Electronic Supplementary Material (ESI) for Green Chemistry.
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One-pot synthesis of 3-(furan-2-yl)-4*H*-chromen-4-ones from 1-(2-hydroxyphenyl)butane-1,3-diones and 2,5-dimethoxy-2,5-dihydrofuran catalyzed *via* K10 montmorillonite under solvent-free conditions

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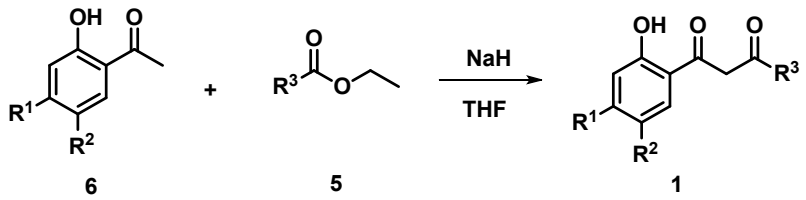
Supporting Information

1. Synthesis of 1-(2-hydroxyphenyl)butane-1,3-diones 1



6 5 1

R^1=H, OH, OMe R^2=H, Me, Br, F, NO_2 R^3=H, Me, i-Pr, Ph, 2-Furyl, 2-Thinyl

Scheme 1 Synthesis of 1-(2-hydroxyphenyl)butane-1,3-diones **1**.

According to the procedure reported by Patonay,[1] 1-(2-hydroxyphenyl)butane-1,3-diones **1** were synthesized (Scheme 1). Sodium hydride (88.2 mmol) was suspended in THF (9 mL). The mixture of 2-hydroxyacetophenone **6a** (22.0 mmol) and EtOAc **5a** (55.1 mmol) in THF (2.5 mL) wasstirred and added dropwise to the above suspension at room temperature. Avigorous reaction was observed, and rose the temperature to reflux. After complete addition, the reaction mixture was stirred for a further 5 min, then quenched by pouring onto ice, then acidified to pH6 with 6 M aq HCl. The mixture was extracted with ethyl acetate (30 mL×3). The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude products were purified by flash column chromatography (silica gel, ethyl acetate/petroleum ether 1:10 as eluent) to afford the desired product **1a**. **1b-1s** were prepared with the same method.

2. Spectroscopic data of 1 and 3

1-(2-Hydroxyphenyl)butane-1,3-dione (1a).

Yield: 74%. Characteristic: a crystalline white solid as a 1:4 mixture of keto/enol tautomers. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) 2.15 (s, 3H), 2.31* (s, 0.75H), 4.10* (s, 0.5H), 6.18 (s, 1H), 6.87 (t, 1H, *J* = 7.6 Hz), 6.91-6.94* (m, 0.25H), 6.97 (q, 1H, *J* = 5.1 Hz), 7.01-7.06* (m, 0.25H), 7.44 (t, 1H, *J* = 7.2 Hz), 7.48-7.52* (m, 0.25H), 7.63 (d, 1H, *J* = 7.0 Hz), 7.90* (d, 0.25H, *J* = 7.8 Hz), 11.93* (s, 0.25H), 12.06 (s, 1H), 14.97 (s, 1H); * = keto (minor) tautomer.[2]

1-(2,4-Dihydroxyphenyl)butane-1,3-dione (1b).

Yield: 19%. Characteristic: a crystalline white solid as a hemiacetal tautomers. m.p. 112.6-113.5 °C. ^{1}H NMR (400 MHz, DMSO-d_6), δ (ppm) 1.58 (s, 3H), 2.58 (d, 1H, *J* = 16.3 Hz), 2.90 (d, 1H, *J* = 16.3 Hz), 6.27 (s, 1H), 6.45 (d, 1H, *J* = 8.5 Hz), 6.89 (s, 1H), 7.57 (d, 1H, *J* = 8.5 Hz), 10.43 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6), δ

(ppm) 27.7, 48.1, 101.5, 103.1, 109.7, 113.4, 127.7, 160.6, 164.5, 189.9; IR (KBr), ν (cm^{-1}) 3356, 2925, 2852, 1641, 1494, 1415, 1342, 1298, 1220, 1124, 1010, 948, 906, 840, 785, 723, 651; HRMS (ESI): calc. for $C_{10}H_{10}O_4$ $[M+Na]^+$ 217.0477, found 217.0477.

1-(2-Hydroxy-4-methoxyphenyl)butane-1,3-dione (1c).

Yield: 65%. Characteristic: a crystalline white solid as a 1:2.5 mixture of keto/enol tautomers. m.p. 69.1-70.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) 2.10 (s, 3H), 2.29* (s, 1.2H), 3.82 (s, 3H), 3.83* (s, 1.2H), 4.00* (s, 0.8H), 6.03 (s, 1H), 6.41 (s, 2H), 6.44* (d, 0.8H, J = 10.4 Hz), 7.52 (d, 1H, J = 8.5 Hz), 7.55* (s, 0.4H), 12.43* (s, 0.4H), 12.54 (s, 1H), 14.80 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm) 22.7, 30.6*, 54.5*, 55.6, 55.8*, 95.0, 101.1*, 101.4, 107.9, 108.4*, 112.1, 113.6*, 130.2, 132.5*, 165.4, 165.8, 165.9*, 166.7*, 181.3, 194.4, 197.5*, 201.9*; * = keto (minor) tautomer; IR (KBr), ν (cm^{-1}) 3348, 3066, 2999, 2949, 2858, 1656, 1589, 1433, 1313, 1265, 1164, 1099, 1055, 970, 948, 871, 819, 661; HRMS (ESI): calc. for $C_{11}H_{12}O_4$ $[M+Na]^+$ 231.0633, found 231.0636.

1-(2-Hydroxy-5-methylphenyl)butane-1,3-dione (1d).

Yield: 77%. Characteristic: a crystalline white solid as a 1:3.3 mixture of keto/enol tautomers. m.p. 105.3-106.0 °C. ^{1}H NMR (600 MHz, $CDCl_3$), δ (ppm) 2.13 (s, 3H), 2.28 (s, 3H), 2.29* (s, 0.9H), 2.30* (s, 0.9H), 4.08* (s, 0.6H), 6.16 (s, 1H), 6.85-6.87 (m, 1H), 6.89* (d, 0.3H, J = 8.5 Hz), 7.24 (dd, 1H, J = 8.4, 1.8 Hz), 7.30* (s, 0.3H), 7.39 (s, 1H), 7.67* (s, 0.3H), 11.78* (s, 0.3H), 11.88 (s, 1H), 15.02 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$), δ (ppm) 20.6, 22.8, 28.6*, 30.6*, 54.5*, 95.5, 118.1*, 118.2, 118.5, 118.6*, 126.2*, 128.2, 128.4, 130.4*, 136.9, 138.5*, 160.5, 160.9*, 182.9, 195.5, 199.8*, 201.7*; * = keto (minor) tautomer; IR (KBr), ν (cm^{-1}) 3267, 2920, 2864, 1664, 1614, 1487, 1423, 1382, 1305, 1234, 1164, 1078, 1055, 952, 885, 833, 723, 651; HRMS (ESI): calc. for $C_{11}H_{12}O_3$ $[M+Na]^+$ 215.0684, found 215.0685.[3]

1-(5-Bromo-2-hydroxyphenyl)butane-1,3-dione (1e).

Yield: 66%. Characteristic: a crystalline white solid as a 1:6.7 mixture of keto/enol tautomers. m.p. 106.4-107.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) 2.16 (s, 3H), 2.32* (s, 0.45H), 4.08* (s, 0.3H), 6.11 (s, 1H), 6.87 (d, 1H, J = 8.8 Hz), 6.91* (d, 0.15H, J = 8.7 Hz), 7.49 (dd, 1H, J = 8.8, 2.0 Hz), 7.56* (dd, 0.15H, J = 8.7, 2.3 Hz), 7.71 (d, 1H, J = 2.0 Hz), 7.99* (d, 0.15H, J = 2.3 Hz), 11.86* (s, 0.15H), 12.01 (s, 1H), 14.86 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm) 22.9, 28.8*, 54.3*, 95.5, 110.8, 113.9*, 119.4*, 119.9, 120.4*, 120.8, 130.9, 133.0*, 138.3, 138.7*, 161.5,

162.2*, 184.2, 194.2, 201.0*, 204.2*; * = keto (minor) tautomer; IR (KBr), ν (cm^{-1}) 3269, 3047, 2987, 2877, 1674, 1631, 1585, 1463, 1413, 1384, 1317, 1282, 1220, 1166, 1126, 1085, 1045, 997, 945, 893, 821, 729, 663; HRMS (ESI): calc. for $C_{10}H_9BrO_3$ $[M+Na]^+$ 278.9633, found 278.9622.

1-(5-Fluoro-2-hydroxyphenyl)butane-1,3-dione (1f).

Yield: 66%. Characteristic: a crystalline yellow solid as a 1:6.7 mixture of keto/enol tautomers. m.p. 99.3-100.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) 2.21 (s, 3H), 2.38* (s, 0.45H), 4.12* (s, 0.3H), 6.13 (s, 1H), 6.98 (dd, 1H, J = 9.1, 4.6 Hz), 7.02* (dd, 0.15H, J = 9.1, 4.6 Hz), 7.19-7.25 (m, 1H), 7.27-7.31* (m, 0.15H), 7.33 (dd, 1H, J = 9.1, 2.8 Hz), 7.59* (d, 0.15H, J = 5.2 Hz), 11.74* (s, 0.15H), 11.88 (s, 1H), 14.98 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm) 22.9, 28.7*, 54.5*, 95.5, 111.8*(d, ^2J = 23.3 Hz), 113.6 (d, ^2J = 23.5 Hz), 118.2 (d, ^3J = 6.4 Hz), 120.0 (d, ^3J = 7.4 Hz), 120.2* (d, ^3J = 7.4 Hz), 121.2* (d, ^3J = 6.5 Hz), 123.2 (d, ^2J = 23.4 Hz), 125.1* (d, ^2J = 23.8 Hz), 155.0* (d, ^1J = 243.7 Hz), 155.2 (d, ^1J = 236.6 Hz), 158.7 (d, ^4J = 1.2 Hz), 159.1* (d, ^4J = 1.3 Hz), 184.1, 194.3 (d, ^4J = 2.6 Hz), 199.1* (d, ^4J = 3.3 Hz), 201.2*; * = keto (minor) tautomer; IR (KBr), ν (cm^{-1}) 3267, 3010, 2925, 2860, 1635, 1556, 1483, 1400, 1313, 1282, 1213, 1182, 1122, 1041, 1002, 937, 908, 819, 777, 721, 678; HRMS (ESI): calc. for $C_{10}H_9FO_3$ $[M+Na]^+$ 219.0433, found 219.0432.

1-(2-Hydroxyphenyl)-4-methylpentane-1,3-dione (1g).

Yield: 74%. Characteristic: a crystalline yellow oil as a 1:5 mixture of keto/enol tautomers. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) 1.16* (s, 0.6H), 1.18* (s, 0.6H), 1.23 (s, 3H), 1.25 (s, 3H), 2.57 (dt, 1H, J = 13.8, 6.9 Hz), 2.83* (t, 0.2H, J = 7.8 Hz), 4.14* (s, 0.4H), 6.18 (s, 1H), 6.87 (t, 1H, J = 7.6 Hz), 6.90-6.94* (m, 0.2H), 6.96 (d, 1H, J = 8.5 Hz), 7.01* (d, 0.2H, J = 8.7 Hz), 7.43 (t, 1H, J = 7.8 Hz), 7.48* (t, 0.2H, J = 7.8 Hz), 7.65 (d, 1H, J = 8.1 Hz), 7.88* (d, 0.2H, J = 7.8 Hz), 11.98* (s, 0.2H), 12.09 (s, 1H), 15.10 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm) 18.1*, 19.9, 35.3, 41.7*, 51.4*, 92.6, 118.3*, 118.7, 118.8, 119.1, 119.4*, 121.5*, 128.6, 130.9*, 135.7, 137.1*, 162.5, 162.9*, 191.1, 196.0, 200.4*, 207.6*; * = keto (minor) tautomer; IR (KBr), ν (cm^{-1}) 3456, 2980, 2892, 1688, 1618, 1482, 1295, 1219, 1154, 1083, 1030, 978, 889, 825, 743, 666, 601; HRMS (ESI): calc. for $C_{12}H_{14}O_3$ $[M+Na]^+$ 229.0841, found 229.0842. [4]

1-(2-Hydroxy-4-methoxyphenyl)-4-methylpentane-1,3-dione (1h).

Yield: 54%. Characteristic: a crystalline white soild as a 1:3.3 mixture of keto/enol tautomers. m.p. 87.5-88.7 °C. ^{1}H NMR (600 MHz, $CDCl_3$), δ (ppm) 1.15* (s, 0.9H),

1.16* (s, 0.9H), 1.22 (s, 3H), 1.23 (s, 3H), 2.53 (dt, 1H, *J* = 13.8, 6.9 Hz), 2.77-2.82* (m, 0.3H), 3.82 (s, 3H), 3.83* (s, 0.9H), 4.05* (s, 0.6H), 6.04 (s, 1H), 6.42 (d, 2H, *J* = 2.2 Hz), 6.44* (d, 0.6H, *J* = 2.4 Hz), 7.53* (s, 0.3H), 7.56 (d, 1H, *J* = 8.8 Hz), 12.46* (s, 0.3H), 12.56 (s, 1H), 14.92 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$), δ (ppm) 18.2*, 20.0, 35.2, 41.6*, 51.5*, 55.6, 55.8*, 92.1, 101.1*, 101.4, 107.9, 108.3*, 112.4, 113.8*, 130.2, 132.7*, 165.4, 165.8, 165.9*, 166.8*, 189.4, 194.9, 198.0*, 207.8*; * = keto (minor) tautomer; IR (KBr), *ν* (cm^{-1}) 3224, 3050, 2991, 2952, 1652, 1559, 1440, 1350, 1259, 1211, 1164, 1114, 1024, 972, 887, 835, 732, 665; HRMS (ESI): calc. for $C_{13}H_{16}O_4$ $[M+Na]^+$ 259.0946, found 259.0937.

1-(5-Bromo-2-hydroxyphenyl)-4-methylpentane-1,3-dione (1i).

Yield: 56%. Characteristic: a crystalline yellow soild as a 1:10 mixture of keto/enol tautomers. m.p. 43.1-44.2 °C. ^{1}H NMR (600 MHz, $CDCl_3$), δ (ppm) 1.17* (d, 0.3H, *J* = 3.5 Hz), 1.18* (d, 0.3H, *J* = 3.4 Hz), 1.23 (d, 3H, *J* = 3.5 Hz), 1.25 (d, 3H, *J* = 3.4 Hz), 2.53-2.61 (m, 1H), 2.75-2.80* (m, 0.1H), 4.10* (d, 0.2H, *J* = 3.2 Hz), 6.09 (d, 1H, *J* = 3.1 Hz), 6.84 (dd, 1H, *J* = 8.8, 3.3 Hz), 6.86-6.89* (m, 0.1H), 7.44-7.48 (m, 1H), 7.50-7.53* (m, 0.1H), 7.70 (d, 1H, *J* = 1.8 Hz), 7.95* (d, 0.1H, *J* = 1.7 Hz), 11.87* (s, 0.1H), 12.01 (s, 1H), 15.00 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$), δ (ppm) 18.0*, 19.9, 35.4, 37.9*, 51.0*, 92.6, 110.7, 114.1*, 120.1, 120.4*, 120.7, 122.2*, 130.7, 133.1*, 138.2, 139.7*, 161.4, 161.7*, 192.2, 194.5, 199.6*, 207.0*; * = keto (minor) tautomer; IR (KBr), ν (cm^{-1}) 3303, 2983, 2886, 1889, 1690, 1611, 1569, 1460, 1381, 1315, 1279, 1170, 1073, 970, 873, 807, 759, 728, 680, 620; HRMS (ESI): calc. for $C_{12}H_{13}BrO_3$ $[M+Na]^+$ 306.9946, found 306.9941.

1-(5-Fluoro-2-hydroxyphenyl)-4-methylpentane-1,3-dione (1j).

Yield: 58%. Characteristic: a crystalline yellow soild as a 1:10 mixture of keto/enol tautomers. m.p. 39.2-40.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) 1.16* (s, 0.3H), 1.18* (s, 0.3H), 1.23 (s, 3H), 1.24 (s, 3H), 2.57 (dt, 1H, *J* = 13.8, 6.9 Hz), 2.77* (dd, 0.1H, *J* = 13.9, 7.0 Hz), 4.09* (s, 0.2H), 6.07 (s, 1H), 6.91 (dd, 1H, *J* = 9.1, 4.7 Hz), 6.93-6.97* (m, 0.1H), 7.14 (td, 1H, *J* = 8.4, 2.8 Hz), 7.20* (dd, 0.1H, *J* = 8.5, 3.0 Hz), 7.29 (dd, 1H, *J* = 9.2, 3.0 Hz), 7.51* (dd, 0.1H, *J* = 8.1, 3.1 Hz), 11.71* (s, 0.1H), 11.81 (s, 1H), 15.05 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm) 18.0*, 19.9, 35.4, 37.9*, 51.3*, 92.6, 113.6 (d, ^2J = 23.5), 115.7* (d, ^2J = 23.4), 118.4 (d, ^3J = 6.4), 119.9 (d, ^3J = 7.3), 120.1* (d, ^3J = 7.2), 121.4* (d, ^3J = 6.5), 123.0 (d, ^2J = 23.4), 124.8* (d, ^2J = 23.7), 154.9* (d, ^1J = 237.6), 155.2 (d, ^1J = 236.4), 158.6 (d, ^4J = 0.9), 159.1* (d, ^4J = 1.5), 192.1, 194.7 (d, ^4J = 2.5), 199.6* (d, ^4J = 2.7), 207.2*; * = keto

(minor) tautomer; IR (KBr), ν (cm^{-1}) 3320, 2982, 2885, 1752, 1703, 1575, 1484, 1398, 1319, 1270, 1173, 1076, 1039, 911, 867, 820, 777, 729, 668, 613; HRMS (ESI): calc. for $C_{12}H_{13}FO_3$ $[M+Na]^+$ 247.0746, found 247.0746.

1-(2-Hydroxyphenyl)-3-phenylpropane-1,3-dione (1k).

It was provided by the Energy Chemical web.

1-(Furan-2-yl)-3-(2-hydroxyphenyl)propane-1,3-dione (1l).

Yield: 69%. Characteristic: a crystalline yellow soild as a 1:4 mixture of keto/enol tautomers. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) 4.50* (s, 0.5H), 6.59* (d, 0.25H, *J* = 2.1 Hz), 6.60 (dd, 1H, *J* = 3.5, 1.7 Hz), 6.78 (s, 1H), 6.92 (t, 1H, *J* = 7.2 Hz), 6.95* (s, 0.25H), 6.99 (d, 1H, *J* = 8.2 Hz), 7.00* (s, 0.25H), 7.17 (d, 1H, *J* = 3.5 Hz), 7.35* (d, 0.25H, *J* = 3.6 Hz), 7.43-7.48 (m, 1H), 7.48-7.53* (m, 0.25H), 7.61 (s, 1H), 7.62* (s, 0.25H), 7.77 (dd, 1H, *J* = 8.0, 1.3 Hz), 7.79* (d, 0.25H, *J* = 1.5 Hz), 11.89* (s, 0.25H), 12.08 (s, 1H), 15.08 (s, 1H); * = keto (minor) tautomer. [5]

1-(2-Hydroxyphenyl)-3-(thiophen-2-yl)propane-1,3-dione (1m).

Yield: 60%. Characteristic: a crystalline yellow soild as a 1:2.5 mixture of keto/enol tautomers. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) 4.55* (s, 0.8H), 6.68 (s, 1H), 6.90 (d, 1H, *J* = 7.3 Hz), 6.93* (s, 0.4H), 6.99 (d, 1H, *J* = 8.4 Hz), 6.99* (d, 0.4H, *J* = 8.4 Hz), 7.13-7.20 (m, 1H), 7.13-7.20* (m, 0.4H), 7.45 (t, 1H, *J* = 8.4 Hz), 7.50* (d, 0.4H, *J* = 7.2 Hz), 7.59 (d, 1H, *J* = 4.5 Hz), 7.68-7.74* (m, 0.4H), 7.68-7.74 (m, 1H), 7.77 (d, 1H, *J* = 3.6 Hz), 7.83* (t, 0.8H, *J* = 6.4 Hz), 11.92* (s, 0.4H), 11.97 (s, 1H), 15.65 (s, 1H); * = keto (minor) tautomer.[5]

3-(2-Hydroxyphenyl)-3-oxopropanal (1n).

Yield: 72%. Characteristic: a crystalline white solid as a hemiacetal tautomers. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) 2.89 (dd, 1H, *J* = 16.8, 4.6 Hz), 3.03 (dd, 1H, *J* = 16.8, 3.3 Hz), 3.74 (d, 1H, *J* = 3.1 Hz), 5.89 (dd, 1H, *J* = 7.5, 3.8 Hz), 6.93-7.10 (m, 2H), 7.45-7.57 (m, 1H), 7.89 (dd, 1H, *J* = 7.8, 1.4 Hz).[6]

3-(2-Hydroxy-4-methoxyphenyl)-3-oxopropanal (1o).

Yield: 73%. Characteristic: a crystalline white solid as a hemiacetal tautomers. m.p. 140.9-141.7 °C. ^{1}H NMR (400 MHz, DMSO-d_6), δ (ppm) 2.60 (dd, 1H, *J* = 16.6, 4.6 Hz), 2.95 (dd, 1H, *J* = 16.6, 2.4 Hz), 3.81 (s, 3H), 5.78 (dd, 1H, *J* = 8.4, 4.6 Hz), 6.51 (d, 1H, *J* = 2.2 Hz), 6.62 (dd, 1H, *J* = 8.7, 2.3 Hz), 7.58 (d, 1H, *J* = 5.0 Hz), 7.66 (d, 1H, *J* = 8.8 Hz); ^{13}C NMR (100 MHz, DMSO-d_6), δ (ppm) 43.9, 55.8, 95.3, 101.6, 109.2, 114.8, 127.4, 160.3, 165.7, 189.6; IR (KBr), *v* (cm^{-1}) 3236, 3074, 2926, 2860, 1649, 1605, 1452, 1360, 1256, 1198, 1148, 1103, 1107, 1016, 978, 860, 818, 773, 727,

679, 635; HRMS (ESI): calc. for $C_{10}H_{10}O_4$ $[M+Na]^+$ 217.0477, found 217.0476.[7]

3-(5-Fluoro-2-hydroxyphenyl)-3-oxopropanal (1p).

Yield: 83%. Characteristic: a crystalline white solid as a hemiacetal tautomers. m.p. 202.7-203.4 °C. ^{1}H NMR (400 MHz, DMSO-d_6), δ (ppm) 2.70 (dd, 1H, J = 16.7, 4.1 Hz), 3.02-3.11 (m, 1H), 5.83 (dd, 1H, J = 8.2, 4.0 Hz), 7.07 (dd, 1H, J = 8.8, 4.3 Hz), 7.35-7.47 (m, 2H), 7.62 (dd, 1H, J = 4.9, 1.2 Hz); ^{13}C NMR (100 MHz, DMSO-d_6), δ (ppm) 43.9, 95.2, 110.5 (d, ^2J = 23.0 Hz), 120.4 (d, ^3J = 7.4 Hz), 121.4 (d, ^3J = 6.2 Hz), 123.5 (d, ^2J = 24.1 Hz), 154.6 (d, ^4J = 1.2 Hz), 156.5 (d, ^1J = 237.5 Hz), 190.7 (d, ^4J = 1.6 Hz); IR (KBr), ν (cm^{-1}) 3277, 1665, 1616, 1483, 1440, 1391, 1329, 1269, 1238, 1175, 1096, 1055, 1005, 897, 833, 690; HRMS (ESI): calc. for $C_9H_7FO_3$ $[M+Na]^+$ 205.0277, found 205.0271.

3-(2-Hydroxy-5-nitrophenyl)-3-oxopropanal (1q).

Yield: 82%. Characteristic: a crystalline yellow solid as a hemiacetal tautomers. m.p. 143.2-143.7 °C. ^{1}H NMR (400 MHz, DMSO-d_6), δ (ppm) 2.81 (dd, 1H, J = 16.6, 3.8 Hz), 3.20 (dd, 1H, J = 16.6, 2.8 Hz), 6.01 (dd, 1H, J = 7.5, 3.5 Hz), 7.26 (d, 1H, J = 9.1 Hz), 8.01 (d, 1H, J = 4.3 Hz), 8.38 (dd, 1H, J = 9.1, 2.9 Hz), 8.45 (d, 1H, J = 2.9 Hz; ^{13}C NMR (100 MHz, DMSO-d_6), δ (ppm) 43.8, 96.4, 120.1, 120.5, 121.5, 130.5, 141.3, 162.7, 189.9; IR (KBr), ν (cm^{-1}) 3468, 3125, 3063, 2928, 2864, 1681, 1605, 1585, 1521, 1475, 1437, 1344, 1275, 1221, 1101, 976, 937, 885, 851, 797, 733, 707, 627; HRMS (ESI): calc. for $C_9H_7NO_5$ $[M+Na]^+$ 232.0222, found 232.0222.

1-(2-Hydroxy-5-nitrophenyl)butane-1,3-dione (1r).

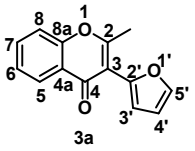
Yield: 44%. Characteristic: a crystalline yellow solid as a 1:6.7 mixture of enol/hemiacetal tautomers. m.p. 152.1-153.9 °C. ^{1}H NMR (400 MHz, DMSO-d_6), δ (ppm) 1.70 (s, 3H), 2.22* (s, 0.45H), 2.85 (d, 1H, J = 16.4 Hz), 3.22 (d, 1H, J = 15.5 Hz), 6.74* (s, 0.15H), 7.16* (d, 0.15H, J = 9.1 Hz), 7.24 (d, 1H, J = 9.1 Hz), 7.51 (s, 1H, 2-OH), 8.28* (ddd, 0.15H, J = 17.4, 9.1, 2.8 Hz), 8.38 (dd, 1H, J = 9.1, 2.6 Hz), 8.47 (d, 1H, J = 2.6 Hz), 8.59* (dd, 0.15H, J = 17.6, 2.6 Hz), 12.39* (s, 0.15H), 16.12* (s, 0.15H); ^{13}C NMR (100 MHz, DMSO-d_6), δ (ppm) 20.0*, 27.3, 47.9, 100.9*, 103.6, 118.2*, 118.7*, 119.9, 120.2, 121.6, 125.5*, 128.6*, 130.3, 139.6*, 141.1, 163.0, 164.3*, 186.4*, 190.5, 194.9*; * = enol (minor) tautomer; IR (KBr), ν (cm^{-1}) 3276, 3132, 3089, 2960, 2920, 1585, 1481, 1342, 1288, 1197, 1116, 1049, 912, 864, 812, 748, 713, 638; HRMS (ESI): calc. for $C_{10}H_9NO_5$ $[M+Na]^+$ 246.0378, found 246.0372.

1-(1-Hydroxynaphthalen-2-yl)butane-1,3-dione (1s).

Yield: 88%. Characteristic: a crystalline white solid as a hemiacetal tautomers. m.p. 164.4-165.4 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 1.68 (s, 3H), 2.78 (d, 1H, *J* = 15.8 Hz), 3.19 (d, 1H, *J* = 15.8 Hz), 7.18 (d, 2H, *J* = 6.4 Hz), 7.43 (t, 1H, *J* = 7.4 Hz), 7.63 (t, 1H, *J* = 7.7 Hz), 7.88 (d, 1H, *J* = 8.0 Hz), 8.10 (d, 1H, *J* = 9.0 Hz), 9.35 (d, 1H, *J* = 8.6 Hz); ^{13}C NMR (100 MHz, DMSO-d_6), δ (ppm) 27.4, 49.6, 101.7, 111.3, 119.5, 124.4, 124.7, 128.5, 128.6, 129.3, 130.7, 137.2, 160.4, 193.3; IR (KBr), ν (cm^{-1}) 3261, 2927, 2864, 1633, 1597, 1506, 1438, 1379, 1220, 1155, 1124, 1070, 968, 864, 840, 746, 684; HRMS (ESI): calc. for $C_{14}H_{12}O_3$ $[M+Na]^+$ 251.0684, found 251.0684.

3-(Furan-2-yl)-2-methyl-4*H*-chromen-4-one (3a).

Yield: 78%. White soild. m.p. 92.8-93.6 °C. ^{1}H NMR (600 MHz, $CDCl_3$), δ (ppm) 2.59 (s, 3H), 6.52 (dd, 1H, *J* = 3.2, 1.8 Hz), 6.97 (d, 1H, *J* = 3.2 Hz), 7.35-7.39 (m, 1H), 7.40 (d, 1H, *J* = 8.4 Hz), 7.50 (d, 1H, *J* = 1.8 Hz), 7.59-7.64 (m, 1H), 8.23 (d, 1H, *J* = 7.9 Hz); ^{13}C NMR (150 MHz, $CDCl_3$), δ (ppm) 20.5, 111.3, 112.4, 114.3, 117.7, 123.1, 125.1, 126.3, 133.5, 141.8, 145.9, 155.5, 164.8, 175.3; IR (KBr), *v* (cm^{-1}) 3105, 3065, 2930, 1967, 1733, 1624, 1541, 1460, 1394, 1352, 1286, 1220, 1150, 1103, 1004, 900, 819, 742, 648; HRMS (ESI): calc.for $C_{14}H_{10}O_3$ $[M+Na]^+$ 249.0528, found 249.0525.



3a

Position	δ_H	δ_C	DEPT (135°) δ_C	H,H-COSY cross-signal with δ_H	HSQC cross-signal with $\delta_H(\delta_C)$	HMBC cross-signal with $\delta_H(\delta_C)$
2		164.8				2.59(164.8)
3		114.3				2.59(114.3)
4		175.3				8.23(175.3)
5	8.23 (d, 7.9)	126.3	126.3	7.35-7.39	8.23(126.3)	
6	7.35-7.39 (m)	125.1	125.1	7.59-7.64, 8.23	7.35-7.39(125.1)	
7	7.59-7.64 (m)	133.5	133.5	7.35-7.39, 7.40	7.59-7.64(133.5)	
8	7.40 (d, 8.4)	117.7	117.7	7.59-7.64	7.40(117.7)	
8a		123.1				7.40(123.1)
4a		155.5				8.23(155.5)
2-Me	2.59(s)	20.5	20.5		2.59(20.5)	
2'		145.7				6.97(145.7)
3'	6.97(d, 3.2)	112.4	112.4	6.52	6.97(112.4)	
4'	6.52(dd, 3.2, 1.8)	111.3	111.3	6.97, 7.50	6.52(111.3)	
5'	7.50 (d, 1.8)	141.8	141.8	6.52	7.50(141.8)	

3-(Furan-2-yl)-7-hydroxy-2-methyl-4*H*-chromen-4-one (3b).

Yield: 64%. White soild. m.p. 225.7-226.4 °C. ^{1}H NMR (600 MHz, DMSO-d_6), δ (ppm) 2.46 (s, 3H), 6.58 (dd, 1H, *J* = 3.2, 1.8 Hz), 6.80 (d, 1H, *J* = 3.2 Hz), 6.81 (d, 1H, *J* = 2.2 Hz), 6.90 (dd, 1H, *J* = 8.7, 2.2 Hz), 7.74 (d, 1H, *J* = 1.8 Hz), 7.89 (d, 1H, *J* = 8.7 Hz), 10.81 (s, 1H); ^{13}C NMR (150 MHz, DMSO-d_6), δ (ppm) 19.8, 101.9, 111.1, 111.7, 112.9, 115.1, 115.2, 127.1, 142.4, 145.8, 156.7, 162.7, 164.4, 173.6; IR (KBr), *v* (cm^{-1}) 3160, 3065, 2958, 2925, 1742, 1631, 1587, 1539, 1475, 1394, 1346, 1265, 1223, 1161, 1109, 1016, 989, 899, 820, 737, 662; HRMS (ESI): calc. for $C_{14}H_{10}O_4$ $[M+Na]^+$ 265.0477, found 265.0468.

3-(Furan-2-yl)-7-methoxy-2-methyl-4*H*-chromen-4-one (3c).

Yield: 79%. White soild. m.p. 118.4-119.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) 2.54 (s, 3H), 3.86 (s, 3H), 6.51 (dd, 1H, *J* = 3.2, 1.0 Hz), 6.77 (d, 1H, *J* = 3.2 Hz), 6.91 (dd, 1H, *J* = 8.9, 1.7 Hz), 6.94 (d, 1H, *J* = 1.7 Hz), 7.48 (d, 1H, *J* = 1.0 Hz), 8.10 (d, 1H, *J* = 8.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm) 20.3, 55.8, 99.9, 111.2, 112.3, 114.0, 114.4, 116.9, 127.6, 141.7, 146.0, 157.2, 163.9, 164.2, 174.8; IR (KBr), *v* (cm^{-1}) 3091, 2956, 2925, 2858, 1737, 1618, 1575, 1500, 1434, 1381, 1346, 1247, 1194, 1155, 1105, 1028, 920, 824, 723, 694; HRMS (ESI): calc. for $C_{15}H_{12}O_4$ $[M+Na]^+$ 279.0633, found 279.0630.

3-(Furan-2-yl)-2,6-dimethyl-4*H*-chromen-4-one (3d).

Yield: 77%. Yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$), δ (ppm) 2.41 (s, 3H), 2.55 (s, 3H), 6.51 (dd, 1H, *J* = 3.2, 1.8 Hz), 6.95 (d, 1H, *J* = 3.2 Hz), 7.27 (d, 1H, *J* = 8.5 Hz), 7.40 (d, 1H, *J* = 8.5Hz), 7.48 (d, 1H, *J* = 1.8 Hz), 7.98 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$), δ (ppm) 20.4, 21.0, 111.2, 112.2, 114.1, 117.4, 122.7, 125.5, 134.7, 135.0, 141.7, 146.1, 153.8, 164.6, 175.3; IR (KBr), *v* (cm^{-1}) 3141, 3042, 2978, 2920, 1726, 1645, 1550, 1489, 1431, 1396, 1352, 1284, 1232, 1146, 1026, 976, 893, 822, 741, 671; HRMS (ESI): calc. for $C_{15}H_{12}O_3$ $[M+Na]^+$ 263.0684, found 263.0679.

6-Bromo-3-(furan-2-yl)-2-methyl-4*H*-chromen-4-one (3e).

Yield: 75%. White soild. m.p. 104.8-105.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) 2.58 (s, 3H), 6.52 (dd, 1H, *J* = 3.2, 1.8 Hz), 6.97 (d, 1H, *J* = 3.2 Hz), 7.28 (d, 1H, *J* = 8.8 Hz), 7.49 (d, 1H, *J* = 1.8 Hz), 7.67 (dd, 1H, *J* = 8.8, 2.3 Hz), 8.30 (d, 1H, *J* = 2.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm) 20.6, 111.3, 112.7, 114.3, 118.4, 119.7, 124.3, 128.8, 136.4, 141.9, 145.4, 154.2, 164.9, 173.9; IR (KBr), *v* (cm^{-1}) 3090, 2924,

2862, 1745, 1633, 1543, 1440, 1384, 1344, 1265, 1217, 1147, 1083, 1012, 898, 813, 738, 661; HRMS (ESI): calc. for $C_{14}H_9BrO_3$ $[M+Na]^+$ 326.9633, found 326.9629.

6-Fluoro-3-(furan-2-yl)-2-methyl-4*H*-chromen-4-one (3f).

Yield: 78%. White soild. m.p. 102.2-102.8 °C. ^{1}H NMR (600 MHz, $CDCl_3$), δ (ppm) 2.55 (s, 3H), 6.49 (dd, 1H, *J* = 3.3, 1.8 Hz), 6.95 (d, 1H, *J* = 3.3 Hz), 7.27-7.31 (m, 1H), 7.36 (dd, 1H, *J* = 9.1, 4.2 Hz), 7.46 (d, 1H, *J* = 1.8 Hz), 7.78 (dd, 1H, *J* = 8.3, 3.1 Hz); ^{13}C NMR (150 MHz, $CDCl_3$), δ (ppm) 20.5, 110.9 (d, ^2J = 23.6 Hz), 111.3, 112.6, 113.6, 119.9 (d, ^3J = 8.1 Hz), 121.6 (d, ^2J = 25.3 Hz), 124.1 (d, ^3J = 7.4 Hz), 141.9, 145.5, 151.6, 159.5 (d, ^1J = 244.9 Hz), 165.0, 174.4 (d, ^4J = 1.7 Hz); IR (KBr), *v* (cm^{-1}) 3160, 3065, 2958, 2925, 1742, 1631, 1587, 1539, 1475, 1394, 1346, 1265, 1223, 1161, 1109, 1016, 989, 899, 820, 737, 662; HRMS (ESI): calc. for $C_{14}H_9FO_3$ $[M+Na]^+$ 267.0433, found 267.0426.

3-(Furan-2-yl)-2-isopropyl-4*H*-chromen-4-one (3g).

Yield: 86%. White soild. m.p. 56.5-57.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) 1.33 (s, 3H), 1.35 (s, 3H), 3.32 (hept, 1H, *J* = 6.8 Hz), 6.52 (dd, 1H, *J* = 3.2, 1.8 Hz), 6.75 (d, 1H, *J* = 3.2 Hz), 7.36-7.39 (m, 1H), 7.46 (d, 1H, *J* = 8.4 Hz), 7.52 (d, 1H, *J* = 1.8 Hz), 7.60-7.69 (m, 1H), 8.23 (d, 1H, *J* = 7.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm) 20.3, 31.9, 111.2, 112.2, 112.8, 117.7, 123.2, 125.1, 126.3, 133.5, 142.2, 145.6, 155.7, 172.3, 176.2; IR (KBr), *v* (cm^{-1}) 2980, 2930, 1726, 1651, 1553, 1468, 1395, 1364, 1288, 1229, 1117, 1065, 1016, 980, 912, 868, 814, 743, 673; HRMS (ESI): calc. for $C_{16}H_{14}O_3$ $[M+Na]^+$ 277.0841, found 277.0842.

3-(Furan-2-yl)-2-isopropyl-7-methoxy-4*H*-chromen-4-one (3h).

Yield: 75%. White soild. m.p. 88.5-89.4 °C. ^{1}H NMR (600 MHz, $CDCl_3$), δ (ppm) 1.32 (s, 3H), 1.33 (s, 3H), 3.29 (hept, 1H, *J* = 6.8 Hz), 3.89 (s, 3H), 6.51 (dd, 1H, *J* = 3.2, 1.9 Hz), 6.72 (d, 1H, *J* = 3.2 Hz), 6.84 (d, 1H, *J* = 2.3 Hz), 6.93 (dd, 1H, *J* = 8.9, 2.3 Hz), 7.50 (d, 1H, *J* = 1.9 Hz), 8.11 (d, 1H, *J* = 8.9 Hz); ^{13}C NMR (150 MHz, $CDCl_3$), δ (ppm) 20.3, 31.7, 55.9, 99.9, 111.1, 112.1, 112.6, 114.5, 117.1, 127.7, 142.2, 145.8, 157.4, 164.1, 171.8, 175.6; IR (KBr), *v* (cm^{-1}) 3098, 2974, 2930, 2880, 1730, 1630, 1499, 1442, 1404, 1350, 1250, 1202, 1159, 1103, 1067, 1020, 955, 912, 820, 731, 681; HRMS (ESI): calc. for $C_{17}H_{16}O_4$ $[M+Na]^+$ 307.0946, found 307.0943.

6-Bromo-3-(furan-2-yl)-2-isopropyl-4*H*-chromen-4-one (3i).

Yield: 68%. Yellow soild. m.p. 106.9-107.8 °C. ^{1}H NMR (600 MHz, $CDCl_3$), δ (ppm) 1.32 (s, 3H), 1.33 (s, 3H), 3.33 (hept, 1H, *J* = 6.8 Hz), 6.52 (dd, 1H, *J* = 3.2, 1.9 Hz), 6.75 (d, 1H, *J* = 3.2 Hz), 7.36 (d, 1H, *J* = 8.9 Hz), 7.52 (d, 1H, *J* = 1.9 Hz), 7.71 (dd,

1H, J = 8.9, 2.4 Hz), 8.33 (d, 1H, J = 2.4 Hz); ^{13}C NMR(150 MHz, $CDCl_3$), δ (ppm) 20.2, 31.9, 111.2, 112.5, 113.0, 118.5, 119.8, 124.6, 128.9, 136.5, 142.4, 145.1, 154.5, 172.5, 174.8; IR (KBr), v (cm^{-1}) 3067, 2978, 2928, 2866, 1946, 1792, 1736, 1643, 1547, 1462, 1431, 1344, 1265, 1221, 1140, 1061, 1011, 890, 824, 735, 687; HRMS (ESI): calc. for $C_{16}H_{13}BrO_3$ $[M+Na]^+$ 354.9946, found 354.9942.

6-Fluoro-3-(furan-2-yl)-2-isopropyl-4*H*-chromen-4-one (3j).

Yield: 65%. White soild. m.p. 78.0-78.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) 1.32 (s, 3H), 1.33 (s, 3H), 3.33 (hept, 1H, J = 6.9 Hz), 6.51 (dd, 1H, J = 3.3, 1.9 Hz), 6.75 (d, 1H, J = 3.3 Hz), 7.33-7.38 (m, 1H), 7.44-7.48 (m, 1H), 7.51 (d, 1H, J = 1.9 Hz), 7.83 (dd, 1H, J = 8.2, 3.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm) 20.2, 31.9, 110.9 (d, ^2J = 23.6 Hz), 111.2, 112.2, 112.3, 119.9 (d, ^3J = 8.0 Hz), 121.7 (d, ^2J = 25.4 Hz), 124.3 (d, ^3J = 7.4 Hz), 142.3, 145.2, 151.9 (d, ^4J = 1.3 Hz), 159.5 (d, ^1J = 244.8 Hz), 172.6, 175.3 (d, ^4J = 2.1 Hz); IR (KBr), v (cm^{-1}) 3134, 3084, 2972, 2926, 2874, 1726, 1638, 1549, 1472, 1400, 1354, 1261, 1148, 1111, 1069, 1013, 984, 895, 829, 760, 737, 679, 640, 600; HRMS (ESI): calc. for $C_{16}H_{13}FO_3$ $[M+Na]^+$ 295.0746, found 295.0743.

3-(Furan-2-yl)-2-phenyl-4*H*-chromen-4-one (3k).

Yield: 89%. Yellow soild. m.p. 133.8-134.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) 6.47 (dd, 1H, J = 3.3, 1.8 Hz), 6.74 (d, 1H, J = 3.3 Hz), 7.31 (d, 1H, J = 1.8 Hz), 7.35-7.45 (m, 6H), 7.52 (d, 1H, J = 8.4 Hz), 7.65-7.69 (m, 1H), 8.30 (d, 1H, J = 7.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm) 111.6, 112.8, 113.5, 118.1, 123.3, 125.4, 126.4, 128.3, 128.8, 130.6, 133.6, 134.0, 142.0, 145.3, 155.9, 162.8, 176.4; IR (KBr), v (cm^{-1}) 3148, 3074, 2974, 2924, 1740, 1641, 1545, 1462, 1389, 1354, 1294, 1229, 1117, 1061, 1007, 889, 819, 750, 698; HRMS (ESI): calc. for $C_{19}H_{12}O_3$ $[M+Na]^+$ 311.0684, found 311.0678.

2,3-Di(furan-2-yl)-4*H*-chromen-4-one (3l).

Yield: 68%. Yellow soild. m.p. 161.4-162.3 °C. ^{1}H NMR (600 MHz, $CDCl_3$), δ (ppm) 6.28 (d, 1H, J = 3.6 Hz), 6.48 (dd, 1H, J = 3.6, 1.6 Hz), 6.59 (dd, 1H, J = 3.2, 1.9 Hz), 6.66 (d, 1H, J = 3.2 Hz), 7.40-7.42 (m, 1H), 7.54 (d, 1H, J = 1.9 Hz), 7.55 (d, 1H, J = 8.4 Hz), 7.57 (d, 1H, J = 1.6 Hz), 7.67-7.71 (m, 1H), 8.24 (dd, 1H, J = 7.9, 1.4 Hz); ^{13}C NMR (150 MHz, $CDCl_3$), δ (ppm) 111.1, 111.9, 112.4, 112.5, 116.4, 118.0, 123.4, 125.5, 126.3, 134.0, 142.5, 144.6, 145.7, 145.8, 153.9, 155.4, 176.3; IR (KBr), v (cm^{-1}) 3128, 3040, 2976, 2924, 2868, 1726, 1639, 1570, 1458, 1375, 1254, 1211,

1153, 1123, 1075, 1015, 961, 880, 839, 754; HRMS (ESI): calc. for $C_{17}H_{10}O_4$ $[M+Na]^+$ 301.0477, found 301.0474.

3-(Furan-2-yl)-2-(thiophen-2-yl)-4*H*-chromen-4-one (3m).

Yield: 80%. Yellow soild. m.p. 132.7-133.2 °C. ^{1}H NMR (600 MHz, $CDCl_3$), δ (ppm) 6.61 (dd, 1H, *J* = 3.2, 1.9 Hz), 6.65 (d, 1H, *J* = 3.2 Hz), 7.00-7.07 (m, 1H), 7.16 (d, 1H, *J* = 3.8 Hz), 7.38-7.41 (m, 1H), 7.50-7.57 (m, 2H), 7.57 (d, 1H, *J* = 1.9 Hz), 7.65-7.70 (m, 1H), 8.22 (dd, 1H, *J* = 7.9, 1.4 Hz); ^{13}C NMR (150 MHz, $CDCl_3$), δ (ppm) 111.3, 112.0, 113.2, 117.8, 123.1, 125.4, 126.3, 127.8, 131.3, 131.7, 134.0, 134.5, 142.9. 144.5, 155.5, 158.2, 176.5; IR (KBr), *v* (cm^{-1}) 3867, 3253, 3117, 2960, 2936, 2856, 1630, 1553, 1468, 1418, 1369, 1294, 1232, 1131, 1043, 1013, 949, 862, 812, 752, 716; HRMS (ESI): calc. for $C_{17}H_{10}O_3S$ $[M+Na]^+$ 317.0248, found 317.0246.

3-(Furan-2-yl)-4*H*-chromen-4-one (3n).

Yield: 27%. White soild. m.p. 135.3-136.1 °C. ^{1}H NMR (600 MHz, $CDCl_3$), δ (ppm) 6.48 (dd, 1H, *J* = 3.2, 1.8 Hz), 7.34 (d, 1H, *J* = 3.2 Hz), 7.36-7.40 (m, 2H), 7.43 (d, 1H, *J* = 8.4 Hz), 7.60-7.63 (m, 1H), 8.27 (dd, 1H, *J* = 8.0, 1.5 Hz), 8.42 (s, 1H); ^{13}C NMR(150 MHz, $CDCl_3$), δ (ppm) 111.2, 111.8, 116.2, 118.2, 124.1, 125.3, 126.1, 133.6, 141.2, 145.5, 151.4, 155.7, 173.9; IR (KBr), *v* (cm^{-1}) 3125, 3090, 1940, 1730, 1649, 1609, 1554, 1460, 1412, 1350, 1280, 1225, 1151, 1107, 1004, 827, 746, 700; HRMS (ESI): calc. for $C_{13}H_8O_3$ $[M+Na]^+$ 235.0371, found 235.0369.[8]

3-(Furan-2-yl)-7-methoxy-4*H*-chromen-4-one (3o).

Yield: 29%. White soild. m.p. 161.9-162.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) 3.87 (s, 3H), 6.49 (dd, 1H, *J* = 3.3, 1.8 Hz), 6.81 (d, 1H, *J* = 3.3 Hz), 6.96 (dd, 1H, *J* = 8.9, 2.4 Hz), 7.33 (d, 1H, *J* = 2.4 Hz), 7.38 (d, 1H, *J* = 1.8 Hz), 8.17 (d, 1H, *J* = 8.9 Hz), 8.36 (s, 1H); ^{13}C NMR(100 MHz, $CDCl_3$), δ (ppm) 55.9, 100.2, 111.2, 111.8, 114.8, 116.2, 118.1, 127.5, 141.1, 145.7, 151.2, 157.6, 164.1, 173.5; IR (KBr), *v* (cm^{-1}) 3153, 3094, 2930, 2852, 1609, 1443, 1362, 1267, 1221, 1192, 1105, 1061, 1015, 905, 853, 816, 740; HRMS (ESI): calc. for $C_{14}H_{10}O_4$ $[M+Na]^+$ 265.0477, found 265.0473.[8]

6-Fluoro-3-(furan-2-yl)-4*H*-chromen-4-one (3p).

Yield: 29%. Yellow soild. m.p. 137.2-137.8 °C. ^{1}H NMR (600 MHz, $CDCl_3$), δ (ppm) 6.50 (dd, 1H, *J* = 3.2, 1.8 Hz), 7.33 (d, 1H, *J* = 3.2 Hz), 7.35-7.39 (m, 1H), 7.40 (d, 1H, *J* = 1.8 Hz), 7.48 (dd, 1H, *J* = 9.2, 4.2 Hz), 7.91 (dd, 1H, *J* = 8.3, 3.1 Hz), 8.46 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$), δ (ppm) 111.0 (d, ^2J = 23.7 Hz), 111.5, 111.9, 115.8, 120.4 (d, ^3J = 8.1 Hz), 122.0 (d, ^2J = 25.5 Hz), 125.3 (d, ^3J = 7.3 Hz), 141.5,

145.2, 151.7, 152.1 (d, ^4J = 1.3 Hz), 159.7 (d, ^1J = 245.5 Hz), 173.3 (d, ^4J = 2.2 Hz); IR (KBr), ν (cm^{-1}) 3119, 3067, 2968, 2916, 2849, 1641, 1558, 1470, 1404, 1360, 1323, 1261, 1217, 1155, 1099, 1049, 1011, 887, 820, 729, 635; HRMS (ESI): calc. for $C_{13}H_7FO_3$ $[M+Na]^+$ 253.0277, found 253.0269.[8]

3-(Furan-2-yl)-6-nitro-4*H*-chromen-4-one (3q).

Yield: 26%. Yellow soild. m.p. 204.2-205.6 °C. ^{1}H NMR (400 MHz, DMSO-d_6), δ (ppm) 6.65 (dd, 1H, J = 3.3, 1.8 Hz), 7.25 (d, 1H, J = 3.3 Hz), 7.80 (d, 1H, J = 1.8 Hz), 7.98 (d, 1H, J = 9.2 Hz), 8.58 (dd, 1H, J = 9.2, 2.7 Hz), 8.84 (d, 1H, J = 2.7 Hz), 8.94 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6), δ (ppm) 111.5, 111,9, 115.5, 120.9, 121.5, 123.3, 128.3, 142.7, 144.3, 144.5, 153.1, 158.2, 172.2; IR (KBr), ν (cm^{-1}) 3082, 2970, 2934, 2857, 1736, 1651, 1624, 1526, 1458, 1402, 1344, 1263, 1211, 1130, 1097, 1045, 1024, 932, 903, 854, 810, 745, 700, 642; HRMS (ESI): calc. for $C_{13}H_7NO_5$ $[M+Na]^+$ 280.0222, found 280.0216.

3-(Furan-2-yl)-2-methyl-6-nitro-4*H*-chromen-4-one (3r).

Yield: 27%. Yellow soild. m.p. 153.2-154.3 °C. ^{1}H NMR (600 MHz, $CDCl_3$), δ (ppm) 2.68 (s, 3H), 6.54 (dd, 1H, J = 3.2, 1.8 Hz), 7.06 (d, 1H, J = 3.2 Hz), 7.52 (d, 1H, J = 1.8 Hz), 7.58 (d, 1H, J = 9.1 Hz), 8.46 (dd, 1H, J = 9.1, 2.7 Hz), 9.07 (d, 1H, J = 2.7 Hz); ^{13}C NMR (150 MHz, $CDCl_3$), δ (ppm) 20.6, 111.6, 113.4, 114.9, 119.6, 123.1, 127.8, 142.3, 144.6, 144.8, 158.2, 165.1, 173.7; IR (KBr), ν (cm^{-1}) 3101, 2920, 2860, 1647, 1742, 1524, 1454, 1396, 1340, 1394, 1243, 1213, 1107, 1028, 897, 816, 748, 899, 679; HRMS (ESI): calc. for $C_{14}H_9NO_5$ $[M+Na]^+$ 294.0378, found 294.0374.

3-(Furan-2-yl)-2-methyl-4*H*-benzo[h]chromen-4-one (3s).

Yield: 53%. White soild. m.p. 120.5-121.4 °C. ^{1}H NMR (600 MHz, $CDCl_3$), δ (ppm) 2.58 (s, 3H), 6.57 (dd, 1H, J = 3.2, 1.8 Hz), 7.02 (d, 1H, J = 3.2 Hz), 7.40 (d, 1H, J = 9.0 Hz), 7.56 (d, 1H, J = 1.8 Hz), 7.57-7.59 (m, 1H), 7.70-7.73 (m, 1H), 7.84 (d, 1H, J = 8.0 Hz), 7.98 (d, 1H, J = 9.0 Hz), 10.05 (d, 1H, J = 8.7 Hz); ^{13}C NMR (150 MHz, $CDCl_3$), δ (ppm) 19.9, 111.3, 112.5, 116.2, 116.6, 117.3, 126.5, 127.1, 128.3, 129.2, 130.6, 130.7, 135.3, 142.0, 146.2, 156.6, 162.3, 177.1; IR (KBr), ν (cm^{-1}) 3113, 3053, 2960, 2925, 2858, 1971, 1917, 1728, 1612, 1510, 1434, 1406, 1340, 1252, 1151, 1078, 1022, 908, 862, 814, 756; HRMS (ESI): calc. for $C_{18}H_{12}O_3$ $[M+Na]^+$ 299.0684, found 299.0678.

4*H*-Chromen-4-one (3n*).

Yield: 45%. White soild. m.p. 58.6-59.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) 6.32 (d, 1H, J = 6.1 Hz), 7.36-7.44 (m, 2H), 7.63-7.67 (m, 1H), 7.84 (d, 1H, J = 6.0

Hz), 8.18 (dd, 1H, J = 8.0, 1.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm) 113.1, 118.3, 125.0, 125.3, 125.9, 133.9, 155.4, 156.6, 177.7; IR (KBr), v (cm^{-1}) 3070, 3041, 2964, 2933, 1733, 1639, 1562, 1462, 1404, 1332, 1244, 1191, 1128, 1031, 1001, 960, 848, 759, 678; HRMS (ESI): calc. for $C_9H_6O_2$ $[M+Na]^+$ 169.0265, found 169.0259.[9]

References

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^{1}H NMR ^{13}C NMR and HRMS Spectra of 1 and 3

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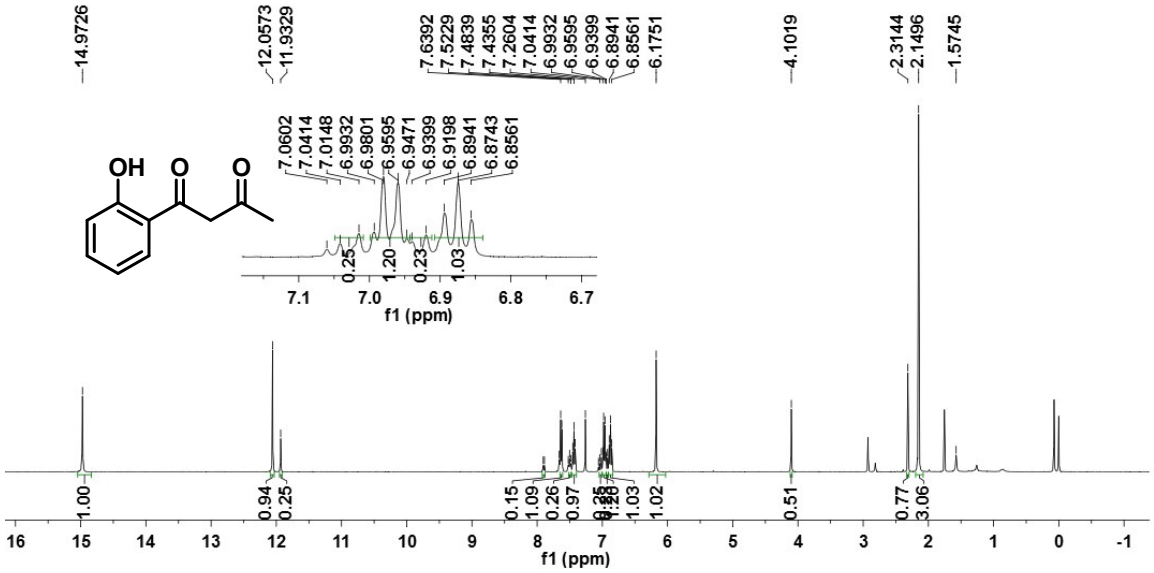

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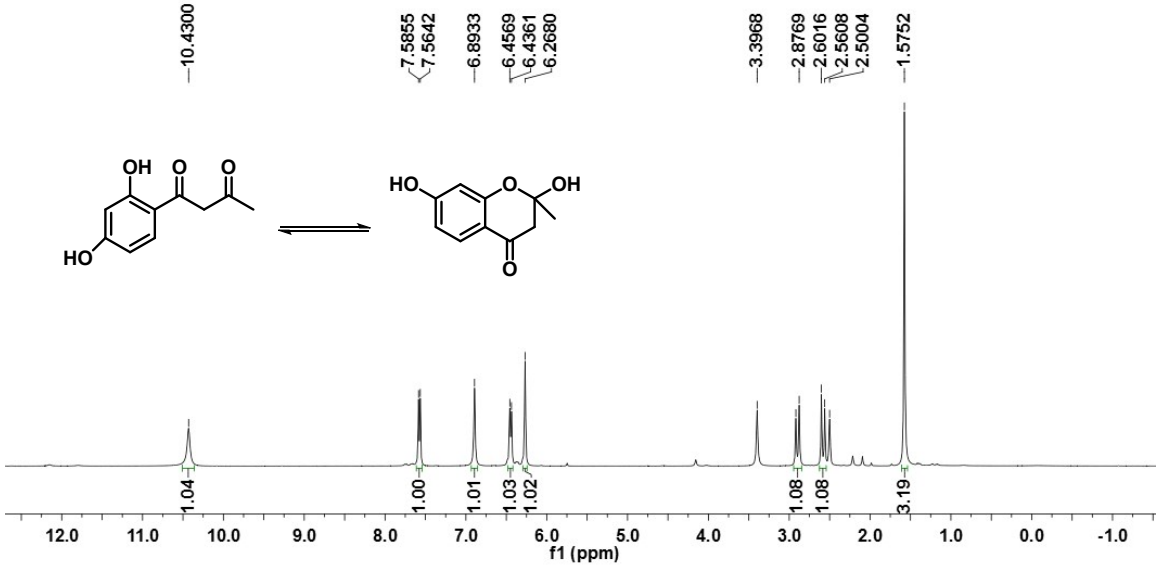

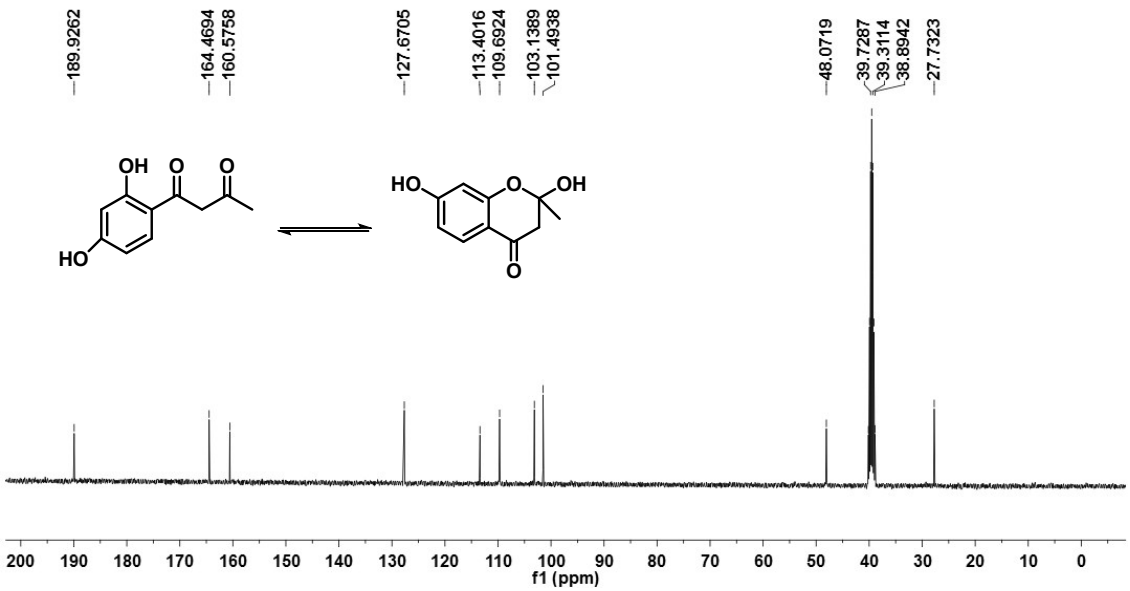
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HO
HO
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OH
O
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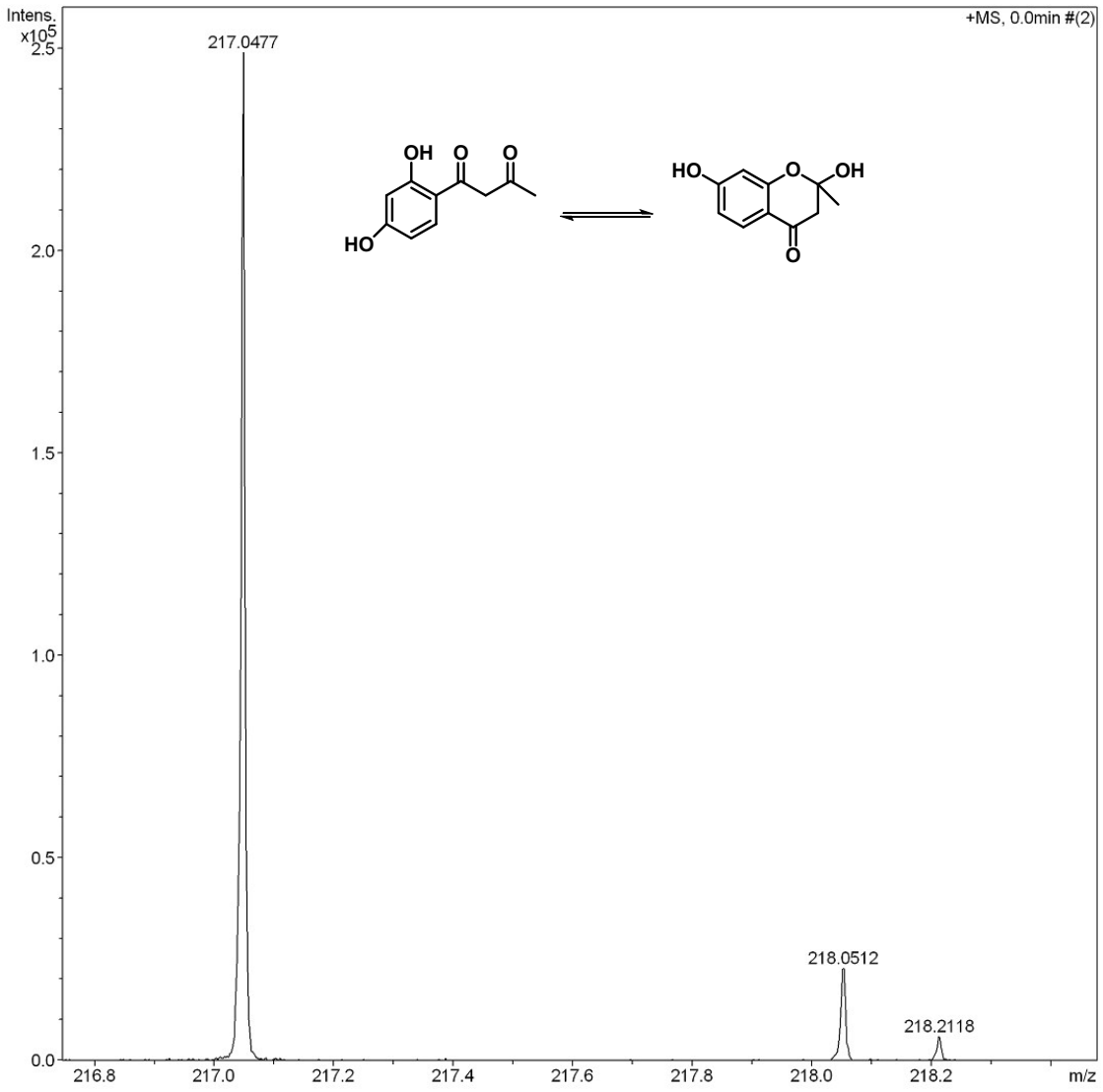
f1 (ppm)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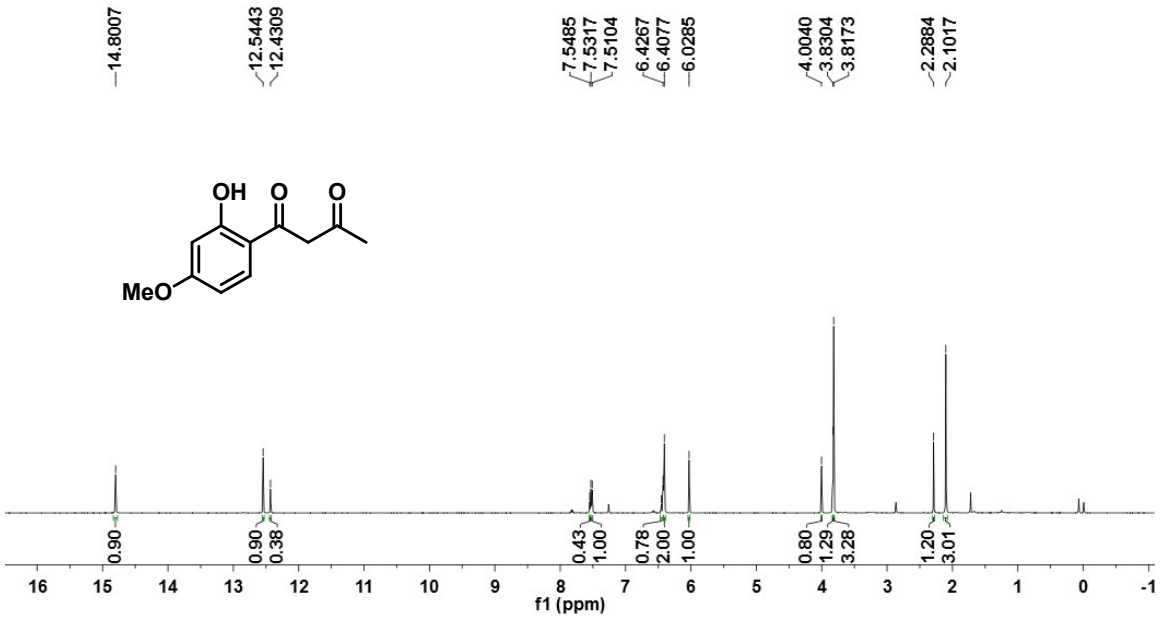
218.2
m/z

1c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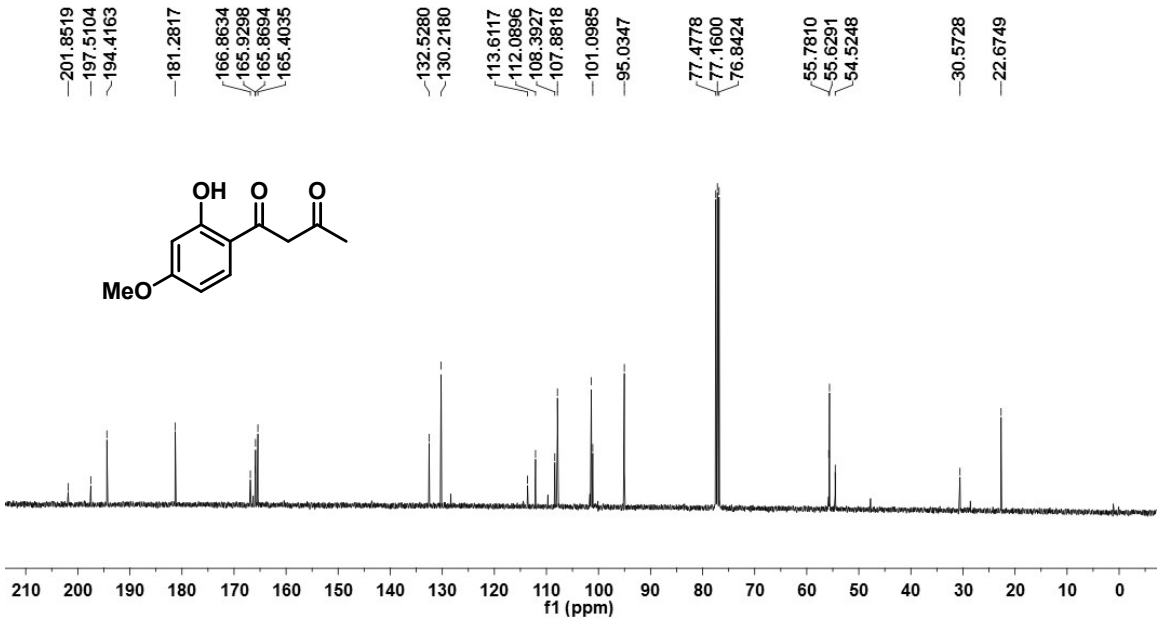
f1 (ppm)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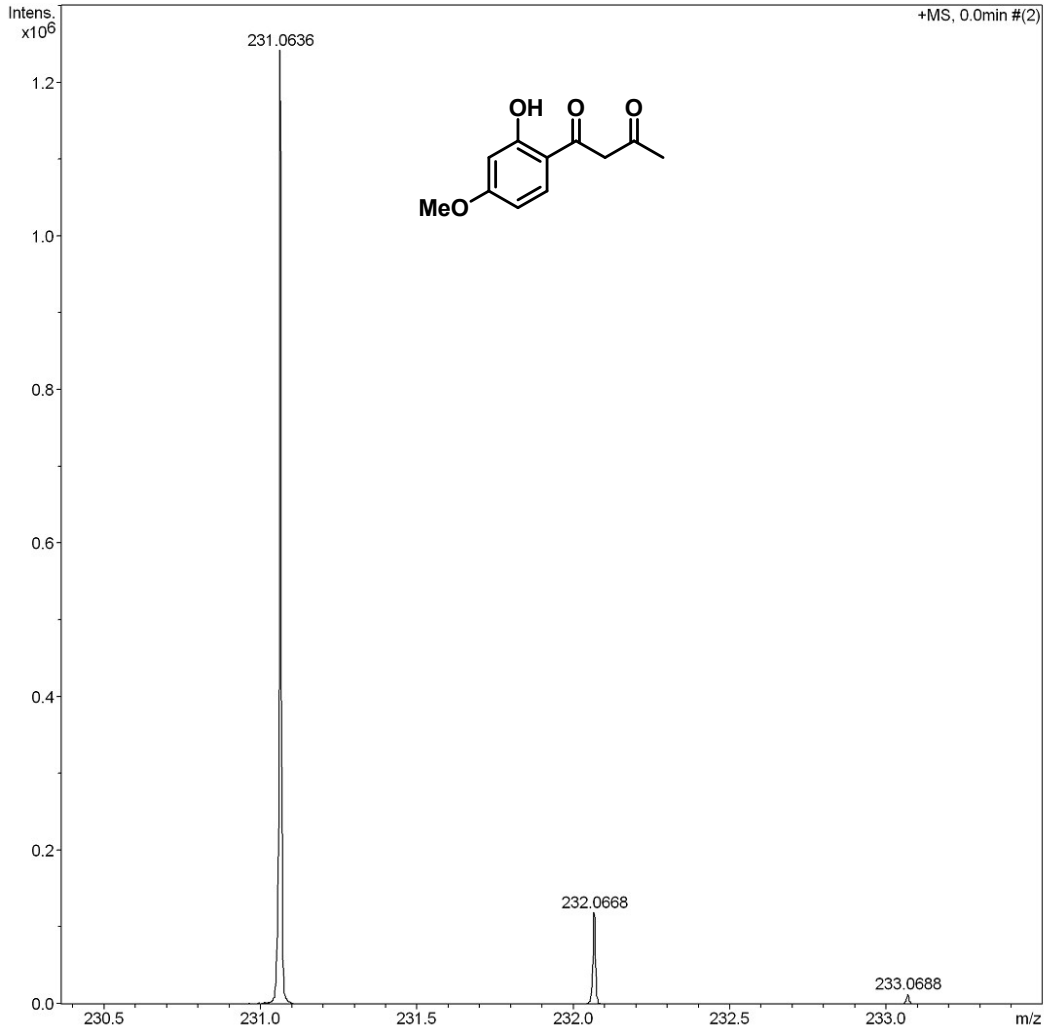
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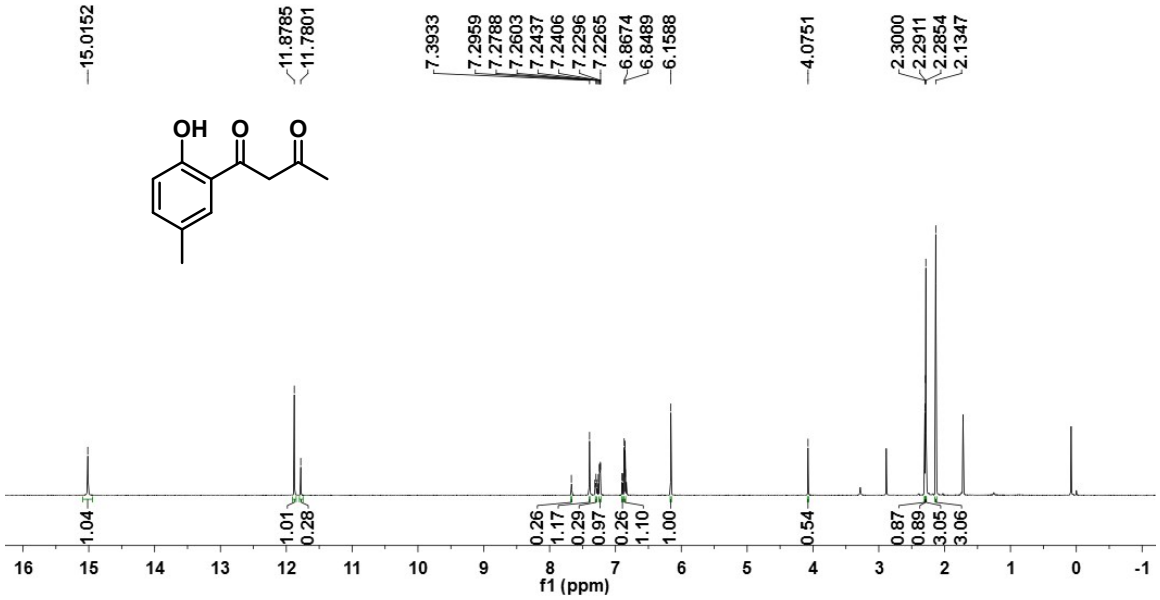
m/z

1d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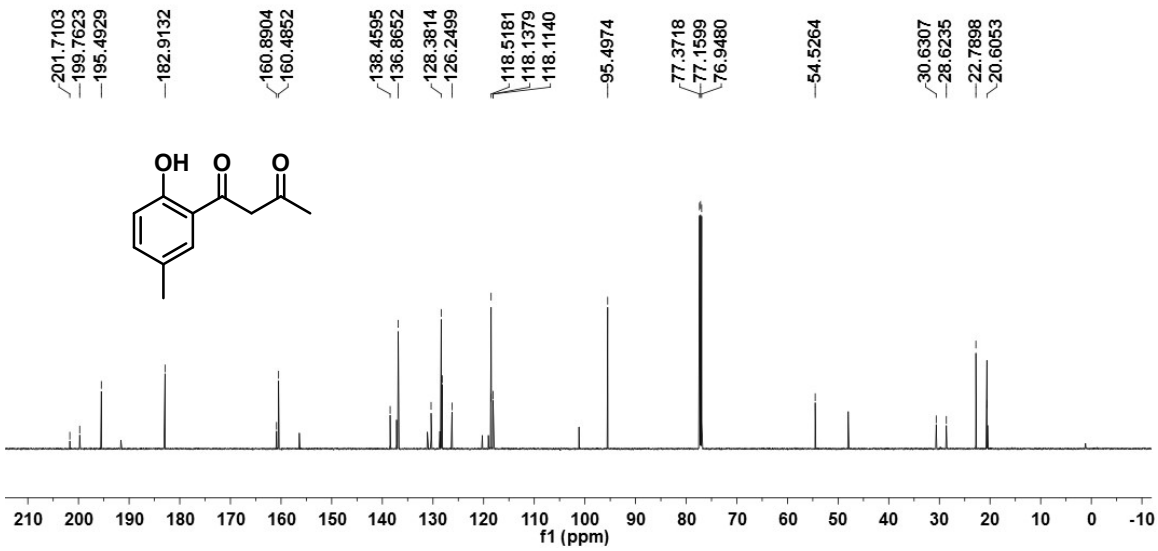
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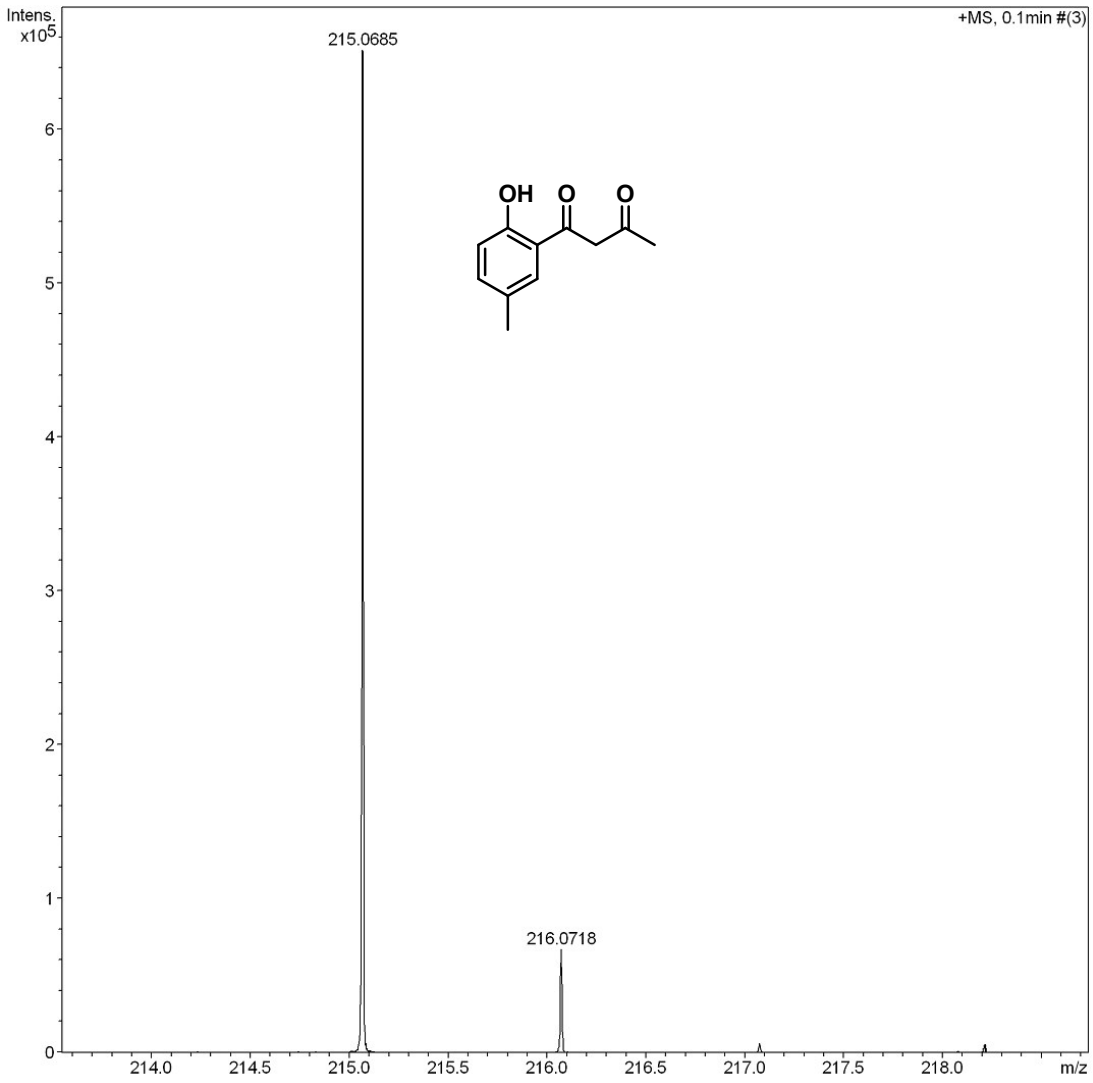
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m/z

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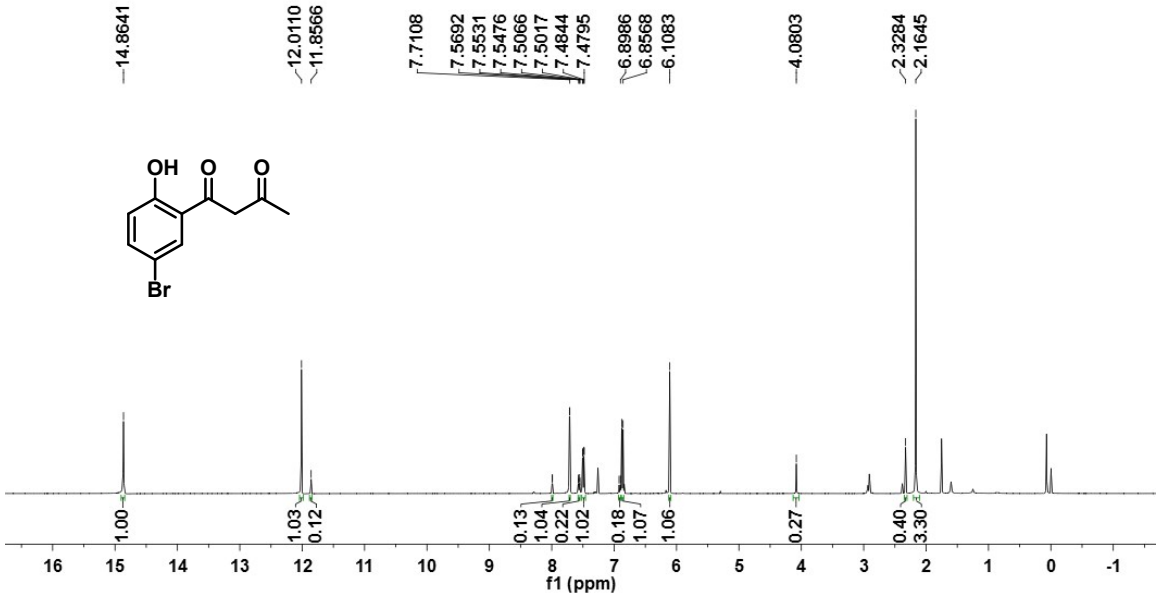
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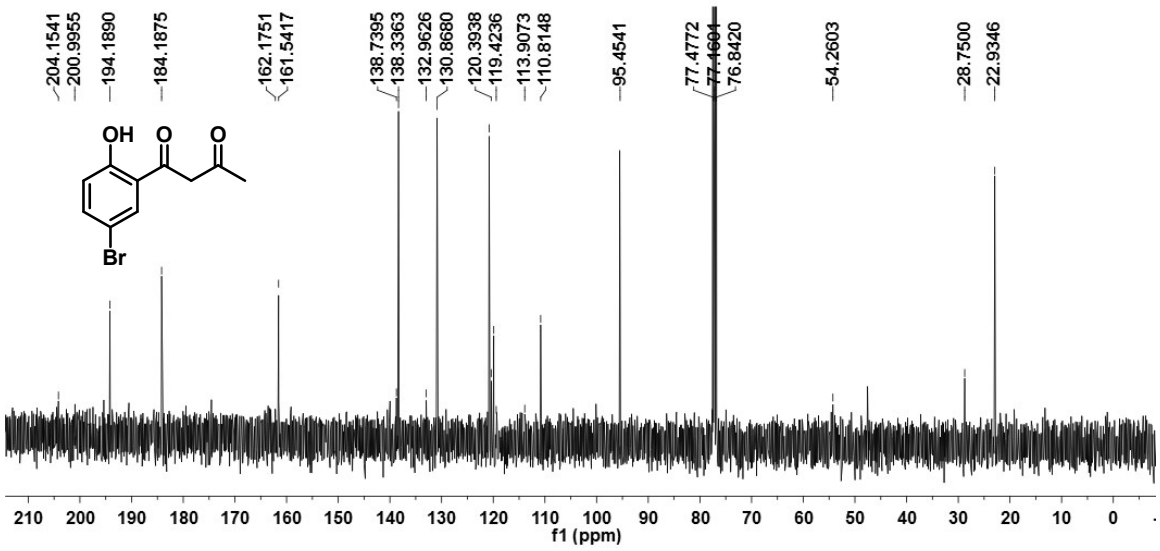
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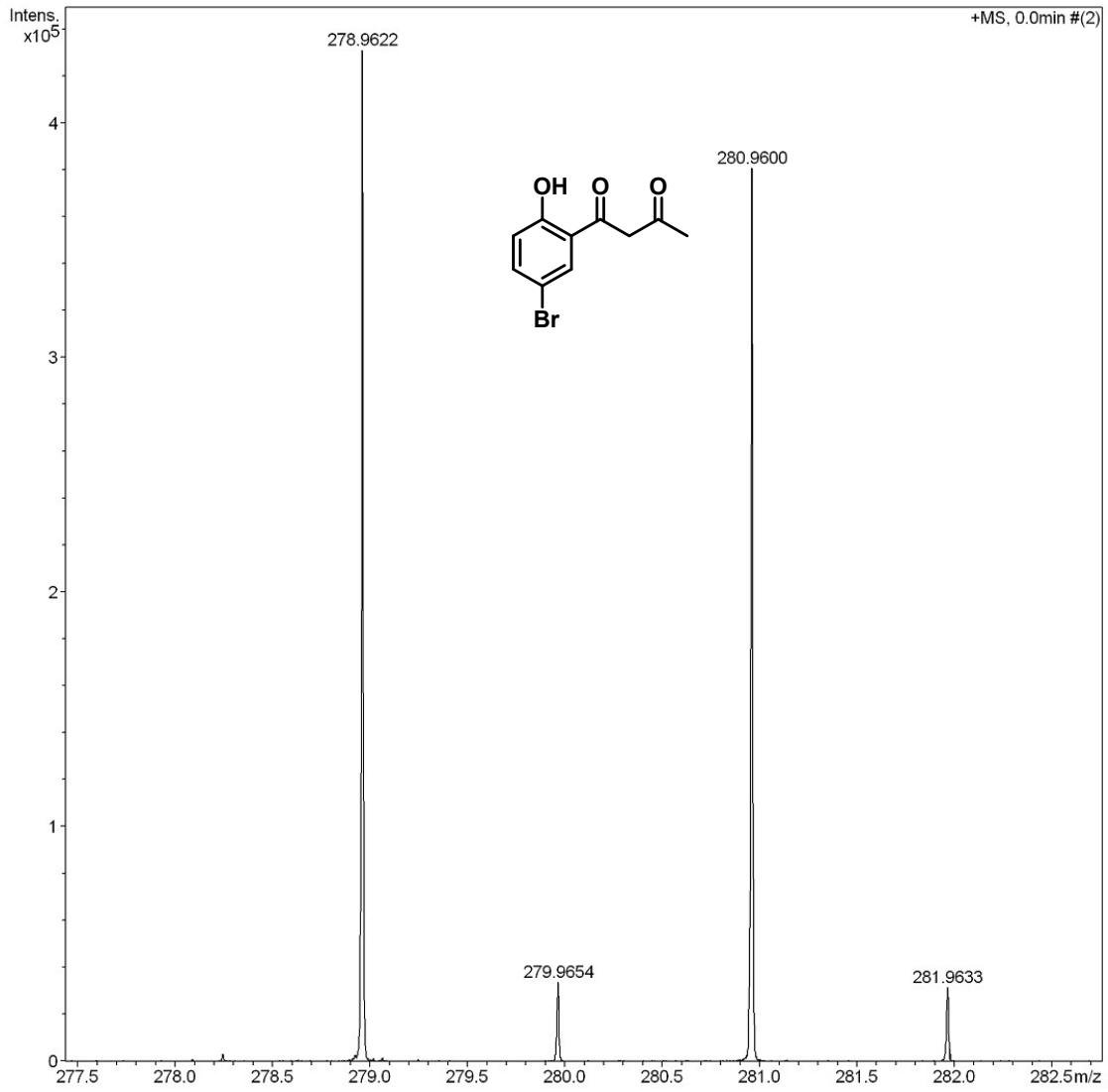
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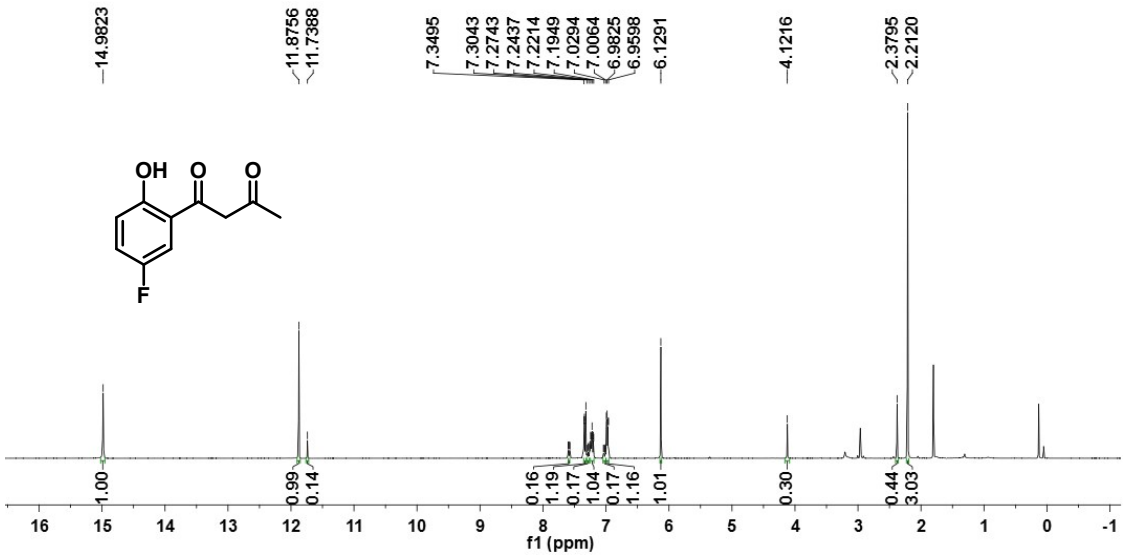
1f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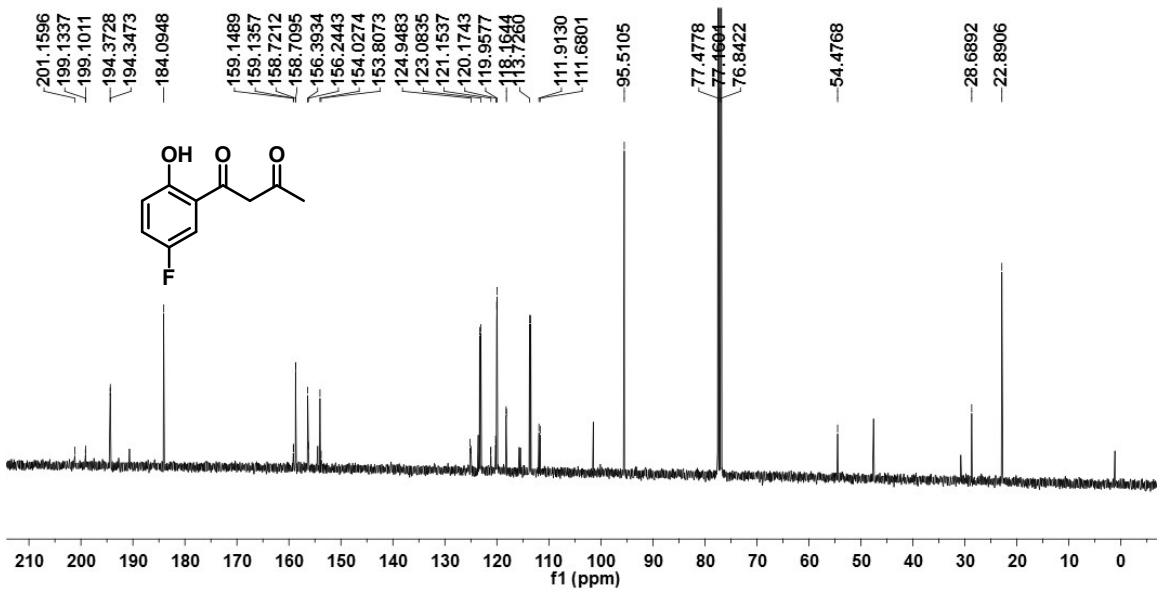
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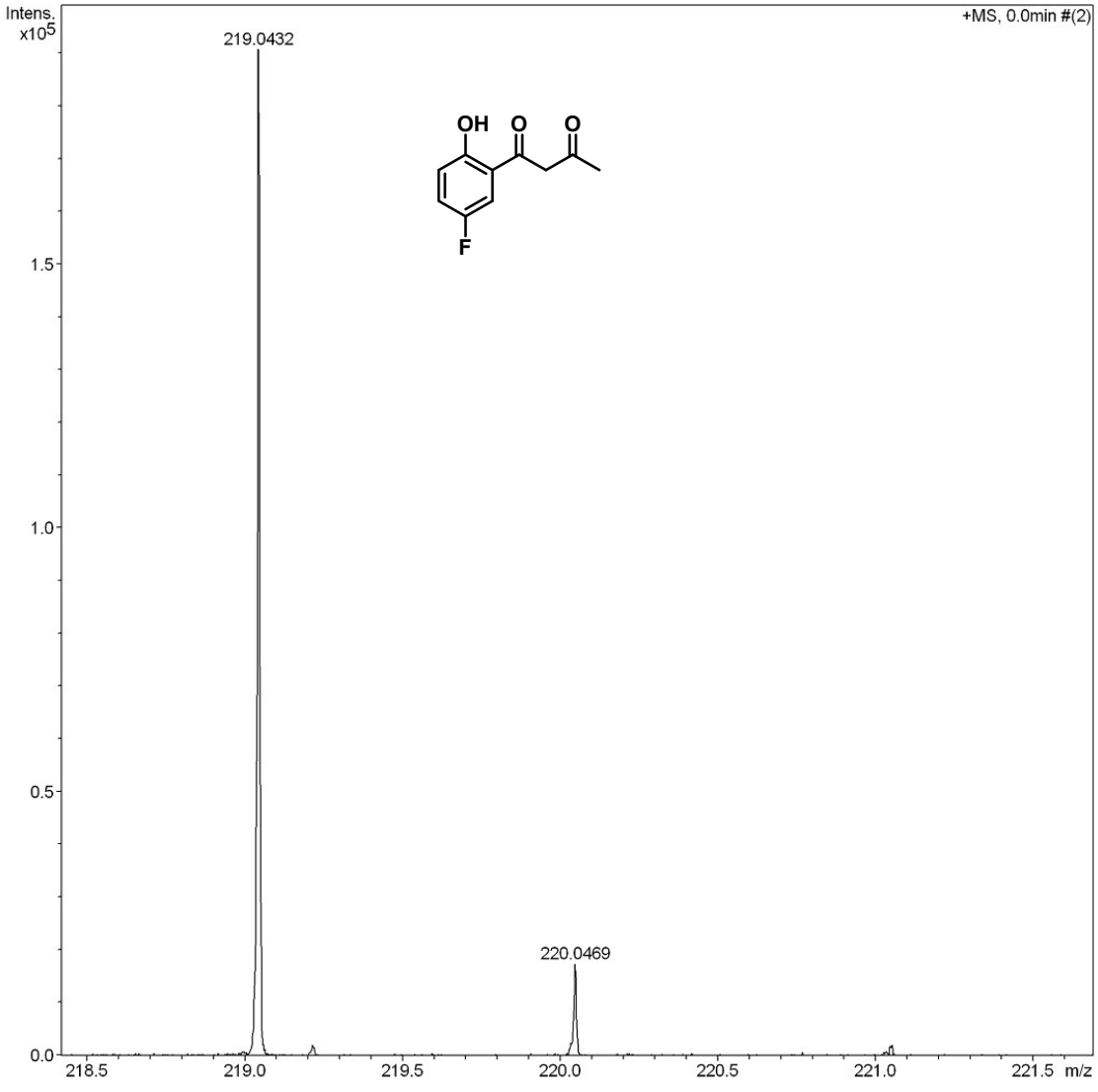
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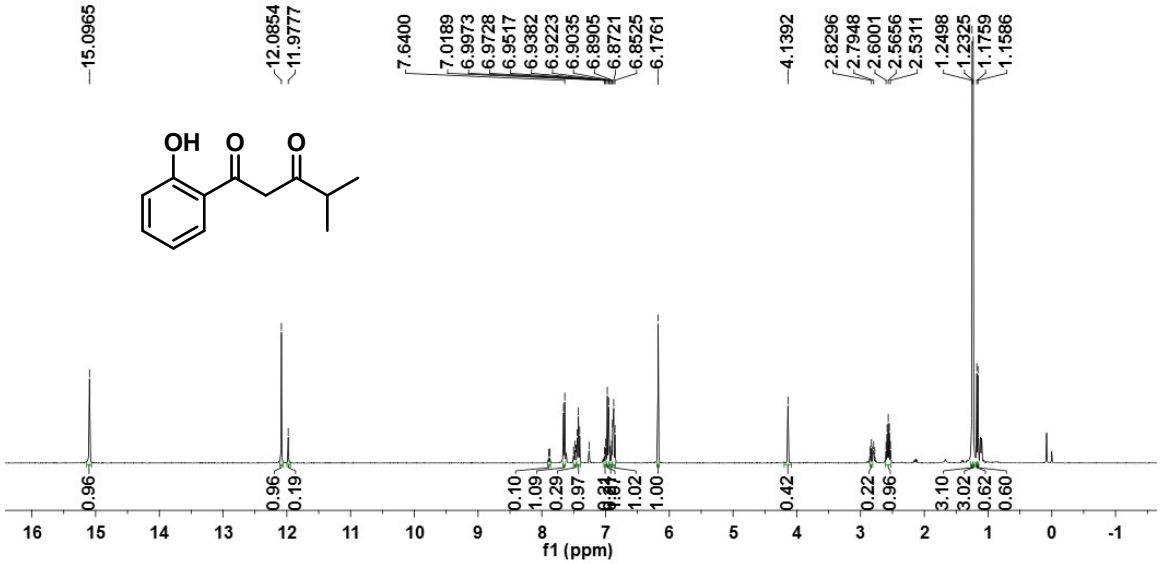
1g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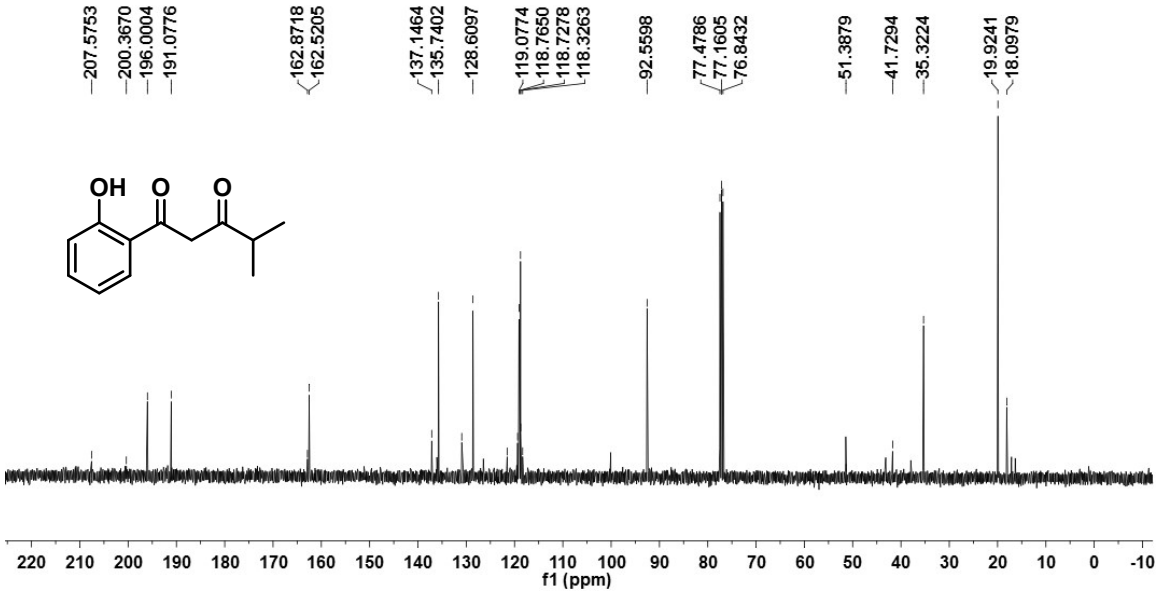
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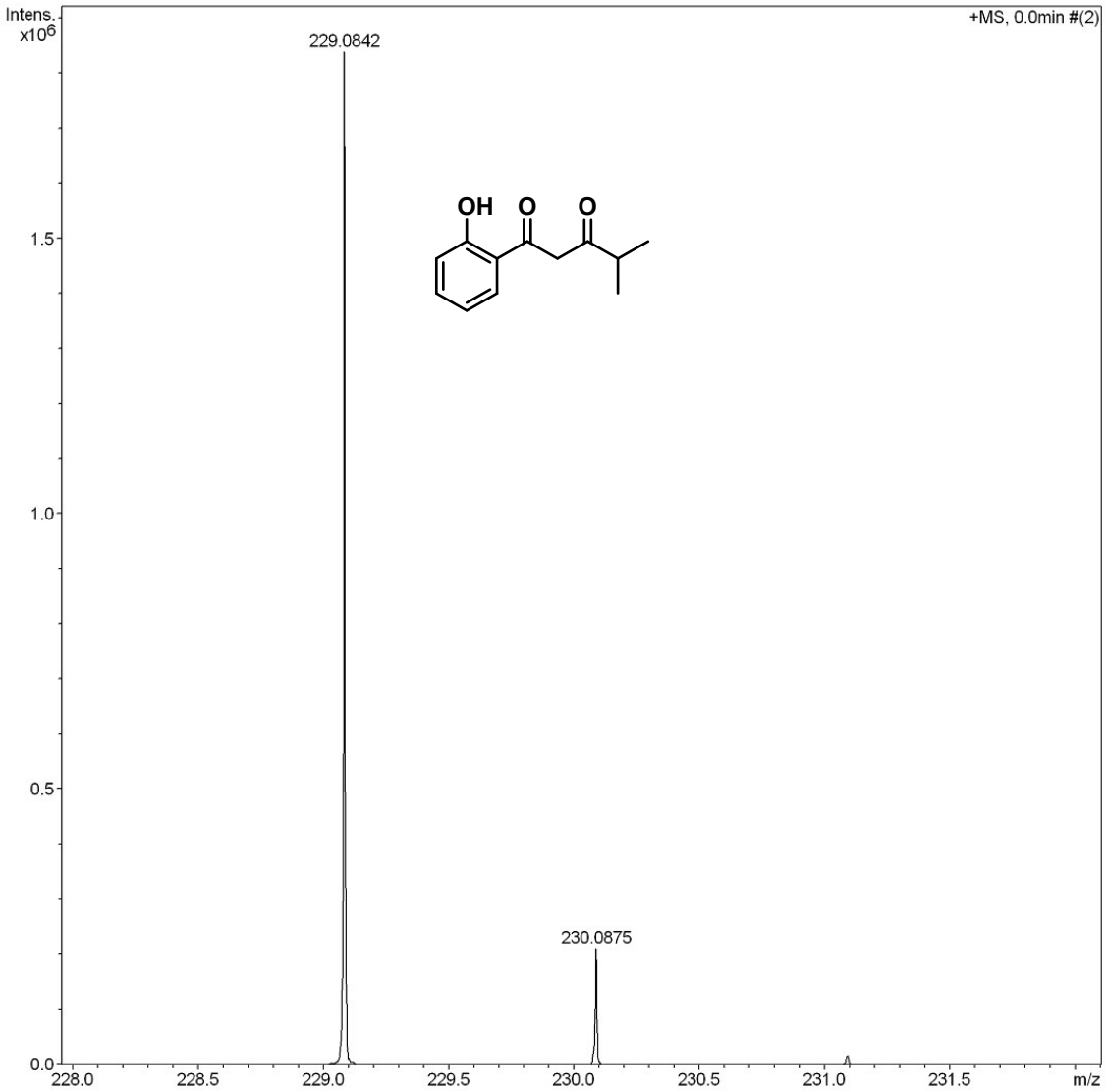
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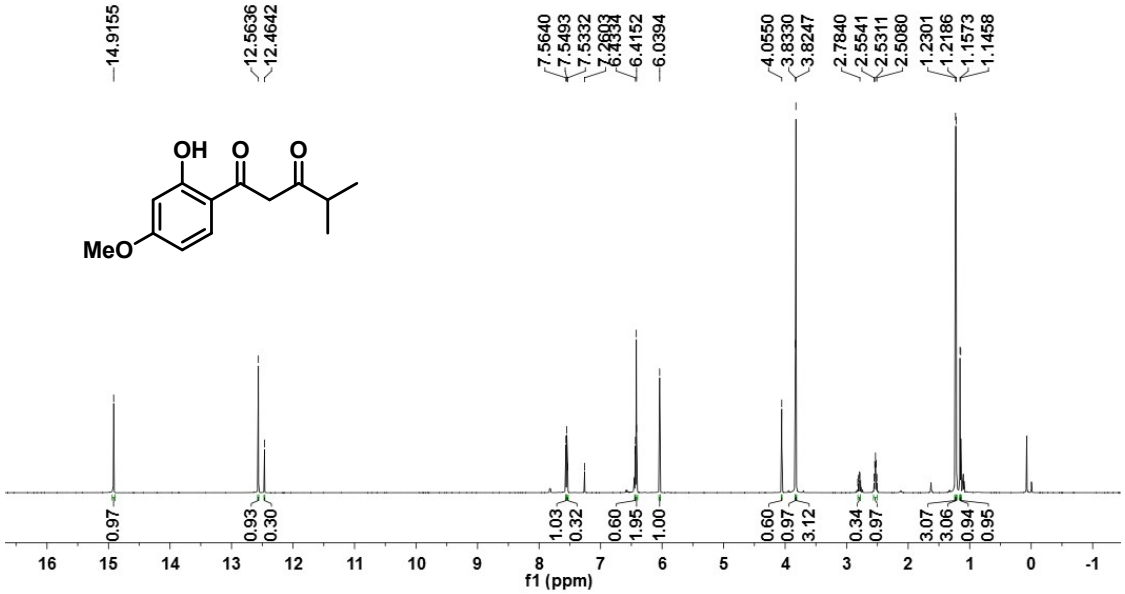
231.5
m/z

1h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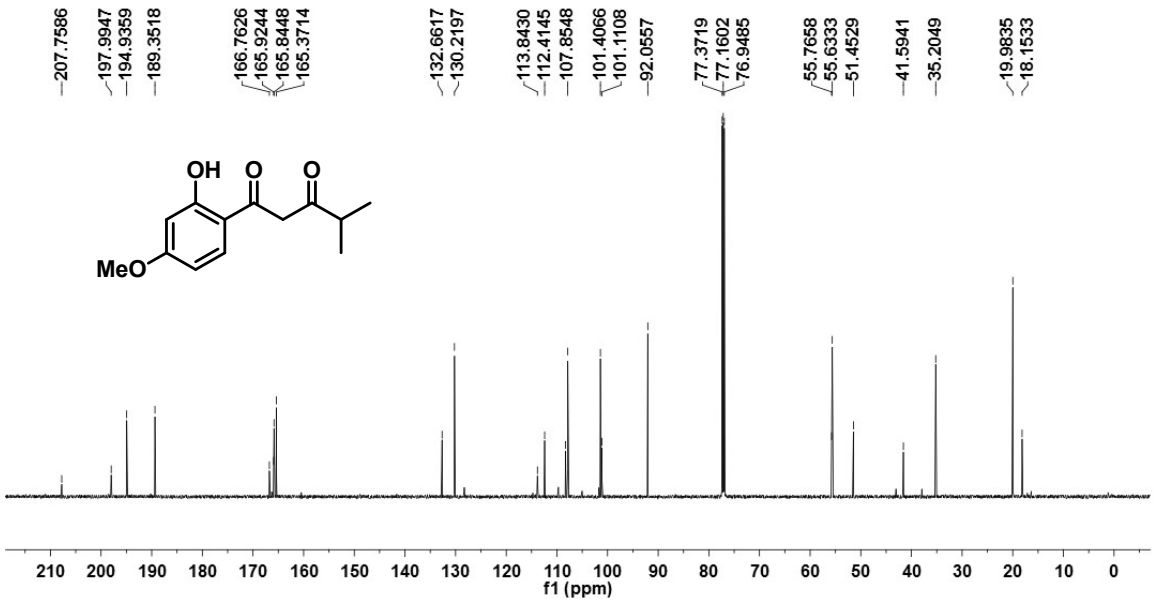
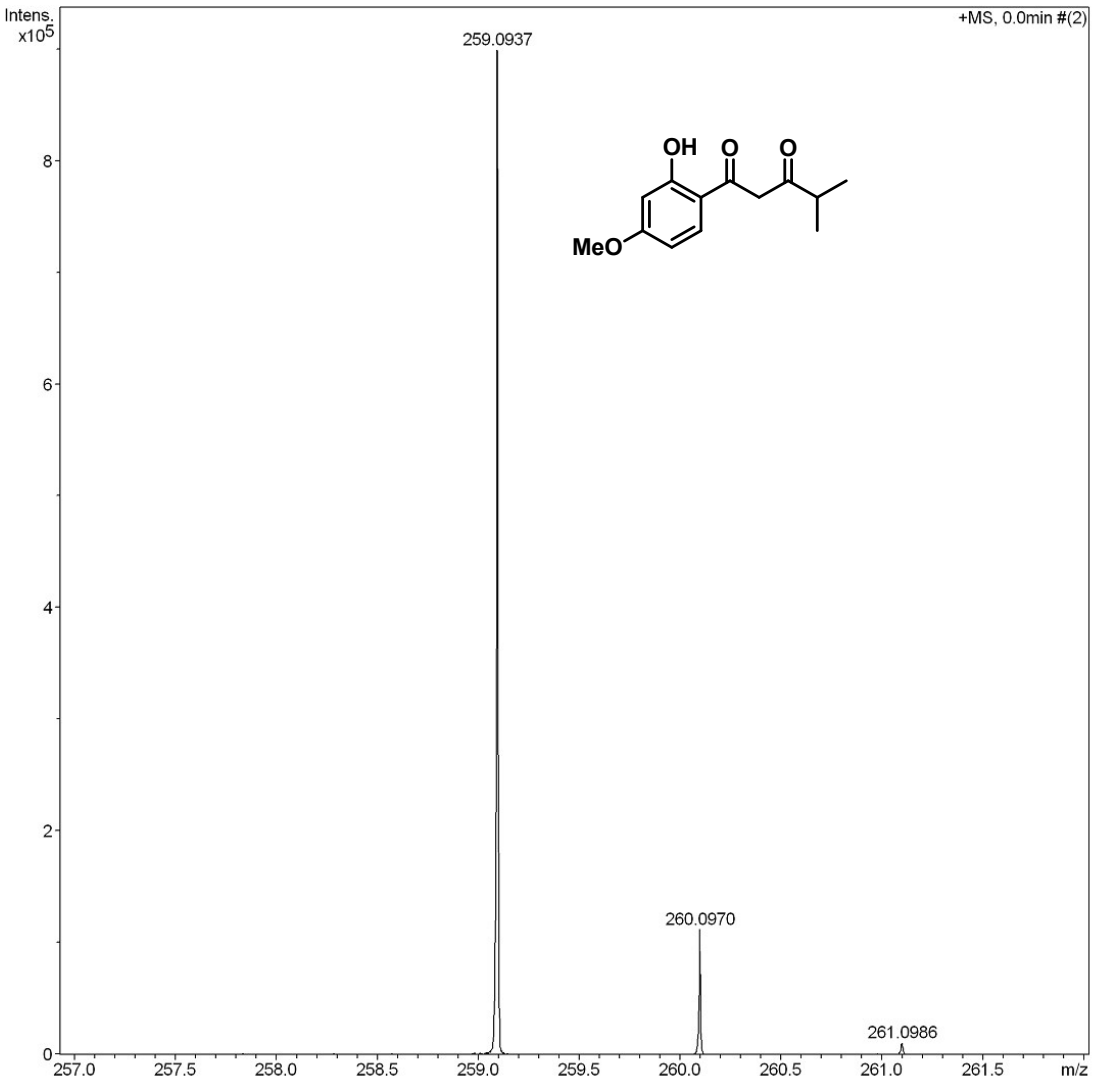
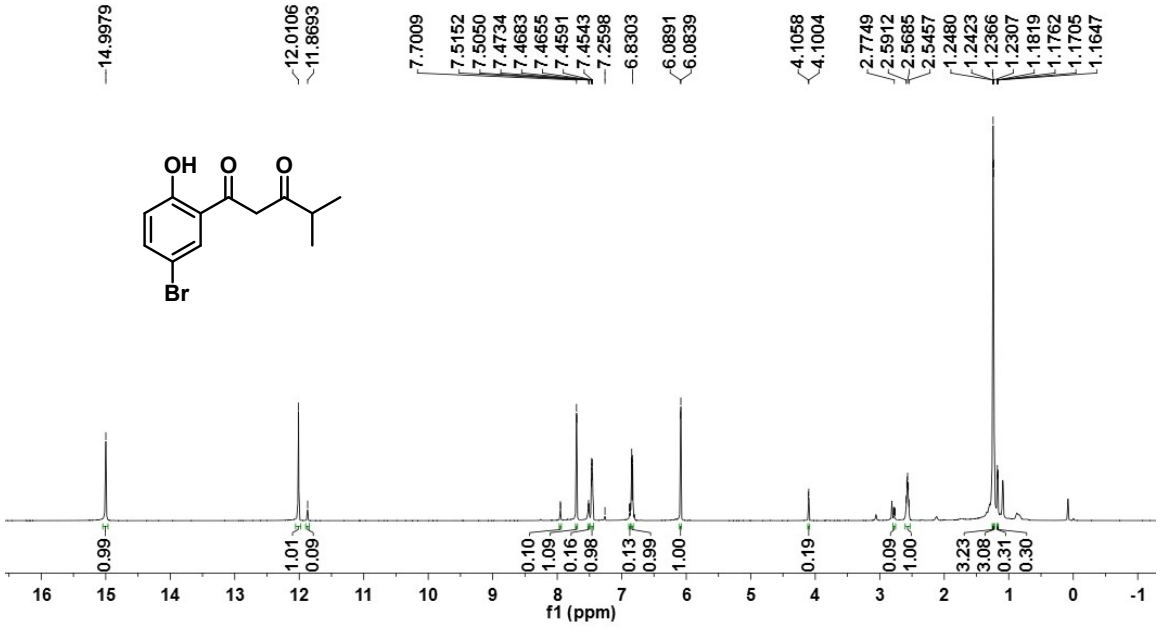
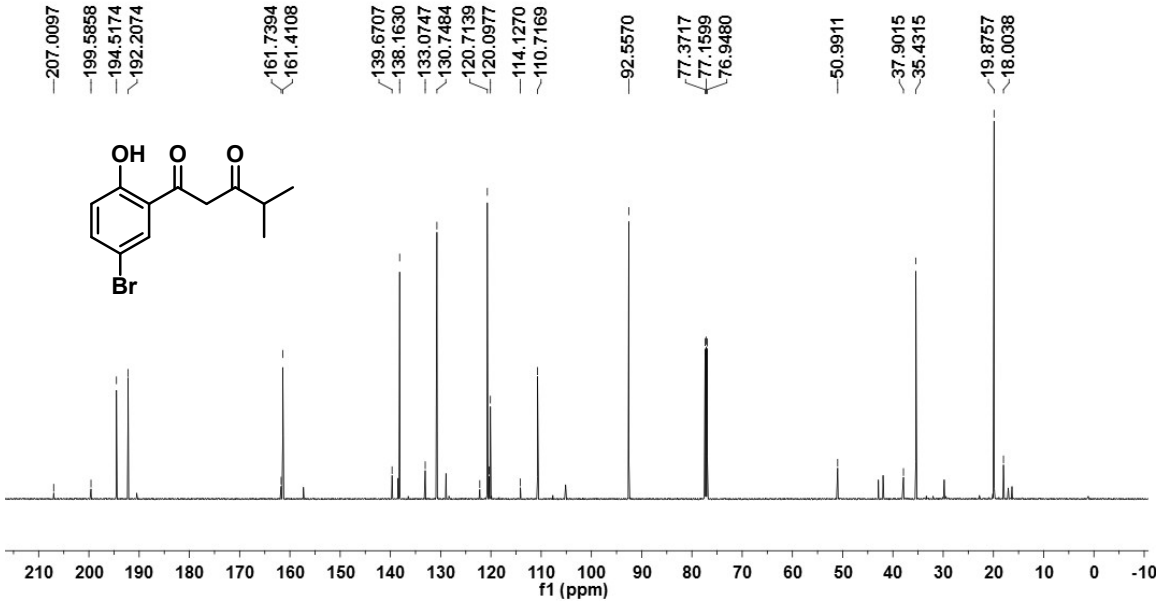
1.2301
1.2186
1.1573
1.1458
OH
O
O
MeO
0.97
0.93
0.30
1.03
0.32
0.60
1.95
1.00
0.60
0.97
3.12
0.34
0.97
3.07
3.06
0.94
0.95
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

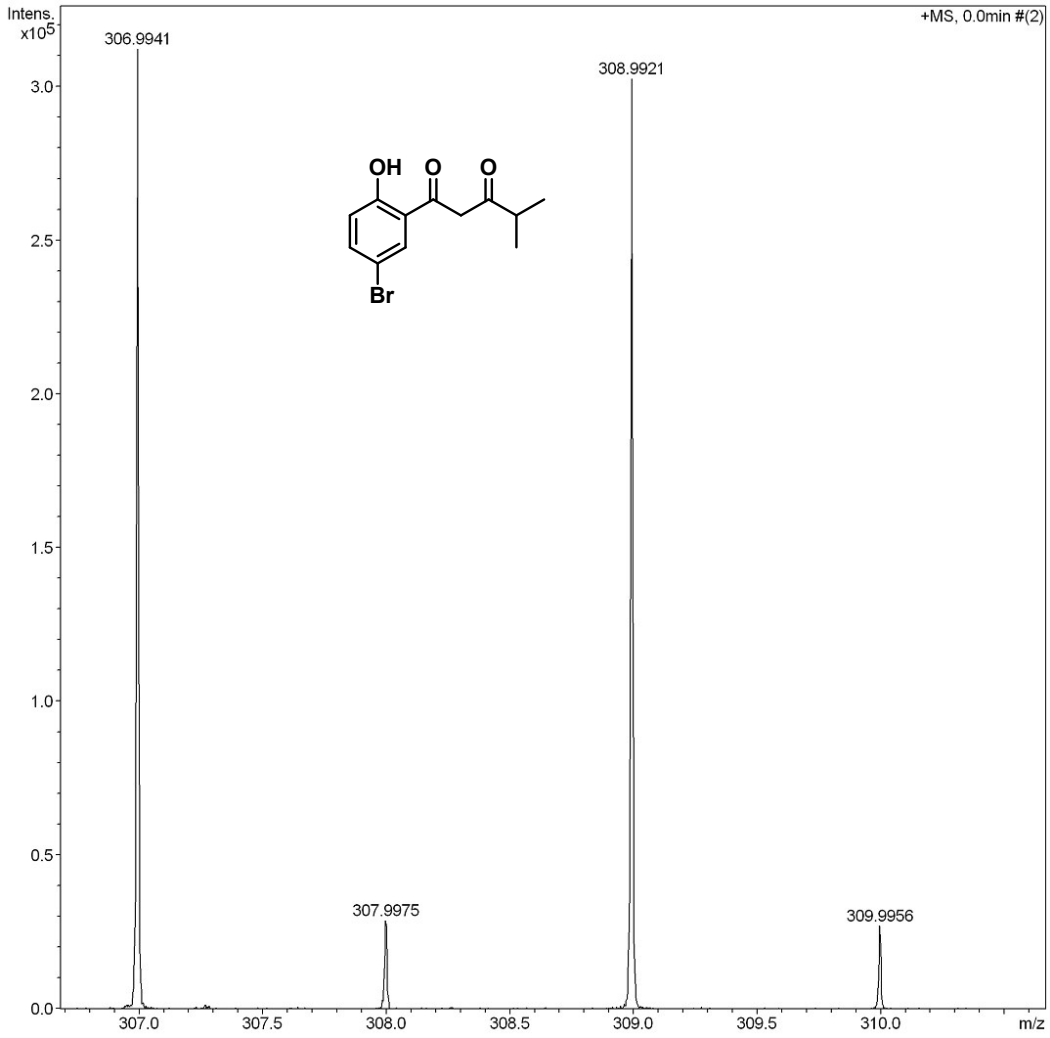

207.7586
197.9947
194.9359
189.3518
166.7626
165.9244
165.8448
165.3714
132.6617
130.2197
113.8430
112.4145
107.8548
101.4066
101.1108
92.0557
77.3719
77.1602
76.9485
55.7658
55.6333
51.4529
41.5941
35.2049
19.9835
18.1533
OH
O
O
MeO
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Intens.
x10^5
+MS, 0.0min #(2)
259.0937
260.0970
261.0986
OH
O
O
MeO
8
6
4
2
0
257.0 257.5 258.0 258.5 259.0 259.5 260.0 260.5 261.0 261.5 m/z

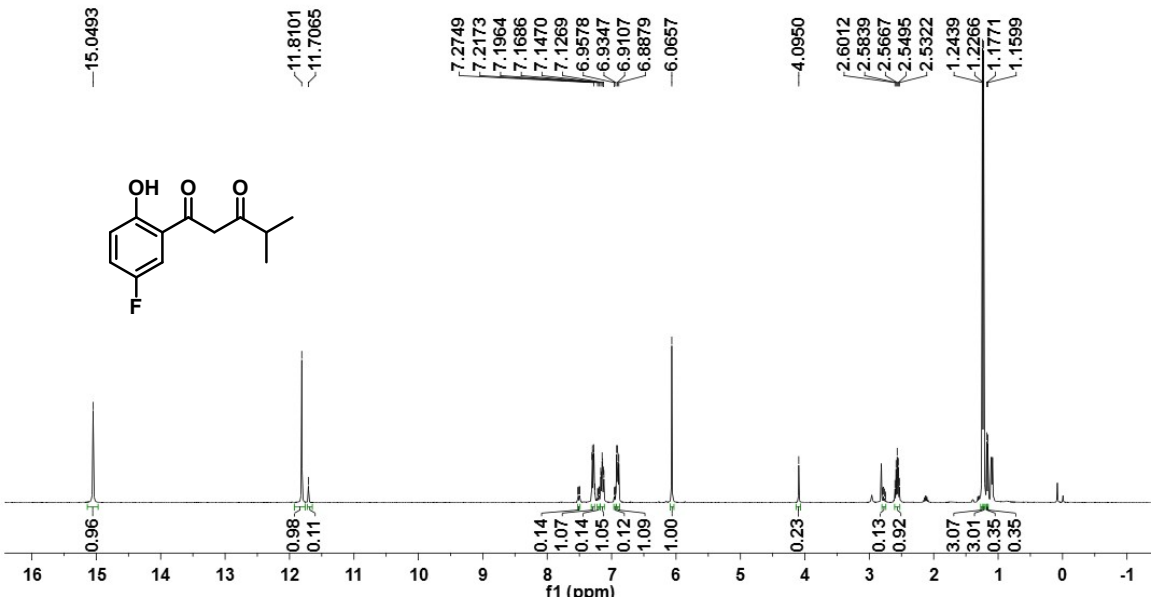
1i

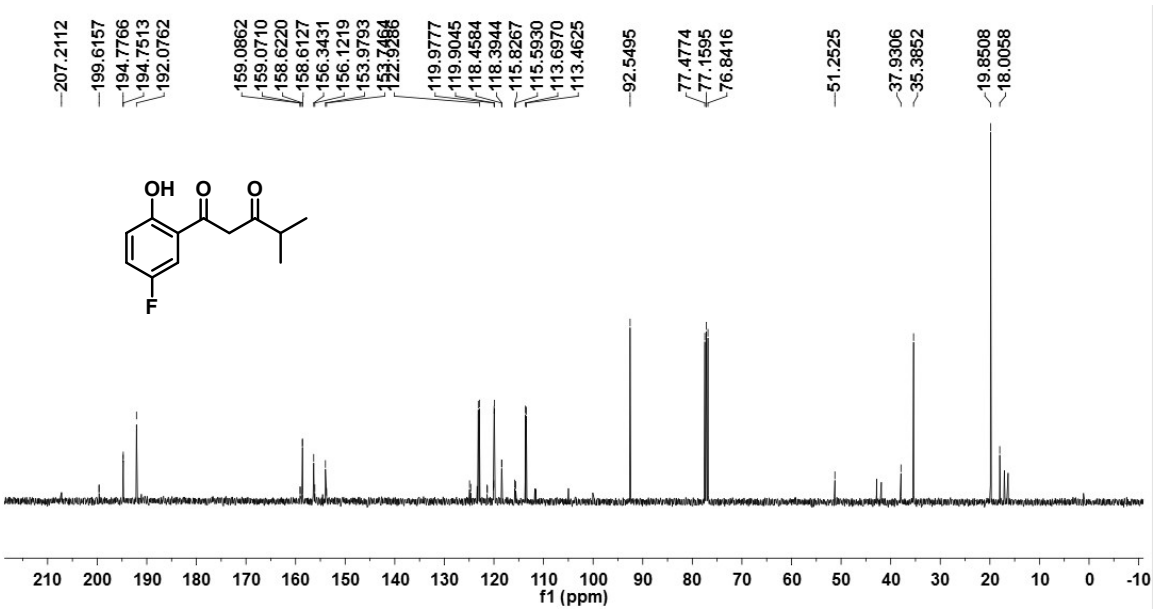

14.9979
12.0106
11.8693
7.7009
7.5152
7.5050
7.4734
7.4683
7.4655
7.4591
7.4543
7.2598
6.8303
6.0891
6.0839
4.1058
4.1004
2.7749
2.5912
2.5685
2.5457
1.2480
1.2423
1.2366
1.2307
1.1819
1.1762
1.1705
1.1647
OH
O
O
Br
0.99
1.01
0.09
0.10
1.09
0.16
0.98
0.13
0.99
1.00
0.19
0.09
1.00
3.23
3.08
0.31
0.30
f1 (ppm)

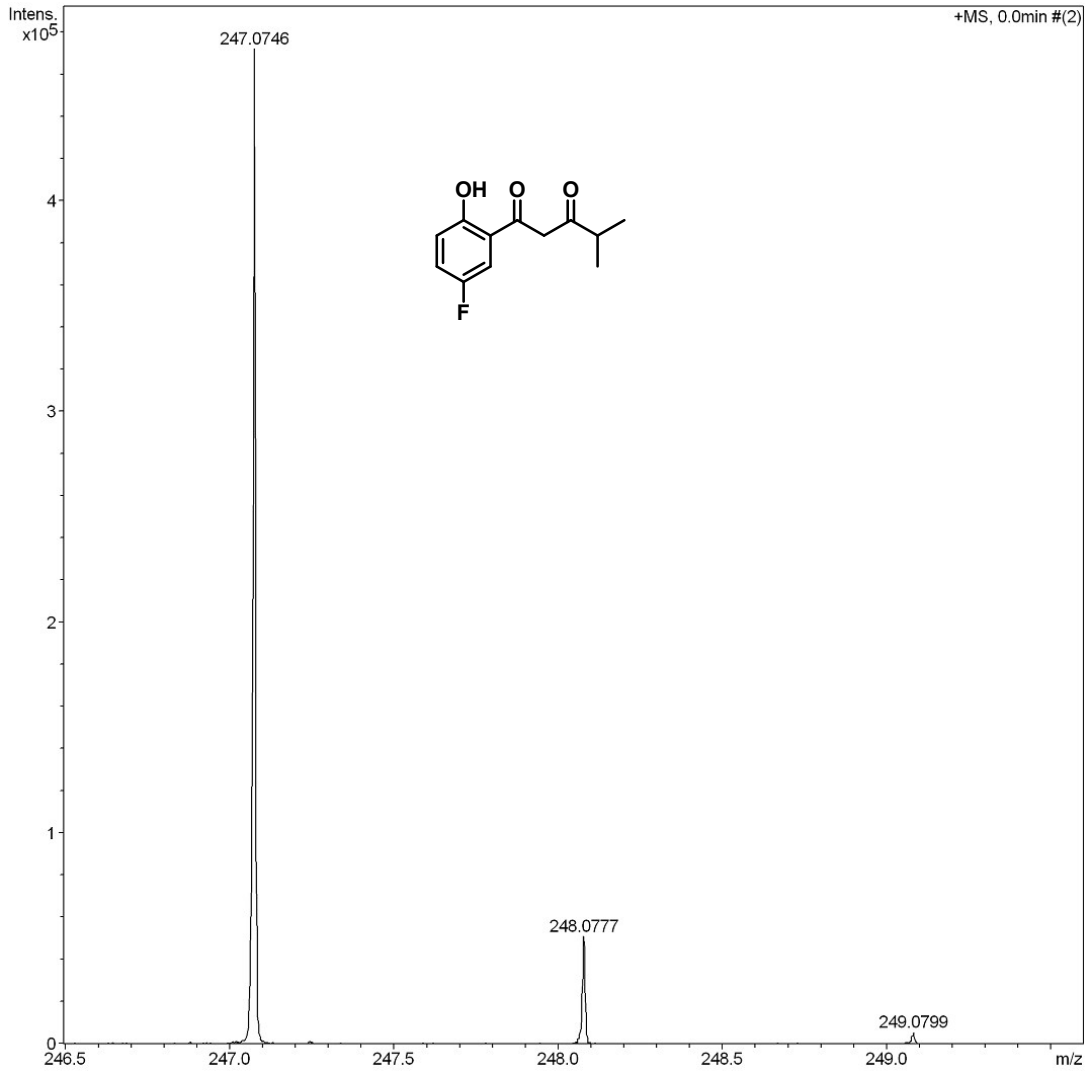

207.0097
199.5858
194.5174
192.2074
161.7394
161.4108
139.6707
138.1630
133.0747
130.7484
120.7139
120.0977
114.1270
110.7169
92.5570
77.3717
77.1599
76.9480
50.9911
37.9015
35.4315
19.8757
18.0038
OH
O
O
Br
f1 (ppm)


Intens.
x10^5
+MS, 0.0min #(2)
306.9941
308.9921
307.9975
309.9956
OH
O
O
Br
m/z

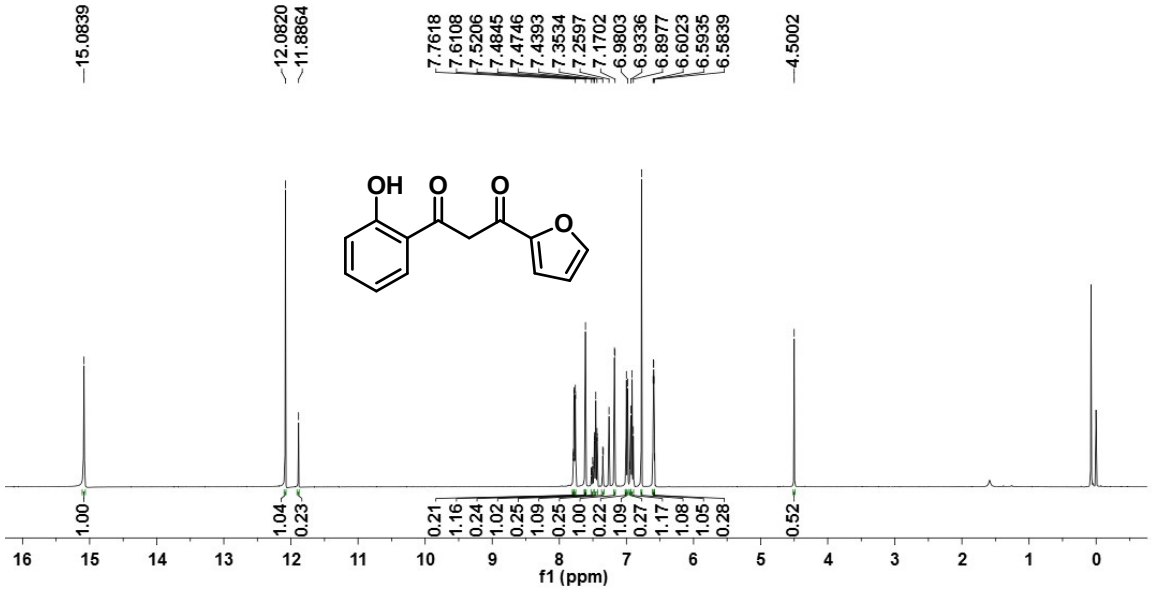
1j


15.0493
11.8101
11.7065
7.2749
7.2173
7.1964
7.1686
7.1470
7.1269
6.9578
6.9347
6.9107
6.8879
6.0657
4.0950
2.6012
2.5839
2.5667
2.5495
2.5322
1.2439
1.2266
1.1771
1.1599
OH
O
O
F
f1 (ppm)

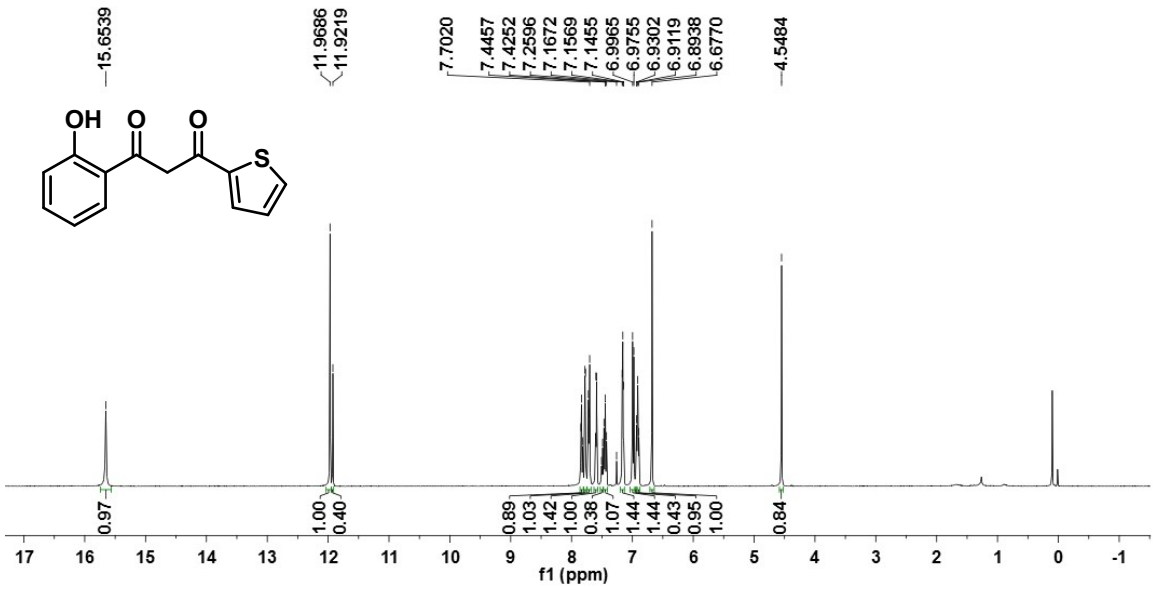

207.2112
199.6157
194.7766
194.7513
192.0762
159.0862
159.0710
158.6220
158.6127
156.3431
156.1219
153.9793
119.9777
119.9045
118.4584
118.3944
115.8267
115.5930
113.6970
113.4625
92.5495
77.4774
77.1595
76.8416
51.2525
37.9306
35.3852
19.8508
18.0058
OH
O
O
F
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Intens.
x10^5
+MS, 0.0min #(2)
247.0746
248.0777
249.0799
OH
O
O
F
4
3
2
1
0
246.5
247.0
247.5
248.0
248.5
249.0
m/z

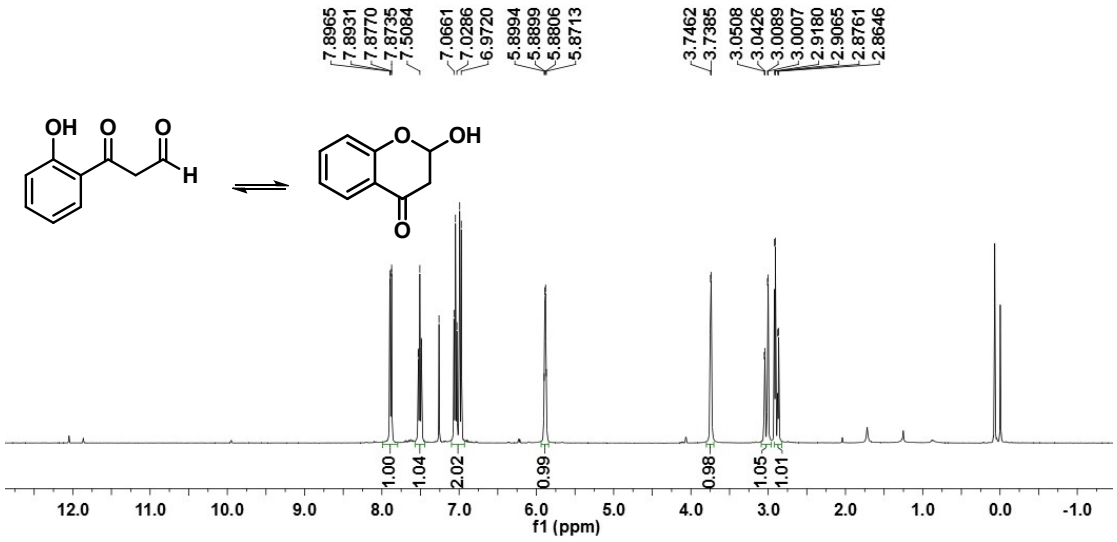
1l


15.0839
12.0820
11.8864
7.7618
7.6108
7.5206
7.4845
7.4746
7.4393
7.3534
7.2597
7.1702
6.9803
6.9336
6.8977
6.6023
6.5935
6.5839
4.5002
OH
O
O
O
1.00
1.04
0.23
0.21
1.16
0.24
1.02
0.25
1.09
0.25
1.00
0.22
1.09
0.27
1.17
1.08
1.05
0.28
0.52
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

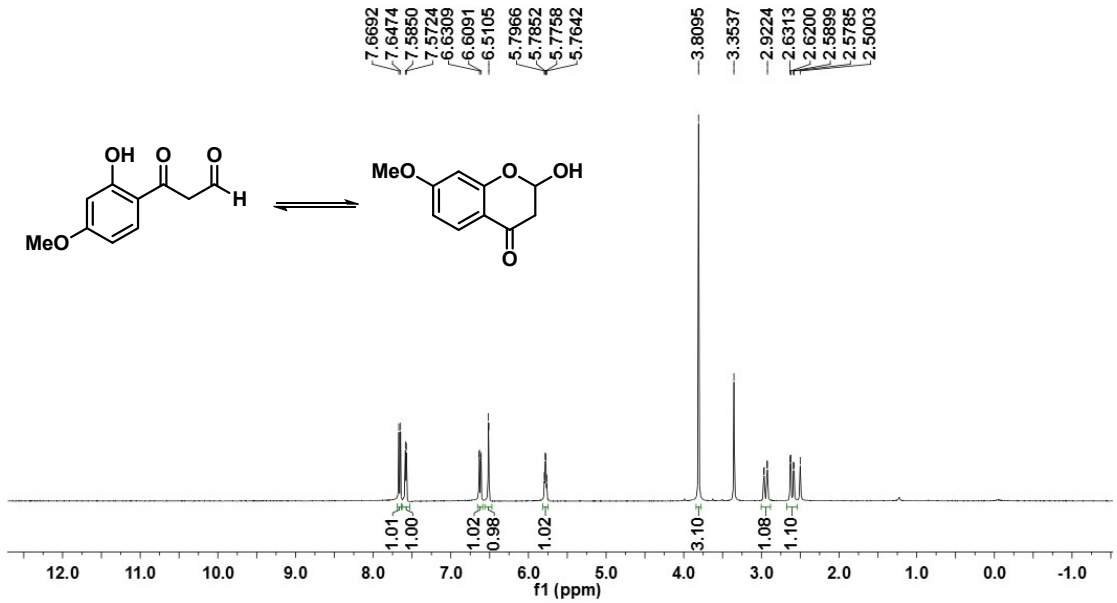
1m

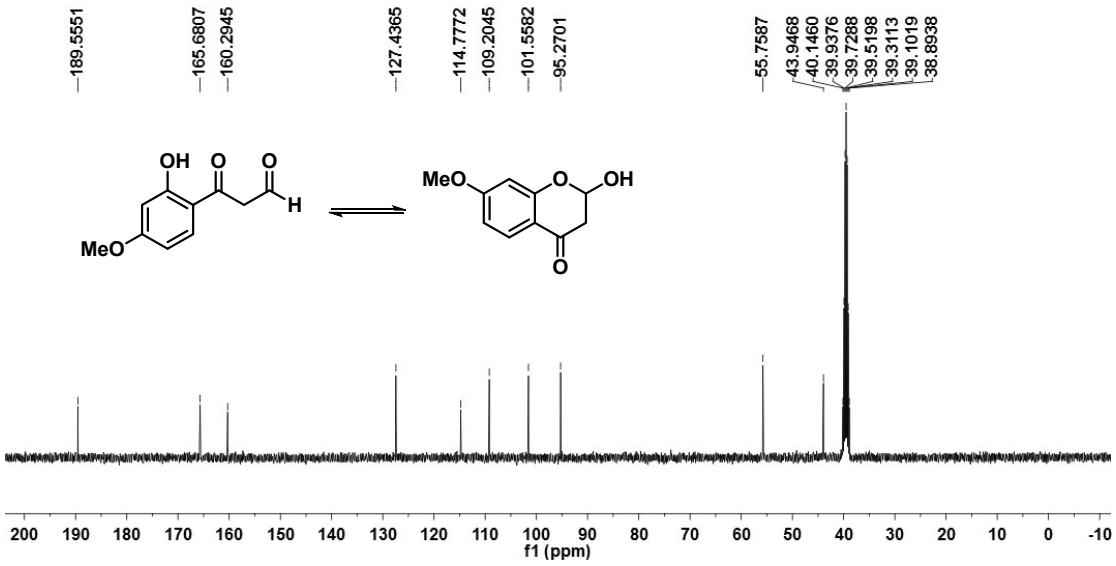

15.6539
11.9686
11.9219
7.7020
7.4457
7.4252
7.2596
7.1672
7.1569
7.1455
6.9965
6.9755
6.9302
6.9119
6.8938
6.6770
4.5484
OH
O
O
S
0.97
1.00
0.40
0.89
1.03
1.42
1.00
0.38
1.07
1.44
1.44
0.43
0.95
1.00
0.84
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

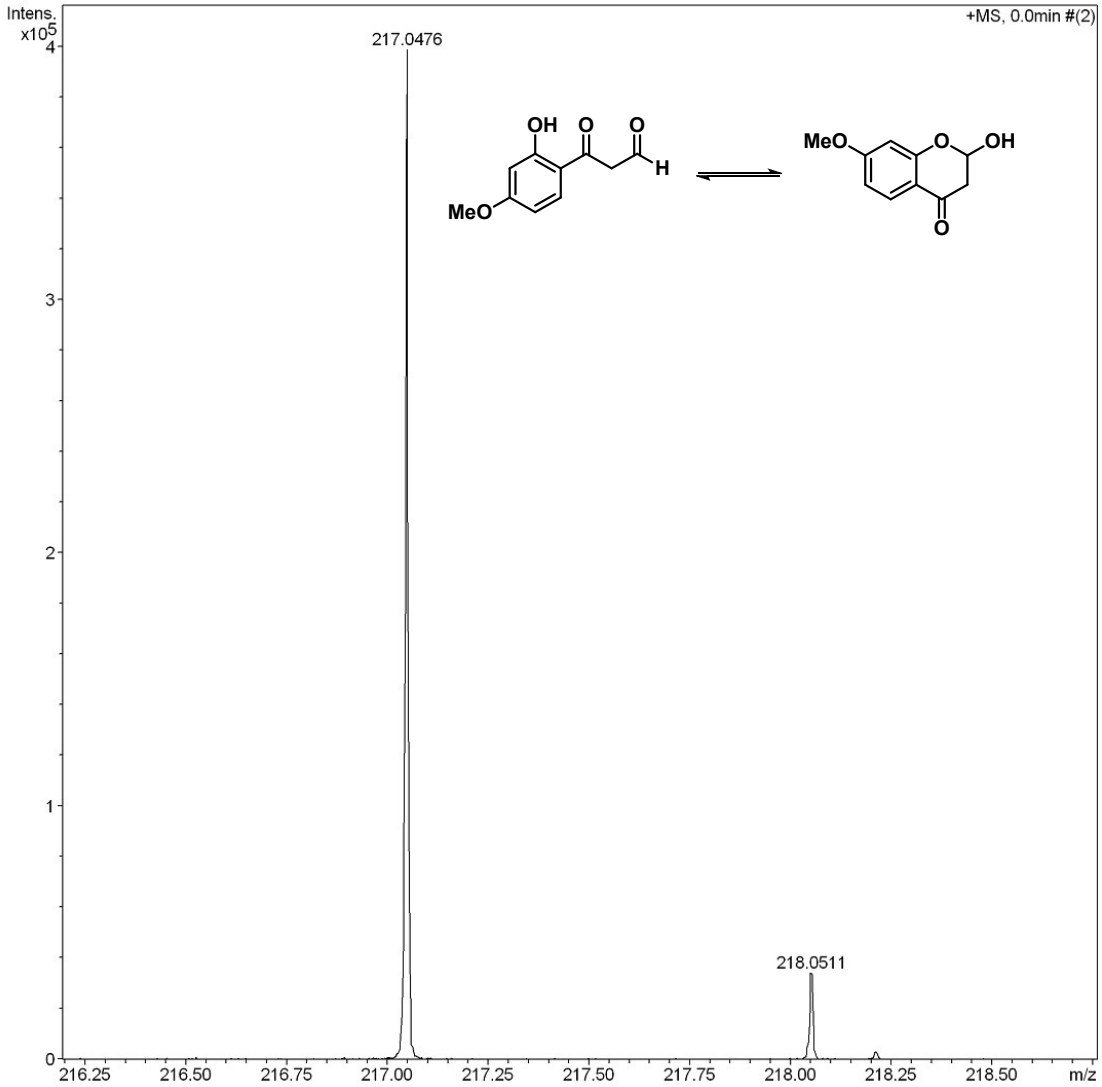
1n


7.8965
7.8931
7.8770
7.8735
7.7084
7.0661
7.0286
6.9720
5.8994
5.8899
5.8806
5.8713
3.7462
3.7385
3.0508
3.0426
3.0089
3.0007
2.9180
2.9065
2.8761
2.8646
OH
O
O
H
O
OH
O
1.00
1.04
2.02
0.99
0.98
1.05
1.01
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

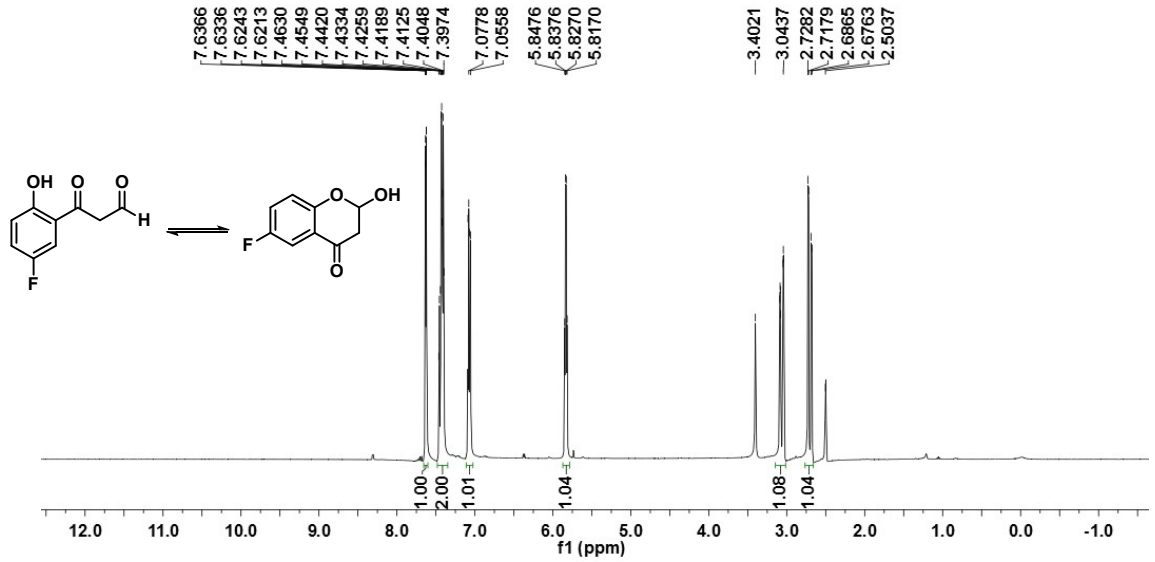
1o

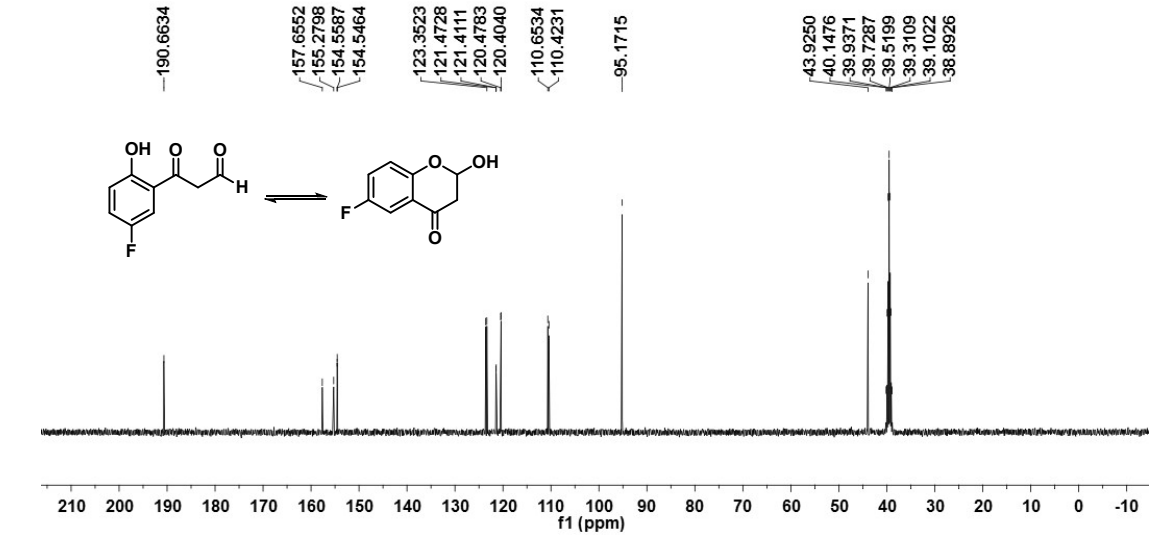

7.6692
7.6474
7.5850
7.5724
6.6309
6.6091
6.5105
5.7966
5.7852
5.7758
5.7642
3.8095
3.3537
2.9224
2.6313
2.6200
2.5899
2.5785
2.5003
OH
O
O
H
MeO
MeO
O
OH
O
1.01
1.00
1.02
0.98
1.02
3.10
1.08
1.10
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

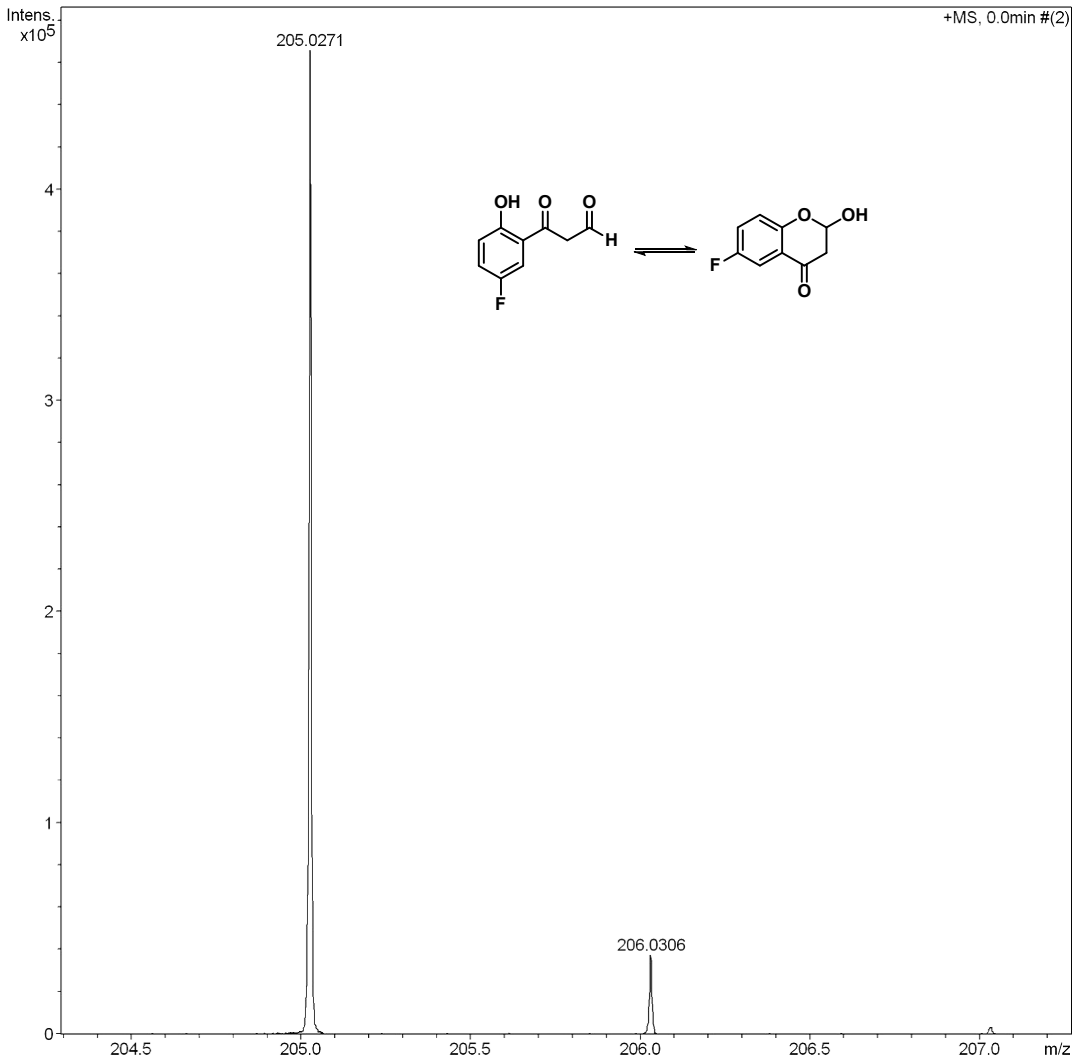

189.5551
165.6807
160.2945
127.4365
114.7772
109.2045
101.5582
95.2701
55.7587
43.9468
40.1460
39.9376
39.7288
39.5198
39.3113
39.1019
38.8938
OH
O
O
H
MeO
MeO
O
OH
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Intens.
x10^5
+MS, 0.0min #(2)
217.0476
218.0511
OH
O
O
H
MeO
MeO
O
OH
O
0
1
2
3
4
216.25
216.50
216.75
217.00
217.25
217.50
217.75
218.00
218.25
218.50
m/z

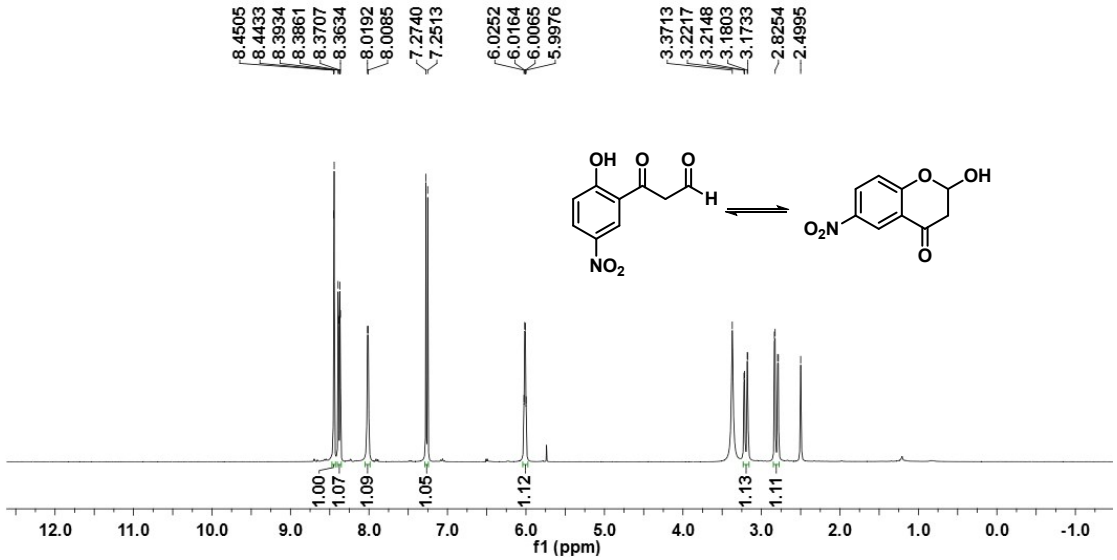
1p

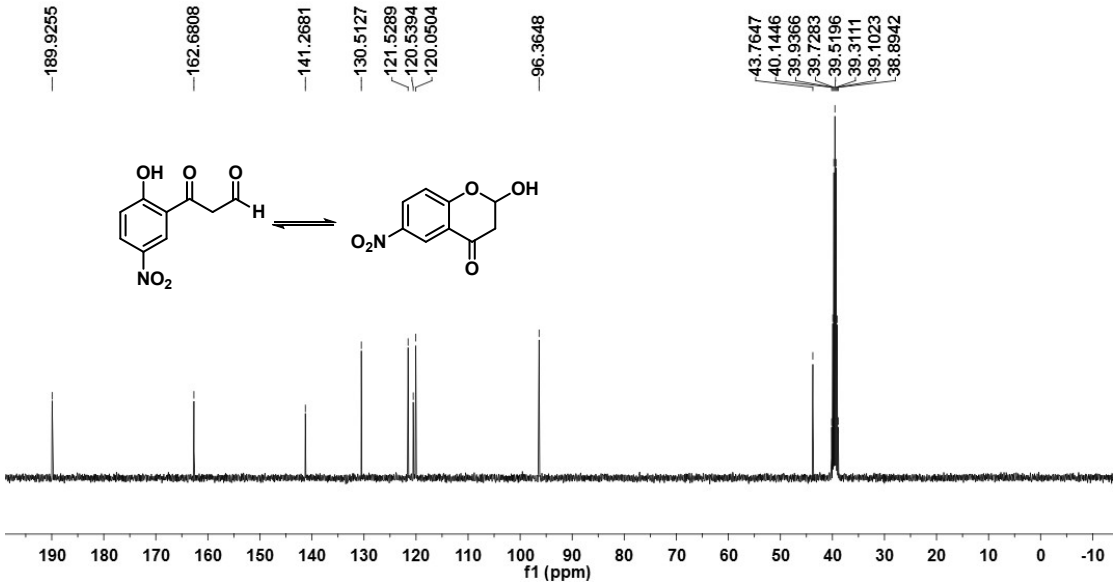

7.6366
7.6336
7.6243
7.6213
7.4630
7.4549
7.4420
7.4334
7.4259
7.4189
7.4125
7.4048
7.3974
7.0778
7.0558
5.8476
5.8376
5.8270
5.8170
3.4021
3.0437
2.7282
2.7179
2.6865
2.6763
2.5037
OH
O
O
H
F
O
OH
F
O
1.00
2.00
1.01
1.04
1.08
1.04
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

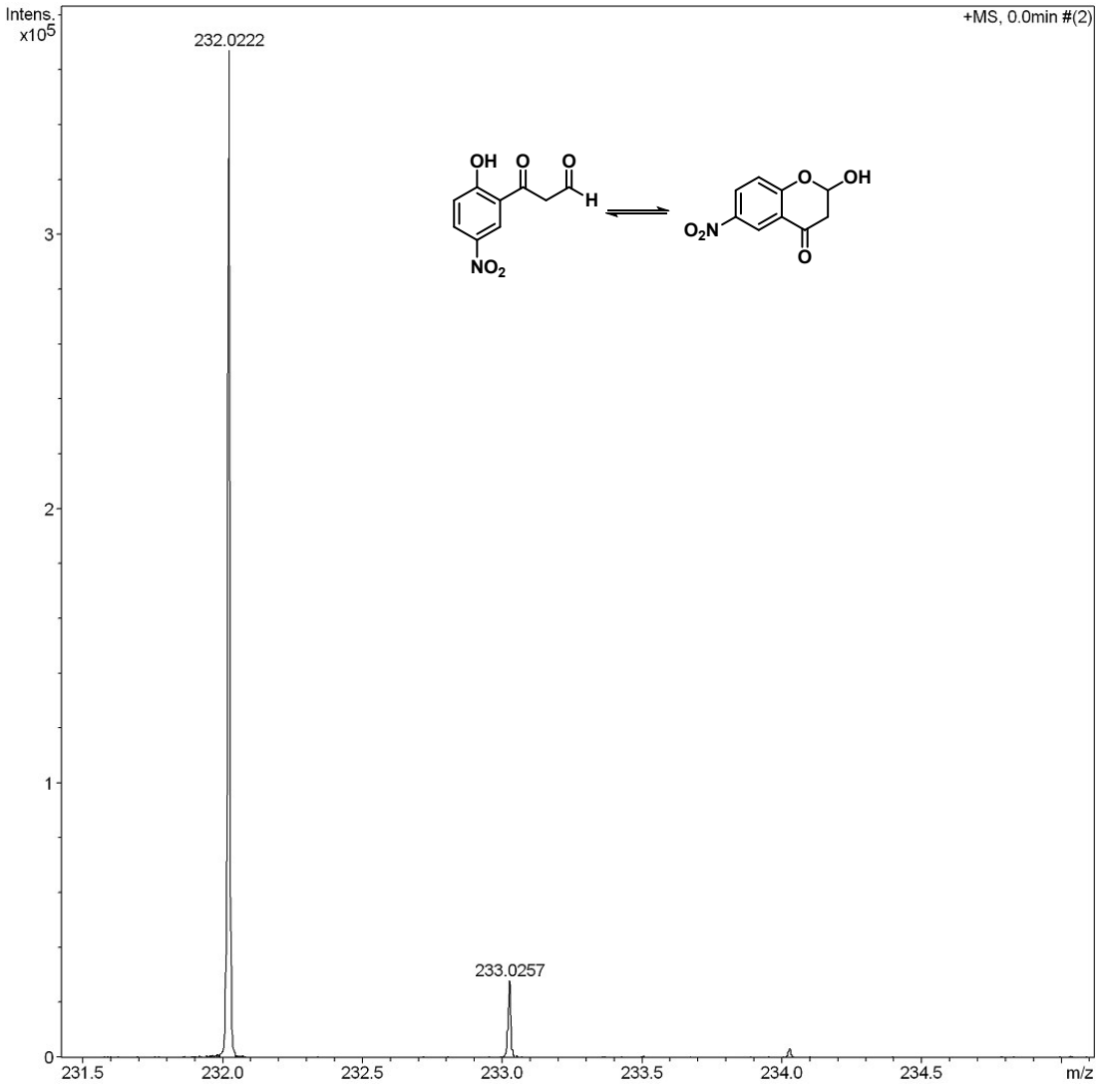

190.6634
157.6552
155.2798
154.5587
154.5464
123.3523
121.4728
121.4111
120.4783
120.4040
110.6534
110.4231
95.1715
43.9250
40.1476
39.9371
39.7287
39.5199
39.3109
39.1022
38.8926
OH
O
O
H
F
O
OH
F
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Intens.
x10^5
+MS, 0.0min #(2)
205.0271
206.0306
OH
O
O
H
F
O
OH
F
O
0
1
2
3
4
204.5
205.0
205.5
206.0
206.5
207.0
m/z

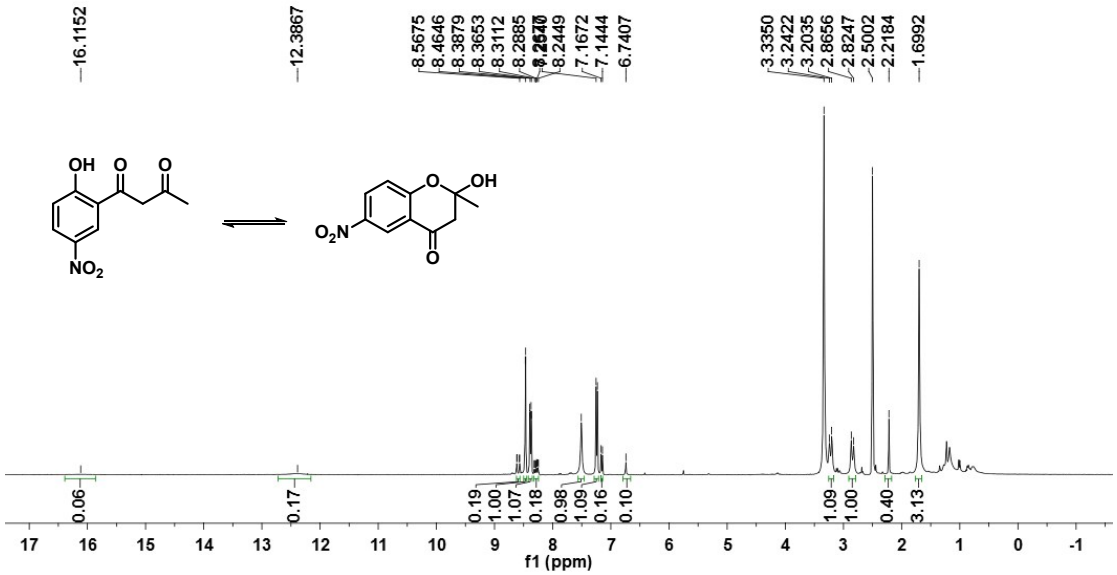
1q

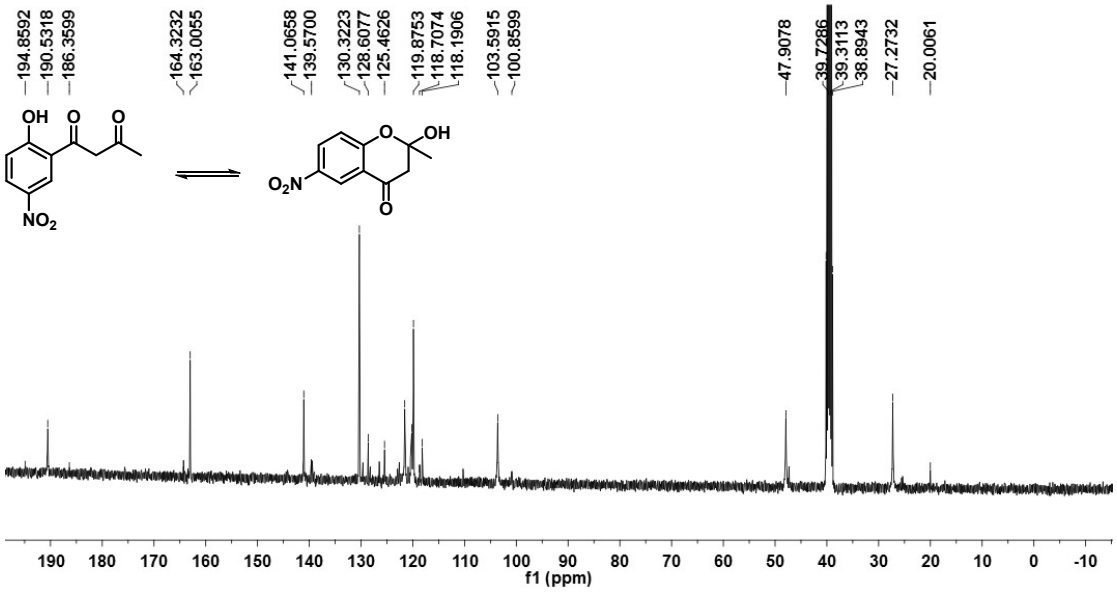

8.4505
8.4433
8.3934
8.3861
8.3707
8.3634
8.0192
8.0085
7.2740
7.2513
6.0252
6.0164
6.0065
5.9976
3.3713
3.2217
3.2148
3.1803
3.1733
2.8254
2.4995
OH
O
O
H
NO2
O
OH
O2N
O
1.00
1.07
1.09
1.05
1.12
1.13
1.11
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

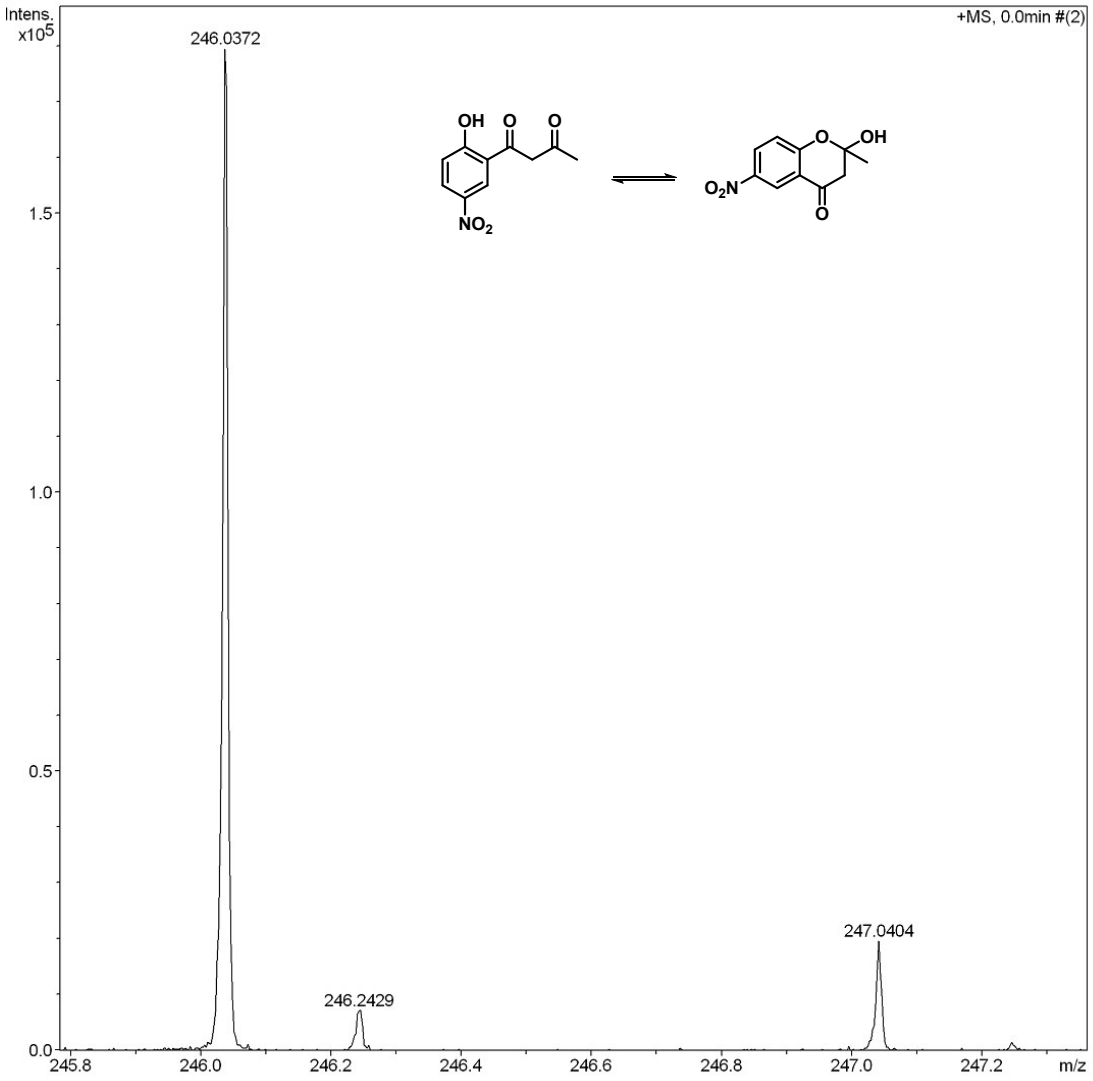

189.9255
162.6808
141.2681
130.5127
121.5289
120.5394
120.0504
96.3648
43.7647
40.1446
39.9366
39.7283
39.5196
39.3111
39.1023
38.8942
OH
O
O
H
NO2
O2N
O
OH
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Intens.
x10^5
+MS, 0.0min #(2)
232.0222
233.0257
OH
O
O
H
NO2
O2N
O
OH
0
1
2
3
231.5
232.0
232.5
233.0
233.5
234.0
234.5
m/z

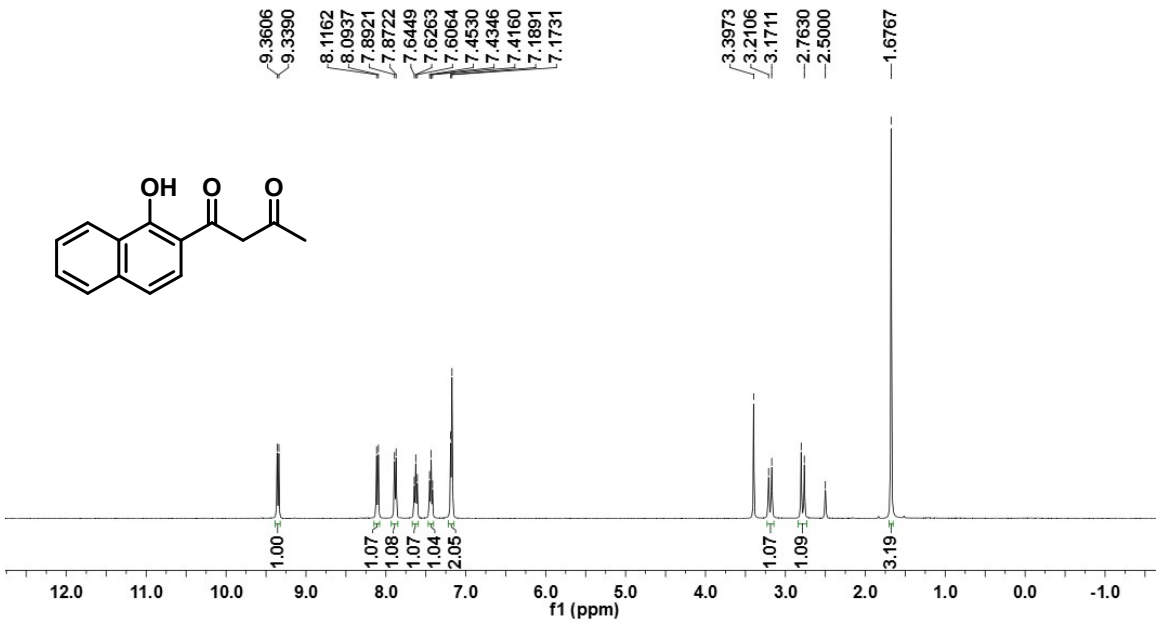
1r


16.1152
12.3867
8.5675
8.4646
8.3879
8.3653
8.3112
8.2885
8.2449
7.1672
7.1444
6.7407
3.3350
3.2422
3.2035
2.8656
2.8247
2.5002
2.2184
1.6992
OH
O
O
NO2
O2N
OH
O
0.06
0.17
0.19
1.00
1.07
0.18
0.98
1.09
0.16
0.10
1.09
1.00
0.40
3.13
f1 (ppm)

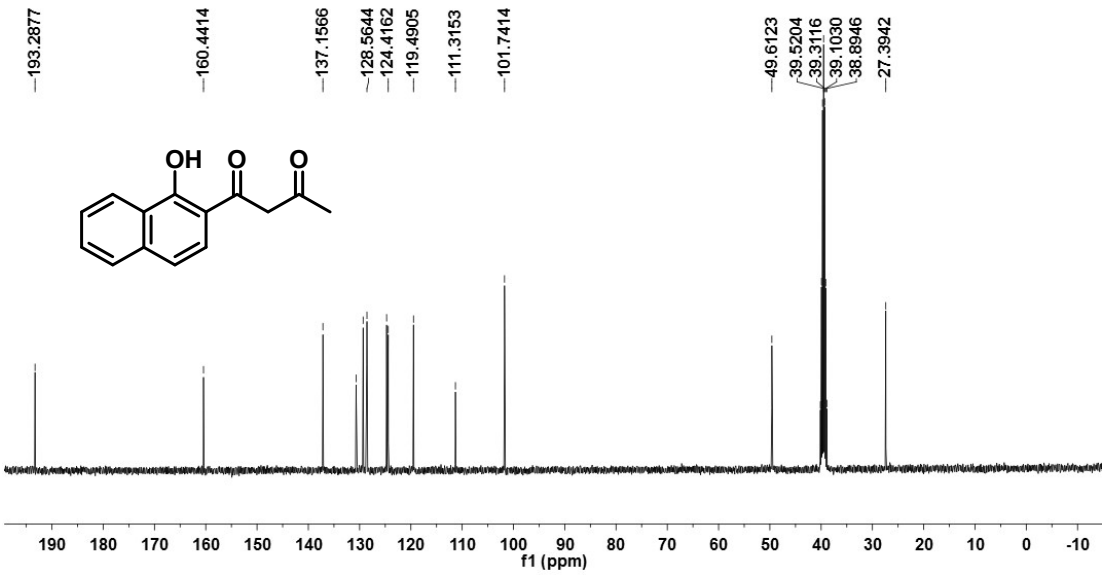

194.8592
190.5318
186.3599
164.3232
163.0055
141.0658
139.5700
130.3223
128.6077
125.4626
119.8753
118.7074
118.1906
103.5915
100.8599
47.9078
39.7286
39.3113
38.8943
27.2732
20.0061
OH
O
O
NO2
O2N
OH
O
f1 (ppm)

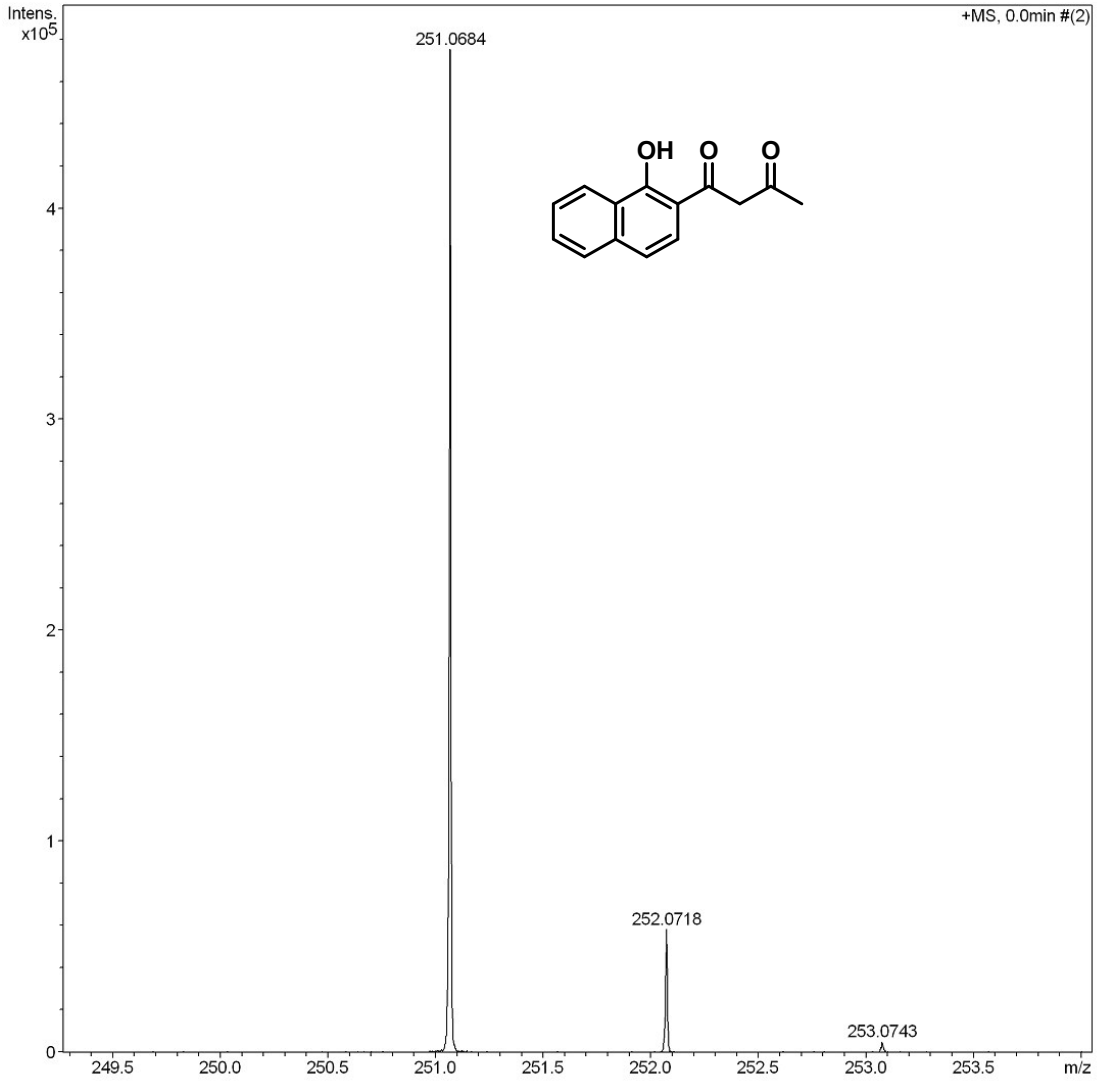

Intens.
x10^5
+MS, 0.0min #(2)
246.0372
247.0404
246.2429
OH
O
O
NO2
O2N
OH
O
O
1.5
1.0
0.5
0.0
245.8
246.0
246.2
246.4
246.6
246.8
247.0
247.2
m/z

1s

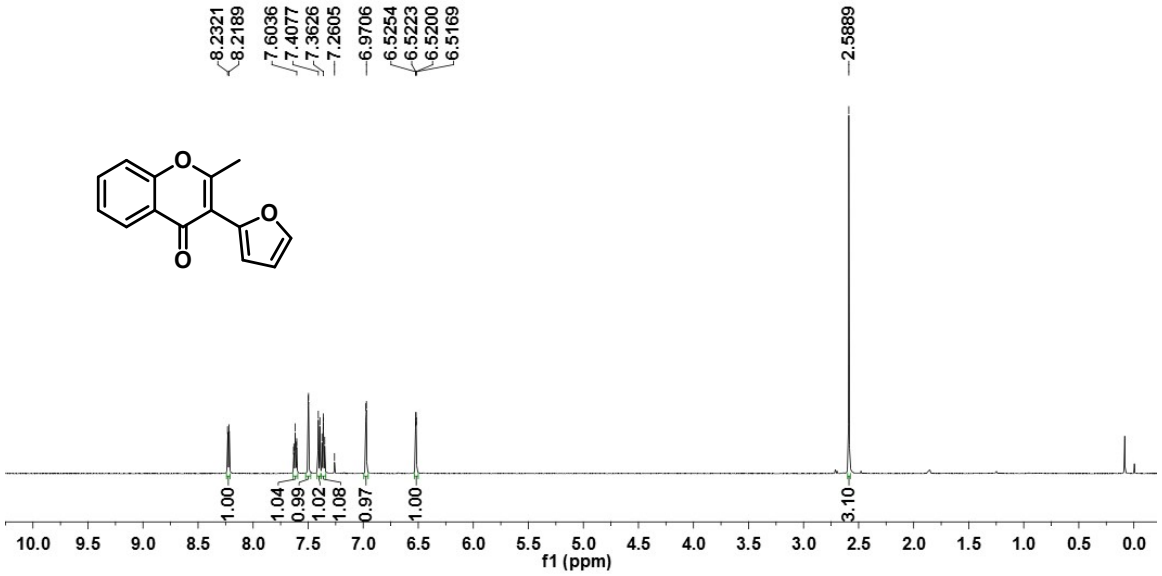

9.3606
9.3390
8.1162
8.0937
7.8921
7.8722
7.6449
7.6263
7.6064
7.4530
7.4346
7.4160
7.1891
7.1731
3.3973
3.2106
3.1711
2.7630
2.5000
1.6767
OH
O
O
1.00
1.07
1.08
1.07
1.04
2.05
1.07
1.09
3.19
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

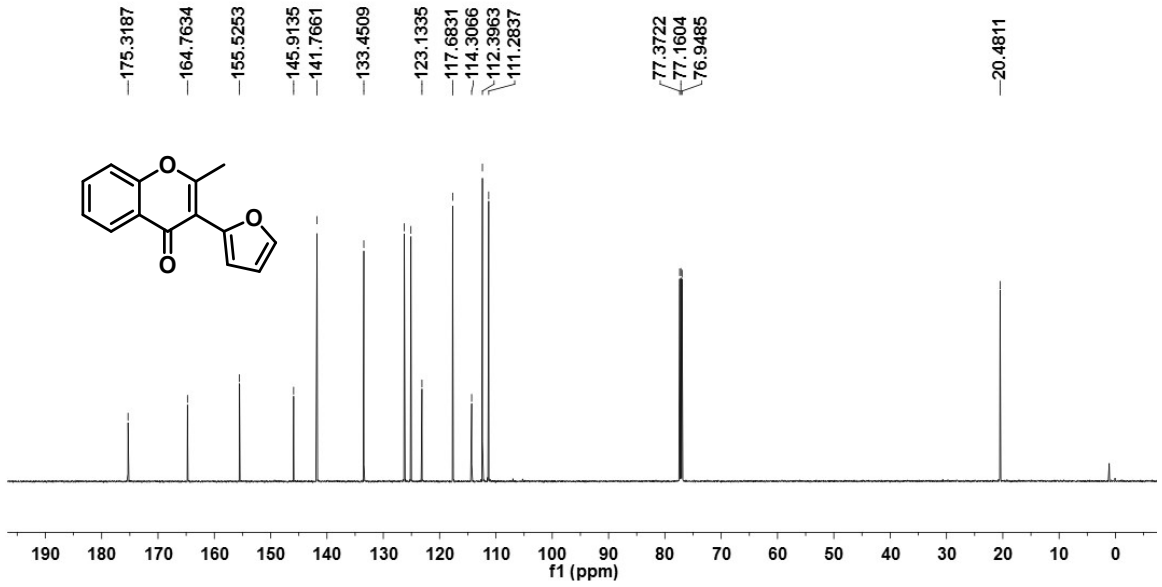
36


193.2877
160.4414
137.1566
128.5644
124.4162
119.4905
111.3153
101.7414
49.6123
39.5204
39.3116
39.1030
38.8946
27.3942
OH
O
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

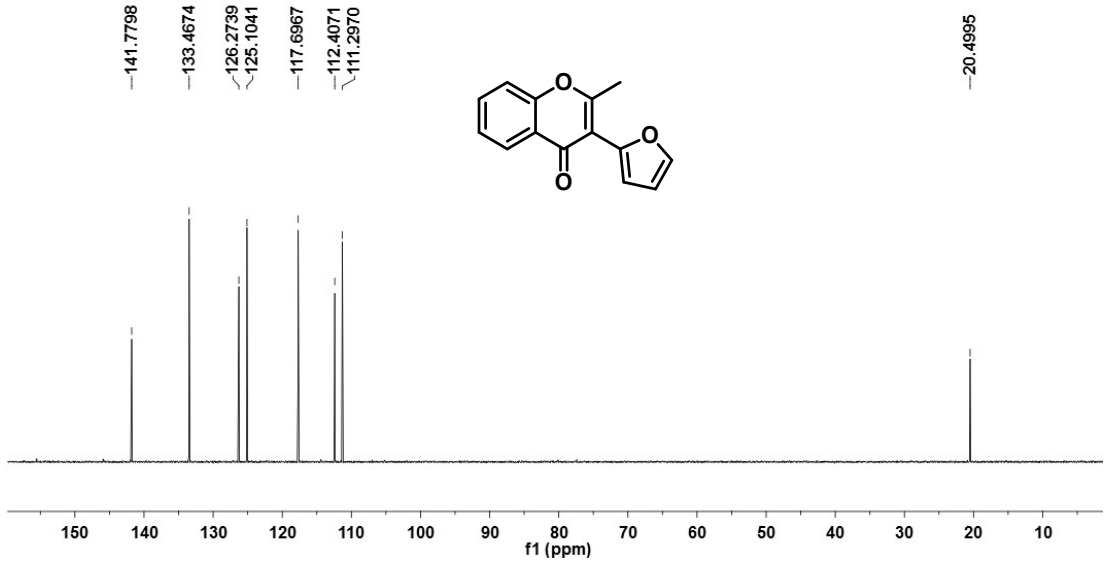

Intens.
x10^5
+MS, 0.0min #(2)
251.0684
OH
O
O
252.0718
253.0743
0
1
2
3
4
249.5 250.0 250.5 251.0 251.5 252.0 252.5 253.0 253.5
m/z

3a

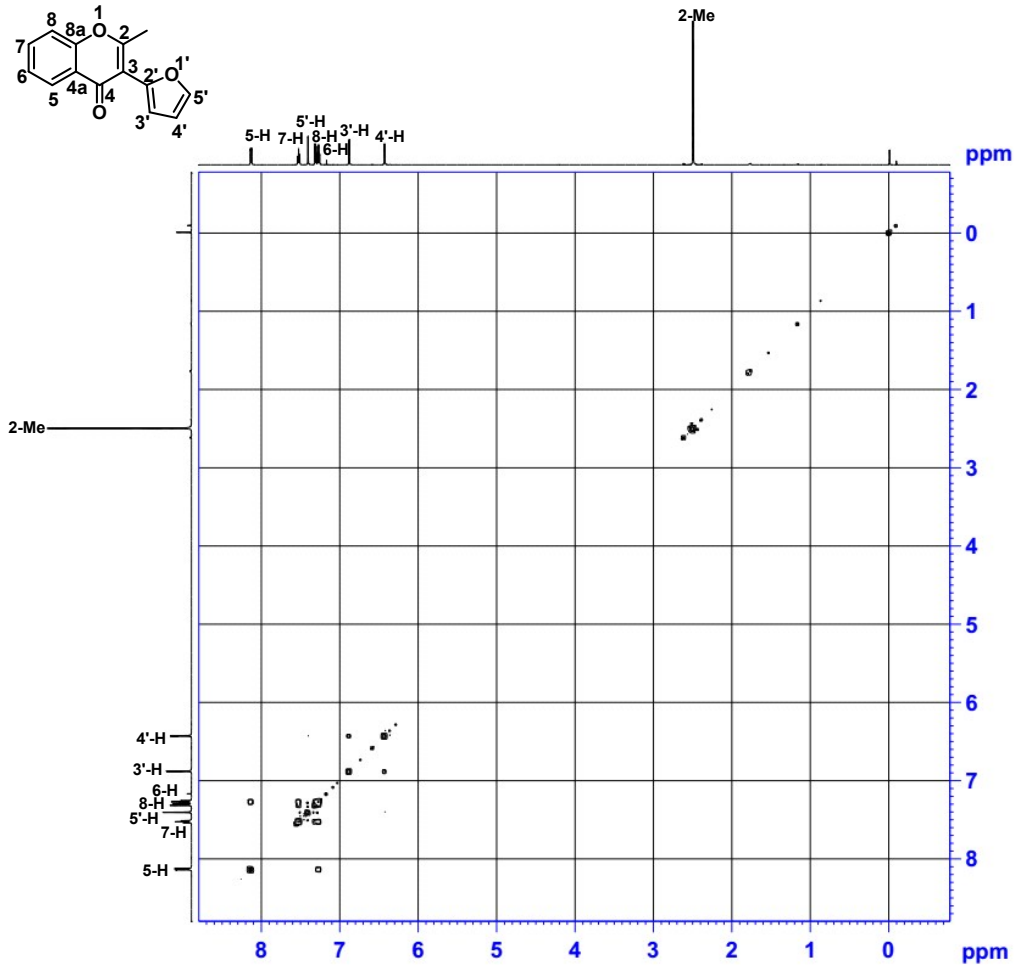

8.2321
8.2189
7.6036
7.4077
7.3626
7.2605
6.9706
6.5254
6.5223
6.5200
6.5169
2.5889
1.00
1.04
0.99
1.02
1.08
0.97
1.00
3.10
f1 (ppm)

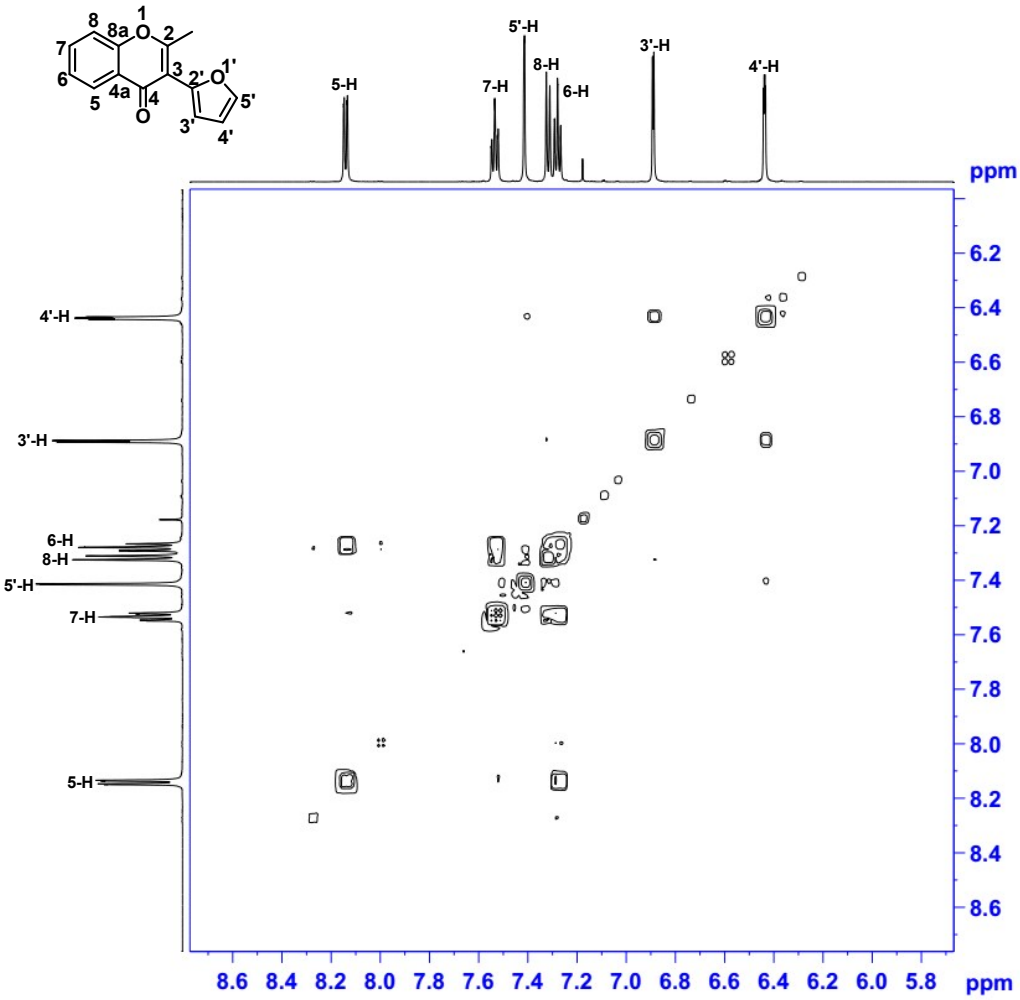

175.3187
164.7634
155.5253
145.9135
141.7661
133.4509
123.1335
117.6831
114.3066
112.3963
111.2837
77.3722
77.1604
76.9485
20.4811
f1 (ppm)

DEPT(135°)

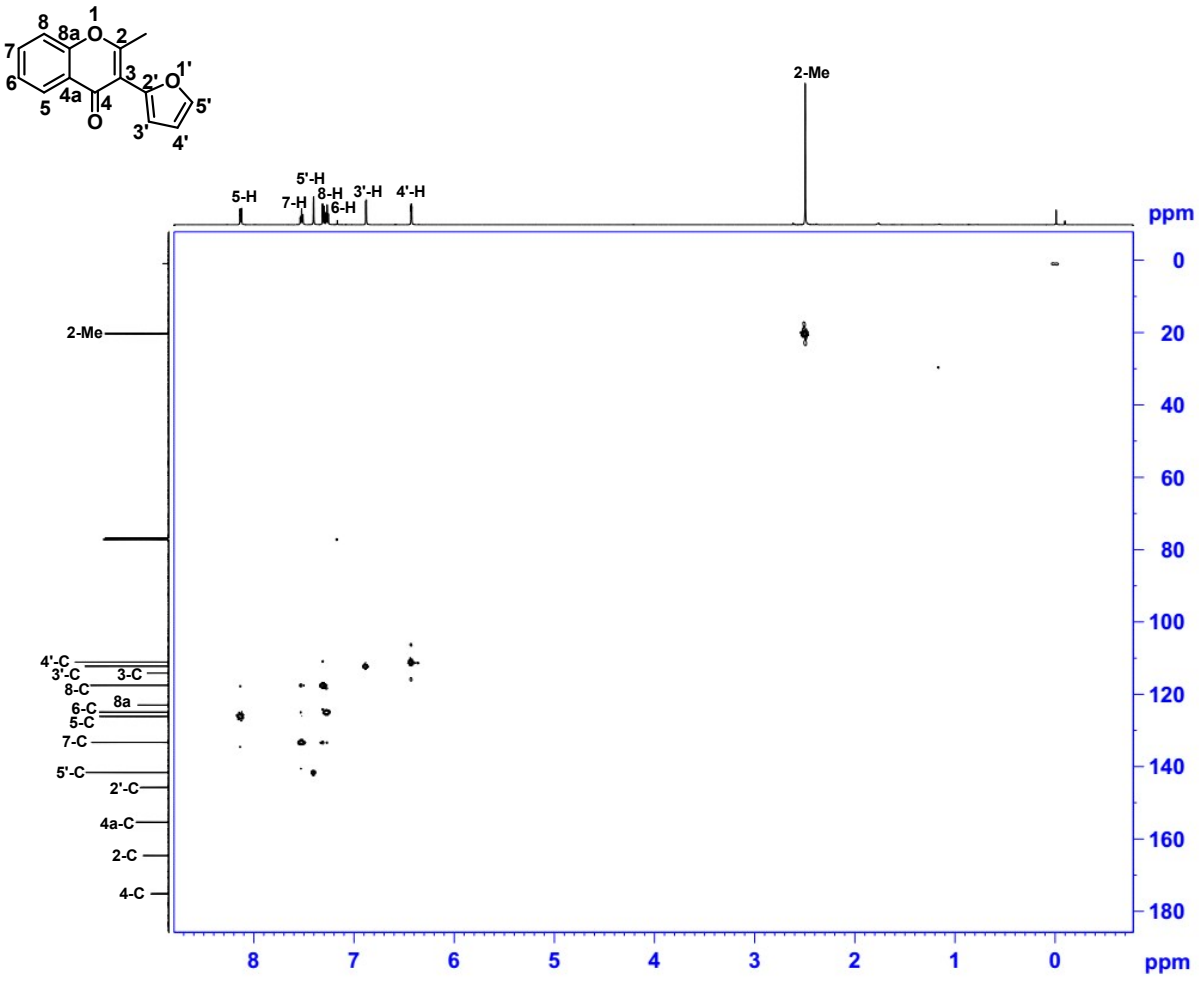


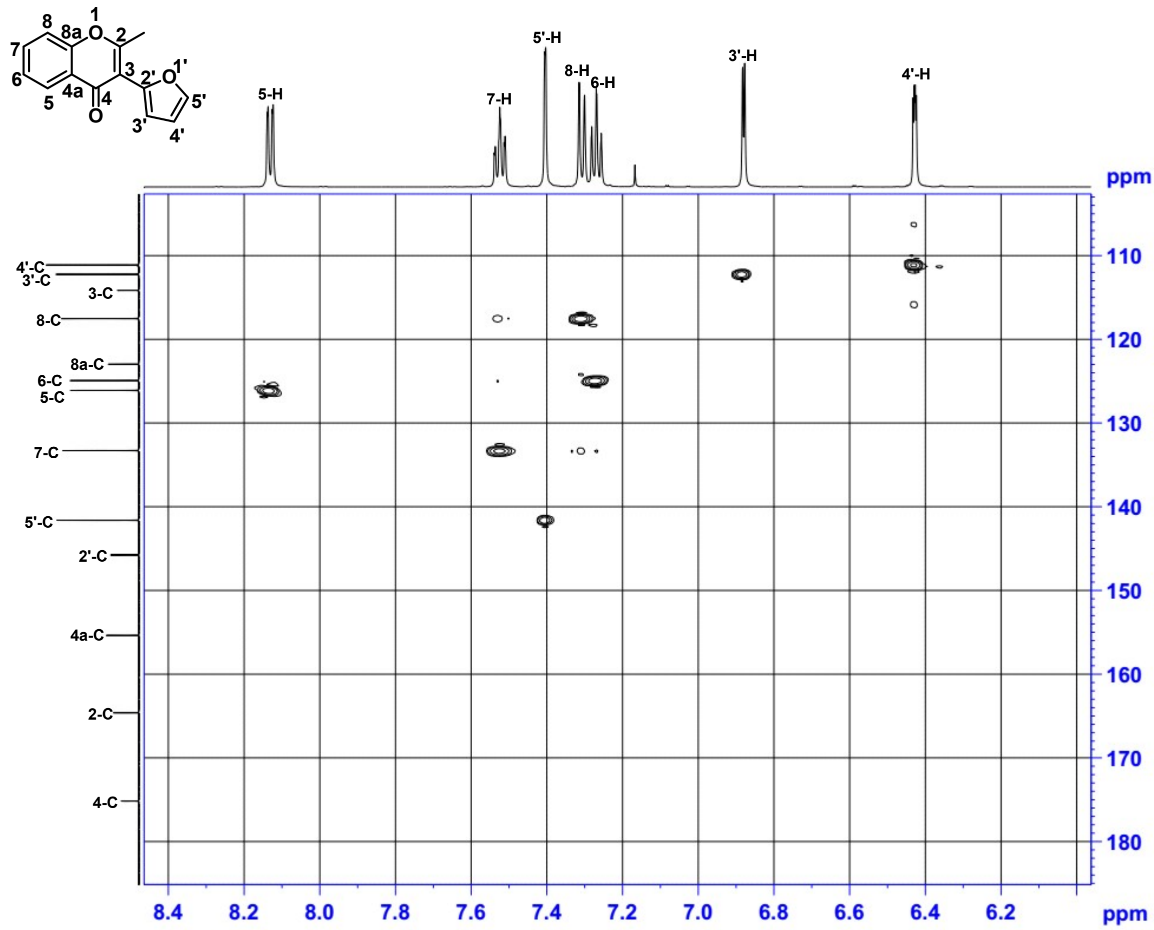
H,H-COSY




8
8a
1
O
2
7
3
6
4a
2'
1'
O
5'
5
4
O
3'
4'
5-H
7-H
5'-H
8-H
6-H
3'-H
4'-H
ppm
6.2
6.4
6.6
6.8
7.0
7.2
7.4
7.6
7.8
8.0
8.2
8.4
8.6
4'-H
3'-H
6-H
8-H
5'-H
7-H
5-H
8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8
ppm

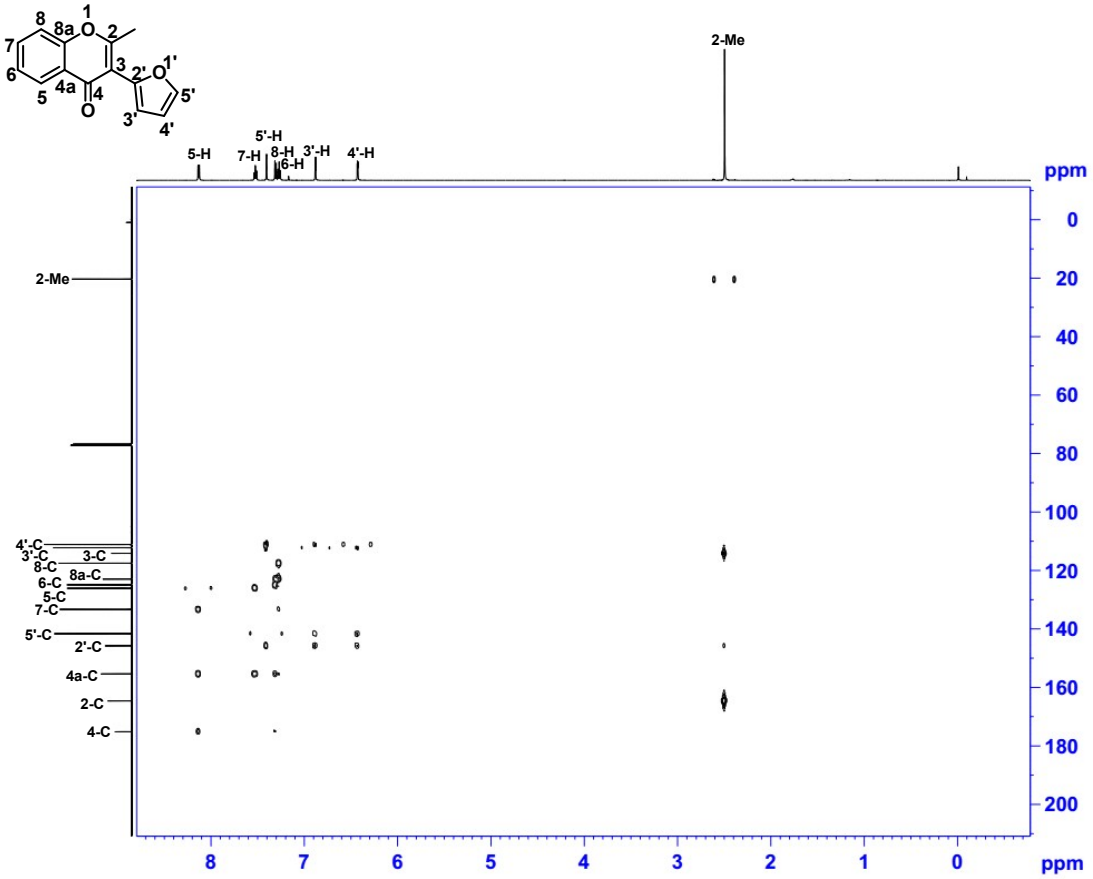
HSQC

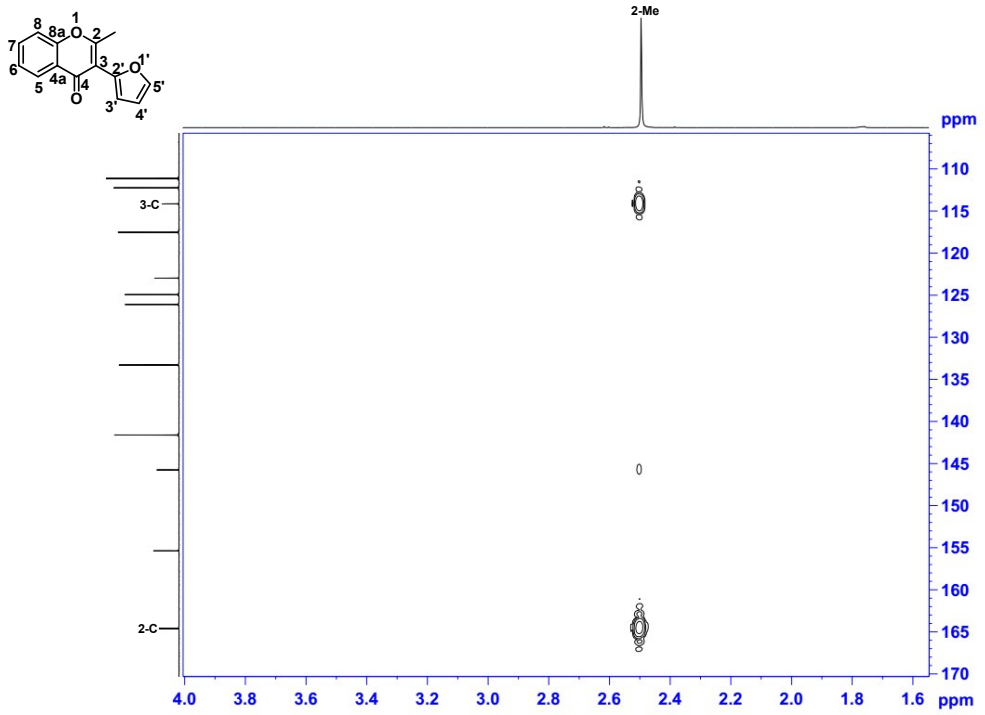

8
1
8a
O
2
7
3
2'
O
1'
6
4a
4
5'
5
O
3'
4'
2-Me
5'-H
5-H
7-H
8-H
6-H
3'-H
4'-H
ppm
0
20
40
60
80
100
120
140
160
180
2-Me
4'-C
3'-C
3-C
8-C
8a
6-C
5-C
7-C
5'-C
2'-C
4a-C
2-C
4-C
8
7
6
5
4
3
2
1
0
ppm

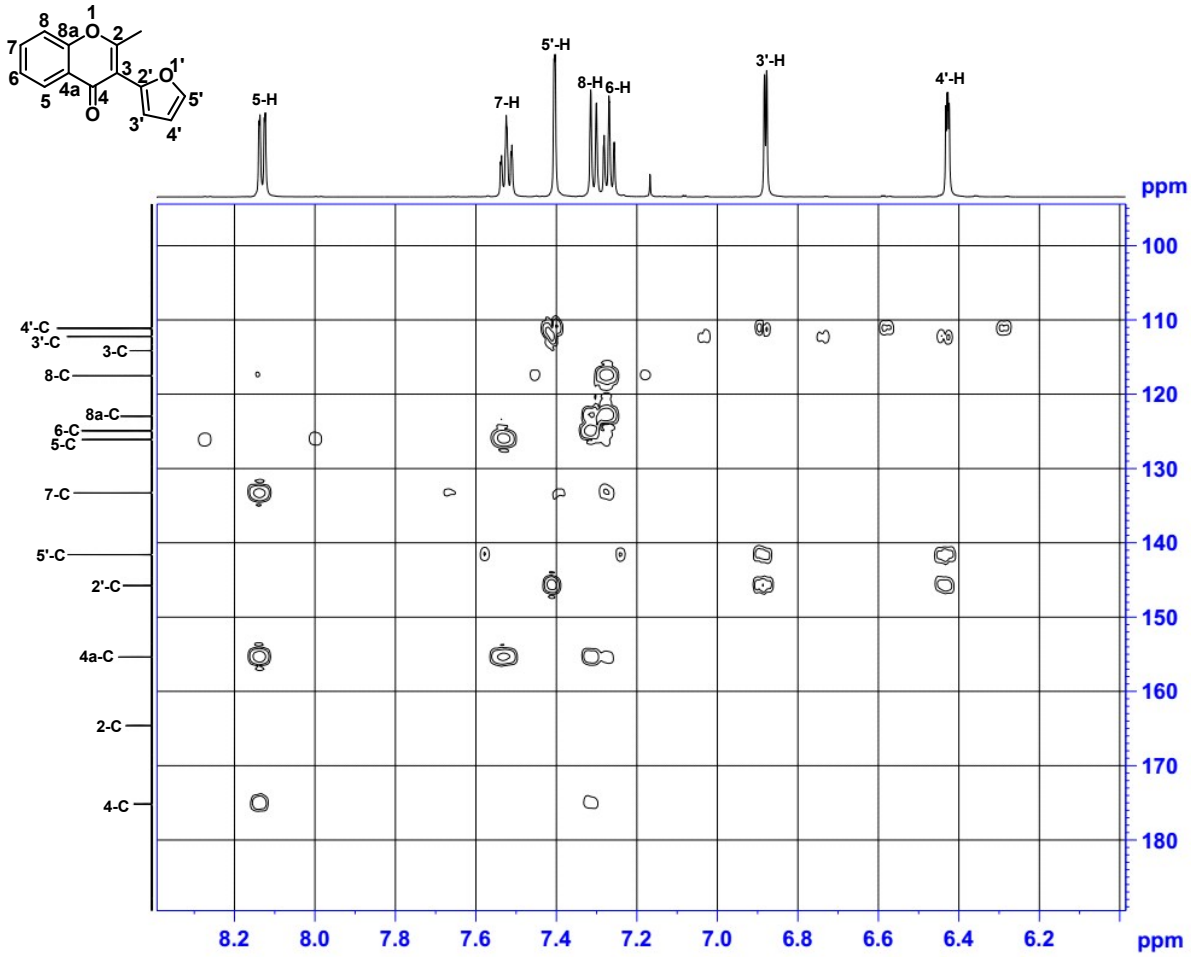


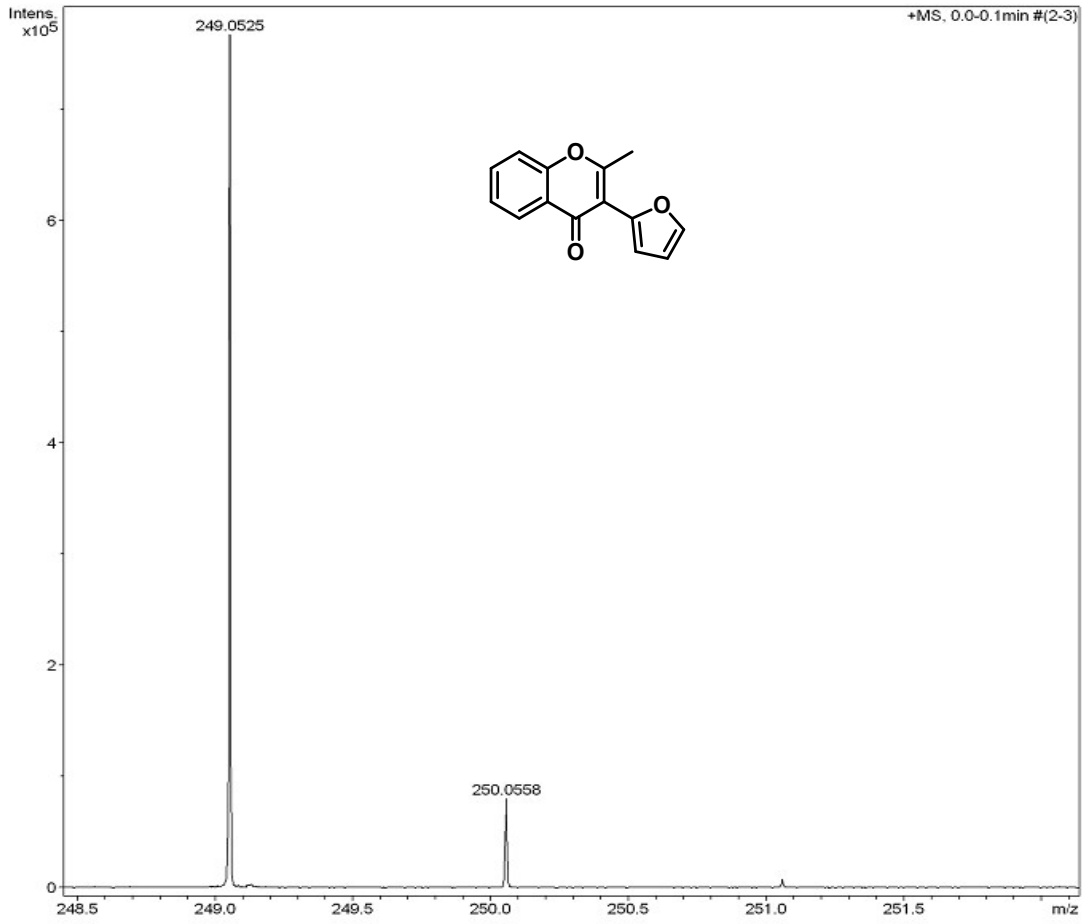
5-H
7-H
5'-H
8-H
6-H
3'-H
4'-H
4'-C
3'-C
3-C
8-C
8a-C
6-C
5-C
7-C
5'-C
2'-C
4a-C
2-C
4-C
ppm
110
120
130
140
150
160
170
180
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
ppm

HMBC

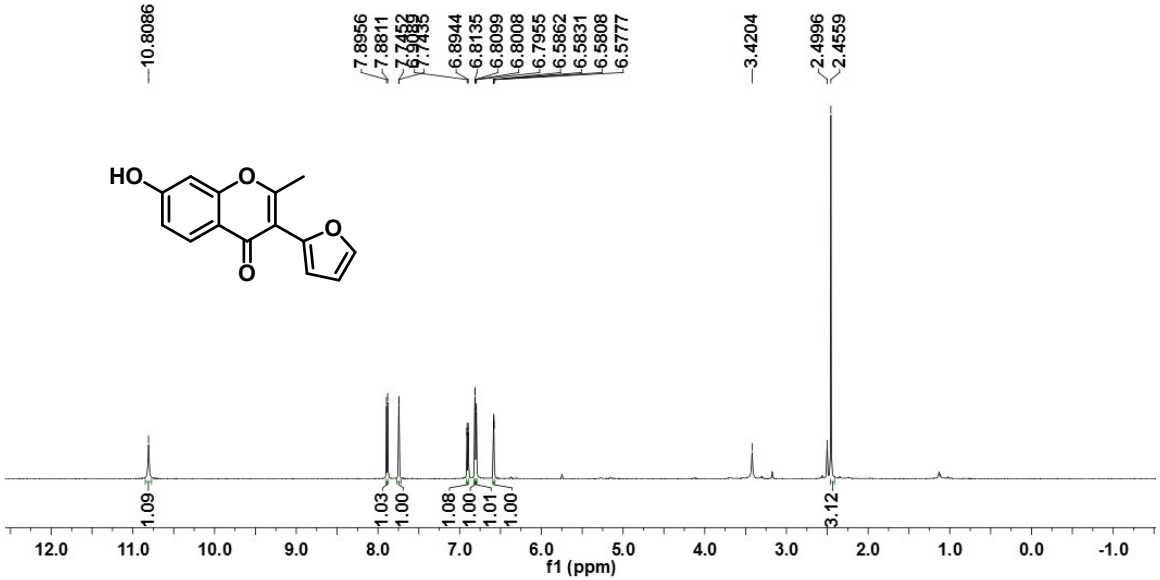

2-Me
5-H
7-H
5'-H
8-H
6-H
3'-H
4'-H
ppm
2-Me
4'-C
3'-C
3-C
8-C
8a-C
6-C
5-C
7-C
5'-C
2'-C
4a-C
2-C
4-C
0
20
40
60
80
100
120
140
160
180
200
8
7
6
5
4
3
2
1
0
ppm

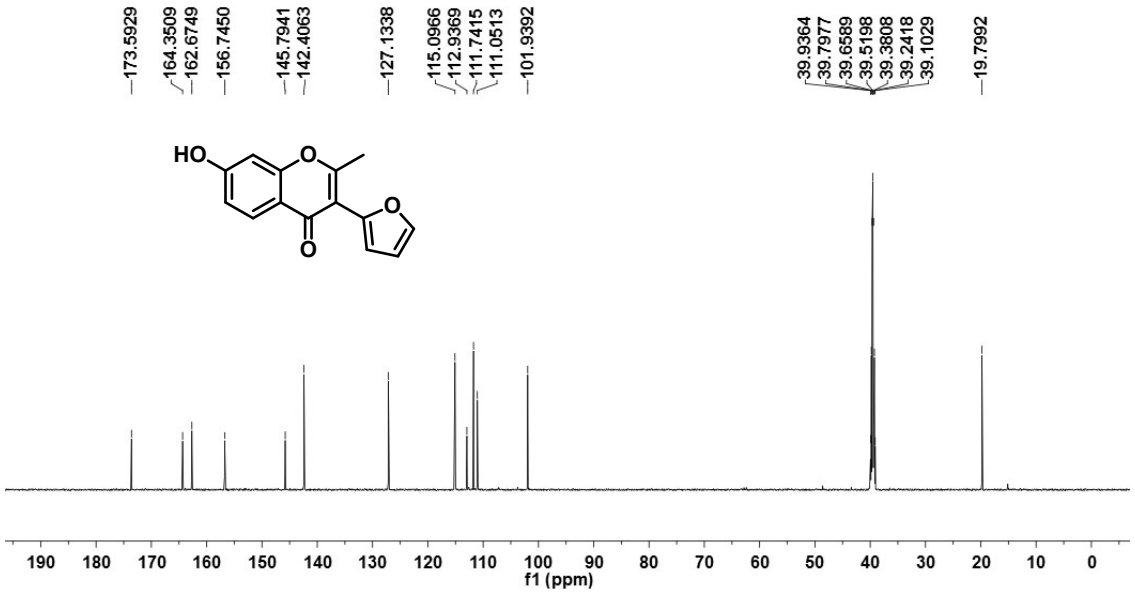

2-Me
ppm
3-C
2-C
110
115
120
125
130
135
140
145
150
155
160
165
170
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
ppm

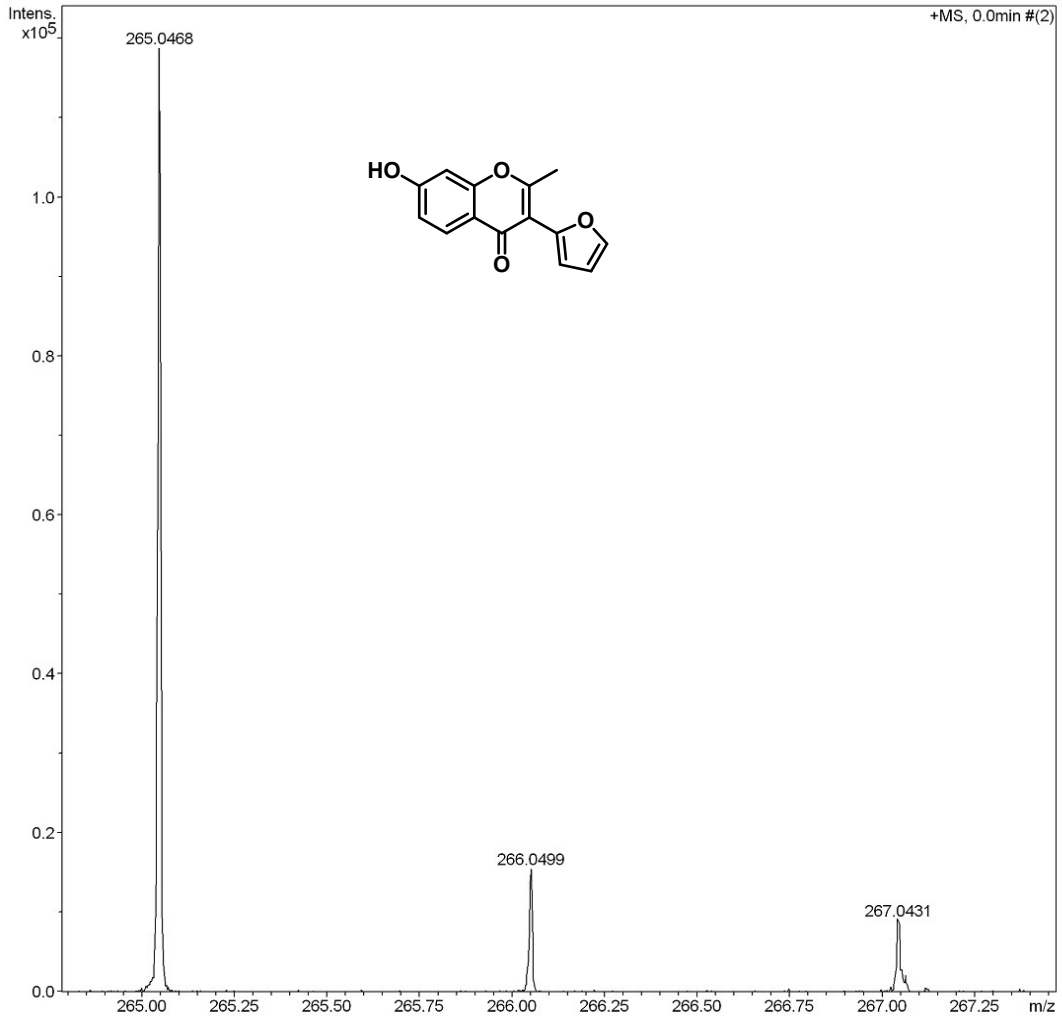

5-H
7-H
5'-H
8-H
6-H
3'-H
4'-H
ppm
4'-C
3'-C
3-C
8-C
8a-C
6-C
5-C
7-C
5'-C
2'-C
4a-C
2-C
4-C
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
ppm


Intens.
x10^5
+MS, 0.0-0.1min #(2-3)
249.0525
250.0558
O
O
O
6
4
2
0
248.5
249.0
249.5
250.0
250.5
251.0
251.5
m/z

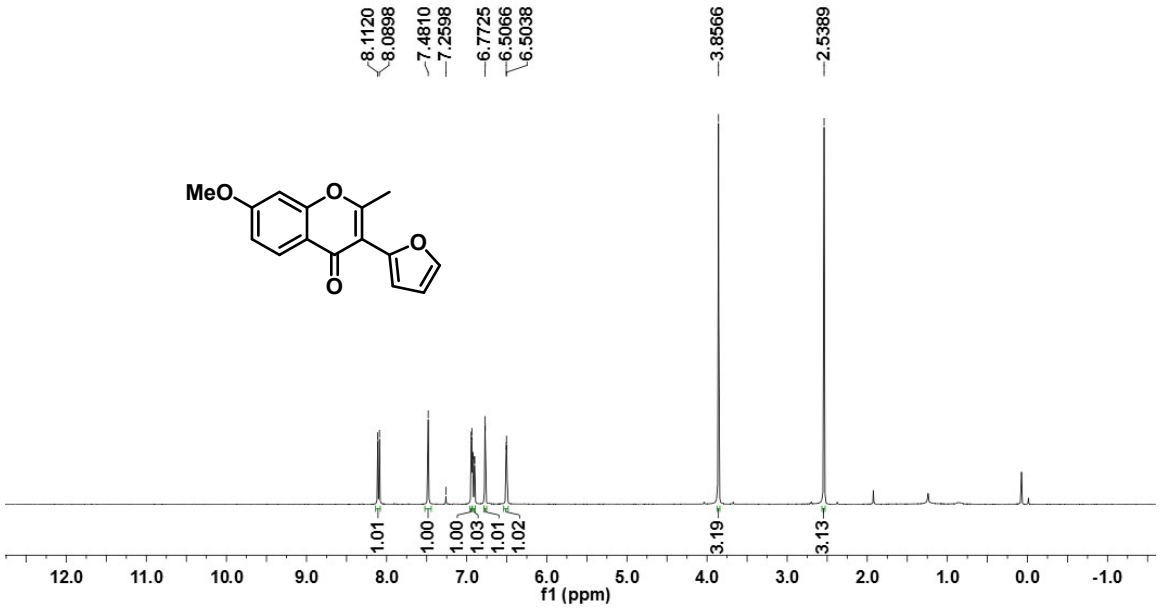
3b

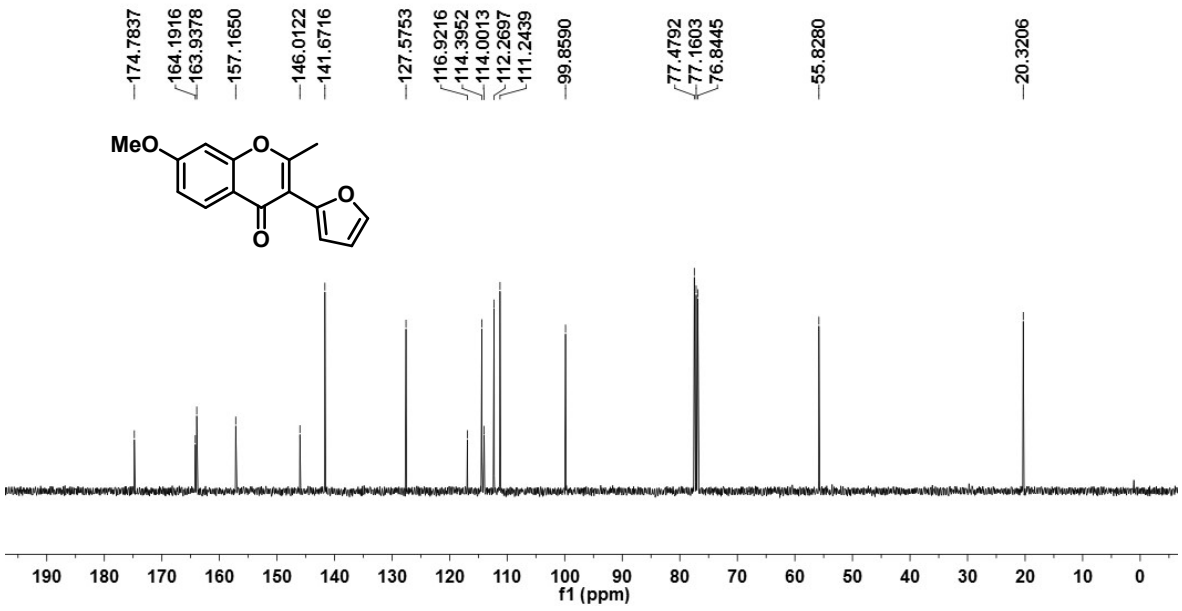

10.8086
7.8956
7.8811
7.7452
7.7435
6.8944
6.8135
6.8099
6.8008
6.7955
6.5862
6.5831
6.5808
6.5777
3.4204
2.4996
2.4559
HO
O
O
O
1.09
1.03
1.00
1.08
1.00
1.01
1.00
3.12
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

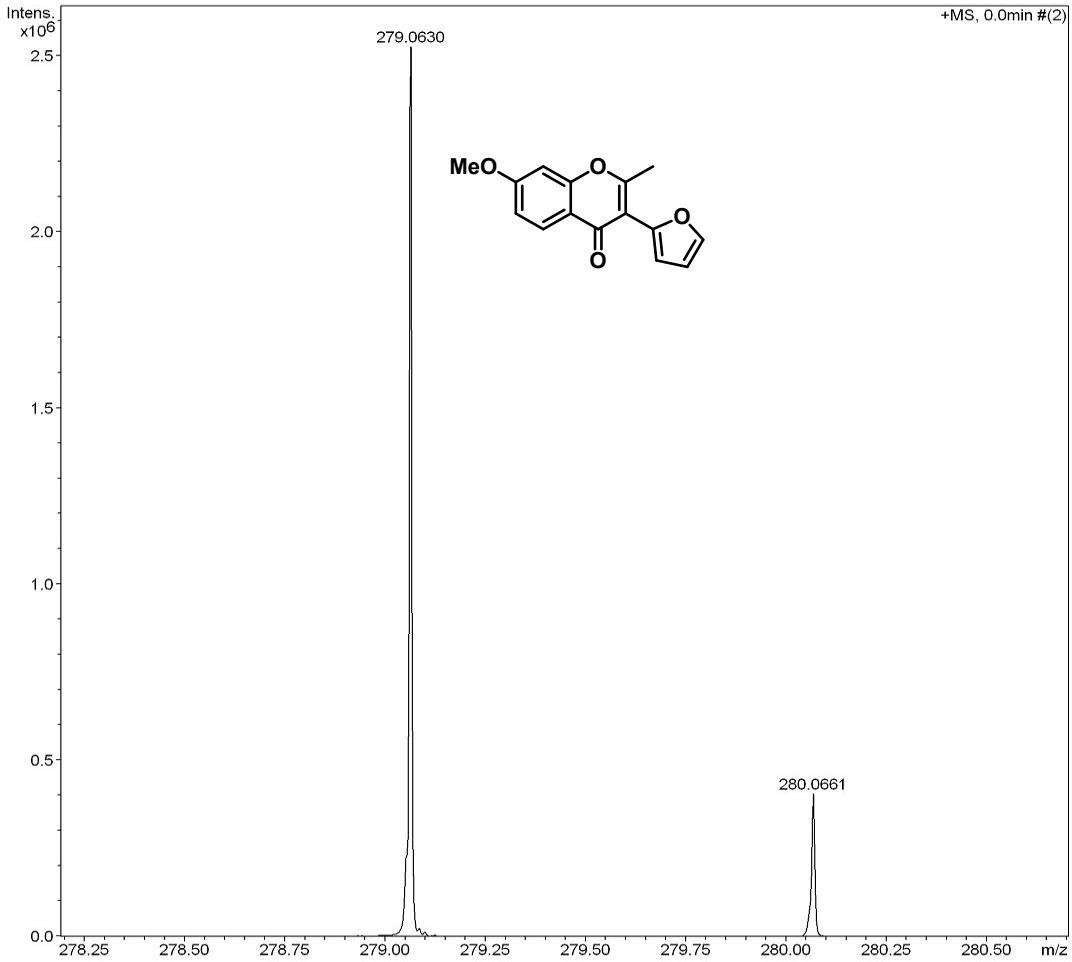

173.5929
164.3509
162.6749
156.7450
145.7941
142.4063
127.1338
115.0966
112.9369
111.7415
111.0513
101.9392
39.9364
39.7977
39.6589
39.5198
39.3808
39.2418
39.1029
19.7992
HO
O
O
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Intens.
x10^5
+MS, 0.0min #(2)
265.0468
266.0499
267.0431
HO
O
O
O
1.0
0.8
0.6
0.4
0.2
0.0
265.00 265.25 265.50 265.75 266.00 266.25 266.50 266.75 267.00 267.25 m/z

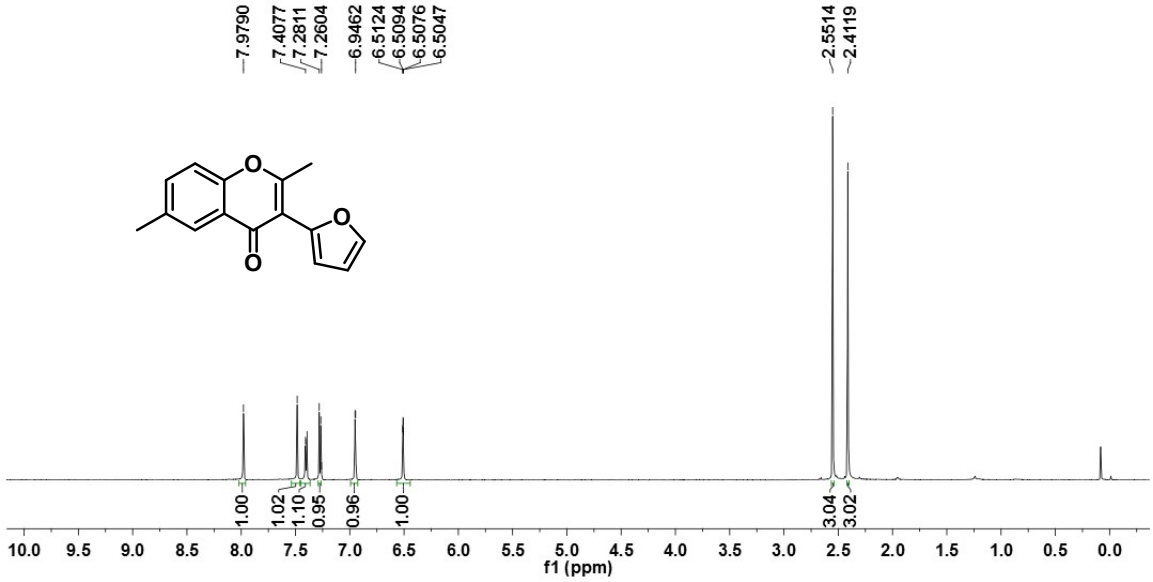
3c

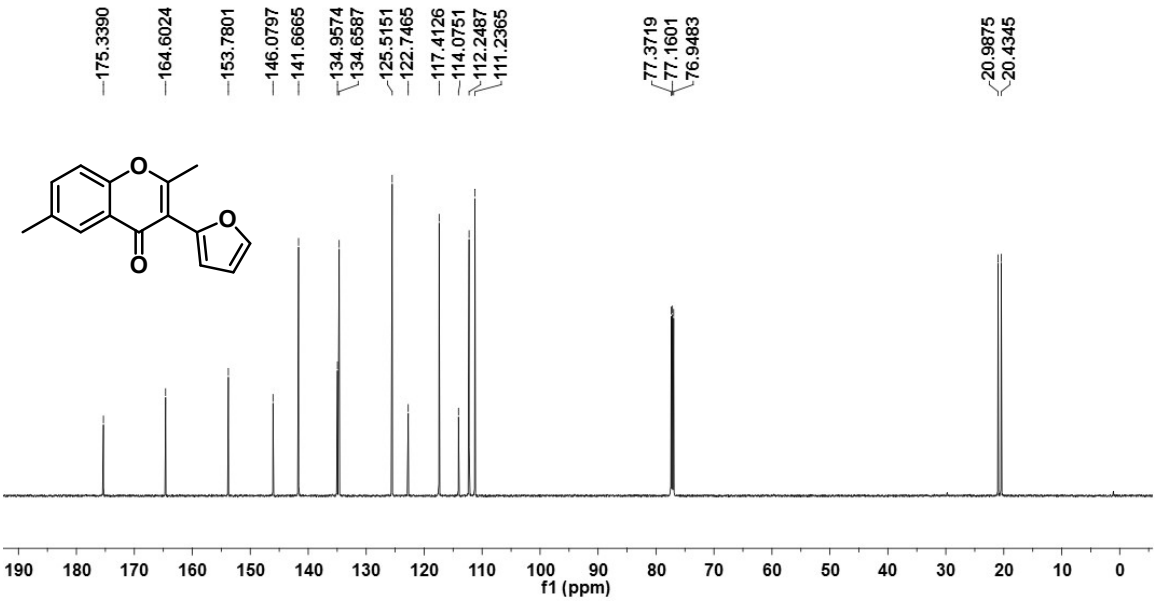

8.1120
8.0898
7.4810
7.2598
6.7725
6.5066
6.5038
3.8566
2.5389
MeO
O
O
O
1.01
1.00
1.00
1.03
1.01
1.02
3.19
3.13
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

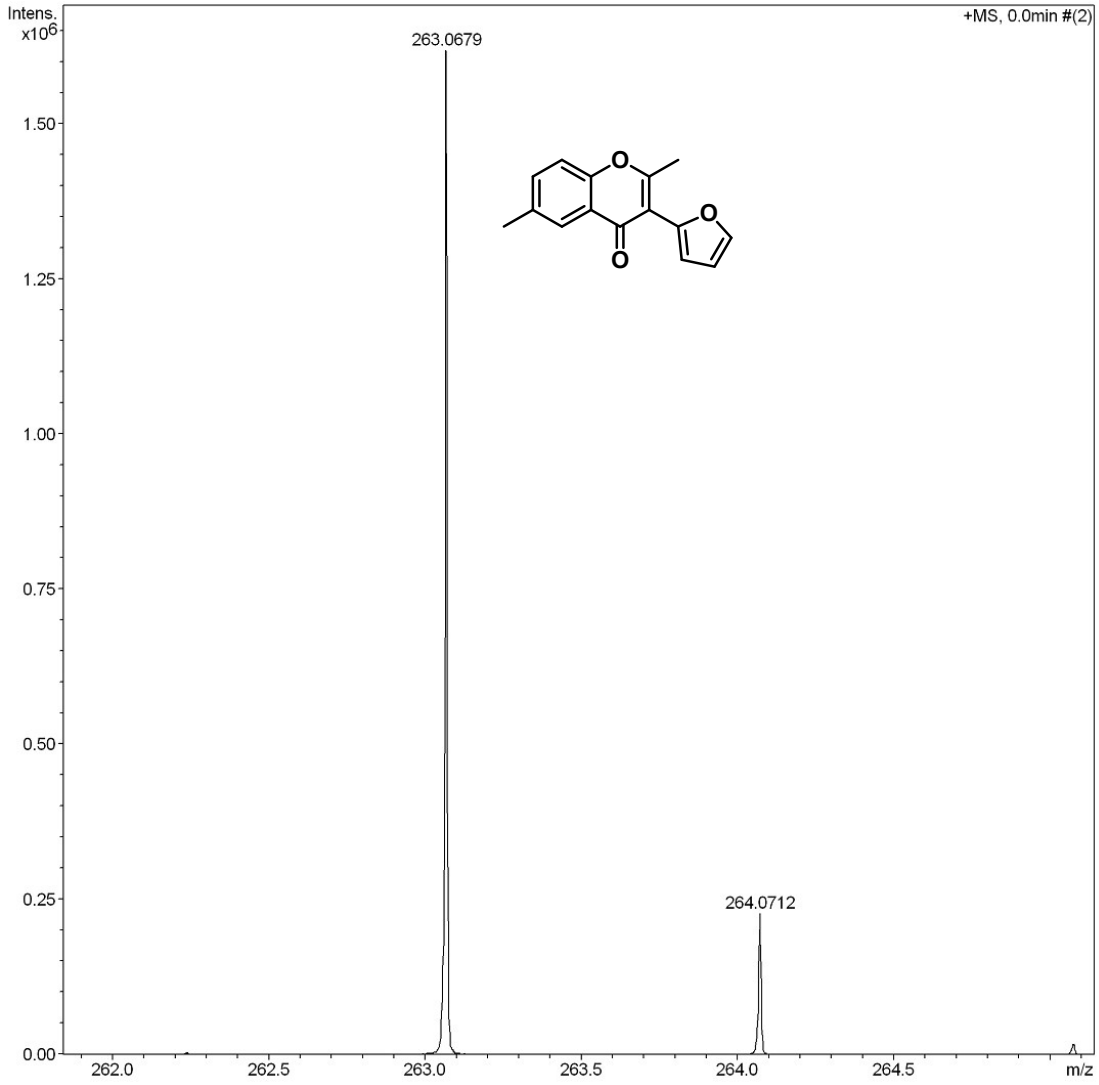

174.7837
164.1916
163.9378
157.1650
146.0122
141.6716
127.5753
116.9216
114.3952
114.0013
112.2697
111.2439
99.8590
77.4792
77.1603
76.8445
55.8280
20.3206
MeO
O
O
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Intens.
x10^6
+MS, 0.0min #(2)
279.0630
280.0661
MeO
O
O
O
2.5
2.0
1.5
1.0
0.5
0.0
278.25
278.50
278.75
279.00
279.25
279.50
279.75
280.00
280.25
280.50
m/z

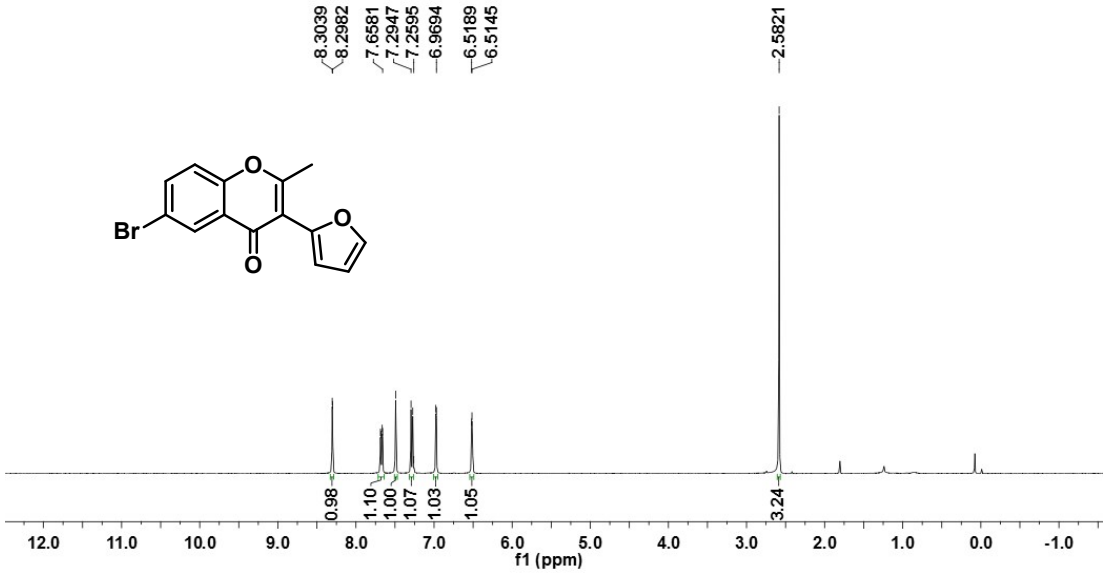
3d

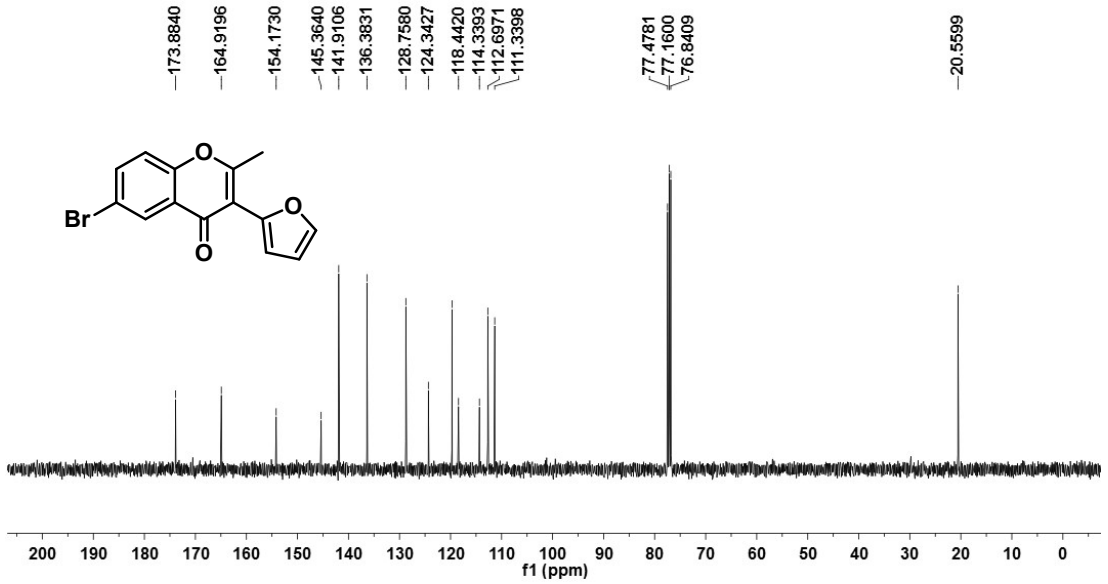

7.9790
7.4077
7.2811
7.2604
6.9462
6.5124
6.5094
6.5076
6.5047
2.5514
2.4119
O
O
O
1.00
1.02
1.10
0.95
0.96
1.00
3.04
3.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

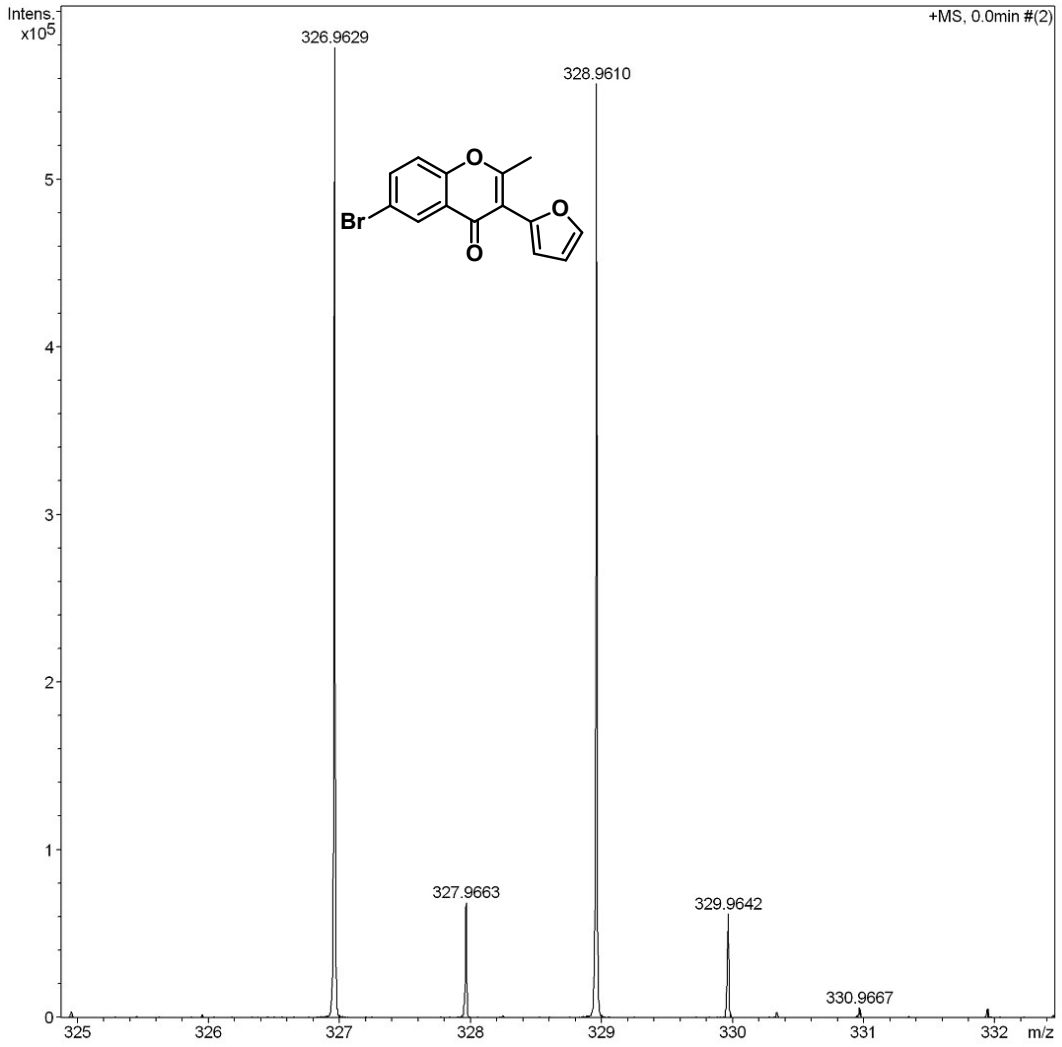

175.3390
164.6024
153.7801
146.0797
141.6665
134.9574
134.6587
125.5151
122.7465
117.4126
114.0751
112.2487
111.2365
77.3719
77.1601
76.9483
20.9875
20.4345
O
O
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Intens.
x10^6
+MS, 0.0min #(2)
263.0679
264.0712
1.50
1.25
1.00
0.75
0.50
0.25
0.00
262.0
262.5
263.0
263.5
264.0
264.5
m/z
O
O
O

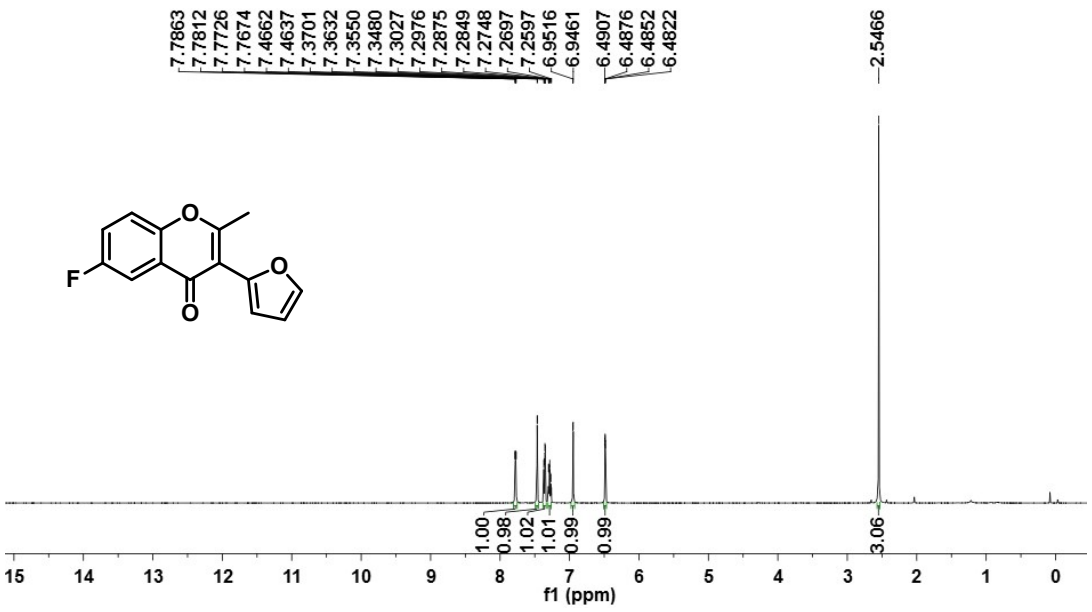
3e


8.3039
8.2982
7.6581
7.2947
7.2595
6.9694
6.5189
6.5145
2.5821
Br
O
O
O
0.98
1.10
1.00
1.07
1.03
1.05
3.24
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

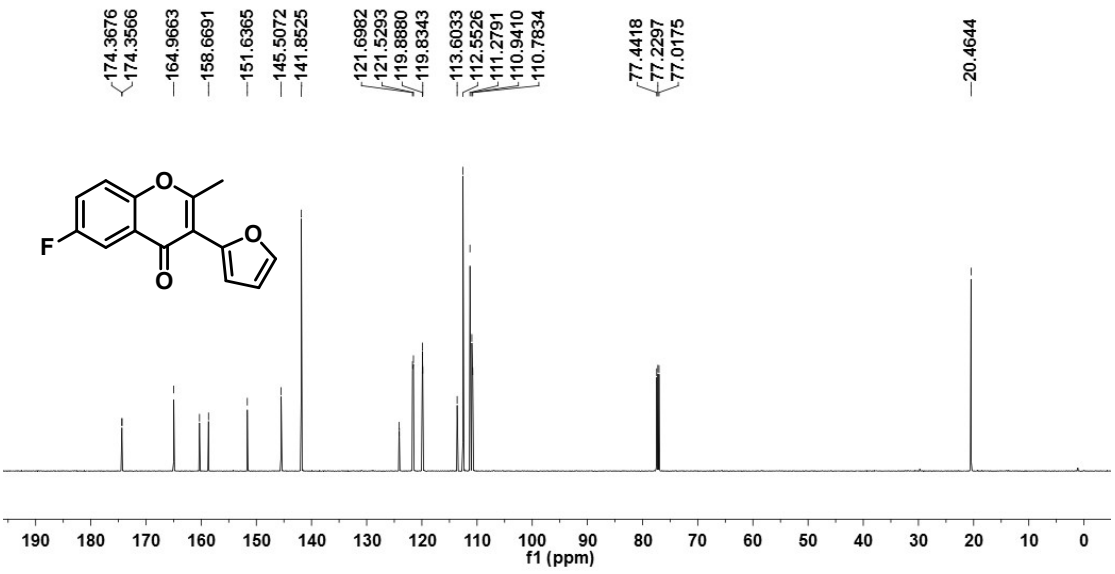

173.8840
164.9196
154.1730
145.3640
141.9106
136.3831
128.7580
124.3427
118.4420
114.3393
112.6971
111.3398
77.4781
77.1600
76.8409
20.5599
Br
O
O
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

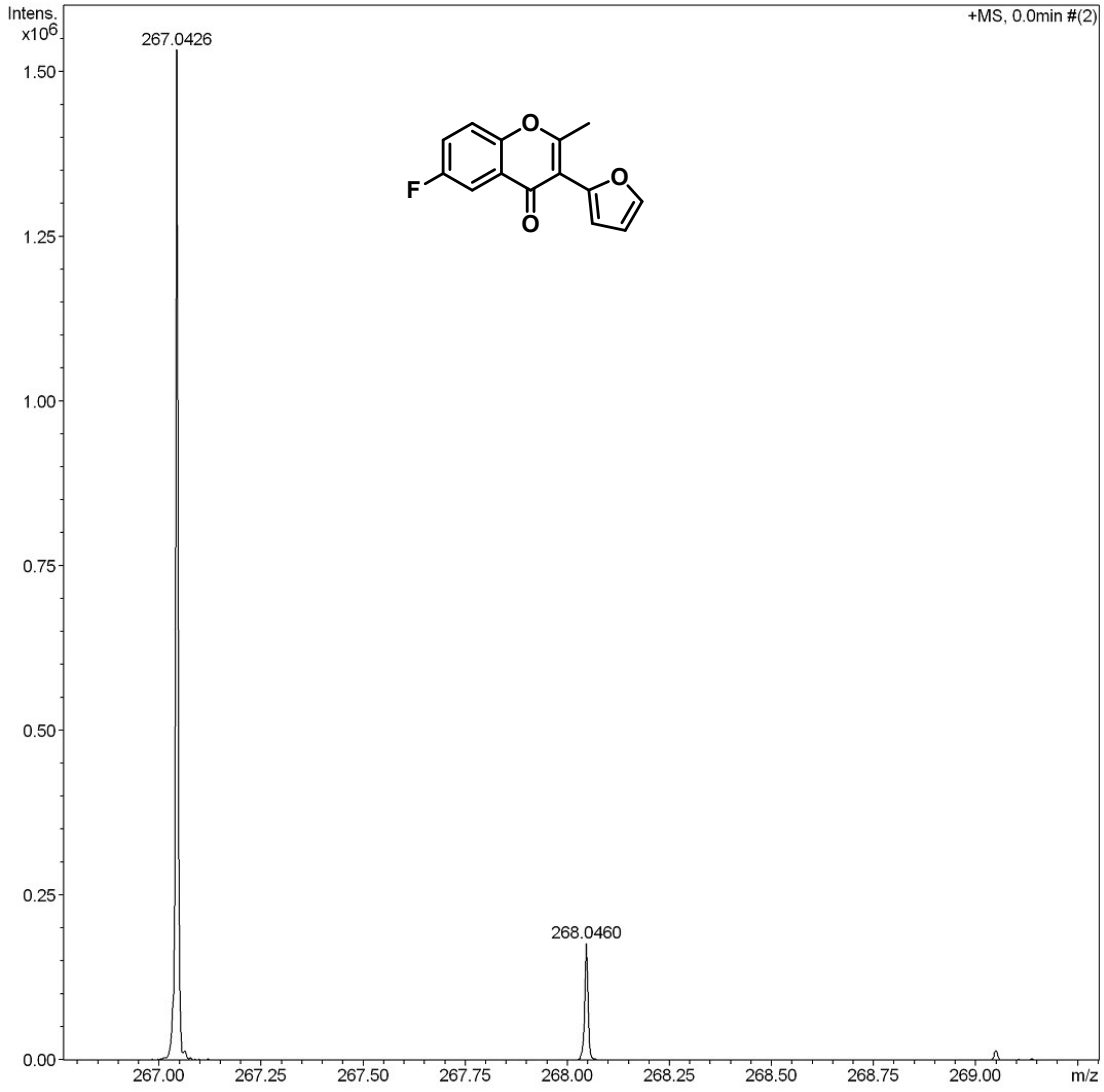

Intens.
x10^5
+MS, 0.0min #(2)
326.9629
328.9610
327.9663
329.9642
330.9667
Br
O
O
O
0
1
2
3
4
5
325
326
327
328
329
330
331
332
m/z

3f

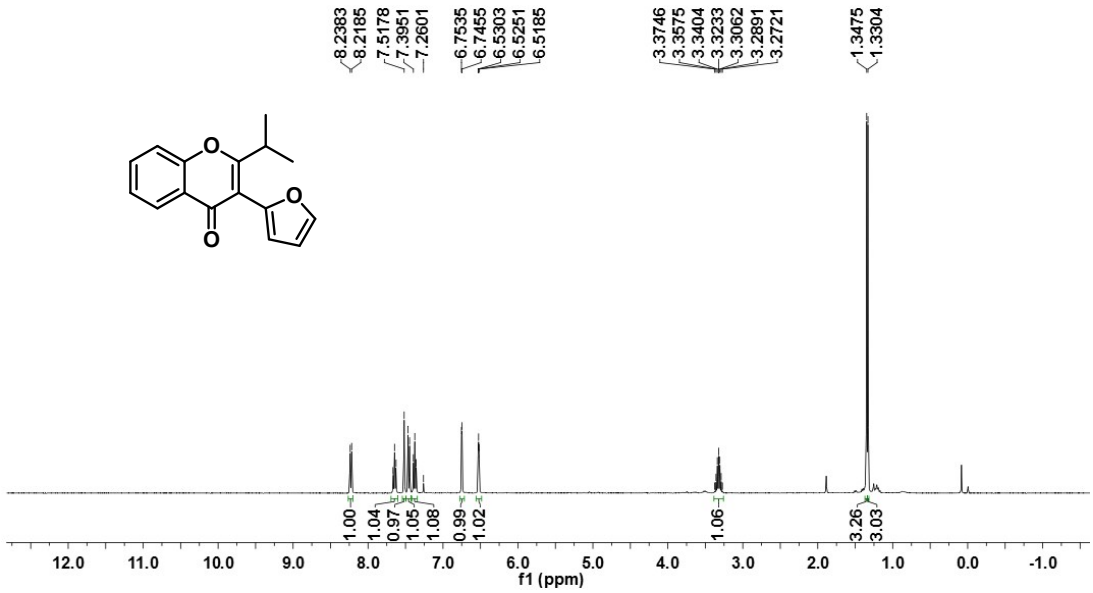

7.7863
7.7812
7.7726
7.7674
7.4662
7.4637
7.3701
7.3632
7.3550
7.3480
7.3027
7.2976
7.2875
7.2849
7.2748
7.2697
7.2597
6.9516
6.9461
6.4907
6.4876
6.4852
6.4822
2.5466
F
O
O
O
1.00
0.98
1.02
1.01
0.99
0.99
3.06
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

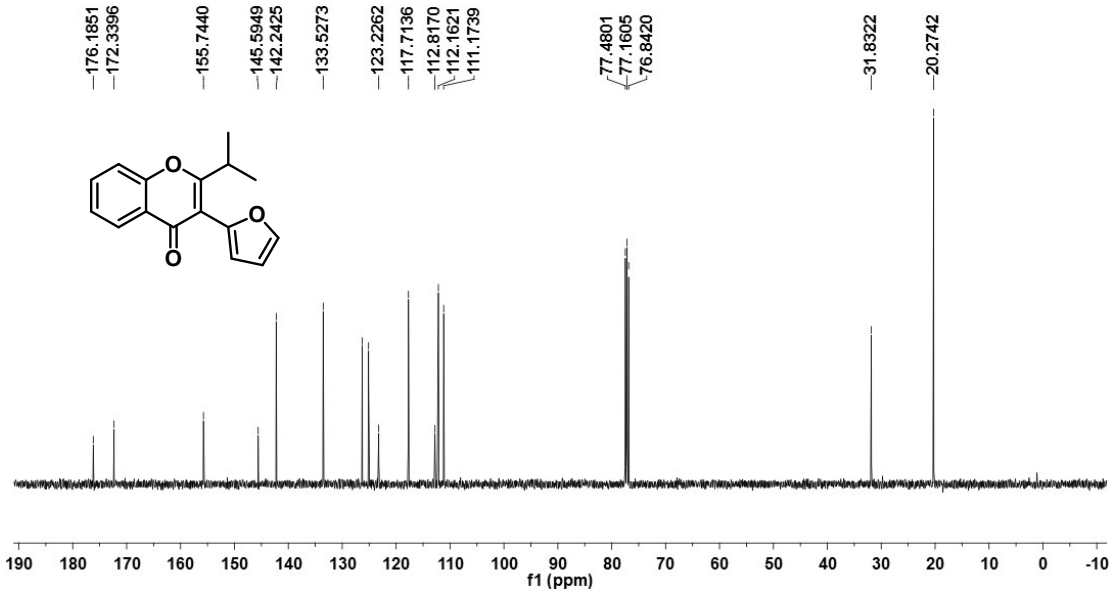
51

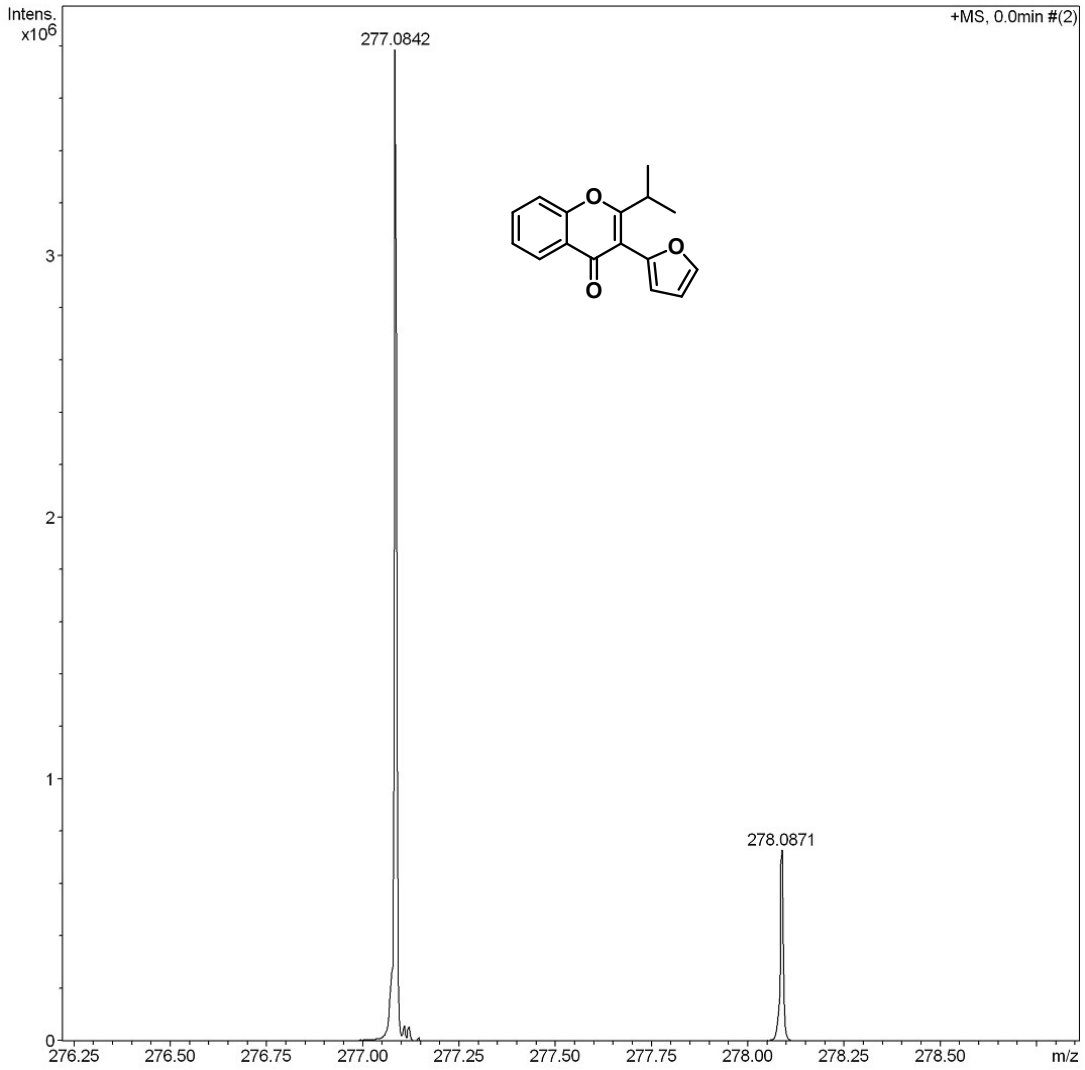

174.3676
174.3566
164.9663
158.6691
151.6365
145.5072
141.8525
121.6982
121.5293
119.8880
119.8343
113.6033
112.5526
111.2791
110.9410
110.7834
77.4418
77.2297
77.0175
20.4644
F
O
O
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Intens.
x10^6
+MS, 0.0min #(2)
267.0426
268.0460
1.50
1.25
1.00
0.75
0.50
0.25
0.00
267.00 267.25 267.50 267.75 268.00 268.25 268.50 268.75 269.00
m/z
F
O
O
O

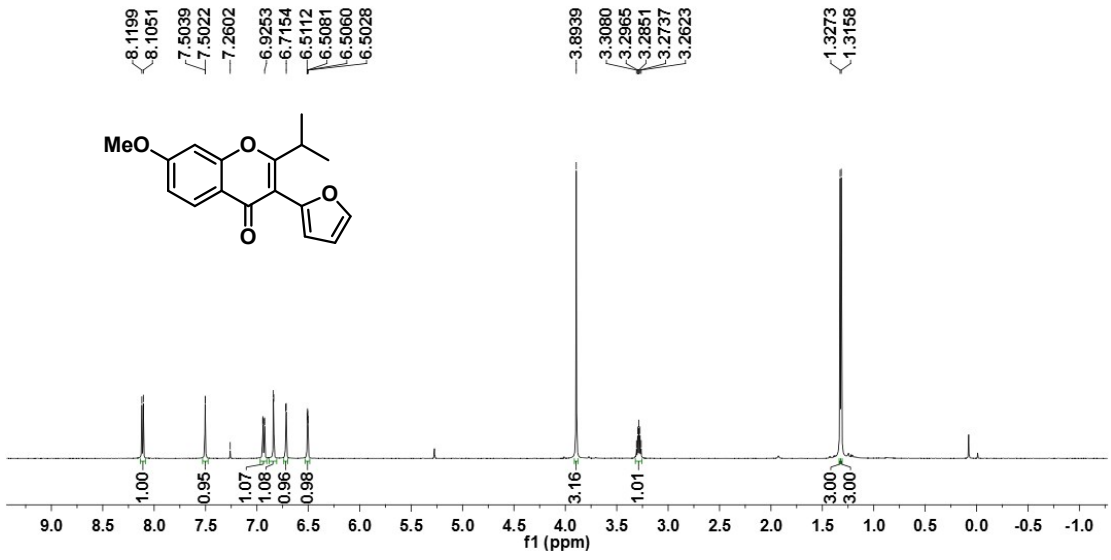
3g

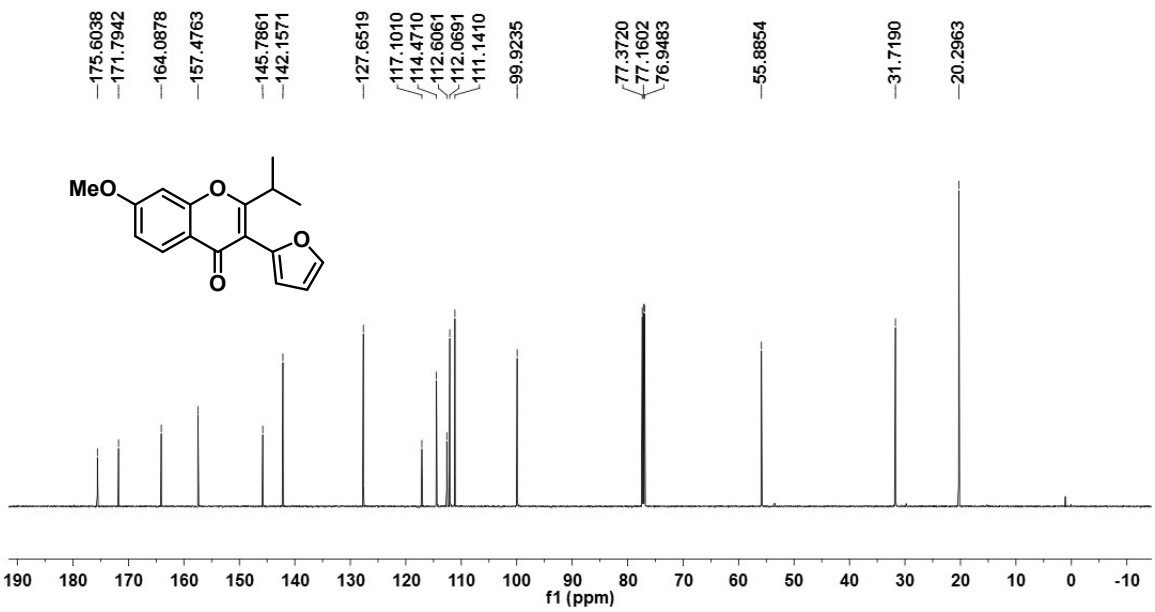

8.2383
8.2185
7.5178
7.3951
7.2601
6.7535
6.7455
6.5303
6.5251
6.5185
3.3746
3.3575
3.3404
3.3233
3.3062
3.2891
3.2721
1.3475
1.3304
1.00
1.04
0.97
1.05
1.08
0.99
1.02
1.06
3.26
3.03
f1 (ppm)

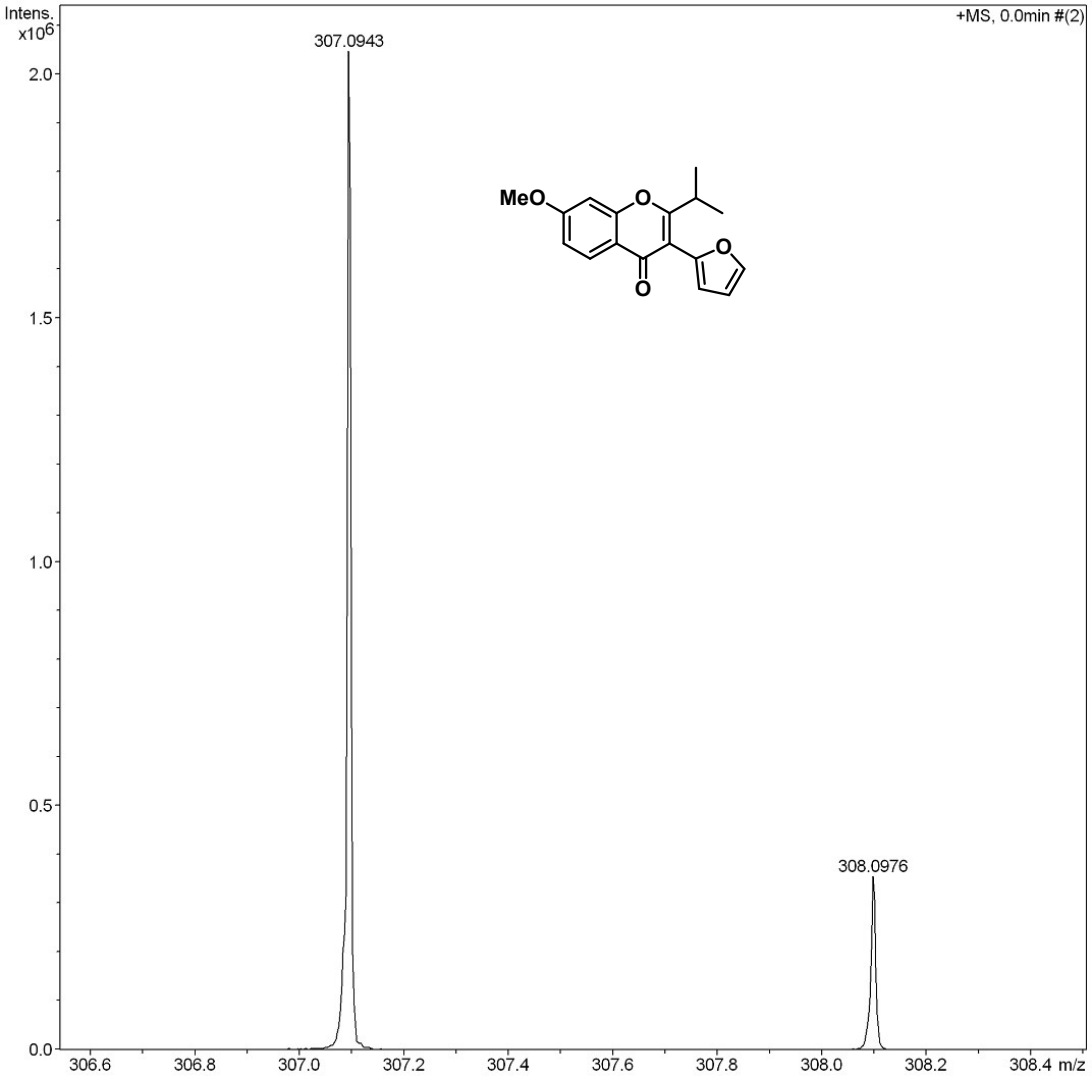

176.1851
172.3396
155.7440
145.5949
142.2425
133.5273
123.2262
117.7136
112.8170
112.1621
111.1739
77.4801
77.1605
76.8420
31.8322
20.2742
f1 (ppm)


Intens.
x10^6
+MS, 0.0min #(2)
277.0842
278.0871
O
O
O
0
1
2
3
276.25
276.50
276.75
277.00
277.25
277.50
277.75
278.00
278.25
278.50
m/z

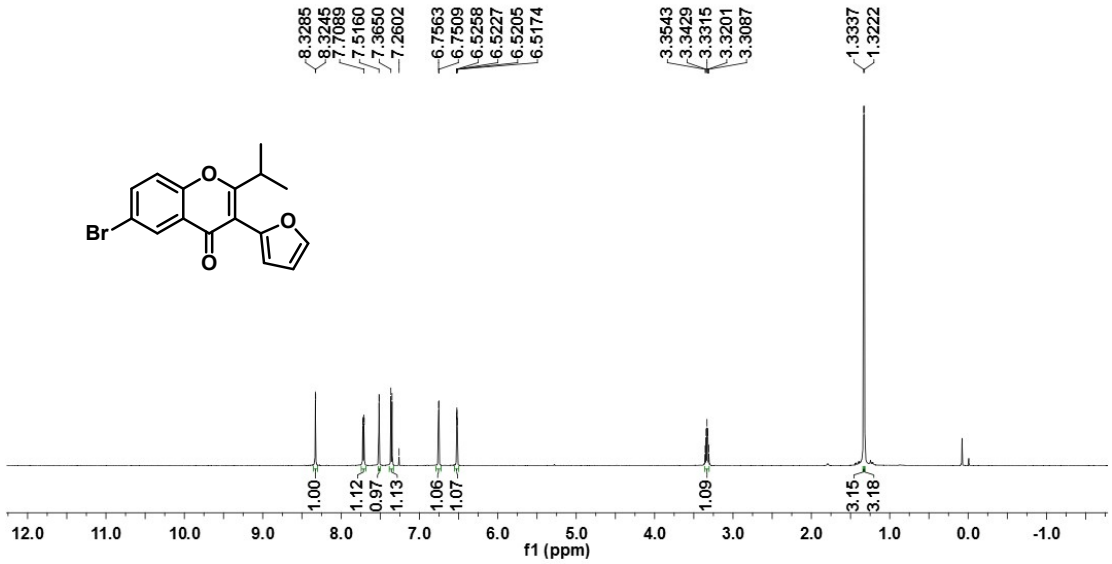
3h

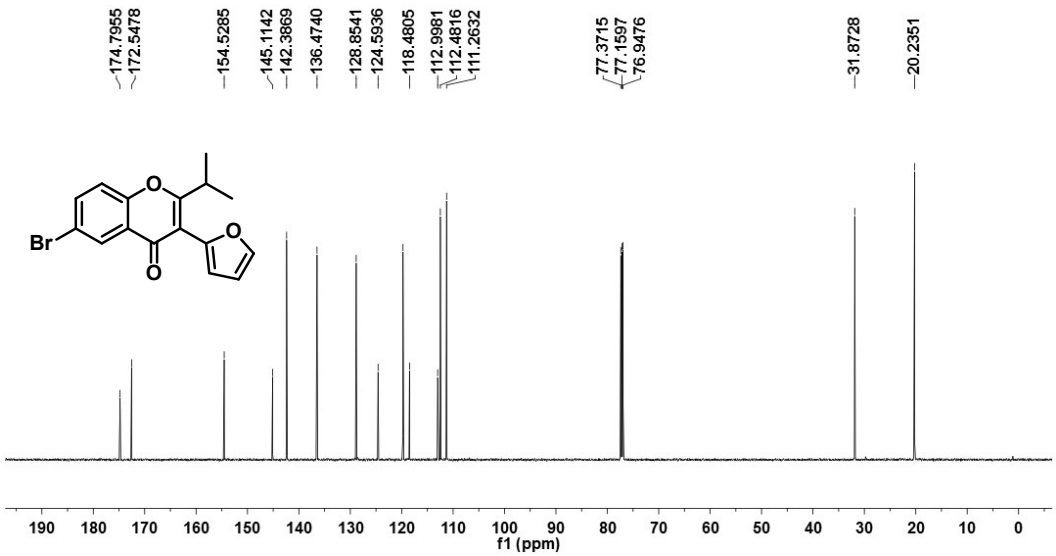

8.1199
8.1051
7.5039
7.5022
7.2602
6.9253
6.7154
6.5112
6.5081
6.5060
6.5028
3.8939
3.3080
3.2965
3.2851
3.2737
3.2623
1.3273
1.3158
MeO
O
O
O
1.00
0.95
1.07
1.08
0.96
0.98
3.16
1.01
3.00
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

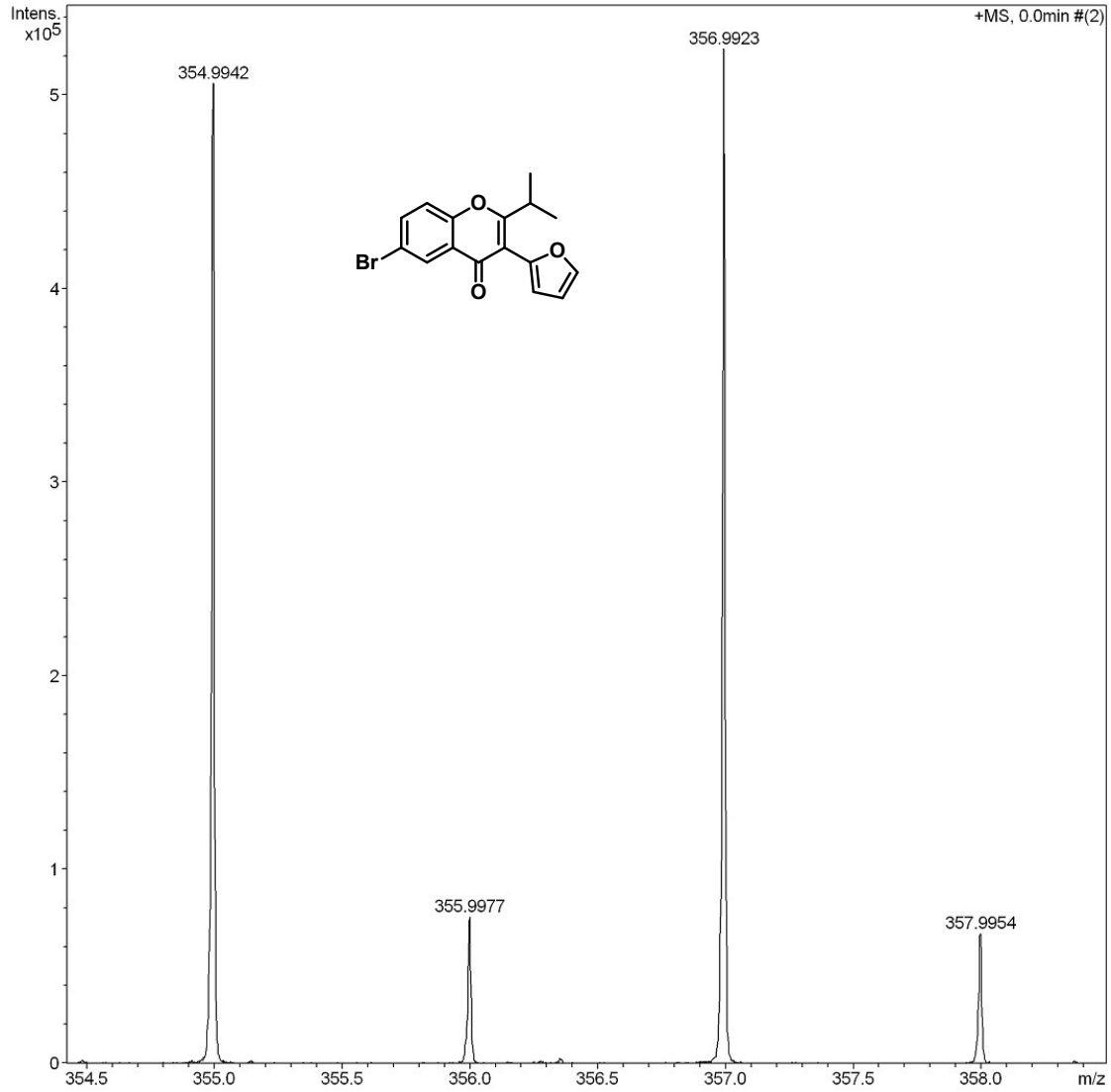

175.6038
171.7942
164.0878
157.4763
145.7861
142.1571
127.6519
117.1010
114.4710
112.6061
112.0691
111.1410
99.9235
77.3720
77.1602
76.9483
55.8854
31.7190
20.2963
MeO
O
O
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Intens.
x10^6
+MS, 0.0min #(2)
307.0943
308.0976
MeO
O
O
O
2.0
1.5
1.0
0.5
0.0
306.6 306.8 307.0 307.2 307.4 307.6 307.8 308.0 308.2 308.4 m/z

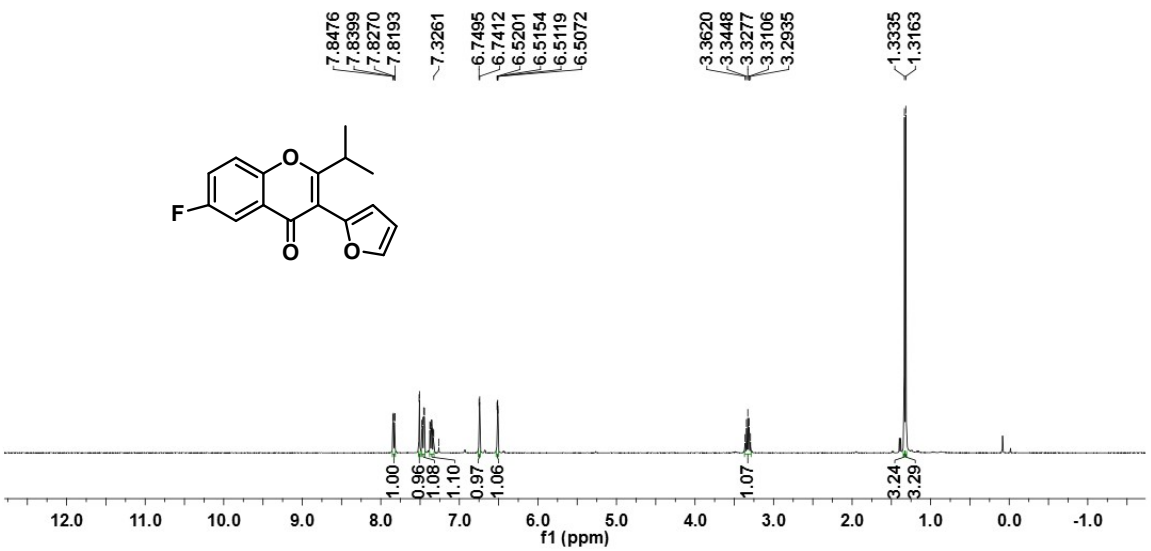
3i

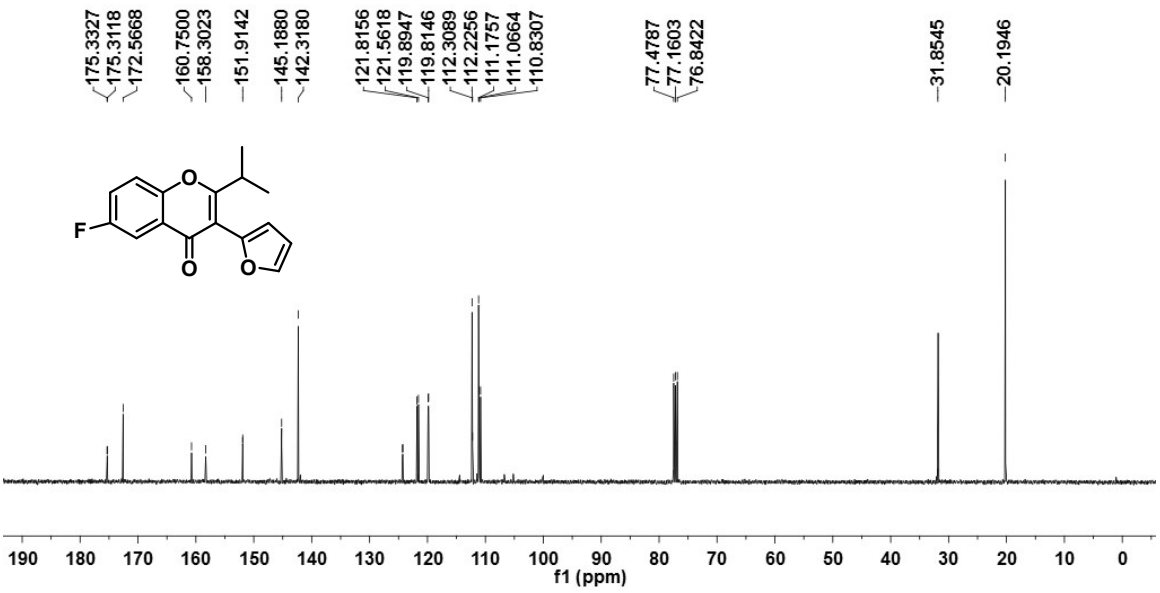

8.3285
8.3245
7.7089
7.5160
7.3650
7.2602
6.7563
6.7509
6.5258
6.5227
6.5205
6.5174
3.3543
3.3429
3.3315
3.3201
3.3087
1.3337
1.3222
Br
O
O
O
1.00
1.12
0.97
1.13
1.06
1.07
1.09
3.15
3.18
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

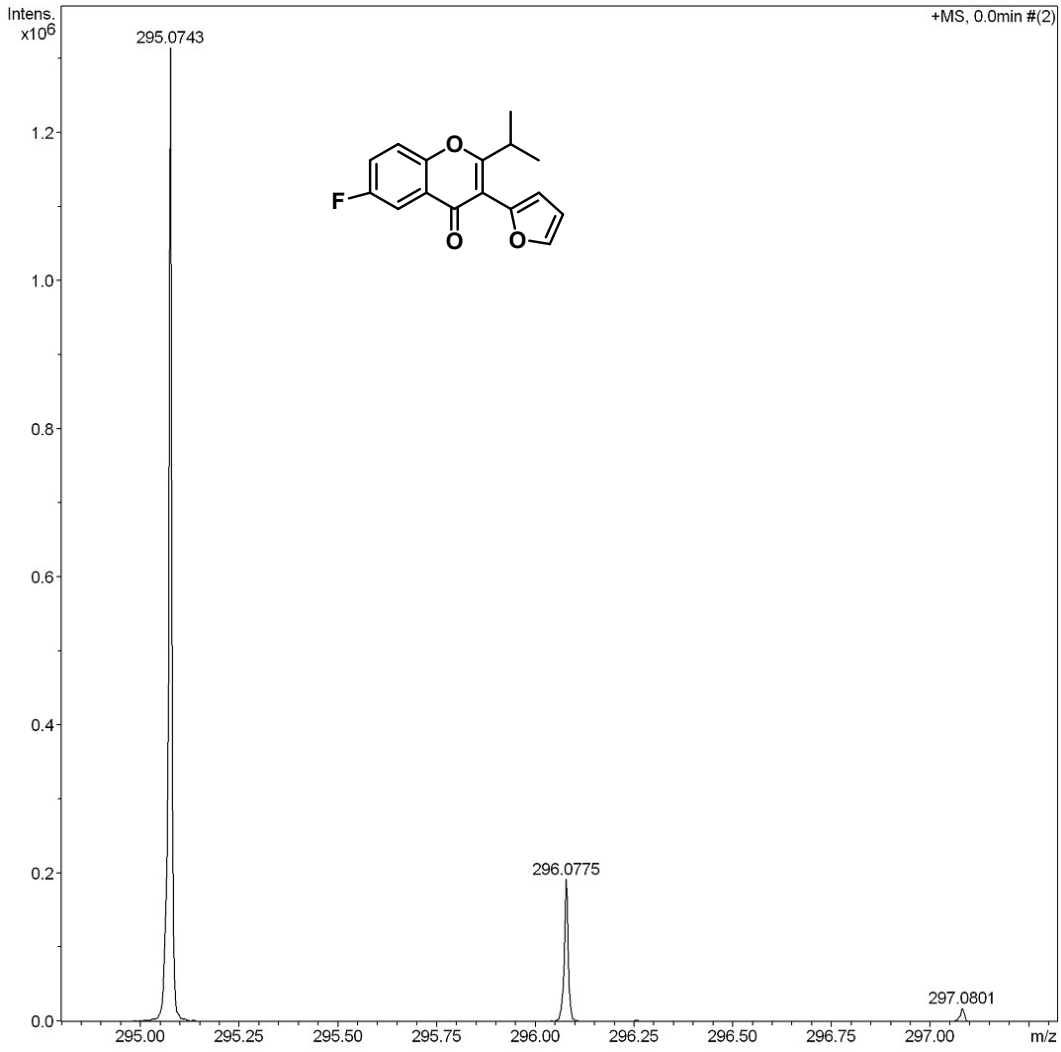

174.7955
172.5478
154.5285
145.1142
142.3869
136.4740
128.8541
124.5936
118.4805
112.9981
112.4816
111.2632
77.3715
77.1597
76.9476
31.8728
20.2351
Br
O
O
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Intens.
x10^5
+MS, 0.0min #(2)
354.9942
356.9923
355.9977
357.9954
Br
O
O
O
0
1
2
3
4
5
354.5
355.0
355.5
356.0
356.5
357.0
357.5
358.0
m/z

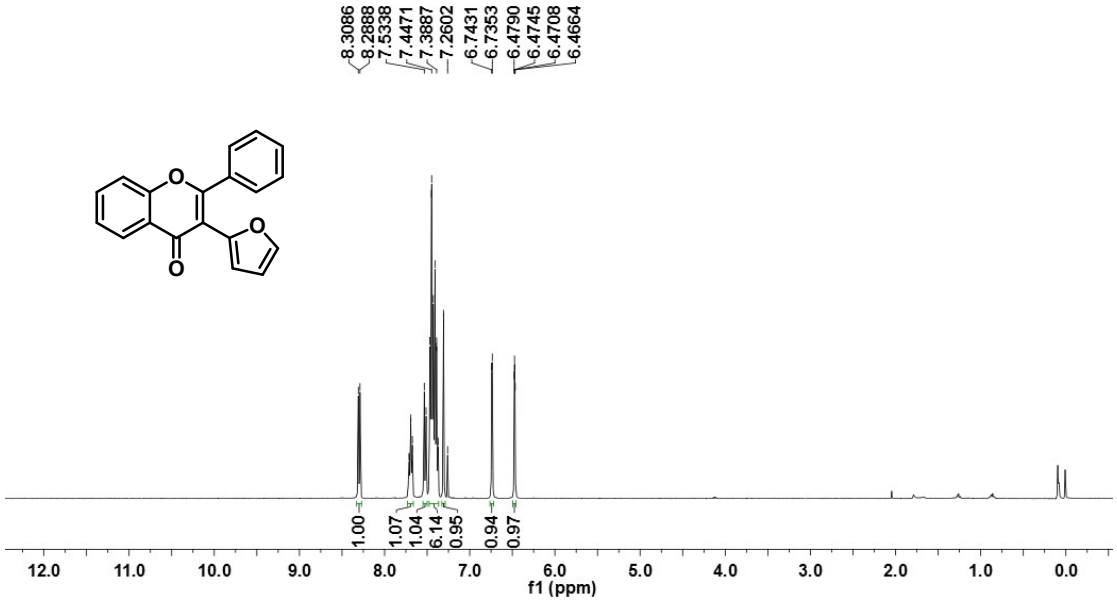
3j

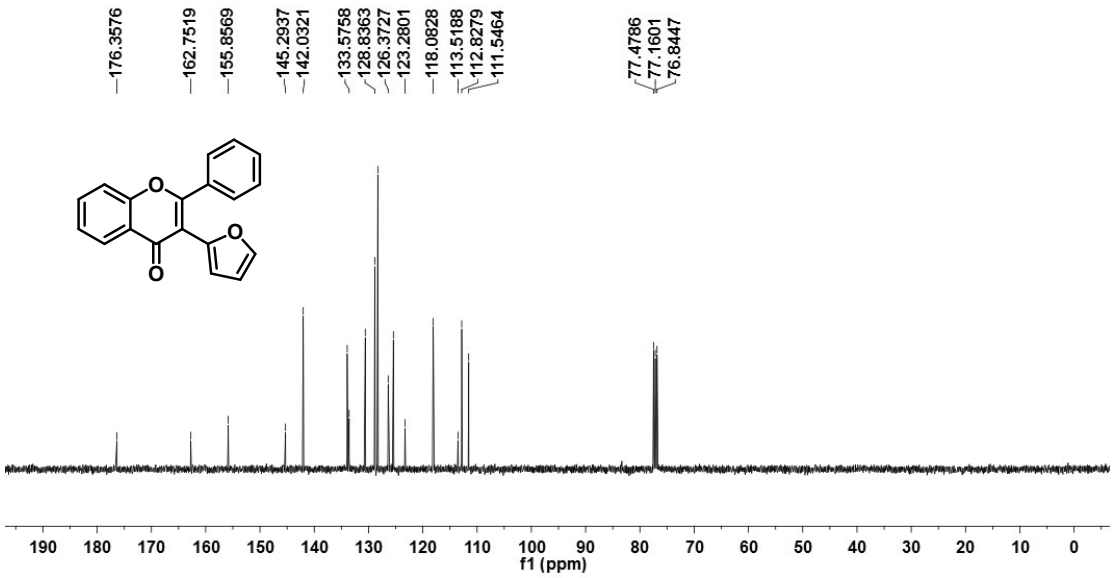

7.8476
7.8399
7.8270
7.8193
7.3261
6.7495
6.7412
6.5201
6.5154
6.5119
6.5072
3.3620
3.3448
3.3277
3.3106
3.2935
1.3335
1.3163
F
O
O
1.00
0.96
1.08
1.10
0.97
1.06
1.07
3.24
3.29
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

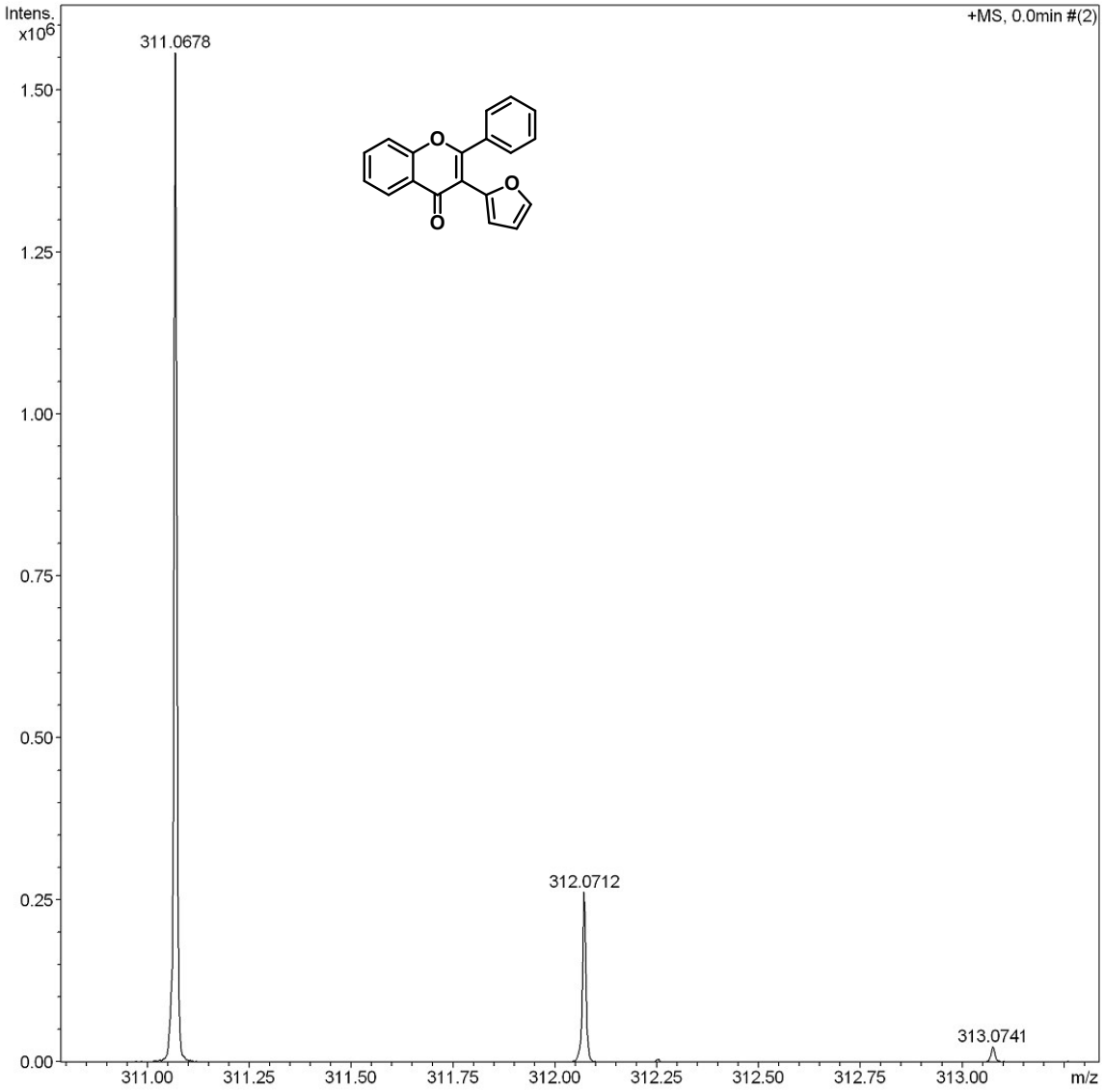

175.3327
175.3118
172.5668
160.7500
158.3023
151.9142
145.1880
142.3180
121.8156
121.5618
119.8947
119.8146
112.3089
112.2256
111.1757
111.0664
110.8307
77.4787
77.1603
76.8422
31.8545
20.1946
F
O
O
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Intens.
x10^6
+MS, 0.0min #(2)
295.0743
296.0775
297.0801
F
O
O
O
1.2
1.0
0.8
0.6
0.4
0.2
0.0
295.00 295.25 295.50 295.75 296.00 296.25 296.50 296.75 297.00
m/z

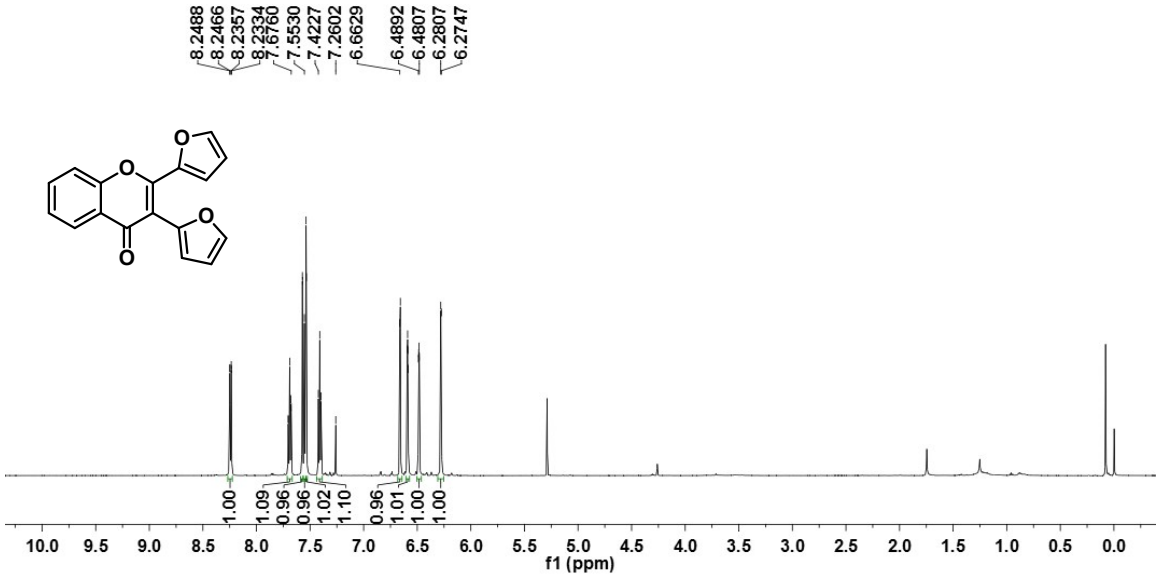
3k

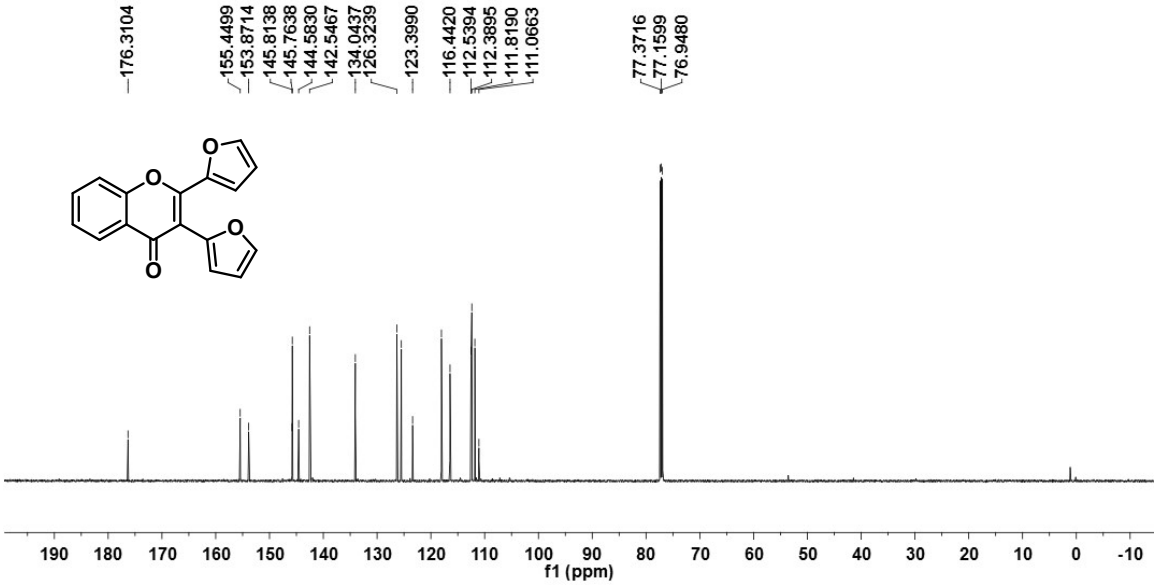

8.3086
8.2888
7.5338
7.4471
7.3887
7.2602
6.7431
6.7353
6.4790
6.4745
6.4708
6.4664
1.00
1.07
1.04
6.14
0.95
0.94
0.97
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

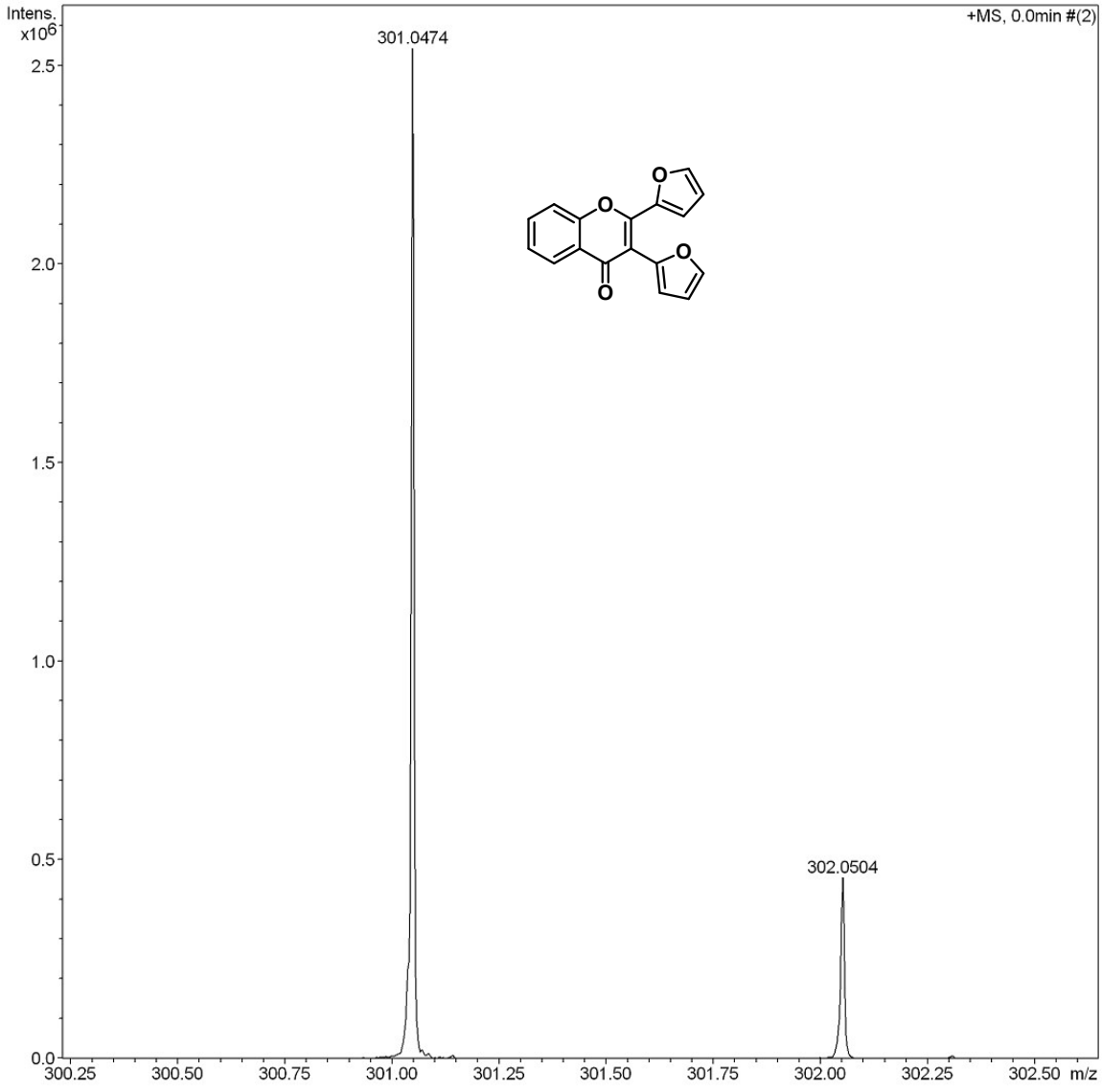

176.3576
162.7519
155.8569
145.2937
142.0321
133.5758
128.8363
126.3727
123.2801
118.0828
113.5188
112.8279
111.5464
77.4786
77.1601
76.8447
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Intens.
x10^6
+MS, 0.0min #(2)
311.0678
312.0712
313.0741
1.50
1.25
1.00
0.75
0.50
0.25
0.00
311.00
311.25
311.50
311.75
312.00
312.25
312.50
312.75
313.00
m/z

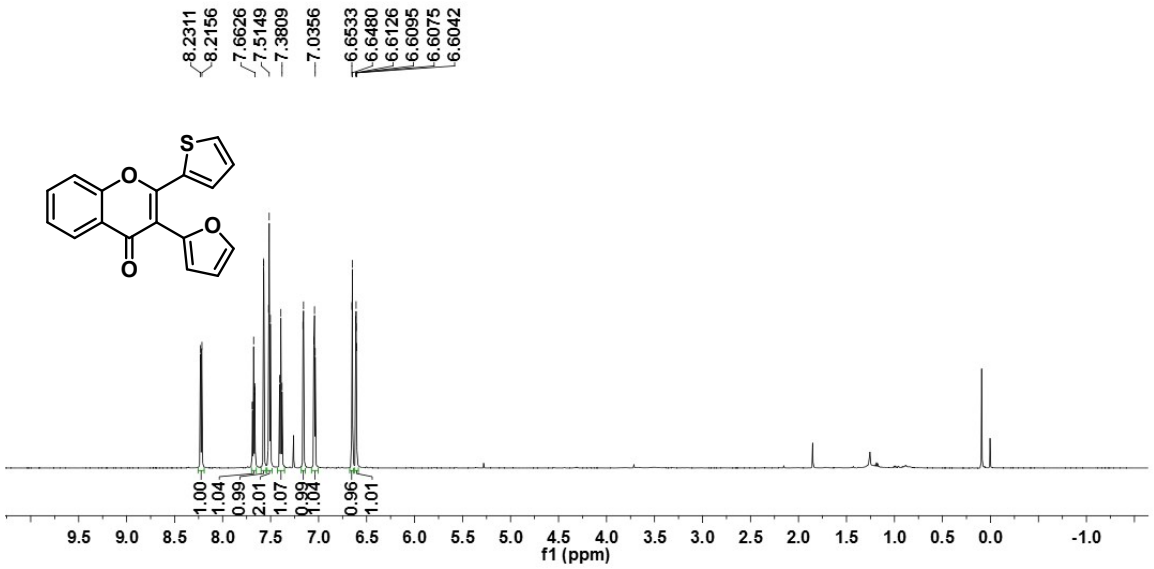
3l

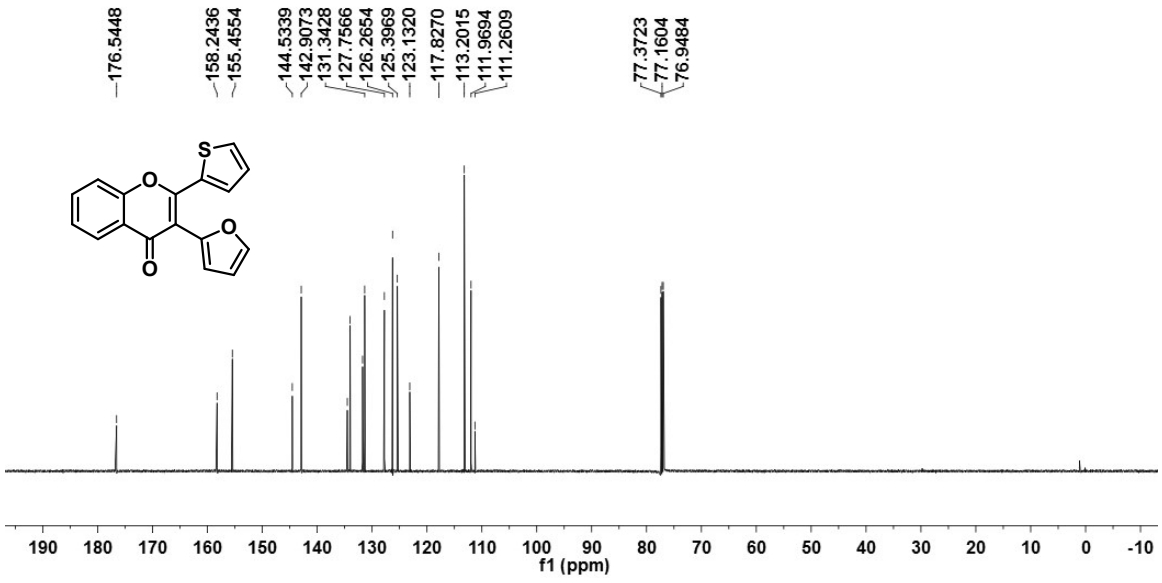

8.2488
8.2466
8.2357
8.2334
7.6760
7.5530
7.4227
7.2602
6.6629
6.4892
6.4807
6.2807
6.2747
1.00
1.09
0.96
0.96
1.02
1.10
0.96
1.01
1.00
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

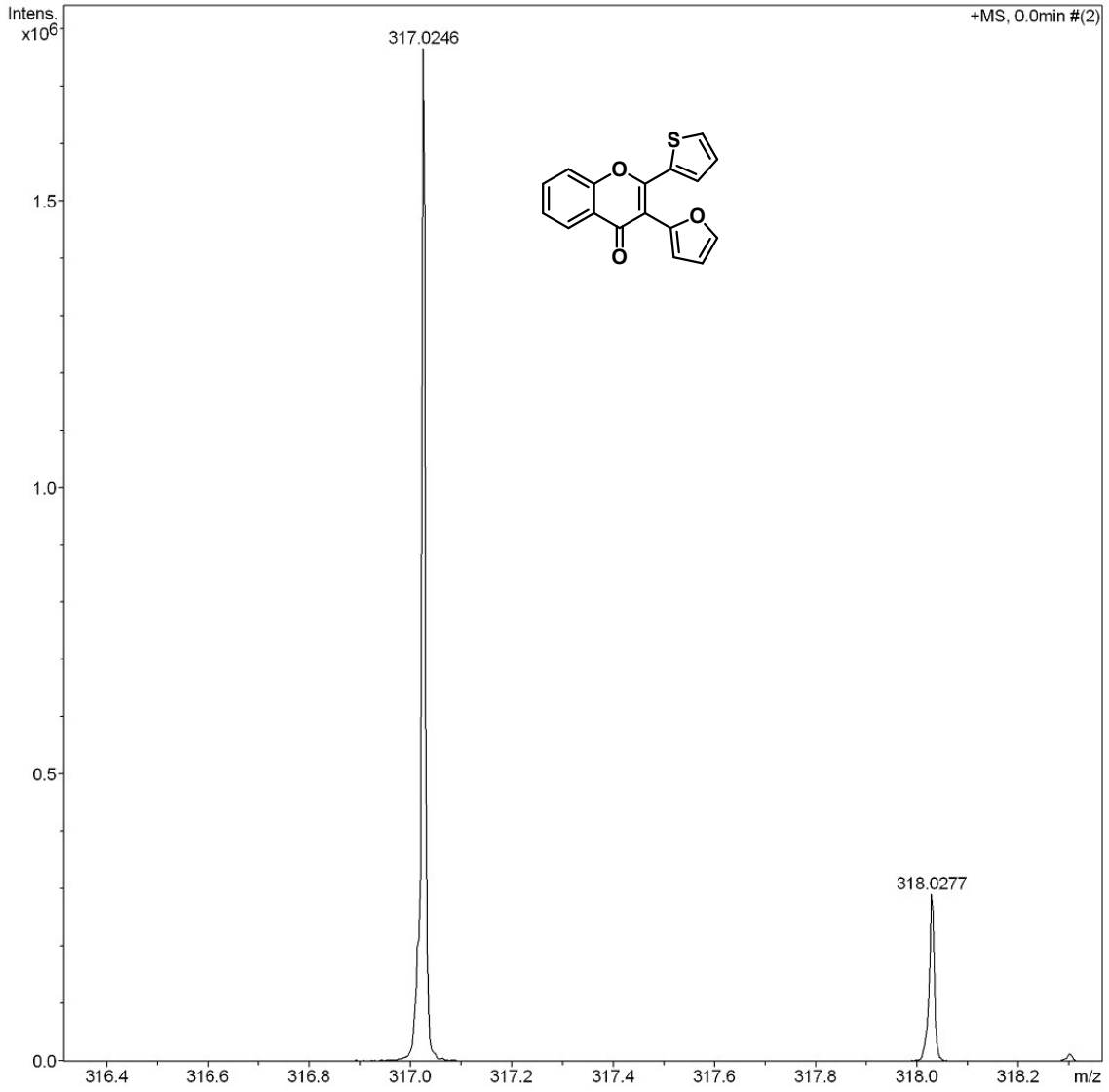

176.3104
155.4499
153.8714
145.8138
145.7638
144.5830
142.5467
134.0437
126.3239
123.3990
116.4420
112.5394
112.3895
111.8190
111.0663
77.3716
77.1599
76.9480
O
O
O
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Intens.
x10^6
+MS, 0.0min #(2)
301.0474
302.0504
O
O
O
O
2.5
2.0
1.5
1.0
0.5
0.0
300.25 300.50 300.75 301.00 301.25 301.50 301.75 302.00 302.25 302.50 m/z

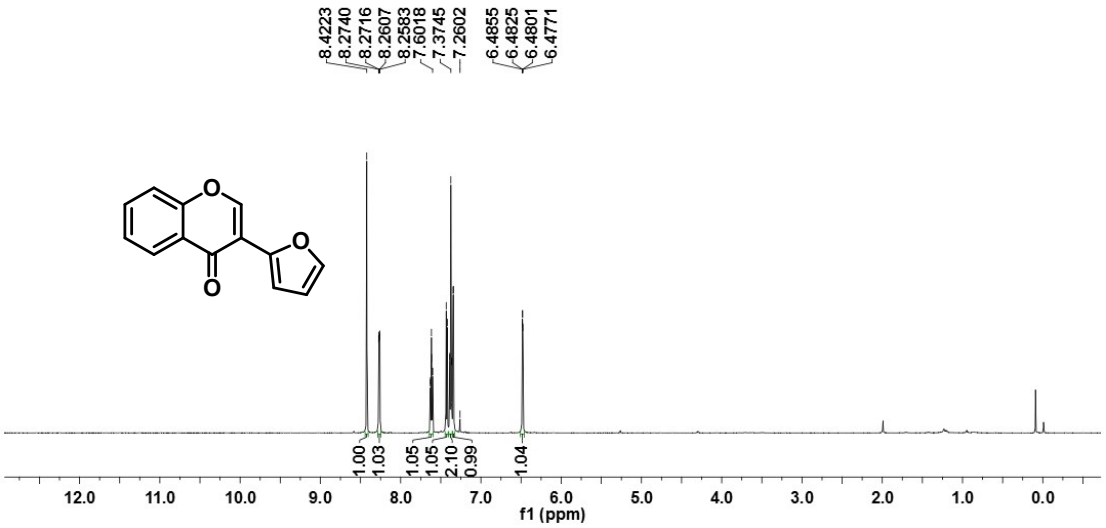
3m


8.2311
8.2156
7.6626
7.5149
7.3809
7.0356
6.6533
6.6480
6.6126
6.6095
6.6075
6.6042
S
O
O
O
1.00
1.04
0.99
2.01
1.07
0.99
1.04
0.96
1.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -1.0
f1 (ppm)

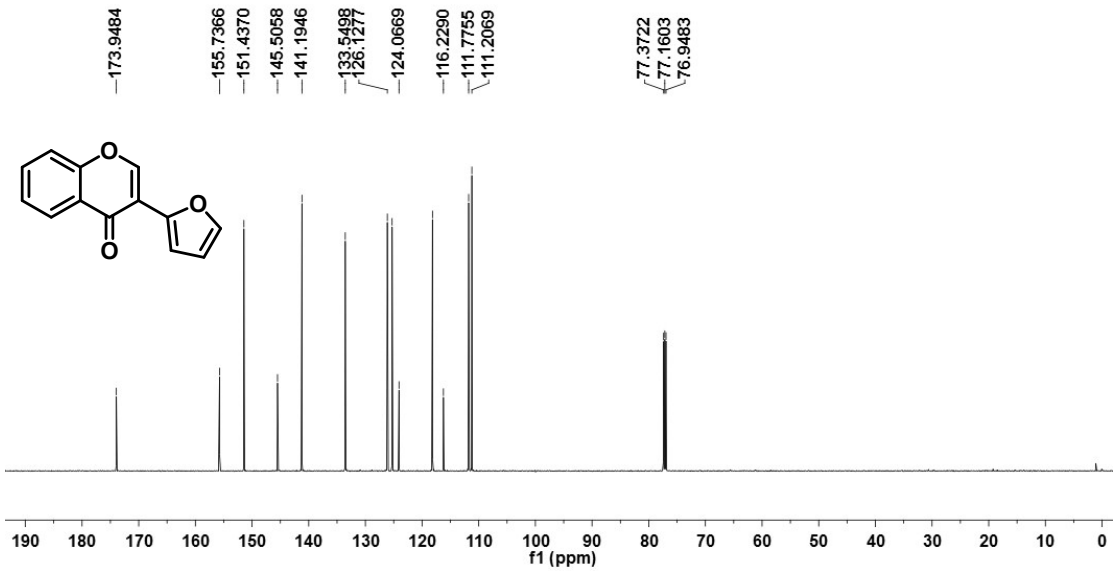

176.5448
158.2436
155.4554
144.5339
142.9073
131.3428
127.7566
126.2654
125.3969
123.1320
117.8270
113.2015
111.9694
111.2609
77.3723
77.1604
76.9484
S
O
O
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

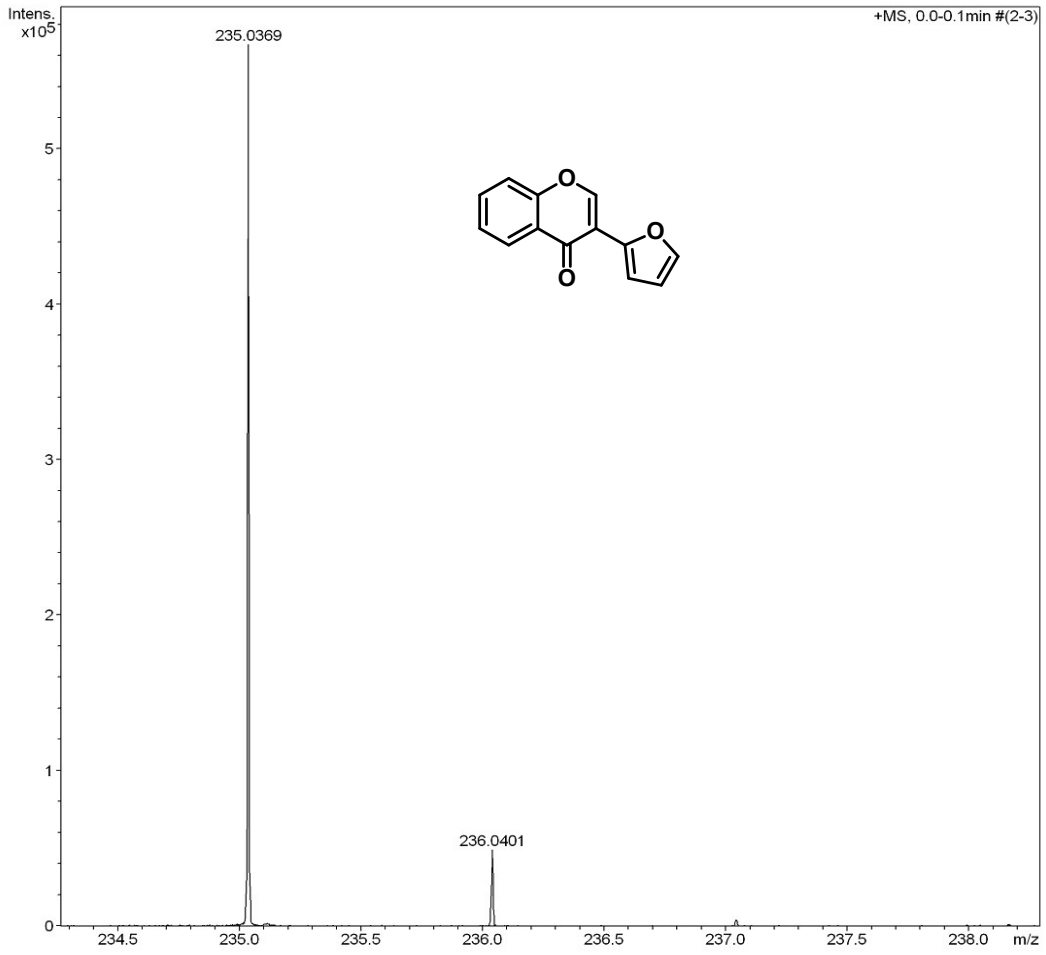

Intens.
x10^6
+MS, 0.0min #(2)
317.0246
318.0277
1.5
1.0
0.5
0.0
316.4
316.6
316.8
317.0
317.2
317.4
317.6
317.8
318.0
318.2
m/z
S
O
O
O

3n

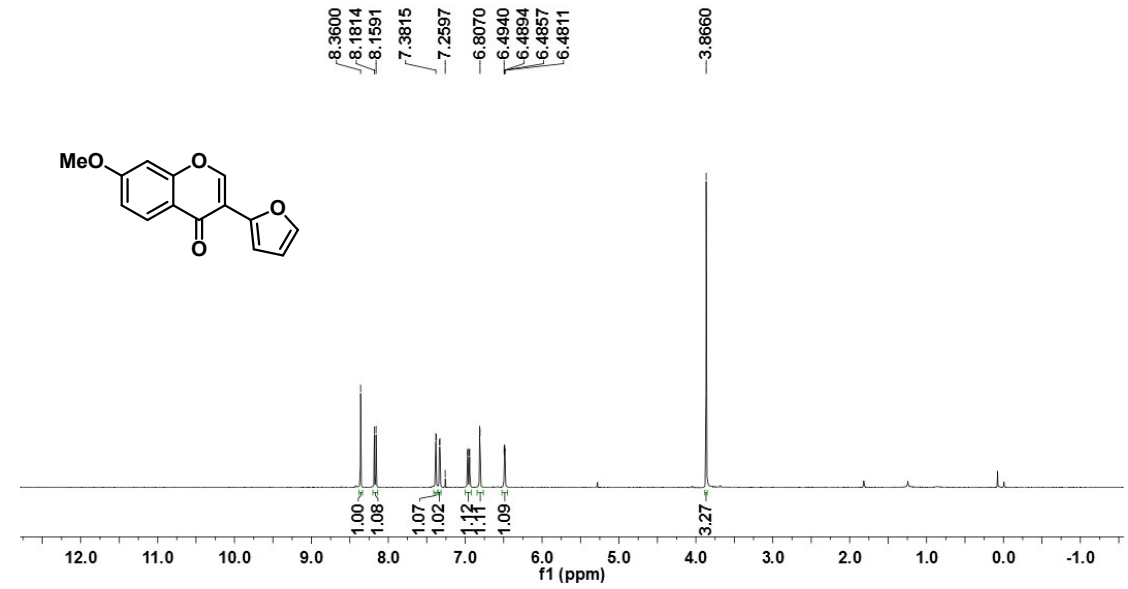

8.4223
8.2740
8.2716
8.2607
8.2583
7.6018
7.3745
7.2602
6.4855
6.4825
6.4801
6.4771
1.00
1.03
1.05
1.05
2.10
0.99
1.04
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)
O
O
O

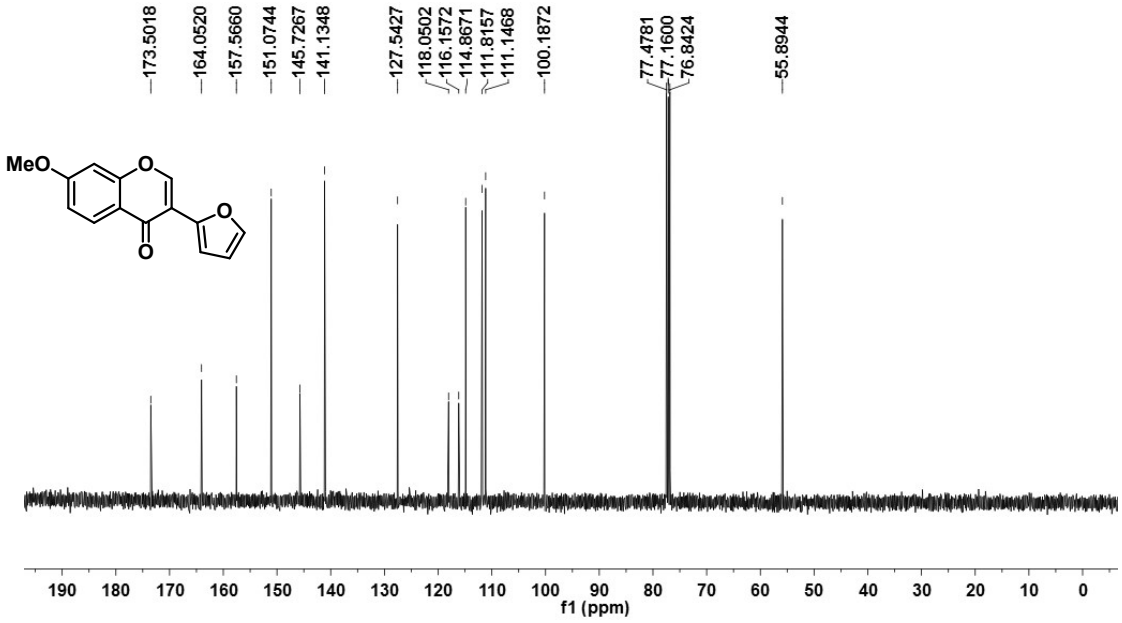
63

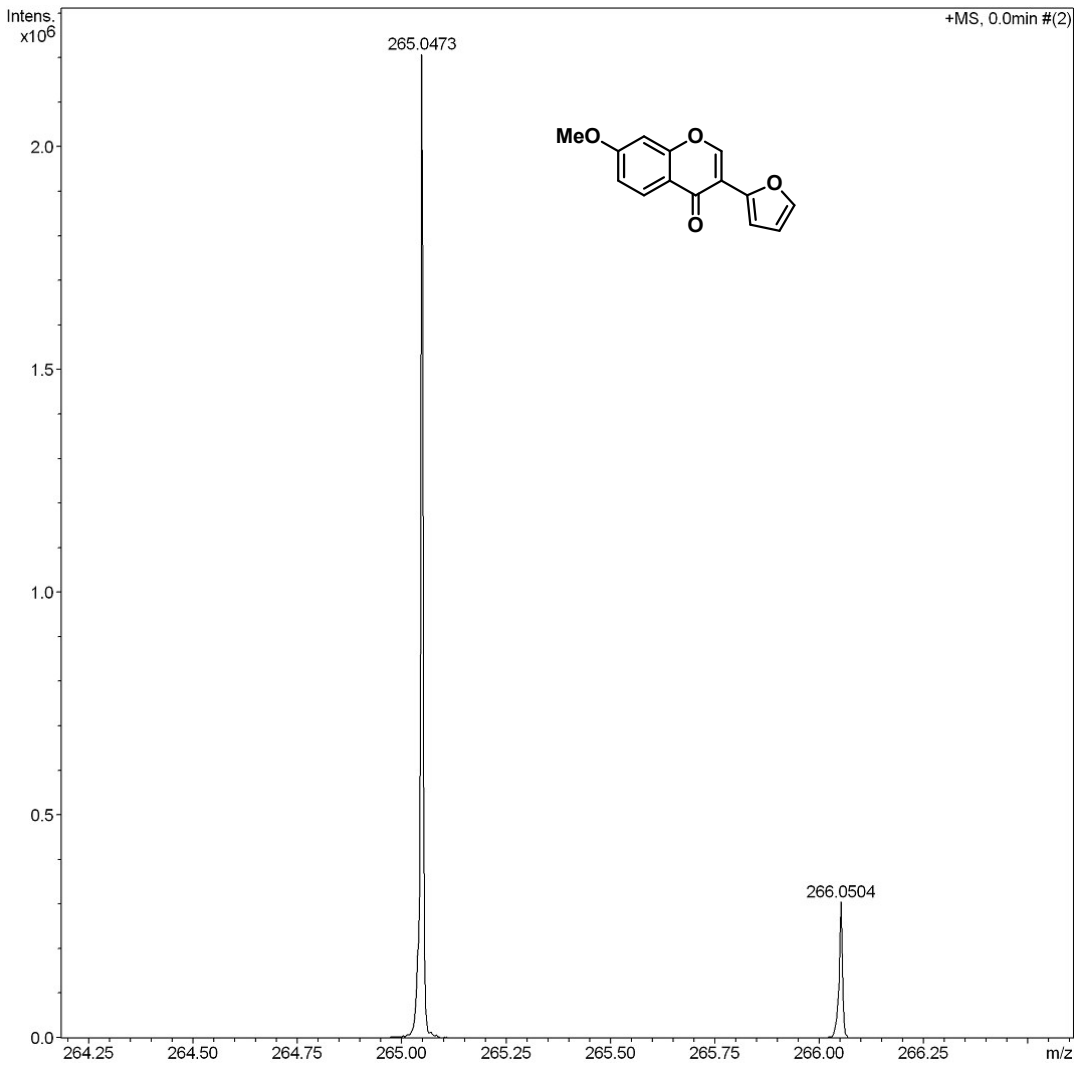

173.9484
155.7366
151.4370
145.5058
141.1946
133.5498
126.1277
124.0669
116.2290
111.7755
111.2069
77.3722
77.1603
76.9483
O
O
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Intens.
x10^5
+MS, 0.0-0.1min #(2-3)
235.0369
236.0401
O
O
O
5
4
3
2
1
0
234.5 235.0 235.5 236.0 236.5 237.0 237.5 238.0 m/z

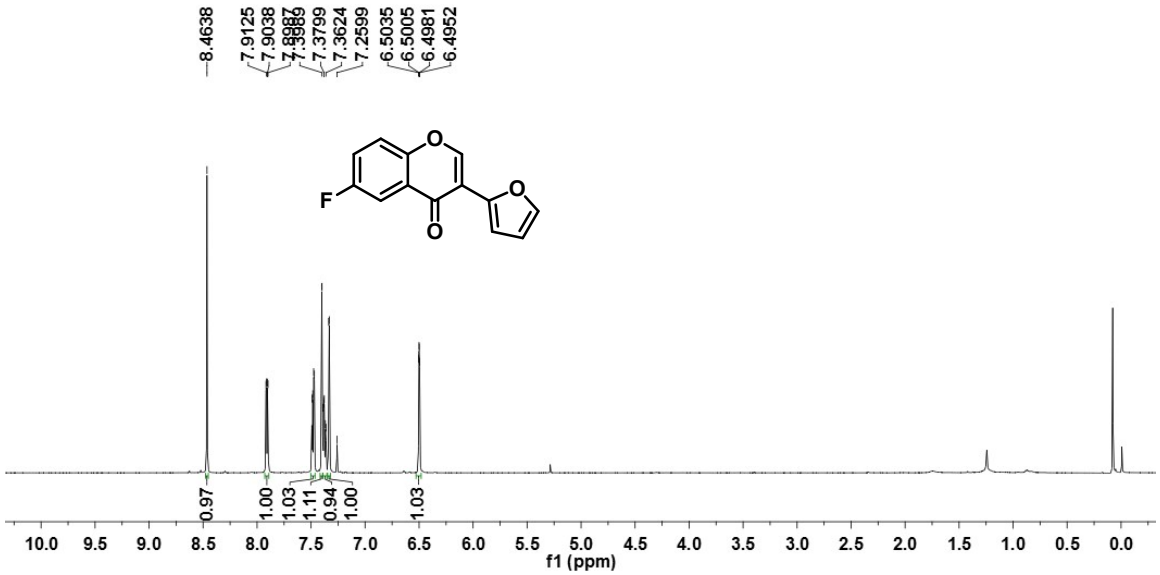
3o


8.3600
8.1814
8.1591
7.3815
7.2597
6.8070
6.4940
6.4894
6.4857
6.4811
3.8660
MeO
O
O
O
1.00
1.08
1.07
1.02
1.12
1.11
1.09
3.27
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

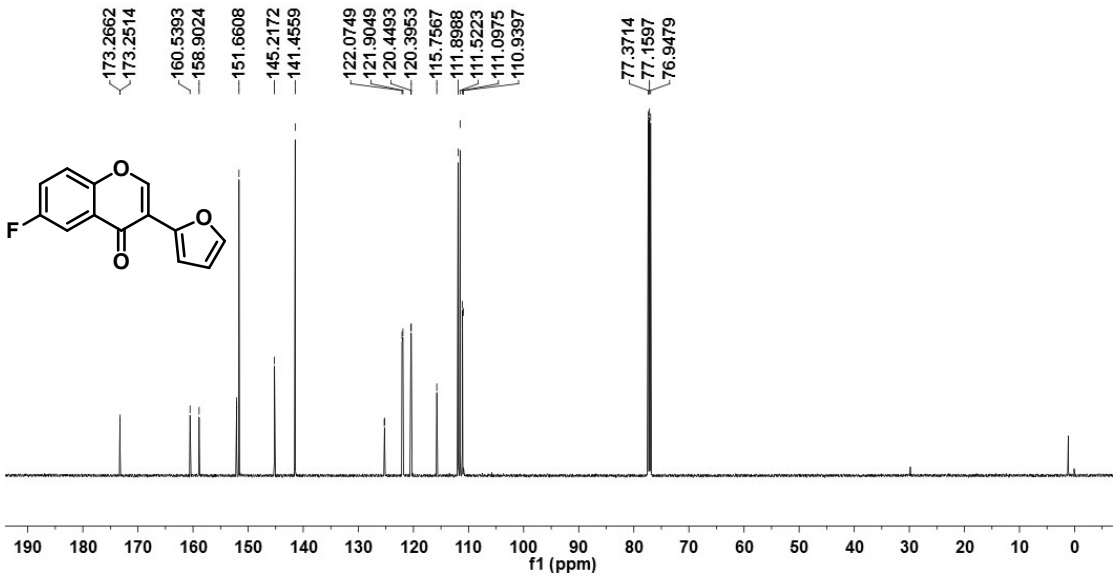

173.5018
164.0520
157.5660
151.0744
145.7267
141.1348
127.5427
118.0502
116.1572
114.8671
111.8157
111.1468
100.1872
77.4781
77.1600
76.8424
55.8944
MeO
O
O
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

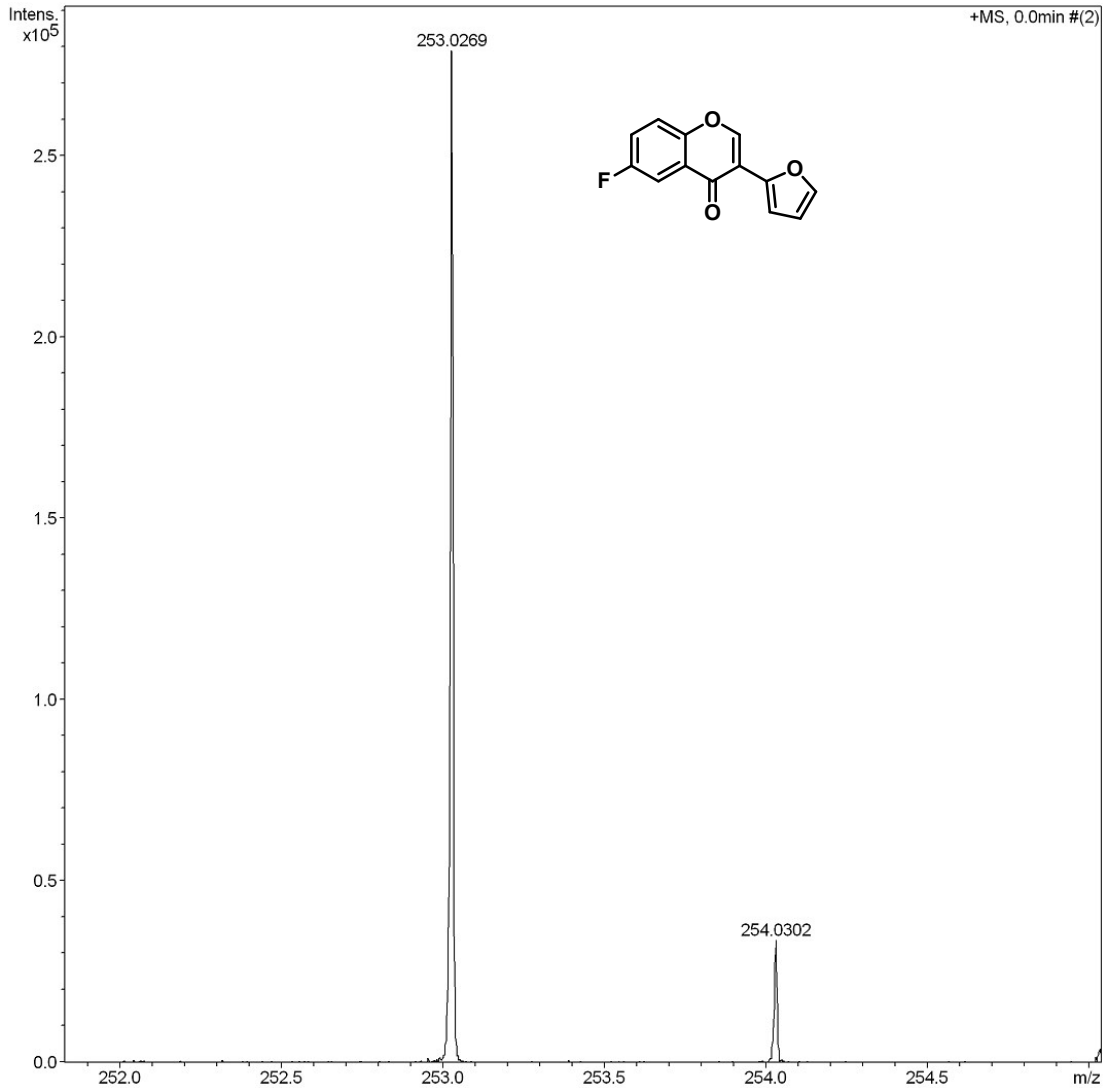

Intens.
x10^6
+MS, 0.0min #(2)
265.0473
266.0504
MeO
O
O
O
2.0
1.5
1.0
0.5
0.0
264.25
264.50
264.75
265.00
265.25
265.50
265.75
266.00
266.25
m/z

3p

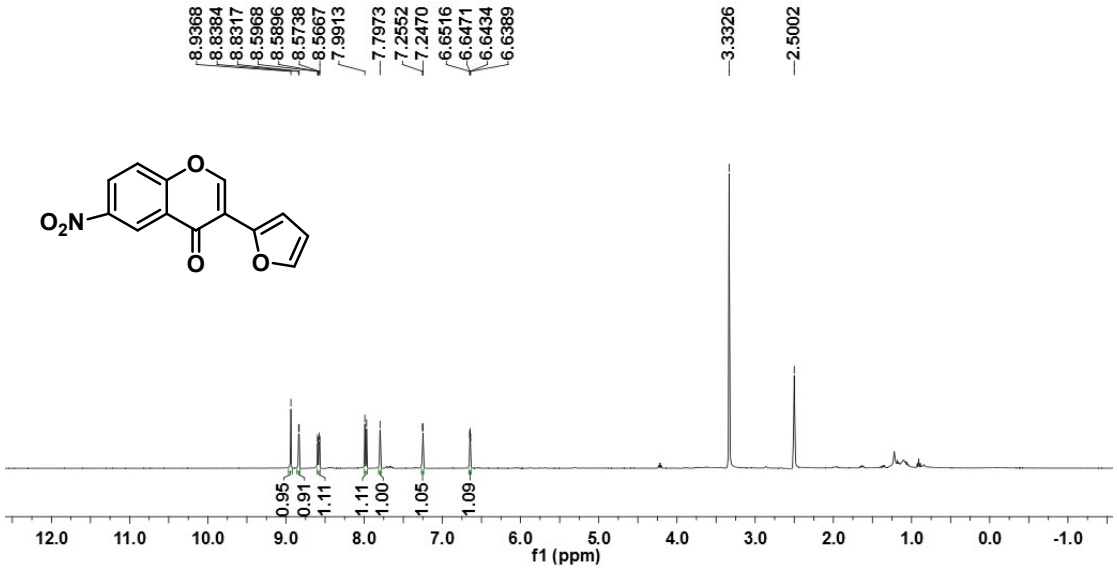

8.4638
7.9125
7.9038
7.3799
7.3624
7.2599
6.5035
6.5005
6.4981
6.4952
F
O
O
O
0.97
1.00
1.03
1.11
0.94
1.00
1.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

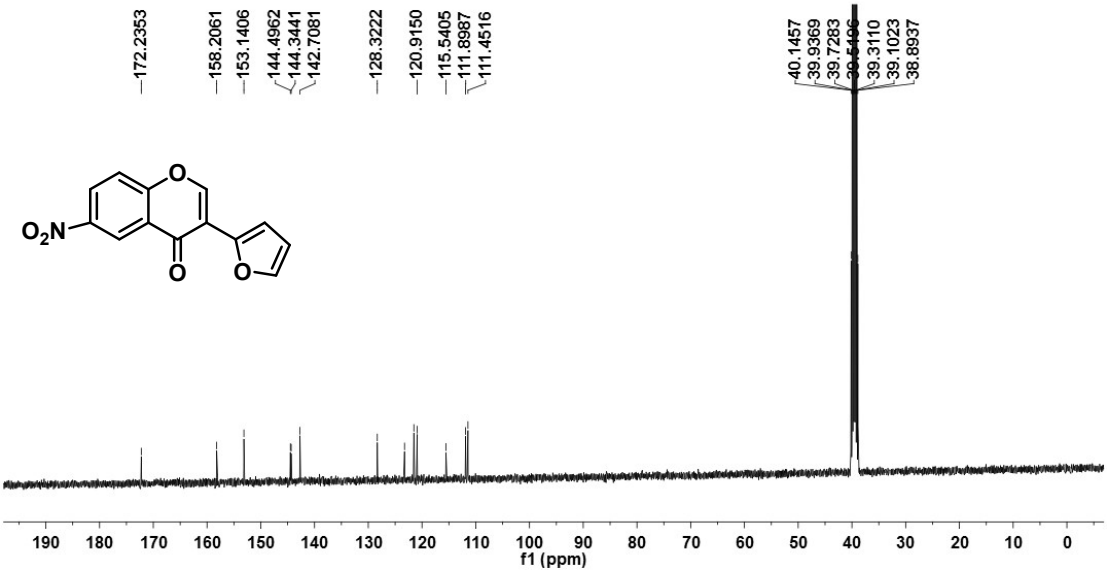
66

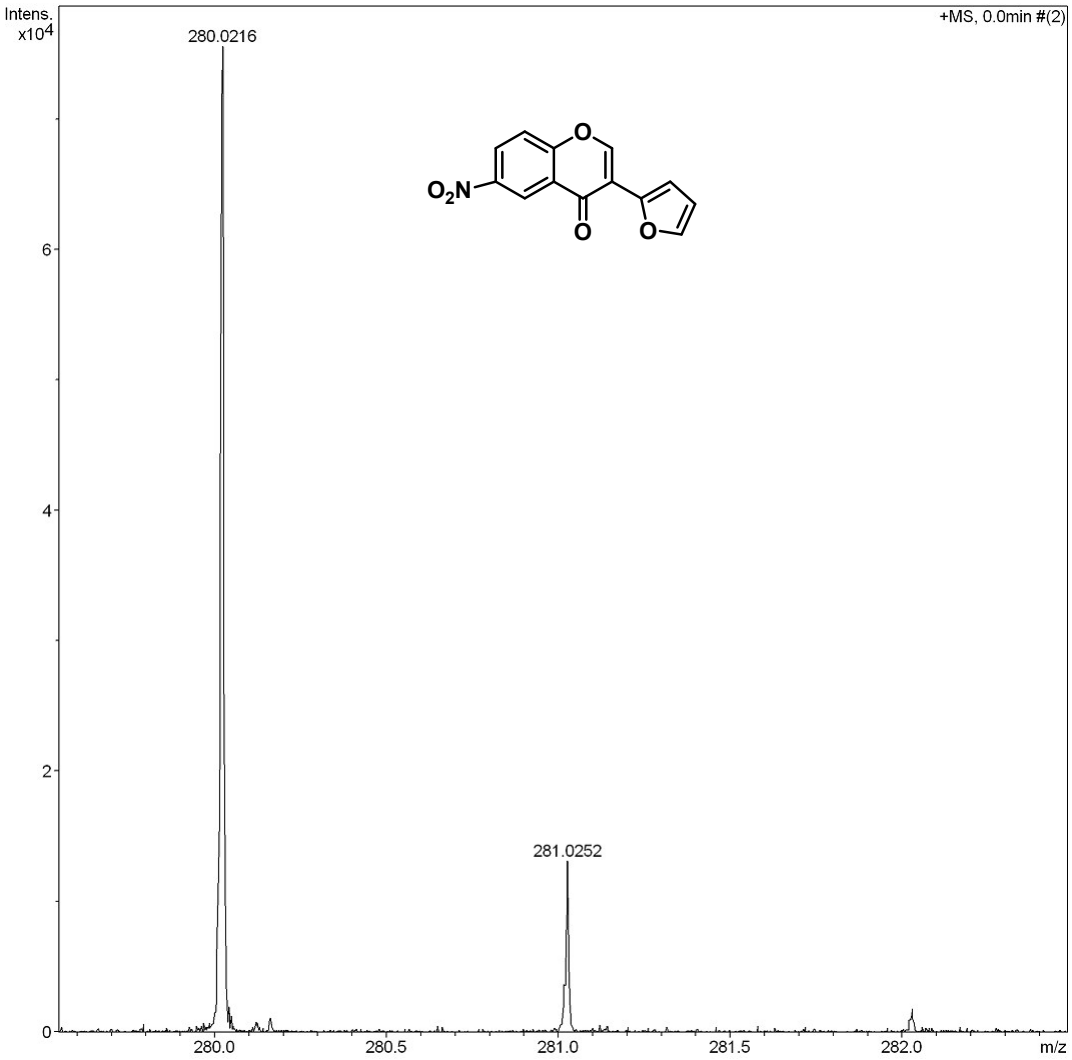

173.2662
173.2514
160.5393
158.9024
151.6608
145.2172
141.4559
122.0749
121.9049
120.4493
120.3953
115.7567
111.8988
111.5223
111.0975
110.9397
77.3714
77.1597
76.9479
F
O
O
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Intens.
x10^5
+MS, 0.0min #(2)
253.0269
254.0302
F
O
O
O
2.5
2.0
1.5
1.0
0.5
0.0
252.0
252.5
253.0
253.5
254.0
254.5
m/z

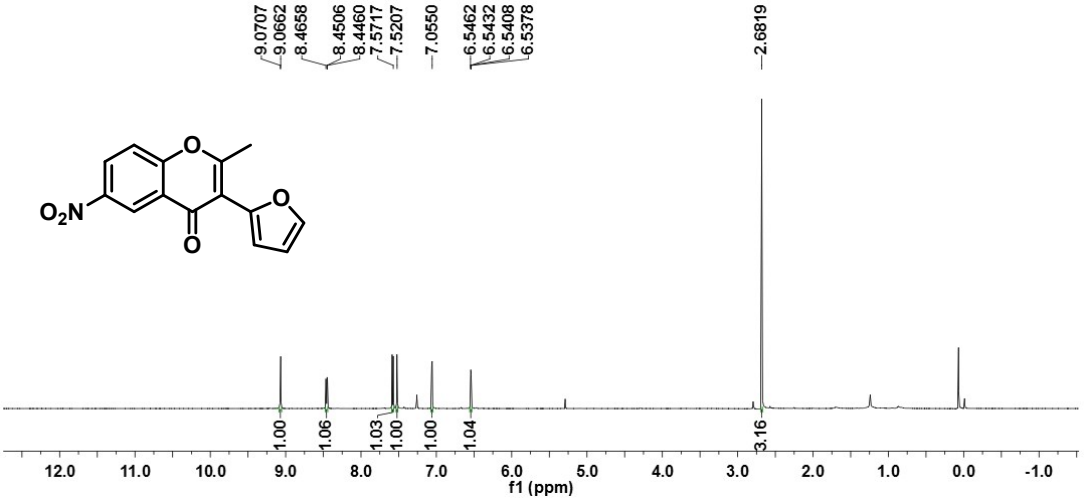
3q

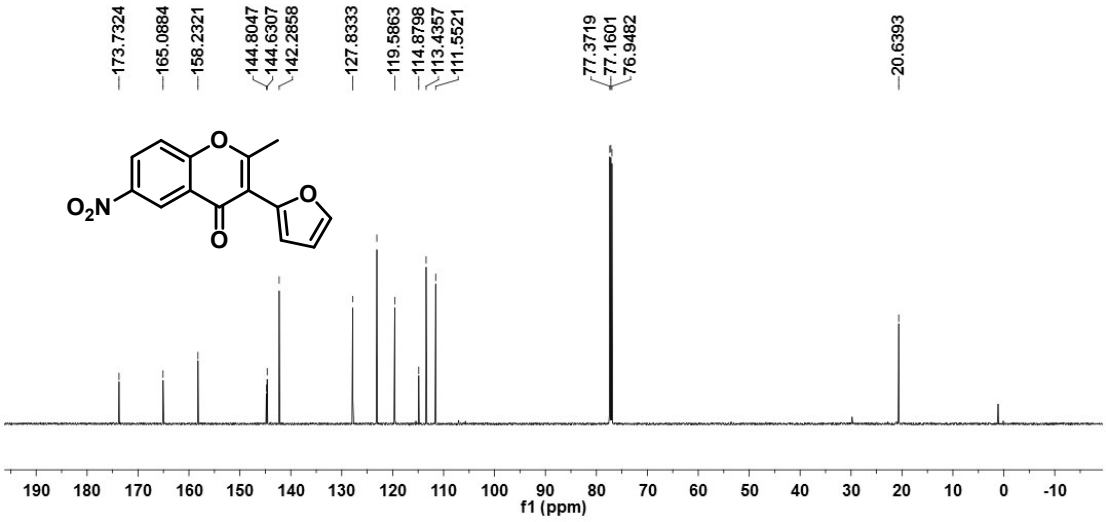

8.9368
8.8384
8.8317
8.5968
8.5896
8.5738
8.5667
7.9913
7.7973
7.2552
7.2470
6.6516
6.6471
6.6434
6.6389
3.3326
2.5002
O2N
O
O
O
0.95
0.91
1.11
1.11
1.00
1.05
1.09
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

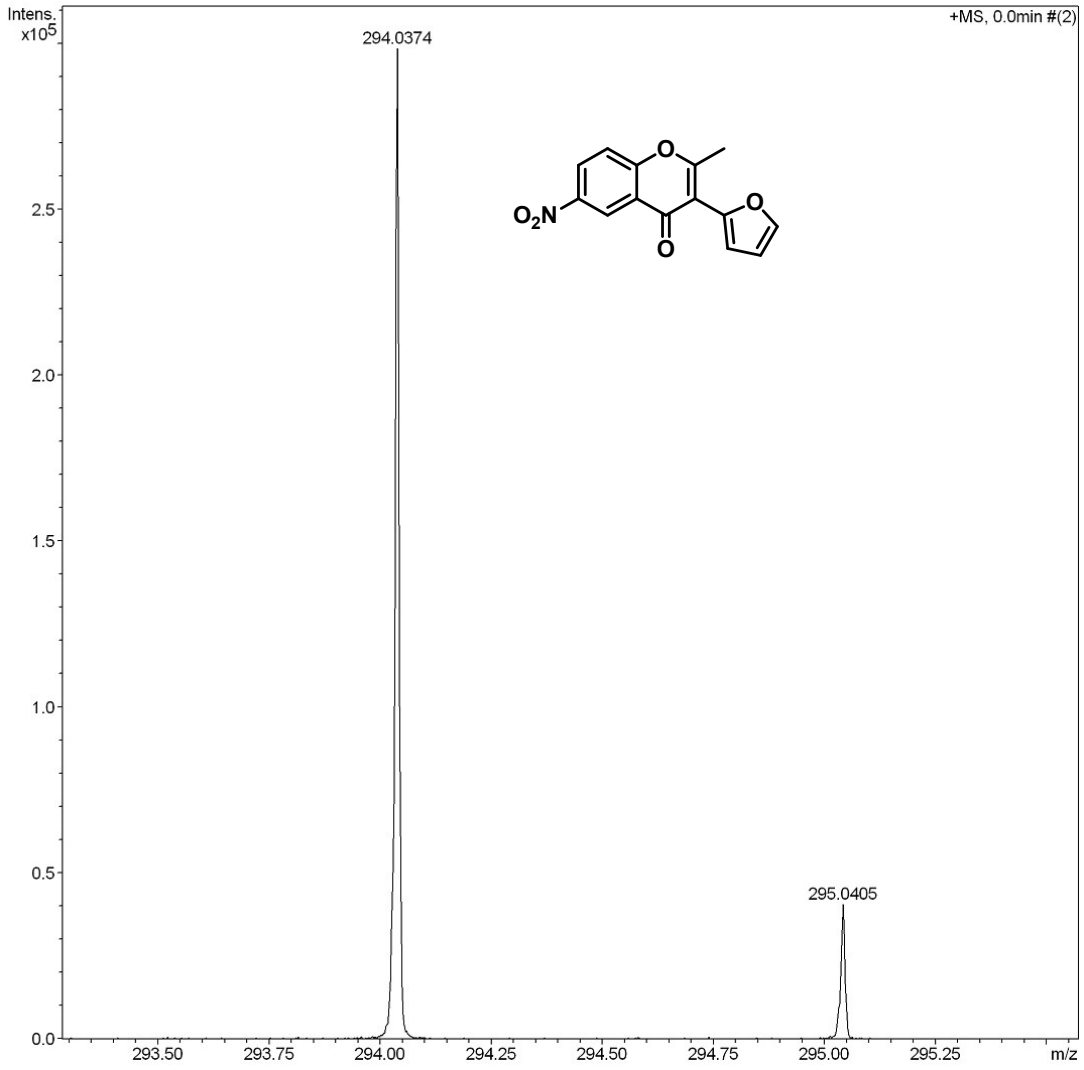

172.2353
158.2061
153.1406
144.4962
144.3441
142.7081
128.3222
120.9150
115.5405
111.8987
111.4516
40.1457
39.9369
39.7283
39.3110
39.1023
38.8937
O2N
O
O
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Intens.
x10^4
+MS, 0.0min #(2)
280.0216
281.0252
O2N
O
O
O
6
4
2
0
280.0
280.5
281.0
281.5
282.0
m/z

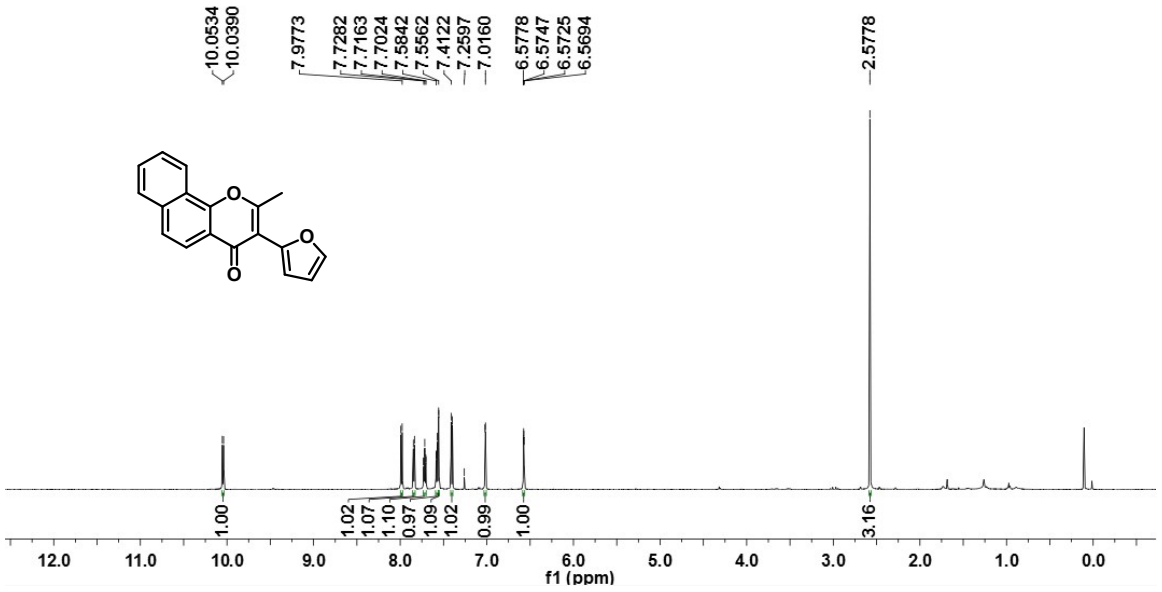
3r

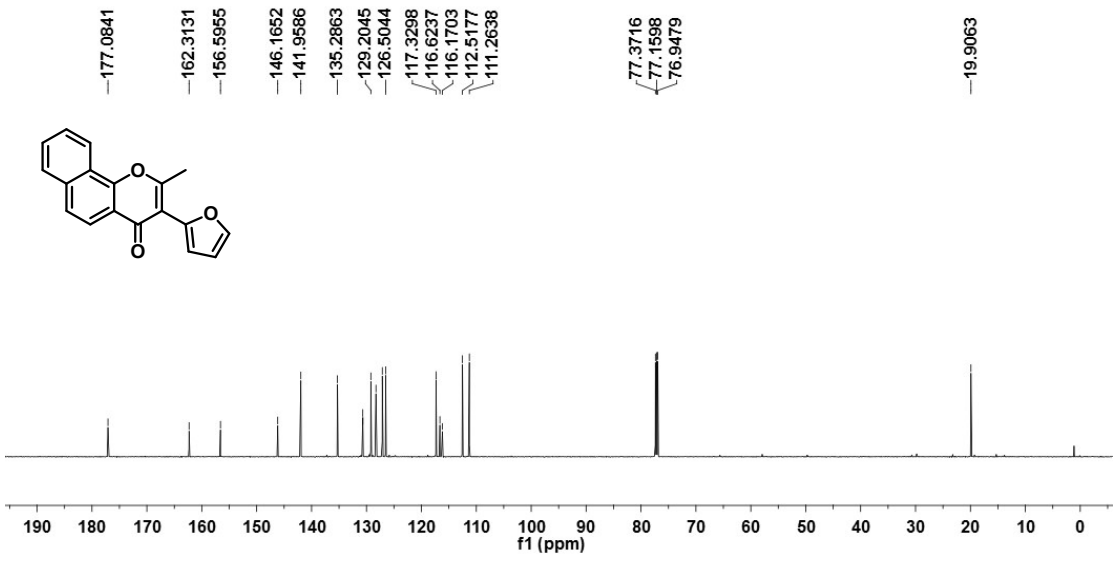

9.0707
9.0662
8.4658
8.4506
8.4460
7.5717
7.5207
7.0550
6.5462
6.5432
6.5408
6.5378
2.6819
O2N
O
O
O
1.00
1.06
1.03
1.00
1.00
1.04
3.16
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

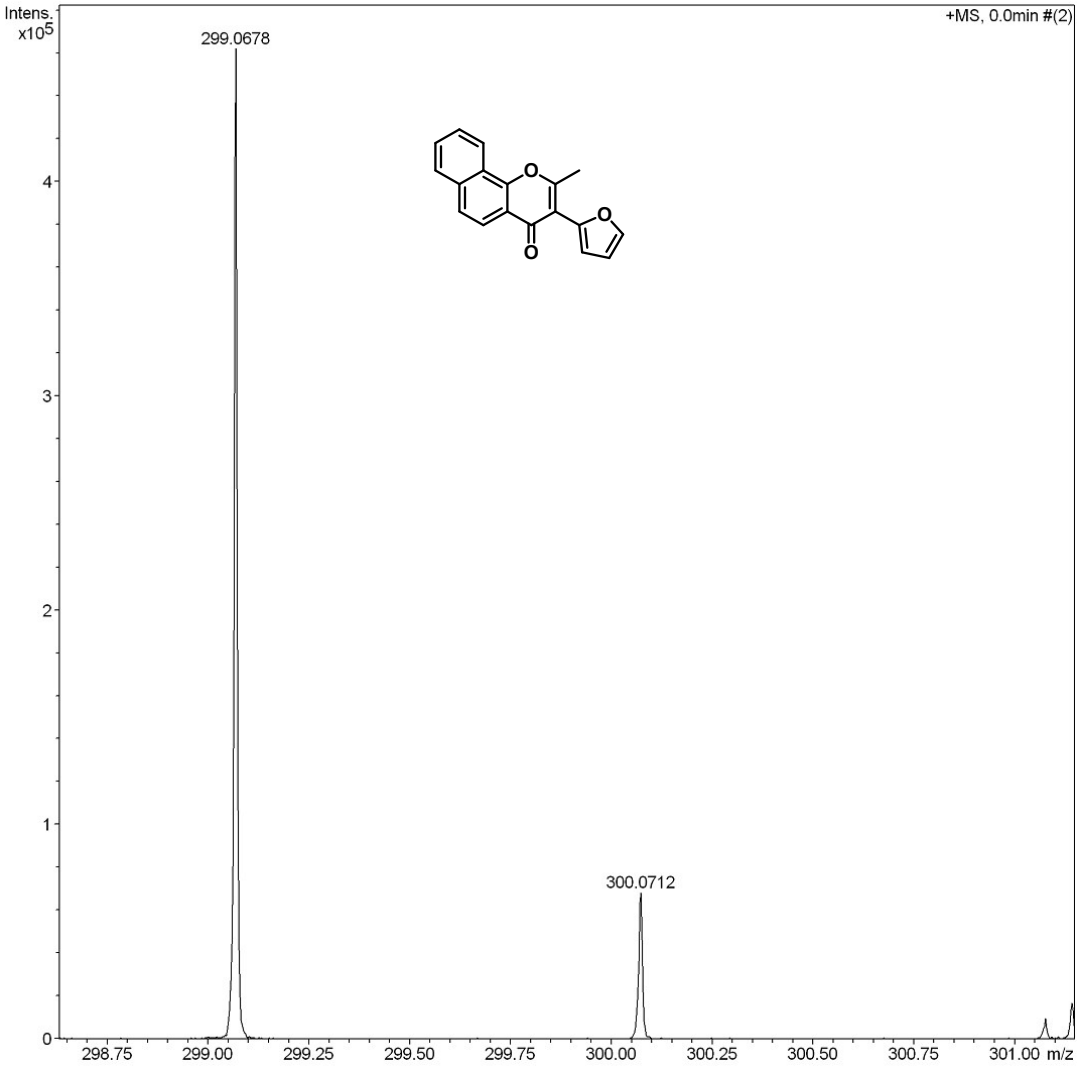

173.7324
165.0884
158.2321
144.8047
144.6307
142.2858
127.8333
119.5863
114.8798
113.4357
111.5521
77.3719
77.1601
76.9482
20.6393
O2N
O
O
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Intens.
x10^5
+MS, 0.0min #(2)
294.0374
295.0405
O2N
O
O
O
2.5
2.0
1.5
1.0
0.5
0.0
293.50
293.75
294.00
294.25
294.50
294.75
295.00
295.25
m/z

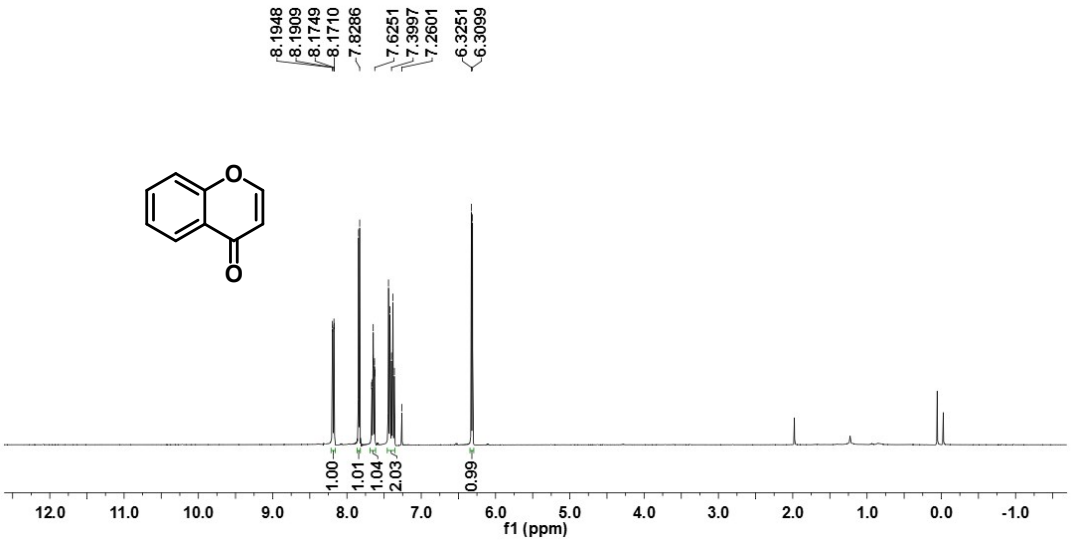
3s

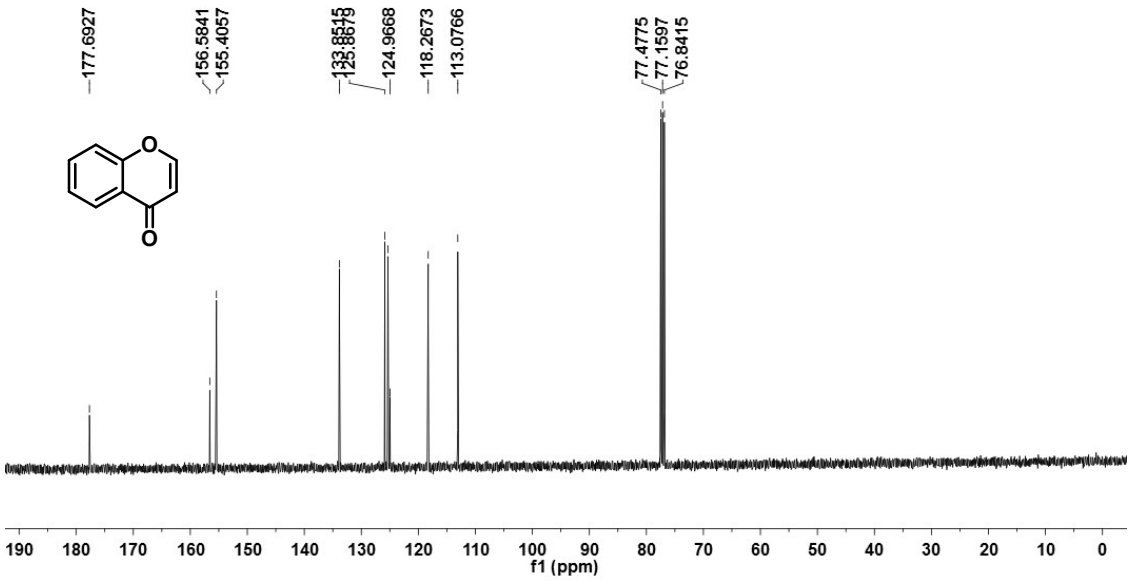

10.0534
10.0390
7.9773
7.7282
7.7163
7.7024
7.5842
7.5562
7.4122
7.2597
7.0160
6.5778
6.5747
6.5725
6.5694
2.5778
1.00
1.02
1.07
1.10
0.97
1.09
1.02
0.99
1.00
3.16
f1 (ppm)

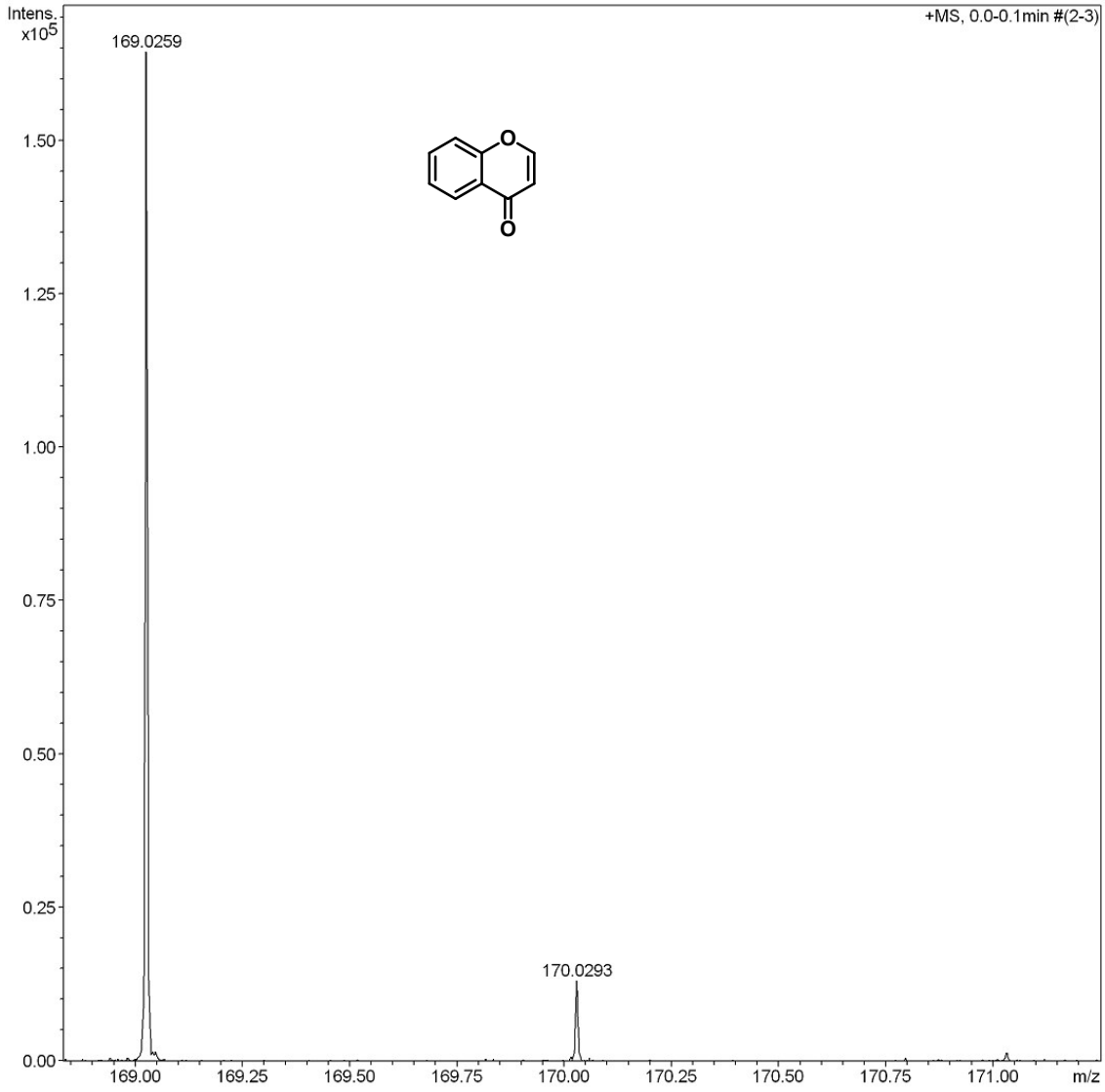

177.0841
162.3131
156.5955
146.1652
141.9586
135.2863
129.2045
126.5044
117.3298
116.6237
116.1703
112.5177
111.2638
77.3716
77.1598
76.9479
19.9063
f1 (ppm)


Intens.
x10^5
+MS, 0.0min #(2)
299.0678
300.0712
0
1
2
3
4
298.75
299.00
299.25
299.50
299.75
300.00
300.25
300.50
300.75
301.00 m/z

3n*


8.1948
8.1909
8.1749
8.1710
7.8286
7.6251
7.3997
7.2601
6.3251
6.3099
1.00
1.01
1.04
2.03
0.99
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)


177.6927
156.5841
155.4057
124.9668
118.2673
113.0766
77.4775
77.1597
76.8415
O
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Intens.
x10^5
+MS, 0.0-0.1min #(2-3)
169.0259
170.0293
O
O
1.50
1.25
1.00
0.75
0.50
0.25
0.00
169.00 169.25 169.50 169.75 170.00 170.25 170.50 170.75 171.00
m/z