Supporting Information

Sustainable and selective synthesis of 3,4-dihydroquinolizin-2-one and quinolizin-2-one derivatives *via* the reactions of penta-3,4-dien-2-ones

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I. Experimental details and spectroscopic data

1. General experimental information

Thin-layer chromatography was visualized with UV light (254 and 365 nm). ^{1}H and ^{13}C NMR spectra were determined on a Bruker AC 400 spectrometer as $CDCl_3$ solutions. Chemical shifts were expressed in parts per million (δ) downfield from the internal standard tetramethylsilane and were reported as s (singlet), d (doublet), t (triplet), m (multiplet) and coupling constants J were given in Hz. High resolution mass spectra (HRMS) were performed on a time-of-flight (microTOF) mass spectrometer.

Penta-3,4-dien-2-ones (**1**), except for 5-phenylpenta-3,4-dien-2-one, were prepared through oxidation of homo- propargyl alcohols,[1] which were prepared through zinc promoted propargylation of aldehydes.[2] 5-Phenylpenta-3,4-dien-2-one was synthesized *via* reaction of 1-(triphenylphosphoranylidene)-2-propanone with phenylacetyl chloride.[3] Pyridines, quinoline, isoquinoline, and phenanthridine are commercial reagents.

2. Typical procedure for the preparation of 4-methyl-1-phenyl-1*H*-quinolizin-2(9*aH*)-one (3a)

To a flask containing pyridine (**2a**, 1 mmol), AcOH (0.2 mmol), EtOH (95%, 2 mL) was added 1-phenylpenta-3,4-dien-2-one (**1a**, 1 mmol). The mixture was stirred at rt for 2 h. Upon completion, the resulting mixture was treated with water (3 mL), and the mixture was let to stand at 0 ^{o}C overnight. The solids thus precipitated were collected by filtration to give **3a**. **3b-3y** and **6a-6r** were obtained in a similar manner.

4-Methyl-1-phenyl-1*H*-quinolizin-2(9*aH*)-one (3a)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.14 (s, 3H), 3.77 (d, J = 15.2 Hz, 1H), 4.86 (d, J = 16.0 Hz, 1H), 5.03 (d, J = 9.6 Hz, 1H), 5.18 (t, J = 6.4 Hz, 1H), 5.45 (s, 1H), 5.85-5.88 (m, 1H), 6.54 (d, J = 8.0 Hz, 1H), 7.13 (d, J = 7.6 Hz, 2H), 7.27-7.38 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.5, 57.5, 60.6, 103.4, 106.1, 120.0, 122.2, 125.9, 127.5, 128.9, 129.9, 136.3, 155.7, 190.8. MS: m/z 238 $[MH]^+$. HRMS calcd for $C_{16}H_{16}NO$: 238.1232 [M+H], found: 238.1236.

1-(2-Fluorophenyl)-4-methyl-1*H*-quinolizin-2(9*aH*)-one (3b)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.16 (s, 3H), 4.09-4.12 (m, 1H), 4.95-5.04 (m, 2H), 5.18 (t, *J* = 6.8 Hz, 1H), 5.44 (s, 1H), 5.87-5.92 (m, 1H), 6.54 (d, *J* = 7.6 Hz, 1H), 7.05-7.17 (m, 3H), 7.27-7.32 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.4, 59.3, 60.6, 103.4, 105.4, 115.6, 115.8, 119.7, 122.4, 123.2, 123.3, 124.5, 124.6, 125.9, 129.3, 129.4, 156.0, 171.1, 189.7. MS: m/z 256 $[MH]^+$. HRMS calcd for $C_{16}H_{15}FNO$: 256.1137 [M+H], found: 256.1139.

1-(4-Fluorophenyl)-4-methyl-1*H*-quinolizin-2(9*aH*)-one (3c)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.16 (s, 3H), 3.77 (d, *J* = 15.6 Hz, 1H), 4.82 (d, *J* = 16.0 Hz, 1H), 5.01-5.03 (m, 1H), 5.21 (t, *J* = 6.4 Hz, 1H), 5.45 (s, 1H), 5.89-5.91 (m 1H), 6.54 (d, *J* = 7.6 Hz, 1H), 7.06-7.10 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.5, 56.8, 60.6, 103.4, 106.1, 115.7, 115.9, 119.7, 122.4, 125.8, 131.3, 131.4, 131.5, 131.91, 131.94, 155.6, 163.4, 190.5. MS: m/z 256 $[MH]^+$. HRMS calcd for $C_{16}H_{15}FNO$: 256.1137 [M+H], found: 256.1131.

4-Methyl-1-*p*-tolyl-1*H*-quinolizin-2(9*aH*)-one (3d)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.16 (s, 3H), 2.33 (s, 3H), 3.73 (d, *J* = 15.6 Hz, 1H), 4.83 (d, *J* = 16.4 Hz, 1H), 5.08 (d, *J* = 6.4 Hz, 1H), 5.17-5.21 (m, 1H), 5.46 (s, 1H), 5.85-5.89 (m, 1H), 6.54 (d, *J* = 7.6 Hz, 1H), 7.02 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 7.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.5, 21.2, 57.1, 60.6, 103.4, 106.1, 120.2, 122.1, 125.8, 129.6, 129.7, 133.1, 137.1, 155.5, 191.1. MS: m/z 252 $[MH]^+$. HRMS calcd for $C_{17}H_{18}NO$: 252.1388 [M+H], found: 252.1390.

1-(4-Methoxyphenyl)-4-methyl-1*H*-quinolizin-2(9*aH*)-one (3e)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.13 (s, 3H), 3.70 (d, *J* = 16.4 Hz, 1H), 3.77 (s, 3H), 4.78 (d, *J* = 16.0 Hz, 1H), 5.06 (d, *J* = 10.0 Hz, 1H), 5.16-5.19 (m, 1H), 5.43 (s, 1H), 5.85-5.88 (m, 1H), 6.52 (d, *J* = 7.6 Hz, 1H), 6.89 (d, *J* = 8.4 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.4, 55.3, 56.7, 60.7, 103.4, 106.1, 114.4, 120.2, 122.1, 125.9, 128.2, 130.9, 155.5, 158.9, 191.2. MS: m/z 268 $[MH]^+$. HRMS calcd for $C_{17}H_{18}NO_2$:

268.1337 [M+H], found: 268.1340.

1-(3,4-Dimethoxyphenyl)-4-methyl-1*H*-quinolizin-2(9*aH*)-one (3f)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.16 (s, 3H), 3.70 (d, *J* = 15.2 Hz, 1H), 3.85 (s, 3H), 3.86 (s, 3H), 4.82 (d, *J* = 16.0 Hz, 1H), 5.06-5.09 (m, 1H), 5.20 (t, *J* = 6.8 Hz, 1H), 5.46 (s, 1H), 5.87-5.90 (m, 1H), 6.54 (d, *J* = 7.6 Hz, 1H), 6.61 (d, *J* = 1.6 Hz, 1H), 6.69-6.72 (m, 1H), 6.86 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.4, 55.9, 57.2, 60.7, 103.4, 106.1, 111.5, 112.5, 120.2, 122.1, 122.3, 125.8, 128.6, 148.4, 149.3, 155.5, 191.0. MS: m/z 298 $[MH]^+$. HRMS calcd for $C_{18}H_{20}NO_3$: 298.1443 [M+H], found: 298.1444.

4-Methyl-1-(thiophen-2-yl)-1*H*-quinolizin-2(9*aH*)-one (3g)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.08 (s, 3H), 3.58 (d, *J* = 4.0 Hz, 1H), 5.04 (t, *J* = 7.2 Hz, 1H), 5.14-5.37 (m, 3H), 5.82-5.85 (m, 1H), 6.44 (d, *J* = 8.0 Hz, 1H), 6.89 (t, *J* = 4.0 Hz, 1H), 6.95 (d, *J* = 2.4 Hz, 1H), 7.15 (d, *J* = 4.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.2, 51.4, 60.7, 102.8, 103.3, 120.5, 122.7, 125.1, 125.2, 126.5, 126.6, 135.6, 156.1, 189.1. MS: m/z 244 $[MH]^+$. HRMS calcd for $C_{14}H_{14}NOS$: 244.0796 [M+H], found: 244.0799.

1-Benzyl-4-methyl-1*H*-quinolizin-2(9*aH*)-one (3h)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.03 (s, 3H), 2.82-2.88 (m, 1H), 3.06 (dd, J_1 = 14.8 Hz, J_2 = 4.4 Hz, 1H), 3.46 (dd, J_1 = 14.8 Hz, J_2 = 3.6 Hz, 1H), 4.24 (d, *J* = 15.2 Hz, 1H), 5.18 (t, *J* = 6.4 Hz, 1H), 5.33 (s, 1H), 5.64-5.67 (m, 1H), 5.96-5.99 (m, 1H), 6.46 (d, *J* = 8.0 Hz, 1H), 7.19-7.22 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.5, 30.7, 50.0, 57.6, 103.8, 105.6, 119.5, 122.7, 126.5, 128.35, 128.44, 129.6, 138.5, 155.5, 190.5. MS: m/z 252 $[MH]^+$. HRMS calcd for $C_{17}H_{18}NO$: 252.1388 [M+H], found: 252.1397.

4-Benzyl-1*H*-quinolizin-2(9a*H*)-one (3i)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.72 (s, 2H), 4.27 (s, 1H), 4.74-4.78 (m, 1H), 5.04 (t, *J* = 6.4 Hz, 1H), 5.28 (s, 1H), 5.31-5.34 (m, 1H), 5.90-5.95 (m, 1H), 6.46 (d, *J* = 8.0 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.24-7.36 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 39.3, 42.7, 56.2, 103.3, 106.7, 121.5, 122.0, 126.0, 127.3, 128.3, 129.1,

135.0, 157.4, 190.7. MS: m/z 238 $[MH]^+$. HRMS calcd for $C_{16}H_{16}NO$: 238.1232 [M+H], found: 238.1234.

3,4-Dimethyl-1-phenyl-1*H*-quinolizin-2(9*aH*)-one (3j)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.94 (s, 3H), 2.18 (s, 3H), 3.79 (d, J = 16.8 Hz, 1H), 4.81 (d, J = 16.8 Hz, 1H), 4.94-4.97 (m, 1H), 5.11 (t, J = 6.4 Hz, 1H), 5.83-5.88 (m, 1H), 6.59 (d, J = 7.6 Hz, 1H), 7.11-7.13 (m, 2H), 7.26-7.37 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 11.6, 16.7, 57.7, 60.0, 102.1, 111.3, 119.4, 122.2, 126.6, 127.3, 128.7, 129.9, 136.8, 152.3, 190.1. MS: m/z 252 $[MH]^+$. HRMS calcd for $C_{17}H_{18}NO$: 252.1388 [M+H], found: 252.1385.

3-Ethyl-1-(4-methoxyphenyl)-4-methyl-1*H*-quinolizin-2(9*aH*)-one (3k)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.98 (t, J = 7.6 Hz, 3H), 2.18 (s, 3H), 2.31-2.37 (m, 1H), 2.50-2.55 (m, 1H), 3.72 (d, J = 16.0 Hz, 1H), 3.78 (s, 3H), 4.74 (dd, J_1 = 16.0 Hz, J_2 = 2.0 Hz, 1H), 4.96-4.99 (m, 1H), 5.08-5.12 (m, 1H), 5.82-5.87 (m, 1H), 6.57 (d, J = 7.6 Hz, 1H), 6.87-6.90 (m, 2H), 7.00-7.03 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.4, 16.2, 19.3, 55.3, 56.9, 60.1, 102.0, 114.2, 117.9, 119.5, 122.1, 126.6, 128.7, 130.8, 151.9, 158.7, 190.1. MS: m/z 296 $[MH]^+$. HRMS calcd for $C_{19}H_{22}NO_2$: 296.1651 [M+H], found: 296.1638.

1-Phenyl-4-propyl-1*H*-quinolizin-2(9*aH*)-one (3l)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.02 (t, J = 7.4 Hz, 3H), 1.62-1.68 (m, 2H), 2.39-2.43 (m, 2H), 3.78 (d, J = 15.6 Hz, 1H), 4.86 (d, J = 16.0 Hz, 1H), 5.00-5.03 (m, 1H), 5.17 (t, J = 6.6 Hz, 1H), 5.48 (s, 1H), 5.84-5.88 (m, 1H), 6.55 (d, J = 8.0 Hz, 1H), 7.14 (d, J = 7.6 Hz, 2H), 7.26-7.38 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.9, 20.4, 35.1, 57.6, 60.9, 103.1, 105.4, 120.2, 122.1, 125.6, 127.5, 128.9, 129.9, 136.3, 159.2, 191.2. MS: m/z 266 $[MH]^+$. HRMS calcd for $C_{18}H_{20}NO$: 266.1545 [M+H], found: 266.1547.

4-Benzyl-1-phenyl-1*H*-quinolizin-2(9*aH*)-one (3m)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.80 (s, 2H), 3.84 (d, J = 15.2 Hz, 1H), 4.92-5.08 (m, 3H), 5.50 (s, 1H), 5.81-5.85 (m, 1H), 6.52 (d, J = 8.0 Hz, 1H), 7.15-7.39 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 39.5, 57.7, 61.1, 103.1, 107.5, 120.0, 122.1, 125.9, 127.3, 127.5, 128.4, 128.9, 129.1, 129.9, 135.2, 136.2, 156.8, 191.1.

MS: m/z 314 $[MH]^+$. HRMS calcd for $C_{22}H_{20}NO$: 314.1545 [M+H], found: 314.1548.

4,6-Dimethyl-1-phenyl-1*H*-quinolizin-2(9*aH*)-one (3n)

^1H NMR (400 MHz, $CDCl_3$) δ: 1.27 (s, 3H), 2.13 (s, 3H), 4.29 (s, 1H), 5.19-5.31 (m, 3H), 5.81-5.84 (m, 1H), 6.47 (d, *J* = 7.6 Hz, 1H), 7.21 (d, *J* = 6.8 Hz, 2H), 7.30-7.37 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 15.1, 21.0, 61.4, 62.7, 104.2, 104.5, 120.0, 124.8, 125.3, 127.4, 127.9, 133.9, 154.4, 190.3. MS: m/z 252 $[MH]^+$. HRMS calcd for $C_{17}H_{18}NO$: 252.1388 [M+H], found: 252.1390.

6-Methyl-1-phenyl-4-propyl-1*H*-quinolizin-2(9*aH*)-one (3o)

^1H NMR (400 MHz, $CDCl_3$) δ: 1.02 (t, *J* = 7.4 Hz, 3H), 1.26 (s, 3H), 1.61-1.66 (m, 2H), 2.35-2.40 (m, 2H), 4.29 (s, 1H), 5.18-5.27 (m, 2H), 5.32 (s, 1H), 5.80-5.84 (m, 1H), 6.48 (d, *J* = 8.0 Hz, 1H), 7.20-7.37 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.9, 15.1, 20.4, 35.3, 61.4, 62.8, 103.5, 104.2, 119.9, 125.05, 125.08, 127.4, 127.9, 134.0, 158.0, 190.6. MS: m/z 280 $[MH]^+$. HRMS calcd for $C_{19}H_{22}NO$: 280.1701 [M+H], found: 280.1712.

1-(4-Methoxyphenyl)-4,6-dimethyl-1*H*-quinolizin-2(9*aH*)-one (3p)

^1H NMR (400 MHz, $CDCl_3$) δ: 1.23 (s, 3H), 2.11 (s, 3H), 3.78 (s, 3H), 4.23 (s, 1H), 5.20-5.28 (m, 3H), 5.79-5.83 (m, 1H), 6.45 (d, *J* = 7.6 Hz, 1H), 6.88 (d, *J* = 9.2 Hz, 2H), 7.11 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 15.0, 20.9, 55.2, 60.5, 62.7, 104.1, 104.5, 113.5, 119.9, 124.9, 125.3, 125.8, 154.4, 158.9, 190.6. MS: m/z 282 $[MH]^+$. HRMS calcd for $C_{18}H_{20}NO_2$: 282.1494 [M+H], found: 282.1495.

4,6-Dimethyl-1-*p*-tolyl-1*H*-quinolizin-2(9*aH*)-one (3q)

^1H NMR (400 MHz, $CDCl_3$) δ: 1.26 (s, 3H), 2.11 (s, 3H), 2.34 (s, 3H), 4.25 (s, 1H), 5.21-5.30 (m, 3H), 5.79-5.83 (m, 1H),6.47 (d, *J* = 7.6 Hz, 1H), 7.10 (d, *J* = 7.6 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 15.0, 21.0, 21.2, 61.0, 62.7, 104.2, 104.5, 119.9, 124.9, 125.3, 128.7, 130.8, 137.0, 154.3, 190.5. MS: m/z 266 $[MH]^+$. HRMS calcd for $C_{18}H_{20}NO$: 266.1545 [M+H], found: 266.1533.

4,8-Dimethyl-1-phenyl-1*H*-quinolizin-2(9*aH*)-one (3r)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.66 (s, 3H), 2.15 (s, 3H), 2.59 (d, *J* = 4.8 Hz, 1H), 3.70 (d, *J* = 15.6 Hz, 1H), 4.76 (s, 1H), 5.09 (d, *J* = 8.0 Hz, 1H), 5.43 (s, 1H), 6.53 (d, *J* = 8.0 Hz, 1H), 7.13 (d, *J* = 8.4 Hz, 2H), 7.27-7.38 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.6, 21.3, 57.6, 60.5, 105.9, 107.2, 115.1, 125.4, 127.4, 128.8, 130.0, 130.6, 131.1, 136.6, 155.5, 191.3. MS: m/z 252 $[MH]^+$. HRMS calcd for $C_{17}H_{18}NO$: 252.1388 [M+H], found: 252.1387.

1-(4-Methoxyphenyl)-4,8-dimethyl-1*H*-quinolizin-2(9*aH*)-one (3s)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.65 (s, 3H), 2.12 (s, 3H), 3.63 (d, *J* = 16.0 Hz, 1H), 3.78 (s, 3H), 4.70 (d, *J* = 15.6 Hz, 1H), 4.79 (s, 1H), 5.07 (d, *J* = 7.2 Hz, 1H), 5.40 (s, 1H), 6.51 (d, *J* = 7.6 Hz, 1H), 6.89 (d, *J* = 8.4 Hz, 2H), 7.03 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.5, 20.6, 55.2, 56.7, 60.6, 105.8, 107.2, 114.3, 115.2, 125.4, 128.4, 130.5, 130.9, 155.4, 158.8, 191.6. MS: m/z 282 $[MH]^+$. HRMS calcd for $C_{18}H_{20}NO_2$: 282.1494 [M+H], found: 282.1499.

4,8-Dimethyl-1-*p*-tolyl-1*H*-quinolizin-2(9*aH*)-one (3t)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.66 (s, 3H), 2.15 (s ,3H), 2.34 (s, 3H), 3.66 (d, *J* = 16.0 Hz, 1H), 4.75 (d, *J* = 16.4 Hz, 1H), 4.80 (s, 1H), 5.08-5.10 (m, 1H), 5.44 (s, 1H), 6.53 (d, *J* = 8.0 Hz, 1H), 7.02 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.45, 20.54, 21.2, 57.2, 60.4, 105.9, 107.2, 115.2, 125.4, 129.6, 130.5, 130.9, 133.4, 137.0, 155.3, 191.5. MS: m/z 266 $[MH]^+$. HRMS calcd for $C_{18}H_{20}NO$: 266.1545 [M+H], found: 266.1541

1-(4-Fluorophenyl)-4,8-dimethyl-1*H*-quinolizin-2(9*aH*)-one (3u)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.67 (s, 3H), 2.15 (s, 3H), 3.70 (d, *J* = 16.0 Hz, 1H), 4.72 (d, *J* = 6.8 Hz, 2H), 5.08-5.11 (m, 1H), 5.42 (s, 1H), 6.53 (d, *J* = 7.6 Hz, 1H), 7.03-7.10 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.4, 20.5, 56.7, 60.5, 105.7, 107.2, 114.7, 115.6, 115.8, 125.3, 130.8, 131.3, 131.4, 132.17, 132.21, 155.5, 160.9, 163.3, 190.9. MS: m/z 270 $[MH]^+$. HRMS calcd for $C_{17}H_{17}FNO$: 270.1294 [M+H], found: 270.1282.

1-(3,4-Dimethoxyphenyl)-4,8-dimethyl-1*H*-quinolizin-2(9*aH*)-one (3v)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.61 (s, 3H), 2.08 (s, 3H), 3.55-3.59 (m, 1H), 3.79 (s, 3H), 3.80 (s, 3H), 4.68 (d, *J* = 15.6 Hz, 1H), 4.73 (s, 1H), 5.03 (d, *J* = 8.0 Hz, 1H), 5.35 (s, 1H), 6.47 (d, *J* = 8.0 Hz, 1H), 6.56 (s, 1H), 6.64 (d, *J* = 8.0 Hz, 1H), 6.80-6.82 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.4, 20.6, 55.8, 57.1, 60.5, 105.7, 107.1, 111.4, 112.4, 115.1, 122.2, 125.4, 128.9, 130.5, 148.2, 149.1, 155.4, 191.3. MS: m/z 312 $[MH]^+$. HRMS calcd for $C_{19}H_{22}NO_3$: 312.1599 [M+H], found: 312.1608.

1-Benzyl-4,8-dimethyl-1*H*-quinolizin-2(9*aH*)-one (3w)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.78 (s, 3H), 2.05 (s, 3H), 2.77-2.83 (m, 1H), 3.05 (dd, J_1 = 15.2 Hz, J_2 = 4.8 Hz, 1H), 3.51 (dd, J_1 = 14.8 Hz, J_2 = 4.0 Hz, 1H), 4.18 (d, *J* = 16.0 Hz, 1H), 5.09 (dd, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H), 5.31 (s, 1H), 5.40 (s, 1H), 6.46 (d, *J* = 7.2 Hz, 1H), 7.14-7.26 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.5, 20.7, 30.7, 50.1, 57.5, 105.5, 107.4, 114.7, 126.0, 126.2, 128.3, 129.7, 131.0, 138.5, 155.1, 190.9. MS: m/z 266 $[MH]^+$. HRMS calcd for $C_{18}H_{20}NO$: 266.1545 [M+H], found: 266.1547.

4,8-Dimethyl-1-(thiophen-2-yl)-1*H*-quinolizin-2(9*aH*)-one (3x)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.65 (s, 3H), 2.07 (s, 3H), 3.54 (d, *J* = 3.6 Hz, 1H), 4.86-5.23 (m, 4H), 6.41 (d, *J* = 7.6 Hz, 1H), 6.86-6.90 (m, 1H), 6.99-7.00 (m, 1H), 7.12-7.13 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.1, 20.7, 51.4, 60.7, 103.1, 106.6, 115.4, 124.6, 125.1, 126.38, 126.44, 127.9, 130.9, 155.9, 189.7. MS: m/z 258 $[MH]^+$. HRMS calcd for $C_{15}H_{16}NOS$: 258.0953 [M+H], found: 258.0955.

3,4,6-Trimethyl-1-phenyl-1*H*-quinolizin-2(9*aH*)-one (3y)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.49 (s, 3H), 1.82 (s, 3H), 2.18 (s, 3H), 3.36 (s, 1H), 4.90-4.93 (m, 1H), 5.06-5.10 (m, 1H), 5.62-5.66 (m, 1H), 6.46 (d, *J* = 7.6 Hz, 1H), 7.21-7.34 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 11.2, 16.9, 22.9, 61.0, 61.5, 103.3, 119.9, 125.1, 126.1, 127.3, 128.5, 128.9, 136.7, 189.9. MS: m/z 266 $[MH]^+$. HRMS calcd for $C_{18}H_{20}NO$: 266.1545 [M+H], found: 266.1533.

1-Methyl-4-phenyl-4,4*a*-dihydro-3*H*-pyrido[1, 2-*a*]quinolin-3-one (6a)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.94 (s, 3H), 3.80 (d, *J* = 4.8 Hz, 1H), 4.75-4.77 (m, 1H), 5.39 (s, 1H), 5. 90 (dd,

J_1 = 9.2 Hz, J_2 = 2.8 Hz, 1H), 6.53 (dd, J_1 = 9.2 Hz, J_2 = 2.8 Hz, 1H), 7.08-7.40 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 22.0, 55.7, 62.1, 106.6, 123.4, 125.7, 127.2, 127.3, 127.5, 127.9, 128.0, 128.8, 128.9, 131.7, 138.2, 138.7, 159.2, 191.2. MS: m/z 288 $[MH]^+$. HRMS calcd for $C_{20}H_{18}NO$: 288.1388 [M+H], found: 288.1396.

4-(4-Methoxyphenyl)-1-methyl-4,4*a*-dihydro-3*H*-pyrido[1,2-*a*]quinolin-3-one (6b)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.92 (s, 3H), 3.63 (s, 1H), 3.72 (s, 3H), 4.69-4.71 (m, 1H), 5.35 (s, 1H), 5.86 (dd, J_1 = 9.6 Hz, J_2 = 2.8 Hz, 1H), 6.50 (dd, J_1 = 10.0 Hz, J_2 = 2.4 Hz, 1H), 6.83 (dd, J_1 = 6.8 Hz, J_2 = 2.4 Hz, 2H), 7.05-7.11 (m, 3H), 7.17-7.19 (m, 1H), 7.27-7.29 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.9, 54.9, 55.2, 62.2, 106.6, 114.2, 123.3, 125.6, 127.16, 127.19, 127.9, 128.9, 129.0, 130.2, 131.6, 138.7, 158.9, 159.0, 191.6. MS: m/z 318 $[MH]^+$. HRMS calcd for $C_{21}H_{20}NO_2$: 318.1494 [M+H], found: 318.1499.

4-Benzyl-1-methyl-4,4*a*-dihydro-3*H*-pyrido[1,2-*a*]quinolin-3-one (6c)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.75 (s, 3H), 2.69-2.73 (m, 1H), 2.93-3.00 (m, 1H), 3.08-3.13 (m, 1H), 4.23 (d, J = 2.0 Hz, 1H), 5.24 (s, 1H), 5.92 (dd, J_1 = 9.2 Hz, J_2 = 2.4 Hz, 1H), 6.48 (dd, J_1 = 9.2 Hz, J_2 = 2.8 Hz, 1H), 7.10 (d, J = 7.6 Hz, 1H), 7.18-7.28 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 22.1, 37.4, 51.6, 58.2, 104.2, 125.3, 126.6, 126.9, 127.0, 127.6, 127.7, 128.6, 129.4, 130.7, 134.0, 138.3, 140.0, 159.1, 193.5. MS: m/z 302 $[MH]^+$. HRMS calcd for $C_{21}H_{20}NO$: 302.1545 [M+H], found: 302.1548.

1-(4-Methoxyphenyl)-4-methyl-1*H*-pyrido[2,1-*a*]isoquinolin-2(11*bH*)-one (6d)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.17 (s, 3H), 3.79 (s, 3H), 4.14 (d, J = 12.4 Hz, 1H), 5.37 (d, J = 12.8 Hz, 1H), 5.50 (s, 1H), 5.79 (d, J = 7.6 Hz, 1H), 6.22 (d, J = 8.0 Hz, 1H), 6.56 (d, J = 8.0 Hz, 1H), 6.76 (t, J = 7.6 Hz, 1H), 6.85 (d, J = 8.8 Hz, 2H), 6.95 (d, J = 8.0 Hz, 1H), 7.01 (d, J = 8.8 Hz, 2H), 7.08 (t, J = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.4, 55.3, 55.9, 63.1, 107.1, 114.1, 124.2, 125.7, 126.0, 127.0, 127.8, 127.9, 129.3, 130.6, 131.2, 156.3, 158.9, 191.8. MS: m/z 318 $[MH]^+$. HRMS calcd for $C_{21}H_{20}NO_2$: 318.1494 [M+H], found: 318.1488.

4-Methyl-1-*p*-tolyl-1*H*-pyrido[2,1-*a*]isoquinolin-2(11*bH*)-one (6e)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.15 (s, 3H), 2.35 (s, 3H), 4.18 (d, *J* = 12.0 Hz, 1H), 5.40 (d, *J* = 12.4 Hz, 1H), 5.50 (s, 1H), 5.82 (d, *J* = 7.6 Hz, 1H), 6.32 (d, *J* = 7.6 Hz, 1H), 6.57-6.59 (m, 1H), 6.78 (t, *J* = 7.6 Hz, 1H), 6.96 (d, *J* = 7.6 Hz, 1H), 7.04 (d, *J* = 7.6 Hz, 2H), 7.08 (t, *J* = 7.6 Hz, 1H), 7.13 (d, *J* = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.4, 21.3, 56.1, 62.8, 106.8, 107.4, 124.2, 126.0, 126.1, 126.9, 127.9, 128.1, 129.4, 130.0, 130.8, 134.4, 137.0, 156.3, 191.5. MS: m/z 302 $[MH]^+$. HRMS calcd for $C_{21}H_{20}NO$: 302.1545 [M+H], found: 302.1547.

1-Benzyl-4-methyl-1*H*-pyrido[2,1-*a*]isoquinolin-2(11*bH*)-one (6f)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.98 (s, 3H), 3.16-3.19 (m, 2H), 3.39-3.41 (m, 1H), 4.66 (d, *J* = 5.2 Hz, 1H), 5.13 (s, 1H), 6.16 (d, *J* = 6.8 Hz, 1H), 6.70 (d, *J* = 7.6 Hz, 1H), 7.06-7.08 (m, 1H), 7.18-7.28 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.1, 37.2, 47.1, 59.3, 102.5, 114.5, 123.6, 124.6, 126.6, 127.5, 127.9, 128.5, 129.2, 129.6, 131.0, 132.1, 138.3, 156.3, 193.1. MS: m/z 302 $[MH]^+$. HRMS calcd for $C_{21}H_{20}NO$: 302.1545 [M+H], found: 302.1548.

4-Benzyl-1*H*-pyrido[2,1-*a*]isoquinolin-2(11b*H*)-one (6g)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.80 (s, 2H), 5.25-5.31 (m, 1H), 5.36 (s, 1H), 5.57 (d, *J* = 7.6 Hz, 1H), 6.58 (d, *J* = 8.4 Hz, 1H), 6.93-6.95 (m, 1H), 7.11 (d, *J* = 6.0 Hz, 1H), 7.15-7.21 (m, 4H), 7.24-7.35 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 39.8, 41.9, 57.2, 106.1, 106.8, 124.4, 124.9, 125.2, 127.2, 128.2, 128.3, 129.1, 129.8, 130.1, 135.1, 157.9, 190.9. MS: m/z 288 $[MH]^+$. HRMS calcd for $C_{20}H_{18}NO$: 288.1388 [M+H], found: 288.1390.

3,4-Dimethyl-1-phenyl-1*H*-pyrido[2,1-*a*]isoquinolin-2(11*bH*)-one (6h)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.93 (s, 3H), 2.19 (s, 3H), 4.25 (d, *J* = 13.2 Hz, 1H), 5.35 (d, *J* = 12.4 Hz, 1H), 5.67 (d, *J* = 8.0 Hz, 1H), 5.87 (d, *J* = 7.6 Hz, 1H), 6.47 (d, *J* = 8.0 Hz, 1H), 6.61 (t, *J* = 7.6 Hz, 1H), 6.90 (d, *J* = 7.6 Hz, 1H), 6.93-6.96 (m, 2H), 7.01 (t, *J* = 7.9 Hz, 1H), 7.22-7.27 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 11.1, 17.4, 57.3, 63.7, 104.6, 115.4, 123.6, 125.3, 126.4, 127.1, 127.4, 127.8, 128.3, 130.5, 130.6, 131.0, 137.1,

153.0, 192.1. MS: m/z 302 $[MH]^+$. HRMS calcd for $C_{21}H_{20}NO$: 302.1545 [M+H], found: 302.1548.

1-(4-Fluorophenyl)-3,4-dimethyl-1*H*-pyrido[2,1-*a*]isoquinolin-2(11*bH*)-one (6i)

^{1}H NMR (400 MHz, $CDCl_3$) δ:1.94 (s, 3H), 2.16 (s, 3H), 4.24 (d, *J* = 13.2 Hz, 1H), 5.30 (d, *J* = 13.2 Hz, 1H), 5.66 (d, *J* = 7.6 Hz, 1H), 5.85 (d, *J* = 8.0 Hz, 1H), 6.45 (d, *J* = 7.6 Hz, 1H), 6.65 (t, *J* = 7.6 Hz, 1H), 6.87-6.97 (m, 5H), 7.03 (t, *J* = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 11.1, 17.4, 56.5, 63.8, 104.5, 115.1, 115.2, 115.3, 123.8, 125.4, 126.3, 127.5, 127.9, 130.5, 132.1, 132.2, 132.79, 132.83, 153.3, 160.8, 163.3, 191.7. MS: m/z 320 $[MH]^+$. HRMS calcd for $C_{21}H_{19}FNO$: 320.1451 [M+H], found: 320.1462.

3,4-Dimethyl-1-*p*-tolyl-1*H*-pyrido[2,1-*a*]isoquinolin-2(11*bH*)-one (6j)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.94 (s, 3H), 2.16 (s, 3H), 2.33 (s, 3H), 4.22 (d, *J* = 13.2 Hz, 1H), 5.34 (d, *J* = 13.2 Hz, 1H), 5.68 (d, *J* = 7.6 Hz, 1H), 5.98 (d, *J* = 8.0 Hz, 1H), 6.47 (d, *J* = 8.0 Hz, 1H), 6.65 (t, *J* = 7.6 Hz, 1H), 6.86 (d, *J* = 8.4 Hz, 2H), 6.91 (d, *J* = 7.6 Hz, 1H), 7.01-7.08 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 11.1, 17.4, 21.2, 57.0, 63.6, 104.6, 115.1, 123.6, 125.4, 126.6, 126.9, 127.5, 127.7, 129.1, 130.3, 130.6, 134.1, 136.7, 153.0, 192.2. MS: m/z 316 $[MH]^+$. HRMS calcd for $C_{22}H_{22}NO$: 316.1701 [M+H], found: 316.1716.

1-(4-Methoxyphenyl)-3,4-dimethyl-1*H*-pyrido[2,1-*a*]isoquinolin-2(11*bH*)-one (6k)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.97 (s, 3H), 2.22 (s, 3H), 3.65 (s, 3H), 3.76 (d, *J* = 4.4 Hz, 1H), 5.32 (d, *J* = 7.6 Hz, 1H), 5.75 (d, *J* = 4.0 Hz, 1H), 6.48 (d, *J* = 7.6 Hz, 1H), 6.62 (d, *J* = 8.8 Hz, 2H), 6.78-6.80 (m, 1H), 6.89 (d, *J* = 8.8 Hz, 2H), 7.07-7.10 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 11.3, 16.8, 55.0, 55.4, 61.8, 103.6, 111.6, 113.6, 124.7, 125.0, 125.6, 126.68, 126.74, 127.8, 127.9, 129.8, 130.3, 152.9, 158.6, 190.9. MS: m/z 332 $[MH]^+$. HRMS calcd for $C_{22}H_{22}NO_2$: 332.1650 [M+H], found: 332.1656.

1-(3,4-Dimethoxyphenyl)-3,4-dimethyl-1*H*-pyrido[2,1-*a*]isoquinolin-2(11*bH*)-one (6l)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.88 (s, 3H), 2.12 (s, 3H), 3.66 (s, 3H), 3.78 (s, 3H), 4.12 (d, *J* = 13.2 Hz, 1H), 5.25 (d, *J* = 12.4 Hz, 1H), 5.61 (d, *J* = 8.0 Hz, 1H), 5.87 (d, *J* = 8.0 Hz, 1H), 6.35 (d, *J* = 2.0 Hz, 1H), 6.41 (d, *J* = 7.6 Hz, 1H), 6.46-6.48 (m, 1H), 6.57-6.60 (m, 1H), 6.71 (d, *J* = 8.4 Hz, 1H), 6.85 (d, *J* = 6.8 Hz, 1H), 6.96 (d,

J = 6.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 11.1, 17.4, 55.8, 56.9, 63.7, 104.4, 111.1, 114.0, 115.2, 122.7, 123.6, 125.3, 126.4, 126.6, 127.5, 127.7, 129.4, 130.4, 148.1, 148.6, 153.0, 192.0. MS: m/z 362 $[MH]^+$. HRMS calcd for $C_{23}H_{24}NO_3$: 362.1756 [M+H], found: 362.1755.

3-Ethyl-4-methyl-1-phenyl-1*H*-pyrido[2,1-*a*]isoquinolin-2(11*bH*)-one (6m)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.06 (t, *J* = 7.4 Hz, 3H), 2.21 (s, 3H), 2.41-2.48 (m, 2H), 4.25 (d, *J* = 13.6 Hz, 1H), 5.35 (d, *J* = 13.6 Hz, 1H), 5.68 (d, *J* = 7.6 Hz, 1H), 5.88 (d, *J* = 7.6 Hz, 1H), 6.48 (d, *J* = 8.0 Hz, 1H), 6.62 (t, *J* = 7.2 Hz, 1H), 6.90-7.04 (m, 4H), 7.24 (d, *J* = 2.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.2, 16.9, 19.0, 57.5, 63.7, 104.5, 121.8, 123.7, 125.3, 126.5, 126.7, 127.1, 127.4, 127.8, 128.3, 130.5, 130.6, 137.1, 152.7, 191.7. MS: m/z 316 $[MH]^+$. HRMS calcd for $C_{22}H_{22}NO$: 316.1701 [M+H], found: 316.1691.

3-Ethyl-1-(4-methoxyphenyl)-4-methyl-1*H*-pyrido [2,1-*a*]isoquinolin-2(11*bH*)-one (6n)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.04 (t, *J* = 7.2 Hz, 3H), 2.19 (s, 3H), 2.39-2.48 (m, 2H), 3.78 (s, 3H), 4.18 (d, *J* = 12.8 Hz, 1H), 5.29 (d, *J* = 13.6 Hz, 1H), 5.66 (d, *J* = 8.0 Hz, 1H), 5.93 (d, *J* = 8.0 Hz, 1H), 6.47 (d, *J* = 7.6 Hz, 1H), 6.65 (t, *J* = 7.6 Hz, 1H), 6.79 (d, *J* = 7.6 Hz, 2H), 6.85 (d, *J* = 8.0 Hz, 2H), 6.90 (d, *J* = 7.6 Hz, 1H), 7.02 (t, *J* = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.2, 16.8, 18.9, 55.3, 56.6, 63.8, 104.4, 113.8, 121.7, 123.6, 125.3, 126.4, 126.8, 127.6, 127.7, 129.2, 130.5, 131.5, 152.5, 158.7, 192.0. MS: m/z 346 $[MH]^+$. HRMS calcd for $C_{23}H_{24}NO_2$: 346.1807 [M+H], found: 346.1809.

4-Ethyl-1-phenyl-1*H*-pyrido [2,1-*a*]isoquinolin-2(11*bH*)-one (6o)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.24-1.29 (m, 3H), 2.53 (q, *J* = 7.6 Hz, 2H), 3.83 (d, *J* = 4.0 Hz, 1H), 5.45 (d, *J* = 8.4 Hz, 1H), 5.51 (s, 1H), 5.84 (d, *J* = 4.4 Hz, 1H), 6.51 (d, *J* = 8.0 Hz, 1H), 6.83-6.85 (m, 1H), 7.05-7.17 (m, 7H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 11.7, 26.2, 55.7, 62.2, 104.2, 105.2, 124.3, 125.1, 127.0, 127.2, 127.9, 128.1, 128.2, 128.8, 129.9, 134.4, 161.2, 191.9. MS: m/z 302 $[MH]^+$. HRMS calcd for $C_{21}H_{20}NO$: 302.1545 [M+H], found: 302.1547.

1-Phenyl-4-propyl-1*H*-pyrido [2,1-*a*]isoquinolin-2(11*bH*)-one (6p)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.00 (t, *J* = 7.4 Hz, 3H), 1.64 (q, *J* = 7.6 Hz, 2H), 2.34-2.55 (m, 2H), 4.21 (d, *J* = 12.0 Hz, 1H), 5.40 (d, *J* = 12.8 Hz, 1H), 5.60 (s, 1H), 5.77 (d, *J* = 8.0 Hz, 1H), 6.02 (d, *J* = 8.0 Hz, 1H), 6.53 (d, *J* = 7.6 Hz, 1H), 6.66-6.70 (m, 1H), 6.94 (d, *J* = 7.6 Hz, 1H), 7.04-7.08 (m, 3H), 7.26-7.30 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.8, 20.4, 35.1, 57.1, 63.8, 106.4, 107.8, 124.1, 125.6, 125.7, 127.2, 127.3, 127.4, 127.9, 128.5, 130.48, 130.52, 136.9, 160.5, 192.4. MS: m/z 316 $[MH]^+$. HRMS calcd for $C_{22}H_{22}NO$: 316.1701 [M+H], found: 316.1704.

1-(4-Methoxyphenyl)-4-propyl-1*H*-pyrido[2,1-*a*]isoquinolin-2(11*bH*)-one (6q)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.99 (t, *J* = 7.2 Hz, 3H), 1.63 (q, *J* = 7.2 Hz, 2H), 2.33-2.55 (m, 2H), 3.79 (s, 3H), 4.14 (d, *J* = 12.0 Hz, 1H), 5.34 (d, *J* = 12.4 Hz, 1H), 5.57 (s, 1H), 5.75 (d, *J* = 7.6 Hz, 1H), 6.07 (d, *J* = 7.6 Hz, 1H), 6.51 (d, *J* = 7.6 Hz, 1H), 6.71 (t, *J* = 7.6 Hz, 1H), 6.82 (d, *J* = 8.8 Hz, 2H), 6.92-6.96 (m, 3H), 7.06 (t, *J* = 7.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.8, 20.4, 35.1, 55.3, 56.2, 63.8, 106.3, 107.7, 114.0, 124.0, 125.6, 125.7, 127.3, 127.5, 127.8, 128.9, 130.5, 131.4, 158.9, 160.4, 192.7. MS: m/z 346 $[MH]^+$. HRMS calcd for $C_{23}H_{24}NO_2$: 346.1807 [M+H], found: 346.1810.

7-Ethyl-6-methyl-9-phenyl-9,9*a*-dihydro-8*H*-pyrido[1,2-*f*]phenanthridin-8-one (6r)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.81-1.85 (m, 3H), 1.82 (s, 3H), 2.04-2.11 (m, 1H), 2.40-2.46 (m, 1H), 4.39 (s, 1H), 4.94 (s, 1H), 7.21-7.54 (m, 11H), 7.79-7.83 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.2, 17.7, 18.5, 50.0, 62.7, 114.8, 124.3, 125.0, 126.7, 127.0, 127.3, 127.7, 127.9, 128.17, 128.19, 128.7, 130.8, 132.5, 136.5, 138.5, 142.0, 154.3, 189.3. MS: m/z 366 $[MH]^+$. HRMS calcd for $C_{26}H_{24}NO$: 366.1858 [M+H], found: 366.1860.

3. The typical procedure for the synthesis of 4-methyl-1-phenyl-2*H*-quinolizin-2-one (4a)

To a flask containing pyridine (**2a**, 1 mmol), AcOH (0.2 mmol), EtOH (95%, 2 mL) was added 1-phenylpenta-3,4-dien-2-one (**1a**, 1 mmol). The mixture was stirred at 80 ^{o}C for 12 h. Upon completion, the resulting mixture was treated with water (3 mL), and the mixture was let to stand at 0 ^{o}C overnight. The solids thus precipitated were collected by filtration to give **4a**. **4a-4n** and **7a-7f** were obtained in a similar

manner.

4-Methyl-1-phenyl-2*H*-quinolizin-2-one (4a)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.57 (s, 3H), 6.64 (t, *J* = 7.2 Hz, 1H), 6.89 (s, 1H), 6.94-6.98 (m, 1H), 7.15 (d, *J* = 9.2 Hz, 1H), 7.26-7.35 (m, 3H), 7.41-7.45 (m, 2H), 7.81 (d, *J* = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.4, 112.5, 123.4, 123.5, 127.5, 127.8, 127.9, 128.8, 131.1, 134.7, 140.9, 142.7, 173.6. MS: m/z 236 $[MH]^+$. HRMS calcd for $C_{16}H_{14}NO$: 236.1075 [M+H], found: 236.1078.

1-(4-Fluorophenyl)-4-methyl-2*H*-quinolizin-2-one (4b)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.64 (s, 3H), 6.74 (t, *J* = 6.4 Hz, 1H), 7.02-7.30 (m, 7H), 7.89 (d, *J* = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.6, 114.5, 115.9, 116.1, 121.9, 123.7, 128.6, 129.2, 129.4, 132.7, 132.8, 141.9, 143.4, 161.3, 163.7, 174.1. MS: m/z 254 $[MH]^+$. HRMS calcd for $C_{16}H_{13}FNO$: 254.0981 [M+H], found: 254.0985.

1-Benzyl-4-methyl-2*H*-quinolizin-2-one (4c)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.55 (s, 3H), 4.23 (s, 2H), 6.66 (t, *J* = 6.8 Hz, 1H), 6.97 (s, 1H), 7.07-7.25 (m, 6H), 7.43 (d, *J* = 9.6 Hz, 1H), 7.80 (d, *J* = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.3, 29.8, 112.5, 122.2, 122.5, 125.9, 128.30, 128.34, 128.37, 128.44, 140.4, 140.5, 142.6, 174.1. MS: m/z 250 $[MH]^+$. HRMS calcd for $C_{17}H_{16}NO$: 250.1232 [M+H], found: 250.1230.

3,4-Dimethyl-1-phenyl-2*H*-quinolizin-2-one (4d)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.33 (s, 3H), 2.60 (s, 3H), 6.58 (t, *J* = 6.8 Hz, 1H), 6.90 (t, *J* = 7.6 Hz, 1H), 7.13 (d, *J* = 9.2 Hz, 1H), 7.30 (t, *J* = 8.4 Hz, 3H), 7.41 (t, *J* = 7.2 Hz, 2H), 7.87 (d, *J* = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ:13.3, 16.9, 112.0, 120.9, 123.1, 127.0, 127.1, 127.9, 128.6, 130.1, 131.3, 135.6, 137.4, 141.4, 172.7. MS: m/z 250 $[MH]^+$. HRMS calcd for $C_{17}H_{16}NO$: 250.1232 [M+H], found: 250.1221.

3-Ethyl-1-(4-methoxyphenyl)-4-methyl-2*H*-quinolizin-2-one (4e)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.14 (t, *J* = 7.6 Hz, 3H), 2.60 (s, 3H), 2.86 (q, *J* = 7.6 Hz, 2H), 3.80 (s, 3H),

6.56 (t, *J* = 7.2 Hz, 1H), 6.87-6.91 (m, 1H), 6.95 (t, *J* = 8.8 Hz, 2H),7.18 (d, *J* = 8.8 Hz, 1H), 7.23 (d, *J* = 8.8 Hz, 2H), 7.85 (d, *J* = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.4, 16.4, 20.6, 55.3, 111.8, 114.0, 121.0, 123.3, 126.8, 127.6, 127.9, 132.4, 135.7, 137.1, 141.5, 158.7, 172.3. MS: m/z 294 $[MH]^+$. HRMS calcd for $C_{19}H_{20}NO_2$: 294.1494 [M+H], found: 294.1495.

1-(4-Methoxyphenyl)-4-propyl-2*H*-quinolizin-2-one (4f)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.08 (t, *J* = 7.4 Hz, 3H), 1.78 (q, *J* = 7.6 Hz, 2H), 2.80 (t, *J* = 7.6 Hz, 2H), 3.62 (s, 3H), 3.84 (s, 3H), 6.37 (d, *J* = 7.6 Hz, 2H), 6.77 (s, 1H), 6.99 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 7.79 (d, *J* = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.8, 20.1, 34.7, 55.3, 55.5, 98.2, 108.0, 114.4, 120.4, 121.0, 127.5, 129.2, 132.1, 143.4, 145.4, 157.9, 158.8, 173.4. MS: m/z 294 $[MH]^+$. HRMS calcd for $C_{19}H_{20}NO_2$: 294.1494 [M+H], found: 294.1498.

1-(4-Fluorophenyl)-4,8-dimethyl-2*H*-quinolizin-2-one (4g)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.21 (s, 3H), 2.62 (s, 3H), 6.60 (dd, J_1 = 7.2 Hz, J_2 = 2.0 Hz, 1H), 6.94 (d, *J* = 12.0 Hz, 2H), 7.16 (t, *J* = 8.6 Hz, 2H), 7.26-7.29 (m, 2H), 7.83 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.6, 21.3, 115.9, 116.1, 117.5, 120.4, 121.1, 121.3, 128.2, 129.36, 129.40, 132.7, 132.8, 141.3, 141.6, 143.6, 170.2. MS: m/z 268 $[MH]^+$. HRMS calcd for $C_{17}H_{15}FNO$: 268.1138 [M+H], found: 268.1145.

1-Benzyl-4,8-dimethyl-2*H*-quinolizin-2-one (4h)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.21 (s, 3H), 2.48 (s, 3H), 4.18 (s, 2H), 6.47 (dd, J_1 = 7.2 Hz, J_2 = 1.6 Hz, 1H), 6.83 (s, 1H), 7.09-7.22 (m, 6H), 7.68 (d, *J* = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.2, 21.4, 29.8, 115.2, 119.0, 119.7, 122.0, 125.8, 127.8, 128.2, 128.3, 128.4, 139.5, 140.1, 140.6, 142.8, 174.1. MS: m/z 264 $[MH]^+$. HRMS calcd for $C_{18}H_{18}NO$: 264.1388 [M+H], found: 264.1385.

3,4,8-Trimethyl-1-phenyl-2*H*-quinolizin-2-one (4i)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.08 (s, 3H), 2.28 (s, 3H), 2.52 (s, 3H), 6.39 (dd, J_1 = 7.2 Hz, J_2 = 2.0 Hz, 1H), 6.83 (s, 1H), 7.25-7.29 (m, 3H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.78 (d, *J* = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$)

δ: 13.2, 16.9, 20.9, 114.8, 119.4, 120.3, 126.9, 127.6, 128.5, 129.3, 131.3, 136.0, 137.1, 138.1, 141.6, 172.7. MS: m/z 264 $[MH]^+$. HRMS calcd for $C_{18}H_{18}NO$: 264.1388 [M+H], found: 264.1389.

8-Methoxy-4-methyl-1-phenyl-2*H*-quinolizin-2-one (4j)

^1H NMR (400 MHz, $CDCl_3$) δ: 2.52 (s, 3H), 3.59 (s, 3H), 6.31 (s, 1H), 6.38-6.40 (m, 1H), 6.75 (s, 1H), 7.26-7.33 (m, 3H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.75 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.3, 55.5, 97.9, 108.3, 120.8, 121.9, 127.4, 128.9, 129.7, 131.0, 135.4, 140.2, 145.1, 158.2, 173.1. MS: m/z 266 $[MH]^+$. HRMS calcd for $C_{17}H_{16}NO_2$: 266.1181 [M+H], found: 266.1188.

8-Methoxy-1-(4-methoxyphenyl)-4-methyl-2*H*-quinolizin-2-one (4k)

^1H NMR (400 MHz, $CDCl_3$) δ: 2.53 (s, 3H), 3.62 (s, 3H), 3.82 (s, 3H), 6.36-6.42 (m, 2H), 6.77 (s, 1H), 6.98 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 9.2 Hz, 2H), 7.75 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.3, 55.3, 55.5, 98.0, 108.3, 114.4, 121.7, 127.3, 129.6, 132.1, 140.0, 145.3, 158.1, 158.8, 173.2. MS: m/z 296 $[MH]^+$. HRMS calcd for $C_{18}H_{18}NO_3$: 296.1287 [M+H], found: 296.1277.

8-Methoxy-3,4-dimethyl-1-phenyl-2*H*-quinolizin-2-one (4l)

^1H NMR (400 MHz, $CDCl_3$) δ: 2.26 (s, 3H), 2.50 (s,. 3H), 3.53 (s, 3H), 6.25-6.30 (m, 2H), 7.25-7.28 (m, 3H), 7.38 (t, *J* = 7.4 Hz, 2H), 7.80 (d, *J* = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.0, 16.9, 55.3, 97.4, 107.5, 118.5, 127.0, 128.1, 128.6, 130.0, 131.2, 136.3, 136.7, 143.7, 157.6, 172.3. MS: m/z 280 $[MH]^+$. HRMS calcd for $C_{18}H_{18}NO_2$: 280.1338 [M+H], found: 280.1329.

8-Methoxy-3,4-dimethyl-1-*p*-tolyl-2*H*-quinolizin-2-one (4m)

^1H NMR (400 MHz, $CDCl_3$) δ: 2.25 (s, 3H), 2.32 (s, 3H), 2.49 (s, 3H), 3.55 (s, 3H), 6.25-6.30 (m, 2H), 7.15-7.19 (m, 4H), 7.78 (d, *J* = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.0, 16.9, 21.3, 55.4, 97.5, 107.4, 118.5, 128.0, 129.4, 129.9, 131.0, 133.1, 136.4, 136.5, 143.7, 157.4, 172.5. MS: m/z 294 $[MH]^+$. HRMS calcd for $C_{19}H_{20}NO_2$: 294.1494 [M+H], found: 294.1495.

3-Ethyl-8-methoxy-1-(4-methoxyphenyl)-4-methyl-2*H*-quinolizin-2-one (4n)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.12 (t, *J* = 7.6 Hz, 3H), 2.54 (s, 3H), 2.81 (q, *J* = 7.6 Hz, 2H), 3.59 (s, 3H), 3.80 (s, 3H), 6.28-6.34 (m, 2H), 6.94-6.96 (m, 2H), 7.23-7.26 (m, 2H), 7.78 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.5, 16.4, 20.3, 55.3, 55.4, 97.5, 107.3, 114.1, 118.6, 128.3, 129.7, 132.3, 133.9, 136.2, 143.8, 157.3, 158.4, 172.1. MS: m/z 324 $[MH]^+$. HRMS calcd for $C_{20}H_{22}NO_3$: 324.1600 [M+H], found: 324.1602.

1-Methyl-4-phenyl-3*H*-pyrido[1,2-*a*]quinolin-3-one (7a)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.77 (s, 3H), 6.87 (s, 1H), 6.97 (d, *J* = 9.2 Hz, 1H), 7.15 (d, *J* = 9.2 Hz, 1H), 7.32-7.50 (m, 7H), 7.56 (d, *J* = 7.6 Hz, 1H), 7.66 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 23.7, 122.0, 123.2, 123.5, 126.1, 126.2, 127.90, 127.93, 128.0, 128.6, 128.7, 131.3, 134.0, 134.8, 142.7, 145.6, 175.6. MS: m/z 286 $[MH]^+$. HRMS calcd for $C_{20}H_{16}NO$: 286.1232 [M+H], found: 286.1235.

4-(4-Methoxyphenyl)-1-methyl-3*H*-pyrido[1,2-*a*]quinolin-3-one (7b)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.76 (s, 3H), 3.84 (s, 3H), 6.90 (s, 1H), 6.98-7.04 (m, 3H), 7.16 (d, *J* = 9.6 Hz, 1H), 7.26 (d, *J* = 8.4 Hz, 1H), 7.42-7.58 (m, 4H), 7.66 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 23.7, 55.3, 114.2, 122.0, 123.2, 126.2, 126.3, 127.88, 127.93, 128.4, 128.5, 128.6, 132.2, 132.5, 134.8, 142.7, 145.6, 159.3, 175.7. MS: m/z 316 $[MH]^+$. HRMS calcd for $C_{21}H_{18}NO_2$: 316.1338 [M+H], found: 316.1340.

1-(4-Methoxyphenyl)-4-methyl-2*H*-pyrido[2,1-*a*]isoquinolin-2-one (7c)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.59 (s, 3H), 3.84 (s, 3H), 6.79 (d, *J* = 6.8 Hz, 2H), 6.95-7.02 (m, 3H), 7.20 (s, 2H), 7.37-7.44 (m, 3H), 7.56 (d, *J* = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.3, 55.3, 113.1, 114.8, 124.0, 126.0, 126.8, 129.9, 130.6, 131.3, 131.9, 141.1, 142.2, 148.2, 159.0, 175.1. MS: m/z 316 $[MH]^+$. HRMS calcd for $C_{21}H_{18}NO_2$: 316.1338 [M+H], found: 316.1346.

4-Methyl-1-*p*-tolyl-2*H*-pyrido[2,1-*a*]isoquinolin-2-one (7d)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.39 (s, 3H), 2.59 (s, 3H), 6.79 (d, *J* = 8.4 Hz, 2H), 6.98 (t, *J* = 7.2 Hz, 1H), 7.15-7.23 (m, 4H), 7.35-7.43 (m, 3H), 7.56 (d, *J* = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.2, 21.4, 113.0, 124.0, 125.9, 126.0, 126.7, 129.9, 130.0, 130.5, 130.7, 131.3, 134.5, 137.2., 142.2, 153.1, 175.2. MS:

m/z 300 $[MH]^+$. HRMS calcd for $C_{21}H_{18}NO$: 300.1388 [M+H], found: 300.1381.

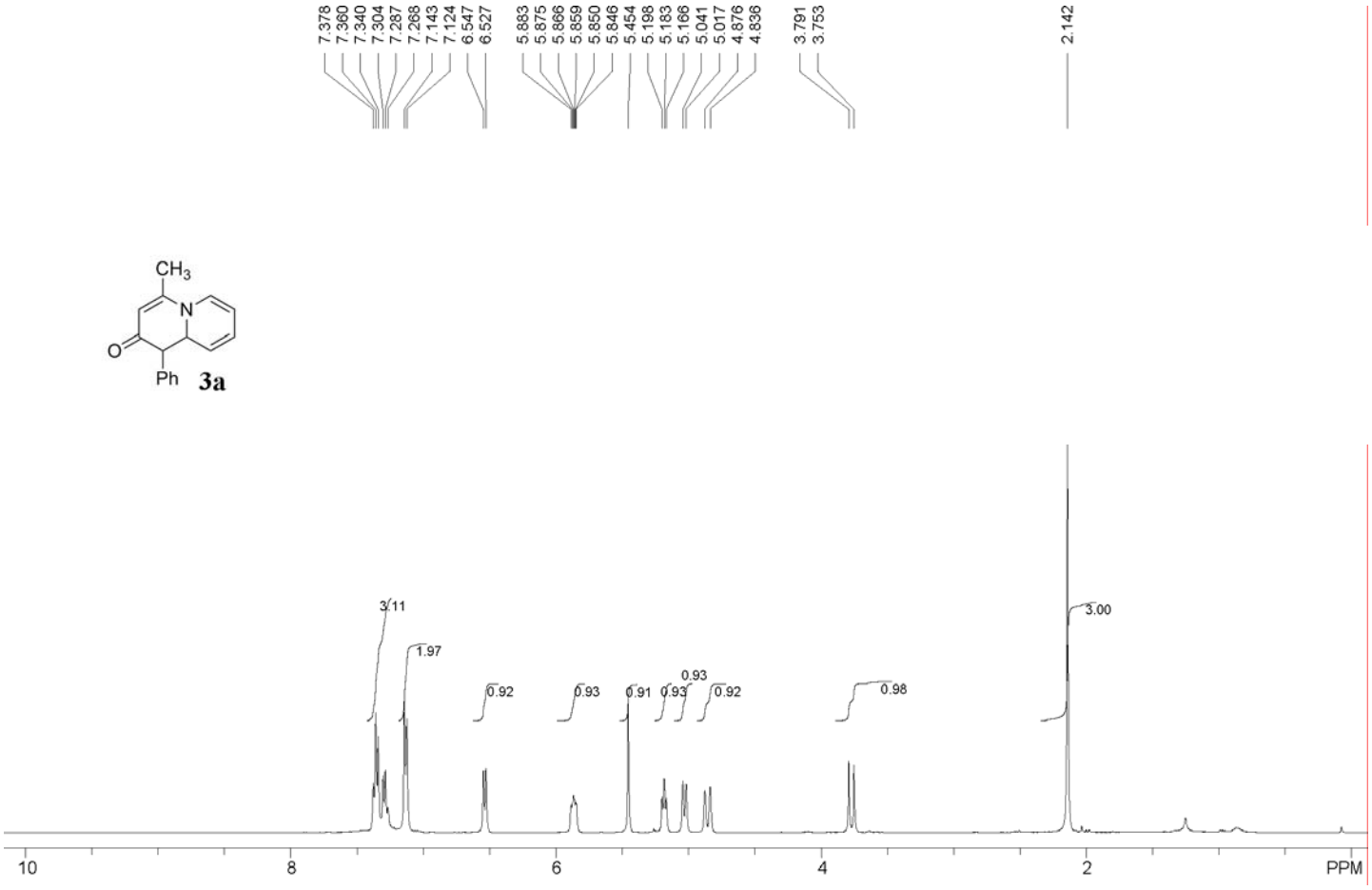
1-(4-Fluorophenyl)-3,4-dimethyl-2*H*-pyrido[2,1-*a*]isoquinolin-2-one (7e)

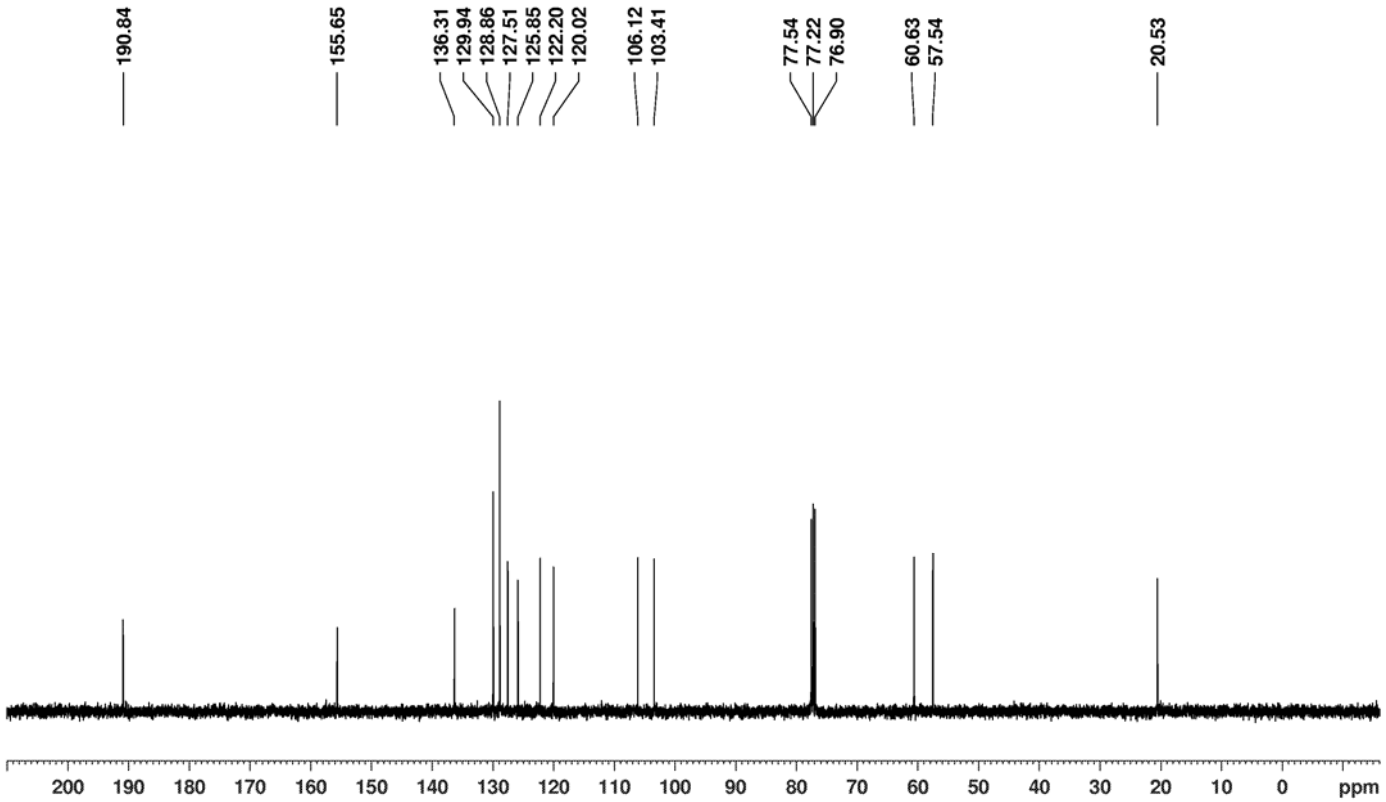
^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.31 (s, 3H), 2.64 (s, 3H), 6.79 (d, *J* = 7.2 Hz, 1H), 7.00-7.11 (m, 3H), 7.23-7.43 (m, 5H), 7.64 (d, *J* = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 12.9, 17.6, 112.3, 115.9, 116.1, 123.5, 124.5, 125.6, 125.8, 126.6, 127.1, 129.8, 130.4, 131.2, 132.7, 132.8, 134.18, 134.21, 139.8, 140.3, 140.7, 145.3, 160.9, 163.4, 175.3. MS: m/z 318 $[MH]^+$. HRMS calcd for $C_{21}H_{17}FNO$: 318.1294 [M+H], found: 318.1284.

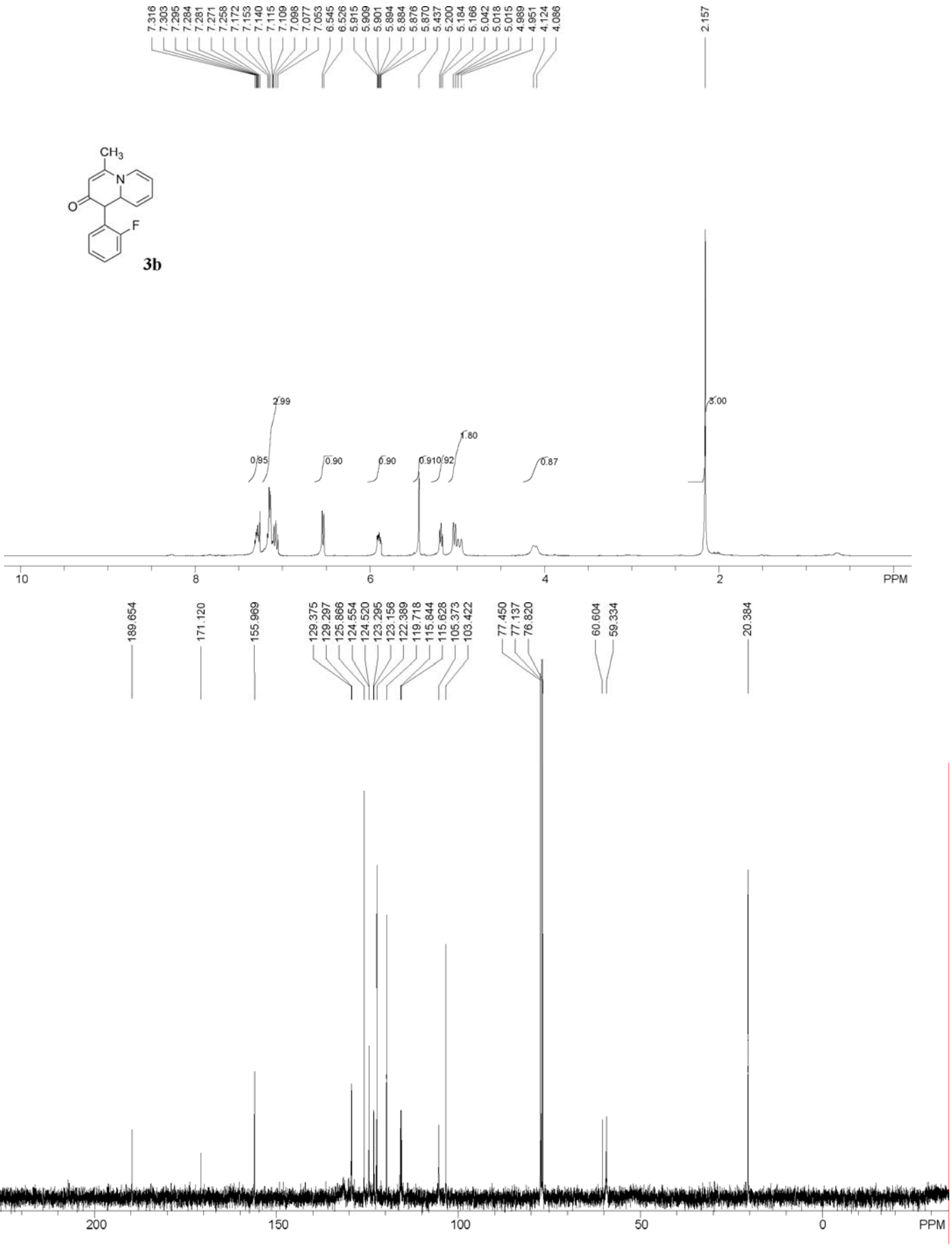
4-Benzyl-2*H*-pyrido[2,1-*a*]isoquinolin-2-one (7f)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.29 (s, 2H), 6.77 (d, *J* = 7.6 Hz, 1H), 6.85 (d, *J* = 1.2 Hz, 1H), 7.18 (d, *J* = 7.2 Hz, 2H), 7.27-7.35 (m, 4H), 7.50 (d, *J* = 7.6 Hz, 1H), 7.52-7.62 (m, 2H), 7.66 (d, *J* = 1.6 Hz, 1H), 7.26 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 39.9, 109.4, 113.8, 122.9, 123.9, 124.6, 125.3, 126.9, 127.7, 128.1, 129.2, 129.4, 131.4, 134.6, 144.2, 145.4, 174.4, 176.6, 185.7. MS: m/z 286 $[MH]^+$. HRMS calcd for $C_{20}H_{16}NO$: 286.1232 [M+H], found: 286.1235.

II. Copies of ^{1}H and ^{13}C NMR spectra of compounds 3a-3y



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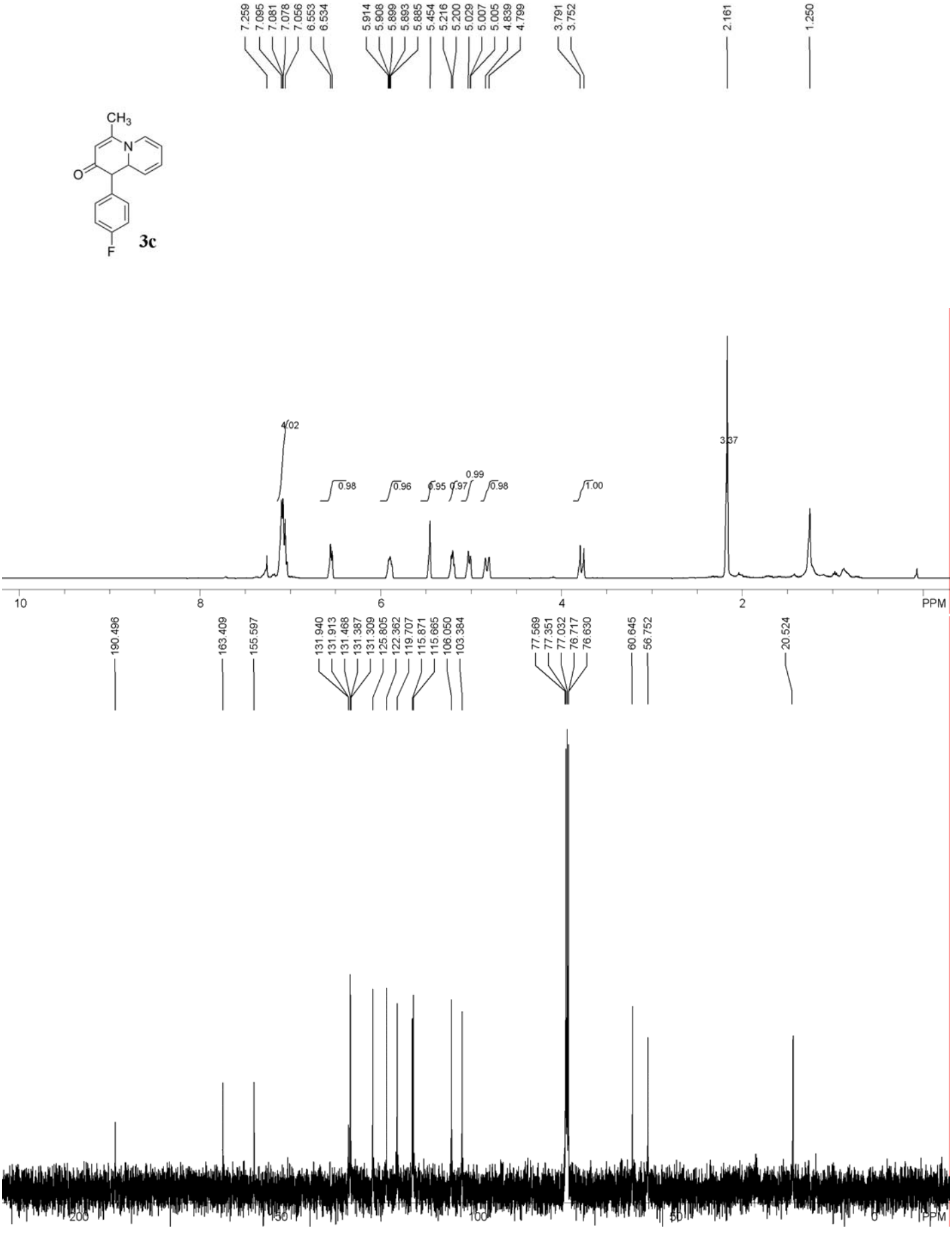
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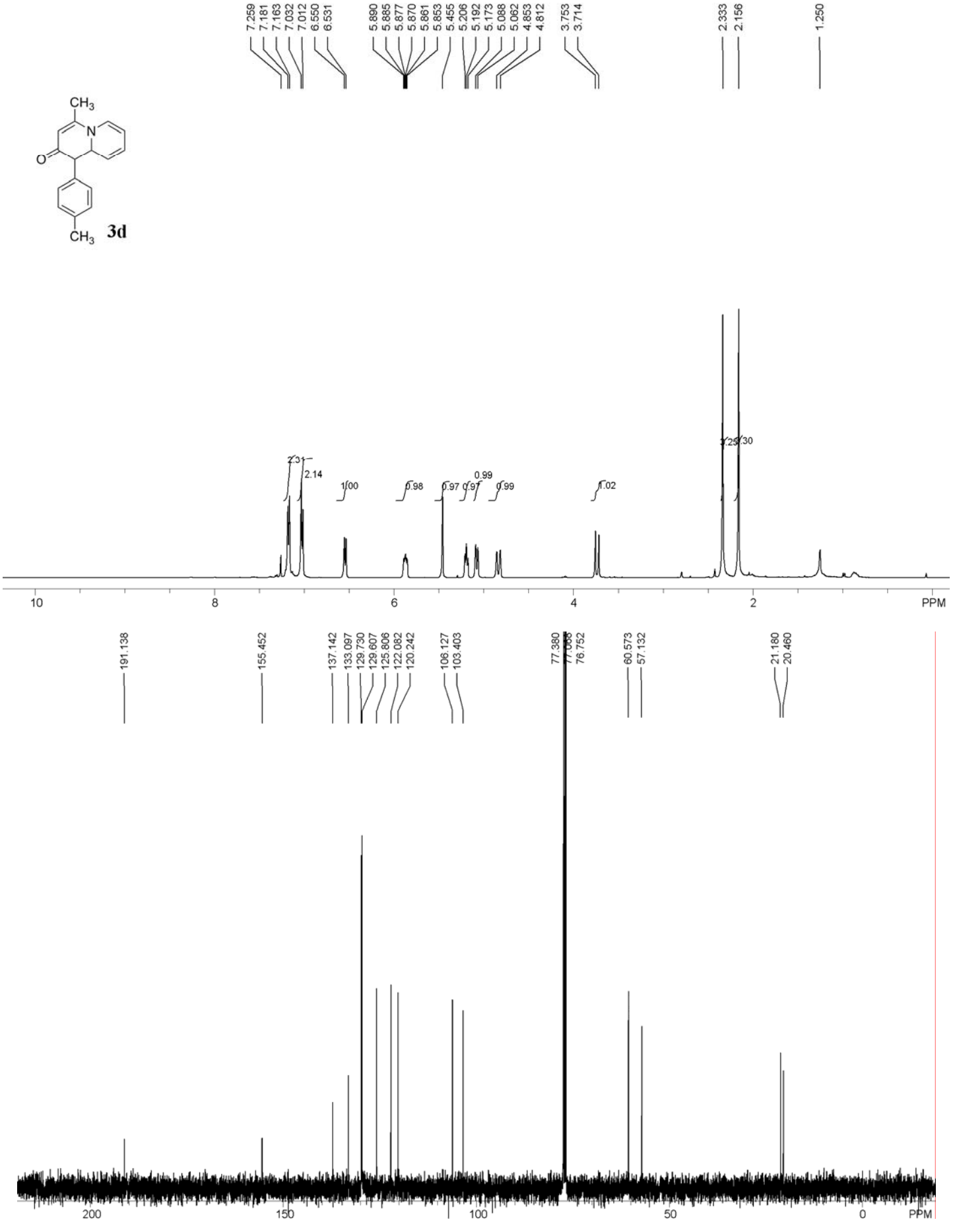

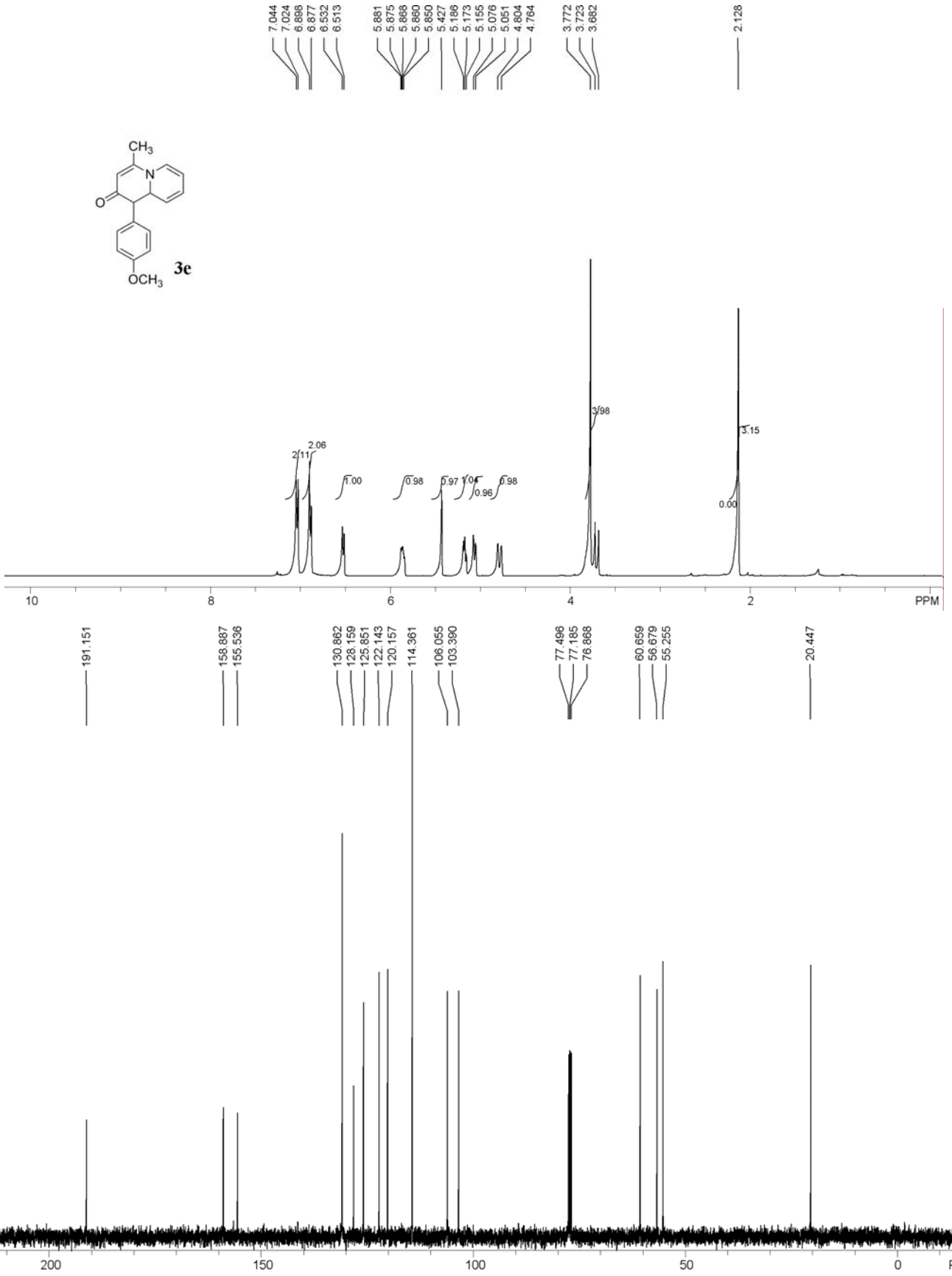
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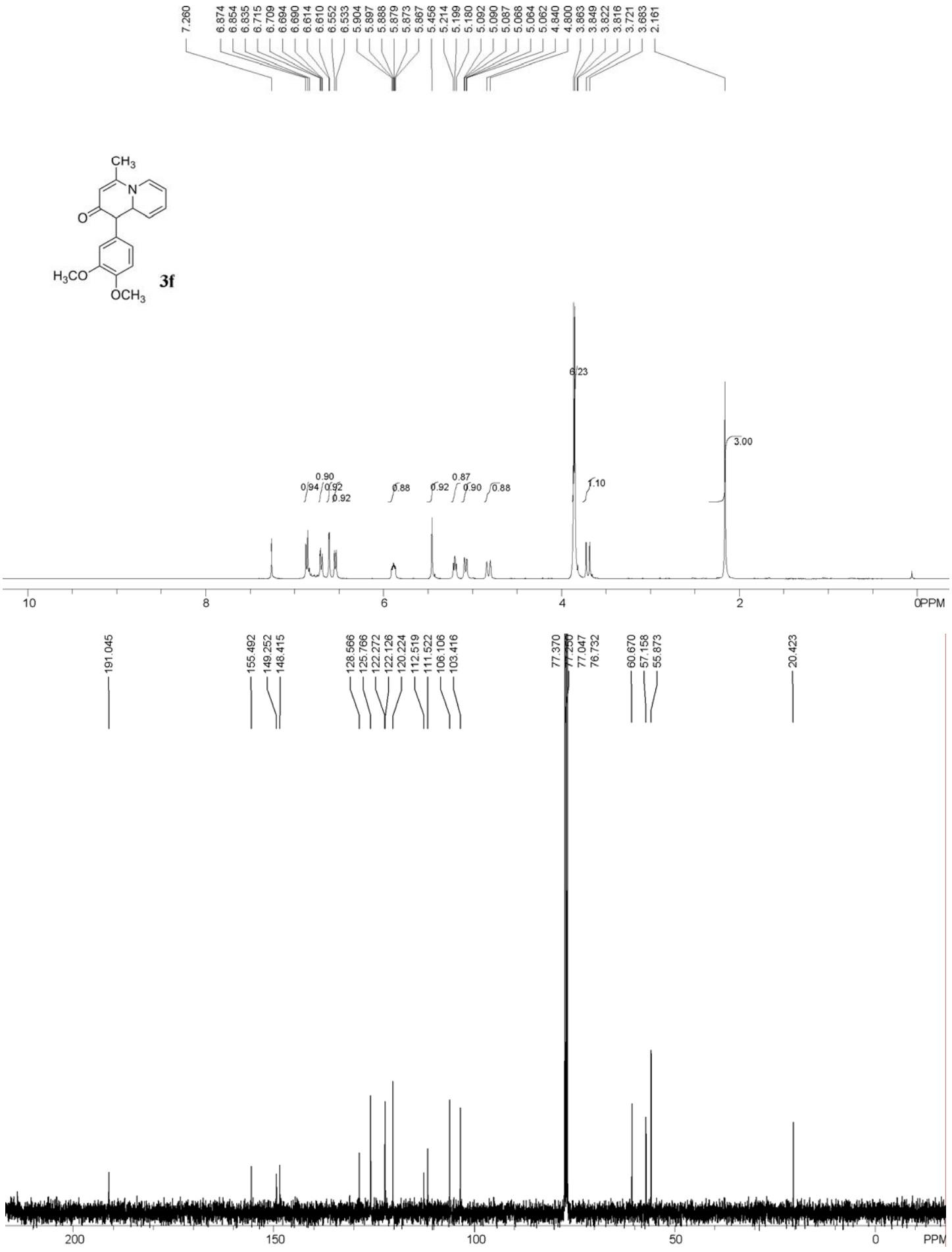

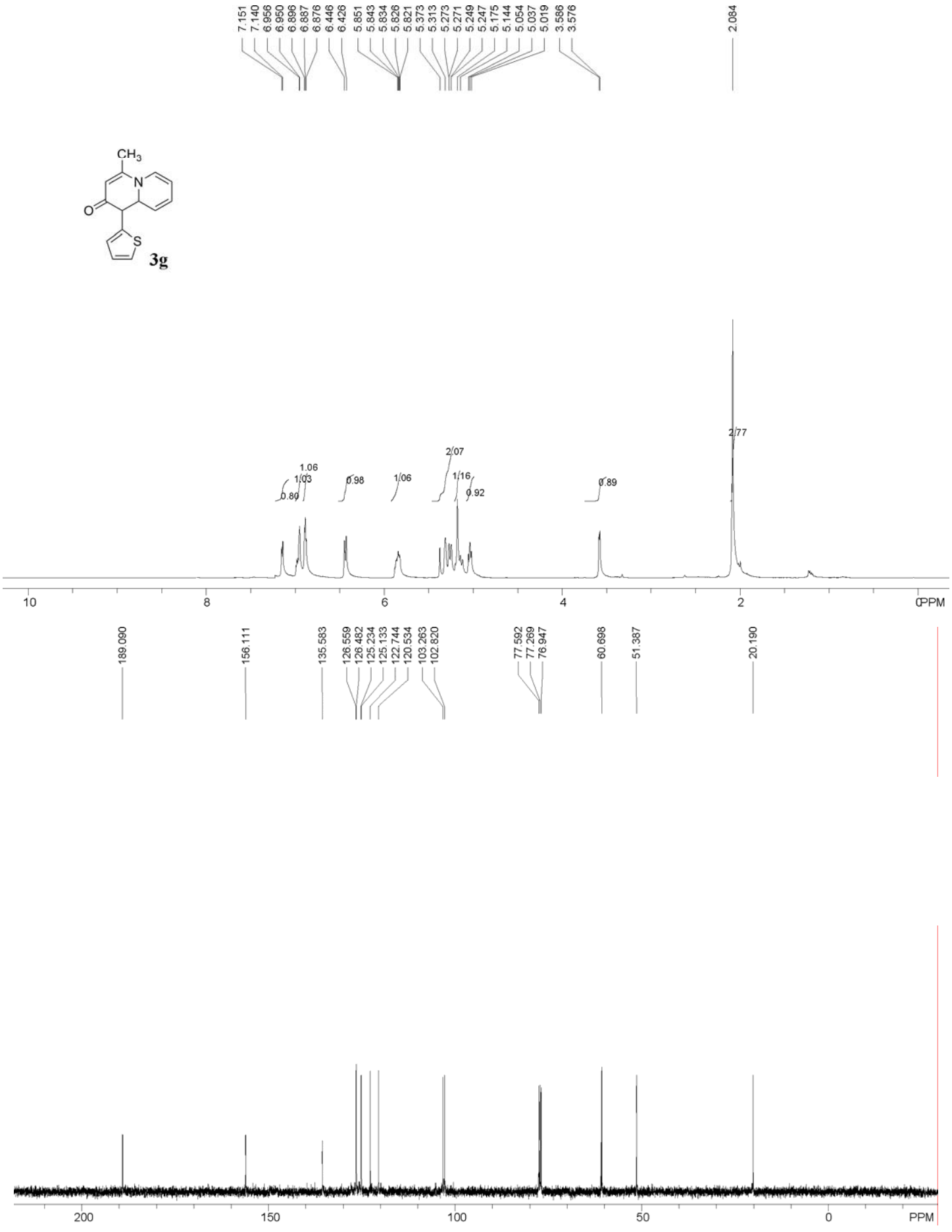

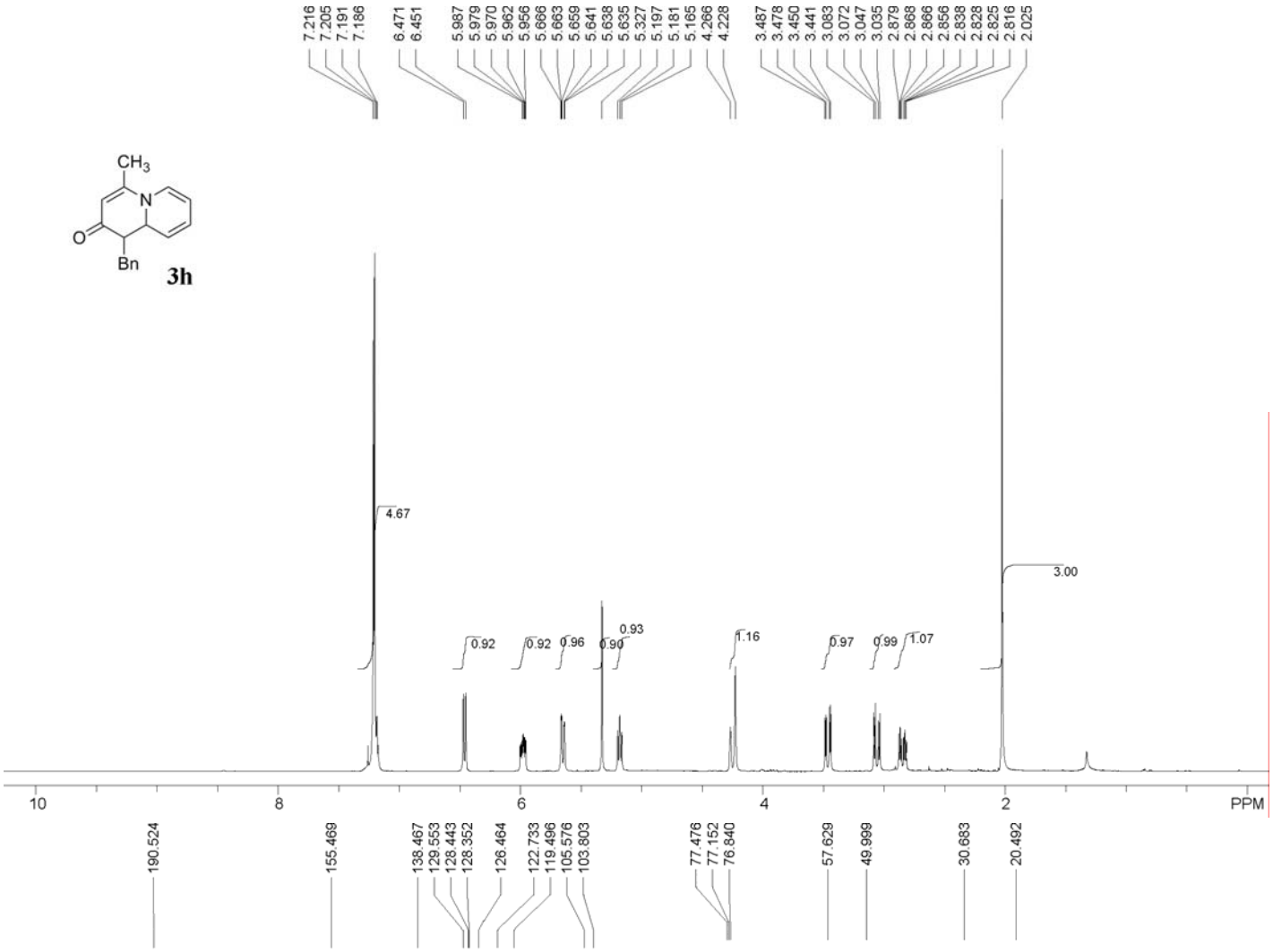
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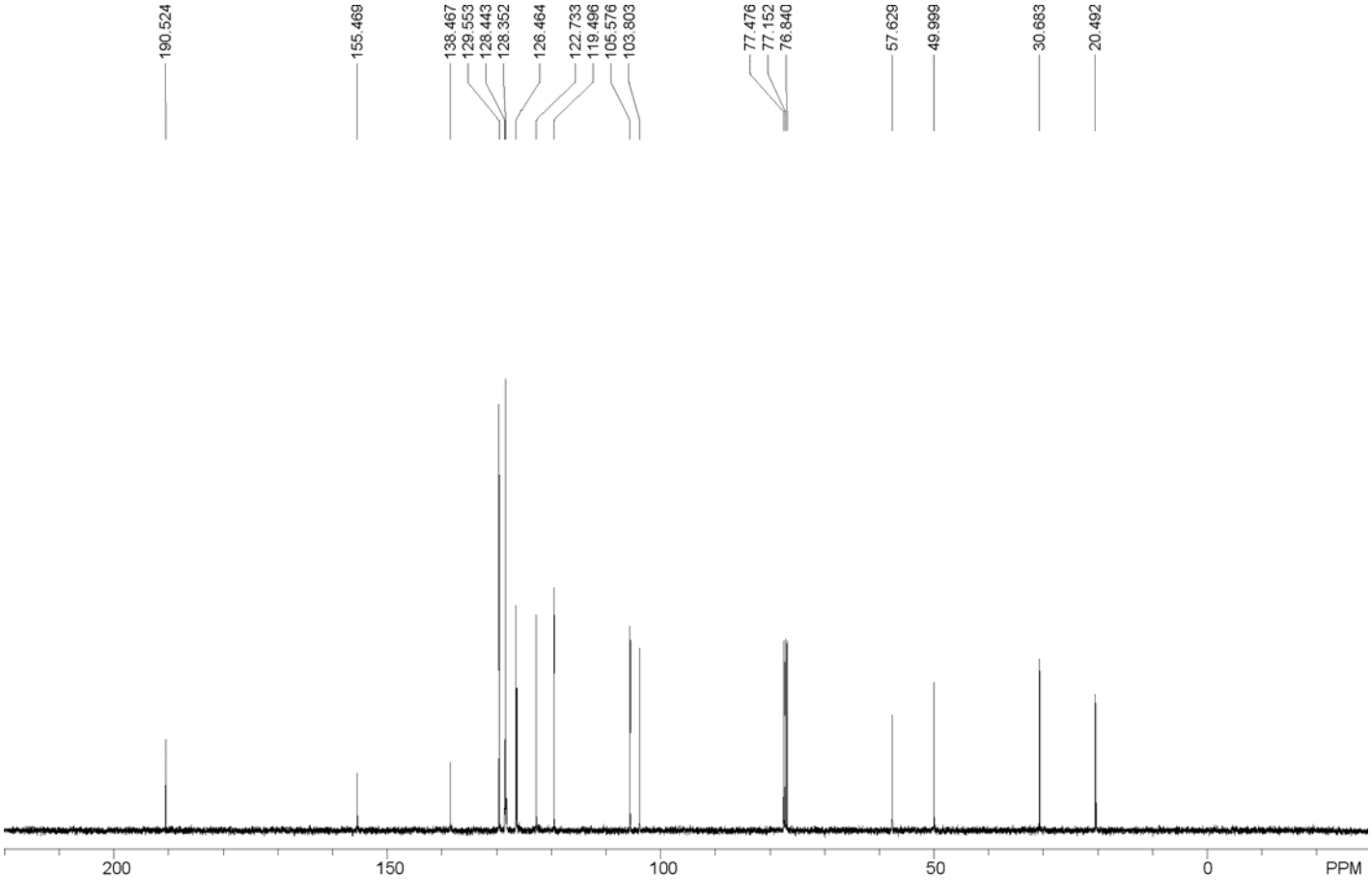
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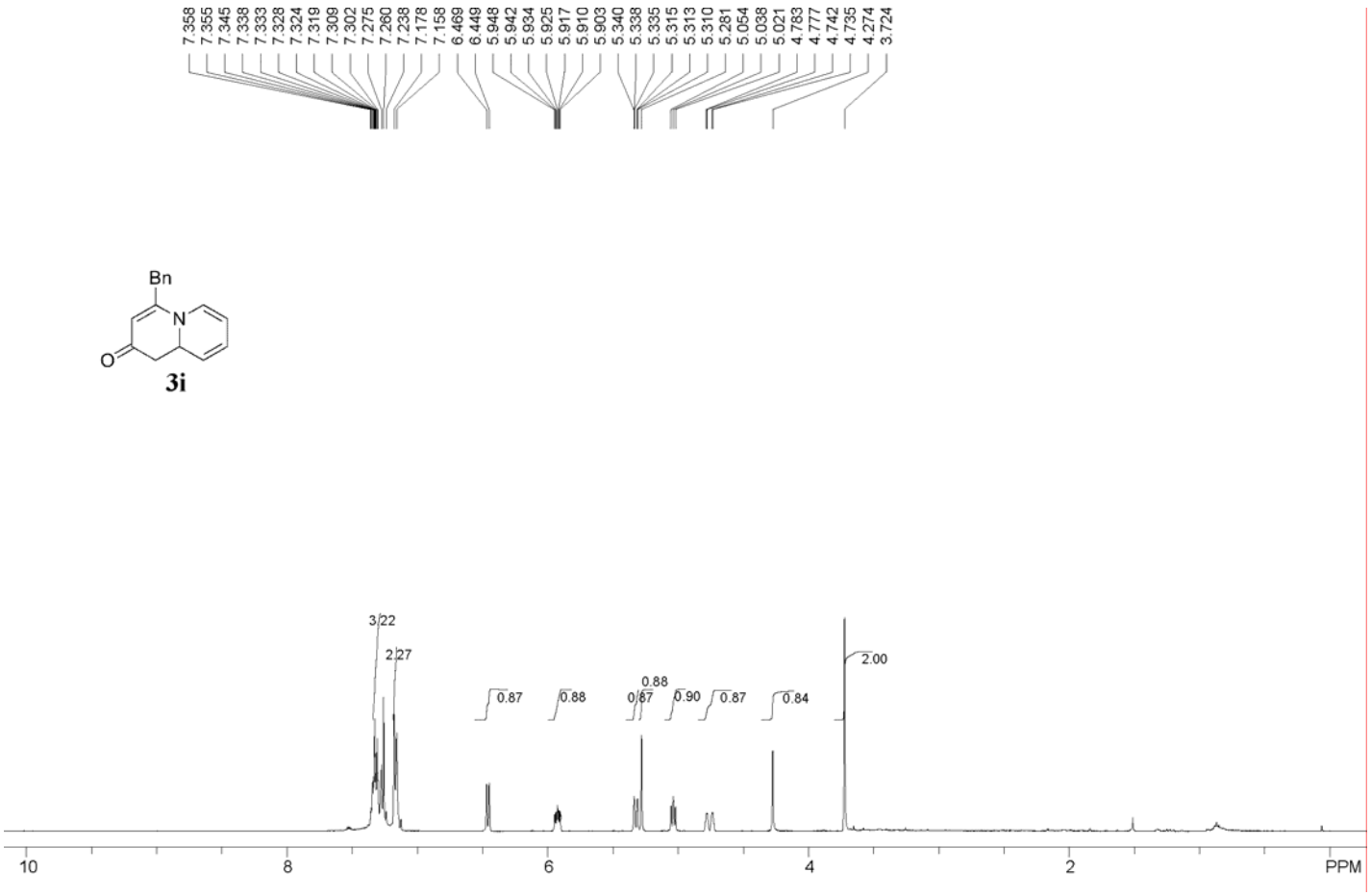
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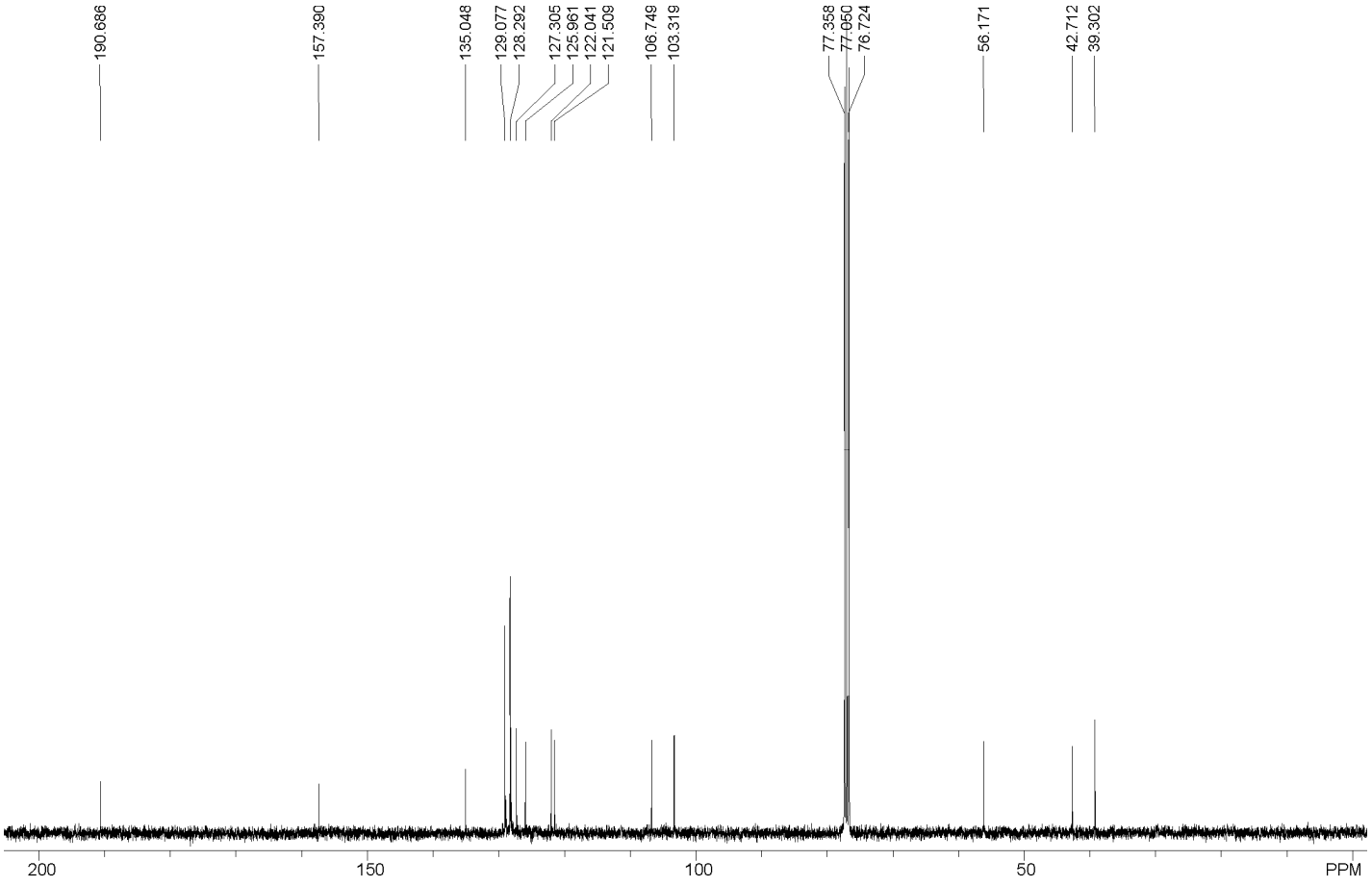
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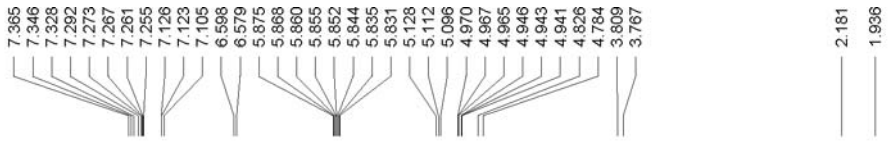
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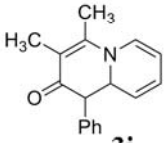
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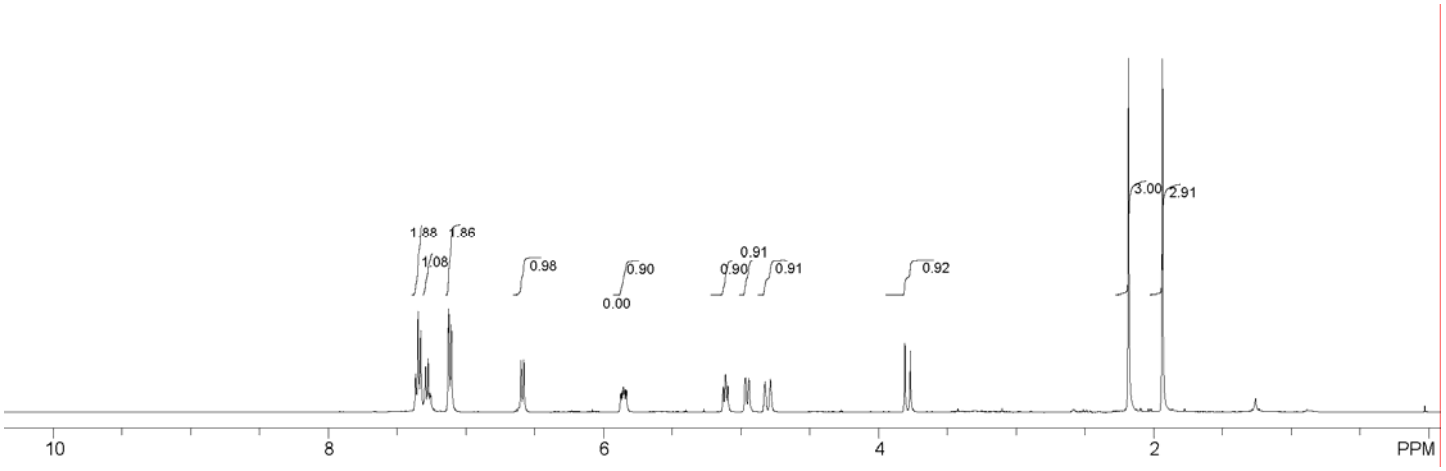
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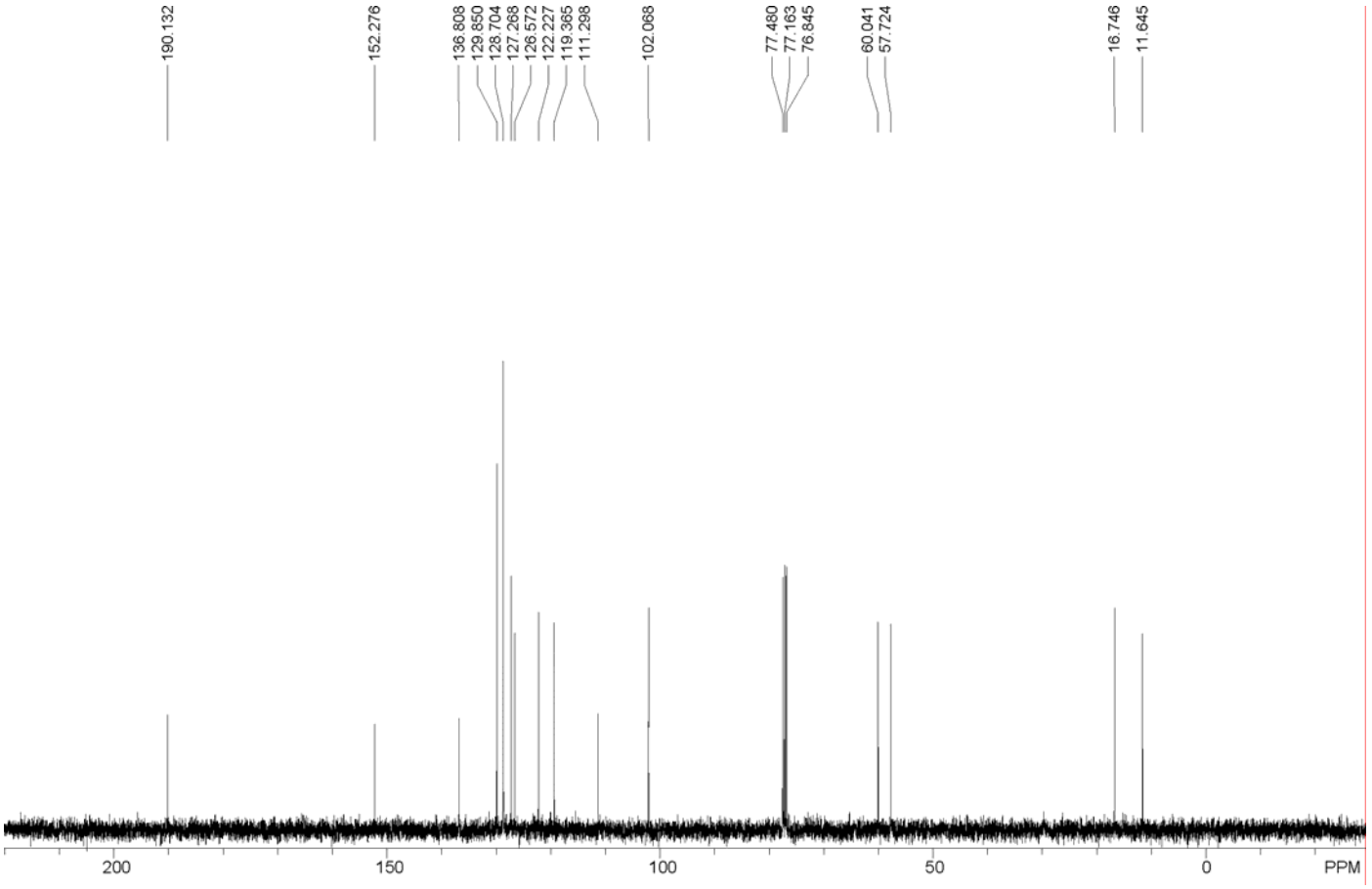
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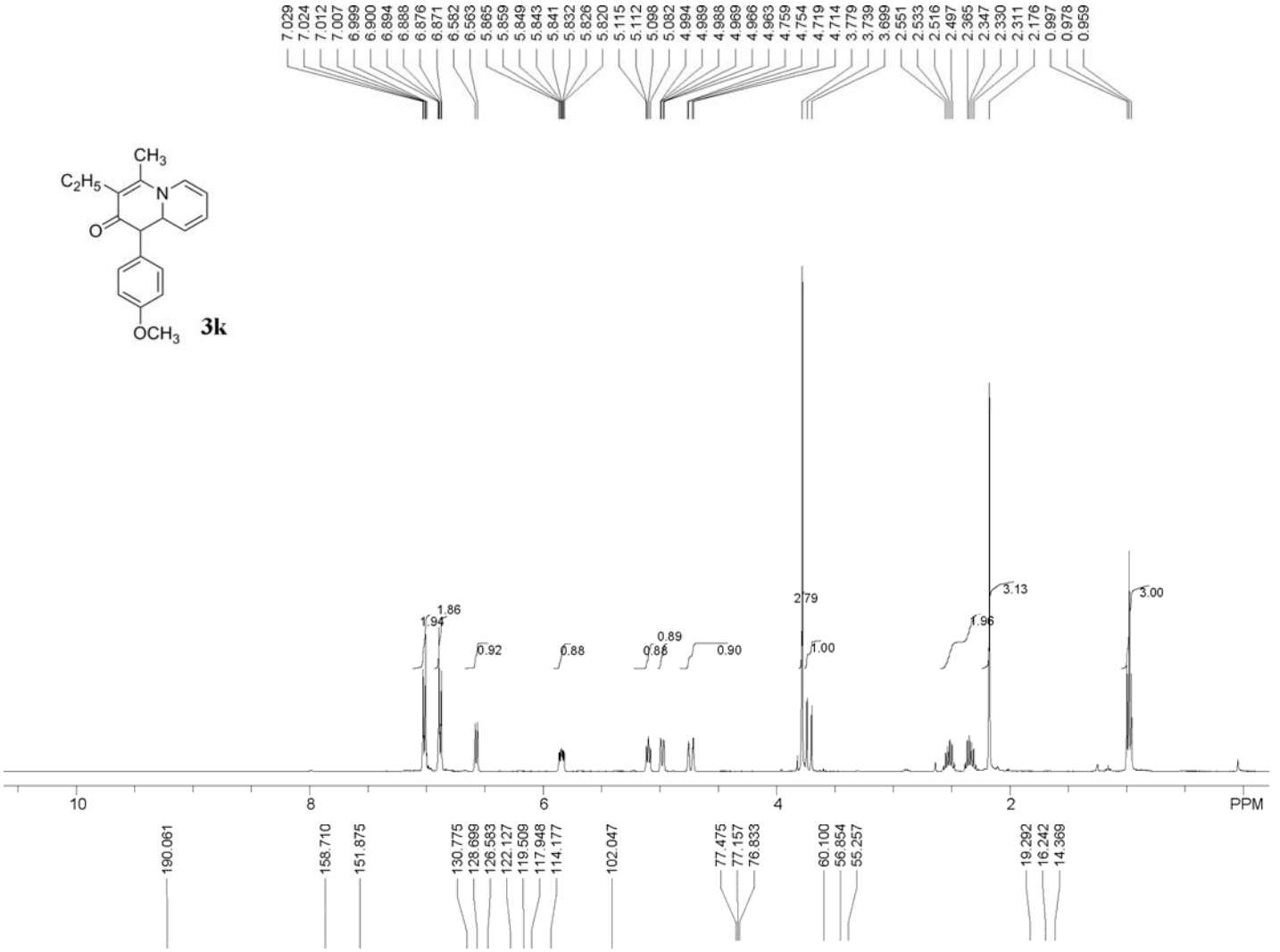
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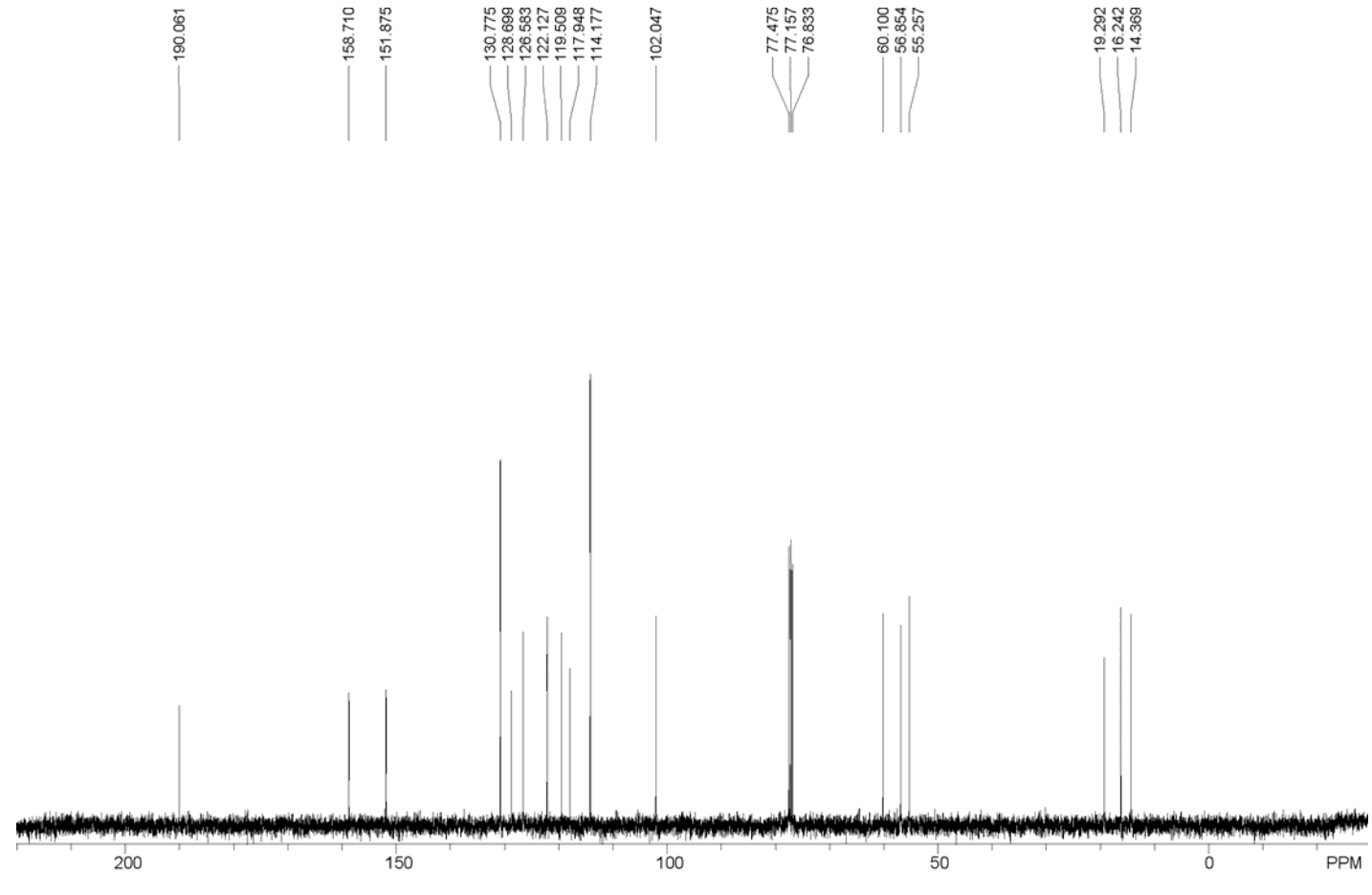
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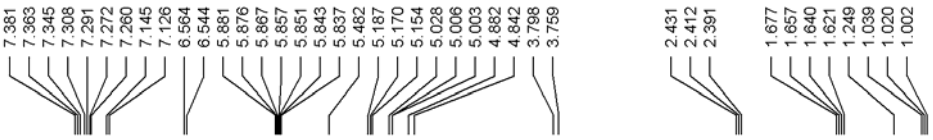
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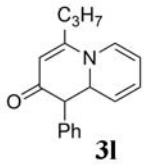
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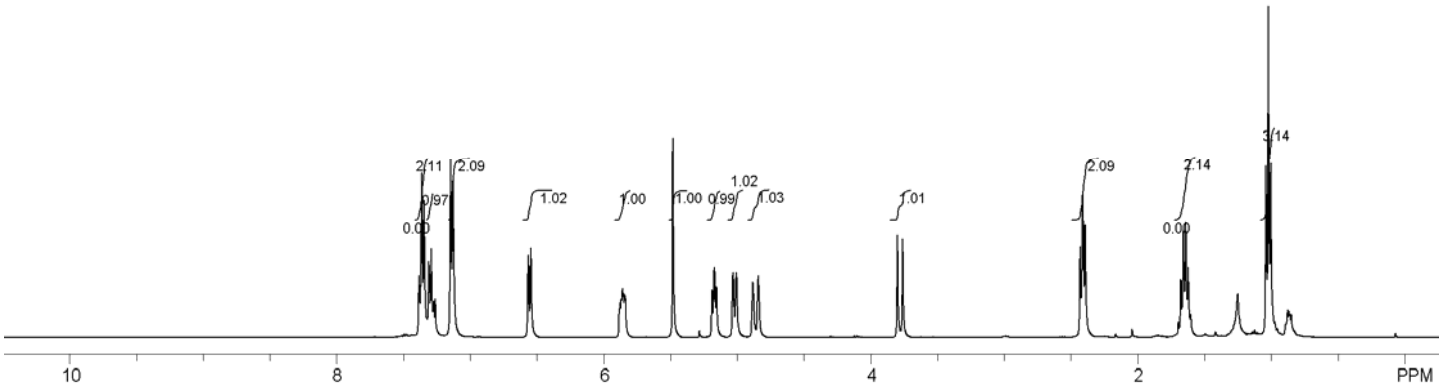
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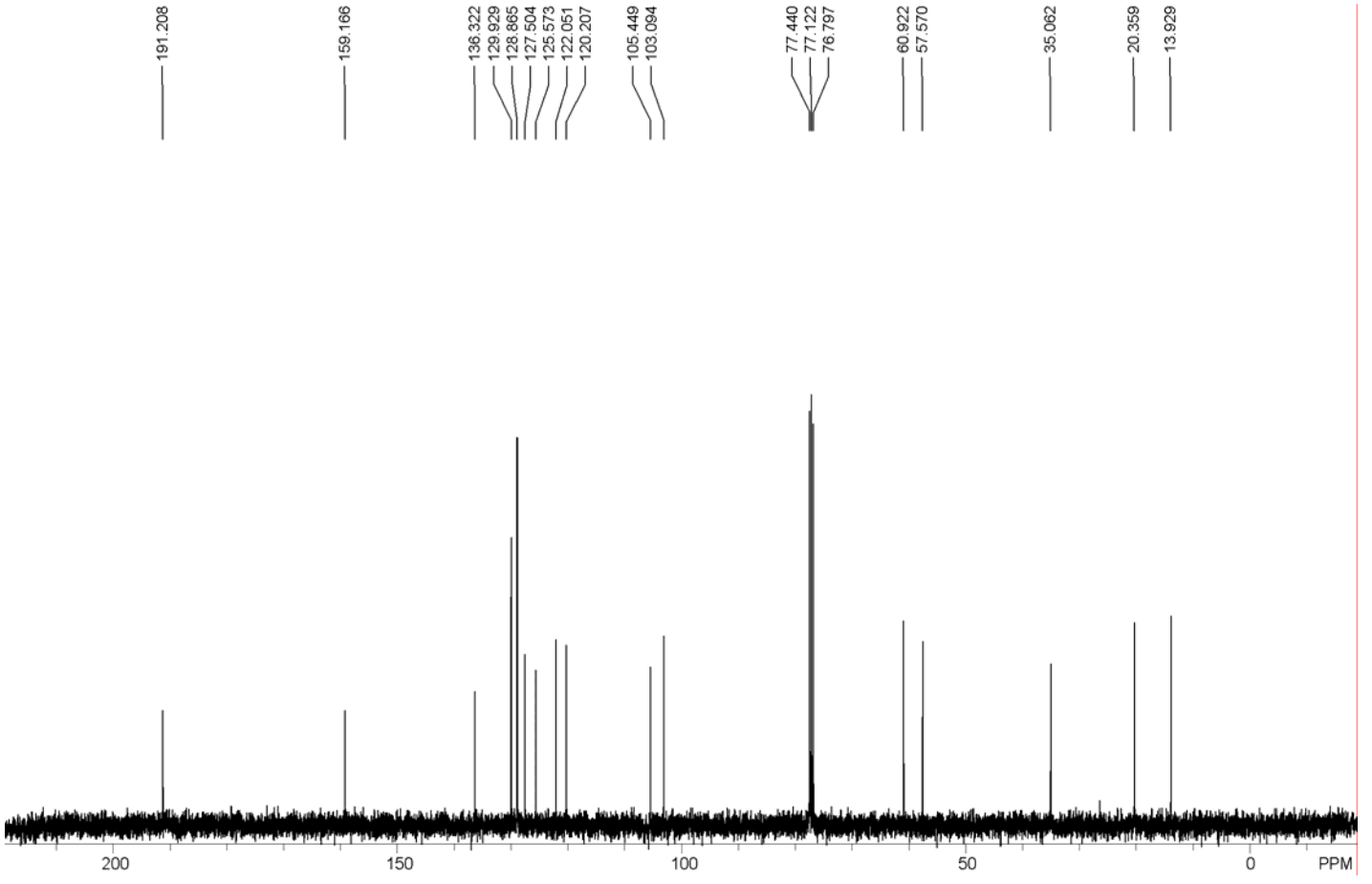
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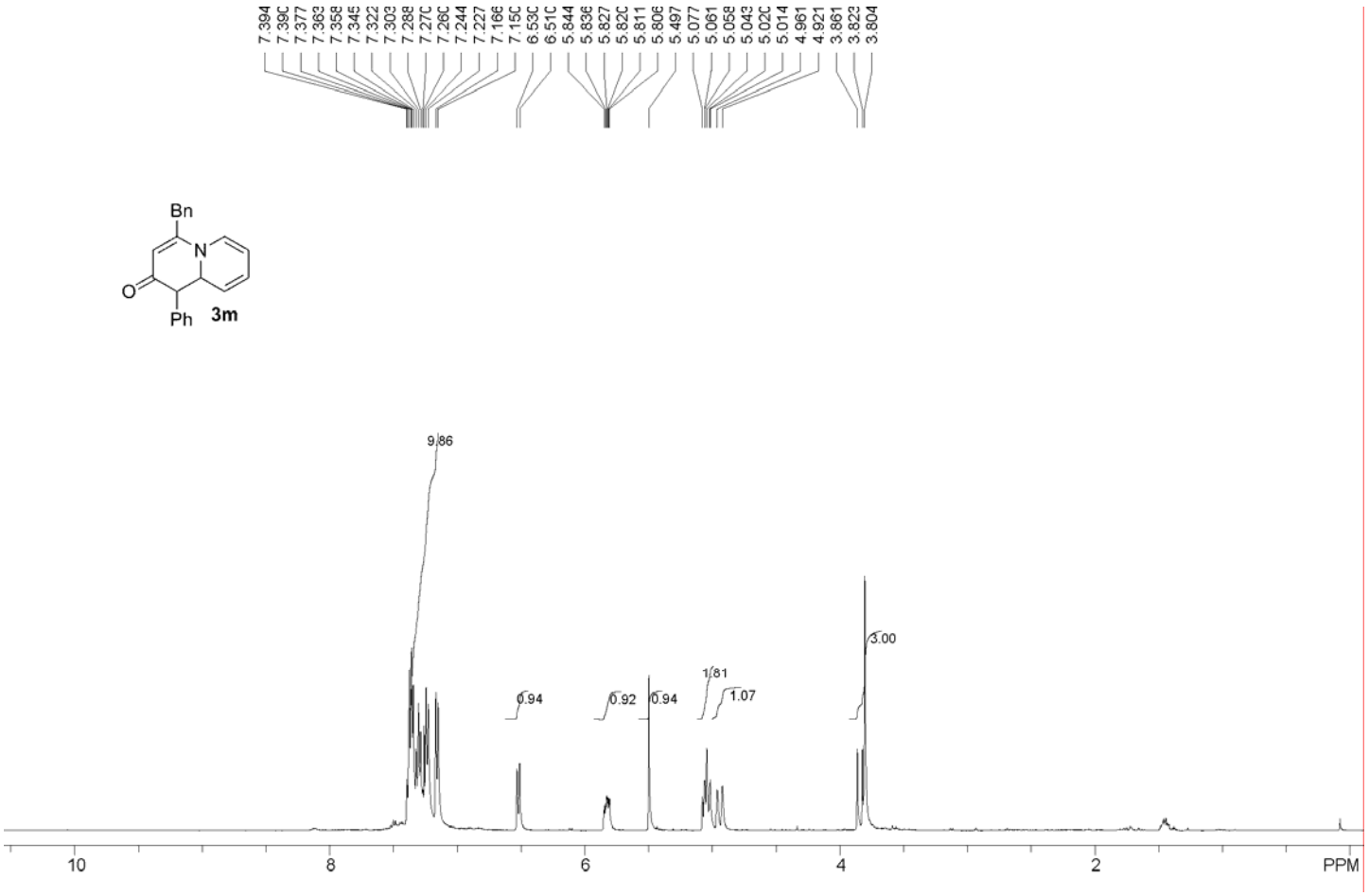
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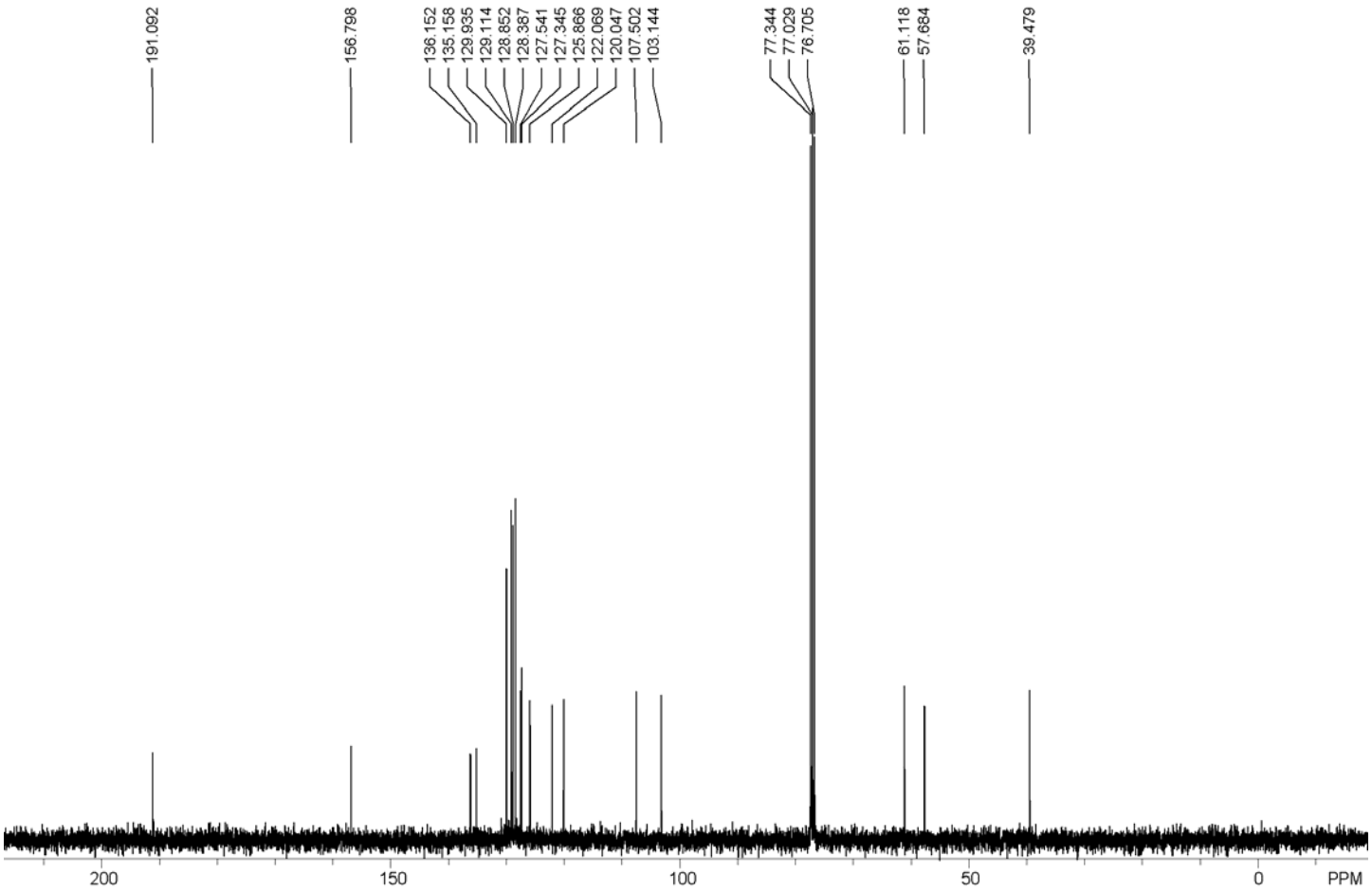
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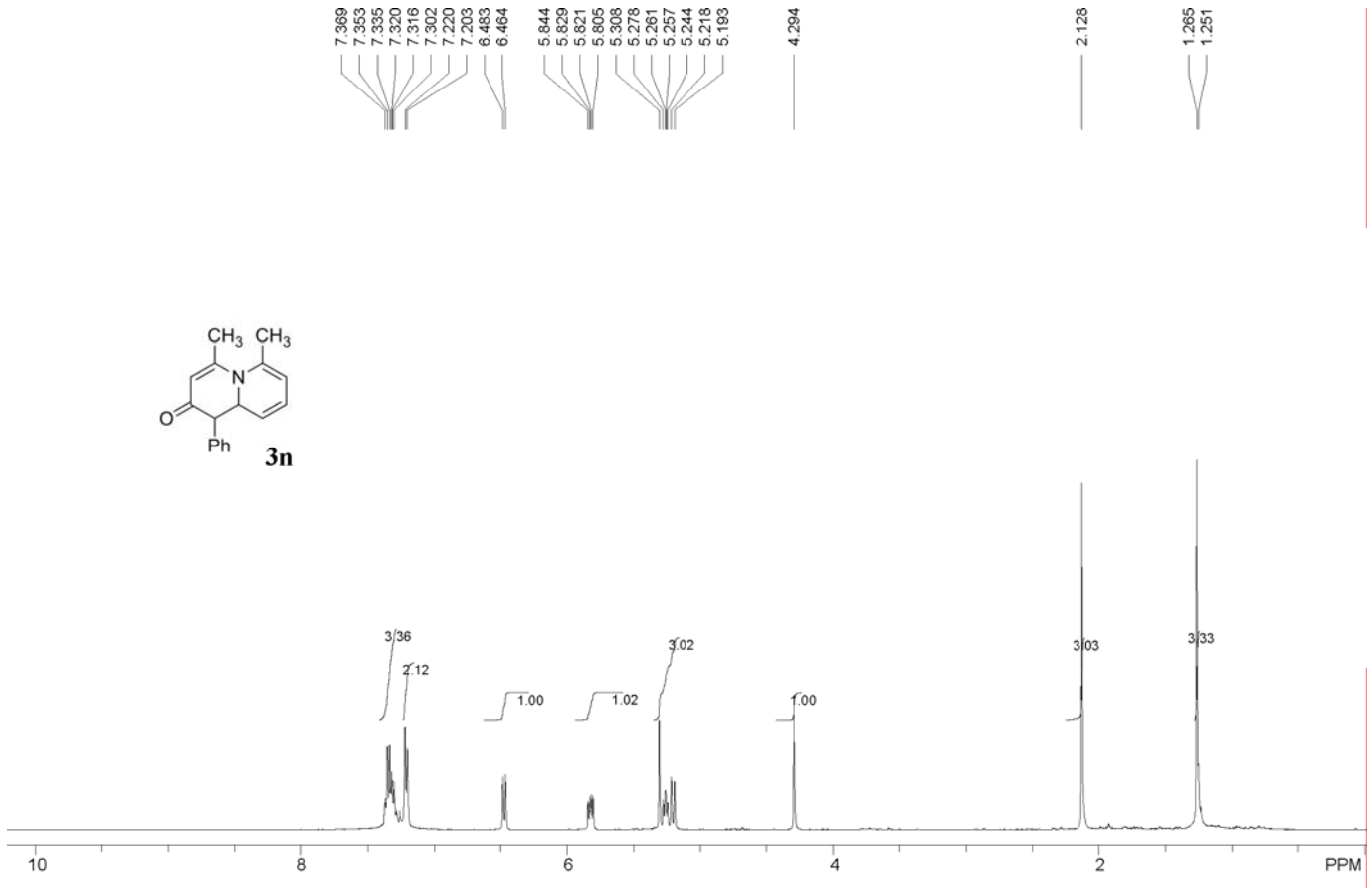
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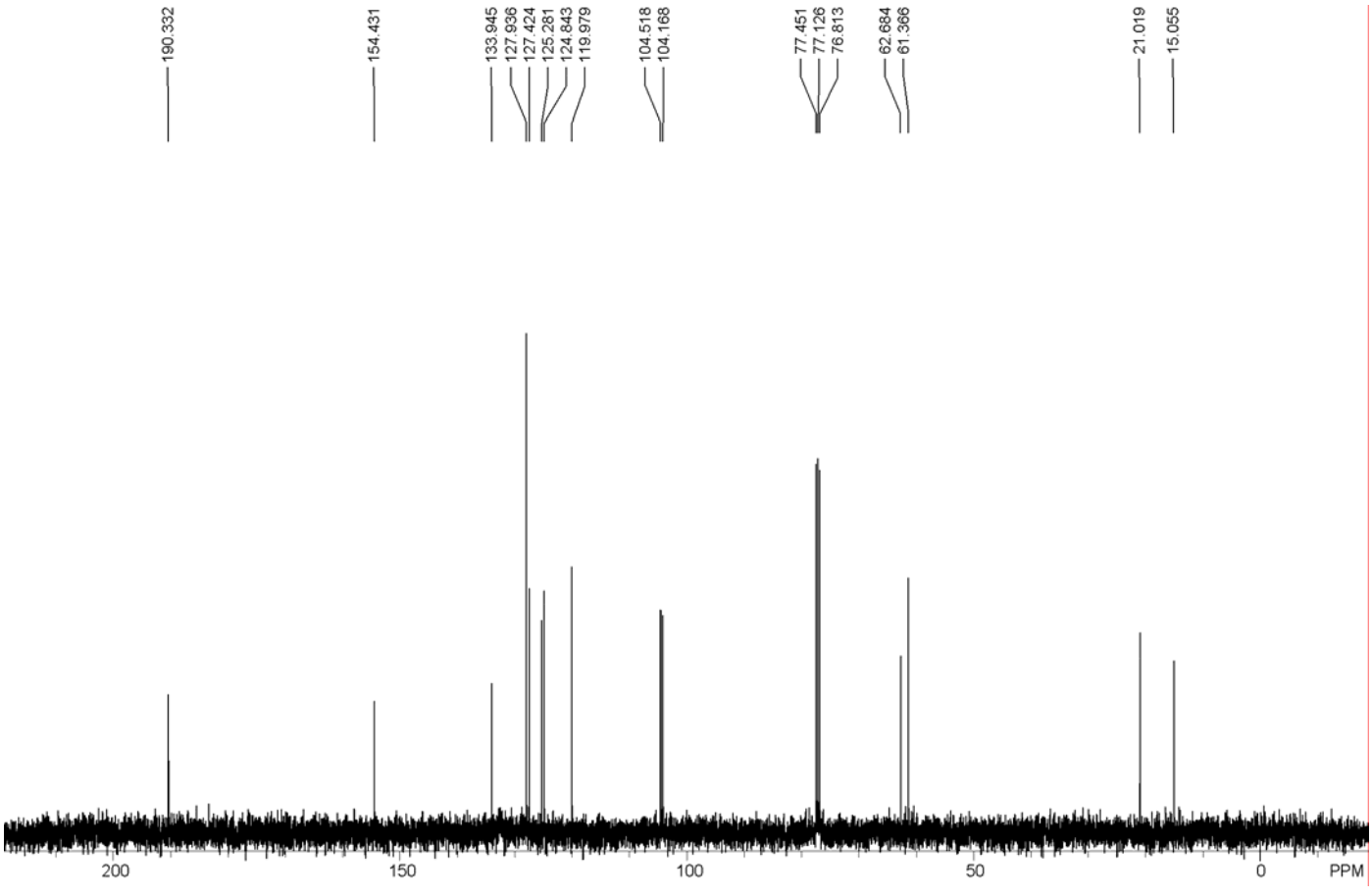
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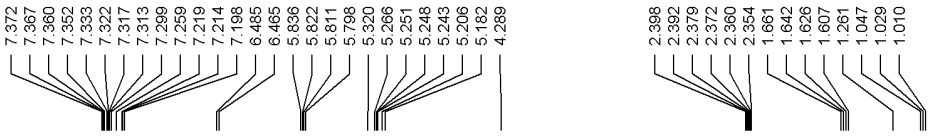
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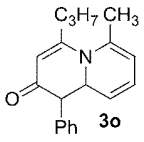
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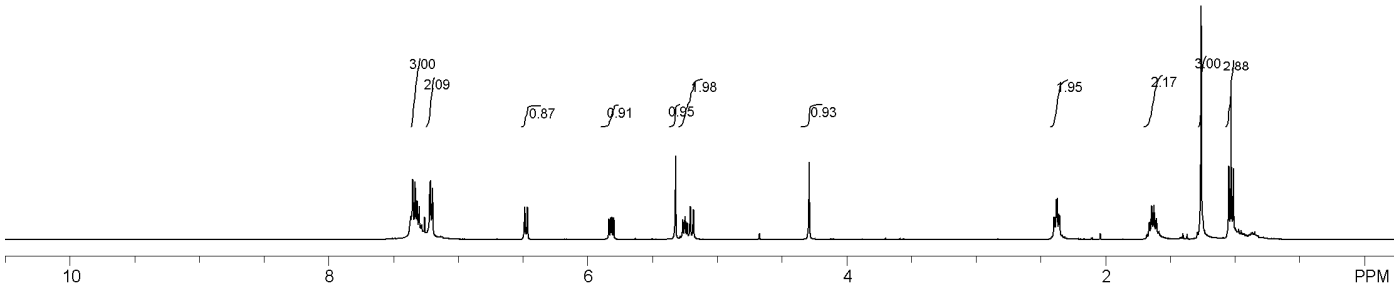
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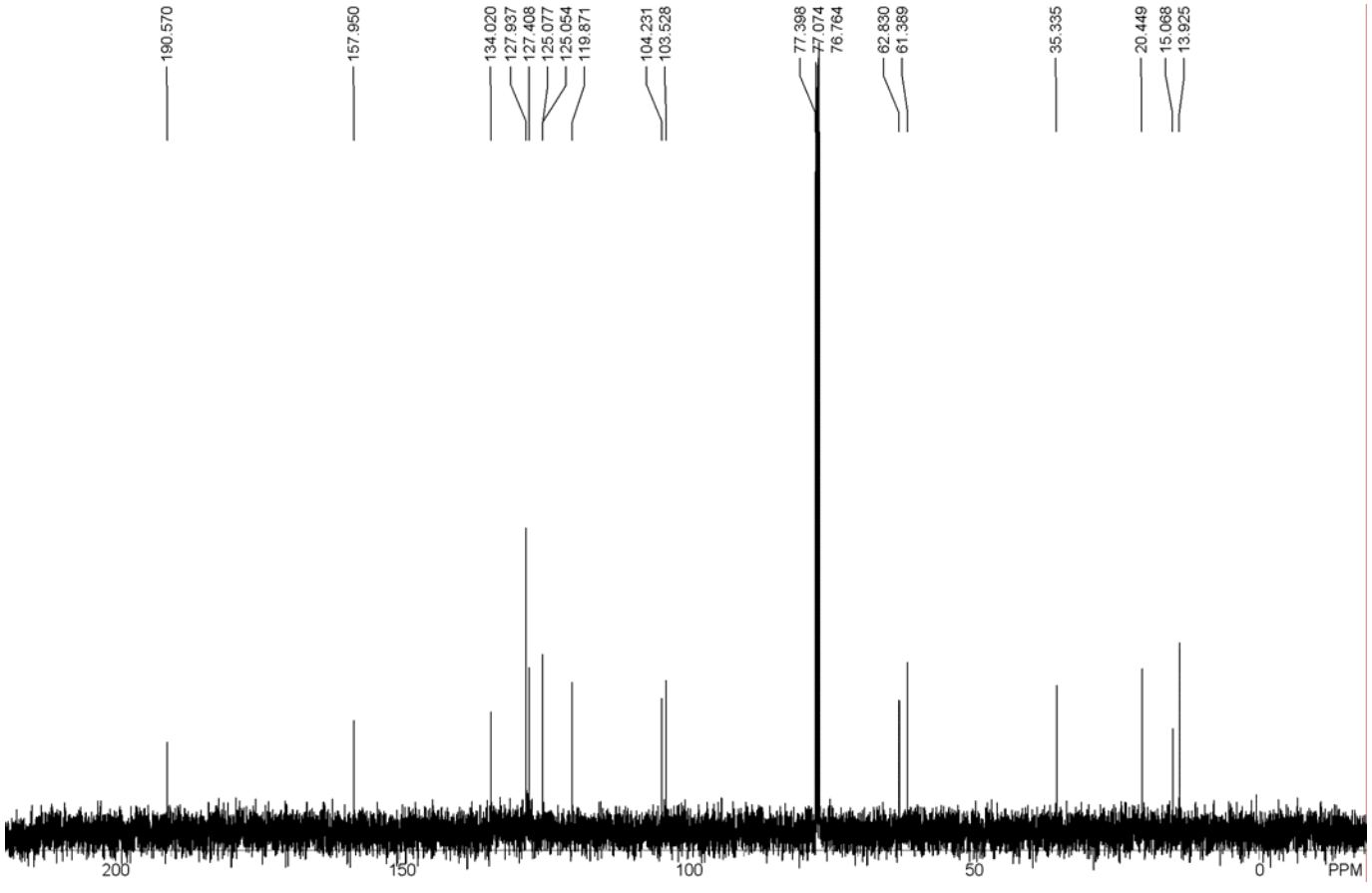
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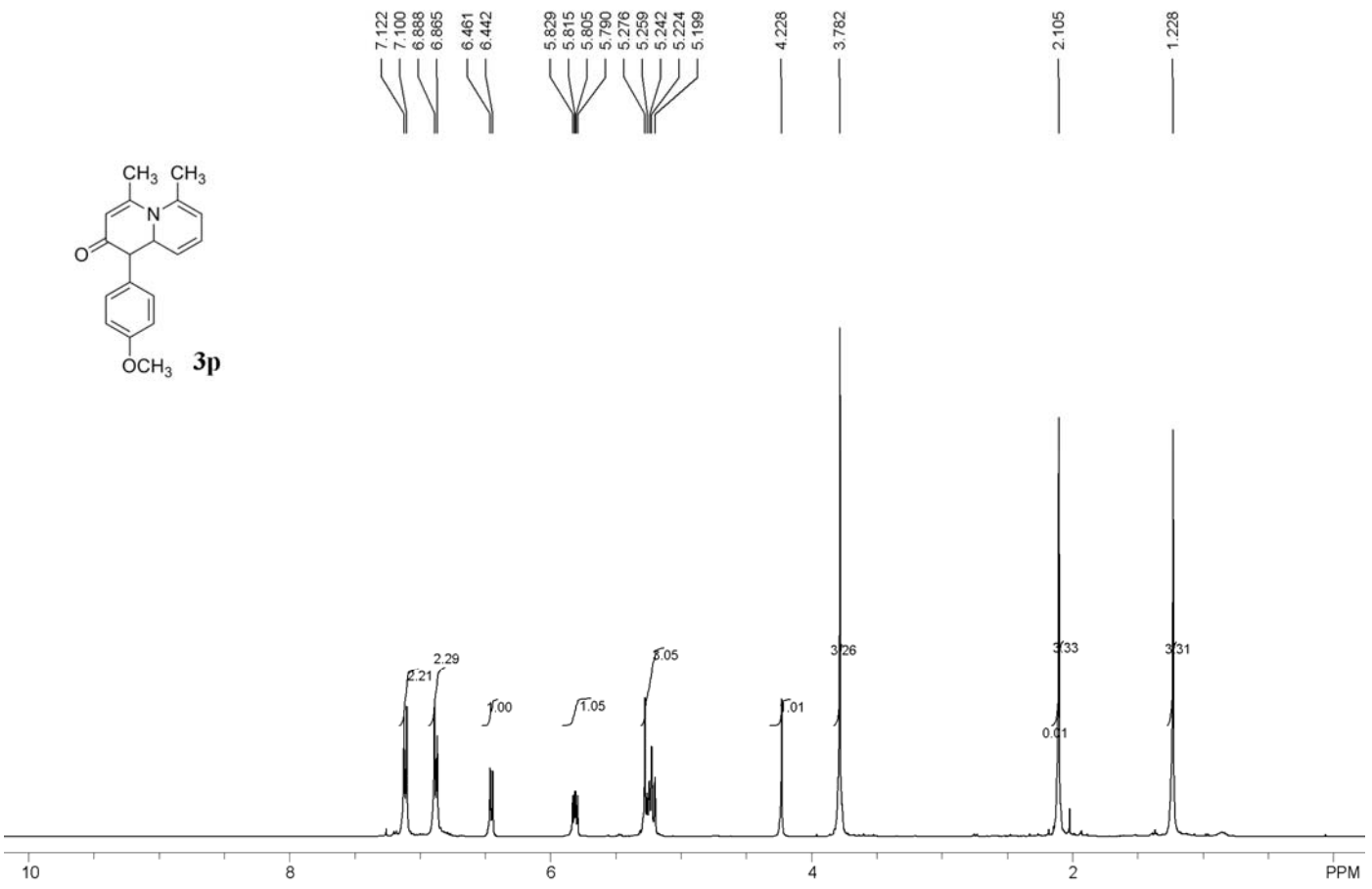

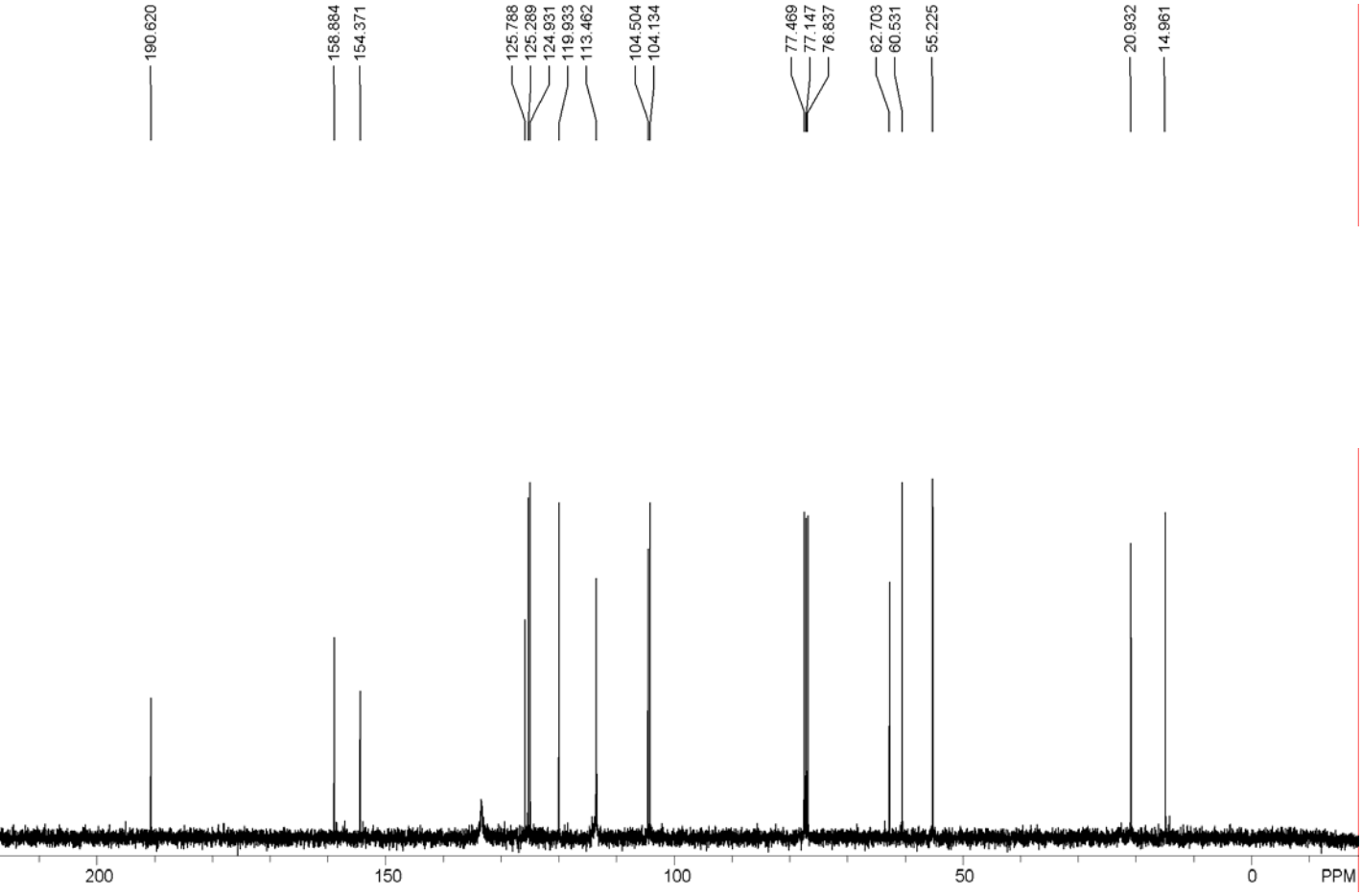

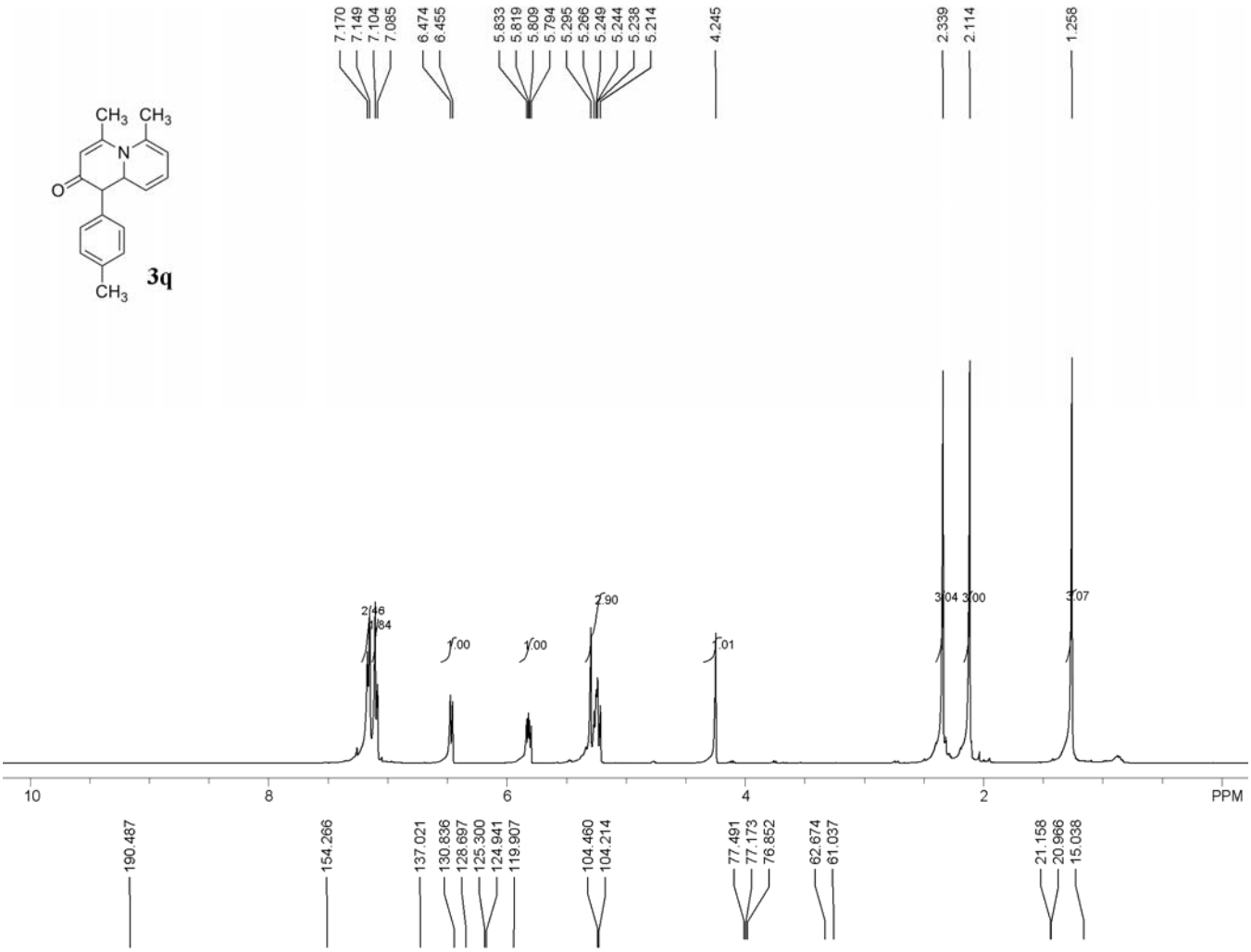

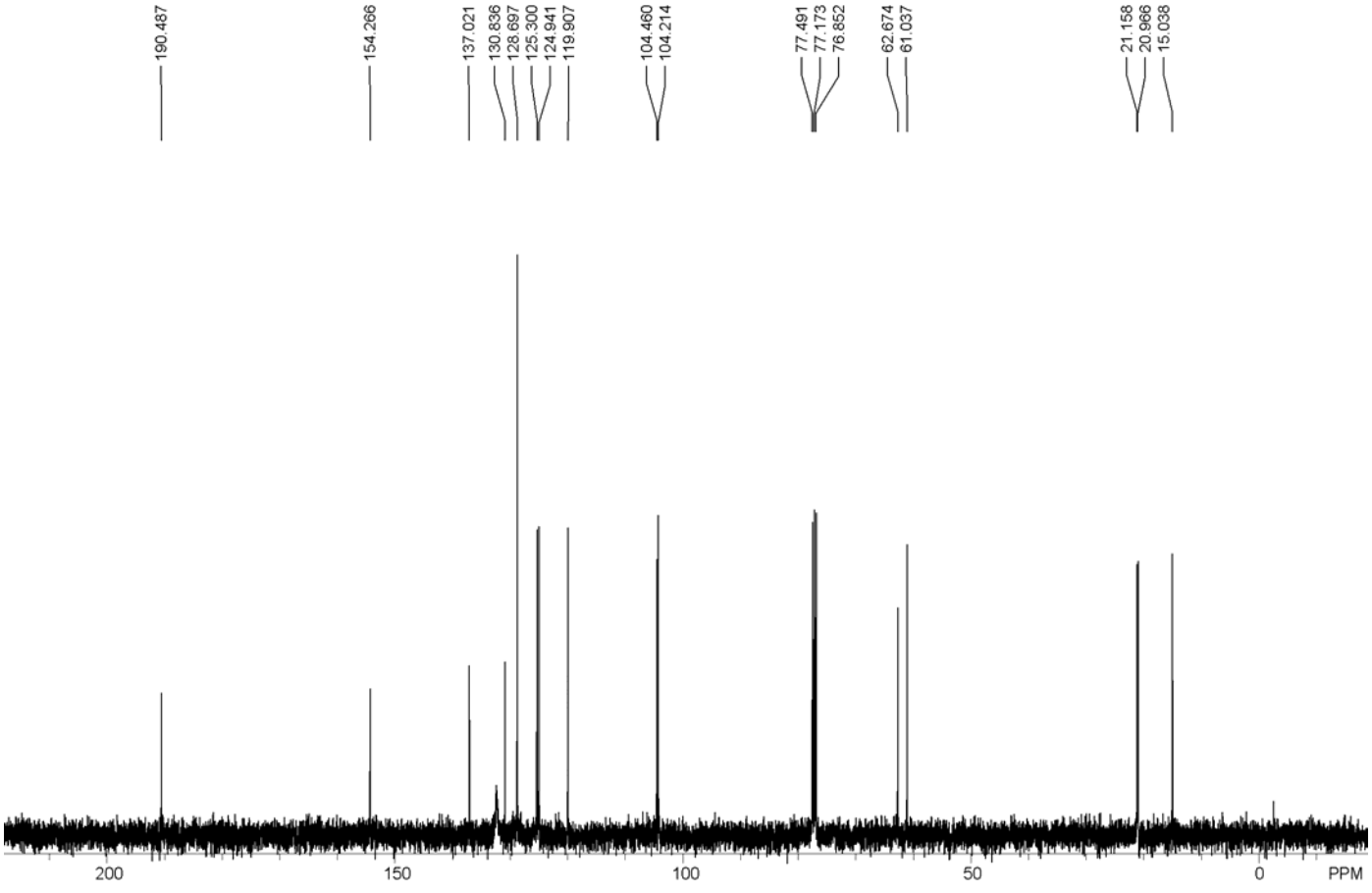

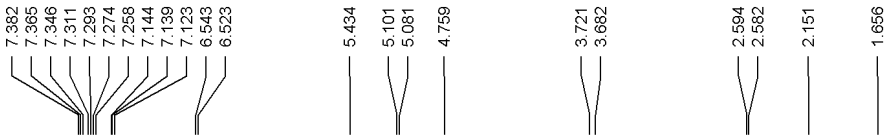

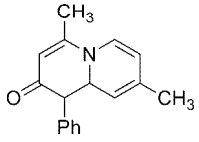

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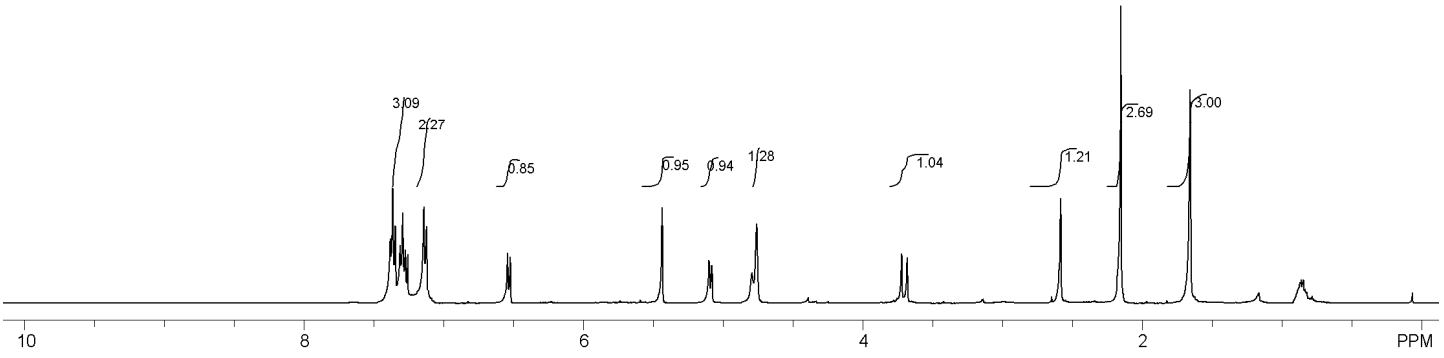

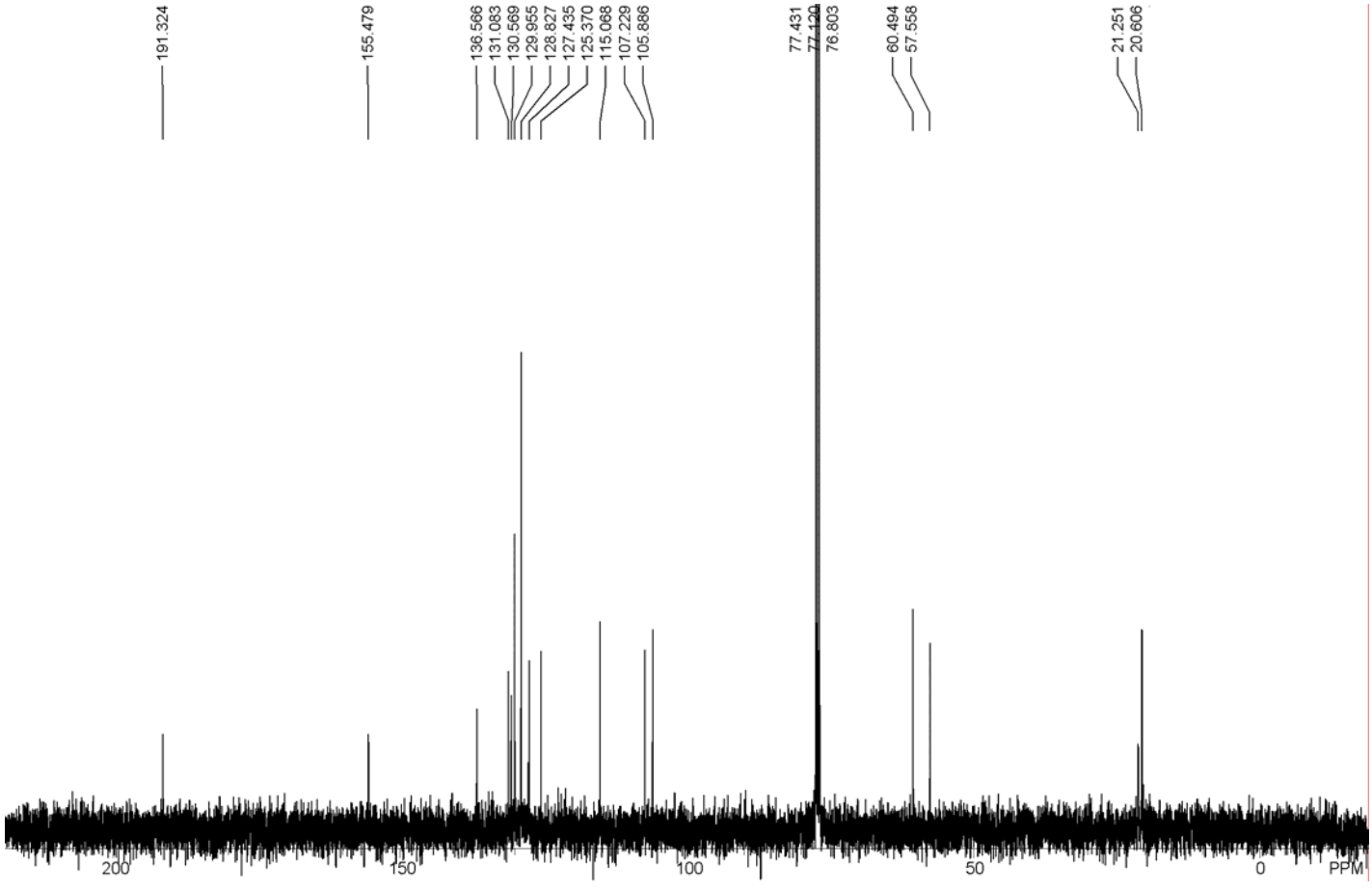

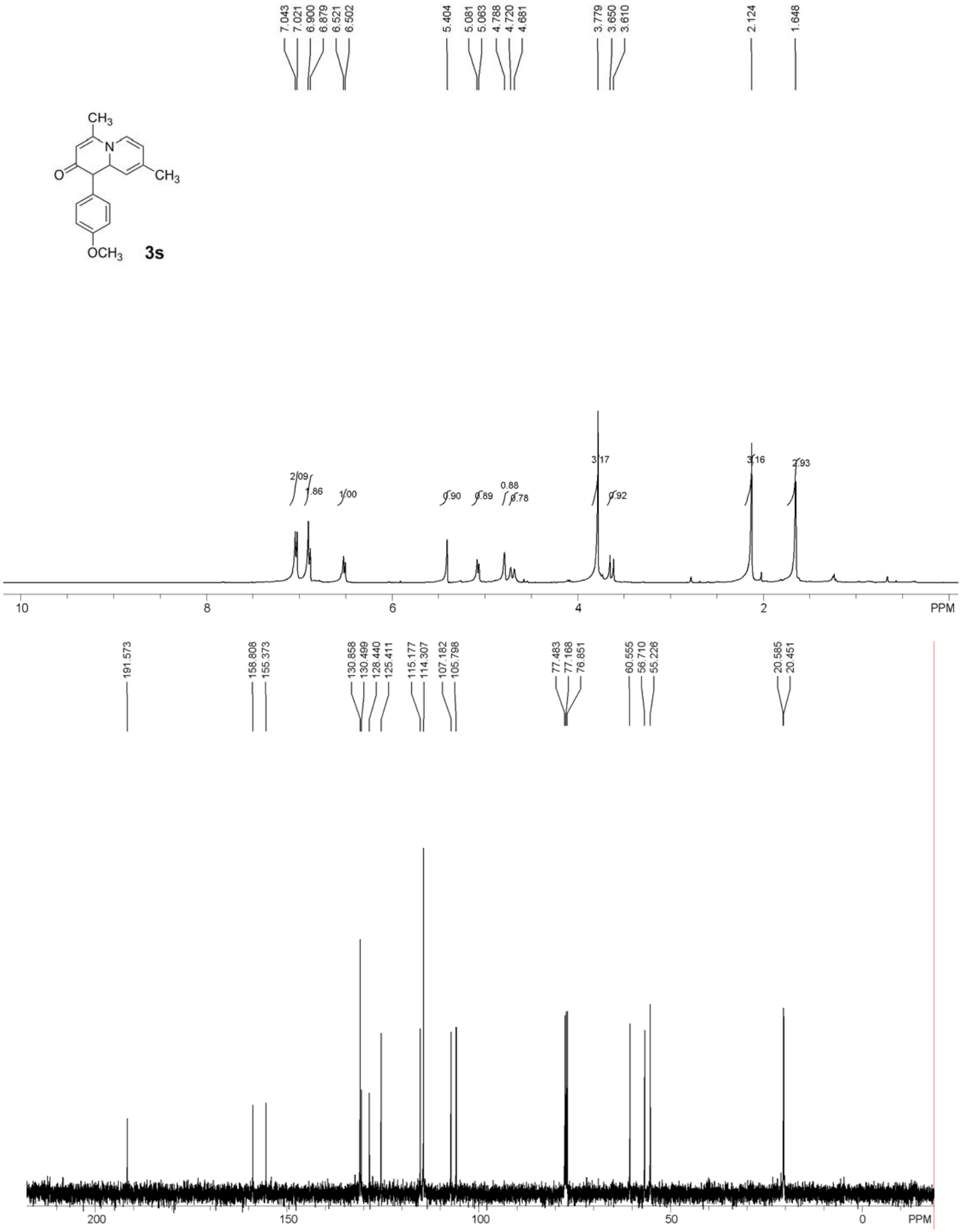
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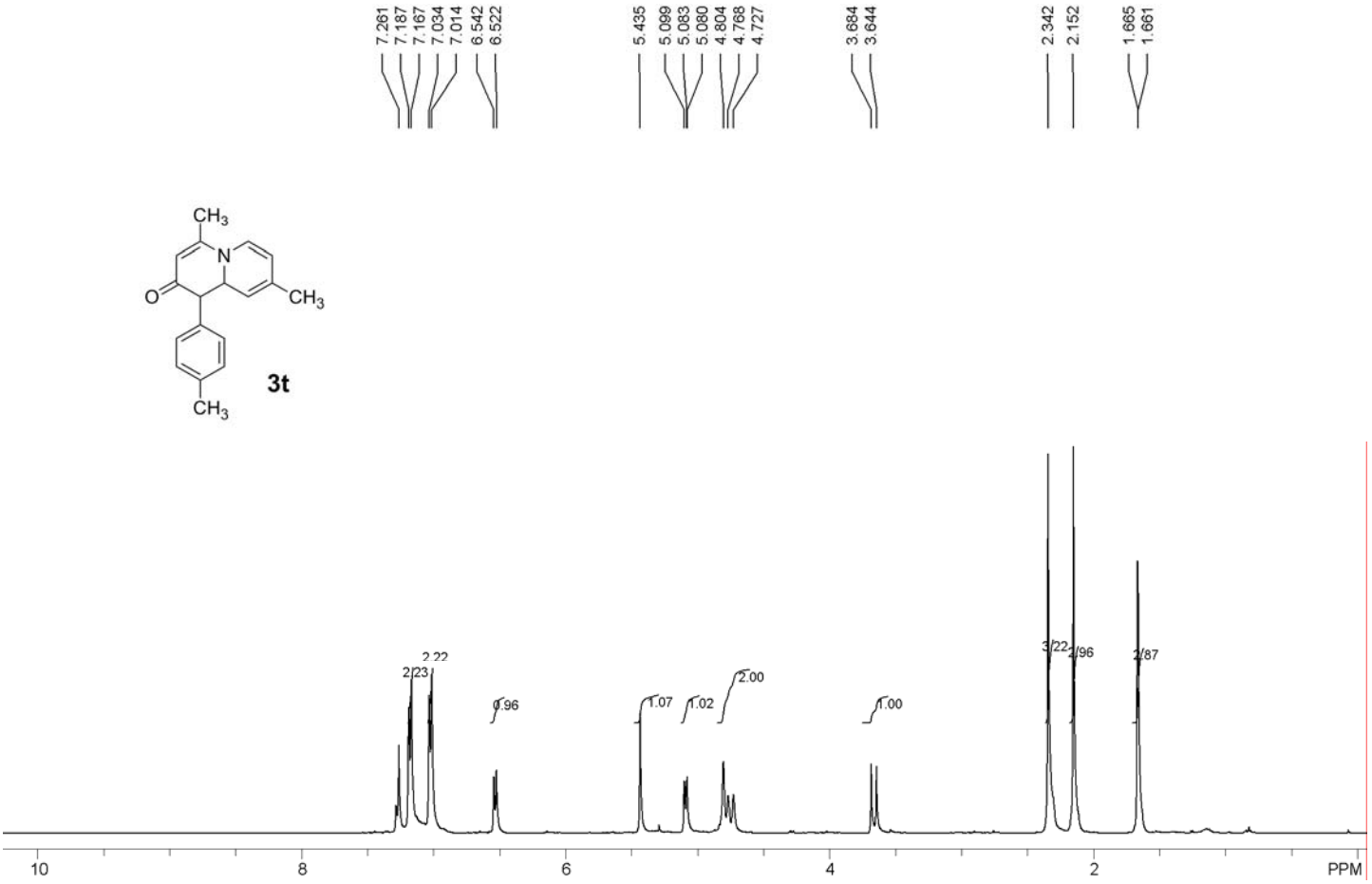

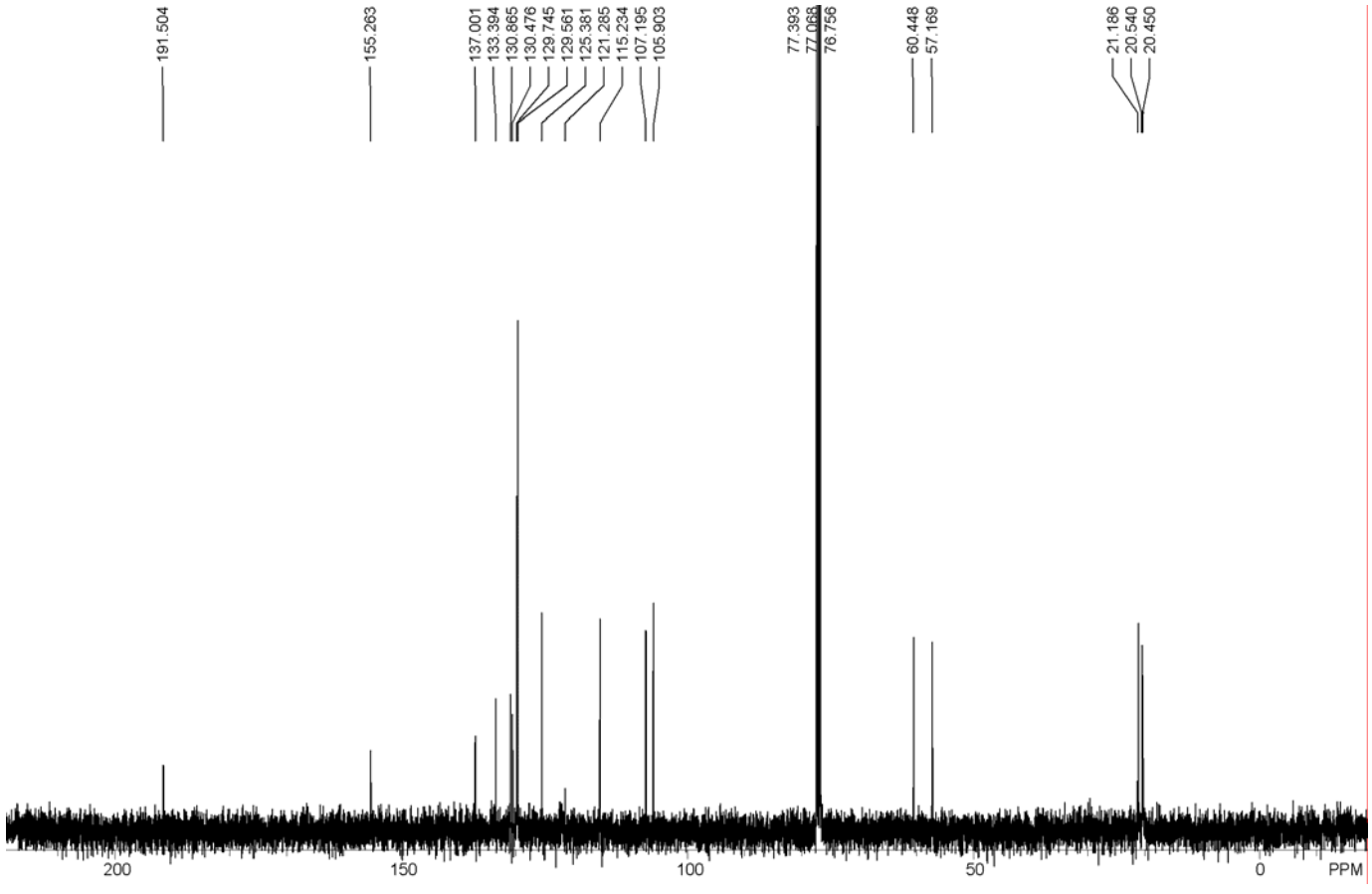

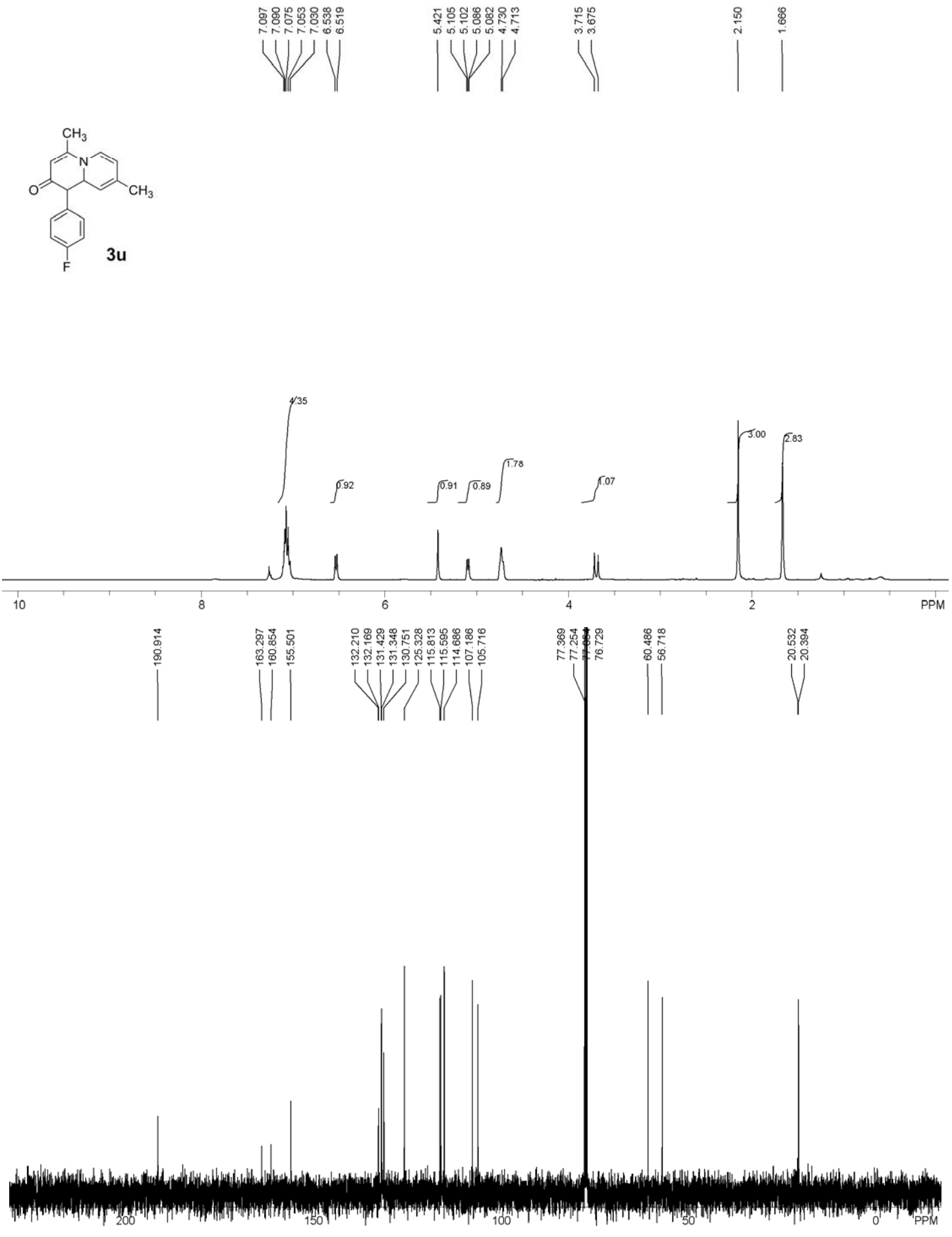

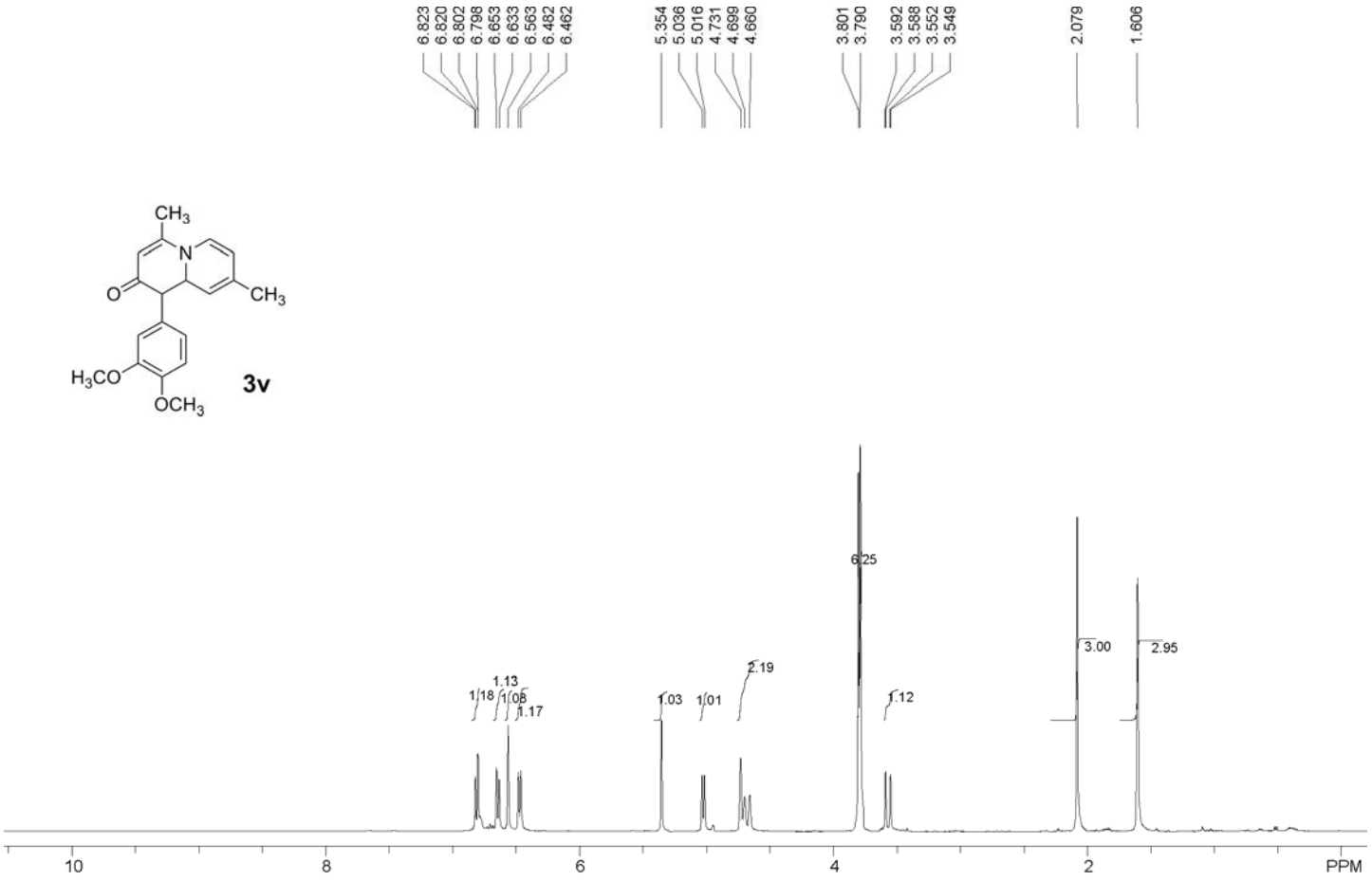
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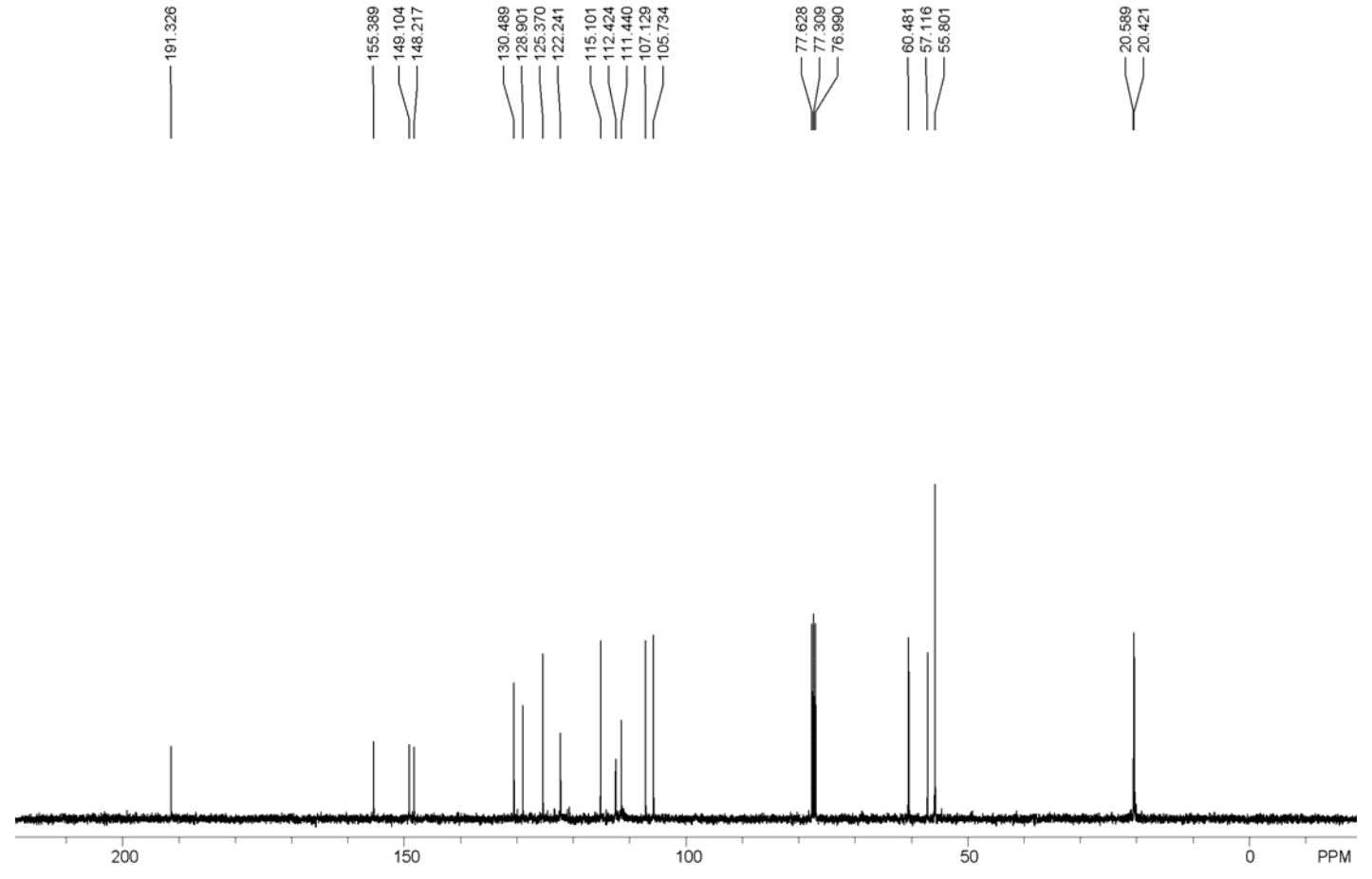
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148.217
130.489
128.901
125.370
122.241
115.101
112.424
111.440
107.129
105.734
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76.990
60.481
57.116
55.801
20.589
20.421
200
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100
50
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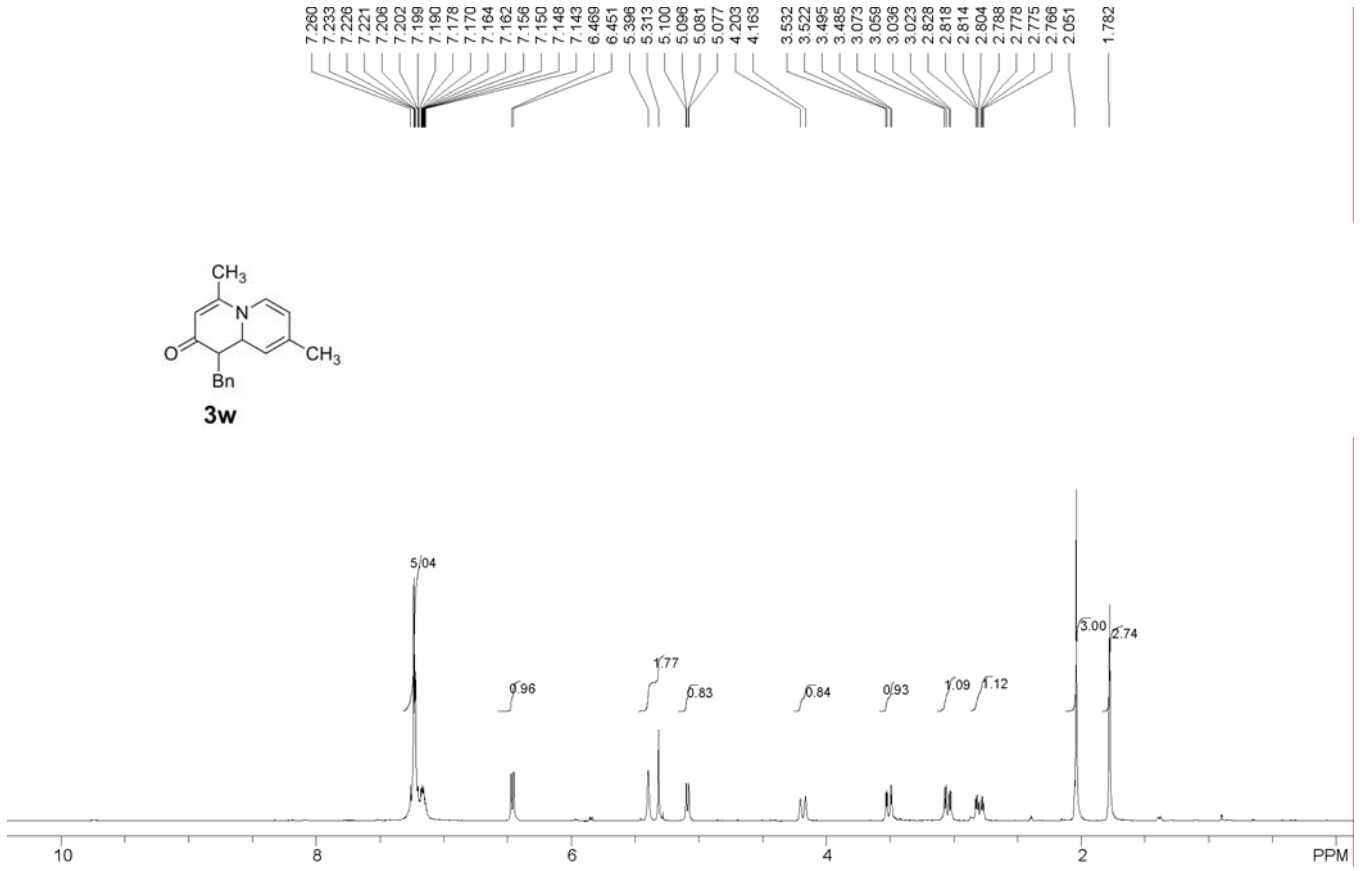
PPM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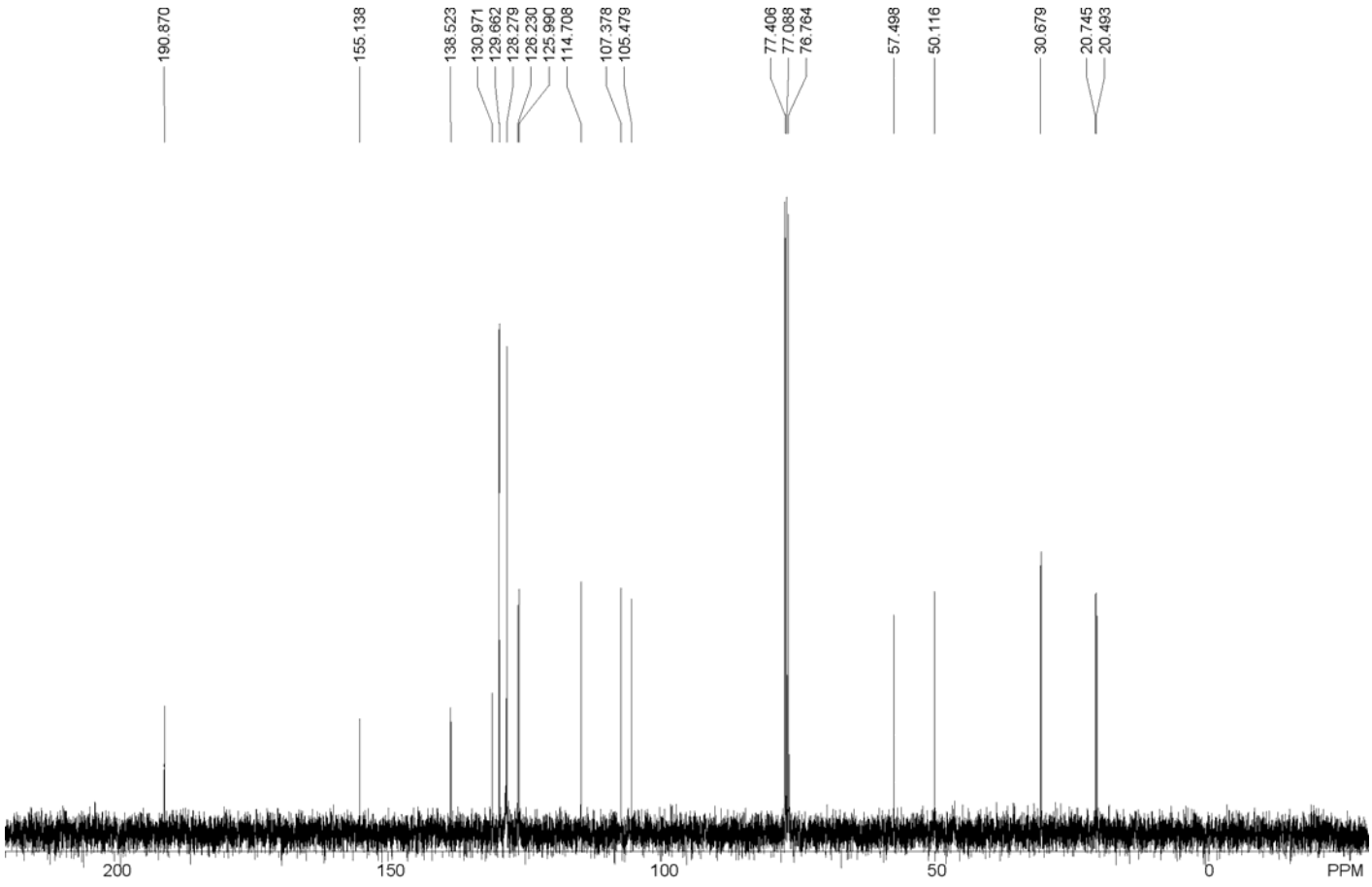
7.202
7.199
7.190
7.178
7.170
7.164
7.162
7.156
7.150
7.148
7.143
6.469
6.451
5.396
5.313
5.100
5.096
5.081
5.077
4.203
4.163
3.532
3.522
3.495
3.485
3.073
3.059
3.036
3.023
2.828
2.818
2.814
2.804
2.788
2.778
2.775
2.766
2.051
1.782
CH3
N
O
CH3
Bn
3w
5.04
0.96
1.77
0.83
0.84
0.93
1.09
1.12
3.00
2.74
10
8
6
4
2
PPM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125.990
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105.479
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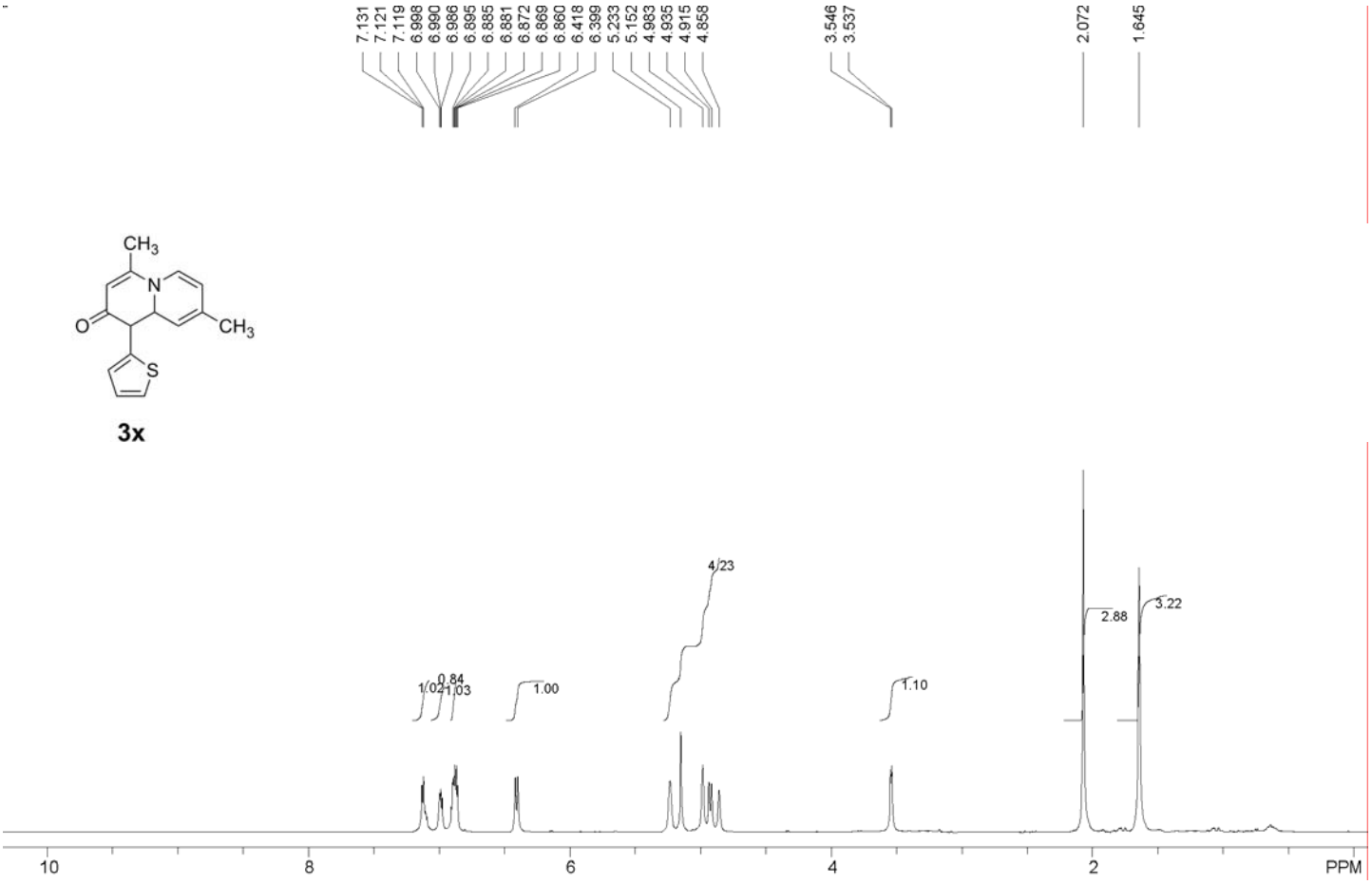
77.088
76.764
57.498
50.116
30.679
20.745
20.493
200
150
100
50
0
PPM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7.121
7.119
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6.990
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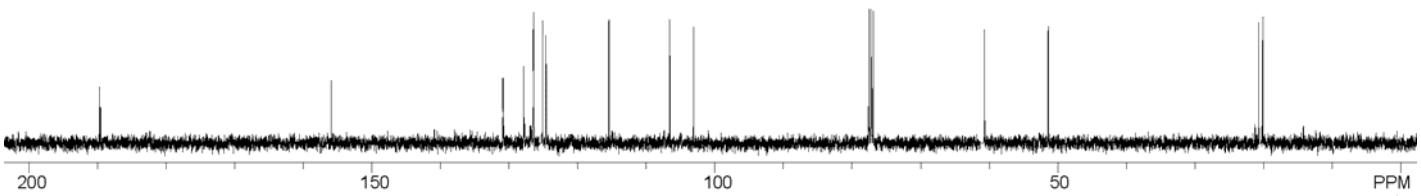
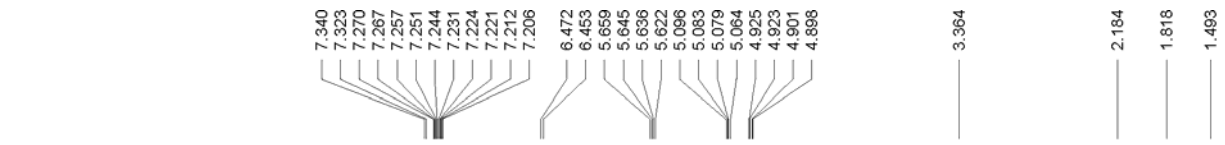
6.895
6.885
6.881
6.872
6.869
6.860
6.418
6.399
5.233
5.152
4.983
4.935
4.915
4.858
3.546
3.537
2.072
1.645
CH3
N
O
CH3
S
3x
4.23
2.88
3.22
0.84
1.02
1.03
1.00
1.10
10
8
6
4
2
PPM


189.705
155.898
130.879
127.856
126.435
126.376
125.112
124.610
115.441
106.562
103.106
77.555
77.239
76.921
60.685
51.404
20.715
20.126


200
150
100
50
PPM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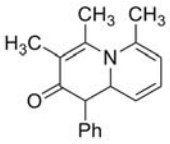
7.323
7.270
7.267
7.257
7.251
7.244
7.231
7.224
7.221
7.212
7.206
6.472
6.453
5.659
5.645
5.636
5.622
5.096
5.083
5.079
5.064
4.925
4.923
4.901
4.898
3.364
2.184
1.818
1.493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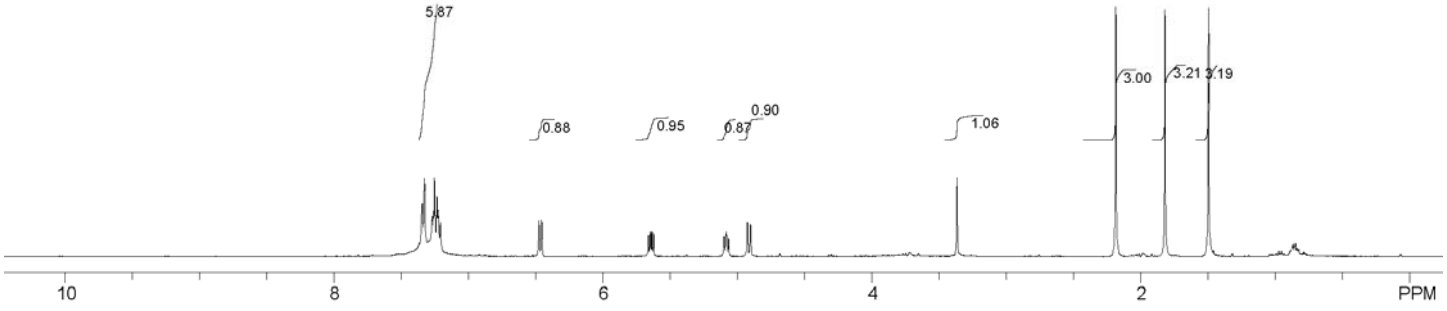
CH3
H3C
N
O
Ph

3y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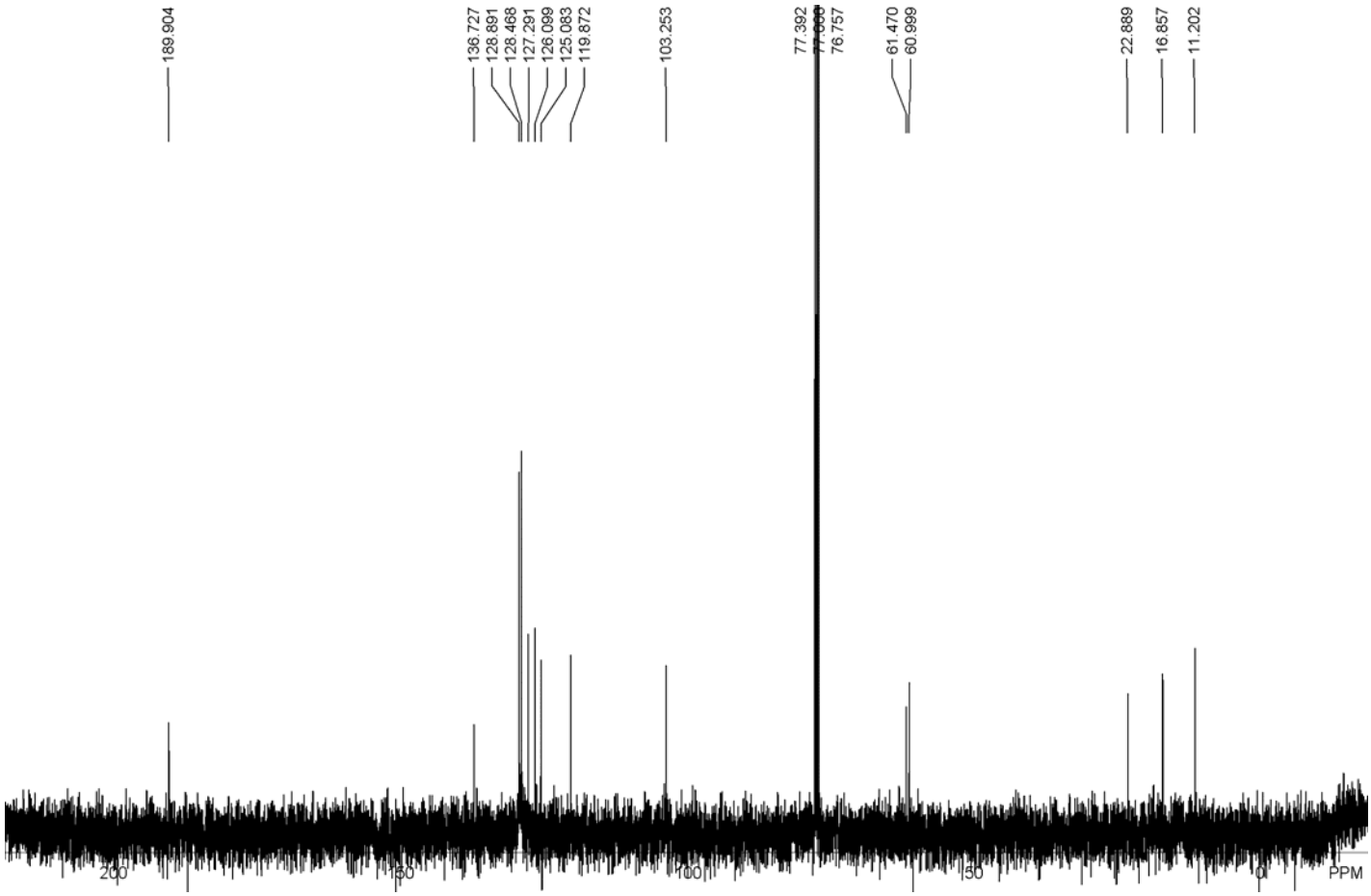
0.87
0.90
1.06
3.00
3.21
3.19
10
8
6
4
2
PPM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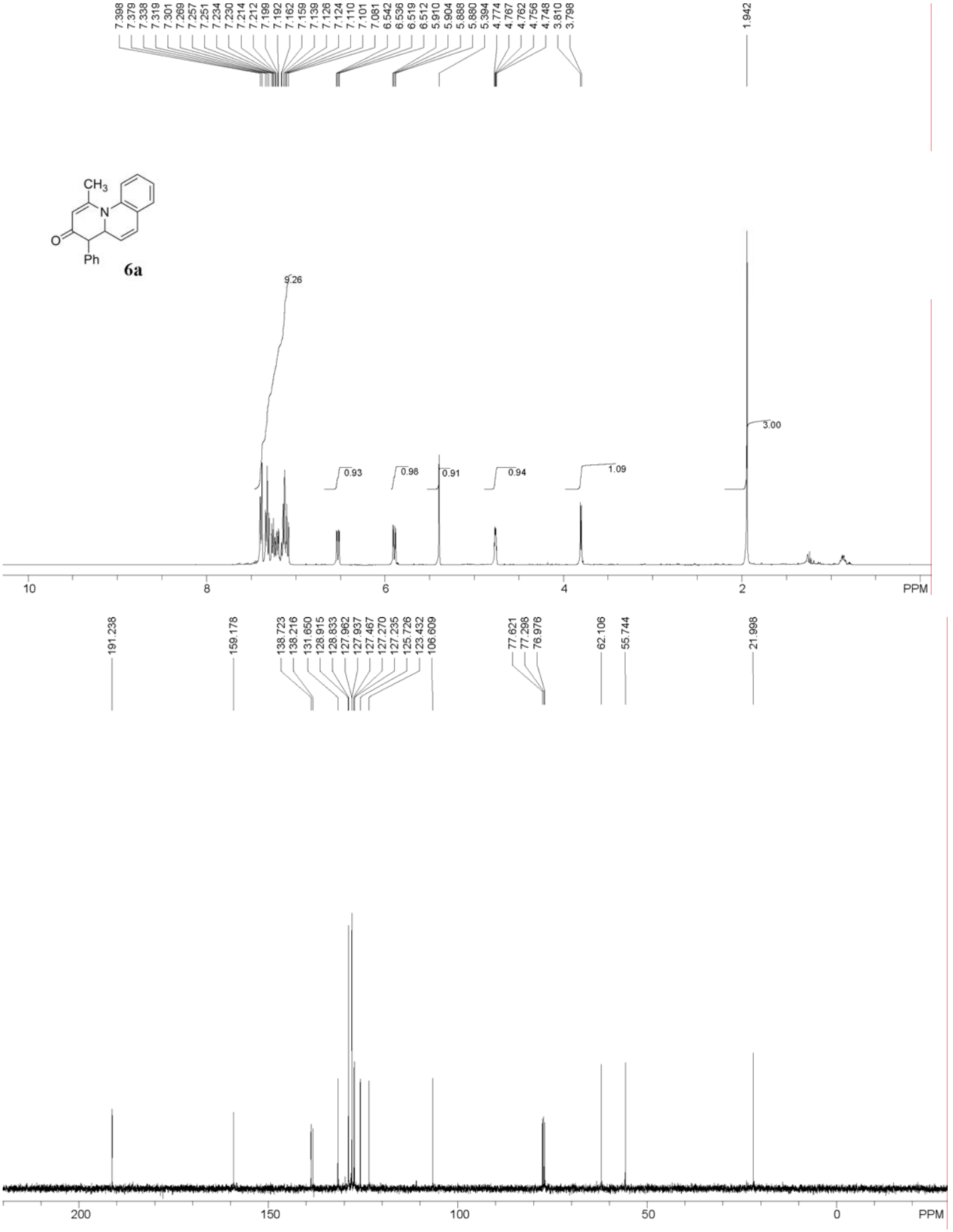
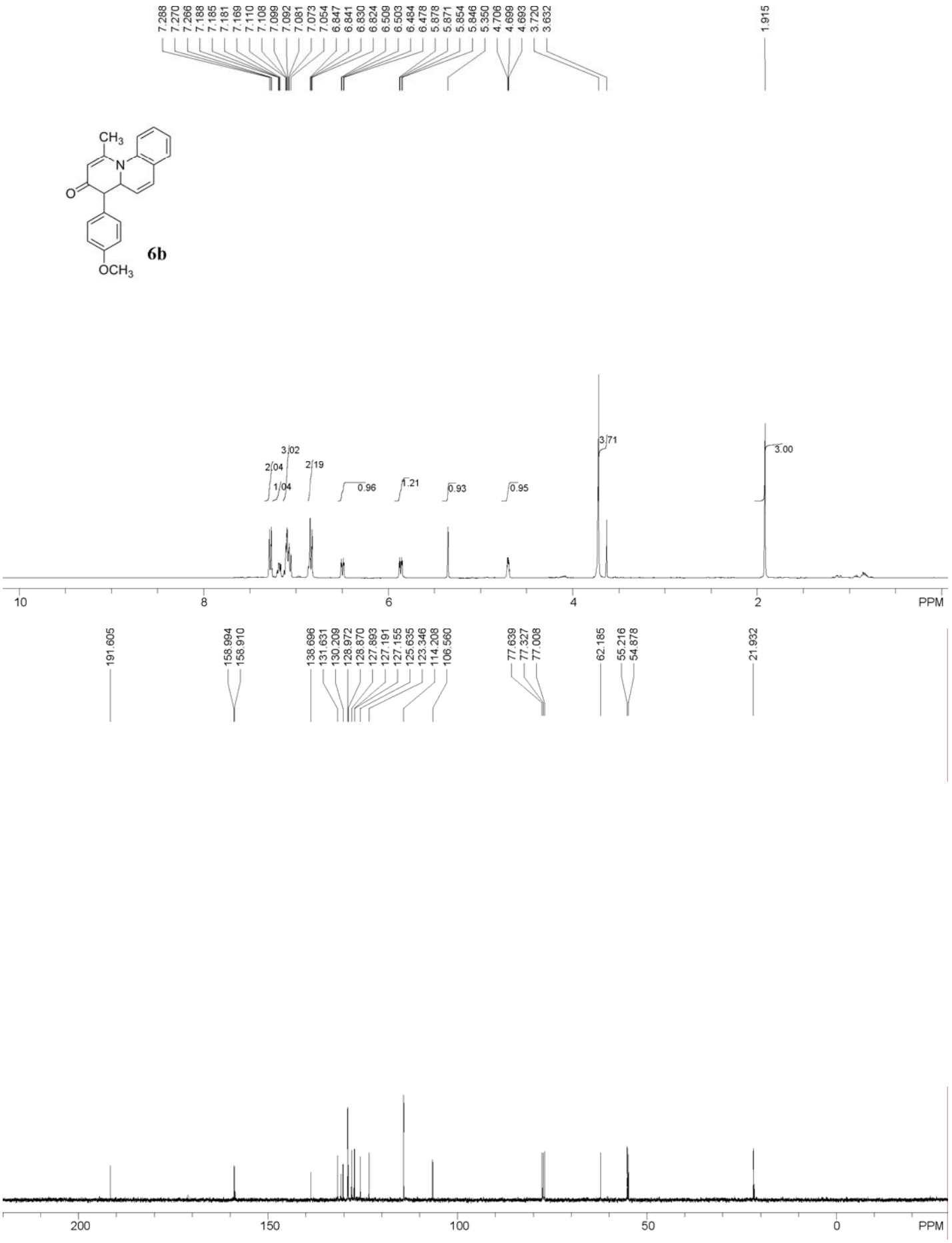
136.727
128.891
128.468
127.291
126.099
125.083
119.872
103.253
77.392
77.000
76.757
61.470
60.999
22.889
16.857
11.202
200
150
100
50
0
PPM

III. Copies of ^{1}H and ^{13}C NMR spectra of compounds 6a-6r

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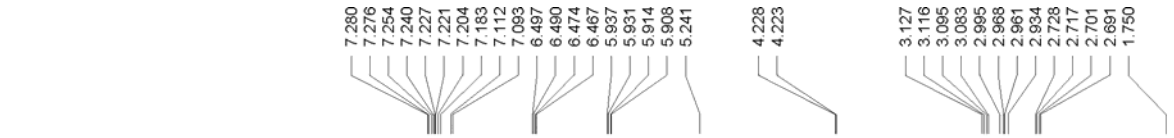
7.270
7.266
7.188
7.185
7.181
7.169
7.110
7.108
7.099
7.092
7.081
7.073
7.054
6.847
6.841
6.830
6.824
6.509
6.503
6.484
6.478
5.878
5.871
5.854
5.846
5.350
4.706
4.699
4.693
3.720
3.632
1.915
CH3
N
O
OCH3
6b
3.02
2.04
2.19
1.04
0.96
1.21
0.93
0.95
3.71
3.00
10
8
6
4
2
PPM
191.605
158.994
158.910
138.696
131.631
130.209
128.972
128.870
127.893
127.191
127.155
125.635
123.346
114.208
106.560
77.639
77.327
77.008
62.185
55.216
54.878
21.932
200
150
100
50
0
PPM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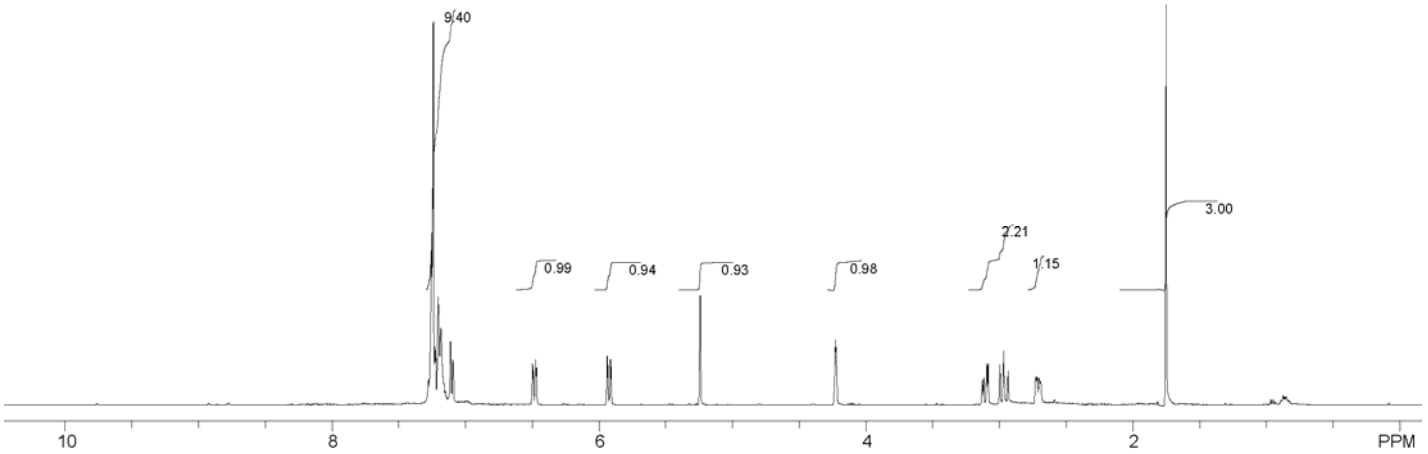
7.276
7.254
7.240
7.227
7.221
7.204
7.183
7.112
7.093
6.497
6.490
6.474
6.467
5.937
5.931
5.914
5.908
5.241
4.228
4.223
3.127
3.116
3.095
3.083
2.995
2.968
2.961
2.934
2.728
2.717
2.701
2.691
1.750


CH3
N
O
Bn

6c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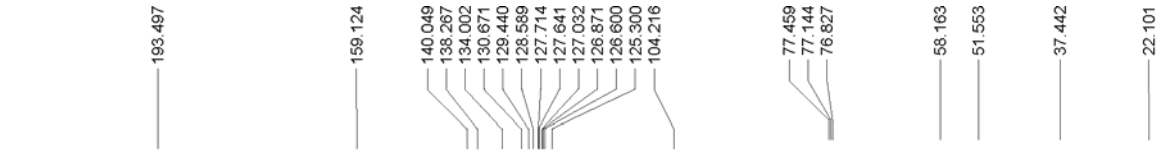
0.99
0.94
0.93
0.98
2.21
1.15
3.00
10
8
6
4
2
PPM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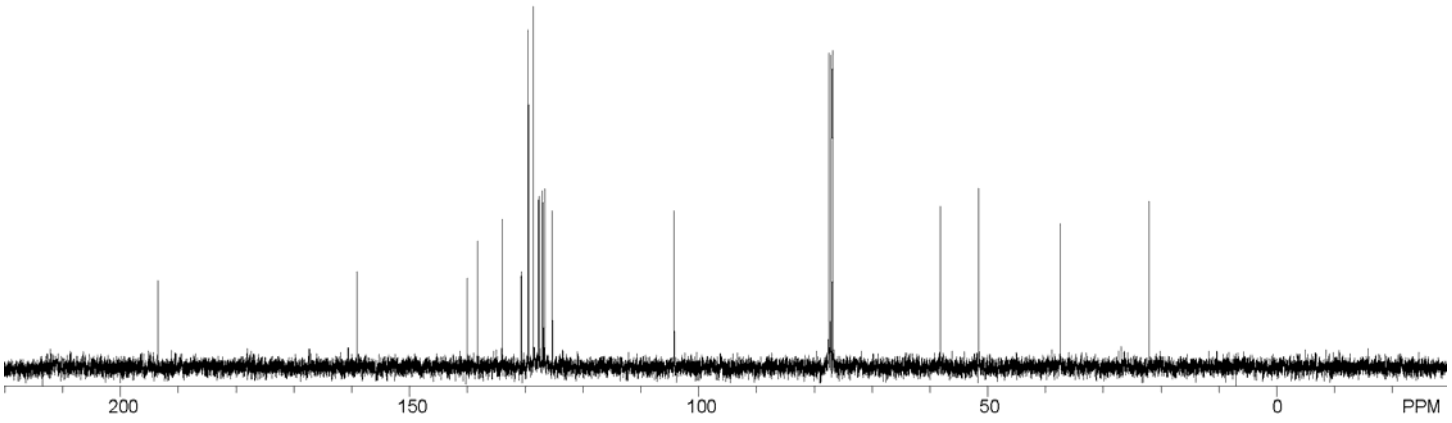
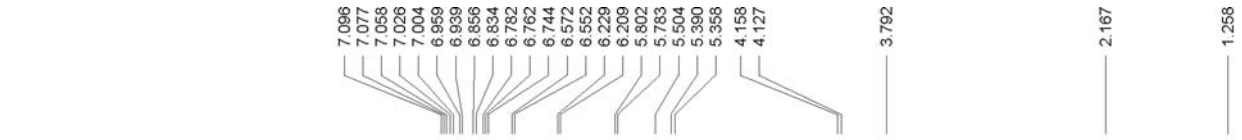
140.049
138.267
134.002
130.671
129.440
128.589
127.714
127.641
127.032
126.871
126.600
125.300
104.216
77.459
77.144
76.827
58.163
51.553
37.442
22.101


200
150
100
50
0
PPM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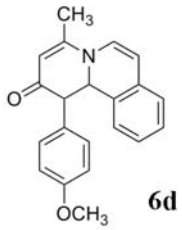
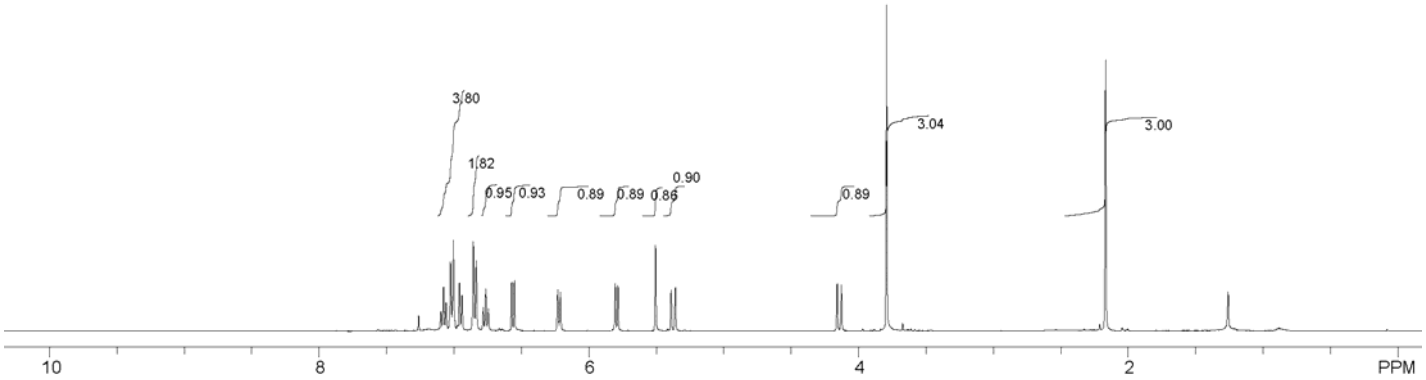
7.077
7.058
7.026
7.004
6.959
6.939
6.856
6.834
6.782
6.762
6.744
6.572
6.552
6.229
6.209
5.802
5.783
5.504
5.390
5.358
4.158
4.127
3.792
2.167
1.258


CH3
N
O
OCH3

6d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0.95
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0.89
0.89
0.86
0.90
0.89
3.04
3.00
10
8
6
4
2
PPM


191.821
158.891
156.323
131.219
130.607
129.266
127.855
127.763
127.024
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125.706
124.195
114.103
107.075
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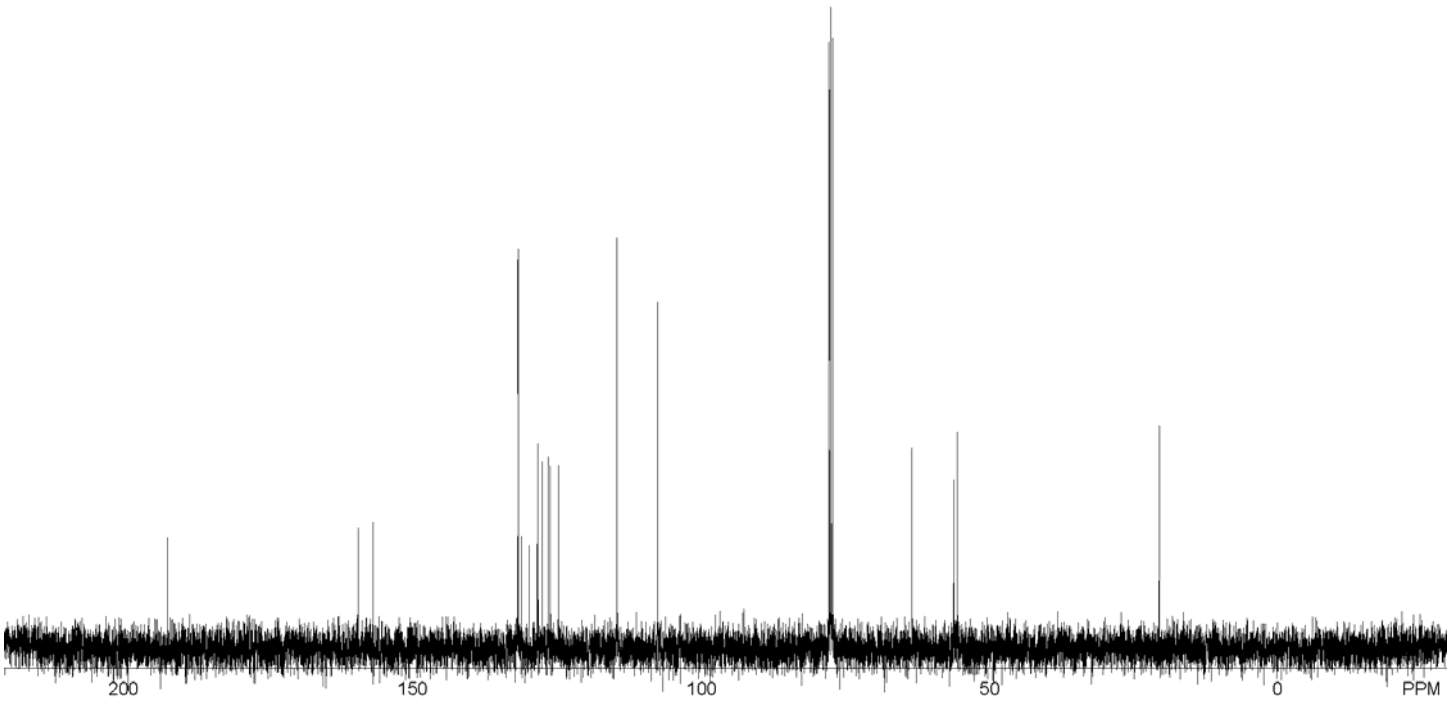
77.093
76.777
63.081
55.864
55.287
20.367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150
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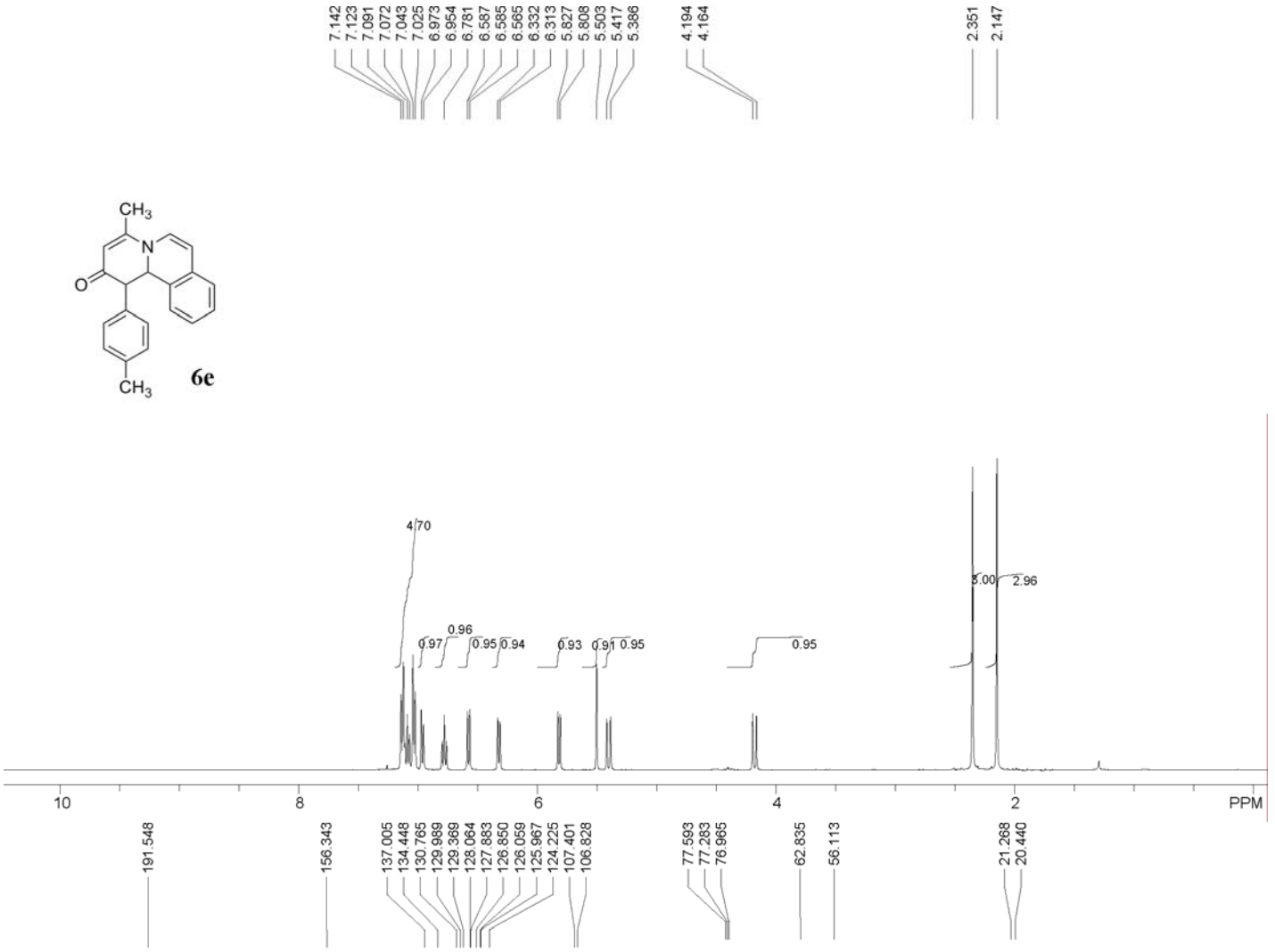
50
0
PPM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6.954
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6.587
6.585
6.565
6.332
6.313
5.827
5.808
5.503
5.417
5.386
4.194
4.164
2.351
2.147
CH3
N
O
CH3
6e
4.70
0.97
0.96
0.95
0.94
0.93
0.91
0.95
0.95
5.00
2.96
10
8
6
4
2
PPM
191.548
156.343
137.005
134.448
130.765
129.989
129.369
128.064
127.883
126.850
126.059
125.967
124.225
107.401
106.828
77.593
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76.965
62.835
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21.268
20.440
200
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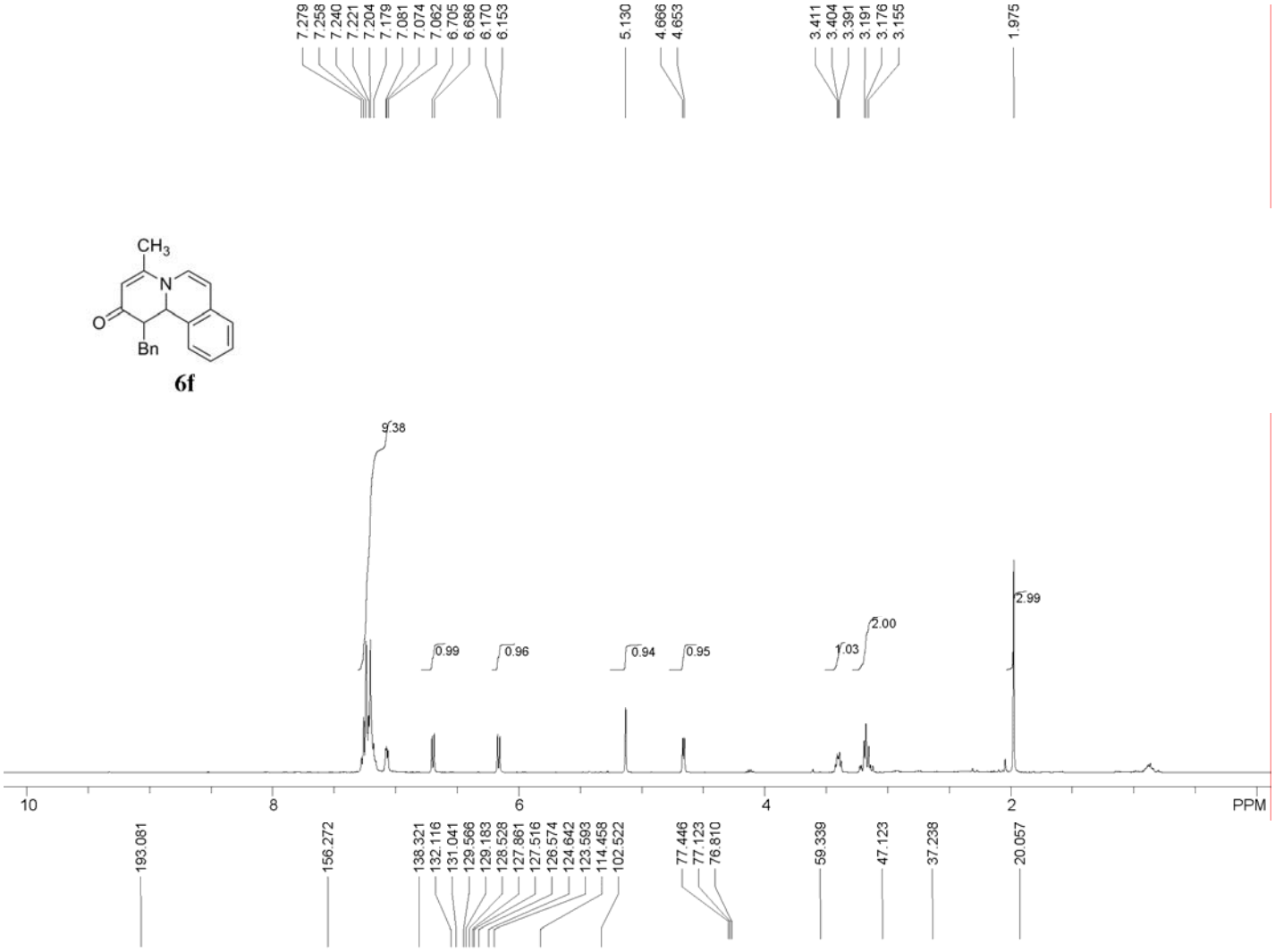
50
0
PPM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7.240
7.221
7.204
7.179
7.081
7.074
7.062
6.705
6.686
6.170
6.153
5.130
4.666
4.653
3.411
3.404
3.391
3.191
3.176
3.155
1.975
CH3
N
O
Bn
9.38
0.99
0.96
0.94
0.95
1.03
2.00
2.99
10
8
6
4
2
PPM
193.081
156.272
138.321
132.116
131.041
129.566
129.183
128.528
127.861
127.516
126.574
124.642
123.593
114.458
102.522
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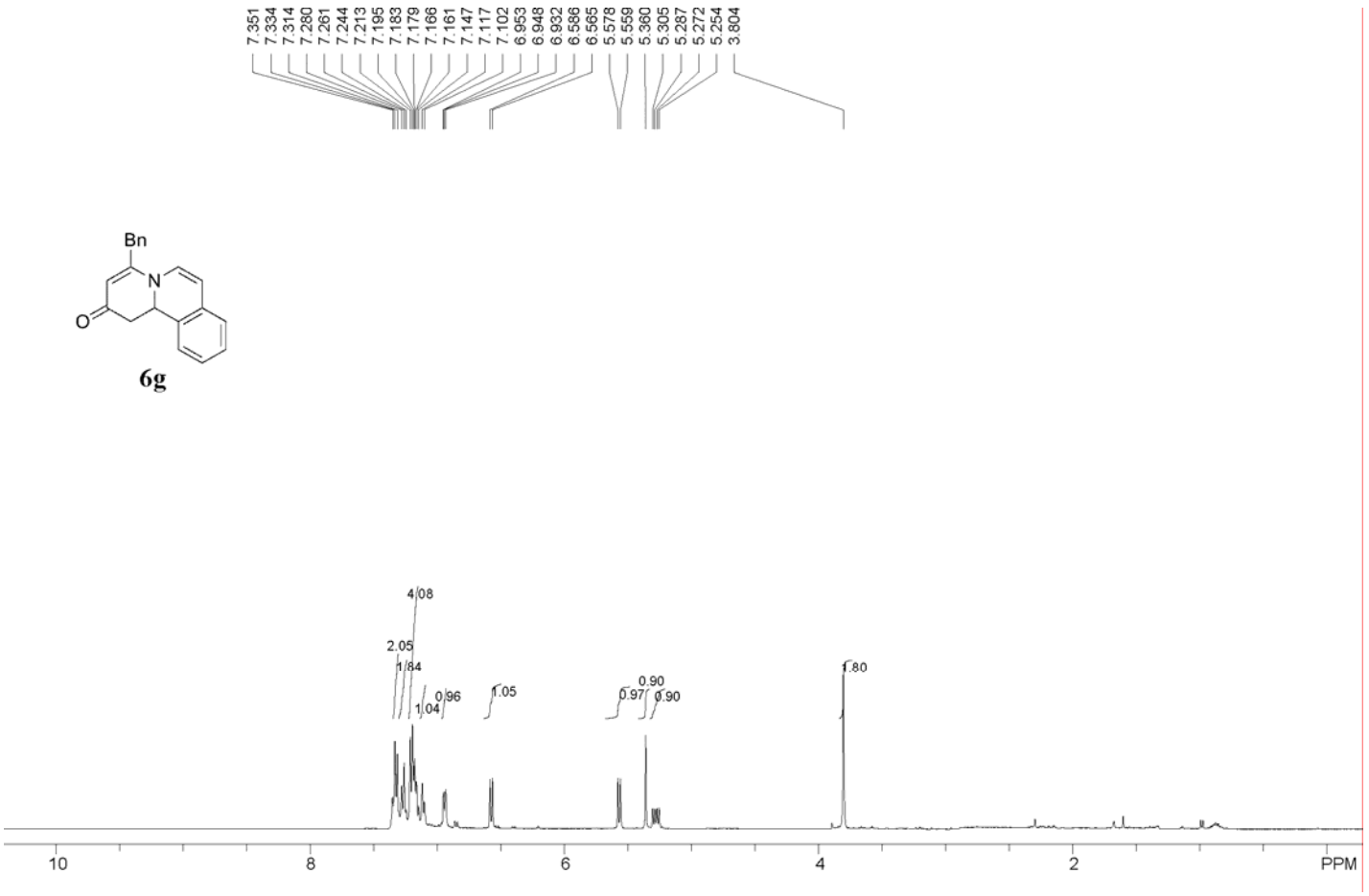
77.123
76.810
59.339
47.123
37.238
20.057
200
150
100
50
0
PPM

6f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7.244
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7.195
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7.179
7.166
7.161
7.147
7.117
7.102
6.953
6.948
6.932
6.586
6.565
5.578
5.559
5.360
5.305
5.287
5.272
5.254
3.804
Bn
N
O
4.08
2.05
1.84
1.04
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1.05
0.97
0.90
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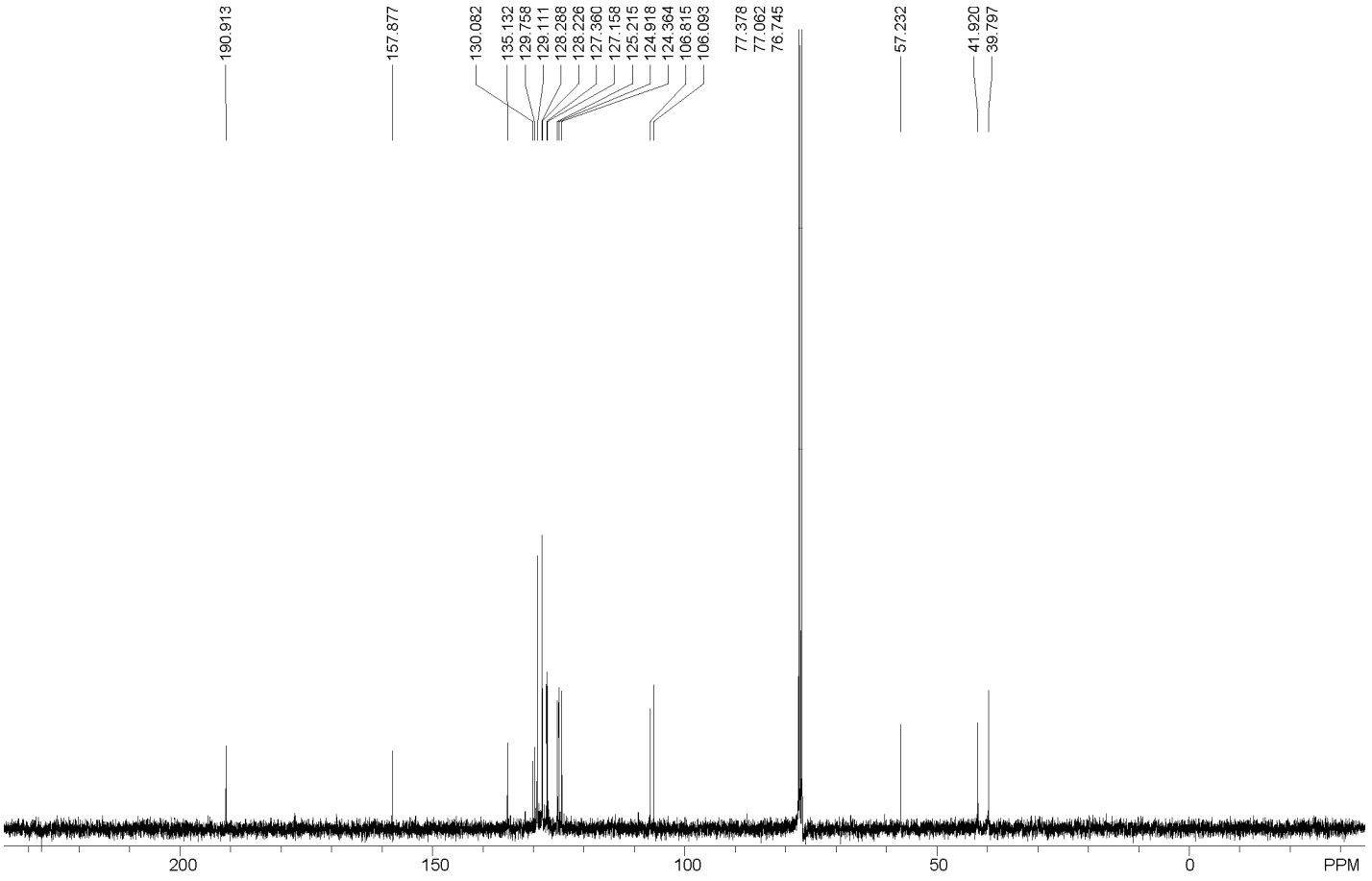
1.80
10
8
6
4
2
PPM

6g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125.215
124.918
124.364
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77.378
77.062
76.745
57.232
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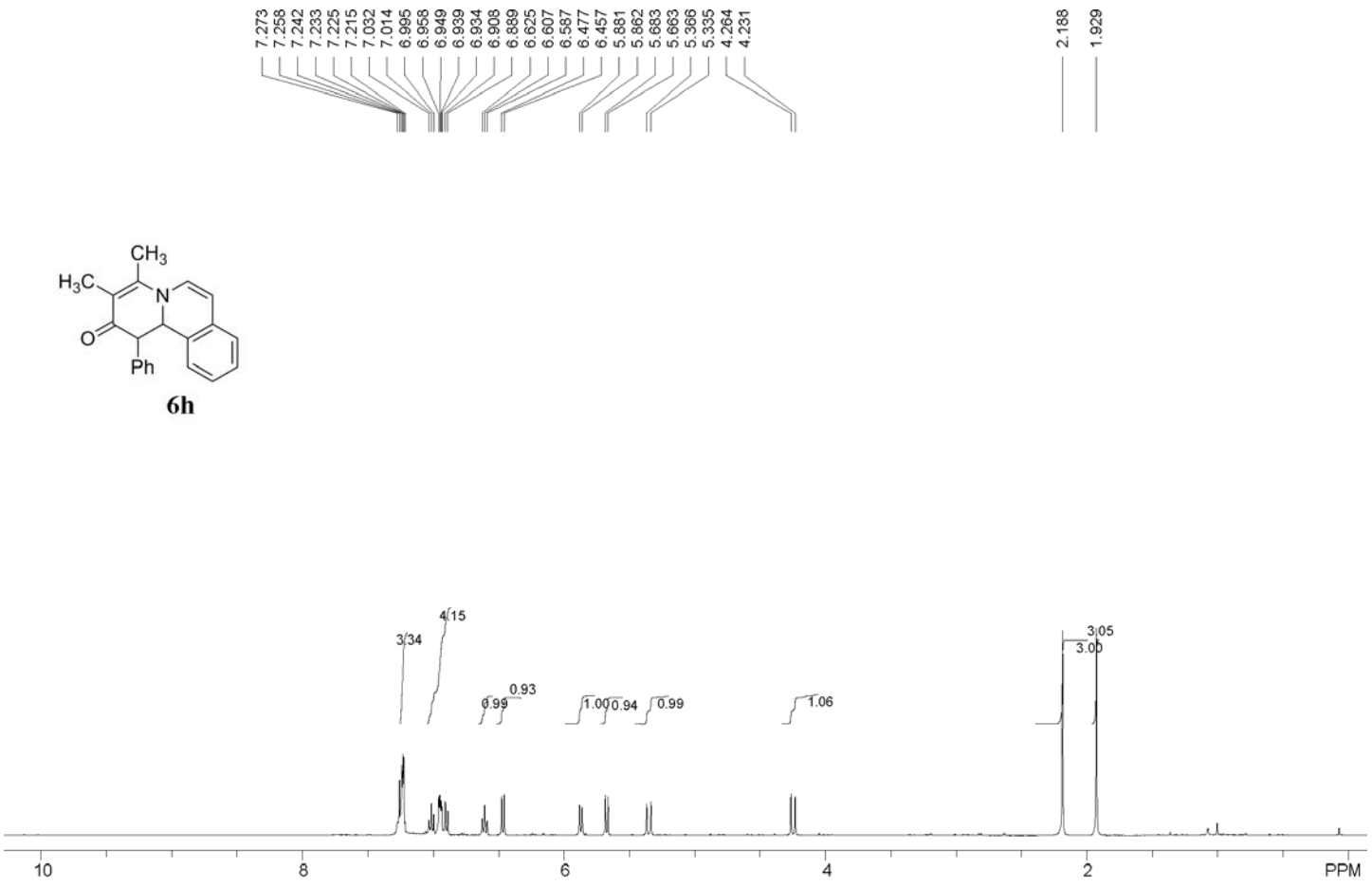
150
100
50
0
PPM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7.233
7.225
7.215
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7.014
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6.958
6.949
6.939
6.934
6.908
6.889
6.625
6.607
6.587
6.477
6.457
5.881
5.862
5.683
5.663
5.366
5.335
4.264
4.231
2.188
1.929
CH3
H3C
N
O
Ph
6h
4.15
3.34
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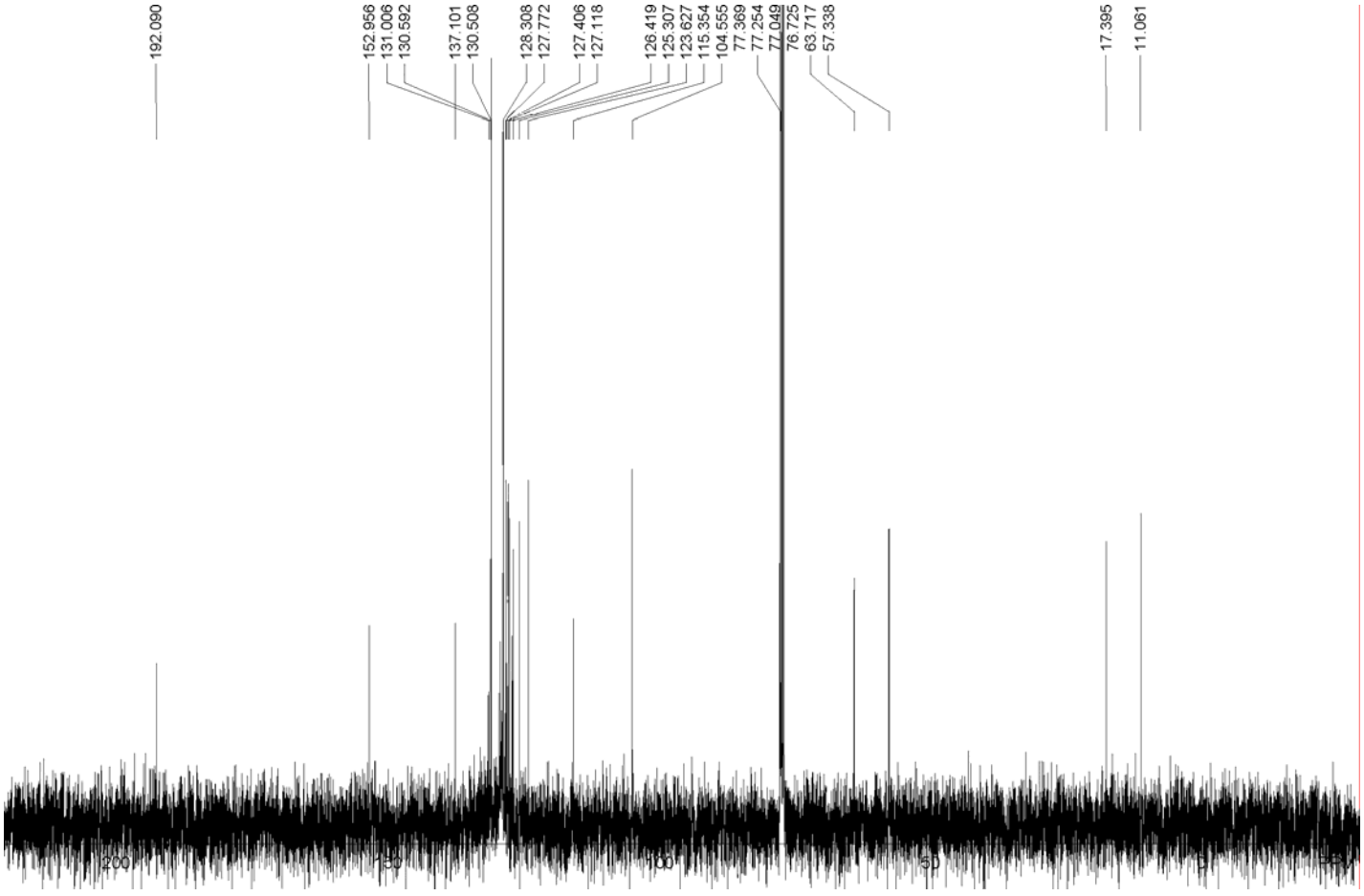
1.00
0.94
0.99
1.06
3.05
3.00
10
8
6
4
2
PPM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137.101
130.508
128.308
127.772
127.406
127.118
126.419
125.307
123.627
115.354
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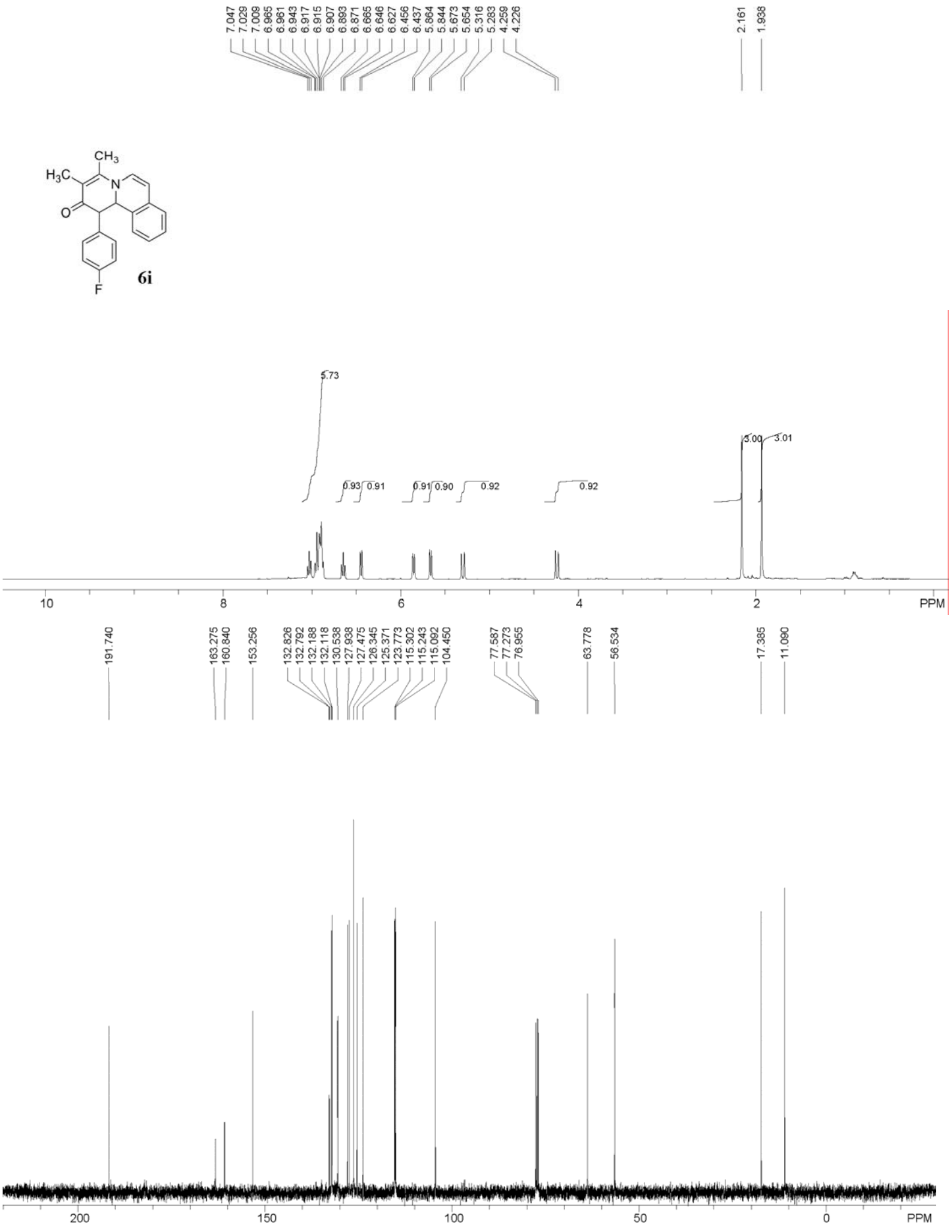
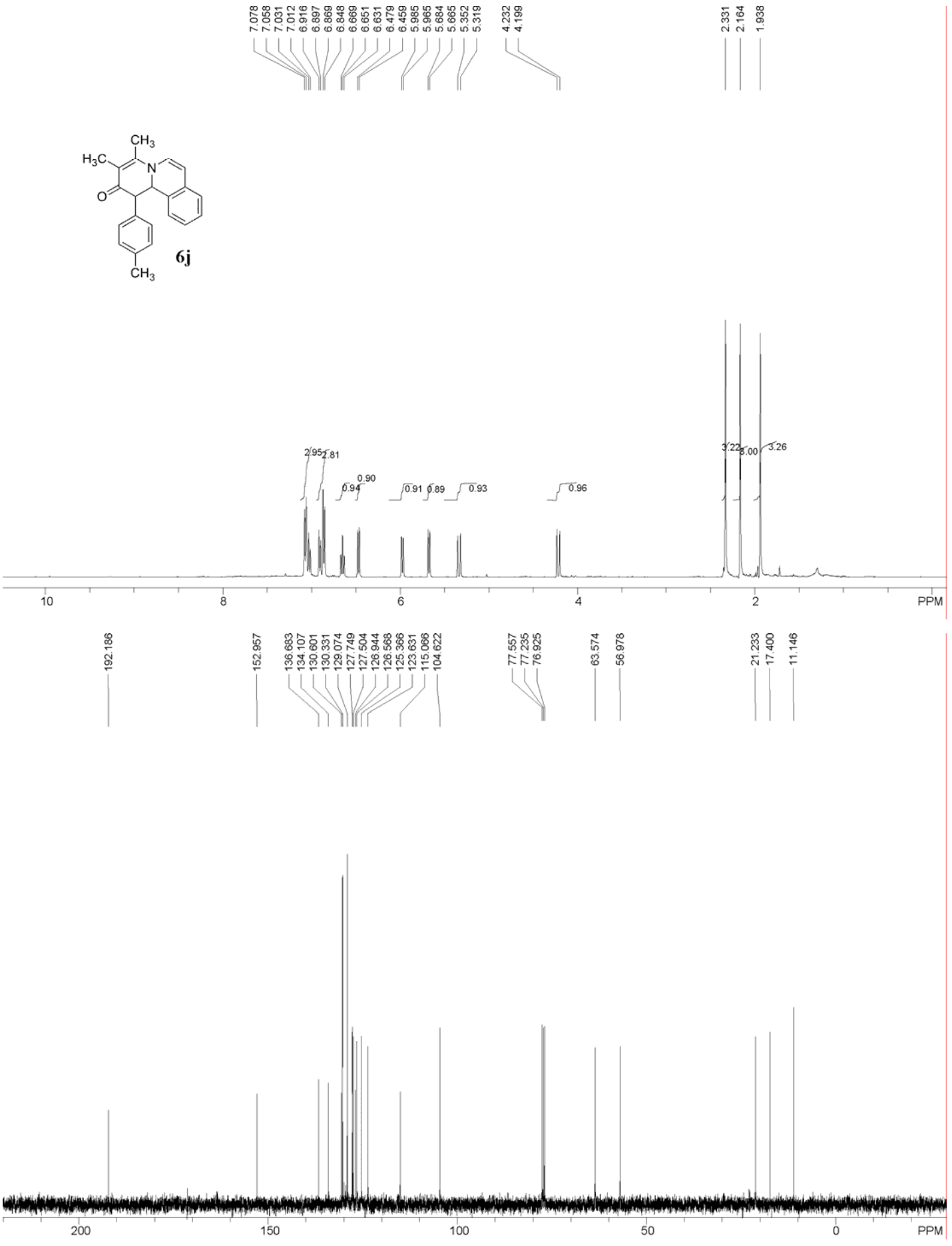
77.254
77.049
76.725
63.717
57.338
17.395
11.061
200
150
100
50
0

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6.479
6.459
5.985
5.965
5.684
5.665
5.352
5.319
4.232
4.199
2.331
2.164
1.938
CH3
H3C
N
O
CH3
6j
2.95
2.81
0.90
0.94
0.91
0.89
0.93
0.96
3.22
3.00
3.26
10
8
6
4
2
PPM
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134.107
130.601
130.331
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126.568
125.366
123.631
115.066
104.622
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63.574
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11.146
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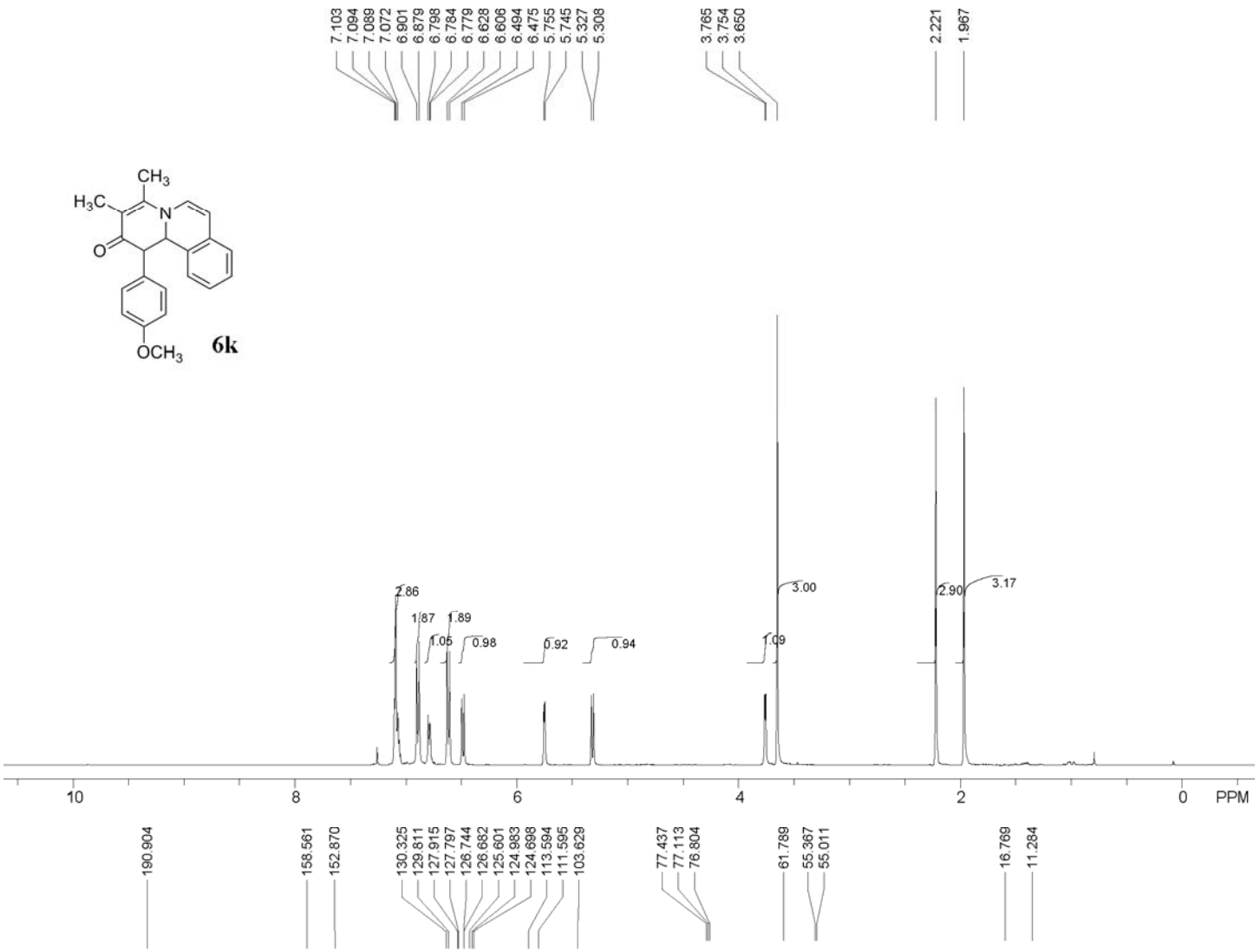
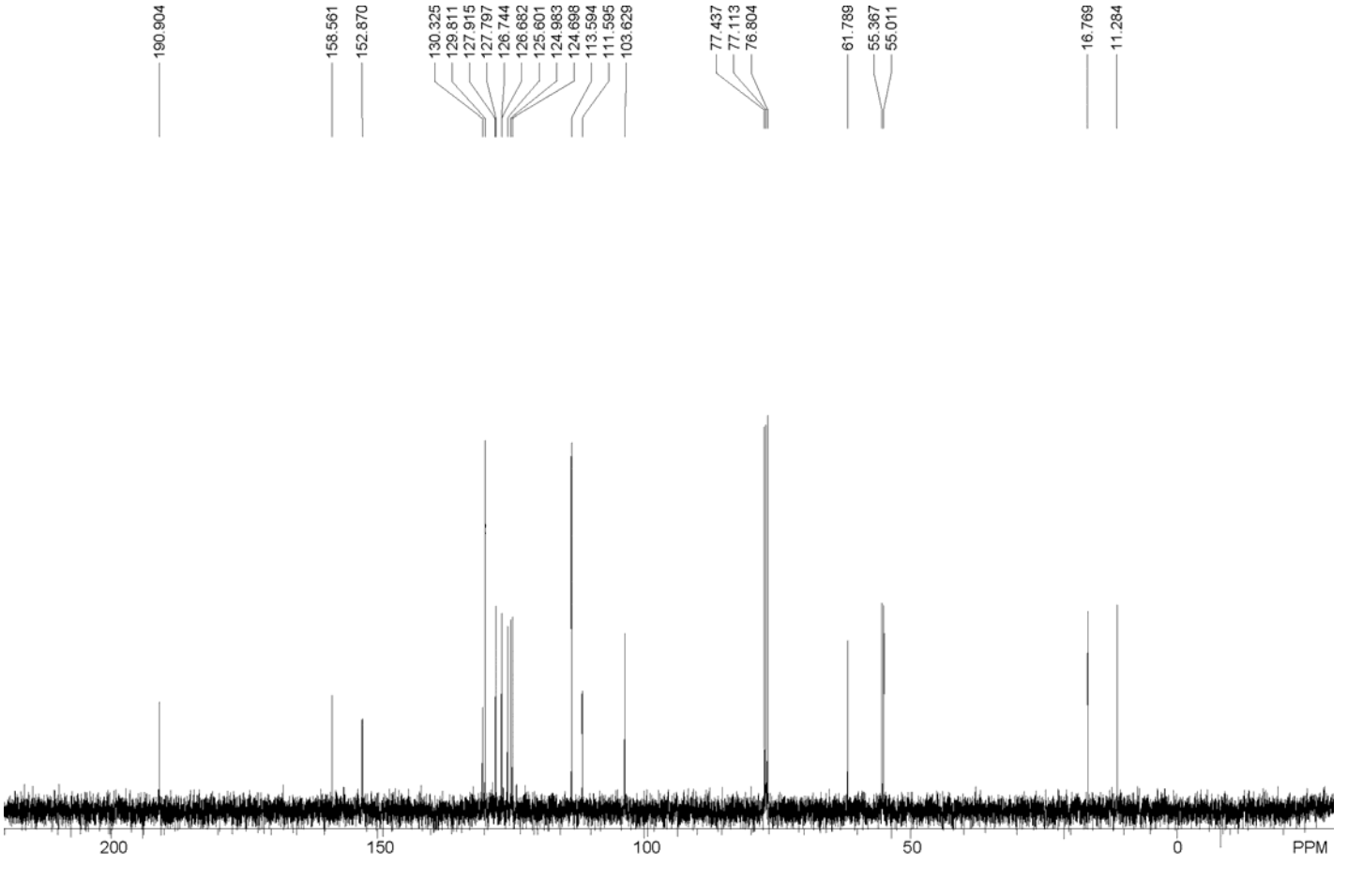
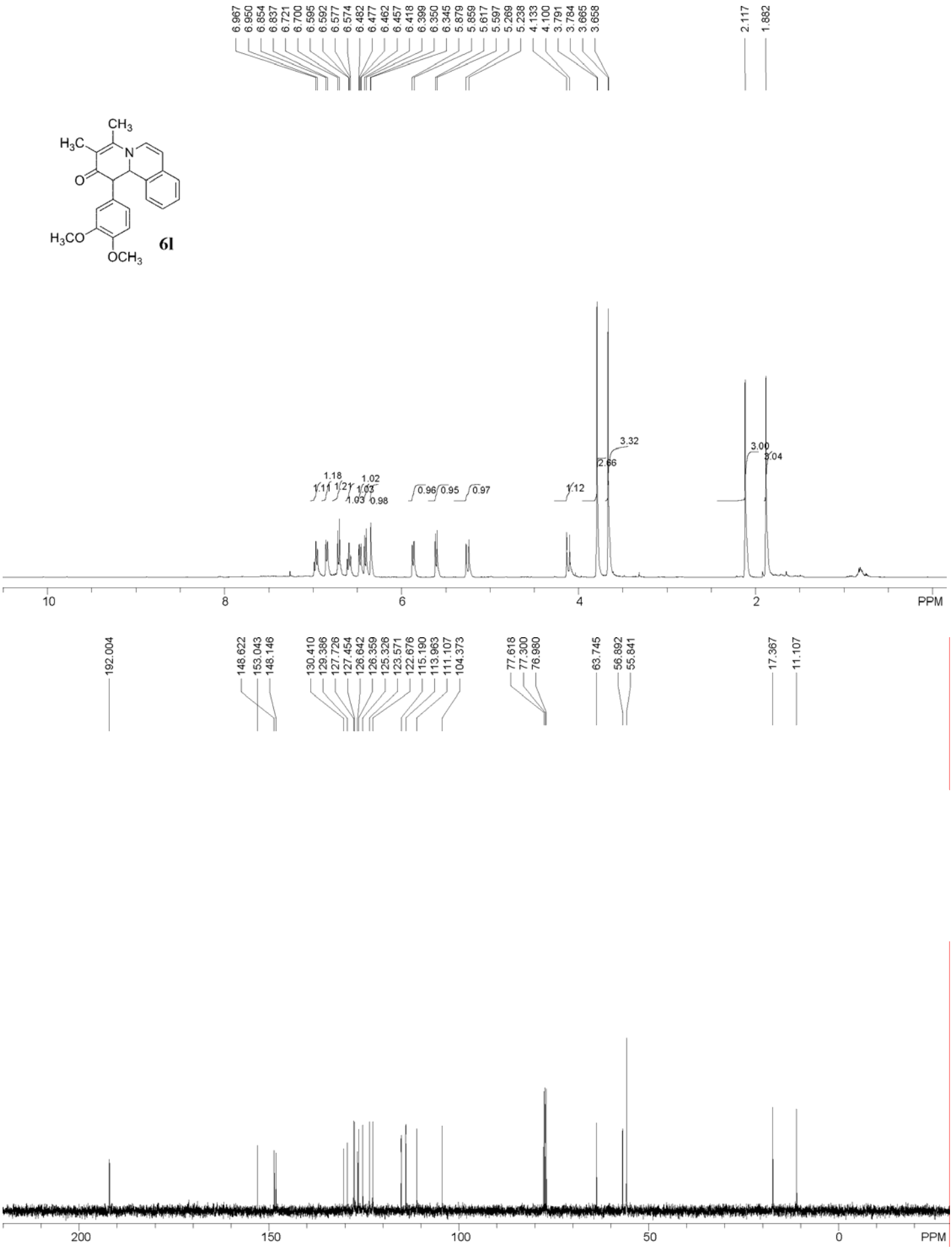
150
100
50
0
PPM



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6.574
6.482
6.477
6.462
6.457
6.418
6.399
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6.345
5.879
5.859
5.617
5.597
5.269
5.238
4.133
4.100
3.791
3.784
3.665
3.658
2.117
1.882
CH3
H3C
N
O
H3CO
OCH3
6l
1.18
1.11
1.21
1.02
1.03
1.03
0.98
0.96
0.95
0.97
1.12
3.32
2.66
3.00
3.04
10
8
6
4
2
PPM
192.004
148.622
153.043
148.146
130.410
129.386
127.726
127.454
126.642
126.359
125.326
123.571
122.676
115.190
113.963
111.107
104.373
77.618
77.300
76.980
63.745
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55.841
17.367
11.107
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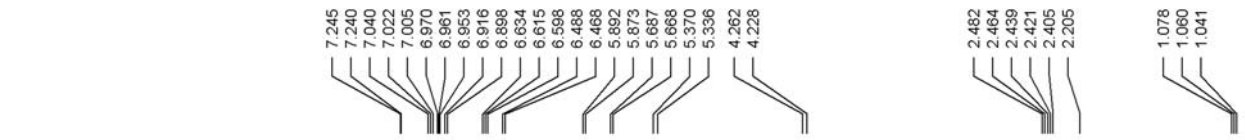
150
100
50
0
PPM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6.961
6.953
6.916
6.898
6.634
6.615
6.598
6.488
6.468
5.892
5.873
5.687
5.668
5.370
5.336
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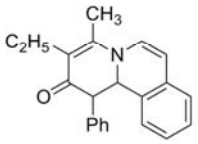
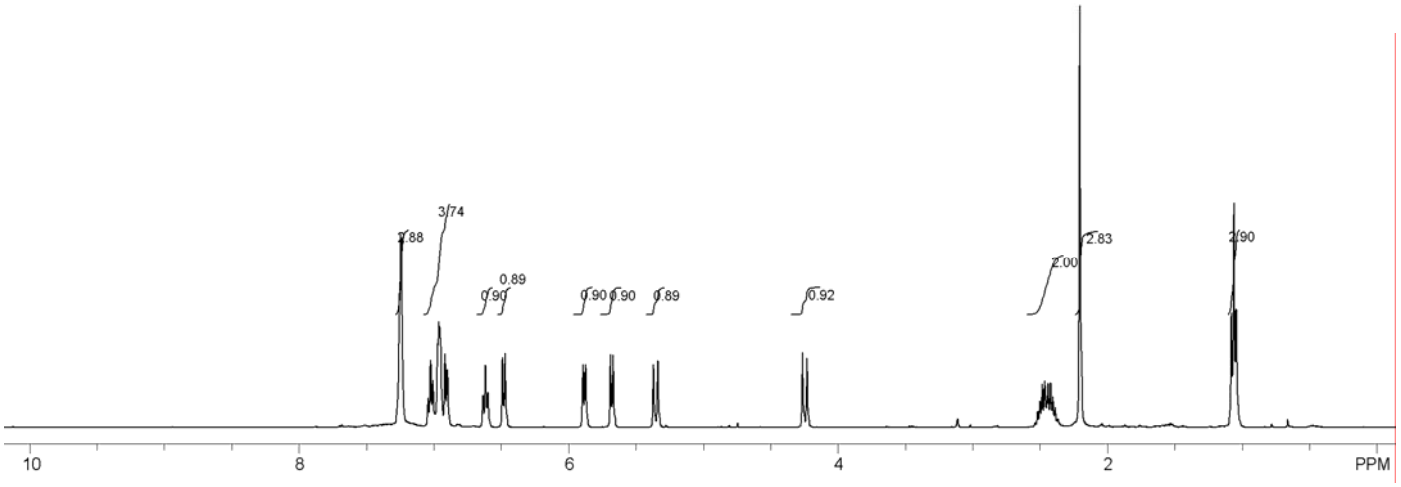
4.228
2.482
2.464
2.439
2.421
2.405
2.205
1.078
1.060
1.041


CH3
C2H5
N
O
Ph

6m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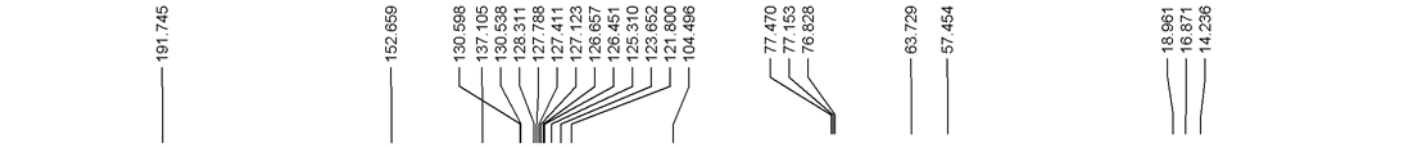
2.88
0.89
0.90
0.90
0.90
0.89
0.92
2.00
2.83
2.90
10
8
6
4
2
PPM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152.659
130.598
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130.538
128.311
127.788
127.411
127.123
126.657
126.451
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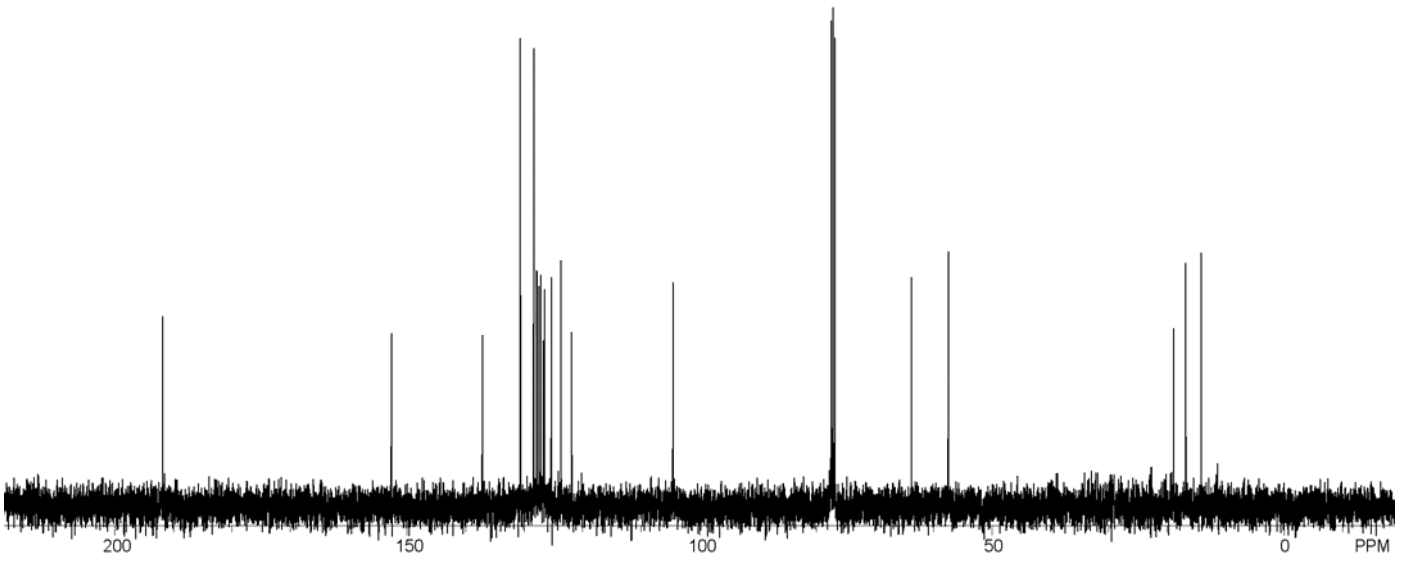
14.236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150
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50
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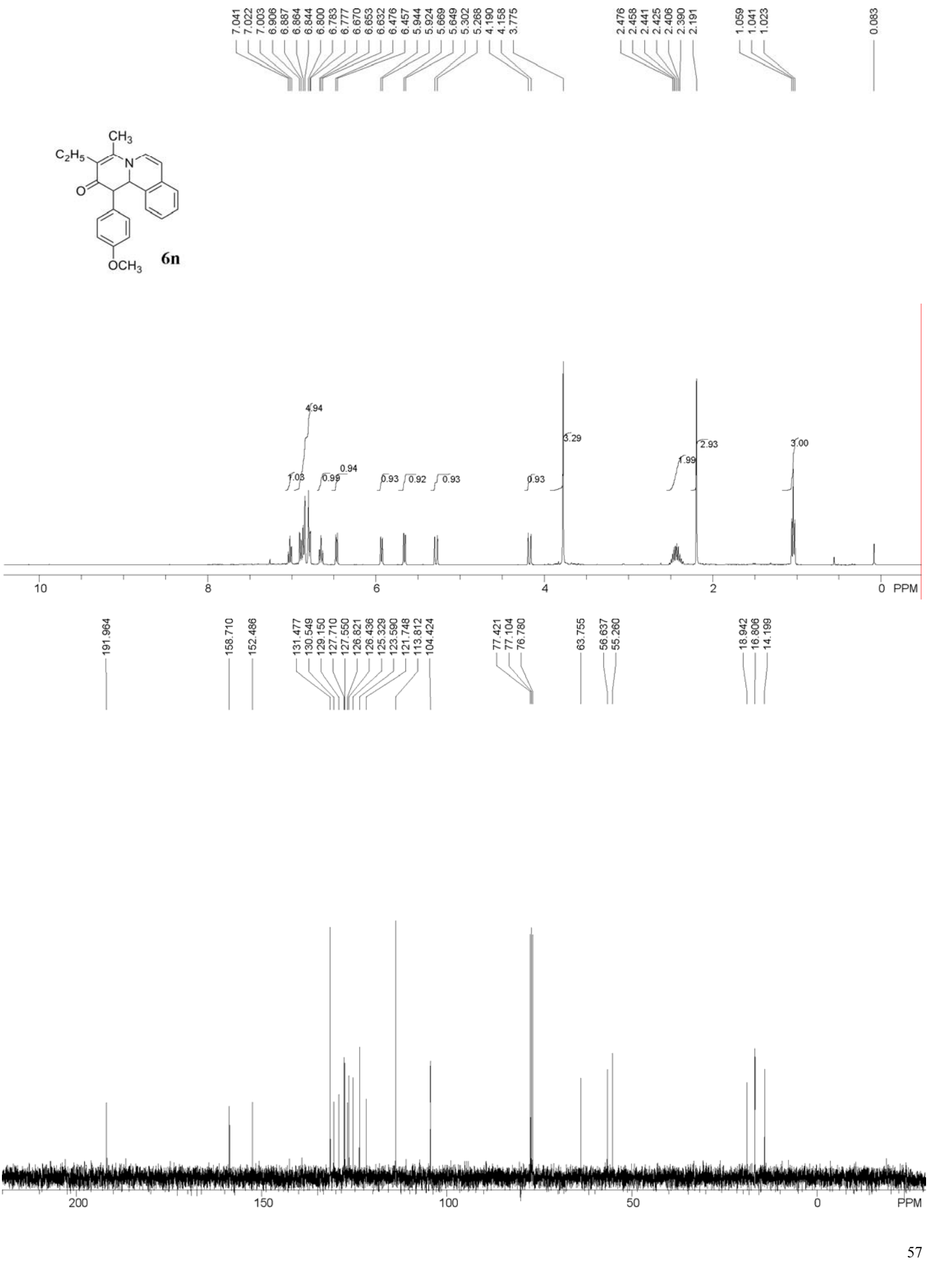
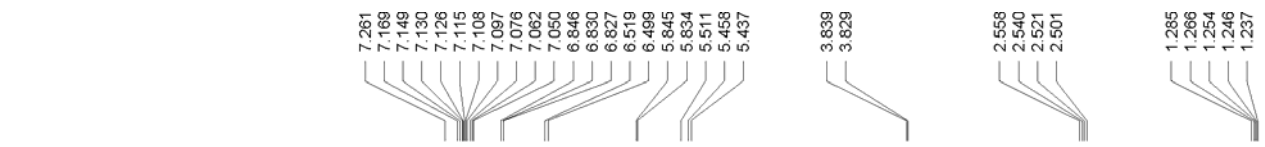
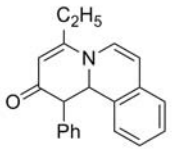
PPM







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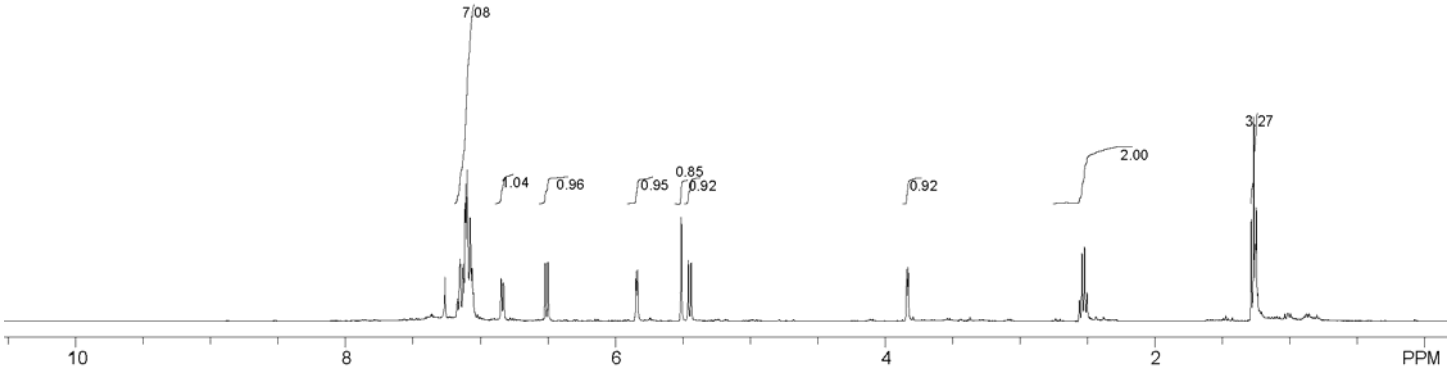

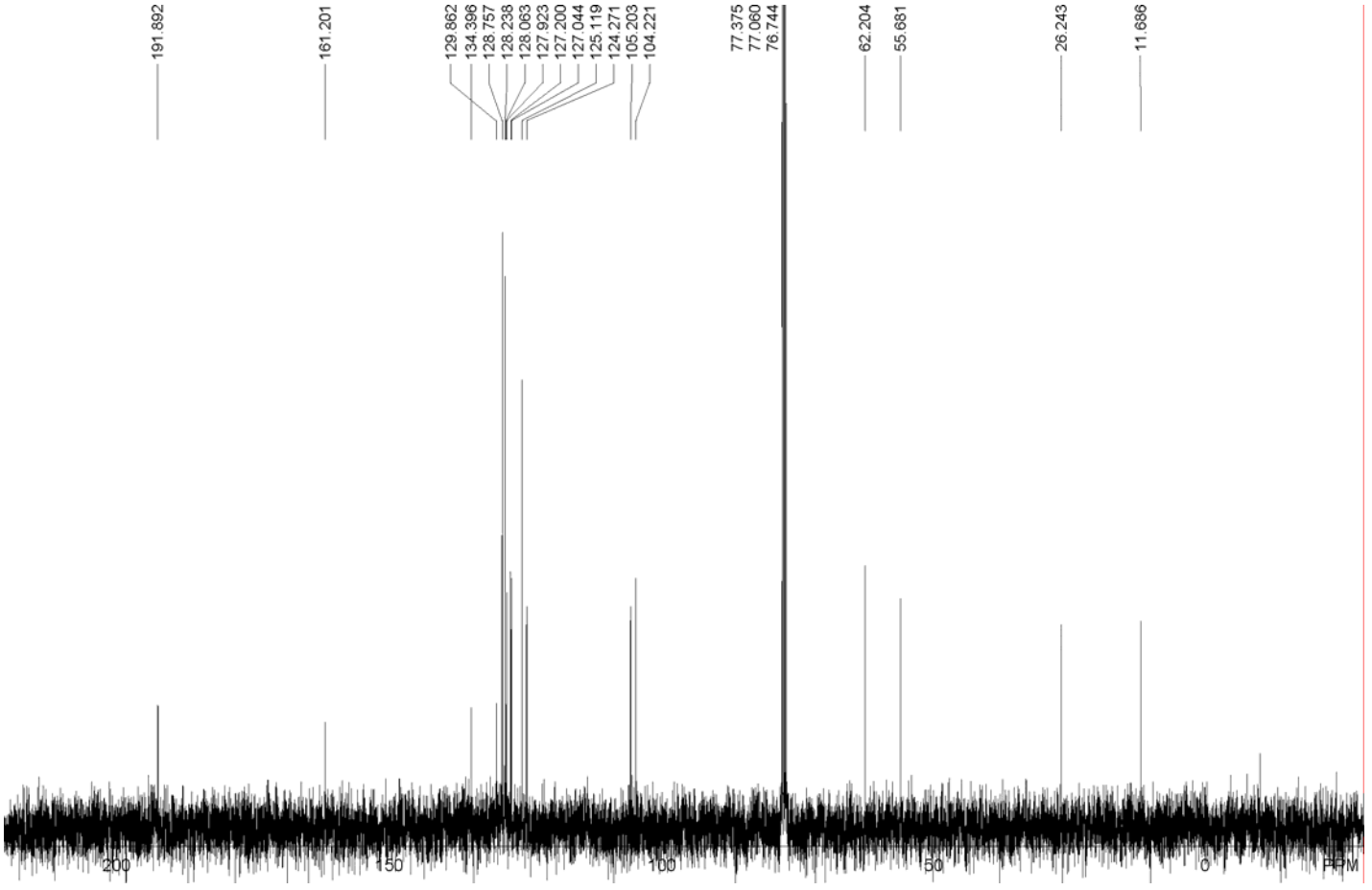

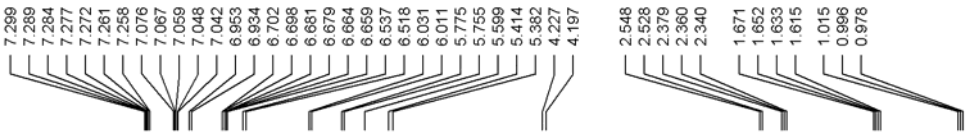
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7.284
7.277
7.272
7.261
7.258
7.076
7.067
7.059
7.048
7.042
6.953
6.934
6.702
6.698
6.681
6.679
6.664
6.659
6.537
6.518
6.031
6.011
5.775
5.755
5.589
5.414
5.382
4.227
4.197
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2.379
2.360
2.340
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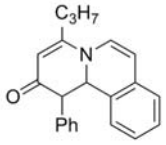
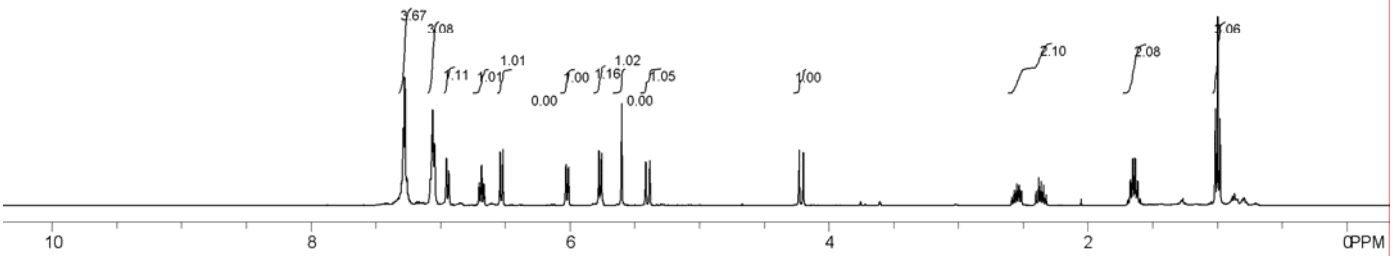
1.652
1.633
1.615
1.015
0.996
0.978


C3H7
N
O
Ph

6p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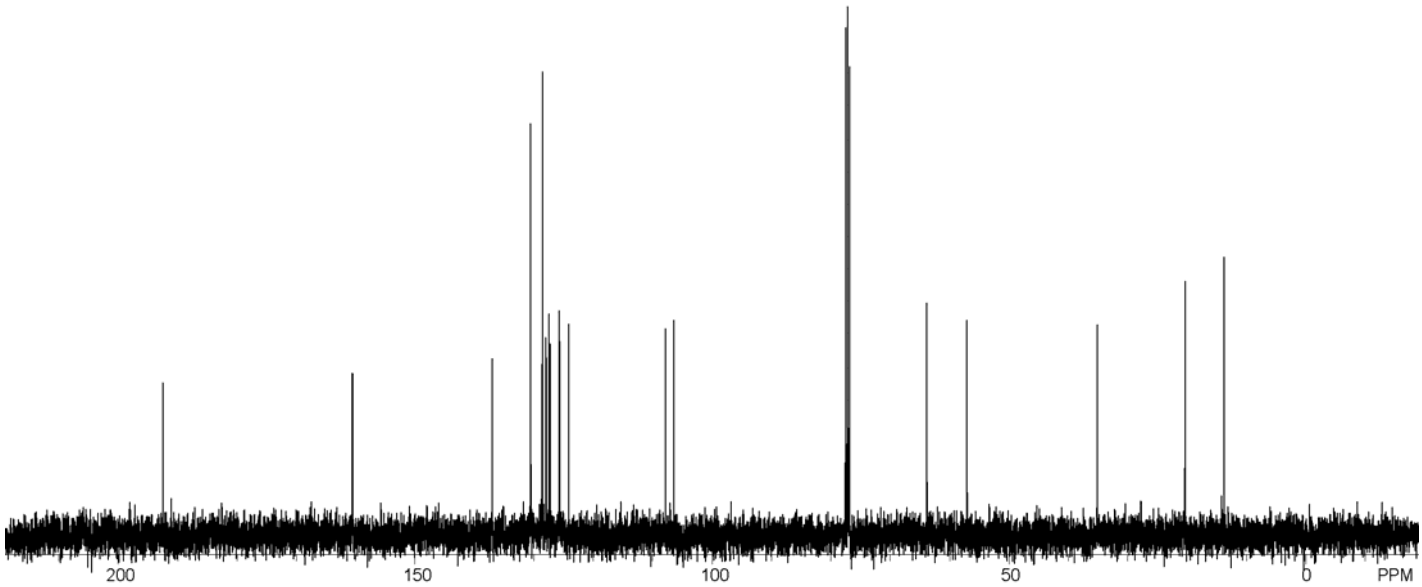
3.08
1.11
1.01
1.01
0.00
1.00
1.16
1.02
1.05
0.00
1.00
2.10
2.08
3.06
10
8
6
4
2
0
PPM


192.444
160.507
130.521
136.934
130.477
128.523
127.902
127.404
127.346
127.176
125.722
125.646
124.088
107.772
106.405
77.479
77.157
76.841
63.813
57.054
35.132
20.375
13.814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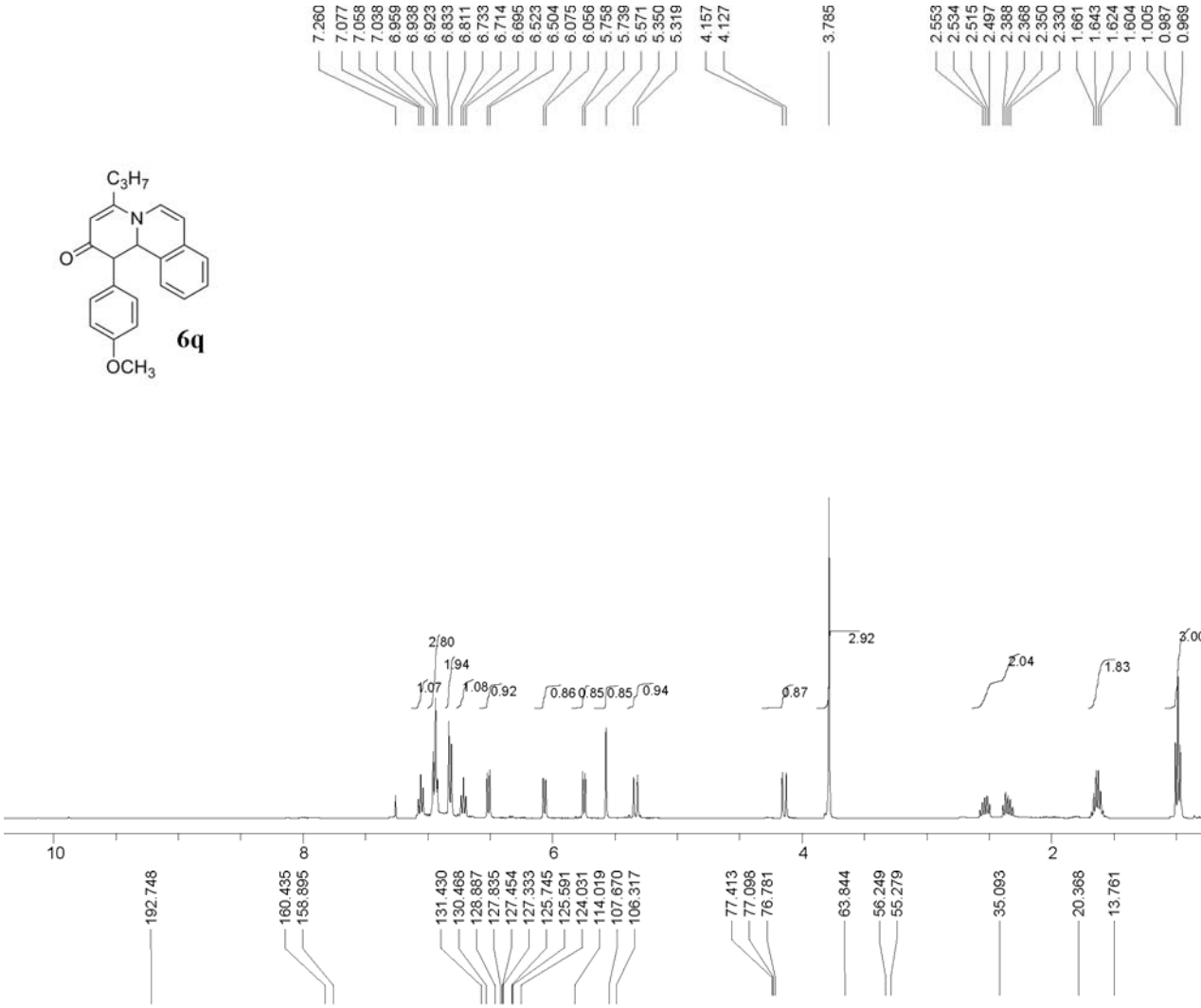
150
100
50
0
PPM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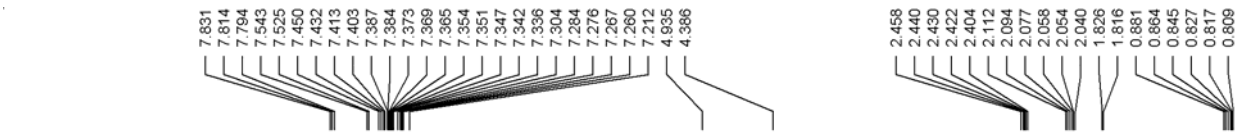
7.077
7.058
7.038
6.959
6.938
6.923
6.833
6.811
6.733
6.714
6.695
6.523
6.504
6.075
6.056
5.758
5.739
5.571
5.350
5.319
4.157
4.127
3.785
2.553
2.534
2.515
2.497
2.388
2.368
2.350
2.330
1.661
1.643
1.624
1.604
1.005
0.987
0.969
C3H7
N
O
OCH3
6q
2.80
1.94
1.07
1.08
0.92
0.86
0.85
0.85
0.94
0.87
2.92
2.04
1.83
3.00
10
8
6
4
2
0PPM
192.748
160.435
158.895
131.430
130.468
128.887
127.835
127.454
127.333
125.745
125.591
124.031
114.019
107.670
106.317
77.413
77.098
76.781
63.844
56.249
55.279
35.093
20.368
13.761
200
150
100
50
0
PPM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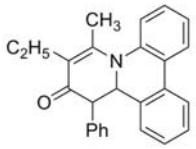
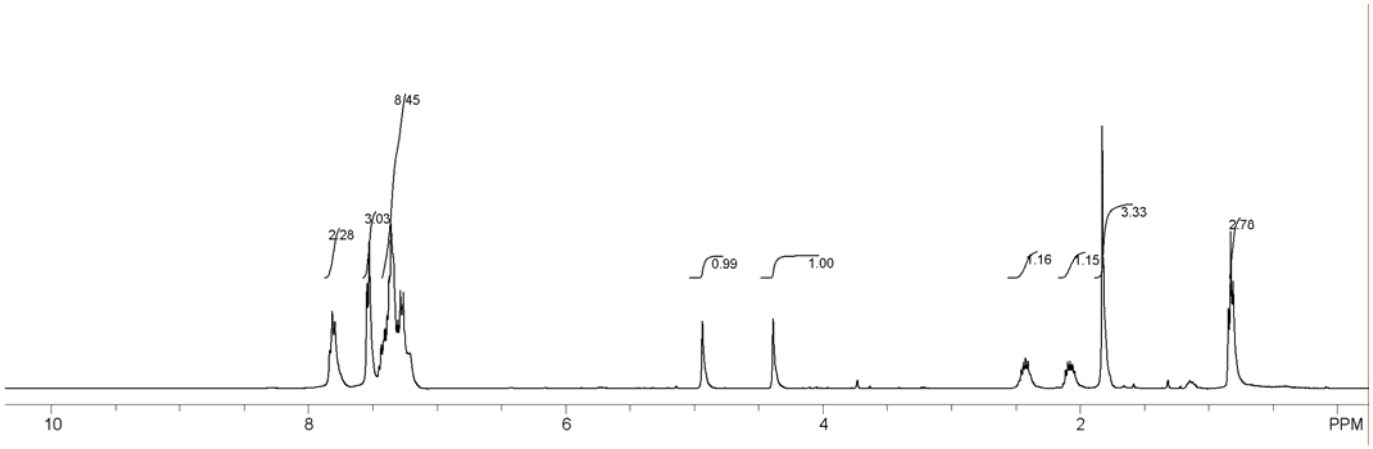
7.794
7.543
7.525
7.450
7.432
7.413
7.403
7.387
7.384
7.373
7.369
7.365
7.354
7.351
7.347
7.342
7.336
7.304
7.284
7.276
7.267
7.260
7.212
4.935
4.386
2.458
2.440
2.430
2.422
2.404
2.112
2.094
2.077
2.058
2.054
2.040
1.826
1.816
0.881
0.864
0.845
0.827
0.817
0.809


CH3
C2H5
N
O
Ph

6r


8.45
3.03
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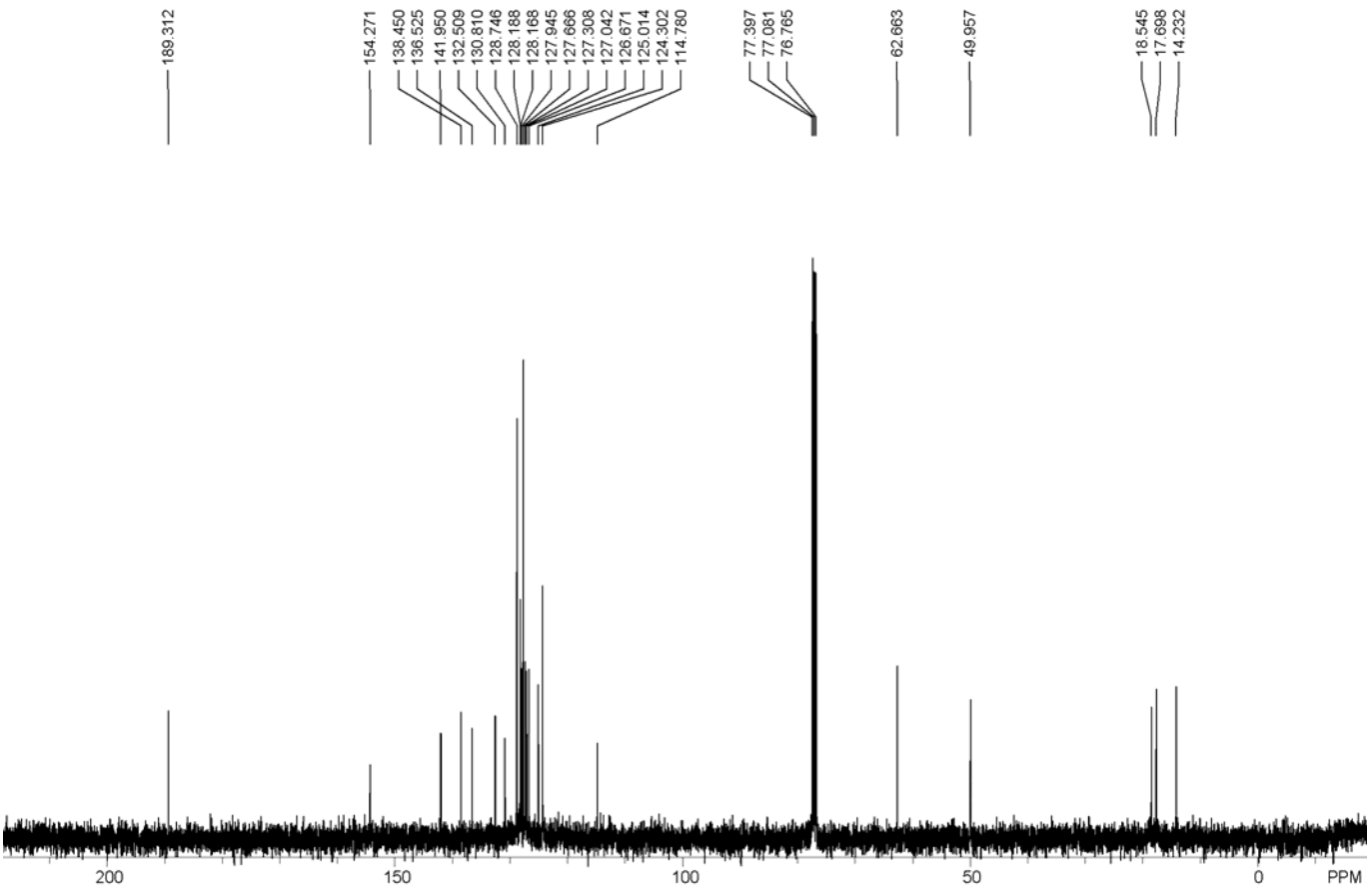
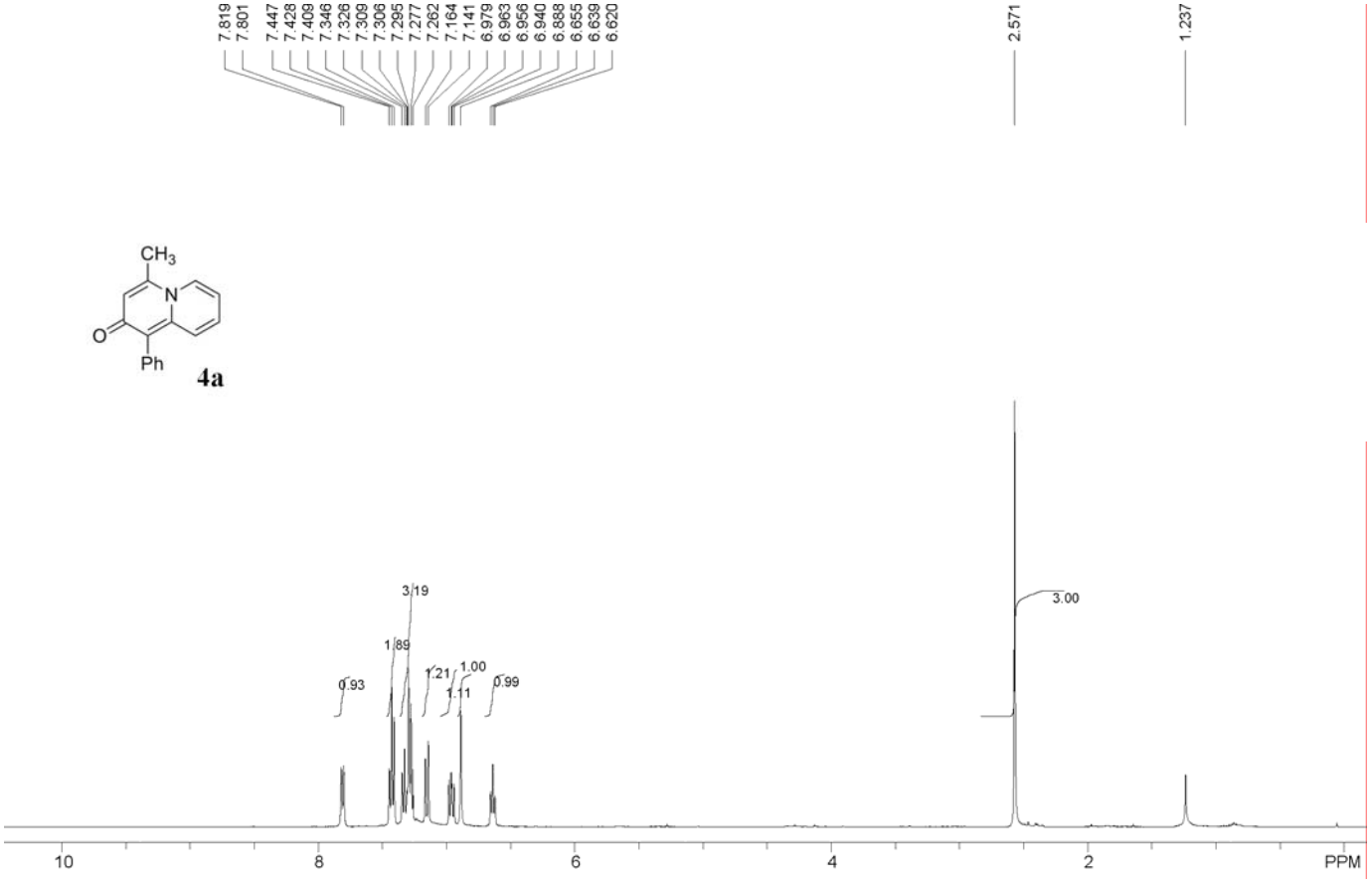
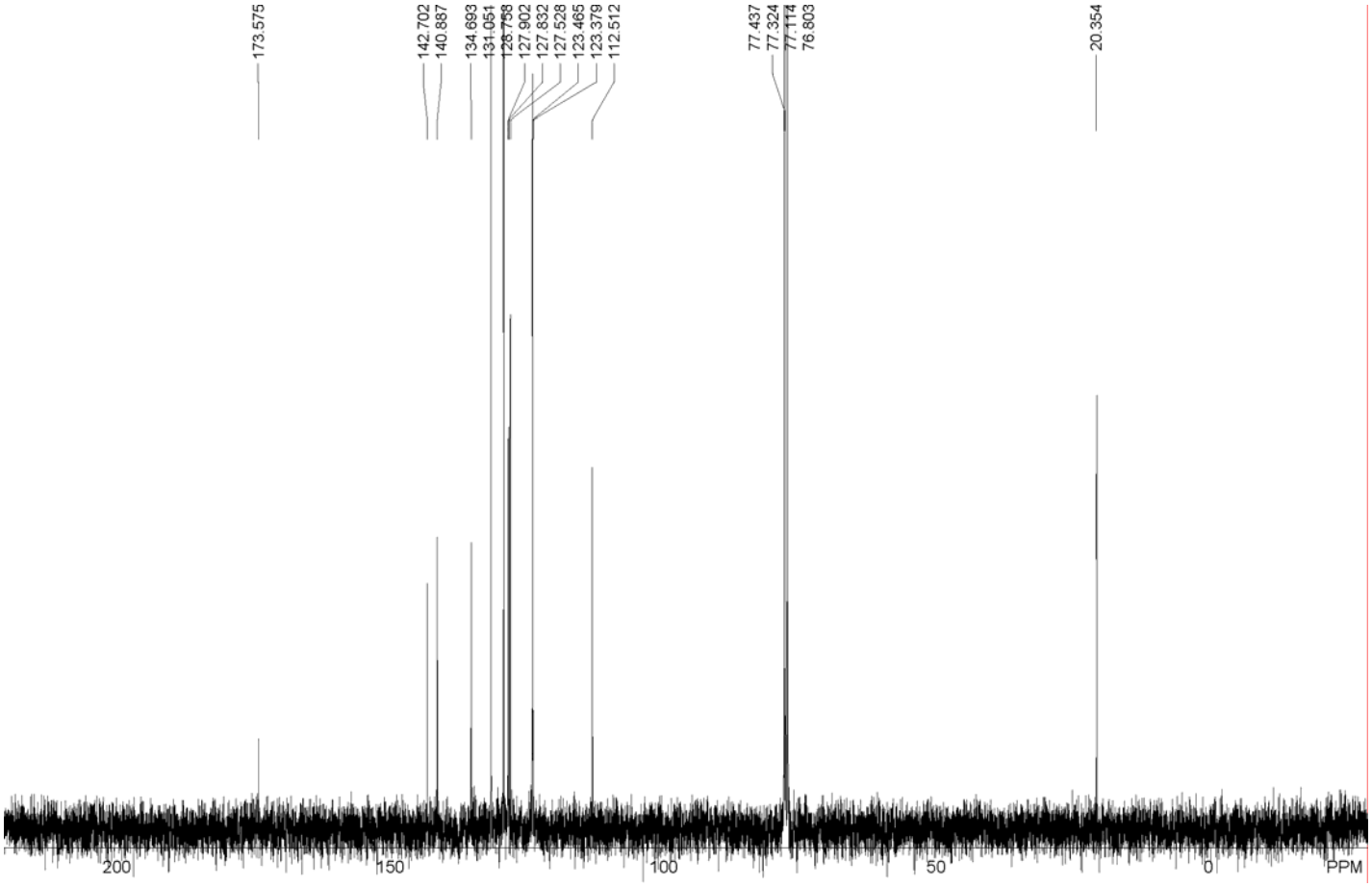
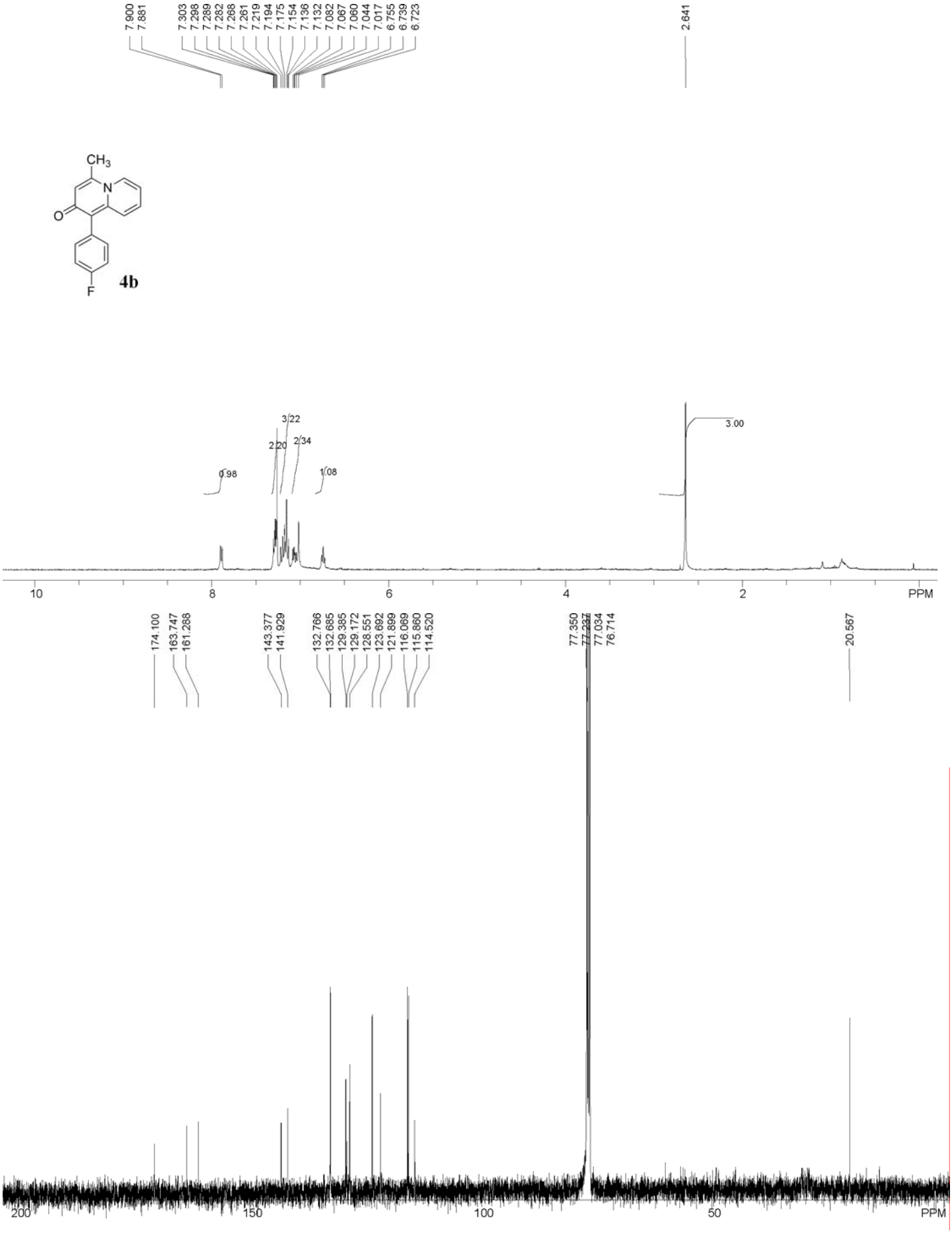
0.99
1.00
1.16
1.15
3.33
2.76
10
8
6
4
2
PPM


189.312
154.271
138.450
136.525
141.950
132.509
130.810
128.746
128.188
128.168
127.945
127.666
127.308
127.042
126.671
125.014
124.302
114.780
77.397
77.081
76.765
62.663
49.957
18.545
17.698
14.232
200
150
100
50
0
PPM

IV. Copies of ^{1}H and ^{13}C NMR spectra of compounds 4a-4n



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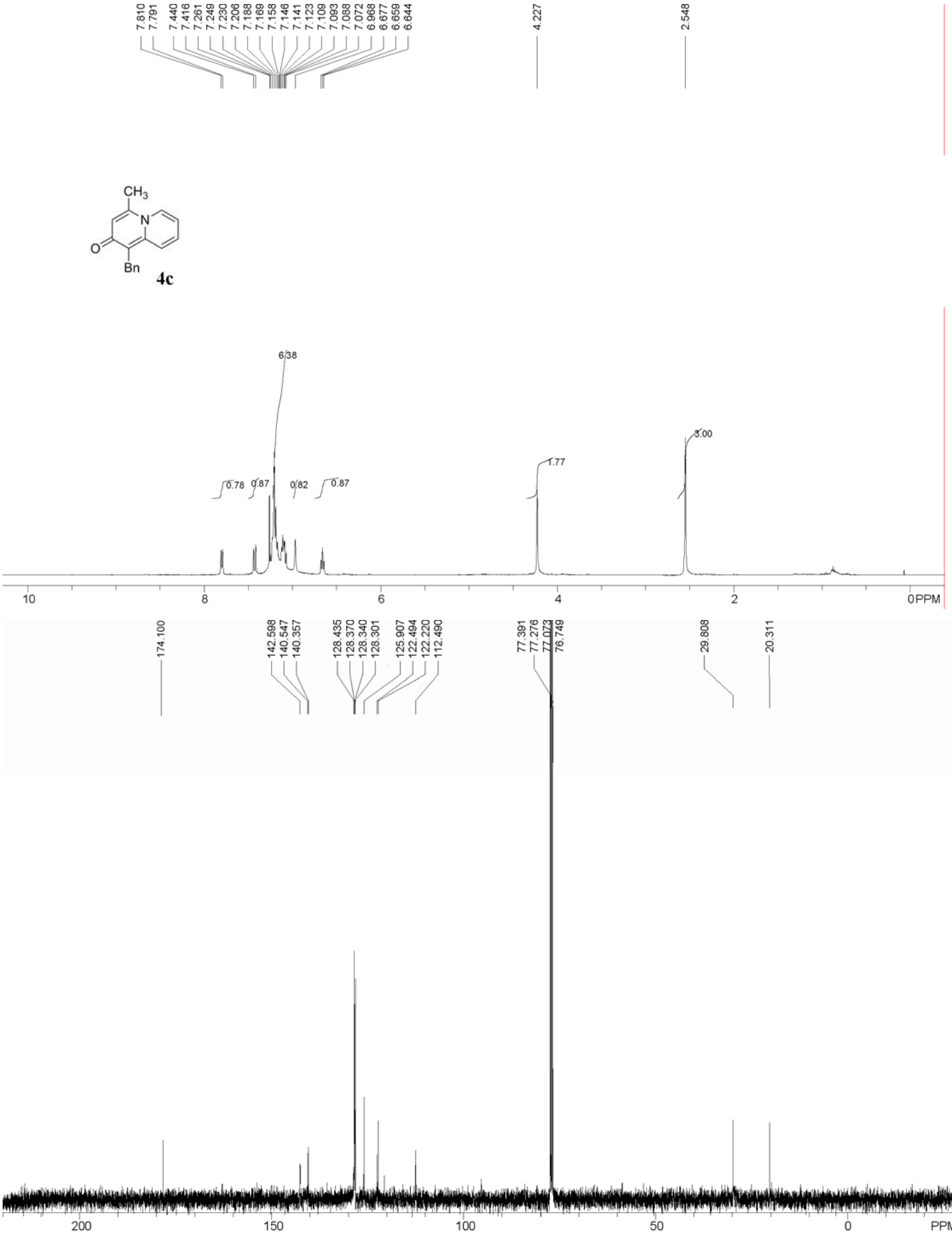
7.268
7.261
7.219
7.194
7.175
7.154
7.136
7.132
7.082
7.067
7.060
7.044
7.017
6.755
6.739
6.723
2.641
CH3
N
O
F
4b
3.22
2.20
2.34
0.98
1.08
3.00
10
8
6
4
2
PPM
174.100
163.747
161.288
143.377
141.929
132.766
132.685
129.385
129.172
128.551
123.692
121.899
116.069
115.860
114.520
77.350
77.237
77.034
76.714
20.567
200
150
100
50
PPM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7.249
7.230
7.206
7.188
7.169
7.158
7.146
7.141
7.123
7.109
7.093
7.088
7.072
6.968
6.677
6.659
6.644
4.227
2.548
CH3
N
O
Bn
4c
6.38
0.78
0.87
0.82
0.87
1.77
3.00
10
8
6
4
2
0PPM
174.100
142.598
140.547
140.357
128.435
128.370
128.340
128.301
125.907
122.494
122.220
112.490
77.391
77.276
77.073
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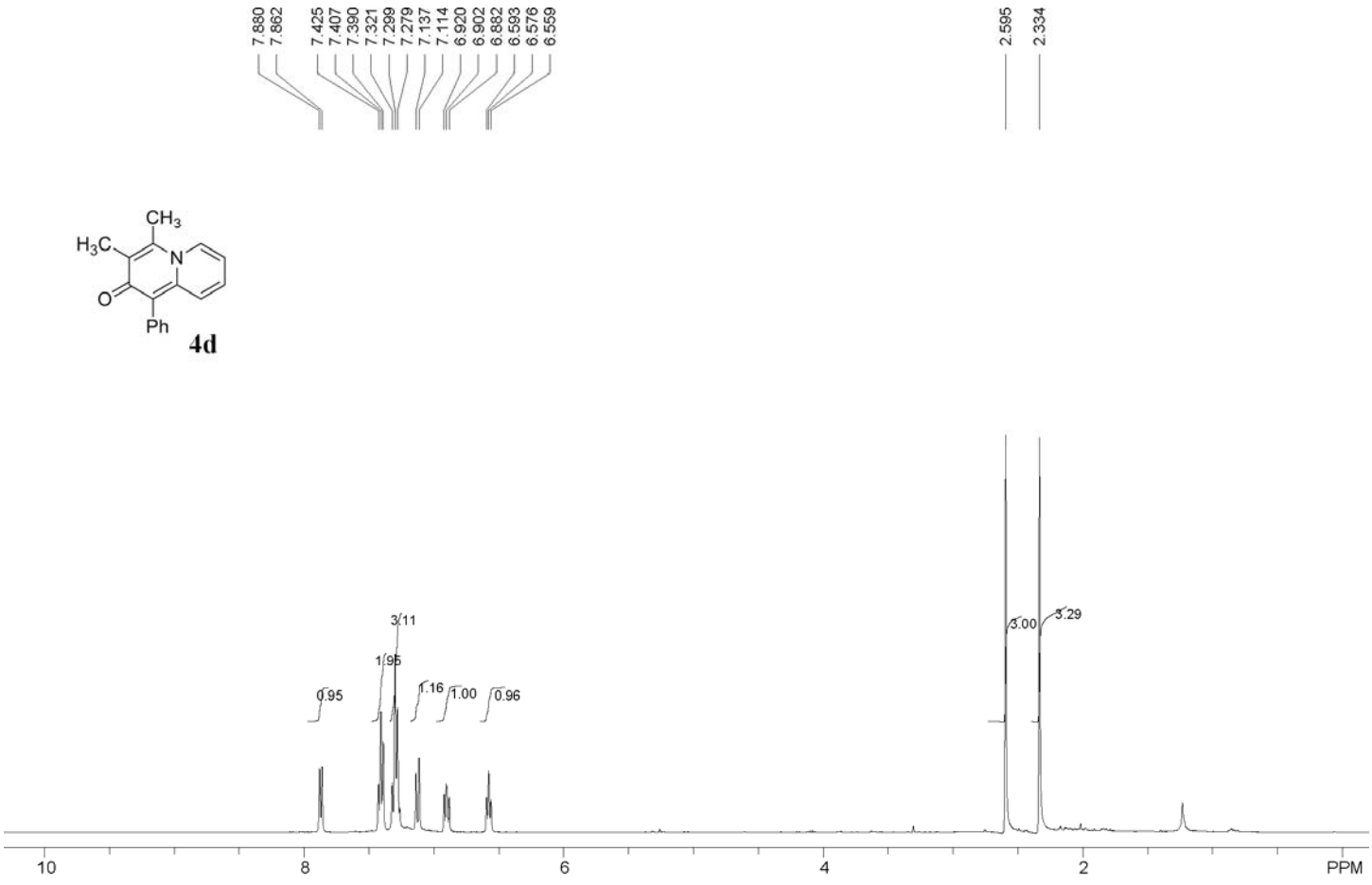
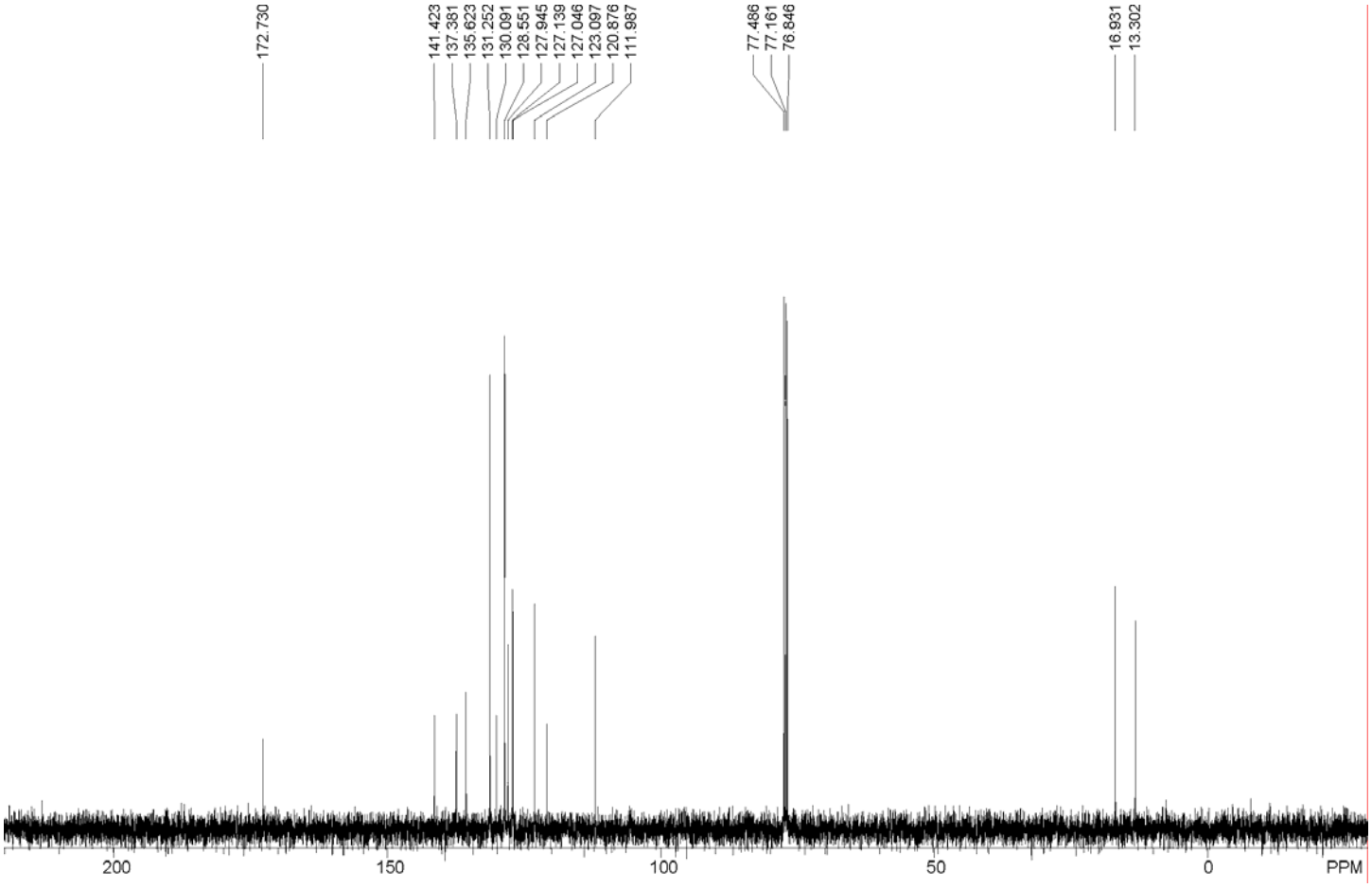
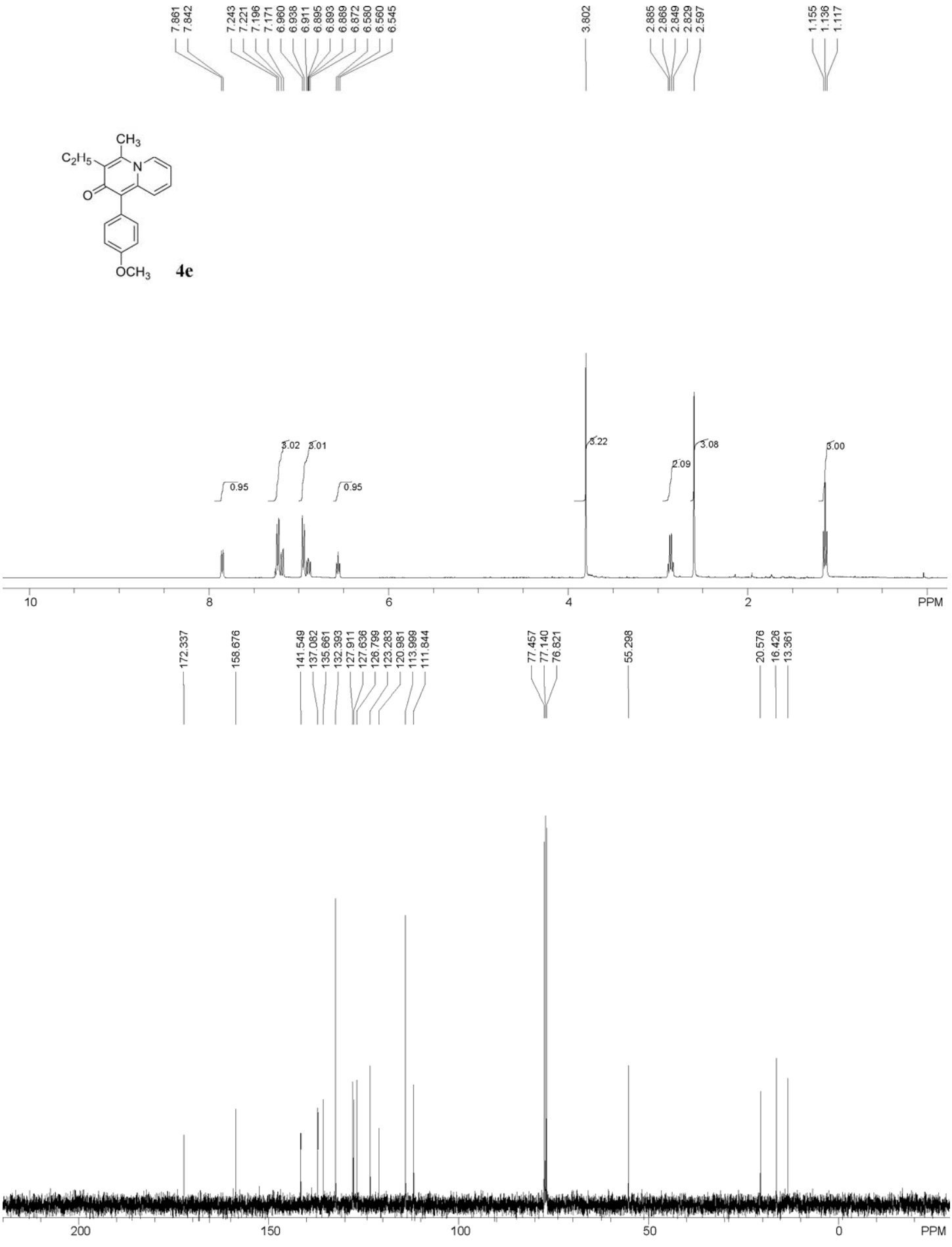
29.808
20.311
200
150
100
50
0
PPM



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7.842
7.243
7.221
7.196
7.171
6.960
6.938
6.911
6.895
6.893
6.889
6.872
6.580
6.560
6.545
3.802
2.885
2.868
2.849
2.829
2.597
1.155
1.136
1.117
CH3
C2H5
N
O
OCH3
4e
0.95
3.02
3.01
0.95
3.22
2.09
3.08
3.00
10
8
6
4
2
PPM
172.337
158.676
141.549
137.082
135.661
132.393
127.911
127.636
126.799
123.283
120.981
113.999
111.844
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77.140
76.821
55.298
20.576
16.426
13.361
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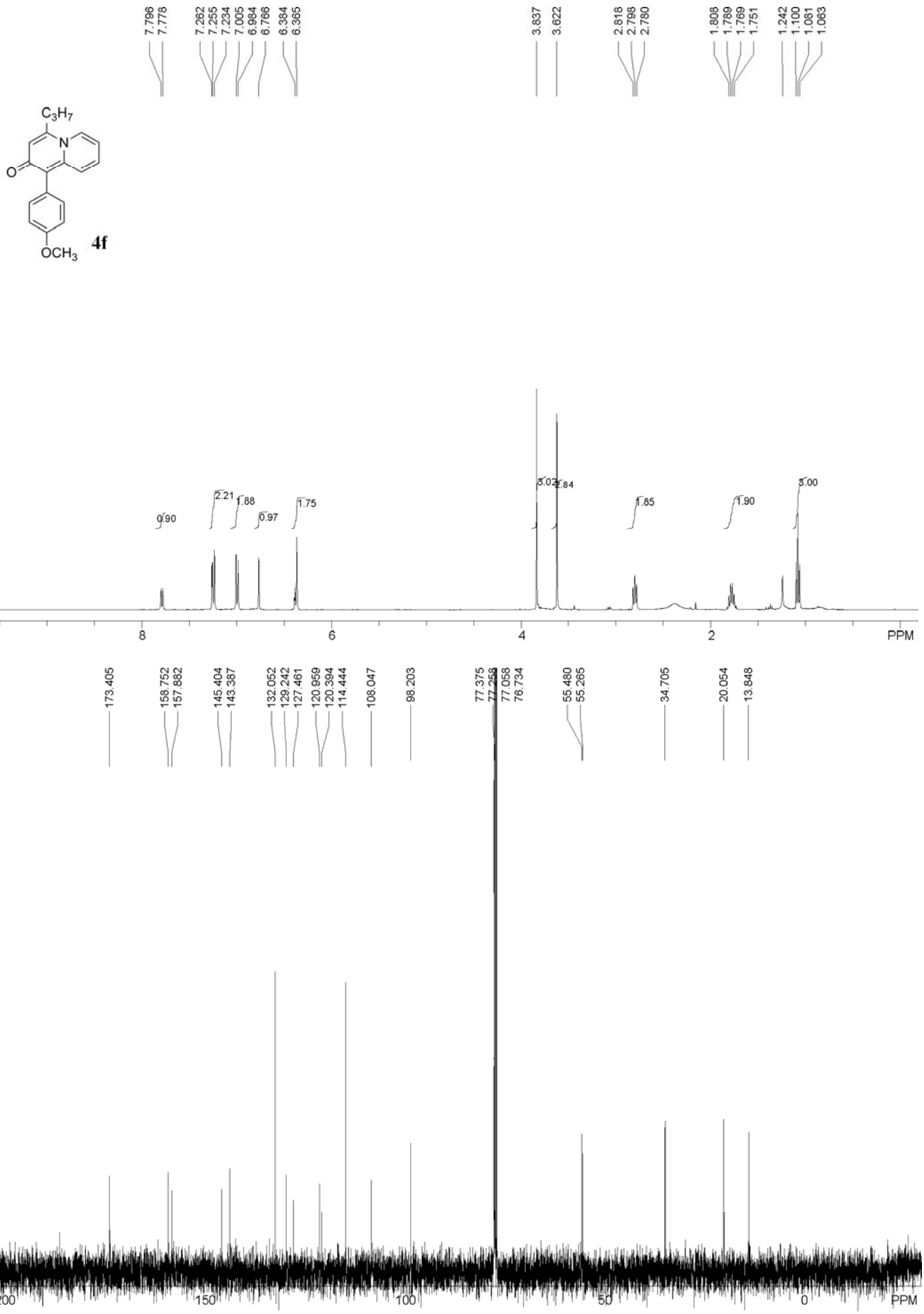
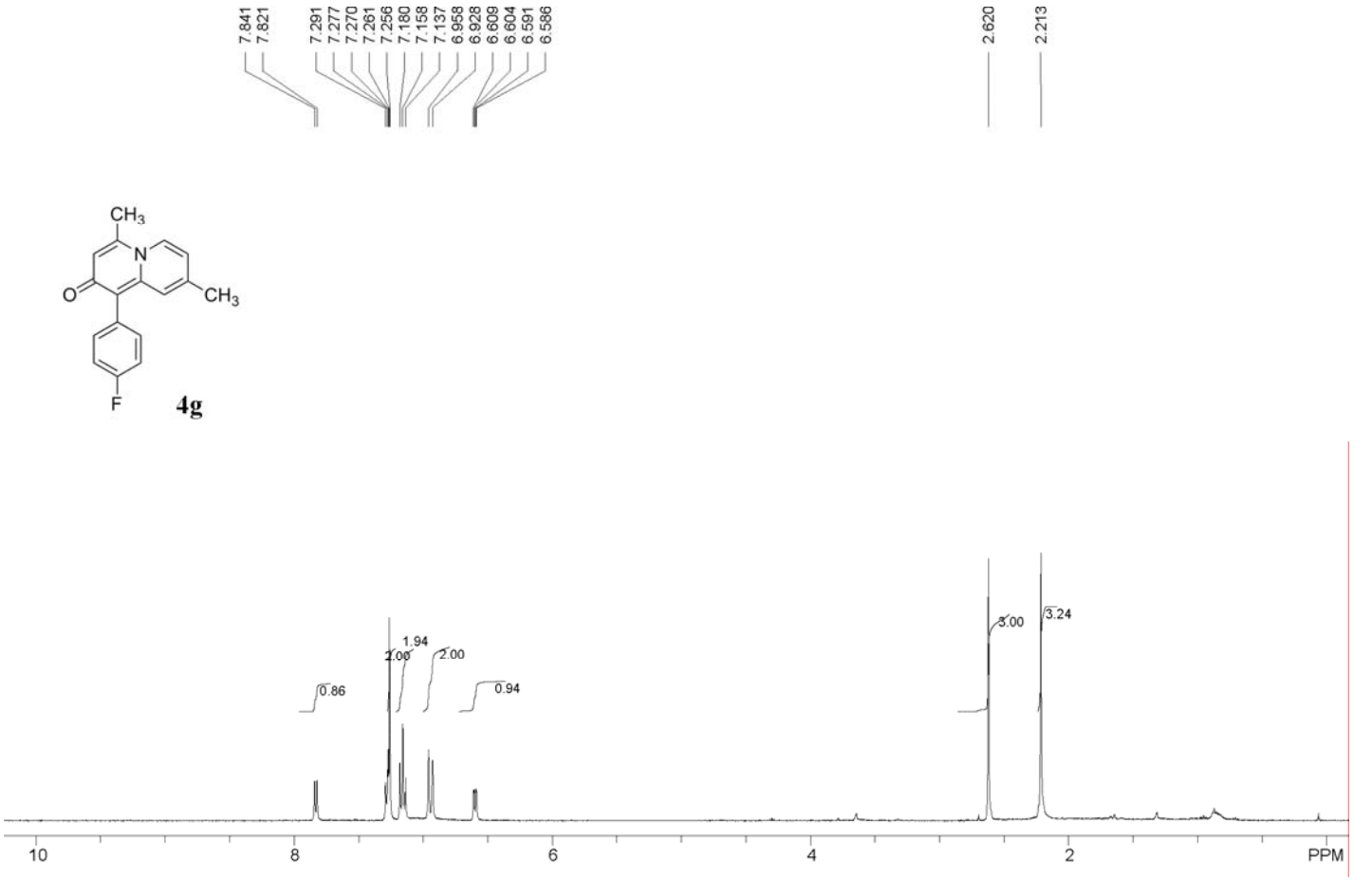
150
100
50
0
PPM

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7.180
7.158
7.137
6.958
6.928
6.609
6.604
6.591
6.586
2.620
2.213
CH3
N
O
CH3
F
4g
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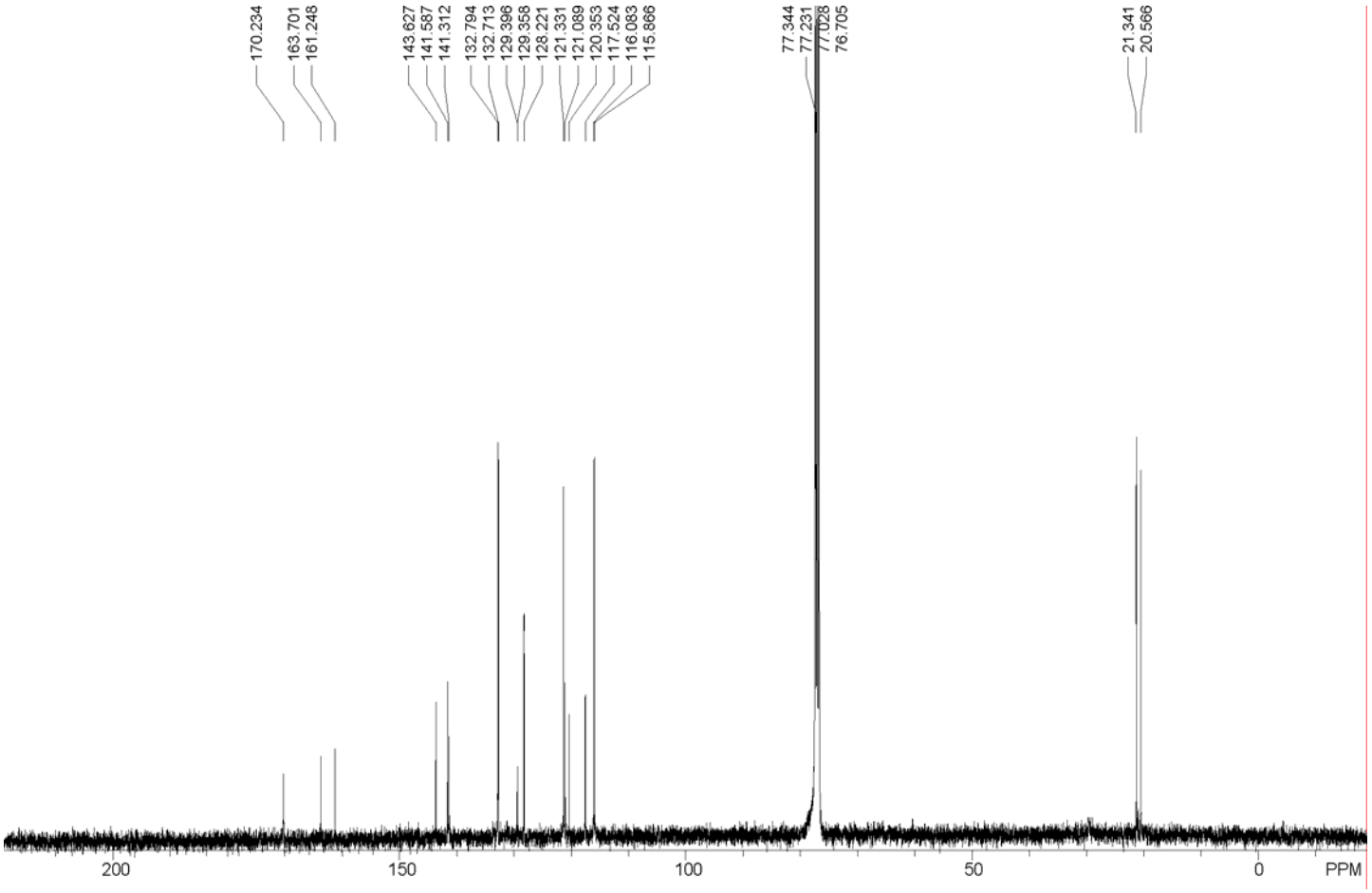
1.94
2.00
2.00
0.94
3.00
3.24
10
8
6
4
2
PPM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143.627
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141.312
132.794
132.713
129.396
129.358
128.221
121.331
121.089
120.353
117.524
116.083
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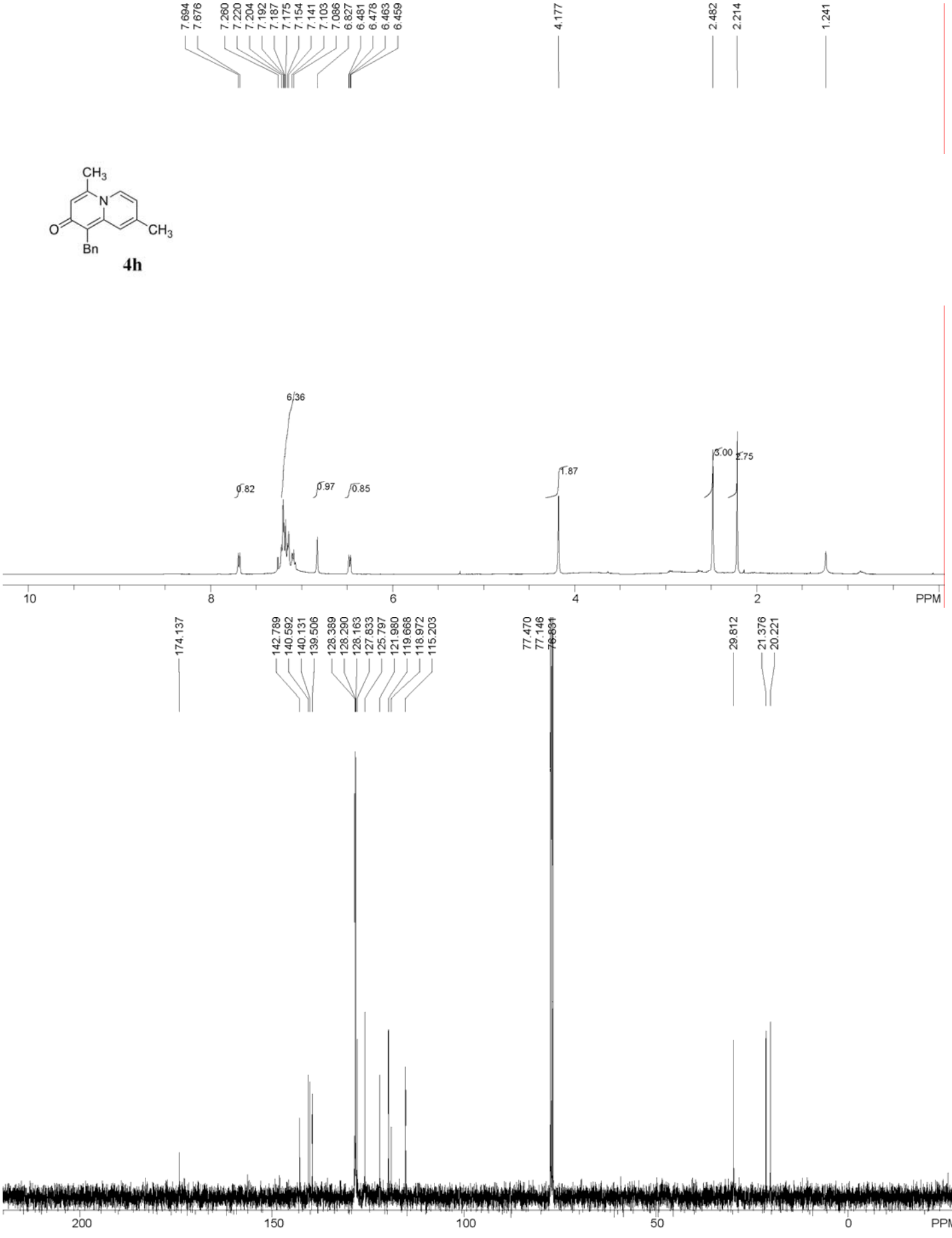
77.344
77.231
77.028
76.705
21.341
20.566
200
150
100
50
0
PPM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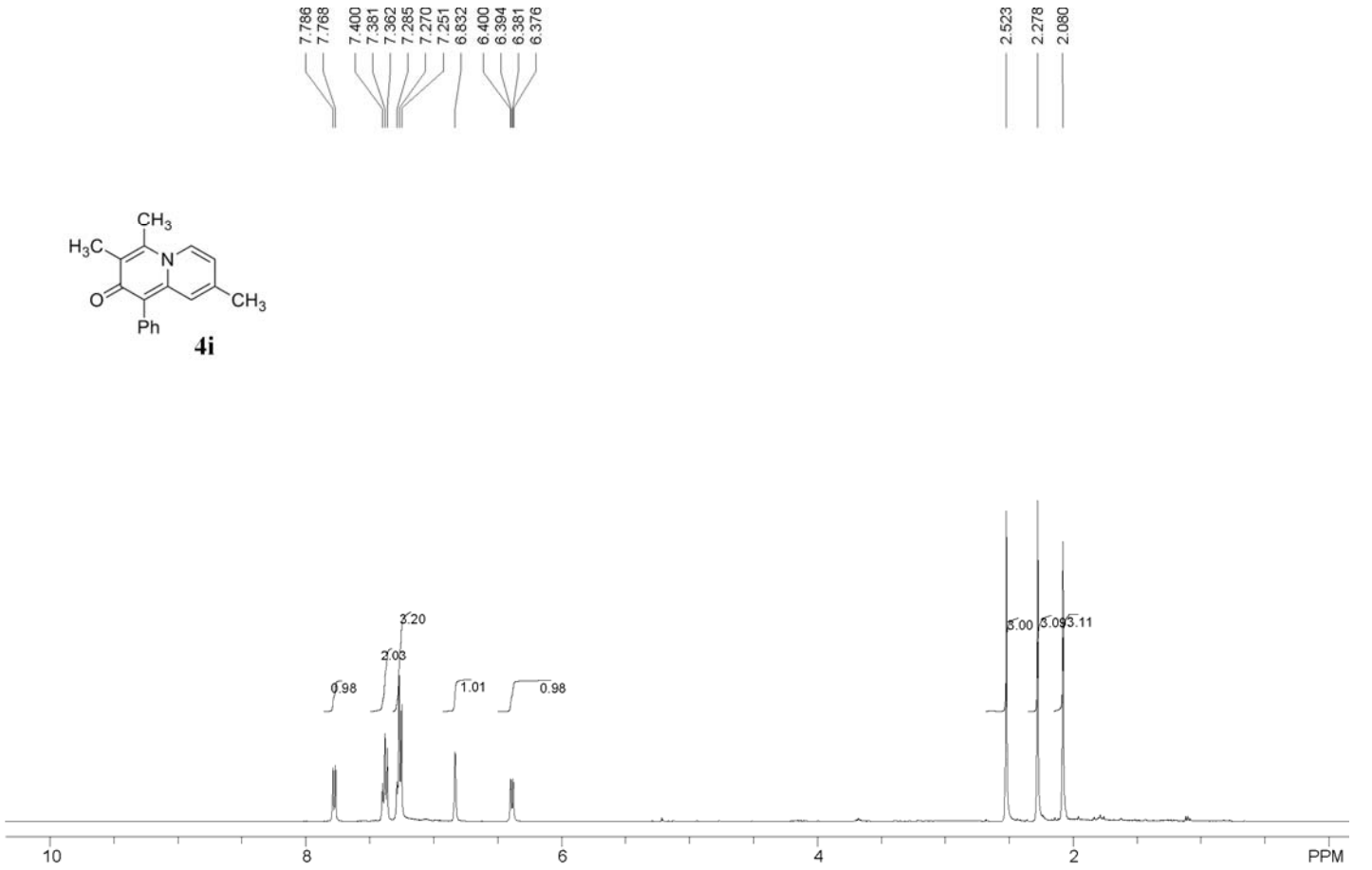
7.187
7.175
7.154
7.141
7.103
7.086
6.827
6.481
6.478
6.463
6.459
4.177
2.482
2.214
1.241
CH3
N
O
CH3
Bn
4h
6.36
0.82
0.97
0.85
1.87
3.00
2.75
10
8
6
4
2
PPM
174.137
142.789
140.592
140.131
139.506
128.389
128.290
128.163
127.833
125.797
121.980
119.668
118.972
115.203
77.470
77.146
76.831
29.812
21.376
20.221
200
150
100
50
0
PPM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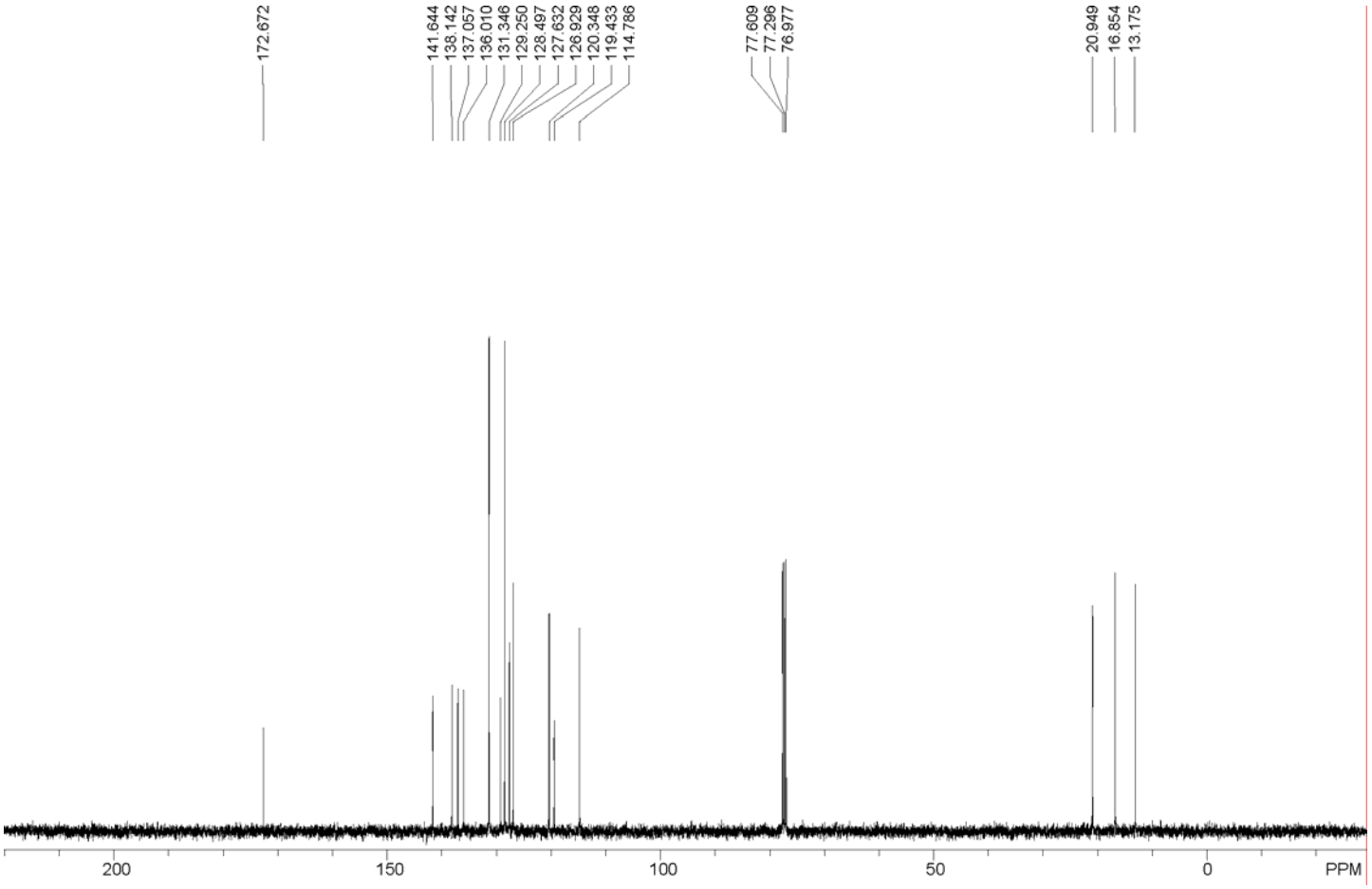
7.381
7.362
7.285
7.270
7.251
6.832
6.400
6.394
6.381
6.376
2.523
2.278
2.080
CH3
H3C
N
O
CH3
Ph
4i
0.98
2.03
3.20
1.01
0.98
3.00
3.09
3.11
10
8
6
4
2
PPM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137.057
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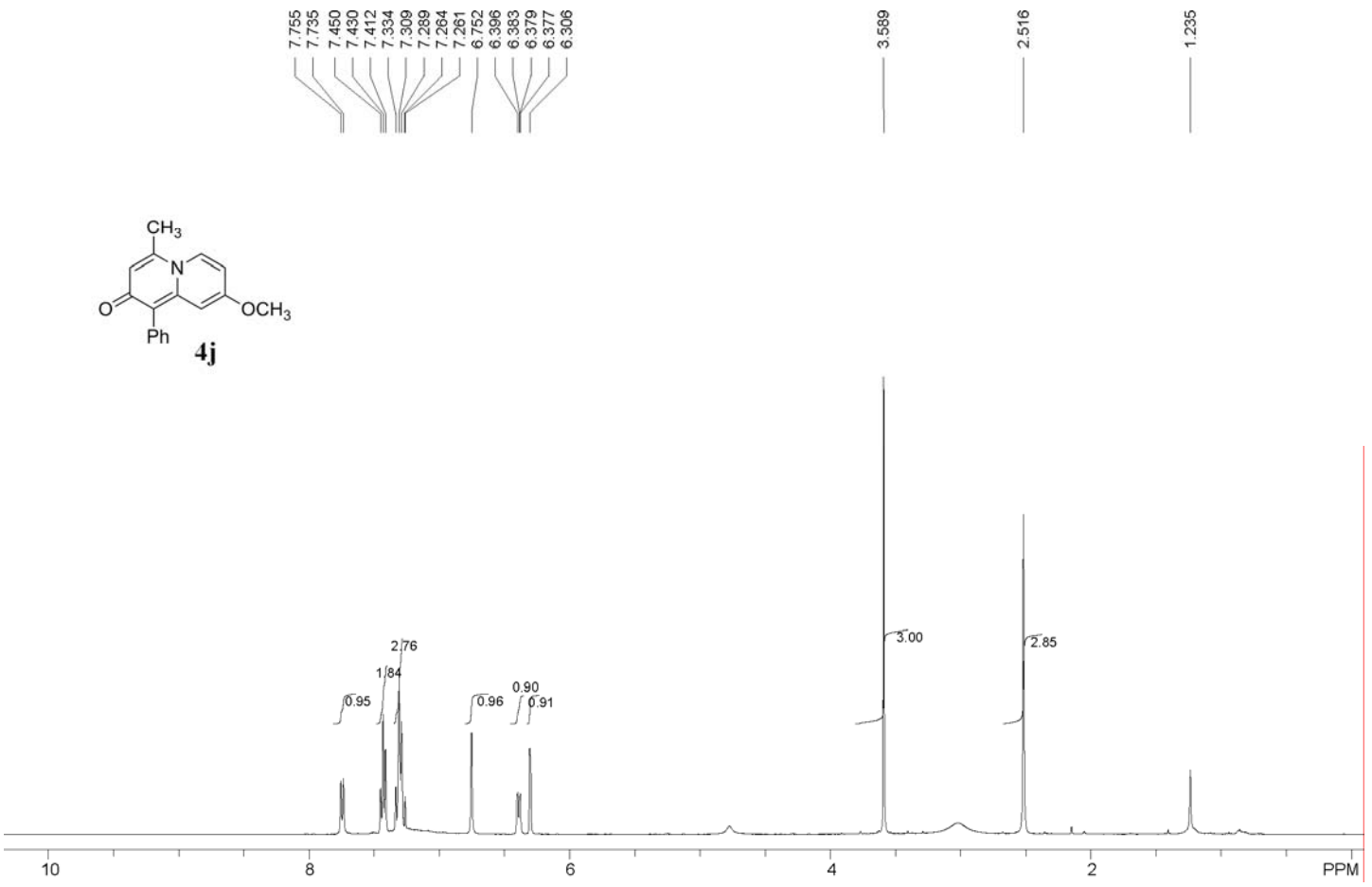
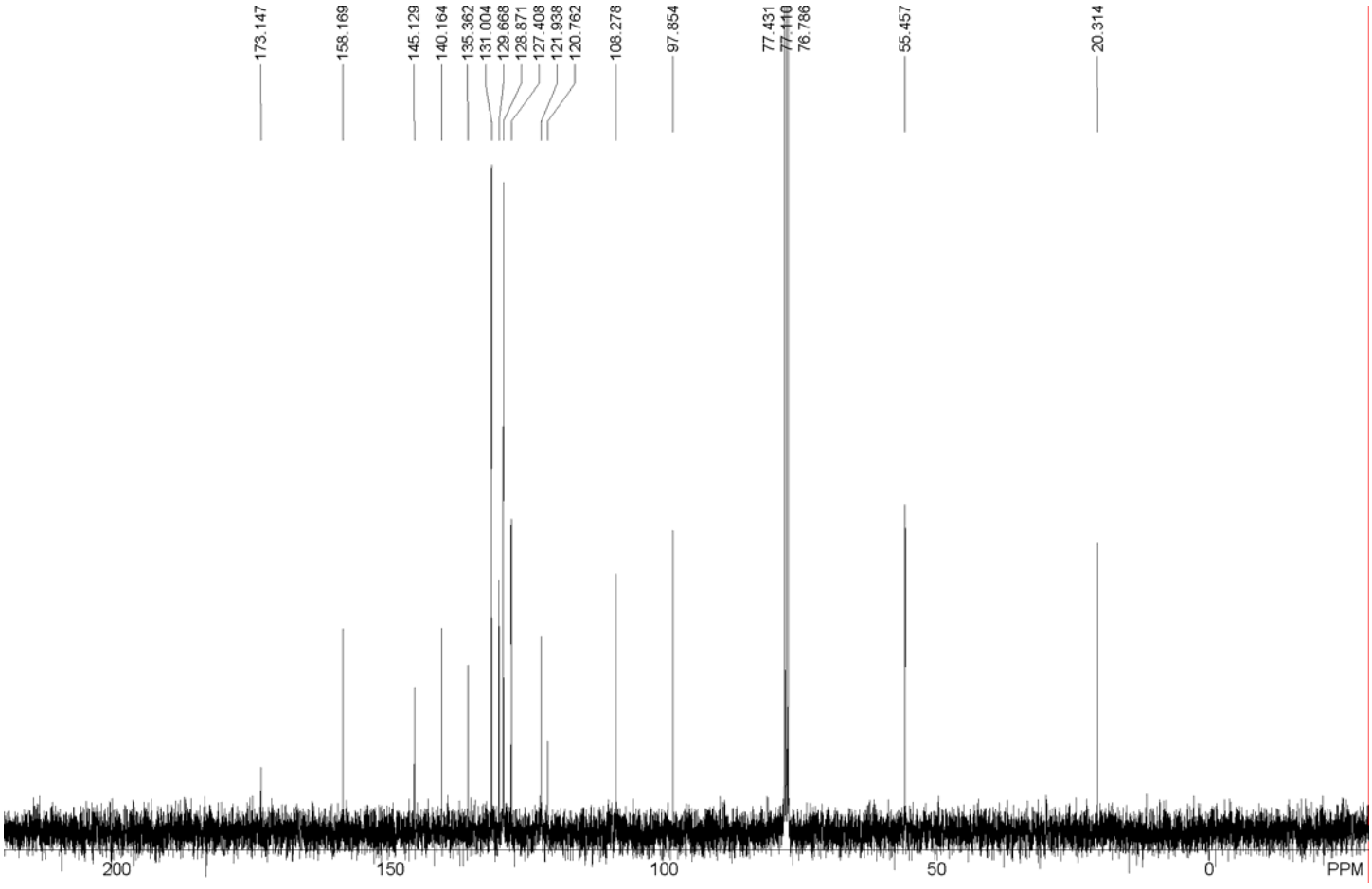
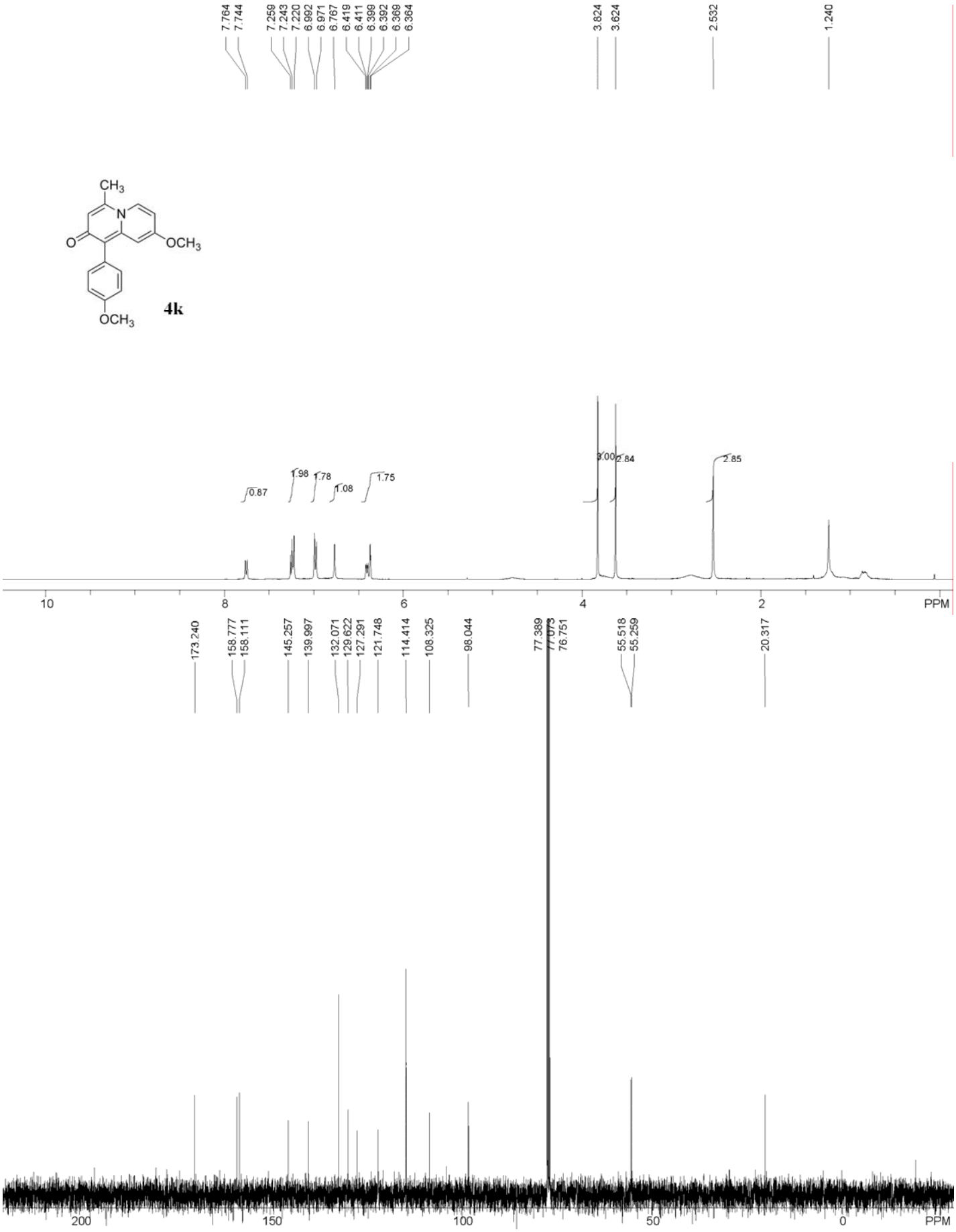
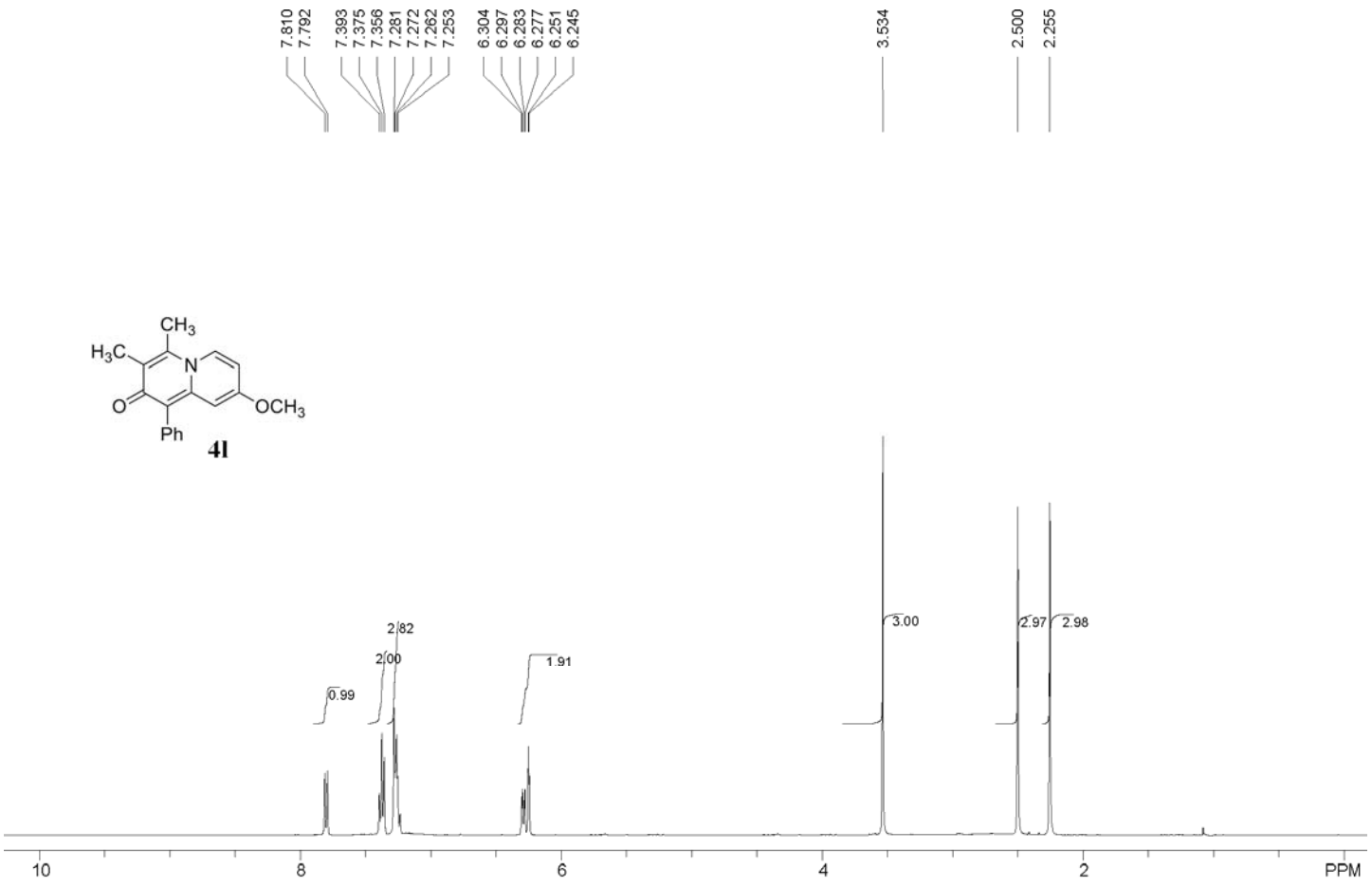
126.929
120.348
119.433
114.786
77.609
77.296
76.977
20.949
16.854
13.175
200
150
100
50
0
PPM









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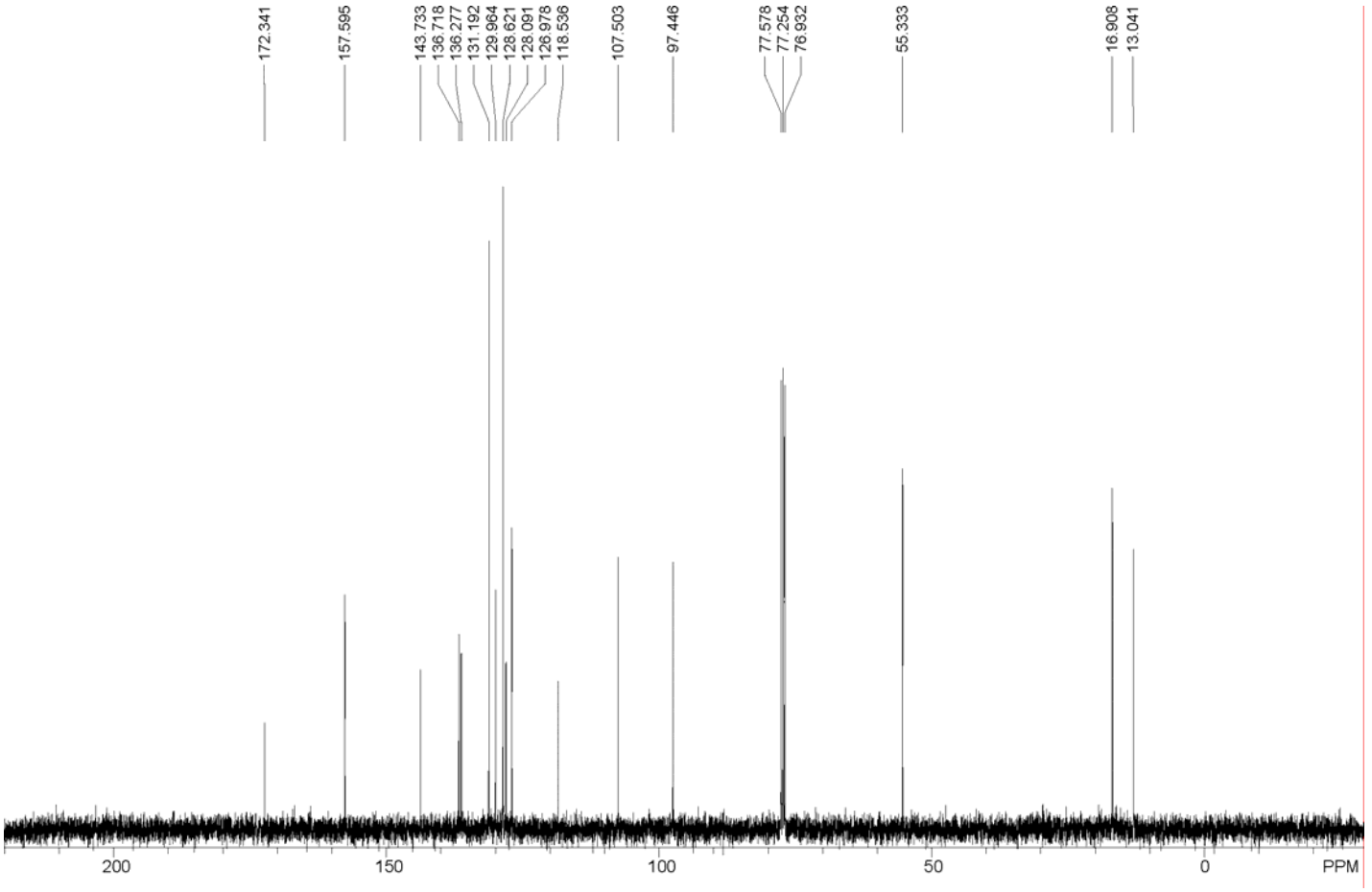

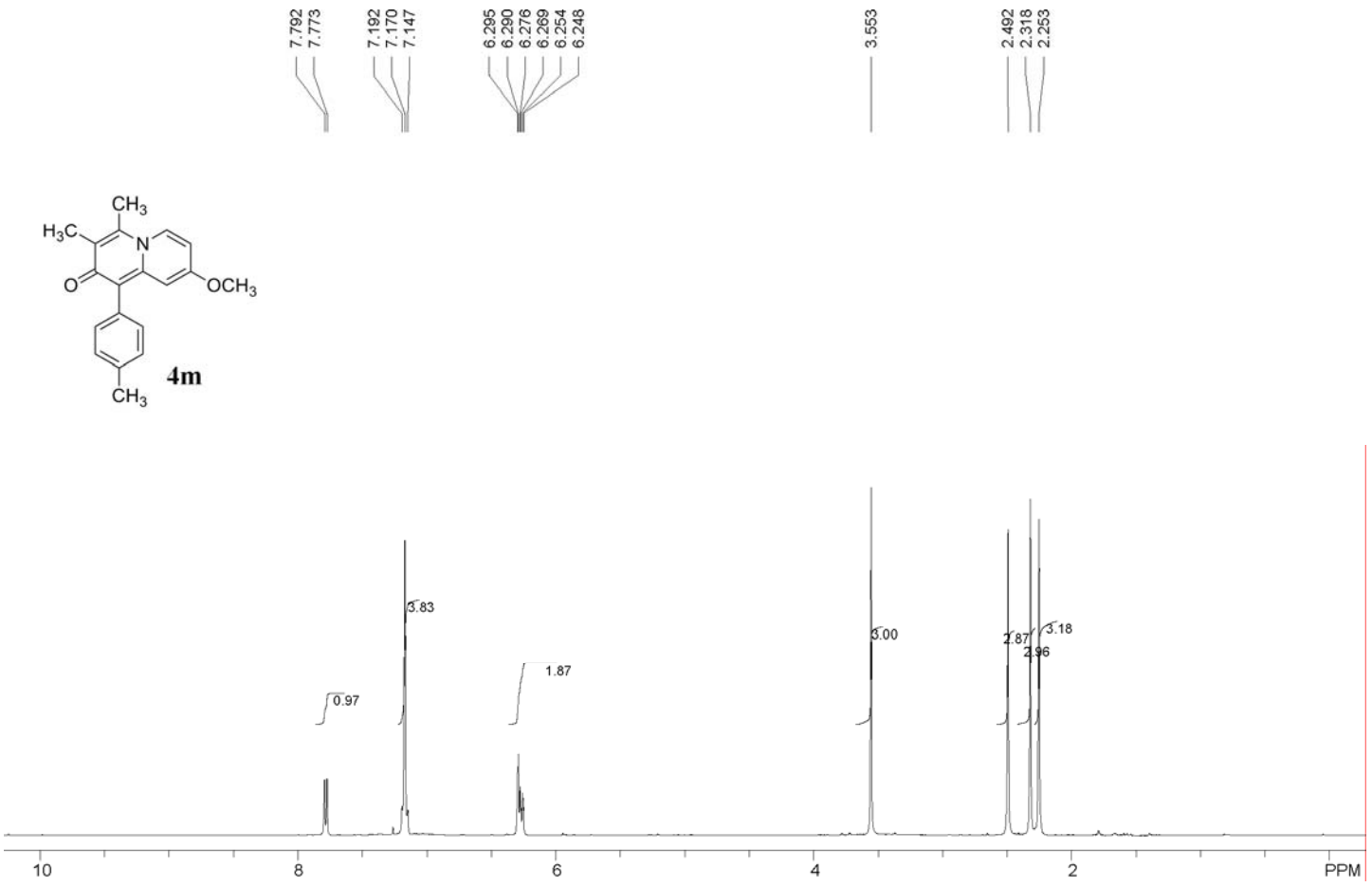

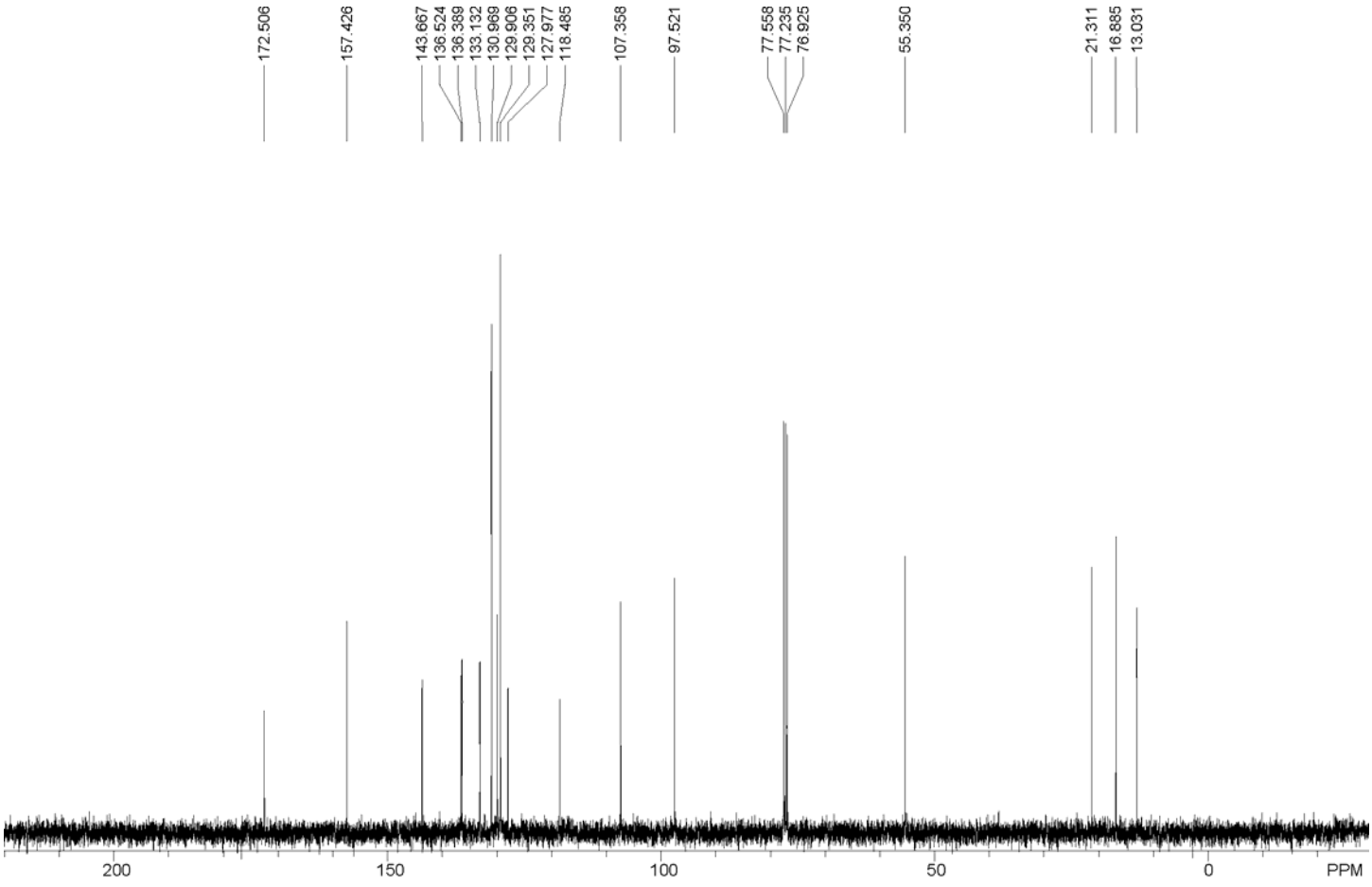

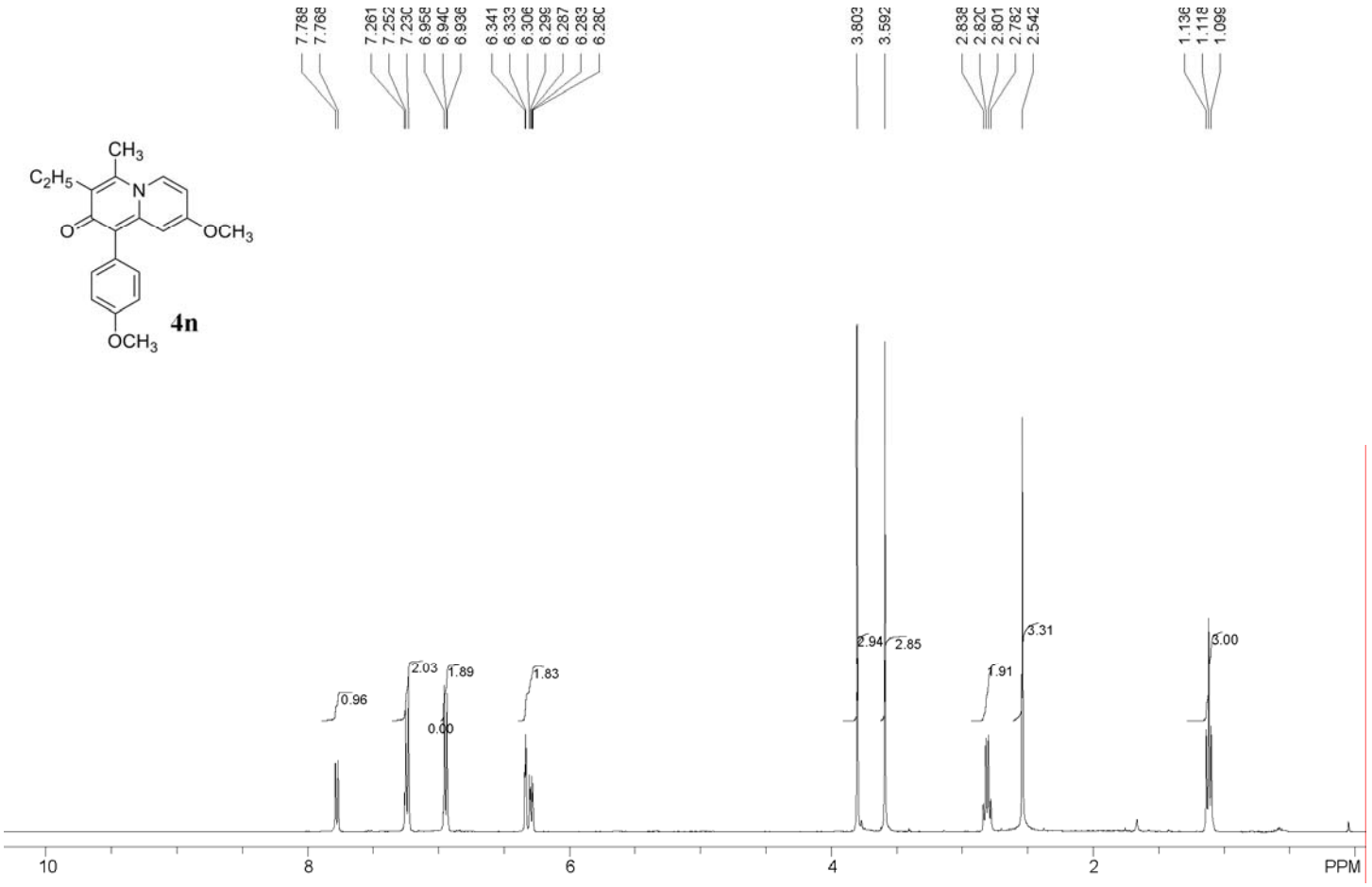
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6.936
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6.333
6.306
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6.287
6.283
6.280
3.803
3.592
2.838
2.820
2.801
2.782
2.542
1.136
1.118
1.098
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C2H5
N
O
OCH3
OCH3
4n
0.96
2.03
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2.94
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1.91
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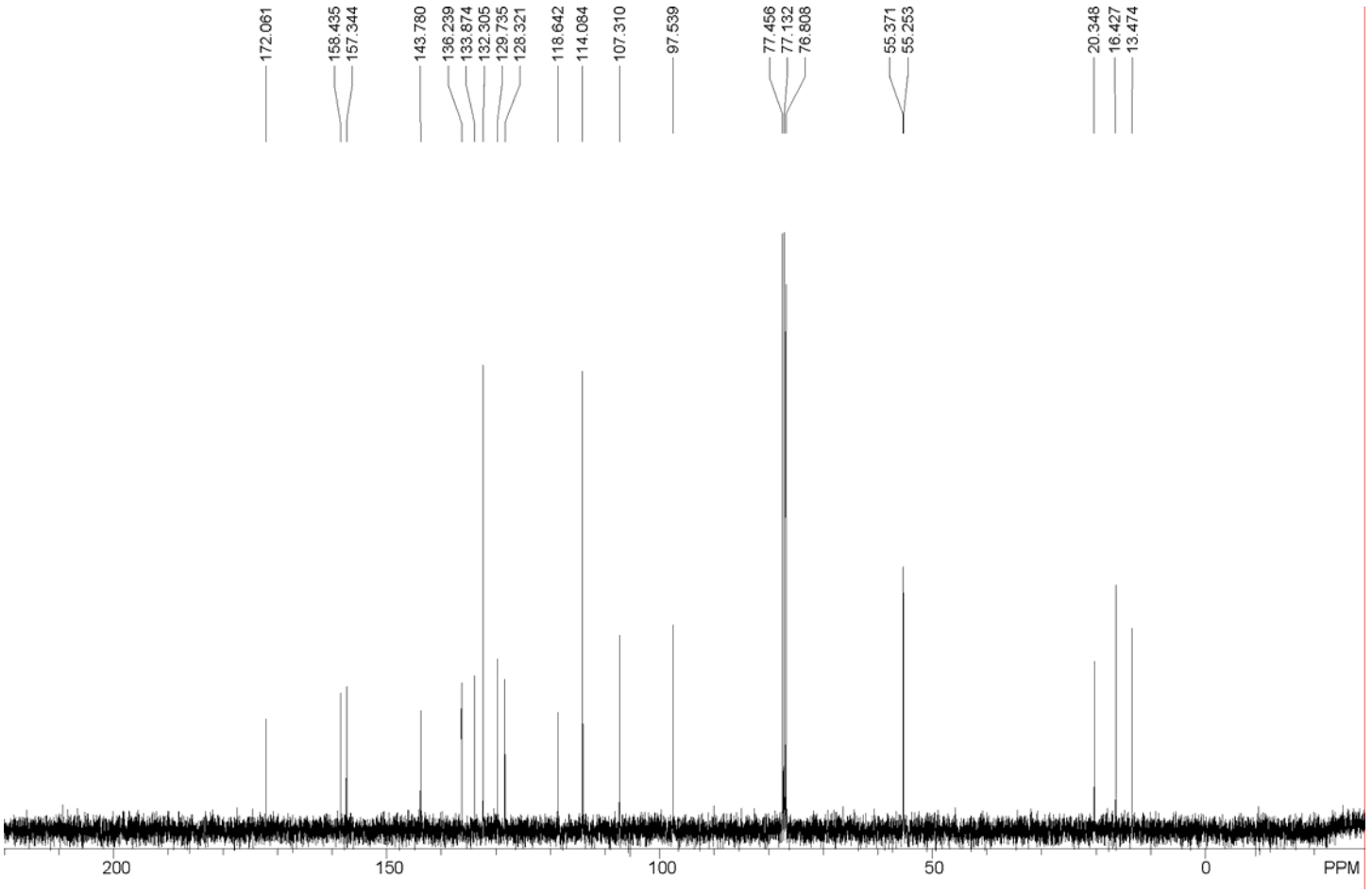
3.00
10
8
6
4
2
PPM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129.735
128.321
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77.456
77.132
76.808
55.371
55.253
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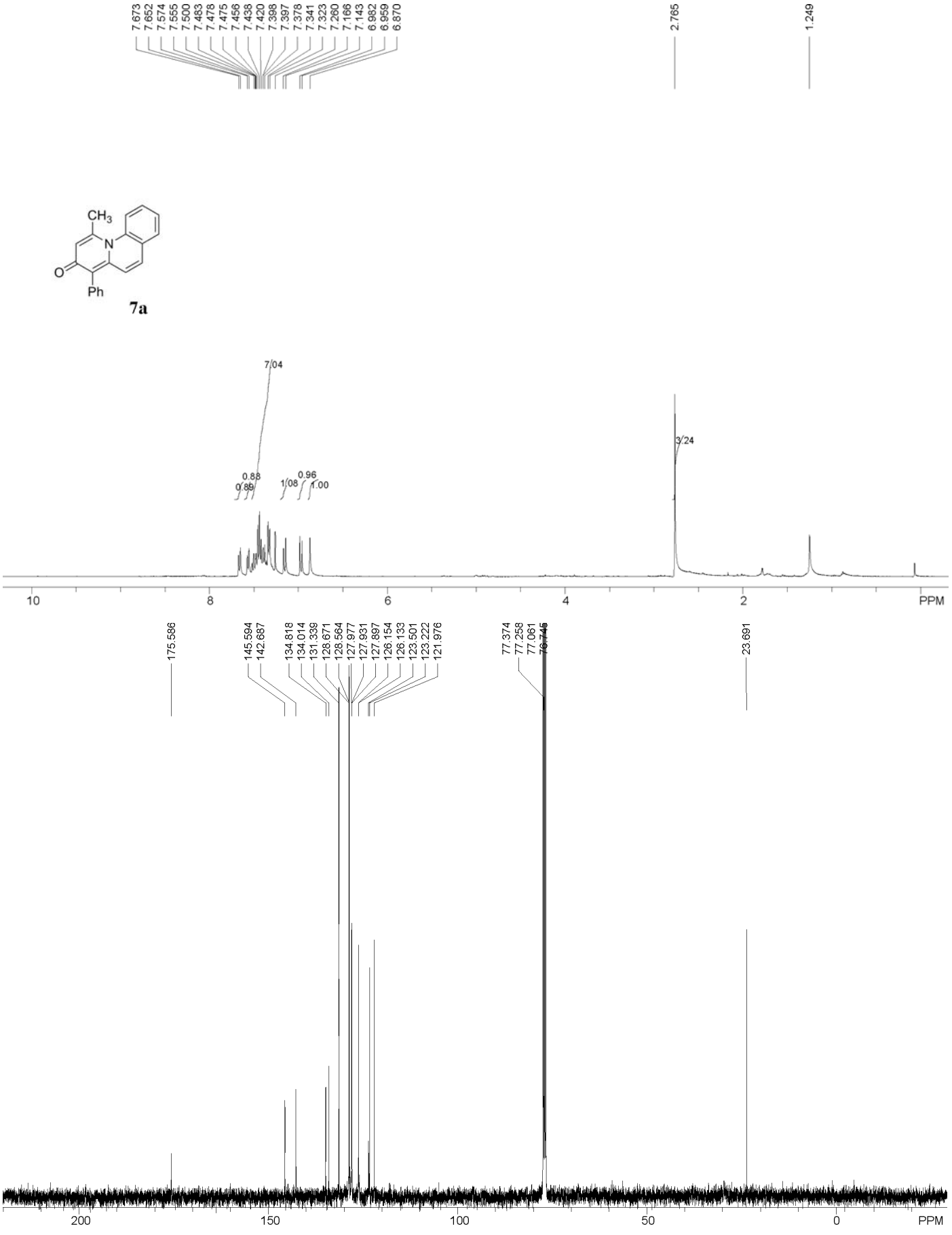
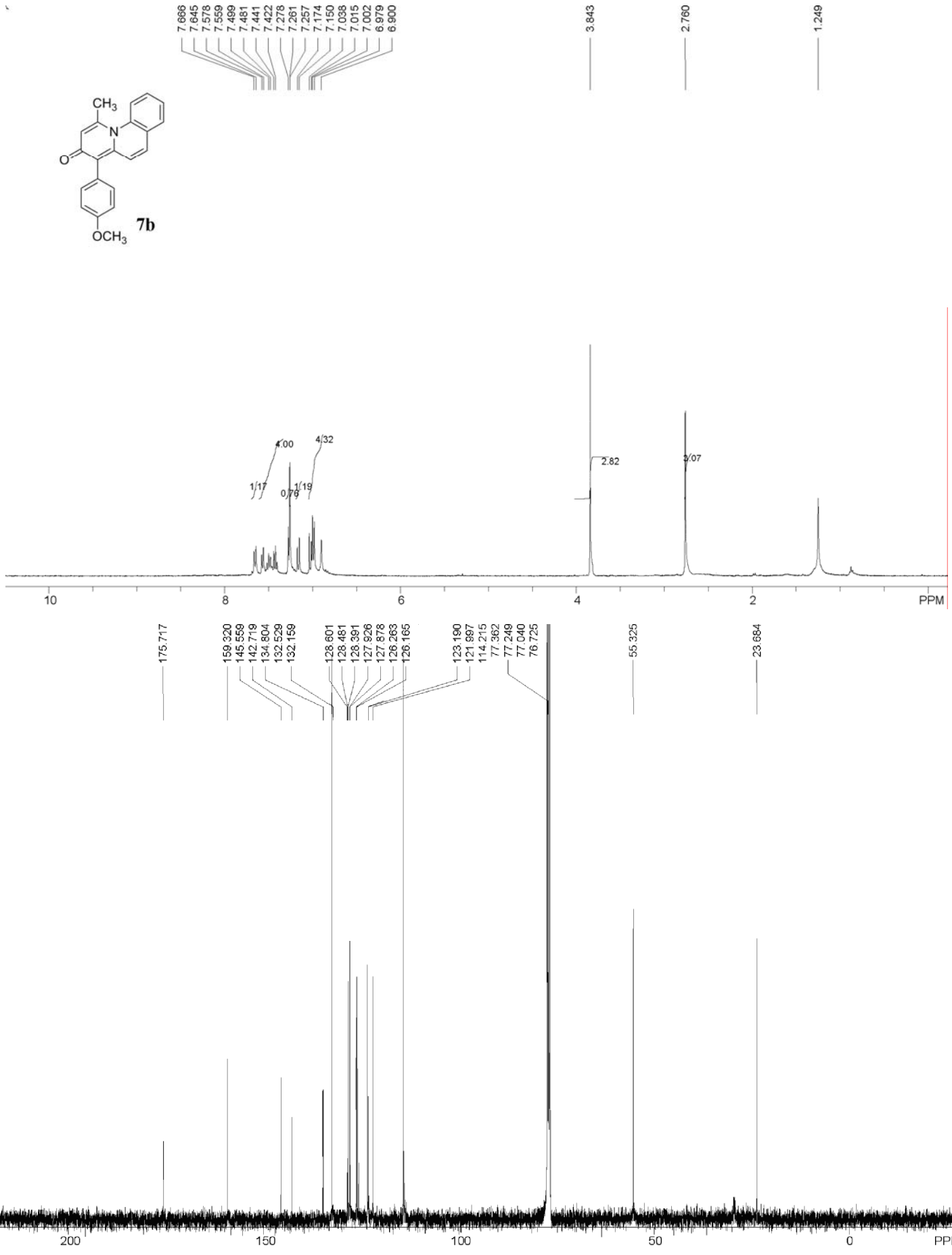
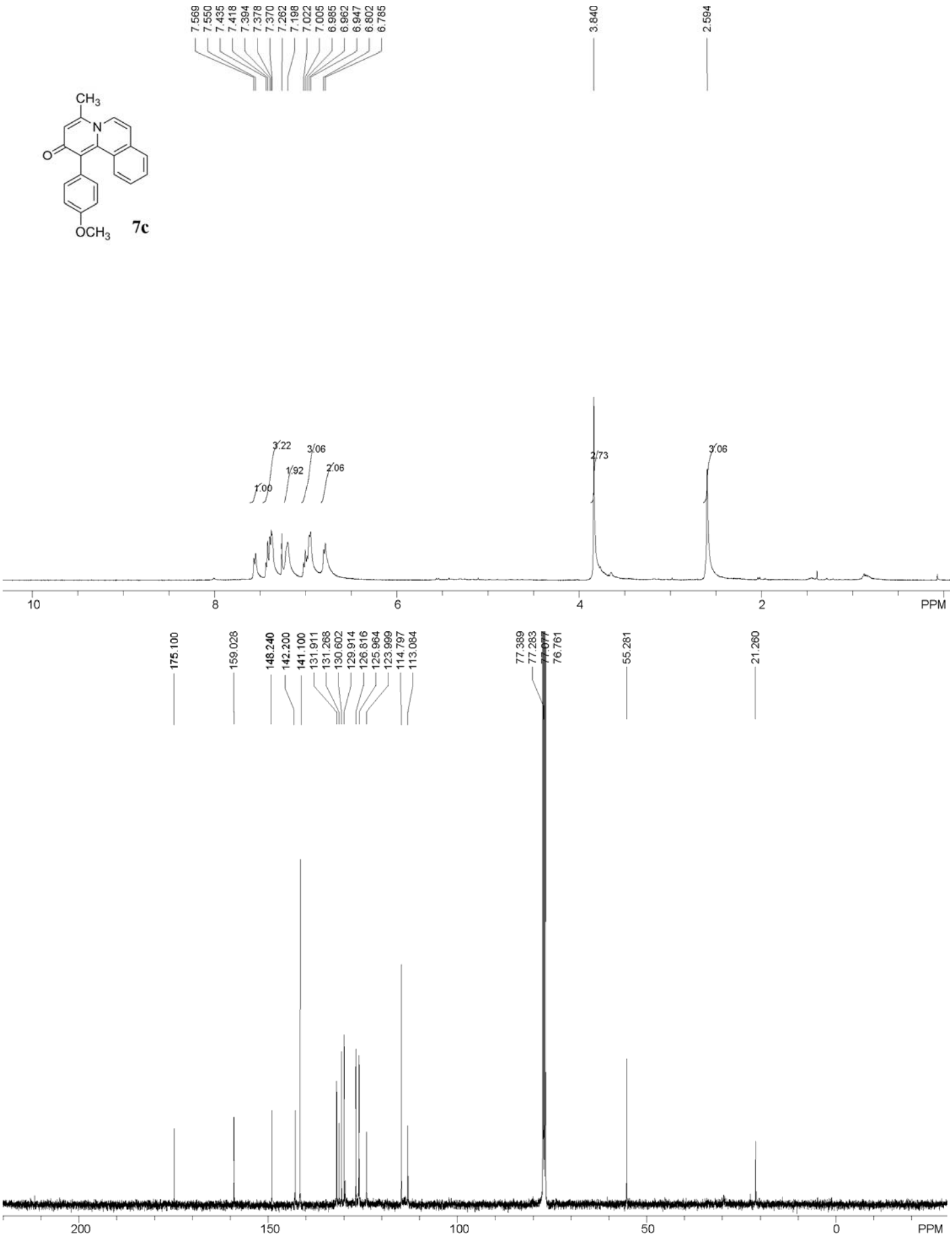
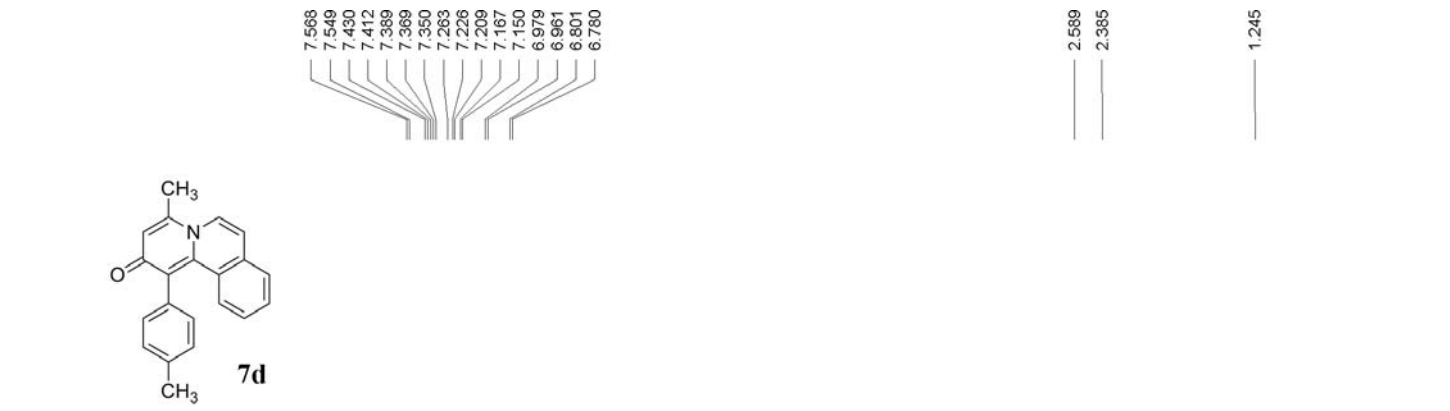
200
150
100
50
0
PPM

V. Copies of ^{1}H and ^{13}C NMR spectra of compounds 7a-7f





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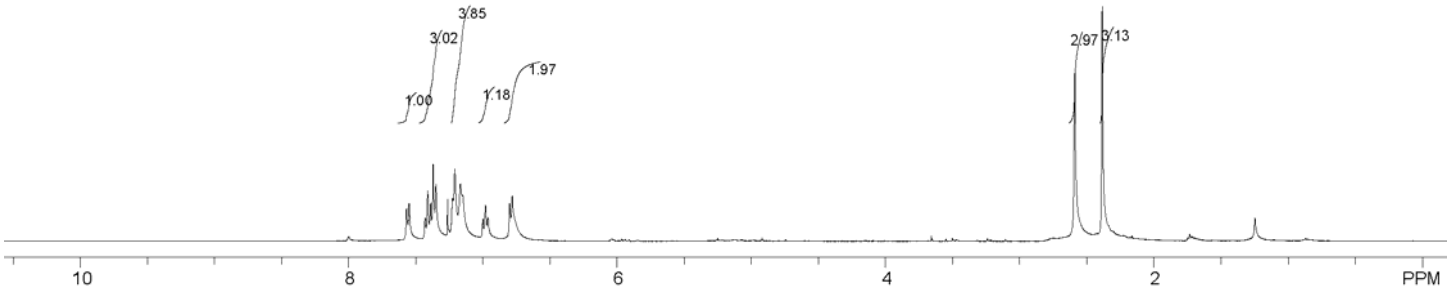
6.961
6.801
6.780
2.589
2.385
1.245

CH3
N
O
CH3

7d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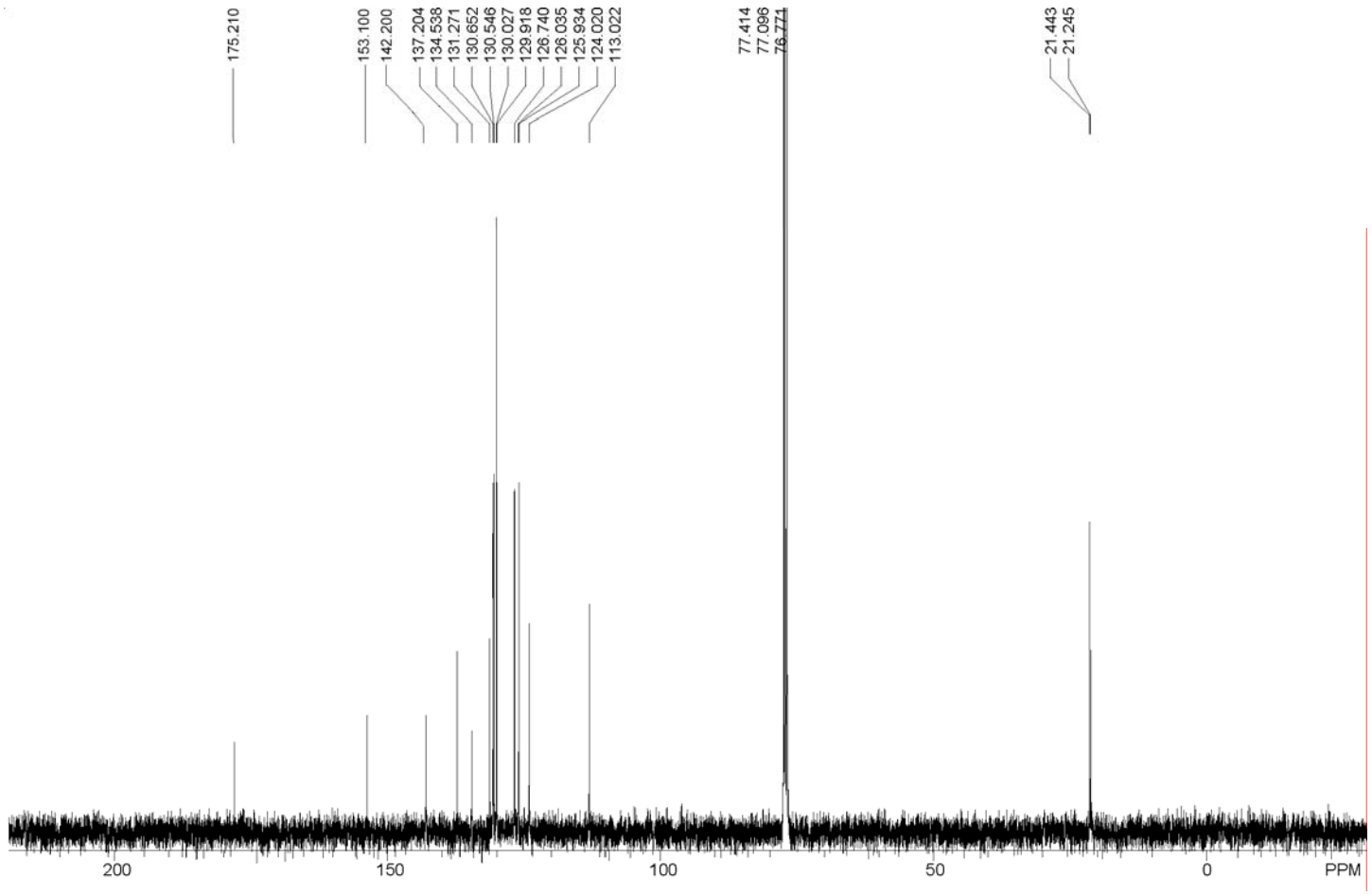
10
8
6
4
2
PPM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137.204
134.538
131.271
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129.918
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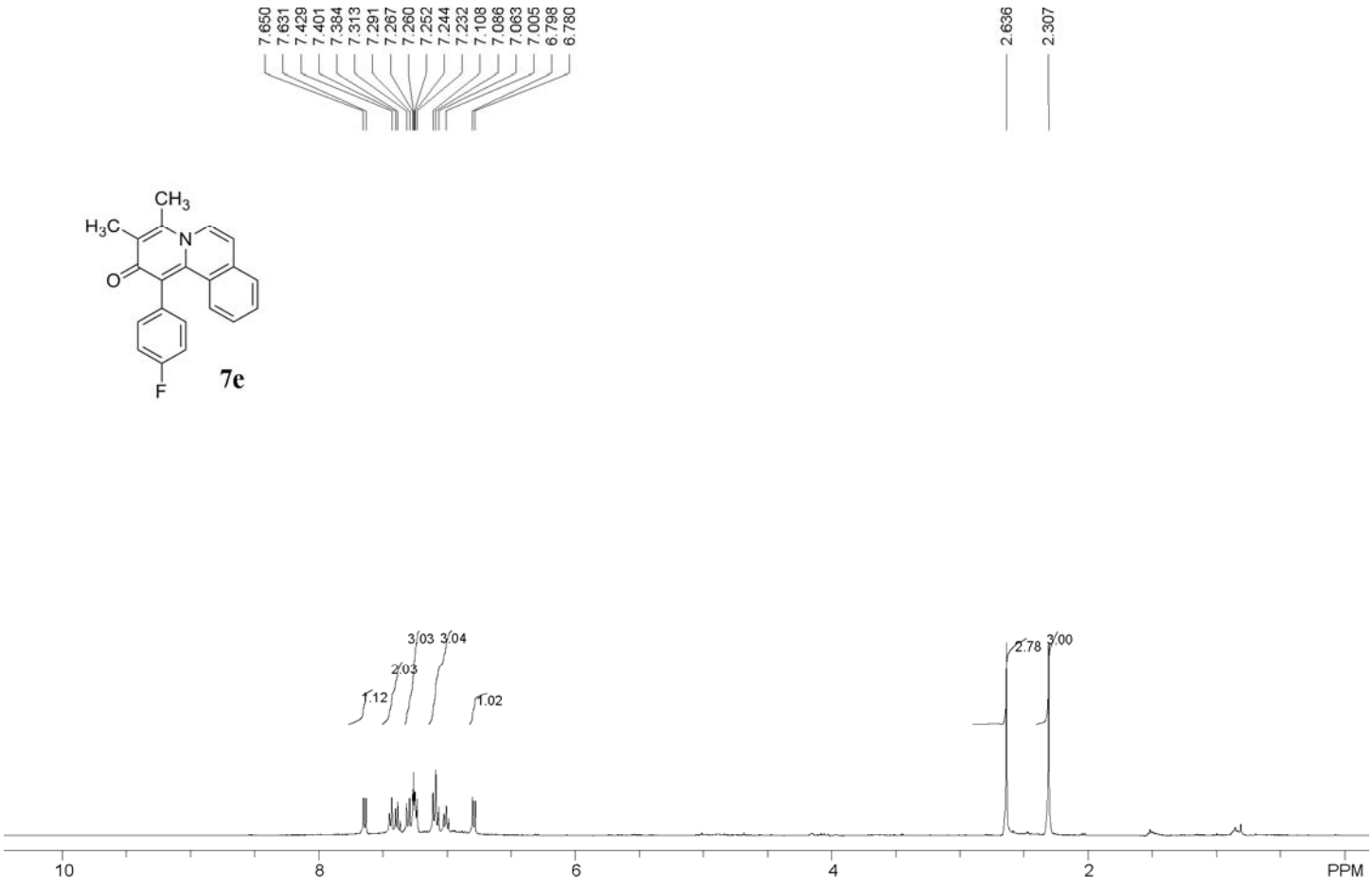
113.022
77.414
77.096
76.771
21.443
21.245
200
150
100
50
0
PPM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7.063
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2.307
CH3
H3C
N
O
F
7e
3.03
3.04
2.03
1.12
1.02
2.78
3.00
10
8
6
4
2
PPM
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160.940
140.685
140.331
139.780
145.329
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134.180
132.760
132.689
131.156
130.352
129.778
127.086
126.606
125.766
125.631
124.525
123.497
116.134
115.919
112.275
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77.252
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76.728
17.634
12.866
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150
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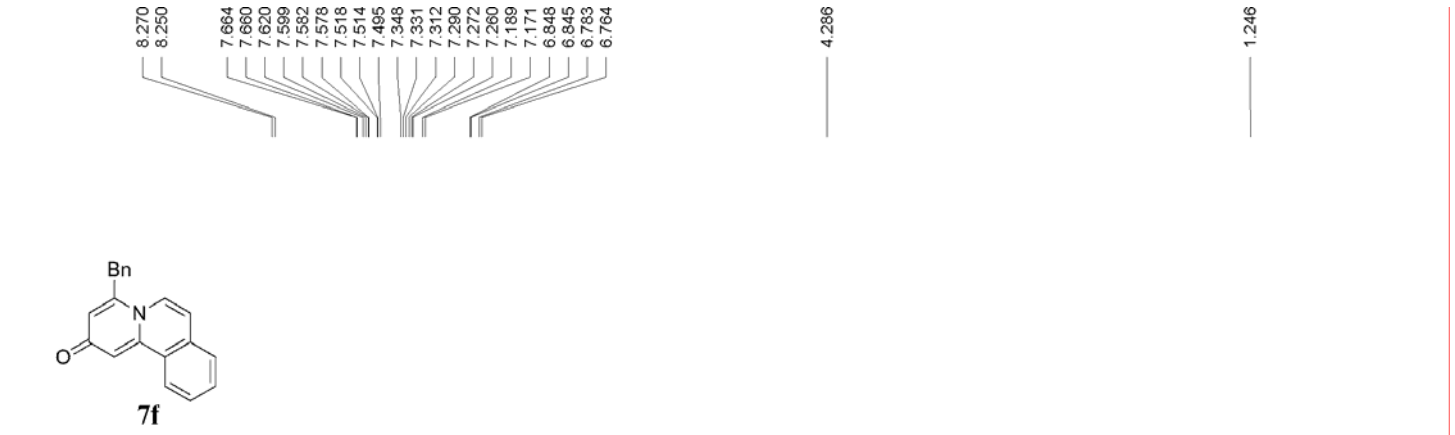
50
0
PPM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8.250
7.664
7.660
7.620
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7.582
7.578
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7.514
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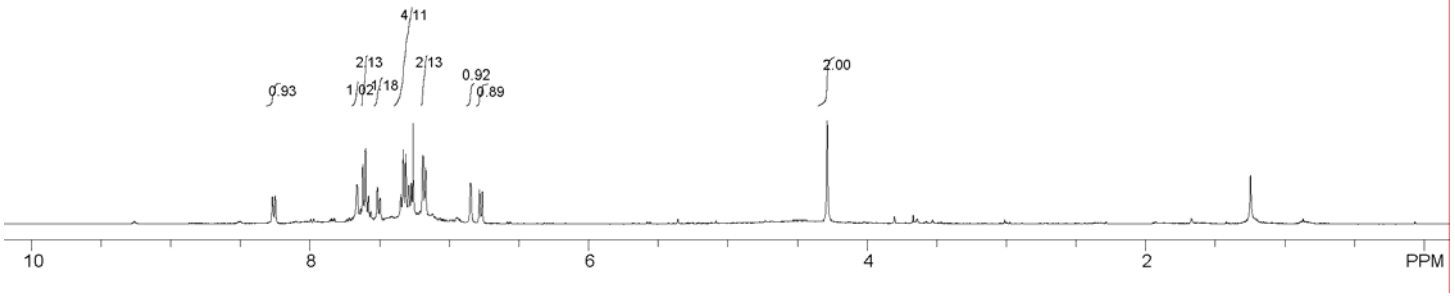
7.312
7.290
7.272
7.260
7.189
7.171
6.848
6.845
6.783
6.764
4.286
1.246

Bn
N
O

7f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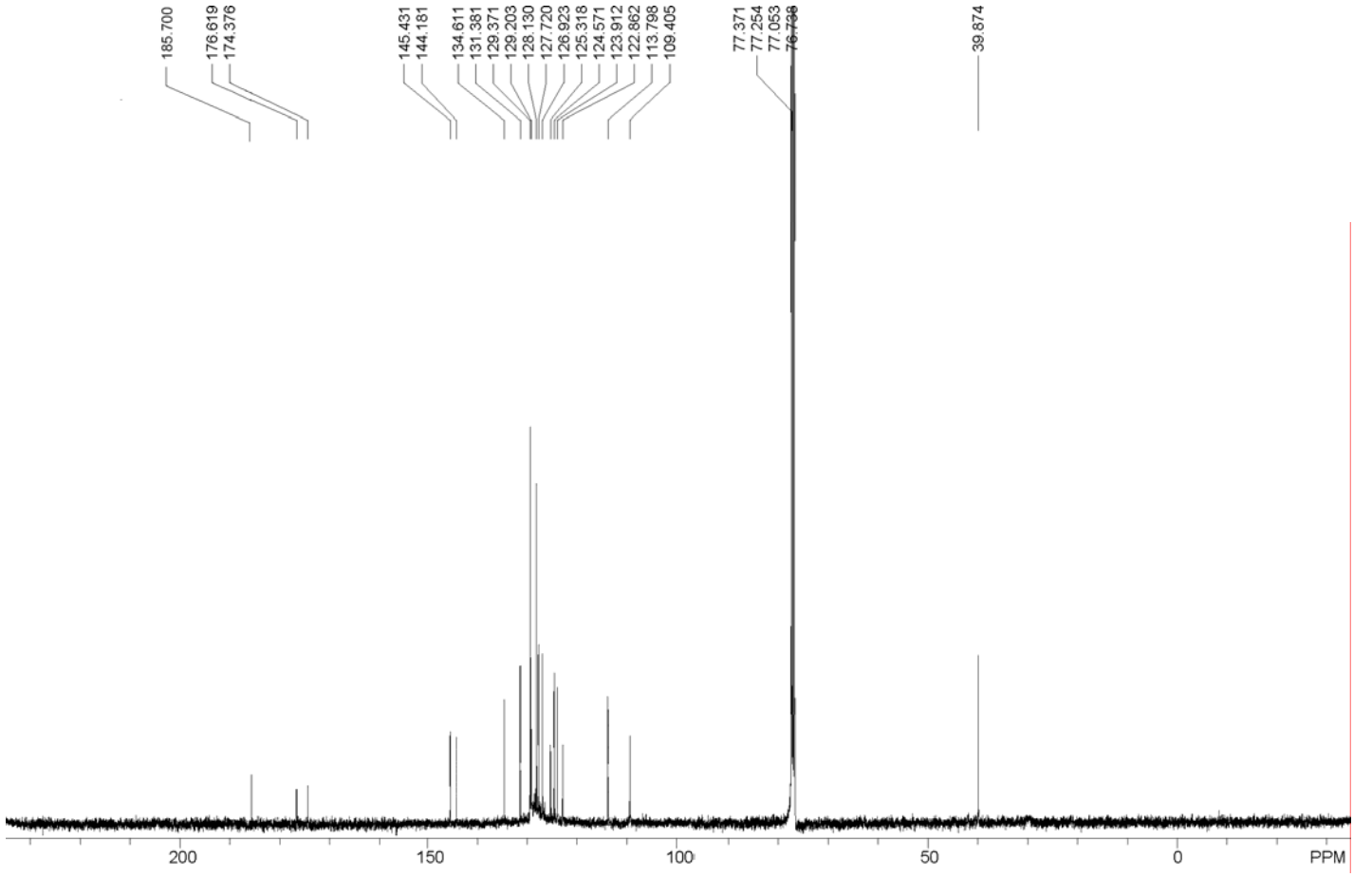
10
8
6
4
2
PPM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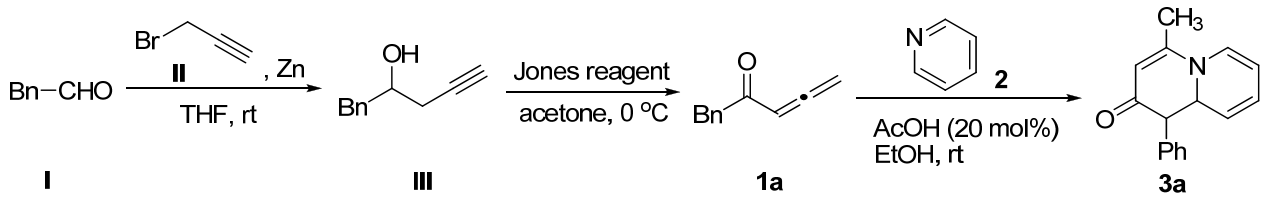
124.571
123.912
122.862
113.798
109.405
77.371
77.254
77.053
76.736
39.874
200
150
100
50
0
PPM

VI. E-factors of the overall process for the synthesis of 3a and 4a.

1. E-factor of the overall process for the synthesis of 3a run on a 100 mmol scale.

1.1 Synthetic procedure toward 4-methyl-1-phenyl-1*H*-quinolizin-2(9*aH*)-one (3a) starting from commercially available 2-phenylacetaldehyde (I) and 3-bromoprop-1-yne (II)



Step 1. Preparation of 1-phenylpent-4-yn-2-ol (**III**): To a flask containing 2-phenylacetaldehyde (**I**, 24.30 g, 200 mmol), THF (100 mL), propargyl bromide (**II**, 47.18 g, 400 mmol) were added activated zinc dust (38.36 g, 600 mmol) portion-wise with stirring. The mixture was then stirred at room temperature. Upon completion, it was treated with NH_4Cl (21.20 g, 400 mmol). Then, the mixture was filtrated and the filtrate was concentrated under vacuum.

Step 2. Preparation of 1-phenylpenta-3,4-dien-2-one (**1a**): To a solution of the residue resulting from step 1 in acetone (450 mL) cooled to 0 ºC was added Jones reagent (79.20 mL) in a dropwise manner. Upon complete consumption of the starting material as monitored by TLC, the reaction mixture was dried over Na_2SO_4. Then, the solvent was filtered and the filtrate was concentrated under vacuum. The residue were purified by column chromatography on silica gel with EtOAc/petroleum (20%) to give 1-phenylpenta-3,4-dien-2-one (**1a**, 25.61 g, 81% as an overall yield from **I**).

Step 3. Preparation of 4-methyl-1-phenyl-1*H*-quinolizin-2(9*aH*)-one (**3a**): To a flask containing pyridine (**2a**, 7.90 g, 100 mmol), AcOH (1.20 g, 20 mmol), EtOH (95%, 50 mL) was added 1-phenylpenta-3,4-dien-2-one (**1a**, 15.81 g, 100 mmol). The mixture was stirred at rt for 2 h. Upon completion, the resulting mixture was treated with water (100 mL), and the mixture was let to stand at 0 °C overnight. The solids thus precipitated were collected by filtration to give **3a** (17.78 g, 75%).

1.2 Mass balance and E-factor of the overall process for the synthesis of 3a starting from commercially available 2-phenylacetaldehyde (I) and 3-bromoprop-1-yne (II)[4]

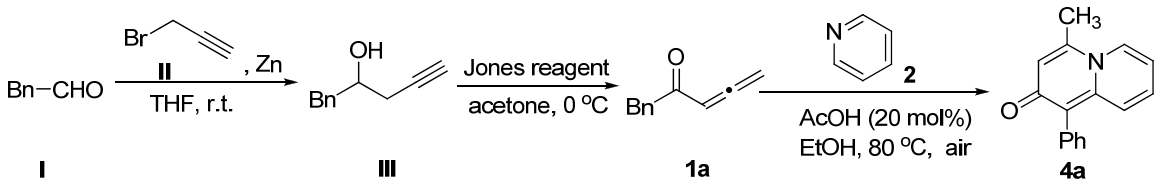
Table 1 Mass balance [a] and E-factor of the overall process to **3a**.

Input	Quantity/kg	Output	Quantity/kg
THF	3.0864	THF	3.0864
Zn	1.3314	Inorganic salts	2.0673
NH_4Cl	0.7359		
Jones' reagent	3.7487	Inorganic salts	8.2471
Na_2SO_4	4.4984		
Acetone	12.2534	Acetone	12.2534
Silica gel	5.6230	Silica gel	5.6230
EtOAc	2.0288	EtOAc	2.0288
Petroleum	7.1975	Petroleum	7.1975
AcOH	0.0675	AcOH	0.0675
EtOH (95%)	0.4694	EtOH (95%)	0.4694
2-phenylacetaldehyde	0.8334	By-products	1.9153
3-bromoprop-1-yne	1.6375		
Pyridine **2a**	0.4444	4-Methyl-1-phenyl-1*H*-quinolizin-2(9*aH*)-one **3a**	1.0
Total	43.9557	Total	43.9557
		E-factor[b]	43

[a] Mass balance calculated for the hypothetical production of 1 kg 4-methyl-1-phenyl-1*H*-quinolizin-2(9*aH*)-one (**3a**). [b] E-factor = (amount of total waste)[kg]/(amount of product)[kg]; the E-factor was given above without decimal places (E = 43); the calculated E-factor with decimal places is 42.9557.

2. E-factor of the overall process for the synthesis of 4a run on a 100 mmol scale.

2.1 Synthetic procedure toward 4-methyl-1-phenyl-2*H*-quinolizin-2-one (4a) starting from commercially available 2-phenylacetaldehyde (I) and 3-bromoprop-1-yne (II)



Step 1. Preparation of 1-phenylpent-4-yn-2-ol (**III**): To a flask containing 2-phenylacetaldehyde (**I**, 24.30 g, 200 mmol), THF (100 mL), propargyl bromide (**II**, 47.18 g, 400 mmol) were added activated zinc dust (38.36 g, 600 mmol) portion-wise with stirring. The mixture was then stirred at room temperature. Upon completion, it was treated with NH_4Cl (21.20 g, 400 mmol). Then, the mixture was filtrated and the filtrate was concentrated under vacuum.

Step 2. Preparation of 1-phenylpenta-3,4-dien-2-one (**1a**): To a solution of the residue resulting from step 1 in acetone (450 mL) cooled to 0 ºC was added Jones reagent (79.20 mL) in a dropwise manner. Upon complete consumption of the starting material as monitored by TLC, the reaction mixture was dried over Na_2SO_4. Then, the solvent was filtered and the filtrate was concentrated under vacuum. The residue were purified by column chromatography on silica gel with EtOAc/petroleum (20%) to give 1-phenylpenta-3,4-dien-2-one (**1a**, 25.61 g, 81% as an overall yield from **I**).

Step 3. Preparation of 4-methyl-1-phenyl-2*H*-quinolizin-2-one (**4a**): To a flask containing pyridine (**2a**, 7.90 g, 100 mmol), AcOH (1.20 g, 20 mmol), EtOH (95%, 50 mL) was added 1-phenylpenta-3,4-dien-2-one (**1a**, 15.81 g, 100 mmol). The mixture was stirred at 80 ^{o}C for 12 h. Upon completion, the resulting mixture was treated with water (100 mL), and the mixture was let to stand at 0 ^{o}C overnight. The solids thus precipitated were collected by filtration to give **4a** (15.28 g, 65%).

2.2 Mass balance and E-factor of the overall process for the synthesis of 4a starting from commercially available 2-phenylacetaldehyde (I) and 3-bromoprop-1-yne (II)[4]

Table 2 Mass balance [a] and E-factor of the overall process to **4a**.

Input	Quantity/kg	Output	Quantity/kg
THF	3.5920	THF	3.5920
Zn	1.5494	Inorganic salts	2.4058
NH_4Cl	0.8564		
Jones' reagent	4.3627	Inorganic salts	9.5980

Na_2SO_4	5.2353		
Acetone	14.2605	Acetone	14.2605
Silica gel	6.5441	Silica gel	6.5441
EtOAc	2.3611	EtOAc	2.3611
Petroleum	8.3764	Petroleum	8.3764
AcOH	0.0785	AcOH	0.0785
EtOH (95%)	1.0925	EtOH (95%)	0.5462
O_2	0.0105	By-products	2.4034
2-phenylacetaldehyde	0.9700		
3-bromoprop-1-yne	1.9057	4-Methyl-1-phenyl-2*H*-quinolizi	1.0
Pyridine **2a**	0.5172	n-2-one **4a**	
Total	51.7123	Total	51.1660
		E-factor [b]	50

[a] Mass balance calculated for the hypothetical production of 1 kg 4-Methyl-1-phenyl-2*H*-quinolizin-2-one **4a**. [b] E-factor = (amount of total waste)[kg]/(amount of product)[kg]; the E-factor was given above without decimal places (E = 50); the calculated E-factor with decimal places is 50.1660.

VII. References

(1) A. Sniady, M. S. Morreale and R. Dembinski, *Org. Synth.,* 2007, **84**, 199.

(2) W. L. Wu, Z. J. Yao, Y. L. Li, J. C. Li, Y. Xia and Y. L. Wu, *J. Org. Chem*., 1995, **60**, 3257.

(3) N. A. Petasis and K. A. Teets, *J. Am. Chem. Soc.,* 1992, **114***,* 10328.

(4) M. Weiß, T. Brinkmann and H. Gröger, *Green Chem*., 2010, **12**, 1580.