Electronic supporting information

Reinvestigation of the Reaction Between 1, 3-Diketones and 2-Hydroxyarylaldehydes: A Short, Atom-Economical Entry to Tetrahydroxanthenones

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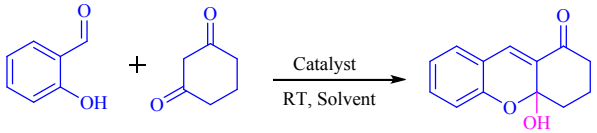
Experimental Part

General information: Salicyladehydes, *β*-diketones, DABCO 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 deuterated chloroform ($CDCl_3$) or $CDCl_3$+DMSO (deuterated dimethyl sulfoxide) (6:4) on Avance 300 or Avance 500 spectrometers. Chemical shifts (δ) are reported in parts per million (ppm) relative to residual $CHCl_3$ (^{1}H: δ 7.26 ppm, ^{13}C: 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. All signals in ^{13}C NMR spectra appeared as singlets and we have performed ^{13}C by using CPD (composite pulse decoupling) method. 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), cyclohexane 1,3-dione (1mmol), DABCO (5 mol%) THF (2 mL) were placed in a 10ml round-bottomed flask and stirred at room temperature for 2 h. After completion of the reaction (monitored by TLC), 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.

Table: Screening of different different solvents



1a **2a** **3a**

S.No	Solvent	Time (h)	Yield (%)[b]
1	H2O	12	-
2	MeOH	5	15
3	THF	2	82
4	CH3CN	5	56
5	Toluene	5	38
6	DMF	5	24
7	DCM	5	41

[a]Reaction conditions: Salicylaldehyde (1 mmol), Cyclohexane 1,3-dione (1 mmol) and DABCO (5 mol%) stirred in 2 mL solvent. [b]Isolated yield of pure product.

AT63 Crystallographic Data

Crystallographic data for 3p: $C_{19}H_{18}O_3$, M = 294.33, colourless block, 0.32 x 0.28 x 0.22 mm^3, monoclinic, space group $P2_1/c$ (No. 14), a = 11.6133(8), b = 6.8128(5), c = 20.3843(13) Å, □ β = 108.514(3)°, V = 1529.32(18) Å^3, Z = 4, D_c = 1.278 g/cm^3, F_{000} = 624, CCD area detector, MoKα radiation, □ λ = 0.71073 Å, T = 293(2)K, $2\theta_{max}$ = 50.0º, 11536 reflections collected, 2685 unique (R_{int} = 0.0233), Final *GooF* = 1.056, *R1* = 0.0535, *wR2* = 0.1274, *R* indices based on 2392 reflections with I >2σ(I) (refinement on F^2), 205 parameters, μ = 0.086 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 1032788. The data can be obtained free of charge from http://www.ccdc.cam.ac.uk/Community/Requestastructure/Pages/DataRequest.aspx 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

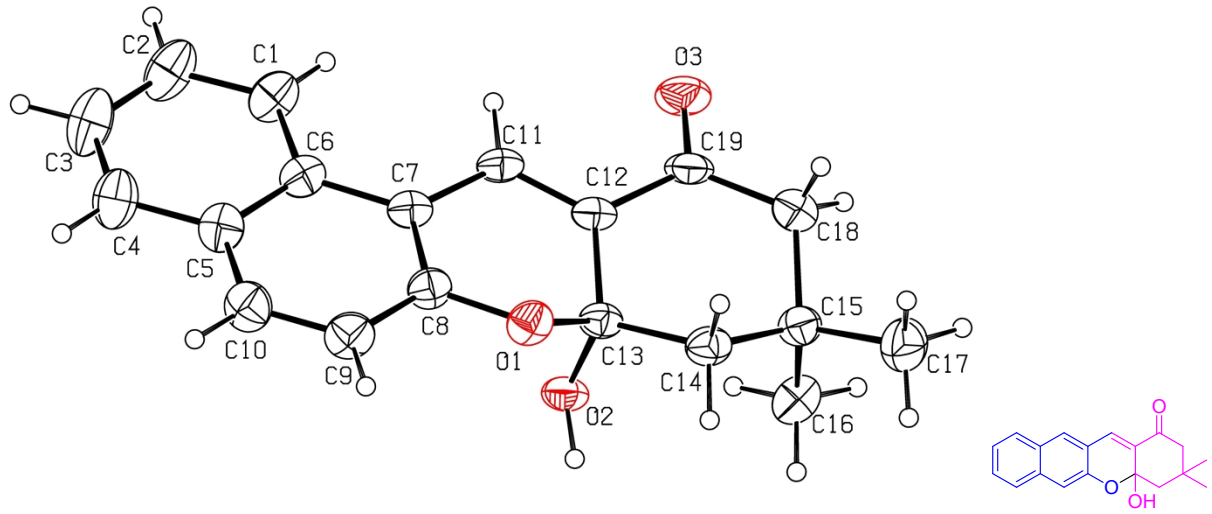
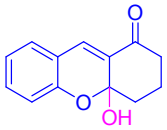


Figure caption: The ORTEP diagram of compound **3p** with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radius.

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 3771 reflections for AT63 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. All 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.

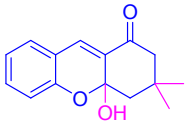
1. SMART & SAINT. Software Reference manuals. Versions 6.28a & 5.625, Bruker Analytical X-ray Systems Inc., Madison, Wisconsin, U.S.A., 2001.
2. Sheldrick, G. M. SHELXS97 and SHELXL97, Programs for crystal structure solution and refinement; University of Gottingen: Germany, 1997.

4a-hydroxy-2,3,4,4a-tetrahydro-1*H*-xanthen-1-one (table 2, 3a):



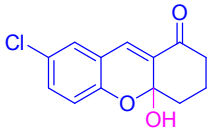
White solid; Mp 155-157 ^{o}C; IR: ν_{max} 3243, 2956, 2927, 1627, 1604, 1561, 1454, 1294, 1172, 979, 842, 761 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$+DMSO): δ 7.47 (s,1 H), 7.28-7.37 (m, 2 H), 6.97-7.07 (m, 2 H), 6.34 (s, 1 H), 2.43-2.68 (m, 2 H), 2.28-2.42 (m, 1 H), 2.07-2.23 (m, 2 H), 1.91-2.04 (m, 1 H), ^{13}C NMR (75 MHz, $CDCl_3$+DMSO): δ 197.2, 152.7, 130.9, 130.5, 128.9, 128.6, 120.9, 119.7, 116.2, 95.9, 38.3, 35.4, 17.5; m/z (ESI); 199 $[M\text{-}H_2O]H^+$.

4a-hydroxy-3,3-dimethyl-2,3,4,4a-tetrahydro-1*H*-xanthen-1-one (table 2, 3b):



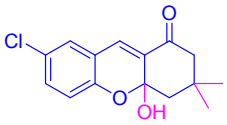
White solid; Mp 128-130 ^{o}C; IR: ν_{max} 3246, 2958, 2915, 1624, 1609, 1559, 1457, 1293, 1165, 968, 844, 768 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$+DMSO): δ 7.43 (s, 1 H), 7.27-7.39 (m, 2 H), 6.96-7.04 (m, 2 H), 6.38 (s, 1 H), 2.87 (s, 3 H), 2.37-2.60 (m, 2 H), 2.19-2.31 (m, 2 H), 1.18 (s, 3 H), 1.10 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$+DMSO): δ 198.0, 152.7, 131.3, 129.6, 129.4, 129.0, 121.3, 120.1, 116.7, 96.3, 52.3, 48.7, 31.3, 30.2, 27.9; m/z (ESI); 227 $[M\text{-}H_2O]H^+$. HRMS calcd for $C_{15}H_{15}O_2$: 227.10666, found: 227.10576.

7-chloro-4a-hydroxy-2,3,4,4a-tetrahydro-1*H*-xanthen-1-one (table 2, 3c):



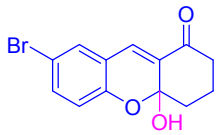
White solid; Mp 168-170 ^{o}C; IR: ν_{max} 3346, 2959, 1720, 1670, 1607, 1547, 1469, 1390, 1259, 1133, 1059, 931, 819 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$+DMSO): δ 7.46 (d, J = 2.3 Hz, 1 H), 7.39 (dd, J_1 = 2.3 Hz, J_2 = 8.7 Hz, 1 H), 6.91 (d, J = 8.69 Hz, 1 H), 6.63 (s, 1 H), 2.89 (s, 1 H), 2.56-2.69 (m, 1 H), 2.27-2.54 (m, 2 H), 1.92-2.24 (m, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$+DMSO): δ 196.5, 151.4, 131.2, 130.5, 126.7, 121.4, 117.8, 112.3, 95.8, 38.0, 34.9, 17.2; m/z (ESI); 233 $[M\text{-}H_2O]H^+$. HRMS calcd for $C_{13}H_{10}O_2Cl$: 233.03638, found: 233.03538.

7-chloro-4a-hydroxy-3,3-dimethyl-2,3,4,4a-tetrahydro-1*H*-xanthen-1-one (table 2, 3d):



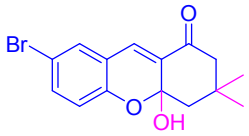
White solid; Mp 131-133 ^{o}C; IR: ν_{max} 3337, 2943, 1717, 1664, 1507, 1445, 1383, 1261, 1147, 1052, 928, 814 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$+DMSO): δ 7.41 (s, 1 H), 7.34 (d, J = 1.9 Hz, 1 H), 7.30 (dd, J_1 = 2.4 Hz, J_2 = 8.7 Hz, 1 H), 6.99 (d, J = 8.7 Hz, 1 H), 2.99 (s, 1 H), 2.49-2.54 (m, 1 H), 2.28-2.37 (m, 3 H), 1.18 (s, 3 H), 1.12 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$+DMSO): δ 197.1, 150.8, 130.3, 130.1, 127.7, 126.8, 125.1, 121.1, 90.0, 51.9, 47.9, 30.8, 29.7, 27.1; m/z (ESI); 261 $[M\text{-}H_2O]H^+$. HRMS $C_{15}H_{15}O_2Cl$: found: 261.08969.

7-bromo-4a-hydroxy-2,3,4,4a-tetrahydro-1*H*-xanthen-1-one (table 2, 3e):



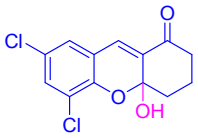
White solid; Mp 172-174 ^{o}C; IR: ν_{max} 3261, 2976, 2943, 1658, 1605, 1547, 1463, 1284, 1190, 1011, 928, 813 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$+DMSO): δ 7.45 (s, 1 H), 7.34 (d, J = 2.6 Hz, 1 H), 7.30 (dd, J_1 = 2.4 Hz, J_2 = 8.7 Hz, 1 H), 6.99 (d, J = 8.7 Hz, 1 H), 2.97 (s, 1 H), 2.49-2.54 (m, 1 H), 2.67-2.73 (m, 1 H), 2.32-2.42 (m, 1 H), 2.10-2.26 (m, 2 H), 1.99-2.05 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$+DMSO): δ 196.6, 151.4, 132.9, 131.1, 130.5, 126.8, 121.3, 117.9, 112.3, 95.8, 38.0, 34.9, 17.2; m/z (ESI); 277 [M-H_2O]H^+.

7-bromo-4a-hydroxy-3,3-dimethyl-2,3,4,4a-tetrahydro-1*H*-xanthen-1-one (table 2, 3f):



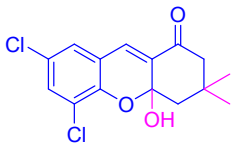
White solid; Mp 135-137 ^{o}C; IR: ν_{max} 3257, 2980, 2953, 1660, 1602, 1549, 1466, 1282, 1189, 1000, 914, 817 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$+DMSO): δ 7.49 (d, J = 2.3 Hz, 1 H), 7.30 (dd, J_1 = 2.4 Hz, J_2 = 8.7 Hz, 1 H), 6.93 (d, J = 8.4 Hz, 1 H), 3.00 (s, 1 H), 2.49-2.54 (m, 1 H), 2.28-2.37 (m, 3 H), 1.18 (s, 3 H), 1.12 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$+ $CDCl_3$+DMSO): δ 197.1, 150.8, 130.3, 130.1, 127.7, 126.8, 125.1, 121.1, 90.0, 51.9, 47.9, 30.8, 29.7, 27.1; m/z (ESI); 305 [M-H_2O]H^+. HRMS calcd for $C_{15}H_{14}O_2Br$: 305.01717, found: 305.01588.

5,7-dichloro-4a-hydroxy-2,3,4,4a-tetrahydro-1*H*-xanthen-1-one (table 2, 3g):



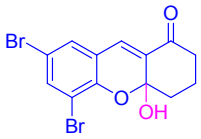
White solid; Mp 170-172 ^{o}C; IR: ν_{max} 3311, 2974, 2952, 2919, 1664, 1601, 1558, 1448, 1339, 1207, 1189, 1026, 984, 763 cm^{-1}; ^{1}H NMR (300 MHz $CDCl_3$+DMSO): δ 7.42 (s, 1 H), 7.40 (d, J = 2.4 Hz, 1 H), 7.26 (d, J = 2.4 Hz, 1 H), 3.15 (s, 1 H), 2.68-2.74 (m, 1 H), 2.53-2.58 (m, 1 H), 2.27-2.43 (m, 2 H), 2.02-2.19 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$+DMSO): δ 196.9, 147.4, 132.2, 130.4, 126.9, 125.4, 122.2, 122.1, 97.2, 38.5, 35.3, 17.6; m/z (ESI); 267 [M-H_2O]H^+.

5,7-dichloro-4a-hydroxy-3,3-dimethyl-2,3,4,4a-tetrahydro-1*H*-xanthen-1-one (table 2, 3h):



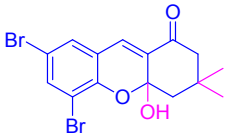
White solid; Mp 144-146 ^{o}C; IR: ν_{max} 3305, 2972, 2955, 2923, 1660, 1605, 1561, 1456, 1344, 1211, 1186, 1018, 998, 756 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$+DMSO): δ 7.40 (d, J = 2.4 Hz, 1 H), 7.38 (s, 1 H), 7.26 (d, J = 2.4 Hz, 1 H), 3.18 (s, 1 H), 2.50-2.55 (m, 1 H), 2.39-2.46 (m, 2 H), 2.28-2.33 (m, 1 H), 1.19 (s, 3 H), 1.13 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$+DMSO): δ 197.3, 147.2, 131.2, 130.3, 126.7, 125.3, 122.4, 122.1, 97.2, 52.2, 47.9, 31.1, 30.1, 27.2; m/z (ESI); 295 [M-H_2O]H^+. HRMS for $C_{15}H_{14}O_2Cl_2$: 295.02727.

5,7-dibromo-4a-hydroxy-2,3,4,4a-tetrahydro-1*H*-xanthen-1-one (table 2, 3i):



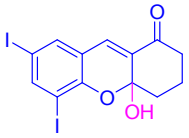
White solid; Mp 158-160 °C; IR: v_{max} 3308, 3143, 2956, 2887, 1681, 1594, 1540, 1429, 1265, 1193, 985, 858 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$+DMSO): δ 7.65 (d, *J* = 2.1 Hz, 1 H), 7.50 (s, 1 H), 7.44 (d, *J* = 2.3 Hz, 1 H), 6.92 (d, *J* = 0.9 Hz, 1 H), 2.56-2.71 (m, 2 H), 1.94-2.44 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$+DMSO): δ 196.6, 148.7, 135.5, 132.0, 130.1, 126.5, 125.5, 112.4, 111.0, 97.1, 38.3, 35.0, 17.3; m/z (ESI); 355 $[M-H_2O]H^+$. HRMS calcd for $C_{13}H_9O_2Br_2$: 354.89638, found: 354.89503.

5,7-dibromo-4a-hydroxy-3,3-dimethyl-2,3,4,4a-tetrahydro-1*H*-xanthen-1-one (table 2, 3j):



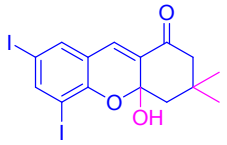
White solid; Mp 151-154 °C; IR: v_{max} 3311, 3150, 2961, 2882, 1685, 1598, 1539, 1439, 1276, 1200, 1156, 978, 947, 864 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$+DMSO): δ 7.70 (d, *J* = 2.3 Hz, 1 H), 7.45 (d, *J* = 2.3 Hz, 1 H), 7.37 (s, 1 H), 3.04 (s, 1 H), 2.27-2.59 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$+DMSO): δ 195.4, 147.0, 133.7, 129.8, 129.6, 129.1, 124.7, 121.7, 110.7, 109.4, 95.8, 50.5, 45.8, 29.4, 28.5, 25.4; m/z (ESI); 384 $[M-H_2O]H^+$. HRMS calcd for $C_{15}H_{13}O_2Br_2$: 382.92768, found: 382.92612.

4a-hydroxy-5,7-diiodo-2,3,4,4a-tetrahydro-1*H*-xanthen-1-one (table 2, 3k):



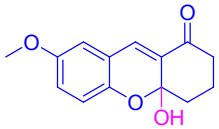
White solid; Mp 174-176 °C; IR: v_{max} 3229, 2950, 2867, 1666, 1609, 1525, 1434, 1317, 1282, 1155, 1098, 981, 856 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$+DMSO): δ 8.00 (s, 1 H), 7.62 (s, 1 H), 6.95 (s, 1 H), 2.51-2.68 (m, 2 H), 1.88-2.44 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$+DMSO): δ 196.5, 151.8, 146.5, 136.8, 131.8, 126.3, 122.3, 97.3, 85.9, 83.1, 38.2, 34.9, 17.3; m/z (ESI); 451 $[M-H_2O]H^+$. HRMS calcd for $C_{13}H_9O_2I_2$: 450.86864, found: 450.86643.

4a-hydroxy-5,7-diiodo-3,3-dimethyl-2,3,4,4a-tetrahydro-1*H*-xanthen-1-one (table 2, 3l):



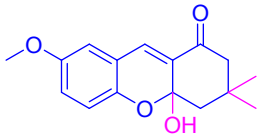
White solid; Mp 146-148 °C; IR: v_{max} 3234, 2946, 2863, 1662, 1605, 1529, 1428, 1314, 1278, 1158, 1094, 983, 850 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$+DMSO): δ 8.00 (s, 1 H), 7.63 (s, 1 H), 6.93 (s, 1 H), 3.04 (s, 1 H), 2.40-2.61 (m, 2 H), 2.22-2.34 (m, 2 H), 1.17 (s, 3 H), 1.11 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$+DMSO): δ 196.8, 151.6, 146.4, 136.8, 130.7, 122.5, 97.3, 85.9, 83.0, 52.0, 47.7, 30.9, 29.9, 27.0; m/z (ESI); 479 $[M-H_2O]H^+$. HRMS calcd for $C_{15}H_{13}O_2I_2$: 478.89754, found: 478.89719.

4a-hydroxy-7-methoxy-2,3,4,4a-tetrahydro-1*H*-xanthen-1-one (table 2, 3m):



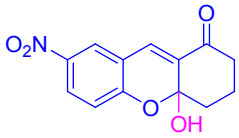
White solid; Mp 128-130 °C; IR: ν_{max} 3305, 3011, 2938, 1669, 1610, 1564, 1487, 1239, 1171, 1059, 980, 865 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.43 (d, *J* = 2.3 Hz, 1 H), 6.82-6.99 (m, 2 H), 6.02-6.09 (m, 1 H), 3.80 (s, 3 H), 1.83-2.64 (m, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 197.2, 153.5, 146.9, 131.5, 128.4, 120.5, 117.9, 117.1, 113.1, 96.1, 55.4, 38.4, 35.4, 17.8; m/z (ESI); 229 $[M\text{-}H_2O]H^+$. HRMS for $C_{13}H_{13}O_3$: found: 229.08490.

4a-hydroxy-7-methoxy-3,3-dimethyl-2,3,4,4a-tetrahydro-1*H*-xanthen-1-one (table 2, 3n):



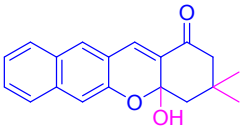
White solid; Mp 132-134 °C; IR: ν_{max} 3311, 3005, 2941, 1672, 1607, 1573, 1484, 1246, 1178, 1049, 977, 862 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$+DMSO): δ 7.44 (s, 1 H), 6.92-6.99 (m, 2 H), 6.85 (d, *J* = 2.9 Hz, 1 H), 3.79 (s, 3 H), 3.09 (s, 1 H), 2.47-2.52 (m, 1 H), 2.26-2.37 (m, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$+DMSO): δ 198.1, 154.4, 146.4, 130.0, 129.7, 120.1, 119.1, 118.2, 112.7, 96.4, 55.7, 52.5, 48.8, 30.6, 28.0; m/z (ESI); 257 $[M\text{-}H_2O]H^+$. HRMS calcd for $C_{16}H_{17}O3$: 257.11482, found: 257.11599.

4a-hydroxy-7-nitro-2,3,4,4a-tetrahydro-1*H*-xanthen-1-one (table 2, 3o):



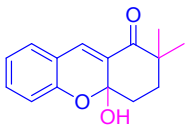
White solid; Mp 164-166 °C; IR: ν_{max} 3396, 3092, 2949, 2879, 1674, 1605, 1569, 1529, 1346, 1271, 1210, 1161, 974, 841 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$+DMSO): δ 8.28 (d, *J* = 2.8 Hz, 1 H), 8.19 (dd, J_1 = 2.6 Hz, J_2 = 8.9 Hz, 1 H), 7.47 (s, 1 H), 7.10-7.15 (m, 2 H), 2.51-2.73 (m, 2 H), 2.32-2.47 (m, 1 H), 1.95-2.27 (m, 3 H), 3.00 (s, 1H), 2.49-2.54 (m, 1H), 2.28-2.37 (m, 3H), 1.18 (s, 3H), 1.12 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$+DMSO): δ 196.7, 157.7, 141.3, 132.3, 126.6, 125.8, 124.4, 119.8, 117.0, 97.5, 38.4, 35.2, 17.5; m/z (ESI); 244 $[M\text{-}H_2O]H^+$.

4a-hydroxy-3,3-dimethyl-2,3,4,4a-tetrahydro-1*H*-benzo[b]xanthen-1-one (table 2, 3p):



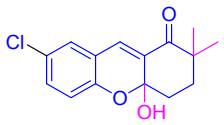
White solid; Mp 124-126 °C; IR: ν_{max} 3280, 2966, 2929, 1628, 1576, 1476, 1373, 1289, 1242, 964, 823 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$+DMSO): δ 8.26 (s, 1 H), 8.16 (d, *J* = 8.5 Hz, 1 H), 7.77-7.88 (m, 2 H), 7.55-7.63 (m, 1 H), 7.41-7.48 (m, 1 H), 7.21-7.28 (m, 1 H), 3.20 (s, 1 H), 2.28-2.57 (m, 4 H), 1.21 (s, 3 H), 1.13 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$+DMSO): δ 197.2, 151.5, 131.6, 128.4, 127.9, 127.1, 126.8, 124.7, 123.6, 120.9, 117.6, 113.0, 96.1, 51.9, 48.2, 30.8, 29.9, 27.3; m/z (ESI); 277 $[M\text{-}H_2O]H^+$. HRMS calcd for $C_{19}H_{18}O_3Na$: 317.11482, found: 317.11330.

4a-hydroxy-2,2-dimethyl-2,3,4,4a-tetrahydro-1*H*-xanthen-1-one (table 4, 4a):



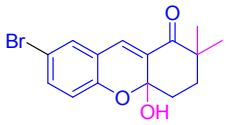
White solid; Mp 133-135 °C; IR: ν_{max} 3237, 2948, 2913, 1625, 1611, 1546, 1462, 1284, 1179, 963, 851, 764 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$+DMSO): δ 7.42 (s, 1 H), 7.27-7.37 (m, 2 H), 6.96-7.03 (m, 2 H), 6.59 (d, *J* = 3.4 Hz, 1 H), 2.57-2.61 (m, 1 H), 2.34-2.38 (m, 1 H), 2.02-2.15 (m, 1 H), 1.63-1.73 (m, 1 H), 1.19 (s, 3 H), 1.12 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$+DMSO): δ 202.2, 152.4, 130.8, 129.6, 129.3, 128.7, 120.9, 119.7, 116.1, 95.8, 42.1, 32.3, 32.1, 25.0, 24.9; m/z (ESI); 227 $[M\text{-}H_2O]H^+$. HRMS calcd for $C_{15}H_{15}O_2$: 227.10666, found: 227.10563.

7-chloro-4a-hydroxy-2,2-dimethyl-2,3,4,4a-tetrahydro-1*H*-xanthen-1-one (table 4, 4b):



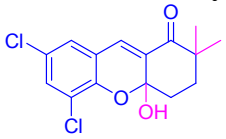
White solid; Mp 161-163 ^{o}C; IR: ν_{max} 3311, 3056, 2964, 2938, 2861, 1663, 1624, 1559, 1455, 1387, 1180, 1050, 930, 818, 750 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$+DMSO): δ 7.34 (s, 1 H), 7.32 (d, J = 2.5 Hz, 2 H), 7.25 (dd, J_1 = 2.5 Hz, J_2 = 8.69 Hz, 1 H), 6.95 (d, J = 8.69 Hz, 2 H), 6.67 (s, 1 H), 2.24-2.40 (m, 2 H), 2.01-2.13 (m, 1 H), 1.63-1.73 (m, 1 H), 1.19 (s, 3 H), 1.12 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$+DMSO): δ 201.4, 150.5, 130.3, 127.3, 127.2, 124.7, 120.7, 117.1, 95.7, 41.7, 31.7, 31.4, 24.4; m/z (ESI); 261 [M-H_2O]H^{+}. HRMS for $C_{15}H_{15}O_2Cl$: found: 261.08969.

7-bromo-4a-hydroxy-2,2-dimethyl-2,3,4,4a-tetrahydro-1*H*-xanthen-1-one (table 4, 4c):



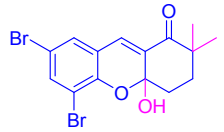
White solid; Mp 155-157 ^{o}C; IR: ν_{max} 3269, 2968, 2924, 2861, 1673, 1620, 1556, 1472, 1245, 1152, 1048, 943, 816 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$+DMSO): δ 7.47 (d, J = 2.5 Hz, 1 H), 7.38 (dd, J_1 = 2.5 Hz, J_2 = 8.7 Hz, 1 H), 7.33 (s, 1 H), 6.91 (d, J = 2.5 Hz, 1 H), 6.74 (s, 1 H), 2.29-2.37 (m, 2 H), 2.00-2.13 (m, 1 H), 1.63-1.73 (m, 1 H), 1.19(s, 3 H), 1.12 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$+DMSO): δ 201.9, 151.3, 132.9, 130.5, 127.7, 121.6, 117.9, 112.5, 96.1, 42.1, 32.1, 31.8, 24.8; m/z (ESI); 305 [M-H_2O]H^{+}. HRMS calcd for $C_{15}H_{14}O_2Br$: 305.01717, found: 305.01565.

5,7-dichloro-4a-hydroxy-2,2-dimethyl-2,3,4,4a-tetrahydro-1*H*-xanthen-1-one (table 4, 4d):



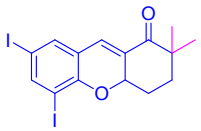
White solid; Mp 137-139 ^{o}C; IR: ν_{max} 3312, 2978, 2946, 2924, 1659, 1607, 1562, 1445, 1333, 1226, 1191, 1012, 988, 751 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.01 (d, J = 8.3 Hz, 1 H), 7.60 (d, J = 8.3 Hz, 1 H), 6.64 (s, 1 H), 2.41-2.61 (m, 2 H), 1.99-2.16 (m, 1 H), 1.65-1.77 (m, 1 H), 1.20 (s, 3 H), 1.12 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 202.3, 147.1, 131.6, 131.5, 129.5, 129.1, 127.3, 127.2, 97.5, 43.1, 32.7, 25.3, 25.2; m/z (ESI); 295 [M-H_2O]H^{+}. HRMS calcd for $C_{15}H_{13}O_2Cl_2$: 295.02871, found: 295.02727.

5,7-dibromo-4a-hydroxy-2,2-dimethyl-2,3,4,4a-tetrahydro-1*H*-xanthen-1-one (table 4, 4e):



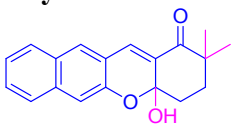
White solid; Mp 144-146 ^{o}C; IR: ν_{max} 165-167^{o} C; IR: ν_{max} 3317, 3148, 2953, 2874, 1687, 1589, 1536, 1433, 1264, 1187, 1151, 945, 861 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$+DMSO): δ 7.65 (s, 1 H), 7.42 (s, 1 H), 7.32 (s, 1 H), 6.73 (s, 1 H), 2.48-2.62 (m, 2 H), 2.01-2.18 (m, 1 H), 1.64-1.76 (m, 1 H), 1.20 (s, 3 H), 1.12 (s, 3 H); m/z (ESI); 383 [M-H_2O]H^{+}.

4a-hydroxy-5,7-diiodo-2,2-dimethyl-2,3,4,4a-tetrahydro-1*H*-xanthen-1-one (table 4, 4f):



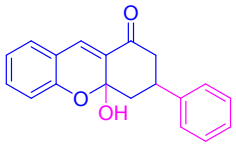
White solid; Mp 163-165 °C; IR: ν_{max} 3237, 2951, 2864, 1668, 1609, 1523, 1422, 1315, 1282, 1156, 1098, 981, 855 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$+DMSO): δ 7.35-7.39 (m, 1 H), 7.31-7.35 (m, 2 H), 7.09 (s, 1 H), 2.29-2.56 (m, 2 H), 1.94-2.12 (m, 1 H), 1.65-1.76 (m, 1 H), 1.18 (s, 3 H), 1.11 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$+DMSO): δ 201.8, 147.0, 131.4, 129.9, 127.3, 126.4, 125.1, 122.1, 121.8, 97.1, 42.3, 32.1, 31.8, 24.8, 24.7; m/z (ESI); 479 $[M-H_2O]H^+$.

4a-hydroxy-2,2-dimethyl-2,3,4,4a-tetrahydro-1*H*-benzo[b]xanthen-1-one (table 4, 4g):



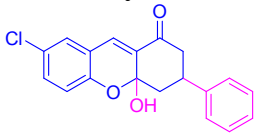
White solid; Mp 161-163 °C; IR: ν_{max} 3280, 2966, 2929, 1628, 1576, 1476, 1373, 1289, 1123, 964, 823 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$+DMSO): δ 8.23 (s, 1 H), 8.16 (d, *J* = 1.7 Hz, 1 H), 7.77-7.86 (m, 2 H), 7.53-7.61 (m, 1 H), 7.38-7.45 (m, 1 H), 7.23 (d, *J* = 1.7 Hz, 1 H), 6.59 (s, 1 H), 2.55-2.60 (m, 1 H), 2.41-2.46 (m, 1 H), 2.08-2.20 (m, 1 H), 1-68-1.76 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$+DMSO): δ 202.2, 151.7, 131.7, 130.5, 128.6, 128.1, 127.4, 126.9, 125.7, 123.7, 120.9, 117.7, 112.9, 96.2, 42.0, 32.4, 32.1, 25.2; m/z (ESI); 277 $[M-H_2O]H^+$.

4a-hydroxy-3-phenyl-2,3,4,4a-tetrahydro-1*H*-xanthen-1-one (table 5, 5a):



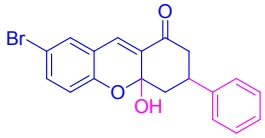
White solid; Mp 146-148 °C; IR: ν_{max} 3389, 3030, 2922, 2852, 1669, 1604, 1558, 1453, 1297, 1261, 1200, 1163, 1094, 970, 765 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$+DMSO): δ 7.56 (s, 1 H), 7.20-7.44 (s, 7 H), 6.99-7.08 (m, 2 H), 3.72 (s, 1 H), 3.44-3.59 (m, 1 H), 2.77-2.90 (m, 1 H), 2.62-2.74 (m, 1 H), 2.40-2.57 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$+DMSO): δ 196.3, 152.8, 142.8, 131.2, 129.6, 129.1, 128.2, 126.1, 121.2, 119.8, 116.4, 95.7, 46.4, 42.6, 35.4; m/z (ESI); 275 $[M-H_2O]H^+$. HRMS for $C_{19}H_{15}O_2$: found: 275.10542.

7-chloro-4a-hydroxy-3-phenyl-2,3,4,4a-tetrahydro-1*H*-xanthen-1-one (table 5, 5b):



White solid; Mp 159-161 °C; IR: ν_{max} 3390, 3030, 2929, 1675, 1617, 1555, 1470, 1283, 1200, 1162, 1081, 967, 824 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$+DMSO): δ 7.50 (s, 1H), 7.22-7.46 (m, 7 H), 3.46-3.60 (m, 1 H), 3.38 (s, 1 H), 2.83-3.03 (m, 1 H), 2.43-2.73 (m, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$+DMSO): δ 195.6, 150.9, 142.3, 130.3, 130.2, 127.8, 127.7, 127.2, 125.8, 125.2, 120.8, 117.5, 95.6, 46.0, 42.1, 34.9; m/z (ESI); 309 $[M-H_2O]H^+$. HRMS for $C_{19}H_{14}O_2Cl$: found: 309.06605.

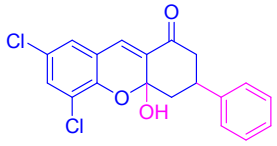
7-bromo-4a-hydroxy-3-phenyl-2,3,4,4a-tetrahydro-1*H*-xanthen-1-one (table 5, 5c):



White solid; Mp 154-156 °C; IR: ν_{max} 3384, 3036, 2937, 1683, 1613, 1552, 1466, 1278, 1201, 1167, 1078, 965, 826 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$+DMSO): δ 7.50 (d, *J* = 2.1 Hz, 1 H), 7.43 (s, 1 H), 7.32-7.41 (m, 2 H), 7.22-7.29

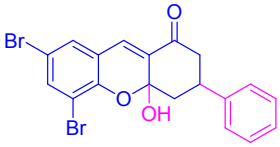
(m, 2 H), 6.98 (s, 1 H), 6.93 (d, J = 8.3 Hz, 1 H), 3.45-3.59 (m, 1 H), 2.95 (s, 1 H), 2.78-2.89 (m, 1 H), 2.65-2.74 (m, 1 H), 2.37-2.61 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$+DMSO): δ 196.2, 151.8, 142.7, 136.6, 131.1, 130.6, 128.3, 127.7, 126.3, 126.2, 121.8, 118.4, 113.1, 96.0, 46.5, 42.6, 35.4; m/z (ESI); 353 $[M\text{-}H_2O]H^+$. HRMS calcd for $C_{19}H_{14}O_2Br$: 353.01717, found: 353.01595.

5,7-dichloro-4a-hydroxy-3-phenyl-2,3,4,4a-tetrahydro-1*H*-xanthen-1-one (table 5, 5d):



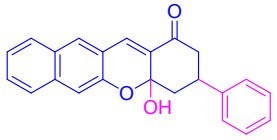
White solid; Mp 168-170 °C; IR: ν_{max} 3392, 3035, 2926, 1678, 1614, 1557, 1471, 1285, 1204, 1169, 1083, 962, 828 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$+DMSO): δ 7.50 (s, 1 H), 7.43 (d, J = 2.4 Hz, 1 H), 7.35-7.40 (m, 2 H), 7.26-7.31 (m, 4 H), 3.50-3.58 (m, 1 H), 3.11 (s, 1 H), 2.91-2.97 (m, 1 H), 2.75-2.80 (m, 1 H), 2.53-2.64 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$+DMSO): δ 195.7, 147.2, 142.3, 131.2, 130.2, 128.0, 126.9, 126.1, 126.0, 125.2, 122.0, 121.9, 96.7, 46.2, 42.3, 35.1; m/z (ESI); 343 $[M\text{-}H_2O]H^+$.

5,7-dibromo-4a-hydroxy-3-phenyl-2,3,4,4a-tetrahydro-1*H*-xanthen-1-one (table 5, 5e):



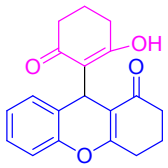
White solid; Mp 172-174 °C; IR: ν_{max} 3390, 3030, 2929, 1675, 1617, 1555, 1470, 1283, 1200, 1162, 1081, 967, 824 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$+DMSO): δ 7.53-7.72 (m, 2 H), 7.15-7.52 (m, 7 H), 2.39-2.86 (m, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$+DMSO): δ 194.7, 147.7, 141.5, 134.5, 130.3, 129.5, 127.1, 125.7, 125.2, 121.8, 111.5, 109.9, 95.9, 45.1, 41.2, 34.2; m/z (ESI); 431 $[M\text{-}H_2O]H^+$.

4a-hydroxy-3-phenyl-2,3,4,4a-tetrahydro-1*H*-benzo[b]xanthen-1-one (table 5, 5f):



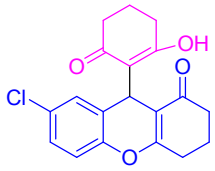
White solid; Mp 155-157 °C; IR: ν_{max} 3389, 3030, 2922, 2852, 1669, 1604, 1558, 1453, 1297, 1261, 1200, 1163, 1094, 970, 765 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.37 (s, 1 H), 8.19 (d, J = 8.3 Hz, 1 H), 7.72-7.89 (m, 2 H), 7.52-7.64 (m, 1 H), 7.22-7.49 (m, 8 H), 3.52-3.66 (m, 1 H), 3.47 (s, 1 H), 2.86-3.00 (m, 1 H), 2.66-2.81 (m, 1 H), 2.48-2.63 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.4, 152.7, 142.8, 131.2, 129.6, 129.2, 129.1, 128.2, 126.1, 121.2, 119.7, 116.4, 95.7, 46.4, 42.6, 35.4; m/z (ESI); 325 $[M\text{-}H_2O]H^+$.

9-(2-hydroxy-6-oxocyclohex-1-en-1-yl)-2,3,4,9-tetrahydro-1*H*-xanthen-1-one (table 6, 6a):



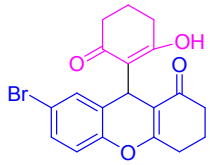
White solid; IR: ν_{max} 3150, 2920, 2880, 1640, 1570, 1550, 1485, 1440,1360, 1280, 1220, 1180, 1051, 991, 970, 905, 840 cm^{-1}; 1H NMR (300 MHz, $CDCl_3$+DMSO): 10.81 (s, 1 H), 7.01–7.20 (m, 1 H), 6.98–7.05 (m, 3 H), 4.60 (s, 1 H), 1.92–2.75 (m, 12 H); m/z (ESI); 310 $[M+H]^+$.

7-chloro-9-(2-hydroxy-6-oxocyclohex-1-en-1-yl)-2,3,4,9-tetrahydro-1*H*-xanthen-1-one (table 6, 6b):



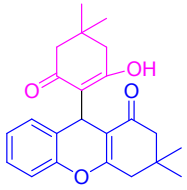
White solid; IR: v_{max} 3110, 2989, 2884, 1675, 1642, 1580, 1481, 1376, 1219, 1210, 1186, 1072, 982, 810, 764 cm^{-1}; 1H NMR (300 MHz, $CDCl_3$+DMSO): 10.56 (s, 1 H), 7.54 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1 H), 7.09 (d, J = 2.4 Hz, 1 H), 6.94 (d, J = 8.4 Hz, 1 H), 4.64 (s, 1 H), 1.84–2.82 (m, 12 H); m/z (ESI); 367 $[M+H]^+$.

7-bromo-9-(2-hydroxy-6-oxocyclohex-1-en-1-yl)-2,3,4,9-tetrahydro-1*H*-xanthen-1-one (table 6, 6c):



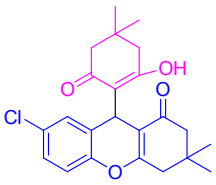
White solid; IR: v_{max} 3112, 2950, 2884, 1676, 1650, 1598, 1481, 1370, 1271, 1219, 1188, 1070, 982, 910, 820, 765 cm^{-1}; 1H NMR (300MHz, $CDCl_3$+DMSO): 10.71 (s, 1 H), 7.32 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1 H), 7.20 (d, J = 2.4 Hz, 1 H), 6.93 (d, J = 8.4 Hz, 1 H), 4.50 (s, 1 H), 1.91–2.78 (m, 12 H); m/z (ESI); 389 $[M+H]^+$.

9-(2-hydroxy-4,4-dimethyl-6-oxocyclohex-1-en-1-yl)-3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one (table 6, 6d):



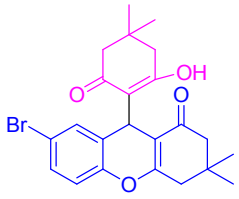
White solid; IR: v_{max} 3182, 2951, 2860, 1652, 1591, 1481, 1372, 1320, 1246, 1185, 1140, 1013, 985, 810, 756 cm^{-1}; 1H NMR (300MHz, $CDCl_3$+DMSO): 10.40 (s, 1 H), 6.98–7.22 (m, 4 H), 4.62 (s, 1 H), 1.96–2.72 (m, 8 H), 1.12 (s, 3 H), 1.04 (s, 6 H), 1.01 (s, 3 H); m/z (ESI); 366 $[M+H]^+$.

7-chloro-9-(2-hydroxy-4,4-dimethyl-6-oxocyclohex-1-en-1-yl)-3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one (table 6, 6e):



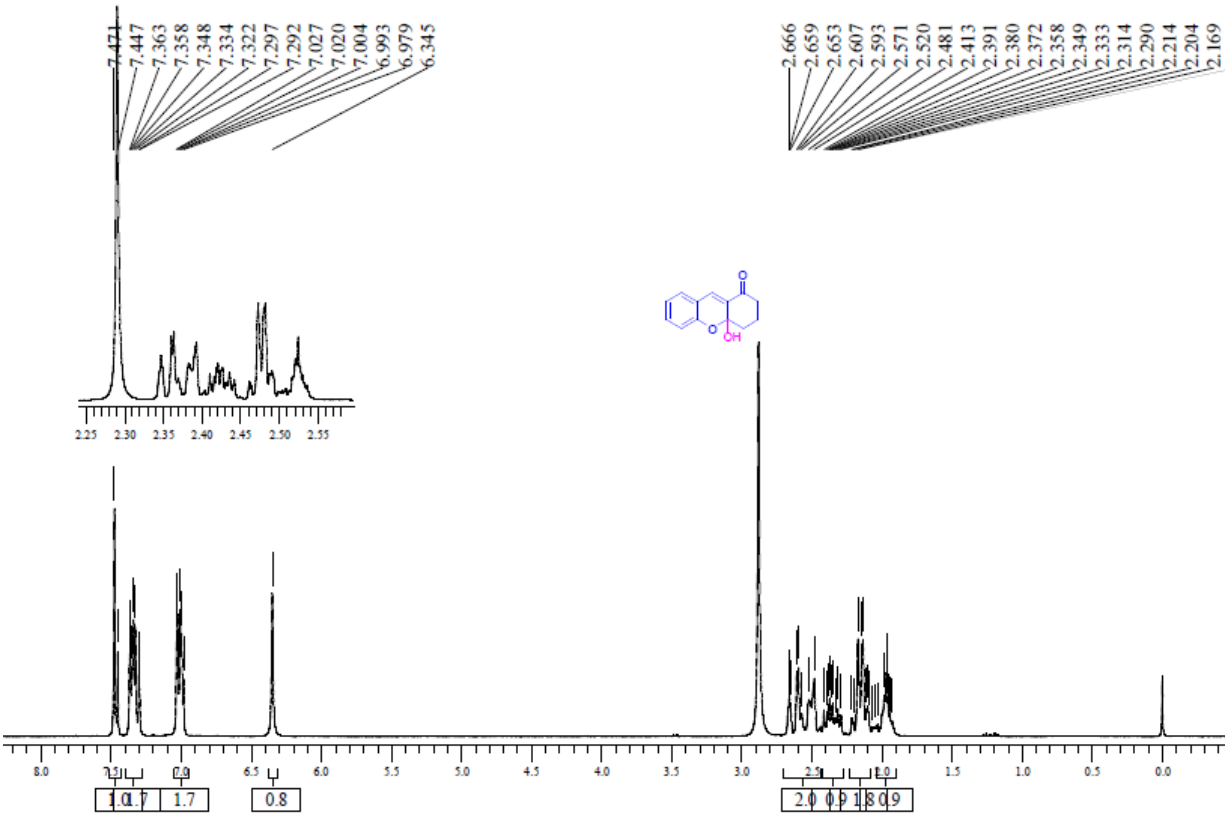
White solid; IR: v_{max} 3184, 2960, 2862, 1650, 1596, 1481, 1460, 1371, 1313, 1247, 1188, 1016, 985, 810, 755 cm^{-1}; 1H NMR (300MHz, $CDCl_3$+DMSO): 10.41 (s, 1 H), 7.10 (dd, J_1 = 8.8 Hz, J_2 = 2.4 Hz, 1 H), 6.99 (d, J = 2.4 Hz), 6.93 (d, J = 8.8 Hz, 1 H), 4.63 (s, 1 H), 1.94–2.56 (m, 8 H), 1.13 (s, 3 H), 1.06 (s, 6 H), 0.98 (s, 3 H); m/z (ESI); 400 $[M+H]^+$.

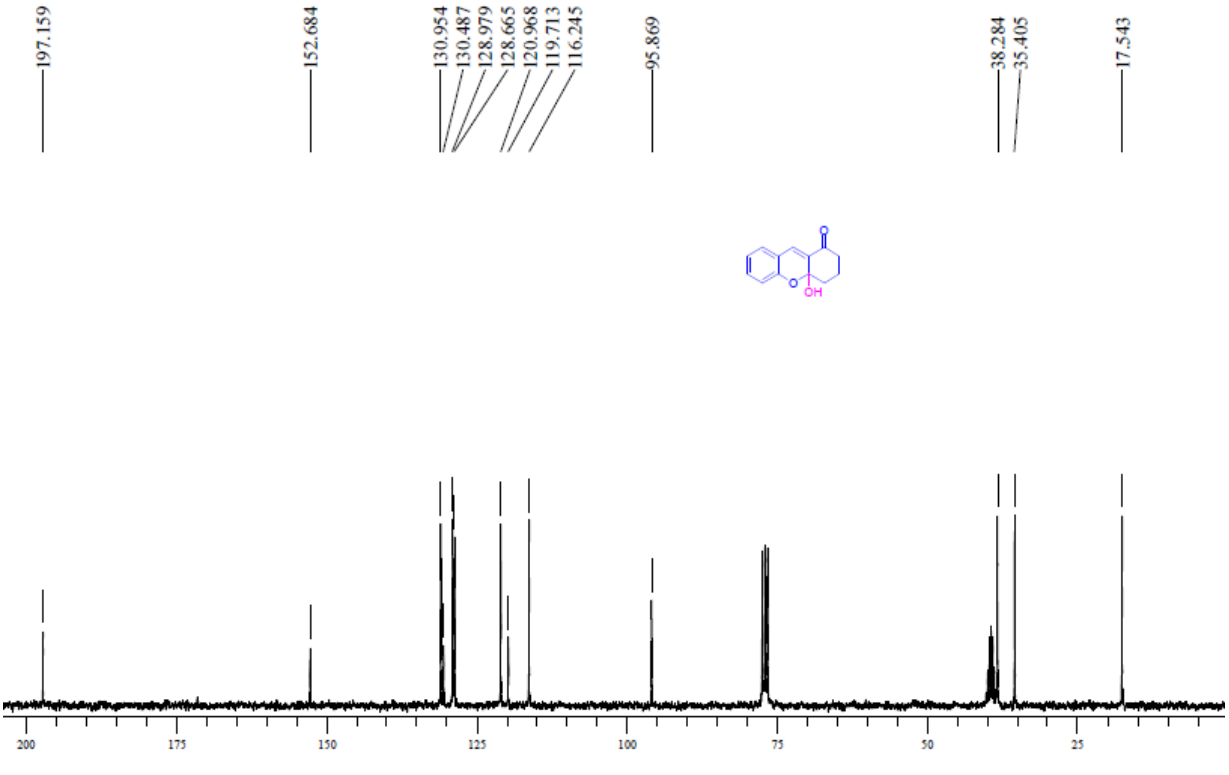
7-bromo-9-(2-hydroxy-4,4-dimethyl-6-oxocyclohex-1-en-1-yl)-3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one (table 6, 6f):



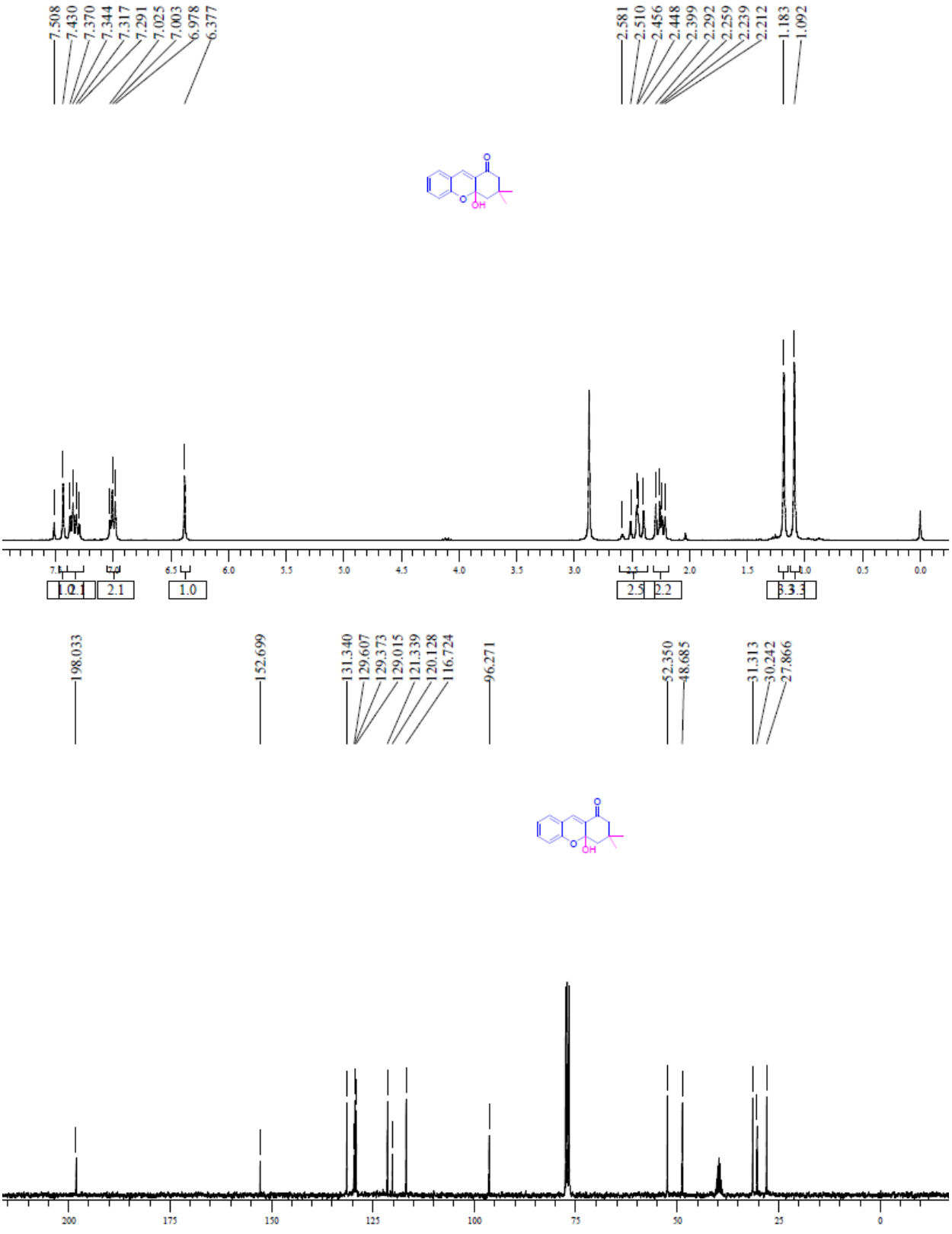
White solid; IR: v_{max} 3121, 2962, 2873, 1619, 1561, 1477, 1372, 1294, 1229, 1178, 1152, 1070, 1032, 886, 819 cm_1; 1H NMR (300 MHz, $CDCl_3$+DMSO): 10.52 (s, 1 H), 7.19 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1 H), 6.93 (d, J = 8.4 Hz, 1 H), 7.12 (d, J = 2.4 Hz, 1 H), 4.61 (s, 1 H), 1.98–2.60 (m, 8 H), 1.11 (s, 3 H), 1.04 (s, 6 H), 0.99 (s, 3 H); m/z (ESI); 446 [M+H].

^{1}H and ^{13}C spectra of compound 3a

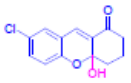


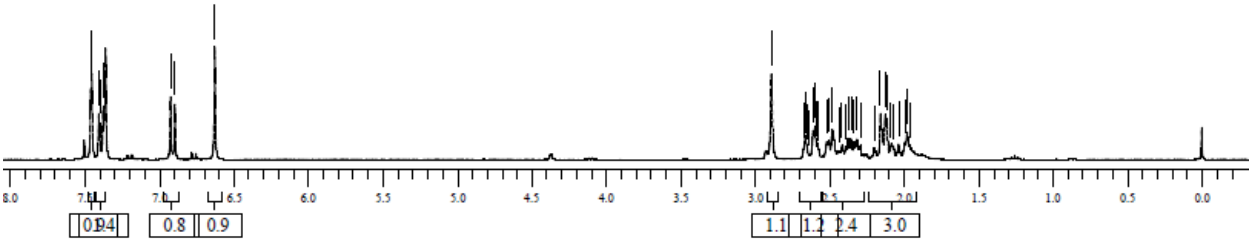


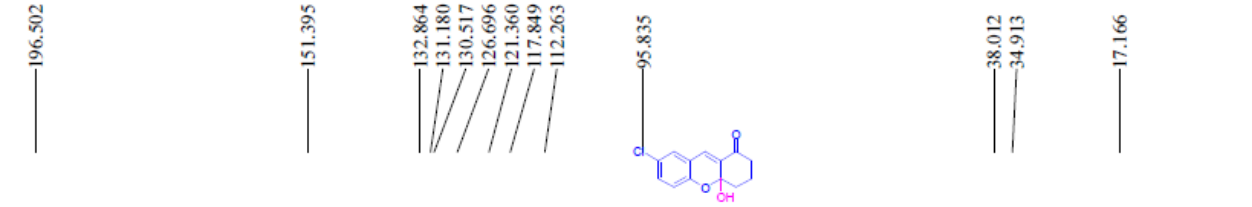
^{1}H and ^{13}C spectra of compound 3b

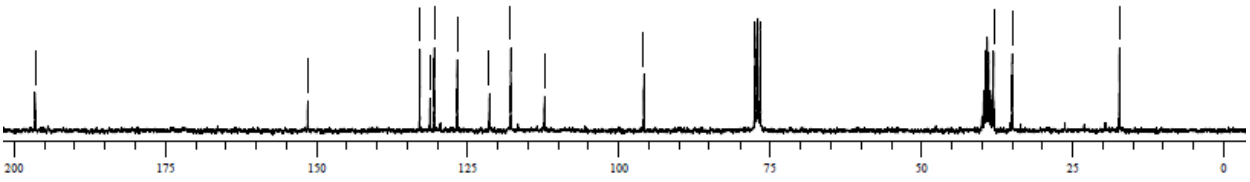


^{1}H and ^{13}C spectra of compound 3c

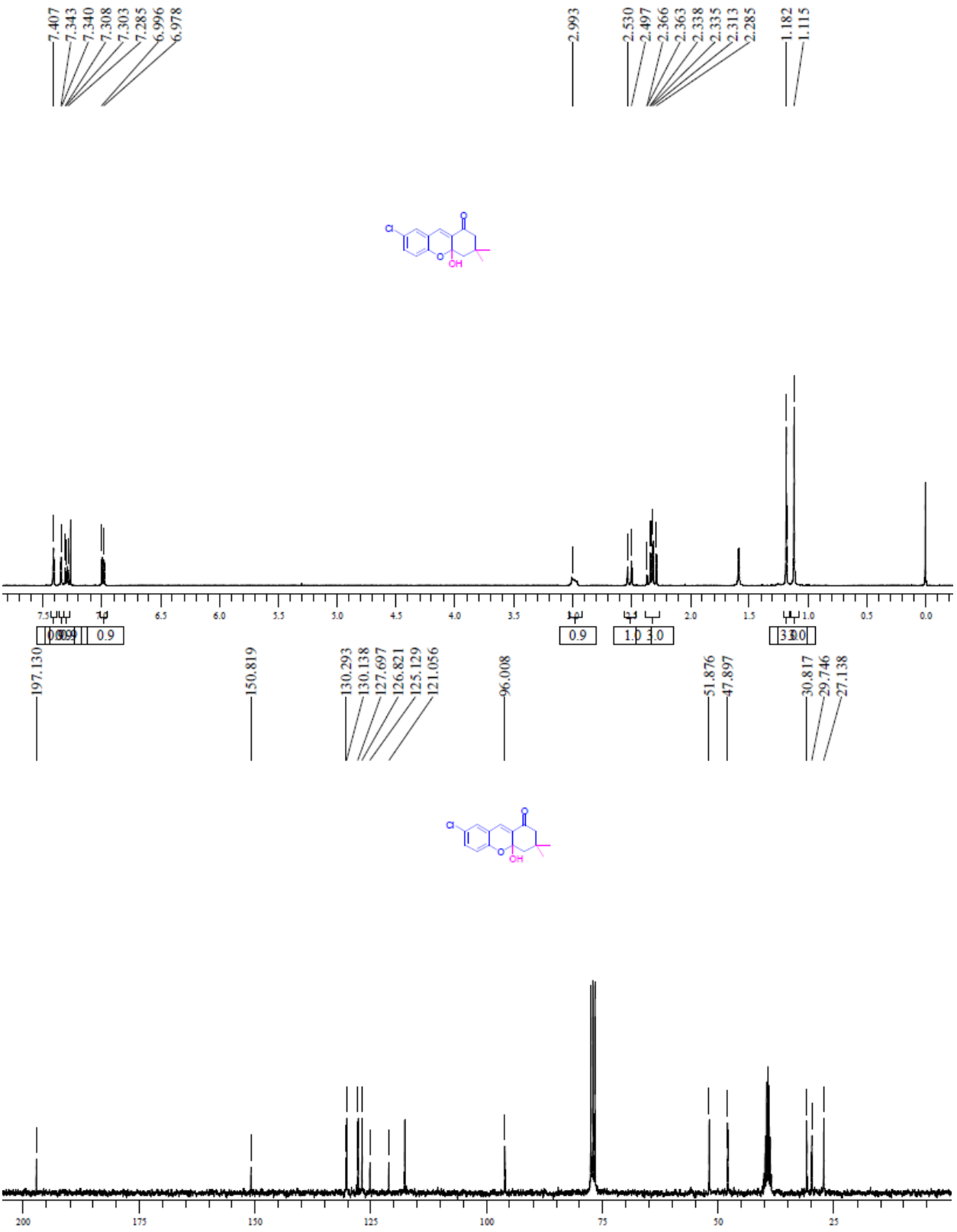




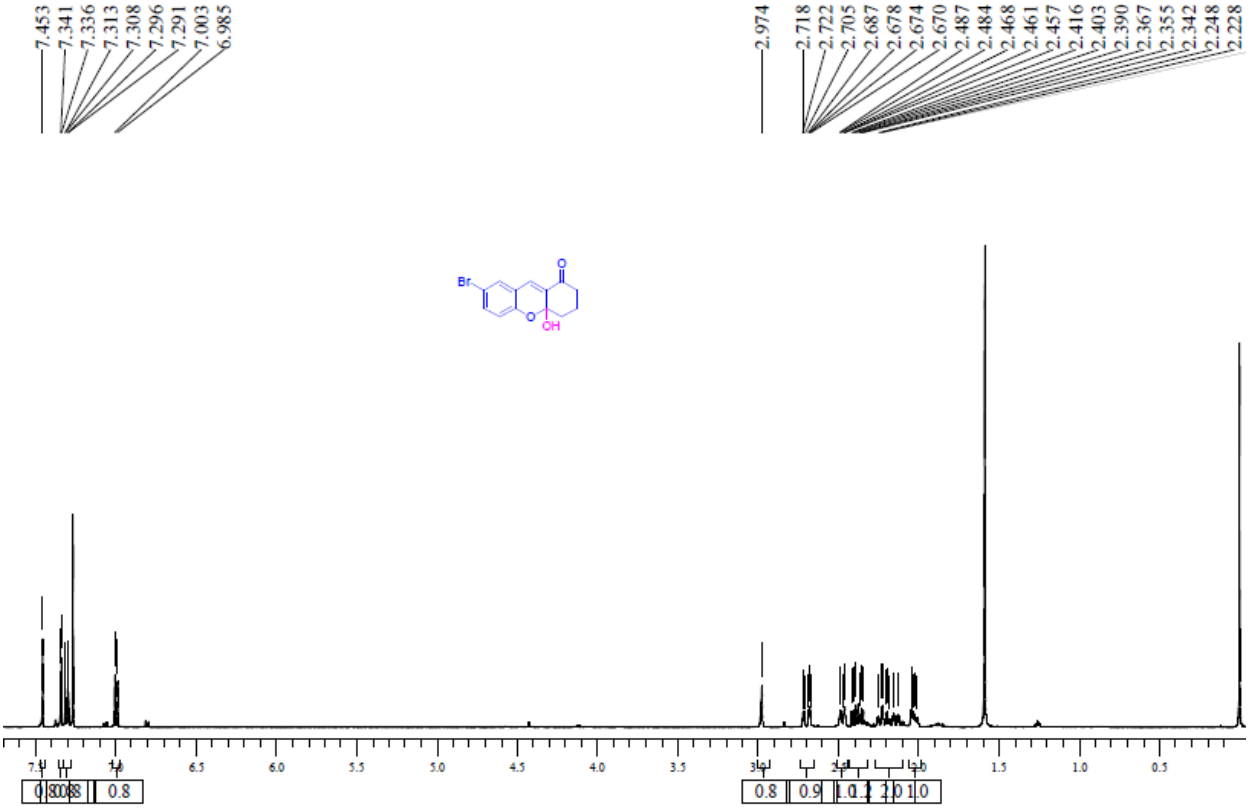


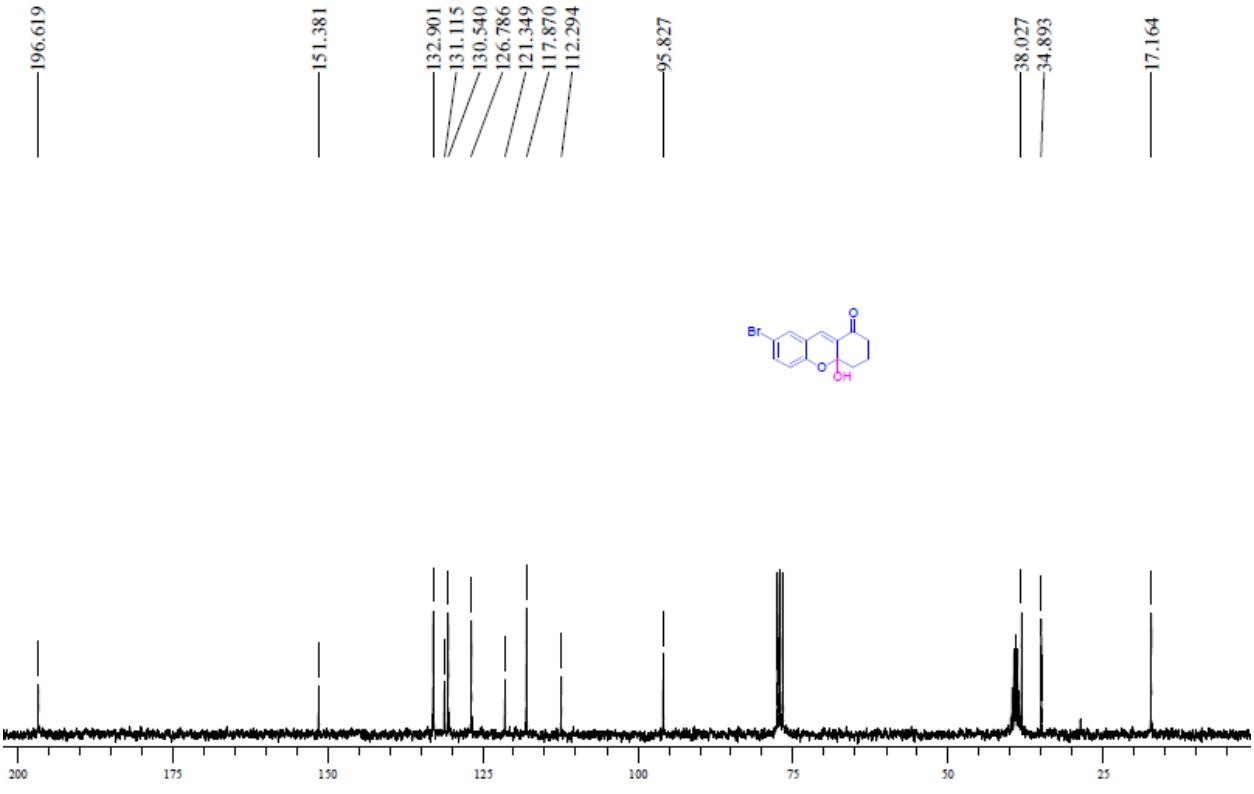


^{1}H and ^{13}C spectra of compound 3d

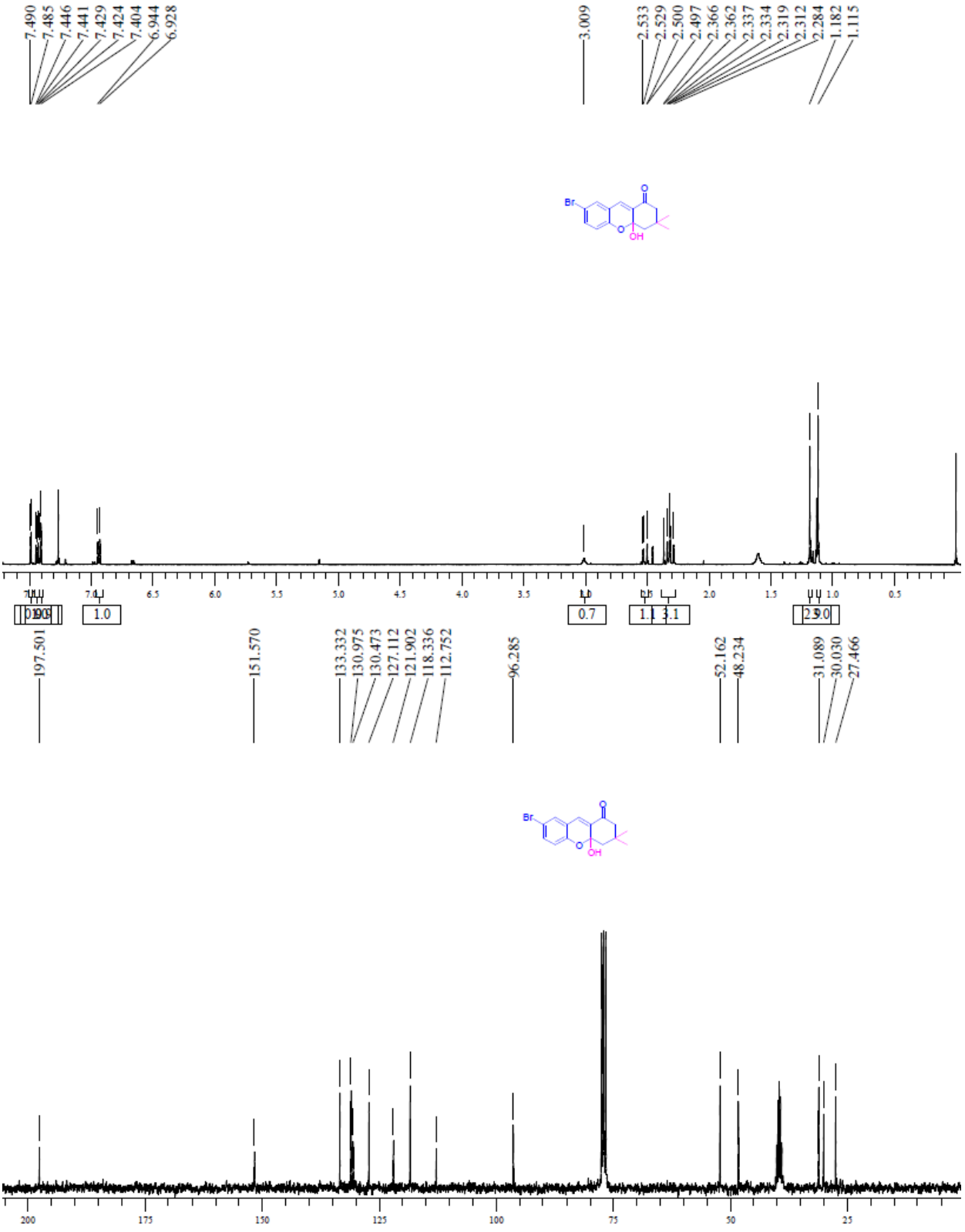


^{1}H and ^{13}C spectra of compound 3e

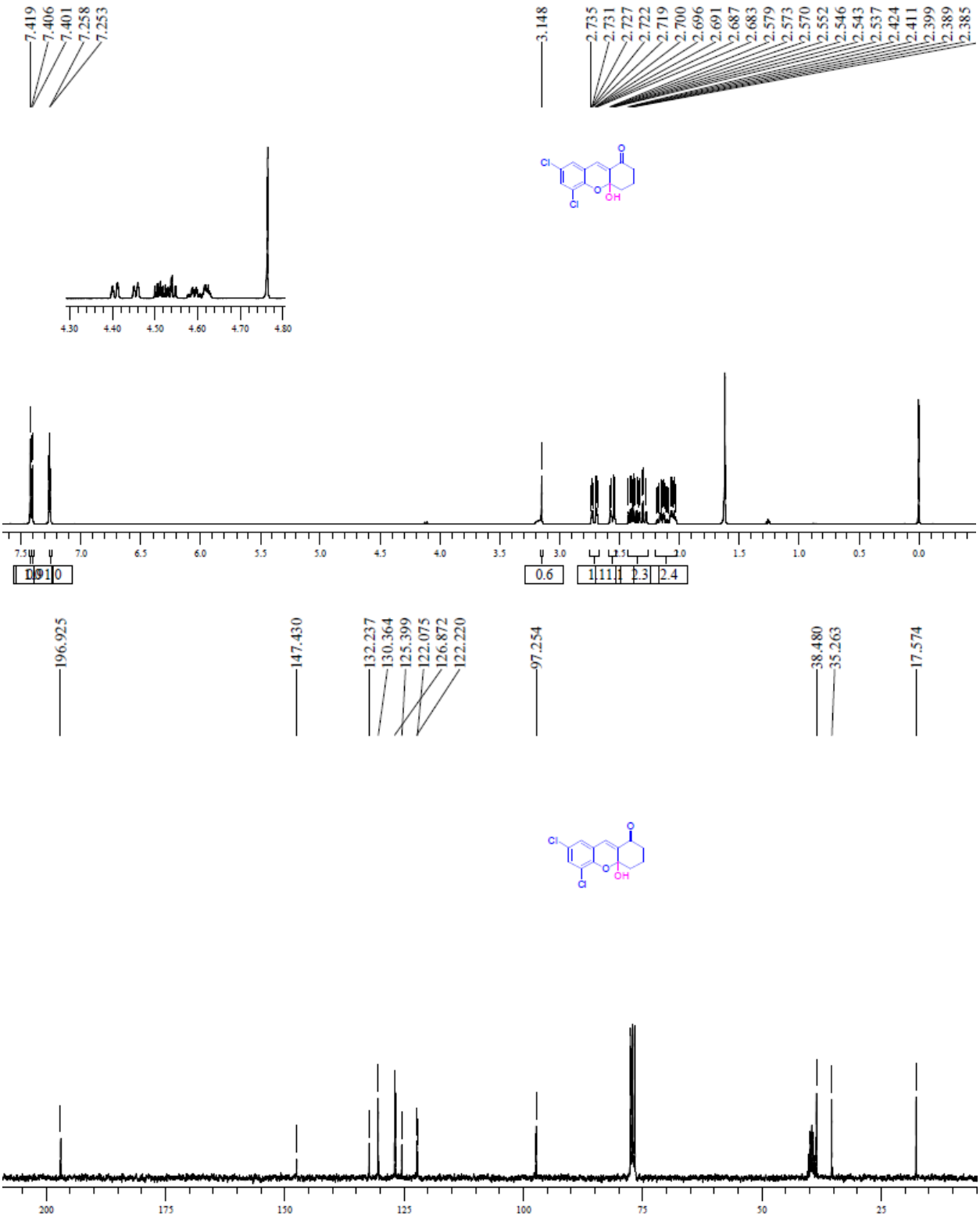




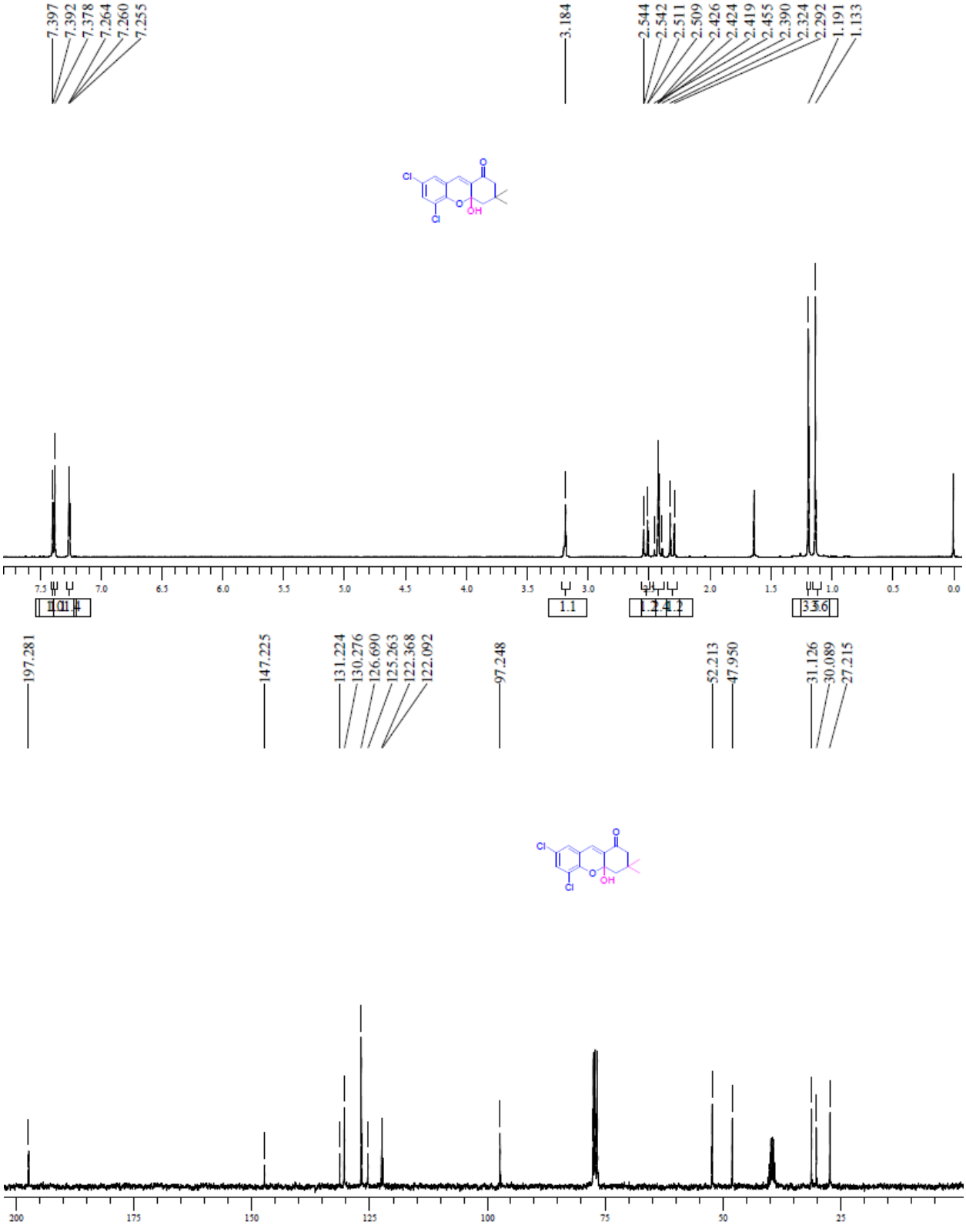
^{1}H and ^{13}C spectra of compound 3f



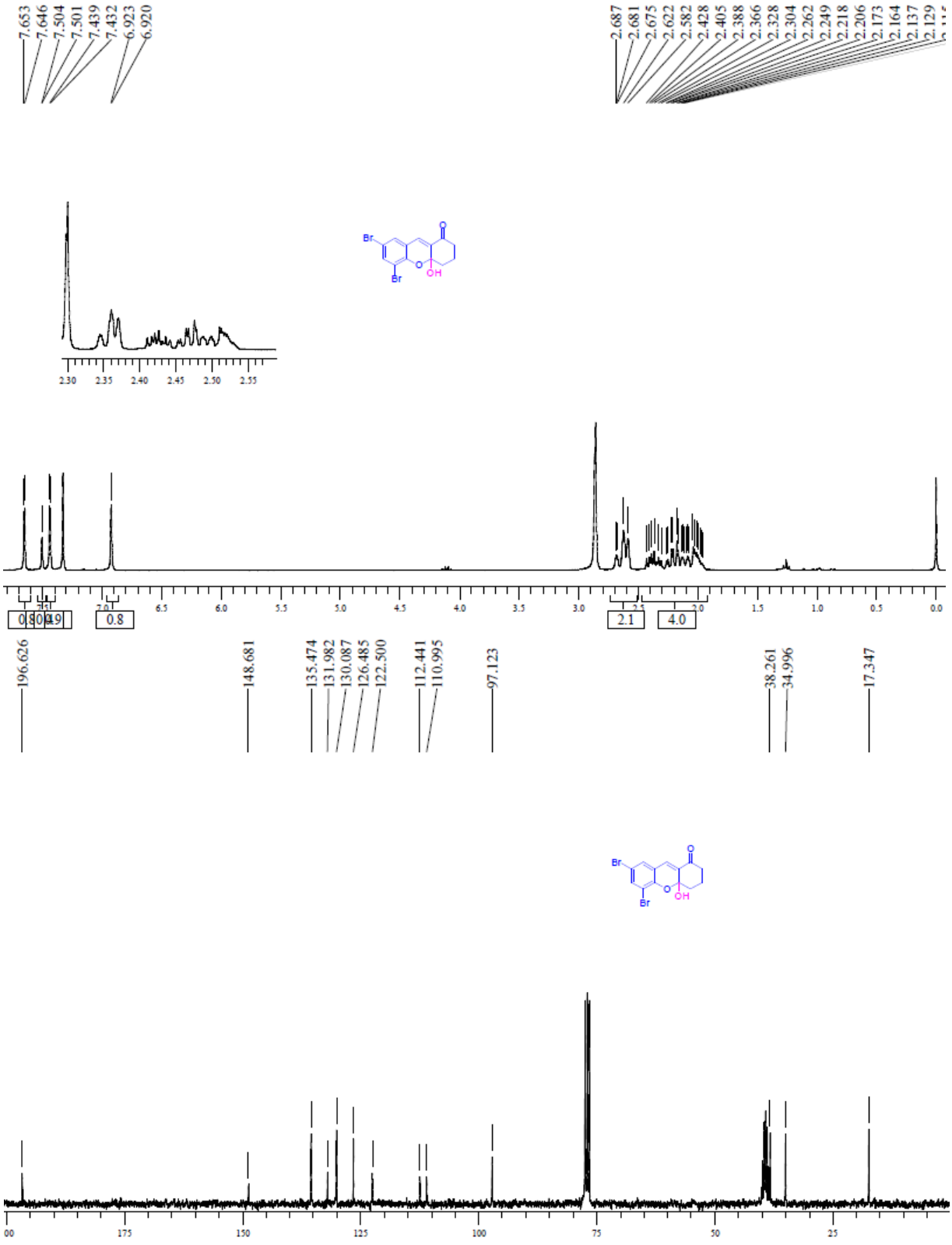
^{1}H and ^{13}C spectra of compound 3g



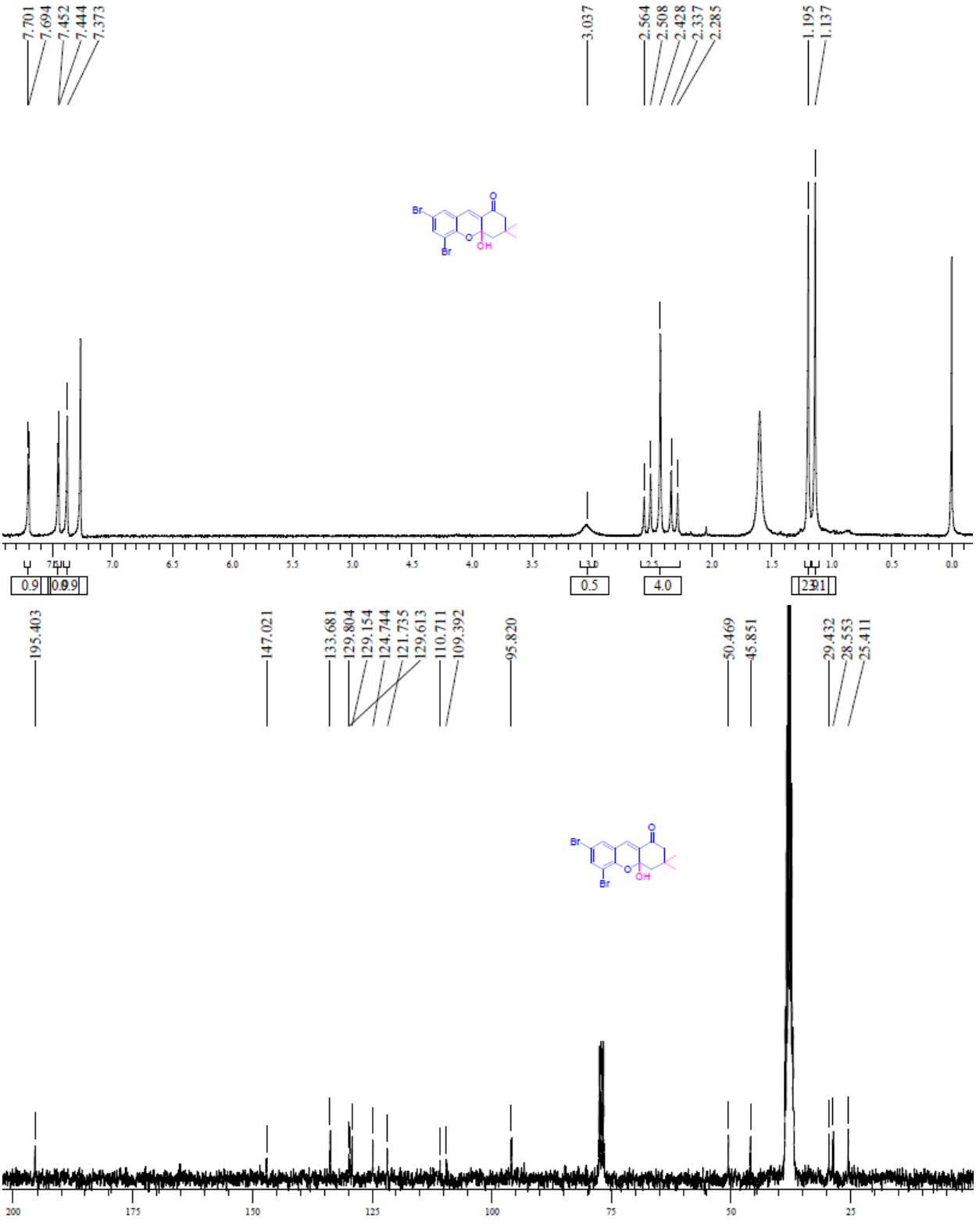
^{1}H and ^{13}C spectra of compound 3h



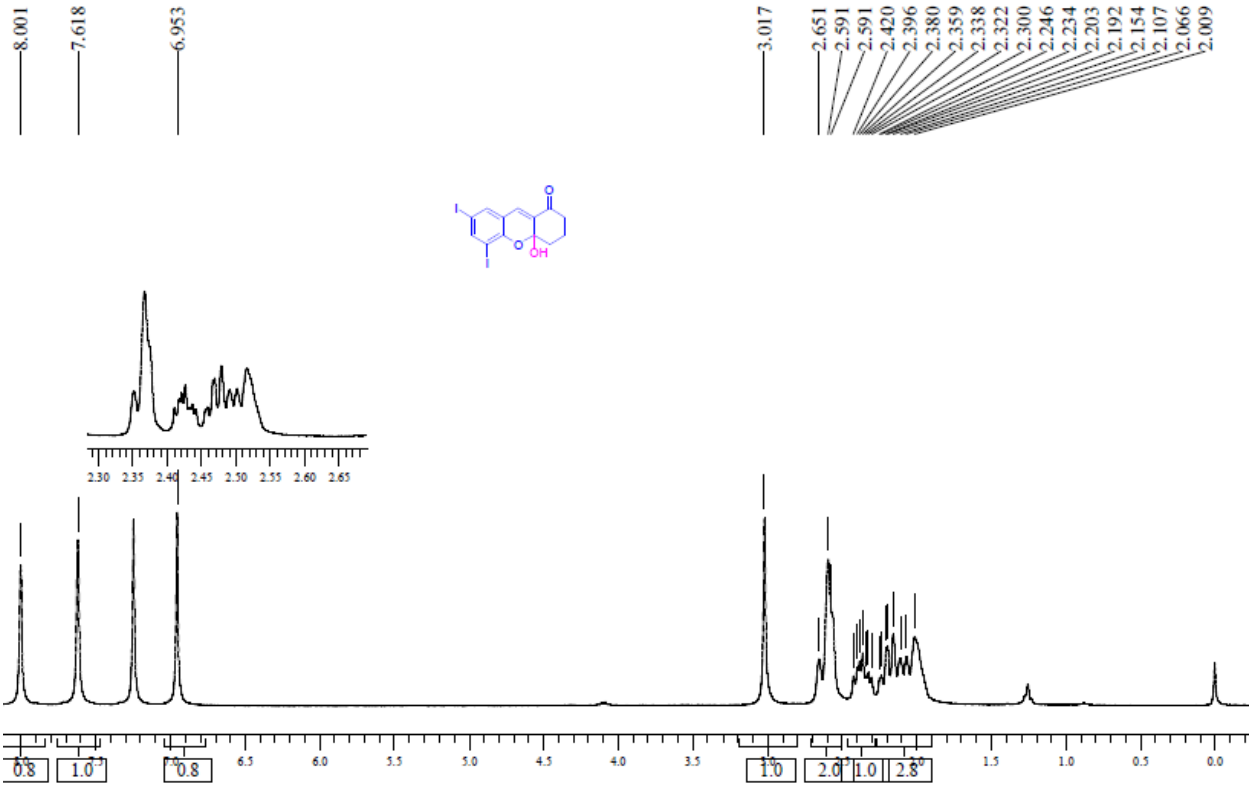
^{1}H and ^{13}C spectra of compound 3i

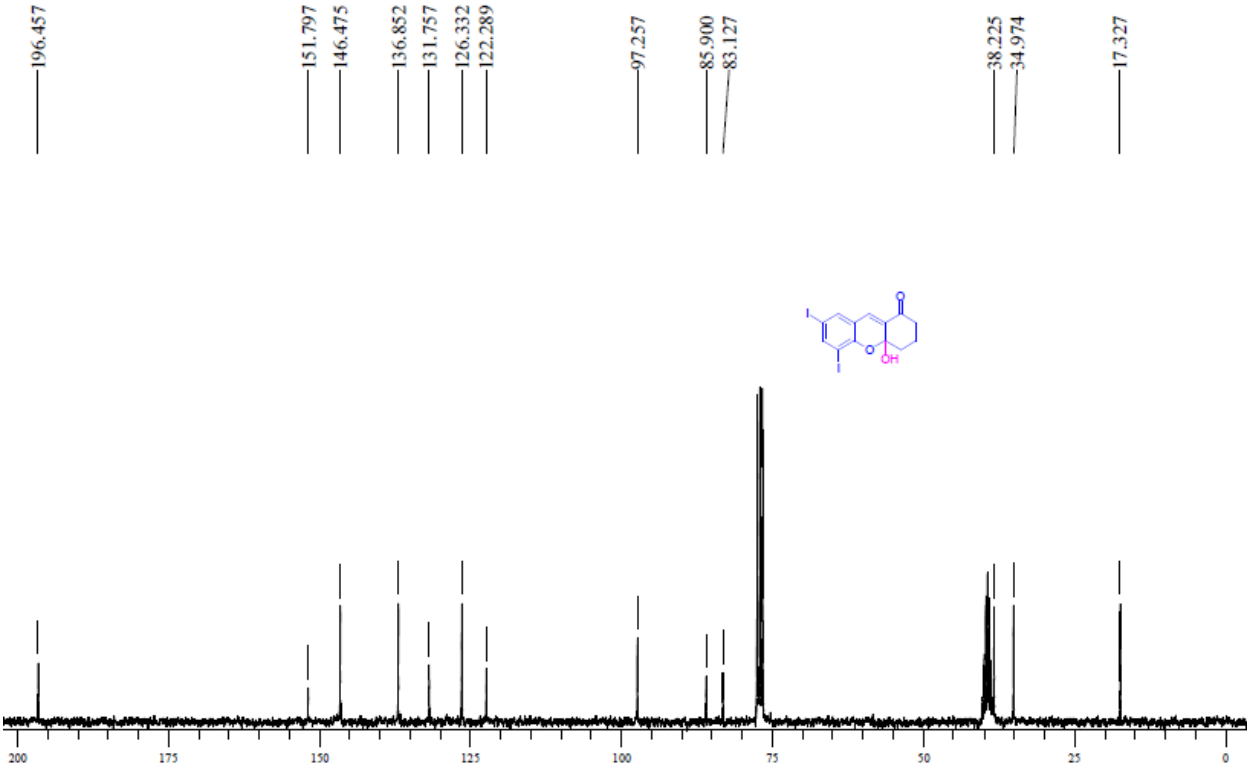


^{1}H and ^{13}C spectra of compound 3j

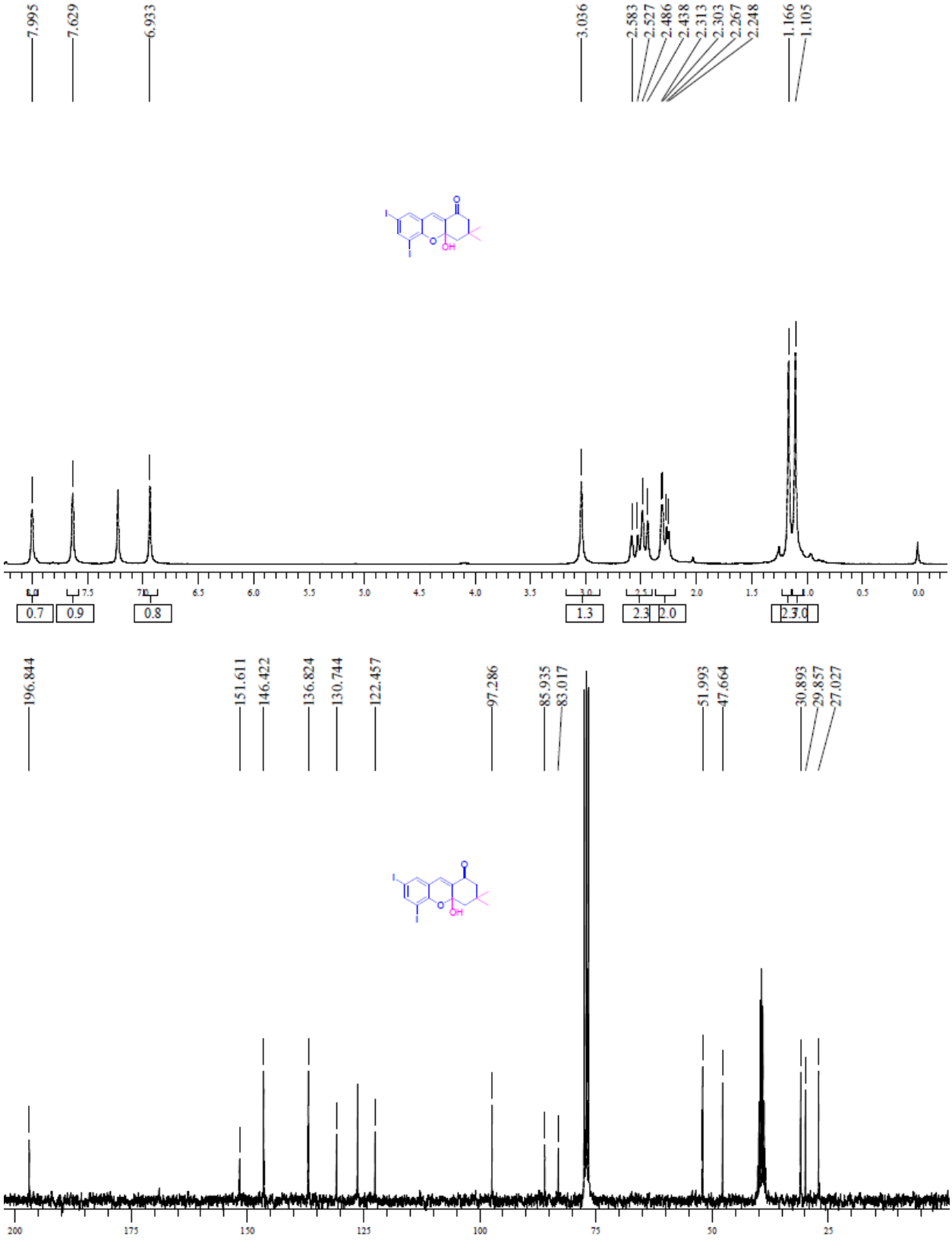


^{1}H and ^{13}C spectra of compound 3k

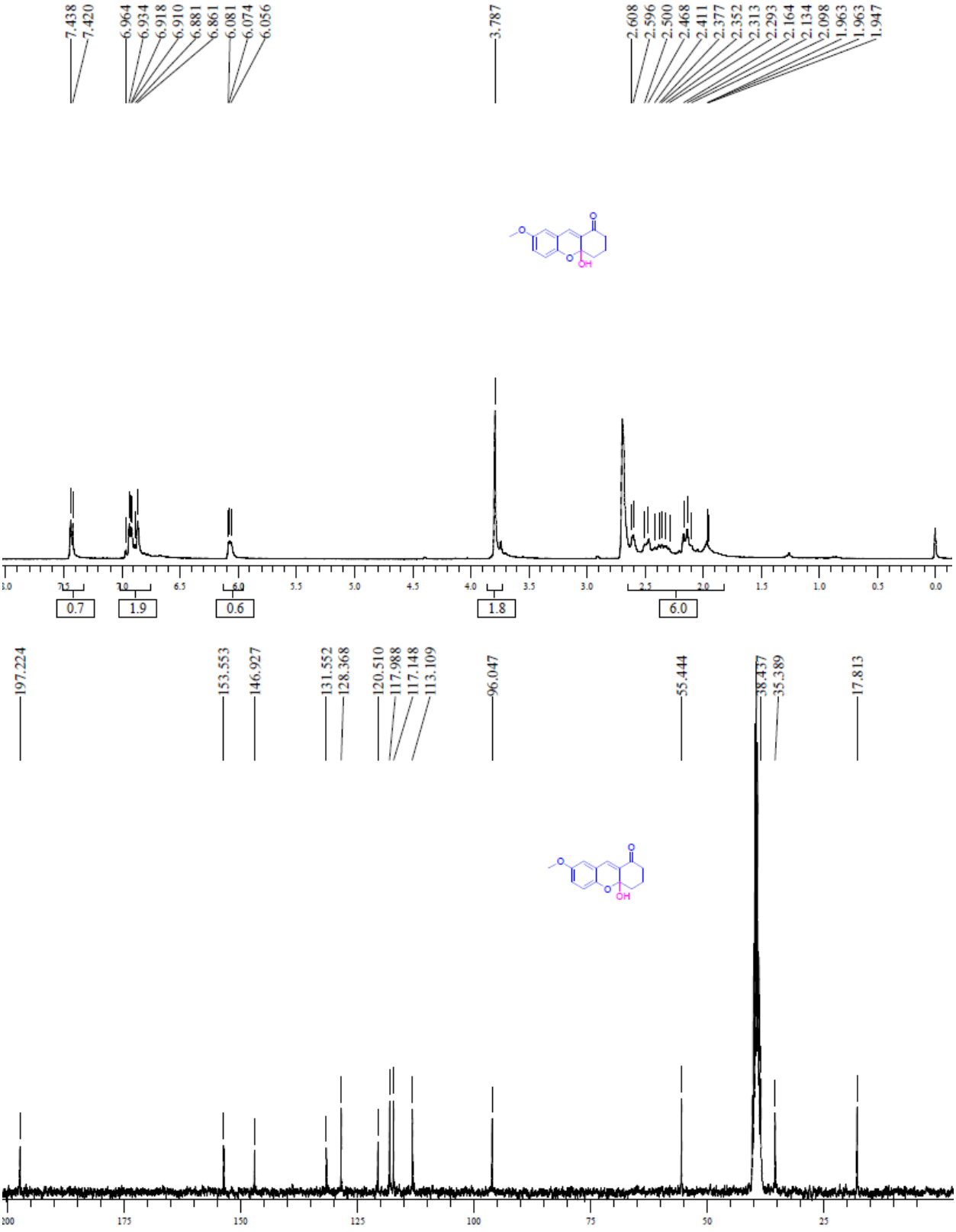




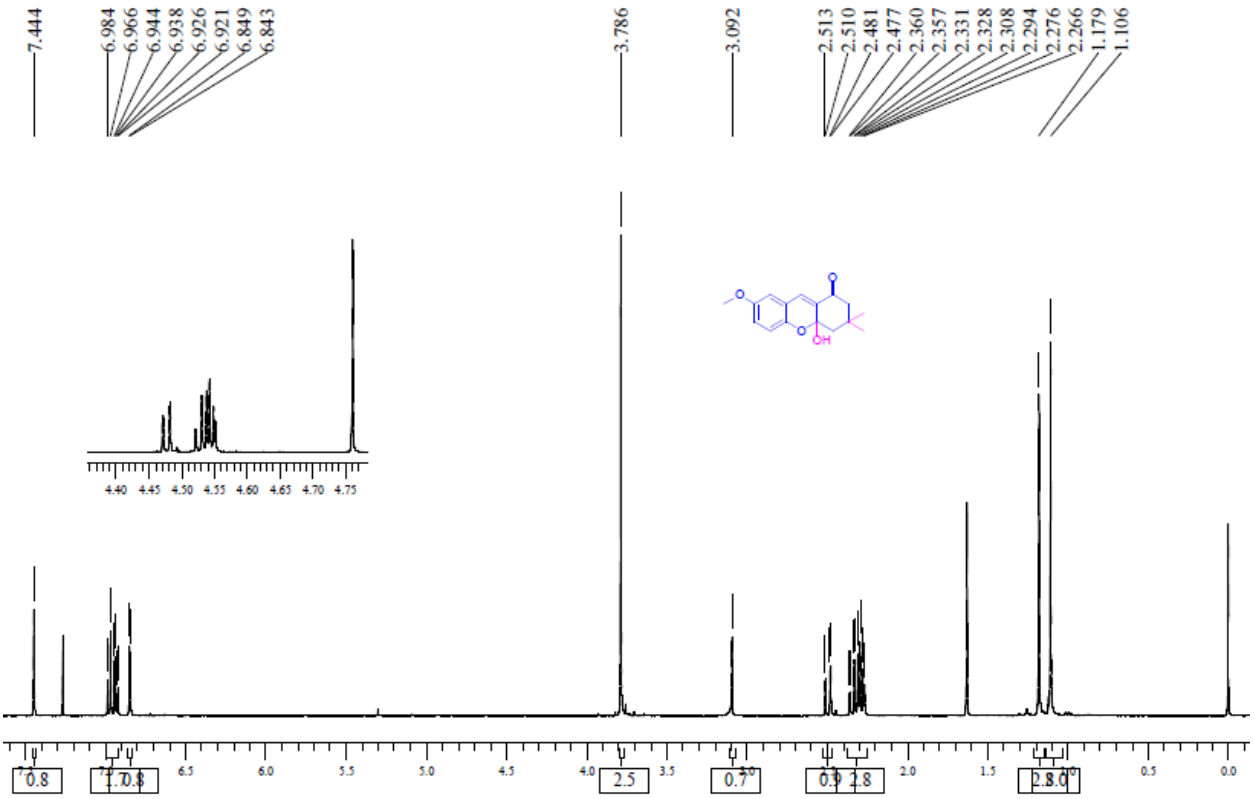
^{1}H and ^{13}C spectra of compound 3l

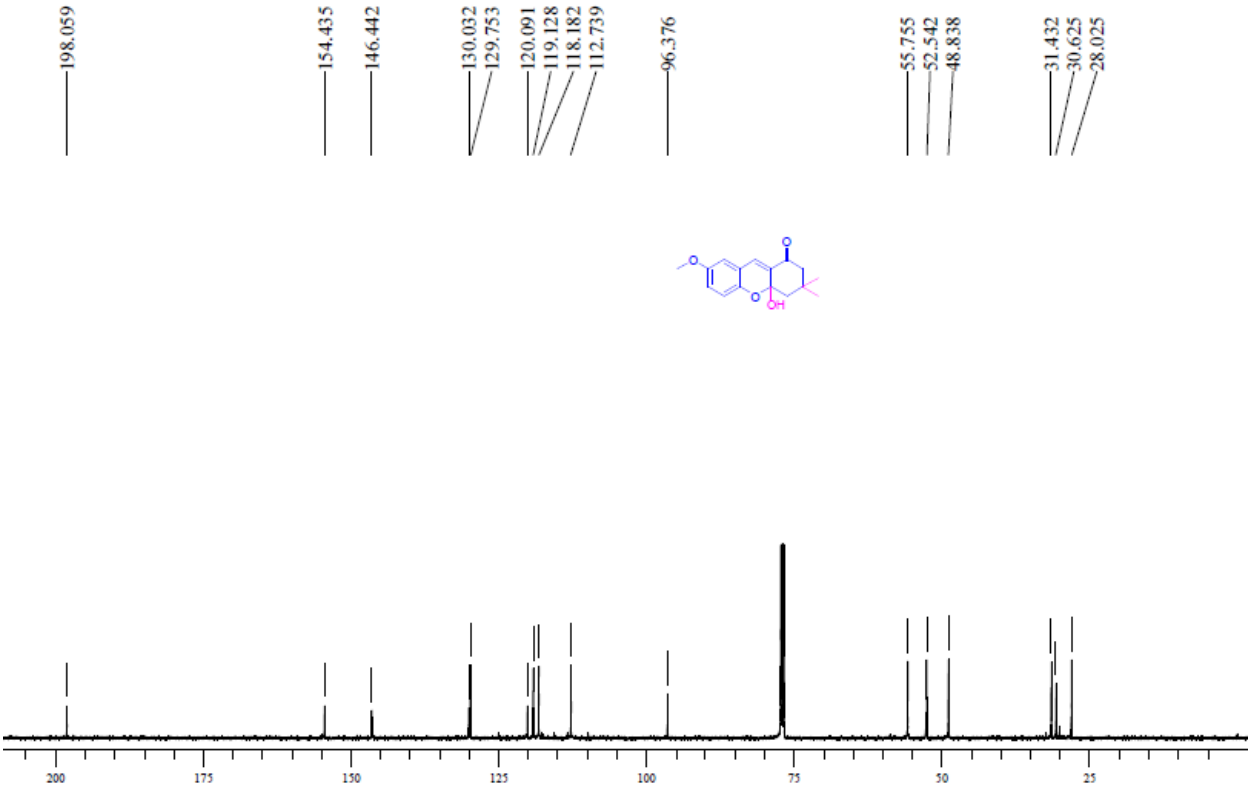


^{1}H and ^{13}C spectra of compound 3m

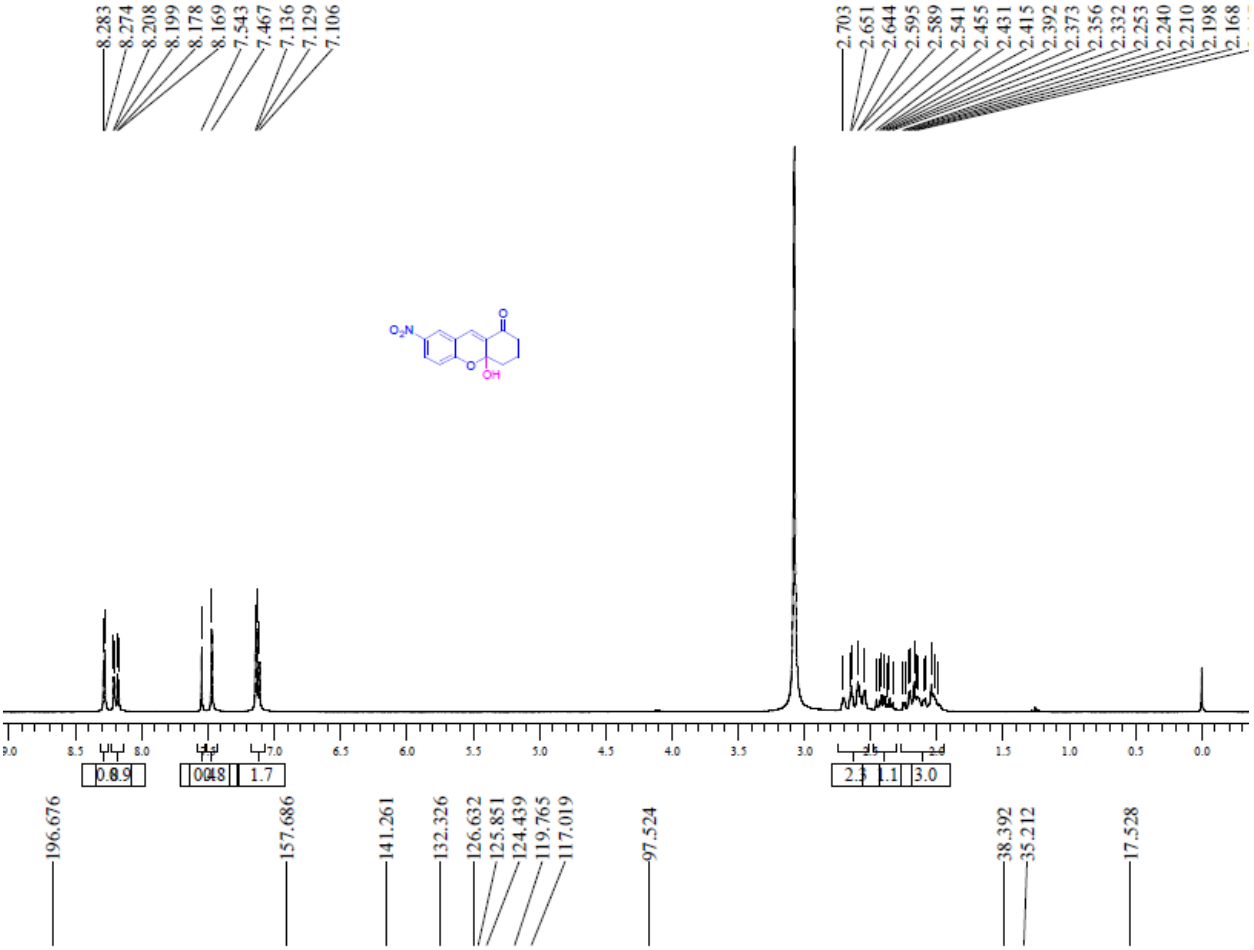


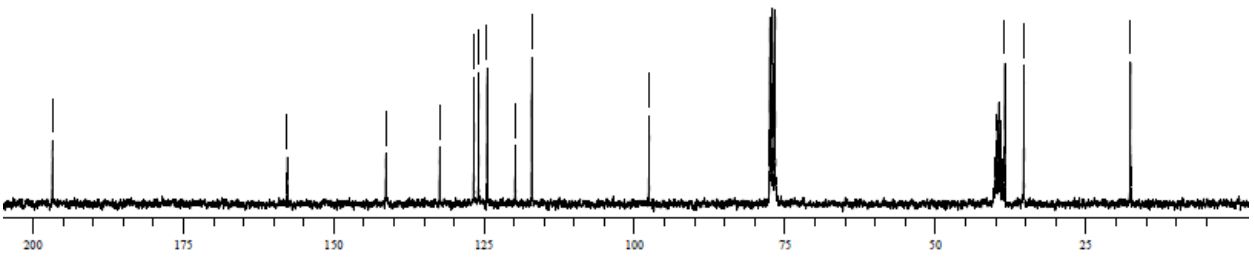
^{1}H and ^{13}C spectra of compound 3n



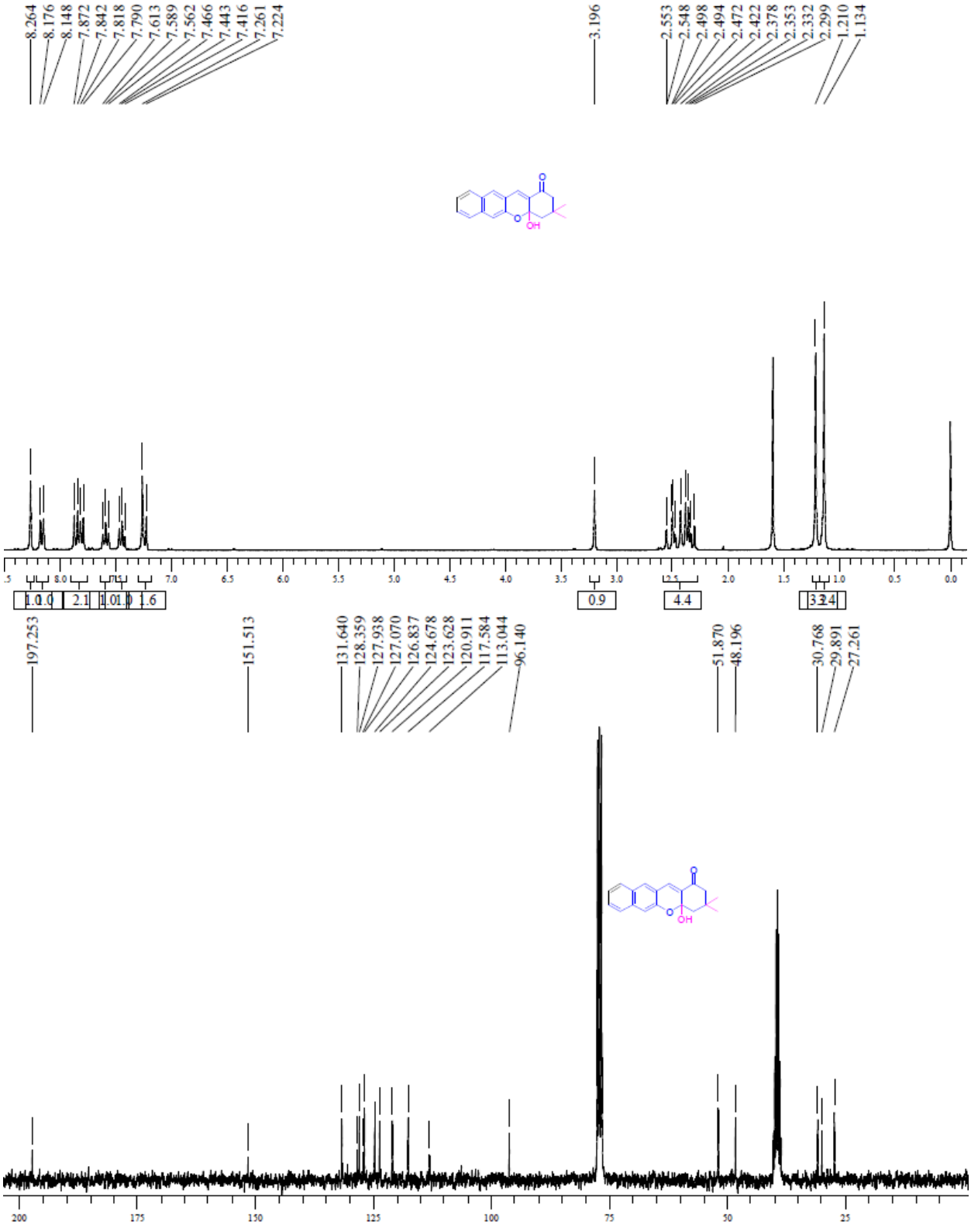


^{1}H and ^{13}C spectra of compound 3o

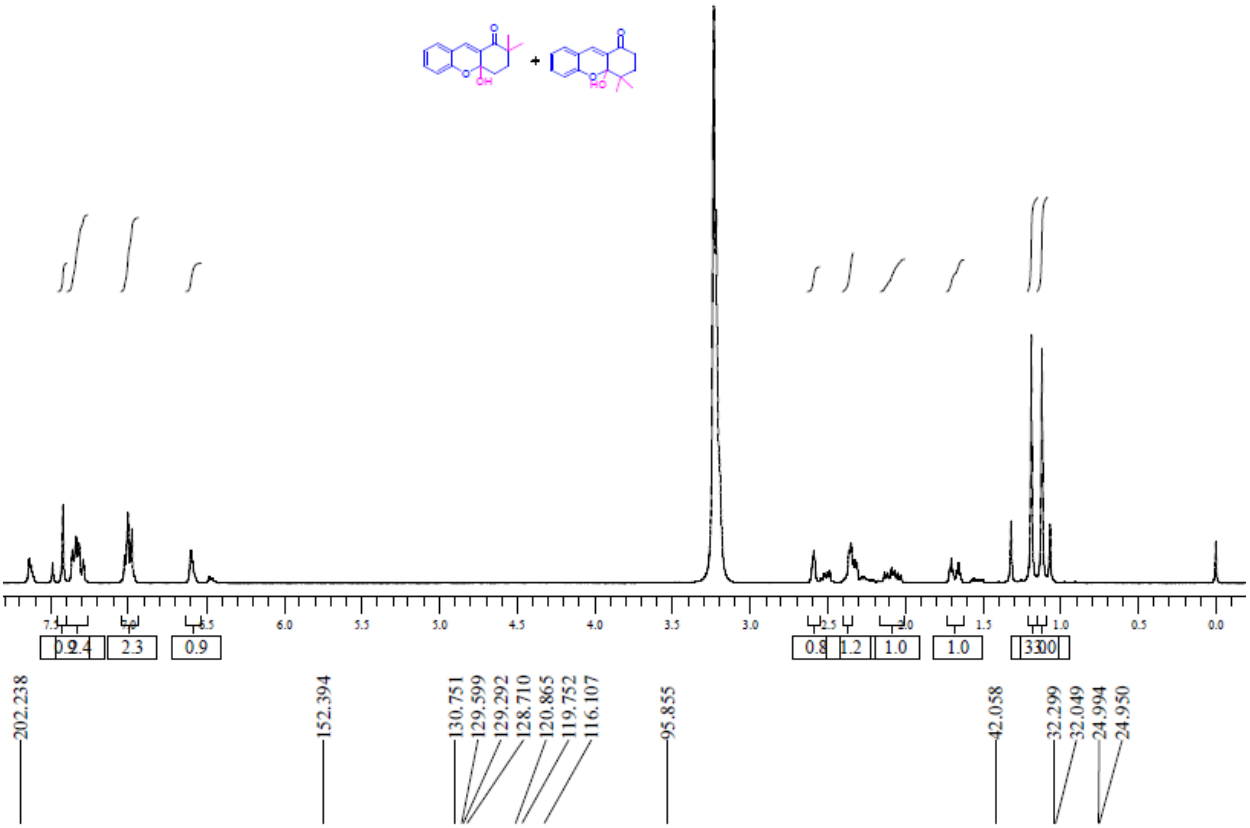


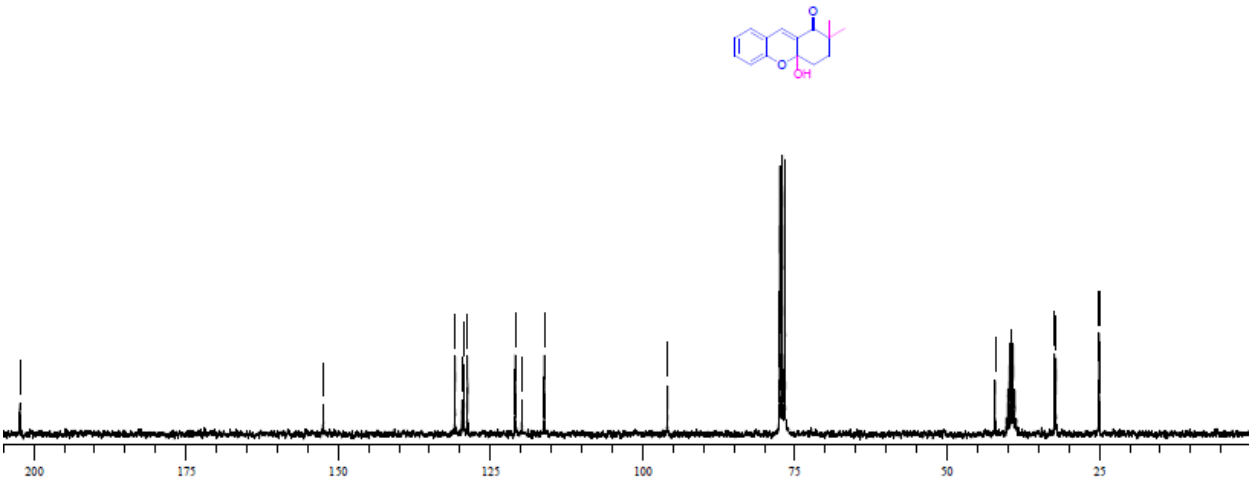


^{1}H and ^{13}C spectra of compound 3p

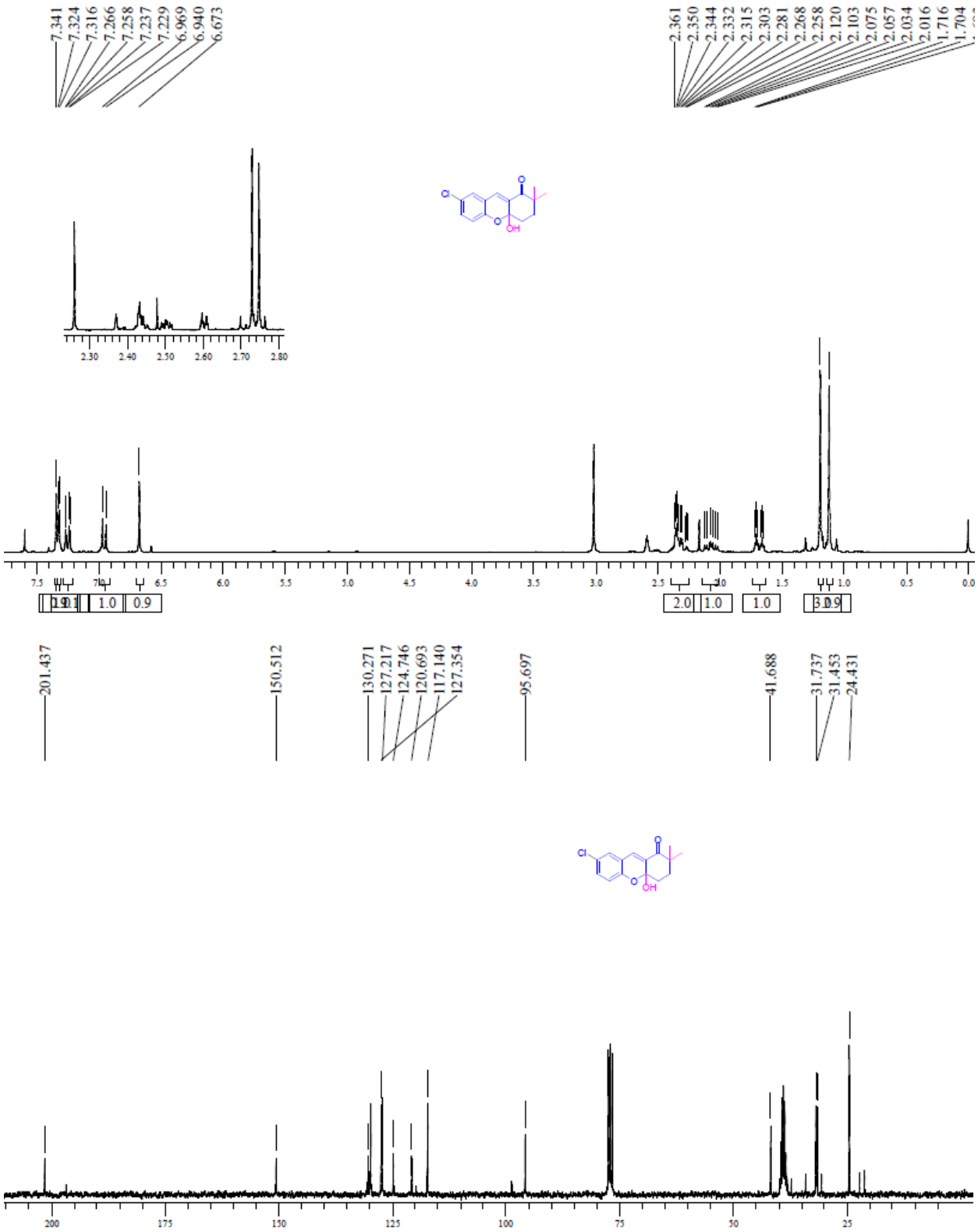


^{1}H and ^{13}C spectra of compound 4a (with minor isomer)

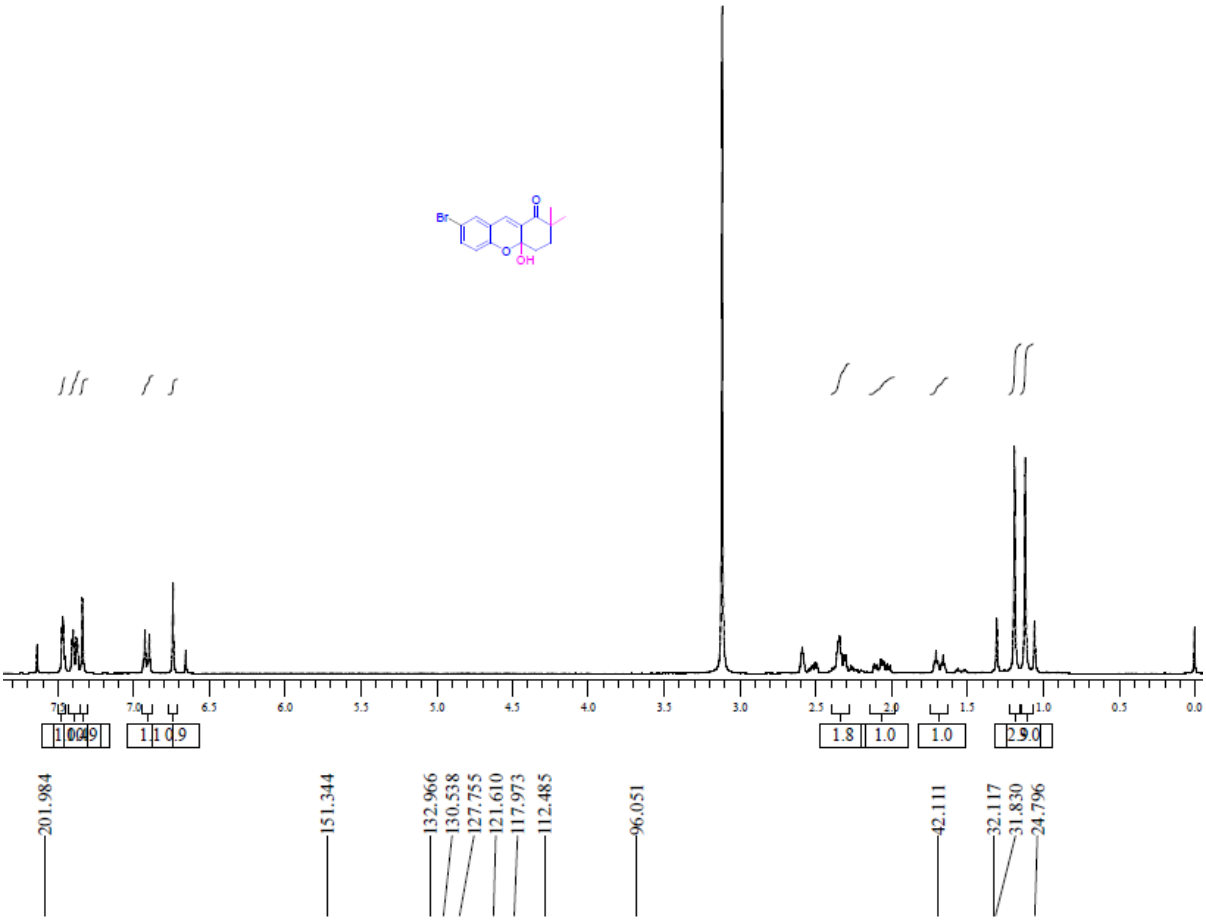


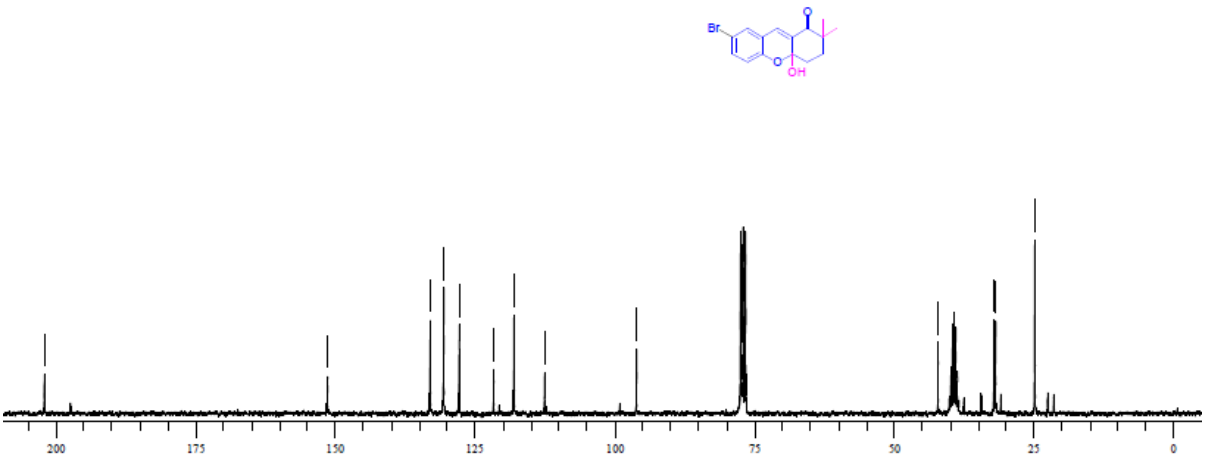


^{1}H and ^{13}C spectra of compound 4b (with minor isomer)

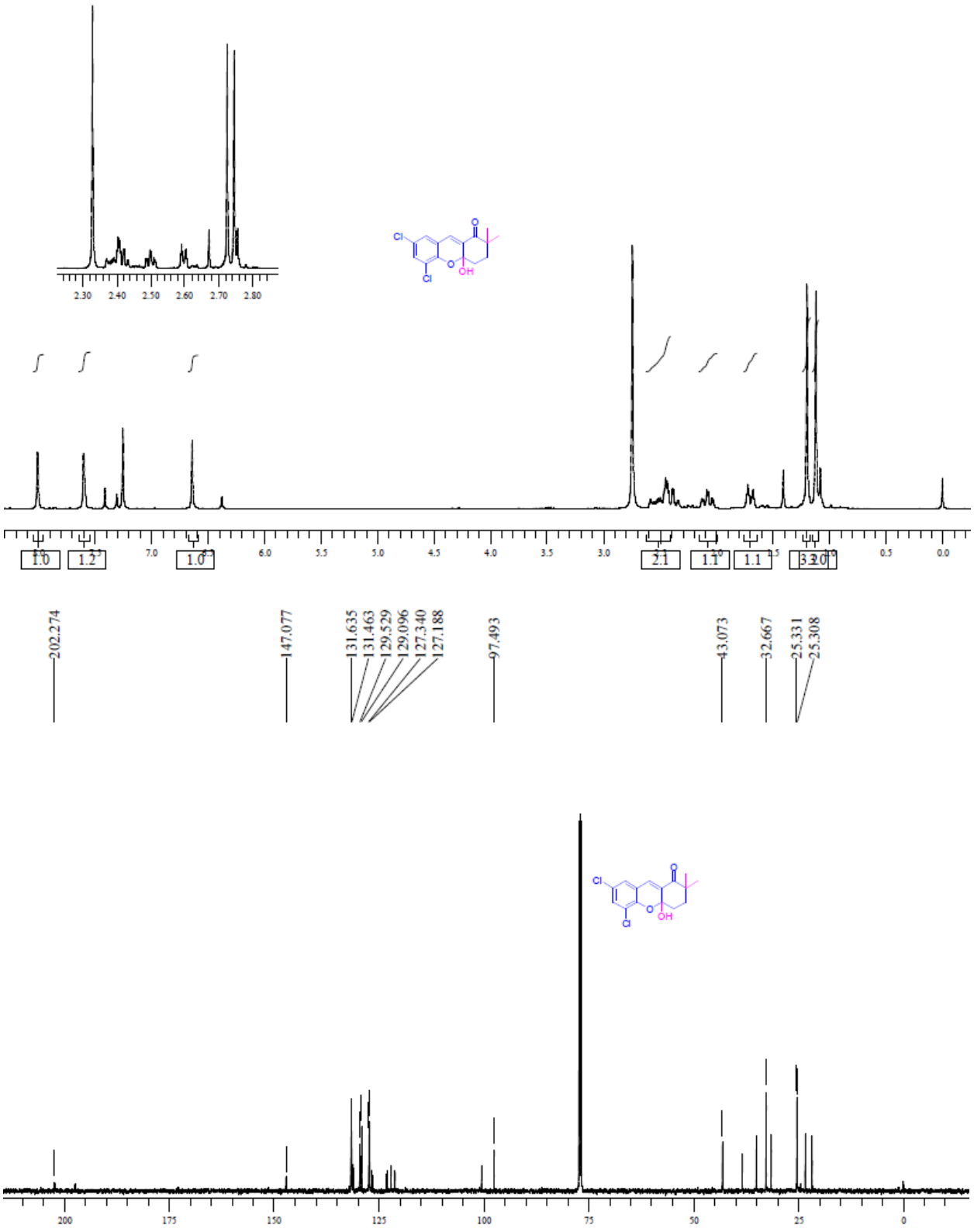


^{1}H and ^{13}C spectra of compound 4c (with minor isomer)

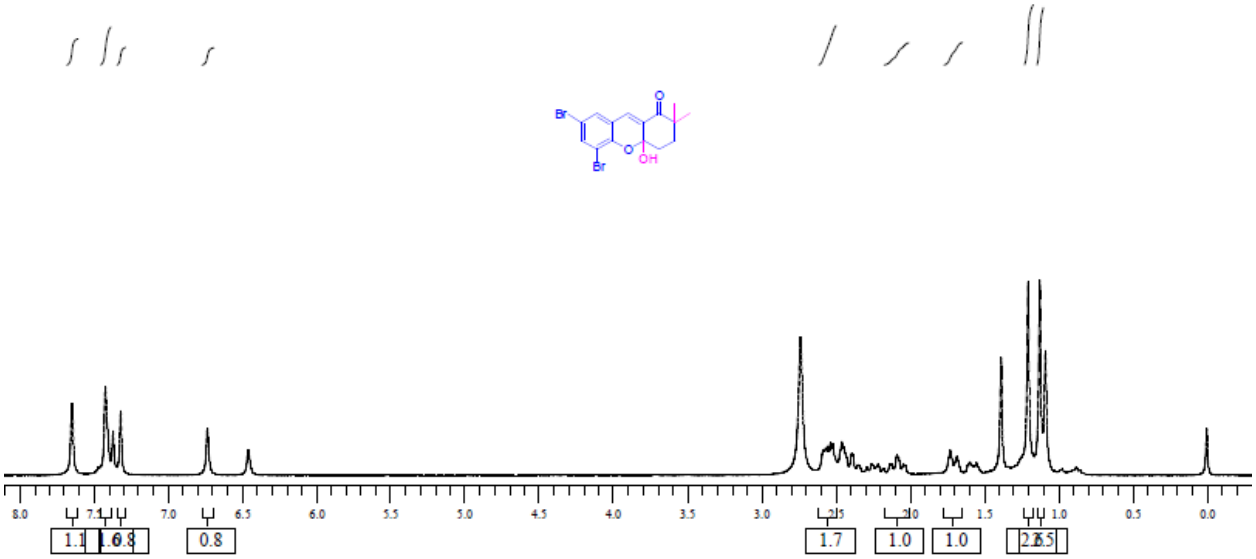




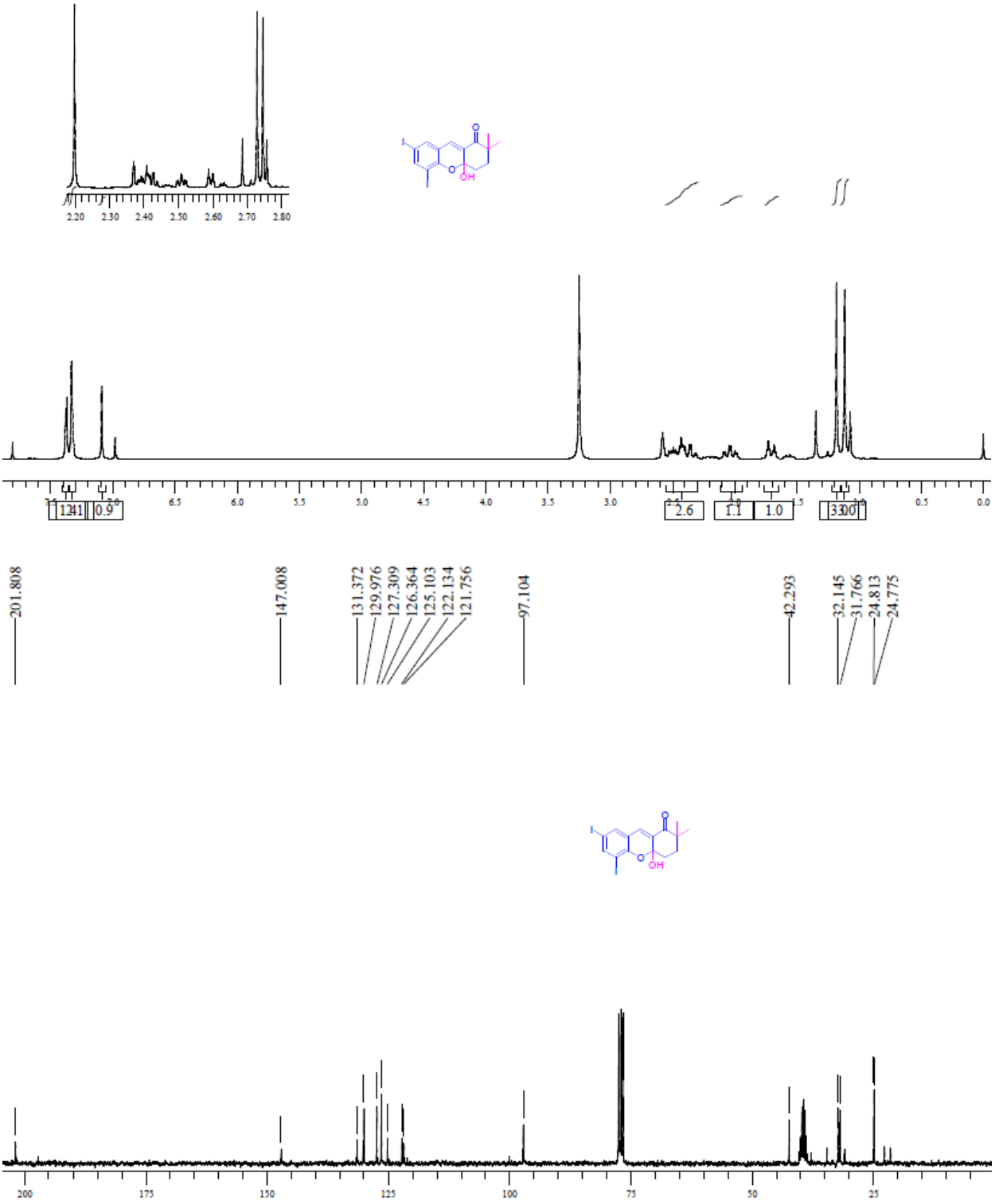
^{1}H and ^{13}C spectra of compound 4d (with minor isomer)



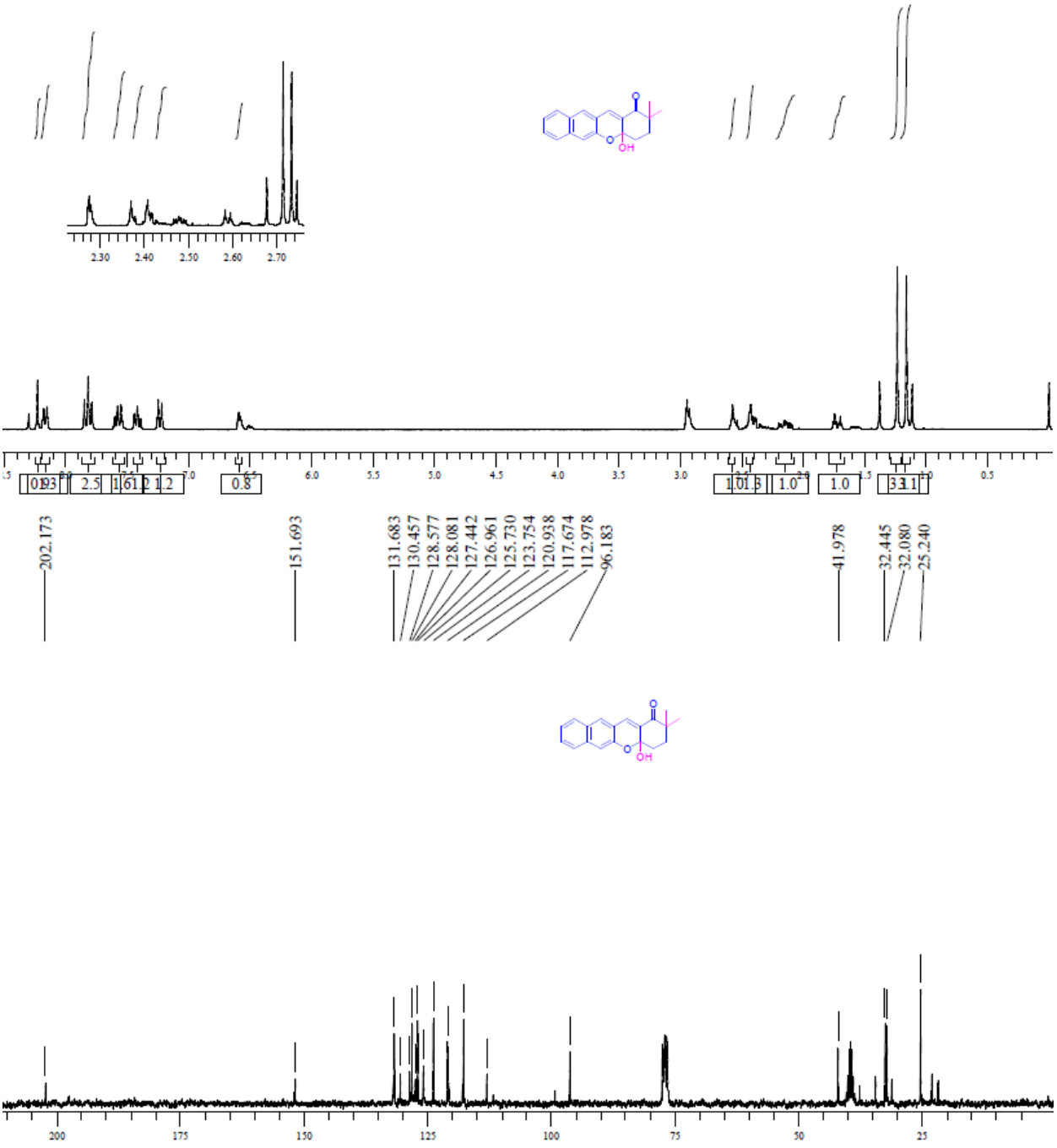
^{1}H spectra of compound 4e (with minor isomer)



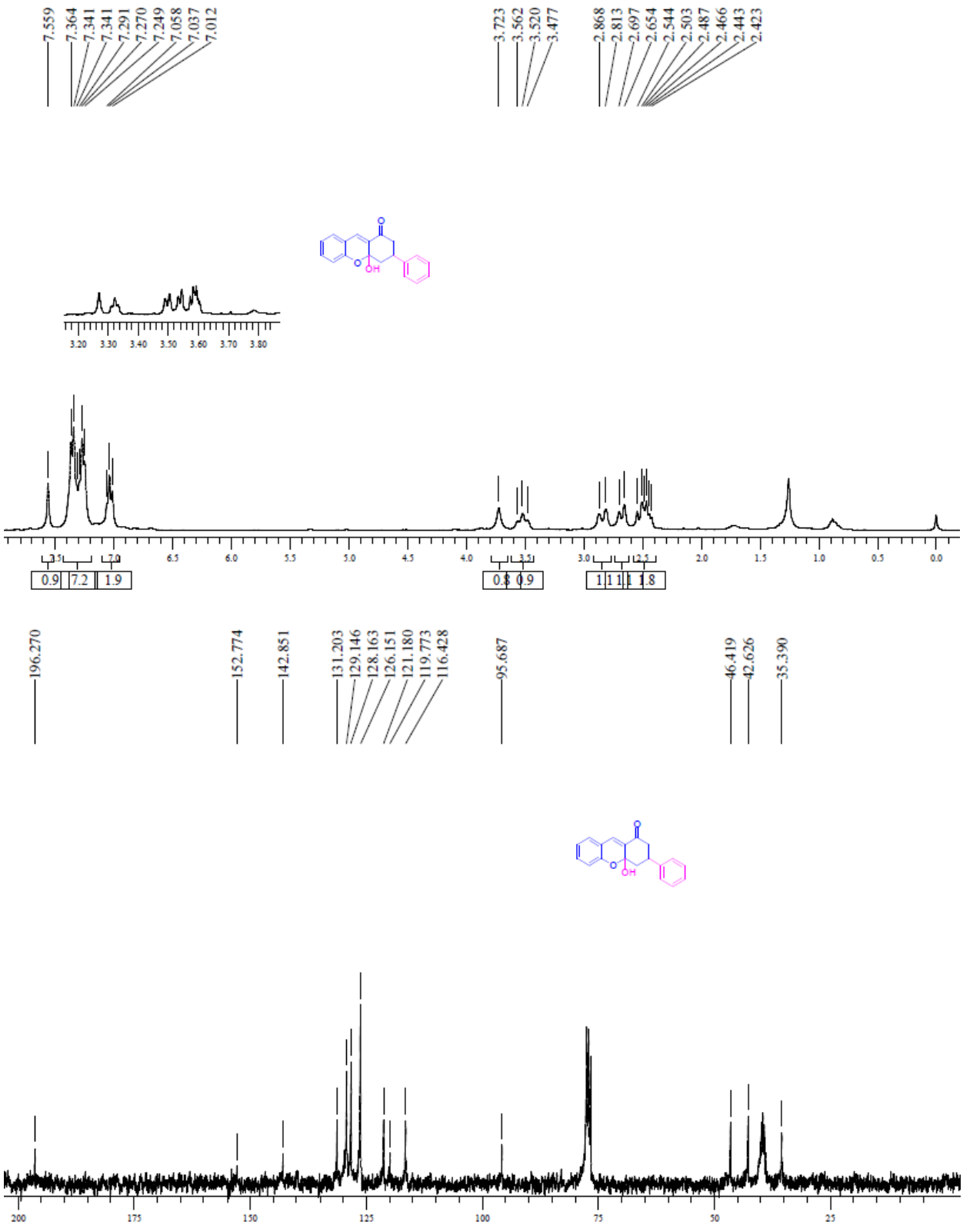
^{1}H and ^{13}C spectra of compound 4f (with minor isomer)



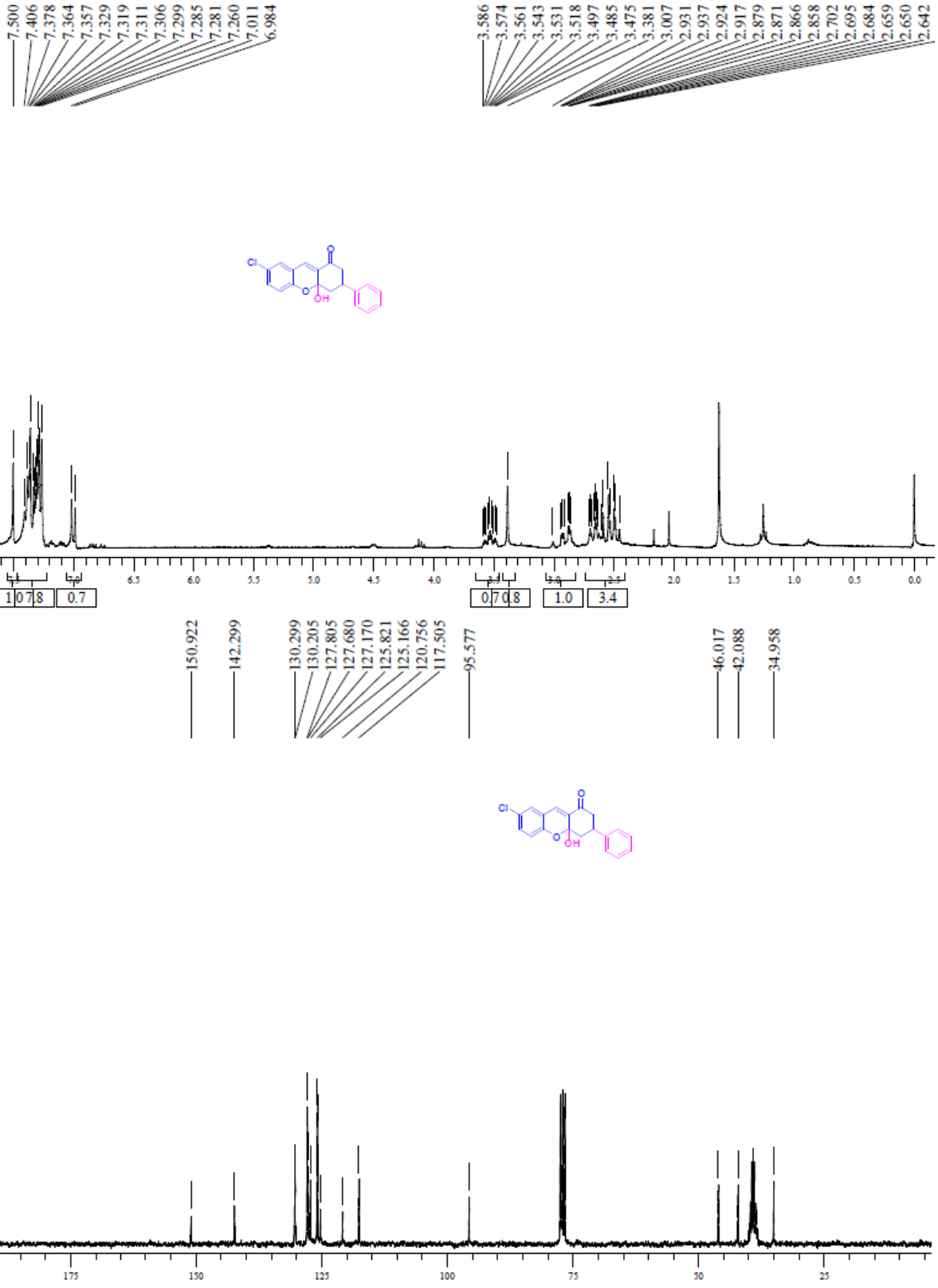
^{1}H and ^{13}C spectra of compound 4g (with minor isomer)



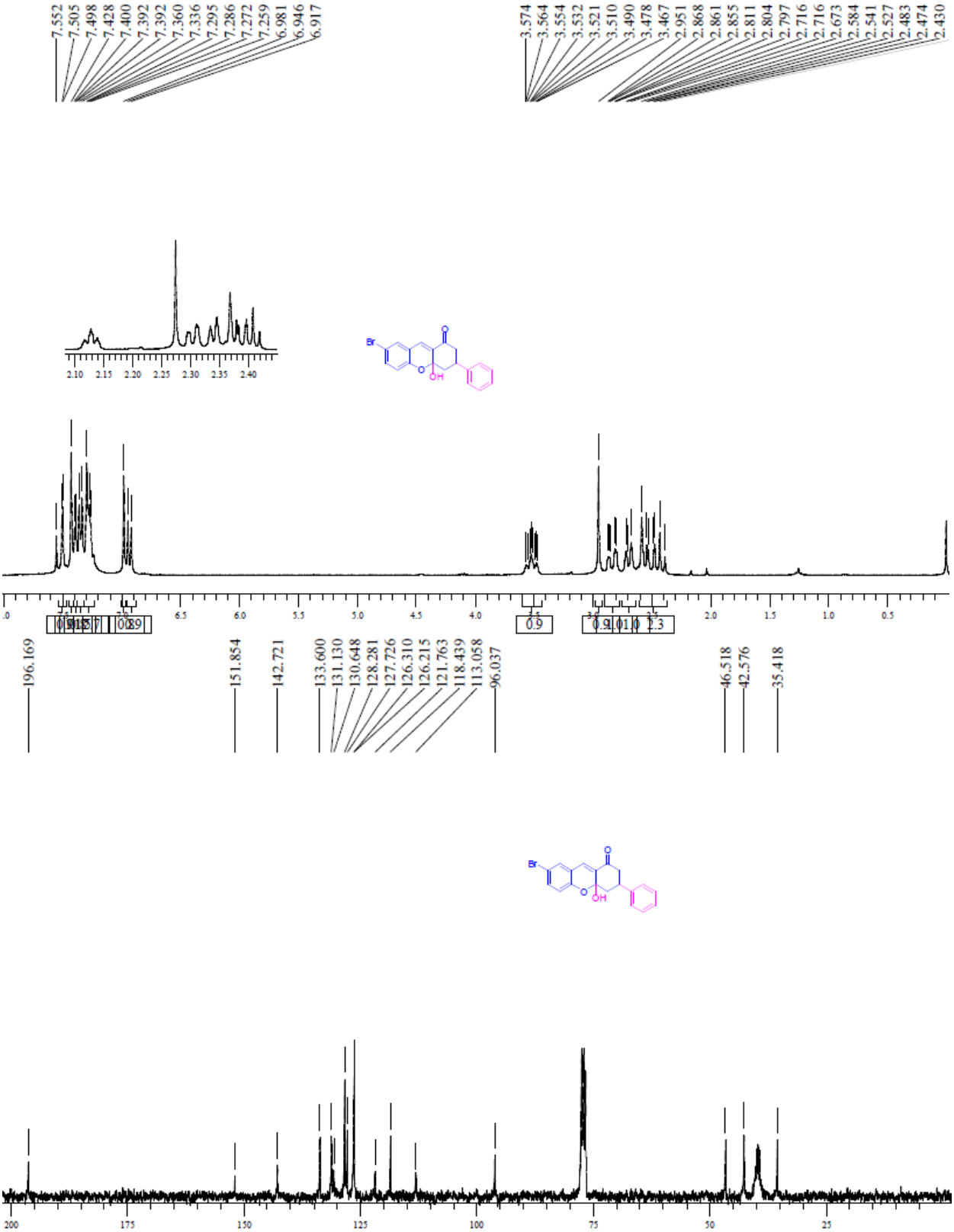
^{1}H and ^{13}C spectra of compound 5a (with minor isomer)



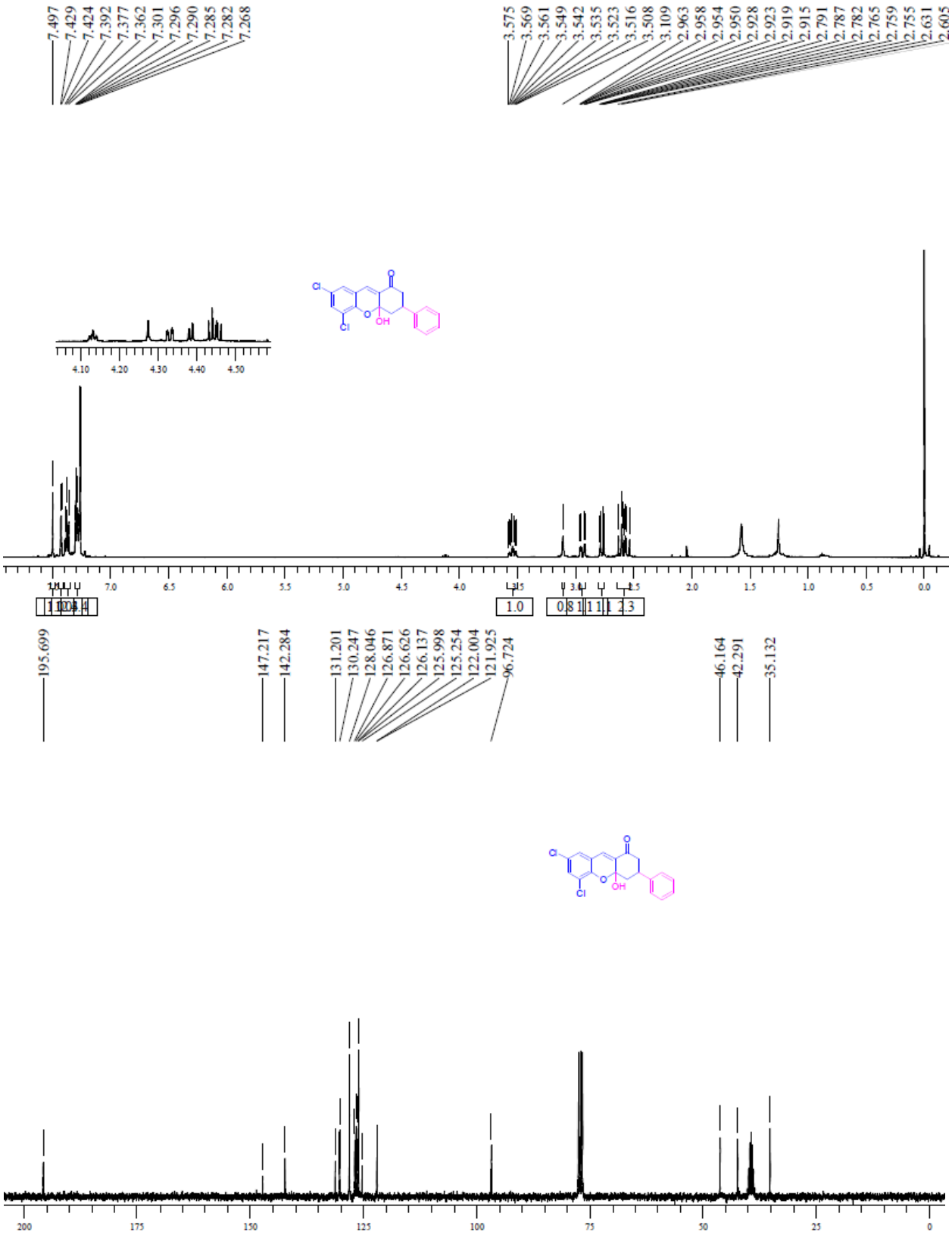
^{1}H and ^{13}C spectra of compound 5b (with minor isomer)



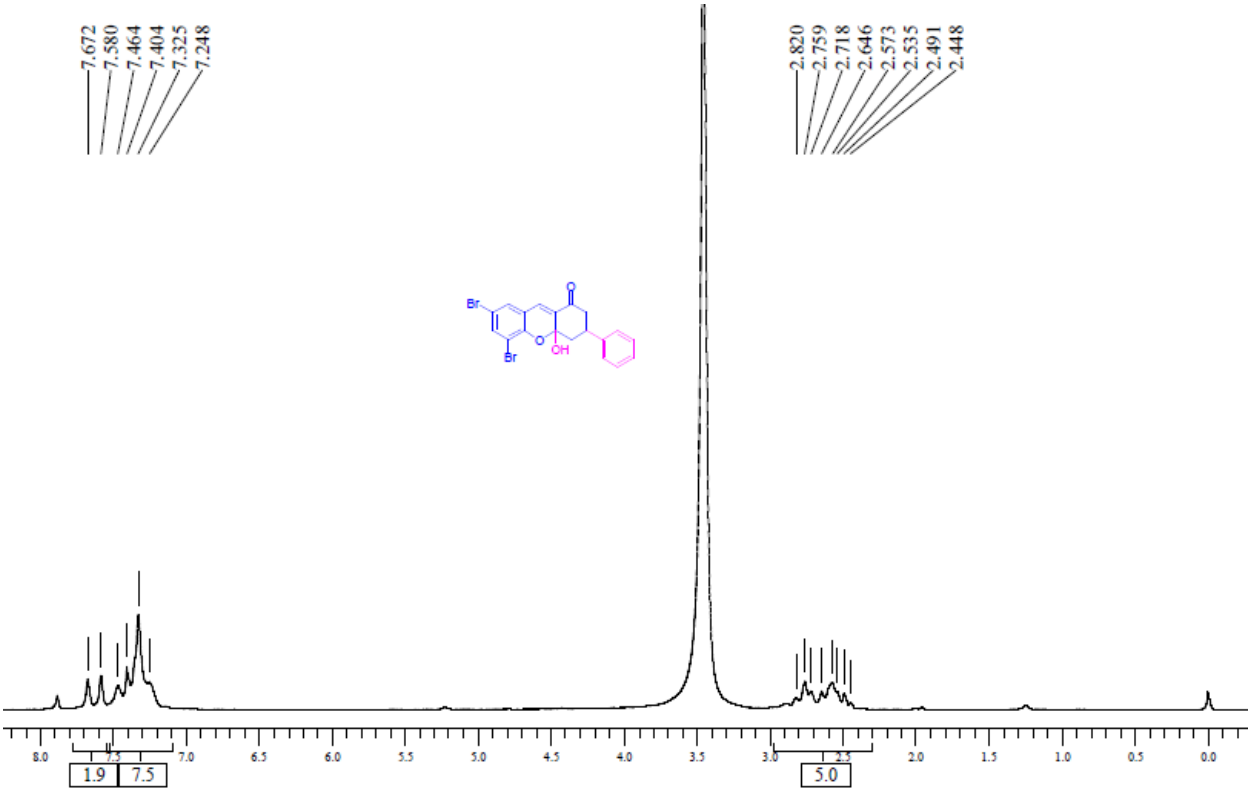
^{1}H and ^{13}C spectra of compound 5c (with minor isomer)

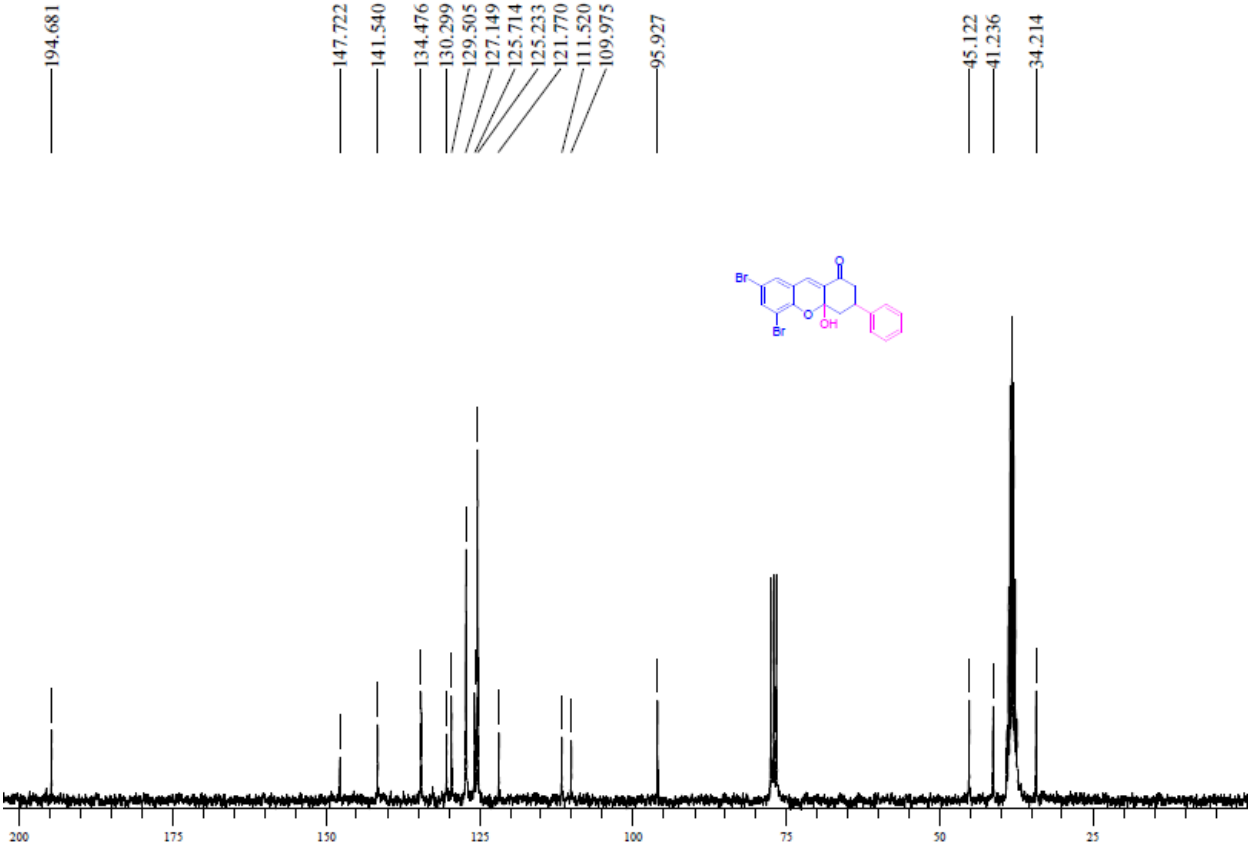


^{1}H and ^{13}C spectra of compound 5d (with minor isomer)



^{1}H and ^{13}C spectra of compound 5e (with minor isomer)





^{1}H and ^{13}C spectra of compound 5f (with minor isomer)