Supporting Information

Copper-Catalyzed Oxidative Cascade Coupling of *N*-Alkyl-*N*-phenylacrylamides with Aryl Aldehydes

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Experimental section

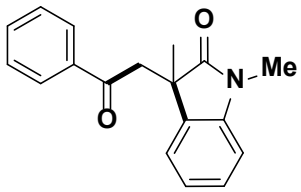
General: All reactions were carried out under an atmosphere of nitrogen; stirring was achieved with an oven-dried magnetic stirring bar. Solvents were purified by standard methods unless otherwise noted. Commercially available reagents were purchased from Aladdin Company in China and used throughout 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 synthesis of compounds 3a-i

N-Methyl-*N*-phenylacrylamide (2.0 mmol, 1.0 equiv) was added to a dried flask, followed by the addition of $CuCl_2$ (0.4 mmol, 0.2 equiv), benzaldehyde (7.0 mmol, 3.5 equiv), then aqueous TBHP (2.5 equiv., 70 wt% in water) was injected into the flask in two portions under N_2. The reaction mixture was stirred at 90 ^{o}C for 6 hrs; another half portion of TBHP was

injected into the flask. The reaction was stirred for another 12 hrs. After the reaction was completed, the reaction mixture was concentrated under reduced pressure and purified by flash chromatography (Petroleum ether: EtOAc =12:1) to provide the title compound **3a** as a sticky solid in a 70% yield. The same procedure for catalyst screening and other compounds **3b-i**.

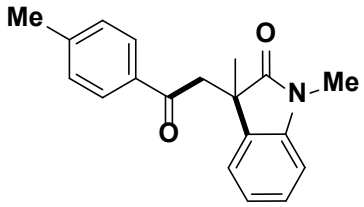
1,3-Dimethyl-3-(2-oxo-2-phenylethyl)indolin-2-one



3a

^{1}H-NMR ($CDCl_3$, 400MHz)：δ (ppm) 7.86-6.91 (aromatic H, 9H), 3.72 (d, *J*=16.2 Hz, 1H), 3.70 (d, *J*=16.2 Hz, 1H), 3.33 (s, 3H), 1.46 (s, 3H); **^{13}C-NMR** ($CDCl_3$,100 Hz): 196.2, 180.6, 143.9, 136.4, 133.8, 133.2, 128.5, 127.9, 127.8, 122.2, 121.8, 108.2, 46.0, 24.9; **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

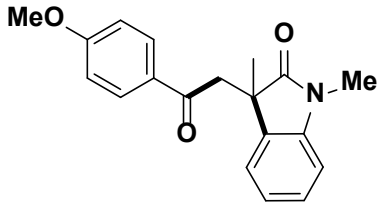
1,3-Dimethyl-3-(2-oxo-2-phenylethyl)indolin-2-one



3b

^{1}H-NMR ($CDCl_3$, 400MHz)：δ (ppm) 7.77-6.90 (aromatic H, 8H), 3.70 (d, *J*=16.2 Hz, 1H), 3.66 (d, *J*=16.2 Hz, 1H), 3.33 (s, 3H), 2.37 (s, 3H), 1.46 (s, 3H); **^{13}C-NMR** ($CDCl_3$,100Hz): 195.8, 180.6, 143.9, 143.8, 134.0, 133.9, 129.2, 128.1, 122.2, 121.8, 108.2, 45.9, 45.3, 26.5, 24.9, 21.6; **IR:** 2962，2924，2851，1712，1614, 735，701 cm^{-1}; **MS** (ESI) m/z calculated for $C_{19}H_{19}NNaO_2$ 316.13, found 316.36.

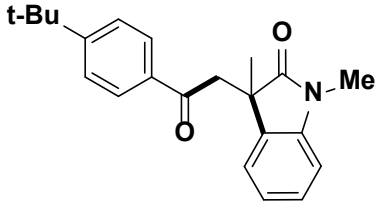
3-(2-(4-Methoxyphenyl)-2-oxoethyl)-1,3-Dimethylindolin-2-one



3c

^{1}H-NMR ($CDCl_3$, 400MHz)：δ (ppm) 7.84-6.85 (aromatic H, 8H), 3.82 (s, 3H), 3.69 (d, *J*=18.0 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): 194.6, 180.8, 163.5, 143.8, 130.2, 129.3, 127.8, 121.8, 113.6, 108.1, 55.4, 45.7, 45.4, 26.5, 24.9; **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.

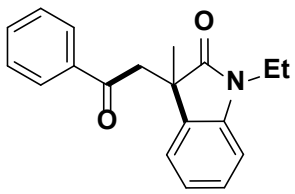
3-(2-(4-(*tert*-Butyl)phenyl)-2-oxoethyl)-1,3-Dimethylindolin-2-one



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*=17.6 Hz, 1H), 3.33 (s, 3H), 1.46 (s, 3H), 1.32 (s, 9H); **^{13}C-NMR** ($CDCl_3$, 100Hz):195.8, 180.8, 156.9, 143.9, 139.3, 133.9, 128.0, 125.4, 122.2, 108.2, 45.9, 45.4, 31.1, 26.5, 24.9; **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.

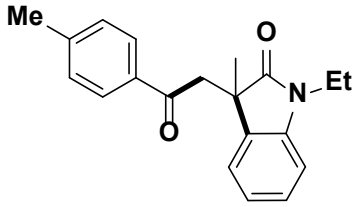
1-Ethyl-3-methyl-3-(2-oxo-2-phenylethyl)indolin-2-one



3e

^{1}H-NMR ($CDCl_3$, 400MHz): δ (ppm) 7.87-6.93 (aromatic H, 9H), 3.87 (m, 2H), 3.73 (d, *J*=17.6 Hz, 1H), 3.66 (d, *J*=17.6 Hz, 1H), 1.45 (s, 3H), 1.37 (t, *J*=8.0 Hz, 3H); **^{13}C-NMR** ($CDCl_3$, 100Hz): 196.0, 180.1, 142.9, 136.5, 134.0, 133.1, 128.0, 127.7, 126.5, 125.4, 121.9, 108.3, 45.9, 45.3, 34.8, 25.0, 12.4; **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.

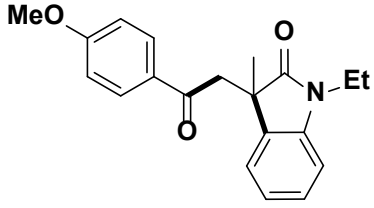
1-Ethyl-3-methyl-3-(2-oxo-2-(p-tolyl)ethyl)indolin-2-one



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): 195.6, 180.2, 143.8, 143.0, 134.1, 129.4, 129.1, 128.4, 128.1, 127.7, 121.9, 108.4, 45.8, 45.3, 34.7, 25.0, 21.6, 12.4; **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-(2-(4-methoxyphenyl)-2-oxoethyl)-3-methylindolin-2-one

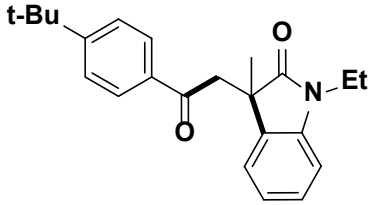


3g

^{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): 195.6, 180.2, 143.8, 143.0, 134.1, 129.4, 129.1, 128.4, 128.1, 127.7, 121.9, 108.4, 45.8, 45.3, 34.7, 25.0, 21.6, 12.4;

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.

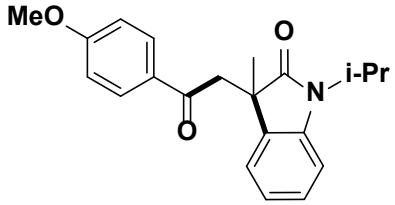
3-(2-(4-(*tert*-Butyl)phenyl)-2-oxoethyl)-1-ethyl-3-methylindolin-2-one



3h

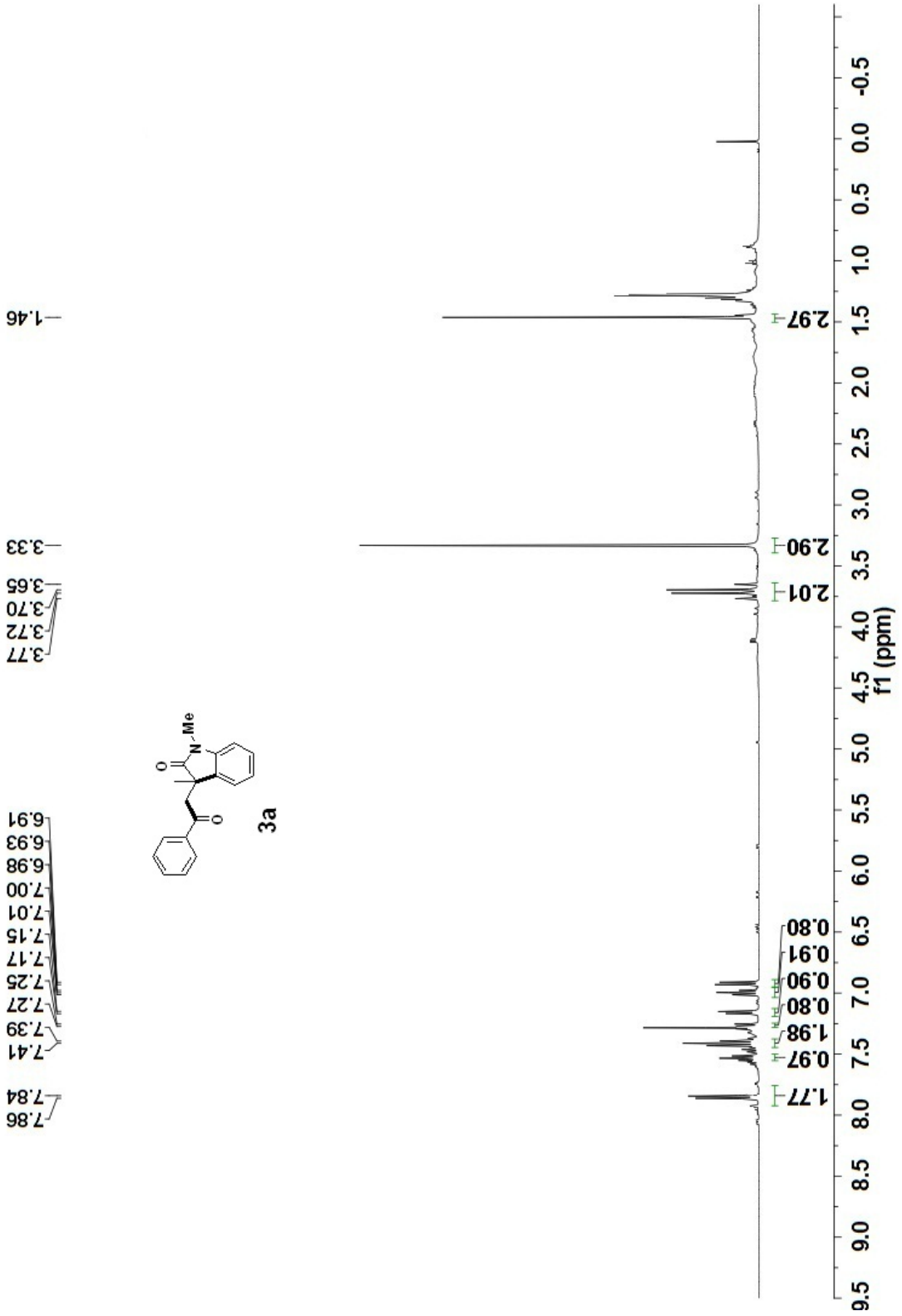
^{1}H-NMR ($CDCl_3$, 400MHz): δ (ppm) 7.82-6.90 (aromatic H, 8H), 3.84 (m, 2H), 3.72 (d, *J*=17.6 Hz, 1H), 3.65 (d, *J*=17.6 Hz, 1H), 1.45 (s, 3H), 1.33 (t, *J*=7.8 Hz, 3H); **^{13}C-NMR** ($CDCl_3$, 100 Hz): 195.6, 180.2, 143.8, 156.7, 142.9, 134.1, 128.4, 128.0, 127.7, 122.0, 121.8, 108.2, 45.8, 45.3, 35.1, 34.7, 31.1, 25.4, 12.4; **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.

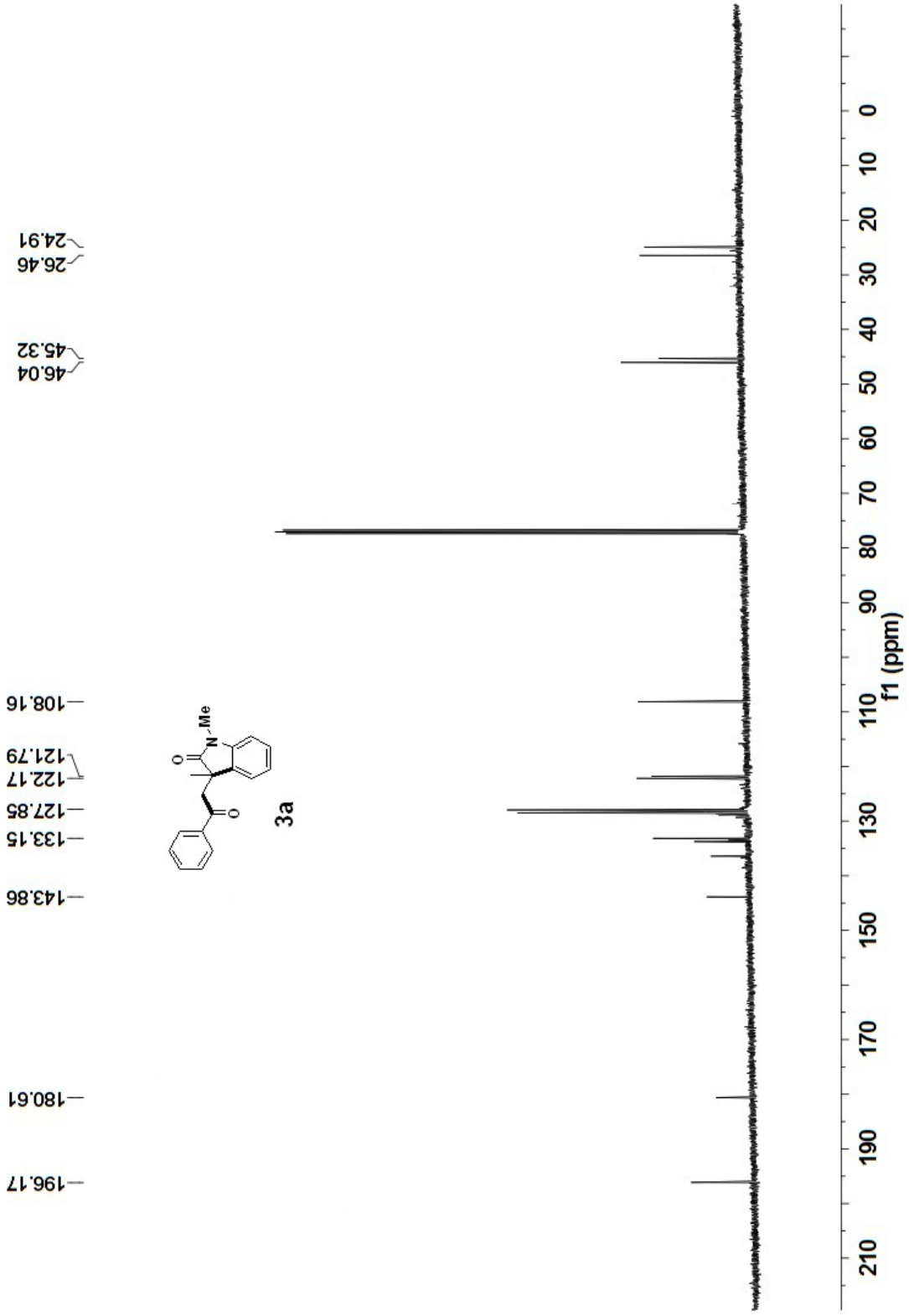
1-*iso*-Propyl-3-(2-(4-methoxyphenyl)-2-oxoethyl)-3-methylindolin-2-one

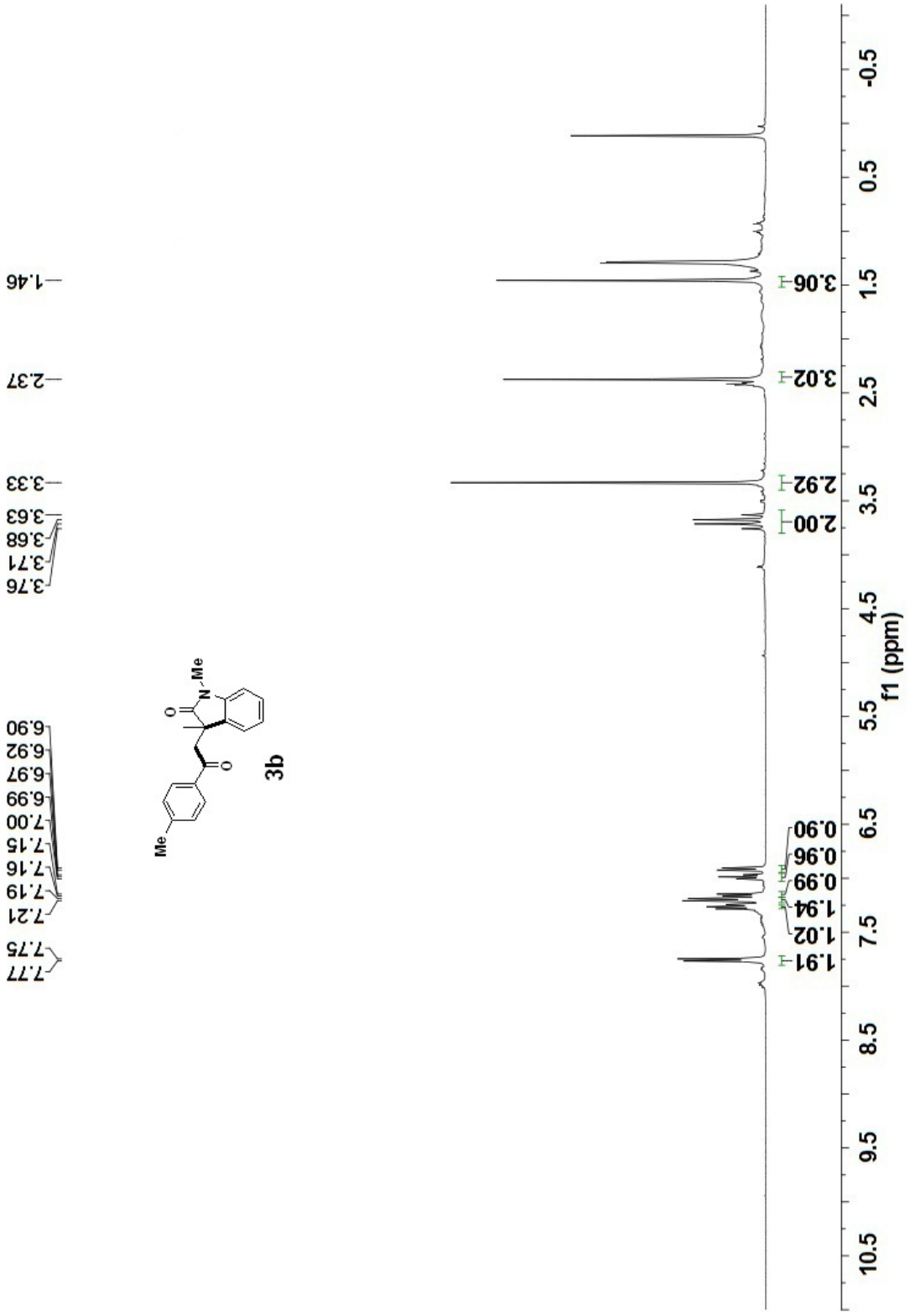


3i

^{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): 195.6, 180.2, 163.4, 142.5, 134.4, 130.3, 129.7, 128.0, 127.4, 122.0, 113.6, 109.9, 55.4, 45.8, 45.1, 25.2, 19.0; **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.






1.46
2.37
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3.63
3.68
3.71
3.76
6.90
6.92
6.97
6.99
7.00
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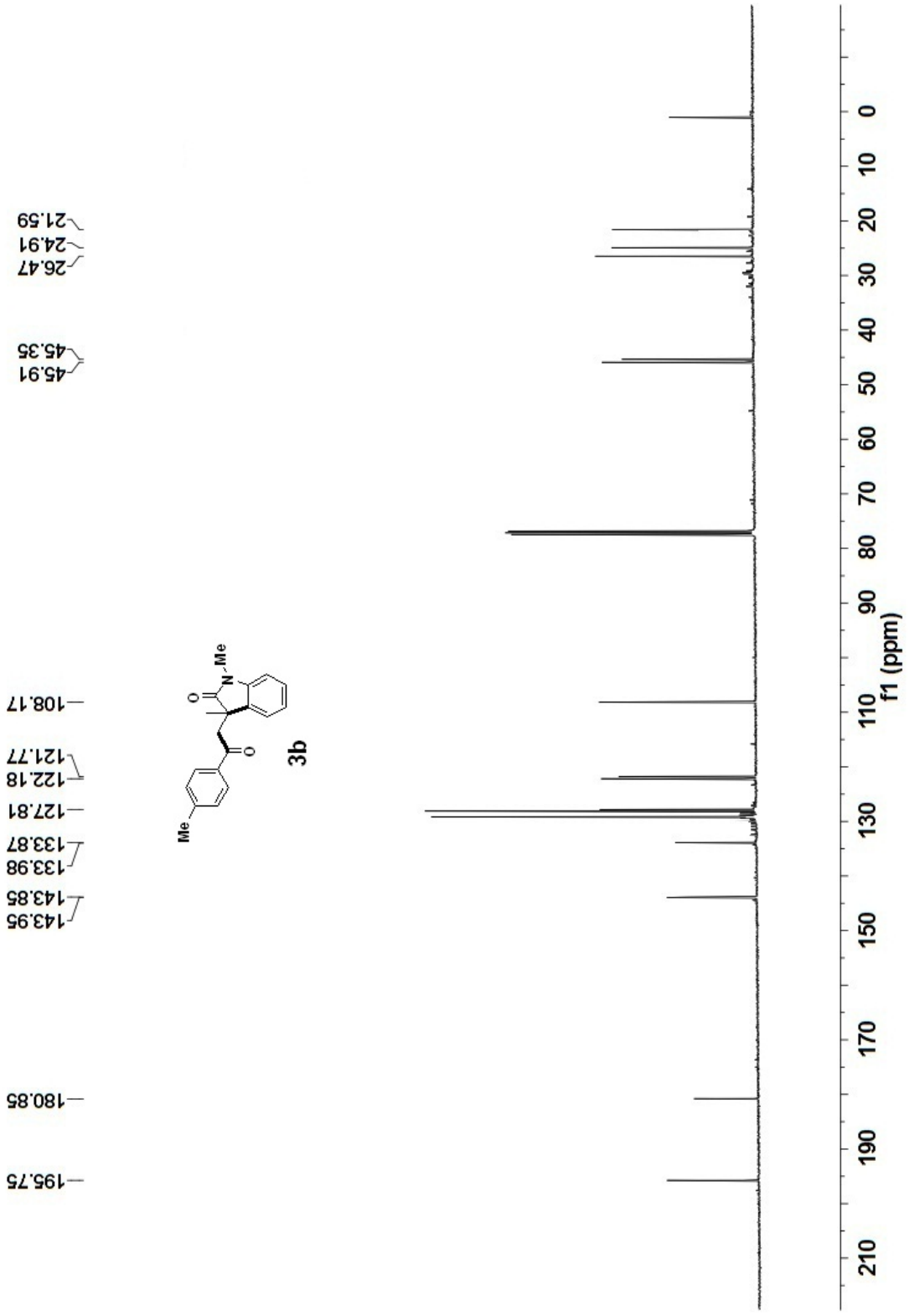
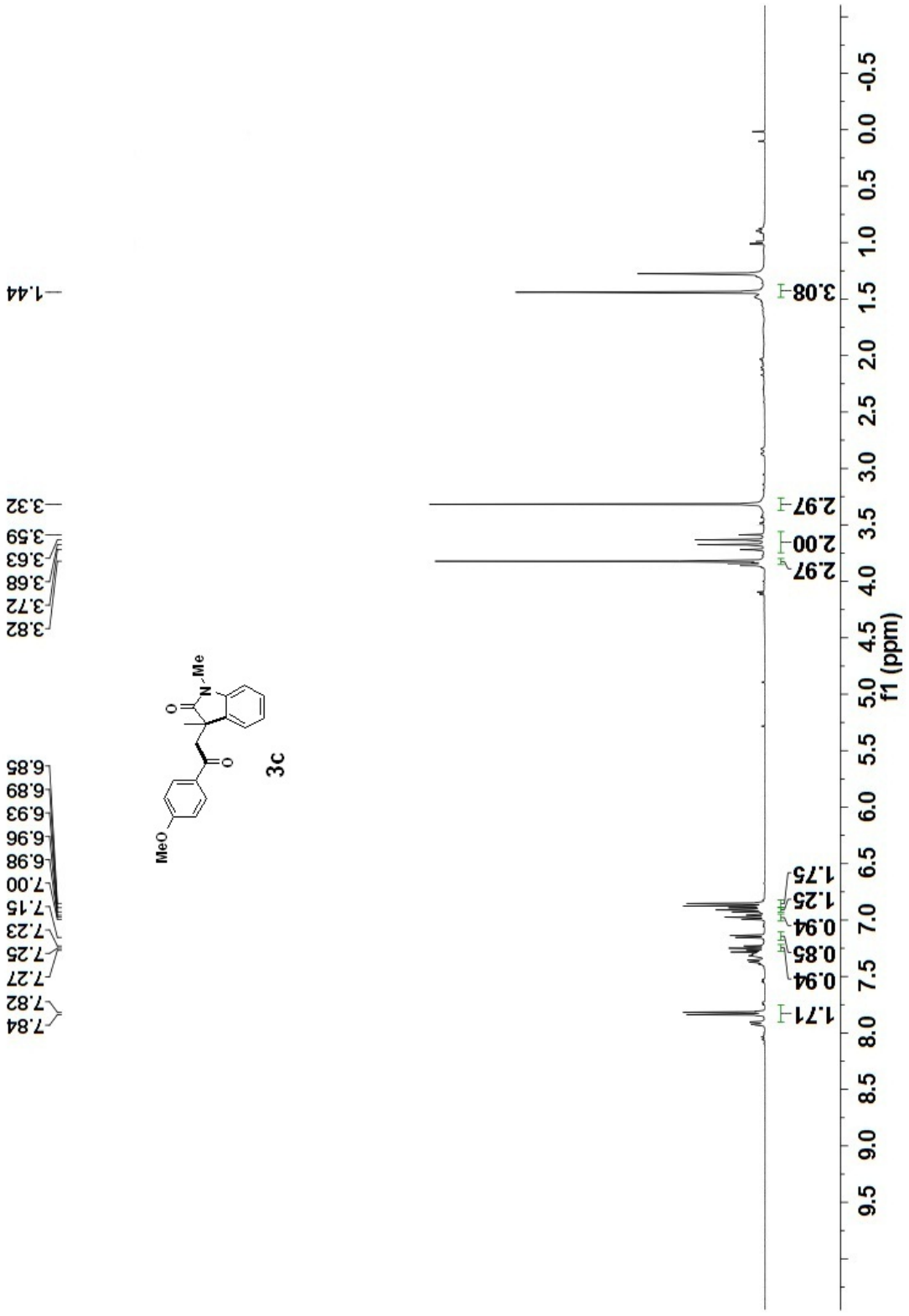
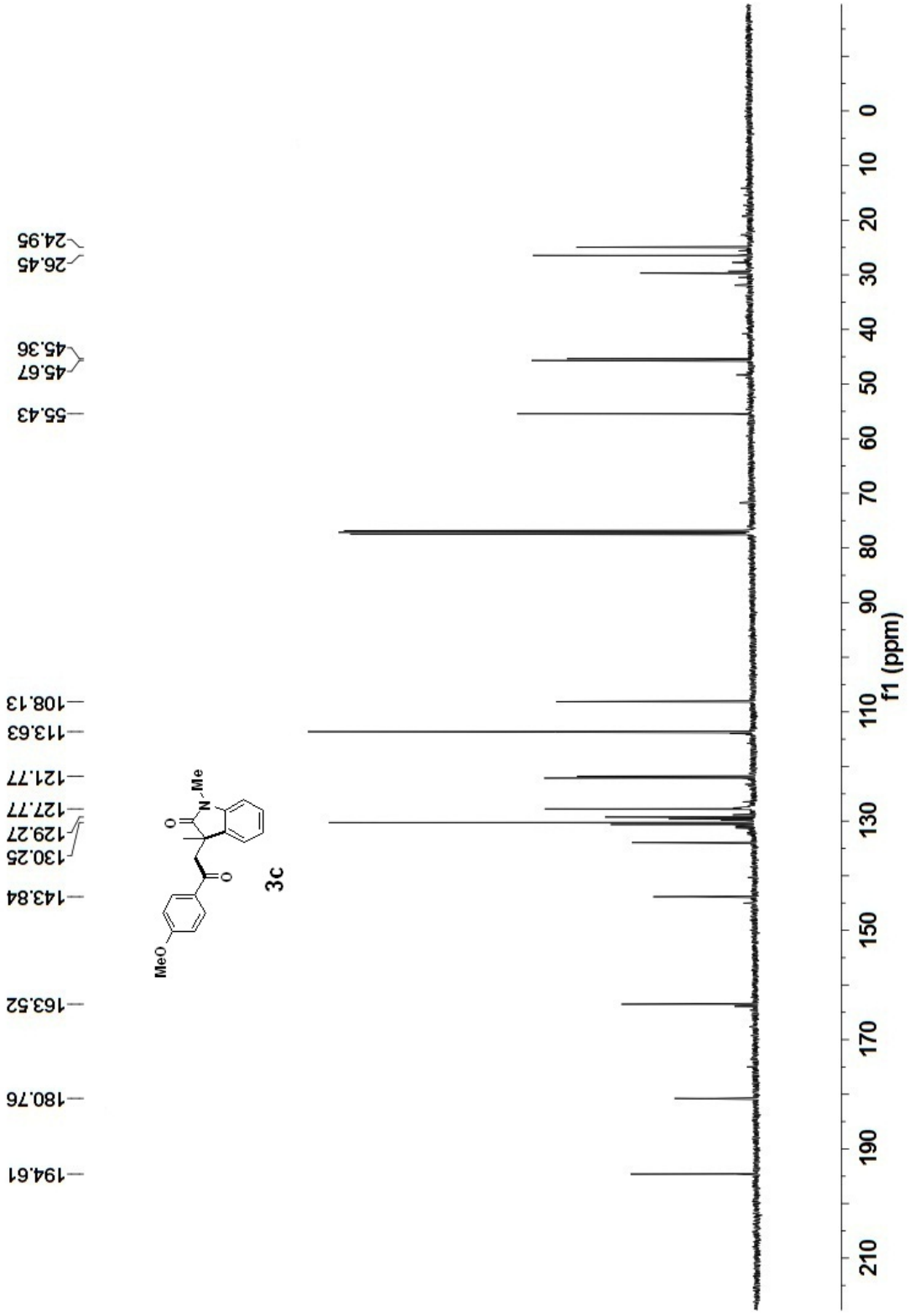
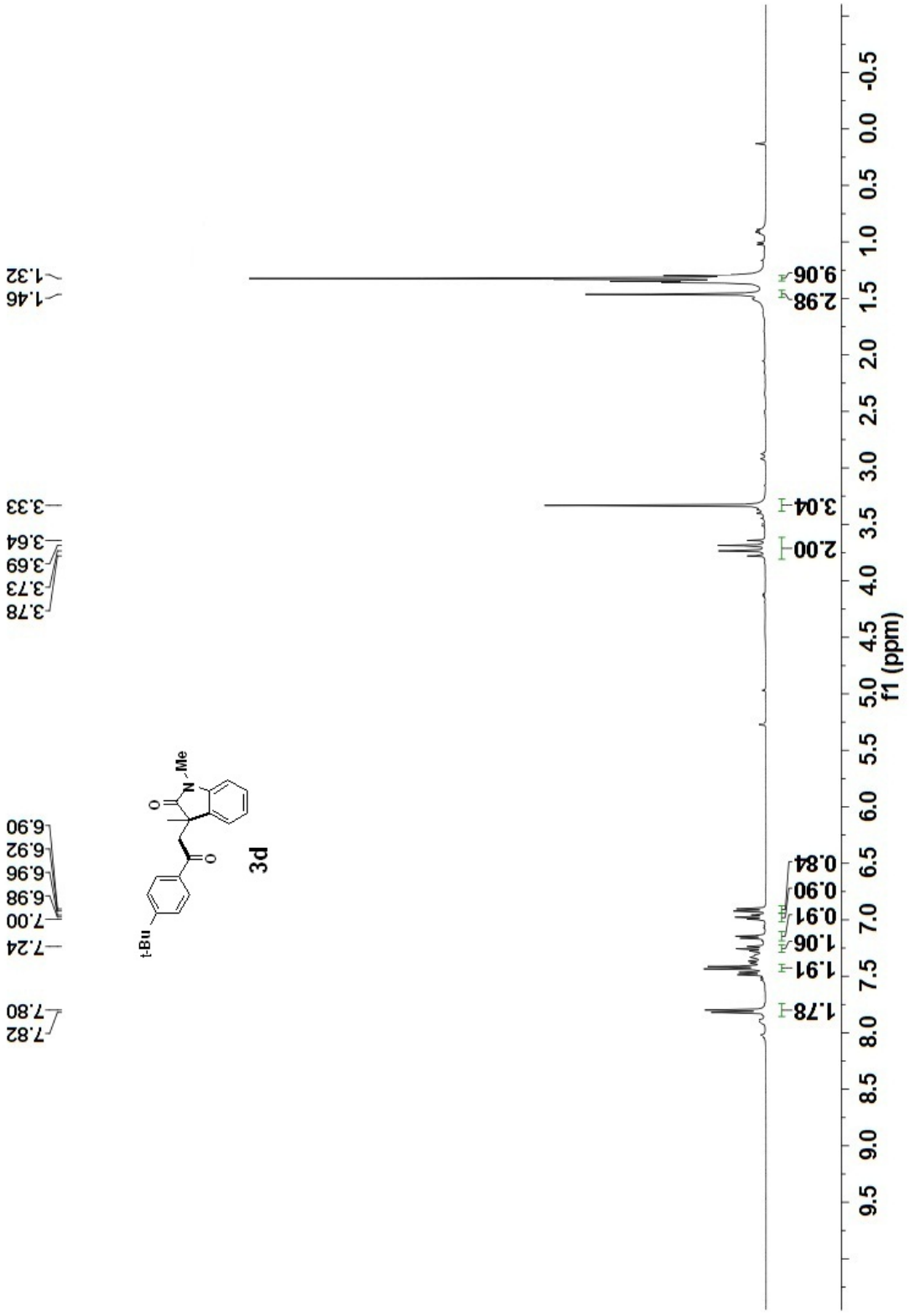
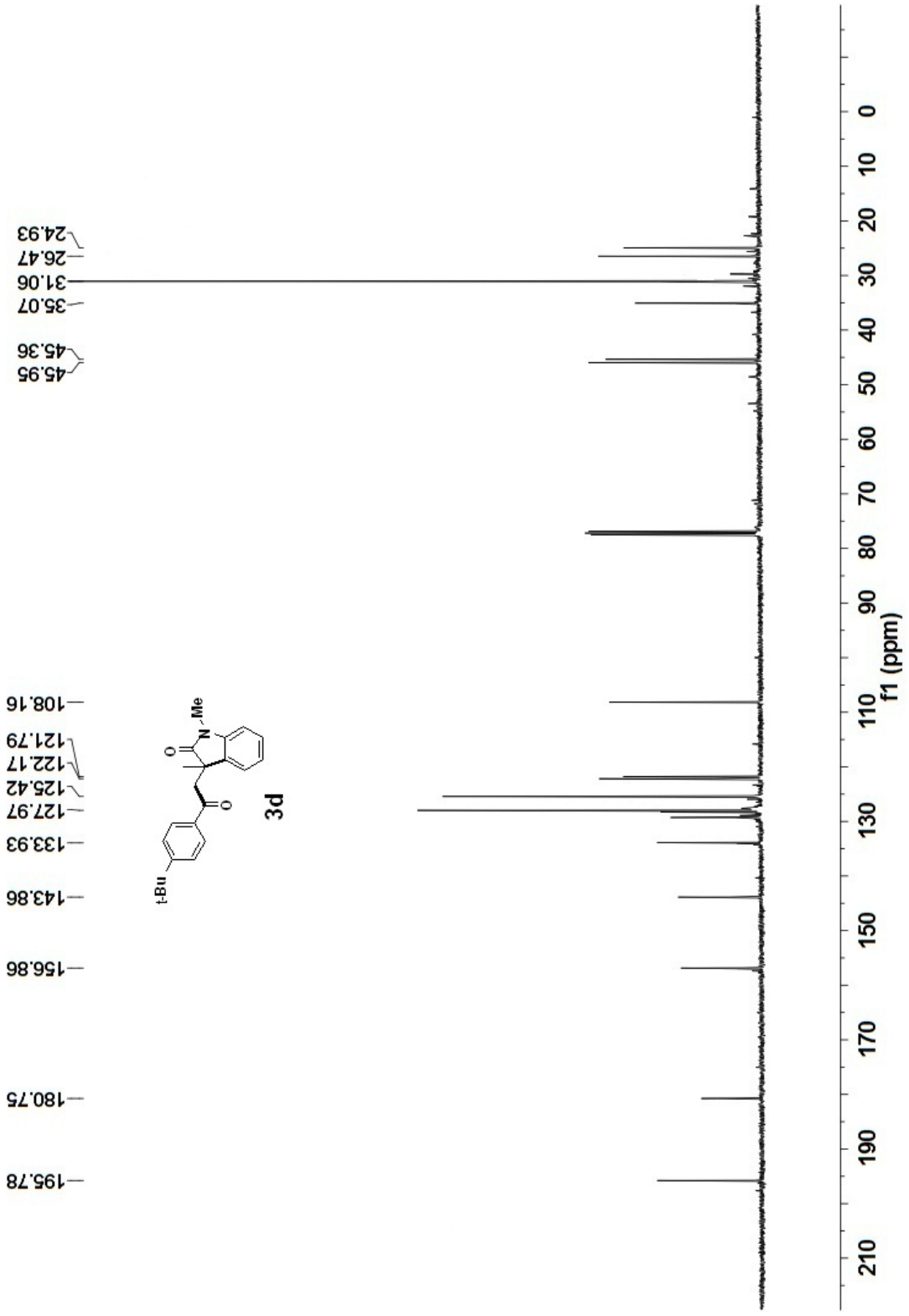
7.16
7.19
7.21
7.75
7.77
Me
N
Me
O
O
3b
3.06
3.02
2.92
2.00
1.91
1.02
1.94
0.99
0.96
0.90
-0.5
0.5
1.5
2.5
3.5
4.5
5.5
6.5
7.5
8.5
9.5
10.5
f1 (ppm)

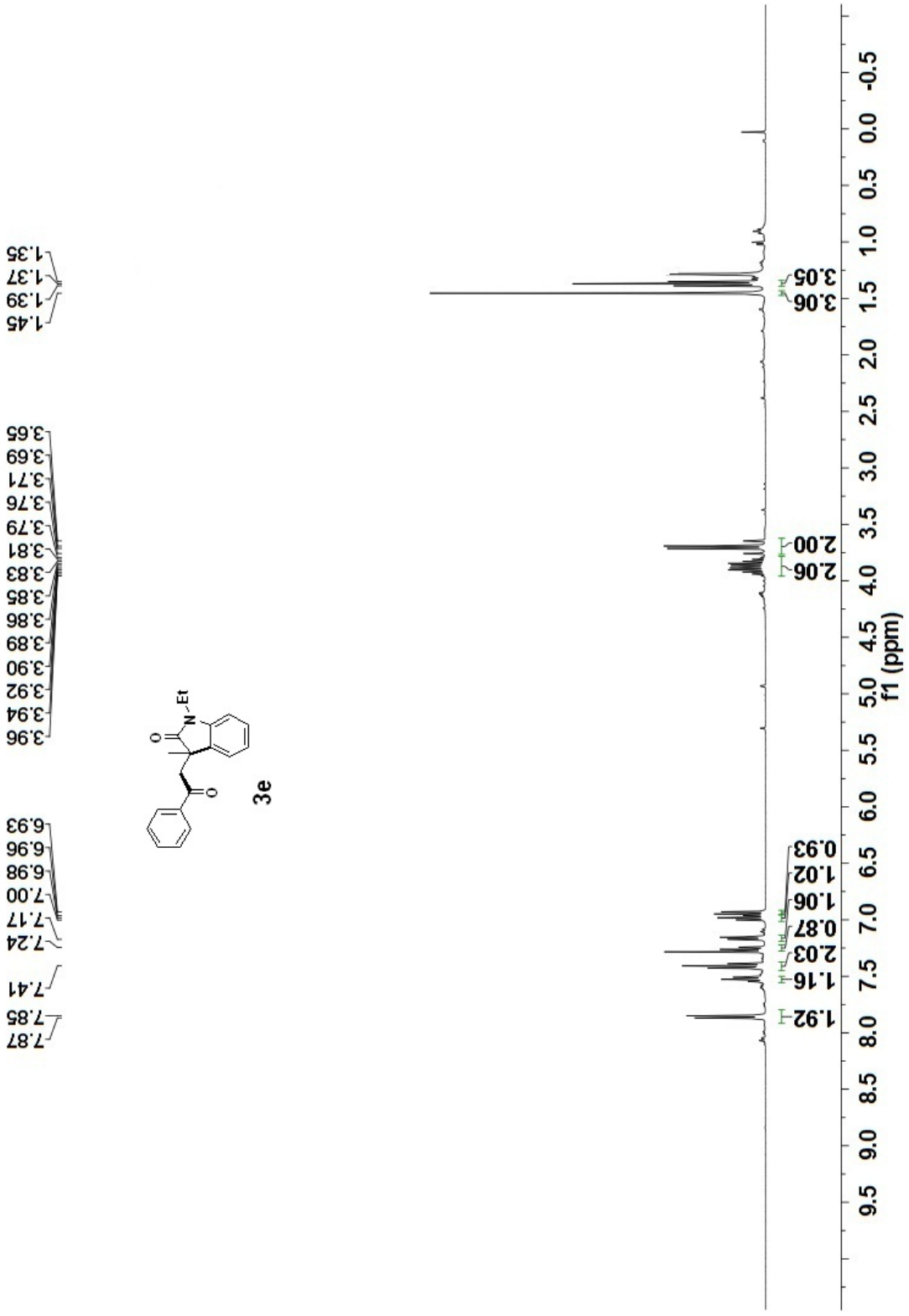


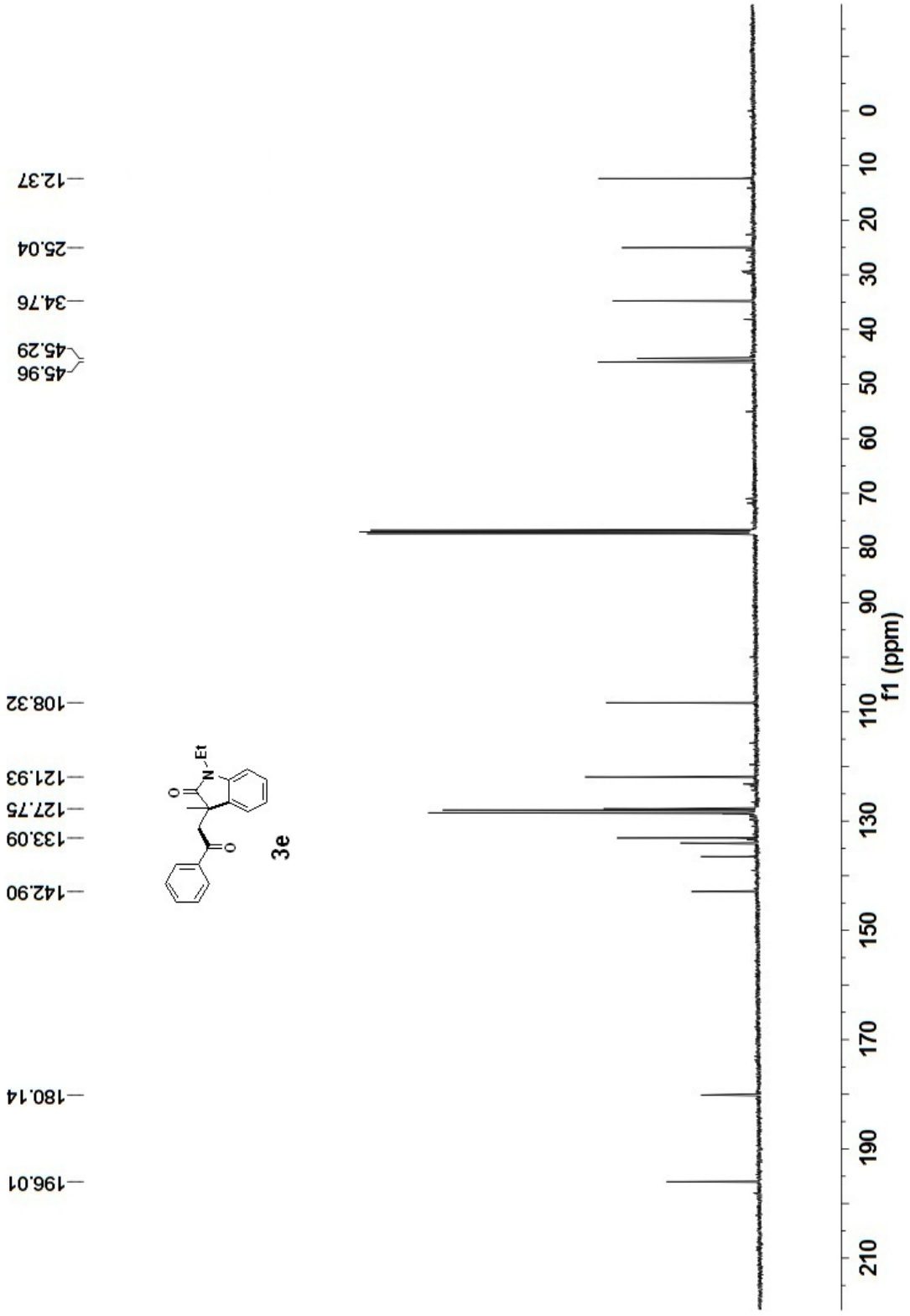


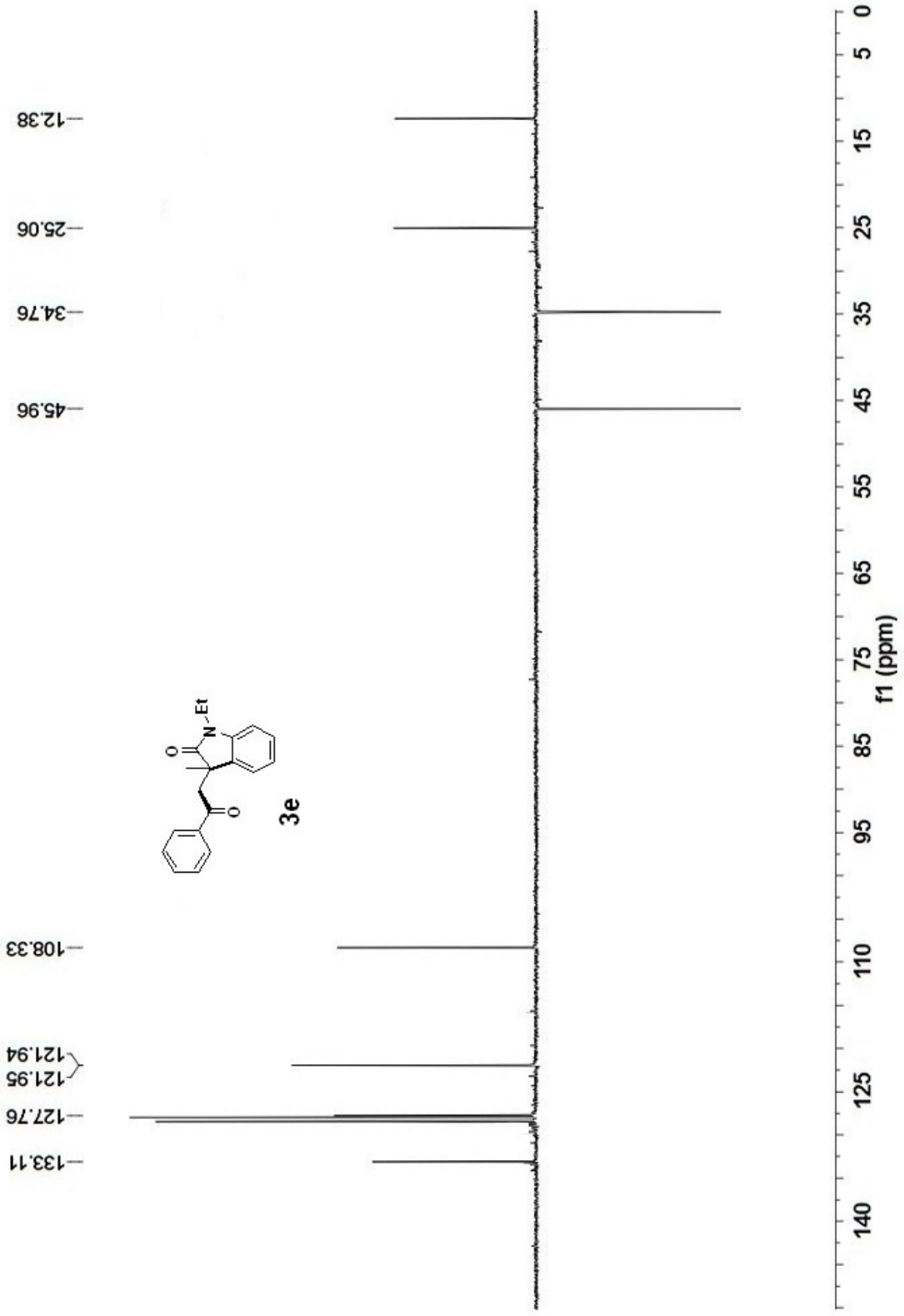








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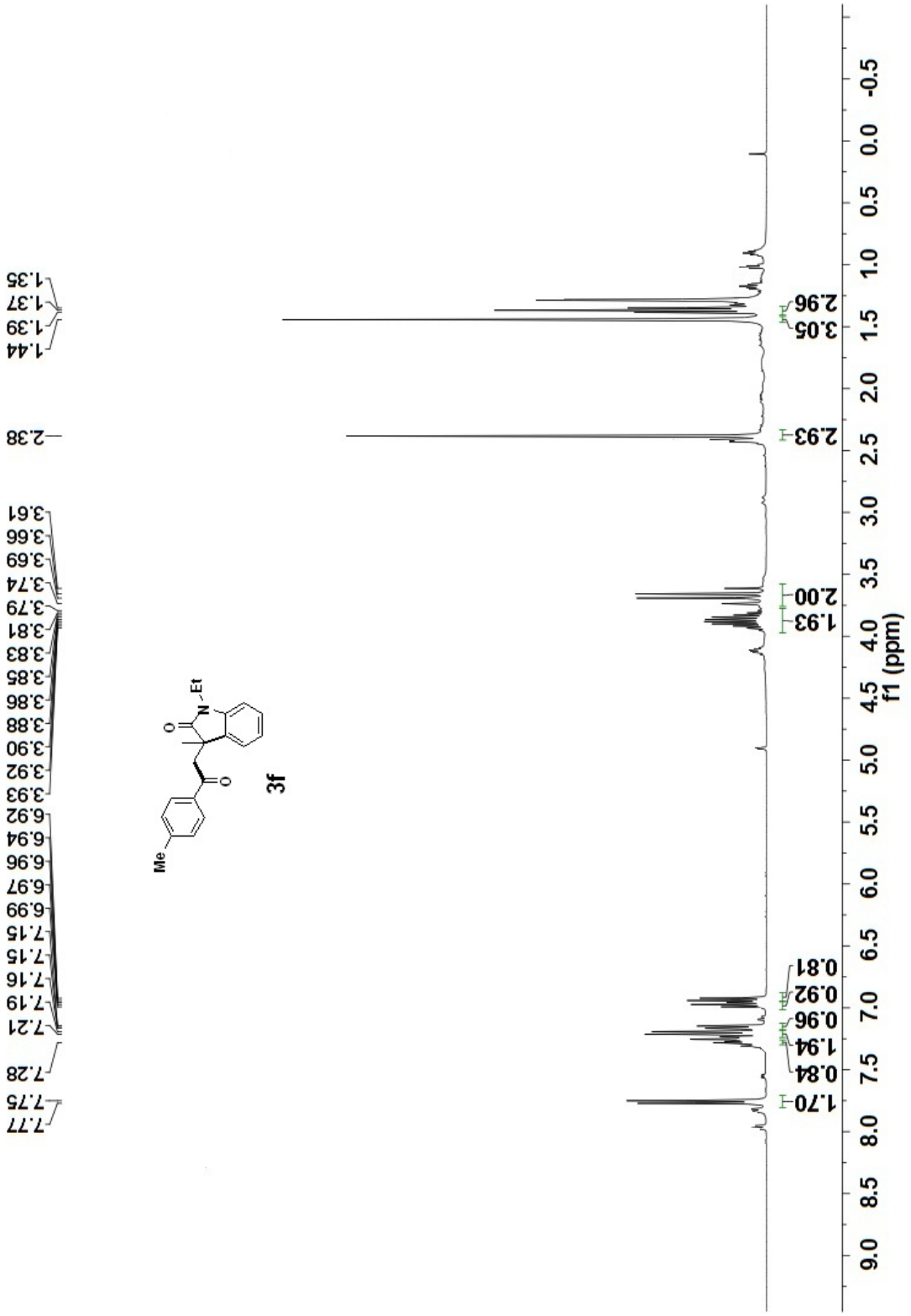
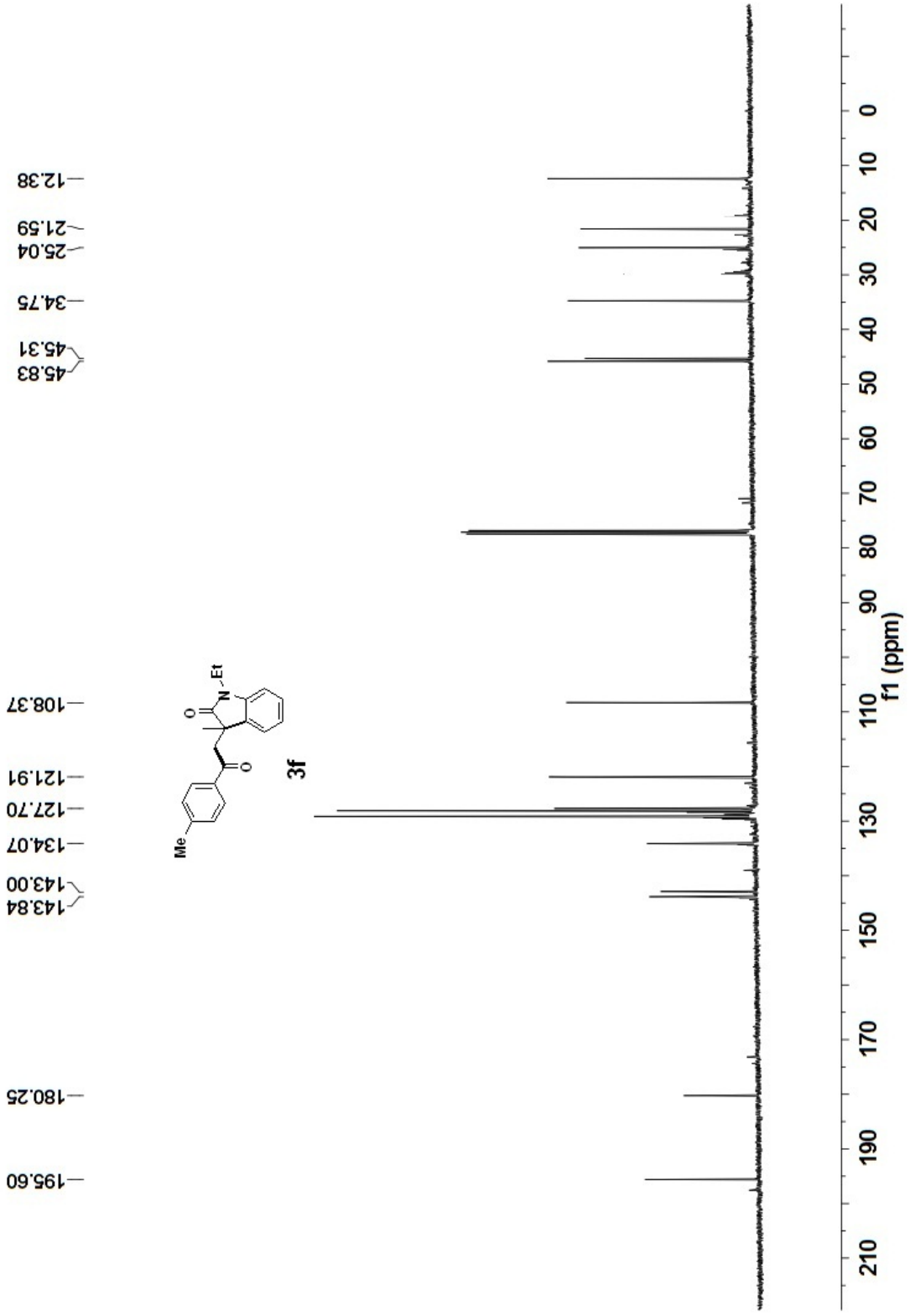
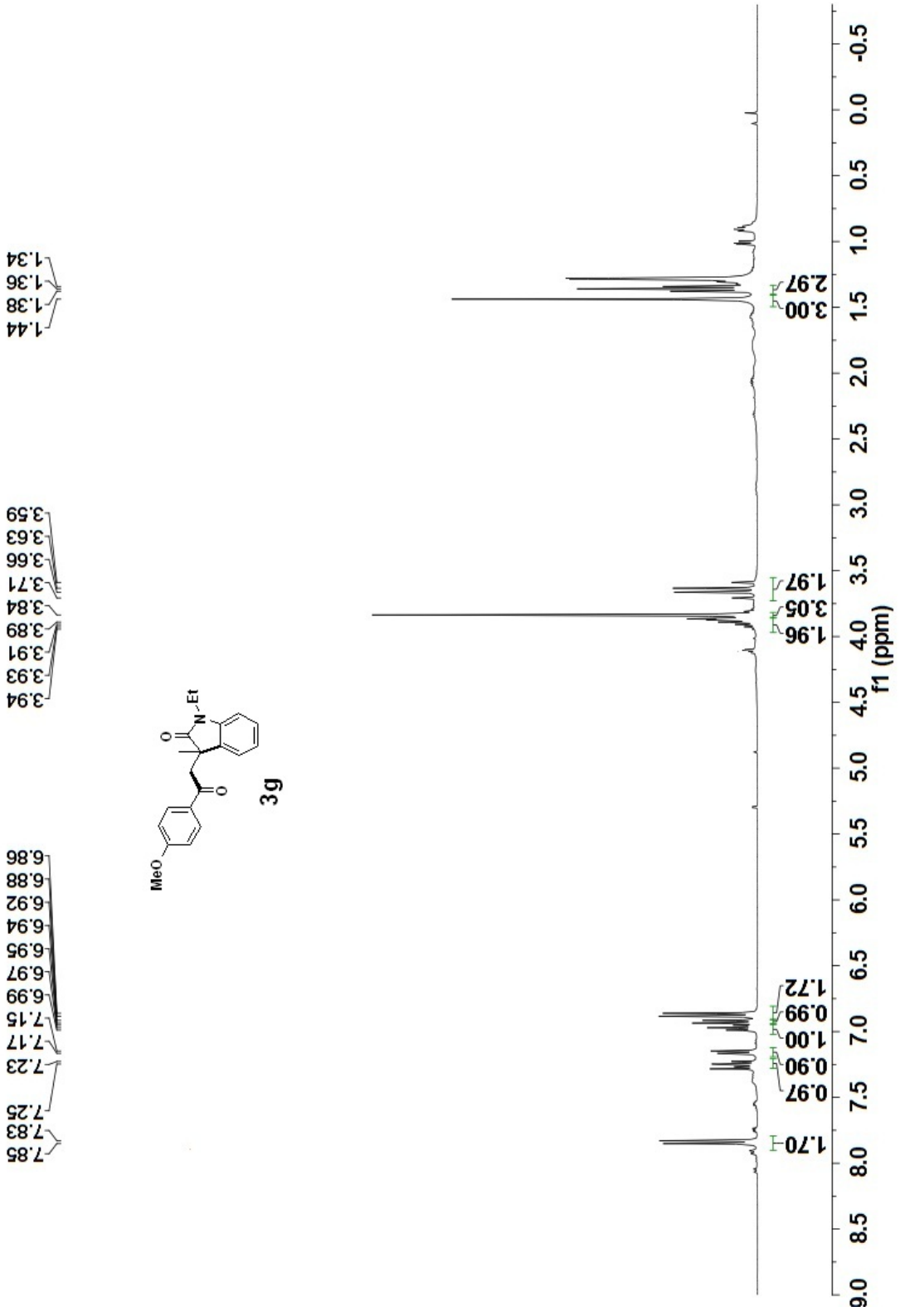
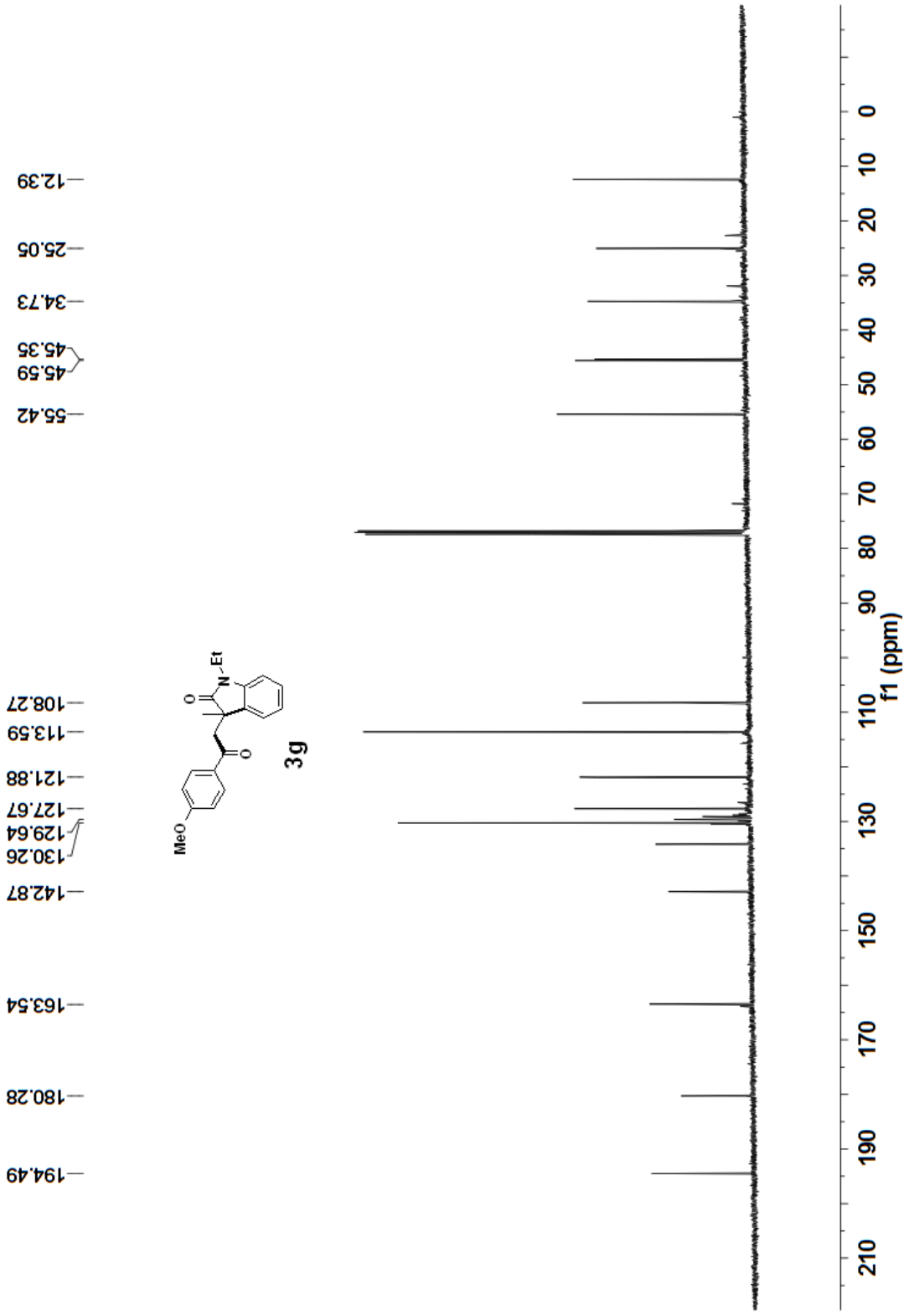
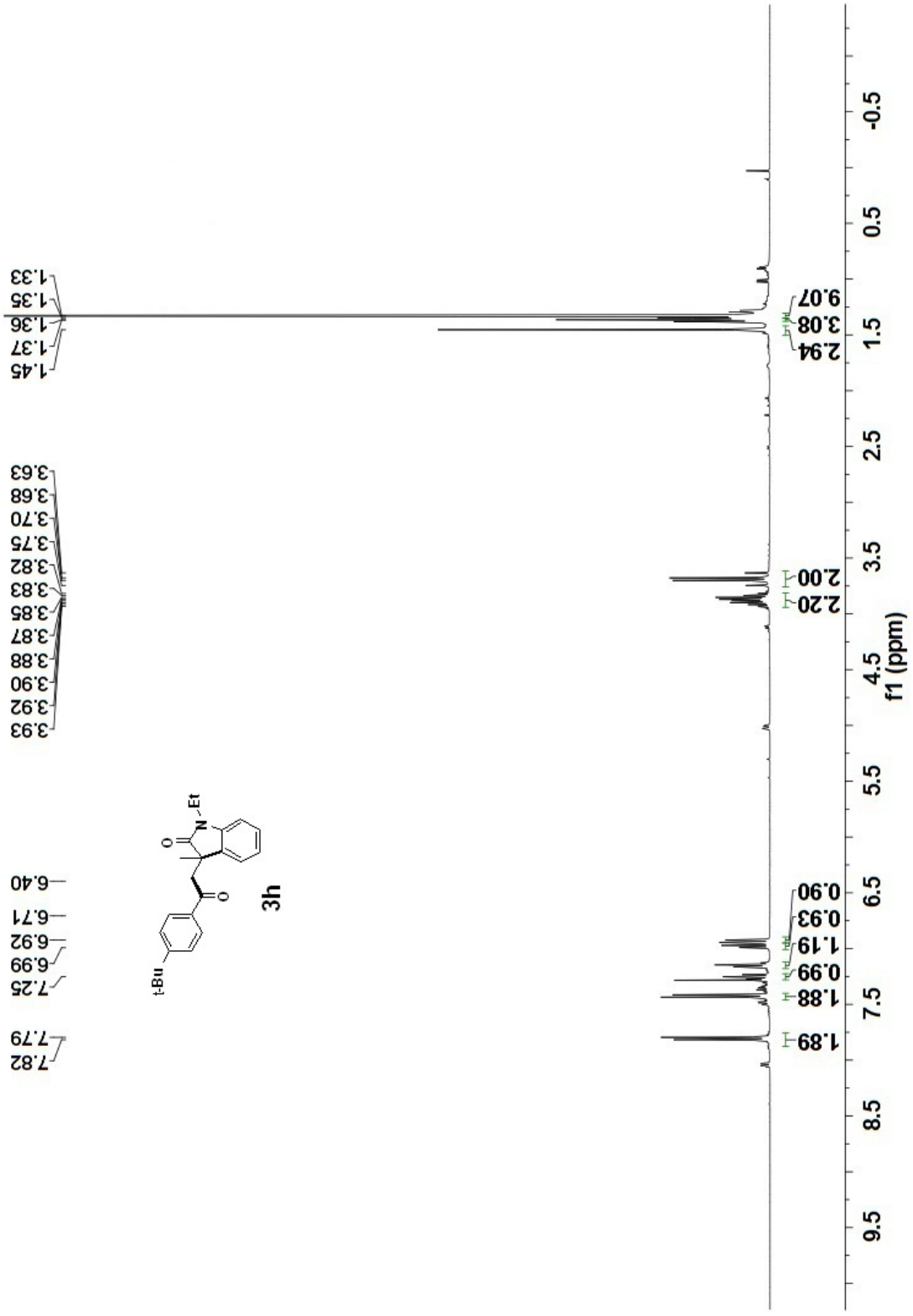
108.33
121.94
121.95
127.76
133.11
3e
f1 (ppm)

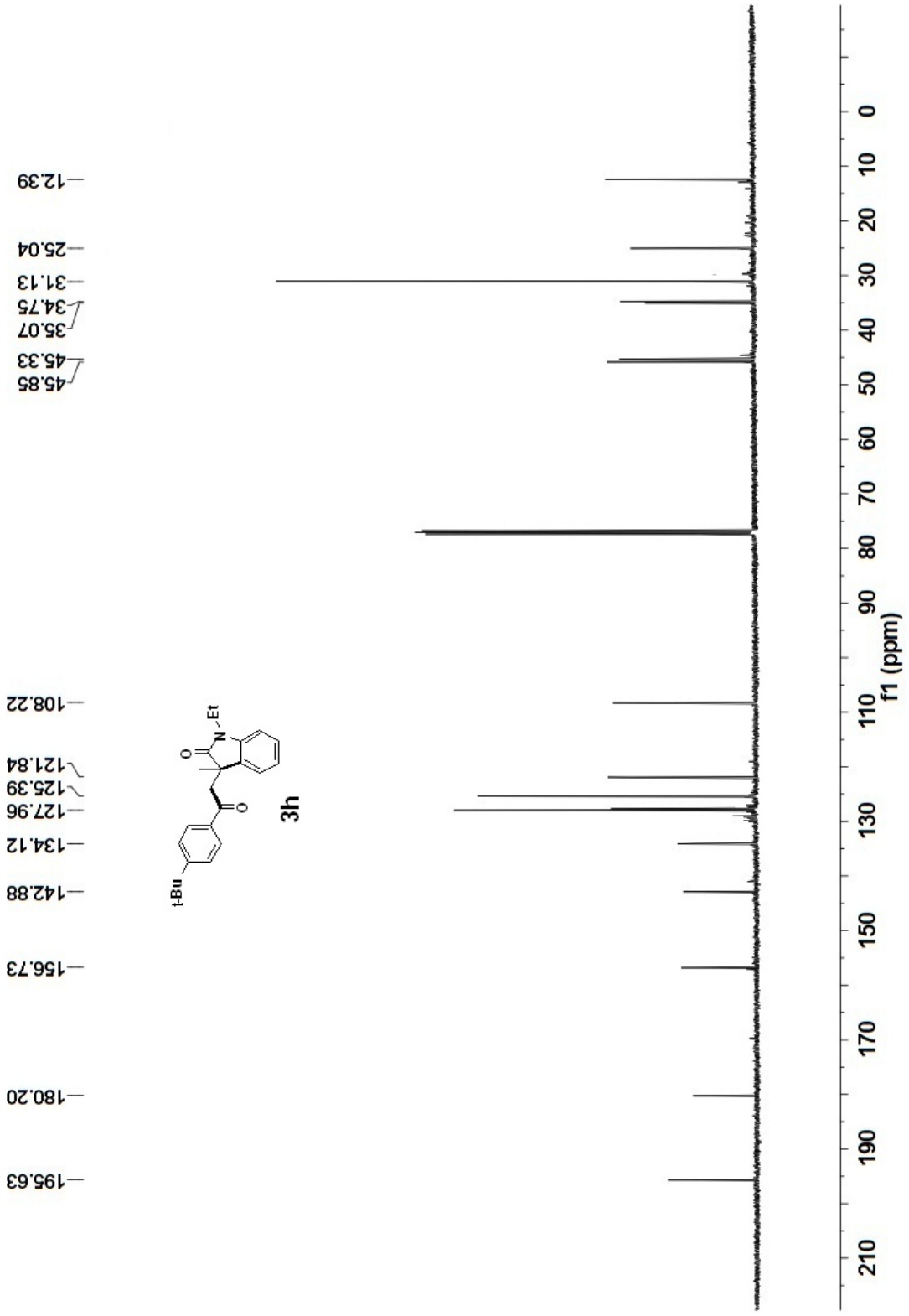











12.39
25.04
31.13
34.75
35.07
45.33
45.85
108.22
121.84
125.39
127.96
134.12
142.88
156.73
180.20
195.63
f1 (ppm)
3h