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A Simple and Efficient One-Pot Synthesis of 2-Alkyl/aryl/pyridyl Substituted 2*H*-Chromenes

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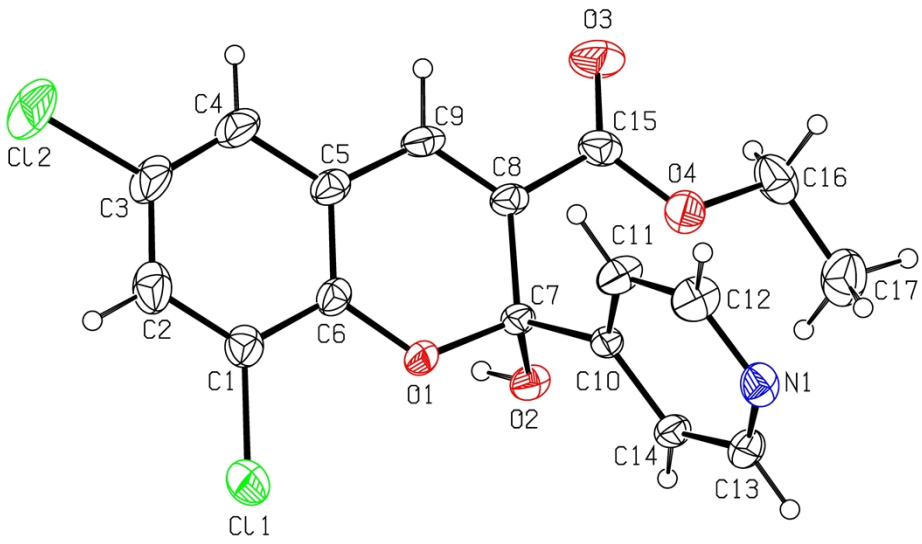
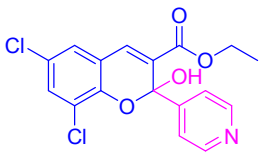
3f Crystallographic Data

Crystallographic data for 3f: $C_{17}H_{13}Cl_2NO_4$, M = 366.18, colourless block, 0.43 x 0.27 x 0.14 mm^3, triclinic, space group $P\bar{1}$ (No. 2), a = 7.7181(13), b = 8.3117(14), c = 14.132(2) Å, α = 99.319(3), β = 103.875(2), γ = 106.460(3)°, V = 817.9(2) Å^3, Z = 2, D_c = 1.487 g/cm^3, F_{000} = 376, CCD area detector, MoKα radiation, λ = 0.71073 Å, T = 293(2)K, $2\theta_{max}$ = 50.0°, 7594 reflections collected, 2869 unique (R_{int} = 0.0273), Final *GooF* = 1.121, *R1* = 0.0554, *wR2* = 0.1352, *R* indices based on 2434 reflections with I >2σ(I) (refinement on F^2), 222 parameters, μ = 0.418 mm^{-1}. Crystallographic data for the structure in this paper has been deposited with the Cambridge Crystallographic Data Centre and obtained a unique depository number, CCDC 1048680. The data can be obtained free of charge from https://summary.ccdc.cam.ac.uk/structure-summary-form or by writing to 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





3f

Figure caption: The ORTEP diagram of 3f with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radius.

Data collection: X-ray data for the compound were 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. Unit cell dimensions were determined using 3682 reflections for 3f data. Integration and scaling of intensity data were accomplished using SAINT program.[1] The structure was 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. O-bound H atom was located from the difference Fourier map. All other H atoms were positioned geometrically and treated as riding on their parent C atoms with C-H distances of 0.93--0.97 Å, and with $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}$ for methyl atoms.

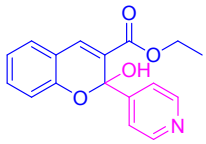
1. SMART & SAINT. Software Reference manuals. Versions 6.28a & 5.625, Bruker Analytical X-ray Systems Inc., Madison, Wisconsin, U.S.A., 2001.
2. Sheldrick, G. M. SHELXS97 and SHELXL97, Programs for crystal structure solution and refinement; University of Gottingen: Germany, 1997.

Experimental Part

General: Salicyladehydes, β-keto esters, L-proline, TBAB and all solvents were purchased from Sigma Aldrich and Alpha Aesar company and used without further purification as received. All ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ or $CDCl_3$+DMSO on Avance 300 or Avance 500 spectrometers. Chemical shifts (δ) are reported in parts per million (ppm) relative to residual CHCl3 (1H: δ 7.26 ppm, 13C: δ 77.00 ppm) as an internal reference. Coupling constants (J) are reported in Hertz (Hz). Peak multiplicity is indicated as follows: s—singlet, d—doublet, t—triplet, q—quartet, m—multiplet and dd—doublet of doublet. Melting points were measured on a BUCHI melting point machine. IR spectra were recorded on Thermo Nicolet FT/IR-5700 spectrometer. Mass spectra were recorded using Waters mass spectrometer. High resolution mass spectrums (HRMS) were recorded using Applied Bio-Sciences HRMS spectrometer at national center for mass spectroscopy-IICT.

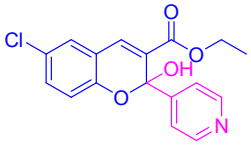
General procedure: In a typical experiment the salicylaldehyde (1mmol), β-keto ester or β-diketone (1mmol), L-proline (30 mol%) catalytic amount of TBAB (5 mol%) in H_2O (2 ml) were placed in a 10ml round-bottomed flask and stirred at room temperature for 6 h. After completion of the reaction (monitored by TLC), extracted with ethylacetate and dried over Na_2SO_4 and the solvent was removed under reduced pressure and the crude product was purified by column chromatography using ethyl acetate/hexane. All compounds were characterized by (NMR, Mass, and IR) spectral data. Further, we have done the reaction up to 5g scales.

Ethyl 2-hydroxy-2-(pyridin-4-yl)-2H-chromene-3-carboxylate (table 2, 3a):



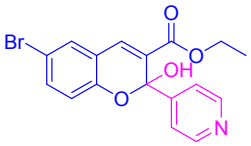
White solid; Mp 145-147 ^{o}C; IR: ν_{max} 3061, 2919, 2808, 2649, 1717, 1632, 1602, 1451, 1360, 1209, 1157, 1068, 926, 762 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$+DMSO): δ 8.55 (d, *J* = 5.47 Hz, 2H), 7.94 (br-s, 1H), 7.80 (s, 1H), 7.56 (d, *J* = 5.47 Hz, 2H), 7.35 (t, *J* = 7.36 Hz, 2H), 7.04 (t, *J* = 7,36 Hz, 1H), 6.94 (d, *J* = 8.49 Hz, 1H), 3.91-4.13 (m, 2H), 1.05 (t, *J* = 7.18 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$+DMSO): δ 163.7, 151.9, 151.7, 148.5, 134.4, 132.0, 128.4, 124.9, 121.4, 121.1, 118.0, 116.2, 97.0, 60.2, 13.4; m/z (ESI); 298 $[M+H]^+$, 320 $[M+23]^+$. HRMS calcd for $C_{17}H_{16}NO_4$: 298.10639, found: 298.10622.

Ethyl 6-chloro-2-hydroxy-2-(pyridin-4-yl)-2H-chromene-3-carboxylate (table 2, 3b):



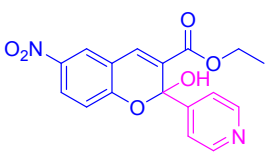
White solid; Mp 165-167 ^{o}C; IR: ν_{max} 3068, 2975, 2736, 1703, 1621, 1600, 1438, 1265, 1209, 1145, 1054, 912, 739 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$+DMSO): δ 8.56 (d, *J* = 5.29 Hz, 2H), 8.11 (br-s, 1H), 7.74 (s, 1H), 7.54 (d, *J* = 5.29 Hz, 2H), 7.36 (s, 1H), 7.30 (dd, J_1 = 8.69 Hz, J_2 = 1.51 Hz, 1H), 6.90 (d, *J* = 8.49 Hz, 1H), 3.92-4.11 (m, 2H), 1.06 (t, *J* = 8.49 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$+DMSO): δ 162.4, 150.5, 149.5, 147.8, 132.2, 130.6, 126.7, 125.4, 125.0, 120.2, 118.7, 116.9, 96.5, 59.5, 12.6; m/z (ESI); 332 $[M+H]^+$. HRMS calcd for $C_{17}H_{15}ClNO_4$: 332.06750, found: 332.06841.

Ethyl 6-bromo-2-hydroxy-2-(pyridin-4-yl)-2H-chromene-3-carboxylate (table 2, 3c):



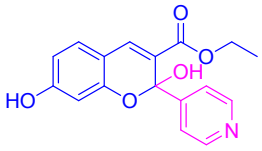
White solid; Mp 172-174 ^{o}C; IR: ν_{max} 3071, 2986, 2748, 1704, 1628, 1605, 1447, 1284, 1217, 1134, 1062, 906, 731 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$+DMSO): δ 8.60 (m, 2H), 7.99 (s, 1H), 7.74 (s, 1H), 7.40-7.60 (m, 4H), 6.83-6.91 (m, 1H), 3.92-4.14 (m, 2H), 1.06 (t, *J* = 7.74 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$+DMSO): δ 163.1, 151.1, 150.6, 148.4, 134.0, 132.7, 130.2, 125.9, 120.8, 119.7, 117.9, 112.8, 97.0, 60.1, 13.1; m/z (ESI); 376 $[M+H]^+$. HRMS calcd for $C_{17}H_{15}BrNO_4$: 376.01771, found: 376.01790.

Ethyl 2-hydroxy-6-nitro-2-(pyridin-4-yl)-2H-chromene-3-carboxylate (table 2, 3d):



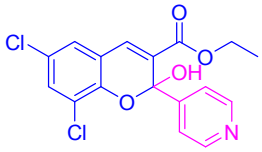
White solid; Mp 191-193 °C; IR: ν_{max} 3063, 2978, 2732, 1706, 1625, 1602, 1439, 1277, 1219, 1144, 1051, 917, 726 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$+DMSO): δ 8.61 (d, J = 5.48 Hz, 2H), 8.37 (d, J = 2.26 Hz, 1H), 8.22 (dd, J_1 = 6.42 Hz, J_2 = 2.45 Hz, 1H), 7.93 (s, 1H), 7.53 (d, J = 5.85 Hz, 2H), 7.06 (d, J = 9.06 Hz, 1H), 3.98-4.12 (m, 2H), 1.09 (t, J = 6.99 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$+DMSO): δ 161.9, 148.0, 140.5, 131.9, 126.2, 123.4, 120.1, 117.2, 115.9, 59.7, 12.6; m/z (ESI); 343 $[M+H]^+$. HRMS calcd for $C_{17}H_{15}N_2O_6$: 343.09164, found: 343.09246.

Ethyl 2,7-dihydroxy-2-(pyridin-4-yl)-2H-chromene-3-carboxylate (table 2, 3e):



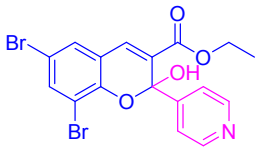
White solid; Mp 250-252 °C; IR: ν_{max} 3305, 3086, 2966, 2718, 1708, 1608, 1601, 1415, 1266, 1208, 1145, 1058, 926, 746 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$+DMSO): δ 9.90 (br-s, 1H), 8.53 (d, J = 4.72 Hz, 2H), 7.88 (s, 1H), 7.74 (s, 1H), 7.50 (d, J = 4.72 Hz, 2H), 7.21 (d, J = 8.31 Hz, 1H), 6.34 (s, 1H), 3.84-4.06 (m, 2H), 3.44 (s, 3H), 1.03 (t, J = 6.99 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$+DMSO): δ 162.6, 160.7, 152.4, 151.1, 147.4, 133.7, 128.7, 119.9, 119.6, 109.1, 108.6, 101.6, 96.5, 58.5, 12.4; m/z (ESI); 314 $[M+H]^+$. HRMS calcd for $C_{17}H_{16}NO_5$: 314.10187, found: 314.10230.

Ethyl 6,8-dichloro-2-hydroxy-2-(pyridin-4-yl)-2H-chromene-3-carboxylate (table 2, 3f):



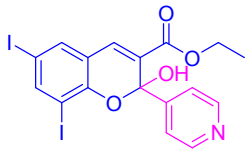
White solid; Mp 173-175 °C; IR: ν_{max} 3324, 3023, 2938, 2842, 1703, 1639, 1519, 1446, 1281, 1228, 1035, 824, 737 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$+DMSO): δ 8.59 (d, J = 5.95 Hz, 2H), 8.36 (br-s, 1H), 7.72 (s, 1H), 7.56 (d, J = 6.10 Hz, 2H), 7.41 (d, J = 2.44 Hz, 1H), 7.31 (d, J = 2.29 Hz, 1H), 3.94-4.11 (m, 2H), 1.07 (t, J = 7.17 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$+DMSO): δ 162.6, 150.3, 148.3, 146.1, 132.1, 130.8, 132.1, 130.8, 126.7, 125.8, 125.3, 120.8, 120.6, 60.2, 13.0; m/z (ESI); 366 $[M+H]^+$. HRMS calcd for $C_{22}H_{14}O_4NCl_2$: 366.02892, found: 366.02944.

Ethyl 6,8-dibromo-2-hydroxy-2-(pyridin-4-yl)-2H-chromene-3-carboxylate (table 2, 3g):



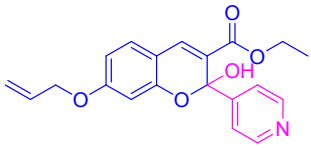
White solid; Mp 248-250 °C; IR: ν_{max} 3324, 3019, 2962, 2831, 1702, 1616, 1524, 1416, 1229, 1208, 1024, 819, 733 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$+DMSO): δ 8.32-8.68 (m, 3H), 7.66-7.79 (m, 2H), 7.48-7.61 (m, 3H), 3.90-4.12 (m, 2H), 1.07 (t, J = 7.17 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$+DMSO): δ 162.6, 150.3, 148.2, 147.6, 136.2, 132.0, 129.7, 126.6, 120.9, 120.5, 112.6, 110.6, 60.2, 13.0; m/z (ESI); 456 $[M+H]^+$. HRMS calcd for $C_{22}H_{14}NO_4Br_2$: 456.92458, found: 456.92025.

Ethyl 2-hydroxy-6,8-diiodo-2-(pyridin-4-yl)-2H-chromene-3-carboxylate (table 2, 3h):



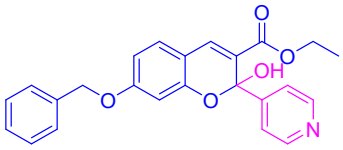
White solid; Mp 163-165 ^{o}C; IR: ν_{max} 3418, 3058, 2926, 2853, 1699, 1625, 1537, 1434, 1278, 1218, 1011, 812, 728 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$+DMSO): δ 8.52-8.64 (m, 2H), 8.37-8.46 (m, 1H), 8.05 (d, J = 2.08 Hz, 1H), 7.85 (d, J = 1.89 Hz, 1H), 7.74 (s, 1H), 7.50 (d, J = 4.34 Hz, 2H), 3.89-4.08 (m, 2H), 1.02 (t, J = 6.99 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$+DMSO): δ 161.3, 149.7, 149.3, 147.3, 145.9, 135.3, 131.2, 125.0, 119.7, 119.4, 97.1, 84.9, 82.7, 58.8, 12.0; m/z (ESI); 550 $[M+H]^+$. HRMS calcd for $C_{22}H_{14}NO_4I_2$: 549.89859, found: 549.90067.

Ethyl 7-(allyloxy)-2-hydroxy-2-(pyridin-4-yl)-2H-chromene-3-carboxylate (table 2, 3i):



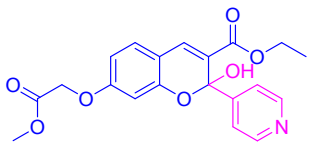
Semi solid; IR: ν_{max} 2984, 1708, 1611, 1560, 1502, 1368, 1284, 1208, 1120, 1002, 756 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.49 (d, J = 5.95 Hz, 2H), 7.74 (s, 1H), 7.52 (d, J = 6.26 Hz, 2H), 7.19 (d, J = 8.39 Hz, 1H), 6.61 (dd, J_1 = 8.39 Hz, J_2 = 2.44 Hz, 1H), 6.49 (d, J = 2.14 Hz, 1H), 5.96-6.05 (m, 1H), 5.37-5.42 (m, 1H), 5.27-5.31 (m, 1H), 4.51 (td, J_1 = 3.82 Hz, J_2 = 1.53 Hz, 2H), 4.07-4.14 (m, 2H), 1.11 (t, J = 7.17 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 164.9, 162.8, 153.5, 151.6, 149.2, 135.3, 132.3, 129.9, 121.9, 120.9, 118.2, 111.4, 110.2, 102.2, 97.8, 69.0, 60.9, 13.9; m/z (ESI); 354 $[M+H]^+$.

Ethyl 7-(benzyloxy)-2-hydroxy-2-(pyridin-4-yl)-2H-chromene-3-carboxylate (table 2, 3j):



White solid; Mp 163-165 ^{o}C; IR: ν_{max} 3419, 3058, 2984, 2830, 1712, 1611, 1568, 1460, 1293, 1218, 1075, 1018, 818, 702 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$+DMSO): δ 8.56 (d, J = 5.85 Hz, 2H), 7.78 (s, 1H), 7.55 (d, J = 5.85 Hz, 2H), 7.24-7.42 (m, 6H), 6.68 (dd, J_1 = 6.42 Hz, J_2 = 2.08 Hz, 1H), 6.55 (d, J = 2.08 Hz, 1H), 5.06 (s, 2H), 3.90-4.11 (m, 2H), 1.05 (t, J = 7.17 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$+DMSO): δ 163.4, 161.6, 152.9, 151.5, 148.1, 135.5, 133.9, 129.1, 127.7, 127.2, 126.6, 121.4, 120.6, 111.2, 108.8, 101.4, 96.9, 69.2, 59.5, 13.0; m/z (ESI); 404 $[M+H]^+$.

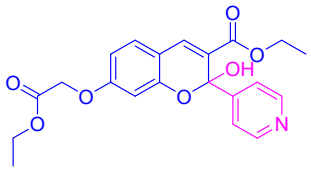
Ethyl 2-hydroxy-7-(2-methoxy-2-oxoethoxy)-2-(pyridin-4-yl)-2H-chromene-3-carboxylate (table 2, 3k):



White solid; Mp 153-155 ^{o}C; IR: ν_{max} 3073, 2790, 2645, 1758, 1705, 1611, 1566, 1454, 1293, 1220, 1065, 999, 855, 718 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.48-8.53 (m, 2H), 7.74 (s, 1H), 7.51 (dd, J_1 = 4.58 Hz, J_2 = 1.68 Hz, 2H), 7.22 (d, J = 8.54 Hz, 1H), 6.60-6.64 (m, 1H), 6.44 (d, J = 2.29 Hz, 1H), 4.62 (s, 2H), 4.00-4.14 (m, 2H), 3.79

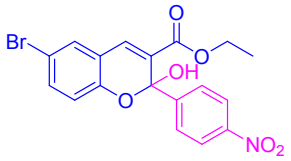
(s, 3H), 1.14 (t, J = 7.17 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.6, 164.6, 161.5, 153.4, 152.1, 148.1, 134.8, 130.0, 122.1, 121.2, 112.3, 109.7, 102.1, 97.8, 64.9, 60.8, 52.3, 13.8; m/z (ESI); 386 $[M+H]^+$.

Ethyl 7-(2-ethoxy-2-oxoethoxy)-2-hydroxy-2-(pyridin-4-yl)-2H-chromene-3-carboxylate (table 2, 3l):



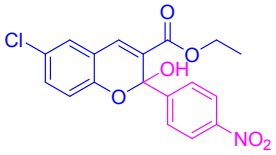
White solid; Mp 157-159 °C; IR: v_{max} 3068, 2792, 2656, 1751, 1704, 1609, 1558, 1446, 1287, 1224, 1068, 976, 856, 727 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.41-8.49 (m, 2H), 7.72 (s, 1H), 7.52 (dd, J_1 = 4.73 Hz, J_2 = 1.37 Hz, 2H), 7.17-7.21 (m, 1H), 6.61 (d, J = 8.39 Hz, 1H), 6.43-6.45 (m, 1H), 4.59 (s, 2H), 4.24 (q, J = 7.17 Hz, 2H), 3.99-4.13 (m, 2H), 1.28 (t, J = 7.17 Hz, 3H), 1.14 (t, J = 7.01 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.1, 164.5, 161.6, 153.4, 152.1, 148.5, 149.8, 134.8, 129.9, 122.1, 121.2, 112.3, 109.7, 102.1, 97.8, 65.1, 61.5, 60.8, 14.0, 13.8; m/z (ESI); 400 $[M+H]^+$.

Ethyl 6-bromo-2-hydroxy-2-(4-nitrophenyl)-2H-chromene-3-carboxylate (table 2, 3m):



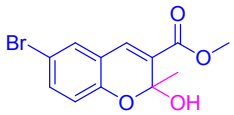
White solid; Mp 127-129 °C; IR: v_{max} 3054, 2789, 2648, 1707, 1605, 1444, 1275, 1213, 1062, 873, 729 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$+DMSO): δ 8.20 (d, J = 8.88 Hz, 2H), 8.02 (s, 1H), 7.83 (d, J = 8.69 Hz, 2H), 7.75 (s, 1H), 7.52 (d, J = 2.08 Hz, 1H), 7.44 (dd, J_1 = 6.42 Hz, J_2 = 2.27 Hz, 1H), 6.85 (d, J = 8.49 Hz 1H), 3.92-4.13 (m, 2H), 1.09 (t, J = 7.18 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$+DMSO): δ 162,9, 150.4, 149.4, 146.7, 133.9, 132.5, 130.1, 126.9, 125.8, 121.9, 119.6, 117.8, 112.7, 97.1, 60.0, 13.1; m/z (ESI); 420 $[M+H]^+$.

Ethyl 6-chloro-2-hydroxy-2-(4-nitrophenyl)-2H-chromene-3-carboxylate (table 2, 3n):



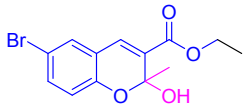
White solid; Mp 121-123 °C; IR: v_{max} 3072, 2803, 2654, 1709, 1606, 1448, 1275, 1229, 1062, 970, 848, 734 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$+DMSO): δ 8.20 (d, J = 8.88 Hz, 2H), 8.02 (s, 1H), 7.83 (d, J = 8.69 Hz, 2H), 7.75 (s, 1H), 7.38 (d, J = 2.45 Hz, 1H), 7.31 (dd, J_1 = 6.23 Hz, J_2 = 2.45 Hz, 1H), 6.91 (d, J = 8.69 Hz 1H), 3.89-4.13 (m, 2H), 1.09 (t, J = 7.18 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$+DMSO): δ 162.8, 149.9, 149.3, 146.6, 132.6, 131.0, 127.1, 126.9, 125.5, 121.8, 118.9, 117.3, 97.1, 59.9, 13.1; m/z (ESI); 376 $[M+H]^+$.

Methyl 6-bromo-2-hydroxy-2-methyl-2H-chromene-3-carboxylate (table 3, 3aa):



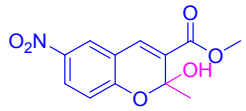
White solid; Mp 106-108 ^{o}C; IR: ν_{max} 3338, 3058, 2975, 1696, 1617, 1524, 1339, 1243, 1051, 945, 760 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.50 (s, 1H), 7.40 (dd, J_1 = 8.69 Hz, J_2 = 2.27 Hz, 1H), 7.36 (d, J = 2.27 Hz, 1H), 6.86 (d, J = 8.69 Hz, 1H), 3.85 (s, 3H), 3.74 (br-s, 1H), 1.96 (s, 3H); m/z (ESI); 321 $[M+Na]^+$, 281 $[M-OH]^+$.

Ethyl 6-bromo-2-hydroxy-2-methyl-2H-chromene-3-carboxylate (table 3, 3ab):



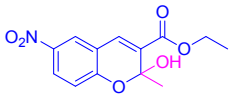
White solid; Mp 128-130 ^{o}C; IR: ν_{max} 3345, 3065, 2987, 1698, 1609, 1524, 1338, 1256, 1067, 941, 762 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.48 (s, 1H), 7.36-7.42 (m, 2H), 6.86 (d, J = 8.49 Hz, 1H), 4.23-4.36 (m, 2H), 3.81 (br-s, 1H), 1.95 (s, 3H), 1.37 (t, J = 7.17 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 164.8, 151.5, 134.7, 132.7, 130.7, 126.7, 120.5, 118.6, 113.6, 98.0, 61.3, 27.4, 14.1; m/z (ESI); 335 $[M+Na]^+$, 295 $[M-OH]^+$.

Methyl 2-hydroxy-2-methyl-6-nitro-2H-chromene-3-carboxylate (table 3, 3ac):



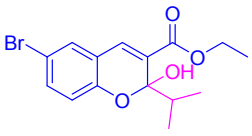
White solid; Mp 143-145 ^{o}C; IR: ν_{max} 3386, 3068, 2984, 1698, 1615, 1507, 1338, 1267, 1053, 951, 772 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$+DMSO): δ 8.22 (dd, J_1 = 6.26 Hz, J_2 = 2.59 Hz, 1H), 8.19 (d, J = 2.59 Hz, 1H), 7.63 (s, 1H), 7.06 (d, J = 8.85 Hz, 1H), 3.98 (s, 3H), 3.80 (br-s, 1H), 2.02 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$+DMSO): δ 163.7, 157.5, 140.7, 131.2, 127.7, 126.1, 123.4, 118.2, 116.4, 98.8, 51.2, 26.8; m/z (ESI); 288 $[M+Na]^+$, 248 $[M-OH]^+$.

Ethyl 2-hydroxy-2-methyl-6-nitro-2H-chromene-3-carboxylate (table 3, 3ad):



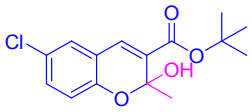
White solid; Mp 132-134 ^{o}C; IR: ν_{max} 3402, 3071, 2993, 1696, 1612, 1519, 1343, 1276, 1076, 947, 774 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$+DMSO): δ 8.17-8.22 (m, 2H), 7.61 (m, 1H), 7.05 (d, J = 9.31 Hz, 1H), 4.29-4.38 (m, 2H), 4.02-4.11 (br-s, 1H), 2.01 (s, 3H), 1.39 (t, J = 7.39 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$+DMSO): δ 162.6, 157.0, 140.2, 130.4, 127.5, 125.6, 122.9, 117.9, 115.9, 98.3, 59.6, 26.2, 13.0; m/z (ESI); 262 $[M-OH]^+$.

Ethyl 6-bromo-2-hydroxy-2-isopropyl-2H-chromene-3-carboxylate (table 3, 3ae):



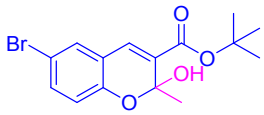
Semi solid; IR: ν_{max} 3068, 2967, 2934, 1702, 1626, 1471, 1361, 1284, 1136, 1052, 915, 828, 768 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.47 (s, 1H), 7.38 (dd, J_1 = 8.69 Hz, J_2 = 2.44 Hz, 1H), 7.33 (d, J = 2.44 Hz, 1H), 6.86 (d, J = 8.69 Hz, 1H), 4.50 (br-s, 1H), 4.27-4.35 (m, 2H), 2.59 (m, 1H), 1.37 (t, J = 7.17 Hz, 3H), 1.11 (d, J = 6.86 Hz, 3H), 0.90 (d, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.8, 152.1, 134.8, 133.3, 130.8, 125.4, 120.4, 118.2, 113.2, 101.7, 61.4, 36.2, 17.4, 14.7, 14.1; m/z (ESI); 363 $[M+Na]^+$, 323 $[M-OH]^+$.

Tert-butyl 6-chloro-2-hydroxy-2-methyl-2H-chromene-3-carboxylate (table 3, 3af):



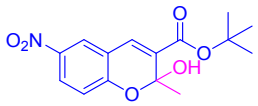
White solid; Mp 102-104 ^{o}C; IR: ν_{max} 3409, 3077, 2965, 2918, 1701, 1639, 1469, 1355, 1282, 1133, 1067, 915, 812, 764 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.34 (s, 1H), 7.23 (dd, J_1 = 6.10 Hz, J_2 = 2.59 Hz, 1H), 7.20 (d, J = 2.44 Hz, 1H), 6.89 (d, J = 8.54 Hz, 1H), 4.04 (br-s, 1H), 1.99 (s, 3H), 1.56 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$+DMSO): δ 162.7, 150.7, 130.6, 130.0, 128.6, 126.6, 124.7, 120.0, 117.1, 97.3, 80.3, 27.3, 26.5; m/z (ESI); 319 $[M+Na]^+$, 279 $[M-OH]^+$.

Tert-butyl 6-bromo-2-hydroxy-2-methyl-2H-chromene-3-carboxylate (table 3, 3ag):



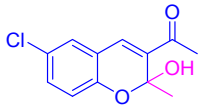
White solid; Mp 110-112 ^{o}C; IR: ν_{max} 3412, 3061, 2974, 2927, 1700, 1632, 1480, 1367, 1293, 1148, 1071, 926, 816, 770 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.37 (dd, J_1 = 6.26 Hz, J_2 = 2.29 Hz, 1H), 7.35 (d, J = 2.29 Hz, 1H), 7.34 (s, 1H), 6.85 (d, J = 8.39 Hz, 1H), 4.01 (br-s, 1H), 1.99 (s, 3H), 1.56 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$+DMSO): δ 162.5, 150.9, 132.5, 130.2, 129.2, 128.3, 120.4, 117.3, 111.5, 96.9, 79.9, 27.0, 26.2; m/z (ESI); 363 $[M+Na]^+$, 325 $[M-OH]^+$.

Tert-butyl 2-hydroxy-2-methyl-6-nitro-2H-chromene-3-carboxylate (table 3, 3ah):



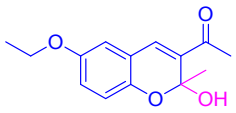
White solid; Mp 115-117 ^{o}C; IR: ν_{max} 3311, 3046, 2968, 2911, 1704, 1619, 1475, 1363, 1288, 1137, 1084, 928, 808, 766 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.17-8.21 (m, 2H), 7.46 (s, 1H), 7.04 (d, J = 8.85 Hz, 1H), 4.15 (br-s, 1H), 1.96 (s, 3H), 1.58 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 163.8, 157.3, 141.9, 131.2, 128.9, 127.2, 124.2, 118.7, 117.2, 99.4, 82.8, 28.1; m/z (ESI); 330 $[M+Na]^+$, 290 $[M-OH]^+$.

1-(6-chloro-2-hydroxy-2-methyl-2H-chromen-3-yl)ethanone (table 3, 3ai):



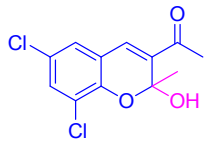
Yellow solid; Mp 93-95 ^{o}C; IR: ν_{max} 3337, 3051, 2996, 2924, 1656, 1622, 1560, 1477, 1376, 1273, 1209, 1076, 935, 869 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.32 (s, 1H), 7.26-7.30 (m, 1H), 7.23 (d, J = 2.44 Hz, 1H), 6.91 (d, J = 8.69 Hz, 1H), 4.58 (br-s, 1H), 2.48 (s, 3H), 1.82 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 198.1, 151.4, 133.9, 132.5, 128.0, 126.5, 120.0, 118.3, 98.9, 27.7, 26.6; m/z (ESI); 261 $[M+Na]^+$, 221 $[M-OH]^+$.

1-(6-ethoxy-2-hydroxy-2-methyl-2H-chromen-3-yl)ethanone (table 3, 3aj):



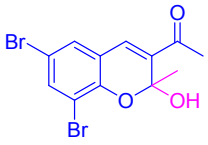
Yellow solid; Mp 143-145 °C; IR: ν_{max} 3327, 3056, 2975, 2931, 1658, 1636, 1553, 1455, 1372, 1240, 1213, 1068, 941, 763 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.34 (s, 1H), 6.76-6.96 (m, 3H), 4.18 (br-s, 1H), 4.10 (q, J = 6.79 Hz, 2H), 2.46 (s, 3H), 1.88 (s, 3H), 1.46 (t, J = 6.79 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 197.8, 147.4, 142.9, 135.2, 133.1, 121.3, 120.9, 119.6, 117.4, 98.8, 65.0, 27.6, 26.6, 14.8; m/z (ESI); 271 $[M+Na]^+$, 231 $[M-OH]^+$.

1-(6,8-dichloro-2-hydroxy-2-methyl-2H-chromen-3-yl)ethanone (table 3, 3ak):



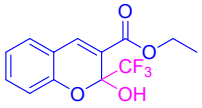
Yellow solid; Mp 123-125 °C; IR: ν_{max} 3324, 3068, 2983, 2932, 1667, 1637, 1558, 1456, 1381, 1259, 1215, 1065, 926, 789 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.38 (d, J = 2.09 Hz, 1H), 7.25 (s, 1H), 7.13 (s, 1H), 3.98 (br-s, 1H), 2.46 (s, 3H), 1.92 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 197.4, 134.6, 132.7, 132.2, 126.5, 126.3, 122.7, 120.9, 99.6, 27.7, 26.7; m/z (ESI); 295 $[M+Na]^+$, 255 $[M-OH]^+$.

1-(6,8-dibromo-2-hydroxy-2-methyl-2H-chromen-3-yl)ethanone (table 3, 3al):



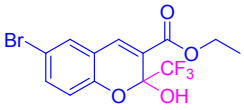
Yellow solid; Mp 138-140 °C; IR: ν_{max} 3349, 3064, 2981, 2928, 1662, 1648, 1566, 1463, 1379, 1247, 1210, 1071, 945, 774 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.67 (d, J = 1.90 Hz, 1H), 7.31 (s, 1H), 7.23 (s, 1H), 3.86 (br-s, 1H), 2.46 (s, 3H), 1.92 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 197.3, 148.9, 137.7, 134.5, 132.7, 130.1, 121.4, 113.5, 111.8, 99.8, 27.8, 26.8; m/z (ESI); 383 $[M+Na]^+$, 343 $[M-OH]^+$.

Ethyl 2-hydroxy-2-(trifluoromethyl)-2H-chromene-3-carboxylate (table 3, 3am):



White solid; Mp 122-124 °C; IR: ν_{max} 3236, 3064, 3011, 1688, 1623, 1454, 1283, 1176, 1035, 957, 829 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.78 (s, 1H), 7.51 (s, 1H), 7.36-7.40 (m, 1H), 7.24-7.27 (m, 1H), 7.01-7.05 (m, 1H), 4.36 (q, J = 7.17 Hz, 2H), 1.40 (t, J = 7.17 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.7, 152.5, 139.3, 133.8, 129.5, 124.5, 122.6, 120.7, 117.5, 115.9, 114.6, 62.4, 13.9; m/z (ESI); 311 $[M+Na]^+$, 271 $[M-OH]^+$.

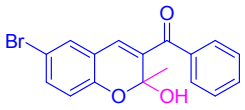
Ethyl 6-bromo-2-hydroxy-2-(trifluoromethyl)-2H-chromene-3-carboxylate (table 3, 3an):



White solid; Mp 133-135 °C; IR: ν_{max} 3247, 3071, 3000, 1684, 1629, 1478, 1288, 1172, 1033, 963, 825 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.69 (s, 1H), 7.44-7.50 (m, 2H), 7.39 (d, J = 2.27 Hz, 1H), 6.94 (d, J = 9.06 Hz, 1H),

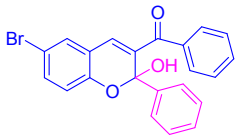
4.38 (q, J = 6.79 Hz, 2H), 1.40 (t, J = 6.79 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.4, 151.5, 137.8, 136.3, 131.6, 124.3, 120.5, 119.2, 117.8, 115.9, 114.7, 62.7, 13.9; m/z (ESI); 389 $[M+Na]^+$, 349 $[M-OH]^+$.

(6-bromo-2-hydroxy-2-methyl-2H-chromen-3-yl)(phenyl)methanone (table 3, 3ao):



Semi solid; IR: ν_{max} 3376, 2935, 2864, 1703, 1628, 1552, 1455, 1271, 1250, 1168, 1063, 846, 687 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.80-7.84 (m, J = 7.17 Hz, 2H), 7.62-7.66 (m, 1H), 7.51 (t, J = 7.48 Hz, 2H), 7.42 (dd, J_1 = 8.69 Hz, J_2 = 2.44 Hz, 1H), 7.29 (d, J_1 = 2.44 Hz, 1H), 6.91-6.94 (m, 2H), 4.25 (br-s, 1H), 1.92 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 195.2, 151.5, 136.9, 134.9, 133.9, 133.4, 133.2, 130.8, 129.8, 128.6, 120.6, 118.9, 113.8, 98.3, 27.1; m/z (ESI); 367 $[M+Na]^+$, 327 $[M-OH]^+$.

(6-bromo-2-hydroxy-2-phenyl-2H-chromen-3-yl)(phenyl)methanone (table 3, 3ap):



Semi solid; IR: ν_{max} 3413, 2924, 2854, 1701, 1633, 1565, 1475, 1289, 1246, 1173, 1067, 851, 692 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.74-7.78 (m, 2H), 7.63-7.67 (m, 2H), 7.57-7.61 (m, 1H), 7.42-7.48 (m, 3H), 7.26-7.36 (m, 4H), 7.08 (s, 1H), 6.92 (d, J = 8.54 Hz, 1H), 5.04 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.9, 150.9, 142.1, 136.1, 135.2, 133.5, 133.4, 133.0, 130.8, 129.8, 128.8, 128.6, 128.2, 125.8, 119.7, 118.8, 113.9, 99.1; m/z (ESI); 429 $[M+Na]^+$, 389 $[M-OH]^+$.


8.559
8.540
7.941
7.804
7.574
7.556
7.375
7.351
7.330
7.064
7.040
7.015
6.952
6.923
4.116
4.093
4.080
4.069
4.057
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3.939
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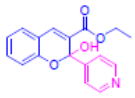
1.030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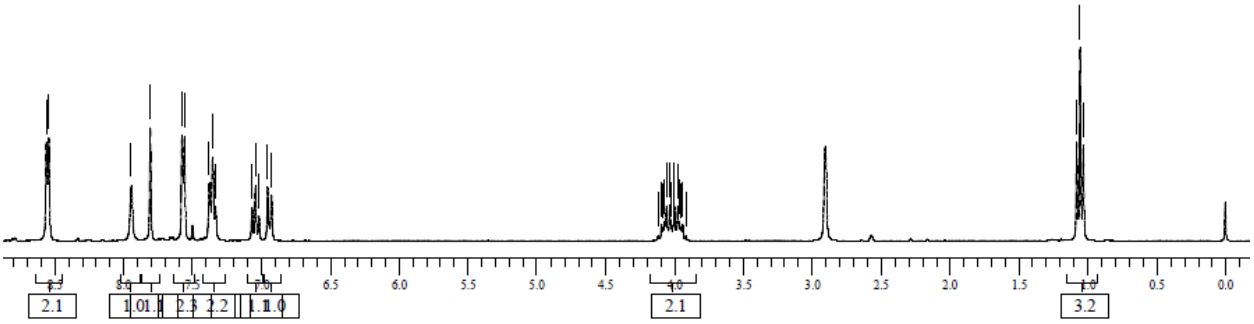
OH
O
N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2.5
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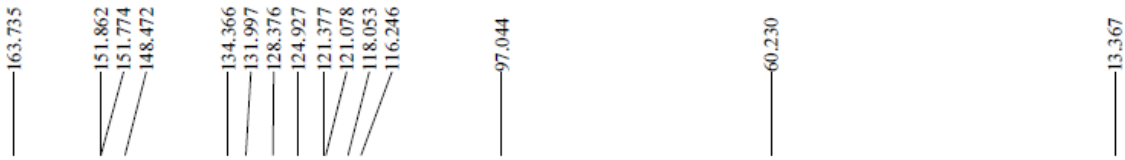
2.1
3.2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131.997
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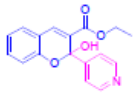
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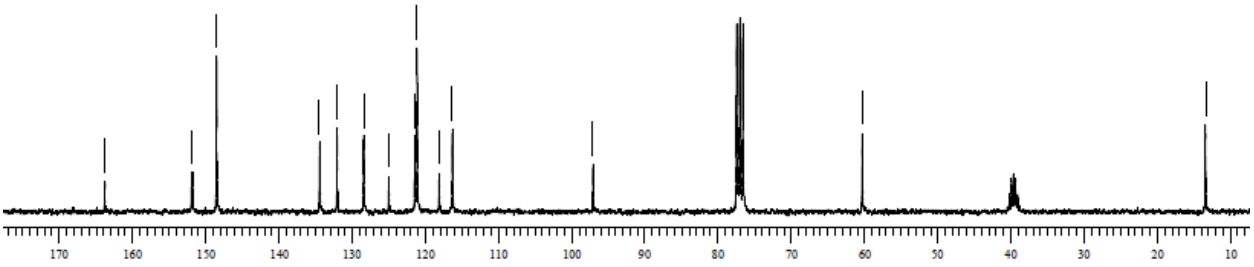


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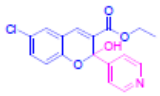
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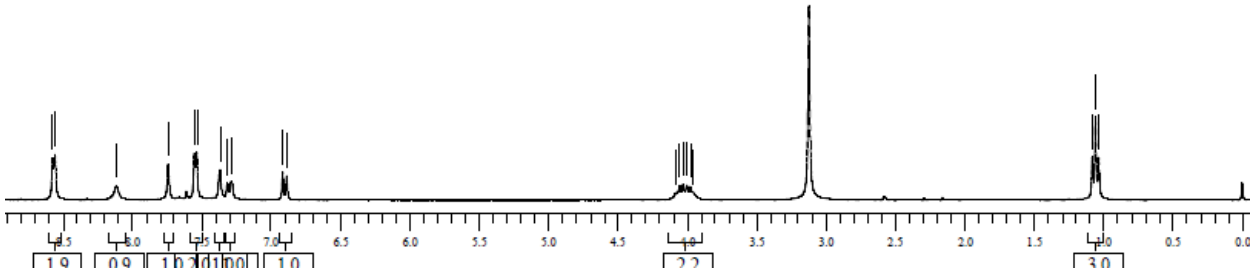
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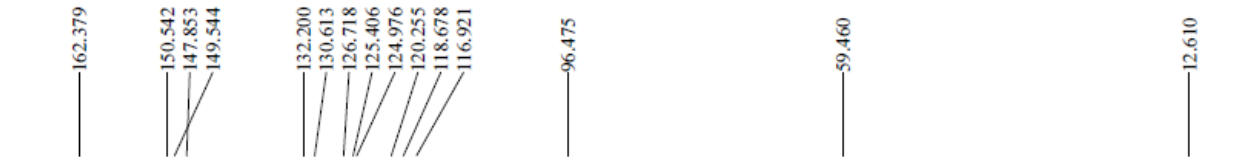
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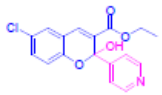
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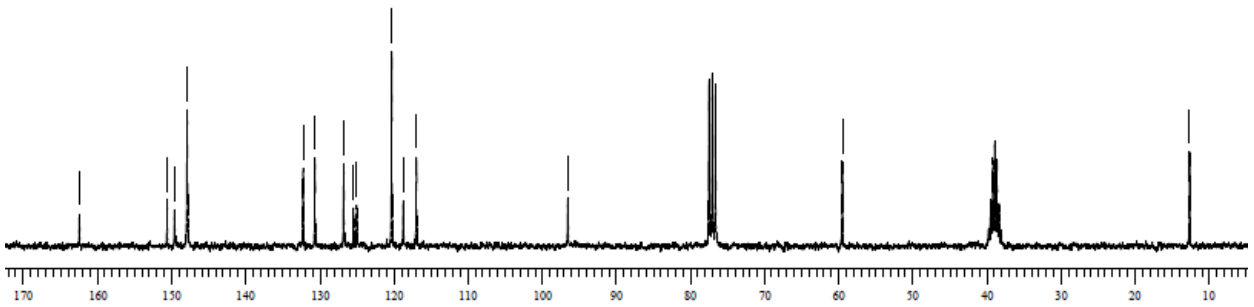
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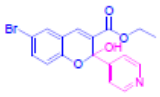
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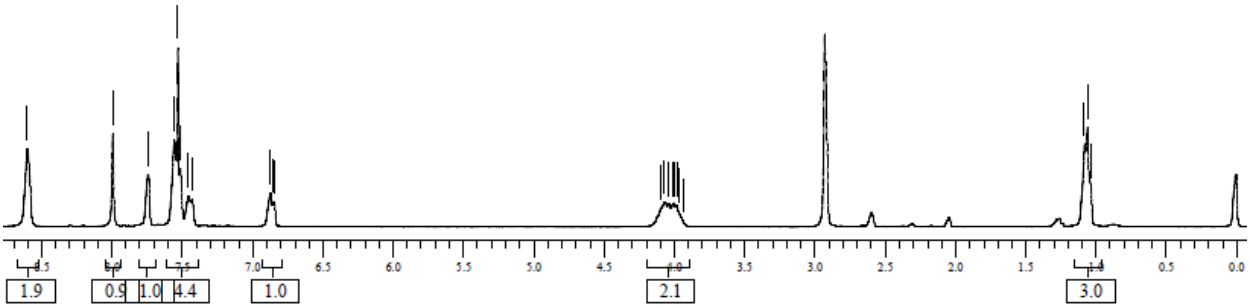
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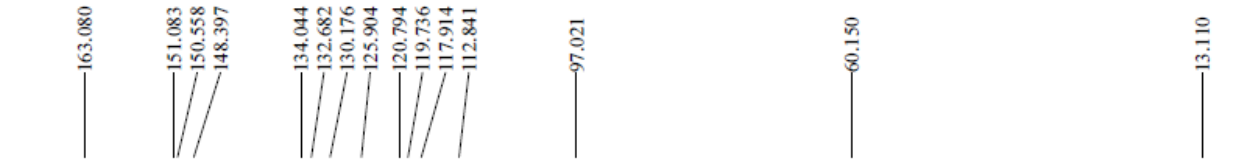
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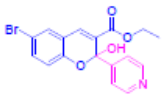
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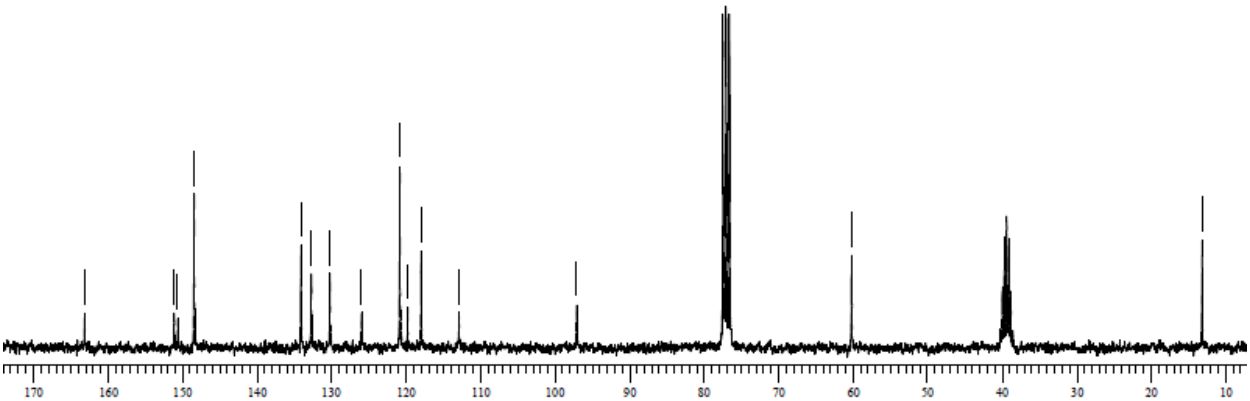

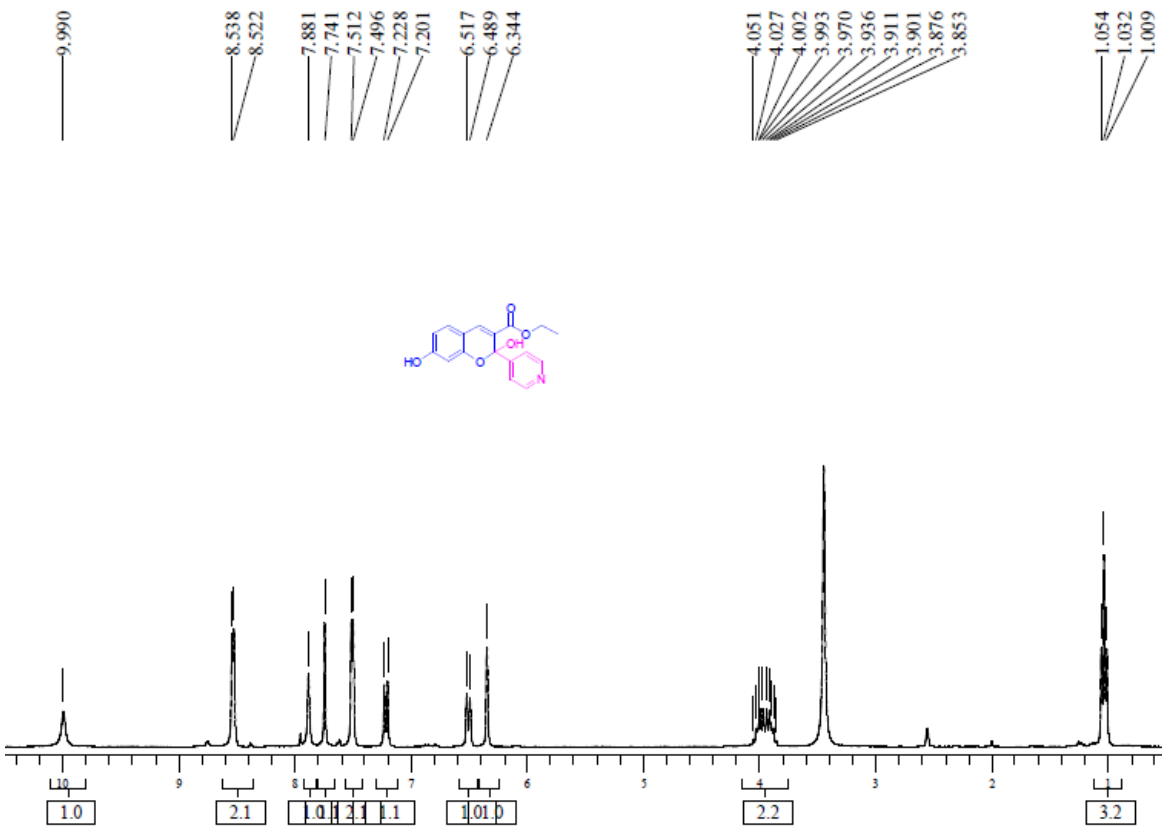
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4.002
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3.876
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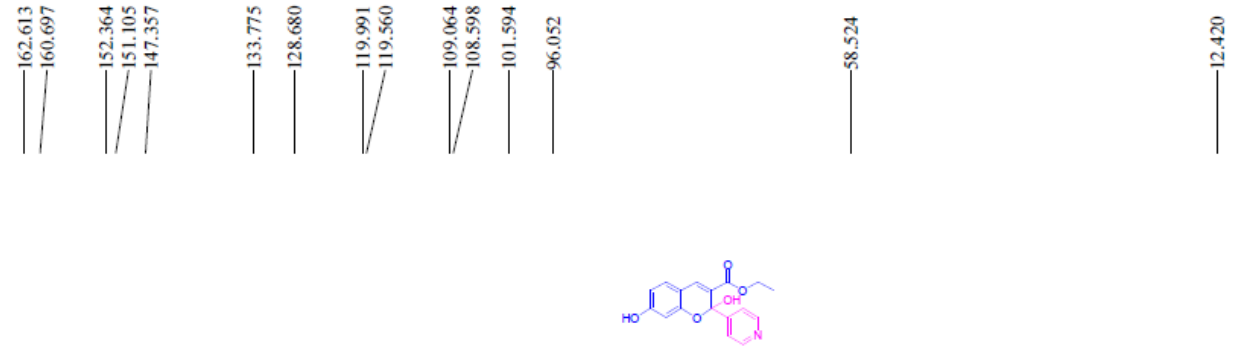
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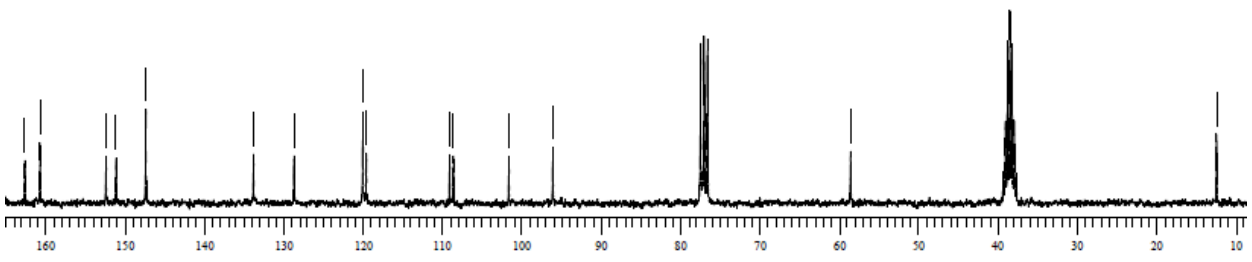

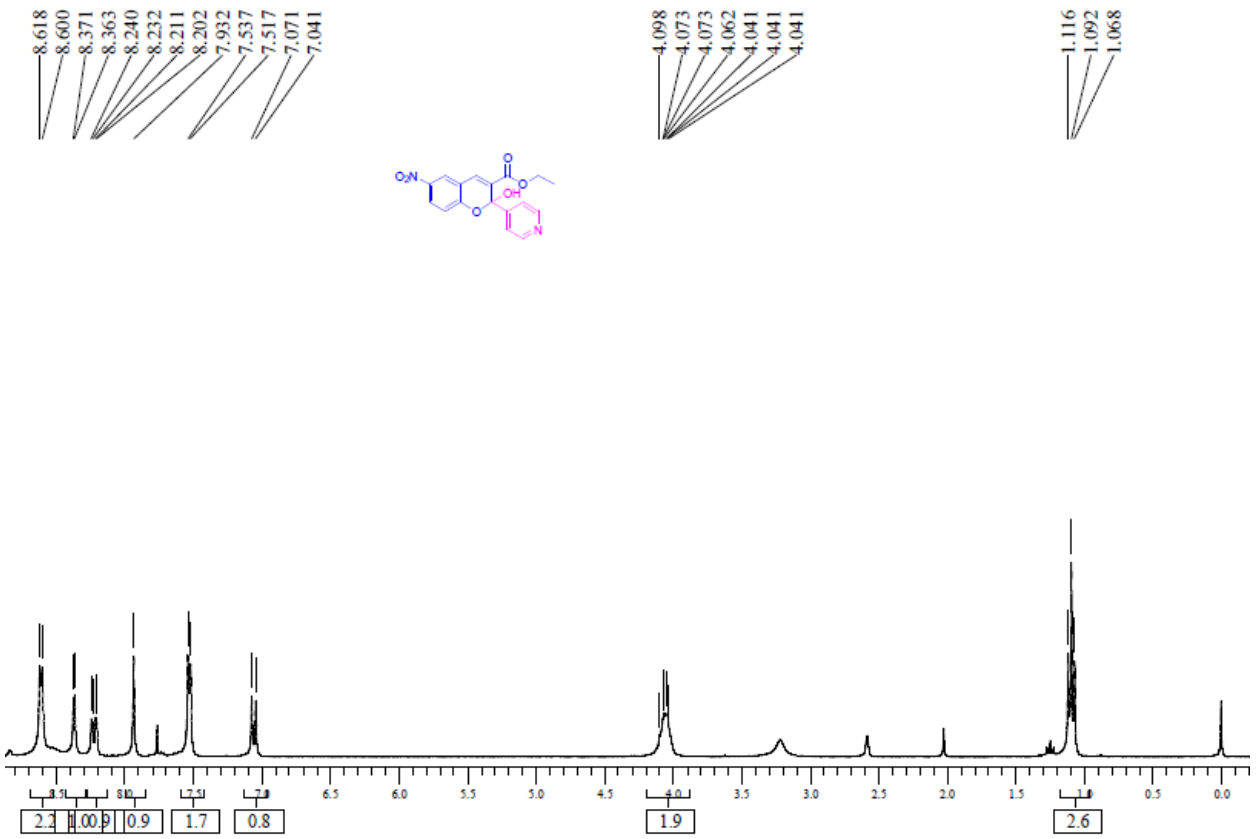
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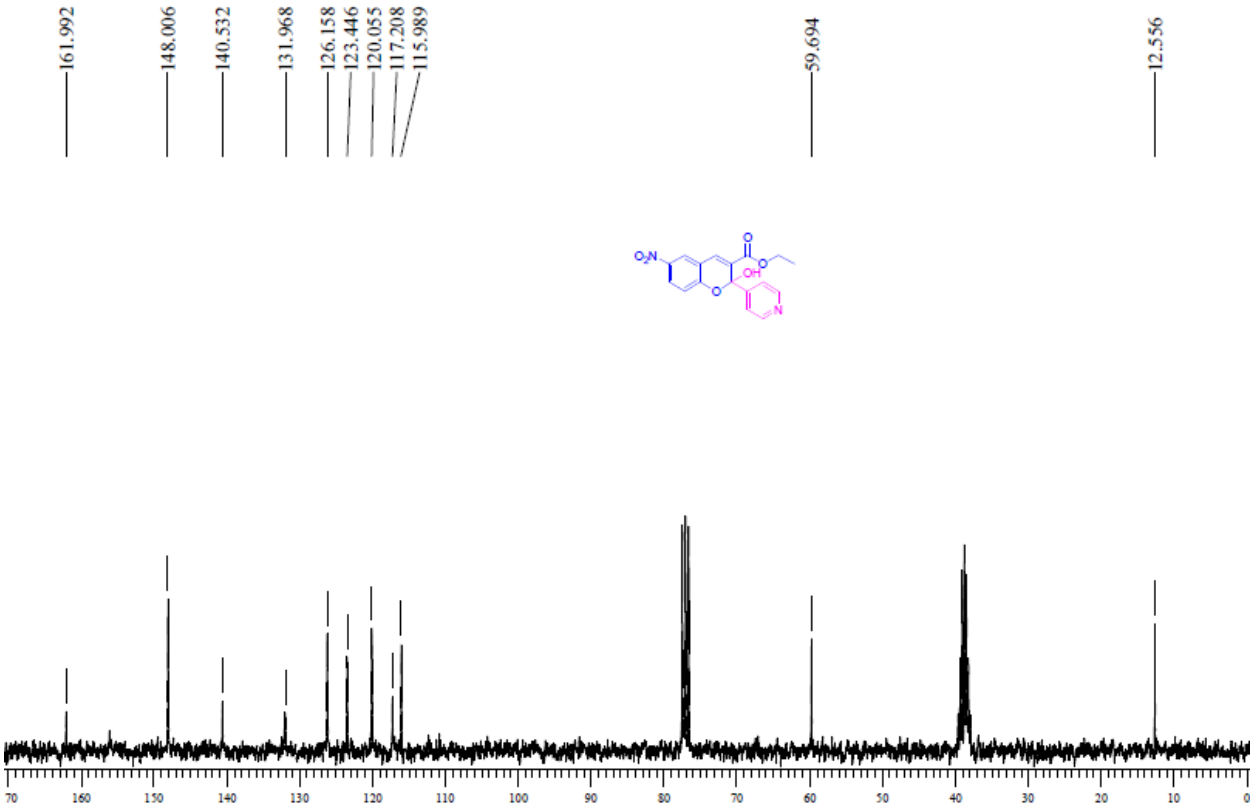
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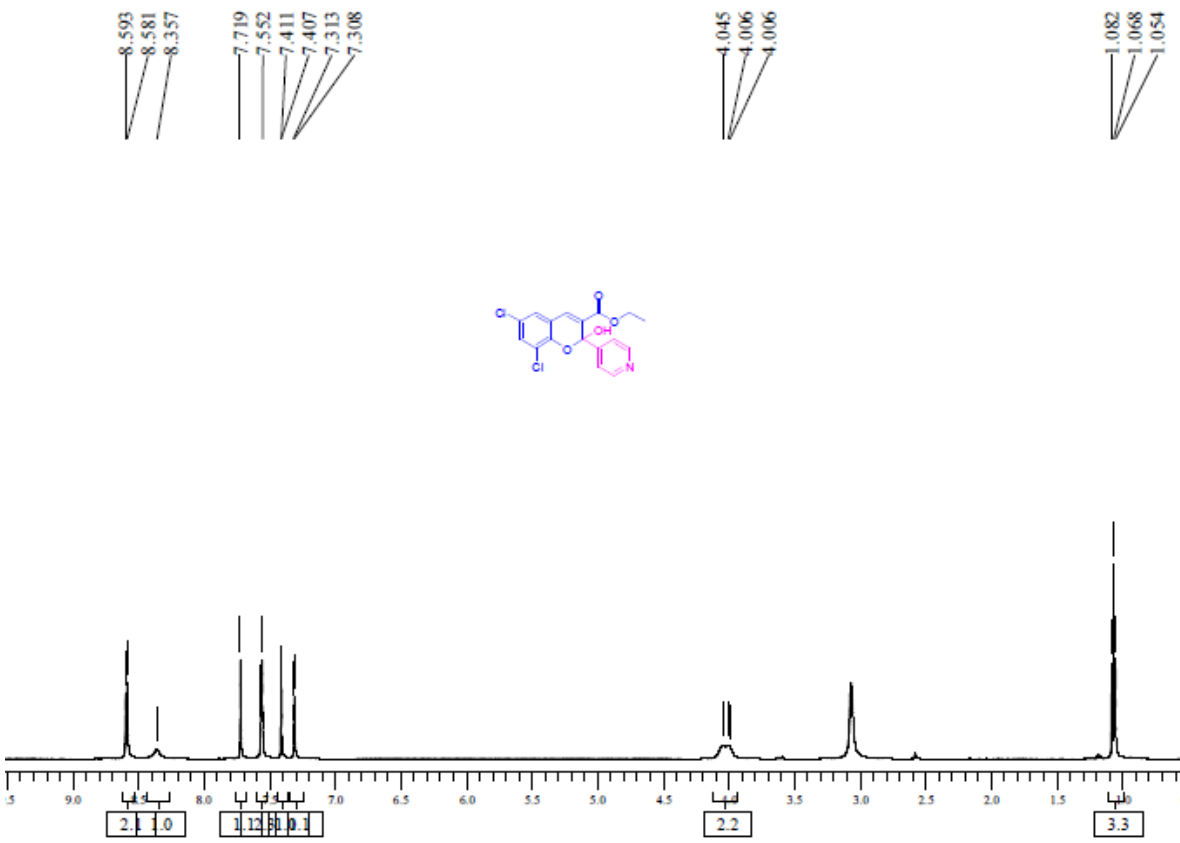
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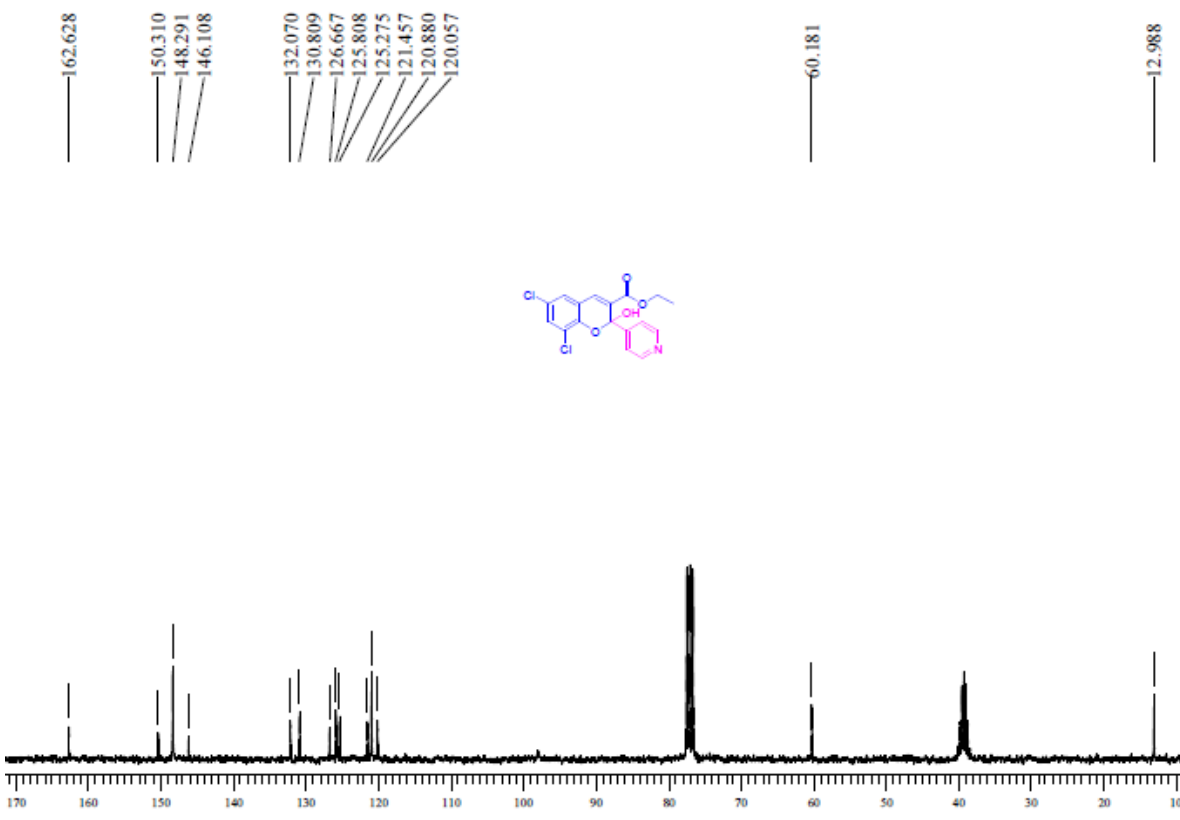
3.3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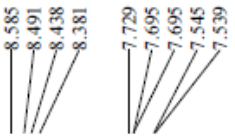
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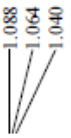
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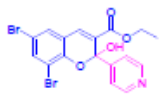
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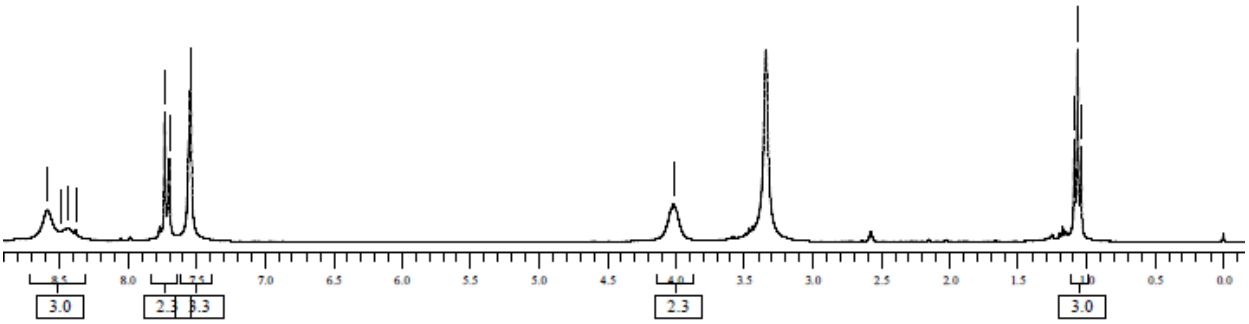
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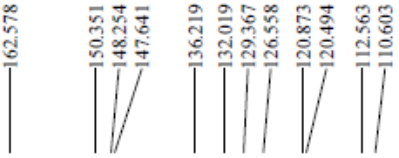
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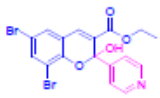
60.179


13.001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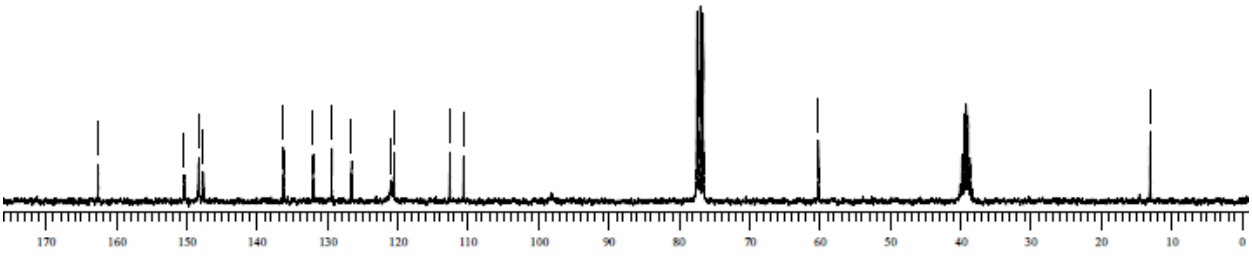

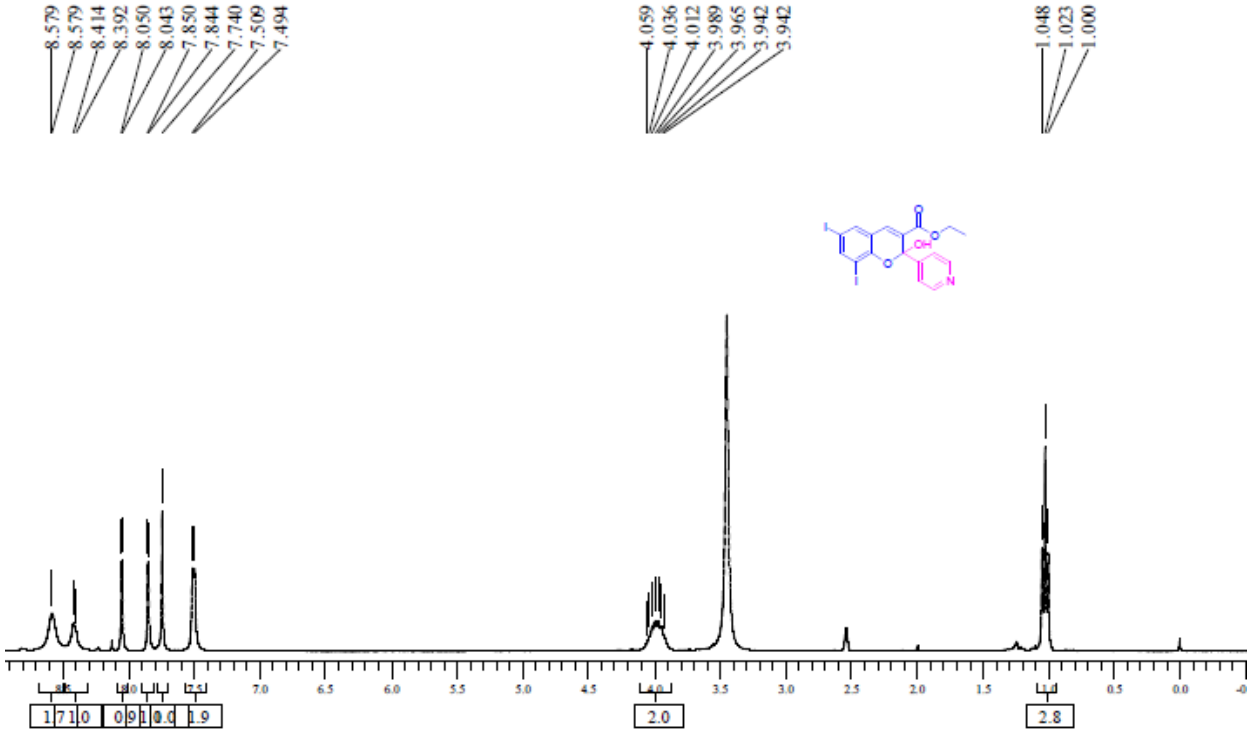
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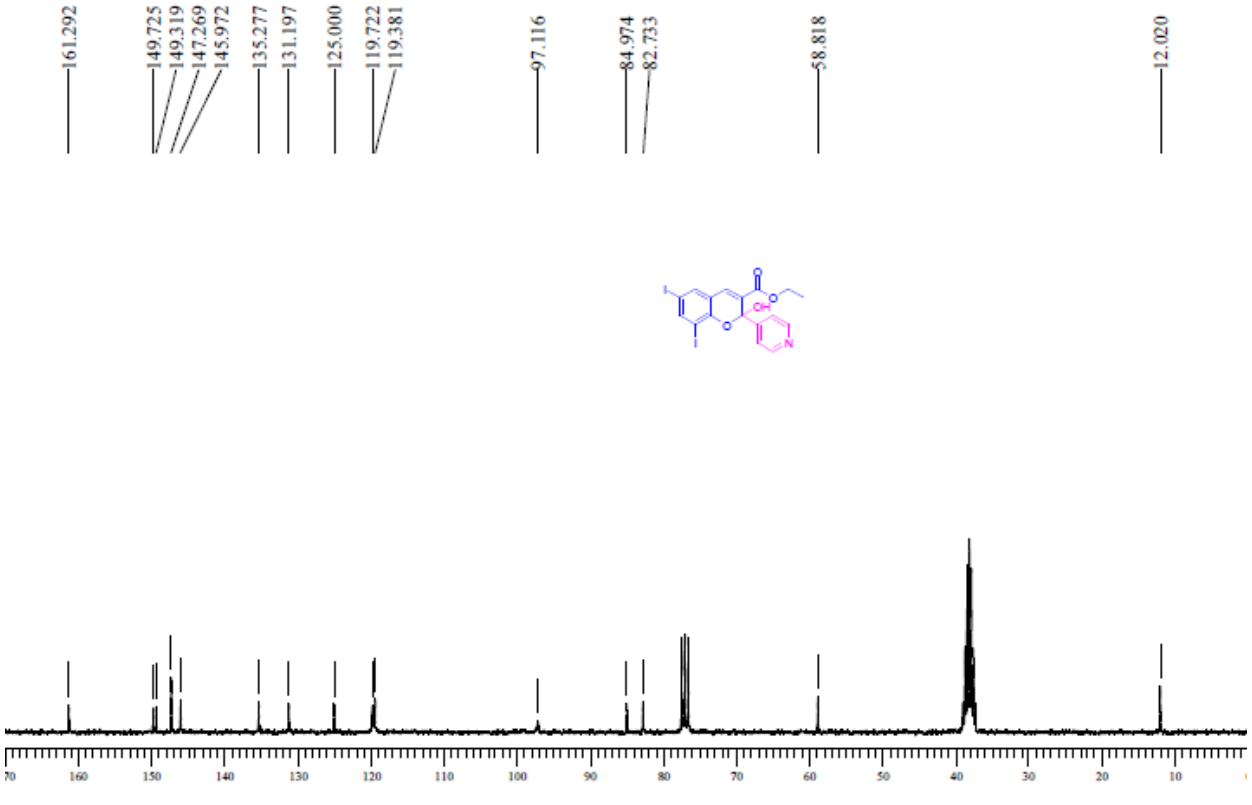
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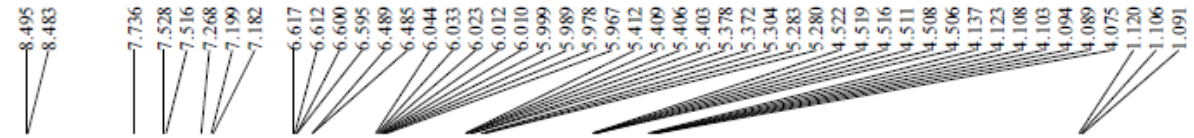
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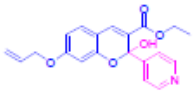

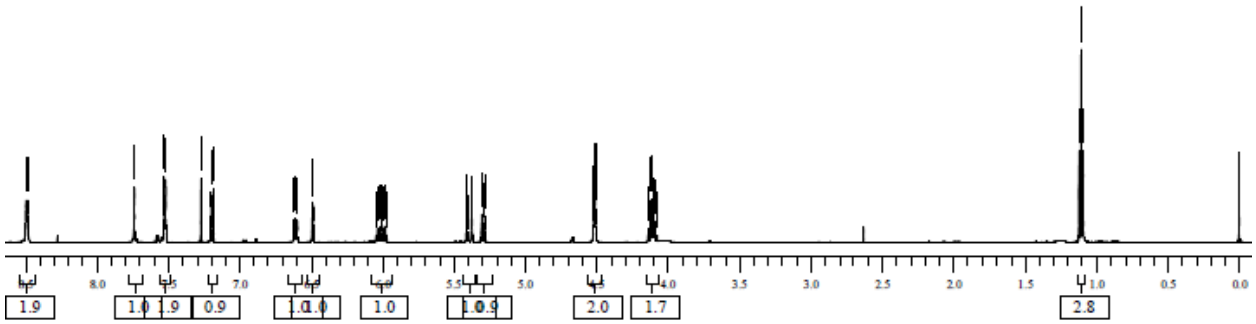
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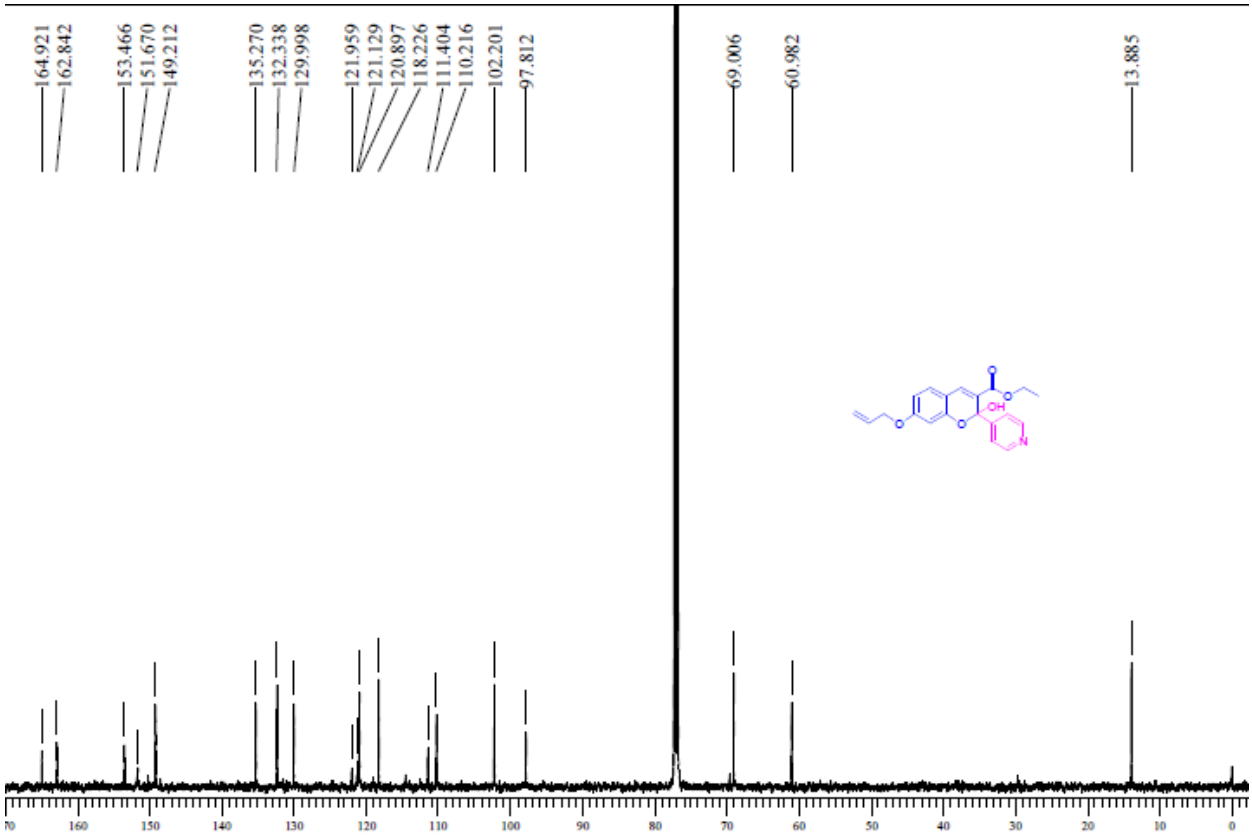
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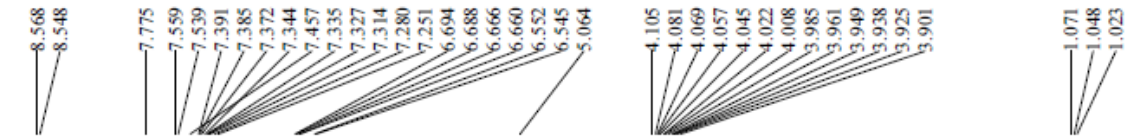
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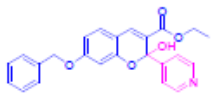
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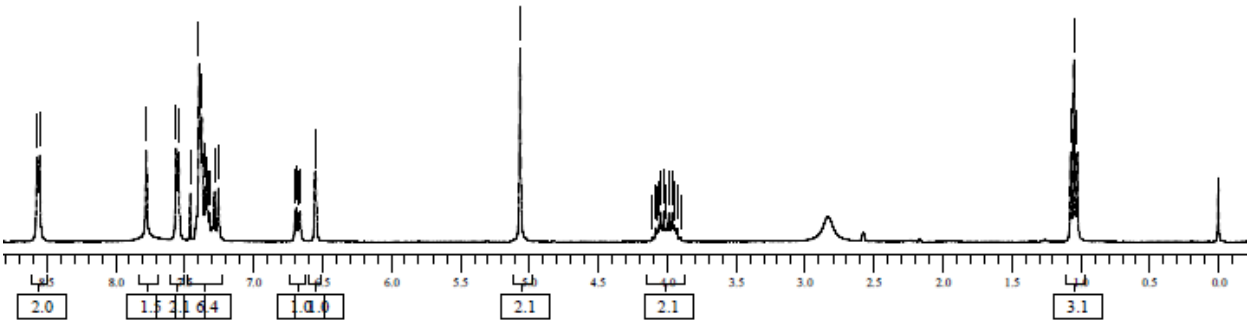
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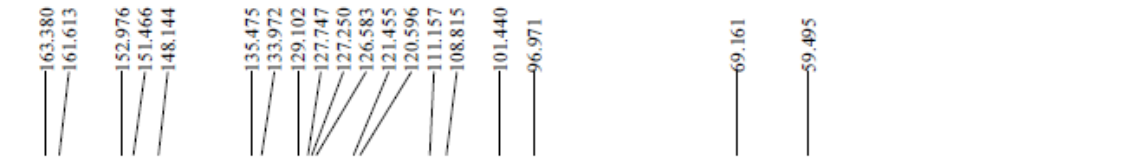
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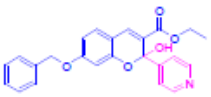
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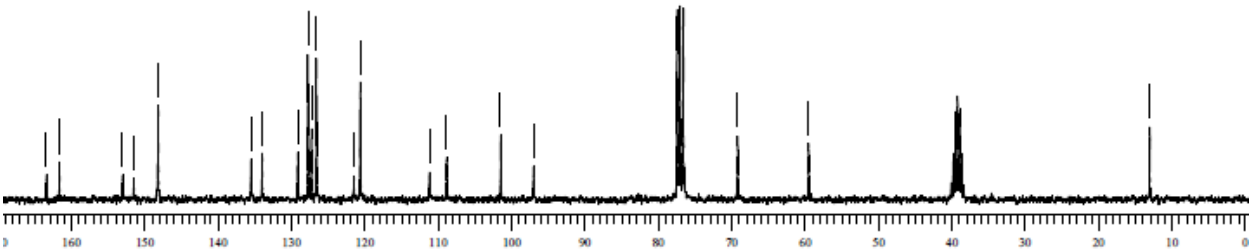
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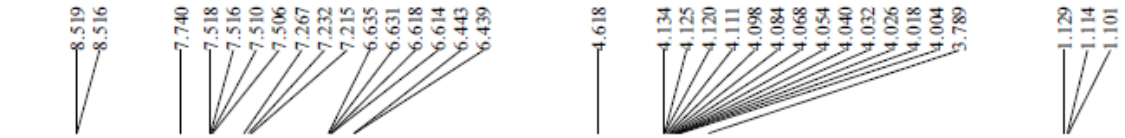
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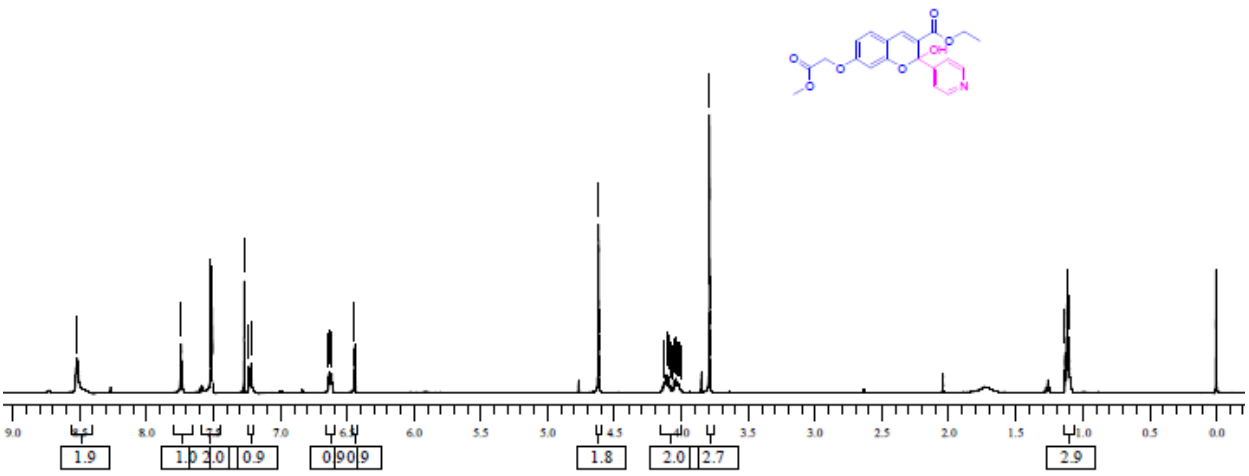
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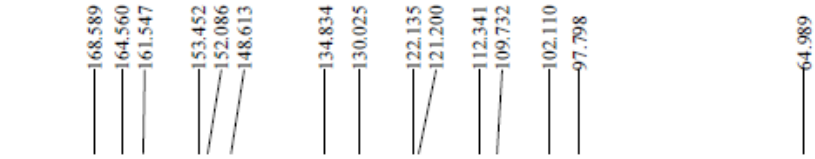
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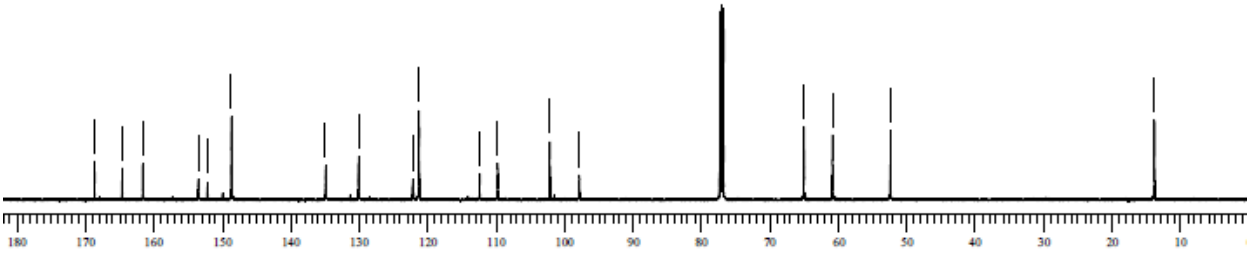

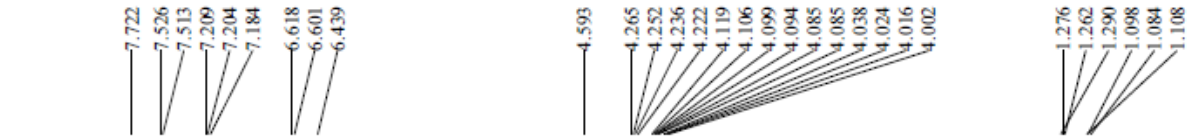
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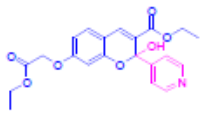

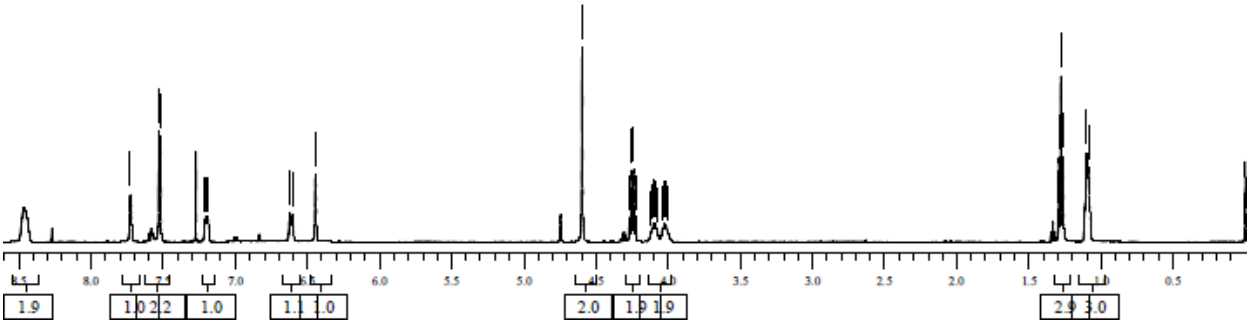
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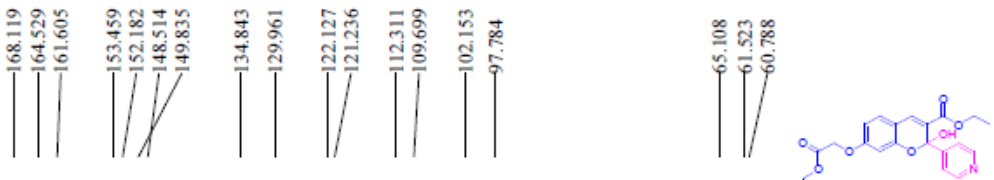
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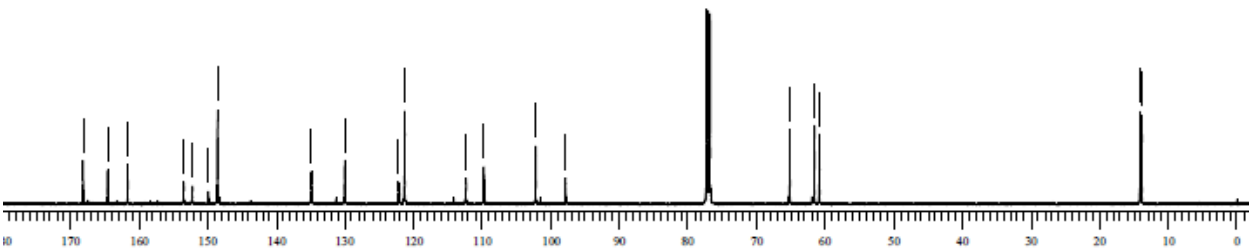

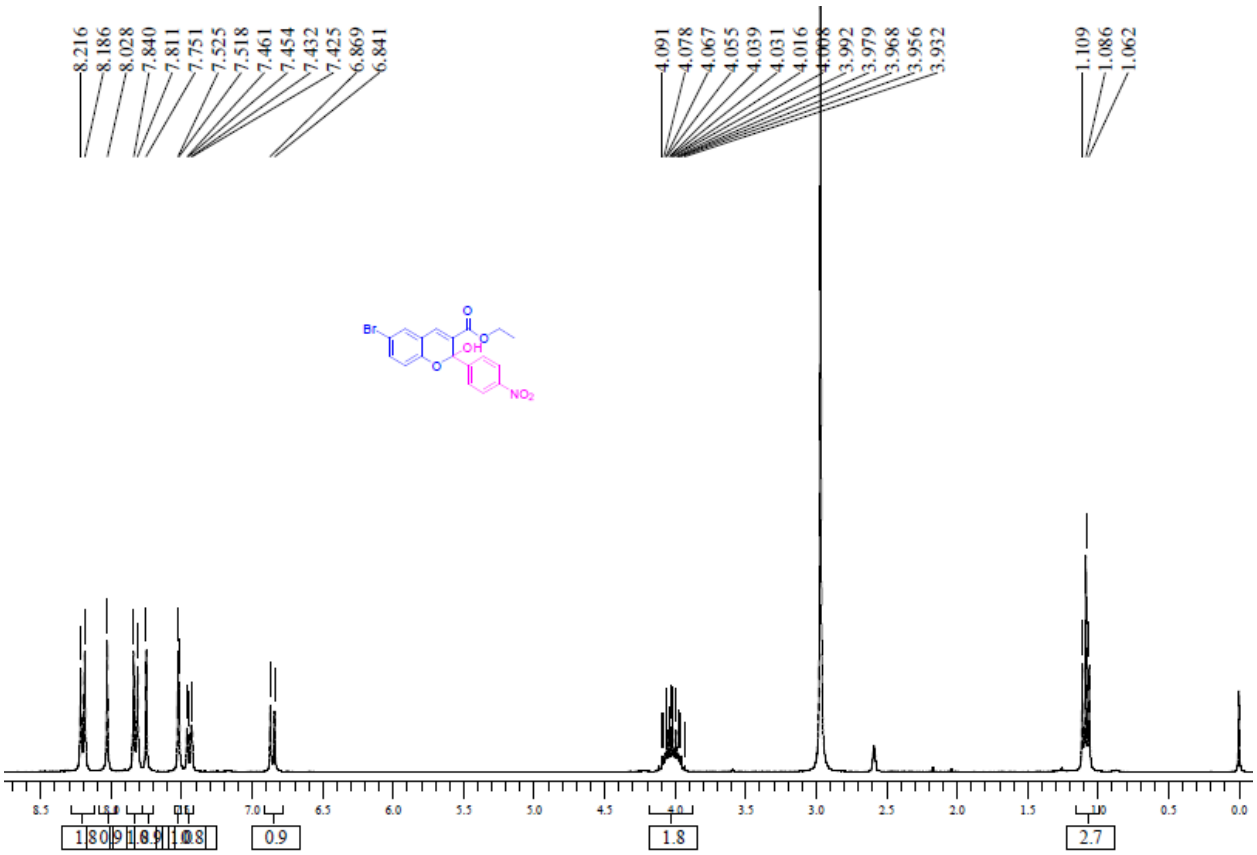
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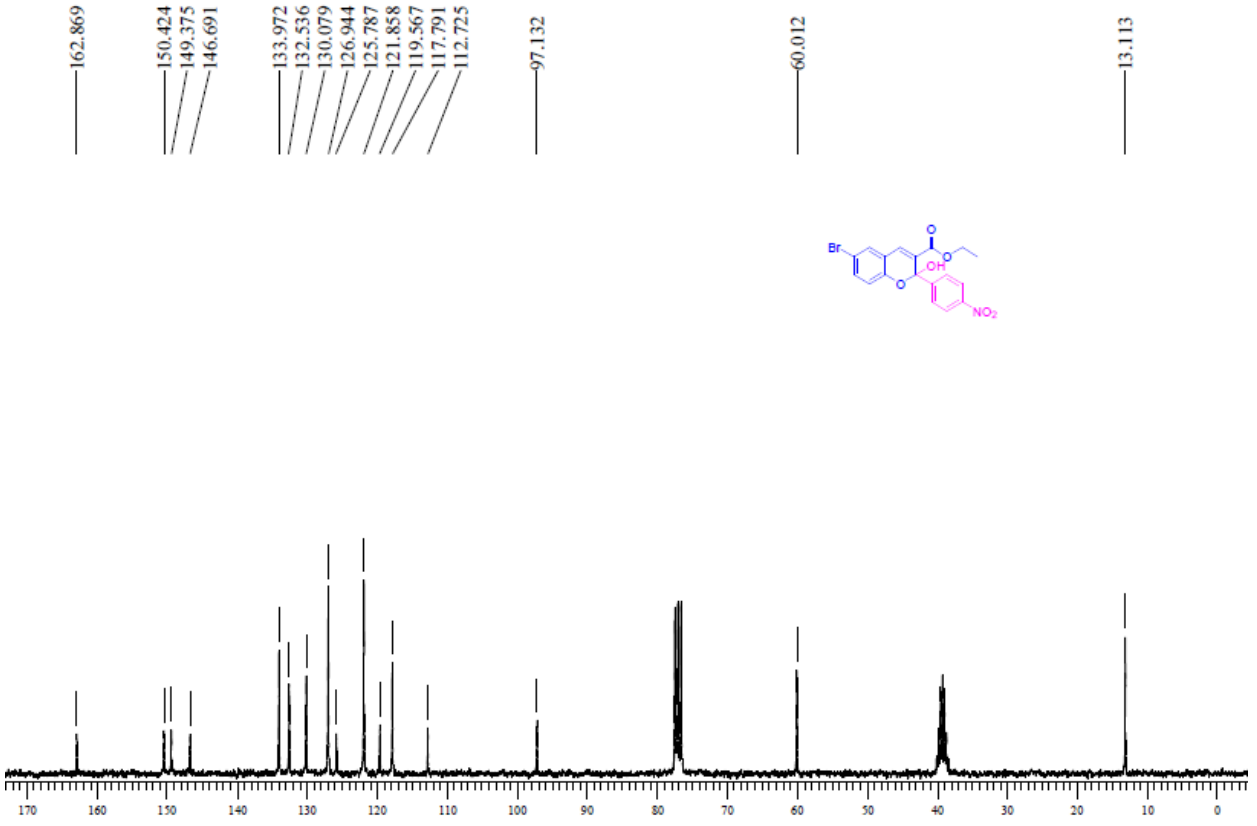
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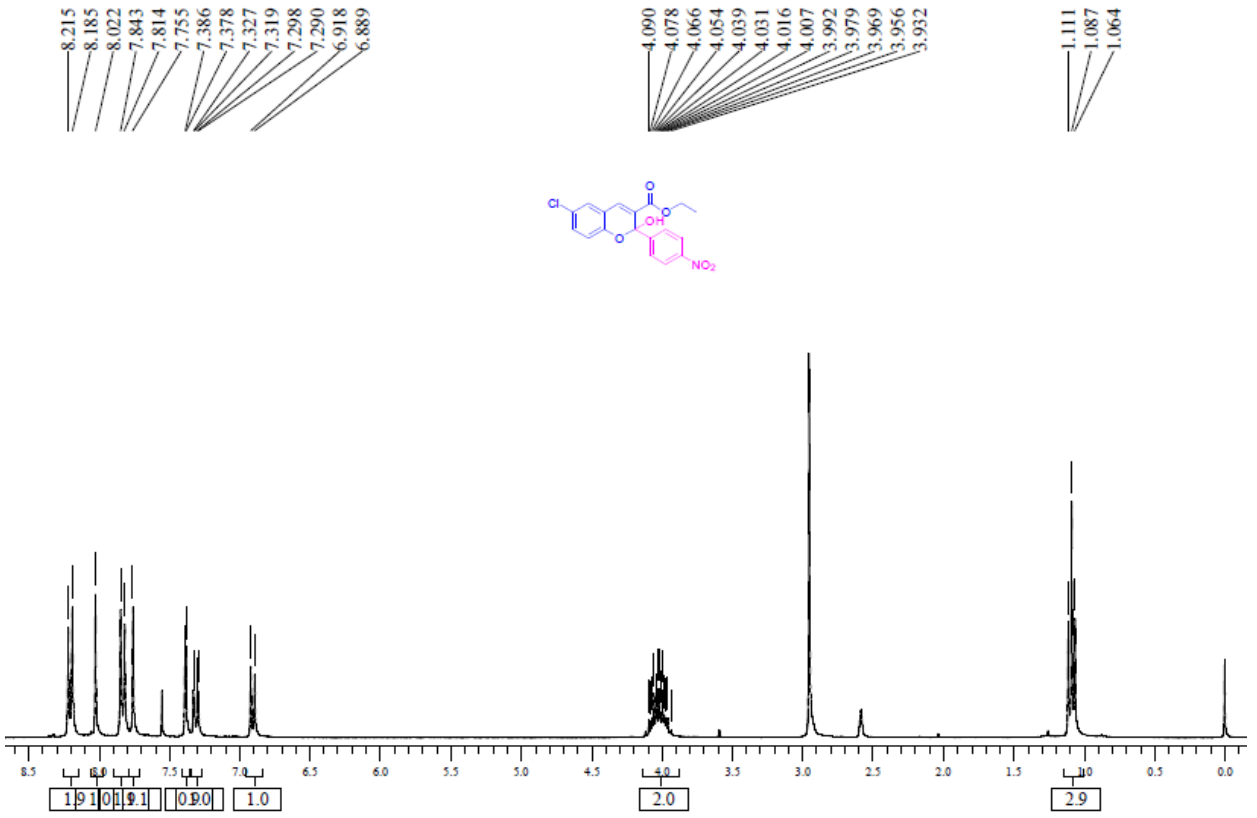
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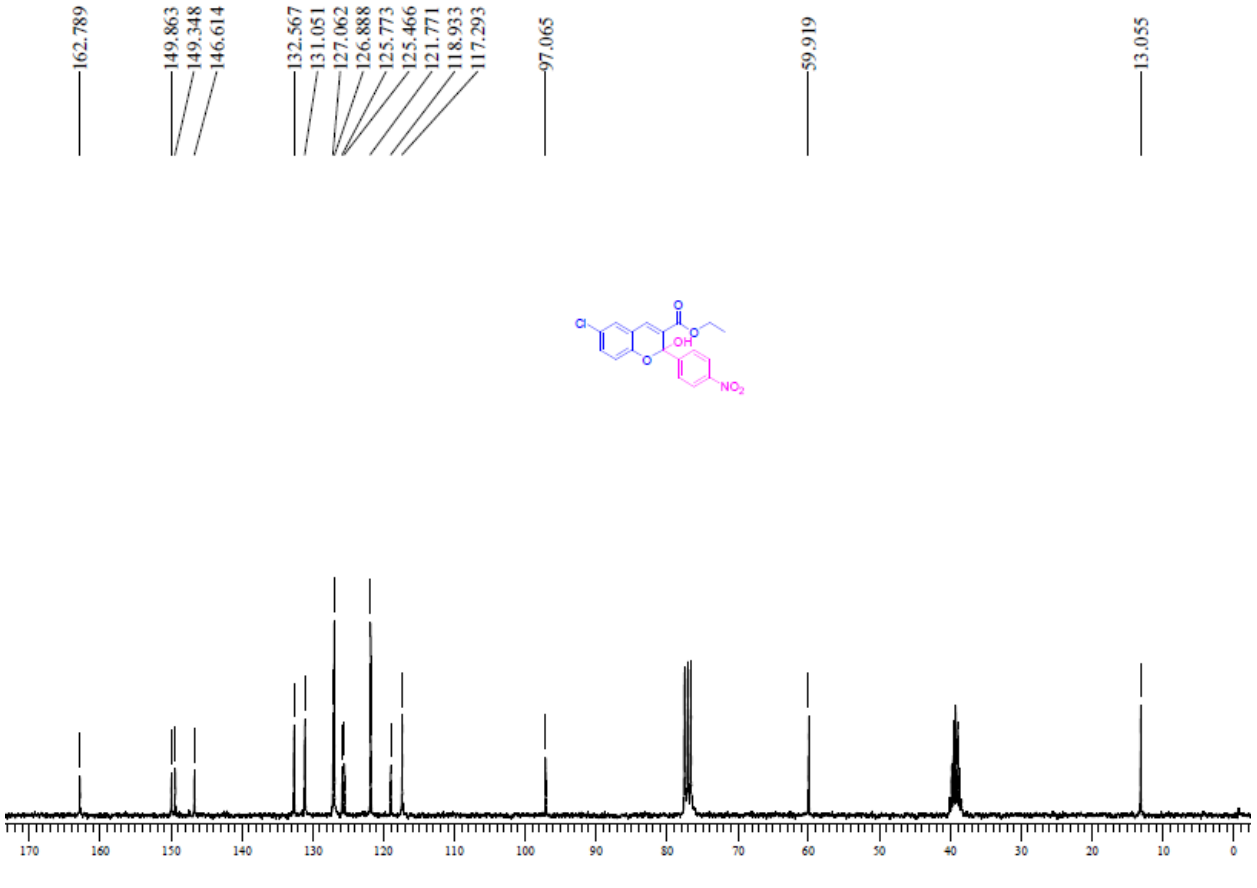
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O
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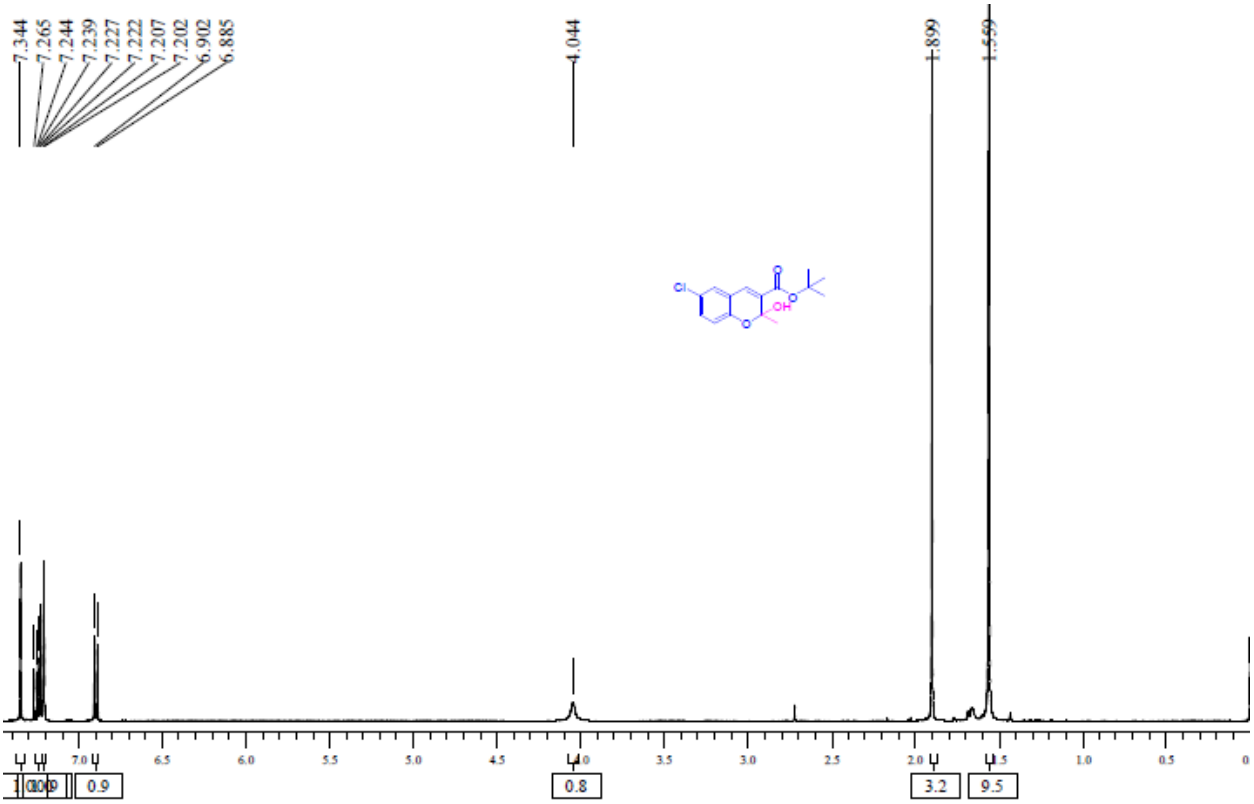
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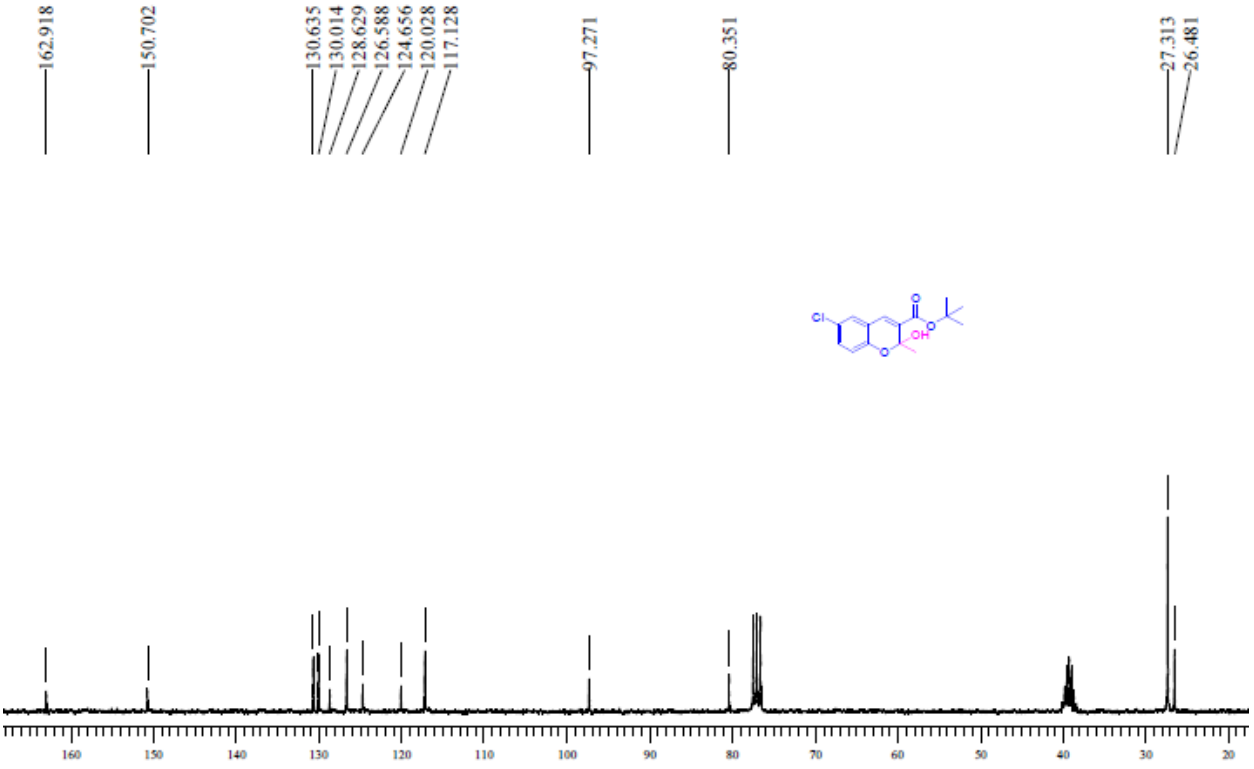
9.5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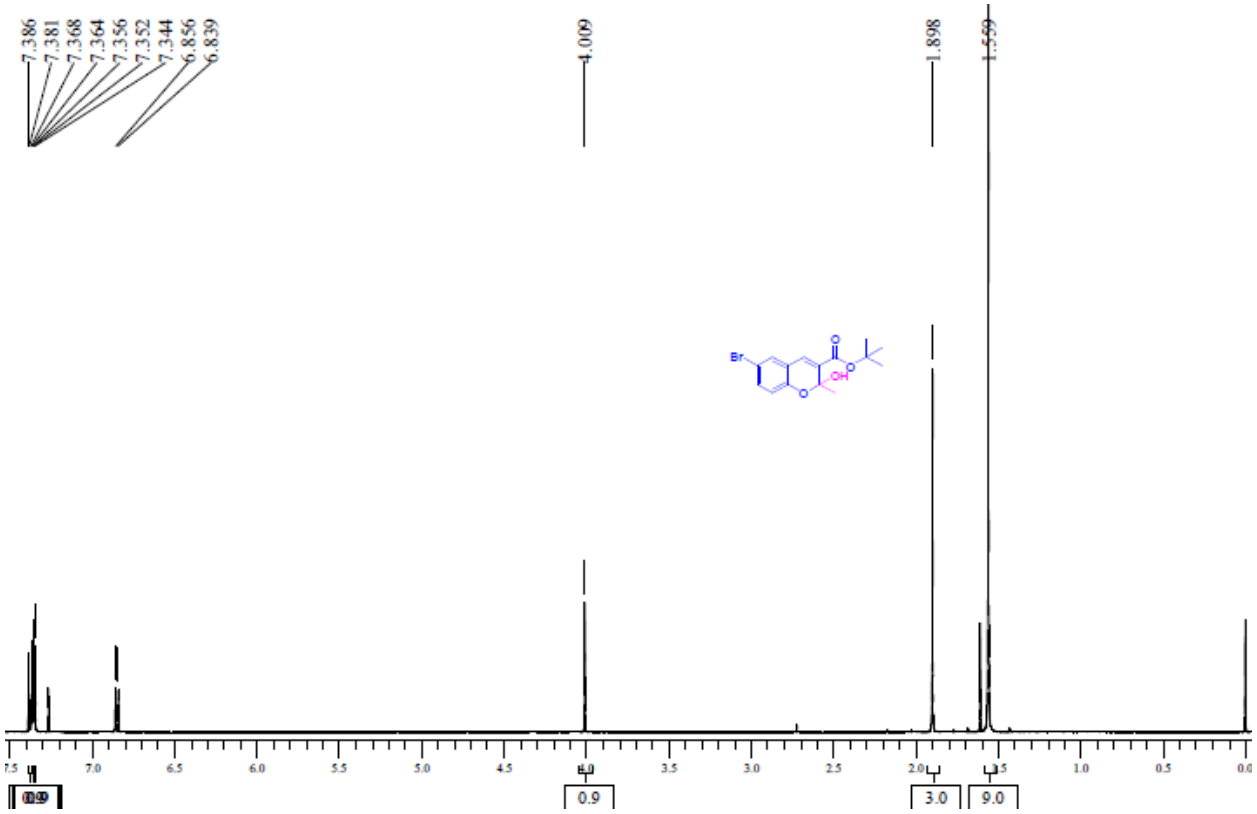
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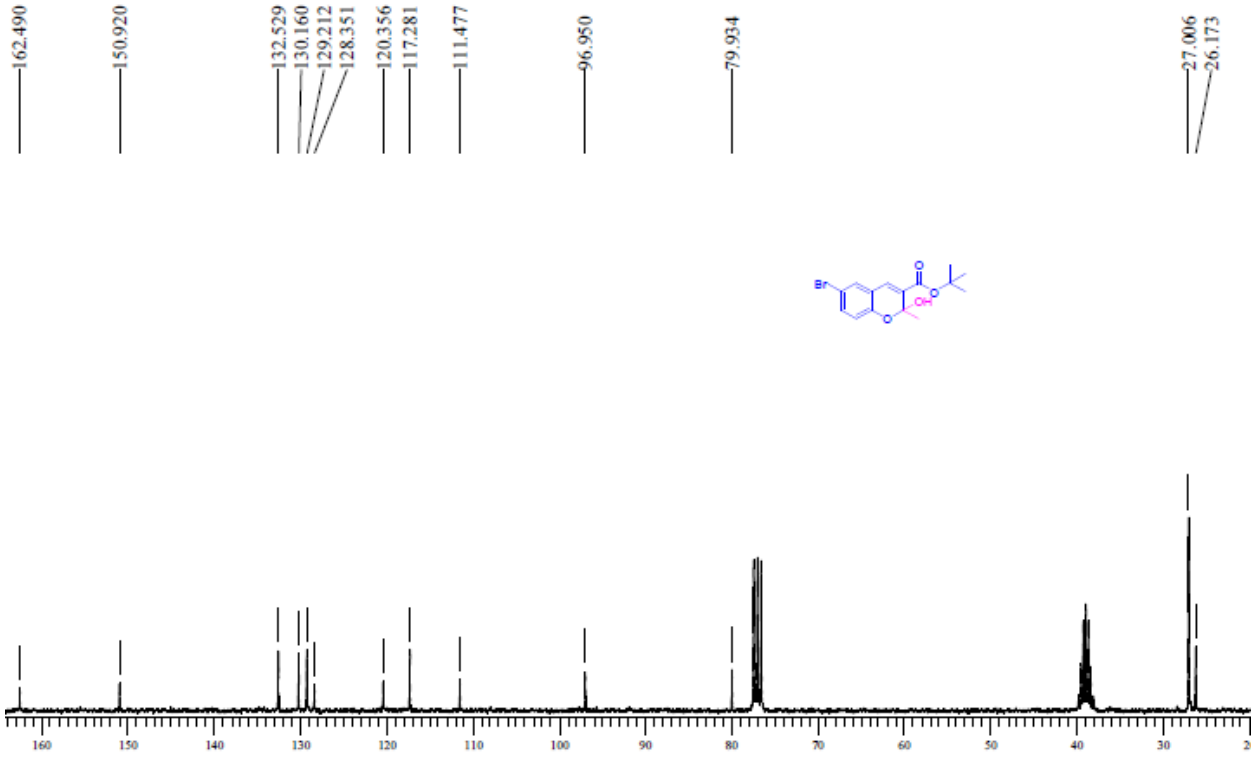
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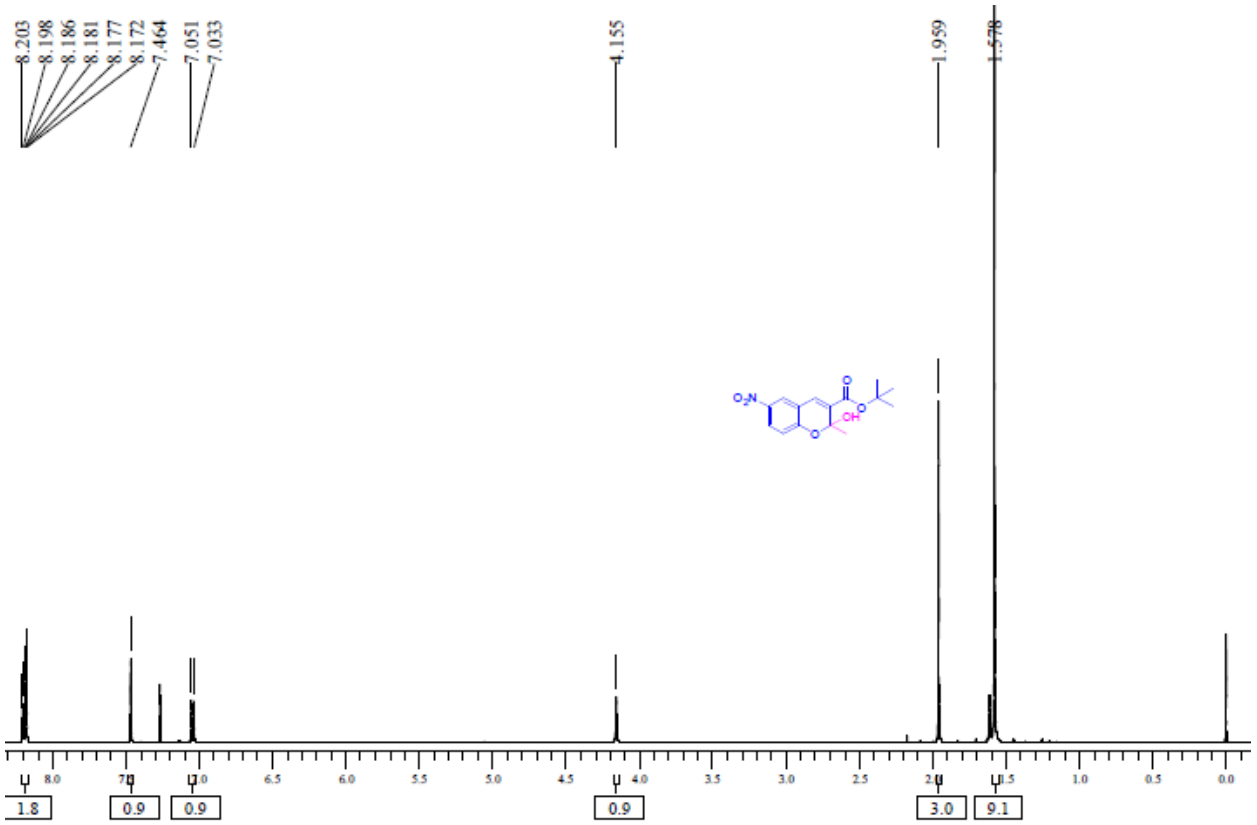
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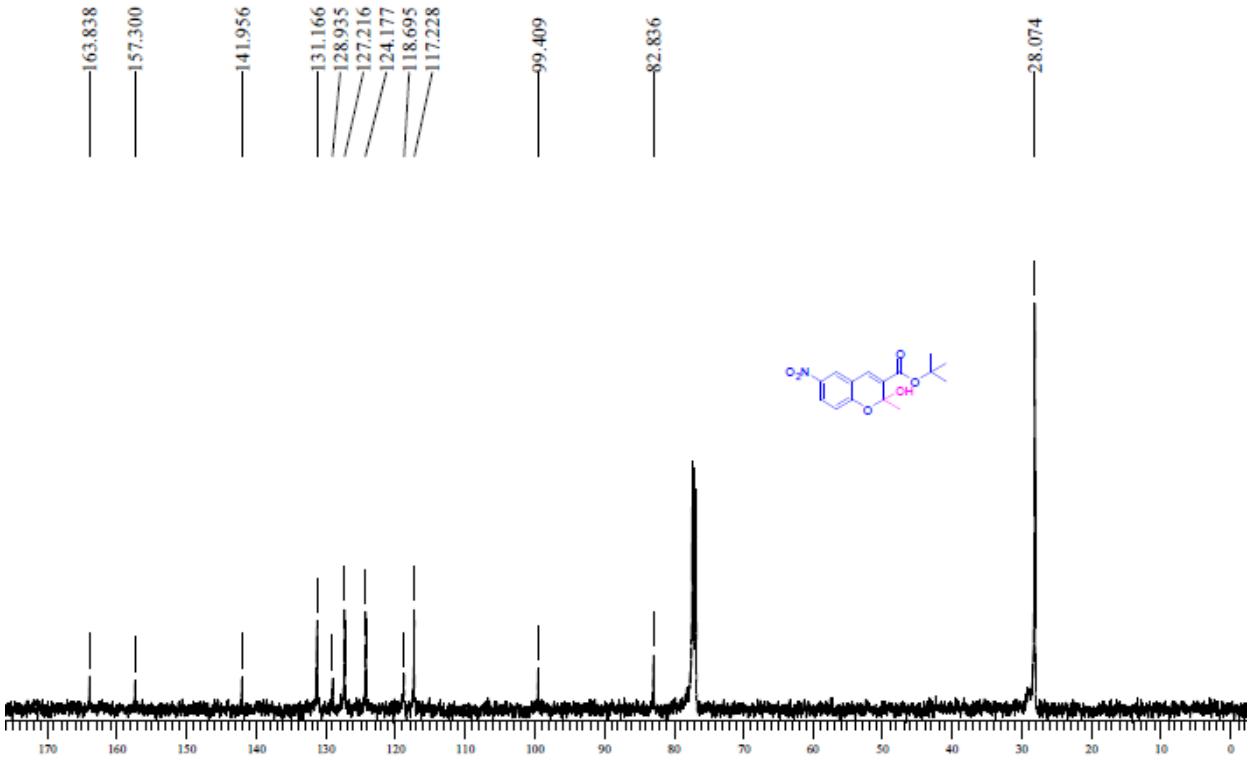
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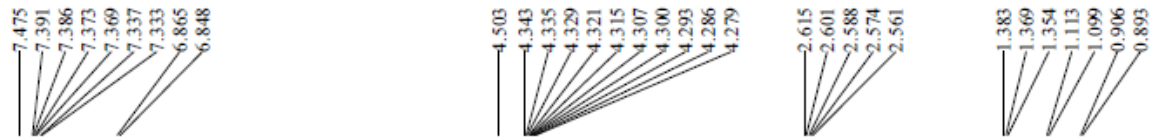
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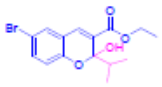
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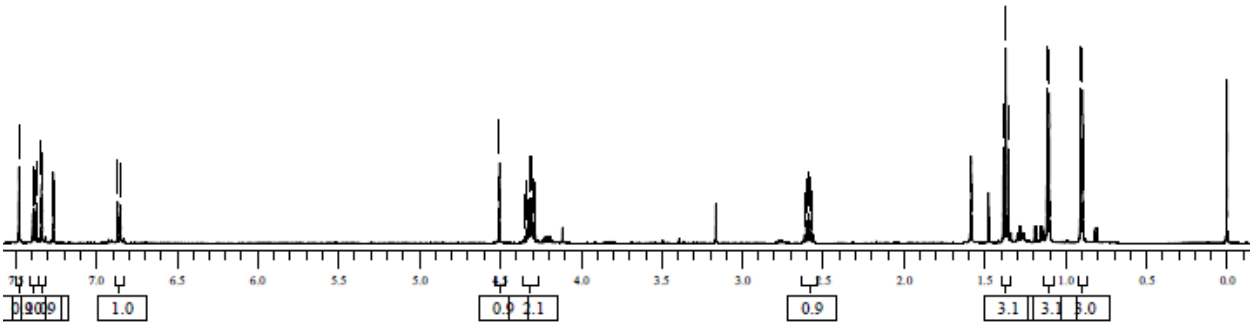
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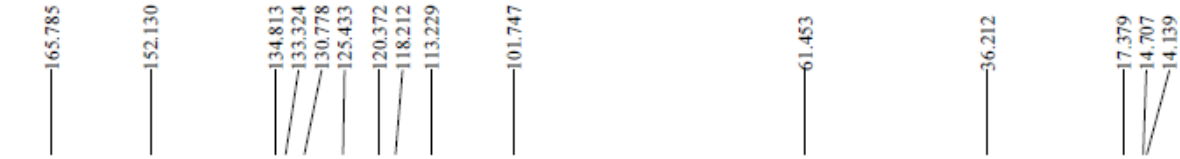
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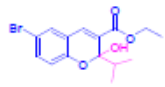
14.139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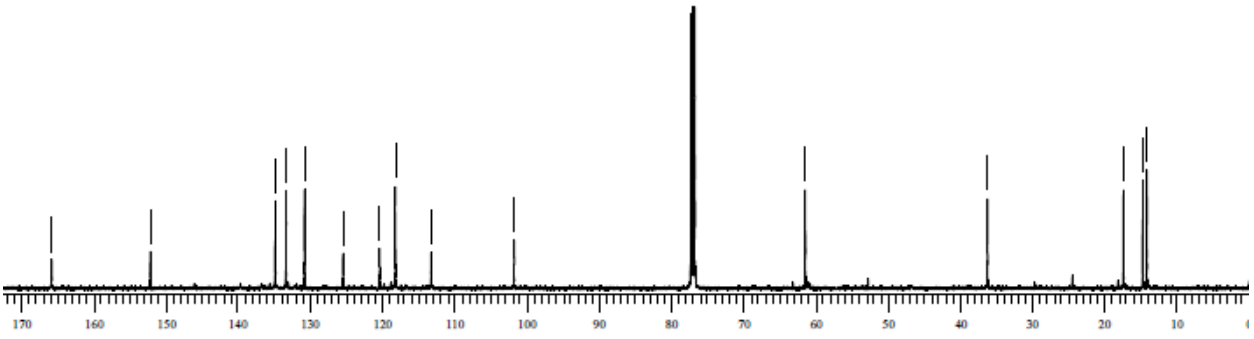

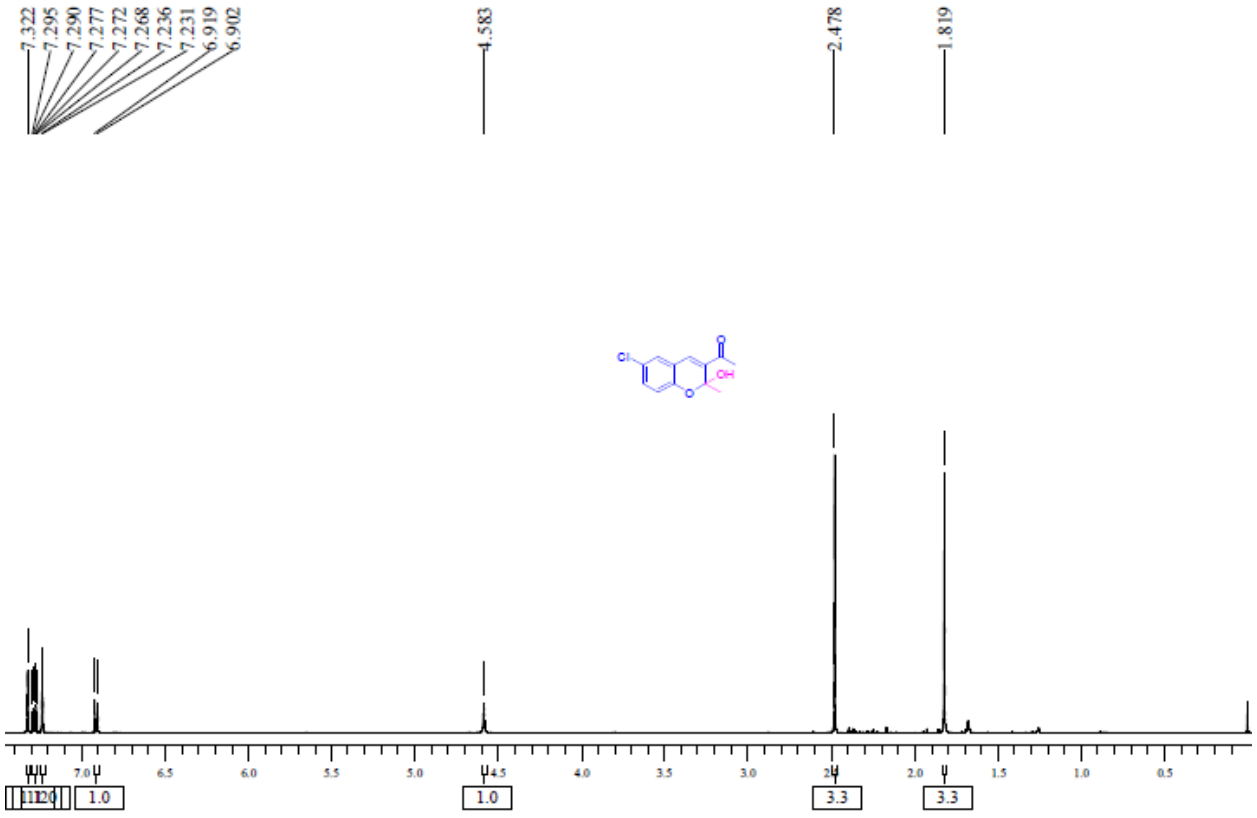
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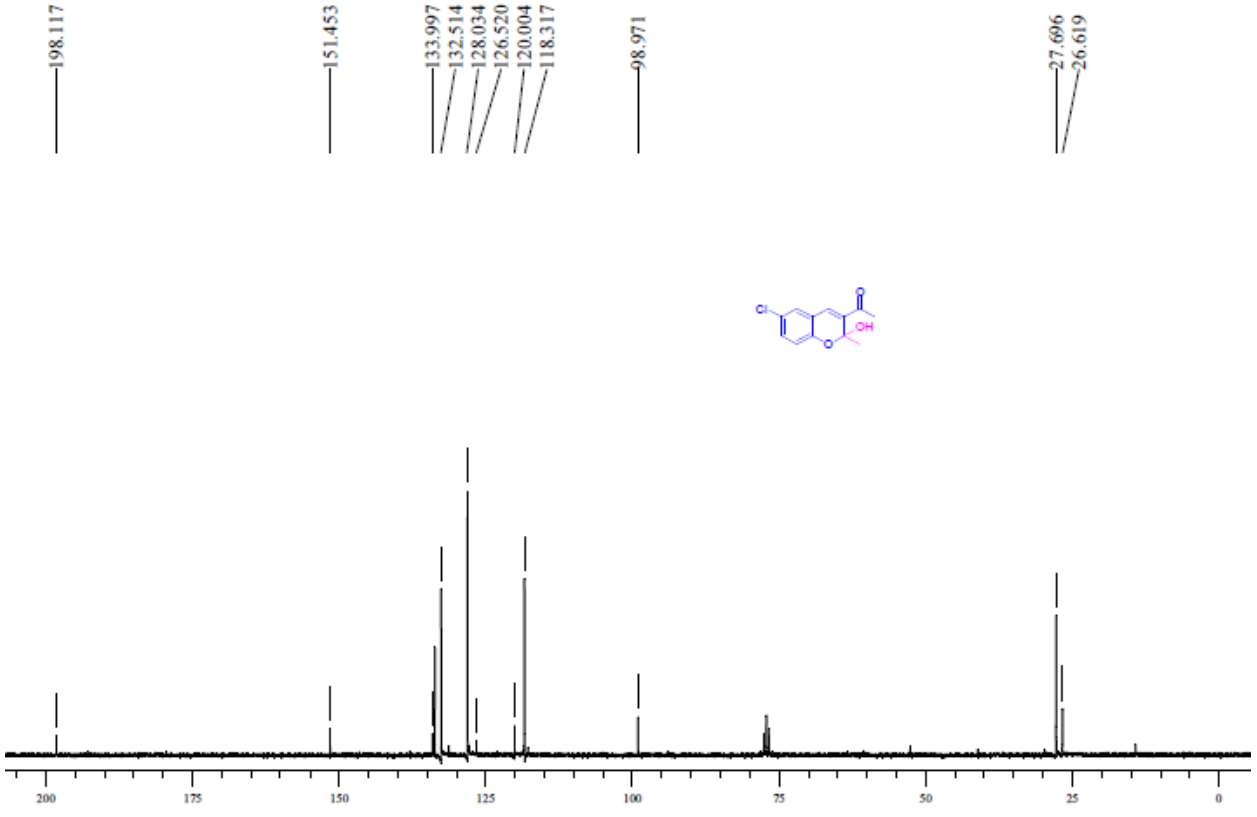
3.3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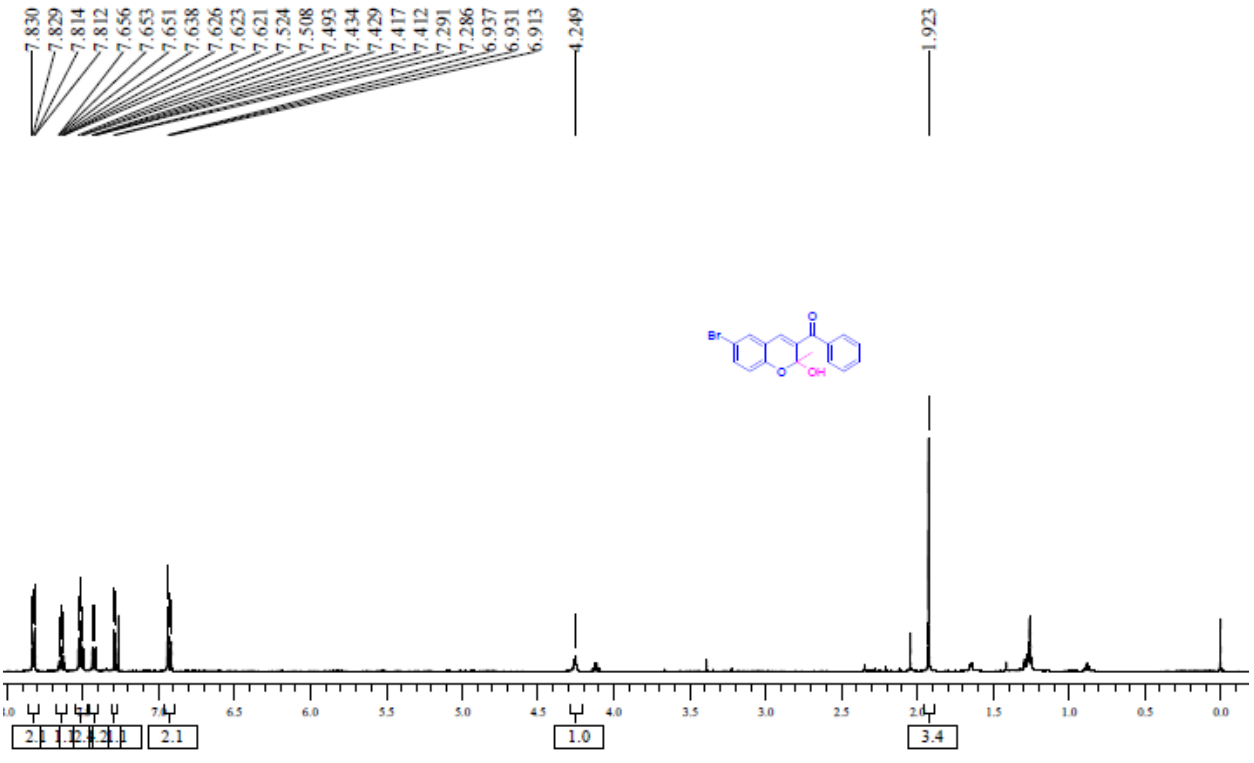
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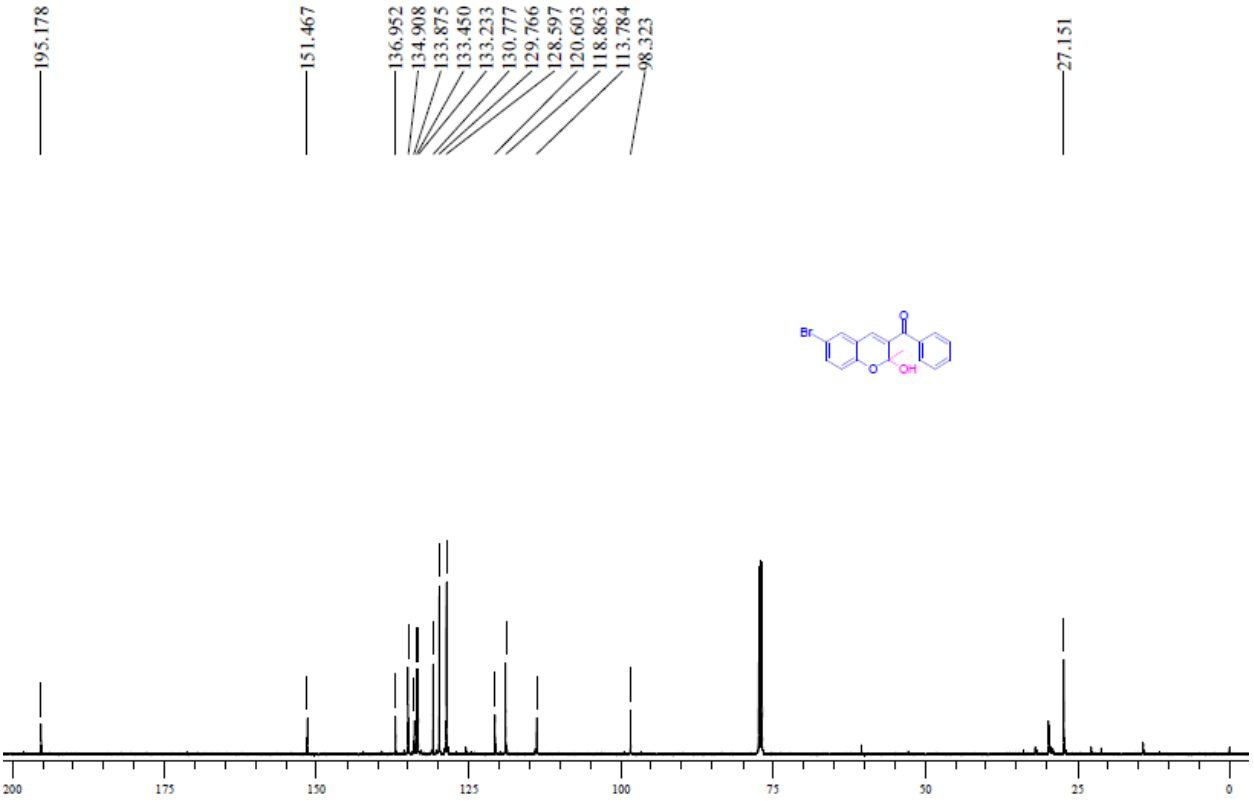
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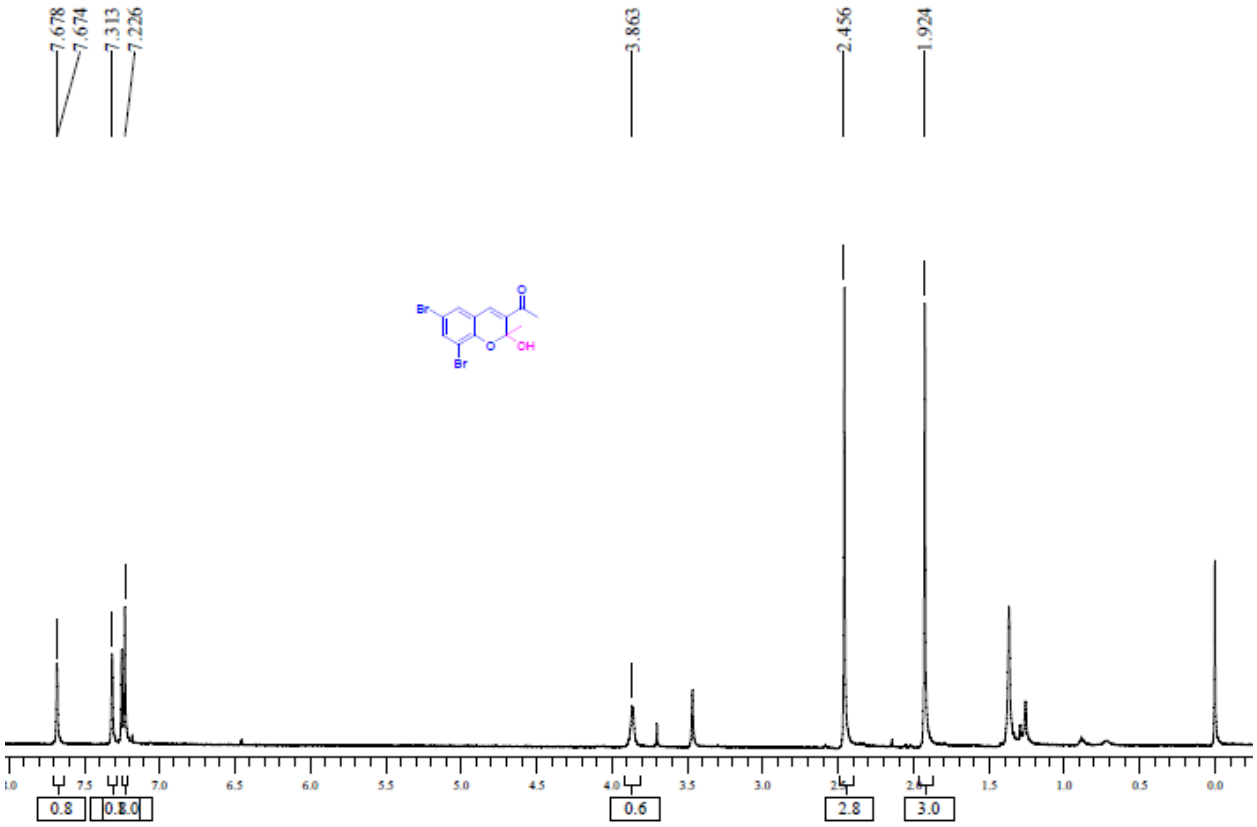
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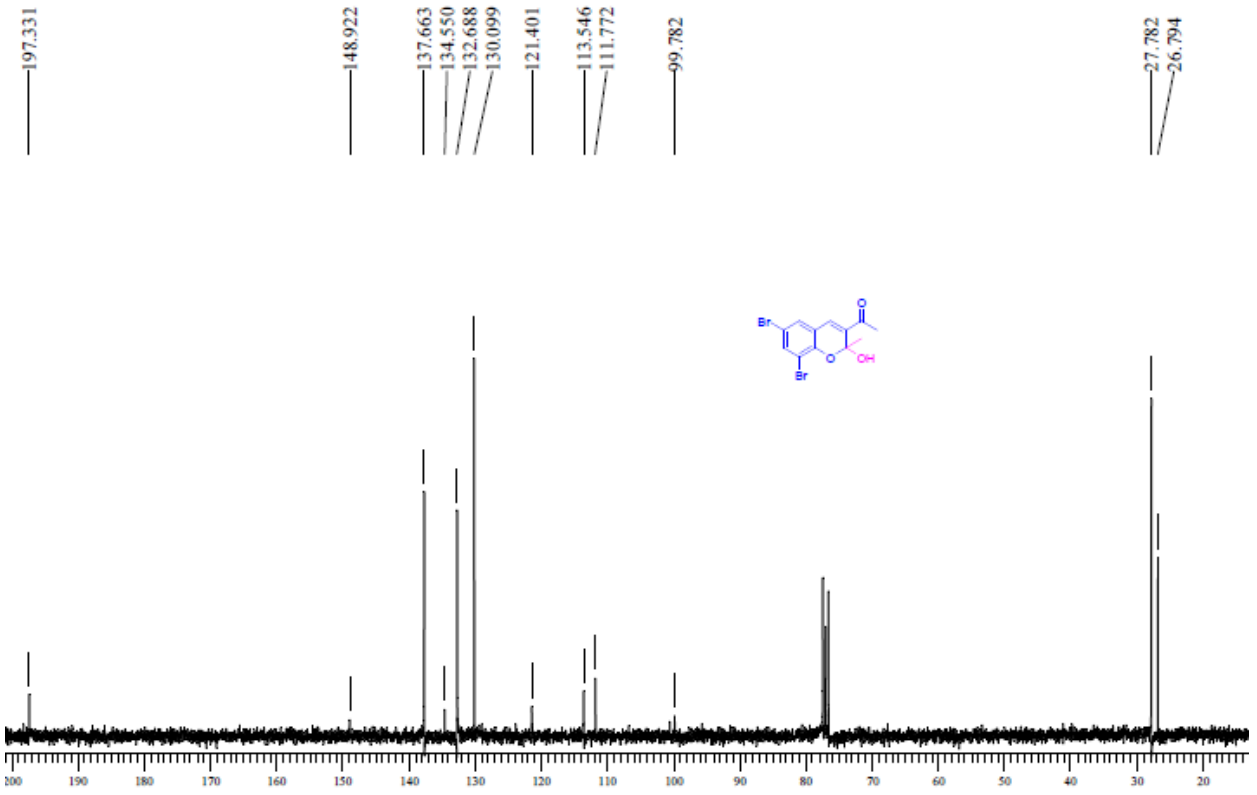
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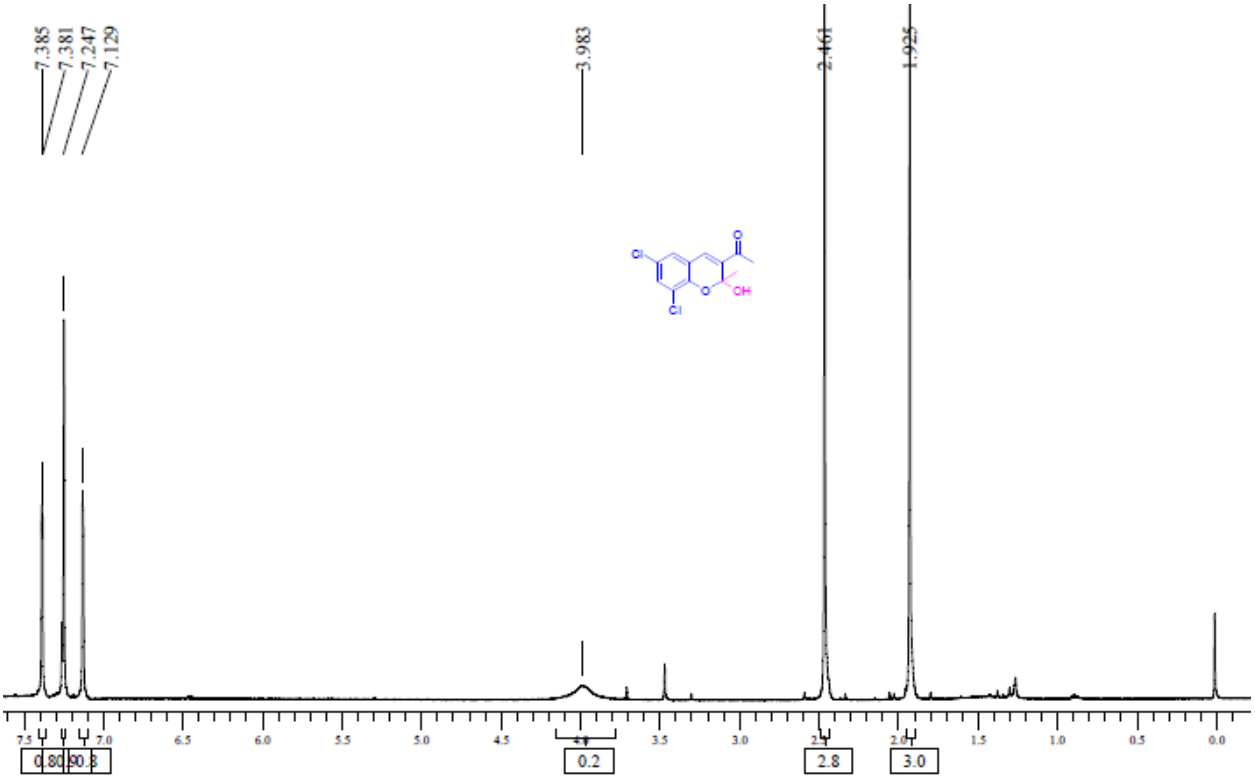
OH
Br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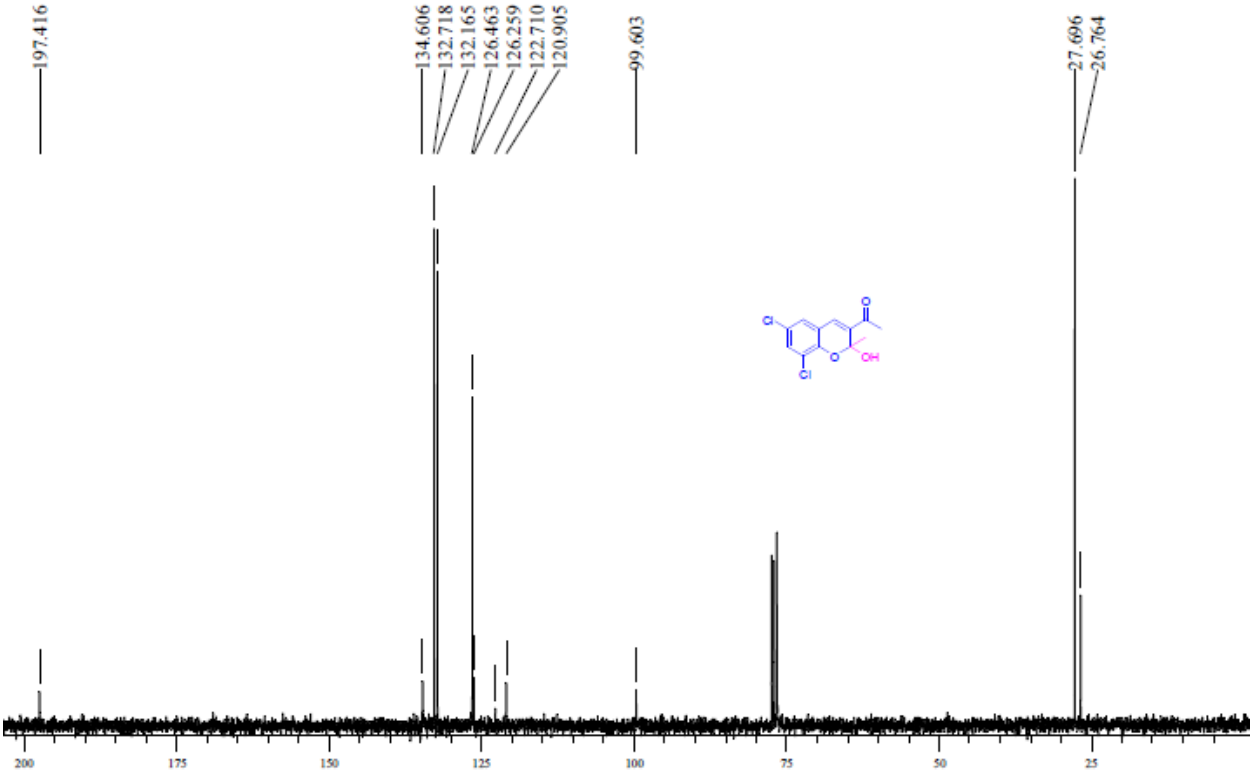
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OH
Cl


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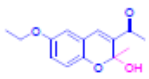
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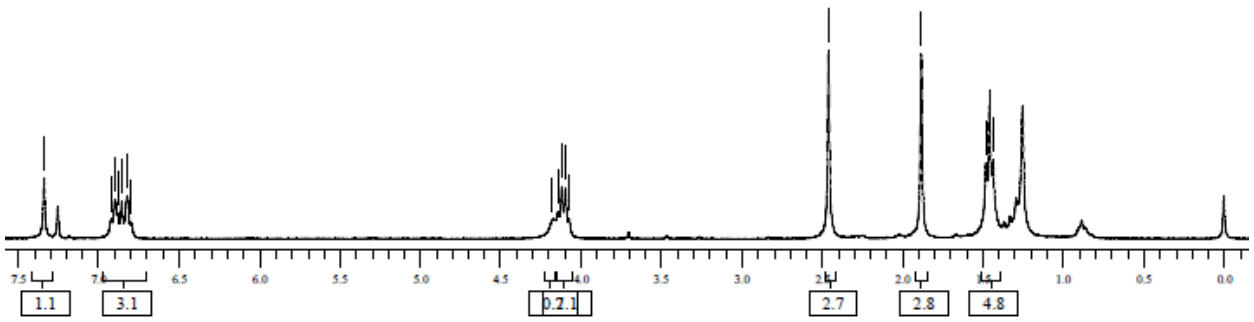
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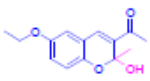
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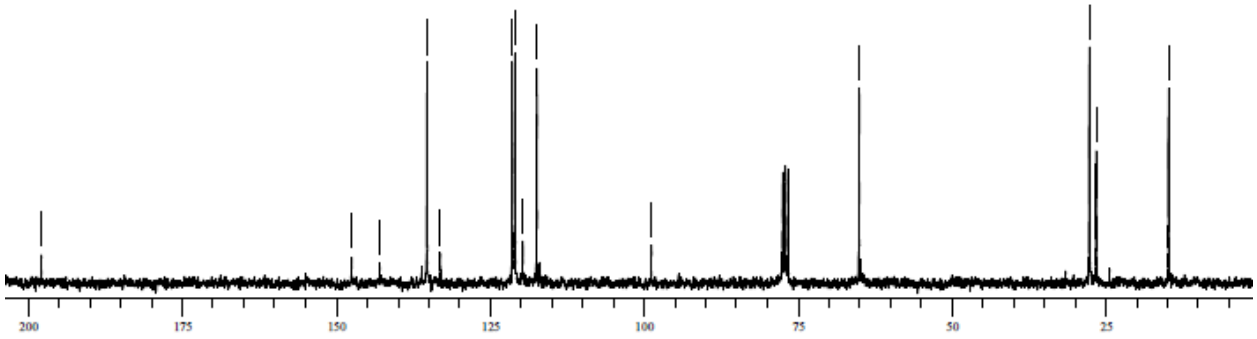
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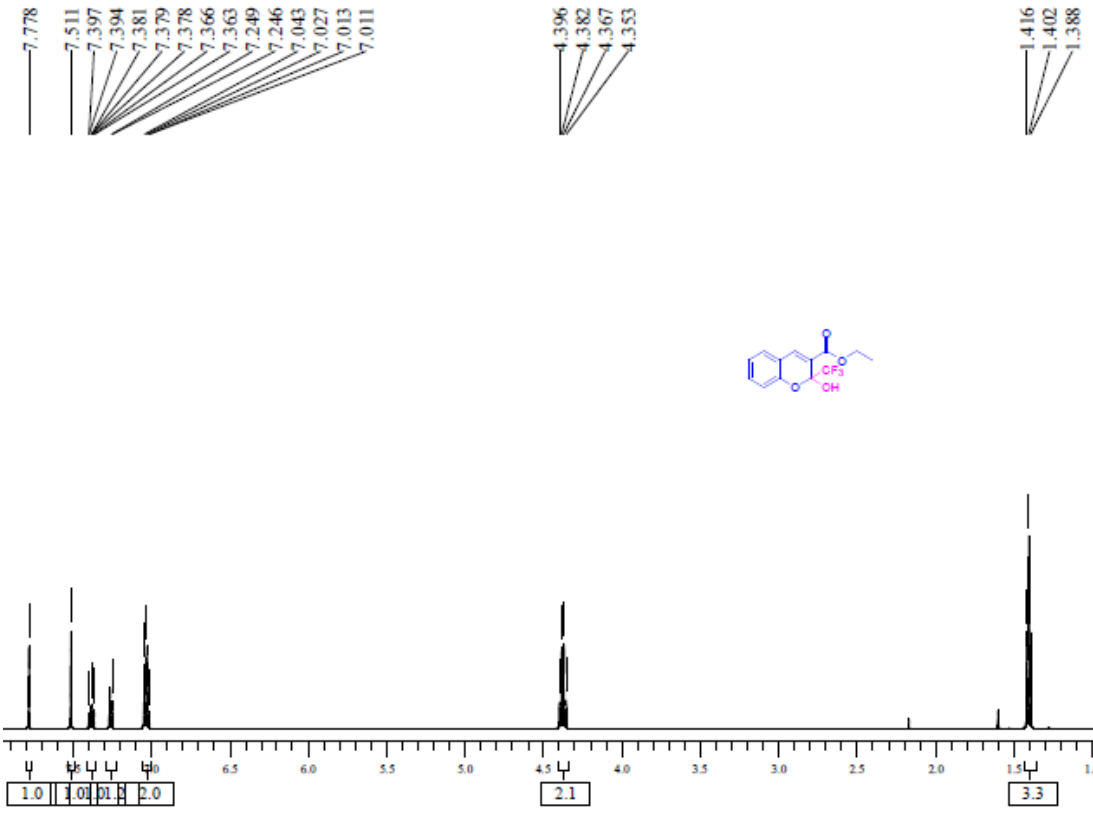
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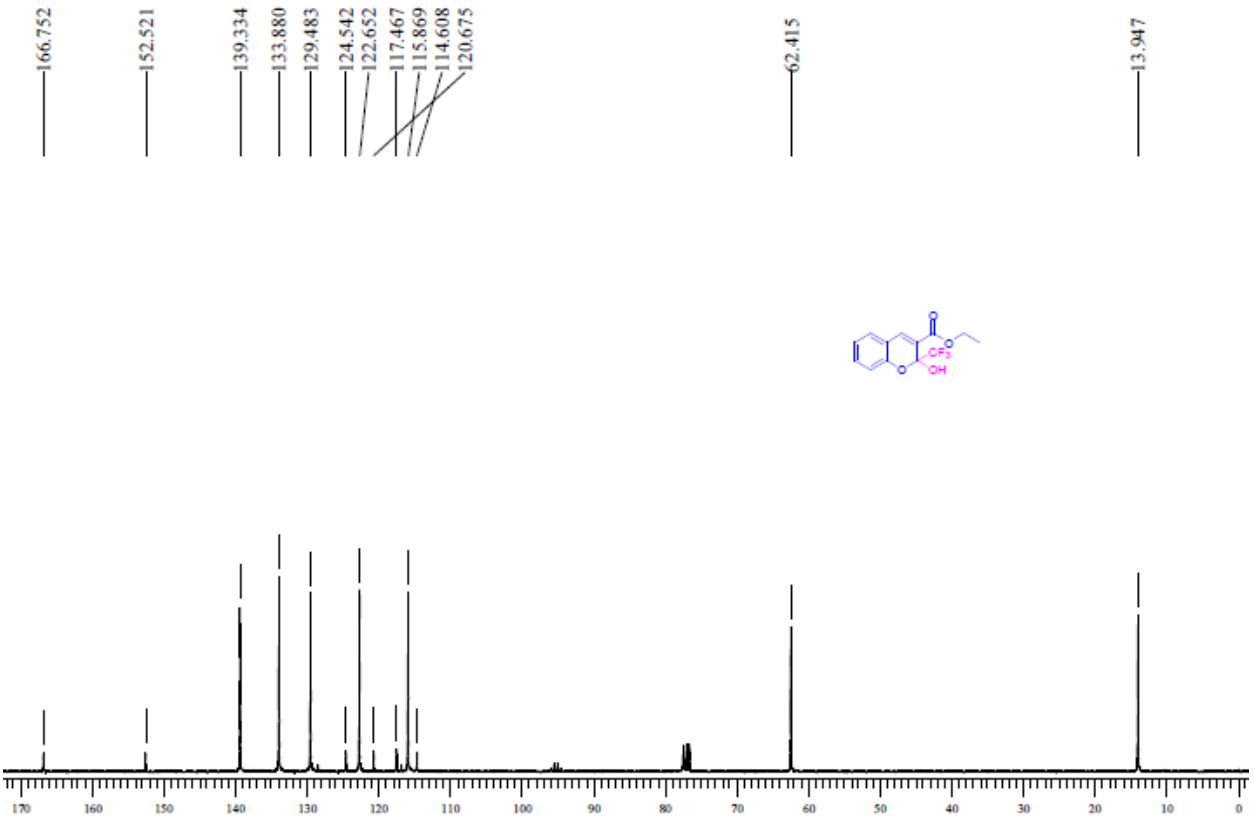
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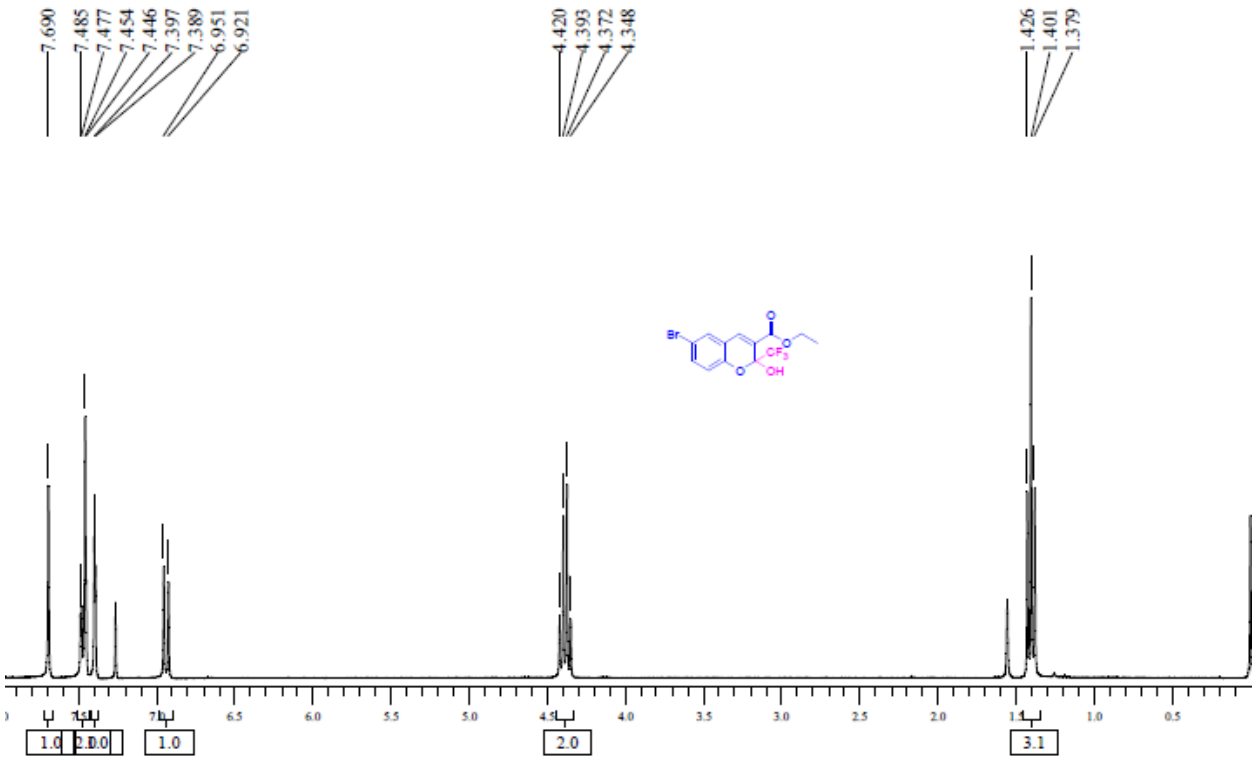
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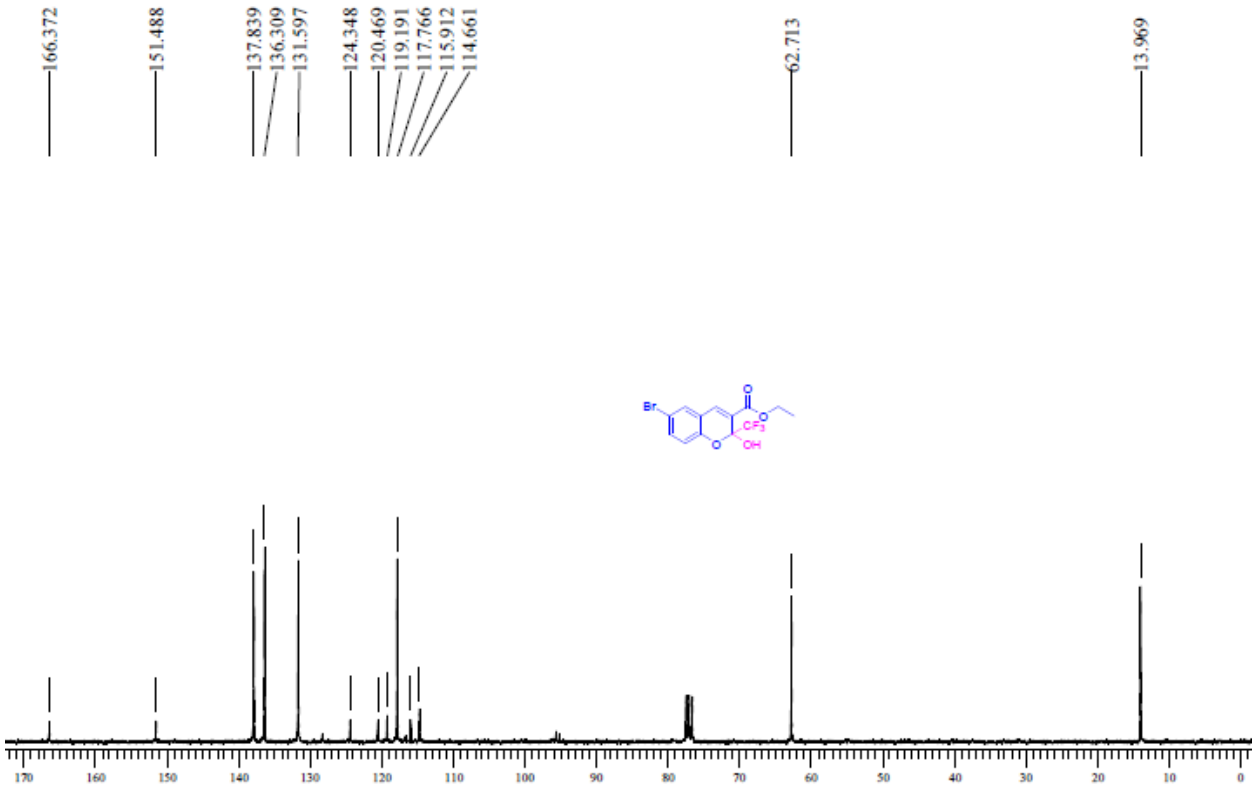
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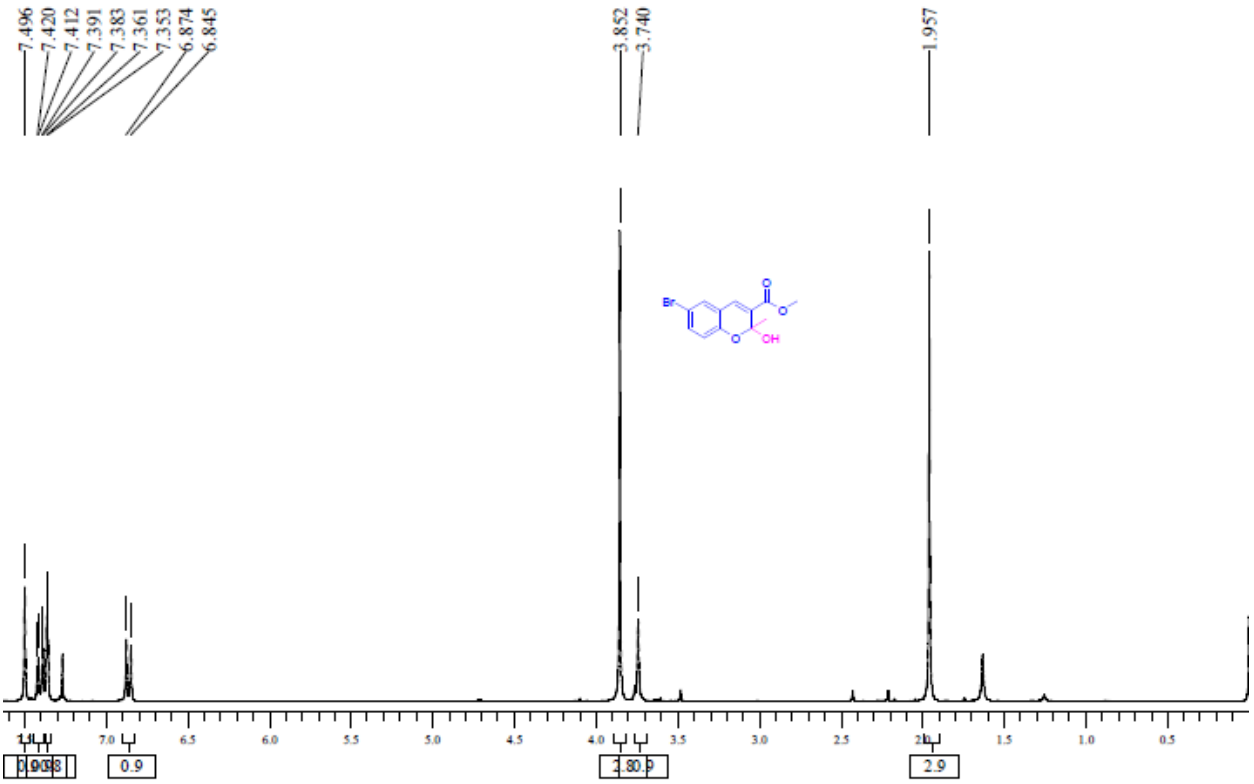
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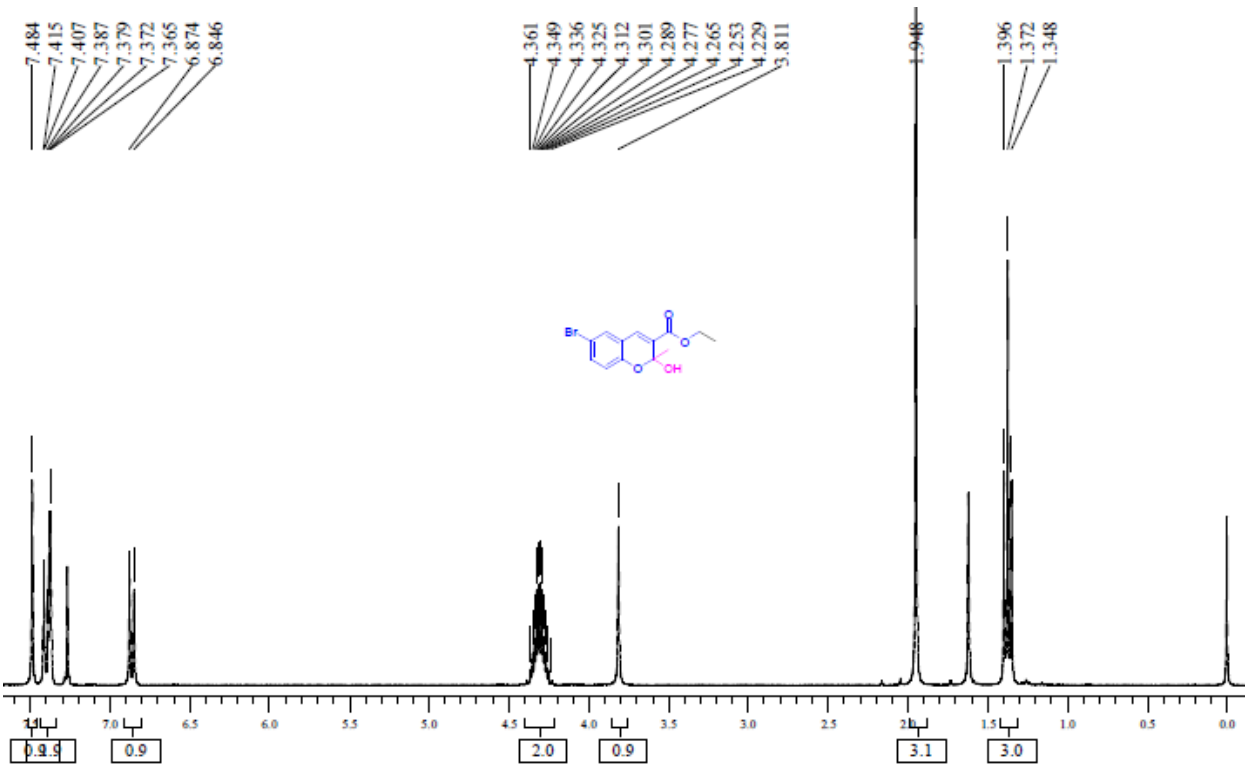
2.9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6.874
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4.325
4.312
4.301
4.289
4.277
4.265
4.253
4.229
3.811
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1.372
1.348
Br
O
O
OH
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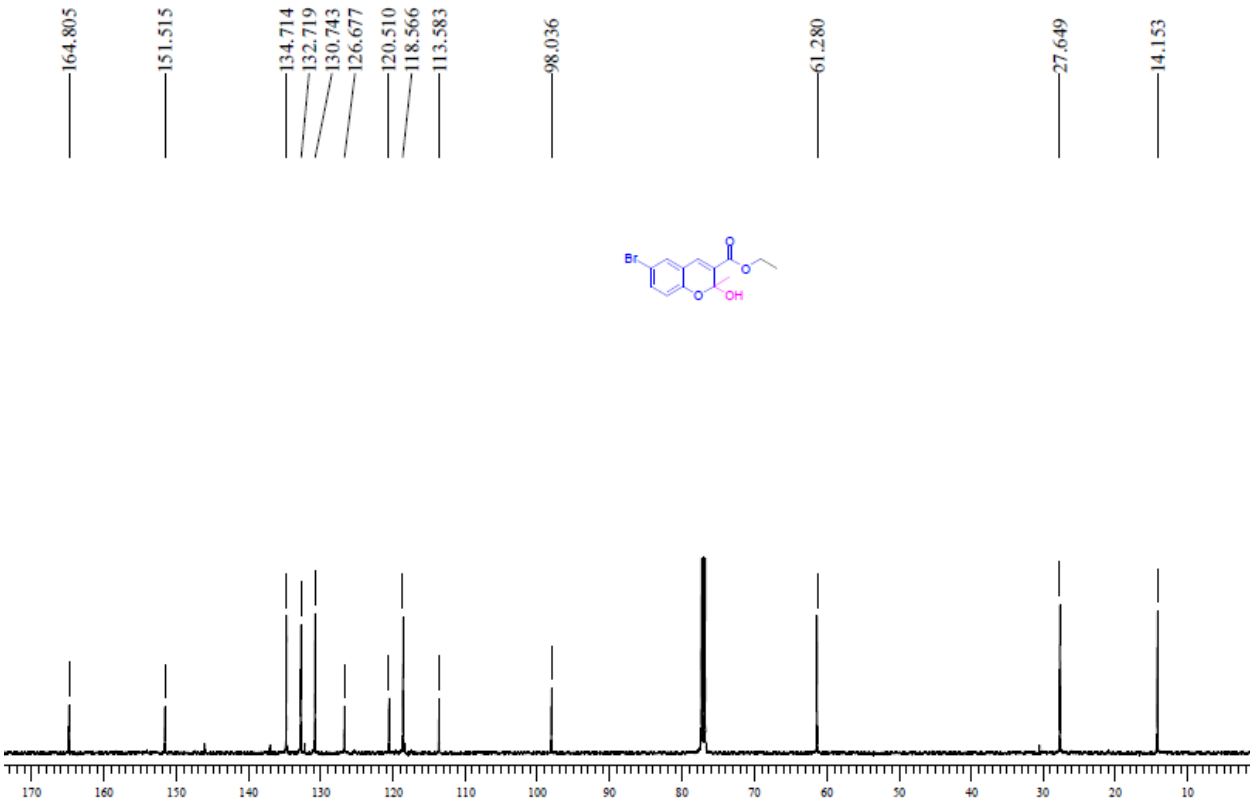
0.9
3.1
3.0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134.714
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126.677
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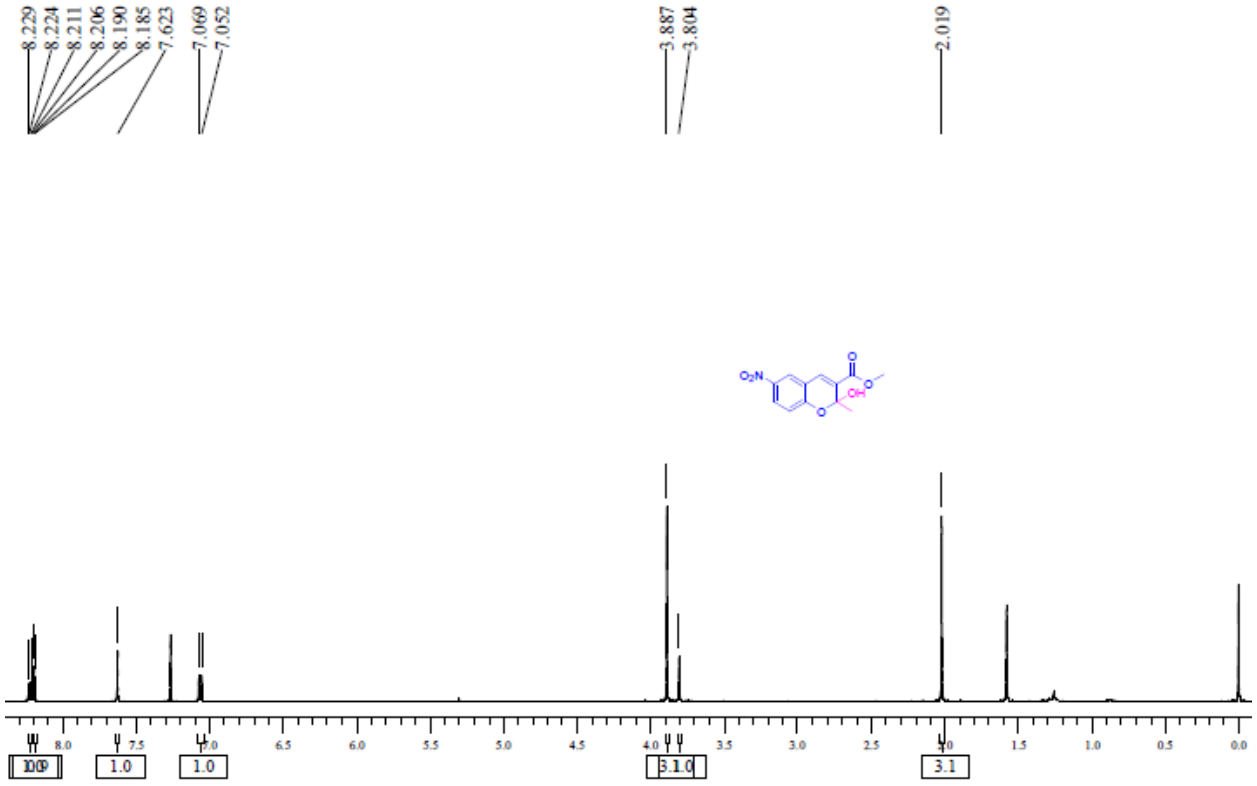
118.566
113.583
98.036
61.280
27.649
14.153
Br
O
O
OH
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10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7.069
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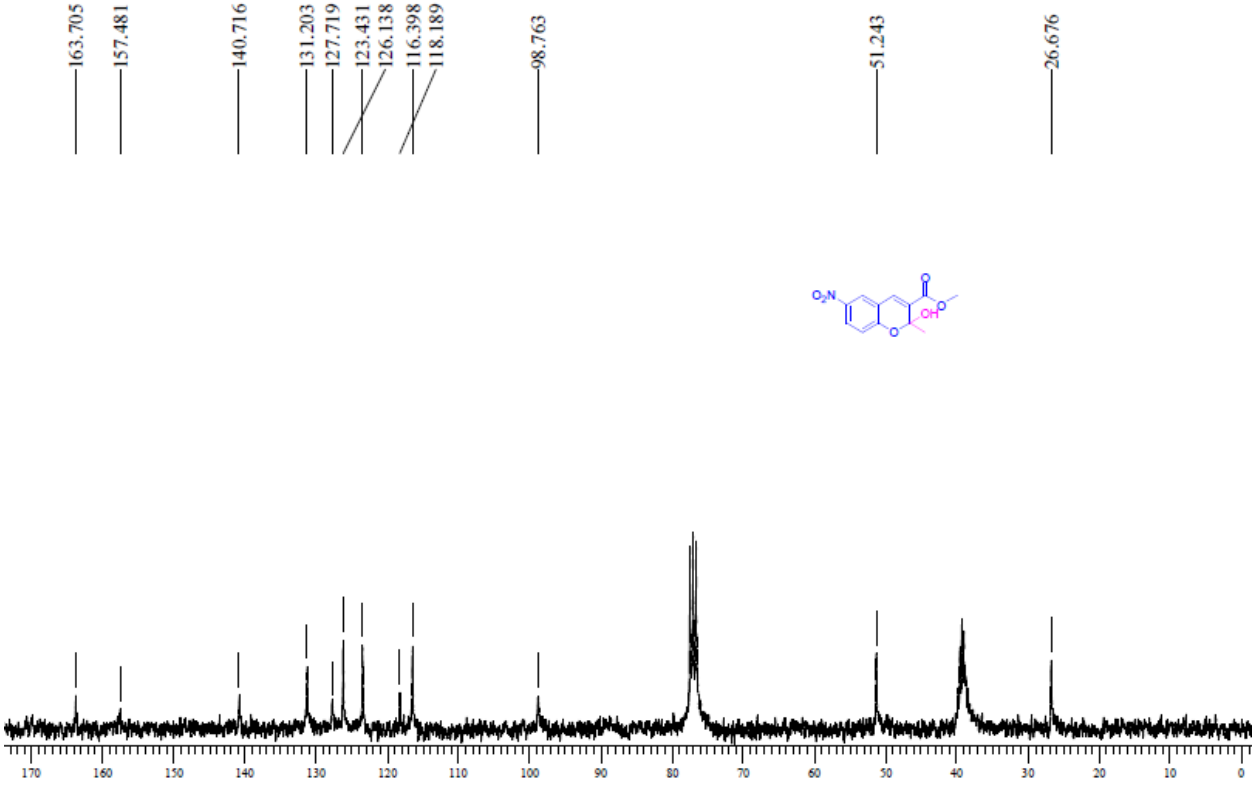
1.0
3.1
3.1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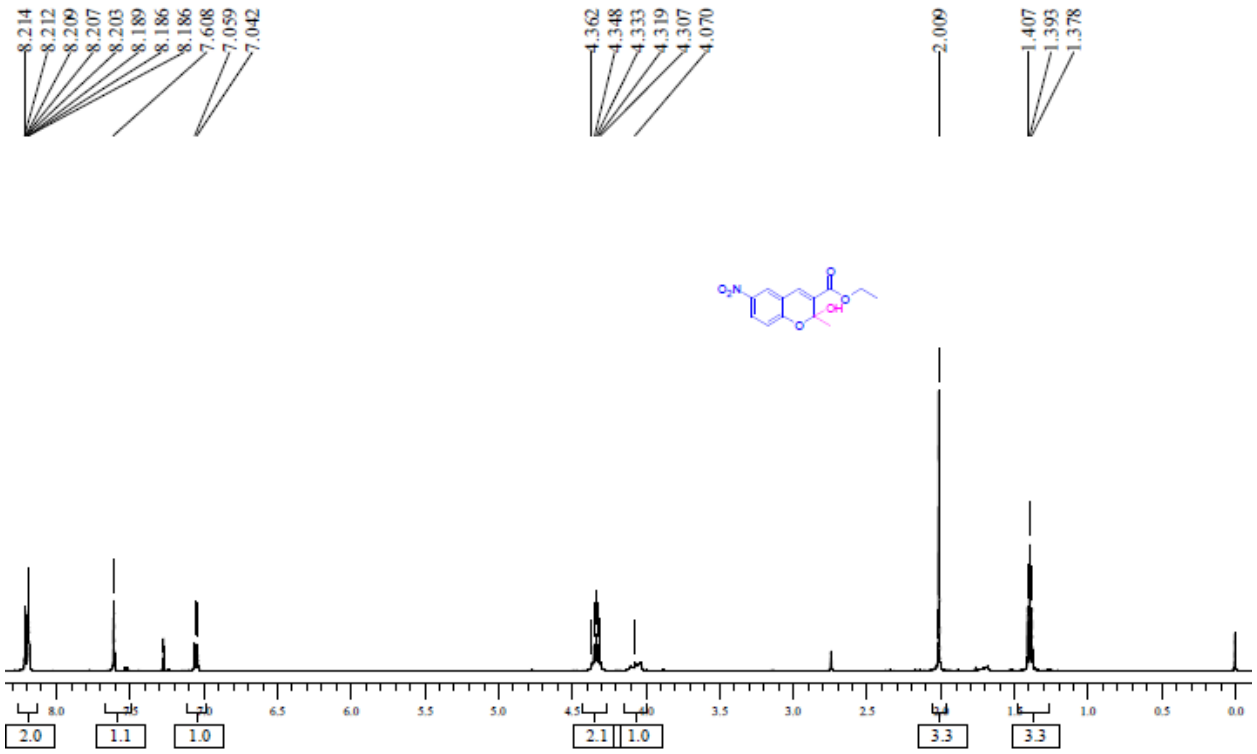
26.676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8.203
8.189
8.186
8.186
7.608
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7.042
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4.348
4.333
4.319
4.307
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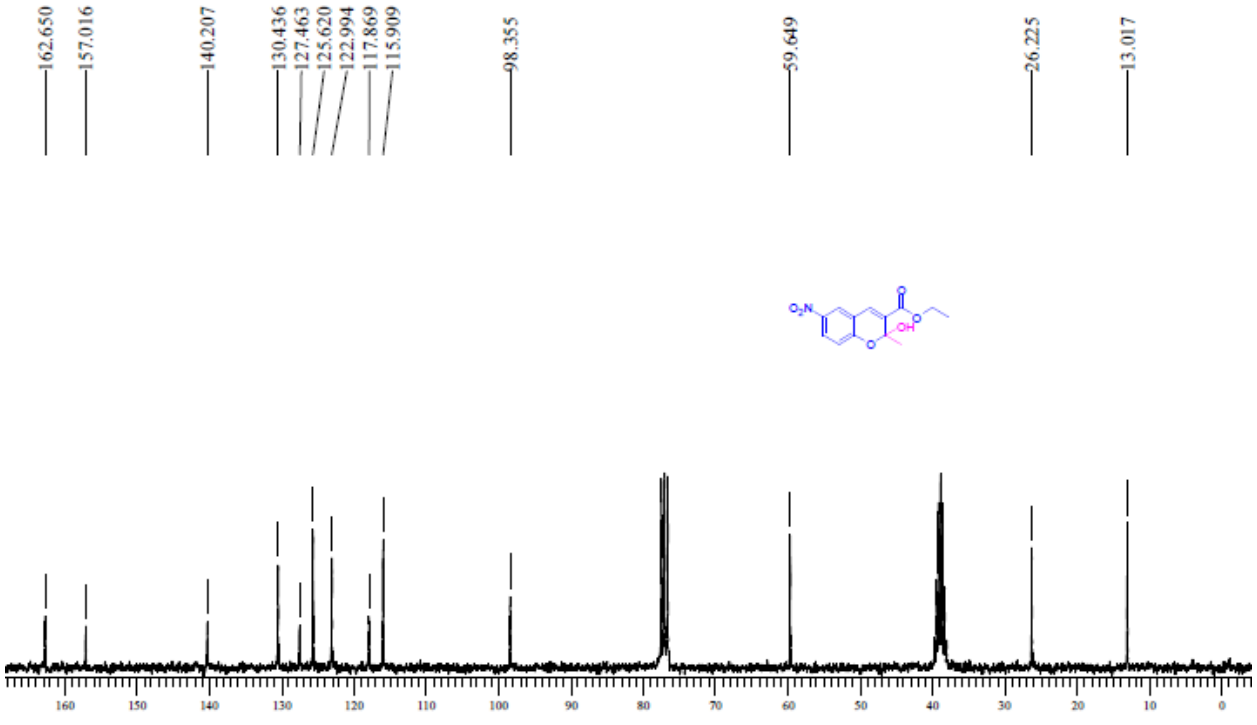
2.1
1.0
3.3
3.3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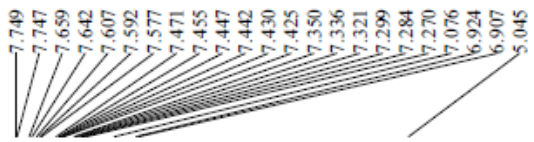
13.017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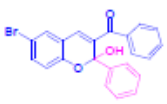
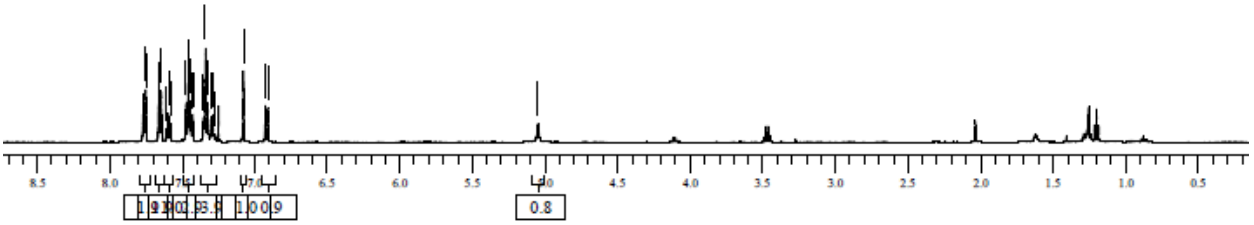
5.045


Br
O
OH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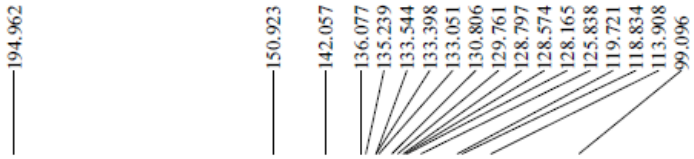
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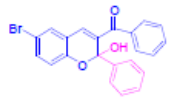
128.165
125.838
119.721
118.834
113.908
99.096


Br
O
OH