Supporting Information

Design, Synthesis of Novel 4-Hydroxyl-3-(2-phenoxyacetyl)-pyran-2-one Derivatives as Herbicides and Evaluation of Their Mode of Action

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General

Unless otherwise stated, all commercially available reagents (purchased from Energy Chemical and Tokyo Chemical Industry) are used without further purification. ^{1}H and ^{13}C NMR spectra are obtained at 400 MHz and 100 MHz, respectively, using an AV400 spectrometer (Bruker, Billerica, MA) in $CDCl_3$ or DMSO-d_6 solution with TMS as the internal standard. Chemical shifts values were given in δ. Coupling constants are reported in hertz (Hz). High-resolution mass spectrometry is conducted using an Ionspec 7.0 T spectrometer (Varian, Palo Alto, CA) by the electrospray ionisation Fourier transform ion cyclotron resonance (ESI-FTICR) technique. The crystal structure is determined on a Saturn 724 CCD area-detector diffractometer (Rigaku, Tokyo, Japan). Real-time PCRs are performed with a Bio-Rad real-time thermal cycling system (Bio-Rad CFX96, USA). High-performance liquid chromatography (HPLC) data is obtained on a SHIMADZU LC-20AT (Japan).

1. Inhibition of the root growth of mustard (*Brassica campestris L.*)

Emulsions of target compounds, mesotrione and 2, 4-D were prepared by dissolving them in 100 μL of DMF adding a few drops of Tween-80 and dispersing in water. A mixture of the same amount of water, DMF and Tween-80 was used as control. Rape seeds were soaked in distilled water for 4 h before being placed on a filter paper in a 6 cm petri plate, to which 2 mL of inhibitor solution had been added in advance. Usually, 15 seeds were used on each plate. The plate was placed in a dark room and allowed to germinate for 65 h at 28 ± 1 °C. The lengths of ten mustard roots randomly selected from each plate were measured, and the means were calculated. Each treatment was performed triplicate. Formulas used in these tests are as follows: Control effect (%) = (the root length of *Brassica campestris L.* of the control − the root length of *Brassica campestris L.* treated by tested compound)/the root length of *Brassica campestris L.* of the control × 100%. The data represented the percent displaying herbicidal damage as compared to the control, where complete control of the target is 100 and no control is 0.

2. Inhibition of the seedling growth of Barnyard Grass [*Echinochloa crusgalli (L.) Beauv.*]

Emulsions of target compounds, mesotrione and 2, 4-D were prepared according to above method. A mixture of the same amount of water, DMF and Tween-80 was used as control. 15 *Echinochloa crusgalli* seeds were placed into a 50 mL cup covered with a layer of glass beads and a piece of filter paper at the bottom, to which 5 mL of inhibitor solution had been added in advance. The cup was placed in a bright room, and the seeds were allowed to germinate for 65 h at 28 ± 1 °C. The heights of the above-ground parts of the seedlings in each cup were measured, and the means were calculated. Formulas used in these tests are as follows: Control effect (%) = (the height of *Echinochloa crusgalli (L.) Beauv.* of the control − the height of *Echinochloa crusgalli (L.) Beauv.* treated by tested compound)/the height of *Echinochloa crusgalli (L.) Beauv.* of the control × 100%. The percentage inhibition was used to describe the control efficiency of the compounds. The data represented the percent displaying herbicidal damage as compared to the control, where complete control of the target is 100 and no control is 0. Each test was performed in triplicate.

3. Greenhouse Tests

The greenhouse herbicidal activities of target compounds and control compounds were evaluated using a standard procedure at Nankai University. Two dicotyledonous species mustard (*Brassica campestris L.*) and amaranth pigweed (*Amaranthus retroflexus L.*), and two monocotyledonous species barnyard grass (*Echinochloa crusgalli (L.) Beauv.*) and crabgrass (*Digitaria sanguinalis (L.) Scop*) were used to test the herbicidal activities of the compounds. For pre-emergence tests, sandy clay (100 g) in a 8-cm-diameter test pot was wetted by water. Then 15 sprouting seeds of the weed were planted to 0.6 cm depth and placed in a greenhouse. All the tested compounds were dissolved in 100 % DMF and then diluted with Tween-80 (concentration: 100 g/L). The resulting solutions were diluted with water to the appropriate concentrations before use. The solutions of the compounds evaluated were sprayed using a laboratory belt sprayer delivering a 750 L ha^{-1} spray volume. The dosage (activity ingredient) for each compound corresponded to 1500 g ha^{-1}. Compounds were sprayed immediately after seed planting. The mixture of same amount of water, *N, N*-dimethylformamide and Tween 80 was sprayed as the control.

For post-emergence tests, the same solution of the compounds was applied at the same rate as for the pre-emergence tests. Compounds were sprayed immediately after the expansion of the first true leaf. After 15 days, the fresh weight of the above-ground tissues in each pot was weighed and the percentage of inhibition calculated. Each treatment was done in triplicate, all the experiments were performed under natural light conditions at 18 – 28 °C. Additionally, adverse weather lighting was provided using sodium vapour lamps with a 12 : 12 h light : dark photoperiod.

Formulas used in these tests are as follows: Control effect (%) = (the weight of live weeds in the control pots − the weight of live weeds in the treated pots)/the weight of live weeds in the control pots × 100%. The data represented the percent displaying herbicidal damage as compared to the control, where complete control of the target is 100 and no control is 0.

4. Crop selectivity

The crops were planted in flowerpots (12 cm diameter) and grown at room temperature in the test soil. Crop safety experiments were conducted at the dosage of 375 g ha^{-1} when the crops had reached the four-leaf stage. After 15 days of treatment by compound **II15**, the crop selectivity was evaluated with three duplicates per experiment.

5. The ^{1}H NMR and ^{13}C NMR Spectrum of Target Compounds

3-(2-phenoxyacetyl)-4-hydroxylcoumarin (**I1**): white solid; yield 52.4%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.10 (dd, J = 8.0, 1.5 Hz, 1H), 7.77 – 7.73 (m, 1H), 7.45 – 7.28 (m, 4H), 7.06 – 6.95 (m, 3H), 5.46 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 200.9, 176.8, 158.8, 156.8, 153.8, 135.6, 128.6, 124.6, 123.8, 120.6, 116.2, 113.7, 113.6, 98.9, 71.0; HRMS: calcd for $C_{17}H_{12}O_5$ $[M+H]^+$ 297.0763, found 297.0766.

3-(2-(2-chlorophenoxy)acetyl)-4-hydroxylcoumarin (**I2**): white solid; yield 56.6%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.10 (dd, J = 8.0, 1.5 Hz, 1H), 7.78 – 7.74 (m, 1H), 7.46 – 7.33 (m, 3H), 7.20 (ddd, J = 8.2, 7.6, 1.6 Hz, 1H), 6.95 (td, J = 7.7, 1.4 Hz, 1H), 6.90 (dd, J = 8.3, 1.3 Hz, 1H), 5.53 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 201.0, 177.8, 159.9, 154.9, 153.5, 136.7, 130.7, 127.7, 125.7, 124.9, 123.2, 122.4, 117.3, 114.6, 113.9, 100.0, 72.7; HRMS: calcd for $C_{17}H_{11}ClO_5$ $[M+H]^+$ 331.0373, found

331.0375.

3-(2-(3-chlorophenoxy)acetyl)-4-hydroxylcoumarin (**I3**): white solid; yield 51.3%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.10 (dd, J = 8.0, 1.5 Hz, 1H), 7.78– 7.74 (m, 1H), 7.44 – 7.33 (m, 2H), 7.25 – 7.19 (td, J = 7.0, 2.0 Hz, 1H), 7.00 – 6.95 (m, 2H), 6.91 – 6.82 (dt, J = 8.4, 2.0 Hz, 1H), 5.44 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 201.3, 177.9, 159.9, 158.6, 154.9, 136.8, 135.0, 130.4, 125.7, 124.9, 121.9, 117.3, 115.3, 114.5, 113.2, 100.0, 72.1; HRMS: calcd for $C_{17}H_{11}ClO_5$ $[M+H]^+$ 331.0373, found 331.0376.

3-(2-(4-chlorophenoxy)acetyl)-4-hydroxylcoumarin (**I4**): white solid; yield 50.1%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.10 (dd, J = 8.0, 1.5 Hz, 1H), 7.78– 7.74 (m, 1H), 7.45 – 7.34 (m, 2H), 7.29 – 7.23 (m, 3H), 6.97-6.87 (m, 2H), 5.43 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 201.5, 177.9, 159.8, 156.5, 154.9, 136.8, 129.5, 126.6, 125.7, 124.9, 117.3, 116.1, 114.5, 100.0, 72.3; HRMS: calcd for $C_{17}H_{11}ClO_5$ $[M+H]^+$ 331.0373, found 331.0376.

3-(2-(2-methylphenoxy)acetyl)-4-hydroxylcoumarin (**I5**): light yellow solid; yield 53.8%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.09 (dd, J = 8.0, 1.6 Hz, 1H), 7.77 – 7.73 (m, 1H), 7.43 – 7.33 (m, 2H), 7.19 (d, J = 7.3 Hz, 1H), 7.16 – 7.09 (m, 1H), 6.91 (t, J = 7.2 Hz, 1H), 6.76 (d, J = 8.1 Hz, 1H), 5.48 (s, 2H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 202.3, 177.8, 159.9, 156.1, 154.9, 136.6, 131.1, 127.2, 126.7, 125.6, 124.8, 121.4, 117.2, 114.7, 111.5, 100.0, 72.3, 16.3; HRMS: calcd for $C_{18}H_{14}O_5$ $[M+H]^+$ 311.0919, found 311.0920.

3-(2-(3-methylphenoxy)acetyl)-4-hydroxylcoumarin (**I6**): white solid; yield 56.7%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.09 (dd, J = 8.0, 1.4 Hz, 1H), 7.77– 7.73 (m, 1H), 7.38 (td, J = 8.4, 4.4 Hz, 2H), 7.22 – 7.14 (m, 1H), 6.84 – 6.75 (m, 3H), 5.44 (s, 2H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 202.1, 177.8, 159.9, 157.8, 154.9, 139.8, 136.6, 129.3, 125.6, 124.9, 122.5, 117.2, 115.5, 114.6, 111.5, 100.0, 71.9, 21.6; HRMS: calcd for $C_{18}H_{14}O_5$ $[M+H]^+$ 311.0919, found 311.0921.

3-(2-(4-methylphenoxy)acetyl)-4-hydroxylcoumarin (**I7**): white solid; yield 61.4%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.09 (dd, J = 8.0, 1.5 Hz, 1H), 7.77– 7.72 (m, 1H), 7.43 – 7.33 (m, 2H), 7.10 (d, J = 8.2 Hz, 2H), 6.93 – 6.84 (m, 2H), 5.43 (s, 2H), 2.29

(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 202.2, 177.8, 159.8, 155.8, 154.9, 136.6, 131.0, 130.0, 125.6, 124.9, 117.2, 114.6, 100.0, 72.2, 20.5; HRMS: calcd for $C_{18}H_{14}O_5$ $[M+H]^+$ 311.0919, found 311.0921.

3-(2-(2-methoxyphenoxy)acetyl)-4-hydroxylcoumarin (**I8**): white solid; yield 48.6%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.09 (dd, J = 8.0, 1.5 Hz, 1H), 7.76 – 7.72 (m, 1H), 7.37 (m, 2H), 7.03 – 6.92 (m, 2H), 6.88 (d, J = 3.6 Hz, 2H), 5.51 (s, 2H), 3.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 200.9, 176.8, 158.8, 153.8, 148.5, 146.2, 135.5, 124.6, 123.8, 121.3, 119.7, 116.2, 113.6, 113.1, 111.0, 98.9, 71.9, 54.9; HRMS: calcd for $C_{18}H_{14}O_6$ $[M+H]^+$ 327.0869, found 327.0871.

3-(2-(3-methoxyphenoxy)acetyl)-4-hydroxylcoumarin (**I9**): white solid; yield 45.1%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.09 (d, J = 7.9 Hz, 1H), 7.77– 7.73 (m, 1H), 7.35 – 7.41 (m, 2H), 7.20 (t, J = 7.6 Hz, 1H), 6.56 (d, J = 7.1 Hz, 3H), 5.44 (s, 2H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 201.9, 177.8, 160.9, 159.8, 159.1, 154.9, 136.7, 130.0, 125.6, 124.9, 117.2, 114.6, 107.4, 106.6, 101.5, 100.0, 72.0, 55.4; HRMS: calcd for $C_{18}H_{14}O_6$ $[M+H]^+$ 327.0869, found 327.0871.

3-(2-(4-methoxyphenoxy)acetyl)-4-hydroxylcoumarin (**I10**): white solid; yield 51.3%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.08 (dd, J = 8.0, 1.4 Hz, 1H), 7.76 – 7.72 (m, 1H), 7.44 – 7.31 (m, 2H), 6.98 – 6.89 (m, 2H), 6.87 – 6.80 (m, 2H), 5.39 (s, 2H), 3.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 201.3, 176.8, 158.7, 153.8, 153.4, 151.0, 135.6, 124.6, 123.8, 116.2, 114.9, 113.7, 113.6, 98.9, 71.9, 54.7; HRMS: calcd for $C_{18}H_{14}O_6$ $[M+H]^+$ 327.0869, found 327.0872.

3-(2-(2, 3-dichlorophenoxy)acetyl)-4-hydroxylcoumarin (**I11**): white solid; yield 56.3%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.09 (dd, J = 8.0, 1.4 Hz, 1H), 7.78– 7.74 (m, 1H), 7.42 – 7.35 (m, 2H), 7.17 – 7.06 (m, 2H), 6.82– 6.78 (m, 1H), 5.53 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 199.5, 176.8, 158.9, 153.9, 153.9, 135.8, 133.2, 126.3, 124.6, 123.9, 122.2, 121.3, 116.2, 113.5, 110.6, 98.9, 71.8; HRMS: calcd for $C_{17}H_{10}Cl_2O_5$ $[M+H]^+$ 364.9984, found 364.9986.

3-(2-(2, 4-dichlorophenoxy)acetyl)-4-hydroxylcoumarin (**I12**): white solid; yield 61.4%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.09 (d, J = 7.7 Hz, 1H), 7.78 – 7.74 (m, 1H), 7.44 – 7.32 (m, 3H), 7.16 (d, J = 8.7 Hz, 1H), 6.82 (d, J = 8.7 Hz, 1H), 5.50 (s, 2H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 199.5, 176.8, 158.8, 153.8, 151.4, 135.8, 129.3, 126.5, 125.8, 124.6, 123.9, 123.0, 116.2, 113.6, 113.4, 98.9, 71.9; HRMS: calcd for $C_{17}H_{10}Cl_2O_5$ $[M+H]^+$ 364.9984, found 364.9987.

3-(2-(2, 5-dichlorophenoxy)acetyl)-4-hydroxylcoumarin (**I13**): white solid; yield 47.2%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.10 (d, J = 7.8 Hz, 1H), 7.79– 7.75 (m, 1H), 7.47 – 7.31 (m, 3H), 6.94 (d, J = 8.3 Hz, 1H), 6.87 (s, 1H), 5.52 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 200.3, 177.8, 159.9, 154.9, 154.0, 136.9, 133.1, 131.1, 125.7, 125.0, 122.4, 121.7, 117.3, 114.5, 114.3, 100.0, 72.7; HRMS: calcd for $C_{17}H_{10}Cl_2O_5$ $[M+H]^+$ 364.9984, found 364.9987.

3-(2-(3, 5-dichlorophenoxy)acetyl)-4-hydroxylcoumarin (**I14**): white solid; yield 51.7%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.04 (dd, J = 8.0, 1.5 Hz, 1H), 7.72– 7.68 (m, 1H), 7.38 – 7.28 (m, 2H), 6.94 (t, J = 1.7 Hz, 1H), 6.80 (d, J = 1.7 Hz, 2H), 5.37 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 199.6, 176.9, 158.9, 157.9, 153.9, 135.9, 134.5, 124.7, 124.0, 121.0, 116.3, 113.5, 112.9, 99.0, 71.1; HRMS: calcd for $C_{17}H_{10}Cl_2O_5$ $[M+H]^+$ 364.9984, found 364.9986.

3-(2-(2-chloro-4-fluorophenoxy)acetyl)-4-hydroxylcoumarin (**I15**): white solid; yield 54.1%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.12 (dd, J = 8.0, 1.5 Hz, 1H), 7.80 – 7.76 (m, 1H), 7.48 – 7.35 (m, 2H), 7.20 (dd, $J_{F\text{-}H}$ = 8.0 Hz, J = 2.8 Hz, 1H), 6.99 – 6.83 (m, 2H), 5.51 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 200.9, 177.8, 159.9, 157.1 (d, $J_{F\text{-}C}$ = 241.9 Hz), 154.9, 150.2 (d, $J_{F\text{-}C}$ = 3.0 Hz), 136.8, 125.7, 125.0, 124.1 (d, $J_{F\text{-}C}$ = 10.4 Hz), 117.9 (d, $J_{F\text{-}C}$ = 26.1 Hz), 117.3, 115.0 (d, $J_{F\text{-}C}$ = 8.8 Hz), 114.5, 114.2 (d, $J_{F\text{-}C}$ = 22.6 Hz), 99.9, 73.5; HRMS: calcd for $C_{17}H_{10}ClFO_5$ $[M+H]^+$ 349.0279, found 349.0282.

3-(2-(4-bromo-2-chlorophenoxy)acetyl)-4-hydroxylcoumarin (**I16**): white solid; yield 57.9%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.09 (dd, J = 8.0, 1.5 Hz, 1H), 7.78– 7.74 (m, 1H), 7.55 (d, J = 2.4 Hz, 1H), 7.45 – 7.34 (m, 2H), 7.30 (dd, J = 8.8, 2.4 Hz, 1H), 6.77 (d, J = 8.8 Hz, 1H), 5.50 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 200.5, 177.8, 159.9, 154.9, 152.9, 136.8, 133.1, 130.5, 125.7, 124.9, 124.4, 117.3, 115.1, 114.5, 113.7, 99.9, 72.8; HRMS: calcd for $C_{17}H_{10}BrClO_5$ $[M+H]^+$ 408.9478, found 408.9481.

3-(2-(4-fluoro-2-methylphenoxy)acetyl)-4-hydroxylcoumarin (**I17**): white solid; yield 52.8%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.10 (dd, J = 8.0, 1.5 Hz, 1H), 7.78–7.73 (m, 1H), 7.43 – 7.34 (m, 2H), 6.91 (dd, $J_{F\text{-}H}$ = 8.9 Hz, J = 2.9 Hz, 1H), 6.80 (td, J = 8.4, 3.0 Hz, 1H), 6.71 (dd, $J_{F\text{-}H}$ = 8.9 Hz, J = 4.5 Hz, 1H), 5.44 (s, 2H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 202.1, 177.84, 159.8, 157.4 (d, $J_{F\text{-}C}$ = 237.8 Hz), 154.9, 152.3 (d, $J_{F\text{-}C}$ = 2.2 Hz), 136.6, 129.3 (d, $J_{F\text{-}C}$ = 7.7 Hz), 125.6, 124.9, 117.7 (d, $J_{F\text{-}C}$ = 22.8 Hz), 117.2, 114.6, 112.7 (d, $J_{F\text{-}C}$ = 8.6 Hz), 112.5 (d, $J_{F\text{-}C}$ = 22.7 Hz), 100.0, 73.1, 16.4; HRMS: calcd for $C_{18}H_{13}FO_5$ $[M+H]^+$ 329.0825, found 329.0828.

3-(2-(4-chloro-2-methylphenoxy)acetyl)-4-hydroxylcoumarin (**I18**): light yellow solid; yield 51.3%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.11 (dd, J = 8.0, 1.4 Hz, 1H), 7.80 – 7.74 (m, 1H), 7.46 – 7.35 (m, 2H), 7.18 (d, J = 2.1 Hz, 1H), 7.09 (dd, J = 8.7, 2.5 Hz, 1H), 6.70 (d, J = 8.7 Hz, 1H), 5.47 (s, 2H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 201.8, 177.8, 159.8, 154.9, 154.8, 136.7, 130.8, 129.2, 126.3, 126.0, 125.6, 124.9, 117.2, 114.6, 112.6, 100.0, 72.5, 16.2; HRMS: calcd for $C_{18}H_{13}ClO_5$ $[M+H]^+$ 345.0530, found 345.0532.

3-(2-(4-bromo-2-methylphenoxy)acetyl)-4-hydroxylcoumarin (**I19**): light yellow solid; yield 54.4%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.10 (dd, J = 8.0, 1.5 Hz, 1H), 7.78– 7.74 (m, 1H), 7.43 – 7.34 (m, 2H), 7.31 (d, J = 2.0 Hz, 1H), 7.22 (dd, J = 8.6, 2.3 Hz, 1H), 6.63 (d, J = 8.7 Hz, 1H), 5.45 (s, 2H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 201.7, 177.8, 159.9, 155.3, 154.9, 136.7, 133.7, 125.7, 124.9, 117.3, 114.6, 113.5, 113.0, 100.0, 72.4, 16.2; HRMS: calcd for $C_{18}H_{13}BrO_5$ $[M+H]^+$ 389.0025, found 389.0027.

3-(2-(2-bromo-4-fluorophenoxy)acetyl)-4-hydroxylcoumarin (**I20**): white solid; yield 50.7%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.10 (dd, J = 8.0, 1.6 Hz, 1H), 7.77–7.74 (m, 1H), 7.45 – 7.31 (m, 3H), 7.00 – 6.95 (m, 1H), 6.85 (dd, $J_{F\text{-}H}$ = 9.1 Hz, J = 4.7 Hz, 1H), 5.49 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 200.9, 177.8, 159.9, 157.2 (d, $J_{F\text{-}C}$ = 242.8 Hz), 154.9, 151.1 (d, $J_{F\text{-}C}$ = 2.9 Hz), 136.8, 125.7, 125.0, 120.8 (d, $J_{F\text{-}C}$ = 25.6 Hz), 117.3, 114.8 (d, $J_{F\text{-}C}$ = 22.6 Hz), 114.6 (d, $J_{F\text{-}C}$ = 8.5 Hz), 114.5, 112.6 (d, $J_{F\text{-}C}$ = 9.8 Hz), 100.0, 73.5; HRMS: calcd for $C_{17}H_{10}BrFO_5$ $[M+H]^+$ 392.9774, found 392.9777.

3-(2-(2-bromo-4-chlorophenoxy)acetyl)-4-hydroxylcoumarin (**I21**): white solid; yield 55.5%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.09 (d, J = 7.9 Hz, 1H), 7.78– 7.74 (m, 1H), 7.58 (d, J = 2.4 Hz, 1H), 7.42 – 7.35 (m, 2H), 7.21 (dd, J = 8.8, 2.4 Hz, 1H), 6.79 (d, J = 8.8 Hz, 1H), 5.50 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 200.5, 177.8, 159.9, 154.9, 153.4, 136.8, 133.2, 128.3, 127.1, 125.7, 125.0, 117.3, 114.5, 114.3, 112.9, 100.0, 73.0; HRMS: calcd for $C_{17}H_{10}BrClO_5$ $[M+H]^+$ 408.9478, found 408.9481.

4-hydroxy-6-methyl-3-(2-phenoxyacetyl)-2*H*-pyran-2-one (**II1**): light yellow solid; yield 53.1%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 15.63 (s, 1H), 7.53 – 7.16 (m, 2H), 7.06 – 6.79 (m, 3H), 6.02 (d, J = 0.5 Hz, 1H), 5.34 (s, 2H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 200.8, 180.7, 169.9, 160.9, 157.9, 129.6, 121.6, 114.7, 101.4, 98.5, 71.8, 20.9; HRMS: calcd for $C_{14}H_{12}O_5$ $[M+H]^+$ 261.0757, found 261.0760.

3-(2-(2-chlorophenoxy)acetyl)-4-hydroxy-6-methyl-2*H*-pyran-2-one (**II2**): white solid; yield 57.2%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 15.52 (s, 1H), 7.41 (dd, J = 7.9, 1.6 Hz, 1H), 7.23 – 7.15 (m, 1H), 6.95 (td, J = 7.7, 1.3 Hz, 1H), 6.86 (dd, J = 8.3, 1.3 Hz, 1H), 6.03 (d, J = 0.7 Hz, 1H), 5.41 (s, 2H), 2.33 (d, J = 0.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 199.9, 180.7, 170.0, 160.9, 153.5, 130.6, 127.7, 123.1, 122.3, 113.8, 101.4, 98.4, 72.5, 20.9; HRMS: calcd for $C_{14}H_{11}ClO_5$ $[M+H]^+$ 295.0368, found 295.0370.

3-(2-(3-chlorophenoxy)acetyl)-4-hydroxy-6-methyl-2*H*-pyran-2-one (**II3**): white solid; yield 48.1%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 15.49 (s, 1H), 7.22 (t, J = 8.1 Hz, 1H), 7.00 – 6.92 (m, 2H), 6.84 (ddd, J = 8.4, 2.5, 0.8 Hz, 1H), 6.03 (d, J = 0.8 Hz, 1H), 5.32 (s, 2H), 2.34 (d, J = 0.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 200.1, 180.7, 170.1, 160.9, 158.6, 134.9, 130.4, 121.8, 115.2, 113.2, 101.4, 98.4, 71.8, 20.9; HRMS: calcd for $C_{14}H_{11}ClO_5$ $[M+H]^+$ 295.0368, found 295.0371.

3-(2-(4-chlorophenoxy)acetyl)-4-hydroxy-6-methyl-2*H*-pyran-2-one (**II4**): light yellow solid; yield 56.8%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 15.51 (s, 1H), 7.43 – 7.06 (m, 2H), 7.01 – 6.71 (m, 2H), 6.03 (d, J = 0.7 Hz, 1H), 5.31 (s, 2H), 2.33 (d, J = 0.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 200.3, 180.7, 170.1, 160.9, 156.5, 129.5, 126.5, 116.1, 101.4, 98.4, 72.0, 20.9; HRMS: calcd for $C_{14}H_{11}ClO_5$ $[M+H]^+$ 295.0368, found 295.0370.

4-hydroxy-3-(2-(2-methylphenoxy)acetyl)-6-methyl-2*H*-pyran-2-one (**II5**): white solid; yield 41.0%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 15.70 (s, 1H), 7.18 (dd, *J* = 7.4, 0.7 Hz, 1H), 7.15 – 7.09 (m, 1H), 6.90 (td, *J* = 7.4, 0.7 Hz, 1H), 6.73 (d, *J* = 8.1 Hz, 1H), 6.01 (d, *J* = 0.7 Hz, 1H), 5.36 (s, 2H), 2.34 (s, 3H), 2.32 (d, *J* = 0.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 201.2, 180.7, 169.8, 160.9, 156.1, 131.0, 127.2, 126.7, 121.3, 111.5, 101.4, 98.5, 72.1, 20.8, 16.3; HRMS: calcd for $C_{15}H_{14}O_5$ $[M+H]^+$ 275.0914, found 275.0917.

4-hydroxy-3-(2-(3-methylphenoxy)acetyl)-6-methyl-2*H*-pyran-2-one (**II6**): white solid; yield 46.9%; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 15.27 (s, 1H), 7.14 (t, *J* = 8.0 Hz, 1H), 6.75 (d, *J* = 7.3 Hz, 2H), 6.70 (dd, *J* = 7.4, 2.0 Hz, 1H), 6.39 (d, *J* = 0.7 Hz, 1H), 5.27 (s, 2H), 2.31 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 200.7, 179.9, 170.9, 160.9, 158.3, 139.5, 129.6, 122.1, 115.5, 111.9, 101.4, 99.0, 71.6, 21.5, 20.6; HRMS: calcd for $C_{15}H_{14}O_5$ $[M+H]^+$ 275.0914, found 275.0916.

4-hydroxy-3-(2-(4-methylphenoxy)acetyl)-6-methyl-2H-pyran-2-one (**II7**): light yellow solid; yield 47.6%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 15.27 (s, 1H), 7.14 (t, *J* = 8.0 Hz, 1H), 6.75 (d, *J* = 7.3 Hz, 2H), 6.70 (dd, *J* = 7.4, 2.0 Hz, 1H), 6.39 (d, *J* = 0.7 Hz, 1H), 5.27 (s, 2H), 2.31 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 201.1, 180.7, 169.9, 160.9, 155.8, 130.9, 130.0, 114.6, 101.4, 98.5, 71.9, 20.8, 20.5; HRMS: calcd for $C_{15}H_{14}O_5$ $[M+H]^+$ 275.0914, found 275.0916.

3-(2-(2-methoxyphenoxy)acetyl)-4-hydroxy-6-methyl-2*H*-pyran-2-one (**II8**): white solid; yield 44.1%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 15.68 (s, 1H), 7.01 – 6.91 (m, 2H), 6.86 (q, *J* = 7.8 Hz, 2H), 6.01 (s, 1H), 5.39 (s, 2H), 3.91 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 200.7, 180.6, 169.8, 160.9, 149.4, 147.2, 122.1, 120.6, 113.8, 111.9, 101.4, 98.4, 72.5, 55.9, 20.8; HRMS: calcd for $C_{15}H_{14}O_6$ $[M+H]^+$ 291.0863, found 291.0865.

3-(2-(3-methoxyphenoxy)acetyl)-4-hydroxy-6-methyl-2*H*-pyran-2-one (**II9**): white solid; yield 43.3%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 15.61 (s, 1H), 7.21 (t, *J* = 8.3 Hz, 1H), 6.56 (t, *J* = 7.1 Hz, 3H), 6.04 (s, 1H), 5.34 (s, 2H), 3.81 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 200.7, 180.7, 160.9, 159.1, 130.0, 107.3, 106.5, 101.4, 98.5, 71.8, 55.3, 20.8; HRMS: calcd for $C_{15}H_{14}O_6$ $[M+H]^+$ 291.0863, found 291.0866.

3-(2-(4-methoxyphenoxy)acetyl)-4-hydroxy-6-methyl-2*H*-pyran-2-one (**II10**): white solid; yield 40.7%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 15.63 (s, 1H), 6.88 (d, *J* = 8.8 Hz, 2H), 6.81 (d, J = 8.8 Hz, 2H), 5.99 (s, 1H), 5.24 (s, 2H), 3.74 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 201.1, 180.6, 169.9, 160.8, 154.3, 152.1, 115.8, 114.6, 101.3, 98.4, 72.6, 55.6, 20.8; HRMS: calcd for $C_{15}H_{14}O_6$ $[M+H]^+$ 291.0863, found 291.0865.

3-(2-(2, 3-dichlorophenoxy)acetyl)-4-hydroxy-6-methyl-2*H*-pyran-2-one (**II11**): white solid; yield 51.6%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 15.42 (s, 1H), 7.16 – 7.08 (m, 2H), 6.77 (m, 1H), 6.04 (d, *J* = 0.7 Hz, 1H), 5.42 (s, 2H), 2.34 (d, *J* = 0.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 199.4, 180.7, 170.2, 160.9, 154.9 134.2, 127.6, 123.2, 122.2, 111.6, 101.4, 98.4, 72.6, 20.9; HRMS: calcd for $C_{14}H_{10}Cl_2O_5$ $[M+H]^+$ 328.9978, found 328.9981.

3-(2-(2, 4-dichlorophenoxy)acetyl)-4-hydroxy-6-methyl-2*H*-pyran-2-one (**II12**): white solid; yield 60.6%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 15.42 (s, 1H), 7.41 (d, *J* = 2.5 Hz, 1H), 7.16 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.79 (d, *J* = 8.8 Hz, 1H), 6.04 (s, 1H), 5.38 (s, 2H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 199.4, 180.7, 170.2, 160.9, 152.5, 130.3, 127.5, 126.7, 123.9, 114.6, 101.4, 98.4, 72.6, 20.9; HRMS: calcd for $C_{14}H_{10}Cl_2O_5$ $[M+H]^+$ 328.9978, found 328.9980.

3-(2-(2, 5-dichlorophenoxy)acetyl)-4-hydroxy-6-methyl-2*H*-pyran-2-one (**II13**): white solid; yield 53.8%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 15.38 (s, 1H), 7.33 (d, *J* = 8.5 Hz, 1H), 6.93 (dd, *J* = 8.5, 2.2 Hz, 1H), 6.83 (d, *J* = 2.2 Hz, 1H), 6.04 (d, *J* = 0.7 Hz, 1H), 5.40 (s, 2H), 2.34 (d, *J* = 0.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 199.1, 180.7, 170.3, 160.9, 154.0, 133.0, 131.1, 122.30, 121.6, 114.2, 101.4, 98.4, 72.5, 20.9; HRMS: calcd for $C_{14}H_{10}Cl_2O_5$ $[M+H]^+$ 328.9978, found 328.9981.

3-(2-(3, 5-dichlorophenoxy)acetyl)-4-hydroxy-6-methyl-2*H*-pyran-2-one (**II14**): white solid; yield 53.3%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 15.37 (s, 1H), 7.00 (t, *J* = 1.7 Hz, 1H), 6.84 (d, *J* = 1.7 Hz, 2H), 6.04 (d, *J* = 0.7 Hz, 1H), 5.31 (s, 2H), 2.34 (d, *J* = 0.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 199.5, 180.7, 170.3, 160.9, 158.9, 135.5, 121.9, 113.9, 101.4, 98.4, 71.9, 20.9; HRMS: calcd for $C_{14}H_{10}Cl_2O_5$ $[M+H]^+$ 328.9978, found 328.9981.

3-(2-(2-chloro-4-fluorophenoxy)acetyl)-4-hydroxy-6-methyl-2*H*-pyran-2-one(**II15**) : light yellow solid; yield 62.7%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 15.48 (s, 1H), 7.17 (dd, $J_{F\text{-}H}$ = 8.0 Hz, J = 2.9 Hz, 1H), 6.94 – 6.83 (m, 2H), 6.03 (s, 1H), 5.36 (s, 2H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 199.8, 180.7, 170.1, 160.9, 157.0 (d, $J_{F\text{-}C}$ = 243.2 Hz), 150.2 (d, $J_{F\text{-}C}$ = 3.0 Hz), 123.9 (d, $J_{F\text{-}C}$ = 10.5 Hz), 117.8 (d, $J_{F\text{-}C}$ = 26.0 Hz), 114.9 (d, $J_{F\text{-}C}$ = 8.8 Hz), 114.1 (d, $J_{F\text{-}C}$ = 22.7 Hz), 101.4, 98.4, 73.3, 20.9; HRMS: calcd for $C_{14}H_{10}ClFO_5$ $[M+H]^+$ 313.0274, found 313.0276.

3-(2-(4-bromo-2-chlorophenoxy)acetyl)-4-hydroxy-6-methyl-2*H*-pyran-2-one (**II16**): white solid; yield 56.6%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 15.41 (s, 1H), 7.55 (d, J = 2.4 Hz, 1H), 7.30 (dd, J = 8.8, 2.4 Hz, 1H), 6.73 (d, J = 8.8 Hz, 1H), 6.03 (d, J = 0.7 Hz, 1H), 5.38 (s, 2H), 2.34 (d, J = 0.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 199.4, 180.67, 170.2, 160.9, 152.9, 133.01, 130.5, 124.3, 114.9, 113.6, 101.4, 98.4, 72.5, 20.9; HRMS: calcd for $C_{14}H_{10}ClBrO_5$ $[M+H]^+$ 372.9473, found 372.9475.

3-(2-(4-fluoro-2-methylphenoxy)acetyl)-4-hydroxy-6-methyl-2*H*-pyran-2-one (**II17**): white solid; yield 52.6%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 15.65 (s, 1H), 6.89 (dd, $J_{F\text{-}H}$ = 8.9 Hz, J = 3.0 Hz, 1H), 6.79 (td, J = 8.5, 3.1 Hz, 1H), 6.67 (dd, $J_{F\text{-}H}$ = 8.9 Hz, J = 4.5 Hz, 1H), 6.02 (d, J = 0.6 Hz, 1H), 5.31 (s, 2H), 2.33 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 201.0, 180.7, 169.9, 160.9, 157.3 (d, $J_{F\text{-}C}$ = 238.8 Hz), 152.3 (d, $J_{F\text{-}C}$ = 2.2 Hz), 129.3 (d, $J_{F\text{-}C}$ = 7.8 Hz), 117.7 (d, $J_{F\text{-}C}$ = 22.8 Hz), 112.7 (d, $J_{F\text{-}C}$ = 8.6 Hz), 112.4 (d, $J_{F\text{-}C}$ = 22.8 Hz), 101.4, 98.4, 72.9, 20.8, 16.4; HRMS: calcd for $C_{15}H_{13}FO_5$ $[M+H]^+$ 293.0820, found 293.0822.

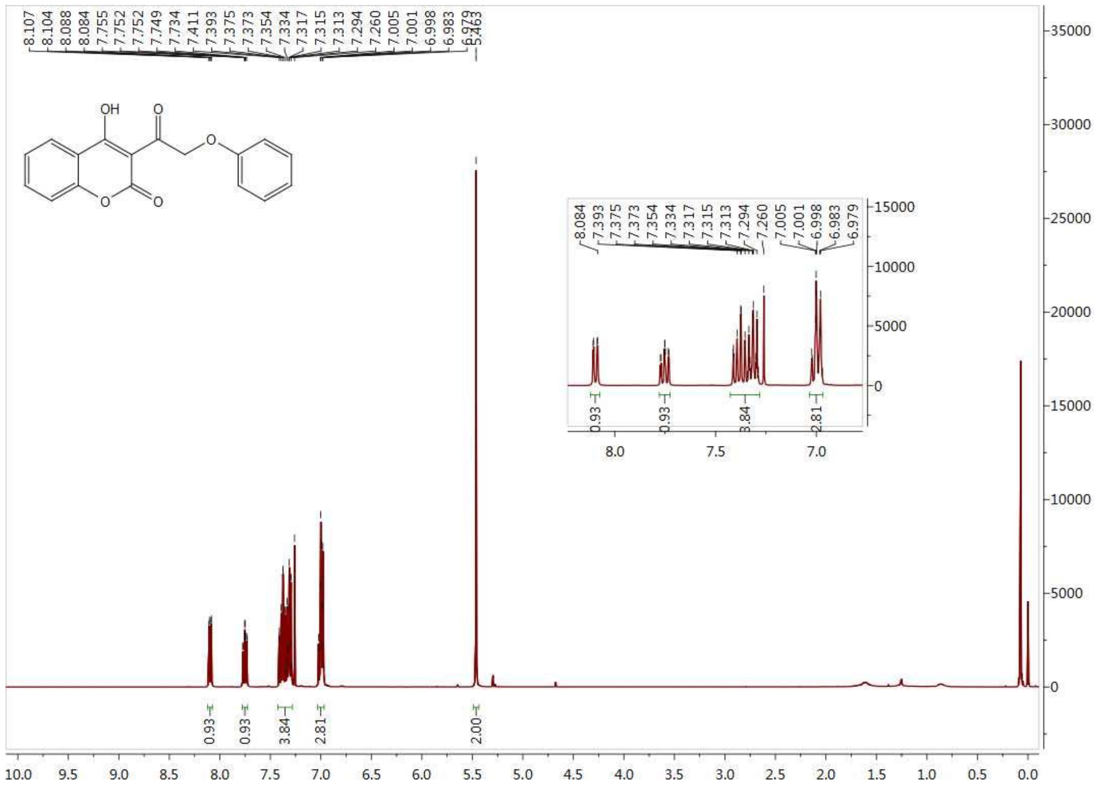
3-(2-(4-chloro-2-methylphenoxy)acetyl)-4-hydroxy-6-methyl-2*H*-pyran-2-one (**II18**): white solid; yield 55.6%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 15.58 (s, 1H), 7.15 (d, J = 2.1 Hz, 1H), 7.07 (dd, J = 8.7, 2.5 Hz, 1H), 6.64 (d, J = 8.7 Hz, 1H), 6.02 (d, J = 0.7 Hz, 1H), 5.33 (s, 2H), 2.33 (d, J = 0.5 Hz, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 200.7, 180.7, 169.9, 160.9, 154.8, 130.8, 129.1, 126.3, 125.9, 112.6, 101.4, 98.4, 72.3, 20.9, 16.2; HRMS: calcd for $C_{15}H_{13}ClO_5$ $[M+H]^+$ 309.0524, found 309.0527.

3-(2-(4-bromo-2-methylpenoxy)acetyl)-4-hydroxy-6-methyl-2*H*-pyran-2-one (**II19**): white solid; yield 57.6%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 15.57 (s, 1H), 7.31 –

7.28 (m, 1H), 7.21 (dd, *J* = 8.6, 2.4 Hz, 1H), 6.59 (d, *J* = 8.7 Hz, 1H), 6.02 (d, *J* = 0.7 Hz, 1H), 5.33 (s, 2H), 2.33 (d, *J* = 0.5 Hz, 3H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 200.6, 180.7, 170.0, 160.9, 155.3, 133.6, 129.6, 129.3, 113.4, 113.0, 101.4, 98.4, 72.2, 20.9, 16.1; HRMS: calcd for $C_{15}H_{13}BrO_5$ $[M+H]^+$ 353.0019, found 353.0021.

3-(2-(2-bromo-4-fluoropenoxy)acetyl)-4-hydroxy-6-methyl-2*H*-pyran-2-one (**II20**): white solid; yield 50.2%; ^1H NMR (400 MHz, $CDCl_3$) *δ*: 15.48 (s, 1H), 7.33 (dd, $J_{F\text{-}H}$ = 7.8 Hz, *J* = 3.0 Hz, 1H), 6.99- 6.94 (m, 1H), 6.81 (dd, $J_{F\text{-}H}$ = 9.1 Hz, *J* = 4.7 Hz, 1H), 6.03 (d, *J* = 0.7 Hz, 1H), 5.36 (s, 2H), 2.33 (d, *J* = 0.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 199.7, 180.7, 170.1, 160.9, 157.2 (d, *J* = 244.1 Hz), 151.2 (d, $J_{F\text{-}C}$ = 2.7 Hz), 120.7 (d, $J_{F\text{-}C}$ = 25.8 Hz), 114.7 (d, $J_{F\text{-}C}$ = 22.6 Hz), 114.5 (d, $J_{F\text{-}C}$ = 8.4 Hz), 112.6 (d, $J_{F\text{-}C}$ = 9.8 Hz), 101.4, 98.4, 73.3, 20.9; HRMS: calcd for $C_{14}H_{10}BrFO_5$ $[M+H]^+$ 356.9768, found 356.9771.

3-(2-(2-bromo-4-chloropenoxy)acetyl)-4-hydroxy-6-methyl-2*H*-pyran-2-one (**II21**): white solid; yield 51.9%; ^1H NMR (400 MHz, $CDCl_3$) *δ*: 15.42 (s, 1H), 7.58 (d, *J* = 2.5 Hz, 1H), 7.21 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.75 (d, *J* = 8.8 Hz, 1H), 6.03 (d, *J* = 0.8 Hz, 1H), 5.38 (s, 2H), 2.33 (d, *J* = 0.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 199.4, 180.7, 170.2, 160.9, 153.4, 133.2, 128.2, 127.0, 114.2, 112.8, 101.4, 98.4, 72.7, 20.9; HRMS: calcd for $C_{14}H_{10}ClFO_5$ $[M+H]^+$ 313.0274, found 313.0276.



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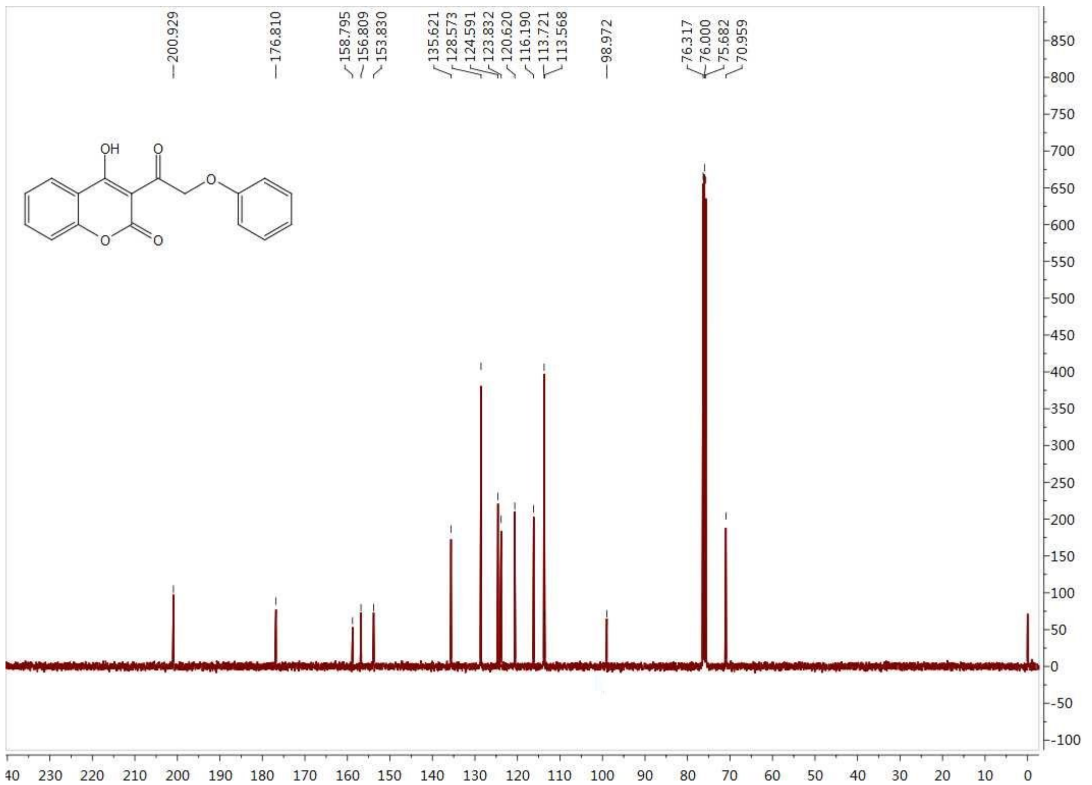

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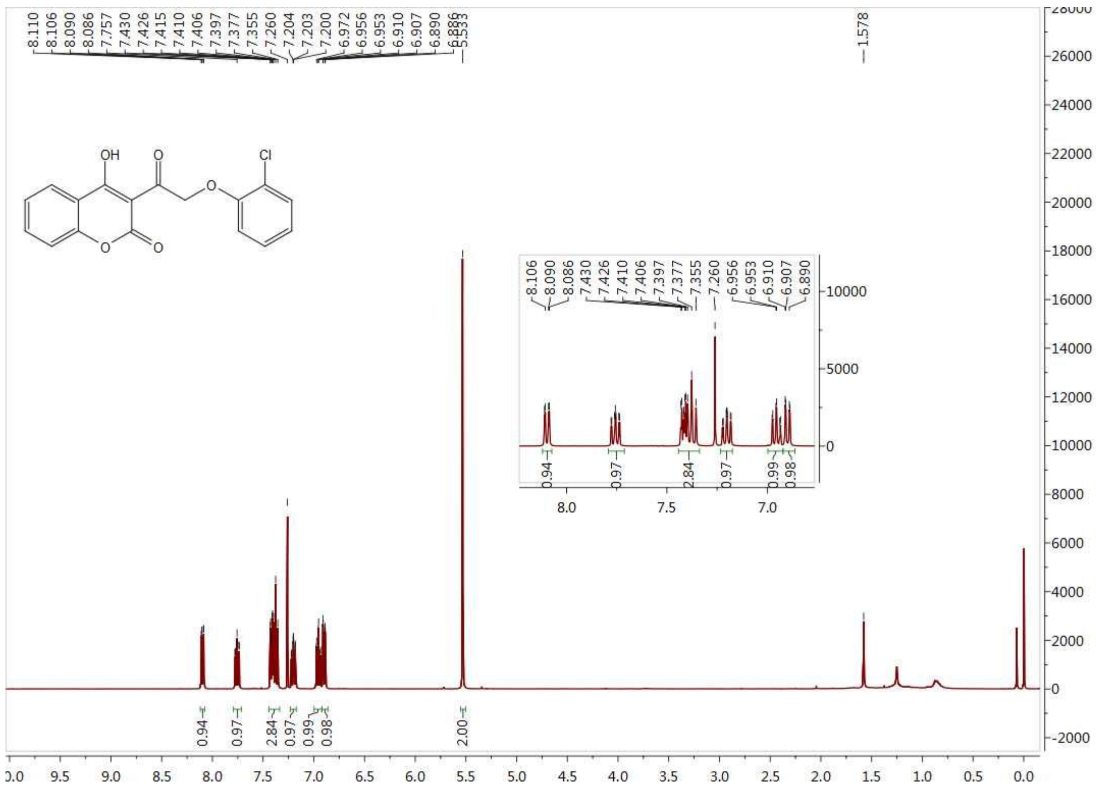
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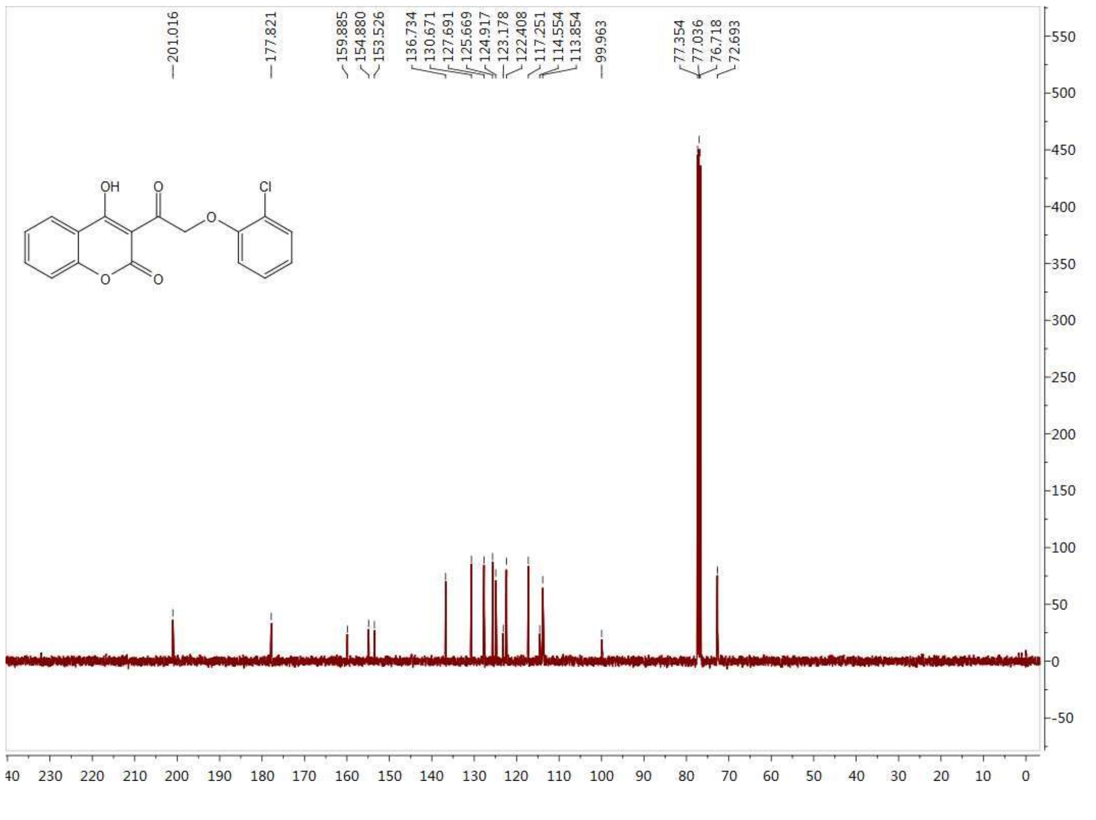
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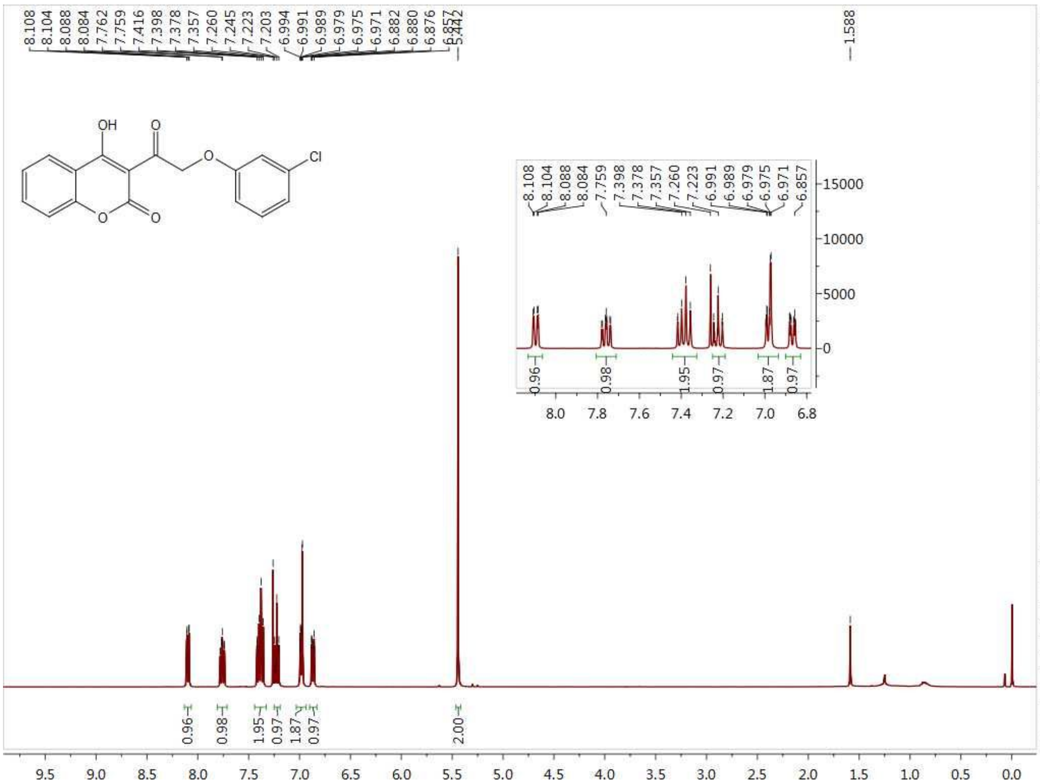
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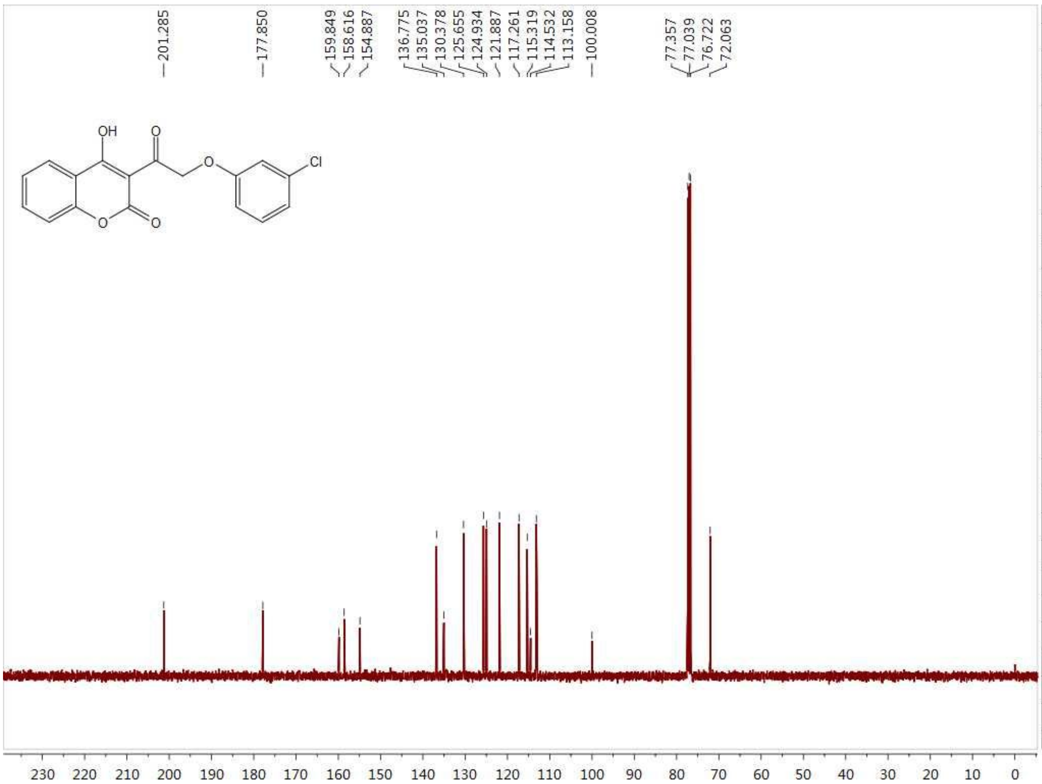
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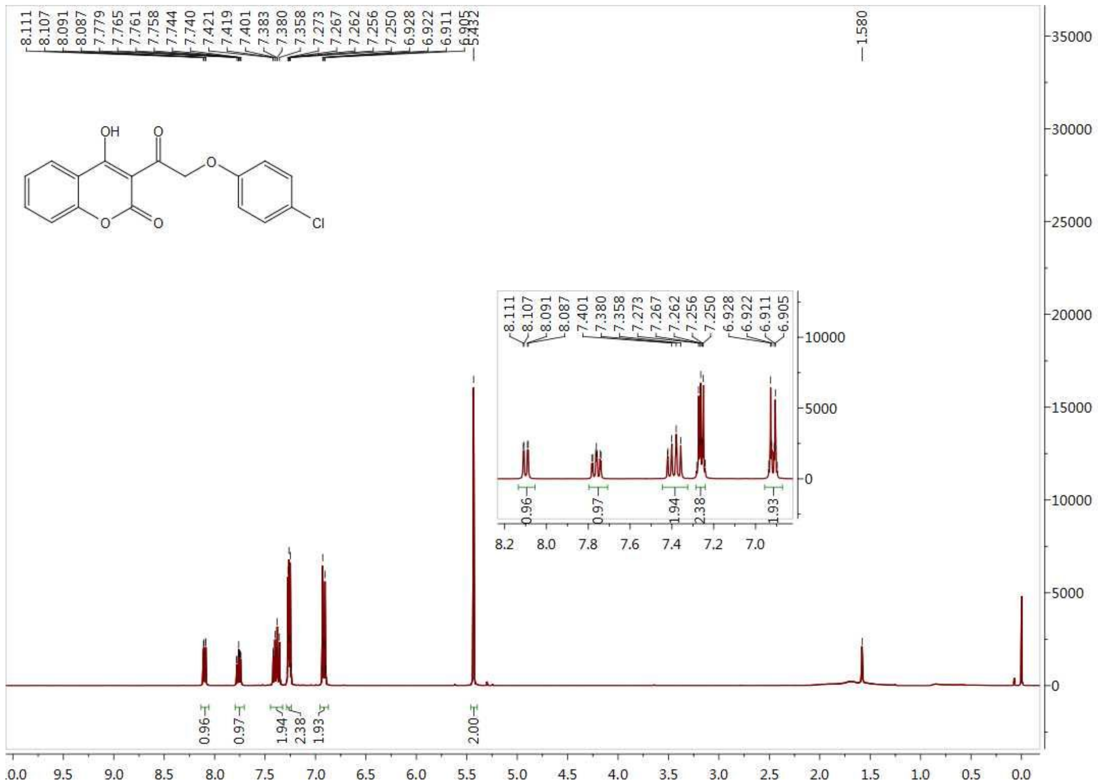
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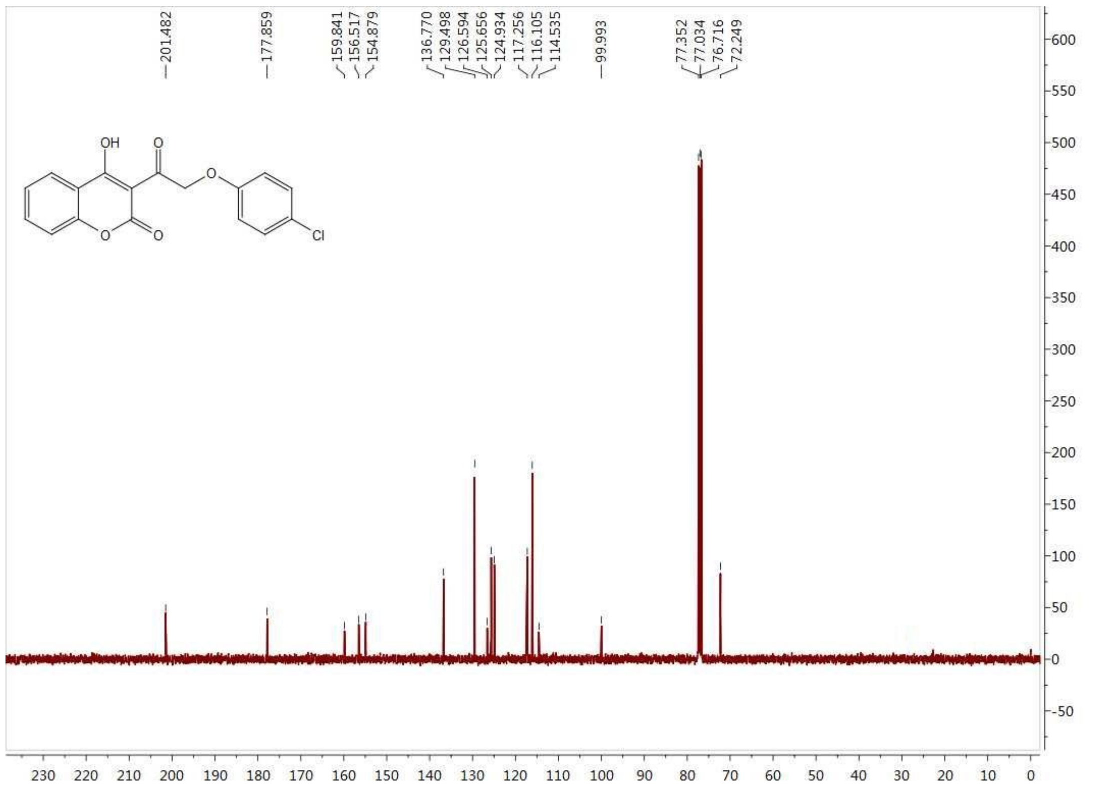
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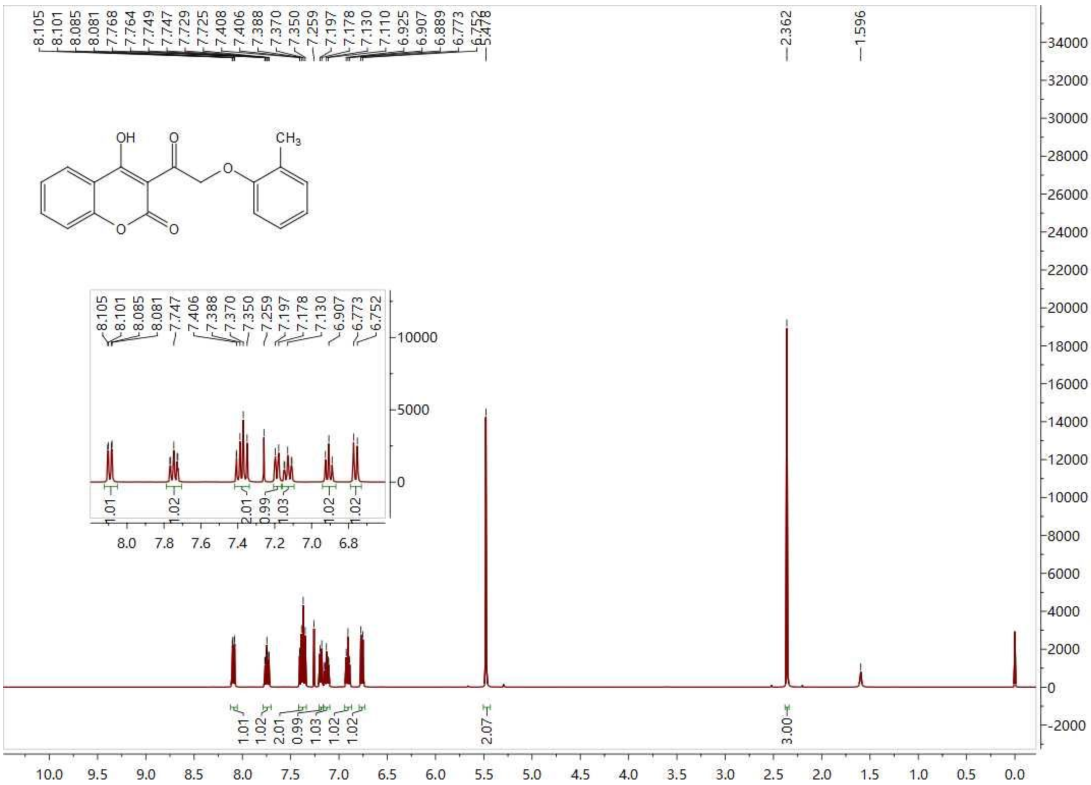

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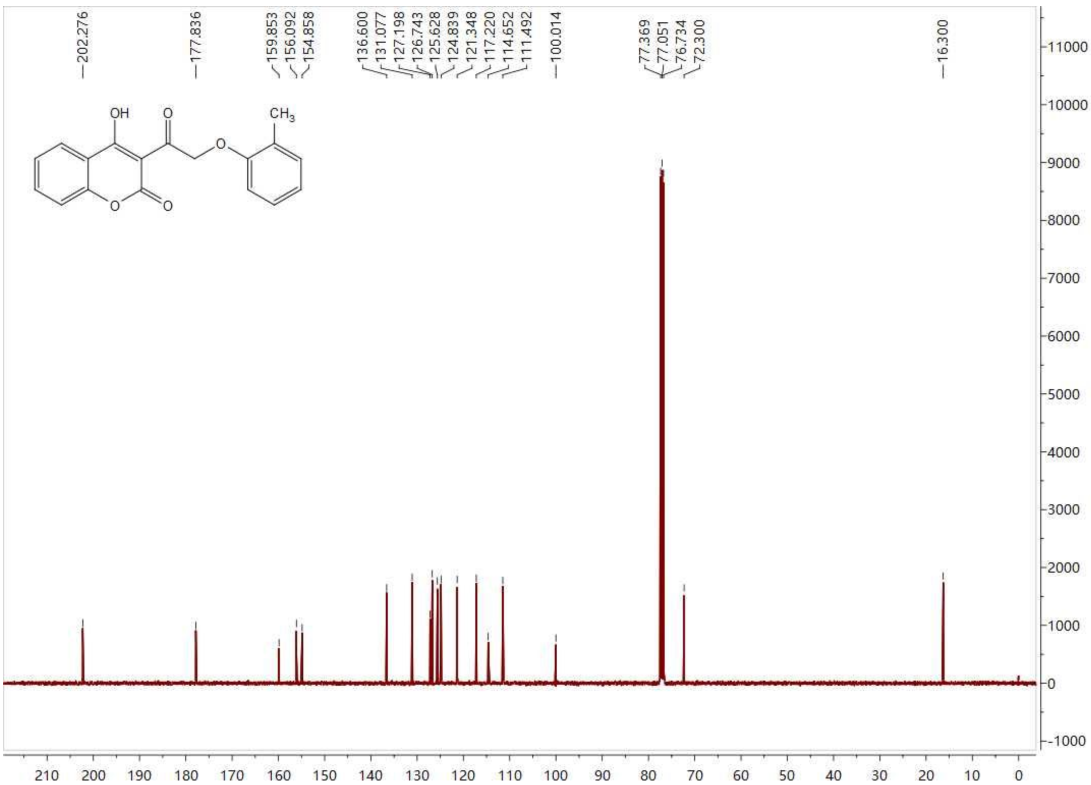

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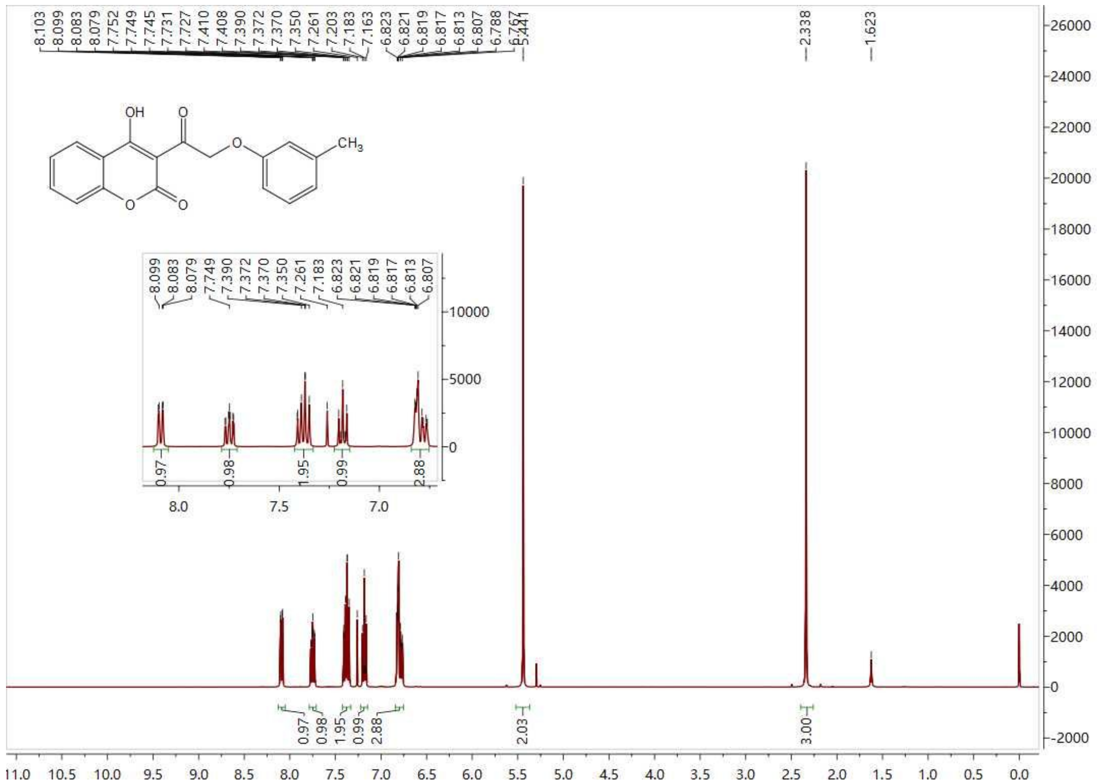
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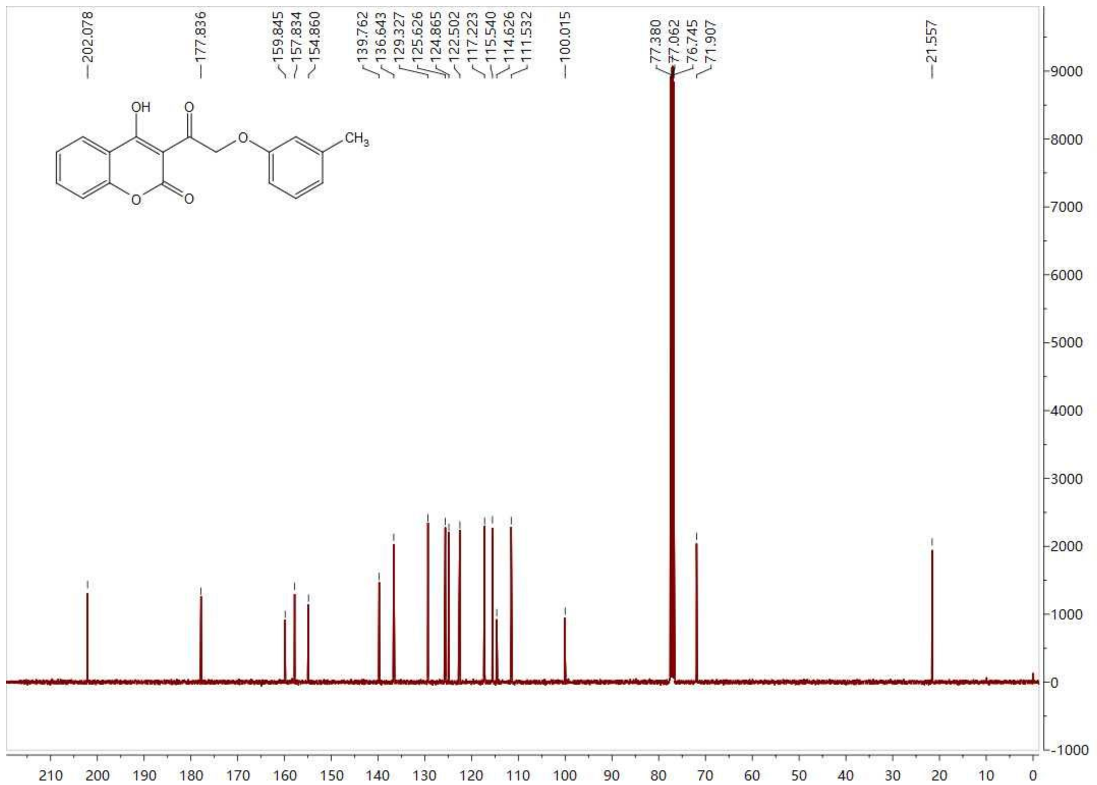
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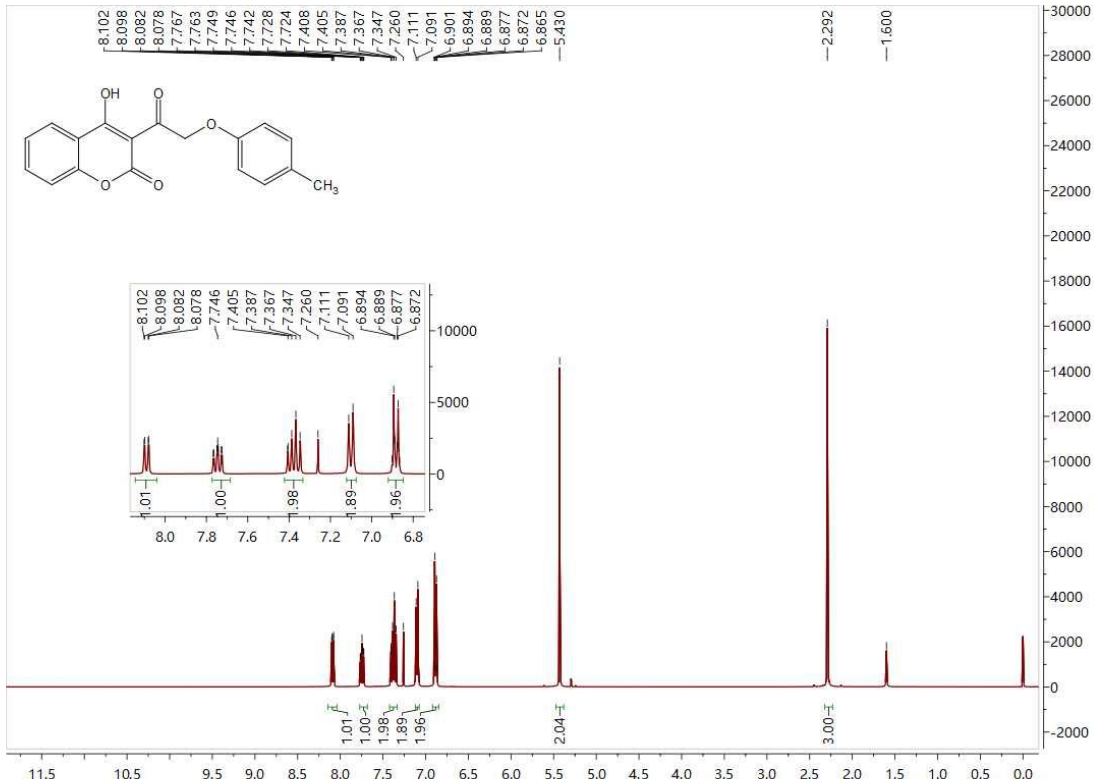

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7.405
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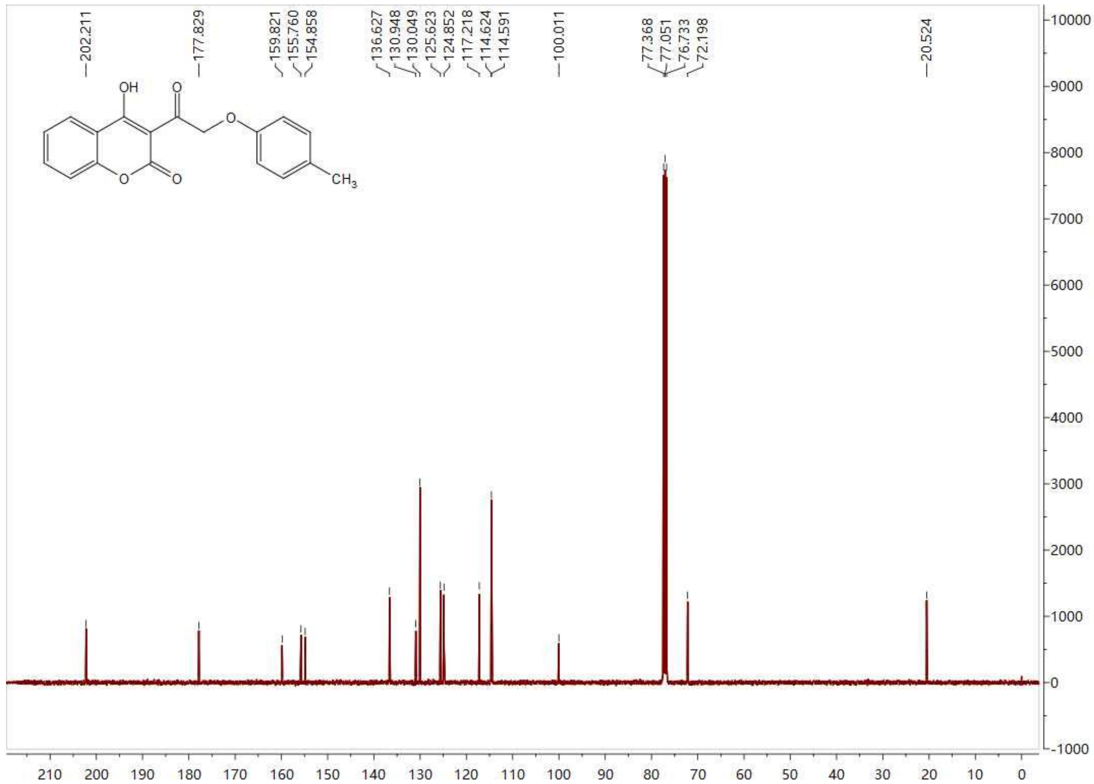

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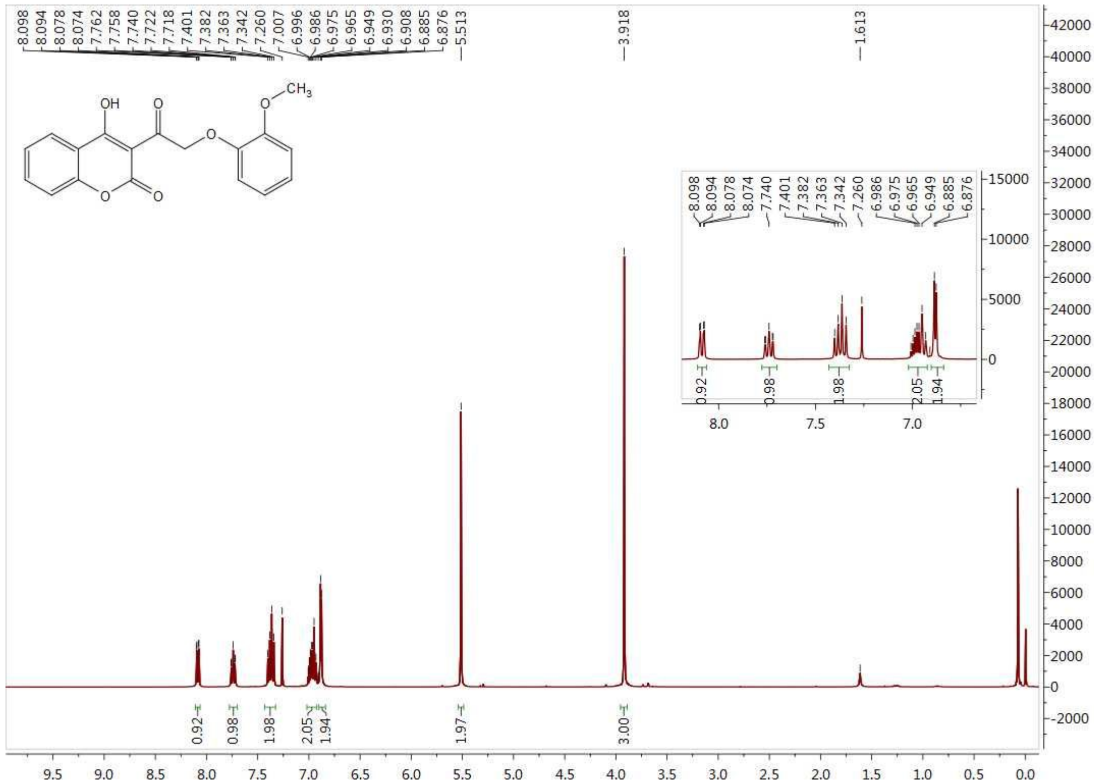
O
CH3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6.965
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6.876
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3.918
1.613
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O
O
CH3
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1.98
2.05
1.94
1.97
3.00
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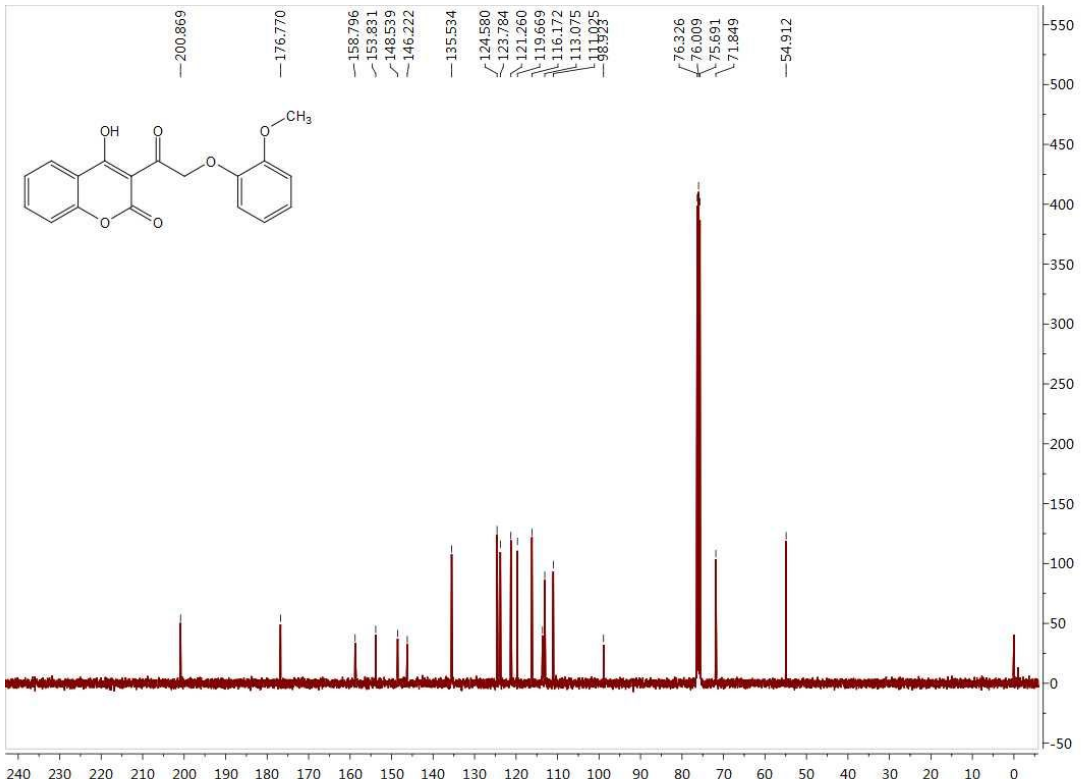
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OH
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O
O
CH3
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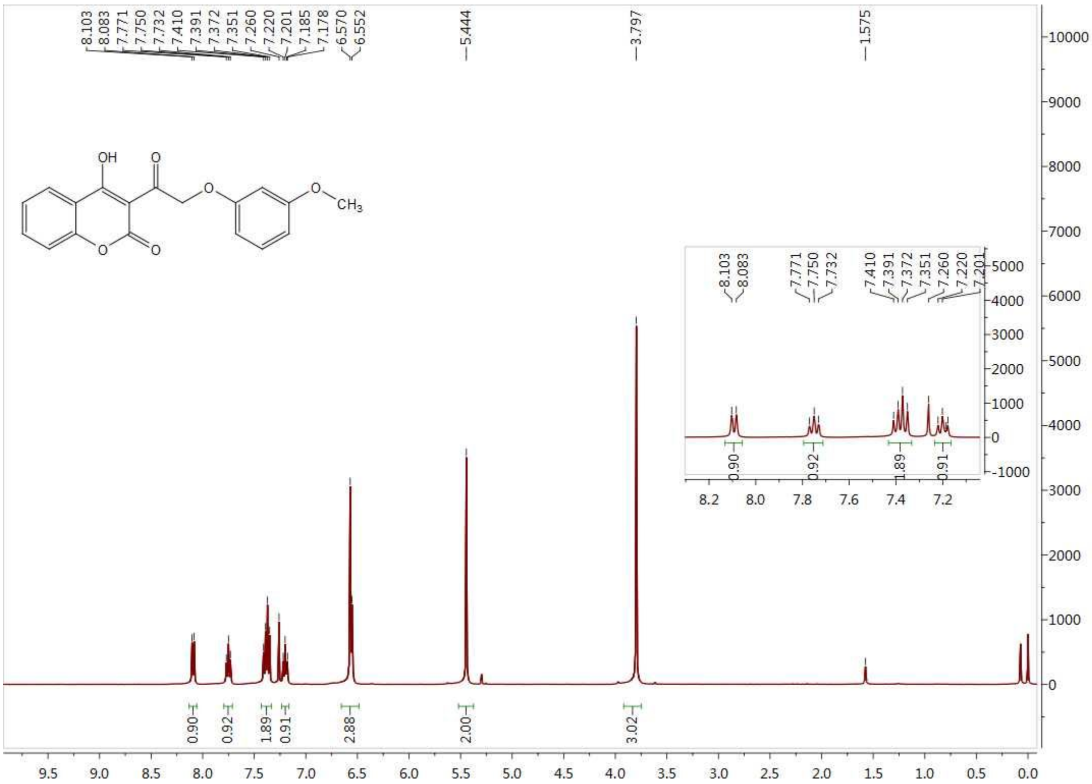
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7.178
6.570
6.552
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1.575
OH
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CH3
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1.89
0.91
2.88
2.00
3.02
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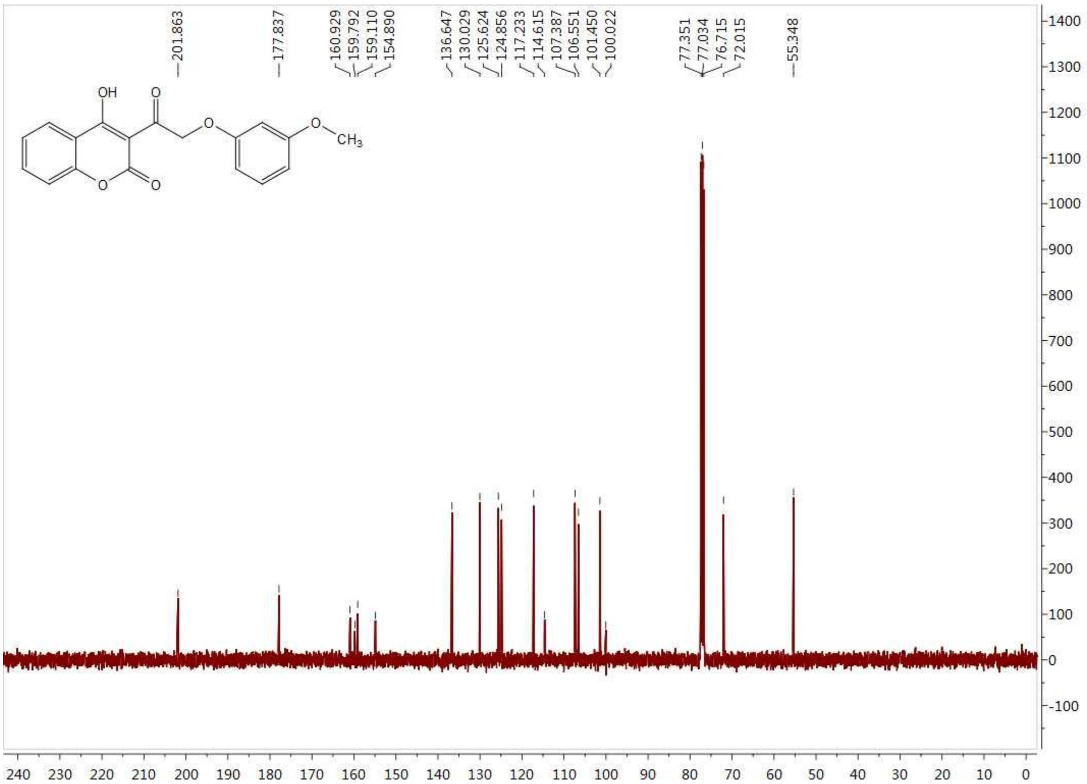
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106.551
101.450
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77.351
77.034
76.715
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O
O
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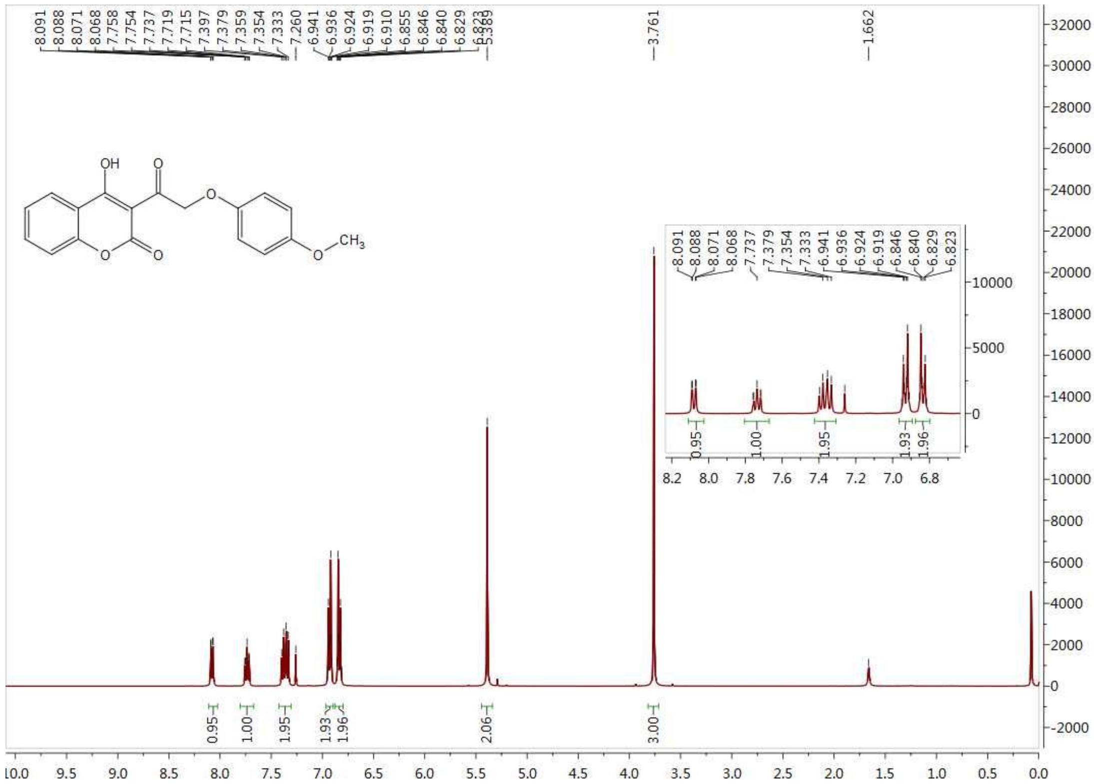
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6.829
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5.389
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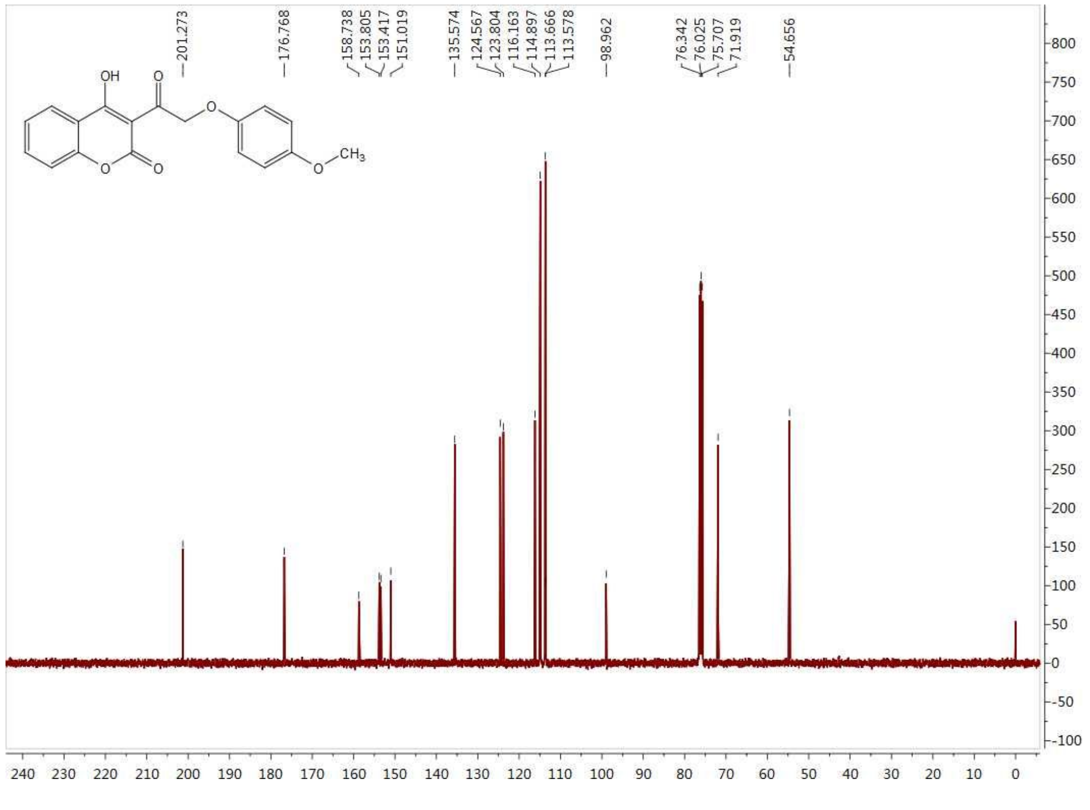
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75.707
71.919
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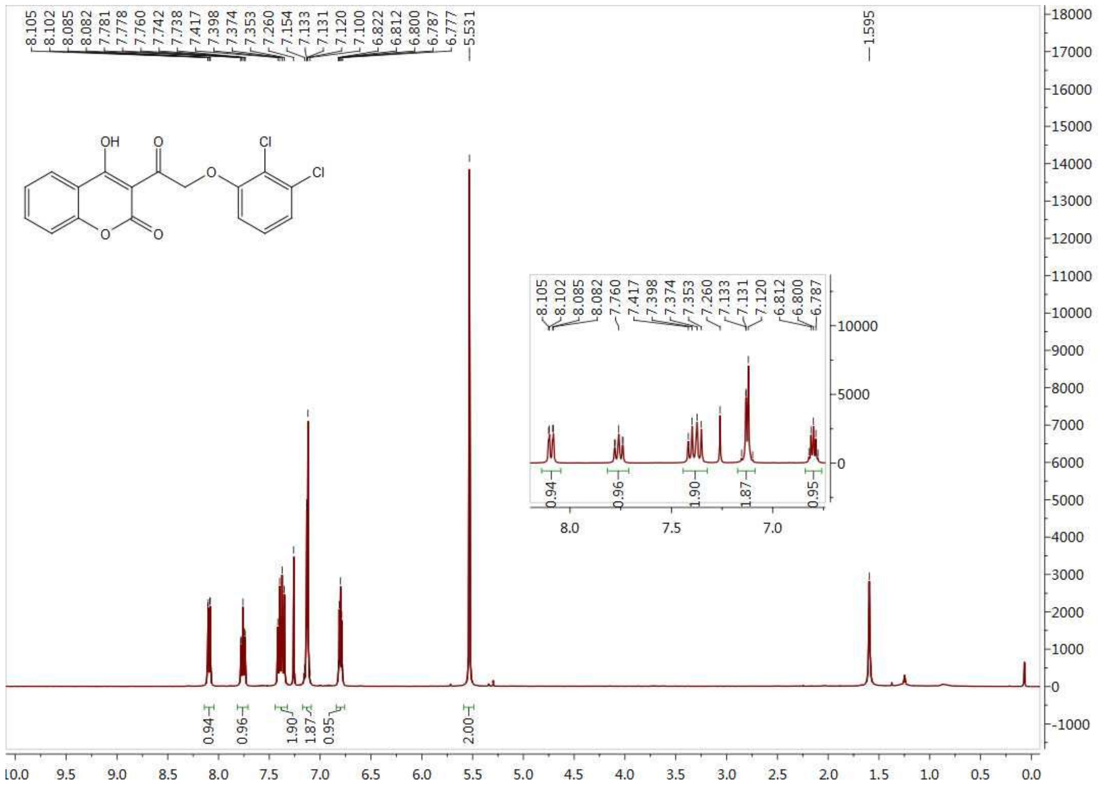
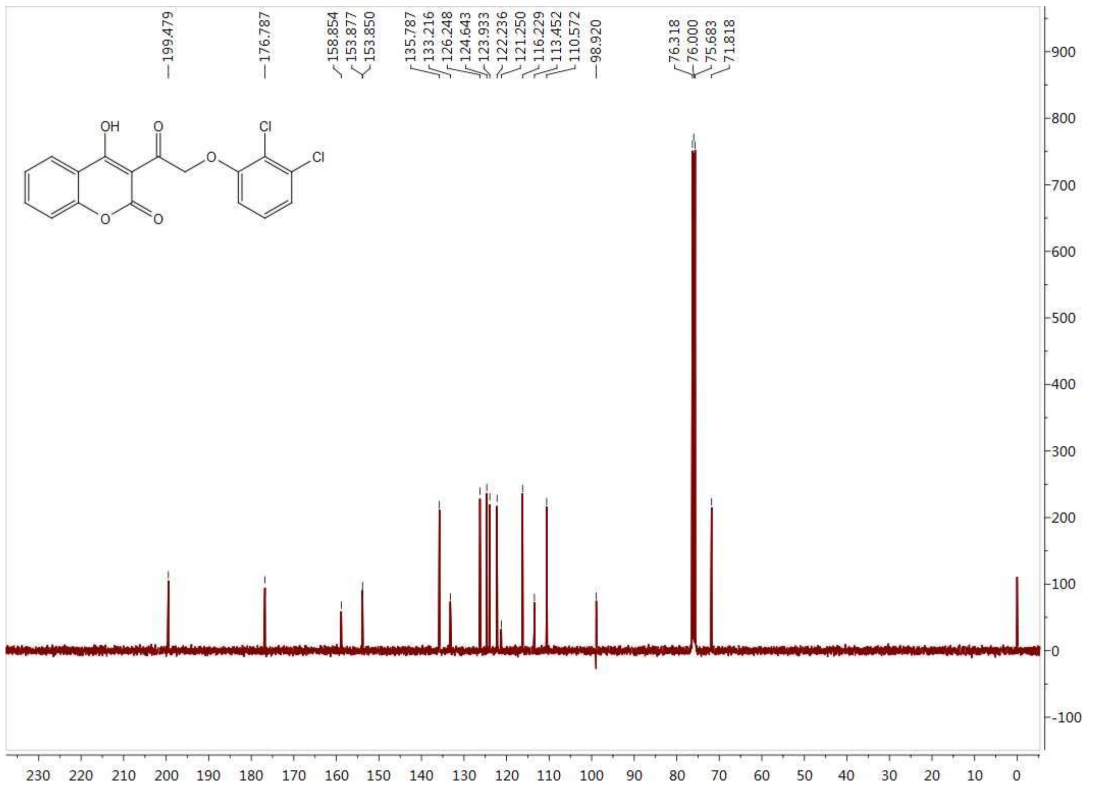
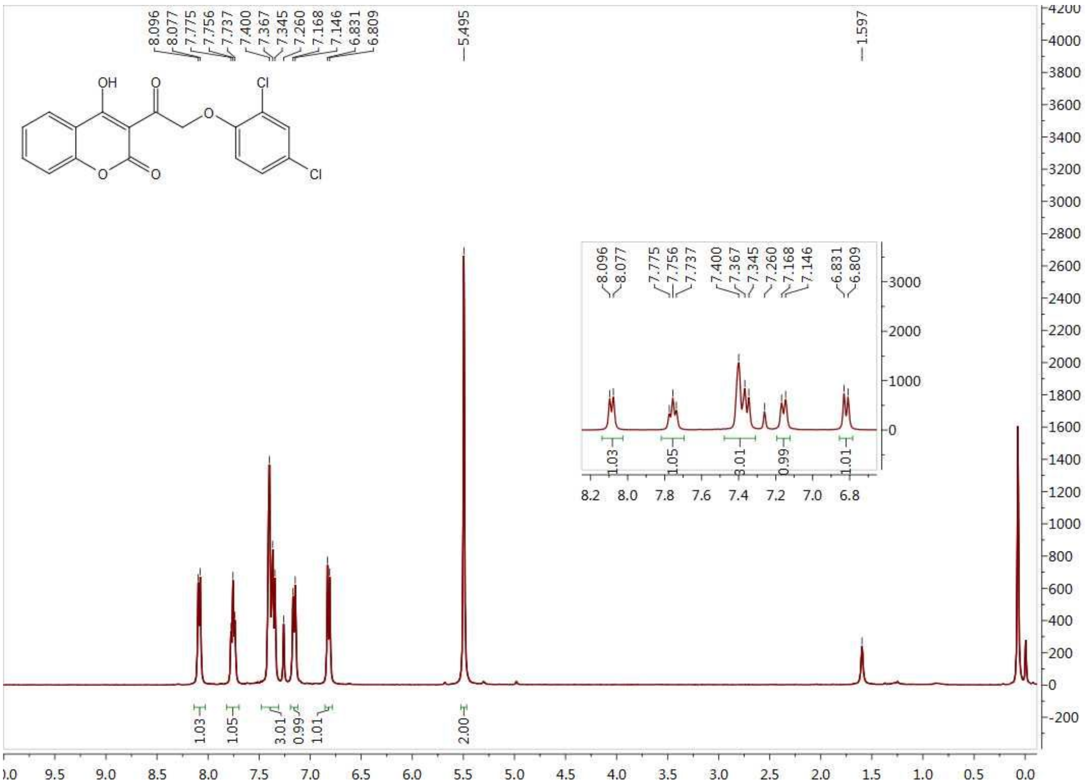
O
O
O
O
CH3

383 

384 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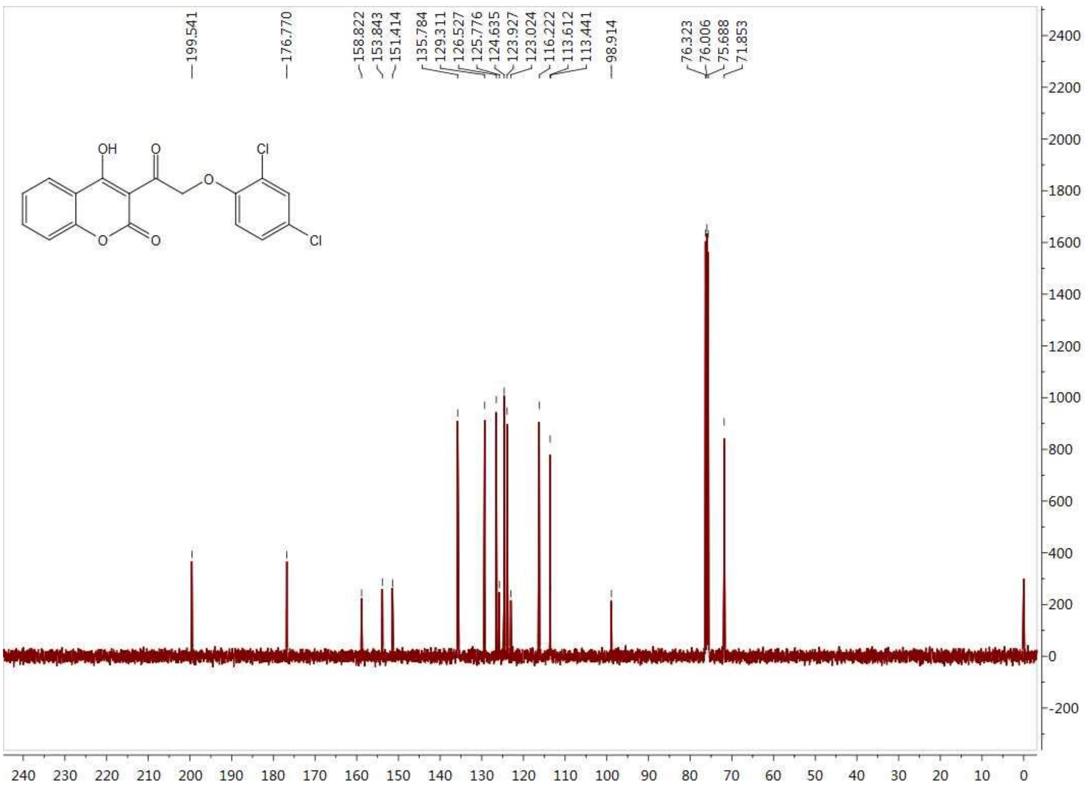
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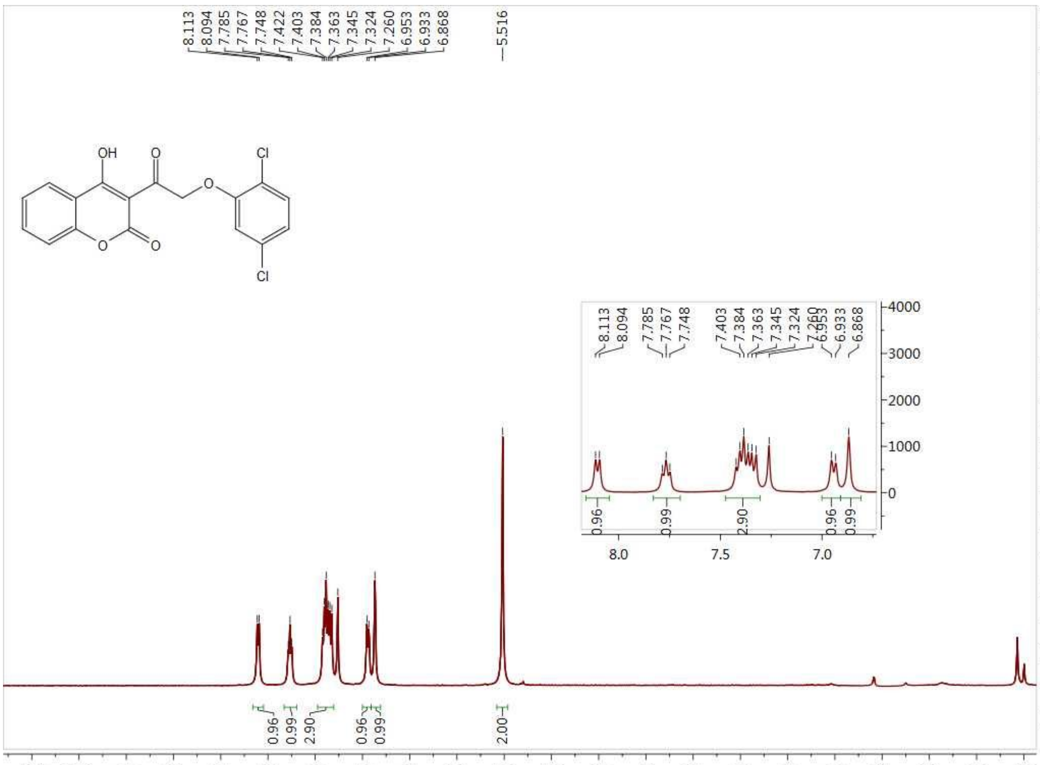
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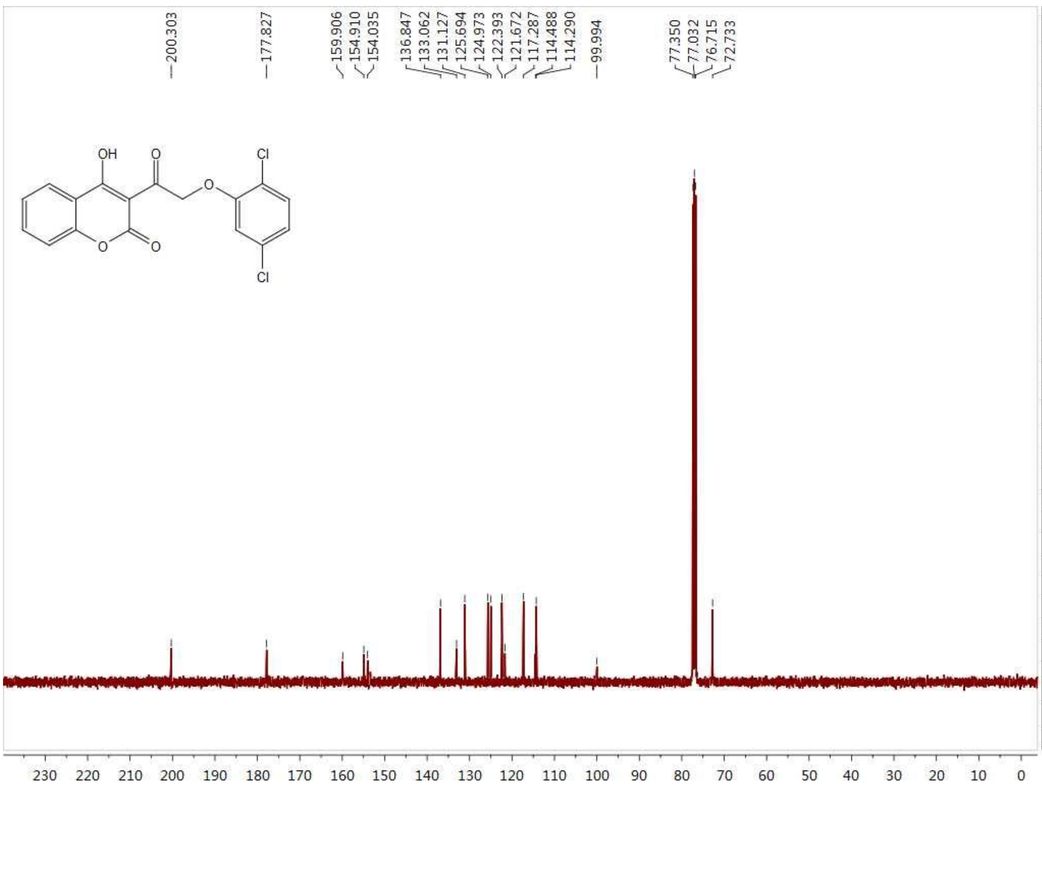
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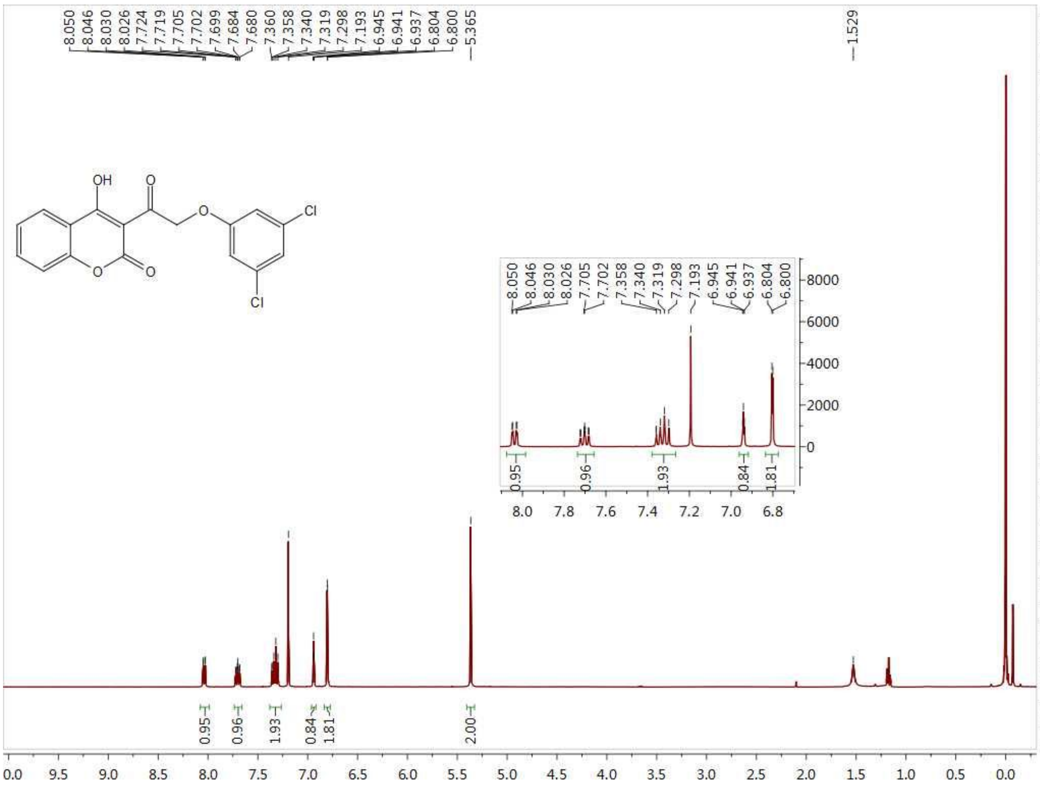
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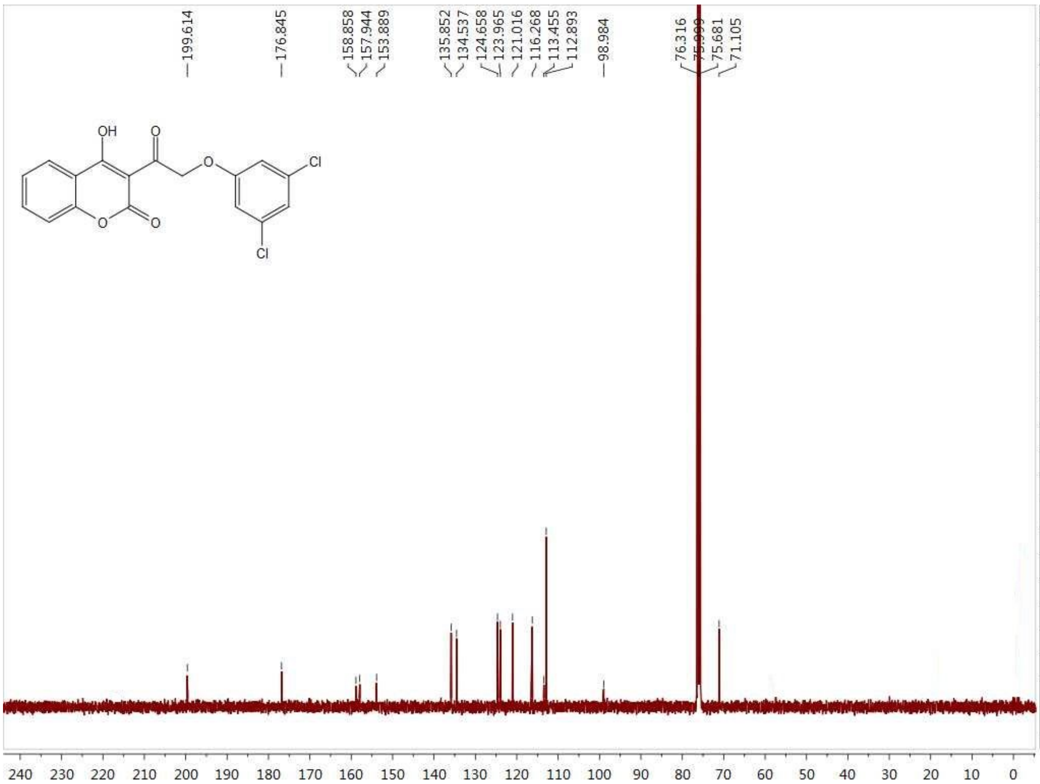
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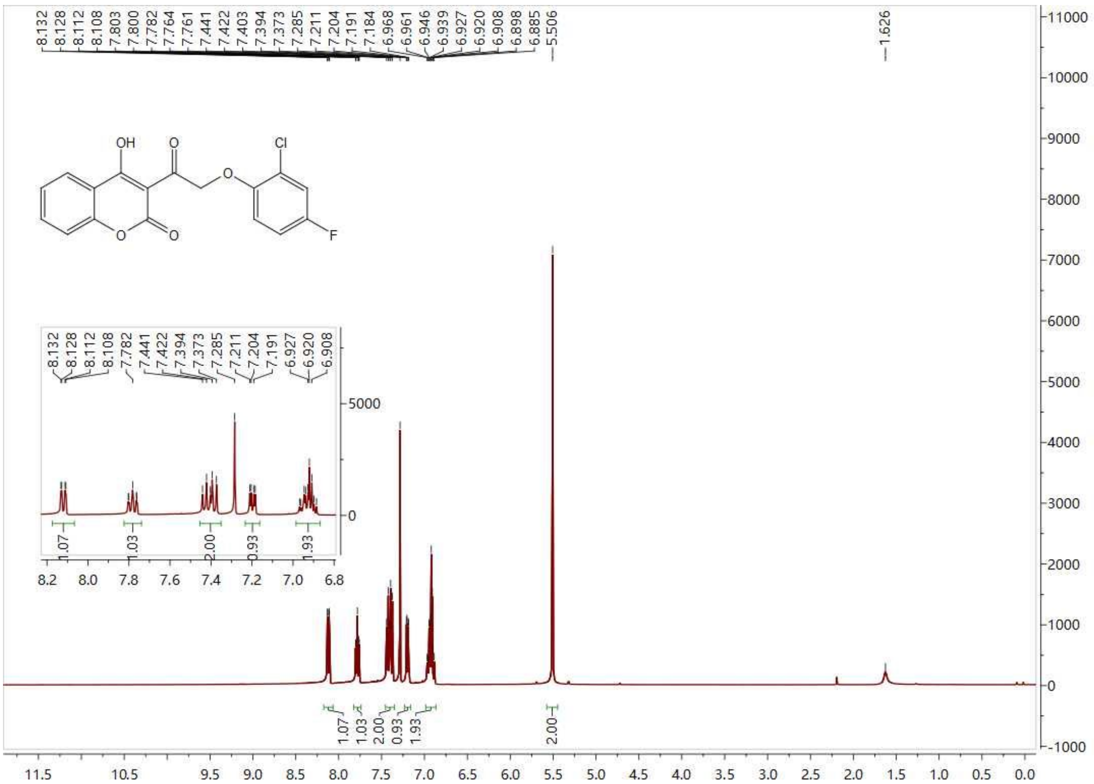
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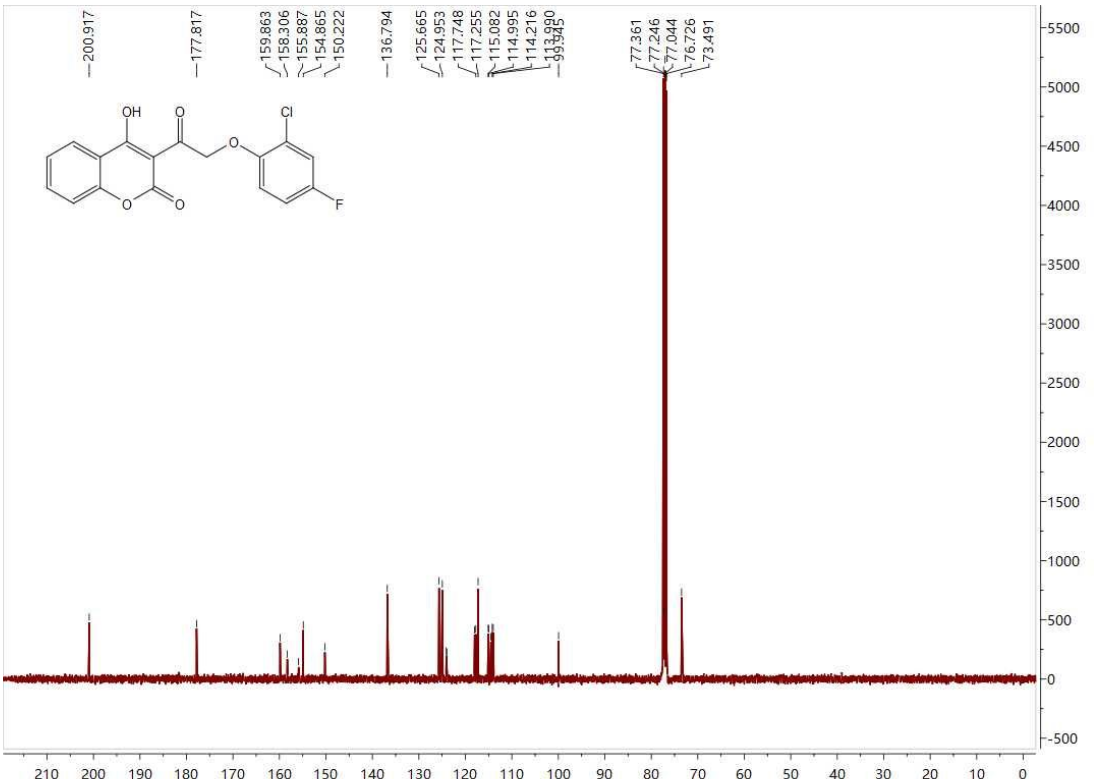
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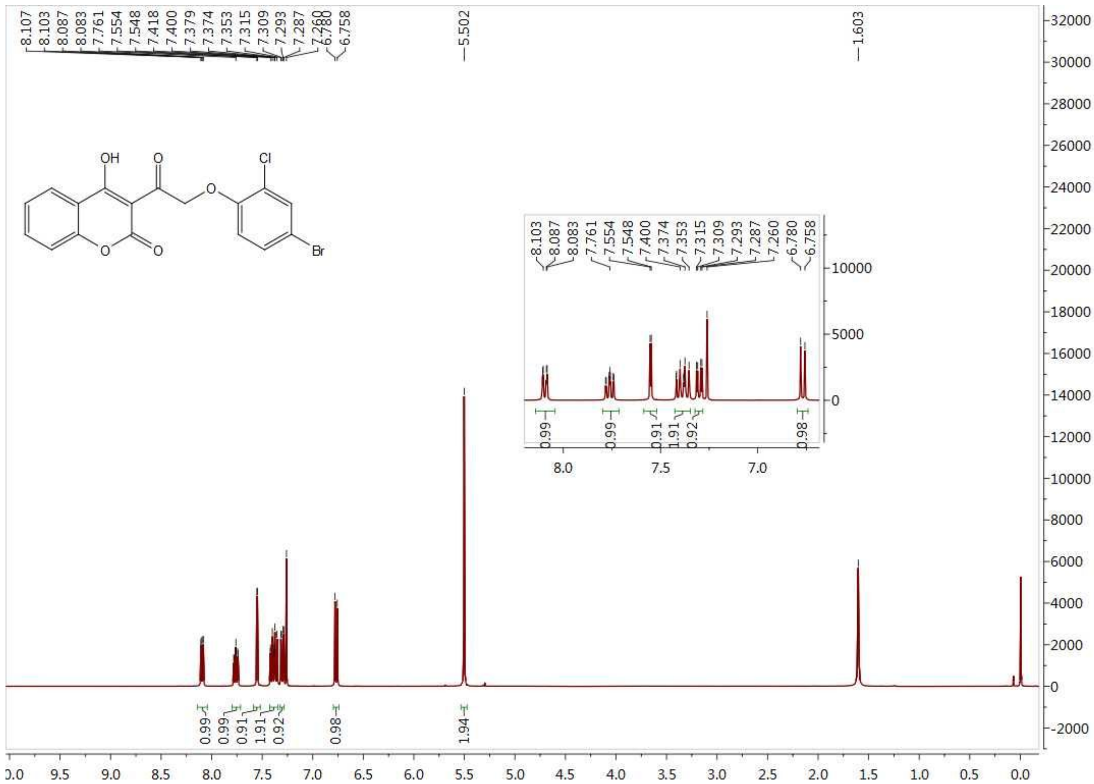
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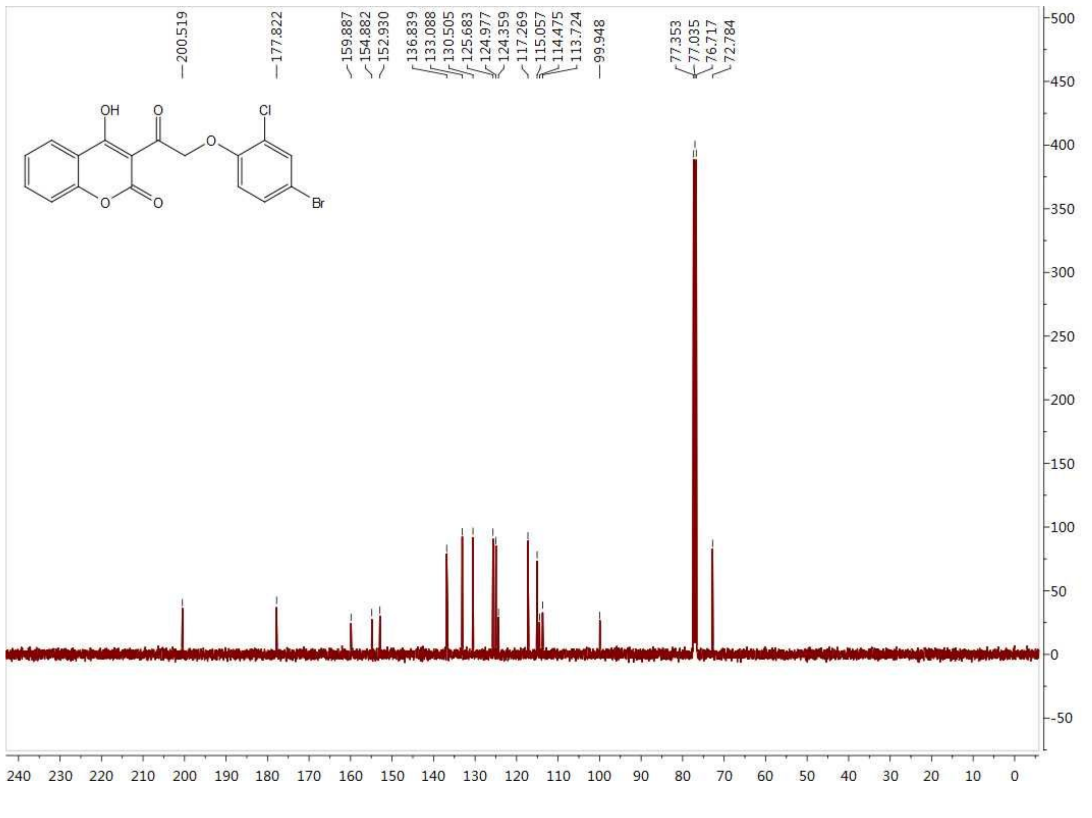
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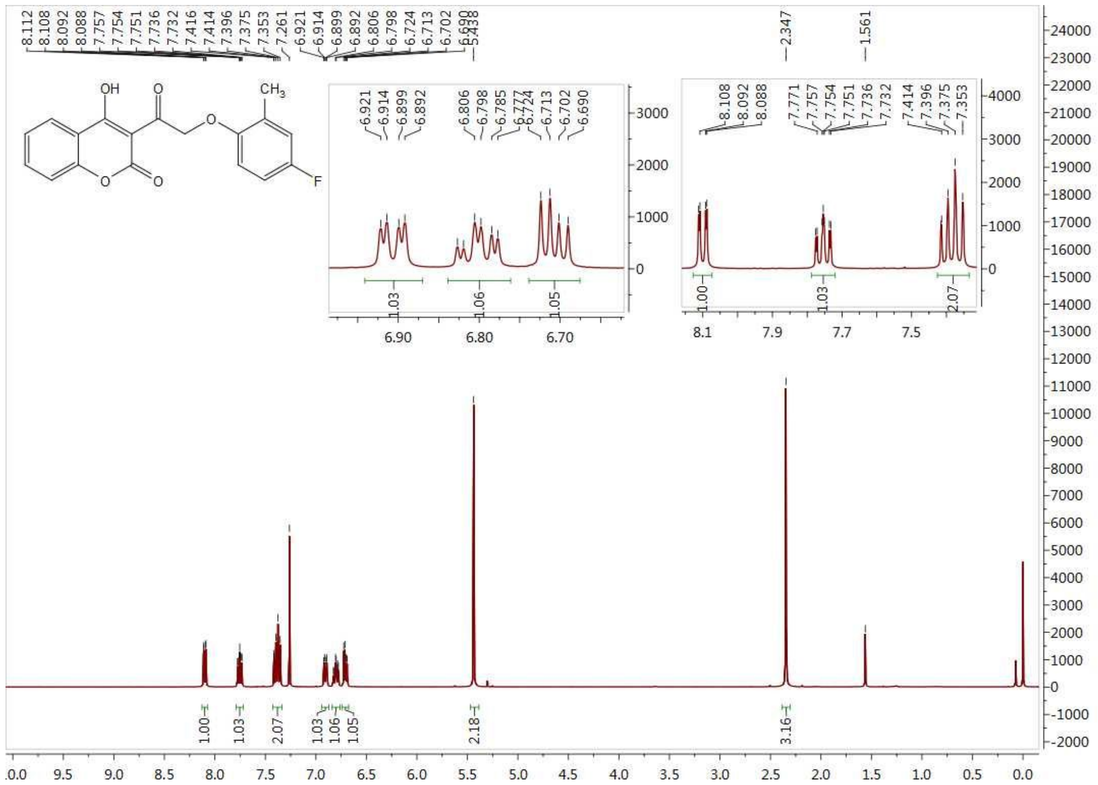
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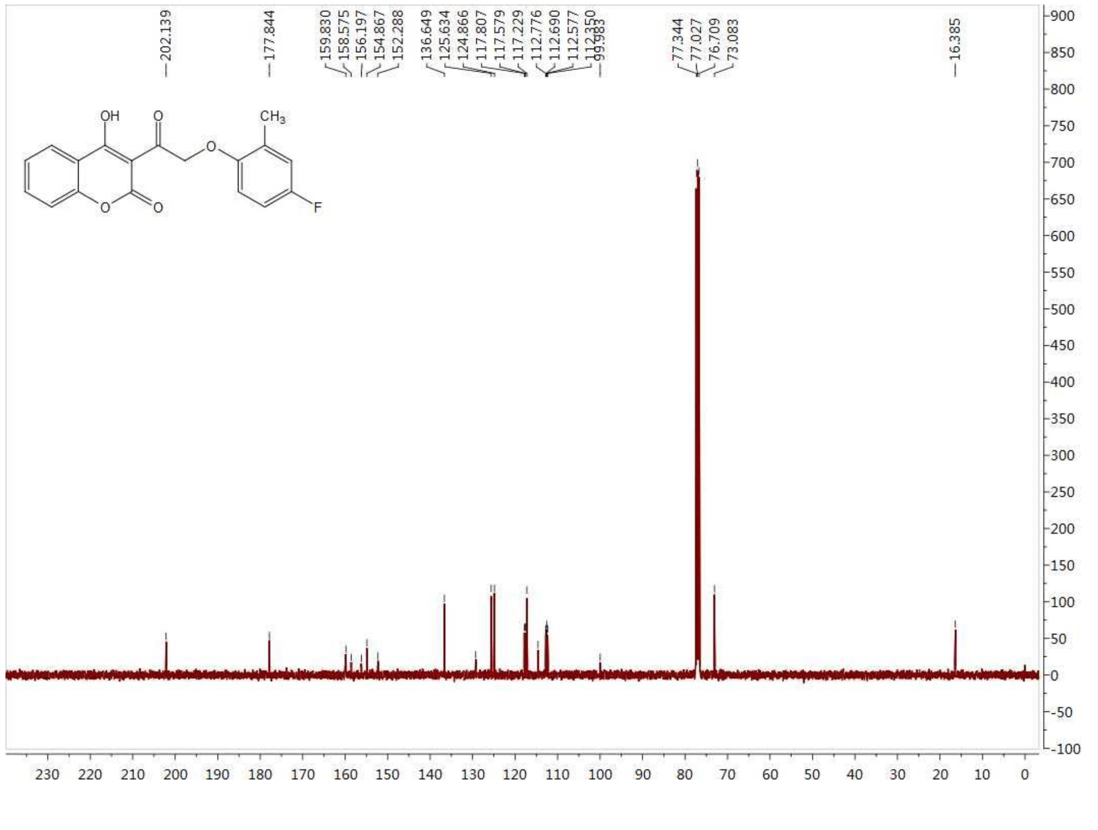
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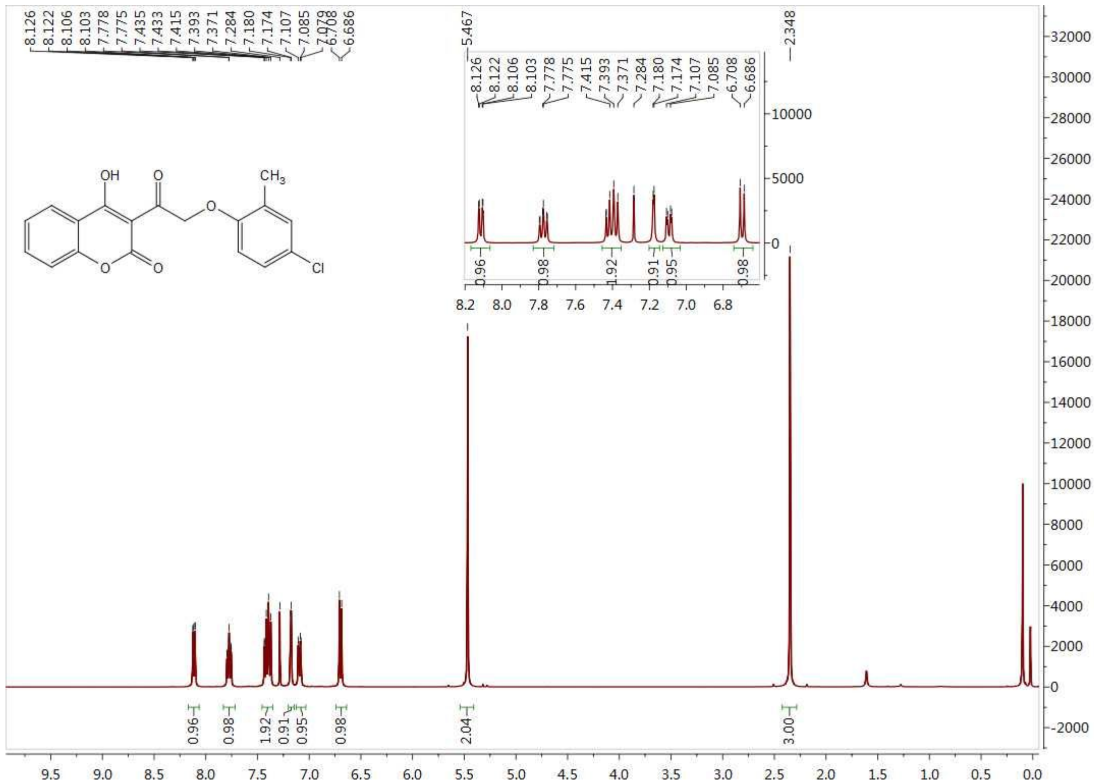
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0.95
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3.00
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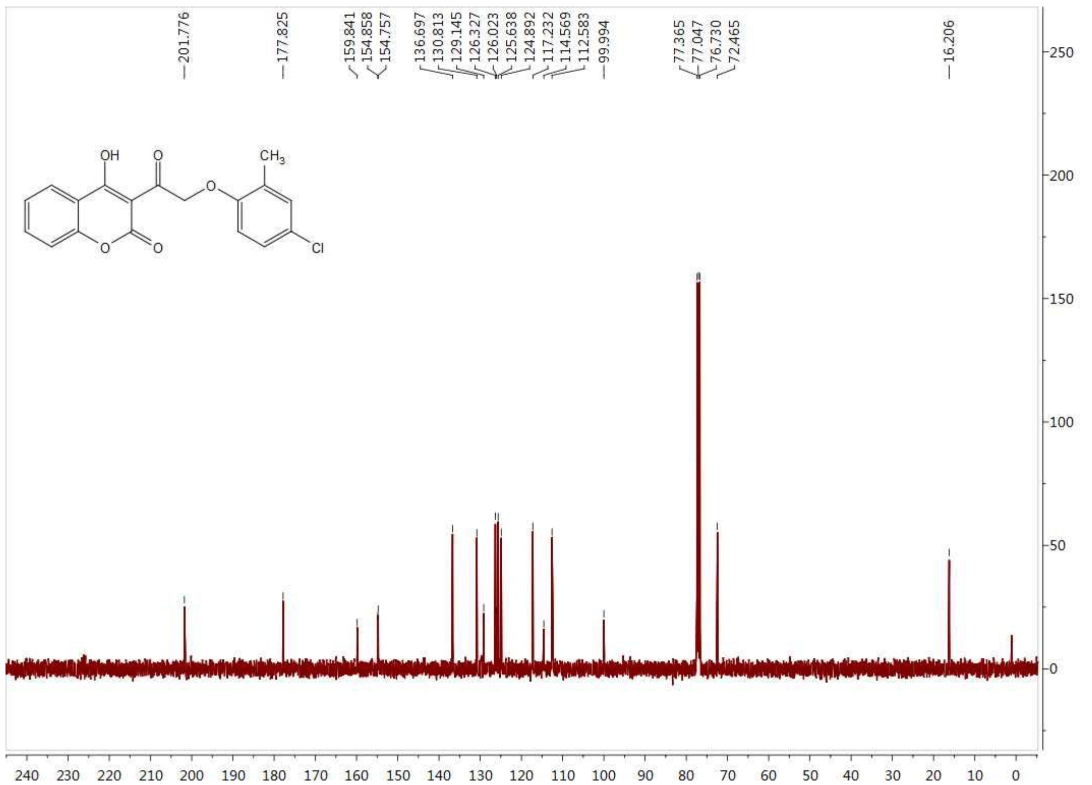
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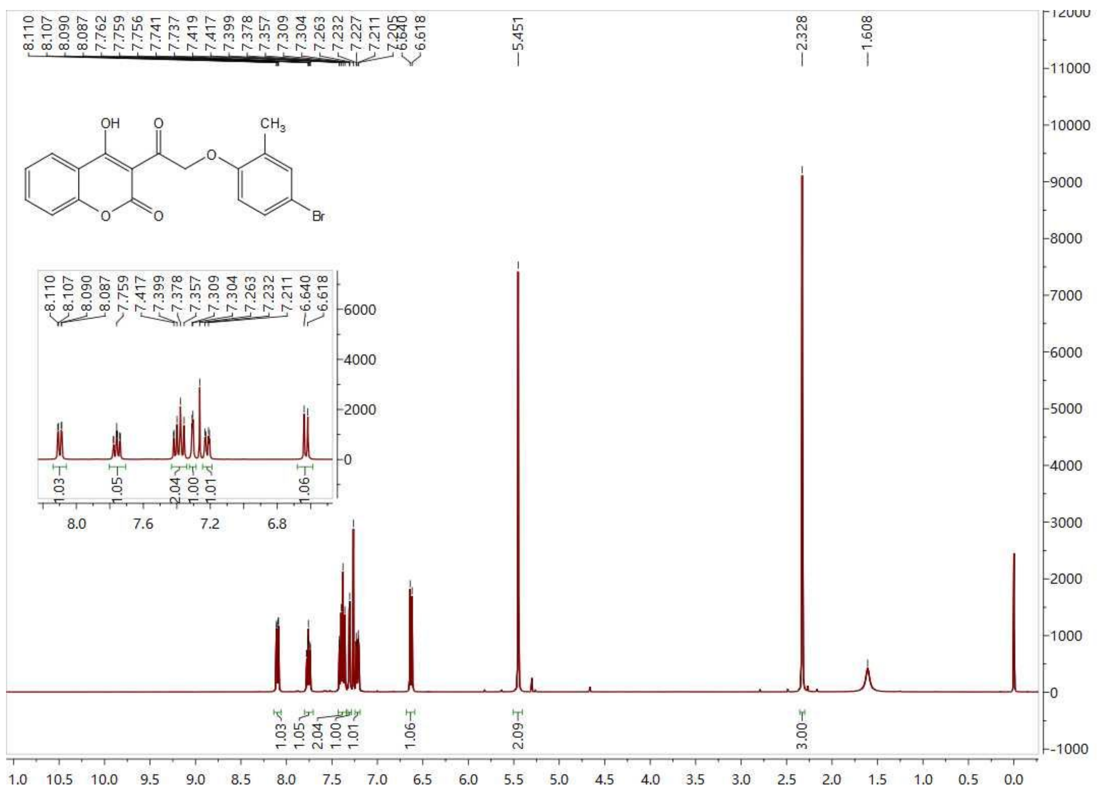
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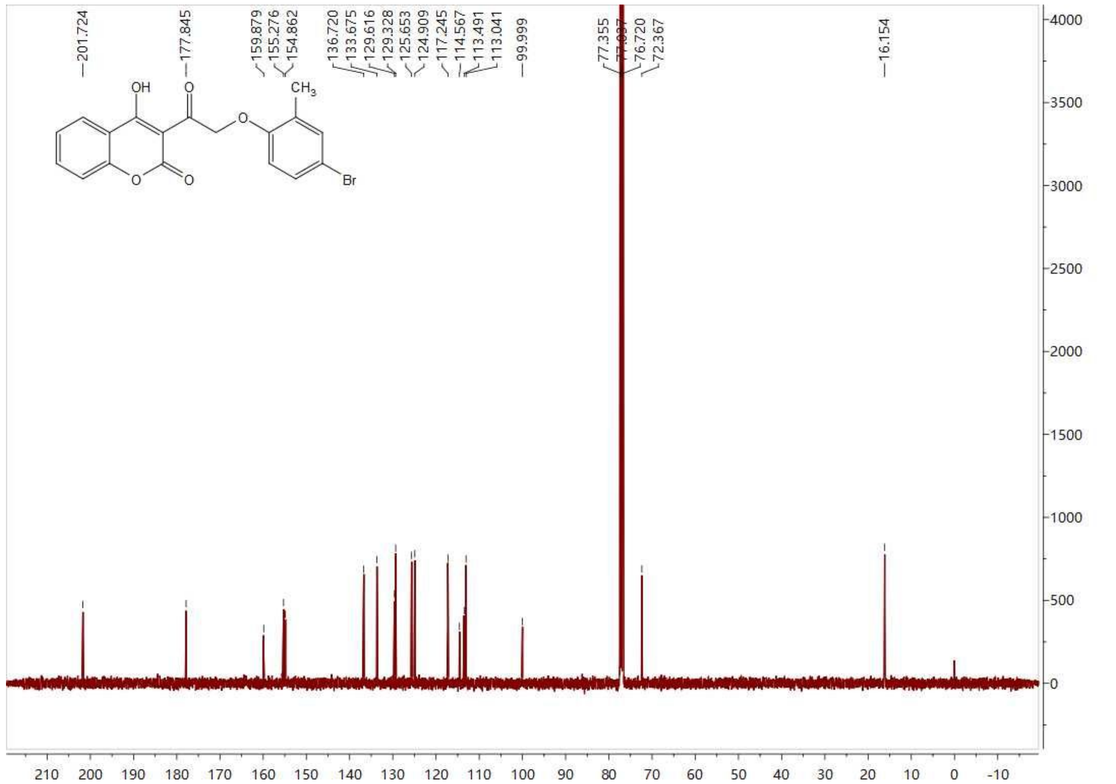
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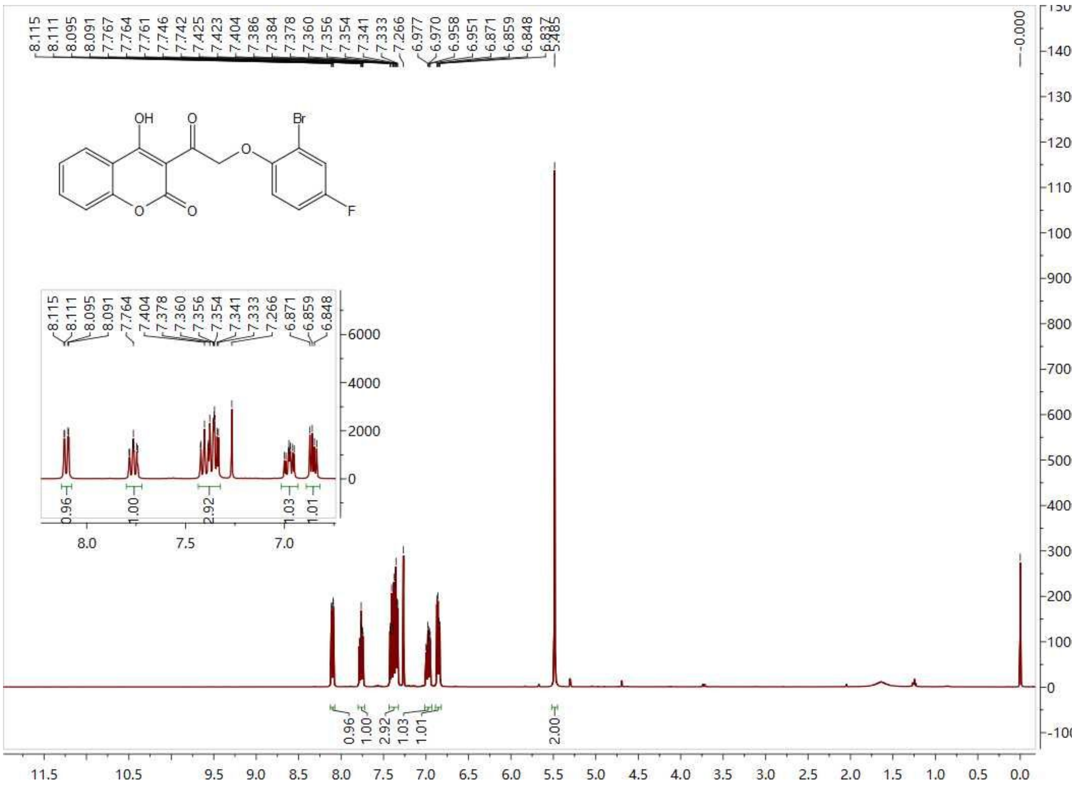

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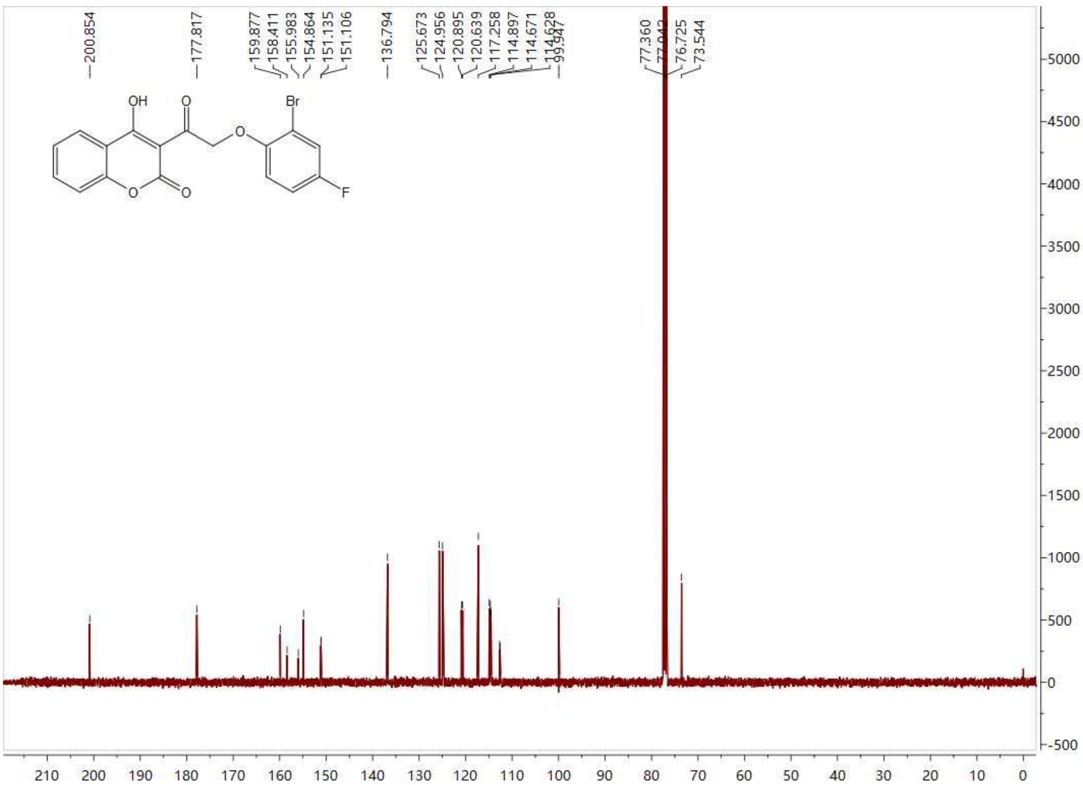

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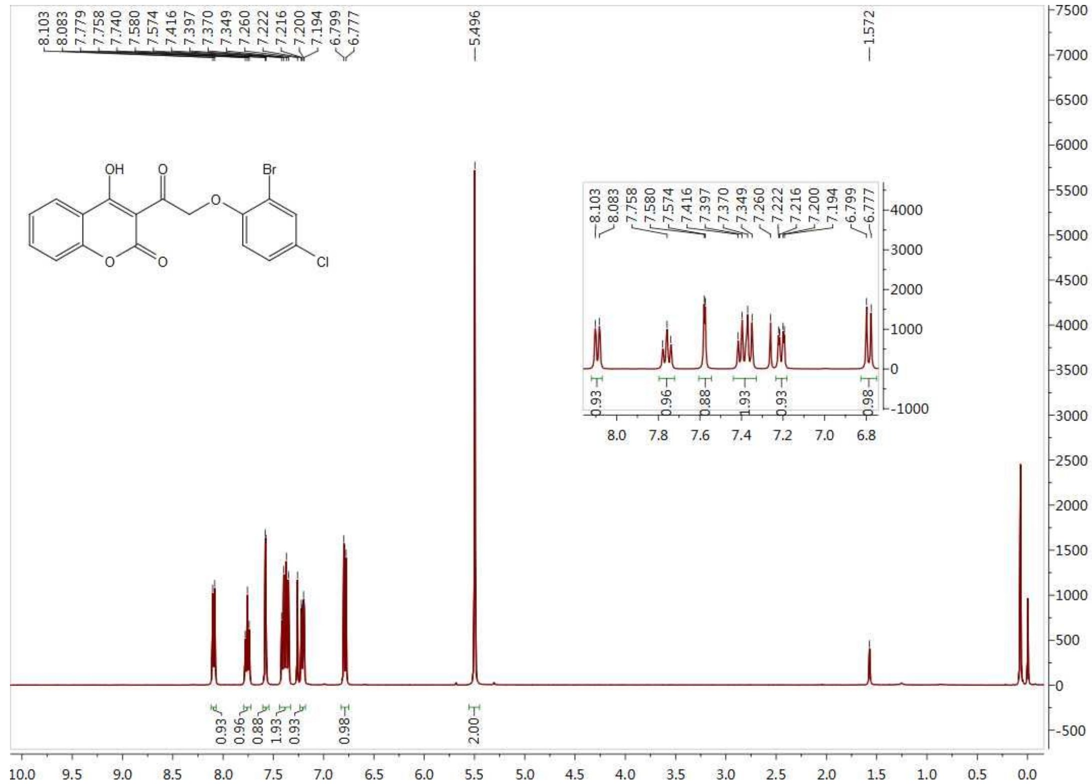
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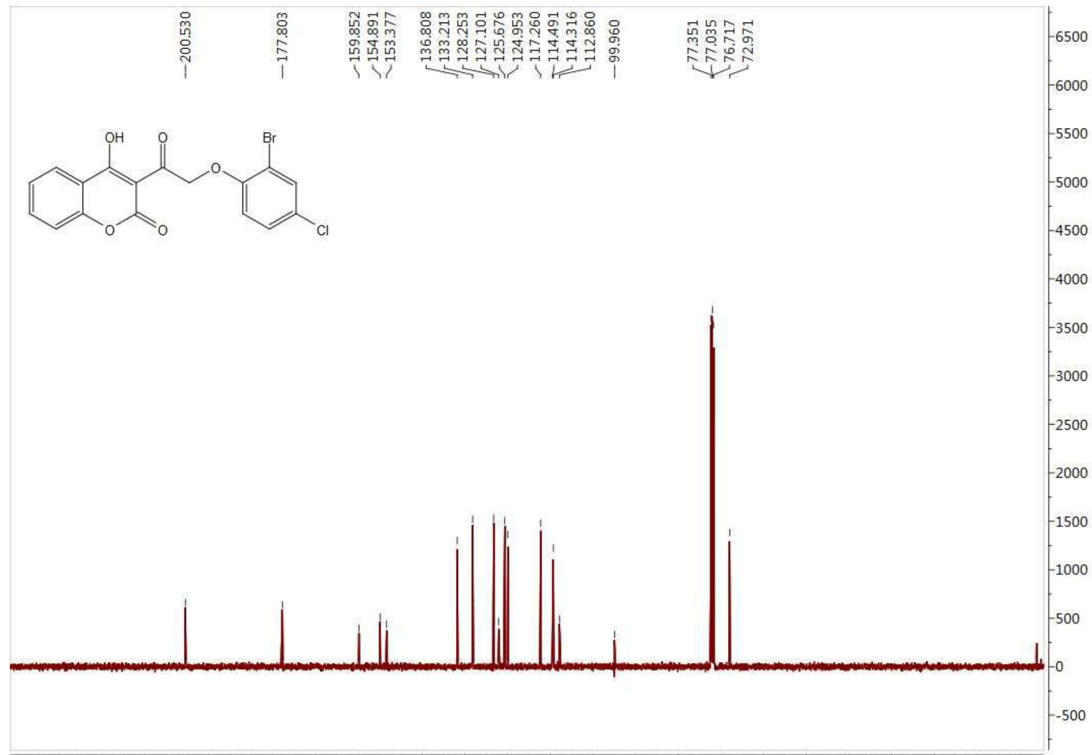
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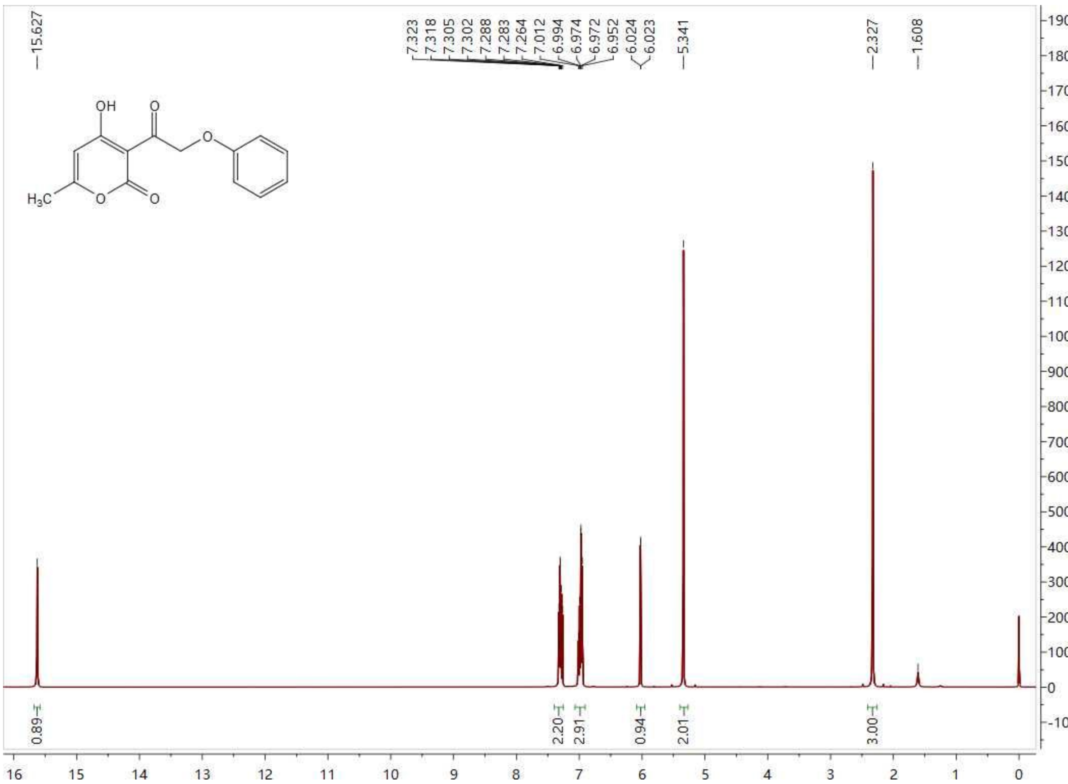
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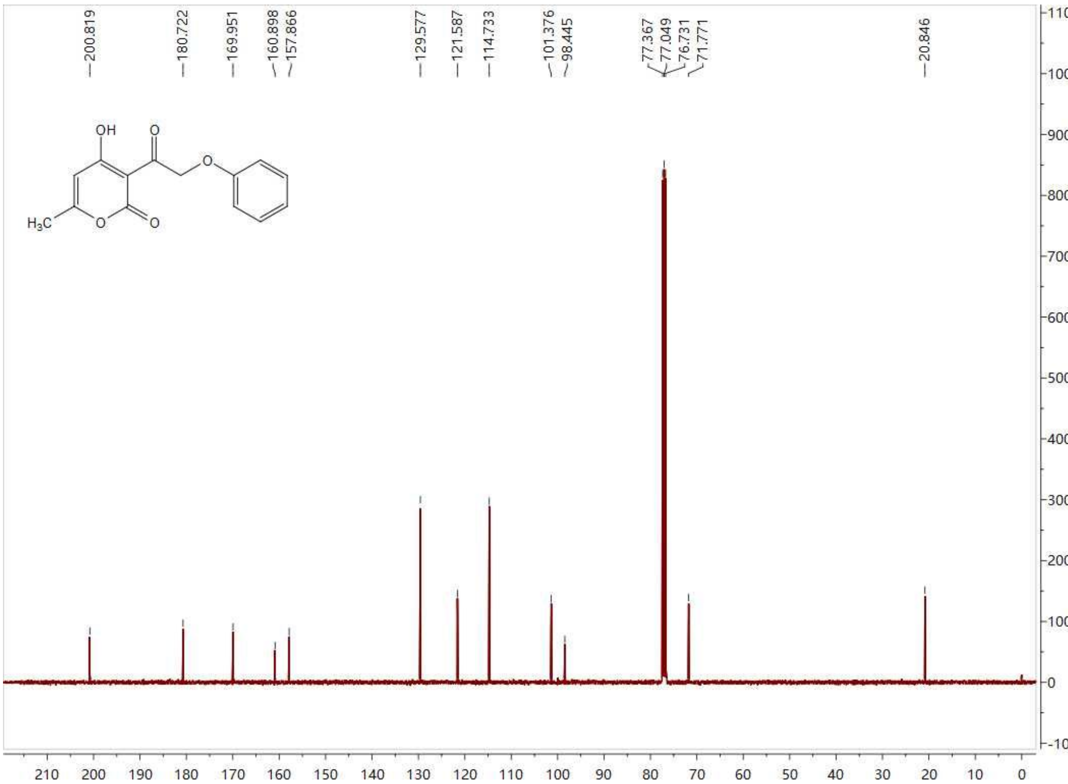
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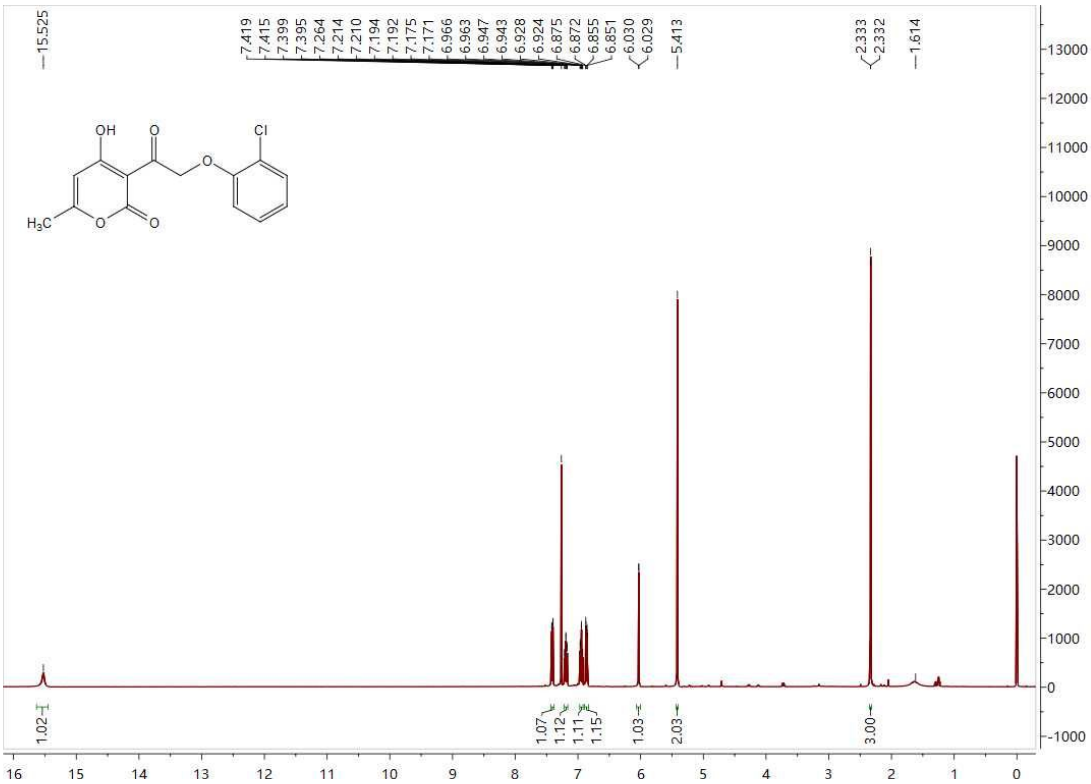
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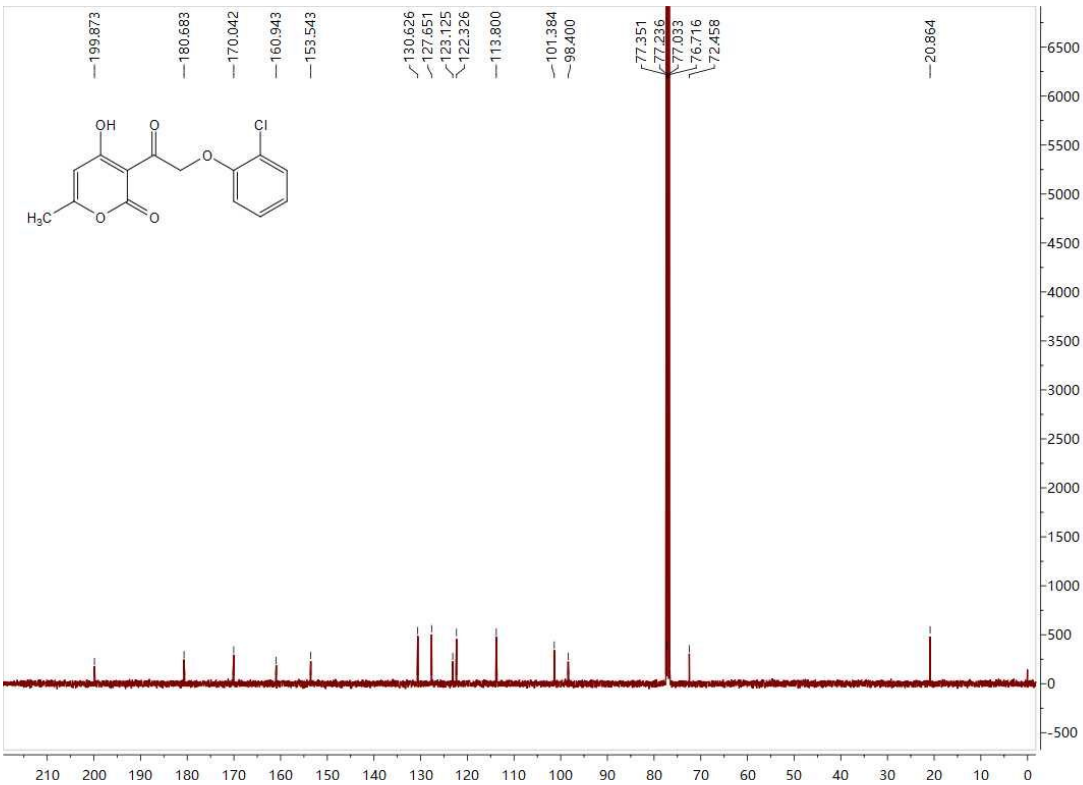
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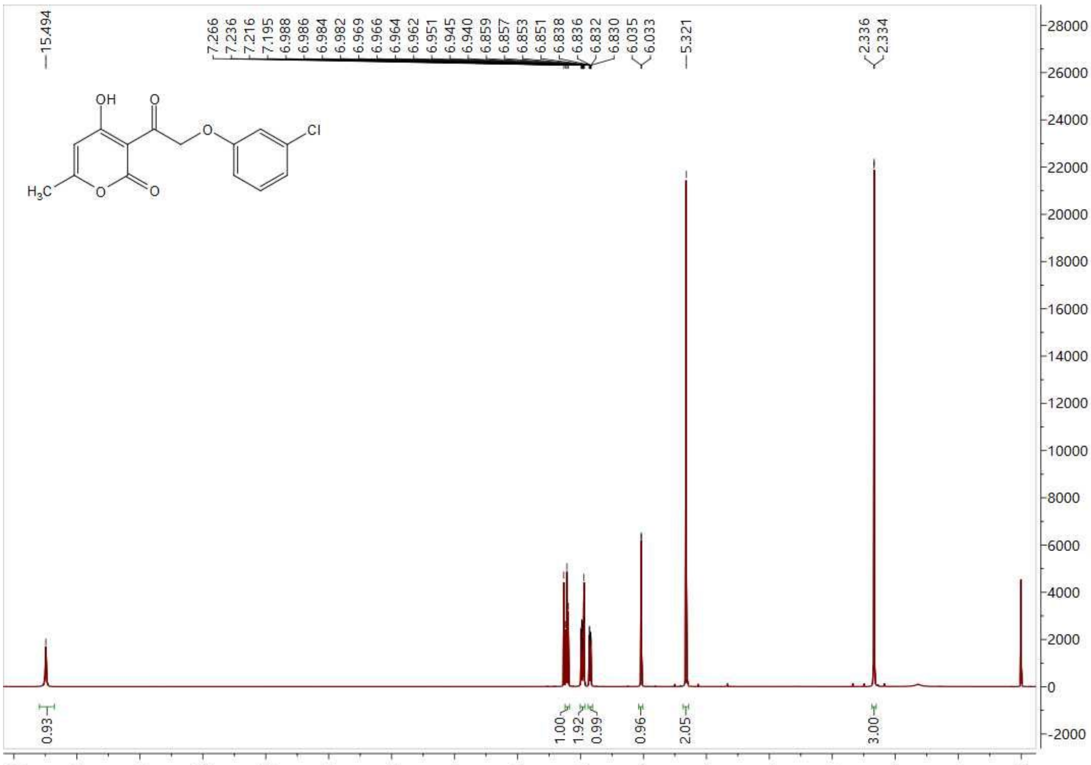
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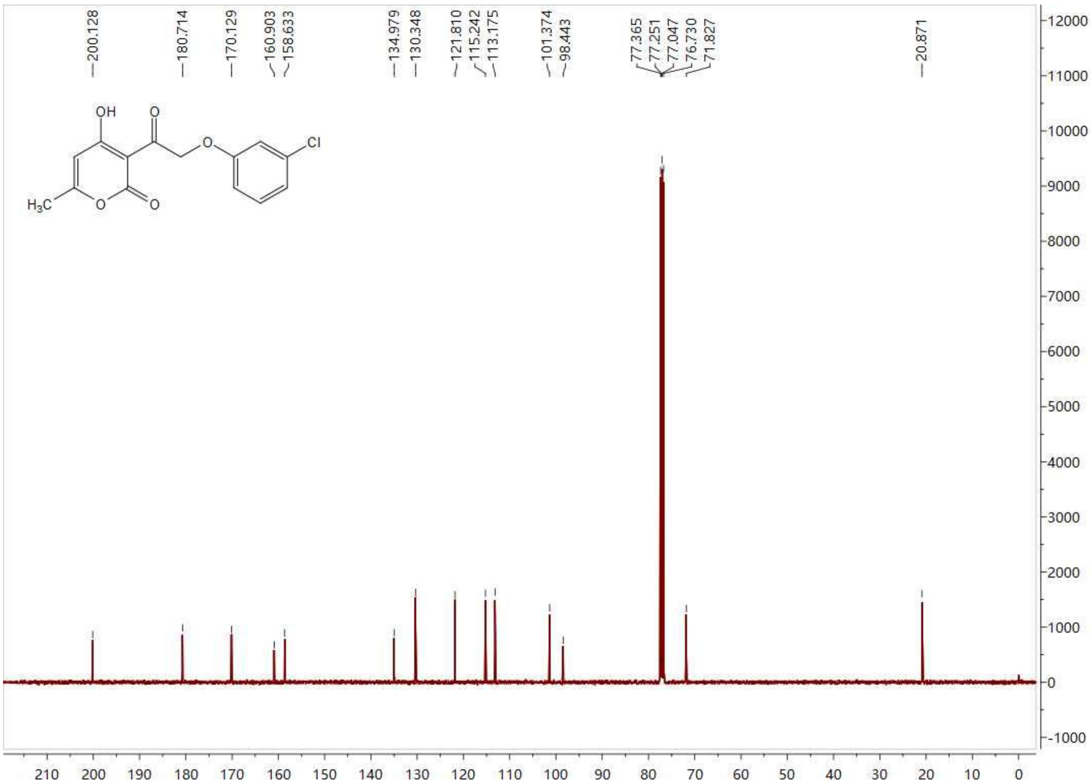
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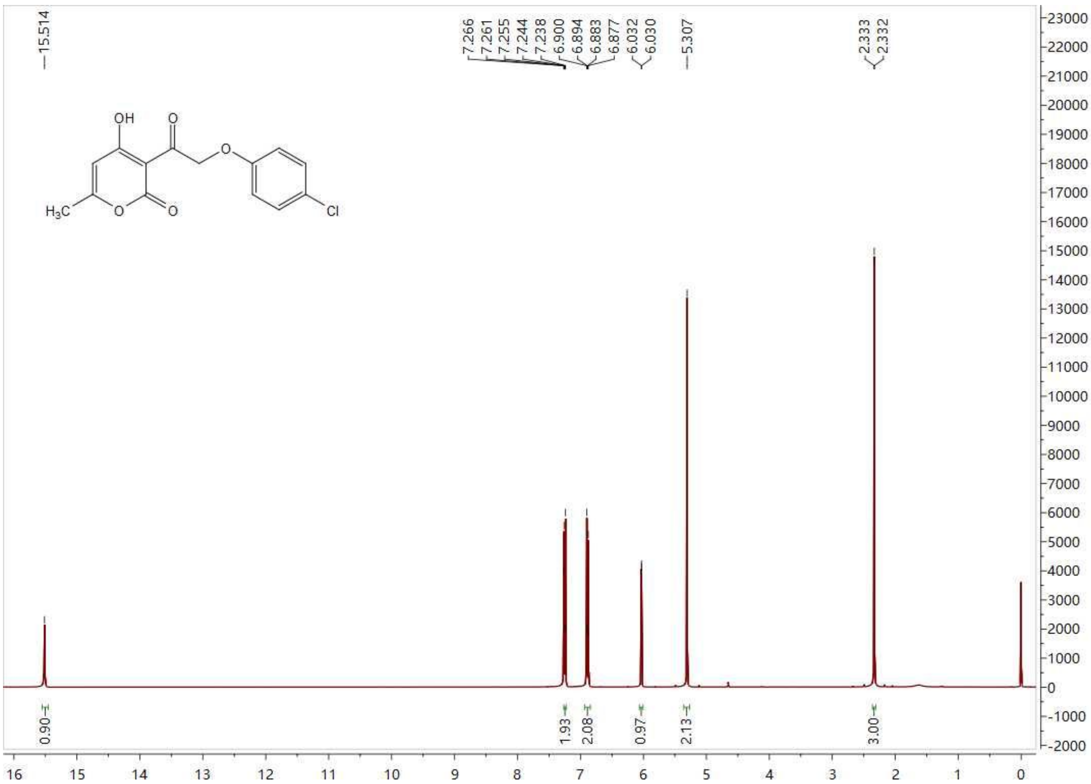
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2.08
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2.13
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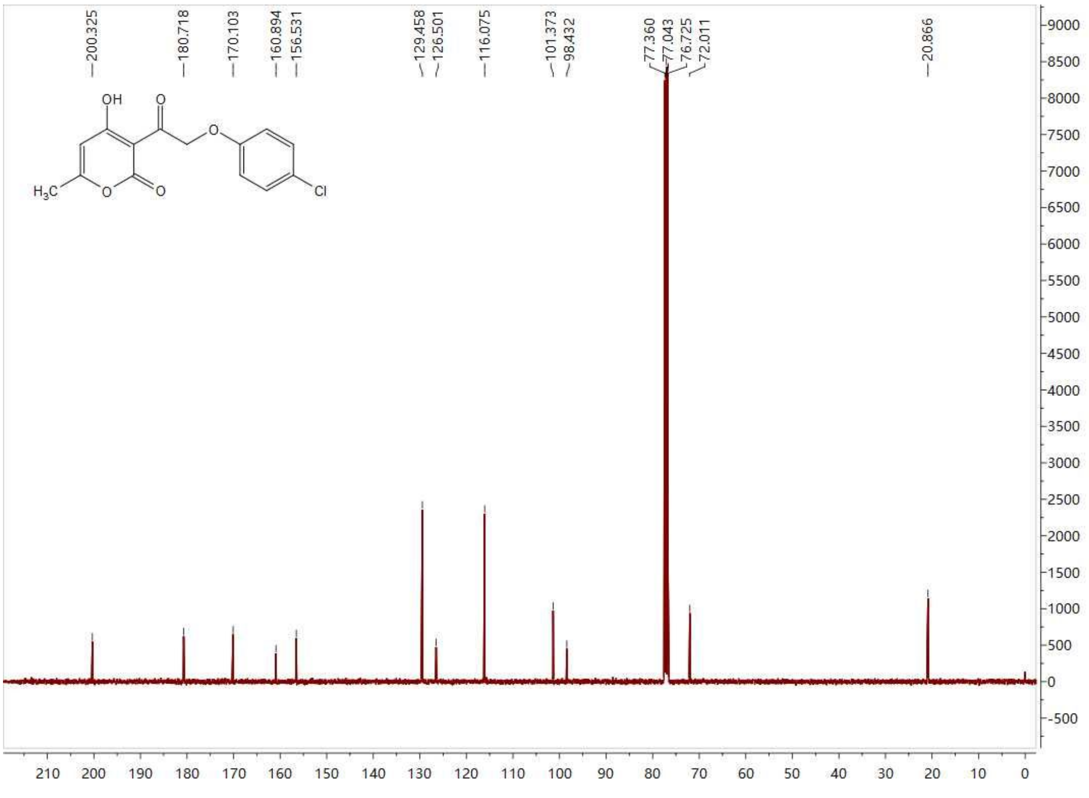
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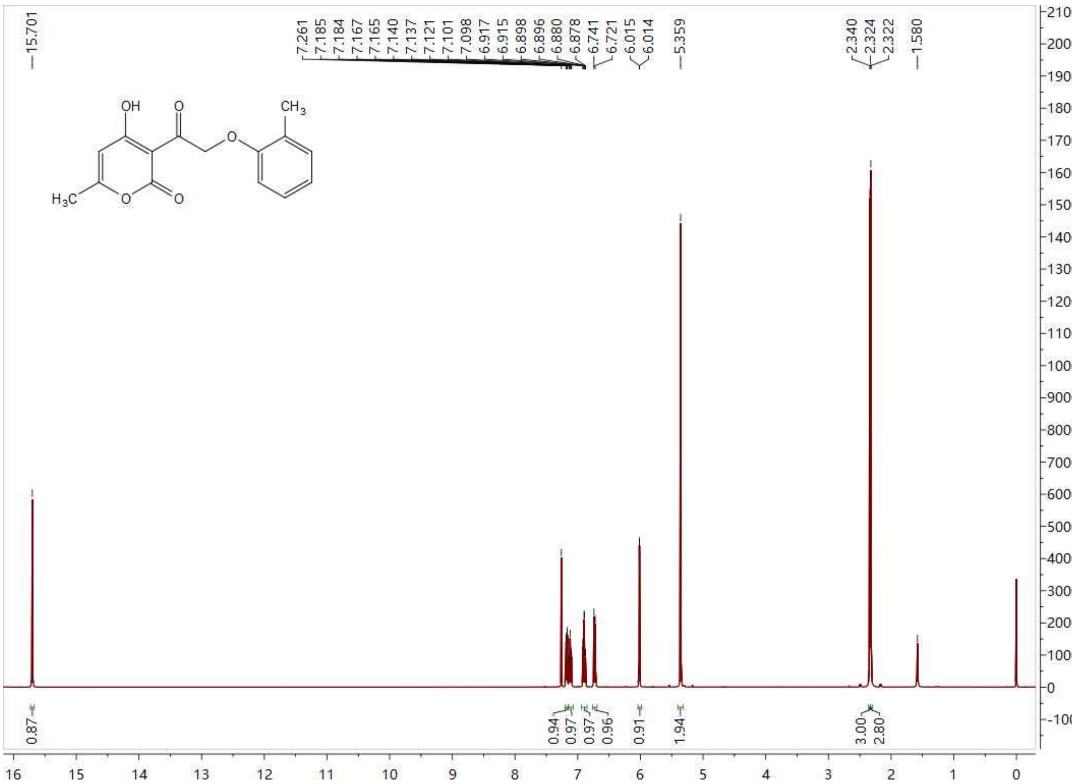

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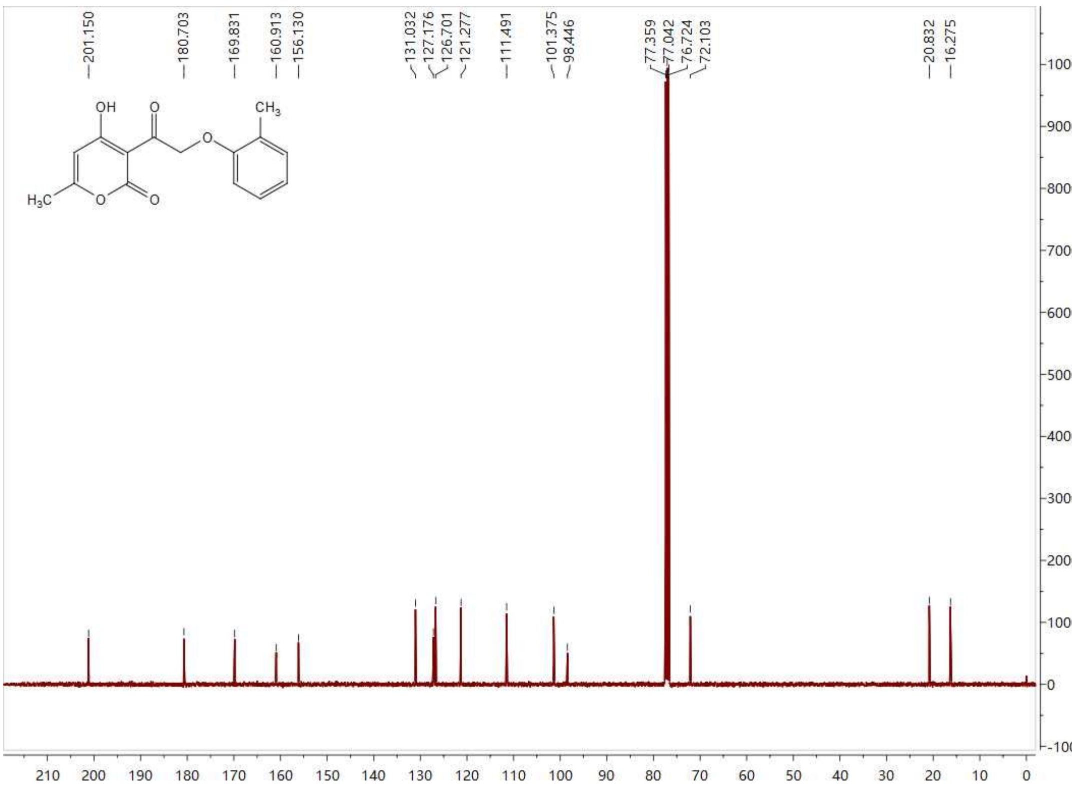

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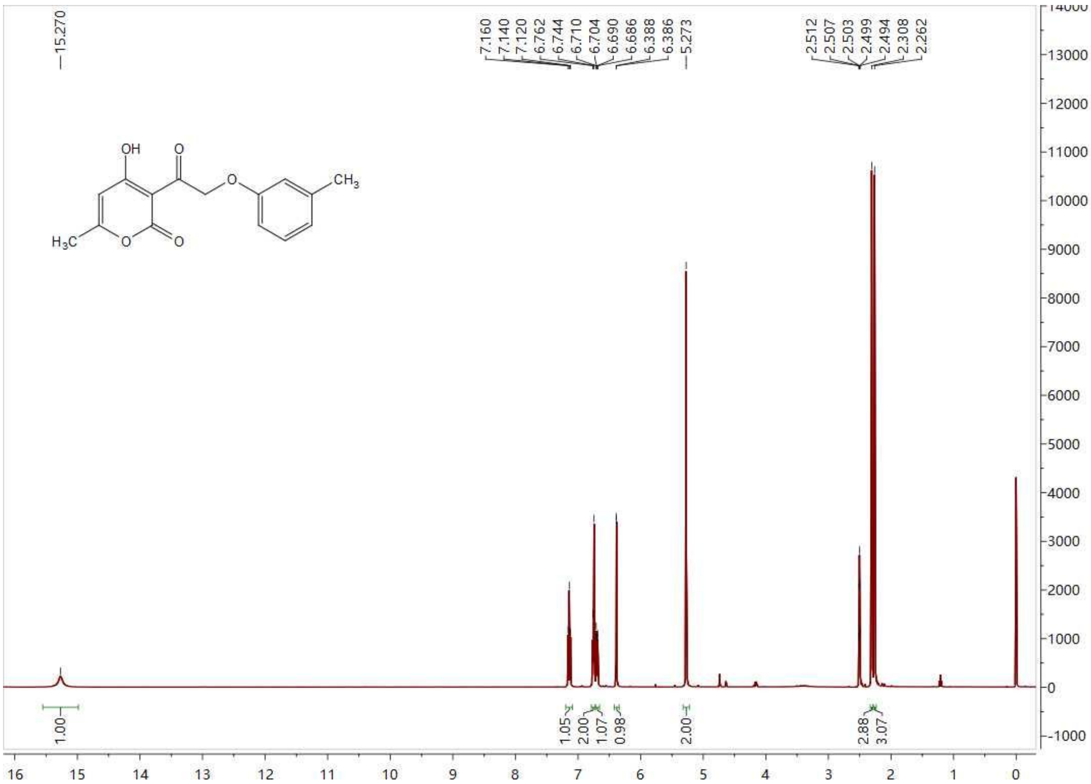
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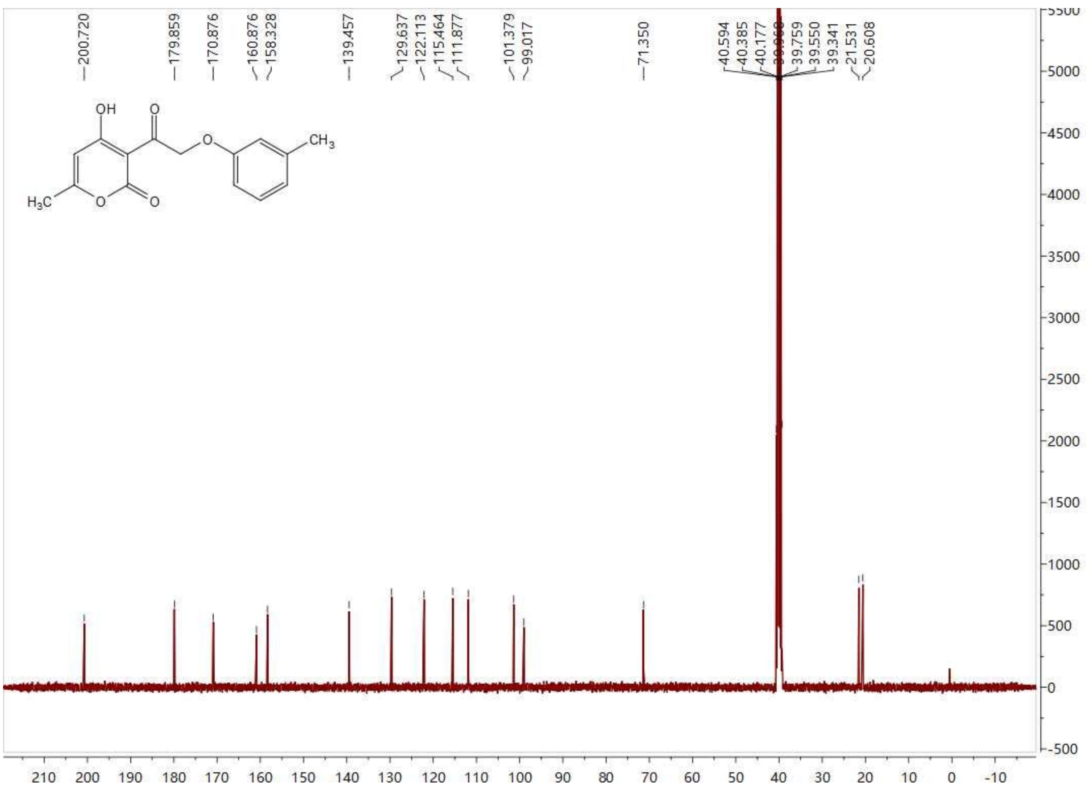
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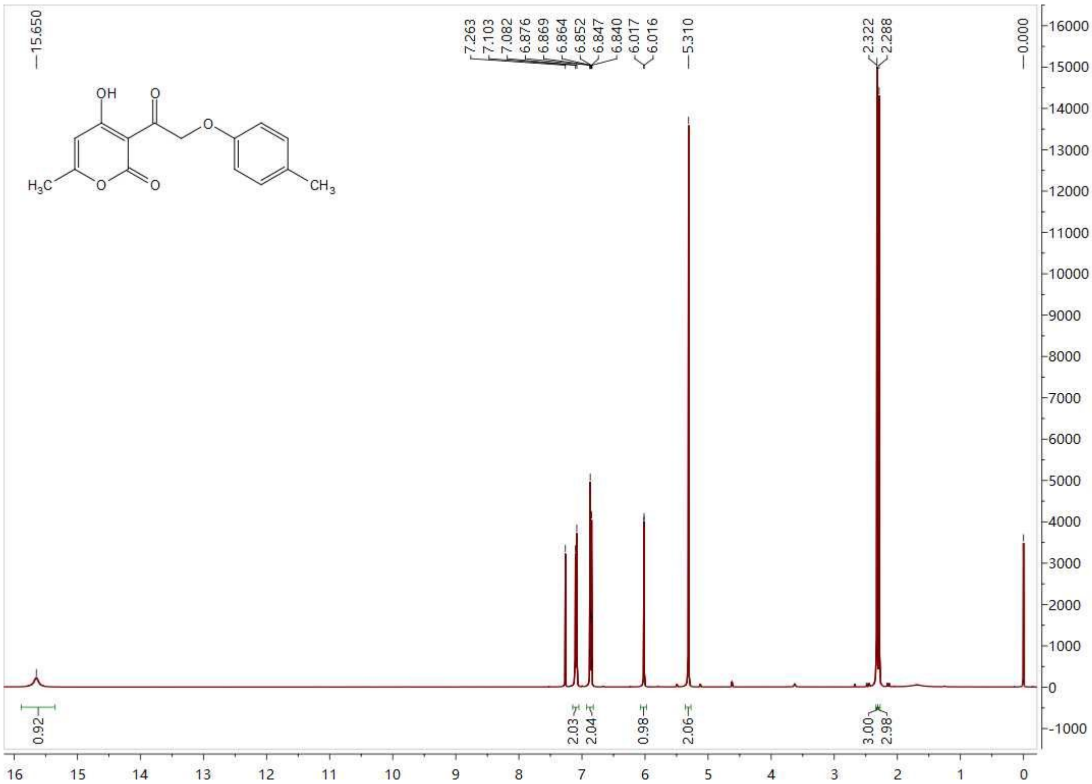

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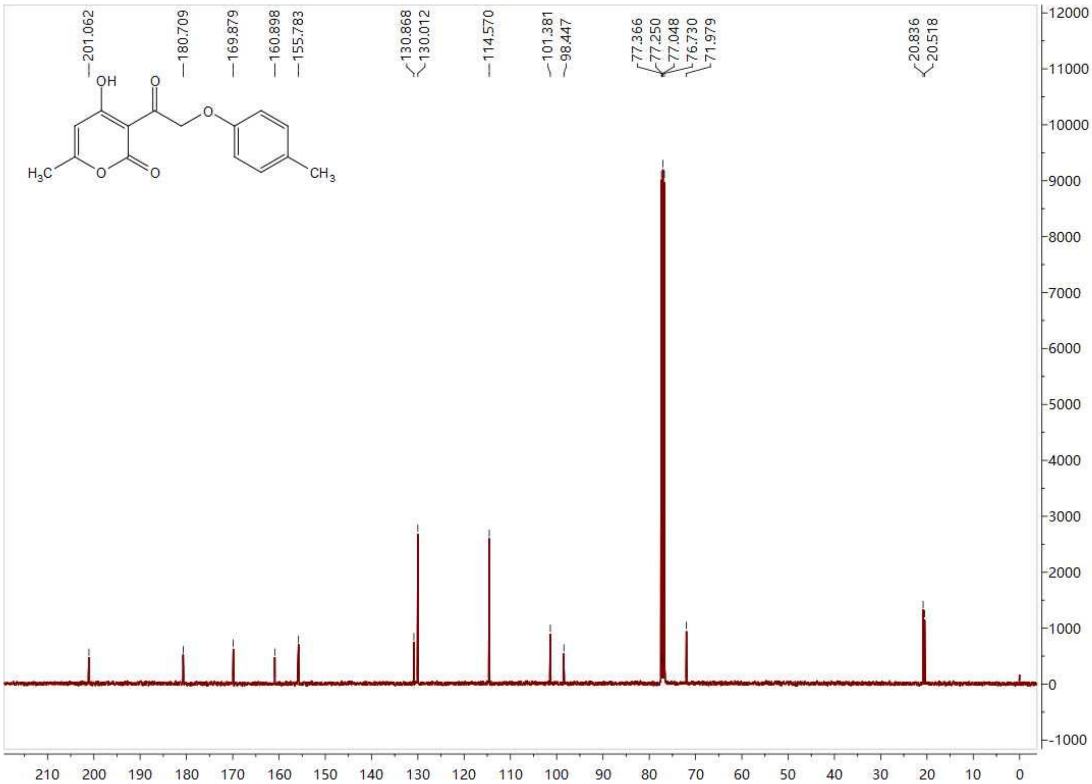

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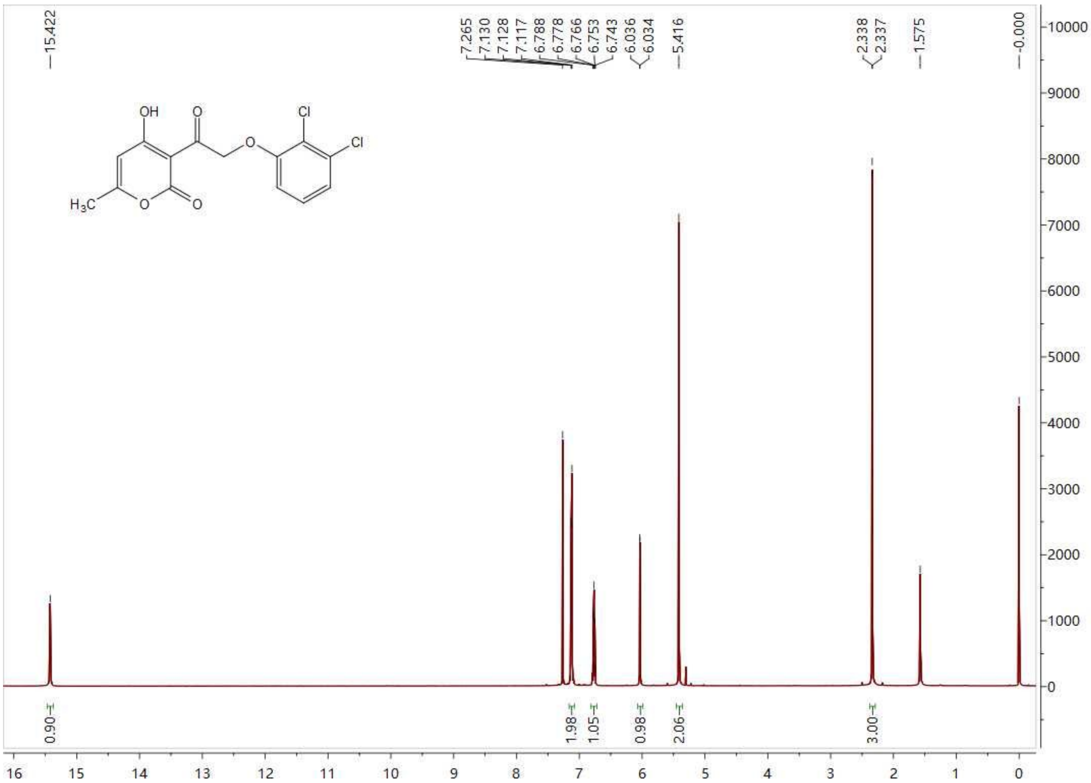

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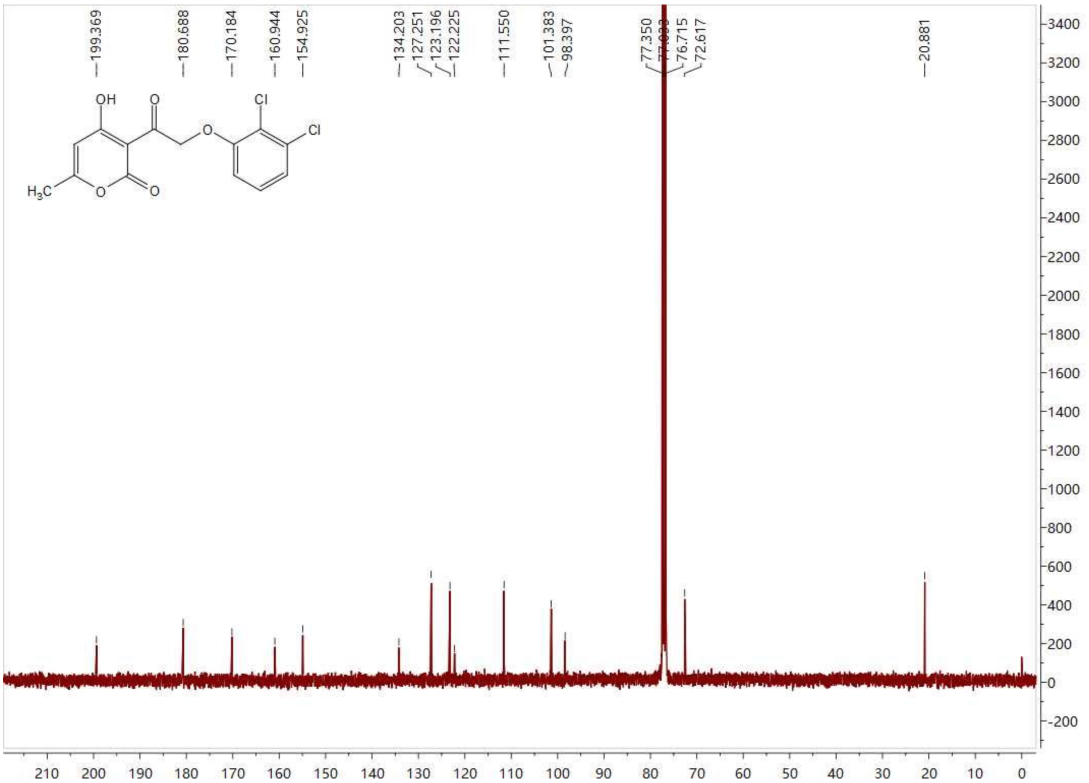

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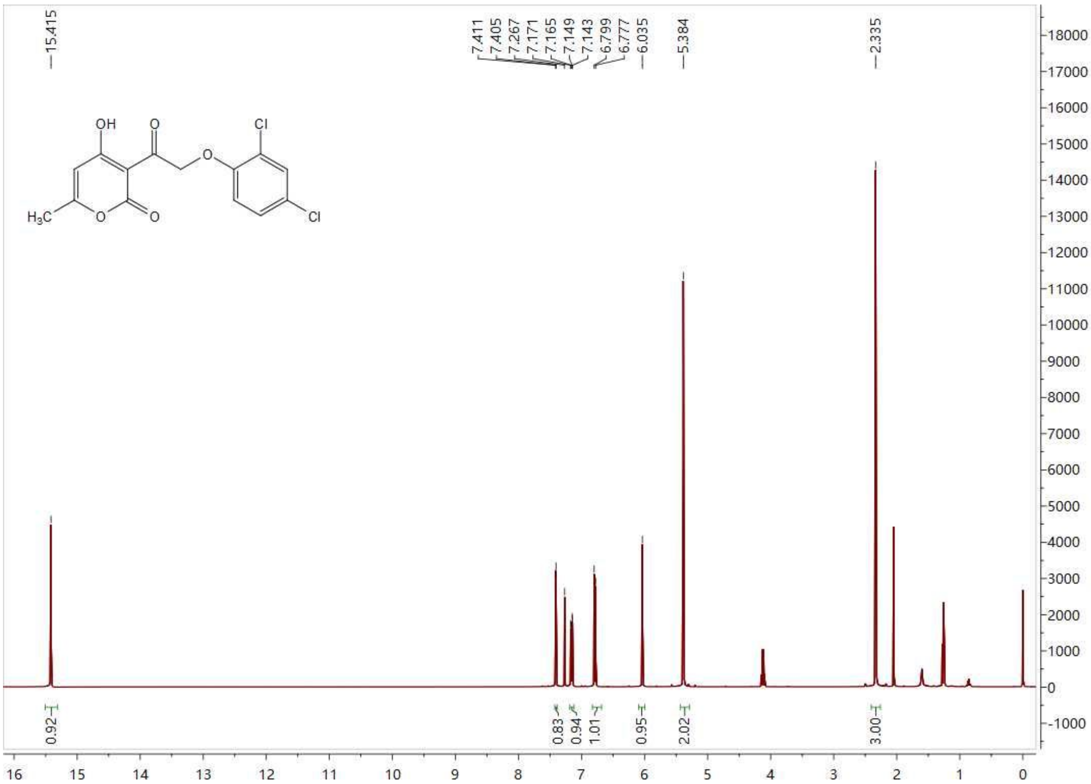
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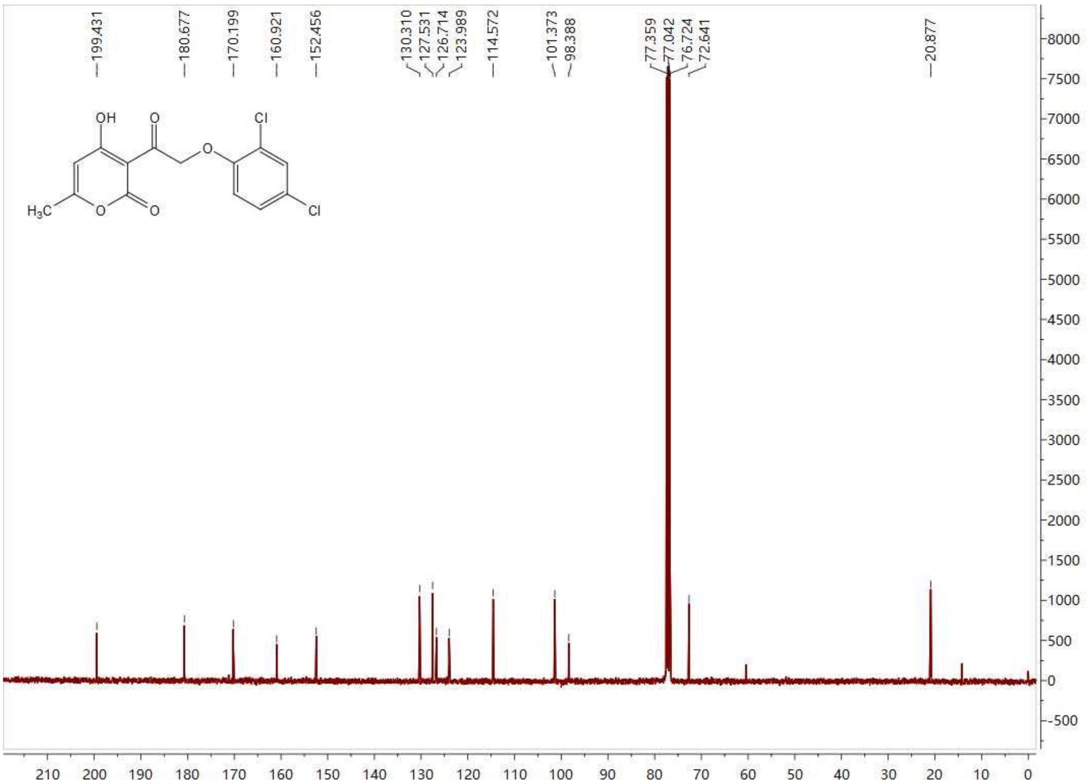
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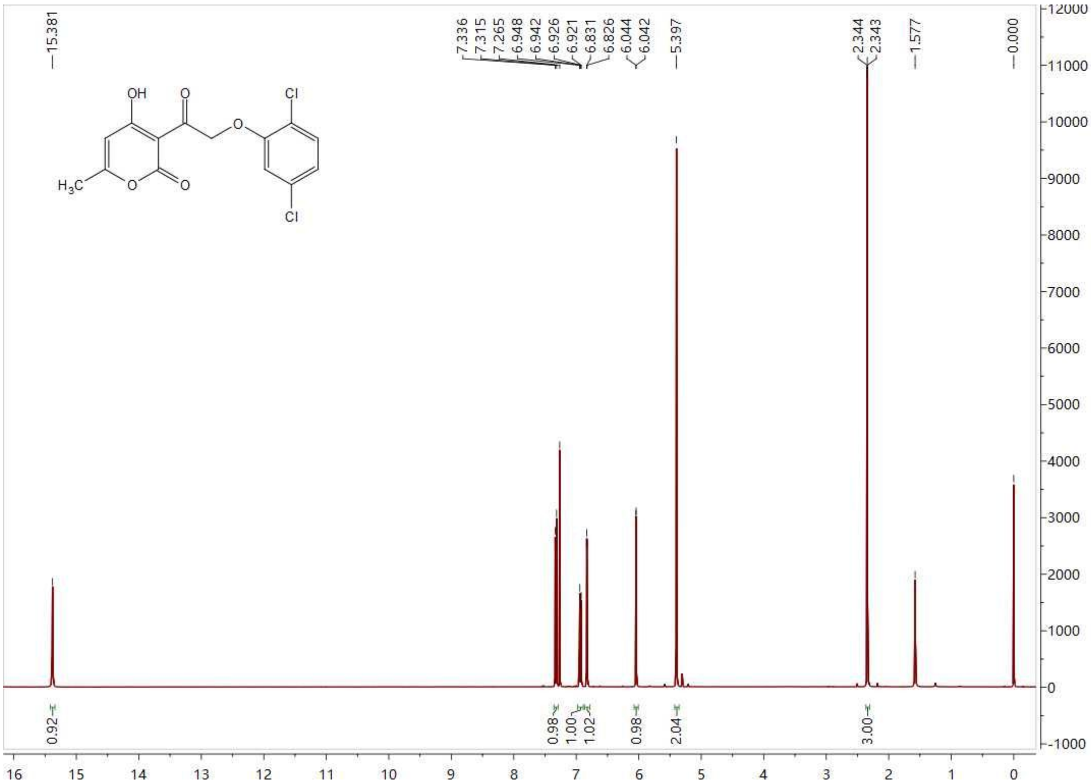
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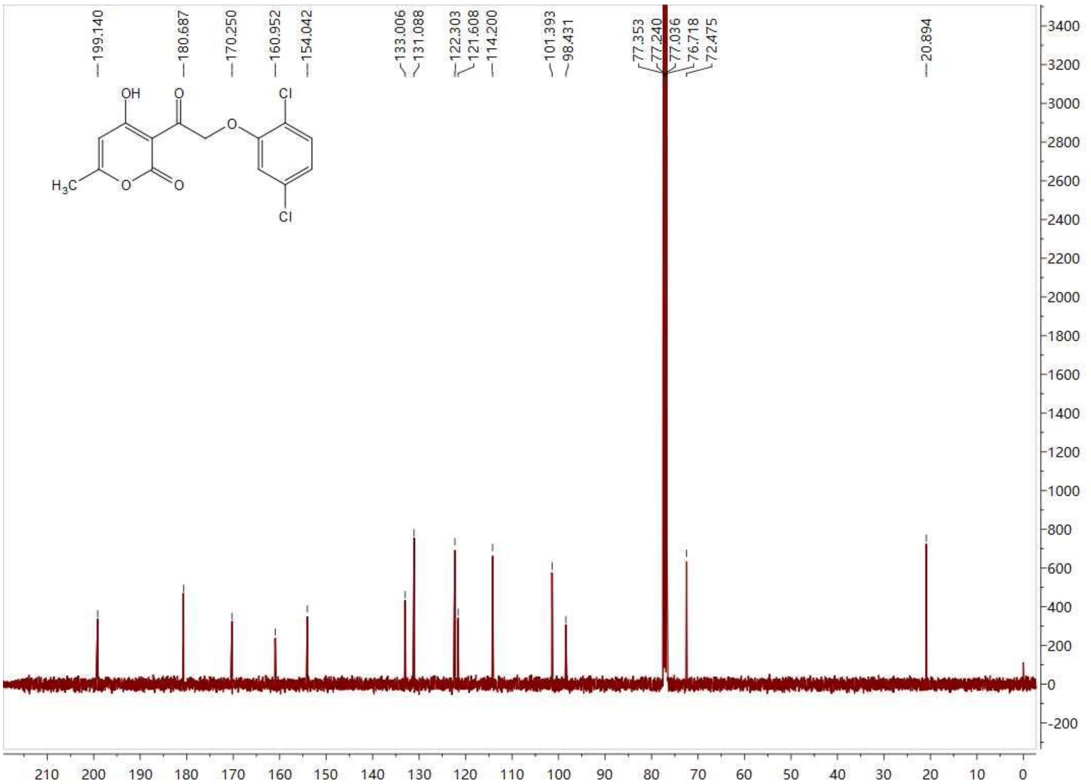
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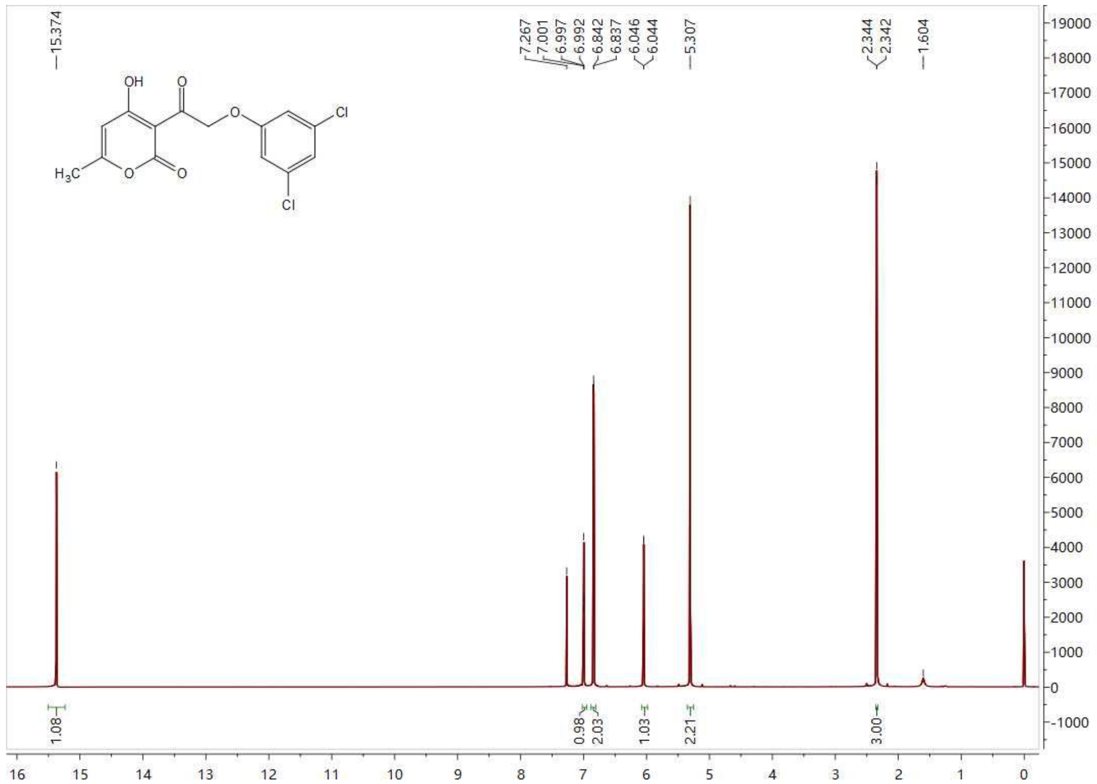
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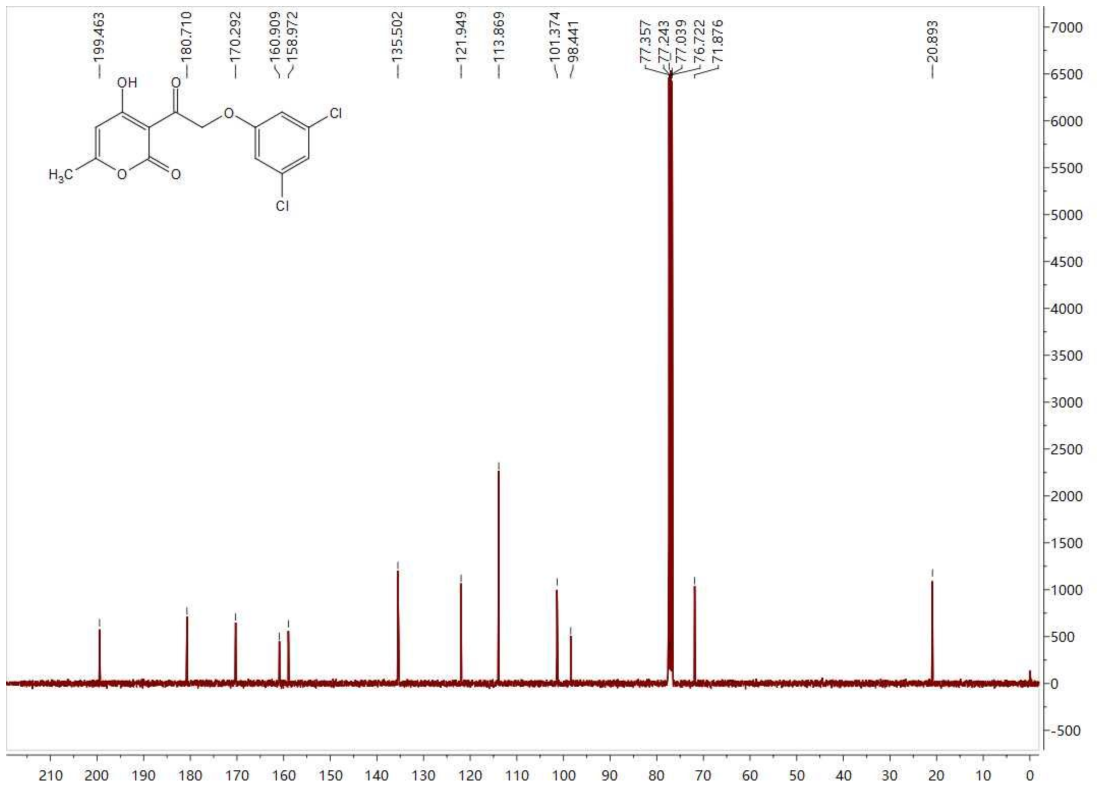
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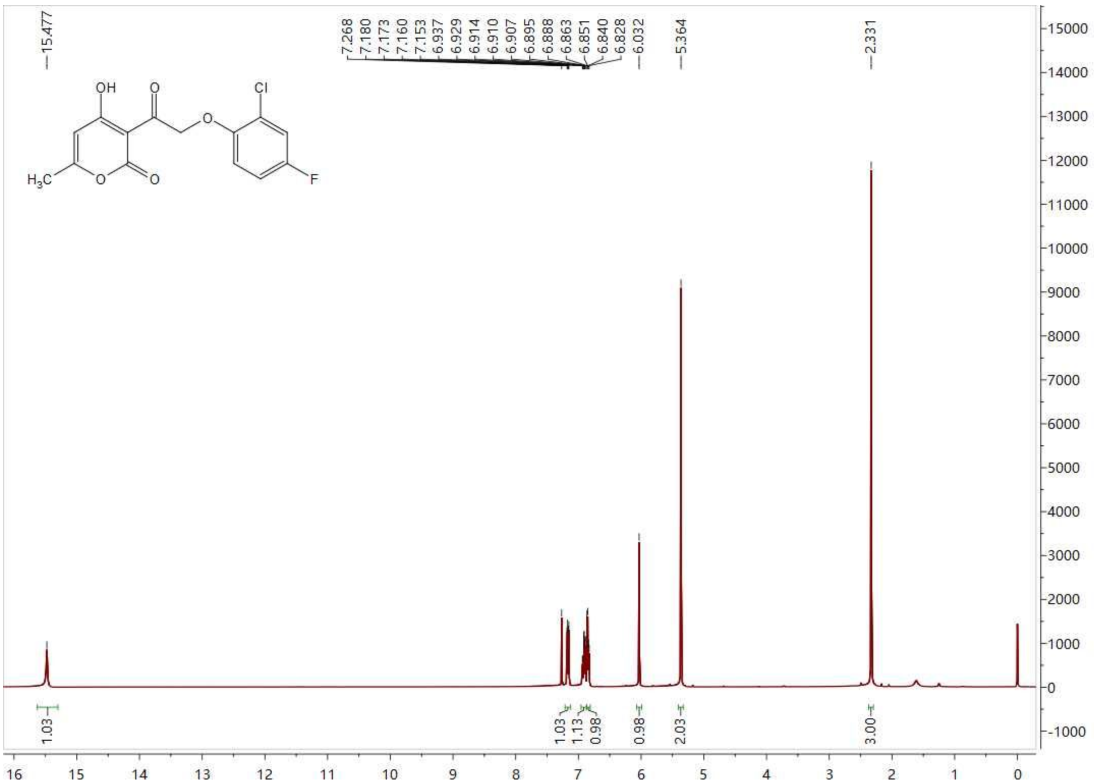
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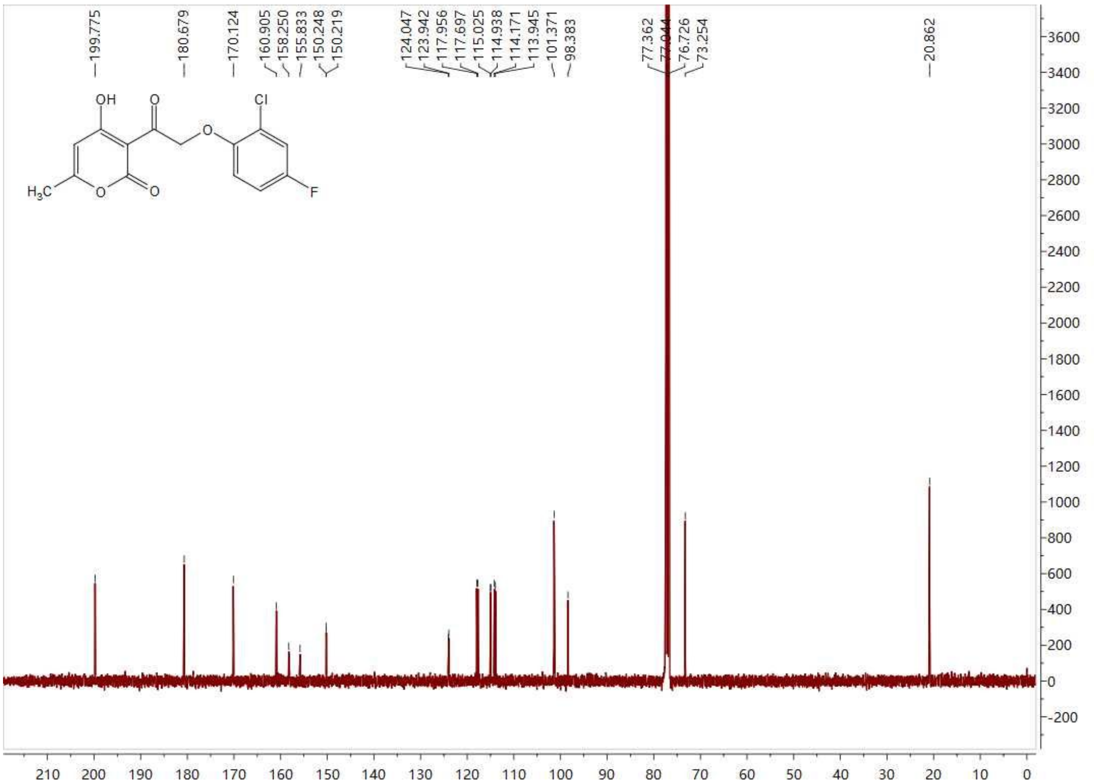
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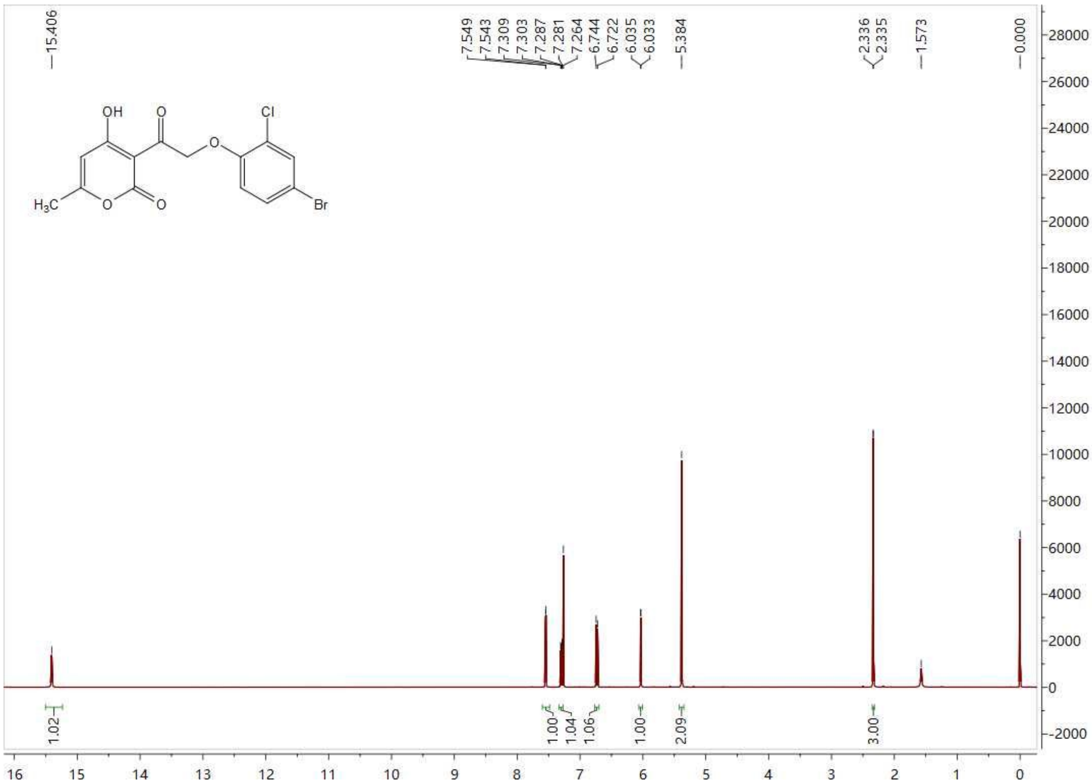

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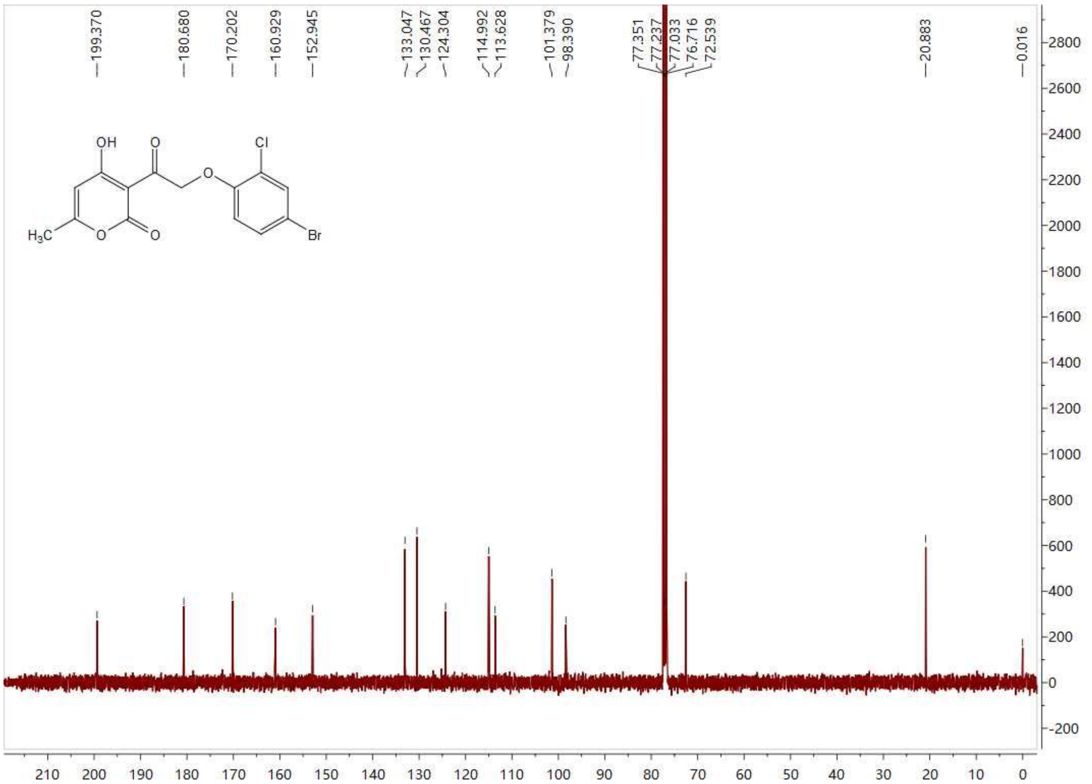

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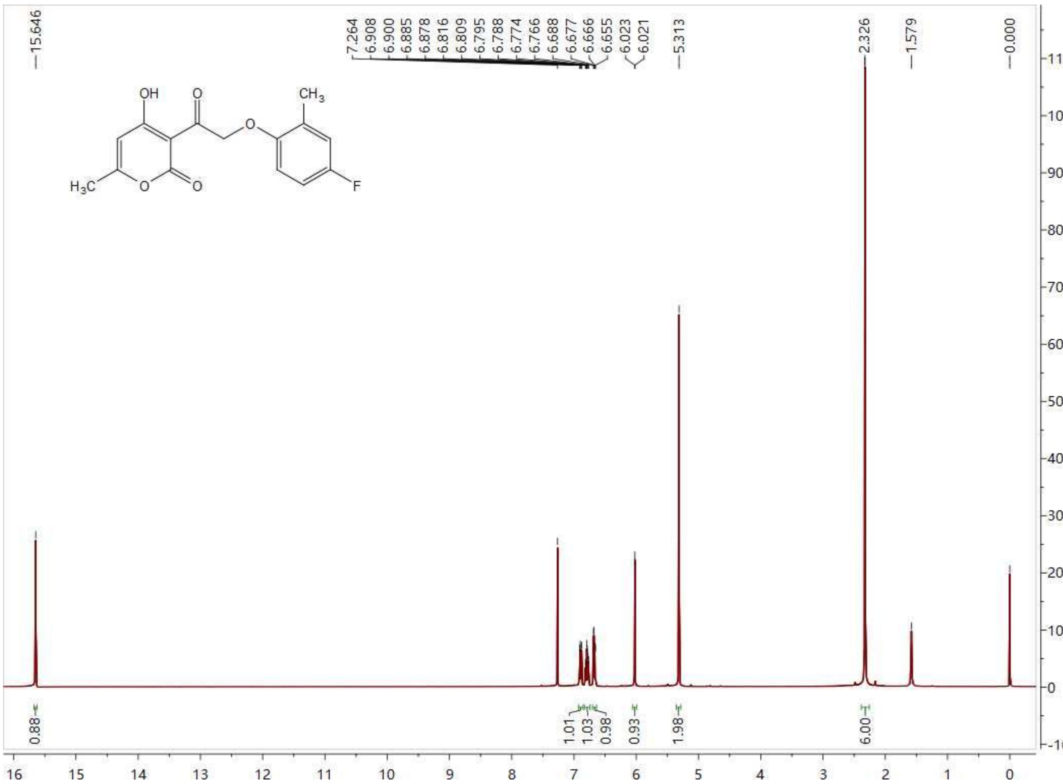

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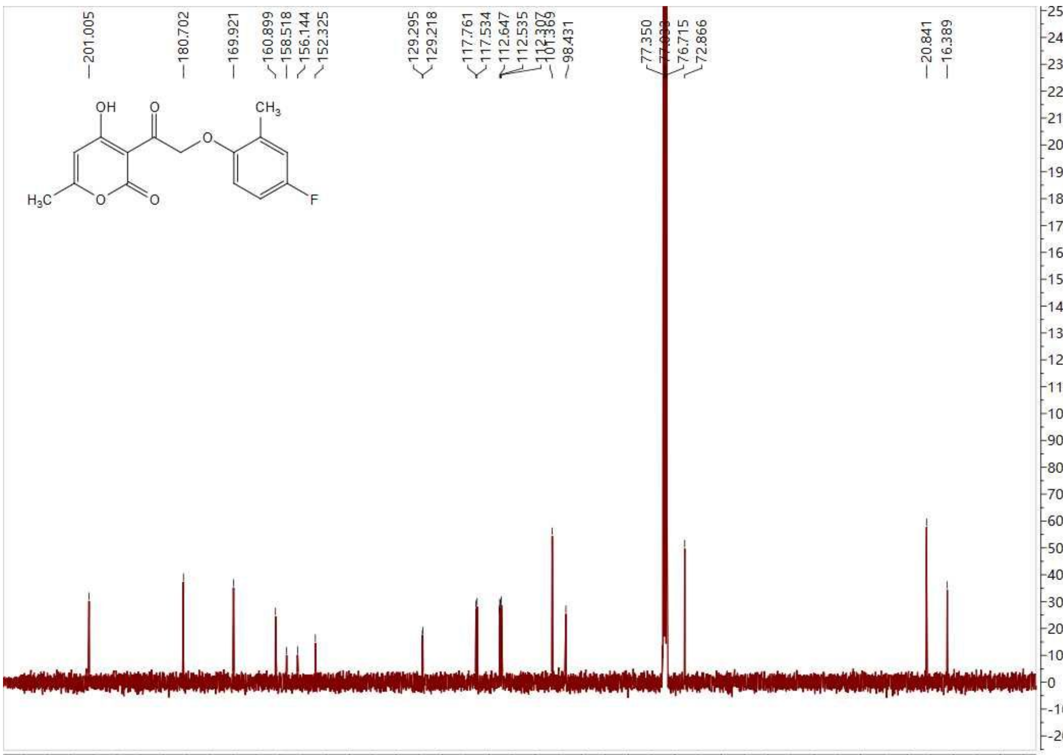

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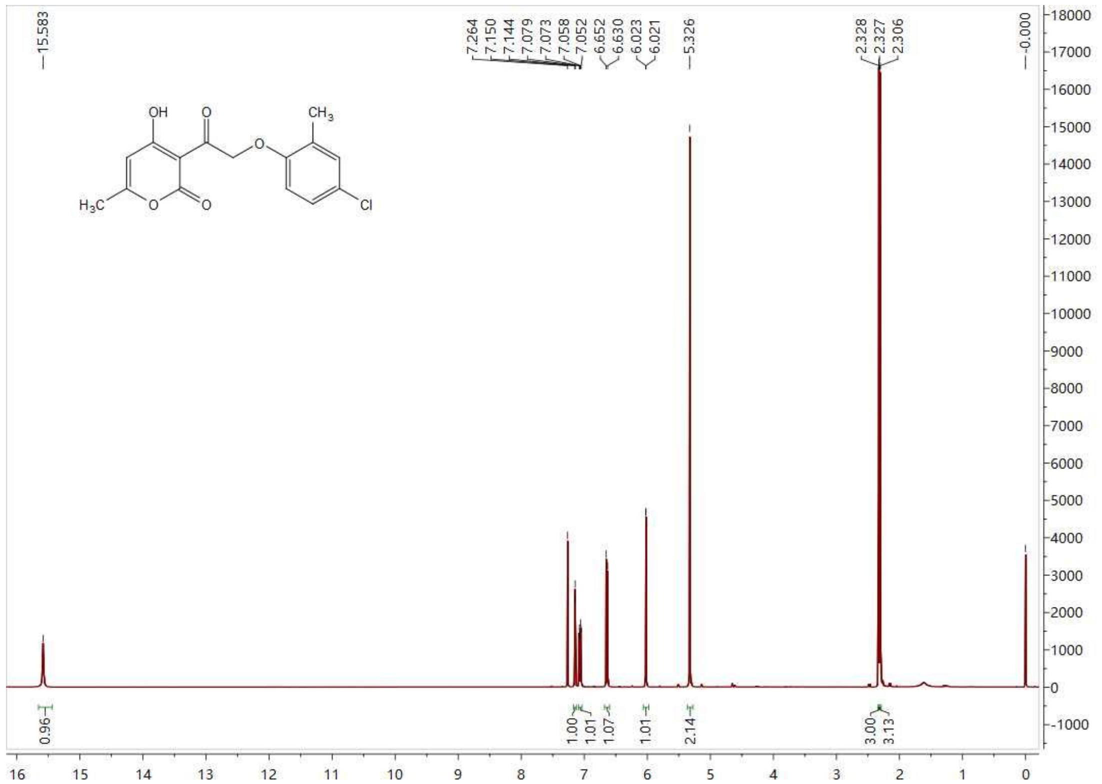
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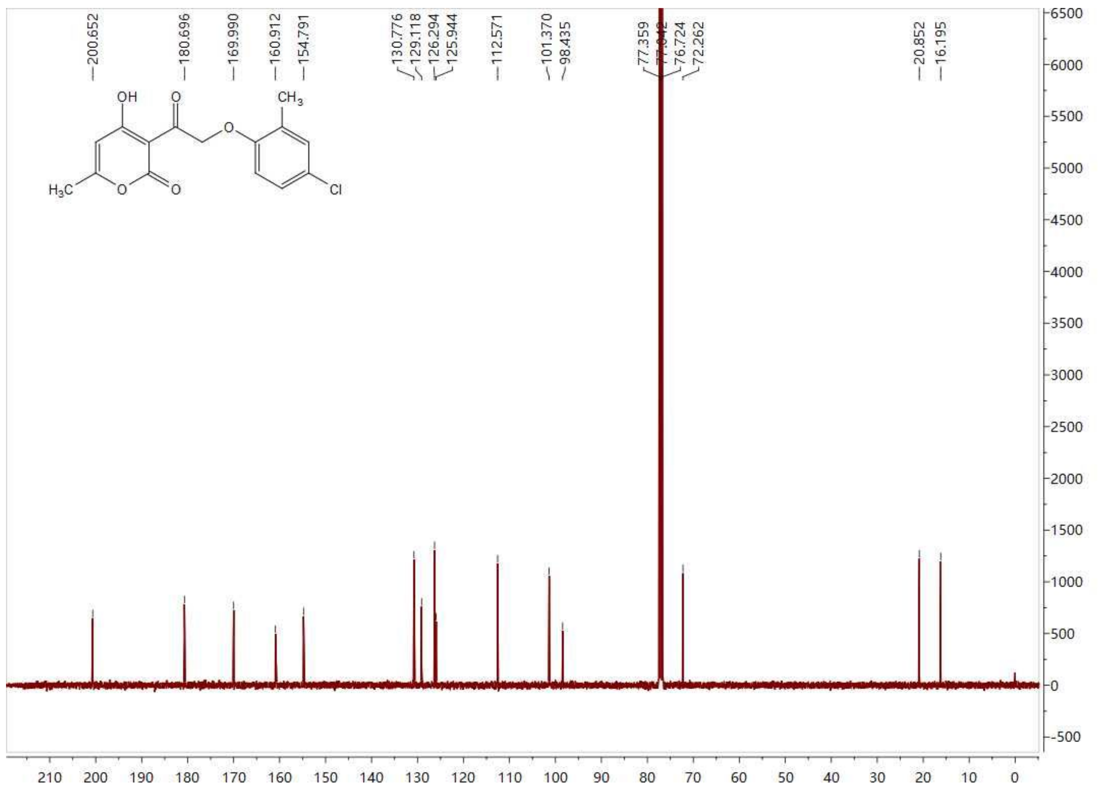
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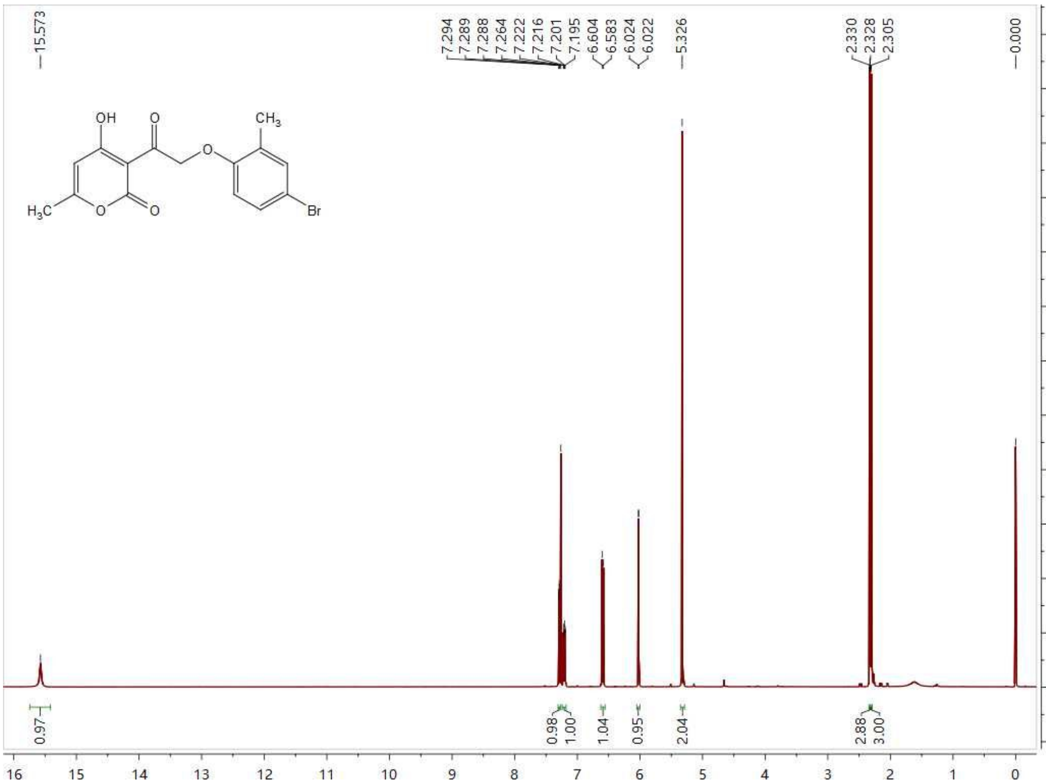

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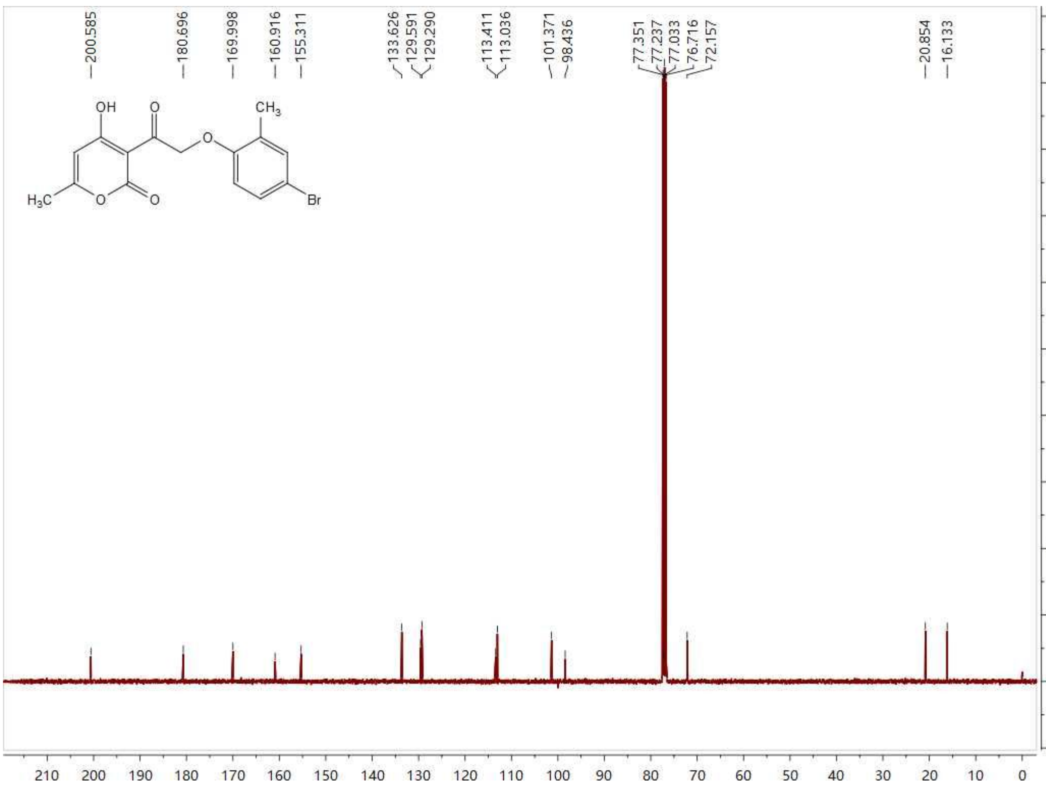
1.04
0.95
2.04
2.88
3.00



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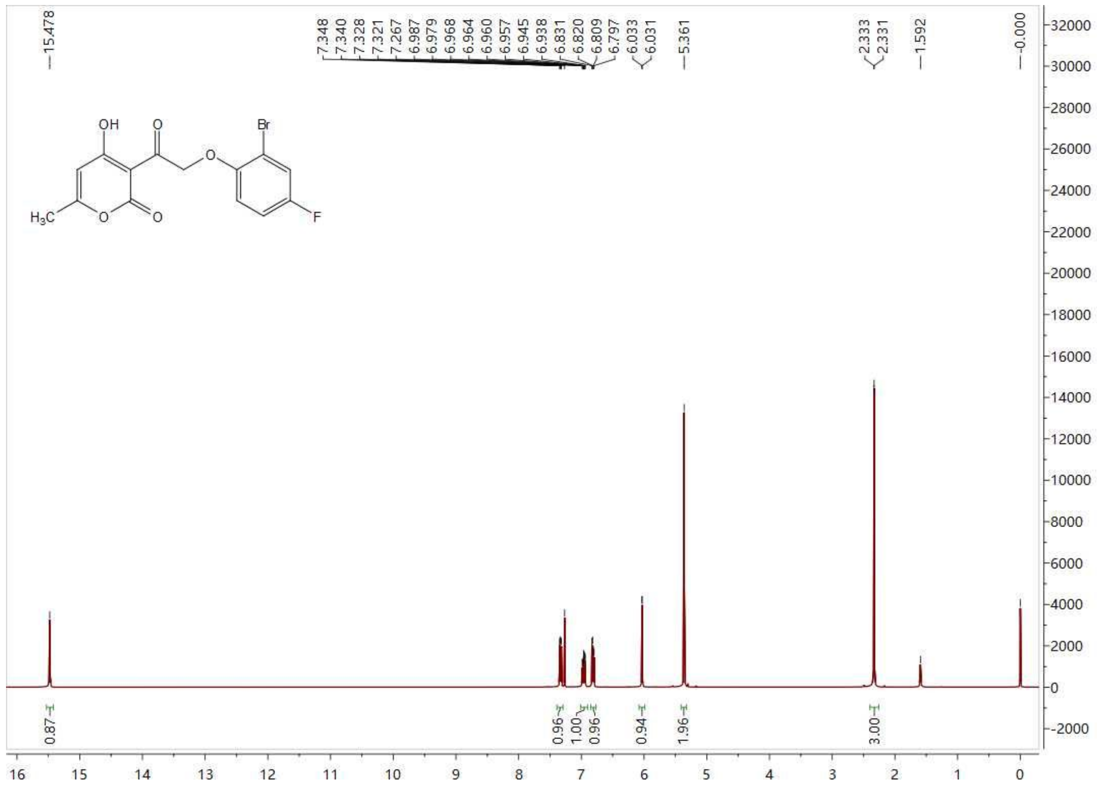
180.696
169.998
160.916
155.311
133.626
129.591
129.290
113.411
113.036
101.371
98.436
77.351
77.237
77.033
76.716
72.157
20.854
16.133
OH
O
CH3
O
H3C
O
O
Br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7.340
7.328
7.321
7.267
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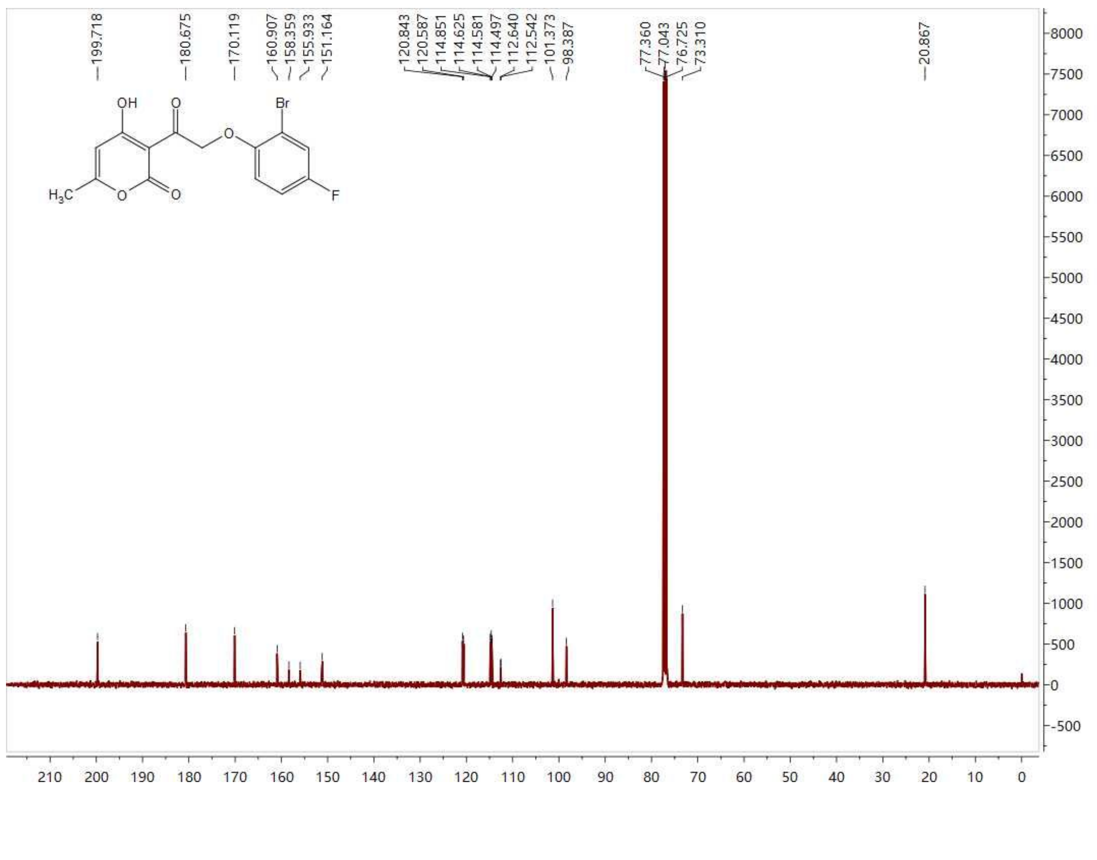
6.979
6.968
6.964
6.960
6.957
6.945
6.938
6.831
6.820
6.809
6.797
6.033
6.031
5.361
2.333
2.331
1.592
-0.000
OH
O
Br
O
H3C
O
O
F
0.87
0.96
1.00
0.96
0.94
1.96
3.00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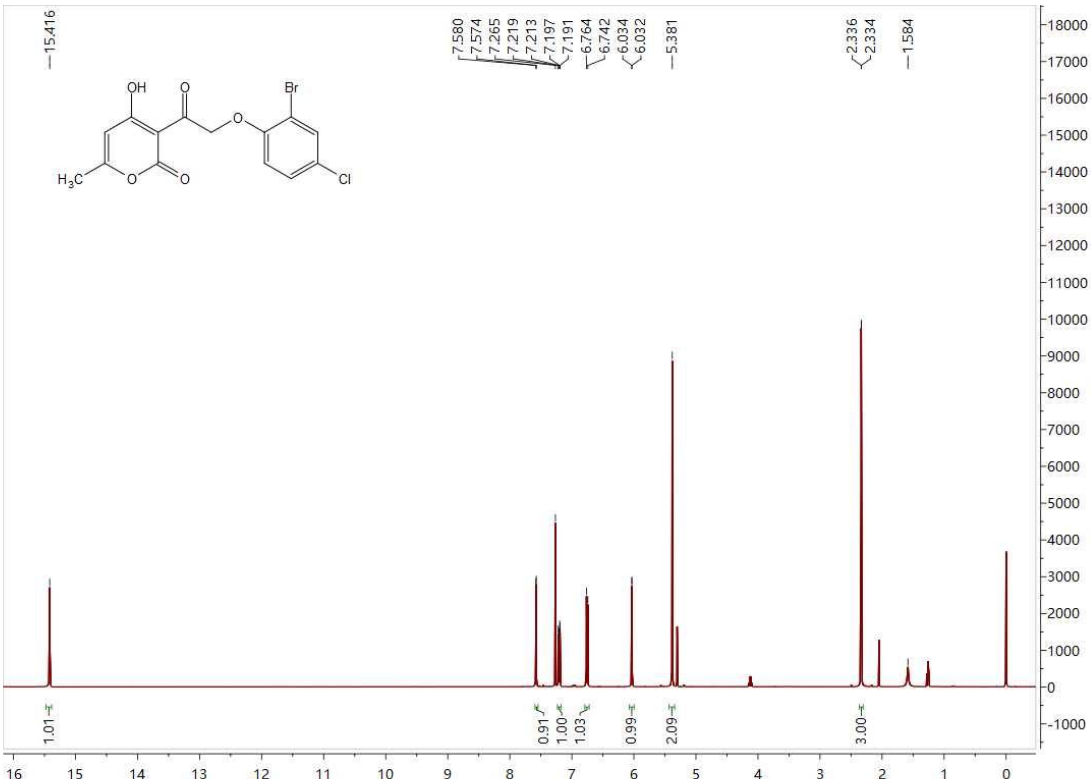
180.675
170.119
160.907
158.359
155.933
151.164
120.843
120.587
114.851
114.625
114.581
114.497
112.640
112.542
101.373
98.387
77.360
77.043
76.725
73.310
20.867
OH
O
Br
O
H3C
O
O
F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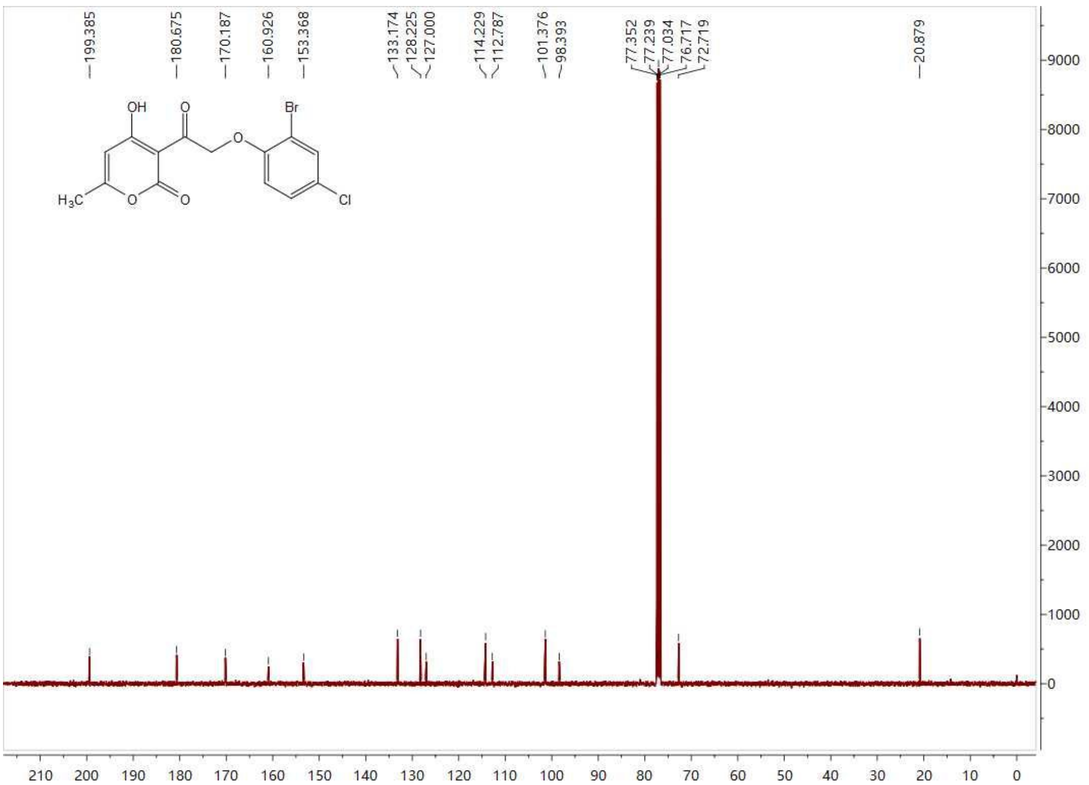
7.580
7.574
7.265
7.219
7.213
7.197
7.191
6.764
6.742
6.034
6.032
5.381
2.336
2.334
1.584
OH
O
Br
O
H3C
O
O
Cl
1.01
0.91
1.00
1.03
0.99
2.09
3.00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127.000
114.229
112.787
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98.393
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77.239
77.034
76.717
72.719
20.879
OH
O
Br
O
H3C
O
O
Cl

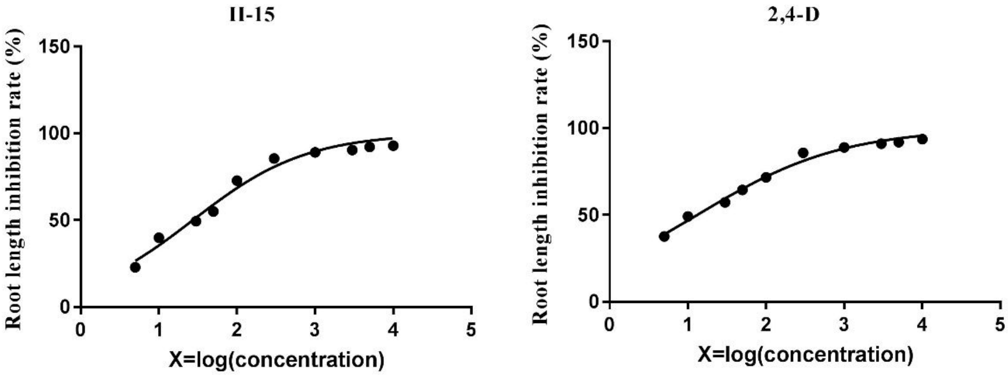

Figure S1

Table S1. Primers for real-time PCR used in this study

Primer names	sequence (5'-3')
AUX1-F	GAAGGAGTAGAAGCGATAGT
AUX1-R	CCGTGCCATAGGAAAT
GH3.3-F	CAAACCAATCCTCCAAATGAC
GH3.3-R	ACTTATCCGCAACCCGACT
IAA5-F	CCGCTCTGCAAATTCTGTT
IAA5-R	TCTCCAGCAAGCATCCAAT
ACTIN2-F	GGTAACATTGTGCTCAGTGGTGG
ACTIN2-R	AACGACCTTAATCTTCATGCTGC