Supporting Information

Metal-free Syntheses of Oxindole Derivatives via a Benzoylation/Substitution/Desulfonylation/Cyclization Cascade

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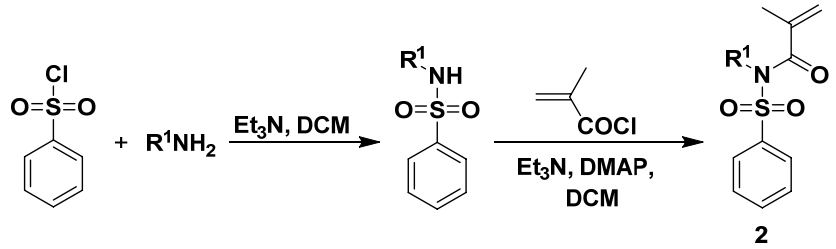
Experimental section

General: All reactions were carried out under an atmosphere of nitrogen; stirring was achieved with an oven-dried magnetic stirring bar. Solvents were purified by standard methods unless otherwise noted. Commercially available reagents were purchased from Aladdin Company in China and used throughout without further purification other than those detailed below. Flash column chromatography was performed on silica gel (200-300 mesh). All reactions were monitored by TLC analysis. Deuterated solvents were purchased from Cambridge Isotope laboratories. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX-400 spectrometer operating at 400 MHz and 100 MHz respectively. Mass spectrometry (LC-MS) was recorded on a LXQ Spectrometer (Thermo Scientific) operating on ESI (MeOH as a solvent)

General procedure for the syntheses of compounds 2



2

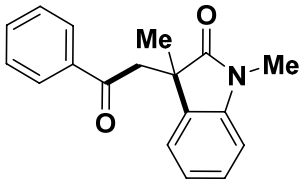
Primary amine (1.2 equiv) and Et_3N (2 equiv) were added to a dried flask, then benzenesulfonyl chloride (1 equiv) in dichloromethane was injected into it. The mixture was stirred at 0°C until TLC showed that benzenesulfonyl chloride was totally consumed. Water was added to the reaction mixture and extracted with dichloromethane. The combined organic layers were dried over Na_2SO_4, concentrated under reduced pressure. Without further purification, the residue was used for the next step.

Methacryloyl chloride (2 equiv) in dichloromethane was added to the mixture of the above residue, triethylamine (2 equiv) and DMAP (0.1 equiv) in dichloromethane. The mixture was stirred overnight at room temperature. Then the reaction mixture was washed with saturated aqueous Na_2CO_3 (5 mL) and extracted with dichloromethane. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by column chromatography (petroleum ether : ethyl acetate =12:1) on silica gel to afford the corresponding product **2** in a total yield of 62~74%.

General procedure for the syntheses of compounds 3a-m

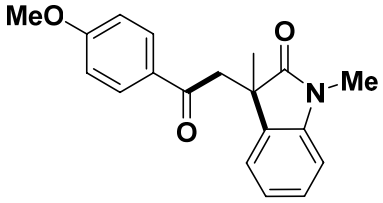
N-Methyl-N-(phenylsulfonyl)methacrylamide (2.0 mmol, 1.0 equiv) was added to a dried flask, followed by the addition of $NaHCO_3$ (2 mmol, 1.0 equiv), Methoxyaldehyde (10.0 mmol, 5 equiv), then aqueous TBHP (2.5 equiv, 70 wt% in water) was injected into the flask under N_2. The reaction mixture was stirred at 90 ^oC for 18 h. After the reaction was completed, the reaction mixture was washed with saturated aqueous Na_2CO_3 (5 mL) and extracted with dichloromethane. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash chromatography (Petroleum ether : EtOAc =10:1) to provide the title compound **3a** as a sticky solid in a 70% yield. The same procedure was applied for producing other compounds **3b-m**.

1,3-Dimethyl-3-(2-oxo-2-phenylethyl)indolin-2-one (3a)



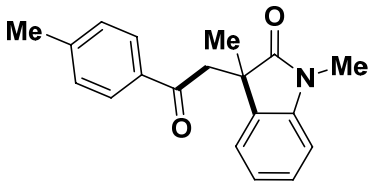
^{1}H-NMR ($CDCl_3$, 400MHz)：δ (ppm) 7.86-6.91 (aromatic H, 9H), 3.72 (d, *J*=17.6 Hz, 1H), 3.70 (d, *J*=17.2 Hz, 1H), 3.33 (s, 3H), 1.46 (s, 3H); **^{13}C-NMR** ($CDCl_3$,100 Hz): 24.9, 26.5, 45.3, 46.0, 108.2, 121.8, 122.2, 127.9, 128.0, 128.5, 128.6, 133.0, 133.2, 133.8, 136.4, 143.9, 180.6, 196.1; **IR:** 2962，2926，2853，1713，1637, 737，700 cm^{-1}; **MS** (ESI) m/z calculated for $C_{18}H_{17}NNaO_2$ 302.12, found 302.36

3-(2-(4-Methoxyphenyl)-2-oxoethyl)-1,3-Dimethylindolin-2-one (3b)



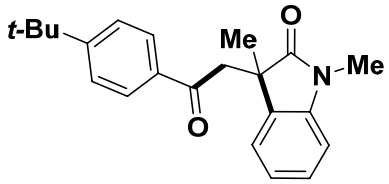
^{1}H-NMR ($CDCl_3$, 400MHz)：δ (ppm) 7.84-6.85 (aromatic H, 8H), 3.82 (s, 3H), 3.69 (d, *J*=17.6 Hz, 1H), 3.65 (d, *J*=18.0 Hz, 1H), 3.32 (s, 3H), 1.44 (s, 3H); **^{13}C-NMR** ($CDCl_3$,100 Hz): 25.0, 26.5, 45.4, 45.7, 55.4, 108.4, 113.6, 121.8, 122.1, 127.8, 129.3, 130.3, 134.0, 143.9, 163.5, 180.8, 194.6; **IR:** 2965，2926，2852，1709，1601, 734，700 cm^{-1}; **MS** (ESI) m/z calculated for $C_{19}H_{19}NNaO_3$ 332.13, found 332.30.

1,3-dimethyl-3-(2-oxo-2-(p-tolyl)ethyl)indolin-2-one (3c)



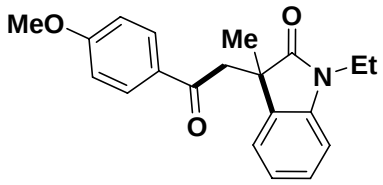
^{1}H-NMR ($CDCl_3$, 400MHz)：δ (ppm) 7.77-6.90 (aromatic H, 8H), 3.70 (d, *J*=18.0 Hz, 1H), 3.66 (d, *J*=17.6 Hz, 1H), 3.33 (s, 3H), 2.37 (s, 3H), 1.46 (s, 3H); **^{13}C-NMR** ($CDCl_3$,100Hz): 21.6, 24.9, 26.5, 45.4, 45.9, 108.2, 121.8, 122.2, 127.8, 128.1, 129.2, 133.9, 134.0, 143.9, 144.0, 180.8, 195.8; **IR:** 2962，2924，2851，1712，1674, 735，701 cm^{-1}; **MS** (ESI) m/z calculated for $C_{19}H_{19}NNaO_2$ 316.13, found 316.36.

3-(2-(4-(*tert*-Butyl)phenyl)-2-oxoethyl)-1,3-Dimethylindolin-2-one (3d)



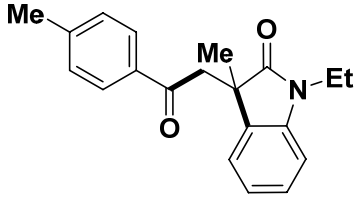
^{1}H-NMR ($CDCl_3$, 400MHz): δ (ppm) 7.82-6.90 (aromatic H, 8H), 3.75 (d, *J*=17.6 Hz, 1H), 3.66 (d, *J*=18.0 Hz, 1H), 3.33 (s, 3H), 1.46 (s, 3H), 1.32 (s, 9H); **^{13}C-NMR** ($CDCl_3$,100Hz): 24.9, 26.5, 31.1, 35.1, 45.4, 46.0, 108.2, 121.8, 122.2, 125.4, 125.5, 127.8, 128.0, 129.3, 133.9, 143.9, 156.9, 180.8, 195.8; **IR:** 2964，2928，2869，1715，1614, 734，700 cm^{-1}; **MS** (ESI) m/z calculated for $C_{22}H_{25}NNaO_2$ 358.18, found 358.28.

1-Ethyl-3-(2-(4-methoxyphenyl)-2-oxoethyl)-3-methylindolin-2-one (3e)



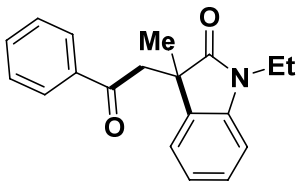
^{1}H-NMR ($CDCl_3$, 400MHz): δ (ppm) 7.85-6.86 (aromatic H, 8H), 3.84 (m, 3H) 3.65 (m, 2H), 1.44 (s, 3H), 1.36 (t, *J*=8.0 Hz, 3H); **^{13}C-NMR** ($CDCl_3$,100 Hz): 12.4, 25.1, 34.7, 45.4, 45.6, 55.4, 108.3, 113.6, 121.9, 122.0, 127.7, 129.6, 130.3, 134.2, 142.9, 163.5, 180.2, 195.6; **IR:** 2969，2928，2854，1711，1602, 736，700 cm^{-1}; **MS** (ESI) m/z calculated for $C_{20}H_{21}NNaO_3$ 346.14, found 346.26.

1-Ethyl-3-methyl-3-(2-oxo-2-(p-tolyl)ethyl)indolin-2-one (3f)



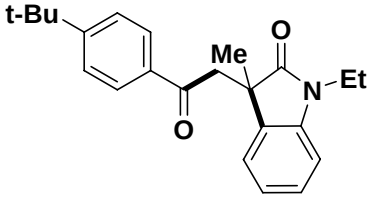
^{1}H-NMR ($CDCl_3$, 400MHz): δ (ppm) 7.77-6.92 (aromatic H, 8H), 3.86 (m, 2H), 3.72 (d, *J*=17.6 Hz, 1H), 3.63 (d, *J*=17.6 Hz, 1H), 2.38 (s, 3H) 1.44 (s, 3H), 1.37 (t, *J*=8.0 Hz, 3H); **^{13}C-NMR** ($CDCl_3$,100Hz): 12.4, 21.6, 25.04, 34.8, 45.3, 45.8, 108.3, 121.9, 122.0, 127.7, 128.1, 129.1, 129.3, 134.13, 142.9, 143.9, 180.3, 195.6; **IR:** 2969，2928，2853，1711，1602, 736，700 cm^{-1}; **MS** (ESI) m/z calculated for $C_{20}H_{21}NNaO_2$ 330.15, found 330.29.

1-Ethyl-3-methyl-3-(2-oxo-2-phenylethyl)indolin-2-one (3g)



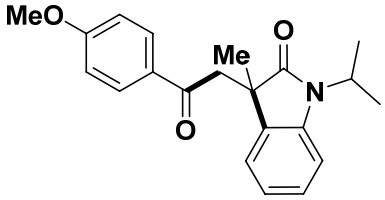
^{1}H-NMR ($CDCl_3$, 400MHz): δ (ppm) 7.52-6.93 (aromatic H, 9H), 3.89 (m, 2H), 3.73 (d, *J*=18.0 Hz, 1H), 3.66 (d, *J*=18.0 Hz, 1H), 1.45 (s, 3H), 1.37 (t, *J*=7.2 Hz, 3H); **^{13}C-NMR** ($CDCl_3$,100Hz): 12.4, 25.1, 29.7，34.8, 45.3, 46.0, 108.3, 121.9, 122.0, 127.8, 128.0, 128.5, 133.1, 134.0, 136.49, 142.9, 180.1, 196.0; **IR:** 2970，2918，2849，1709，1613, 738，700 cm^{-1}; **MS** (ESI) m/z calculated for $C_{19}H_{19}NNaO_2$ 316.13, 316.36.

3-(2-(4-(*tert*-Butyl)phenyl)-2-oxoethyl)-1-ethyl-3-methylindolin-2-one (3h)



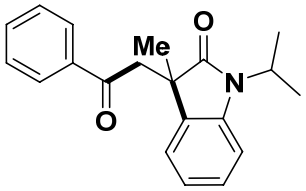
^{1}H-NMR ($CDCl_3$, 400MHz): δ (ppm) 7.82-6.92 (aromatic H, 8H), 3.84 (m, 2H), 3.72 (d, *J*=17.6 Hz, 1H), 3.65 (d, *J*=17.6 Hz, 1H), 1.45 (s, 3H), 1.33 (t, *J*=7.8 Hz, 3H); **^{13}C-NMR** ($CDCl_3$,100 Hz): 12.4, 25.1, 31.1, 34.8, 45.3, 45.9, 108.3, 121.9, 122.0, 125.4, 127.7, 128.0, 134.0, 134.1, 142.9, 156.8, 180.2, 195.7; **IR:** 2965，2931，2870，1713，1612, 742，700 cm^{-1}; **MS** (ESI) m/z calculated for $C_{23}H_{27}NNaO_2$, 372.19, found 372.34.

1-*iso*-Propyl-3-(2-(4-methoxyphenyl)-2-oxoethyl)-3-methylindolin-2-one (3i)



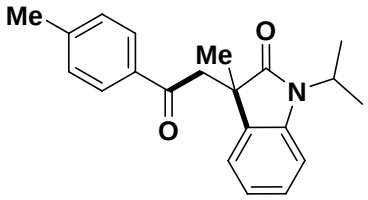
^{1}H-NMR ($CDCl_3$, 400MHz): δ (ppm) 7.86-6.86 (aromatic H, 8H), 4.74 (m, 1H), 3.84 (s, 3H), 3.65 (d, *J*=17.6 Hz, 1H), 3.63 (d, *J*=17.6 Hz, 1H), 1.60 (d, *J*=6.8 Hz, 3H), 1.58 (d, *J*=6.8 Hz, 3H), 1.43 (s, 3H); **^{13}C-NMR** ($CDCl_3$,100 Hz): 19.0, 19.5, 25.3, 43.7, 45.1, 45.8, 55.4, 109.9, 113.6, 121.5, 122.0, 127.4, 129.7, 130.3, 134.5, 142.5, 163.4, 180.4, 194.4; **IR:** 2965，2932，2870，1712，1608, 739，700 cm^{-1}; **MS** (ESI) m/z calculated for $C_{21}H_{23}NNaO_3$ 360.16, found 360.36.

1-isopropyl-3-methyl-3-(2-oxo-2-phenylethyl)indolin-2-one (3j)



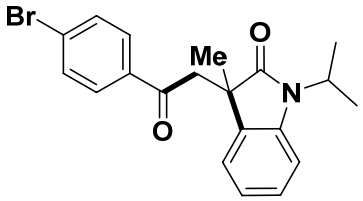
^{1}H-NMR ($CDCl_3$, 400MHz): δ (ppm) 7.87-6.95 (aromatic H, 9H), 4.74 (m, 1H), 3.71 (d, *J*=17.6 Hz, 1H), 3.69 (d, *J*=17.6 Hz, 1H), 1.60 (d, *J*=6.8 Hz, 3H), 1.58 (d, *J*=6.8 Hz, 3H), 1.44 (s, 3H); **^{13}C-NMR** ($CDCl_3$,100 Hz): 19.0, 19.5, 25.3, 43.7, 45.1, 46.1, 110.0, 121.6, 122.0 , 127.5, 128.0, 128.5, 133.1, 134.3, 136.5, 142.5, 180.3, 196.0 ; **IR:** 2972，2928，2860，1709，1611, 750，690 cm^{-1}; **MS** (ESI) m/z calculated for $C_{20}H_{21}NNaO_2$ 330.16, found 330.33.

1-isopropyl-3-methyl-3-(2-oxo-2-(p-tolyl)ethyl)indolin-2-one (3k)



^{1}H-NMR ($CDCl_3$, 400MHz): δ (ppm) 7.77-6.96 (aromatic H, 8H), 4.74 (m, 1H), 3.84 (s, 3H), 3.69(d, *J*=17.6 Hz, 1H), 3.66 (d, *J*=17.6 Hz, 1H), 2.38 (s, 3H), 1.60 (d, *J*=6.8 Hz, 3H), 1.58 (d, *J*=6.8 Hz, 3H), 1.43 (s, 3H); **^{13}C-NMR** ($CDCl_3$,100 Hz): 19.0, 19.5, 21.6, 25.2, 43.7, 45.1, 46.0, 109.9, 121. 6, 122.0, 127.0, 127.2, 128.1, 129.1, 134.4, 142.5, 143.8, 180.4, 195.6; **IR:** 2965，2926，2855，1708，1608, 753，696 cm^{-1}; **MS** (ESI) m/z calculated for $C_{21}H_{23}NNaO_3$ 344.16, found 344.36.

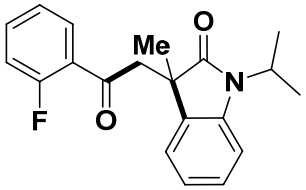
3-(2-(4-bromophenyl)-2-oxoethyl)-1-isopropyl-3-methylindolin-2-one (3l)



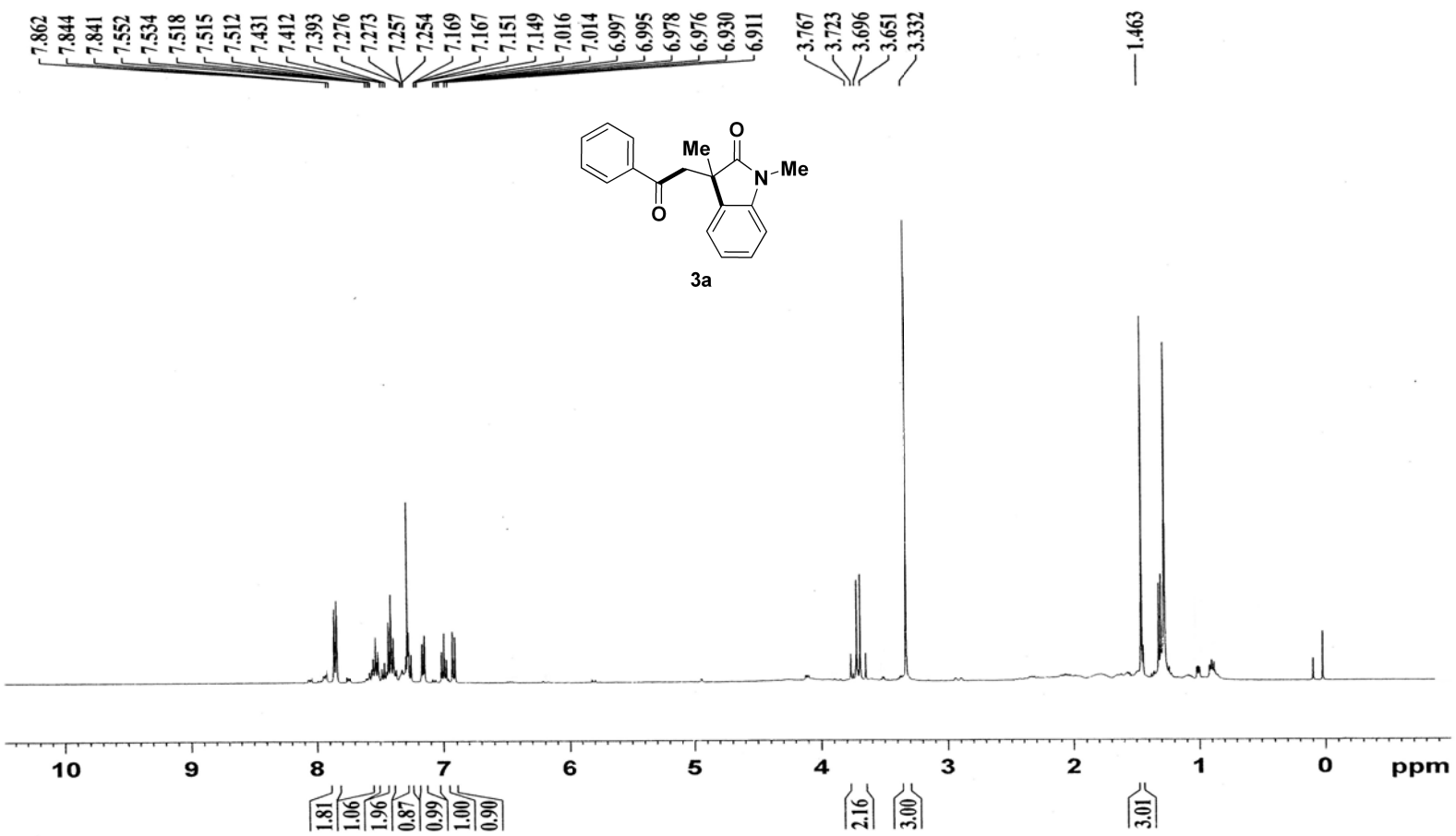
^{1}H-NMR ($CDCl_3$, 400MHz): δ (ppm) 7.73-6.95 (aromatic H, 8H), 4.73 (m, 1H), 3.65 (d, *J*=17.6 Hz, 1H), 3.64 (d, *J*=17.6 Hz, 1H), 1.60 (d, *J*=6.8 Hz, 3H), 1.58 (d, *J*=6.8 Hz, 3H), 1.43 (s, 3H); **^{13}C-NMR** ($CDCl_3$,100 Hz): 19.0, 19.5, 25.3, 43.8, 45.0, 46.1, 110.0, 121.7, 121.9, 127.6, 128.3,

129.6, 131.8, 134.1, 135.1, 142.5, 180.1, 195.0; **IR:** 2965，2933，2863，1709，1608, 742，696 cm^{-1}; **MS** (ESI) m/z calculated for $C_{20}H_{20}NNaO_2$ 408.07, found 408.22.

(S)-3-(2-(2-fluorophenyl)-2-oxoethyl)-1-isopropyl-3-methylindolin-2-one (3m)



^{1}H-NMR ($CDCl_3$, 400MHz): δ (ppm) 7.47-6.95 (aromatic H, 8H), 4.75 (m, 1H), 3.71 (d, *J*=3.2 Hz, 1H), 3.70 (d, *J*=3.2 Hz, 1H), 1.62 (d, *J*=7.2 Hz, 3H), 1.57 (d, *J*=7.2 Hz, 3H), 1.40 (s, 3H); **^{13}C-NMR** ($CDCl_3$, 100 Hz): 19.0, 19.5, 25.3, 43.7, 45.1, 50.9, 110.00, 116.6, 121.5, 121.8, 128.1, 130.7, 134.7, 142.5, 160.7, 163.2, 180.2, 194.1; **IR:** 2961，2919，2877，1709，1618, 1497, 1378, 1235, 1056, 742， 696 cm^{-1}; **MS** (ESI) m/z calculated for $C_{20}H_{20}FNNaO_2$ 348.14, found 348.22.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1.71

ppm
0
20
40
60
80
100
120
140
160
180
200
24.95
26.45
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3c

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143.95
180.78
195.75
Me
N
Me
O
Me
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3c
0
20
40
60
80
100
120
140
160
180
200
ppm

7.820
7.799
7.487
7.466
7.435
7.414
7.277
7.275
7.255
7.236
7.163
7.145
6.995
6.977
6.958
6.923
6.903
3.779
3.735
3.687
3.642
3.332
1.464
1.323
1.80
1.96
1.05
0.96
0.97
0.90
2.08
3.00
3.08
9.00
ppm
0
1
2
3
4
5
6
7
8
Me
N
O
Me
O
t-Bu
3d

ppm
0
20
40
60
80
100
120
140
160
180
200
24.93
26.47
31.06
35.07
45.35
45.94
108.16
121.79
122.17
125.42
127.80
127.97
129.29
133.88
143.86
156.86
180.75
195.78
Me
N
Me
O
O
t-Bu
3d

1.438
1.377
1.359
1.341
3.926
3.908
3.890
3.873
3.866
3.836
3.707
3.663
3.633
3.589
6.861
6.883
6.915
6.935
6.952
6.971
6.989
7.148
7.165
7.227
7.230
7.247
7.249
7.266
7.268
7.829
7.851
Et
N
O
Me
O
MeO
3e
ppm
0
1
2
3
4
5
6
7
8
9
10
3.08
3.01
2.00
3.06
1.97
1.76
1.14
1.02
0.95
0.95
1.73

12.39
25.05
34.73
45.35
45.59
55.42
108.27
113.59
121.88
127.67
129.64
130.26
142.87
163.54
180.28
194.49
Et
N
O
Me
O
MeO
3e
0
10
20
30
40
50
60
70
80
90
110
130
150
170
190
210
f1 (ppm)

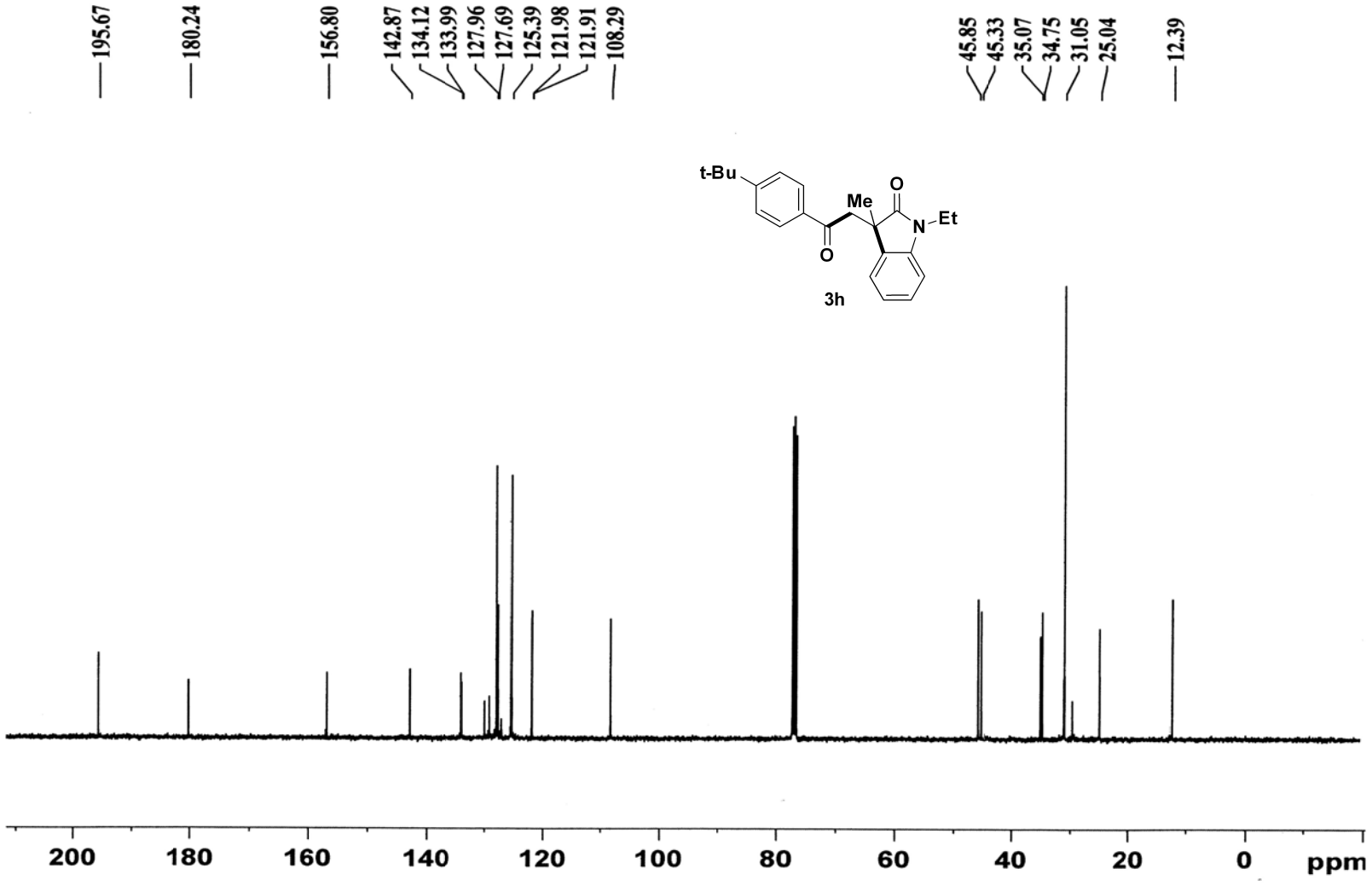
7.771
7.750
7.263
7.255
7.252
7.236
7.233
7.212
7.192
7.165
7.148
6.992
6.973
6.956
6.941
6.922
3.935
3.917
3.899
3.882
3.864
3.846
3.829
3.811
3.737
3.692
3.658
3.613
2.383
1.444
1.385
1.367
1.349
Me
O
N
Et
O
Me
3f
1.66
1.17
1.68
0.95
1.72
1.78
1.91
2.57
3.00
2.97
ppm

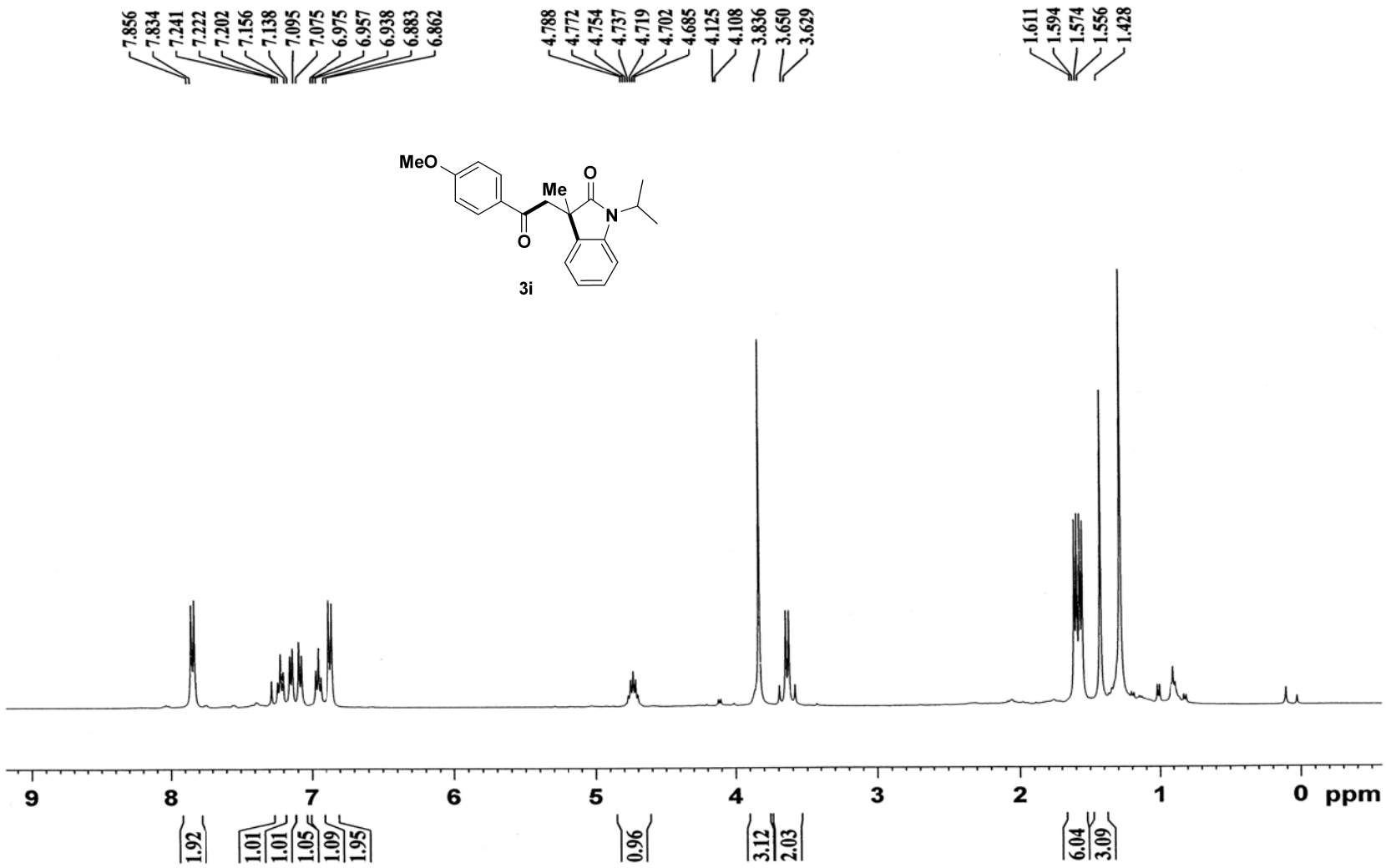
12.38
21.59
25.04
29.70
34.75
45.31
45.83
108.29
121.91
121.96
127.70
128.11
129.13
134.07
134.13
142.89
143.84
180.24
195.60
Et
N
O
Me
O
Me
3f
ppm
0
20
40
60
80
100
120
140
160
180
200

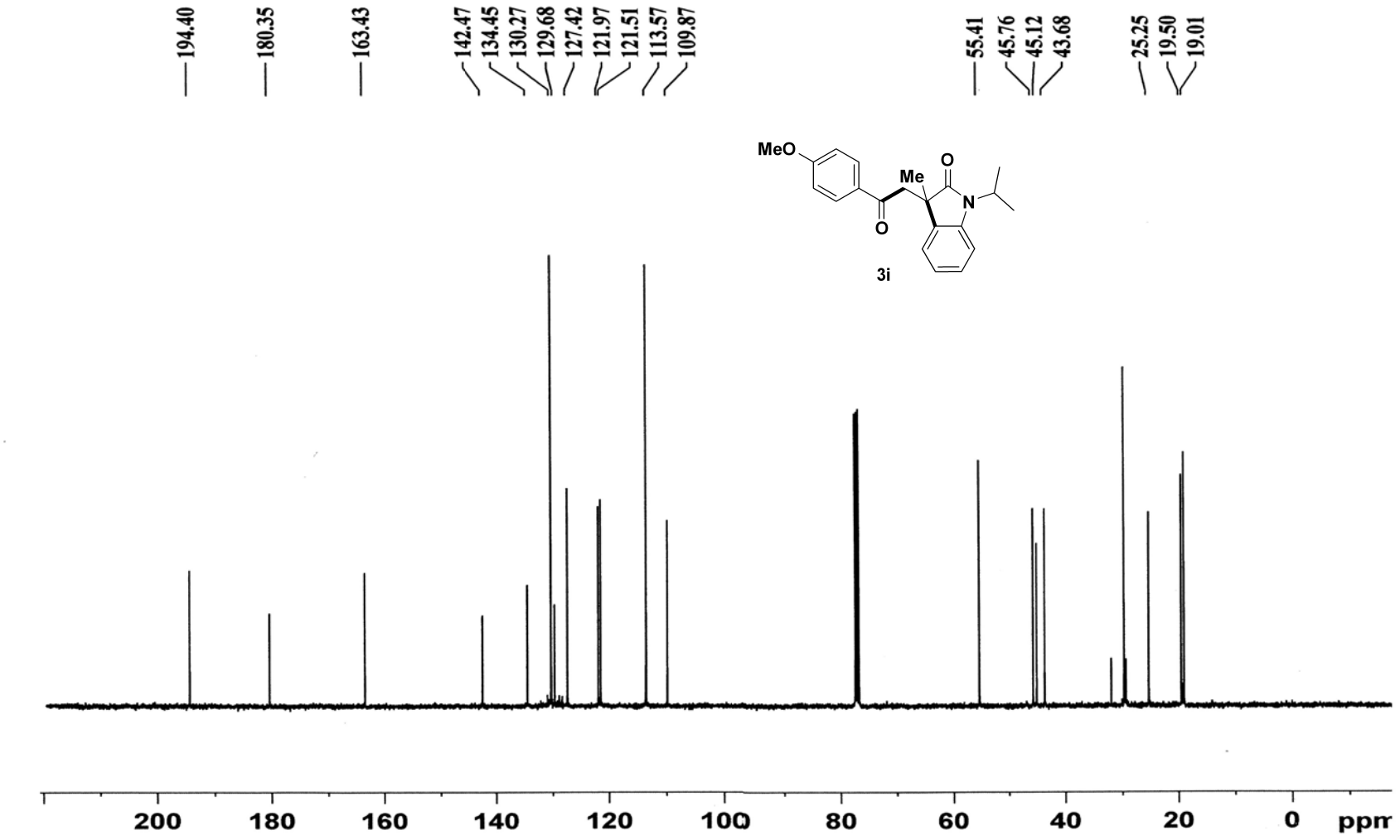
7.523
7.512
7.509
7.506
7.428
7.408
7.389
7.264
7.261
7.245
7.242
7.173
7.171
7.155
7.002
7.000
6.982
6.965
6.963
6.949
6.929
3.939
3.921
3.904
3.886
3.863
3.845
3.828
3.810
3.758
3.713
3.692
3.647
1.454
1.447
1.388
1.370
1.352
Et
N
O
Me
O
3g
ppm
0
1
2
3
4
5
6
7
8
3.11
3.00
1.89
1.96
1.88
1.04
0.77
2.14
1.30
1.82

12.38
25.05
29.70
34.76
45.29
45.96
Et
N
O
Me
O
3g
108.32
121.93
121.95
127.75
127.98
128.47
133.10
134.01
136.48
142.90
180.14
196.01
ppm
0
20
40
60
80
100
120
140
160
180
200

1.329
1.454
3.633
3.678
3.701
3.745
3.817
3.835
3.852
3.864
3.870
3.882
3.888
3.900
3.917
3.935
6.924
6.943
6.953
6.955
6.972
6.973
6.990
6.992
7.146
7.162
7.164
7.234
7.237
7.253
7.256
7.272
7.275
7.414
7.435
7.795
7.816
t-Bu
Me
O
N
Et
O
3h
2.92
3.23
9.00
2.20
2.00
1.77
1.87
0.98
1.02
1.84
0 ppm
1
2
3
4
5
6
7
8
9


195.67
180.24
156.80
142.87
134.12
133.99
127.96
127.69
125.39
121.98
121.91
108.29
45.85
45.33
35.07
34.75
31.05
25.04
12.39
t-Bu
Me
O
N
Et
O
3h
200
180
160
140
120
100
80
60
40
20
0
ppm


7.856
7.834
7.241
7.222
7.202
7.156
7.138
7.095
7.075
6.975
6.957
6.938
6.883
6.862
4.788
4.772
4.754
4.737
4.719
4.702
4.685
4.125
4.108
3.836
3.650
3.629
1.611
1.594
1.574
1.556
1.428
MeO
Me
O
O
N
3i
9
8
7
6
5
4
3
2
1
0 ppm
1.92
1.01
1.01
1.05
1.09
1.95
0.96
3.12
2.03
6.04
3.09

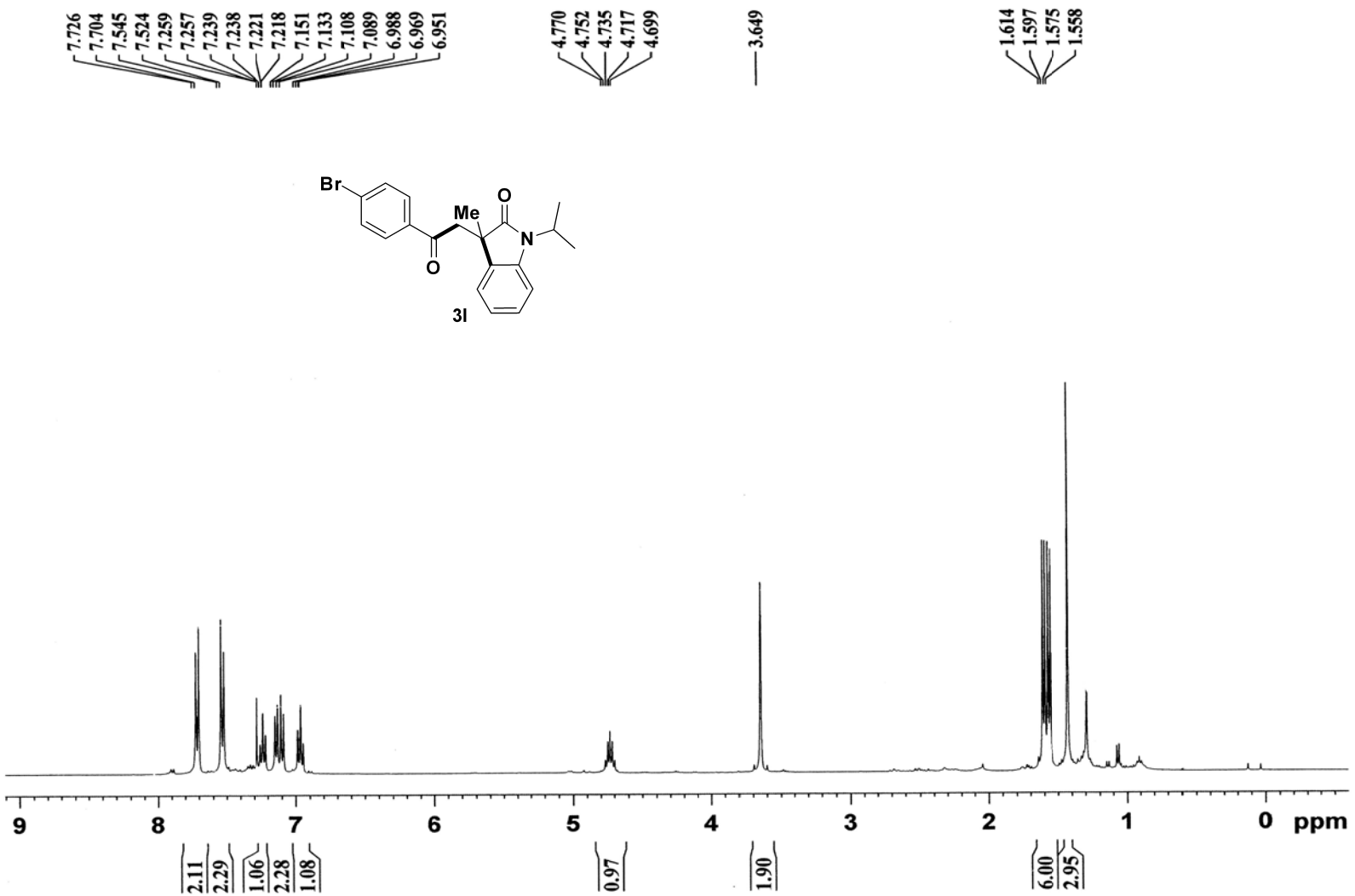

194.40
180.35
163.43
142.47
134.45
130.27
129.68
127.42
121.97
121.51
113.57
109.87
55.41
45.76
45.12
43.68
25.25
19.50
19.01
MeO
Me
O
N
O
3i
200
180
160
140
120
100
80
60
40
20
0
ppm

1.442
1.563
1.580
1.601
1.619
3.690
3.701
4.706
4.724
4.741
4.759
4.777
6.947
6.949
6.966
6.968
6.984
6.986
7.088
7.108
7.141
7.143
7.159
7.161
7.215
7.218
7.234
7.237
7.254
7.257
7.388
7.406
7.426
7.506
7.509
7.525
Me
N
O
O
3j
9
8
7
6
5
4
3
2
1
0
ppm
1.95
1.42
2.13
1.10
1.08
1.00
0.98
1.11
1.90
3.03
3.03
3.11

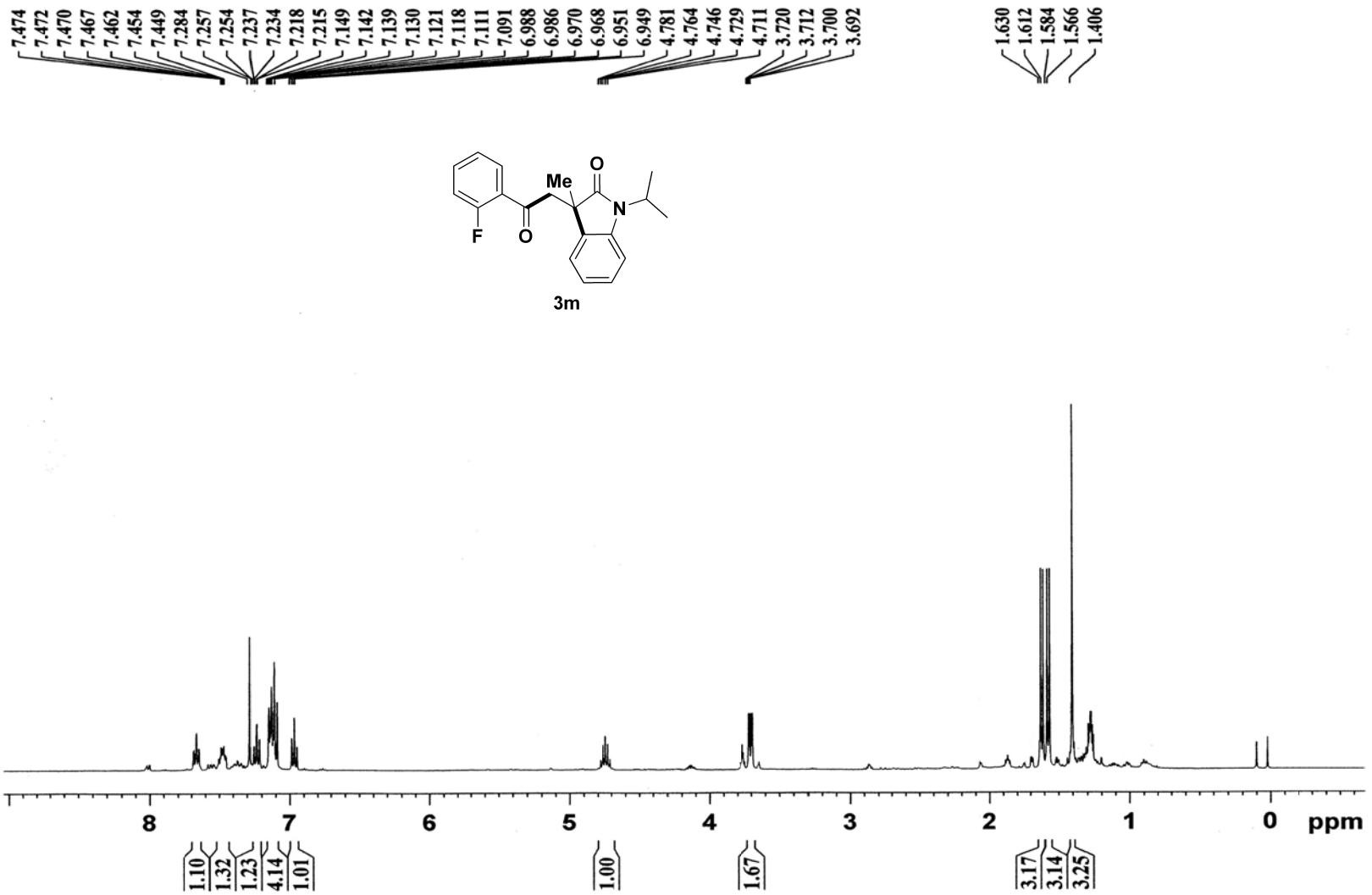
195.93
180.26
142.49
136.49
134.28
133.06
128.45
127.99
127.50
126.95
121.95
121.58
109.94
46.11
45.06
43.73
25.25
19.50
19.01
Me
O
N
O
3j
ppm
0
20
40
60
80
100
120
140
160
180
200

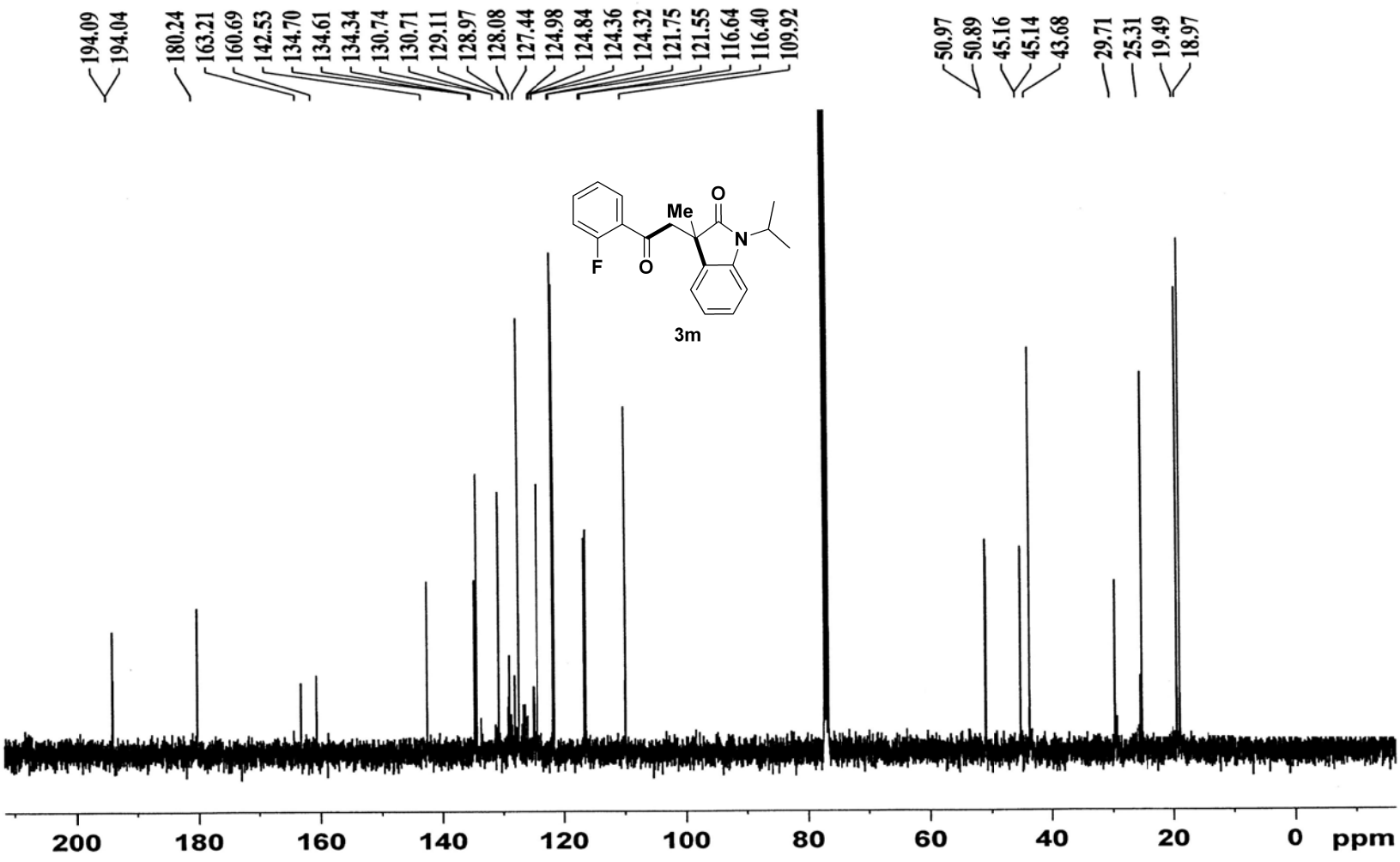
1.431
1.560
1.578
1.599
1.617
2.380
3.619
3.663
3.683
3.728
4.724
4.741
4.759
4.776
6.939
6.941
6.958
6.959
6.976
6.978
7.083
7.102
7.136
7.153
7.154
7.188
7.209
7.225
7.228
7.245
7.247
7.283
7.487
7.505
7.508
7.524
7.547
7.550
7.568
Me
N
O
O
Me
3k
1.97
3.21
1.02
0.99
1.01
1.00
1.99
3.15
5.97
3.08
9
8
7
6
5
4
3
2
1
0
ppm

195.56
180.42
143.81
142.45
134.39
134.06
129.12
129.01
128.12
127.45
126.95
121.94
121.58
109.94
46.10
45.99
45.10
43.72
29.71
25.24
23.71
21.59
19.50
19.00
Me
O
N
O
Me
3k
ppm
0
20
40
60
80
100
120
140
160
180
200


7.726
7.704
7.545
7.524
7.259
7.257
7.239
7.238
7.221
7.218
7.151
7.133
7.108
7.089
6.988
6.969
6.951
4.770
4.752
4.735
4.717
4.699
3.649
1.614
1.597
1.575
1.558
Br
Me
O
N
O
3l
9
8
7
6
5
4
3
2
1
0
ppm
2.11
2.29
1.06
2.28
1.08
0.97
1.90
6.00
2.95

194.95
180.10
142.46
135.11
134.07
131.78
129.56
128.29
127.63
121.91
121.66
110.01
46.05
45.01
43.75
25.29
19.52
19.01
Me
O
O
N
Br
3l
200
180
160
140
120
100
80
60
40
20
0
ppm


7.474
7.472
7.470
7.467
7.462
7.454
7.449
7.284
7.257
7.254
7.237
7.234
7.218
7.215
7.149
7.142
7.139
7.130
7.121
7.118
7.111
7.091
6.988
6.986
6.970
6.968
6.951
6.949
4.781
4.764
4.746
4.729
4.711
3.720
3.712
3.700
3.692
1.630
1.612
1.584
1.566
1.406
Me
O
N
F
O
3m
8
7
6
5
4
3
2
1
0
ppm
1.10
1.32
1.23
4.14
1.01
1.00
1.67
3.17
3.14
3.25


194.09
194.04
180.24
163.21
160.69
142.53
134.70
134.61
134.34
130.74
130.71
129.11
128.97
128.08
127.44
124.98
124.84
124.36
124.32
121.75
121.55
116.64
116.40
109.92
50.97
50.89
45.16
45.14
43.68
29.71
25.31
19.49
18.97
Me
O
N
F
O
3m
200
180
160
140
120
100
80
60
40
20
0
ppm