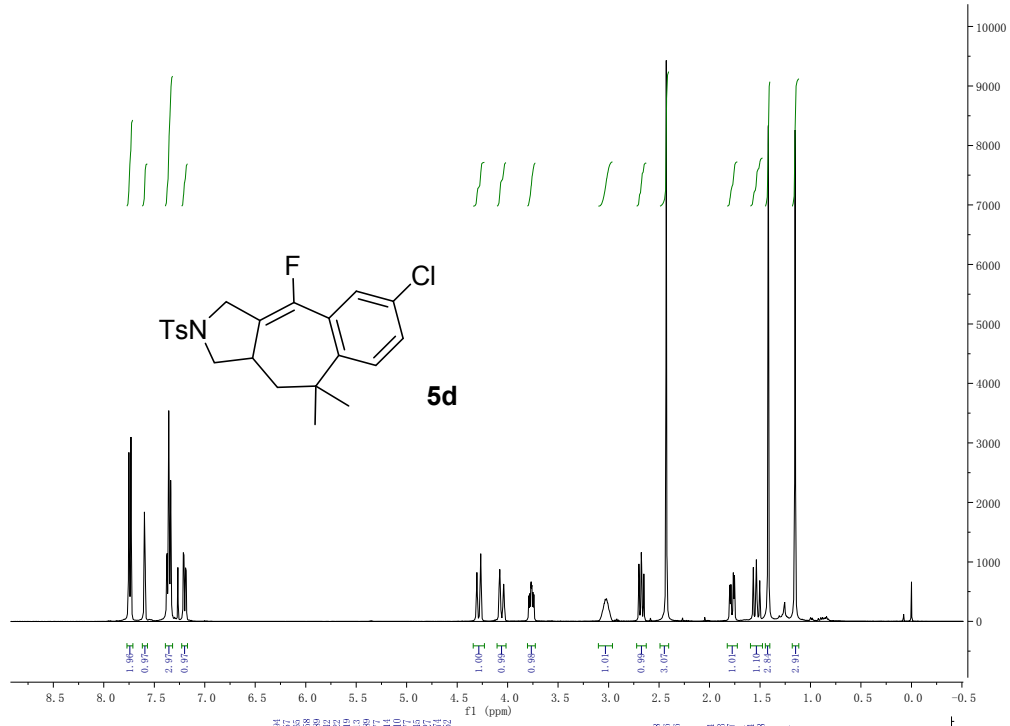
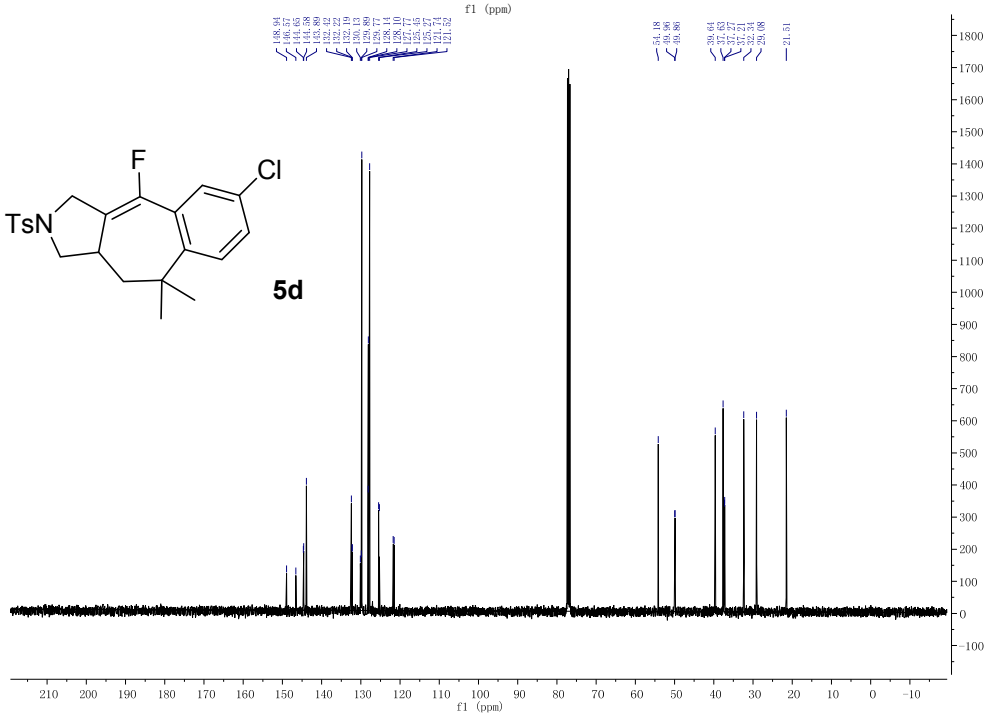
129.79
128.56
128.46
128.37
127.86
126.60
126.57
126.38
126.25
125.63
125.49
120.12
119.95
F
23
22
12
19
24
11, d
13, d
14, d
10, d
8, d
9,d
f1 (ppm)

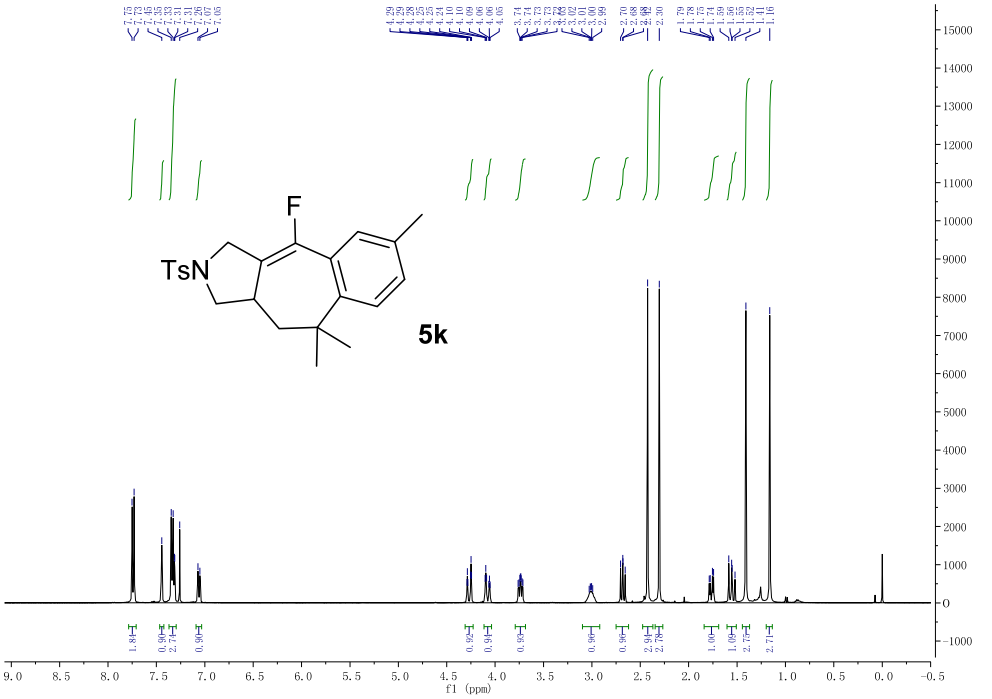

F
TsN
5a
COSY
f2 (ppm)
f1 (ppm)

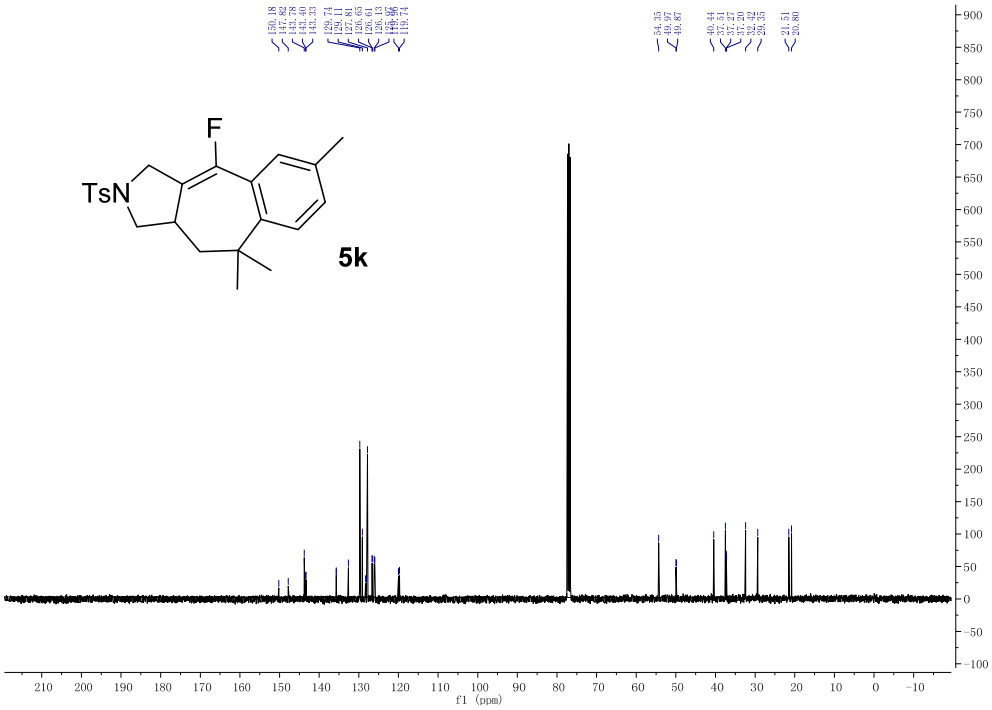

F
TsN
5a
HSQC
f2 (ppm)
f1 (ppm)

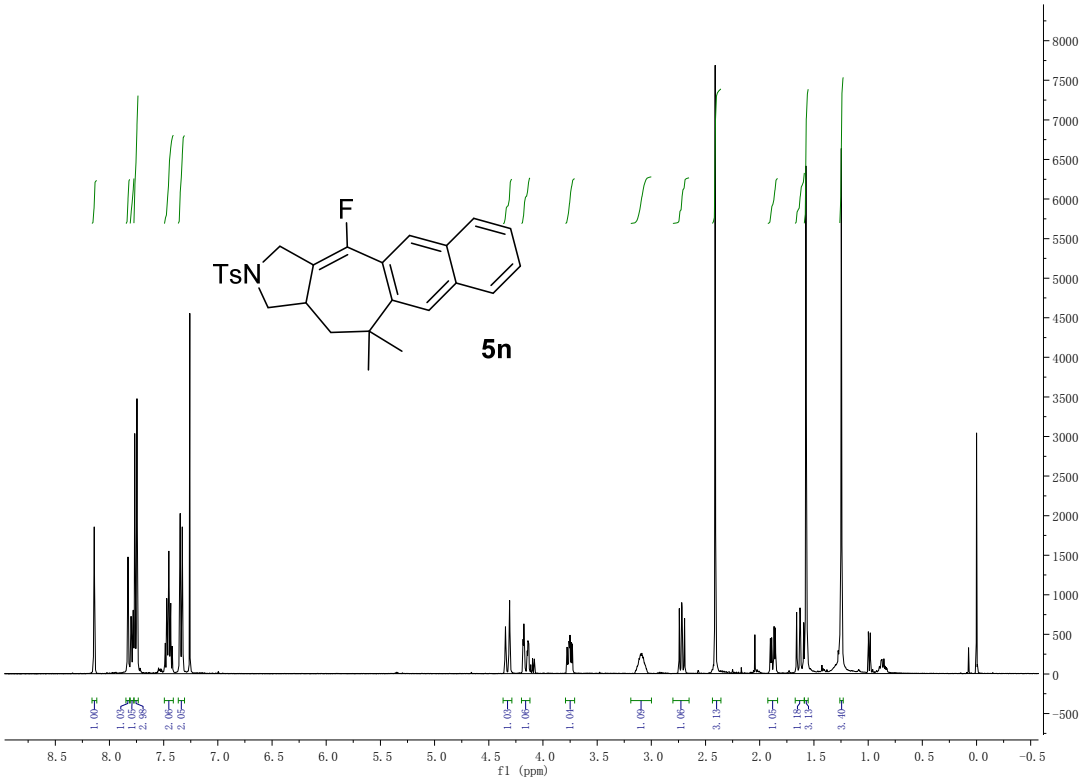

F
TsN
5a
19F
200000
190000
180000
170000
160000
150000
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
-20000
100
50
0
-50
-100
-150
-200
f1 (ppm)

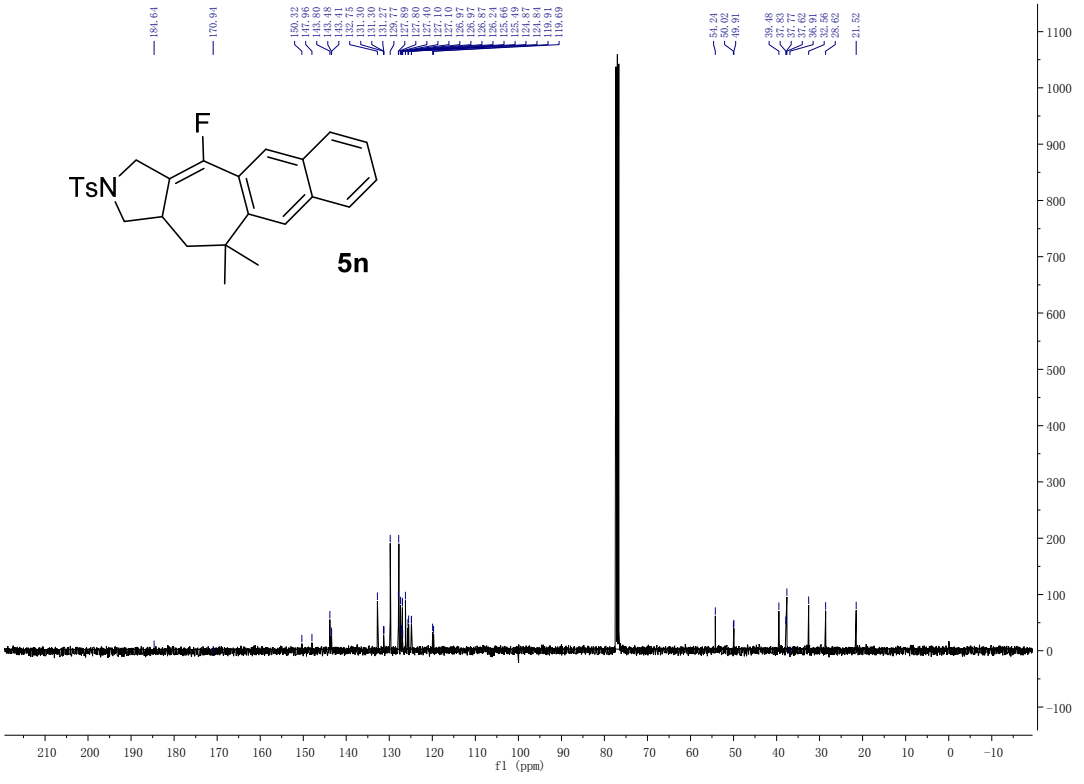

F
Cl
TsN
5d
f1 (ppm)

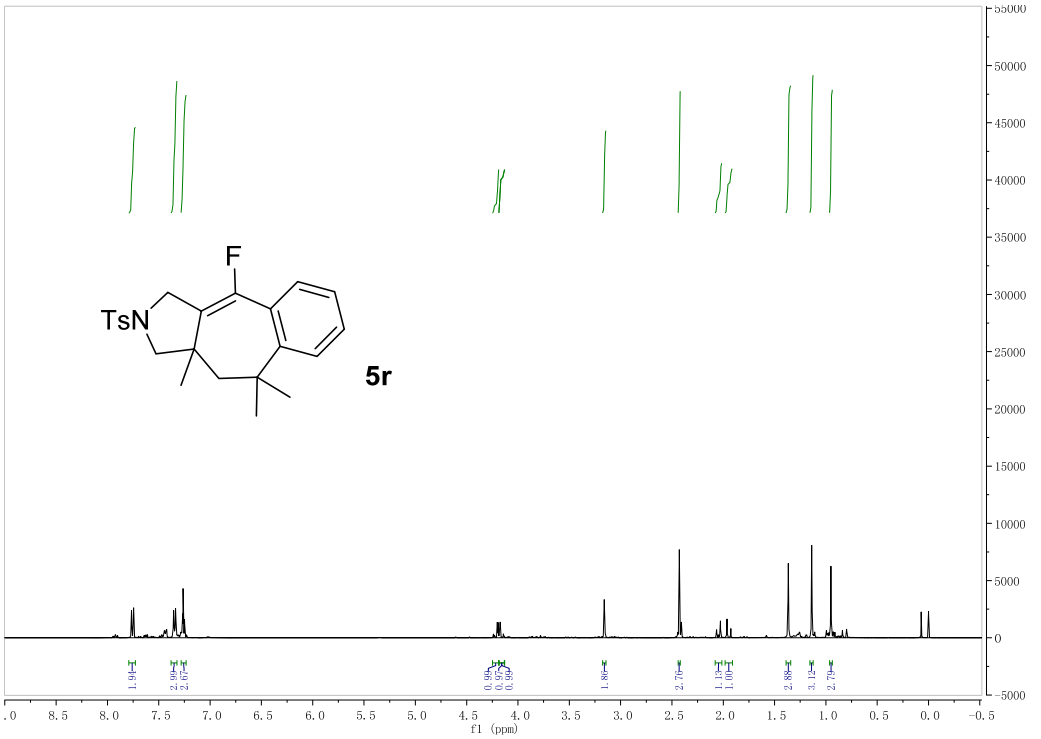

F
Cl
TsN
5d
f1 (ppm)

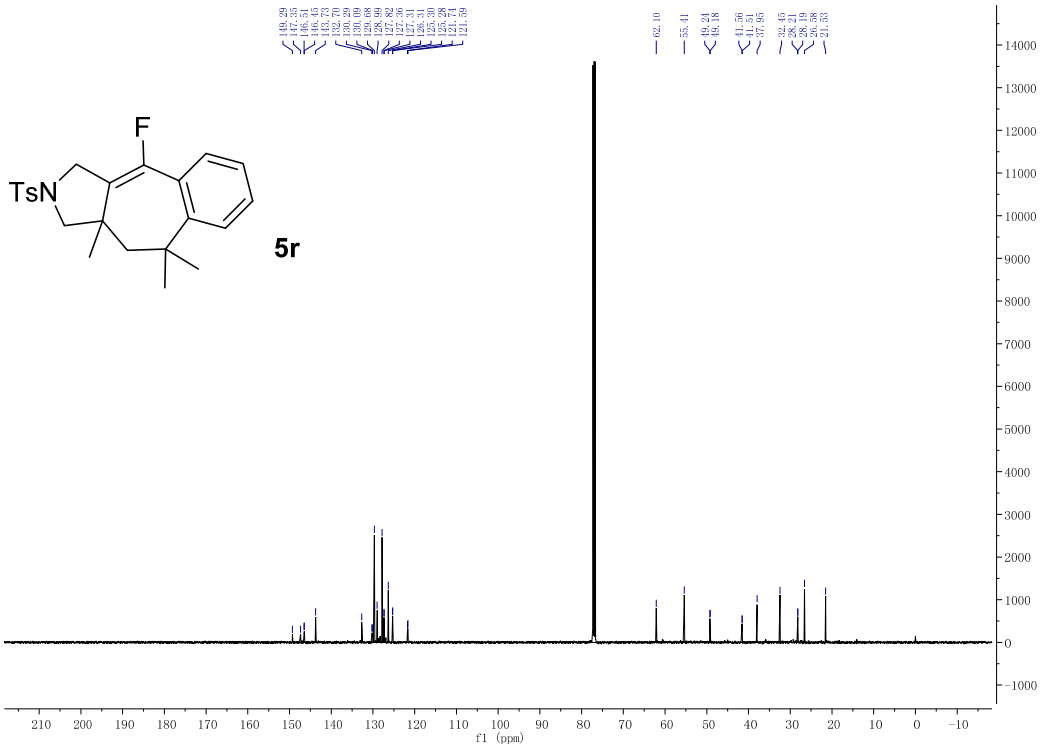

F
TsN
5k
f1 (ppm)


F
TsN
5k
f1 (ppm)


F
TsN
5n
f1 (ppm)


F
TsN
5n
f1 (ppm)


F
TsN
5r
1.94
2.09
2.67
0.99
0.97
0.99
1.88
2.70
1.13
1.09
2.88
3.12
2.79
f1 (ppm)


F
TsN
5r
149.39
147.35
146.51
146.45
143.73
132.70
130.29
130.09
128.68
128.09
127.82
127.36
127.31
126.31
125.30
125.28
121.74
121.39
62.10
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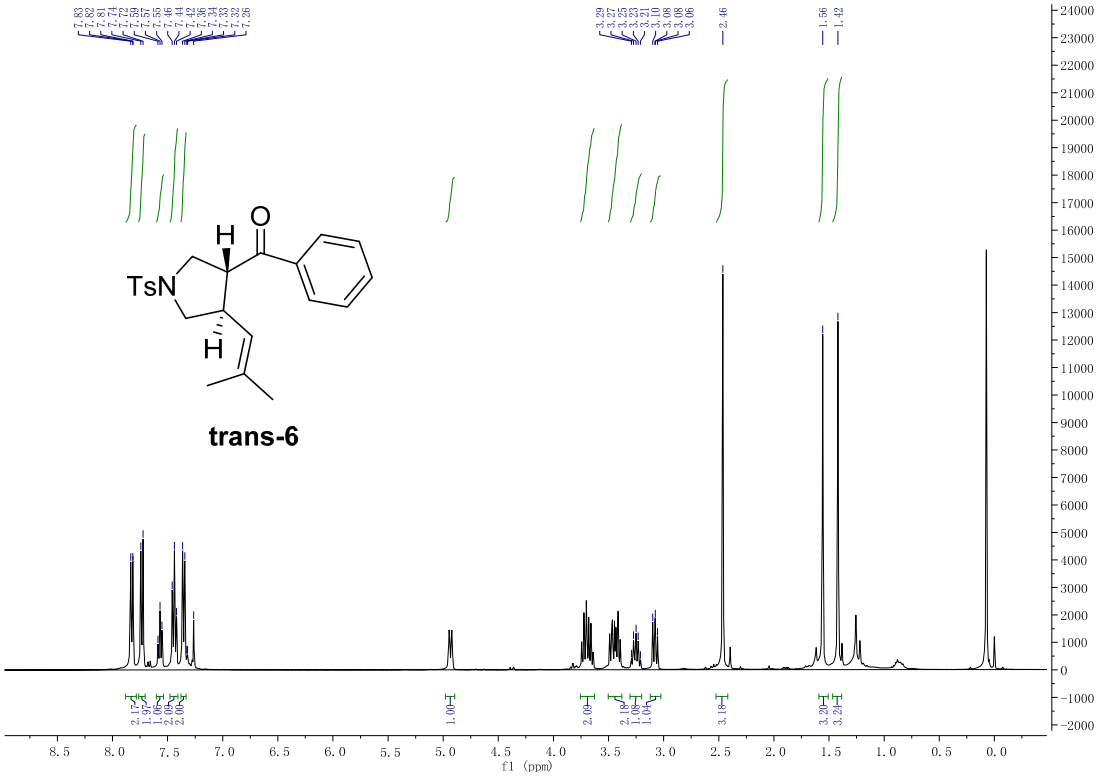
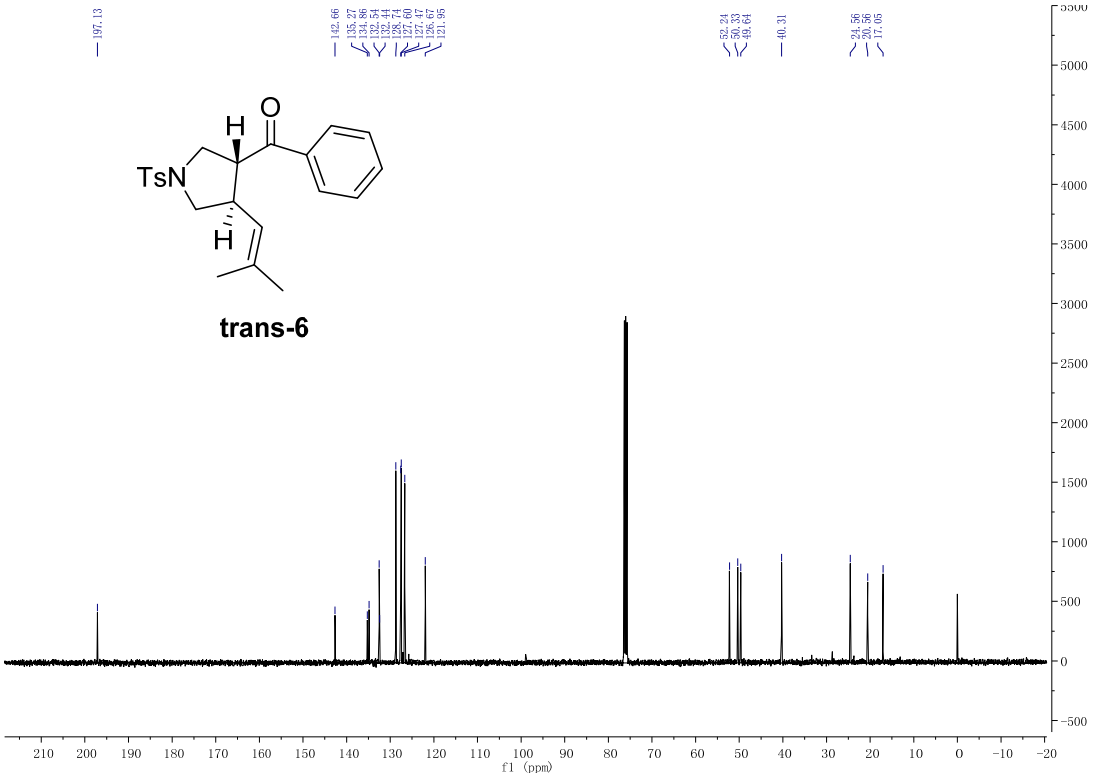
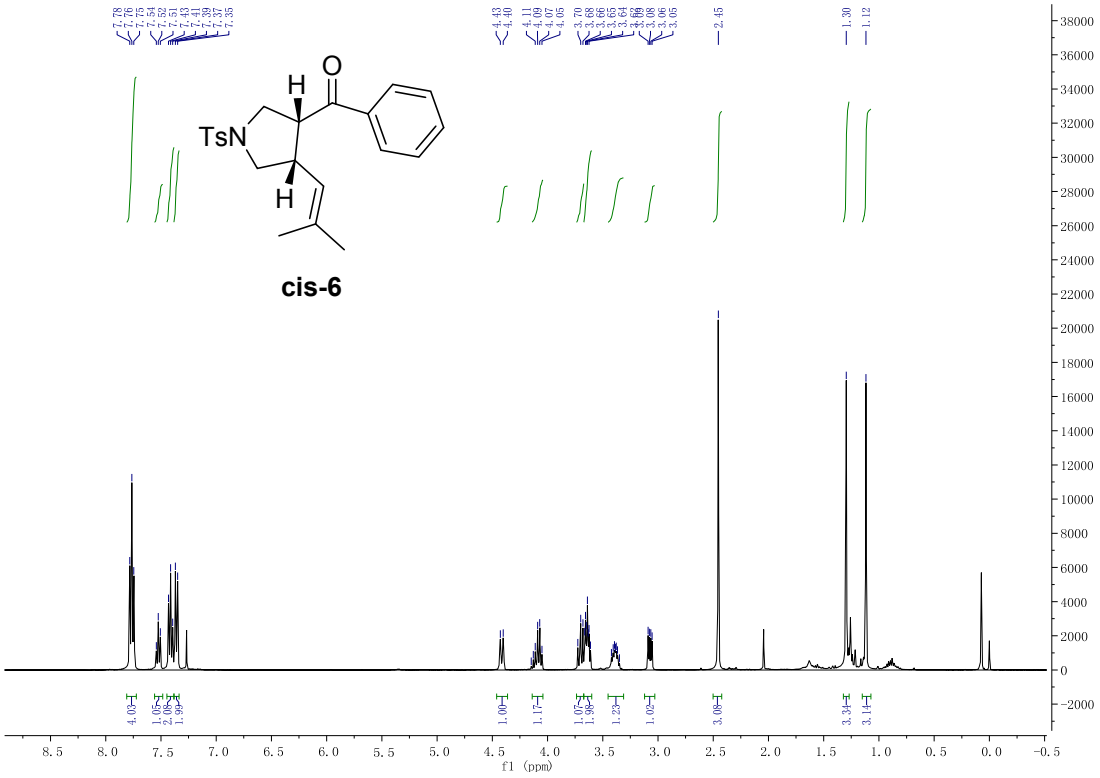
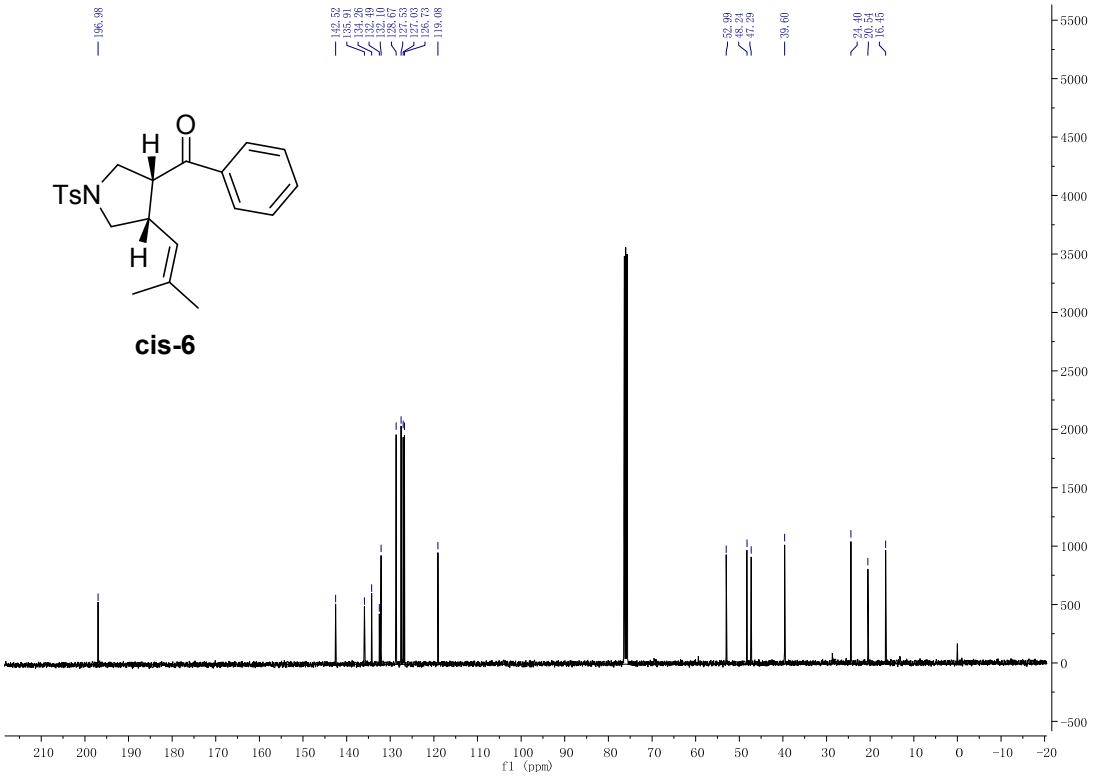
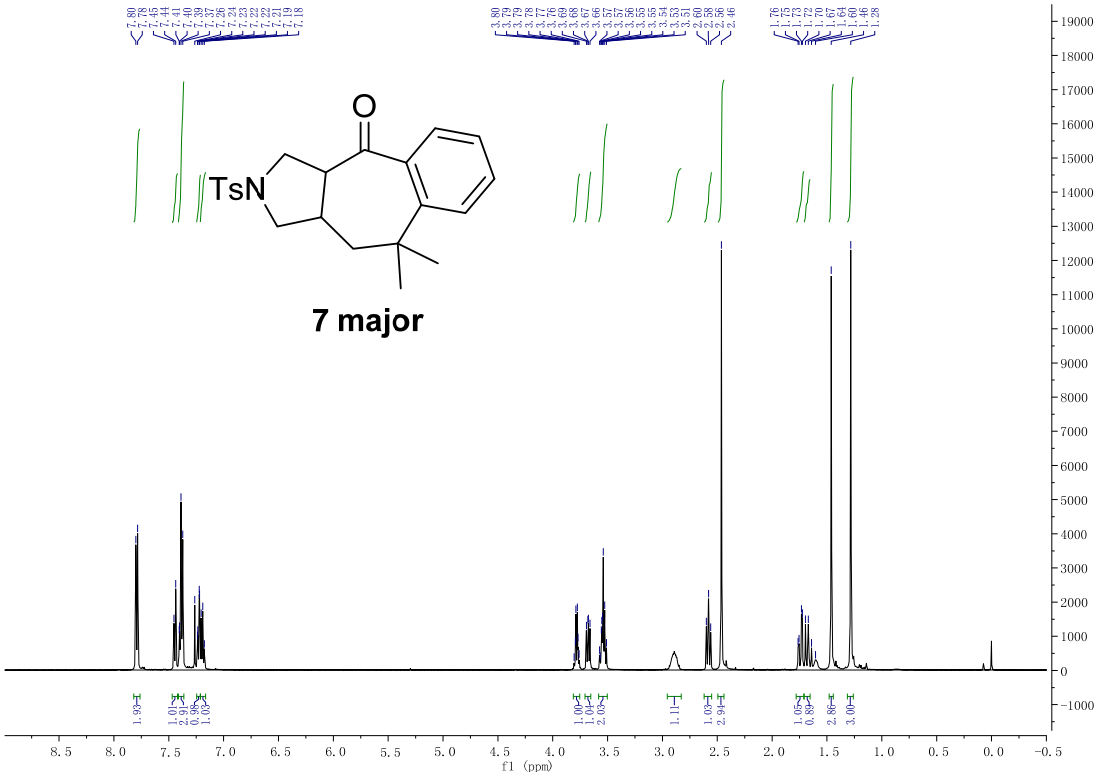
28.21
28.19
26.88
21.53
f1 (ppm)

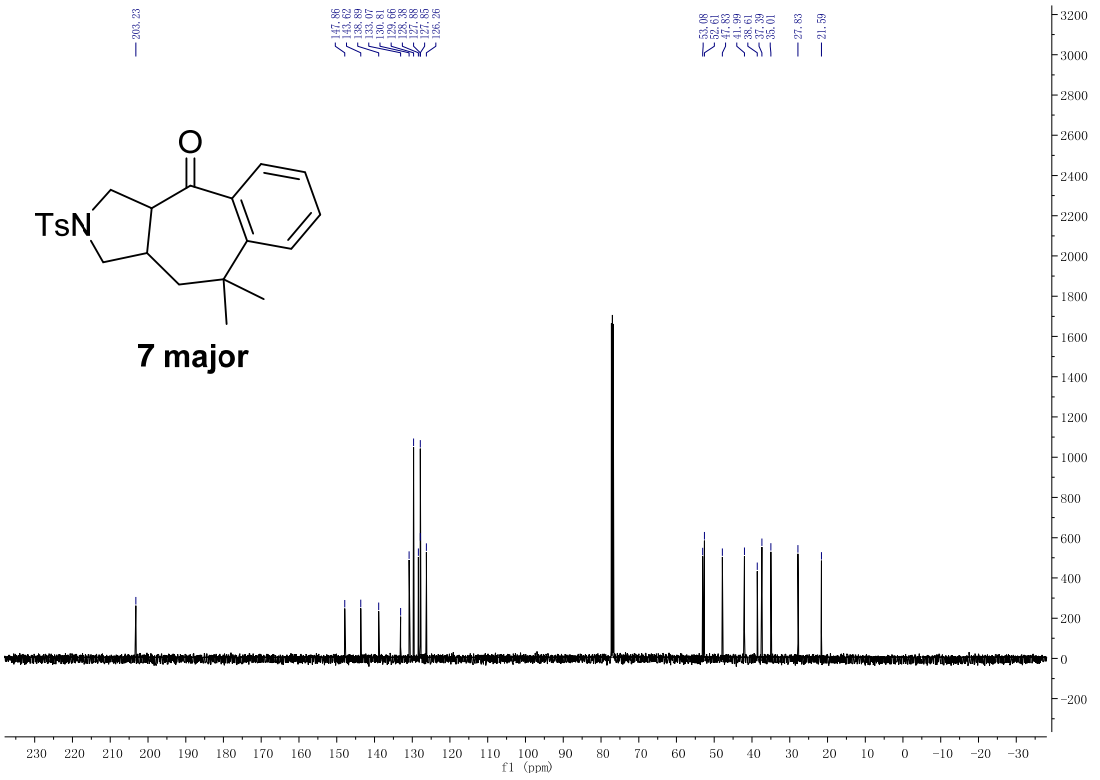

trans-6
f1 (ppm)

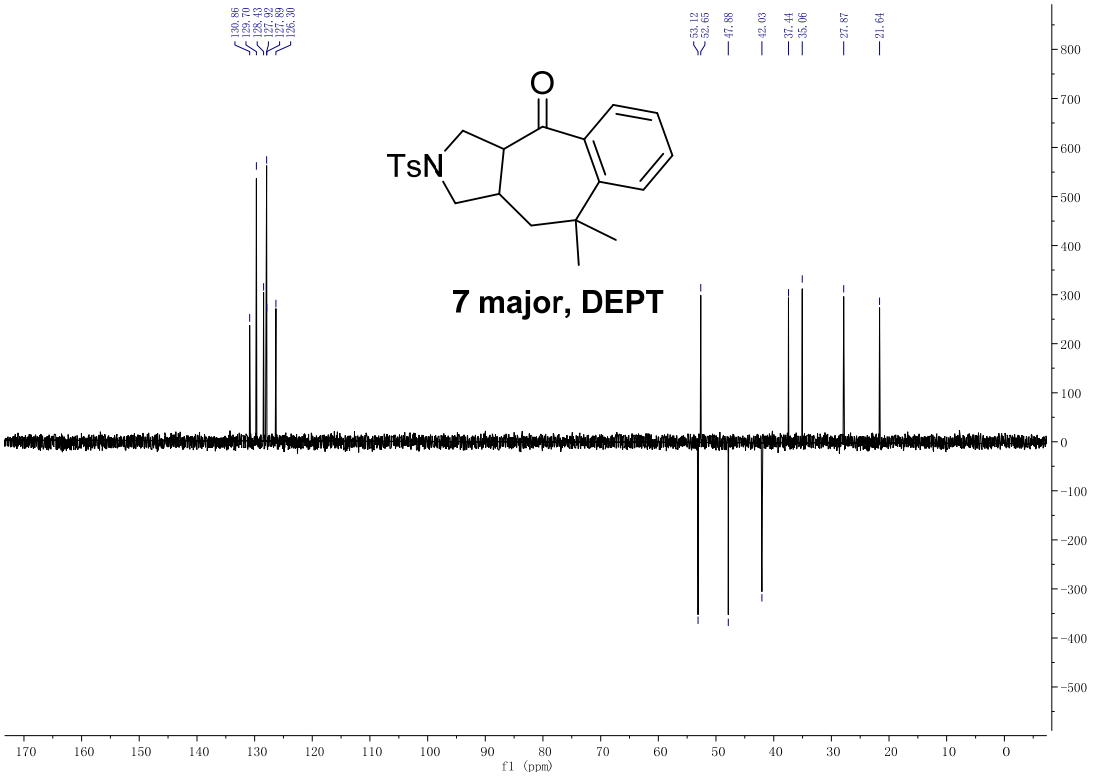

trans-6
f1 (ppm)

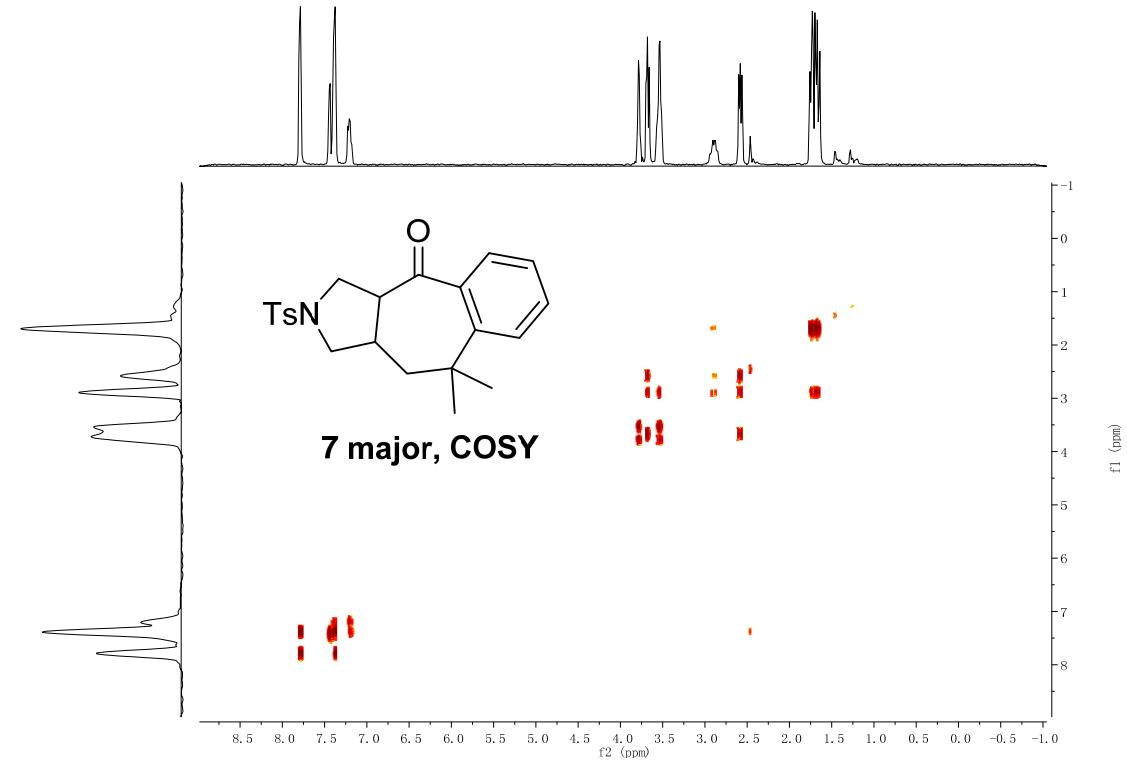

TsN
H
O
H
cis-6
f1 (ppm)

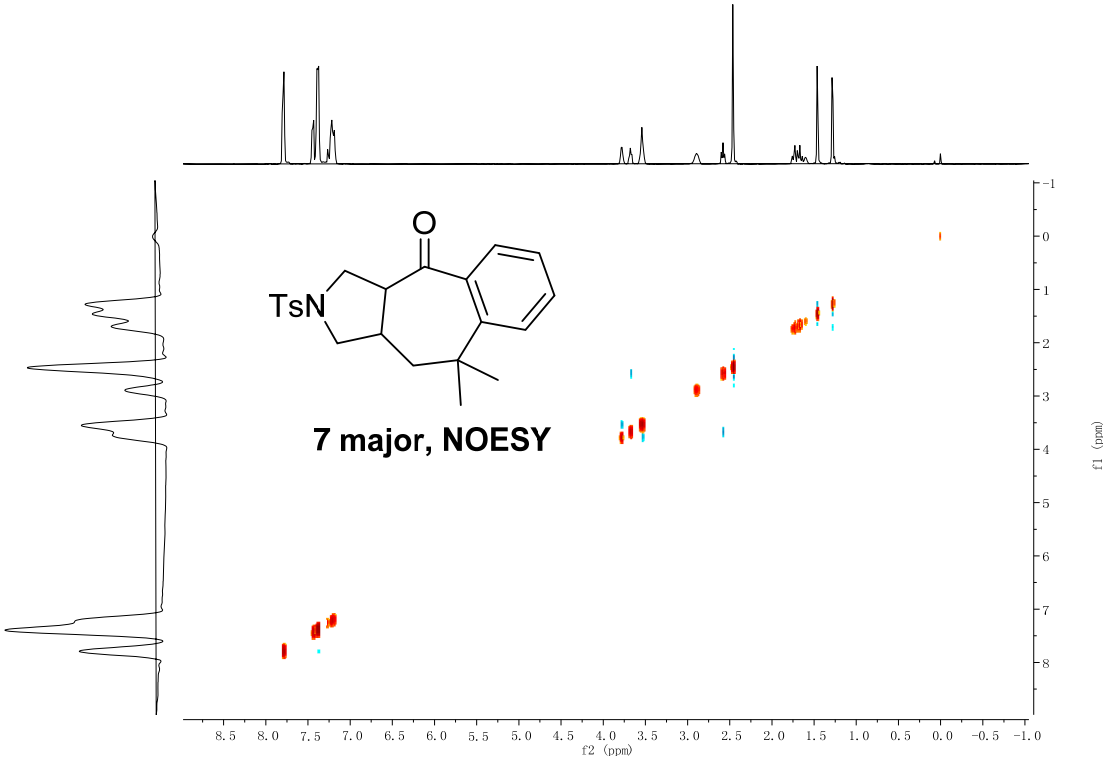

TsN
H
O
H
cis-6
f1 (ppm)

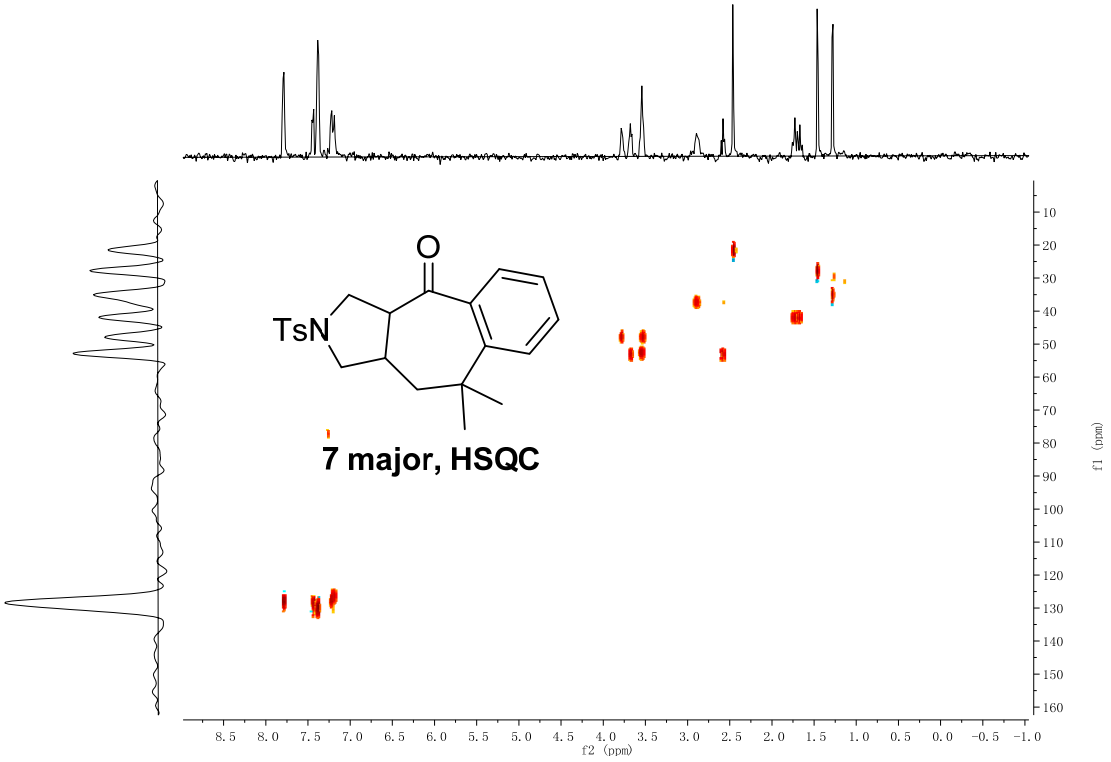

O
TsN
7 major
f1 (ppm)

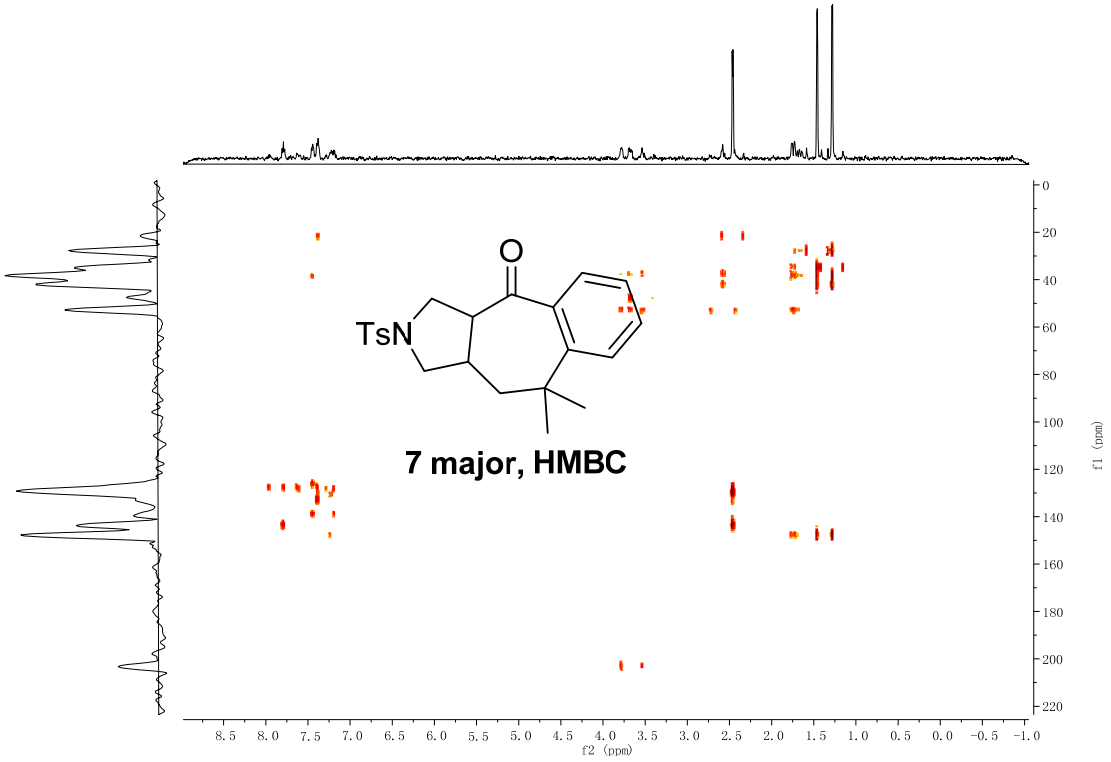

O
TsN
7 major
f1 (ppm)

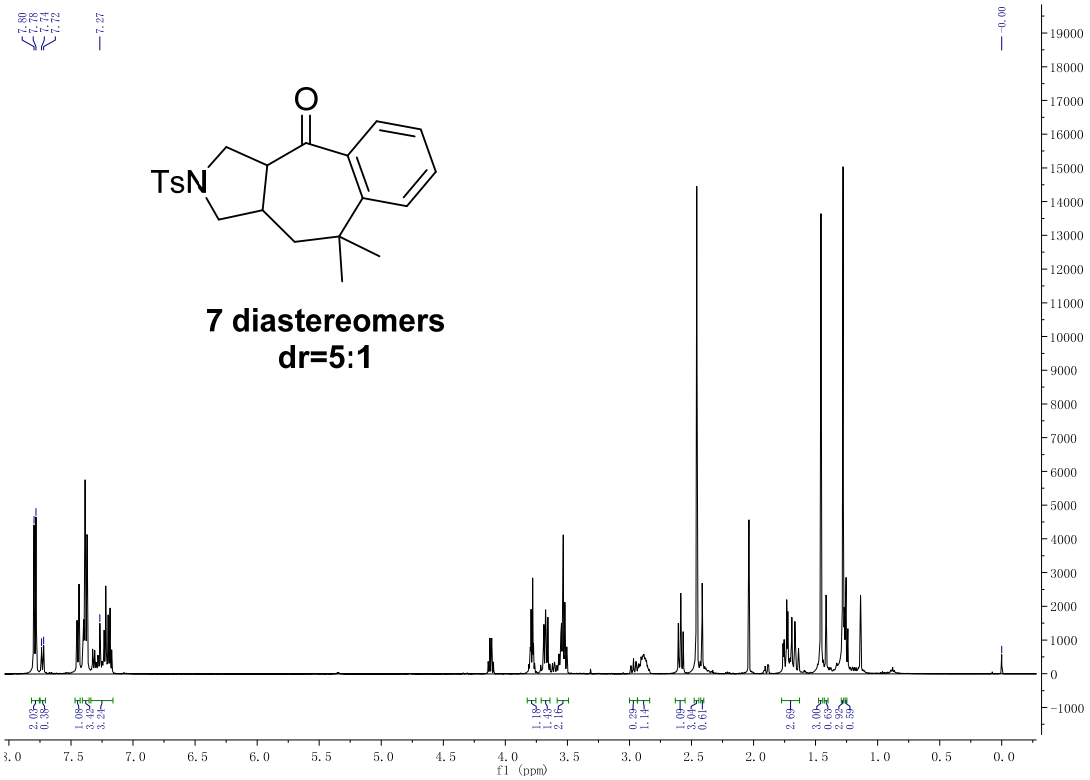

130.86
129.70
128.43
127.92
127.88
126.30
53.12
52.65
47.88
42.03
37.44
35.06
27.87
21.64
O
TsN
7 major, DEPT
f1 (ppm)

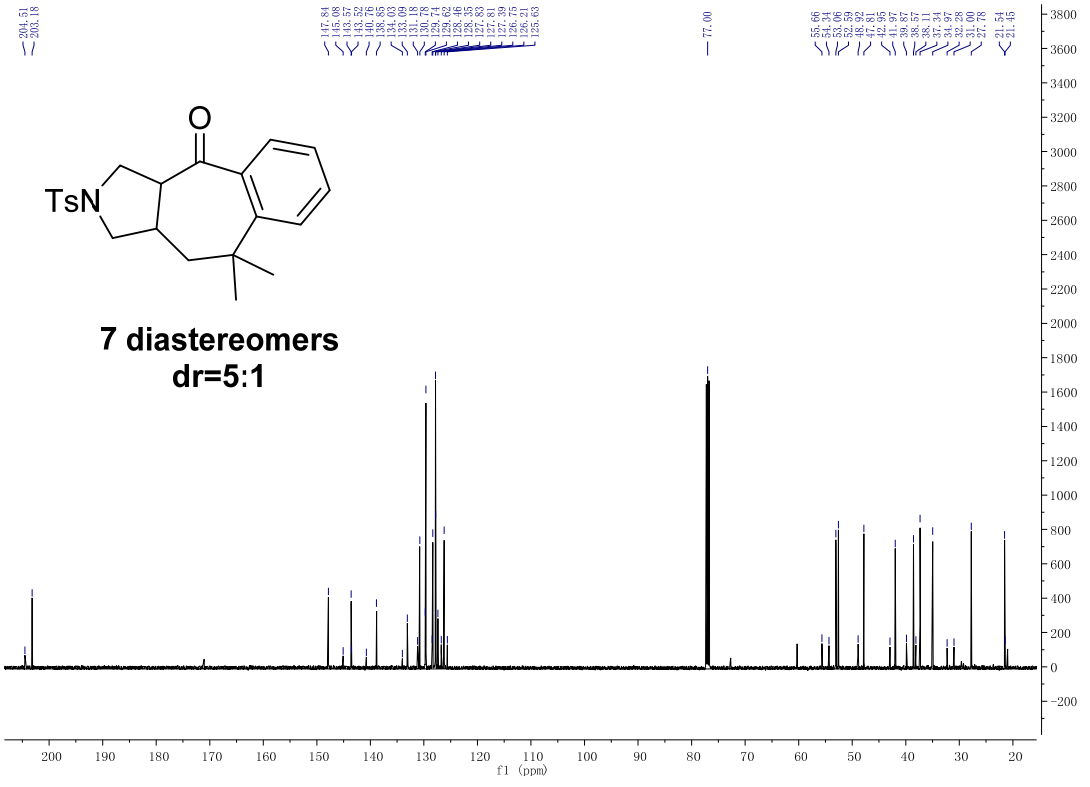

O
TsN
7 major, COSY
f2 (ppm)
f1 (ppm)

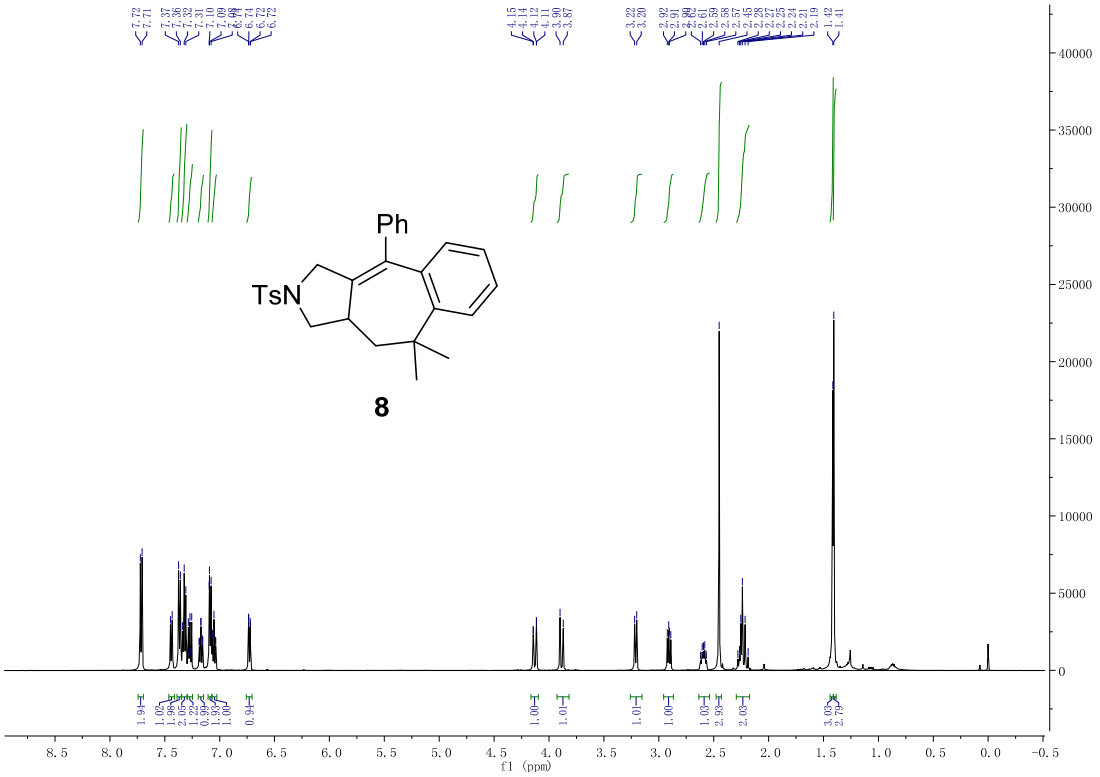

O
TsN
7 major, NOESY
f2 (ppm)
f1 (ppm)

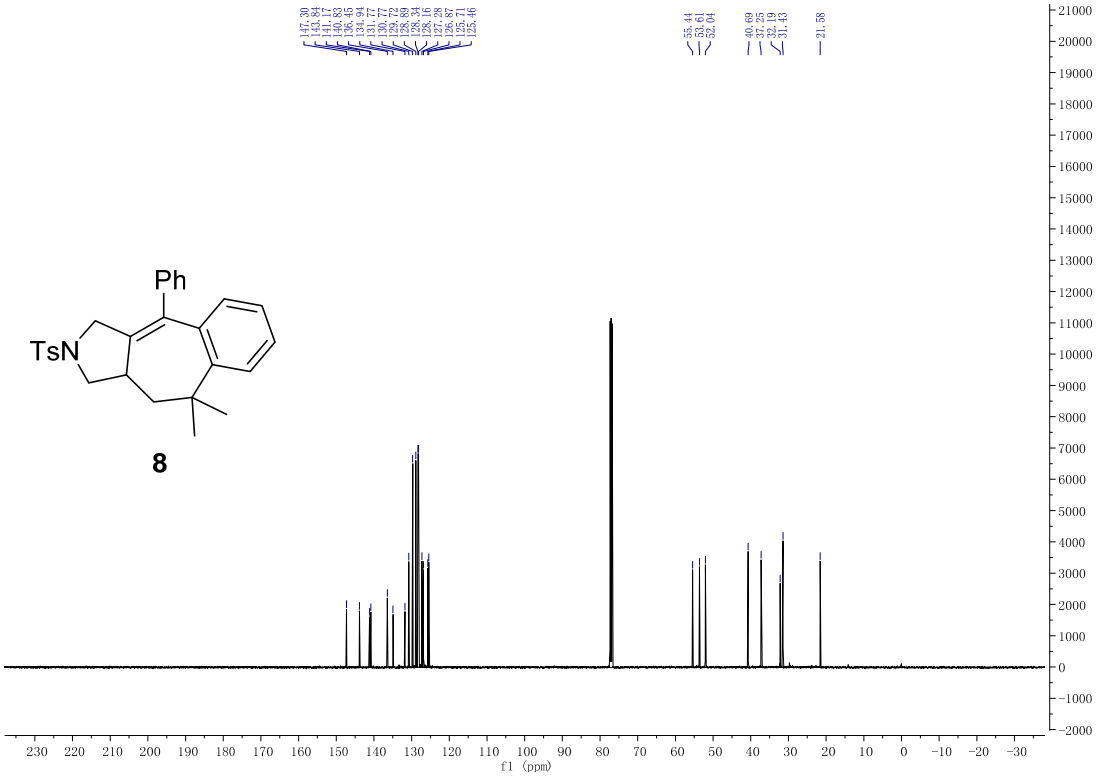

O
TsN
7 major, HSQC
f2 (ppm)
f1 (ppm)

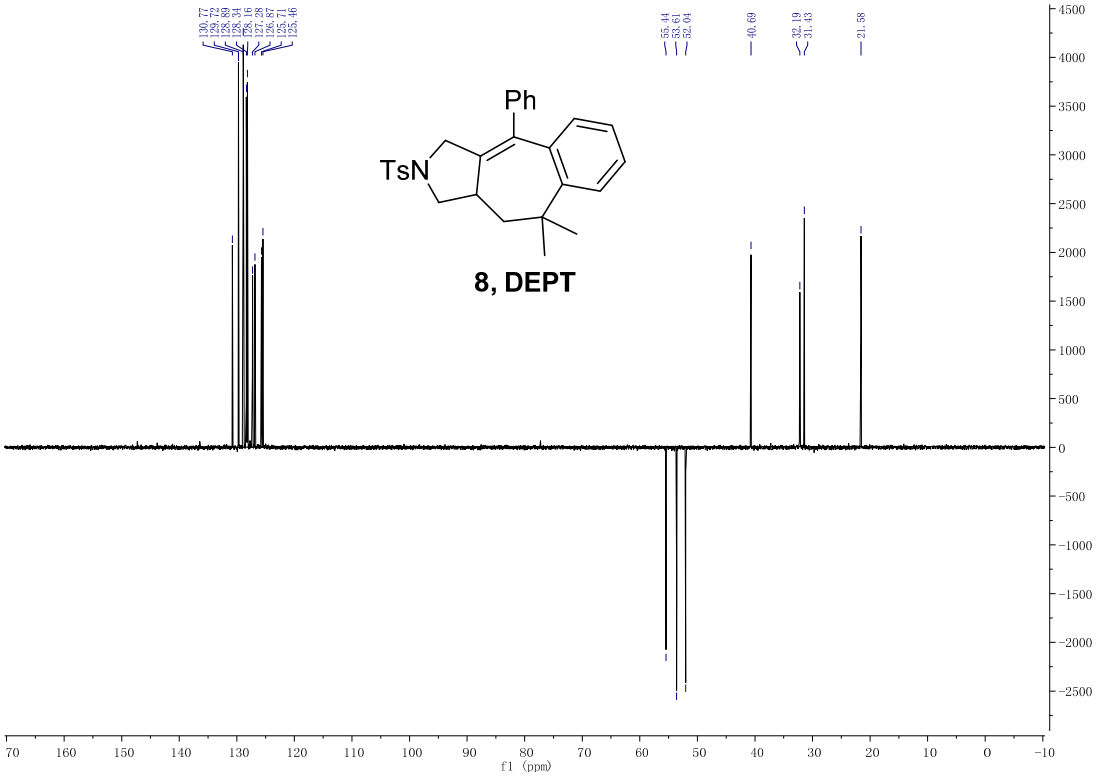

O
TsN
7 major, HMBC
f2 (ppm)
f1 (ppm)

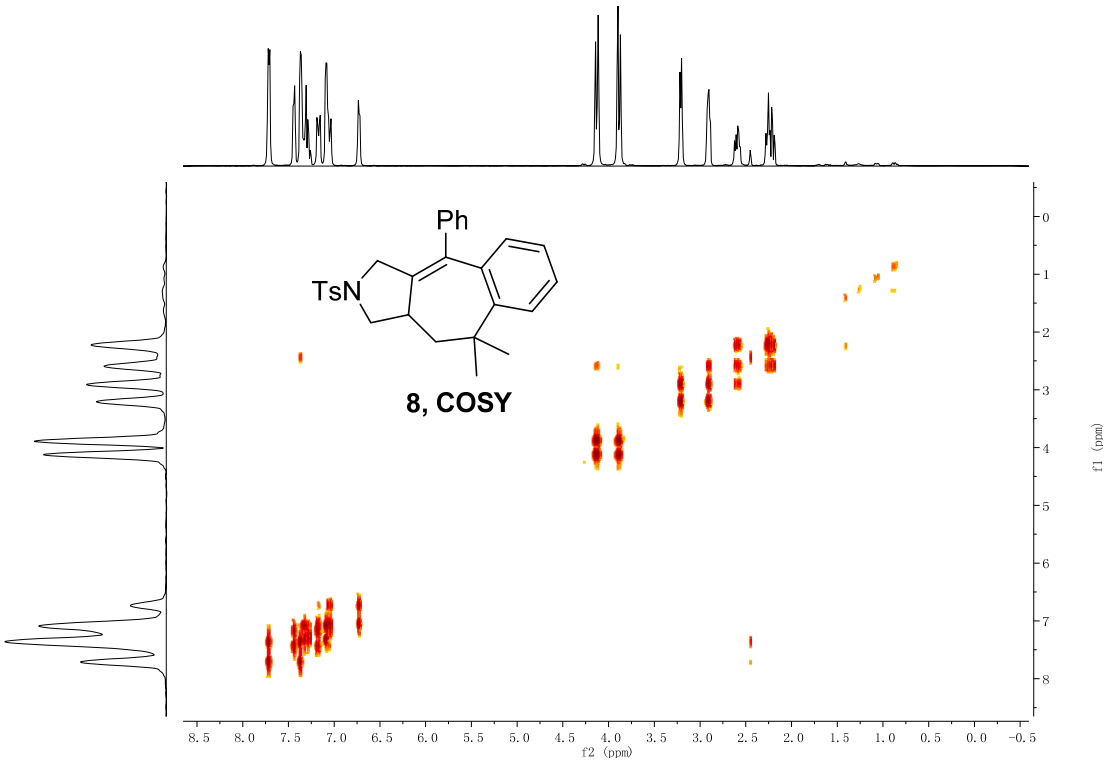

TsN
O
7 diastereomers
dr=5:1
f1 (ppm)

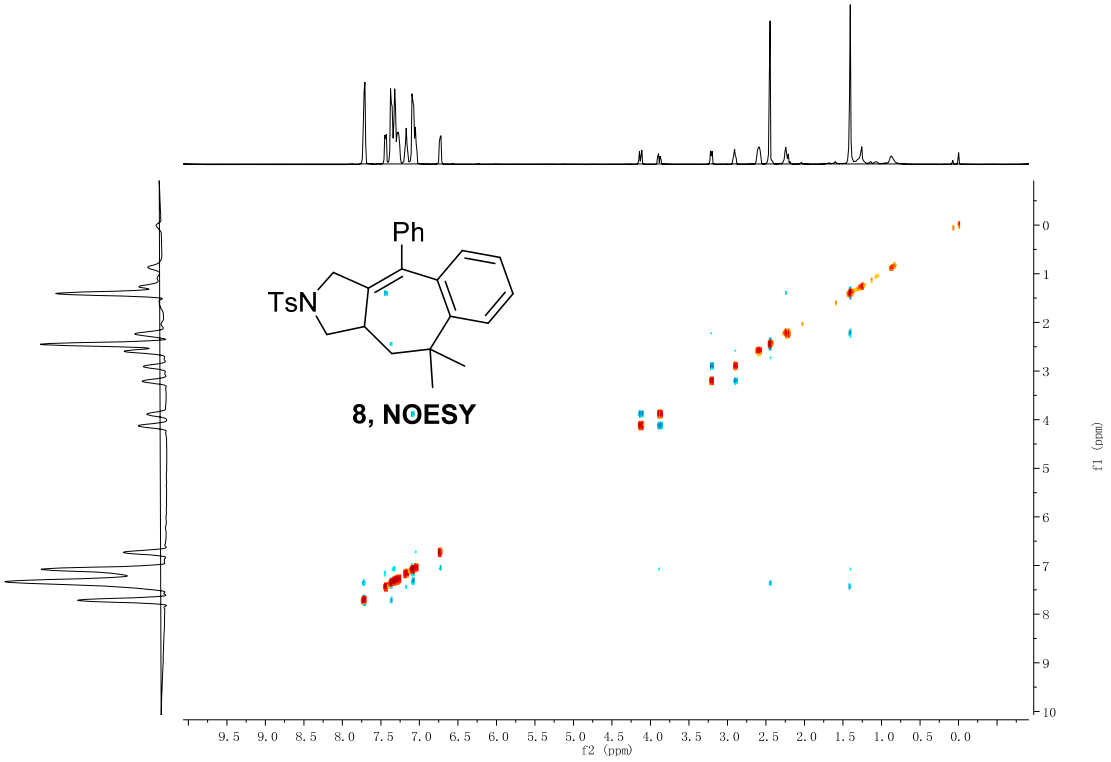

TsN
O
7 diastereomers
dr=5:1
f1 (ppm)

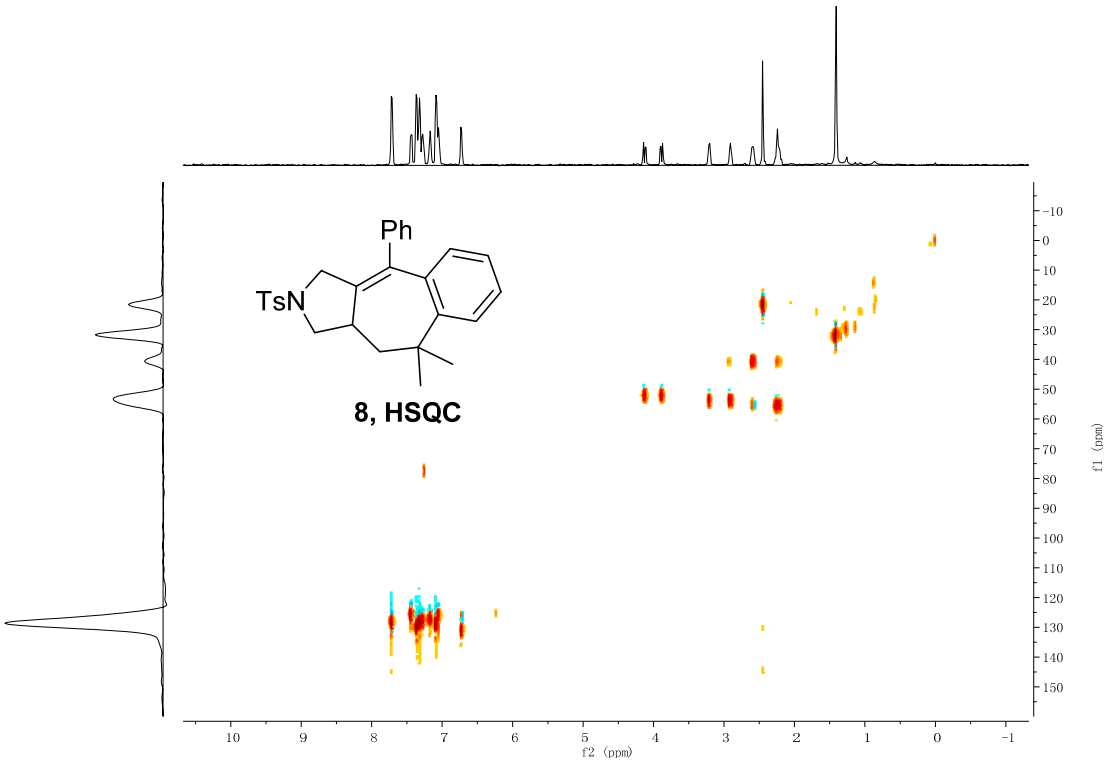

Ph
TsN
8
f1 (ppm)

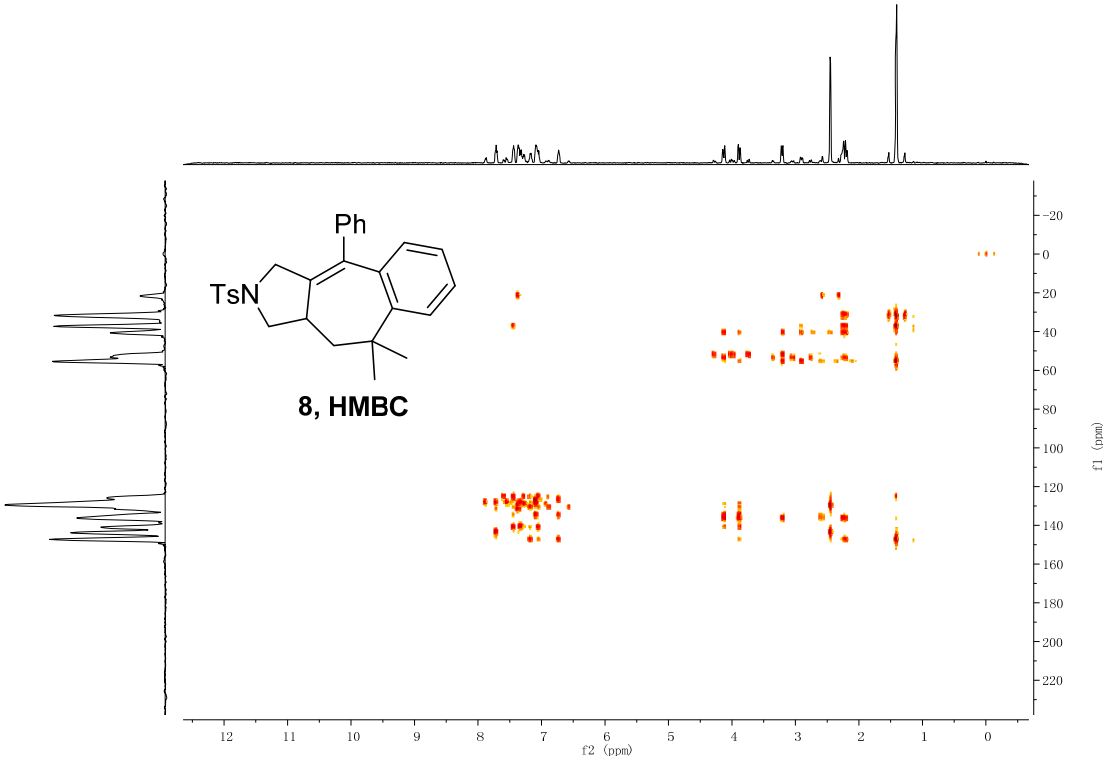

Ph
TsN
8
f1 (ppm)


Ph
TsN
8, DEPT
f1 (ppm)


Ph
TsN
8, COSY
f2 (ppm)
f1 (ppm)

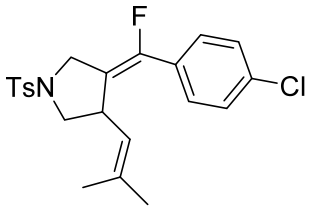

Ph
TsN
8, NOESY
f2 (ppm)
f1 (ppm)


Ph
TsN
8, HSQC
f2 (ppm)
f1 (ppm)

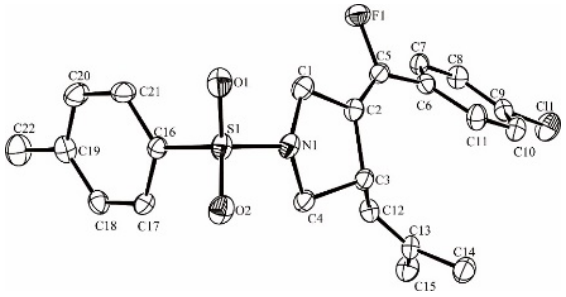

Ph
TsN
8, HMBC
f2 (ppm)
f1 (ppm)

## 3. X-ray Data

**X-ray Data of 4b (exp_6623).:**




**4b**




Ellipsoids are drawn at 30% probability

**Table 1 Crystal data and structure refinement for exp_6623.**

| | |
|---|---|
| Identification code | exp_6623 |
| Empirical formula | $C_{22}H_{23}NO_2SFCl$ |
| Formula weight | 419.92 |
| Temperature/K | 180.00(10) |
| Crystal system | monoclinic |
| Space group | $P2_1/c$ |
| a/Å | 20.142(3) |
| b/Å | 8.359(2) |
| c/Å | 12.4889(17) |
| α/° | 90 |
| β/° | 91.811(14) |
| γ/° | 90 |
| Volume/Å$^3$ | 2101.8(7) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.327 |
| μ/mm$^{-1}$ | 0.307 |
| F(000) | 880.0 |
| Crystal size/mm$^3$ | 0.1 × 0.1 × 0.05 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 6.072 to 52.04 |
| Index ranges | -20 ≤ h ≤ 24, -10 ≤ k ≤ 5, -15 ≤ l ≤ 15 |
| Reflections collected | 8145 |
| Independent reflections | 4133 [$R_{int}$ = 0.0723, $R_{sigma}$ = 0.1389] |
| Data/restraints/parameters | 4133/0/256 |
| Goodness-of-fit on F$^2$ | 1.020 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0626, $wR_2$ = 0.0905 |
| Final R indexes [all data] | $R_1$ = 0.1448, $wR_2$ = 0.1249 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.30/-0.44 |

**Table 2 Fractional Atomic Coordinates (×10$^4$) and Equivalent Isotropic Displacement Parameters (Å$^2$×10$^3$) for exp_6623. $U_{eq}$ is defined as 1/3 of of the trace of the orthogonalised $U_{IJ}$ tensor.**

| Atom | *x* | *y* | *z* | U(eq) |
|---|---|---|---|---|
| C1 | 3008.8(16) | 4118(6) | 7150(3) | 39.5(12) |
| C2 | 2473.0(16) | 3668(6) | 6331(3) | 34.8(11) |
| C3 | 2139.4(16) | 5173(6) | 5888(3) | 34.8(11) |
| C4 | 2642.8(15) | 6473(6) | 6239(2) | 36.9(11) |
| C5 | 2364.1(16) | 2180(6) | 6029(3) | 38.8(12) |
| C6 | 1866.8(16) | 1483(6) | 5285(3) | 35.8(11) |
| C7 | 2041.7(17) | 336(6) | 4547(3) | 39.2(11) |
| C8 | 1586.6(17) | -231(6) | 3793(3) | 45.4(12) |
| C9 | 946.7(17) | 359(6) | 3770(3) | 41.7(12) |
| C10 | 746.0(17) | 1435(7) | 4522(3) | 49.6(13) |
| C11 | 1206.3(16) | 2017(6) | 5279(3) | 46.0(12) |
| C12 | 2024.1(16) | 5185(6) | 4687(3) | 38.2(11) |
| C13 | 1471.3(15) | 5511(6) | 4147(3) | 38.1(11) |
| C14 | 826.1(15) | 5979(7) | 4627(3) | 53.1(14) |
| C15 | 1451.5(17) | 5385(7) | 2931(3) | 51.7(14) |
| C16 | 4204.0(15) | 6850(5) | 7133(3) | 31.2(10) |
| C17 | 4222.8(16) | 7844(6) | 6239(3) | 38.1(11) |
| C18 | 4773.6(16) | 7804(6) | 5599(3) | 40.6(12) |
| C19 | 5311.1(17) | 6826(6) | 5855(3) | 43.1(12) |
| C20 | 5290.4(17) | 5856(6) | 6757(3) | 49.1(13) |
| C21 | 4733.4(16) | 5845(6) | 7385(3) | 42.8(12) |
| C22 | 5915.5(17) | 6815(8) | 5158(3) | 66.0(16) |
| Cl1 | 373.5(5) | -314(2) | 2795.8(8) | 68.5(5) |
| F1 | 2786.6(9) | 1032(3) | 6452.4(16) | 49.7(7) |
| N1 | 2917.2(12) | 5848(5) | 7267(2) | 36.8(9) |
| O1 | 3651(1) | 5928(4) | 8873.3(16) | 46.4(9) |
| O2 | 3259.6(11) | 8458(4) | 8004.4(18) | 46.8(8) |
| S1 | 3496.9(4) | 6846.4(16) | 7924.2(7) | 37.9(3) |

**Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for exp_6623. The Anisotropic displacement factor exponent takes the form: $-2π^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+…]$.**

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| C1 | 36(2) | 47(4) | 35(2) | -4(2) | -1.3(17) | 3(2) |
| C2 | 32.5(19) | 42(4) | 29.9(19) | -3(2) | -0.4(16) | -2(2) |
| C3 | 27.5(17) | 42(3) | 35.0(19) | 3(2) | -2.0(16) | -1(2) |
| C4 | 32.1(19) | 41(3) | 37(2) | 2(2) | -3.2(17) | 1.6(19) |
| C5 | 31(2) | 49(4) | 37(2) | 10(2) | 2.3(17) | 4(2) |
| C6 | 35(2) | 36(3) | 37(2) | 3(2) | 5.3(18) | -2(2) |
| C7 | 32.4(19) | 43(4) | 42(2) | 0(2) | 4.5(18) | 0(2) |
| C8 | 46(2) | 46(4) | 45(2) | -9(2) | 2.3(19) | -2(2) |
| C9 | 38(2) | 48(4) | 39(2) | 0(2) | 2.1(18) | -8(2) |
| C10 | 35(2) | 53(4) | 62(3) | 2(3) | 3(2) | 0(2) |
| C11 | 37(2) | 50(4) | 52(2) | -11(2) | 8.9(19) | -2(2) |
| C12 | 35.5(19) | 42(3) | 37(2) | -3(2) | 2.3(18) | -7(2) |
| C13 | 28.4(19) | 47(4) | 39(2) | -2(2) | 1.3(17) | -5(2) |
| C14 | 39(2) | 68(5) | 52(2) | 9(3) | 3.2(19) | 4(2) |
| C15 | 48(2) | 67(4) | 40(2) | -3(2) | -3.6(18) | -1(2) |
| C16 | 28.5(18) | 32(3) | 33.2(19) | -4.6(19) | 0.0(16) | 0.4(18) |
| C17 | 32.9(19) | 41(3) | 40(2) | 2(2) | -9.0(17) | 1(2) |
| C18 | 41(2) | 47(4) | 33.6(19) | 5(2) | 0.4(19) | -11(2) |
| C19 | 41(2) | 44(4) | 45(2) | -14(2) | 12(2) | -4(2) |
| C20 | 38(2) | 53(4) | 57(2) | 5(3) | 5(2) | 12(2) |
| C21 | 43(2) | 44(4) | 41(2) | 12(2) | 3.0(19) | 5(2) |
| C22 | 51(2) | 78(5) | 70(3) | -9(3) | 18(2) | -2(3) |
| Cl1 | 57.0(6) | 86.4(14) | 60.9(7) | -13.2(7) | -16.9(6) | -3.2(7) |
| F1 | 51.7(12) | 42(2) | 55.5(13) | 1.8(13) | -6.5(11) | 5.1(13) |
| N1 | 29.9(15) | 47(3) | 32.8(15) | -3.9(18) | -1.8(13) | 0.6(17) |
| O1 | 44.3(14) | 68(3) | 26.6(12) | 1.8(15) | -2.8(11) | -9.9(15) |
| O2 | 39.1(13) | 46(3) | 55.2(15) | -15.3(16) | 4.1(12) | 6.6(14) |
| S1 | 31.4(5) | 48.4(9) | 33.9(5) | -5.2(5) | 0.0(4) | -4.1(5) |

**Table 4 Bond Lengths for exp_6623.**

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| C1 | C2 | 1.511(4) | C10 | C11 | 1.391(5) |
| C1 | N1 | 1.466(6) | C12 | C13 | 1.313(4) |
| C2 | C3 | 1.522(6) | C13 | C14 | 1.500(5) |

| | | | | | |
|---|---|---|---|---|---|
| C2 | C5 | 1.316(6) | C13 | C15 | 1.521(4) |
| C3 | C4 | 1.541(5) | C16 | C17 | 1.394(5) |
| C3 | C12 | 1.510(4) | C16 | C21 | 1.386(5) |
| C4 | N1 | 1.477(4) | C16 | S1 | 1.759(3) |
| C5 | C6 | 1.466(5) | C17 | C18 | 1.388(5) |
| C5 | F1 | 1.377(5) | C18 | C19 | 1.386(5) |
| C6 | C7 | 1.383(5) | C19 | C20 | 1.390(6) |
| C6 | C11 | 1.403(5) | C19 | C22 | 1.518(5) |
| C7 | C8 | 1.377(5) | C20 | C21 | 1.389(5) |
| C8 | C9 | 1.379(5) | N1 | S1 | 1.635(3) |
| C9 | C10 | 1.371(6) | O1 | S1 | 1.438(3) |
| C9 | Cl1 | 1.744(4) | O2 | S1 | 1.434(3) |

**Table 5 Bond Angles for exp_6623.**

| Atom | Atom | Atom | Angle/˚ | Atom | Atom | Atom | Angle/˚ |
|---|---|---|---|---|---|---|---|
| N1 | C1 | C2 | 102.9(3) | C12 | C13 | C14 | 125.5(3) |
| C1 | C2 | C3 | 109.8(4) | C12 | C13 | C15 | 119.6(3) |
| C5 | C2 | C1 | 122.5(4) | C14 | C13 | C15 | 114.9(3) |
| C5 | C2 | C3 | 127.5(3) | C17 | C16 | S1 | 119.6(3) |
| C2 | C3 | C4 | 101.6(3) | C21 | C16 | C17 | 120.2(3) |
| C12 | C3 | C2 | 114.7(4) | C21 | C16 | S1 | 120.2(3) |
| C12 | C3 | C4 | 110.9(3) | C18 | C17 | C16 | 119.3(4) |
| N1 | C4 | C3 | 102.9(3) | C19 | C18 | C17 | 121.0(4) |
| C2 | C5 | C6 | 131.4(4) | C18 | C19 | C20 | 119.2(3) |
| C2 | C5 | F1 | 117.0(3) | C18 | C19 | C22 | 120.4(4) |
| F1 | C5 | C6 | 111.6(4) | C20 | C19 | C22 | 120.4(4) |
| C7 | C6 | C5 | 121.0(3) | C21 | C20 | C19 | 120.5(4) |
| C7 | C6 | C11 | 118.6(3) | C16 | C21 | C20 | 119.8(4) |
| C11 | C6 | C5 | 120.4(4) | C1 | N1 | C4 | 107.9(3) |
| C8 | C7 | C6 | 121.1(3) | C1 | N1 | S1 | 117.6(2) |
| C7 | C8 | C9 | 119.5(4) | C4 | N1 | S1 | 119.8(3) |
| C8 | C9 | Cl1 | 119.8(3) | N1 | S1 | C16 | 107.28(15) |
| C10 | C9 | C8 | 121.0(3) | O1 | S1 | C16 | 107.84(16) |
| C10 | C9 | Cl1 | 119.1(3) | O1 | S1 | N1 | 105.88(18) |
| C9 | C10 | C11 | 119.4(3) | O2 | S1 | C16 | 108.4(2) |
| C10 | C11 | C6 | 120.2(4) | O2 | S1 | N1 | 106.28(16) |
| C13 | C12 | C3 | 127.8(3) | O2 | S1 | O1 | 120.51(17) |

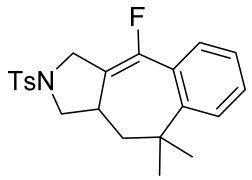
**Table 6 Hydrogen Atom Coordinates (Å×10$^4$) and Isotropic Displacement Parameters (Å$^2$×10$^3$) for exp_6623.**

| Atom | *x* | *y* | *z* | U(eq) |
|---|---|---|---|---|
| H1A | 2946 | 3557 | 7838 | 47 |
| H1B | 3456 | 3866 | 6889 | 47 |
| H3 | 1709 | 5352 | 6249 | 42 |
| H4A | 2995 | 6596 | 5710 | 44 |
| H4B | 2421 | 7517 | 6338 | 44 |
| H7 | 2483 | -68 | 4561 | 47 |
| H8 | 1712 | -1022 | 3293 | 55 |
| H10 | 297 | 1779 | 4527 | 60 |
| H11 | 1073 | 2779 | 5794 | 55 |
| H12 | 2397 | 4925 | 4274 | 46 |
| H14A | 496 | 5136 | 4488 | 80 |
| H14B | 668 | 6983 | 4304 | 80 |
| H14C | 893 | 6122 | 5401 | 80 |
| H15A | 1905 | 5283 | 2677 | 78 |
| H15B | 1245 | 6349 | 2622 | 78 |
| H15C | 1192 | 4443 | 2710 | 78 |
| H17 | 3862 | 8542 | 6069 | 46 |
| H18 | 4782 | 8456 | 4976 | 49 |
| H20 | 5660 | 5197 | 6946 | 59 |
| H21 | 4715 | 5149 | 7984 | 51 |
| H22A | 5771 | 6748 | 4403 | 99 |
| H22B | 6195 | 5889 | 5344 | 99 |
| H22C | 6171 | 7800 | 5278 | 99 |

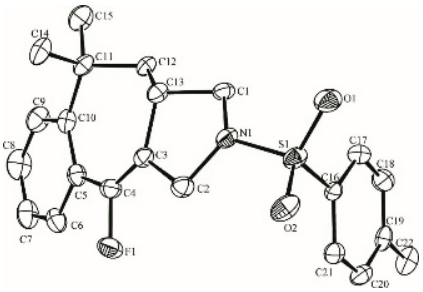
**Experimental**

Single crystals of $C_{22}H_{23}NO_2SFCl$ [exp_6623] were developped in a mixture solvent of hexane and ethyl acetate under temperature below 10℃. A suitable crystal was selected and diffracted on a SuperNova diffractometer. The crystal was kept at 180.00(10) K during data collection. Using Olex2 [1], the structure was solved with the Superflip [2] structure solution program using Charge Flipping and refined with the ShelXL [3] refinement package using Least Squares minimisation.

## X-ray Data of 5a (exp_6671).:




**5a**



Ellipsoids are drawn at 30% probability

**Table 1 Crystal data and structure refinement for exp_6671.**

| | |
|---|---|
| Identification code | exp_6671 |
| Empirical formula | $C_{22}H_{24}FNO_2S$ |
| Formula weight | 385.48 |
| Temperature/K | 180.01(10) |
| Crystal system | triclinic |
| Space group | P-1 |
| a/Å | 6.2637(9) |
| b/Å | 11.6536(11) |
| c/Å | 13.7124(15) |
| α/° | 72.602(9) |
| β/° | 87.821(10) |
| γ/° | 87.697(10) |
| Volume/Å$^3$ | 954.01(19) |
| Z | 2 |
| $\rho_{calc}$g/cm$^3$ | 1.342 |
| μ/mm$^{-1}$ | 0.196 |
| F(000) | 408.0 |
| Crystal size/mm$^3$ | 0.1 × 0.05 × 0.05 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 6.512 to 52.044 |
| Index ranges | -7 ≤ h ≤ 7, -14 ≤ k ≤ 11, -16 ≤ l ≤ 16 |
| Reflections collected | 5923 |
| Independent reflections | 3730 [$R_{int}$ = 0.0754, $R_{sigma}$ = 0.1044] |
| Data/restraints/parameters | 3730/0/247 |
| Goodness-of-fit on F$^2$ | 1.036 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0727, $wR_2$ = 0.1574 |
| Final R indexes [all data] | $R_1$ = 0.1100, $wR_2$ = 0.1979 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.34/-0.52 |

**Table 2 Fractional Atomic Coordinates (×10$^4$) and Equivalent Isotropic Displacement Parameters (Å$^2$×10$^3$) for exp_6671. $U_{eq}$ is defined as 1/3 of of the trace of the orthogonalised $U_{IJ}$ tensor.**

| Atom | *x* | *y* | *z* | U(eq) |
|---|---|---|---|---|
| C1 | 3100(5) | 4955(3) | 8524(2) | 36.3(8) |
| C2 | -488(5) | 4253(3) | 8602(2) | 39.9(8) |
| C3 | -101(5) | 5264(3) | 7638(2) | 35.0(8) |
| C4 | -1181(5) | 5374(3) | 6804(3) | 40.2(8) |
| C5 | -1065(5) | 6173(3) | 5735(2) | 40.5(8) |
| C6 | -2385(6) | 5884(4) | 5052(3) | 51.5(10) |
| C7 | -2441(7) | 6532(4) | 4033(3) | 63.6(12) |
| C8 | -1140(8) | 7481(5) | 3674(3) | 71.5(13) |
| C9 | 218(7) | 7791(4) | 4331(3) | 58.8(11) |
| C10 | 294(5) | 7167(3) | 5372(2) | 43.2(9) |
| C11 | 1721(5) | 7638(3) | 6041(2) | 41.5(8) |
| C12 | 2987(5) | 6603(3) | 6810(2) | 36.8(8) |
| C13 | 1773(5) | 5945(3) | 7773(2) | 37.3(8) |
| C14 | 263(6) | 8338(3) | 6613(3) | 53.8(10) |
| C15 | 3400(7) | 8489(4) | 5421(3) | 60.2(11) |
| C16 | 3100(5) | 1995(3) | 9454(2) | 32.3(7) |
| C17 | 5197(5) | 2076(3) | 9092(3) | 48.4(9) |
| C18 | 5941(5) | 1300(3) | 8553(3) | 50.7(10) |
| C19 | 4669(6) | 447(3) | 8379(2) | 41.9(9) |
| C20 | 2604(6) | 360(3) | 8775(2) | 43.1(8) |
| C21 | 1789(5) | 1145(3) | 9295(2) | 36.8(8) |
| C22 | 5519(7) | -363(3) | 7772(3) | 60.0(11) |
| F1 | -2758(3) | 4544.5(19) | 6937.5(15) | 53.0(6) |
| N1 | 1415(4) | 4251(2) | 9197.6(19) | 36.7(7) |
| O1 | 3748(4) | 3298(2) | 10635.4(18) | 57.2(7) |
| O2 | 119(4) | 2544(2) | 10602.7(16) | 49.5(7) |
| S1 | 2061.0(14) | 3019.2(8) | 10084.2(6) | 40.0(3) |

**Table 3 Anisotropic Displacement Parameters (Å$^2$×10$^3$) for exp_6671. The Anisotropic displacement factor exponent takes the form: -2π$^2$[h$^2$a*$^2$$U_{11}$+2hka*b*$U_{12}$+…].**

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|

| | | | | | | |
|---|---|---|---|---|---|---|
| C1 | 43.4(17) | 30.5(19) | 33.1(18) | -4.5(15) | -4.1(14) | -12.9(15) |
| C2 | 37.9(17) | 38(2) | 42(2) | -8.5(17) | 5.0(14) | -6.8(16) |
| C3 | 37.6(16) | 29.8(18) | 38.5(19) | -11.8(15) | 2.5(14) | -0.4(14) |
| C4 | 35.9(16) | 40(2) | 46(2) | -16.1(18) | 0.8(15) | -4.8(15) |
| C5 | 40.1(17) | 44(2) | 38.3(19) | -14.6(17) | -1.9(14) | 6.3(16) |
| C6 | 46.4(19) | 61(3) | 51(2) | -23(2) | -11.5(16) | 9.3(19) |
| C7 | 75(3) | 75(3) | 41(2) | -20(2) | -19(2) | 20(3) |
| C8 | 95(3) | 81(3) | 30(2) | -6(2) | -10(2) | 13(3) |
| C9 | 80(3) | 49(2) | 40(2) | -2.8(19) | -3.2(19) | 1(2) |
| C10 | 51(2) | 40(2) | 37(2) | -9.5(16) | -2.8(15) | 10.7(17) |
| C11 | 53(2) | 28.3(19) | 38.6(19) | -3.3(16) | 5.5(15) | -4.4(16) |
| C12 | 46.5(18) | 24.5(17) | 36.6(18) | -4.5(15) | 0.8(14) | -3.3(15) |
| C13 | 45.9(18) | 31.5(19) | 36.0(18) | -12.3(16) | -0.6(14) | -2.5(15) |
| C14 | 79(3) | 34(2) | 45(2) | -7.5(18) | -4.9(19) | 11(2) |
| C15 | 75(3) | 46(2) | 48(2) | 1(2) | 7(2) | -7(2) |
| C16 | 38.7(16) | 23.8(17) | 29.9(17) | -0.2(14) | -6.4(13) | -3.8(14) |
| C17 | 40.0(18) | 41(2) | 63(2) | -12.4(19) | -5.8(17) | -9.5(17) |
| C18 | 36.8(18) | 51(2) | 64(2) | -16(2) | -0.1(17) | 0.0(18) |
| C19 | 55(2) | 35(2) | 26.0(17) | 4.0(15) | -2.1(15) | 7.5(18) |
| C20 | 58(2) | 30.0(19) | 39.0(19) | -6.0(16) | -1.8(16) | -9.5(17) |
| C21 | 44.4(17) | 36(2) | 25.5(16) | -1.8(15) | -2.0(13) | -5.3(16) |
| C22 | 83(3) | 47(2) | 47(2) | -11.3(19) | 1(2) | 11(2) |
| F1 | 41(1) | 60.0(14) | 55.9(13) | -12.0(11) | -5.3(9) | -13.9(10) |
| N1 | 46.4(15) | 27.5(15) | 35.0(15) | -6.6(13) | -1.4(12) | -5.5(13) |
| O1 | 82.4(18) | 44.5(16) | 47.3(15) | -13.5(13) | -22.0(13) | -13.0(14) |
| O2 | 70.7(16) | 37.3(15) | 37.6(13) | -8.0(11) | 16.3(12) | -10.2(12) |
| S1 | 57.6(6) | 32.1(5) | 29.9(5) | -7.3(4) | -2.6(4) | -8.3(4) |

**Table 4 Bond Lengths for exp_6671.**

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| C1 | C13 | 1.536(4) | C11 | C12 | 1.556(4) |
| C1 | N1 | 1.477(4) | C11 | C14 | 1.543(4) |
| C2 | C3 | 1.504(4) | C11 | C15 | 1.524(5) |
| C2 | N1 | 1.470(4) | C12 | C13 | 1.508(4) |
| C3 | C4 | 1.322(4) | C16 | C17 | 1.383(4) |
| C3 | C13 | 1.490(4) | C16 | C21 | 1.383(4) |
| C4 | C5 | 1.484(5) | C16 | S1 | 1.763(3) |
| C4 | F1 | 1.379(4) | C17 | C18 | 1.386(5) |

| | | | | | |
|---|---|---|---|---|---|
| C5 | C6 | 1.395(5) | C18 | C19 | 1.378(5) |
| C5 | C10 | 1.420(5) | C19 | C20 | 1.379(5) |
| C6 | C7 | 1.375(5) | C19 | C22 | 1.504(4) |
| C7 | C8 | 1.358(6) | C20 | C21 | 1.390(4) |
| C8 | C9 | 1.395(6) | N1 | S1 | 1.628(3) |
| C9 | C10 | 1.396(5) | O1 | S1 | 1.425(3) |
| C10 | C11 | 1.531(5) | O2 | S1 | 1.430(2) |

**Table 5 Bond Angles for exp_6671.**

| Atom | Atom | Atom | Angle/˚ | Atom | Atom | Atom | Angle/˚ |
|---|---|---|---|---|---|---|---|
| N1 | C1 | C13 | 101.7(2) | C13 | C12 | C11 | 115.7(3) |
| N1 | C2 | C3 | 103.1(3) | C3 | C13 | C1 | 101.5(3) |
| C4 | C3 | C2 | 121.4(3) | C3 | C13 | C12 | 116.2(3) |
| C4 | C3 | C13 | 129.0(3) | C12 | C13 | C1 | 114.0(3) |
| C13 | C3 | C2 | 109.1(3) | C17 | C16 | S1 | 119.7(3) |
| C3 | C4 | C5 | 134.7(3) | C21 | C16 | C17 | 120.6(3) |
| C3 | C4 | F1 | 113.7(3) | C21 | C16 | S1 | 119.6(2) |
| F1 | C4 | C5 | 111.5(3) | C16 | C17 | C18 | 118.5(3) |
| C6 | C5 | C4 | 115.7(3) | C19 | C18 | C17 | 122.1(3) |
| C6 | C5 | C10 | 119.2(3) | C18 | C19 | C20 | 118.2(3) |
| C10 | C5 | C4 | 125.1(3) | C18 | C19 | C22 | 120.6(3) |
| C7 | C6 | C5 | 122.6(4) | C20 | C19 | C22 | 121.2(4) |
| C8 | C7 | C6 | 118.8(4) | C19 | C20 | C21 | 121.1(3) |
| C7 | C8 | C9 | 120.3(4) | C16 | C21 | C20 | 119.3(3) |
| C10 | C9 | C8 | 122.5(4) | C1 | N1 | S1 | 119.7(2) |
| C5 | C10 | C11 | 125.0(3) | C2 | N1 | C1 | 109.7(2) |
| C9 | C10 | C5 | 116.6(3) | C2 | N1 | S1 | 118.0(2) |
| C9 | C10 | C11 | 118.3(3) | N1 | S1 | C16 | 106.67(14) |
| C10 | C11 | C12 | 112.0(3) | O1 | S1 | C16 | 107.76(15) |
| C10 | C11 | C14 | 107.4(3) | O1 | S1 | N1 | 106.98(15) |
| C14 | C11 | C12 | 110.7(3) | O1 | S1 | O2 | 120.38(14) |
| C15 | C11 | C10 | 112.8(3) | O2 | S1 | C16 | 107.41(15) |
| C15 | C11 | C12 | 105.7(3) | O2 | S1 | N1 | 106.91(14) |
| C15 | C11 | C14 | 108.2(3) | | | | |

**Table 6 Hydrogen Atom Coordinates (Å×10$^4$) and Isotropic Displacement Parameters (Å$^2$×10$^3$) for exp_6671.**

| Atom | *x* | *y* | *z* | U(eq) |
|---|---|---|---|---|
| H1A | 3949 | 4461 | 8167 | 44 |
| H1B | 4068 | 5298 | 8912 | 44 |
| H2A | -1807 | 4408 | 8969 | 48 |
| H2B | -601 | 3477 | 8453 | 48 |
| H6 | -3281 | 5214 | 5299 | 62 |
| H7 | -3374 | 6320 | 3589 | 76 |
| H8 | -1156 | 7935 | 2972 | 86 |
| H9 | 1127 | 8451 | 4061 | 71 |
| H12A | 3486 | 6012 | 6455 | 44 |
| H12B | 4270 | 6943 | 7005 | 44 |
| H13 | 1264 | 6545 | 8128 | 45 |
| H14A | -400 | 9037 | 6118 | 81 |
| H14B | 1117 | 8609 | 7081 | 81 |
| H14C | -853 | 7812 | 7003 | 81 |
| H15A | 4300 | 8073 | 5025 | 90 |
| H15B | 4290 | 8746 | 5886 | 90 |
| H15C | 2690 | 9195 | 4955 | 90 |
| H17 | 6108 | 2651 | 9211 | 58 |
| H18 | 7375 | 1358 | 8295 | 61 |
| H20 | 1724 | -246 | 8690 | 52 |
| H21 | 345 | 1099 | 9539 | 44 |
| H22A | 5243 | 17 | 7046 | 90 |
| H22B | 4807 | -1134 | 8009 | 90 |
| H22C | 7062 | -498 | 7866 | 90 |

**Experimental**

Single crystals of $C_{22}H_{24}FNO_2S$ [exp_6671] were developped in a mixture solvent of hexane and ethyl acetate under temperature below 10℃. A suitable crystal was selected and diffracted on a SuperNova diffractometer. The crystal was kept at 180.01(10) K during data collection. Using Olex2 [1], the structure was solved with the Superflip [2] structure solution program using Charge Flipping and refined with the ShelXL [3] refinement package using Least Squares minimisation.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