Bargellini condensation of ninhydrin as a ketone and substituted anilines as nucleophiles

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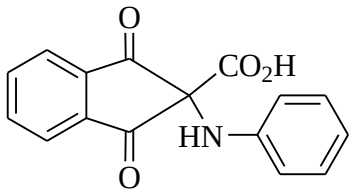
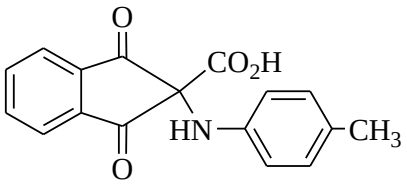
SUPPORTING INFORMATION

1,3-Dioxo-2-(phenylamino)-2,3-dihydro-1*H*-indene-2-carboxylic acid (3a)



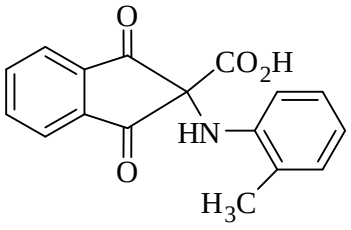
White powder (Yield: 87%). mp: 147 °C. IR (KBr) (ν_{max}/ cm^{-1}): 3338, 1796, 1775, 1670; ^{1}H NMR (DMSO-d_6, 400 MHz): δ: 6.22 (1H, s, NH), 7.33-7.80 (9H, m, ArH), 10.64 (1H, s, OH); ^{13}C NMR (DMSO-d_6, 100 MHz): δ: 79.1, 120.4, 123.1, 124.8, 124.9, 125.7, 129.3, 130.5, 135.3, 138.3, 146.2, 164.9, 170.2; Anal. Calcd for $C_{16}H_{11}NO_4$: C, 68.32; H, 3.94; N, 4.98; Found C, 68.35; H, 4.99; N, 4.95; MS: *m/z* 281.07.

1,3-Dioxo-2-(*p*-tolylamino)-2,3-dihydro-1*H*-indene-2-carboxylic acid (3b)



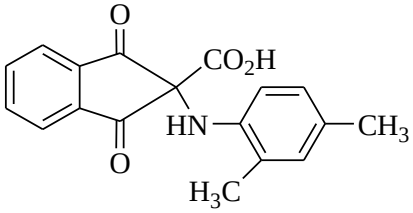
White powder (Yield: 89%). mp: 169 °C. IR (KBr) (ν_{max}/ cm^{-1}): 3343, 1769, 1669, 1599; ^{1}H NMR (DMSO-d_6, 400 MHz): δ: 2.24 (3H, s, CH_3), 6.19 (1H, s, NH), 7.11-7.92 (8H, m, ArH), 10.54 (1H, s, OH); ^{13}C NMR (DMSO-d_6, 100 MHz): δ: 20.92, 79.21, 120.4, 123.1, 124.9, 125.6, 129.6, 130.5, 133.8, 135.3, 135.8, 146.3, 164.7, 170.1; Anal. Calcd for $C_{17}H_{13}NO_4$: C, 69.15; H, 4.44; N, 4.74; Found C, 69.18; H, 4.48; N, 4.70; MS: *m/z* 295.08.

1,3-Dioxo-2-(o-tolylamino)-2,3-dihydro-1*H*-indene-2-carboxylic acid (3c)



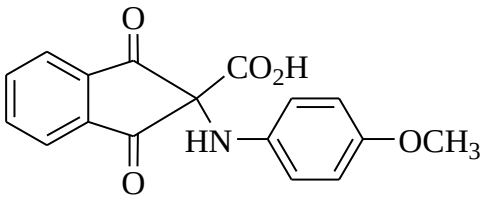
Cream powder (Yield: 81%). mp: 140 °C. IR (KBr) (ν_{max}/ cm^{-1}): 3349, 1769, 1690, 1531; ^{1}H NMR (DMSO-*d*$_6$, 400 MHz): δ: 2.13 (3H, s, CH_3), 6.28 (1H, s, NH), 7.14-7.93 (8H, m, ArH), 10.09 (1H, s, OH); ^{13}C NMR (DMSO-*d*$_6$, 100 MHz): δ: 18.1, 78.0, 123.1, 123.4, 124.9, 125.7, 126.0, 126.6, 126.7, 130.5, 130.9, 133.1, 135.3, 135.5, 147.4, 165.2, 170.2 ; Anal. Calcd for $C_{17}H_{13}NO_4$: C, 69.15; H, 4.44; N, 4.74; Found C, 69.11; H, 4.39; N, 4.77; MS: *m/z* 295.08.

2-(2,4-Dimethylphenylamino)-1,3-dioxo-2,3-dihydro-1*H*-indene-2-carboxylic acid (3d)



Cream powder (Yield: 83%). mp: 147 °C. IR (KBr) (ν_{max}/ cm^{-1}): 3343, 1796, 1669, 1599; ^{1}H NMR (DMSO-*d*$_6$, 400 MHz): δ: 2.07 (3H, s, CH_3), 2.17 (3H, s, CH_3), 6.25 (1H, s, NH), 6.95-7.91 (7H, m, ArH), 9.99 (1H, s, OH); ^{13}C NMR (DMSO-*d*$_6$, 100 MHz): δ: 18.0, 20.9, 79.1, 123.1, 124.9, 125.6, 126.0, 127.0, 130.4, 131.4, 132.9, 133.0, 135.2, 135.8, 146.5, 165.2, 170.2; Anal. Calcd for $C_{18}H_{15}NO_4$: C, 69.89; H, 4.89; N, 4.53; Found C, 69.92; H, 4.85; N, 4.50; MS: *m/z* 309.10.

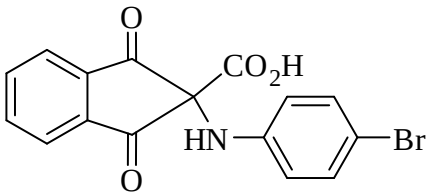
2-(4-Methoxyphenylamino)-1,3-dioxo-2,3-dihydro-1*H*-indene-2-carboxylic acid (3e)



White powder (Yield: 91%). mp: 147 °C. IR (KBr) (ν_{max}/ cm^{-1}): 3280, 1777, 1674, 1606; ^{1}H NMR (DMSO-d_6, 400 MHz): δ: 3.71 (3H, s, OCH_3), 6.18 (1H, s, NH), 6.88-7.92 (8H, m, ArH), 10.49 (1H, s, OH); ^{13}C NMR (DMSO-d_6, 100 MHz): δ: 55.6, 79.1, 114.1, 114.3, 122.0, 123.1, 124.9, 125.6, 130.5, 131.4, 135.3, 146.4, 156.3, 164.5, 170.2; Anal. Calcd for $C_{17}H_{13}NO_5$: C, 65.59; H, 4.21; N, 4.50; Found C, 65.62; H, 4.19; N, 4.47; MS: *m/z* 311.08.

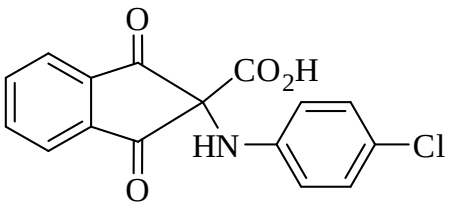
Due to very low solubility of the products **3f**, we cannot report the 13C NMR data for this product.

2-(4-Bromophenylamino)-1,3-dioxo-2,3-dihydro-1*H*-indene-2-carboxylic acid (3f)



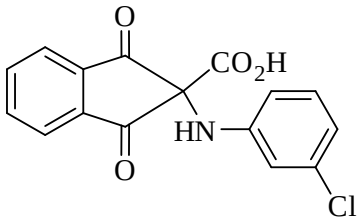
White powder (Yield: 84%). mp: 220 °C. IR (KBr) (ν_{max}/ cm^{-1}): 3419, 1778, 1683, 1592; ^{1}H NMR (DMSO-*d6*, 400 MHz): δ: 6.23 (1H, s, NH), 7.51-7.94 (8H, m, ArH), 10.74 (1H, s, OH); Anal. Calcd for $C_{16}H_{10}BrNO_4$: C, 53.36; H, 2.80; N, 3.89; Found C, 53.40; H, 2.85; N, 3.93; MS: *m/z* 358.98, 360.18.

2-(4-Chlorophenylamino)-1,3-dioxo-2,3-dihydro-1*H*-indene-2-carboxylic acid (3g)



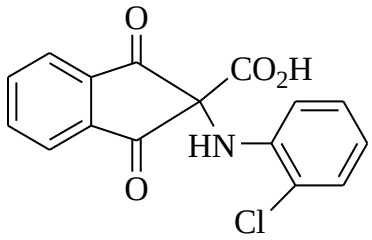
White powder (Yield: 80%). mp: 180 °C. IR (KBr) (ν_{max}/ cm^{-1}): 3347, 1770, 1690, 1597; ^{1}H NMR (DMSO-*d6*, 400 MHz): δ: 6.21 (1H, s, NH), 7.37-7.92 (8H, m, ArH), 10.75 (1H, s, OH); ^{13}C NMR (DMSO-d_6, 100 MHz): δ: 84.0, 126.9, 128.0, 129.6, 130.5, 133.2, 134.0, 135.4, 140.1, 142.1, 150.9, 169.9, 174.9.; Anal. Calcd for $C_{16}H_{10}ClNO_4$: C, 60.87; H, 3.19; N, 4.44; Found C, 60.91; H, 3.24; N, 4.49; MS: *m/z* 315.03.

2-(3-Chlorophenylamino)-1,3-dioxo-2,3-dihydro-1*H*-indene-2-carboxylic acid (3h)



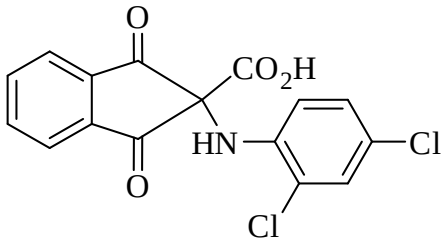
White powder (Yield: 76%). mp: 148 °C. IR (KBr) (ν_{max}/ cm^{-1}): 3437, 1684, 1596, 1538; ^{1}H NMR (DMSO-*d6*, 400 MHz): δ: 6.11 (1H, s, NH), 7.08-7.89 (8H, m, ArH), 10.17 (1H, s, OH); ^{13}C NMR (DMSO-d_6, 100 MHz): δ: 70.7, 118.5, 119.5, 123.5, 127.8, 127.9, 130.1, 130.7, 131.1, 132.0, 133.4, 140.6, 141.7, 169.5, 171.7; Anal. Calcd for $C_{16}H_{10}ClNO_4$: C, 60.87; H, 3.19; N, 4.44; Found C, 60.84; H, 3.15; N, 4.48; MS: *m/z* 315.03.

2-(2-Chlorophenylamino)-1,3-dioxo-2,3-dihydro-1*H*-indene-2-carboxylic acid (3i)



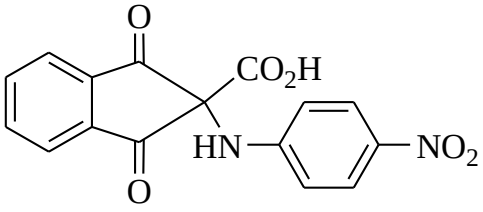
White powder (Yield: 72%). mp: 132 °C. IR (KBr) (ν_{max}/ cm^{-1}): 3385, 1786, 1685, 1596; ^{1}H NMR (DMSO-*d6*, 400 MHz): δ: 6.34 (1H, s, NH), 7.25-7.91 (8H, m, ArH), 10.33 (1H, s, OH); ^{13}C NMR (DMSO-d_6, 100 MHz): δ: 78.9, 123.3, 124.8, 125.7, 127.4, 128.0, 128.0, 128.2, 130.1, 130.5, 134.1, 135.3, 146.1, 165.5, 170.1; Anal. Calcd for $C_{16}H_{10}ClNO_4$: C, 60.87; H, 3.19; N, 4.44; Found C, 60.89; H, 3.16; N, 4.46; MS: *m/z* 315.03.

2-(2,4-Dichlorophenylamino)-1,3-dioxo-2,3-dihydro-1*H*-indene-2-carboxylic acid (3j)



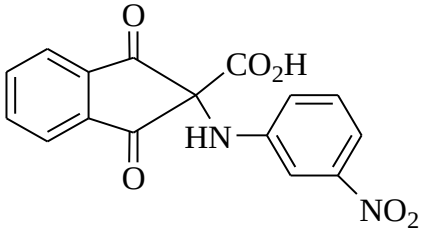
Cream powder (Yield: 76%). mp: 176 °C. IR (KBr) (ν_{max}/ cm^{-1}): 3423, 1774, 1663, 1605; ^{1}H NMR (DMSO-*d6*, 400 MHz): δ: 6.16 (1H, s, NH), 6.88-8.11 (7H, m, ArH), 9.68 (1H, s, OH); ^{13}C NMR (DMSO-d_6, 100 MHz): δ: 70.1, 123.3, 124.8, 128.0, 128.1, 128.3, 128.6, 129.2, 130.2, 131.0, 132.2, 134.0, 141.0, 169.6, 171.2; Anal. Calcd for $C_{16}H_9Cl_2NO_4$: C, 54.88; H, 2.59; N, 4.00; Found C, 54.83; H, 2.63; N, 4.06; MS: *m/z* 348.99.

2-(4-Nitrophenylamino)-1,3-dioxo-2,3-dihydro-1*H*-indene-2-carboxylic acid (3k)



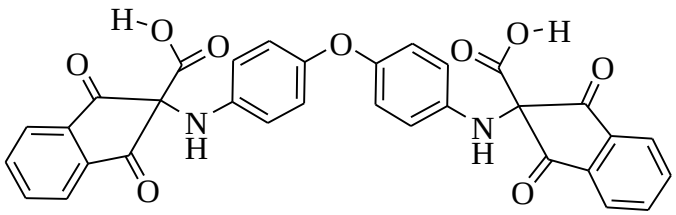
Yellow powder (Yield: 70%). mp: 250 °C. IR (KBr) (ν_{max}/ cm^{-1}): 3317, 1788, 1692, 1600; ^{1}H NMR (DMSO-*d6*, 400 MHz): δ: 6.28 (1H, s, NH), 7.80-8.25 (8H, m, ArH), 12.20 (1H, s, OH); ^{13}C NMR (DMSO-d_6, 100 MHz): δ: 79.1, 120.4, 123.3, 124.8, 125.3, 125.8, 130.7, 135.4, 143.5, 144.4, 145.7, 166.0, 170.0; Anal. Calcd for $C_{16}H_{10}N_2O_6$: C, 58.90; H, 3.09; N, 8.59; Found C, 58.93; H, 3.11; N, 8.62; MS: *m/z* 326.05.

2-(3-Nitrophenylamino)-1,3-dioxo-2,3-dihydro-1*H*-indene-2-carboxylic acid (3l)



Cream powder (Yield: 72%). mp: 202 °C. IR (KBr) (ν_{max}/ cm^{-1}): 3322, 1738, 1688, 1600; ^{1}H NMR (DMSO-*d6*, 400 MHz): δ: 6.24 (1H, s, NH), 6.66-8.58 (8H, m, ArH), 11.00 (1H, s, OH); ^{13}C NMR (DMSO-d_6, 100 MHz): δ: 79.0, 114.8, 119.3, 123.3, 124.8, 125.7, 126.5, 130.6, 130.7, 135.4, 139.4, 145.8, 148.4, 165.9, 169.9; Anal. Calcd for $C_{16}H_{10}N_2O_6$: C, 58.90; H, 4.21; N, 8.59; Found C, 58.92; H, 4.18; N, 8.62; MS: *m/z* 326.05.

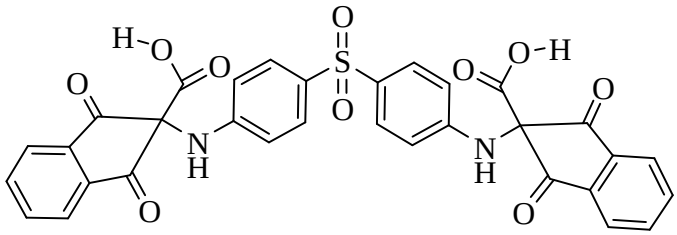
2,2'-(4,4'-Oxybis(4,1-phenylene)bis(azanediyl))bis(1,3-dioxo-2,3-dihydro-1*H*-indene-2-carboxylic acid) (3m)



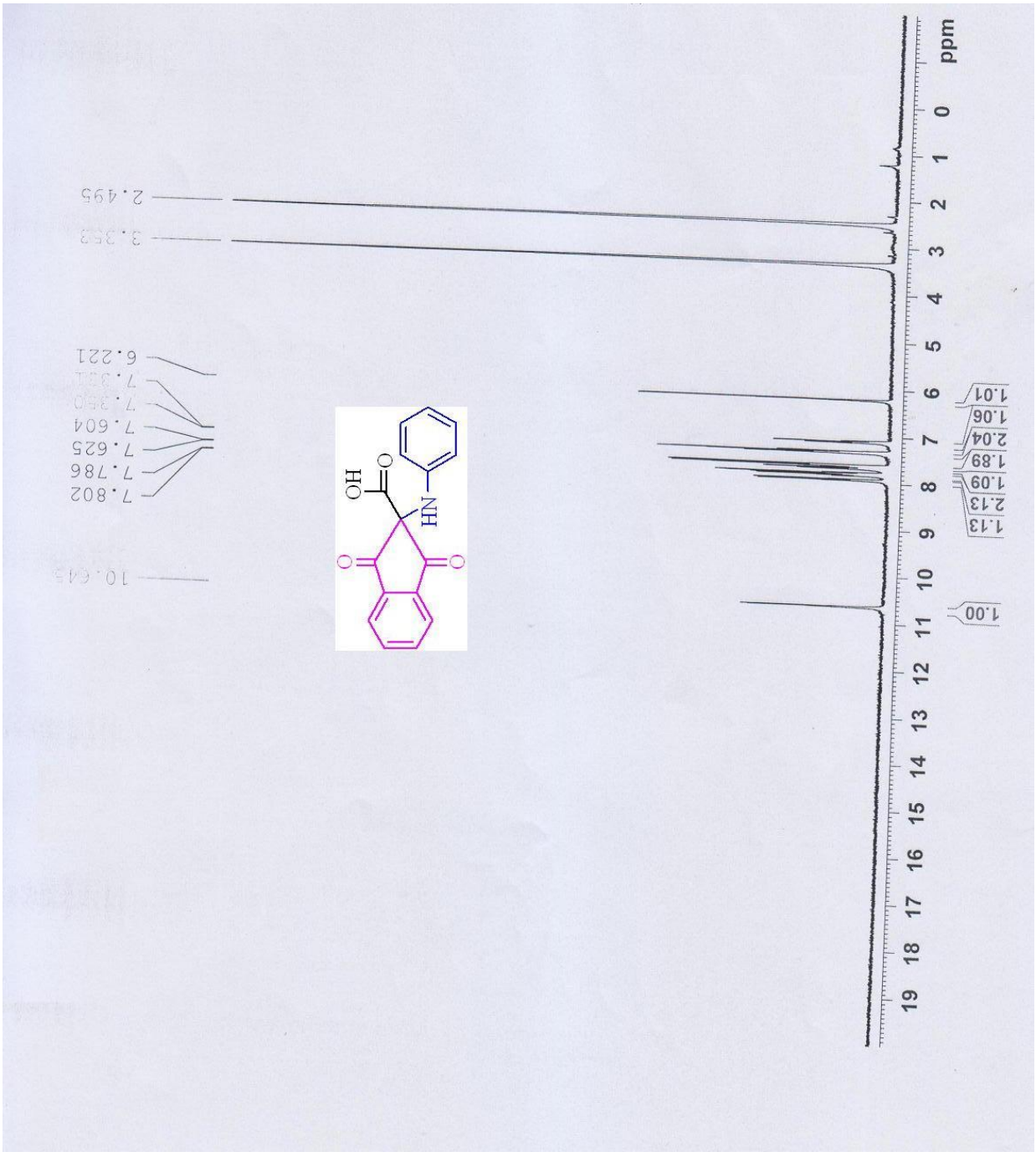
Yellow powder (Yield: 85%). mp: 187 °C. IR (KBr) (ν_{max}/ cm^{-1}): 3407, 1773, 1679, 1607; ^{1}H NMR (DMSO-*d6*, 400 MHz): δ: 6.18 (1H, s, NH), 6.95-7.90 (8H, m, ArH), 10.59 (1H, s, OH); ^{13}C NMR (DMSO-d_6, 100 MHz): δ: 79.1, 119.2, 122.2, 123.1, 124.9, 125.7, 130.5, 135.3, 146.3, 153.6, 164.8, 170.2; Anal. Calcd for $C_{32}H_{20}N_2O_9$: C, 66.67; H, 3.50; N, 4.86; Found C, 66.69; H, 3.47; N, 4.89; MS: *m/z* 576.12.

Due to very low solubility of the products **3n**, we cannot report the 13C NMR data for this product.

2,2'-(4,4'-Sulfonylbis(4,1-phenylene)bis(azanediyl))bis(1,3-dioxo-2,3-dihydro-1*H*-indene-2-carboxylic acid) (3n)



Yellow powder (Yield: 83%). mp: 165 °C. IR (KBr) (ν_{max}/ cm^{-1}): 3441, 1777, 1694, 1593; ^{1}H NMR (DMSO-*d6*, 400 MHz): δ: 6.22 (2H, s, 2NH), 7.64-7.88 (16H, m, ArH), 10.99 (2H, s, 2OH); Anal. Calcd for $C_{32}H_{20}N_2O_{10}S$: C, 61.54; H, 3.23; N, 4.49; Found C, 61.59; H, 3.27; N, 4.46; MS: *m/z* 624.08.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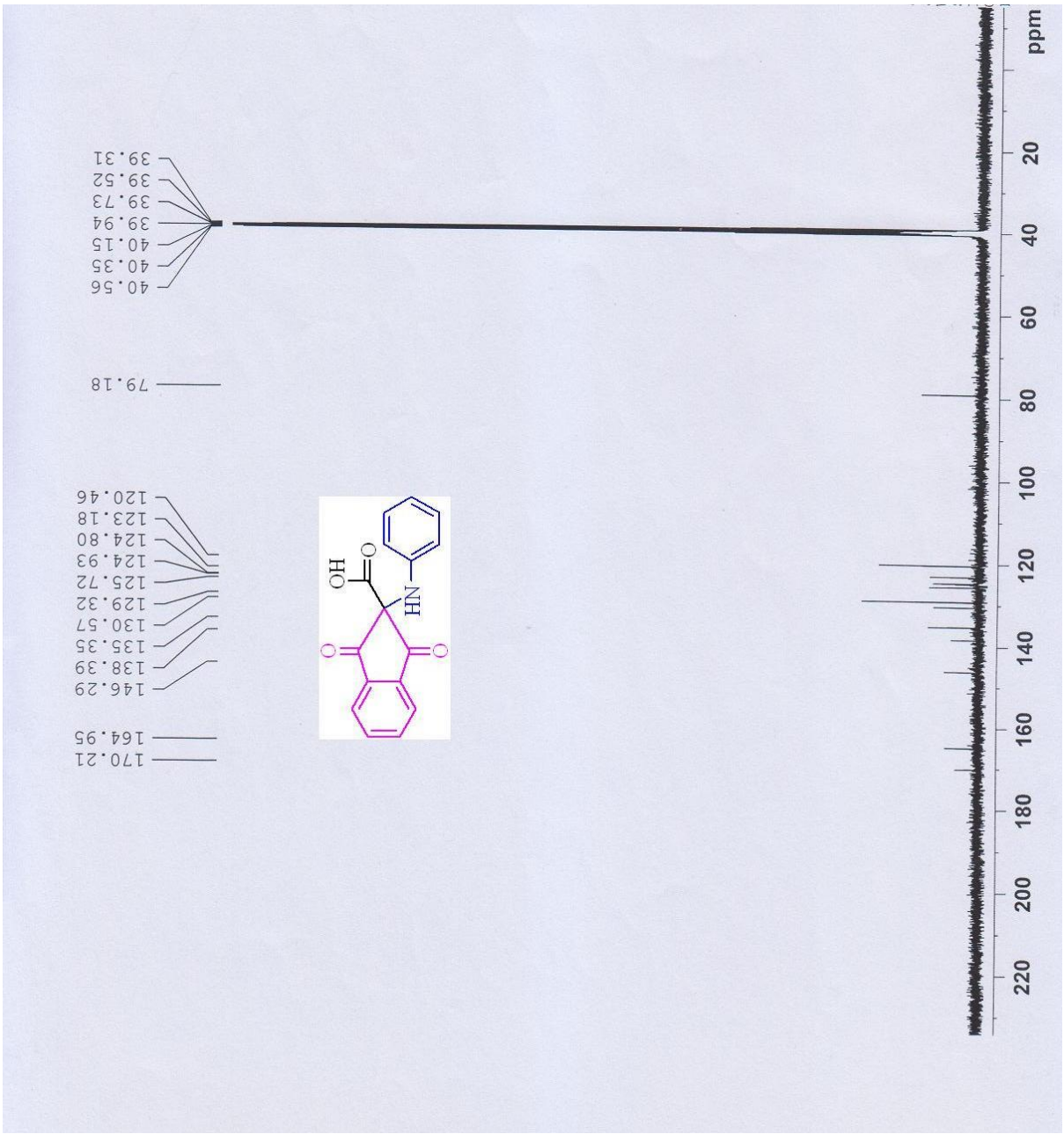
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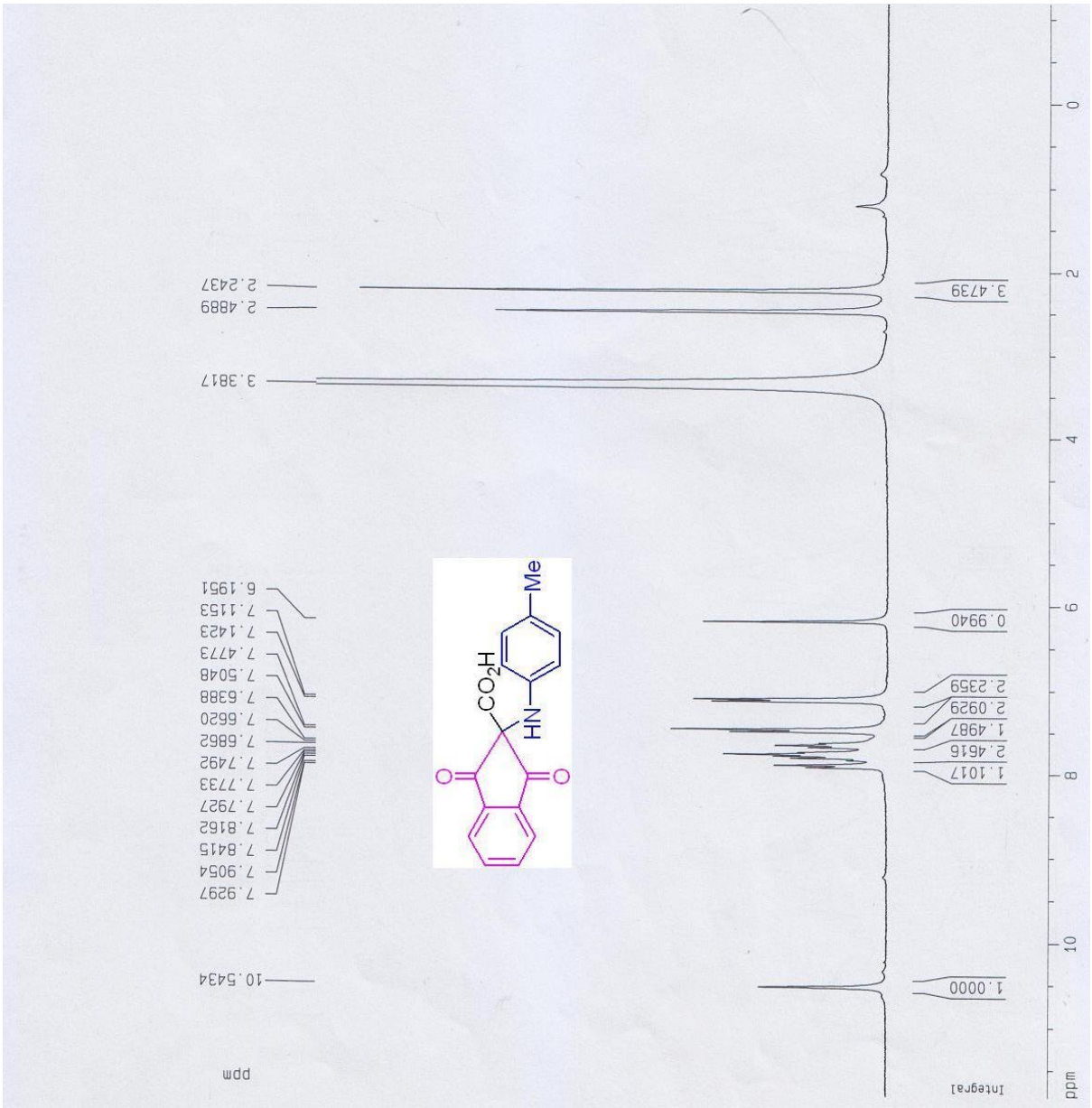
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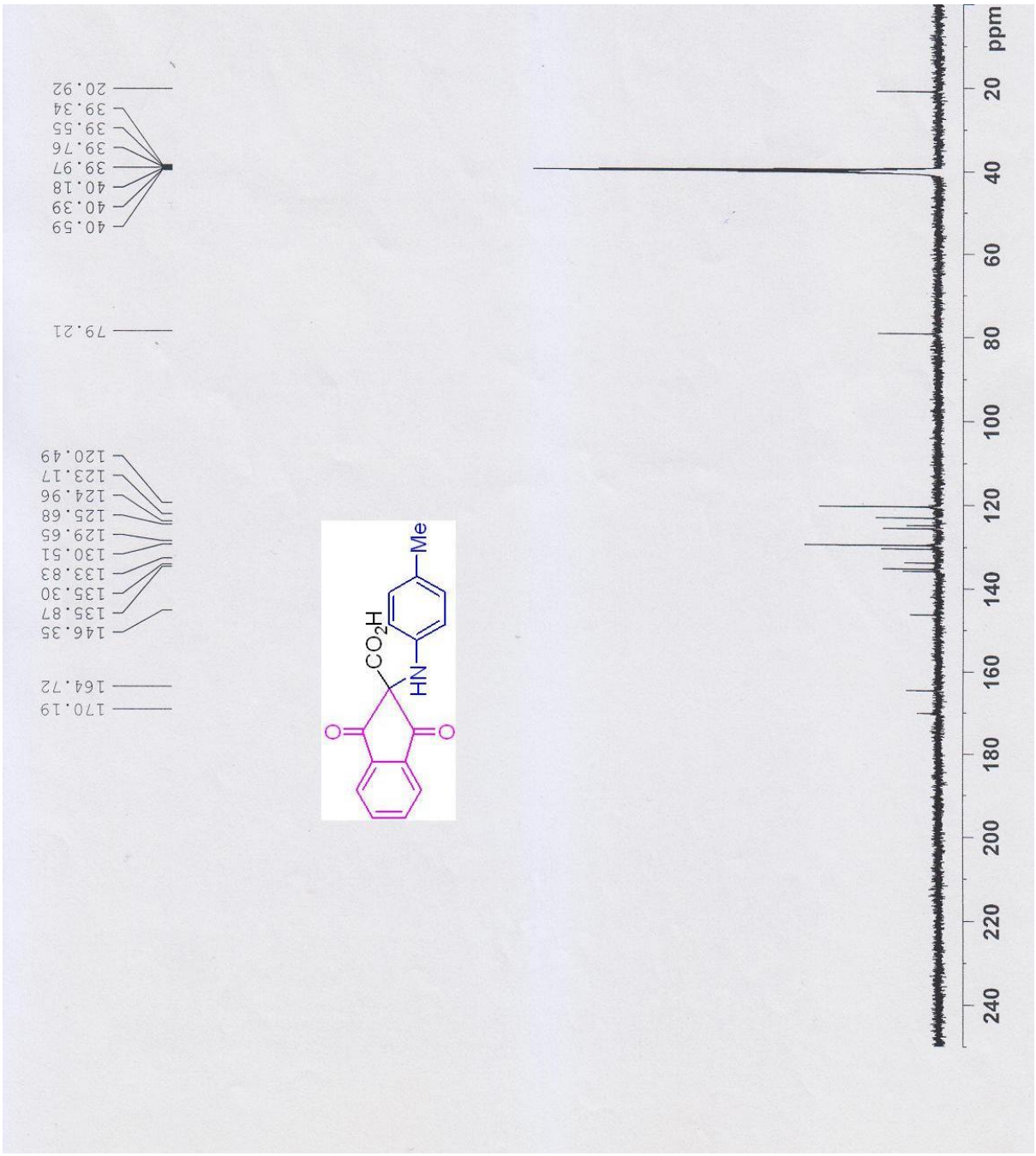
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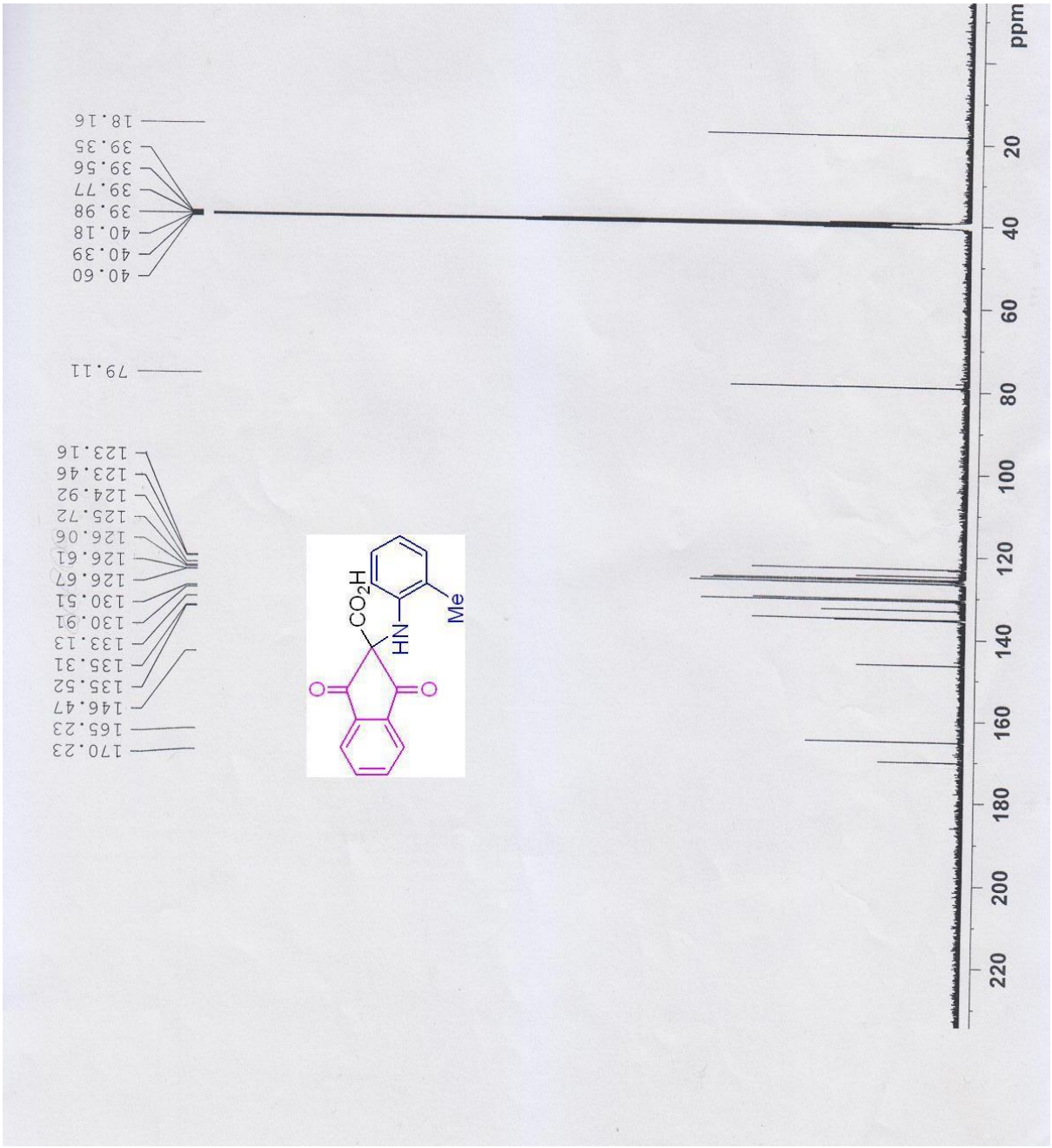
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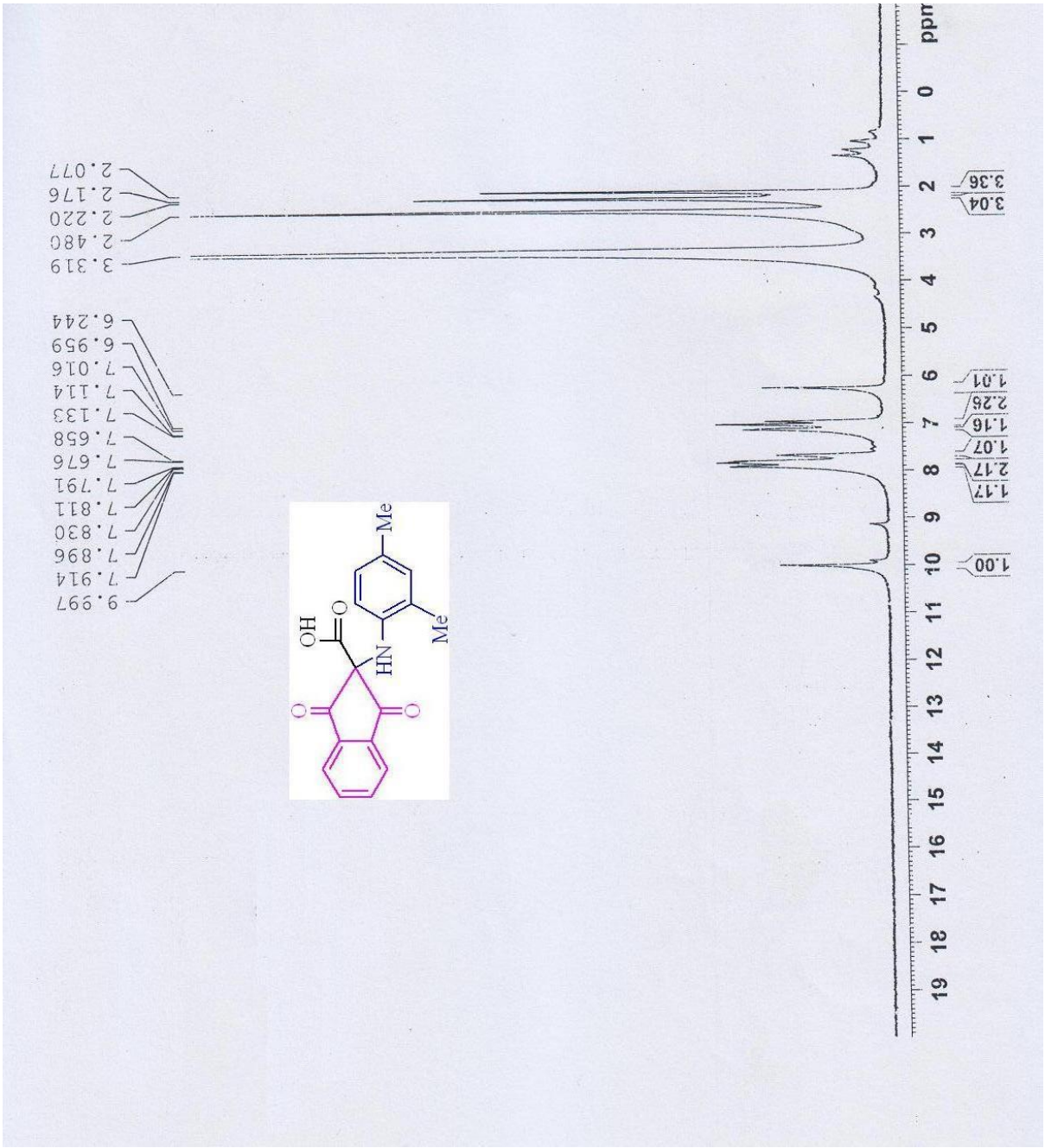
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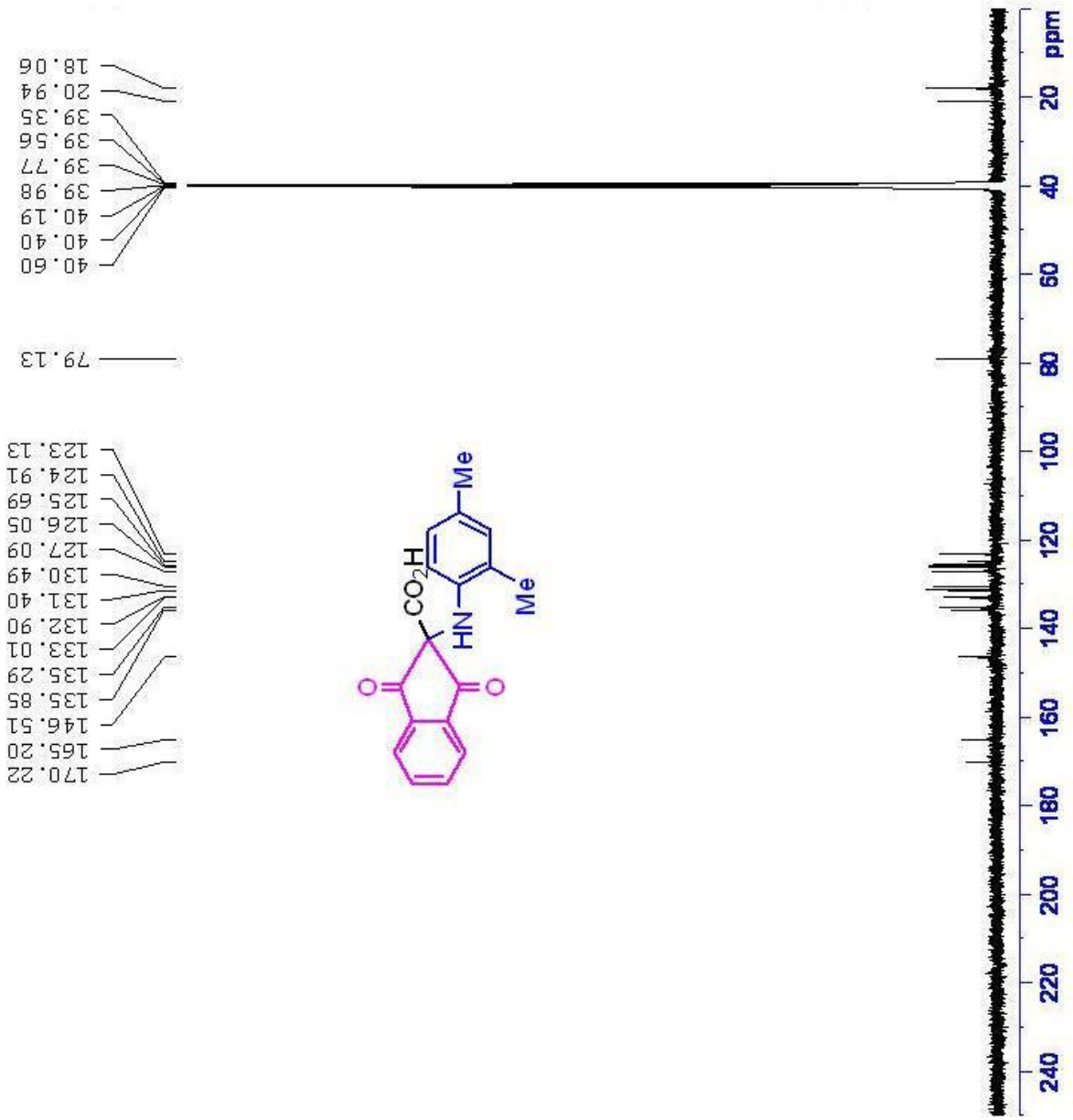
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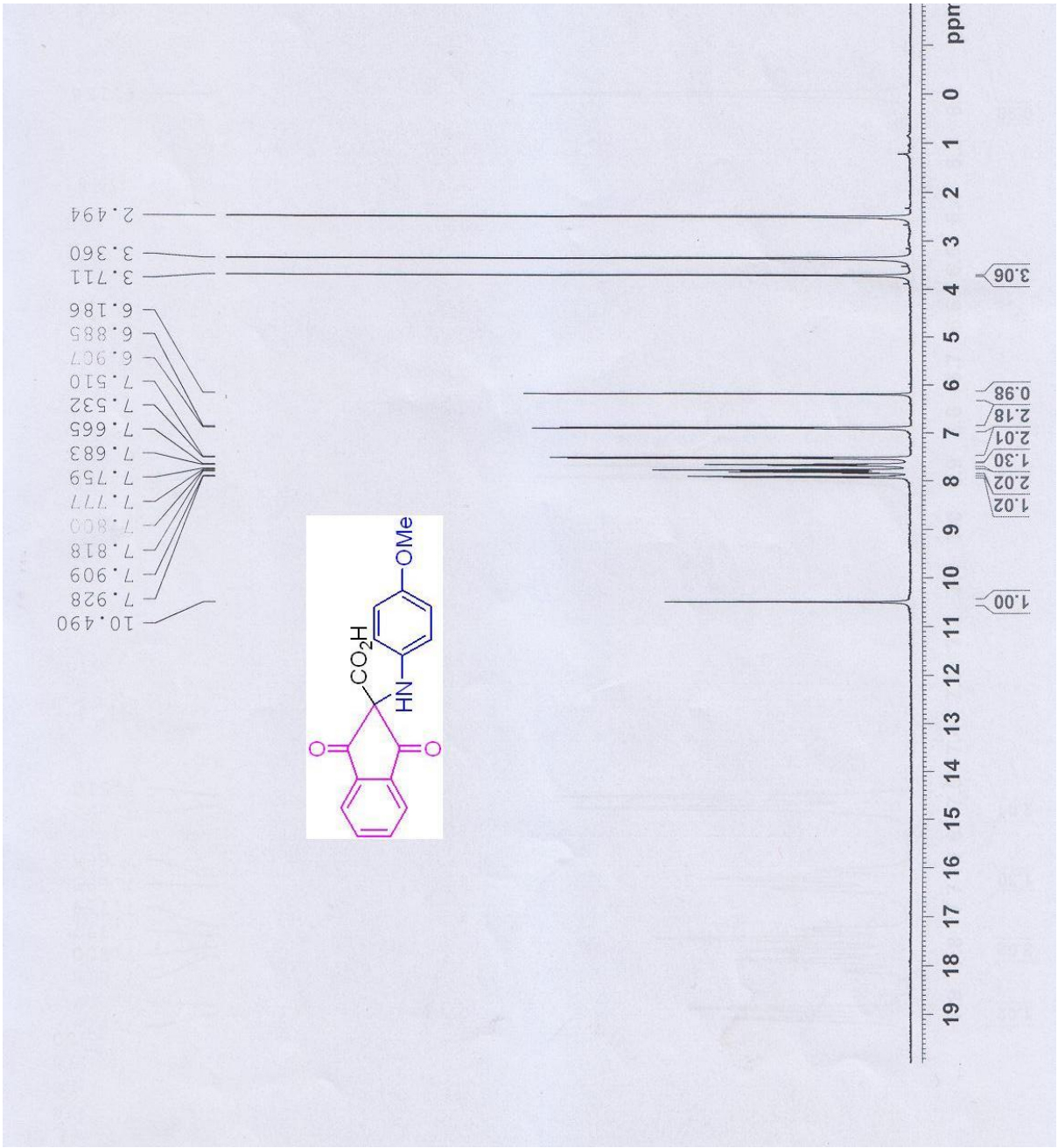
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7.800
7.818
7.909
7.928
10.490
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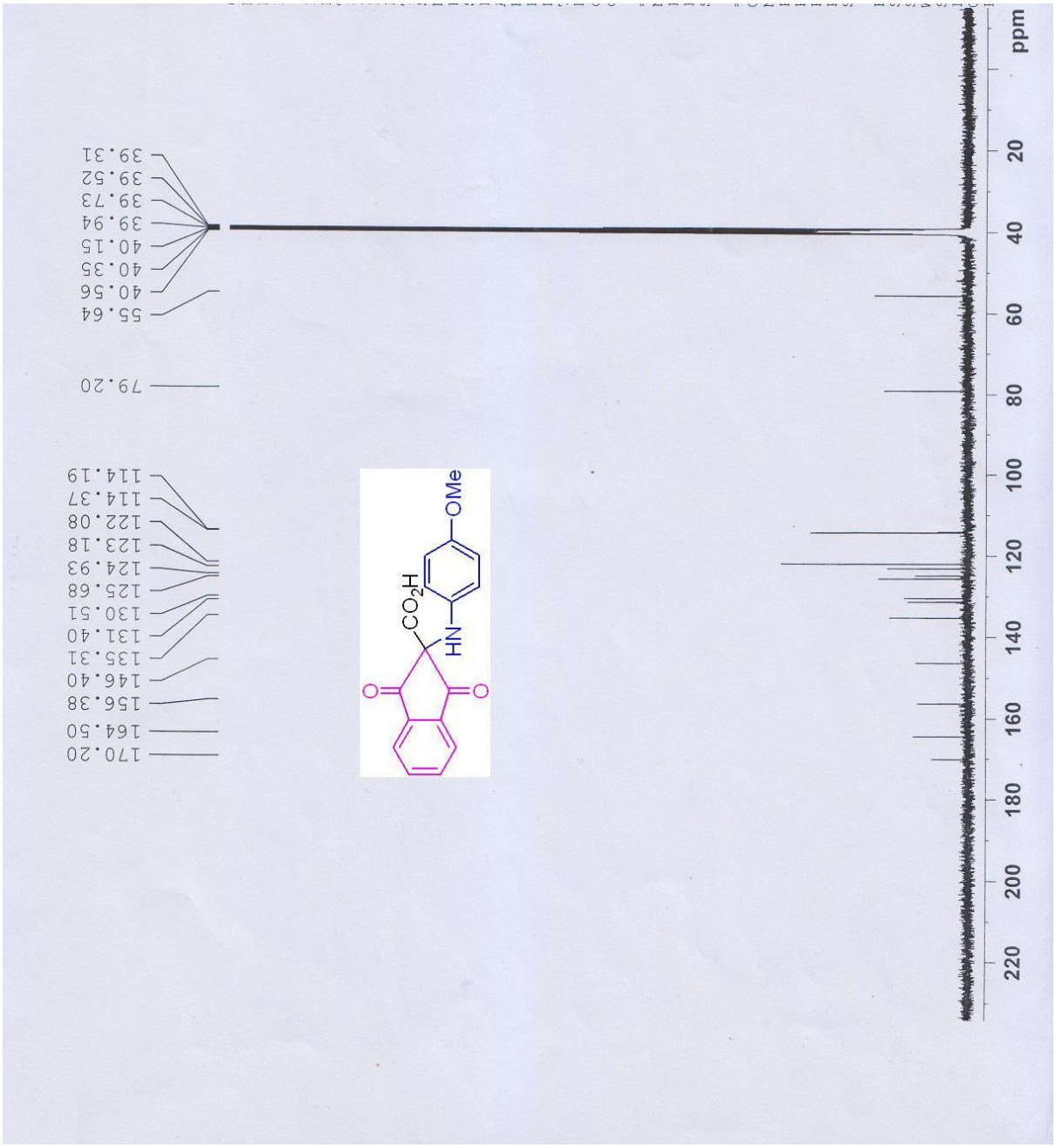
1.30
2.02
1.02
1.00
ppm
OMe
CO2H
HN
O
O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40.35
40.56
55.64
79.20
114.19
114.37
122.08
123.18
124.93
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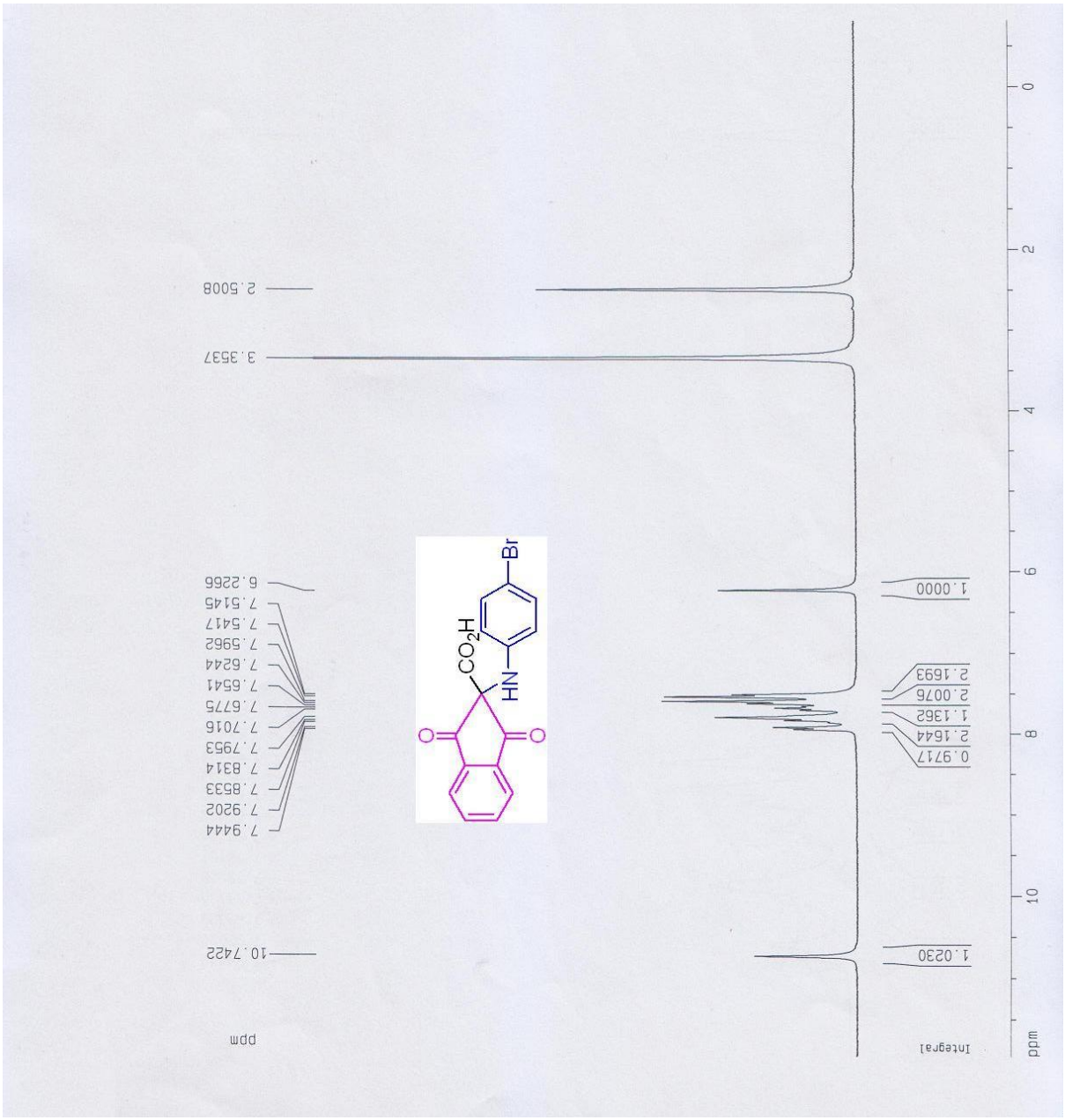
131.40
135.31
146.40
156.38
164.50
170.20
OMe
HN
CO2H
O
O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7.5962
7.5417
7.5145
6.2266
2.5008
3.3537
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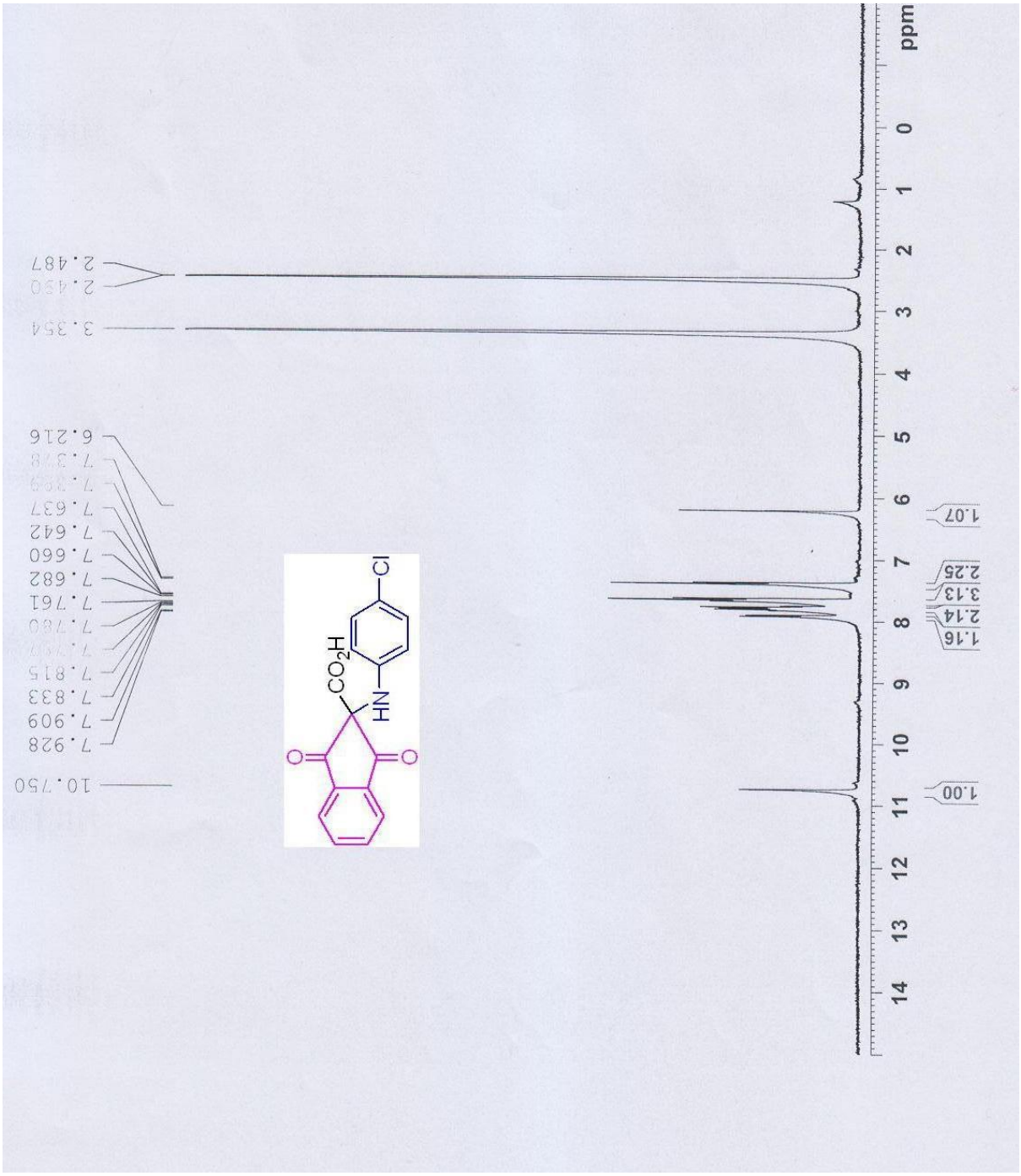
1.0230
Integral
ppm
Br
HN
CO2H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3
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7
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11
12
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14
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3.13
2.25
1.07
10.750
7.928
7.909
7.833
7.815
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7.642
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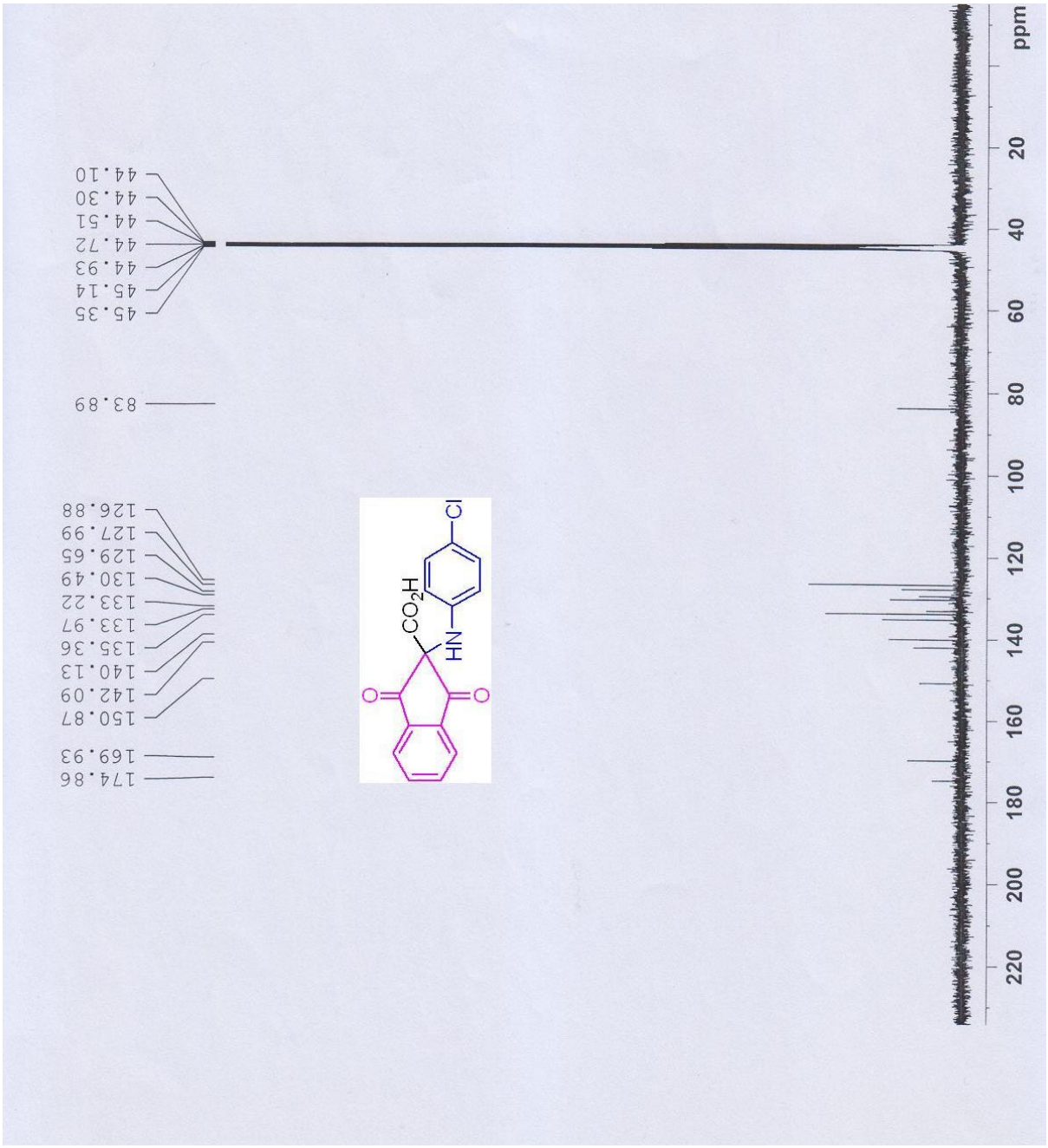
HN
O
O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200
220
44.10
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44.72
44.93
45.14
45.35
83.89
126.88
127.99
129.65
130.49
133.22
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135.36
140.13
142.09
150.87
169.93
174.86
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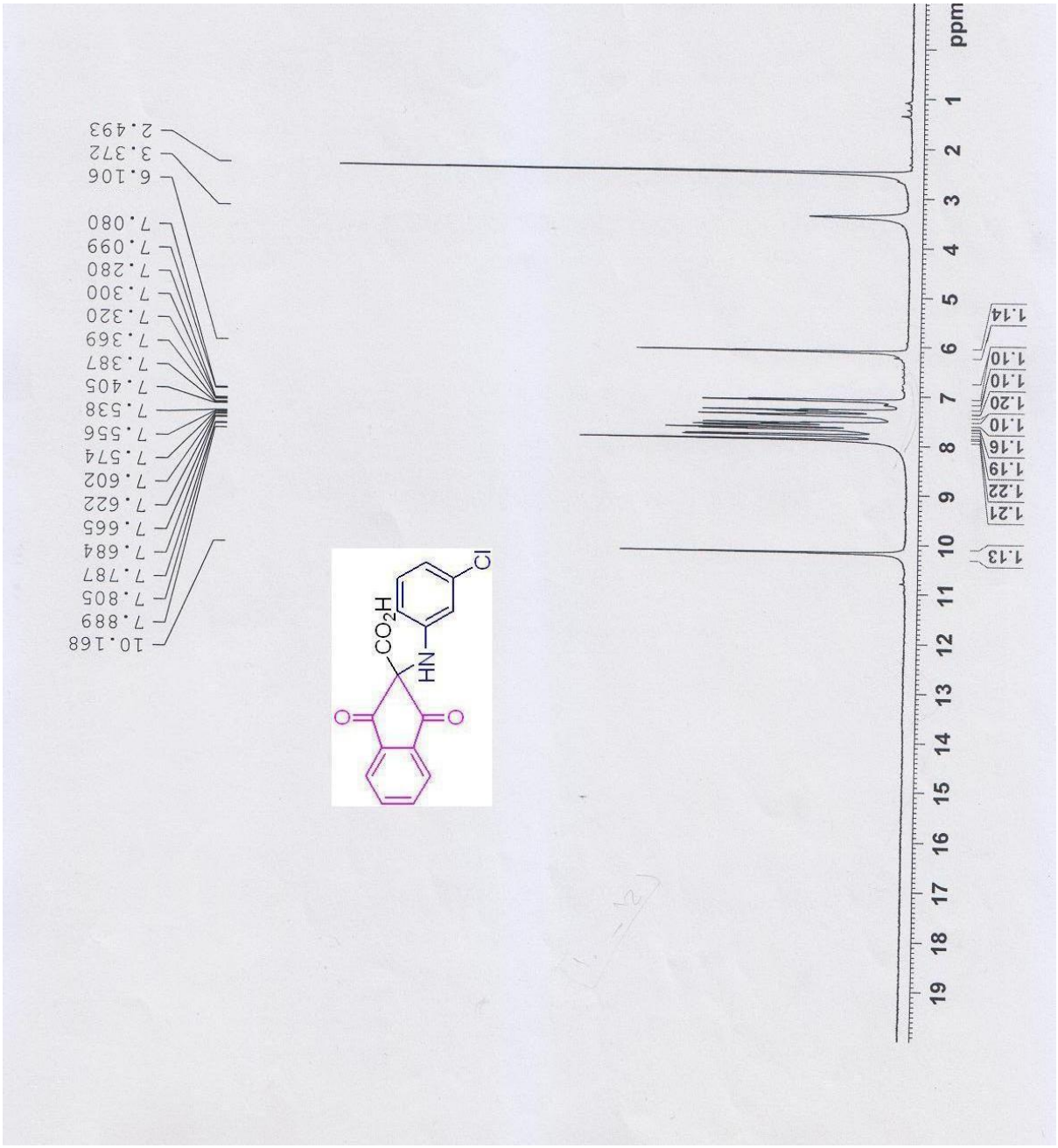
HN
O
O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1.10
1.16
1.19
1.22
1.21
1.13
2.493
3.372
6.106
7.080
7.099
7.280
7.300
7.320
7.369
7.387
7.405
7.538
7.556
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7.665
7.684
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10.168
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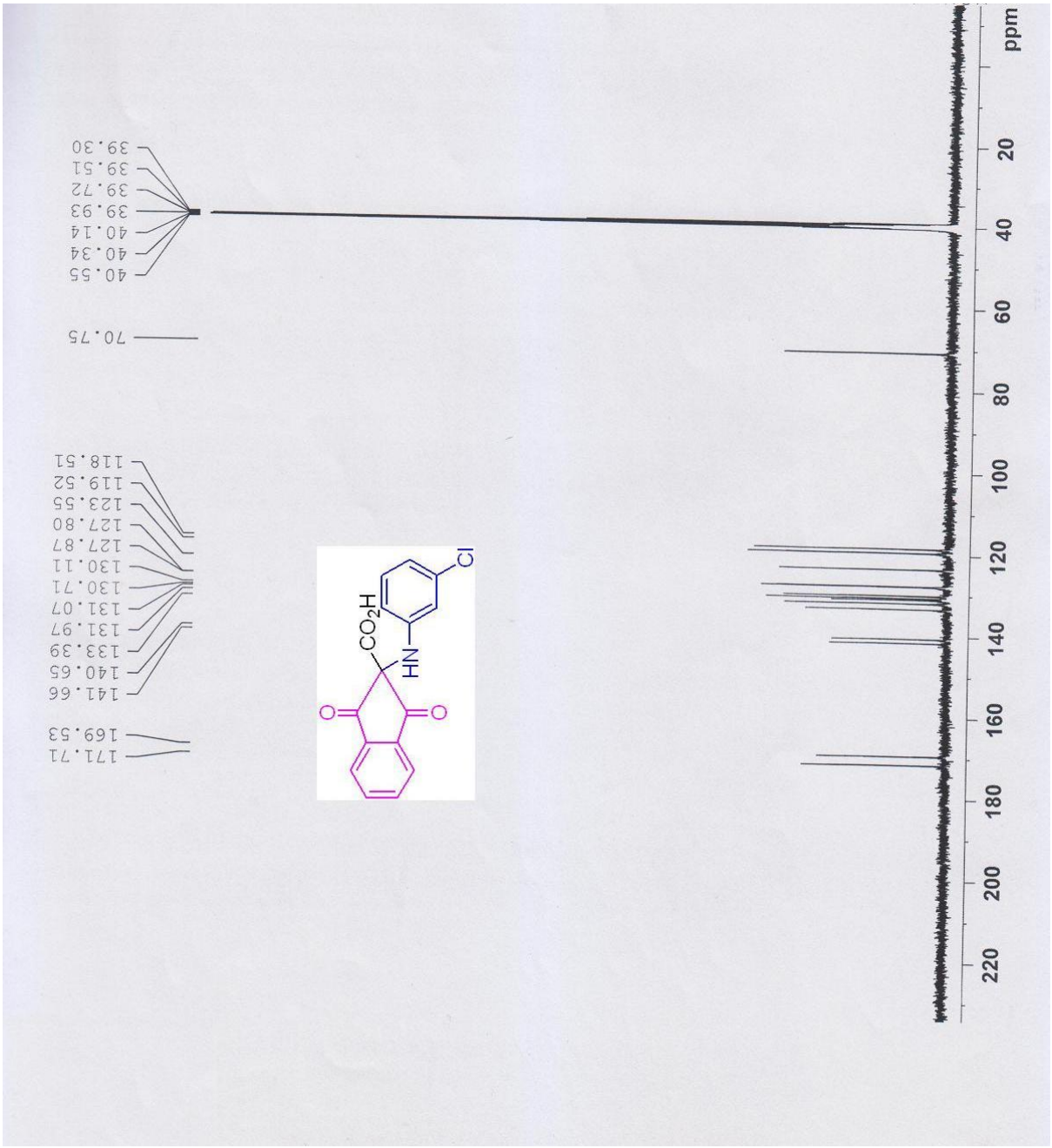
HN
O
O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119.52
123.55
127.80
127.87
130.11
130.71
131.07
131.97
133.39
140.65
141.66
169.53
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CO2H
HN
Cl
O
O
ppm
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160
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80
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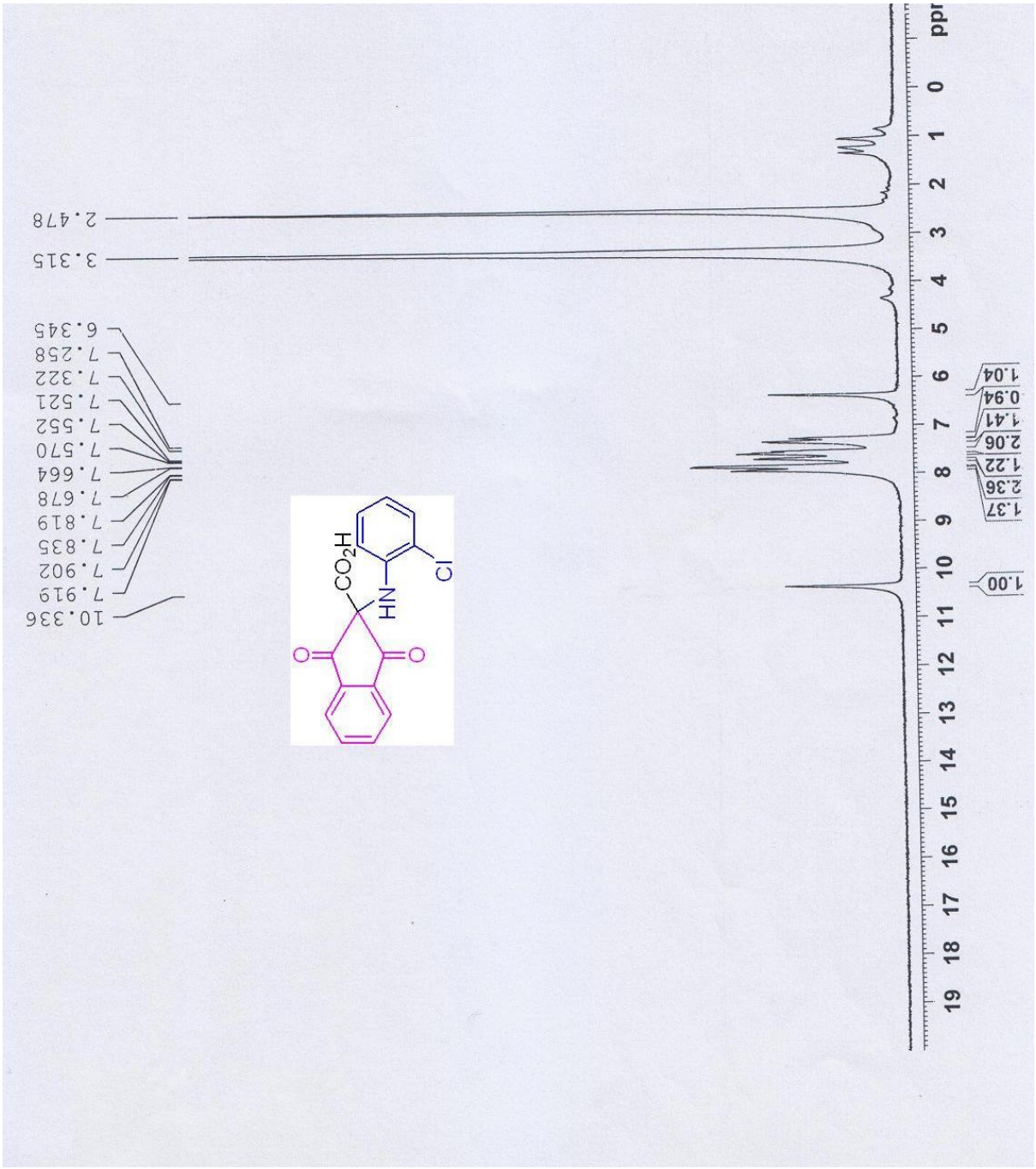
40
20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7.552
7.570
7.664
7.678
7.819
7.835
7.902
7.919
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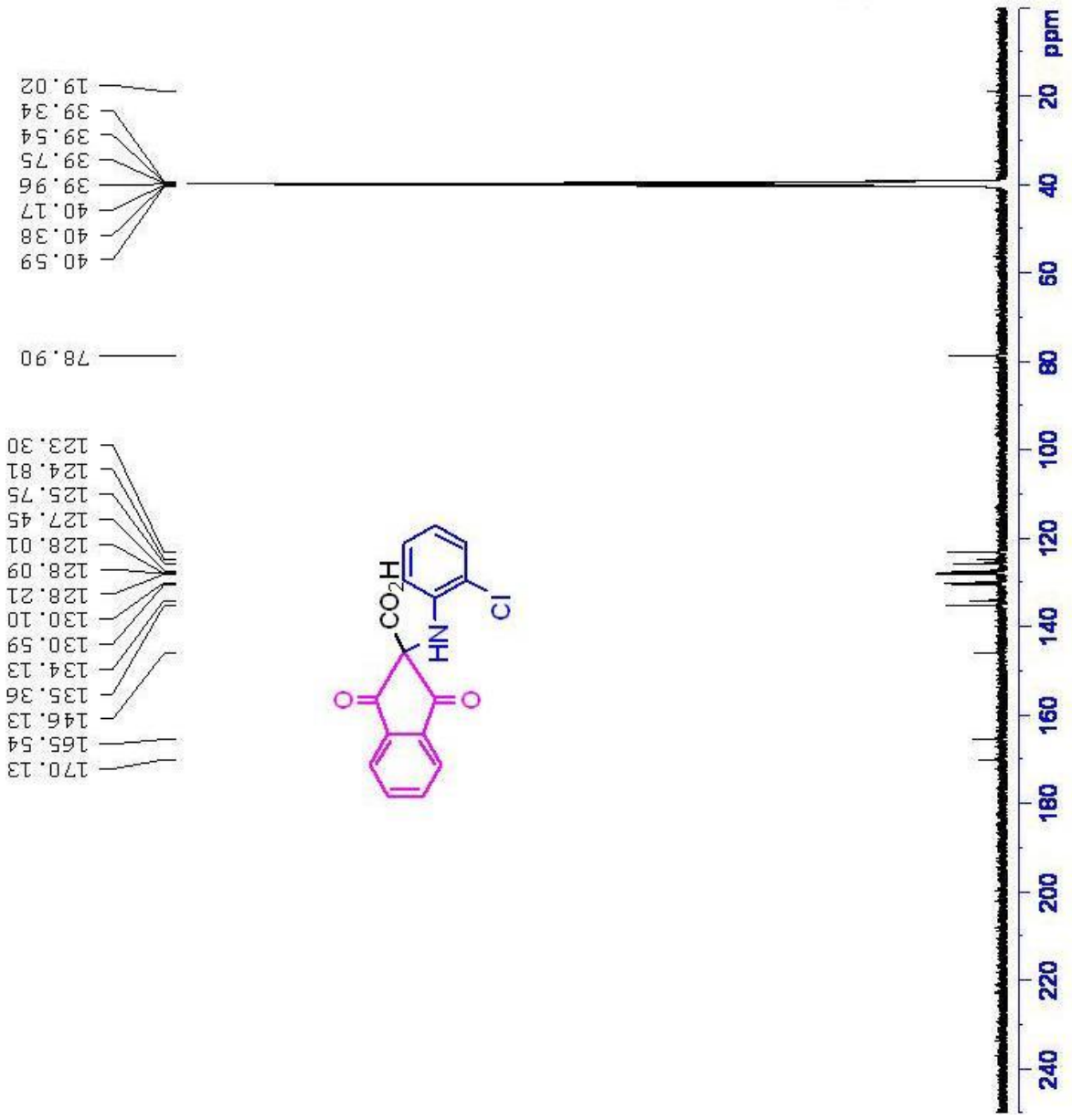
2.36
1.22
2.06
1.41
0.94
1.04
1.00
ppm
CO2H
HN
Cl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124.81
125.75
127.45
128.01
128.09
128.21
130.10
130.59
134.13
135.36
146.13
165.54
170.13
ppm
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60
80
100
120
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200
220
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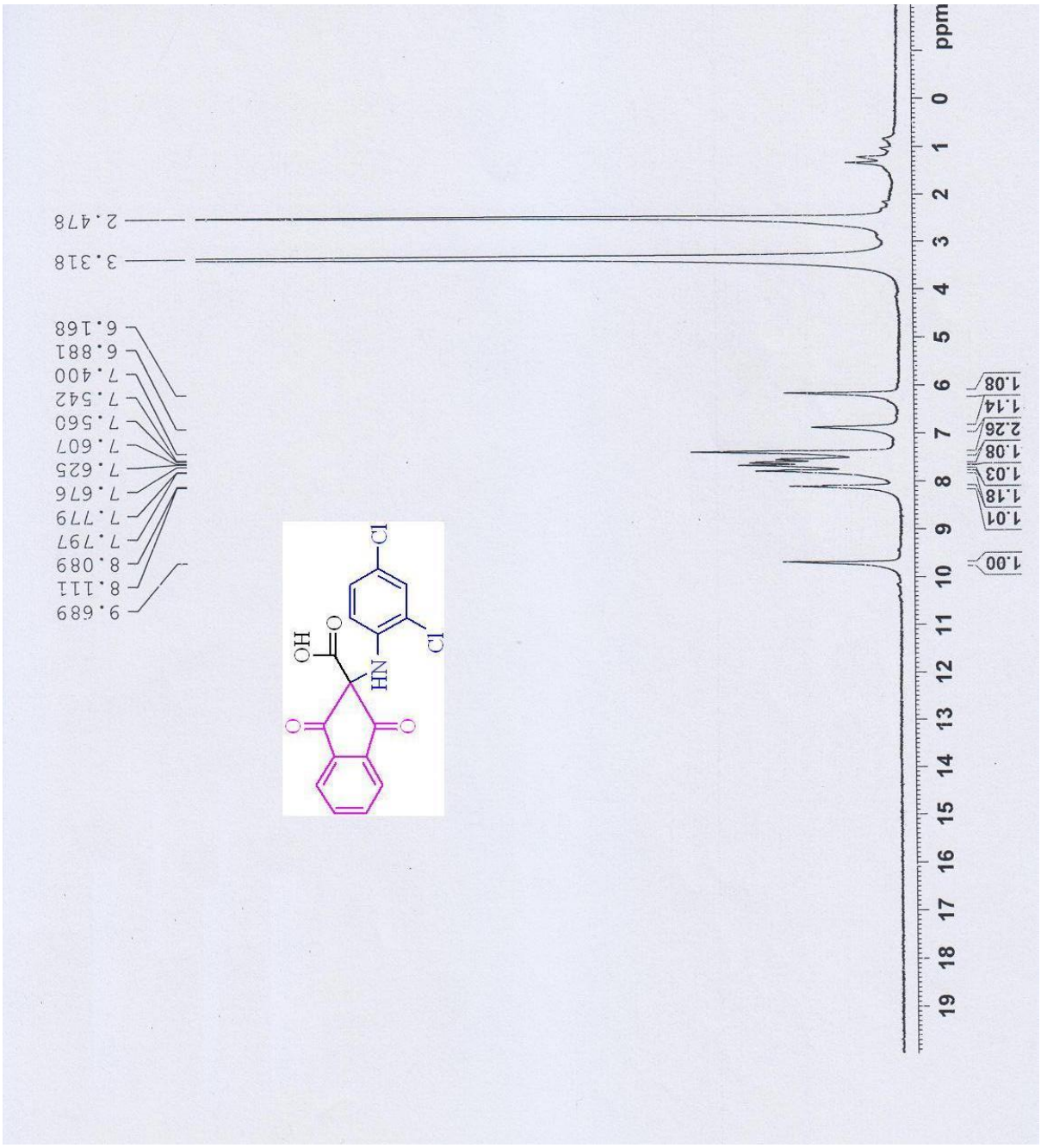
CO2H
HN
Cl
O
O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15
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17
18
19
1.00
1.01
1.18
1.03
1.08
2.26
1.14
1.08
2.478
3.318
6.168
6.881
7.400
7.542
7.560
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7.625
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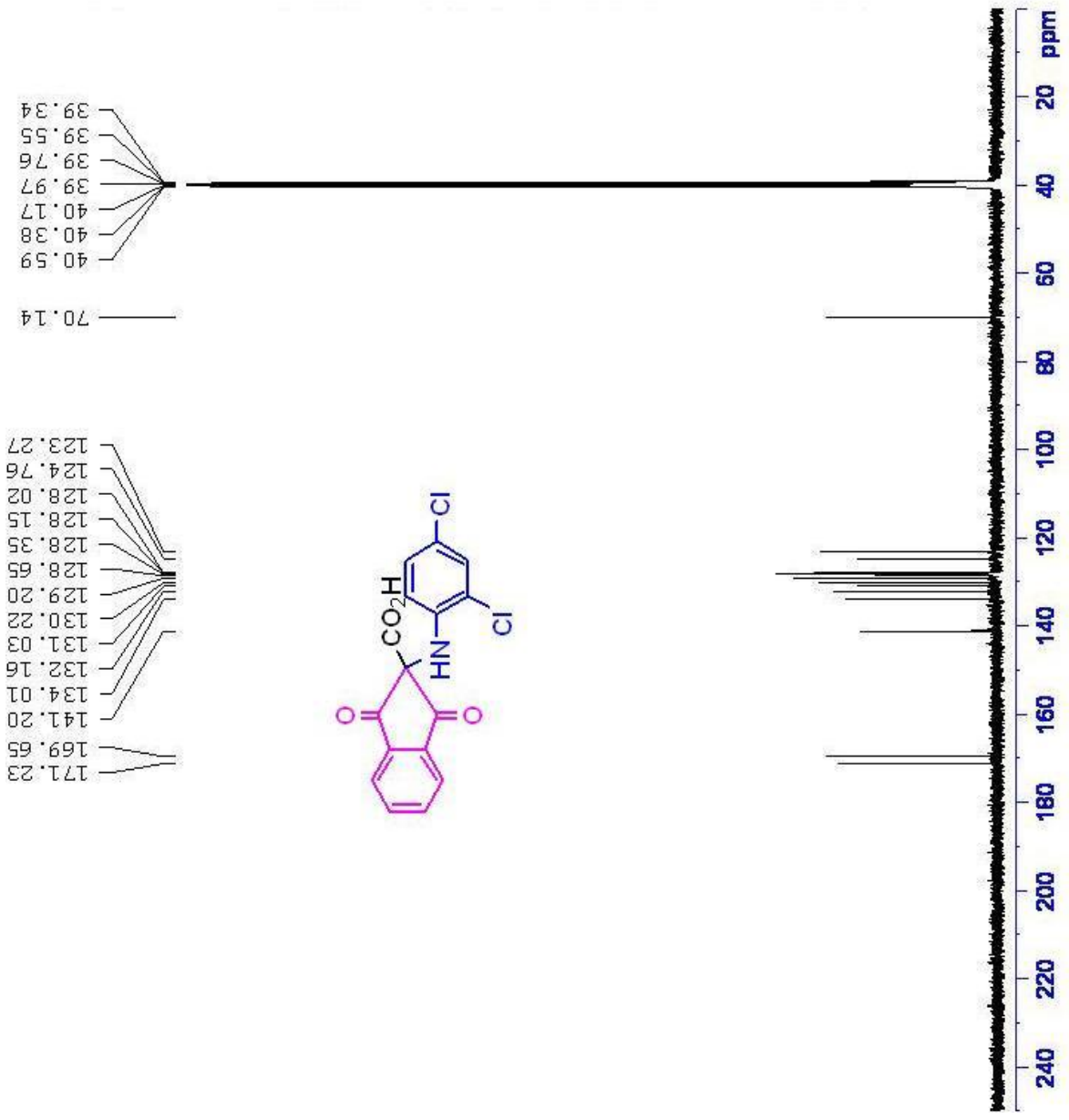
7.779
7.797
8.089
8.111
9.689
Cl
Cl
HN
O
OH
O
O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40.38
40.59
70.14
123.27
124.76
128.02
128.15
128.35
128.65
129.20
130.22
131.03
132.16
134.01
141.20
169.65
171.23
Cl
Cl
HN
CO2H
O
O
ppm
20
40
60
80
100
120
140
160
180
200
220
240

ppm
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2.07
2.02
3.23
1.07
1.01
2.488
3.331
6.284
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7.904
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8.252
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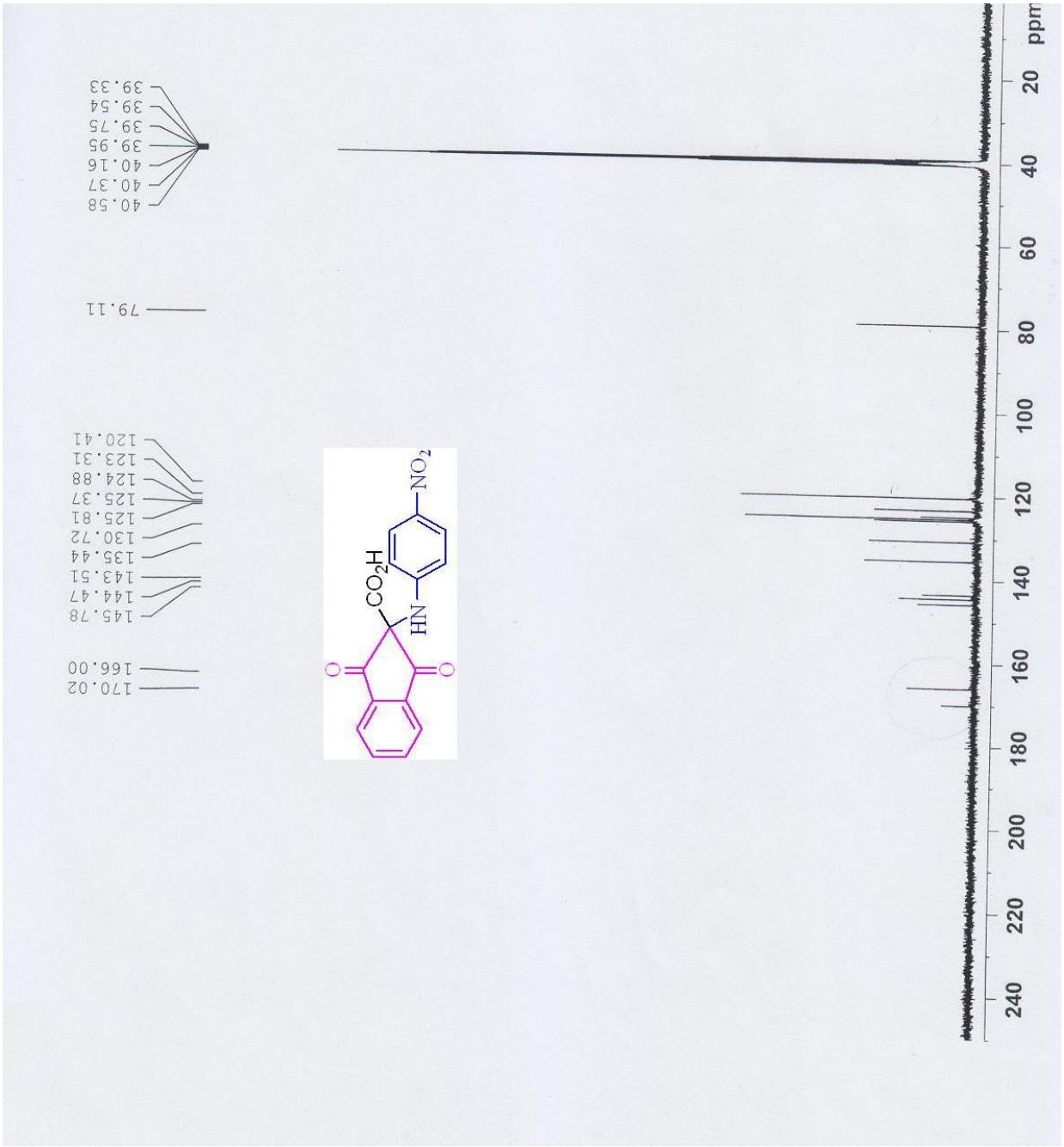
HN
O
O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125.37
125.81
130.72
135.44
143.51
144.47
145.78
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HN
CO2H
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40
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80
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120
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200
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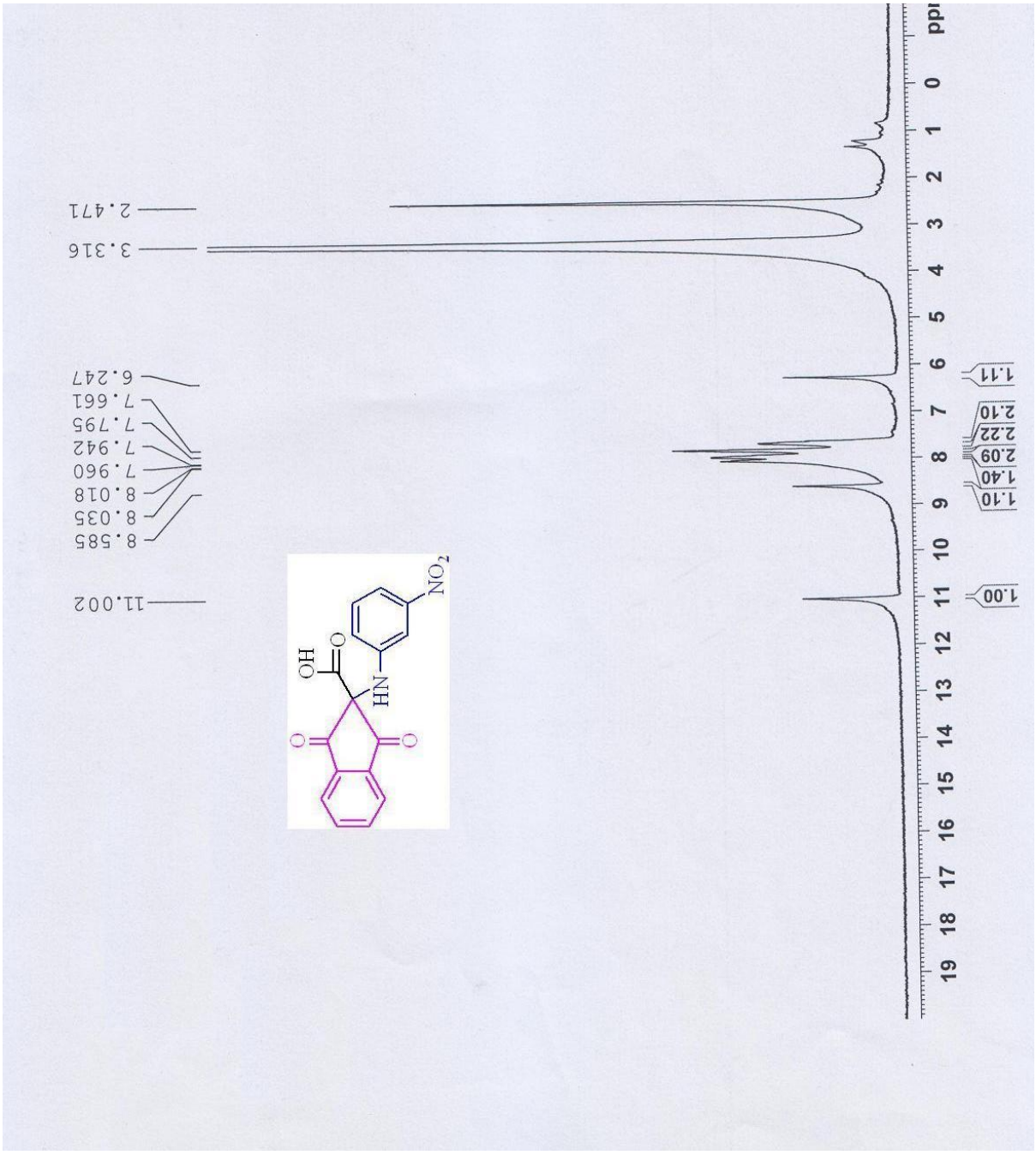
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1.40
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2.10
1.11
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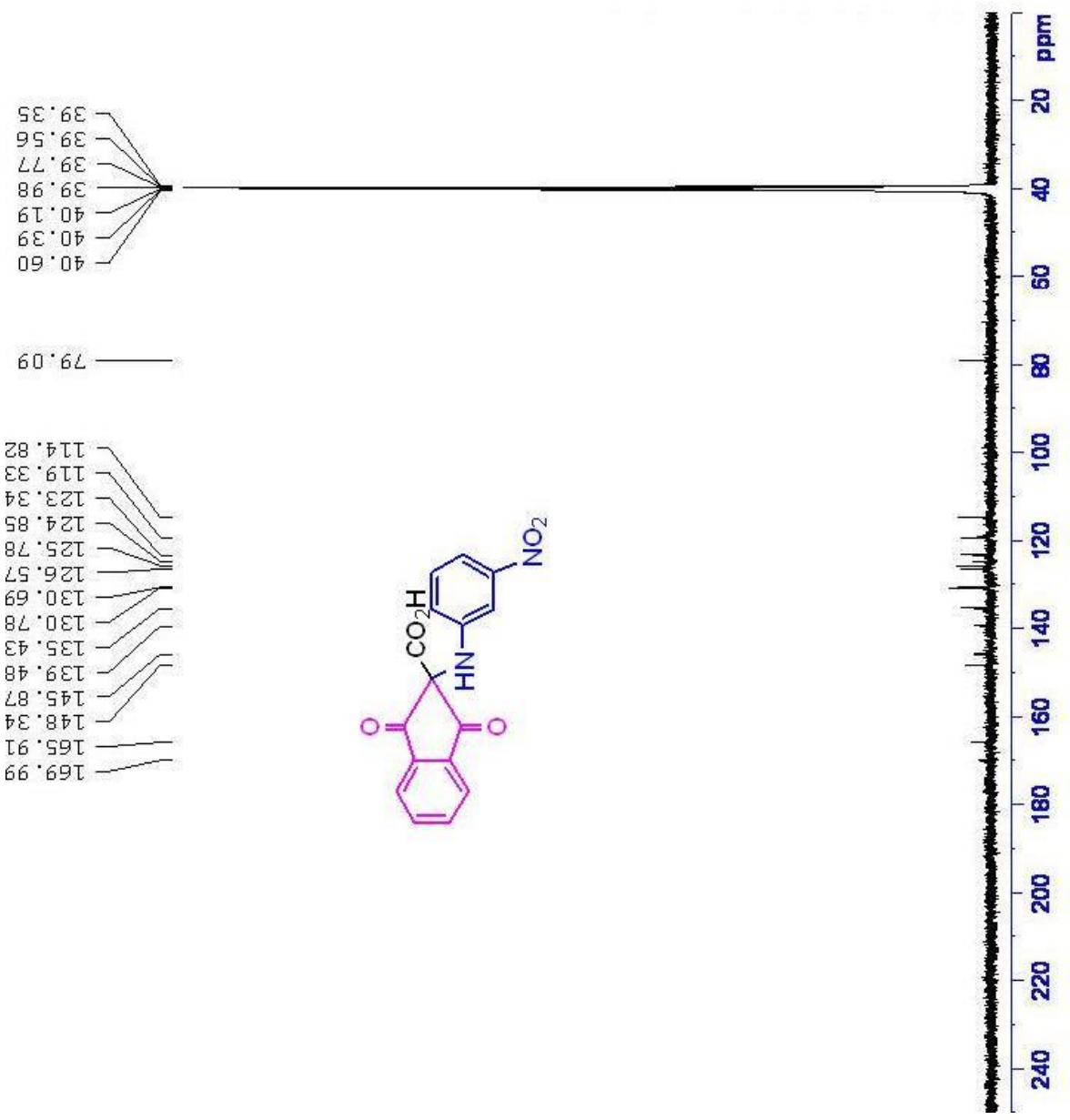
OH
HN
NO2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130.78
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139.48
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148.34
165.91
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ppm
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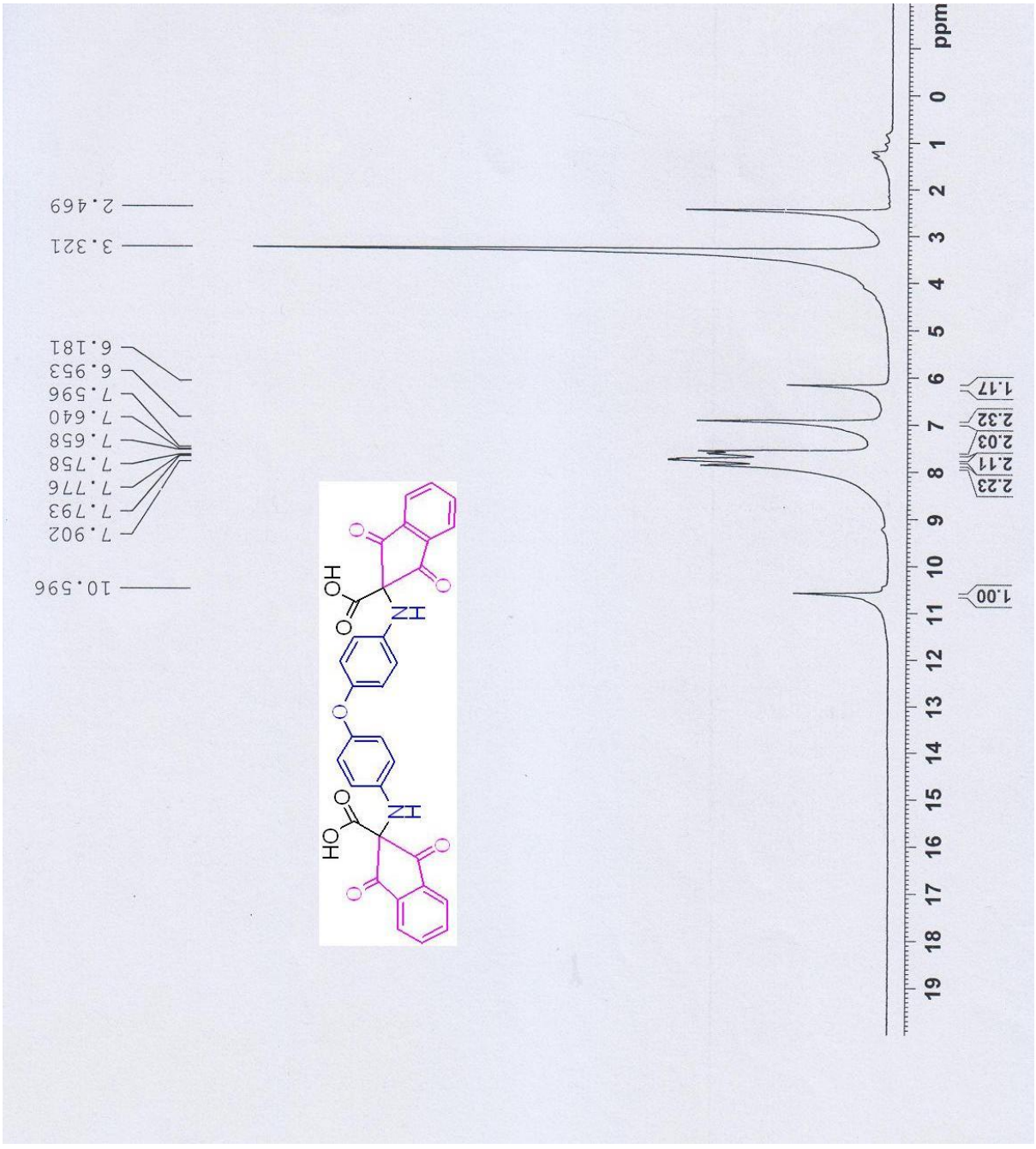
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1.17
2.32
2.03
2.11
2.23
10.596
7.902
7.793
7.776
7.758
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6.181
3.321
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O
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HO
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HN
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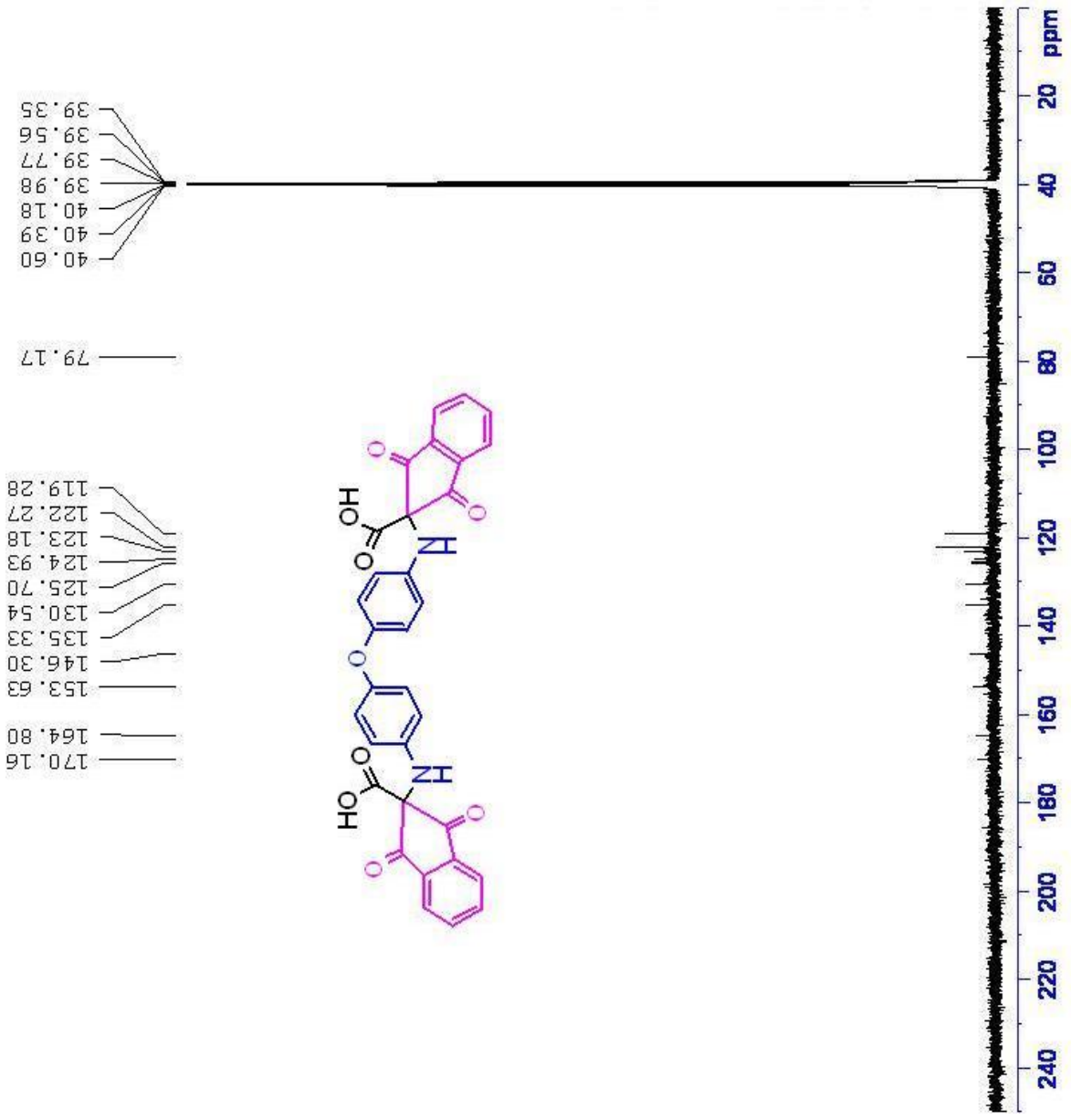
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153.63
164.80
170.16
HO
O
N
O
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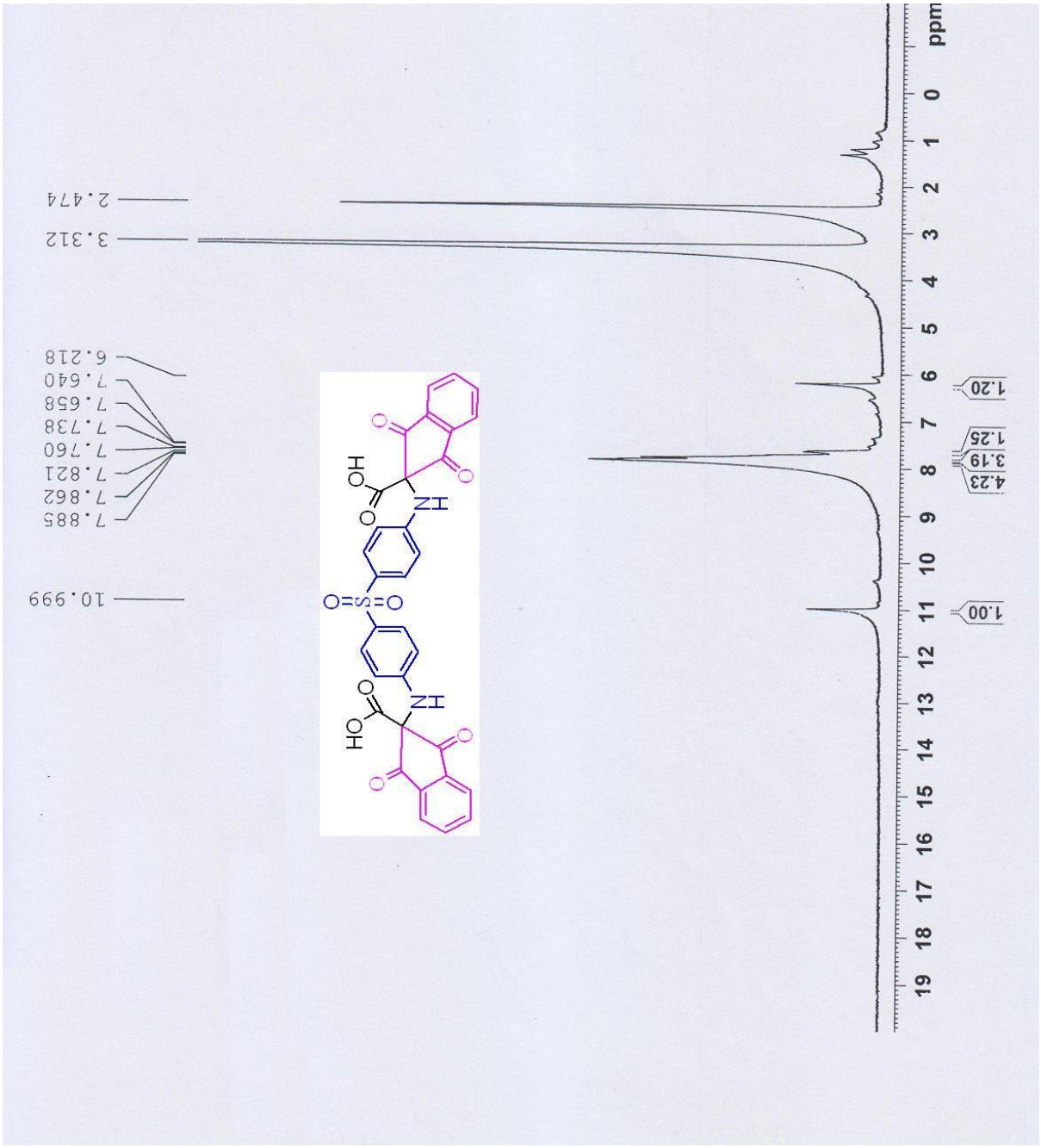
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1.25
3.19
4.23
1.00
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3.312
6.218
7.640
7.658
7.738
7.760
7.821
7.862
7.885
10.999
HO
O
NH
O=S=O
NH
O
OH