

Supporting Information

**Rh-catalyzed domino synthesis of 4-hydroxy-3-methylcoumarins
via branch-selective hydroacylation**

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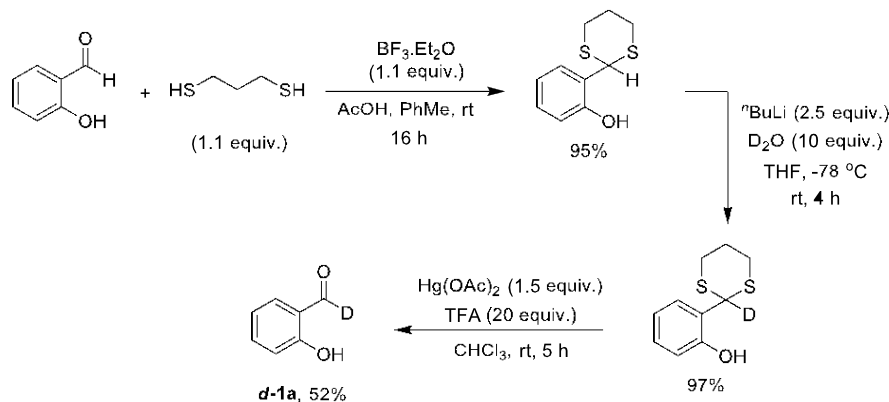
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1. General Information

The coupling reactions were performed in dry Schlenk tubes under nitrogen atmosphere conditions. Standard procedures were followed to dry various solvents used in coupling reactions. All the NMR (^1H and ^{13}C) spectra were recorded on a JEOL ECS-400/ECX-500 spectrometer in CDCl_3 with TMS as the internal standard. Data have shown as chemical shift in ppm, multiplicity and coupling constant (Hz). Infrared spectra (IR) were obtained using a PerkinElmer FT/IR spectrometer and absorptions are reported in reciprocal centimeters. High resolution mass spectra (HRMS) were obtained using Waters GCT Premier-CAB155 and Waters-Q-ToF Premier-HAB213 instruments with Electron ionisation and Electrospray ionisation techniques. Melting points were determined using a Yamato melting point apparatus. Column chromatography was performed with silica-gel (100-200 mesh). All the acrylates and *N,N*-dimethylacrylamide were purchased commercially and used without further purifications. The salicylaldehyde, 3-methoxysalicylaldehyde, 5-bromosalicylaldehyde, 3-bromo-5-chloro and 2-hydroxy-1-naphthaldehyde were purchased from commercial suppliers. The other substituted salicylaldehydes which includes 5-methyl,^a 5-fluoro,^a 5-chloro,^b 5-acetyl,^c 5-cyano,^d 5-methoxycarbonyl,^d 5-formyl,^d 5-nitro,^d 3,5-dichloro,^d 4-hydroxy,^e 4-methoxy^f and 3,4,5-trimethoxysalicylaldehyde^g were prepared from the literature known procedures.

2. Synthesis of starting materials

Preparation of deuterium-labeled salicylaldehyde (*d*-1a):^h

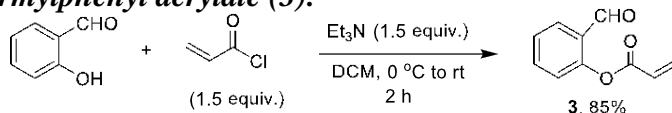


2-(2'-Hydroxyphenyl)-1,3-dithiane: In an oven-dried 150 mL R.B flask kept under nitrogen atmosphere, $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (9.9 mmol, 1.22 mL) was added to the solution of salicylaldehyde (9 mmol, 1.1 g), 1,3-propane dithiol (9.9 mmol, 1 mL) and acetic acid (9 mL) in toluene (20 mL). The reaction mixture was stirred at room temperature for 16 h and quenched with water, extracted with ethyl acetate. The organic contents was washed with saturated NaHCO_3 solution, brine and dried over anhydrous MgSO_4 . The solvent was evaporated and purified by column chromatography to obtain dithiane (1.82 g, 95%) as colourless solid.

Deuterated 2-(2'-hydroxyphenyl)-1,3-dithiane: In an oven-dried 100 mL R.B flask kept under nitrogen atmosphere, dithiane (4.7 mmol, 1 g) was taken in THF (40 mL) and cooled to -78°C . To this, *n*-BuLi in hexane (11.78 mmol, 7.5 mL) was added dropwise and stirred for 2 h. Reaction mixture was quenched with D_2O (47.1 mmol, 0.9 mL) at -78°C , brought to room temperature and quenched with dil.HCl. THF was removed and the residue was extracted with DCM, washed with saturated NaHCO_3 solution, brine and dried over anhydrous MgSO_4 . The solvent was evaporated and the product was purified by column chromatography to obtain dithiane-*d* (0.98 g, 97%) as colourless solid.

Deuterium-labeled salicylaldehyde (*d*-1a):ⁱ In an oven-dried 100 mL R.B flask, Hg(OAc)₂ (2.84 mmol, 0.9 g) was taken in trifluoroacetic acid (4 mL). It was stirred at room temperature for 2 h. To this dithiane-*d* (1.88 mmol, 0.4 g) in chloroform was added and stirred for 5 h. The mixture was filtered through celite and the organic contents was washed with water, brine, dried over anhydrous MgSO₄. Solvent was evaporated and the crude was purified by column chromatography to obtain deuterated salicylaldehyde (*d*-1a) (0.12 g, 52%) as colourless liquid. ¹H NMR (400 MHz, CDCl₃) δ 11.04 (s, 1H, OH), 7.58-7.51 (m, 2H, Ar-H), 7.04-6.98 (m, 2H, Ar-H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 196.41 (t, *J*_{C-D} = 27.1 Hz), 161.83, 137.17, 133.84, 120.70, 119.99, 117.77 ppm.

Preparation of 2-formylphenyl acrylate (*3*):^j

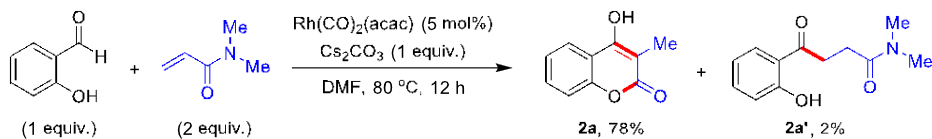


In an oven-dried 100 mL R.B flask, salicylaldehyde (16.38 mmol, 2 g) was taken in DCM (50 mL). It was cooled to 0 °C and then added triethylamine (24.57 mmol, 3.45 mL), acryloyl chloride (24.57 mmol, 2 mL) sequentially. The mixture was stirred at room temperature for 2 h and quenched with water, extracted with DCM. The organic content was washed with brine and dried over anhydrous MgSO₄. The solvent was evaporated and product was subjected to column chromatography to obtain 2-formylphenyl acrylate (*3*) (2.45 g, 85%) as colourless liquid. ¹H NMR (400 MHz, CDCl₃) δ 10.15 (s, 1H, CHO), 7.92 (dd, *J* = 7.6, 1.7 Hz, 1H, Ar-H), 7.66 (dd, *J* = 7.8, 1.7 Hz, 1H, Ar-H), 7.41 (t, *J* = 7.5 Hz, 1H, Ar-H), 7.26-7.23 (m, 1H, Ar-H), 6.68 (d, *J* = 18.1 Hz, 1H, CH), 6.39 (dd, *J* = 17.5, 10.5 Hz, 1H, CH), 6.11 (dd, *J* = 10.4, 1.0 Hz, 1H, CH) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 188.57, 164.35, 151.94, 135.47, 133.92, 130.49, 128.21, 127.23, 126.65, 123.51 ppm. IR (KBr, cm⁻¹): 3080, 2859, 2758, 1746, 1701, 1604, 1403, 1245, 1208, 1144, 759.

3. General procedure for coupling reactions

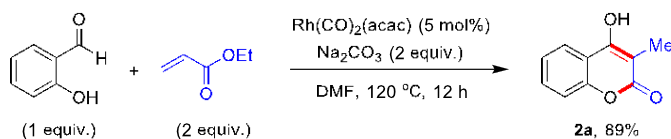
Conditions-A:

The coupling reaction was performed by charging a dry Schlenk tube with salicylaldehyde (61 mg, 0.5 mmol), *N,N*-dimethylacrylamide (99.1 mg, 1 mmol), Rh(CO)₂(acac) (6.4 mg, 0.025 mmol), Cs₂CO₃ (163 mg, 0.5 mmol) and DMF (2 mL) solvent. The mixture was stirred at 80 °C in an oil bath for 12 h. It was brought to rt, quenched with dil. HCl and extracted with ethyl acetate (30 mL). The organic content was washed with water (15 mL), brine (15 mL), dried over anhydrous MgSO₄ and concentrated. The crude product was purified by silica gel column chromatography using ethyl acetate/hexane as eluent. The product *2a* was obtained as colourless solid (67 mg, 78%) along with linear hydroacylation product *2a'* as yellow solid (3 mg, 2%).



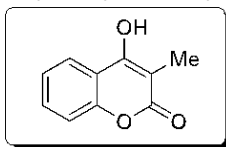
Conditions-B:

The coupling reaction was performed by charging a dry Schlenk tube with salicylaldehyde (61 mg, 0.5 mmol), ethyl acrylate (100.1 mg, 1.0 mmol), Rh(CO)₂(acac) (6.4 mg, 0.025 mmol), Na₂CO₃ (106 mg, 1 mmol) and DMF (2 mL) solvent. The mixture was stirred at 120 °C in an oil bath for 12 h. It was brought to rt, quenched with dil. HCl and extracted with ethyl acetate (30 mL). The organic content was washed with water (15 mL), brine (15 mL), dried over anhydrous MgSO₄ and concentrated. The crude was purified by silica gel column chromatography using ethyl acetate/hexane as eluent. The product **2a** was obtained as colourless solid (79 mg, 89%).

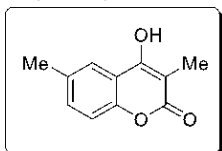


4. Characterization data for the products

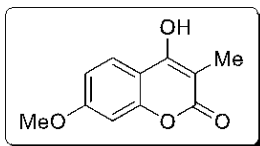
4-Hydroxy-3-methyl-2H-chromen-2-one (2a):^k Colourless solid (79 mg, 89%); mp 214-216 °C. ¹H NMR (500 MHz, DMSO-*d*₆) δ 11.28 (s, 1H, OH), 7.90-7.88 (m, 1H, Ar-H), 7.58-7.55 (m, 1H, Ar-H), 7.35-7.31 (m, 2H, Ar-H), 1.99 (s, 3H, Me) ppm. ¹³C NMR (125 MHz, DMSO-*d*₆) δ 163.14, 159.77, 151.65, 131.38, 123.78, 122.95, 116.31, 116.02, 100.26, 9.74 ppm. IR (KBr, cm⁻¹): 3177, 2926, 2854, 1668, 1615, 1570, 1236, 1209, 1185, 1089, 750. HRMS (ESI⁺): calcd for C₁₀H₉O₃ [M+H]⁺ 177.0552; found 177.0547.



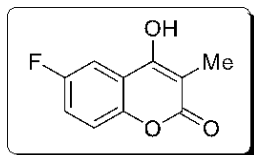
4-Hydroxy-3,6-dimethyl-2H-chromen-2-one (2b):^k Colourless solid (59 mg, 62%); mp 222-224 °C. ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.69 (s, 1H, Ar-H), 7.38 (d, *J* = 8.0 Hz, 1H, Ar-H), 7.23 (d, *J* = 8.3 Hz, 1H, Ar-H), 2.37 (s, 3H, Me), 1.98 (s, 3H, Me) ppm. ¹³C NMR (100 MHz, DMSO-*d*₆) δ 163.28, 159.76, 149.80, 132.98, 132.21, 122.60, 115.98, 115.82, 100.15, 20.47, 9.77 ppm. IR (KBr, cm⁻¹): 3156, 1666, 1617, 1579, 1502, 1239, 1199, 1097, 812. HRMS (ESI⁺): calcd for C₁₁H₁₁O₃ [M+H]⁺ 191.0708; found 191.0707.



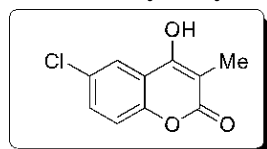
4-Hydroxy-7-methoxy-3-methyl-2H-chromen-2-one (2c):^l Colourless solid (71 mg, 69%); mp 206-208 °C. ¹H NMR (400 MHz, DMSO-*d*₆) δ 11.14 (s, 1H, OH), 7.79 (d, *J* = 9.6 Hz, 1H, Ar-H), 6.93-6.90 (m, 2H, Ar-H), 3.83 (s, 3H, OMe), 1.95 (s, 3H, Me) ppm. ¹³C NMR (100 MHz, DMSO-*d*₆) δ 163.53, 161.92, 160.30, 153.39, 124.08, 111.67, 109.49, 100.25, 97.45, 55.79, 9.55 ppm. IR (KBr, cm⁻¹): 3087, 3017, 1671, 1631, 1609, 1573, 1519, 1311, 1235, 1160, 1088, 1029, 851, 754. HRMS (ESI⁺): calcd for C₁₁H₁₁O₄ [M+H]⁺ 207.0657; found 207.0643.



6-Fluoro-4-hydroxy-3-methyl-2H-chromen-2-one (2d): Colourless solid (65 mg, 67%); mp 204-206 °C. ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.64-7.61 (m, 1H, Ar-H), 7.47-7.39 (m, 2H, Ar-H), 1.99 (s, 3H, Me) ppm. ¹³C NMR (125 MHz, DMSO-*d*₆) δ 162.96, 158.99 (d, *J*_{C-F} = 2.8 Hz), 157.93 (d, *J*_{C-F} = 238.5 Hz), 147.95 (d, *J*_{C-F} = 1.9 Hz), 118.64 (d, *J*_{C-F} = 24.4 Hz), 118.11 (d, *J*_{C-F} = 8.6 Hz), 117.51 (d, *J*_{C-F} = 8.9 Hz), 108.53 (d, *J*_{C-F} = 25.4 Hz), 101.20, 9.83 ppm. IR (KBr, cm⁻¹): 3157, 1676, 1620, 1579, 1498, 1229, 1186, 1082, 830, 737. HRMS (ESI⁺): calcd for C₁₀H₈FO₃ [M+H]⁺ 195.0457; found 195.0451.

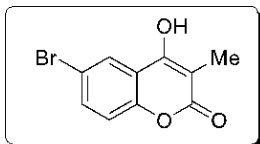


6-Chloro-4-hydroxy-3-methyl-2H-chromen-2-one (2e):^m Colourless solid (78 mg, 74%); mp 222-224 °C. ¹H NMR (500 MHz, DMSO-*d*₆) δ 7.85 (d, *J* = 2.4 Hz, 1H, Ar-H), 7.59 (dd, *J* = 8.8, 2.5 Hz, 1H, Ar-H), 7.37 (d, *J* = 8.7 Hz, 1H, Ar-H), 1.98 (s, 3H, Me) ppm. ¹³C NMR (100 MHz, DMSO-*d*₆) δ 162.74, 158.65, 150.24, 131.04, 127.89, 122.20, 118.14, 117.81, 101.33, 9.87 ppm. IR (KBr, cm⁻¹): 3170, 1678, 1611, 1569, 1489, 1237, 1206, 1177, 818. HRMS (ESI⁺): calcd for C₁₀H₈ClO₃ [M+H]⁺ 211.0162; found

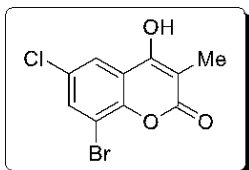


211.0162.

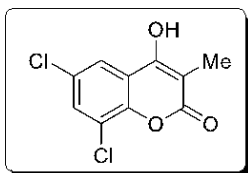
6-Bromo-4-hydroxy-3-methyl-2H-chromen-2-one (2f): Brown solid (66 mg, 52%); mp 226-228 °C. ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.00 (d, *J* = 2.4 Hz, 1H, Ar-H), 7.72 (dd, *J* = 8.8, 2.4 Hz, 1H, Ar-H), 7.32 (d, *J* = 8.8 Hz, 1H, Ar-H), 1.99 (s, 3H, Me) ppm. ¹³C NMR (100 MHz, DMSO-*d*₆) δ 162.70, 158.57, 150.67, 133.87, 125.16, 118.47, 118.26, 115.66, 101.35, 9.86 ppm. IR (KBr, cm⁻¹): 3182, 1678, 1611, 1566, 1492, 1233, 1202, 1175, 812. HRMS (ESI⁺): calcd for C₁₀H₈BrO₃ [M+H]⁺ 254.9657; found 254.9657.



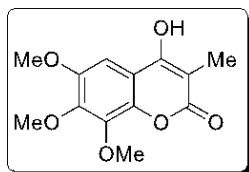
8-Bromo-6-chloro-4-hydroxy-3-methyl-2H-chromen-2-one (2g): Colourless solid (76 mg, 52%); mp 231-234 °C. ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.98 (d, *J* = 2.4 Hz, 1H, Ar-H), 7.85 (d, *J* = 2.4 Hz, 1H, Ar-H), 2.00 (s, 3H, Me) ppm. ¹³C NMR (100 MHz, DMSO-*d*₆) δ 161.94, 158.43, 147.27, 133.46, 128.18, 121.98, 118.86, 110.03, 101.71, 9.97 ppm. IR (KBr, cm⁻¹): 3087, 1705, 1677, 1607, 1559, 1224, 1204, 1173, 1082, 864, 790. HRMS (ESI⁺): calcd for C₁₀H₇BrClO₃ [M+H]⁺ 288.9267; found 288.9269.



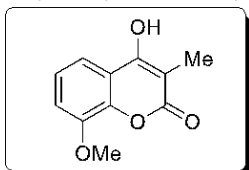
6,8-Dichloro-4-hydroxy-3-methyl-2H-chromen-2-one (2h): Colourless solid (88 mg, 72%); mp 240-242 °C. ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.85 (s, 1H, Ar-H), 7.79-7.78 (m, 1H, Ar-H), 1.99 (s, 3H, Me) ppm. ¹³C NMR (100 MHz, DMSO-*d*₆) δ 161.77, 158.41, 146.17, 130.60, 127.77, 121.39, 120.90, 118.94, 101.80, 9.96 ppm. IR (KBr, cm⁻¹): 3286, 3100, 1706, 1609, 1569, 1474, 1225, 1206, 1182, 1075, 866, 828. HRMS (ESI⁺): calcd for C₁₀H₇Cl₂O₃ [M+H]⁺ 244.9772; found 244.9770.



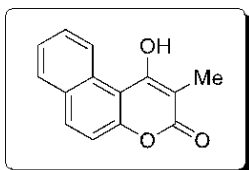
4-Hydroxy-6,7,8-trimethoxy-3-methyl-2H-chromen-2-one (2i): Colourless solid (101 mg, 76%); mp 214-216 °C. ¹H NMR (400 MHz, DMSO-*d*₆) δ 11.21 (s, 1H, OH), 7.19 (s, 1H, Ar-H), 3.88 (s, 3H, OMe), 3.84 (s, 6H, OMe), 1.97 (s, 3H, Me) ppm. ¹³C NMR (100 MHz, DMSO-*d*₆) δ 163.05, 159.90, 149.27, 144.57, 140.38, 140.30, 111.66, 99.38, 99.30, 61.40, 60.96, 56.09, 9.74 ppm. IR (KBr, cm⁻¹): 2952, 2842, 1663, 1623, 1571, 1500, 1406, 1371, 1250, 1110, 1089, 751, 586. HRMS (ESI⁺): calcd for C₁₃H₁₅O₆ [M+H]⁺ 267.0869; found 267.0865.



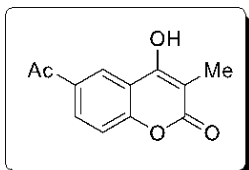
4-Hydroxy-8-methoxy-3-methyl-2H-chromen-2-one (2j): Colourless solid (85 mg, 82%); mp 200-202 °C. ¹H NMR (400 MHz, DMSO-*d*₆) δ 11.21 (s, 1H, OH), 7.44 (dd, *J* = 6.1, 3.4 Hz, 1H, Ar-H), 7.25-7.23 (m, 2H, Ar-H), 3.88 (s, 3H, OMe), 1.99 (s, 3H, Me) ppm. ¹³C NMR (100 MHz, DMSO-*d*₆) δ 162.87, 160.00, 146.52, 141.30, 123.58, 116.97, 114.09, 113.42, 100.35, 56.01, 9.75 ppm. IR (KBr, cm⁻¹): 3610, 2979, 1680, 1612, 1580, 1492, 1279, 1180, 1098, 1004, 747. HRMS (ESI⁺): calcd for C₁₁H₁₁O₄ [M+H]⁺ 207.0657; found 207.0650.



1-Hydroxy-2-methyl-3H-benzo[f]chromen-3-one (2k):ⁿ Brown solid (65 mg, 57%); mp 206-208 °C. ¹H NMR (400 MHz, DMSO-*d*₆) δ 9.39 (d, *J* = 8.6 Hz, 1H, Ar-H), 8.11 (d, *J* = 9.1 Hz, 1H, Ar-H), 8.01 (d, *J* = 7.3 Hz, 1H, Ar-H), 7.67 (ddd, *J* = 8.6, 7.0, 1.3 Hz, 1H, Ar-H), 7.59-7.55 (m, 1H, Ar-H), 7.49 (d, *J* = 9.0 Hz, 1H, Ar-H), 2.09 (s, 3H, Me) ppm. ¹³C NMR (100 MHz, DMSO-*d*₆) δ 163.70, 162.54, 152.35, 132.99, 130.54, 128.94, 128.86, 127.93, 126.18, 125.36, 116.90, 109.29, 100.68, 10.07 ppm. IR (KBr, cm⁻¹): 3061, 1687, 1662, 1623, 1549, 1200, 1061, 808, 738. HRMS (ESI⁺): calcd for C₁₄H₁₁O₃ [M+H]⁺ 227.0708; found 227.0717.

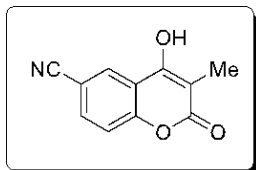


6-Acetyl-4-hydroxy-3-methyl-2H-chromen-2-one (2l): Colourless solid (88 mg, 80%); mp 246-248 °C. ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.43 (d, *J* = 1.9 Hz, 1H, Ar-H), 8.09 (dd, *J* = 8.7, 2.0 Hz, 1H, Ar-H), 7.41 (d, *J* = 8.7 Hz, 1H, Ar-H), 2.61 (s, 3H, COMe), 1.99 (s, 3H, Me) ppm. ¹³C NMR (100 MHz, DMSO-*d*₆) δ 196.48, 162.73, 159.63, 154.50, 132.44, 131.07, 123.76, 116.57, 116.26, 100.91, 26.73, 9.84 ppm. IR (KBr, cm⁻¹):

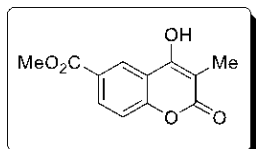


3106, 1686, 1612, 1361, 1250, 1233, 1189, 1094, 828. HRMS (ESI⁺): calcd for C₁₂H₁₁O₄ [M+H]⁺ 219.0657; found 219.0658.

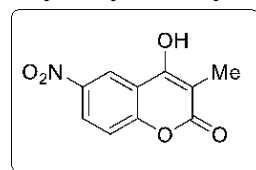
4-Hydroxy-3-methyl-2-oxo-2H-chromene-6-carbonitrile (2m): Colourless solid (65 mg, 64%); mp 232-234 °C. ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.29 (d, *J* = 2.0 Hz, 1H, Ar-H), 8.00 (dd, *J* = 8.6, 2.0 Hz, 1H, Ar-H), 7.53 (d, *J* = 8.6 Hz, 1H, Ar-H), 2.00 (s, 3H, Me) ppm. ¹³C NMR (100 MHz, DMSO-*d*₆) δ 162.33, 158.60, 154.12, 134.57, 128.10, 118.21, 117.70, 117.45, 106.68, 101.62, 9.87 ppm. IR (KBr, cm⁻¹): 3070, 2234, 1659, 1622, 1394, 1369, 1267, 1096, 843. HRMS (ESI⁺): calcd for C₁₁H₈NO₃ [M+H]⁺ 202.0504; found 202.0504.



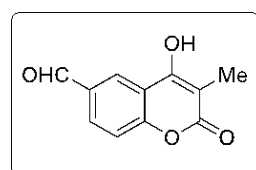
Methyl 4-hydroxy-3-methyl-2-oxo-2H-chromene-6-carboxylate (2n): Colourless solid (72 mg, 61%); mp 264-266 °C. ¹H NMR (400 MHz, DMSO-*d*₆) δ 11.59 (s, 1H, OH), 8.46 (d, *J* = 2.2 Hz, 1H, Ar-H), 8.09-8.07 (m, 1H, Ar-H), 7.44 (d, *J* = 8.7 Hz, 1H, Ar-H), 3.88 (s, 3H, CO₂Me), 2.00 (s, 3H, Me) ppm. ¹³C NMR (125 MHz, DMSO-*d*₆) δ 165.32, 162.69, 159.65, 154.61, 131.73, 125.05, 124.73, 116.70, 116.67, 100.77, 52.34, 9.84 ppm. IR (KBr, cm⁻¹): 3388, 3248, 2352, 1731, 1693, 1681, 1618, 1295, 1232, 1129, 1083, 1096, 763. HRMS (ESI⁺): calcd for C₁₂H₁₁O₅ [M+H]⁺ 235.0606; found 235.0608.



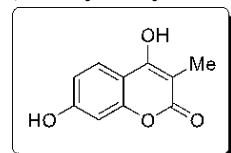
4-Hydroxy-3-methyl-6-nitro-2H-chromen-2-one (2o): Brown solid (72 mg, 65%); mp 228-230 °C. ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.66 (d, *J* = 2.7 Hz, 1H, Ar-H), 8.37 (dd, *J* = 9.2, 2.8 Hz, 1H, Ar-H), 7.56 (d, *J* = 9.2 Hz, 1H, Ar-H), 2.01 (s, 3H, Me) ppm. ¹³C NMR (100 MHz, DMSO-*d*₆) δ 162.21, 158.69, 155.31, 143.20, 126.10, 119.01, 117.70, 116.90, 101.86, 9.90 ppm. IR (KBr, cm⁻¹): 3092, 2931, 1658, 1630, 1618, 1525, 1486, 1371, 1347, 1279, 1258, 1084, 915, 654. HRMS (ESI⁺): calcd for C₁₀H₆NO₅ [M-H]⁻ 220.0246; found 220.0237.



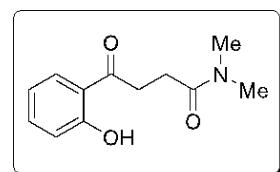
4-Hydroxy-3-methyl-2-oxo-2H-chromene-6-carbaldehyde (2p): Colourless solid (79 mg, 77%); mp 220-222 °C. ¹H NMR (400 MHz, DMSO-*d*₆) δ 10.04 (s, 1H, CHO), 8.41 (d, *J* = 2.0 Hz, 1H, Ar-H), 8.05 (dd, *J* = 8.6, 2.0 Hz, 1H, Ar-H), 7.51 (d, *J* = 8.6 Hz, 1H, Ar-H), 2.01 (s, 3H, Me) ppm. ¹³C NMR (100 MHz, DMSO-*d*₆) δ 191.78, 162.58, 159.35, 155.31, 131.99, 131.44, 125.82, 117.21, 116.86, 101.04, 9.85 ppm. IR (KBr, cm⁻¹): 3308, 3067, 1728, 1680, 1625, 1605, 1337, 1235, 1207, 1005, 903, 628. HRMS (ESI⁺): calcd for C₁₁H₇O₄ [M-H]⁻ 203.0344; found 203.0348.



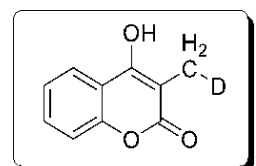
4,7-Dihydroxy-3-methyl-2H-chromen-2-one (2q):ⁿ Yellow solid (58 mg, 60%); mp 300-302 °C. ¹H NMR (400 MHz, DMSO-*d*₆) δ 10.36 (s, 1H, OH), 7.71 (d, *J* = 8.8 Hz, 1H, Ar-H), 6.76 (dd, *J* = 8.8, 2.3 Hz, 1H, Ar-H), 6.65 (d, *J* = 2.3 Hz, 1H, Ar-H), 1.93 (s, 3H, Me) ppm. ¹³C NMR (100 MHz, DMSO-*d*₆) δ 163.63, 160.69, 160.56, 153.44, 124.25, 112.35, 108.41, 101.71, 96.57, 9.47 ppm. IR (KBr, cm⁻¹): 3239, 2926, 2854, 1728, 1617, 1376, 1246, 852, 800. HRMS (ESI⁺): calcd for C₁₀H₉O₄ [M+H]⁺ 193.0501; found 193.0503.



4-(2-Hydroxyphenyl)-*N,N*-dimethyl-4-oxobutanamide (2a!):^o Yellow solid (5 mg, 4%); mp 74-76 °C. ¹H NMR (400 MHz, CDCl₃) δ 12.14 (s, 1H, OH), 7.87-7.84 (m, 1H, Ar-H), 7.46-7.41 (m, 1H, Ar-H), 6.94 (dd, *J* = 8.5, 0.8 Hz, 1H, Ar-H), 6.90-6.86 (m, 1H, Ar-H), 3.41-3.37 (m, 2H, CH₂), 3.10 (s, 3H, NMe), 2.97 (s, 3H, NMe), 2.78-2.75 (m, 2H, CH₂) ppm. ¹³C NMR (125 MHz, CDCl₃) δ 205.29, 171.70, 162.34, 136.43, 130.15, 119.55, 119.14, 118.50, 37.37, 35.85, 33.46, 27.07 ppm. IR (KBr, cm⁻¹): 2925, 2854, 1719, 1639, 1489, 1450, 1286, 1155, 756. HRMS (ESI⁺): calcd for C₁₂H₁₆NO₃ [M+H]⁺ 222.1130; found 222.1138.



4-Hydroxy-3-methyl-2H-chromen-2-one (d-2a): Colourless solid (23 mg, 52%); mp 198-200 °C. ¹H NMR (400 MHz, DMSO-*d*₆) δ 11.29 (s, 1H, OH), 7.90 (dd, *J* = 7.9, 1.3 Hz, 1H, Ar-H), 7.60-7.55 (m, 1H, Ar-H), 7.34 (t, *J* = 8.2 Hz, 2H, Ar-H), 1.98-1.97 (m, 2H, CH₂D) ppm. ¹³C NMR (100 MHz, DMSO-*d*₆) δ 163.20, 159.87, 151.68, 131.46, 123.84, 123.00, 116.35, 116.07, 100.19, 9.56 (t, *J*_{C-D} = 19.6 Hz) ppm. IR (KBr, cm⁻¹): 3158,

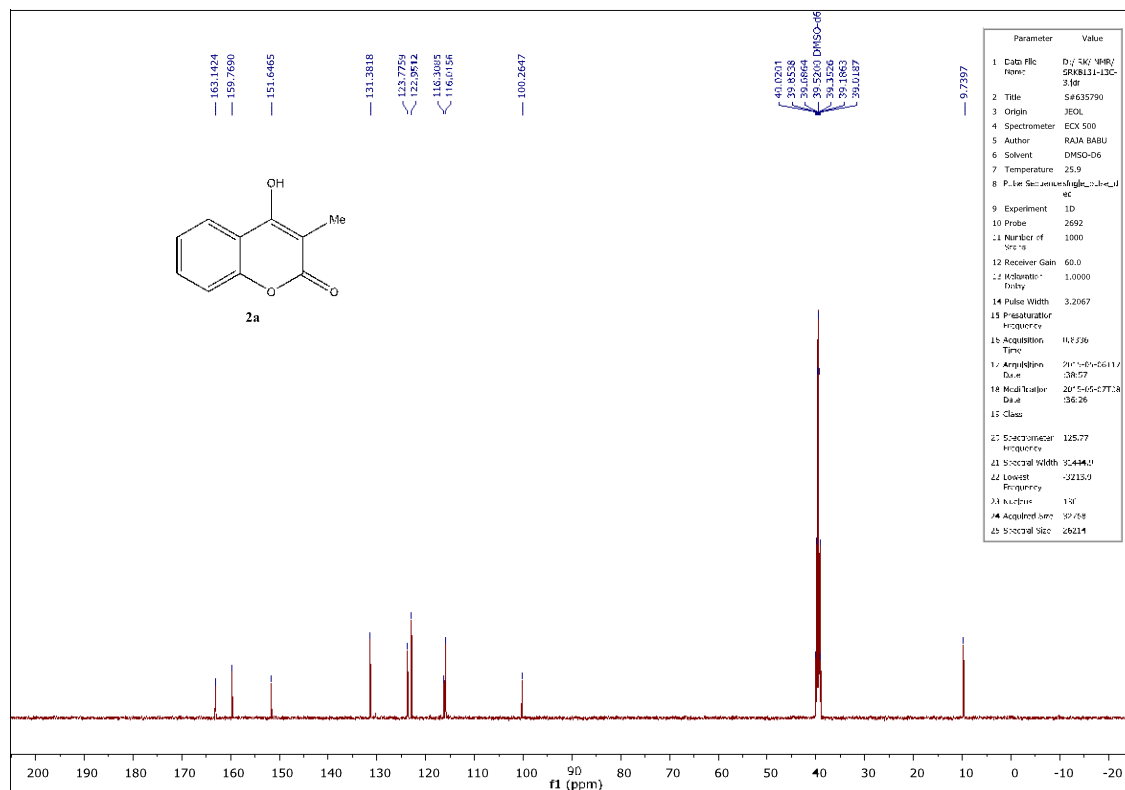
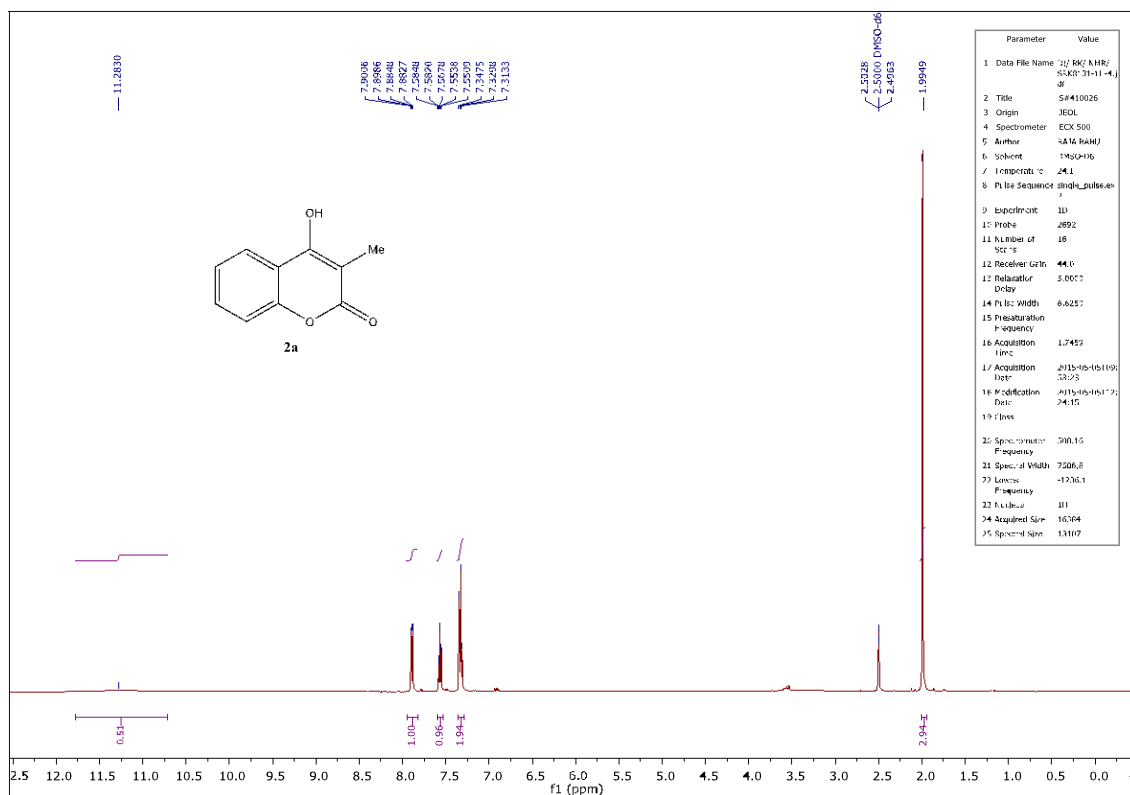


2924, 2853, 1716, 1665, 1608, 1563, 1233, 1204, 1174, 1077, 746, 733, 658. HRMS (ESI⁺): calcd for C₁₀H₈DO₃ [M+H]⁺ 178.0614; found 178.0616.

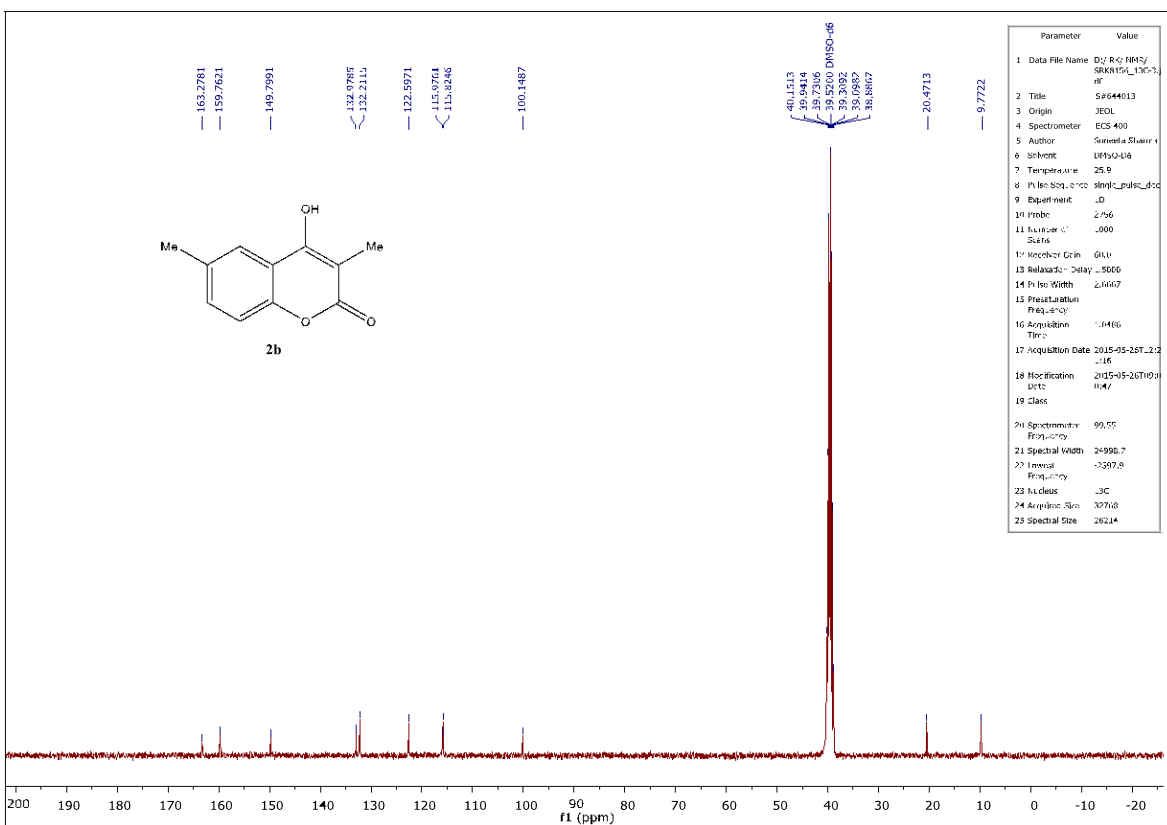
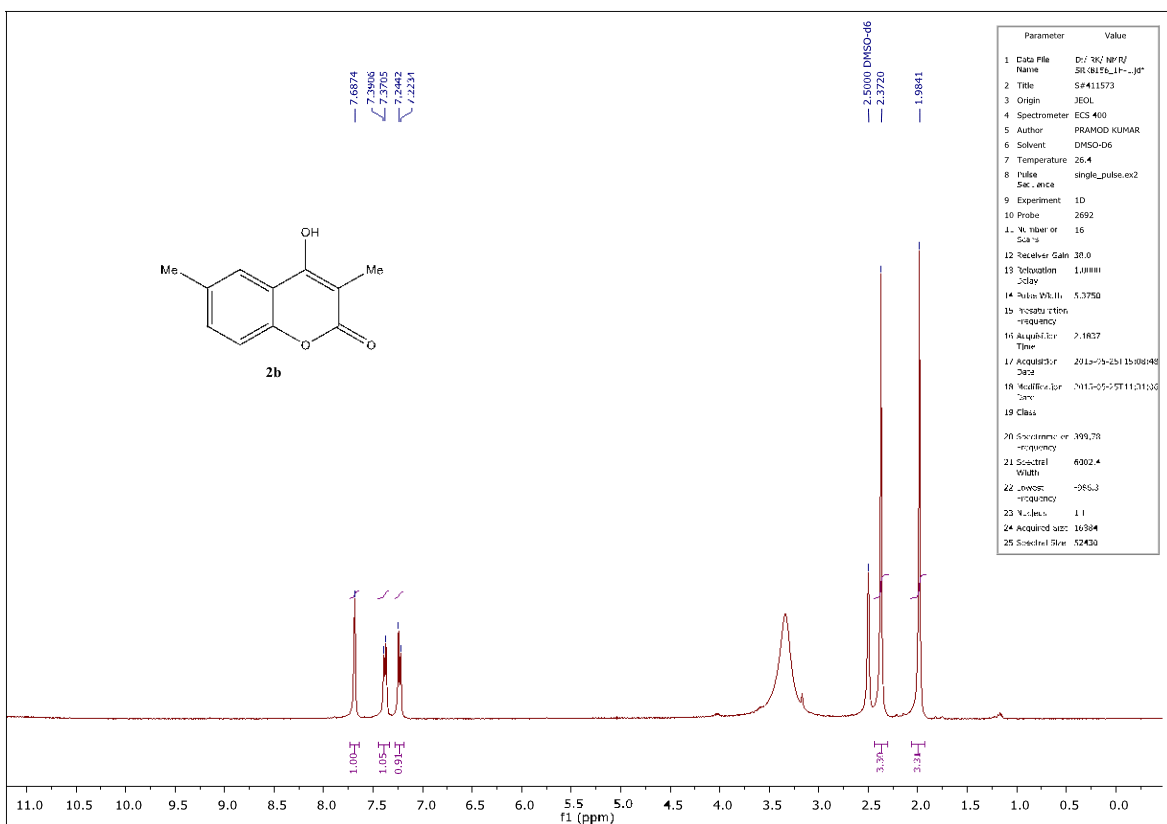
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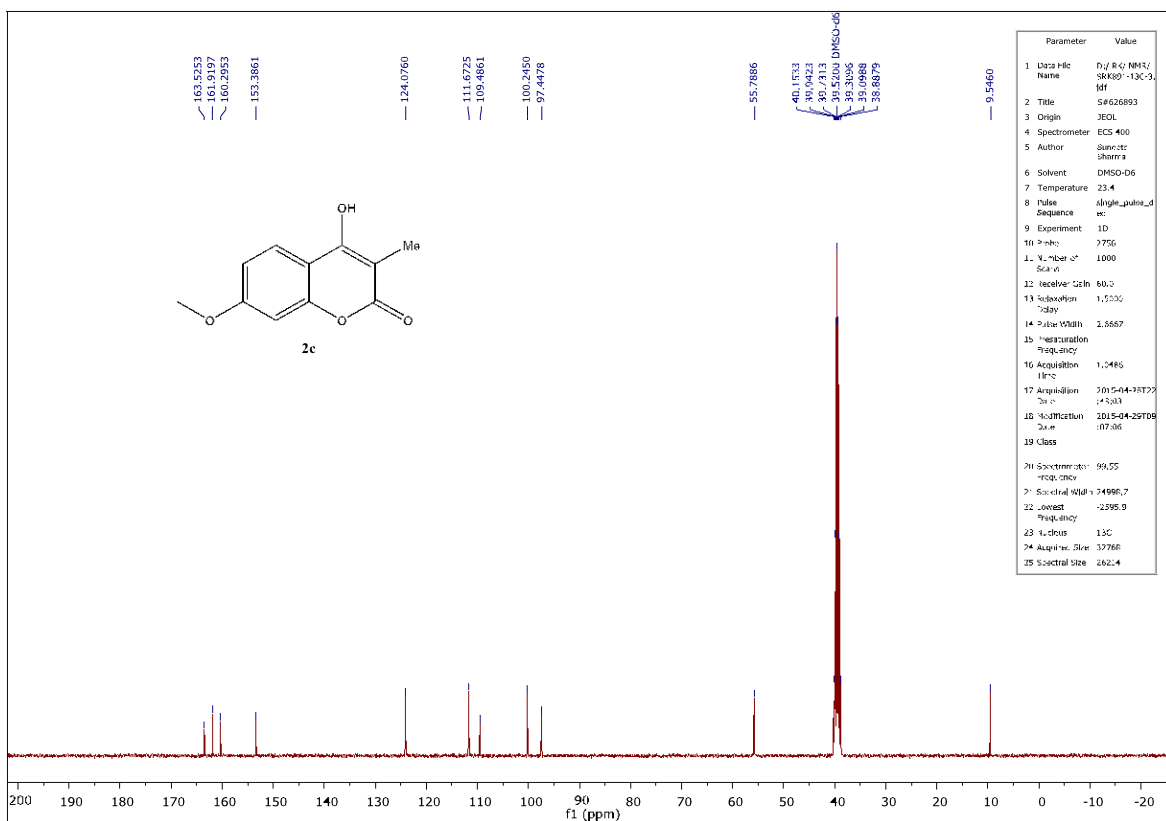
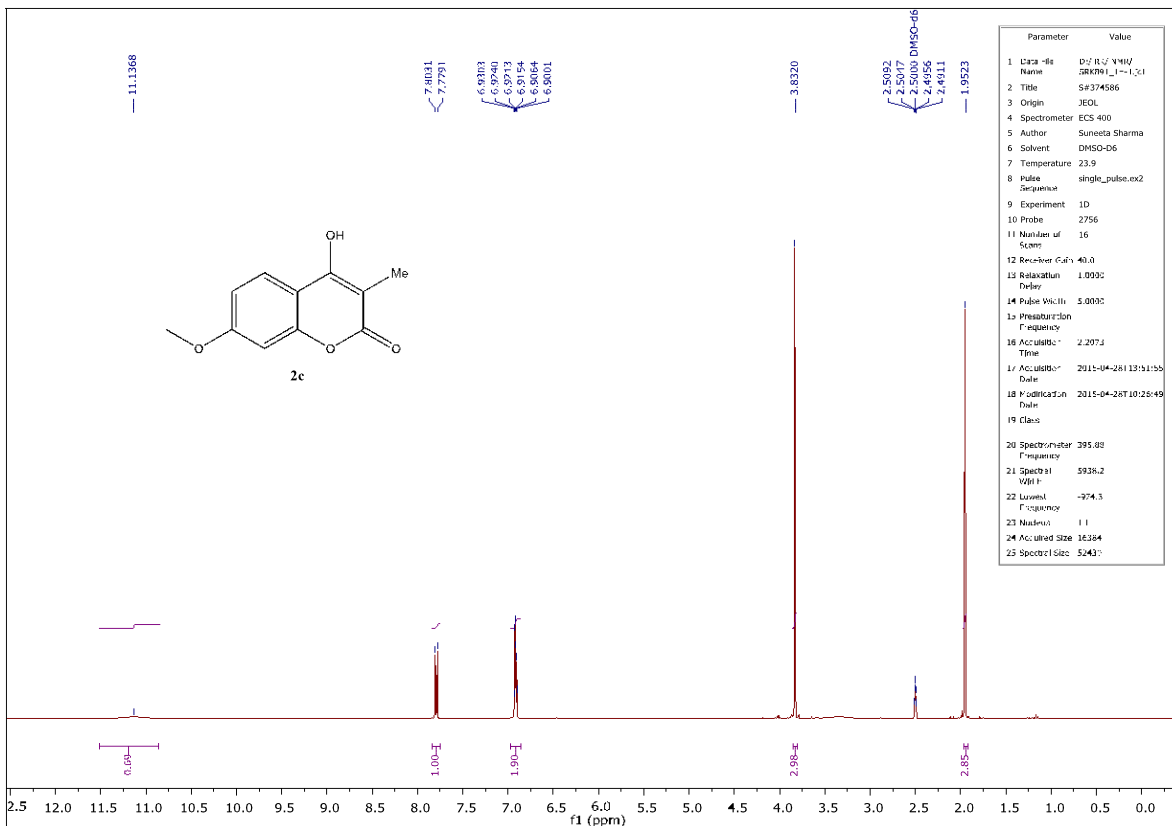
6. Copies of ^1H and ^{13}C NMR spectra of products



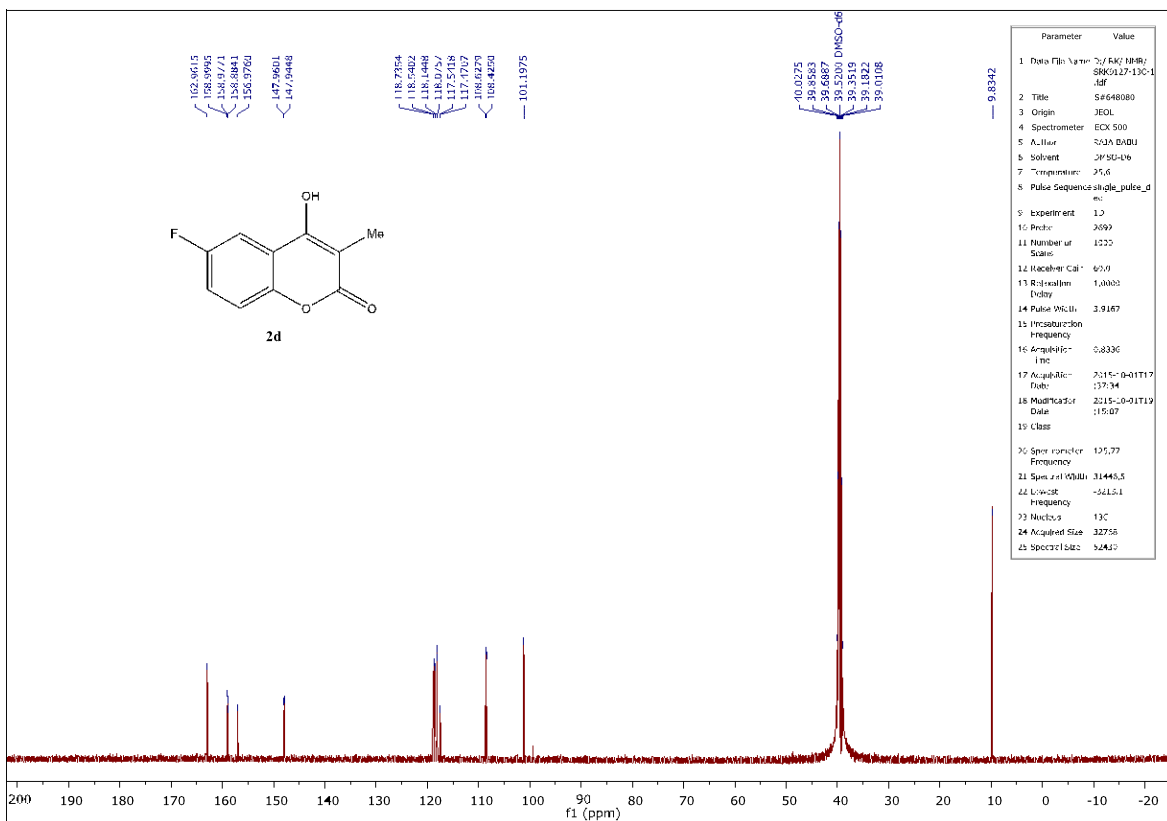
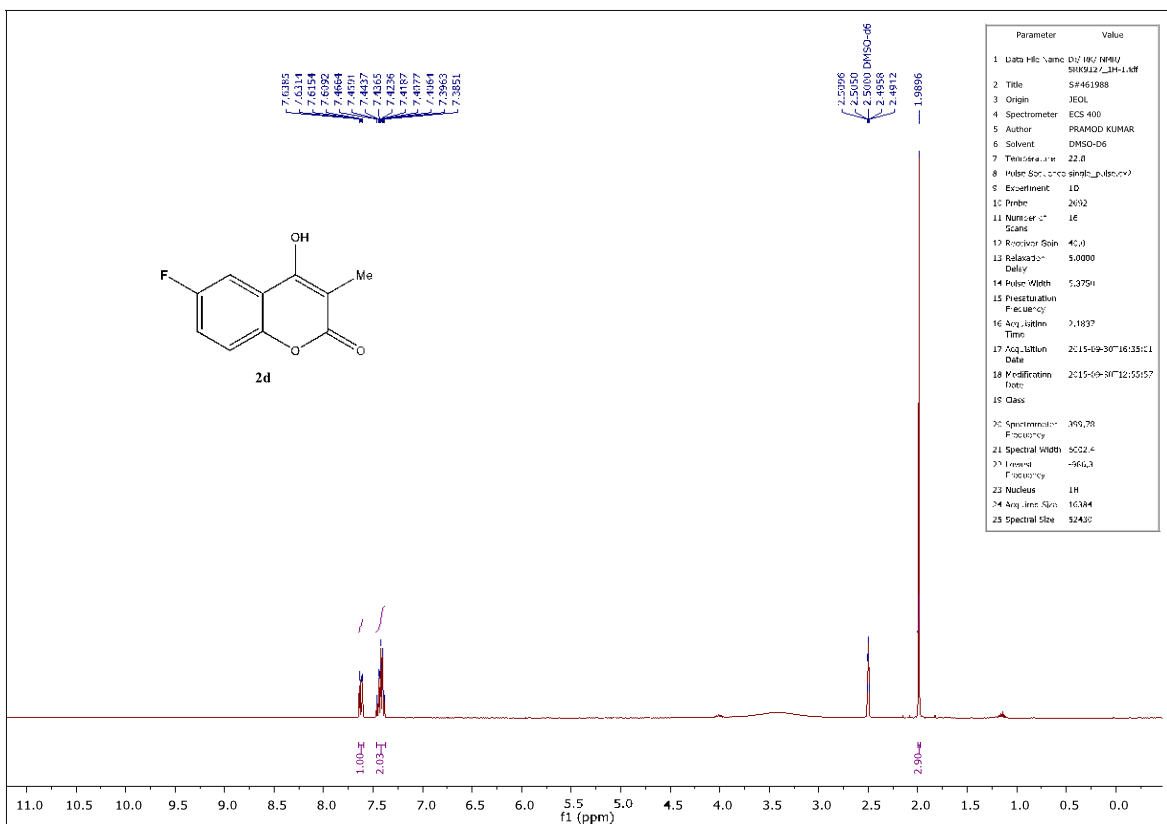
^1H and ^{13}C NMR spectra of compound 4-hydroxy-3-methyl-2H-chromen-2-one (**2a**)



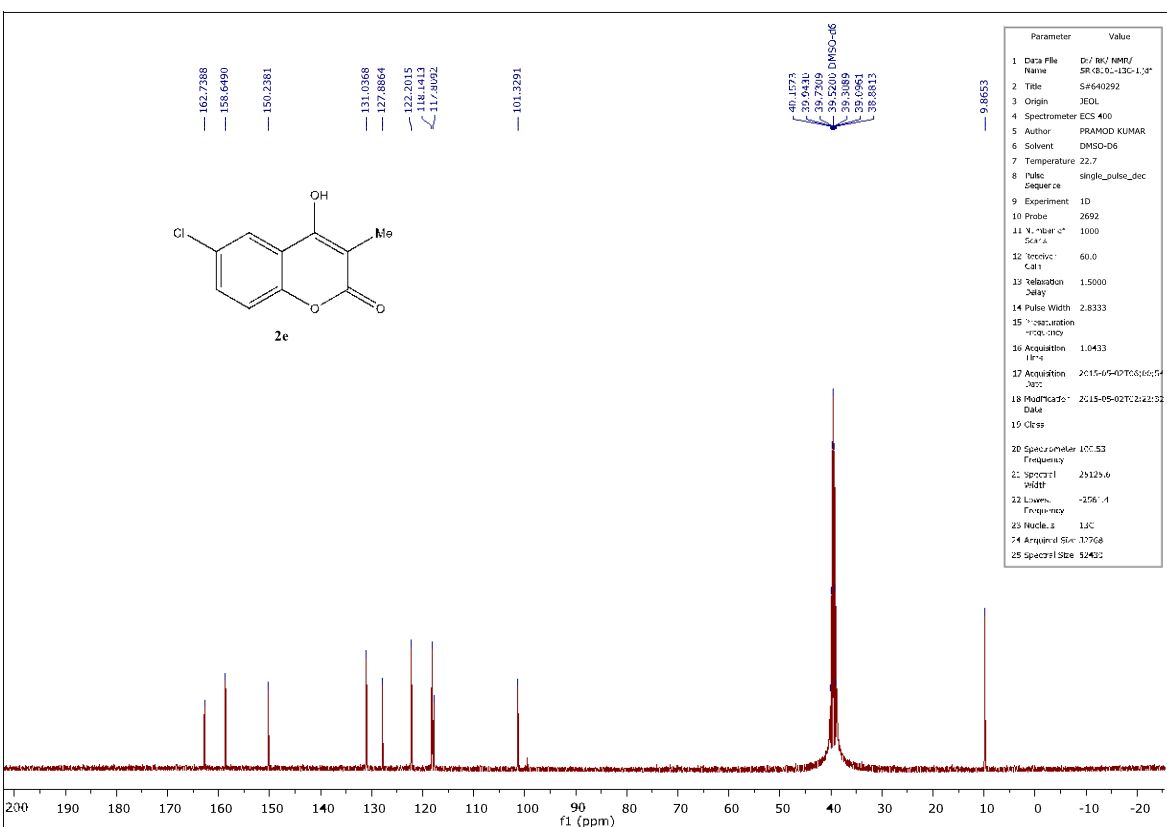
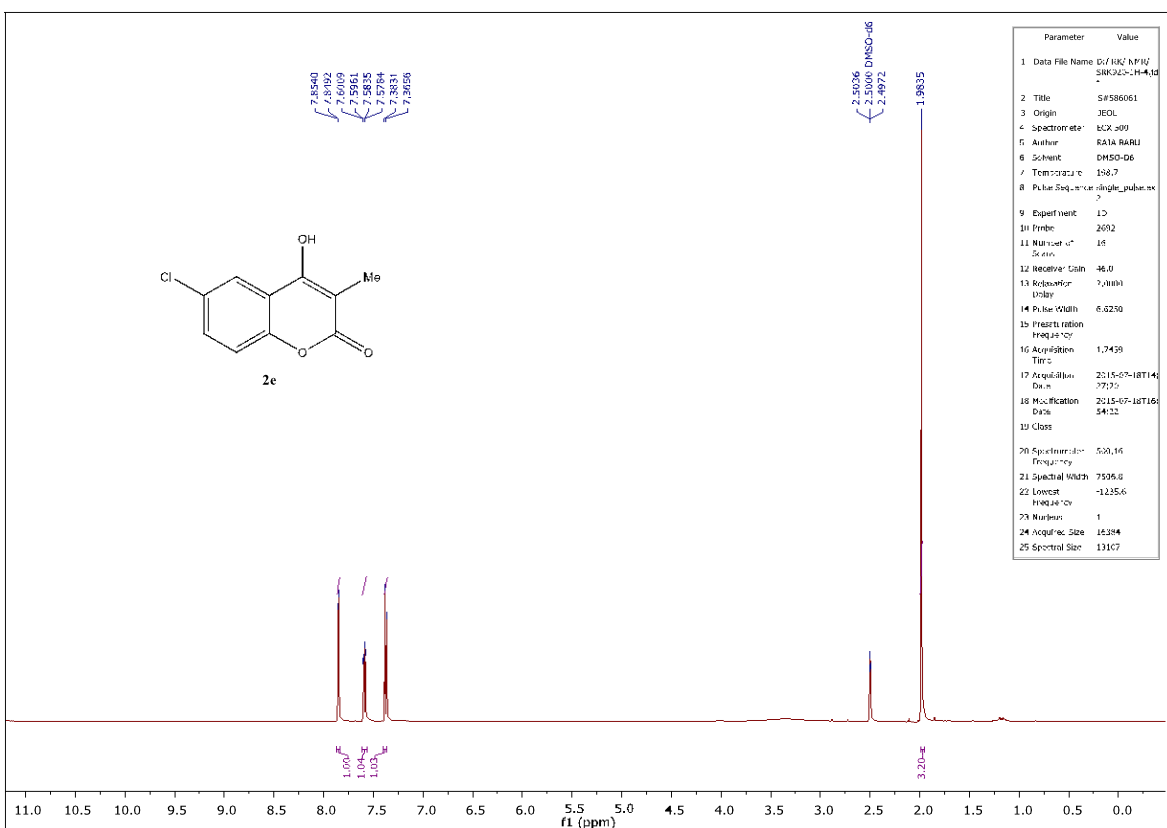
¹H and ¹³C NMR spectra of compound 4-hydroxy-3,6-dimethyl-2H-chromen-2-one (2b)



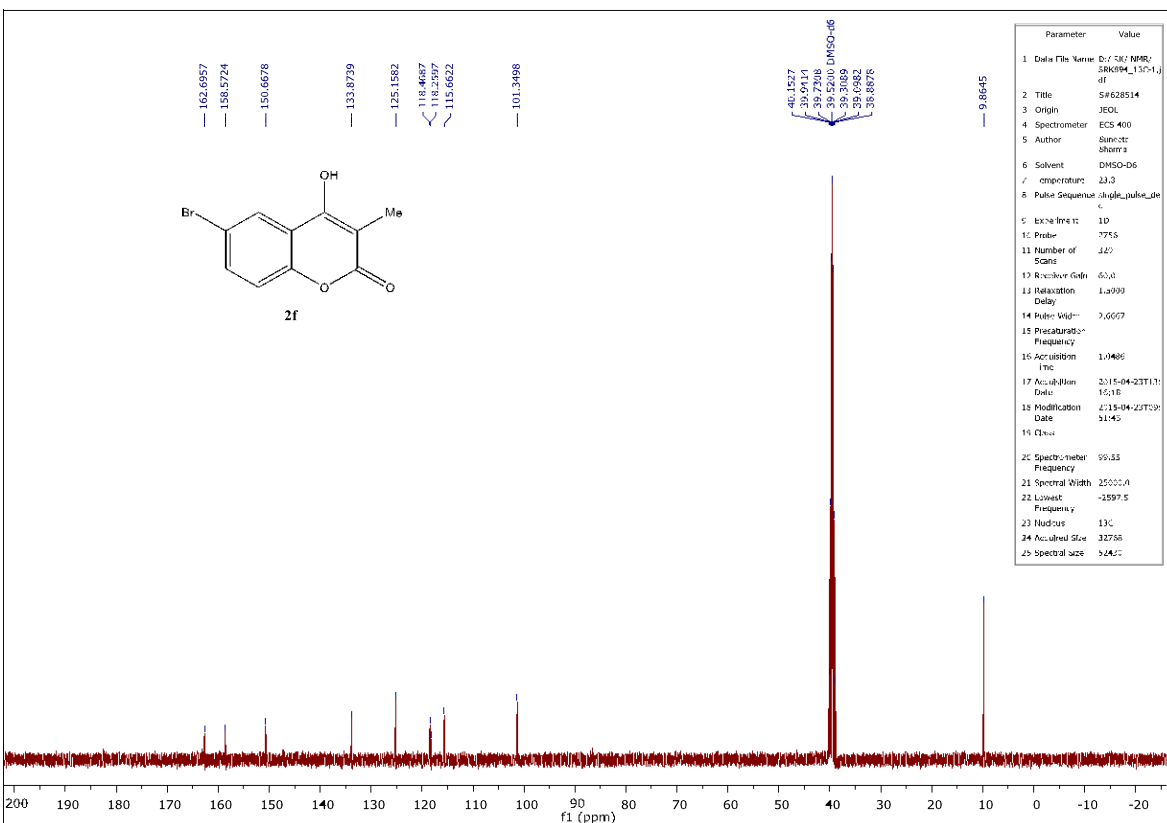
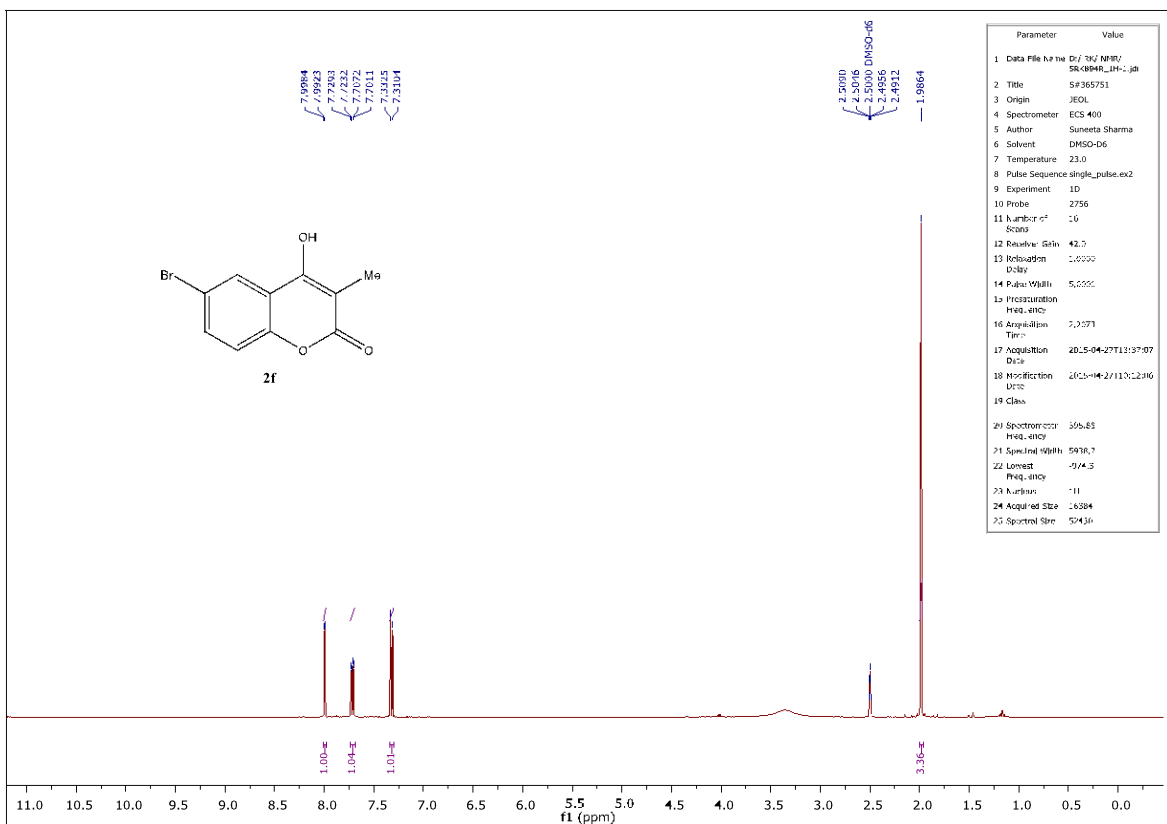
¹H and ¹³C NMR spectra of compound 4-hydroxy-7-methoxy-3-methyl-2*H*-chromen-2-one (**2c**)



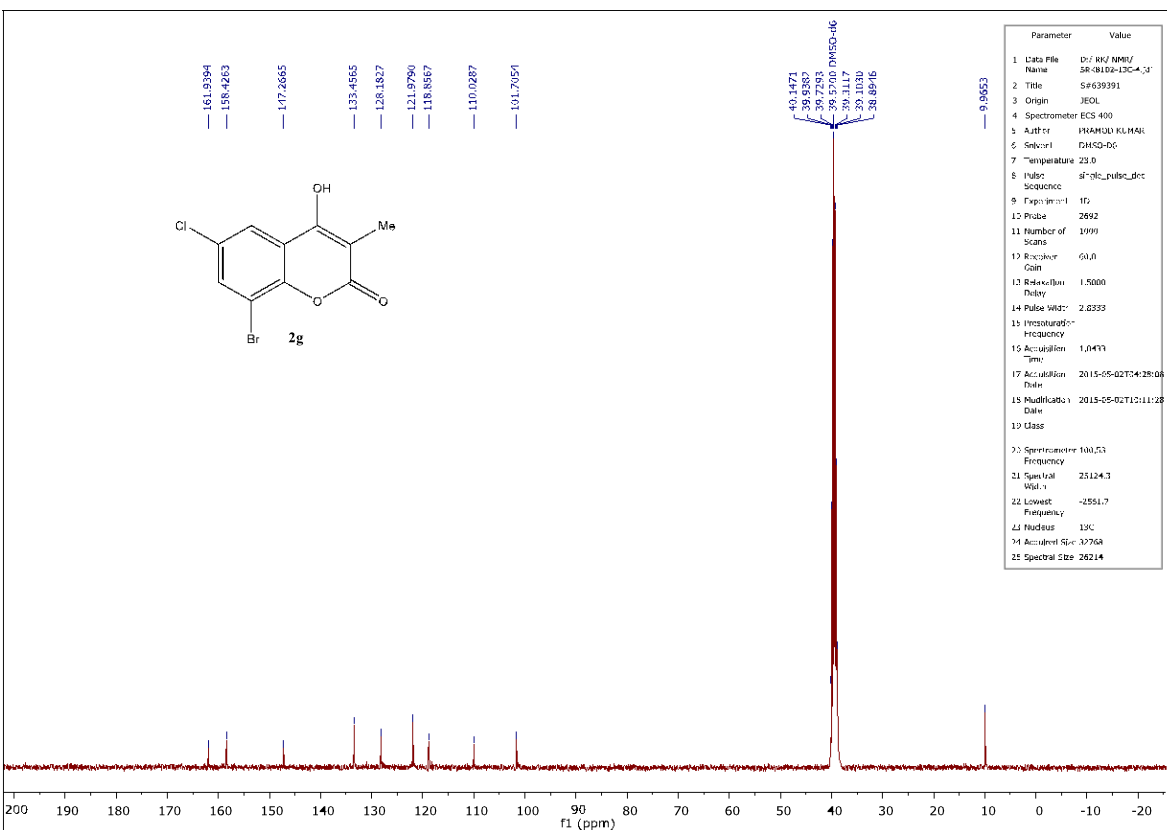
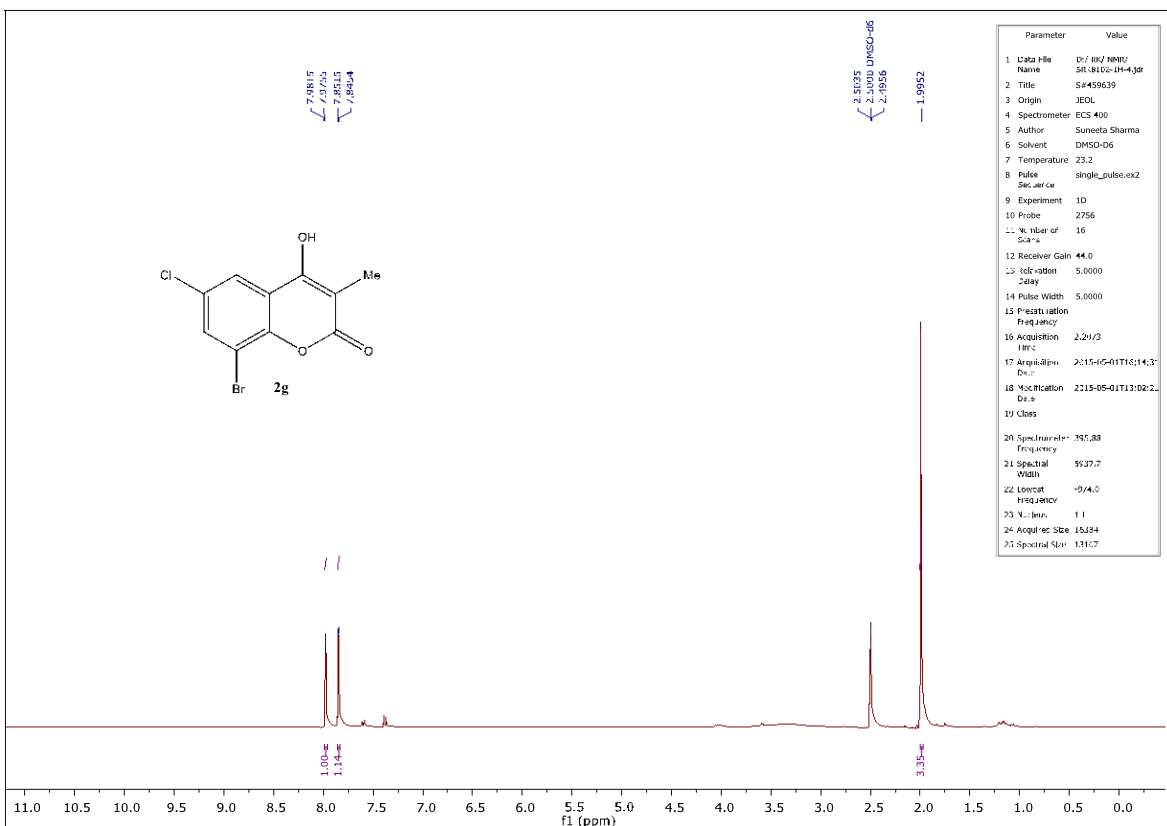
¹H and ¹³C NMR spectra of compound 6-fluoro-4-hydroxy-3-methyl-2H-chromen-2-one (**2d**)



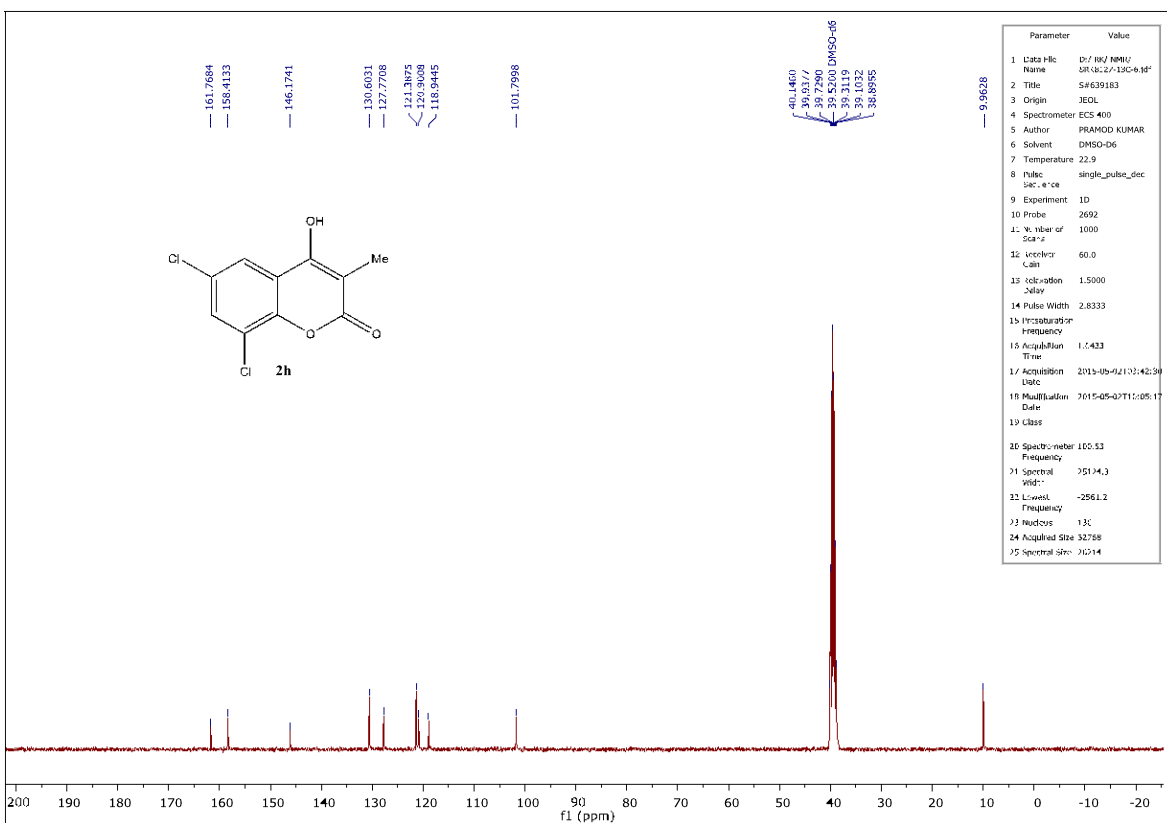
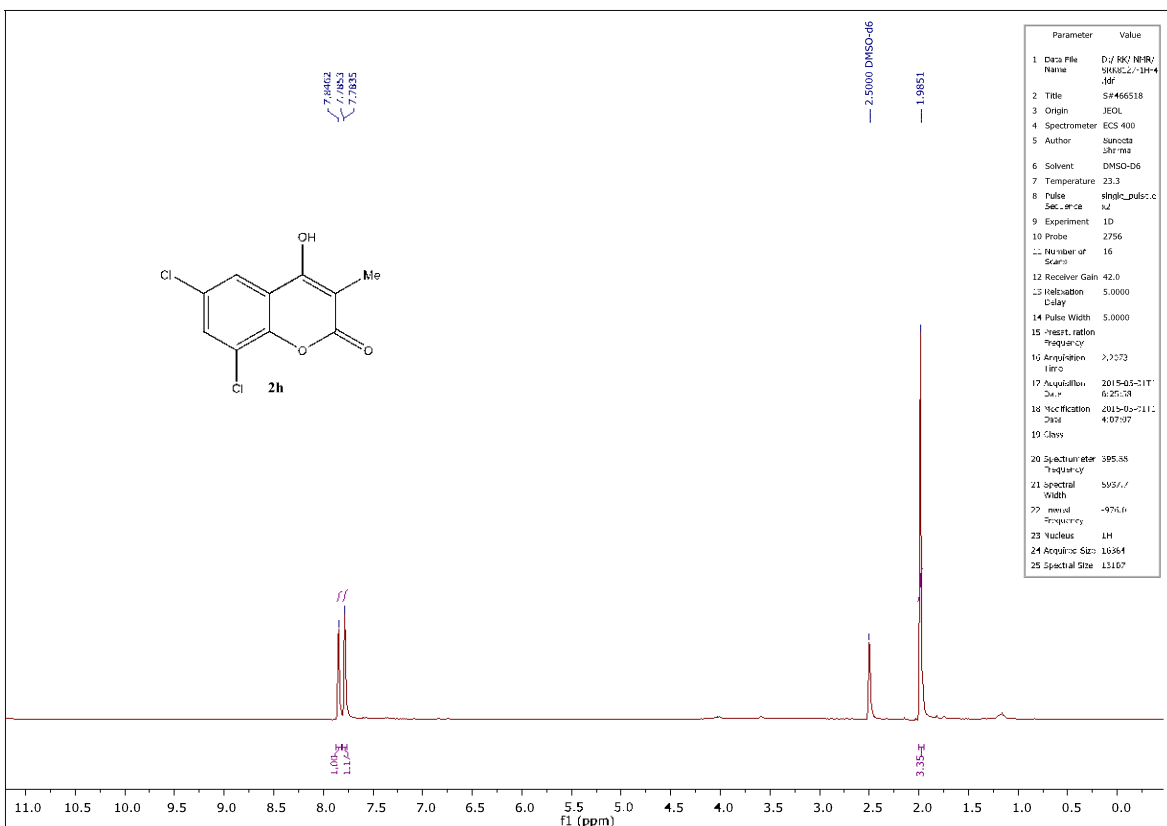
¹H and ¹³C NMR spectra of compound 6-chloro-4-hydroxy-3-methyl-2H-chromen-2-one (2e)



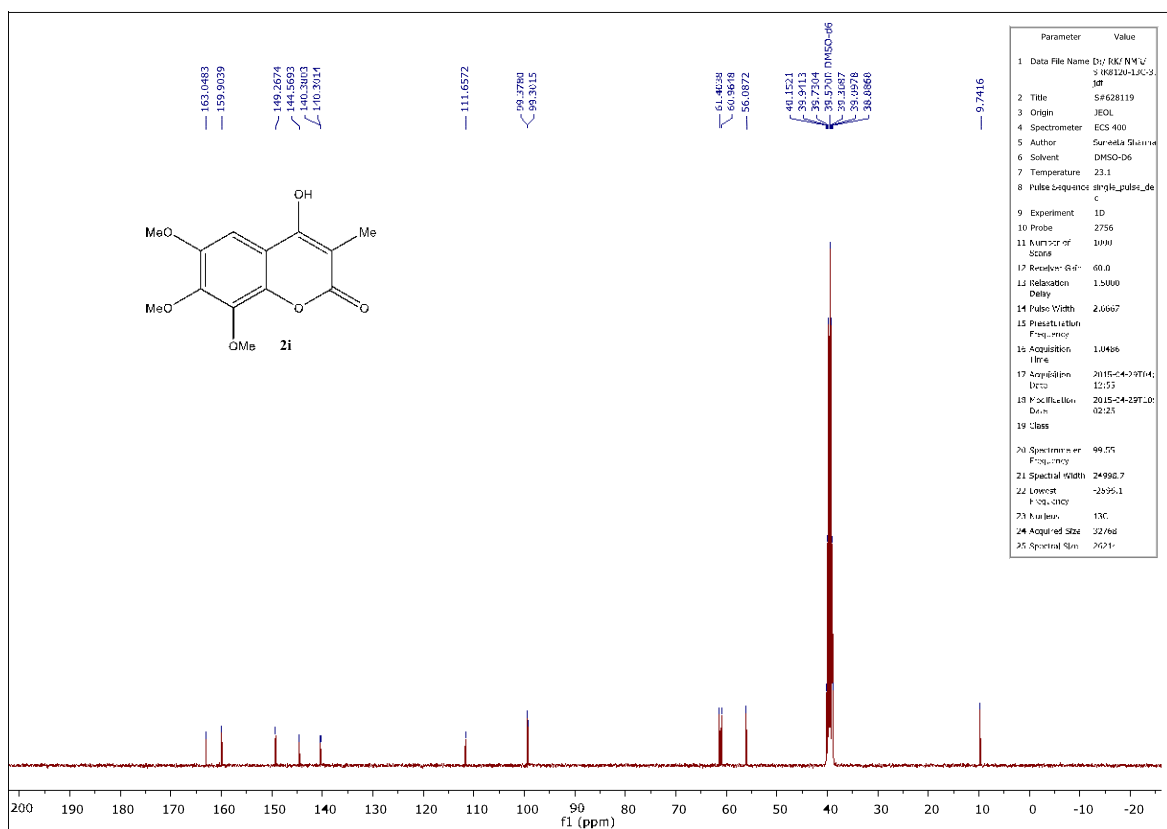
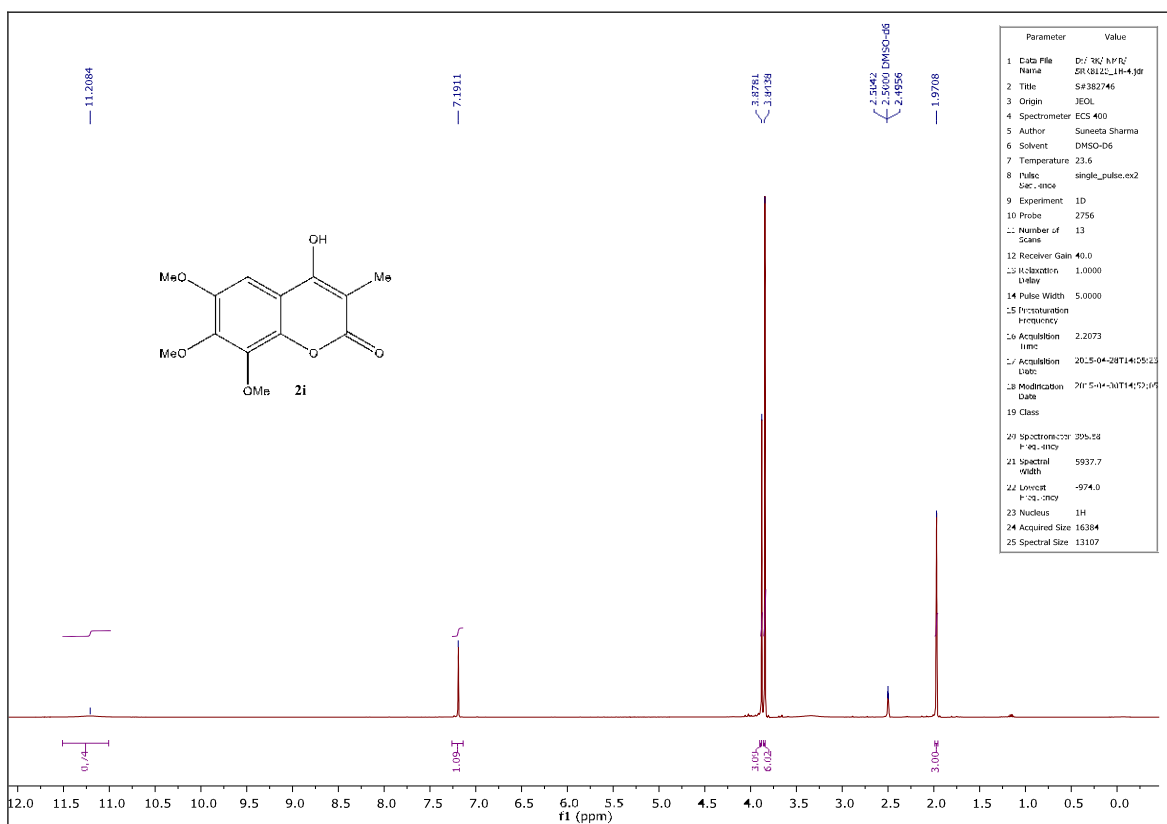
¹H and ¹³C NMR spectra of compound 6-bromo-4-hydroxy-3-methyl-2H-chromen-2-one (**2f**)



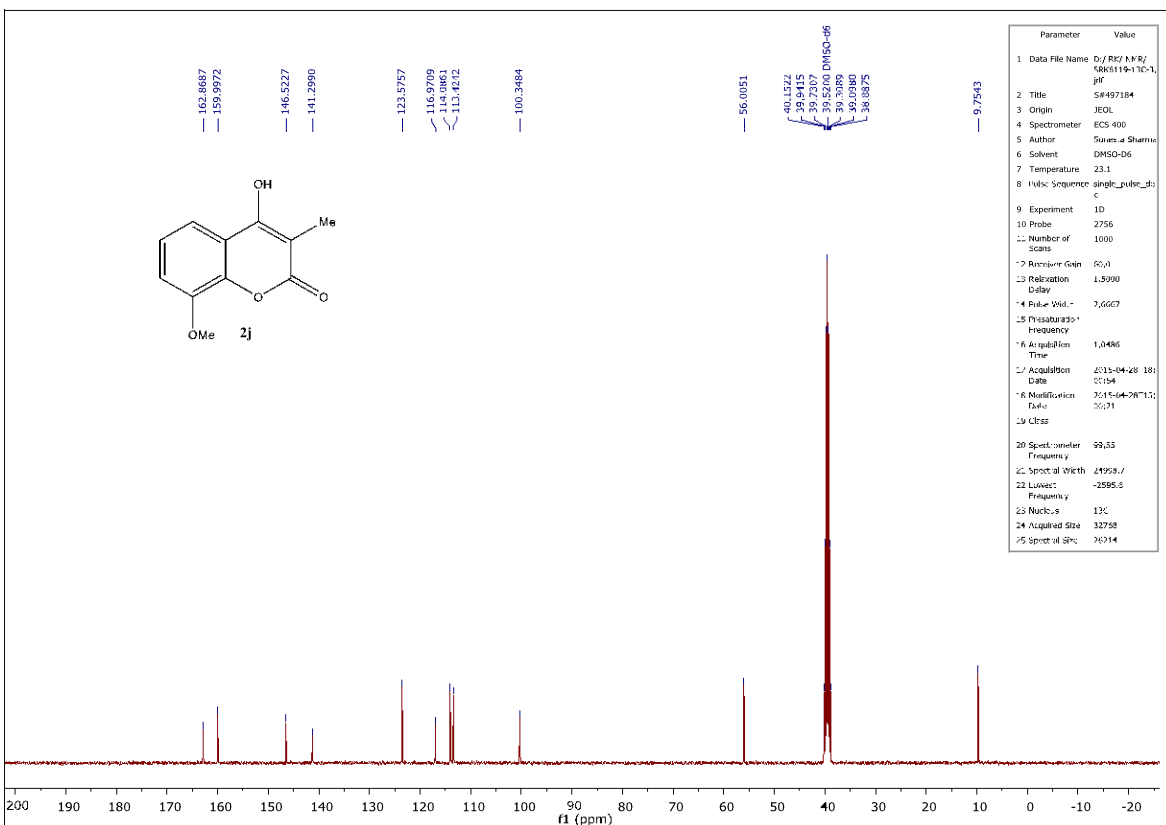
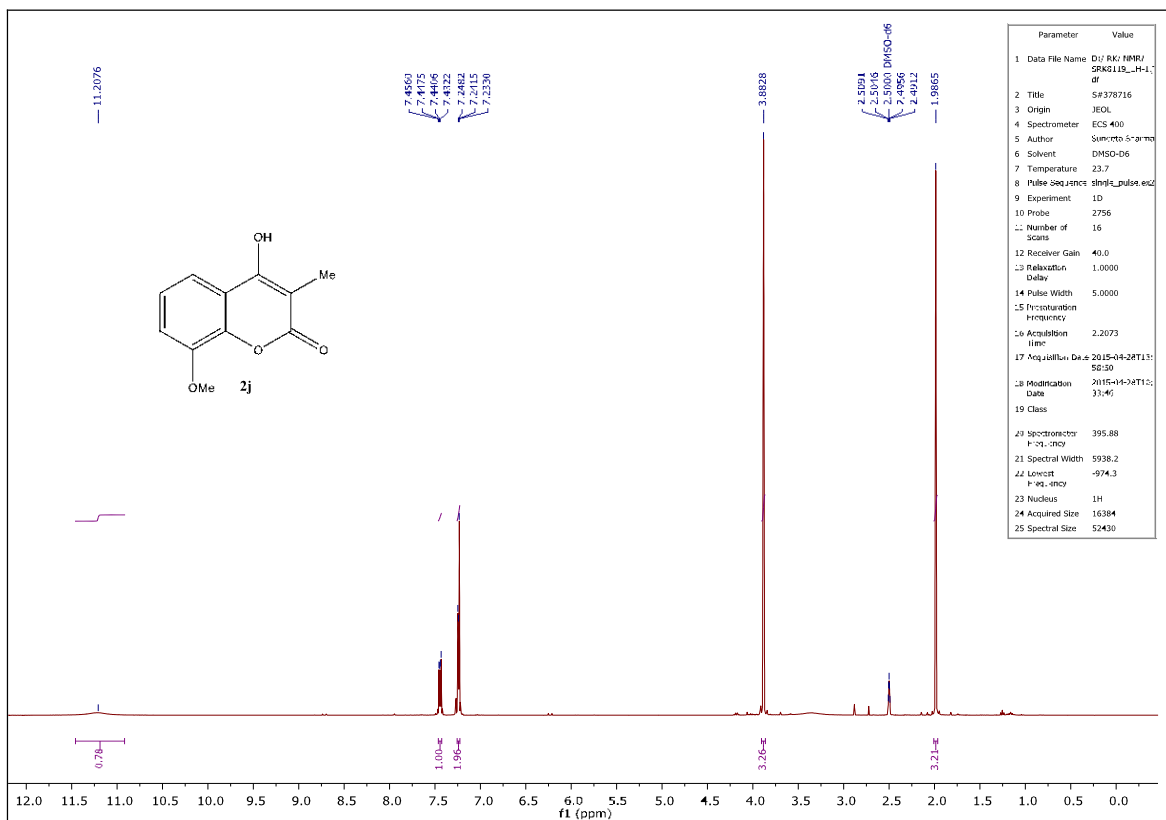
¹H and ¹³C NMR spectra of compound 8-bromo-6-chloro-4-hydroxy-3-methyl-2H-chromen-2-one (2g)



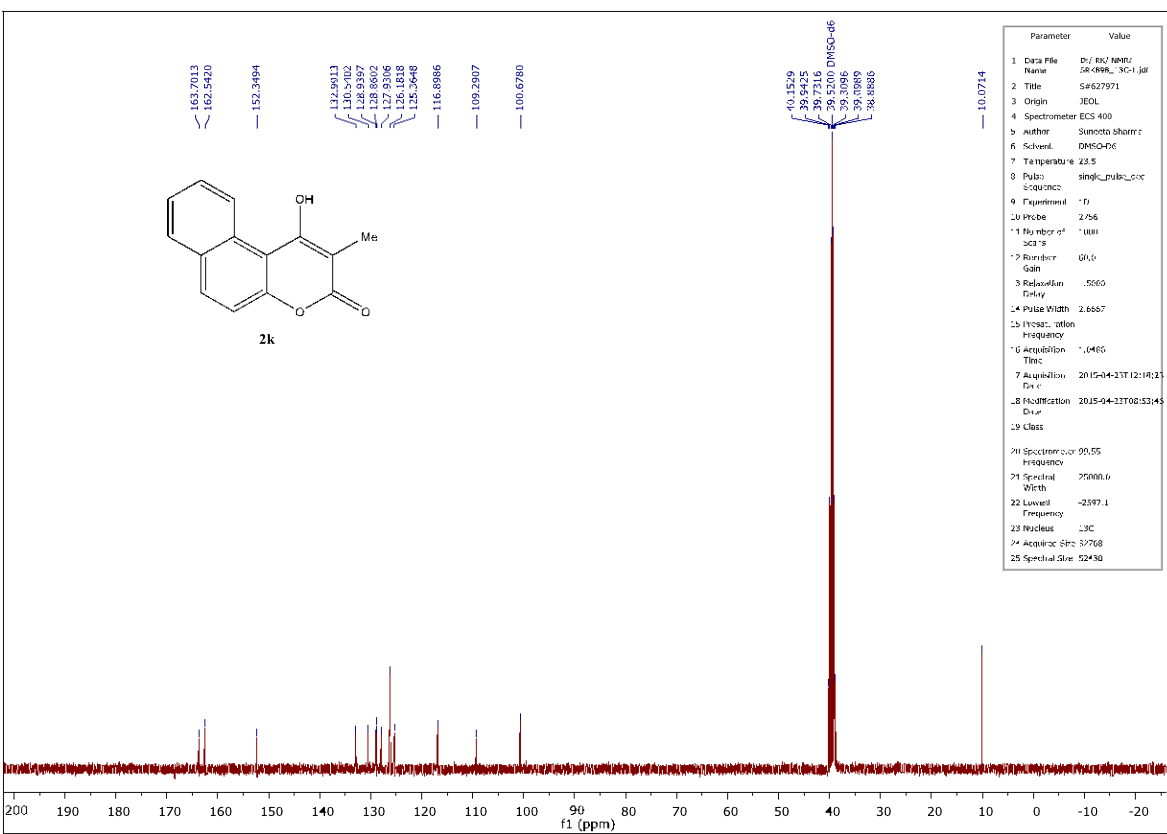
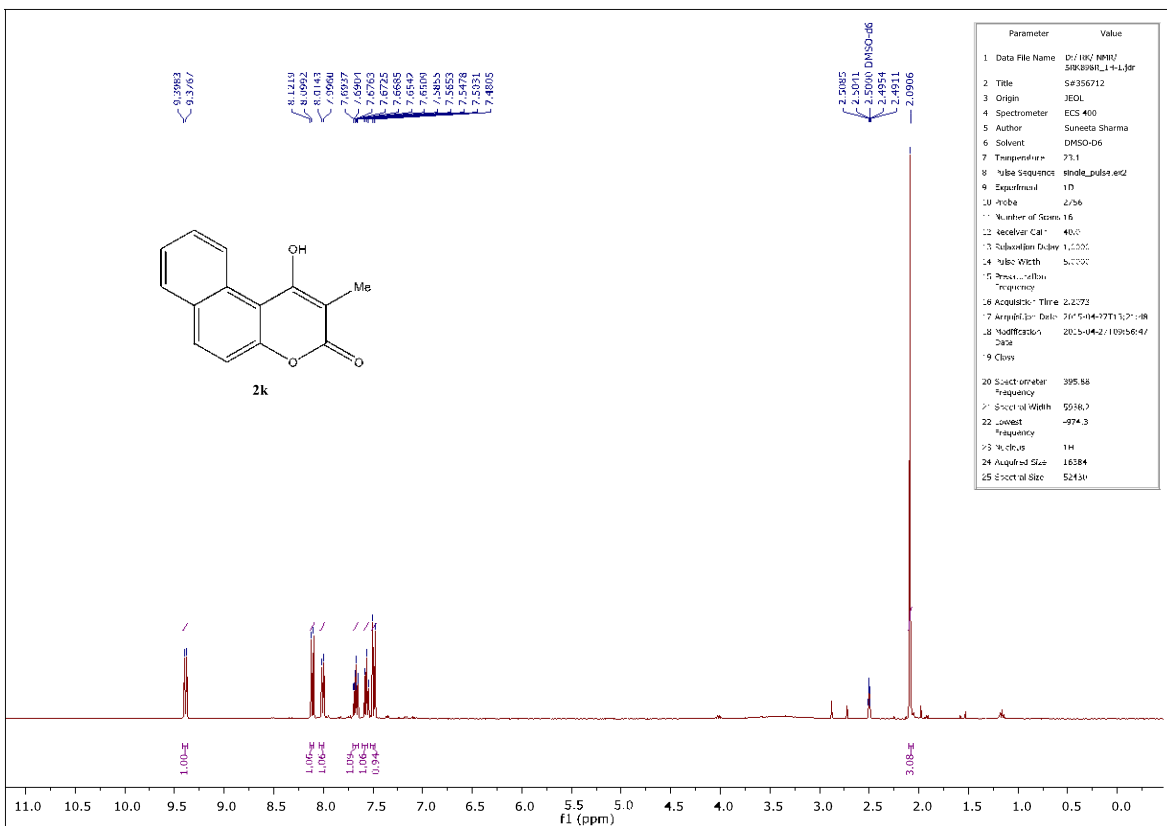
¹H and ¹³C NMR spectra of compound 6,8-dichloro-4-hydroxy-3-methyl-2H-chromen-2-one (**2h**)



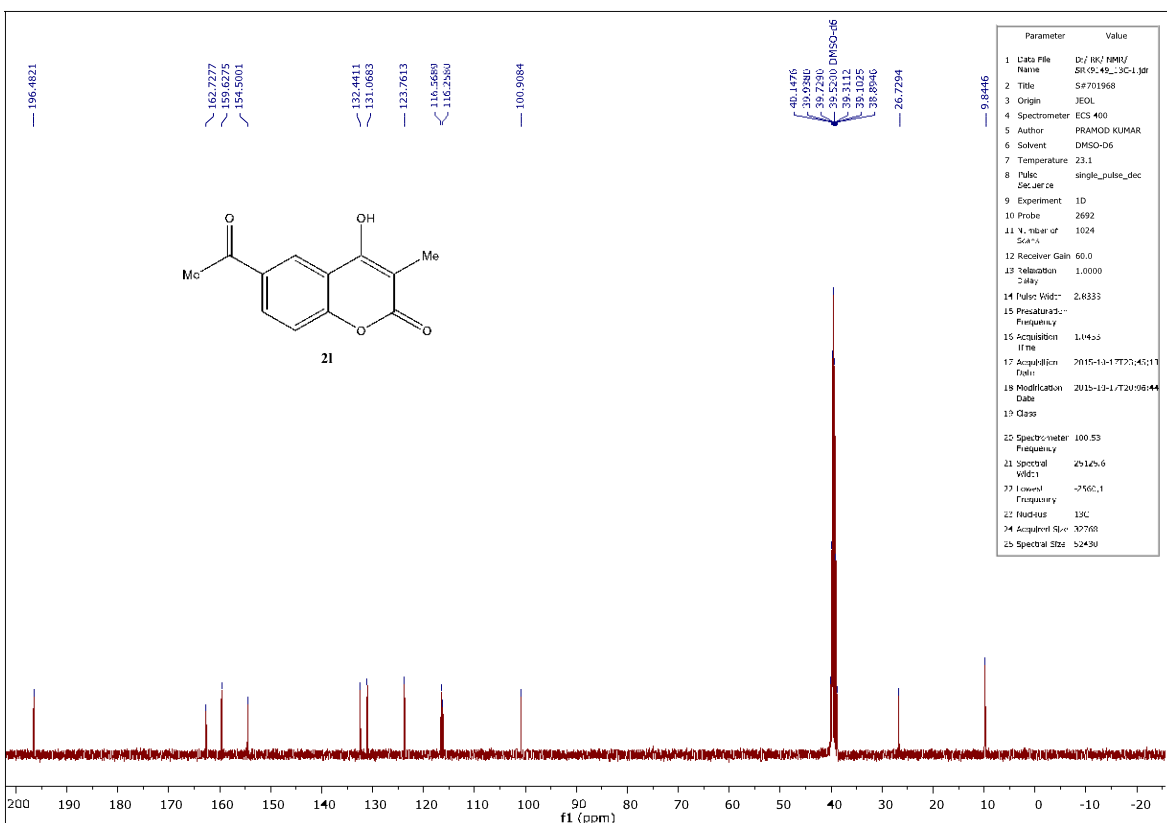
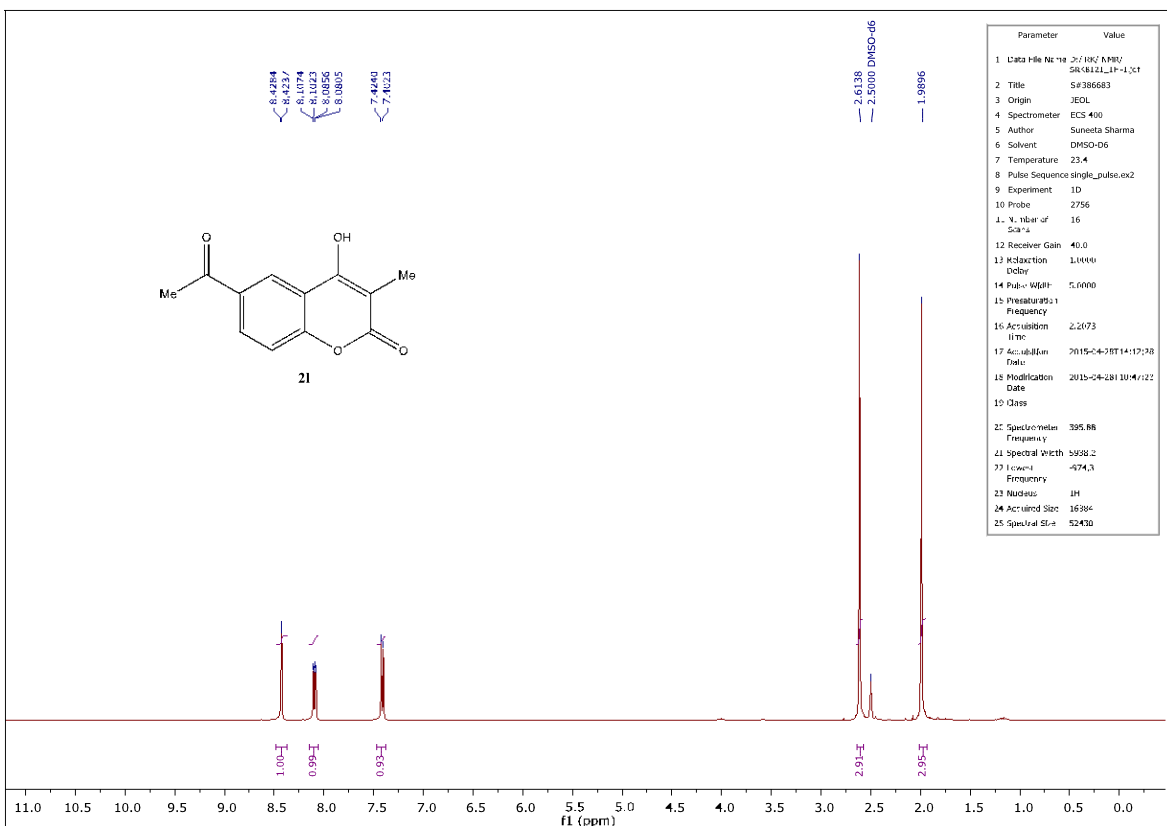
¹H and ¹³C NMR spectra of compound 4-hydroxy-6,7,8-trimethoxy-3-methyl-2*H*-chromen-2-one (**2i**)



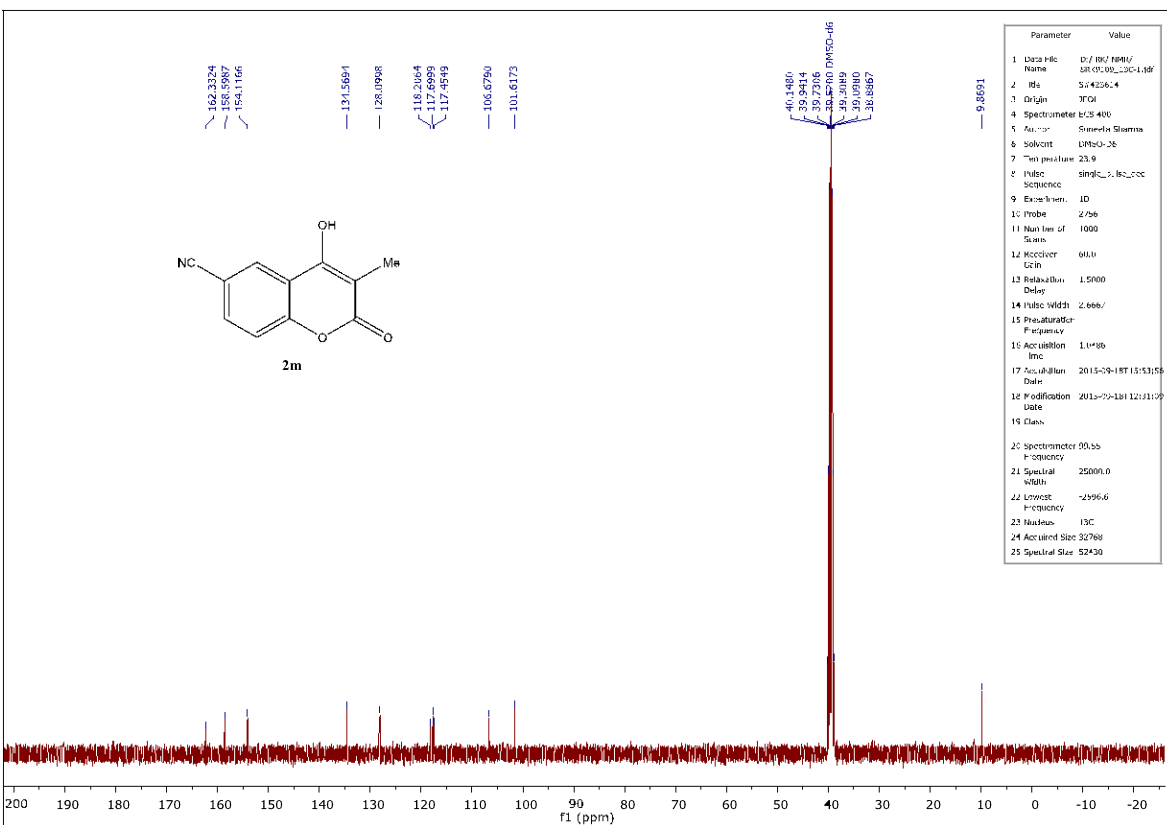
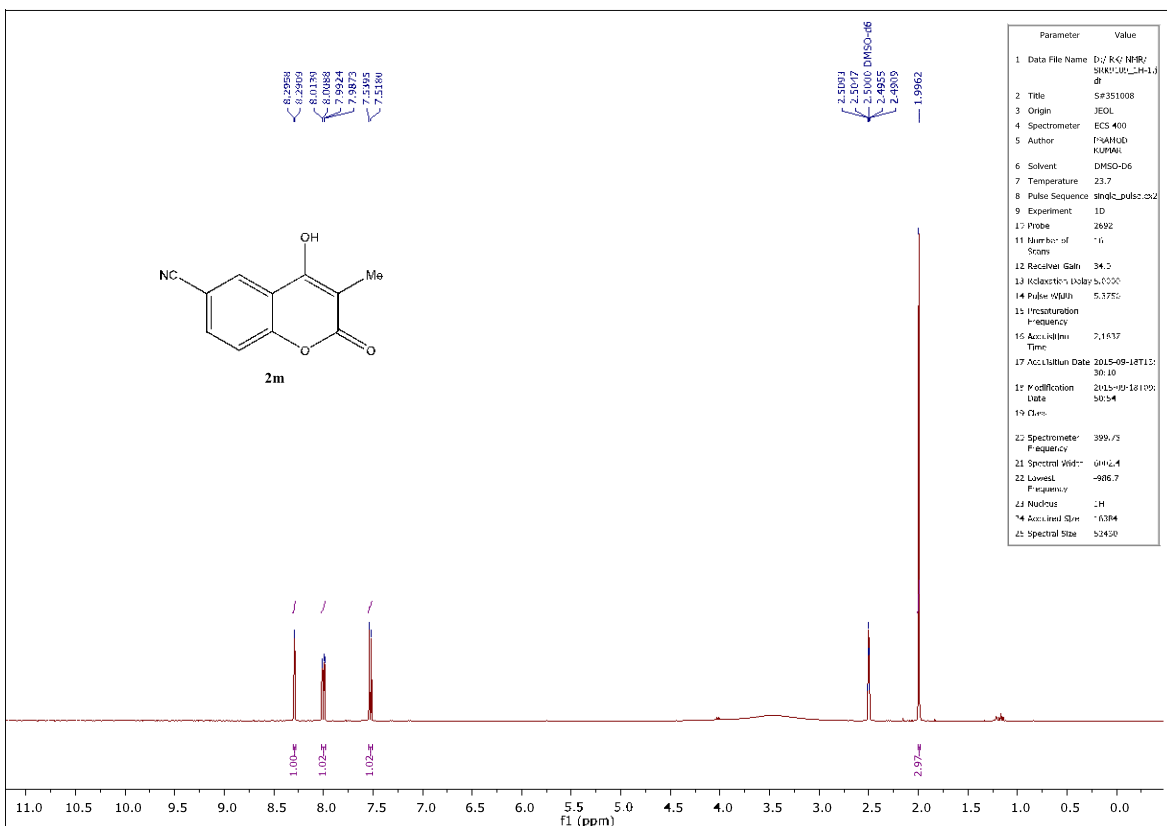
¹H and ¹³C NMR spectra of compound 4-hydroxy-8-methoxy-3-methyl-2H-chromen-2-one (2j)



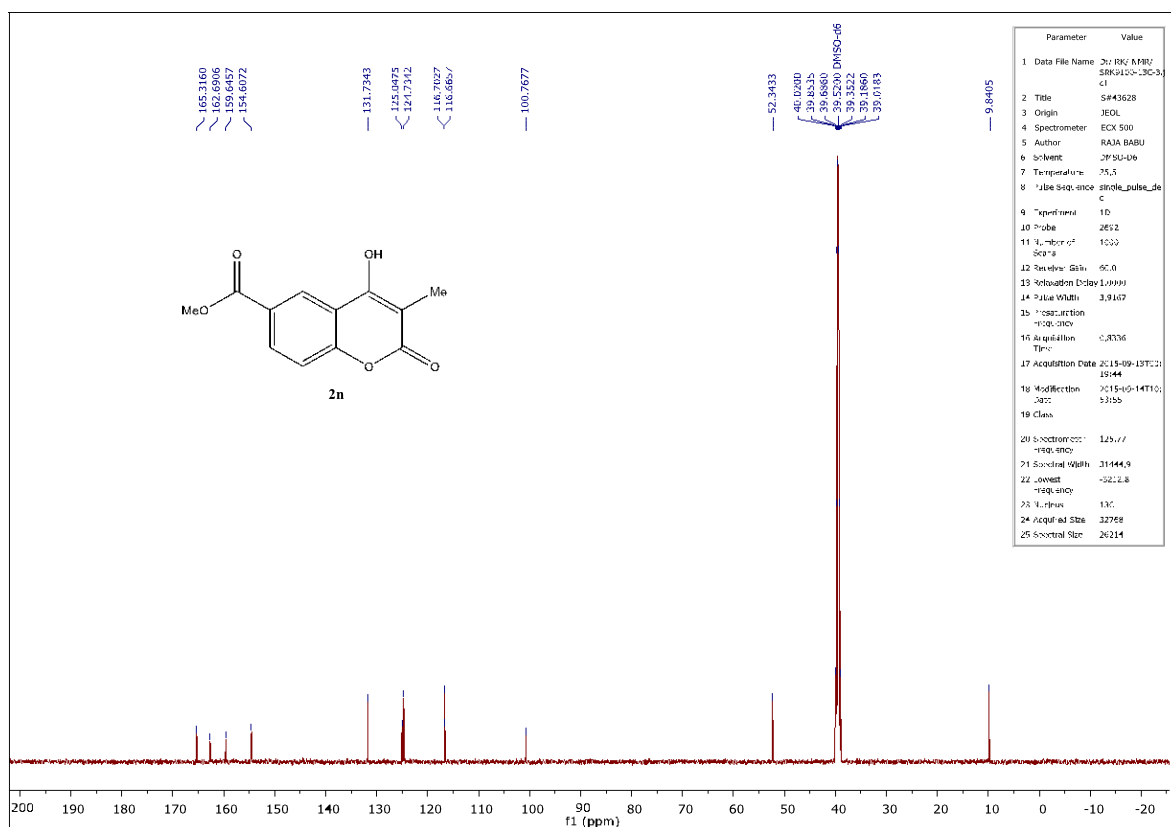
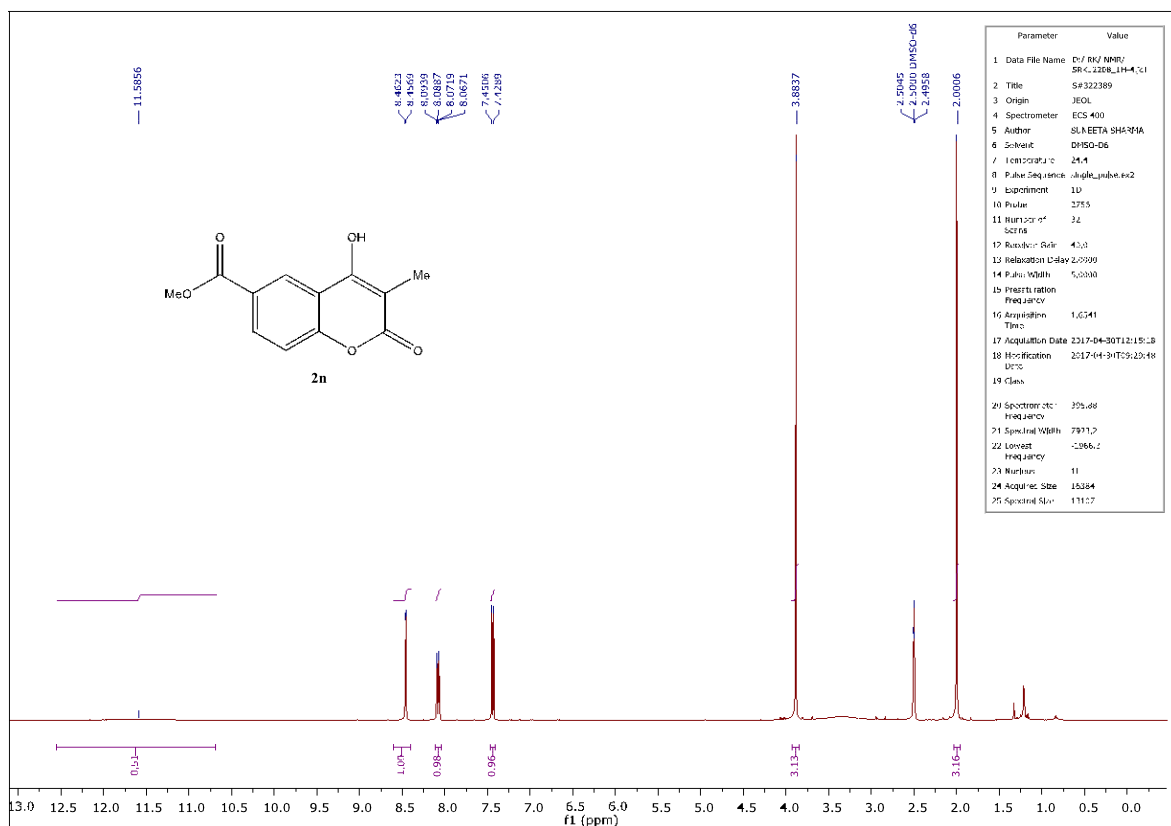
¹H and ¹³C NMR spectra of compound 1-hydroxy-2-methyl-3H-benzo[f]chromen-3-one (**2k**)



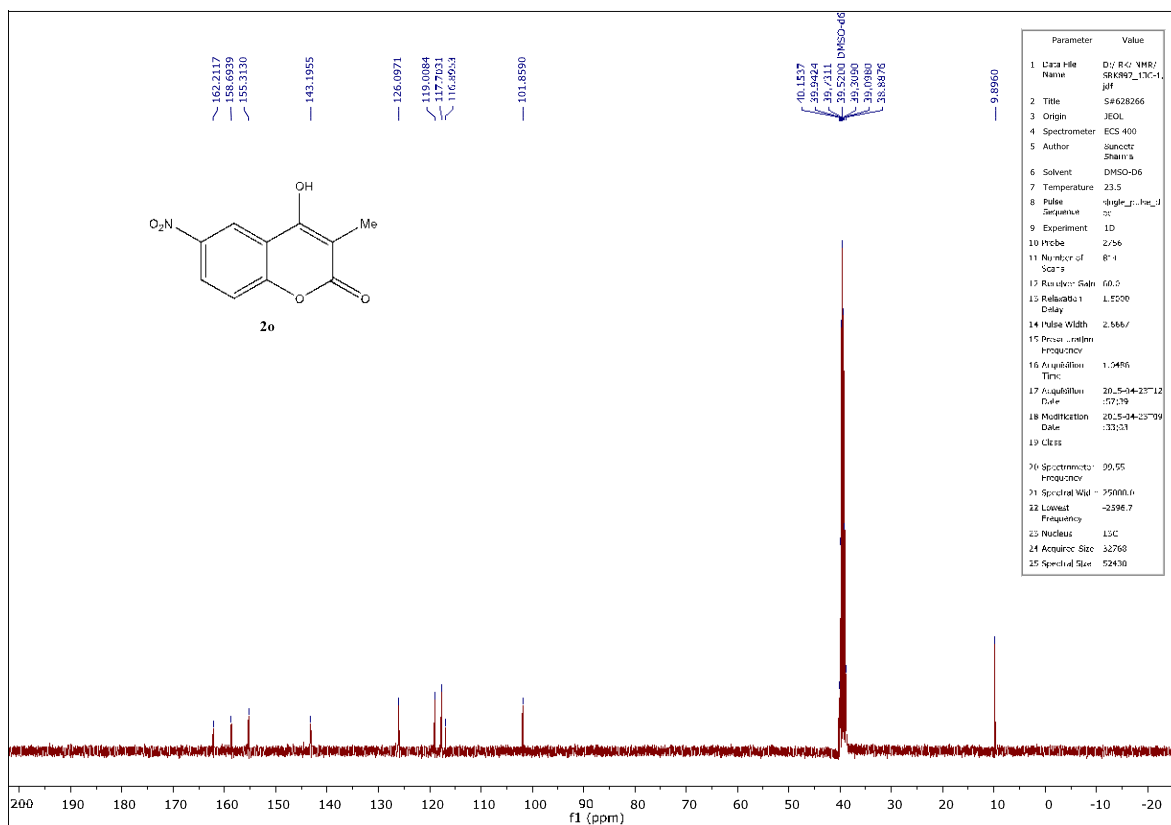
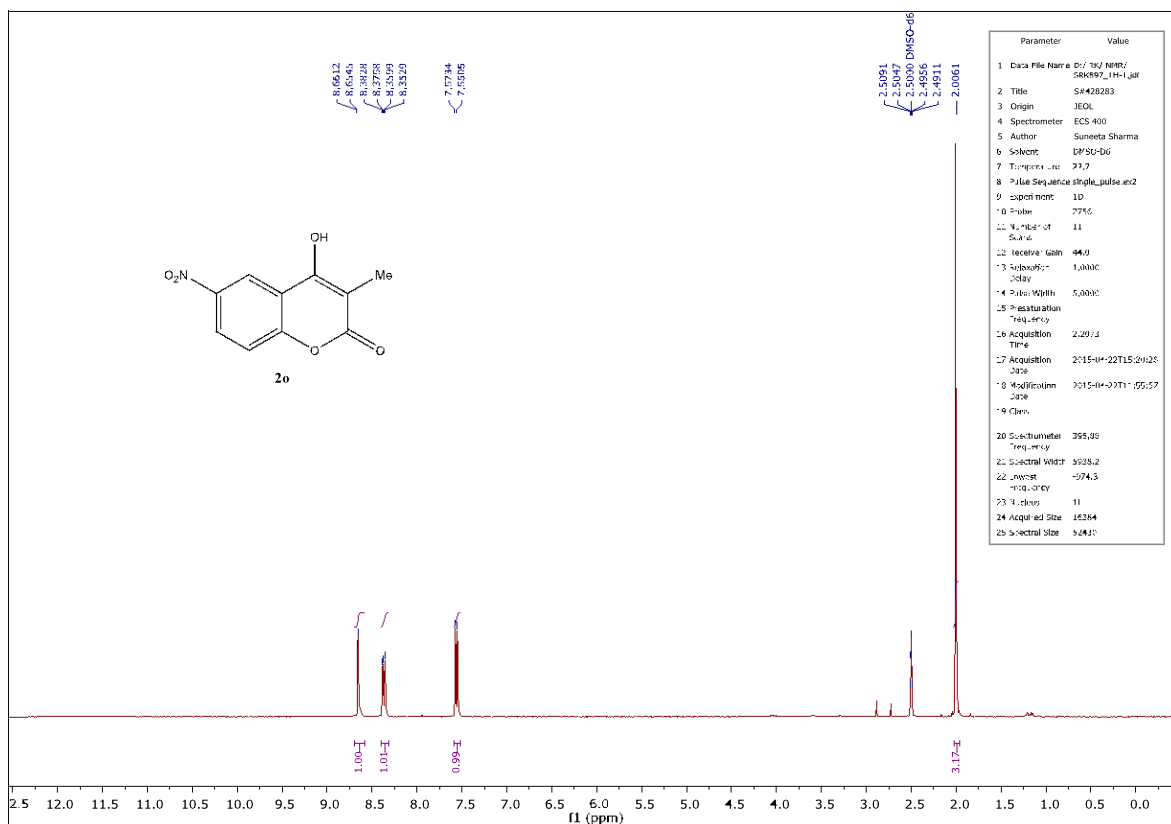
¹H and ¹³C NMR spectra of compound 6-acetyl-4-hydroxy-3-methyl-2H-chromen-2-one (21)



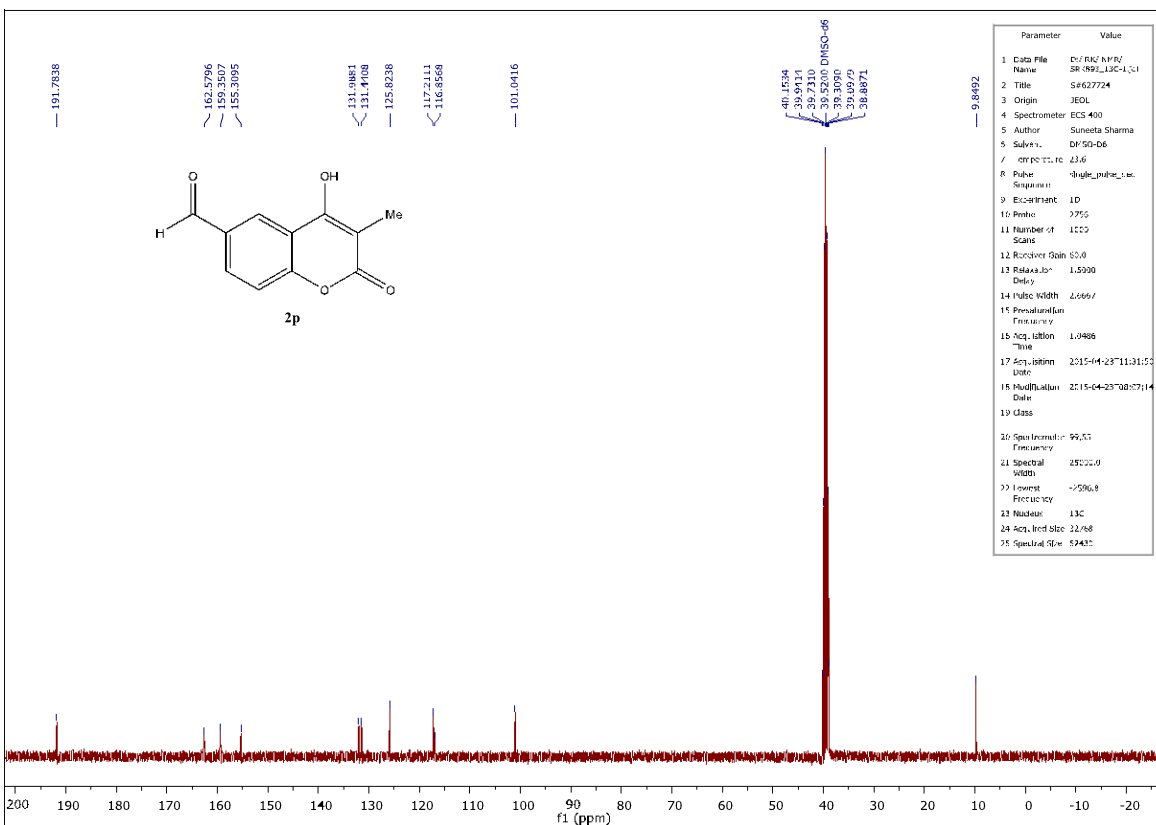
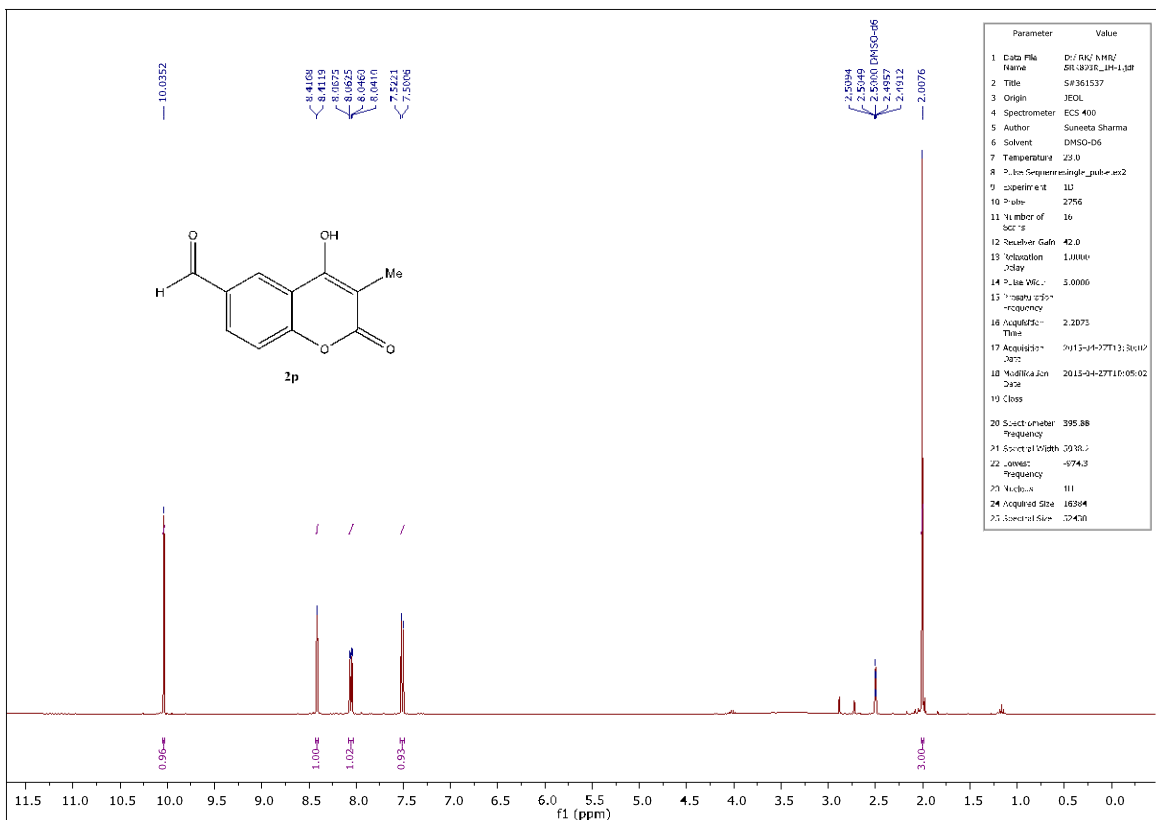
¹H and ¹³C NMR spectra of compound 4-hydroxy-3-methyl-2-oxo-2H-chromene-6-carbonitrile (**2m**)



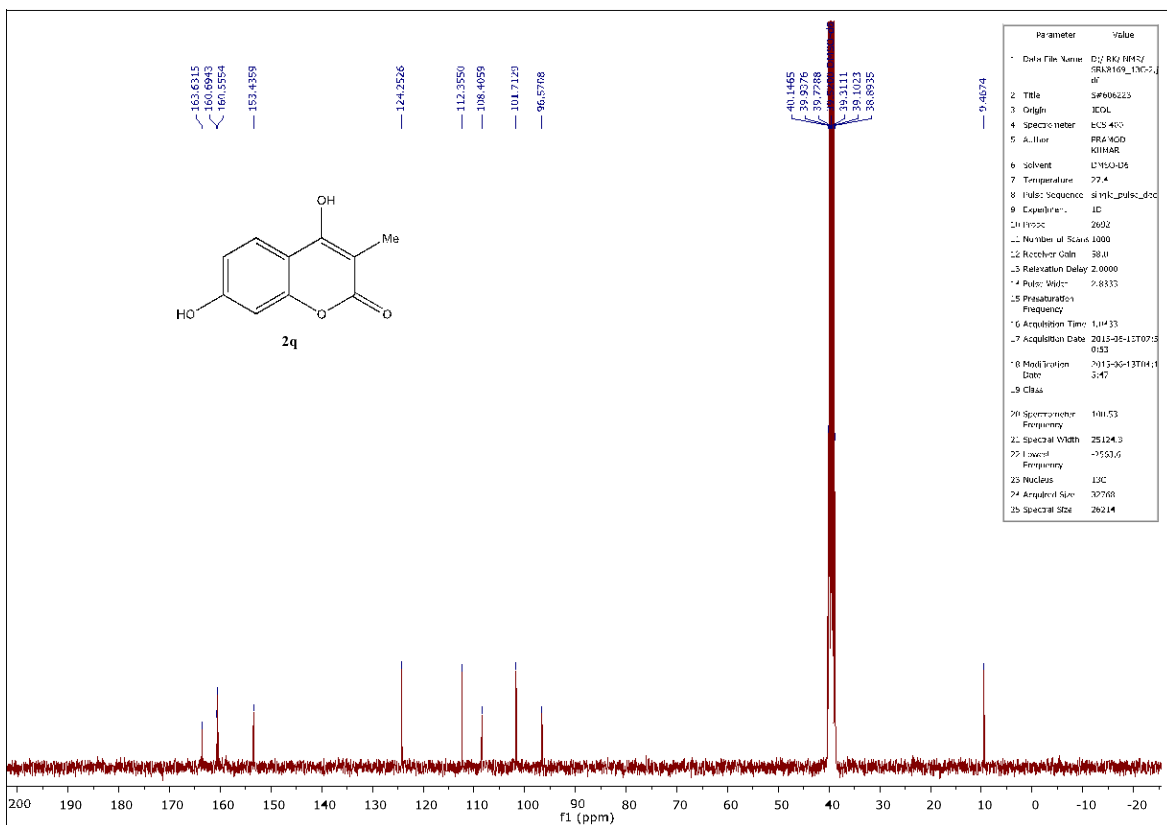
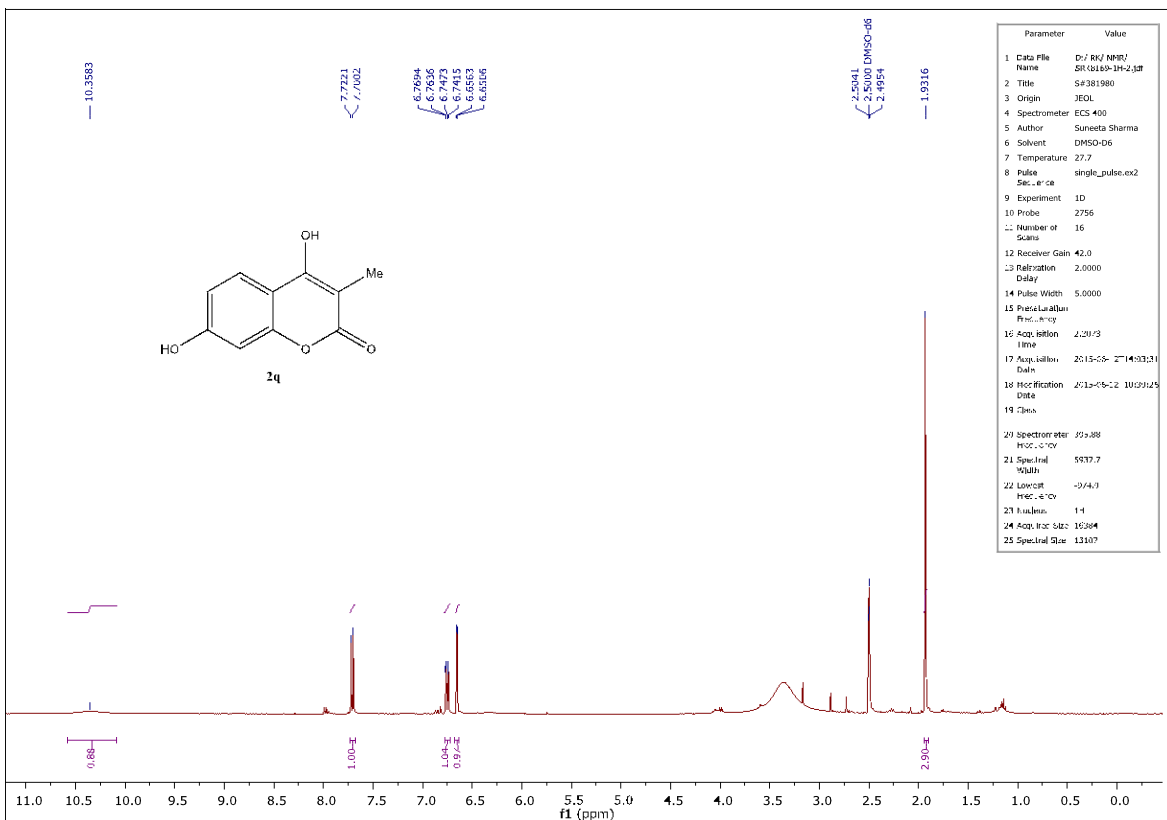
^1H and ^{13}C NMR spectra of compound methyl 4-hydroxy-3-methyl-2-oxo-2*H*-chromene-6-carboxylate (**2n**)



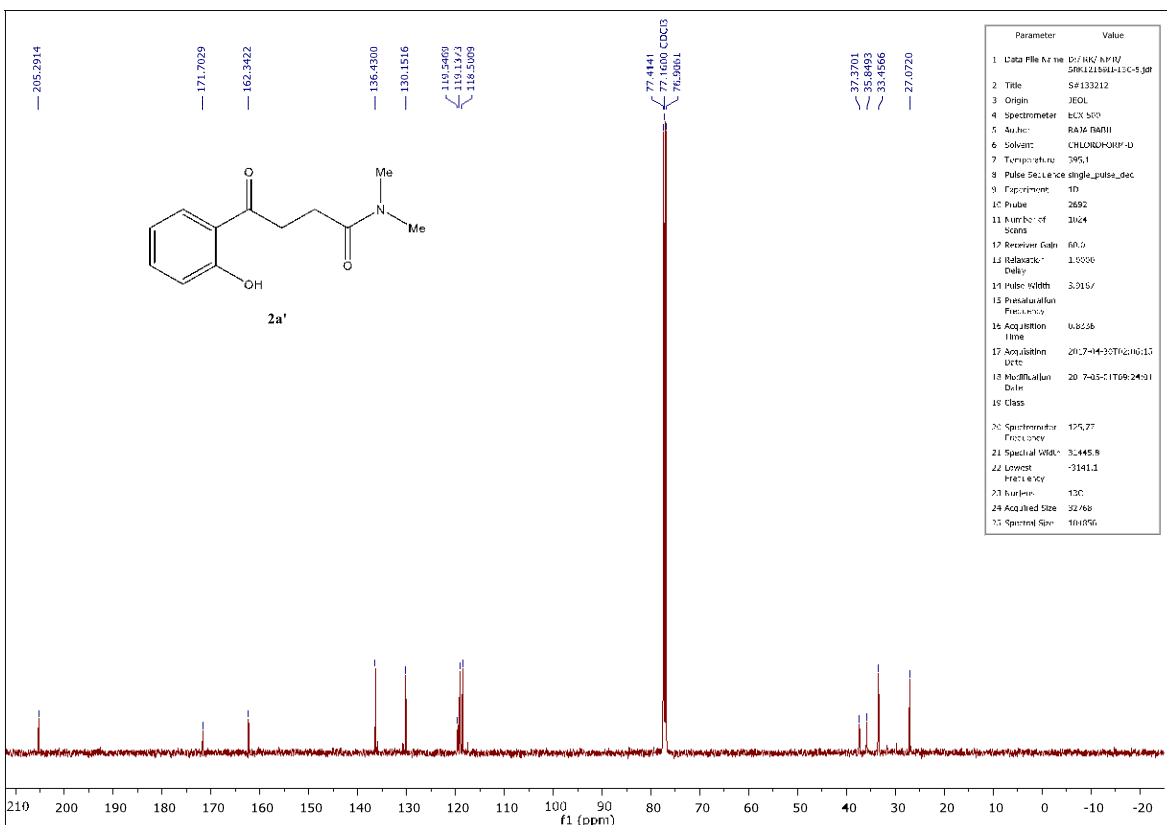
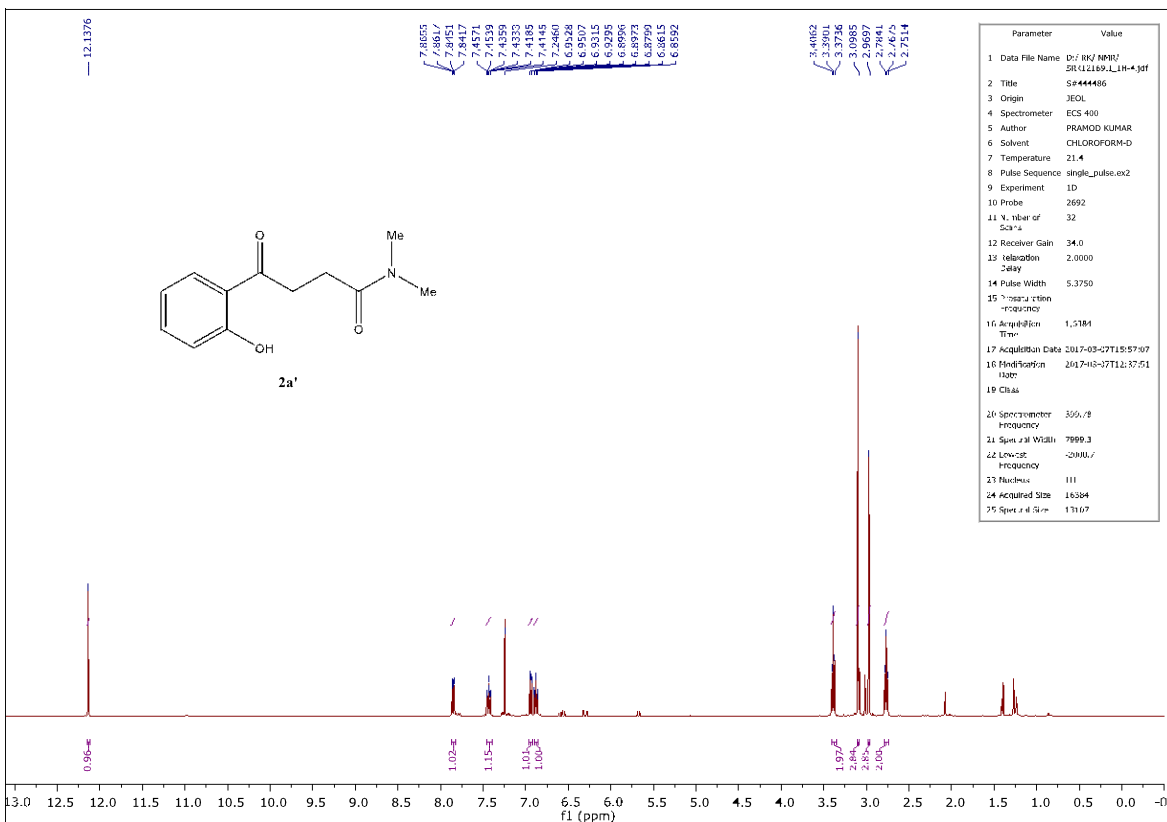
¹H and ¹³C NMR spectra of compound 4-hydroxy-3-methyl-6-nitro-2H-chromen-2-one (2o)



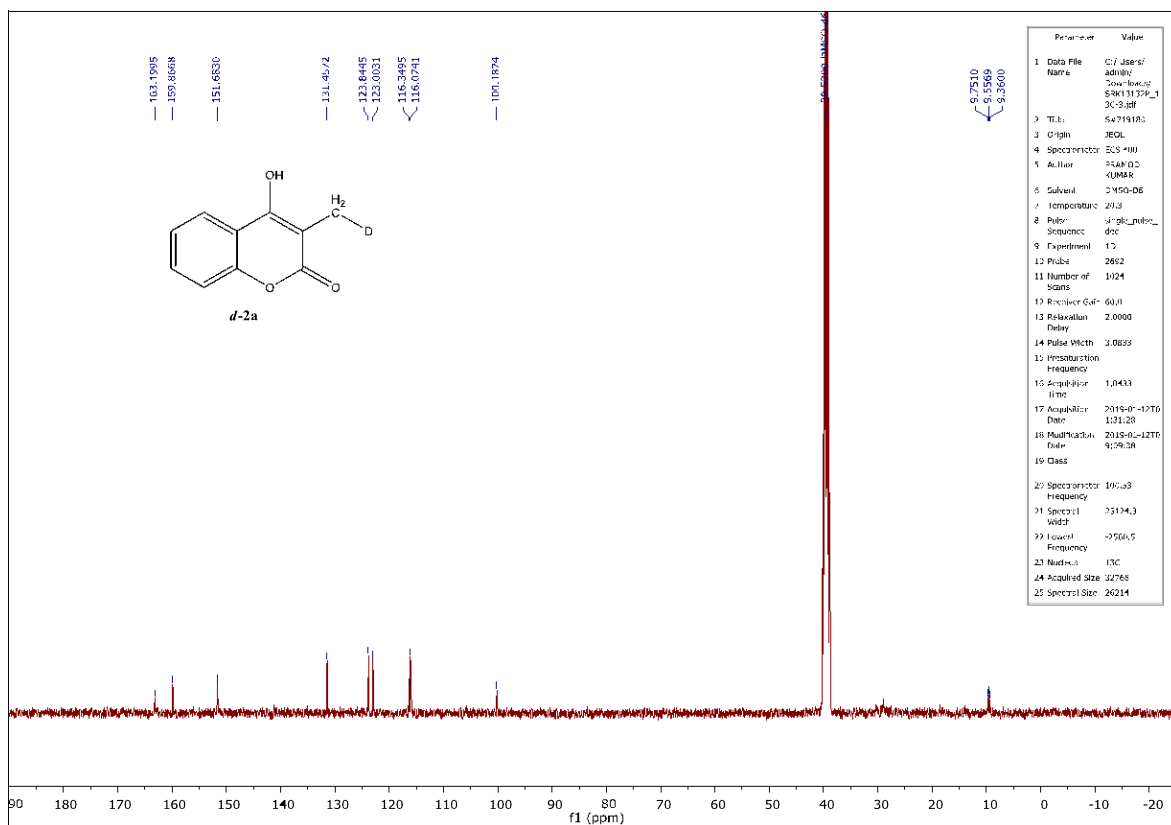
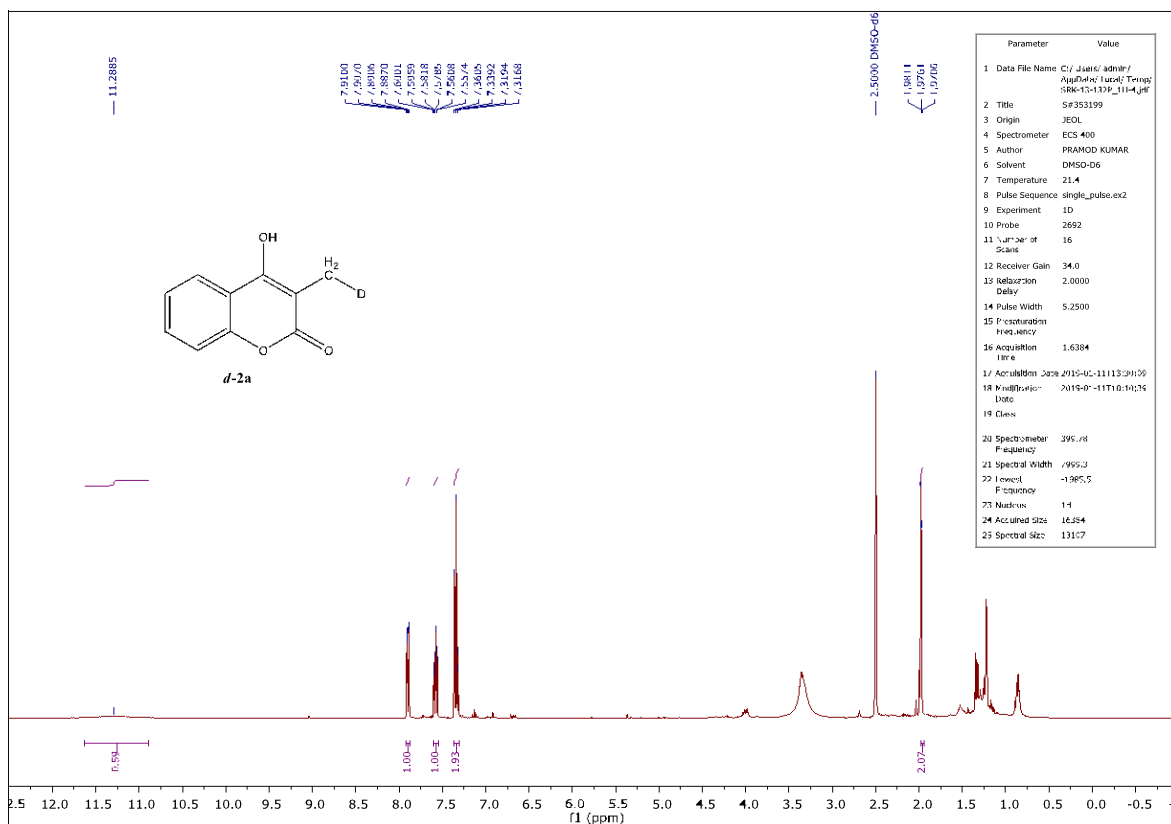
¹H and ¹³C NMR spectra of compound 4-hydroxy-3-methyl-2-oxo-2H-chromene-6-carbaldehyde (**2p**)



^1H and ^{13}C NMR spectra of compound 4,7-dihydroxy-3-methyl-2H-chromen-2-one (**2q**)

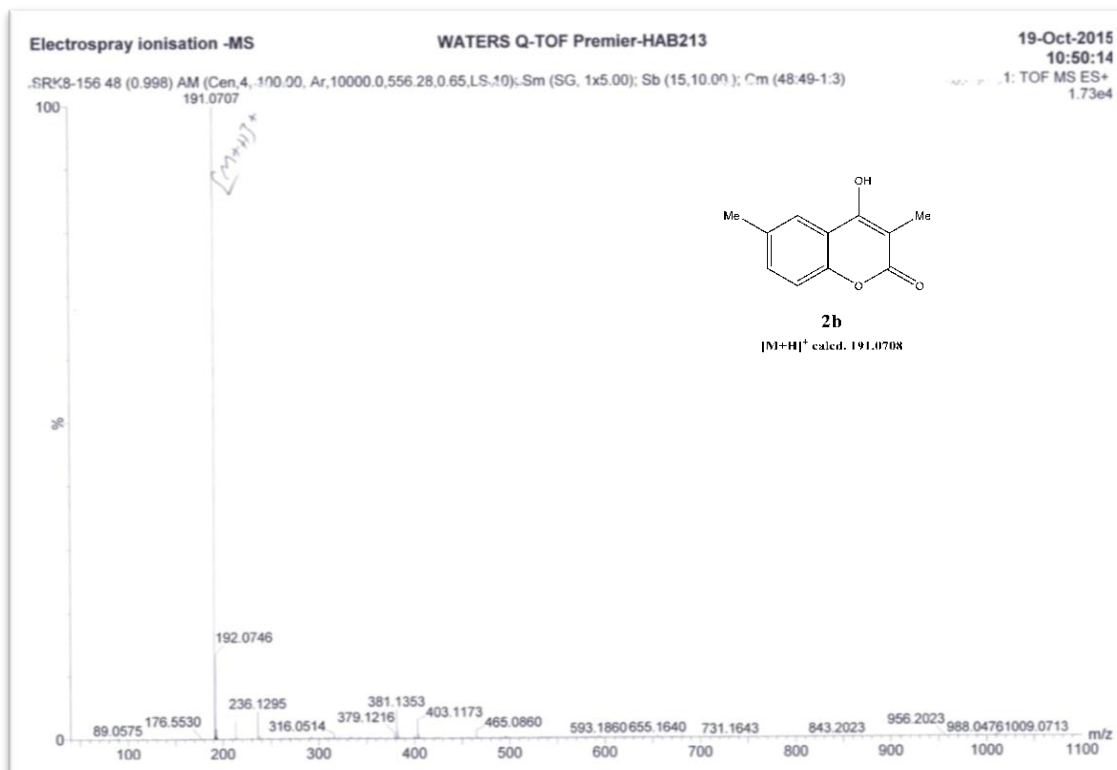
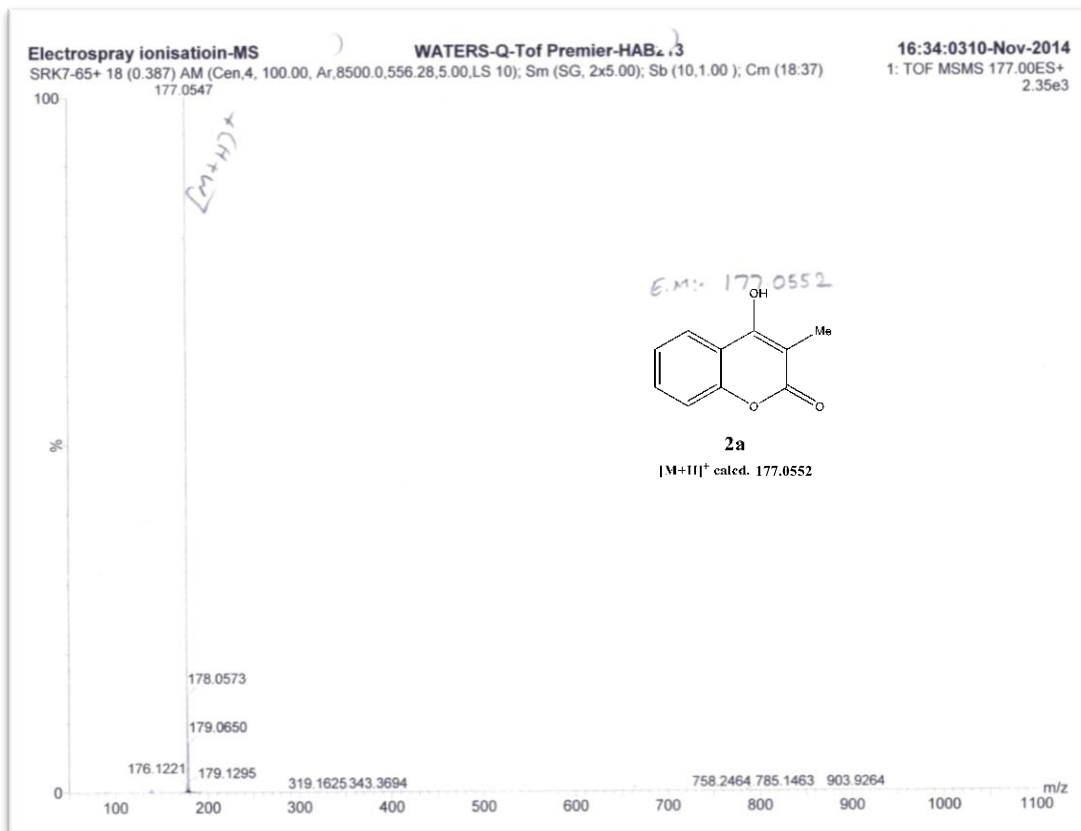


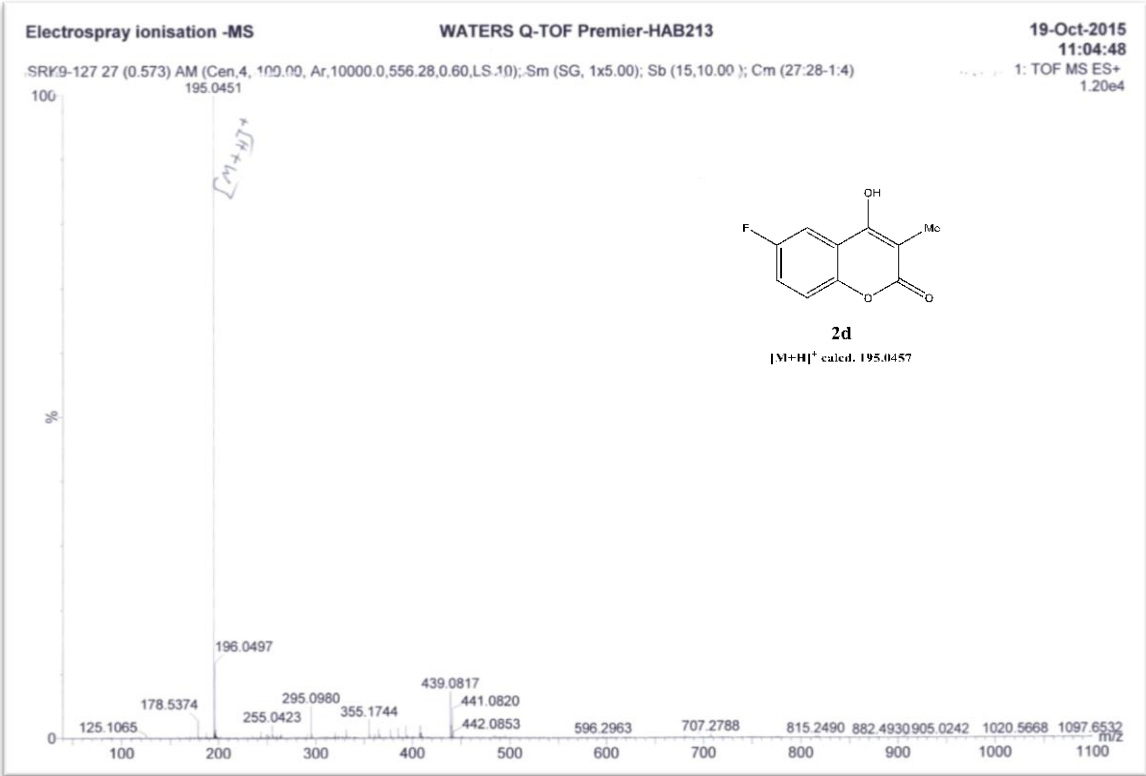
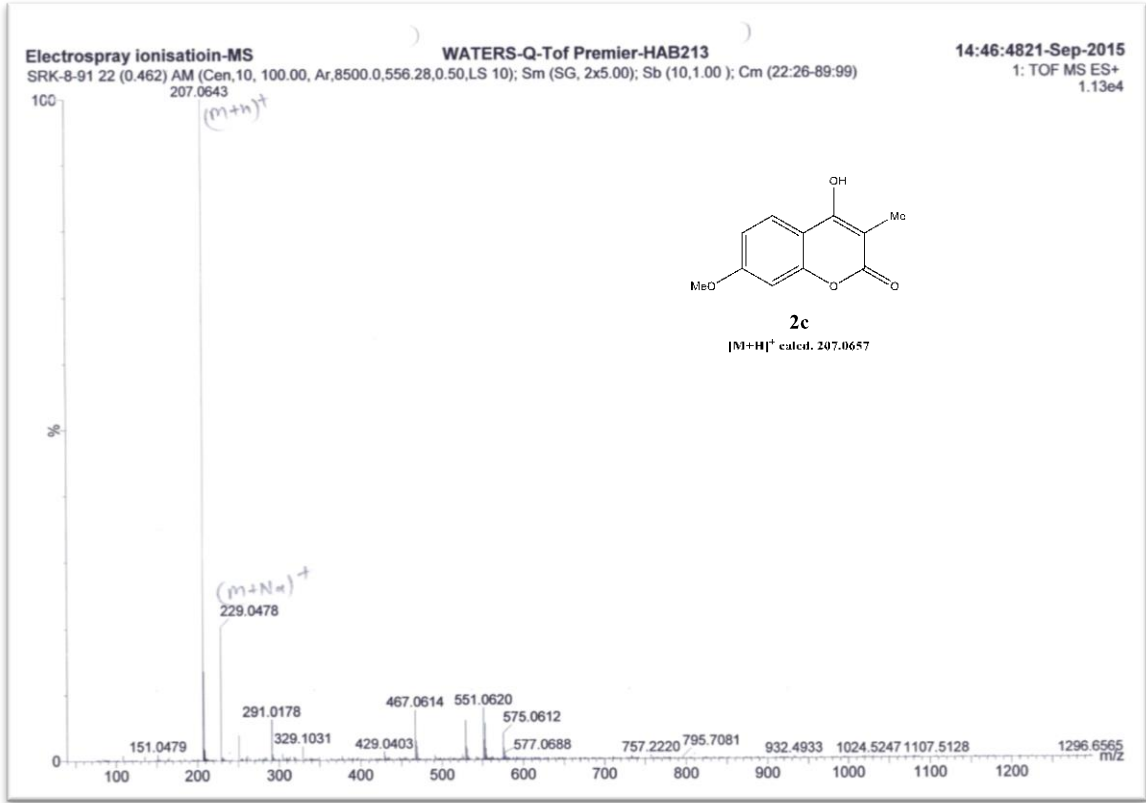
¹H and ¹³C NMR spectra of compound 4-(2-hydroxyphenyl)-*N,N*-dimethyl-4-oxobutanamide (**2a'**)

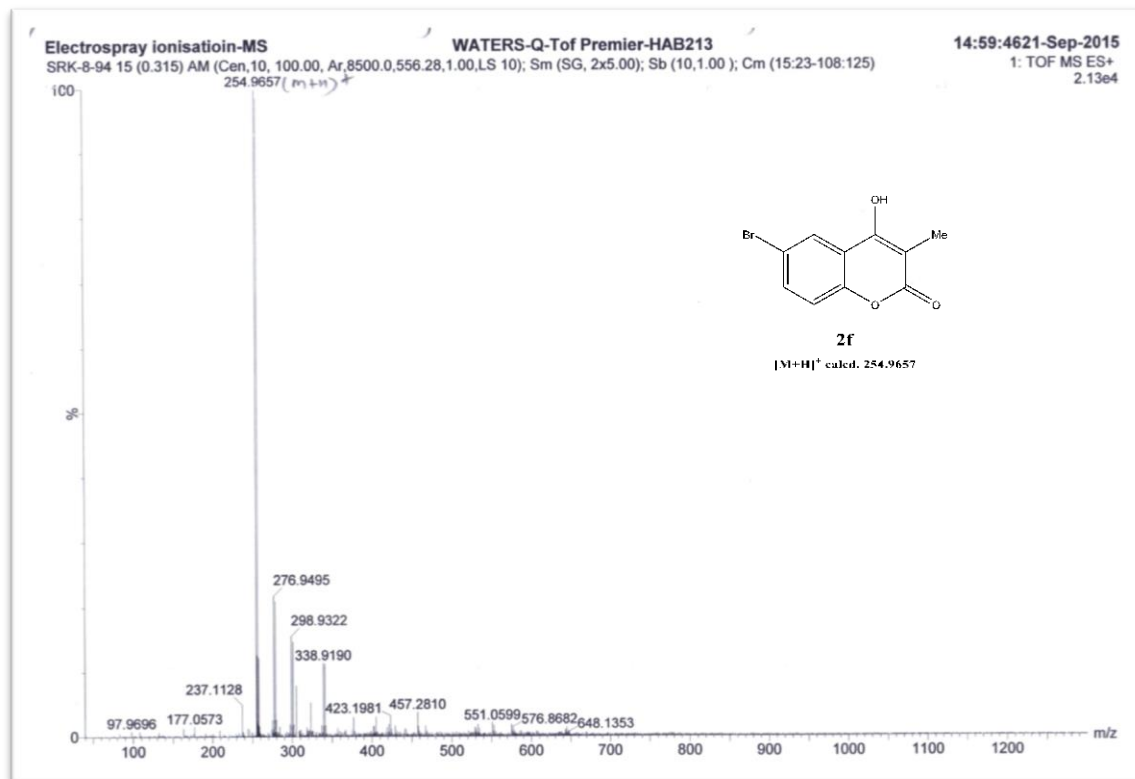
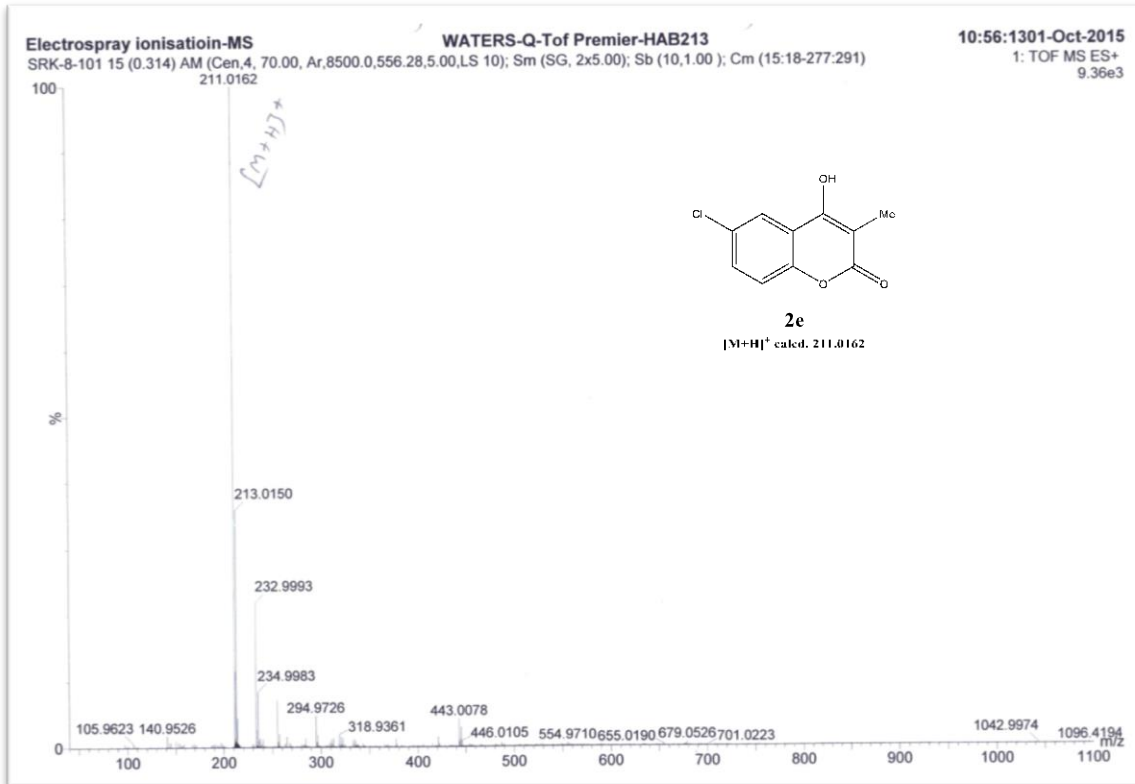


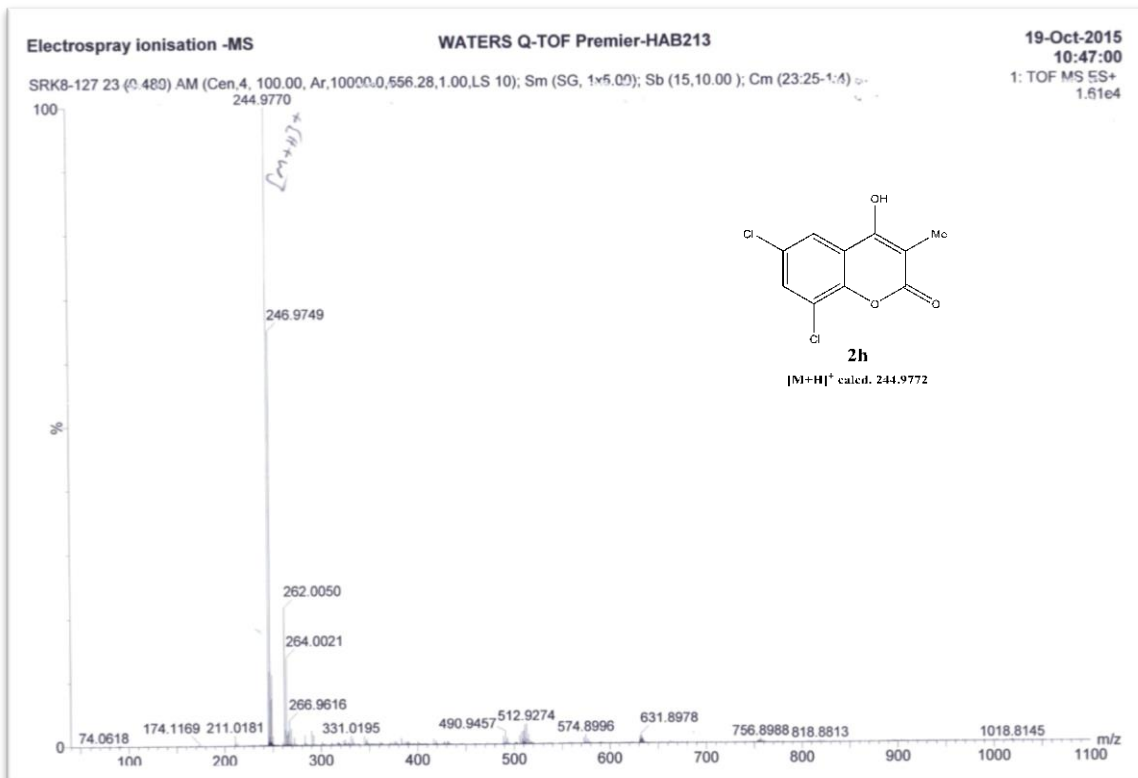
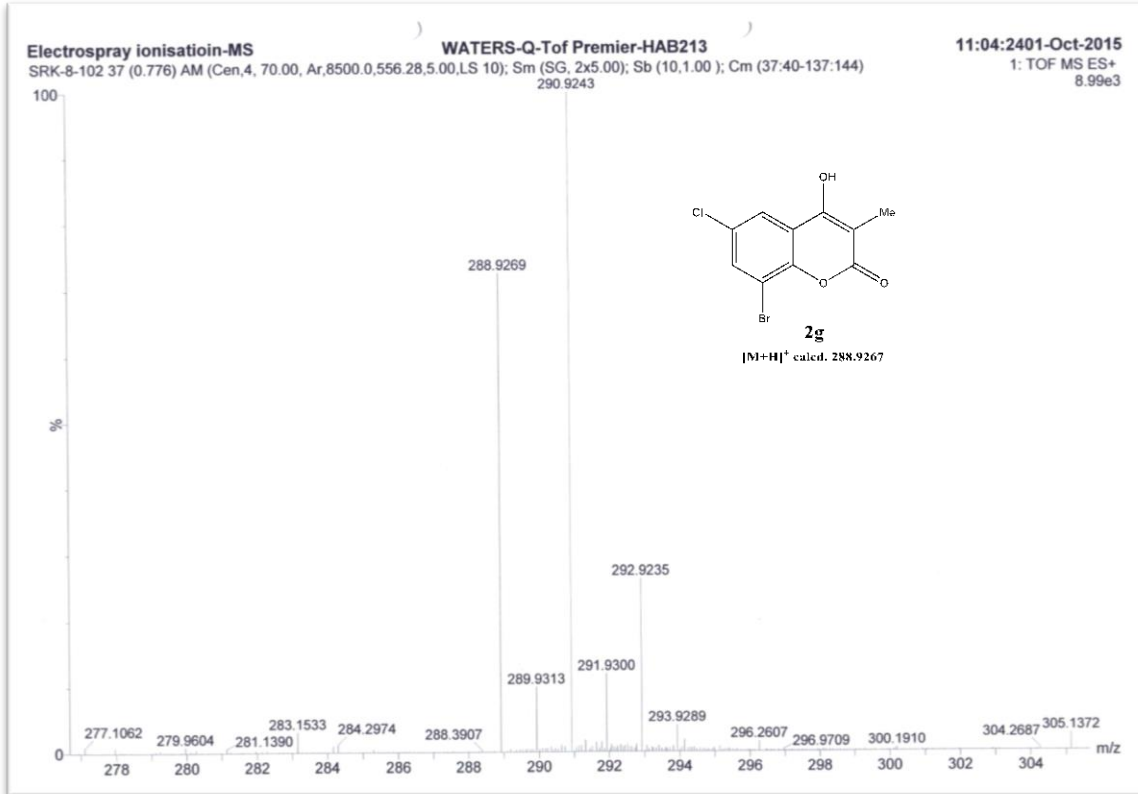
1H and ^{13}C NMR spectra of compound 4-hydroxy-3-methyl-2H-chromen-2-one (*d-2a*)

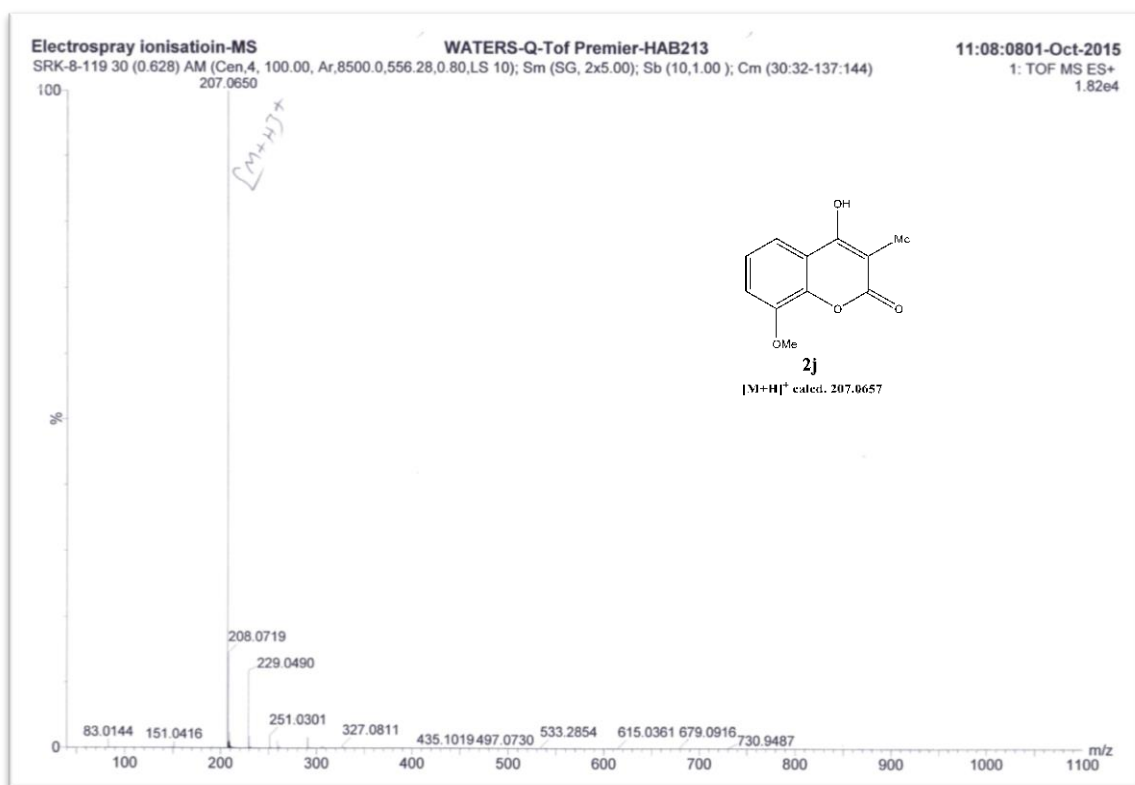
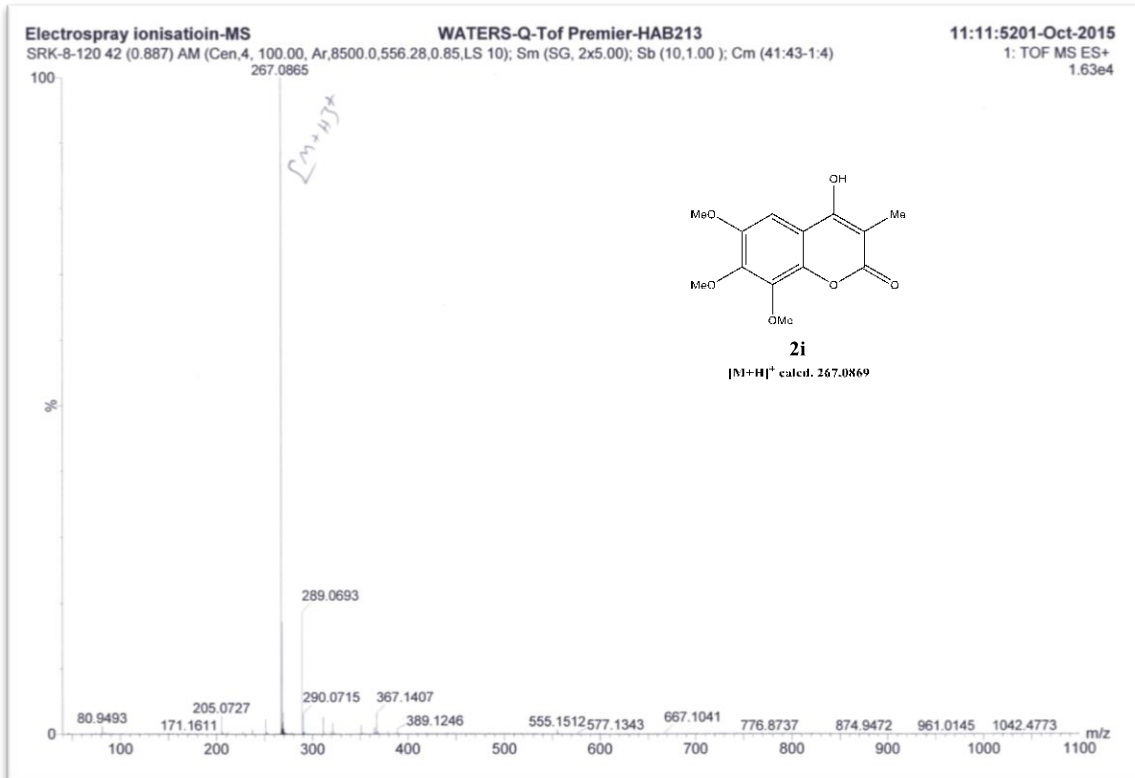
7. Copies of HRMS spectra of products

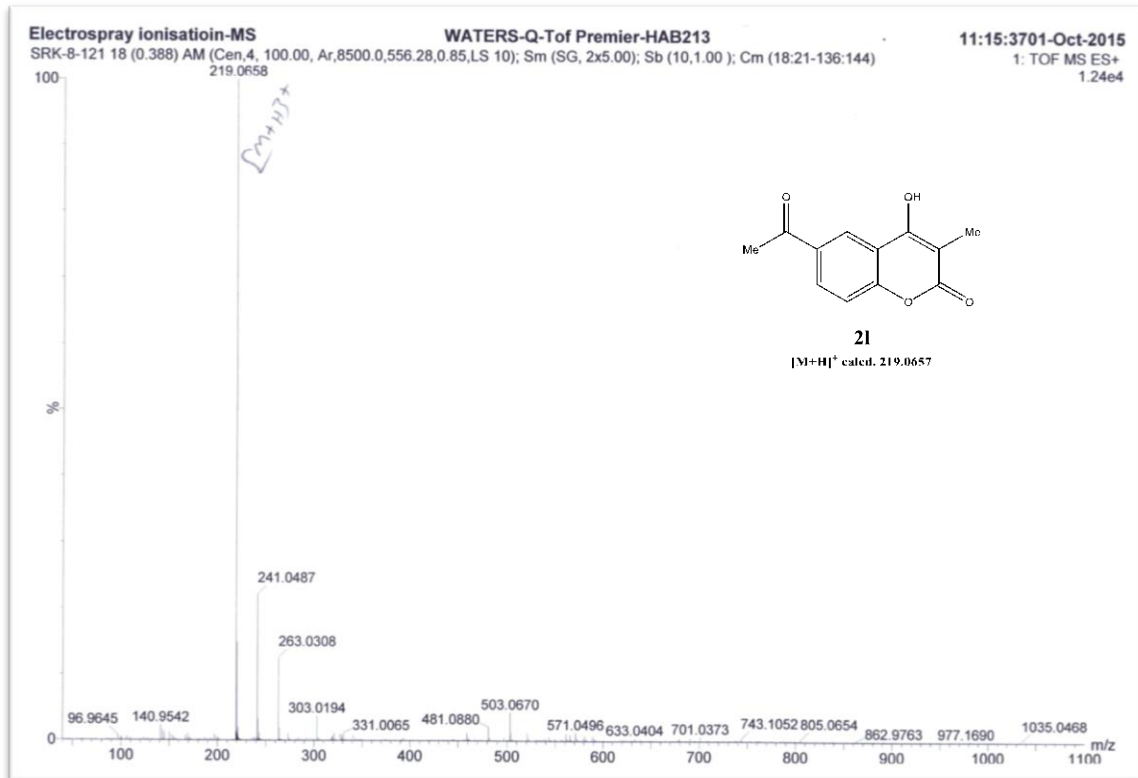
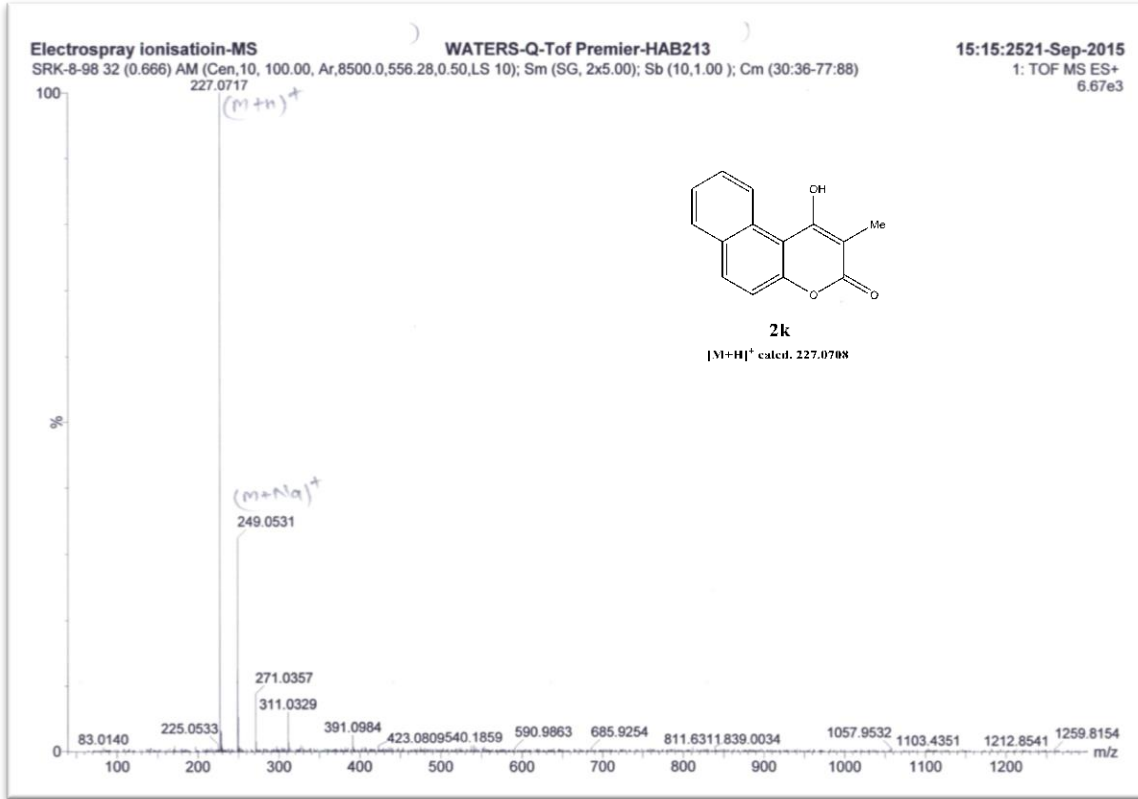


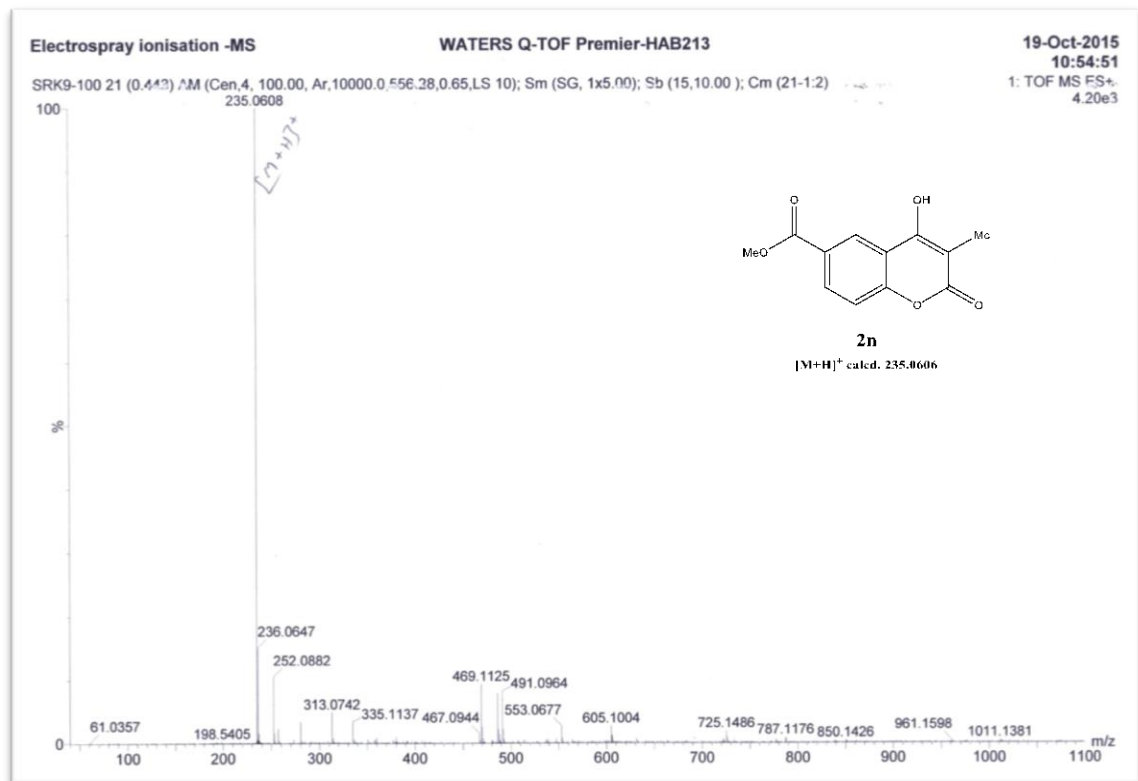
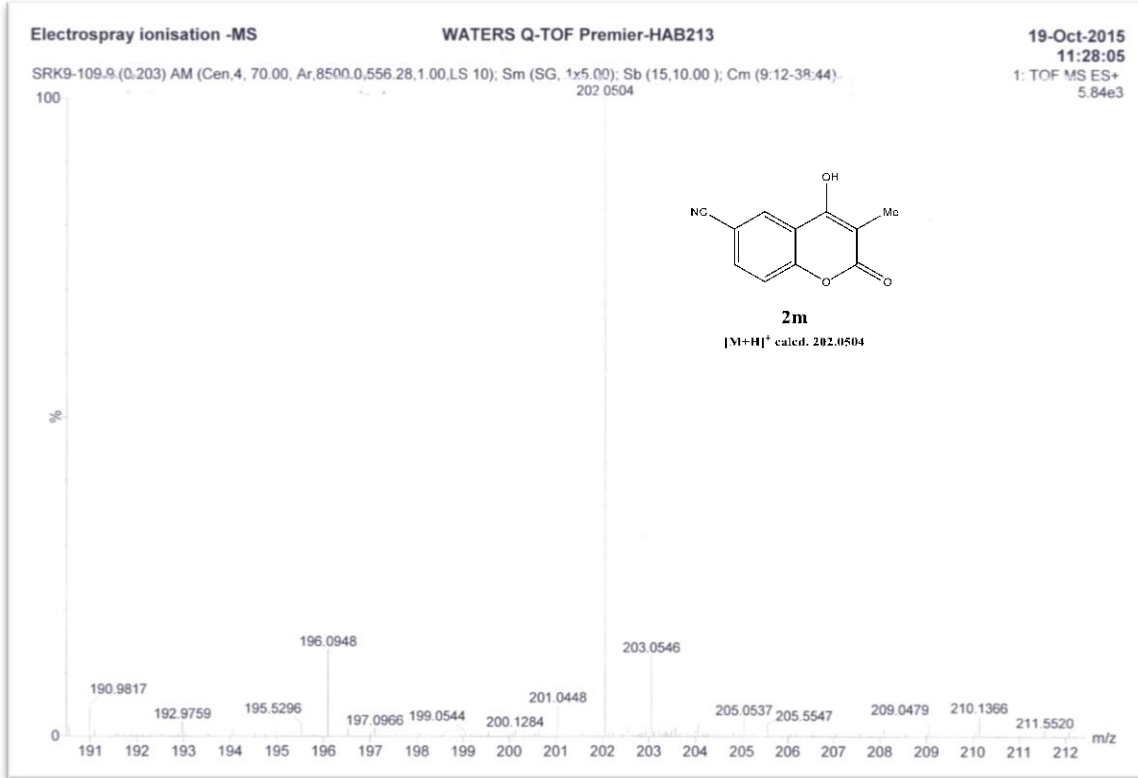


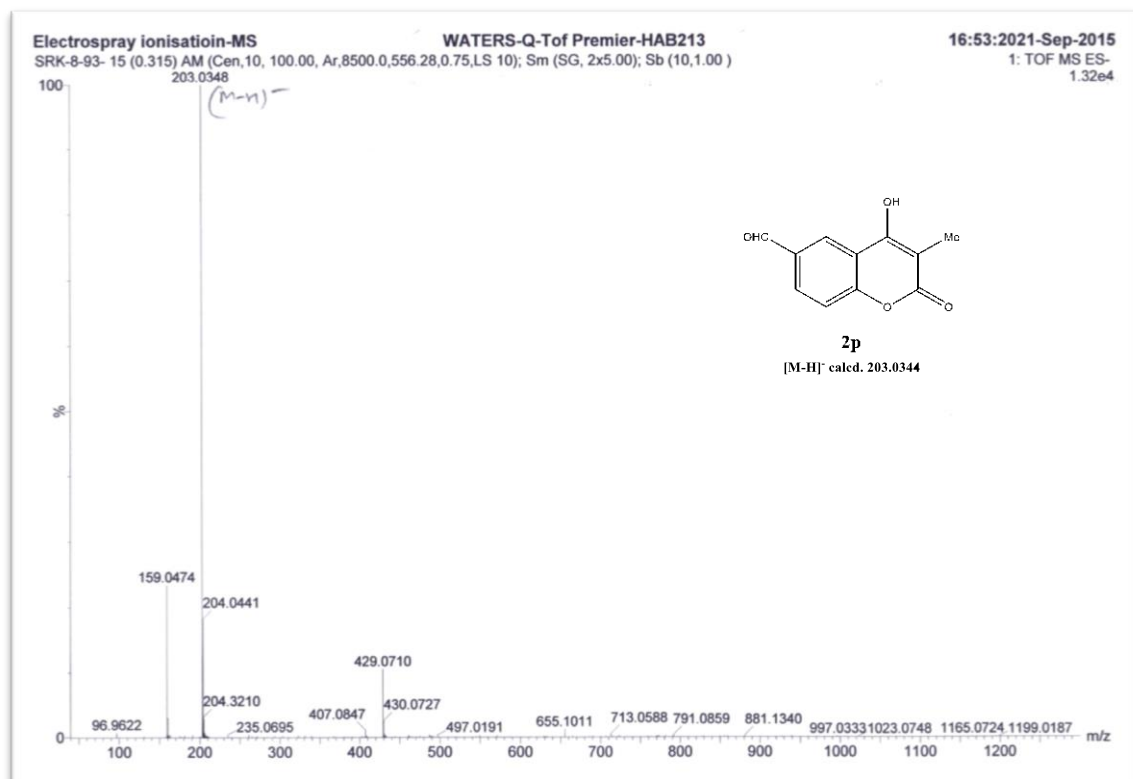
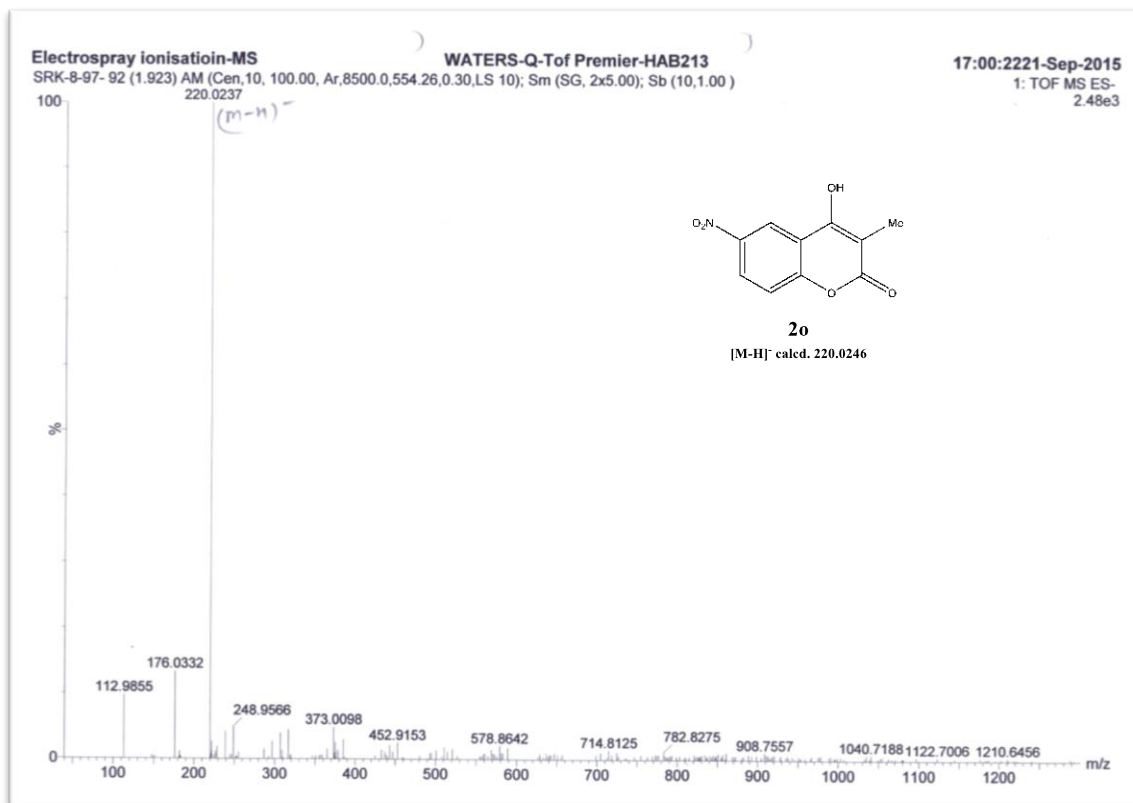


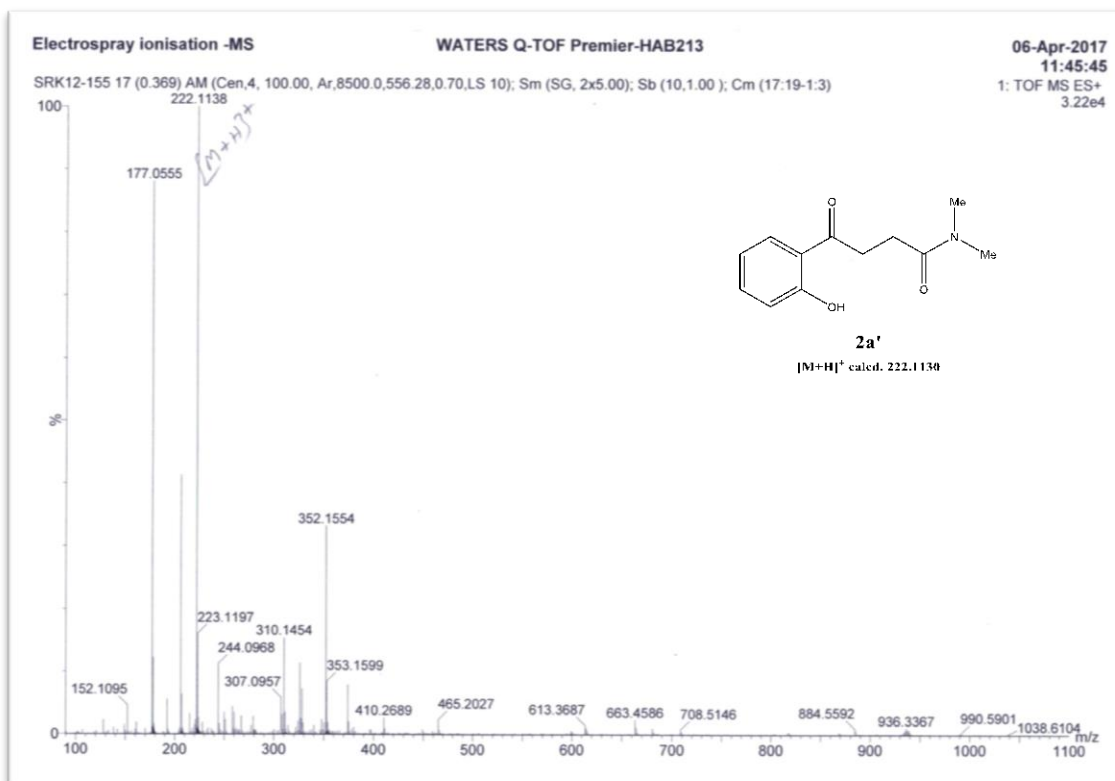
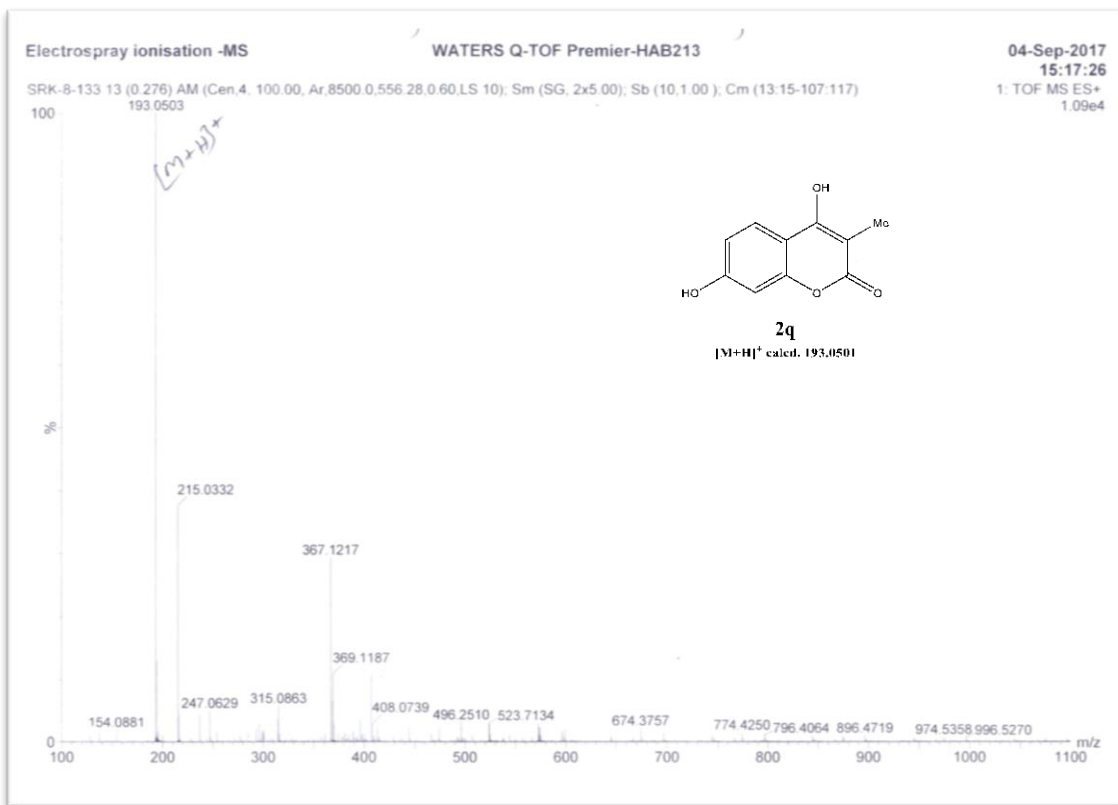












Electrospray ionisation -MS

WATERS Q-TOF Premier-HAB213

15-Jan-2019

16:18:25

SRK13-132 9 (0.203) AM (Cen,4, 80.00, Ar,8500.0,556.28,20.00,LS 10); Sm (SG, 2x5.00); Sb (10,1.00); Cm (9:10)

1: TOF MS ES+
2.19e3

