

Electronic Supporting Information

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

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General remarks:

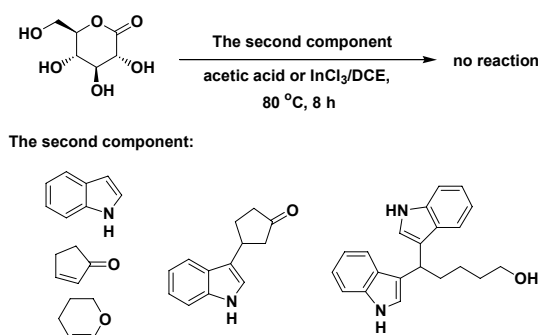
Indole, *N*-methylindole, 2-methylindole, 4-chloroindole, 5-methoxyindole, 2-methyl-5-methoxyindole, 5-bromoindole, 6-fluoroindole, 6-methylindole, β -nitro-3,4-dimethoxystyrene, cyclopent-2-enone, 1-phenyl-2-buten-1-one, 2-furfurylideneacetone, 2-thienylidenacetone, 3, 4-dihydro-2*H*-pyran, D-gluconic acid solution (50%), ($\pm$)-1-(4-methoxyphenyl)-1-ethanol, veratryl alcohol, 9-hydroxyxanthene, ($\pm$)-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, FeCl₃ (anhydrous), SnCl₄, ZnCl₂, H₃BO₃, CuCl₂, NiCl₂, 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 ¹³C NMR spectra were recorded on a Bruker AV-400. Chemical shifts are expressed in ppm relative to Me₄Si in CDCl₃. 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 °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 $\times$ 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 °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-2H-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 °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 °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.



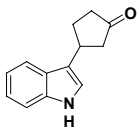
Scheme S1. Reactivity of gluconic acid lactone toward **1a**, **2a**, **3a**, **4a** and **5a**.

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

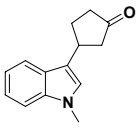
Solvent data	before reaction	after application
pH	1.52	2.22
Conductivity (ms/cm)	0.92	0.91

Spectroscopic data of known compounds

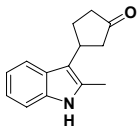
3-(1*H*-indol-3-yl)cyclopentanone (3a)¹

 Yellow oil, ¹H NMR (CDCl₃): 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); ¹³C NMR (CDCl₃): 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

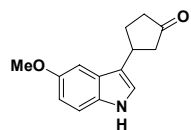
 Red solid, mp: 59-60°C, ¹H NMR (CDCl₃): 2.03-2.12 (m, 1H), 2.26 (quint, *J* = 9.2 Hz, 1H), 2.32-2.43 (m, 2H), 2.43-2.51 (m, 1H), 2.69 (dd, *J*_a = 8.0 Hz, *J*_b = 18.4 Hz, 1H), 3.65 (quint, *J* = 7.2 Hz, 1H), 3.69 (s, 3H), 6.79 (s, 1H), 7.10 (dt, *J*_a = 0.8 Hz, *J*_b = 7.6 Hz, 1H), 7.22 (t, *J* = 7.2 Hz, 1H), 7.27 (d, *J* = 8.0 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 1H); ¹³C NMR (CDCl₃): 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°C, ¹H NMR (CDCl₃): 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); ¹³C NMR (CDCl₃): 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,

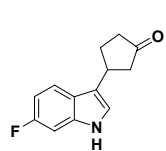
566.

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



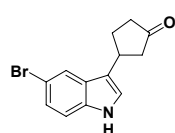
Red oil, ¹H NMR (CDCl₃): 1.86-1.99 (m, 1H), 2.10-2.39 (m, 4H), 2.69 (dd, *J*_a = 7.6 Hz, *J*_b = 18.4 Hz, 1H), 3.50 (quint, *J* = 8.4 Hz, 1H), 3.73 (s, 3H), 6.72-6.79 (m, 2H), 6.93 (d, *J* = 2.0 Hz, 1H), 7.09 (d, *J* = 8.8 Hz, 1H), 8.38 (bs, 1H); ¹³C NMR (CDCl₃): 29.8, 33.7, 38.2, 45.4, 56.1, 101.2, 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



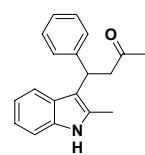
Red oil, ¹H NMR (CDCl₃): 1.98-2.11 (m, 1H), 2.23-2.42 (m, 3H), 2.42-2.53 (m, 1H), 2.71 (dd, *J*_a = 8.0 Hz, *J*_b = 18.4 Hz, 1H), 3.63 (quint, *J* = 7.2 Hz, 1H), 6.86 (dd, *J*_a = 2.0 Hz, *J*_b = 8.8 Hz, 1H), 6.89-6.94 (m, 1H), 7.01 (dd, *J*_a = 2.0 Hz, *J*_b = 9.6 Hz, 1H), 7.48 (dd, *J*_a = 5.2 Hz, *J*_b = 8.4 Hz, 1H), 8.61 (bs, 1H); ¹³C NMR (CDCl₃): 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, ¹H NMR (CDCl₃): 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); ¹³C NMR (CDCl₃): 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.

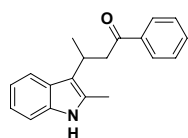
4-(2-Methyl-1*H*-indol-3-yl)-4-phenyl-2-butanone (3j)⁷



Red solid, mp: 97-99°C, ¹H NMR (CDCl₃): 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); ¹³C NMR (CDCl₃): 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,

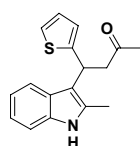
131.9, 135.5, 144.1, 208.1.

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



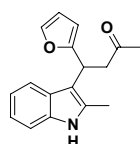
Red oil, ¹H NMR (CDCl₃): 1.48 (d, J = 8.0 Hz, 3H), 2.30 (s, 3H), 3.35 (dd, J_a = 7.6 Hz, J_b = 16.4 Hz, 1H), 3.50 (dd, J_a = 6.4 Hz, J_b = 16.0 Hz, 1H), 3.73 (sext, J = 7.2 Hz, 1H), 7.05 (td, J_a = 3.6 Hz, J_b = 10.0 Hz, 2H), 7.14-7.20 (m, 1H), 7.33 (t, J = 8.0 Hz, 2H), 7.45 (t, J = 7.2 Hz, 1H), 7.66 (q, J = 3.2 Hz, 1H), 7.84 (d, J = 7.2 Hz, 2H), 7.93 (bs, 1H); ¹³C NMR (CDCl₃): 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)



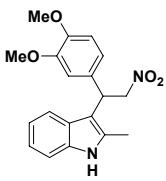
Red oil, ¹H NMR (CDCl₃): 1.98 (s, 3H), 2.03 (d, J = 2.8 Hz, 2H), 2.34 (s, 3H), 3.33 (dd, J_a = 7.6 Hz, J_b = 16.8 Hz, 1H); 3.42 (q, J = 8.0 Hz, 1H); 5.01 (t, J = 7.6 Hz, 1H), 6.74-6.79 (m, 1H), 6.83 (dd, J_a = 3.6 Hz, J_b = 4.8 Hz, 1H), 6.99 (dt, J_a = 1.2 Hz, J_b = 8.0 Hz, 1H), 7.03-7.09 (m, 2H), 7.17 (t, J = 7.6 Hz, 1H), 7.42 (d, J = 8.0 Hz, 1H), 7.88 (bs, 1H); ¹³C NMR (CDCl₃): 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 C₁₇H₁₇NNaOS [M + Na]⁺ 306.0929 found 306.0925.

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



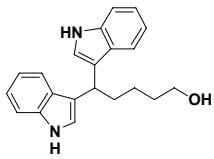
Red oil, ¹H NMR (CDCl₃): 2.01 (s, 3H), 2.35 (s, 3H), 3.22 (q, J = 8.0 Hz, 1H), 3.34 (dd, J_a = 6.0 Hz, J_b = 15.6 Hz, 1H), 4.83 (t, J = 7.2 Hz, 1H), 5.94 (d, J = 3.2 Hz, 1H), 6.22 (q, J = 1.6 Hz, 1H), 6.99 (dt, J_a = 0.8 Hz, J_b = 8.0 Hz, 1H), 7.06 (dt, J_a = 0.8 Hz, J_b = 8.0 Hz, 1H), 7.18 (d, J = 8.0 Hz, 1H), 7.27 (s, 1H), 7.43 (d, J = 7.6 Hz, 1H), 7.92 (bs, 1H); ¹³C NMR (CDCl₃): 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 C₁₇H₁₇NNaO₂ [M + Na]⁺ 290.1157 found 290.1146.

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

 Red solid, mp: 154-156°C, ¹H NMR (CDCl₃): 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); ¹³C NMR (CDCl₃): 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.

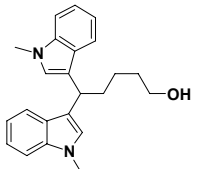
5,5-di(1H-indol-3-yl)pentanol (5a)¹⁰

Red oil, ¹H NMR (CDCl₃): 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); ¹³C NMR (CDCl₃): 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.



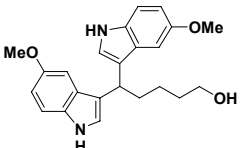
5,5-bis(1-methyl-1H-indol-3-yl)pentanol (5b)¹¹

Red oil, ¹H NMR (CDCl₃): 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); ¹³C NMR (CDCl₃): 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.



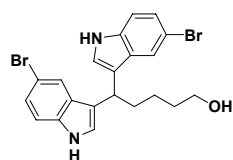
5,5-bis(5-methoxy-1H-indol-3-yl)pentanol (5c)¹²

Red oil, ¹H NMR (CDCl₃): 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); ¹³C NMR (CDCl₃): 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,



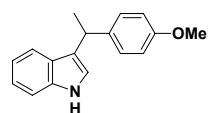
127.5, 132.1, 153.4.

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



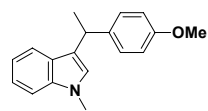
Red oil, ¹H NMR (CDCl₃): 1.27-1.37 (m, 2H), 1.52 (quint, *J* = 6.8 Hz, 2H), 1.91 (bs, 1H), 2.07 (q, *J* = 8.0 Hz, 2H), 3.51 (t, *J* = 6.8 Hz, 2H), 4.22 (t, *J* = 7.6 Hz, 1H), 6.83 (d, *J* = 2.4 Hz, 2H), 7.05 (d, *J* = 8.8 Hz, 2H), 7.16 (dd, *J*_{*a*} = 2.0 Hz, *J*_{*b*} = 8.8 Hz, 2H), 7.61 (d, *J* = 1.6 Hz, 2H), 8.11 (bs, 1H); ¹³C NMR (CDCl₃): 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



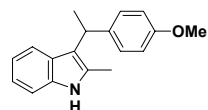
White solid, mp: 156-157°C, ¹H NMR (acetone-*d*₆): 1.64 (d, *J* = 7.2 Hz, 3H), 3.70 (s, 3H), 4.31 (q, *J* = 7.2 Hz, 1H), 6.78 (d, *J* = 8.8 Hz, 2H), 6.88 (dt, *J*_{*a*} = 0.8 Hz, *J*_{*b*} = 8.0 Hz, 1H), 7.03 (dt, *J*_{*a*} = 0.8 Hz, *J*_{*b*} = 8.0 Hz, 1H), 7.19 (t, *J* = 8.8 Hz, 3H), 7.33 (q, *J* = 8.8 Hz, 2H), 9.96 (bs, 1H); ¹³C 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



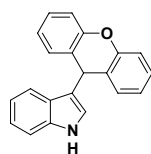
Red oil, ¹H NMR (acetone-*d*₆): 1.62 (d, *J* = 6.8 Hz, 3H), 3.69 (s, 3H), 3.73 (s, 3H), 4.29 (q, *J* = 6.8 Hz, 1H), 6.78 (d, *J* = 8.4 Hz, 2H), 6.89 (t, *J* = 8.0 Hz, 1H), 7.02 (s, 1H), 7.09 (dt, *J*_{*a*} = 0.8 Hz, *J*_{*b*} = 6.8 Hz, 1H), 7.19 (d, *J* = 8.8 Hz, 2H), 7.29 (t, *J* = 9.2 Hz, 2H); ¹³C 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



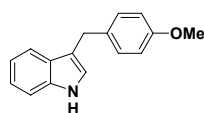
Red oil, ¹H NMR (acetone-*d*₆): 1.62 (d, *J* = 7.2 Hz, 3H), 2.34 (s, 3H), 3.68 (s, 3H), 4.27 (q, *J* = 7.2 Hz, 1H), 6.72 (dd, *J*_{*a*} = 0.4 Hz, *J*_{*b*} = 8.0 Hz, 1H), 6.77 (td, *J*_{*a*} = 3.2 Hz, *J*_{*b*} = 9.6 Hz, 2H), 7.06 (d, *J* = 1.6 Hz, 1H), 7.14 (s, 1H), 7.15-7.21 (m, 3H), 9.76 (bs, 1H); ¹³C 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



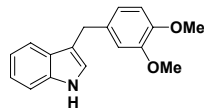
Black solid, mp: 134-135°C, ¹H NMR (CDCl₃): 5.52 (s, 1H), 6.89 (dt, *J*_a = 0.8 Hz, *J*_b = 8.0 Hz, 2H), 6.95 (t, *J* = 7.2 Hz, 1H), 6.99 (d, *J* = 2.4 Hz, 1H), 7.06-7.19 (m, 7H), 7.27 (d, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.89 (bs, 1H); ¹³C NMR (CDCl₃): 35.6, 111.3, 116.4, 119.7, 119.7, 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



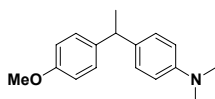
Yellow solid, mp: 72-75°C, ¹H NMR (CDCl₃): 3.76 (s, 3H), 4.00-4.06 (m, 2H), 6.78-6.88 (m, 3H), 7.03-7.16 (m, 2H), 7.16-7.21 (m, 2H), 7.24-7.34 (m, 1H), 7.49-7.56 (m, 1H), 7.78-8.14 (m, 1H); ¹³C NMR (CDCl₃): 30.8, 55.3, 111.1, 113.8, 113.8, 116.3, 119.2, 119.4, 122.1, 122.3, 129.6, 133.4, 136.5, 157.8.

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



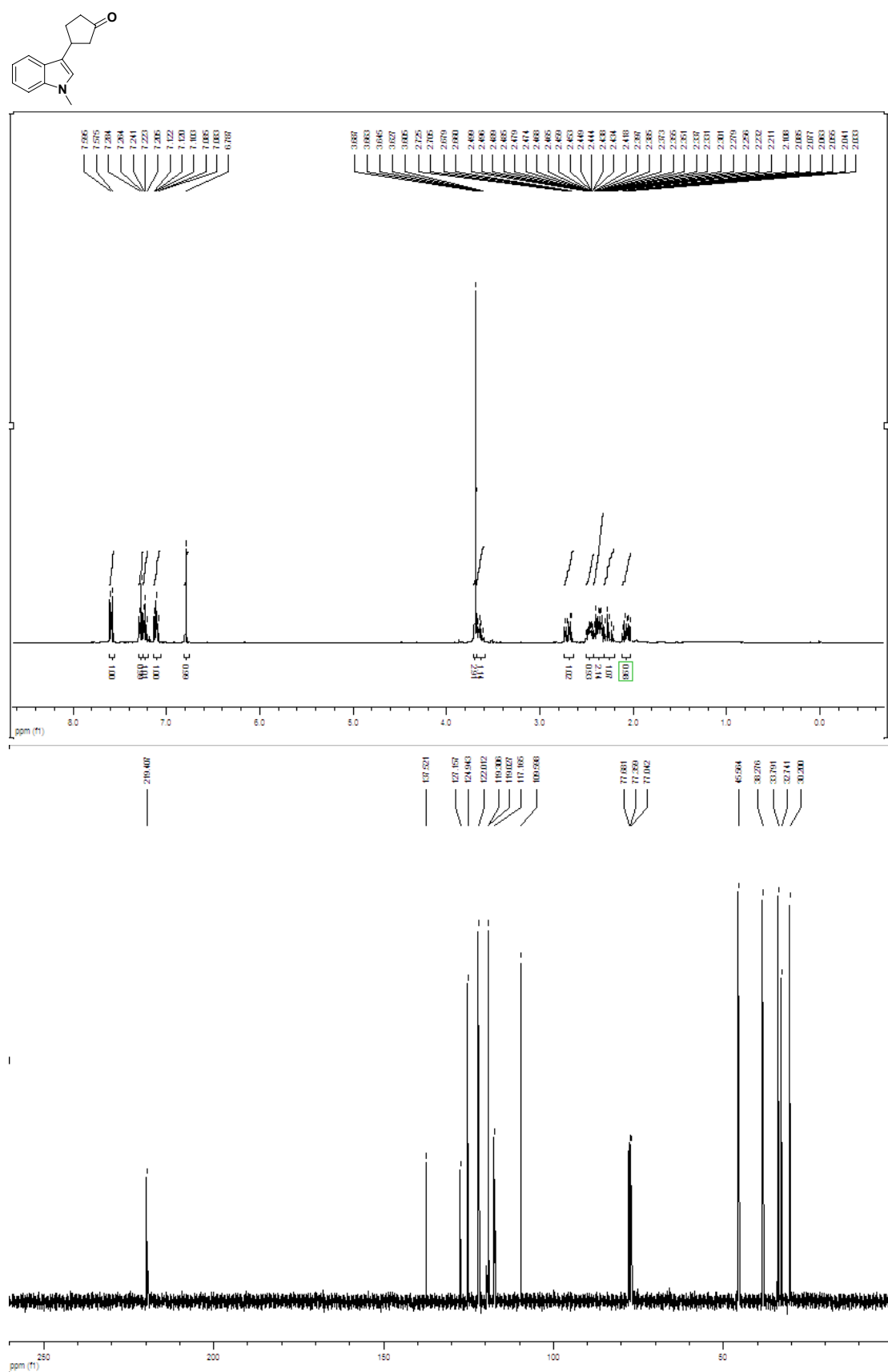
Yellow solid, mp: 121-122 °C, ¹H NMR (CDCl₃): 3.78 (s, 3H), 3.82 (s, 3H), 4.01-4.06 (m, 2H), 6.72-6.88 (m, 4H), 7.03-7.12 (m, 1H), 7.16 (dt, *J*_a = 0.8 Hz, *J*_b = 8.0 Hz, 1H), 7.22-7.32 (m, 1H), 7.46-7.58 (m, 1H), 7.95-8.19 (m, 1H); ¹³C NMR (CDCl₃): 31.3, 55.8, 56.0, 111.2, 112.1, 116.0, 119.2, 119.3, 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

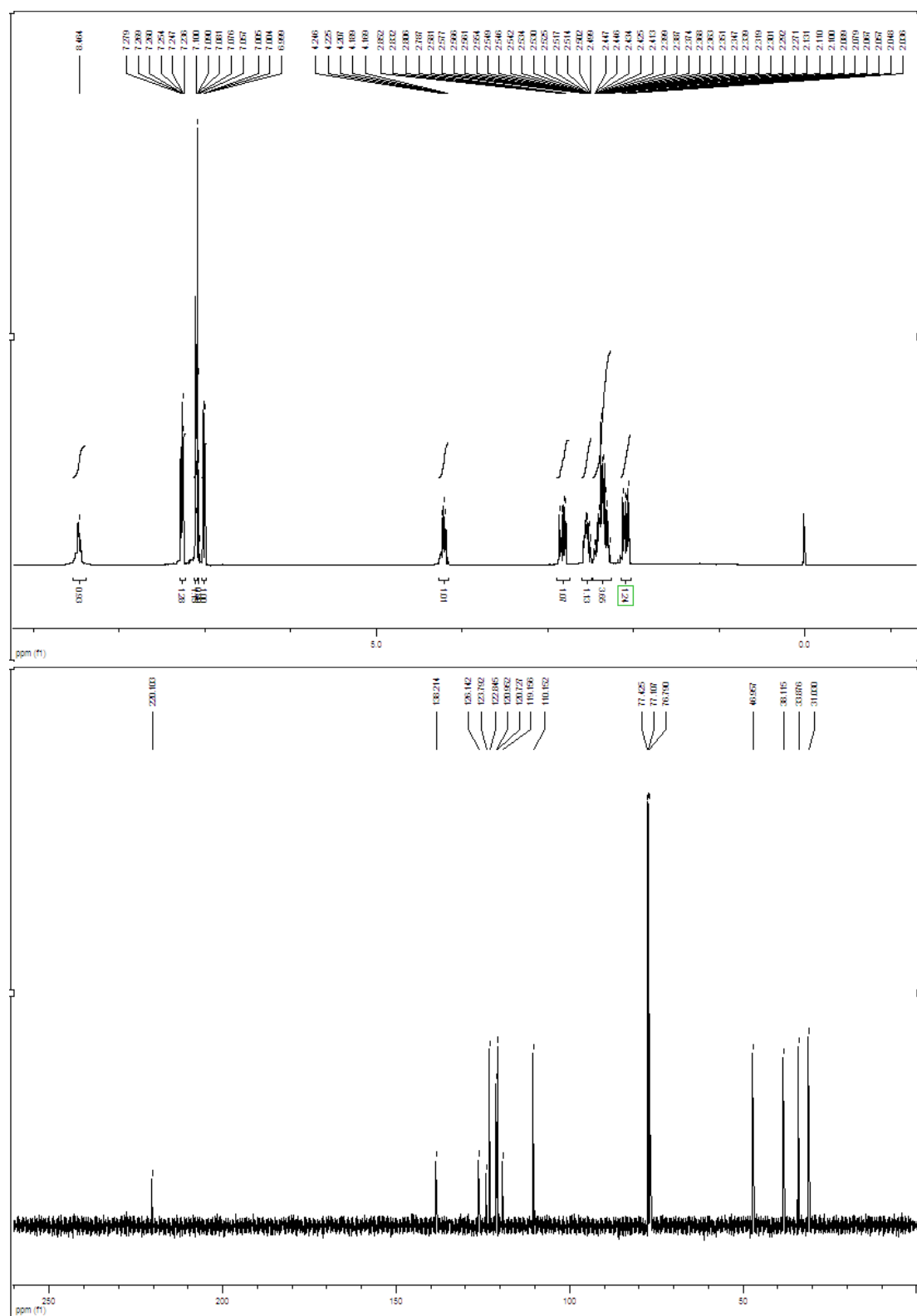
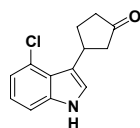


Yellow oil, ¹H NMR (CDCl₃): 1.55 (d, *J* = 7.2 Hz, 3H), 2.84 (s, 6H), 3.69 (s, 3H), 3.99 (q, *J* = 7.2 Hz, 1H), 6.64 (d, *J* = 8.4 Hz, 2H), 6.78 (d, *J* = 8.4 Hz, 2H), 7.05 (d, *J* = 8.4 Hz, 2H), 7.10 (d, *J* = 8.4 Hz, 2H); ¹³C NMR (CDCl₃): 22.5, 41.0, 43.2, 55.3, 113.0, 113.8, 128.3, 128.6, 135.1, 139.6, 149.2, 157.9.



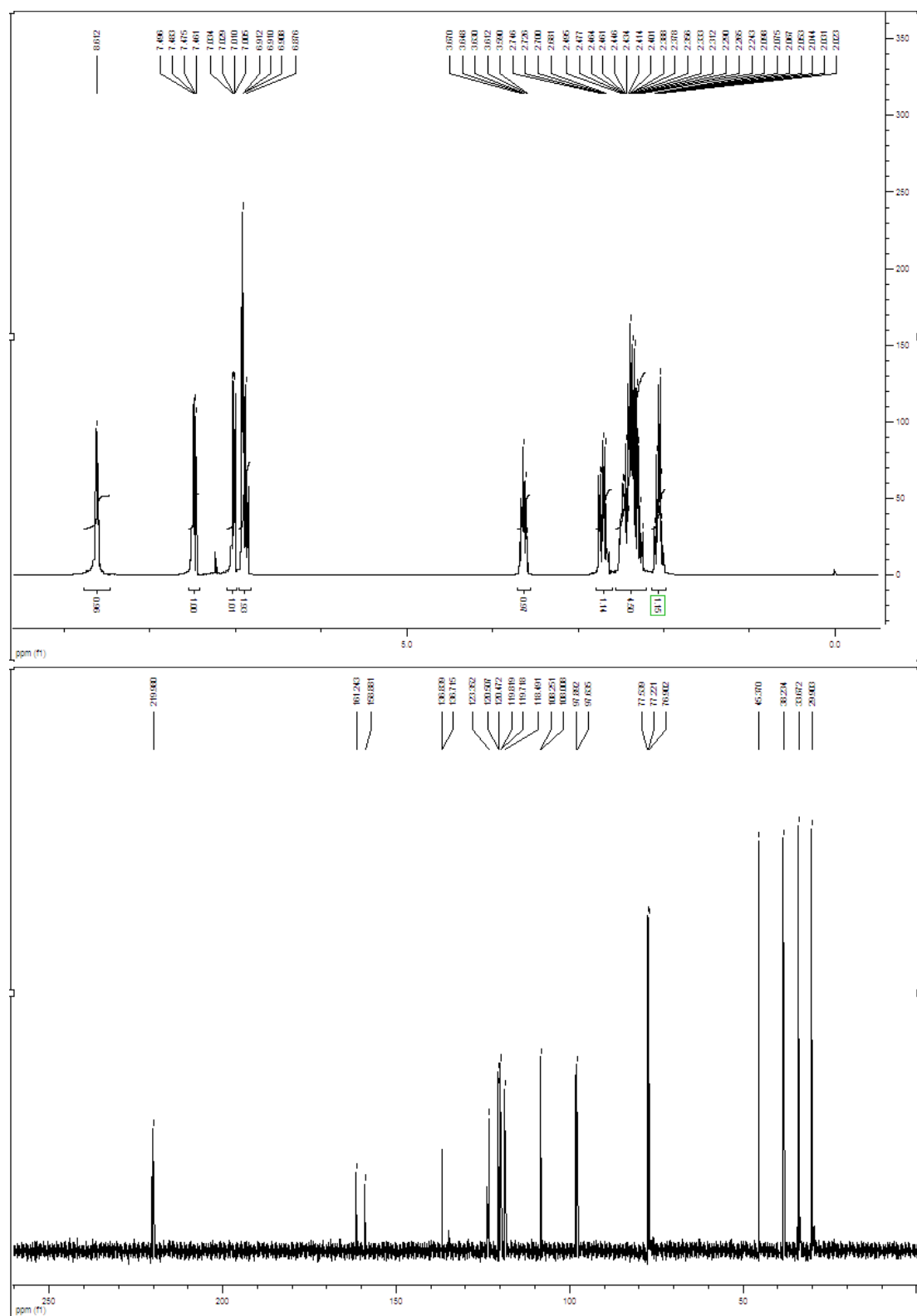
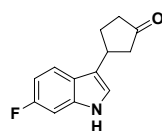


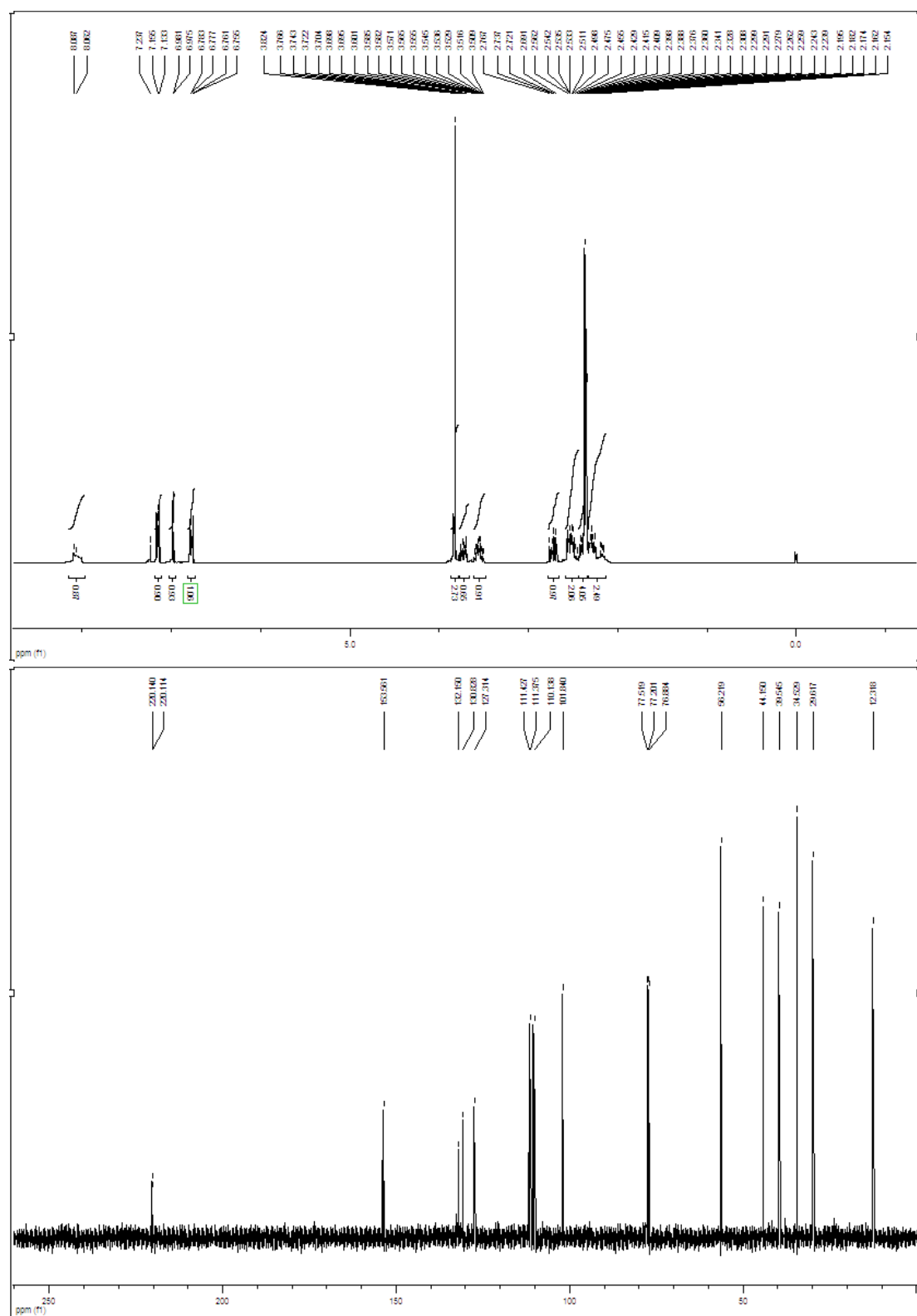
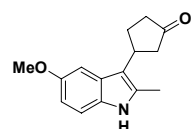




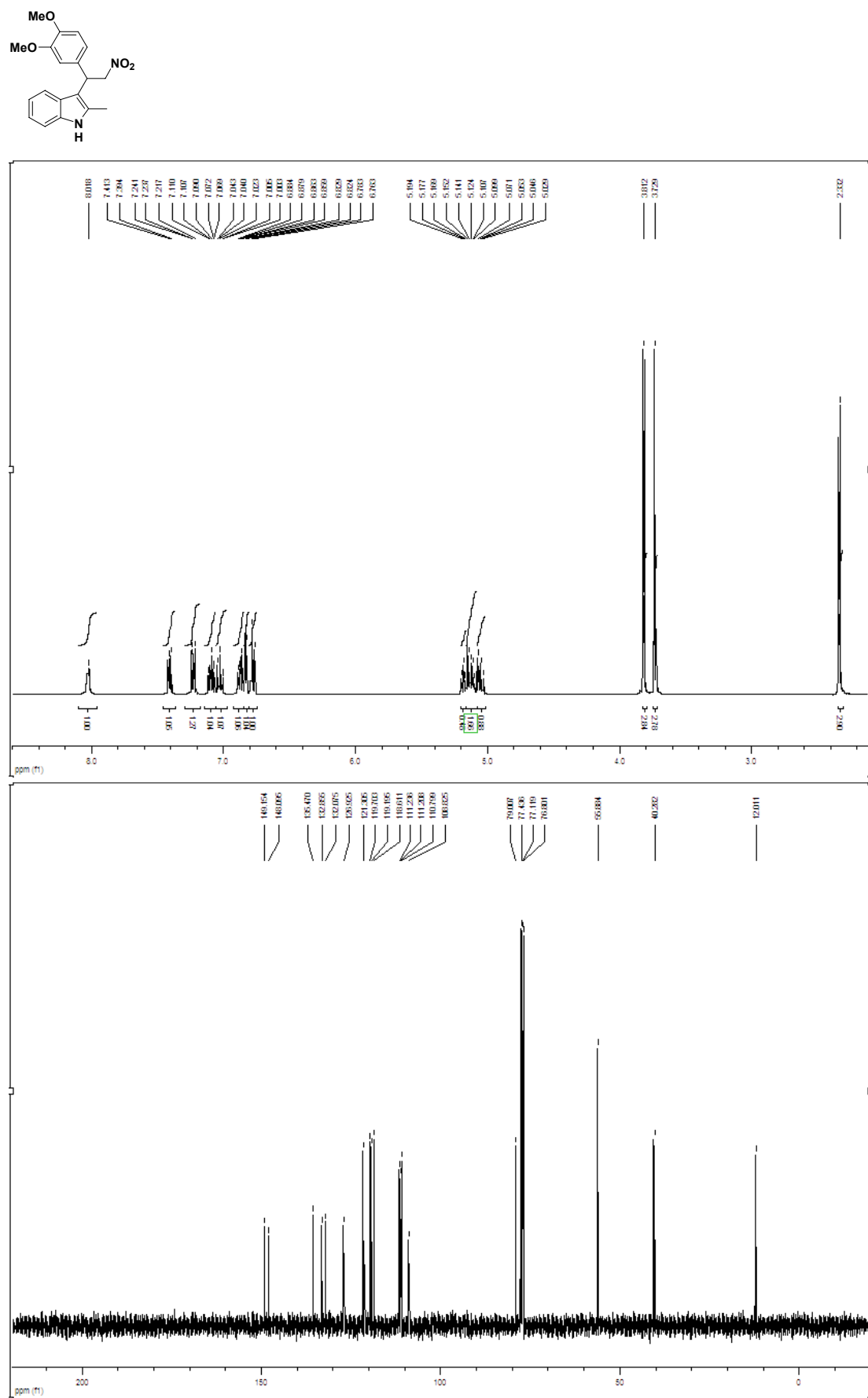


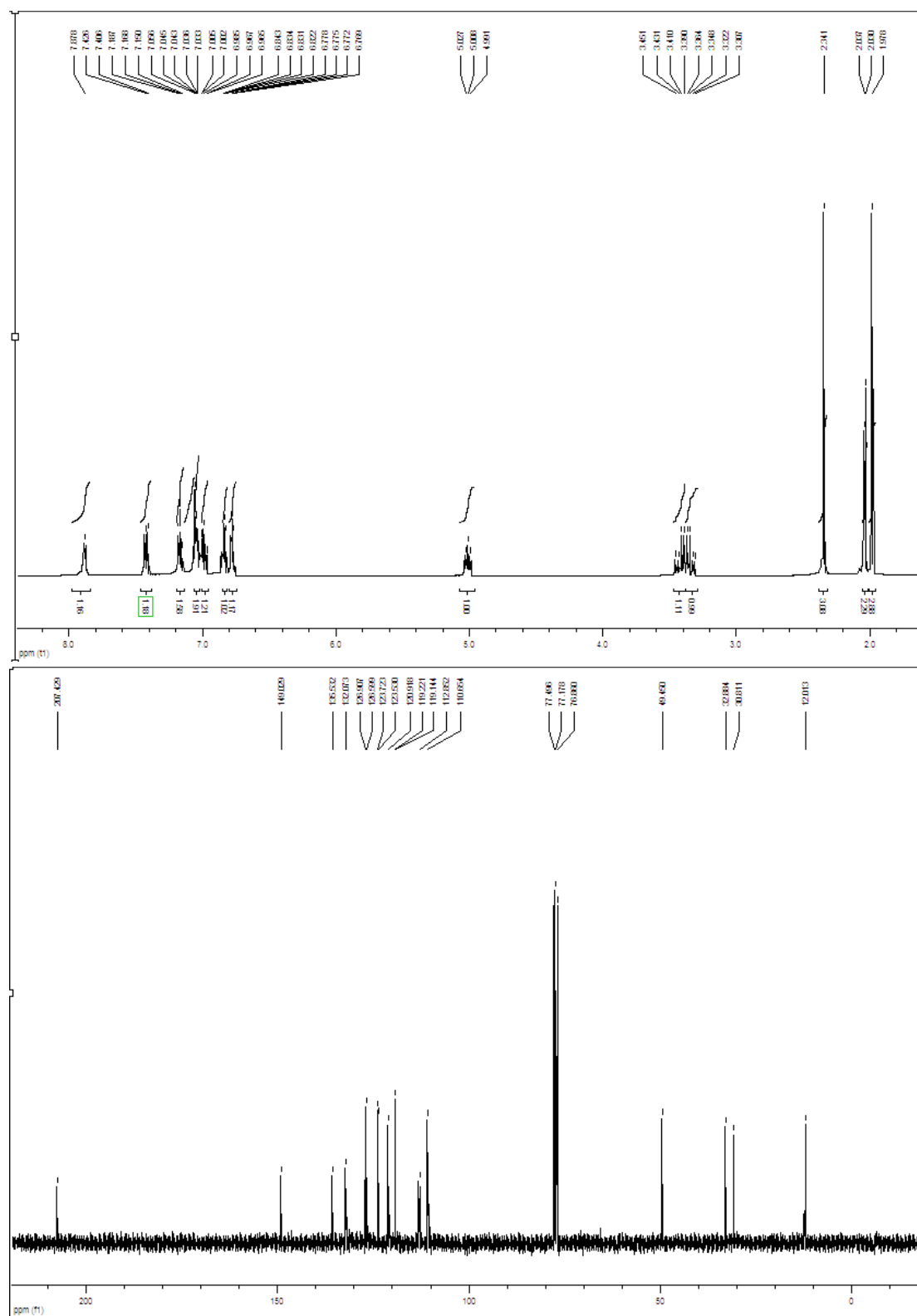
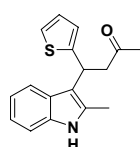


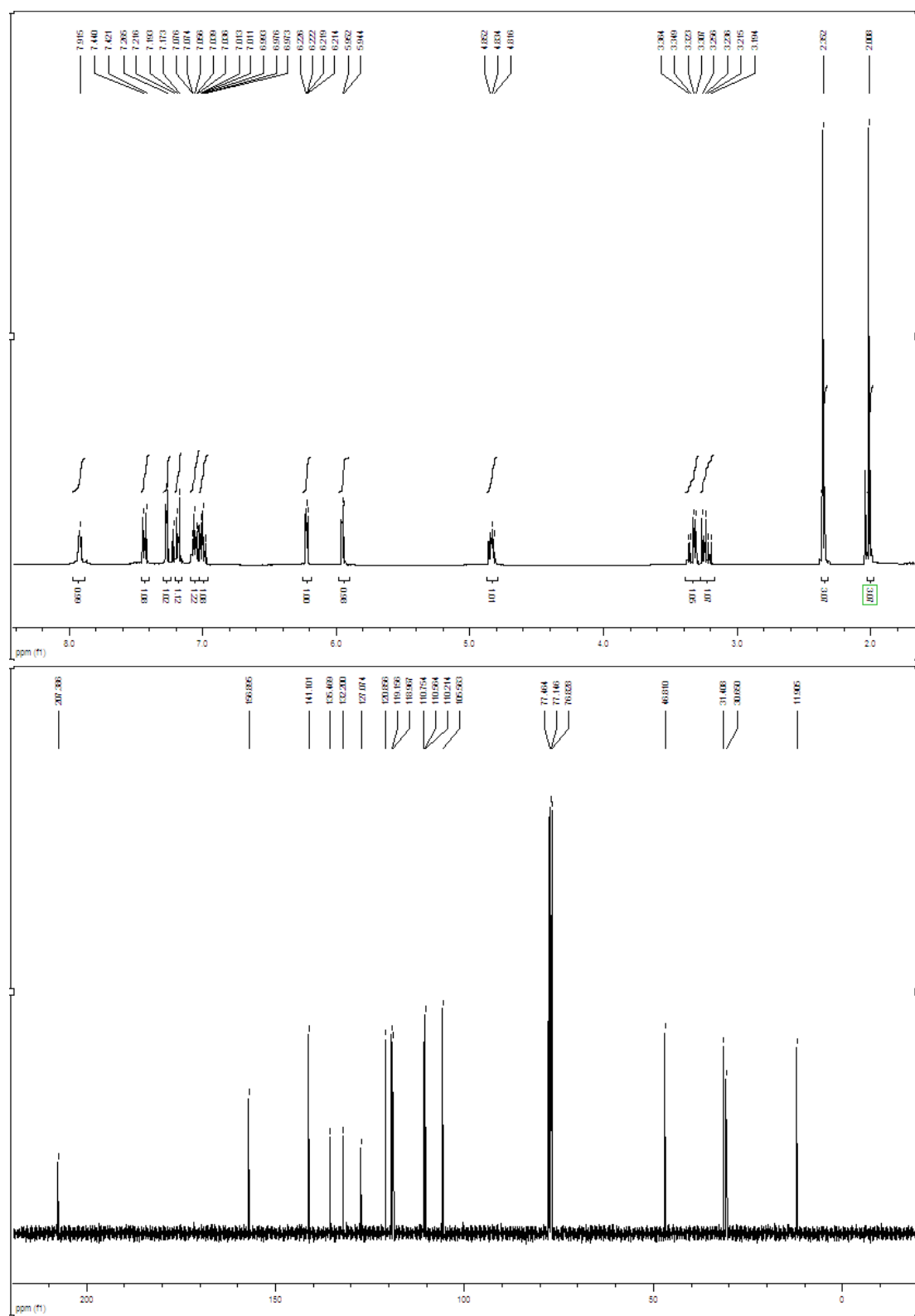
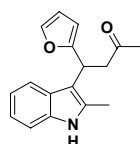


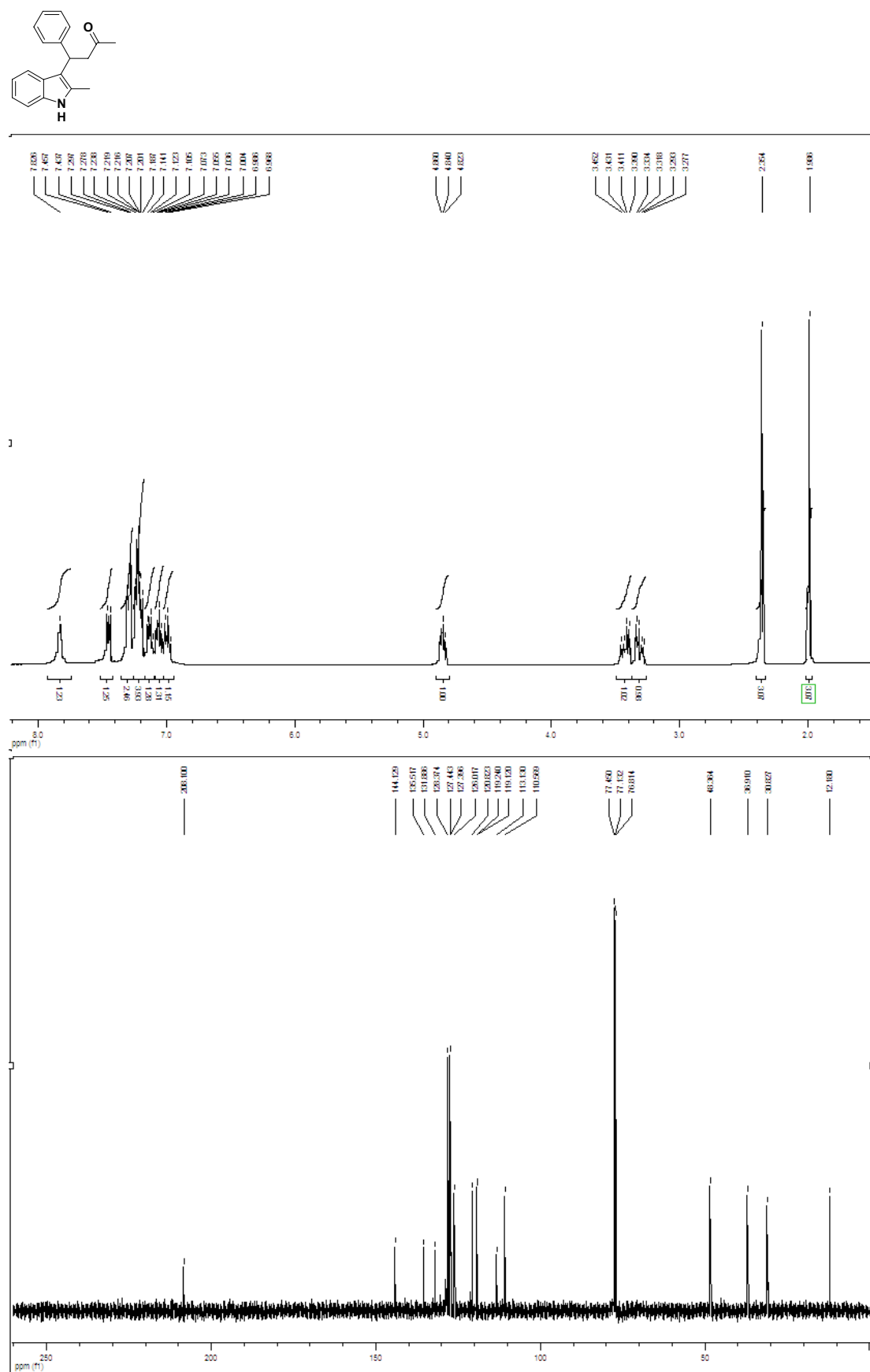


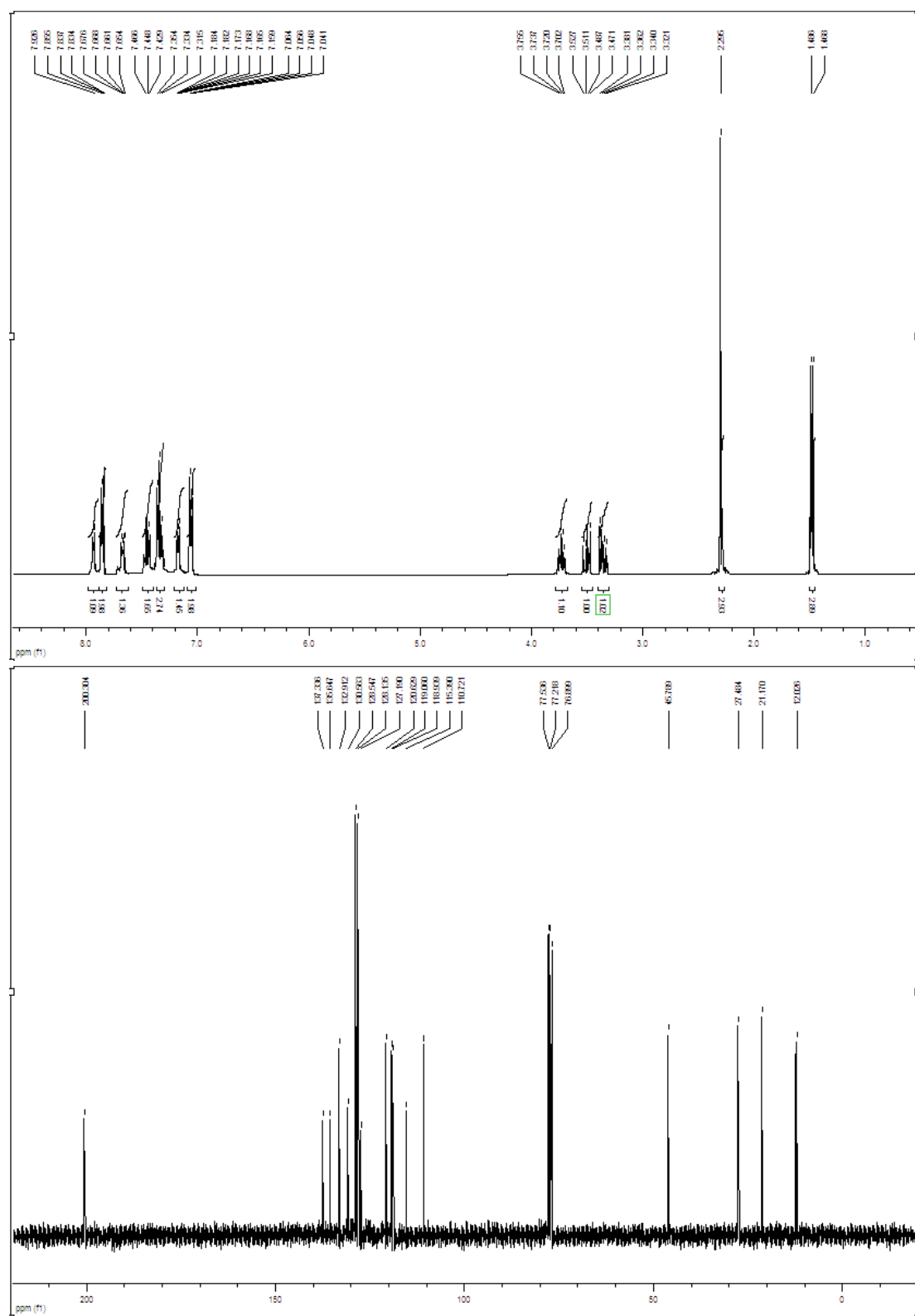
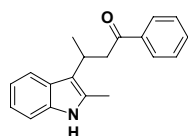


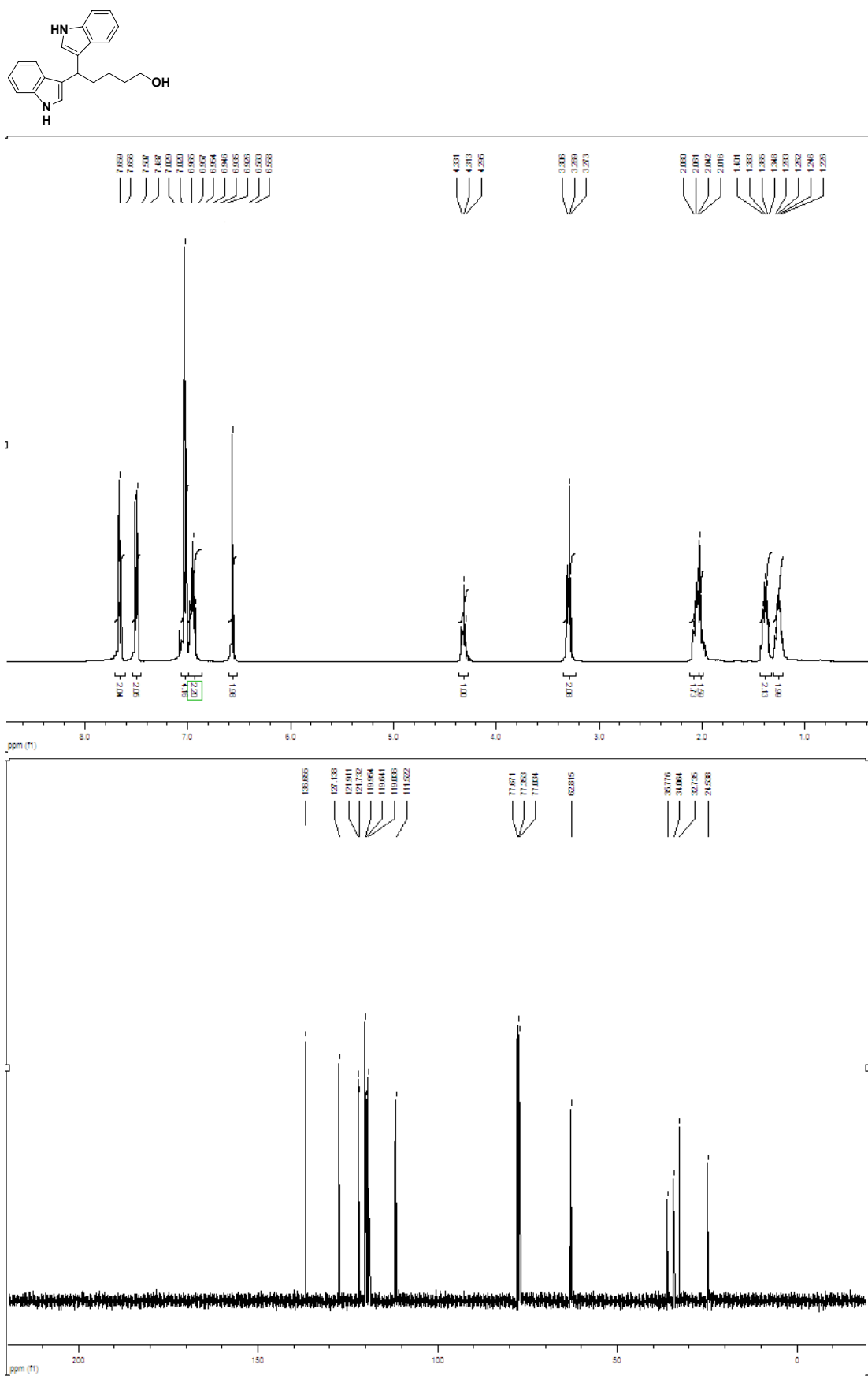


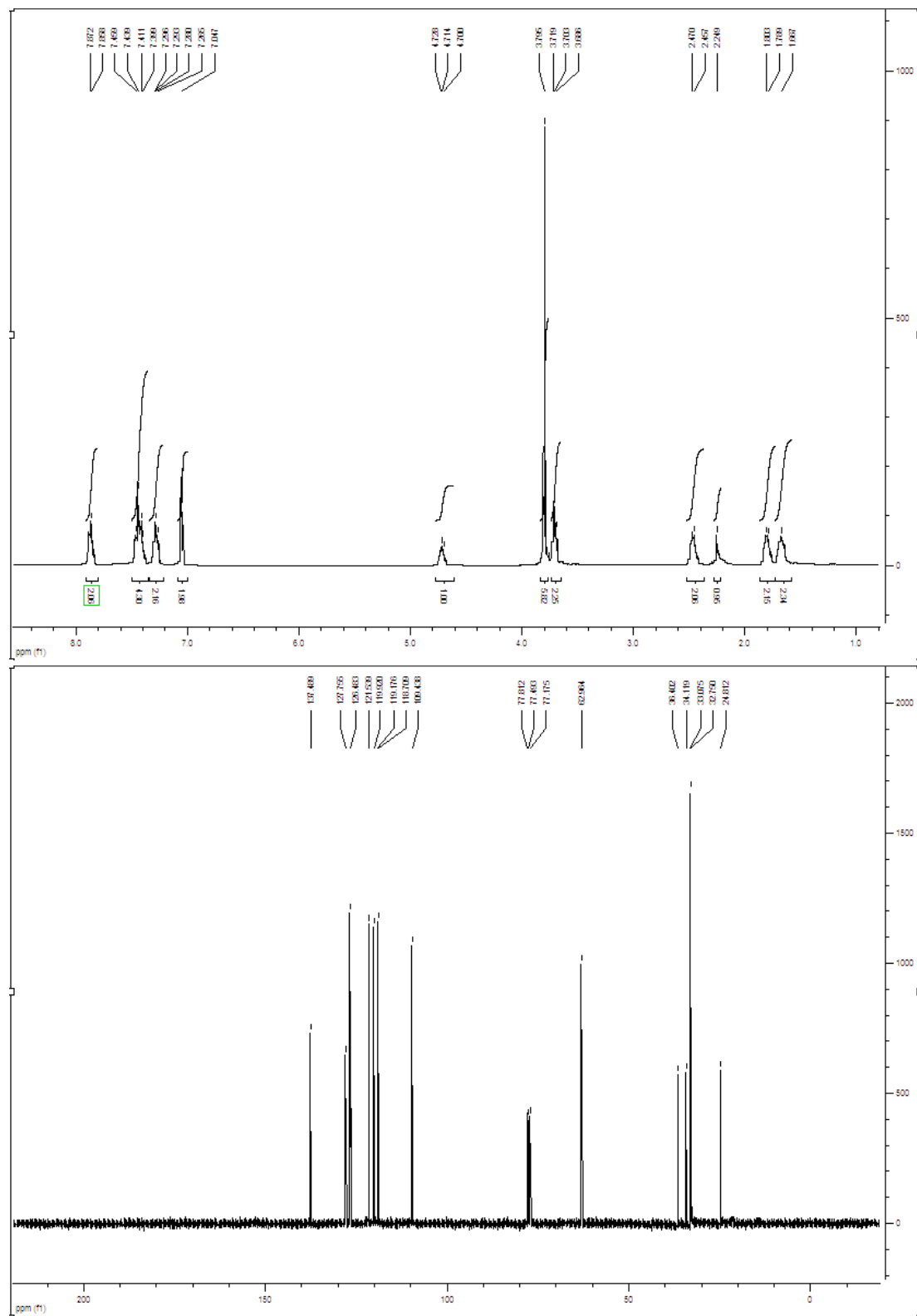
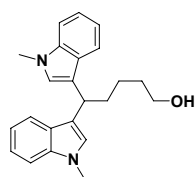


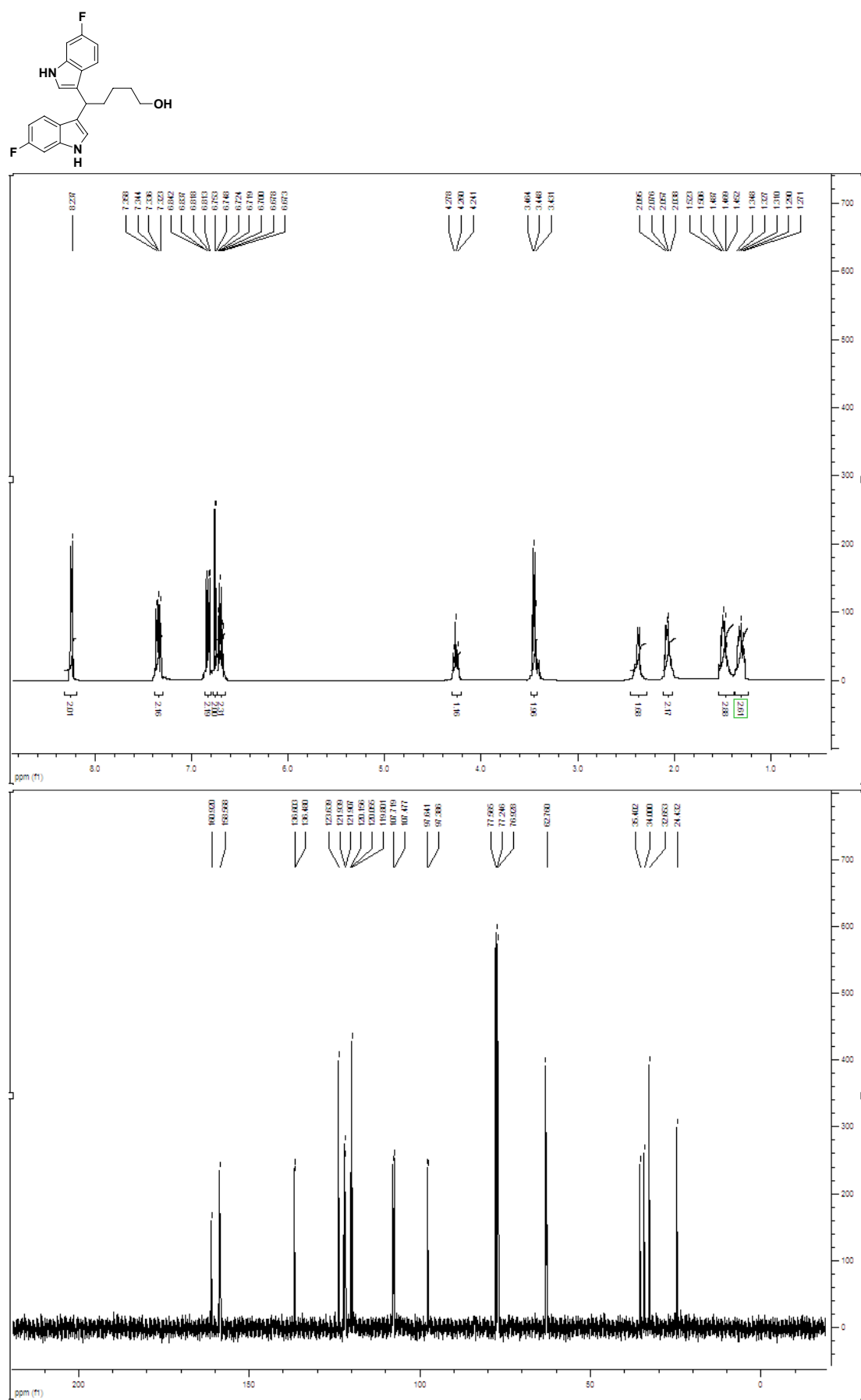


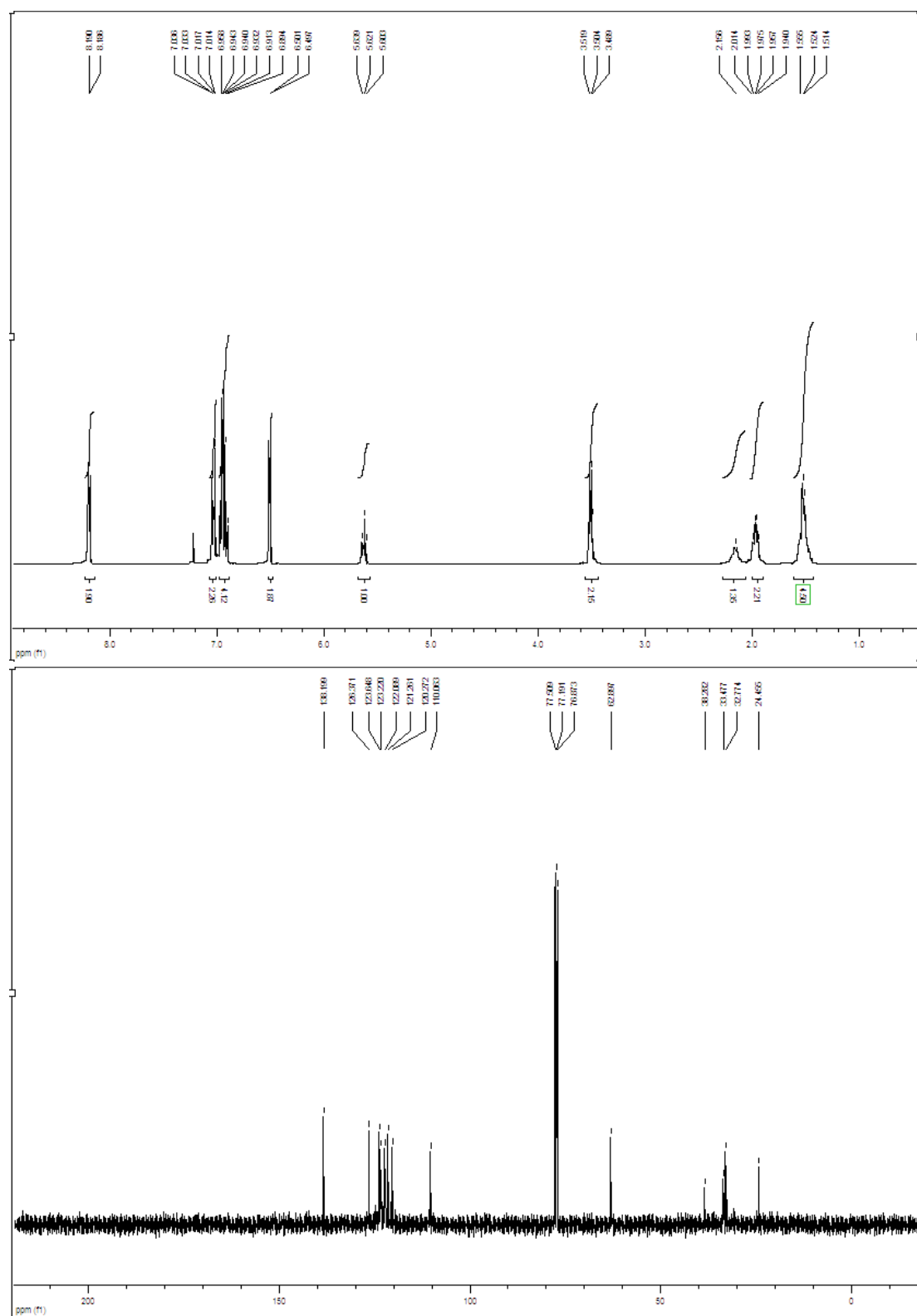
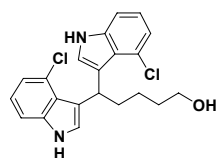


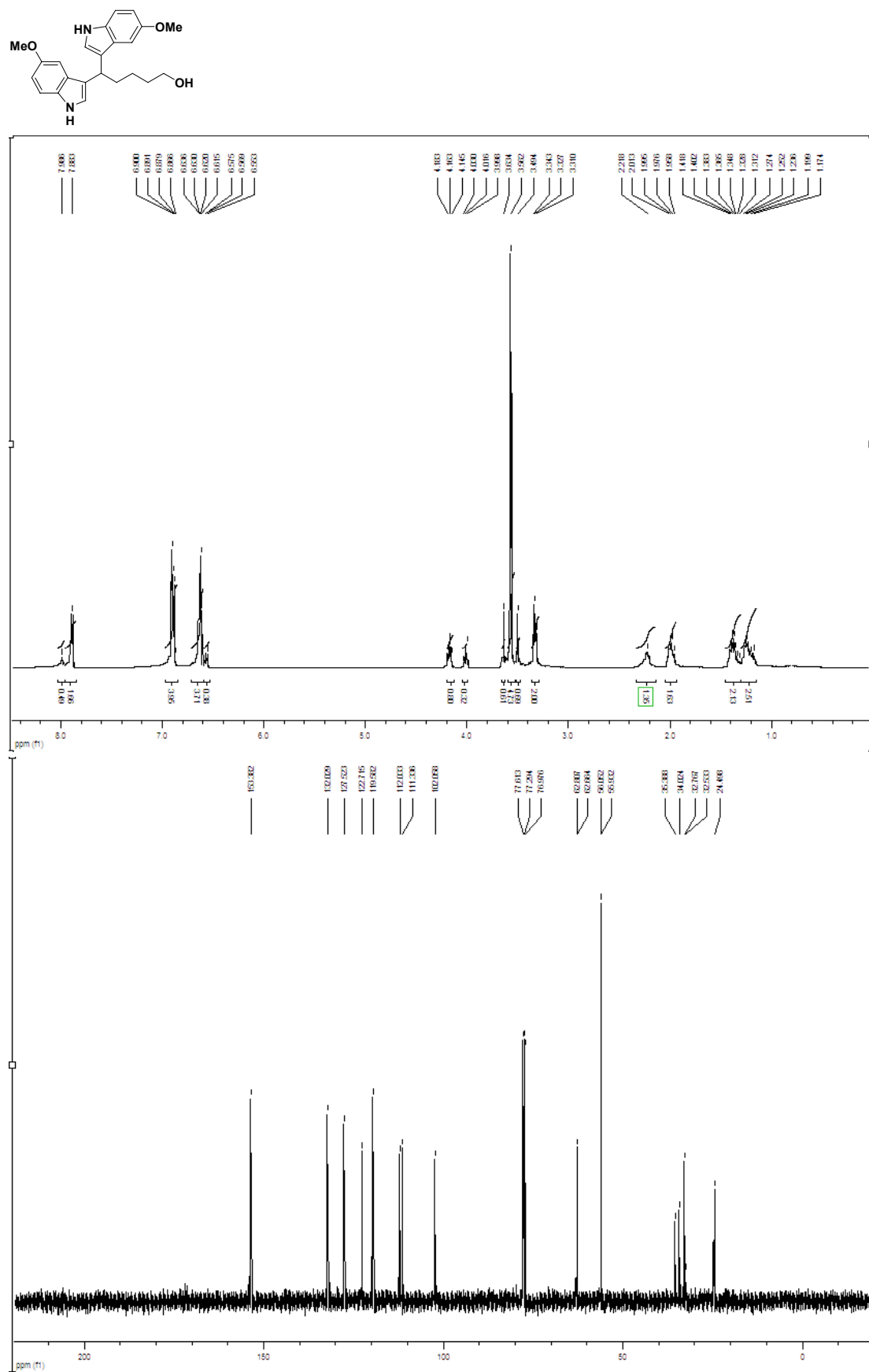




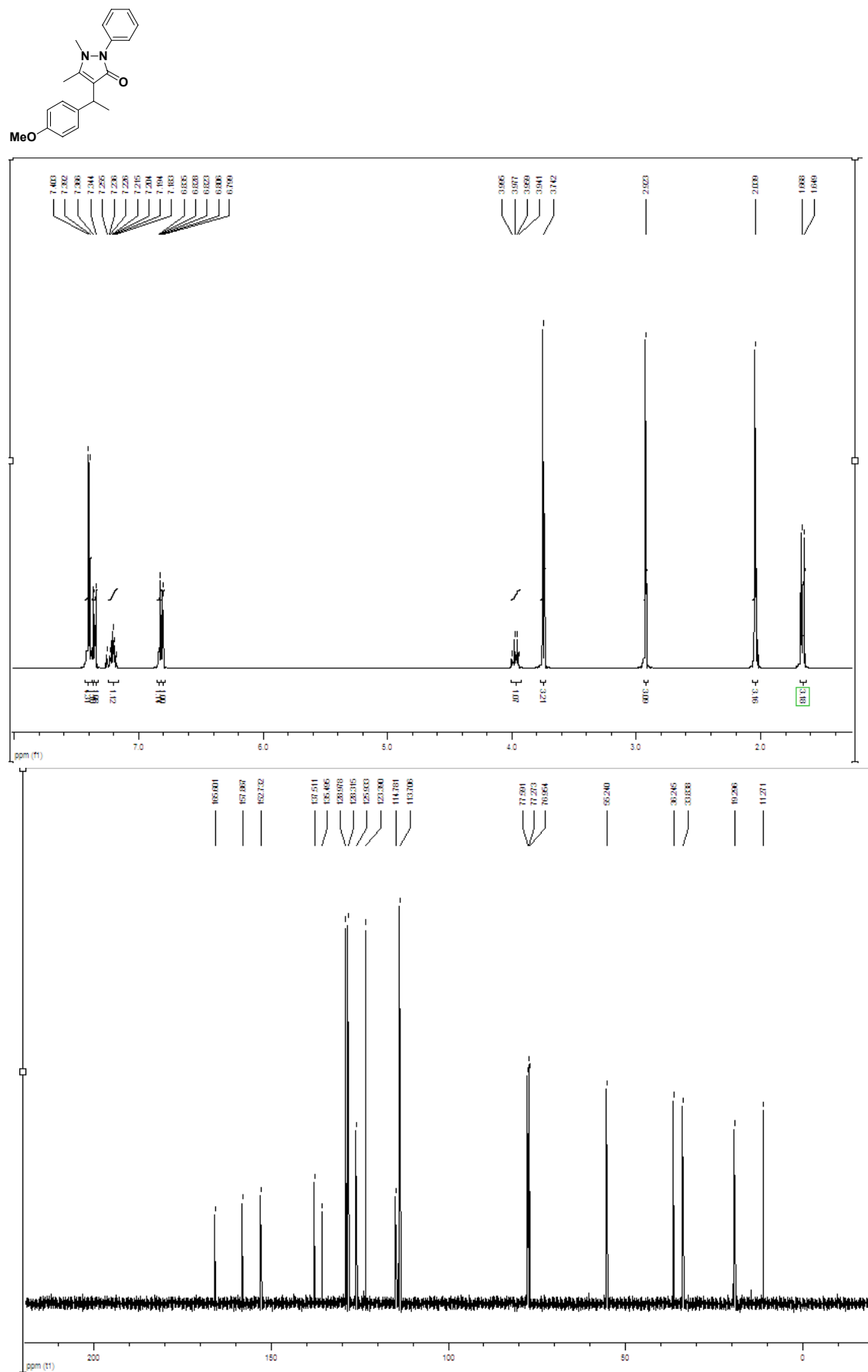


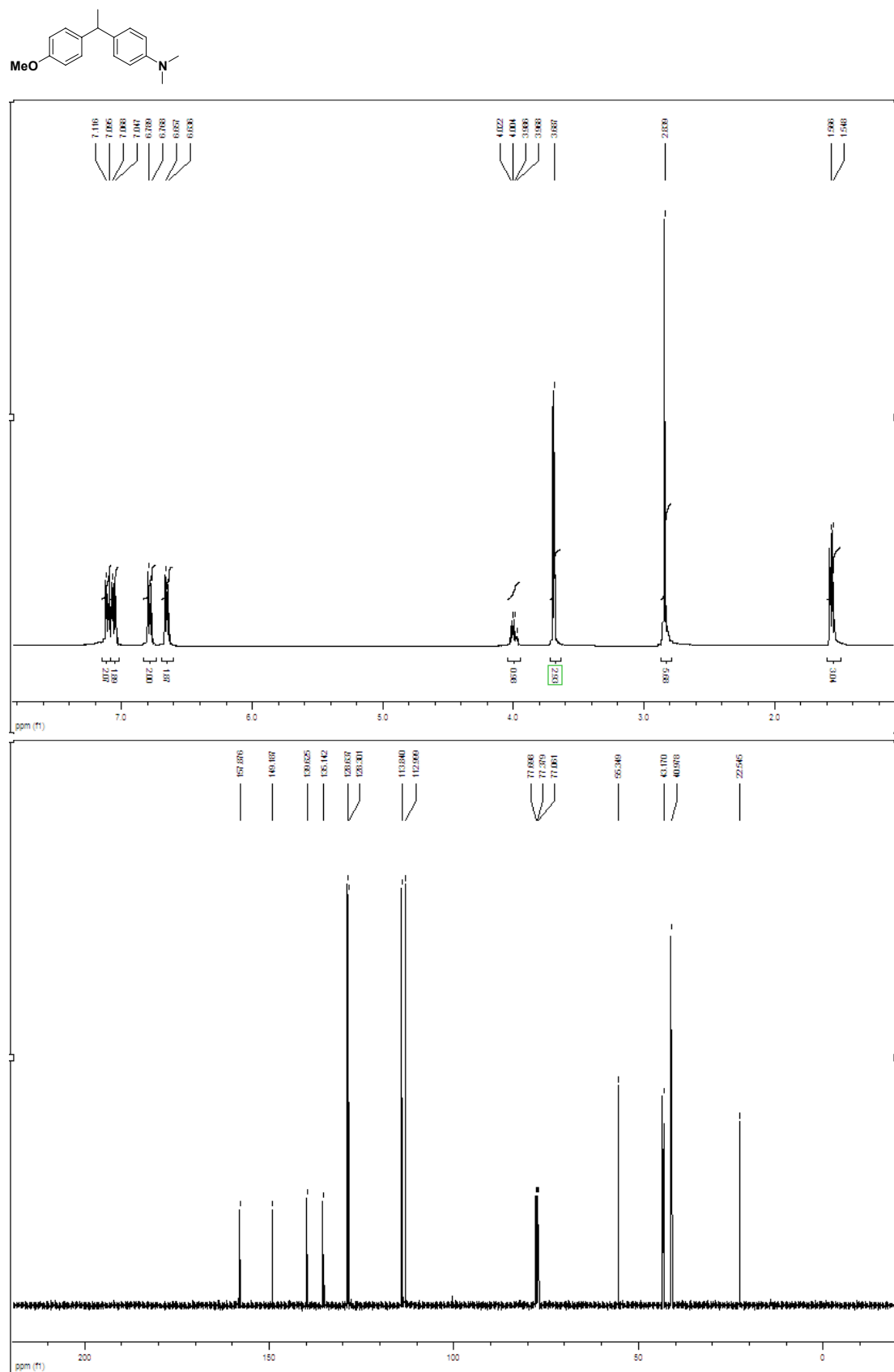


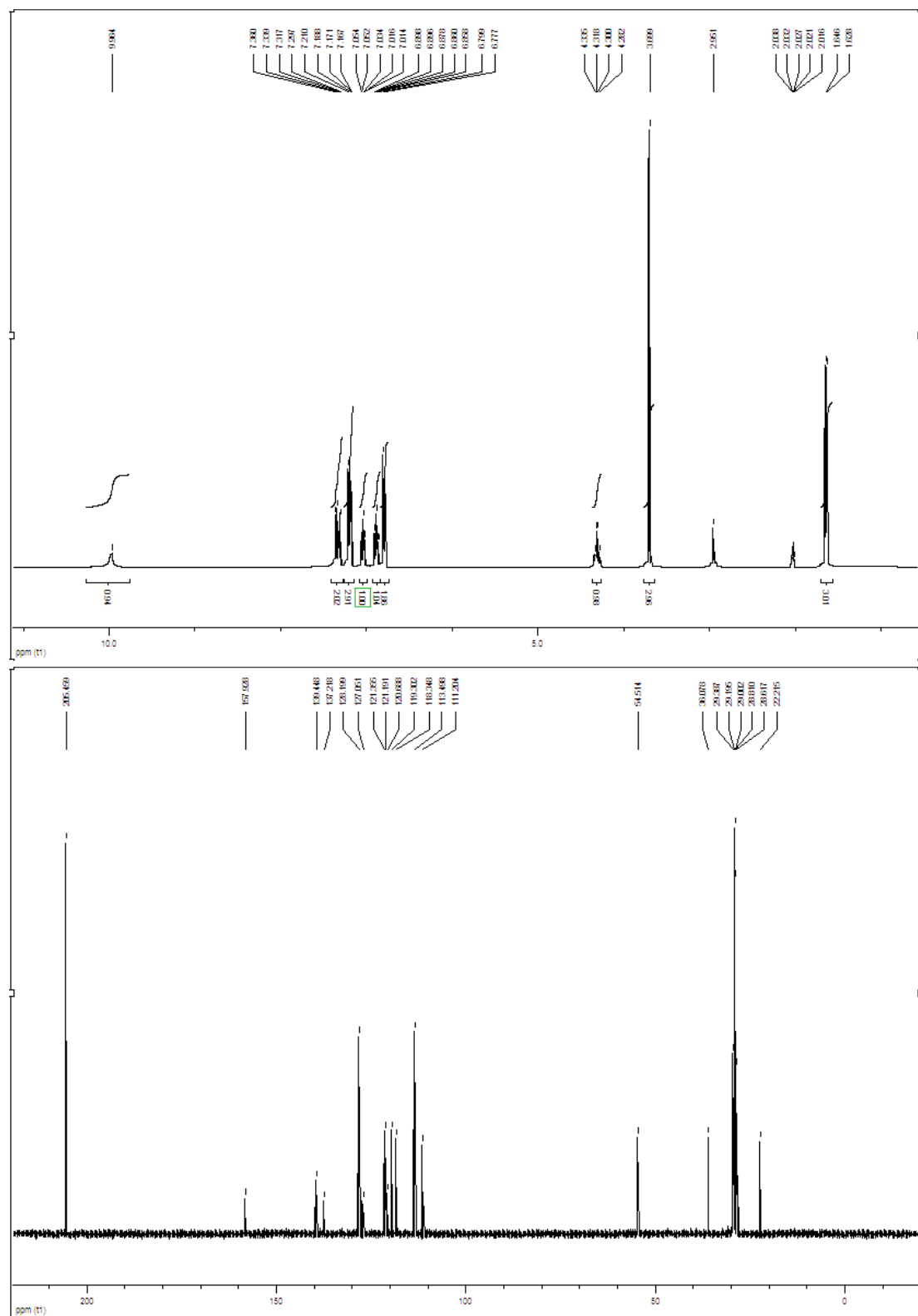
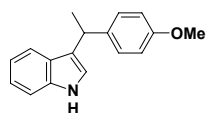




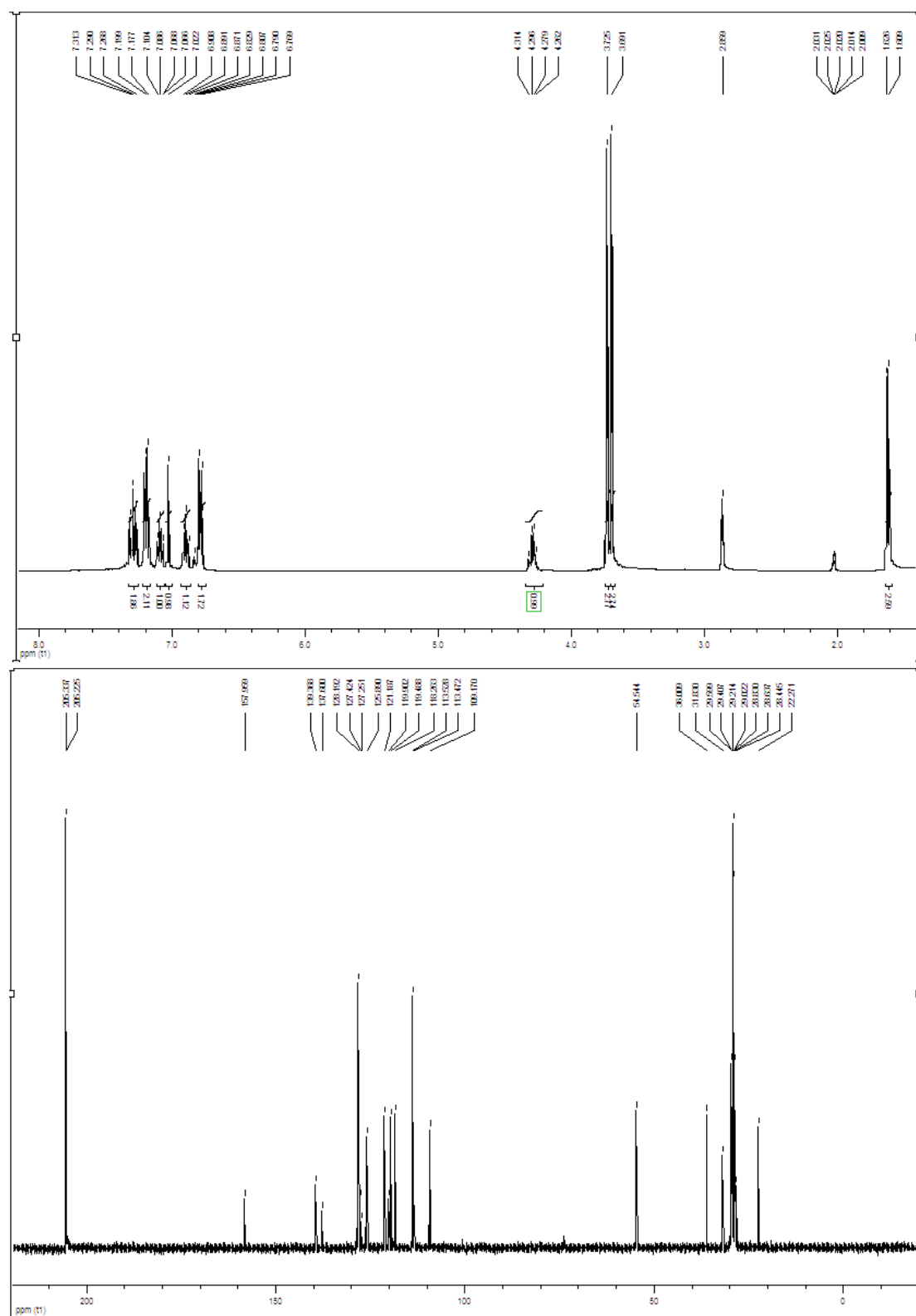
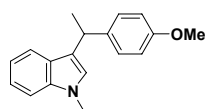


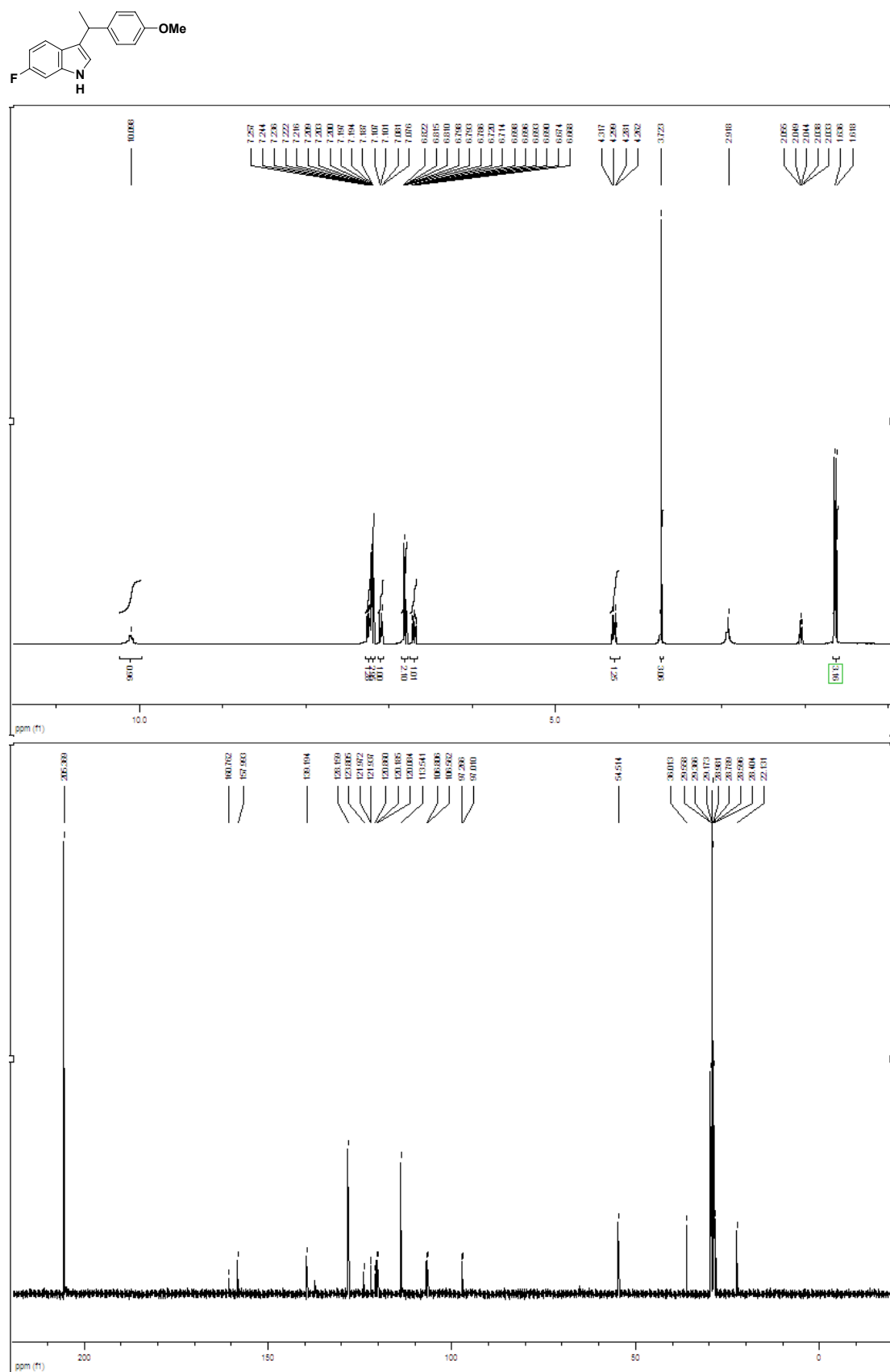


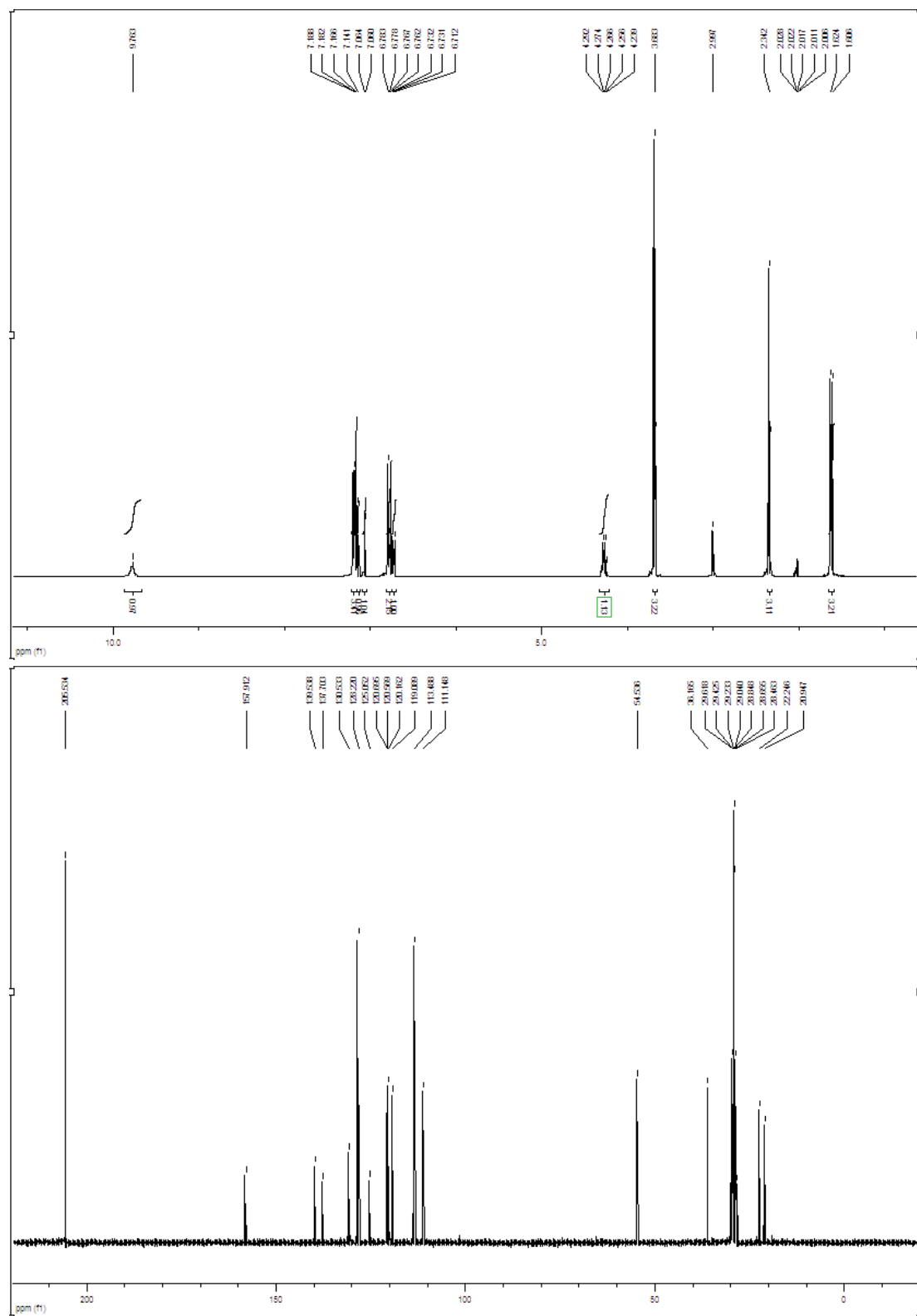
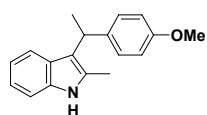


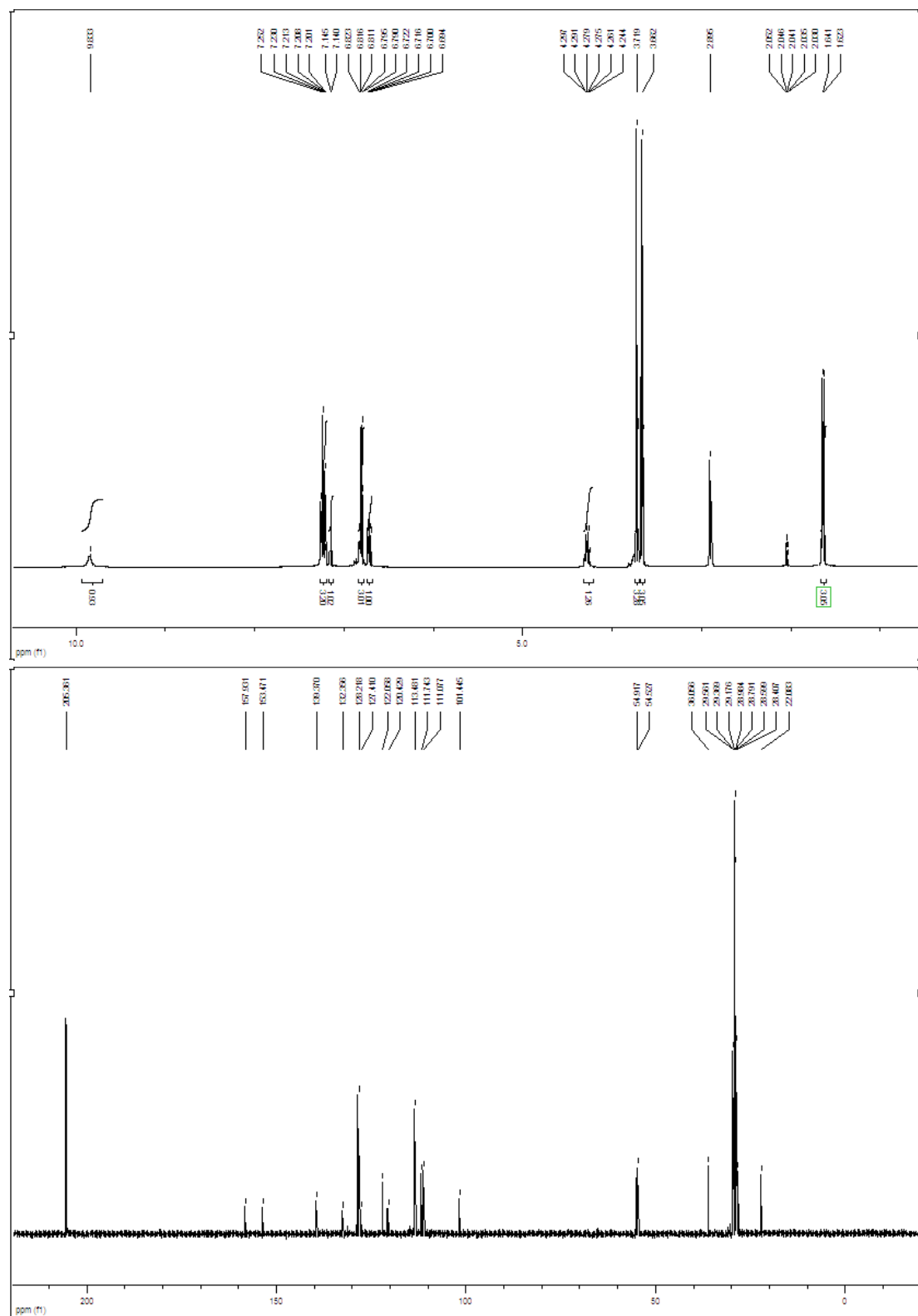
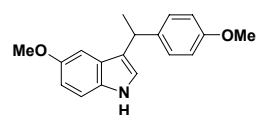


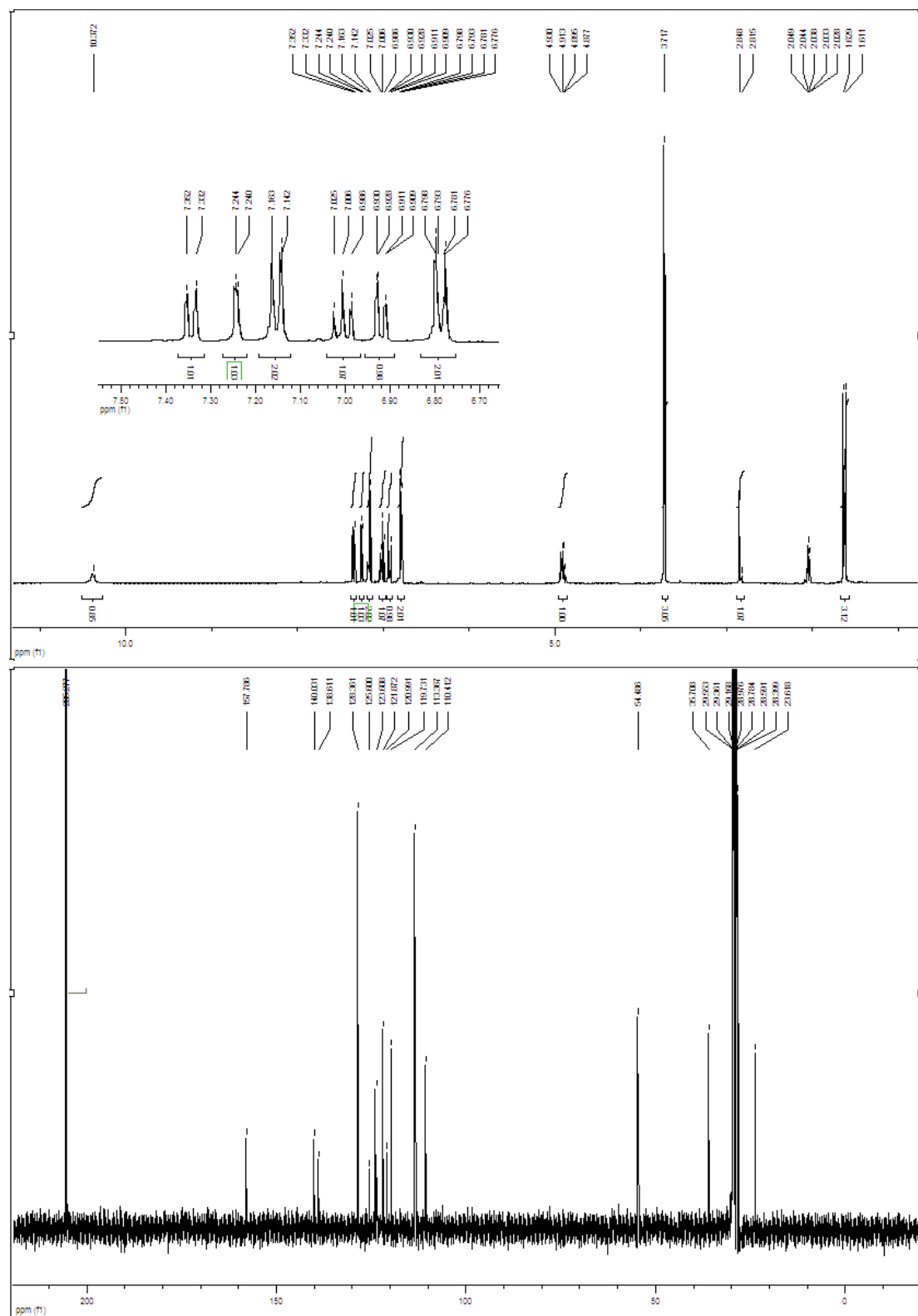
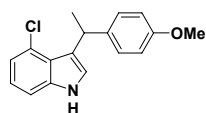


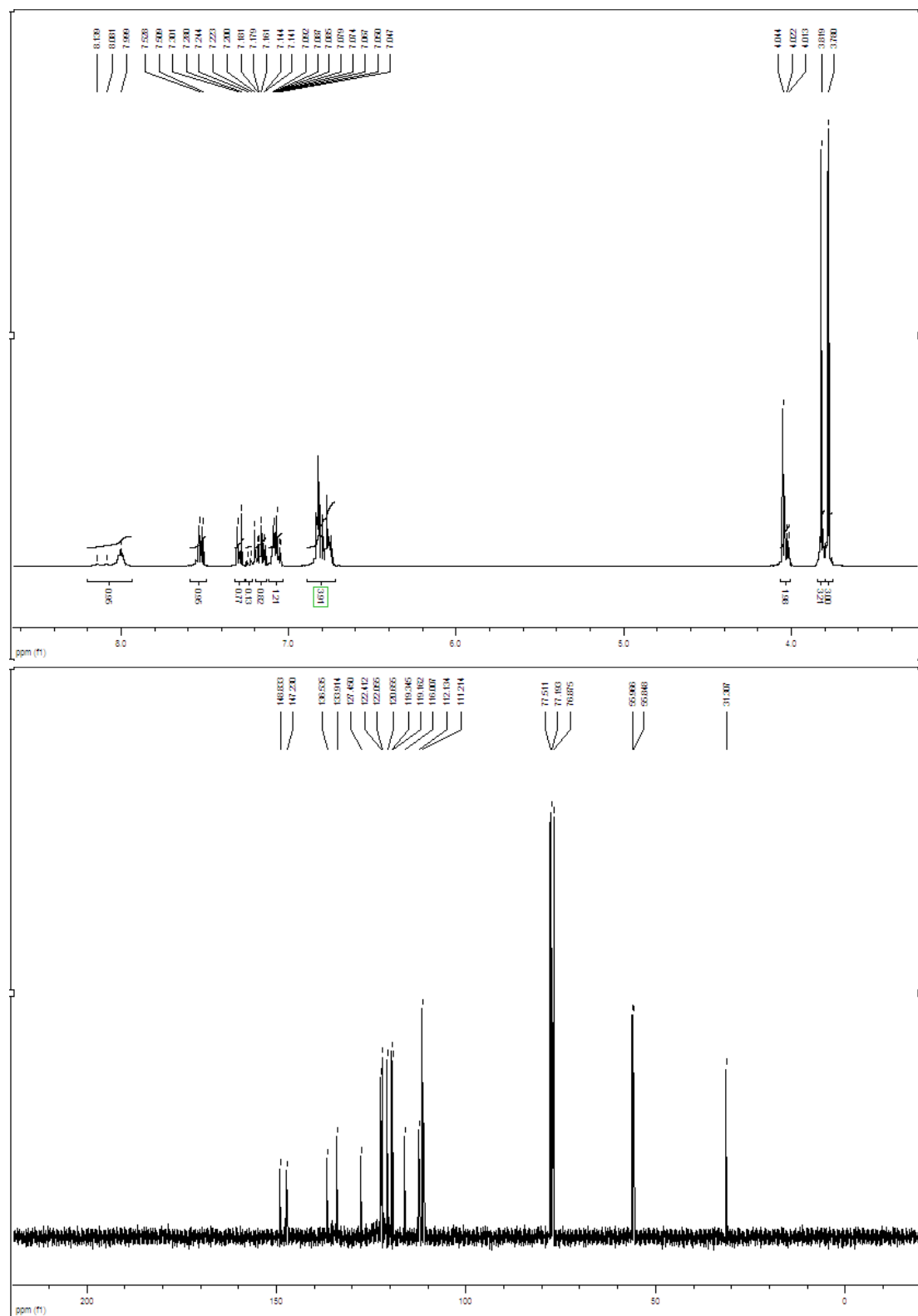
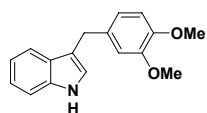


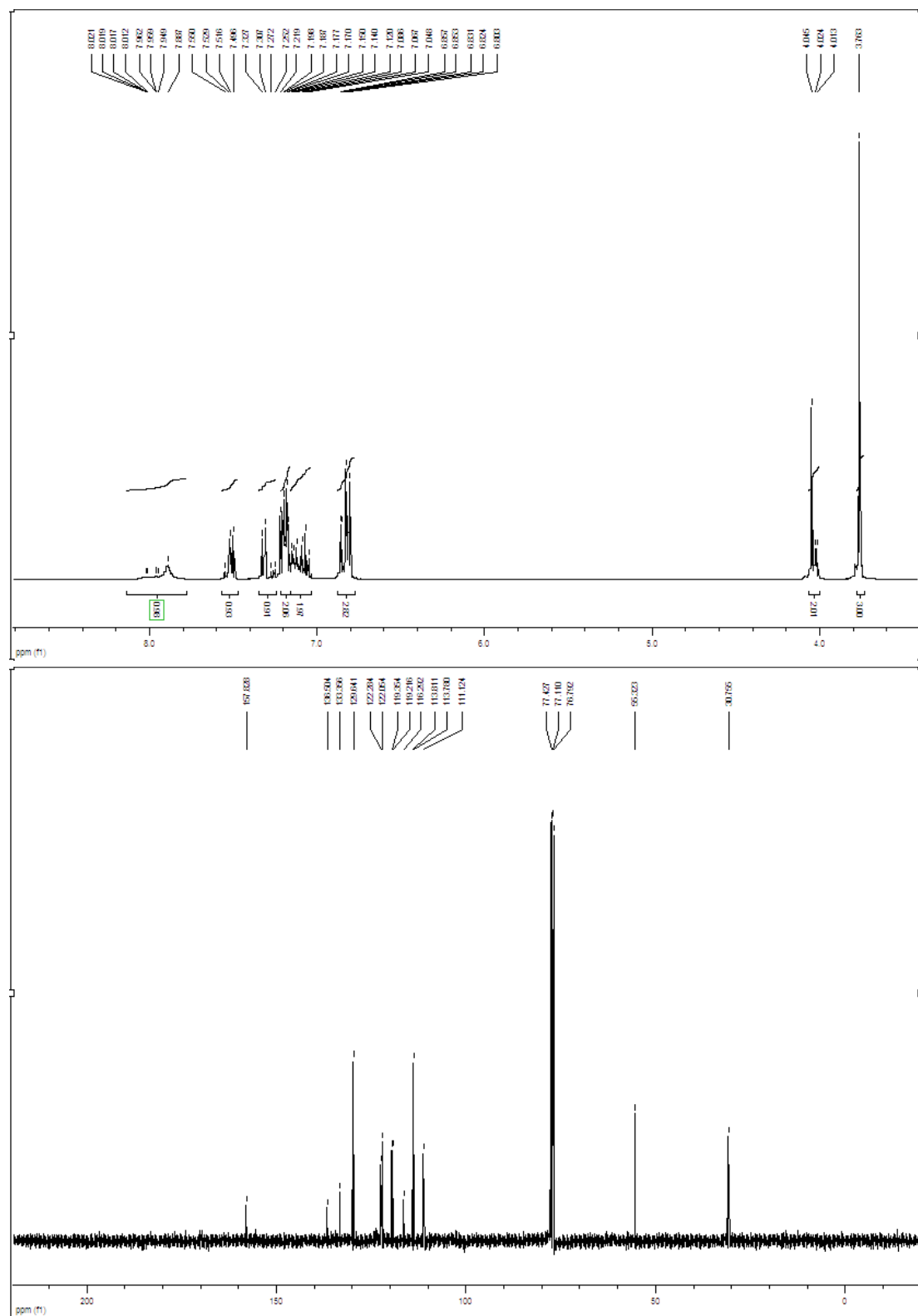
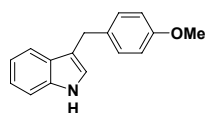




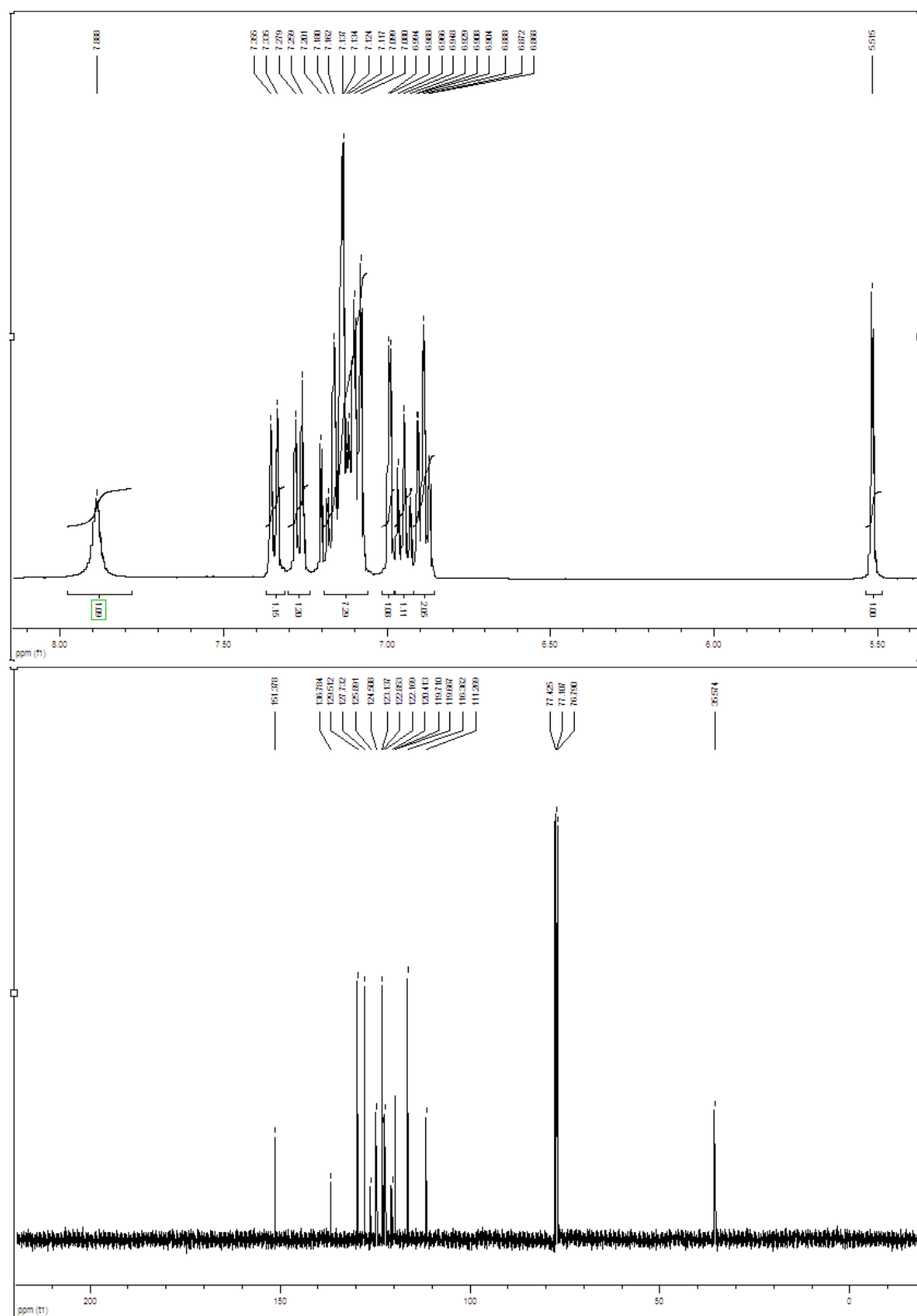
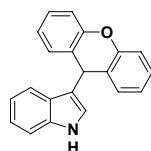












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