Supporting Information for

Gallium Bromide-Promoted Dearomative Indole Insertion in 3-Indolylmethanols: Chemoselective and (*Z*/*E*)-Selective Synthesis of 3,3'-Bisindole Derivatives

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E-mail: fshi@jsnu.edu.cn; guangjianM@126.com

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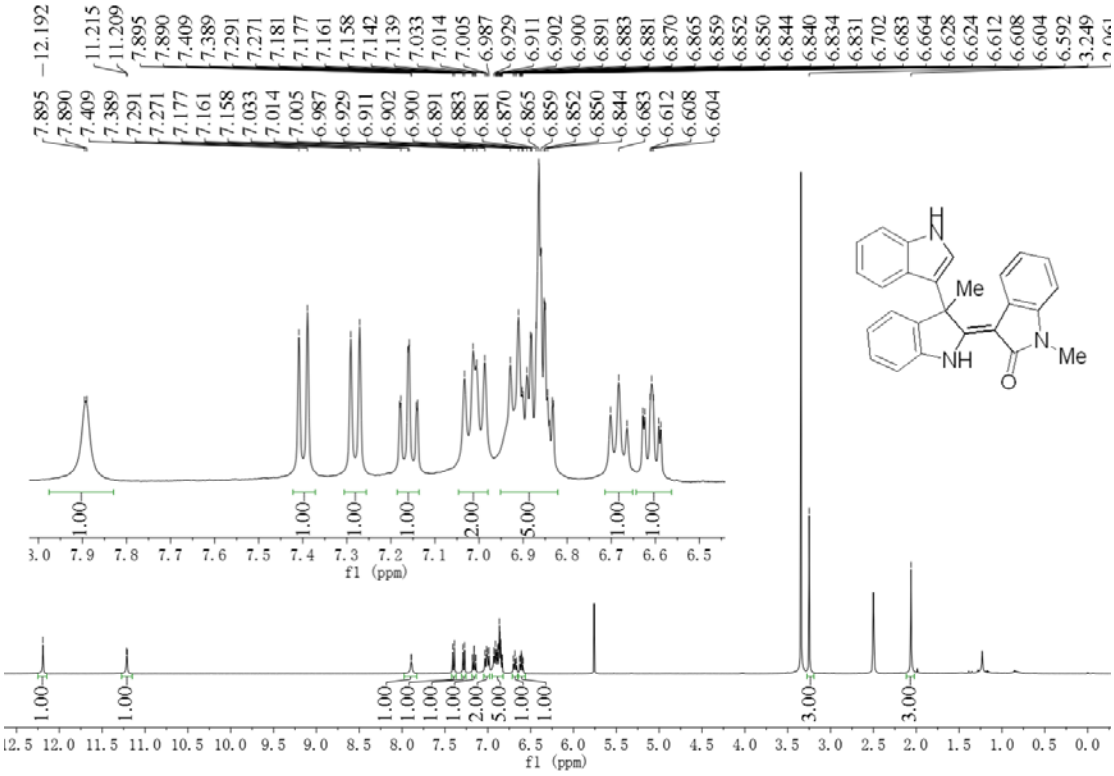
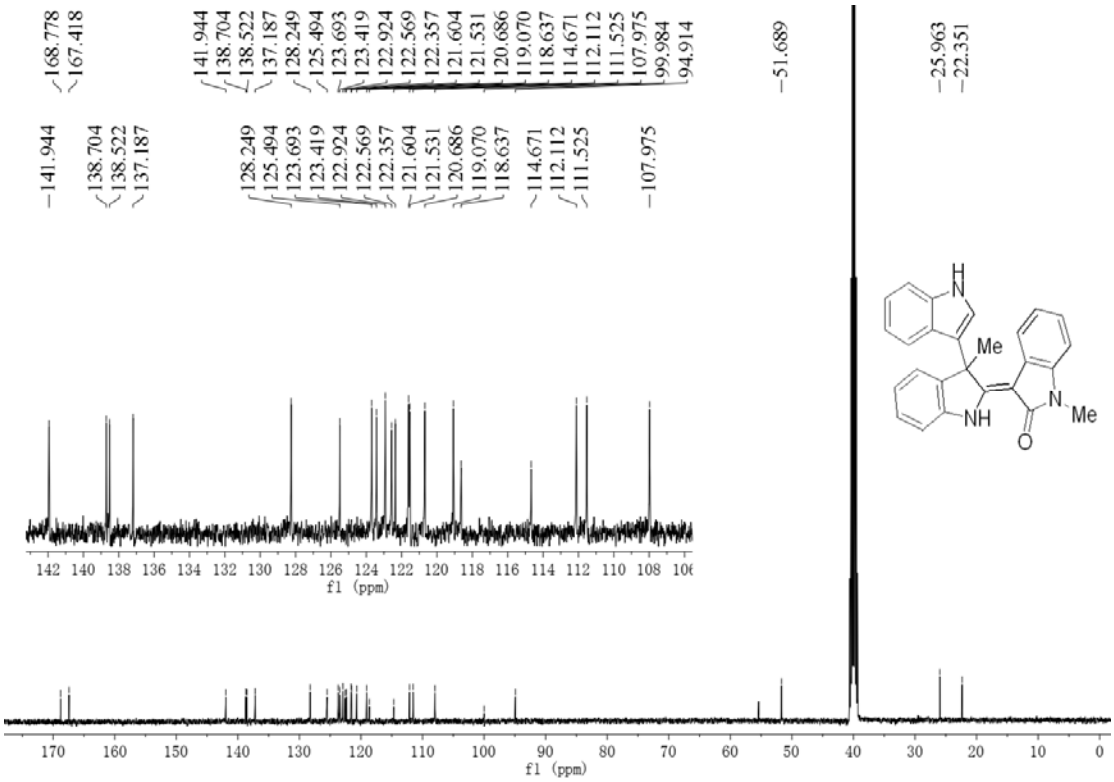
1. NMR spectra of all products 3

3aa





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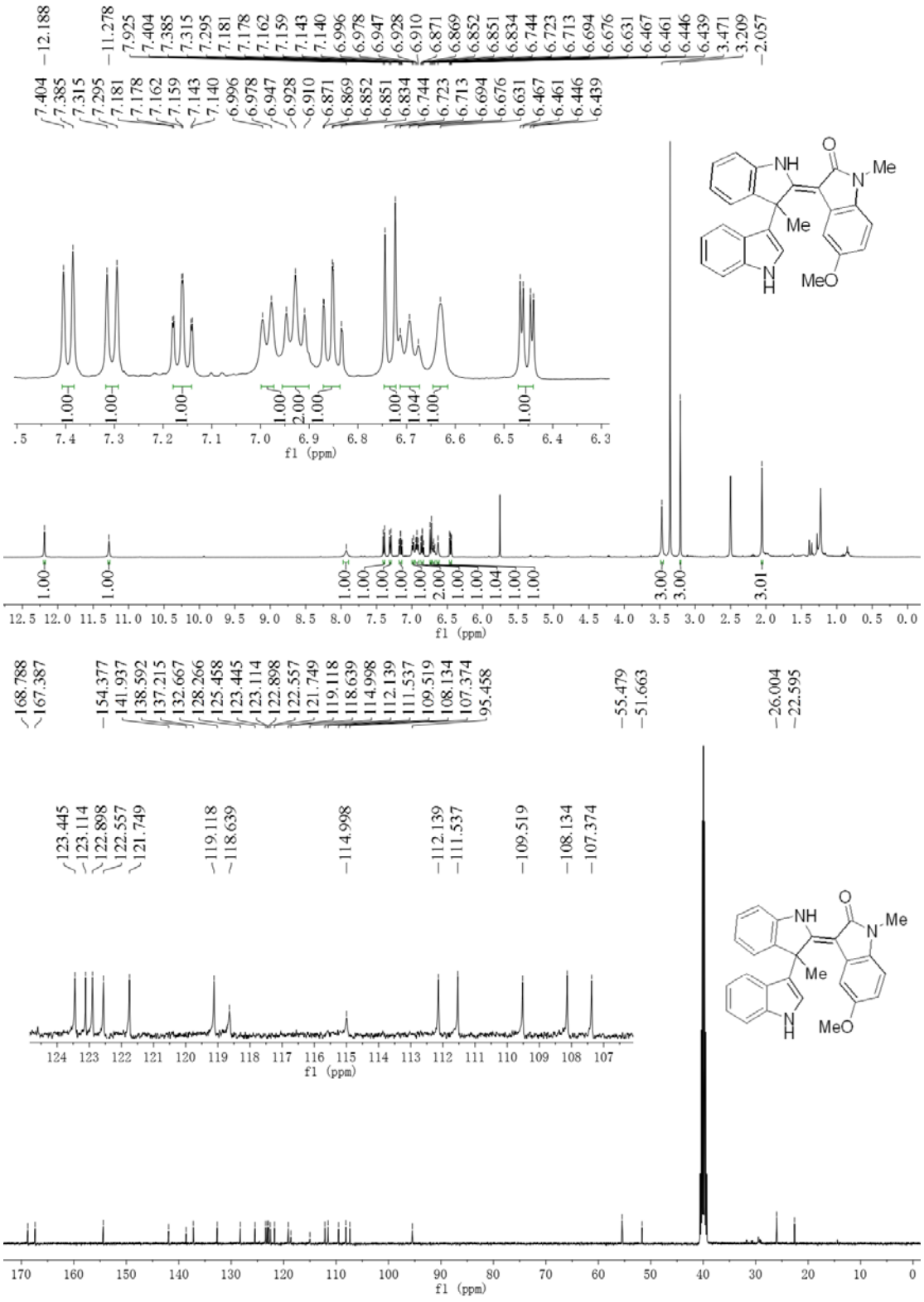
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6.467
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2.057
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N
Me
Me
MeO
f1 (ppm)
168.788
167.387
154.377
141.937
138.592
137.215
132.667
128.266
125.458
123.445
123.114
122.898
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f1 (ppm)

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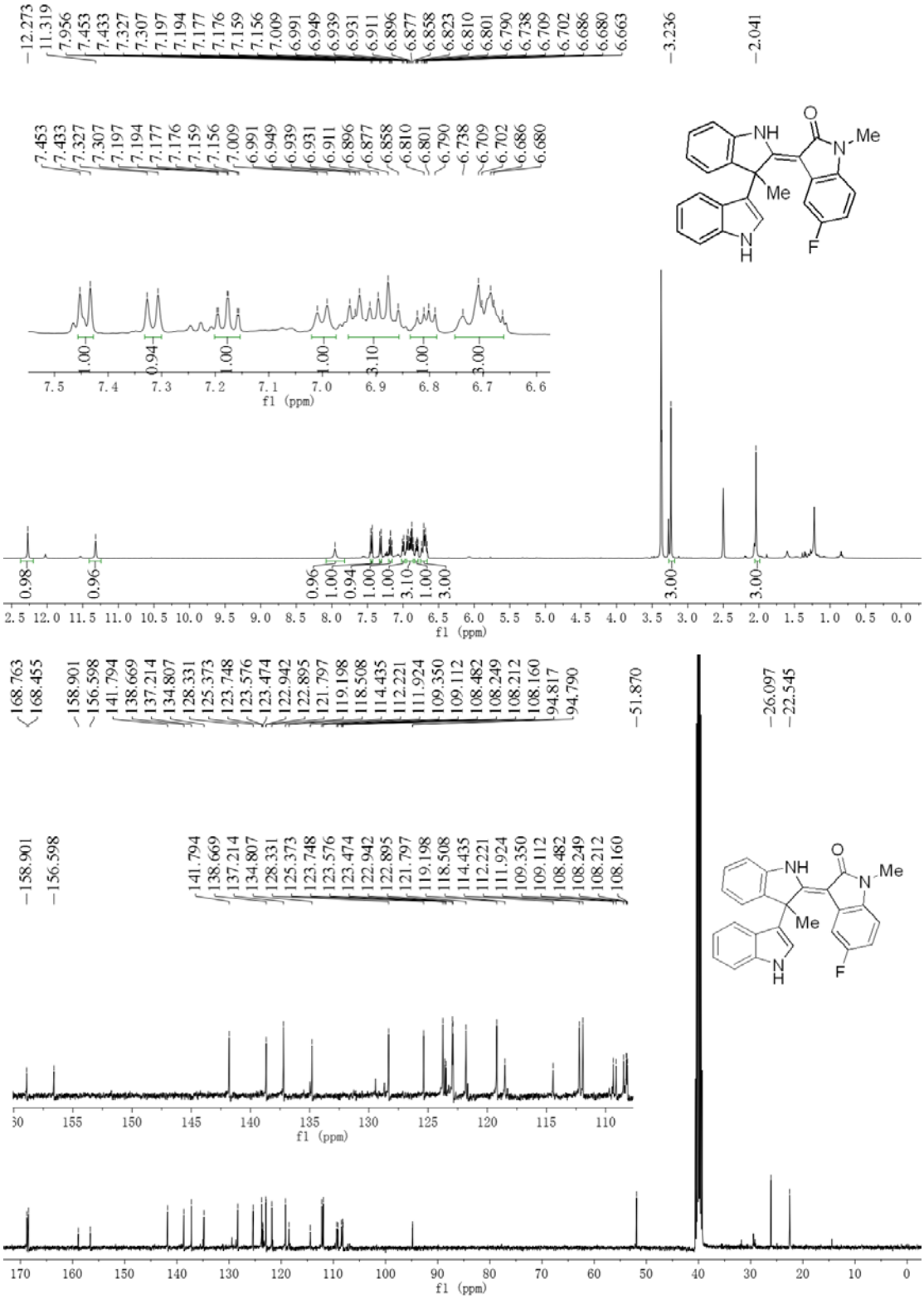
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7.009
6.991
6.949
6.939
6.931
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6.858
6.823
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6.801
6.790
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6.702
6.686
6.680
6.663
3.236
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NH
O
N
Me
Me
N
H
F
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0.94
1.00
1.00
3.10
1.00
3.00
f1 (ppm)
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0.96
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1.00
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1.00
1.00
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1.00
3.00
3.00
3.00
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168.455
158.901
156.598
141.794
138.669
137.214
134.807
128.331
125.373
123.748
123.576
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122.895
121.797
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118.508
114.435
112.221
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109.350
109.112
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22.545
f1 (ppm)
f1 (ppm)

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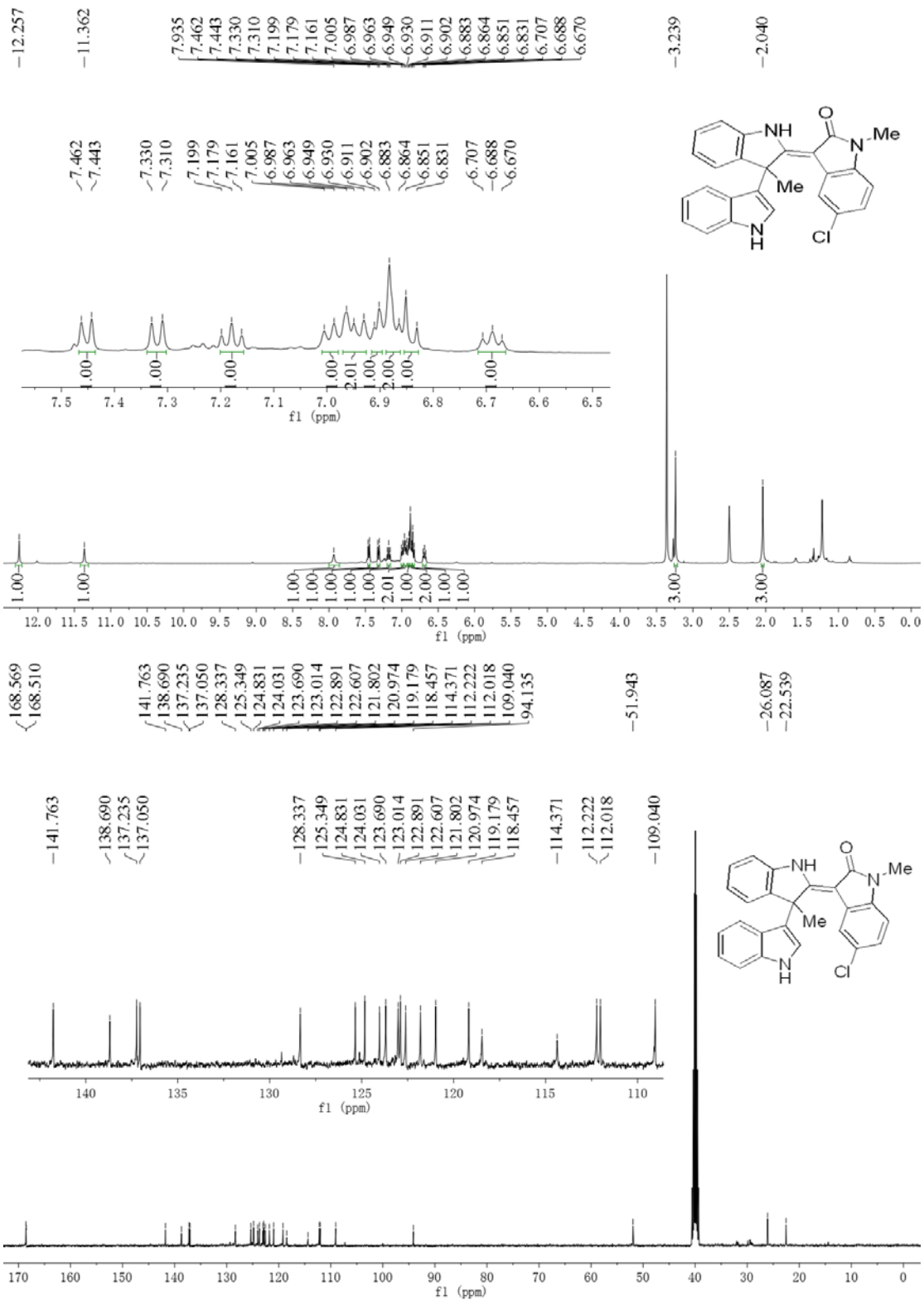
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Me
Me
N
H
Cl
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138.690
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124.831
124.031
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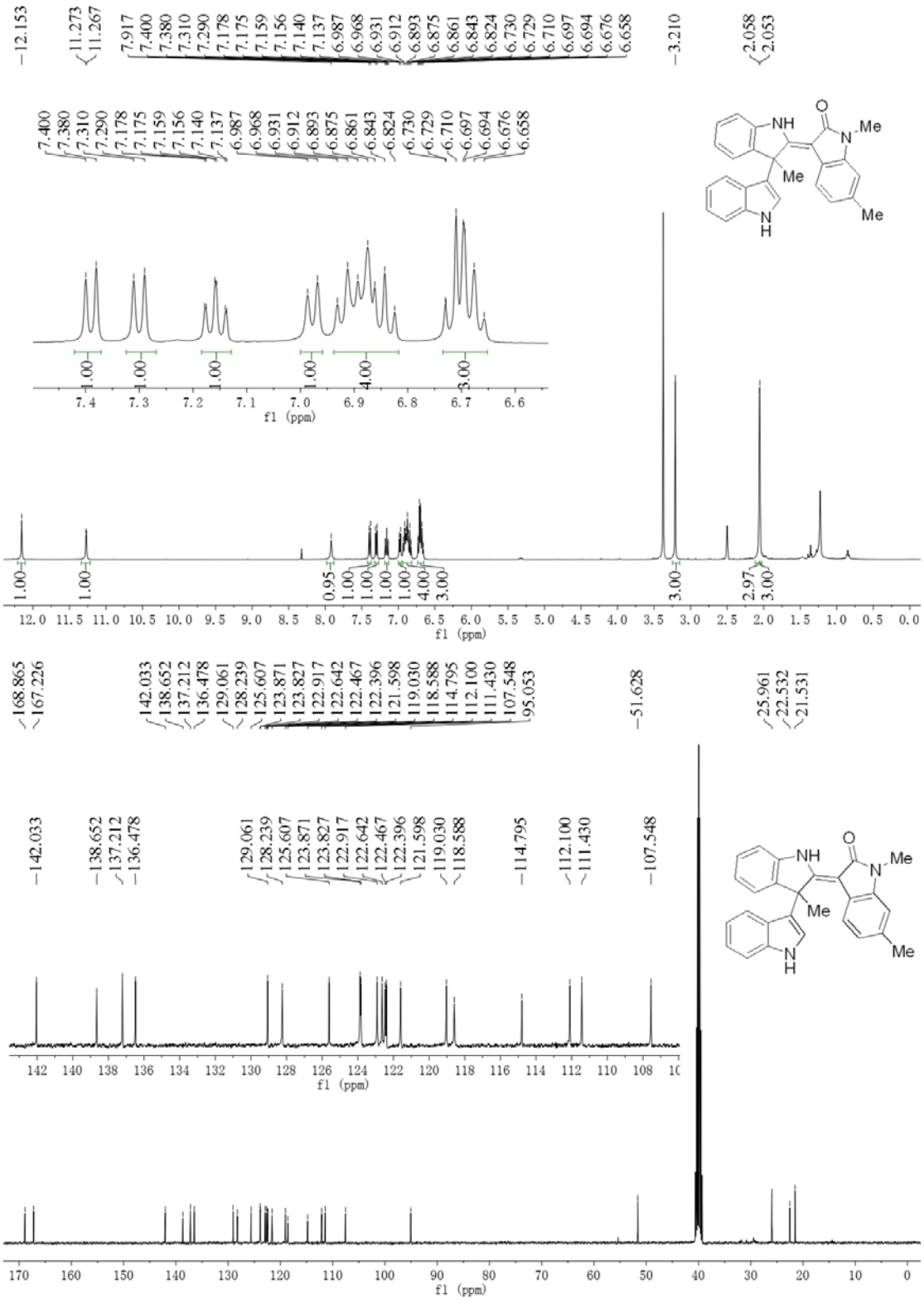
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6.697
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3.210
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N
Me
Me
Me
H
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1.00
1.00
1.00
4.00
3.00
f1 (ppm)
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1.00
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1.00
1.00
4.00
3.00
3.00
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3.00
f1 (ppm)
168.865
167.226
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138.652
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129.061
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119.030
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f1 (ppm)

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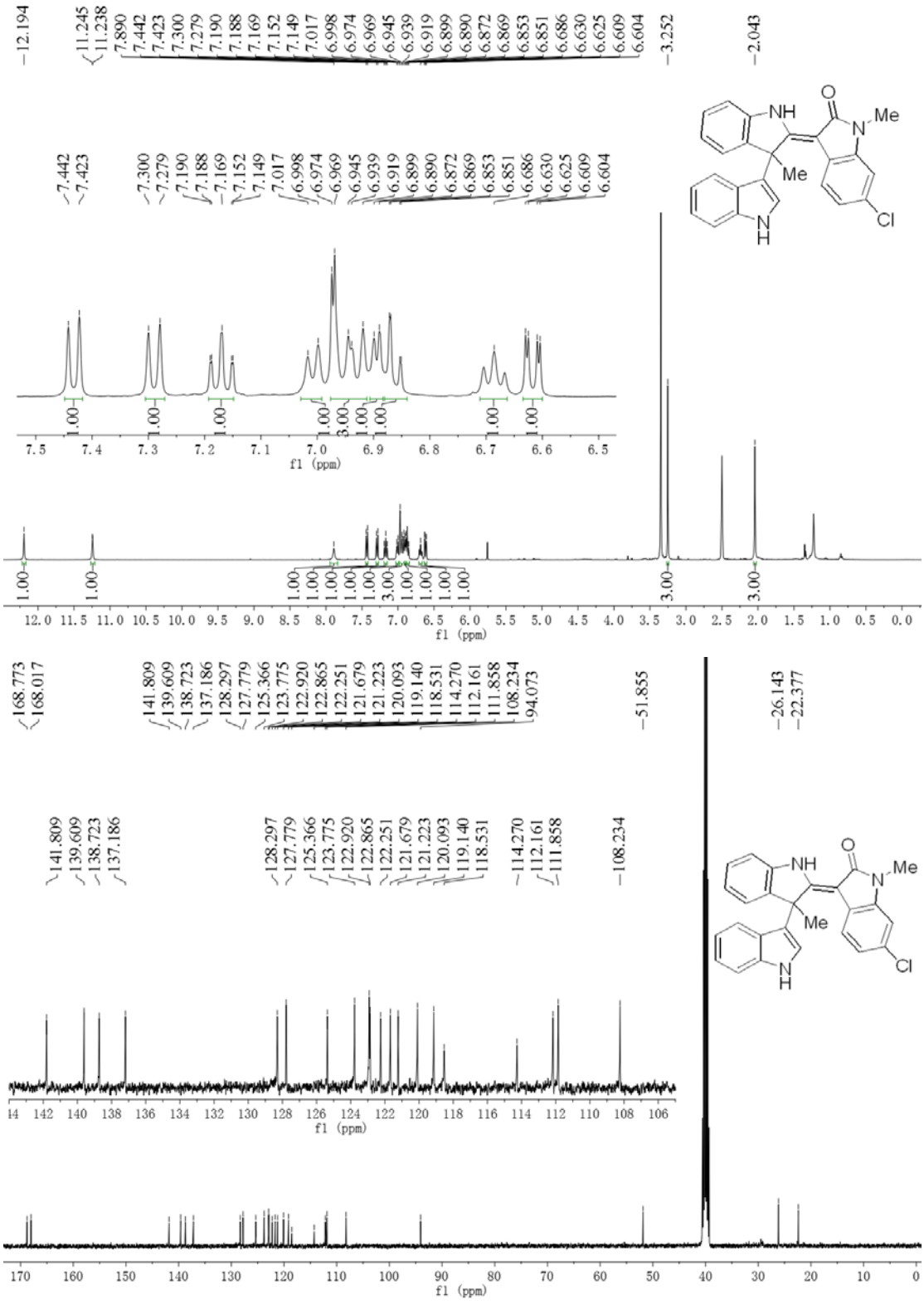
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7.152
7.149
7.017
6.998
6.974
6.969
6.945
6.939
6.919
6.899
6.890
6.872
6.869
6.853
6.851
6.686
6.630
6.625
6.609
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3.252
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O
N
Me
Me
Cl
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138.723
137.186
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127.779
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123.775
122.920
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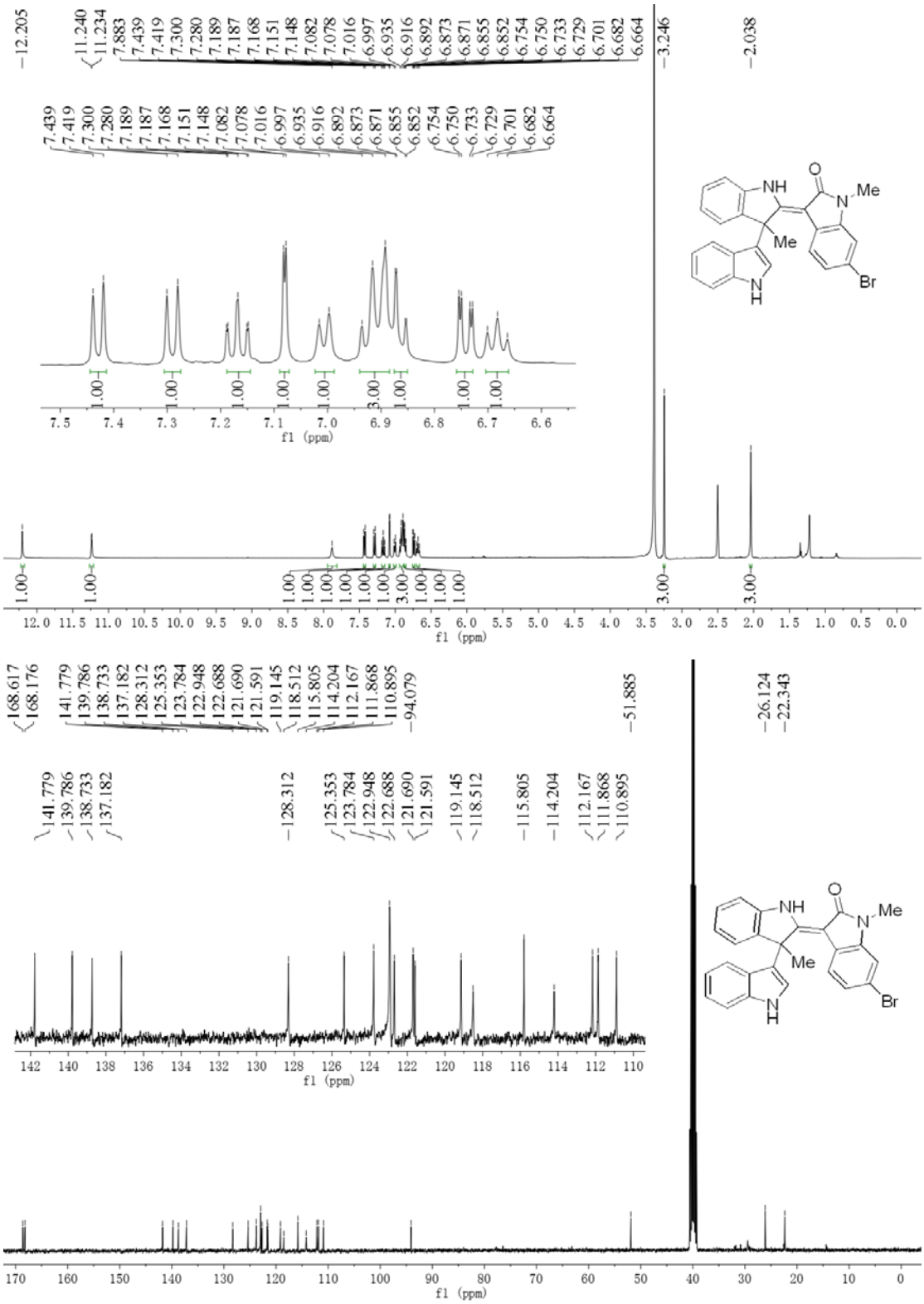
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7.082
7.078
7.016
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6.935
6.916
6.892
6.873
6.871
6.855
6.852
6.754
6.750
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6.729
6.701
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Me
Me
Br
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139.786
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137.182
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123.784
122.948
122.688
121.690
121.591
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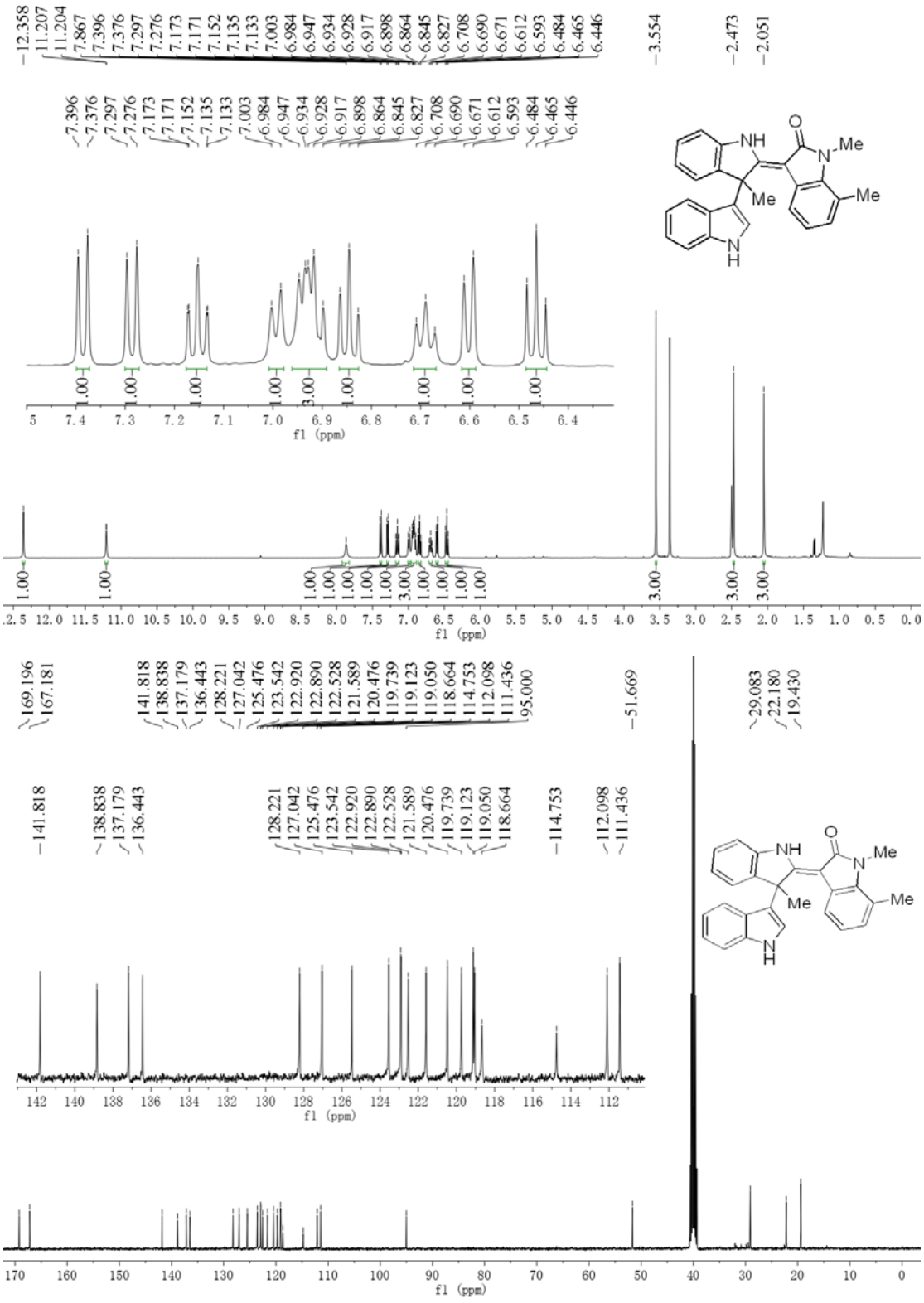
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6.446
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Me
Me
Me
N
H
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169.196
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f1 (ppm)

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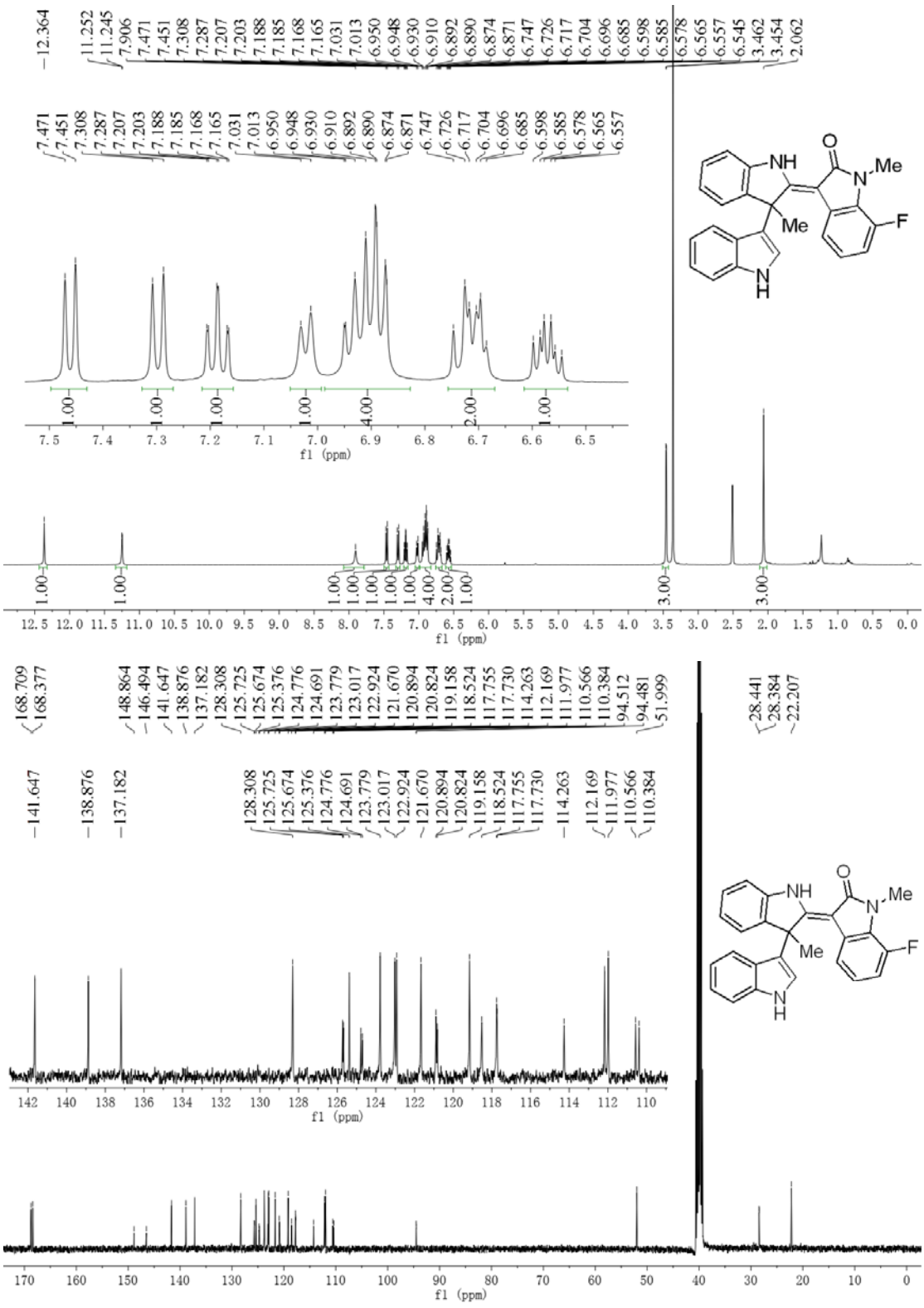
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6.585
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NH
N
Me
Me
F
H
f1 (ppm)
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168.377
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125.376
124.776
124.691
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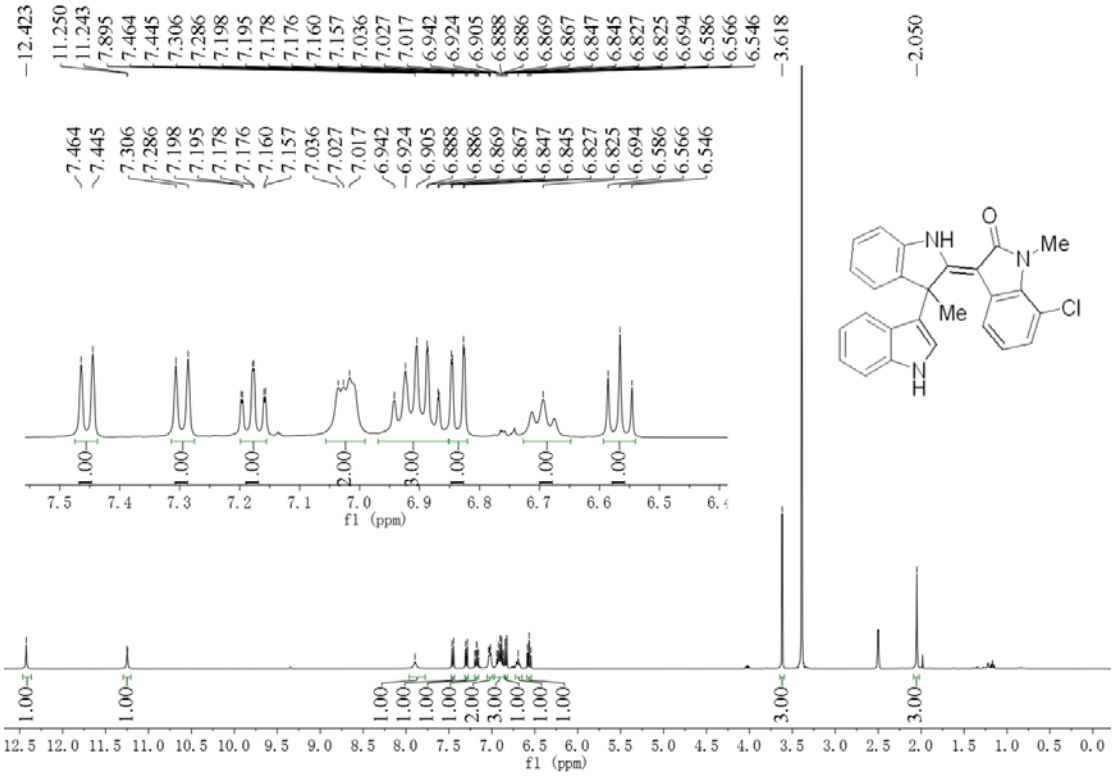
f1 (ppm)
f1 (ppm)

3ja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7.157
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6.825
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Cl
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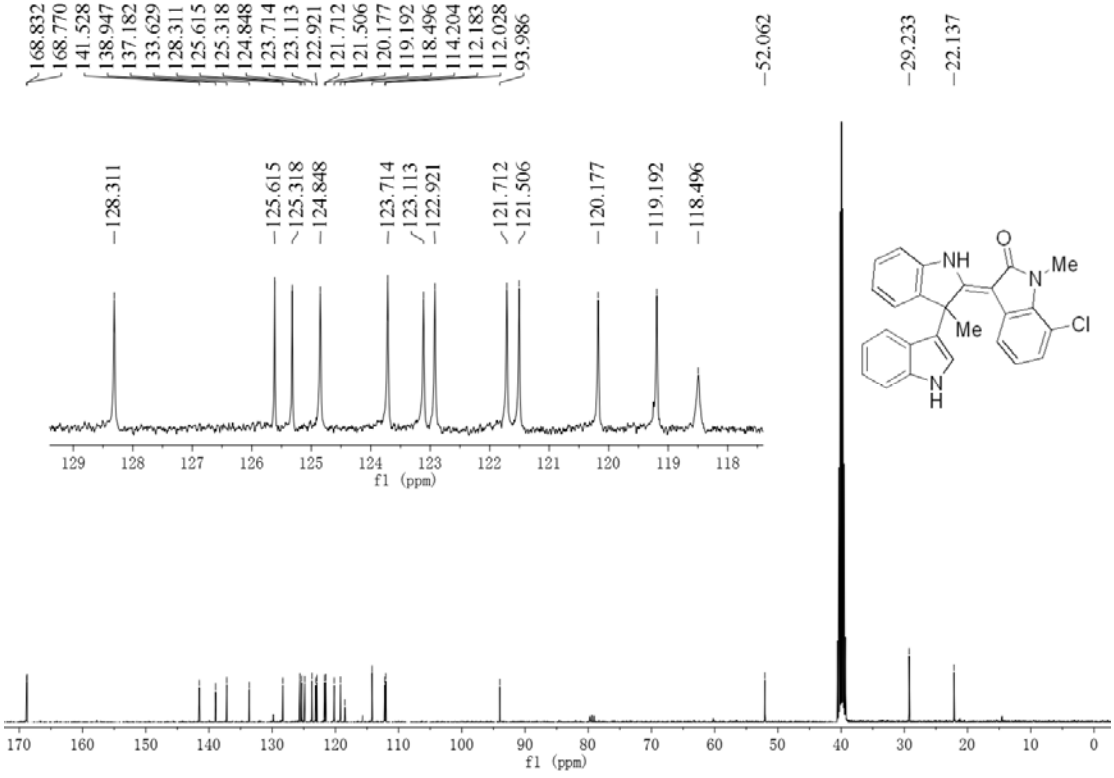
H
f1 (ppm)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121.712
121.506
120.177
119.192
118.496
114.204
112.183
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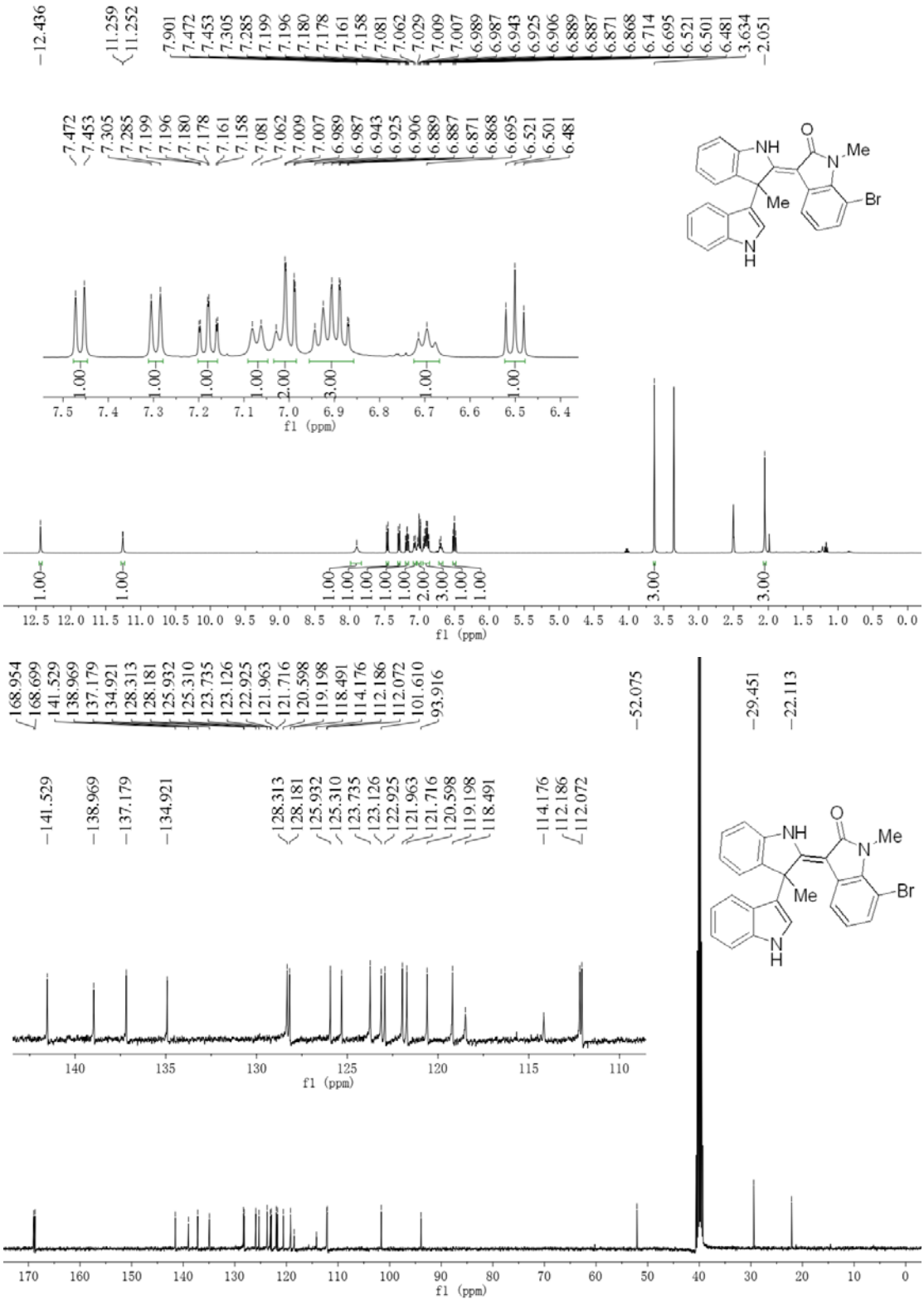
Me
Me
Cl
N
H
f1 (ppm)

3ka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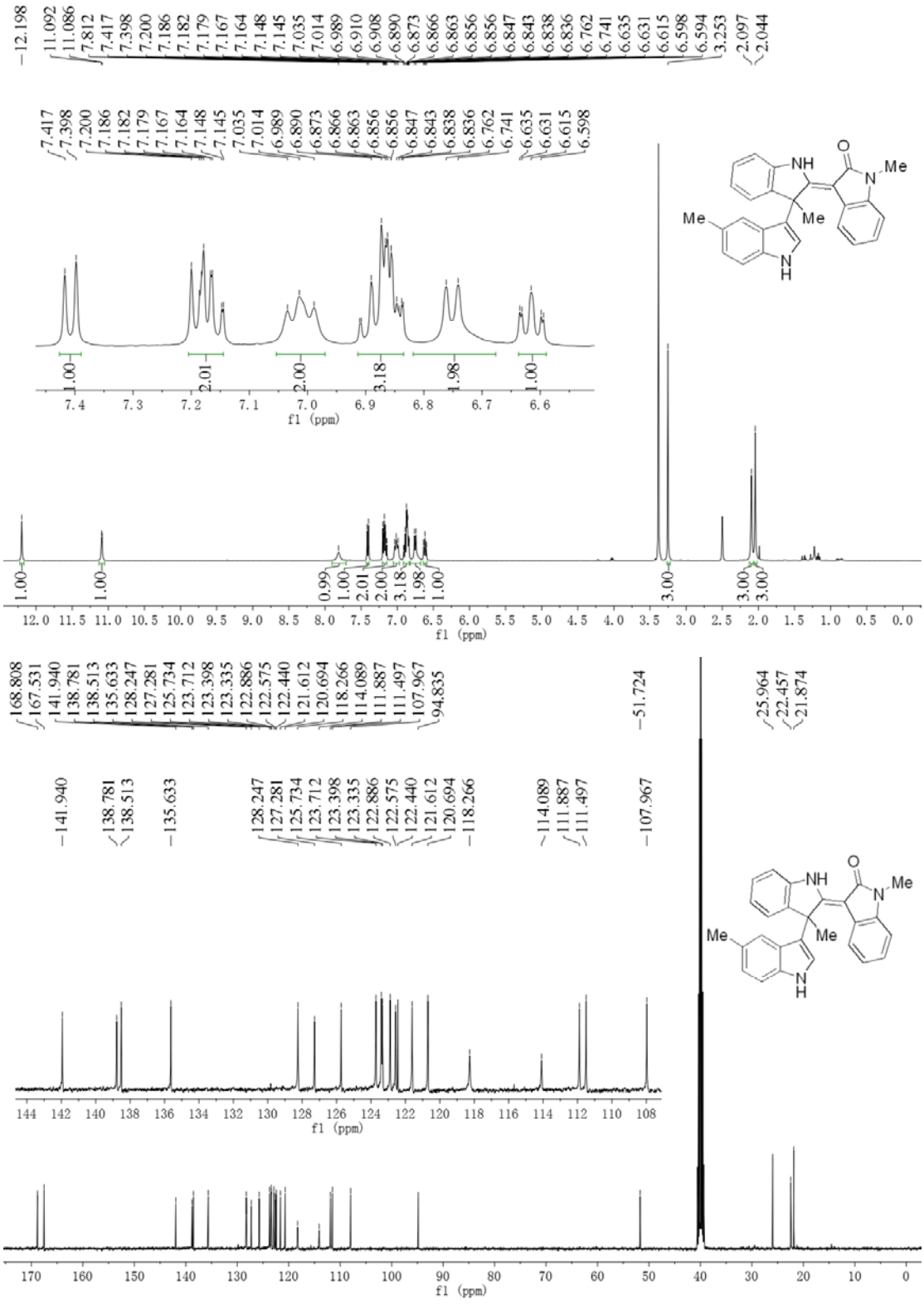
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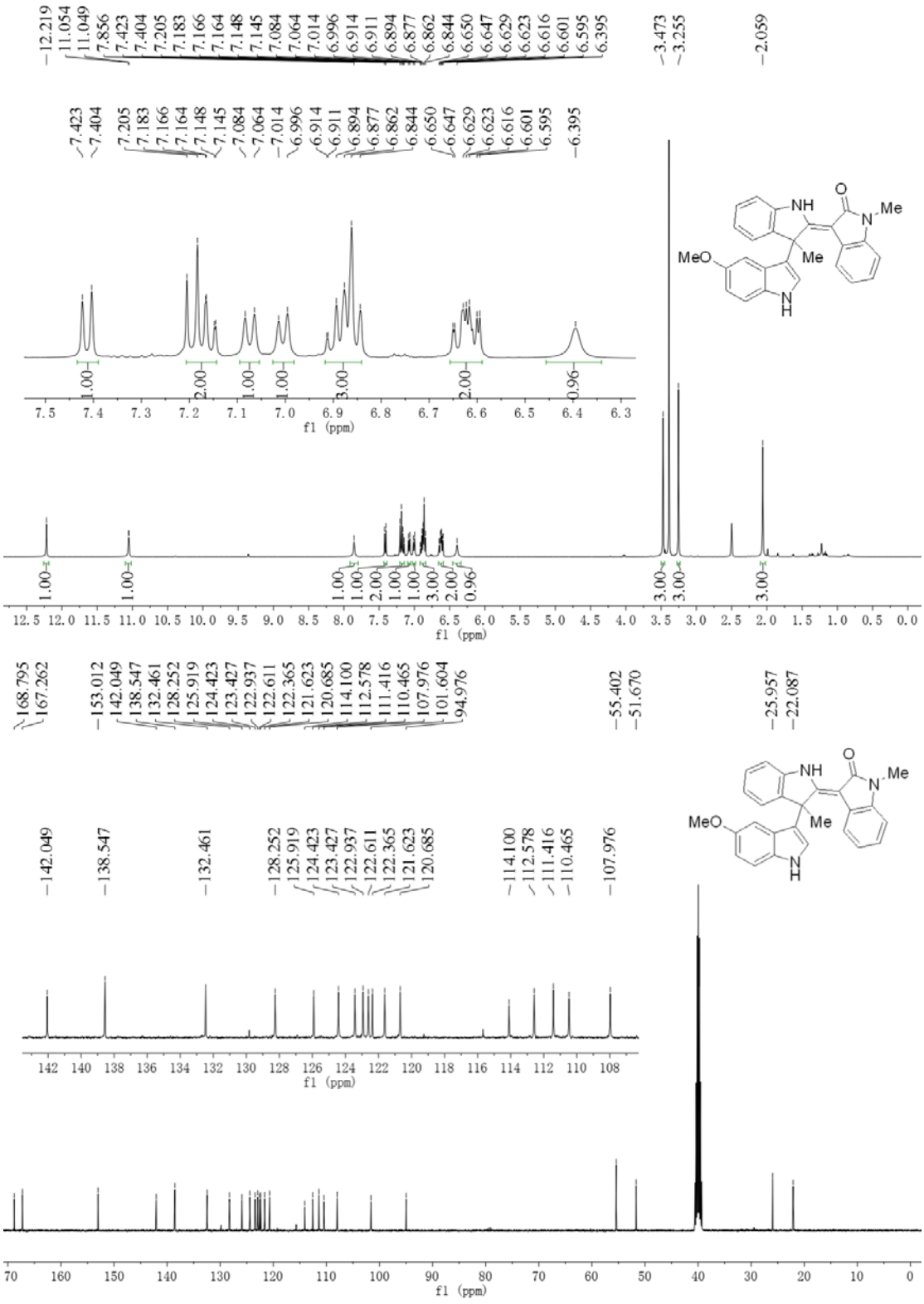
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O
N
Me
MeO
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H
f1 (ppm)
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167.262
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142.049
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125.919
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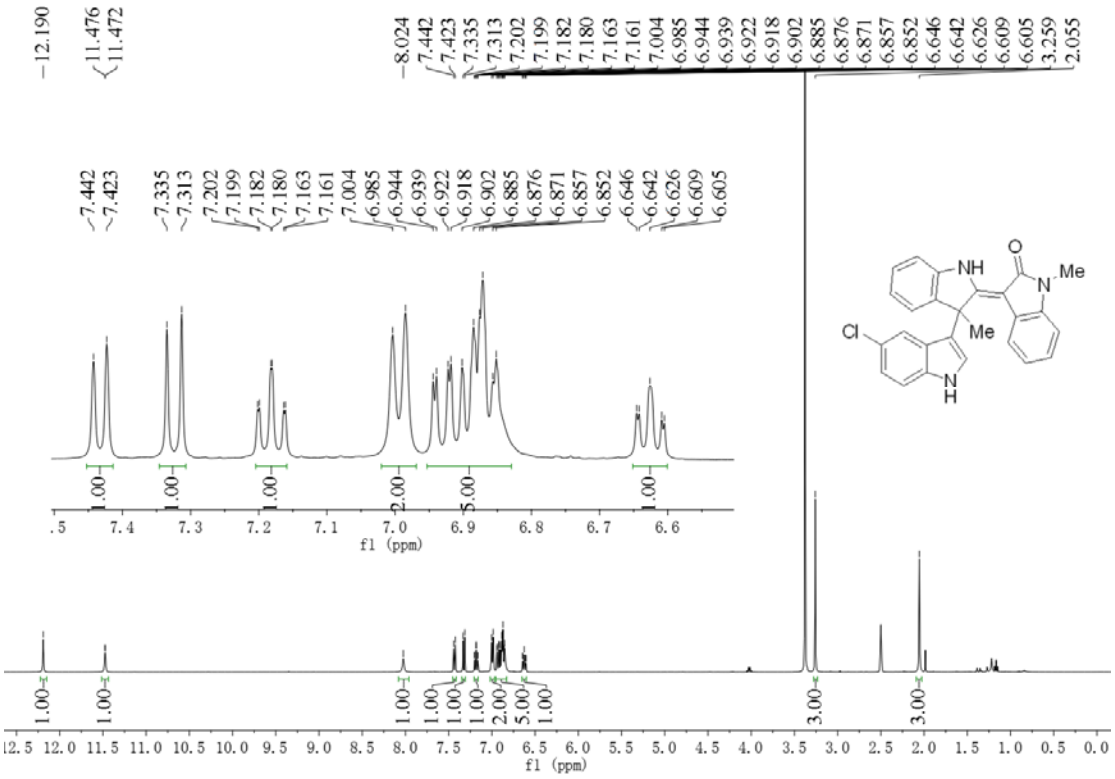
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6.626
6.609
6.605
3.259
2.055
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O
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Me
Me
Cl
N
H
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1.00
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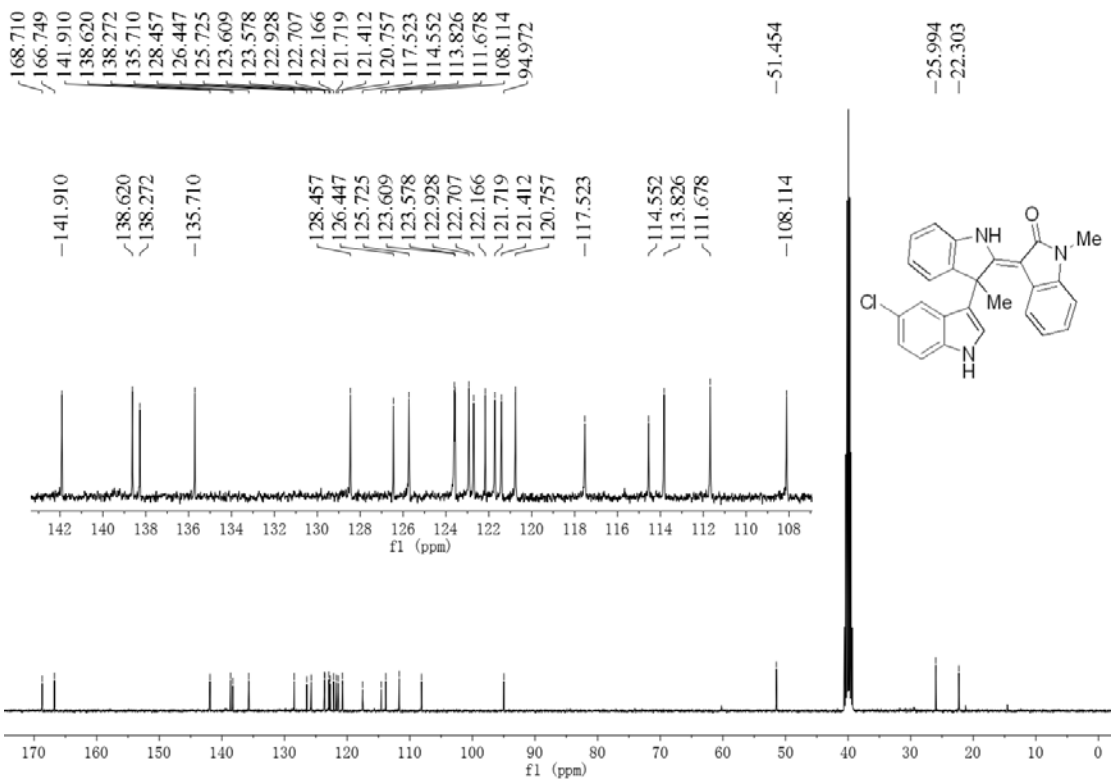
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Me
Cl
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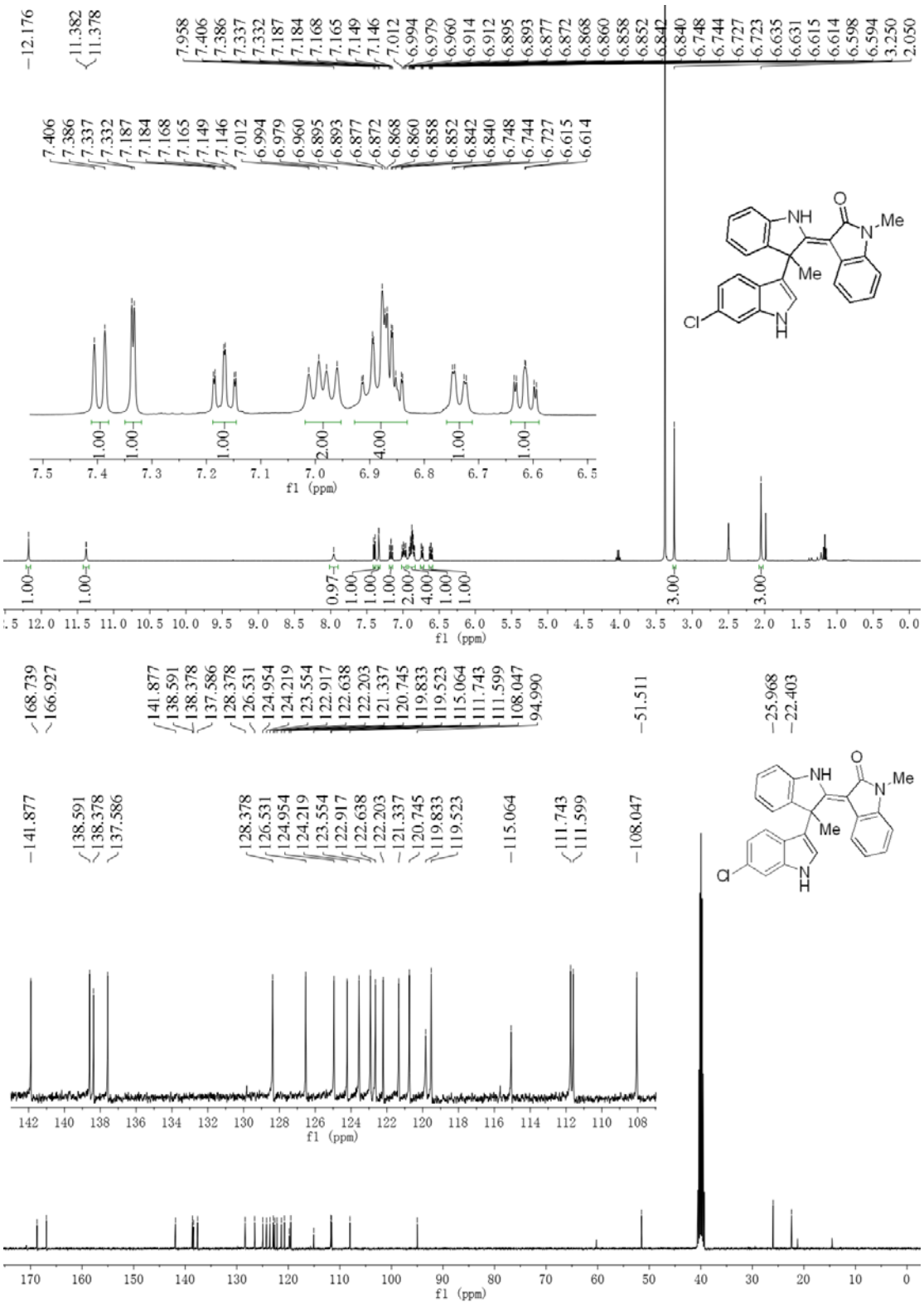
f1 (ppm)
f1 (ppm)

3oa



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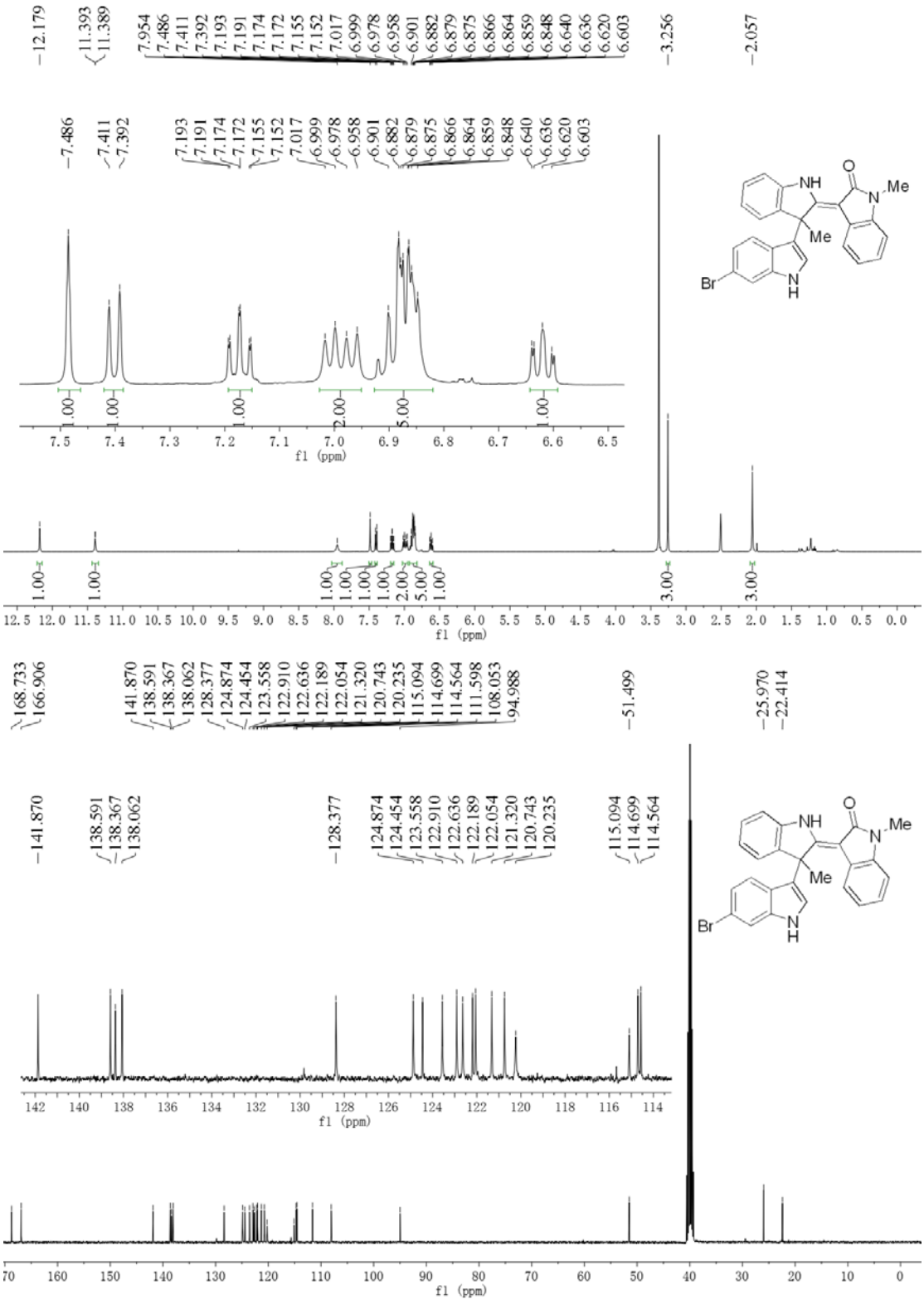
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Me
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f1 (ppm)
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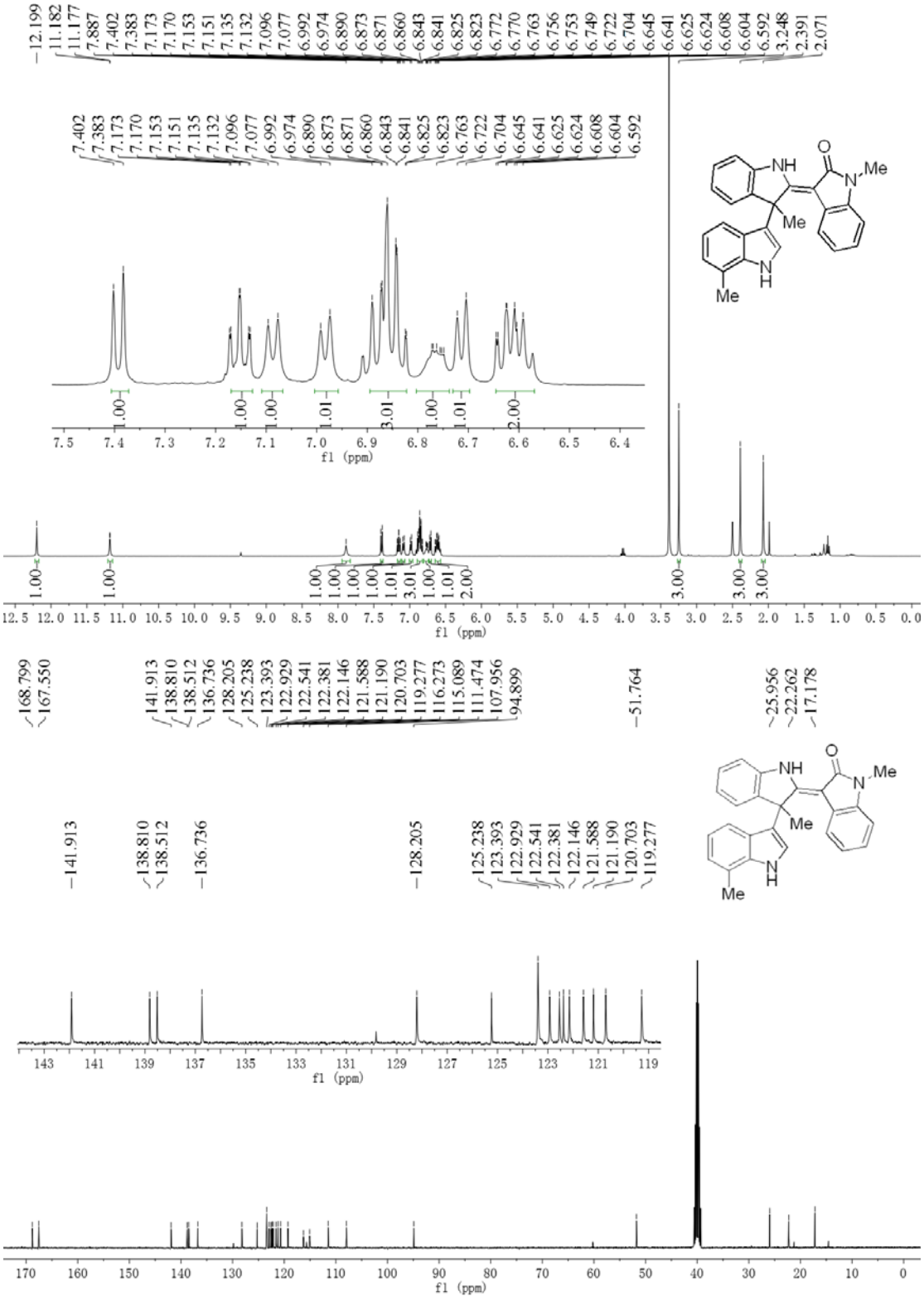
3qa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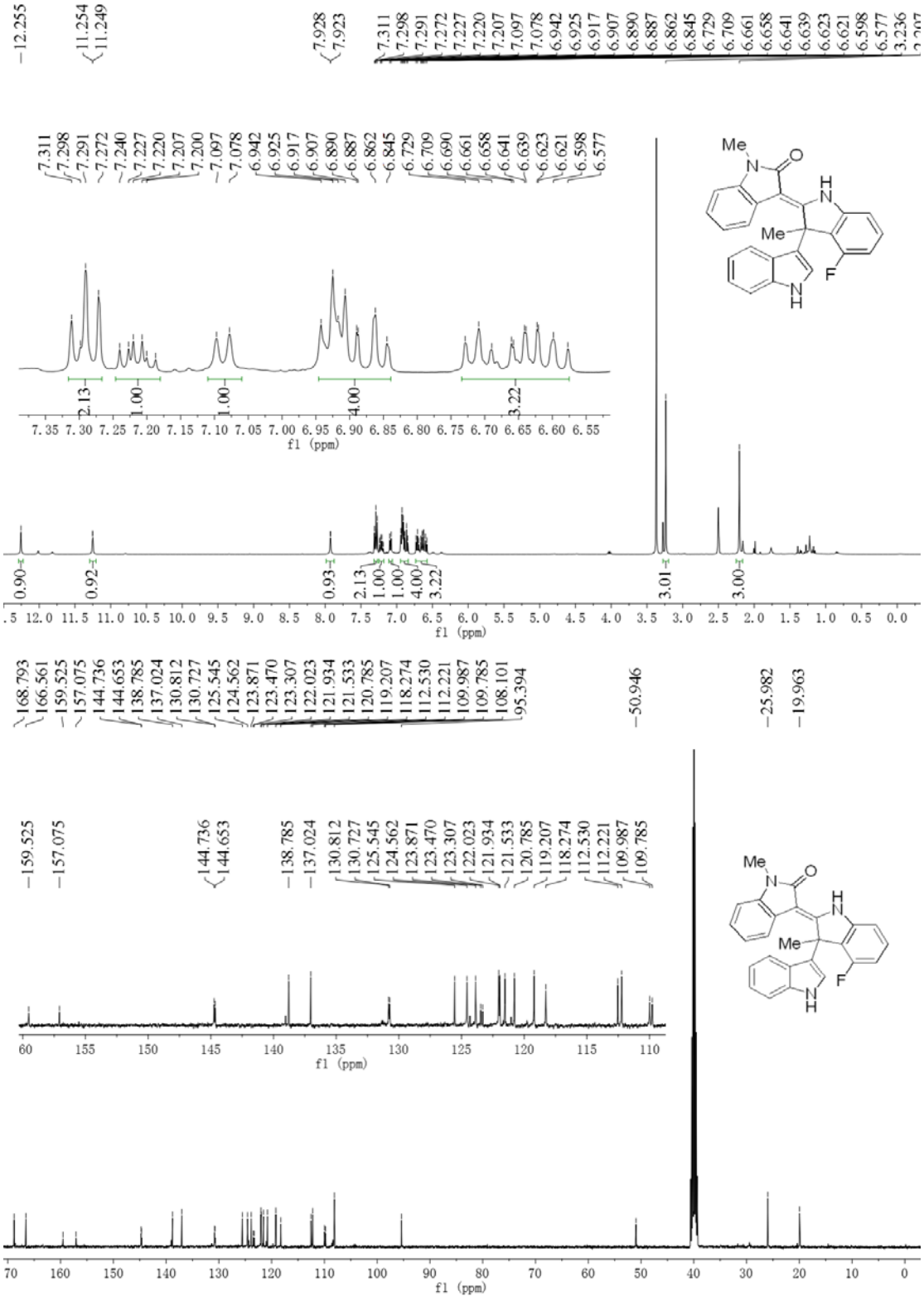
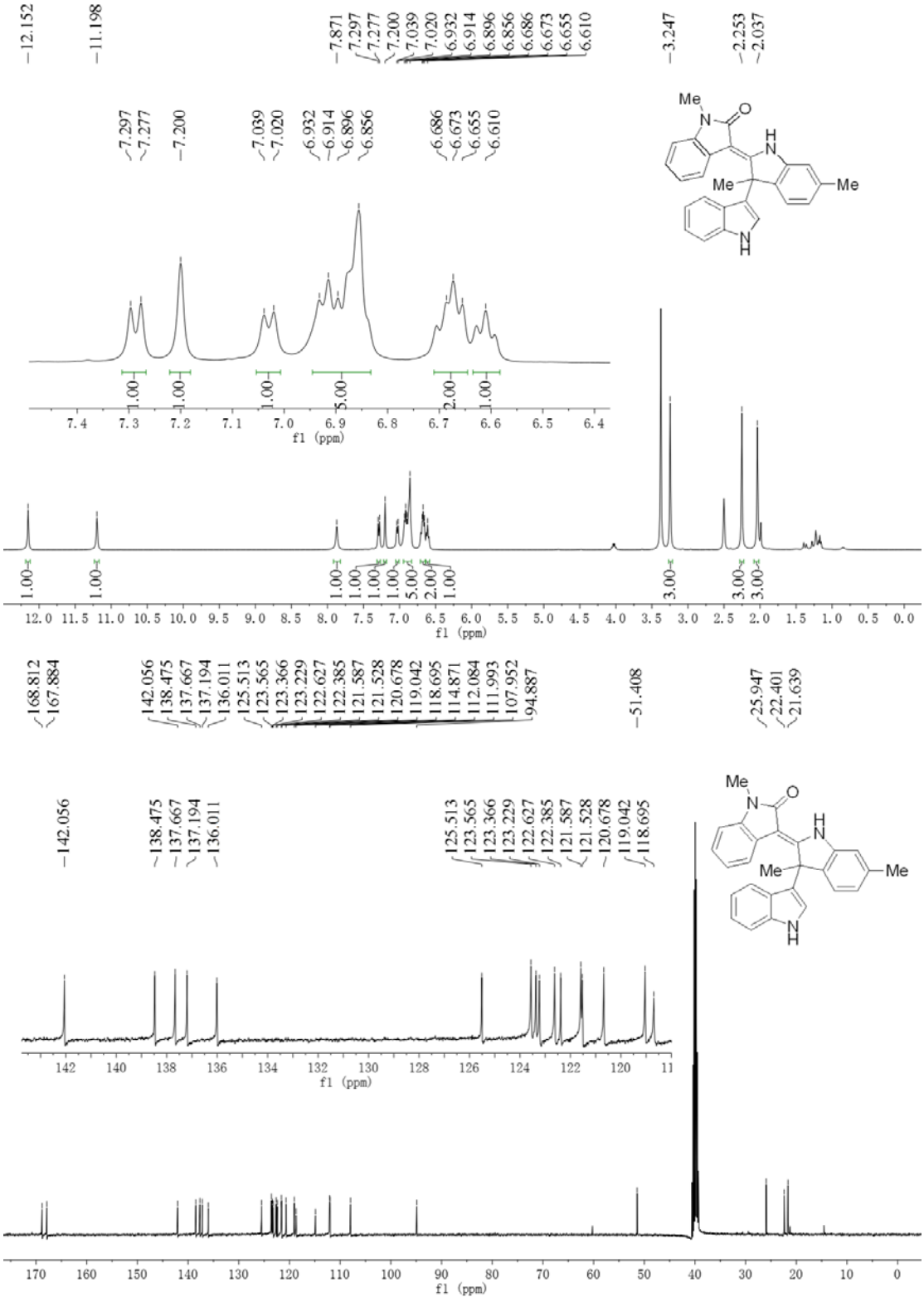
6.825
6.823
6.772
6.770
6.763
6.756
6.753
6.749
6.722
6.704
6.645
6.641
6.625
6.624
6.608
6.604
6.592
3.248
2.391
2.071
NH
O
N
Me
Me
N
H
Me
f1 (ppm)
168.799
167.550
141.913
138.810
138.512
136.736
128.205
125.238
123.393
122.929
122.541
122.381
122.146
121.588
121.190
120.703
119.277
116.273
115.089
111.474
107.956
94.899
51.764
25.956
22.262
17.178
f1 (ppm)

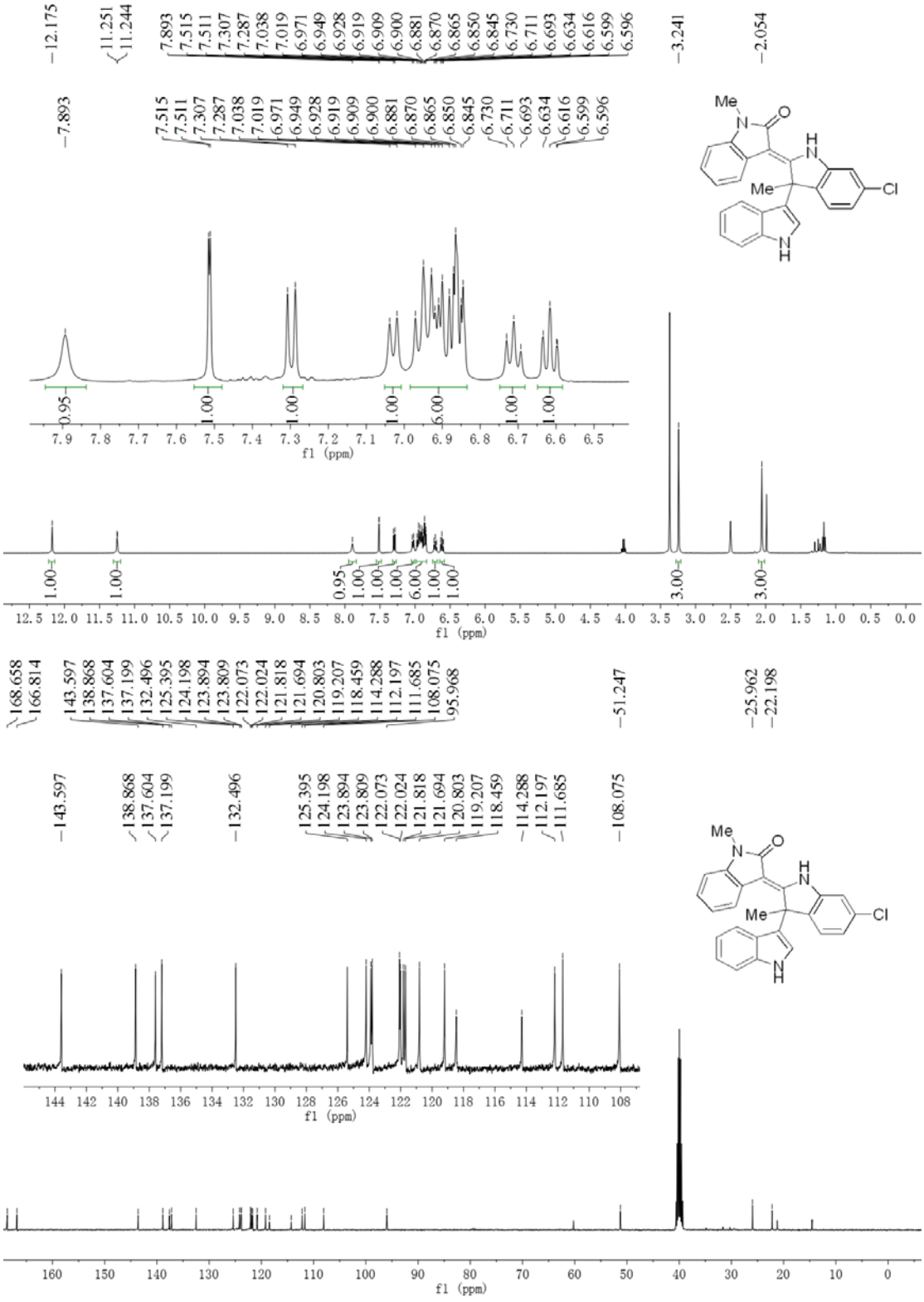
3ab


12.255
11.254
11.249
7.928
7.923
7.311
7.298
7.291
7.272
7.240
7.227
7.220
7.207
7.200
7.097
7.078
6.942
6.925
6.917
6.907
6.890
6.887
6.862
6.845
6.729
6.709
6.690
6.661
6.658
6.641
6.639
6.623
6.621
6.598
6.577
Me
N
O
H
N
Me
F
H
N
2.13
1.00
1.00
4.00
3.22
f1 (ppm)
0.90
0.92
0.93
2.13
1.00
1.00
4.00
3.22
3.01
3.00
f1 (ppm)
168.793
166.561
159.525
157.075
144.736
144.653
138.785
137.024
130.812
130.727
125.545
124.562
123.871
123.470
123.307
122.023
121.934
121.533
120.785
119.207
118.274
112.530
112.221
109.987
109.785
108.101
95.394
50.946
25.982
19.963
159.525
157.075
144.736
144.653
138.785
137.024
130.812
130.727
125.545
124.562
123.871
123.470
123.307
122.023
121.934
121.533
120.785
119.207
118.274
112.530
112.221
109.987
109.785
Me
N
O
H
N
Me
F
H
f1 (ppm)
f1 (ppm)

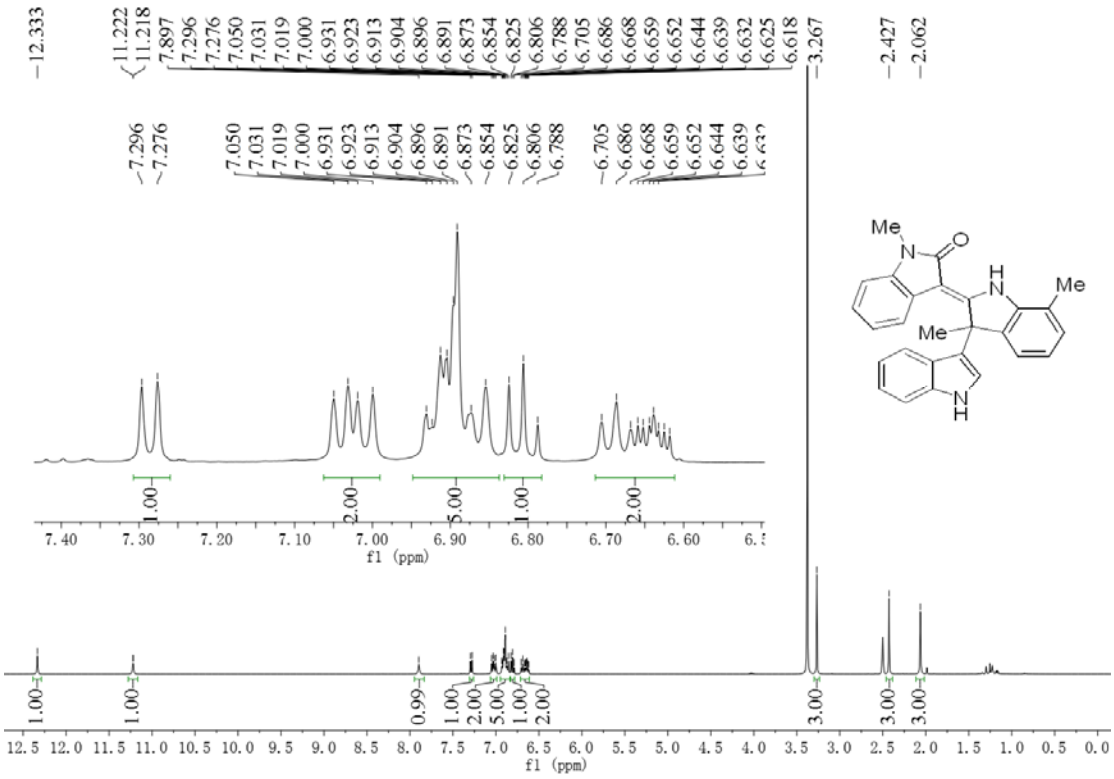
3ac

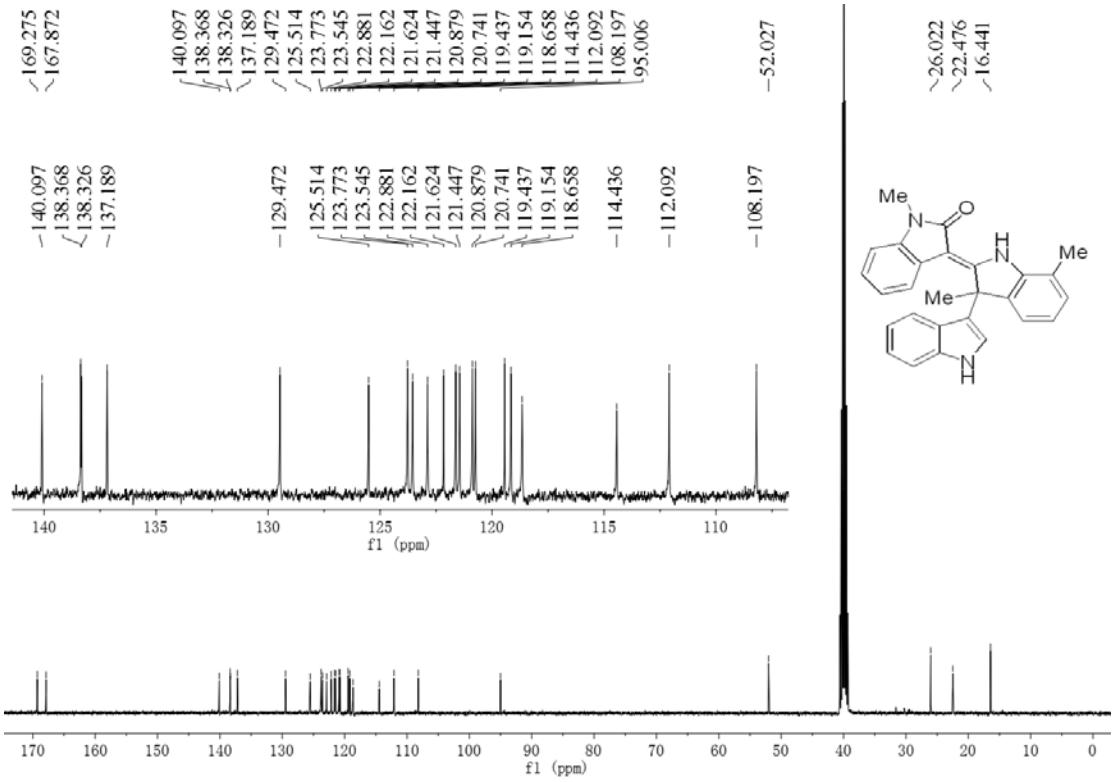

12.152
11.198
7.871
7.297
7.277
7.200
7.039
7.020
6.932
6.914
6.896
6.856
6.686
6.673
6.655
6.610
3.247
2.253
2.037
Me
N
O
H
N
Me
Me
f1 (ppm)
168.812
167.884
142.056
138.475
137.667
137.194
136.011
125.513
123.565
123.366
123.229
122.627
122.385
121.587
121.528
120.678
119.042
118.695
114.871
112.084
111.993
107.952
94.887
51.408
25.947
22.401
21.639

3ad

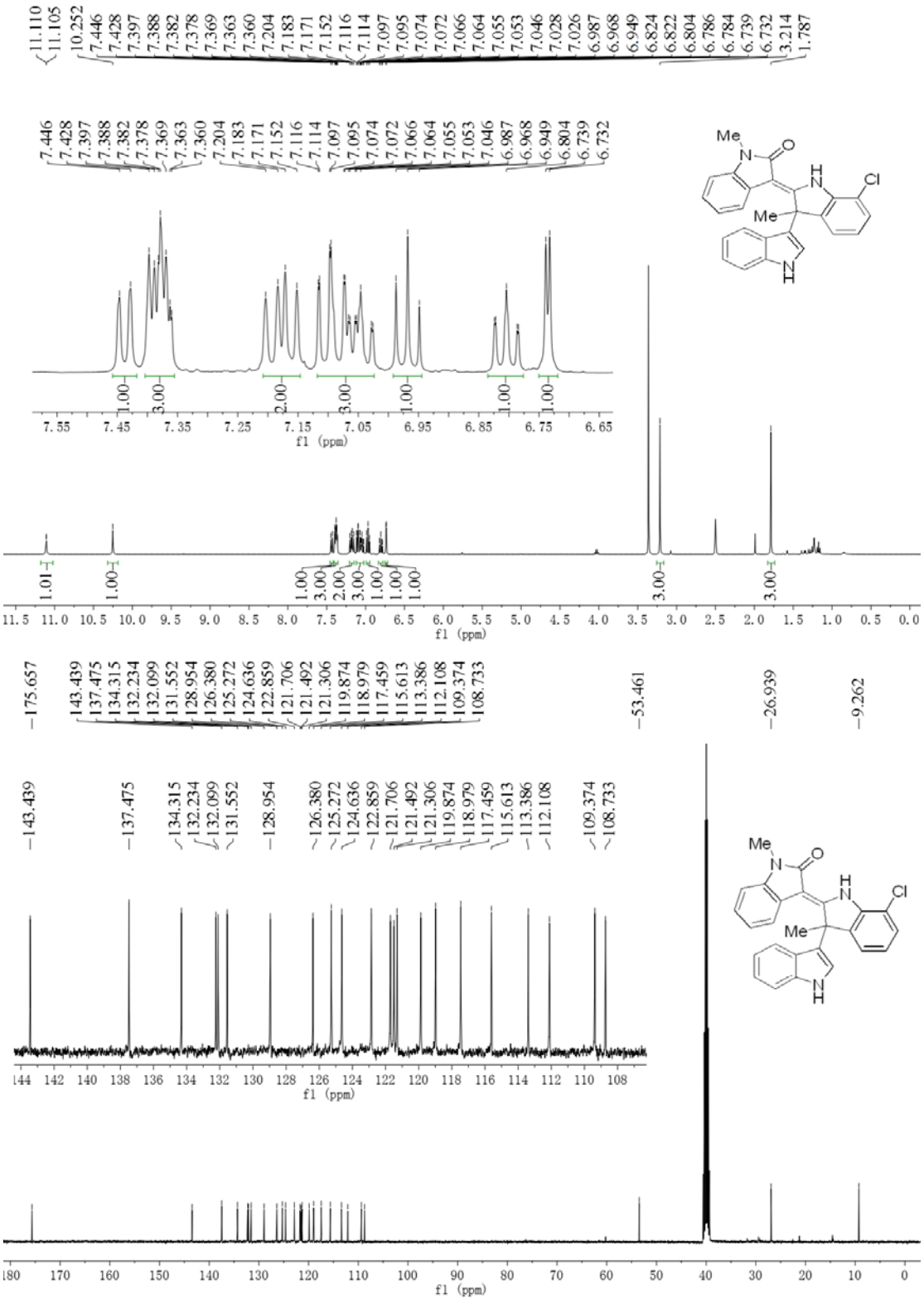

12.175
11.251
11.244
7.893
7.515
7.511
7.307
7.287
7.038
7.019
6.971
6.949
6.928
6.919
6.909
6.900
6.881
6.870
6.865
6.850
6.845
6.730
6.711
6.693
6.634
6.616
6.599
6.596
3.241
2.054
Me
N
O
H
N
Me
Cl
H
N
f1 (ppm)
168.658
166.814
143.597
138.868
137.604
137.199
132.496
125.395
124.198
123.894
123.809
122.073
122.024
121.818
121.694
120.803
119.207
118.459
114.288
112.197
111.685
108.075
95.968
51.247
25.962
22.198
f1 (ppm)
f1 (ppm)

3ae

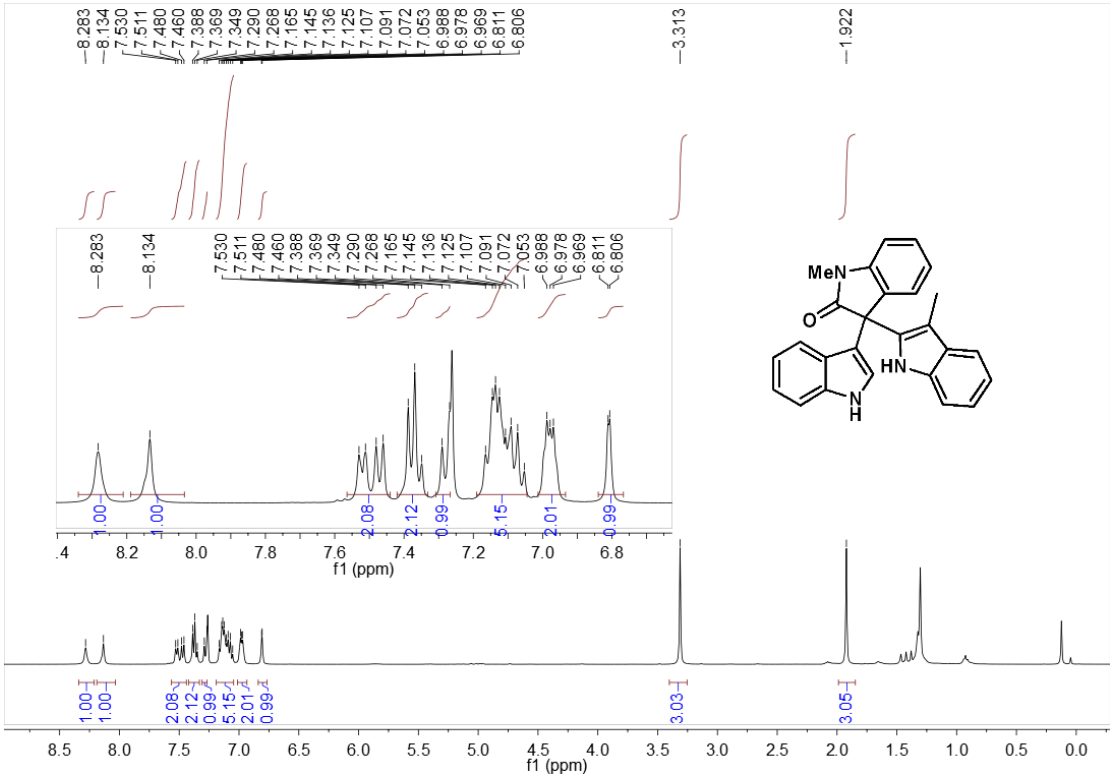

12.333
11.222
11.218
7.897
7.296
7.276
7.050
7.031
7.019
7.000
6.931
6.923
6.913
6.904
6.896
6.891
6.873
6.854
6.825
6.806
6.788
6.705
6.686
6.668
6.659
6.652
6.644
6.639
6.632
6.625
6.618
3.267
2.427
2.062
Me
N
O
H
N
Me
Me
N
H
1.00
2.00
5.00
1.00
2.00
f1 (ppm)
0.99
3.00

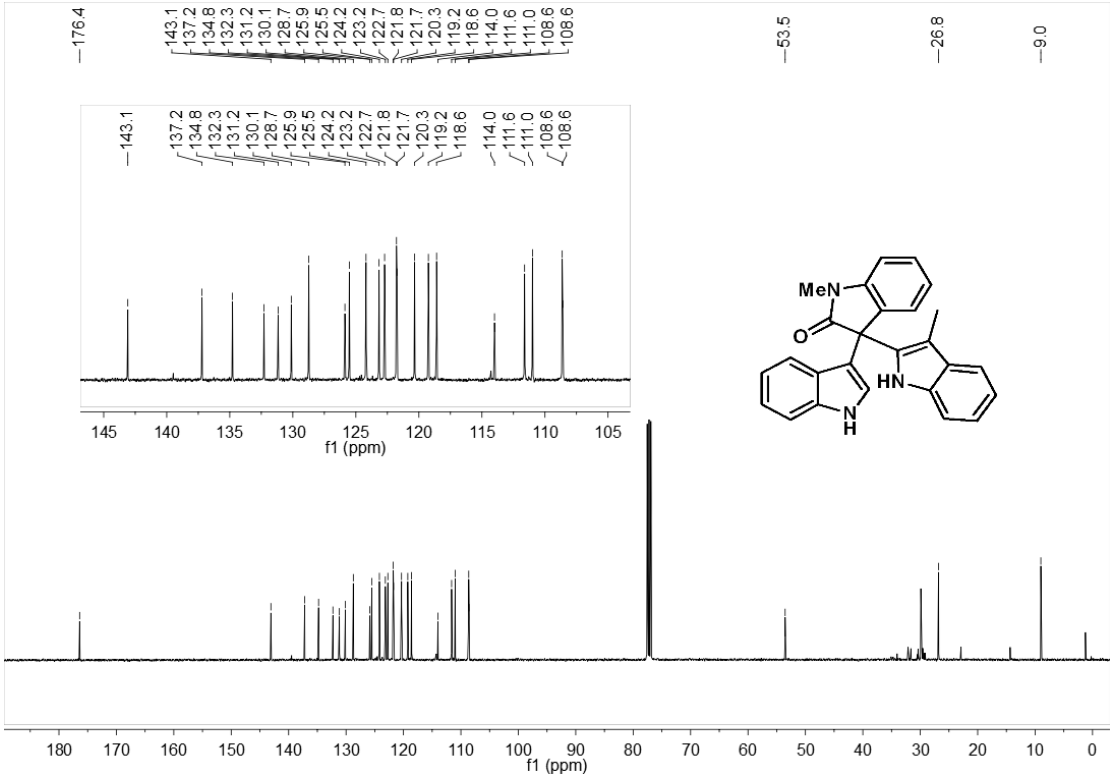

169.275
167.872
140.097
138.368
138.326
137.189
129.472
125.514
123.773
123.545
122.881
122.162
121.624
121.447
120.879
120.741
119.437
119.154
118.658
114.436
112.092
108.197
95.006
52.027
26.022
22.476
16.441
Me
N
O
H
N
Me
Me
N
H
f1 (ppm)

3af

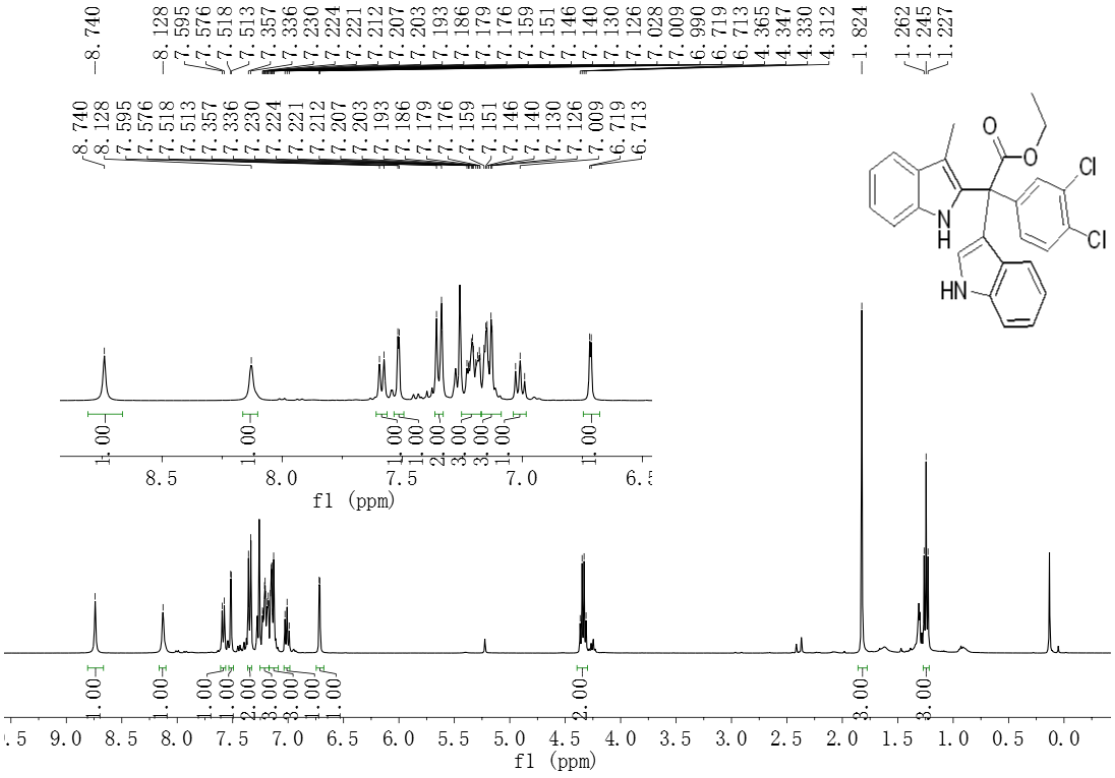

11.110
11.105
10.252
7.446
7.428
7.397
7.388
7.382
7.378
7.369
7.363
7.360
7.204
7.183
7.171
7.152
7.116
7.114
7.097
7.095
7.074
7.072
7.066
7.064
7.055
7.053
7.046
7.028
7.026
6.987
6.968
6.949
6.824
6.822
6.804
6.786
6.784
6.739
6.732
3.214
1.787
Me
N
O
H
N
Cl
Me
H
N
1.00
3.00
2.00
3.00
1.00
1.00
1.00
7.55
7.45
7.35
7.25
7.15
7.05
6.95
6.85
6.75
6.65
f1 (ppm)
1.01
1.00
1.00
3.00
2.00
3.00
1.00
1.00
1.00
3.00
3.00
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
175.657
143.439
137.475
134.315
132.234
132.099
131.552
128.954
126.380
125.272
124.636
122.859
121.706
121.492
121.306
119.874
118.979
117.459
115.613
113.386
112.108
109.374
108.733
53.461
26.939
9.262
144
142
140
138
136
134
132
130
128
126
124
122
120
118
116
114
112
110
108
f1 (ppm)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

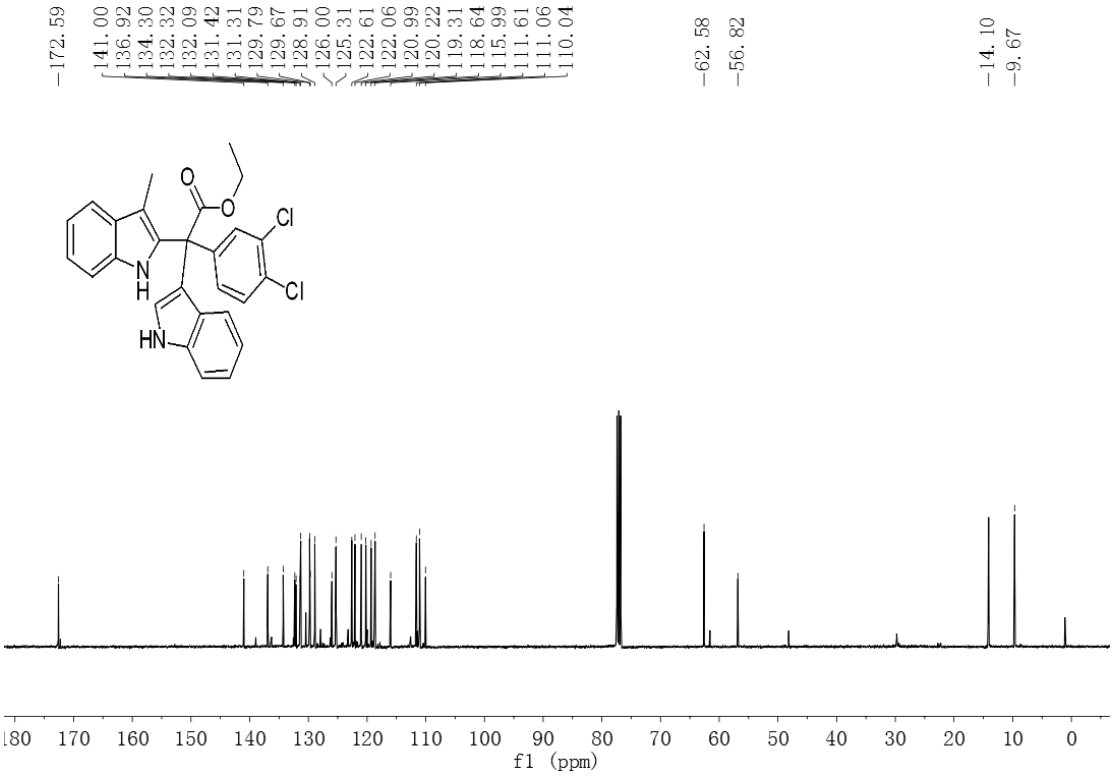
4aa


8.283
8.134
7.530
7.511
7.480
7.460
7.388
7.369
7.349
7.290
7.268
7.165
7.145
7.136
7.125
7.107
7.091
7.072
7.053
6.988
6.978
6.969
6.811
6.806
3.313
1.922
MeN
O
HN
N
H
1.00
1.00
2.08
2.12
0.99
5.15
2.01
0.99
3.03
3.05
f1 (ppm)

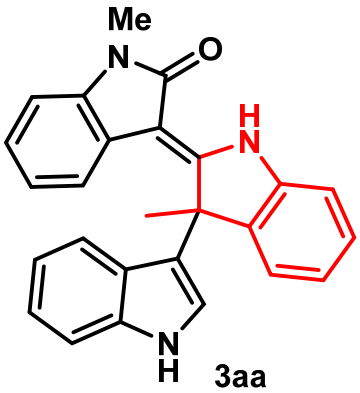

176.4
143.1
137.2
134.8
132.3
131.2
130.1
128.7
125.9
125.5
124.2
123.2
122.7
121.8
121.7
120.3
119.2
118.6
114.0
111.6
111.0
108.6
108.6
53.5
26.8
9.0
MeN
O
HN
N
H
f1 (ppm)

4ra

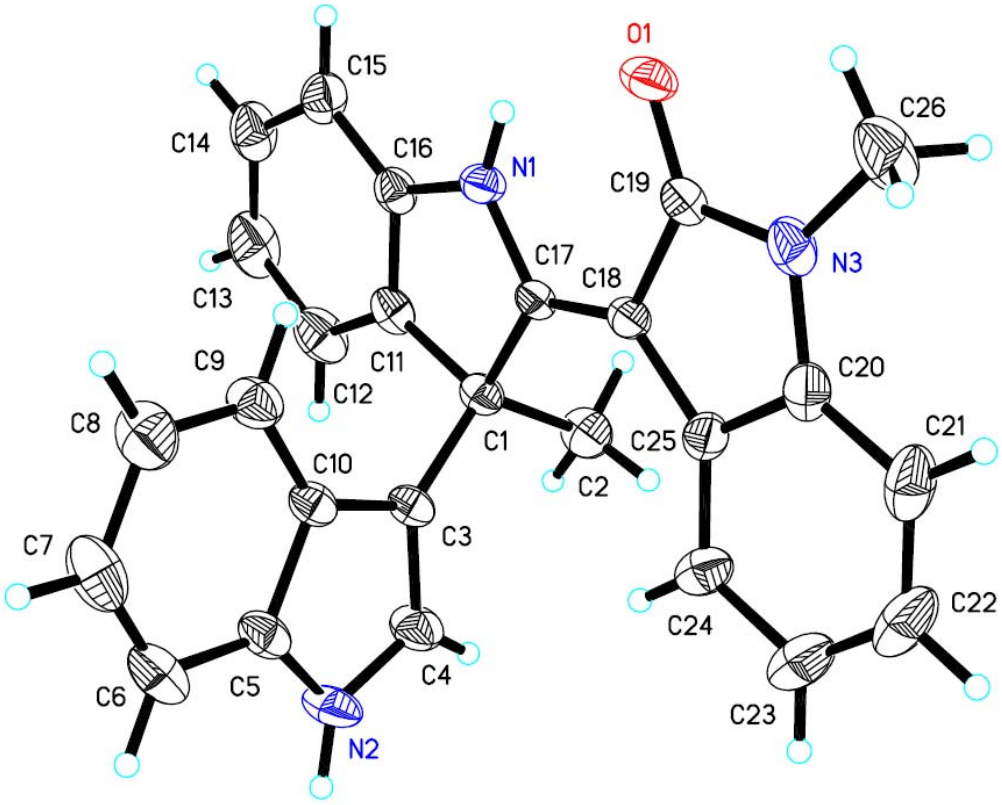

8.740
8.128
7.595
7.576
7.518
7.513
7.357
7.336
7.230
7.224
7.221
7.212
7.207
7.203
7.193
7.186
7.179
7.176
7.159
7.151
7.146
7.140
7.130
7.126
7.009
6.719
6.713
4.365
4.347
4.330
4.312
1.824
1.262
1.245
1.227
Cl
Cl
N
H
HN
O
O
f1 (ppm)


172.59
141.00
136.92
134.30
132.32
132.09
131.42
131.31
129.79
129.67
128.91
126.00
125.31
122.61
122.06
120.99
120.22
119.31
118.64
115.99
111.61
111.06
110.04
62.58
56.82
14.10
9.67
Cl
Cl
N
H
HN
O
O
f1 (ppm)

2. X-ray single crystal data for compounds 3aa and 4aa



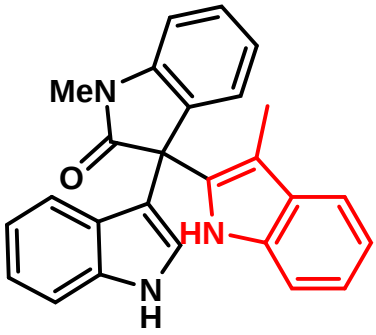
3aa



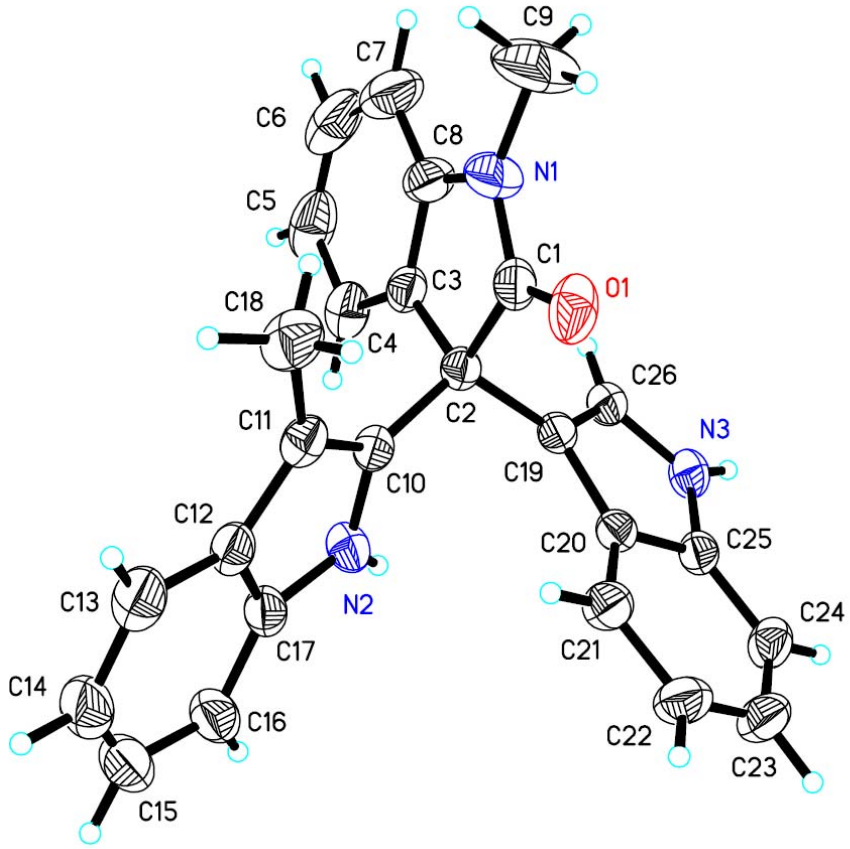
The thermal ellipsoid was drawn at the 30% probability level.

Empirical formula	C26 H21 N3 O	
Formula weight	391.46	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 10.0804(4) Å	α= 90°.
	b = 13.1042(6) Å	β= 105.516(2)°.
	c = 15.9458(7) Å	γ = 90°.

Volume	2029.60(15) $Å^3$
Z	4
Density (calculated)	1.281 Mg/m^3
Absorption coefficient	0.080 mm^{-1}
F(000)	824
Crystal size	0.260 x 0.220 x 0.150 mm^3
Theta range for data collection	2.043 to 27.506°.
Index ranges	-13<=h<=13, -15<=k<=17, -19<=l<=20
Reflections collected	17943
Independent reflections	4651 [R(int) = 0.0308]
Completeness to theta = 25.242°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.6657
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4651 / 0 / 273
Goodness-of-fit on F^2	1.061
Final R indices [I>2sigma(I)]	R1 = 0.0490, wR2 = 0.1306
R indices (all data)	R1 = 0.0774, wR2 = 0.1539
Extinction coefficient	n/a
Largest diff. peak and hole	0.214 and -0.235 $e.Å^{-3}$



4aa



The thermal ellipsoid was drawn at the 30% probability level.

Empirical formula	C26 H21 N3 O	
Formula weight	391.46	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 10.0804(4) Å	α= 90°.
	b = 13.1042(6) Å	β= 105.516(2)°.
	c = 15.9458(7) Å	γ = 90°.

Volume	2029.60(15) $Å^3$
Z	4
Density (calculated)	1.281 Mg/m^3
Absorption coefficient	0.080 mm^{-1}
F(000)	824
Crystal size	0.260 x 0.220 x 0.150 mm^3
Theta range for data collection	2.043 to 27.506°.
Index ranges	-13<=h<=13, -15<=k<=17, -19<=l<=20
Reflections collected	17943
Independent reflections	4651 [R(int) = 0.0308]
Completeness to theta = 25.242°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.6657
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4651 / 0 / 273
Goodness-of-fit on F^2	1.061
Final R indices [I>2sigma(I)]	R1 = 0.0490, wR2 = 0.1306
R indices (all data)	R1 = 0.0774, wR2 = 0.1539
Extinction coefficient	n/a
Largest diff. peak and hole	0.214 and -0.235 $e.Å^{-3}$