Electronic Supporting Information

Gluconic acid aqueous solution as a sustainable and recyclable promoting medium for organic reactions

Binghua Zhou,[a] Jie Yang,[a] Minghao Li[a] and Yanlong Gu[a,b*]

[a]: Institute of Physical Chemistry and Industrial Catalysis, Hubei Key Laboratory of Material Chemistry and Service Failure, School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, 1037 Luoyu road, Hongshan District, Wuhan 430074, China.

[b]: State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Lanzhou, 730000, China

General remarks:

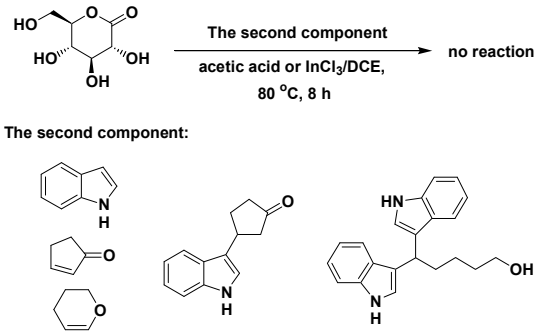
Indole, *N*-methylindole, 2-methylindole, 4-chloroindole, 5-methoxyindole, 2-methyl-5-methoxyindole, 5-bromoindole, 6-fluoroindole, 6-methylindole, *β*-nitro-3,4-dimethoxystyrene, cyclopent-2-enone, 1-phenyl-2-buten-1-one, 2-furfurylideneacetone, 2-thienylidenacetone, 3, 4-dihydro-2*H*-pyran, D-gluconic acid solution (50%), (±)-1-(4-methoxyphenyl)-1-ethanol, veratryl alcohol, 9-hydroxyxanthene, (±)-1-(6-methoxynaphthyl)ethanol and chloroform-*d* were purchased from Alfa Aesar Chemical Company. 2-Naphthol, methyl acetoacetate, pyrrole, ethyl acetoacetate, acetylacetone, *N,N*-dimethylaniline, *p*-toluenesulfonic acid, $FeCl_3$ (anhydrous), $SnCl_4$, $ZnCl_2$, H_3BO_3, $CuCl_2$, $NiCl_2$, DMSO, 1,4-dioxane, 1,2-dichloroethane, acetic acid, acetonitrile, nitromethane, DMF, toluene, ethyl acetate, and formaldehyde aqueous solution (37wt%) were purchased from Sinopharm Chemical Reagent Co., Ltd. ^1H and ^{13}C NMR spectra were recorded on a Bruker AV-400. Chemical shifts are expressed in ppm relative to Me_4Si in $CDCl_3$. IR spectra were recorded on a FT-IR Bruker (VERTEX 70) using KBr technology.

A typical procedure for Michael reaction of indole: All reactions were conducted in a 10 mL of V-type flask equipped with triangle magnetic stirring. In a typical reaction, gluconic acid aqueous solution (1.0 ml) was mixed with indole (***1a***, 58.5 mg, 0.50 mmol) and cyclopent-2-enone (***2a***, 49.3 mg, 0.60 mmol) under air. The mixture was stirred for 10 hours at 100 ^oC. After reaction, the mixture was cooled to room temperature and the reaction mixture was extracted with a mixed solution composed of ethyl acetate and heptane (v/v = 2/1, 6 ml × 3). After concentration of the combined organic phase under reduced pressure, the desired product, ***3a***, was obtained by preparative TLC using a mixed solution of ethyl acetate and petro ether as eluting solvent (the ratio of ethyl acetate/petroether is 1/7). 82.7 mg, Yield = 83%. The recovered GAAS phase could

be reused after 20 min of treatment at 70 ^{o}C under reduced pressure (10 mmg Hg). The 20 mmol scale reaction of ***1a*** and ***2a*** was performed in a 100 ml flask by using increased amount of GAAS (60 ml) as medium. Experiments for substrate scope were all performed according to a similar procedure.

A typical procedure for electrophilic ring-opening of 3,4-dihydro-2*H*-pyran with indole: All reactions were conducted in a 10 mL of V-type flask equipped with triangle magnetic stirring. In a typical reaction, gluconic acid aqueous solution (1.0 ml) was mixed with indole (***1a***, 58.6 mg, 0.50 mmol) and 3,4-dihydro-2H-pyran (***4a***, 31.5 mg, 0.38 mmol) under air. The mixture was stirred for 11 hours at 100 ^{o}C. After reaction, the mixture was cooled to room temperature and the reaction mixture was extracted with a mixed solution composed of ethyl acetate and heptane (v/v = 2/1, 6 ml × 3). After concentration of the combined organic phase under reduced pressure, the desired product, ***5a***, was obtained by preparative TLC using a mixed solution of ethyl acetate and petro ether as eluting solvent (the ratio of ethyl acetate/petroether is 1/7). 65.2 mg, Yield = 82%. Experiments for substrate scope were all performed according to a similar procedure.

A typical procedure for Friedel-Crafts alkylation of indoles with benzyl alcohols: All reactions were conducted in a 10 mL of V-type flask equipped with triangle magnetic stirring. In a typical reaction, gluconic acid aqueous solution (1.0 ml) was mixed with(±)-1-(4-methoxyphenyl)-1-ethanol (***6a***, 76.1 mg, 0.5 mol) and indole (***1a***, 64.5 mg, 0.55 mmol) under air. The mixture was stirred for 6 hours at 50 ^{o}C. After reaction, the mixture was cooled to room temperature and the reaction mixture was extracted with a mixed solution composed of ethyl acetate and heptane (v/v = 1/1, 6 ml × 3). After concentration of the combined organic phase under reduced pressure, the desired product was obtained by preparative TLC using a mixed solution of ethyl acetate and petro ether as eluting solvent (the ratio of ethyl acetate/petroether is 1/7). Experiments for substrate scope were all performed according to a similar procedure. In the reaction of indole, because the product solidified well at the end of the reaction, by adding water into the reaction system, the solid product could be precipitated out directly. After many times of washing with water and drying at atmospheric pressure, the product could be obtained with high purity.



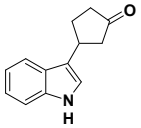
Scheme S1. Reactivity of gluconic acid lactone toward **1a**, **2a**, **3a**, **4a** and **5a**.

Table S1. pH and conductivity change of GAAS before and after use in the first model reaction

Solvent data	before reaction	after application
pH	1.52	2.22
Conductivity (ms/cm)	0.92	0.91

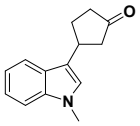
Spectroscopic data of known compounds

3-(1*H*-indol-3-yl)cyclopentanone (3a)[1]



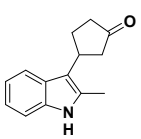
Yellow oil, ^{1}H NMR ($CDCl_3$): 1.95-2.15 (m, 1H), 2.14-2.25 (m, 1H), 2.26-2.42 (m, 3H), 2.65 (dd, J_a = 7.6 Hz, J_b = 18.0 Hz, 1H), 3.55 (quint, J = 7.6 Hz, 1H), 6.79 (d, J = 2.0 Hz, 1H), 7.09 (t, J = 7.6 Hz, 1H), 7.16 (t, J = 7.2 Hz, 1H), 7.26 (d, J = 8.0 Hz, 1H), 8.50 (bs, J = 1H); ^{13}C NMR ($CDCl_3$): 30.2, 34.0, 38.5, 45.7, 111.8, 118.5, 119.4, 119.6, 120.5, 122.5, 126.9, 137.1, 220.5.

3-(1-Methyl-1*H*-indol-3-yl)cyclopentanone (3b)[2]



Red solid, mp: 59-60^{o}C, ^{1}H NMR ($CDCl_3$): 2.03-2.12 (m, 1H), 2.26 (quint, J = 9.2 Hz, 1H), 2.32-2.43 (m, 2H), 2.43-2.51 (m, 1H), 2.69 (dd, J_a = 8.0 Hz, J_b = 18.4 Hz, 1H), 3.65 (quint, J = 7.2 Hz, 1H), 3.69 (s, 3H), 6.79 (s, 1H), 7.10 (dt, J_a = 0.8 Hz, J_b = 7.6 Hz, 1H), 7.22 (t, J = 7.2 Hz, 1H), 7.27 (d, J = 8.0 Hz, 1H), 7.59 (d, J = 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$): 30.2, 32.7, 33.8, 38.3, 45.6, 109.6, 117.2, 119.0, 119.3, 122.0, 124.9, 127.2, 137.5, 219.4.

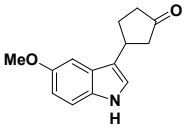
3-(2-Methyl-1*H*-indol-3-yl)cyclopentanone (3c)[3]



Red solid, mp: 140-142^{o}C, ^{1}H NMR ($CDCl_3$): 1.16-2.23 (m, 2H), 2.33 (s, 3H), 2.36-2.46 (m, 1H), 2.46-2.52 (m, 1H), 2.54 (d, J = 8.0 Hz, 1H), 2.72 (dd, J_a = 0.8 Hz, J_b = 11.6 Hz, 0.61 H), 2.76 (dd, J_a = 0.8 Hz, J_b = 11.6 Hz, 0.39 H), 3.50-3.60 (m, 1H), 7.03 (dt, J_a = 0.80 Hz, J_b = 8.0 Hz, 1H), 7.09 (dt, J_a = 0.8 Hz, J_b = 7.6 Hz, 1H), 7.22 (d, J = 7.6 Hz, 1H), 7.50 (d, J = 7.6 Hz, 1H), 8.15 (bs, 1H); ^{13}C NMR ($CDCl_3$): 12.2, 29.9, 34.6, 39.6, 44.5, 111.0, 111.7, 118.7, 119.2, 121.0, 126.9, 131.3, 135.7, 220.5; IR (cm^{-1}) 3342, 3057, 2962, 2896, 1729, 1620, 1461, 1395, 1307, 1248, 1231, 1170, 1137, 1016, 970, 915, 881, 743, 667, 620,

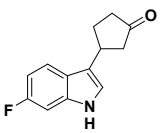
566.

3-(5-Methoxy-1*H*-indol-3-yl)cyclopentanone (3e)[4]



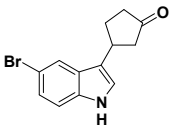
Red oil, ^{1}H NMR ($CDCl_3$): 1.86-1.99 (m, 1H), 2.10-2.39 (m, 4H), 2.69 (dd, J_a = 7.6 Hz, J_b = 18.4 Hz, 1H), 3.50 (quint, J = 8.4 Hz, 1H), 3.73 (s, 3H), 6.72-6.79 (m, 2H), 6.93 (d, J = 2.0 Hz, 1H), 7.09 (d, J = 8.8 Hz, 1H), 8.38 (bs, 1H); ^{13}C NMR ($CDCl_3$): 29.8, 33.7, 38.2, 45.4, 56.1, 101.2, 112.2, 112.3, 118.1, 121.0, 127.1, 132.0, 153.9, 219.9.

3-(6-Fluoro-1*H*-indol-3-yl)cyclopentanone (3g)[5]



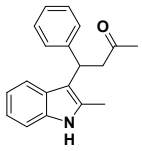
Red oil, ^{1}H NMR ($CDCl_3$): 1.98-2.11 (m, 1H), 2.23-2.42 (m, 3H), 2.42-2.53 (m, 1H), 2.71 (dd, J_a = 8.0 Hz, Jb = 18.4 Hz, 1H), 3.63 (quint, J = 7.2 Hz, 1H), 6.86 (dd, J_a = 2.0 Hz, J_b = 8.8 Hz, 1H), 6.89-6.94 (m, 1H), 7.01 (dd, J_a = 2.0 Hz, J_b = 9.6 Hz, 1H), 7.48 (dd, J_a = 5.2 Hz, J_b = 8.4Hz, 1H), 8.61 (bs, 1H); ^{13}C NMR ($CDCl_3$): 29.9, 33.7, 38.2, 45.4, 97.6, 97.9, 108.0, 108.3, 118.5, 119.7, 119.8, 120.5, 120.5, 123.4, 136.7, 136.8, 158.9, 161.2, 220.0.

3-(5-Bromo-1*H*-indol-3-yl)cyclopentanone (3i)[6]



Red oil, ^{1}H NMR ($CDCl_3$): 2.00-2.11 (m, 1H), 2.24-2.43 (m, 3H), 2.43-2.54 (m, 1H), 2.71 (dd, J_a = 7.2 Hz, J_b = 18.0 Hz, 1H), 3.61 (quint, J = 7.2 Hz, 1H), 6.95 (d, J = 2.0 Hz, 1H), 7.22 (d, J = 8.4 Hz, 1H), 7.27 (dd, J_a = 1.6 Hz, J_b = 8.8 Hz, 1H), 7.72 (d, J = 1.6 Hz, 1H), 8.48 (bs, 1H); ^{13}C NMR ($CDCl_3$): 29.9, 33.6, 38.2, 45.3, 112.7, 113.0, 118.1, 121.4, 121.7, 125.1, 128.4, 135.4, 219.6.

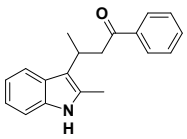
4-(2-Methyl-1*H*-indol-3-yl)-4-phenyl-2-butanone (3j)[7]



Red solid, mp: 97-99^{o}C, ^{1}H NMR ($CDCl_3$): 1.99 (s, 3H), 2.35 (s, 3H), 3.30 (dd, J_a = 6.4 Hz, J_b = 16.4 Hz, 1H), 3.42 (dd, J_a = 8.4 Hz, J_b = 16.4 Hz, 1H), 4.84 (t, J = 8.0 Hz, 1H), 6.99 (t, J = 7.2 Hz, 1H), 7.06 (t, J = 7.2 Hz, 1H), 7.12 (t, J = 7.2 Hz, 1H), 7.17-7.26 (m, 3H), 7.29 (d, J = 7.6 Hz, 1H), 7.44 (d, J = 8.0 Hz, 1H), 7.83 (s, 1H); ^{13}C NMR ($CDCl_3$): 12.2, 30.8, 36.9, 48.4, 110.6, 113.1, 119.1, 119.2, 120.8, 126.0, 127.4, 127.4, 128.4,

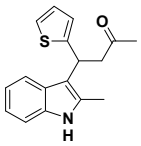
131.9, 135.5, 144.1, 208.1.

3-(2-Methyl-1*H*-indol-3-yl)-1-phenyl-1-butanone (3k)[8]



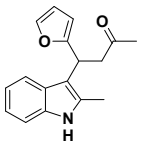
Red oil, ^{1}H NMR ($CDCl_3$): 1.48 (d, J = 8.0 Hz, 3H), 2.30 (s, 3H), 3.35 (dd, J_a = 7.6 Hz, J_b = 16.4 Hz, 1H), 3.50 (dd, J_a = 6.4 Hz, J_b = 16.0 Hz, 1H), 3.73 (sext, J = 7.2 Hz, 1H), 7.05 (td, J_a = 3.6 Hz, J_b = 10.0 Hz, 2H), 7.14-7.20 (m, 1H), 7.33 (t, J = 8.0 Hz, 2H), 7.45 (t, J = 7.2 Hz, 1H), 7.66 (q, J = 3.2 Hz, 1H), 7.84 (d, J = 7.2 Hz, 2H), 7.93 (bs, 1H); ^{13}C NMR ($CDCl_3$): 12.0, 21.2, 27.5, 45.8, 110.7, 115.4, 118.9, 119.1, 120.6, 127.2, 128.1, 128.5, 130.6, 132.9, 135.6, 137.3, 200.3.

4-(2-Methyl-1H-indol-3-yl)-4-(2-thienyl)-2-butanone (3l)



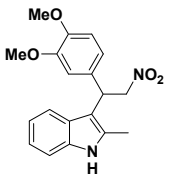
Red oil, ^{1}H NMR ($CDCl_3$): 1.98 (s, 3H), 2.03 (d, J = 2.8 Hz, 2H), 2.34 (s, 3H), 3.33 (dd, J_a = 7.6 Hz, J_b = 16.8 Hz, 1H); 3.42 (q, J = 8.0 Hz, 1H); 5.01 (t, J = 7.6 Hz, 1H), 6.74-6.79 (m, 1H), 6.83 (dd, J_a = 3.6 Hz, J_b = 4.8 Hz, 1H), 6.99 (dt, J_a = 1.2 Hz, J_b = 8.0 Hz, 1H), 7.03-7.09 (m, 2H), 7.17 (t, J = 7.6 Hz, 1H), 7.42 (d, J = 8.0 Hz, 1H), 7.88 (bs, 1H); ^{13}C NMR ($CDCl_3$): 12.0, 30.8, 32.9, 49.5, 110.7, 112.9, 119.1, 119.2, 120.9, 123.5, 123.7, 126.6, 126.9, 132.1, 135.5, 149.0, 207.4; IR (cm^{-1}) 3401, 3057, 2962, 2918, 1709, 1617, 1583, 1488, 1460, 1432, 1359, 1300, 1245, 1162, 1133, 1040, 966, 848, 827, 743, 699, 601, 584, 530; HRMS m/z (ESI) calcd for $C_{17}H_{17}NNaOS$ $[M + Na]^+$ 306.0929 found 306.0925.

4-(2-Methyl-1H-indol-3-yl)-4-(2-furyl)-2-butanone (3m)



Red oil, ^{1}H NMR ($CDCl_3$): 2.01 (s, 3H), 2.35 (s, 3H), 3.22 (q, J = 8.0 Hz, 1H), 3.34 (dd, J_a = 6.0 Hz, J_b = 15.6 Hz, 1H), 4.83 (t, J = 7.2 Hz, 1H), 5.94 (d, J = 3.2 Hz, 1H), 6.22 (q, J = 1.6 Hz, 1H), 6.99 (dt, J_a = 0.8 Hz, J_b = 8.0 Hz, 1H), 7.06 (dt, J_a = 0.8 Hz, J_b = 8.0 Hz, 1H), 7.18 (d, J = 8.0 Hz, 1H), 7.27 (s, 1H), 7.43 (d, J = 7.6 Hz, 1H), 7.92 (bs, 1H); ^{13}C NMR ($CDCl_3$): 11.9, 30.7, 31.4, 46.8, 105.6, 110.2, 110.6, 110.8, 119.0, 119.2, 120.9, 127.1, 132.2, 135.5, 141.1, 156.9, 207.4; IR (cm^{-1}) 3401, 3115, 3056, 2919, 1710, 1616, 1586, 1501, 1460, 1429, 1359, 1301, 1246, 1161, 1076, 1010, 968, 912, 884, 806, 739, 597, 534, 505; HRMS m/z (ESI) calcd for $C_{17}H_{17}NNaO_2$ $[M + Na]^+$ 290.1157 found 290.1146.

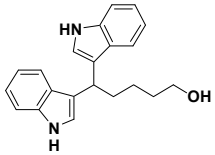
3-[1-(3,4-Dimethoxyphenyl)-2-nitroethyl]-2-methyl-1*H*-indole (3n)[9]



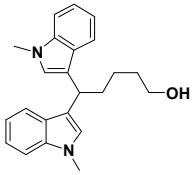
Red solid, mp: 154-156°C, ^{1}H NMR ($CDCl_3$): 2.33 (s, 3H), 3.73 (s, 3H), 3.81 (s, 3H), 5.05 (dd, J_a = 7.2 Hz, J_b = 10.0 Hz, 1H), 5.02-5.20 (m, 2H), 6.77 (d, J = 8.0 Hz, 1H), 6.82 (d, J = 2.0 Hz, 1H), 6.87 (dd, J_a = 2.0 Hz, J_b = 8.4 Hz, 1H), 7.02 (dt, J_a = 1.2 Hz, J_b = 8.0 Hz, 1H), 7.09 (J_a = 1.2 Hz, J_b = 8.0 Hz, 1H), 7.23 (d, J = 8.0 Hz, 1H), 7.40 (d, J = 8.4 Hz, 1H), 8.02 (bs, 1H); ^{13}C NMR ($CDCl_3$): 12.0, 40.3, 55.9, 79.0, 108.8, 110.8, 111.2, 111.2, 118.6, 119.2, 119.7, 121.3, 126.9, 132.1, 132.9, 135.5, 148.1, 149.2; IR (cm^{-1}) 3359, 3022, 2958, 2933, 2836, 1591, 1549, 1511, 1459, 1378, 1329, 1304, 1260, 1226, 1135, 1018, 910, 850, 816, 763, 735, 667, 601, 568.

5,5-di(1*H*-indol-3-yl)pentanol (5a)[10]

Red oil, ^{1}H NMR ($CDCl_3$): 1.22-1.30 (m, 2H), 1.37 (q, J = 7.2 Hz, 2H), 2.02 (bs, 1H), 2.05 (q, J = 7.6 Hz, 2H), 3.29 (t, J = 6.8 Hz, 2H), 4.31 (t, J = 7.2 Hz, 1H), 6.56 (d, J = 2.0 Hz, 2H), 6.90-6.99 (m, 2H), 7.02 (d, J = 3.6 Hz, 4H), 7.49 (d, J = 8.0 Hz, 2H), 7.66 (bs, 2H); ^{13}C NMR ($CDCl_3$): 24.5, 32.7, 34.1, 35.8, 62.8, 111.5, 119.0, 119.6, 120.0, 121.7, 121.9, 127.1, 136.7.

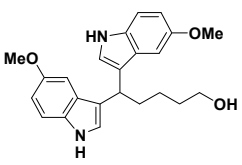


5,5-bis(1-methyl-1*H*-indol-3-yl)pentanol (5b)[11]



Red oil, ^{1}H NMR ($CDCl_3$): 1.60-1.72 (m, 2H), 1.73-1.86 (m, 2H), 2.25 (bs, 1H), 2.40-2.52 (m, 2H), 3.66-3.74 (m, 2H), 3.80 (s, 6H), 4.66-4.77 (m, 1H), 7.05 (s, 2H), 7.28 (t, J = 5.2 Hz, 2H), 7.36-7.50 (m, 4H), 7.86 (d, J = 5.6 Hz, 2H); ^{13}C NMR ($CDCl_3$): 24.8, 32.8, 33.1, 34.1, 36.4, 63.0, 109.4, 118.7, 119.2, 119.9, 121.5, 126.5, 127.8, 137.5.

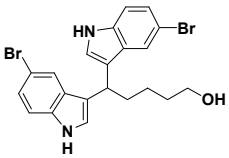
5,5-bis(5-methoxy-1*H*-indol-3-yl)pentanol (5c)[12]



Red oil, ^{1}H NMR ($CDCl_3$): 1.15-1.30 (m, 2H), 1.37 (sext, J = 6.4 Hz, 2H), 1.98 (q, J = 7.2 Hz, 2H), 2.22 (bs, 1H), 3.33 (t, J = 6.4 Hz, 2H), 3.49 (s, 0.6H), 3.56 (s, 4.8H), 3.63 (s, 0.6H), 4.02 (t, J = 5.6 Hz, 0.2H), 4.16 (t, J = 8.0 Hz, 0.8H), 6.53-6.68 (m, 4H), 6.86-6.95 (m, 4H), 7.88 (s, 1.6H), 7.99 (s, 0.4H); ^{13}C NMR ($CDCl_3$): 24.5, 32.5, 32.8, 34.0, 35.4, 55.9, 56.1, 62.7, 62.8, 102.1, 111.3, 112.0, 119.6, 122.7,

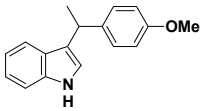
127.5, 132.1, 153.4.

5-Bromo-ε-(5-Bromo-1*H*-indol-3-yl)-1*H*-indole-3-pentanol (5e)[12]



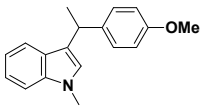
Red oil, ^{1}H NMR ($CDCl_3$): 1.27-1.37 (m, 2H), 1.52 (quint, J = 6.8 Hz, 2H), 1.91 (bs, 1H), 2.07 (q, J = 8.0 Hz, 2H), 3.51 (t, J = 6.8 Hz, 2H), 4.22 (t, J = 7.6 Hz, 1H), 6.83 (d, J = 2.4 Hz, 2H), 7.05 (d, J = 8.8 Hz, 2H), 7.16 (dd, J_a = 2.0 Hz, J_b = 8.8 Hz, 2H), 7.61 (d, J = 1.6 Hz, 2H), 8.11 (bs, 1H); ^{13}C NMR ($CDCl_3$): 24.4, 32.6, 34.0, 35.1, 62.9, 112.3, 112.8, 119.1, 121.9, 122.9, 124.6, 128.6, 135.3.

3-[1-(4-Methoxyphenyl)ethyl]-1*H*-indole (7a)[13]



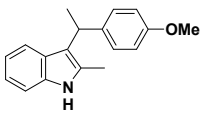
White solid, mp: 156-157°C, ^{1}H NMR (acetone-d_6): 1.64 (d, J = 7.2 Hz, 3H), 3.70 (s, 3H), 4.31 (q, J = 7.2 Hz, 1H), 6.78 (d, J = 8.8 Hz, 2H), 6.88 (dt, J_a = 0.8 Hz, J_b = 8.0 Hz, 1H), 7.03 (dt, J_a = 0.8 Hz, J_b = 8.0 Hz, 1H), 7.19 (t, J = 8.8 Hz, 3H), 7.33 (q, J = 8.8 Hz, 2H), 9.96 (bs, 1H); ^{13}C NMR (acetone-d_6): 22.2, 36.1, 54.5, 111.2, 113.5, 118.3, 119.3, 120.7, 121.2, 121.4, 127.1, 128.2, 137.2, 139.4, 157.9.

3-[1-(4-Methoxyphenyl)ethyl]-1-methyl-1*H*-indole (7b)[13]



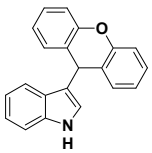
Red oil, ^{1}H NMR (acetone-d_6): 1.62 (d, J = 6.8 Hz, 3H), 3.69 (s, 3H), 3.73 (s, 3H), 4.29 (q, J = 6.8 Hz, 1H), 6.78 (d, J = 8.4 Hz, 2H), 6.89 (t, J = 8.0 Hz, 1H), 7.02 (s, 1H), 7.09 (dt, J_a = 0.8 Hz, J_b = 6.8 Hz, 1H), 7.19 (d, J = 8.8 Hz, 2H), 7.29 (t, J = 9.2 Hz, 2H); ^{13}C NMR (acetone-d_6): 22.3, 31.8, 36.0, 54.5, 109.2, 113.5, 113.5, 118.3, 119.5, 119.9, 121.2, 125.9, 127.3, 127.4, 128.2, 137.6, 139.4, 158.0.

3-[1-(4-Methoxyphenyl)ethyl]-2-methyl-1*H*-indole (7c)[13]



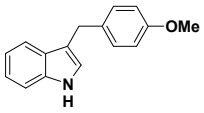
Red oil, ^{1}H NMR (acetone-d_6): 1.62 (d, J = 7.2 Hz, 3H), 2.34 (s, 3H), 3.68 (s, 3H), 4.27 (q, J = 7.2 Hz, 1H), 6.72 (dd, J_a = 0.4 Hz, J_b = 8.0 Hz, 1H), 6.77 (td, J_a = 3.2 Hz, J_b = 9.6 Hz, 2H), 7.06 (d, J = 1.6 Hz, 1H), 7.14 (s, 1H), 7.15-7.21 (m, 3H), 9.76 (bs, 1H); ^{13}C NMR (acetone-d_6): 20.9, 22.2, 36.2, 54.5, 111.1, 113.5, 119.1, 120.2, 120.6, 120.7, 125.1, 128.2, 130.5, 137.7, 139.5, 157.9; IR (cm^{-1}) 3401, 3325, 3057, 2965, 2835, 1678, 1614, 1510., 1460, 1325, 1300, 1244, 1178, 1136, 1033, 967, 886, 745, 696, 652, 549, 507.

3-(9*H*-xanthen-9-yl)-1*H*-indole (7i)[14]



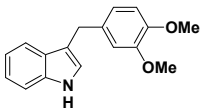
Black solid, mp: 134-135°C, ^{1}H NMR ($CDCl_3$): 5.52 (s, 1H), 6.89 (dt, J_a = 0.8 Hz, J_b = 8.0 Hz, 2H), 6.95 (t, J = 7.2 Hz, 1H), 6.99 (d, J = 2.4 Hz, 1H), 7.06-7.19 (m, 7H), 7.27 (d, J = 8.0 Hz, 1H), 7.33 (d, J = 8.0 Hz, 1H), 7.89 (bs, 1H); ^{13}C NMR ($CDCl_3$): 35.6, 111.3, 116.4, 119.7, 119.7, 120.4, 122.2, 122.9, 123.1, 124.5, 125.9, 127.7, 129.5, 136.8, 151.4.

3-[(4-Methoxyphenyl)methyl]-1*H*-indole (7j)[15]



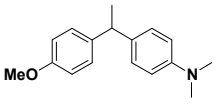
Yellow solid, mp: 72-75°C, ^{1}H NMR ($CDCl_3$): 3.76 (s, 3H), 4.00-4.06 (m, 2H), 6.78-6.88 (m, 3H), 7.03-7.16 (m, 2H), 7.16-7.21 (m, 2H), 7.24-7.34 (m, 1H), 7.49-7.56 (m, 1H), 7.78-8.14 (m, 1H); ^{13}C NMR ($CDCl_3$): 30.8, 55.3, 111.1, 113.8, 113.8, 116.3, 119.2, 119.4, 122.1, 122.3, 129.6, 133.4, 136.5, 157.8.

3-[(3,4-Dimethoxyphenyl)methyl]-1*H*-indole (7k)[16]

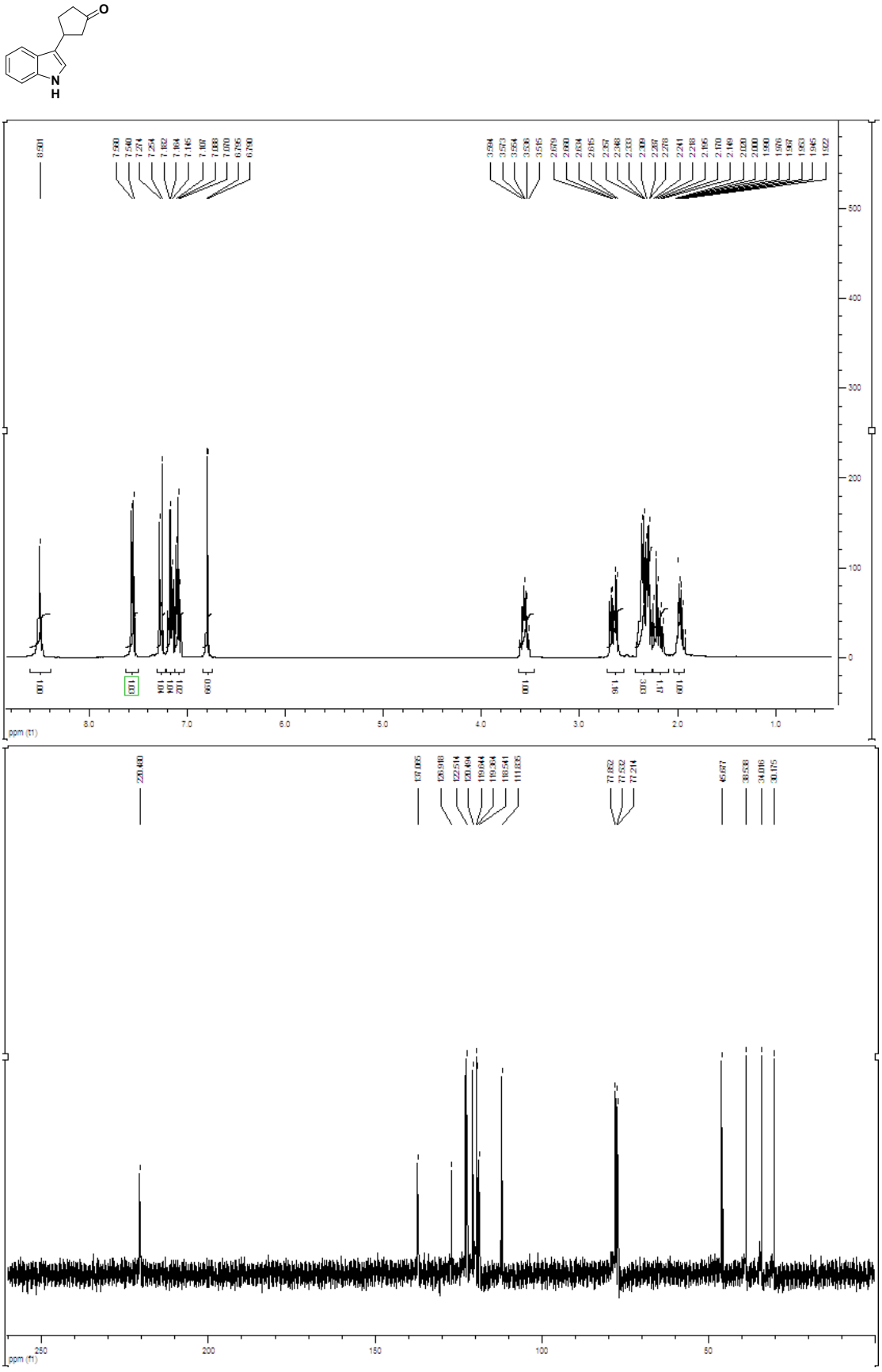


Yellow solid, mp: 121-122 °C, ^{1}H NMR ($CDCl_3$): 3.78 (s, 3H), 3.82 (s, 3H), 4.01-4.06 (m, 2H), 6.72-6.88 (m, 4H), 7.03-7.12 (m, 1H), 7.16 (dt, J_a = 0.8 Hz, J_b = 8.0 Hz, 1H), 7.22-7.32 (m, 1H), 7.46-7.58 (m, 1H), 7.95-8.19 (m, 1H); ^{13}C NMR ($CDCl_3$): 31.3, 55.8, 56.0, 111.2, 112.1, 116.0, 119.2, 119.3, 120.7, 122.1, 122.4, 127.5, 133.9, 136.5, 147.2, 148.8.

4-[1-(4-methoxyphenyl)ethyl]- *N,N*-dimethylbenzenamine (9a)[17]



Yellow oil, ^{1}H NMR ($CDCl_3$): 1.55 (d, J = 7.2 Hz, 3H), 2.84 (s, 6H), 3.69 (s, 3H), 3.99 (q, J = 7.2 Hz, 1H), 6.64 (d, J = 8.4 Hz, 2H), 6.78 (d, J = 8.4 Hz, 2H), 7.05 (d, J = 8.4 Hz, 2H), 7.10 (d, J = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$): 22.5, 41.0, 43.2, 55.3, 113.0, 113.8, 128.3, 128.6, 135.1, 139.6, 149.2, 157.9.


O
N
H
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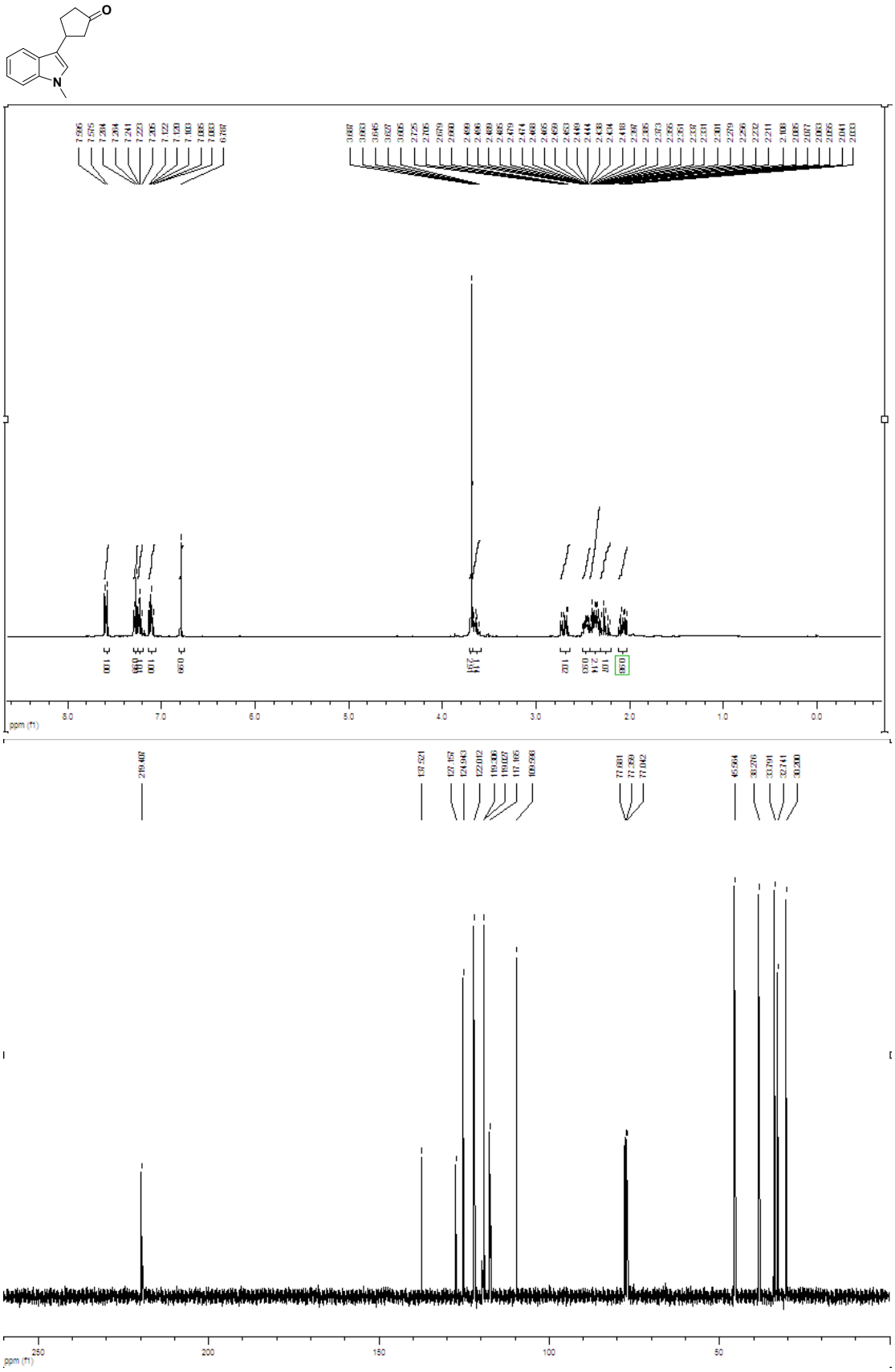
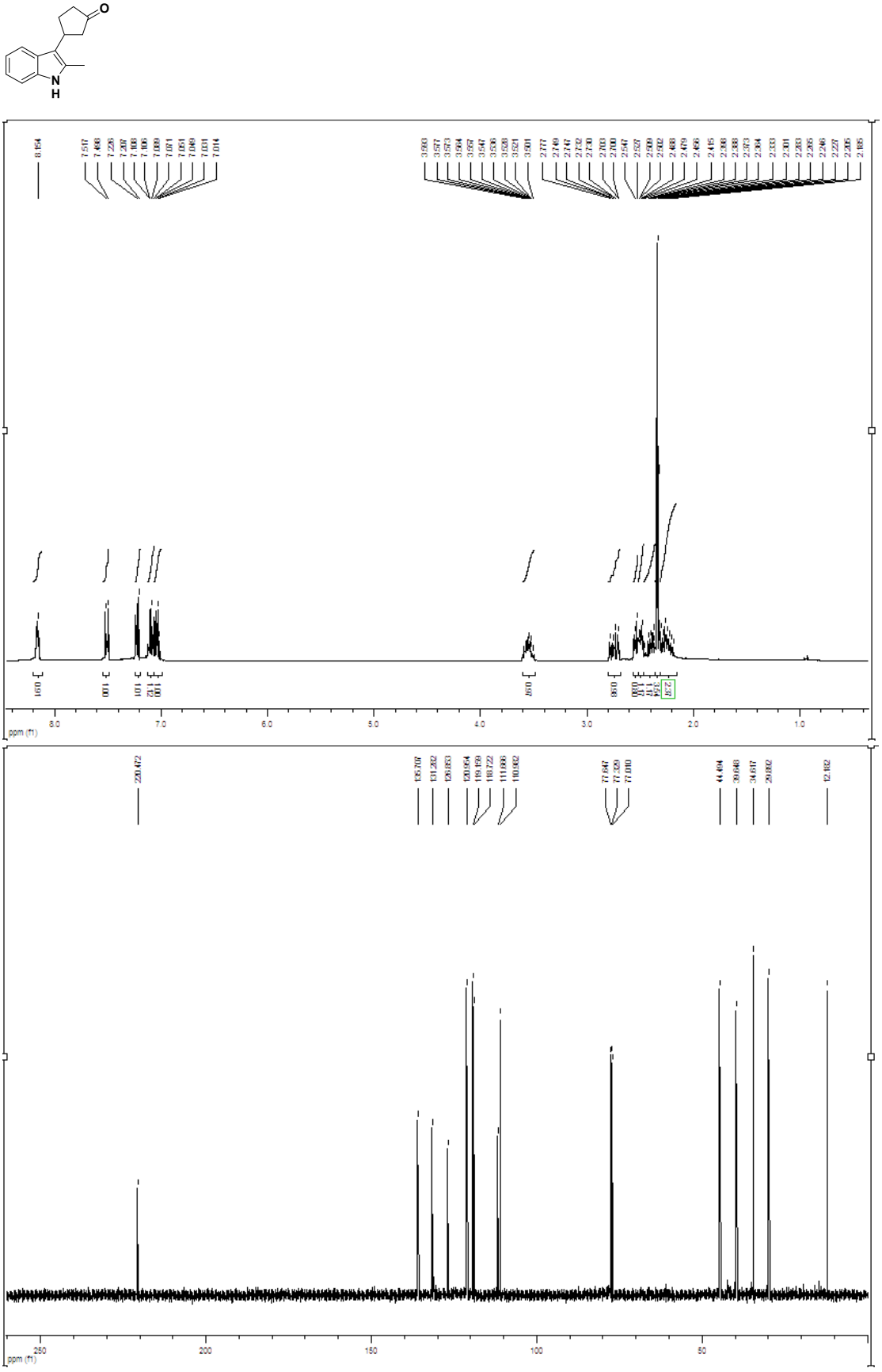
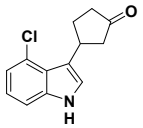
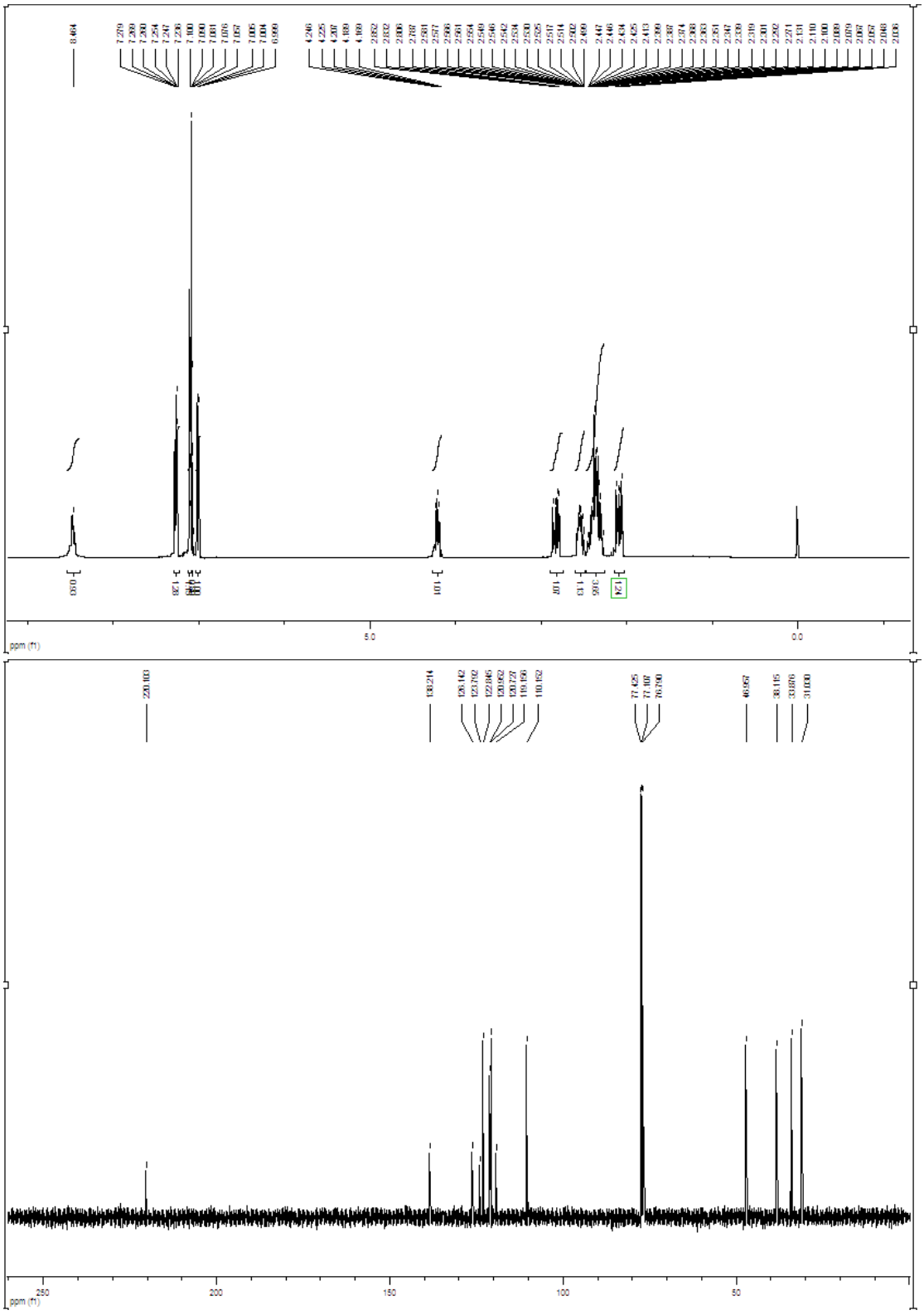
7.590
7.540
7.274
7.254
7.182
7.164
7.145
7.107
7.088
7.070
6.795
6.790
3.594
3.573
3.554
3.536
3.515
2.679
2.660
2.634
2.615
2.257
2.248
2.233
2.209
2.197
2.178
2.241
2.218
2.195
2.170
2.149
2.020
2.000
1.990
1.976
1.967
1.953
1.945
1.922
ppm (t1)
220.480
137.095
126.998
122.514
120.494
119.044
119.364
118.541
111.835
77.262
77.032
77.214
45.677
30.538
34.016
30.175
ppm (f1)






Cl
O
N
H


8.464
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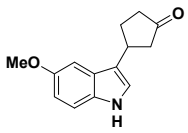
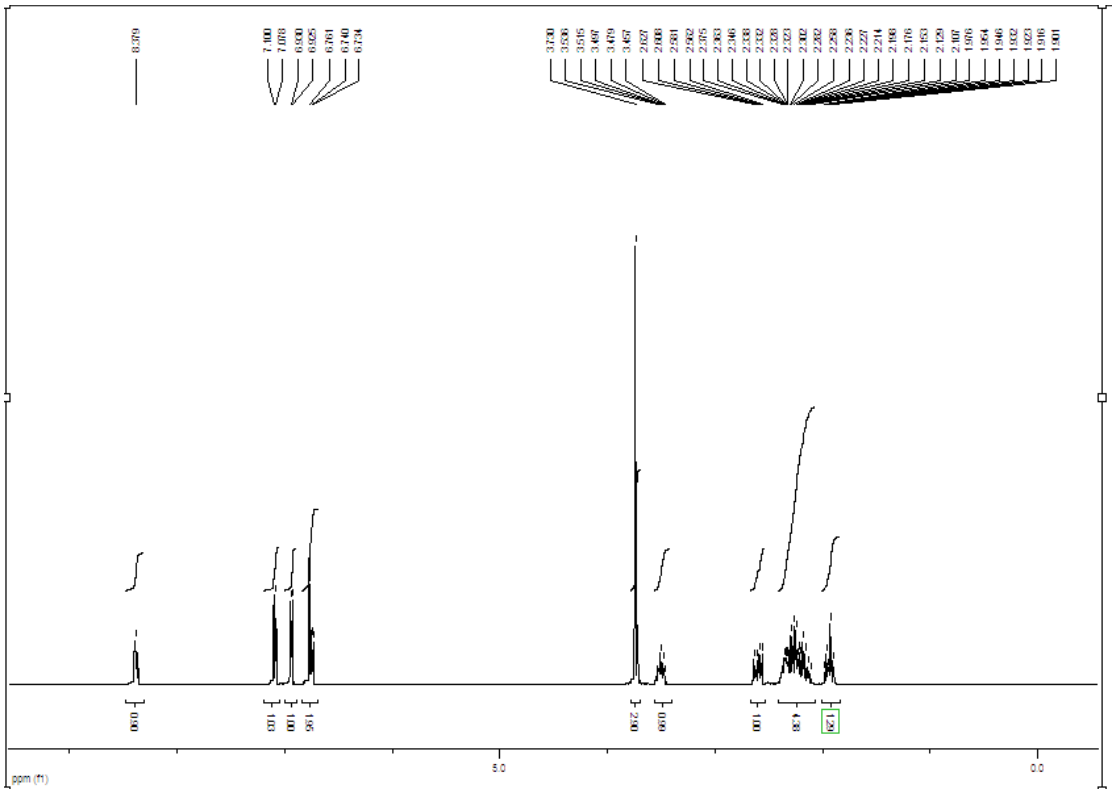
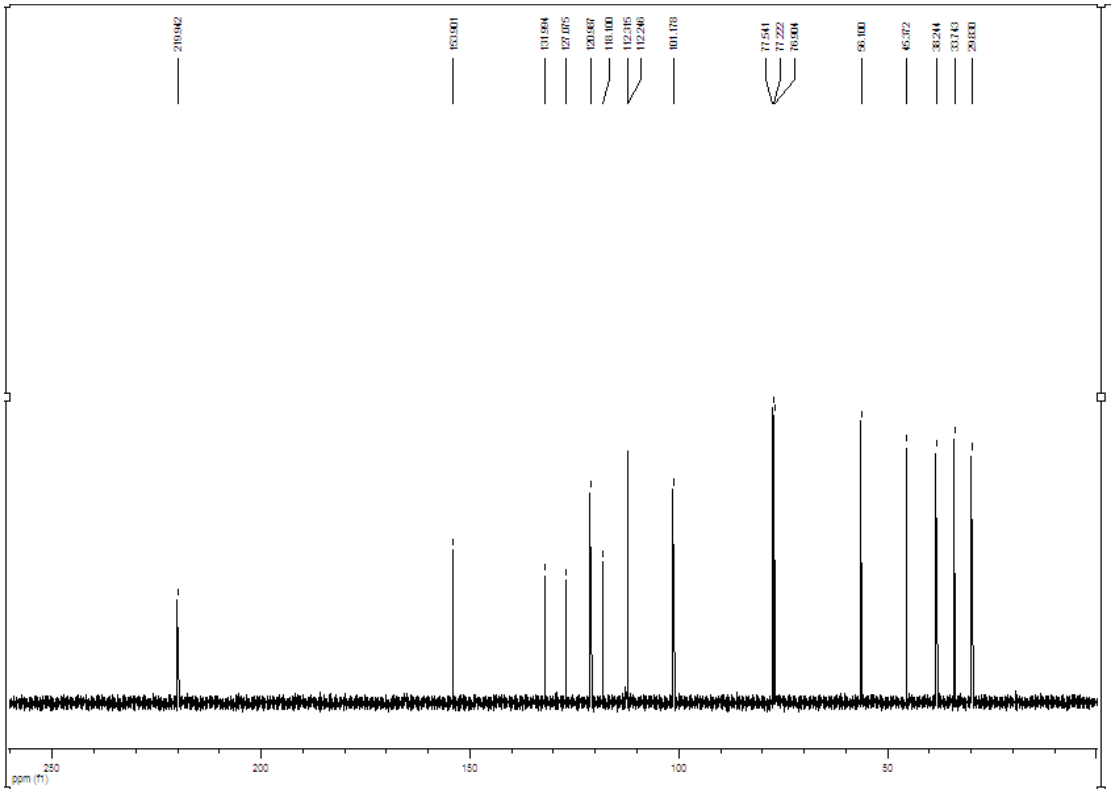
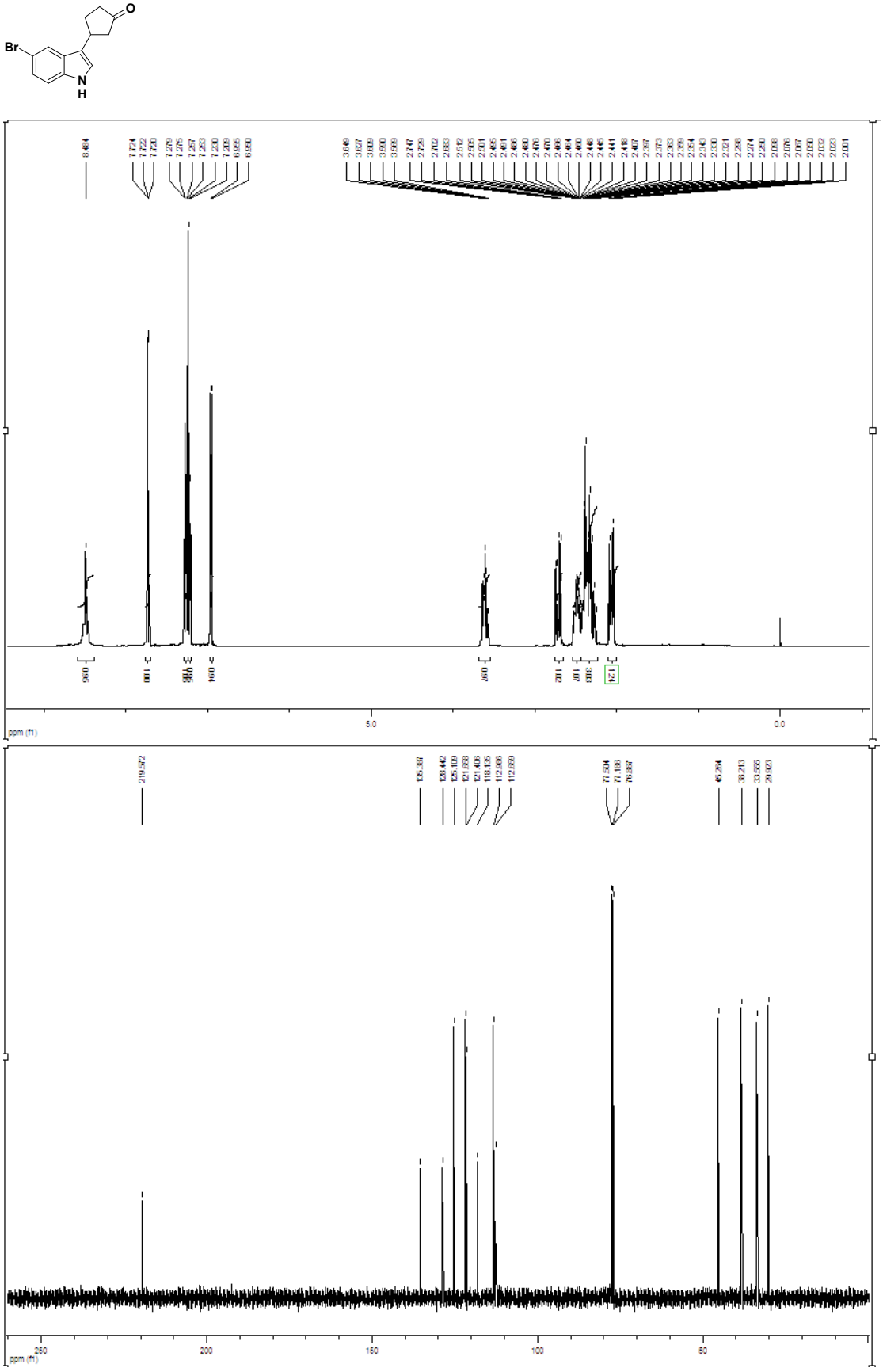
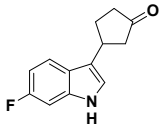
7.269
7.260
7.254
7.247
7.236
7.100
7.090
7.081
7.076
7.057
7.005
7.004
6.999
4.246
4.225
4.207
4.189
4.169
2.882
2.832
2.806
2.787
2.781
2.577
2.566
2.561
2.554
2.549
2.546
2.542
2.534
2.530
2.525
2.517
2.514
2.502
2.499
2.447
2.446
2.434
2.425
2.413
2.399
2.387
2.374
2.368
2.363
2.351
2.347
2.339
2.319
2.301
2.292
2.271
2.131
2.110
2.100
2.089
2.079
2.067
2.057
2.046
2.036
0.93
1.36
1.01
1.01
1.13
3.05
1.24
5.0
0.0
ppm (f1)
220.103
138.214
126.142
123.752
122.946
120.652
120.727
119.156
110.152
77.425
77.107
76.790
46.967
36.115
33.676
31.030
250
200
150
100
50
ppm (f1)

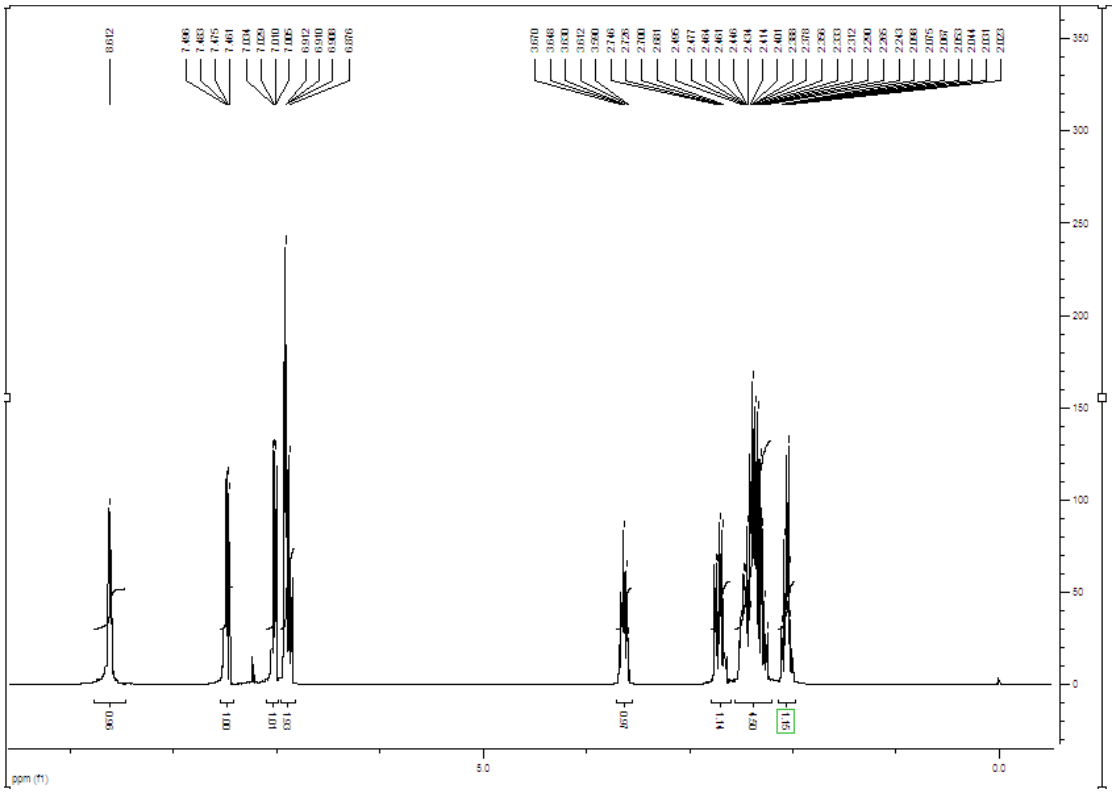

MeO
O
N
H


8.379
7.100
7.078
6.930
6.925
6.761
6.740
6.734
3.730
3.536
3.515
3.496
3.479
3.457
2.627
2.008
2.001
2.002
2.375
2.363
2.346
2.338
2.332
2.328
2.323
2.302
2.282
2.258
2.236
2.227
2.214
2.198
2.176
2.153
2.129
2.107
1.976
1.954
1.946
1.932
1.923
1.916
1.901
0.90
3.31
1.00
1.96
2.00
0.99
1.00
4.38
1.21
5.0
0.0
ppm (f1)


209.942
153.901
131.964
127.075
120.867
118.100
112.315
112.246
101.178
77.541
77.222
76.904
56.100
45.372
38.244
33.743
29.830
250
200
150
100
50
ppm (f1)


Br
O
N
H
ppm (f1)
5.0
0.0
ppm (f1)
250
200
150
100
50


O
F
N
H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7.034
7.029
7.010
7.005
6.912
6.910
6.908
6.886
3.670
3.648
3.630
3.612
3.590
2.746
2.725
2.700
2.681
2.495
2.477
2.464
2.451
2.446
2.434
2.414
2.401
2.388
2.378
2.296
2.333
2.312
2.290
2.265
2.243
2.208
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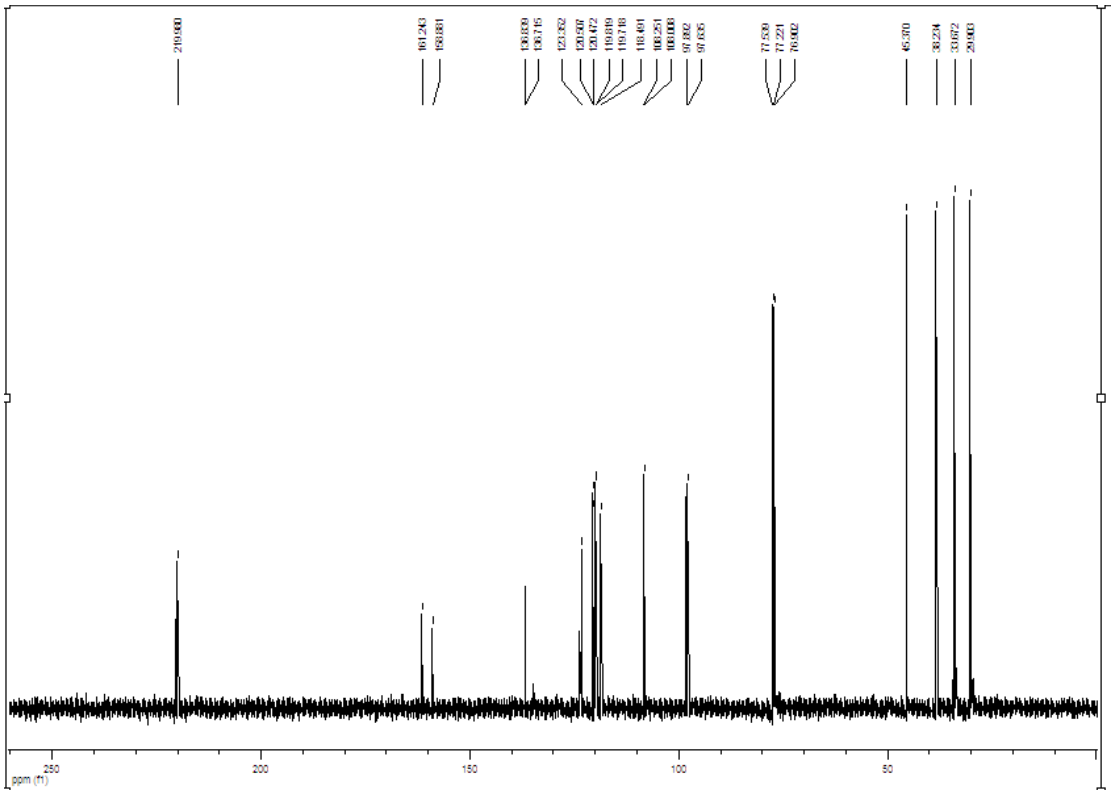
2.053
2.044
2.031
2.023
9.60
1.00
1.01
1.51
3.50
1.14
4.20
5.11
5.0
0.0
ppm (f1)


209.980
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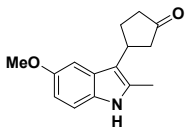
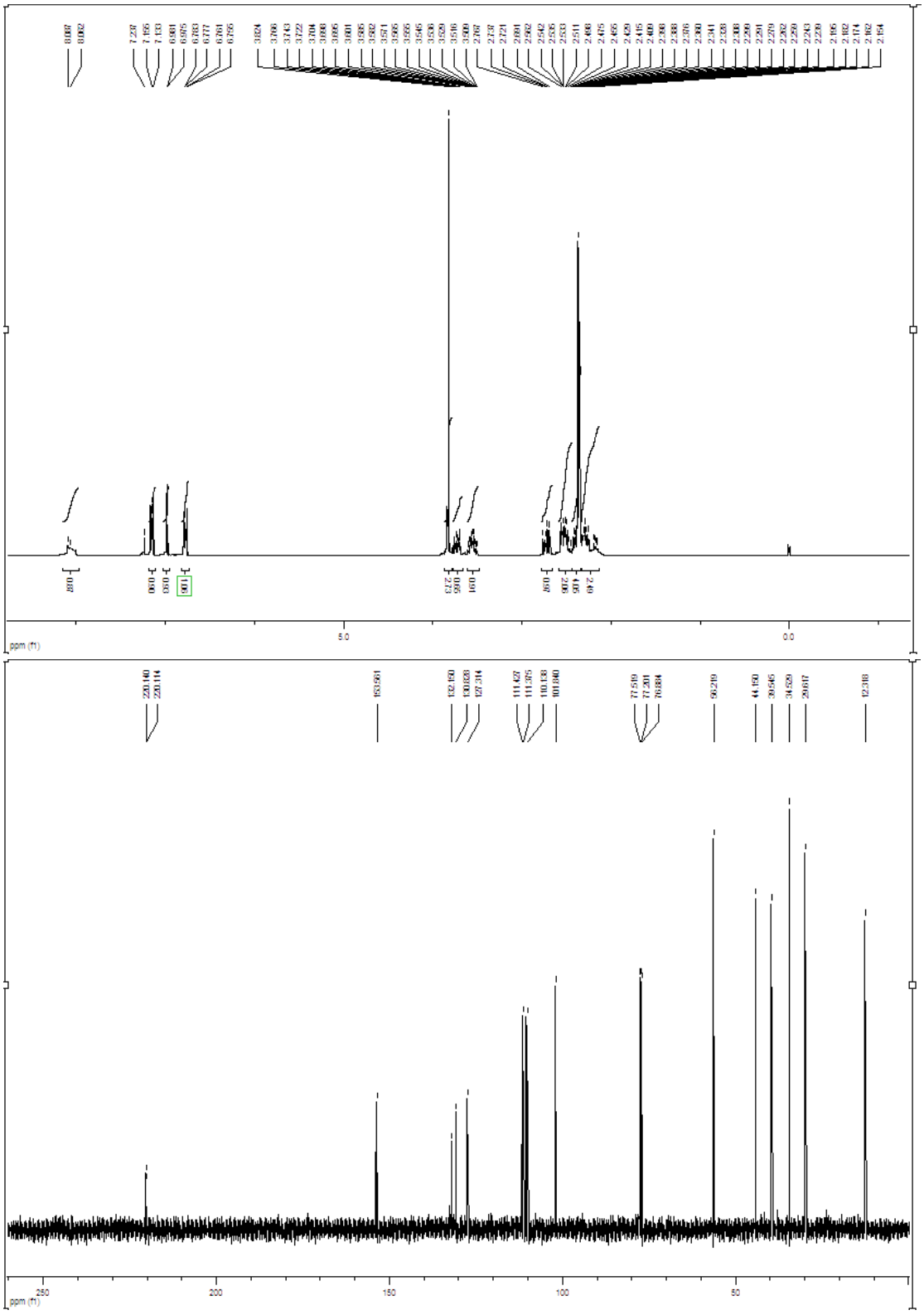
159.381
139.839
139.715
123.362
120.567
120.472
119.919
119.718
118.491
118.251
118.008
97.992
97.635
77.539
77.221
76.902
45.370
38.224
33.672
29.903
250
200
150
100
50
ppm (f1)


MeO
O
N
H


8.007
8.002
7.237
7.195
7.133
6.981
6.975
6.783
6.777
6.761
6.755
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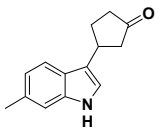
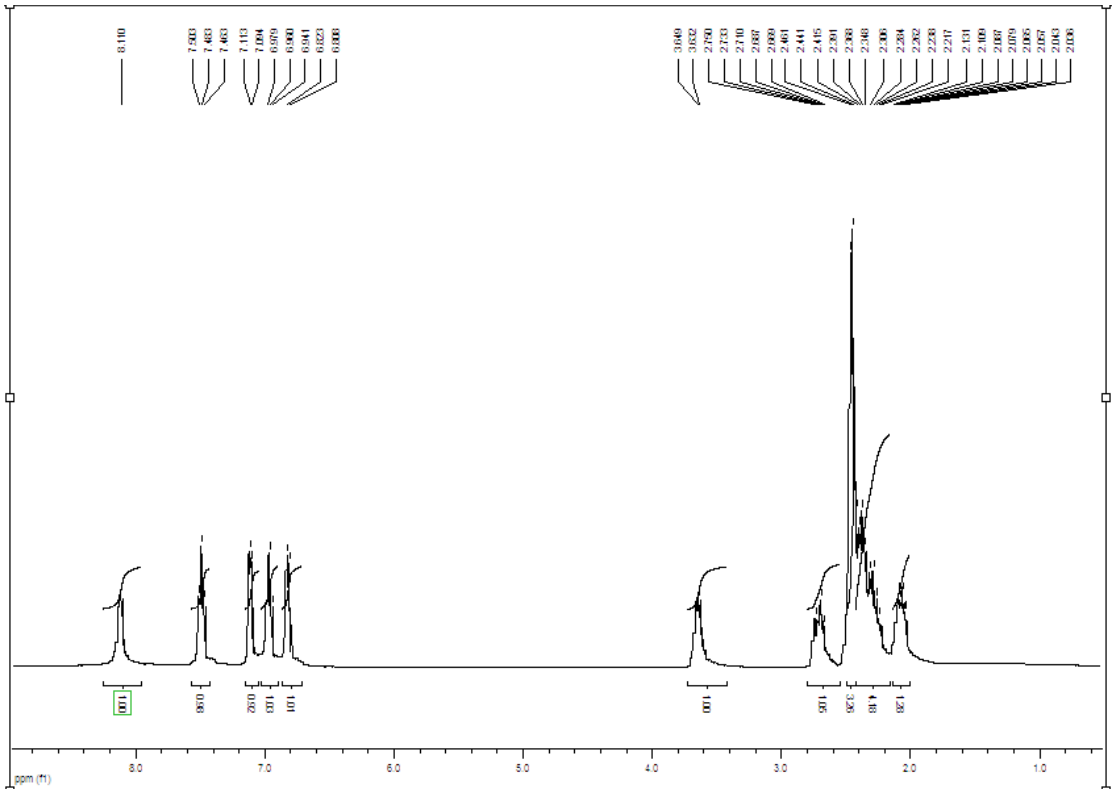
3.786
3.743
3.722
3.704
3.698
3.695
3.691
3.686
3.682
3.671
3.666
3.646
3.636
3.629
3.616
3.609
3.587
2.737
2.721
2.691
2.662
2.542
2.535
2.533
2.511
2.498
2.475
2.455
2.439
2.415
2.400
2.388
2.388
2.376
2.360
2.341
2.333
2.308
2.299
2.291
2.279
2.262
2.259
2.243
2.239
2.195
2.182
2.174
2.162
2.154
0.97
0.90
0.93
1.00
2.73
0.95
1.01
0.97
2.06
0.99
2.49
ppm (f1)
5.0
0.0
220.140
220.074
153.961
132.150
130.033
127.314
111.427
111.375
110.138
101.840
77.519
77.201
76.884
56.219
44.150
39.545
34.529
29.617
12.318
250
200
150
100
50
ppm (f1)


O
N
H


8.110
7.503
7.483
7.463
7.113
7.094
6.979
6.960
6.941
6.823
6.808
3.649
3.632
2.790
2.733
2.710
2.687
2.669
2.461
2.441
2.415
2.391
2.368
2.348
2.306
2.284
2.262
2.238
2.217
2.131
2.109
2.087
2.079
2.065
2.057
2.043
2.036
1.00
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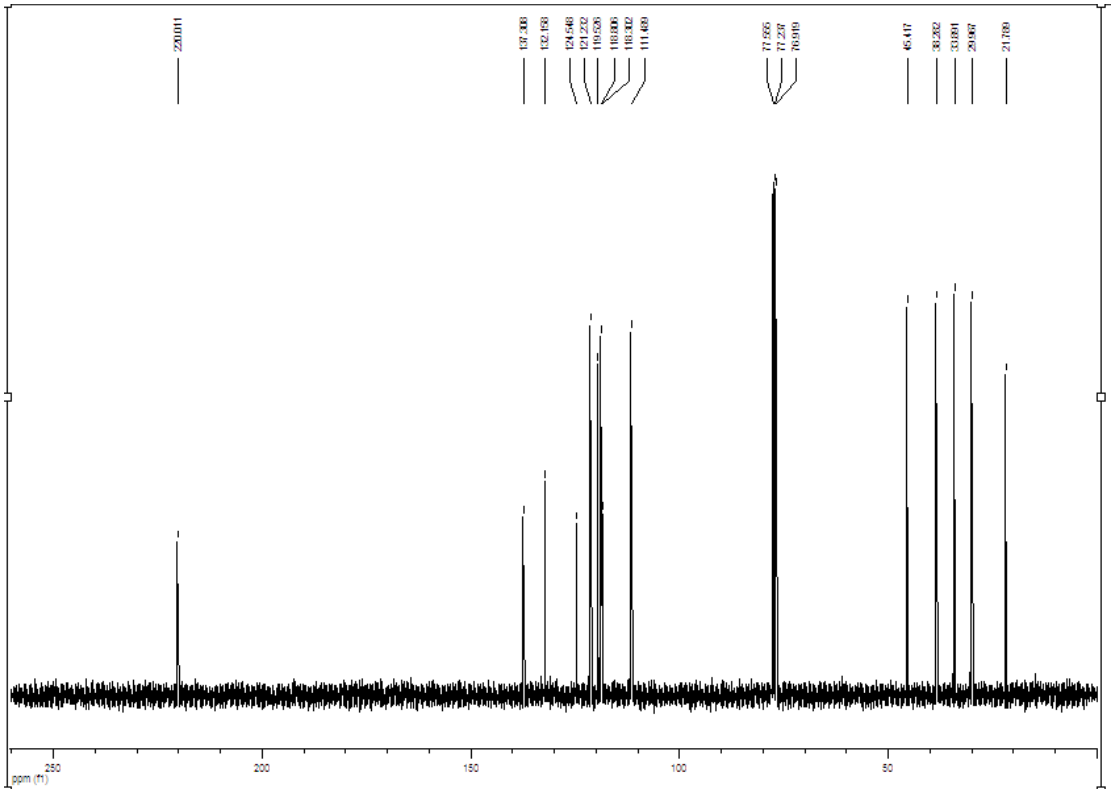
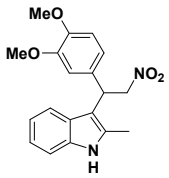
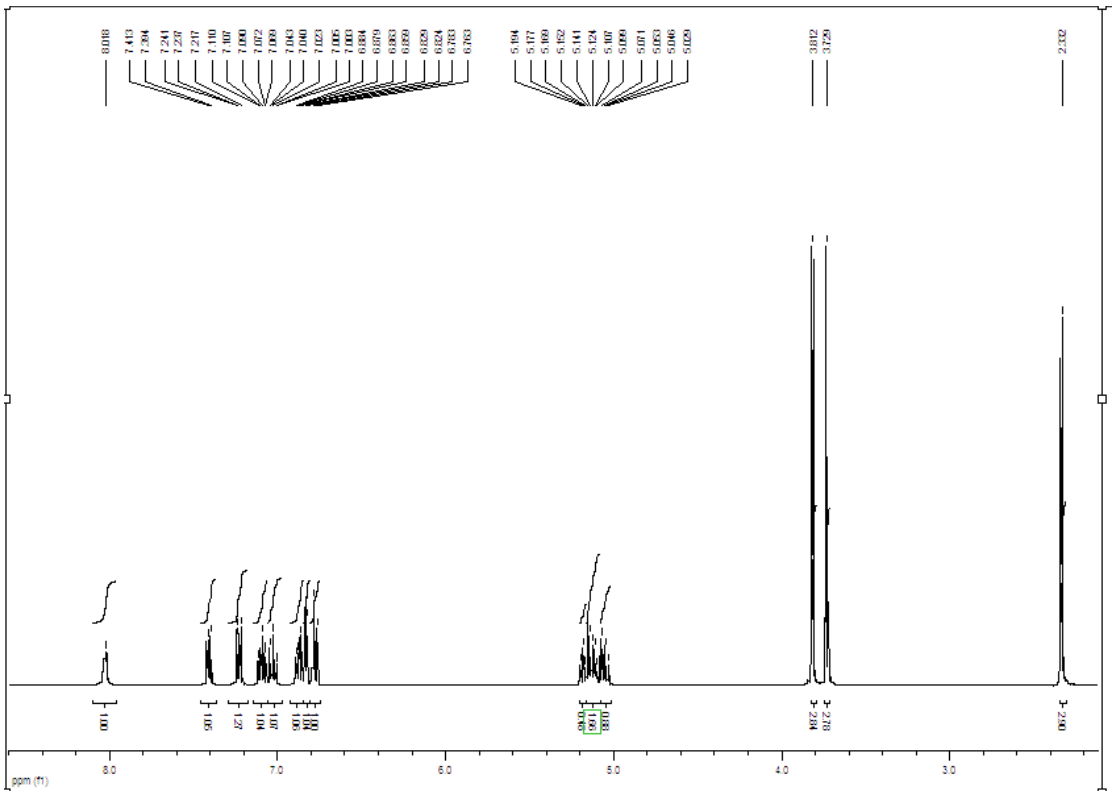
2.50
1.31
1.01
1.00
9.01
3.36
4.18
1.28
ppm (f1)


220.011
137.308
132.158
124.546
121.232
119.526
118.806
118.302
111.489
77.595
77.237
76.919
45.417
36.282
33.081
29.967
21.789
ppm (f1)


MeO
MeO
NO2
N
H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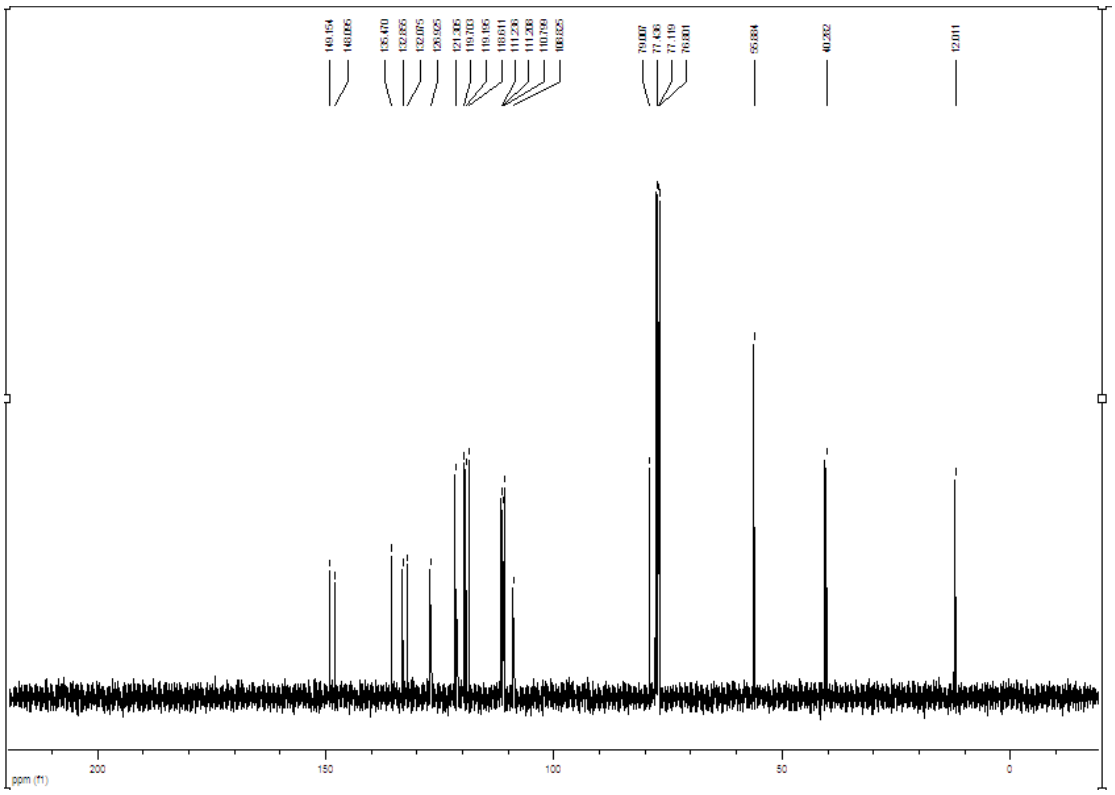
7.394
7.241
7.238
7.237
7.110
7.107
7.000
7.072
7.069
7.043
7.040
7.023
7.006
7.003
6.884
6.879
6.863
6.859
6.829
6.824
6.783
6.763
5.194
5.177
5.169
5.162
5.141
5.124
5.107
5.099
5.071
5.063
5.046
5.029
3.812
3.729
2.332
1.00
5.01
1.37
1.01
1.01
1.00
1.00
0.98
1.06
1.08
2.24
2.18
3.00
8.0
7.0
6.0
5.0
4.0
3.0
ppm (f1)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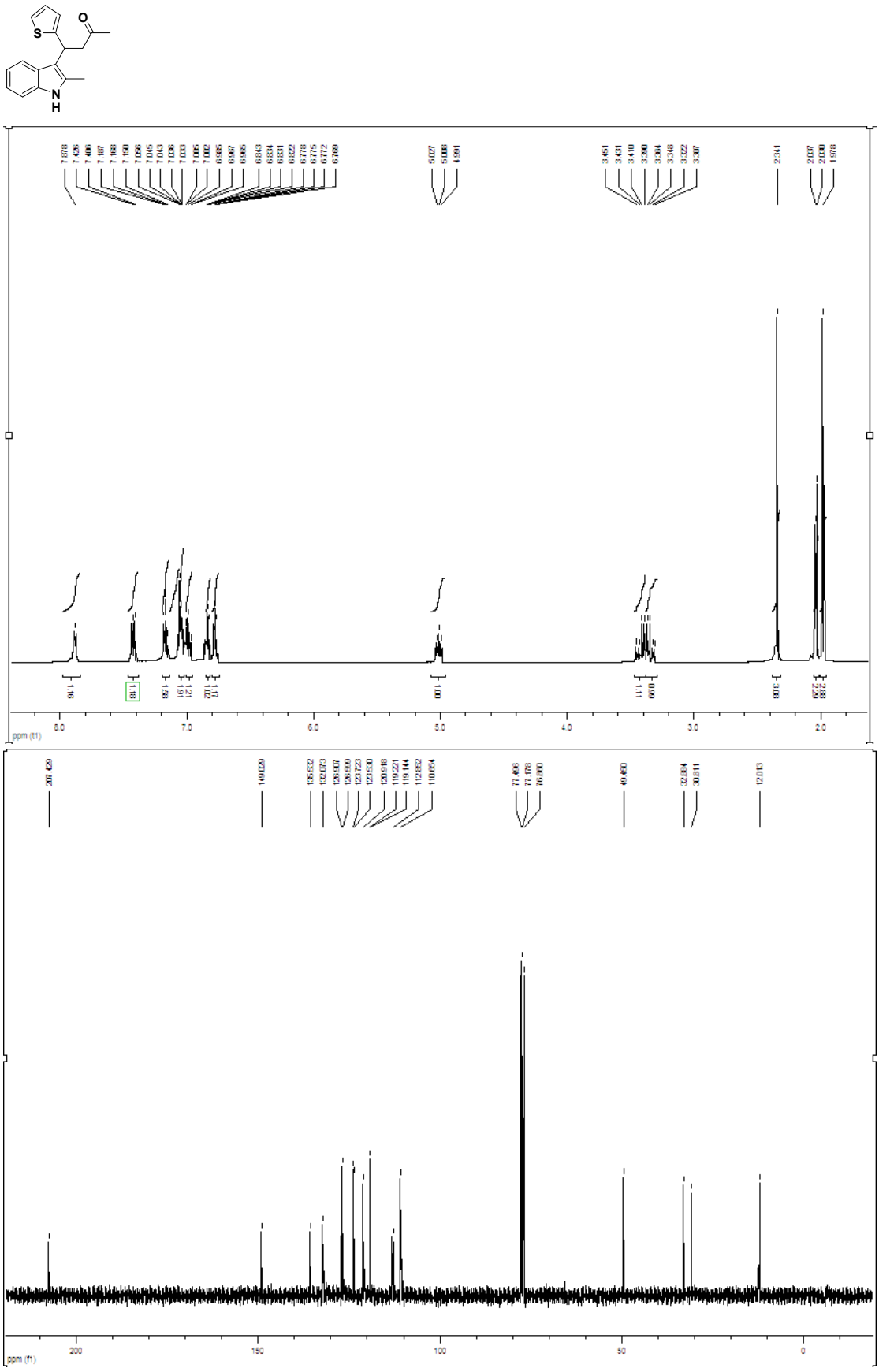
148.066
135.470
132.855
132.075
126.925
121.305
119.703
119.195
118.611
111.230
111.208
110.759
108.825
79.007
77.436
77.119
76.801
55.884
40.252
12.011
200
150
100
50
0
ppm (f1)


S
O
N
H
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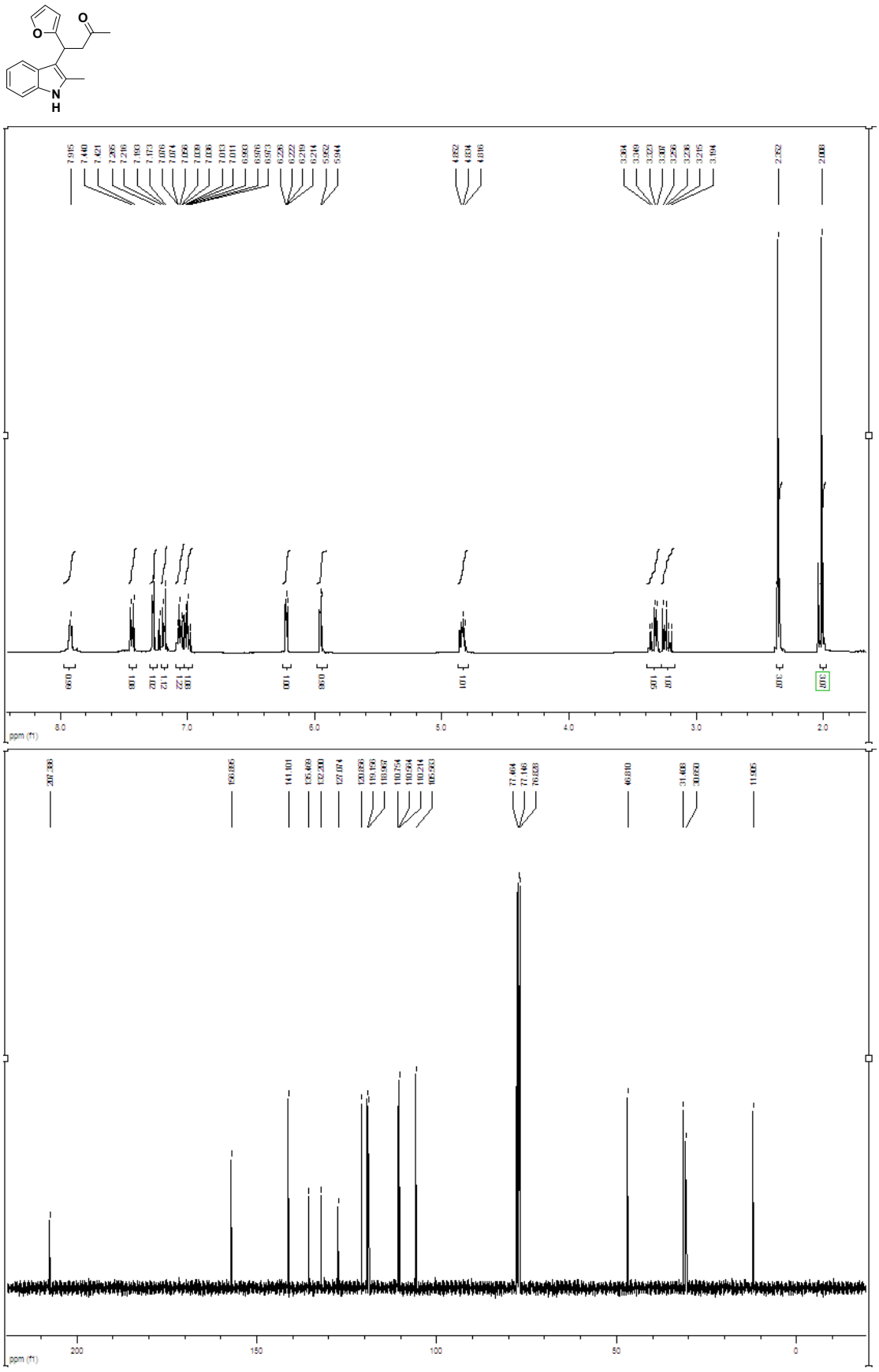
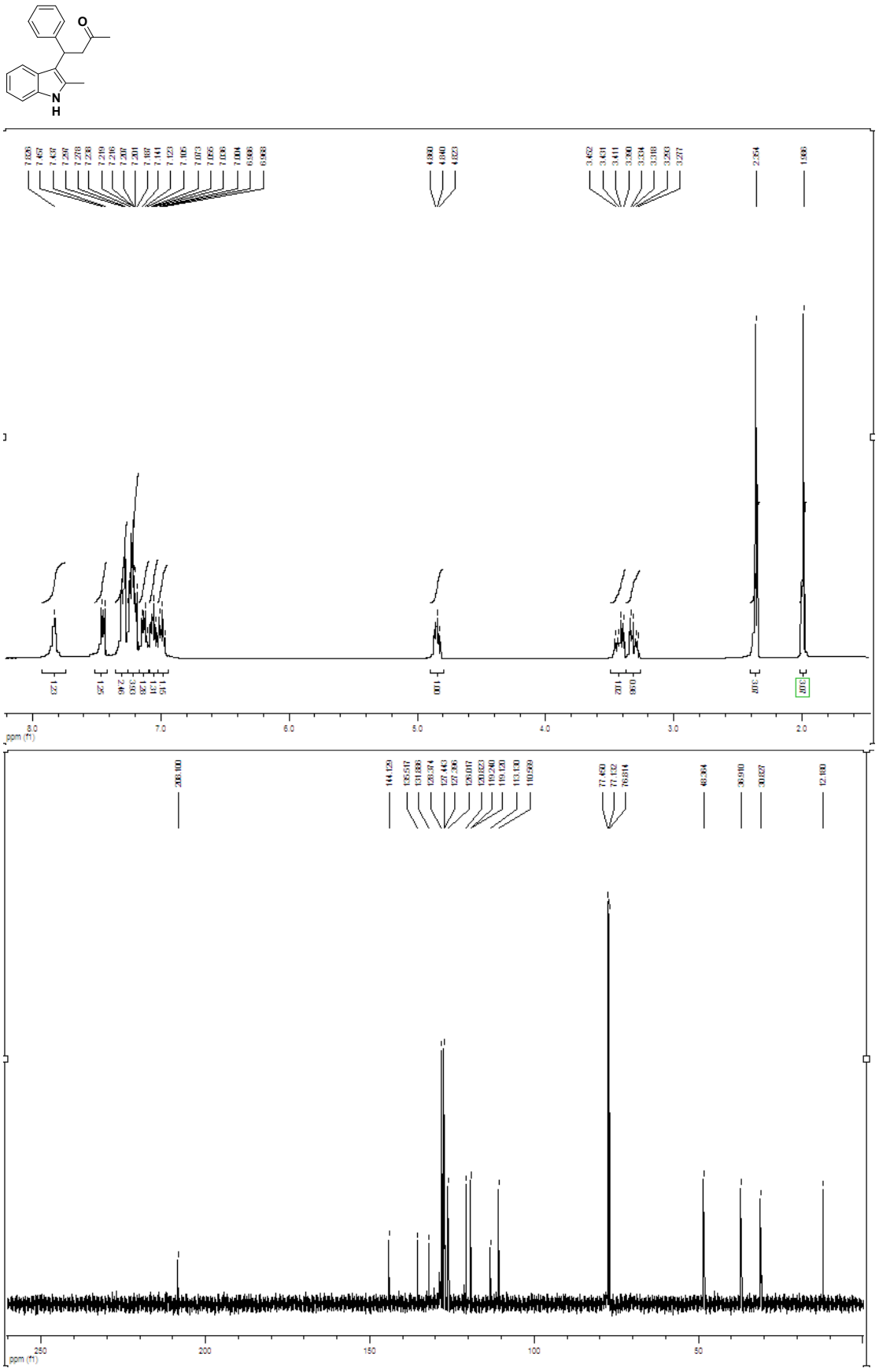
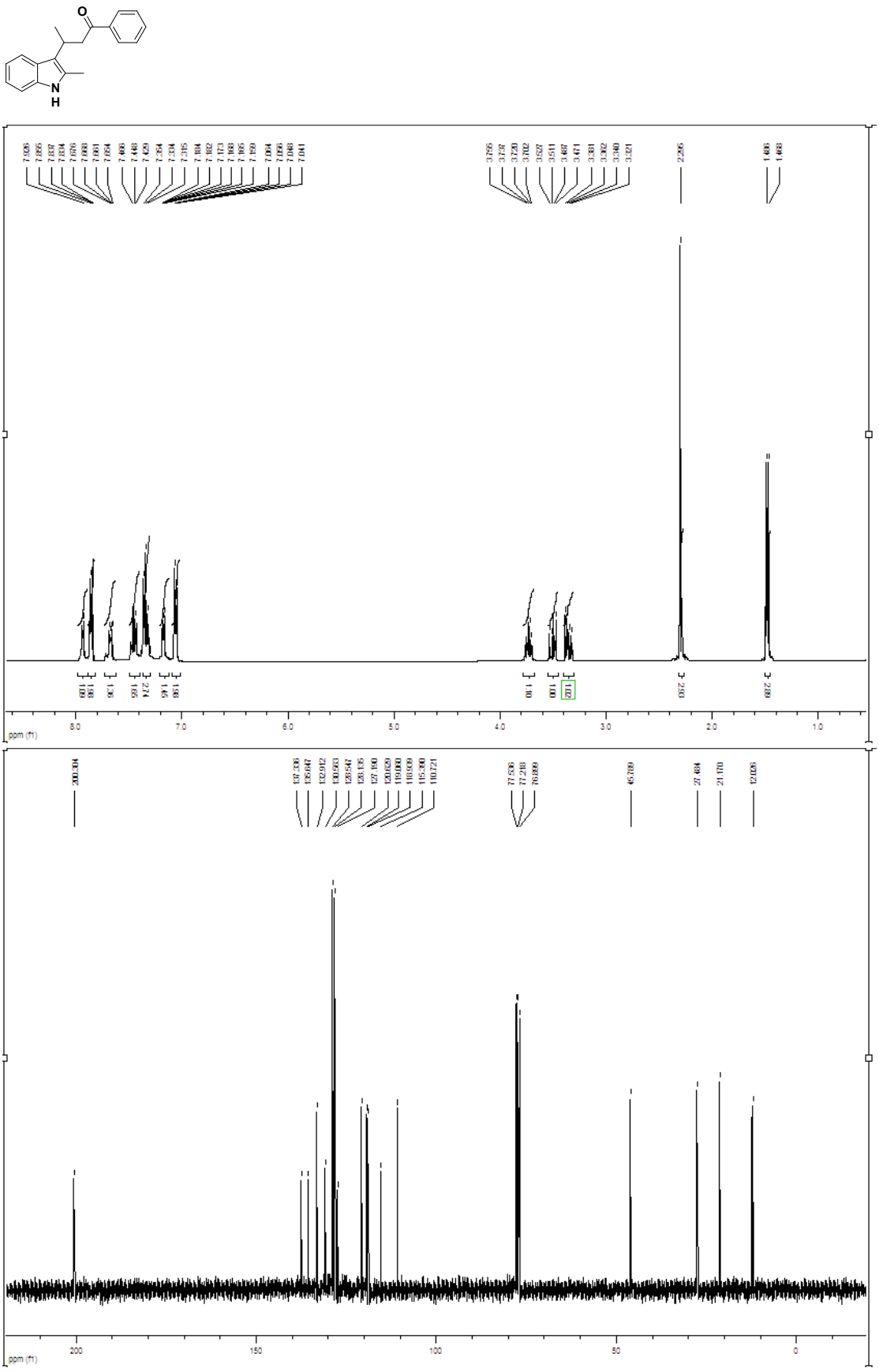
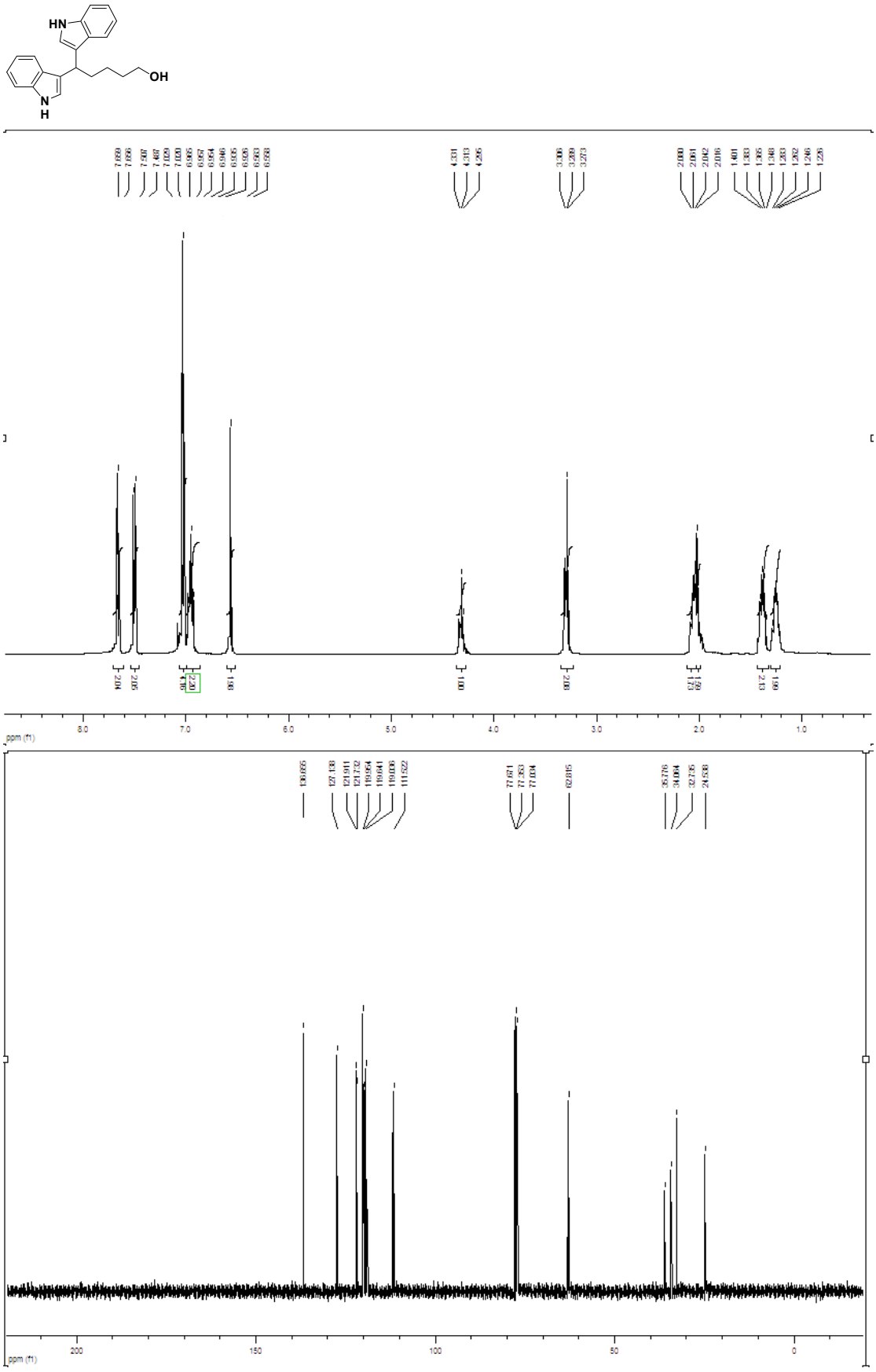
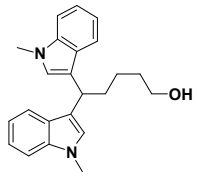
7.406
7.197
7.168
7.150
7.056
7.045
7.043
7.036
7.033
7.005
7.002
6.995
6.967
6.965
6.843
6.834
6.831
6.822
6.778
6.775
6.772
6.769
5.027
5.008
4.991
3.451
3.431
3.410
3.390
3.364
3.348
3.322
3.307
2.341
2.037
2.030
1.978
1.16
1.00
1.58
1.51
1.24
2.01
1.17
1.00
1.11
0.60
3.00
2.29
2.00
ppm (t1)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
207.429
149.029
135.632
132.073
126.967
126.599
123.723
123.530
120.918
119.221
119.144
112.852
110.854
77.496
77.178
76.860
49.450
32.884
30.811
12.013
ppm (f1)
200
150
100
50
0

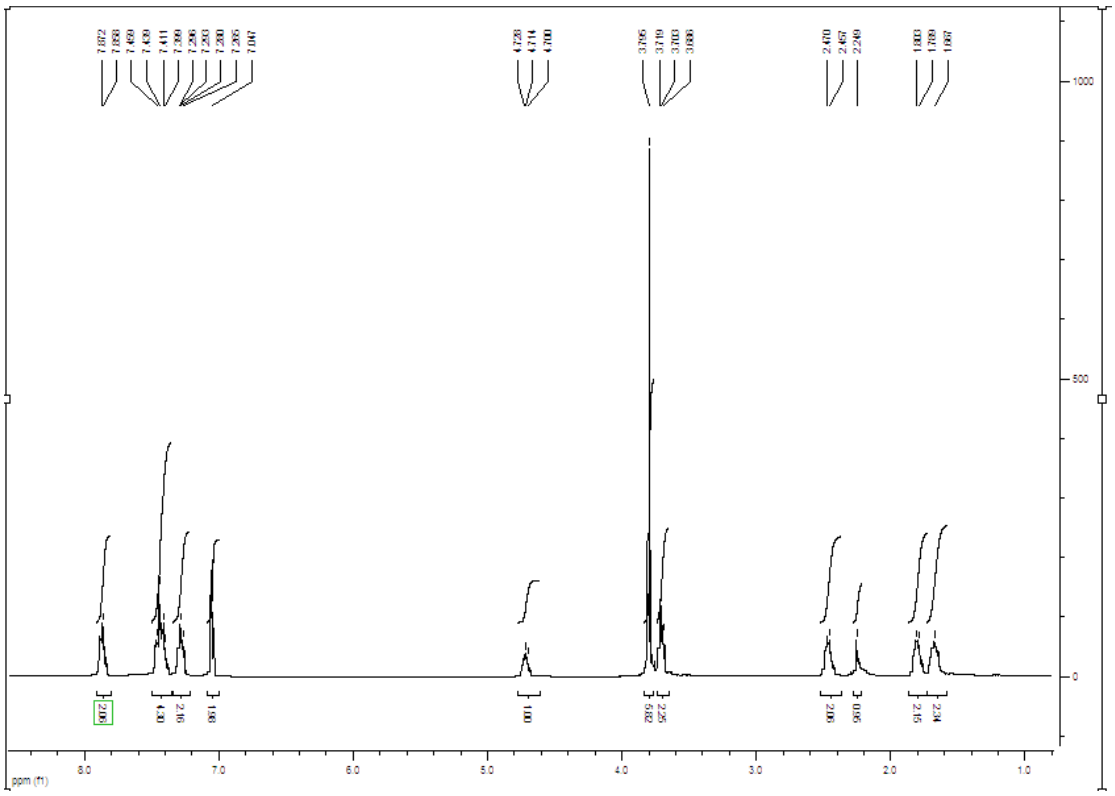


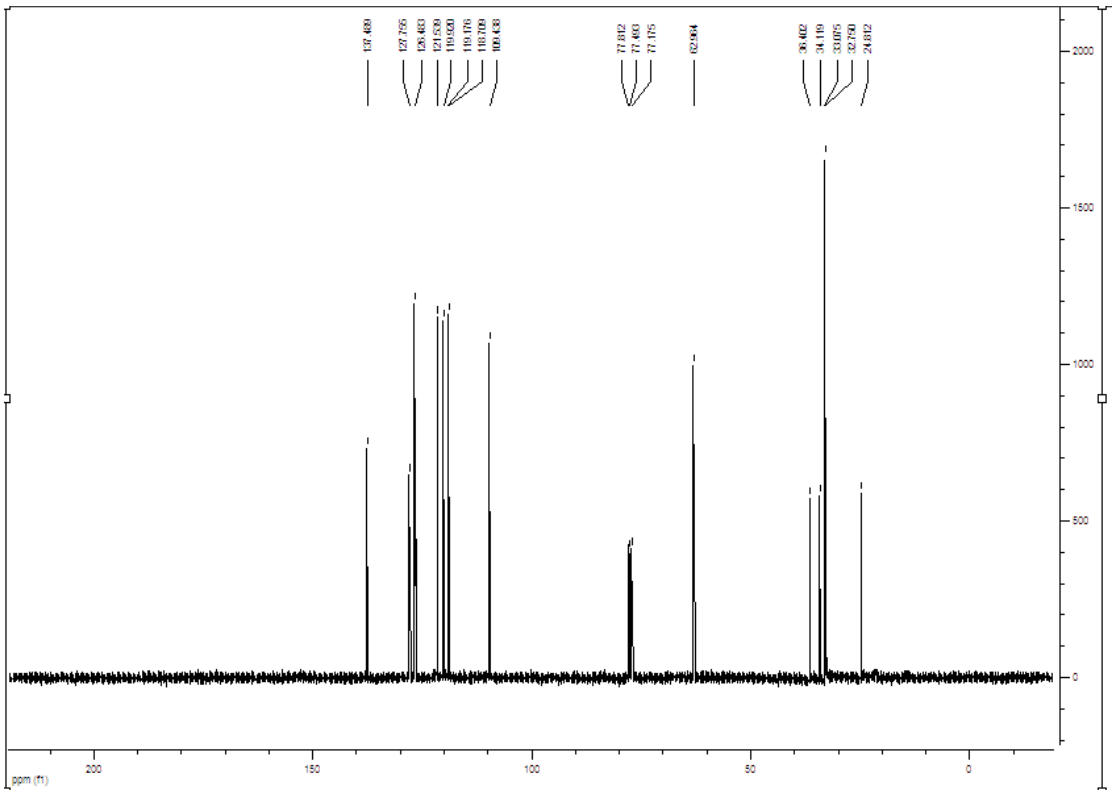

O
N
H
ppm (f1)

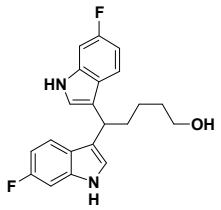


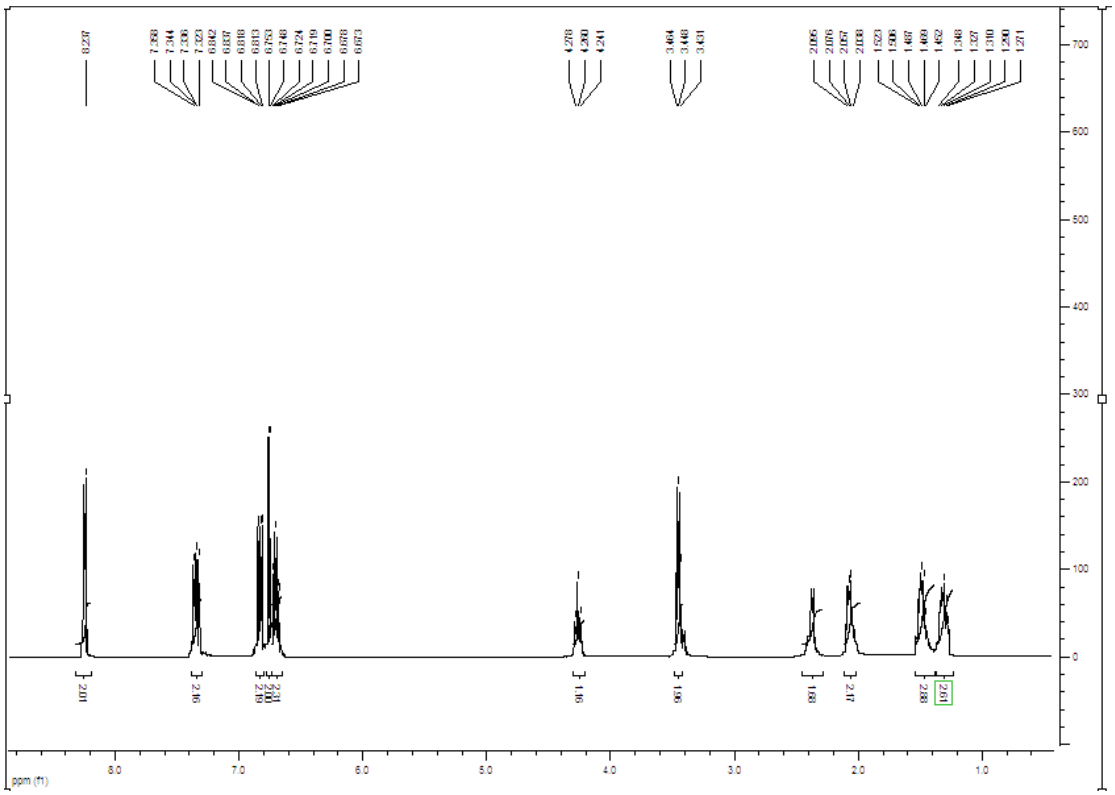

HN
OH
N
H
ppm (f1)
ppm (f1)

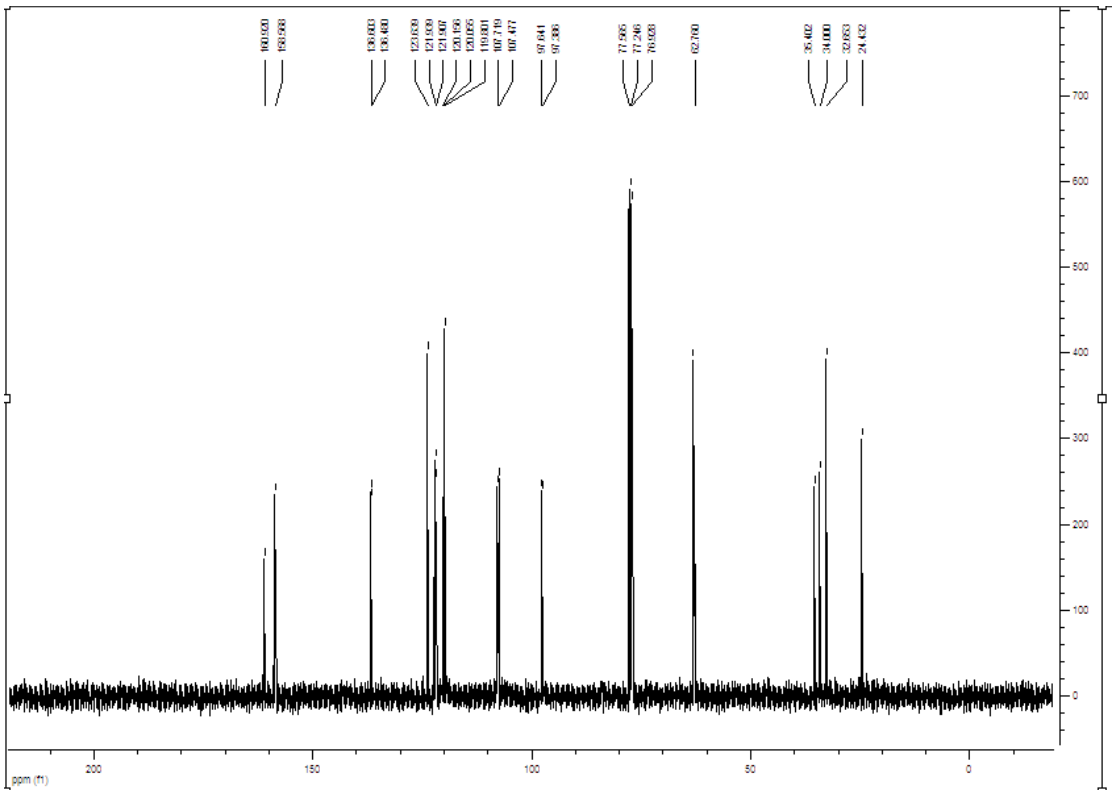

N
OH
N

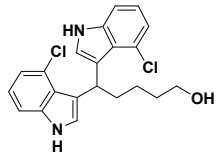

7.672
7.668
7.459
7.439
7.411
7.399
7.396
7.393
7.390
7.295
7.047
4.728
4.714
4.700
3.795
3.719
3.703
3.688
2.470
2.457
2.249
1.803
1.789
1.667
2.06
0.30
2.16
1.96
1.00
2.35
5.62
2.06
0.95
2.15
2.34
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)

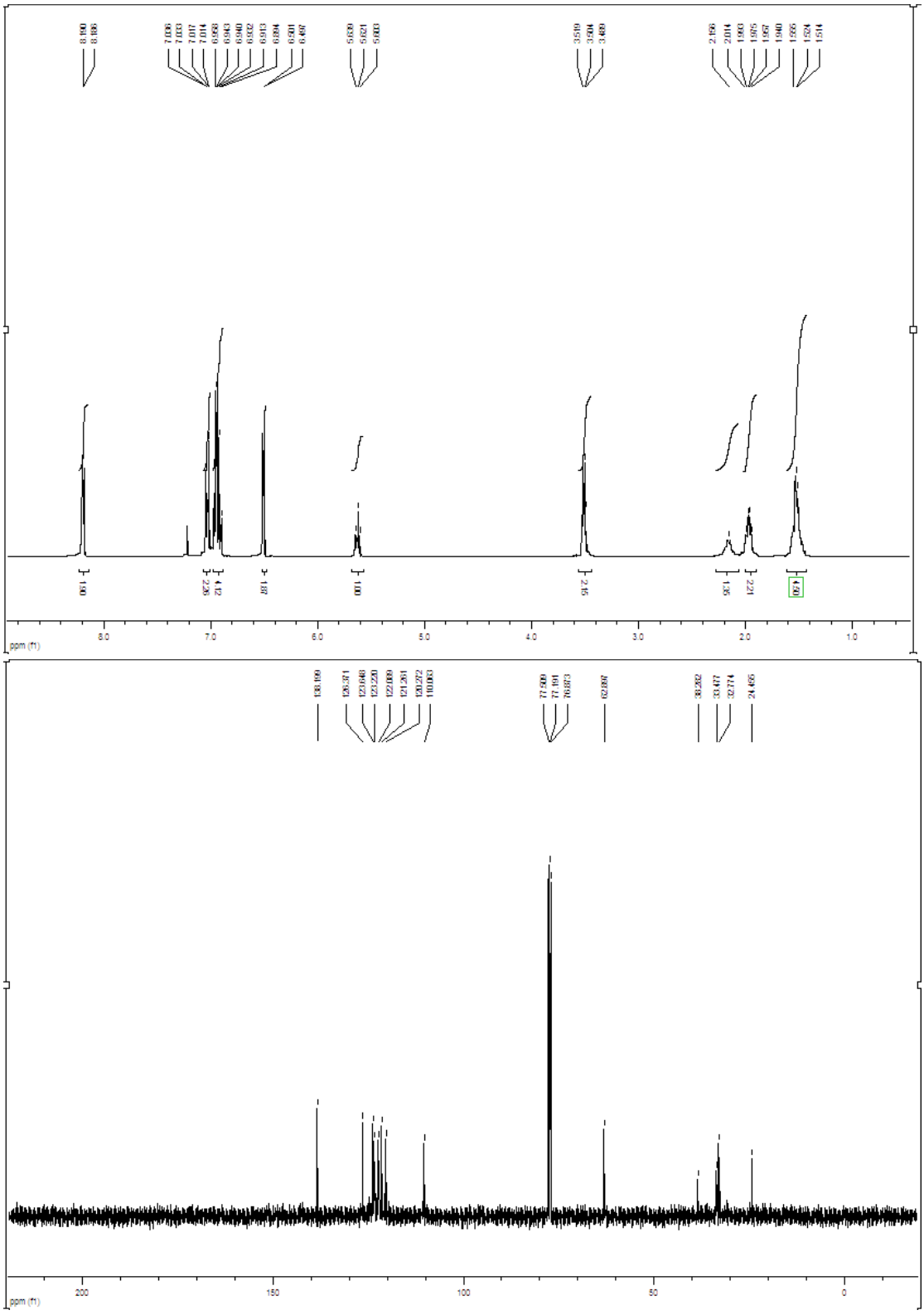

137.489
127.755
126.483
121.539
119.550
119.176
118.709
109.438
77.812
77.493
77.175
62.964
30.482
34.119
33.075
32.750
24.812
200
150
100
50
0
ppm (f1)

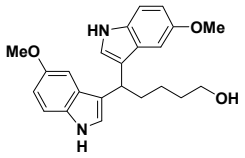

F
HN
OH
F
N
H

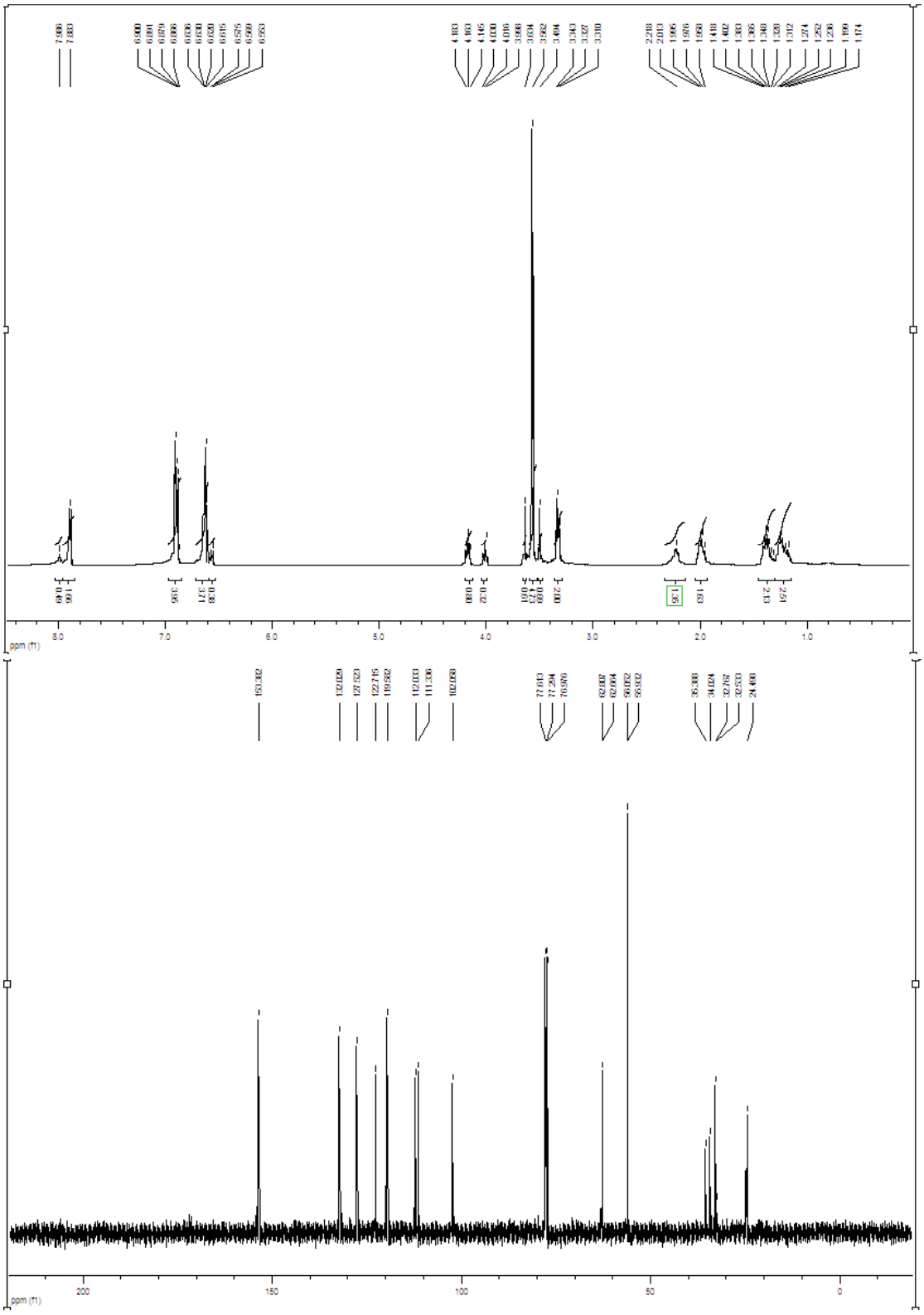

8.237
7.358
7.344
7.336
7.323
6.642
6.637
6.618
6.613
6.753
6.748
6.724
6.719
6.700
6.698
6.693
4.278
4.260
4.241
3.464
3.448
3.431
2.095
2.076
2.057
2.038
1.523
1.506
1.487
1.469
1.452
1.348
1.327
1.310
1.290
1.271
2.01
2.16
1.19
1.96
1.68
2.17
2.38
2.01
ppm (f1)

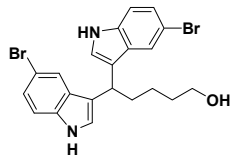

136.603
136.480
123.939
121.939
121.907
120.156
120.065
119.801
112.719
112.477
97.641
97.386
77.305
77.246
76.928
62.760
35.402
34.000
32.663
24.432
ppm (f1)

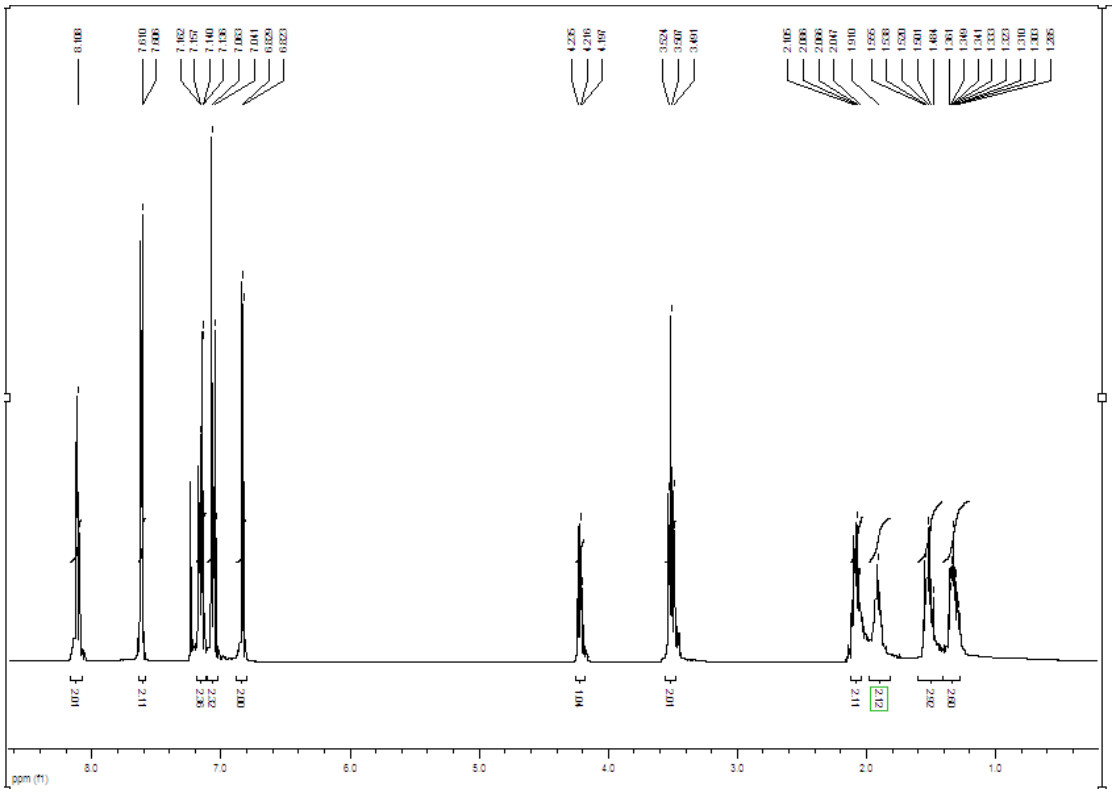


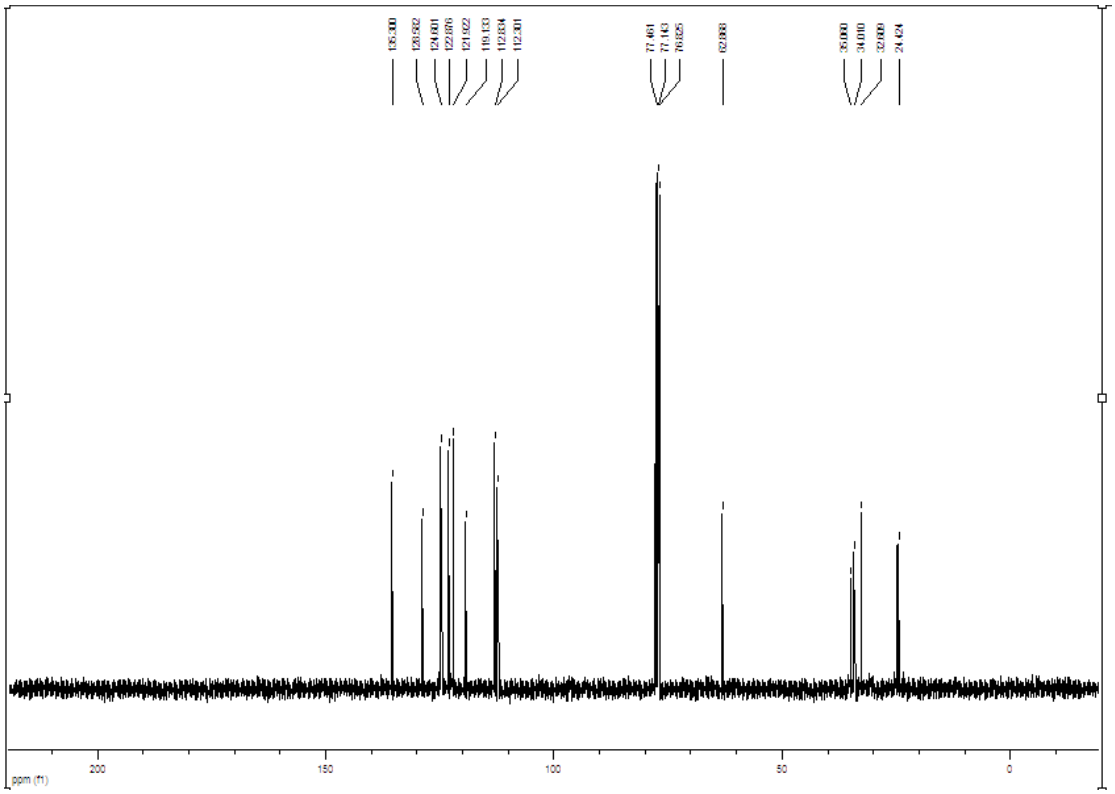


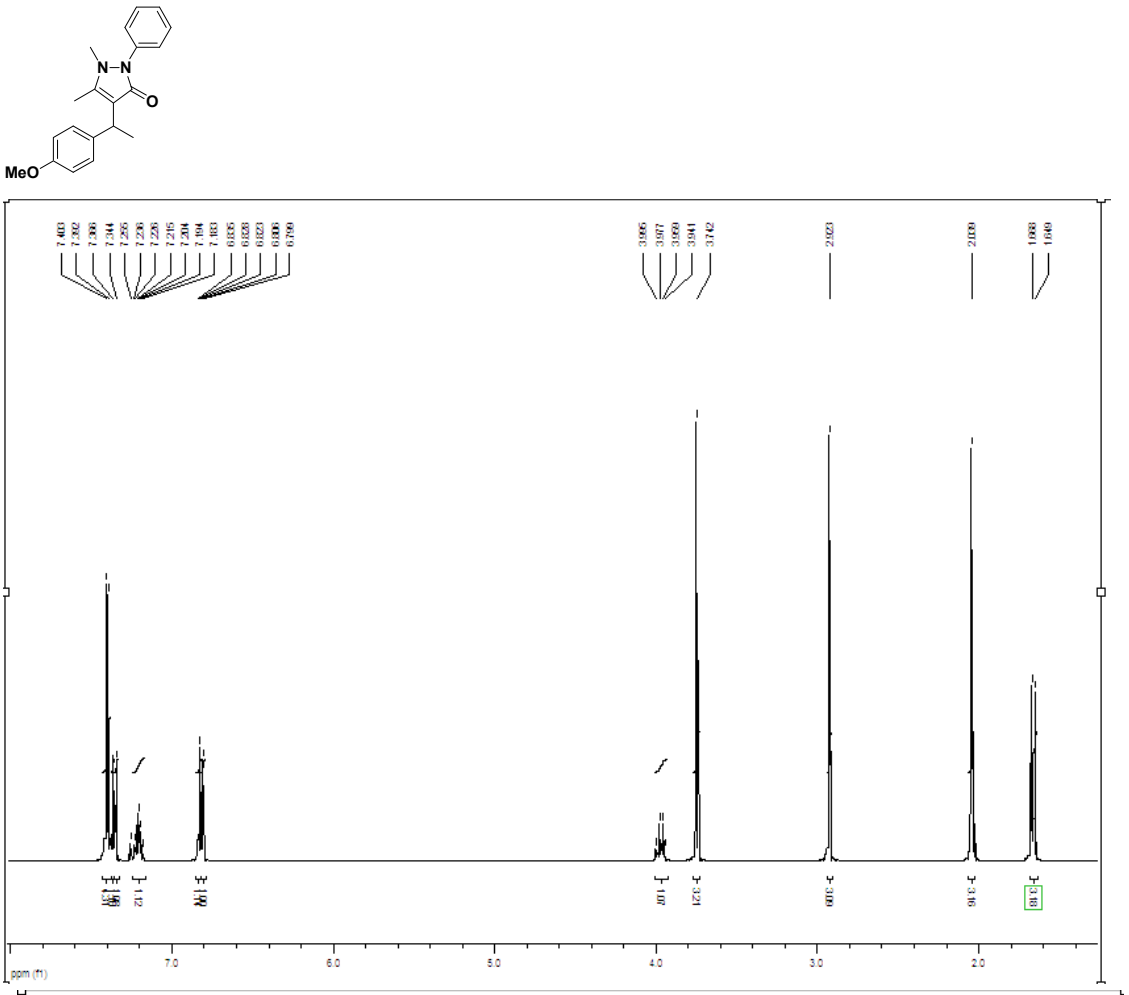

HN
OMe
MeO
OH
N
H

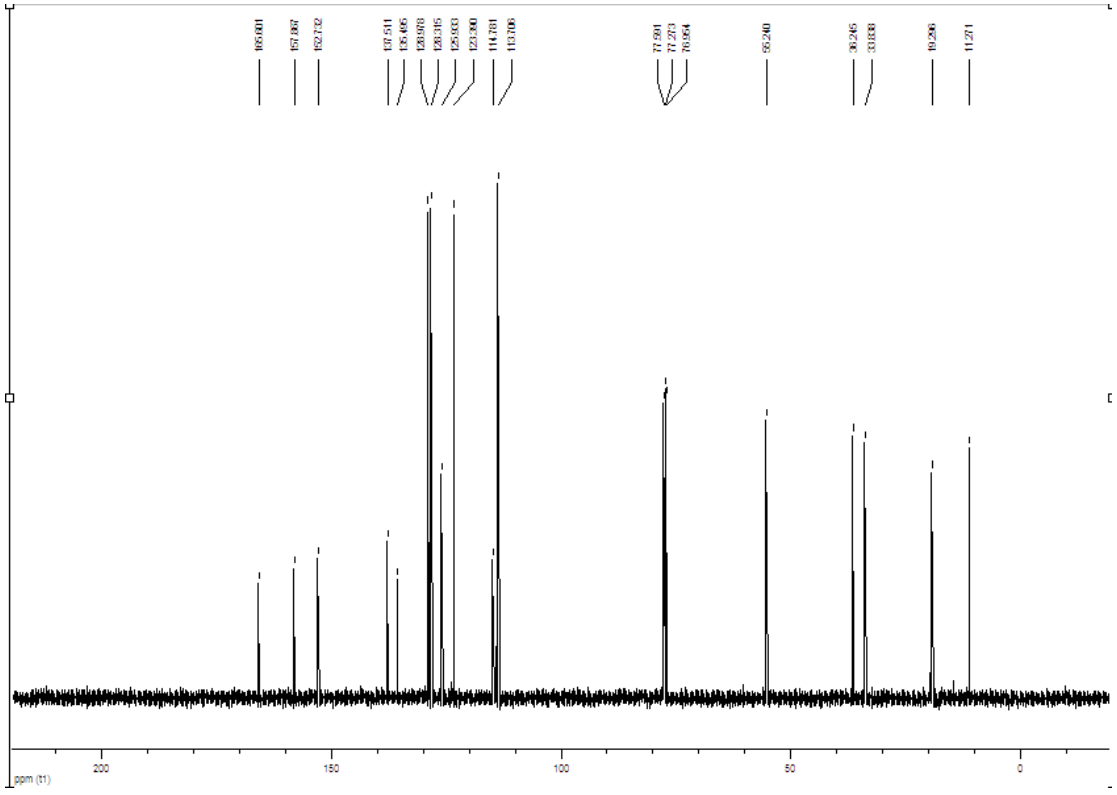


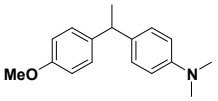

HN
Br
Br
OH
N
H

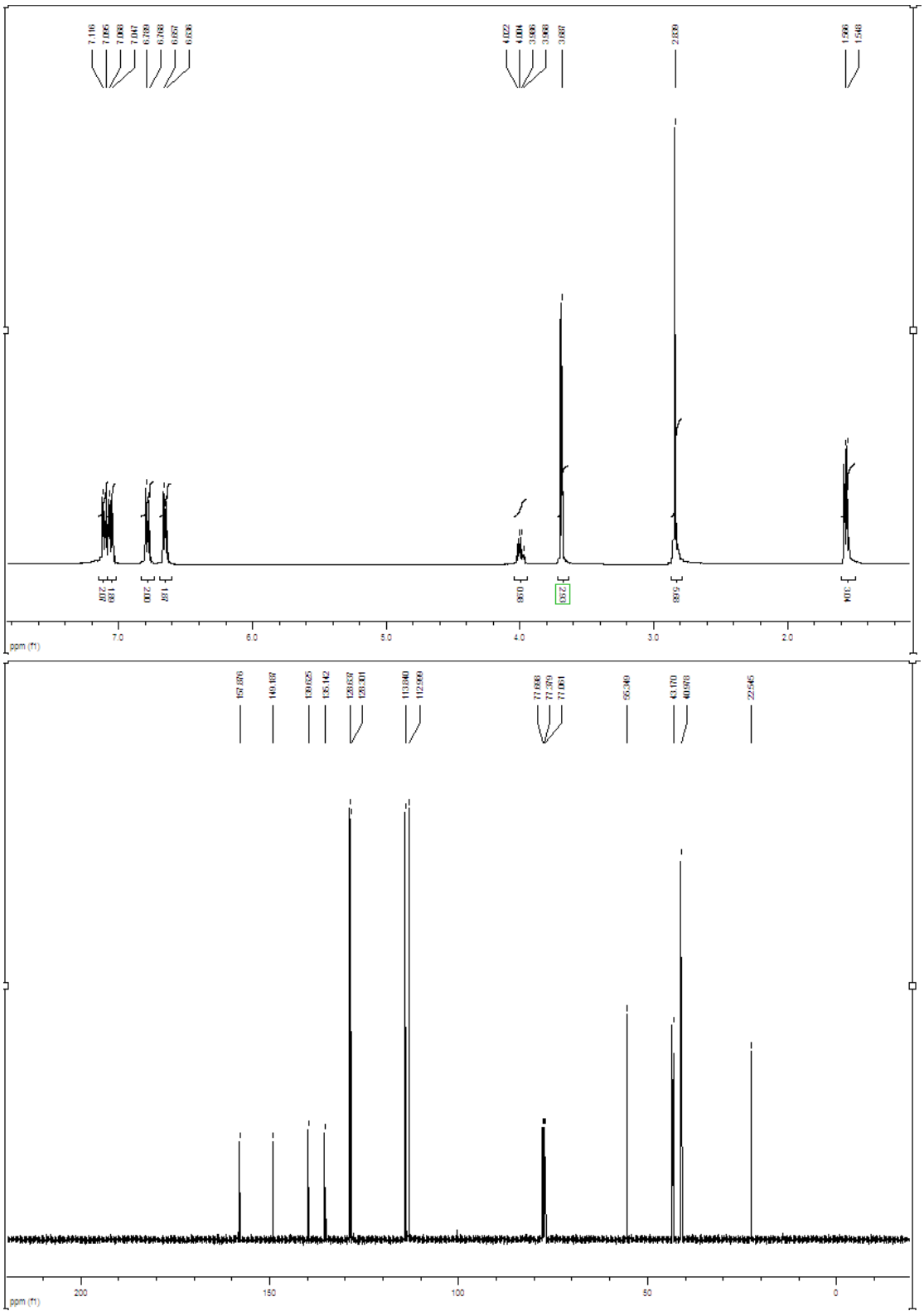

8.108
7.610
7.605
7.162
7.157
7.140
7.136
7.063
7.041
6.929
6.923
4.235
4.216
4.197
3.524
3.507
3.491
2.105
2.066
2.056
2.047
1.910
1.895
1.538
1.520
1.501
1.484
1.361
1.349
1.341
1.333
1.323
1.310
1.303
1.285
2.01
2.11
2.36
2.32
2.00
1.04
2.01
2.11
2.12
2.92
2.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)

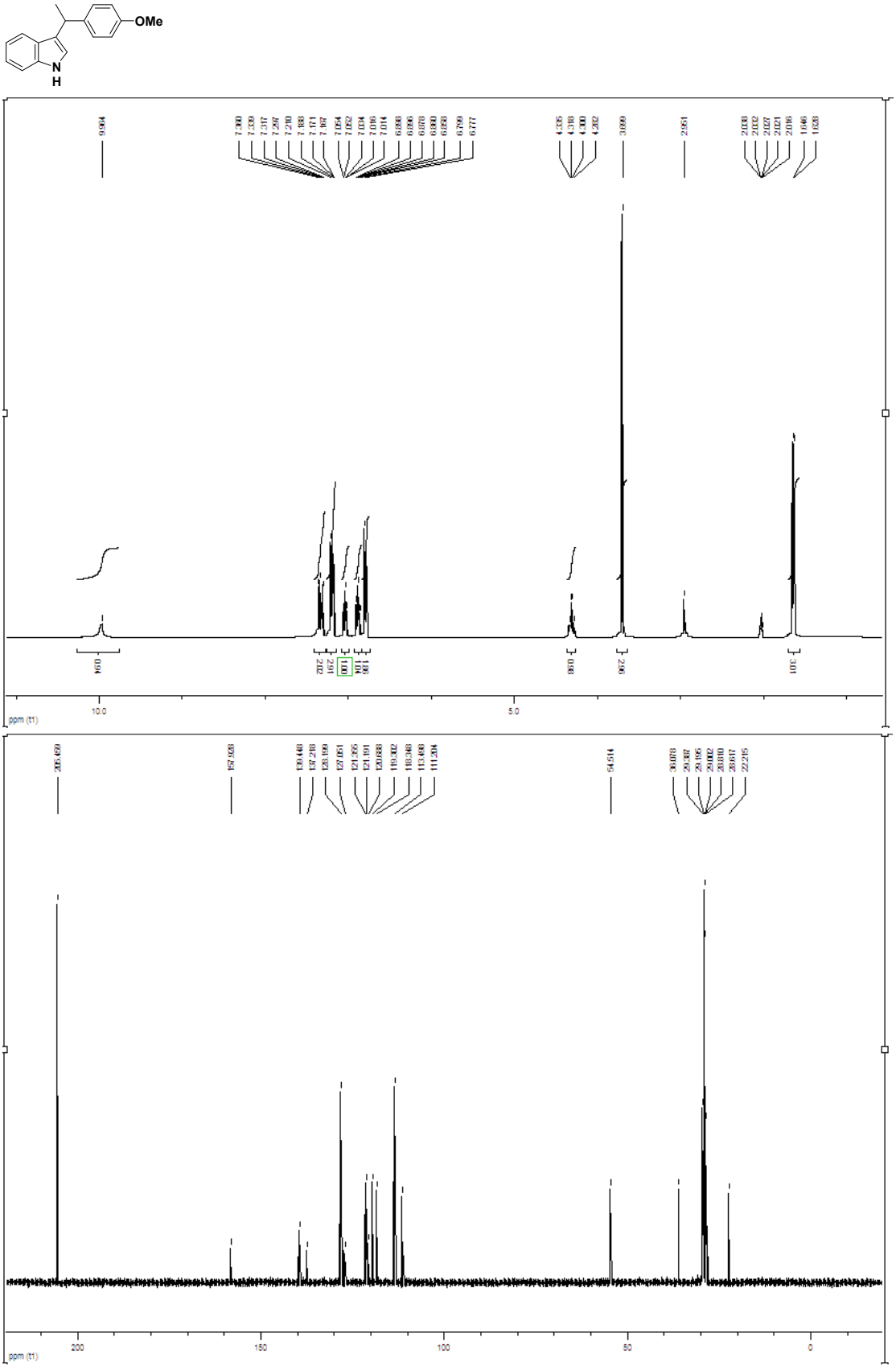

135.300
126.582
124.601
122.586
121.922
119.133
112.854
112.301
77.461
77.143
76.825
62.888
35.000
34.010
32.889
24.424
200
150
100
50
0
ppm (f1)

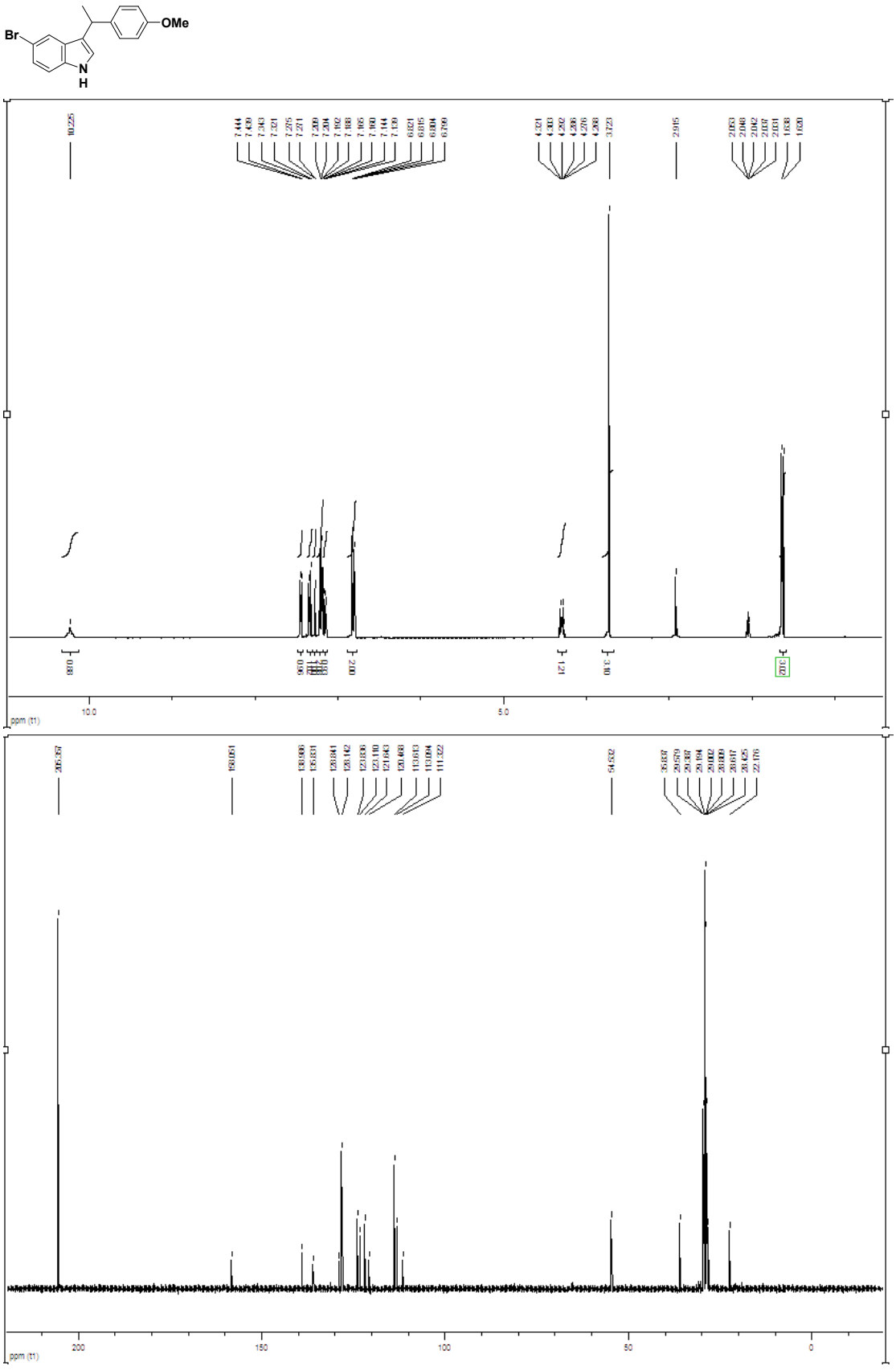

N–N
O
MeO
7.403
7.392
7.386
7.344
7.256
7.228
7.215
7.204
7.194
7.183
6.835
6.828
6.823
6.806
6.799
3.995
3.987
3.969
3.941
3.742
2.923
2.039
1.988
1.649
1.00
3.24
3.09
3.16
3.18
ppm (f1)

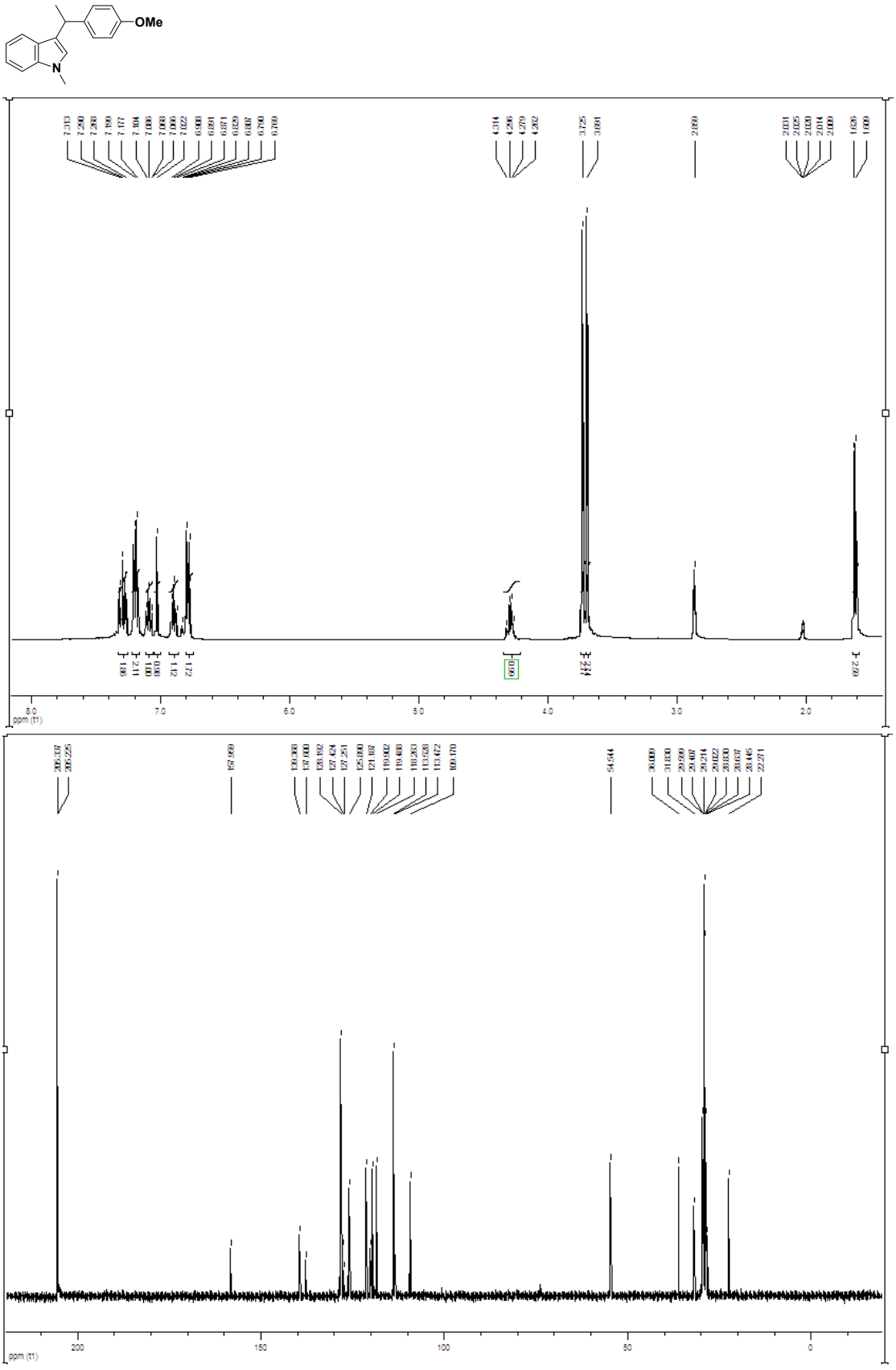

165.601
157.067
132.732
137.511
135.495
128.978
128.315
125.933
123.300
114.781
113.706
77.591
77.273
76.954
55.240
36.245
33.038
19.296
11.271
ppm (f1)

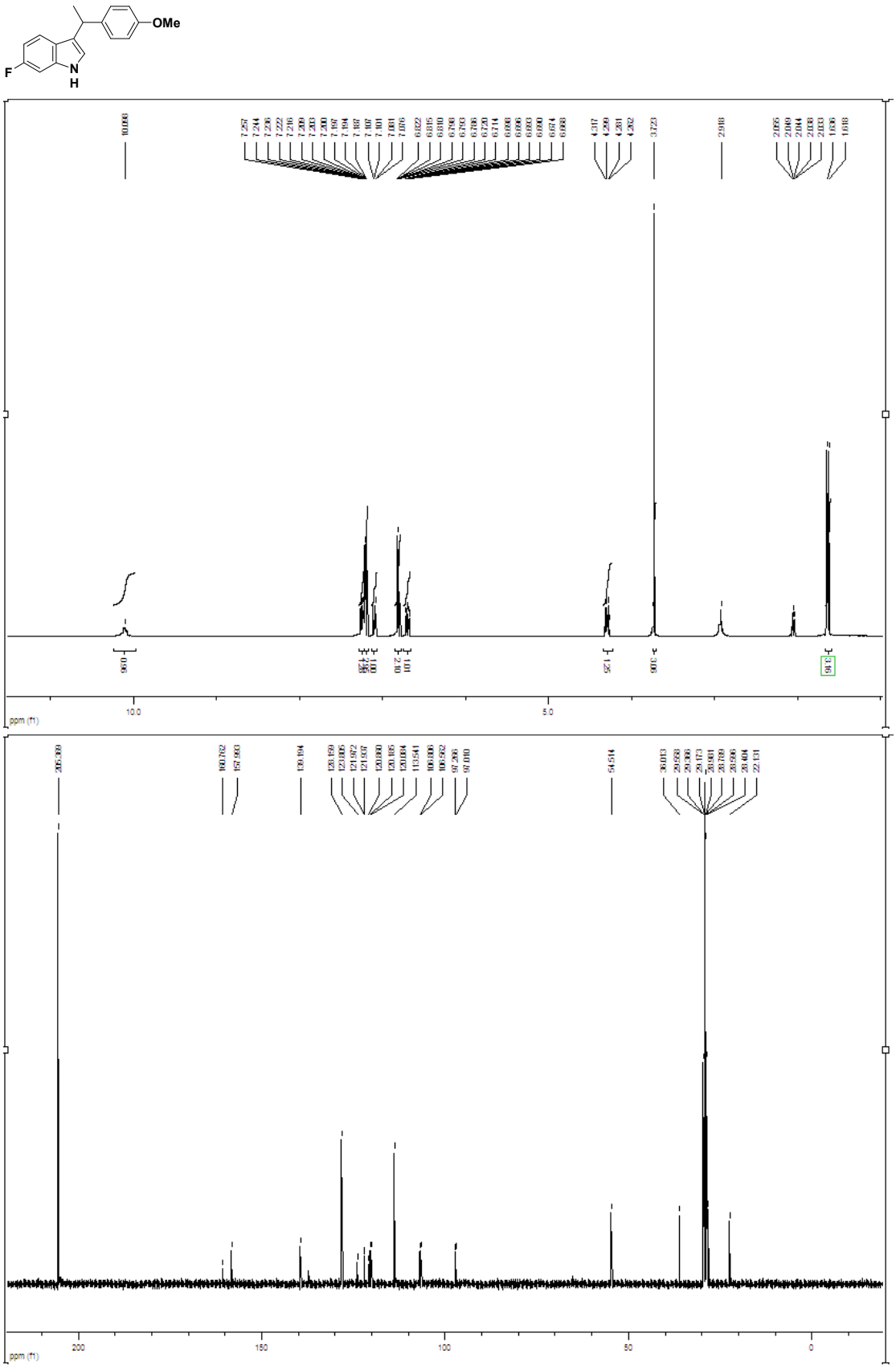

MeO
N

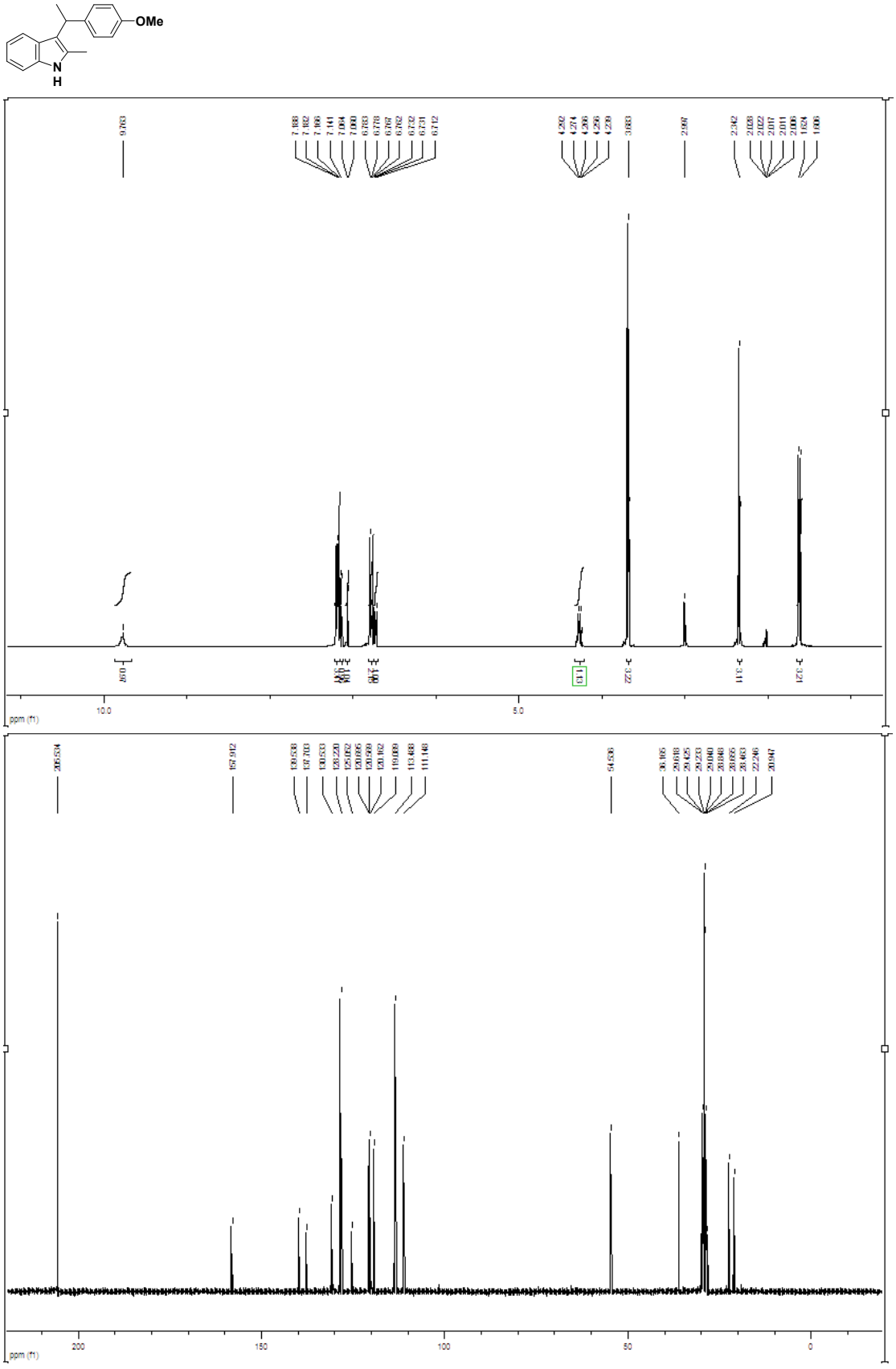

7.116
7.095
7.088
7.047
6.789
6.687
6.636
4.022
4.004
3.996
3.968
3.887
2.839
1.596
1.548
2.07
1.89
2.00
1.87
0.98
3.00
5.88
3.04
ppm (f1)
7.0
6.0
5.0
4.0
3.0
2.0
157.876
140.887
130.625
130.142
126.637
126.301
113.840
112.990
77.098
77.379
77.061
55.349
43.170
40.978
22.545
ppm (f1)
200
150
100
50
0

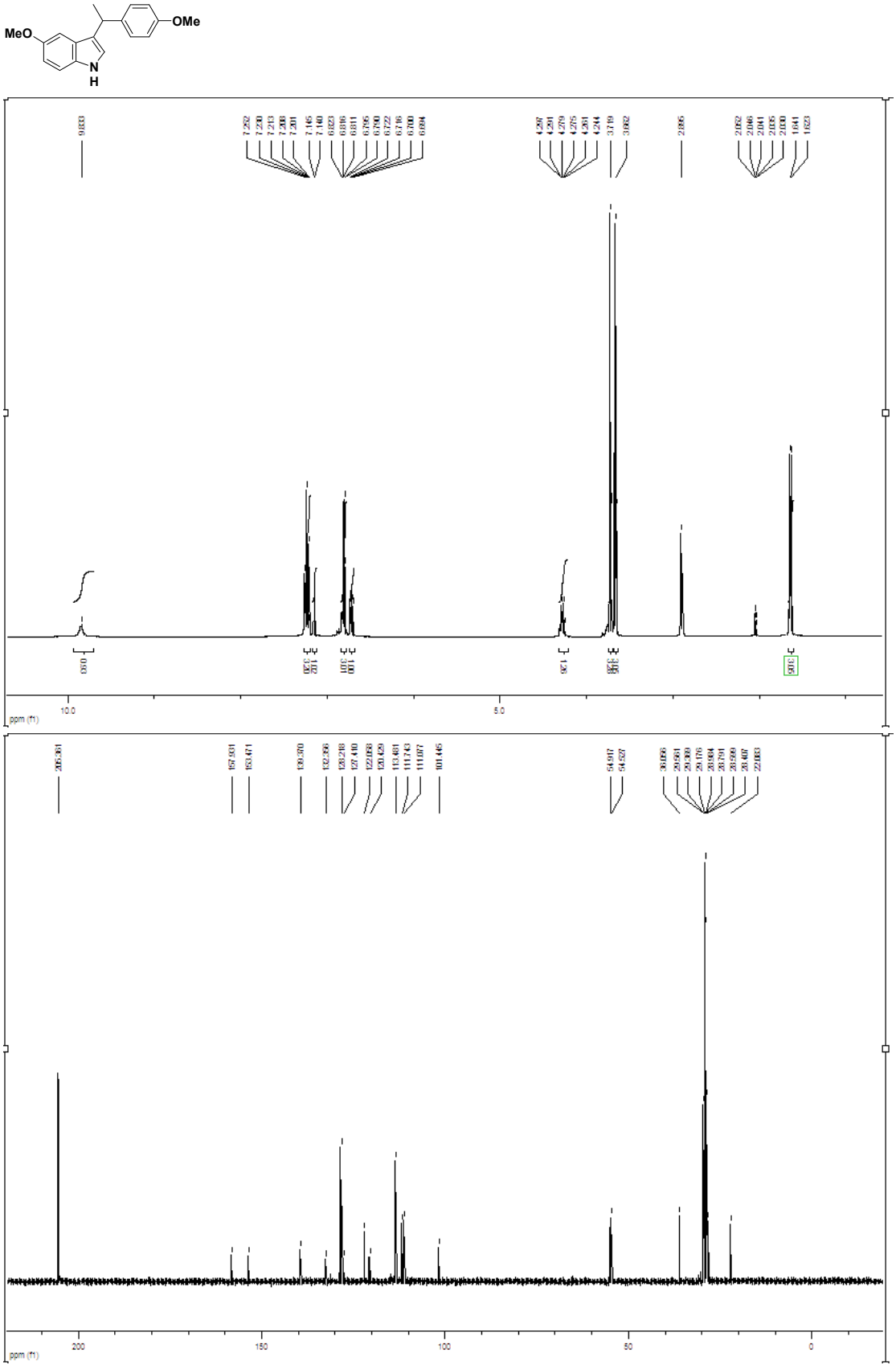

OMe
N
H
9.964
7.390
7.339
7.317
7.298
7.210
7.188
7.171
7.167
7.054
7.052
7.034
7.016
7.014
6.898
6.896
6.878
6.860
6.858
6.799
6.777
4.335
4.318
4.300
4.282
3.899
2.951
2.038
2.032
2.027
2.021
2.016
1.646
1.628
0.94
2.02
2.91
1.00
1.04
1.88
0.98
2.96
3.01
10.0
5.0
ppm (t1)
205.459
157.938
130.448
127.218
126.999
122.051
121.355
121.191
120.888
119.302
118.348
113.408
111.204
54.514
36.078
29.382
29.195
29.002
28.810
20.617
22.215
200
150
100
50
0
ppm (t1)

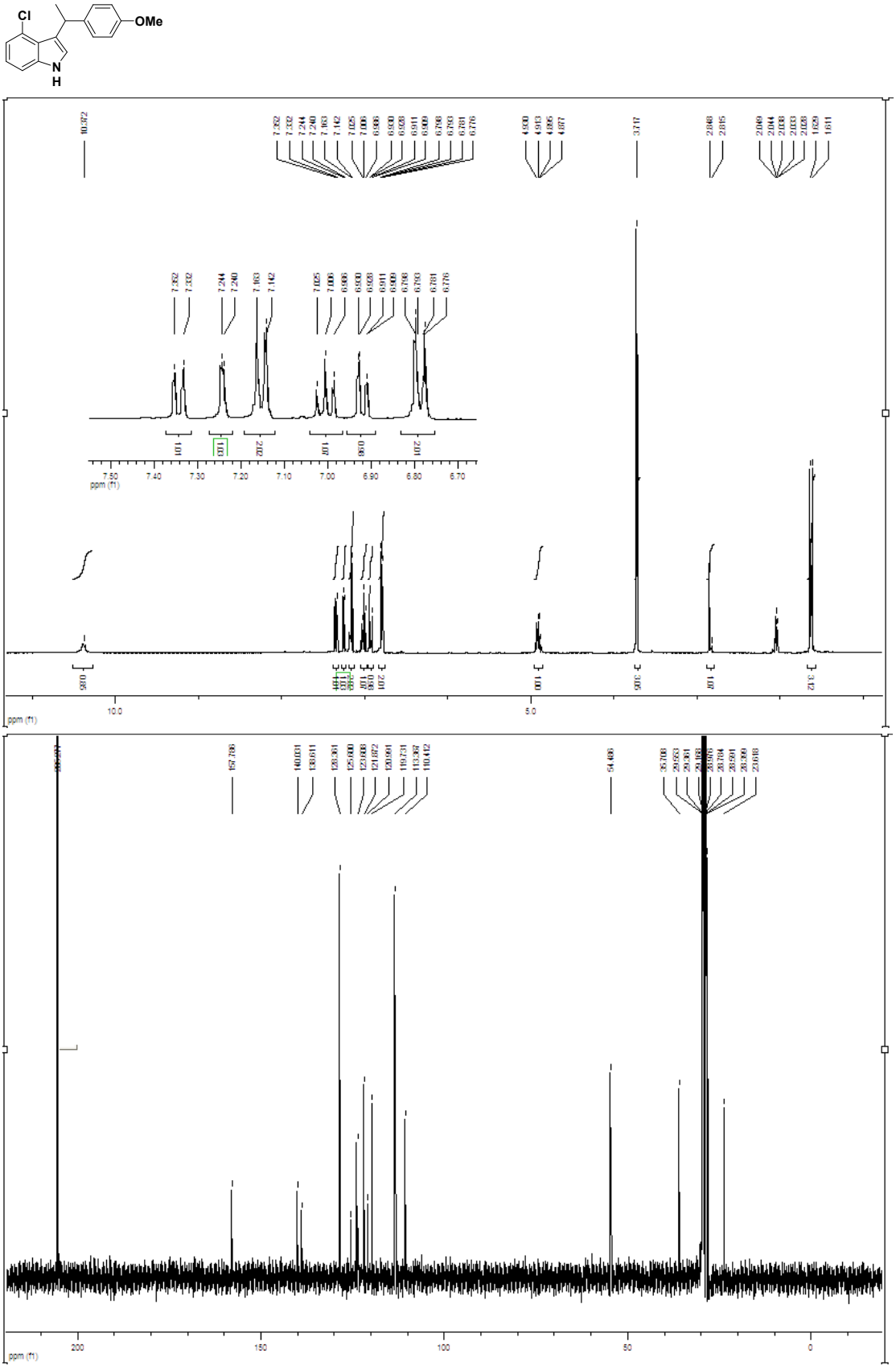

Br
OMe
N
H
10.225
7.444
7.439
7.343
7.321
7.275
7.271
7.200
7.194
7.192
7.188
7.165
7.160
7.144
7.139
6.821
6.815
6.804
6.799
4.321
4.303
4.292
4.286
4.276
4.268
3.723
2.915
2.063
2.048
2.042
2.037
2.031
1.638
1.630
0.98
9.60
2.00
1.71
3.10
2.02
10.0
5.0
ppm (t1)
205.367
158.051
130.986
130.831
128.841
128.142
123.836
123.110
121.643
120.468
113.613
113.094
111.322
54.532
35.837
29.579
29.367
29.194
29.102
29.009
28.917
28.425
22.116
200
150
100
50
0
ppm (t1)

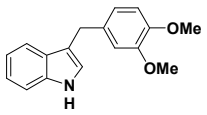

OMe
N
7.313
7.290
7.268
7.199
7.177
7.104
7.086
7.063
7.006
7.022
6.908
6.891
6.871
6.829
6.807
6.790
6.769
4.314
4.296
4.279
4.262
3.725
3.691
2.899
2.031
2.025
2.020
2.014
2.009
1.626
1.000
1.86
2.11
1.00
0.98
1.12
1.72
0.99
3.24
2.29
8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)
205.337
205.225
157.959
130.368
127.600
126.192
127.424
127.251
125.890
121.187
119.902
119.488
118.283
113.538
113.472
109.170
54.594
36.009
31.830
29.599
29.467
29.214
29.022
28.830
28.637
28.445
22.271
200
150
100
50
0
ppm (t1)

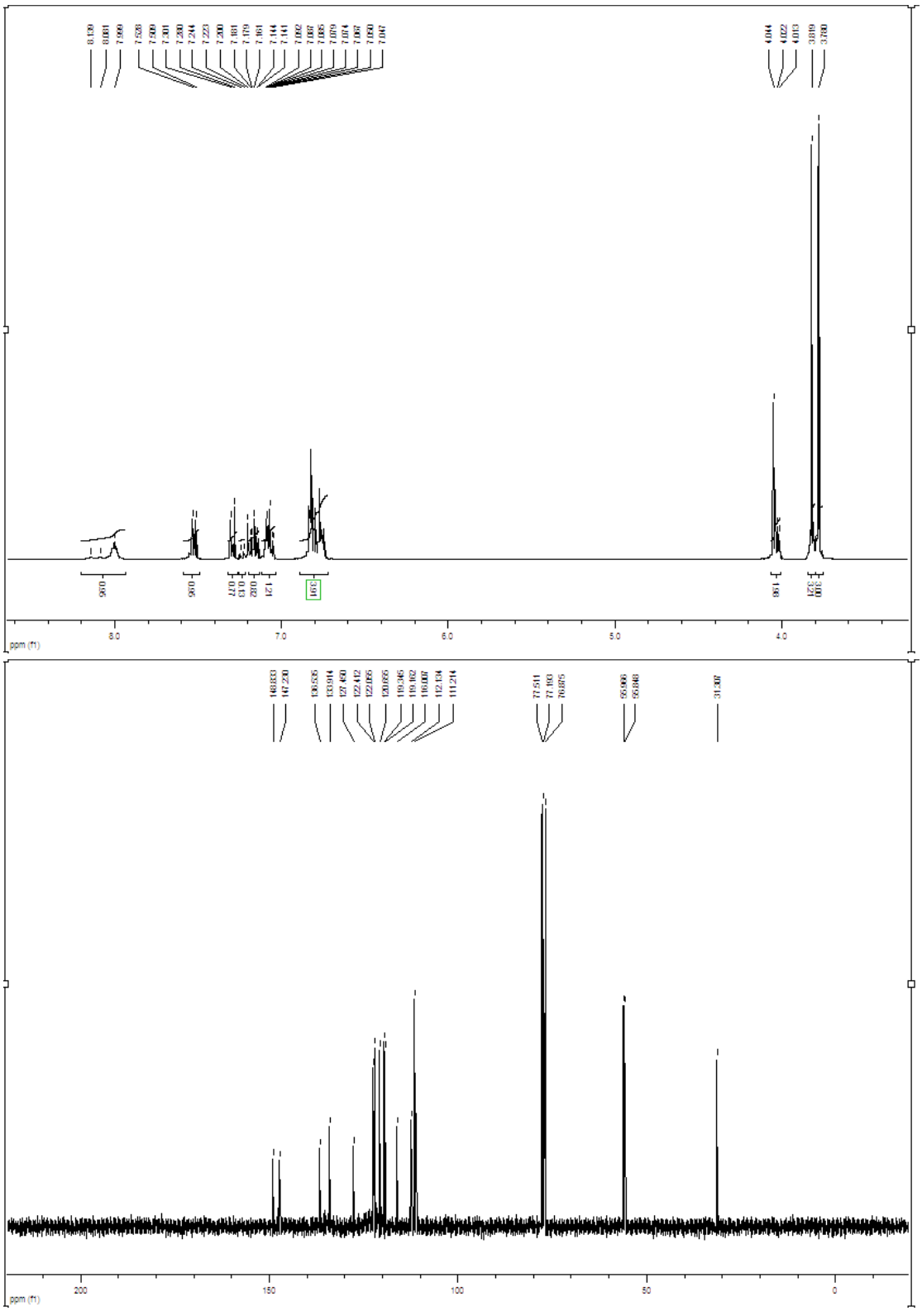

OMe
F
N
H
10.086
7.257
7.244
7.236
7.222
7.216
7.209
7.203
7.200
7.197
7.194
7.187
7.107
7.101
7.081
7.076
6.822
6.815
6.810
6.796
6.795
6.788
6.730
6.714
6.696
6.696
6.693
6.690
6.674
6.668
4.317
4.299
4.281
4.262
3.723
2.918
2.065
2.049
2.044
2.038
2.033
1.636
1.618
0.60
2.39
1.01
2.10
1.01
1.26
3.06
2.16
10.0
5.0
ppm (f1)
205.309
160.762
157.963
130.164
126.159
123.385
121.972
121.937
120.930
120.885
120.884
113.541
106.806
106.562
97.266
97.010
54.514
36.013
29.693
29.306
29.173
29.161
28.789
28.596
28.464
22.131
200
150
100
50
0
ppm (f1)

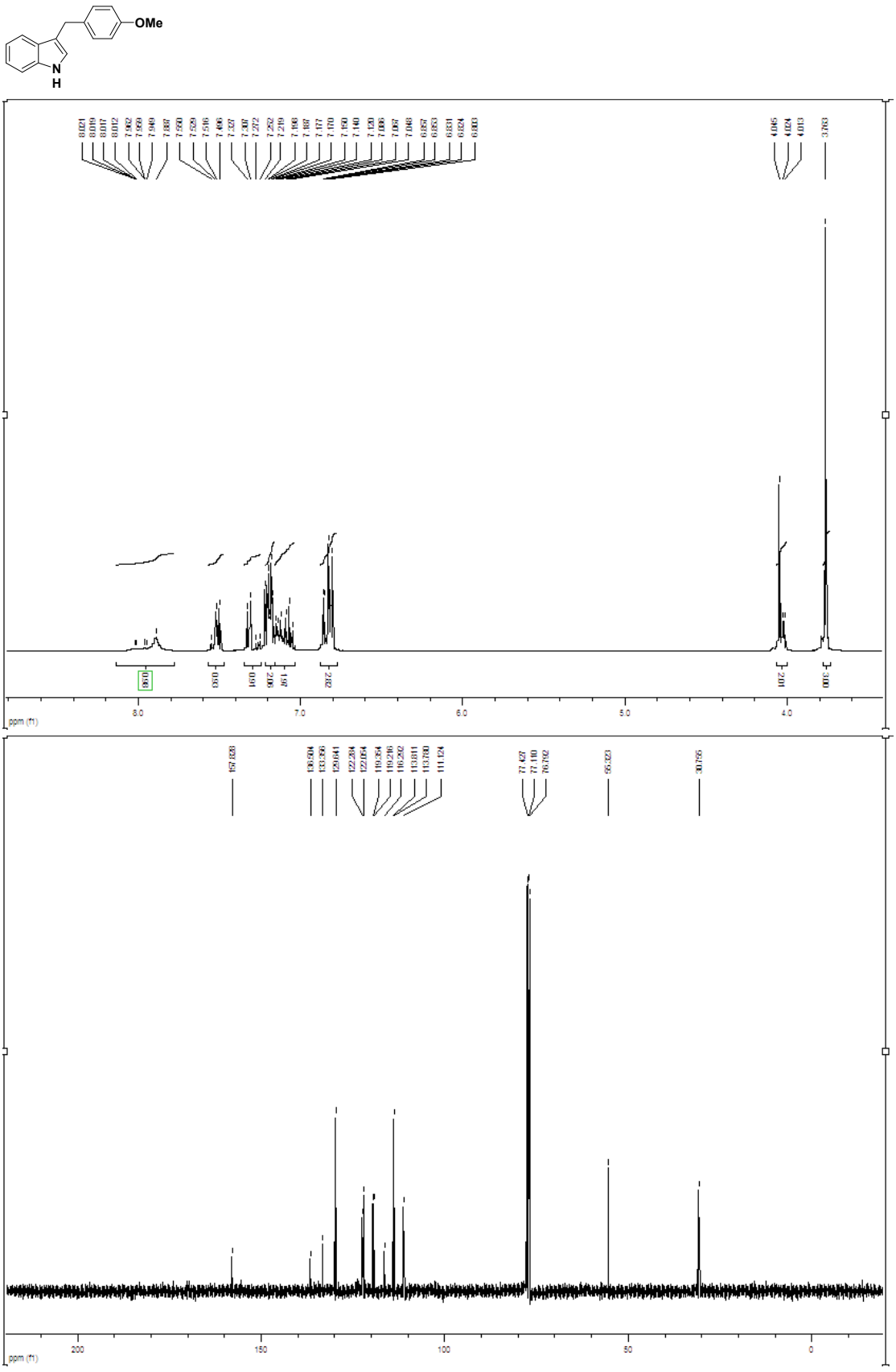

OMe
N
H
9.763
7.188
7.182
7.166
7.141
7.084
7.080
6.783
6.778
6.767
6.762
6.732
6.731
6.712
4.292
4.274
4.256
4.238
3.883
2.998
2.342
2.028
2.022
2.017
2.011
2.006
1.624
1.606
0.97
2.48
1.03
3.22
3.11
3.21
10.0
5.0
ppm (f1)
205.534
157.912
130.538
127.703
130.533
128.220
125.052
120.995
120.989
120.162
110.089
113.488
111.148
54.936
36.165
29.618
29.425
29.233
29.090
28.948
28.805
28.463
22.246
20.947
200
150
100
50
0
ppm (f1)

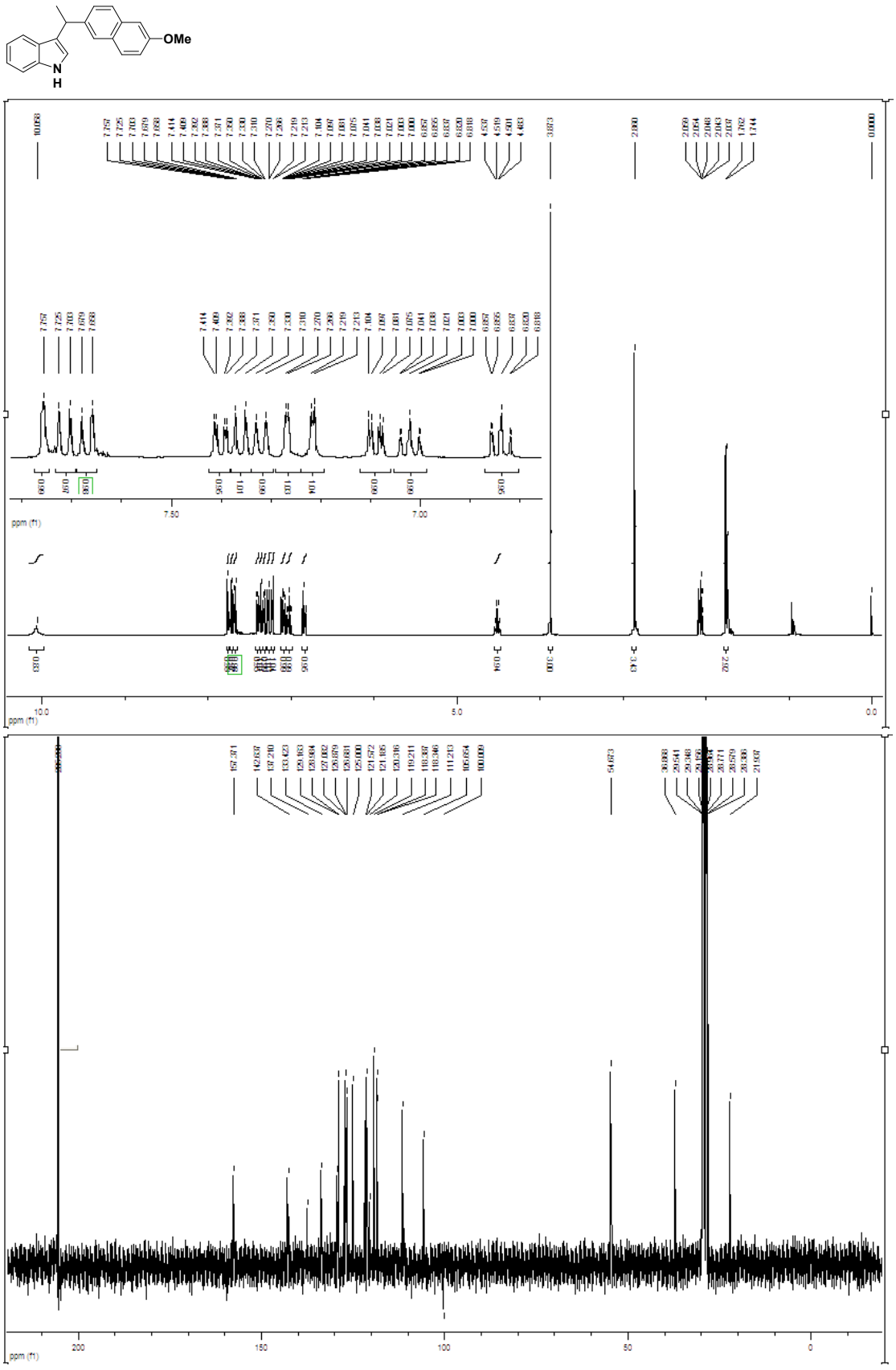

MeO
OMe
N
H

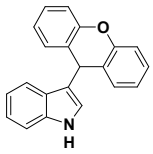

Cl
OMe
N
H
ppm (f1)

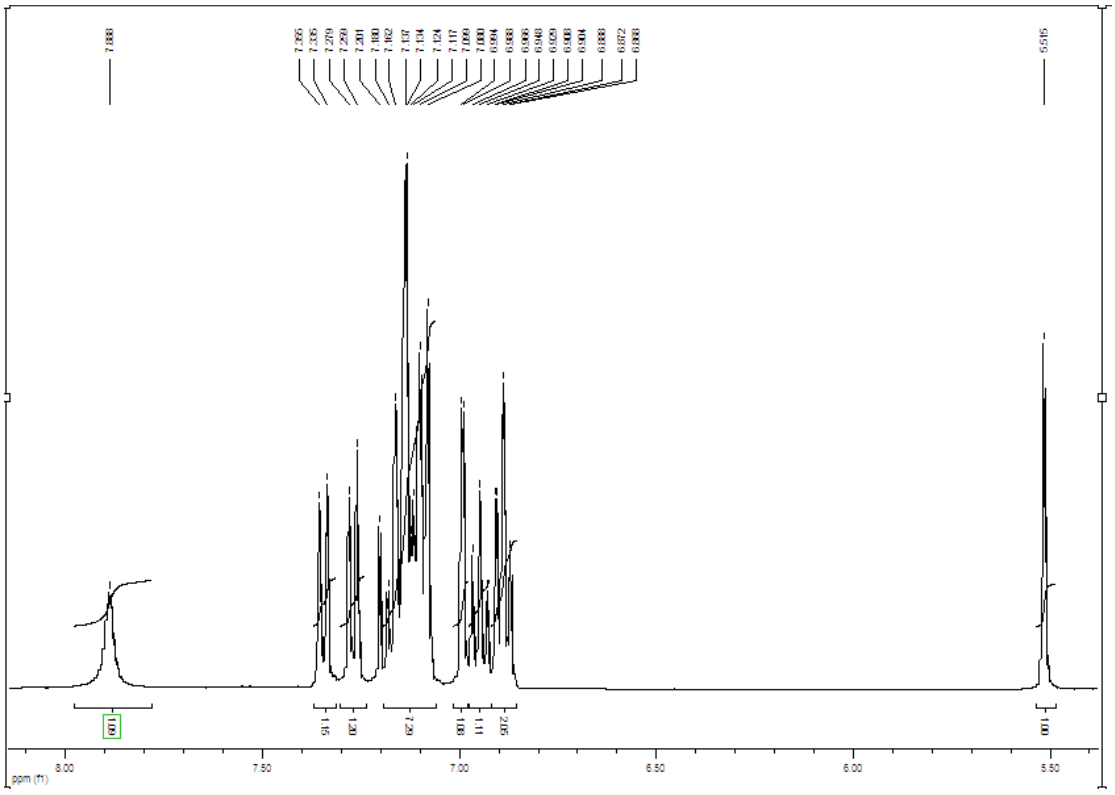

OMe
OMe
N
H

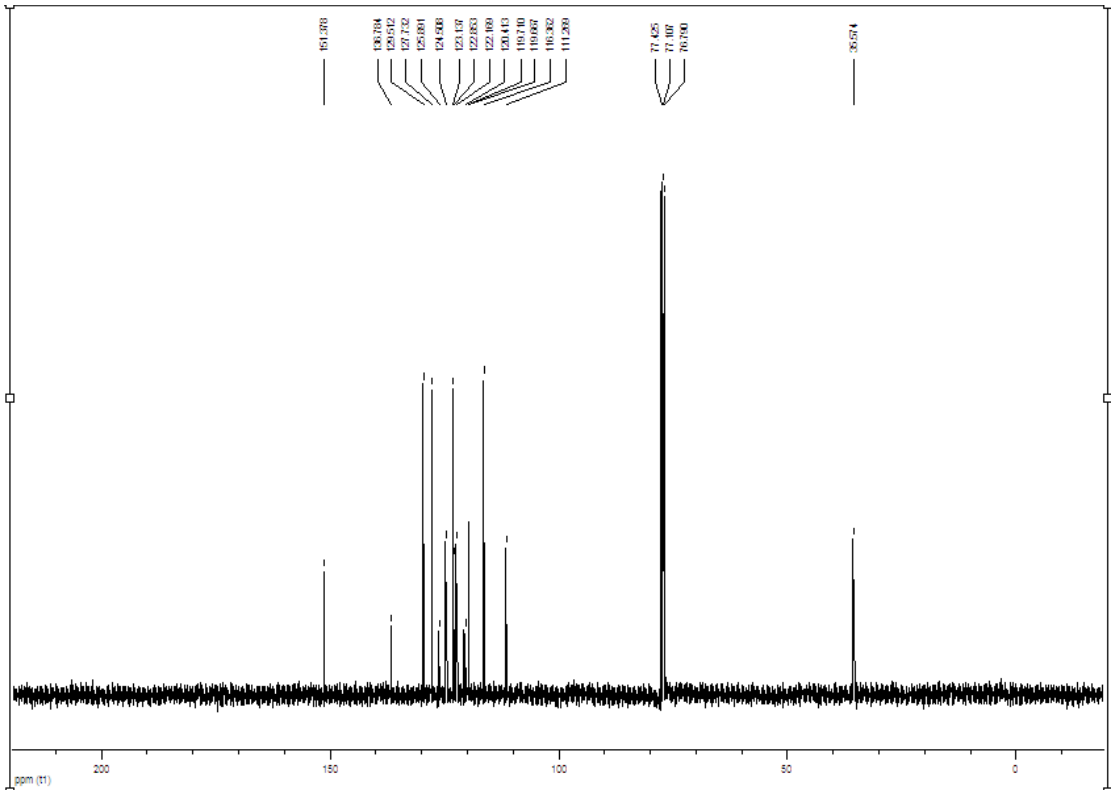

8.139
8.001
7.999
7.528
7.509
7.301
7.290
7.244
7.223
7.200
7.181
7.179
7.161
7.144
7.141
7.092
7.087
7.085
7.079
7.074
7.067
7.050
7.047
4.044
4.022
4.013
3.919
3.780
9.60
9.60
0.27
0.13
0.82
1.21
16.00
1.96
3.24
ppm (f1)
8.0
7.0
6.0
5.0
4.0
148.833
147.230
136.535
133.914
127.450
122.412
122.055
120.035
119.345
119.162
118.007
112.134
111.214
77.511
77.193
76.875
55.966
55.848
31.307
ppm (f1)
200
150
100
50
0


OMe
N
H
8.021
8.019
8.017
8.012
7.962
7.959
7.949
7.887
7.590
7.529
7.516
7.496
7.337
7.308
7.272
7.252
7.219
7.198
7.167
7.177
7.170
7.150
7.140
7.120
7.106
7.067
7.048
6.857
6.853
6.831
6.824
6.803
4.045
4.024
4.013
3.763
9.70
5.10
1.50
2.06
2.11
2.12
2.01
3.00
8.0
7.0
6.0
5.0
4.0
ppm (f1)
157.833
136.504
133.356
129.641
122.284
122.054
119.354
119.216
118.252
113.811
113.730
111.124
77.427
77.110
76.792
55.323
30.795
200
150
100
50
0
ppm (f1)


OMe
N
H


O
N
H


7.888
7.335
7.335
7.279
7.259
7.201
7.180
7.162
7.137
7.134
7.124
7.117
7.099
7.080
6.994
6.983
6.966
6.948
6.929
6.908
6.904
6.888
6.872
6.868
5.515
1.00
1.15
1.30
2.29
0.88
1.11
2.06
1.00
8.00
7.50
7.00
6.50
6.00
5.50
ppm (f1)


151.378
136.784
129.512
127.732
125.861
124.508
122.137
122.053
122.169
120.413
119.710
119.057
116.362
111.269
77.425
77.107
76.790
35.574
200
150
100
50
0
ppm (f1)

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