

Supporting Information

A Facile Route to Isoflavone Quinones via the Direct Cross-Coupling of Chromones and Quinones

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I. General Methods and Materials S2

II. Experimental Procedure S2

Appendix I

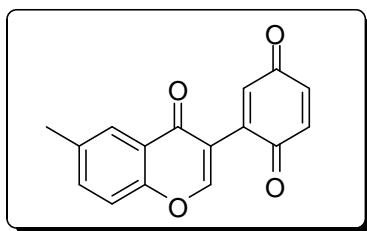
Spectral Copies of ¹H- and ¹³C-NMR Data Obtained in this Study S16

I. General Methods and Materials. Unless stated otherwise, reactions were performed in flame-dried glassware under a positive pressure of nitrogen. Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 F²⁵⁴ plates and visualization on TLC was achieved by UV light (254 and 354 nm). Flash column chromatography was undertaken on silica gel (400-630 mesh). ¹H NMR was recorded on 300 MHz or 400 MHz and chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak or 0.0 ppm for tetramethylsilane. The following abbreviations were used to describe peak splitting patterns when appropriate: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet, td = doublet of triplet. Coupling constants, *J*, were reported in hertz unit (Hz). ¹³C NMR was recorded on 100 MHz and was fully decoupled by broad band proton decoupling. Chemical shifts were reported in ppm referenced to the center line of a triplet at 77.0 ppm of Chloroform-d. High-resolution mass spectrometry (HRMS) data were recorded on LC-TOF. Unless otherwise stated, all commercial reagents and solvents were used without additional purification.

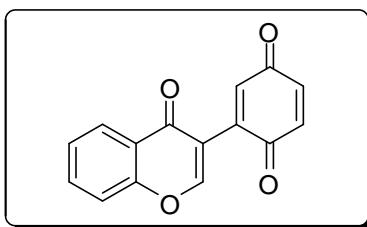
II. Experimental Procedure

General procedure (GP): Chromone derivative (0.088 mmol), quinone (4 equiv), Pd(OAc)₂ (0.2 equiv), AgOAc (2.5 equiv) and PivOH (2 equiv) were combined in dioxane (1 mL) in a cap test tube. The reaction mixture was heated to 100 °C. The reaction was stirred for 12–24 h until the starting material, chromone derivative disappeared (monitored by TLC using EtOAc and *n*-hexane = 1:3 as the mobile phase). After cooled to RT, the dioxane solvent was removed under reduced pressure. The reaction mixture was diluted with CH₂Cl₂ and the aqueous NaHCO₃ was added to neutralize the PivOH. After stirring the mixture for 10 min, the residue was extracted with aqueous NH₄Cl (3×30 ml). The organic layer was dried over MgSO₄. After removal of solvent, the residue was purified by flash chromatography on silica gel to give desired product.

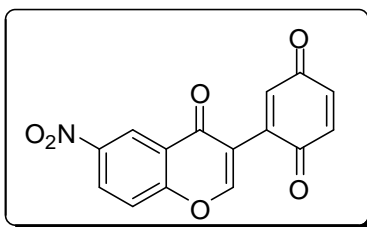
Compound characterizations:



2-(6-methyl-4-oxo-4H-chromen-3-yl)cyclohexa-2,5-diene-1,4-dione (3a). Yield 89% (20.4 mg) as yellow solid; mp 183–185 °C; ^1H NMR (300 MHz, Chloroform- d) δ 8.19 (s, 1H), 8.01 (d, J = 2.1 Hz, 1H), 7.50 (dd, J = 8.6, 2.2 Hz, 1H), 7.42 – 7.31 (m, 2H), 6.91 – 6.76 (m, 2H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 187.2, 185.8, 175.0, 156.9, 153.9, 137.2, 136.9, 136.4, 136.0, 135.6, 135.4, 125.7, 123.8, 117.9, 116.1, 21.0; HRMS (EI^+) m/z calcd. for $\text{C}_{16}\text{H}_{10}\text{NaO}_4^+$ [$\text{M}+\text{Na}$] $^+$: 289.0471, found: 289.0475.

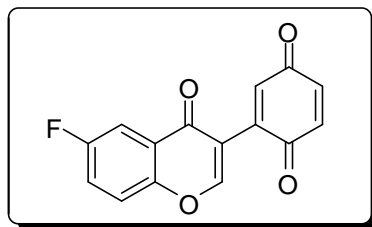


2-(4-oxo-4H-chromen-3-yl)cyclohexa-2,5-diene-1,4-dione (3b). Yield 74% (16.6 mg) as yellow solid; mp 210–212 °C; ^1H NMR (300 MHz, Chloroform- d) δ 8.23 (d, J = 6.9 Hz, 2H), 7.70 (ddd, J = 8.8, 7.1, 1.7 Hz, 1H), 7.45 (dd, J = 16.8, 8.3 Hz, 2H), 7.34 (d, J = 2.3 Hz, 1H), 6.91 – 6.75 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 187.2, 185.8, 175.0, 157.0, 155.6, 137.0, 136.9, 136.4, 135.7, 134.2, 126.4, 125.9, 124.1, 118.1, 116.3; HRMS (EI^+) m/z calcd. for $\text{C}_{15}\text{H}_8\text{NaO}_4^+$ [$\text{M}+\text{Na}$] $^+$: 275.0315, found: 275.0338.

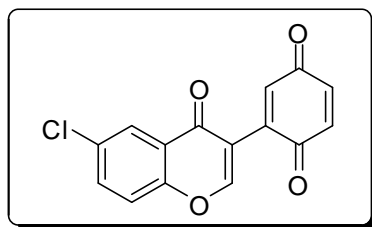


2-(6-nitro-4-oxo-4H-chromen-3-yl)cyclohexa-2,5-diene-1,4-dione (3c). Yield 66% (17.4 mg) as yellow solid; mp 212–214 °C; ^1H NMR (300 MHz, Chloroform- d) δ 9.11 (d, J = 2.8 Hz, 1H), 8.54 (dd, J = 9.2, 2.8 Hz, 1H), 8.30 (s, 1H), 7.67 (d, J = 9.1 Hz, 1H), 7.35 (d, J = 2.2 Hz, 1H), 7.00 – 6.75 (m, 2H); ^{13}C

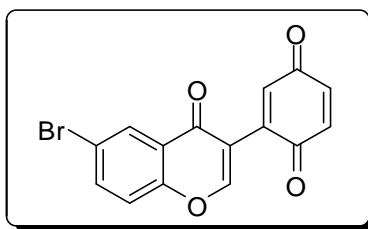
NMR (100 MHz, CDCl₃) δ 186.8, 185.3, 173.6, 158.3, 157.2, 145.2, 136.9, 136.6, 136.2, 135.9, 128.6, 124.2, 123.2, 120.0, 117.0; HRMS (EI⁺) m/z calcd. for C₁₅H₇NNaO₆⁺ [M+Na]⁺: 320.0166, found: 320.0157.



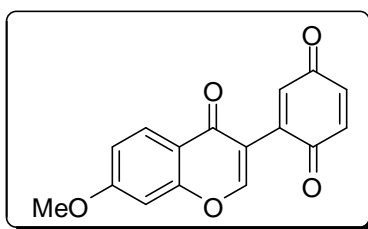
2-(6-fluoro-4-oxo-4H-chromen-3-yl)cyclohexa-2,5-diene-1,4-dione (3d). Yield 71% (16.9 mg) as yellow solid; mp 228–230 °C; ¹H NMR (300 MHz, Chloroform-d) δ 8.24 (s, 1H), 7.87 (dd, *J* = 8.2, 3.0 Hz, 1H), 7.57 – 7.40 (m, 2H), 7.34 (d, *J* = 2.3 Hz, 1H), 6.91 – 6.77 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 187.1, 185.7, 174.3, 174.2, 161.1, 158.7, 157.2, 151.9, 151.9, 136.9, 136.7, 136.5, 135.8, 125.4, 125.3, 122.7, 122.4, 120.4, 120.3, 115.7, 111.5, 111.2; HRMS (EI⁺) m/z calcd. for C₁₅H₇FNao₄⁺ [M+Na]⁺: 293.0221, found: 293.0215.



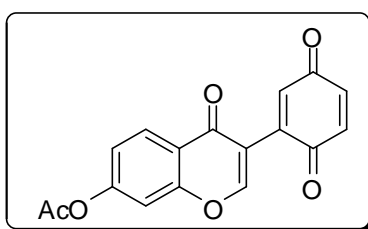
2-(6-chloro-4-oxo-4H-chromen-3-yl)cyclohexa-2,5-diene-1,4-dione (3e). Yield 92% (23.4 mg) as yellow solid; mp 226–228 °C; ¹H NMR (300 MHz, Chloroform-d) δ 8.23 (s, 1H), 8.19 (d, *J* = 2.6 Hz, 1H), 7.64 (dd, *J* = 8.9, 2.5 Hz, 1H), 7.46 (d, *J* = 8.9 Hz, 1H), 7.33 (d, *J* = 2.3 Hz, 1H), 6.90 – 6.77 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 187.0, 185.6, 173.8, 157.1, 154.0, 136.9, 136.6, 136.5, 135.9, 134.5, 132.0, 125.8, 125.0, 119.9, 116.4; HRMS (EI⁺) m/z calcd. for C₁₅H₇ClNaO₄⁺ [M+Na]⁺: 308.9925, found: 308.9927.



2-(6-bromo-4-oxo-4H-chromen-3-yl)cyclohexa-2,5-diene-1,4-dione (3f). Yield 93% (27.4 mg) as yellow solid; mp 217–219 °C; ^1H NMR (300 MHz, Chloroform-d) δ 8.36 (d, $J = 2.4$ Hz, 1H), 8.23 (s, 1H), 7.78 (dd, $J = 8.9, 2.5$ Hz, 1H), 7.39 (d, $J = 8.9$ Hz, 1H), 7.33 (d, $J = 2.3$ Hz, 1H), 6.92 – 6.76 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 187.0, 185.6, 173.7, 157.1, 154.4, 137.3, 136.9, 136.6, 136.5, 135.8, 129.0, 125.4, 120.1, 119.4, 116.4; HRMS (EI^+) m/z calcd. for $\text{C}_{15}\text{H}_7\text{BrNaO}_4^+$ [$\text{M}+\text{Na}$] $^+$: 352.9420, found: 352.9409.

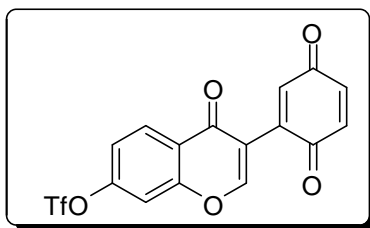


2-(7-methoxy-4-oxo-4H-chromen-3-yl)cyclohexa-2,5-diene-1,4-dione (3g). Yield 73% (18.2 mg) as yellow solid; mp 235–237 °C; ^1H NMR (400 MHz, Chloroform-d) δ 8.15 – 8.12 (m, 2H), 7.34 (d, $J = 2.4$ Hz, 1H), 7.00 (dd, $J = 8.9, 2.4$ Hz, 1H), 6.86 – 6.79 (m, 3H), 3.91 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 187.2, 185.9, 174.3, 164.5, 157.4, 156.6, 137.2, 136.9, 136.4, 135.7, 127.9, 118.0, 116.3, 115.1, 100.3, 55.9; HRMS (EI^+) m/z calcd. for $\text{C}_{16}\text{H}_{10}\text{NaO}_5^+$ [$\text{M}+\text{Na}$] $^+$: 305.0420, found: 305.0411.

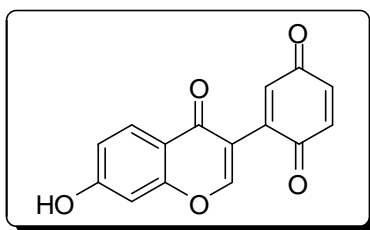


3-(3,6-dioxocyclohexa-1,4-dienyl)-4-oxo-4H-chromen-7-yl acetate (3h). Yield 90% (24.6 mg) as yellow solid; mp 185–187 °C; ^1H NMR (400 MHz, Chloroform-d) δ 8.24 (dd, $J = 8.7, 0.4$ Hz, 1H), 8.20

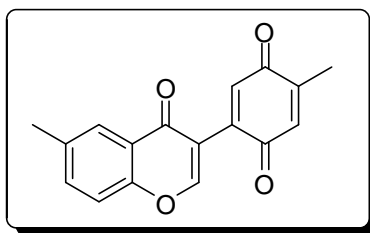
(s, 1H), 7.37 – 7.30 (m, 2H), 7.18 (dd, $J = 8.7, 2.1$ Hz, 1H), 6.88 – 6.78 (m, 2H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 187.1, 185.6, 174.2, 168.3, 157.1, 156.1, 154.9, 136.9, 136.7, 136.4, 135.8, 127.8, 121.8, 120.1, 116.5, 111.0, 21.1; HRMS (EI^+) m/z calcd. for $\text{C}_{17}\text{H}_{10}\text{NaO}_6^+$ $[\text{M}+\text{Na}]^+$: 333.0370, found: 333.0368.



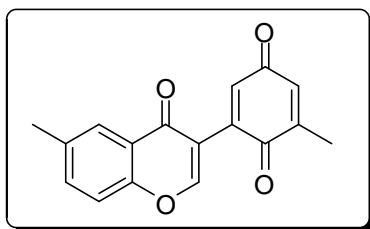
3-(3,6-dioxocyclohexa-1,4-dienyl)-4-oxo-4H-chromen-7-yl trifluoromethanesulfonate (3i). Yield 85% (30 mg) as yellow solid; mp 168–170 °C; ^1H NMR (400 MHz, Chloroform- d) δ 8.35 (d, $J = 8.9$ Hz, 1H), 8.25 (s, 1H), 7.47 (d, $J = 2.3$ Hz, 1H), 7.36 (dd, $J = 8.9, 2.3$ Hz, 1H), 7.32 (d, $J = 2.4$ Hz, 1H), 6.93 – 6.79 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 186.9, 185.4, 173.7, 157.4, 155.8, 152.5, 136.9, 136.5, 136.3, 136.0, 129.2, 123.8, 120.2, 119.3, 117.0, 111.6, 104.1; HRMS (EI^+) m/z calcd. for $\text{C}_{16}\text{H}_7\text{F}_3\text{NaO}_7\text{S}^+$ $[\text{M}+\text{Na}]^+$: 422.9757, found: 422.9752.



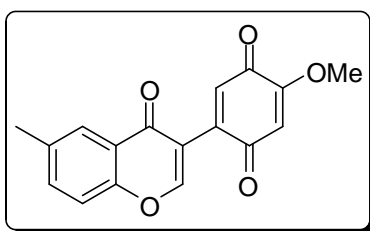
2-(7-hydroxy-4-oxo-4H-chromen-3-yl)cyclohexa-2,5-diene-1,4-dione (3j). Yield 63% (14.9 mg) as yellow solid; mp 206–208 °C; ^1H NMR (300 MHz, Dimethyl sulfoxide- d_6) δ 8.35 (s, 1H), 7.91 (d, $J = 8.7$ Hz, 1H), 7.10 (d, $J = 2.6$ Hz, 1H), 7.05 – 6.83 (m, 4H); ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$) δ 187.9, 185.7, 173.8, 163.5, 157.7, 156.9, 139.6, 137.6, 136.8, 135.0, 127.7, 117.3, 116.5, 116.1, 102.8; HRMS (EI^+) m/z calcd. for $\text{C}_{15}\text{H}_8\text{NaO}_5^+$ $[\text{M}+\text{Na}]^+$: 291.0264, found: 291.0259.



2-methyl-5-(6-methyl-4-oxo-4H-chromen-3-yl)cyclohexa-2,5-diene-1,4-dione (3k, major). Overall yield 81% (20 mg) as yellow solid; mp 163–165 °C; ^1H NMR (300 MHz, Chloroform- d) δ 8.20 (s, 1H), 8.01 (s, 1H), 7.50 (d, $J = 8.6$ Hz, 1H), 7.37 (d, $J = 10.2$ Hz, 2H), 6.68 (s, 1H), 2.45 (s, 3H), 2.08 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 187.3, 185.7, 174.6, 156.6, 153.4, 145.4, 136.4, 135.4, 135.2, 134.9, 133.1, 125.2, 123.3, 117.4, 115.5, 20.5, 15.0; HRMS (EI^+) m/z calcd. for $\text{C}_{17}\text{H}_{12}\text{NaO}_4^+$ $[\text{M}+\text{Na}]^+$: 303.0628, found: 303.0618.

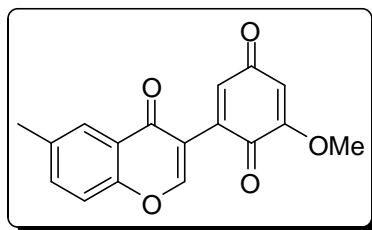


2-methyl-6-(6-methyl-4-oxo-4H-chromen-3-yl)cyclohexa-2,5-diene-1,4-dione (3k). Yellow solid; mp 208–210 °C; ^1H NMR (300 MHz, Chloroform- d) δ 8.13 (s, 1H), 8.01 (s, 1H), 7.50 (d, $J = 9.0$ Hz, 1H), 7.38 (d, $J = 8.6$ Hz, 1H), 7.17 (d, $J = 2.6$ Hz, 1H), 6.65 (s, 1H), 2.45 (s, 3H), 2.10 (d, $J = 1.6$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 187.2, 186.2, 175.1, 156.2, 154.1, 146.2, 137.9, 135.9, 135.6, 135.4, 133.3, 125.7, 123.8, 117.9, 117.1, 21.0, 16.4; HRMS (EI^+) m/z calcd. for $\text{C}_{17}\text{H}_{12}\text{NaO}_4^+$ $[\text{M}+\text{Na}]^+$: 303.0628, found: 303.0618.

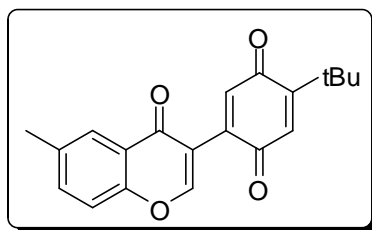


2-methoxy-5-(6-methyl-4-oxo-4H-chromen-3-yl)cyclohexa-2,5-diene-1,4-dione (3l, major). Overall yield 77% (19.9 mg) as yellow solid; mp 225–227 °C; ^1H NMR (300 MHz, Chloroform- d) δ 8.22 (s, 1H),

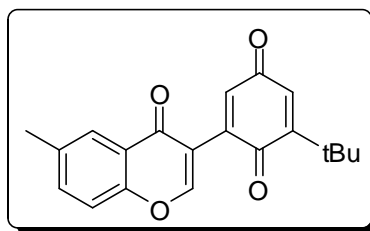
8.01 (s, 1H), 7.50 (dd, $J = 8.5, 2.1$ Hz, 1H), 7.37 (d, $J = 11.2$ Hz, 2H), 6.01 (s, 1H), 3.85 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 186.1, 181.9, 175.1, 158.6, 157.6, 153.8, 137.3, 135.9, 135.4, 133.7, 125.7, 123.8, 117.8, 115.8, 107.9, 56.3, 21.0; HRMS (EI^+) m/z calcd. for $\text{C}_{17}\text{H}_{12}\text{NaO}_5^+$ $[\text{M}+\text{Na}]^+$: 319.0577, found: 319.0578.



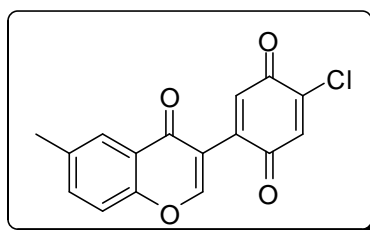
2-methoxy-6-(6-methyl-4-oxo-4H-chromen-3-yl)cyclohexa-2,5-diene-1,4-dione (3l). Yellow solid; mp 240–242 °C; ^1H NMR (400 MHz, Dimethyl sulfoxide- d_6) δ 8.47 (s, 1H), 7.87 (d, $J = 2.2$ Hz, 1H), 7.68 (dd, $J = 8.6, 2.2$ Hz, 1H), 7.61 (d, $J = 8.6$ Hz, 1H), 6.98 (d, $J = 2.4$ Hz, 1H), 6.19 (d, $J = 2.4$ Hz, 1H), 3.83 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) δ 187.0, 179.4, 178.7, 174.1, 158.9, 156.7, 153.7, 137.4, 135.7, 135.2, 124.5, 123.0, 118.3, 117.2, 107.4, 56.6, 20.4; HRMS (EI^+) m/z calcd. for $\text{C}_{17}\text{H}_{12}\text{NaO}_5^+$ $[\text{M}+\text{Na}]^+$: 319.0577, found: 319.0578.



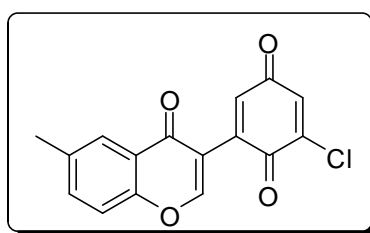
2-tert-butyl-5-(6-methyl-4-oxo-4H-chromen-3-yl)cyclohexa-2,5-diene-1,4-dione (3m). Overall yield 92% (25.8 mg) as yellow oil; ^1H NMR (300 MHz, Chloroform- d) δ 8.23 (s, 1H), 8.02 (s, 1H), 7.50 (dd, $J = 8.5, 2.2$ Hz, 1H), 7.37 (d, $J = 8.6$ Hz, 1H), 7.28 (s, 1H), 6.66 (s, 1H), 2.45 (s, 3H), 1.29 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 187.4, 187.0, 175.2, 157.0, 156.1, 153.9, 137.7, 135.9, 135.4, 135.4, 131.9, 125.7, 123.8, 117.9, 115.7, 35.2, 29.1, 21.0; HRMS (EI^+) m/z calcd. for $\text{C}_{20}\text{H}_{18}\text{NaO}_4^+$ $[\text{M}+\text{Na}]^+$: 345.1097, found: 345.1092.



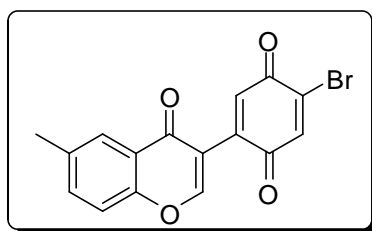
2-tert-butyl-6-(6-methyl-4-oxo-4H-chromen-3-yl)cyclohexa-2,5-diene-1,4-dione (3m, major). Yellow oil; ^1H NMR (300 MHz, Chloroform- d) δ 8.06 (s, 1H), 8.01 (s, 1H), 7.50 (dd, $J = 8.7, 2.1$ Hz, 1H), 7.37 (d, $J = 8.6$ Hz, 1H), 7.03 (d, $J = 2.6$ Hz, 1H), 6.63 (d, $J = 2.7$ Hz, 1H), 2.45 (s, 3H), 1.30 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 187.9, 185.7, 175.2, 156.6, 155.7, 154.2, 140.1, 135.9, 135.4, 134.1, 131.5, 125.7, 123.8, 118.0, 117.9, 35.6, 29.3, 21.0; HRMS (EI^+) m/z calcd. for $\text{C}_{20}\text{H}_{18}\text{NaO}_4^+$ $[\text{M}+\text{Na}]^+$: 345.1097, found: 345.1092.



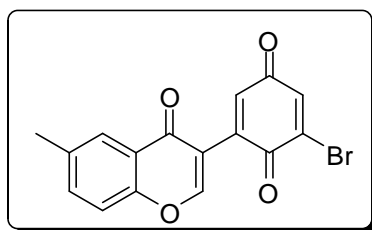
2-chloro-5-(6-methyl-4-oxo-4H-chromen-3-yl)cyclohexa-2,5-diene-1,4-dione (3n, major). Overall yield 69% (17.3 mg) as yellow solid; mp 175–177 °C; ^1H NMR (400 MHz, Chloroform- d) δ 8.24 (s, 1H), 8.01 (dd, $J = 2.2, 1.0$ Hz, 1H), 7.57 (s, 1H), 7.54 – 7.48 (m, 1H), 7.38 (d, $J = 8.5$ Hz, 1H), 7.07 (s, 1H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 183.9, 179.4, 174.8, 157.6, 153.8, 144.0, 137.3, 136.2, 135.6, 135.0, 133.9, 125.7, 123.7, 117.9, 115.3, 21.0; HRMS (EI^+) m/z calcd. for $\text{C}_{16}\text{H}_9\text{ClNaO}_4^+$ $[\text{M}+\text{Na}]^+$: 323.0082, found: 323.0085.



2-chloro-6-(6-methyl-4-oxo-4H-chromen-3-yl)cyclohexa-2,5-diene-1,4-dione (3n). Yellow solid; mp 216–218 °C; ^1H NMR (400 MHz, Chloroform- d) δ 8.22 (s, 1H), 8.01 (dd, $J = 1.5, 0.7$ Hz, 1H), 7.52 (ddd, $J = 8.6, 2.2, 0.6$ Hz, 1H), 7.39 (d, $J = 8.6$ Hz, 1H), 7.36 (d, $J = 2.5$ Hz, 1H), 7.04 (d, $J = 2.5$ Hz, 1H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 184.7, 178.5, 174.7, 157.0, 153.9, 144.2, 137.2, 136.2, 135.8, 135.6, 133.6, 125.7, 123.7, 117.9, 116.1, 21.0; HRMS (EI^+) m/z calcd. for $\text{C}_{16}\text{H}_9\text{ClNaO}_4^+$ $[\text{M}+\text{Na}]^+$: 323.0082, found: 323.0085.

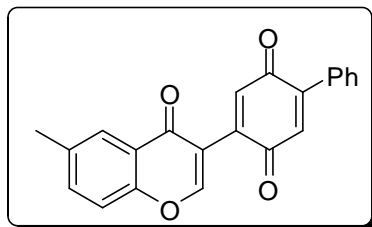


2-chloro-5-(6-methyl-4-oxo-4H-chromen-3-yl)cyclohexa-2,5-diene-1,4-dione (3o, major). Overall yield 55% (16.6 mg) as yellow solid; mp 152–154 °C; ^1H NMR (300 MHz, Chloroform- d) δ 8.24 (s, 1H), 8.01 (d, $J = 2.1$ Hz, 1H), 7.61 (s, 1H), 7.51 (dd, $J = 8.6, 2.3$ Hz, 1H), 7.38 (d, $J = 11.0$ Hz, 2H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 183.5, 179.4, 174.8, 157.5, 153.8, 138.3, 137.4, 137.2, 136.2, 135.6, 134.8, 125.7, 123.7, 117.9, 115.4, 21.0; HRMS (EI^+) m/z calcd. for $\text{C}_{16}\text{H}_9\text{BrNaO}_4^+$ $[\text{M}+\text{Na}]^+$: 366.9576, found: 366.9571.

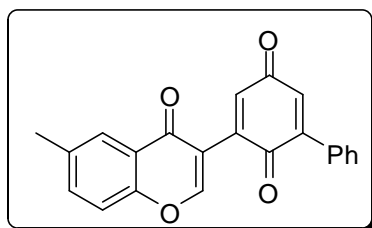


2-bromo-6-(6-methyl-4-oxo-4H-chromen-3-yl)cyclohexa-2,5-diene-1,4-dione (3o). Yellow solid; mp 202–204 °C; ^1H NMR (400 MHz, Chloroform- d) δ 8.21 (s, 1H), 8.02 (d, $J = 1.6$ Hz, 1H), 7.52 (dd, $J = 8.5, 2.2$ Hz, 1H), 7.39 (d, $J = 8.5$ Hz, 1H), 7.37 (d, $J = 2.5$ Hz, 1H), 7.33 (d, $J = 2.5$ Hz, 1H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 184.5, 178.4, 174.7, 157.0, 153.9, 138.1, 137.5, 136.9, 136.2, 135.7, 135.6,

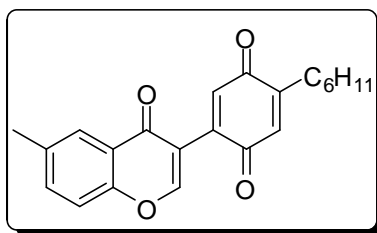
125.7, 123.7, 117.9, 116.3, 21.0; HRMS (EI⁺) m/z calcd. for C₁₆H₉BrNaO₄⁺ [M+Na]⁺: 366.9576, found: 366.9571.



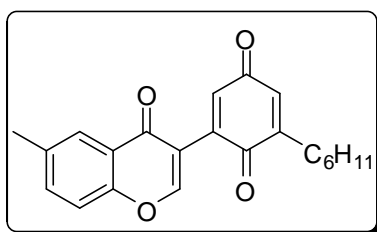
2-(6-methyl-4-oxo-4H-chromen-3-yl)-5-phenylcyclohexa-2,5-diene-1,4-dione (3p, major). Overall Yield 71% (21.1 mg) as yellow solid; mp 223–225 °C; ¹H NMR (400 MHz, Methylene chloride-d₂) δ 8.31 (s, 1H), 8.02 (dd, *J* = 1.6, 0.8 Hz, 1H), 7.61 – 7.50 (m, 3H), 7.52 – 7.44 (m, 3H), 7.47 – 7.39 (m, 2H), 6.95 (s, 1H), 2.48 (s, 3H); ¹³C NMR (100 MHz, CD₂Cl₂) δ 187.1, 186.5, 175.3, 157.6, 154.4, 146.0, 137.5, 136.5, 136.2, 135.8, 133.4, 133.1, 130.4, 129.7, 128.8, 125.8, 124.2, 118.3, 116.3, 21.1; HRMS (EI⁺) m/z calcd. for C₂₂H₁₄NaO₄⁺ [M+Na]⁺: 365.0784, found: 365.0782.



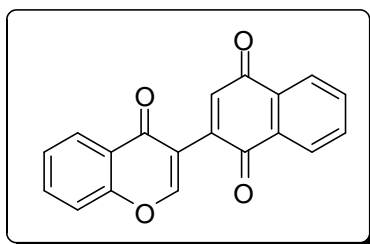
2-(6-methyl-4-oxo-4H-chromen-3-yl)-6-phenylcyclohexa-2,5-diene-1,4-dione (3p). Yellow solid: mp 195–197 °C; ¹H NMR (300 MHz, Chloroform-d) δ 8.16 (s, 1H), 8.03 (d, *J* = 1.5 Hz, 1H), 7.55 – 7.36 (m, 7H), 7.25 (d, *J* = 2.7 Hz, 1H), 6.89 (d, *J* = 2.7 Hz, 1H), 2.46 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 187.2, 185.2, 175.2, 156.2, 154.1, 146.7, 138.5, 136.0, 135.4, 135.2, 133.1, 132.4, 130.1, 129.3, 128.5, 125.7, 123.8, 117.9, 117.4, 21.0; HRMS (EI⁺) m/z calcd. for C₂₂H₁₄NaO₄⁺ [M+Na]⁺: 365.0784, found: 365.0782.



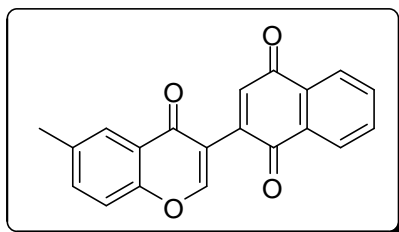
2-cyclohexyl-5-(6-methyl-4-oxo-4H-chromen-3-yl)cyclohexa-2,5-diene-1,4-dione (3q). Overall yield 88% (26.8 mg) as yellow oil; ^1H NMR (400 MHz, Chloroform- d) δ 8.21 (s, 1H), 8.01 (dd, $J = 2.2, 1.0$ Hz, 1H), 7.49 (ddd, $J = 8.5, 2.2, 0.6$ Hz, 1H), 7.37 (d, $J = 8.6$ Hz, 1H), 7.33 (s, 1H), 6.56 (d, $J = 1.1$ Hz, 1H), 2.78 – 2.65 (m, 1H), 2.45 (s, 3H), 1.86 – 1.68 (m, 5H), 1.47 – 1.31 (m, 2H), 1.28 – 1.08 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 187.1, 186.8, 175.2, 157.1, 154.0, 153.9, 136.3, 136.2, 135.9, 135.4, 131.1, 125.7, 123.8, 117.9, 116.0, 36.2, 32.0, 26.3, 26.0, 21.0; HRMS (EI^+) m/z calcd. for $\text{C}_{22}\text{H}_{20}\text{NaO}_4^+$ $[\text{M}+\text{Na}]^+$: 371.1254, found: 371.1238.



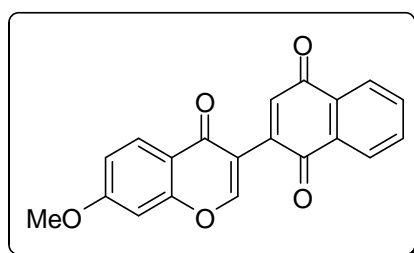
2-cyclohexyl-6-(6-methyl-4-oxo-4H-chromen-3-yl)cyclohexa-2,5-diene-1,4-dione (3q, major). Yellow oil; ^1H NMR (400 MHz, Chloroform- d) δ 8.11 (s, 1H), 8.01 (dd, $J = 2.1, 0.9$ Hz, 1H), 7.50 (dd, $J = 8.5, 2.1$ Hz, 1H), 7.37 (d, $J = 8.6$ Hz, 1H), 7.12 (d, $J = 2.6$ Hz, 1H), 6.53 (dd, $J = 2.7, 1.2$ Hz, 1H), 2.83 – 2.69 (m, 1H), 2.45 (s, 3H), 1.89 – 1.67 (m, 5H), 1.47 – 1.31 (m, 2H), 1.28 – 1.10 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 187.8, 185.5, 175.2, 156.1, 154.4, 154.1, 138.4, 135.9, 135.4, 135.0, 130.6, 125.7, 123.8, 117.9, 117.5, 36.9, 32.2, 26.3, 26.0, 21.0; HRMS (EI^+) m/z calcd. for $\text{C}_{22}\text{H}_{20}\text{NaO}_4^+$ $[\text{M}+\text{Na}]^+$: 371.1254, found: 371.1238.



2-(4-oxo-4H-chromen-3-yl)naphthalene-1,4-dione (3r). Yield 76% (20.3 mg) as yellow solid; mp 266–268 °C; ^1H NMR (300 MHz, Chloroform-d) δ 8.31 (s, 1H), 8.27 (d, J = 8.1 Hz, 1H), 8.19 – 8.07 (m, 2H), 7.81 – 7.73 (m, 2H), 7.70 (d, J = 7.1 Hz, 1H), 7.55 – 7.40 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 184.7, 183.7, 175.1, 156.9, 155.8, 139.3, 138.1, 134.2, 134.0, 133.8, 132.2, 132.0, 127.1, 126.5, 126.1, 125.8, 124.2, 118.2, 117.2; HRMS (EI^+) m/z calcd. for $\text{C}_{19}\text{H}_{10}\text{NaO}_4^+$ [$\text{M}+\text{Na}$] $^+$: 325.0471, found: 325.0465.

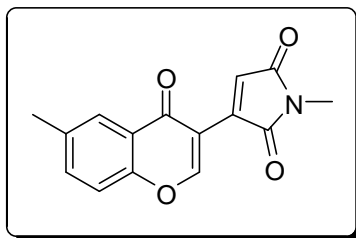


2-(6-methyl-4-oxo-4H-chromen-3-yl)naphthalene-1,4-dione (3s). Yield 87% (24 mg) as yellow solid; mp 234–236 °C; ^1H NMR (300 MHz, Chloroform-d) δ 8.28 (s, 1H), 8.15 – 8.08 (m, 2H), 8.04 (s, 1H), 7.80 – 7.70 (m, 2H), 7.56 – 7.45 (m, 2H), 7.40 (d, J = 8.5 Hz, 1H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 184.8, 183.8, 175.2, 156.8, 154.0, 139.5, 138.0, 135.9, 135.4, 134.0, 133.8, 132.2, 132.0, 127.1, 126.1, 125.7, 123.9, 117.9, 117.0, 21.0; HRMS (EI^+) m/z calcd. for $\text{C}_{20}\text{H}_{12}\text{NaO}_4^+$ [$\text{M}+\text{Na}$] $^+$: 339.0628, found: 339.0617.



2-(7-methoxy-4-oxo-4H-chromen-3-yl)naphthalene-1,4-dione (3t). Yield 56% (16.5 mg) as yellow solid; mp 233–235 °C; ^1H NMR (400 MHz, Chloroform-d) δ 8.23 (s, 1H), 8.16 (d, J = 9.0 Hz, 1H), 8.14 – 8.07 (m, 2H), 7.78 – 7.71 (m, 2H), 7.48 (s, 1H), 7.00 (dd, J = 8.9, 2.4 Hz, 1H), 6.87 (d, J = 2.4 Hz, 1H), 3.91 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 184.7, 183.8, 174.4, 164.4, 157.5, 156.4, 139.5, 138.0, 133.9,

133.8, 132.2, 132.0, 127.9, 127.0, 126.1, 118.1, 117.1, 115.1, 100.3, 55.9; HRMS (EI⁺) m/z calcd. for C₂₀H₁₂NaO₅⁺ [M+Na]⁺: 355.0577, found: 355.0572.

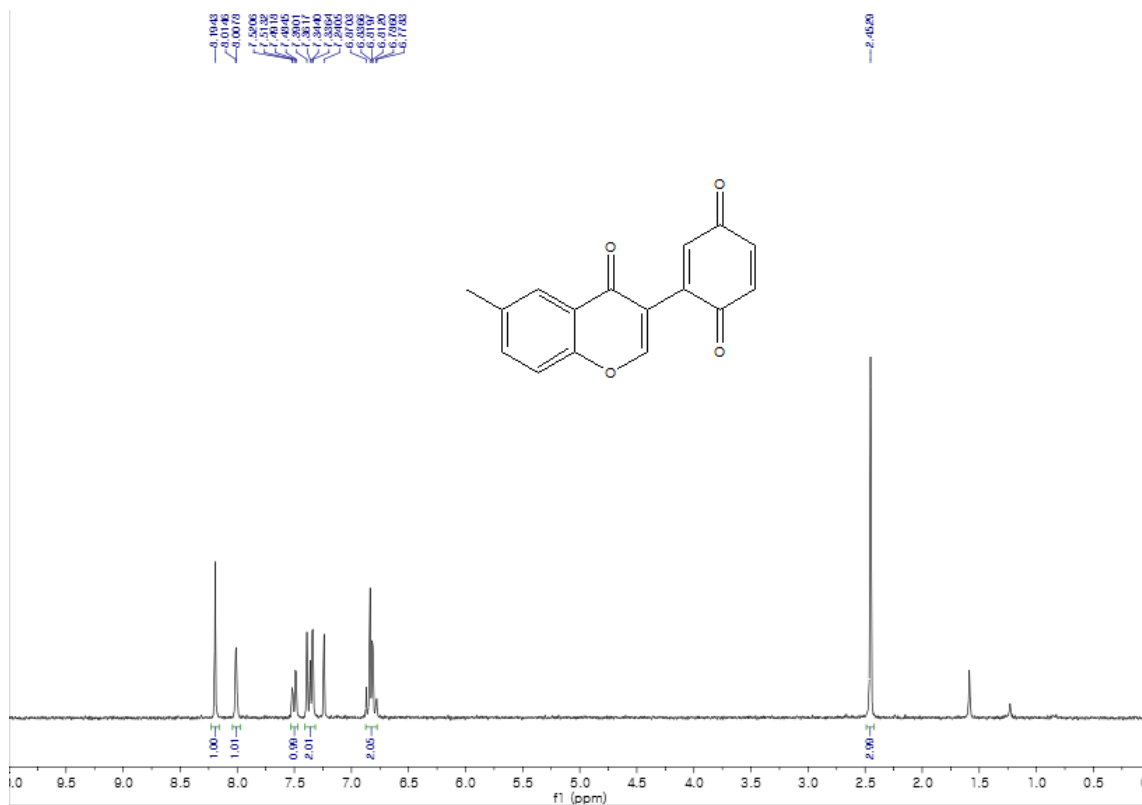


1-methyl-3-(6-methyl-4-oxo-4H-chromen-3-yl)-1H-pyrrole-2,5-dione (3u). Yield 52% (12.1 mg) as white solid; mp 256–258 °C; ¹H NMR (300 MHz, Chloroform-d) δ 9.34 (s, 1H), 8.03 (d, *J* = 1.2 Hz, 1H), 7.78 (s, 1H), 7.52 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.40 (d, *J* = 8.5 Hz, 1H), 3.05 (s, 3H), 2.46 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 175.4, 171.5, 171.2, 158.9, 153.6, 136.3, 135.6, 134.9, 127.9, 125.5, 123.6, 118.0, 114.2, 23.8, 21.0; HRMS (EI⁺) m/z calcd. for C₁₅H₁₁NNaO₄⁺ [M+Na]⁺: 292.0580, found: 292.0582.

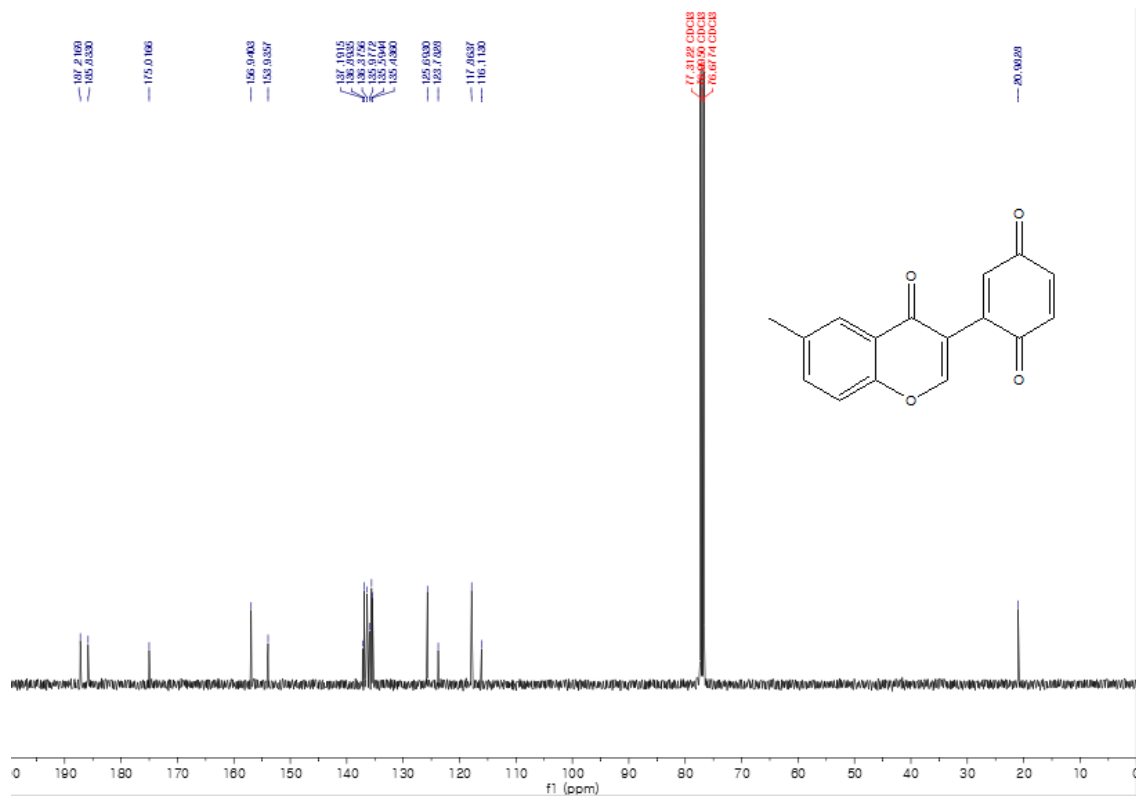
Appendix I

Spectral Copies of ^1H and ^{13}C NMR Data Obtained in this Study

2-(6-methyl-4-oxo-4H-chromen-3-yl)cyclohexa-2,5-diene-1,4-dione (3a)

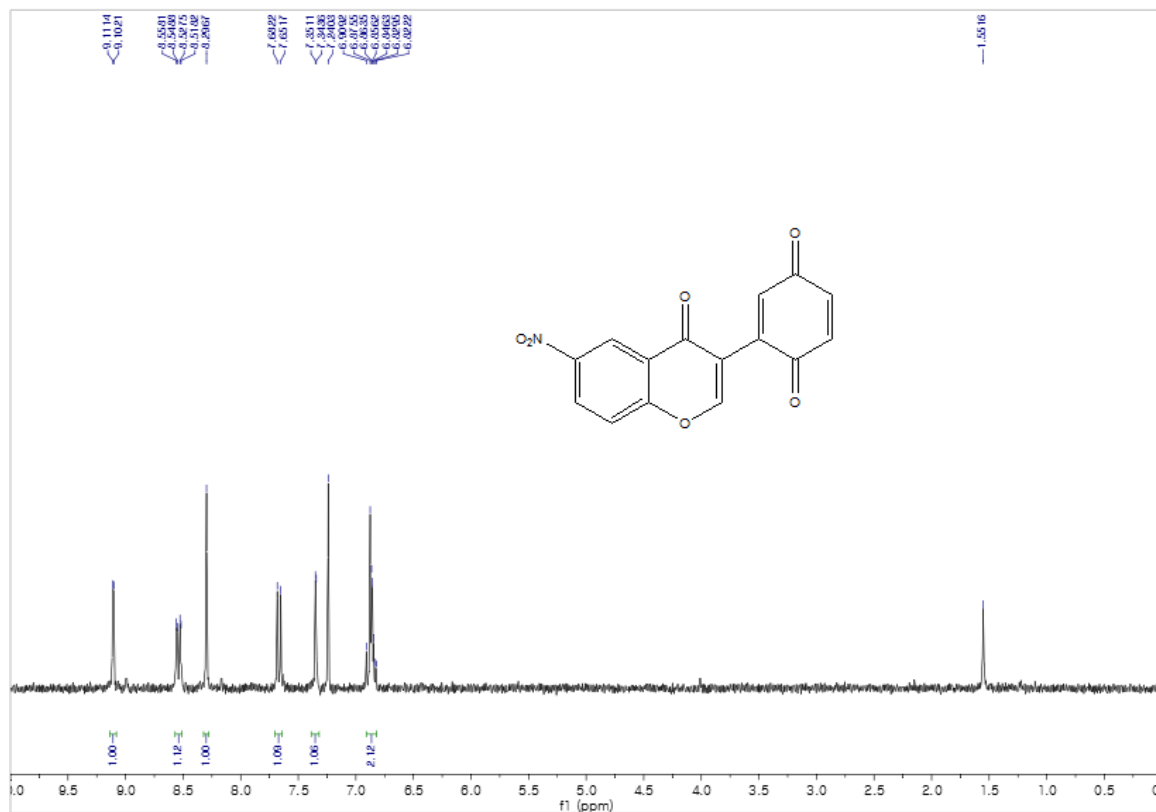


300 MHz, ^1H NMR in CDCl_3

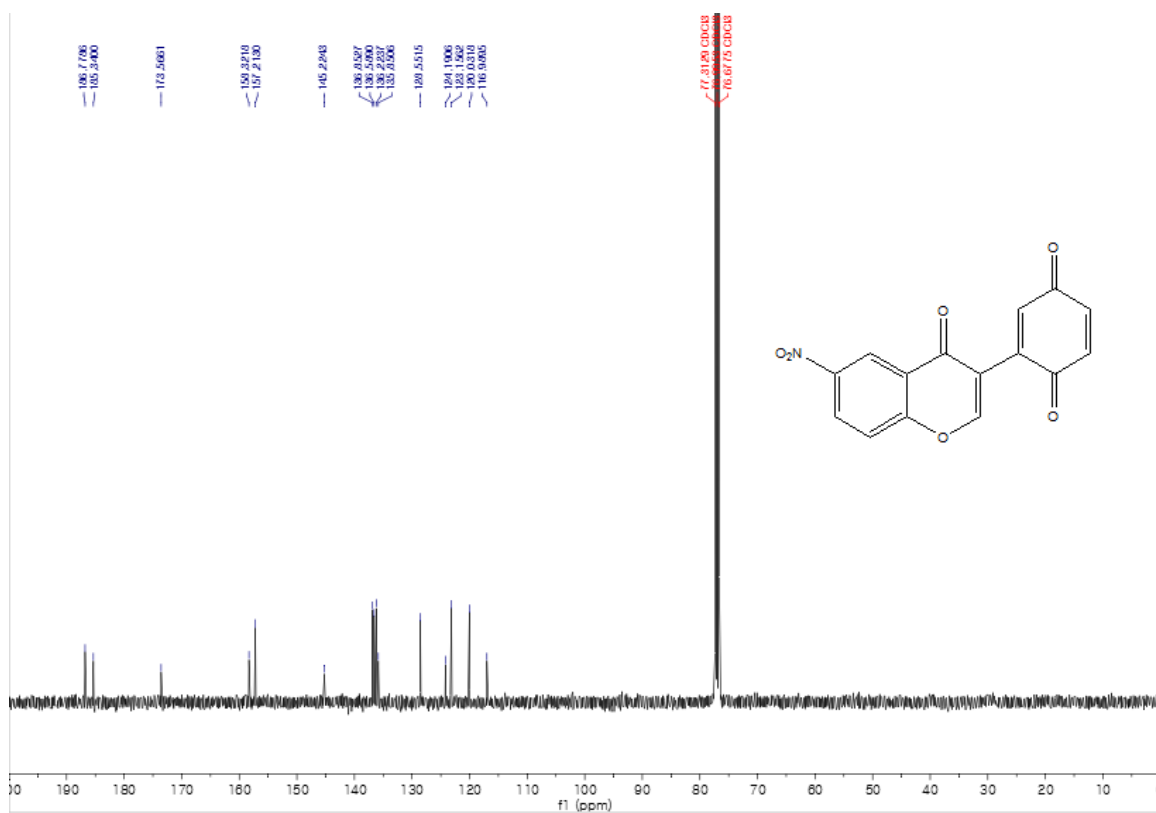


100 MHz, ^{13}C NMR in CDCl_3

2-(6-nitro-4-oxo-4H-chromen-3-yl)cyclohexa-2,5-diene-1,4-dione (3c)

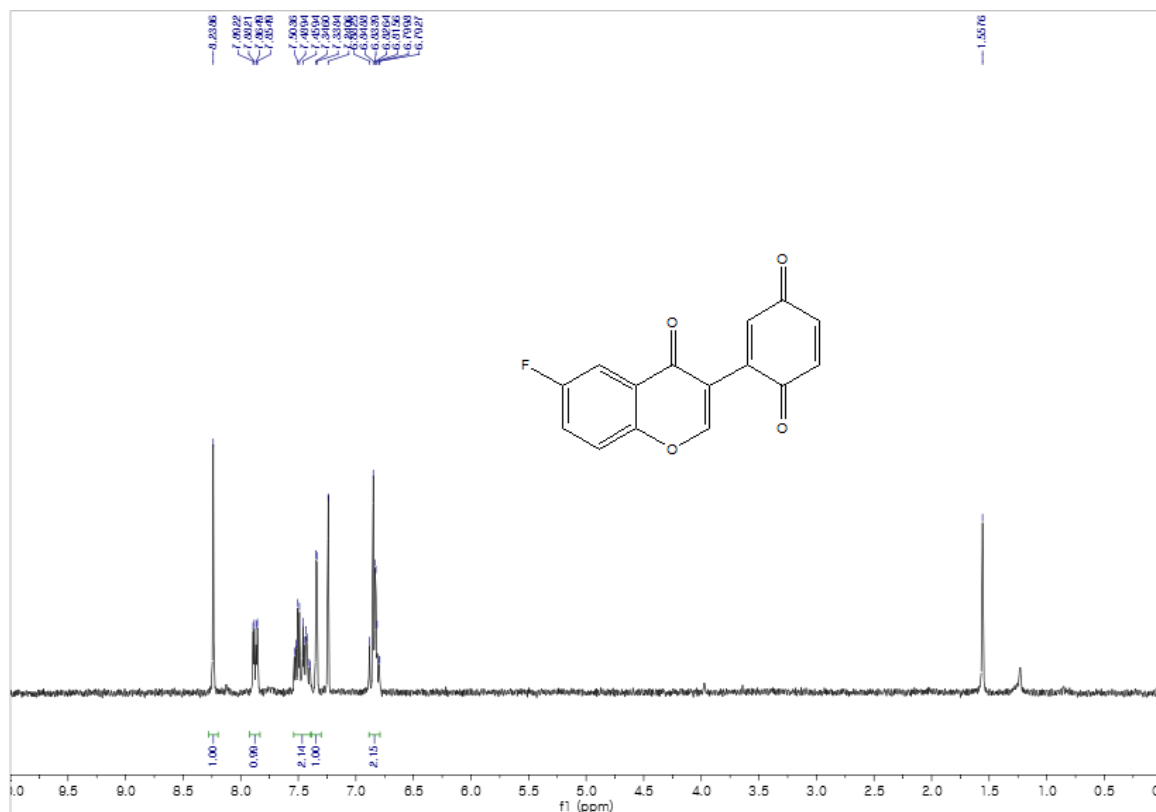


300 MHz, ^1H NMR in CDCl_3

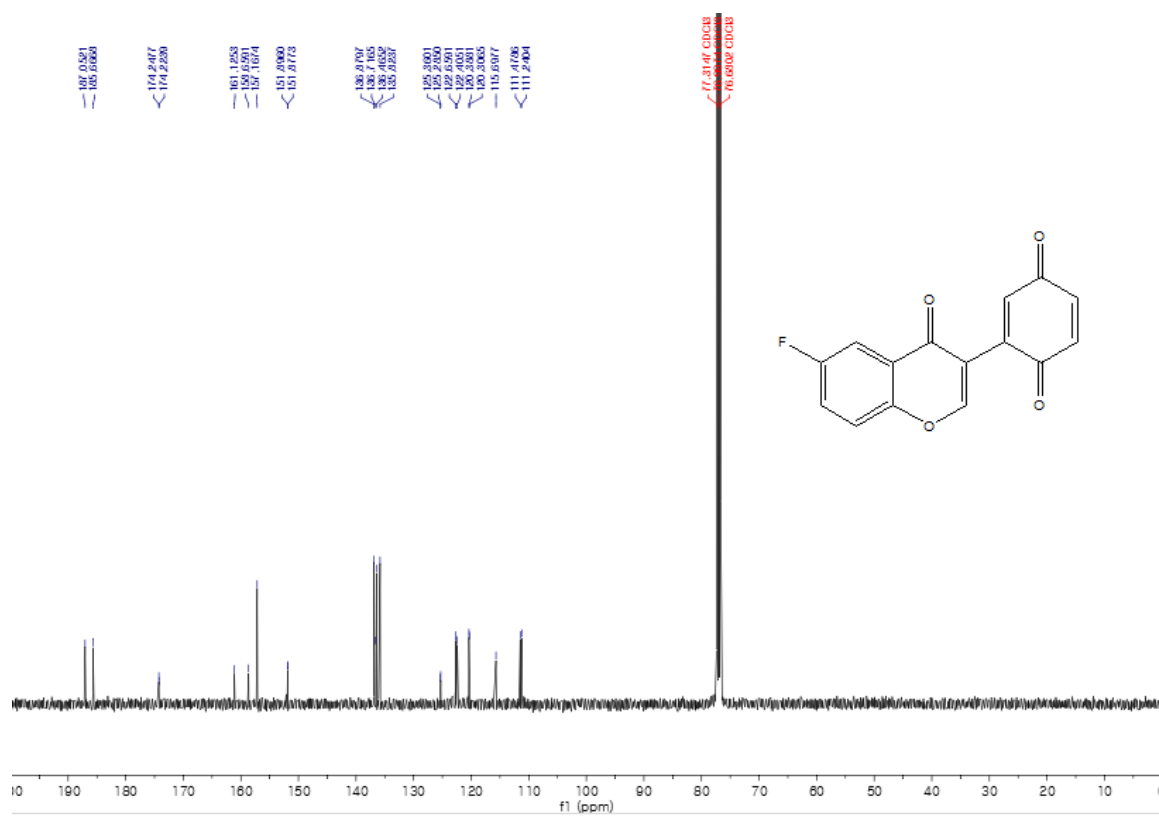


100 MHz, ^{13}C NMR in CDCl_3

2-(6-fluoro-4-oxo-4H-chromen-3-yl)cyclohexa-2,5-diene-1,4-dione (3d)

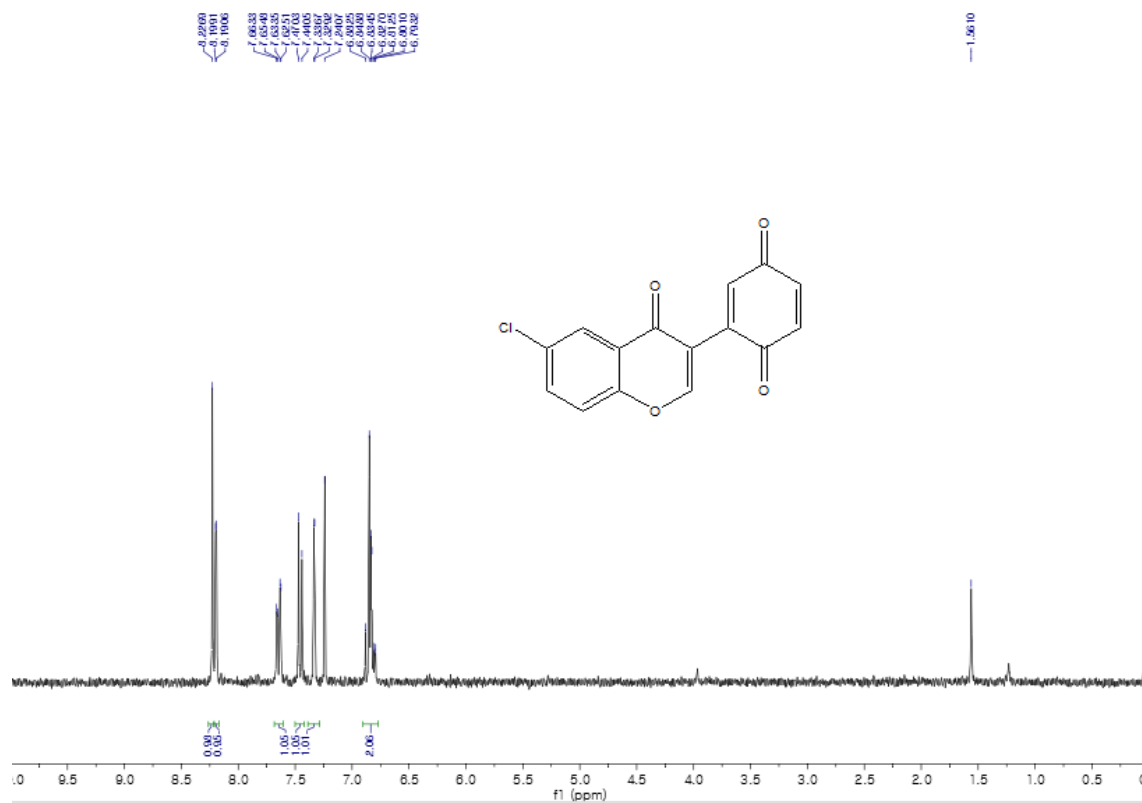


300 MHz, ^1H NMR in CDCl_3

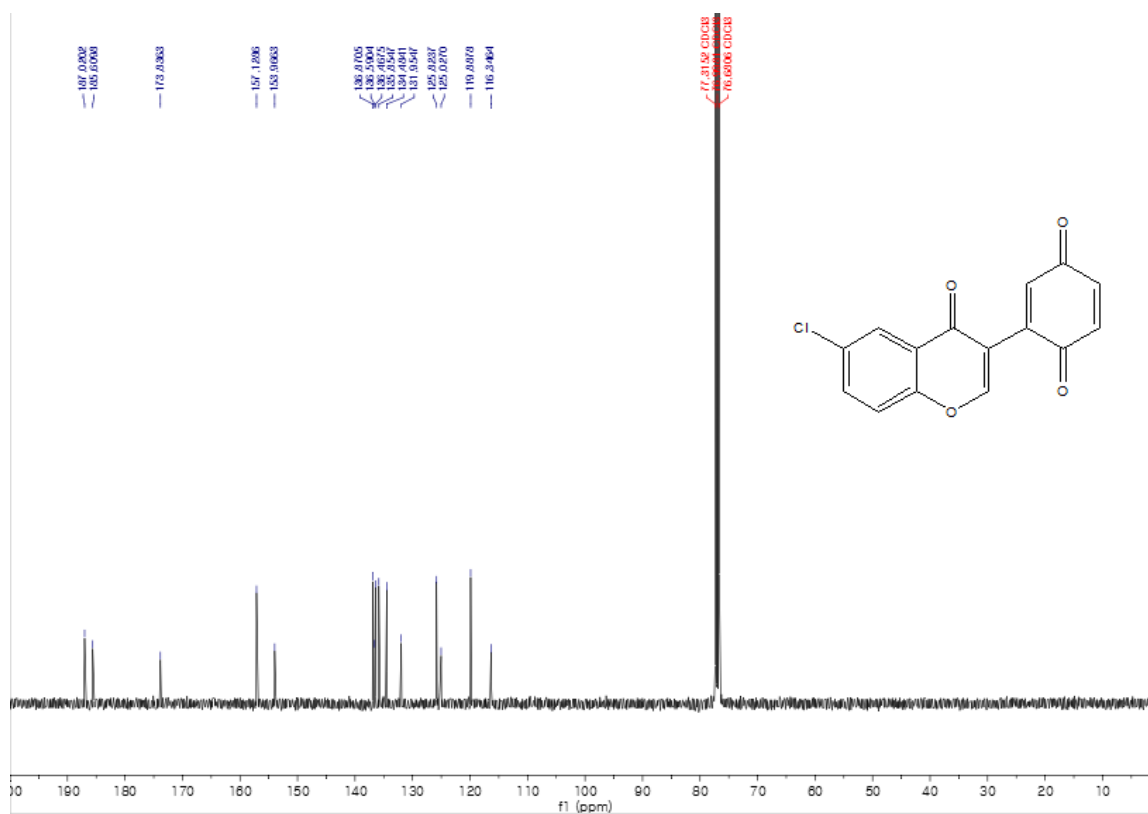


100 MHz, ^{13}C NMR in CDCl_3

2-(6-chloro-4-oxo-4H-chromen-3-yl)cyclohexa-2,5-diene-1,4-dione (3e)

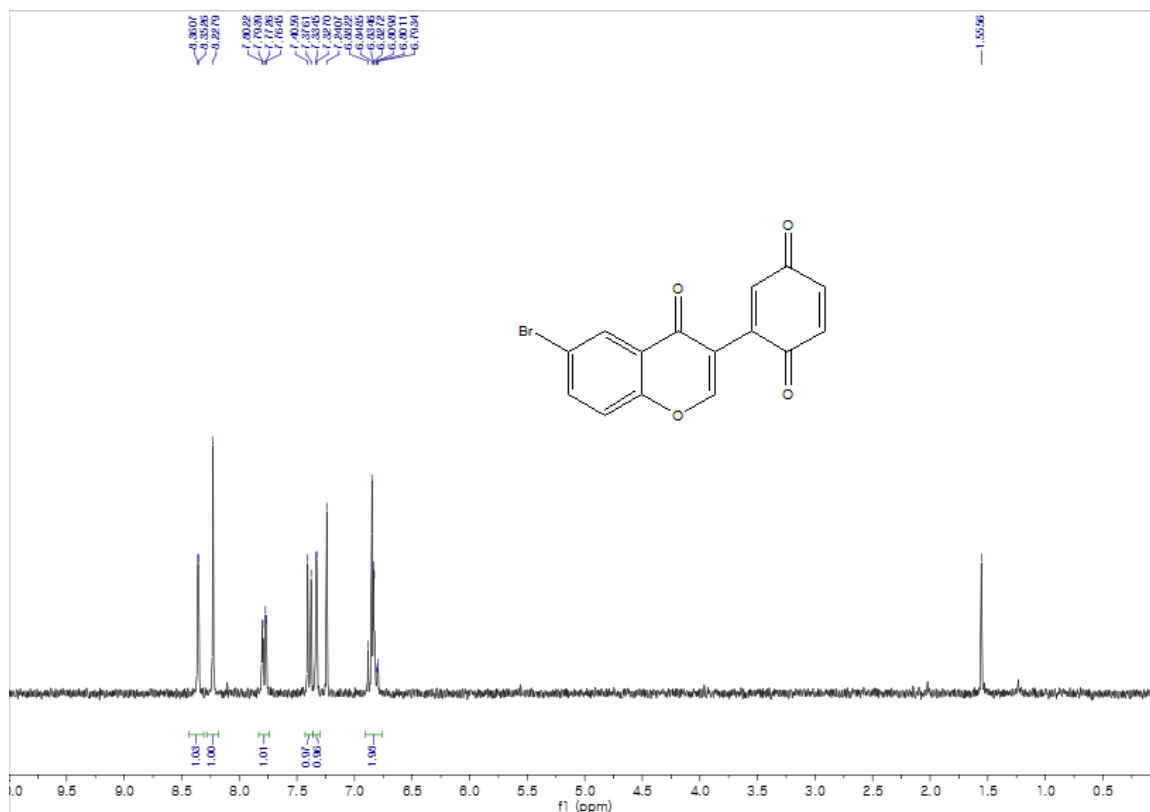


300 MHz, ^1H NMR in CDCl_3

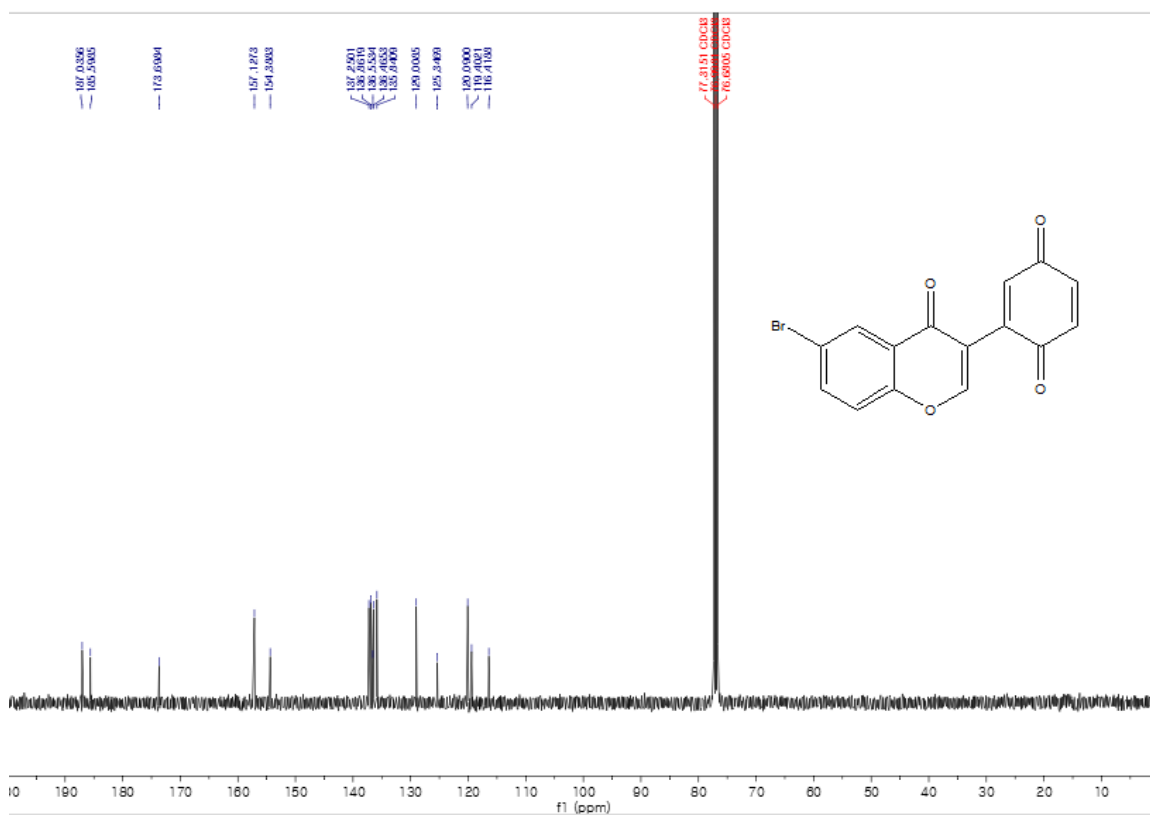


100 MHz, ^{13}C NMR in CDCl_3

2-(6-bromo-4-oxo-4H-chromen-3-yl)cyclohexa-2,5-diene-1,4-dione (3f)

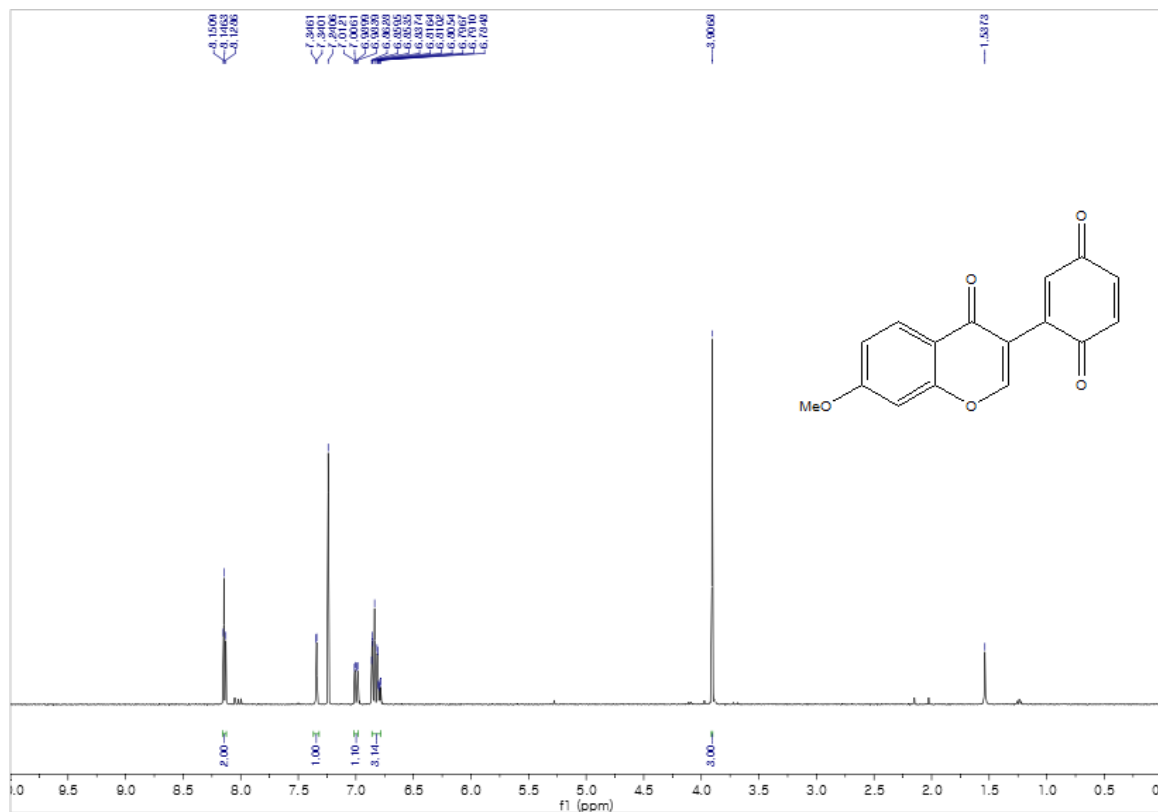


300 MHz, ¹H NMR in CDCl₃

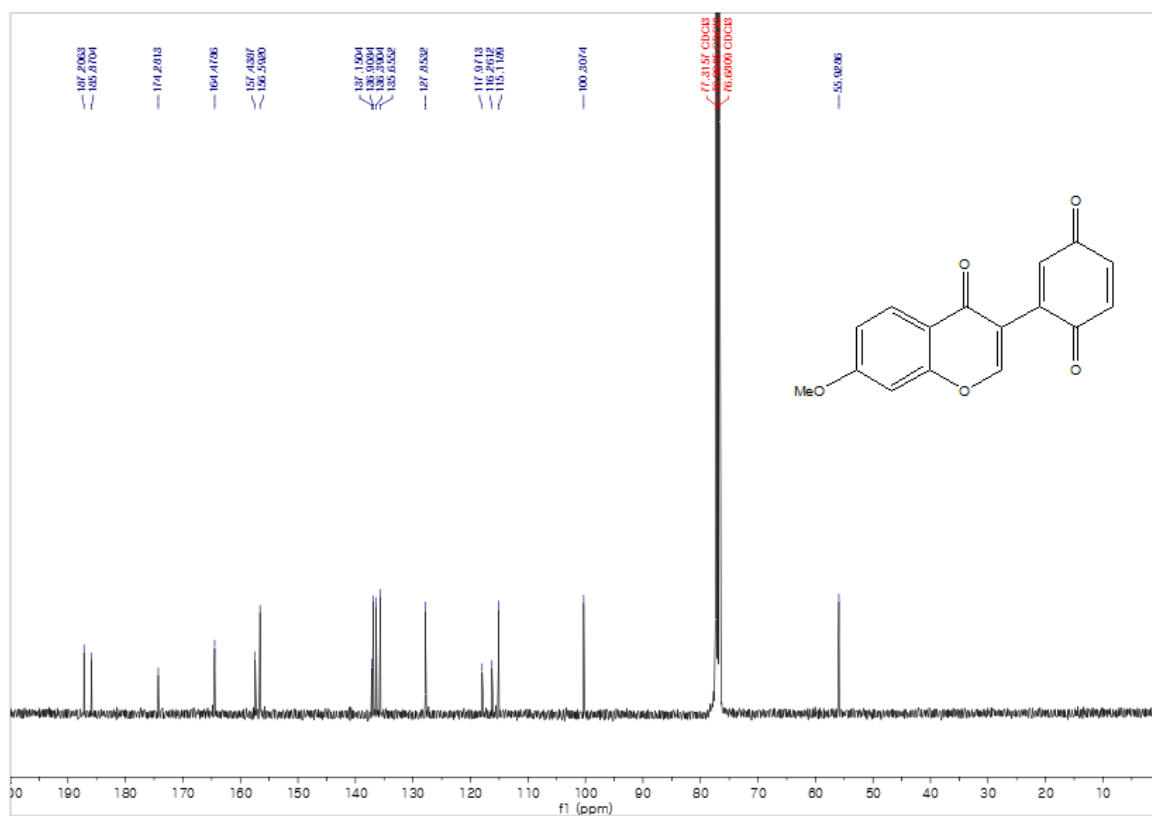


100 MHz, ¹³C NMR in CDCl₃

2-(7-methoxy-4-oxo-4H-chromen-3-yl)cyclohexa-2,5-diene-1,4-dione (3g)

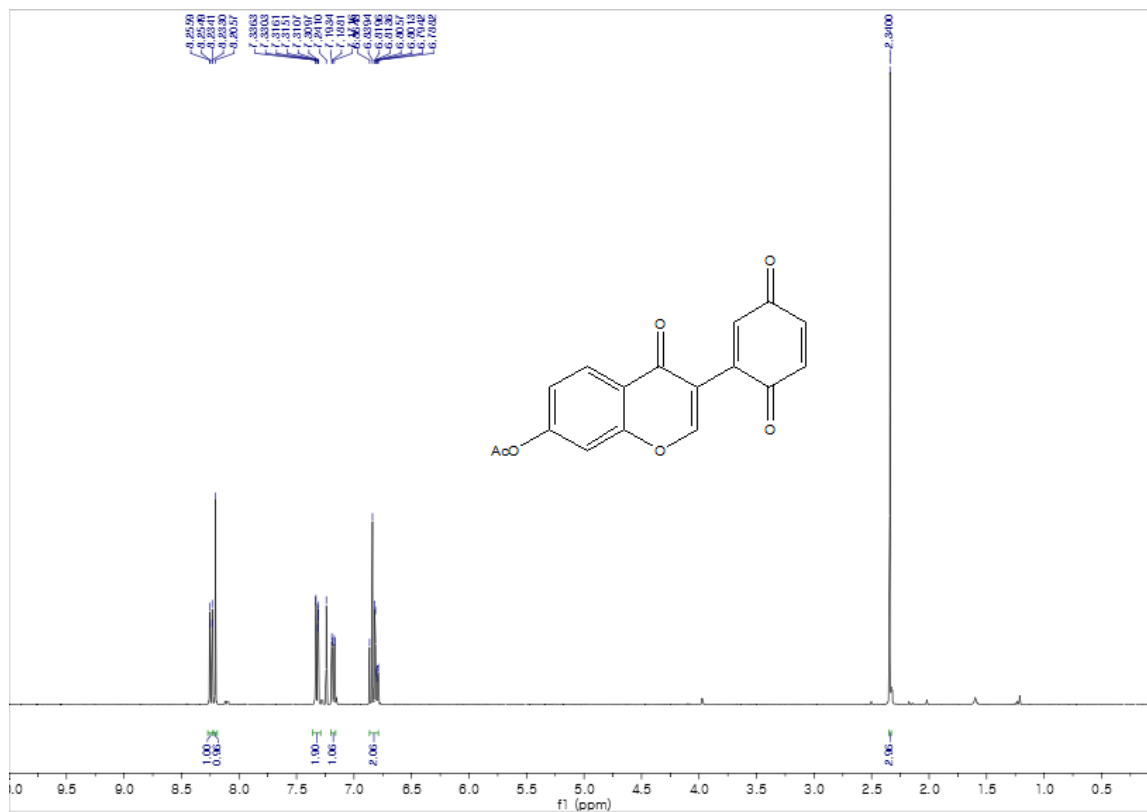


400 MHz, ^1H NMR in CDCl_3

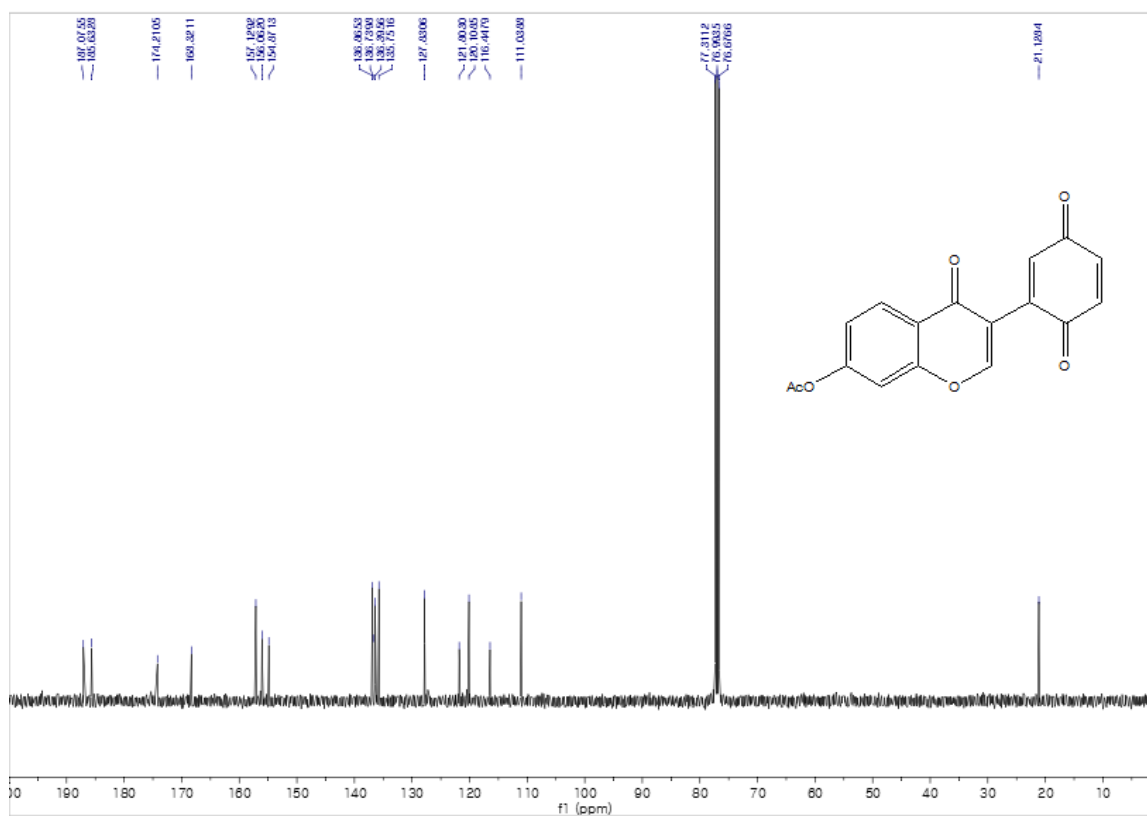


100 MHz, ^{13}C NMR in CDCl_3

3-(3,6-dioxocyclohexa-1,4-dienyl)-4-oxo-4H-chromen-7-yl acetate (3h)

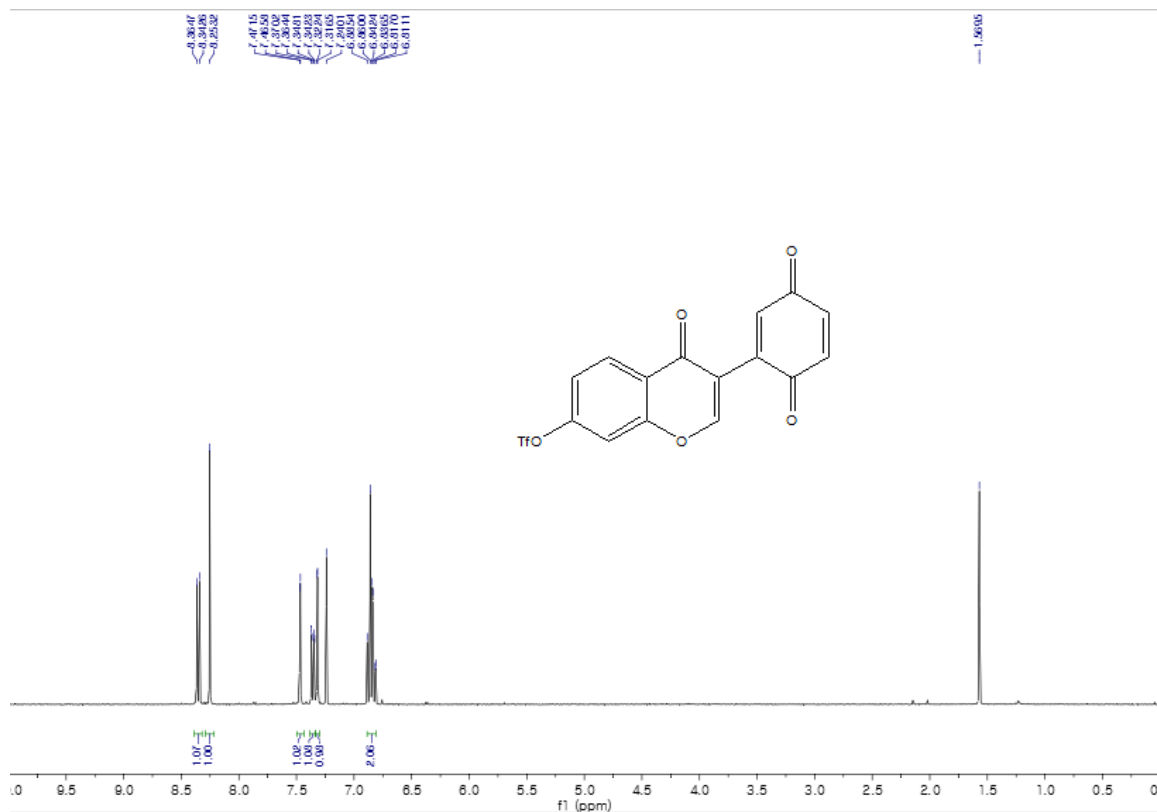


400 MHz, ^1H NMR in CDCl_3

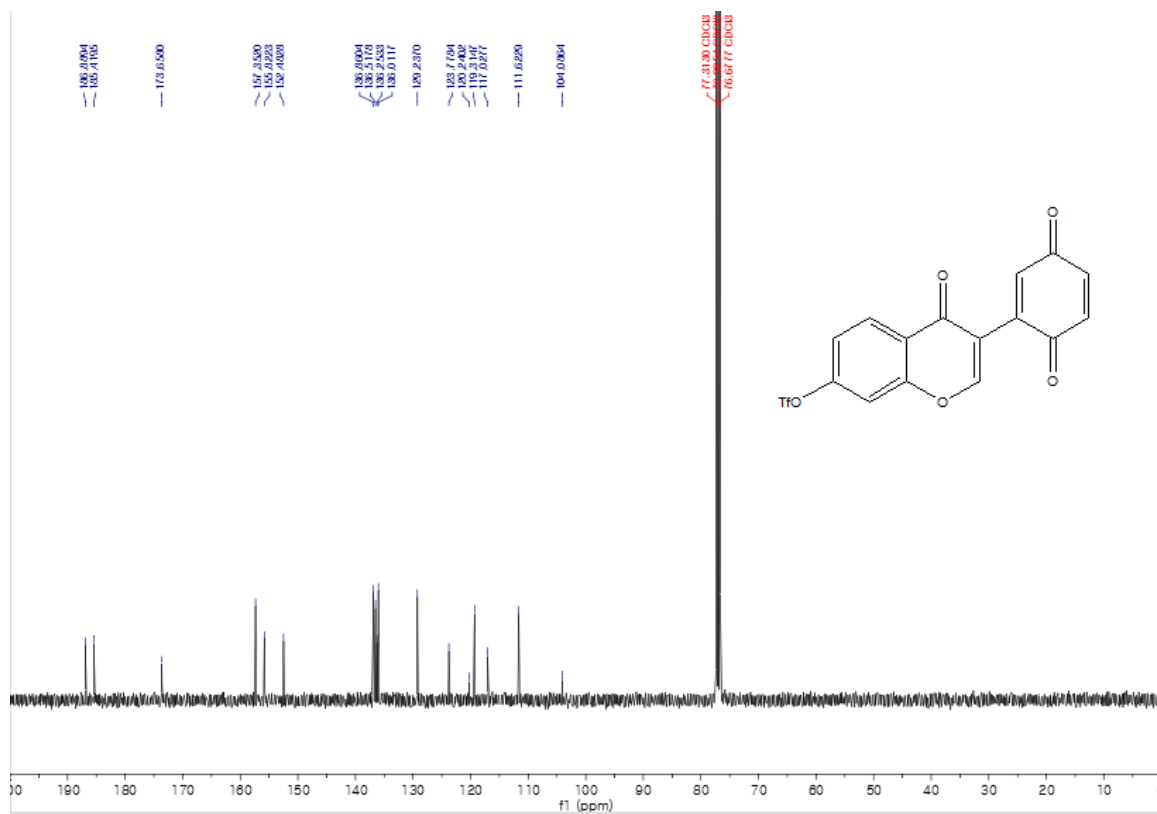


100 MHz, ^{13}C NMR in CDCl_3

3-(3,6-dioxocyclohexa-1,4-dienyl)-4-oxo-4H-chromen-7-yl trifluoromethanesulfonate (3i)

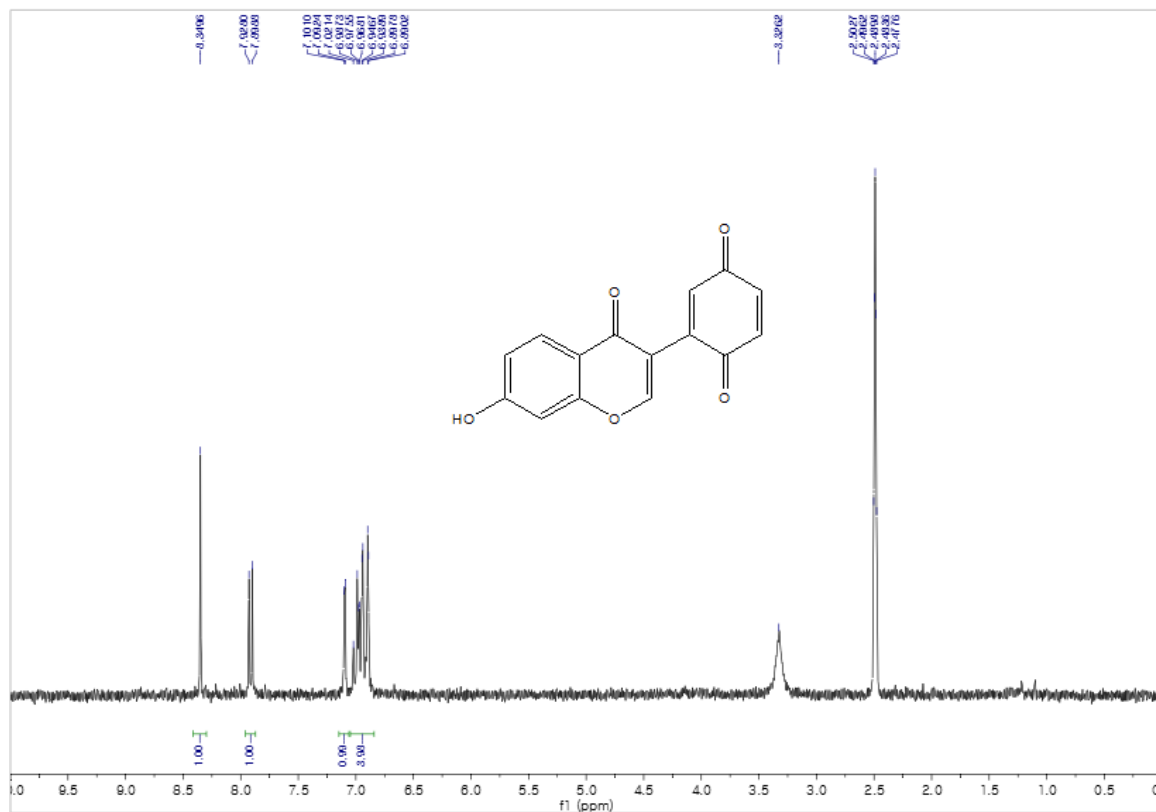


400 MHz, ^1H NMR in CDCl_3

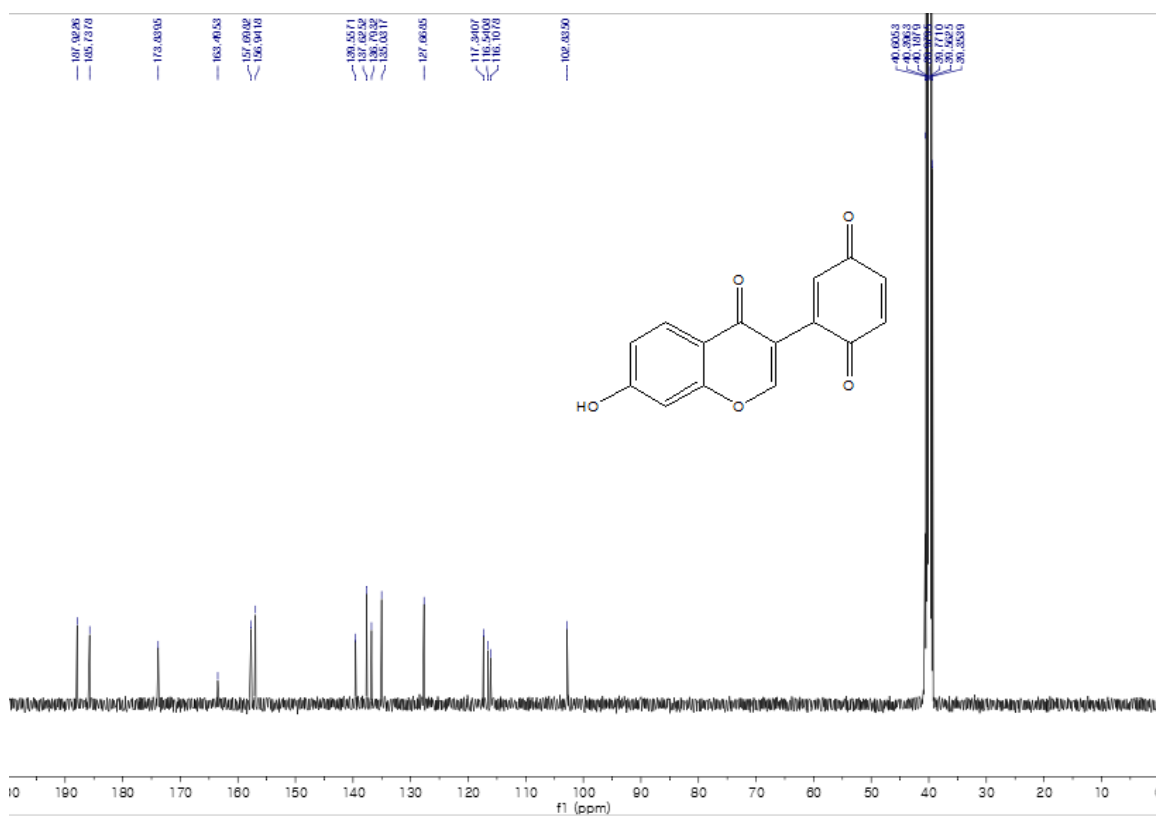


100 MHz, ^{13}C NMR in CDCl_3

2-(7-hydroxy-4-oxo-4H-chromen-3-yl)cyclohexa-2,5-diene-1,4-dione (3j)

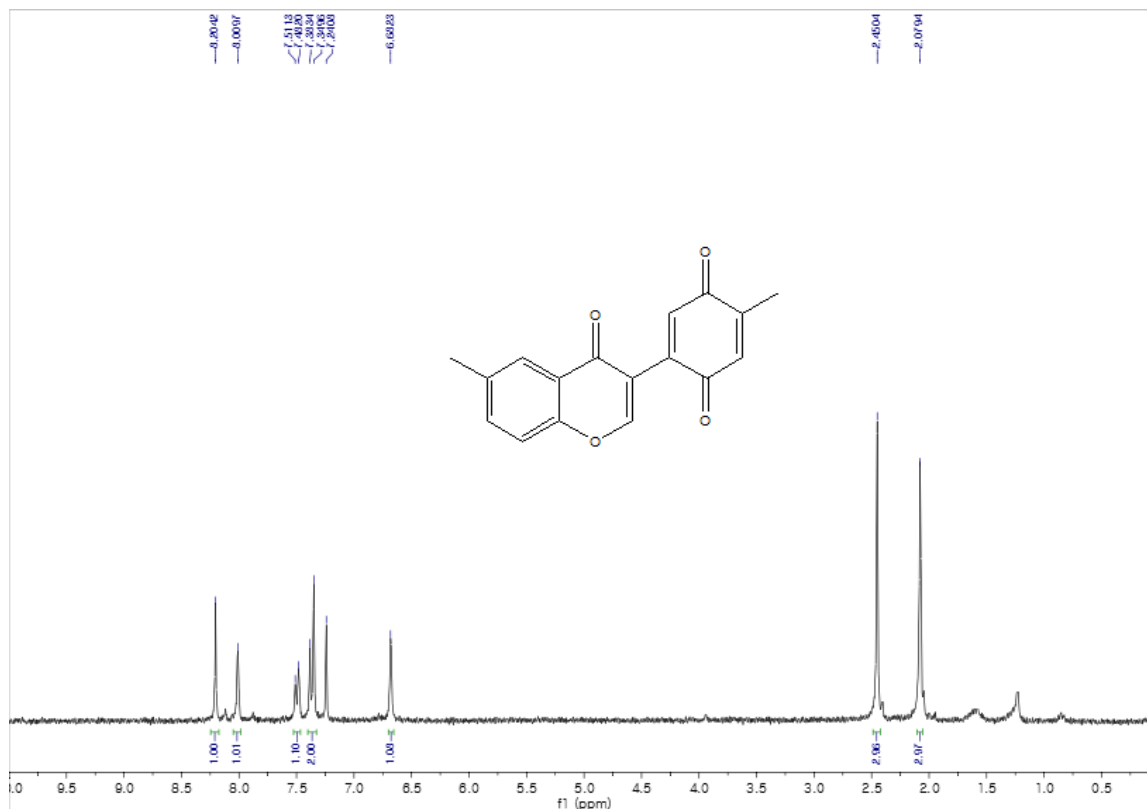


300 MHz, ^1H NMR in DMSO-d_6

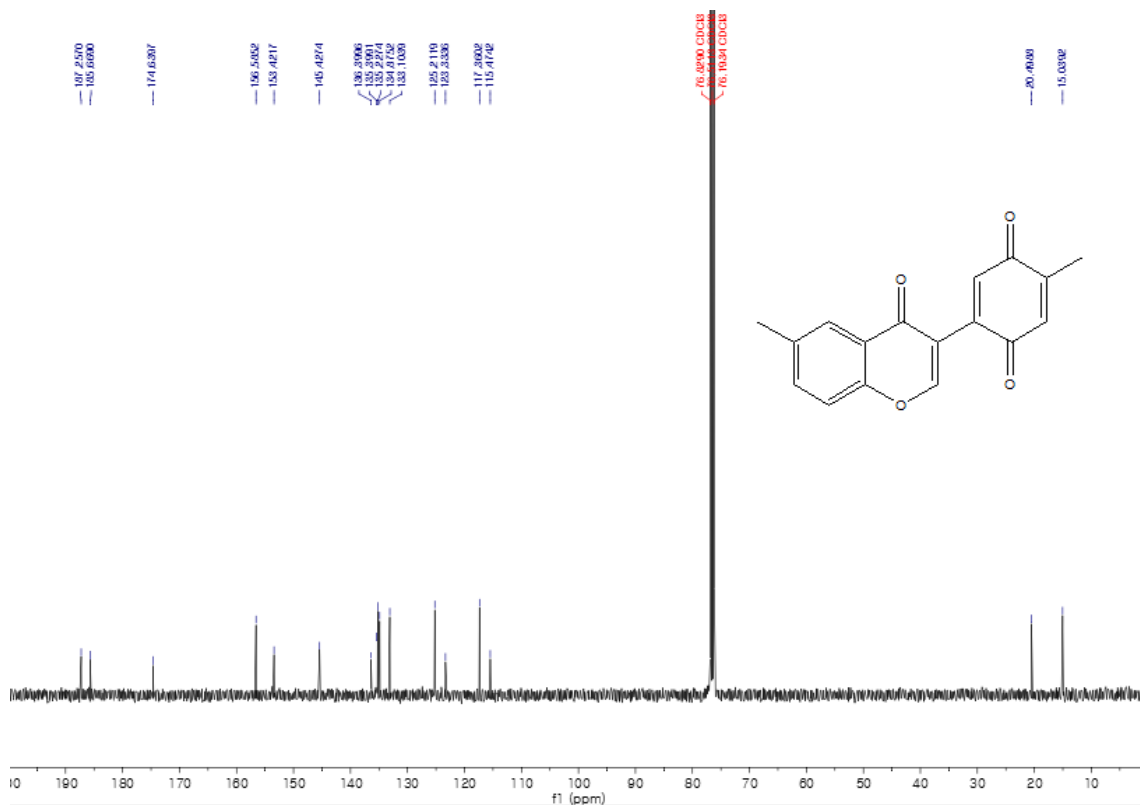


100 MHz, ^{13}C NMR in DMSO-d_6

2-methyl-5-(6-methyl-4-oxo-4H-chromen-3-yl)cyclohexa-2,5-diene-1,4-dione (3k, major)

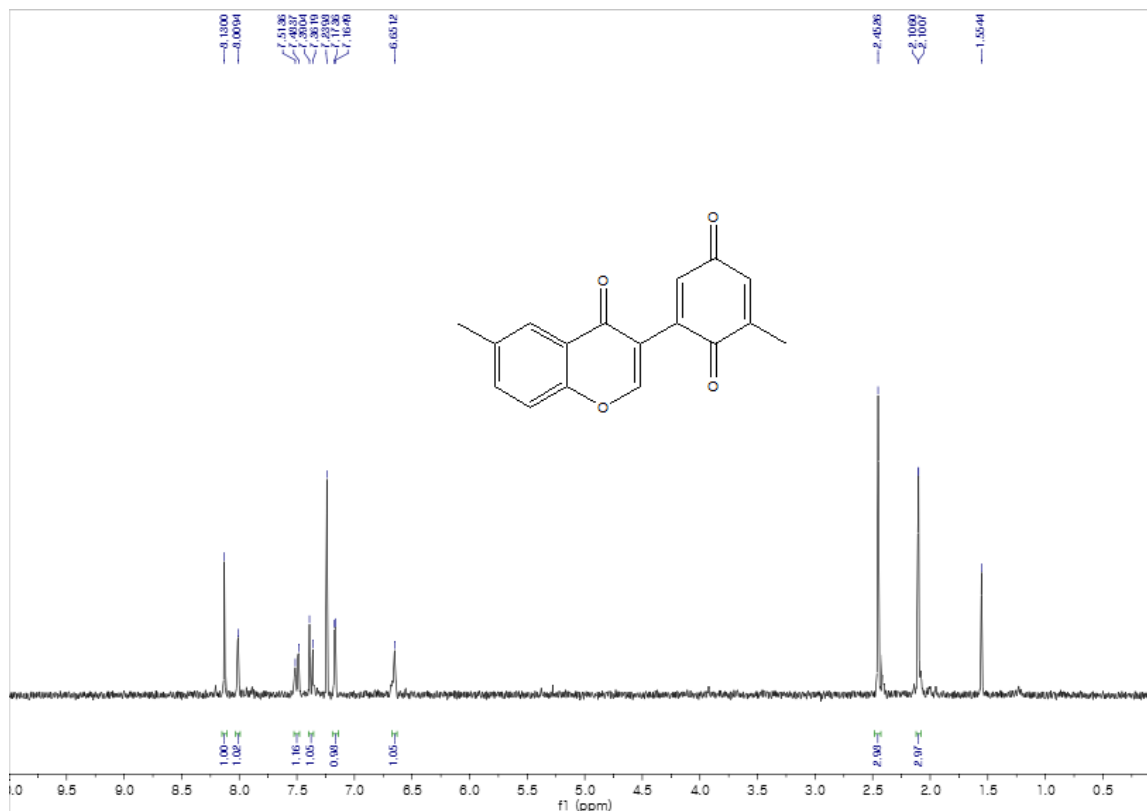


300 MHz, ¹H NMR in CDCl₃

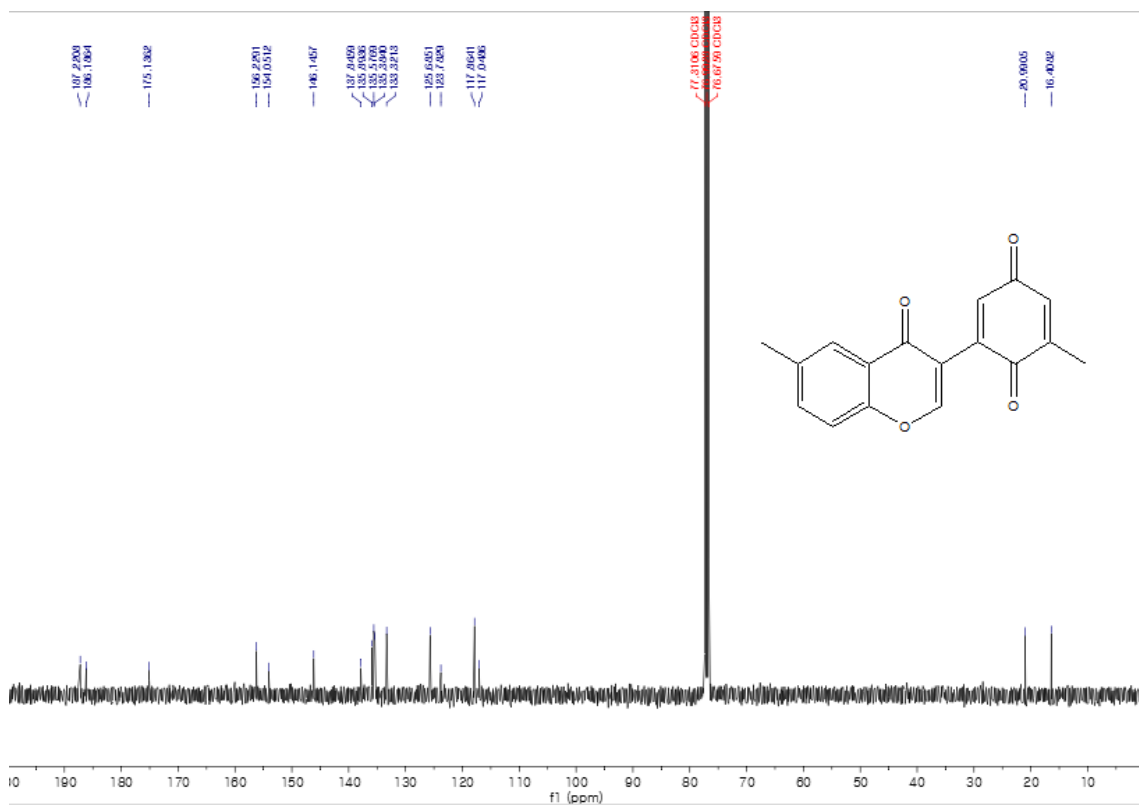


100 MHz, ¹³C NMR in CDCl₃

2-methyl-6-(6-methyl-4-oxo-4H-chromen-3-yl)cyclohexa-2,5-diene-1,4-dione (3k)

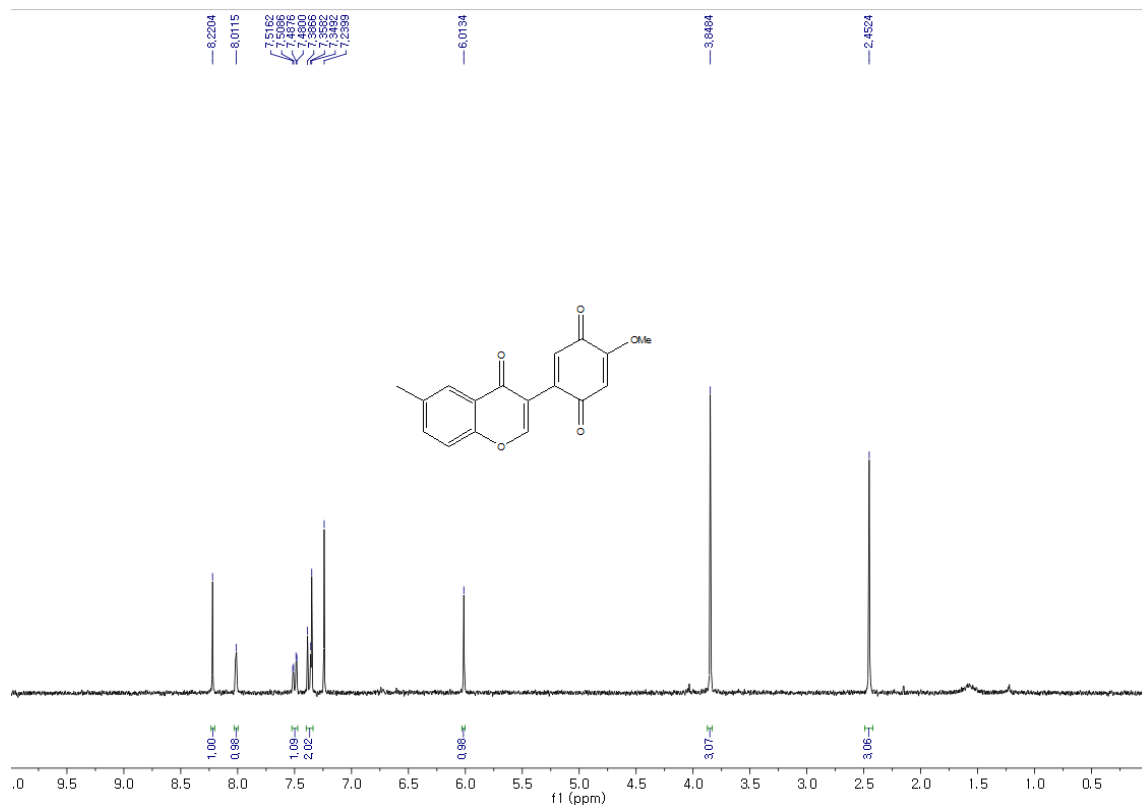


300 MHz, ^1H NMR in CDCl_3

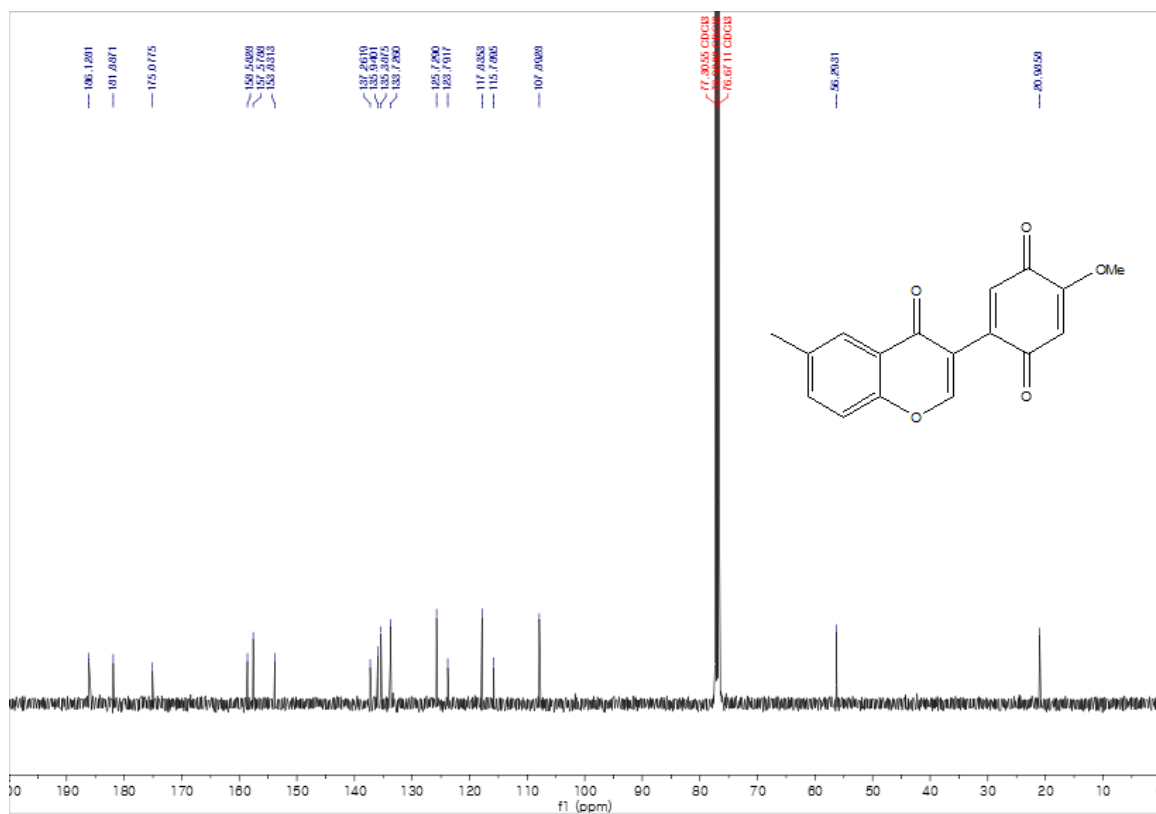


100 MHz, ^{13}C NMR in CDCl_3

2-methoxy-5-(6-methyl-4-oxo-4H-chromen-3-yl)cyclohexa-2,5-diene-1,4-dione (31, major)

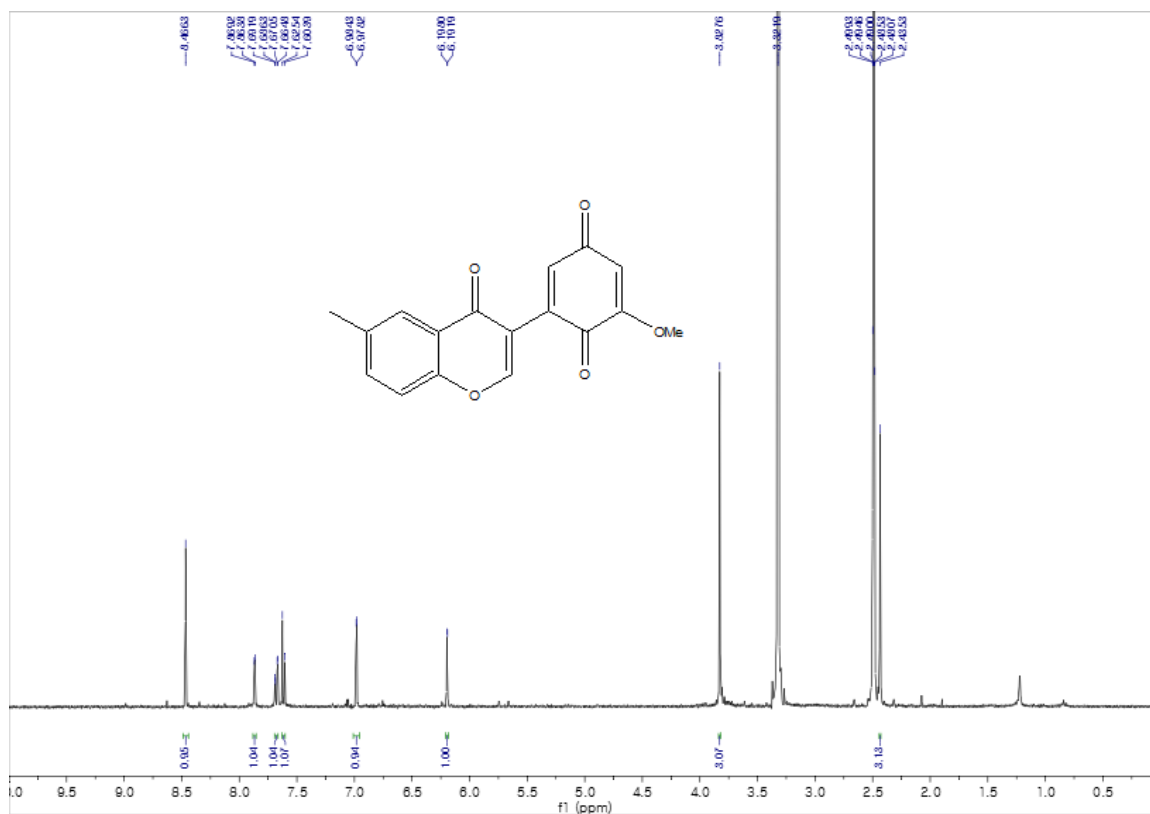


300 MHz, ¹H NMR in CDCl₃

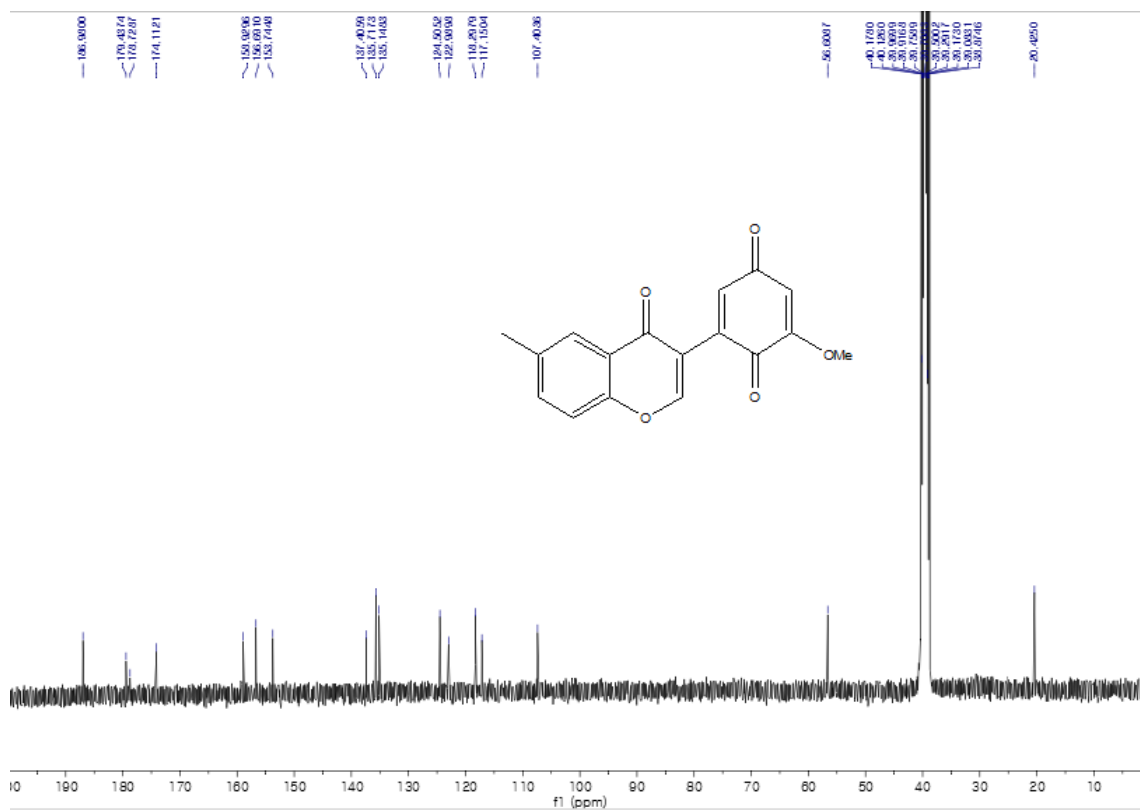


100 MHz, ¹³C NMR in CDCl₃

2-methoxy-6-(6-methyl-4-oxo-4H-chromen-3-yl)cyclohexa-2,5-diene-1,4-dione (3l)

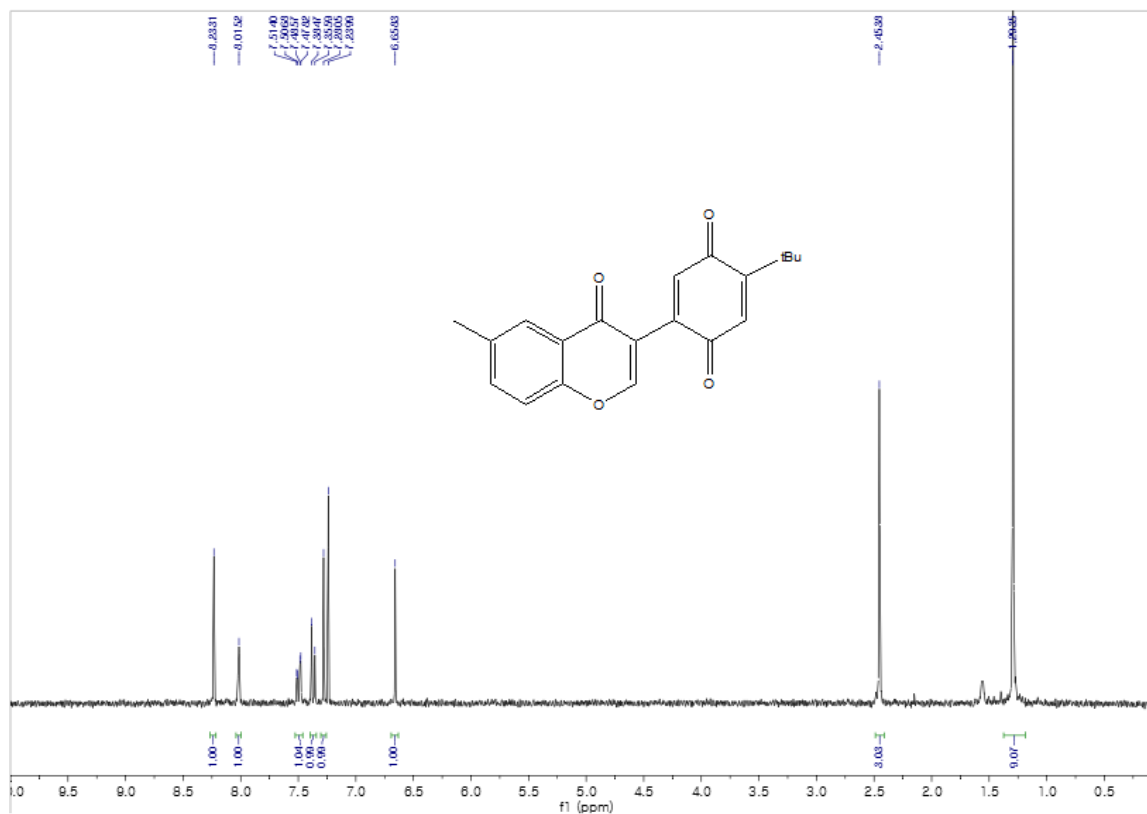


400 MHz, ^1H NMR in DMSO-d_6

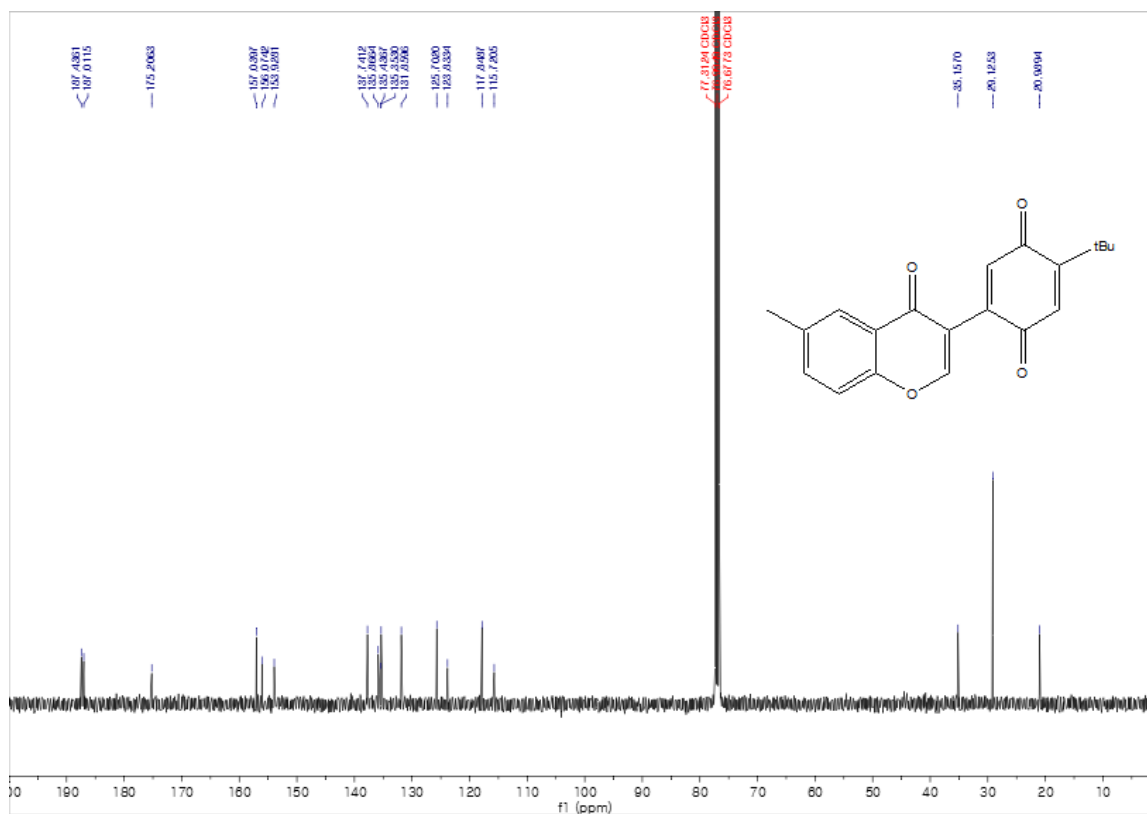


100 MHz, ^{13}C NMR in DMSO-d_6

2-tert-butyl-5-(6-methyl-4-oxo-4H-chromen-3-yl)cyclohexa-2,5-diene-1,4-dione (3m)

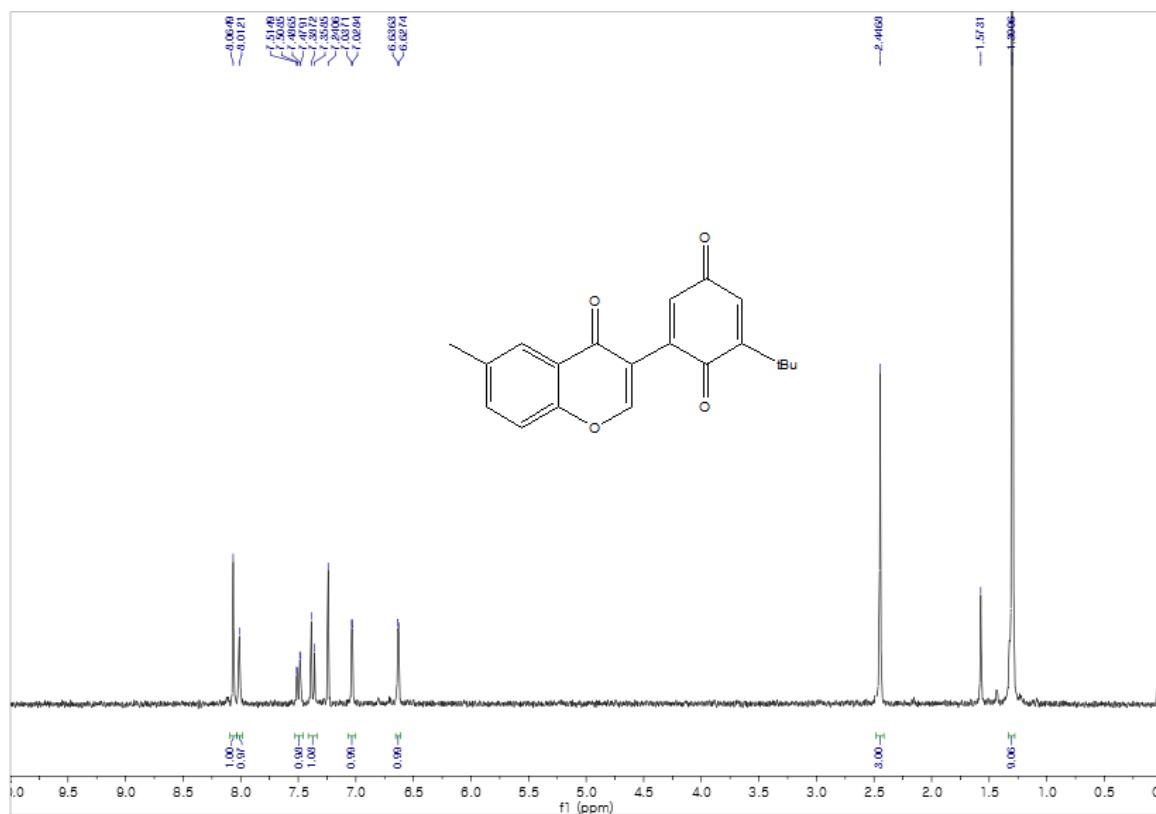


300 MHz, $^1\text{H NMR}$ in CDCl_3

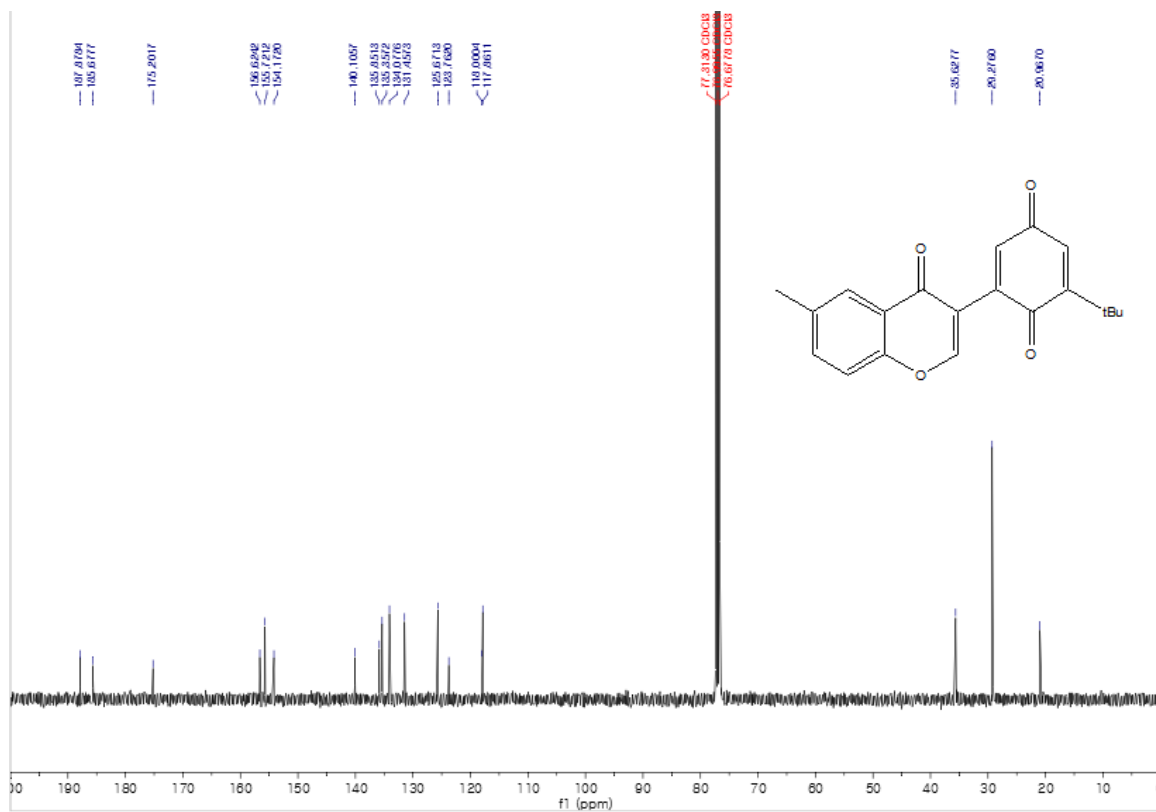


100 MHz, $^{13}\text{C NMR}$ in CDCl_3

2-tert-butyl-6-(6-methyl-4-oxo-4H-chromen-3-yl)cyclohexa-2,5-diene-1,4-dione (3m, major)

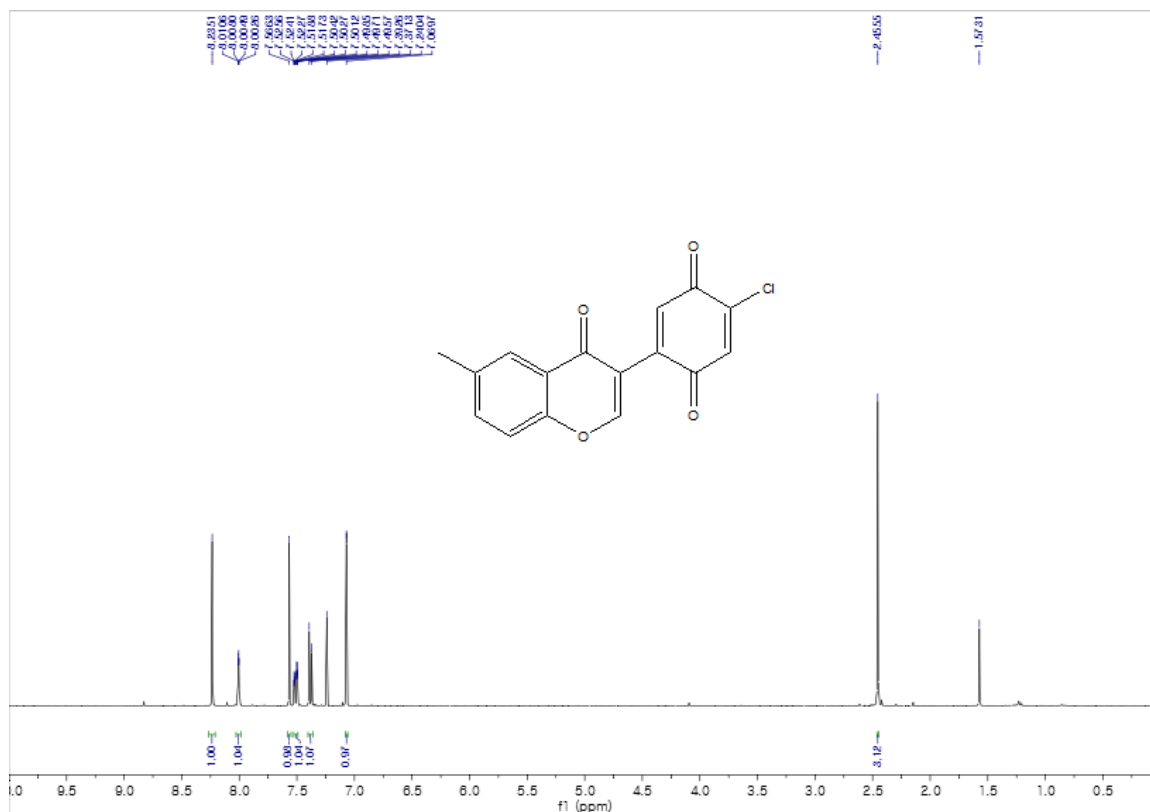


300 MHz, ¹H NMR in CDCl₃

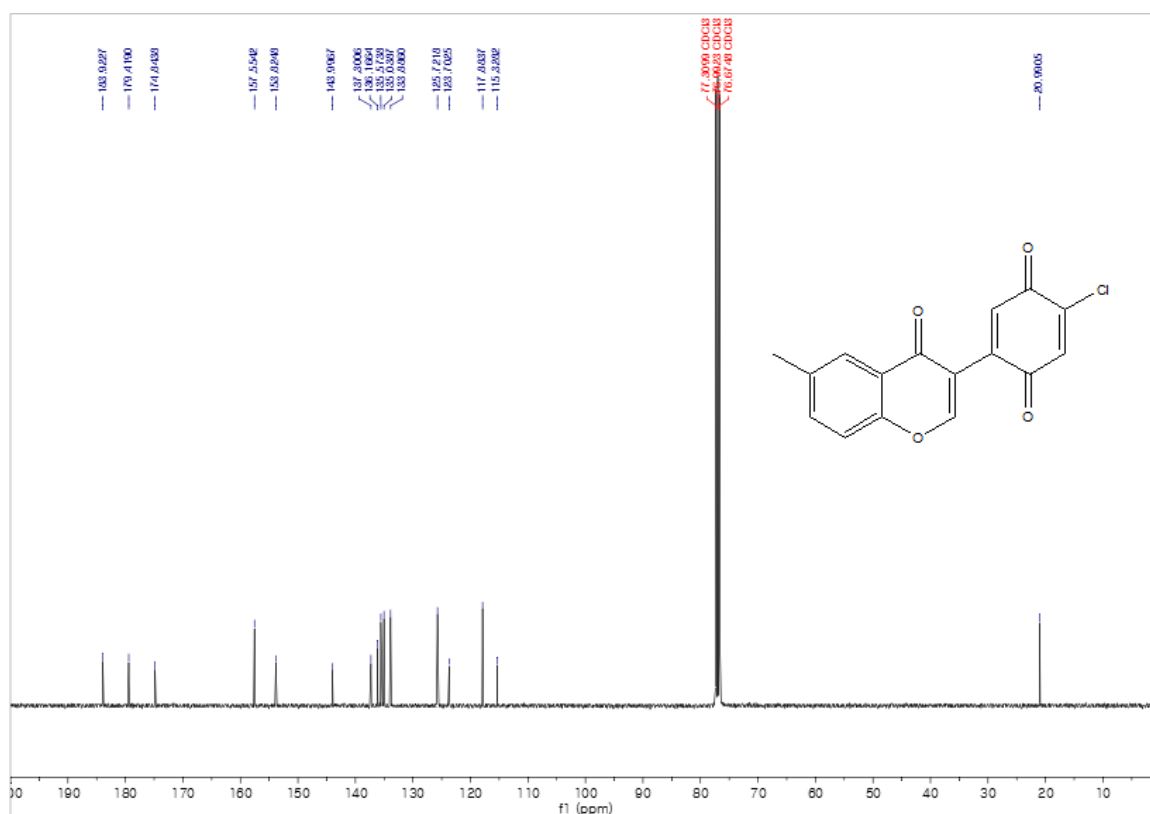


100 MHz, ¹³C NMR in CDCl₃

2-chloro-5-(6-methyl-4-oxo-4H-chromen-3-yl)cyclohexa-2,5-diene-1,4-dione (3n, major)

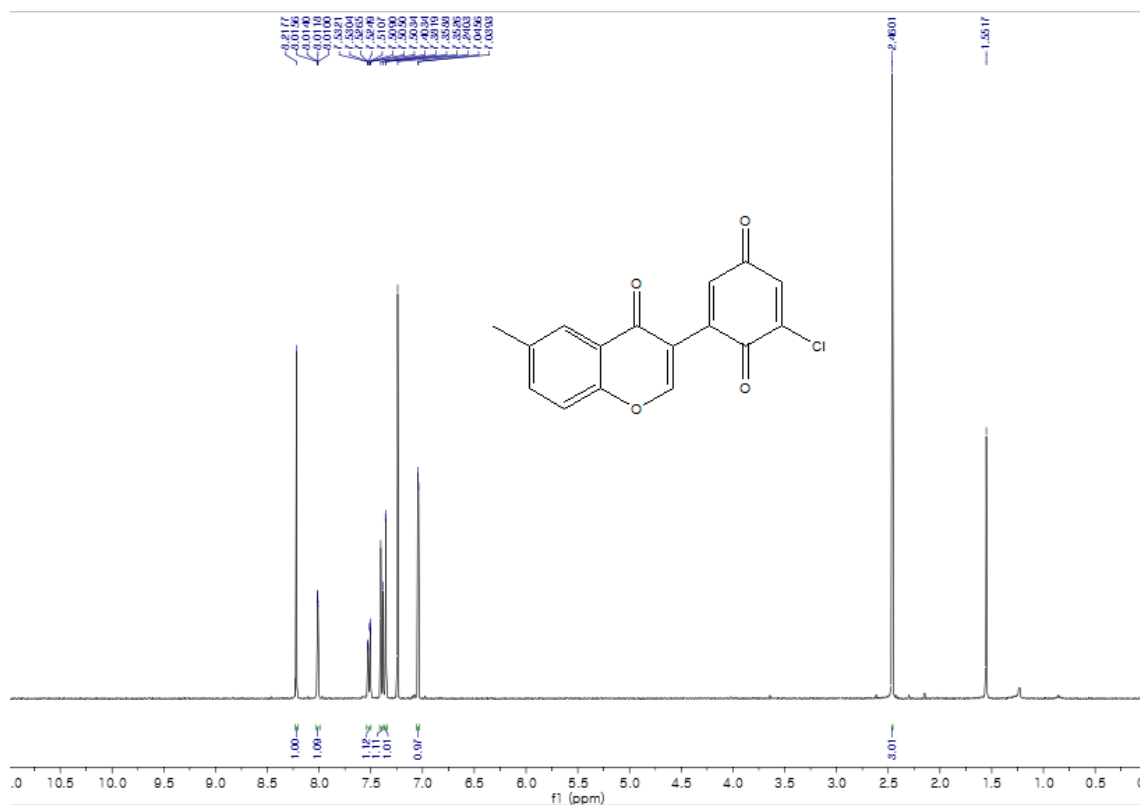


400 MHz, ^1H NMR in CDCl_3

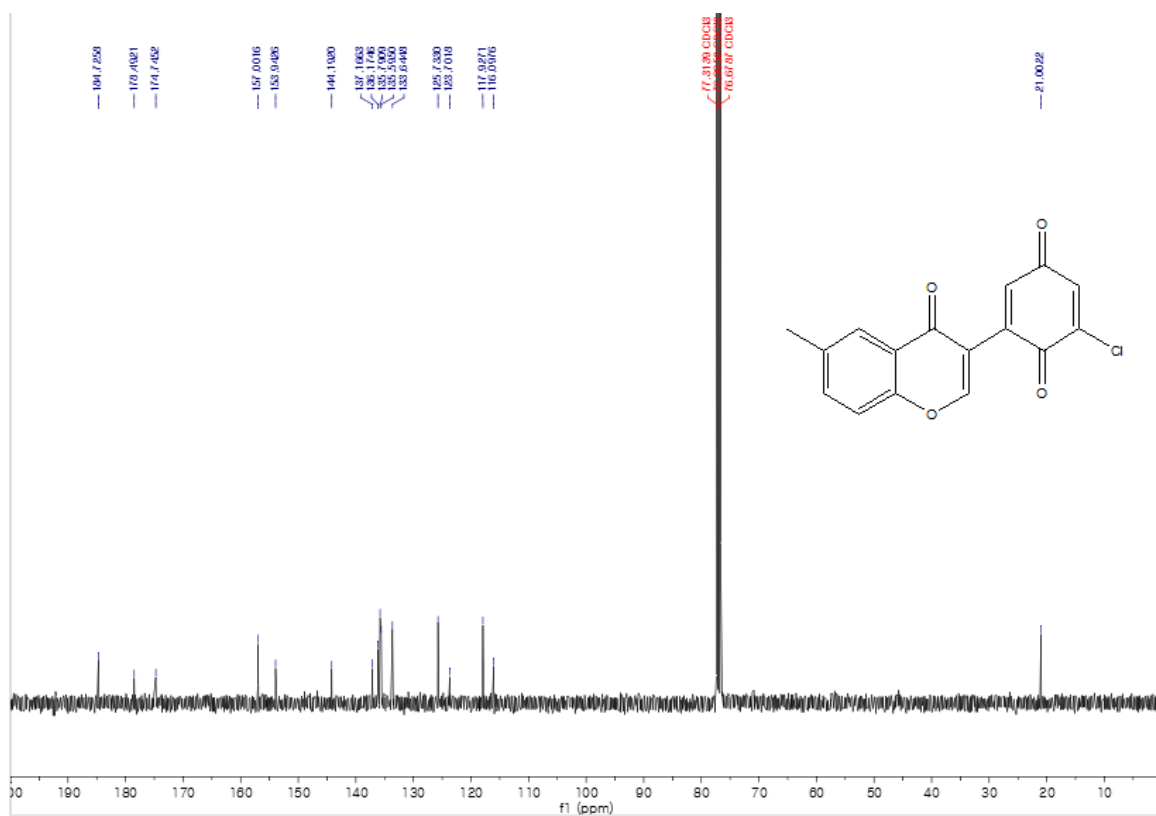


100 MHz, ^{13}C NMR in CDCl_3

2-chloro-6-(6-methyl-4-oxo-4H-chromen-3-yl)cyclohexa-2,5-diene-1,4-dione (3n)



400 MHz, ¹H NMR in CDCl₃

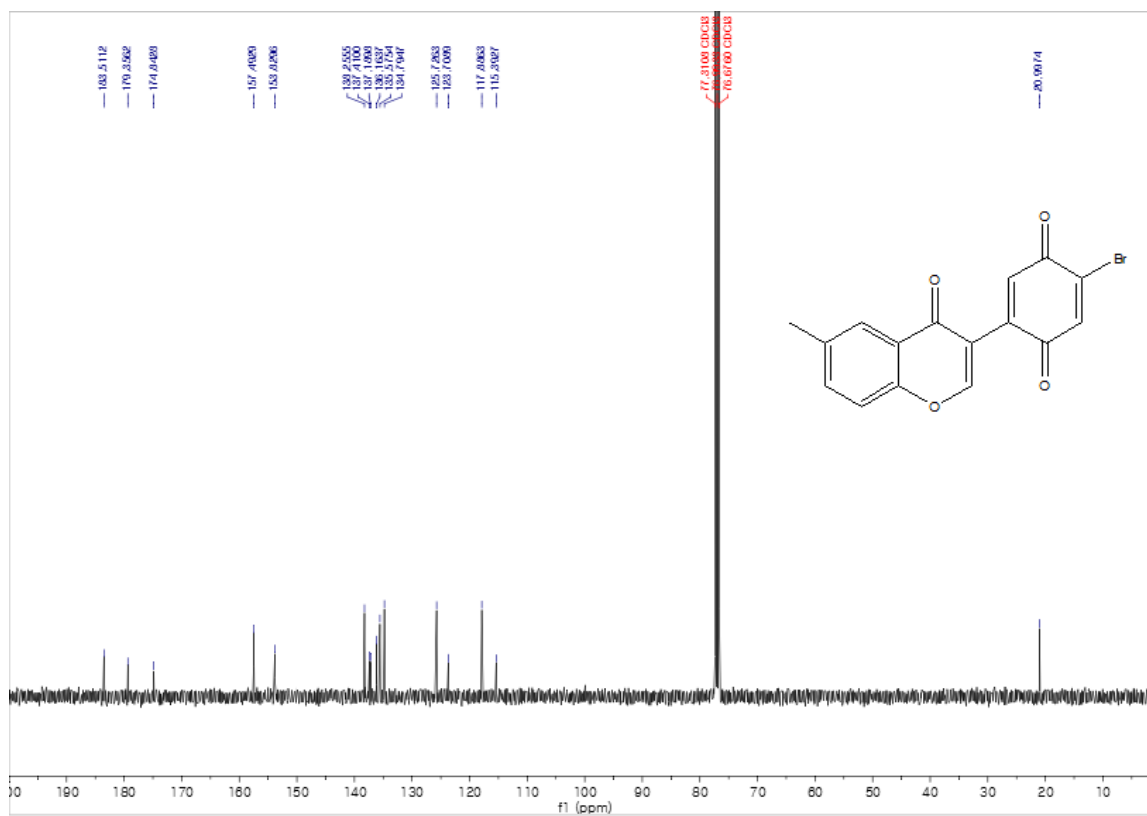


100 MHz, ¹³C NMR in CDCl₃

2-chloro-5-(6-methyl-4-oxo-4H-chromen-3-yl)cyclohexa-2,5-diene-1,4-dione (3o, major)

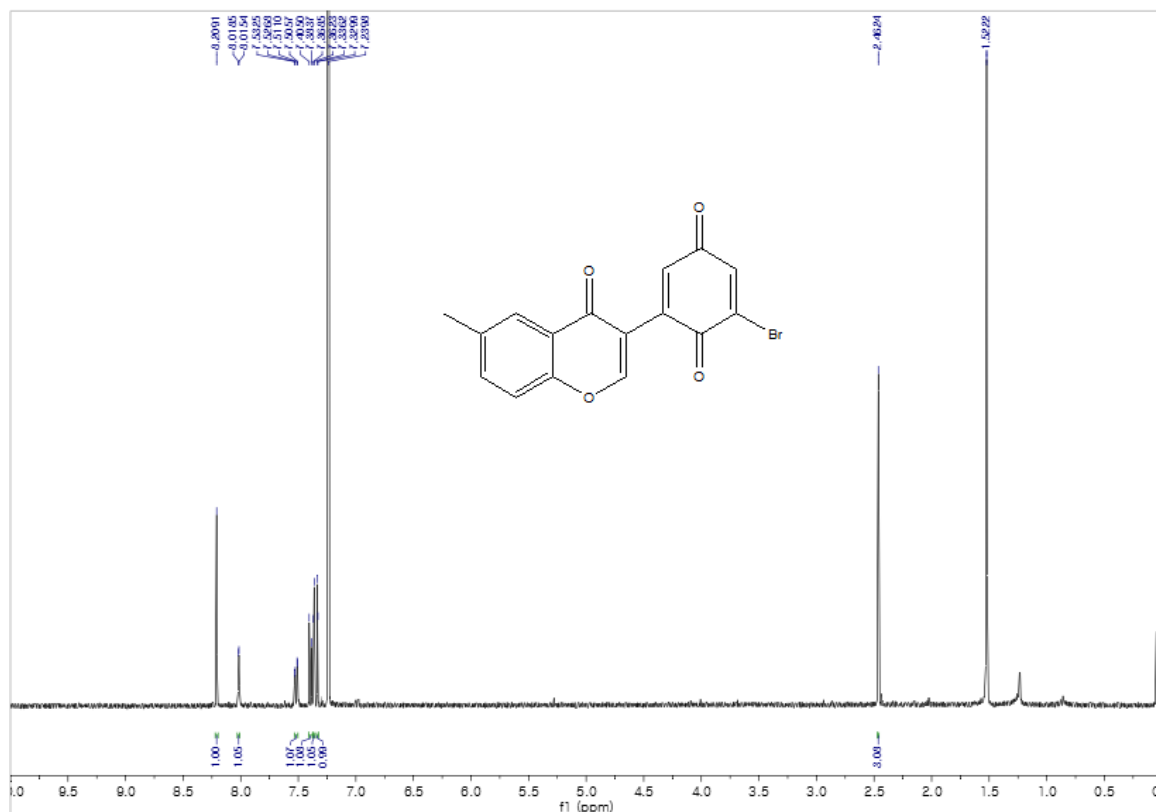


300 MHz, ^1H NMR in CDCl_3

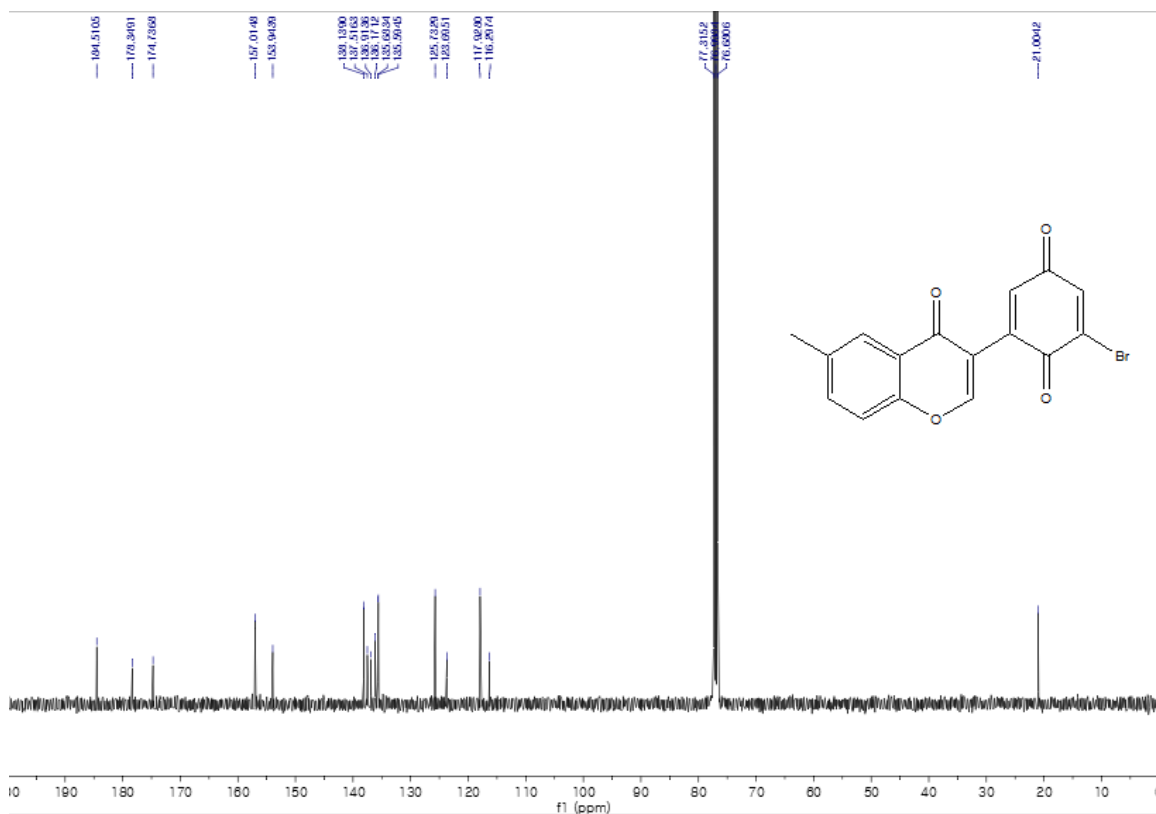


100 MHz, ^{13}C NMR in CDCl_3

2-bromo-6-(6-methyl-4-oxo-4H-chromen-3-yl)cyclohexa-2,5-diene-1,4-dione (3o)

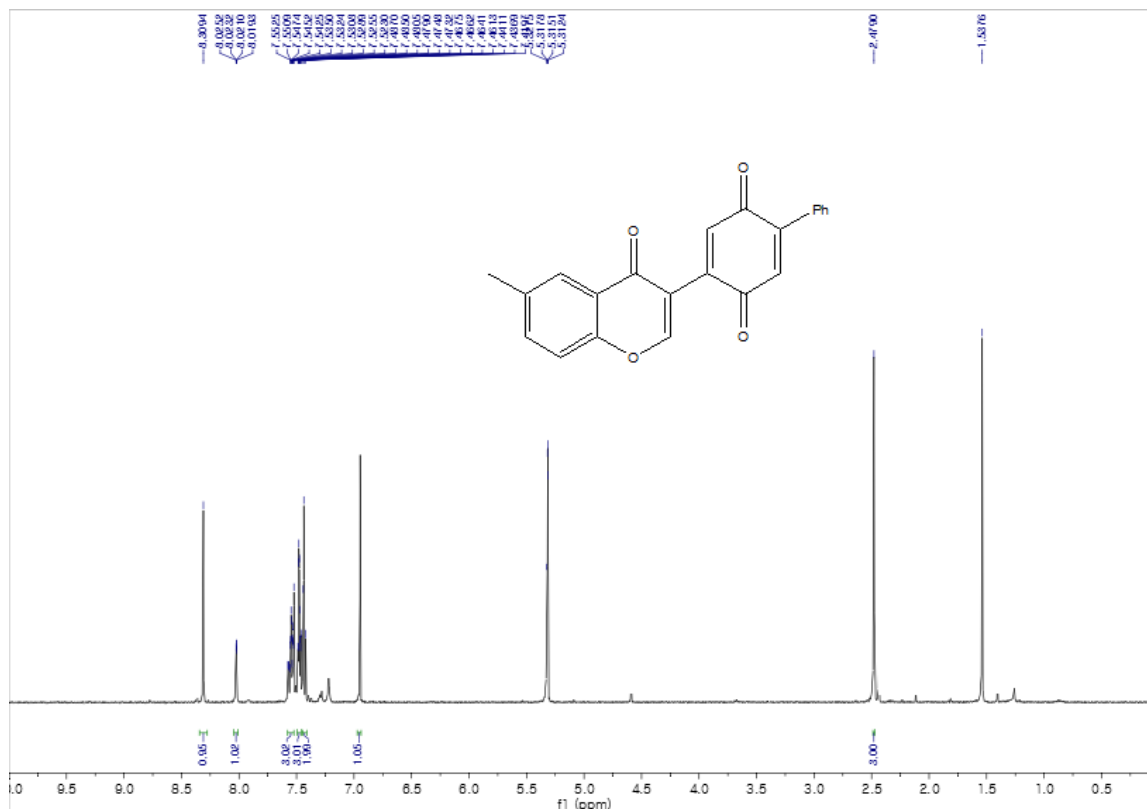


400 MHz, ¹H NMR in CDCl₃

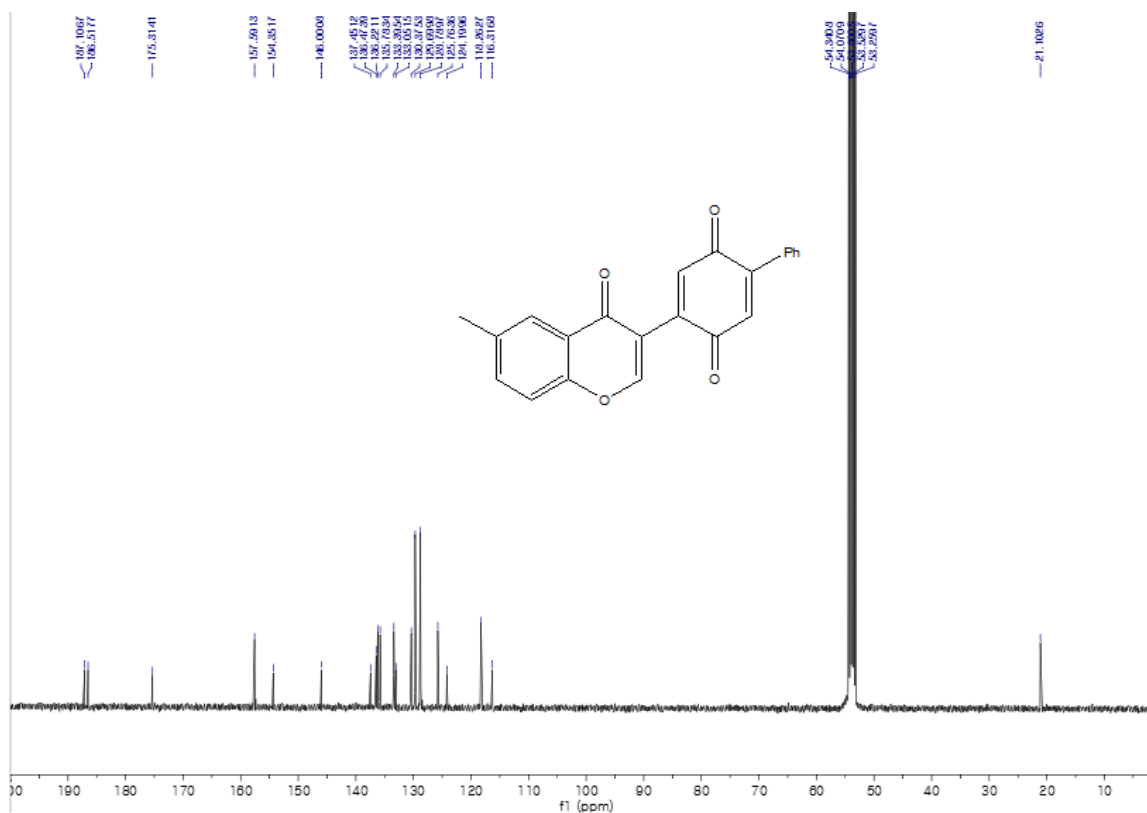


100 MHz, ¹³C NMR in CDCl₃

2-(6-methyl-4-oxo-4H-chromen-3-yl)-5-phenylcyclohexa-2,5-diene-1,4-dione (3p)

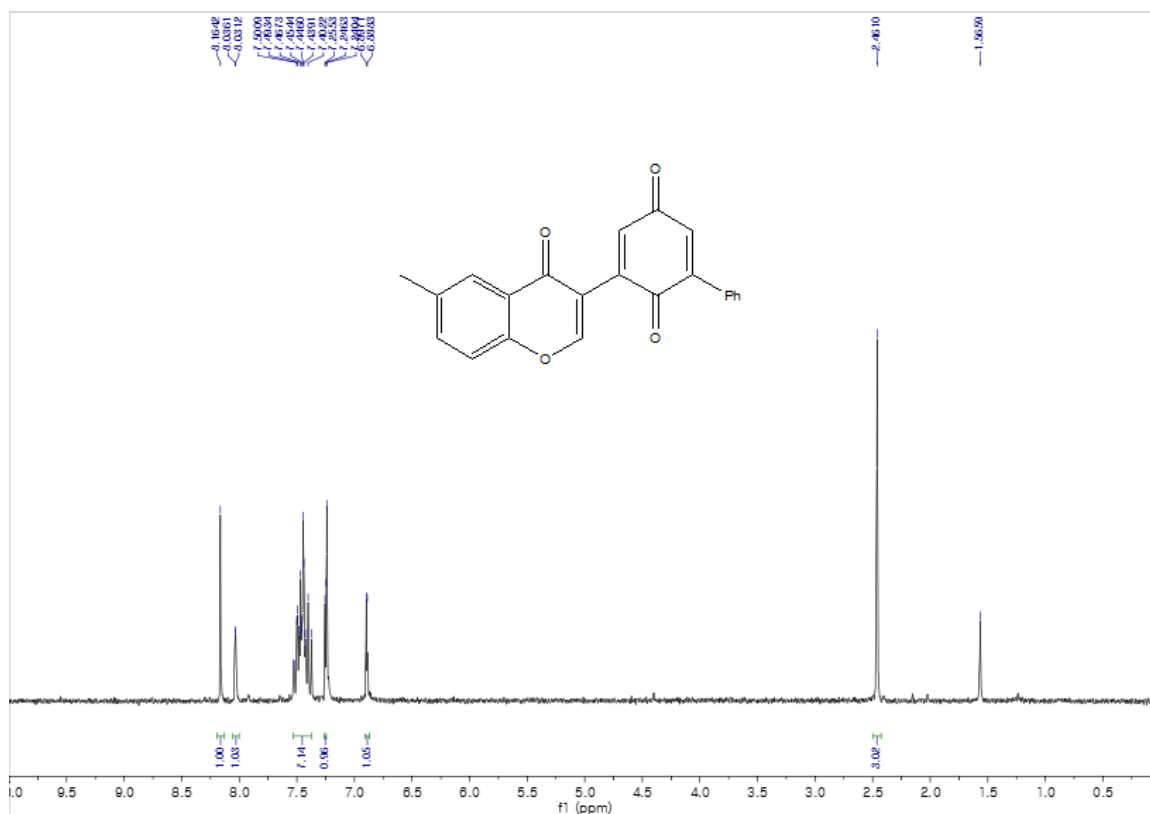


400 MHz, ^1H NMR in CD_2Cl_2

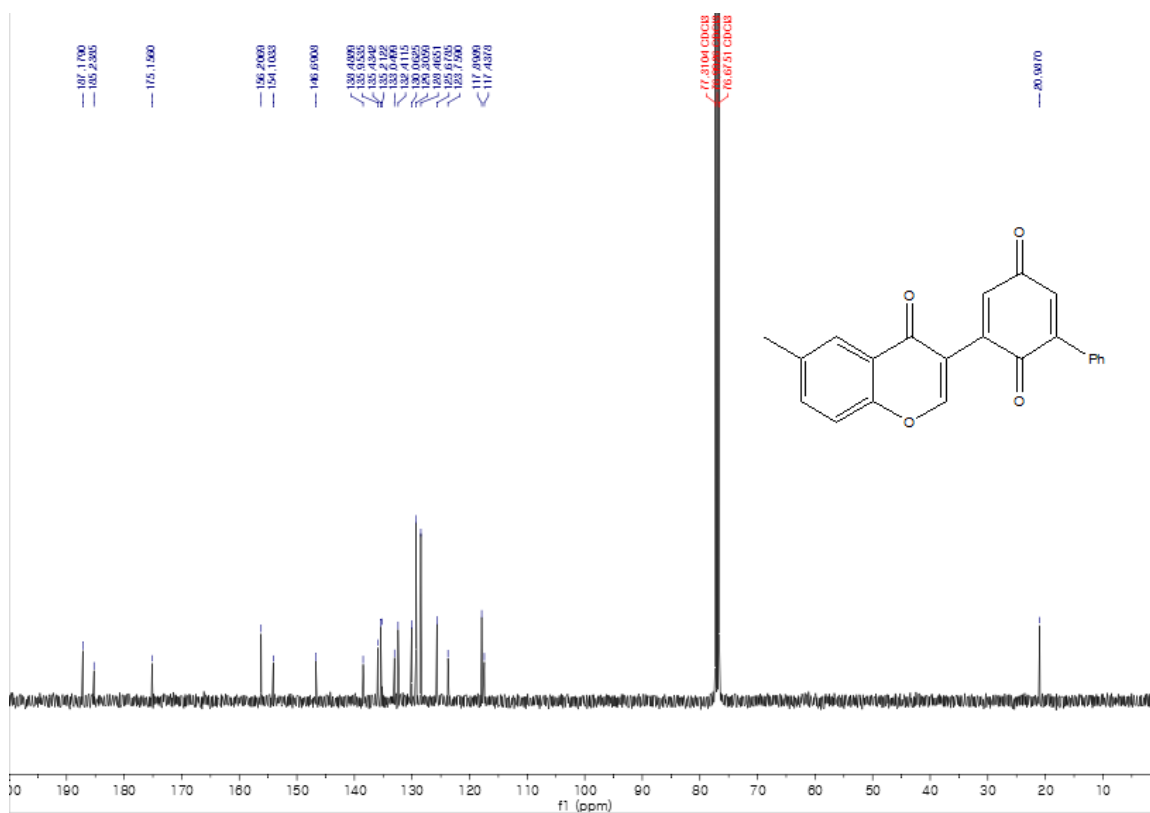


100 MHz, ^{13}C NMR in CD_2Cl_2

2-(6-methyl-4-oxo-4H-chromen-3-yl)-6-phenylcyclohexa-2,5-diene-1,4-dione (3p)

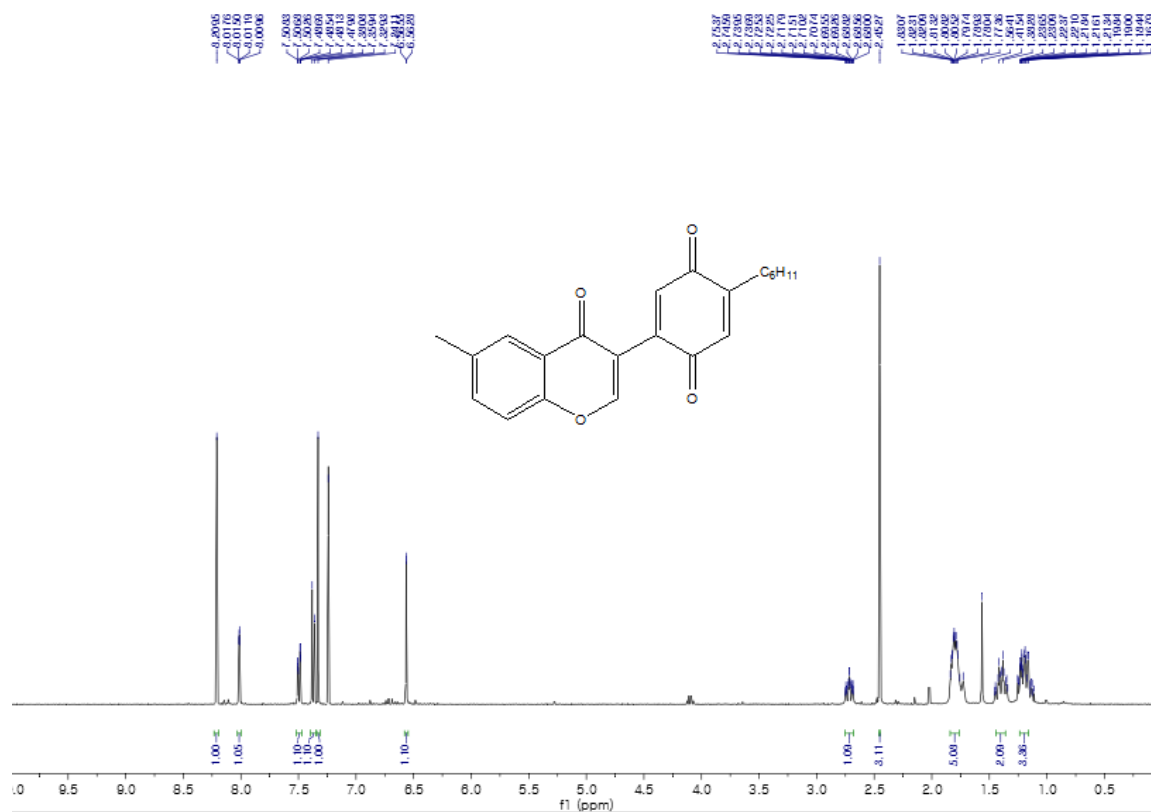


300 MHz, $^1\text{H NMR}$ in CDCl_3

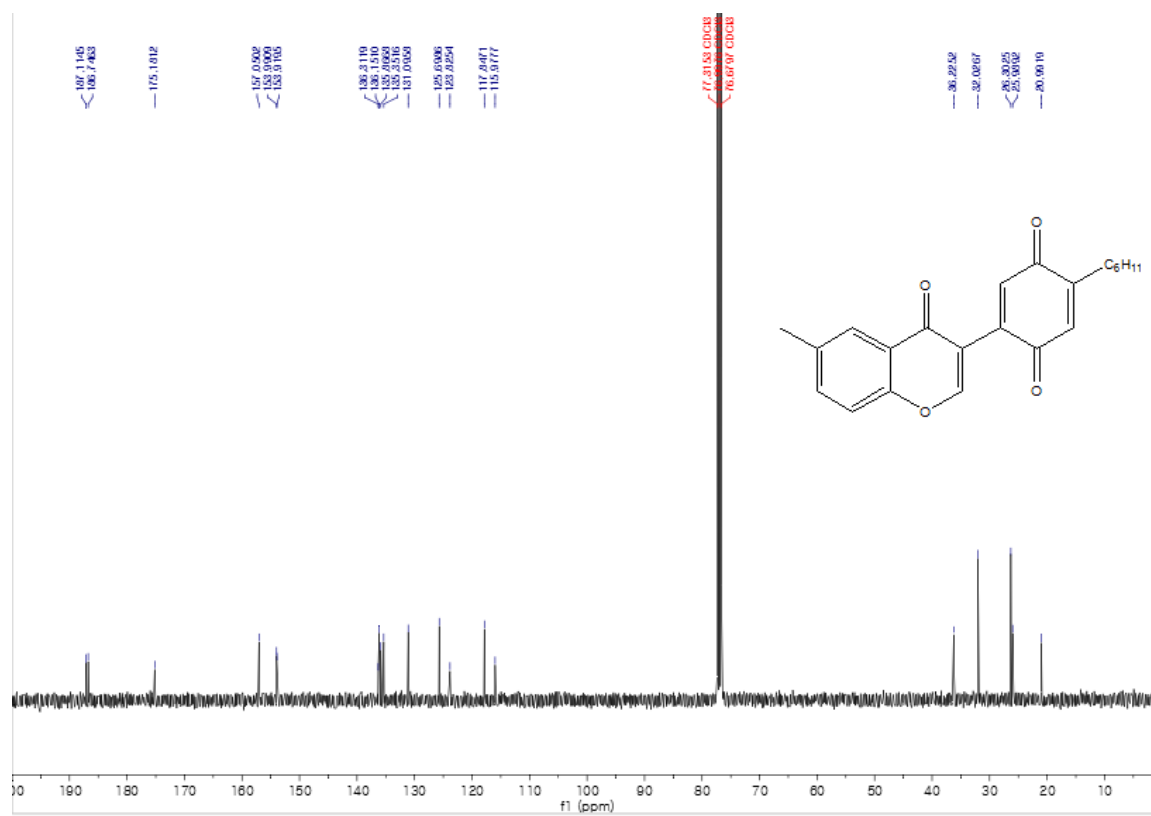


100 MHz, $^{13}\text{C NMR}$ in CDCl_3

2-cyclohexyl-5-(6-methyl-4-oxo-4H-chromen-3-yl)cyclohexa-2,5-diene-1,4-dione (3q)

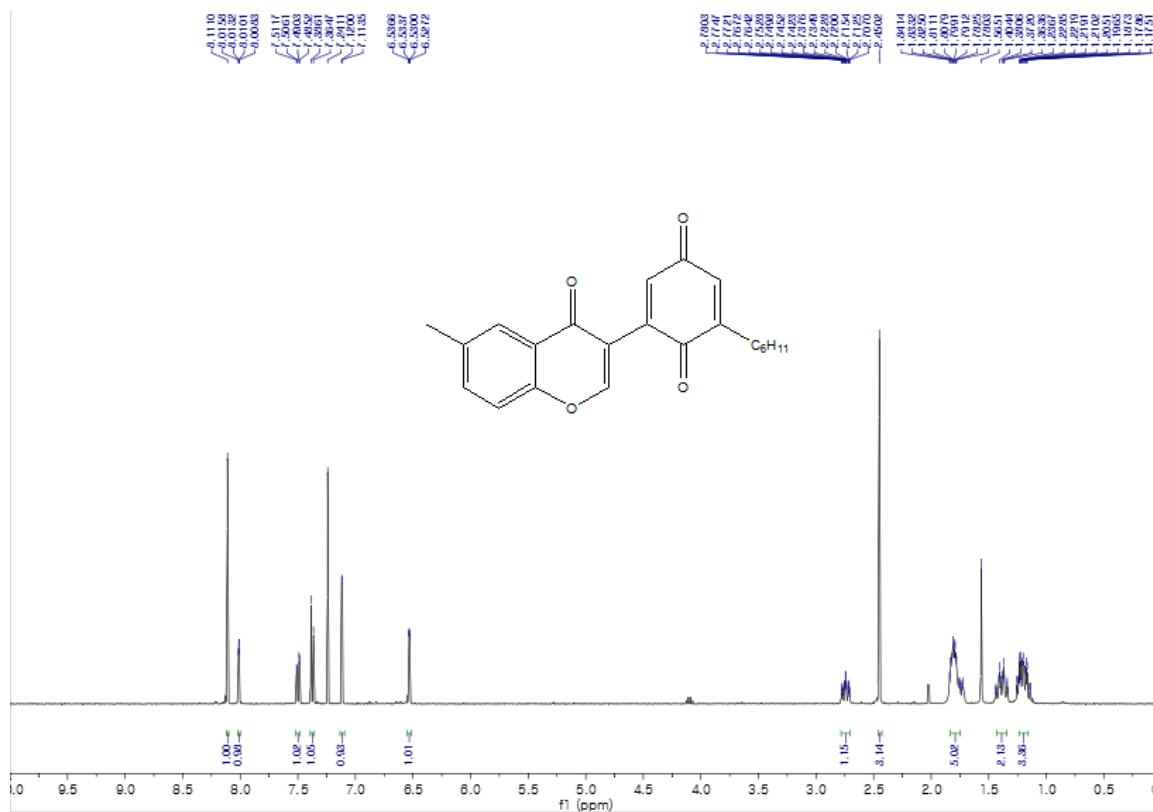


400 MHz, ^1H NMR in CDCl_3

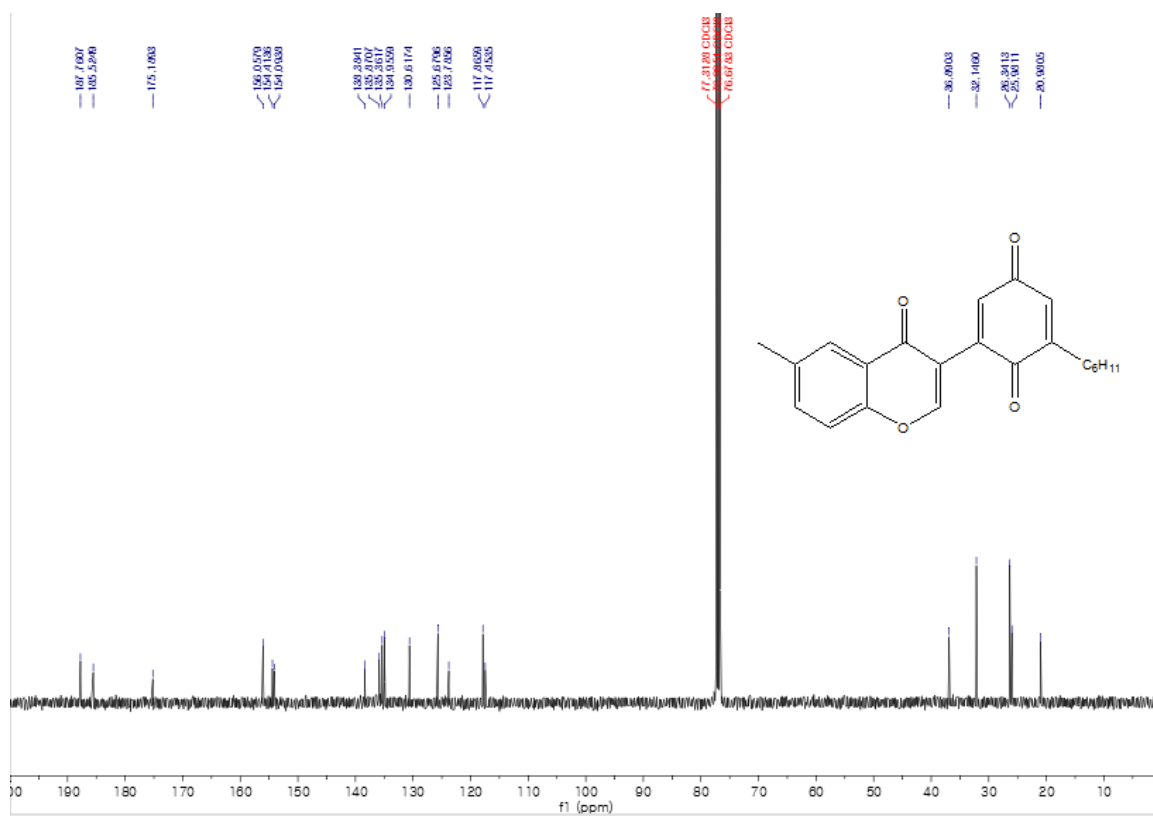


100 MHz, ^{13}C NMR in CDCl_3

2-cyclohexyl-6-(6-methyl-4-oxo-4H-chromen-3-yl)cyclohexa-2,5-diene-1,4-dione (3q, major)

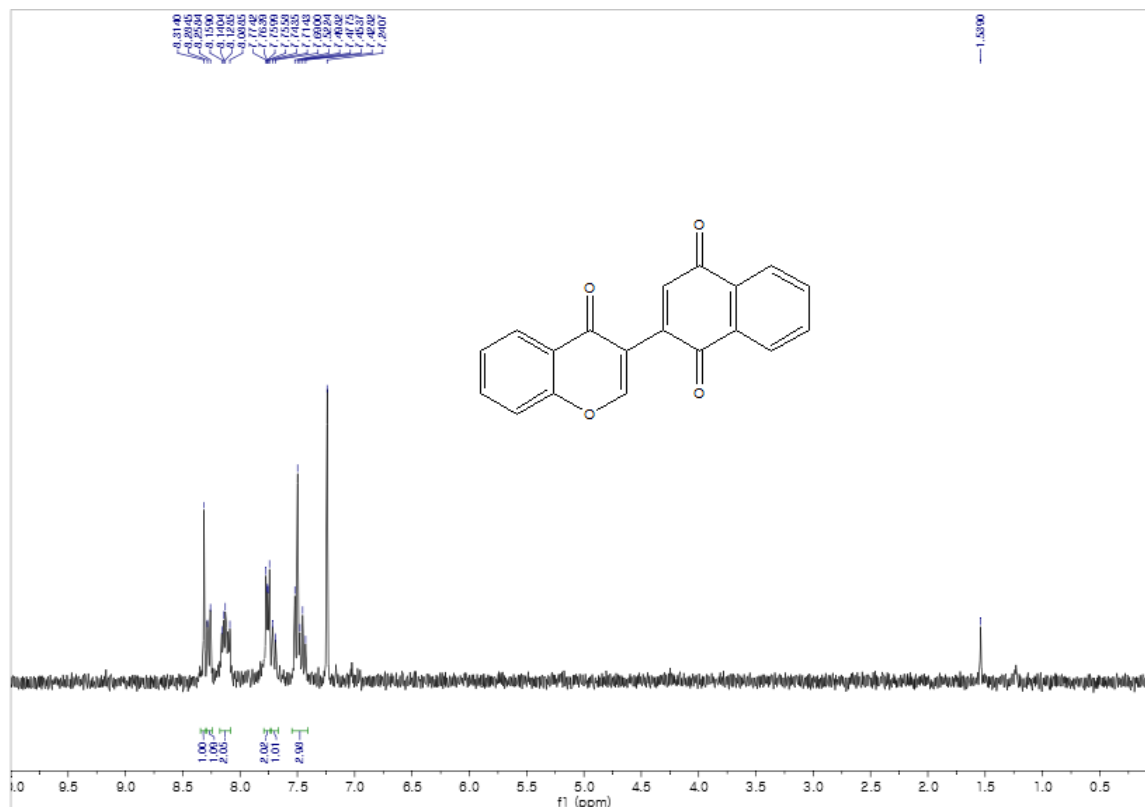


400 MHz, ^1H NMR in CDCl_3

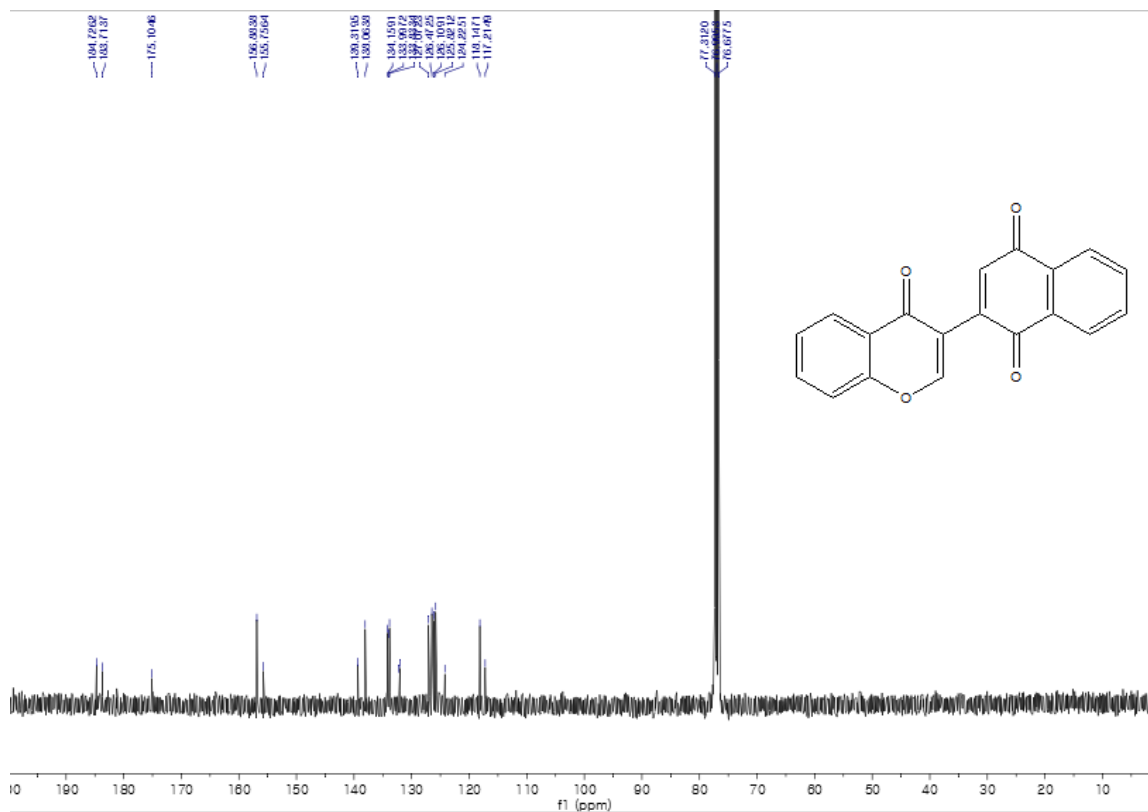


100 MHz, ^{13}C NMR in CDCl_3

2-(4-oxo-4H-chromen-3-yl)naphthalene-1,4-dione (3r)

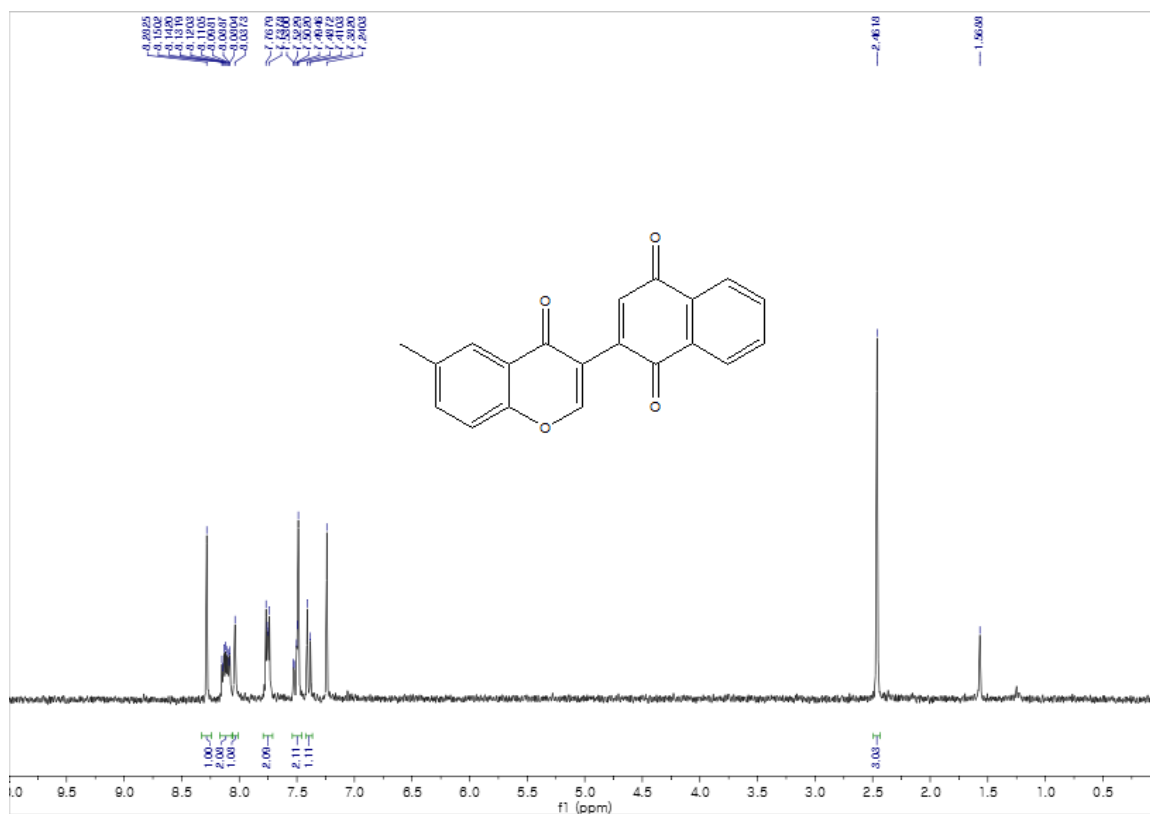


300 MHz, ¹H NMR in CDCl₃

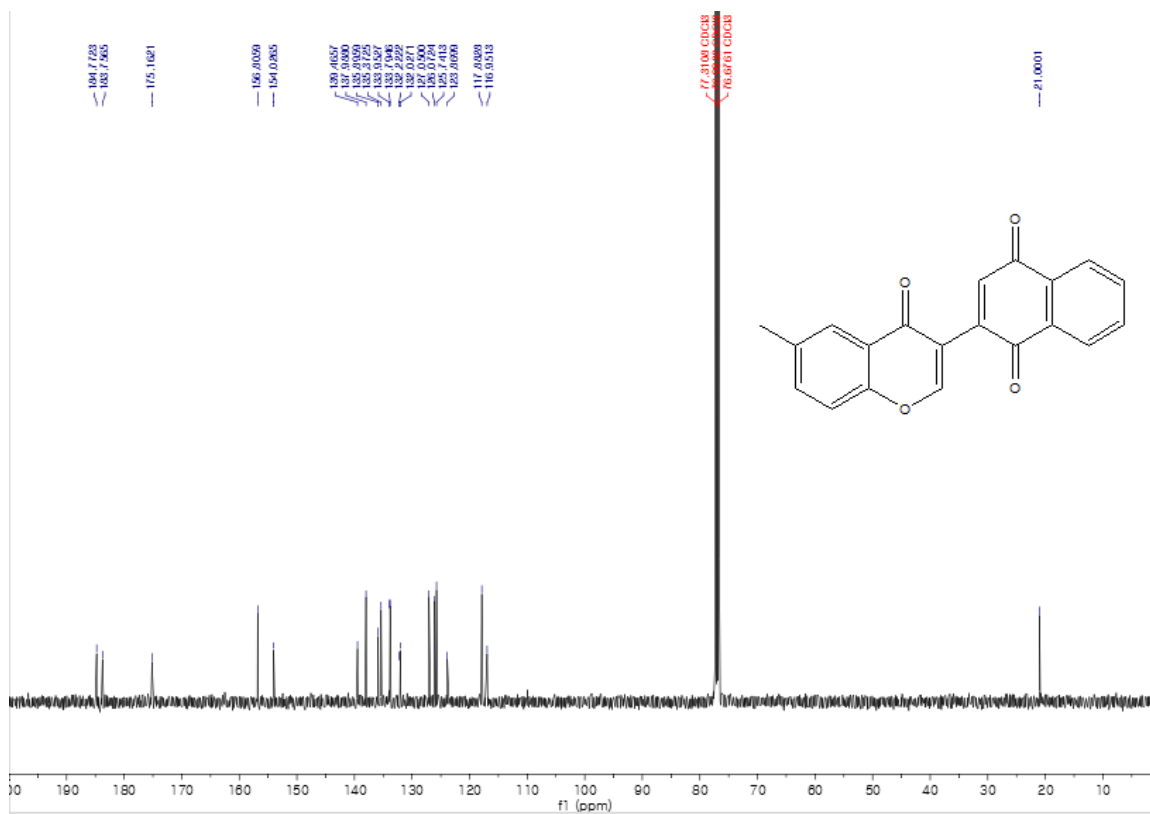


100 MHz, ¹³C NMR in CDCl₃

2-(6-methyl-4-oxo-4H-chromen-3-yl)naphthalene-1,4-dione (3s)

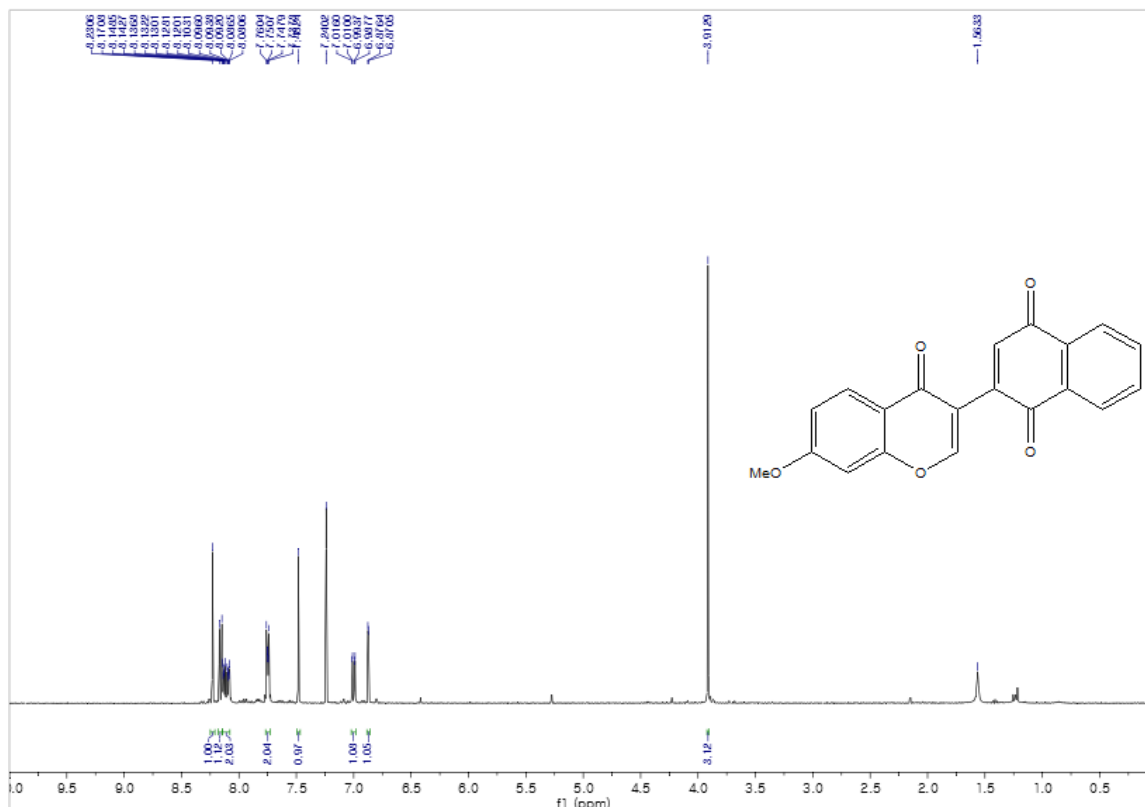


300 MHz, ^1H NMR in CDCl_3

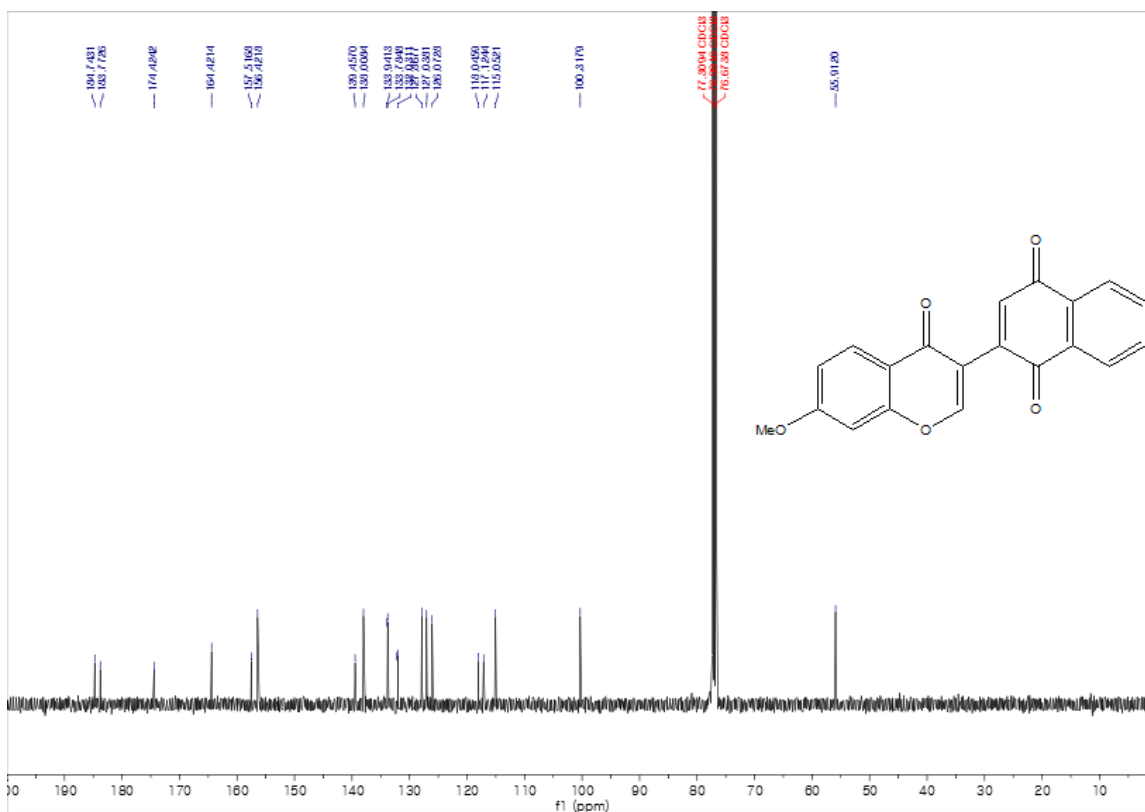


100 MHz, ^{13}C NMR in CDCl_3

2-(7-methoxy-4-oxo-4H-chromen-3-yl)naphthalene-1,4-dione (3t)



400 MHz, ^1H NMR in CDCl_3



100 MHz, ^{13}C NMR in CDCl_3

1-methyl-3-(6-methyl-4-oxo-4H-chromen-3-yl)-1H-pyrrole-2,5-dione (3u)

