Iridium-catalyzed *ortho*-selective carbon−hydrogen amidation of benzamides with sulfonyl azides in ionic liquid

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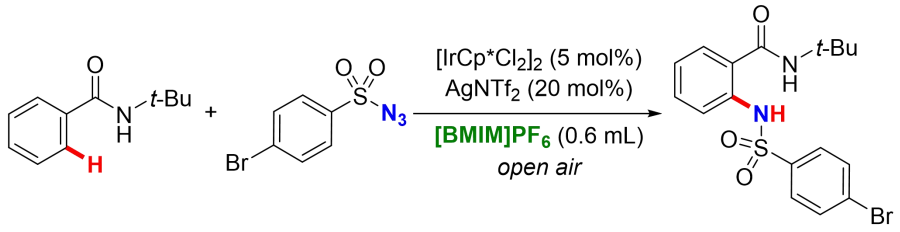
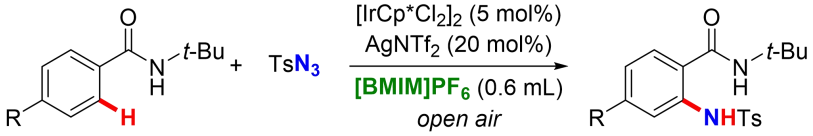
1 Optimization of the Reaction Conditions for Products 3ae, 3fa, 3ga, and 7aa



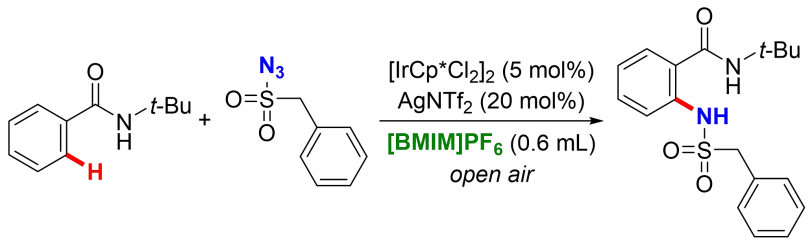
1a (1.0 equiv.) **2e** (1.5 equiv.) **3ae**

Entry	Temperature (°C)	Reaction Time	Isolated Yield (%)
1	40	8	23
2	60	8	86



1f–1g (1.0 equiv.) **2a** (1.5 equiv.)
3fa: R = Cl
3ga:R = Br

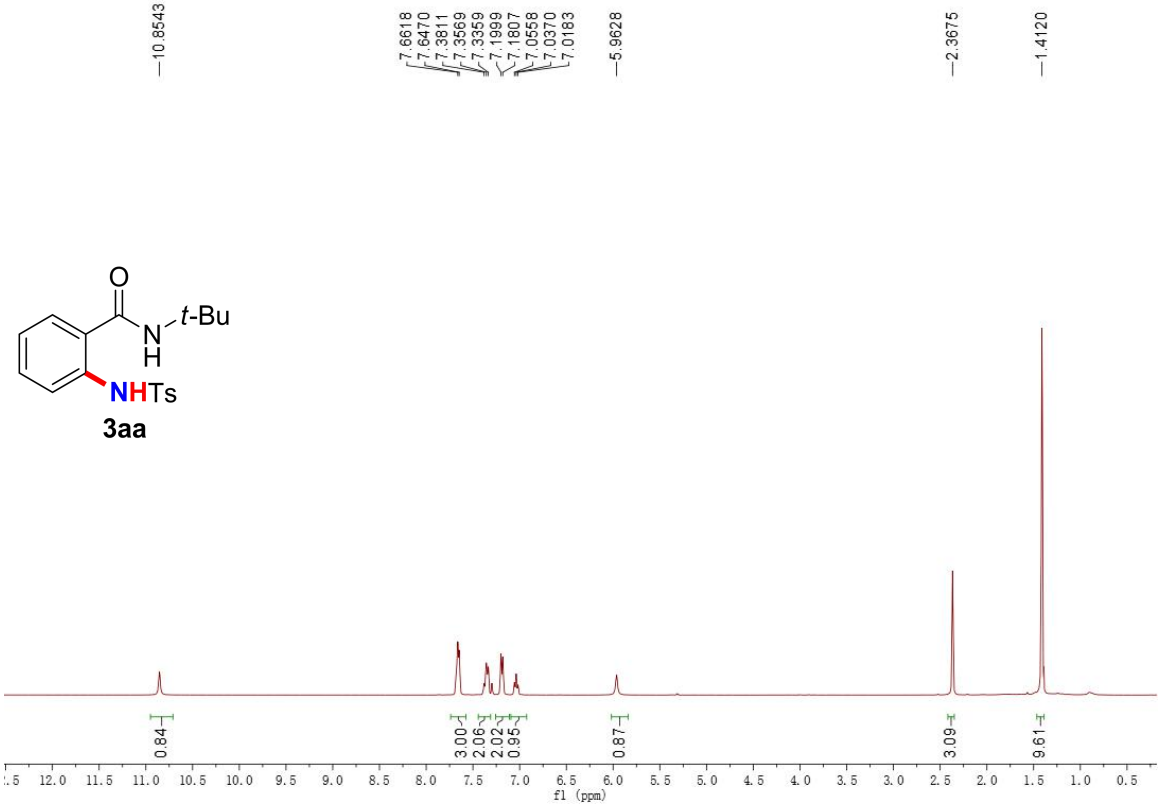
Entry	R	Temperature (°C)	Reaction Time	Isolated Yield (%)
1	4-Cl	40	24	32
2	4-Cl	40	30	37
3	4-Cl	60	8	45
4	4-Cl	80	8	75
5	4-Br	40	8	27
6	4-Br	40	30	30
7	4-Br	60	8	62



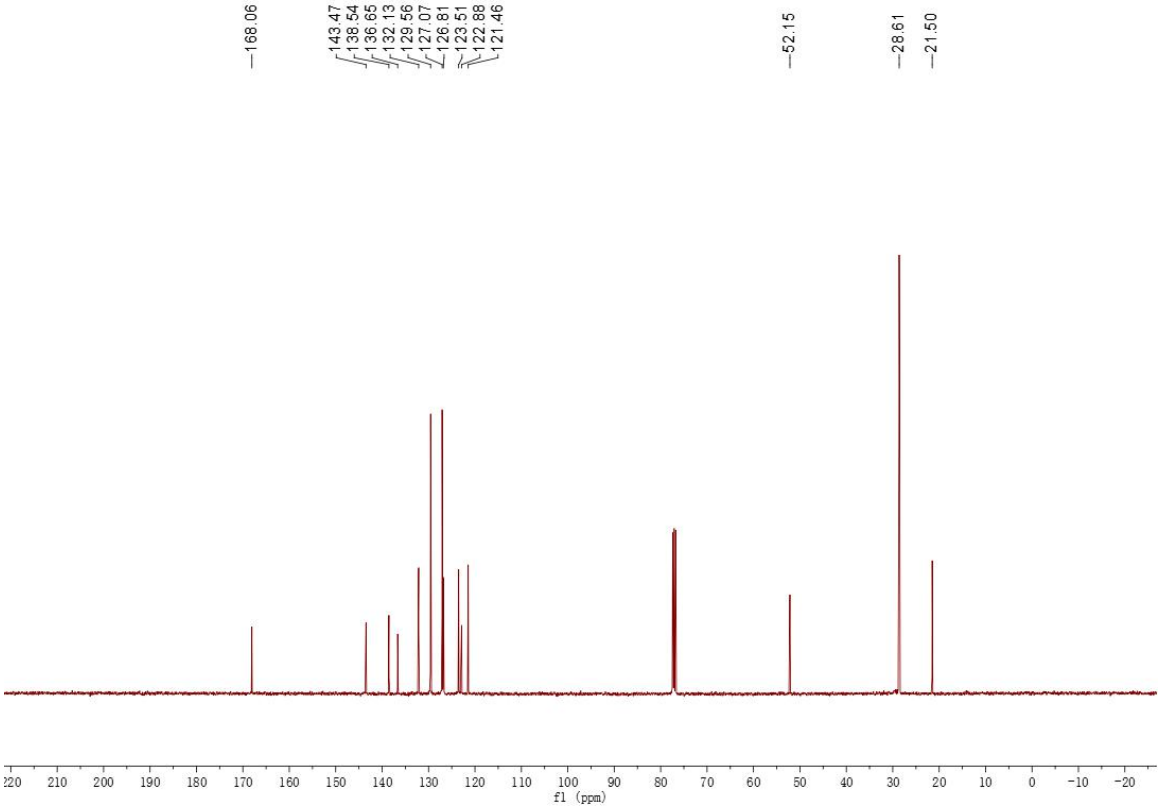
1a (1.0 equiv.) **6a** (1.5 equiv.) **7aa**

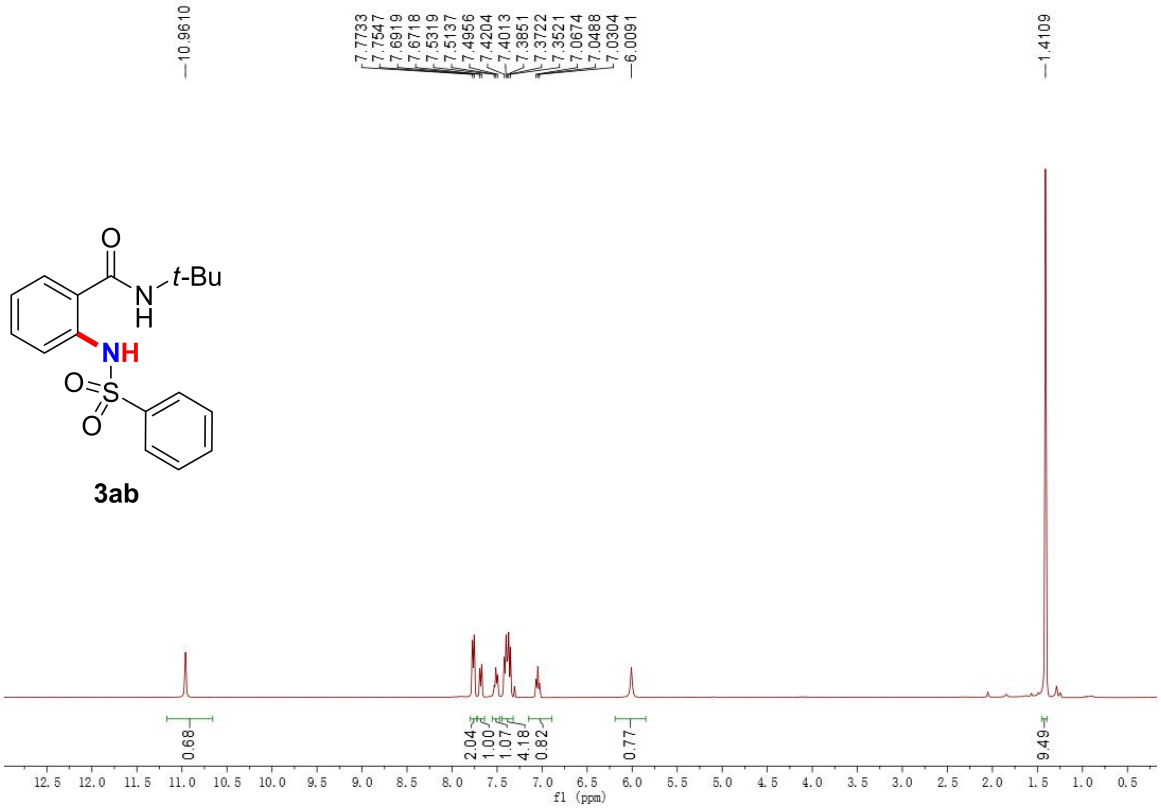
Entry	Temperature (°C)	Reaction Time	Isolated Yield (%)
1	40	8	32
2	60	8	90

2 ^{1}H, ^{13}C, and ^{19}F NMR Spectra of the Amidation Products



3aa

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7.3722
7.3521
7.0674
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7.0304
6.0091
1.4109
t-Bu
N
H
NH
O
S
O
O
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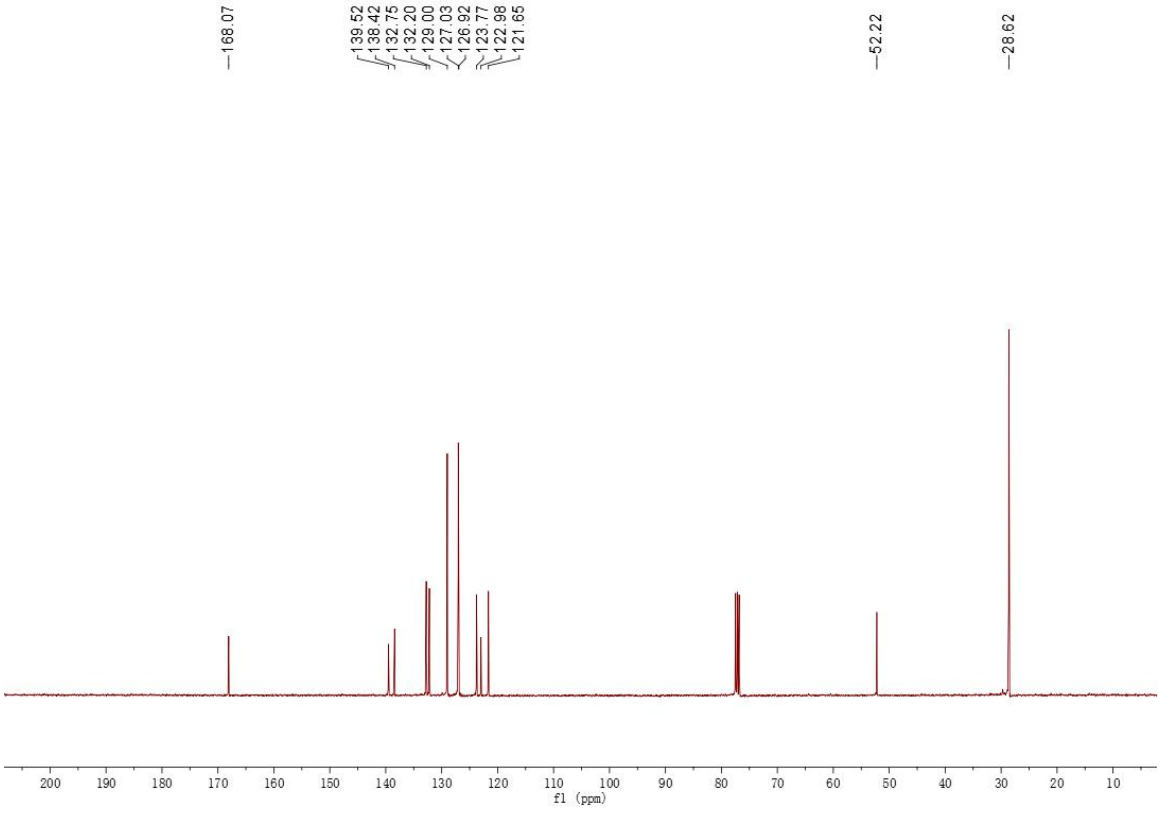
0.77
9.49
f1 (ppm)

3ab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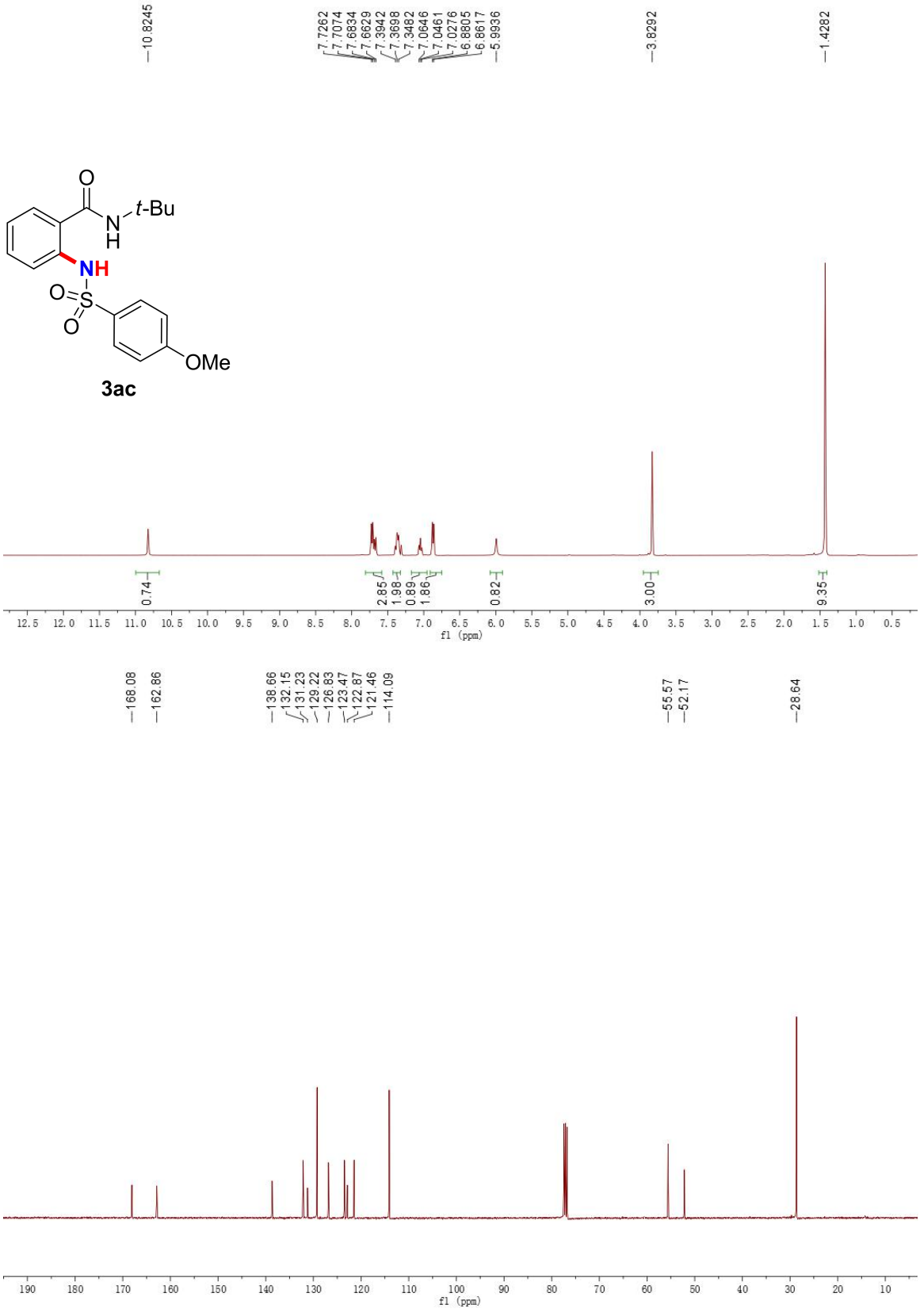
f1 (ppm)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6.8617
5.9936
3.8292
1.4282
O
N
H
t-Bu
NH
O
S
O
OMe
3ac
0.74
2.85
1.98
0.89
1.86
0.82
3.00
9.35
f1 (ppm)
168.08
162.86
138.66
132.15
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129.22
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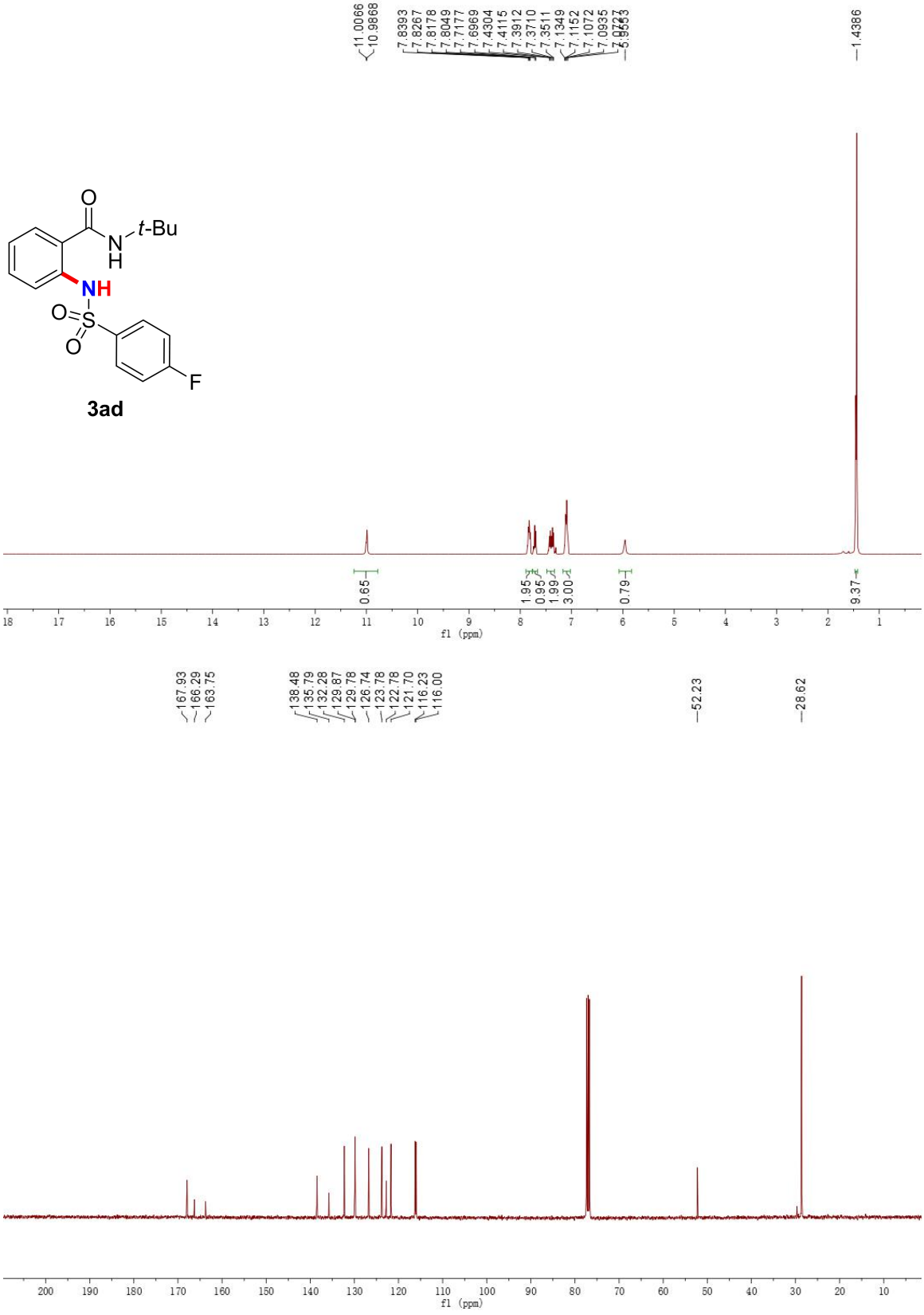
f1 (ppm)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7.3511
7.1349
7.1152
7.1072
7.0935
1.4386
O
N
H
t-Bu
NH
O
S
O
F
3ad
0.65
1.95
0.95
1.99
3.00
0.79
9.37
f1 (ppm)
167.93
166.29
163.75
138.48
135.79
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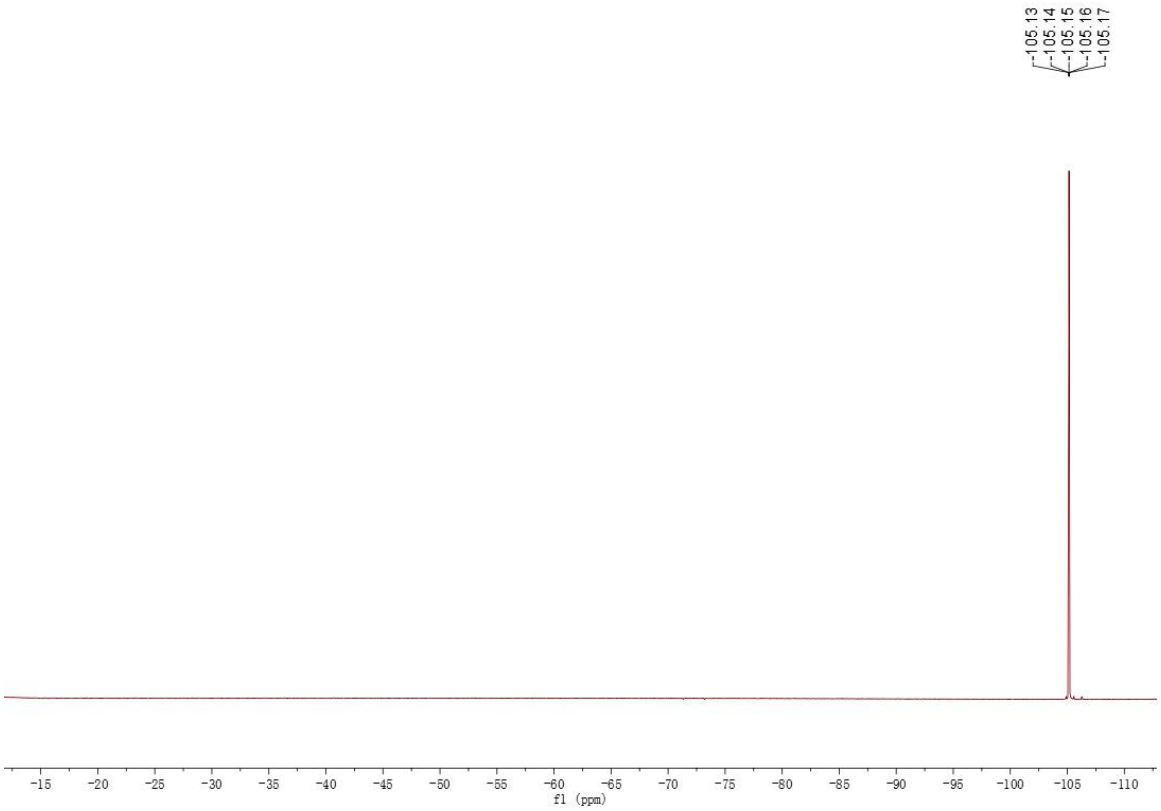
f1 (ppm)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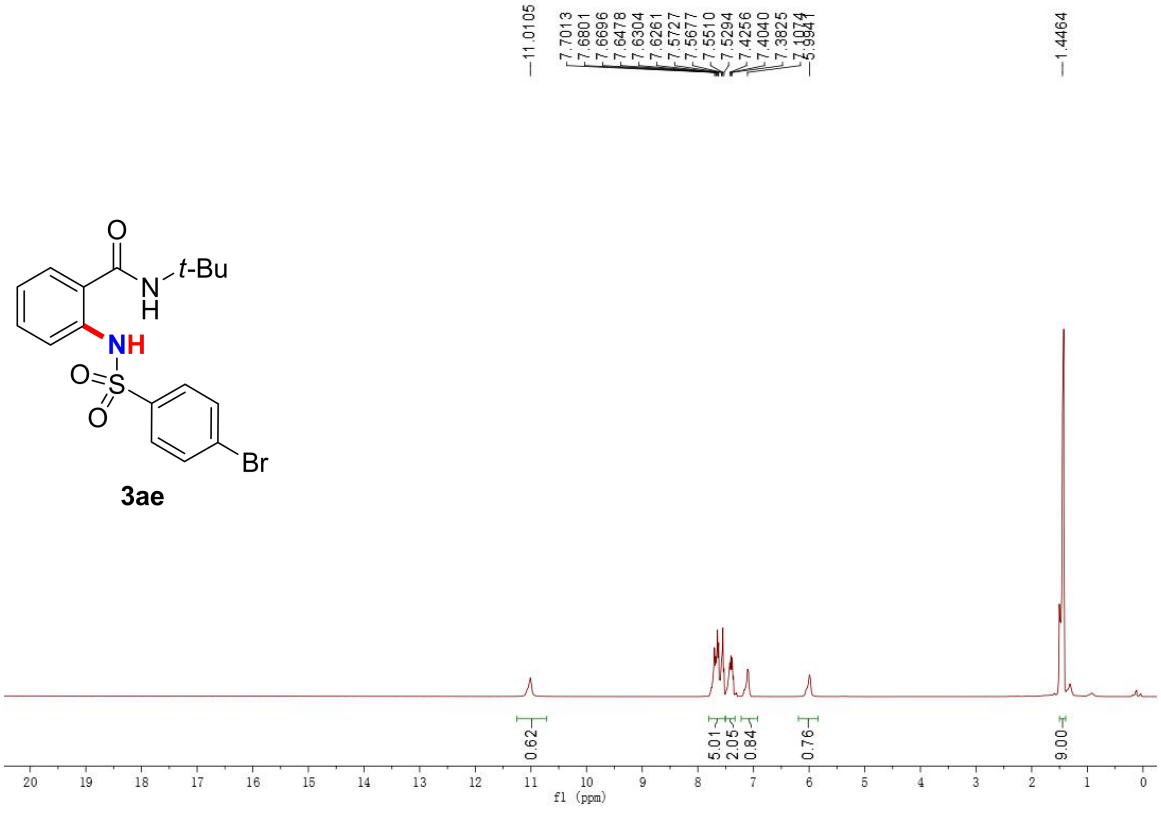
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7.3825
7.1074
5.3941
1.4464
0.62
5.01
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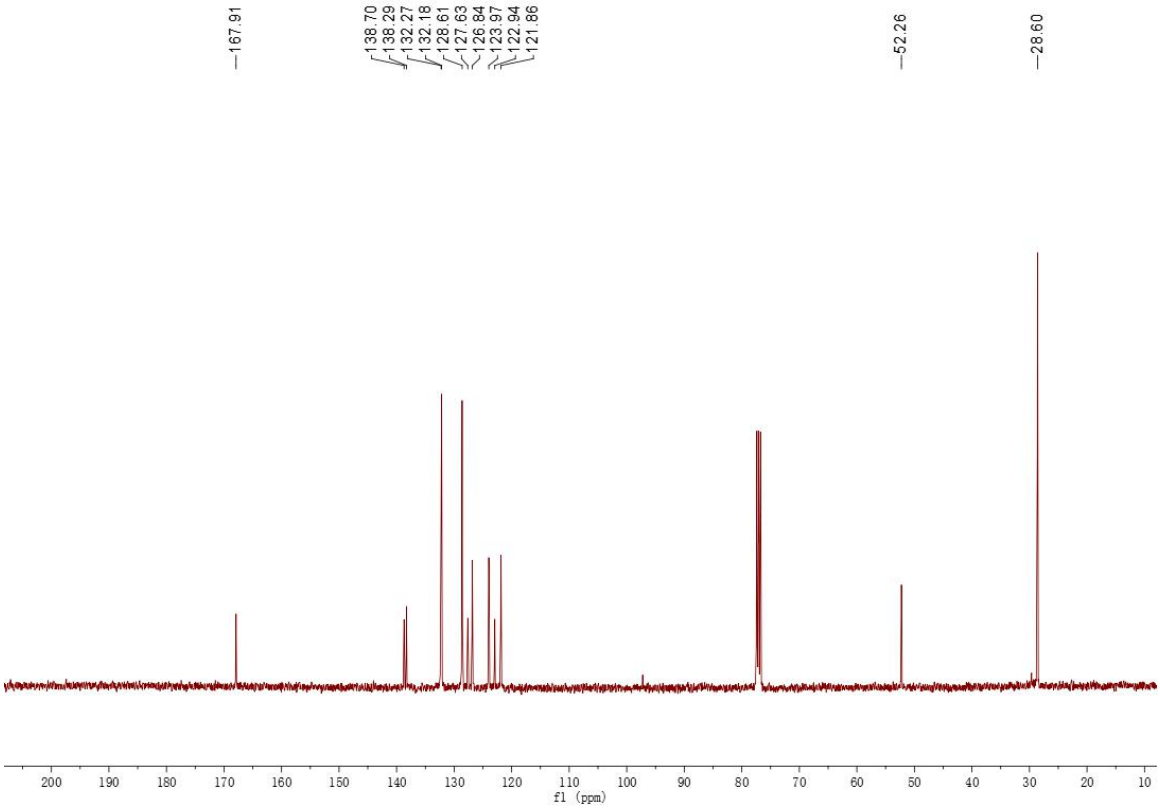
9.00
f1 (ppm)

O
N
H
t-Bu
NH
O
S
O
Br

3ae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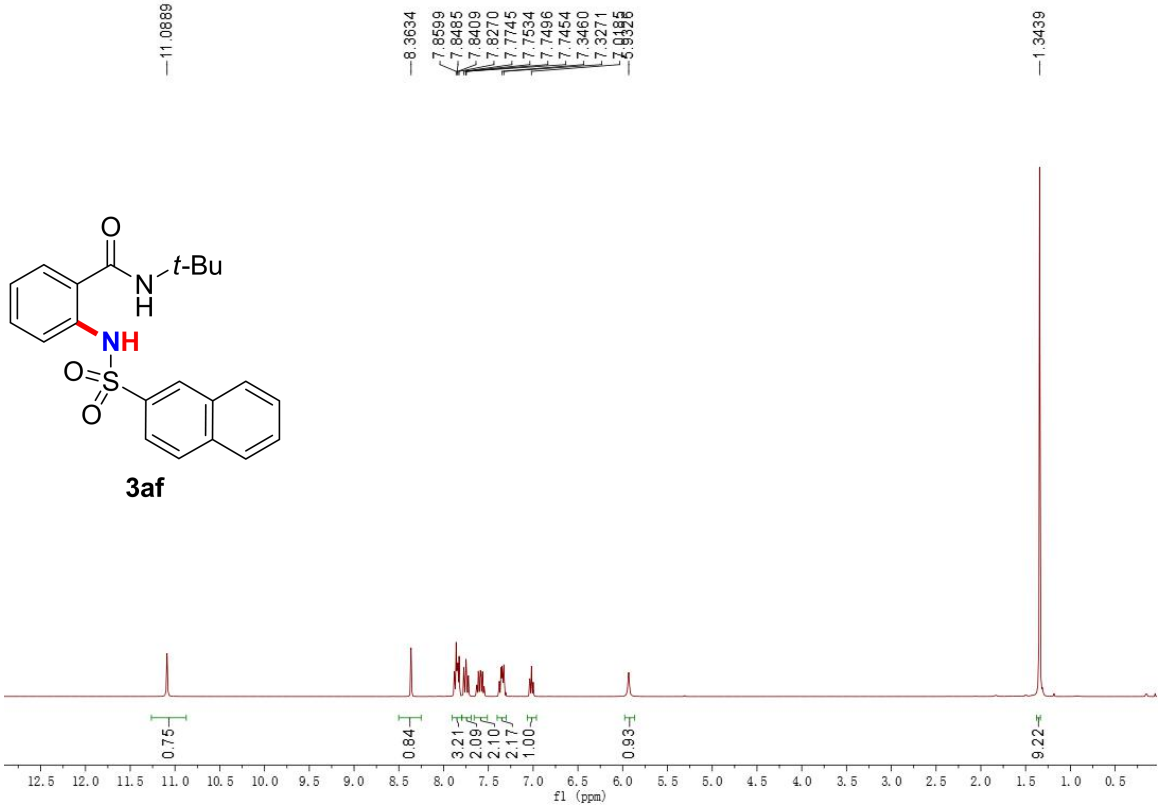
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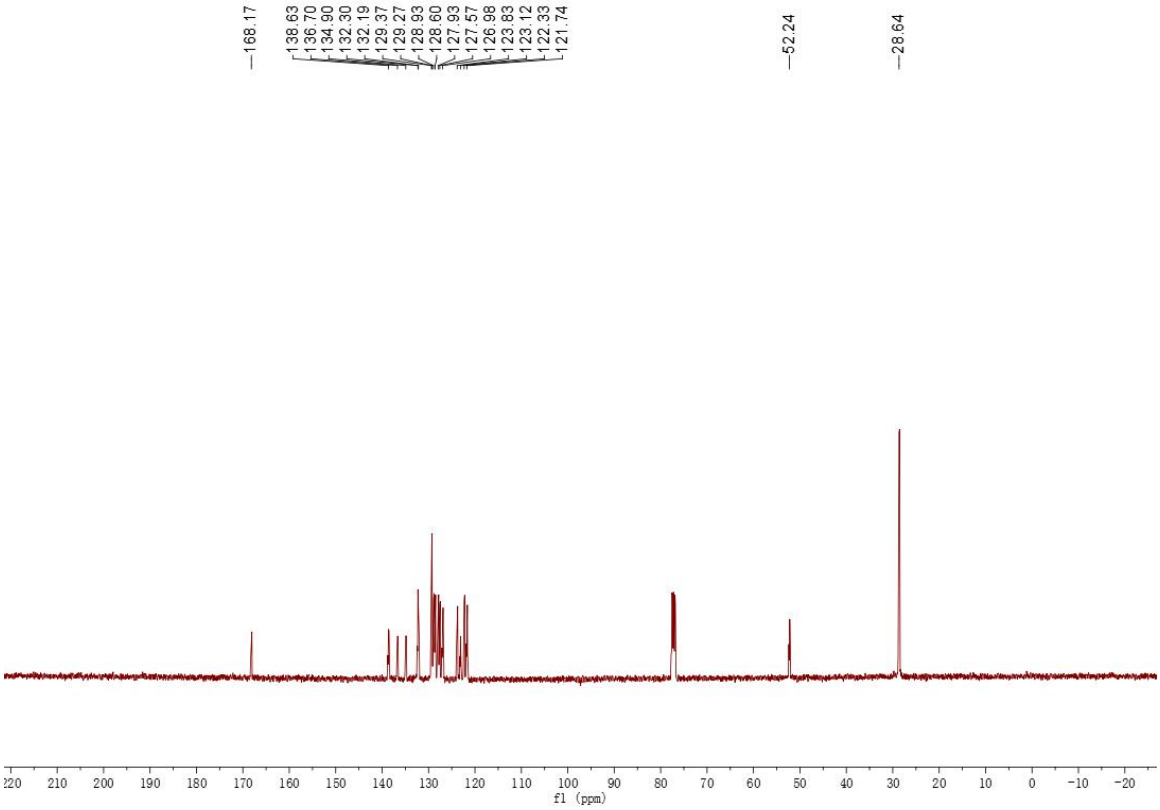
7.7454
7.3460
7.3271
1.3439
0.75
0.84
3.21
2.09
2.10
2.17
1.00
0.93
9.22
f1 (ppm)

O
N
H
t-Bu
NH
O
S
O

3af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122.33
121.74
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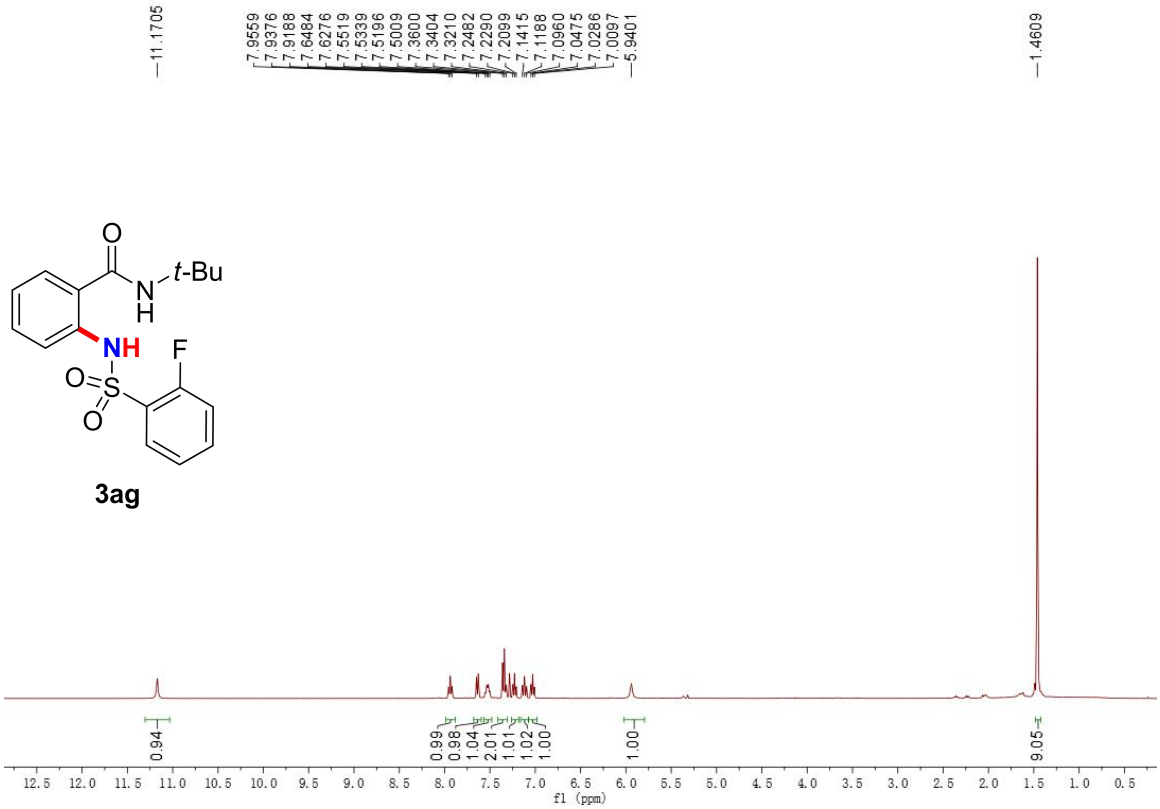
28.64
f1 (ppm)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7.0286
7.0097
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0.99
0.98
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2.01
1.01
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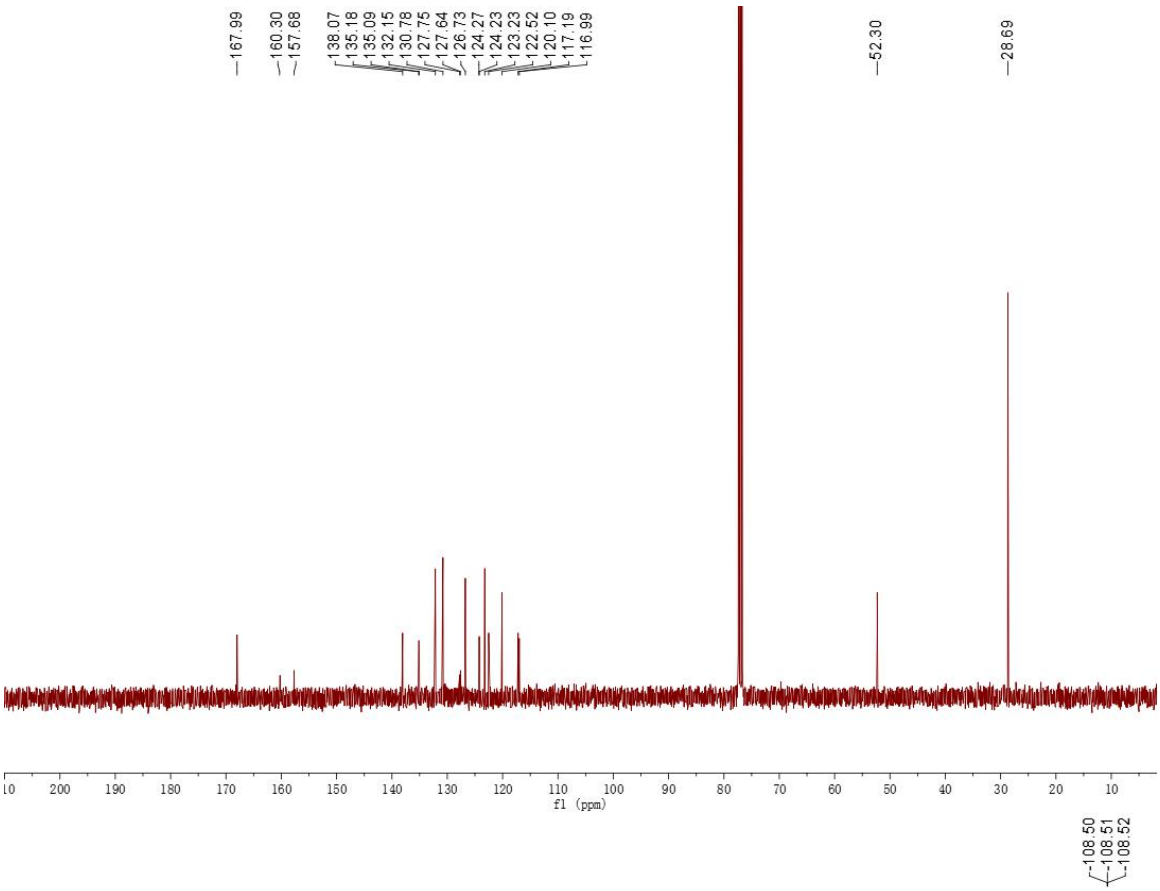
f1 (ppm)

O
N
H
t-Bu
NH
F
O
S
O

3ag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116.99
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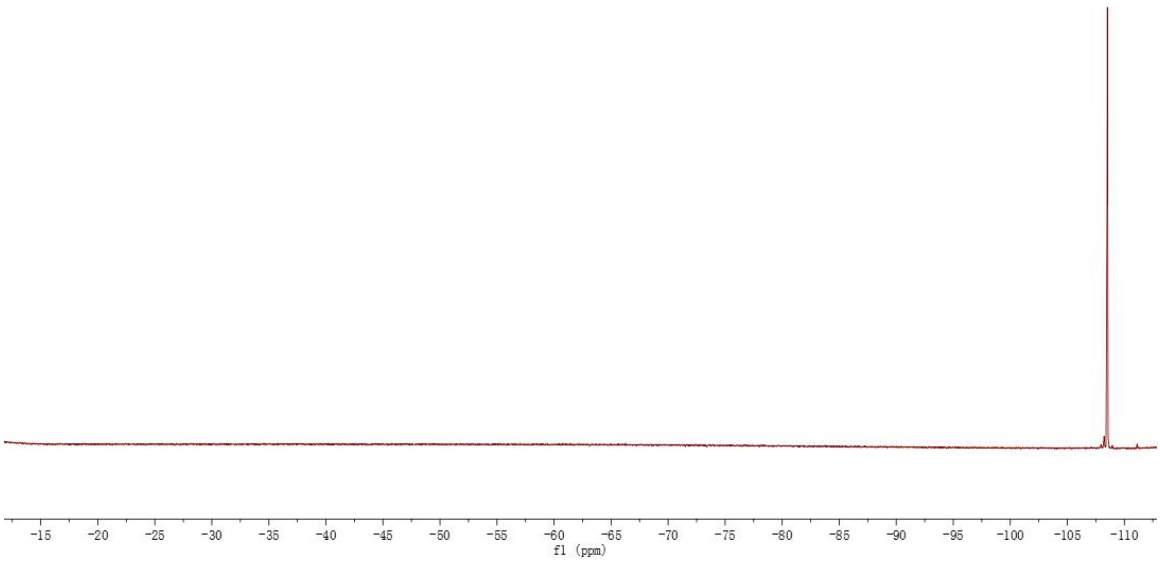
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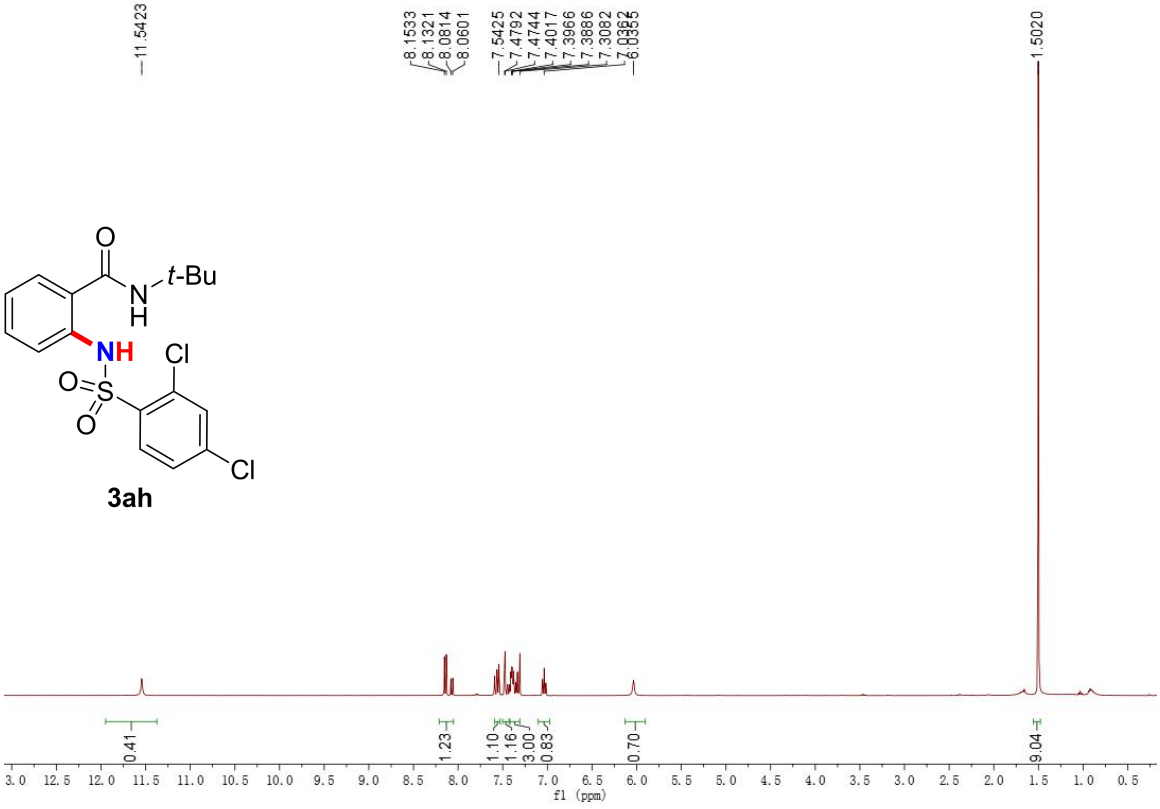
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O
N
H
t-Bu
NH
Cl
O
S
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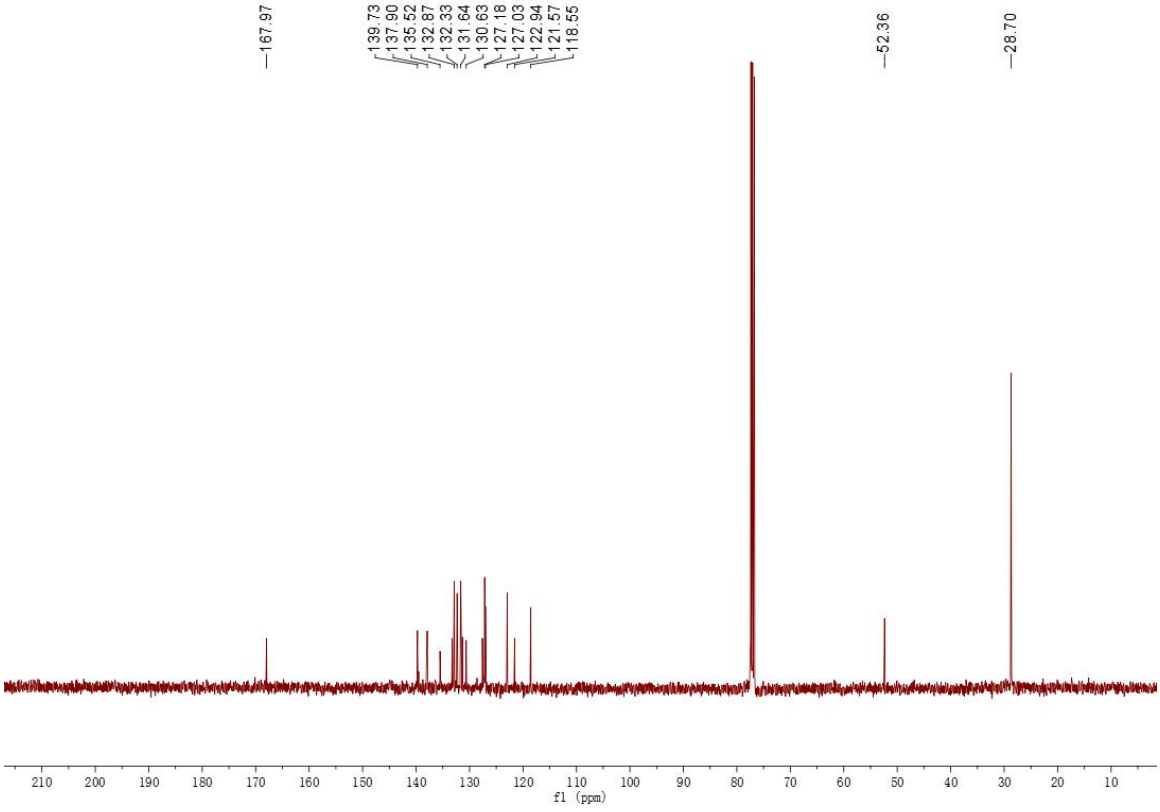
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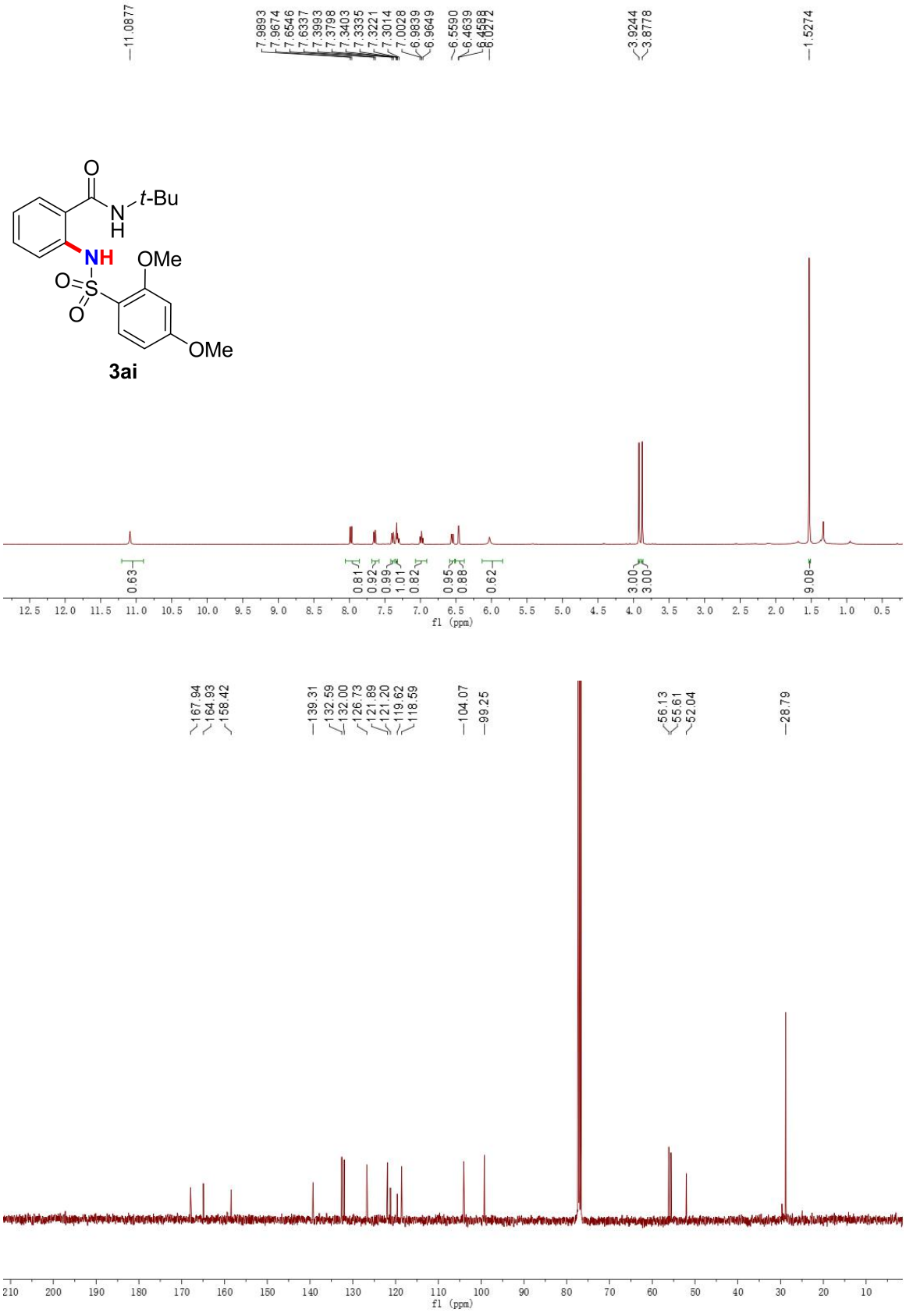
f1 (ppm)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6.5590
6.4639
6.4588
6.0212
3.9244
3.8778
1.5274
t-Bu
N
H
NH
OMe
O
S
O
OMe
3ai
0.63
0.81
0.92
0.99
1.01
0.82
0.95
0.88
0.62
3.00
3.00
9.08
f1 (ppm)
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132.00
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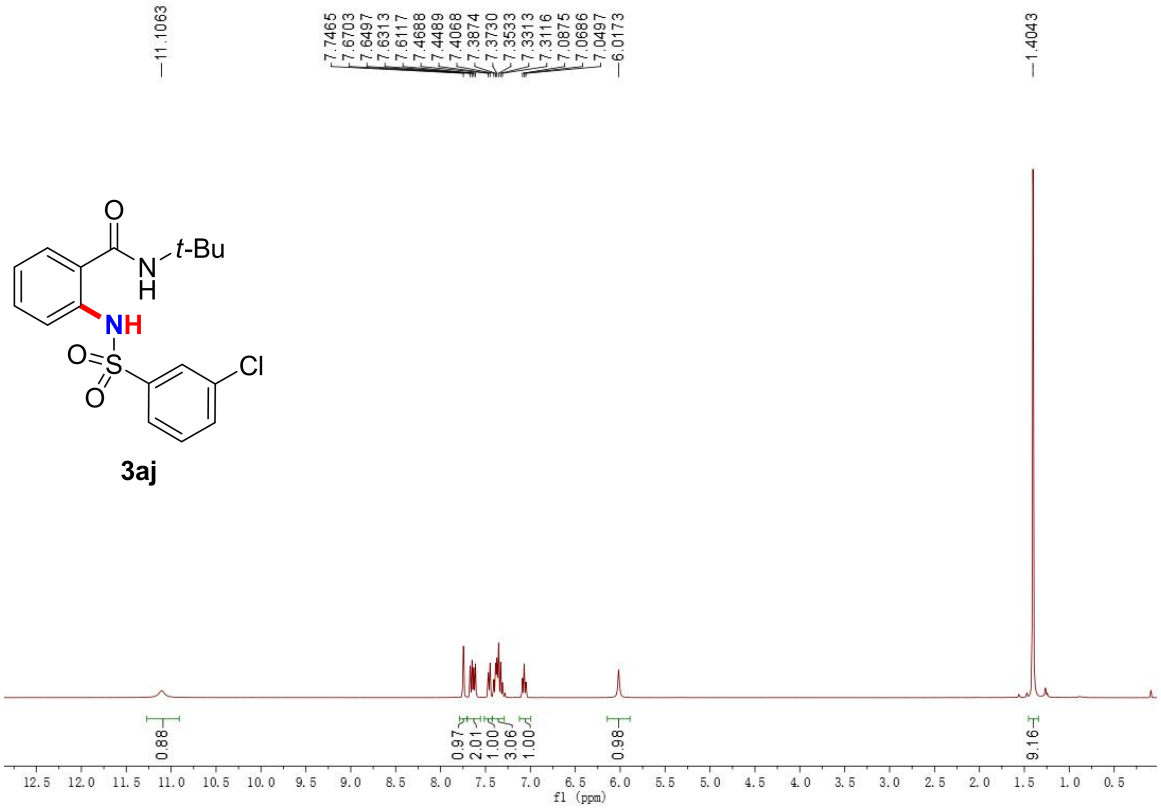
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H
t-Bu
NH
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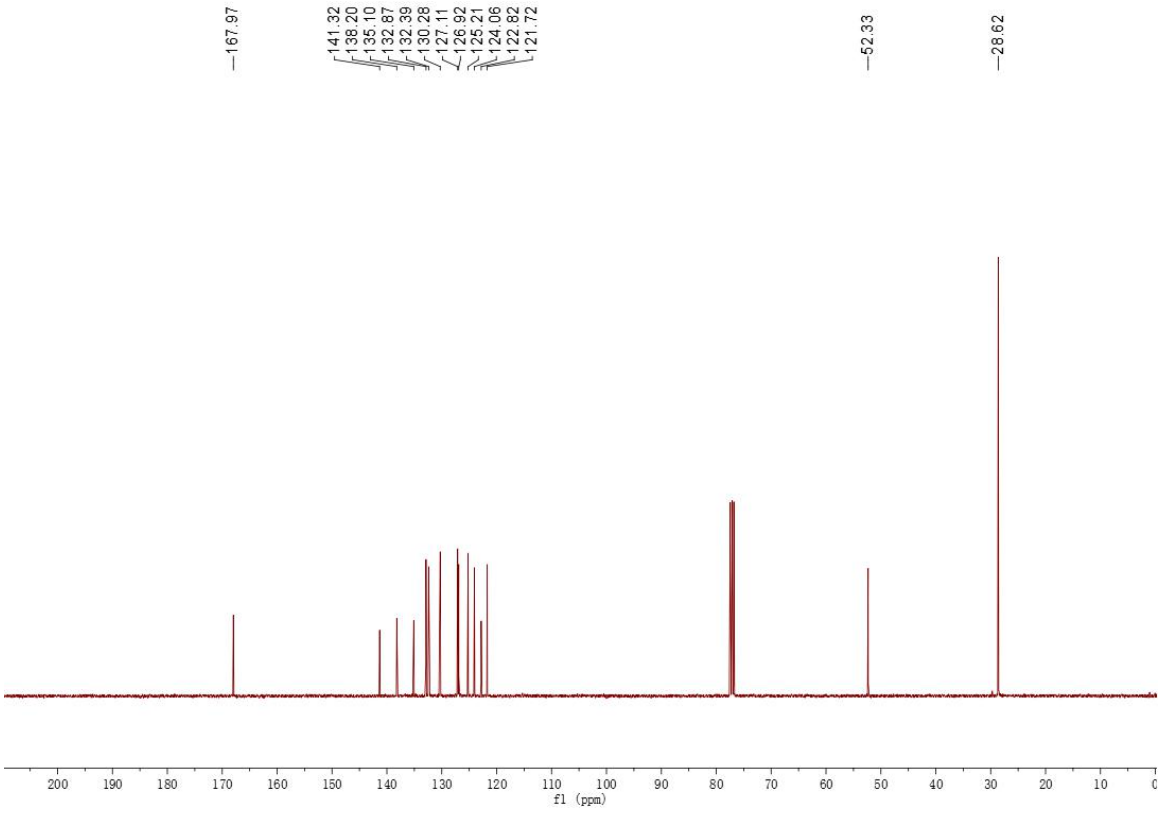
3aj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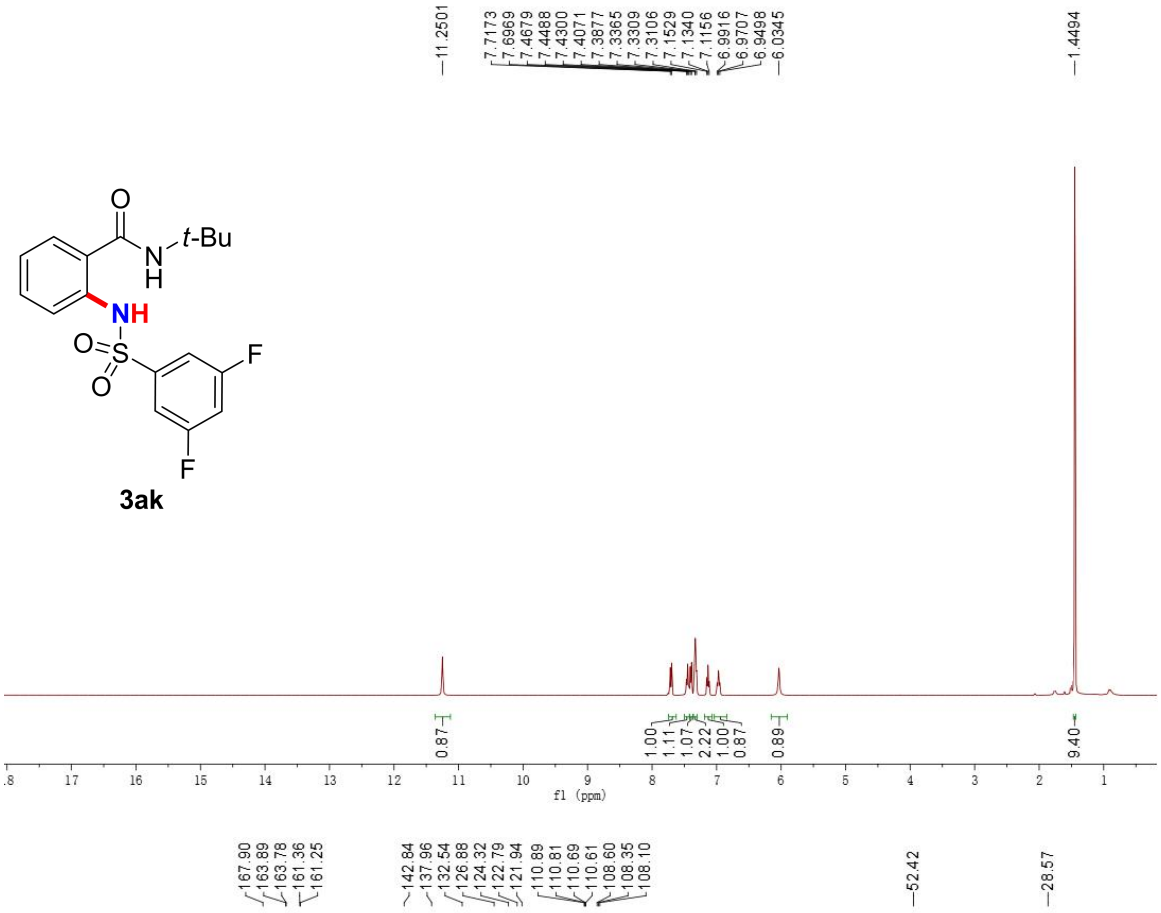
28.62
f1 (ppm)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1.4494
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N
H
t-Bu
NH
O
S
O
F
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9.40
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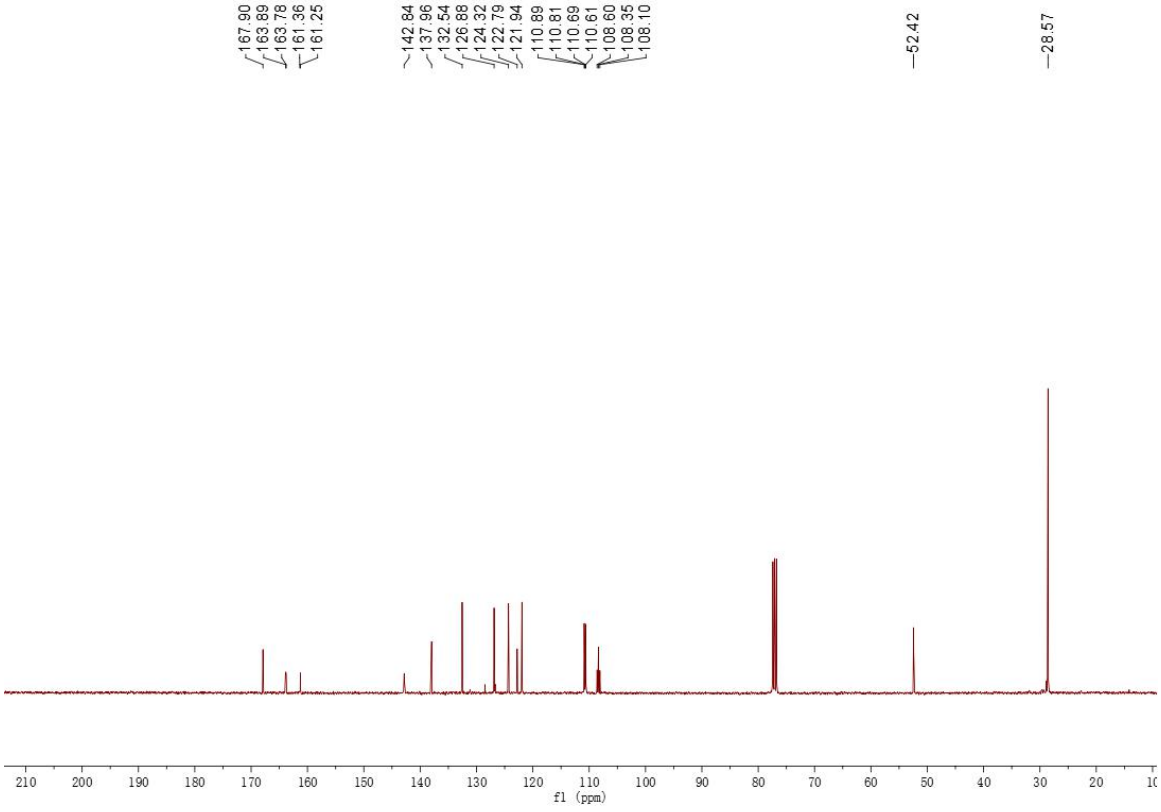
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28.57
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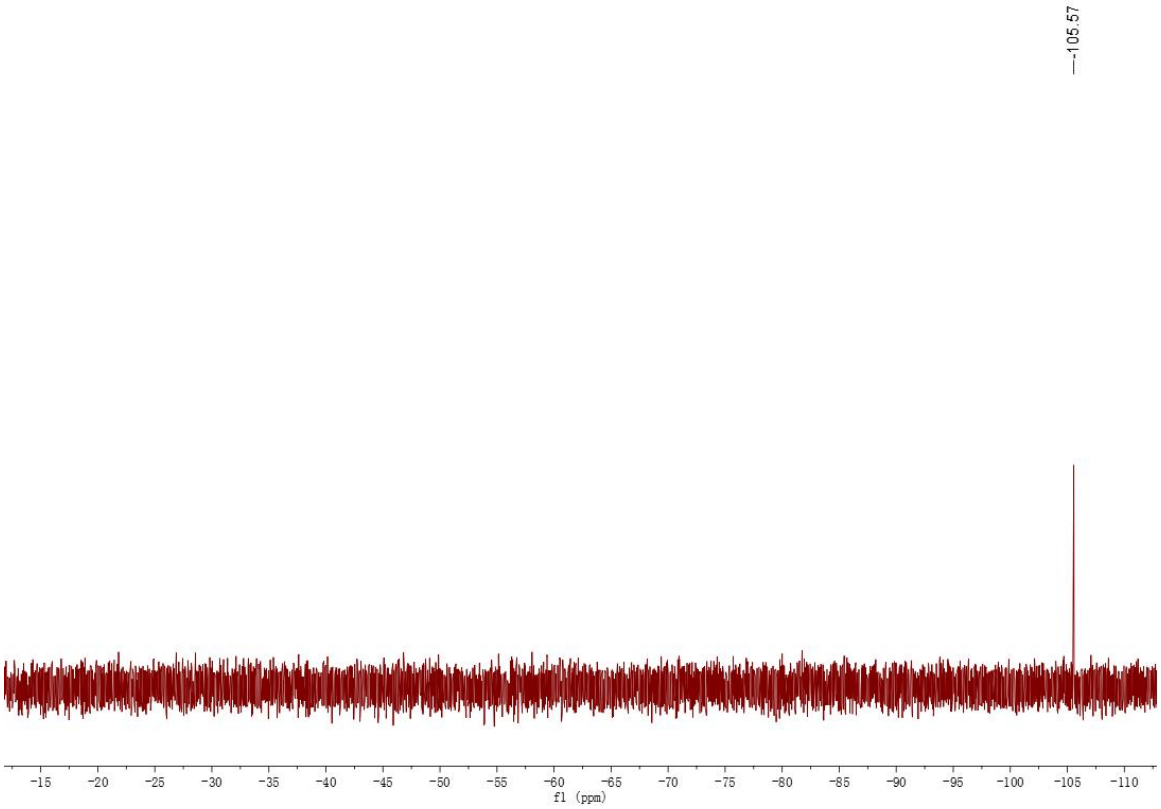
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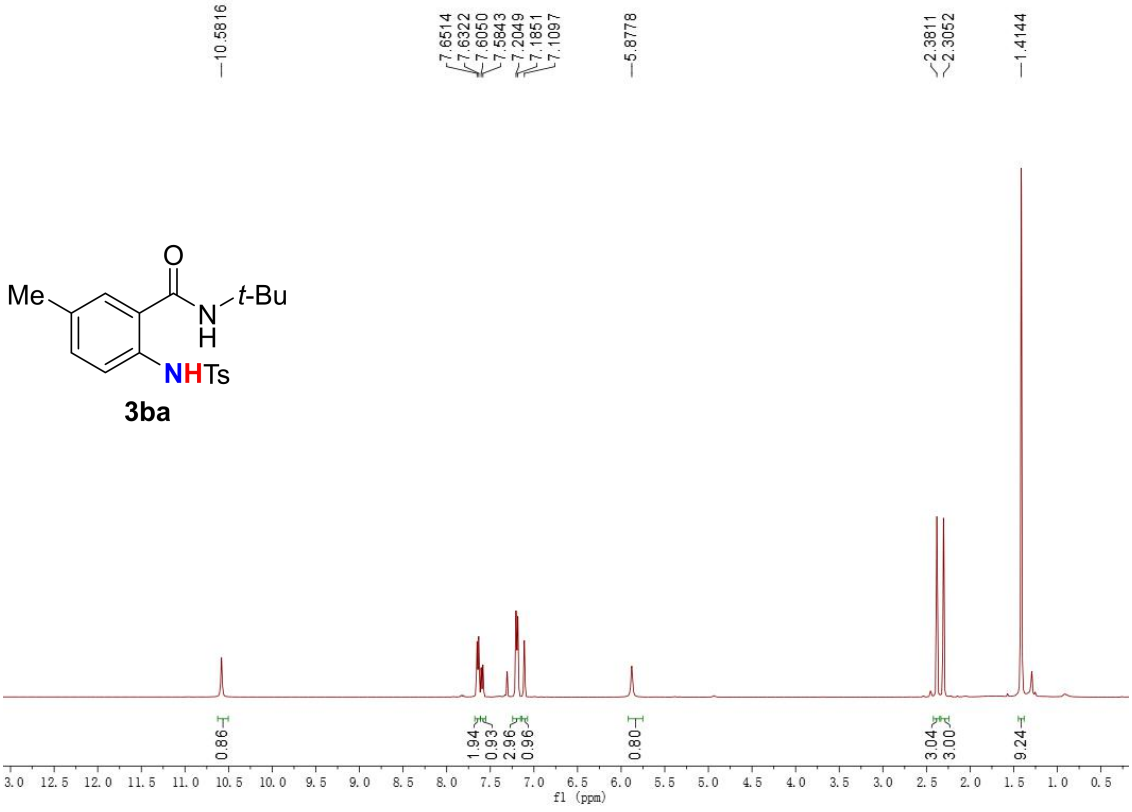
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7.1097
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2.3052
1.4144
0.86
1.94
0.93
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0.96
0.80
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3.00
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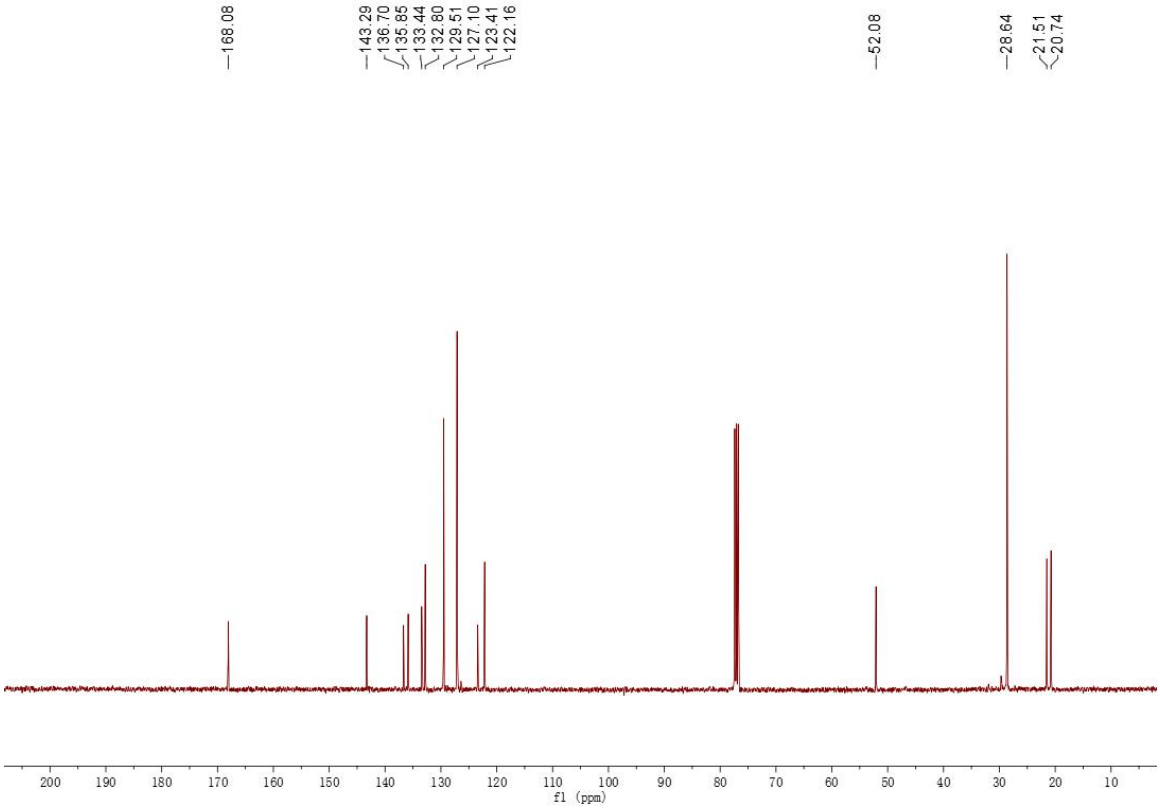
f1 (ppm)

O
Me
N
H
t-Bu
NHTs

3ba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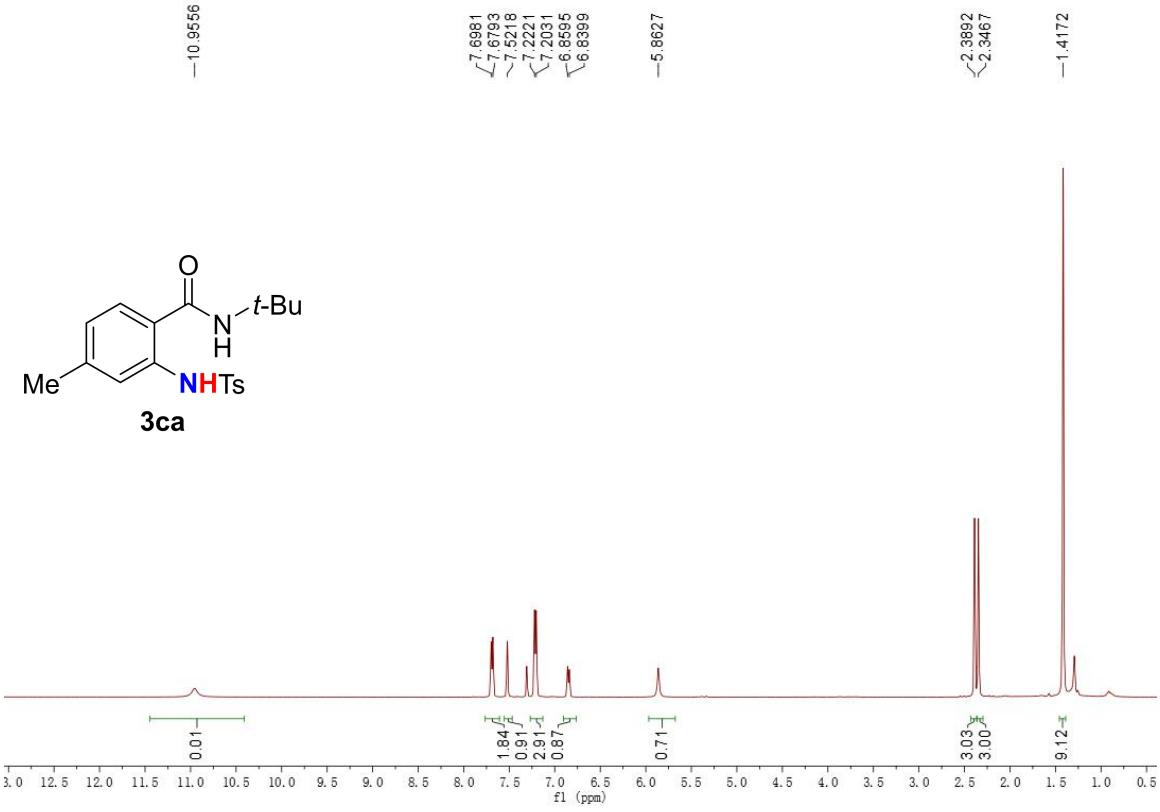
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1.4172
0.01
1.84
0.91
2.91
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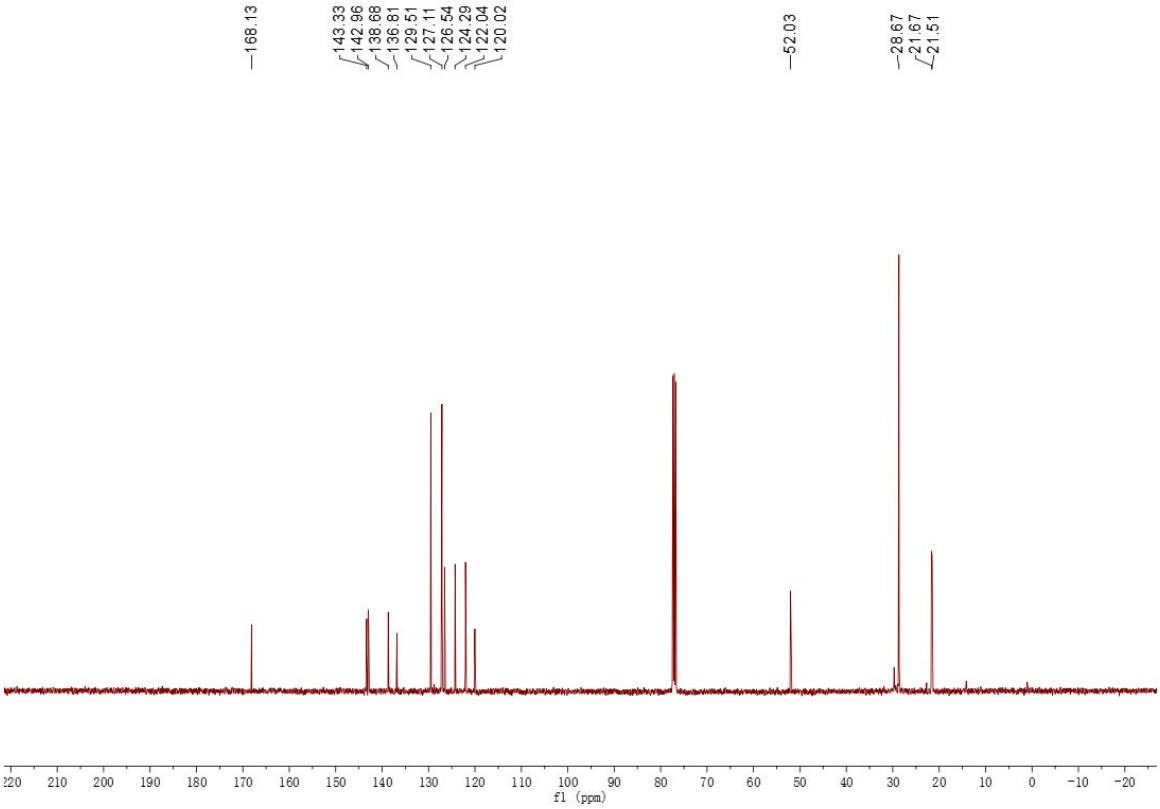
f1 (ppm)

O
N
H
t-Bu
Me
NHTs

3ca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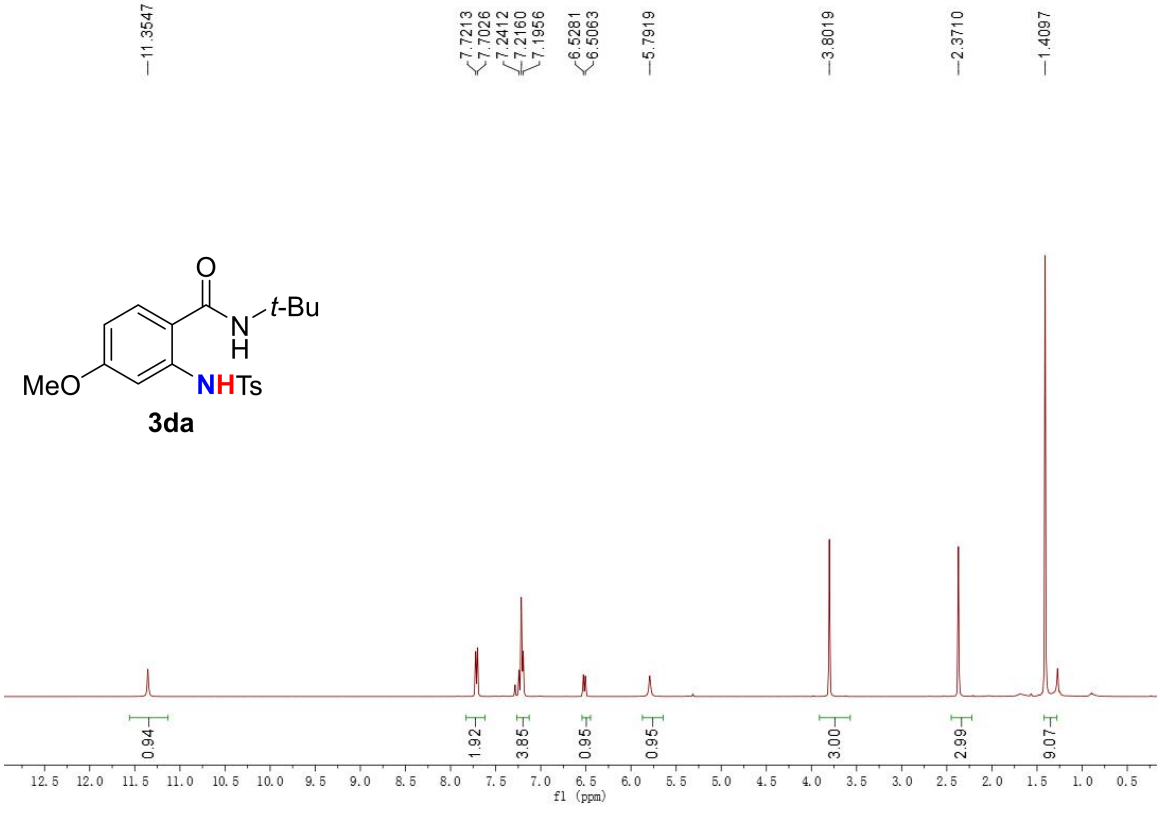
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1.4097
0.94
1.92
3.85
0.95
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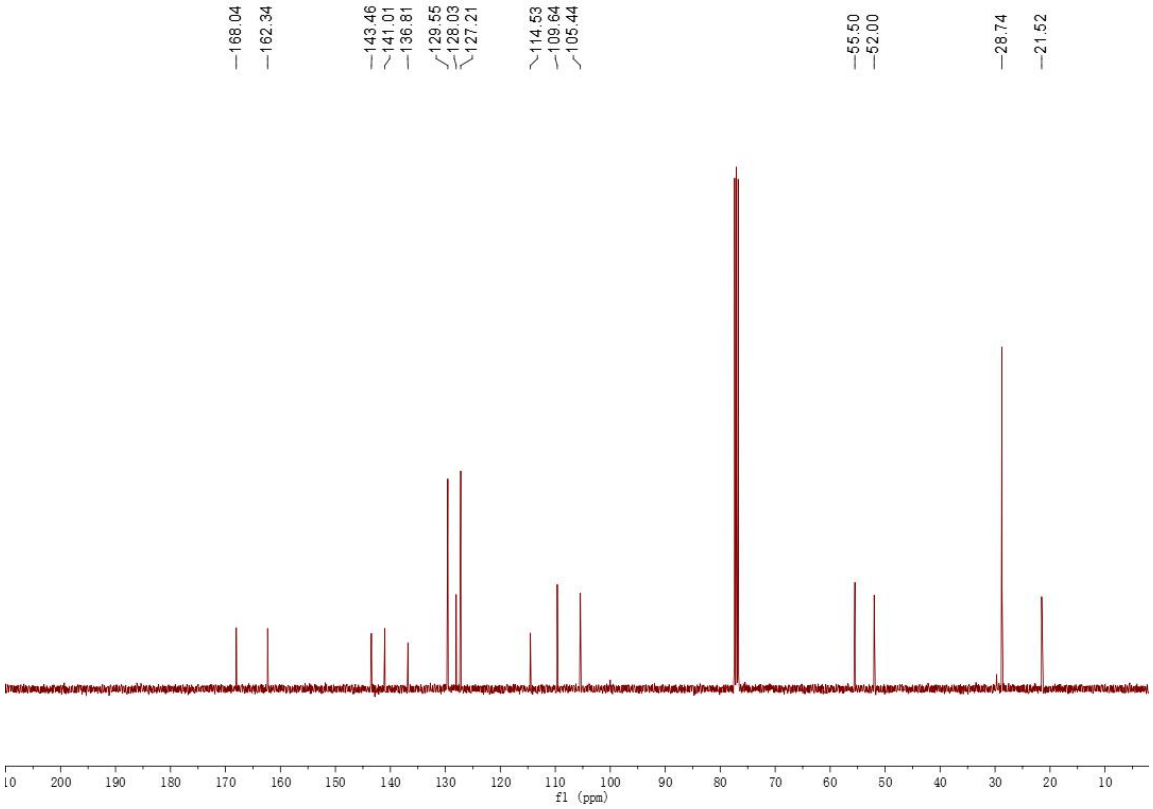
9.07
f1 (ppm)

O
N
H
t-Bu
MeO
NHTs

3da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143.46
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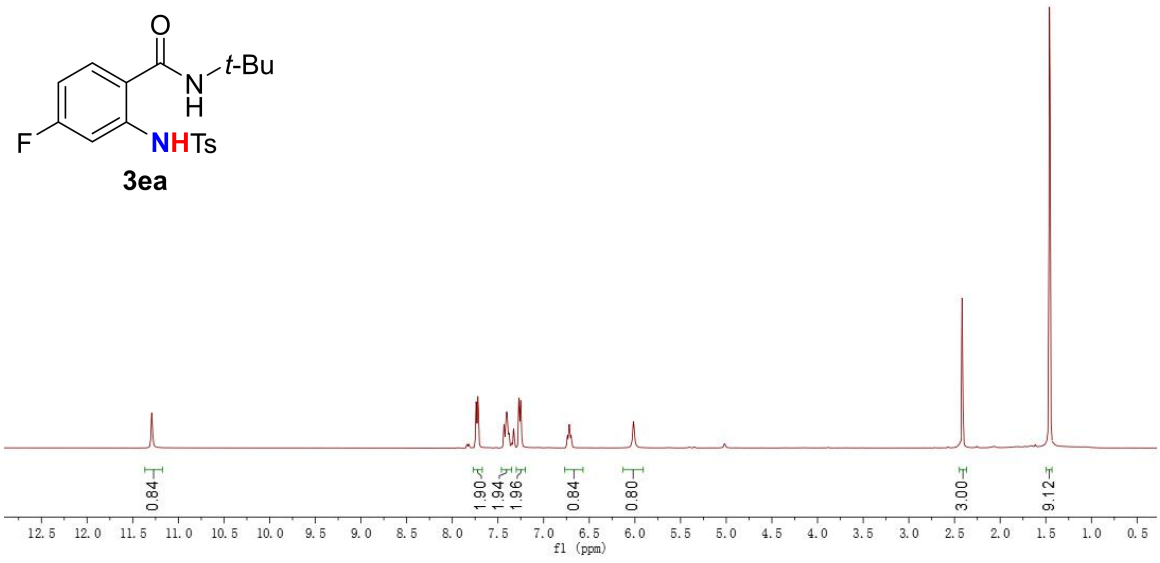
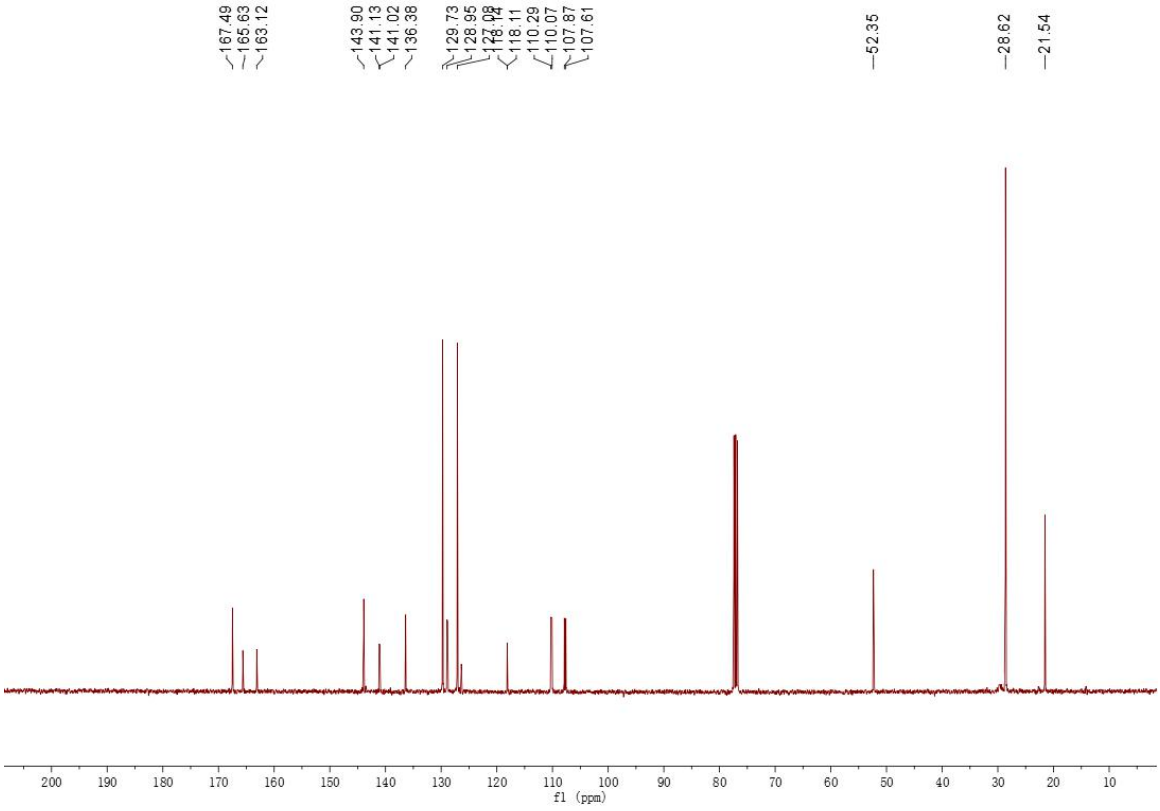
136.81
129.55
128.03
127.21
114.53
109.64
105.44
55.50
52.00
28.74
21.52
f1 (ppm)

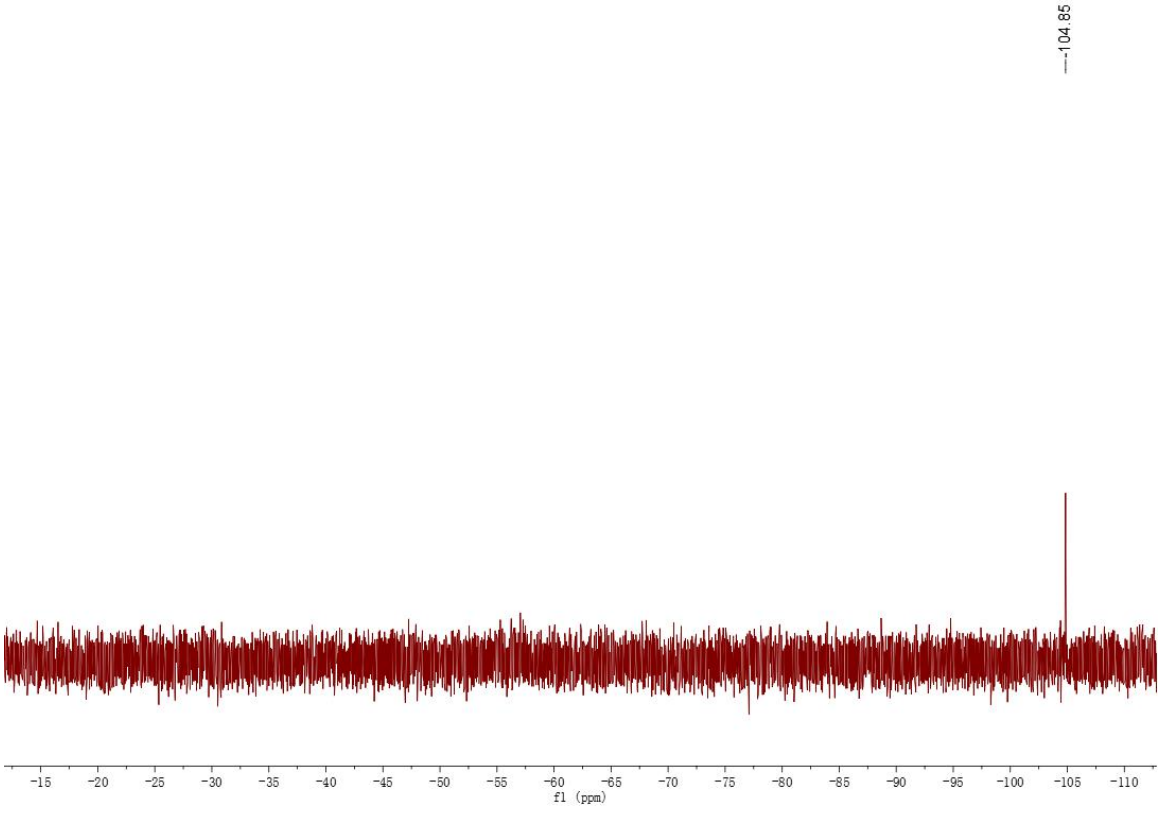

11.2913
7.7391
7.7205
7.4332
7.4046
7.3980
7.3807
7.2695
7.2508
6.7391
6.7189
6.6990
6.0149
2.4167
1.4599

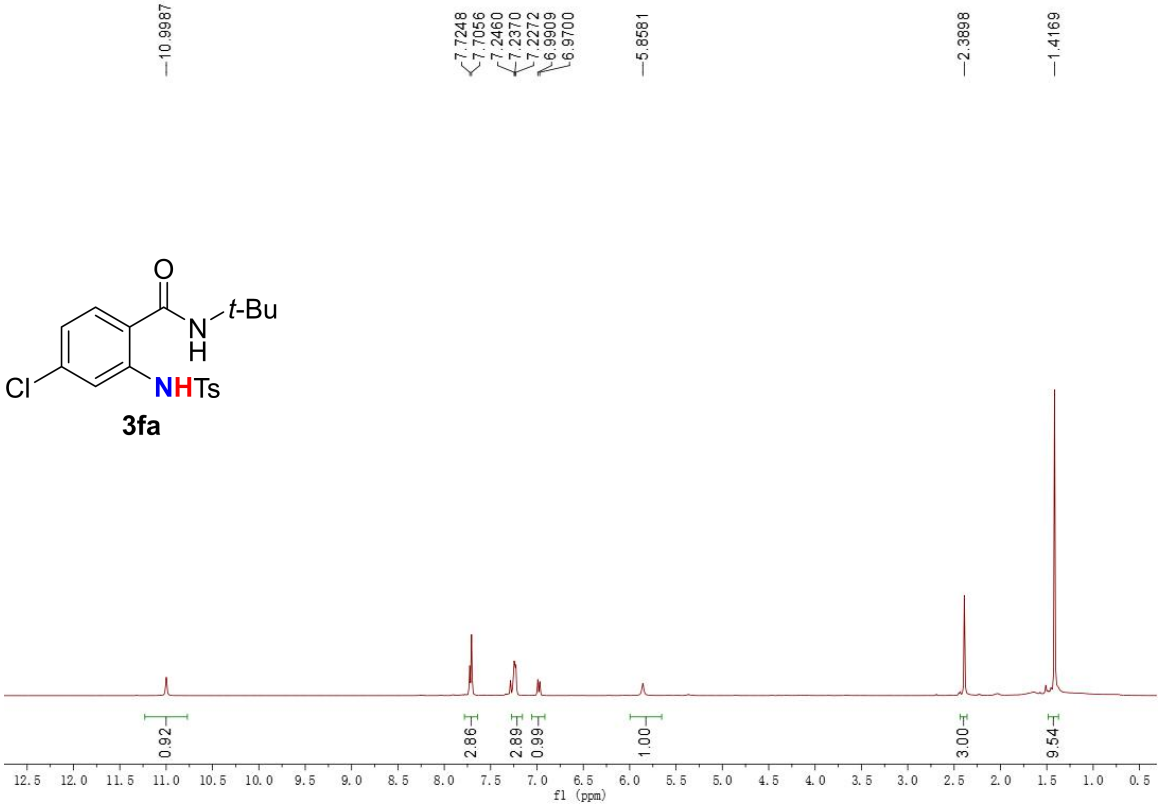
O
N
H
t-Bu
F
NHTs

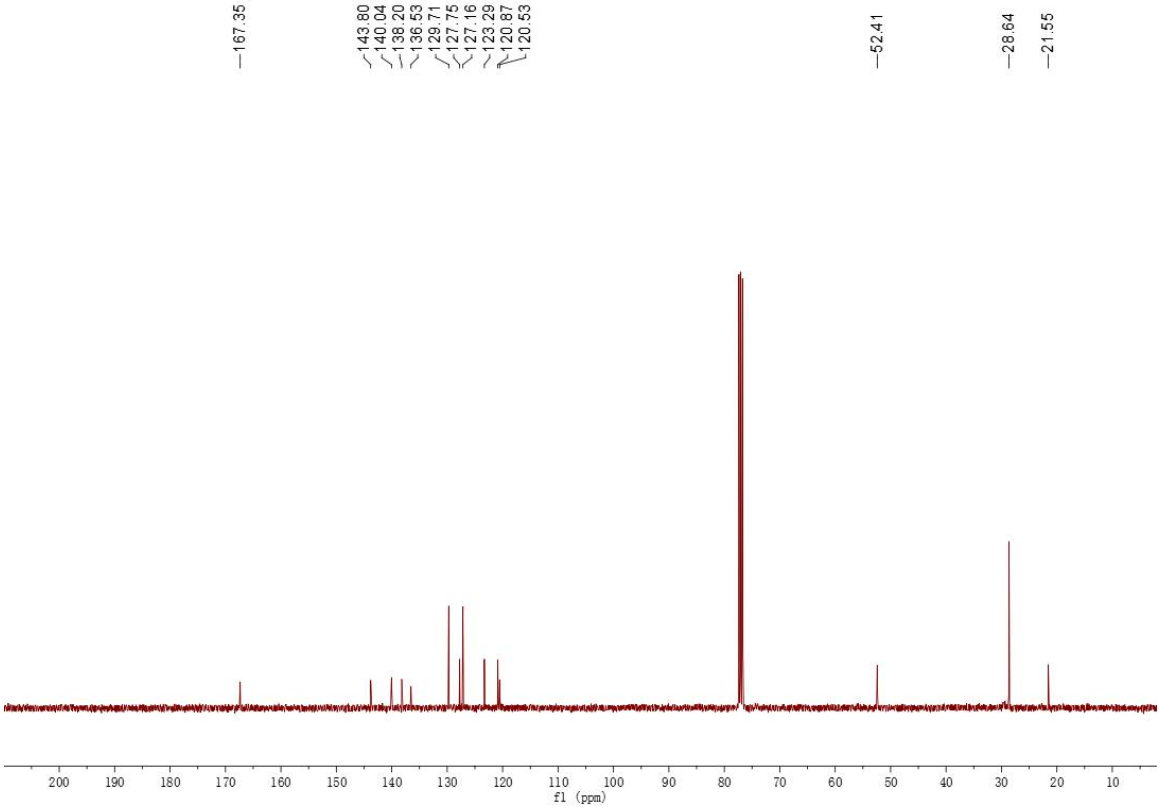
3ea

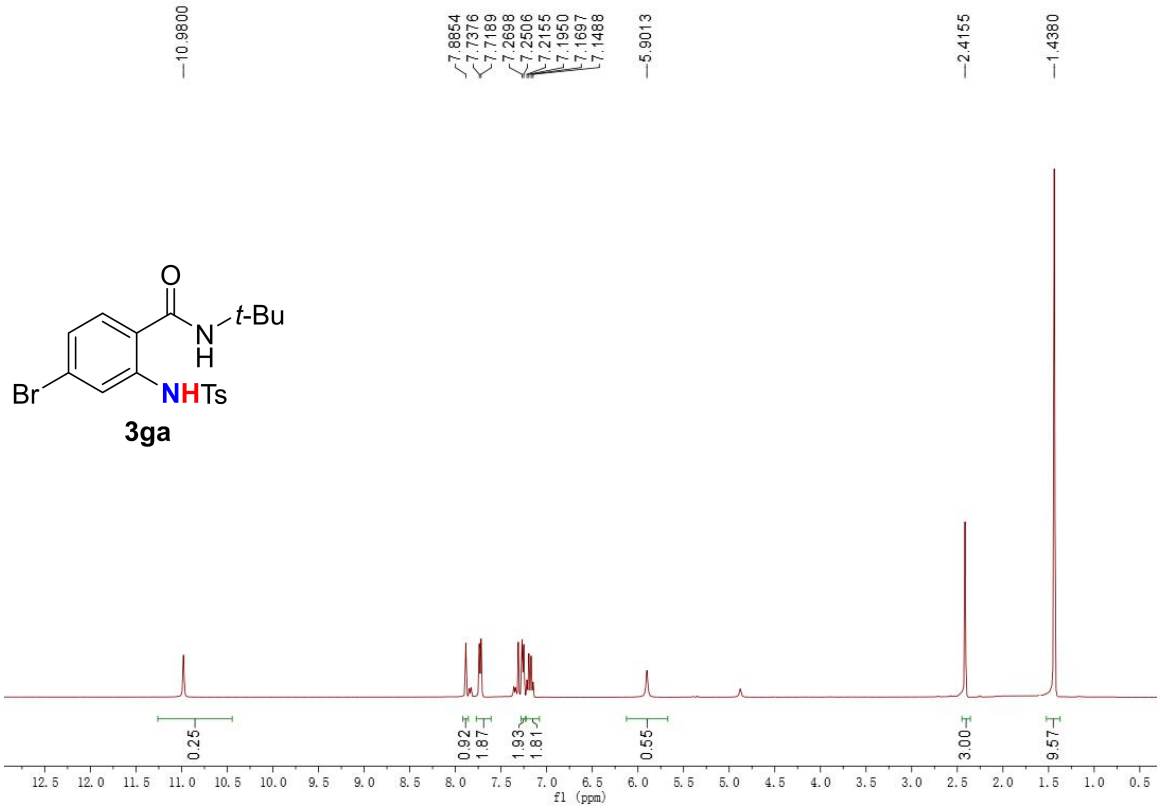

0.84
1.90
1.94
1.96
0.84
0.80
3.00
9.12
f1 (ppm)

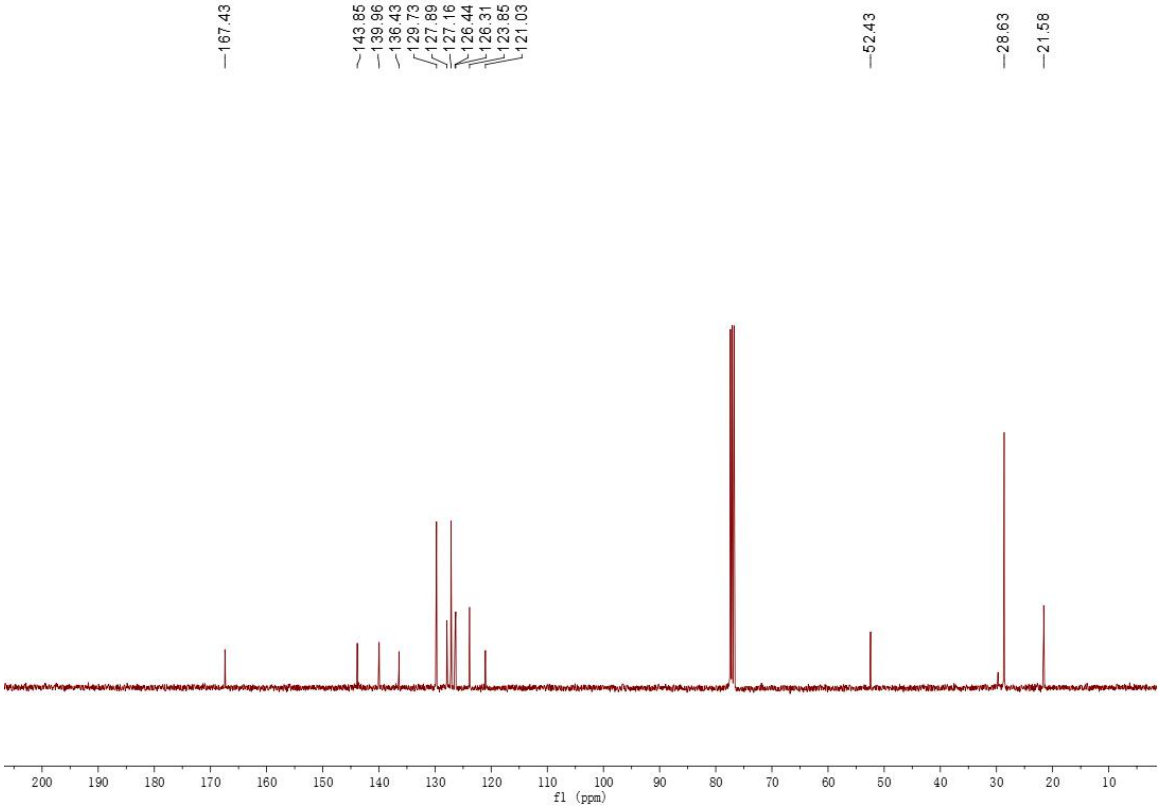

167.49
165.63
163.12
143.90
141.13
141.02
136.38
129.73
128.95
127.08
118.14
118.11
110.29
110.07
107.87
107.61
52.35
28.62
21.54
f1 (ppm)

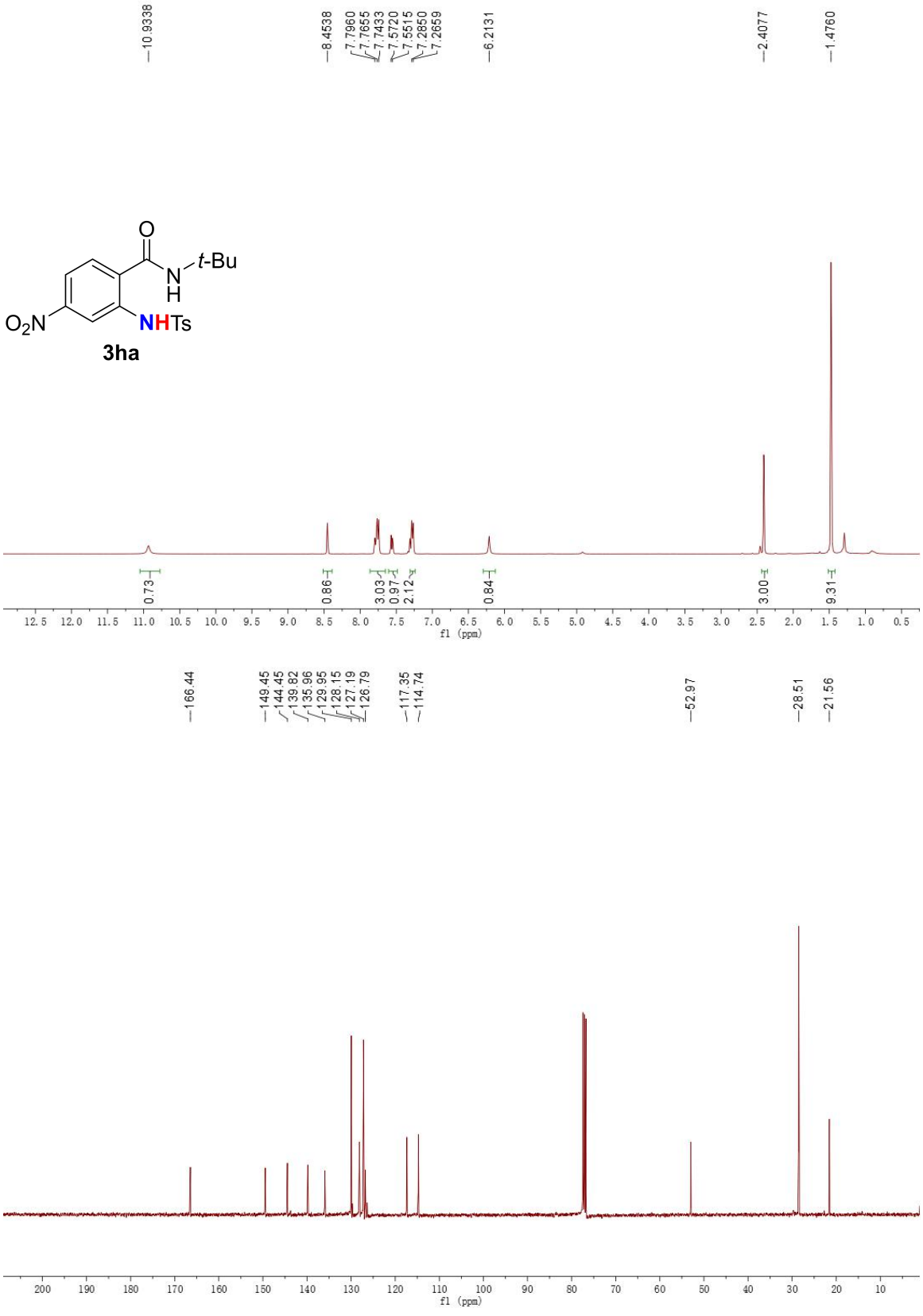

104.85
f1 (ppm)

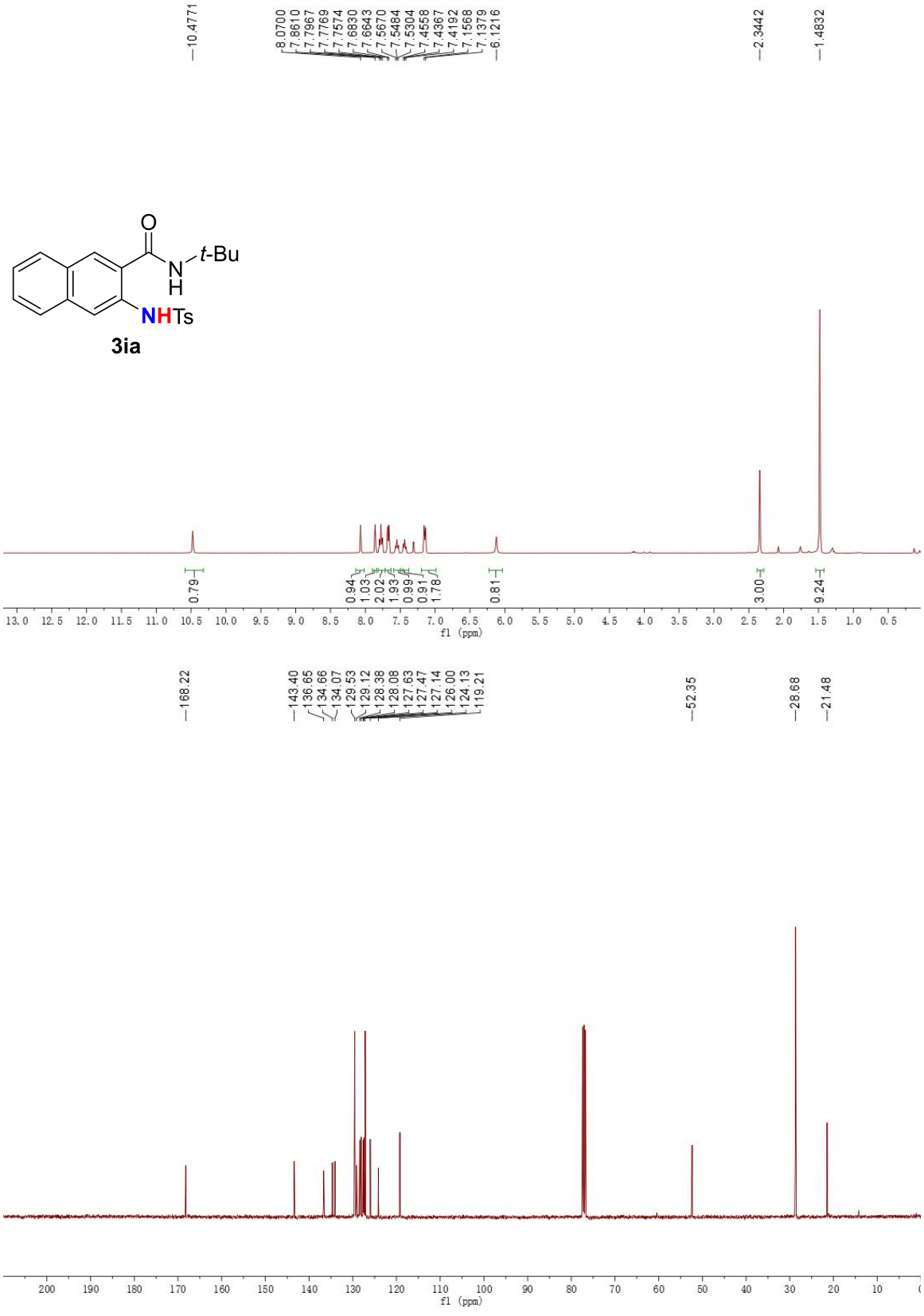

10.9987
7.7248
7.7056
7.2460
7.2370
7.2272
6.9909
6.9700
5.8581
2.3898
1.4169
O
N
H
t-Bu
Cl
NHTs
3fa
0.92
2.86
2.89
0.99
1.00
3.00
9.54
f1 (ppm)

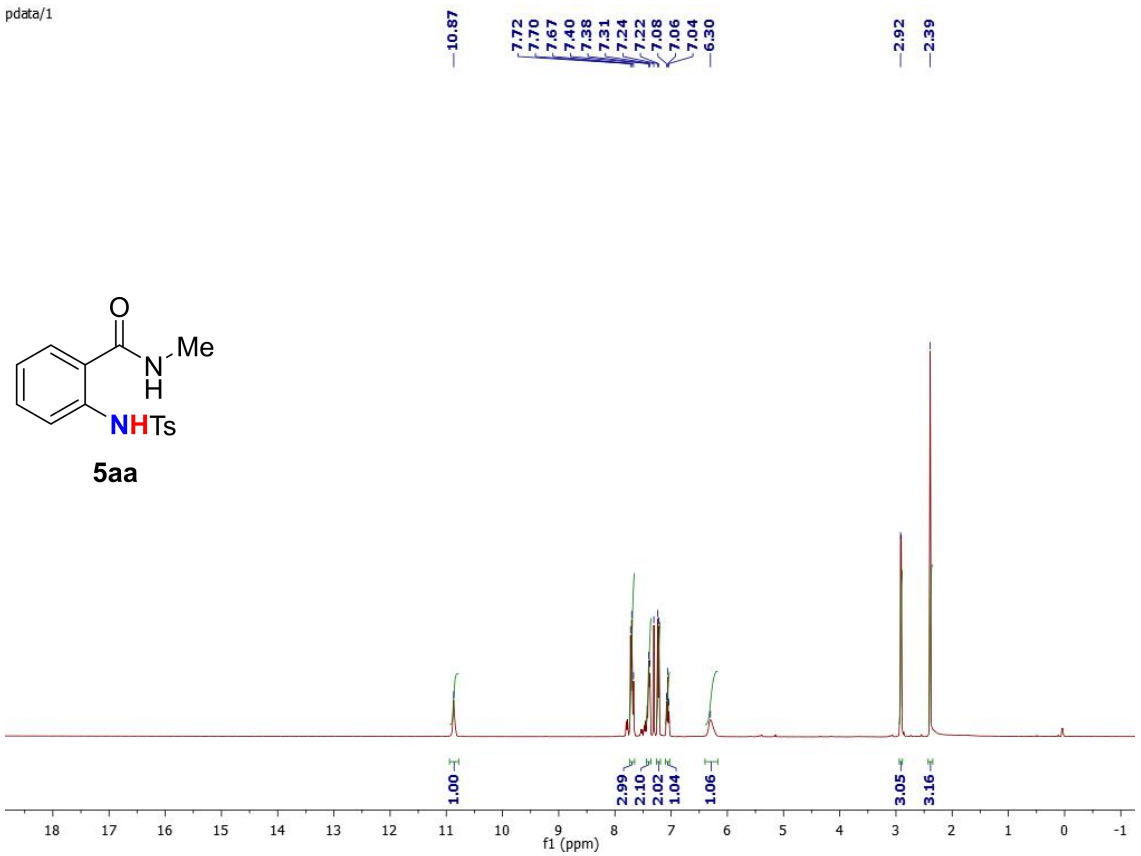

167.35
143.80
140.04
138.20
136.53
129.71
127.75
127.16
123.29
120.87
120.53
52.41
28.64
21.55
f1 (ppm)


10.9800
7.8854
7.7376
7.7189
7.2698
7.2506
7.2155
7.1950
7.1697
7.1488
5.9013
2.4155
1.4380
O
N
H
t-Bu
Br
NHTs
3ga
0.25
0.92
1.87
1.93
1.81
0.55
3.00
9.57
f1 (ppm)

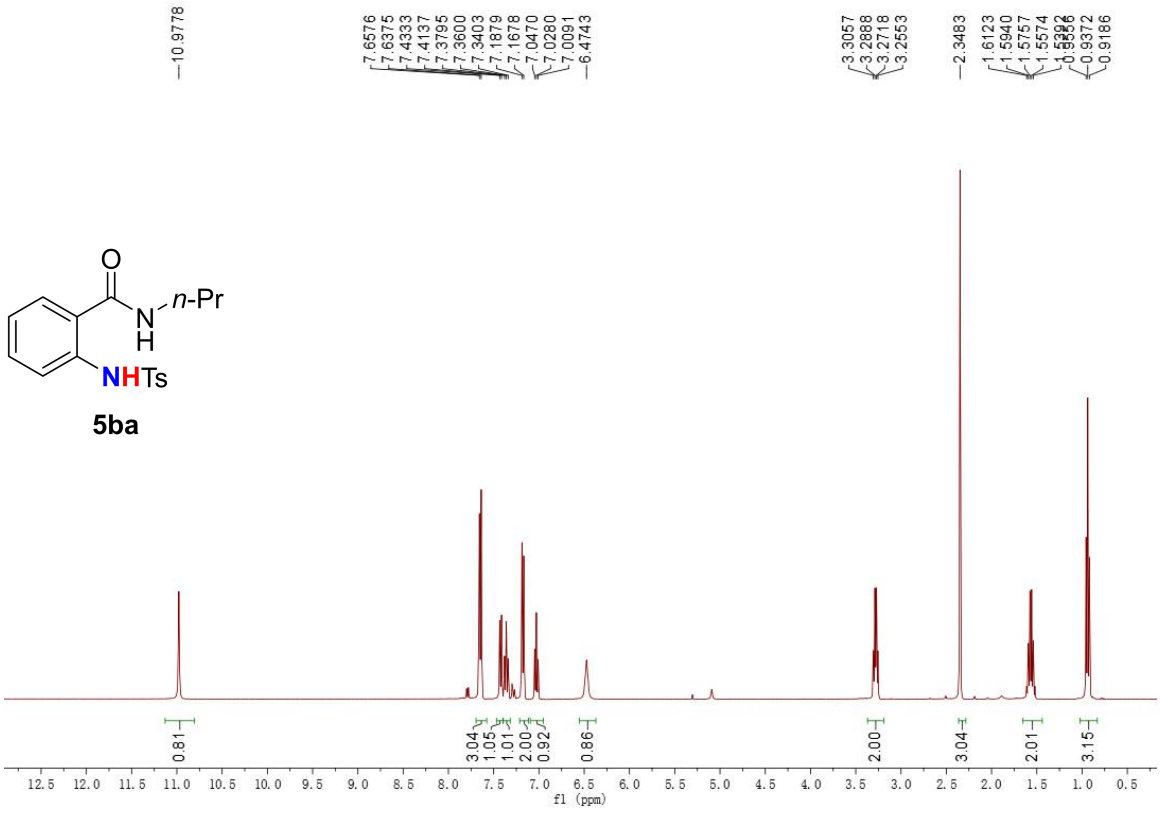

167.43
143.85
139.96
136.43
129.73
127.89
127.16
126.44
126.31
123.85
121.03
52.43
28.63
21.58
f1 (ppm)


10.9338
8.4538
7.7960
7.7655
7.7433
7.5720
7.5515
7.2850
7.2659
6.2131
2.4077
1.4760
O
N
H
t-Bu
O2N
NHTs
3ha
0.73
0.86
3.03
0.97
2.12
0.84
3.00
9.31
f1 (ppm)
166.44
149.45
144.45
139.82
135.96
129.95
128.15
127.19
126.79
117.35
114.74
52.97
28.51
21.56
f1 (ppm)

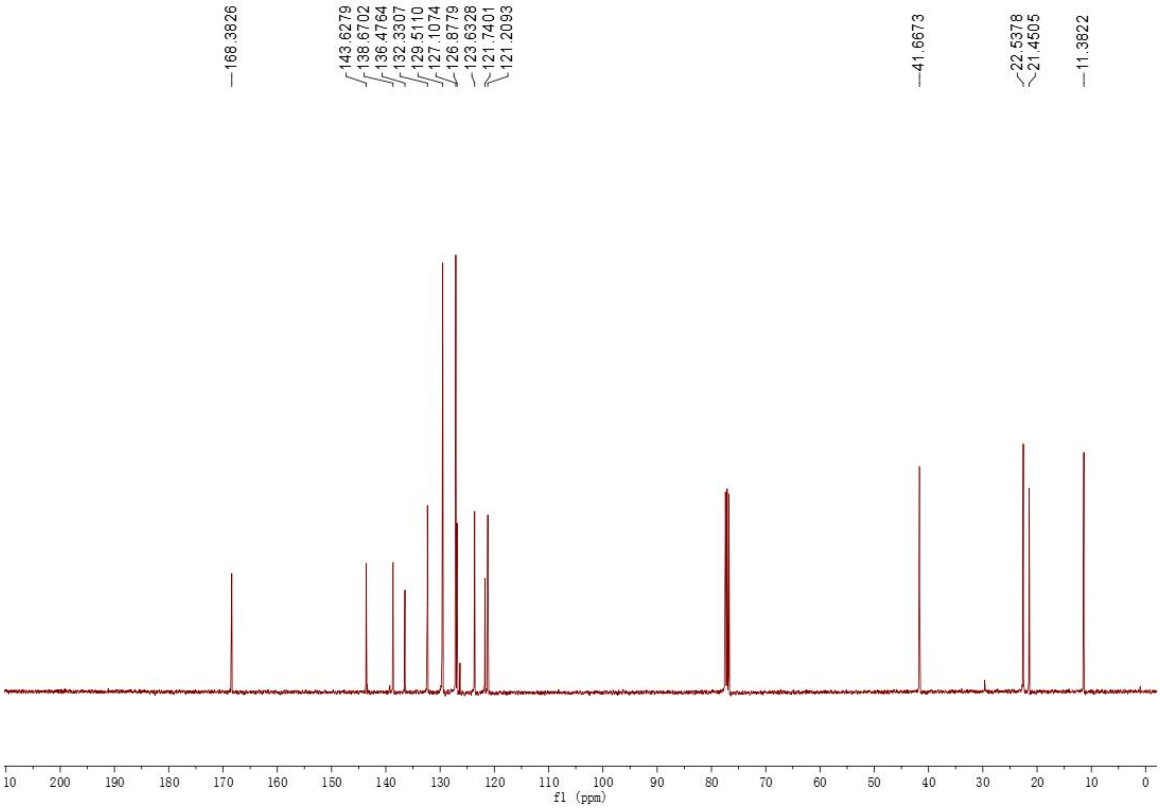

10.4771
8.0700
7.8610
7.7967
7.7769
7.7574
7.6830
7.6643
7.5670
7.5484
7.5304
7.4558
7.4367
7.4192
7.1568
7.1379
6.1216
2.3442
1.4832
O
N
H
t-Bu
NHTs
3ia
0.79
0.94
1.03
2.02
1.93
0.99
0.91
1.78
0.81
3.00
9.24
f1 (ppm)
168.22
143.40
136.65
134.66
134.07
129.53
129.12
128.38
128.08
127.63
127.47
127.14
126.00
124.13
119.21
52.35
28.68
21.48
f1 (ppm)

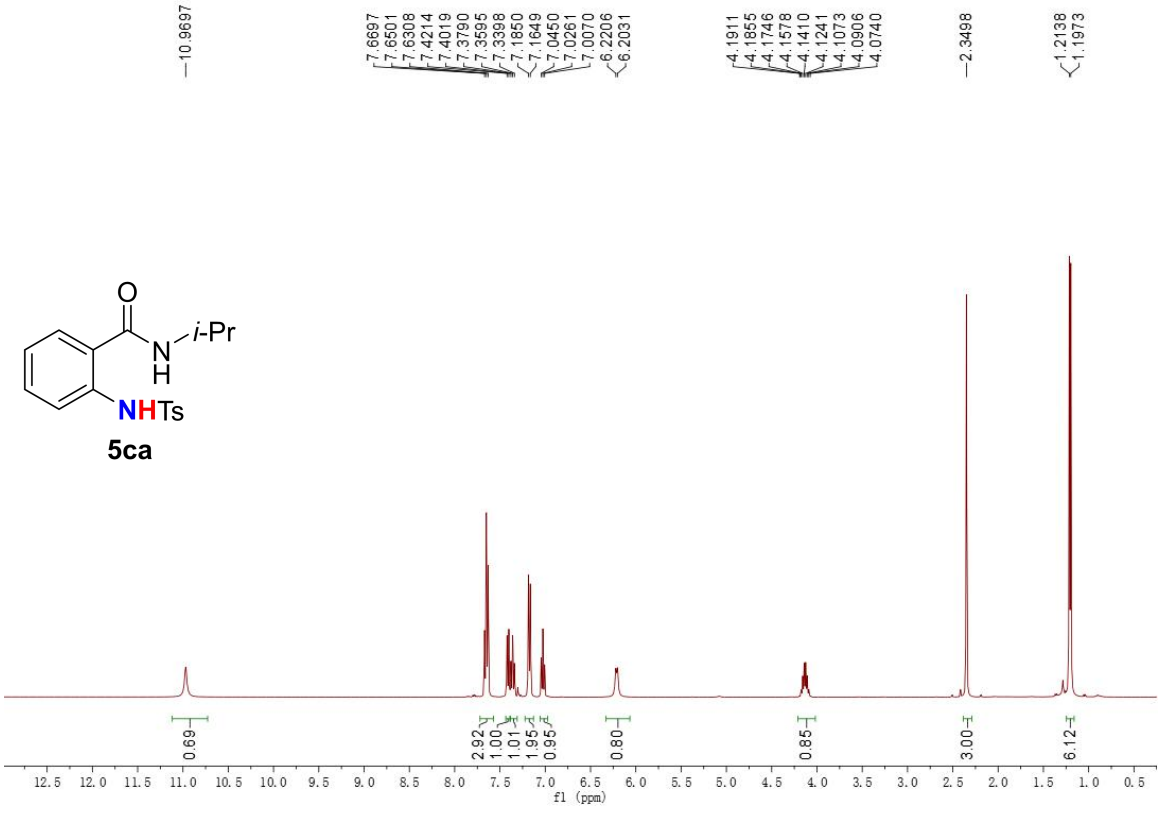

pdata/1
10.87
7.72
7.70
7.67
7.40
7.38
7.31
7.24
7.22
7.08
7.06
7.04
6.30
2.92
2.39
O
N
Me
H
NHTs
1.00
2.99
2.10
2.02
1.04
1.06
3.05
3.16
f1 (ppm)

5aa


10.9778
7.6576
7.6375
7.4333
7.4137
7.3795
7.3600
7.3403
7.1879
7.1678
7.0470
7.0280
7.0091
6.4743
3.3057
3.2888
3.2718
3.2553
2.3483
1.6123
1.5940
1.5757
1.5574
0.9372
0.9186
O
N
n-Pr
H
NHTs
0.81
3.04
1.05
1.01
2.00
0.92
0.86
2.00
3.04
2.01
3.15
f1 (ppm)

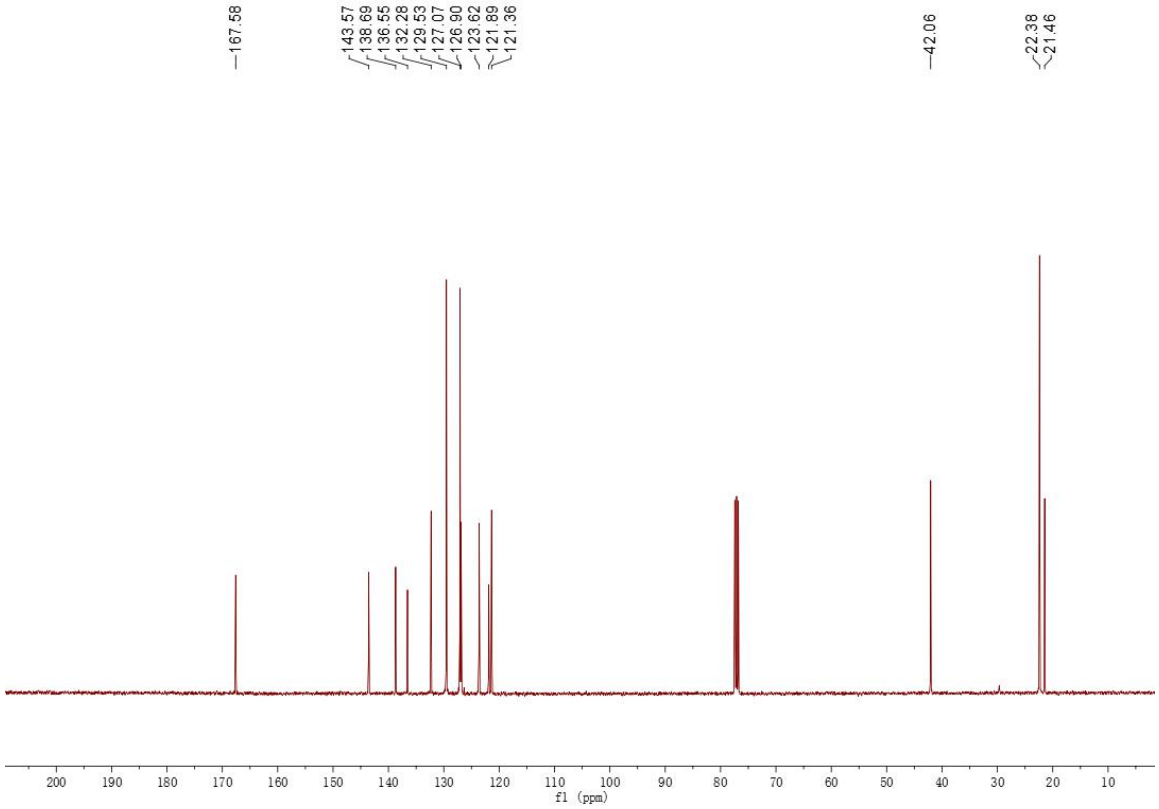
5ba

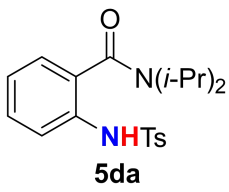

168.3826
143.6279
138.6702
136.4764
132.3307
129.5110
127.1074
126.8779
123.6328
121.7401
121.2093
41.6673
22.5378
21.4505
11.3822
f1 (ppm)


10.9697
7.6697
7.6501
7.6308
7.4214
7.4019
7.3790
7.3595
7.3398
7.1850
7.1649
7.0450
7.0261
7.0070
6.2206
6.2031
4.1911
4.1855
4.1746
4.1578
4.1410
4.1241
4.1073
4.0906
4.0740
2.3498
1.2138
1.1973
0.69
2.92
1.00
1.01
1.95
0.95
0.80
0.85
3.00
6.12
f1 (ppm)

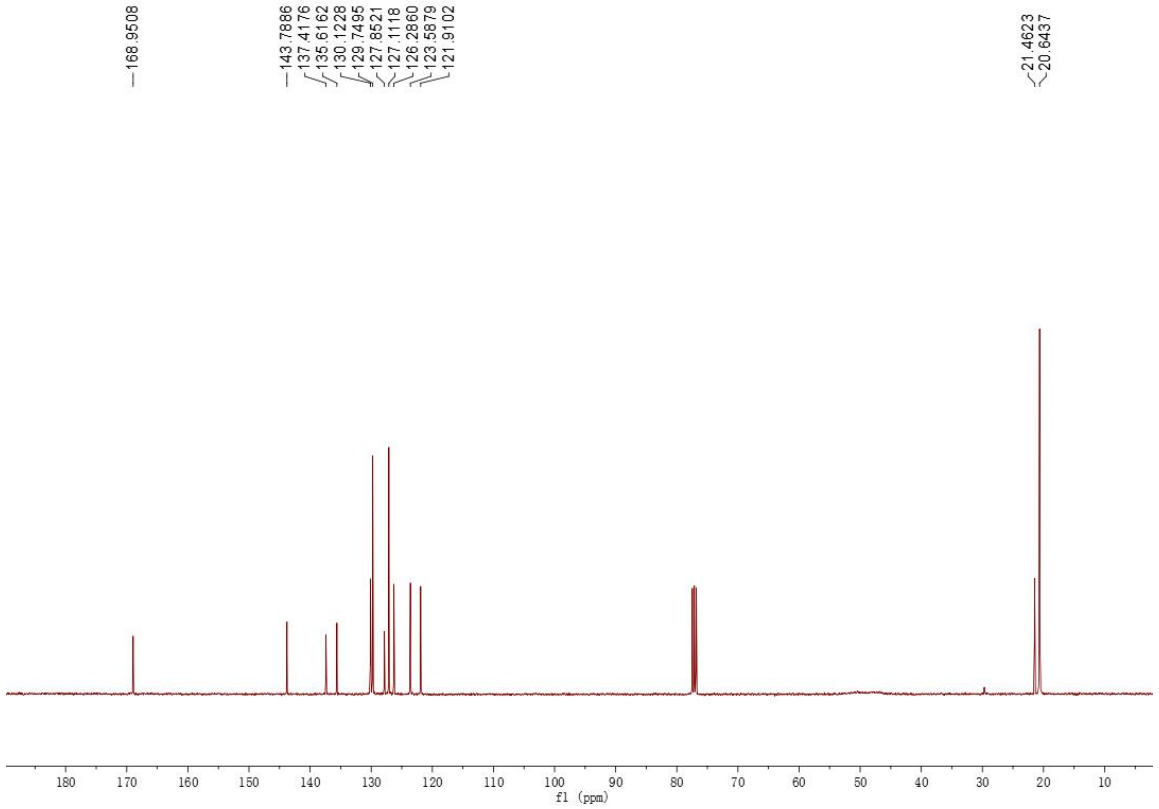
O
N
H
i-Pr
NHTs

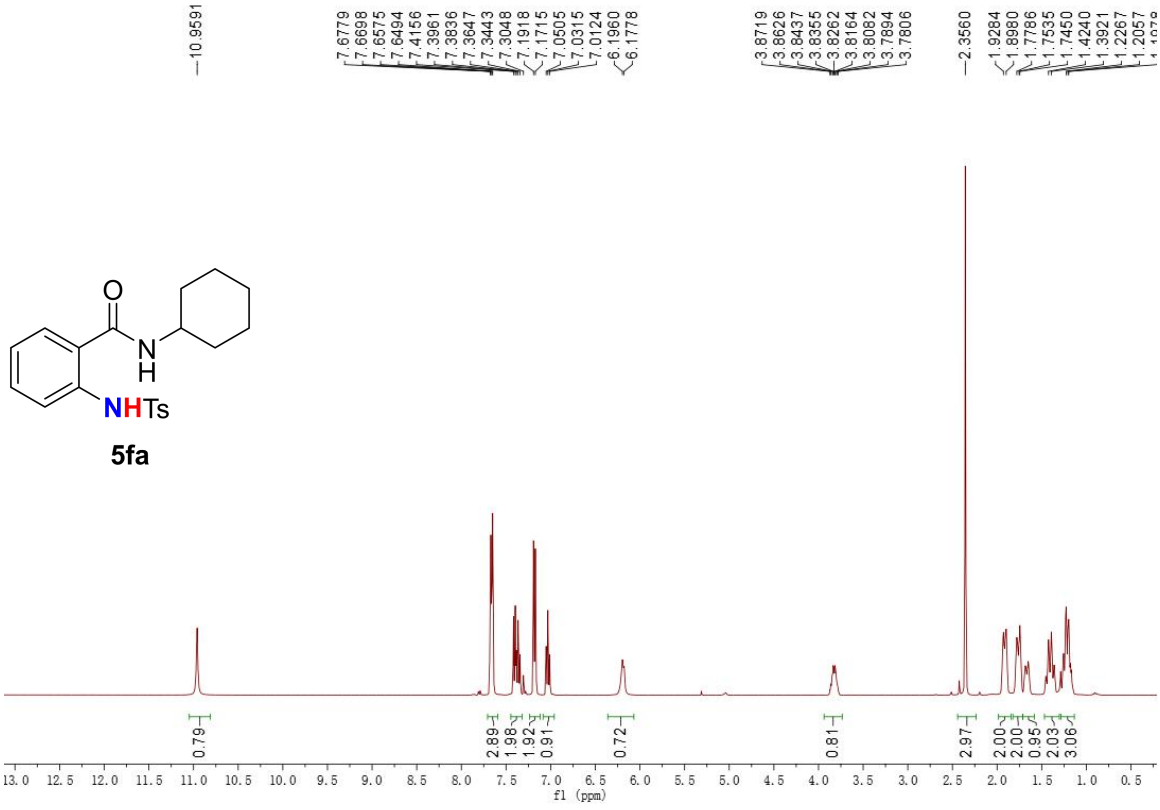
5ca


167.58
143.57
138.69
136.55
132.28
129.53
127.07
126.90
123.62
121.89
121.36
42.06
22.38
21.46
f1 (ppm)
8.3395
7.7612
7.7407
7.6034
7.5827
7.3094
7.3055
7.2975
7.2876
7.2662
7.2581
7.2377
7.1207
7.1051
7.1019
7.0770
7.0587
7.0398
3.6563
2.3693
1.2784
f1 (ppm)

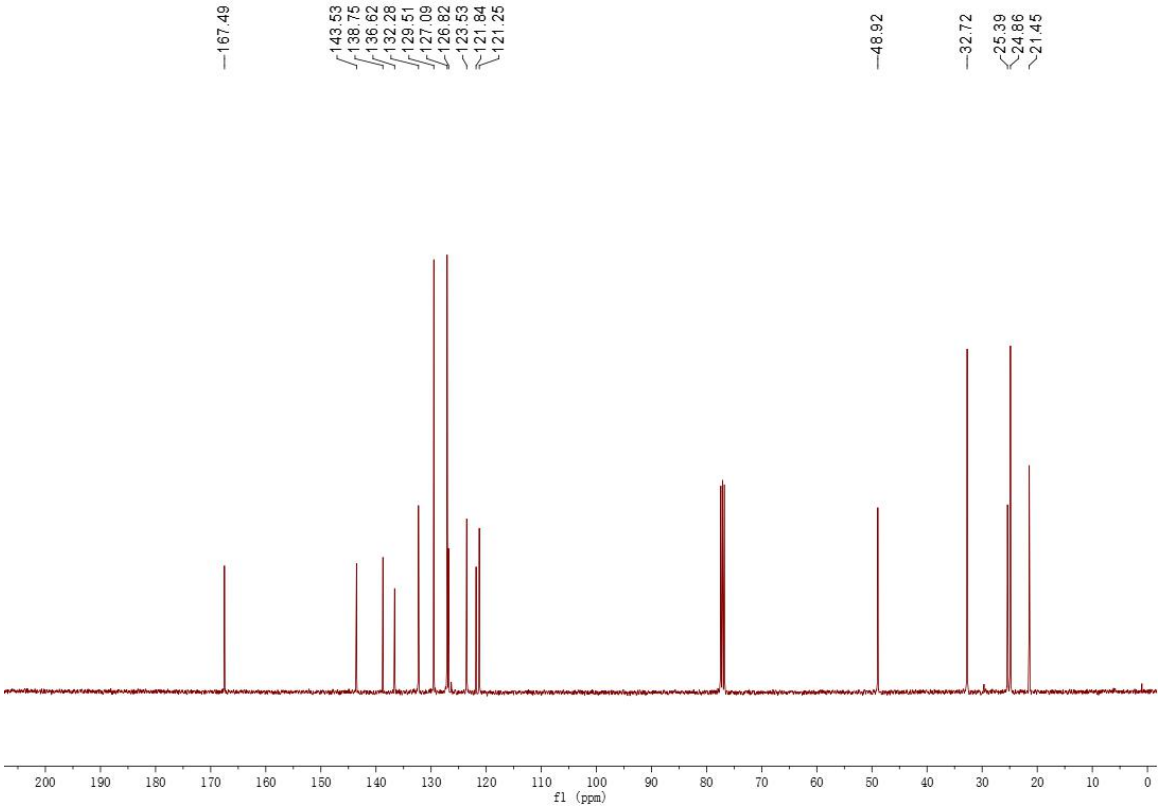

O
N(*i*-Pr)$_2$
NHTs

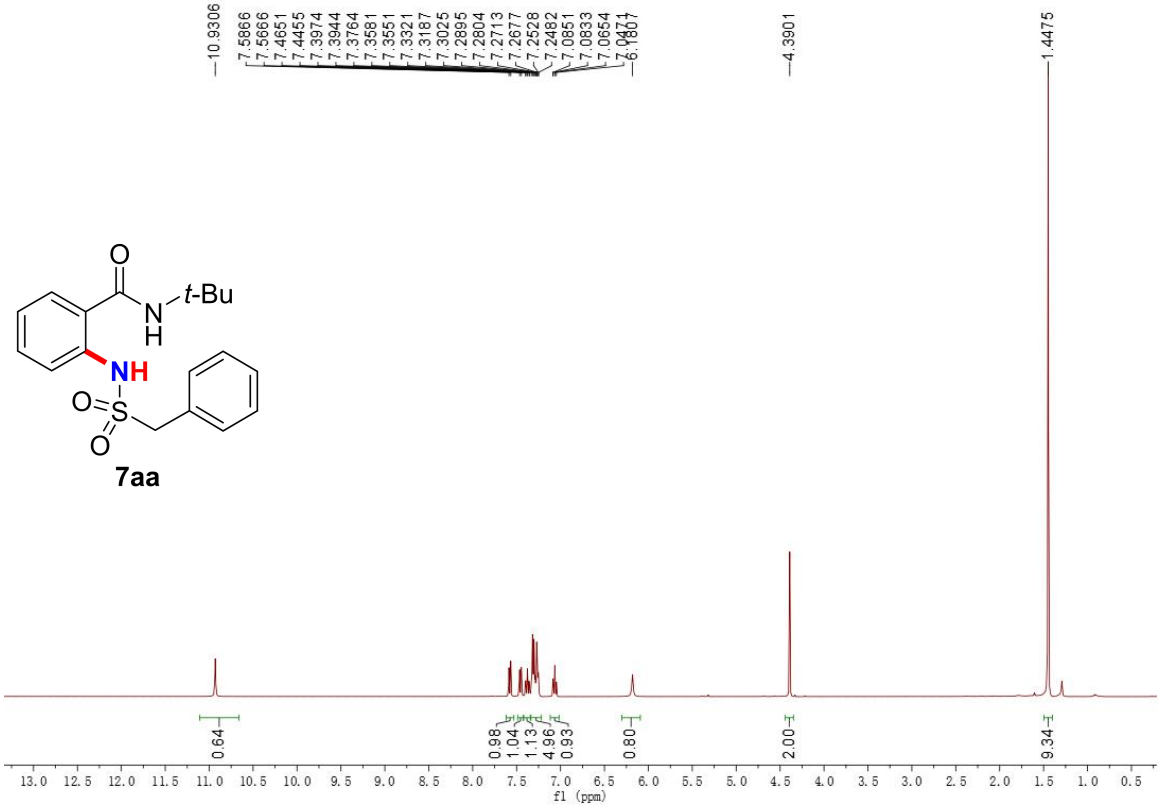
5da


168.9508
143.7886
137.4176
135.6162
130.1228
129.7495
127.8521
127.1118
126.2860
123.5879
121.9102
21.4623
20.6437
f1 (ppm)


10.9591
7.6779
7.6698
7.6575
7.6494
7.4156
7.3961
7.3836
7.3647
7.3443
7.3048
7.1918
7.1715
7.0505
7.0315
7.0124
6.1960
6.1778
3.8719
3.8626
3.8437
3.8355
3.8262
3.8164
3.8082
3.7894
3.7806
2.3560
1.9284
1.8880
1.7786
1.7535
1.7450
1.4240
1.3921
1.2267
1.2057
O
N
H
NHTs
0.79
2.89
1.98
1.92
0.91
0.72
0.81
2.97
2.00
2.00
0.95
2.03
3.06
f1 (ppm)

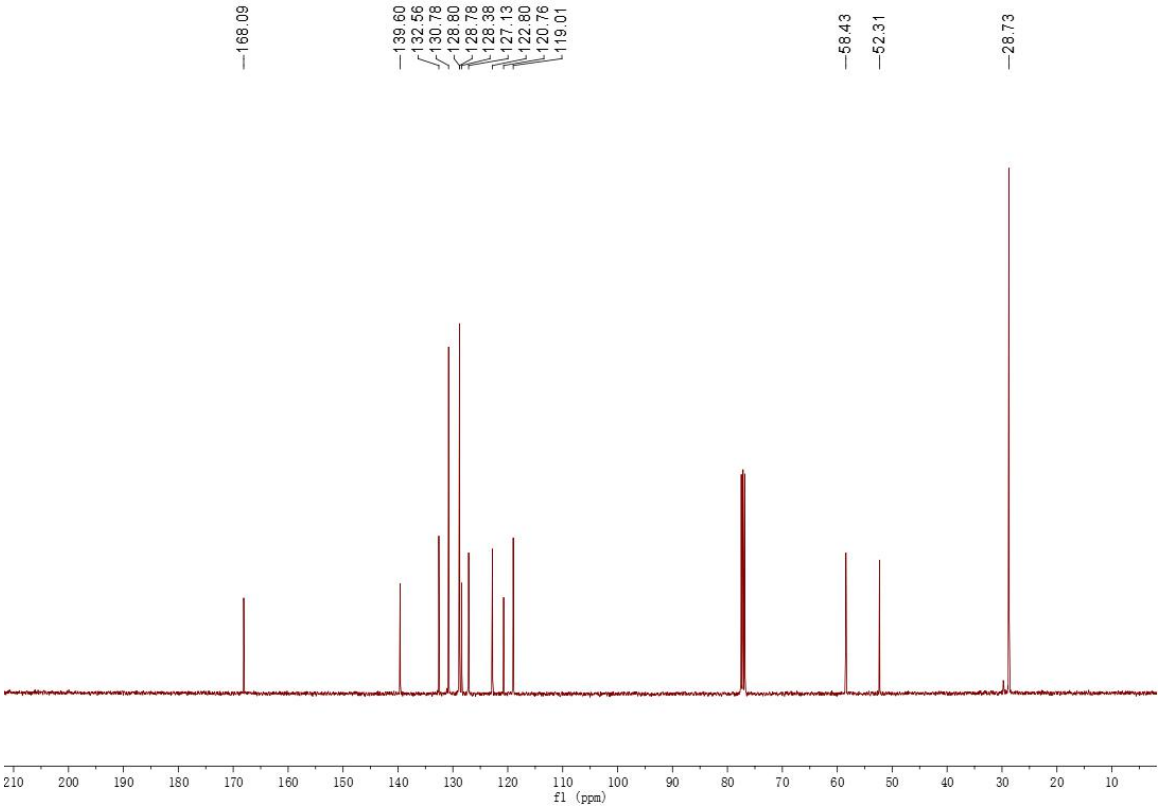
5fa

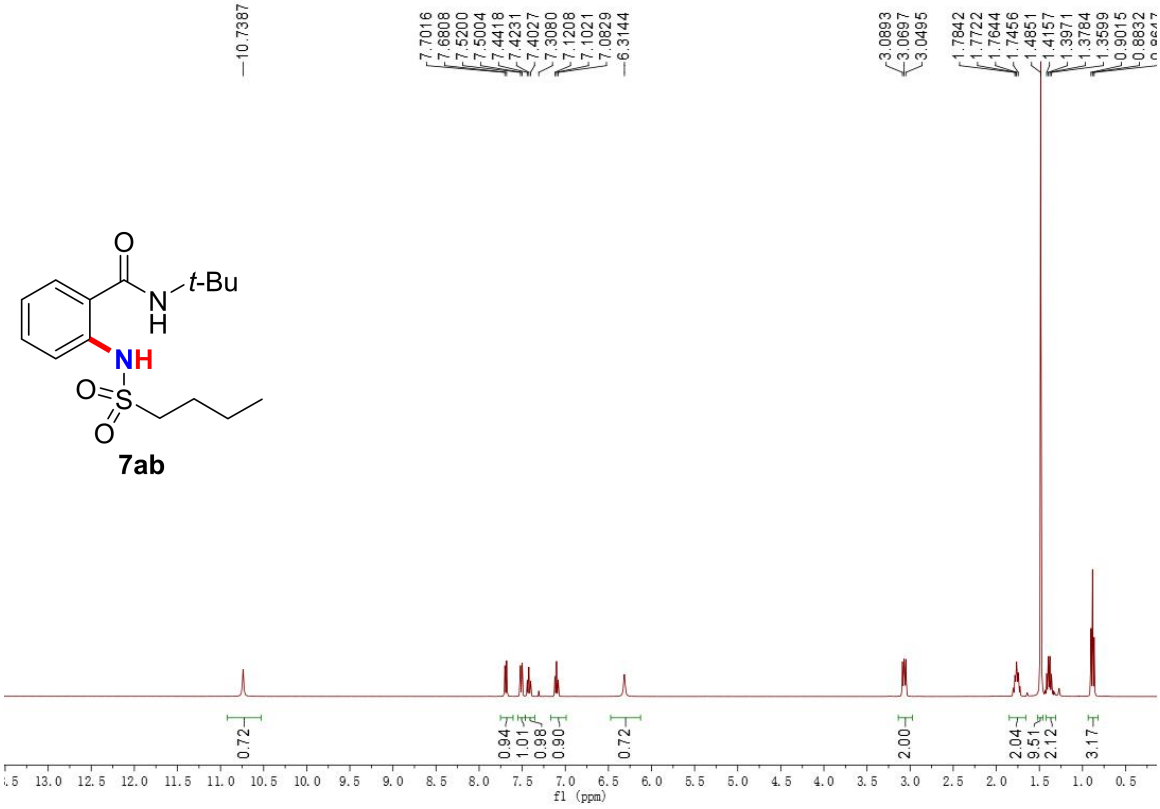

167.49
143.53
138.75
136.62
132.28
129.51
127.09
126.82
123.53
121.84
121.25
48.92
32.72
25.39
24.86
21.45
f1 (ppm)


10.9306
7.5866
7.5666
7.4651
7.4455
7.3974
7.3944
7.3764
7.3581
7.3551
7.3321
7.3187
7.3025
7.2895
7.2804
7.2713
7.2677
7.2528
7.2482
7.0851
7.0833
7.0654
6.1807
4.3901
1.4475
0.64
0.98
1.04
1.13
4.96
0.93
0.80
2.00
9.34
f1 (ppm)

O
N
H
t-Bu
NH
O
S
O

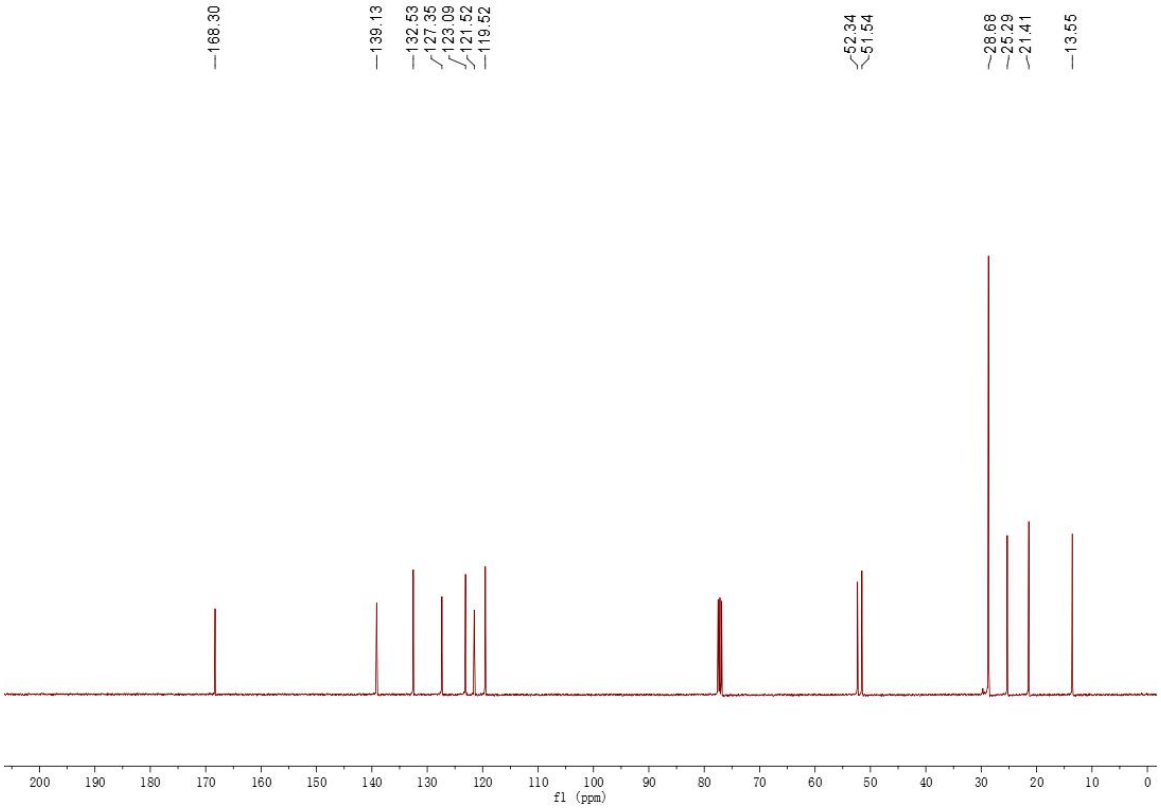
7aa


168.09
139.60
132.56
130.78
128.80
128.78
128.38
127.13
122.80
120.76
119.01
58.43
52.31
28.73
f1 (ppm)


10.7387
7.7016
7.6808
7.5200
7.5004
7.4418
7.4231
7.4027
7.3080
7.1208
7.1021
7.0829
6.3144
3.0893
3.0697
3.0495
1.7842
1.7722
1.7644
1.7456
1.4851
1.4157
1.3971
1.3784
1.3599
0.9015
0.8832
0.72
0.94
1.01
0.98
0.90
0.72
2.00
2.04
9.51
2.12
3.17
f1 (ppm)

O
N
H
t-Bu
NH
O
S
O

7ab


168.30
139.13
132.53
127.35
123.09
121.52
119.52
52.34
51.54
28.68
25.29
21.41
13.55
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)