Supporting Information

Synthesis of pyrano[3,2-*c*]chromene-2,5-diones from 4-hydroxycoumarins and aminocrotonates under solvent-free conditions†

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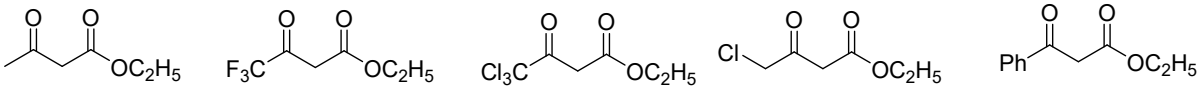
1. General Information: β-Ketoesters were procured from Sigma-Aldrich chemicals, USA. Substituted acetophenones, NaH, diethyl carbonate, Ammonium salts, Et_3N, K_2CO_3, Na_2CO_3, Cs_2CO_3, Imidazole, DABCO, DBU, DMAP, DIPEA, and solvents were procured from local suppliers. All the reactions were monitored by thin layer chromatography (TLC) on pre-coated silica gel 60 F254 (mesh); spots were visualized under UV light. Merck silica gel (60-120, 100-200 mesh) was used for column chromatography. ^1H NMR and ^{13}C NMR spectra were recorded on an Avance 300, 400, 500 MHz spectrometers in $CDCl_3$ using TMS as internal standard. ESI-MS obtained on quarto micro spectrometer. HRMS were measured on Agilent Technologies 6510, Q-TOFLC/MS ESI-Technique. Melting points were determined in open glass capillary tubes on a Stuart melting point apparatus and are uncorrected.

2. General procedure for the preparation of Aminocrotonates (2bg-2bt):

Step 1. To a dried 100-mL Round Bottom Flask were added NaH (0.9 g, 60% w/w, 2.80 equiv.), dimethyl carbonate (3.14 g, 2.0 equiv.) and toluene (10 mL) under nitrogen atmosphere. After the mixture was heated to reflux, acetophenone (2.0 g, 1.0 equiv.) in toluene (10 mL) was added dropwise over 0.5 h. After the evolution of hydrogen ceased (15-20 min), the reaction was cooled down to room temperature. Glacial acetic acid (6 mL) was added dropwise and a heavy pasty solid separated. Ice-cold water was slowly added until the solid was dissolved completely. Then, the reaction system was diluted with 200 mL of EtOAc. The organic layer was separated, washed with water (20 mL) and brine (20 mL) and dried over Na_2SO_4. After the solvent was evaporated, the residue was purified by column chromatography on silica gel (60-120) with EtOAc/hexane (1:3) as eluent to give the desired aryl *β*-ketoester (2.6 g) in 90% yield.

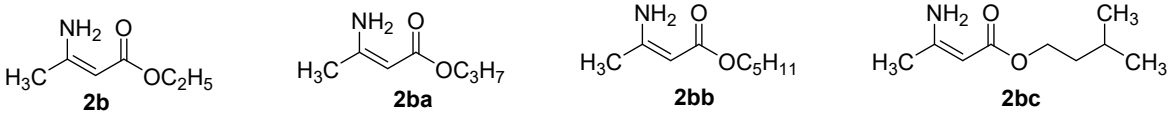
Step 2. Under nitrogen atmosphere, a solution of *β*-ketoester (2.6 g, 1.0 equiv.) and NH_4OAc (1.8 g, 2.0 equiv.) in methanol (12 mL) was stirred under reflux for 16 hr. After the solvent was evaporated under reduced pressure, the residue was suspended in EtOAc (30 mL). The insoluble solid was filtered off and washed with EtOAc (2 x 30 mL). The combined filtrate was washed with water and brine and dried over sodium sulfate. After the solvent was evaporated, the residue was purified by column chromatography on silica gel (60-120) with EtOAc/hexane (1:3) as eluent to give the desired aminocrotonate **2bg** in 80% yield. The remaining aminocrotonates **2bi-2bt** were prepared from corresponding acetophenones under above established procedure. The schematic scheme was depicted below.

Structures of *β*-Ketoesters: 2a, 2aa-2ad

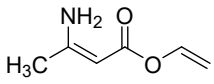


2a **2aa** **2ab** **2ac** **2ad**

Structures of Aminocrotonates: 2b, 2ba-2bd

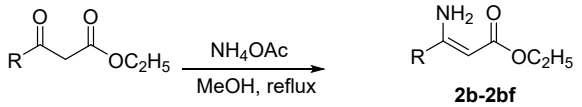


2b **2ba** **2bb** **2bc**

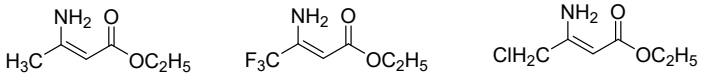


2bd

Structures of Aminocrotonates: 2b, 2be & 2bf

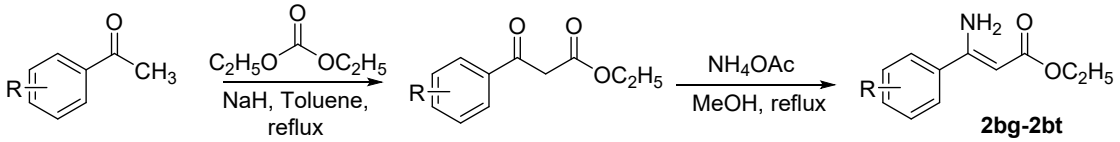


2b-2bf

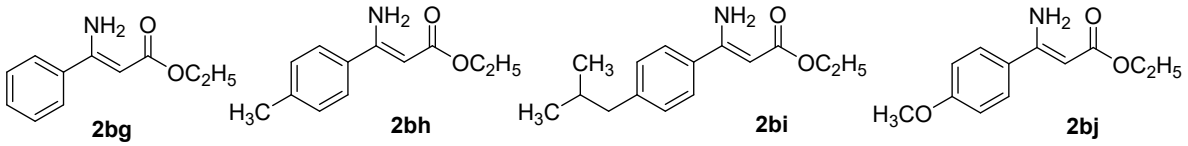


2b **2be** **2bf**

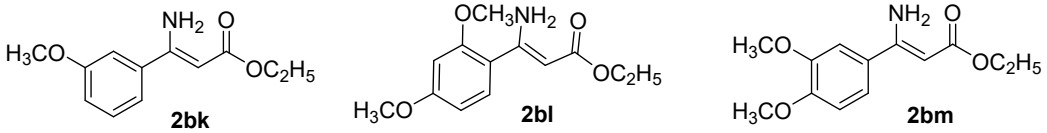
Aminocrotonates: 2bg-2bt



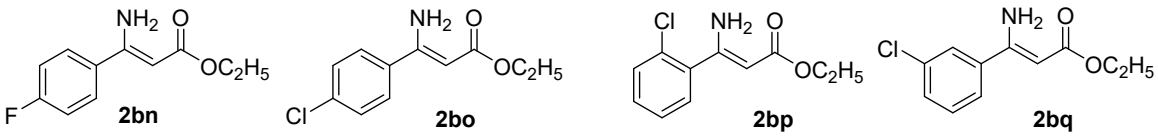
2bg-2bt



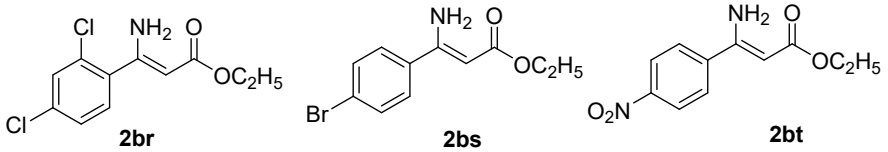
2bg **2bh** **2bi** **2bj**



2bk **2bl** **2bm**



2bn **2bo** **2bp** **2bq**

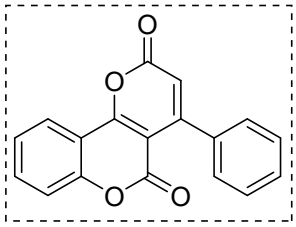


2br **2bs** **2bt**

3. General procedure for the preparation of 4-phenyl-2*H*,5*H*-pyrano[3,2-*c*]chromene-2,5-dione (**3ad**): 4-Hydroxycoumarin (**1a**, 0.1 g, 1.0 equiv.) and ethyl 3-amino-3-phenylacrylate (**2bg**, 0.118 g, 1.0 equiv.) were heated at 130 °C. The reaction mixture was monitored by TLC and after completion of reaction (TLC, 8h), the residue was purified by column chromatography by using silica gel (60:120, ethyl acetate/hexane 5:95) afforded 4-phenyl-2*H*,5*H*-pyrano[3,2-*c*]chromene-2,5-dione **3ad** as colorless solid in 80% yield. The pyranochromenediones **3b-3zc** were prepared by reacting substituted 4-hydroxycoumarins with various aminocrotonates **2bg-2bt** under above optimized reaction conditions.

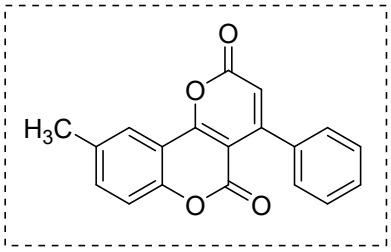
4. Spectral data of compounds:

4-Phenyl-2*H*,5*H*-pyrano[3,2-*c*]chromene-2,5-dione (**3ad**):



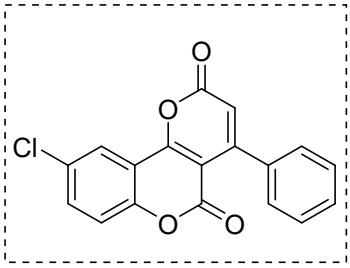
Colorless solid (80%), m.p. 208-210 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (dd, J = 8.0, 1.5 Hz, 1H), 7.70 (td, J = 8.7, 7.4, 1.6 Hz, 1H), 7.50-7.32 (m, 7H), 6.29 (s, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.63, 157.82, 156.96, 153.54, 136.18, 134.7, 129.52, 128.11, 127.44, 125.05, 124.19, 117.04, 113.24, 102.65 ppm. ESI-MS: *m/z* 291 $[M+H]^+$; HRMS-ESI: Calcd for $C_{18}H_{11}O_4$ $[M+H]^+$ 291.0651; found 291.0648.

9-Methyl-4-phenyl-2*H*,5*H*-pyrano[3,2-*c*]chromene-2,5-dione (**3b**):



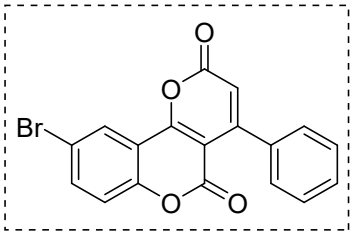
Colorless solid (76%), m.p. 226-228 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (dd, J = 8.0, 1.5 Hz, 1H), 7.76-7.69 (m, 1H), 7.49-7.39 (m, 2H), 7.30 (s, 4H), 6.31 (s, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.67, 157.97, 157.21, 157.06, 151.78, 136.28, 135.93, 135.05, 129.48, 128.08, 127.43, 123.68, 116.79, 115.49, 112.85, 102.54, 20.95 ppm. ESI-MS: *m/z* 303 $[M-H]^+$; HRMS-ESI: Calcd for $C_{19}H_{11}O_4$ $[M-H]^+$ 303.0651; found 303.0663.

9-Chloro-4-phenyl-2*H*,5*H*-pyrano[3,2-*c*]chromene-2,5-dione (**3c**):



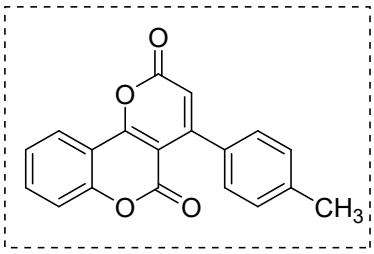
Pale yellow solid (62%), m.p. 228-230 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, J = 2.5 Hz, 1H), 7.63 (dd, J = 8.9, 2.5 Hz, 1H), 7.52-7.42 (m, 3H), 7.34 (dt, J = 4.5, 2.7 Hz, 3H), 6.32 (s, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 161.46, 157.28, 156.61, 156.48, 151.83, 135.86, 134.73, 130.80, 129.66, 128.16, 127.43, 123.56, 118.55, 116.30, 114.28, 103.19 ppm. ESI-MS: *m/z* 325 $[M+H]^+$; HRMS-ESI: Calcd for $C_{18}H_{10}ClO_4$ $[M+H]^+$ 325.0268; found 325.0272.

9-Bromo-4-phenyl-2*H*,5*H*-pyrano[3,2-*c*]chromene-2,5-dione (**3d**):



Pale yellow solid (60%), m.p. 232-234 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, J = 2.5 Hz, 1H), 7.63 (dd, J = 8.9, 2.5 Hz, 1H), 7.52-7.43 (m, 3H), 7.34 (dt, J = 4.5, 2.7 Hz, 3H), 6.32 (s, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 161.35, 157.28, 156.61, 156.42, 152.29, 137.53, 135.85, 129.67, 128.16, 127.42, 126.60, 118.77, 117.95, 116.29, 114.69, 103.18 ppm. ESI-MS: *m/z* 367 $[M+H_2O]^+$; HRMS-ESI: Calcd for $C_{18}H_{10}O_4Br$ $[M+H]^+$ 368.9762; found 368.9745.

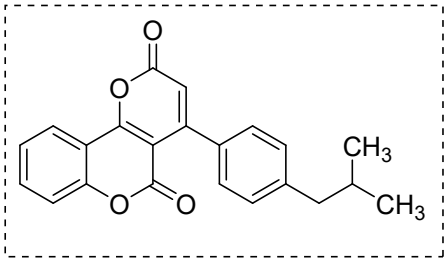
4-(*p*-tolyl)-2*H*,5*H*-Pyrano[3,2-*c*]chromene-2,5-dione (**3e**):



Colorless solid (85%), m.p. 196-197 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (dd, J = 8.0, 1.5 Hz, 1H), 7.76-7.63 (m, 1H), 7.48-7.35 (m, 2H), 7.26 (s, 4H), 6.27 (s, 1H), 2.42 (s, 3H) ppm.

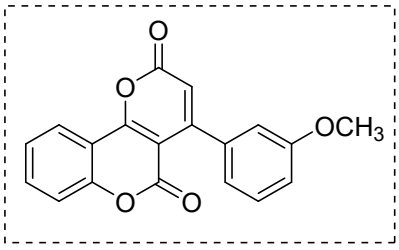
^{13}C NMR (101 MHz, $CDCl_3$): δ 162.59, 157.89, 157.01, 153.50, 139.76, 134.69, 133.27, 128.83, 127.49, 125.00, 124.18, 116.99, 115.42, 113.27, 102.70, 21.50 ppm. ESI-MS: *m/z* 305 $[M+H]^+$; HRMS-ESI: Calcd for $C_{19}H_{13}O_4$ $[M+H]^+$ 305.0814; found 305.0804.

4-(4-Isobutylphenyl)-2*H*,5*H*-pyrano[3,2-*c*]chromene-2,5-dione (**3f**):



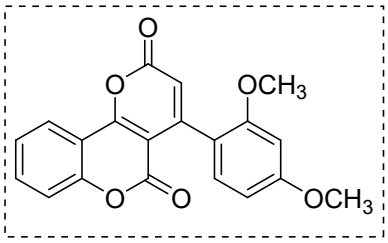
Colorless solid (89%), m.p. 152-154 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.15 (d, J = 7.9 Hz, 1H), 7.74-7.64 (m, 1H), 7.41 (t, J = 7.7 Hz, 1H), 7.37 (d, J = 8.4 Hz, 1H), 7.27 (d, J = 8.2 Hz, 2H), 7.22 (d, J = 8.0 Hz, 2H), 6.29 (s, 1H), 2.54 (t, J = 7.5 Hz, 2H), 1.92 (dd, J = 13.4, 6.7 Hz, 1H), 0.95 (d, J = 6.6 Hz, 6H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ 162.52, 157.85, 157.00, 156.97, 153.47, 143.46, 134.65, 133.49, 128.80, 127.39, 124.98, 124.15, 116.96, 115.41, 113.27, 102.71, 45.33, 30.17, 22.49 ppm. ESI-MS: *m/z* 347 $[M+H]^+$. HRMS-ESI: Calcd for $C_{22}H_{19}O_4$ $[M+H]^+$ 347.1283; found 347.1283.

4-(3-Methoxyphenyl)-2*H*,5*H*-pyrano[3,2-*c*]chromene-2,5-dione (**3h**):



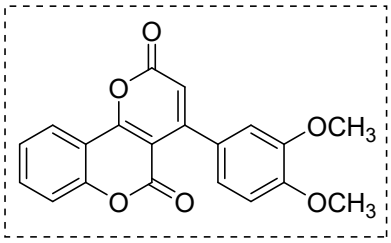
Pale yellow solid (70%), m.p. 175-177 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (dd, J = 8.0, 1.1 Hz, 1H), 7.72-7.64 (m, 1H), 7.40 (s, 1H), 7.36 (d, J = 6.9 Hz, 2H), 6.99 (dd, J = 8.3, 2.1 Hz, 1H), 6.91 (d, J = 7.6 Hz, 1H), 6.87 (d, J = 1.8 Hz, 1H), 6.28 (s, 1H), 3.82 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.57, 159.18, 157.80, 156.76, 153.51 ,137.46, 134.76, 129.24, 125.04, 124.16 , 119.79, 117.00, 115.64, 114.92 , 113.22, 102.68, 55.38 ppm. ESI-MS: *m/z* 321 $[M+H]^+$; HRMS-ESI: Calcd for $C_{19}H_{13}O_5$ $[M+H]^+$ 321.0763; found 321.0748.

4-(2,4-Dimethoxyphenyl)-2*H*,5*H*-pyrano[3,2-*c*]chromene-2,5-dione (**3i**):



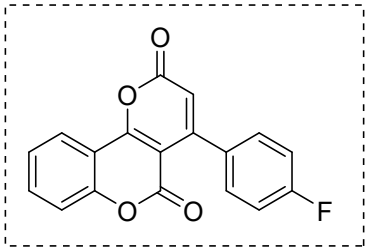
Yellow solid (73%), m.p. 203-205 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, J = 7.7 Hz, 1H), 7.66 (t, J = 7.5 Hz, 1H), 7.44-7.32 (m, 2H), 7.14 (d, J = 8.2 Hz, 1H), 6.57 (d, J = 8.0 Hz, 2H), 6.26 (s, 1H), 3.86 (s, 3H), 3.74 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.51, 161.12, 158.52, 157.99, 157.09, 154.44, 153.25, 134.22, 129.02, 124.82, 124.06, 118.86, 116.92, 115.39, 113.44, 104.48, 98.54, 55.53 ppm. ESI-MS: *m/z* 351 $[M+H]^+$. HRMS-ESI: Calcd for $C_{20}H_{15}O_6$ $[M+H]^+$ 351.0869; found 351.0889.

4-(3,4-Dimethoxyphenyl)-2*H*,5*H*-pyrano[3,2-*c*]chromene-2,5-dione (**3j**):



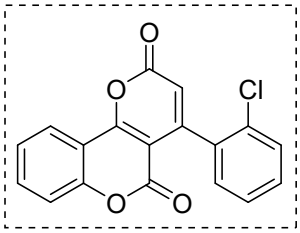
Yellow solid (72%), m.p. 205-207 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, J = 8.0 Hz, 1H), 7.69 (dd, J = 11.4, 4.3 Hz, 1H), 7.41 (d, J = 7.7 Hz, 2H), 7.02-6.94 (m, 2H), 6.88 (d, J = 1.5 Hz, 1H), 6.30 (s, 1H), 3.94 (s, 3H), 3.90 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.66, 157.91, 157.07, 156.53, 153.44, 150.36, 148.39, 134.72, 128.51, 125.02, 124.18, 120.6, 116.93, 115.15, 113.24, 111.28, 110.57, 102.62, 56.06, 55.95 ppm. ESI-MS: *m/z* 351 $[M+H]^+$. HRMS-ESI: Calcd for $C_{20}H_{15}O_6$ $[M+H]^+$ 351.0869; found 351.0867.

4-(4-Fluorophenyl)-2*H*,5*H*-pyrano[3,2-*c*]chromene-2,5-dione (**3k**):



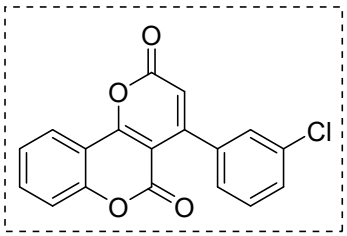
Yellow solid (48%), m.p. 249-251 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.17 (d, J = 7.9 Hz, 1H), 7.71 (t, J = 7.8 Hz, 1H), 7.44 (t, J = 7.7 Hz, 1H), 7.39 (d, J = 8.4 Hz, 1H), 7.35 (dd, J = 8.4, 5.3 Hz, 2H), 7.15 (t, J = 8.5 Hz, 2H), 6.28 (s, 1H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ 164.74, 162.77, 162.26, 157.64, 157.11, 155.89, 153.53, 134.89, 129.56, 125.13, 124.23, 117.05, 115.75, 115.42, 115.20, 102.47 ppm. ESI-MS: *m/z* 309 $[M+H]^+$; HRMS-ESI: Calcd for $C_{18}H_{10}FO_4$ $[M+H]^+$ 309.0563; found 309.0550.

4-(2-Chlorophenyl)-2*H*,5*H*-pyrano[3,2-*c*]chromene-2,5-dione (**3m**):



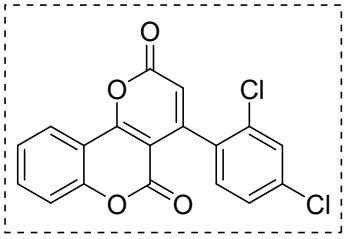
Pale yellow solid (62%), m.p. 147-149 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, J = 7.0 Hz, 1H), 7.68 (d, J = 7.1 Hz, 1H), 7.48-7.34 (m, 5H), 7.24 (s, 1H), 6.27 (s, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.00, 157.81, 156.77, 154.26, 153.51, 135.66, 134.75, 132.03, 130.41, 129.29, 128.40, 126.96, 125.07, 124.09, 117.15, 116.18, 113.19, 103.32 ppm. ESI-MS: *m/z* 325 $[M+H]^+$; HRMS-ESI: Calcd for $C_{18}H_{10}ClO_4$ $[M+H]^+$ 325.0268; found 325.0272.

4-(3-Chlorophenyl)-2*H*,5*H*-pyrano[3,2-*c*]chromene-2,5-dione (**3n**):



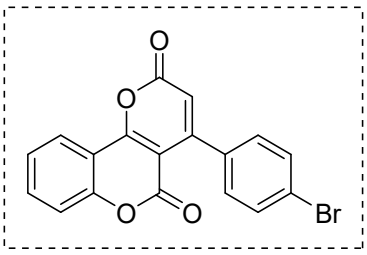
Pale yellow solid (60%), m.p. 192-194 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (dd, J = 8.0, 1.4 Hz, 1H), 7.77-7.67 (m, 1H), 7.51-7.32 (m, 5H), 7.23 (dd, J = 5.1, 3.7 Hz, 1H), 6.27 (s, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.39, 162.05, 161.64, 159.70, 158.16, 142.82, 139.80, 138.38, 134.12, 134.00, 132.27, 130.63, 129.97, 128.83, 121.71, 120.67, 117.84, 107.12 ppm. ESI-MS: *m/z* 325 $[M+H]^+$; HRMS-ESI: Calcd for $C_{18}H_{10}O_4Cl$ $[M+H]^+$ 325.0268; found 325.0259.

4-(2,4-Dichlorophenyl)-2*H*,5*H*-pyrano[3,2-*c*]chromene-2,5-dione (**3o**):



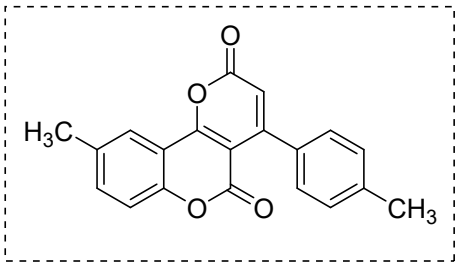
Pale yellow solid (58%), m.p. 205-207 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (dd, J = 8.0, 1.4 Hz, 1H), 7.69 (dd, J = 7.2, 1.3 Hz, 1H), 7.52-7.33 (m, 4H), 7.19 (d, J = 8.2 Hz, 1H), 6.25 (s, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.20, 157.58, 156.83, 153.51, 153.24, 135.82, 134.95, 134.16, 132.95, 129.26, 127.37, 125.18, 124.13, 117.21, 116.33, 113.09, 103.05 ppm. ESI-MS: *m/z* 359 $[M+H]^+$; HRMS-ESI: Calcd for $C_{18}H_9Cl_2O_4$ $[M+H]^+$ 359.9878; found 359.9872.

4-(4-Bromophenyl)-2*H*,5*H*-pyrano[3,2-*c*]chromene-2,5-dione (**3p**):



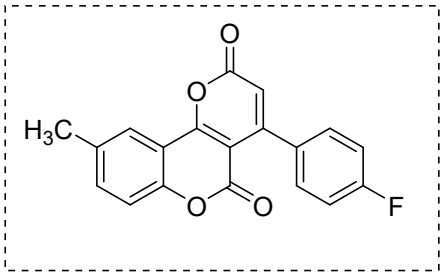
Yellow solid (54%), m.p. 239-241 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.16 (d, J = 7.9 Hz, 1H), 7.70 (t, J = 7.8 Hz, 1H), 7.42 (t, J = 7.7 Hz, 1H), 7.38 (d, J = 8.4 Hz, 1H), 7.33 (dd, J = 8.4, 5.3 Hz, 2H), 7.13 (t, J = 8.5 Hz, 2H), 6.27 (s, 1H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ 162.50, 158.30, 157.26, 154.75, 154.00, 136.15, 135.25, 132.52, 130.91, 129.78, 128.89, 127.45, 125.56, 124.58, 117.64, 116.67, 113.68, 103.81 ppm. ESI-MS: *m/z* 369 $[M+H]^+$; HRMS-ESI: Calcd for $C_{18}H_{10}BrO_4$ $[M+H]^+$ 369.1775; found 369.1769.

9-Methyl-4-(*p*-tolyl)-2*H*,5*H*-pyrano[3,2-*c*]chromene-2,5-dione (**3r**):



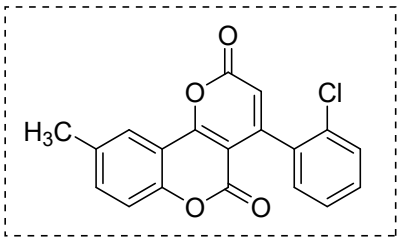
Colorless solid (72%), m.p. 214-216 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (s, 1H), 7.47 (dd, J = 8.5, 1.8 Hz, 1H), 7.33-7.21 (m, 5H), 6.24 (s, 1H), 2.46 (s, 3H), 2.42 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.59, 158.02, 157.21, 157.10, 151.72, 139.68, 135.85, 134.99, 133.36, 128.80, 127.49, 123.65, 116.73, 115.20, 112.87, 102.59, 21.49, 20.94 ppm. ESI-MS: *m/z* 319 $[M+H]^+$; HRMS-ESI: Calcd for $C_{20}H_{15}O_4$ $[M+H]^+$ 319.0970; found 319.0971.

4-(4-Fluorophenyl)-9-Methyl-2*H*,5*H*-pyrano[3,2-*c*]chromene-2,5-dione (**3s**):



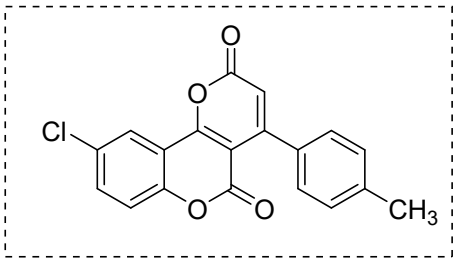
Pale yellow solid (50%), m.p. 244-246 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (s, 1H), 7.50 (d, J = 8.0 Hz, 1H), 7.34 (dd, J = 7.8, 5.2 Hz, 3H), 7.14 (d, J = 8.3 Hz, 1H), 6.85-6.68 (m, 2H), 6.26 (s, 1H), 2.48 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.59, 158.55, 157.53, 154.98, 152.30, 136.47, 136.29, 135.63, 132.57, 130.92, 129.83, 128.90, 127.48, 124.14, 117.46, 116.49, 113.35, 103.76, 21.49 ppm. ESI-MS: *m/z* 323 $[M+H]^+$; HRMS-ESI: Calcd for $C_{19}H_{12}FO_4$ $[M+H]^+$ 323.0872; found 323.0878.

4-(2-Chlorophenyl)-9-Methyl-2*H*,5*H*-pyrano[3,2-*c*]chromene-2,5-dione (**3t**):



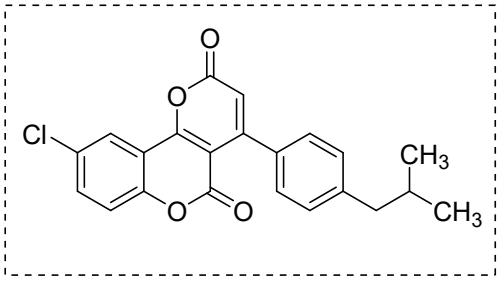
Pale yellow solid (52%), m.p. 210-212 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, J = 0.9 Hz, 1H), 7.49-7.37 (m, 4H), 7.29-7.23 (m, 2H), 6.26 (s, 1H), 2.48 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.05, 158.01, 156.99, 154.43, 151.76, 135.92, 135.75, 135.09, 132.03, 130.37, 129.29, 128.35, 126.93, 123.60, 116.91, 115.95, 112.80, 103.22, 20.94 ppm. ESI-MS: *m/z* 339 $[M+H]^+$; HRMS-ESI: Calcd for $C_{19}H_{12}ClO_4$ $[M+H]^+$ 339.0424; found 339.0414.

9-Chloro-4-(*p*-tolyl)-2*H*,5*H*-pyrano[3,2-*c*]chromene-2,5-dione (**3u**):



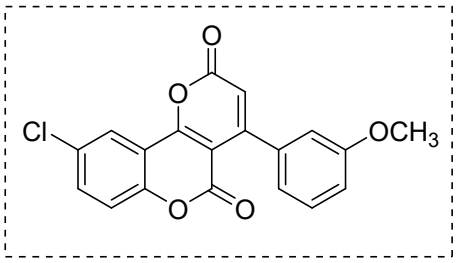
Yellow solid (72%), m.p. 203-205 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (d, J = 2.5 Hz, 2H), 7.63 (dd, J = 8.9, 2.5 Hz, 2H), 7.33 (d, J = 8.9 Hz, 2H), 7.28-7.24 (m, 9H), 6.31 (s, 1H), 2.43 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 161.43, 157.38, 156.70, 156.53, 151.79, 139.95, 134.67, 132.94, 130.76, 128.88, 127.46, 123.56, 118.52, 116.00, 114.31, 103.25, 21.49 ppm. ESI-MS: *m/z* 339 $[M+H]^+$; HRMS-ESI: Calcd for $C_{19}H_{12}ClO_4$ $[M+H]^+$ 339.0424; found 339.0432.

9-Chloro-4-(4-isobutylphenyl)-2*H*,5*H*-pyrano[3,2-c]chromene-2,5-dione (**3v**):



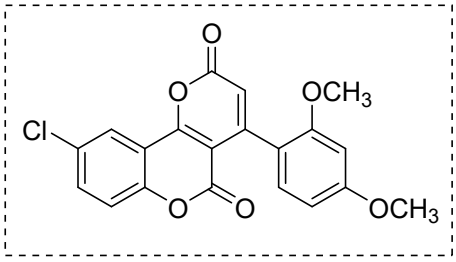
Colorless solid (76%), m.p. 275-277 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (d, J = 1.4 Hz, 1H), 7.64 – 7.60 (m, 1H), 7.32 (d, J = 8.8 Hz, 1H), 7.25 (dd, J = 9.6, 5.5 Hz, 4H), 6.32 (d, J = 0.6 Hz, 1H), 2.55 (d, J = 7.2 Hz, 2H), 1.91 (dd, J = 13.5, 6.7 Hz, 1H), 0.95 (s, 3H), 0.94 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 161.39, 157.39, 156.72, 156.52, 151.79, 143.68, 134.63, 133.15, 130.73, 128.86, 127.36, 123.54, 118.51, 116.00, 114.33, 103.26, 45.32, 30.17, 22.47 ppm. ESI-MS: *m/z* 381 $[M+H]^+$; HRMS-ESI: Calcd for $C_{22}H_{18}O_4Cl$ $[M+H]^+$ 381.0894; found 381.0887.

9-Chloro-4-(3-methoxyphenyl)-2*H*,5*H*-pyrano[3,2-*c*]chromene-2,5-dione (**3w**):



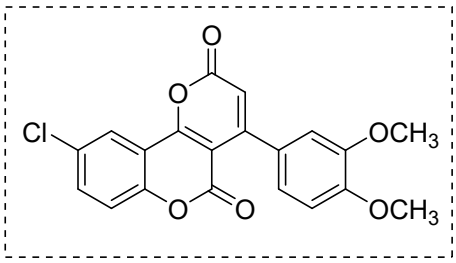
Pale yellow solid (70%), m.p. 171-173 °C; ^{1}H (400 MHz, $CDCl_3$): δ 8.12 (d, J = 2.5 Hz, 1H), 7.62 (dd, J = 8.9, 2.5 Hz, 1H), 7.38-7.30 (m, 3H), 7.02-6.99 (m, 1H), 6.91-6.89 (m, 1H), 6.86-6.84 (m, 1H), 6.32 (s, 1H), 3.83 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 161.39, 159.21, 157.27, 156.37, 156.31, 151.82, 137.13, 134.72, 130.77, 129.30, 123.53, 119.75, 118.55, 116.25, 115.00, 114.26, 113.25, 103.23, 55.39 ppm. ESI-MS: *m/z* 355 $[M+H]^+$; HRMS-ESI: Calcd for $C_{19}H_{12}ClO_5$ $[M+H]^+$ 355.0373; found 355.0365.

9-Chloro-4-(2,4-dimethoxyphenyl)-2*H*,5*H*-pyrano[3,2-*c*]chromene-2,5-dione (**3y**):



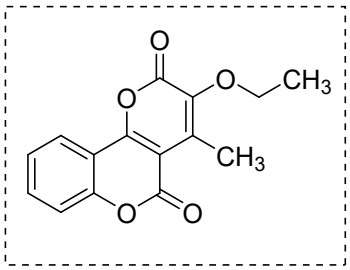
Yellowish solid (60%), m.p. 202-204 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (d, J = 2.1 Hz, 1H), 7.59 (dd, J = 8.8, 2.1 Hz, 1H), 7.30 (d, J = 8.8 Hz, 1H), 7.13 (d, J = 8.3 Hz, 1H), 6.58-6.49 (m, 2H), 6.28 (s, 1H), 3.86 (s, 3H), 3.73 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.63, 159.91, 157.99, 157.97, 156.56, 154.13, 151.52, 134.17, 130.52, 129.08, 123.43, 118.51, 118.43, 115.93, 114.49, 104.85, 104.54, 98.52, 55.56, 55.49 ppm. ESI-MS: *m/z* 385 $[M+H]^+$; HRMS-ESI: Calcd for $C_{20}H_{14}ClO_6$ $[M+H]^+$ 385.0479; found 385.0462.

9-Chloro-4-(3,4-dimethoxyphenyl)-2*H*,5*H*-pyrano[3,2-*c*]chromene-2,5-dione (**3z**):



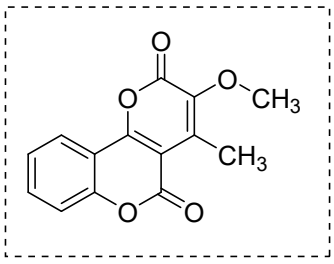
Yellowish solid (62%), m.p. 223-225 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.13 (d, J = 2.4 Hz, 1H), 7.63 (dd, J = 8.9, 2.5 Hz, 1H), 7.33 (d, J = 8.9 Hz, 1H), 6.94 (d, J = 2.0 Hz, 2H), 6.87 (d, J = 1.2 Hz, 1H), 6.33 (s, 1H), 3.94 (s, 3H), 3.89 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ 161.47, 157.37, 156.52, 156.24, 151.74, 150.49, 148.45, 134.67, 130.74, 128.19, 123.53, 120.66, 118.46, 115.71, 114.29, 111.28, 110.62, 103.17, 56.07, 55.96 ppm. ESI-MS: *m/z* 407 $[M+Na]^+$; HRMS-ESI: Calcd for $C_{20}H_{14}ClO_6$ $[M+H]^+$ 385.0479; found 385.0465.

3-Ethoxy-4-methyl-2*H*,5*H*-pyrano[3,2-*c*]chromene-2,5-dione (**4a**):



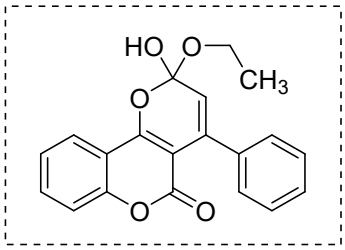
Colorless solid (84%), m.p. 196-198 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.98 (dd, J = 7.8, 1.6 Hz, 1H), 7.56 (dd, J = 8.7, 7.3, 1.6 Hz, 1H), 7.41 (dd, J = 8.4, 1.0 Hz, 1H), 7.35 (td, J = 7.6, 1.1 Hz, 1H), 4.44 (q, J = 7.1 Hz, 2H), 2.68 (s, 3H), 1.44 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 158.97, 158.04, 157.76, 153.45, 141.80, 132.03, 130.27, 124.69, 121.86, 117.35, 112.14, 111.48, 61.41, 14.31, 10.11 ppm. ESI-MS: *m/z* 273 $[M+H]^+$; HRMS-ESI: Calcd for $C_{15}H_{13}O_5$ $[M+H]^+$ 273.0547; found 273.0552.

3-Methoxy-4-methyl-2*H*,5*H*-pyrano[3,2-*c*]chromene-2,5-dione (**4b**):



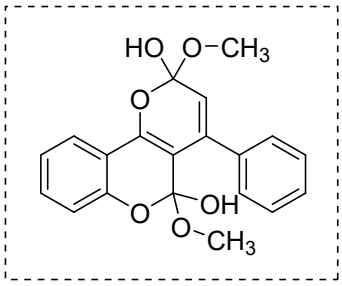
Colorless solid (90%), m.p. 268-270 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (dt, J = 8.1, 1.8 Hz, 1H), 7.64 (dd, J = 8.4, 7.3, 1.7 Hz, 1H), 7.41-7.35 (m, 2H), 3.94 (s, 3H), 2.62 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ 158.47, 157.35, 155.53, 152.43, 141.58, 140.68, 133.68, 124.98, 123.49, 116.73, 113.07, 104.22, 59.99, 14.03 ppm. ESI-MS: *m/z* 259 $[M+H]^+$; HRMS-ESI: Calcd for $C_{14}H_{11}O_5$ $[M+H]^+$ 259.0528; found 259.0600.

2-Ethoxy-2-hydroxy-4-phenyl-2*H*,5*H*-pyrano[3,2-*c*]chromen-5-one (**4c**):



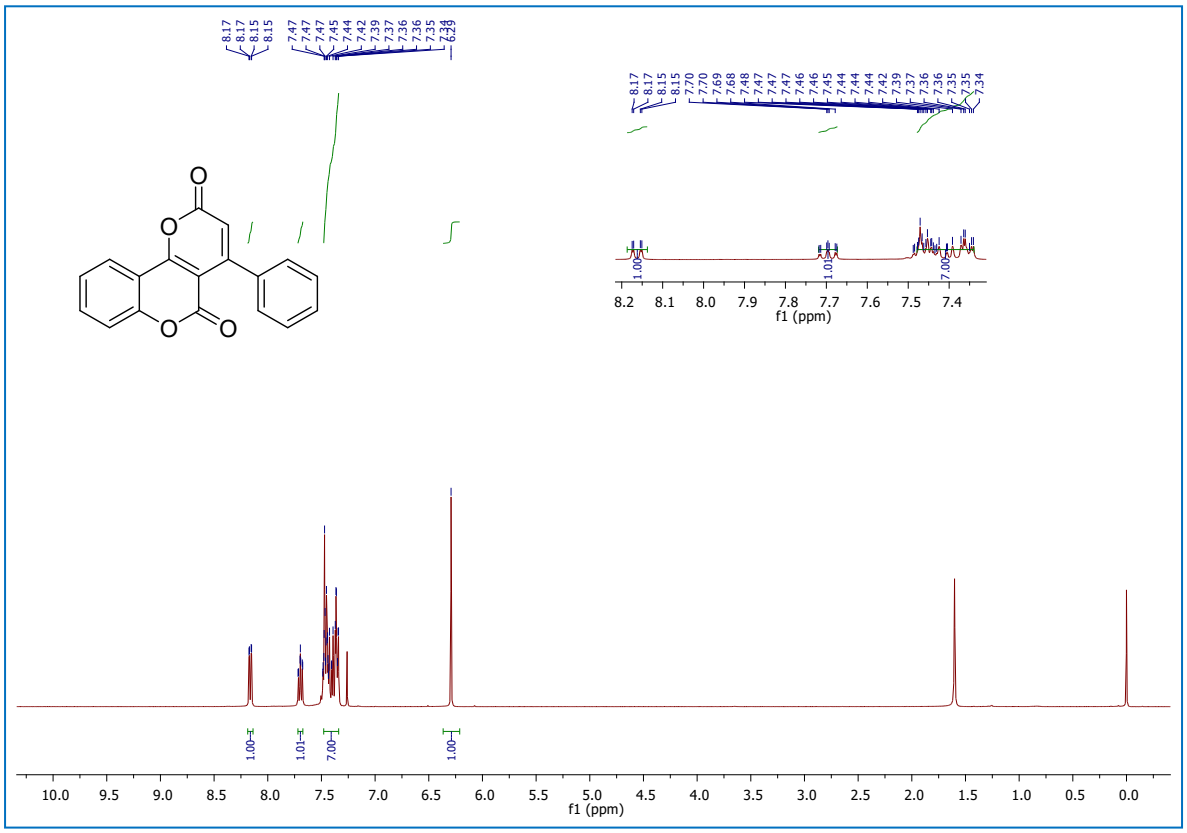
Colorless solid (79%), m.p. 244-246 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.94 (dd, J = 7.9, 1.5 Hz, 1H), 7.63-7.56 (m, 1H), 7.51-7.46 (m, 2H), 7.42-7.29 (m, 6H), 6.66 (s, 1H), 4.15 (t, J = 7.1 Hz, 2H), 1.23 (d, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 165.44, 162.30, 160.91, 152.73, 145.74, 137.33, 131.99, 129.48, 128.32, 126.55, 123.77, 123.51, 121.51, 116.17, 115.84, 103.33, 60.09, 13.40 ppm. ESI-MS: *m/z* 337 $[M+H]^+$; HRMS-ESI: Calcd for $C_{20}H_{16}O_5Na$ $[M+Na]^+$ 359.0895; found 359.0857.

2,5-Dimethoxy-4-phenyl-2*H*,5*H*-pyrano[3,2-*c*]chromene-2,5-diol (**4d**):

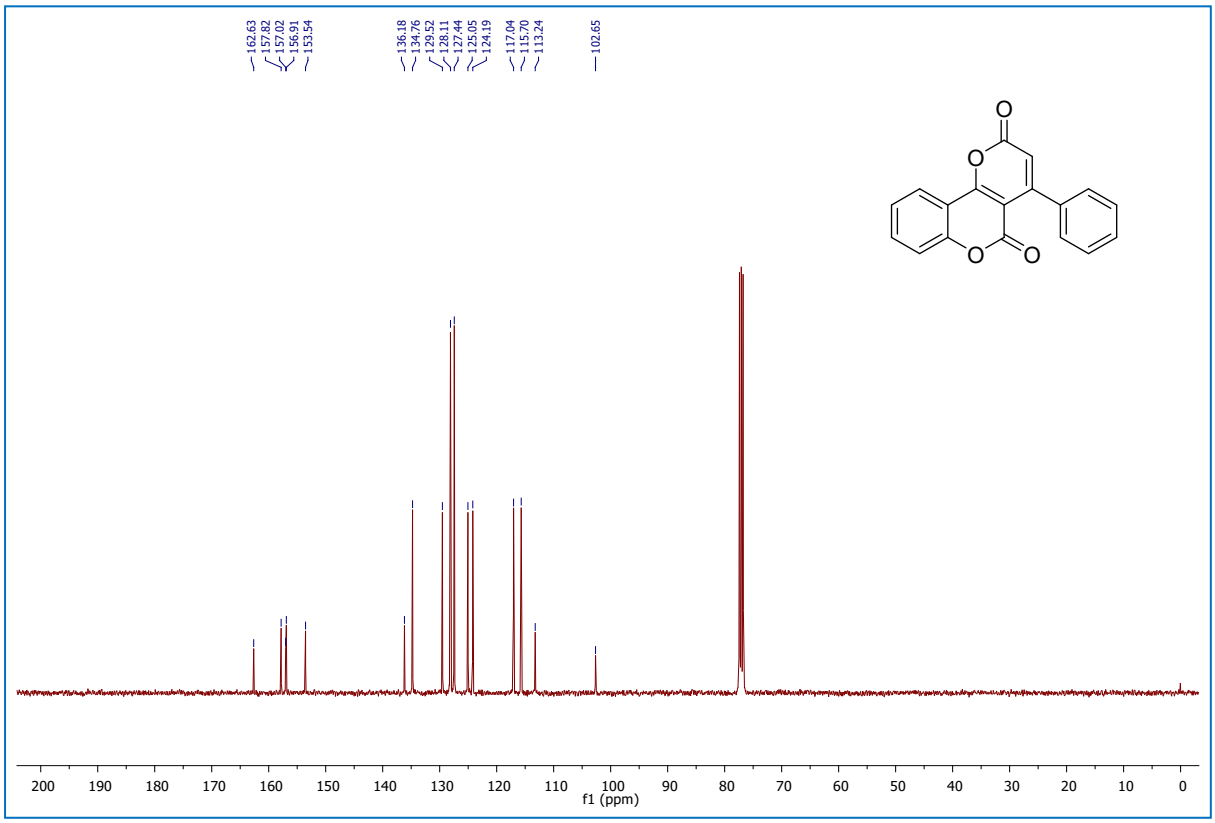


Colorless solid (72%), m.p. 322-324 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.76 (dd, J = 8.0, 1.6 Hz, 1H), 7.47 (dd, J = 9.2, 5.1, 2.0 Hz, 3H), 7.30 (dd, J = 6.3, 2.3 Hz, 4H), 7.29-7.17 (m, 3H), 6.67 (s, 1H), 3.85 (s, 3H), 3.62 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.86, 161.95, 161.86, 152.63, 147.87, 138.29, 132.08, 130.12, 129.01, 126.95, 123.99, 123.93, 120.90, 116.97, 116.57, 107.10, 59.66, 51.61 ppm. ESI-MS: *m/z* 337 $[M+H]^+$; HRMS-ESI: Calcd for $C_{20}H_{19}O_6[M+H]^+$ 355.1062; found 355.1056.

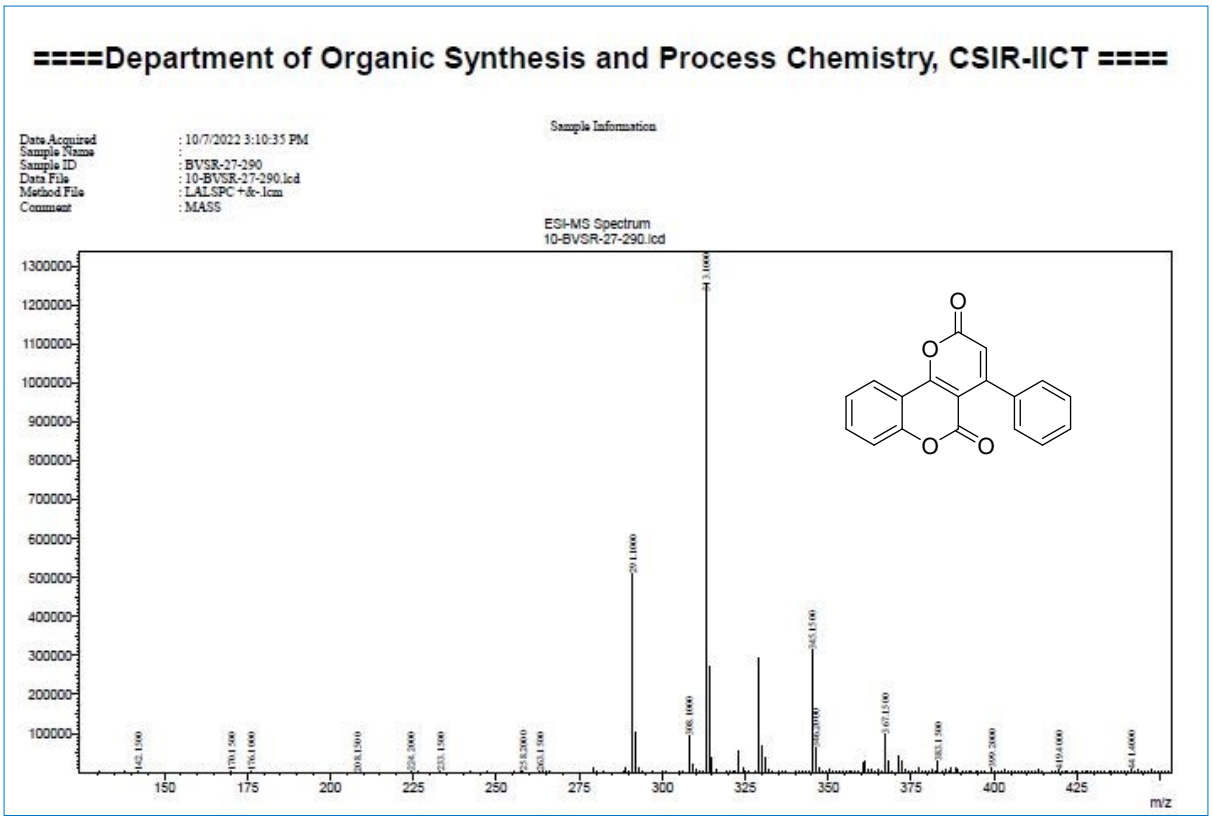
6. Copies of ^{1}H NMR, ^{13}C NMR, HRMS Spectrums (3ad-zc & 4a-d):



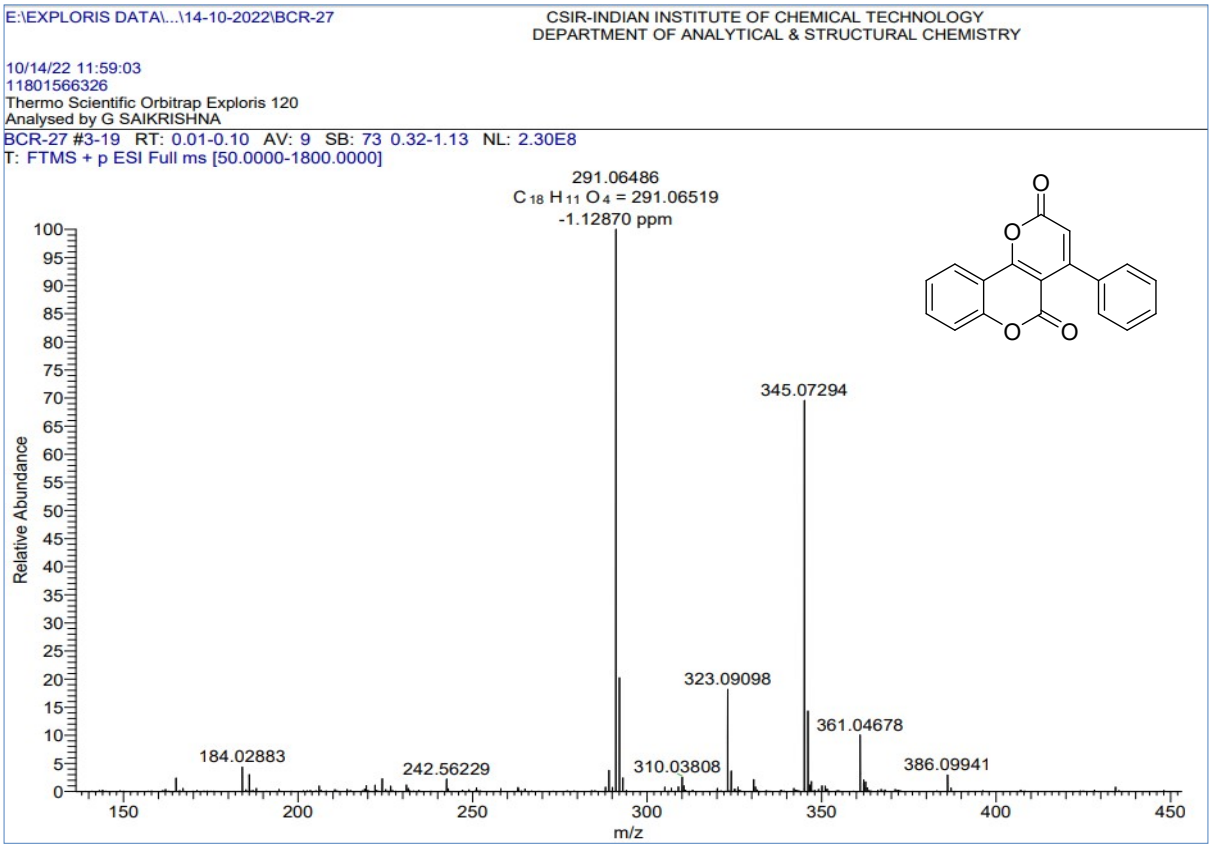
^{1}H-NMR spectrum of compound **3ad**



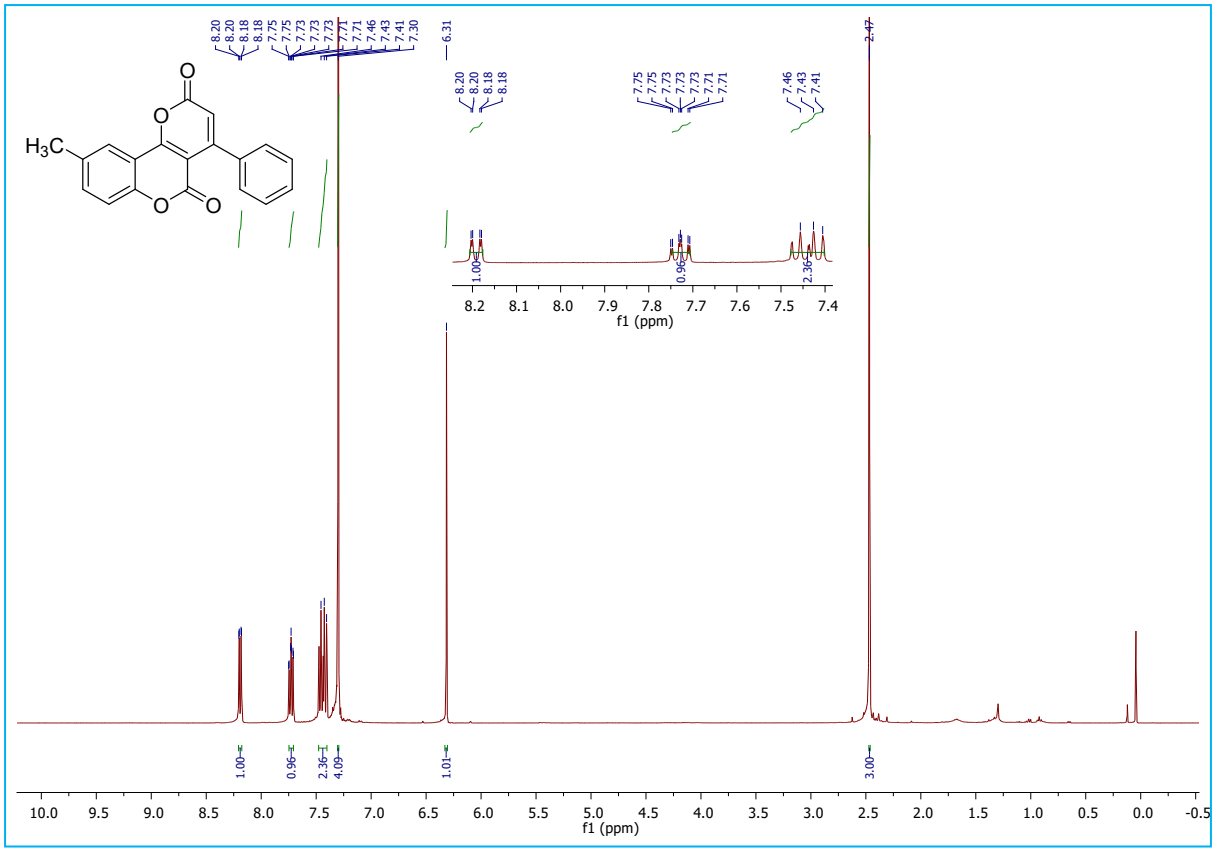
^{13}C-NMR spectrum of compound **3ad**



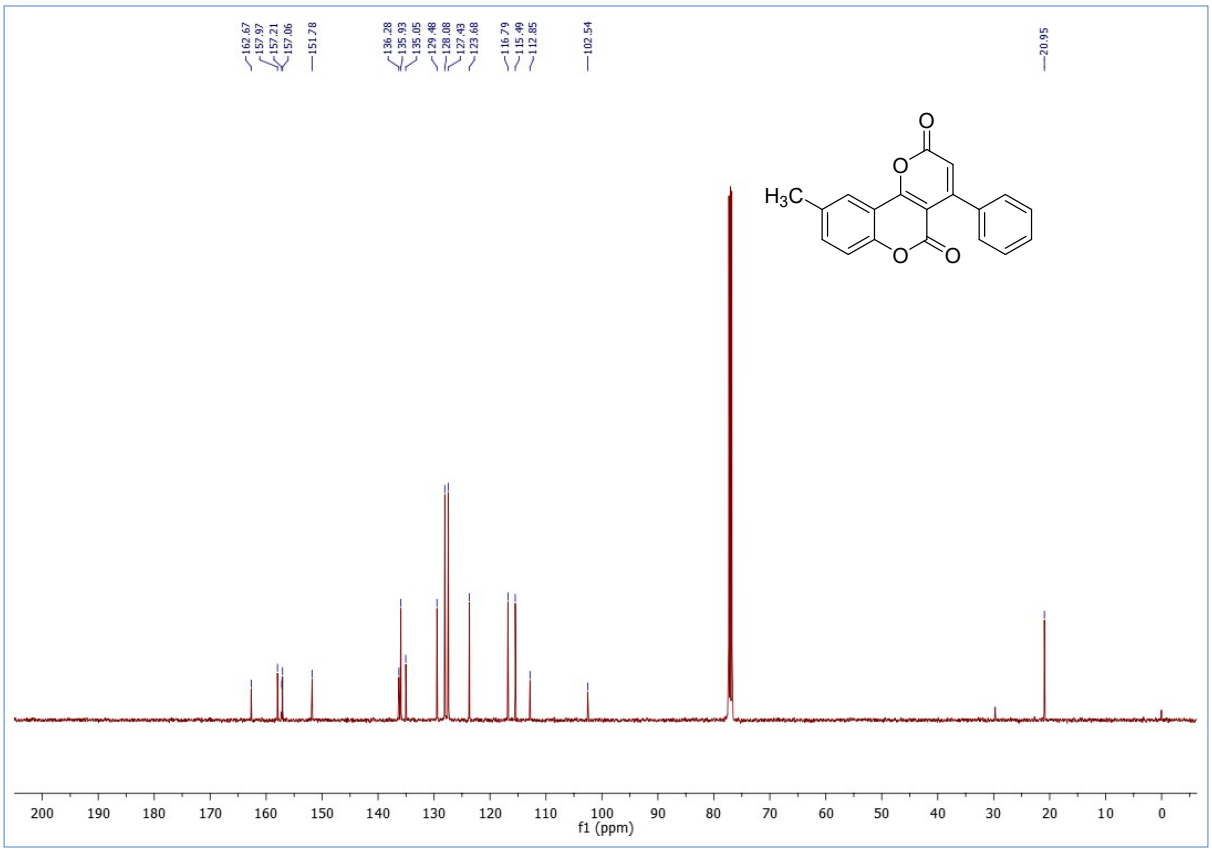
Mass spectrum of compound **3ad**



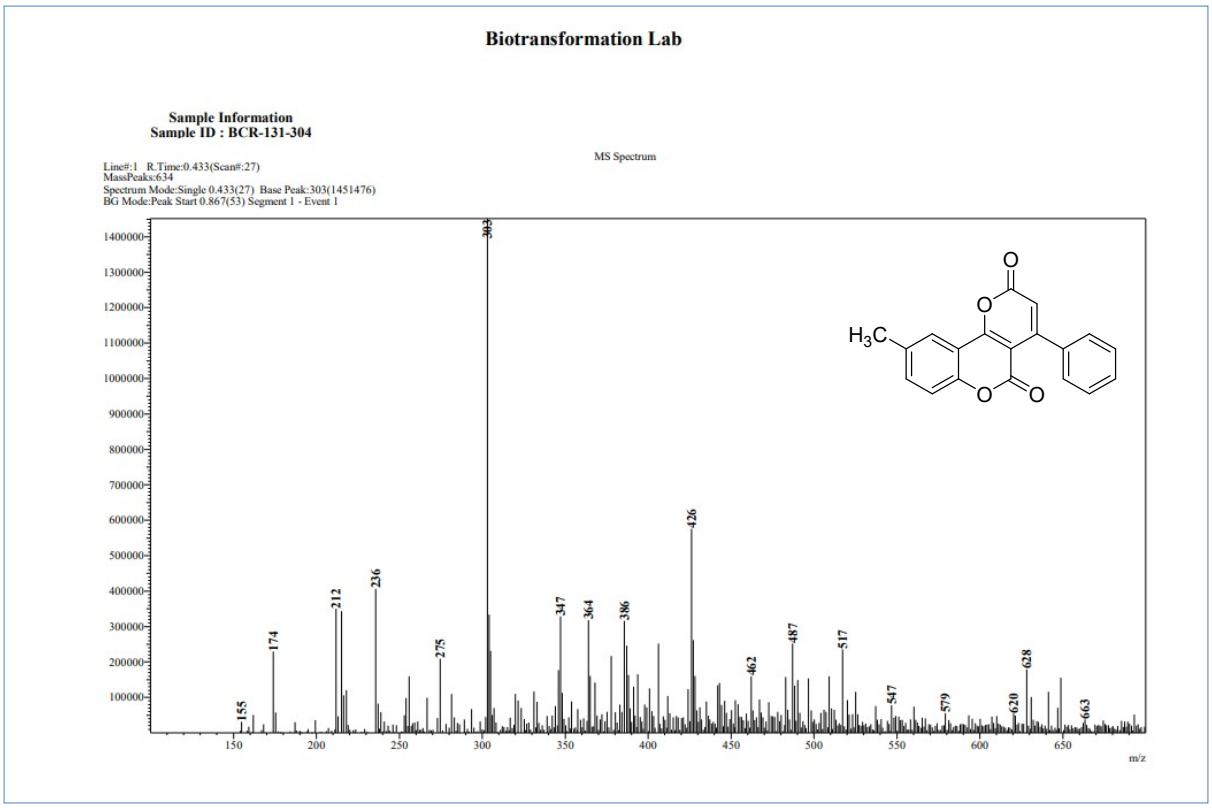
HRMS spectrum of compound **3ad**



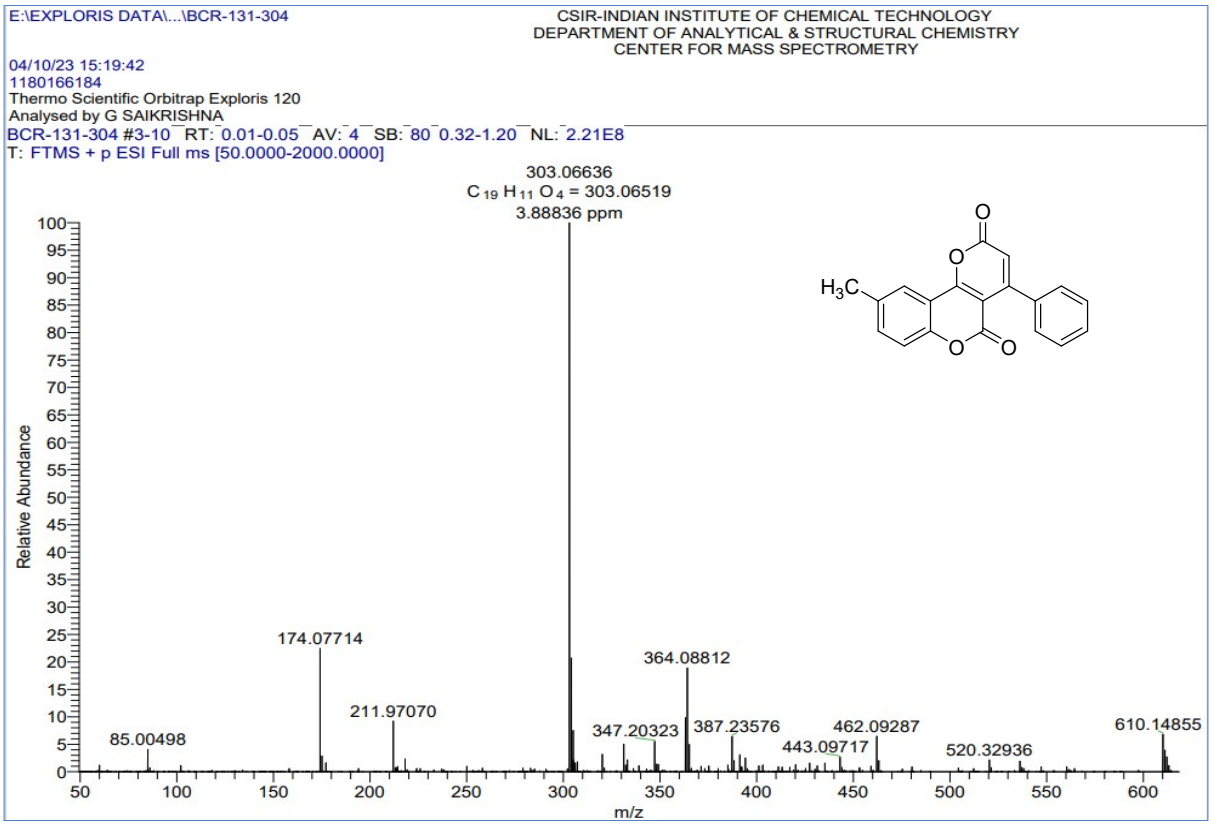
^{1}H-NMR spectrum of compound **3b**



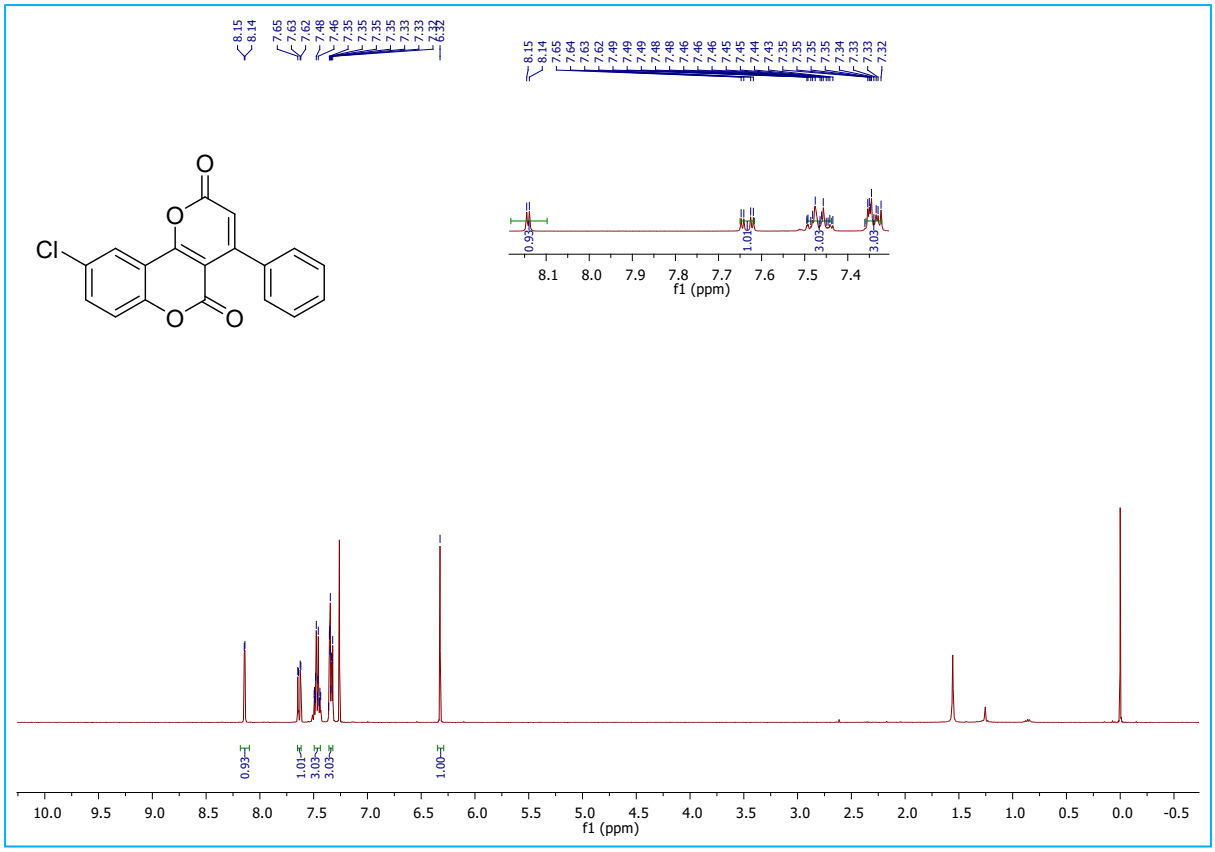
^{13}C-NMR spectrum of compound **3b**



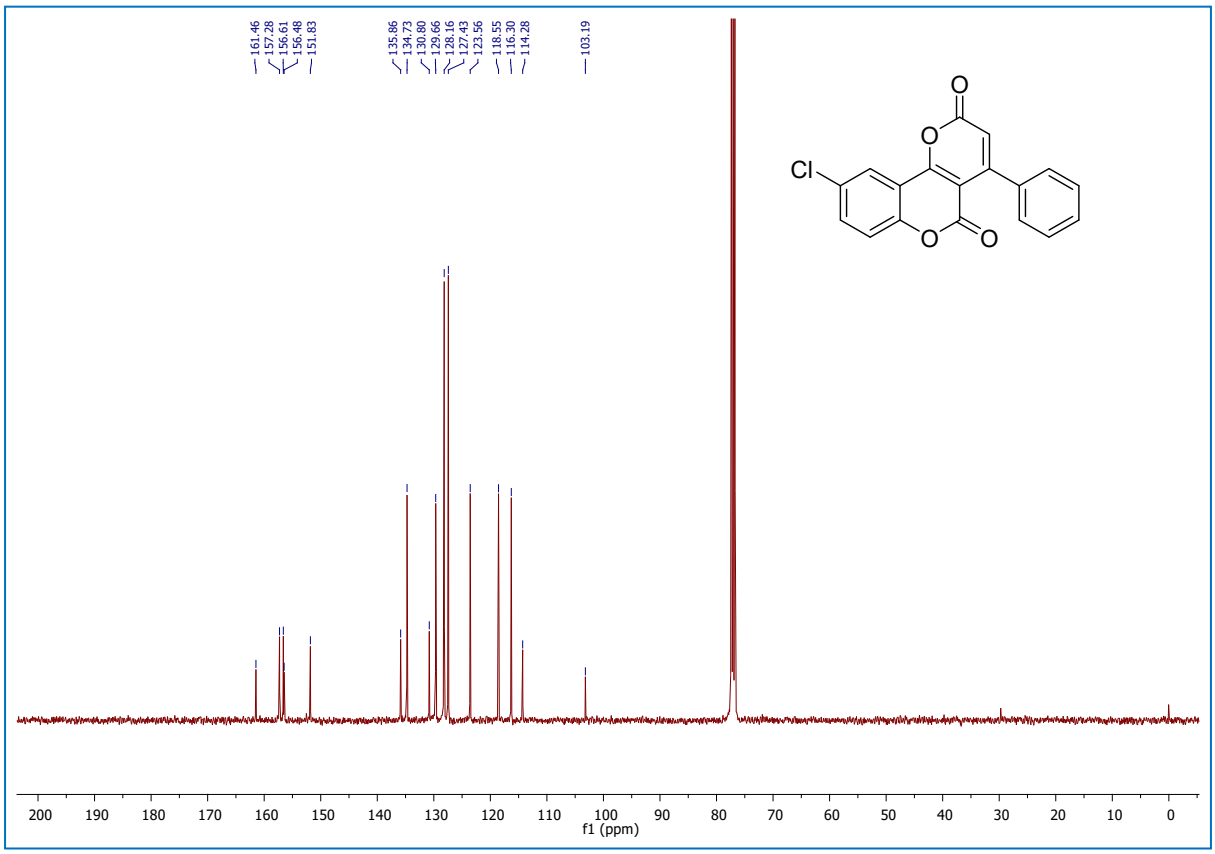
Mass spectrum of compound **3b**



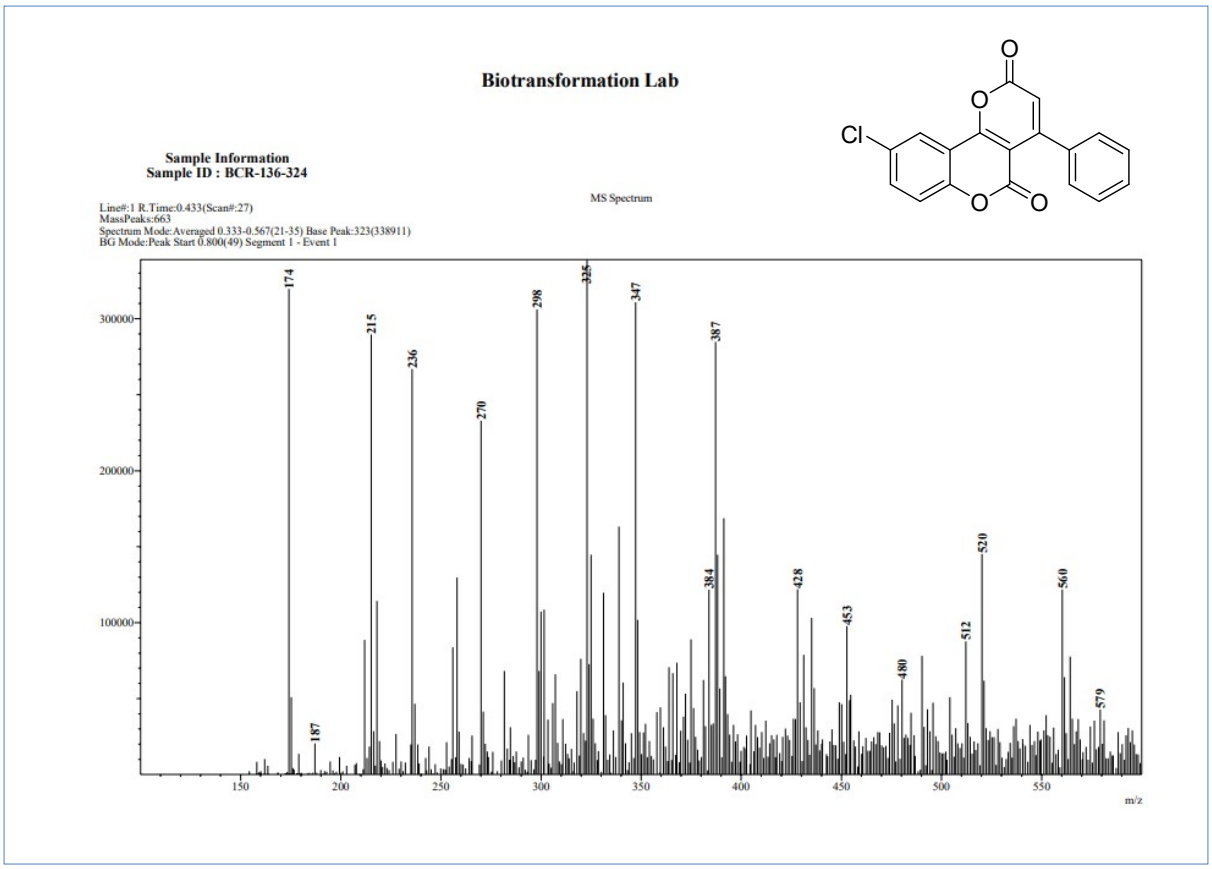
HRMS spectrum of compound **3b**



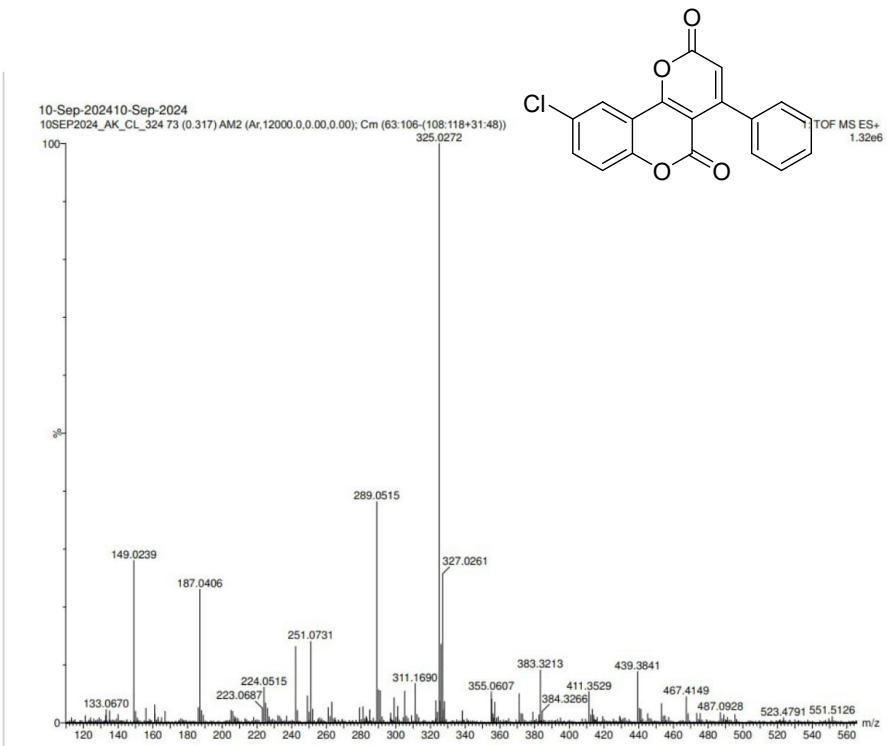
[1]H-NMR spectrum of compound **3c**



[13]C-NMR spectrum of compound **3c**



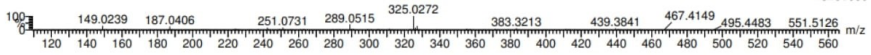
Mass spectrum of compound **3c**



Elemental Composition Report **Page 1**

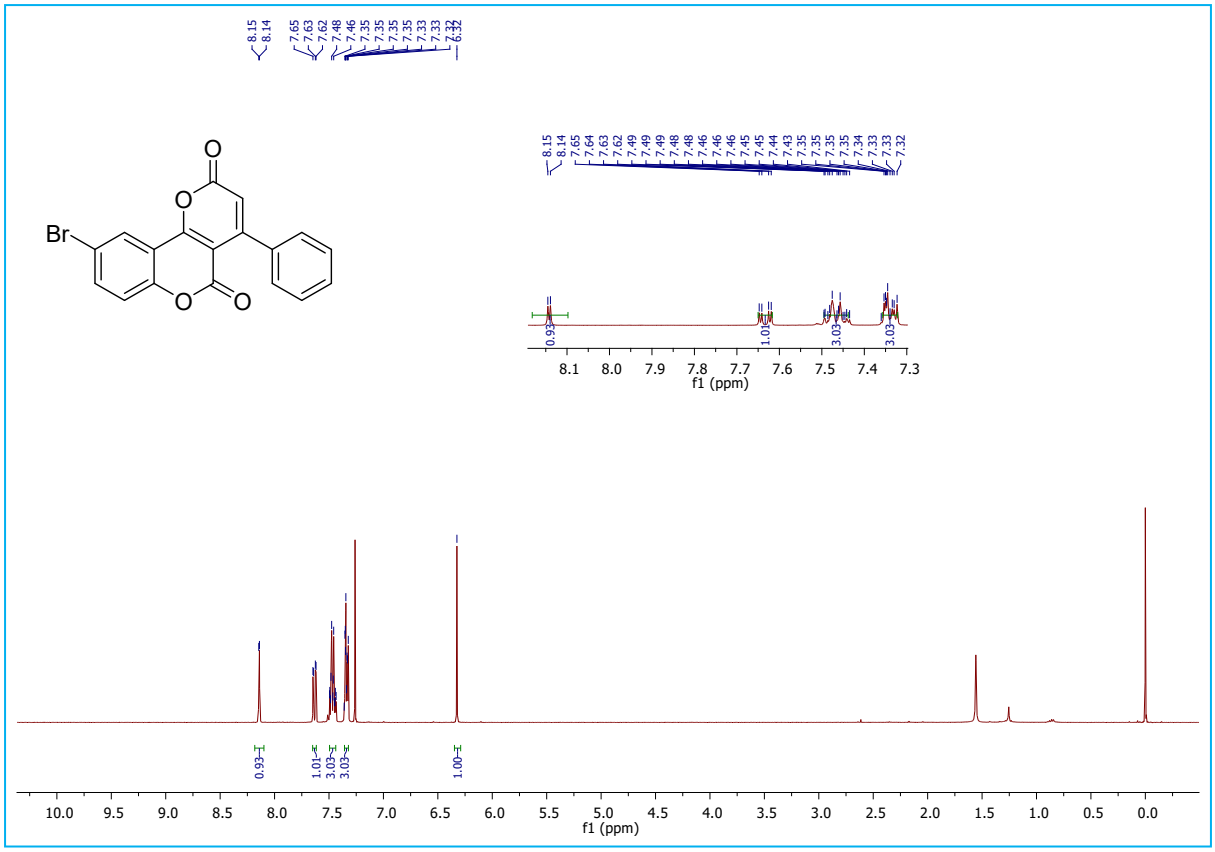
Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
19 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-18 H: 0-10 O: 0-4 P: 0-1 Cl: 0-2
10-Sep-202410-Sep-2024
10SEP2024_AK_CL_324 73 (0.317) AM2 (Ar,12000.0,0.00,0.00); Cm (63:106-(108:118+31:48))
1: TOF MS ES+
1.32e+006

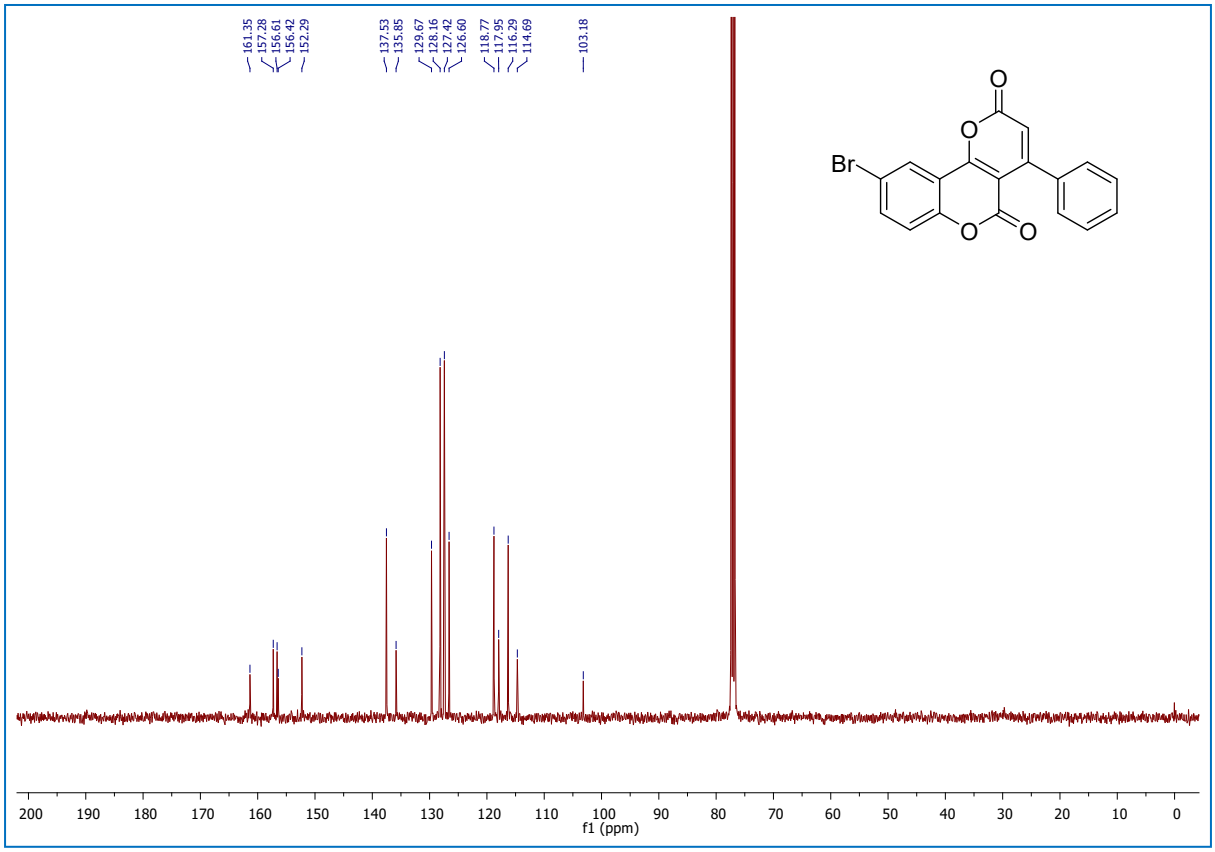


Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
325.0272	325.0268	0.4	1.2	13.5	406.8	n/a	n/a	C18 H10 O4 Cl

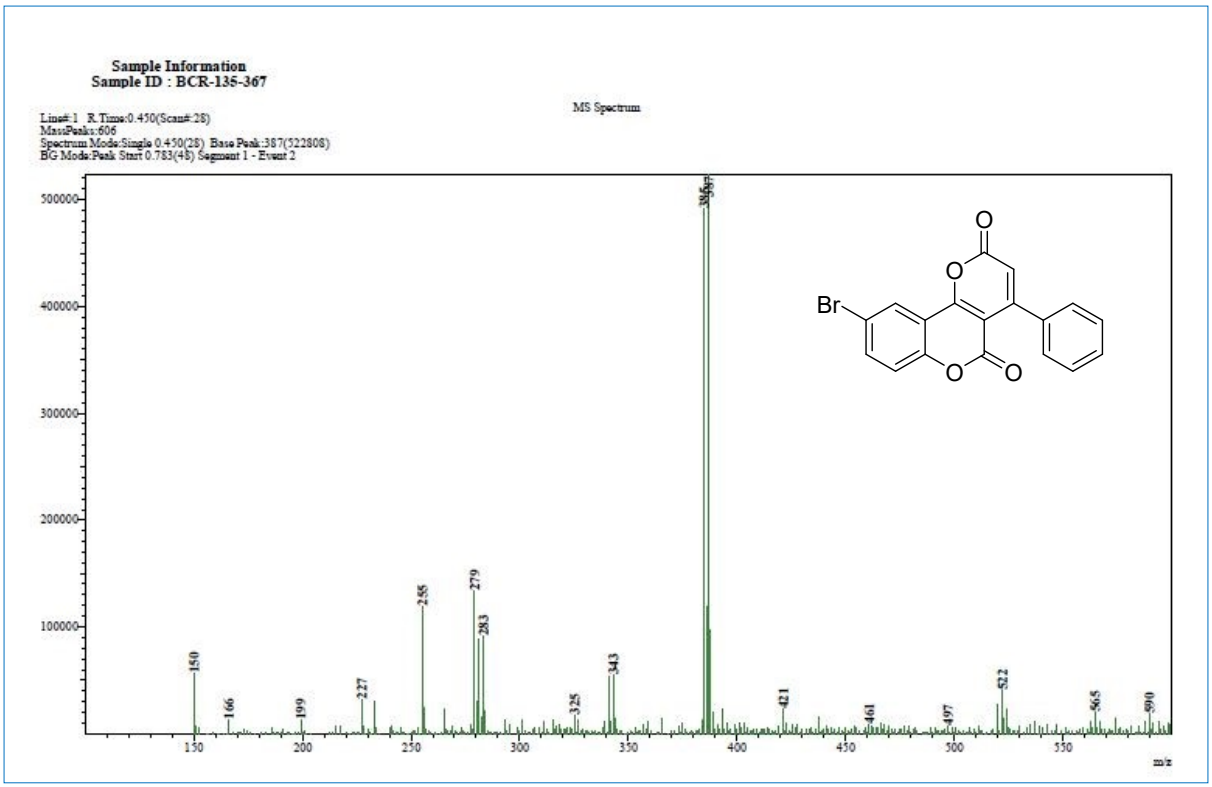
HRMS spectrum of **3c**



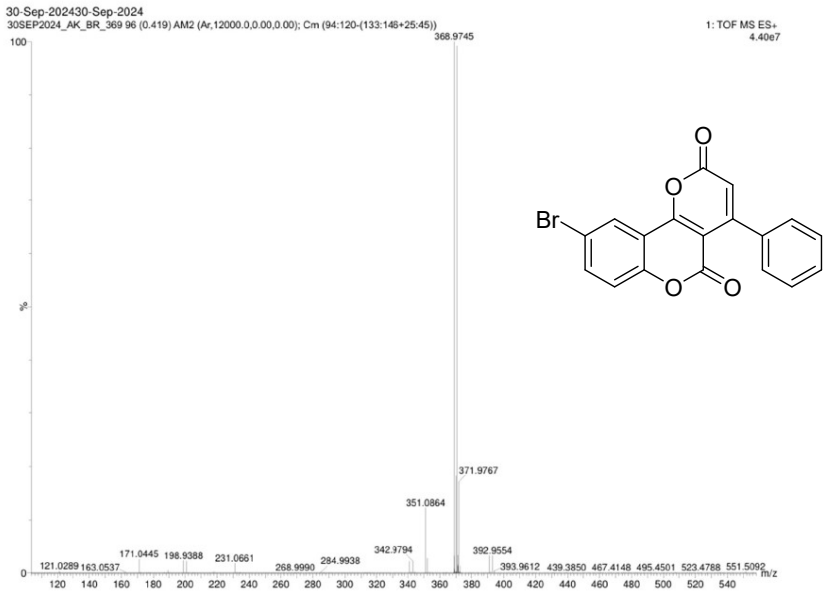
^{1}H-NMR spectrum of compound **3d**



^{13}C-NMR spectrum of compound **3d**



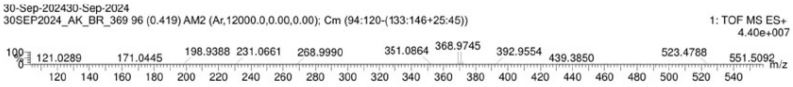
Mass spectrum of compound **3d**



Elemental Composition Report **Page 1**

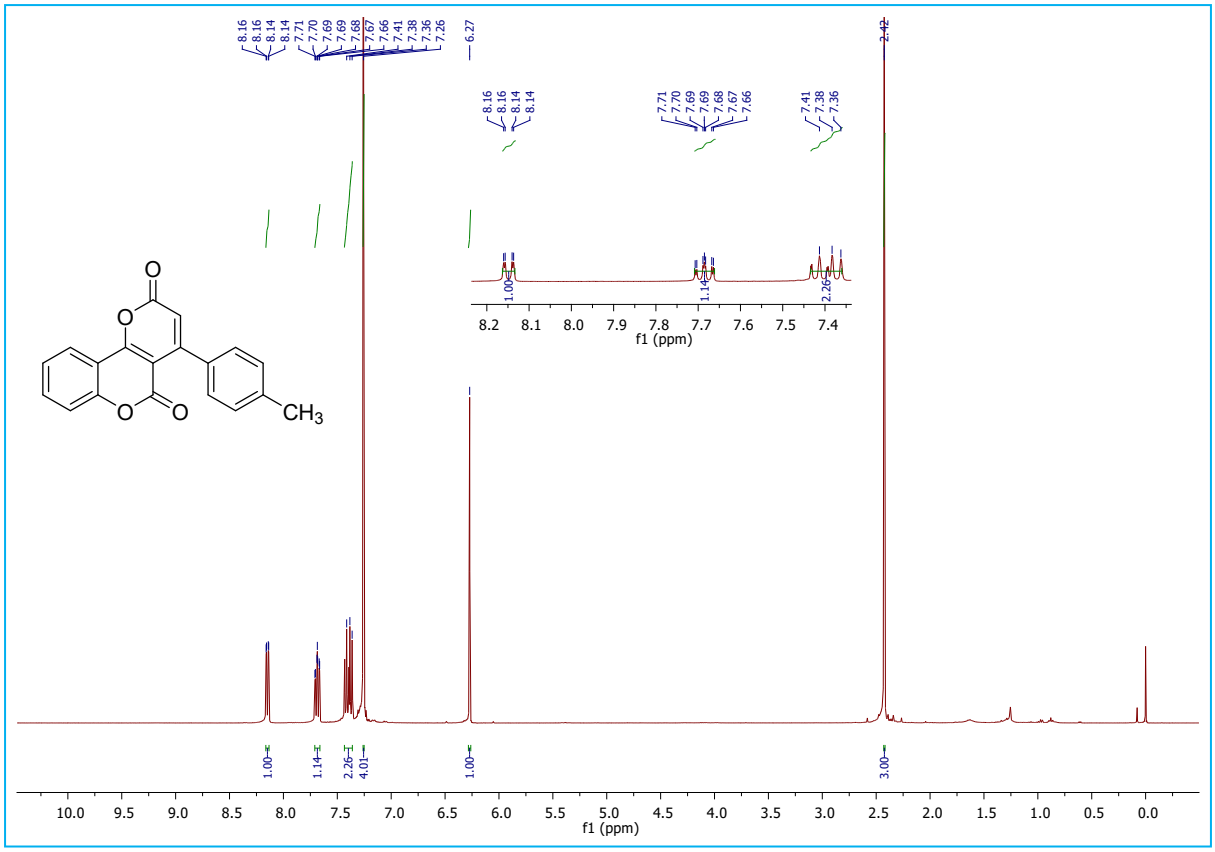
Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
47 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-20 H: 0-15 O: 0-6 S: 0-1 Br: 0-2

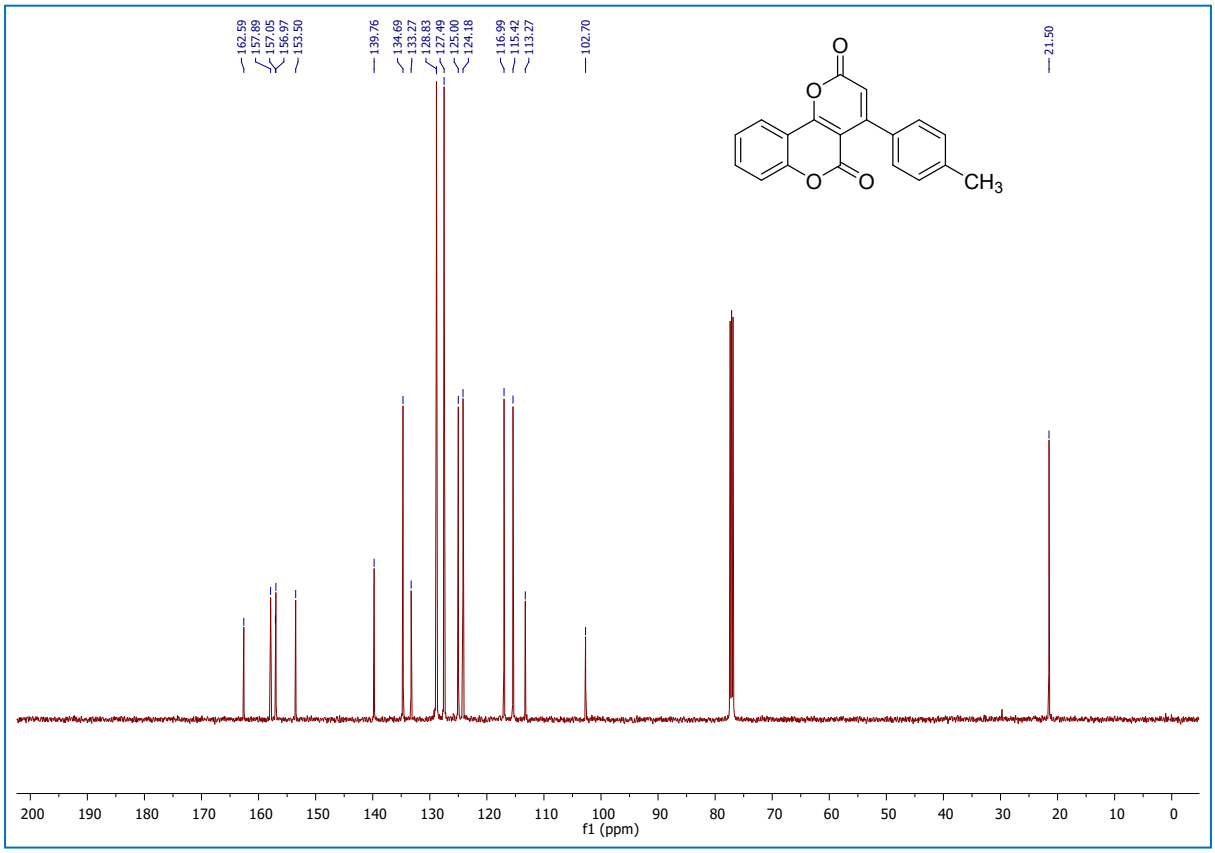


Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
368.9745	368.9762	-1.7	-4.6	13.5	653.6	n/a	n/a	C18 H10 O4 Br

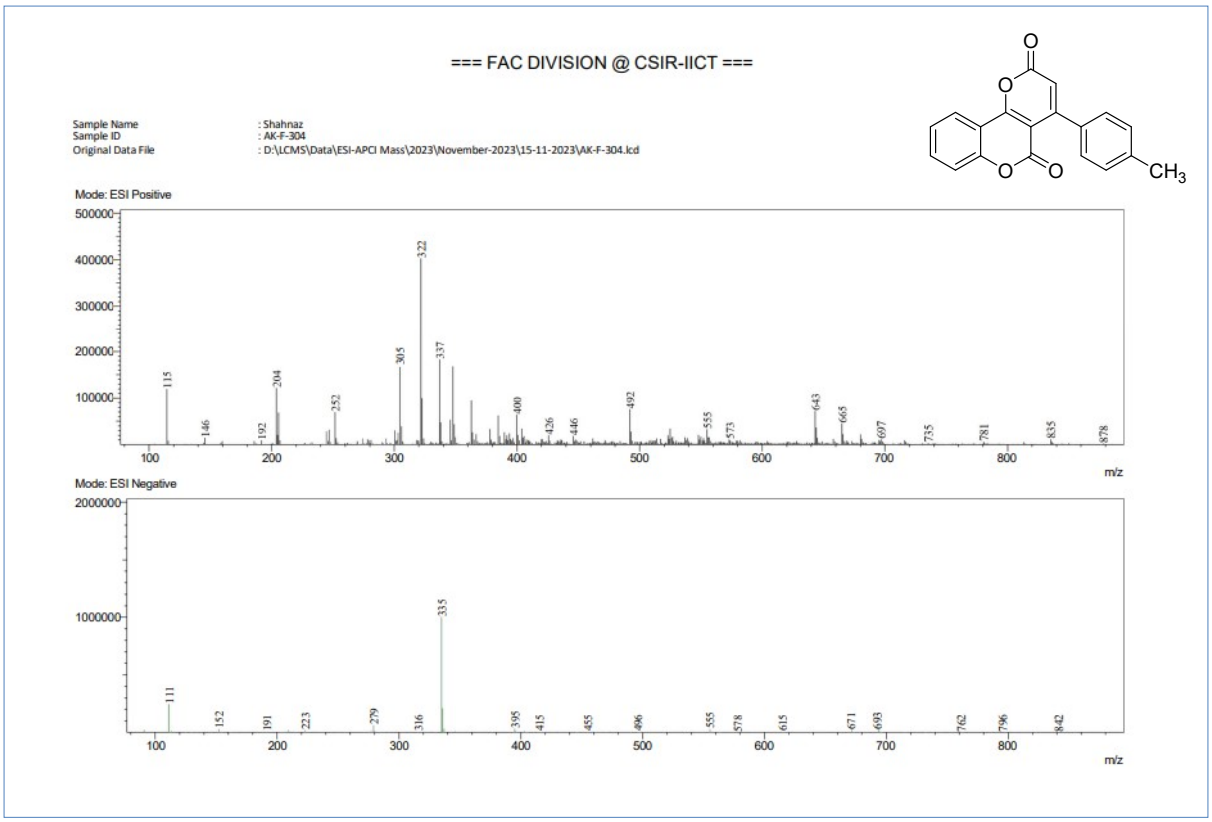
HRMS spectrum of compound **3d**



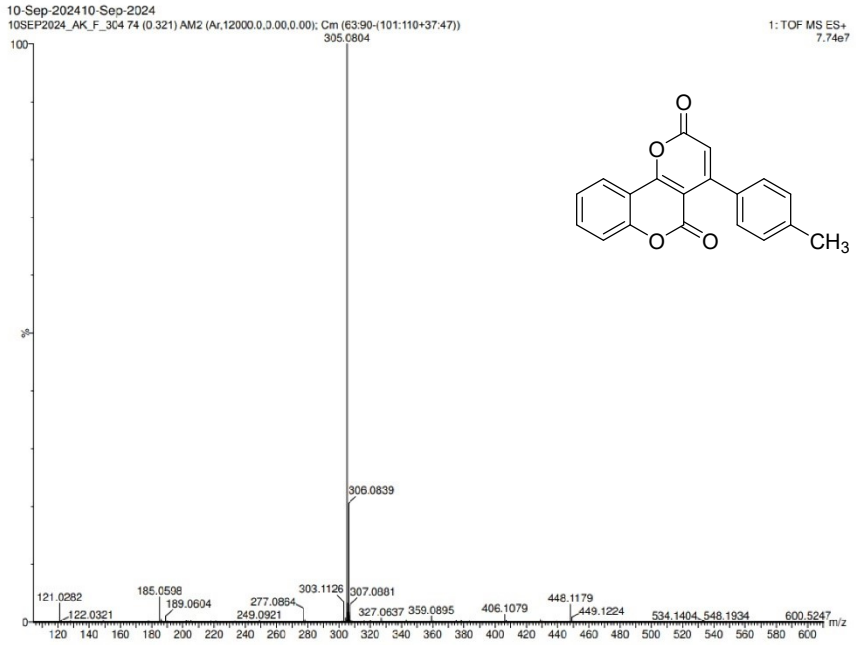
^{1}H-NMR spectrum of compound **3e**



^{13}C-NMR spectrum of compound **3e**



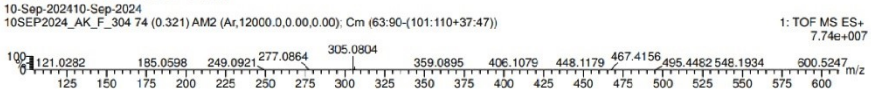
Mass spectrum of compound **3e**



Elemental Composition Report **Page 1**

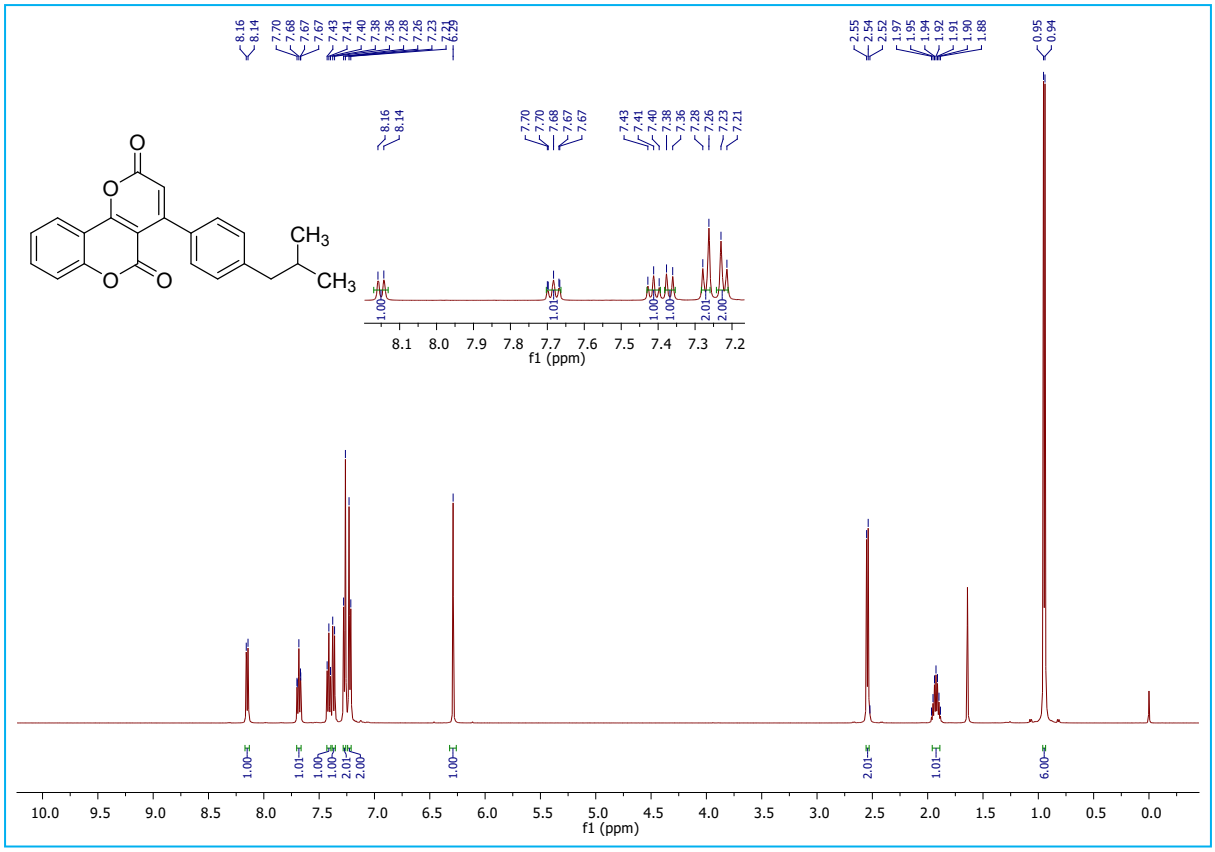
Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
5 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-19 H: 0-13 O: 0-4 P: 0-1

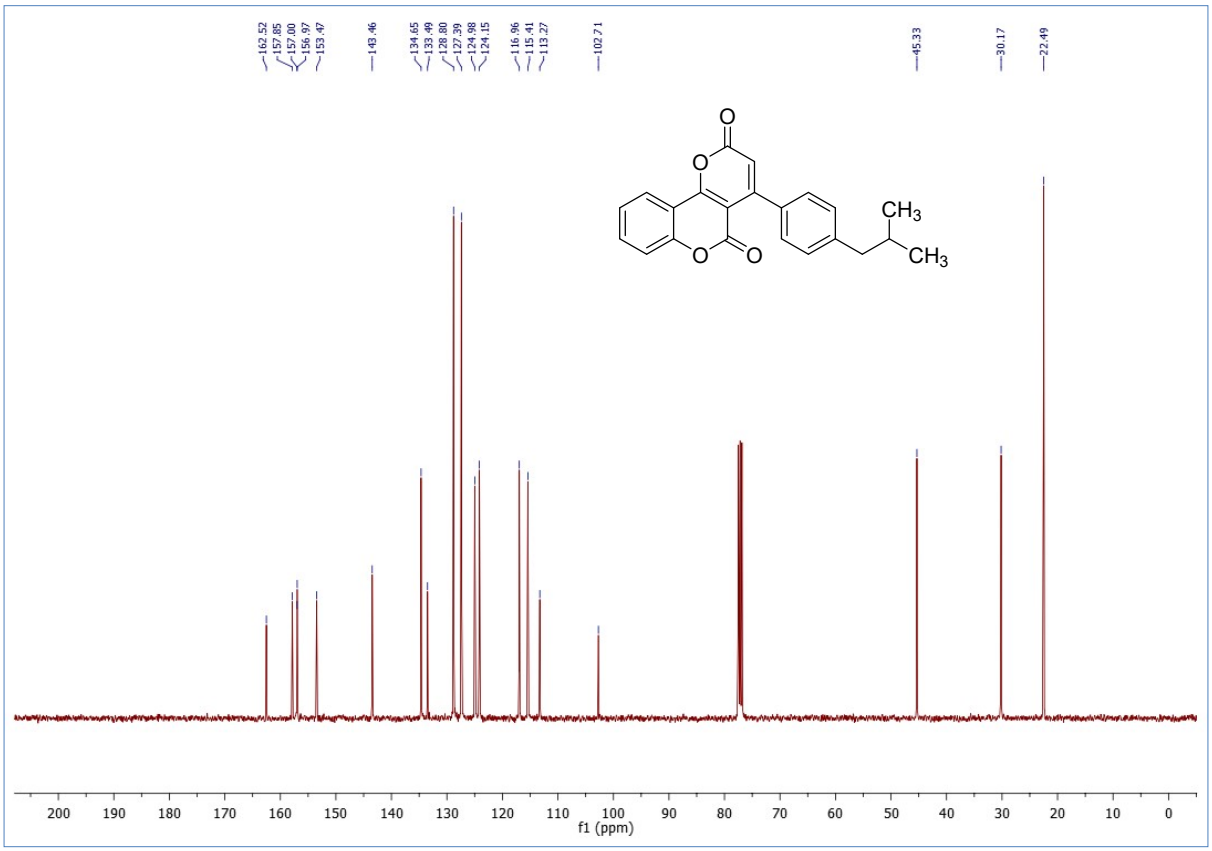


Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
305.0804	305.0814	-1.0	-3.3	13.5	644.2	n/a	n/a	C19 H13 O4

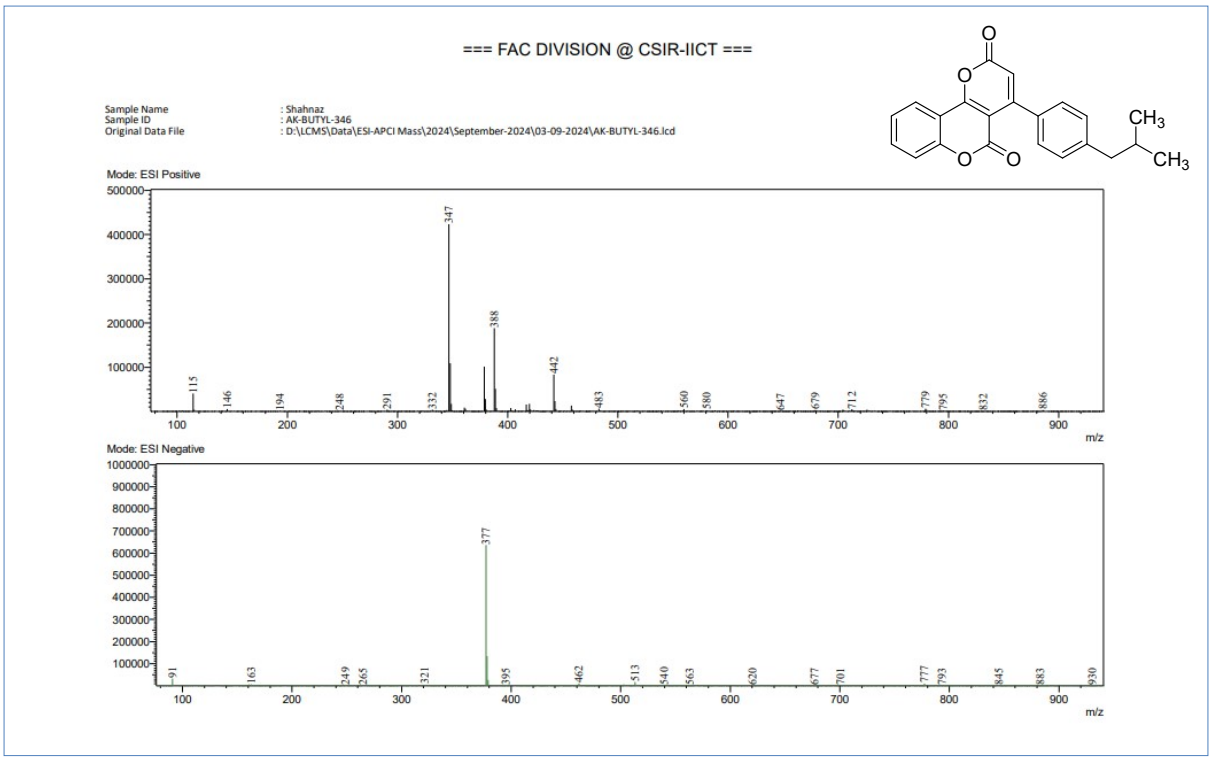
HRMS spectrum of compound **3e**



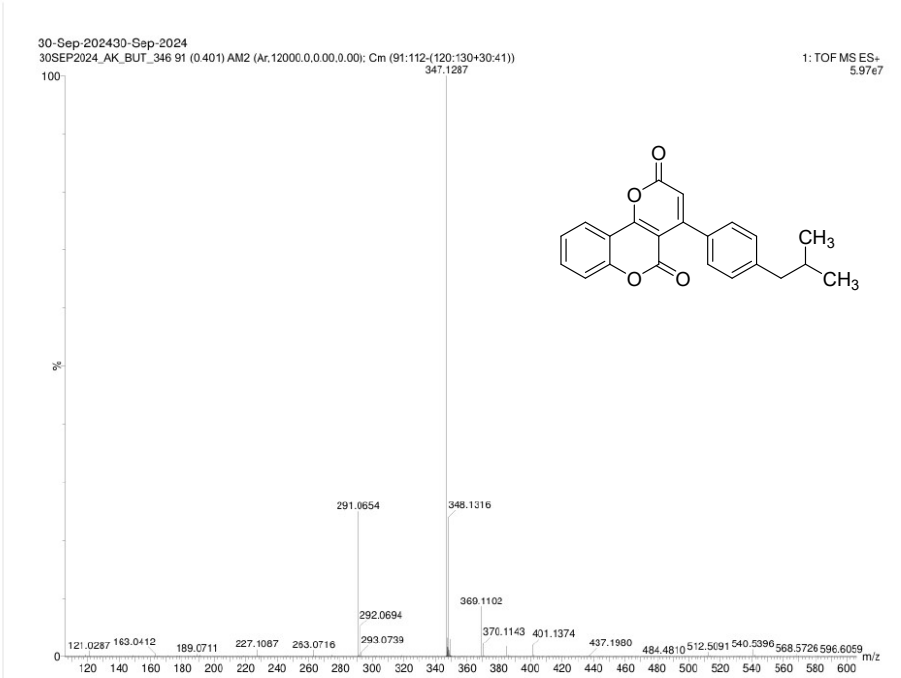
^{1}H-NMR spectrum of compound **3f**



^{13}C-NMR spectrum of compound **3f**



Mass spectrum of compound **3f**

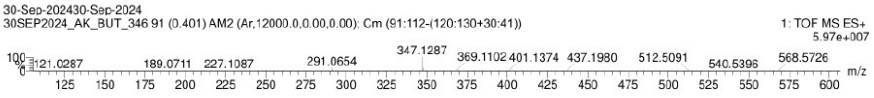


Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

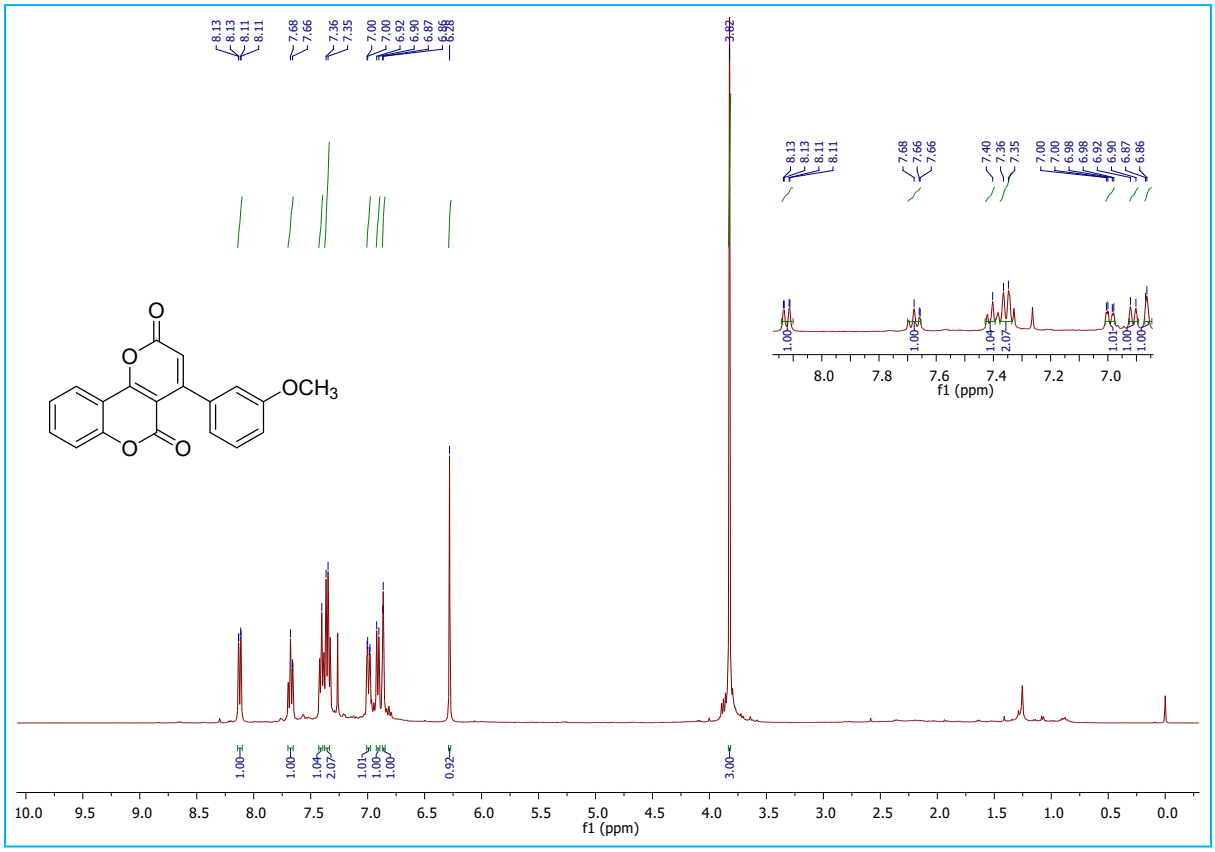
Monoisotopic Mass, Even Electron Ions
16 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-22 H: 0-20 O: 0-6 S: 0-1

30-Sep-202430-Sep-2024
30SEP2024_AK_BUT_346 91 (0.401) AM2 (Ar,12000.0,0.00,0.00); Cm (91:112-(120:130+30:41))
1: TOF MS ES+
5.97e+007

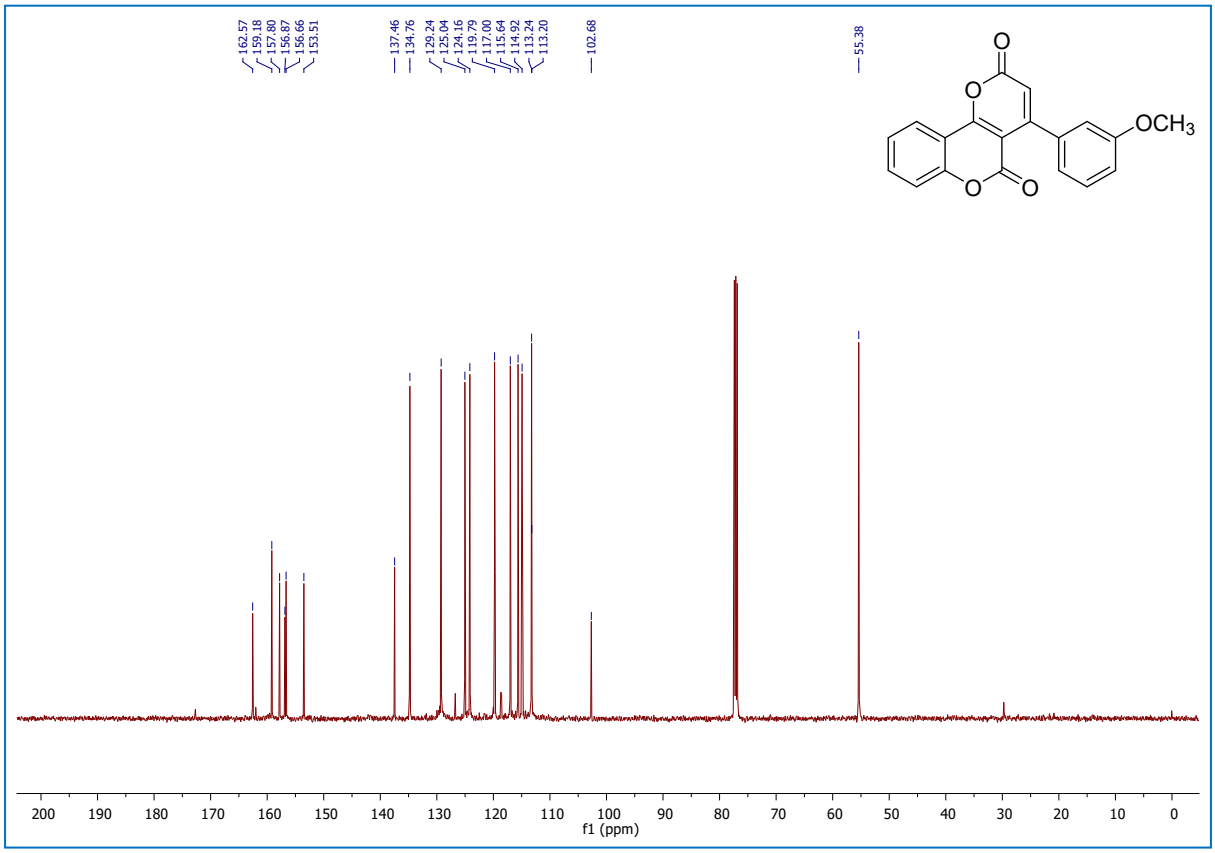


Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
347.1287	347.1283	0.4	1.2	13.5	599.5	n/a	n/a	C22 H19 O4

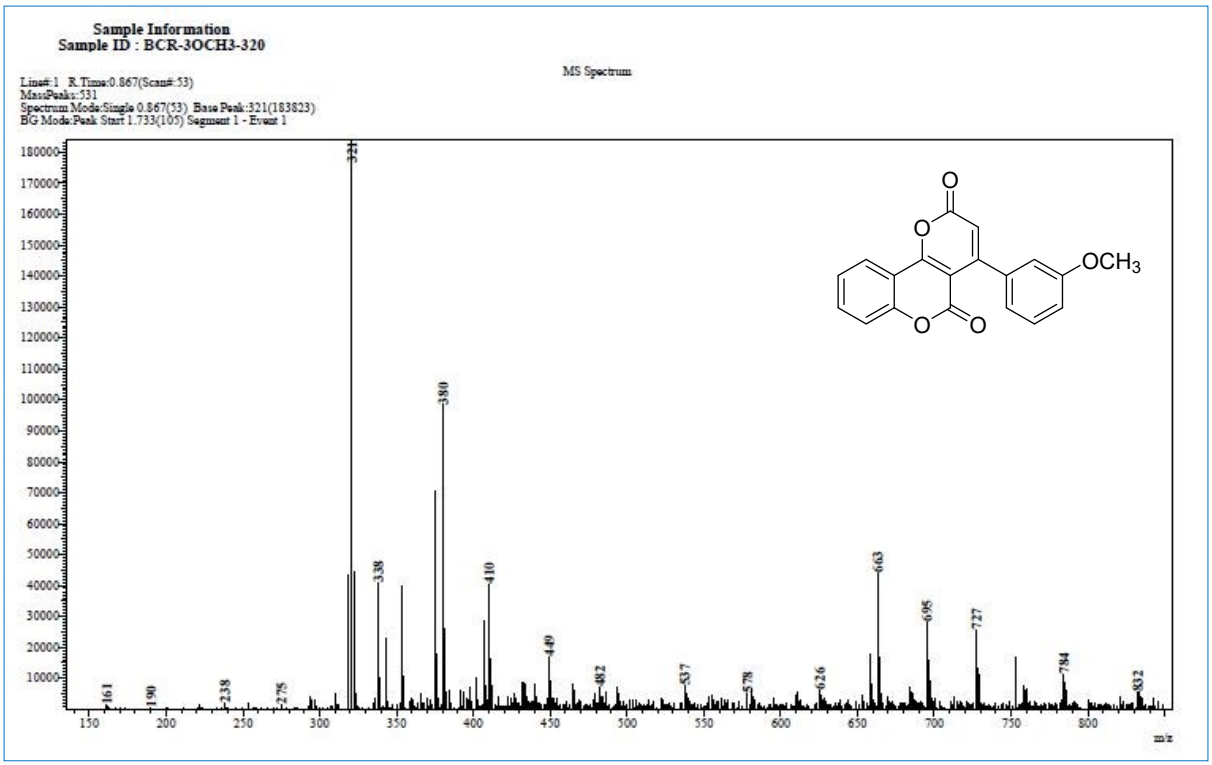
HRMS spectrum of compound **3f**



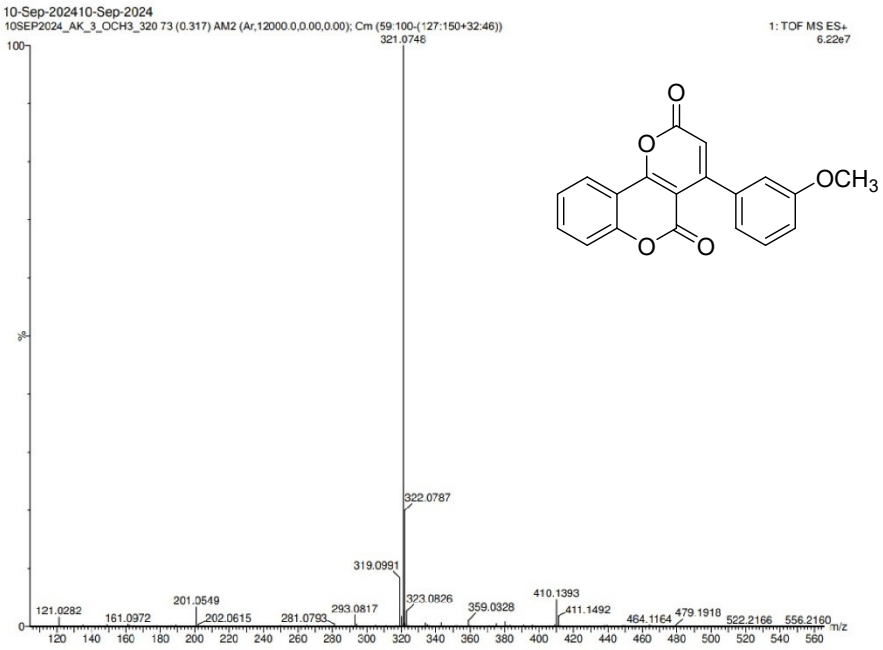
^{1}H-NMR spectrum of compound **3h**



^{13}C-NMR spectrum of compound **3h**



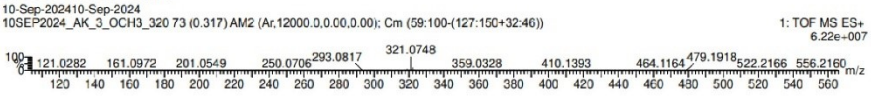
Mass spectrum of compound **3h**



Elemental Composition Report **Page 1**

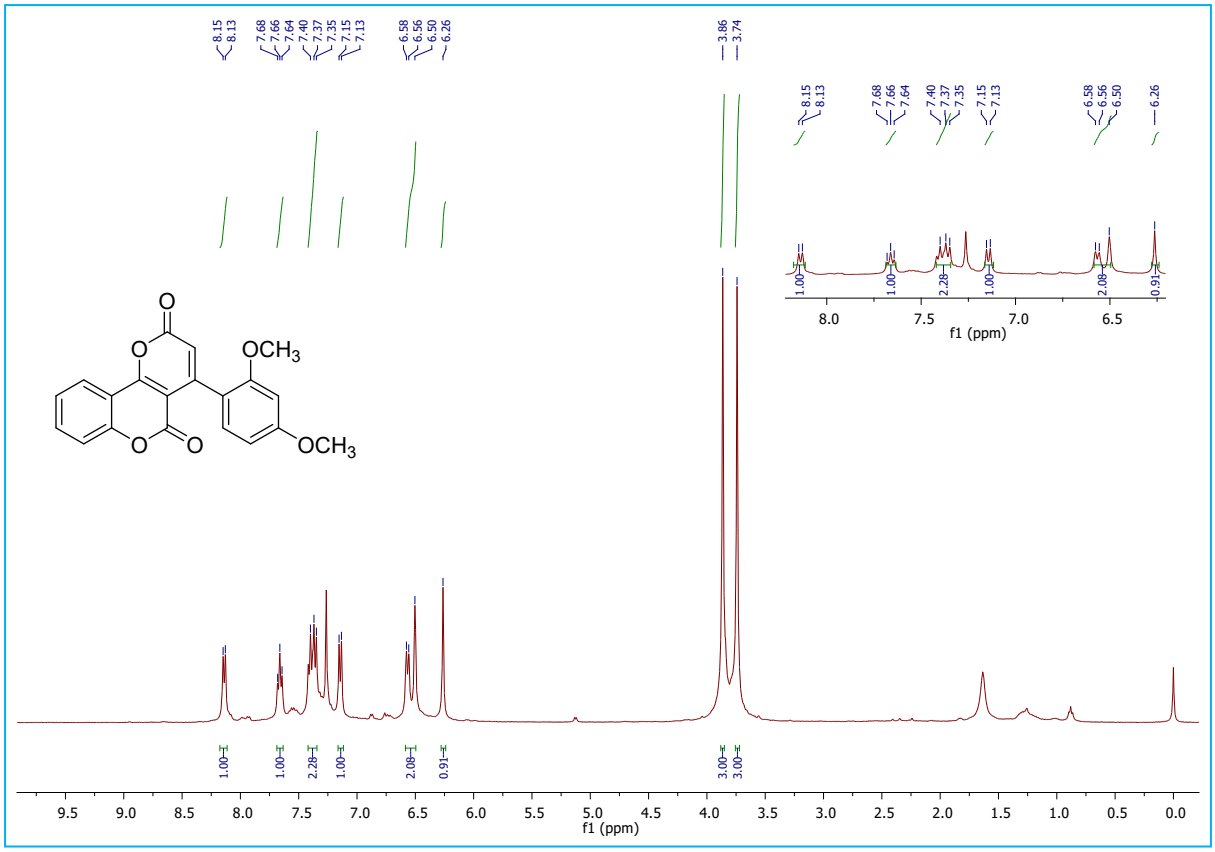
Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
4 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-19 H: 0-15 O: 0-5

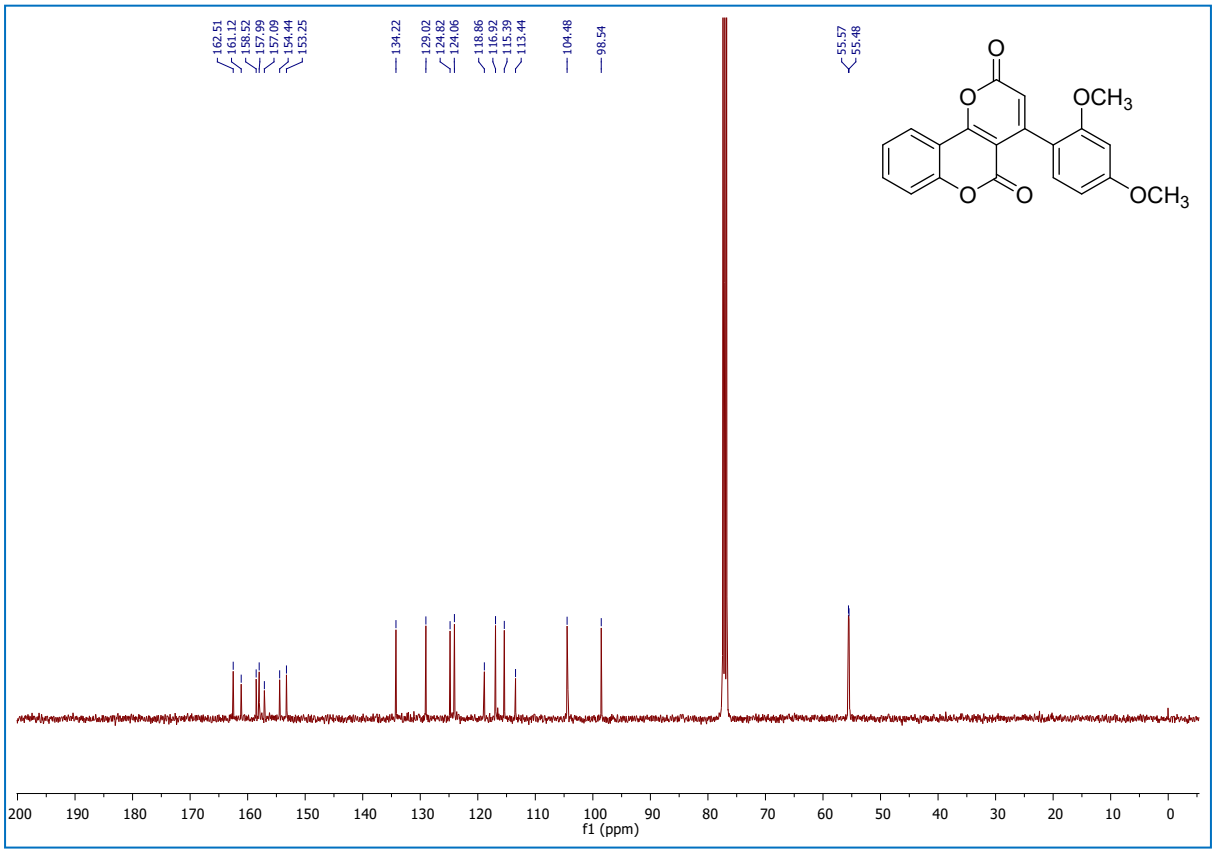


Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
321.0748	321.0763	-1.5	-4.7	13.5	574.9	n/a	n/a	C19 H13 O5

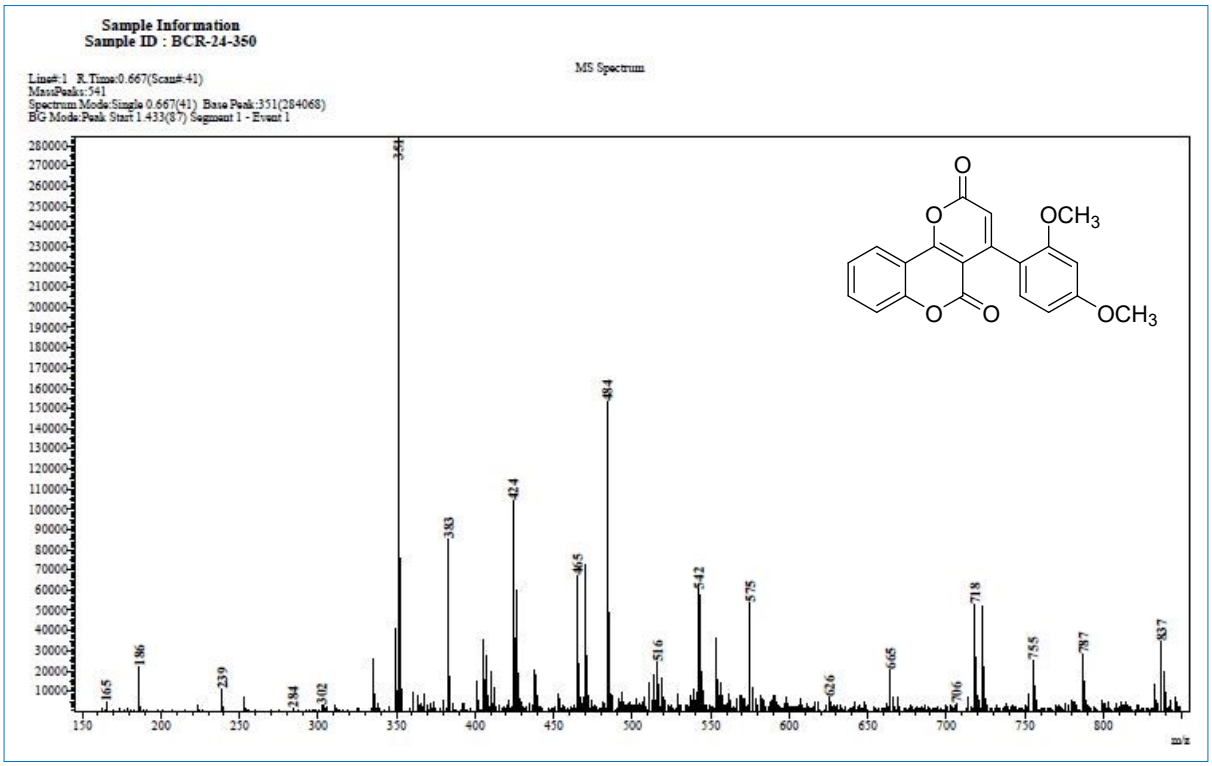
HRMS spectrum of compound **3h**



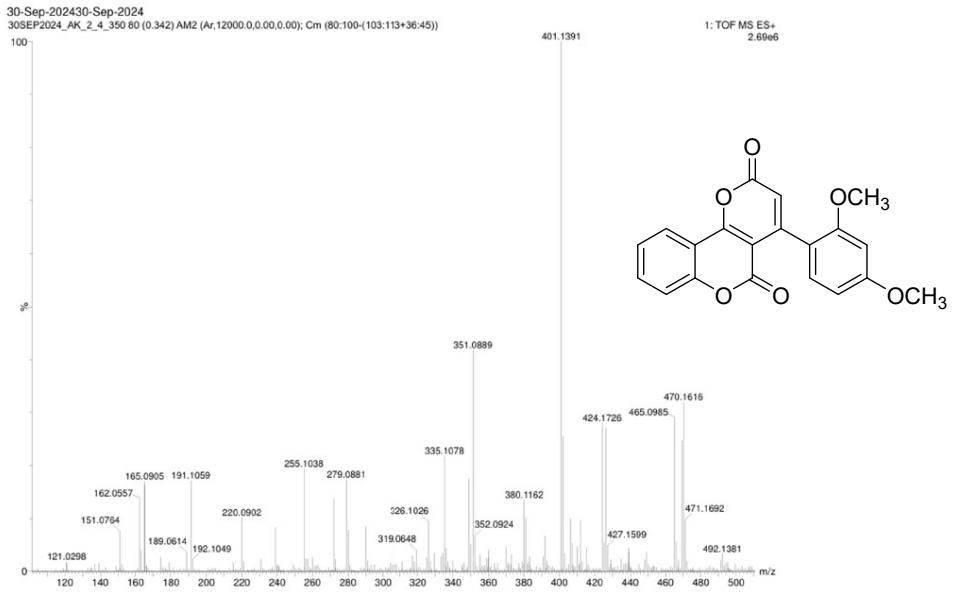
^{1}H-NMR spectrum of compound **3i**



^{13}C-NMR spectrum of compound **3i**



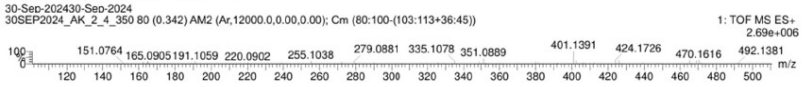
Mass spectrum of compound **3i**



Elemental Composition Report **Page 1**

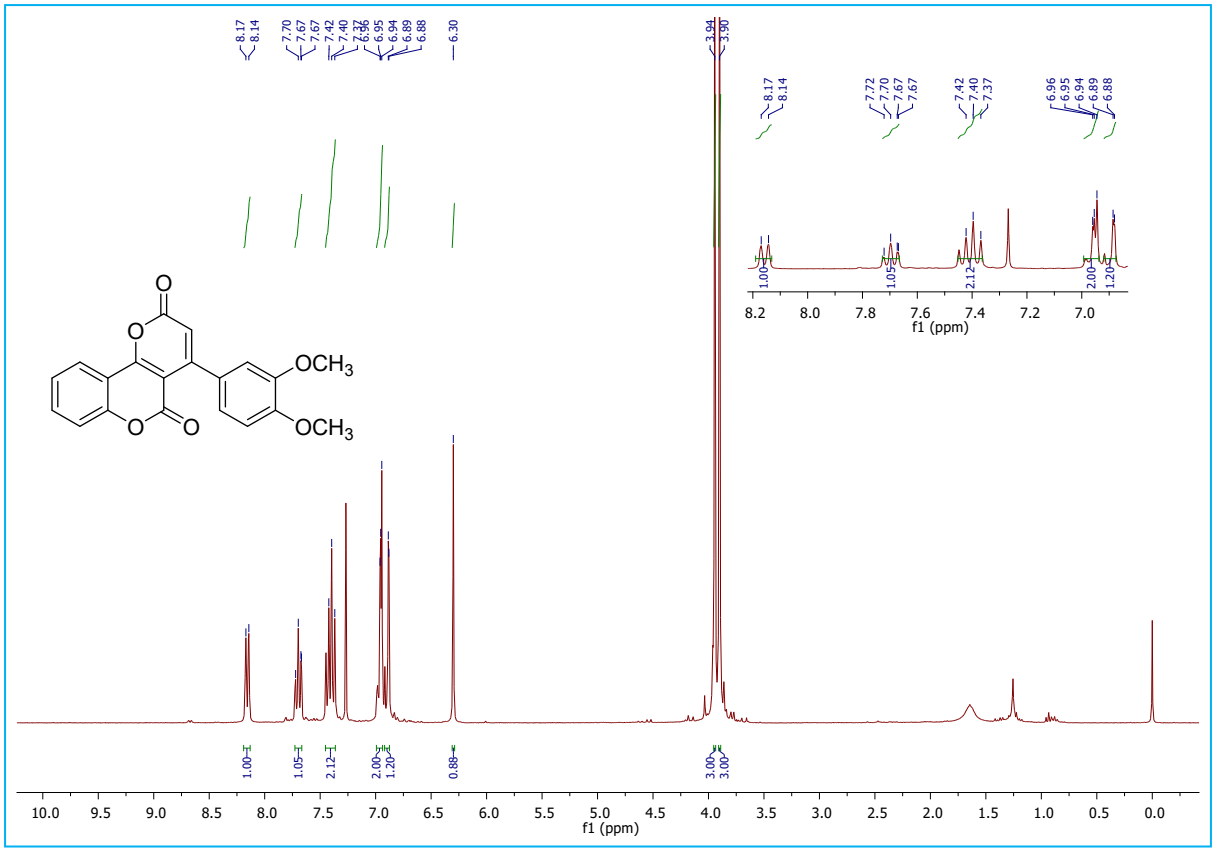
Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
34 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-20 H: 0-16 N: 0-2 O: 0-6 S: 0-1

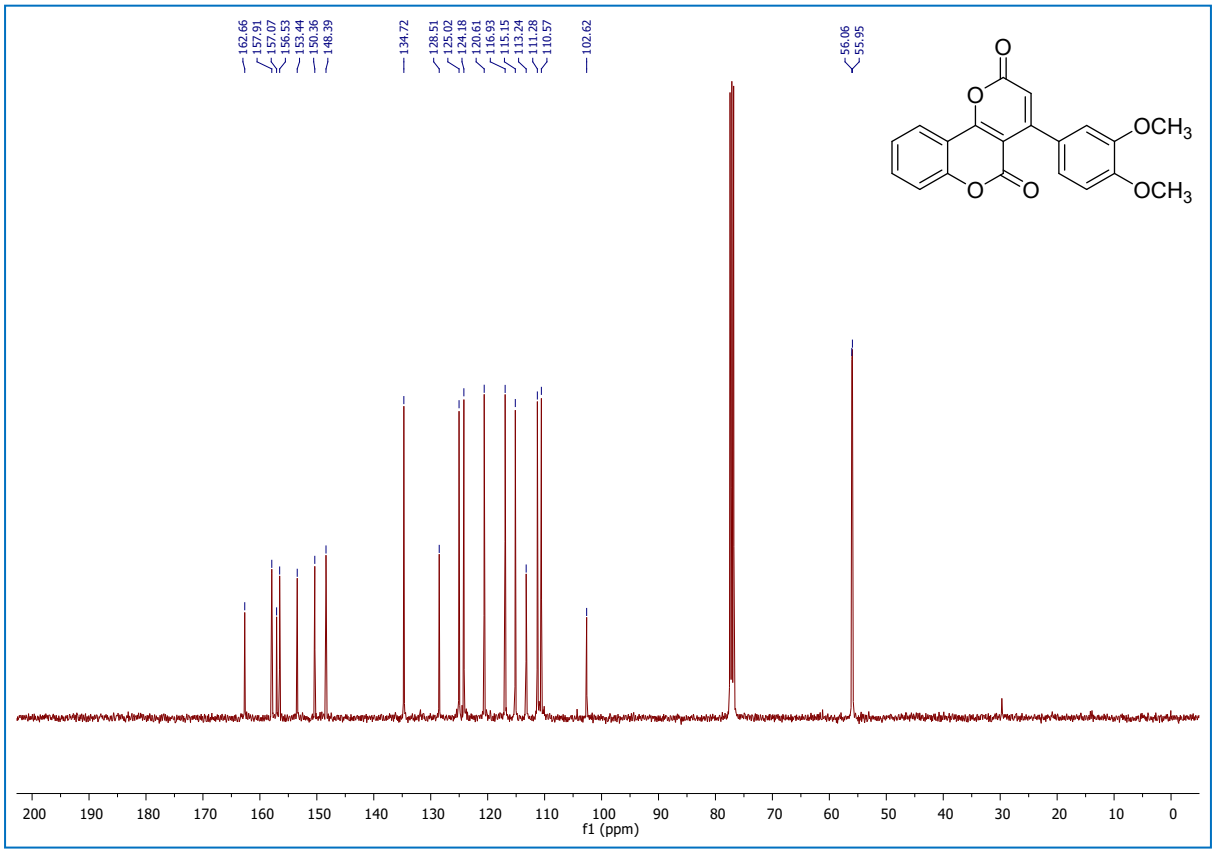


Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
351.0889	351.0869	2.0	5.7	13.5	398.7	n/a	n/a	C20 H15 O6

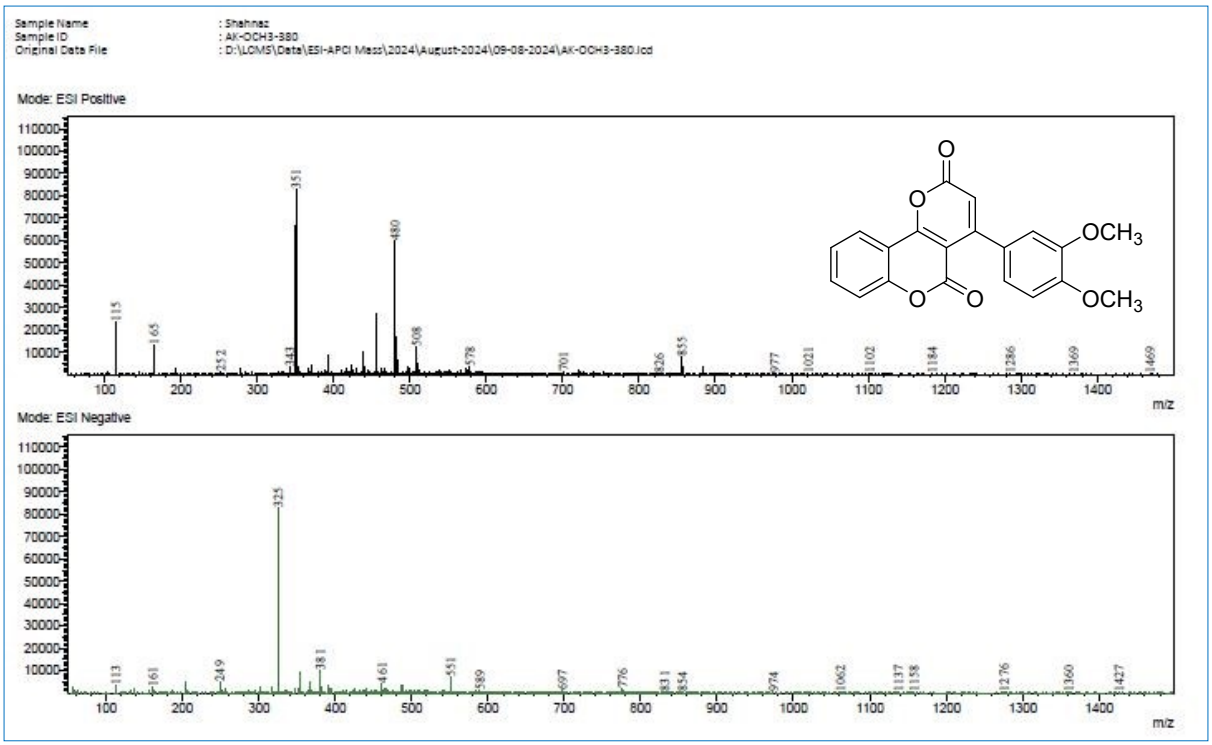
HRMS spectrum of compound **3i**



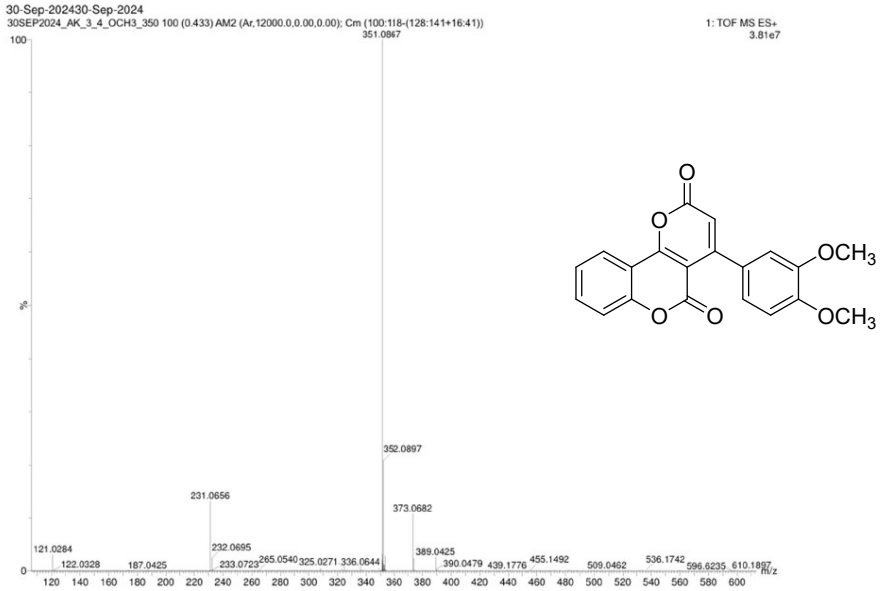
^{1}H-NMR spectrum of compound **3j**



^{13}C-NMR spectrum of compound **3j**



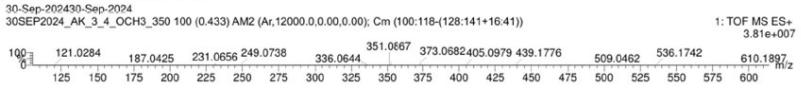
Mass spectrum of compound **3j**



Elemental Composition Report **Page 1**

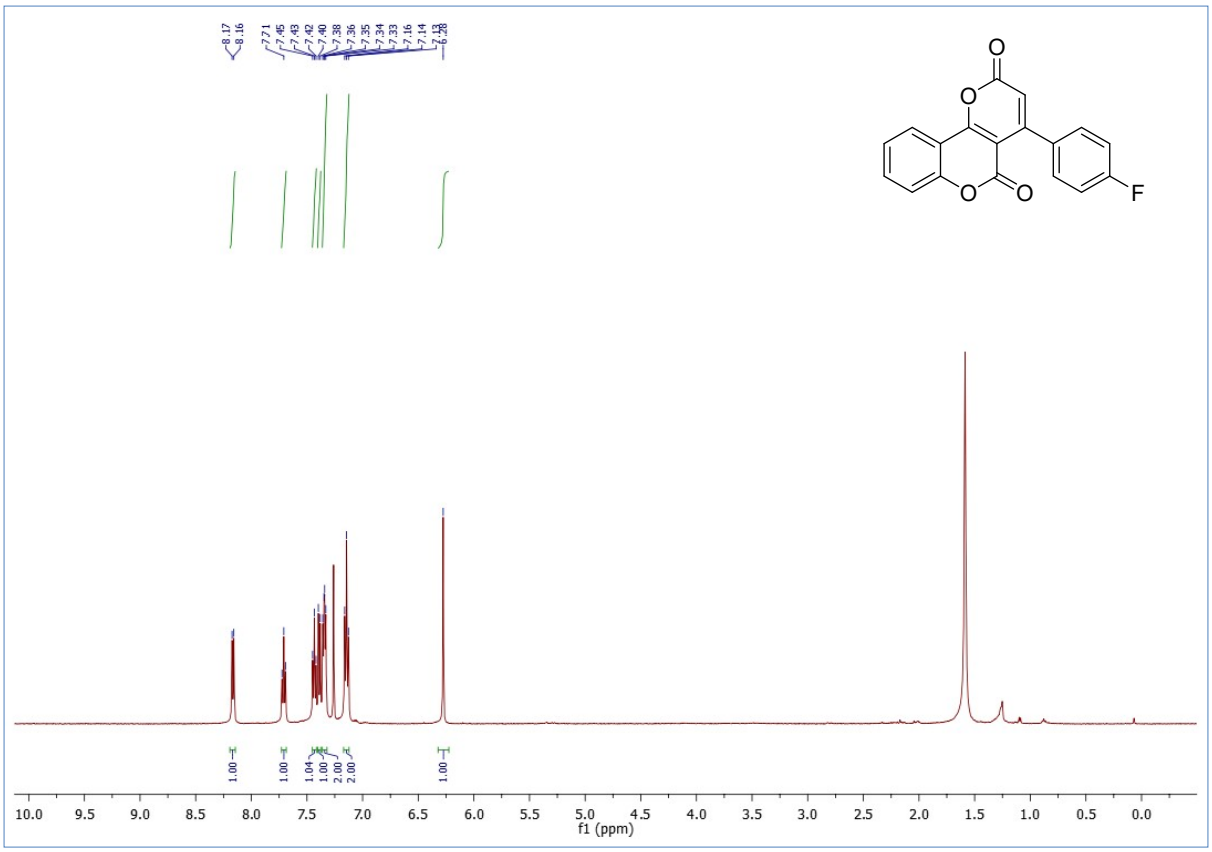
Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
11 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-20 H: 0-15 O: 0-6 S: 0-1

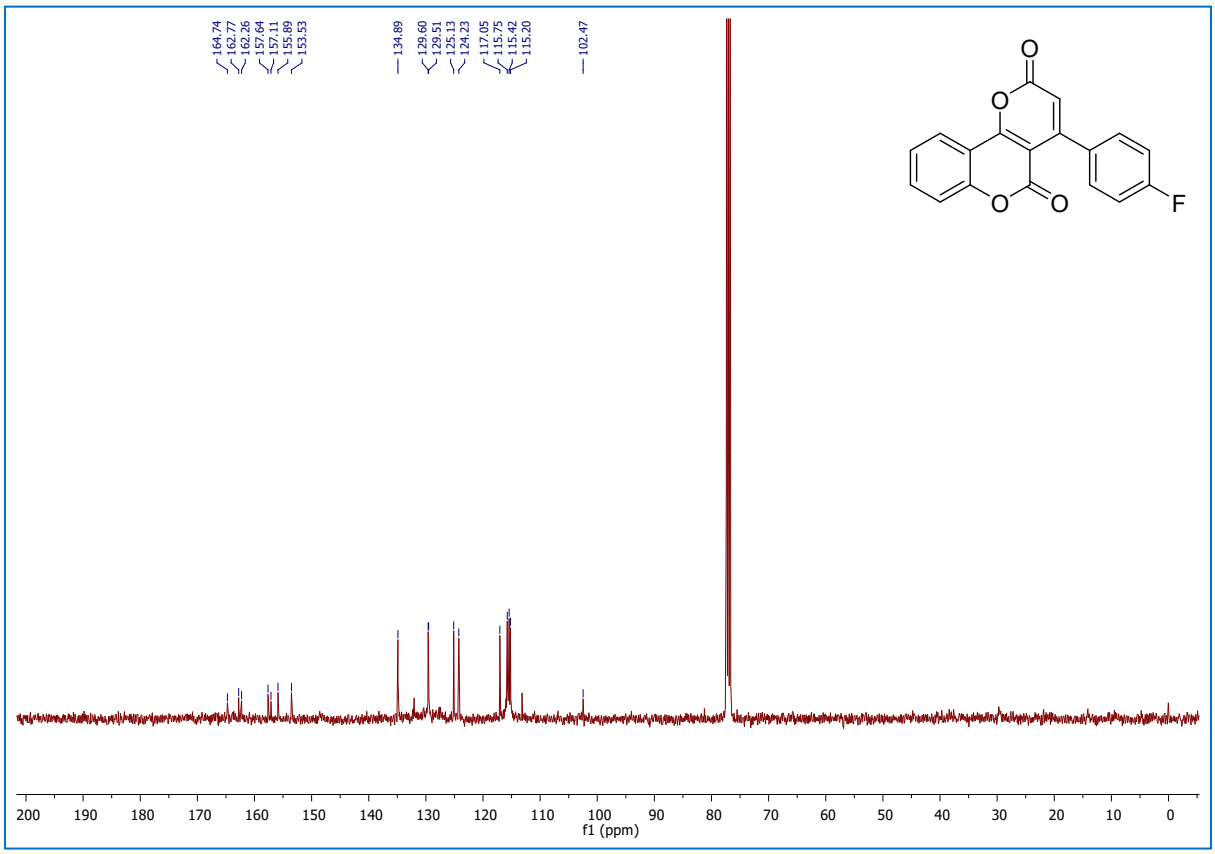


Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
351.0867	351.0869	-0.2	-0.6	13.5	500.1	n/a	n/a	C20 H15 O6

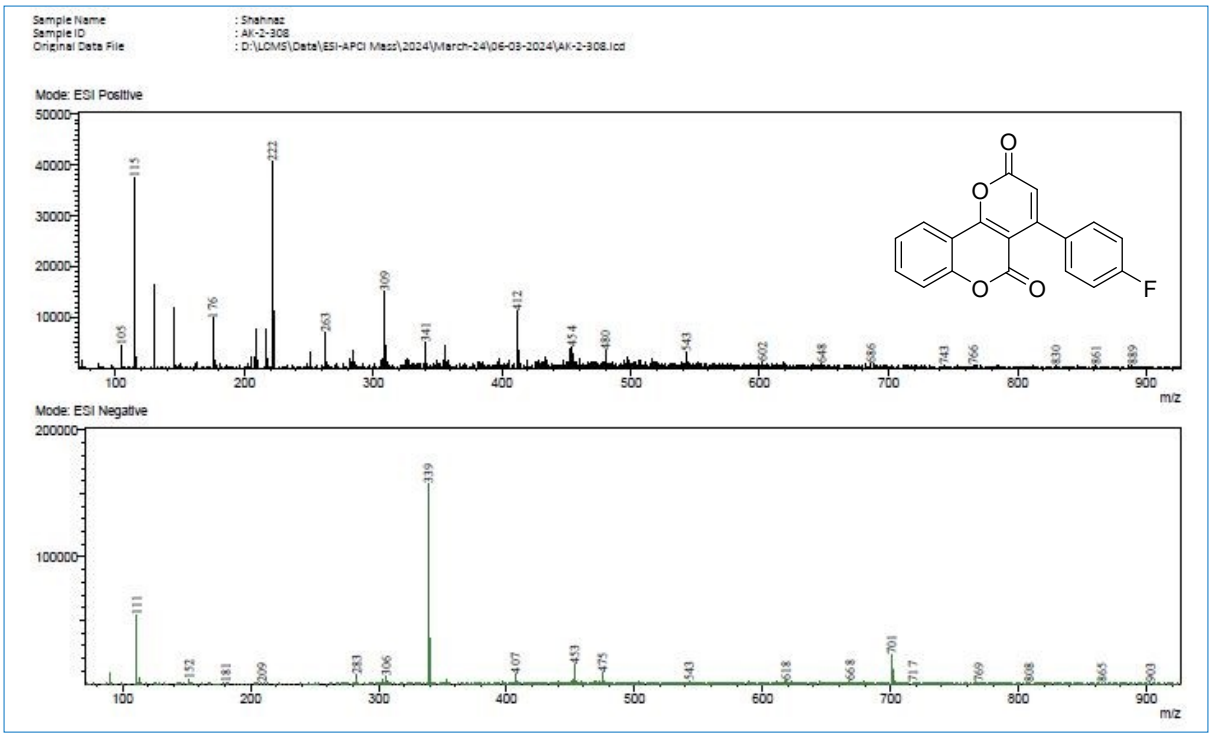
HRMS spectrum of compound **3j**



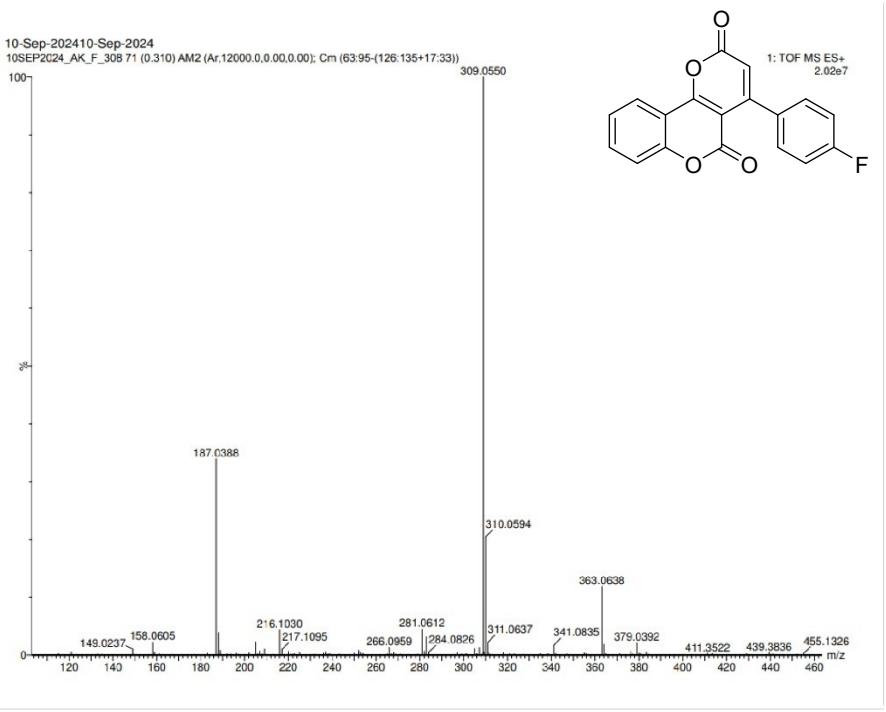
^{1}H-NMR spectrum of compound **3k**



^{13}C-NMR spectrum of compound **3k**



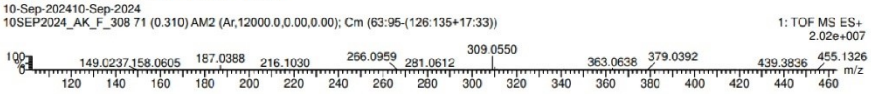
Mass spectrum of compound **3k**



Elemental Composition Report **Page 1**

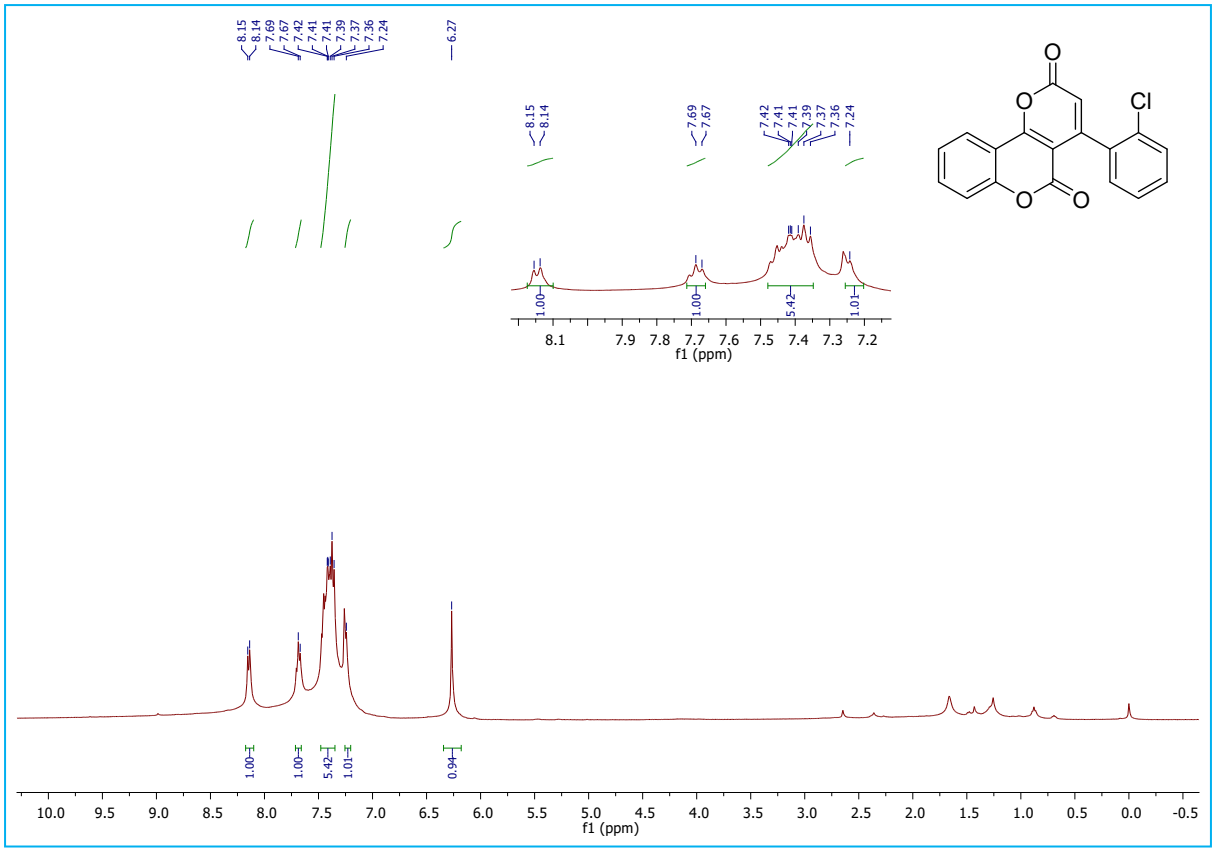
Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
25 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-18 H: 0-10 O: 0-4 F: 0-3 P: 0-1

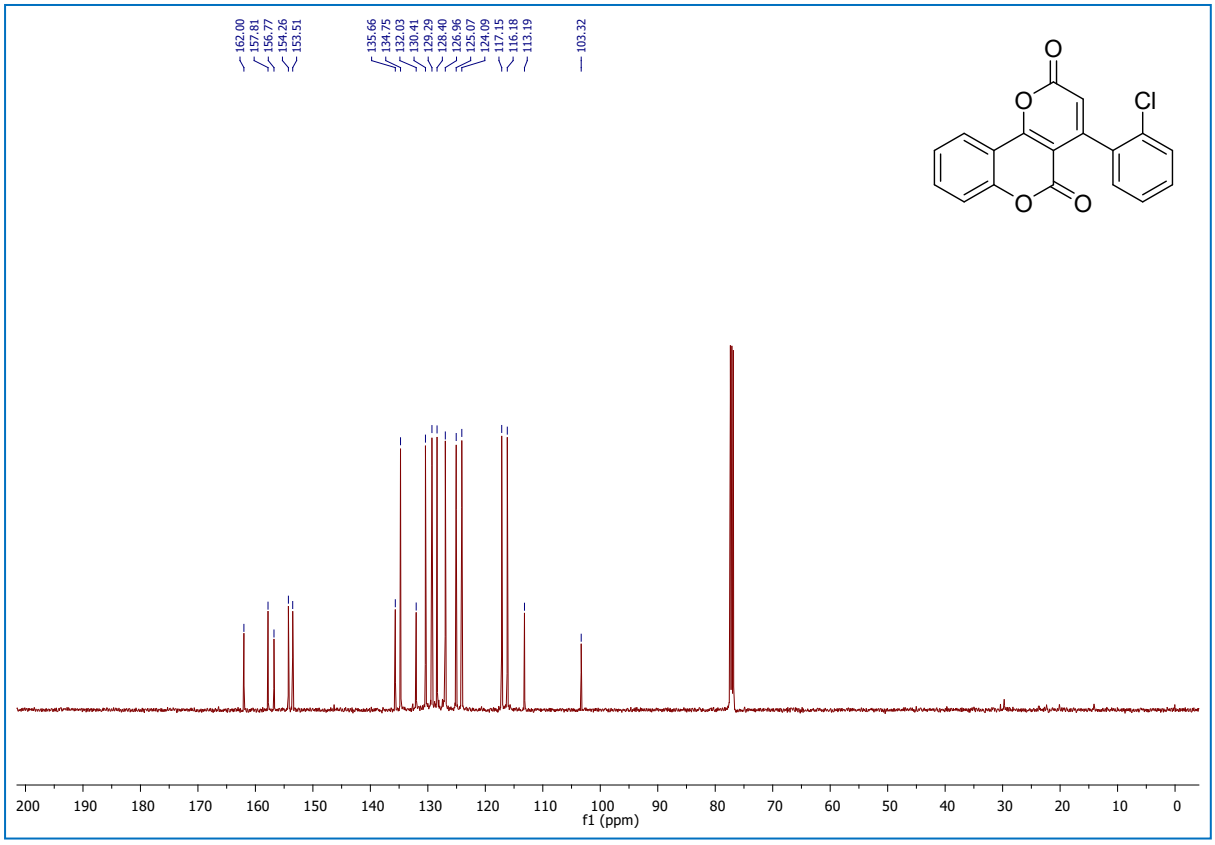


Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
309.0550	309.0563	-1.3	-4.2	13.5	545.2	n/a	n/a	C18 H10 O4 F

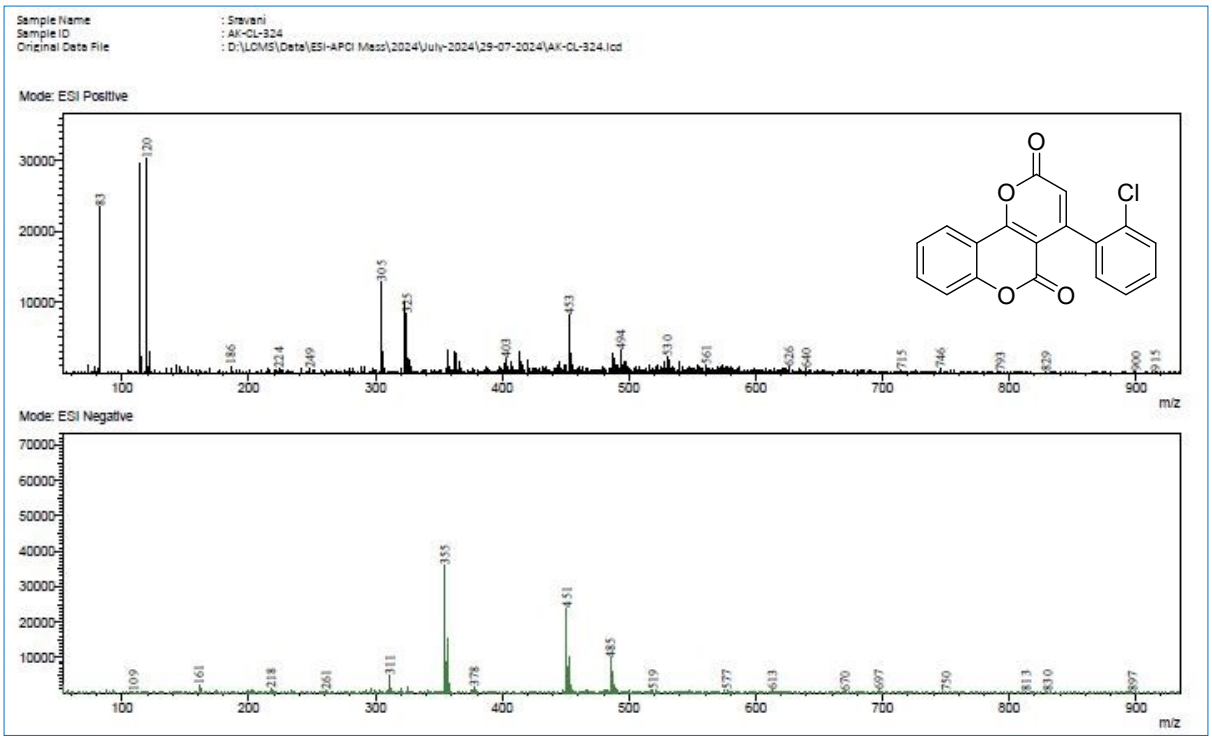
HRMS spectrum of **3k**



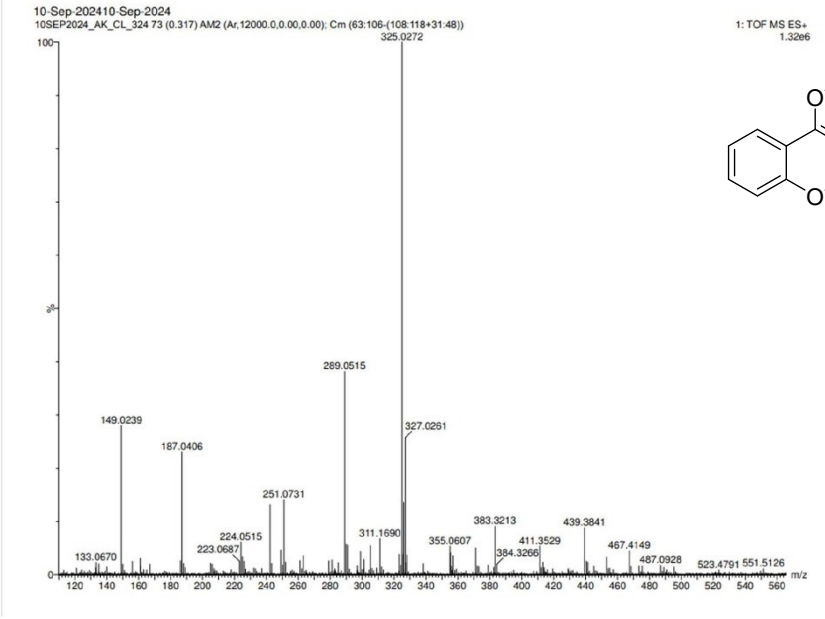
^{1}H-NMR spectrum of compound **3m**



^{13}C-NMR spectrum of compound **3m**



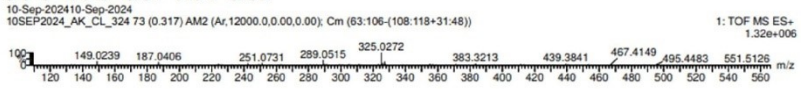
Mass spectrum of compound **3m**



Elemental Composition Report **Page 1**

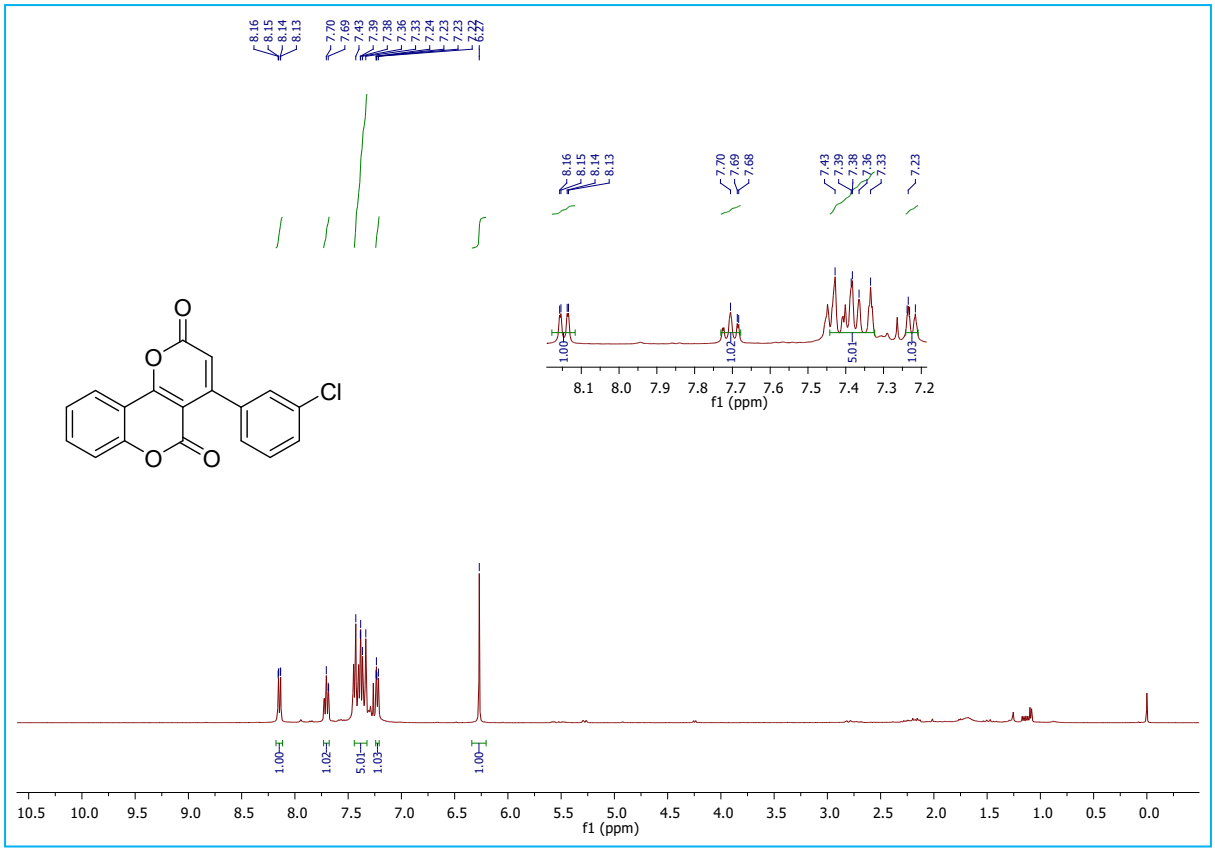
Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
19 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-18 H: 0-10 O: 0-4 P: 0-1 Cl: 0-2

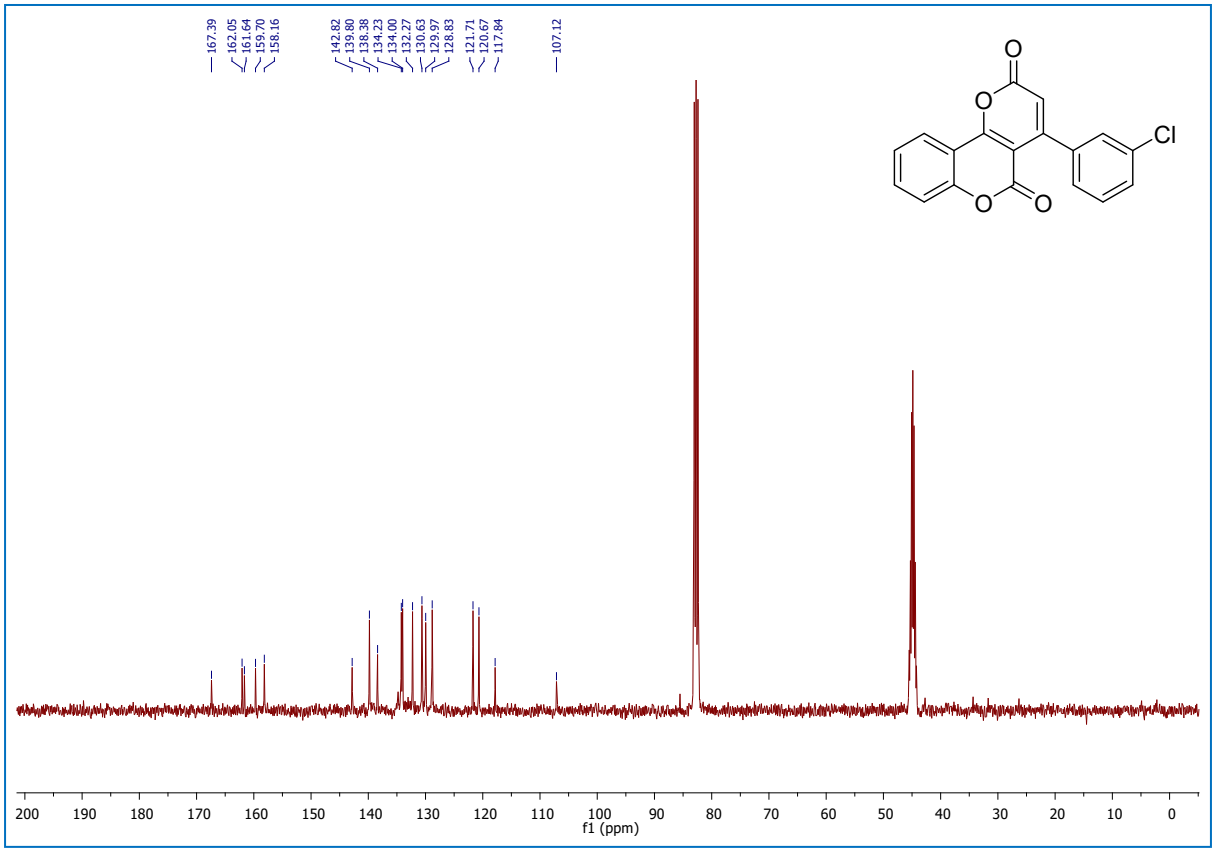


Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
325.0272	325.0268	0.4	1.2	13.5	406.8	n/a	n/a	C18 H10 O4 Cl

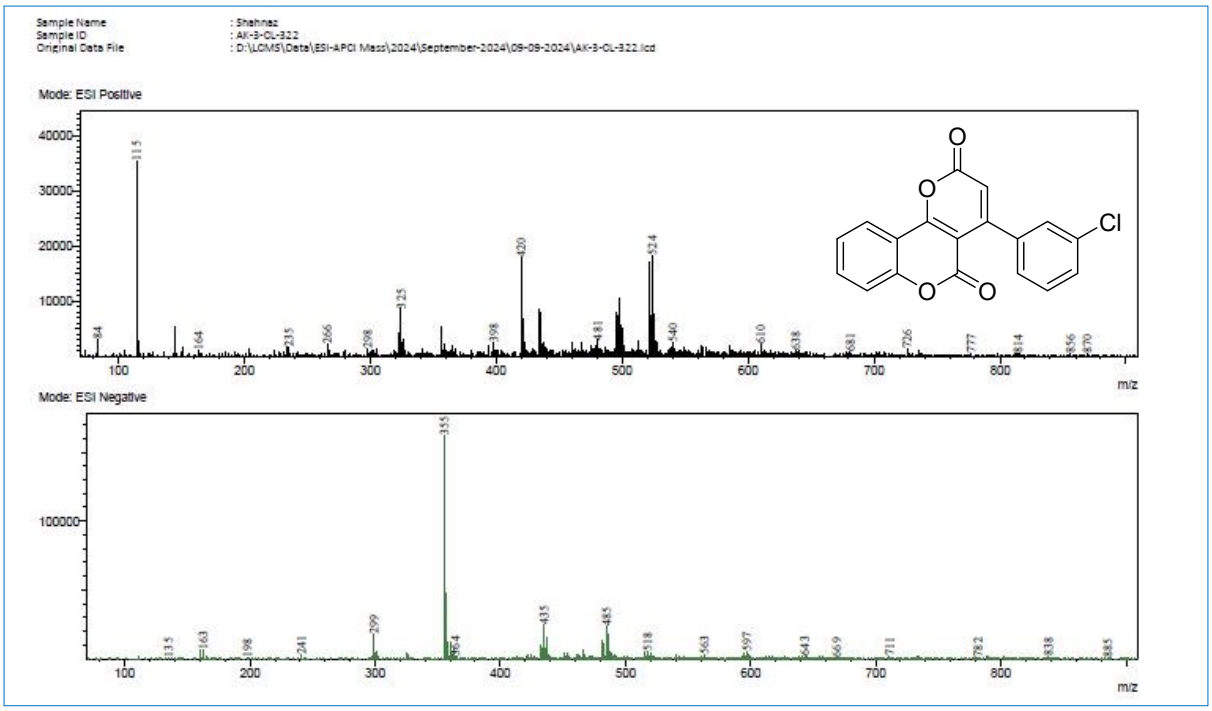
HRMS spectrum of **3m**



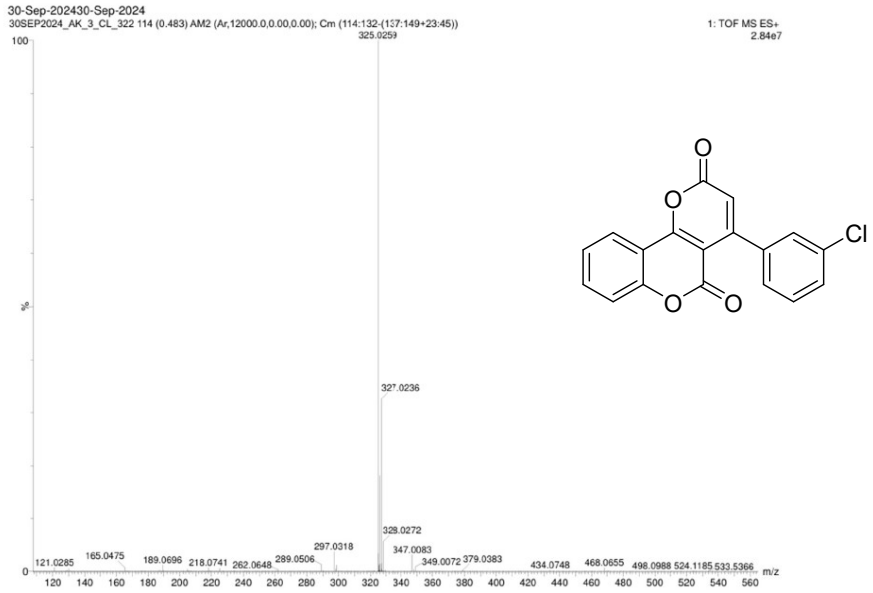
^{1}H-NMR spectrum of compound **3n**



^{13}C-NMR spectrum of compound **3n**



Mass spectrum of compound **3n**



Elemental Composition Report **Page 1**

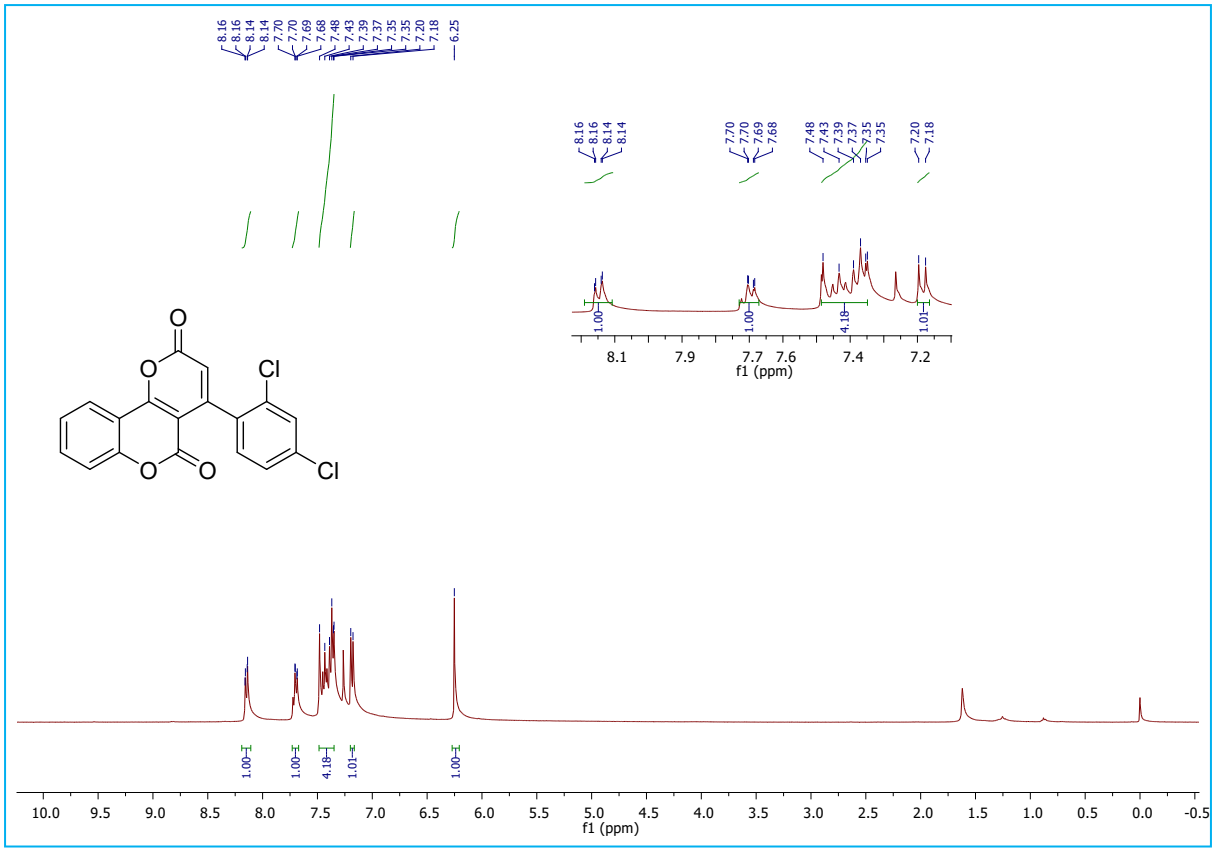
Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
33 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-20 H: 0-10 O: 0-6 S: 0-1 Cl: 0-2

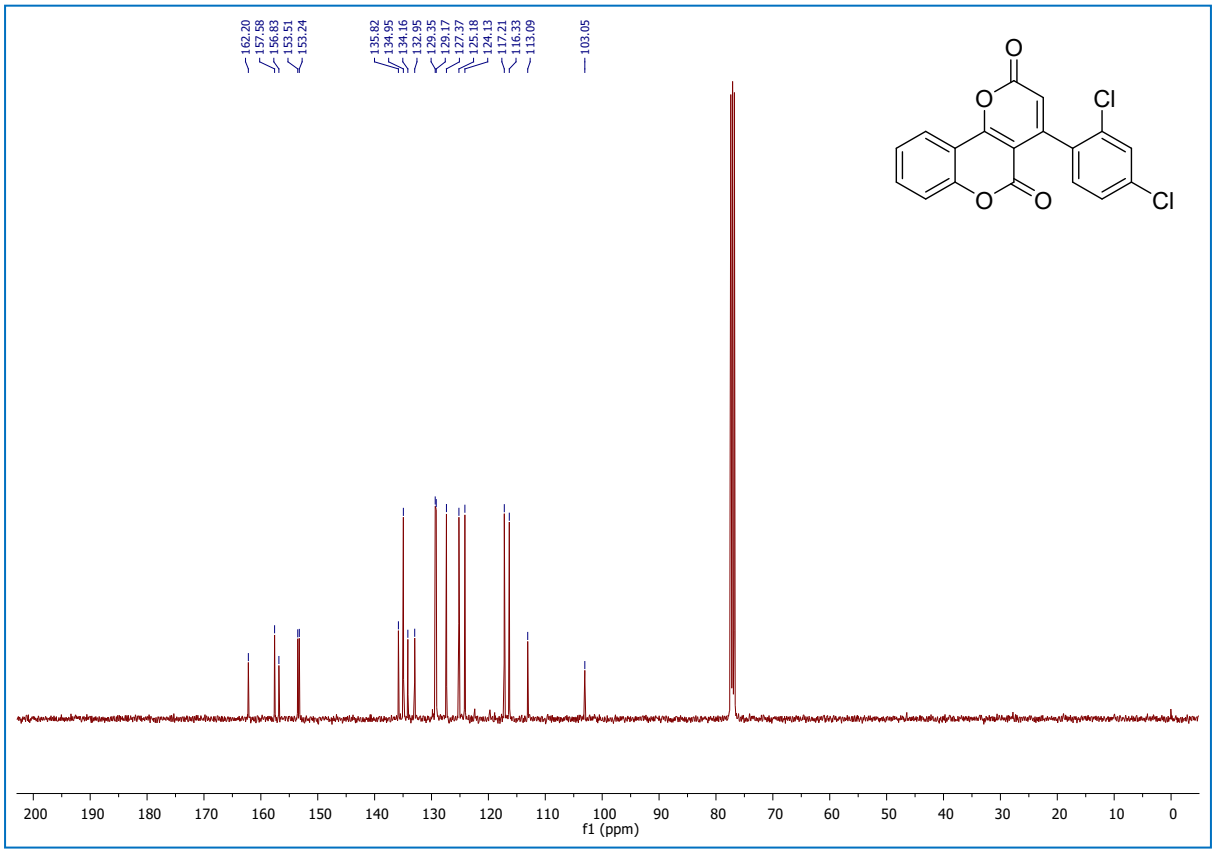
30-Sep-202430-Sep-2024
30SEP2024_AK_3_CL_322 114 (0.483) AM2 (Ar,12000.0,0.00,0.00); Cm (114:132-(137:149+23:45))
1: TOF MS ES+
2.84e+007

Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
325.0259	325.0268	-0.9	-2.8	13.5	624.9	n/a	n/a	C18 H10 O4 Cl

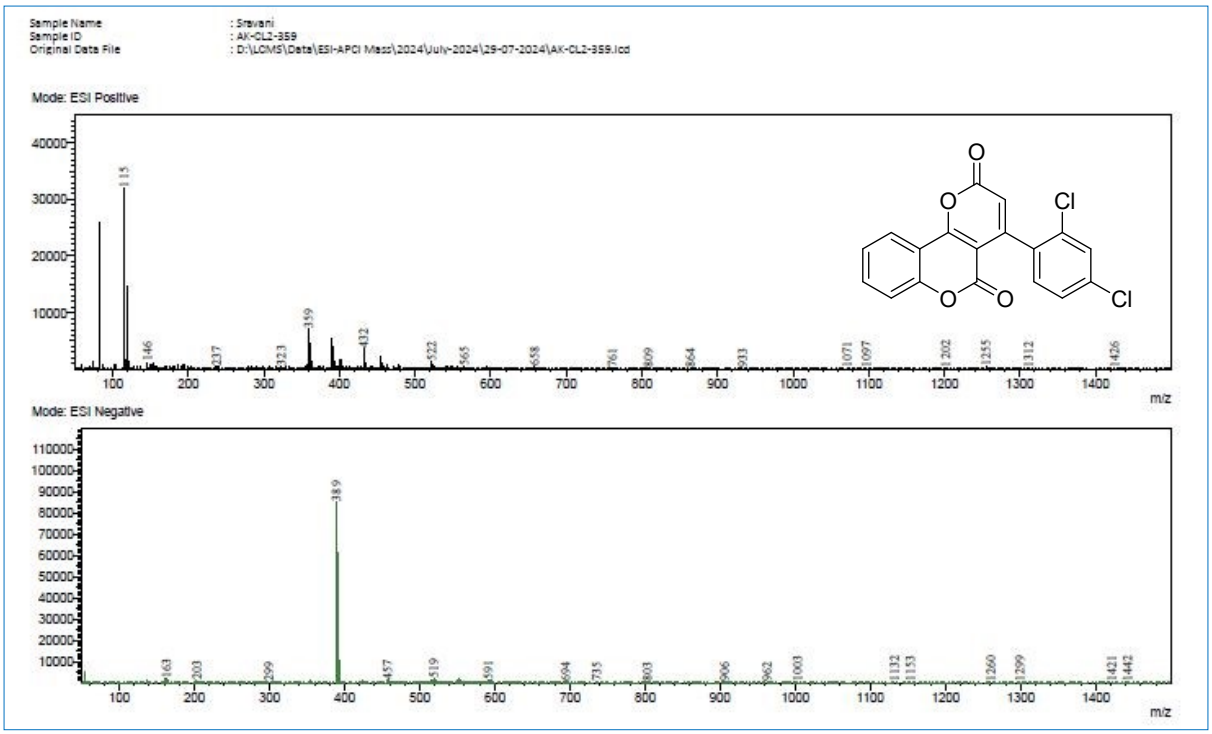
HRMS spectrum of compound **3n**



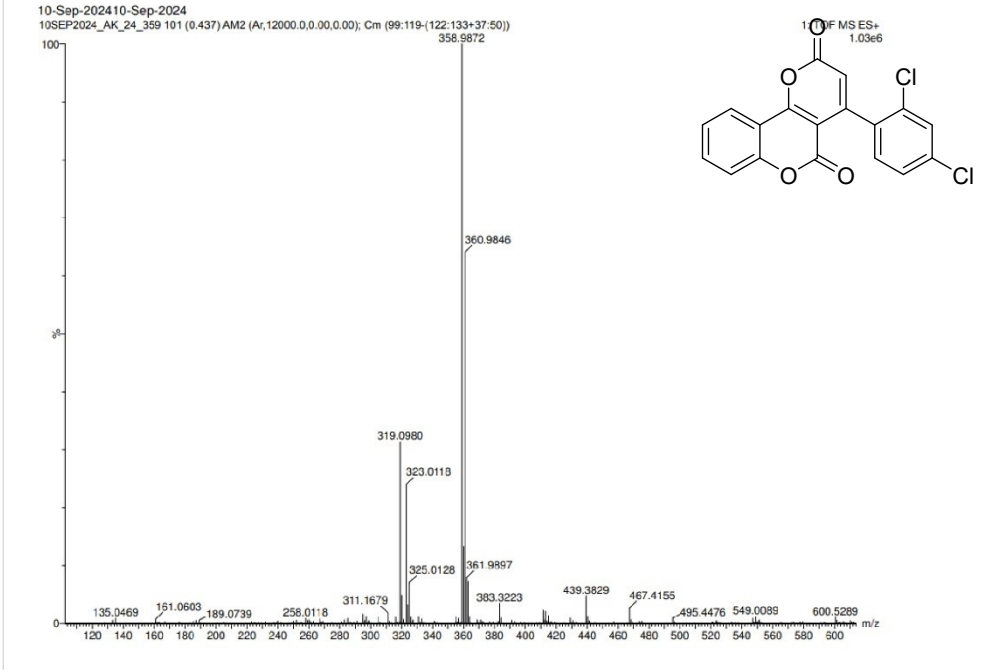
^{1}H-NMR spectrum of compound **3o**



^{13}C-NMR spectrum of compound **3o**



Mass spectrum of compound **3o**

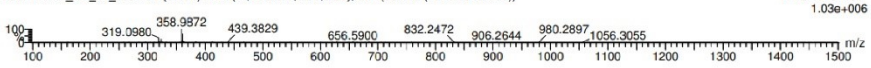


Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

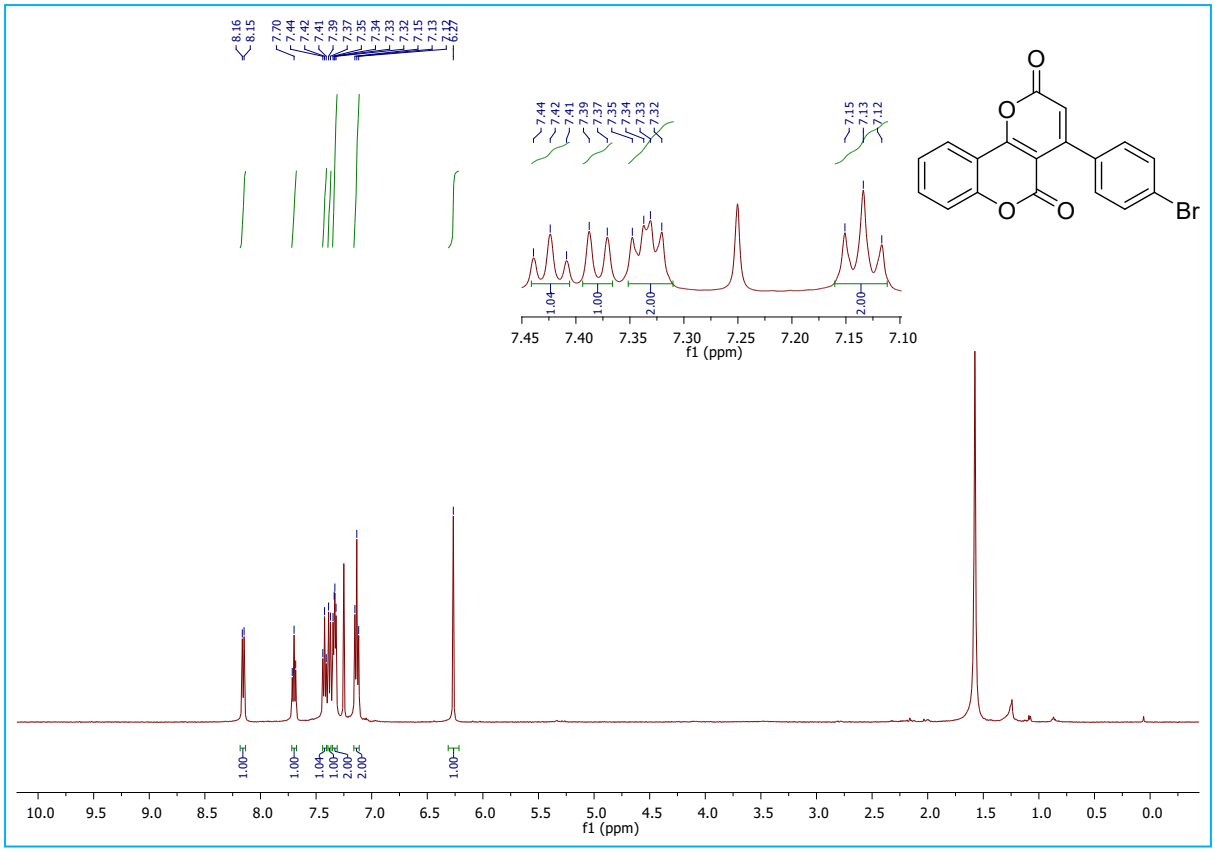
Monoisotopic Mass, Even Electron Ions
21 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-20 H: 0-20 O: 0-6 Cl: 0-2

10-Sep-202410-Sep-2024
10SEP2024_AK_24_359 101 (0.437) AM2 (Ar,12000.0,0.00,0.00); Cm (99:119-(122:133+37:50))
1: TOF MS ES+
1.03e+006

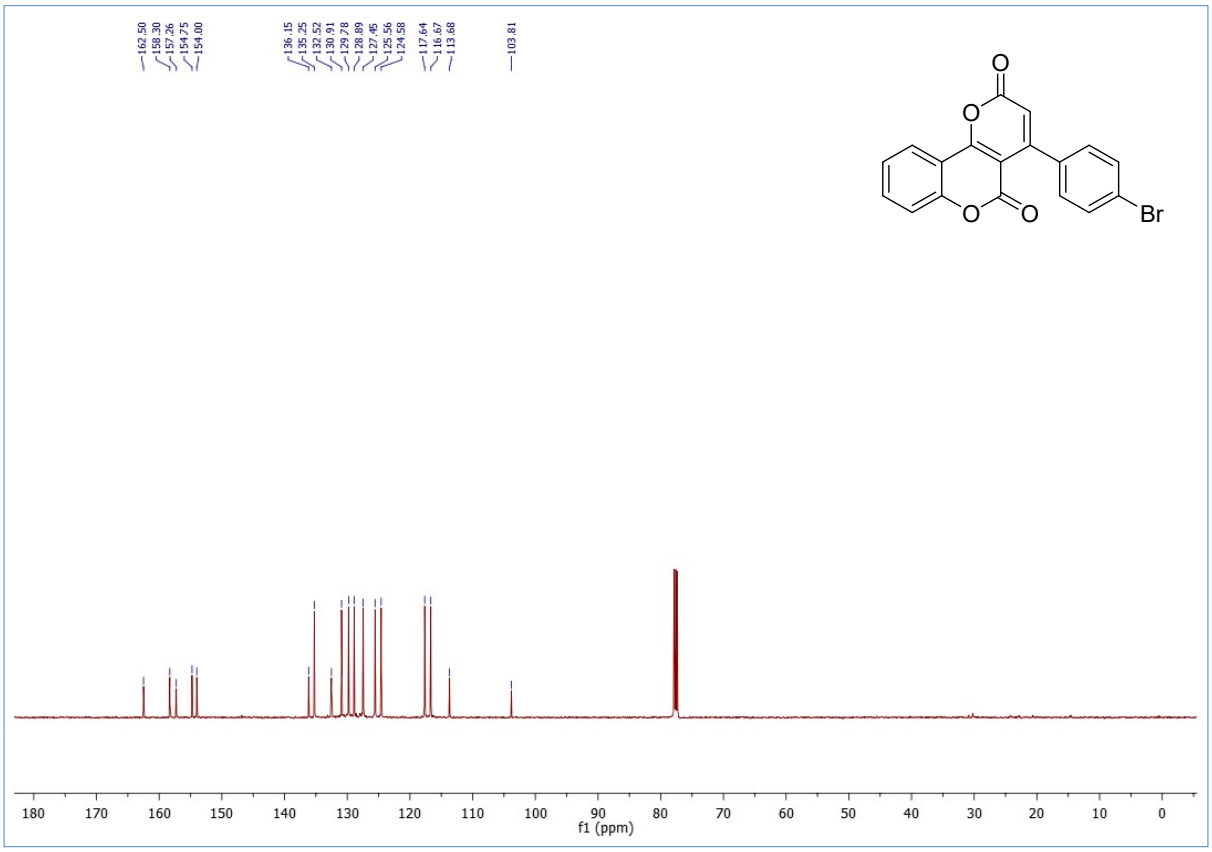


Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
358.9872	358.9878	-0.6	-1.7	13.5	383.3	n/a	n/a	C18 H9 O4 Cl2

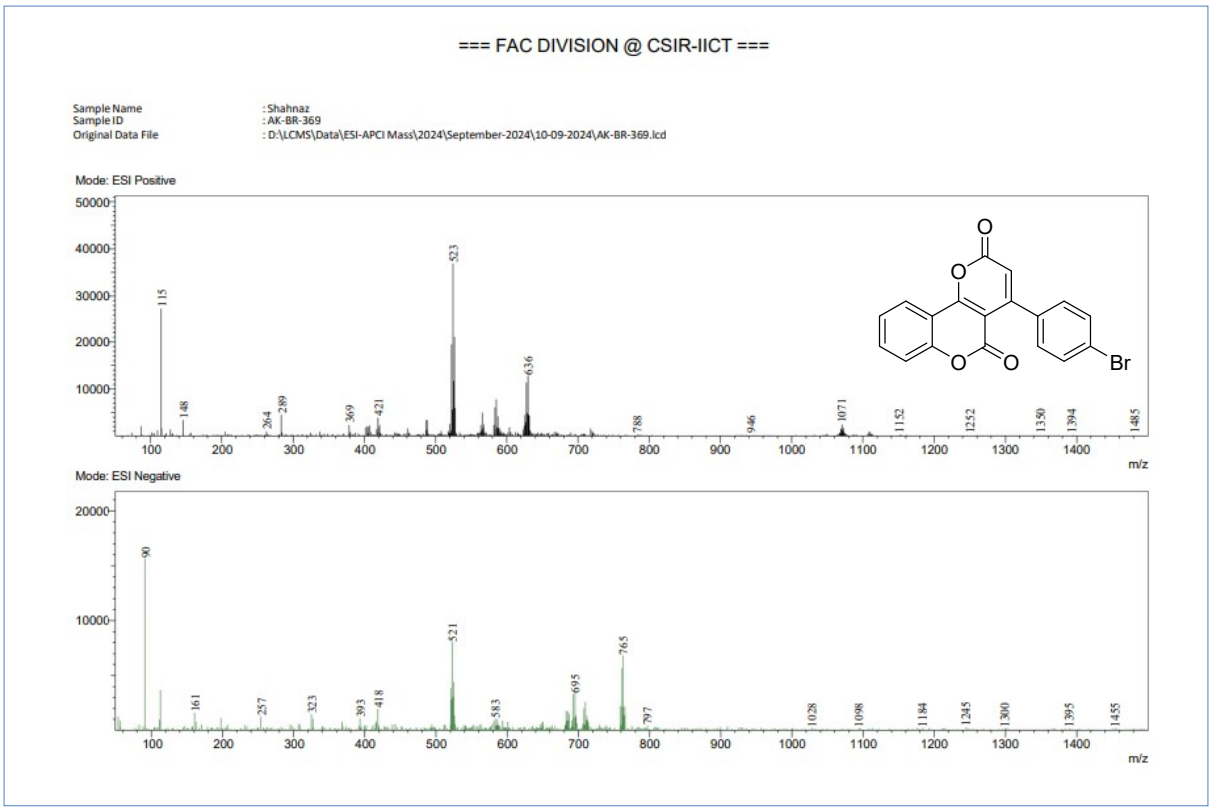
HRMS spectrum of **3o**



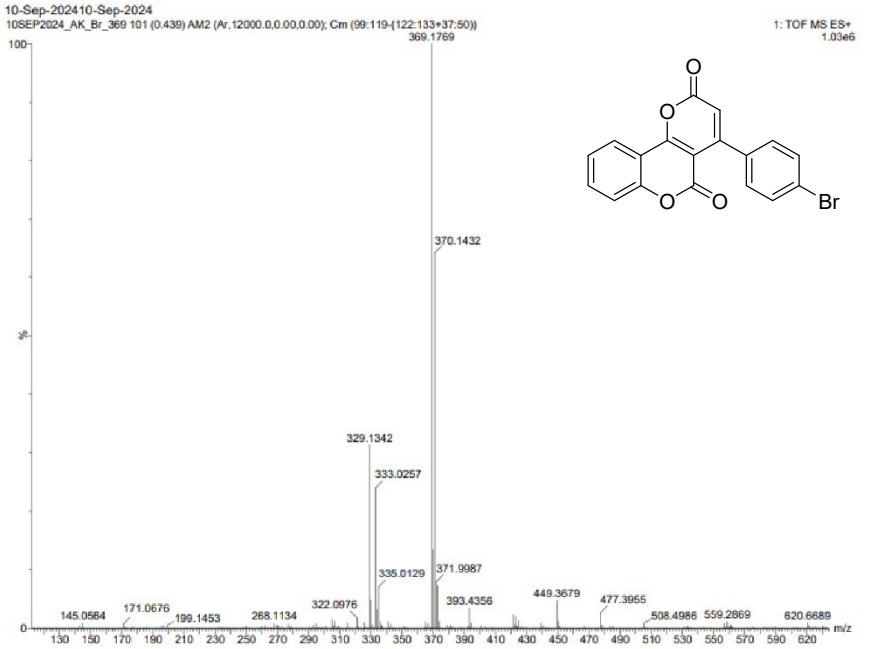
^{1}H-NMR spectrum of compound **3p**



^{13}C-NMR spectrum of compound **3p**



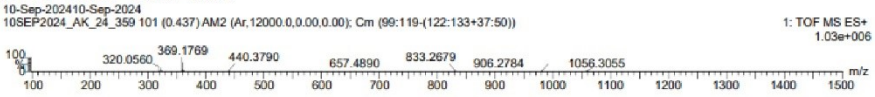
Mass spectrum of compound **3p**



Elemental Composition Report **Page 1**

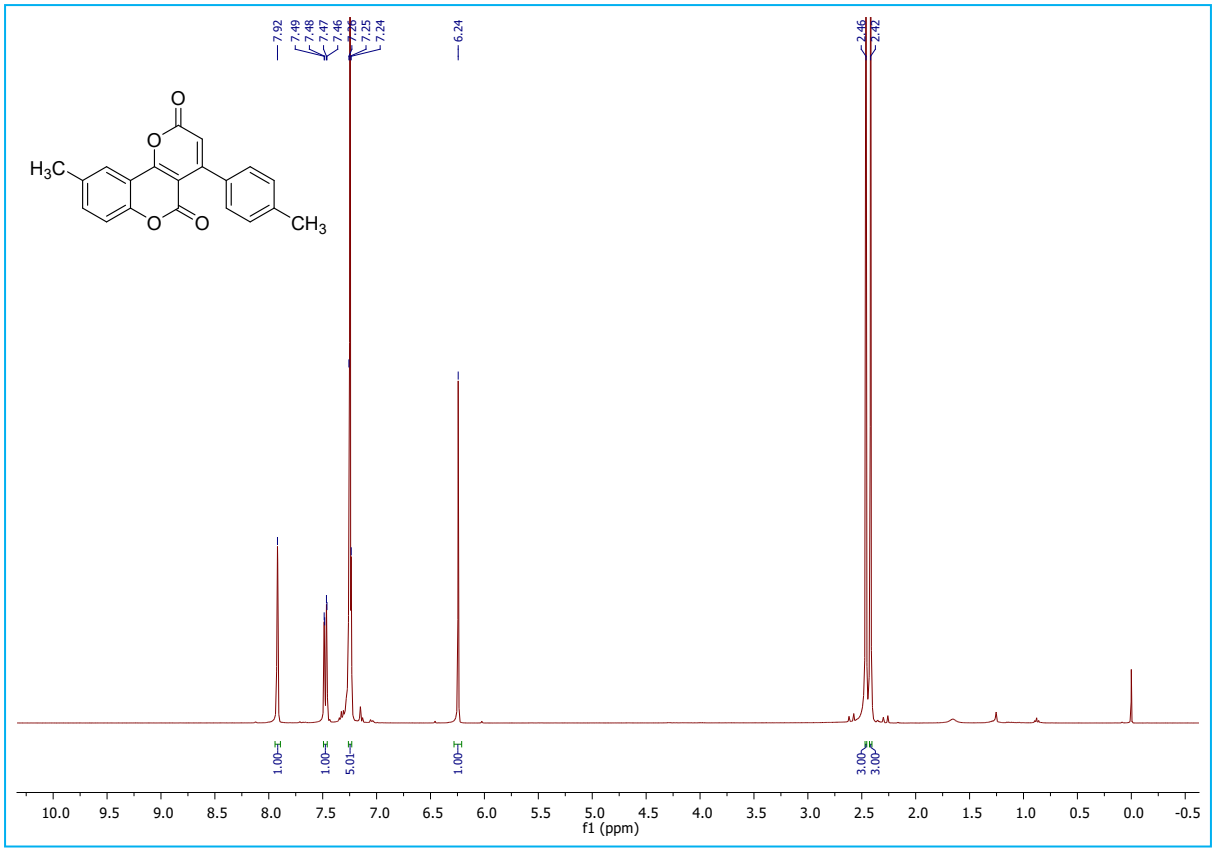
Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
21 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-20 H: 0-20 O: 0-6 Cl: 0-2

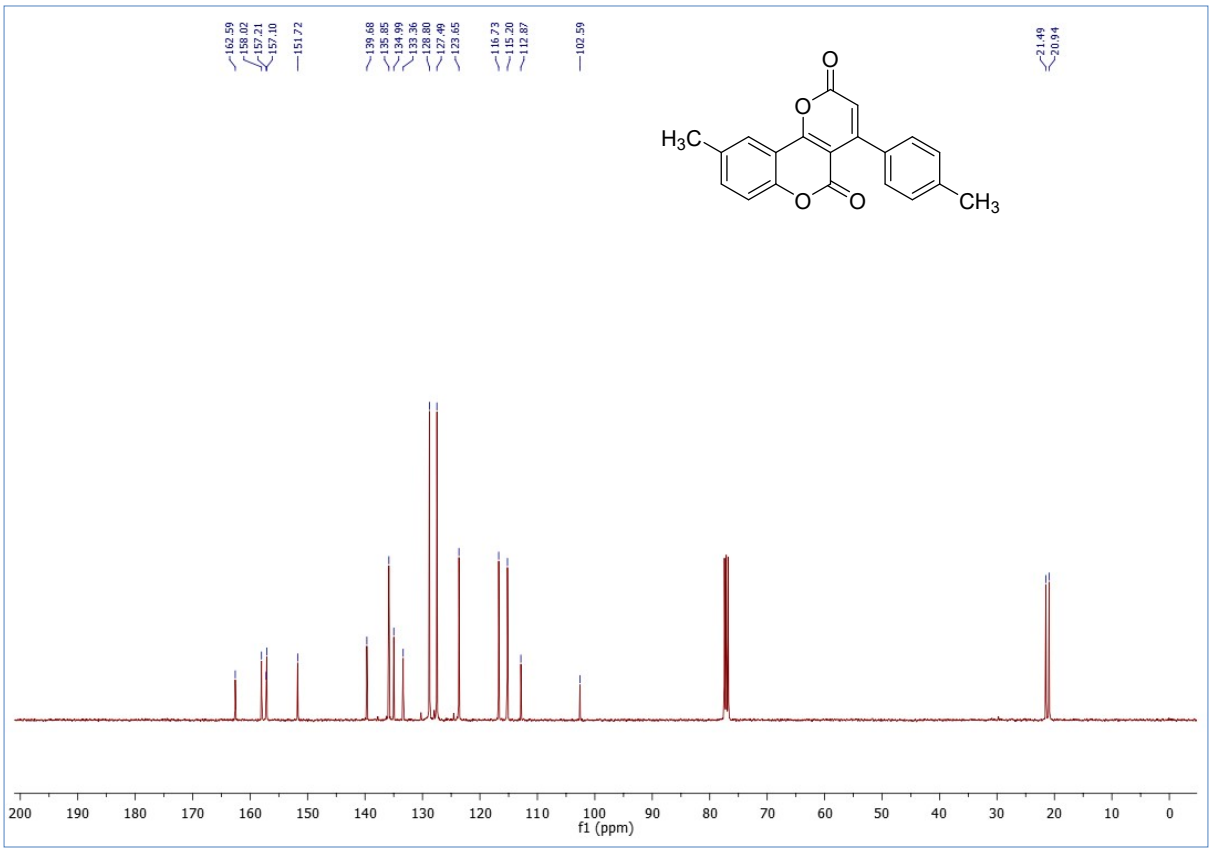


Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
369.1769	369.1775	-0.6	-1.7	13.5	385.3	n/a	n/a	C18 H10 O4 Br

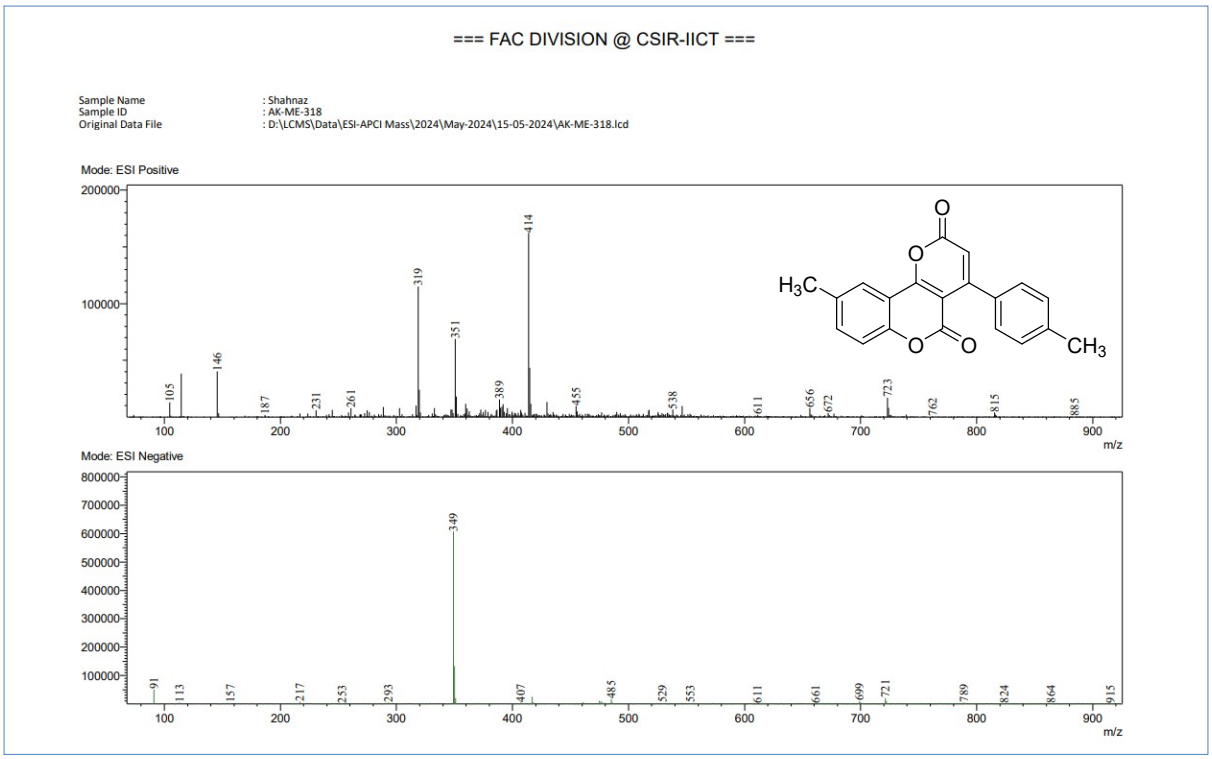
HRMS spectrum of **3p**



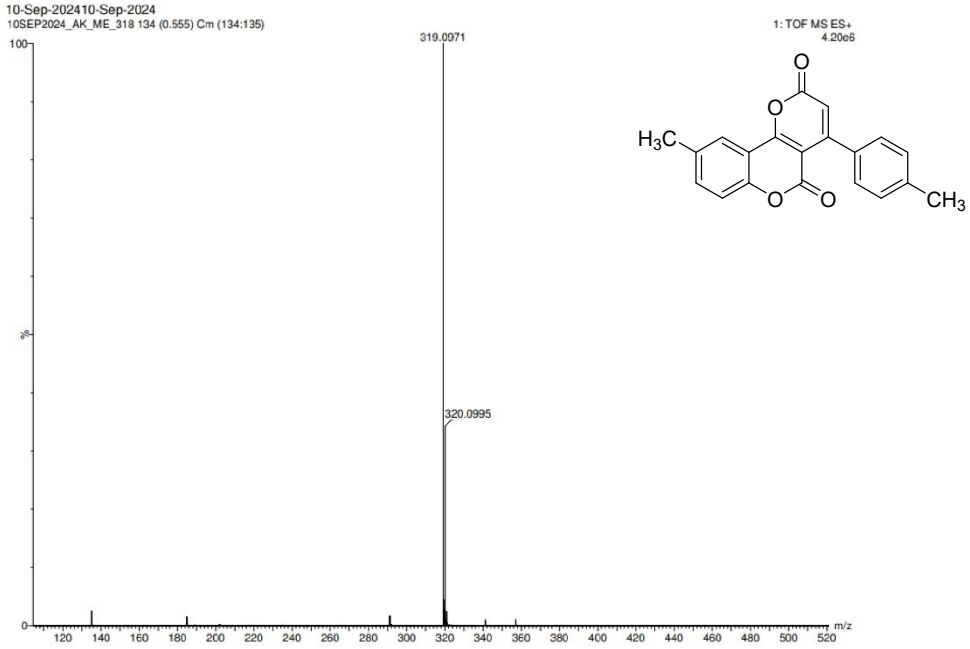
^{1}H-NMR spectrum of compound **3r**



^{13}C-NMR spectrum of compound **3r**



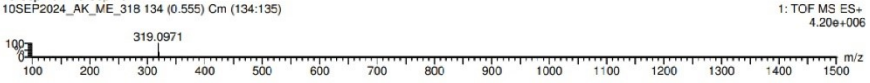
Mass spectrum of compound **3r**



Elemental Composition Report **Page 1**

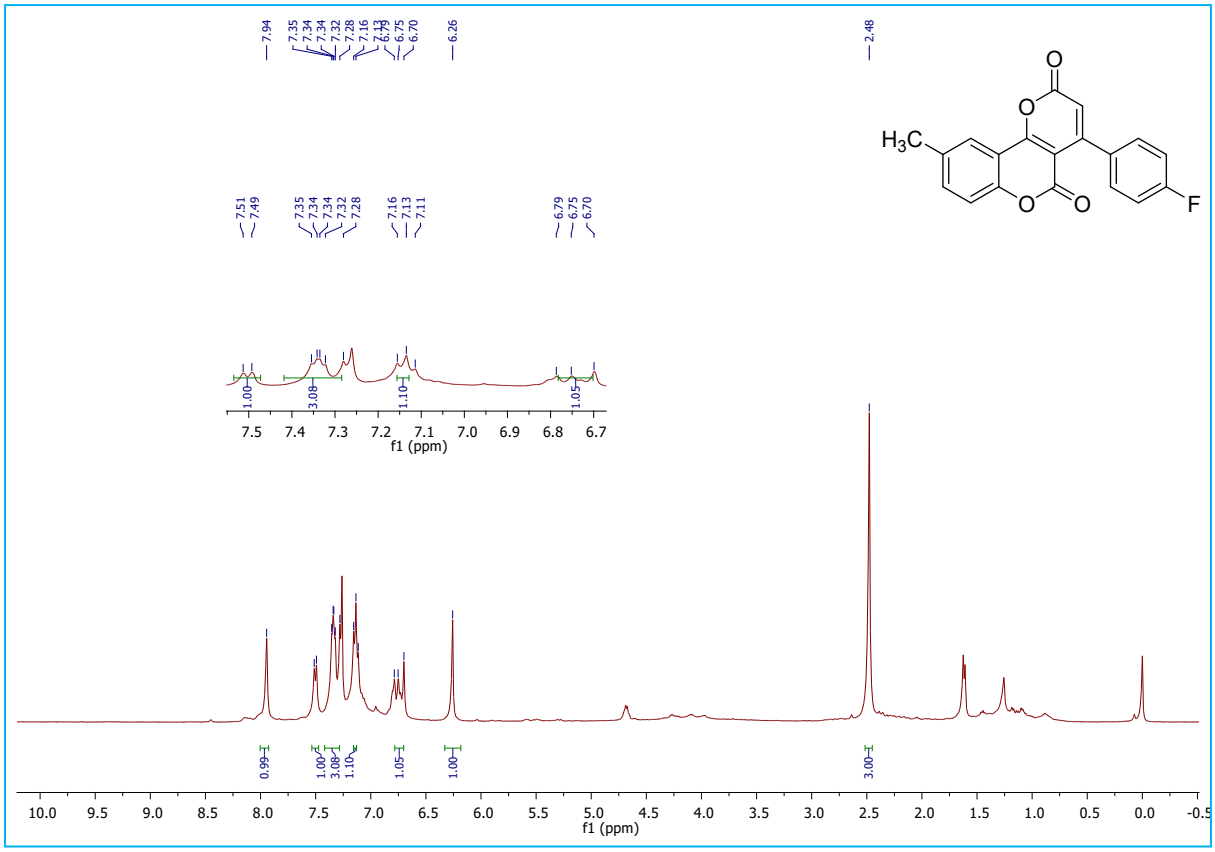
Single Mass Analysis
Tolerance = 100.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off

Monoisotopic Mass, Even Electron Ions
6 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-20 H: 0-15 O: 0-6

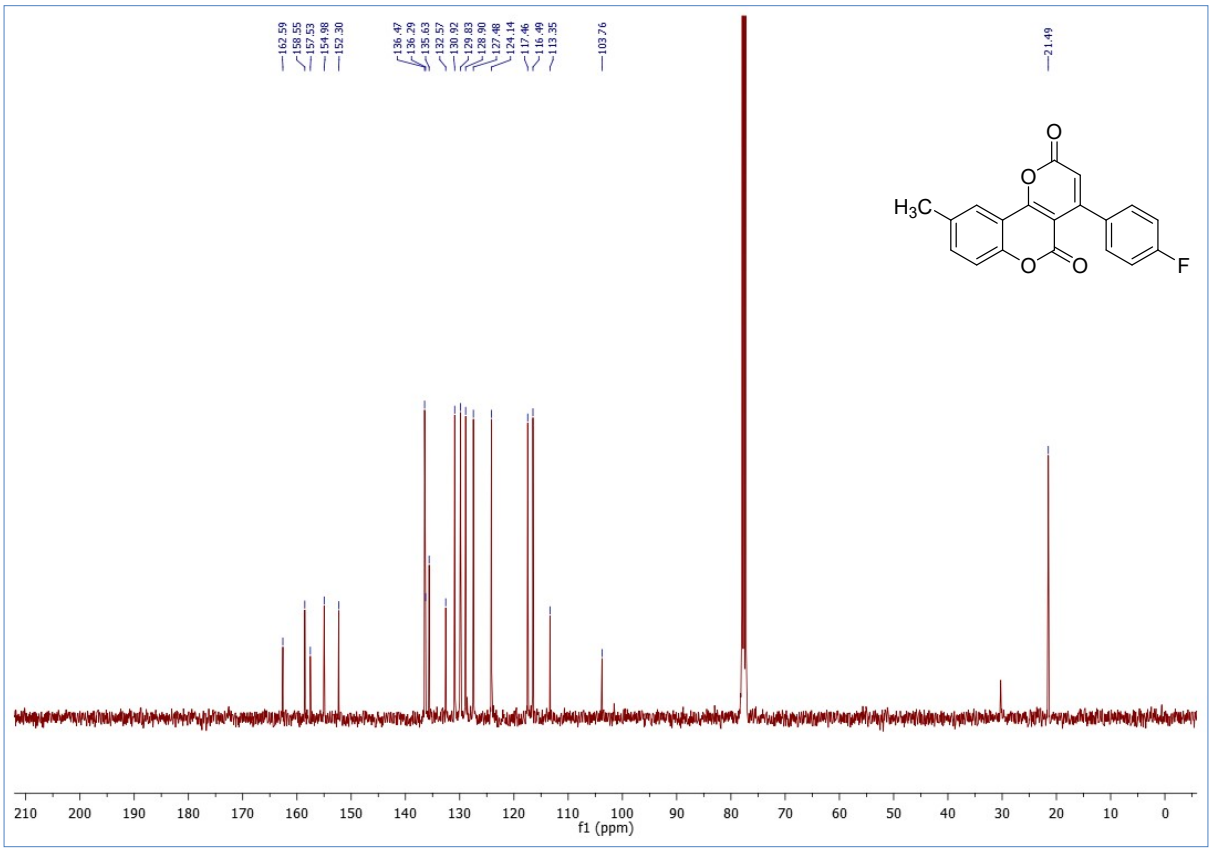


Minimum:				-1.5	
Maximum:		5.0	100.0	50.0	
Mass	Calc. Mass	mDa	PPM	DBE	Formula
319.0971	319.0970	0.1	0.3	13.5	C20 H15 O4

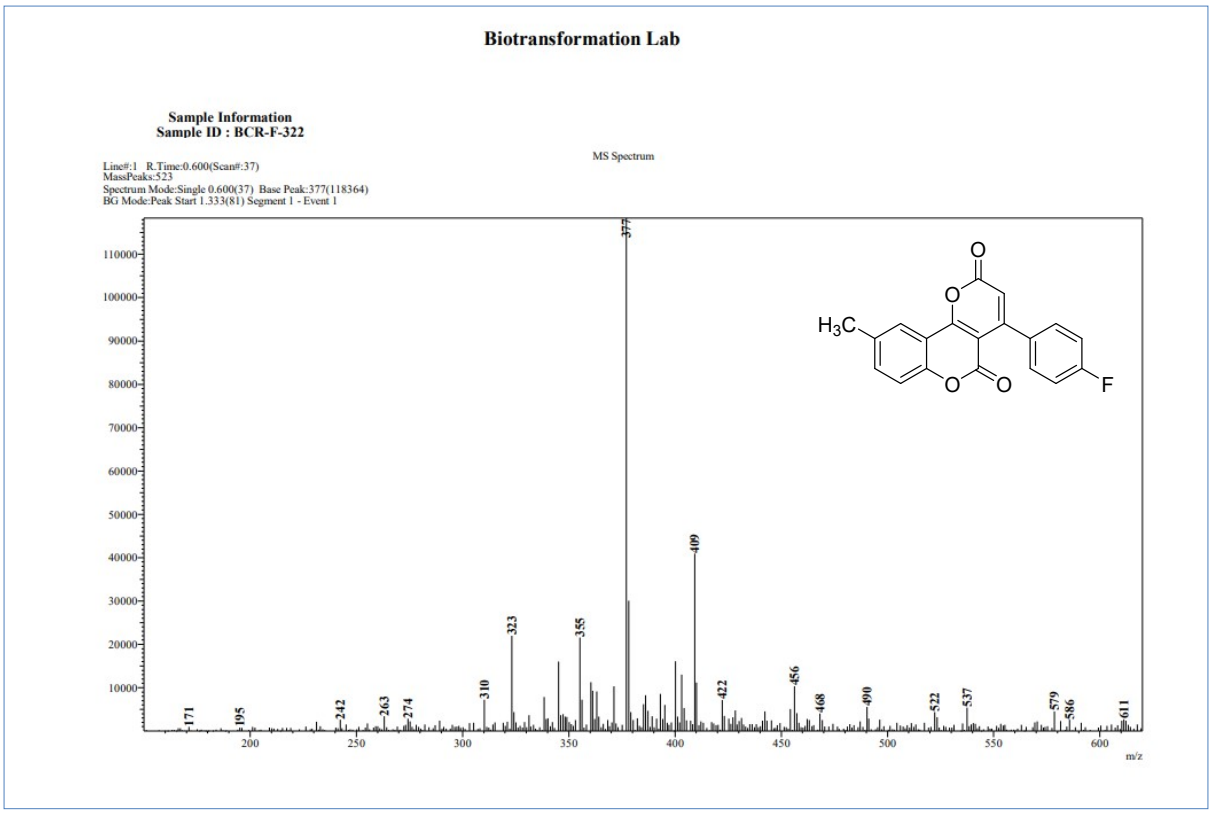
HRMS spectrum of compound **3r**



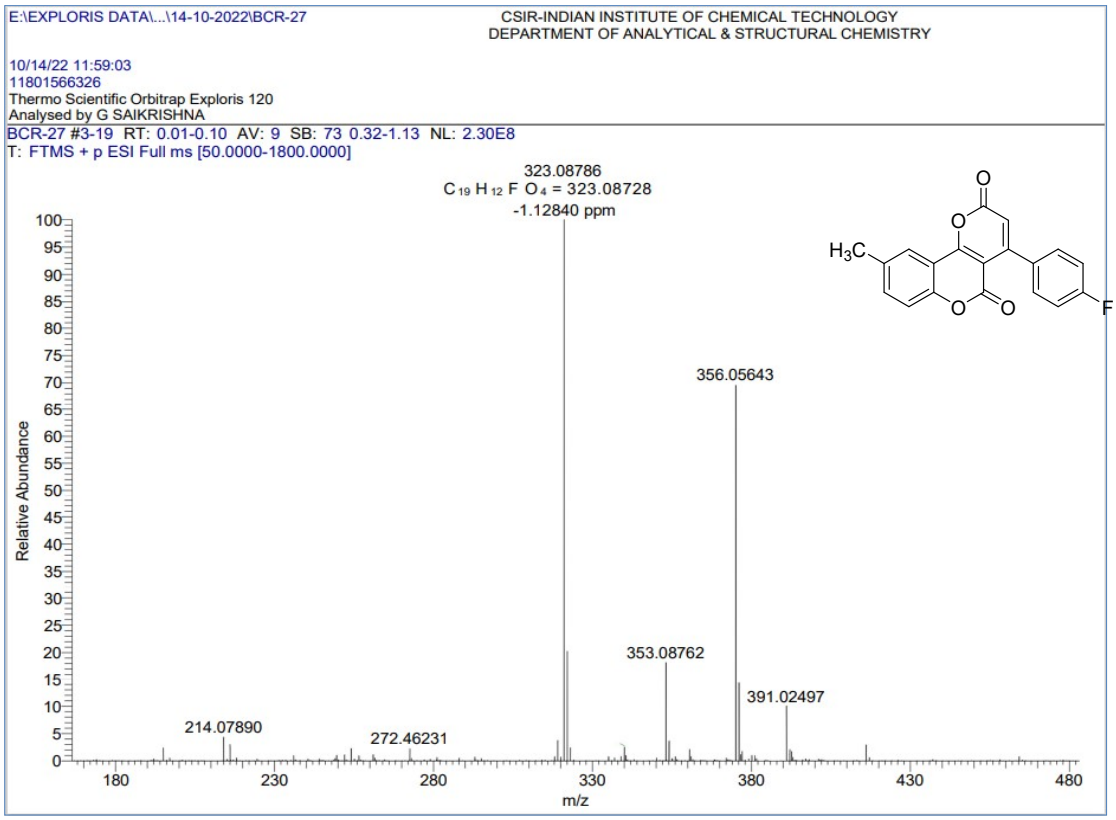
^{1}H-NMR spectrum of compound **3s**



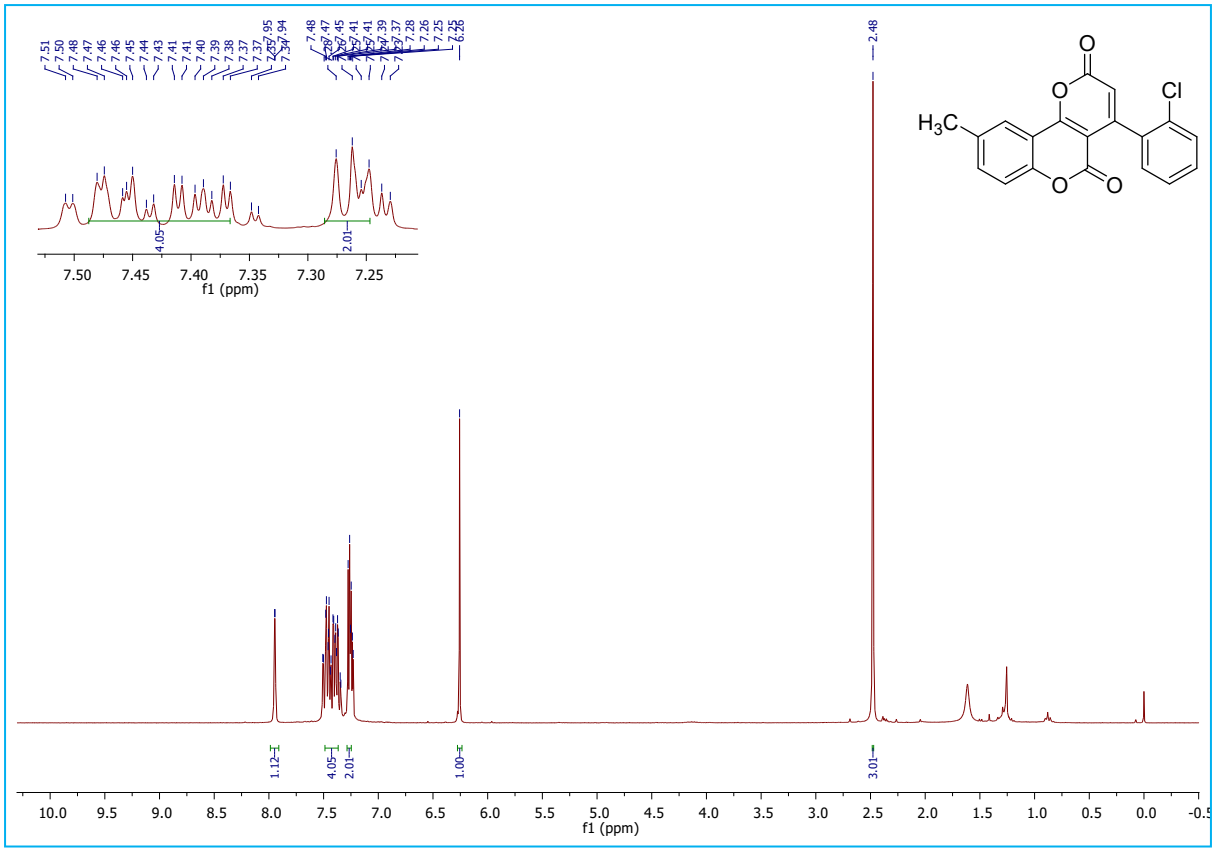
^{13}C-NMR spectrum of compound **3s**



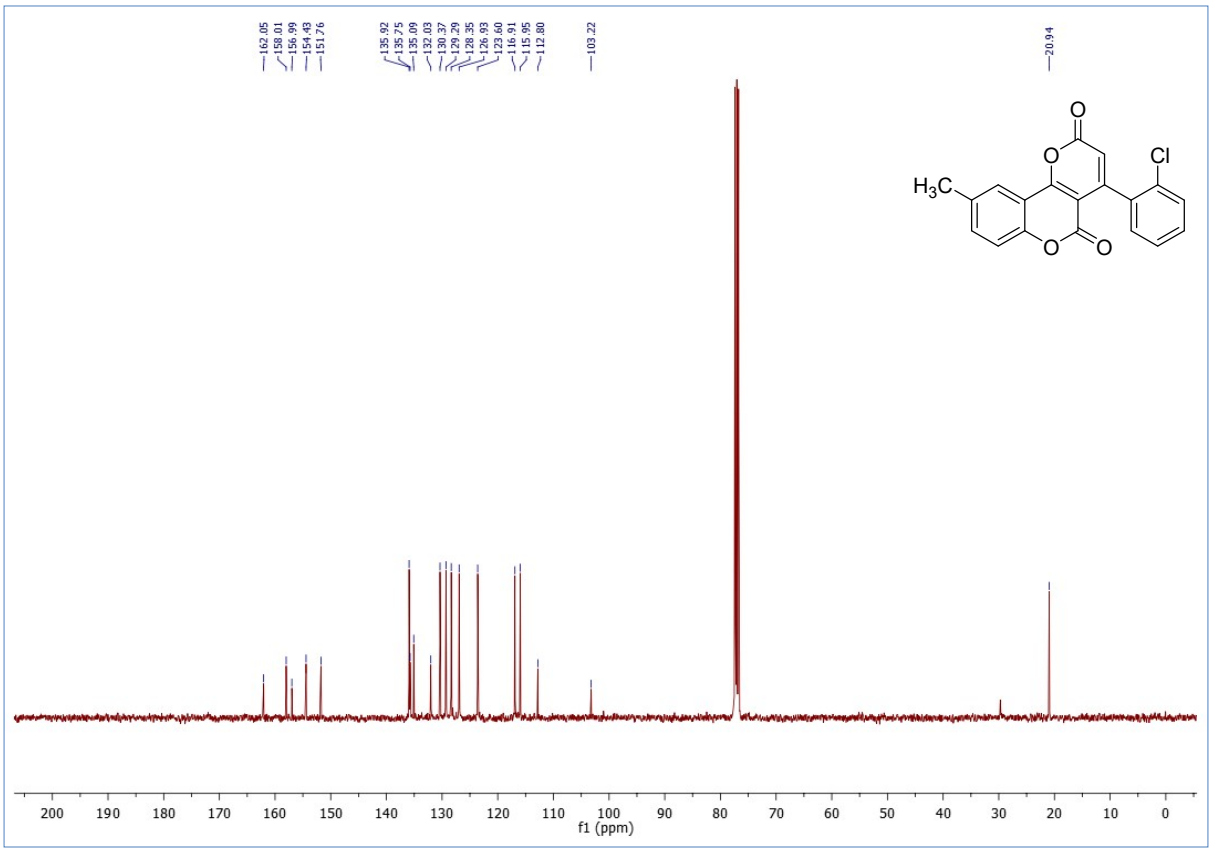
Mass spectrum of compound **3s**



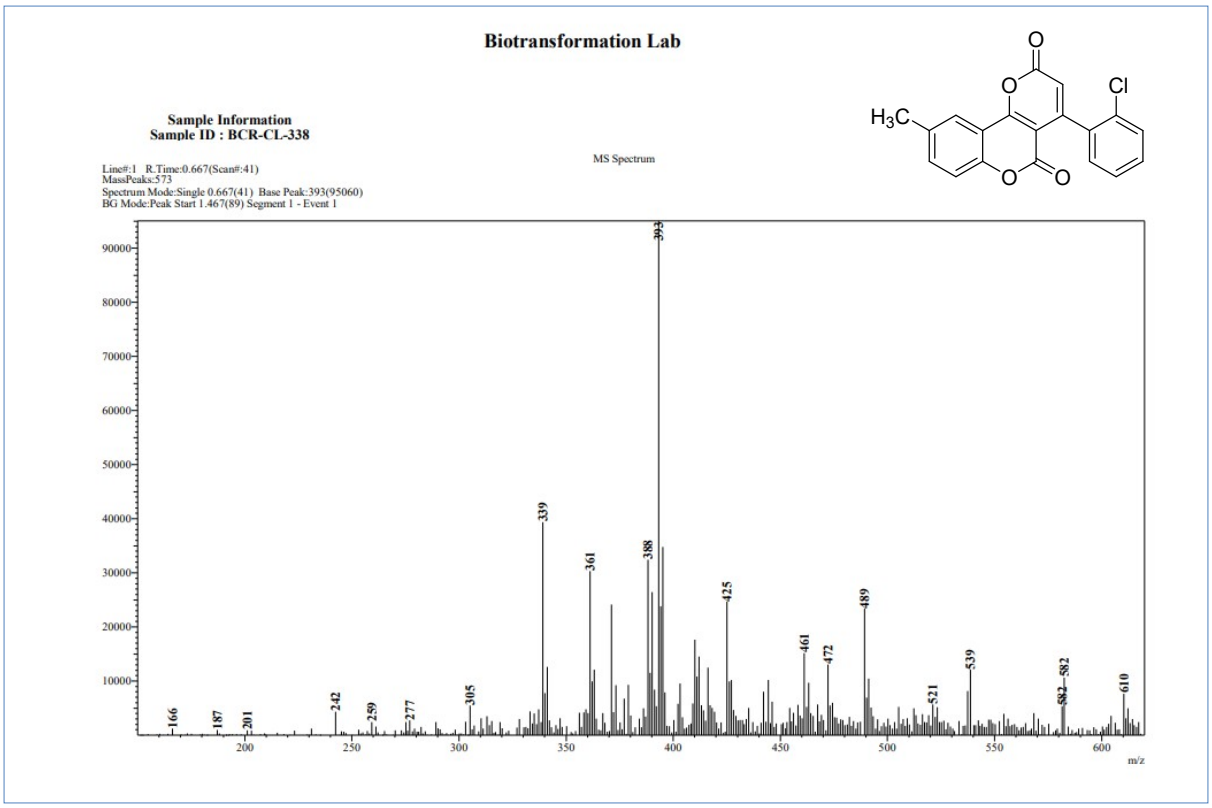
HRMS spectrum of compound **3s**



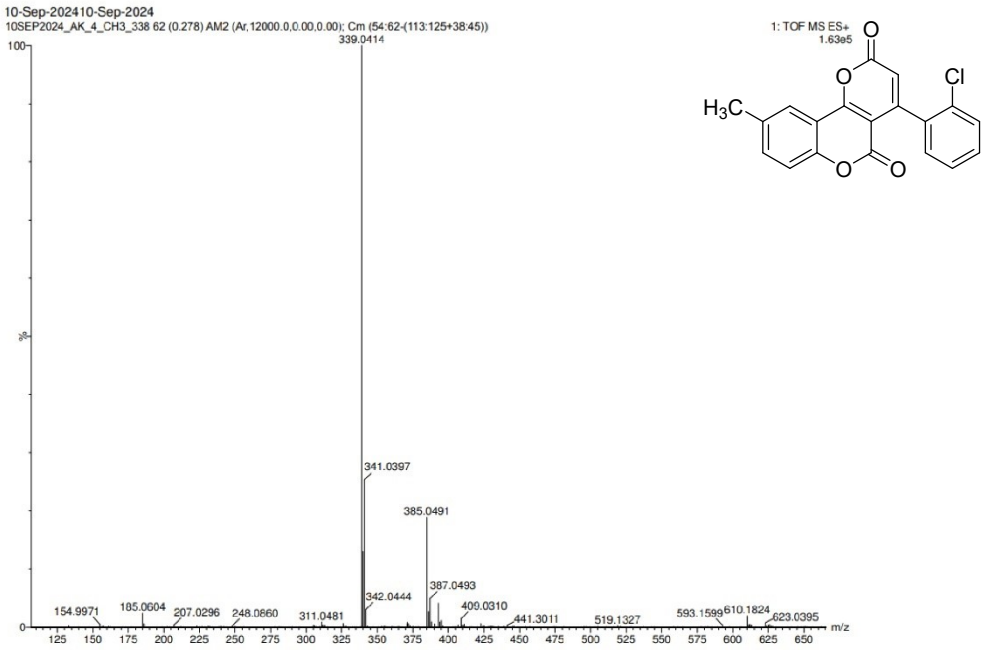
[1]H-NMR spectrum of compound **3t**



[13]C-NMR spectrum of compound **3t**



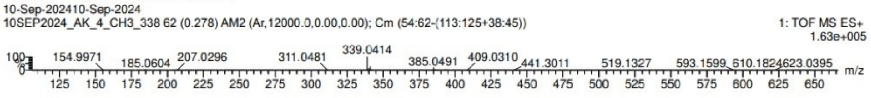
Mass spectrum of compound **3t**



Elemental Composition Report **Page 1**

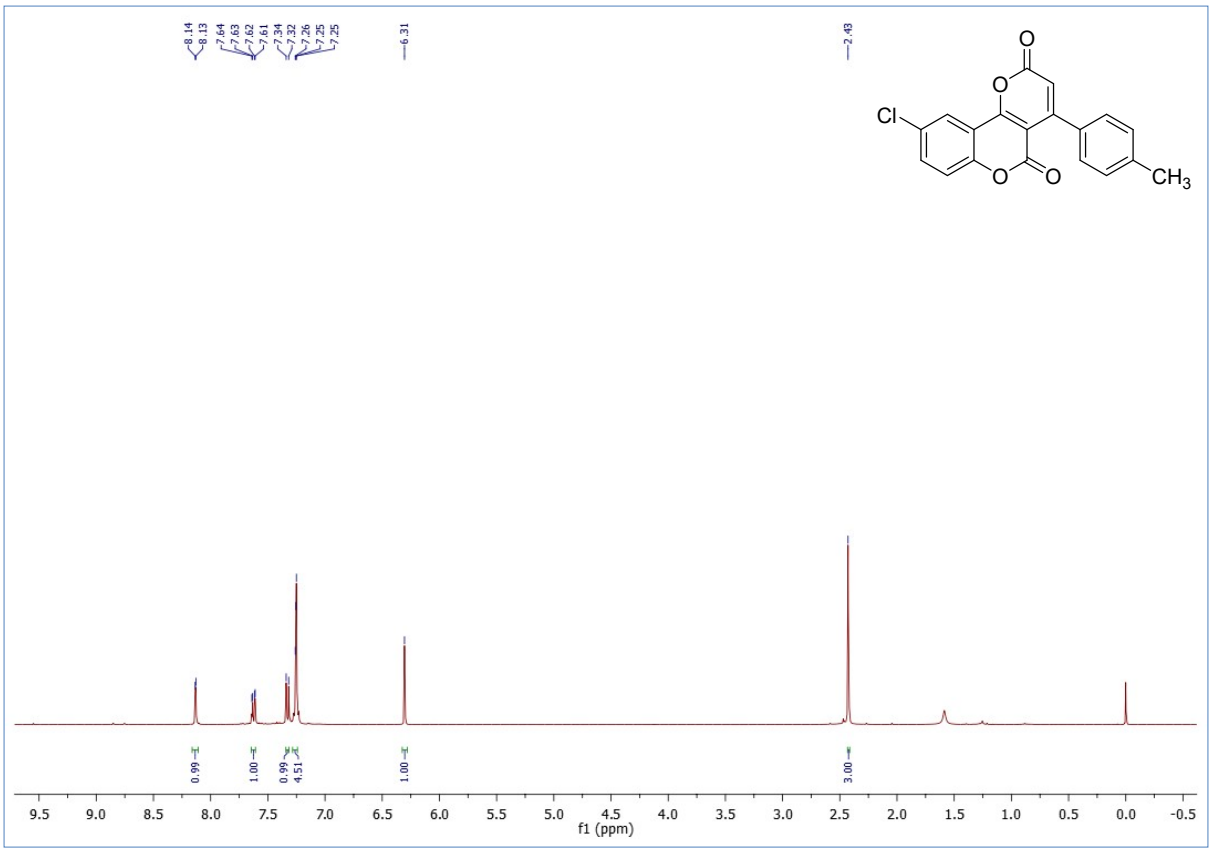
Single Mass Analysis
Tolerance = 100.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
9 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-20 H: 0-14 O: 0-6 Cl: 0-1

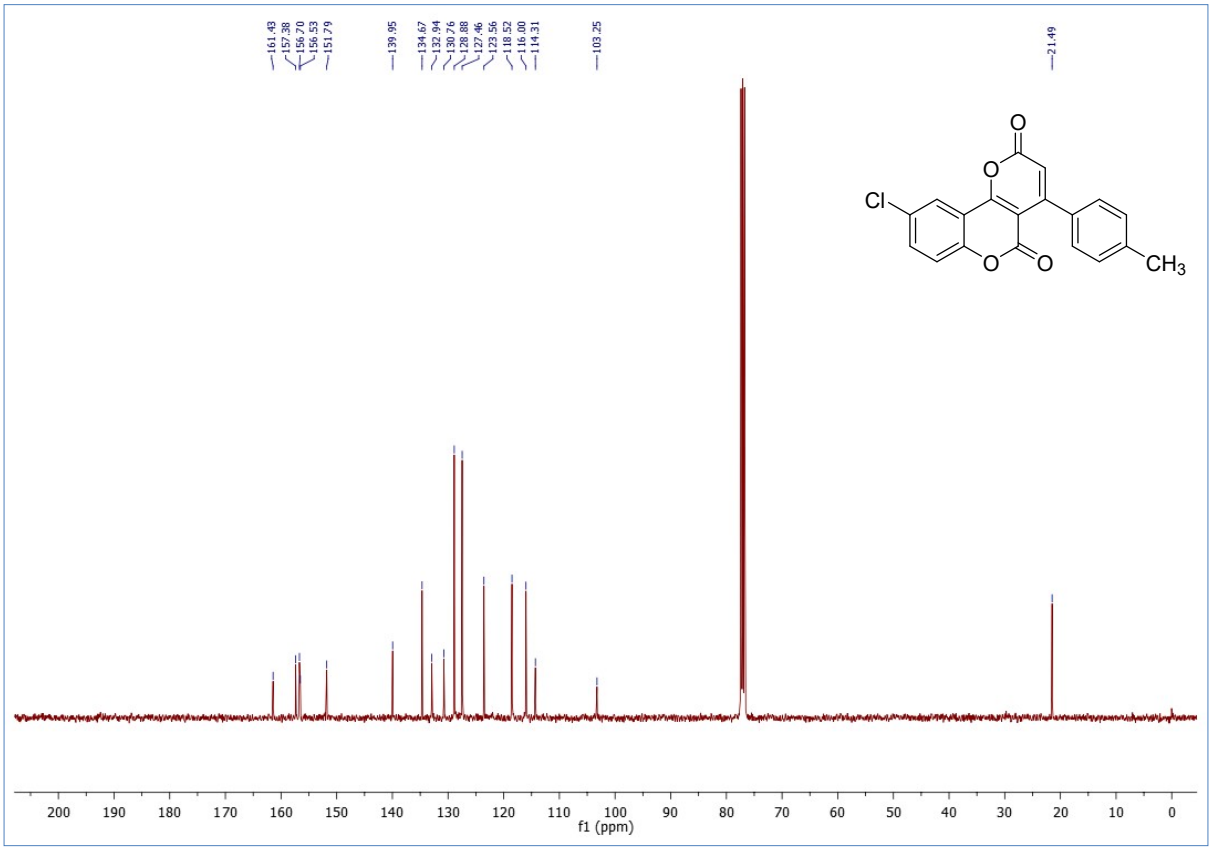


Minimum:				-1.5				
Maximum:		5.0	100.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
339.0414	339.0424	-1.0	-2.9	13.5	235.1	n/a	n/a	C19 H12 O4 Cl

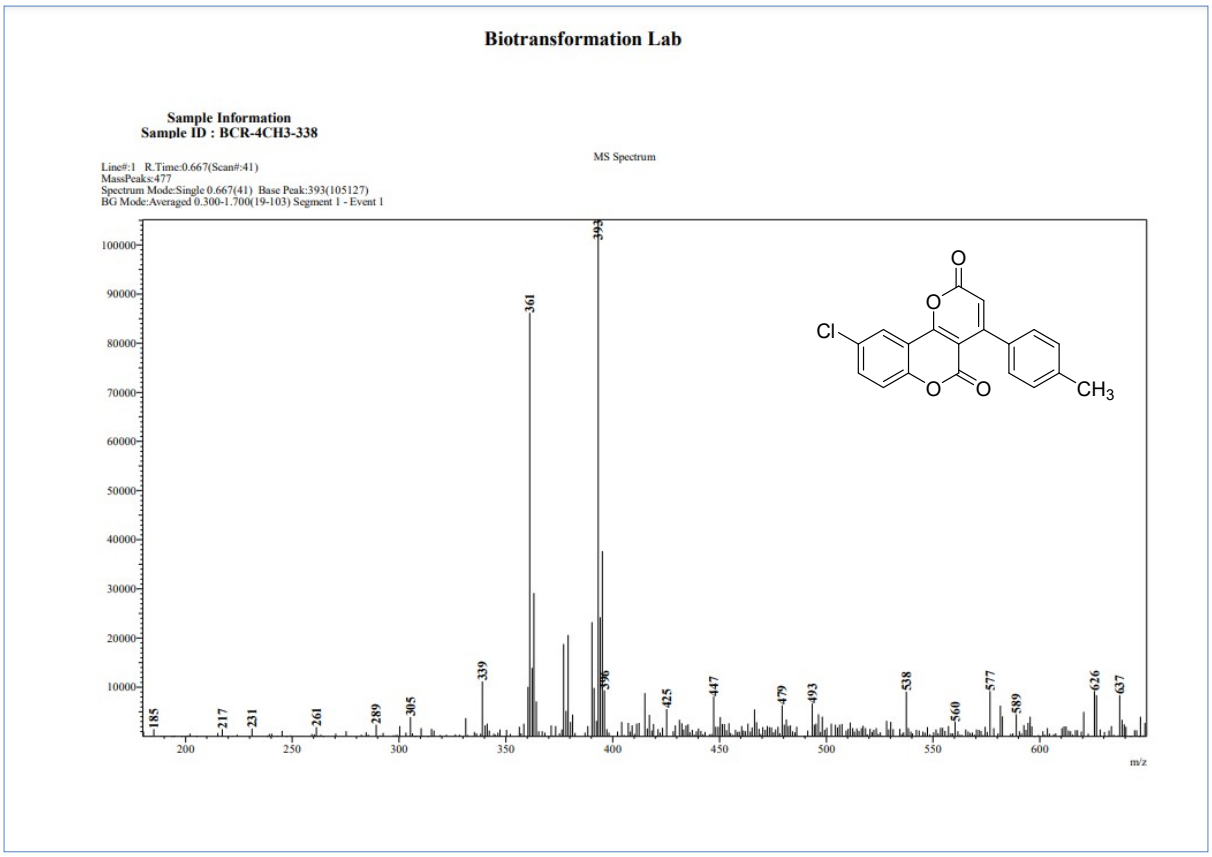
HRMS spectrum of compound **3t**



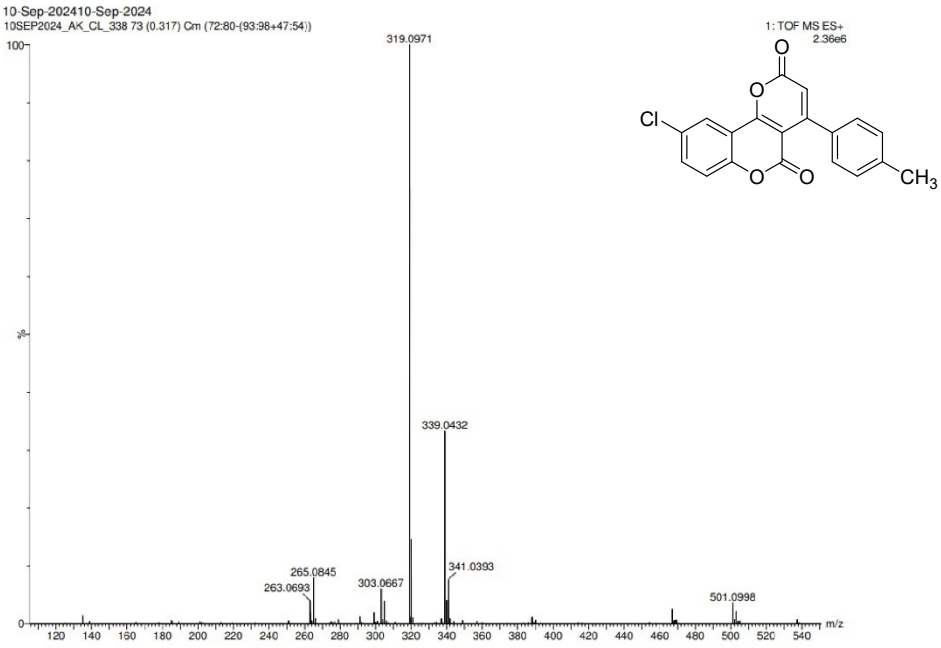
^{1}H-NMR spectrum of compound **3u**



^{13}C-NMR spectrum of compound **3u**



Mass spectrum of compound **3u**

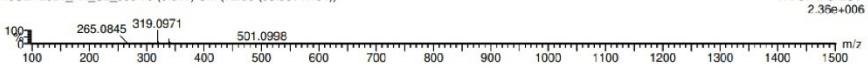


Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off

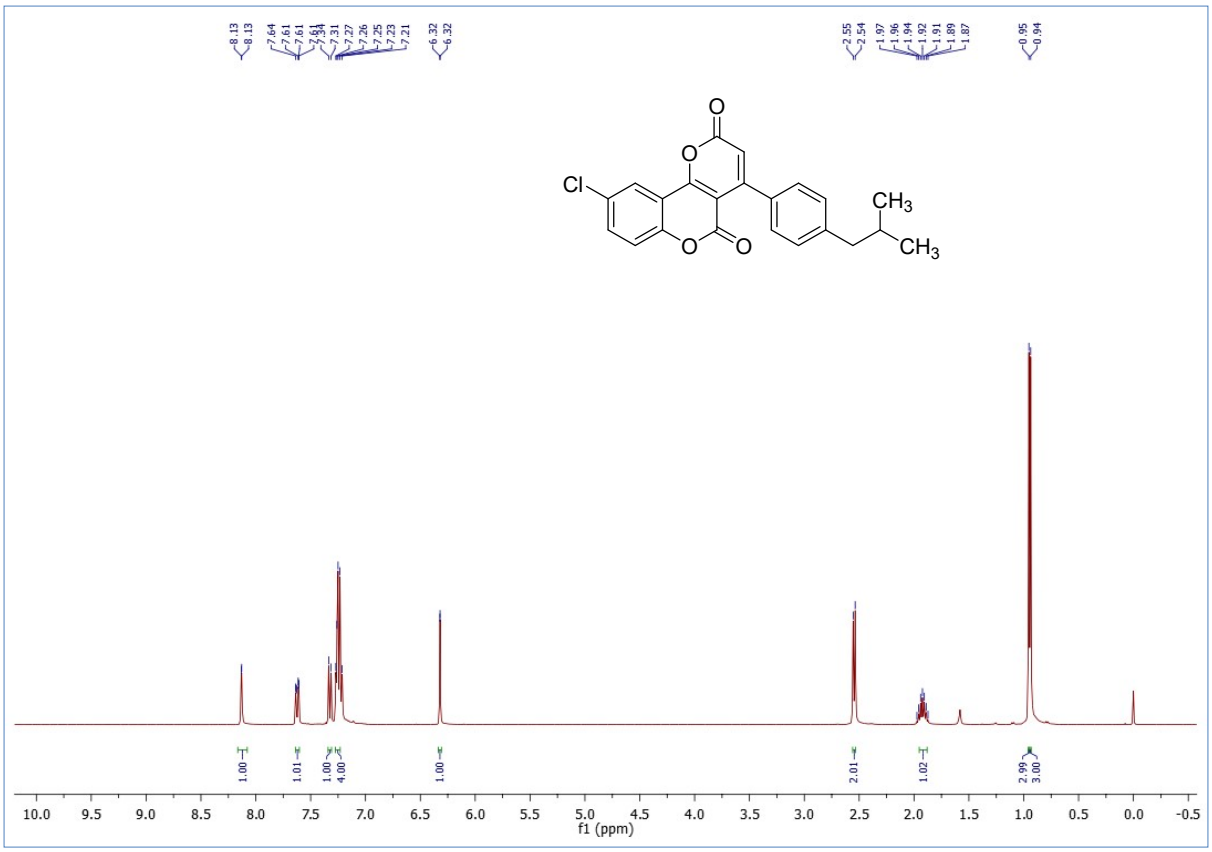
Monoisotopic Mass, Even Electron Ions
14 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-20 H: 0-20 O: 0-6 Cl: 0-1

10-Sep-202410-Sep-2024
10SEP2024_AK_CL_338 73 (0.317) Cm (72:80-(93:98+47:54))
1: TOF MS ES+
2.36e+006

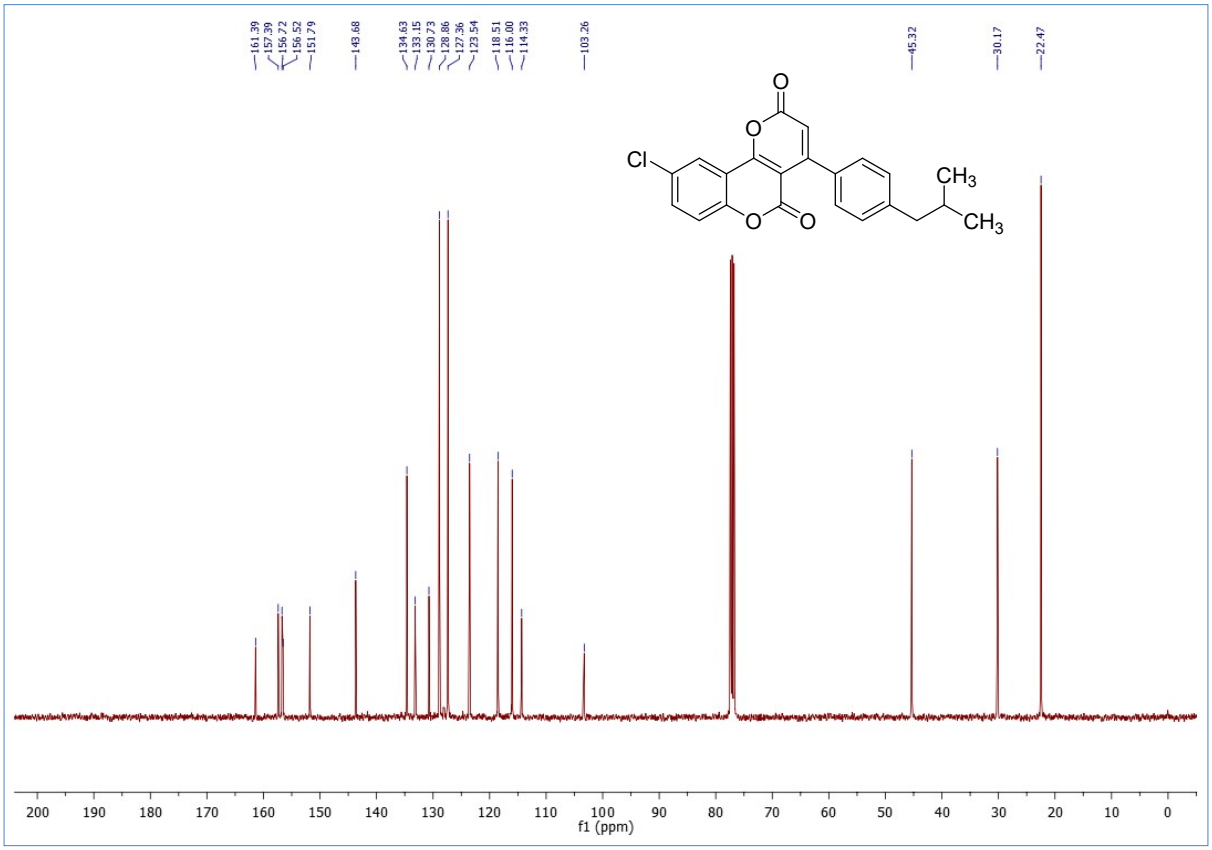


Minimum:				-1.5	
Maximum:		5.0	5.0	50.0	
Mass	Calc. Mass	mDa	PPM	DBE	Formula
339.0432	339.0424	0.8	2.4	13.5	C19 H12 O4 Cl

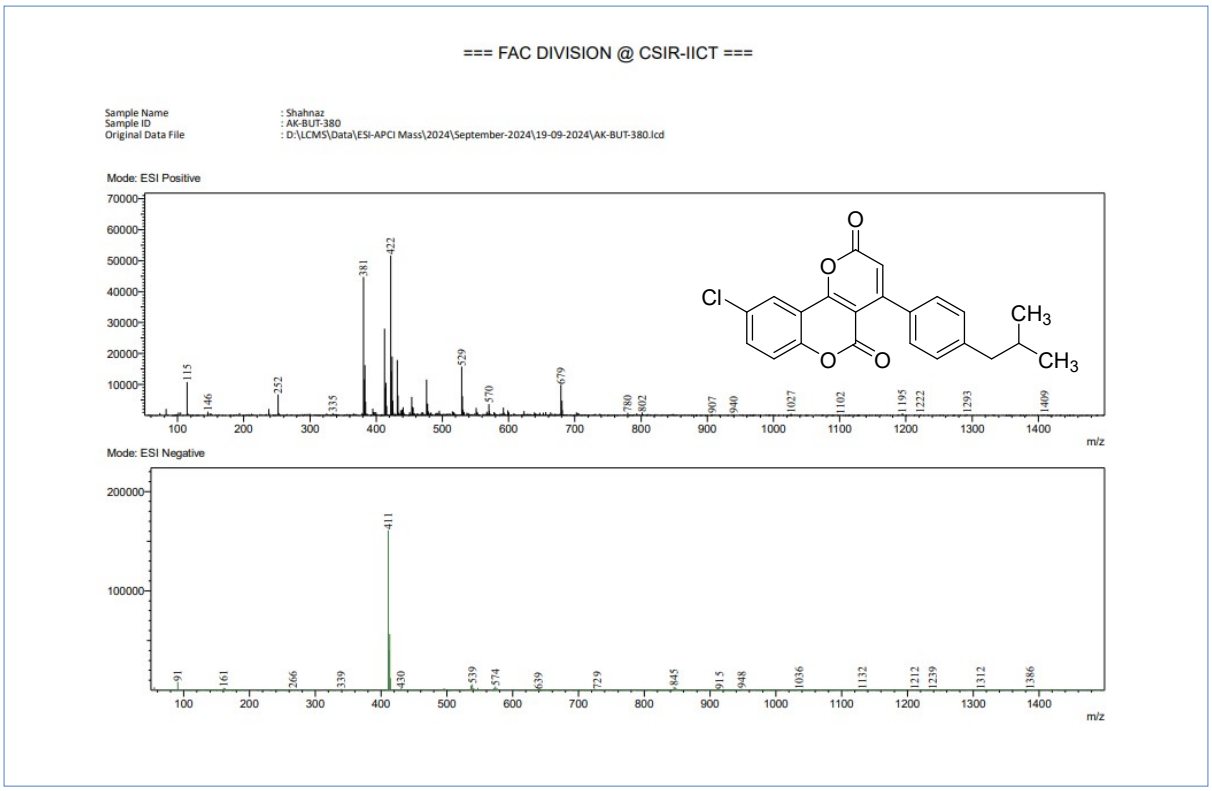
HRMS spectrum of compound **3u**



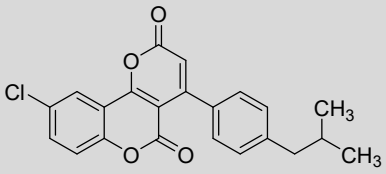
^{1}H-NMR spectrum of compound **3v**



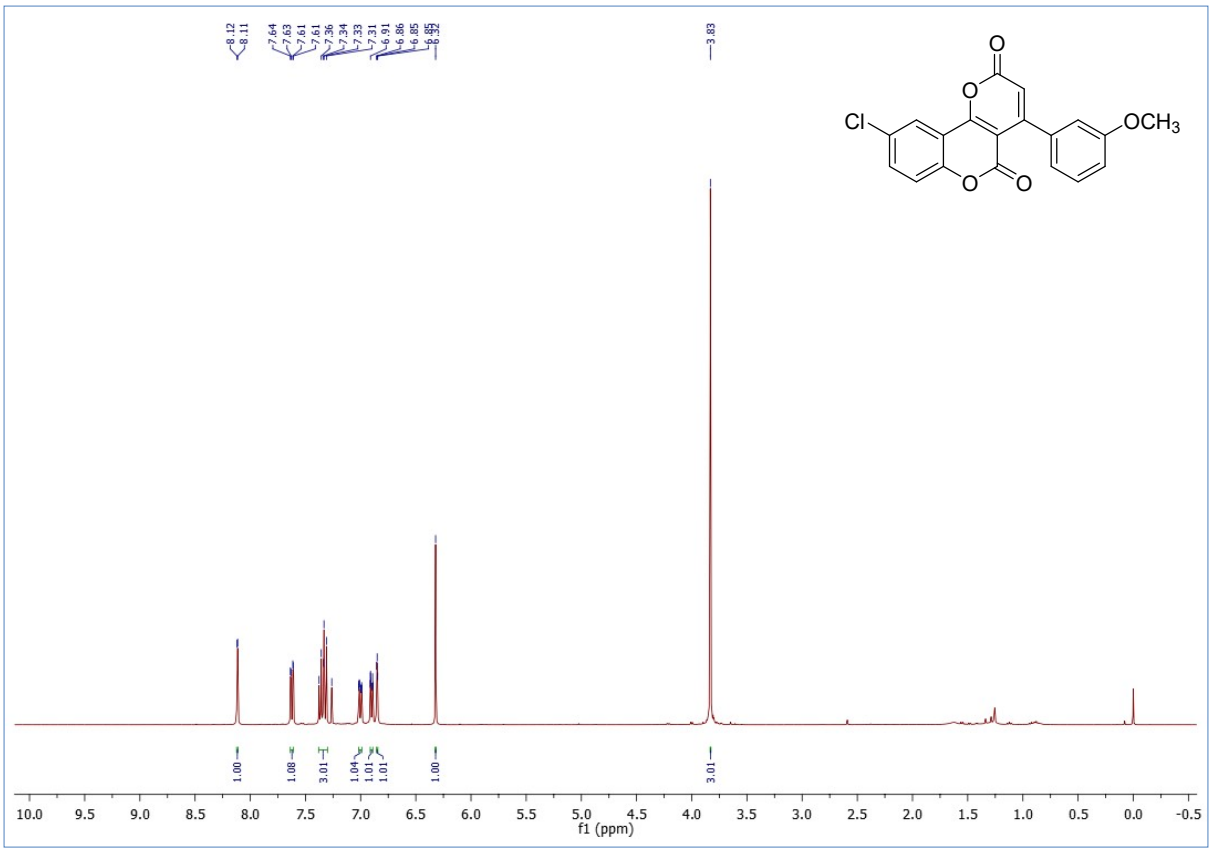
^{13}C-NMR spectrum of compound **3v**



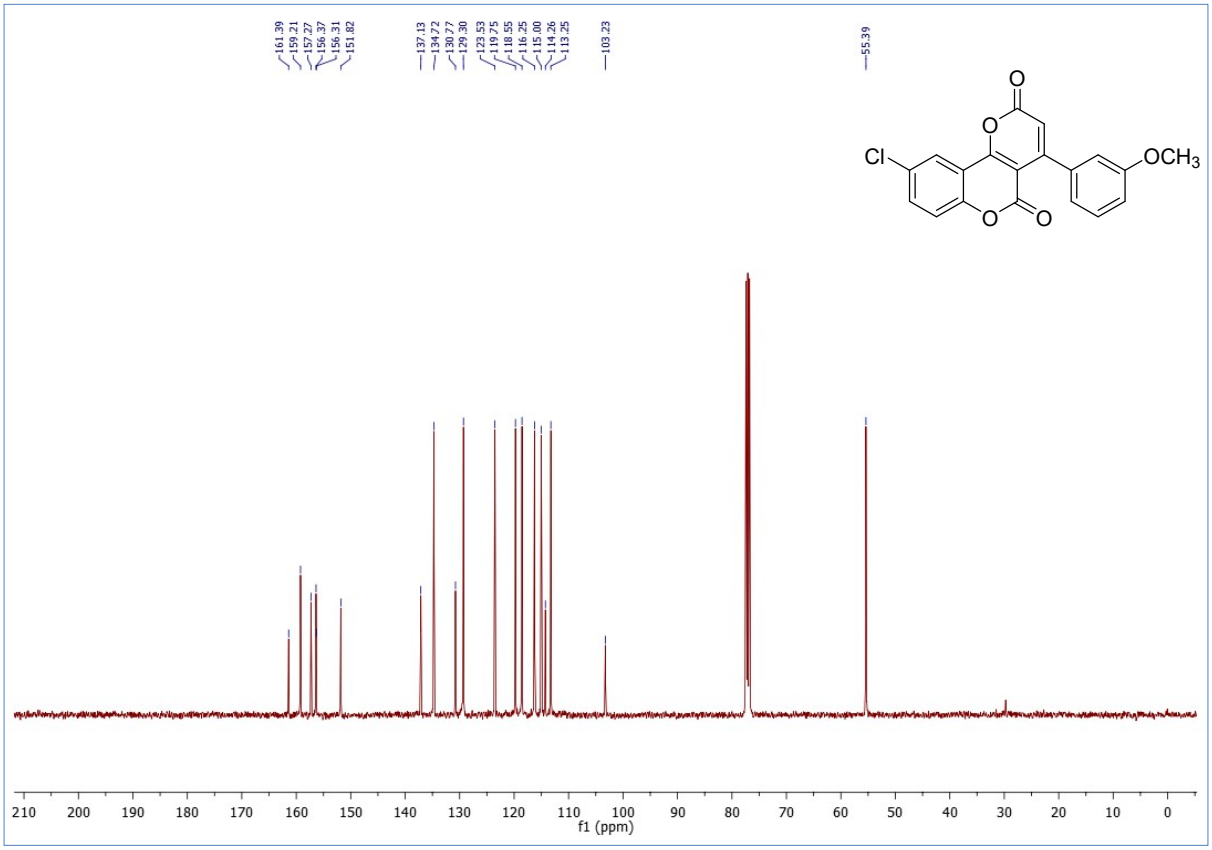
Mass spectrum of compound **3v**



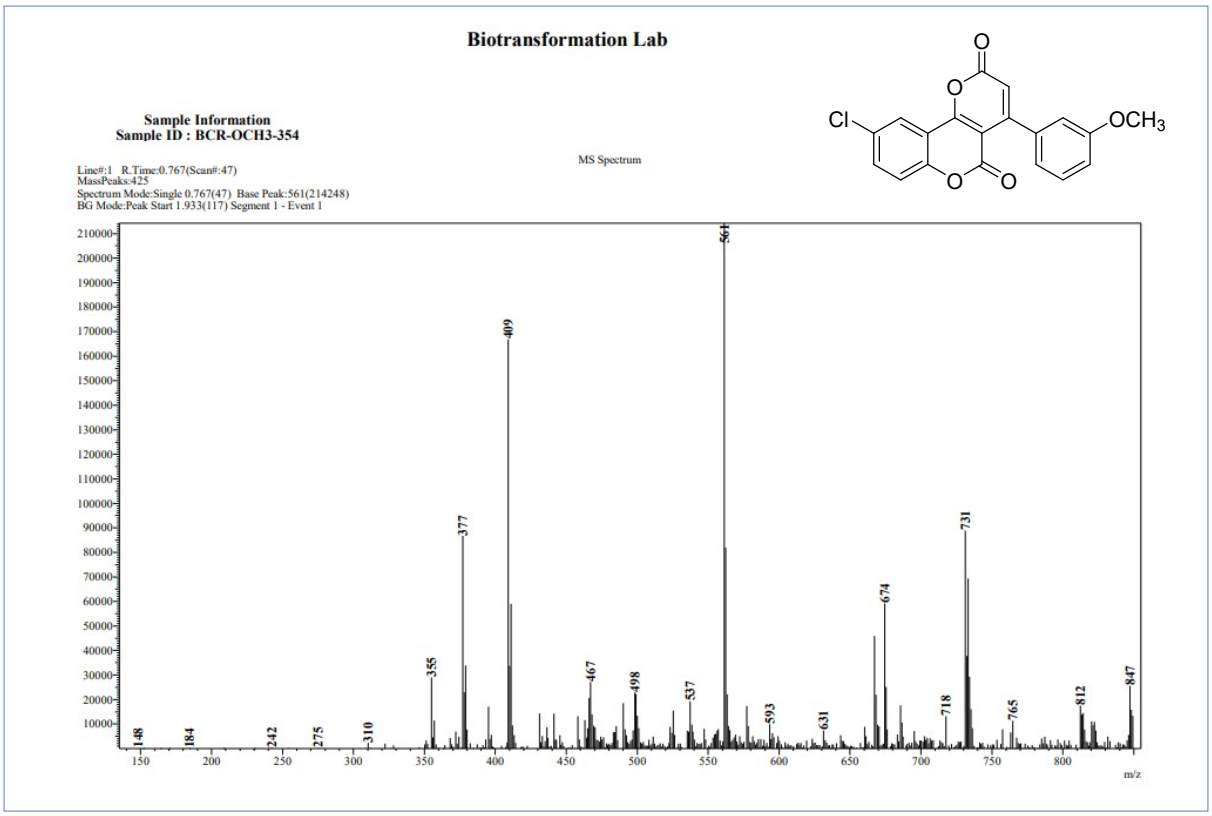
HRMS spectrum of compound **3v**



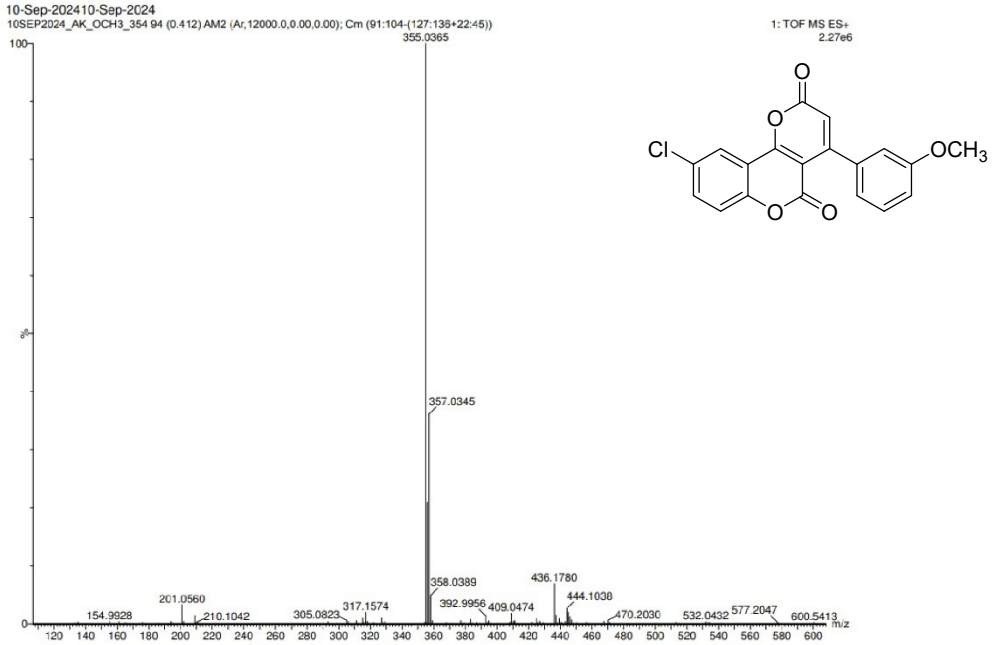
^{1}H-NMR spectrum of compound **3w**



^{13}C-NMR spectrum of compound **3w**



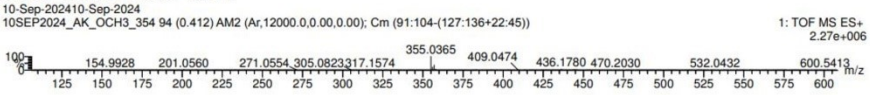
Mass spectrum of compound **3w**



Elemental Composition Report **Page 1**

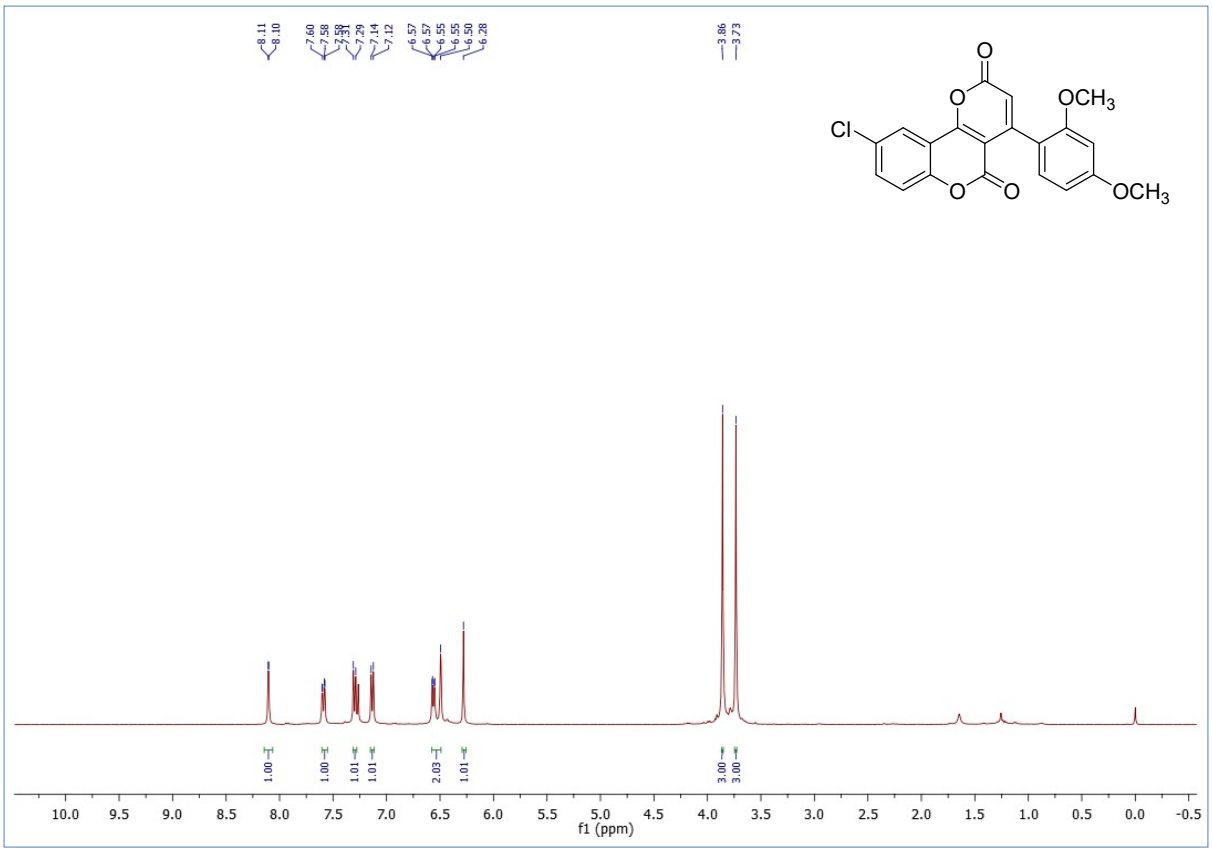
Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
9 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-20 H: 0-12 O: 0-6 Cl: 0-1

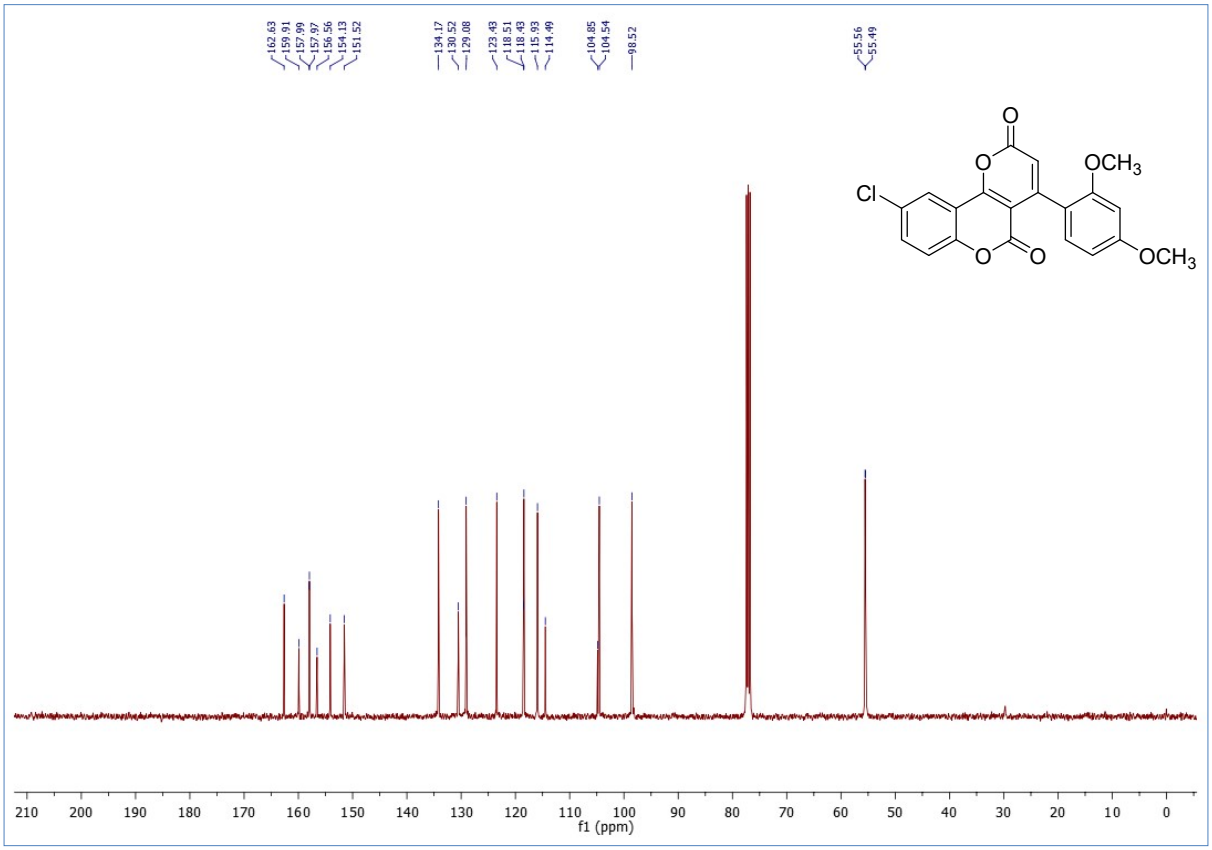


Minimum:			-1.5					
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
355.0365	355.0373	-0.8	-2.3	13.5	353.6	n/a	n/a	C19 H12 O5 Cl

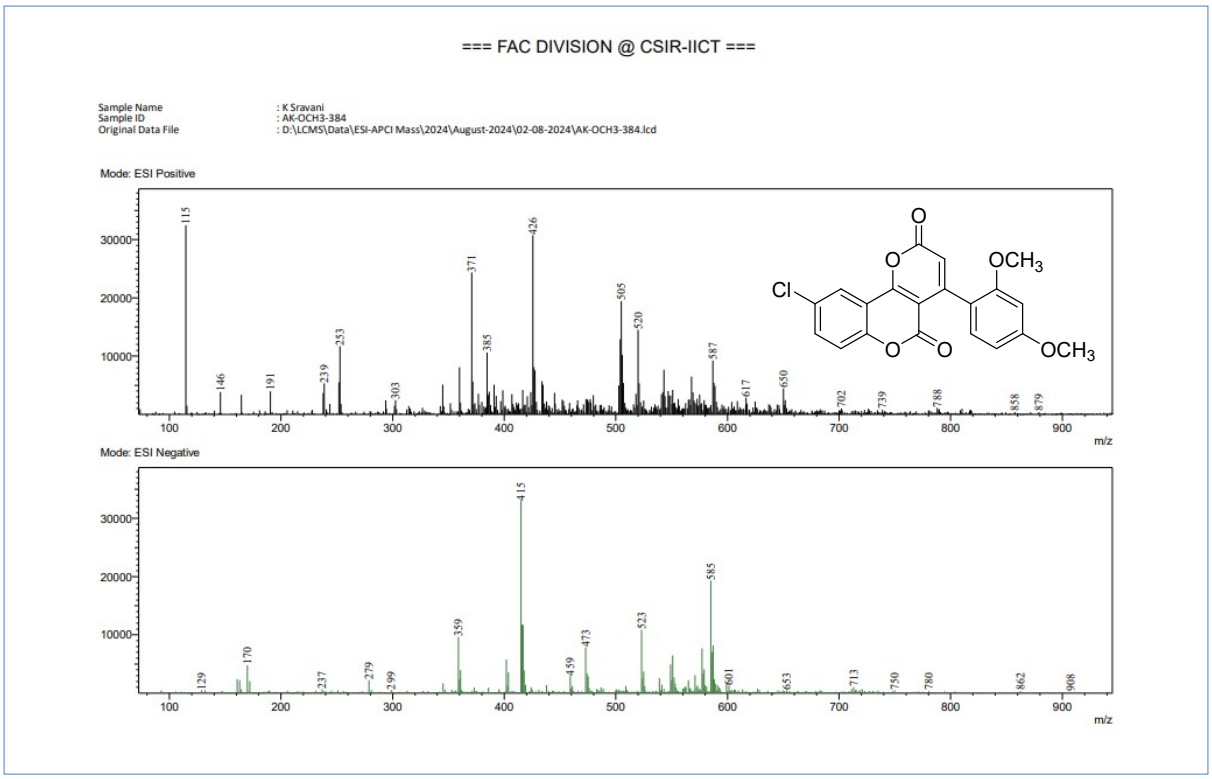
HRMS spectrum of compound **3w**



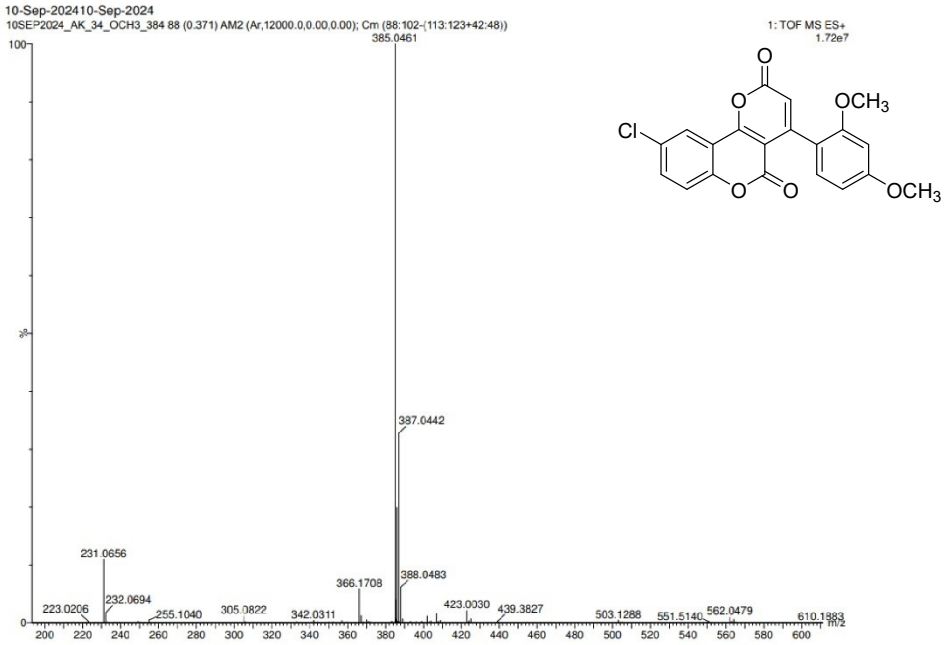
^{1}H-NMR spectrum of compound **3y**



^{13}C-NMR spectrum of compound **3y**



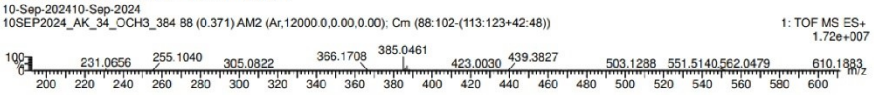
Mass spectrum of compound **3y**



Elemental Composition Report **Page 1**

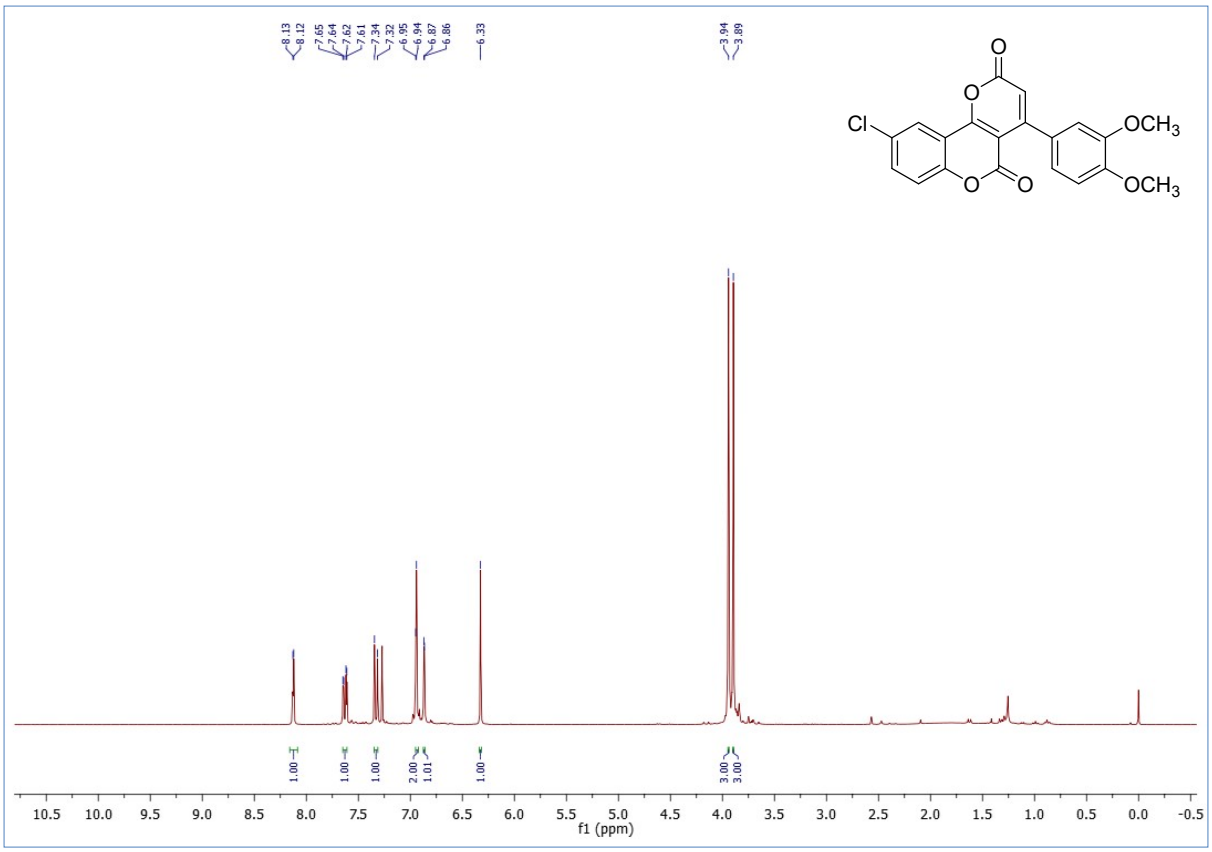
Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
21 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-20 H: 0-15 O: 0-6 P: 0-1 Cl: 0-1

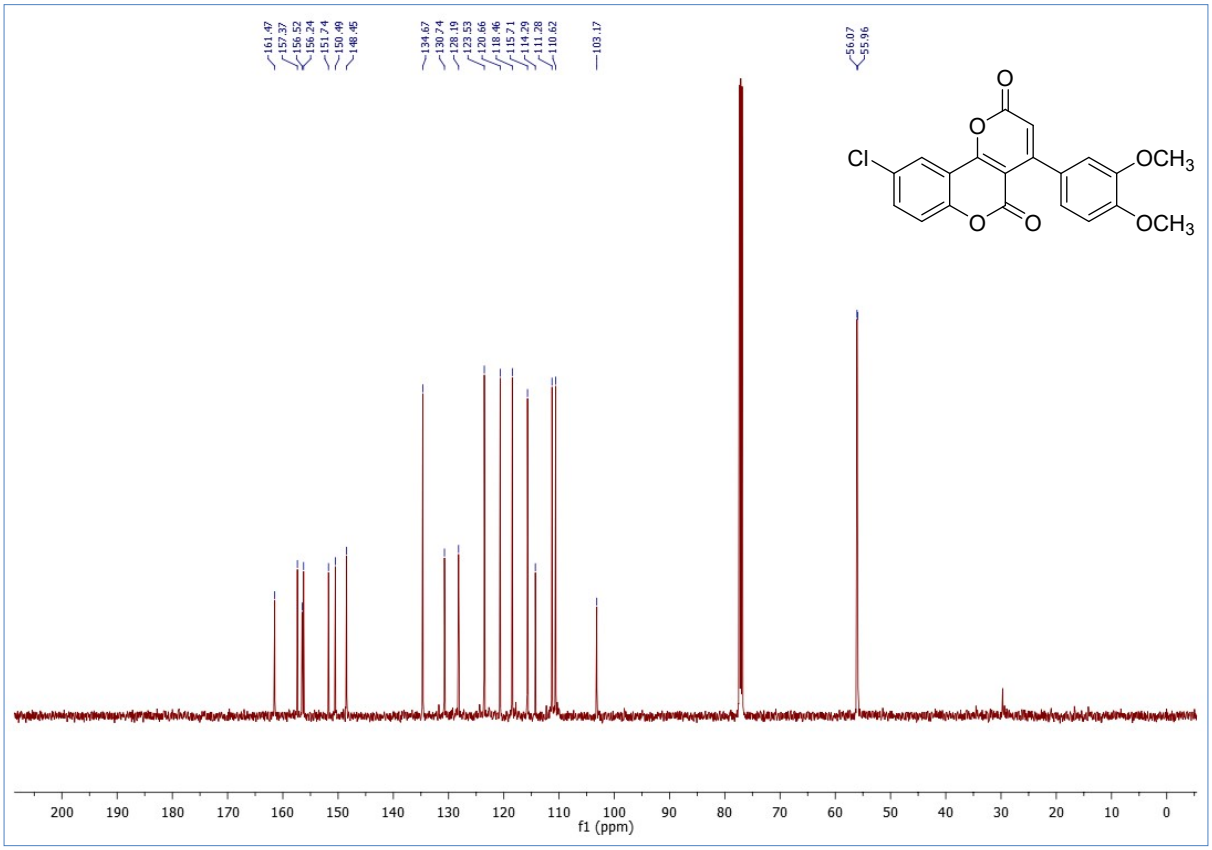


Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
385.0461	385.0479	-1.8	-4.7	13.5	525.4	n/a	n/a	C20 H14 O6 Cl

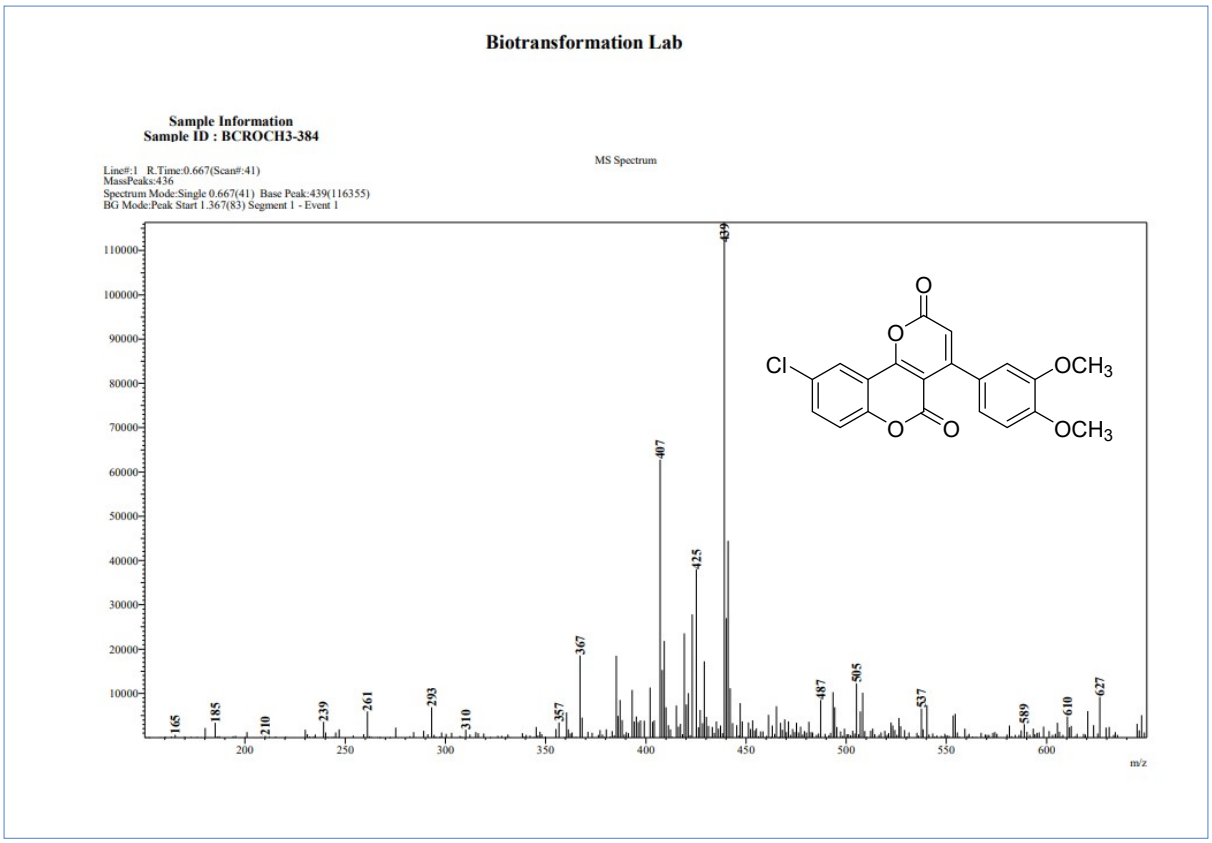
HRMS spectrum of compound **3y**



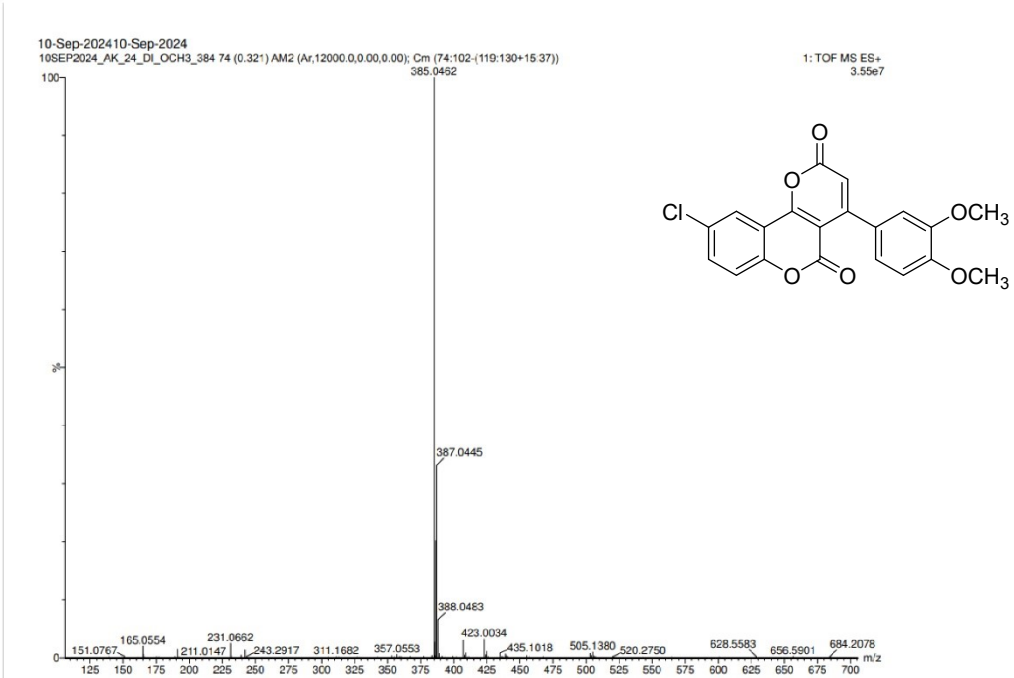
^{1}H-NMR spectrum of compound **3z**



^{13}C-NMR spectrum of compound **3z**



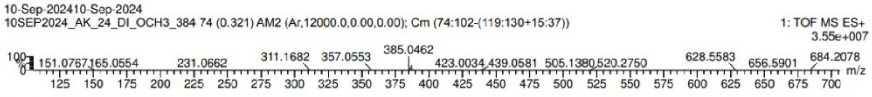
Mass spectrum of compound **3z**



Elemental Composition Report **Page 1**

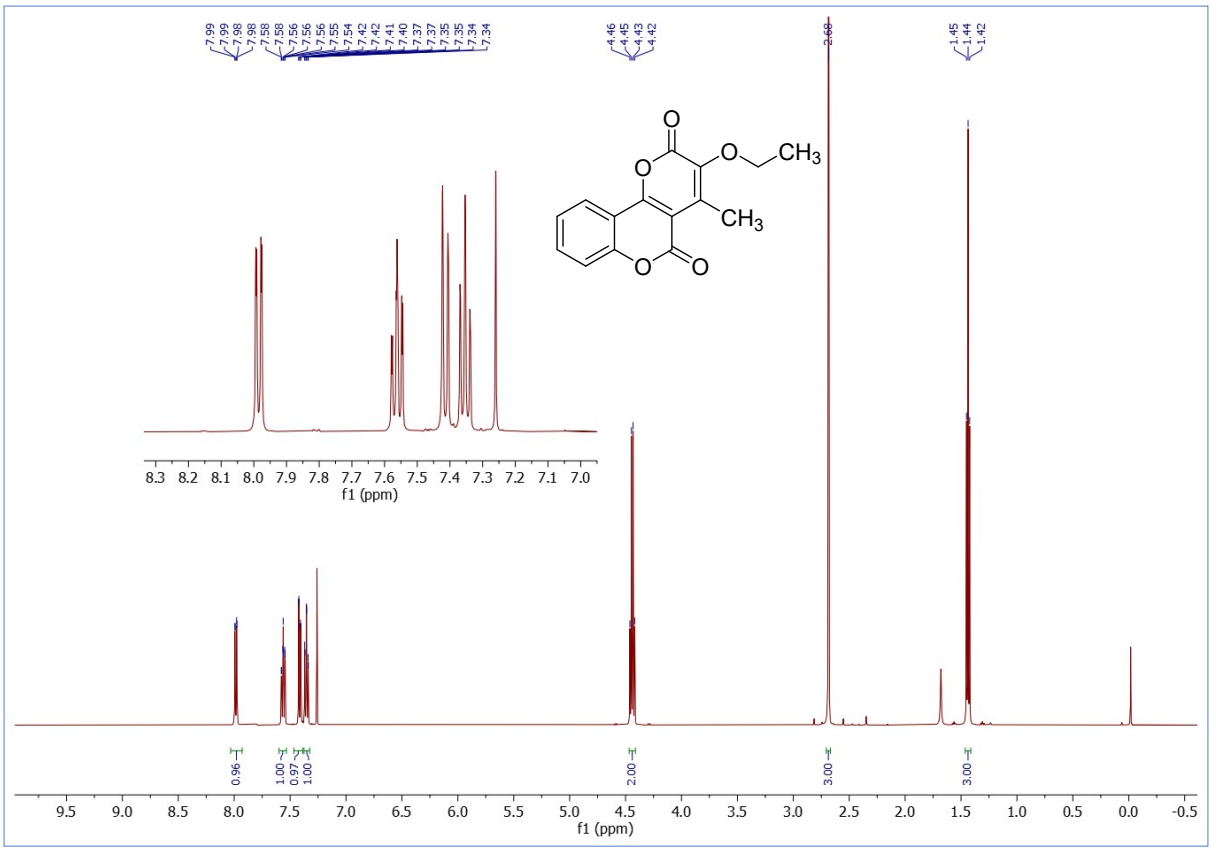
Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Odd and Even Electron Ions
11 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-20 H: 0-14 O: 0-6 Cl: 0-1

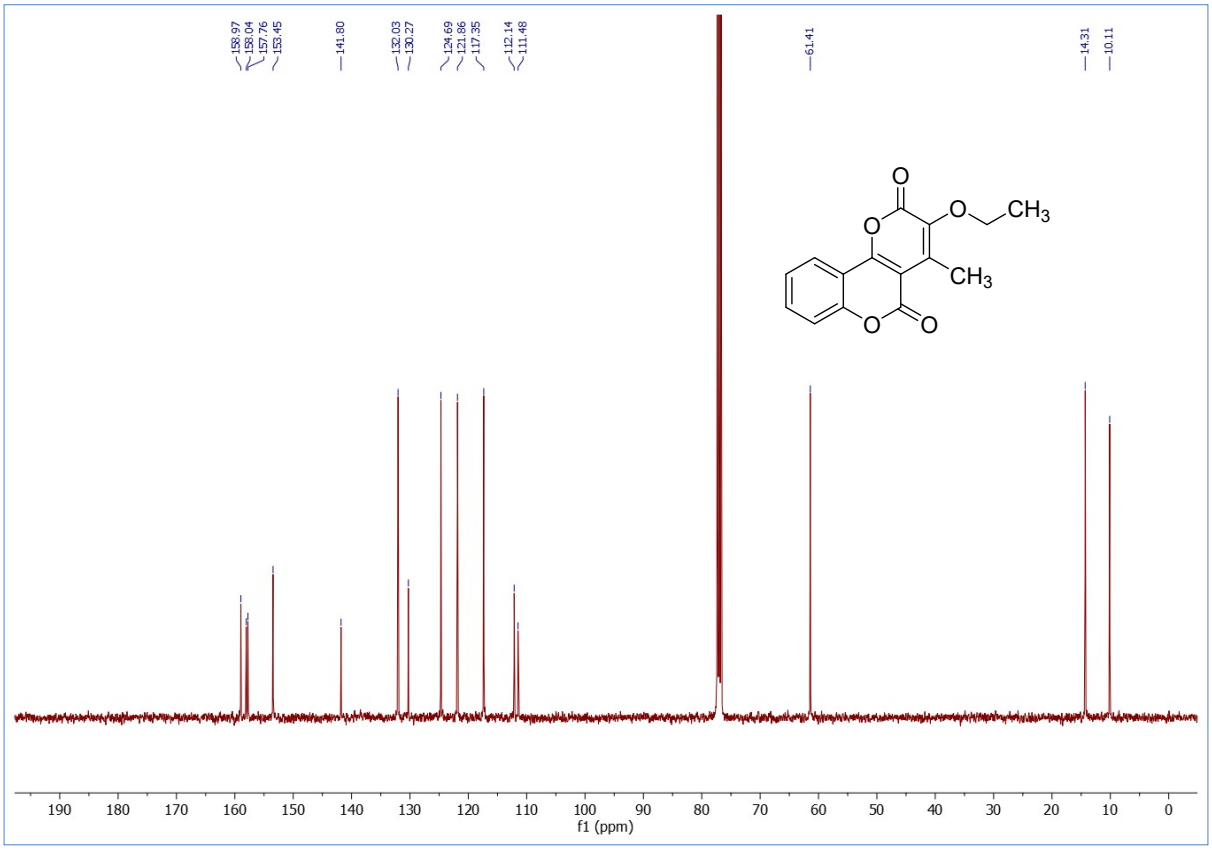


Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
385.0462	385.0479	-1.7	-4.4	13.5	533.1	n/a	n/a	C20 H14 O6 Cl

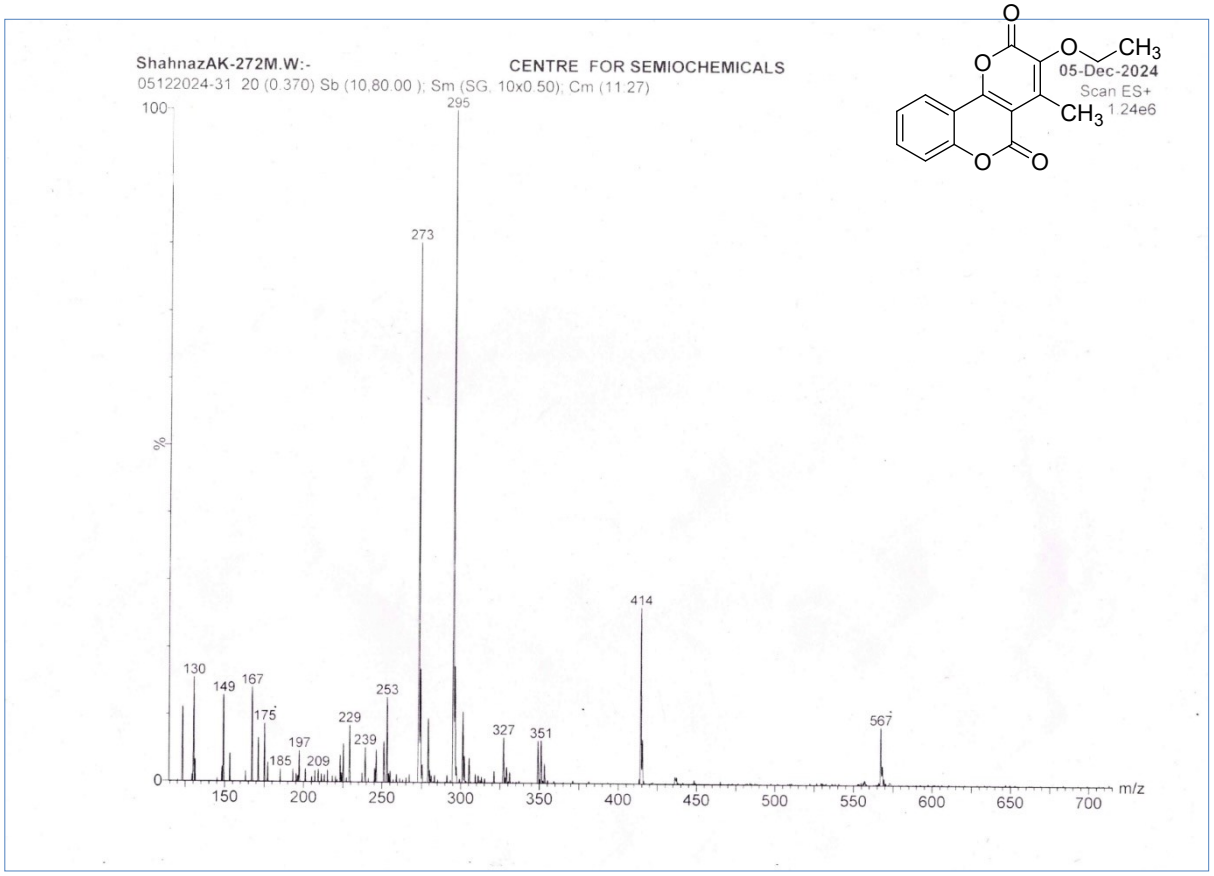
HRMS spectrum of compound **3z**



^{1}H-NMR spectrum of compound **4a**

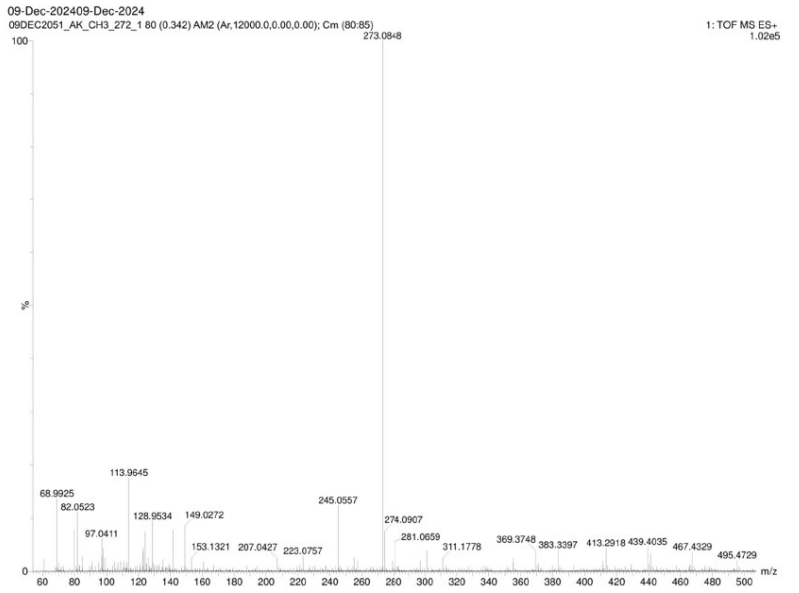


^{13}C-NMR spectrum of compound **4a**



Mass spectrum of compound

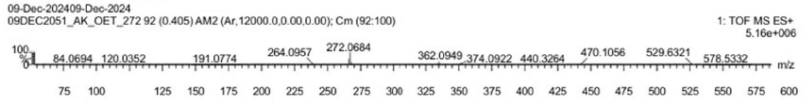
4a



Elemental Composition Report **Page 1**

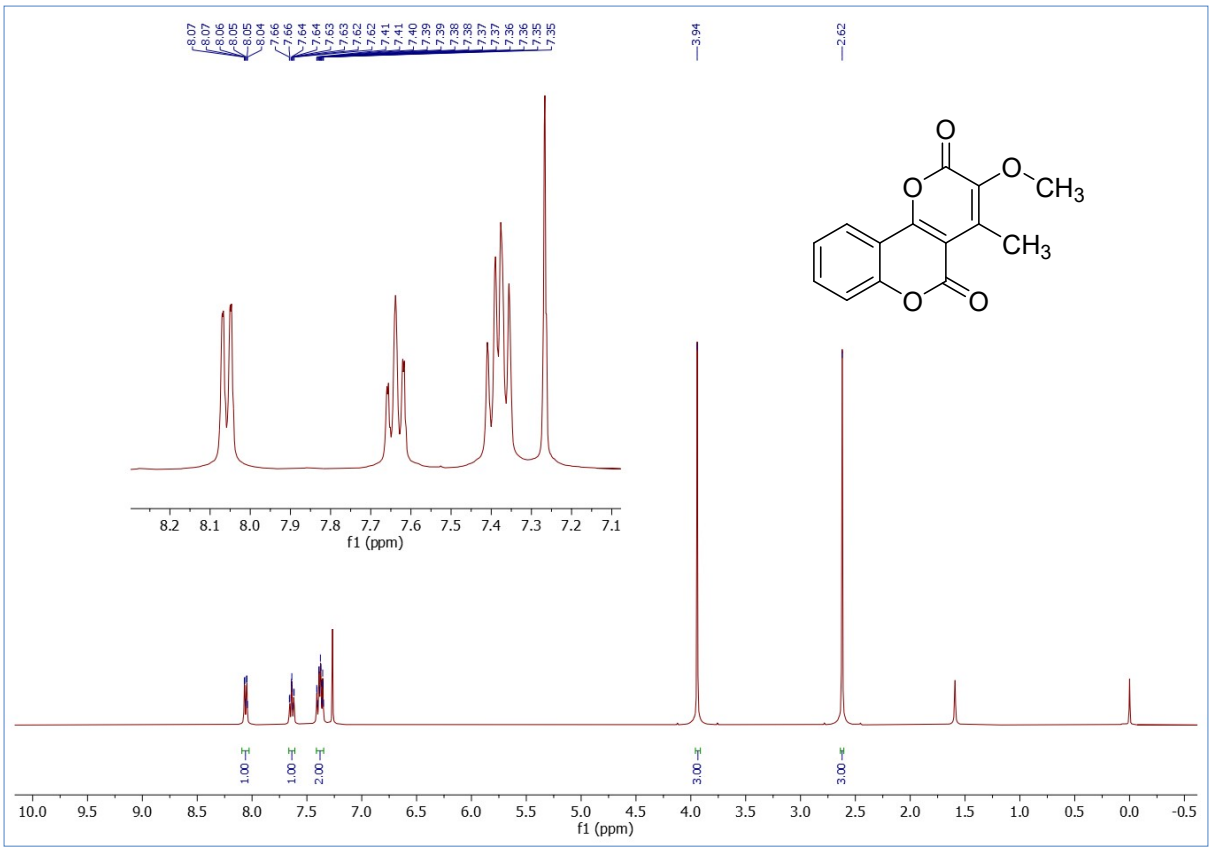
Single Mass Analysis
Tolerance = 100.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 4

Monoisotopic Mass, Even Electron Ions
9 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-15 H: 0-13 O: 0-5

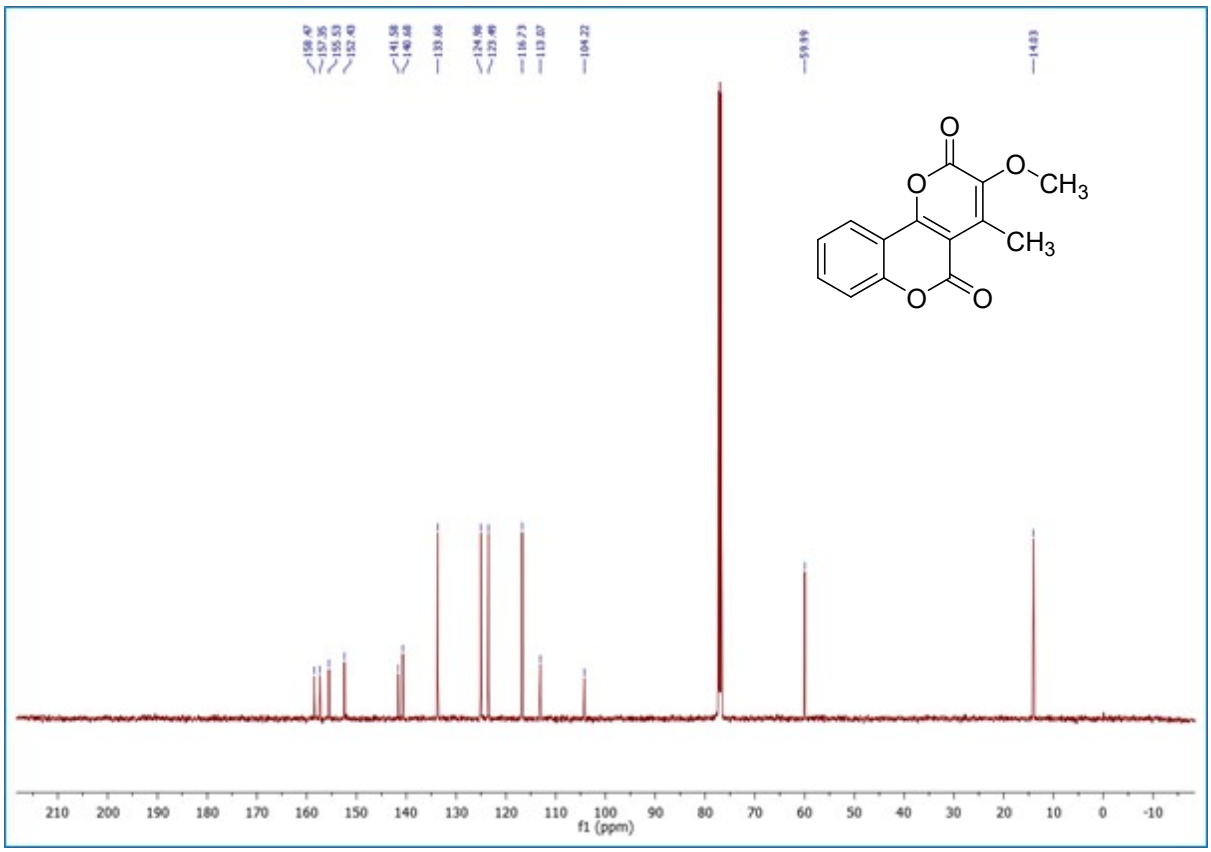


Minimum:				-1.5				
Maximum:		5.0	100.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
273.0547	273.0552	-3.9	-5.4	12.5	272.6	n/a	n/a	C15 H13 O5

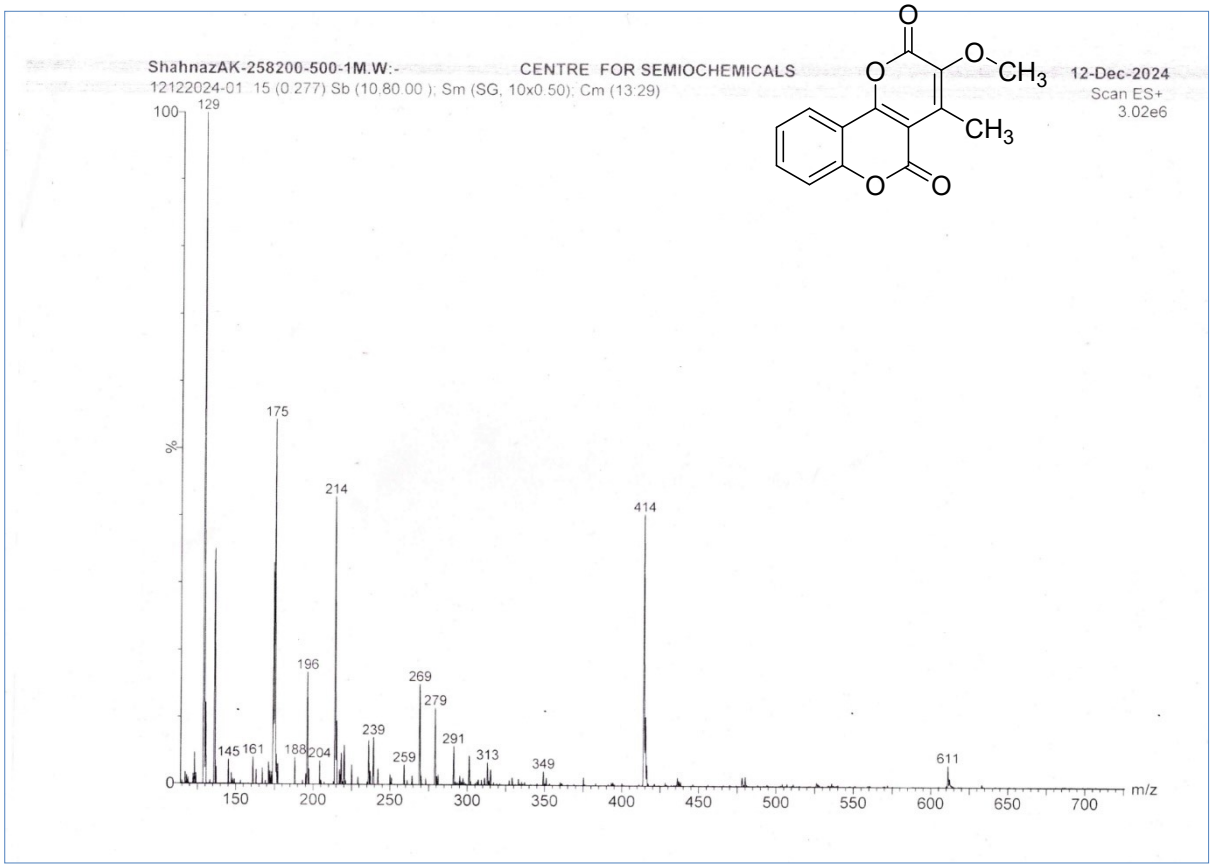
HRMS spectrum of compound **4a**



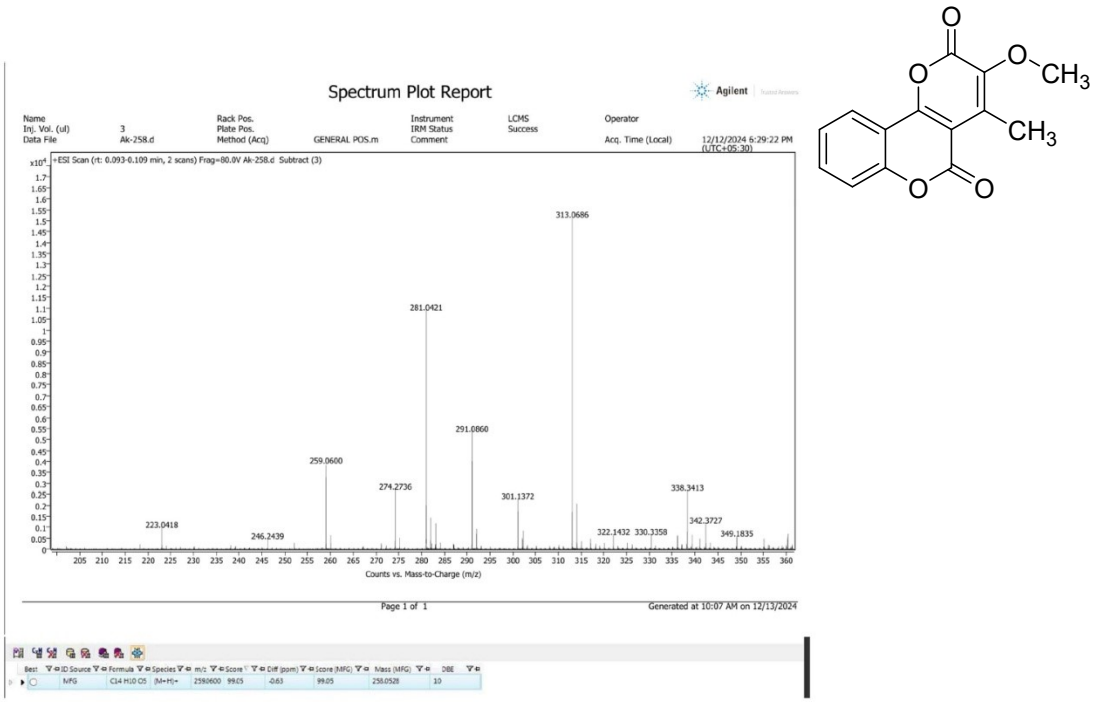
^{1}H-NMR spectrum of compound **4b**



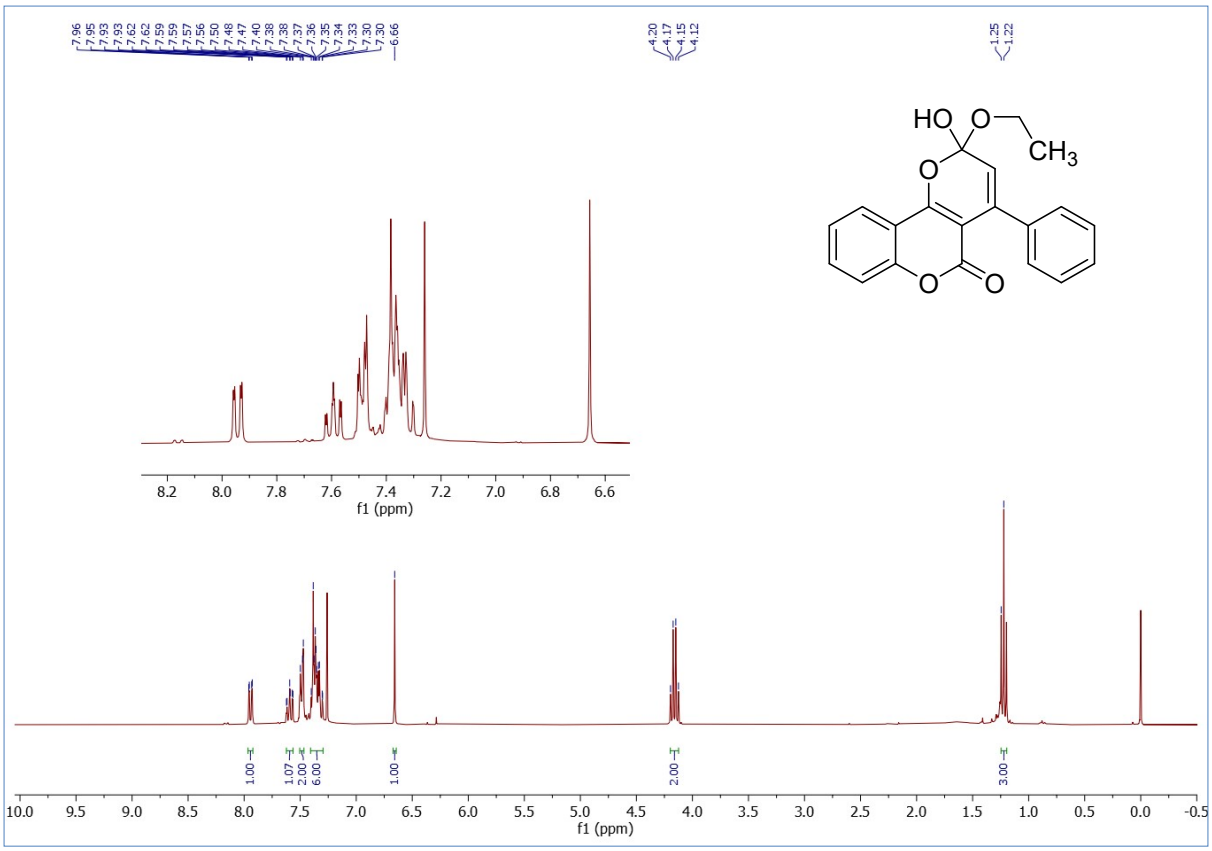
^{13}C-NMR spectrum of compound **4b**



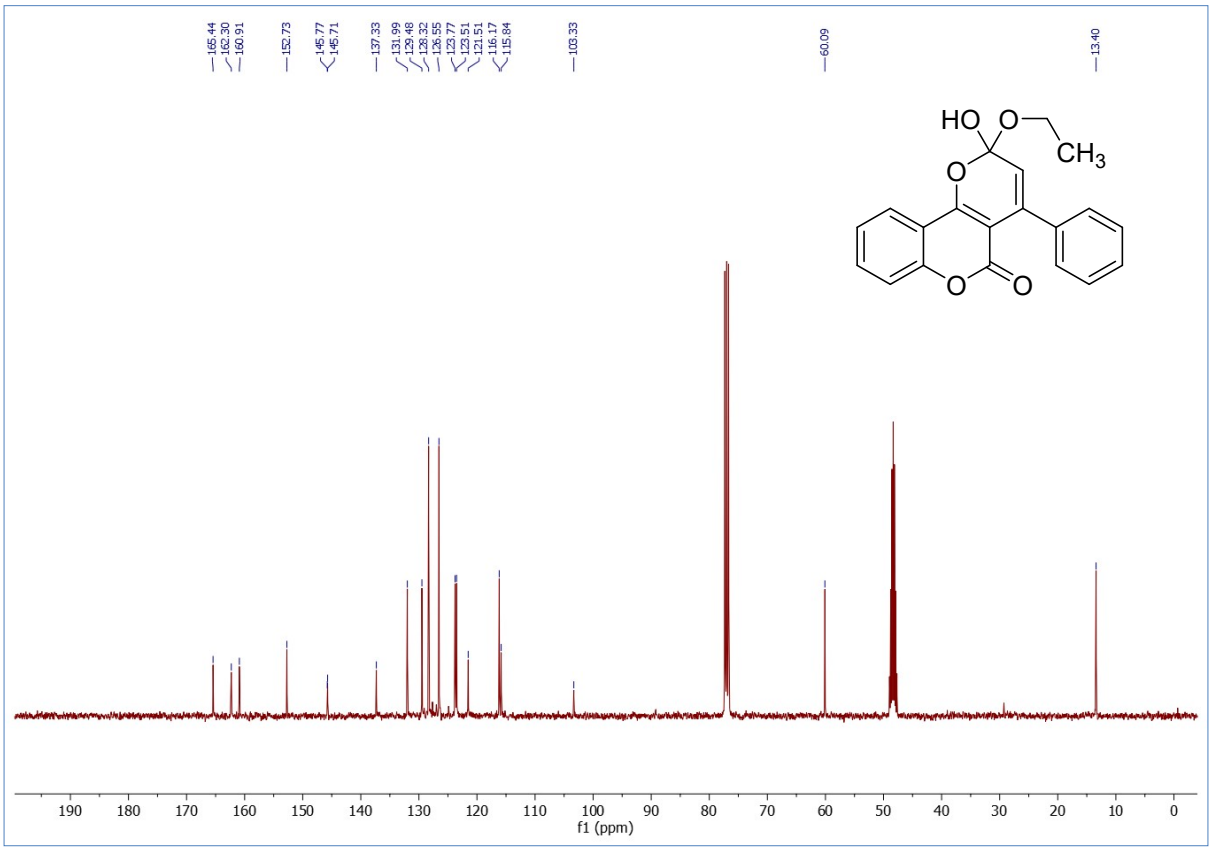
Mass spectrum of compound **4b**



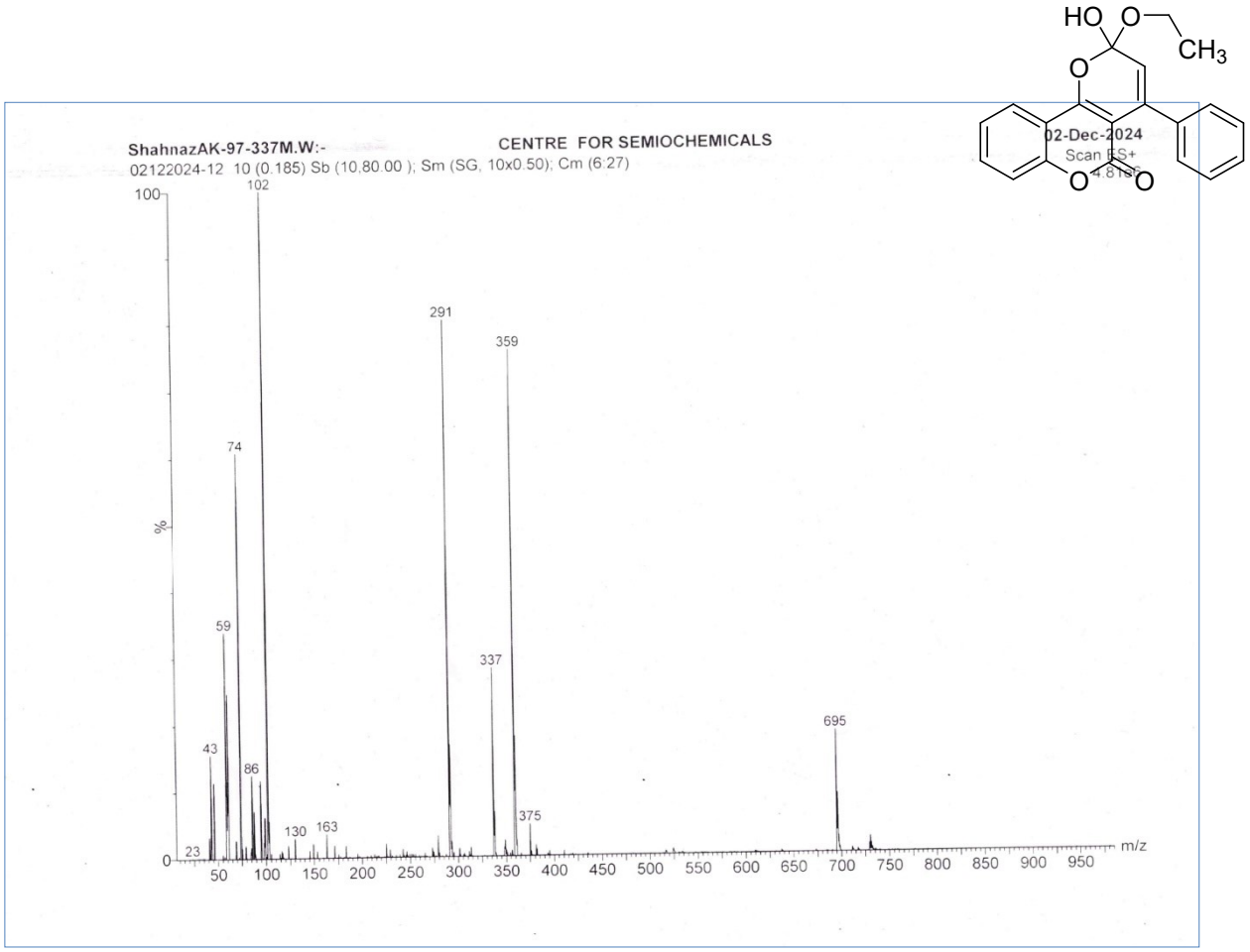
HRMS spectrum of compound **4b**



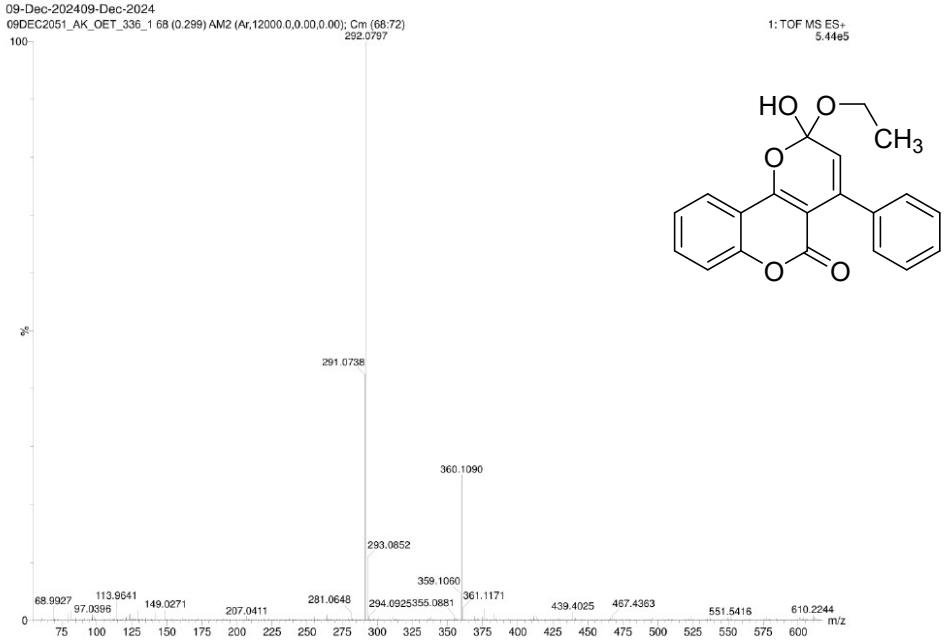
^{1}H-NMR spectrum of compound **4c**



^{13}C-NMR spectrum of compound **4c**



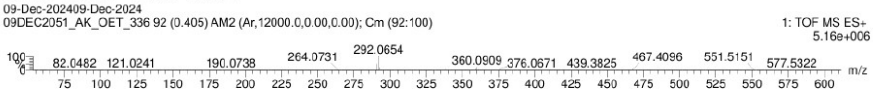
Mass spectrum of compound **4c**



Elemental Composition Report **Page 1**

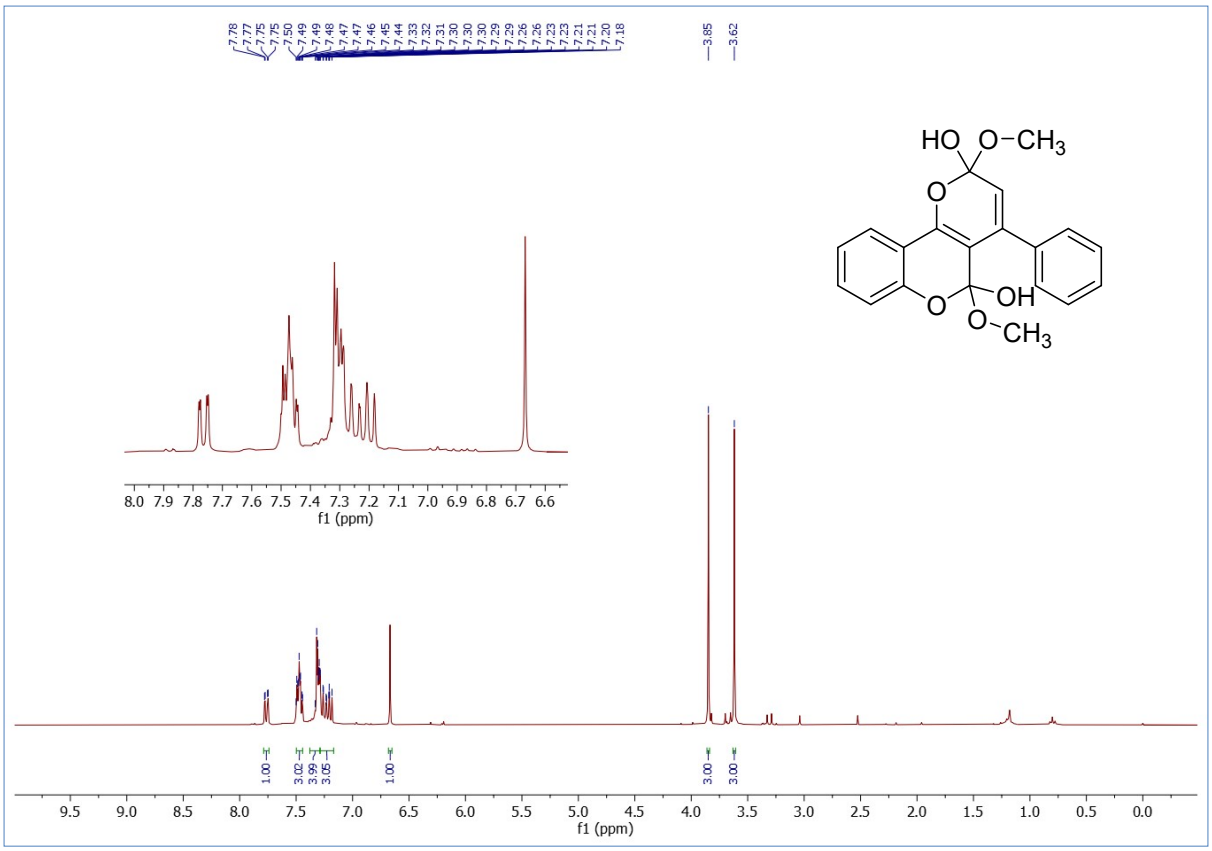
Single Mass Analysis
Tolerance = 100.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
9 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-20 H: 0-18 O: 0-5 Na: 0-1

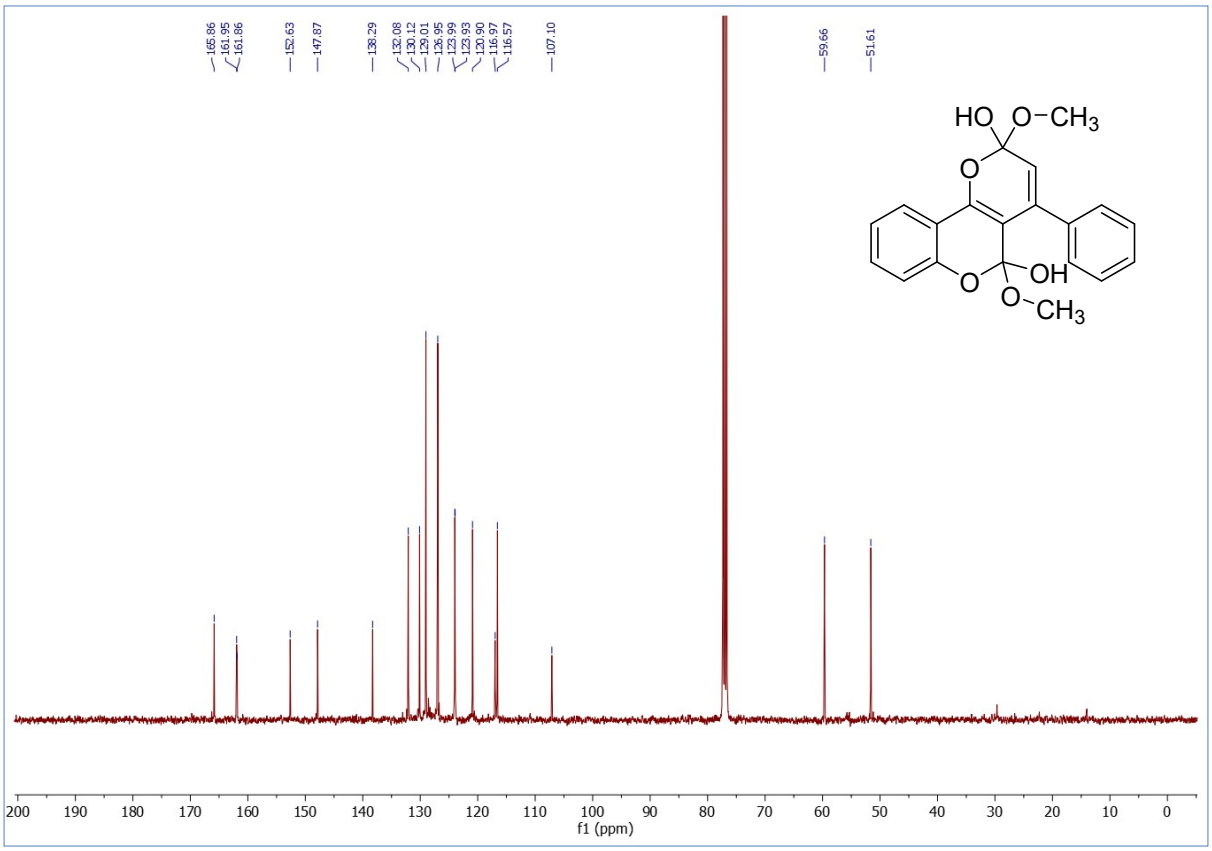


Minimum:				-1.5				
Maximum:		5.0	100.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
359.0857	359.0895	-3.8	-10.6	12.5	308.2	n/a	n/a	C20 H16 O5 Na

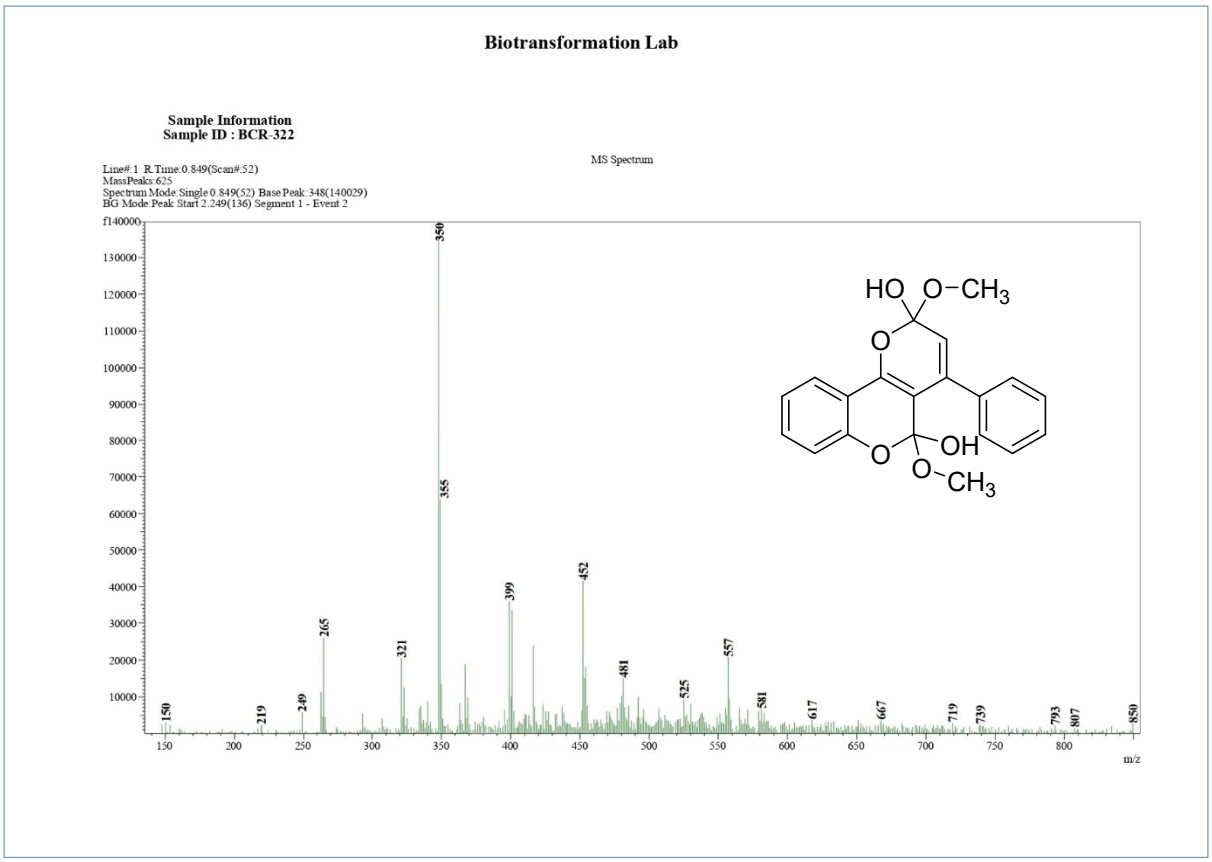
HRMS spectrum of compound **4c**



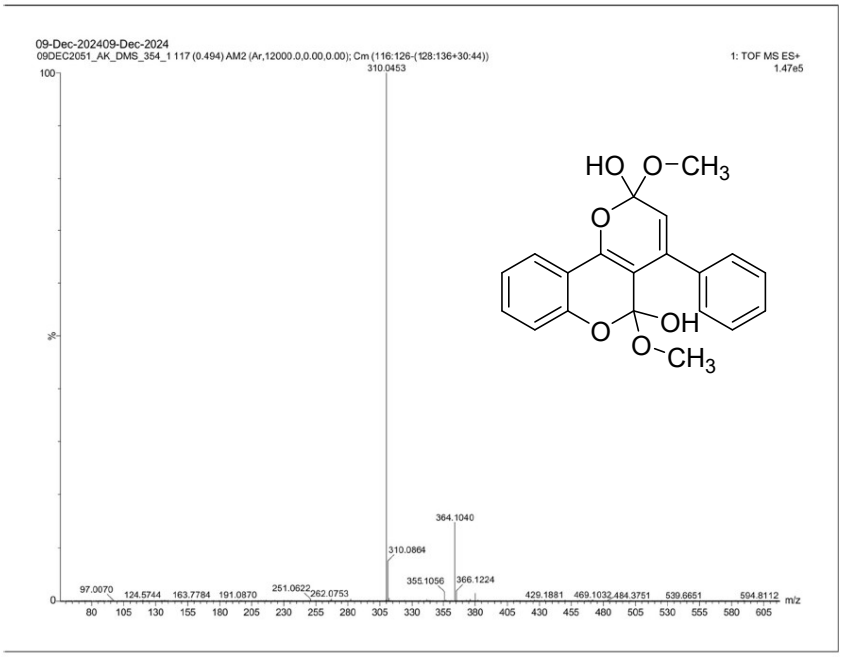
^{1}H-NMR spectrum of compound **4d**



^{13}C-NMR spectrum of compound **4d**



Mass spectrum of compound **4d**

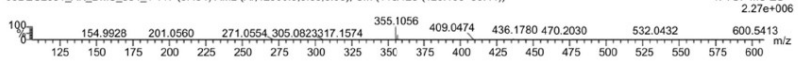


Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
9 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-20 H: 0-19 O: 0-6

09DEC2051_AK_DMS_354_1 117 (0.494) AM2 (Ar,12000.0,0.00,0.00); Cm (116:126-(128:136+30:44))
1: TOF MS ES+
2.27e+006



Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
355.1056	355.1062	-0.8	-2.3	6.5	354.5	n/a	n/a	C20 H19 O6

HRMS spectrum of compound **4d**

X-ray Crystallography

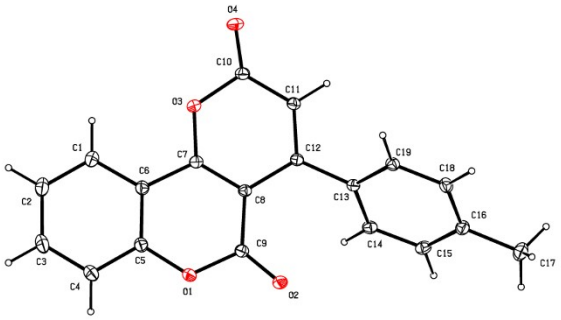
X-ray Crystallography.

X-ray data for the compound was collected at room temperature on a Bruker D8 QUEST instrument with an IμS Mo microsource (λ = 0.7107 Å) and a PHOTON-III detector. The raw data frames were reduced and corrected for absorption effects using the Bruker Apex 3 software suite programs [1]. The structure was solved using intrinsic phasing method [2] and further refined with the SHELXL [2] program and expanded using Fourier techniques. Anisotropic displacement parameters were included for all non-hydrogen atoms. All C bound H atoms were positioned geometrically and treated as riding on their parent C atoms [C-H = 0.93-0.97 Å, and Uiso(H) = 1.5Ueq(C) for methyl H or 1.2Ueq(C) for other H atoms].

Crystal structure determination of compound 3e

Crystal Data for $C_{19}H_{12}O_4$ (M =304.29 g/mol): monoclinic, space group $P2_1/n$ (no. 14), a = 6.4750(3) Å, b = 8.0563(4) Å, c = 27.3771(14) Å, β = 92.317(3)°, V = 1426.95(12) Å^3, Z = 4, T = 294.15 K, μ(MoKα) = 0.100 mm^{-1}, $Dcalc$ = 1.416 g/cm^3, 15912 reflections measured (5.272° ≤ 2Θ ≤ 56.556°), 3541 unique (R_{int} = 0.0300, R_{sigma} = 0.0307) which were used in all calculations. The final R_1 was 0.0455 (I > 2σ(I)) and wR_2 was 0.1266 (all data). **CCDC 2371440** deposition number contains the supplementary crystallographic data for this paper which can be obtained free of charge at https://www.ccdc.cam.ac.uk/structures/

1. Bruker (2016). APEX3, SAINT and SADABS. Bruker AXS, Inc., Madison, Wisconsin, USA.
2. Sheldrick G. M. (2015).ActaCrystallogr C71: 3-8.



Figure

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