Electronic Supporting Information

Ring-opening reactions of 2-aryl-3, 4-dihydropyrans with nucleophiles

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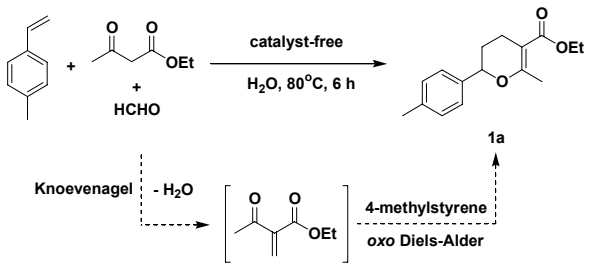
General remarks:

4-Methylstyrene, 4-fluoro-α-methylstyrene, *tert*-butylstyrene, 4-methoxystyrene, 4-ethoxystyrene, 4-chloroindole, 1-methylindole, 5-methoxyindole, 4-hydroxy-6-methyl-2-pyrone, 5-bromoindole, 6-fluoroindole, $Sc(OTf)_3$, $Bi(OTf)_3$, $Y(OTf)_3$, $In(OTf)_3$, Amberlyst-15, $Mn(OAc)_3 \cdot 2H_2O$, montmorillonite K10 and chloroform-*d* were purchased from Alfa Aesar Chemical Company. α-Methylstyrene, $MnBr_2$, indole, methyl acetoacetate, ethyl acetoacetate, acetylacetone, *p*-toluenesulfonic acid, 2-naphthol, $FeCl_3$ (anhydrous), $SnCl_4$, $ZnCl_2$, $Mn(OAc)_2$, $MnCl_2$ (anhydrous), $MnCl_2 \cdot 4H_2O$, 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 Reagents Limited Company (SCRC). 2,5,6-Trisubstituted 3,4-dihydropyrans were prepared in water according to our reported method starting from olefins, 1,3-dicarbonyl compounds and formaldehyde aqueous solution.[1] ^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.

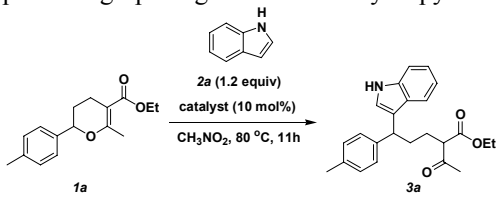


Scheme S1. Tandem Knoevenagel / *oxo* Diels-Alder reaction we have recently reported.

A typical procedure for electrophilic ring-opening reaction of dihydropyran 1a with indole:

All reactions were conducted in a 10 mL of V-type flask equipped with triangle magnetic stirring. In a typical reaction, nitromethane (1.0 ml) was mixed with **1a** (65.1 mg, 0.25 mmol), **2a** (35.1 mg, 0.30 mmol) and $MnCl_2$•$4H_2O$ (5.0 mg, 10 mol%) under air. The mixture was stirred for 11 hours at 80 ^oC. After reaction, the mixture was cooled to room temperature and 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 1/6). 89.7 mg, Yield = 95%. Tests for substrate scope and the reaction of using other nucleohphile were all performed according to an analogous procedure with above mentioned.

Table S1. Electrophilic ring-opening reaction of dihydropyran **1a** with indole **2a**.[a]



Entry	Catalyst	Yield%
1	NH_3SO_3	trace
2	$ZnCl_2$	32
3	$ZrCl_4$	13
4	$FeCl_3$	trace
5	$SnCl_4$	10
6	$AlCl_3$	trace
7	$Y(OTf)_3$	9
8	$MnBr_2$	36
9	$Mn(OAc)_2$	trace
10	$Mn(NO_3)_2$	trace

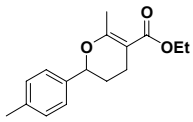
[a]: the reaction was performed in 0.25 mmol scale in 1.0 ml of solvent.

Procedure for synthesis of *7a*: The synthesis was started from preparation of dihydropyran **1c**. In a U-type reaction flask equipped with magnetic stirring, 4-methoxystyrene, **6a** (134.2 mg, 1.0 mmol), was mixed with acetylacetone (**5a**, 200.1 mg, 2.0 mmol) and formaldehyde aqueous solution (37 wt%, 202.8 mg, 2.5 mmol) under air. The mixture was stirred at 80 ^oC for 3 hours. After reaction, the reaction mixture was cooled to room temperature. After addition of brine (5.0 ml), the aqueous phase was extracted with a mixture of ethyl acetate and heptane (v/v = 1/1, 5.0 ml × 3). The obtained organic phases were then combined together and dried with anhydrous Na_2SO_4. After evaporation under reduced pressure, 229.1 mg of the desired product **1c** was obtained by silica gel column chromatography using a mixed solution of ethyl acetate and petro ether as eluting solvent (the ratio of ethyl acetate/petroether is 1/20), yield = 93%. Synthesis of **3o** was performed according to the procedure described in the part of ring-opening reaction. Finally, **3o** was obtained in 91% of yield (307.6 mg). Radical cyclization of **3o** was performed in acetic acid using a V-type flask as reactor. Thus, acetic acid (2.5 ml) was added into the flask that contain the obtained **3o** (0.85 mmol), and then, manganese triacetate dihydrate (559.6 mg, 2.1 mmol) was added. The mixture was then stirred at 60 ^oC for 8 hours. After reaction, Na_2CO_3 aqueous solution (2N, 15 ml) was added and then extracted with a mixture of ethyl acetate and heptane (v/v = 1/1, 20 ml × 3). The obtained organic phases were combined together and dried with anhydrous Na_2SO_4. After evaporation under reduced pressure, **7a** was obtained in 72% of yield (0.61 mmol, 220.2 mg) through a

preparative TLC isolation using a mixed solution of ethyl acetate and petro ether as eluting solvent (the ratio of ethyl acetate/petroether is 1/5).

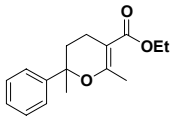
Spectroscopic data of newly synthesized products

Ethyl 6-methyl-2-(p-tolyl)-3,4-dihydro-2H-pyran-5-carboxylate (1a)



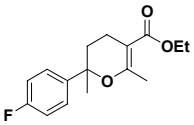
White solid, mp: 40-42 ^{o}C, ^{1}H NMR ($CDCl_3$): 1.28 (t, J = 6.8 Hz, 3H), 1.77-1.90 (m, 1H), 2.03-2.11 (m, 1H), 2.31(t, J = 1.2 Hz, 3H), 2.34 (s, 3H), 2.35-2.50 (m, 2H), 4.17 (q, J = 7.2 Hz, 2H), 4.81 (dd, J_a = 2.4 Hz, J_b = 10.4 Hz, 1H), 7.16 (d, J = 8.4 Hz, 2H), 7.21 (d, J = 8.0 Hz, 2H); ^{13}C NMR: 14.5, 20.4, 21.2, 22.0, 29.2, 59.7, 78.1, 101.4, 125.9, 129.2, 137.7, 137.9, 165.0, 168.6; IR (cm^{-1}): 2979, 2953, 2927, 2857, 1702, 1623, 1516, 1444, 1381, 1207, 1174, 1133, 1076, 1019, 960, 880, 813, 761, 581, 542; HRMS m/z (ESI) calcd for $C_{16}H_{20}NaO_3$ $[M + Na]^+$ 283.1310 found 283.1301.

Ethyl 2,6-dimethyl-2-phenyl-3,4-dihydro-2H-pyran-5-carboxylate



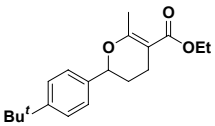
White solid, mp: 38-40 ^{o}C; ^{1}H NMR ($CDCl_3$): 1.54 (s, 3H), 1.83-1.88 (m, 1H), 1.88-1.92 (m, 1H), 1.92-1.99 (m, 1H), 2.15-2.23 (m, 1H), 2.29-2.37 (m, 1H), 2.39 (d, J = 1.2 Hz, 3H), 4.05-4.15 (m, 2H), 7.22-7.30 (m, 3H), 7.30-7.37 (m, 2H); ^{13}C NMR: 14.4, 19.5, 20.5, 29.4, 32.5, 59.6, 79.4, 101.1, 124.4, 127.0, 128.5, 145.0, 163.4, 168.5; IR (cm^{-1}): 3088, 3029, 2980, 2931, 2858, 1705, 1625, 1448, 1379, 1277, 1264, 1232, 1166, 1096, 1028, 1012, 764, 700; HRMS m/z (ESI) calcd for $C_{16}H_{20}NaO_3$ $[M]^+$ 283.1310 found 283.1296.

Ethyl 2-(4-fluorophenyl)-2,6-dimethyl-3,4-dihydro-2H-pyran-5-carboxylate



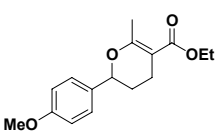
White liquid, mp: 59-61 ^{o}C; ^{1}H NMR ($CDCl_3$): 1.24 (t, J = 7.2 Hz, 3H), 1.52 (s, 3H), 1.82-1.99 (m, 2H), 2.10-2.19 (m, 1H), 2.29-2.37 (m, 1H), 2.37 (d, J = 1.2 Hz, 3H), 4.06-4.16 (m, 2H), 7.01 (tt, J_a = 3.2 Hz, J_b = 8.4 Hz, 2H), 7.21-7.28 (m, 2H); ^{13}C NMR: 14.4, 19.5, 20.5, 29.3, 32.5, 59.6, 79.0, 101.1, 115.1, 115.4, 126.1, 126.1, 140.8, 140.8, 160.5, 163.0, 163.2, 168.4; IR (cm^{-1}): 3069, 3044, 2988, 2942, 2908, 2851, 1696, 1622, 1508, 1480, 1450, 1374, 1278, 1227, 1166, 1094, 1062, 1018, 986, 877, 809, 764, 603, 512; HRMS m/z (ESI) calcd for $C_{16}H_{19}FNaO_3$ $[M + Na]^+$ 301.1216 found 301.1198.

Ethyl 2-(4-(*tert*-butyl)phenyl)-6-methyl-3,4-dihydro-2H-pyran-5-carboxylate



White solid, mp: 54-56 ^{o}C; ^{1}H NMR ($CDCl_3$): 1.32 (s, 9H), 1.81-1.94 (m, 1H), 2.06-2.16 (m, 1H), 2.31 (s, 3H), 2.35-2.53 (m, 2H), 4.18 (q, J = 7.2 Hz, 2H), 4.84 (d, J = 10.0 Hz, 1H), 7.27 (d, J = 8.0 Hz, 2H), 7.40 (d, J = 8.0 Hz, 2H); ^{13}C NMR: 14.5, 20.4, 22.0, 29.1, 31.4, 34.6, 59.7, 78.1, 101.4, 125.5, 125.7, 137.8, 151.0, 165.0, 168.7; IR (cm^{-1}): 3096, 3033, 2953, 2868, 1700, 1620, 1513, 1469, 1447, 1420, 1388, 1371, 1362, 1341, 1208, 1193, 1137, 1110, 1076, 1013, 960, 804, 880, 836, 826, 762, 579; HRMS m/z (ESI) calcd for $C_{19}H_{26}NaO_3$ $[M + Na]^+$ 325.1780 found 325.1767.

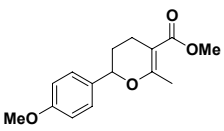
Ethyl 2-(4-methoxyphenyl)-6-methyl-3,4-dihydro-2H-pyran-5-carboxylate (1b)



White solid, mp: 52-54 ^{o}C; ^{1}H NMR ($CDCl_3$): 1.29 (t, J = 7.2 Hz, 3H), 1.80-1.92 (m, 1H), 2.03-2.12 (m, 1H), 2.30 (s, 3H), 2.33-2.43 (m, 1H), 2.43-2.52 (m, 1H), 3.81 (s, 3H), 4.18 (q, J = 7.2 Hz, 2H), 4.81 (dd, J_a = 1.6 Hz, J_b = 10.0 Hz, 1H), 6.90 (d, J = 8.8 Hz, 2H), 7.27 (d, J = 8.8 Hz, 2H); ^{13}C NMR: 14.5, 20.4, 22.1, 29.1, 55.3, 59.7, 77.9, 101.4, 113.9, 127.3, 133.0, 159.4, 165.0, 168.6; IR (cm^{-1}): 2978, 2954, 2933, 2838, 1704, 1621, 1515, 1463,

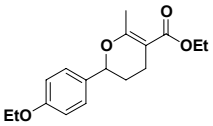
1444, 1381, 1348, 1287, 1270, 1207, 1177, 1133, 1078, 1035, 1019, 961, 879, 828, 761, 590, 551; HRMS m/z (ESI) calcd for $C_{16}H_{20}NaO_4$ $[M + Na]^+$ 299.1259 found 299.1260.

Methyl 3,4-dihydro-2-(4-methoxyphenyl)-6-methyl-2H-pyran-5-carboxylate:[2] White solid, mp: 56-58



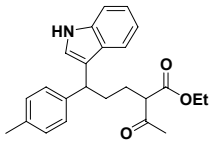
^{o}C; Yield = 83% (ethyl acetate/petroether = 1/4), ^{1}H NMR ($CDCl_3$): 1.71-1.83 (m, 1H), 1.95-2.04 (m, 1H), 2.22 (s, 3H), 2.23-2.43 (m, 2H), 3.63 (s, 3H), 3.72 (s, 3H), 4.72 (d, J = 8.8 Hz, 1H), 6.81 (d, J = 8.4 Hz, 2H), 7.17 (d, J = 8.4 Hz, 2H); ^{13}C NMR: 20.4, 22.0, 29.1, 51.0, 55.3, 78.0, 101.1, 113.9, 127.3, 132.9, 156.4, 165.3, 169.0.

Ethyl 2-(4-ethoxyphenyl)-6-methyl-3,4-dihydro-2H-pyran-5-carboxylate



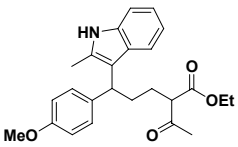
White solid, mp: 49-51 ^{o}C; ^{1}H NMR ($CDCl_3$): 1.29 (t, J = 7.2 Hz, 3H), 1.41 (t, J = 7.2 Hz, 3H), 1.80-1.92 (m, 1H), 2.03-2.12 (m, 1H), 2.30 (s, 3H), 2.32-2.43 (m, 1H), 2.43-2.52 (m, 1H), 4.03 (q, J = 6.8 Hz, 2H), 4.18 (q, J = 7.2 Hz, 2H), 4.81 (dd, J_a = 2.0 Hz, J_b = 10.4 Hz, 1H), 6.89 (d, J = 8.4 Hz, 2H), 7.25 (d, J = 8.4 Hz, 2H); ^{13}C NMR: 14.5, 14.9, 20.4, 22.1, 29.1, 59.7, 63.5, 78.0, 101.4, 114.5, 127.3, 132.8, 158.8, 165.0, 168.7; IR (cm^{-1}): 2981, 2931, 1704, 1622, 1515, 1477, 1445, 1383, 1346, 1270, 1246, 1207, 1175, 1133, 1074, 1048, 1016, 961, 923, 880, 826, 782, 763, 612, 551; HRMS m/z (ESI) calcd for $C_{17}H_{22}NaO_4$ $[M + Na]^+$ 313.1416 found 313.1402.

Ethyl 2-acetyl-5-(1H-indol-3-yl)-5-(p-tolyl)pentanoate (3a)



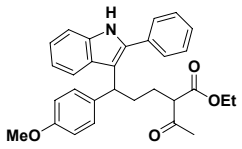
Red liquid; ^{1}H NMR ($CDCl_3$): 1.08 (t, J = 7.2 Hz, 1.5H), 1.10 (t, J = 7.2 Hz, 1.5 H), 1.65-1.89 (m, 3H), 1.95-2.10 (m, 4H), 2.14 (s, 3H), 3.32 (q, J = 7.6 Hz, 1H), 3.95-4.07 (m, 3H), 6.80 (dd, J_a = 2.0 Hz, J_b = 8.4 Hz, 1H), 6.87 (t, J = 8.0 Hz, 1H), 6.92 (d, J = 8.0 Hz, 2H), 6.98 (t, J = 7.2 Hz, 1H), 7.04 (dd, J_a = 1.6 Hz, J_b = 8.0 Hz, 2H), 7.10 (d, J = 8.4 Hz, 1H), 7.31 (dd, J_a = 2.4 Hz, J_b = 7.6 Hz, 1H), 8.08 (s, 1H); ^{13}C NMR: 13.03, 13.0, 19.9, 25.7, 25.8, 27.6, 27.8, 32.6, 32.8, 41.2, 41.3, 58.7, 58.8, 60.3, 110.1, 118.0, 118.8, 118.2, 118.2, 120.2, 120.7, 125.7, 125.8, 126.6, 126.6, 128.0, 134.4, 135.5, 140.6, 168.8, 168.8, 202.5, 202.5; IR (cm^{-1}): 3415, 3051, 2981, 2964, 2926, 2868, 1734, 1731, 1621, 1513, 1458, 1421, 1360, 1341, 1261, 1264, 1226, 1213, 1187, 1151, 1098, 1042, 1022, 913, 811, 744, 617, 530; HRMS m/z (ESI) calcd for $C_{24}H_{27}NNaO_3$ $[M + Na]^+$ 400.1889 found 400.1873.

Ethyl 2-acetyl-5-(4-methoxyphenyl)-5-(2-methyl-1H-indol-3-yl)pentanoate (3b)



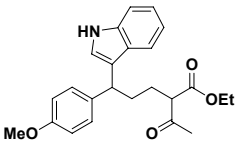
Red liquid; ^{1}H NMR ($CDCl_3$): 1.02 (t, J = 7.2 Hz, 1.5 H), 1.08 (t, J = 7.2 Hz, 1.5 H), 1.56-1.84 (m, 2H), 1.91 (s, 1.5 H), 1.96 (s, 1.5 H), 2.00-2.11 (m, 2H), 2.12 (s, 3H), 3.29 (dd, J_a = 7.6 Hz, J_b = 18.0 Hz, 1H), 3.54 (s, 3H), 3.92-4.04 (m, 3H), 6.62 (d, J = 8.4 Hz, 2H), 6.84 (t, J = 6.8 Hz, 1H), 6.90 (t, J = 6.8 Hz, 1H), 7.02 (d, J = 8.0 Hz, 2H), 7.11 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 8.0 Hz, 1H); ^{13}C NMR: 12.2, 12.2, 14.1, 14.2, 27.2, 27.3, 28.6, 29.0, 32.3, 32.4, 41.1, 41.2, 55.2, 59.8, 60.0, 61.5, 110.7, 113.3, 113.4, 113.7, 119.0, 119.2, 120.7, 127.6, 127.7, 128.6, 131.7, 131.8, 135.6, 137.3, 137.3, 157.7, 169.9, 170.1, 203.8; IR (cm^{-1}): 3397, 3054, 3027, 2958, 2934, 2868, 2836, 1735, 1709, 1613, 1583, 1510, 1460, 1360, 1325, 1300, 1245, 1178, 1150, 1113, 1098, 1033, 969, 912, 831, 742, 590, 542; HRMS m/z (ESI) calcd for $C_{25}H_{29}NNaO_4$ $[M + Na]^+$ 430.1994 found 430.2003.

Ethyl 2-acetyl-5-(4-methoxyphenyl)-5-(2-phenyl-1H-indol-3-yl)pentanoate (3c)



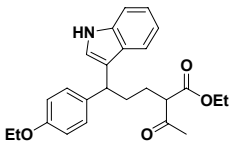
Yellow solid, mp: 78-80 °C; ^{1}H NMR ($CDCl_3$): 1.07 (t, J = 7.2 Hz, 1.6 H), 1.12 (t, J = 7.2 Hz, 1.4 H), 1.52-1.70 (m, 2H), 1.89 (s, 1.5H), 1.91(s, 1.5 H), 2.00-2.35 (m, 2H), 3.18 (dd, J_a = 8.0 Hz, J_b = 16.8 Hz, 1H), 3.66 (d, J = 1.6 Hz, 3H), 3.96-4.08 (m, 2H), 4.22-4.33 (m, 1H), 6.74 (dd, J_a = 2.8 Hz, J_b = 8.8 Hz, 2H), 7.00 (t, J = 7.2 Hz, 1H), 7.10 (t, J = 7.2 Hz, 1H), 7.21-7.33 (m, 6H), 7.36 (d, J = 4.0 Hz, 2H), 7.55 (s, 1H), 8.54 (bs, 1H); ^{13}C NMR: 14.1, 14.2, 26.8, 27.1, 28.4, 28.9, 32.7, 33.0, 40.9, 41.2, 55.3, 59.4, 59.8, 61.4, 61.4, 111.5, 113.8, 113.9, 114.0, 119.6, 120.9, 120.9, 121.0, 122.0, 127.6, 128.0, 128.8, 128.9, 128.9, 133.2, 136.2, 136.3, 136.6, 137.5, 157.7, 169.8, 170.0, 203.6, 203.8; IR (cm^{-1}): 3393, 3054, 3022, 2979, 2935, 2868, 1734, 1709, 1616, 1512, 1488, 1452, 1367, 1310, 1244, 1211, 1152, 1116, 1095, 1045, 1022, 811, 766, 744, 700, 547, 420; HRMS m/z (ESI) calcd for $C_{30}H_{31}NNaO_4$ $[M + Na]^+$ 492.2151 found 492.2152.

Ethyl 2-acetyl-5-(1H-indol-3-yl)-5-(4-methoxyphenyl)pentanoate (3d)



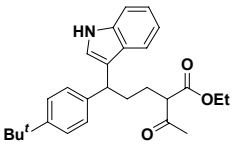
Red liquid; ^{1}H NMR ($CDCl_3$): 1.17 (t, J = 7.2 Hz, 3H), 1.74-1.99 (m, 3H), 2.04-2.21 (m, 4H), 3.36-3.48 (m, 1H), 3.64 (s, 3H), 4.05-4.19 (m, 3H), 6.74 (d, J = 8.0 Hz, 2H), 6.80 (d, J = 8.0 Hz, 1H), 6.97 (t, J = 6.8 Hz, 1H), 7.07 (t, J = 7.2 Hz, 1H), 7.13 (dd, J_a = 2.0 Hz, J_b = 6.8 Hz, 2H), 7.19 (d, J = 8.0 Hz, 1H), 7.39 (s, 1H), 8.27 (bs, 1H); ^{13}C NMR: 14.2, 26.9, 27.0, 28.8, 29.0, 33.9, 34.0, 42.1, 42.1, 55.3, 59.9, 59.9, 61.6, 111.4, 113.9, 119.2, 119.4, 119.6, 121.4, 121.9, 126.9, 127.0, 128.9, 136.8, 137.0, 137.1, 158.0, 170.0, 170.1, 203.8, 203.8; IR (cm^{-1}): 3412, 3056, 3034, 2981, 2957, 2837, 1735, 1710, 1610, 1510, 1458, 1421, 1360, 1338, 1299, 1246, 1178, 1149, 1098, 1033, 912, 836, 815, 743, 580, 541, 424; HRMS m/z (ESI) calcd for $C_{24}H_{27}NNaO_4$ $[M + Na]^+$ 416.1838 found 416.1819.

Ethyl 2-acetyl-5-(4-ethoxyphenyl)-5-(1H-indol-3-yl)pentanoate (3e)



Red liquid; ^{1}H NMR ($CDCl_3$): 1.14-1.24 (m, 3H), 1.31 (m, 3H), 1.75-2.00 (m, 3H), 2.05-2.22 (m, 4H), 3.43 (t, J = 6.4 Hz, 1H), 3.88 (q, J = 7.2 Hz, 2H), 4.05-4.19 (m, 3H), 6.75 (dd, J_a = 2.0 Hz, J_b = 7.2 Hz, 2H), 6.87 (d, J = 7.6 Hz, 1H), 6.98 (t, J = 6.4 Hz, 1H), 7.04-7.11 (m, 1H), 7.11-7.23 (m, 3H), 7.41 (s, 1H), 8.27 (bs, 1H); ^{13}C NMR: 14.2, 15.0, 26.9, 27.0, 28.8, 29.0, 33.9, 34.0, 42.1, 42.2, 59.8, 60.0, 61.6, 63.5, 111.5, 114.5, 119.2, 119.4, 119.6, 121.5, 121.9, 127.0, 128.9, 128.9, 136.8, 136.8, 137.0, 157.4, 170.0, 170.1, 203.8, 203.8; IR (cm^{-1}): 3413, 3056, 3036, 2980, 2932, 2871, 1736, 1709, 1610, 1584, 1509, 1477, 1455, 1421, 1392, 1338, 1299, 1177, 1149, 1113, 1095, 1046, 1016, 918, 838, 813, 743, 584, 540, 421; HRMS m/z (ESI) calcd for $C_{25}H_{29}NNaO_4$ $[M + Na]^+$ 430.1994 found 430.2001.

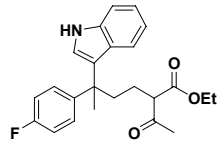
Ethyl 2-acetyl-5-(4-(*tert*-butyl)phenyl)-5-(1H-indol-3-yl)pentanoate (3f)



Red liquid; ^{1}H NMR ($CDCl_3$): 1.19 (t, J = 7.2 Hz, 3H), 1.25 (s, 9H), 1.75-2.00 (m, 3H), 2.09 (d, J = 8.8 Hz, 3H), 2.11-2.30 (m, 1H), 3.37-2.47 (m, 1H), 4.06-4.17 (m, 3H), 6.94 (dd, J_a = 2.0 Hz, J_b = 8.8 Hz, 1H), 6.99 (t, J = 6.8 Hz, 2H), 7.08 (t, J = 7.2 Hz, 1H), 7.15-7.27 (m, 5H), 7.45 (dd, J_a = 2.4 Hz, J_b = 8.0 Hz, 1H), 8.18 (bs, 1H); ^{13}C NMR: 14.2, 14.2, 27.0, 27.1, 28.7, 29.0, 31.5, 33.9, 34.0, 34.4, 42.4, 42.4, 59.9, 60.0, 61.5, 111.3, 119.2, 119.2, 119.4, 121.4, 121.9, 125.4, 127.0, 127.0, 127.4, 127.5, 136.7, 141.8, 141.9, 148.8, 169.9, 170.0, 203.6, 203.6; IR (cm^{-1}): 3415, 3123, 3082, 3054, 2962, 2908, 2868, 1736, 1711, 1619, 1510, 1457,

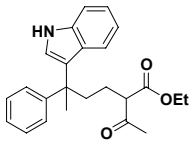
1418, 1396, 1362, 1340, 1269, 1243, 1226, 1207, 1149, 1097, 911, 841, 811, 740, 645, 610, 581, 557; HRMS m/z (ESI) calcd for $C_{27}H_{33}NNaO_3$ $[M + Na]^+$ 442.2358 found 442.2374.

Ethyl 2-acetyl-5-(4-fluorophenyl)-5-(1H-indol-3-yl)hexanoate (3g)



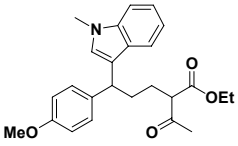
Red liquid; ^{1}H NMR ($CDCl_3$): 1.14 (t, J = 7.2 Hz, 1.4H), 1.21 (t, J = 6.8 Hz, 1.6 H), 1.43-1.60 (m, 0.6 H), 1.66 (d, J = 2.4 Hz, 3H), 1.70-1.87 (m, 1.4 H), 2.00 (s, 1.5 H), 2.03-2.08 (m, 0.4 H), 2.09 (s, 1.5 H), 2.10-2.34 (m, 1.6 H), 3.32 (q, J = 7.2 Hz, 1H), 4.02-4.14 (m, 2H), 6.80-6.87 (m, 3H), 6.90-6.94 (m, 1H), 7.02-7.08 (m, 2H), 7.19 (dd, J_a = 5.6 Hz, J_b = 8.8 Hz, 2H), 7.22-7.26 (m, 1H), 8.34 (bs, 1H); ^{13}C NMR: 14.1, 14.2, 23.7, 23.8, 27.7, 28.0, 28.6, 29.0, 38.8, 38.9, 41.9, 41.9, 60.2, 60.3, 61.6, 111.5, 111.5, 114.6, 114.9, 118.9, 118.9, 121.0, 121.7, 121.7, 121.8, 122.0, 123.0, 123.3, 125.8, 125.8, 128.5, 128.5, 128.5, 128.6, 137.3, 144.2, 144.3, 144.3, 144.3, 159.9, 162.3, 170.0, 170.0, 203.8; IR (cm^{-1}): 3412, 3057, 2972, 2936, 2872, 1736, 1709, 1647, 1602, 1507, 1458, 1419, 1365, 1337, 1226, 1159, 1102, 1016, 911, 836, 741, 587, 541, 424; HRMS m/z (ESI) calcd for $C_{24}H_{26}FNNaO_3$ $[M + Na]^+$ 418.1794 found 418.1802.

Ethyl 2-acetyl-5-(1H-indol-3-yl)-5-phenylhexanoate (3h)



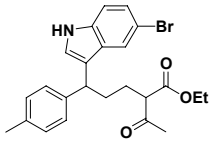
Red liquid; ^{1}H NMR ($CDCl_3$): 1.09 (t, J = 7.2 Hz, 1.4 H), 1.16 (t, J = 7.2 Hz, 1.6 H), 1.46-1.63 (m, 0.6 H), 1.66 (s, 3H), 1.68-1.88 (m, 1.4 H), 1.94 (s, 1.4 H), 2.02 (s, 1.6 H), 2.04-2.28 (m, 2H), 3.21-3.30 (m, 1H), 3.97-4.15 (m, 2H), 6.77 (t, J = 7.2 Hz, 1H), 6.90 (d, J = 7.6 Hz, 1H), 6.96-7.04 (m, 2H), 7.07 (t, J = 6.8 Hz, 1H), 7.14 (t, J = 7.2 Hz, 2H), 7.21 (t, J = 7.6 Hz, 3H), 8.15 (bs, 1H); ^{13}C NMR: 14.1, 14.2, 23.8, 23.9, 27.5, 27.9, 28.5, 28.8, 38.7, 38.9, 42.3, 42.3, 60.3, 60.4, 61.5, 111.4, 118.9, 118.9, 121.2, 121.6, 121.7, 121.8, 122.0, 123.3, 123.6, 125.9, 126.0, 126.0, 127.0, 127.0, 128.1, 137.2, 148.5, 148.6, 170.0, 170.0, 203.8; IR (cm^{-1}): 3415, 3056, 2971, 2936, 2872, 1735, 1701, 1616, 1544, 1491, 1457, 1418, 1363, 1337, 1263, 1243, 1221, 1103, 1018, 910, 742, 702, 586, 516, 426; HRMS m/z (ESI) calcd for $C_{24}H_{27}NNaO_3$ $[M + Na]^+$ 400.1889 found 400.1877.

Ethyl 2-acetyl-5-(4-methoxyphenyl)-5-(1-methyl-1H-indol-3-yl)pentanoate (3i)



Red liquid; ^{1}H NMR ($CDCl_3$): 1.19 (t, J = 8.8 Hz, 3H), 1.75-1.98 (m, 3H), 2.04-2.28 (m, 4H), 3.41 (td, J_a = 7.6 Hz, J_b = 10.4 Hz, 1H), 3.60 (d, J = 2.0 Hz, 3H), 3.66 (s, 3H), 4.06-4.17 (m, 3H), 6.77 (dd, J_a = 1.6 Hz, J_b = 8.8 Hz, 2H), 6.82 (d, J = 8.0 Hz, 1H), 6.97 (dd, J_a = 7.2 Hz, J_b = 8.0 Hz, 1H), 7.12 (t, J = 7.6 Hz, 1H), 7.15-7.22 (m, 3H), 7.40 (dd, J_a = 2.8 Hz, J_b = 8.0 Hz, 1H); ^{13}C NMR: 14.2, 14.2, 26.9, 27.0, 28.7, 28.9, 32.7, 34.0, 34.1, 42.0, 42.1, 55.2, 59.9, 60.0, 61.4, 109.3, 113.9, 118.4, 118.6, 118.8, 119.6, 121.7, 126.0, 127.4, 127.4, 128.8, 128.8, 137.0, 137.1, 137.4, 158.0, 169.9, 169.9, 203.3; IR (cm^{-1}): 3053, 2934, 2872, 2835, 1738, 1713, 1610, 1510, 1467, 1369, 1329, 1300, 1208,1178, 1151, 1094, 1034, 814, 742, 566; HRMS m/z (ESI) calcd for $C_{25}H_{29}NNaO_4$ $[M + Na]^+$ 430.1994 found 430.1982.

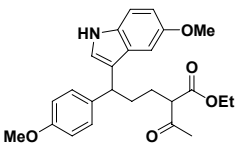
Ethyl 2-acetyl-5-(5-bromo-1H-indol-3-yl)-5-(p-tolyl)pentanoate (3j)



Red liquid; ^{1}H NMR ($CDCl_3$): 1.20 (q, J = 7.2 Hz, 3H), 1.73-2.00 (m, 3H), 2.02-2.11 (m, 1H), 2.13 (d, J = 9.6 Hz, 3H), 2.24 (s, 3H), 3.40-3.50 (m, 1H), 3.99-4.06 (m, 1H), 4.07-4.18 (m, 2H), 6.94 (dd, J_a = 2.0 Hz, J_b = 7.2 Hz, 1H), 7.02 (d, J = 8.0 Hz, 2H), 7.06 (d, J = 8.8 Hz, 1H), 7.08-7.15 (m, 3H), 7.52 (dd, J_a = 2.0 Hz, J_b = 3.2

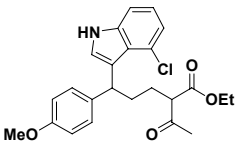
Hz, 1H), 8.43 (bs, 1H); ^{13}C NMR: 14.2, 21.1, 26.8, 27.0, 28.9, 29.1, 33.8, 34.0, 42.2, 42.4, 59.7, 59.9, 61.6, 61.6, 112.4, 112.9, 118.9, 119.1, 121.7, 122.6, 122.7, 124.7, 127.6, 127.6, 128.7, 128.7, 129.3, 135.3, 135.3, 135.9, 141.3, 141.4, 169.9, 170.0, 203.8; IR (cm^{-1}): 3413, 3124, 2980, 2926, 2866, 1734, 1706, 1613, 1565, 1511, 1456, 1419, 1361, 1333, 1211, 1148, 1098, 1048, 1020, 909, 883, 862, 796, 731, 594, 420; HRMS m/z (ESI) calcd for $C_{24}H_{26}BrNNaO_3$ $[M + Na]^+$ 478.0994 found 478.0980.

Ethyl 2-acetyl-5-(5-methoxy-1H-indol-3-yl)-5-(4-methoxyphenyl)pentanoate (3k)



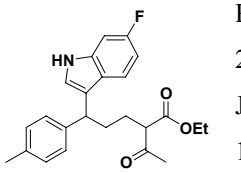
Red liquid; ^{1}H NMR ($CDCl_3$): 1.23 (q, J = 7.2 Hz, 3H), 1.76-2.00 (m, 3H), 2.07-2.20 (m, 4H), 3.44 (q, J = 8.0 Hz, 1H), 3.72 (s, 3H), 3.75 (s, 3H), 4.06 (t, J = 8.0 Hz, 1H), 4.16 (q, J = 7.2 Hz, 2H), 6.75-6.81 (m, 3H), 6.84 (s, 1H), 7.14 (d, J = 8.8 Hz, 1H), 7.17 (dd, J_a = 1.6 Hz, J_b = 8.4 Hz, 2H), 8.19 (bs, 1H); ^{13}C NMR: 14.1, 14.2, 26.8, 26.9, 28.7, 28.9, 33.7, 33.9, 42.0, 42.0, 55.2, 55.9, 59.8, 59.9, 61.5, 101.5, 111.8, 111.9, 113.8, 119.2, 119.4, 122.1, 127.3, 127.3, 128.8, 128.8, 131.8, 136.7, 136.9, 153.6, 157.9, 169.9, 169.9, 203.5; IR (cm^{-1}): 3415, 3030, 2991, 2937, 2868, 2834, 1735, 1710, 1611, 1583, 1510, 1483, 1456, 1360, 1297, 1246, 1175, 1148, 1095, 1033, 924, 830, 799, 773, 732, 424; HRMS m/z (ESI) calcd for $C_{25}H_{29}NNaO_5$ $[M + Na]^+$ 446.1943 found 446.1969.

Ethyl 2-acetyl-5-(4-chloro-1H-indol-3-yl)-5-(4-methoxyphenyl)pentanoate (3l)



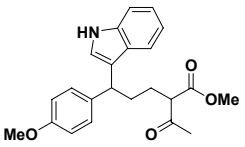
Red liquid; ^{1}H NMR ($CDCl_3$): 1.18 (q, J = 7.2 Hz, 3H), 1.78-2.10 (m, 3H), 2.04-2.20 (m, 4H), 3.47 (q, J = 7.2 Hz, 1H), 3.66 (s, 3H), 4.13 (q, J = 6.8 Hz, 2H), 4.78 (t, J = 7.2 Hz, 1H), 6.76 (dd, J_a = 2.0 Hz, J_b = 8.4 Hz, 2H), 6.87 (dd, J_a = 3.6 Hz, J_b = 18.0 Hz, 1H), 6.92-6.99 (m, 2H), 6.98 (d, J = 7.6 Hz, 1H), 7.03 (dd, J_a = 4.8 Hz, J_b = 8.4 Hz, 2H), 8.61 (bs, 1H); ^{13}C NMR: 14.2, 14.2, 27.1, 27.1, 29.0, 29.1, 35.6, 35.8, 41.4, 41.5, 55.2, 59.8, 60.0, 61.6, 61.6, 110.4, 113.8, 113.8, 120.0, 120.3, 120.6, 122.4, 123.2, 123.5, 123.6, 126.0, 129.2, 129.2, 137.1, 137.4, 138.1, 157.8, 157.9, 170.0, 170.1, 204.0, 204.1; IR (cm^{-1}): 3395, 3125, 3101, 3062, 2979, 2958, 2935, 2867, 2836, 1735, 1710, 1611, 1510, 1482, 1460, 1424, 1359, 1338, 1300, 1247, 1210, 1181, 1147, 1111, 1094, 1034, 936, 820, 778, 741, 550; HRMS m/z (ESI) calcd for $C_{24}H_{26}ClNNaO_4$ $[M + Na]^+$ 450.1448 found 450.1437.

Ethyl 2-acetyl-5-(6-fluoro-1H-indol-3-yl)-5-(p-tolyl)pentanoate (3m)



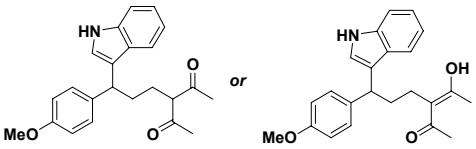
Red liquid; ^{1}H NMR ($CDCl_3$): 1.21 (t, J = 7.2 Hz, 3H), 1.76-2.01 (m, 1.4 H), 2.01-2.10 (m, 1.6 H), 2.10-2.20 (m, 4H), 2.25 (s, 3H), 3.46 (q, J = 6.4 Hz, 1H), 4.12 (dd, J_a = 7.2 Hz, J_b = 15.2 Hz, 2H), 4.80 (t, J = 6.8 Hz, 1H), 6.88 (dd, J_a = 2.4 Hz, J_b = 18.4 Hz, 1H), 6.82-6.89 (m, 2H), 6.94 (dd, J_a = 1.6 Hz, J_b = 8.0 Hz, 2H), 7.00 (d, J = 6.8 Hz, 1H), 7.15 (dd, J_a = 4.8 Hz, J_b = 8.0 Hz, 2H), 8.57 (bs, 1H); ^{13}C NMR: 14.2, 14.2, 21.1, 27.1, 27.1, 28.9, 29.1, 35.6, 35.7, 41.8, 41.9, 59.9, 60.0, 61.5, 61.6, 110.3, 119.8, 120.2, 120.6, 122.3, 123.2, 123.5, 123.6, 126.1, 128.1, 128.2, 129.1, 129.2, 135.5, 135.6, 138.1, 141.9, 142.2, 170.0, 170.1, 203.9, 204.0; IR (cm^{-1}): 3396, 2980, 2960, 2933, 2867, 1735, 1710, 1615, 1561, 1512, 1483, 1425, 1359, 1339, 1268, 1245, 1209, 1186, 1147, 1113, 1094, 1020, 936, 911, 815, 771, 740, 420; HRMS m/z (ESI) calcd for $C_{24}H_{26}FNNaO_3$ $[M + Na]^+$ 418.1794 found 418.1789.

Methyl 2-acetyl-5-(1H-indol-3-yl)-5-(4-methoxyphenyl)pentanoate (3n)



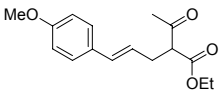
Brown liquid; [1] HNMR ($CDCl_3$): 1.78-1.94 (m, 3H), 2.18-2.15 (m, 4H), 3.42-3.48 (m, 1H), 3.67 (d, J = 2.8 Hz, 3H), 3.73 (s, 3H), 4.10 (t, J = 6.8 Hz, 1H), 6.77 (dd, J_a = 1.6Hz, J_b = 8.4Hz, 2H), 6.94-7.01 (m, 2H), 7.10 (t, J = 7.6Hz, 1H), 7.16 (dd, J_a = 2.8Hz, J_b = 8.8Hz, 1H), 7.26 (d, J = 8.0Hz, 1H), 7.39 (dd, J_a = 2.8Hz, J_b = 8.0Hz, 1H), 8.13 (s, 1H); [13] CNMR: 26.8, 26.9, 28.7, 28.9, 33.7, 33.9, 41.9, 42.0, 52.4, 55.2, 59.6, 59.7, 111.2, 113.8, 119.2, 119.3, 119.4, 119.6, 121.1, 121.9, 126.8, 126.9, 128.7, 136.6, 136.7, 136.9, 157.9, 170.3, 170.4, 203.5; IR (cm^{-1}): 3411, 3001, 2953, 1711, 1610, 1510, 1457, 1358, 1246, 1177, 1150, 1034, 910, 816, 742, 648, 541; HRMS m/z (ESI) calcd for $C_{23}H_{25}NNaO_4$ $[M + Na]^+$ 402.1681 found 402.1864.

3-(3-(1H-indol-3-yl)-3-(4-methoxyphenyl)propyl)pentane-2,4-dione and (Z)-3-(1-hydroxyethylidene)-6-(1H-indol-3-yl)-6-(4-methoxyphenyl)hexan-2-one (3o)



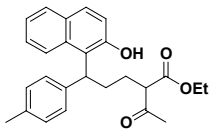
Brown liquid; [1] HNMR ($CDCl_3$): 1.81-1.89 (m, 2H), 1.89-2.00 (m, 2.1H), 2.03-2.04 (m, 2.1H), 2.03-2.04 (m, 2.3), 2.08 (s, 2.5H), 2.13-2.30 (m, 1.1H), 3.60 (t, J = 6.8 Hz, 0.68H), 3.71 (d, J = 8.0Hz, 3H), 4.08 (t, J = 7.6 Hz, 1H), 6.76-6.81 (m, 2H), 6.93-7.02 (m, 2H), 7.10 (t, J = 6.8Hz, 1H), 7.14-7.25 (m, 3H), 7.40 (dd, J_a = 16.8Hz, J_b = 8.0Hz, 1H), 8.17 (d, J = 19.2Hz, 1H); 13 CNMR: 22.8, 26.2, 26.9, 29.0, 29.3, 33.9, 37.0, 42.0, 42.2, 55.2, 68.7, 110.4, 111.2, 111.3, 113.8, 119.2, 119.3, 119.5, 120.1, 121.1, 122.0, 112.1, 126.8, 128.7, 128.8, 136.6, 136.8, 157.8, 157.9, 191.2, 204.8; IR (cm^{-1}): 3411, 3056, 3034, 3001, 2953, 2932, 2863, 2835, 1722, 1696, 1609, 1583, 1510, 1457, 1419, 1358, 1338, 1300, 1246, 1177, 1150, 1107, 1033, 909, 834, 741, 580; HRMS m/z (ESI) calcd for $C_{23}H_{25}NNaO_3$ $[M + Na]^+$ 386.1732 found 386.1724.

(E)-Ehyl 2-acetyl-5-(4-methoxyphenyl)pent-4-enoate (4a)



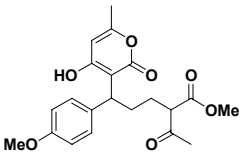
White solid, mp = 41-42°C; [1] HNMR ($CDCl_3$): 1.25 (t, J = 6.8Hz, 3H), 2.25 (s, 3H), 2.72 (t, J = 7.2Hz, 2H), 3.57 (t, J = 7.6Hz, 1H), 3.79 (s, 3H), 4.19 (q, J = 7.2Hz, 2H), 5.96 (dt, J_a = 15.6Hz, J_b = 7.6Hz, 1H), 6.39 (d, J = 15.6 Hz, 1H), 6.82 (d, J = 8.4Hz, 2H), 7.24 (d, J = 8.4Hz, 2H); [13] NMR: 14.1, 29.2, 31.5, 55.2, 59.7, 61.4, 113.9, 123.4, 127.3, 129.8, 132.1, 159.0, 169.2, 202.5; IR (cm^{-1}): 3414, 3031, 2986, 2965, 2916, 2842, 1736, 1710, 1607, 1511, 1457, 1422, 1367, 1303, 1251, 1217, 1175, 1143, 1030, 974, 838, 795; HRMS m/z (ESI) calcd for $C_{16}H_{20}NaO_4$ $[M + Na]^+$ 299.1259 found 299.1256.

Ethyl 2-acetyl-5-(2-hydroxynaphthalen-1-yl)-5-(p-tolyl)pentanoate (6a)



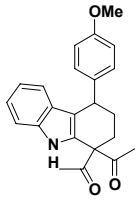
Yellow pale liquid; [1]H NMR ($CDCl_3$): 1.16 (t, J = 7.2 Hz, 1.4 H), 1.21 (t, J = 7.2 Hz, 1.6 H), 1.60-1.82 (m, 1H), 1.83-2.02 (m, 1H), 2.04 (s, 1.4 H), 2.08 (s, 1.6 H), 2.27 (s, 3H), 2.30-2.47 (m, 2H), 3.39 (t, J = 6.8 Hz, 0.46 H), 3.48 (t, J = 7.2 Hz, 0.54 H), 4.05-4.20 (m, 2H), 4.96-5.08 (m, 1H), 5.75 (bs, 1H), 6.99 (d, J = 8.8 Hz, 1H), 7.05 (d, J = 7.6 Hz, 1H), 7.23 (d, J = 7.6 Hz, 2H), 7.29 (d, J = 6.8 Hz, 1H), 7.34-7.48 (m, 1H), 7.61 (d, J = 8.8 Hz, 1H), 7.74 (d, J = 8.0 Hz, 1H), 7.99 (bs, 1H); [13]C NMR: 14.0, 14.1, 21.0, 26.8, 27.0, 28.5, 28.9, 29.5, 29.6, 59.7, 60.0, 61.5, 61.5, 121.7, 121.9, 123.0, 127.4, 128.9, 128.9, 129.4, 152.0, 152.0, 169.9, 170.0, 203.9; IR (cm^{-1}): 3441, 3053, 2980, 2963, 2923, 2870, 1731, 1707, 1625, 1512, 1437, 1369, 1361, 1269, 1148, 1021, 812, 747, 418; HRMS m/z (ESI) calcd for $C_{26}H_{28}NaO_4$ $[M + Na]^+$ 427.1885 found 427.1894.

Ethyl- 2-acetyl-5-(4-methoxyphenyl)-5-(6-methyl-2,4-dioxo-3,4-dihydro-2H-pyran-3-yl)pentanoate



(8a) Colorless liquid; ^{1} HNMR ($CDCl_3$): 1.17 (m, 3H), 1.79 (m, 2H), 1.98 (m, 1H), 2.05 (s, 3H), 2.13 (s, 3H), 2.24 (m, 1H), 3.44 (dt, J_a = 18.8 Hz, J_b = 6.8 Hz, 1H), 3.66 (s, 3H), 4.09 (q, J = 6.8 Hz, 2H), 4.18 (m, 1H), 5.98 (s, 1H), 6.70 (d, J = 8.4 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H); ^{13} CNMR: 14.0, 19.5, 26.9, 27.0, 28.8, 28.9, 29.0, 29.1, 38.7, 39.0, 55.1, 59.6, 59.9, 61.4, 101.7, 104.5, 113.4, 128.8, 128.9, 135.4, 135.5, 157.9, 160.6, 166.9, 167.7, 169.8, 169.9, 203.6; IR (cm^{-1}): 3065, 3032, 2958, 2932, 2658, 1737, 1712, 1671, 1634, 1574, 1511, 1447, 1404, 1375, 1178, 1035, 997, 913, 832, 732, 623, 547; HRMS m/z (ESI) calcd for $C_{21}H_{24}NaO_7$ $[M + Na]^+$ 411.1420 found 411.1412.

1,1'-(1-(4-Methoxyphenyl)-2,3,4,9-tetrahydro-1H-carbazole-4,4-diyl)diethanone (7a)

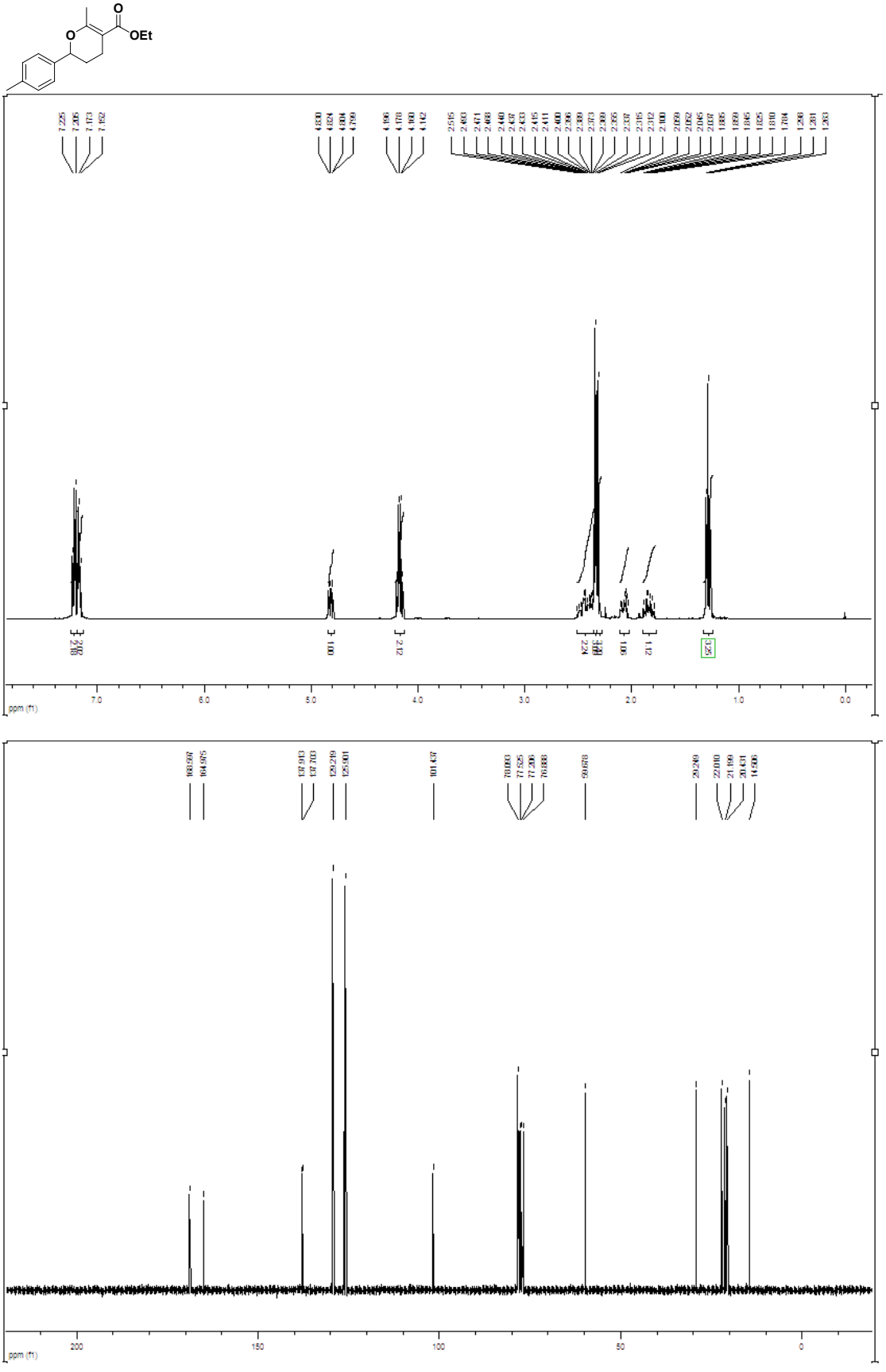


Brown solid, mp = 140-142 ^{o}C; ^{1} HNMR ($CDCl_3$): 1.75-1.83 (m, 1H), 2.18-2.25 (m, 1H), 2.27 (s, 3H), 2.28 (s, 3H), 2.33-2.39 (m, 1H), 2.55-2.61 (m, 1H), 3.76 (s, 3H), 4.21 (t, J = 6.4Hz, 1H), 6.80 (dt, J_a = 2.8Hz, J_b = 8.8Hz, 2H), 6.91 (m, 2H), 7.03 (d, J = 7.2Hz, 2H), 7.14 (sept, J = 2.4Hz, 1H), 7.37 (d, J = 8.0Hz, 1H), 9.12 (s, 1H); ^{13} CNMR: 28.1, 28.2, 28.6, 31.6, 38.3, 55.2, 67.8, 111.2, 113.8, 115.3, 119.5, 120.0, 122.5, 126.4, 128.9, 130.5, 136.6, 136.9, 158.1, 206.5, 207.0; IR (cm^{-1}): 3379, 3049, 2996, 2932, 2861, 2831, 2698, 1610, 1511, 1457, 1433, 1414, 1354, 1293, 1244, 1210, 1176, 1147, 1110, 1028, 962, 830, 747, 682, 578; HRMS m/z (ESI) calcd for $C_{23}H_{23}NNaO_3$ $[M + Na]^+$ 384.1576 found 384.1568.

References

1. Y. Gu, R. De Sousa, G. Frapper, C. Bachmann, J. Barrault, F. Jérôme, *Green Chem*. **2009**, *11*, 1968-1972.

2. Y. Gu, J. Barrault, F. Jerome, *Adv. Synth. Catal.* **2009**, *351*, 3269-3278.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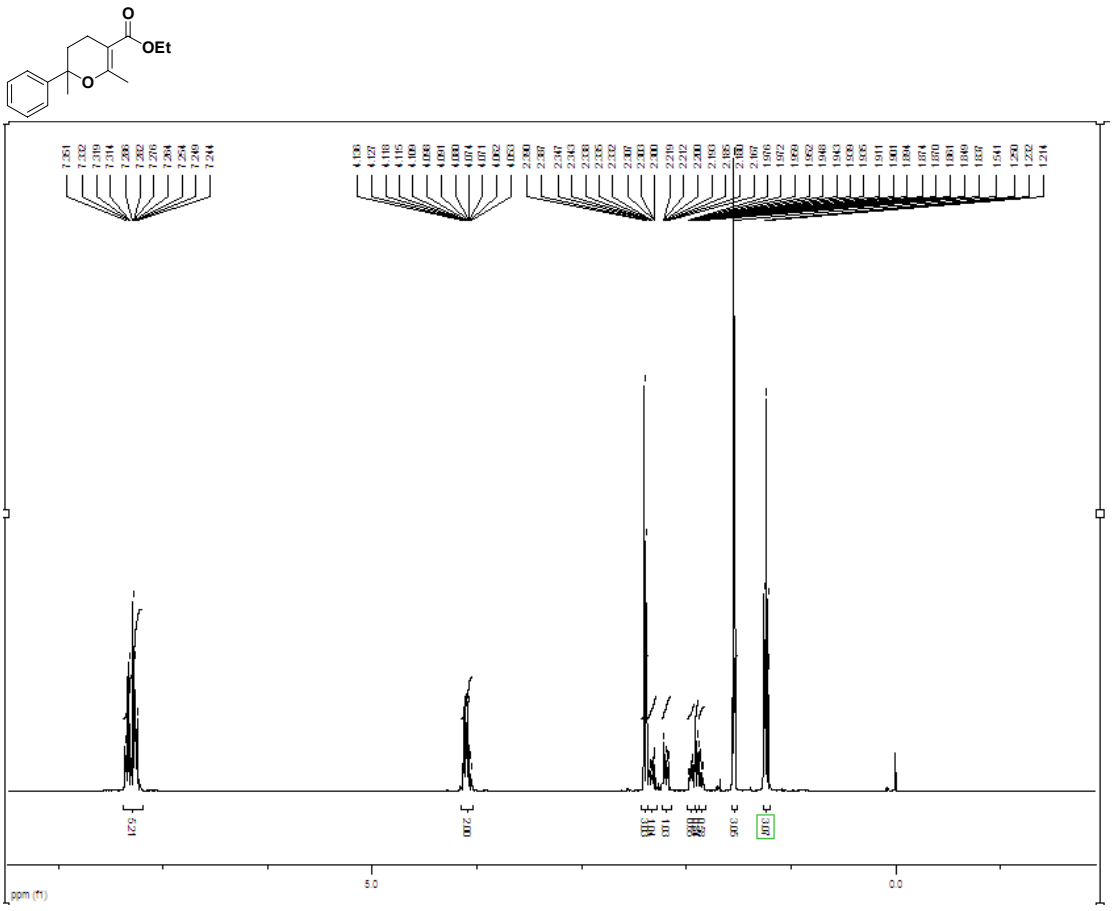
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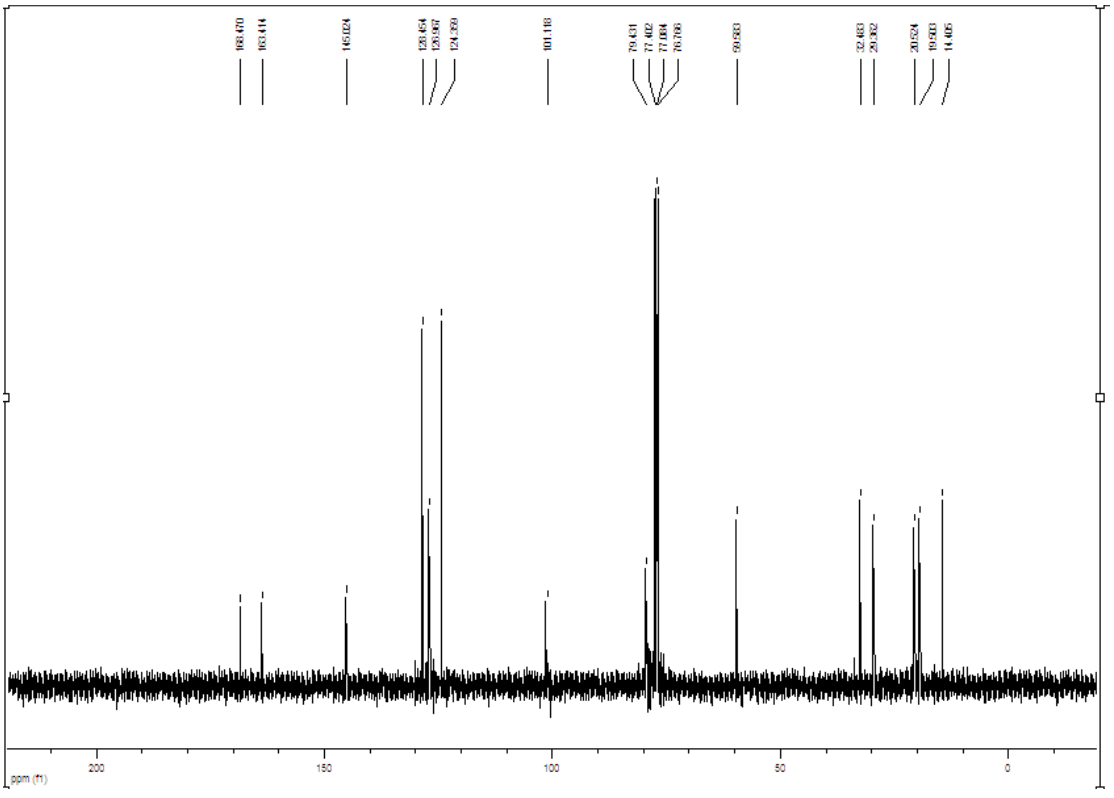
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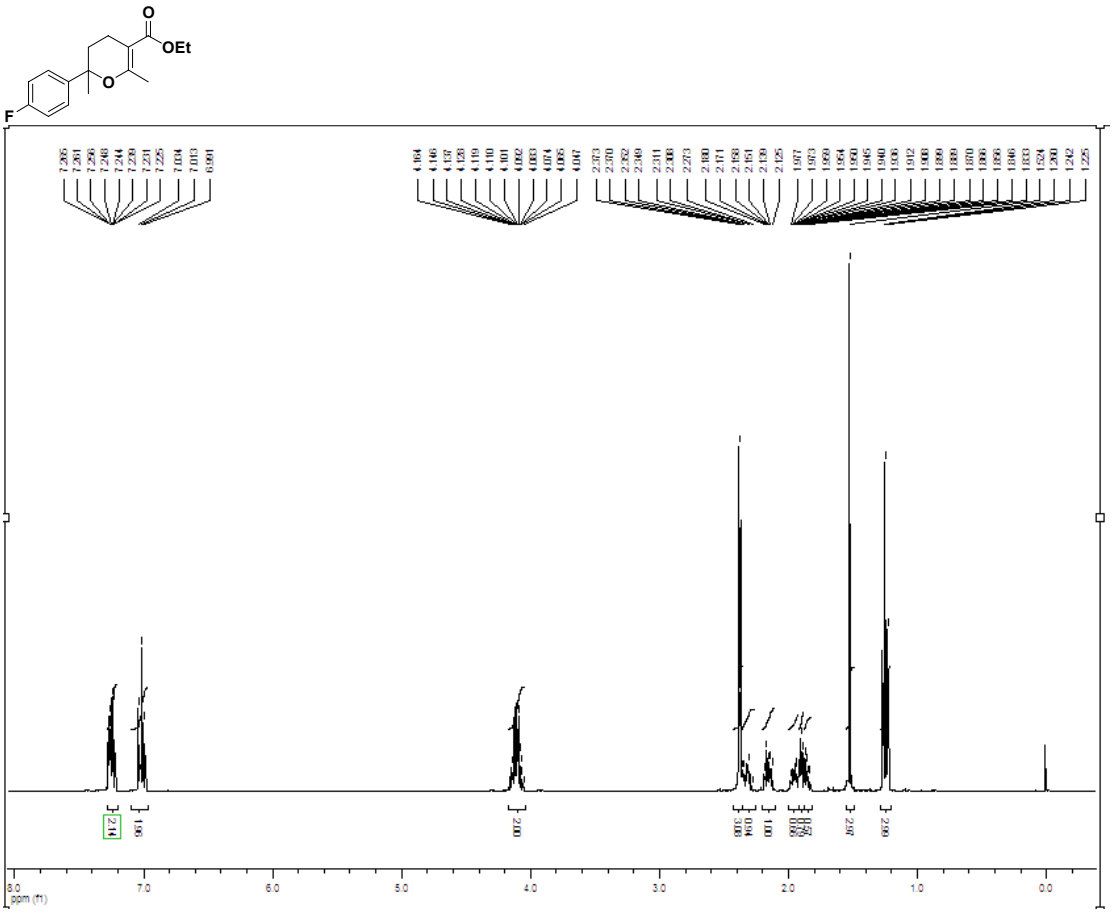
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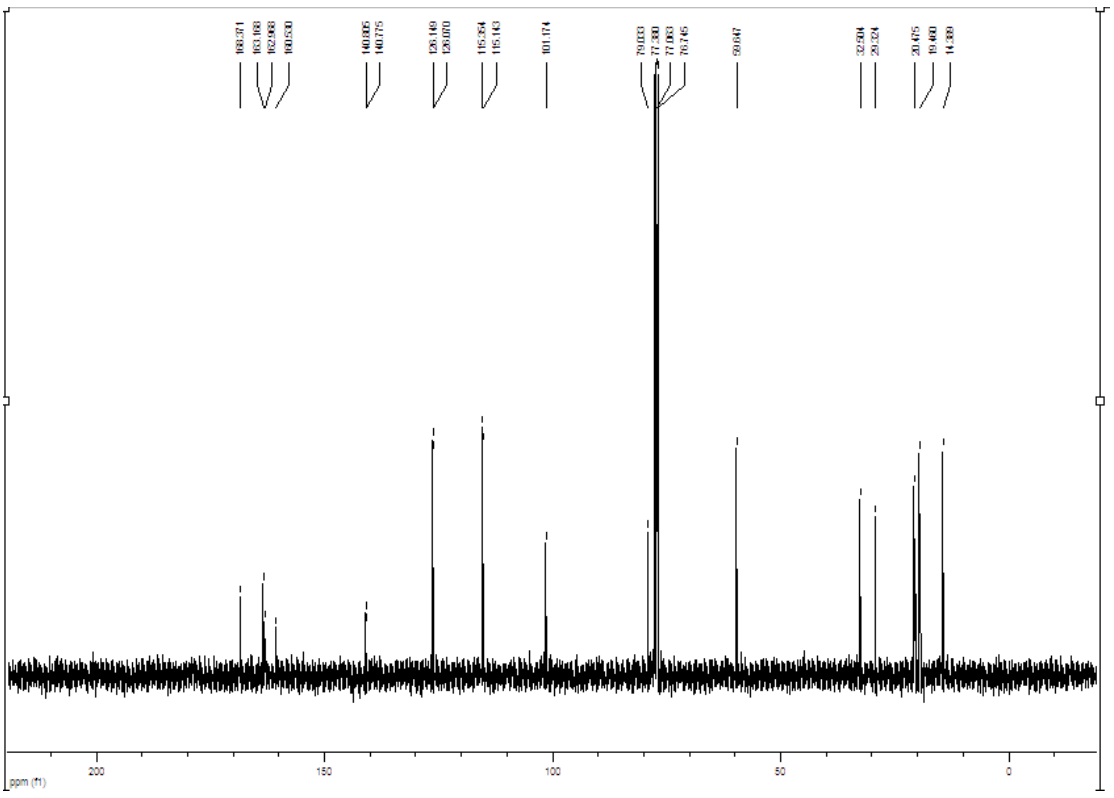

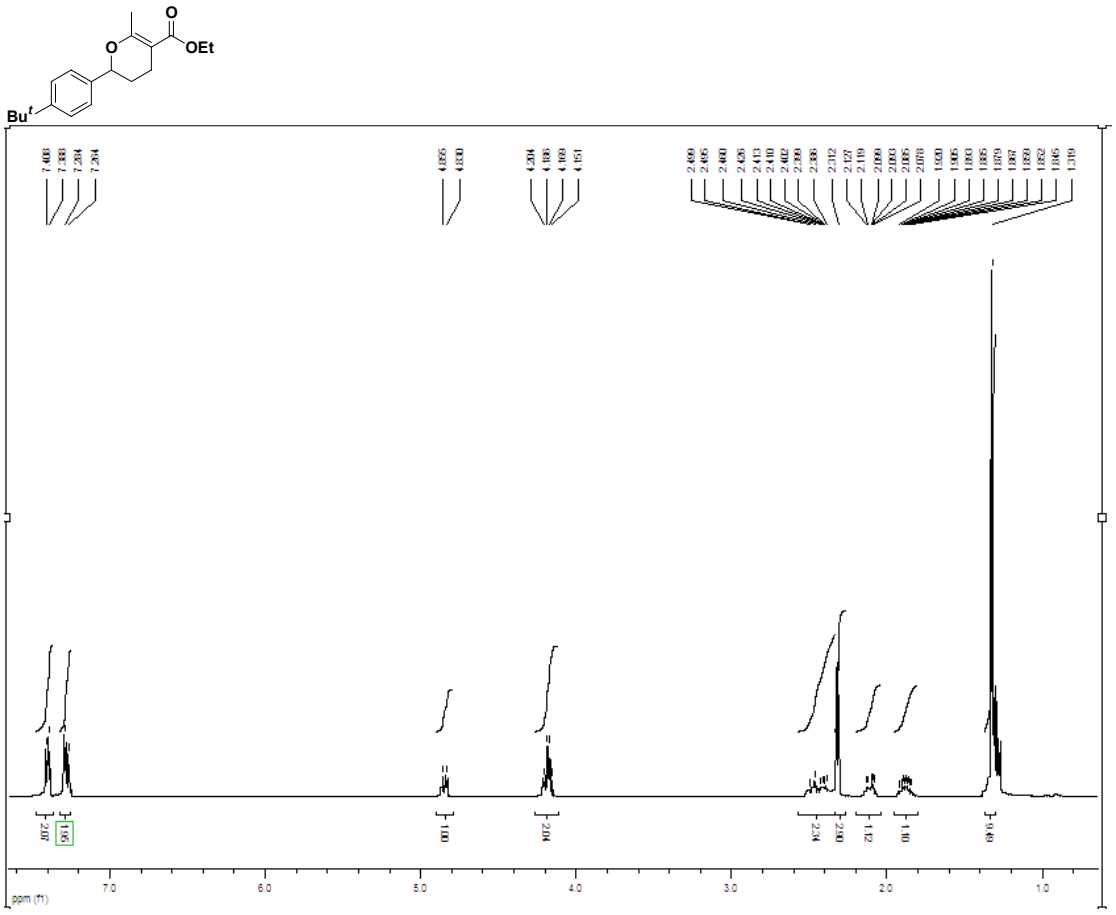
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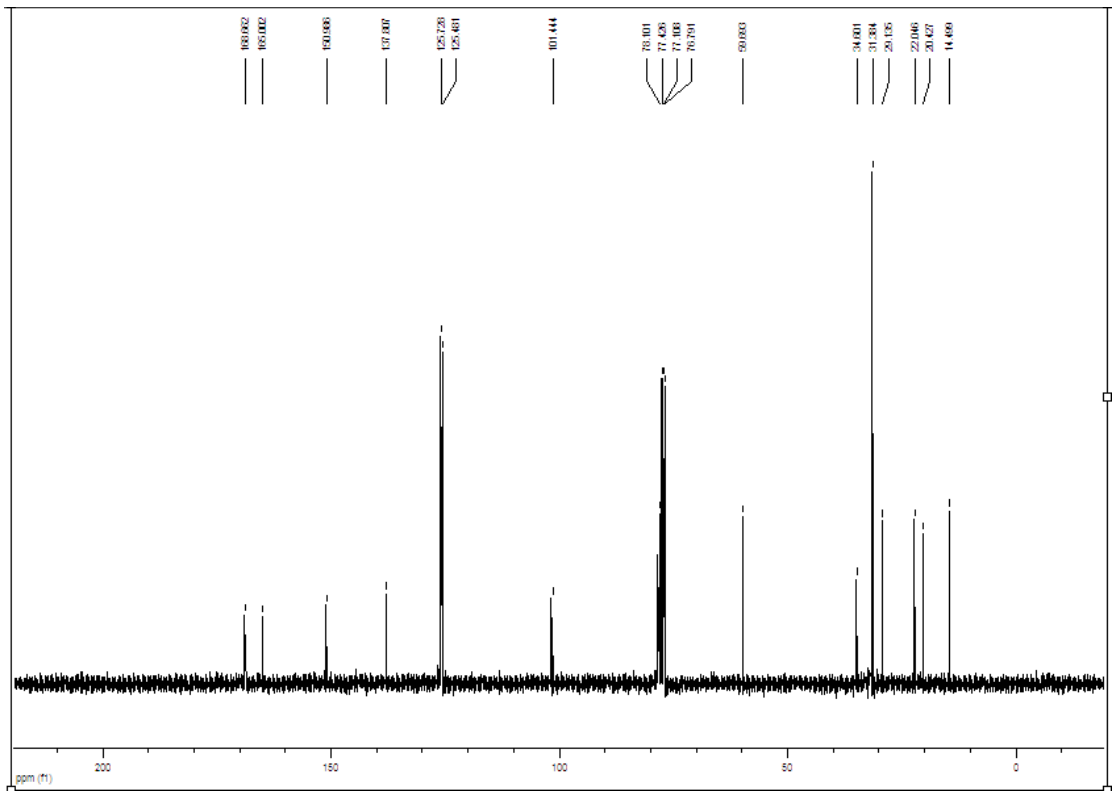
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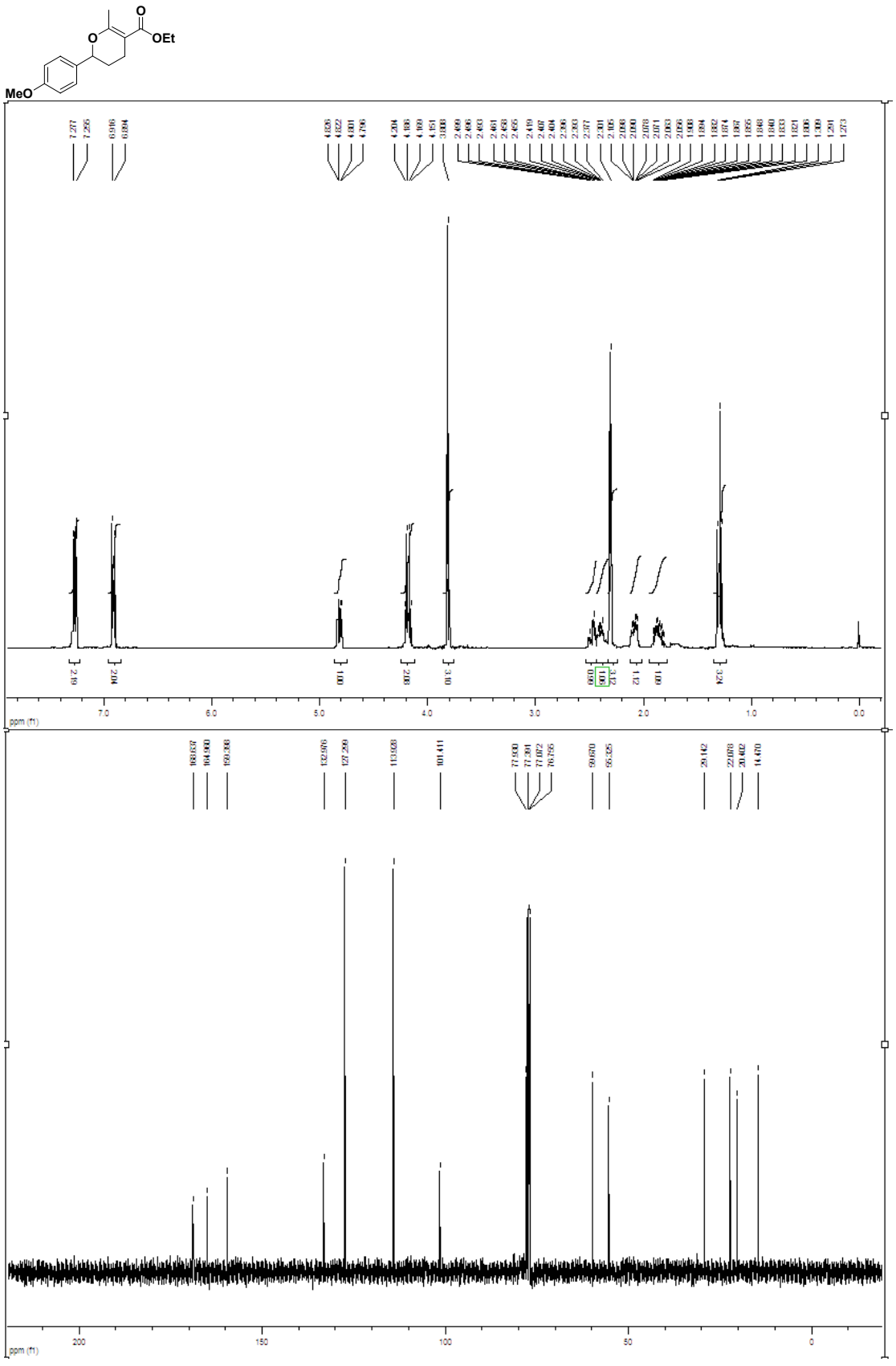
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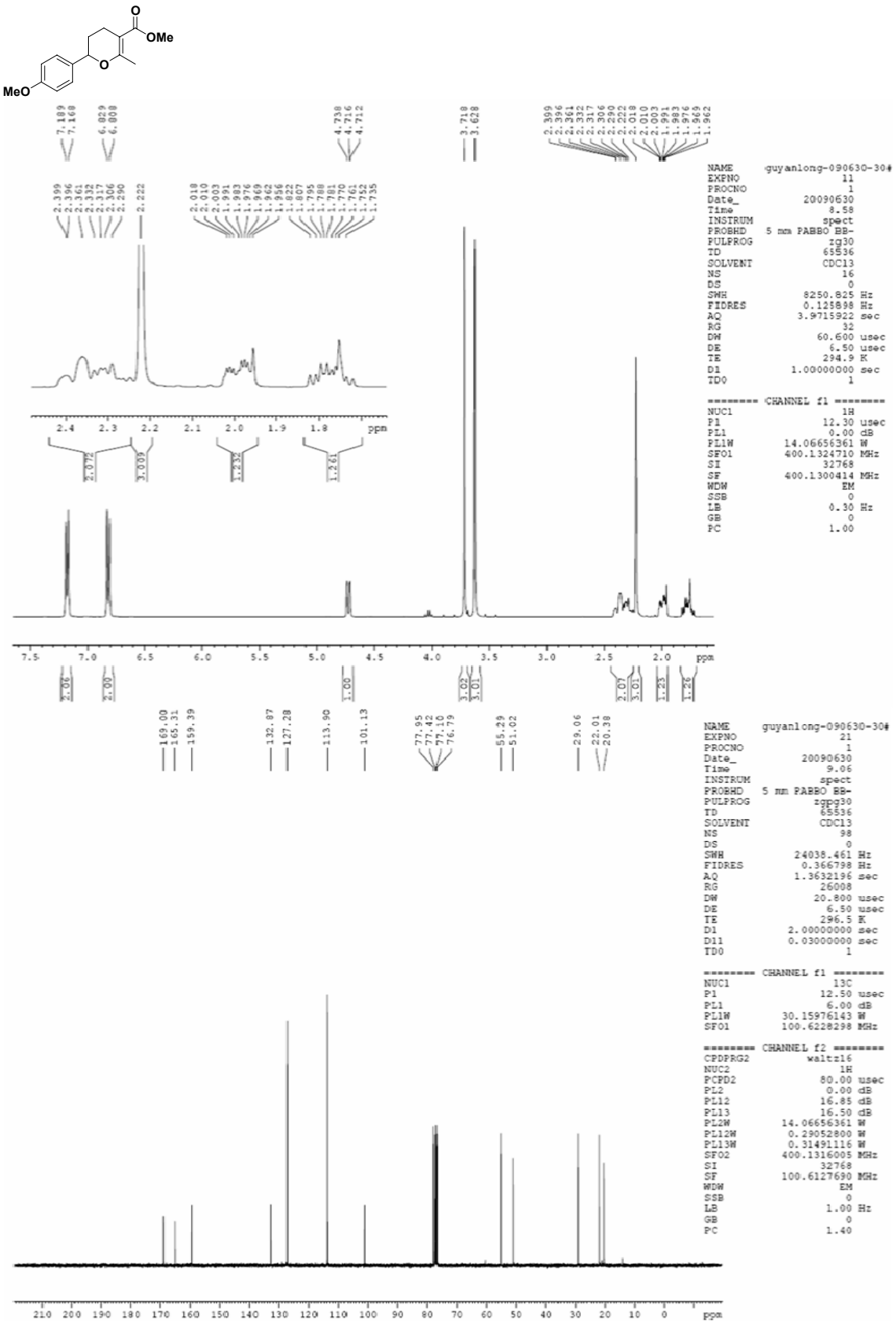

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RG	32
DW	60.600 usec
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TE	294.9 K
D1	1.00000000 sec
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SI	32768
SF	400.1300414 MHz
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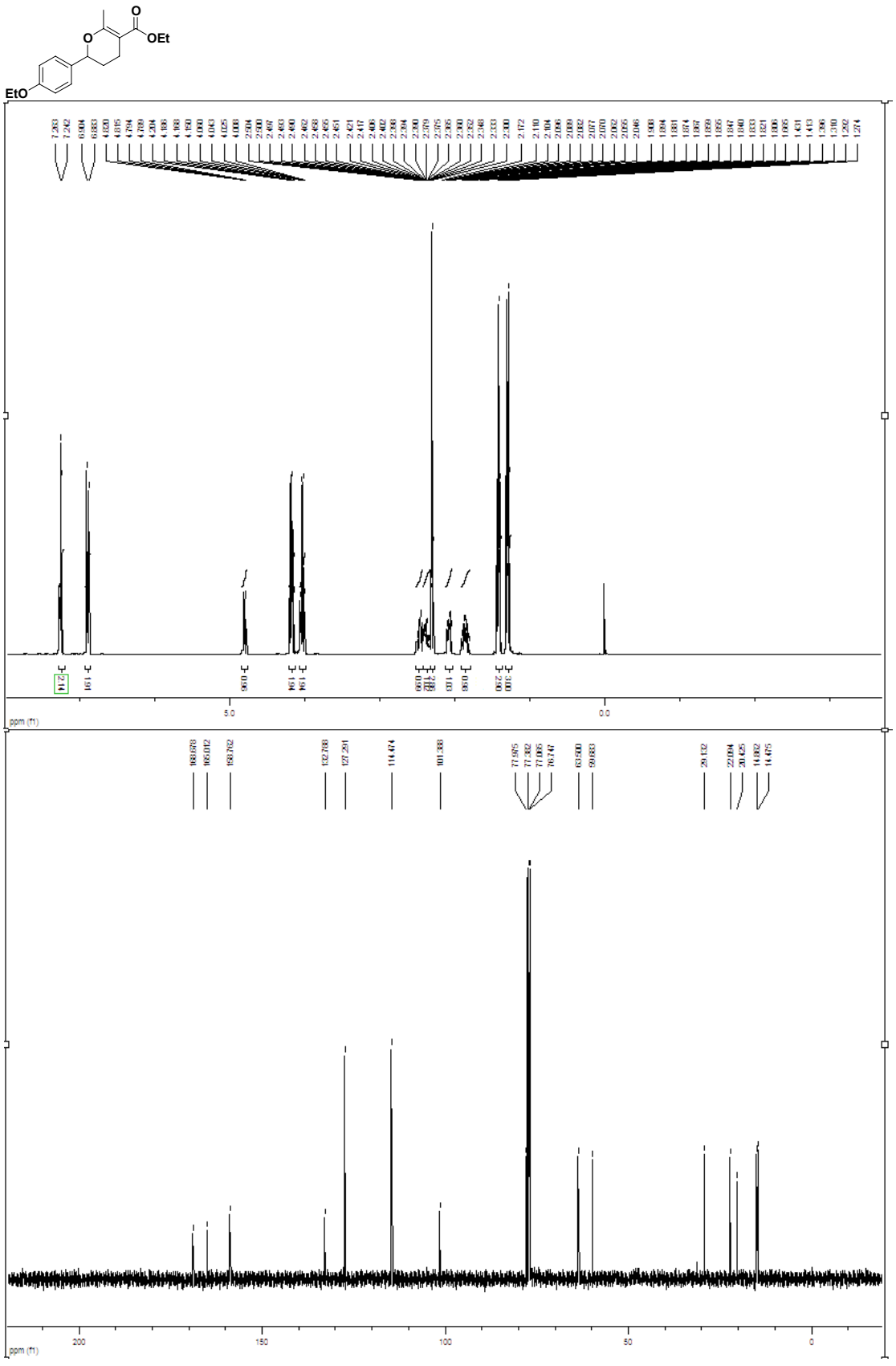
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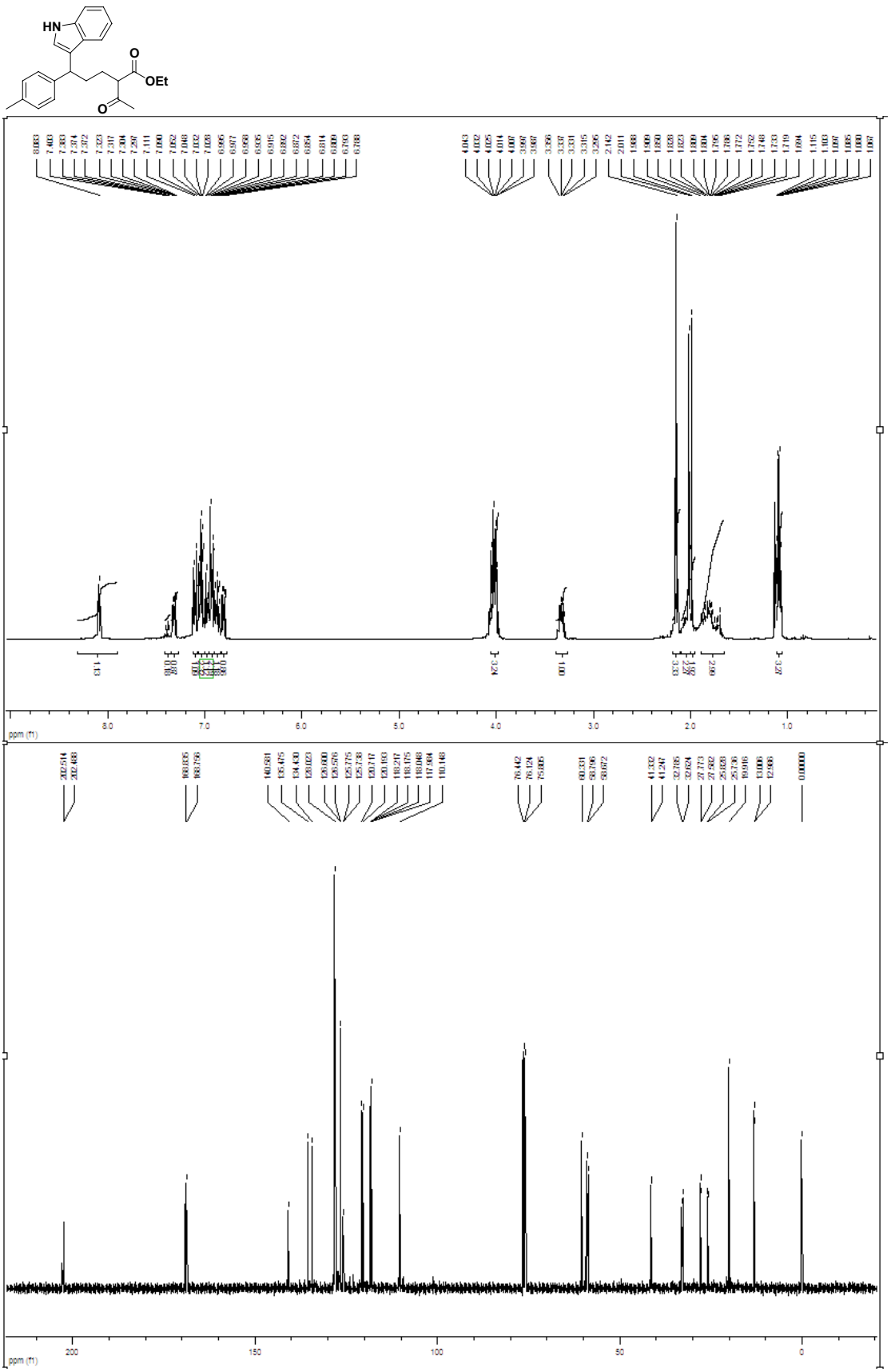
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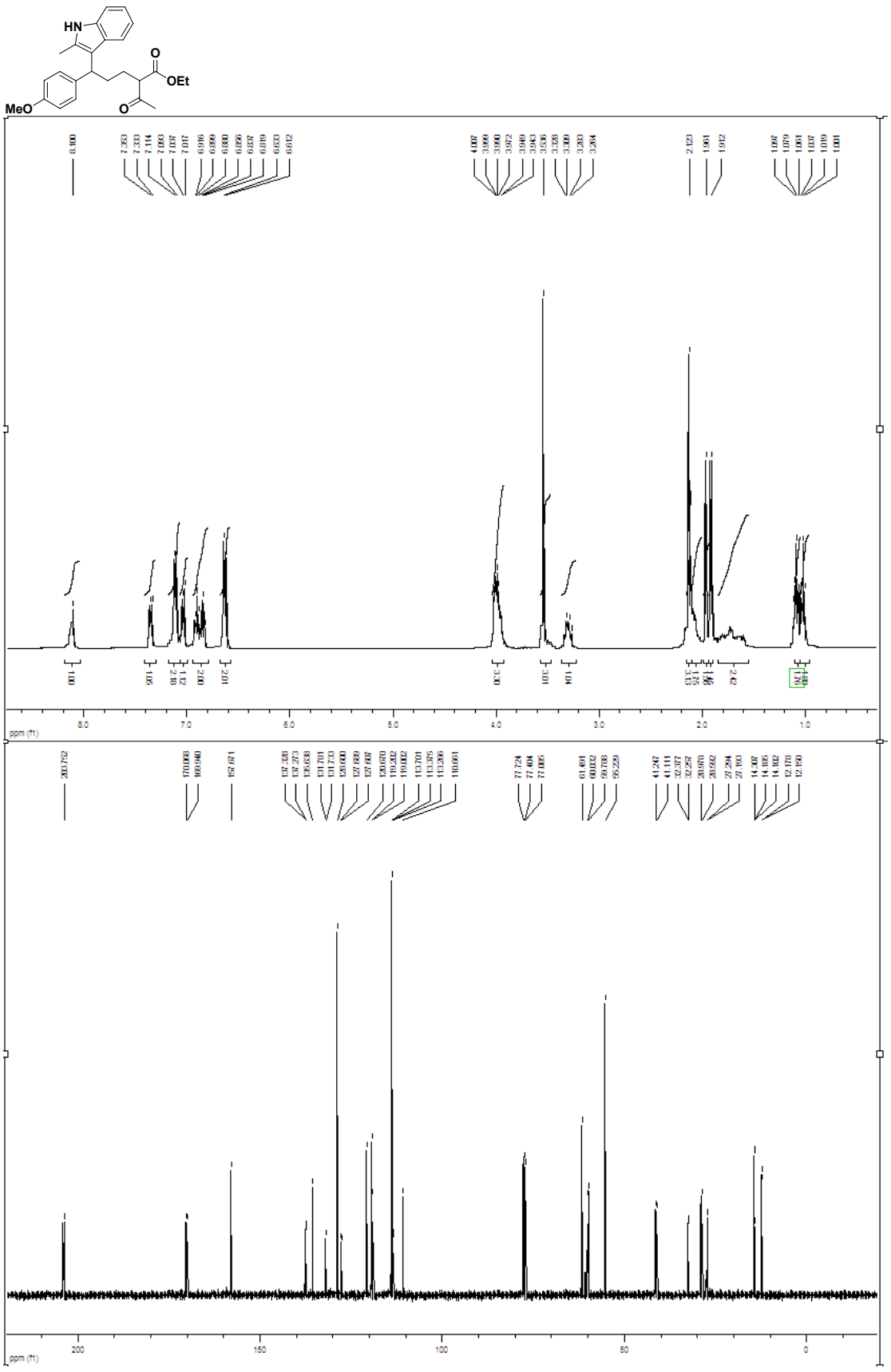
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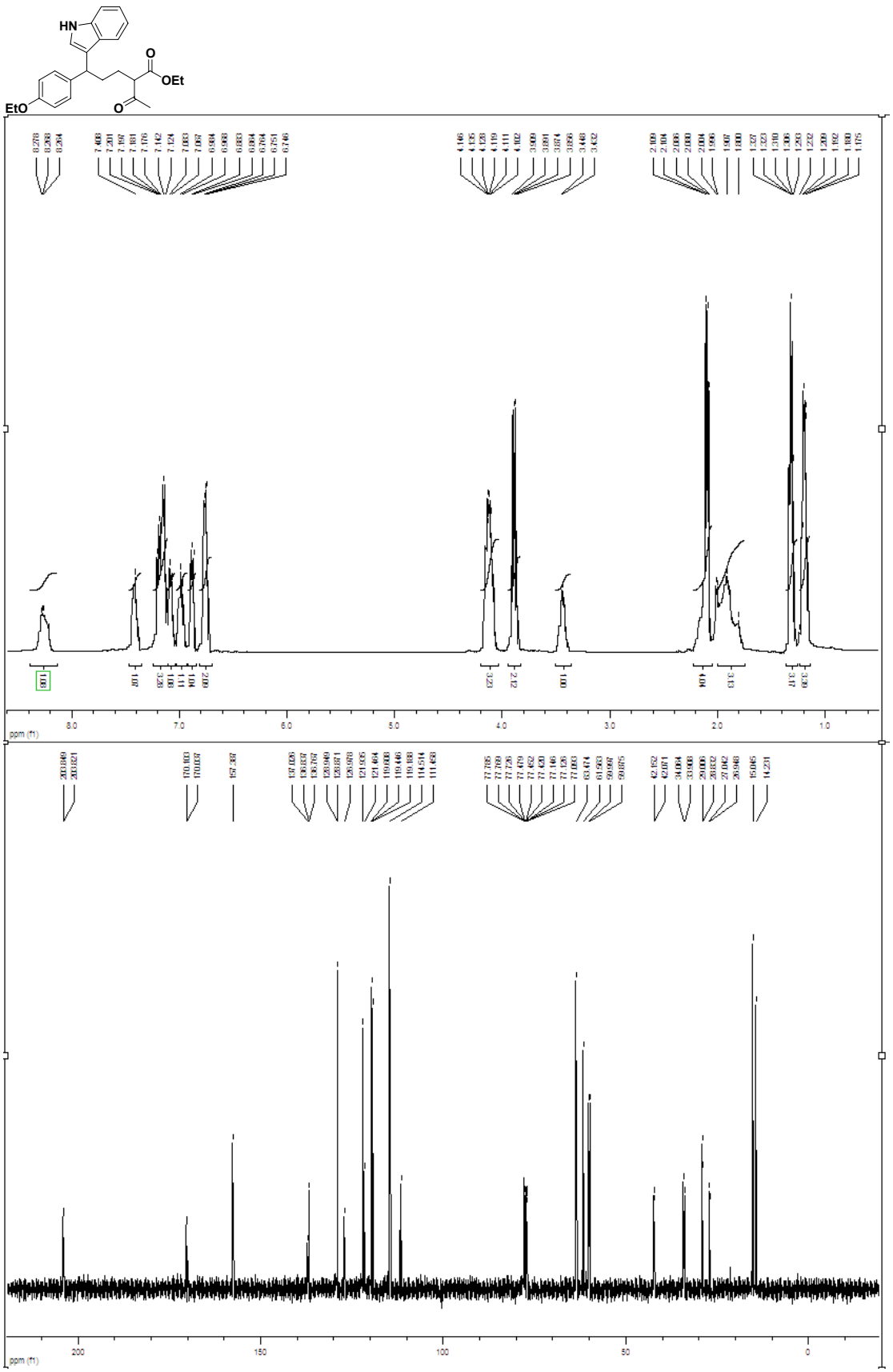
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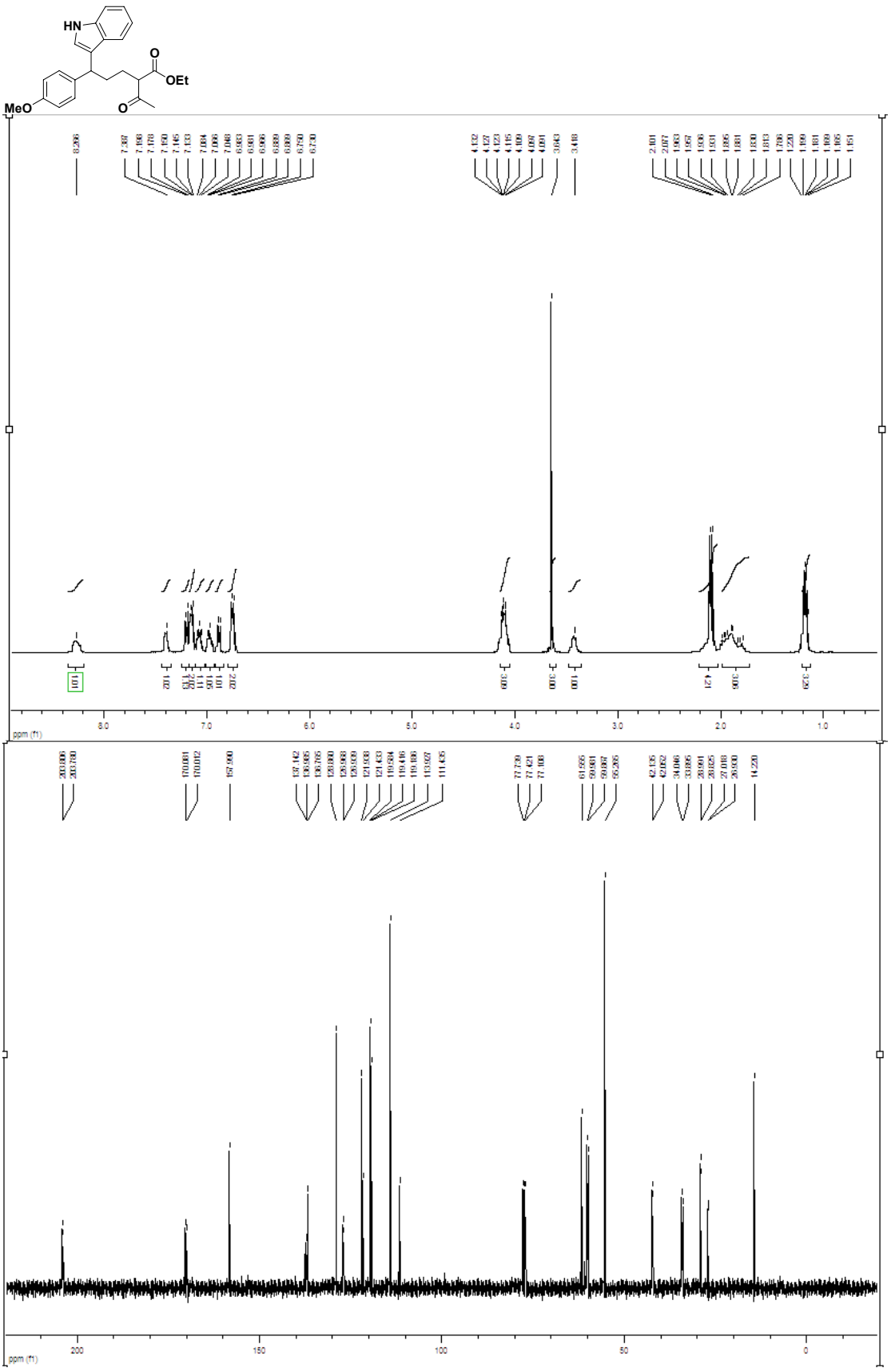
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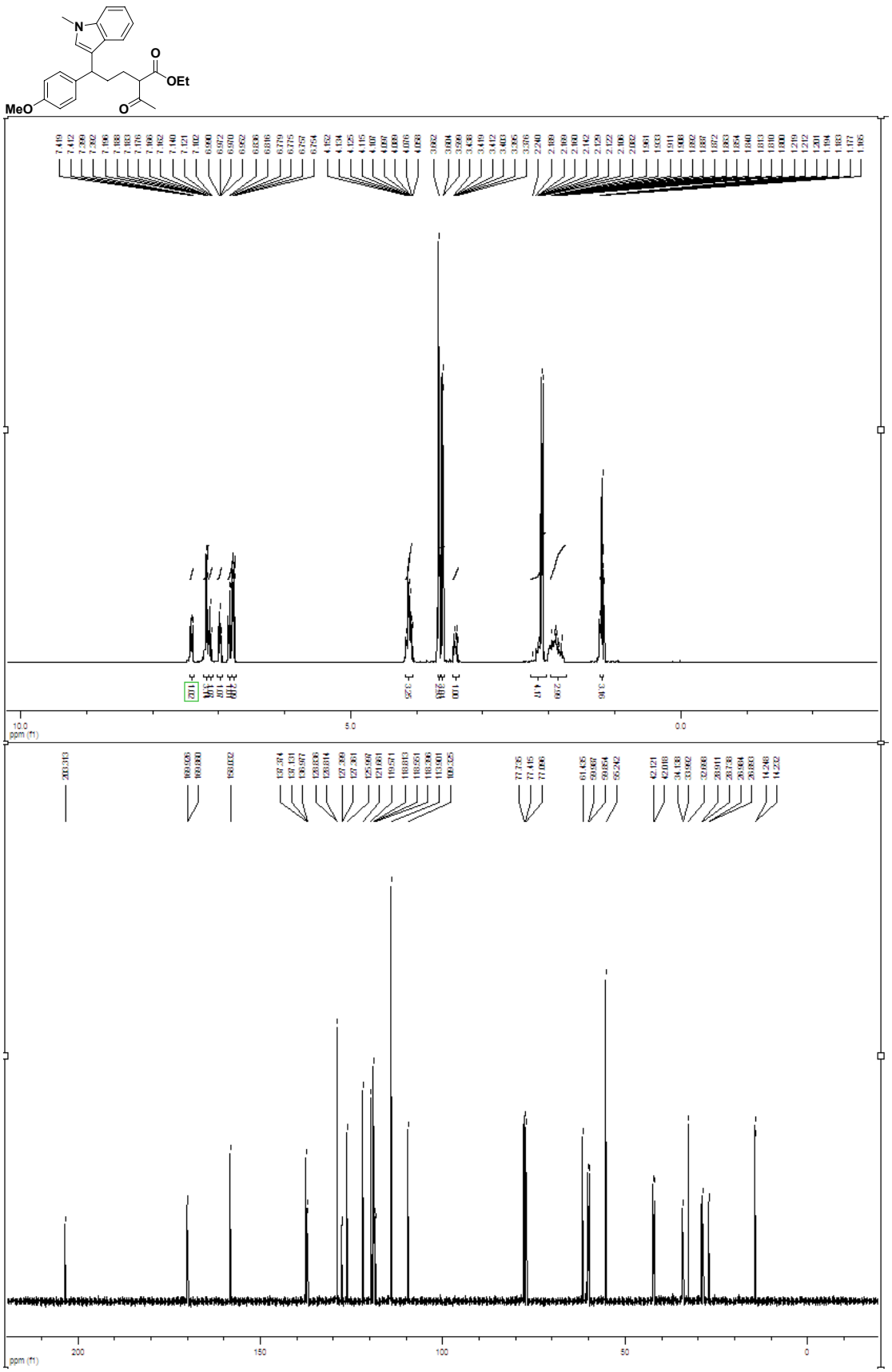
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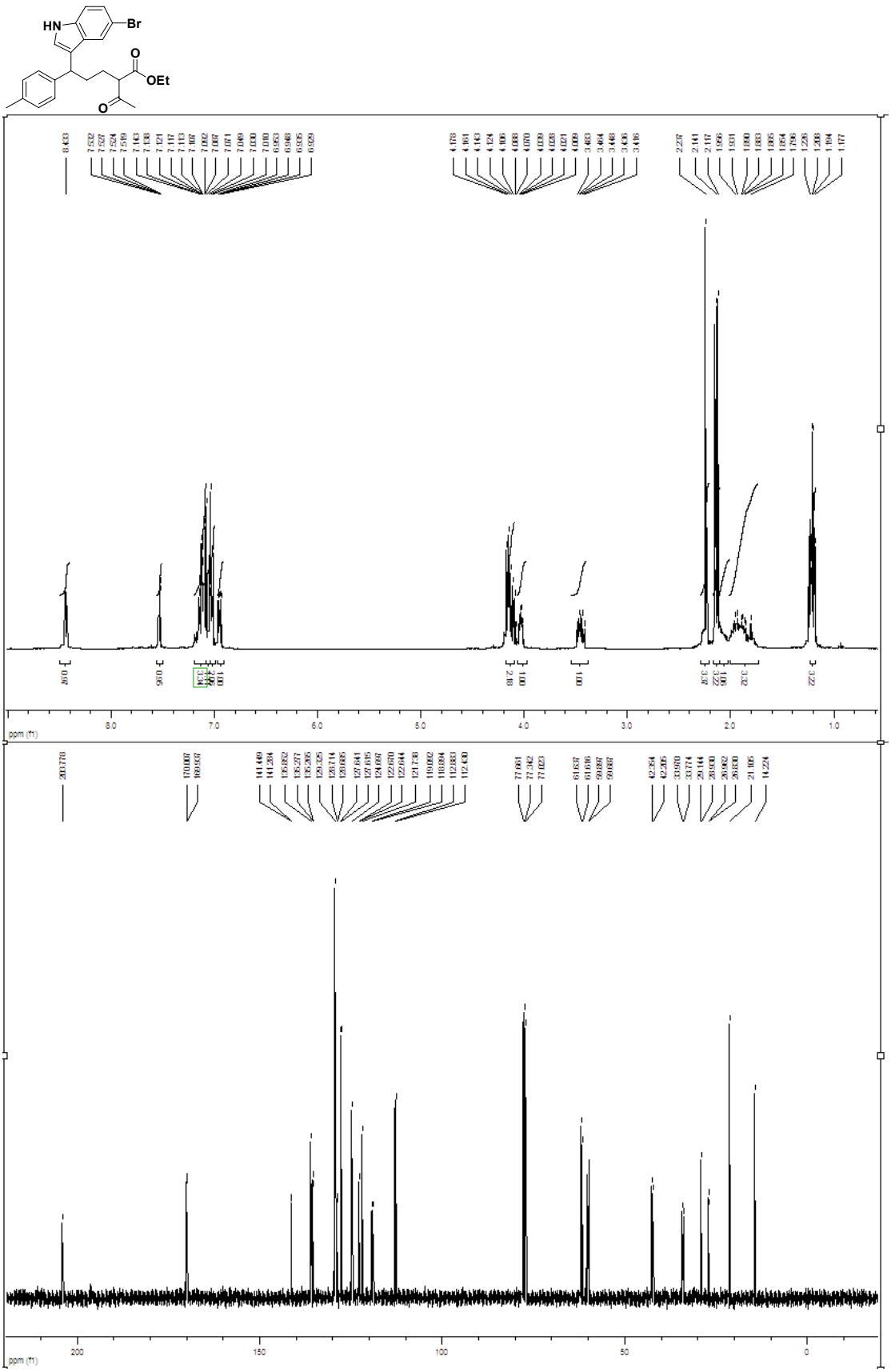
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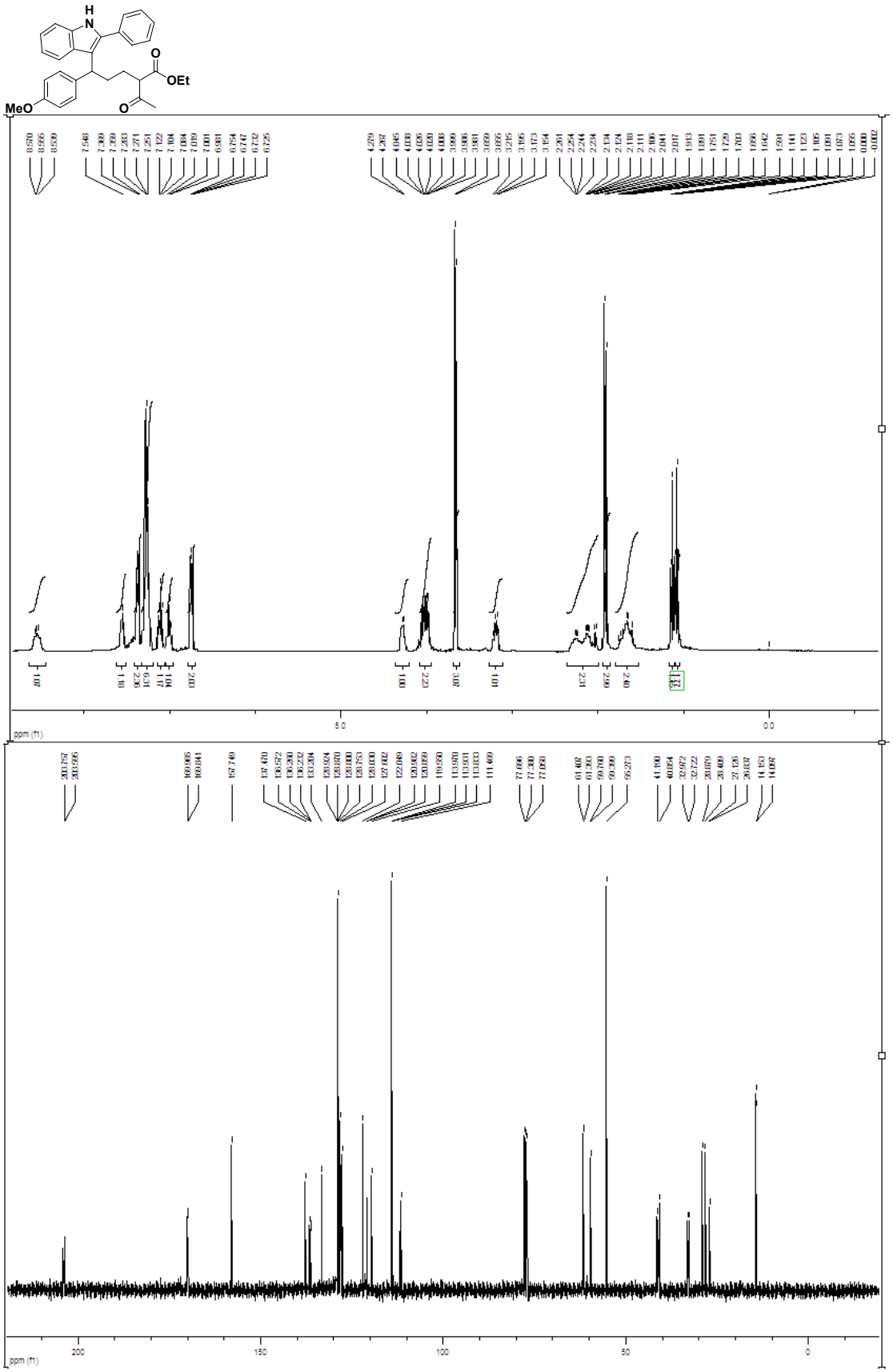
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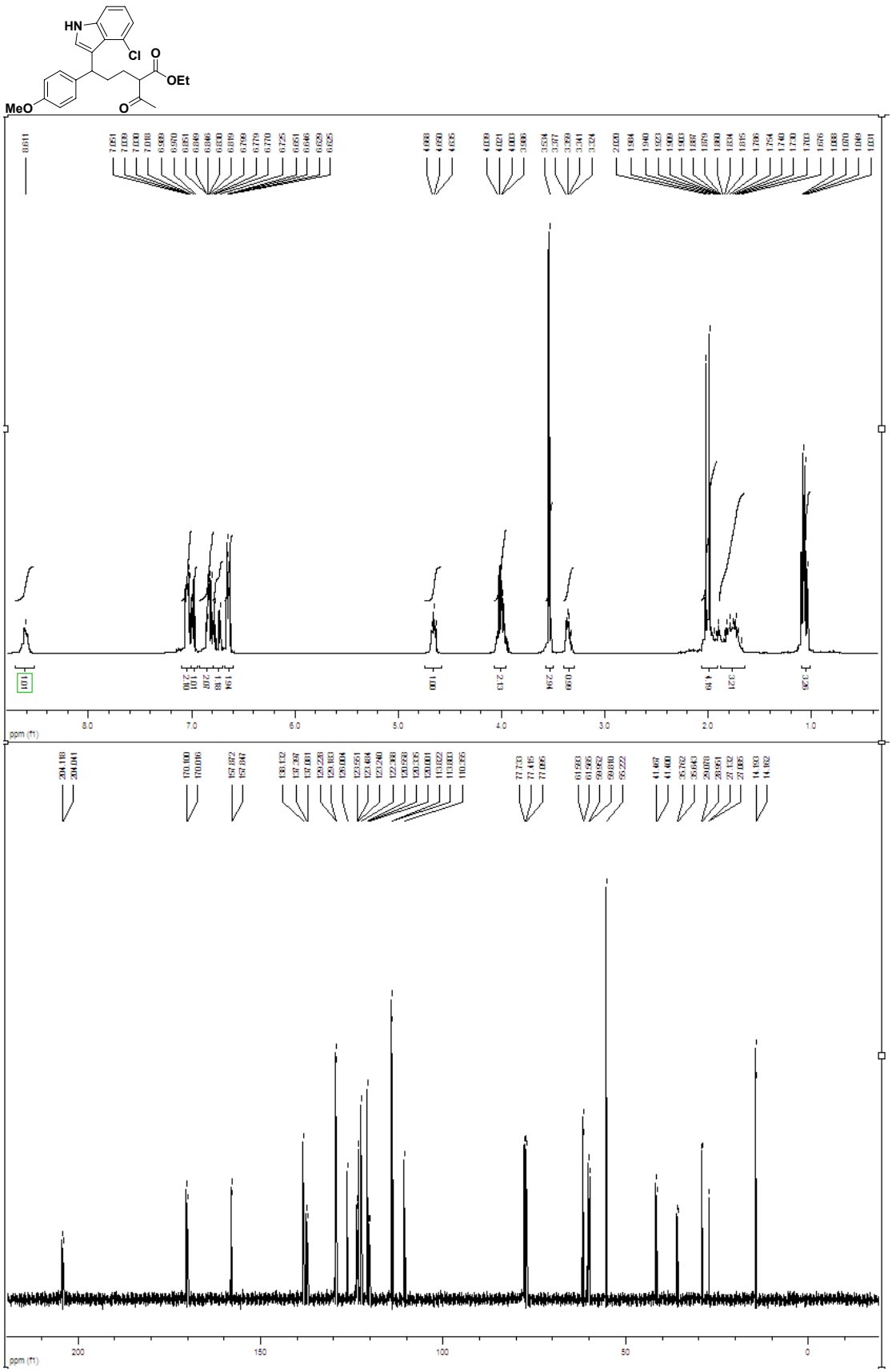
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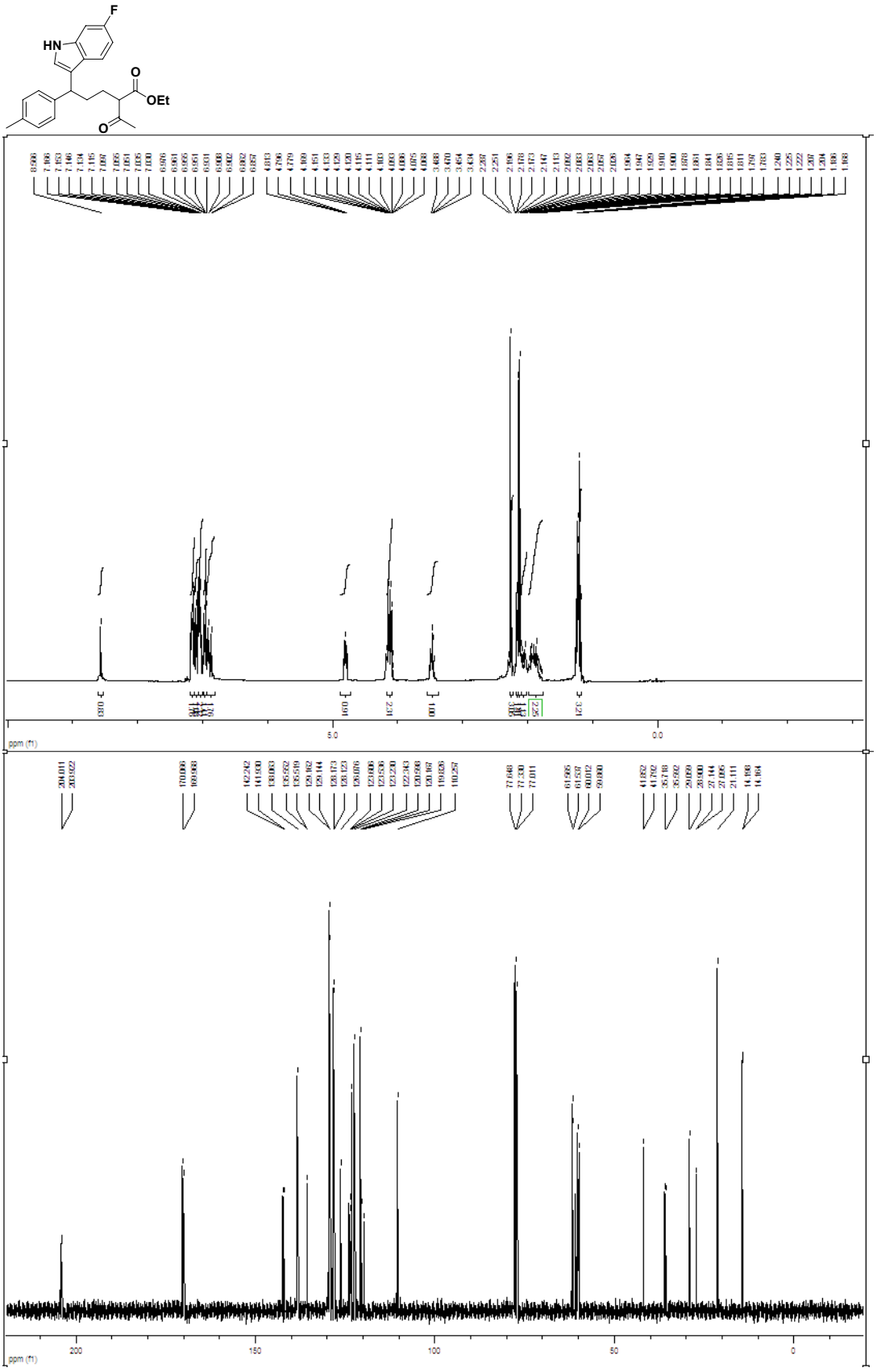
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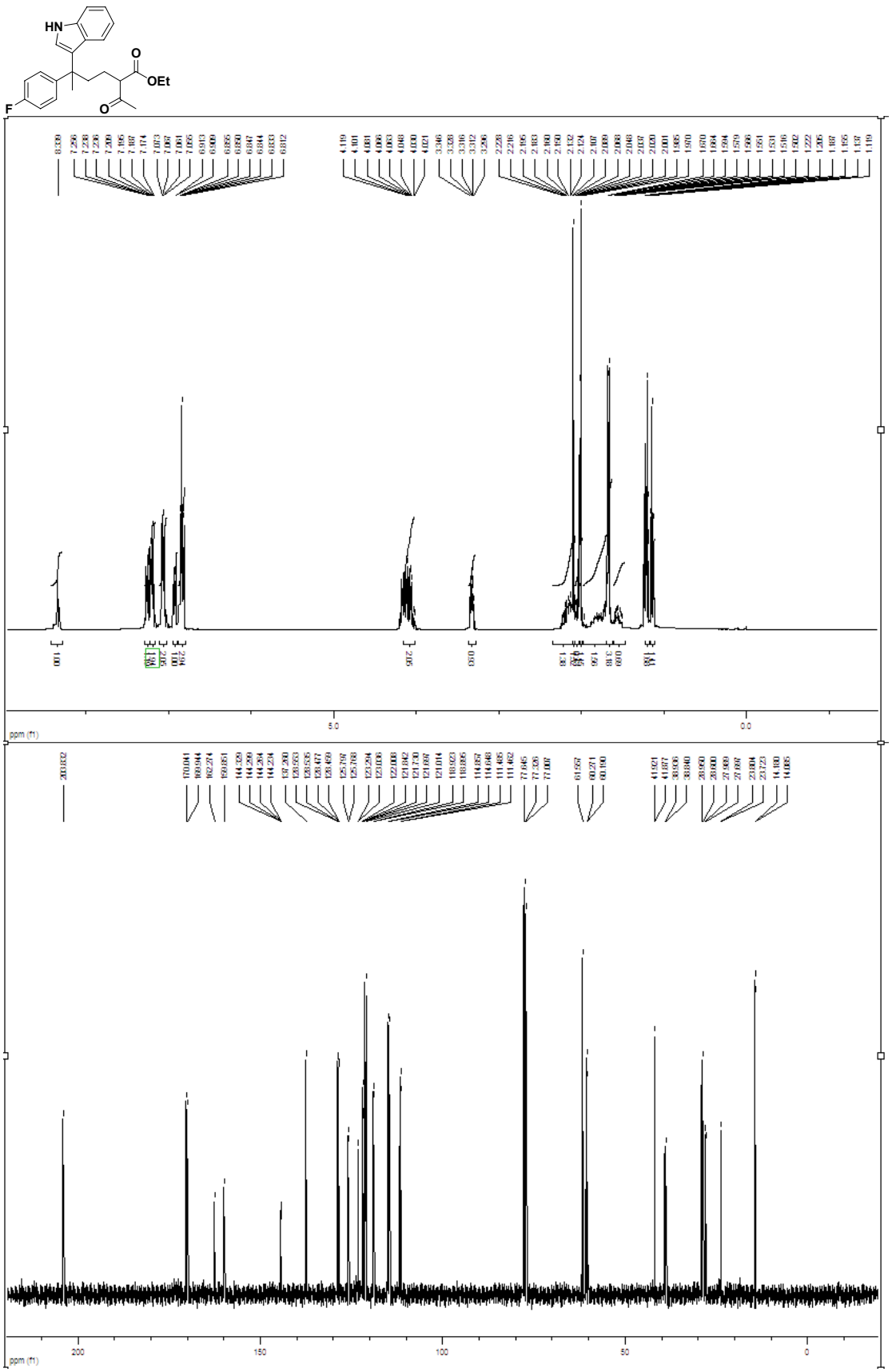
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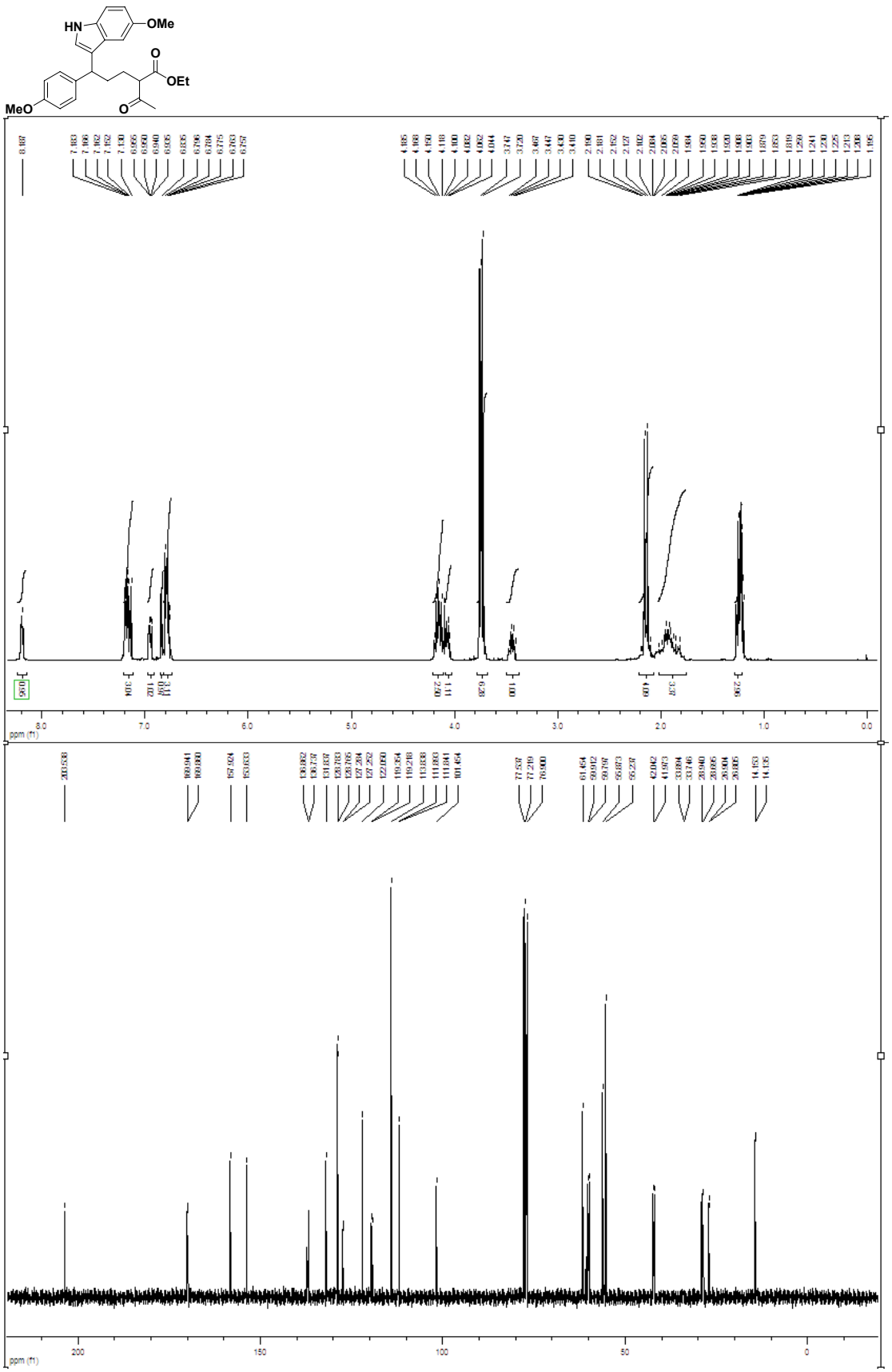
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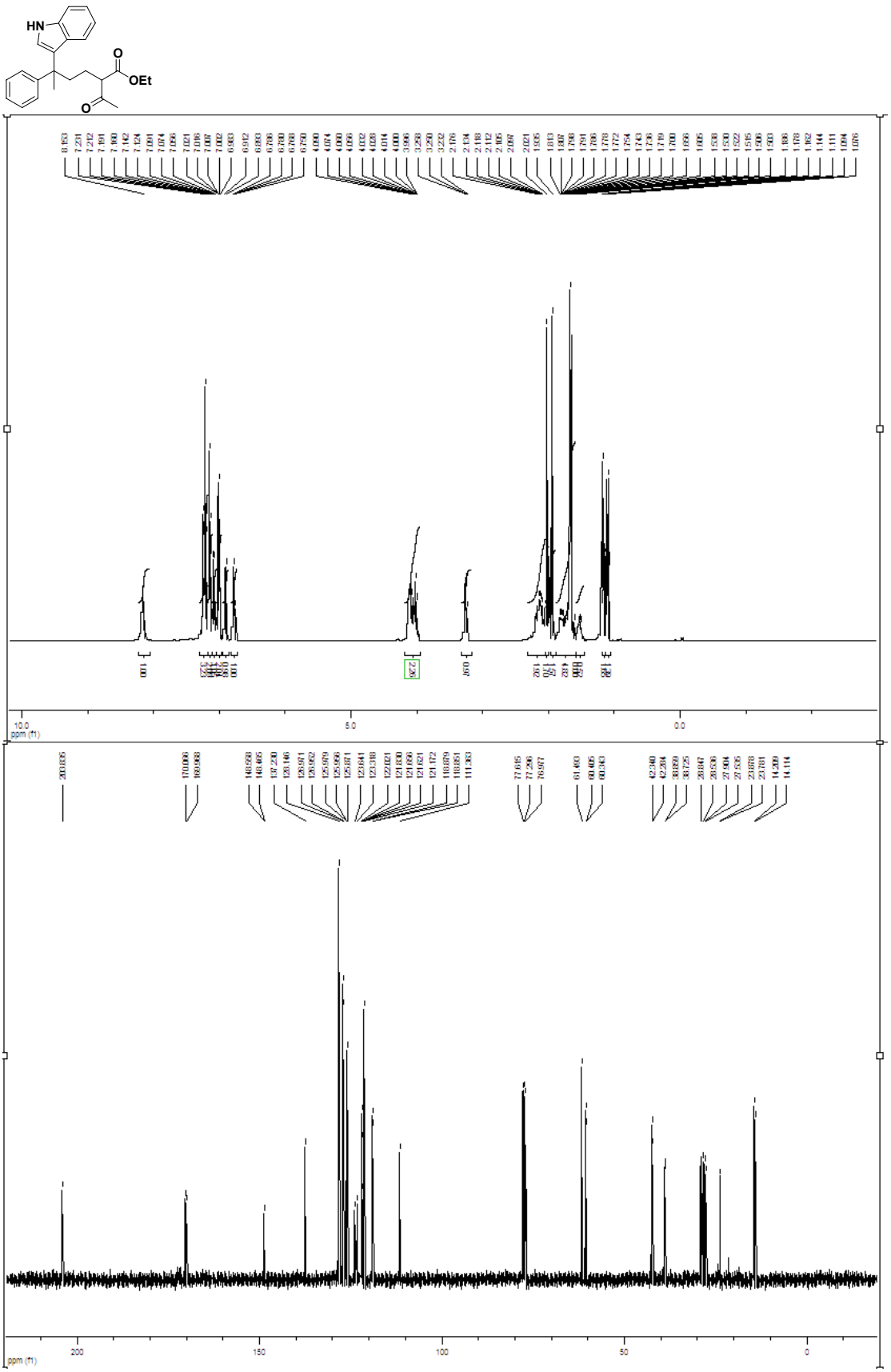
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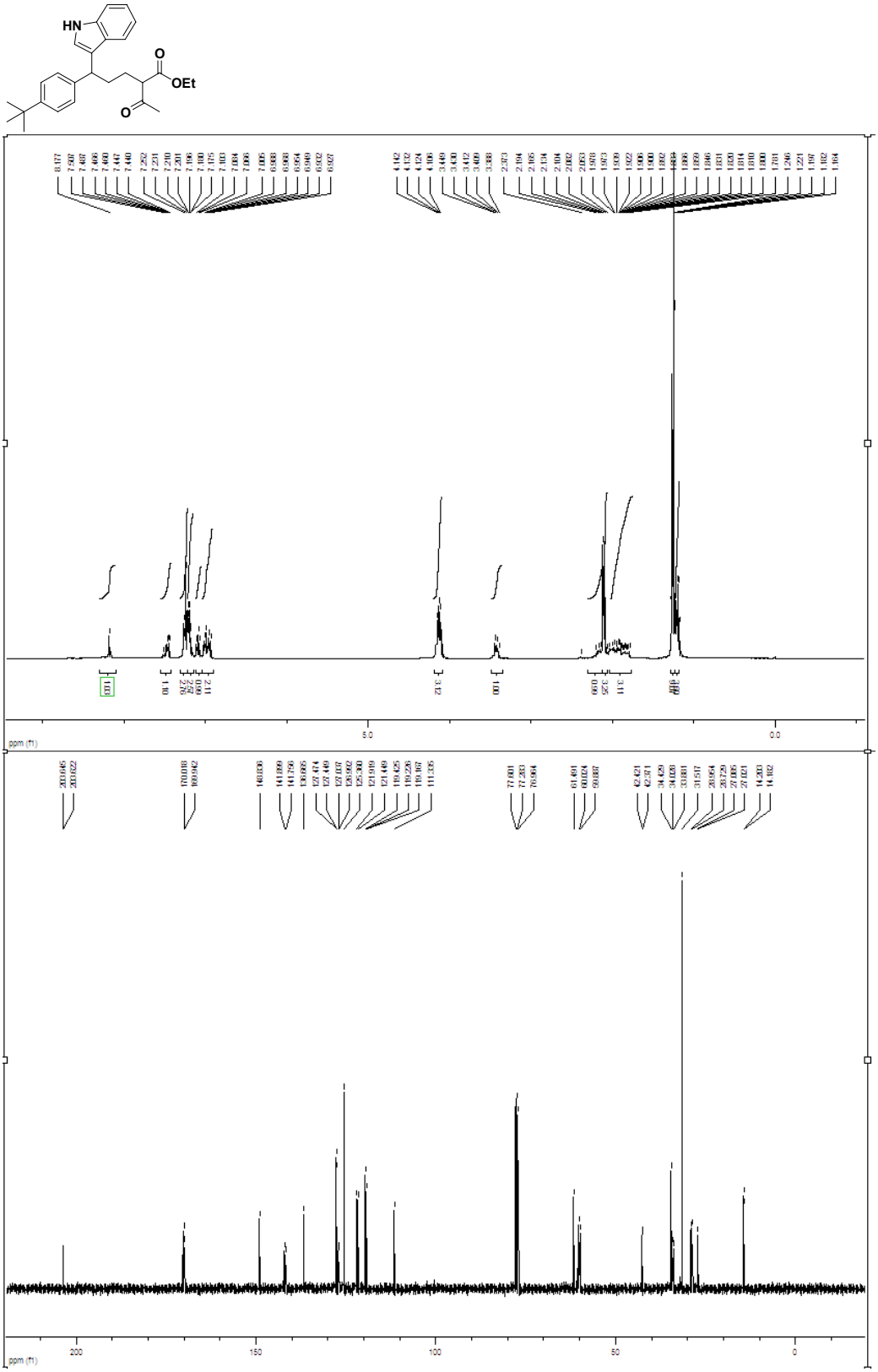
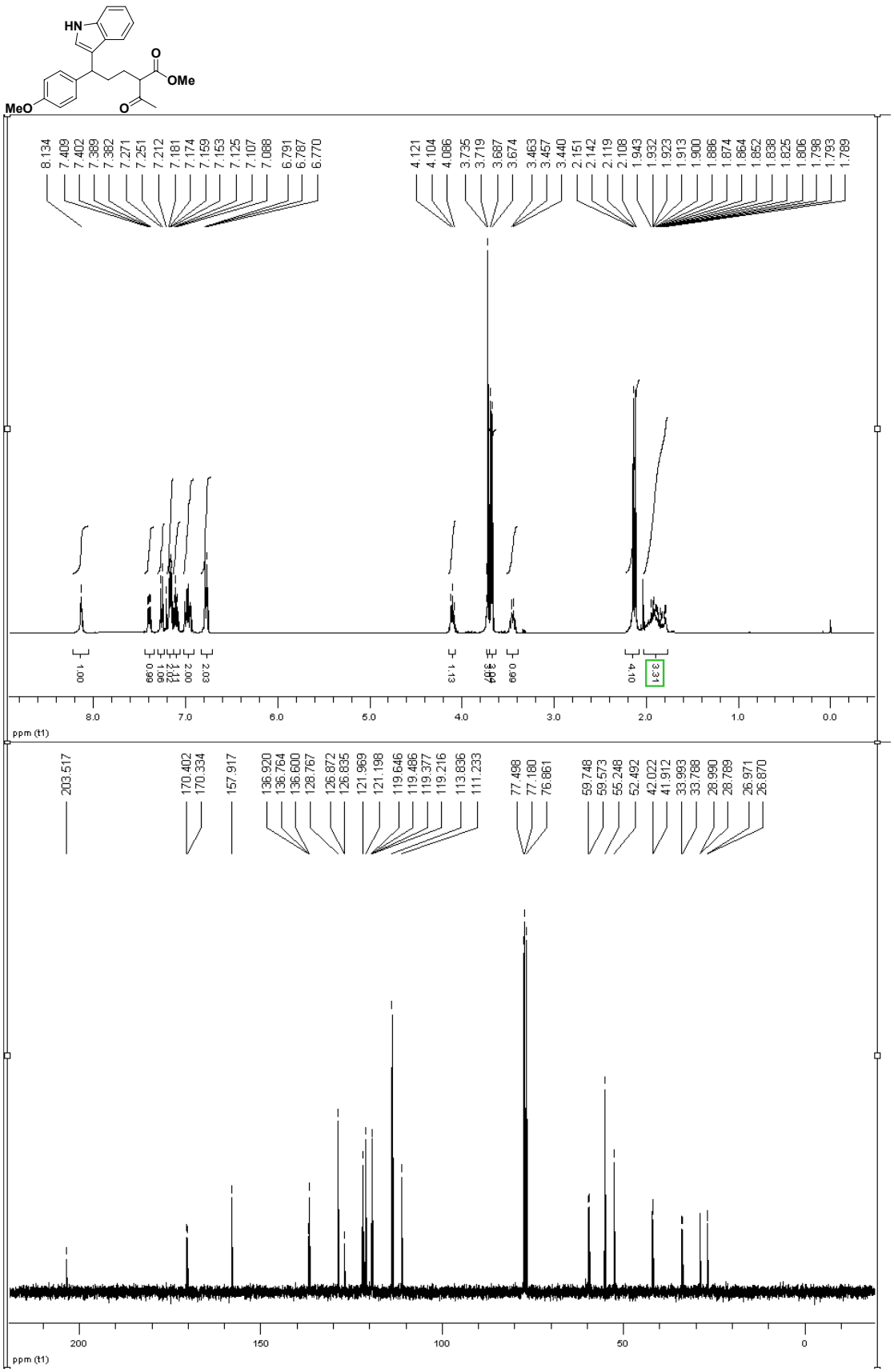
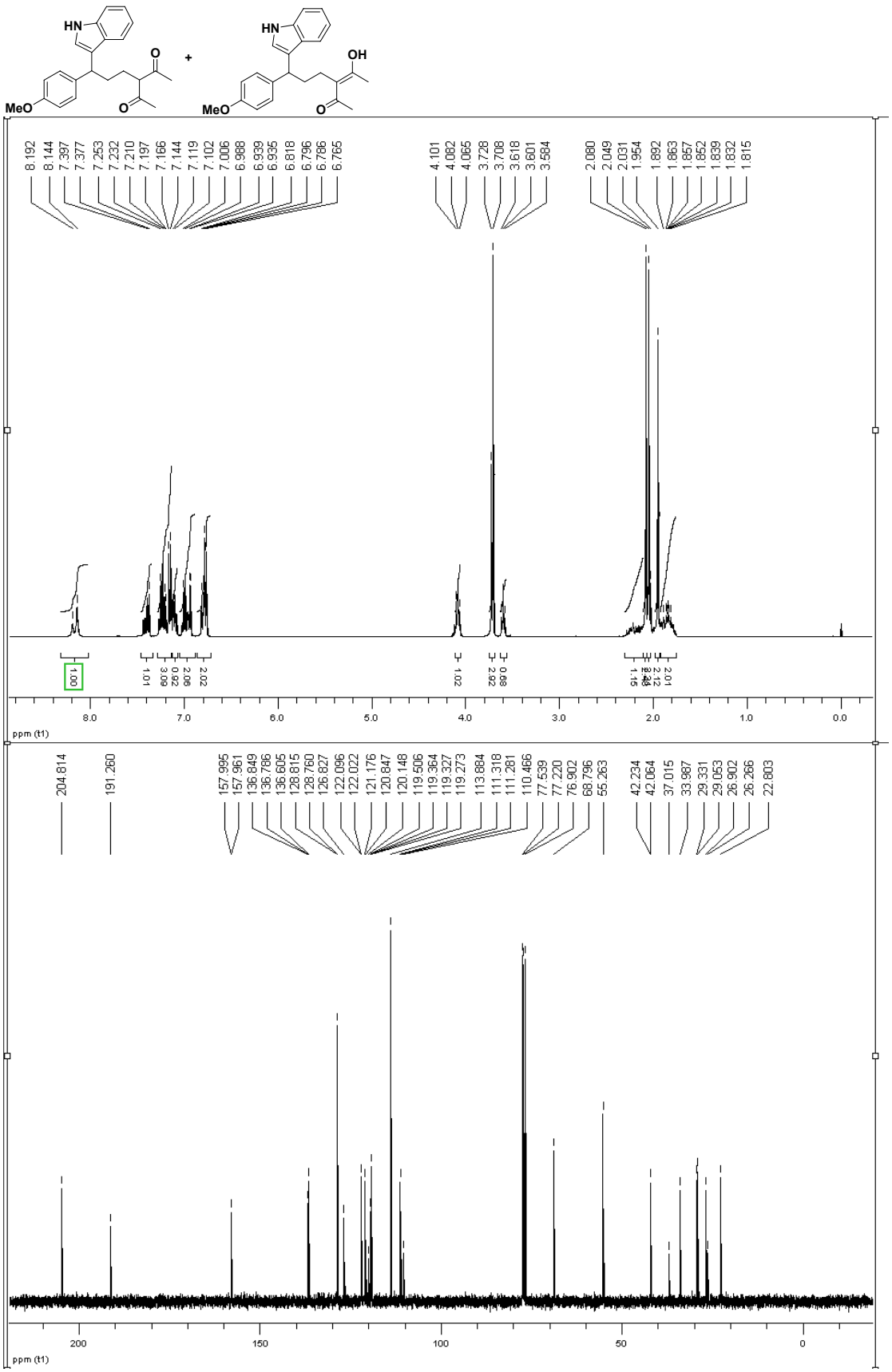
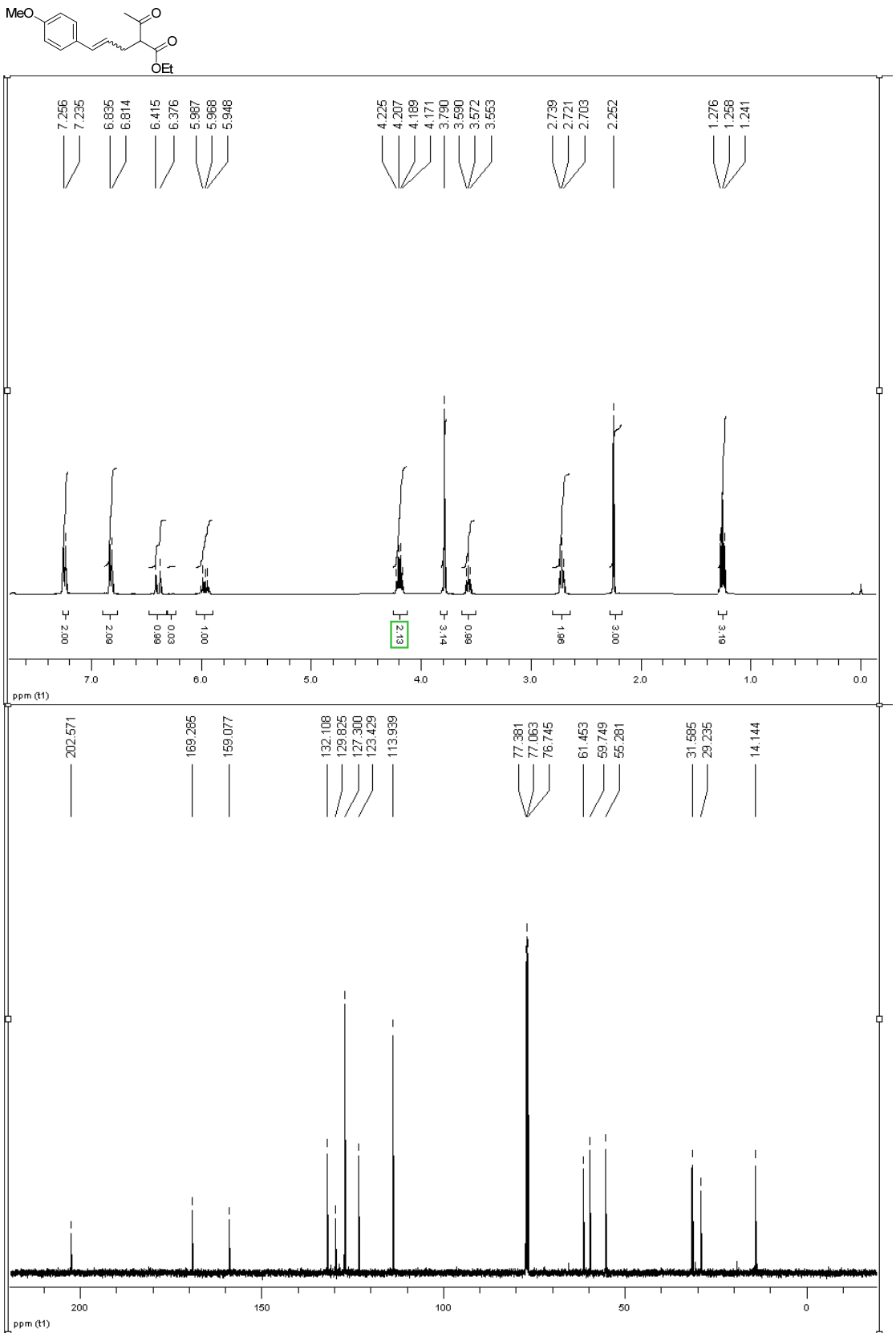
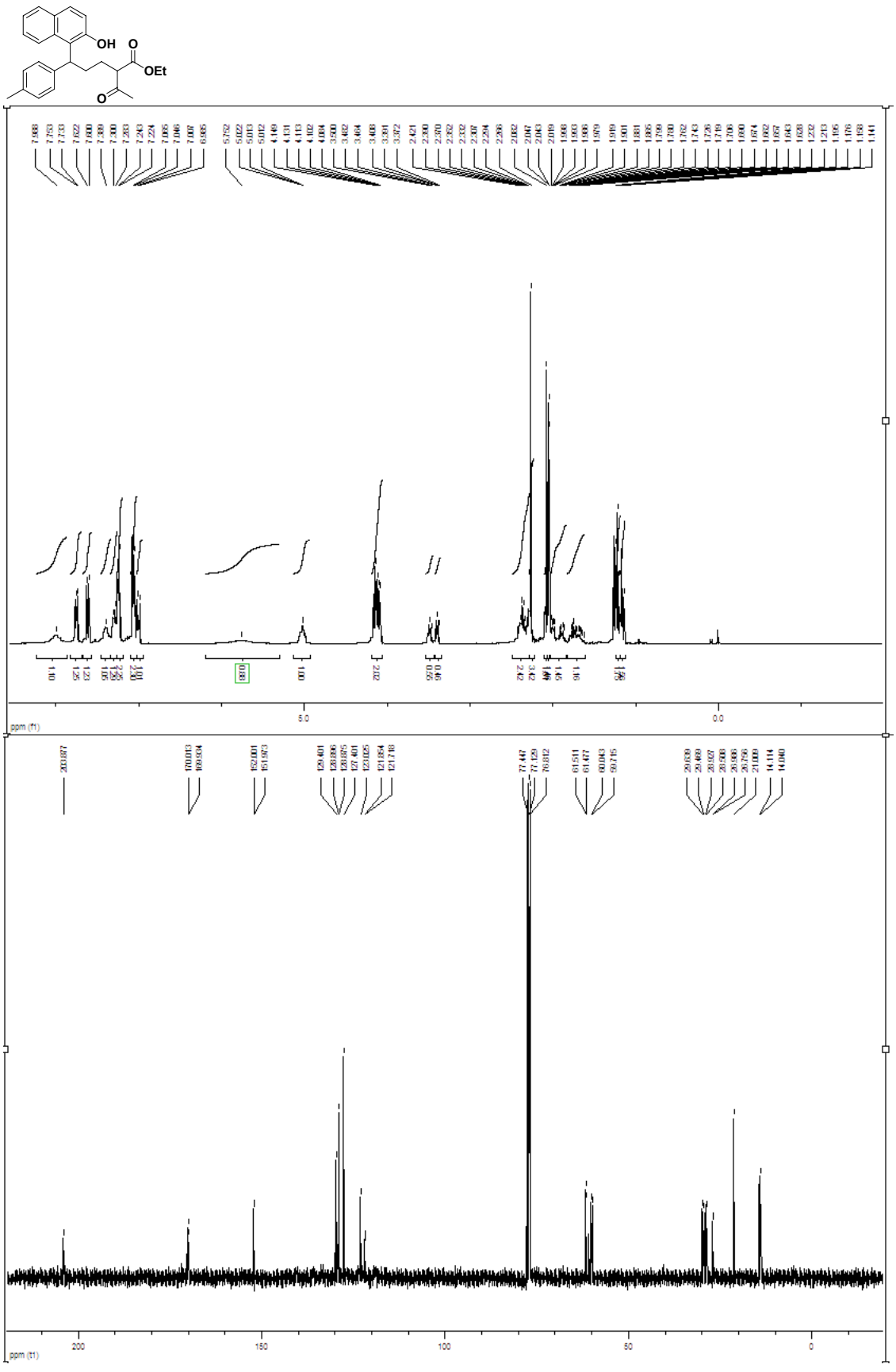
O
ppm (f1)

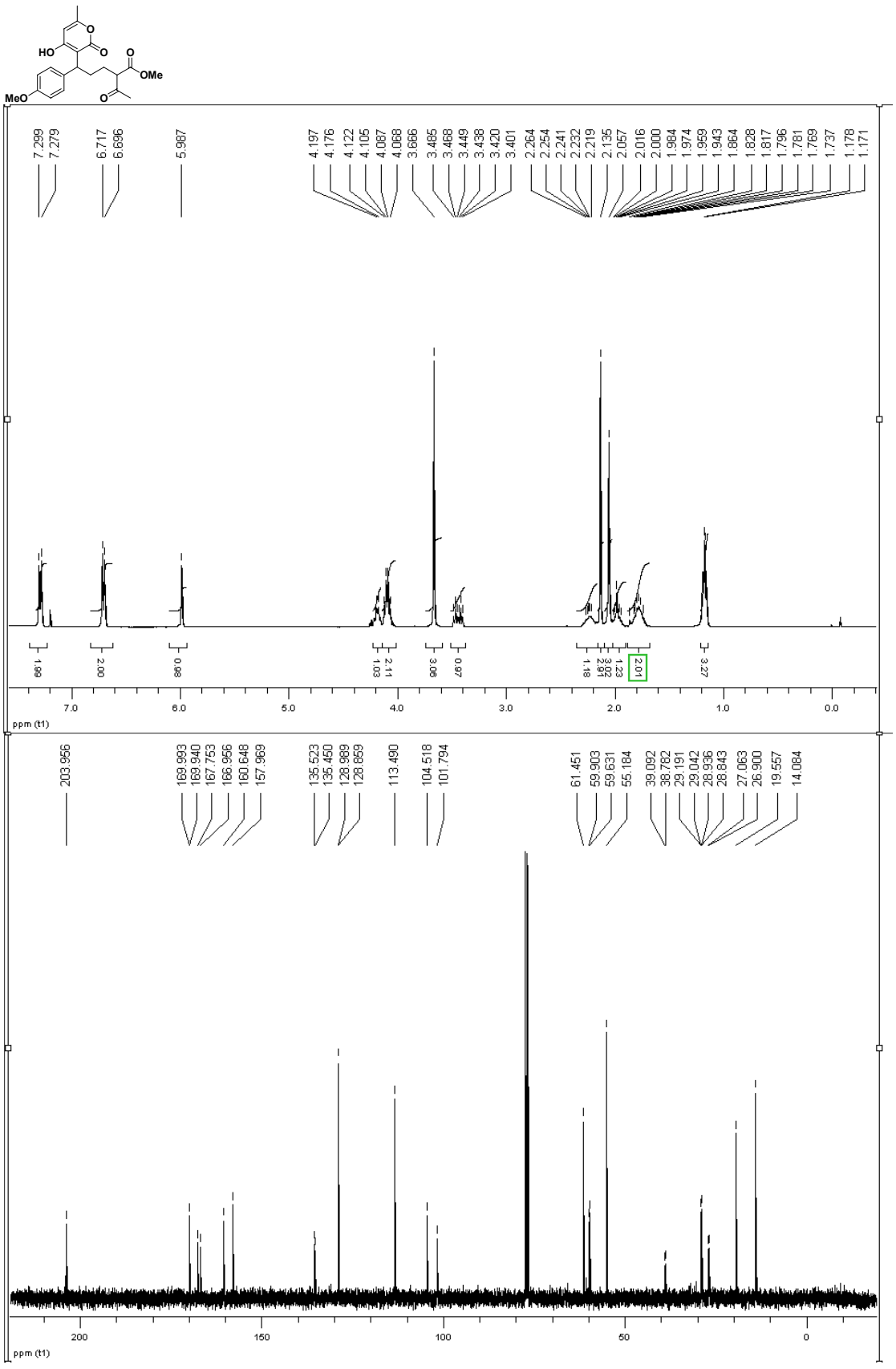

HN
O
OEt
O

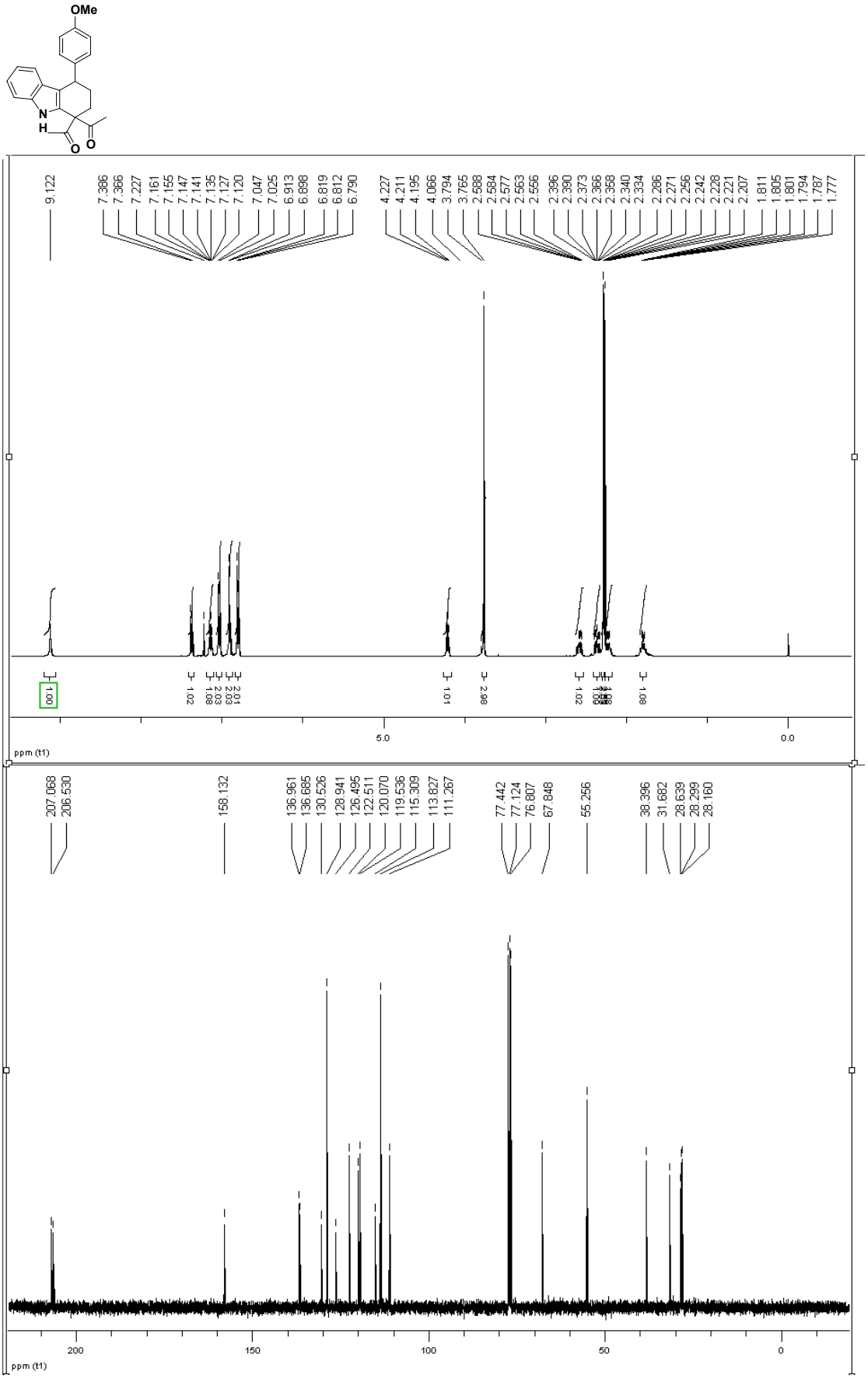

HN
O
OMe
MeO
O
8.134
7.409
7.402
7.389
7.382
7.271
7.251
7.212
7.181
7.174
7.159
7.153
7.125
7.107
7.088
6.791
6.787
6.770
4.121
4.104
4.086
3.735
3.719
3.687
3.674
3.463
3.457
3.440
2.151
2.142
2.119
2.108
1.943
1.932
1.923
1.913
1.900
1.886
1.874
1.864
1.852
1.838
1.825
1.806
1.798
1.793
1.789
1.00
0.99
1.11
1.06
2.00
2.03
1.13
3.84
0.96
4.10
3.31
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)
203.517
170.402
170.334
157.917
136.920
136.764
136.600
128.767
126.872
126.835
121.969
121.198
119.646
119.486
119.377
119.216
113.836
111.233
77.498
77.180
76.861
59.748
59.573
55.248
52.492
42.022
41.912
33.993
33.788
28.990
28.789
26.971
26.870
200
150
100
50
0
ppm (t1)


HN
O
O
MeO
+
HN
OH
O
MeO
8.192
8.144
7.397
7.377
7.253
7.232
7.210
7.197
7.166
7.144
7.119
7.102
7.006
6.988
6.939
6.935
6.818
6.796
6.786
6.765
4.101
4.082
4.065
3.728
3.708
3.618
3.601
3.584
2.080
2.049
2.031
1.954
1.892
1.863
1.857
1.852
1.839
1.832
1.815
1.00
1.01
3.09
0.92
2.06
2.02
1.02
2.92
0.88
1.95
2.12
2.01
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)
204.814
191.260
157.995
157.961
136.849
136.786
136.605
128.815
128.760
126.827
122.096
122.022
121.176
120.847
120.148
119.506
119.364
119.327
119.273
113.884
111.318
111.281
110.466
77.539
77.220
76.902
68.796
55.263
42.234
42.064
37.015
33.987
29.331
29.053
26.902
26.266
22.803
200
150
100
50
0
ppm (t1)


MeO
O
O
OEt
7.256
7.235
6.835
6.814
6.415
6.376
5.987
5.968
5.948
4.225
4.207
4.189
4.171
3.790
3.590
3.572
3.553
2.739
2.721
2.703
2.252
1.276
1.258
1.241
2.00
2.09
0.69
0.03
1.00
2.13
3.14
0.99
1.96
3.00
3.19
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)
202.571
169.285
159.077
132.108
129.825
127.300
123.429
113.939
77.381
77.063
76.745
61.453
59.749
55.281
31.585
29.235
14.144
200
150
100
50
0
ppm (t1)


OH
O
OEt
O
ppm (f1)
5.0
0.0
200
150
100
50
0


HO
O
O
O
OMe
MeO
O
7.299
7.279
6.717
6.696
5.987
4.197
4.176
4.122
4.105
4.087
4.068
3.666
3.485
3.468
3.449
3.438
3.420
3.401
2.264
2.254
2.241
2.232
2.219
2.135
2.057
2.016
2.000
1.984
1.974
1.959
1.943
1.864
1.828
1.817
1.796
1.781
1.769
1.737
1.178
1.171
1.99
2.00
0.98
1.03
2.11
3.00
0.97
1.18
2.01
3.27
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)
203.956
169.993
169.940
167.753
166.956
160.648
157.969
135.523
135.450
128.989
128.859
113.490
104.518
101.794
61.451
59.903
59.631
55.184
39.092
38.782
29.191
29.042
28.936
28.843
27.063
26.900
19.557
14.084
200
150
100
50
0
ppm (t1)


OMe
N
H
O
O
9.122
7.386
7.366
7.227
7.161
7.155
7.147
7.141
7.135
7.127
7.120
7.047
7.025
6.913
6.898
6.819
6.812
6.790
4.227
4.211
4.195
4.066
3.794
3.765
2.588
2.584
2.577
2.563
2.556
2.396
2.390
2.373
2.366
2.358
2.340
2.334
2.286
2.271
2.256
2.242
2.228
2.221
2.207
1.811
1.805
1.801
1.794
1.787
1.777
1.00
1.02
1.08
1.23
1.71
1.01
2.88
1.02
1.08
5.0
0.0
ppm (t1)
207.068
206.530
158.132
136.961
136.685
130.526
128.941
126.495
122.511
120.070
119.536
115.309
113.827
111.267
77.442
77.124
76.807
67.848
55.256
38.396
31.682
28.639
28.299
28.160
200
150
100
50
0
ppm (t1)