**Supporting Information for**

# $Cu(OTf)_2$-catalyzed synthesis of 2,3-disubstituted indoles and 2,4,5-trisubstituted pyrroles from α-diazoketones

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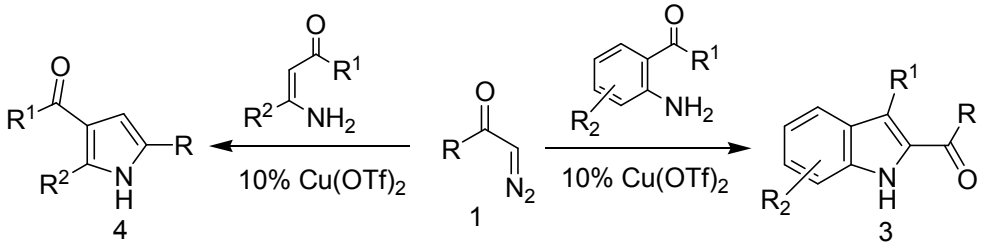


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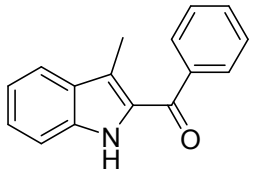
**General**

IR spectra were recorded on FT-IR spectrometer (KBr) and reported in reciprocal centimeters ($cm^{-1}$). $^1H$ NMR spectra were recorded at 500 MHz, 300 MHz and $^{13}C$ NMR at 75 MHz. For $^1H$ NMR, tetramethylsilane (TMS) was used as internal standard ($\delta = 0$) and the values are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t= triplet, q = quartet, m = multiplet, br = broad), and the coupling constants in Hz. For $^{13}C$ NMR, $CDCl_3$ ($\delta = 77.27$) was used as internal standard and spectra were obtained with complete proton decoupling. Low-resolution MS and HRMS data were obtained using ESI ionization. Melting points were measured on micro melting point apparatus. The precursors, α-diazoketones and enamines were prepared according to reported procedures. Commercially available 2-aminoacetophenones, 1,3-diketones, 2-aminobenzophenones, and $Cu(OTf)_2$ were used without further purification. DCE were distilled from CaH under $N_2$ atmosphere.

**General procedure for the synthesis of indoles and pyrroles**

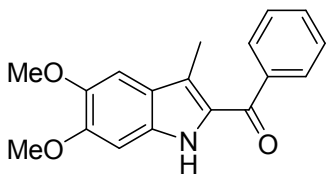
A mixture of *α*-diazoketone (**1**) (1 mmol, 1 eq.), 2-aminoketone (**2)** (1 mmol, 1 eq.) and $Cu(OTf)_2$ (0.1 mmol, 0.1 eq.) in dichloroethane (3mL) was stirred at 80 ˚C for the appropriate time (Table 1 and 2). After completion of the reaction, as indicated by TLC, the solvent was removed in vacuo. The resulting residue was subjected to column chromatography on silica gel using petroleum ether/ethyl acetate as eluent to afford the product **3**.

**(3-Methyl-1*H*-indol-2-yl)(phenyl)methanone (3a):**




Yellow solid, m.p.111-112 °C; $^1H$ NMR (500 MHz, $CDCl_3$): δ 8.91 (brs, 1H), 7.80-7.73 (m, 2H), 7.65-7.44 (m, 4H), 7.39-7.27 (m, 2H), 7.15-7.06 (m, 1H), 2.26 (s, 3H); $^{13}C$ NMR (75 MHz, $CDCl_3$): δ 189.3, 139.3, 136.5, 131.9, 131.5, 129.6, 128.7, 128.4, 127.9, 126.4, 121.2, 120.1, 111.8, 11.2; IR (KBr): υ 3312, 2918, 1607, 1522, 1433, 1330, 1265, 1143, 942, 736 $cm^{-1}$; MS (ESI): *m/z* ($[M+H]^+$): 236; HRMS (ESI): *m/z* calcd for $C_{16}H_{13}NONa$: 258.0894; found: 258.0890.

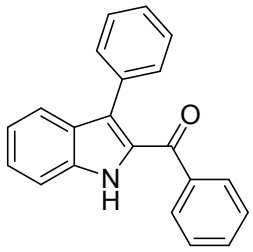
**(5,6-Dimethoxy-3-methyl-1*H*-indol-2-yl)(phenyl)methanone (3b):**




White solid, m.p. 164-166 °C; $^1H$ NMR (500 MHz, $CDCl_3$): δ 8.86 (brs, 1H), 7.71 (d, *J* = 7.9 Hz, 2H), 7.56-7.50 (m, 1H), 7.47 (t, *J* = 7.9 Hz, 2H), 6.89 (s, 1H), 6.76 (s, 1H), 3.92 (s, 6H), 2.19 (s, 3H); $^{13}C$ NMR (75 MHz, $CDCl_3$): δ 188.1, 146.4, 145.9, 139.8, 132.2, 131.4, 129.4, 128.7, 128.6, 128.3, 121.9,

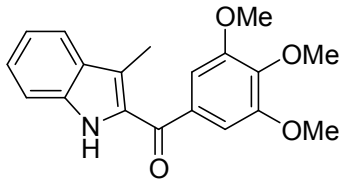
121.0, 101.0, 93.5, 56.1, 56.0, 11.4; IR (KBr): υ 3308, 2923, 2854, 1604, 1522, 1450, 1261, 1211, 1160, 803, 690 $cm^{-1}$; MS (ESI): *m/z* ($[M+H]^+$): 296; HRMS (ESI): *m/z* calcd for $C_{18}H_{17}NO_3Na$: 318.1106; found: 318.1111.

**Phenyl(3-phenyl-1*H*-indol-2-yl)methanone (3c):**



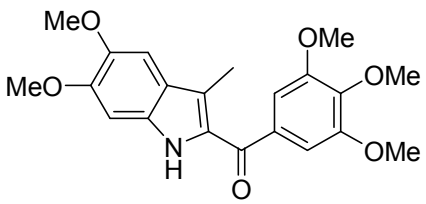

Yellow solid, m.p. 192-193 °C; $^1H$ NMR (500 MHz, $CDCl_3$): δ 9.31 (brs, 1H), 7.69 (d, *J* = 7.9 Hz, 1H), 7.62 (d, *J* = 7.9 Hz, 1H), 7.52-7.40 (m, 4H), 7.38-7.33 (m, 1H), 7.25-7.20 (m, 1H), 7.20-7.07 (m, 4H), 7.07-7.02 (m, 2H); $^{13}C$ NMR (75 MHz, $CDCl_3$): δ 189.5, 143.1, 134.5, 134.1, 133.6, 132.1, 131.6, 130.7, 130.6, 130.1, 129.4, 128.7, 127.9, 127.8, 127.4, 126.7, 126.4, 122.0, 121.0, 111.9; IR (KBr): υ 3316, 2923, 1615, 1482, 1334, 1262, 1015, 740, 693 $cm^{-1}$; MS (ESI): *m/z* ($[M+H]^+$): 298; HRMS (ESI): *m/z* calcd for $C_{21}H_{16}NO$ (M+H): 298.1231; found: 298.1233.

**(3-Methyl-1*H*-indol-2-yl)(3,4,5-trimethoxyphenyl)methanone (3d):**




White solid, m.p. 129-131 °C; $^1H$ NMR (500 MHz, $CDCl_3$): δ 8.86 (brs, 1H), 7.63 (d, *J* = 7.9 Hz, 1H),7.39-7.27 (m, 2H), 7.15-7.08 (m, 1H), 7.03 (s, 2H), 3.91 (s, 3H), 3.89 (s, 6H), 2.37 (s, 3H); $^{13}C$ NMR (75 MHz, $CDCl_3$): δ 188.3, 152.9, 141.5, 136.4, 134.2, 128.8, 126.3, 121.1, 120.1, 119.9, 111.8, 106.4, 60.9, 56.2, 11.4; IR (KBr): υ 3326, 2923, 2842, 1614, 1578, 1422, 1334, 1233, 1129, 966, 729, 667 $cm^{-1}$; MS (ESI): *m/z* ($[M+H]^+$): 326; HRMS (ESI): *m/z* calcd for $C_{19}H_{19}NO_4Na$: 348.1211; found: 348.1220.

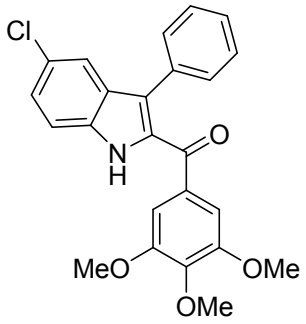
**(5,6-Dimethoxy-3-methyl-1*H*-indol-2-yl-)(3,4,5-trimethoxyphenyl)methanone (3e):**




Yellow solid, m.p. 189-191 °C; $^1H$ NMR (500 MHz, $CDCl_3$): δ 8.82 (brs, 1H), 6.98 (s, 2H), 6.91 (s, 1H), 6.77 (s, 1H), 3.92 (s, 6H), 3.90 (s, 3H), 3.89 (s, 6H), 2.29 (s, 3H); $^{13}C$ NMR (75 MHz, $CDCl_3$): δ 187.1, 152.9, 151.1, 145.9, 141.1, 134.7, 132.1, 130.6, 121.8, 120.5, 106.3, 100.9, 93.5, 60.9, 56.2, 56.1, 56.0,

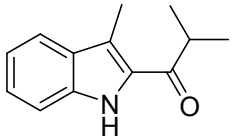
11.6; IR (KBr): υ 3347, 2924, 2849, 1611, 1578, 1454, 1322, 1227, 1126, 1059, 829, 764 $cm^{-1}$; MS (ESI): *m/z* ($[M+H]^+$): 386; HRMS (ESI): *m/z* calcd for $C_{21}H_{23}NO_6Na$: 408.1423; found: 408.1416.

**(5-Chloro-3-phenyl-1*H*-indol-2-yl)(3,4,5-trimethoxyphenyl)methanone (3f):**



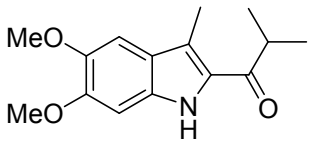

Yellow solid, m.p. 142-144 °C; $^1H$ NMR (500 MHz, $CDCl_3$): δ 9.28 (brs, 1H), 7.65-7.62 (m, 1H), 7.34-7.32 (m, 1H), 7.28-7.23 (m, 1H), 7.19 (s, 1H), 7.17-7.10 (m, 4H), 6.73 (s, 2H), 3.68 (s, 3H), 3.57 (s, 6H); $^{13}C$ NMR (75 MHz, $CDCl_3$): δ 188.2, 152.4, 141.7, 134.6, 133.3, 132.1, 131.6, 130.5, 129.7, 128.4, 128.2, 127.3, 126.9, 123.7, 121.3, 113.1, 107.1, 60.7, 55.9; IR (KBr): υ 3310, 2923, 2854, 1726, 1576, 1454, 1332, 1230, 1118, 996, 764, 690 $cm^{-1}$; MS (ESI): *m/z* ($[M+H]^+$): 422; HRMS (ESI): *m/z* calcd for $C_{24}H_{20}NO_4ClNa$: 444.0978; found: 444.0963.

**2-Methyl-1-(3-methyl-1*H*-indol-2-yl)propan-1-one (3g):**




White solid, m.p.120-121 °C; $^1H$ NMR (500 MHz, $CDCl_3$): δ 9.12 (brs, 1H), 7.63 (d, *J* = 8.3 Hz, 1H), 7.36-7.27 (m, 2H), 7.11-7.05 (m, 1H), 3.50-3.39 (m, 1H), 2.67 (s, 3H), 1.28 (d, *J* = 6.7 Hz, 6H); $^{13}C$ NMR (75 MHz, $CDCl_3$): δ 197.6, 135.9, 131.4, 129.1, 126.2, 121.1, 119.9, 117.4, 111.7, 37.1, 18.8, 10.8; IR (KBr): ν 3320, 2966, 2927, 1629, 1427, 1337, 1225, 1150, 995, 743, 696 $cm^{-1}$; MS (ESI): *m/z* ($[M+H]^+$): 202; HRMS (ESI): *m/z* calcd for $C_{13}H_{16}ON$ (M+H): 202.12264; found: 202.12286.

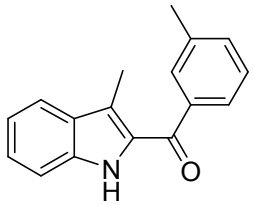
**1-(5,6-Dimethoxy-3-methyl-1*H*-indol-2-yl)-2-methylpropan-1-one (3h):**




White solid, m.p. 170-172 °C; $^1H$ NMR (500 MHz, $CDCl_3$): δ 9.19 (brs, 1H), 6.92 (s, 1H), 6.78 (s, 1H), 3.92 (s, 6H), 3.48-3.35 (m, 1H), 2.61 (s, 3H), 1.28 (d, *J* = 6.7 Hz, 6H); $^{13}C$ NMR (75 MHz, $CDCl_3$): δ 196.5, 150.8, 145.6, 131.7, 130.6, 121.7, 117.8, 100.8, 93.5, 56.1, 55.9, 36.5, 18.9, 11.1; IR (KBr): υ

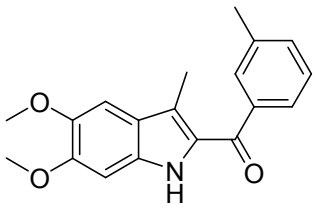
3322, 2924, 1614, 1524, 1418, 1284, 1223, 1160, 998, 830 $cm^{-1}$; MS (ESI): *m/z* ($[M+H]^+$): 262; HRMS (ESI): *m/z* calcd for $C_{15}H_{20}O_3N$ (M+H): 262.14377; found: 262.14410.

**(3-Methyl-1*H*-indol-2-yl)(*m*-tolyl)methanone (3i):**



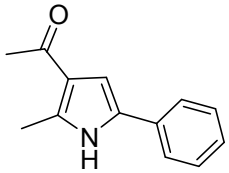
Yellow solid, m.p. 122-124 °C; $^1H$ NMR (500 MHz, $CDCl_3$): δ 8.84 (brs, 1H), 7.65-7.52 (m, 3H),7.38-7.30 (m, 4H), 7.13-7.07 (m, 1H), 2.45 (s, 3H), 2.27 (s, 3H); $^{13}C$ NMR (75 MHz, $CDCl_3$): δ 194.0, 139.2, 138.2, 132.6, 130.0, 129.3, 128.9, 128.4, 128.2, 126.3, 125.9, 121.1, 120.0, 111.8, 21.2, 11.1; IR (KBr): υ 3304, 2918, 2856, 1614, 1525, 1440, 1328, 1269, 1158, 744, 690 $cm^{-1}$; MS (ESI): *m/z* ($[M+H]^+$): 250; HRMS (ESI): *m/z* calcd for $C_{17}H_{16}ON$ (M+H): 250.12264; found: 250.12276.

**(5,6-Dimethoxy-3-methyl-1*H*-indol-2-yl)(*m*-tolyl)methanone (3j):**



Yellow solid, m.p.140-142°C; $^1H$ NMR (500 MHz, $CDCl_3$): δ 8.84 (brs, 1H), 7.65-7.52 (m, 3H),7.38-7.30 (m, 4H), 7.13-7.07 (m, 1H), 2.45(s, 3H), 2.27 (s, 3H); $^{13}C$ NMR (75 MHz, $CDCl_3$): δ 176.4, 166.4, 145.9, 144.6, 139.8, 138.2, 132.2, 129.1, 128.2, 125.7, 101.2, 93.5, 56.2, 56.1, 21.3, 11.3; IR (KBr): υ 3304, 2918, 2856, 1614, 1525, 1440, 1328, 1269, 1158, 744, 690 $cm^{-1}$; MS (ESI): *m/z* ($[M+H]^+$): 310; HRMS (ESI): *m/z* calcd for $C_{19}H_{20}O_3N$ (M+H): 310.14377; found: 310.14363.

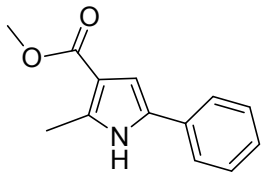
**(3,5-Dimethyl-1*H*-pyrrol-2-yl)(phenyl)methanone (4a):**



White solid, m.p.118-120 °C; $^1H$ NMR (500 MHz, $CDCl_3$): δ 8.55 (brs, 1H), 7.42 (d, *J* = 6.9 Hz, 2H),7.36-7.32 (m, 2H), 7.22-7.18 (m, 1H), 6.71(s, 1H), 2.61 (s, 3H) 2.43 (s, 3H); $^{13}C$ NMR (75 MHz, $CDCl_3$): δ 195.1, 135.8, 131.6, 128.9, 126.7, 123.7, 107.4, 28.4, 14.1; IR (KBr): υ 3260, 2921, 2855,

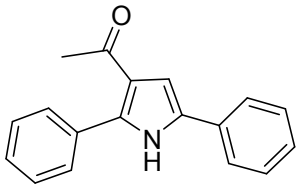
1601, 1438, 1253, 1170, 899, 754 $cm^{-1}$; MS (ESI): *m/z* ($[M+Na]^+$): 222; HRMS (ESI): *m/z* calcd for $C_{13}H_{13}NONa$: 222.0894; found: 222.0892.

**(5-Methoxy-3-methyl-1*H*-pyrrol-2-yl)(phenyl)methanone (4b):**



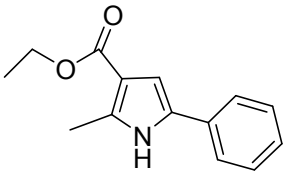
White solid, m.p. 90-92 °C; $^1H$ NMR (500 MHz, $CDCl_3$): δ 8.48 (brs, 1H), 7.50-7.33 (m, 4H), 7.25-7.20 (m, 1H), 6.83 (d, *J* = 3.0 Hz, 1H), 3.83 (s, 3H), 2.60 (s, 3H); $^{13}C$ NMR (75 MHz, $CDCl_3$): δ 173.3, 166.0, 129.9, 129.0, 128.8, 128.6, 126.4, 123.6, 112.9, 107.2, 50.8, 22.6; IR (KBr): υ 3328, 2925, 2854, 1709, 1679, 1453, 1236, 1100, 760 $cm^{-1}$; MS (ESI): *m/z* ($[M+H]^+$): 216; HRMS (ESI): *m/z* calcd for $C_{13}H_{14}O_2N$ (M+H): 216.10191; found: 216.10234.

**(5-Methyl-3-phenyl-1*H*-pyrrol-2-yl)(methanone) (4c):**



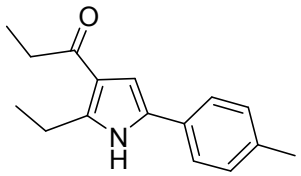
Yellow solid, m.p. 159-160 °C; $^1H$ NMR (500 MHz, $CDCl_3$): δ 8.59 (brs, 1H), 7.88-7.82 (m, 2H), 7.57-7.42 (m, 5H), 7.41-7.34 (m, 2H ), 6.68 (s, *J* = 2.2 Hz, 1H), 2.65 (s, 3H); $^{13}C$ NMR (75 MHz, $CDCl_3$): δ 192.4, 140.4, 137.5, 133.0, 131.6, 131.2, 129.7, 129.1, 129.1, 128.9, 128.9, 128.6, 126.6, 109.1, 13.8; IR (KBr): υ 3261, 3058, 2922, 1598, 1557, 1440, 1254, 1172, 901, 756, 695 $cm^{-1}$; MS (ESI): *m/z* ($[M+H]^+$): 262; HRMS (ESI): *m/z* calcd for $C_{18}H_{16}ON$ (M+H): 262.12264; found: 262.12261

**(5-Ethoxy-3-methyl-1*H*-pyrrol-2-yl)(phenyl)methanone (4d):**



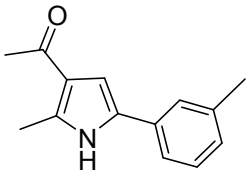
White solid, m.p. 94-96 °C; $^1H$ NMR (500 MHz, $CDCl_3$): δ 8.63 (brs, 1H), 7.51-7.43 (m, 2H), 7.39-7.32 (m, 2H), 7.27-7.17 (m, 1H), 6.84 (d, *J* = 3.0 Hz, 2H), 4.29 (q, *J* = 7.1 Hz, 2H), 2.58 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H); $^{13}C$ NMR (75 MHz, $CDCl_3$): δ 165.7, 136.3, 134.1, 131.8, 130.0, 128.9, 128.8, 128.5, 126.3, 123.6, 107.2, 59.5, 14.4, 13.2; IR (KBr): υ 3314, 2980, 2927, 1672, 1609, 1479, 1448, 1236, 1099, 780 $cm^{-1}$; MS (ESI): *m/z* ($[M+H]^+$): 230; HRMS (ESI): *m/z* calcd for $C_{14}H_{16}O_2N$ (M+H): 230.11756; found: 230.11808

**(3,5-Diethyl-1*H*-pyrrol-2-yl)(*p*-tolyl)methanone (4e):**



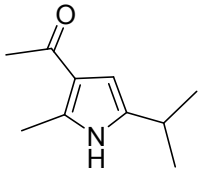
White solid, m.p. 162-164 °C; $^{1}$H NMR (500 MHz, $CDCl_3$): δ 8.44 (brs, 1H), 7.36 (d, *J* = 7.9 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 6.74 (d, *J* = 2.6 Hz, 1H), 3.06 (q, *J* = 7.5 Hz, 2H), 2.83 (q, *J* = 7.3 Hz, 2H), 2.36 (s, 3H), 1.29 (t, *J* = 7.5 Hz, 3H ), 1.19 (t, *J* = 7.3 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ 197.9, 141.4, 136.4, 129.7, 129.6, 129.0, 120.7, 123.7, 106.4, 21.2, 21.1, 13.1, 8.4; IR (KBr): υ 3274, 2974, 2926, 1629, 1460, 1211, 1012, 918, 801 cm$^{-1}$; MS (ESI): *m/z* ([M+H]$^{+}$): 242; HRMS (ESI): *m/z* calcd for $C_{16}H_{20}ON$ (M+H): 242.15394; found: 242.15382.

**(3,5-Dimethyl-1*H*-pyrrol-2-yl)(*m*-tolyl)methanone (4f)**



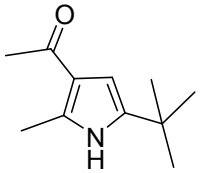
Yellow solid, m.p. 160-162 °C; $^{1}$H NMR (500 MHz, $CDCl_3$): δ 8.58 (brs, 1H), 7.33-7.25 (m, 4H),7.07 (s, 1H), 6.75 (s, 1H), 2.64 (s, 3H) 2.45 (s, 3H) 2.40 (s, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ 195.2, 138.6, 135.9, 131.8, 131.7, 129.9, 128.9, 127.5, 124.3, 107.3, 28.4, 21.5, 13.8; IR (KBr): υ 3289, 2920, 2854, 1635, 1573, 1437, 1239, 1170, 942, 776 cm$^{-1}$; MS (ESI): *m/z* ([M+H]$^{+}$): 214; HRMS (ESI): *m/z* calcd for $C_{14}H_{16}NO$ (M+H): 214.1231; found: 214.1242.

**2-Methyl-1-(3,5-dimethyl-1*H*-pyrrol-2-yl)propan-1-one (4g):**



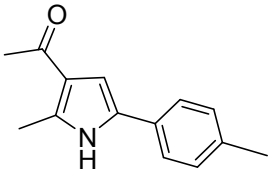
White solid, m.p.116-118 °C; $^{1}$H NMR (500 MHz, $CDCl_3$): δ 7.95 (brs, 1H), 6.09 (s, 1H), 2.86-2.79 (m, 1H) 2.50 (s, 3H), 2.34 (s, 3H), 1.25 (d, *J* = 7.0 Hz, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ 195.1, 136.7, 136.3, 133.7, 104.9, 28.3, 26.7, 22.3, 13.9; IR (KBr): υ 3228, 2963, 2925, 1618, 1463, 1262, 1024, 957, 824 cm$^{-1}$; MS (ESI): *m/z* ([M+H]$^{+}$): 166; HRMS (ESI): *m/z* calcd for $C_{10}H_{15}NONa$: 188.1051; found: 188.1058.

**2,2-Dimethyl-1-(3,5-dimethyl-1*H*-pyrrol-2-yl)propan-1-one (4h):**



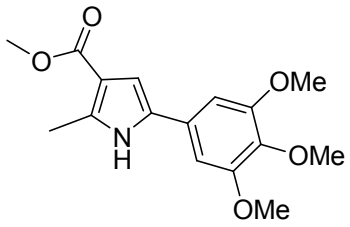
Yellow solid, m.p. 92-94 °C; $^{1}$H NMR (500 MHz, $CDCl_3$): δ 7.94 (brs, 1H), 6.19 (s, 1H), 2.52 (s, 3H), 2.39 (s, 3H), 1.55 (s, 9H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ 195.2, 139.9, 139.8, 134.1, 104.4, 31.2, 30.2, 29.7, 28.4, 26.8, 13.8; IR (KBr): υ 3248, 2960, 1620, 1525, 1455, 1243, 1018, 821, 775 cm$^{-1}$; MS (ESI): *m/z* ($[M+H]^+$): 180; HRMS (ESI): *m/z* calcd for $C_{11}H_{18}ON$ (M+H): 180.13829; found: 180.13874.

**(3,5-Dimethyl-1*H*-pyrrol-2-yl)(*p*-tolyl)methanone (4i):**



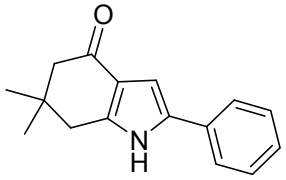
Yellow solid, m.p. 168-170 °C; $^{1}$H NMR (500 MHz, $CDCl_3$): δ 8.66 (brs, 1H), 7.35-7.30 (m, 2H), 7.16-7.13 (s, 2H), 6.65 (s, 1H), 2.60 (s, 3H) 2.42 (s, 3H) 2.36 (s, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ 195.3, 136.4, 135.7, 130.0, 129.5, 128.9, 123.6, 106.7, 28.4, 21.0, 14.0; IR (KBr): υ 3261, 2916, 1637, 1582, 1445, 1236, 1167, 942, 795 cm$^{-1}$; MS (ESI): *m/z* ($[M+H]^+$): 214; HRMS (ESI): *m/z* calcd for $C_{14}H_{16}NO$ (M+H): 214.1231; found: 214.1231.

**(5-Methoxy-3-methyl-1*H*-pyrrol-2-yl)(3,4,5-trimethoxyphenyl)methanone (4j):**



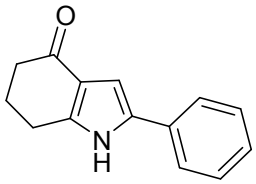
White solid, m.p.192-194 °C; $^{1}$H NMR (500 MHz, $CDCl_3$): δ 9.09 (brs, 1H), 7.16 (s, 2H), 6.66 (d, *J* = 1.0 Hz, 1H), 3.95-3.82 (m, 12H), 2.61 (s, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ 174.2, 153.4, 153.1, 136.8, 136.2, 130.1, 127.8, 127.3, 112.6, 106.9, 105.2, 101.2, 60.8, 56.2, 56.0, 13.1; IR (KBr): υ 3326, 2925, 2850, 1743, 1707, 1679, 1450, 1276, 1234, 1160, 1133, 760, 695 cm$^{-1}$; MS (ESI): *m/z* ($[M+H]^+$): 306; HRMS (ESI): *m/z* calcd for $C_{16}H_{20}O_5N$ (M+H): 306.13360; found: 306.13311.

**6,6-Dimethyl-2-phenyl-6,7-dihydro-1*H*-indol-4(5*H*)-one (4k):**



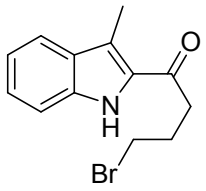
White solid, m.p. 226-227 °C; $^{1}$H NMR (500 MHz, $CDCl_3$): δ 9.07 (brs, 1H), 7.50-7.45 (m, 2 H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.27-7.20 (m, 1H), 6.80 (d, *J* = 3.0 Hz, 1H), 2.73 (s, 3H), 2.38 (s, 3H), 1.14 (s, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ 194.1, 143.7, 133.1, 131.6, 128.8, 126.8, 124.0, 120.4, 102.1, 51.9, 36.8, 35.7, 28.5; IR (KBr): υ 3259, 2954, 1626, 1489, 1224, 1162, 1060, 760, 686 $cm^{-1}$; MS (ESI): *m/z* ($[M+H]^+$): 240; HRMS (ESI): *m/z* calcd for $C_{16}H_{18}ON$ (M+H): 240.13829; found: 240.13827.

**2-Phenyl-6,7-dihydro-1*H*-indol-4(5*H*)-one (4l):**



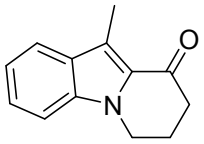
White solid, m.p. 208-210 °C; $^{1}$H NMR (500 MHz, $CDCl_3$): δ 8.85 (brs, 1H), 7.48-7.45 (m, 2H), 7.38-7.34 (m, 2H), 7.28-7.20 (m, 1H), 6.82 (d, *J* = 2.2 Hz, 1H), 2.87 (t, *J* = 6.0 Hz, 2H), 2.51 (t, *J* = 6.0 Hz, 2H), 2.18 (m, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ 194.7, 144.7, 132.9, 131.6, 128.9, 126.9, 124.0, 121.7, 102.3, 37.7, 23.8, 22.8; IR (KBr): υ 3240, 2925, 1631, 1486, 1224, 1181, 1141, 758, 695 $cm^{-1}$; MS (ESI): *m/z* ($[M+H]^+$): 212; HRMS (ESI): *m/z* calcd for $C_{14}H_{14}ON$ (M+H): 212.10699; found: 212.10709.

**4-Bromo-1-(3-methyl-1*H*-indol-2-yl)butan-1-one (6):**



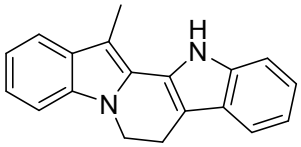
A freshly prepared mixture of 5-bromo-1-diazopentan-2-one (132 mg, 0.7 mmol), 2-aminoacetophenone (**2)** (70 mg, 0.51 mmol) and $Cu(OTf)_2$ (0.1 mmol) in dichloroethane (4 mL) was stirred at 80 ˚C for 5h. The solvent was removed in vacuo and the resulting residue was subjected to column chromatography on silica gel using petroleum ether/ethyl acetate (93:7) as eluent to afford the product **6** in 55% yield.
White solid, m.p. 127-129 °C; $^{1}$H NMR (500 MHz, $CDCl_3$): δ 8.96 (brs, 1H), 7.70 (d, *J* = 7.9 Hz, 1H), 7.38-7.32 (m, 2H), 7.15 (t, *J* = 6.9 Hz, 1H), 3.72 (t, *J* = 5.9 Hz, 2H), 3.14 (t, *J* = 6.9 Hz, 2H), 2.67 (s, 3H), 2.29 (m, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ 191.4, 136.1, 127.1, 125.8, 121.2, 120.0, 109.9, 37.8, 37.7, 22.8, 10.1; IR (KBr): υ 3324, 2988, 2926, 1622, 1420, 1333, 1225, 1050, 998, 743, 698 $cm^{-1}$; MS (ESI): *m/z* ($[M^+]$): 279; HRMS (ESI): *m/z* calcd for $C_{13}H_{15}BrON$ (M+):279.02588; found:279.02754.

**10-Methyl-7,8-[1,2-*a*]indol-9(6*H*)-one (7):**



A mixture of 4-bromo-1-(3-methyl-1*H*-indol-2-yl)butan-1-one (**6**) (100 mg, 0.35 mmol) and $K_2CO_3$ (71 mg, 0.52 mmol) in 3mL of $CH_3CN$ was heated under reflux for 1h. The mixture was filtered off on celite and the filtrate was concentrated in vacuo and purified by column chromatography to give the desired compound **7** in 95% yield.
White solid, m.p. 87-89 °C; $^1$H NMR (500 MHz, $CDCl_3$): δ 7.72 (d, *J* = 8.3 Hz, 1H), 7.39 (t, *J* = 7.3 Hz, 1H), 7.32 (d, *J* = 8.3 Hz, 1H), 7.16 (t, *J* = 7.3 Hz, 1H), 4.22 (t, *J* = 6.2 Hz, 2H), 2.74 (t, *J* = 6.2 Hz, 2H), 2.70 (s, 3H), 2.37 (m, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ 191.4, 136.1, 129.2, 127.1, 125.8, 121.2, 120.0, 119.5, 109.9, 41.3, 37.7, 22.9, 10.1; IR (KBr): υ 3420, 3054, 2924, 2857, 1654, 1538, 1372, 1327, 1230, 1104, 1002, 741, 687 cm$^{-1}$; MS (ESI): *m/z* ([M+H]$^+$): 200; HRMS (ESI): *m/z* calcd for $C_{13}H_{14}ON$ (M+H): 200.10699; found: 200.10786.

**6,7-Dihydro-13-methyl-12*H*-pyrido[1,2-*a*:3,4-*b*]diindole (8):**

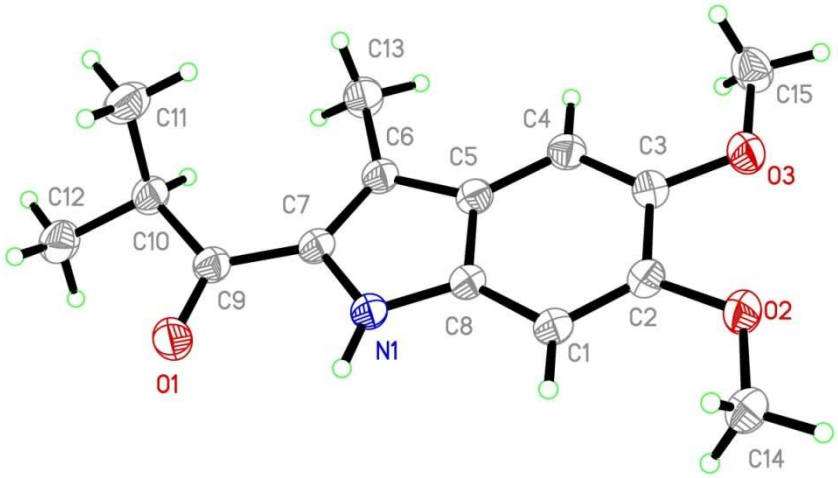


A mixture of phenylhydrazine (50 mg, 0.24 mmol), 10-methyl-7,8-dihydropyrido[1,2-*a*]indol-9(6*H*)-one (**7**) (70 mg, 0.36 mmol) and TsOH (274 mg, 1.44 mmol) in 4 mL of EtOH was heated under reflux for 2h. The solvent was removed in vacuo and the resulting residue was subjected to column chromatography on silica gel using petroleum ether/ethyl acetate(95:5) as eluent to afford the product **8** in 90% yield.
Brown solid, m.p. 163-164 °C; $^1$H NMR (500 MHz, $CDCl_3$): δ 8.35 (brs, 1H), 7.61-7.54 (m, 2H), 7.46-7.41 (m, 1H), 7.35-7.29 (m, 1H), 7.24-7.08 (m, 4H), 4.27 (t, *J* = 6.6 Hz, 2H), 3.25 (t, *J* = 6.6 Hz, 2H), 2.62 (s, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ 137.0, 136.9, 129.2, 128.5, 126.8, 126.4, 122.2, 122.0, 120.1, 119.1, 118.4, 118.2, 111.1, 108.7, 41.1, 21.0, 9.5; IR (KBr): υ 3418, 3044, 2922, 1443, 1343, 1297, 1255, 1202, 1151, 1008, 742 cm$^{-1}$; MS (ESI): *m/z* ([M+H]$^+$): 273; HRMS (ESI): *m/z* calcd for $C_{19}H_{17}N_2$ (M+H): 273.13917; found: 273.13813.

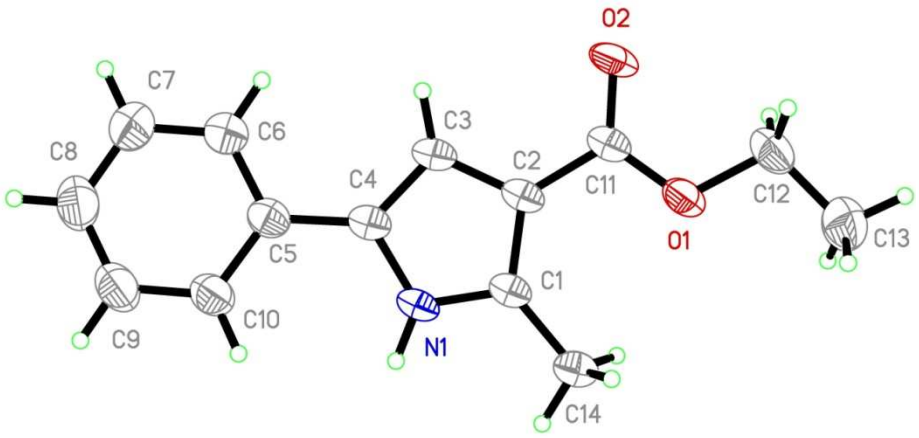
## 5. X-ray crystal structures of product **3h** and **4d**

The structure and stereochemistry of the product **3h** was confirmed by single crystal X-ray crystallography as shown in figure S3. X-ray data was collected at room temperature using a Bruker Smart Apex CCD diffractometer with graphite monochromated MoKα radiation (λ=0.71073Å) with ω-scan method.[1] Preliminary lattice parameters and orientation matrices were obtained from four sets of frames.

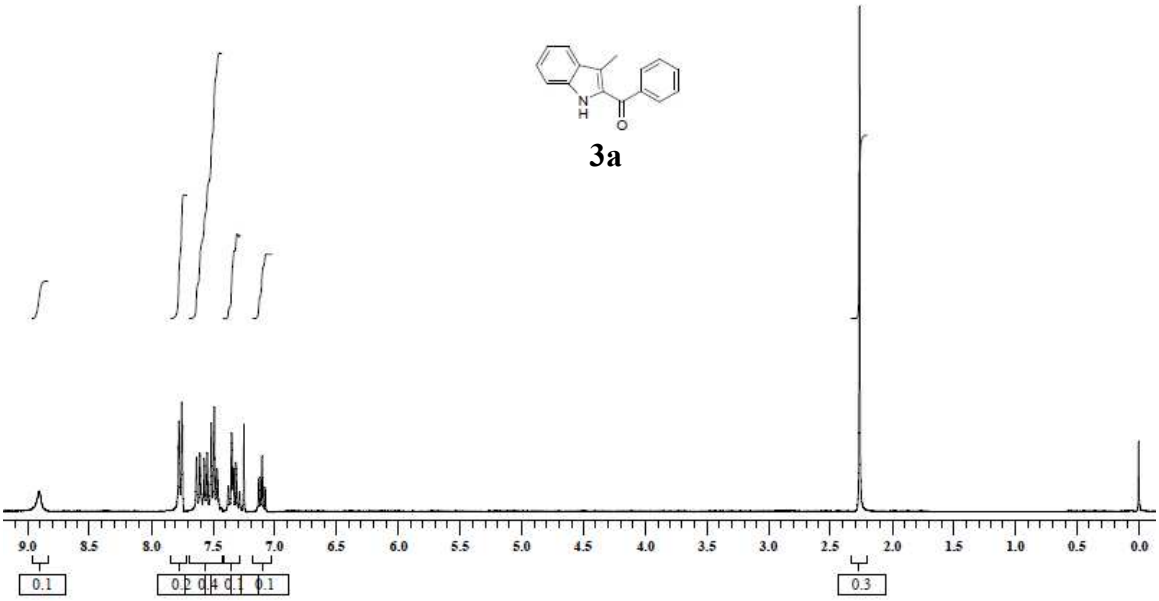
Integration and scaling of intensity data were accomplished using SAINT program.[1] The structures were solved by Direct Methods using SHELXS97[2] and refinement was carried out by full-matrix least-squares technique using SHELXL97.[2] Anisotropic displacement parameters were included for all non-hydrogen atoms. H atom attached to the N atom was located in difference Fourier maps and their positions and isotropic displacement parameters were refined. All other H atoms were located in difference Fourier maps and subsequently geometrically optimized and allowed for as riding atoms, with C-H = 0.93- 0.97 Å, with $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl H or $1.2U_{eq}(C)$. The methyl groups were allowed to rotate but not to tip.



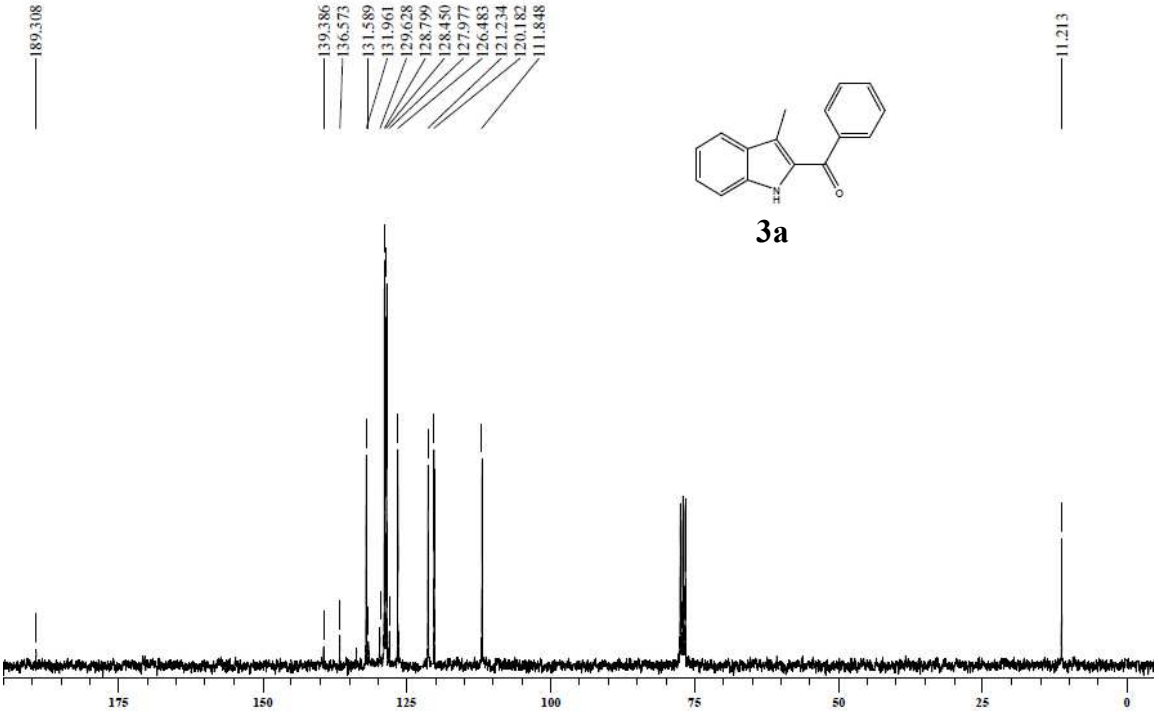

Crystal data for 3h: $C_{15}H_{19}NO_3$, $M$ = 261.31, colorless needle, 0.17 × 0.08 × 0.06 $mm^3$, triclinic, space group $P\bar{1}$ (No. 2), $a$ = 6.9397(7), $b$ = 8.8694(10), $c$ = 11.1168(12) Å, $\alpha$ = 97.572(2), $\beta$ = 94.165(2), $\gamma$ = 92.775(2)°, $V$ = 675.33(13) $Å^3$, $Z$ = 2, $D_c$ = 1.285 $g/cm^3$, $F_{000}$ = 280, CCD Area Detector, MoKα radiation, λ = 0.71073 Å, $T$ = 294(2)K, $2\theta_{max}$ = 50.0º, 6539 reflections collected, 2371 unique ($R_{int}$ = 0.0173). Final *GooF* = 1.049, *R1* = 0.0410, *wR2* = 0.1127, *R* indices based on 2102 reflections with I I>2(I) (refinement on $F^2$), 181 parameters, 0 restraints. Lp and absorption corrections applied, $\mu$ = 0.089 $mm^{-1}$. CCDC 909541 contains supplementary Crystallographic data for the structure.



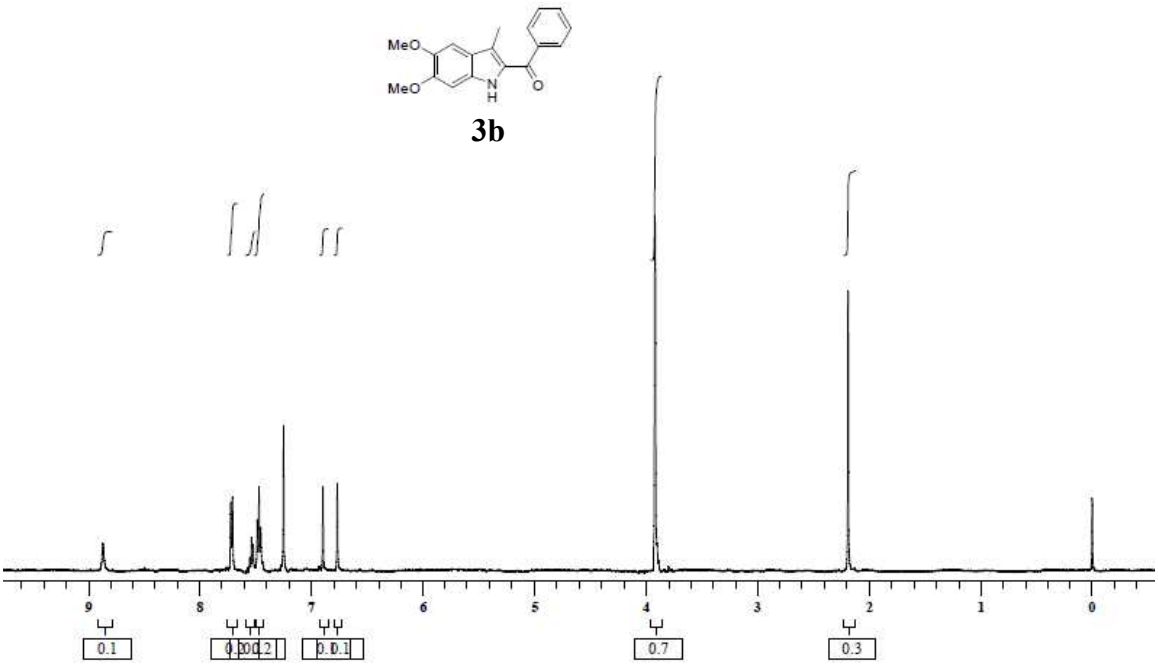

Crystal data for **4d**: $C_{14}H_{15}NO_2$, $M$ = 229.27, colorless block, 0.21 × 0.18 × 0.09 $mm^3$, monoclinic, space group $P2_1/n$ (No. 14), $a$ = 11.7298(8), $b$ = 9.2723(6), $c$ = 11.8853(8) Å, $\beta$ = 103.883(1)°, $V$ = 1254.91(15) $Å^3$, $Z$ = 4, $D_c$ = 1.214 $g/cm^3$, $F_{000}$ = 488, CCD Area Detector, MoKα radiation, λ = 0.71073 Å, $T$ = 294(2)K, $2\theta_{max}$ = 50.0º, 11655 reflections collected, 2198 unique ($R_{int}$ = 0.0241). Final *GooF* = 1.035, *R1* = 0.0396, *wR2* = 0.1124, *R* indices based on 1862 reflections with I>2σ(I) (refinement on $F^2$), 160 parameters, 0 restraints, $\mu$ = 0.081 $mm^{-1}$. CCDC 909542 contains supplementary Crystallographic data for the structure. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0) 1223 336 033; email: deposit@ccdc.cam.ac.uk].

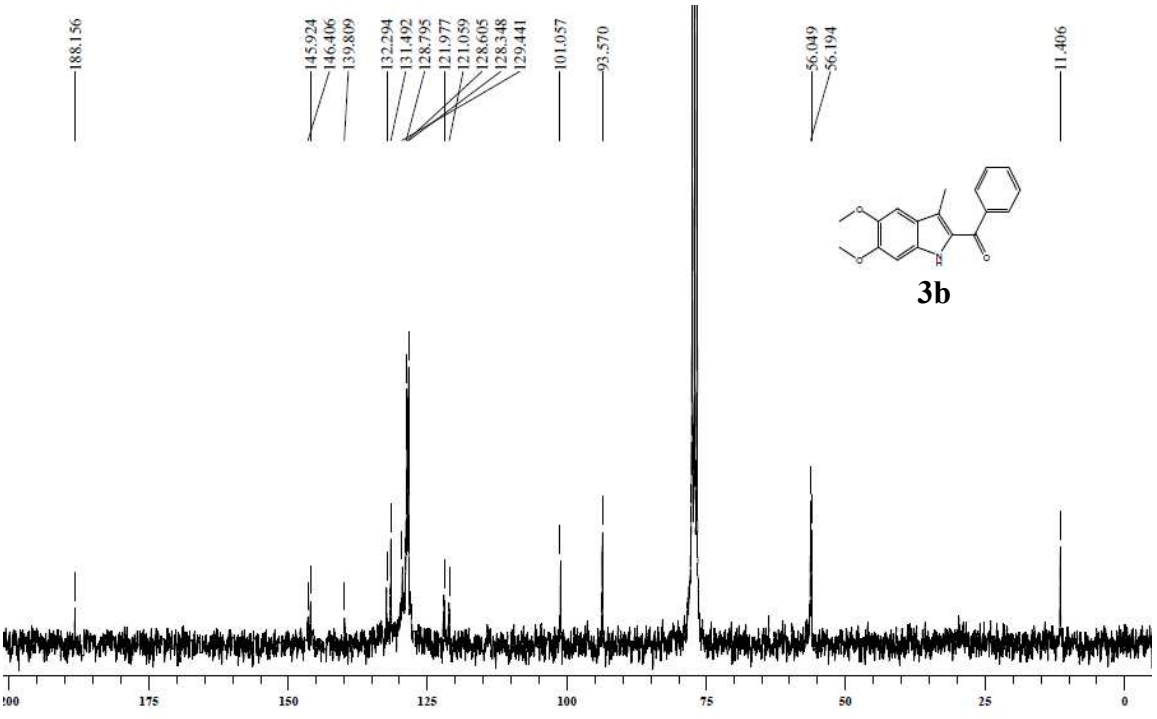


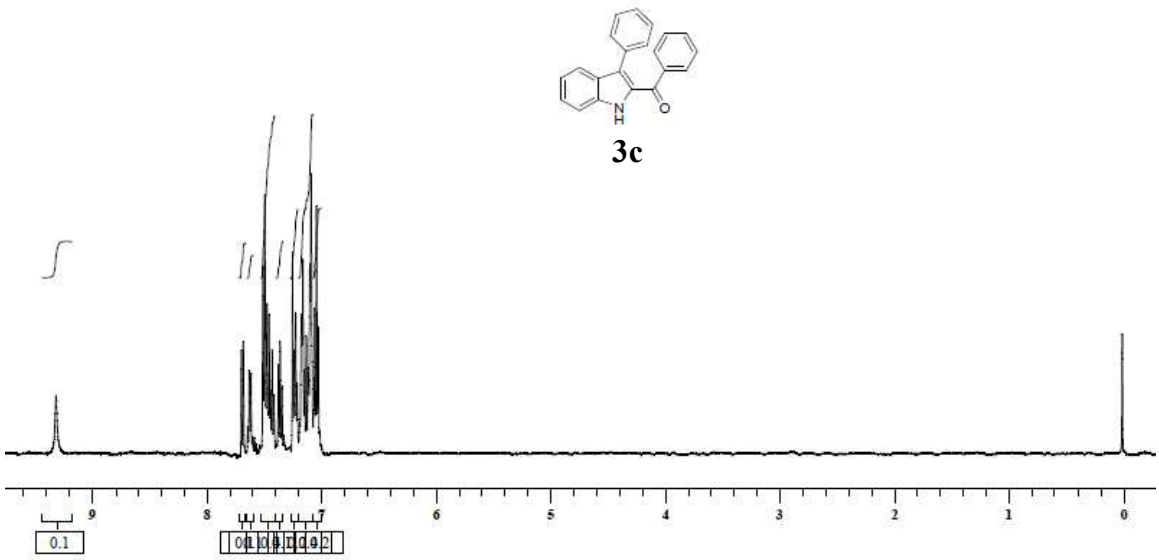
**3a**



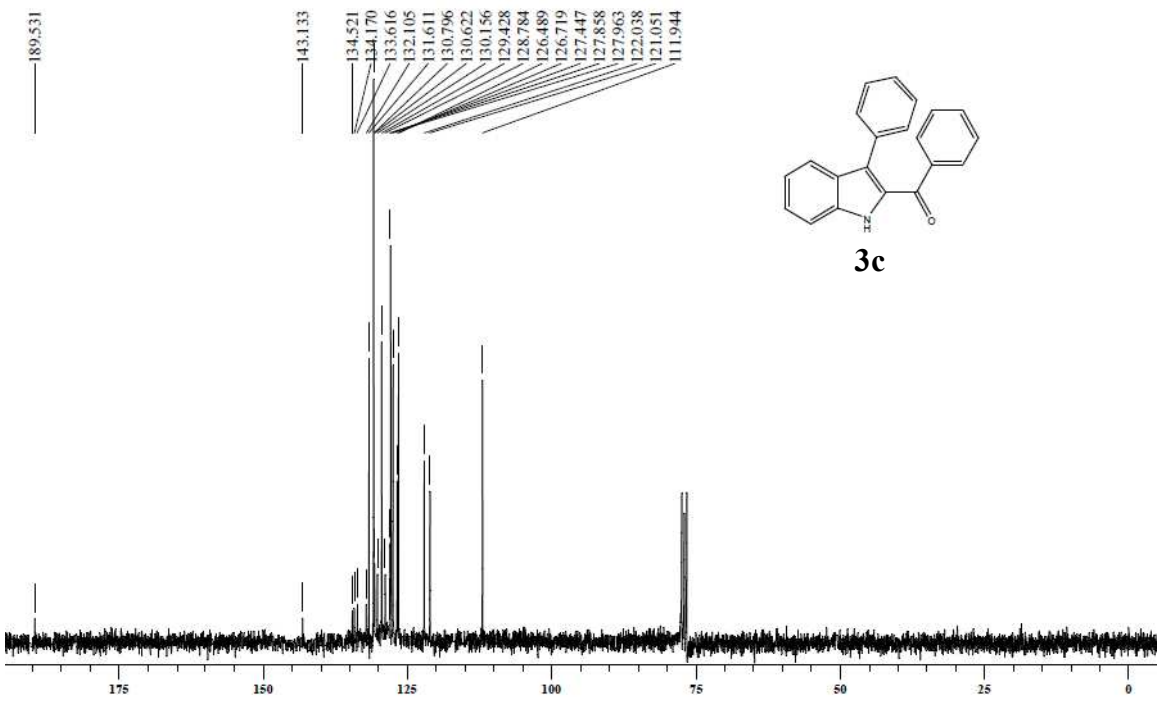
**3a**


MeO
MeO
N
H
O
3b
9
8
7
6
5
4
3
2
1
0
0.1
0.7
0.3


188.156
145.924
146.406
139.809
132.294
131.492
128.795
121.977
121.059
128.605
128.348
129.441
101.057
93.570
56.049
56.194
11.406
3b
200
175
150
125
100
75
50
25
0



**3c**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132.105
131.611
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130.156
129.428
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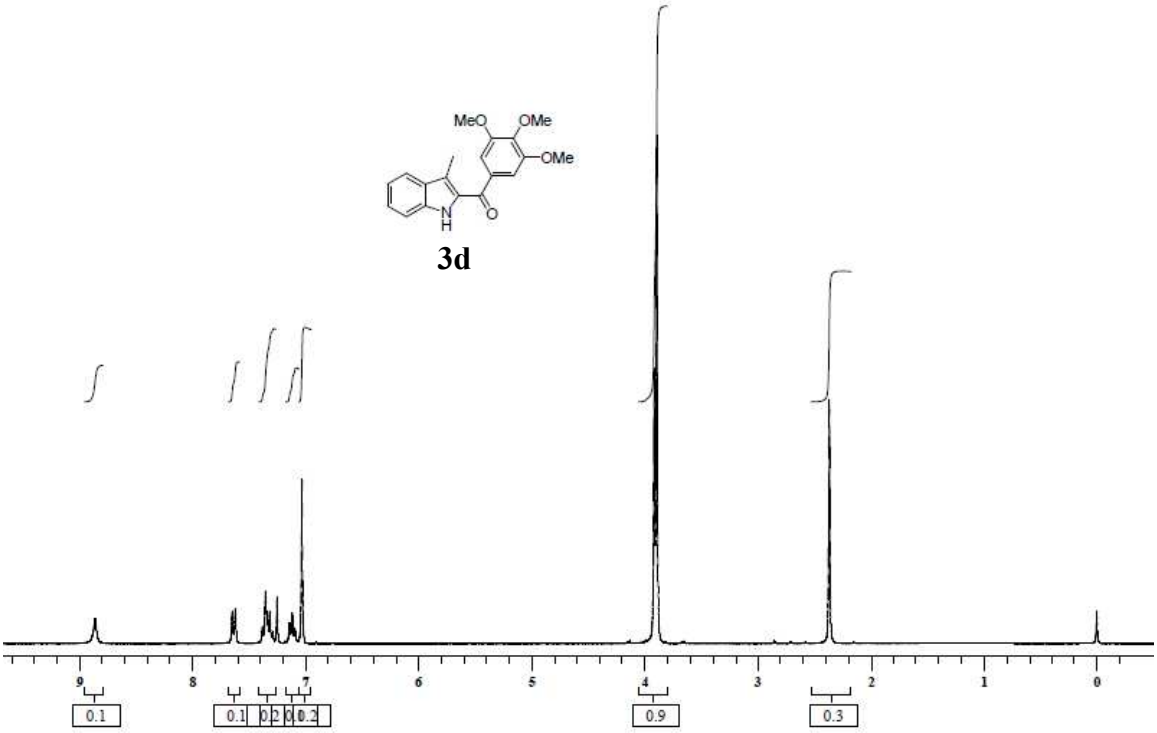
127.963
122.038
121.051
111.944

**3c**


MeO
OMe
OMe
O
N
H
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5
4
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1
0
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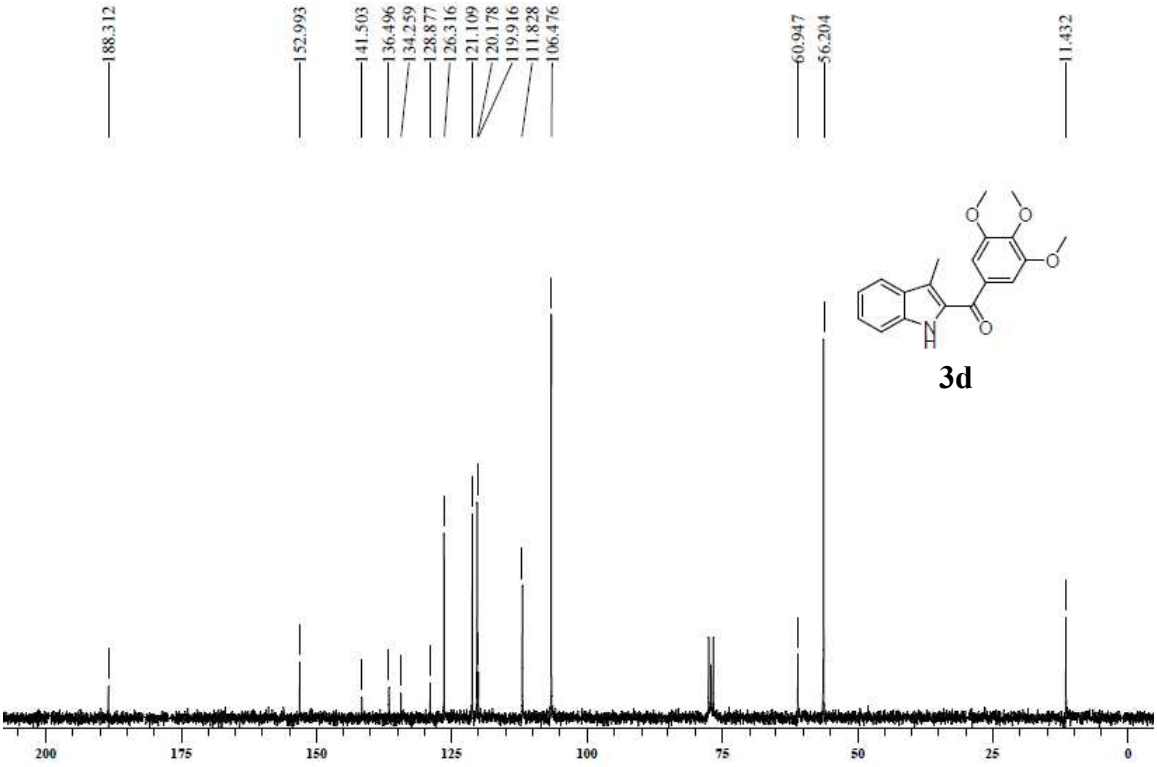
0.2
0.0
0.2
0.9
0.3

**3d**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128.877
126.316
121.109
120.178
119.916
111.828
106.476
60.947
56.204
11.432
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O
N
H
O
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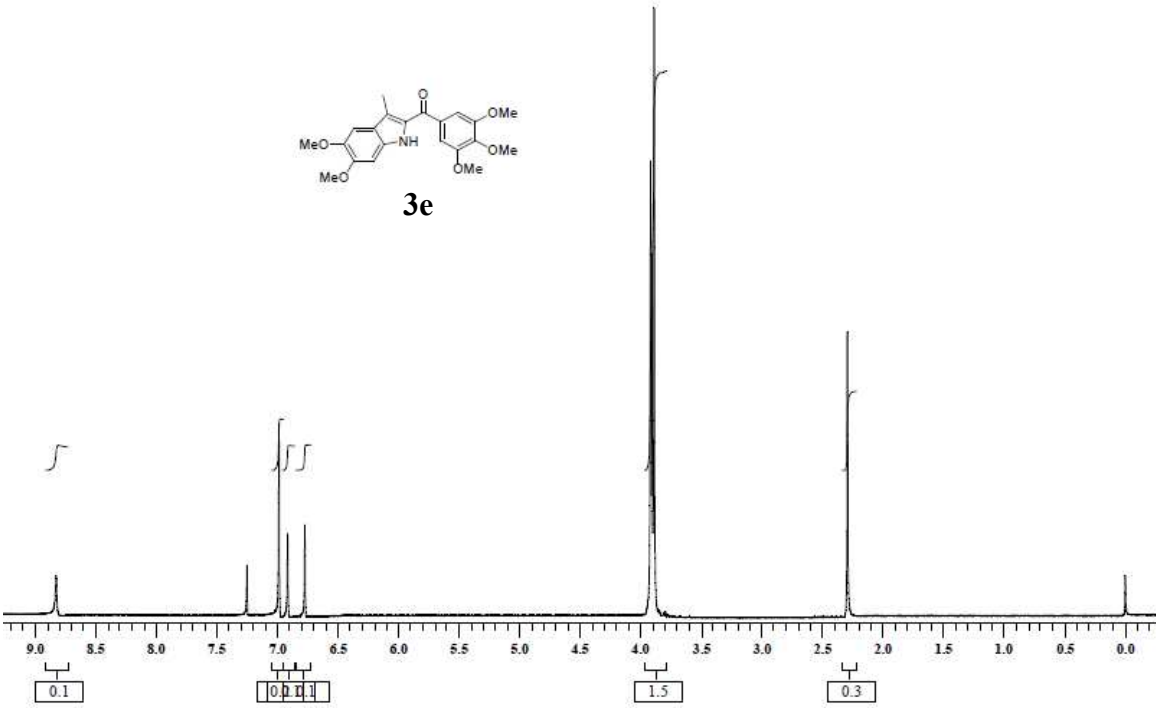
175
150
125
100
75
50
25
0

**3d**


MeO
NH
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MeO
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7.0
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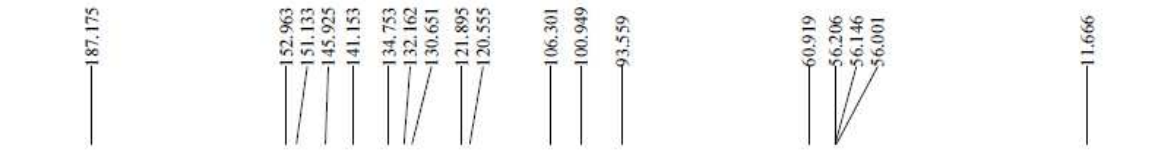
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0.1
1.5
0.3

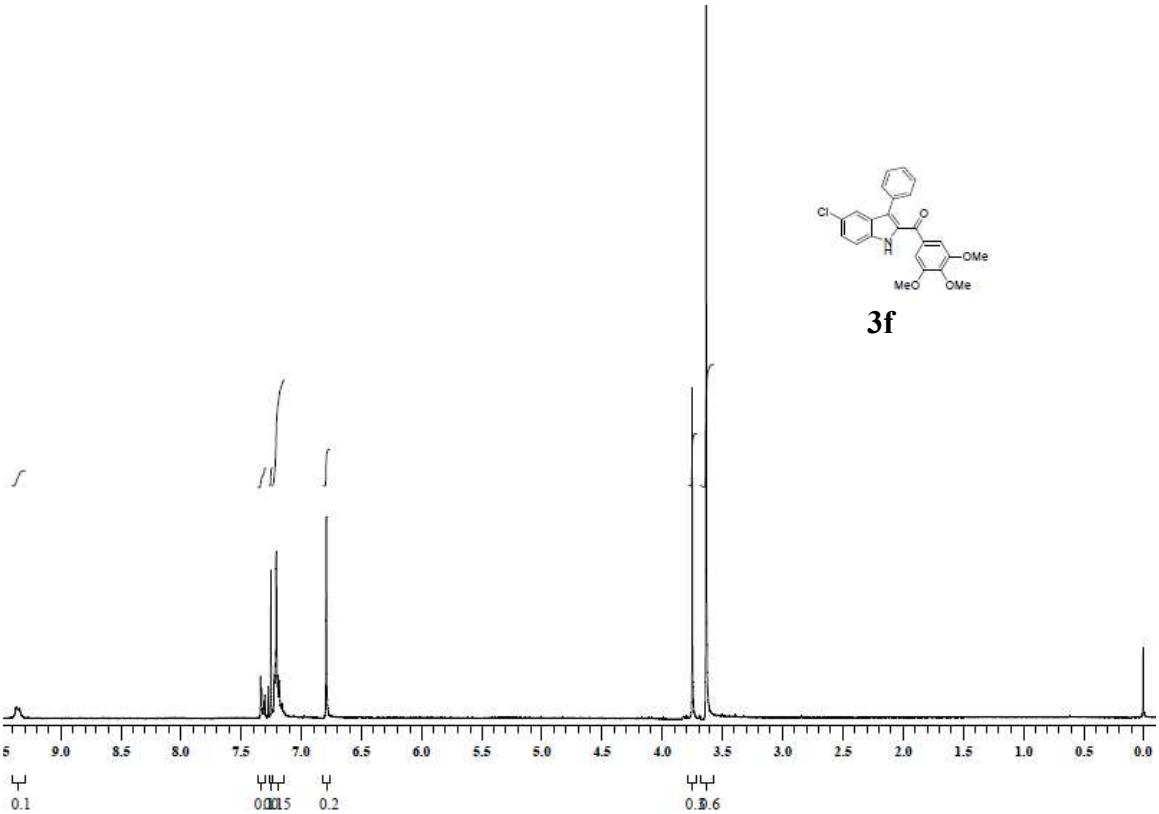
**3e**


187.175
152.963
151.133
145.925
141.153
134.753
132.162
130.651
121.895
120.555
106.301
100.949
93.559
60.919
56.206
56.146
56.001
11.666

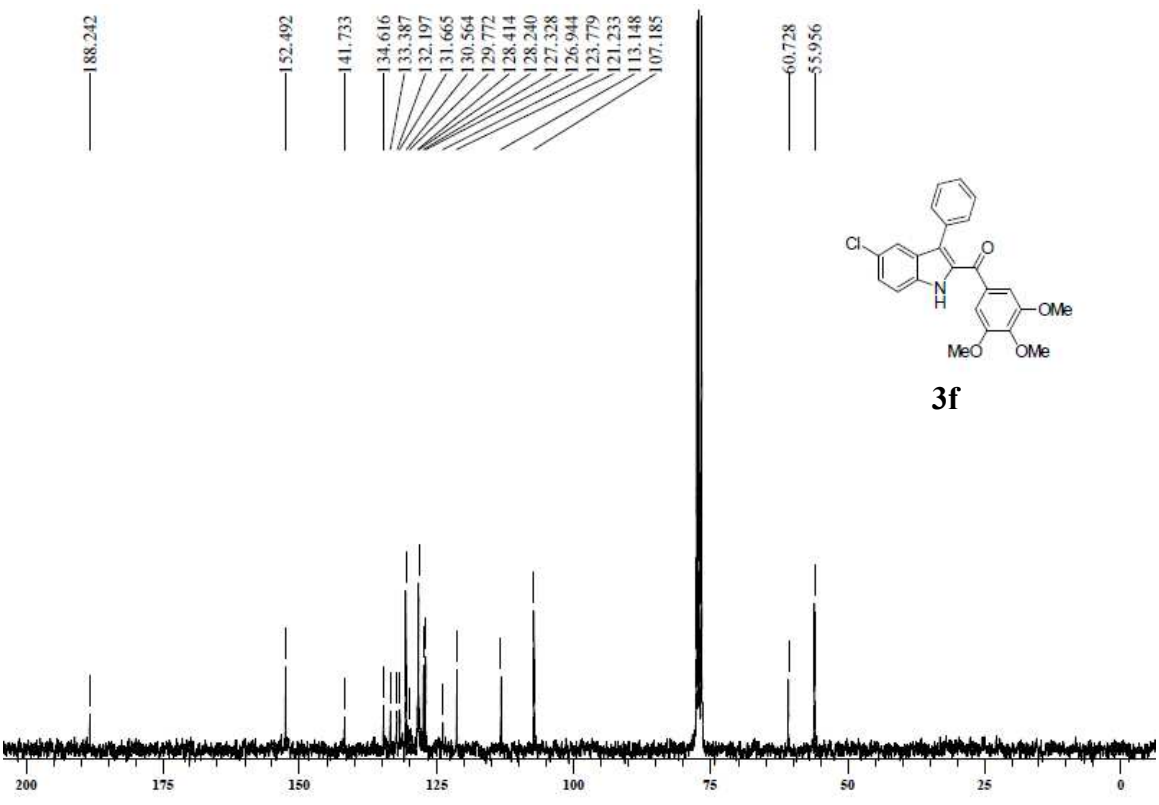

MeO
OMe
OMe
MeO
MeO
N
H
O

**3e**


200
175
150
125
100
75
50
25


Cl
O
H
OMe
MeO
OMe

**3f**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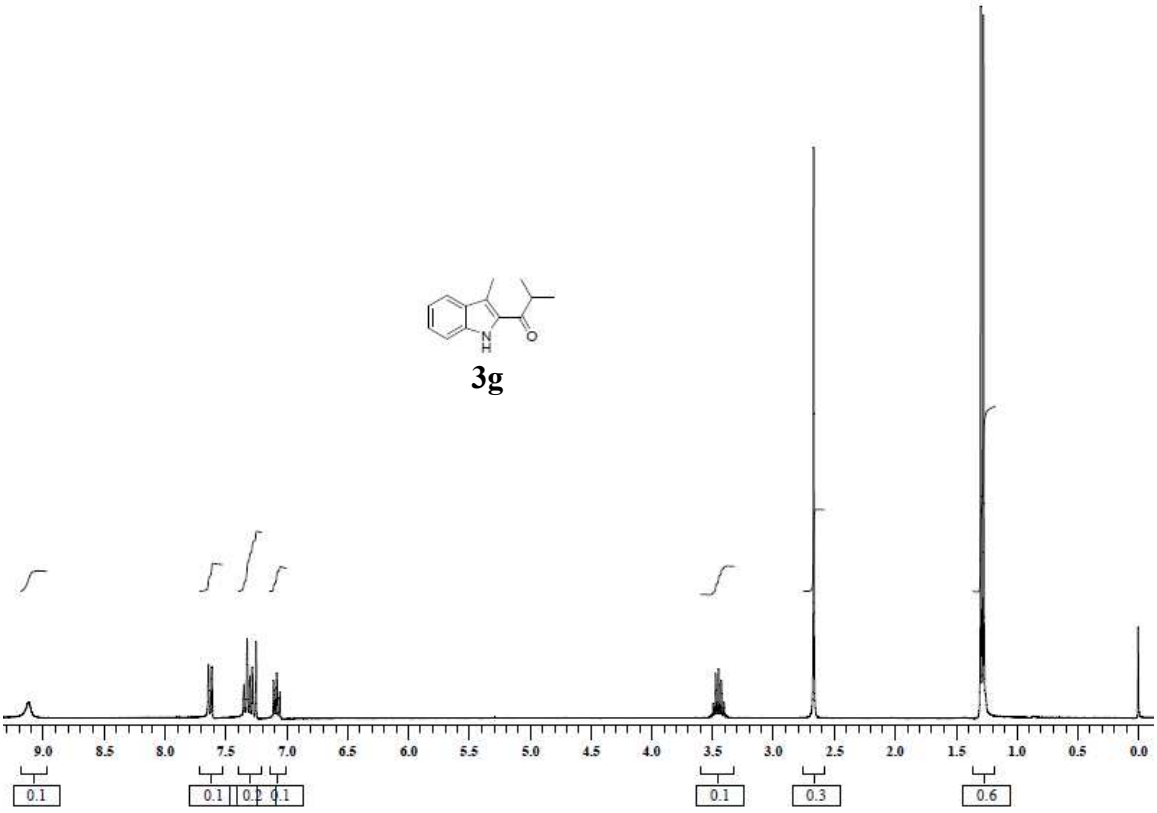
152.492
141.733
134.616
133.387
132.197
131.665
130.564
129.772
128.414
128.240
127.328
126.944
123.779
121.233
113.148
107.185
60.728
55.956


Cl
O
H
OMe
MeO
OMe

**3f**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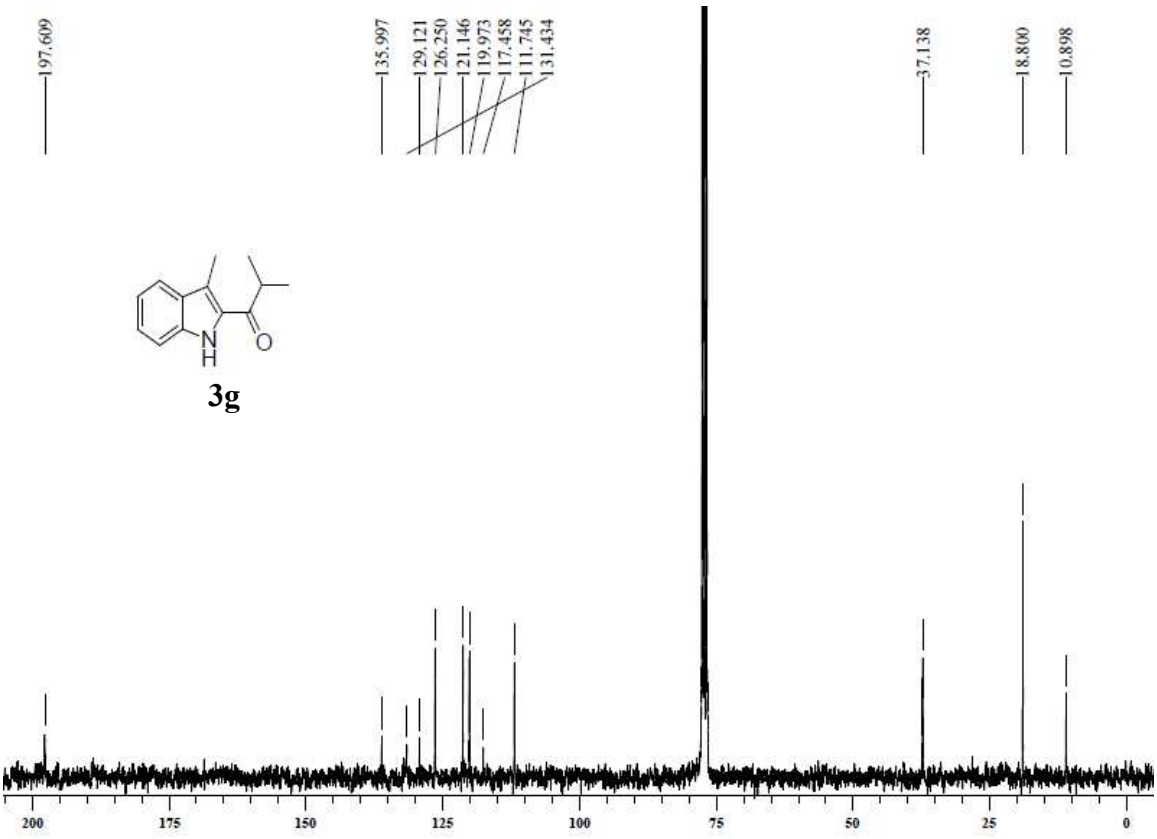
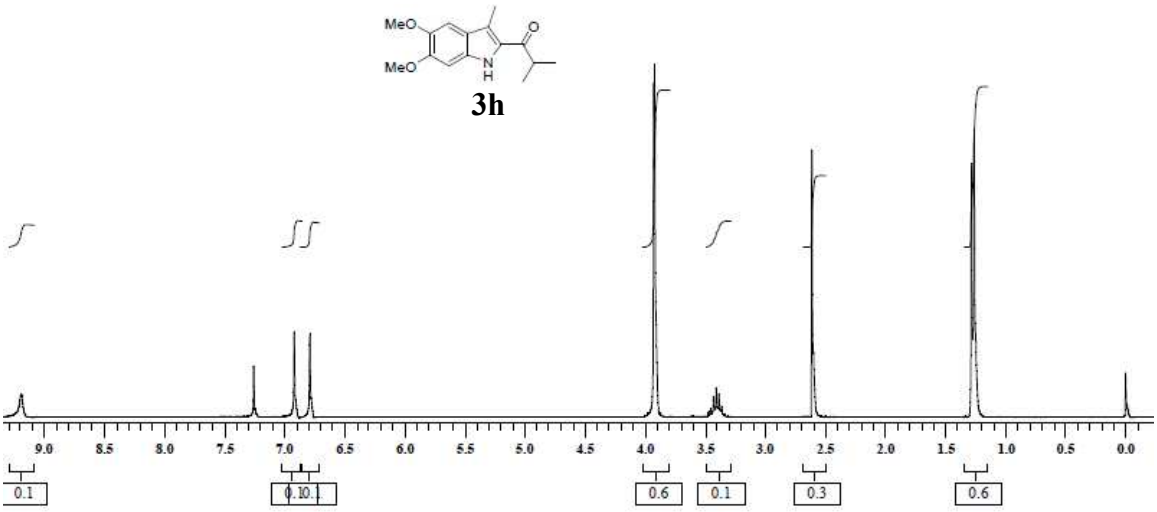
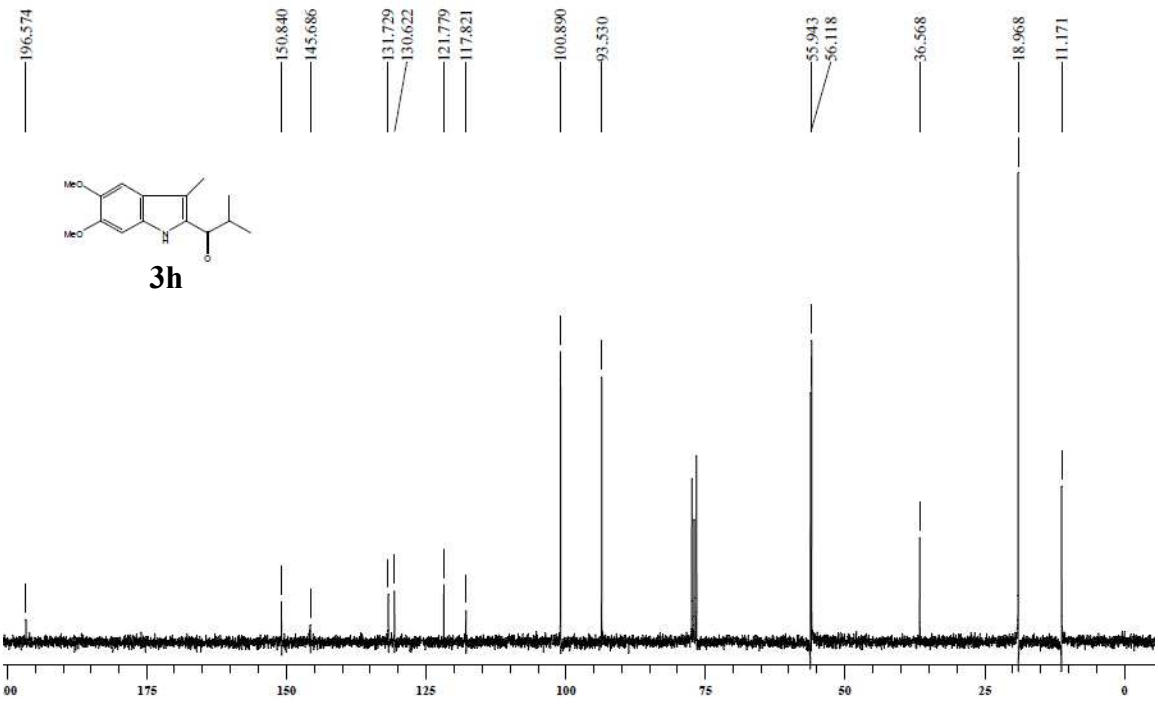
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0.1
0.1
0.2
0.1
0.1
0.3
0.6


197.609
135.997
129.121
126.250
121.146
119.973
117.458
111.745
131.434
37.138
18.800
10.898
3g
200
175
150
125
100
75
50
25
0


MeO
MeO
O
N
H
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0.1
0.6
0.1
0.3
0.6

**3h**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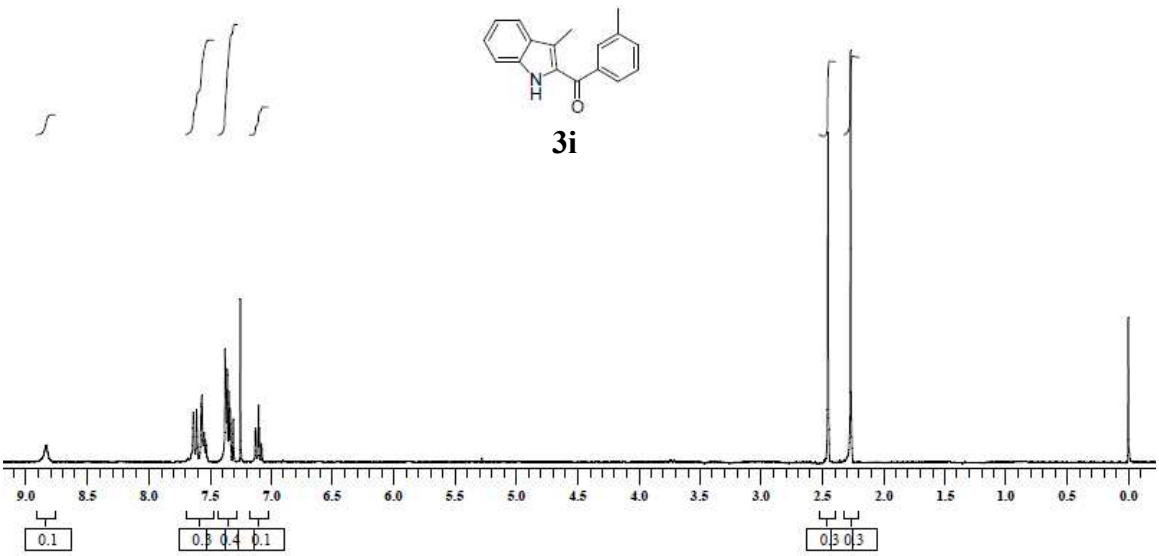
150.840
145.686
131.729
130.622
121.779
117.821
100.890
93.530
55.943
56.118
36.568
18.968
11.171
MeO
MeO
H
O
175
150
125
100
75
50
25
0

**3h**


3i
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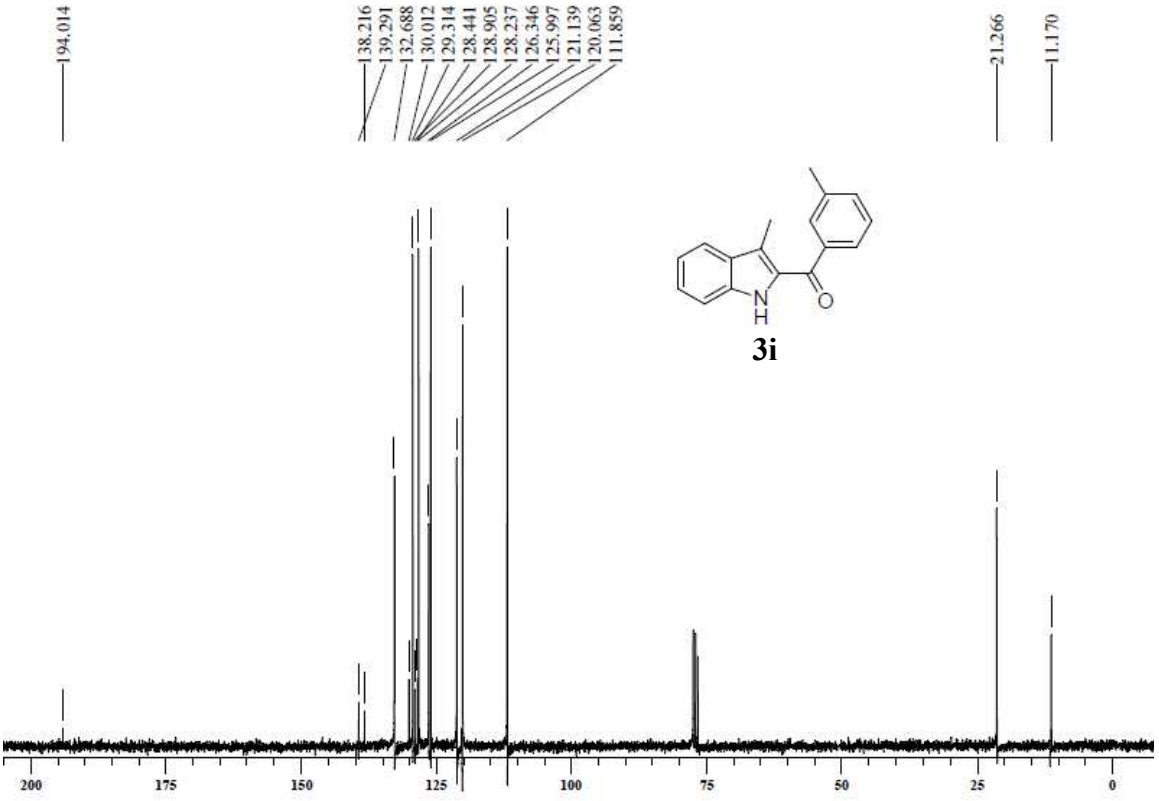
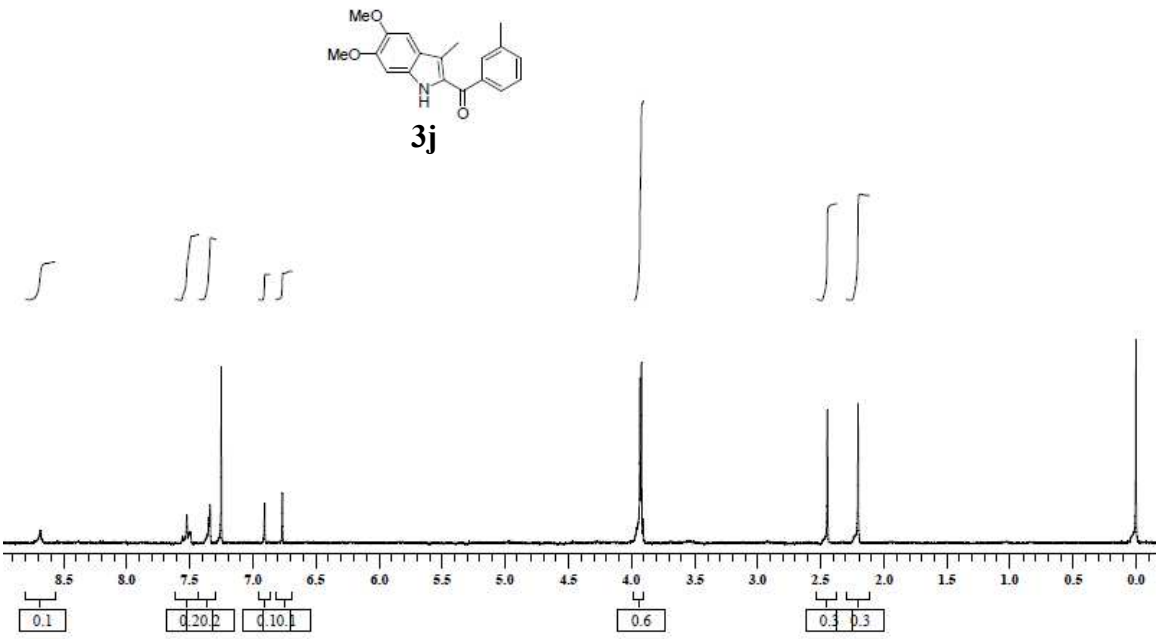
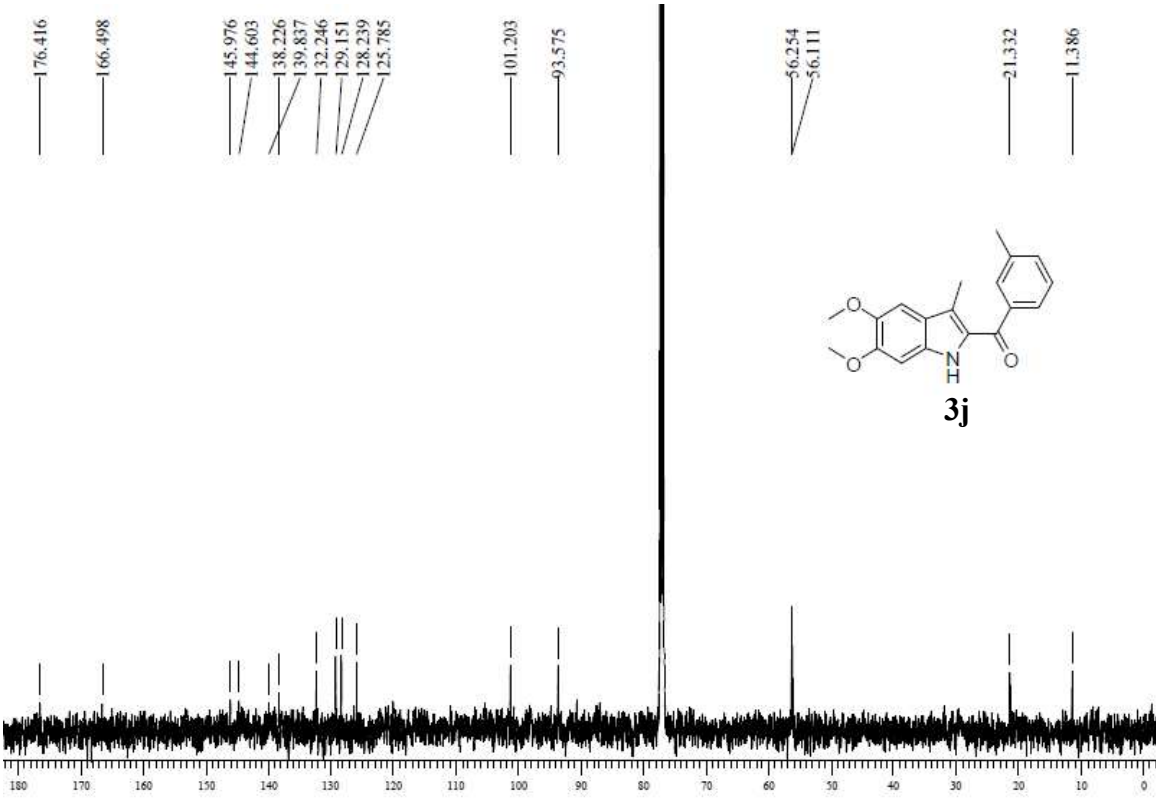
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0.1
0.3
0.4
0.1
0.3
0.3

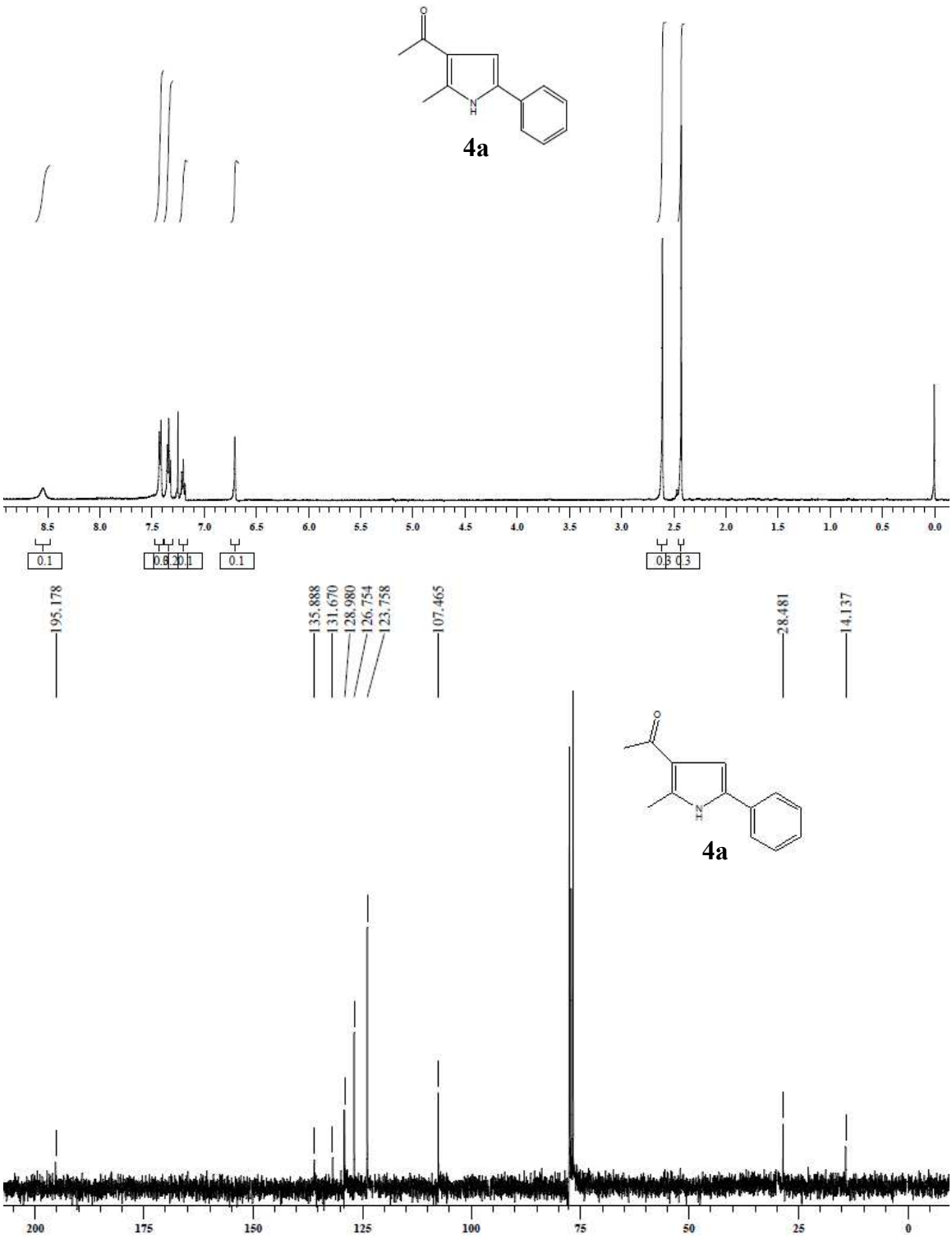

194.014
138.216
139.291
132.688
130.012
129.314
128.441
128.905
128.237
126.346
125.997
121.139
120.063
111.859
21.266
11.170
3i
200
175
150
125
100
75
50
25
0


MeO
MeO
N
H
O
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0.1
0.20.2
0.10.1
0.6
0.3
0.3

**3j**


176.416
166.498
145.976
144.603
138.226
139.837
132.246
129.151
128.239
125.785
101.203
93.575
56.254
56.111
21.332
11.386
O
O
N
H
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

**3j**


4a
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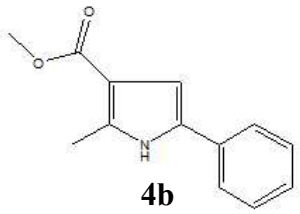
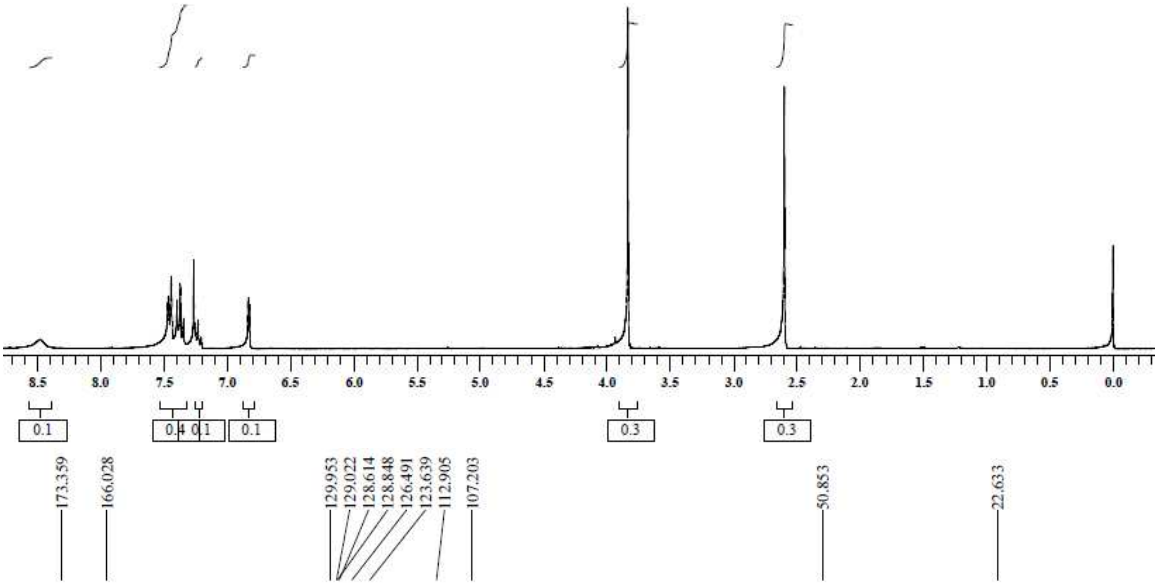
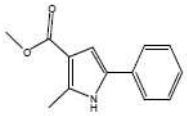
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0.1
0.8
0.2
0.1
0.1
0.3
0.3
195.178
135.888
131.670
128.980
126.754
123.758
107.465
28.481
14.137
4a
200
175
150
125
100
75
50
25
0

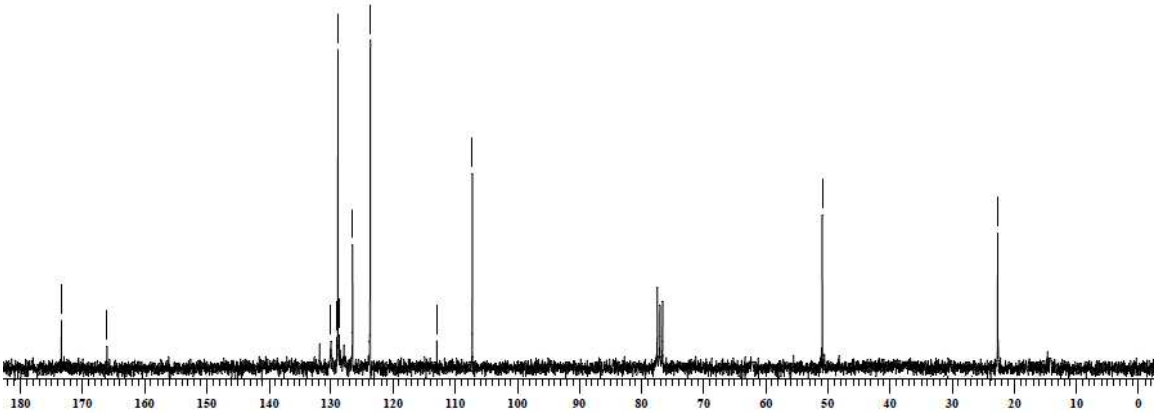


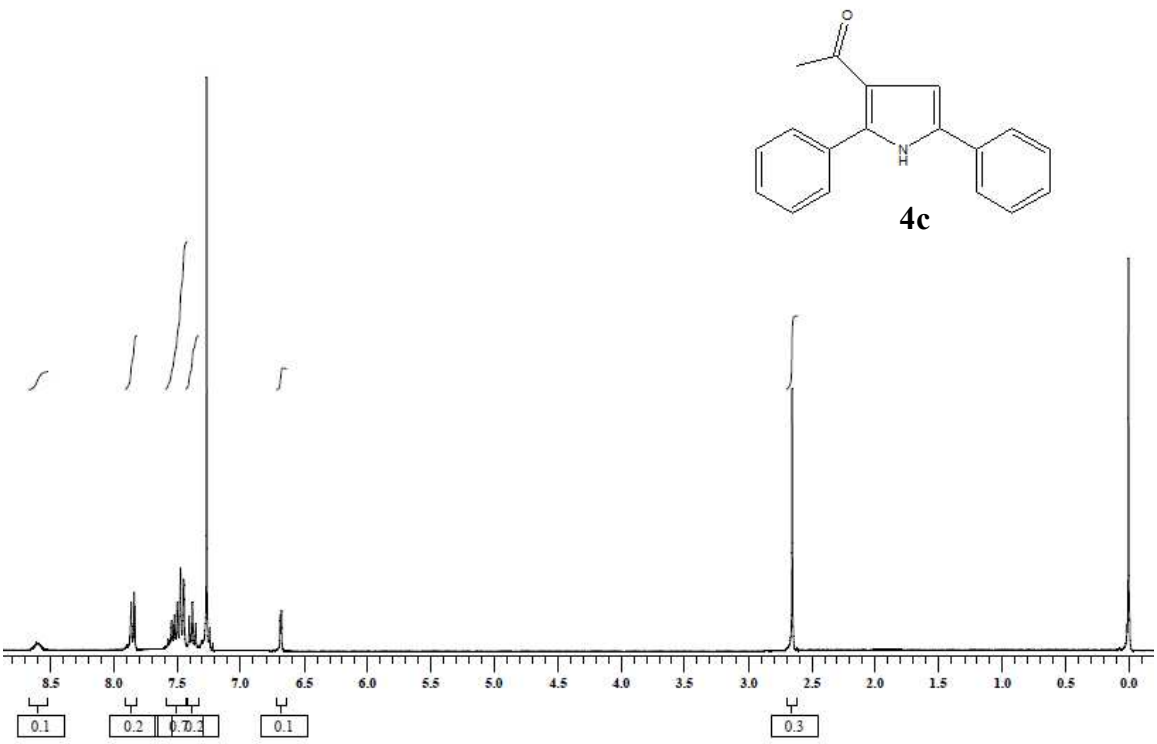
**4b**


8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0.1
0.4
0.1
0.1
0.3
0.3
173.359
166.028
129.953
129.022
128.614
128.848
126.491
123.639
112.905
107.203
50.853
22.633

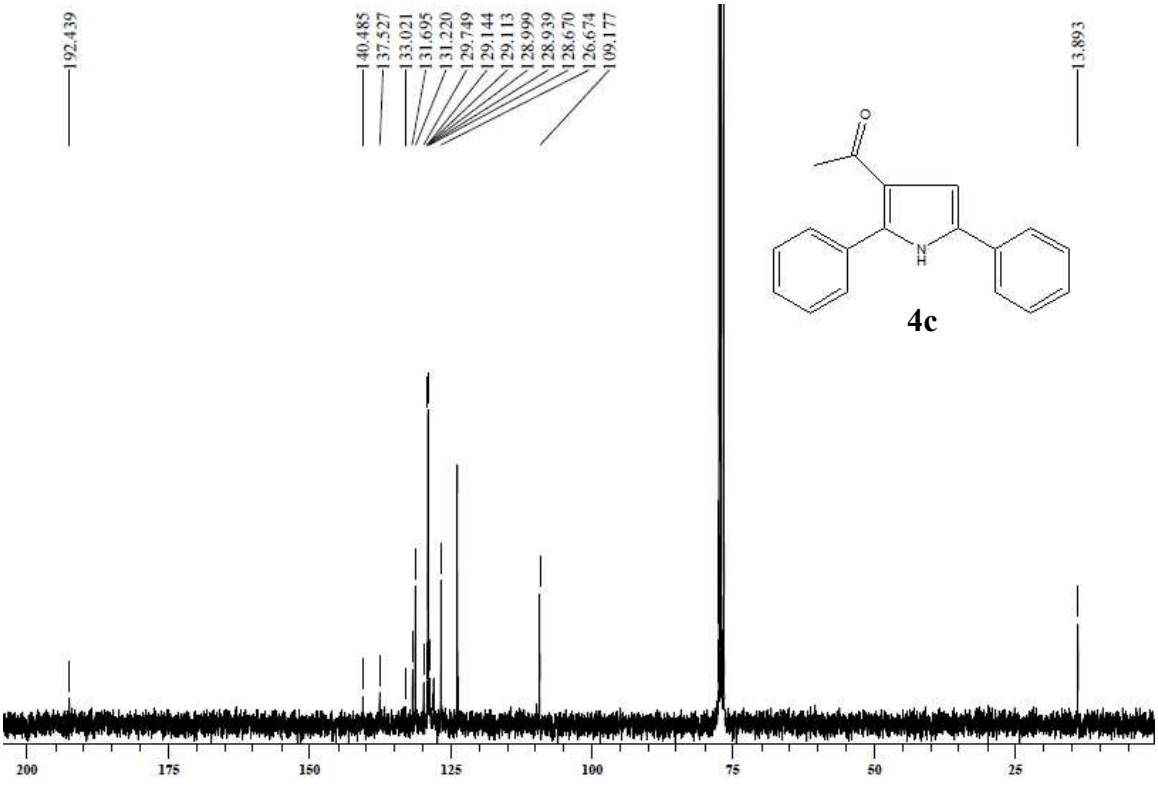


**4b**

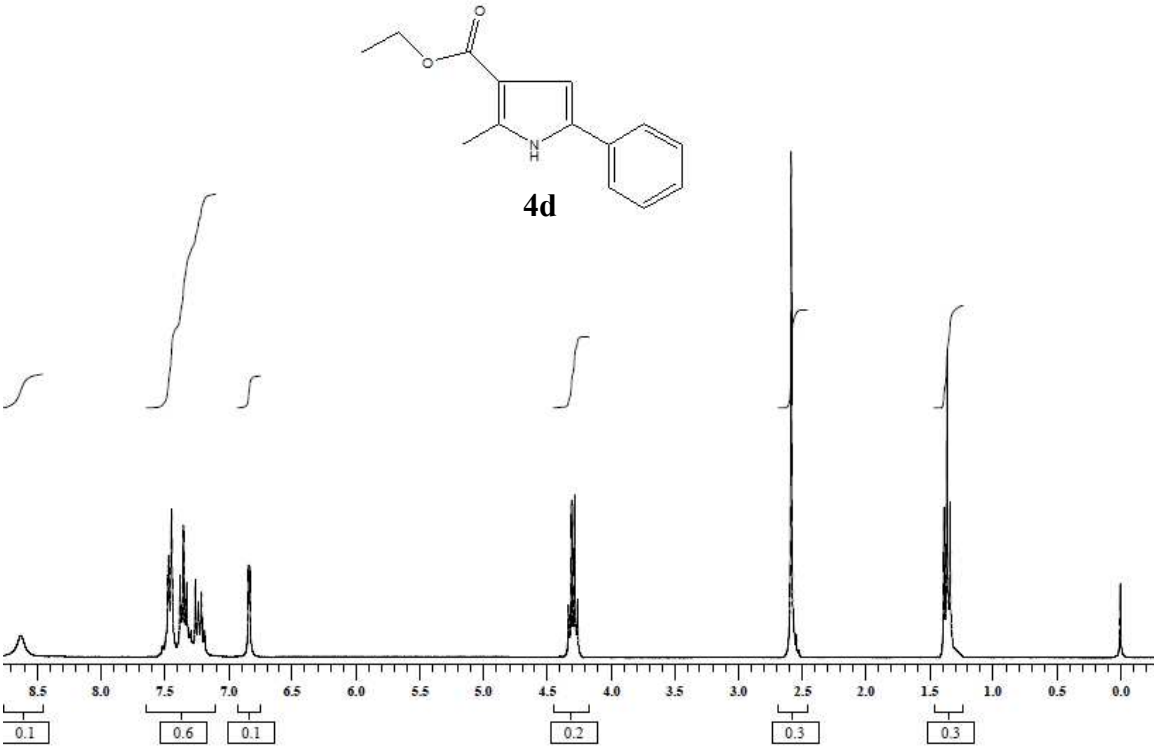

180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


O
N
H
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0.1
0.2
0.3

**4c**

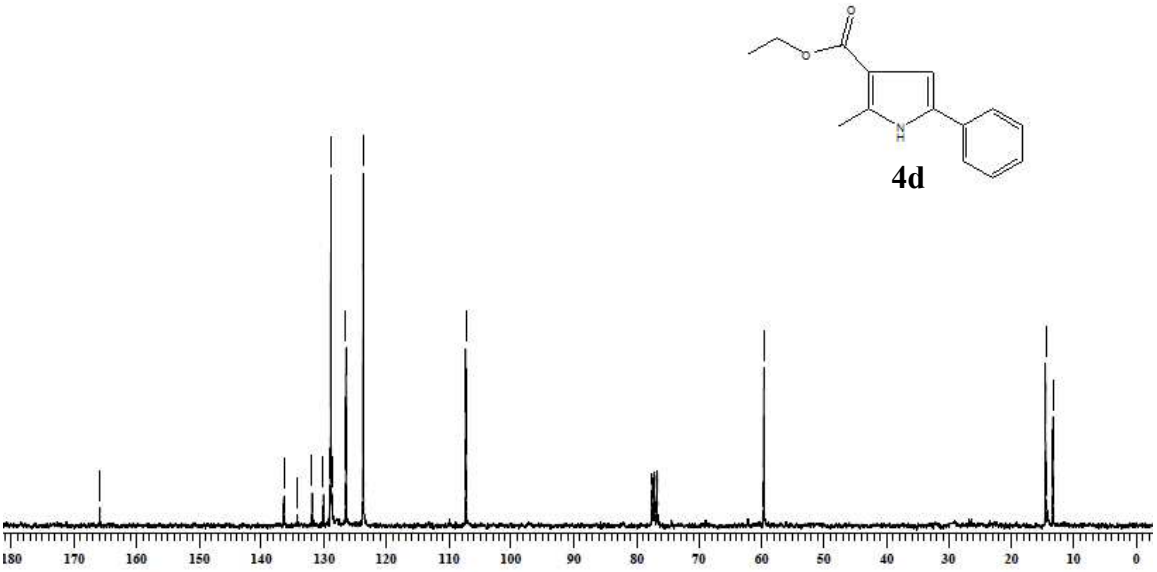

192.439
140.485
137.527
133.021
131.695
131.220
129.749
129.144
129.113
128.999
128.939
128.670
126.674
109.177
13.893
O
N
H
200
175
150
125
100
75
50
25

**4c**

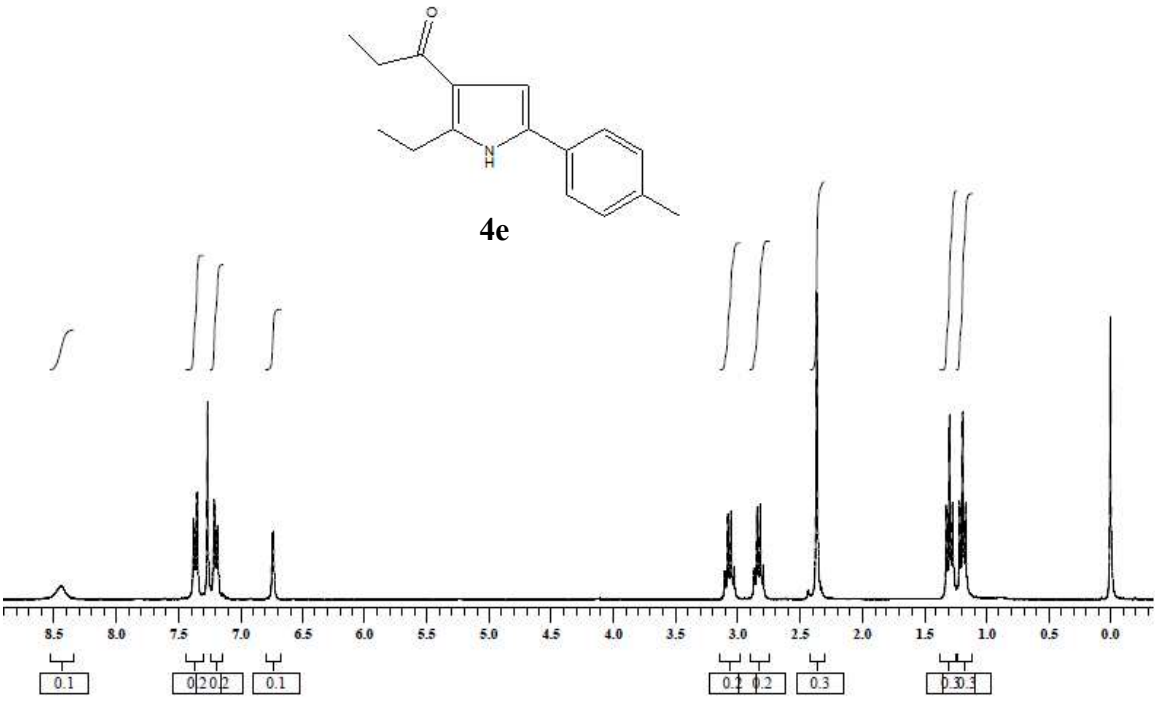


**4d**

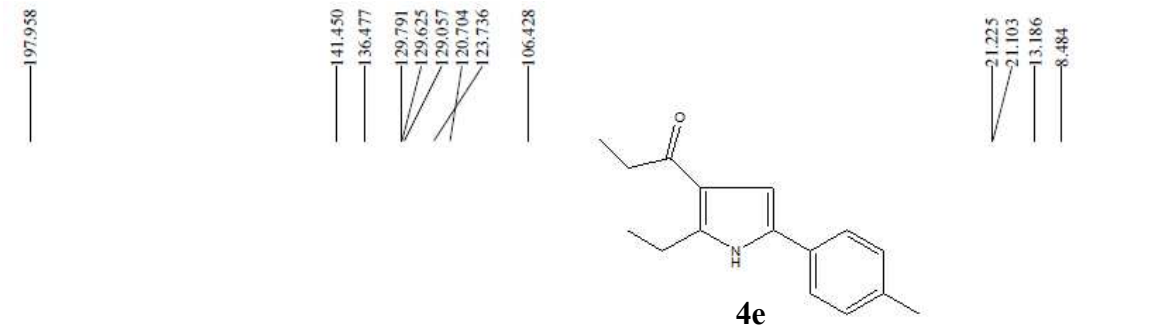

165.761
136.330
134.187
131.822
130.018
128.970
128.806
128.587
126.397
123.643
107.227
59.528
14.455
13.292



**4d**

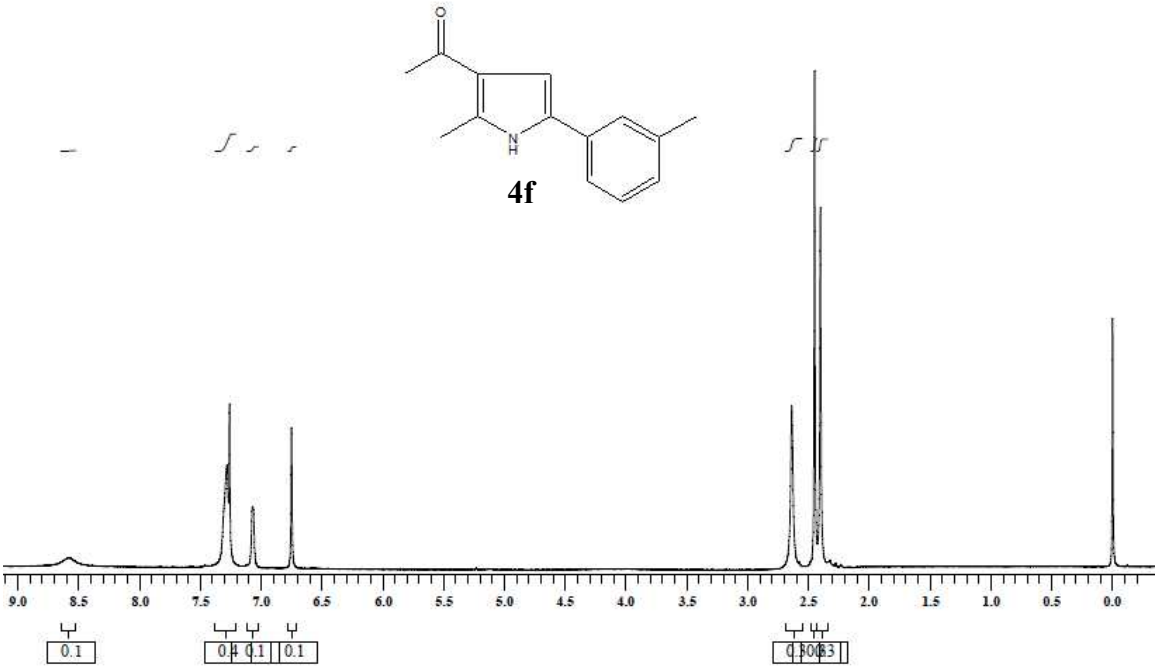


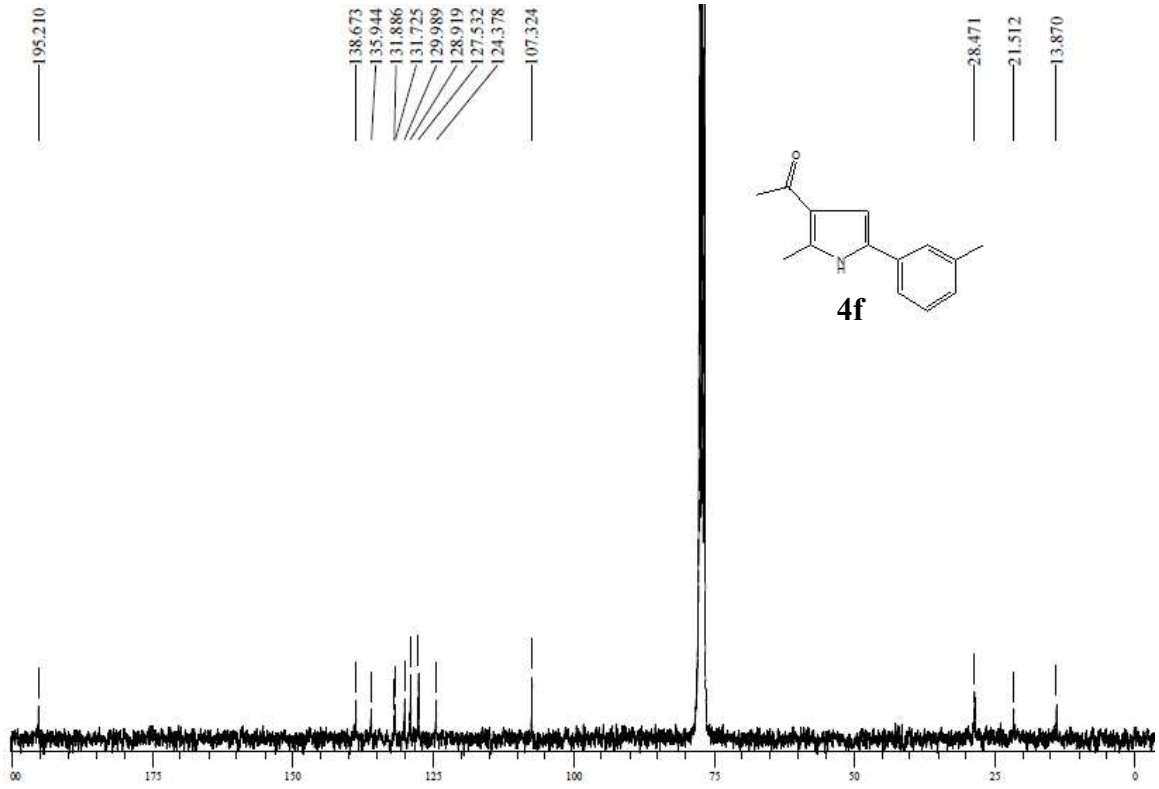
**4e**

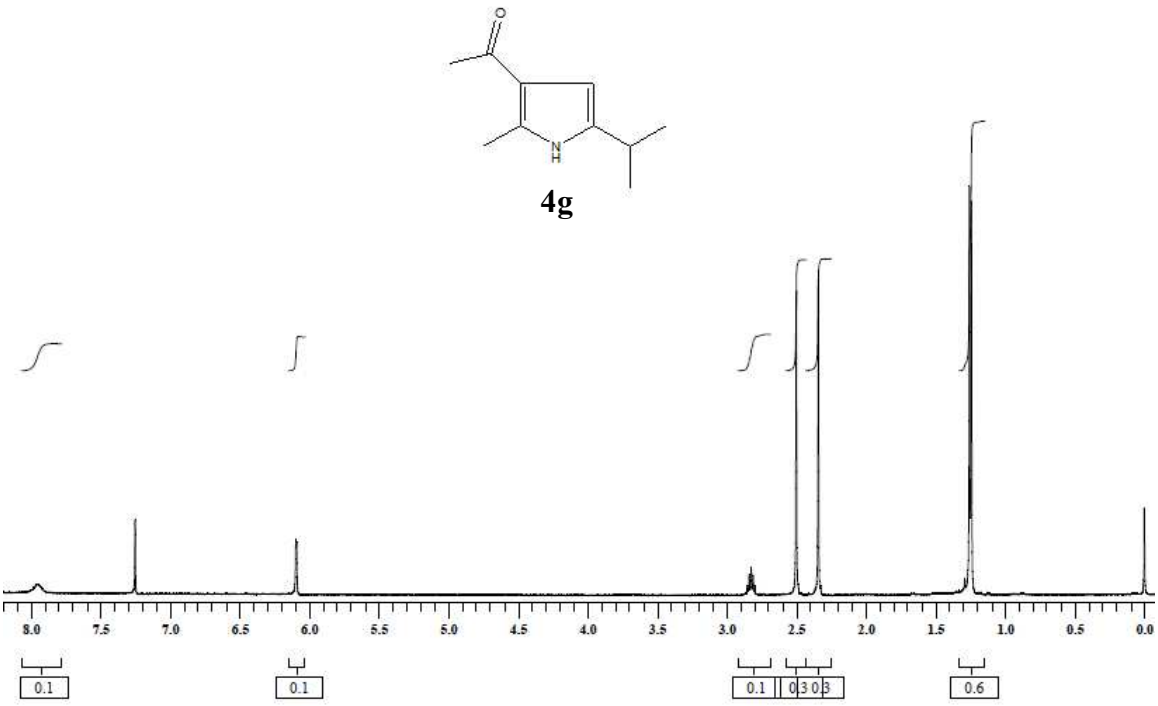




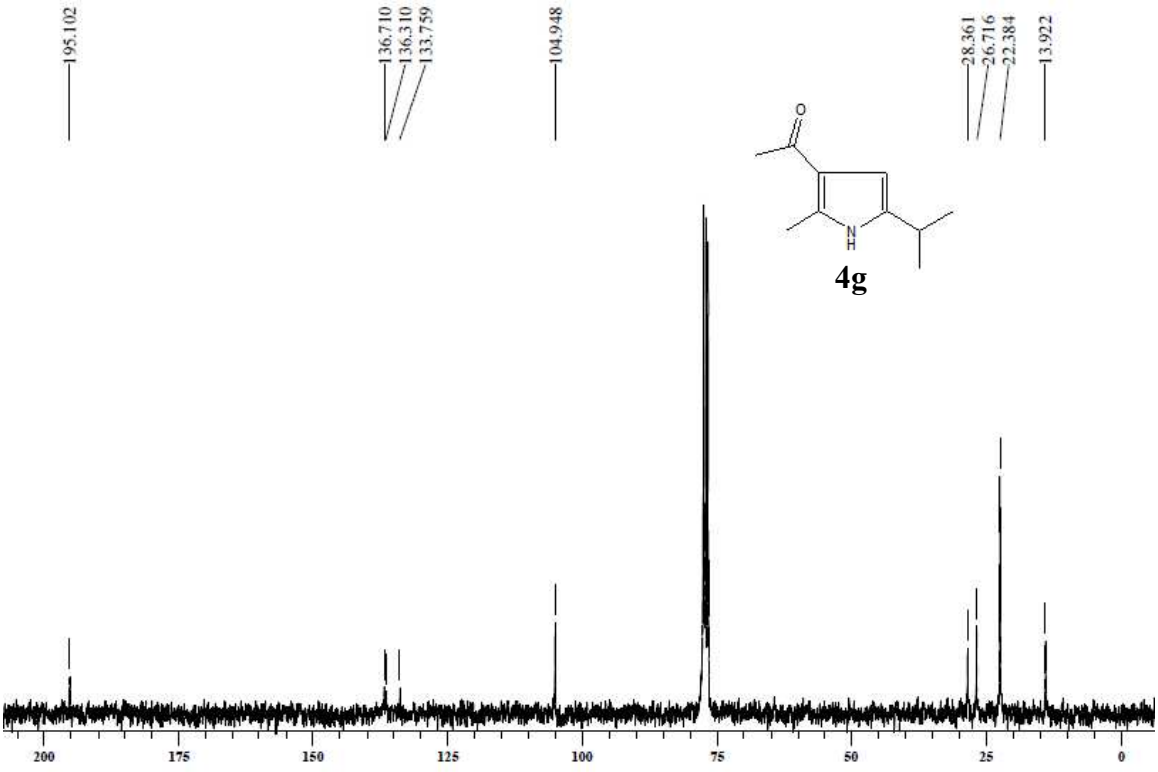
**4e**


4f
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0.1
0.4
0.1
0.1

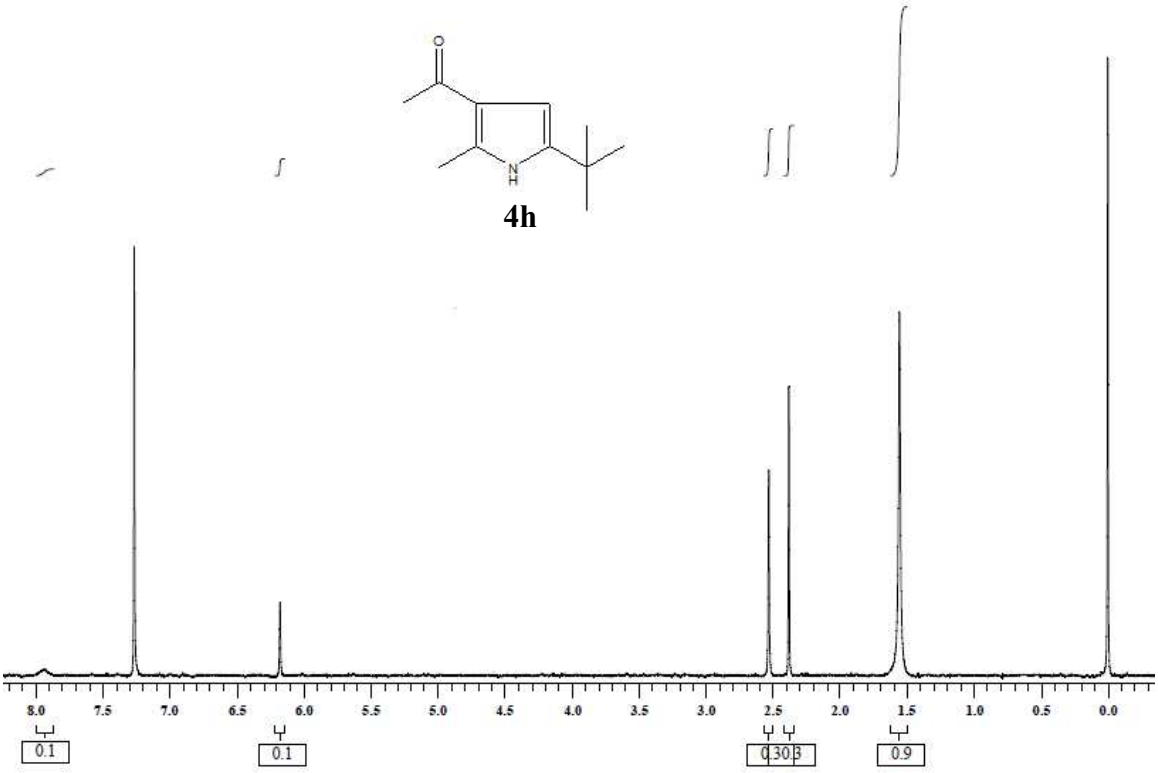

195.210
138.673
135.944
131.886
131.725
129.989
128.919
127.532
124.378
107.324
28.471
21.512
13.870
4f
175
150
125
100
75
50
25
0

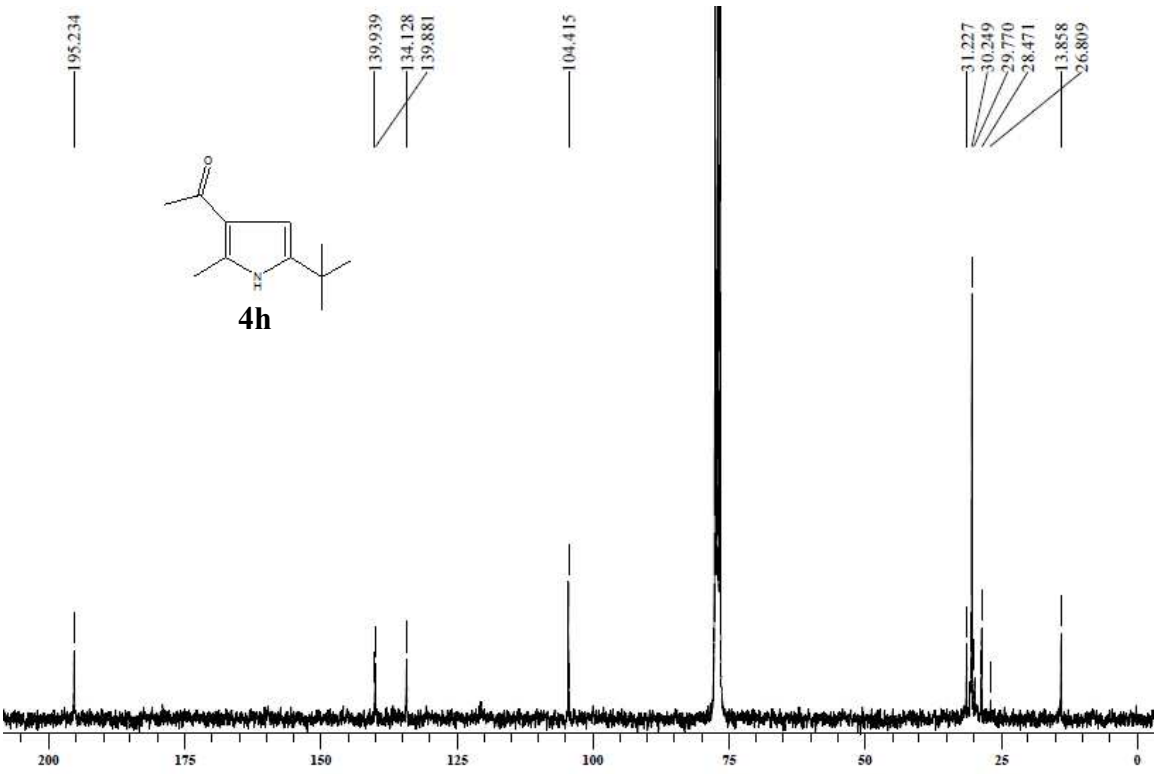

O
N
H
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0.1
0.1
0.1
0.3
0.3
0.6

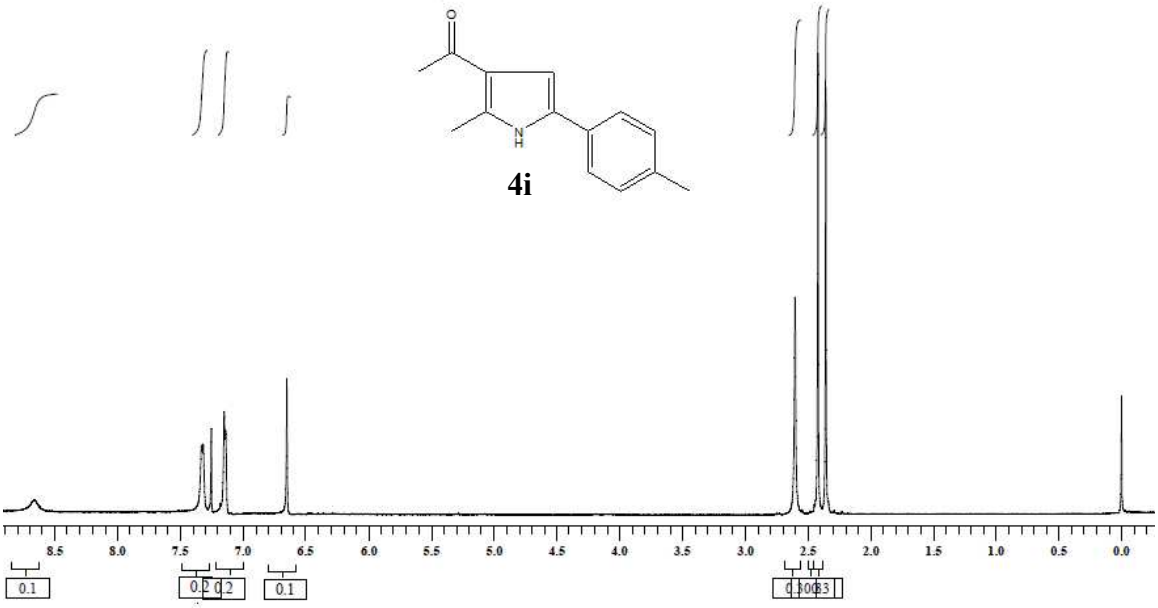
**4g**

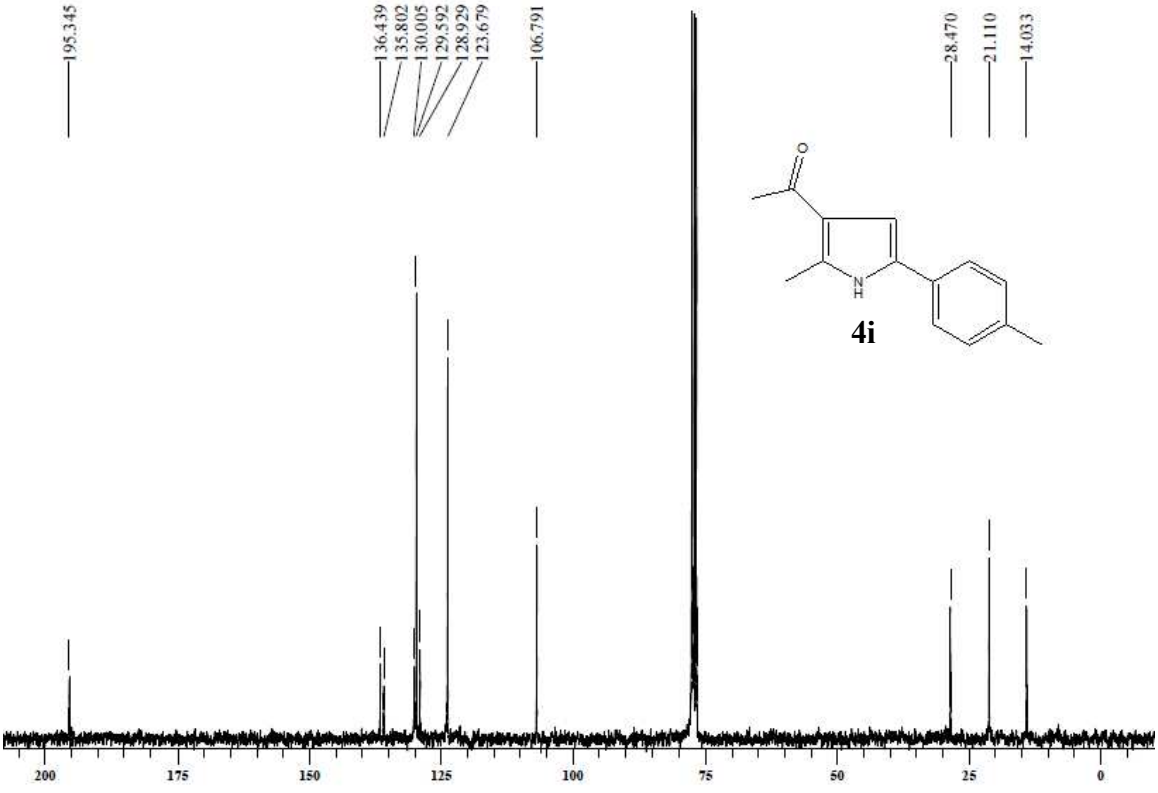

195.102
136.710
136.310
133.759
104.948
28.361
26.716
22.384
13.922
O
N
H
200
175
150
125
100
75
50
25
0

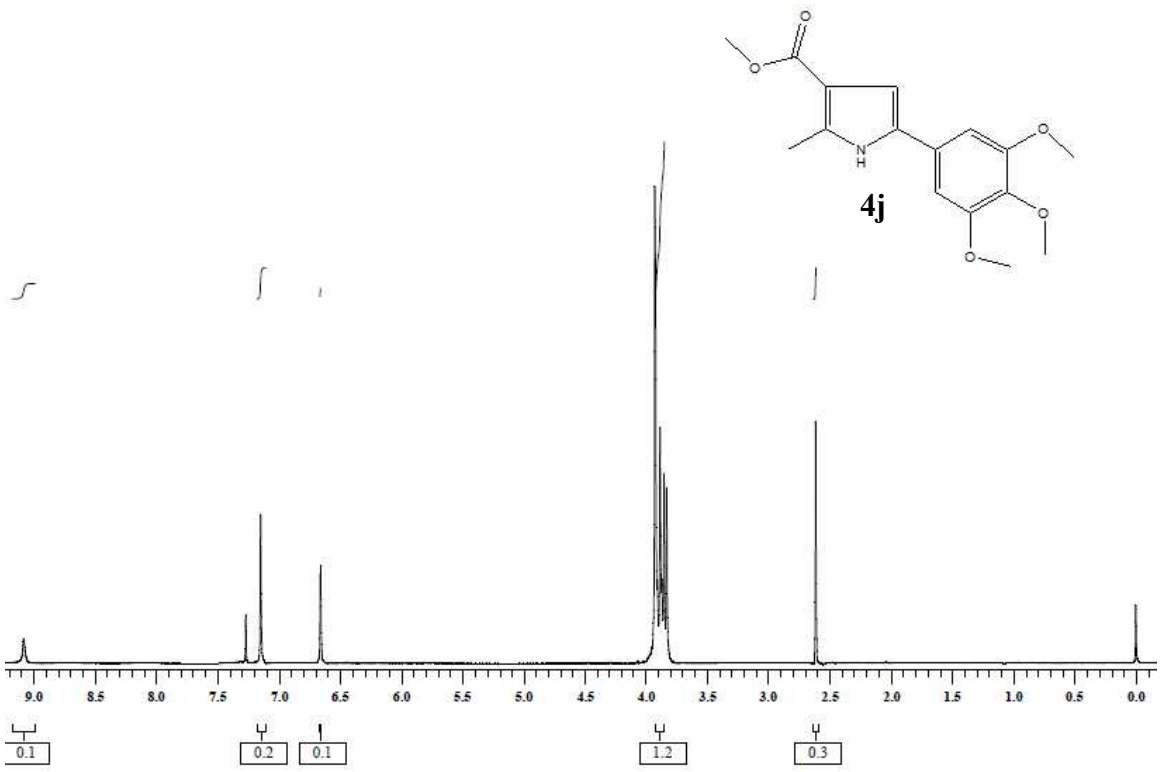
**4g**

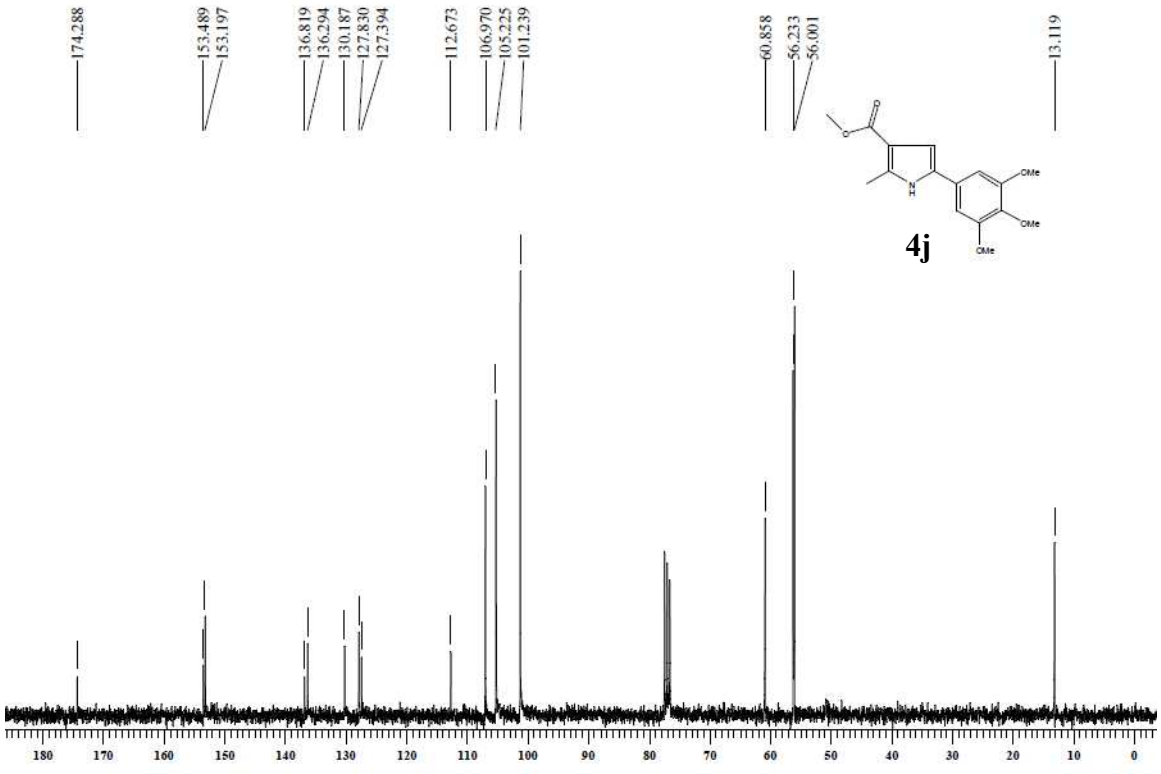

4h
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0.1
0.1
0.30
0.3
0.9

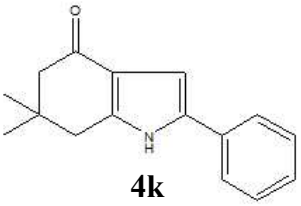

195.234
139.939
134.128
139.881
104.415
31.227
30.249
29.770
28.471
13.858
26.809
4h
200
175
150
125
100
75
50
25
0


4i

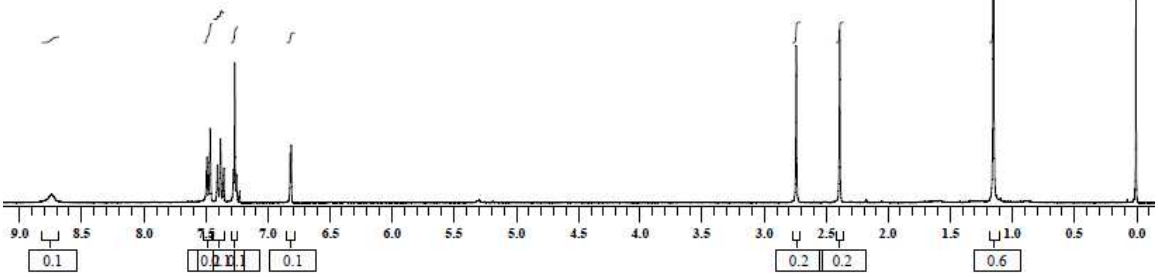

195.345
136.439
135.802
130.005
129.592
128.929
123.679
106.791
28.470
21.110
14.033
4i

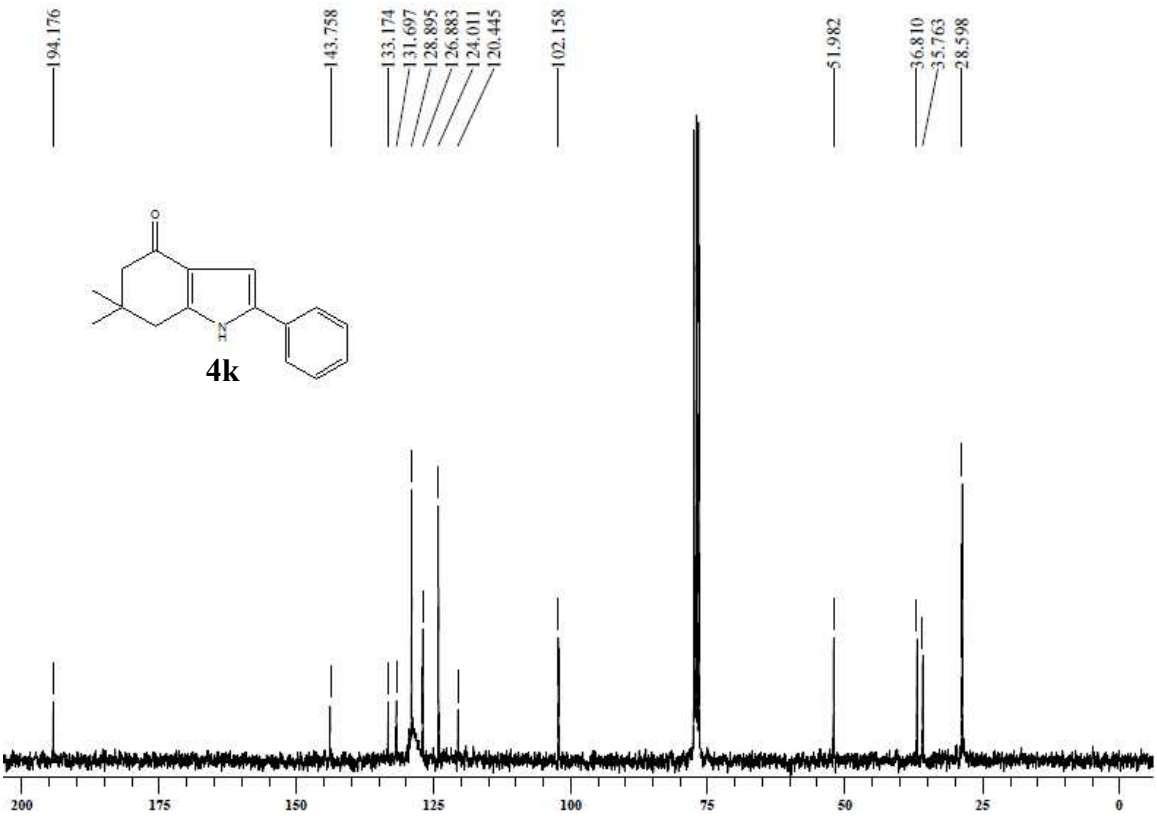

4j
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0.1
0.2
0.1
1.2
0.3


174.288
153.489
153.197
136.819
136.294
130.187
127.830
127.394
112.673
106.970
105.225
101.239
60.858
56.233
56.001
13.119
4j
OMe
OMe
OMe
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



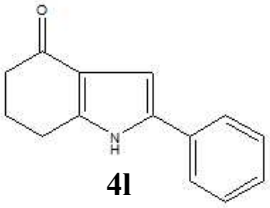
**4k**


9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0.1
0.1
0.2
0.2
0.6

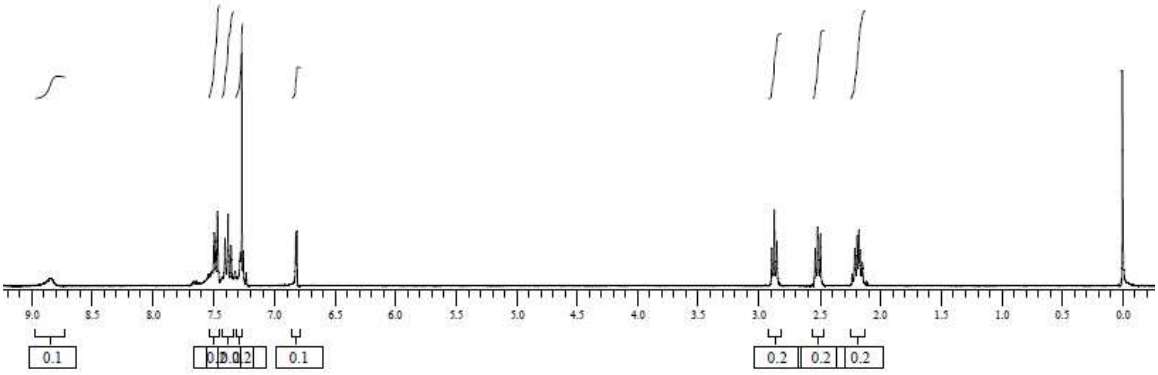

194.176
143.758
133.174
131.697
128.895
126.883
124.011
120.445
102.158
51.982
36.810
35.763
28.598
200
175
150
125
100
75
50
25
0



**4k**



**4l**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8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.5
4.0
3.5
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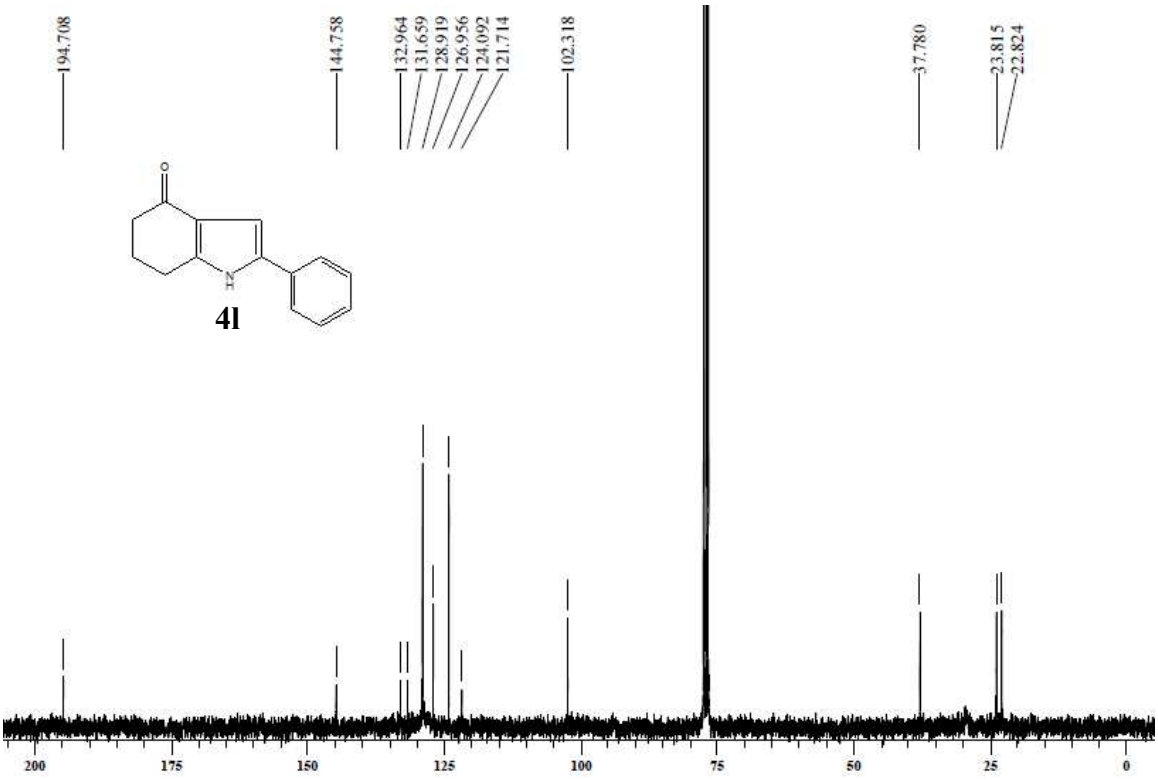
0.1
0.2
0.2
0.2
0.1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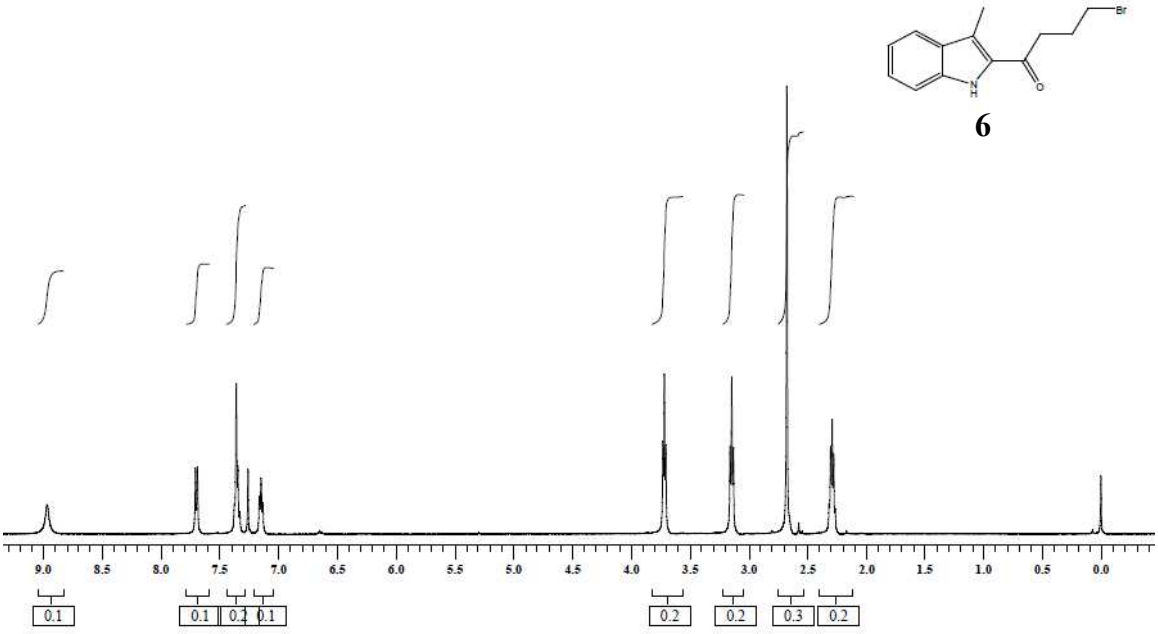
132.964
131.659
128.919
126.956
124.092
121.714
102.318
37.780
23.815
22.824
200
175
150
125
100
75
50
25
0



**4l**


Br
O
H
N
6
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
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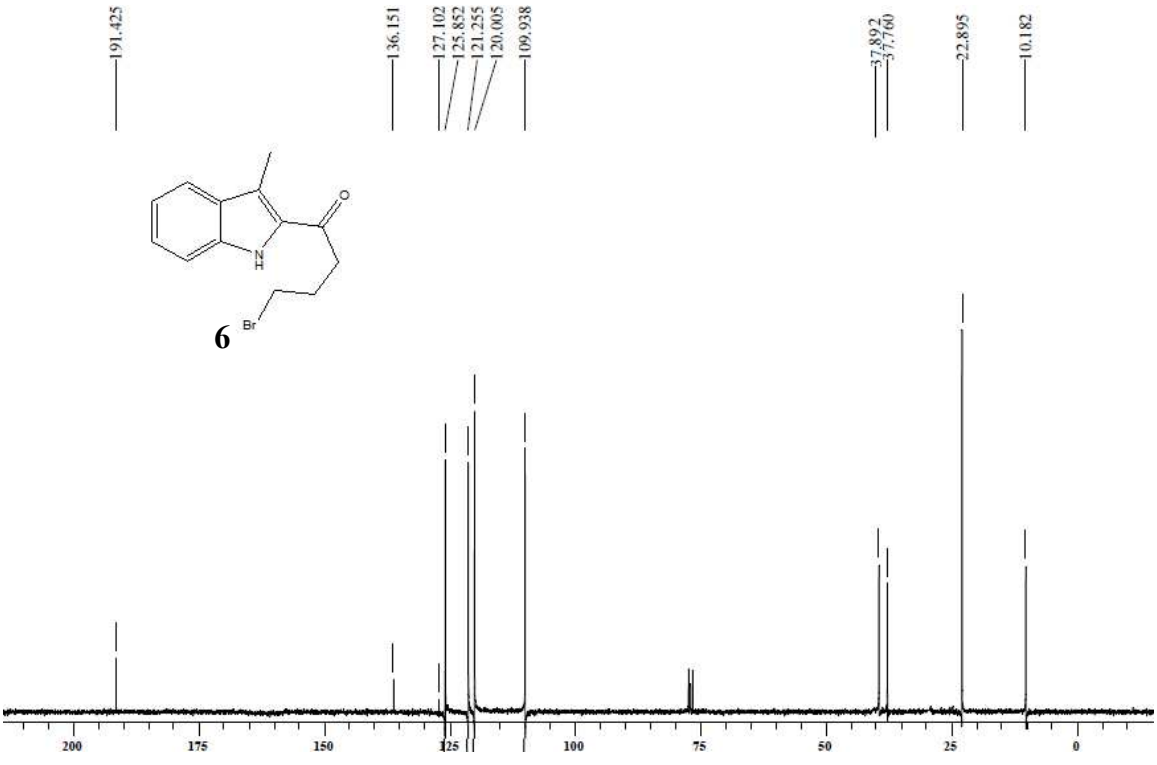
0.2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136.151
127.102
125.852
121.255
120.005
109.938
37.892
37.760
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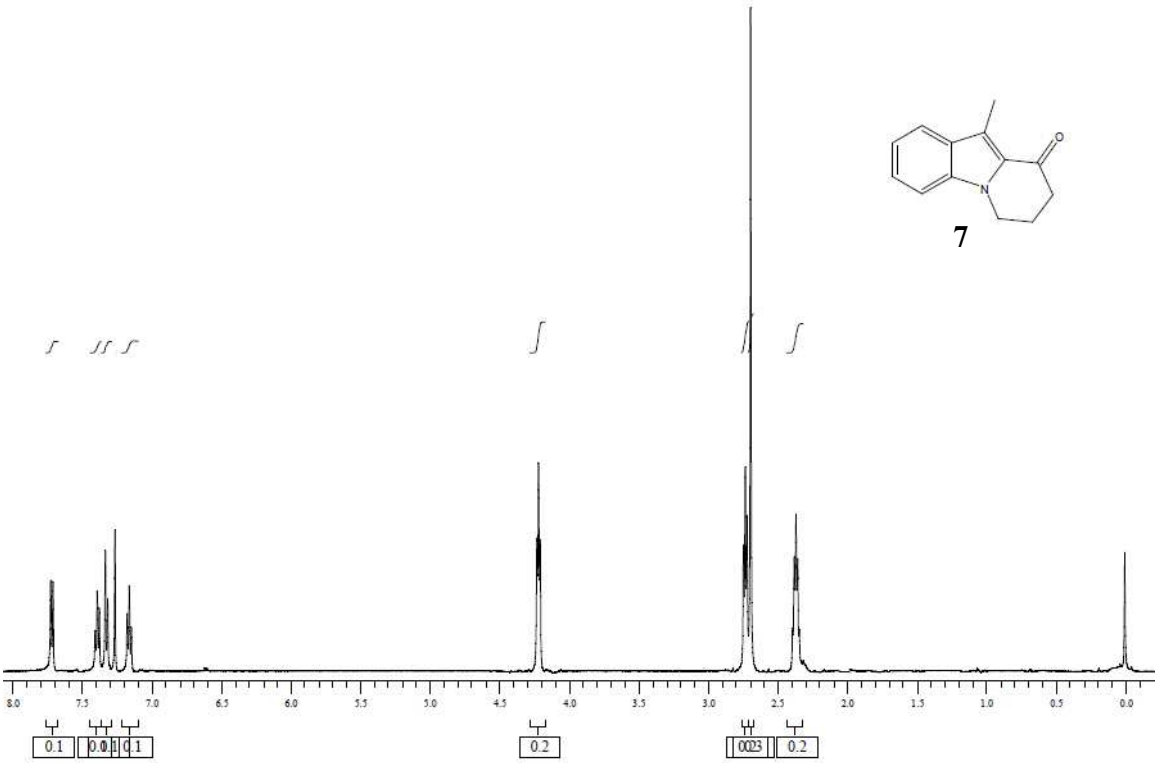
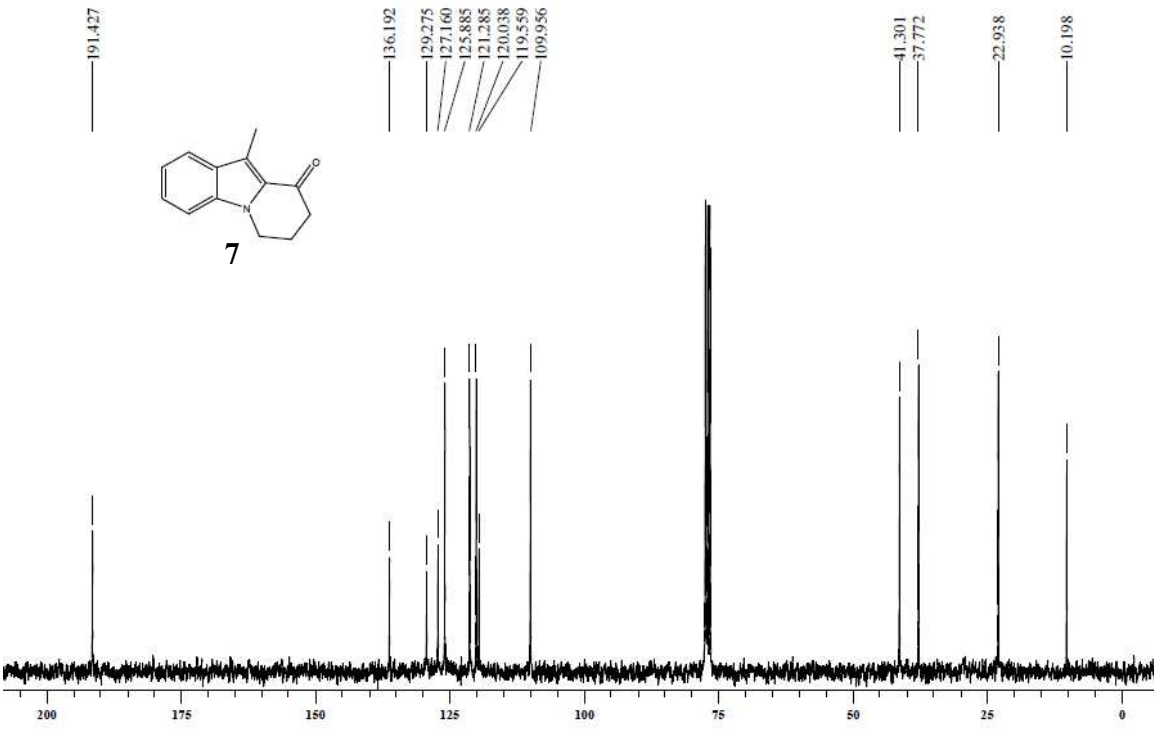
10.182
O
H
N
Br
6
200
175
150
125
100
75
50
25
0


7
0.1
0.2
0.2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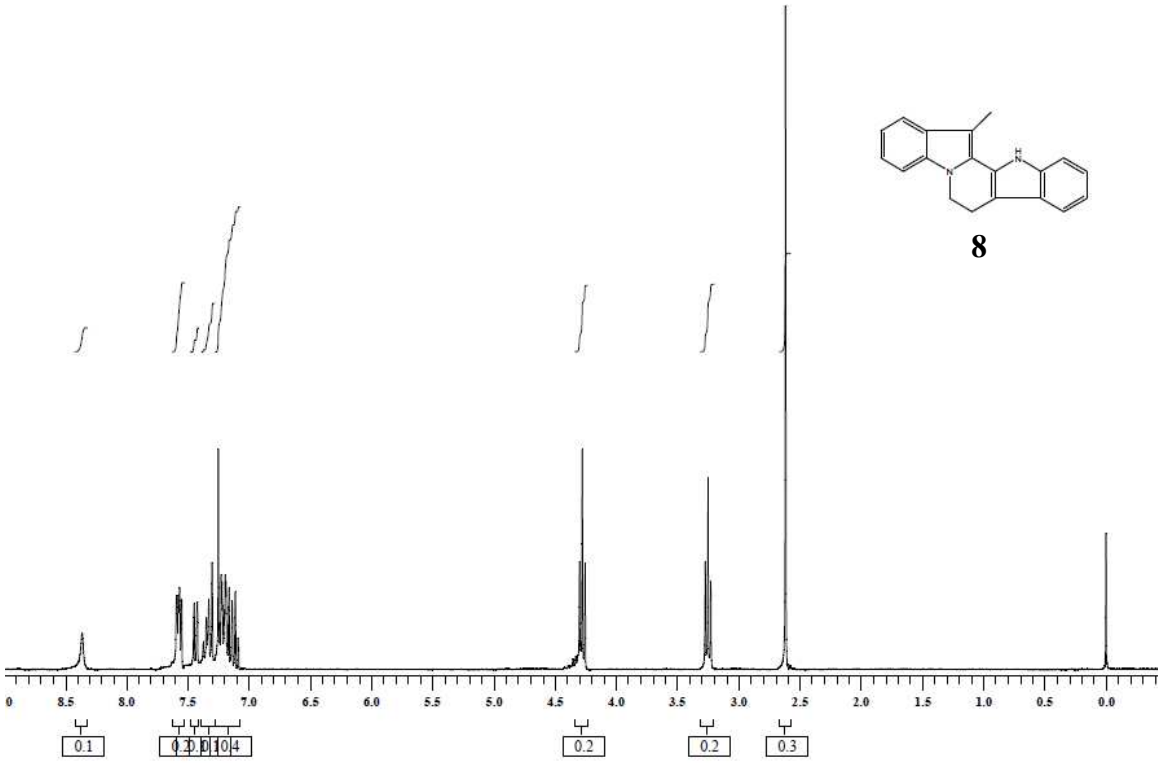
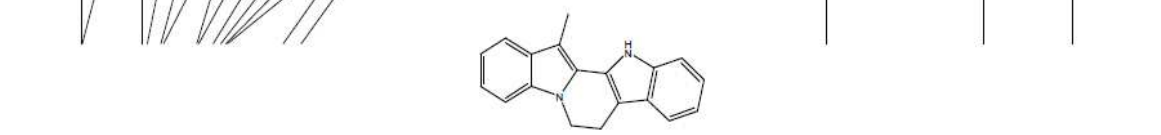
136.192
129.275
127.160
125.885
121.285
120.038
119.559
109.956
41.301
37.772
22.938
10.198
7



**8**





**8**