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Reactions of 3-functionalized chromones with triacetic acid lactone

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NMR spectra were recorded on Bruker DRX-400 (^{1}H – 400 MHz and ^{13}C – 100 MHz) and AVANCE-500 (^{1}H – 500 MHz and ^{13}C – 126 MHz) spectrometers with TMS as an internal standard. IR spectra were recorded on a Shimadzu IR Spirit instrument (ATR mode, diamond prism). Melting points were determined using Stuart SMP30 apparatus.

*3-Methyl-1*H*,5a*H*,11*H*-pyrano[3',4':5,6]pyrano[2,3-*b*]chromene-1,11-dione* **6a**. 3-Formylchromone **2a** (348 mg, 2 mmol) was dissolved in ethyl acetate (40 ml). Triacetic acid lactone **1** (269 mg, 2.13 mmol) and L-proline (115 mg, 1 mmol) were added to the resulting solution. The mixture was stirred for 5 h at room temperature. The precipitate was filtered off and washed with ethyl acetate, then with water and dried. Lemon yellow solid, yield 66%, mp 222–223 ºC (decomp.). IR (ATR, ν/cm^{-1}): 3089, 3058, 2963, 2925, 1714, 1668, 1628, 1602, 1575, 1538, 1464, 1448, 1422. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.34 (s, 3H, Me), 6.05 (s, 1H, H-4), 6.90 (s, 1H, H-5a), 7.10 (d, 1H, H-7, *J* 8.4 Hz), 7.19 (t, 1H, H-9, *J* 7.6 Hz), 7.59 (td, 1H, H-8, *J* 7.8, 1.3 Hz), 7.76 (s, 1H, H-12), 7.99 (dd, 1H, H-10, *J* 7.7, 1.2 Hz). Found (%): C, 68.16; H, 3.61. Calc. for $C_{16}H_{10}O_5$ (%): C, 68.09; H, 3.57.

*9-Chloro-3-methyl-1*H*,5a*H*,11*H*-pyrano[3',4':5,6]pyrano[2,3-*b*]chromene-1,11-dione* **6b**. This compound was obtained similarly to compound **6a**. Yellow solid, yield 60%, mp 216–217 ºC. IR (ATR, ν/cm^{-1}): 3086, 2930, 1736, 1732, 1716, 1667, 1631, 1604, 1573, 1535, 1533, 1469, 1455. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.34 (s, 3H, Me), 6.06 (s, 1H, H-4), 6.88 (s, 1H, H-5a), 7.06 (d, 1H, H-7, *J* 8.8 Hz), 7.52 (dd, 1H, H-8, *J* 8.8, 2.6 Hz), 7.77 (s, 1H, H-12), 7.94 (d, 1H, H-10, *J* 2.6 Hz). Found (%): C, 60.47; H, 2.58. Calc. for $C_{16}H_9ClO_5$ (%): C, 60.68; H, 2.86.

*(*E*)-4-Hydroxy-3-[3-(2-hydroxyphenyl)-3-oxoprop-1-enyl]-6-methyl-2*H*-pyran-2-one* **8**. A mixture of chromone-3-carboxylic acid **7** (150 mg, 0.79 mmol) and lactone **1** (130 mg, 1.06 mmol) in pyridine (5 ml) was stirred at 60 ºC for 2 h. Then 1 M HCl was added to the cooled reaction mixture until the medium became strongly acidic. The precipitate was filtered off, washed with water and dried. Yellow solid, yield 63%, mp 208–209 ºC (decomp.). IR (ATR, ν/cm^{-1}): 3300–2800, 1690, 1647, 1621, 1582, 1544, 1486, 1451, 1416, 1365, 1344, 1307. ^{1}H NMR (500 MHz, DMSO-d_6) δ: 2.27 (s, 3H, Me), 6.20 (s, 1H, H-5 pyrone), 6.95–7.03 (m, 2H, H-3, H-5 Ar), 7.53 (td, 1H, H-4 Ar, *J* 7.8, 1.5 Hz), 7.85 (dd, 1H, H-6 Ar, *J* 8.0, 1.3 Hz), 8.03 (d, 1H, α-H, *J*

15.2 Hz), 8.15 (d, 1H, β-H, *J* 15.2 Hz), 12.73 (br s, 1H, OH), the second OH proton was not observed. ^{13}C NMR (126 MHz, DMSO-d_6) δ: 19.9 (Me), 97.8, 100.2, 117.8, 118.5, 119.2, 120.8, 129.6, 135.8, 161.81, 161.83, 165.4 (C=O lactone), 171.7 (=C–OH lactone), 193.9 (C=O), one C atom was not observed. Found (%): C, 66.21; H, 4.41. Calc. for $C_{15}H_{12}O_5$ (%): C, 66.17; H, 4.44.

*(Z)-3-(1-Hydroxy-3-oxobut-1-en-1-yl)-2*H*,5*H*-pyrano[3,2-*c*]chromene-2,5-dione* **10**. A mixture of methyl chromone-3-carboxylate **9** (150 mg, 0.73 mmol), lactone **1** (92.7 mg, 0.73 mmol) and pyridine (291 mg, 3.8 mmol) was boiled in toluene (10 ml) for 4 h. The resulting solution was cooled and left at –18 ºC overnight. The precipitate was filtered off, washed with toluene and dried in air. Yellow solid, yield 36%, mp 238–239 ºC (decomp.) (lit. [S1] mp 242–243 ºC). IR (ATR, ν/cm^{-1}): 3118, 3093, 3062, 1753, 1723, 1624, 1580, 1555, 1487, 1448, 1392, 1299, 1187, 1176, 1109. ^{1}H NMR (500 MHz, DMSO-d_6) enol (80%), δ: 2.28 (s, 3H, Me), 6.86 (s, 1H, =CH enol), 7.55 (td, 1H, H-9, *J* 7.6, 0.8 Hz), 7.60 (d, 1H, H-7, *J* 8.3 Hz), 7.88 (td, 1H, H-8, *J* 7.8, 1.5 Hz), 8.09 (dd, 1H, H-10, *J* 7.9, 1.4 Hz), 8.59 (s, 1H, H-4), 16.02 (br s, 1H, OH). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 27.6 (Me), 101.3, 103.8, 112.7, 117.7, 119.8, 124.1, 125.5, 135.6, 142.9, 154.3, 155.7, 158.1 (C=O coumarin), 162.9 (C=O lactone), 170.6 (=C–OH), 199.8 (C=O). Found (%): C, 64.21; H, 3.34. Calc. for $C_{16}H_{10}O_6$ (%): C, 64.43; H, 3.38.

*(Z)-3-(1-Hydroxy-3-oxobut-1-en-1-yl)-2*H*-chromeno[2,3-*b*]pyridine-2,5(1*H*)-dione* **12a**. A mixture of 3-cyanochromone **11** (150 mg, 0.857 mmol), lactone **1** (108 mg, 0.857 mmol) and piperidine (2–3 drops) in absolute ethanol (7 ml) was refluxed for 2 h. The precipitate was filtered off. An additional amount of product was obtained from the filtrate by evaporation to dryness and washing the residue with ethanol (2 ml). The resulting product was washed with boiling ethanol (15 ml) and dried in air. Green solid, yield 51%, mp 255–257 ºC (decomp.). IR (ATR, ν/cm^{-1}): 3128, 3070, 3010, 2900–2400, 1641, 1614, 1583, 1563, 1502, 1465, 1401, 1339, 1312, 1243. ^{1}H NMR (500 MHz, DMSO-d_6) enol (89%), δ: 2.22 (s, 3H, Me), 7.03 (s, 1H, =CH enol), 7.55 (t, 1H, H-7, *J* 7.6 Hz), 7.63 (d, 1H, H-9, *J* 8.3 Hz), 7.87 (td, 1H, H-8, *J* 7.8, 1.7 Hz), 8.15 (dd, 1H, H-6, *J* 7.8, 1.6 Hz), 8.80 (s, 1H, H-4), 13.92 (br s, 1H, NH), 16.25 (br s, 1H, OH). Found (%): C, 64.55; H, 3.74; N, 4.77. Calc. for $C_{16}H_{11}NO_5$ (%): C, 64.65; H, 3.73; N, 4.71.

*(Z)-3-(1-Hydroxy-3-oxobut-1-en-1-yl)-1-phenyl-2*H*-chromeno[2,3-*b*]pyridine-2,5(1*H*)-dione* **12b**. A mixture of 2-phenylamino-3-formylchromone **14** (200 mg, 0.78 mmol), lactone **1** (196.7 mg, 1.56 mmol) and Et_3N (0.1 ml) was boiled in ethanol (7 ml) for 7 h. The precipitate formed was filtered off, washed with ethanol and recrystallized from the mixture chloroform–ethanol (2:1). Orange solid, yield 27%, mp >275 ºC. IR (ATR, ν/cm^{-1}): 3126, 3063, 1686, 1659, 1618, 1615, 1605, 1595, 1583, 1524, 1520, 1460, 1439, 1435, 1418, 1370. ^{1}H NMR (400 MHz, $CDCl_3$) enol (97%), δ: 2.18 (s, 3H, Me), 7.06 (s, 1H, =CH enol), 7.14 (d, 1H, H-9, *J* 8.5 Hz), 7.35 (m, 2H, H-7, Ph-H), 7.47 (t, 1H, H-8, *J* 7.5 Hz), 7.58–7.68 (m, 4H, Ph-H), 8.31 (dd, 1H, H-6, *J* 7.5, 1.3 Hz), 9.25 (s, 1H, H-4), 15.92 (s, 1H, OH). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 27.3 (Me), 101.1, 102.5, 117.7, 120.2, 122.0, 126.4, 126.8, 128.1, 129.9, 133.5, 134.6, 139.3, 153.6, 156.8, 159.6 (N–C=O), 173.3 (=C–OH), 173.4 (C=O chromone), 199.0 (C=O), one C atom was not observed. Found (%): C, 70.77; H, 4.06; N, 3.86. Calc. for $C_{22}H_{15}NO_5$ (%): C, 70.77; H, 4.05; N, 3.75.

Single-crystal X-ray diffraction analysis was performed on an Xcalibur 3 automatic diffractometer using the standard procedure (MoK$_6$ irradiation, graphite monochromator, ω-scanning with 1º step, 295(2) K). An empirical adjustment for absorption was introduced. The structures were solved and refined using the OLEX2 software package [S2]. The structures were solved by the direct method using ShelXS program [S3] and refined by fullmatrix least squares method against F^2 using ShelXL program in anisotropic approximation for nonhydrogen atoms. The hydrogen atoms of C–H bonds were placed in geometrically calculated positions and included in the refinement in the “riding” model.

References

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[S2] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339.

[S3] G. M. Sheldrick, *Acta Crystallogr. A*, 2008, **64**, 112.

Table S1 Optimization of the reaction conditions for the synthesis of compound **8**.

Conditions	Time, h	TAL, equiv.	Yield, %
Toluene, reflux	4	1	–[a]
Toluene, Py (5 equiv.), reflux	5	1	15[b]
Toluene, Py (1 equiv.), reflux	8	1	–[a]
Toluene, Py (5 equiv.), reflux	5	1.3	19[b]
Toluene, TEA, (1 equiv.), 90 °C	1	1	–[c]
Toluene, TEA, (1 drop), 70 °C	1	1.3	traces
Toluene, TEA, (1 drop), 70 °C	7	1.3	28[d]
Dioxane, Py (5 equiv.), reflux	3	1.3	30[d]
Ethanol, 60 °C	3	1	13[e]
Pyridine, 60 °C	**2**	**1.3**	**63[b]**

[a] Starting materials were isolated.

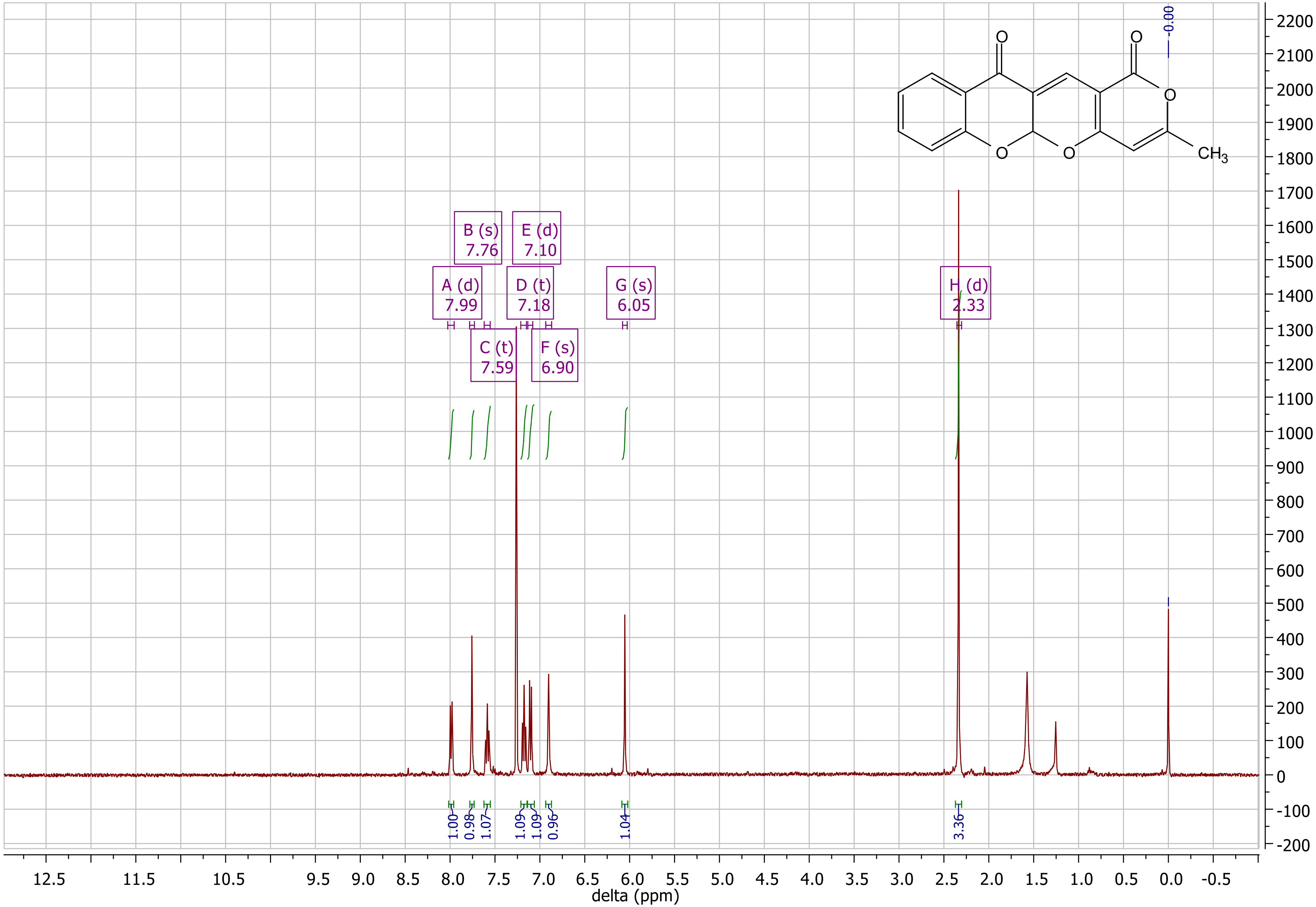
[b] Pyridine salt of the product was obtained, the product was isolated by acidification of the latter.

[c] Resinification.

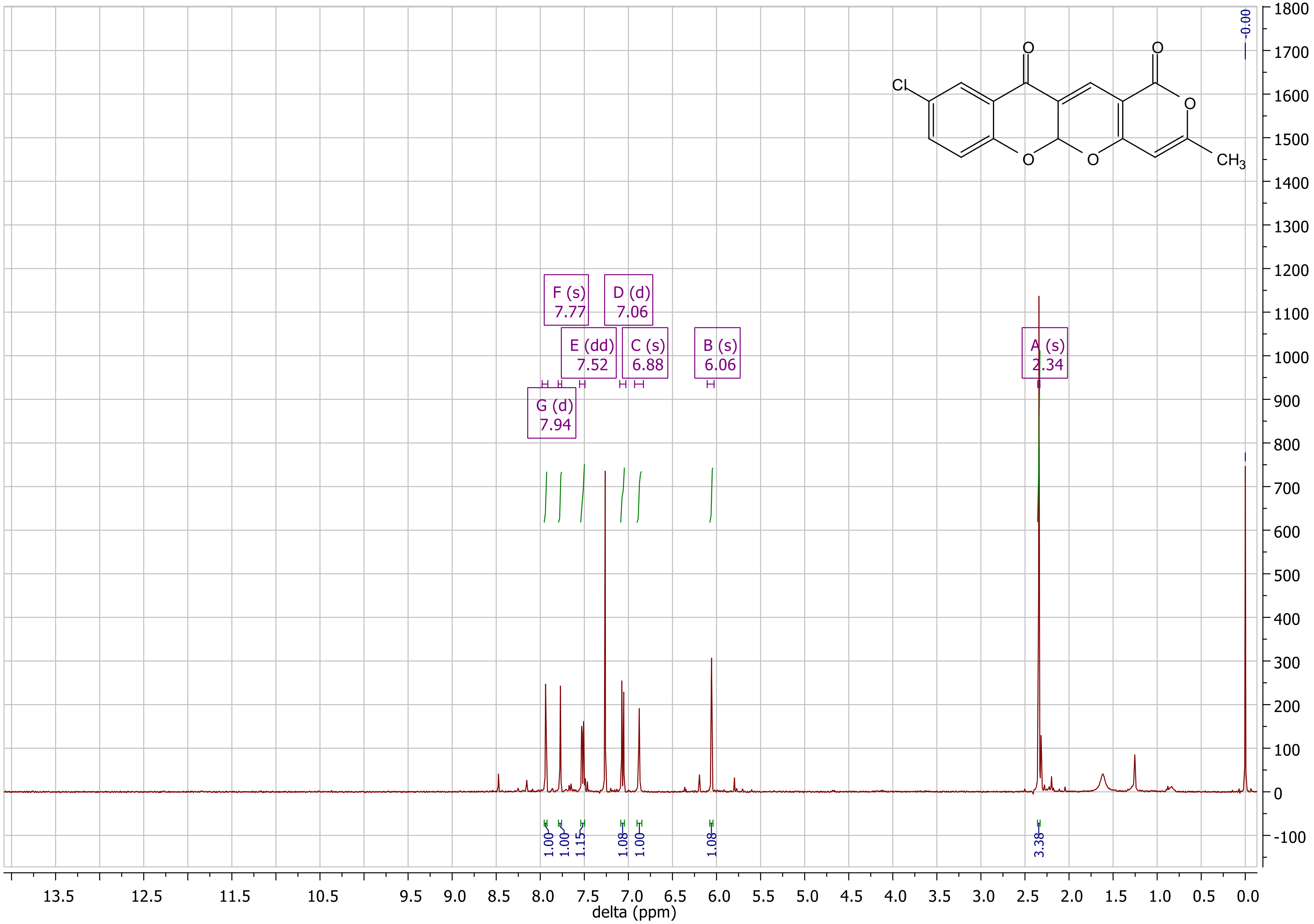
[d] Yield was calculated on the base of the NMR data.

[e] Unsubstituted chromone was obtained as a major product.

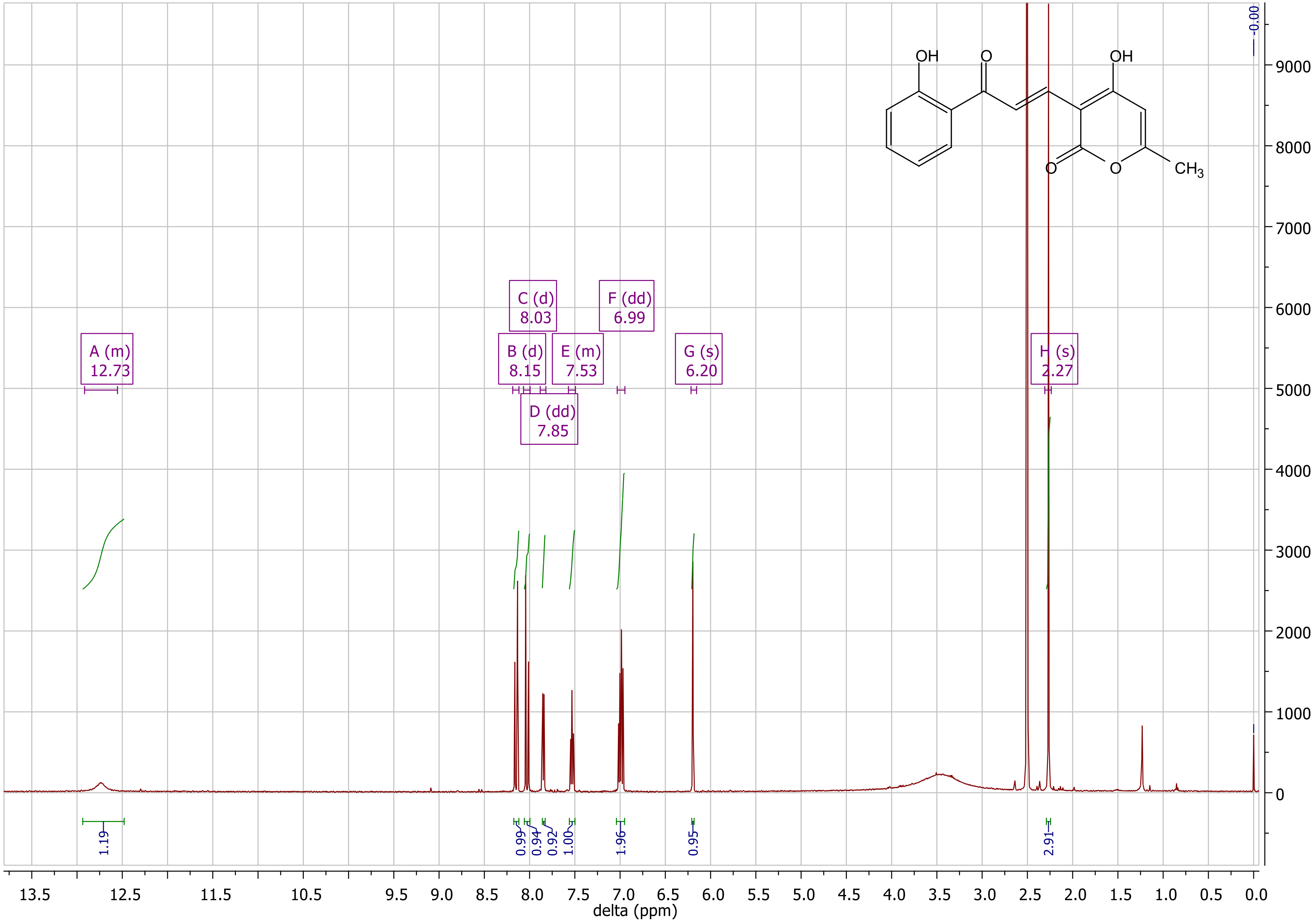
^{1}H NMR spectrum of compound **6a** (CDCl$_3$)



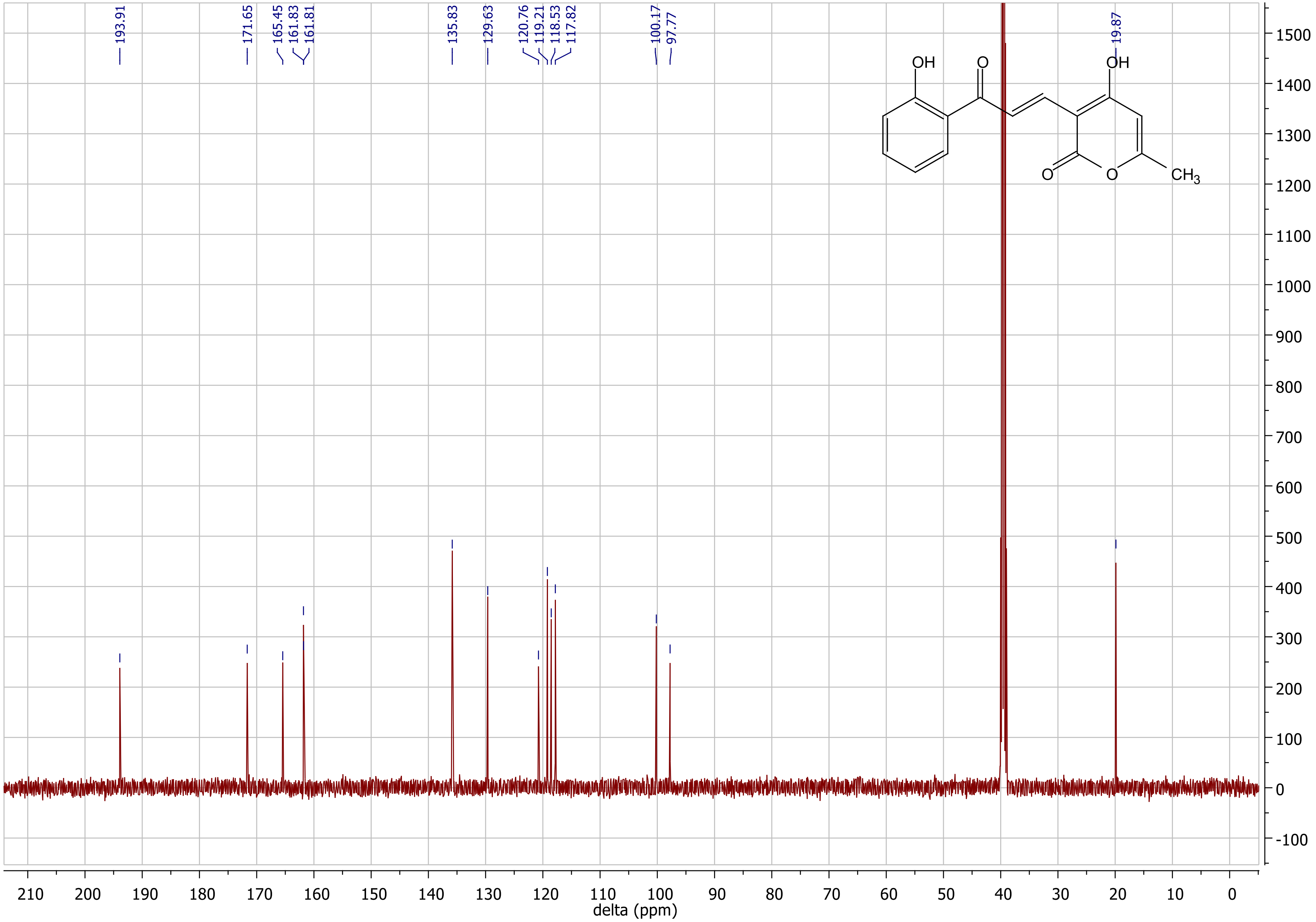
^{1}H NMR spectrum of compound **6b** ($CDCl_3$)



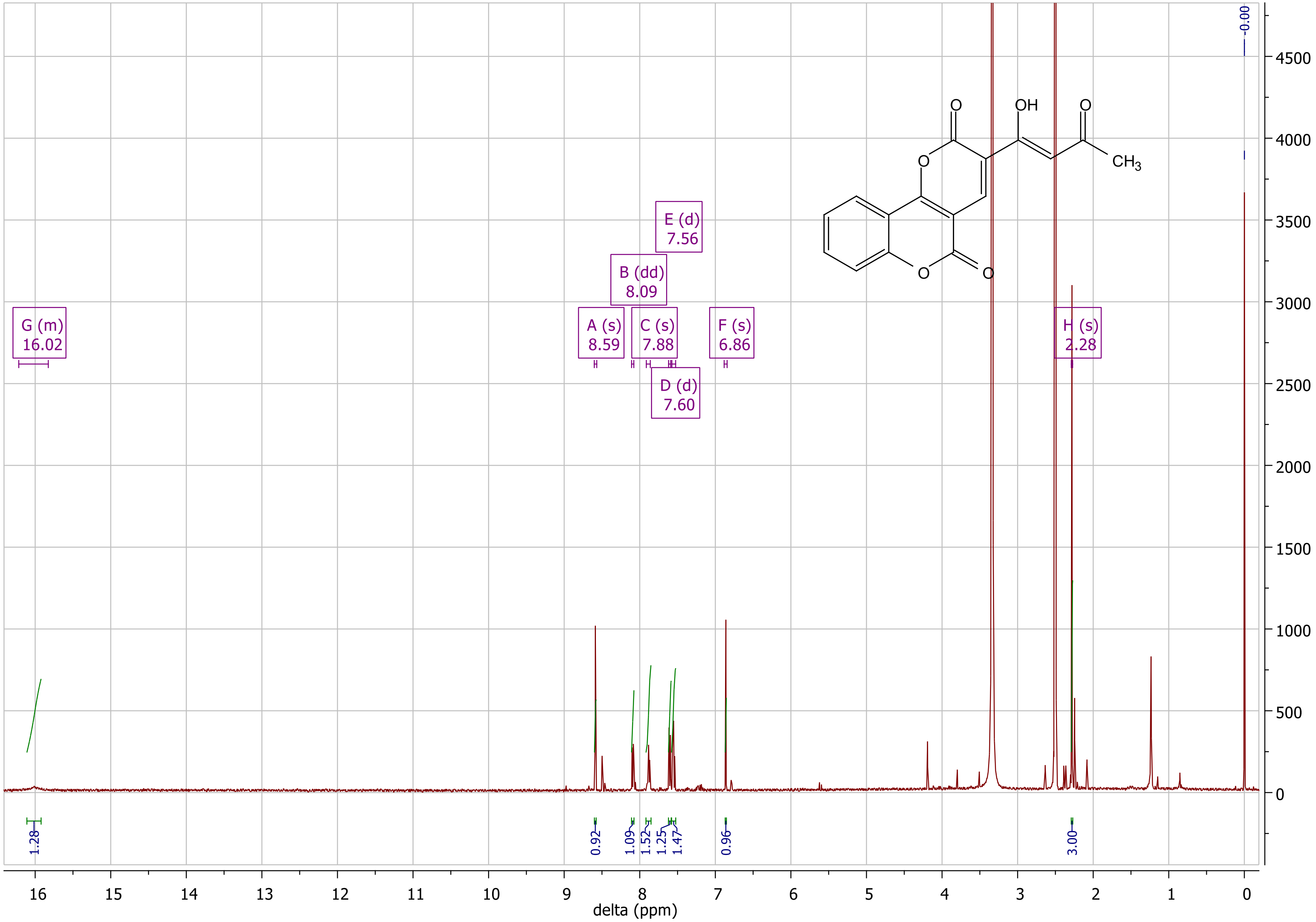
^{1}H NMR spectrum of compound **8** (DMSO-d_6)



^{13}C NMR spectrum of compound **8** (DMSO-d_6)



^{1}H NMR spectrum of compound **10** (DMSO-d_6)



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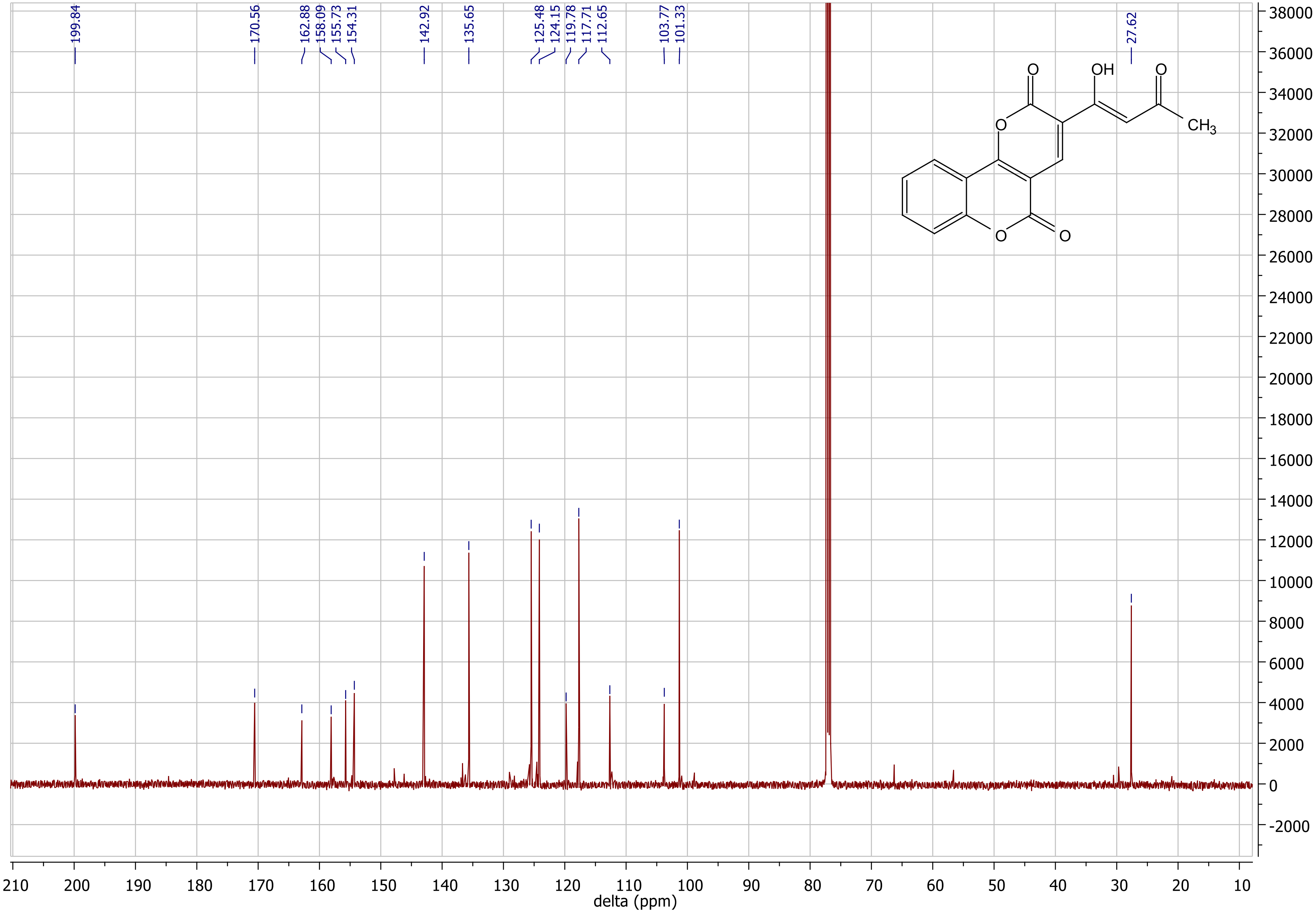
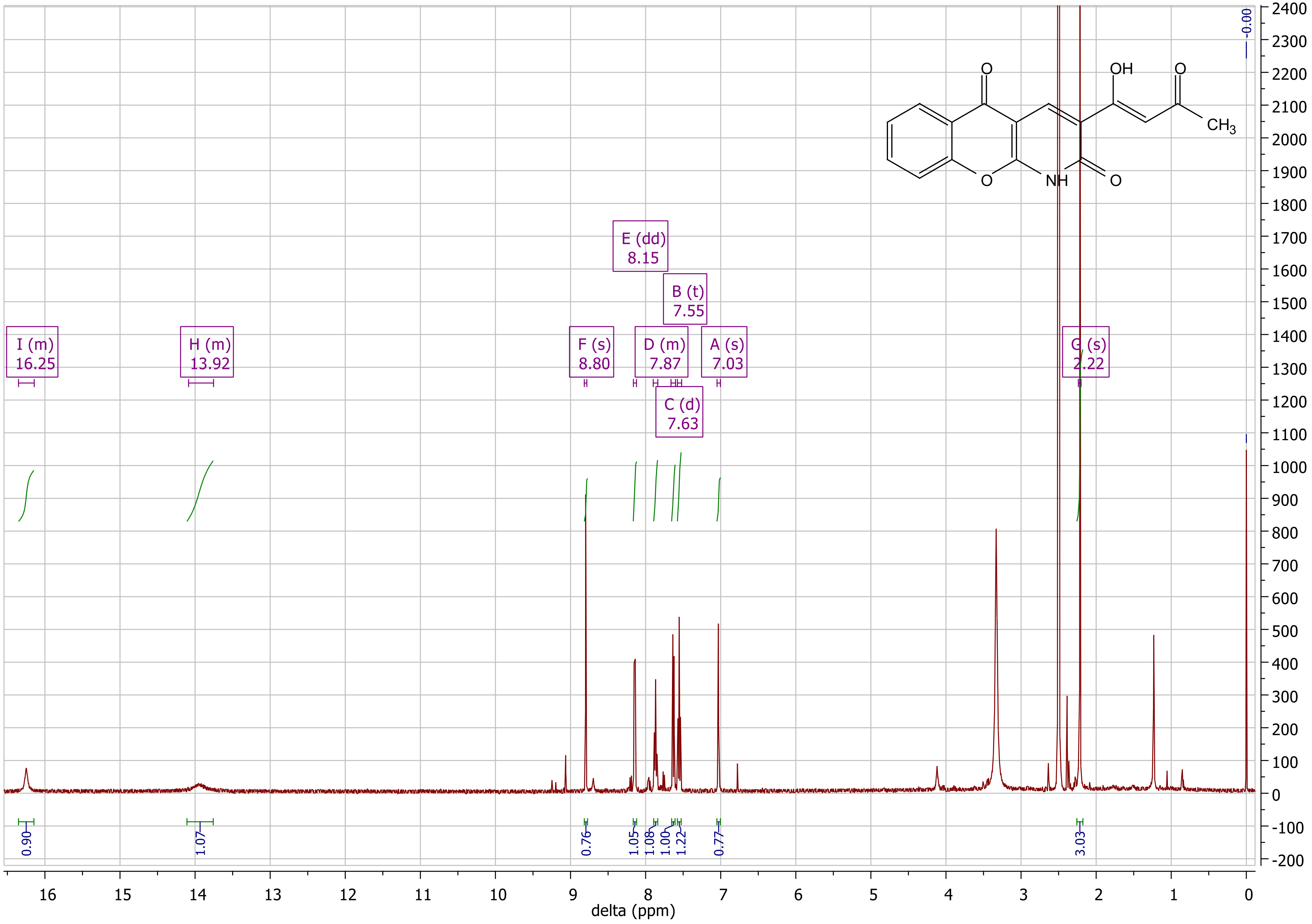
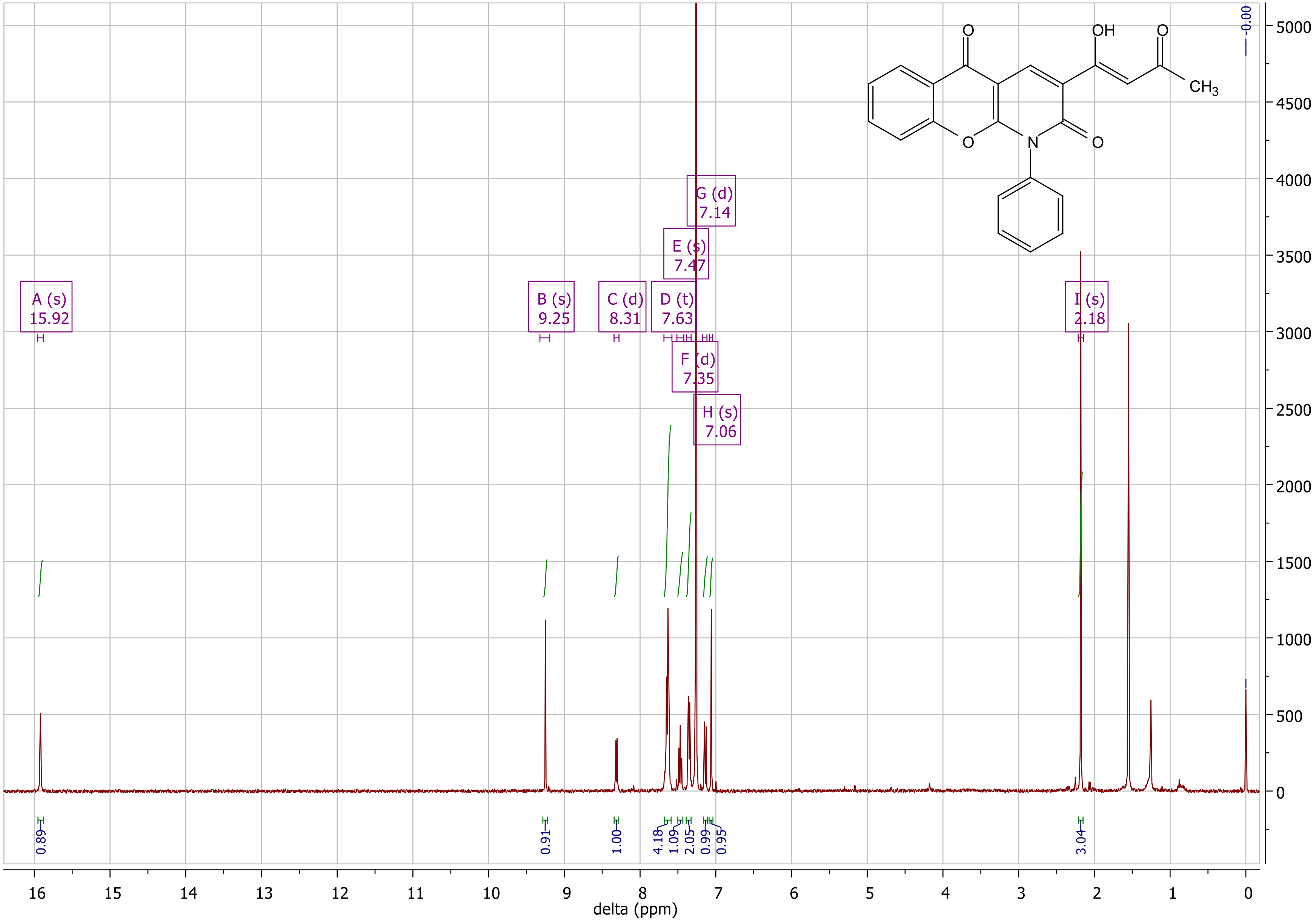


^{1}H NMR spectrum of compound **12a** (DMSO-d_6)



^{1}H NMR spectrum of compound **12b** ($CDCl_3$)



^{13}C NMR spectrum of compound **12b** ($CDCl_3$)