Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Supplementary information

For

Highly enantioselective synthesis of angelmarin

Hang Jiang and Yasumasa Hamada*

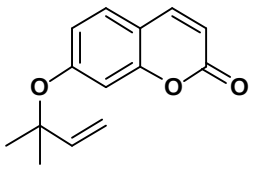
Graduate School of Pharmaceutical Sciences, Chiba University, Yayoi-cho, Inage-ku, Chiba 263-8522, Japan

Contents

ⅰ) Experimental and NMR data of compounds

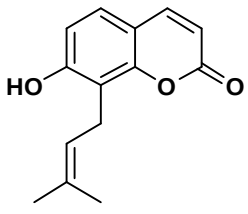
General procedures. Melting points were measured with a SIBATA NEL-270 melting point apparatus. Infrared spectra were on a JASCO FT/IR-230 Fourier Transform infrared spectrophotometer. Optical rotations were measured on a JASCO P-1020 polarimeter with a sodium lamp and were recorded as follows: $[\alpha]_D^T$ (cg/100 mL, solvent). ^{1}H NMR spectra were recorded on JEOL JNM-GSX 400A spectrometer (400 MHz) and JNM ECP400 spectrometer (400 MHz). Chemical shifts are recorded in ppm from tetramethylsilane or chloroform as the internal standard. Mass spectra were obtained on a JEOL HX-110A (LRFAB, LREI) spectrometer. HPLC was carried out using the JASCO high pressure liquid chromatography with UV-970 (Detector) and PU-980 (Pump). Analytical thin layer chromatography was performed on Merck Art. 5715, Kieselgel 60F254/0.25 mm thickness plates. Visualization was accomplished with UV light, phosphomolybdic acid, cerium-phosphomolybdic acid, ninhydrin, and anisaldehyde solution followed by heating. Column chromatography was performed with silica gel BW-820MH (Fuji Davison Co.).

7-(2-mrthylbut-3-en-2-yloxy)-2*H*-chromen-2-one (7)



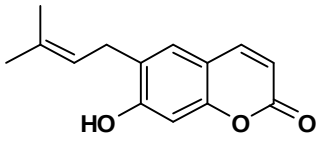
To a stirred solution of 7-hydroxycoumarin (50 mg, 0.31 mmol) and isobutyl 2-methylbut-3-en-2-yl carbonate (101.4 mg, 0.46 mmol, 85 % purity) in THF (2 mL), tetrakis(triphenylphosphine)palladium(0) (3.6 mg, 0.003 mmol) was added. The mixture was stirred at 23 °C for 1.5 h. The reaction mixture was extracted with ethyl acetate. The combined organic extracts were washed with brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (*n*-hexane/ethyl acetate = 2/1) to give **7** (68.7 mg, 97 %) as pale yellow solids: mp 70.5-71.5 °C (ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.54 (s, 6H), 5.25 (d, *J* = 17.6 Hz, 1H), 5.23 (dd, *J* = 10.8, 0.8 Hz, 1H), 6.14 (dd, *J* = 17.6, 10.8 Hz, 1H), 6.24 (d, *J* = 9.2 Hz, 1H), 6.88 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.98 (d, *J* = 2.4 Hz, 1H) 7.30 (d, *J* = 8.8 Hz, 1H), 7.62 (d, *J* = 9.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 27.1, 80.9, 106.7, 112.8, 113.2, 114.5, 117.2, 128.1, 143.3, 143.4, 155.1, 160.0, 161.3; IR (KBr, cm^{-1}): 3990, 3074, 2985, 1732, 1602, 1504, 1402, 1346, 1234, 1117, 991, 852, 754, 698; HRMS (FAB) calcd for $C_{14}H_{15}O_3$: 231.1021 $[M+H]^+$, found: 231.1038.

7-hydroxy-8- (3-methylbut-2-enyl)-2*H*-chromen-2-one (4) and 7-hydroxy-6-(3-methylbut-2-enyl)-2*H*-chromen-2-one (8)



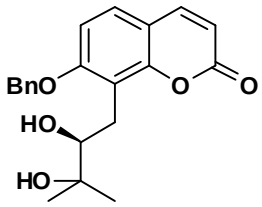
The ether **7** (2.37 g, 10.3 mmol) was heated at 130 °C for 1.5 h. After cooling the reaction mixture to room temperature, the mixture was purified by silica gel column chromatography (*n*-hexane/ethyl acetate = 2/1) to give **8** (0.37 g, 1.6 mmol, 15.4%) as white solids and **4** (1.69 g, 7.4 mmol, 71.4%)

as white solids. Major **4:** mp 105.5-106.5 °C (ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.77 (s, 3H), 1.86 (s, 3H) 3.63 (d, *J* = 6.8 Hz, 2H), 5.275 (t, *J* = 7.2 Hz, 1H), 6.02 (s, 1H), 6.25 (d, *J* = 9.6 Hz, 1H), 6.79 (d, *J* = 8.4 Hz, 1H), 7.24 (d, *J* = 8.4 Hz, 1H), 7.63 (d, *J* = 9.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.0, 22.0, 25.8, 112.3, 112.6, 113.2, 114.8, 120.3, 126.6, 135.9, 144.3, 153.1, 158.4, 161.9; IR (KBr, cm^{-1}): 3379, 1682, 1591, 1504, 1373, 1309, 1252, 1124, 1059, 826; HRMS (FAB) calcd for $C_{14}H_{15}O_3$: 231.1021 $[M+H]^+$, found: 231.1006.



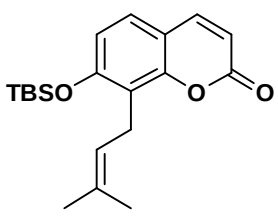
Minor **8:** mp 128-129°C (ethyl acetate/*n*-hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.77 (s, 3H), 1.80 (s, 3H), 3.38 (d, *J* = 7.2 Hz, 2H) 5.31 (t, *J* = 7.2 Hz, 1H), 6.24 (d, *J* = 9.6 Hz, 1H), 6.39 (s, 1H), 6.90 (s, 1H), 7.20 (s, 1H), 7.63 (d, *J* = 9.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.8, 25.8, 28.0, 103.0, 111.7, 112.1, 121.1, 126.3, 128.1, 134.4, 144.8, 153.9, 158.8, 163.0; IR (KBr, cm^{-1}): 3234, 1591, 1363, 1219, 1132, 930, 887, 852, 816, 773, 696; HRMS (FAB) calcd for $C_{14}H_{15}O_3$: 231.1021 $[M+H]^+$, found: 231.1038.

(*S*)-7-(benzyloxy)-8-(2,3-dihydroxy-3-methylbutyl)-2*H*-chromen-2-one (18)



To a stirred mixture of AD-mix-α (516 mg, 140 mg/0.1 mmol) and methane sulfonamide (38.6 mg, 0.41 mmol) in *t*-BuOH/H_2O (1/1) (0.1 M) at 0 °C was added **15** (118.1 mg, 0.37 mmol). During the reaction the temperature was kept at 0 °C. The reaction was quenched by an addition of saturated $Na_2S_2O_3$ at 0 °C and then the resulting mixture was gradually warmed to room temperature. The mixture was extracted with $CHCl_3$. The organic extracts were washed with brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (*n*-hexane/ethyl acetate = 1/2) to give **18** (90.5 mg, 69.2 %, 80% ee) as white solids: mp 139-140 °C (ethyl acetate/*n*-hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.25 (s, 3H), 1.27 (s, 3H), 2.40 (brm, 2H), 3.04 (dd, *J* = 14.0, 10.4 Hz, 1H), 3.13 (dd, *J* = 14.0, 2.8 Hz, 1H), 2.65 (dd, *J* = 14.8, 9.6 Hz, 1H), 3.66 (m, 1H), 5.18 (dd, *J* = 13.2, 11.6 Hz, 2H), 6.25 (d, *J* = 9.6 Hz, 1H), 6.93 (d, *J* = 8.8 Hz, 1H), 7.33 (d, *J* = 8.8 Hz, 1H), 7.43 (m, 5H),7.63 (d, *J* = 9.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 23.8, 25.7, 26.0, 71.0, 73.0, 78.3, 108.3, 113.3, 115.9, 126.9, 127.4, 128.4, 128.8, 135.8, 143.8, 153.5, 159.6, 161.0; IR (KBr, cm^{-1}) 3411, 2970, 1709, 1610, 1493, 1402, 1281, 1088, 831, 760, 721, 671; HRMS (FAB) calcd for $C_{21}H_{23}O_5$: 355.1545 $[M+H]^+$, found: 355.1515. The HPLC analysis using CHIRALPAC AD and *n*-hexane/*i*-PrOH (75/25, 1.0 mL/min), Retention time for minor: 19.5 min; major: 28.4 min.

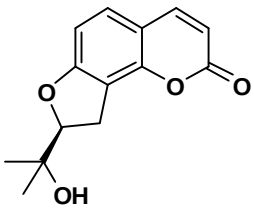
7-(*tert*-butyldimethylsilyloxy)-8-(3-methylbut-2-enyl)-2*H*-chromen-2-one (9)



To a stirred solution of **4** (14.9 g, 64.7 mmol) and imidazole (13.2 g, 194 mmol) in DMF (150 mL) at 0 °C was added TBS-Cl (14.6 g, 97.0 mmol)

and then allowed to gradually warmed to room temperature. After being stirred for 1.5 h, the reaction was quenched with water at 0 °C. The residue was extracted with ethyl acetate. The organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (*n*-hexane/ethyl acetate = 2/1) to give **9** (22.3g, 64.7 mmol, quant) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.29 (s, 6H), 1.03 (s, 9H), 1.66 (s, 3H), 1.83 (s, 3H), 3.52 (d, *J* = 7.2 Hz, 2H), 5.18 (t, *J* = 7.2 Hz, 1H), 6.24 (d, *J* = 9.2 Hz, 1H), 6.75 (d, *J* = 8.4 Hz, 1H), 7.18 (d, *J* = 8.4 Hz, 1H), 7.60 (d, *J* = 9.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ -4.3, - 3.8, 17.9, 18.1, 22.2, 25.4, 112.5, 113.0, 115.2, 120.3, 121.2, 125.6, 132.2, 143.8, 153.2, 156.7, 161.3; IR (KBr, cm^{-1}): 2929, 2857, 1716, 1653, 1600, 1492, 1471, 1403, 1362, 1304, 1282, 1248, 1159, 1115, 1067, 995, 894, 833, 806, 779, 687; HRMS (FAB) calcd for $C_{20}H_{29}O_3Si$: 345.1886 $[M+H]^+$, found: 345.1882.

(*S*)-8-(2-hydroxypropan-2-yl)-8,9-dihydro-2*H*-furo[2,3-*h*]chromen-2-one (2)

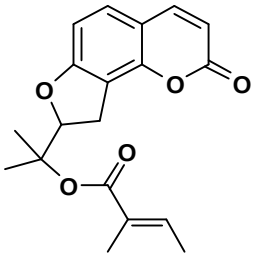


Alkene **9** (10.0 g, 29.0 mmol) and the ketone **13** (1.32 g, 4.35 mmol) were dissolved in acetonitrile/dimethoxymethane (576 mL, 1:2 v/v). A pH = 6 buffer solution (105 mL) and tetrabutylammonium hydrogen sulfate (394.2 mg, 1.16 mmol) were slowly added with stirring, and the mixture was cooled to 0 °C. The flask was equipped with two adding funnels; one of them was filled with a solution of oxone (29.1 g, 47.3 mmol) in the pH = 6 buffer (183 mL), and the other one with a solution of K_2CO_3 (9.63 g, 69.7 mmol) in water (183 mL). The two solutions were added dropwise over a 4 h period. The solution was stirred at 0 °C for 43.5 h. The crude was quenched by addition of water (500 mL) and hexane (150 mL). The reaction mixture was extracted with hexane (300 mL X2). The combined organic extracts were washed with brine (500 mL), dried over sodium sulfate, filtered, and concentrated under reduced pressure. The residue was used in next step without further purification. **10**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.29 (s, 3H), 0.31 (s, 3H), 1.04 (s, 9H), 1.30 (s, 3H), 1.51 (s, 3H), 3.02 (m, 2H), 3.15 (m, 1H), 6.26 (d, *J* = 9.2 Hz, 1H), 6.79 (d, *J* = 8.4 Hz, 1H), 7.25 (d, *J* = 8.8 Hz, 1H), 7.63 (d, *J* = 9.6 Hz, 1H).

To a solution of **10** (12.0 g, 29.0 mmol) in THF (100 mL) at 0 °C was added TBAF (34.8 mL, 34.8 mmol, 1.0 M in THF) and then allowed to gradually warmed to room temperature. After being stirred for 4 h, the reaction was quenched with water. The residue was extracted with ethyl acetate. The organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (*n*-hexane/ethyl acetate = 1/1) to give **2** (6.07 g, 84.9 %, 97% ee) as solids: mp 161-162 °C (ethyl acetate); $[\alpha]_D^{25}$ +183.55° (*c* 1.0, $CHCl_3$) for 100% ee; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.24 (s, 3H), 1.37 (s, 3H) 3.32 (m, 2H), 4.80 (t, *J* = 8.8 Hz, 1H), 6.21 (d, *J* = 9.6 Hz, 1H), 6.75(d, *J* = 8.4 Hz, 1H), 7.27 (d, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 9.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 23.9, 26.0, 27.6, 71.8, 91.3, 106.7, 112.3, 113.1, 114.0,

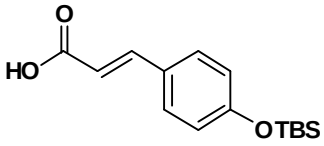
128.7, 144.0, 151.3, 161.0, 163.7; IR (KBr, cm^{-1}): 3502, 2969, 1698, 1609, 1490, 1453, 1406, 1337, 1316, 1254, 1146, 1118, 1065, 1011, 946, 826, 779, 759; HRMS (FAB) calcd for $C_{14}H_{15}O_4$: 247.0970 $[M+H]^+$, found: 247.0956.. The HPLC analysis using CHIRALPAC AD and *n*-hexane/*i*-PrOH (75:25, 0.5 mL.min), Retention time for major: 15.6 min; minor: 22.9 min .

(*E*)-2-(2-oxo-8,9-dihydro-2*H*-furo[2,3-*h*]chromen-8-yl)propan-2-yl 2-methylbut-2-enoate (19)



To a stirred suspension of *rac*-**2** (200 mg, 0.81 mmol) and CuCN (255 mg, 2.84 mmol) in toluene (5 mL) at room temperature was added tigloyl chloride (223 µL, 2.03 mmol) under argon atmosphere. After being stirred for 24 h at 50 °C, the mixture was filtered through a pad of Celite$^{@}$ and the residue was washed with ethyl acetate. The combined filtrates were washed with brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (*n*-hexane/ethyl acetate = 3/1) to give **12** (276 mg, quant) as white solids: mp 96-97 °C (*n*-hexane/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.60 (s, 3H), 1.65 (s, 3H), 1.67 (s, 3H), 1.69 (s, 3H) 3.39 (m, 2H), 5.11 (t, *J* = 7.6 Hz, 1H), 6.22 (d, *J* = 9.6 Hz, 1H), 6.55 (dd, *J* = 13.6, 7.6 Hz, 1H) 6.76(d, *J* = 8.4 Hz, 1H), 7.28 (d, *J* = 8.4 Hz, 1H), 7.64 (d, *J* = 9.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.8, 14.3, 20.9, 22.2, 27.6, 81.8, 89.3, 106.6, 112.1, 112.9, 113.6, 128.8, 129.3, 137.1, 144.0, 151.2, 161.0, 164.0, 167.0; IR (KBr, cm^{-1}): 2979, 2938, 1724, 1608, 1456, 1402, 1263, 1144, 1107, 970, 922, 837, 729; HRMS (FAB) calcd for $C_{19}H_{21}O_5$: 329.1389 $[M+H]^+$, found: 329.1366.

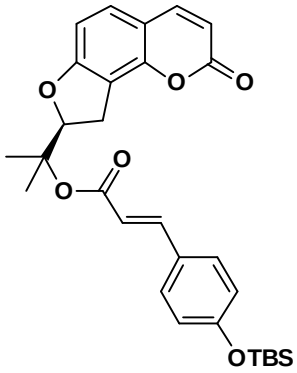
(*E*)-3-(4-(*tert*-butyldimethylsilyloxy)phenyl)acrylic acid (21)



To a stirred solution of *p*-coumaric acid (2.0 g, 12.2 mmol) and imidazole (3.32 g, 48.7 mmol) in CH_2Cl_2 (40 mL) at 0 °C was added TBSCl (4.59 g, 30.5 mmol)in one portion, and then the resulting mixture was warmed to room temperature. After being stirred for 4.5 h, the reaction was quenched with brine (10 mL) and the mixture was extracted with ethyl acetate. The organic extract was washed with brine, dried over Na_2SO_4, filtered, and concentrated in *vacuo.* The residue was used in next step without further purification. The residue was solved in THF (40 mL) and H_2O (10 mL). Lithium hydroxide monohydrate (511.1 mg, 12.18 mmol) was added in one potion. After being stirred for 10 min, the solution was quenched with 0.1 M HCl, extracted with ethyl acetate, washed with brine, dried over Na_2SO_4, filtered, and concentrated in *vacuo.* The residue was purified by silica gel column chromatography (*n*-hexane/ethyl acetate = 3/1) and recrystallized from *n*-hexane and ethyl acetate to give **21** (2.34 g, 68.9 %) as white solids: mp 138-139 °C (*n*-hexane/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.23 (s, 6H), 1.00 (s, 9H), 6.31 (d, *J* = 15.6 Hz, 1H), 6.85 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.72 (d, *J* = 16.0 Hz, 1H); ^{13}C NMR (100

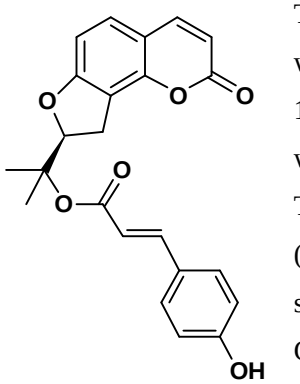
MHz, $CDCl_3$): δ -4.4, 18.2, 25.6, 114.8, 120.6, 127.3, 130.0, 146.8, 158.3, 172.7; IR (KBr, cm^{-1}): 2927, 2855, 2506, 1674, 1596, 1504, 1423, 1247, 1165, 984, 901, 832, 776; HRMS (FAB) calcd for $C_{15}H_{23}O_3Si$: 279.1416 $[M+H]^+$, found: 279.1389.

(*S*,*E*)-2-(2-oxo-8,9-dihydro-2*H*-furo[2,3-*h*]chromen-8-yl)propan-2-yl 3-(4-(*tert*-butyldimethylsilyloxy)phenyl)acrylate (24)



Thionyl chloride (5 mL) was added to **21** (1.36 g, 4.87 mmol) at room temperature under argon atmosphere. After being refluxed for 5 h, the mixture was concentrated in *vacuo.* A solution of the above acid chloride (4.87 mmol) in toluene (10 mL) was added to a stirred suspension of **2** (400 mg, 100% ee) and CuCN (727 mg, 8.12 mmol) in toluene (5 mL) at room temperature under argon atmosphere. After being stirred for 18.5 h at 50 °C, the mixture was filtered through a pad of Celite[@] and the residue was washed with ethyl acetate. The combined filtrates were washed with brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by Al_2O_3 column chromatography and silica gel column chromatography (*n*-hexane/ethyl acetate = 3/1) to give **24** (719.5 mg, 87.4 %) as a brown oil: ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.21 (s, 6H), 0.98 (s, 9H), 1.61 (s, 3H), 1.65 (s, 3H), 3.41 (m, 2H), 5.21 (t, *J* = 9.6 Hz, 1H), 6.17 (d, *J* = 15.6 Hz, 1H), 6.23 (d, *J* = 9.2 Hz, 1H), 6.79 (m, 3H), 7.30 (m, 3H), 7.37 (d, *J* = 16.0 Hz, 1H), 7.66 (d, *J* = 9.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ -4.4, 18.2, 21.2, 22.1, 25.6, 27.7, 82.1, 89.1, 106.7, 112.2, 113.0, 113.6, 116.8, 120.4, 127.6, 128.8, 129.6, 143.9, 144.3, 151.3, 157.8, 161.0, 164.0, 166.3; IR (KBr, cm^{-1}): 2930, 1734, 1706, 1616, 1600, 1508, 1254, 1133, 1108, 978, 905, 829; HRMS (FAB) calcd for $C_{29}H_{35}O_6Si$: 507.2203 $[M+H]^+$, found: 507.2161.

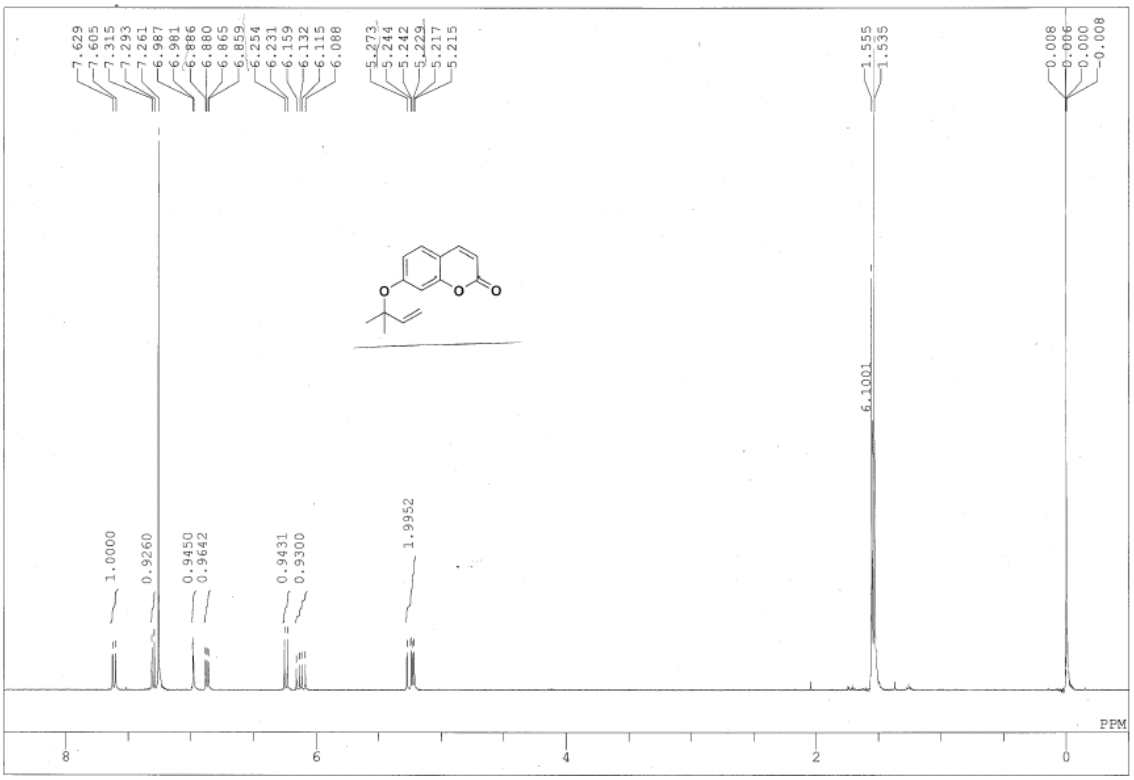
(*S*,*E*)-2-(2-oxo-8,9-dihydro-2*H*-furo[2,3-*h*]chromen-8-yl)propan-2-yl 3-(4-hydroxyphenyl)acrylate (1)

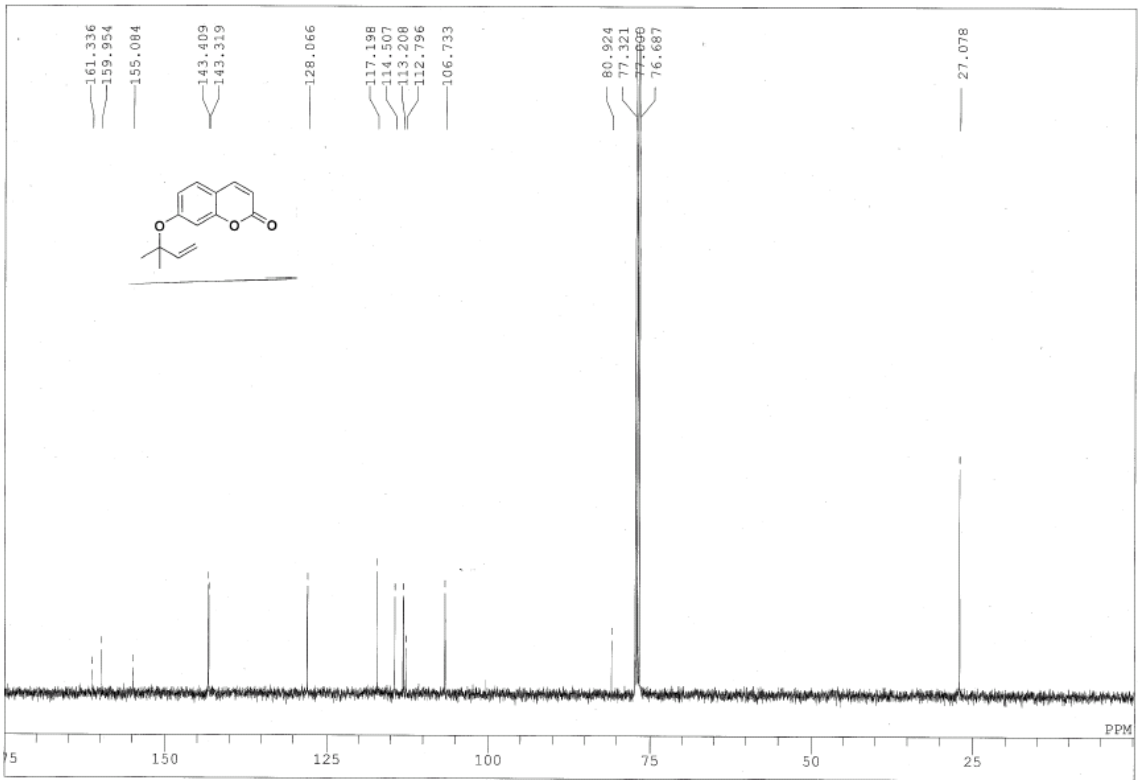


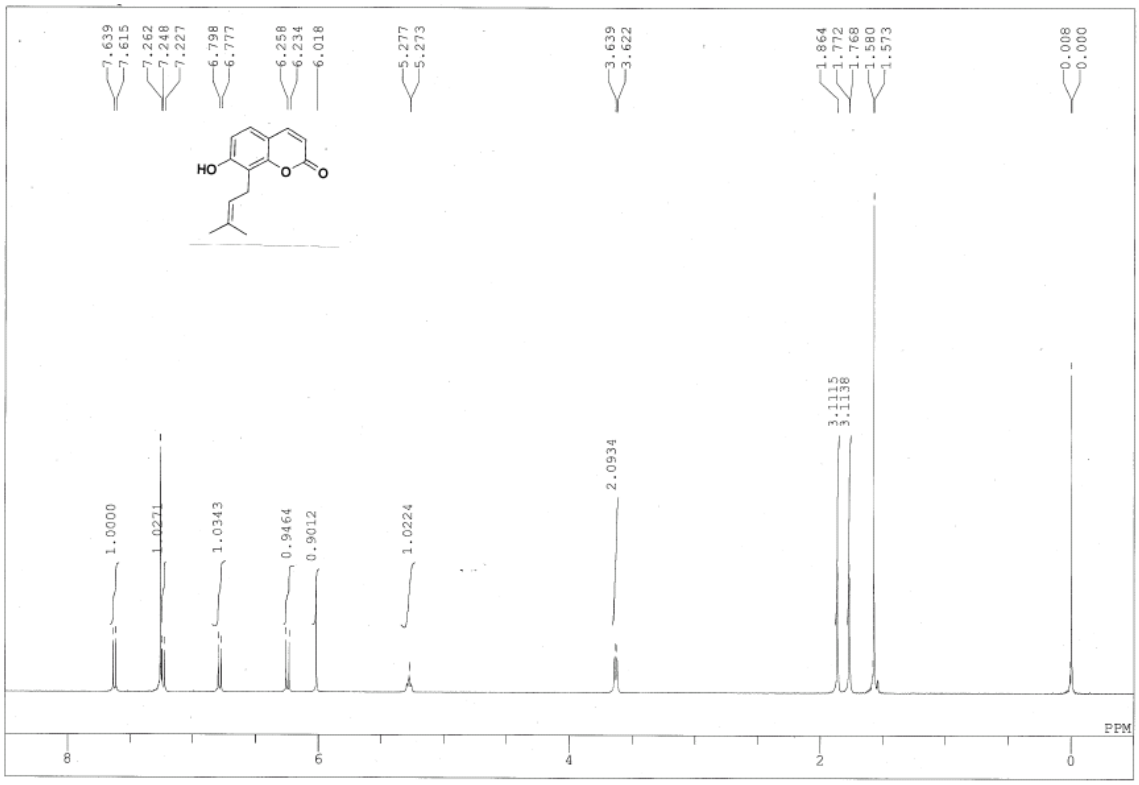
To a stirred solution of **24** (635 mg, 1.25 mmol) in THF (6 mL) at 0 °C was added TBAF (1M in THF, 1.5 mL, 1.5 mmol). After being stirred for 10 min at room temperature, the mixture was diluted with ethyl acetate, washed with brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (*n*-hexane/ethyl acetate = 1/1) to give **1** (510 mg, quant) as a amorphous solid: $[\alpha]_D^{25}$: + 237.8° (*c* 1.025, $CHCl_3$), $[\alpha]_D^{25}$: + 217.5° (*c* 0.028, $CHCl_3$), lit.[4] $[\alpha]_D^{25}$ + 218.7° (*c* 0.025, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.60 (s, 3H), 1.65 (s, 3H), 3.39 (m, 2H), 5.20 (t, *J* = 9.6 Hz, 1H), 6.15 (d, *J* = 16.0 Hz, 1H), 6.24 (d, *J* = 9.2 Hz, 1H), 6.79 (d, *J* = 8.8 Hz, 1H), 6.83 (d, *J* = 8.8 Hz, 2H),

7.30 (m, 3H), 7.35 (d, J = 15.6 Hz, 1H), 7.67 (d, J = 9.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.1, 22.1, 27.6, 82.2, 89.1, 106.9, 112.1, 113.0, 113.6, 115.9, 116.4, 126.9, 128.9, 129.9, 144.2, 144.4, 151.2, 158.0, 161.4, 164.1, 166.4; IR (KBr, cm^{-1}): 3303, 1696, 1602, 1513, 1489, 1455, 1406, 1387, 1369, 1328, 1260, 1200, 1167, 1118, 1065, 976, 871, 828, 753; HRMS (FAB) calcd for $C_{23}H_{21}O_6$: 393.1338 $[M+H]^+$, found: 393.1321.

ii) Copies of ^{1}H NMR and ^{13}C NMR spectra of compounds



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3.622
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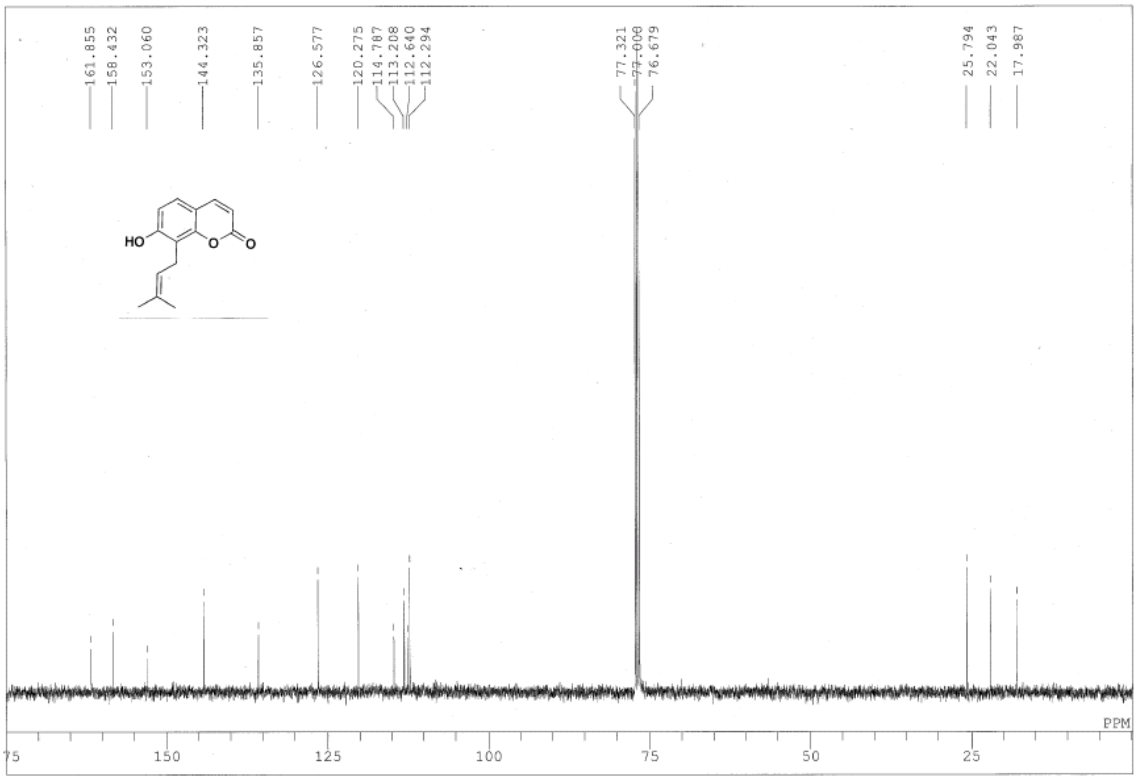
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PPM
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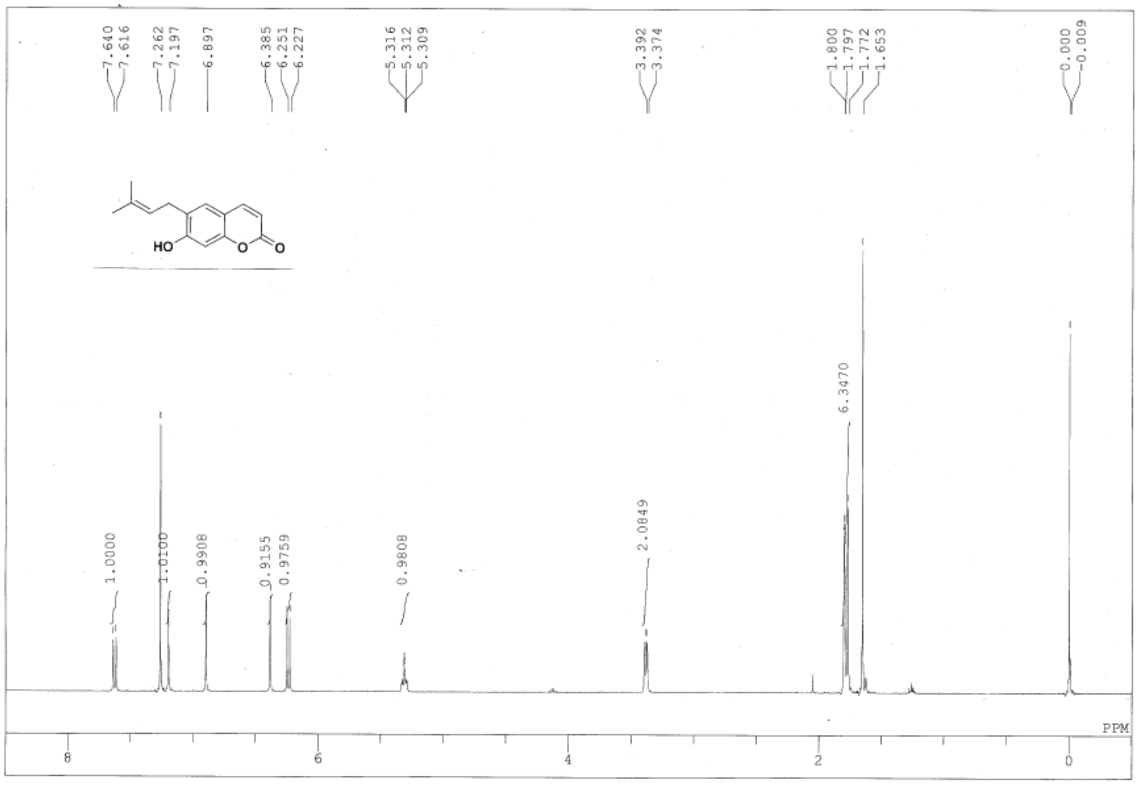
125
100
75
50
25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1.797
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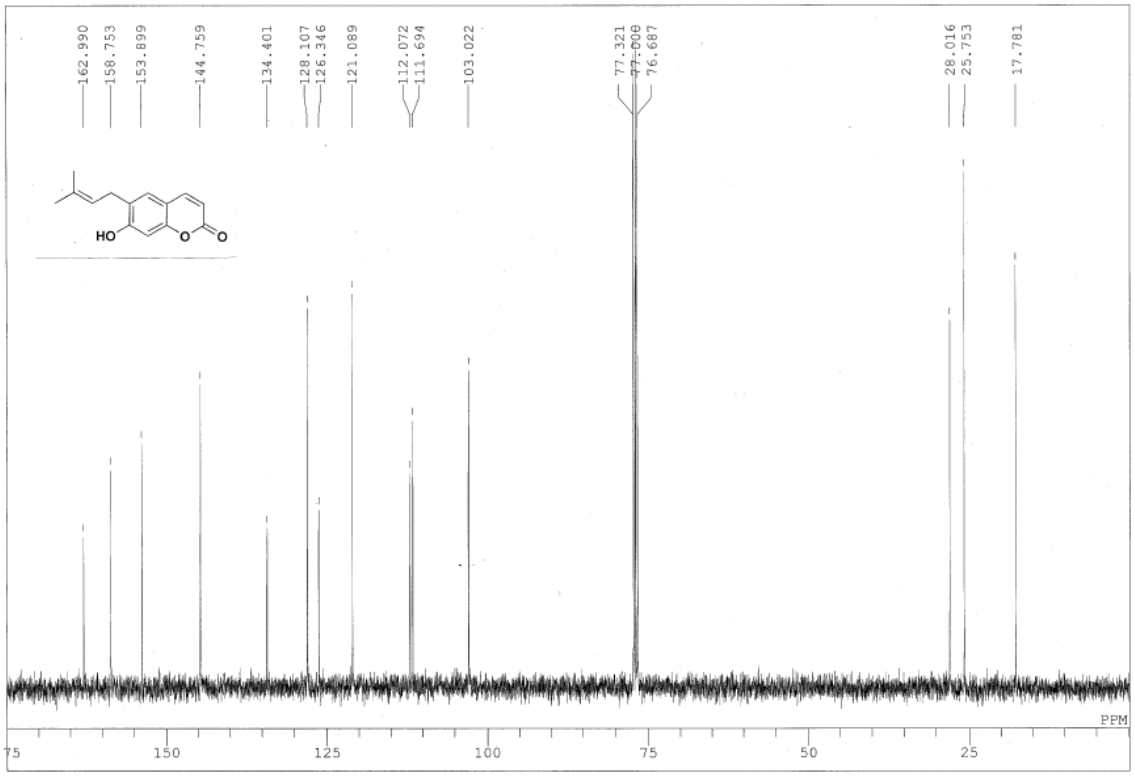
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PPM
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150
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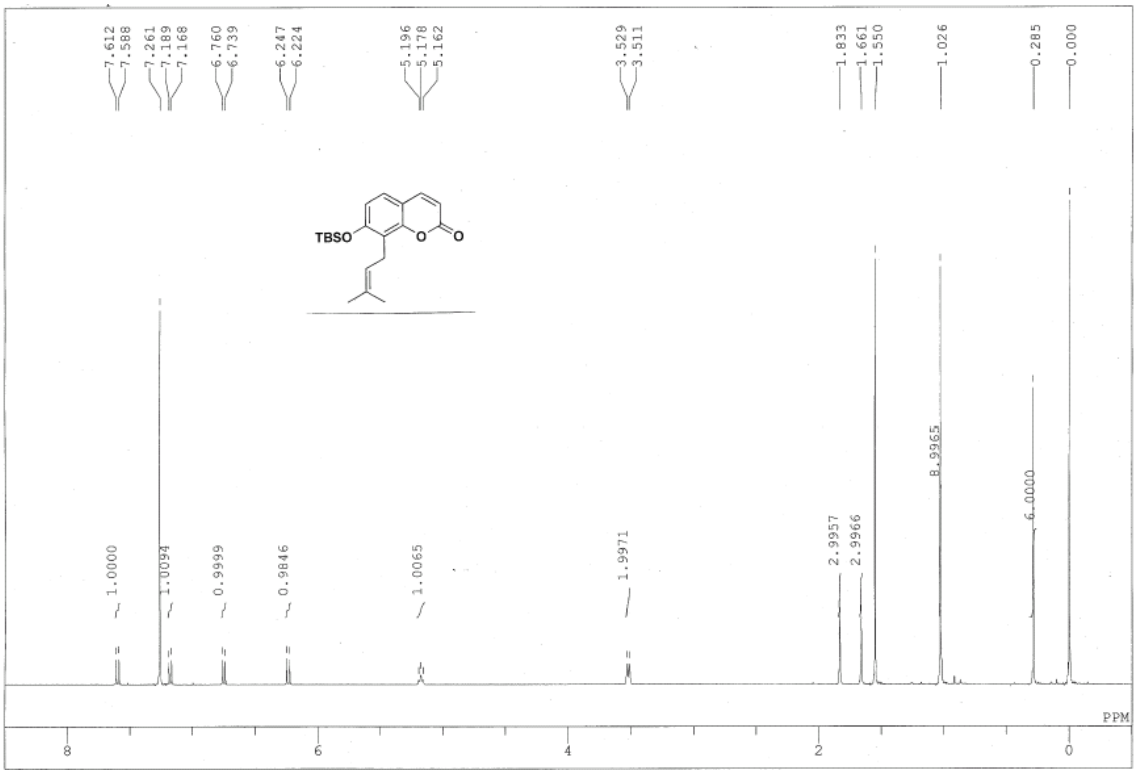
75
50
25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3.529
3.511
1.833
1.661
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1.026
0.285
0.000
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O
O
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1.0094
0.9999
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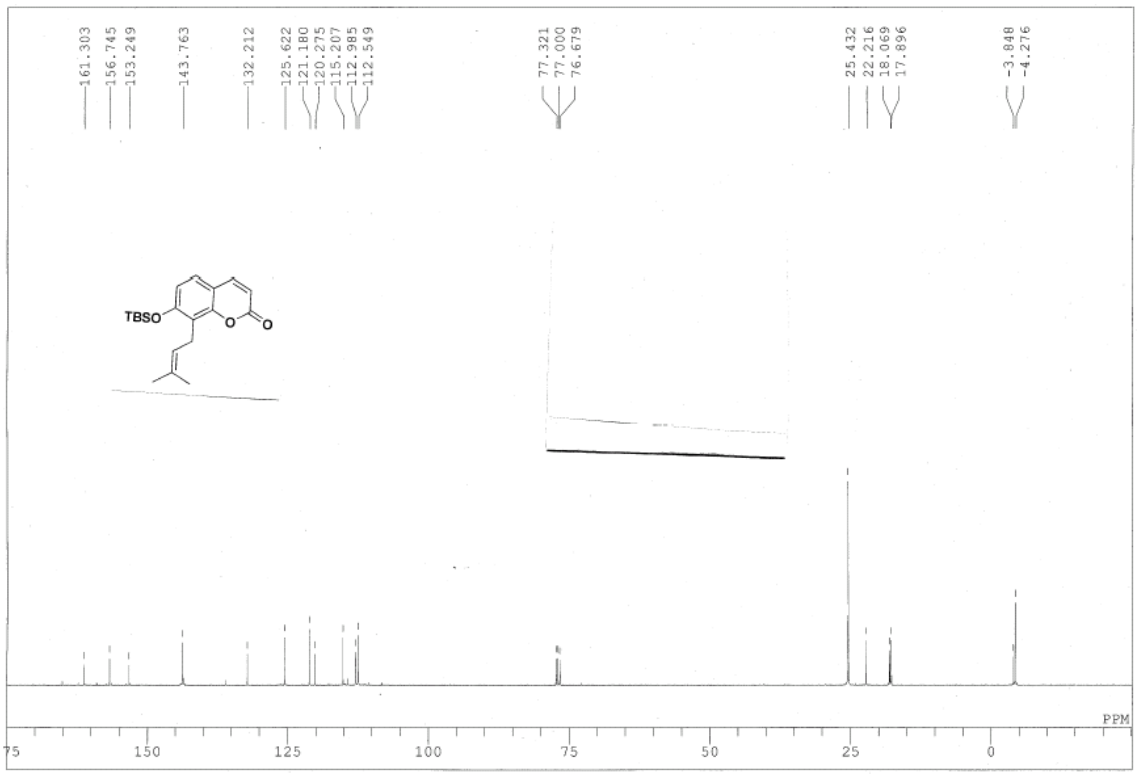
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77.000
76.679
25.432
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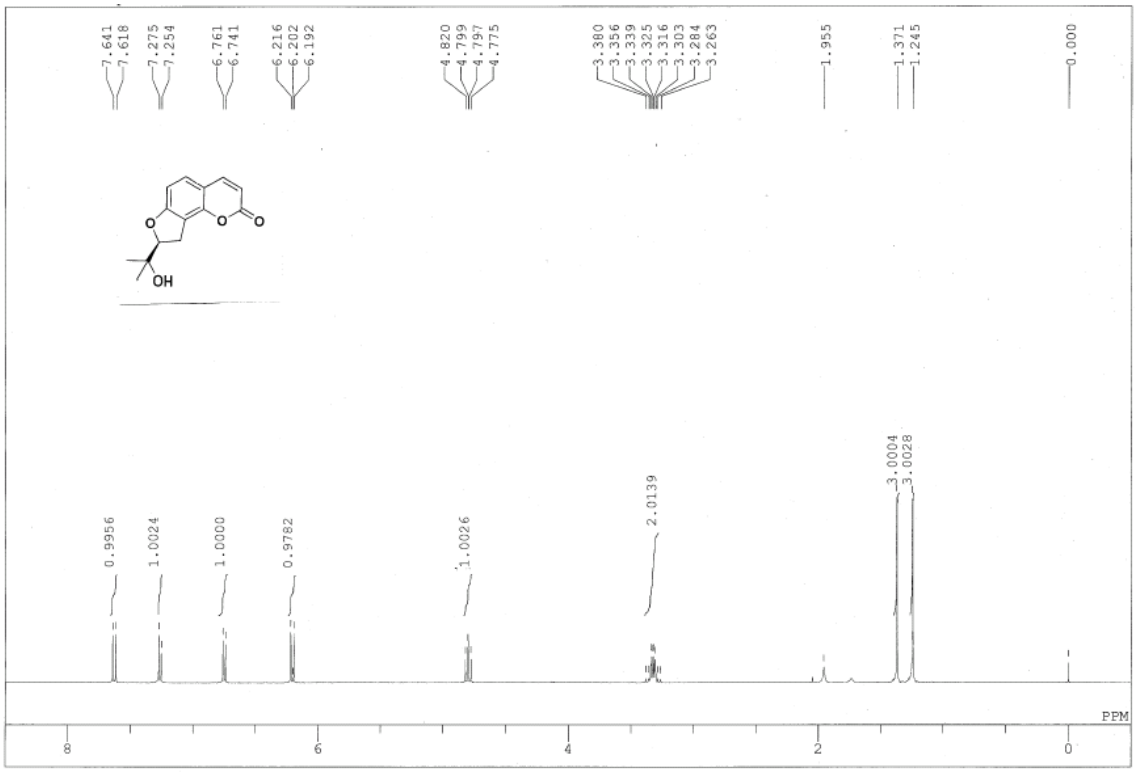
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6.216
6.202
6.192
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4.775
3.380
3.356
3.339
3.325
3.316
3.303
3.284
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1.371
1.245
0.000
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O
OH
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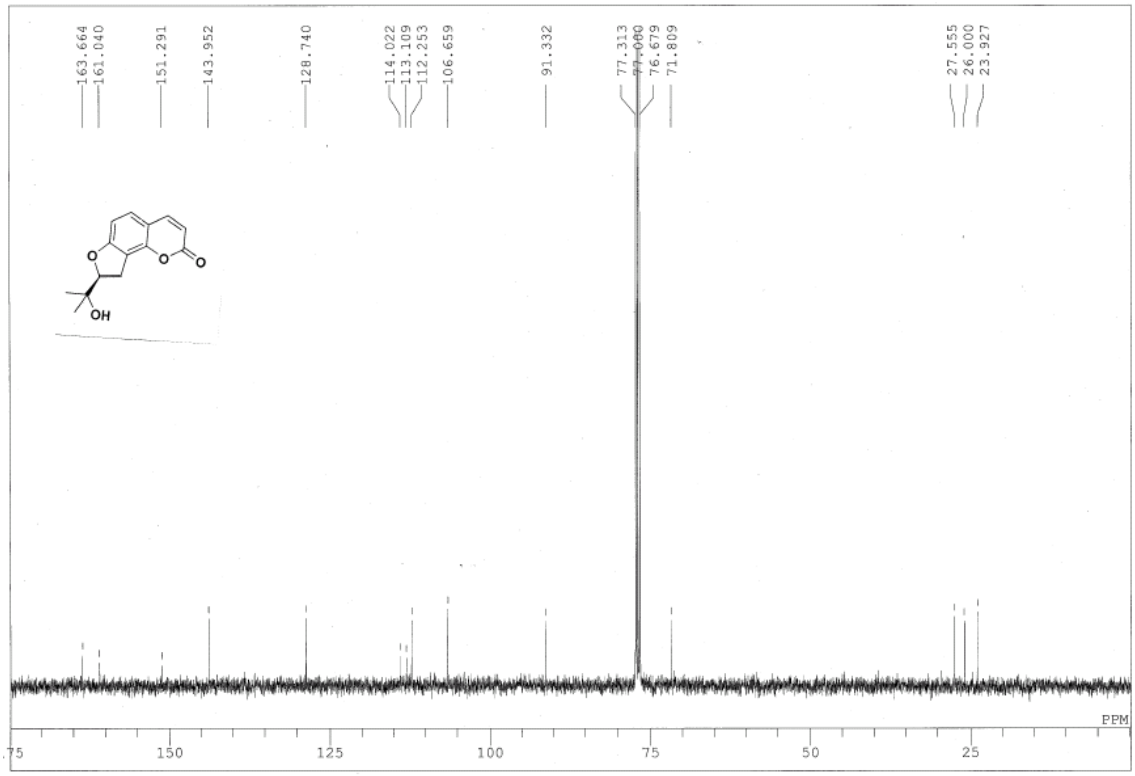
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26.000
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100
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50
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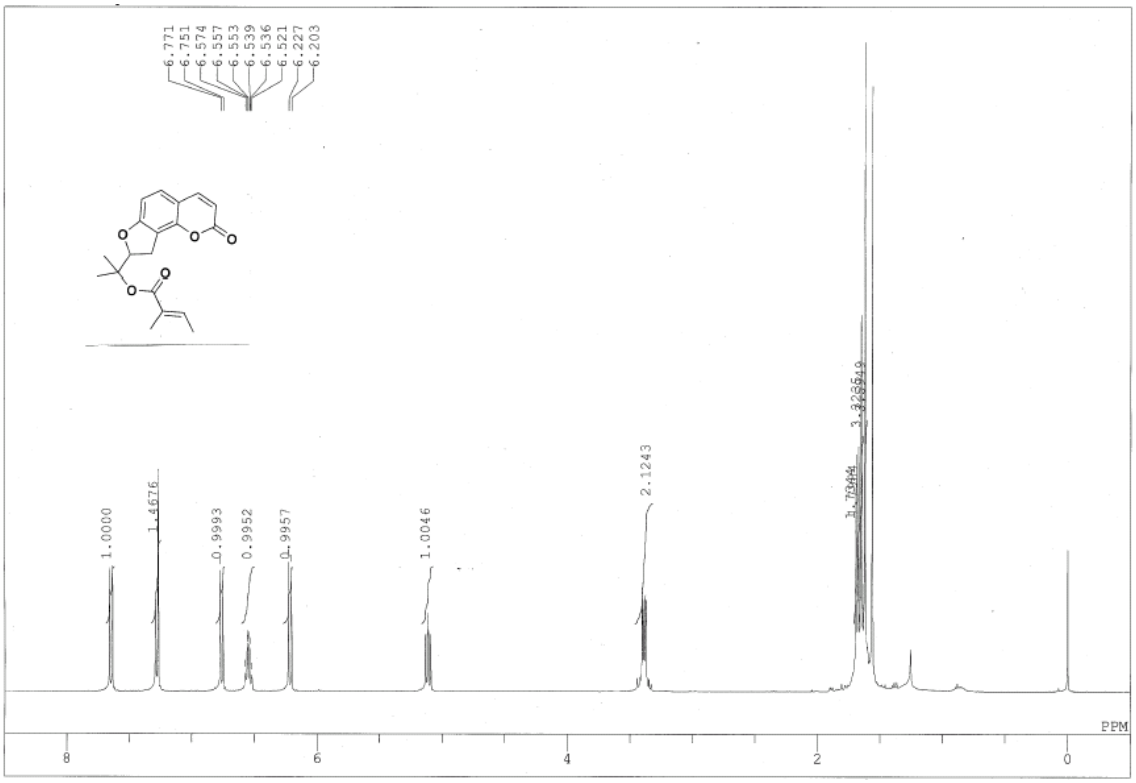
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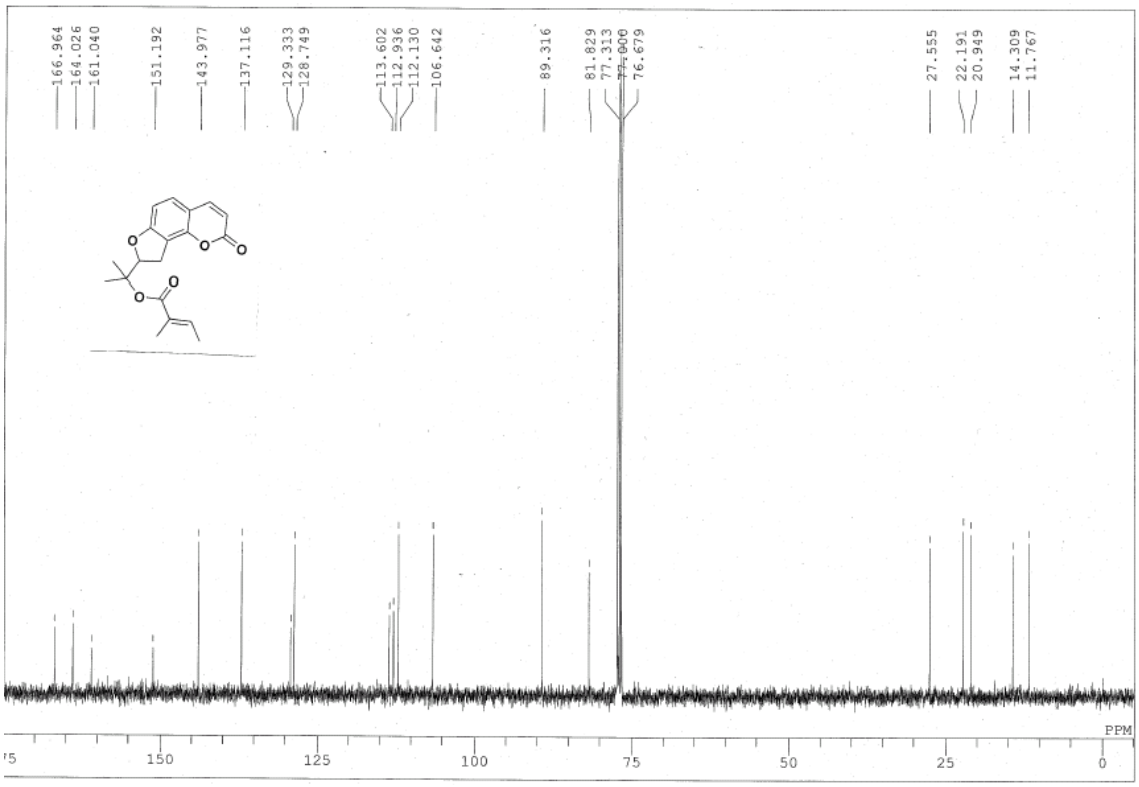
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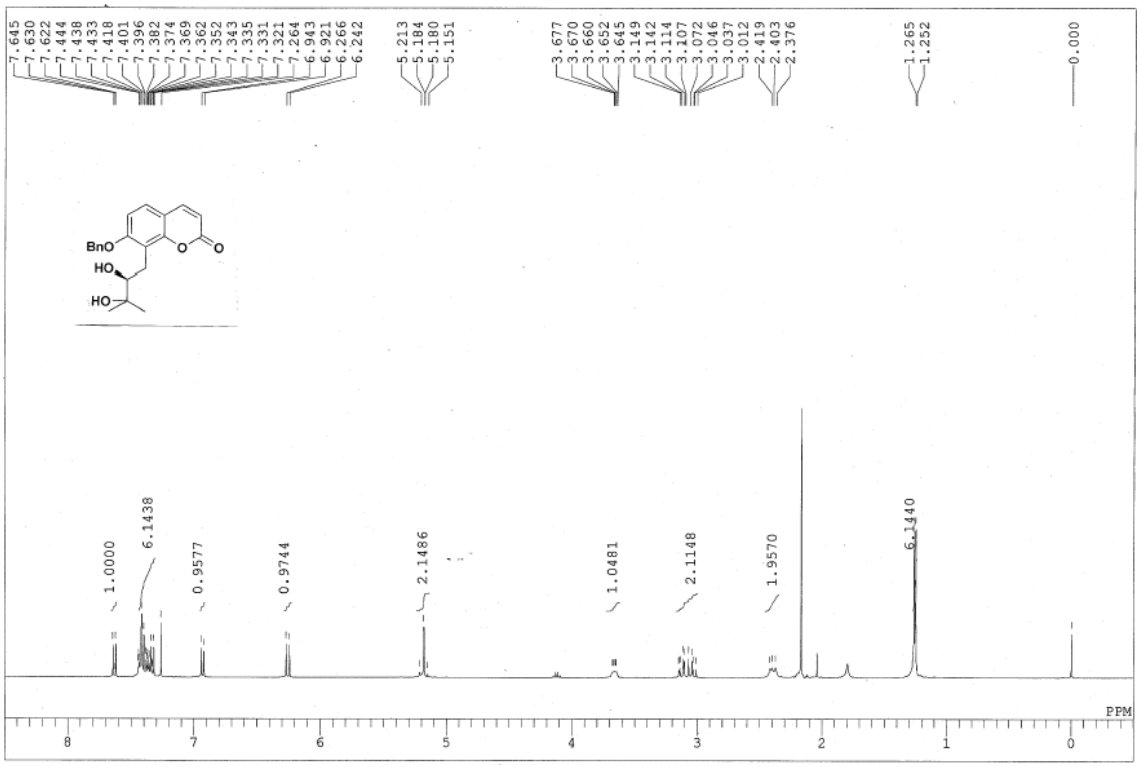
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7.343
7.335
7.331
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3.660
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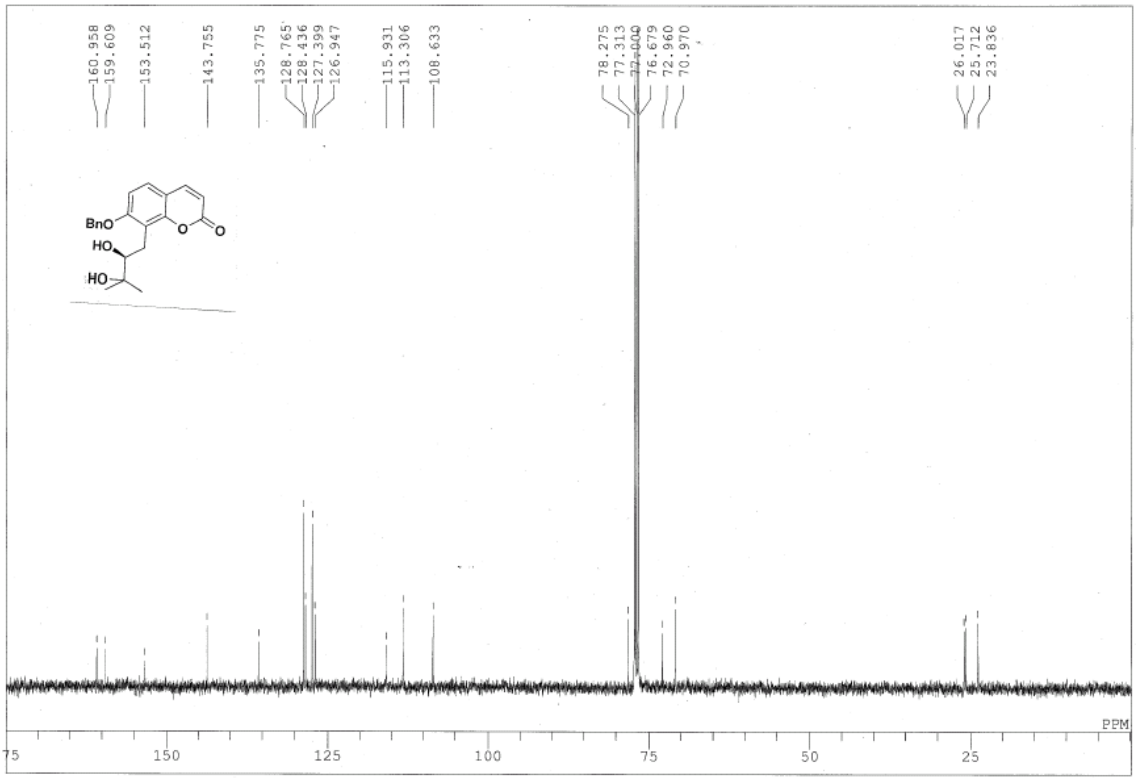
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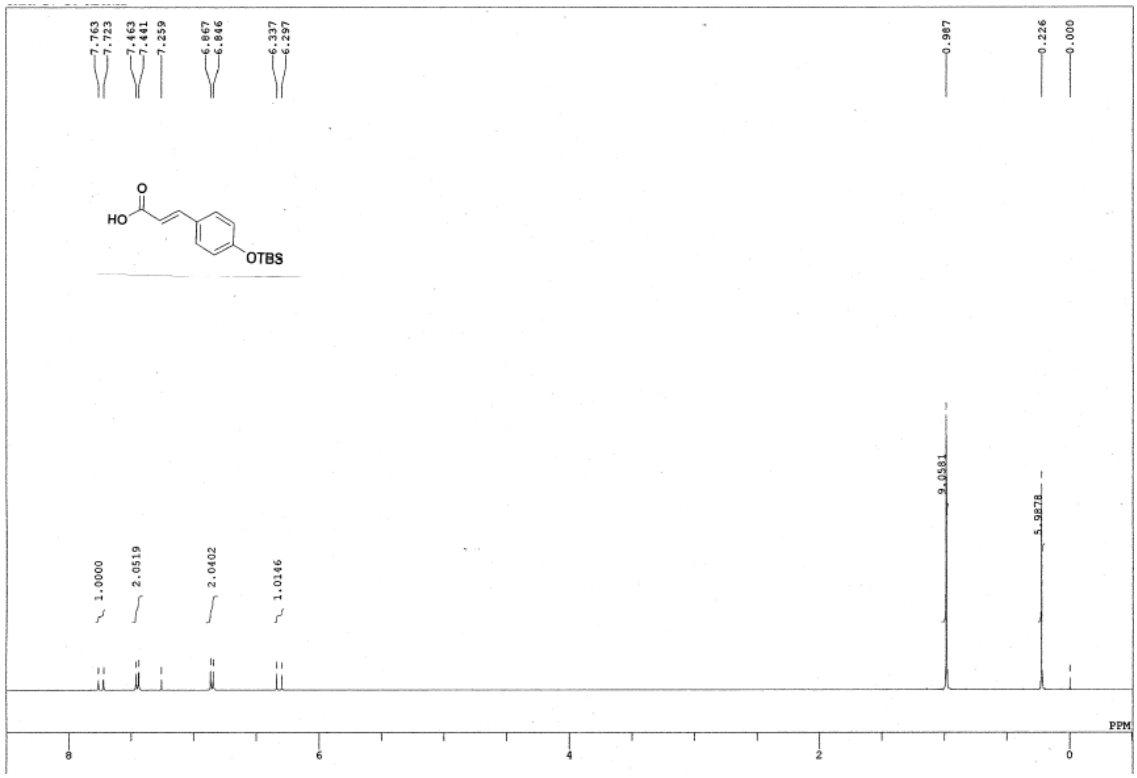
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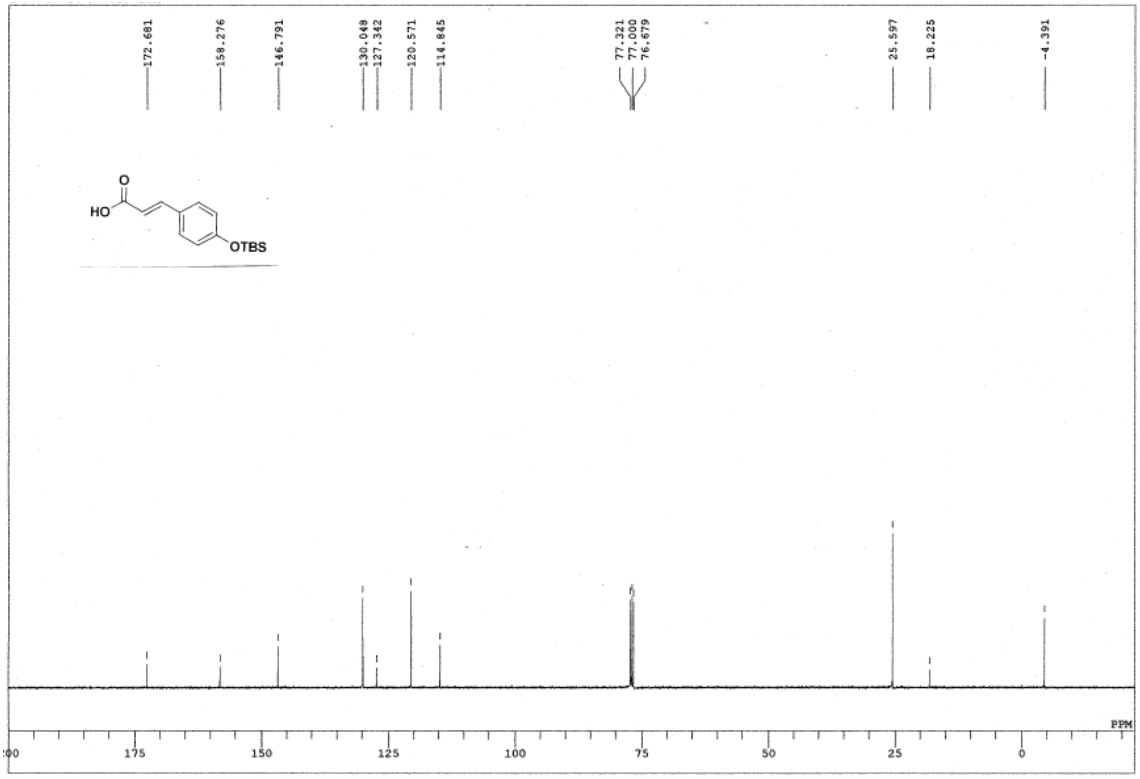
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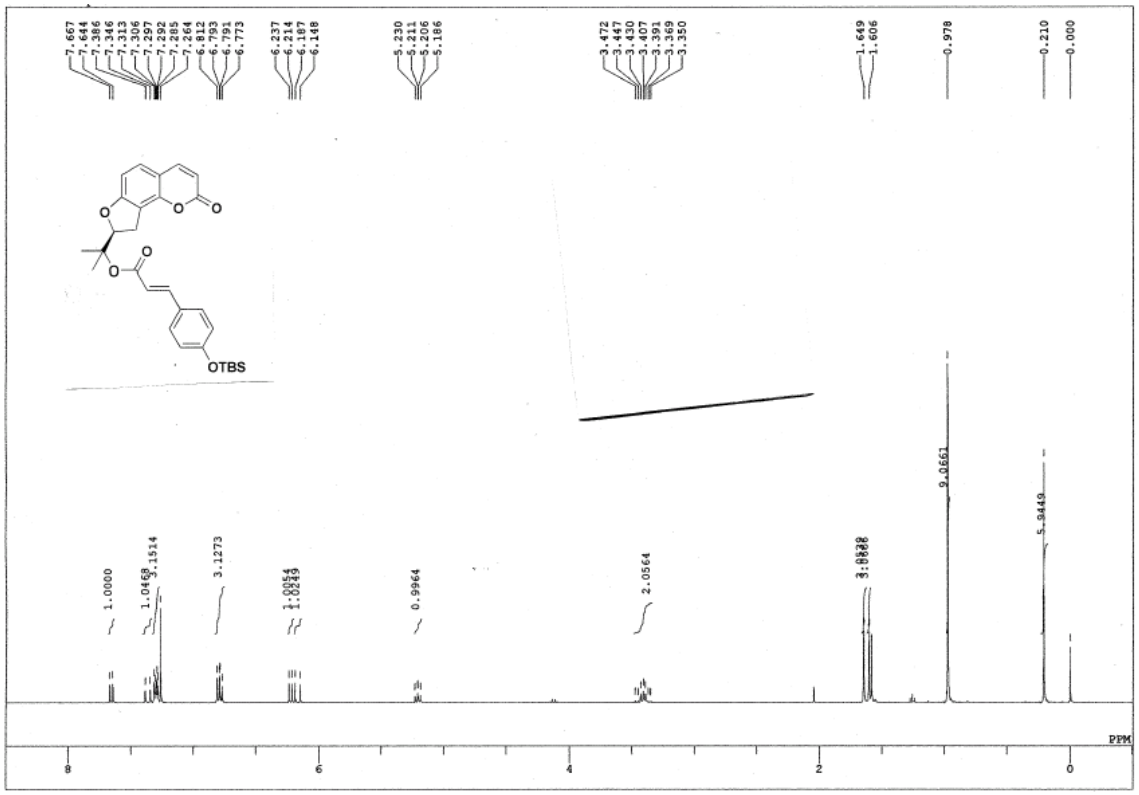
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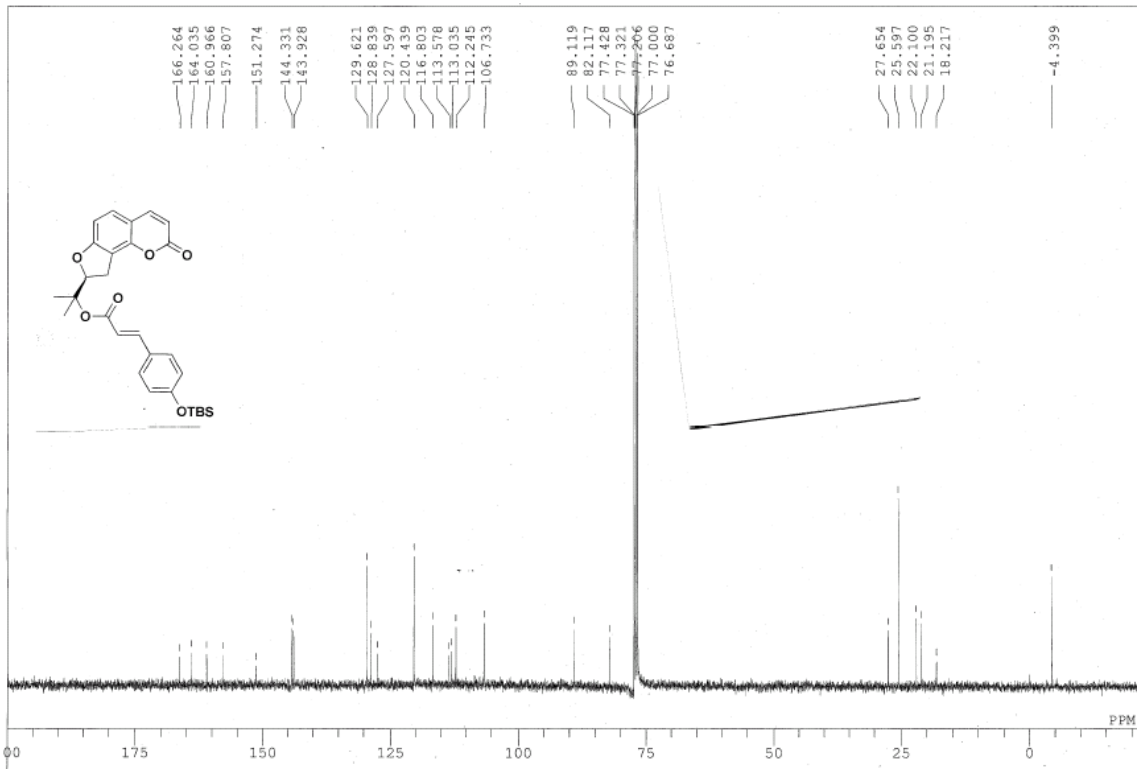
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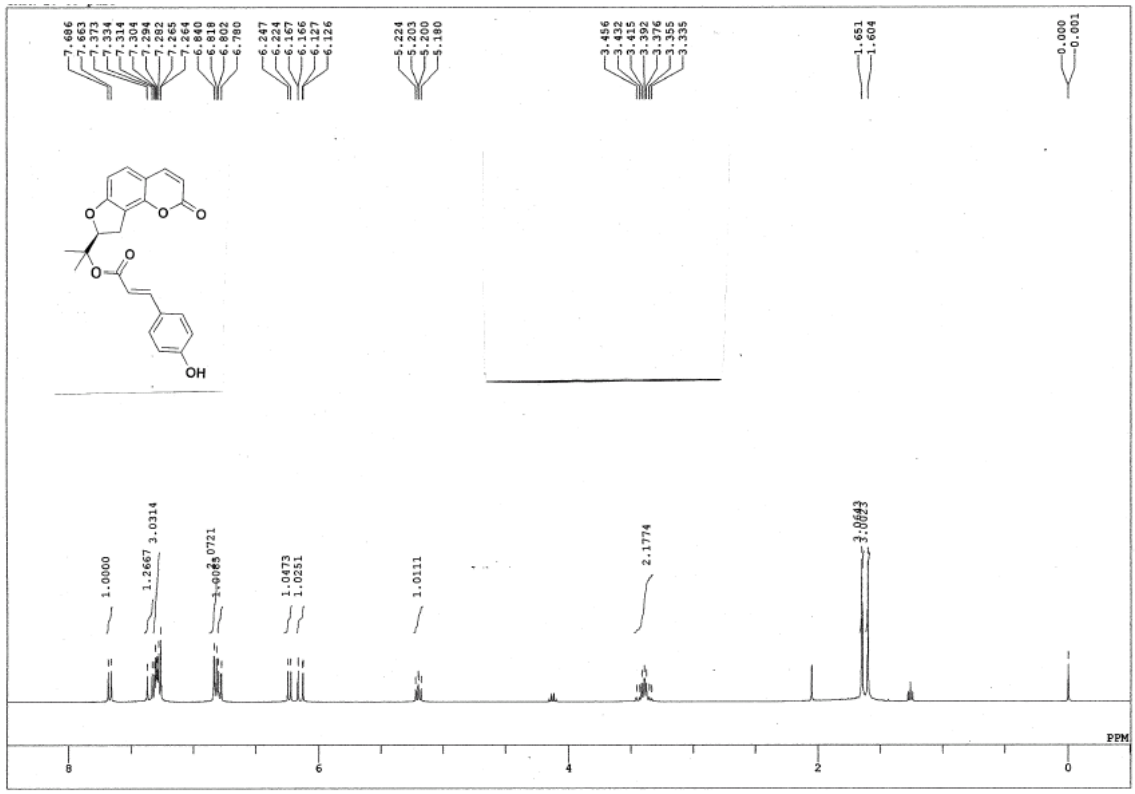
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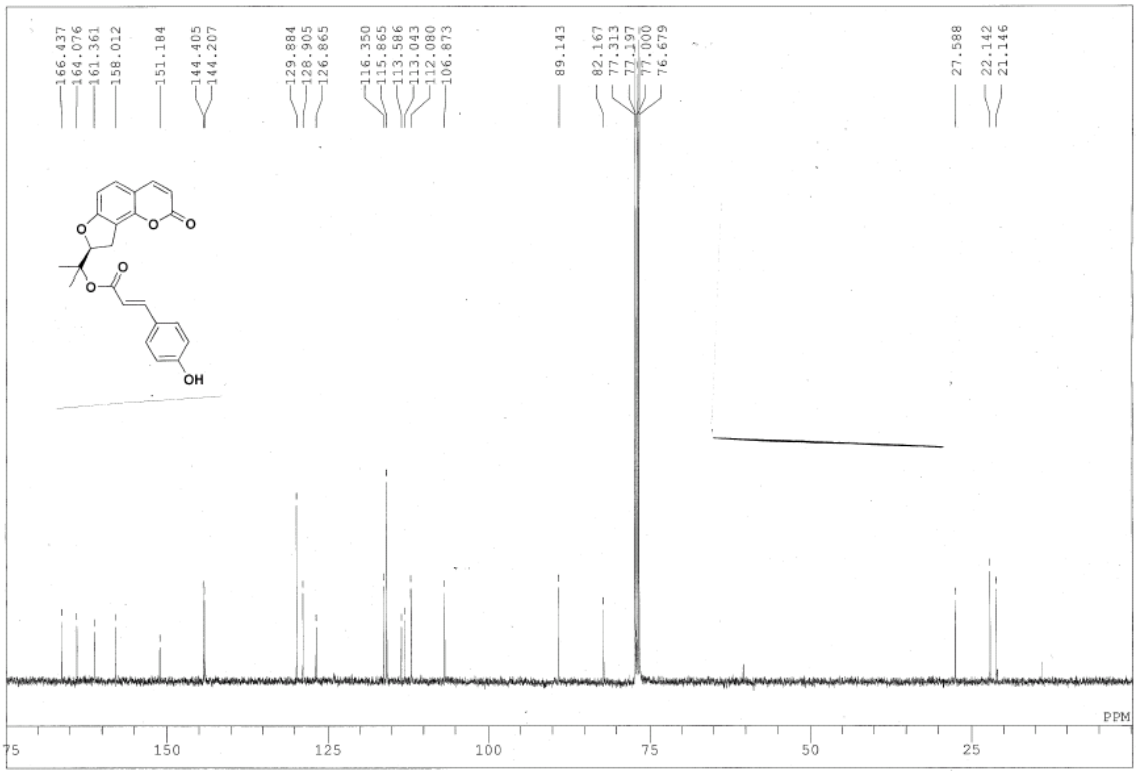
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