Design and Synthesis of an *ortho*-Hydroxyphenyl-containing Spiropyran Thermochromic Colorant

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Supporting Information

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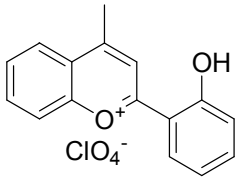
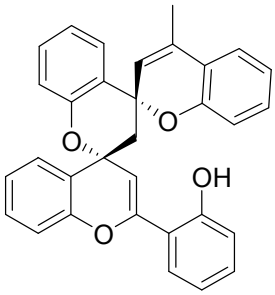
General Experimental

Melting points were determined on a Mel-Temp melting point apparatus in open capillaries and are uncorrected. MS were performed with a JEOL JMS-SX/SX 102A spectrometer. Single-crystal structures were determined with a Bruker AXS SMART-1000 X-ray single-crystal diffractometer. Absorption spectra were recorded using a HP8453 spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded at 300 and 75 MHz on a Varian VXR300 spectrometer. Chemical shifts were reported in parts per million on the δ scale relative to an internal standard (tetramethylsilane, or appropriate solvent peaks) with coupling constants given in hertz. ^{1}H NMR multiplicity data are denoted by s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). Analytical thin-layer chromatography (TLC) was carried out on Merck silica gel 60G-254 plates (25 mm) and developed with the solvents mentioned. Flash chromatography was performed in columns of various diameters with Merck silica gel (230–400 mesh ASTM 9385 kieselgel 60H) by elution with the solvent systems. Solvents, unless otherwise specified, were reagent grade and distilled once prior to use. The commercial chemicals were used as received.

Synthetic procedures

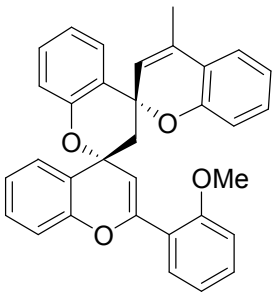


Preparation of 2'-hydroxy-4-methylflavylium perchlorate (2).
To a solution of 2-hydroxyacetophenone (1 g, 7.4 mmol) in acetic acid (30 mL) was added perchloric acid (15 mL) at room temperature. The mixture was refluxed for 13 h. After cooled to room temperature, the precipitate was filtered. The cake was then washed with ethyl acetate and hexanes and then dried under vacuum to give an orange solid in a 66% yield: R_f= 0.30 (15% EtOAc/hexanes); mp 230–231 ^{o}C (lit[1] 230–231 ^{o}C); ^{1}H NMR (CD_3OD, 300 MHz) 9.08 (s, 1H), 8.60–8.21 (m, 4H), 7.98 (t, J = 6.9 Hz, 1H), 7.72 (t, J = 7.2 Hz, 1H), 7.23–7.12 (m, 2H).



Preparation of compound 1.

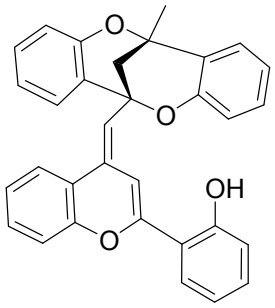
To a solution of **2** (283 mg, 0.6 mmol) in methylene chloride (15 mL) was added triethylamine (303 mg, 1.8 mmol) at room temperature. After the mixture was stirred for 0.5 h. the solution was evaporated under reduced pressure and the crude product was purified by column chromatography (1:12 EtOAc/hexanes) to give a white solid; yield 52%; R_f= 0.42 (15% EtOAc/hexanes); mp 139–140 ^{o}C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.64 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.57 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.51 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.38–7.41 (m, 12H), 6.74 (d, *J* = 7.8 Hz, 1H), 6.39 (s, 1H), 5.44 (s, 1H), 2.86, 2.49 (ABq, *J* = 15.3 Hz, 1H each), 2.10 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 154.1, 152.3, 151.2, 148.7, 147.0, 130.7, 130.4, 130.0, 129.7, 129.5, 129.4, 128.0, 127.1, 124.4, 124.3, 124.1, 123.3, 123.0, 122.3, 121.2 (two peaks overlapped), 120.2, 119.4, 117.8, 117.0, 116.5, 116.4, 102.2, 74.5, 70.2, 46.6, 17.9; IR ν (KBr) 3383, 1483, 1449, 1227, 754 cm^{-1}; HRMS (EI) calcd for $C_{32}H_{24}O_4$ [M^+] 472.1675, found 472.1677.



Preparation of compound 3.

To a solution of **1** (200 mg, 0.4 mmol) in methylene chloride (15 mL) was added an ethereal solution of diazomethane (prepared from the Diazald kit) at 0 ^{o}C. After the reaction was stirred for 1 h, the solvent was removed by evaporation. The crude product was purified by column chromatography (1:22 EtOAc/hexanes) to give a white solid; yield 65%; R_f= 0.65 (10% EtOAc/hexanes); mp 198–199 ^{o}C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.80 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.72 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.53 (td, *J* = 9.8, 1.8 Hz, 1H), 7.31–7.06 (m, 7H), 6.98 (dd, *J* = 7.8, 0.9 Hz, 1H), 6.94–6.80 (m, 4H), 6.77 (dd, *J* = 8.1, 0.9 Hz, 1H), 6.54 (s, 1H), 6.31 (s, 1H), 3.70 (s,

3H), 2.63, 2.40 (ABq, J = 14.1 Hz, 1H each), 1.89 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 157.2, 154.3, 153.4, 151.5, 146.1, 129.8 (three peaks overlapped), 129.4, 128.9, 127.9, 127.1, 126.5, 124.5, 124.1, 123.9, 122.6, 121.8, 121.5, 121.1, 120.6, 120.3, 117.7, 117.4 , 116.9, 115.8, 111.1, 105.1, 75.5, 71.1, 55.0, 39.4, 25.3.; IR ν (KBr) 1637, 1483, 1455, 1295, 1232, 748 cm^{-1}; HRMS (EI) calcd for $C_{33}H_{26}O_4$ [M^+] 486.1831, found 486.1828.



Isolation of compound 6.

To a solution of **1** (50 mg, 0.1 mmol) in chloroform was heated to 40 ^{o}C for 8 h. After cooled down to room temperature, the solvent was evaporated under the reduced pressure and the crude product was purified by column chromatography (1:20 EtOAc/hexanes) to give a white solid; yield 75%; R_f = 0.38 (15% EtOAc/hexanes); mp 183−184 ^{o}C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.80 (dd, J = 8.1, 1.5 Hz, 1H), 7.52 (dd, J = 7.8, 1.5 Hz, 1H), 7.35−7.10 (m, 6H), 6.98 (td, J = 7.8, 1.5 Hz, 1H), 6.92−6.81 (m, 7H), 6.60 (s, 1H), 6.30 (s, 1H), 6.13 (s, 1H), 2.41 (s, 2H), 1.87 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 154.2, 154.1, 153.2, 150.5, 148.7, 130.9, 130.1, 129.8, 129.4, 129.3, 127.8, 126.6, 125.9, 124.8, 124.3, 123.8, 122.9, 121.3, 121.1, 120.8, 120.5, 119.2, 117.5, 117.3 (two peaks overlapped), 117.2, 116.7, 103.2, 75.4, 71.1, 40.1, 25.1; IR ν (KBr) 3383, 3338, 1456, 1455, 1238, 748 cm^{-1}; HRMS (EI) calcd for $C_{32}H_{24}O_4$ [M^+] 472.1675, found 472.1678 .

The UV−vis absorption spectra of 1.

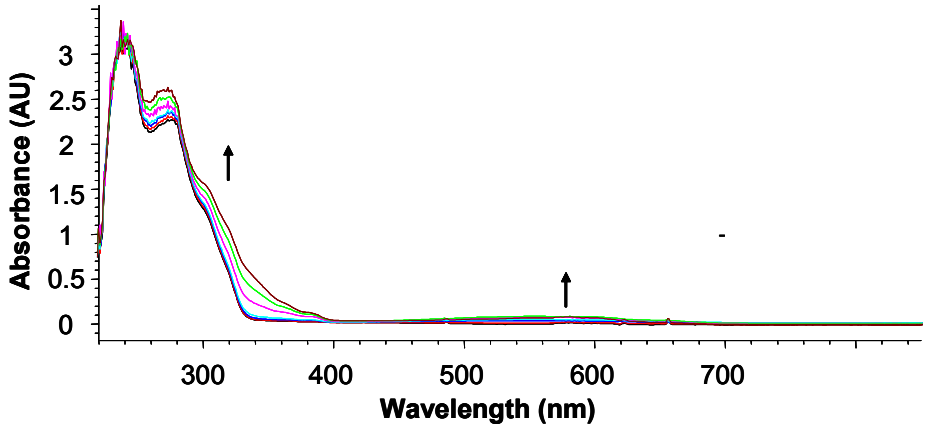


Figure S1. The absorption spectra of **1** (1.9×10^{-5} M in $CHCl_3$) obtained under temperature between -20 to 50 ^{o}C.

X-ray crystallography

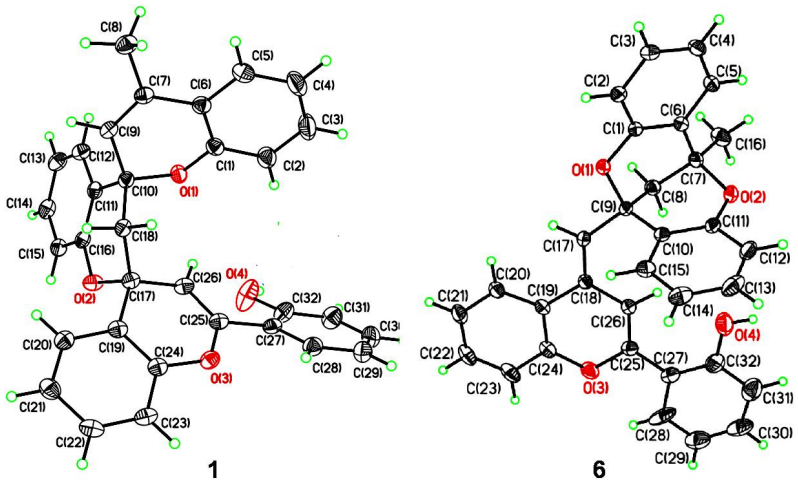


Figure S2. X-ray crystal structures of compounds **1** and **6**.

Variable temperature ^{1}H NMR experiments of 1

Figure S3 shows the partial proton NMR spectra of **1** in $CDCl_3$ obtained under temperature between 20 to 55 ^{o}C. The emergence of three discernible new singlets at 6.29, 5.21, and 4.78 ppm were tentatively assigned to the three olefin hydrogen absorptions of **8**. The new singlet at 5.79 ppm could be the hydroxy hydorgen absorption.

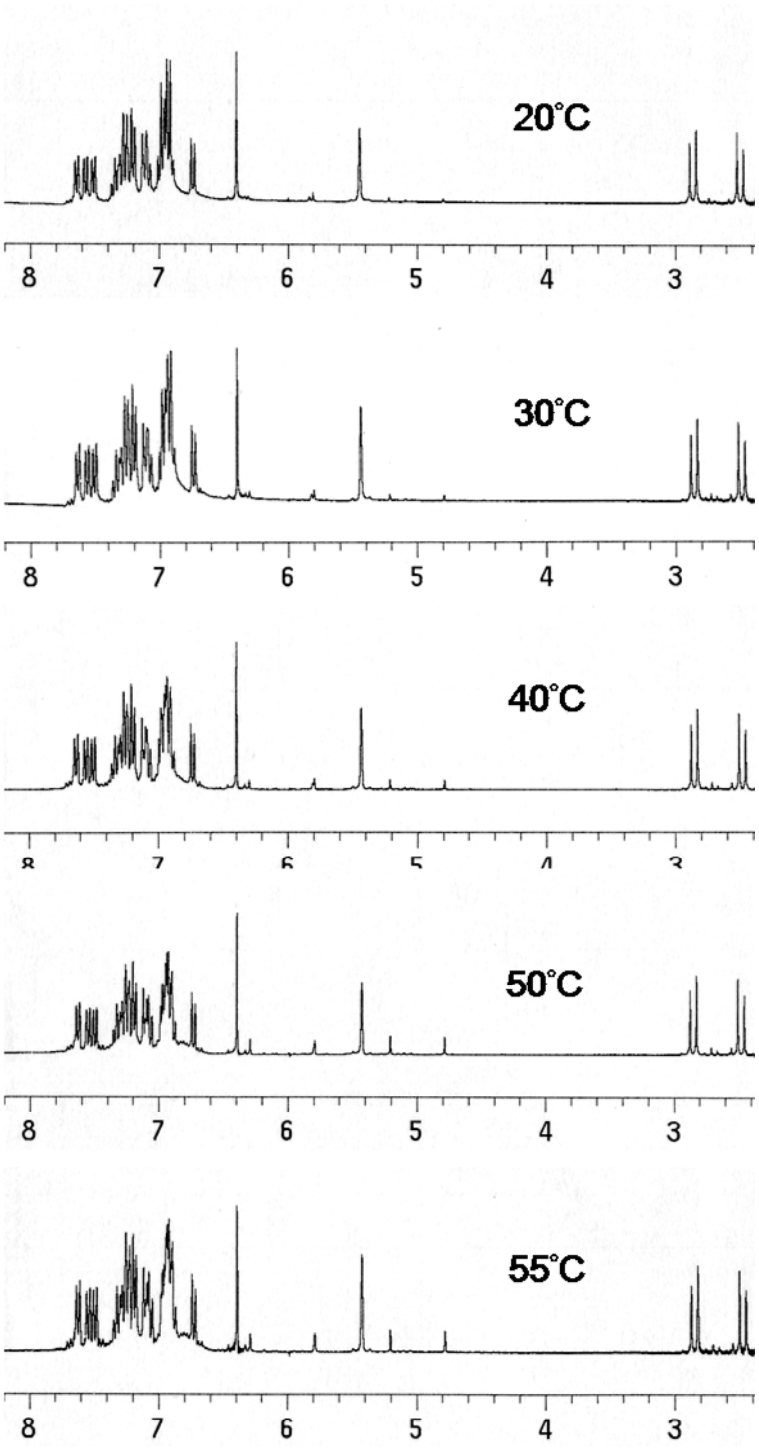
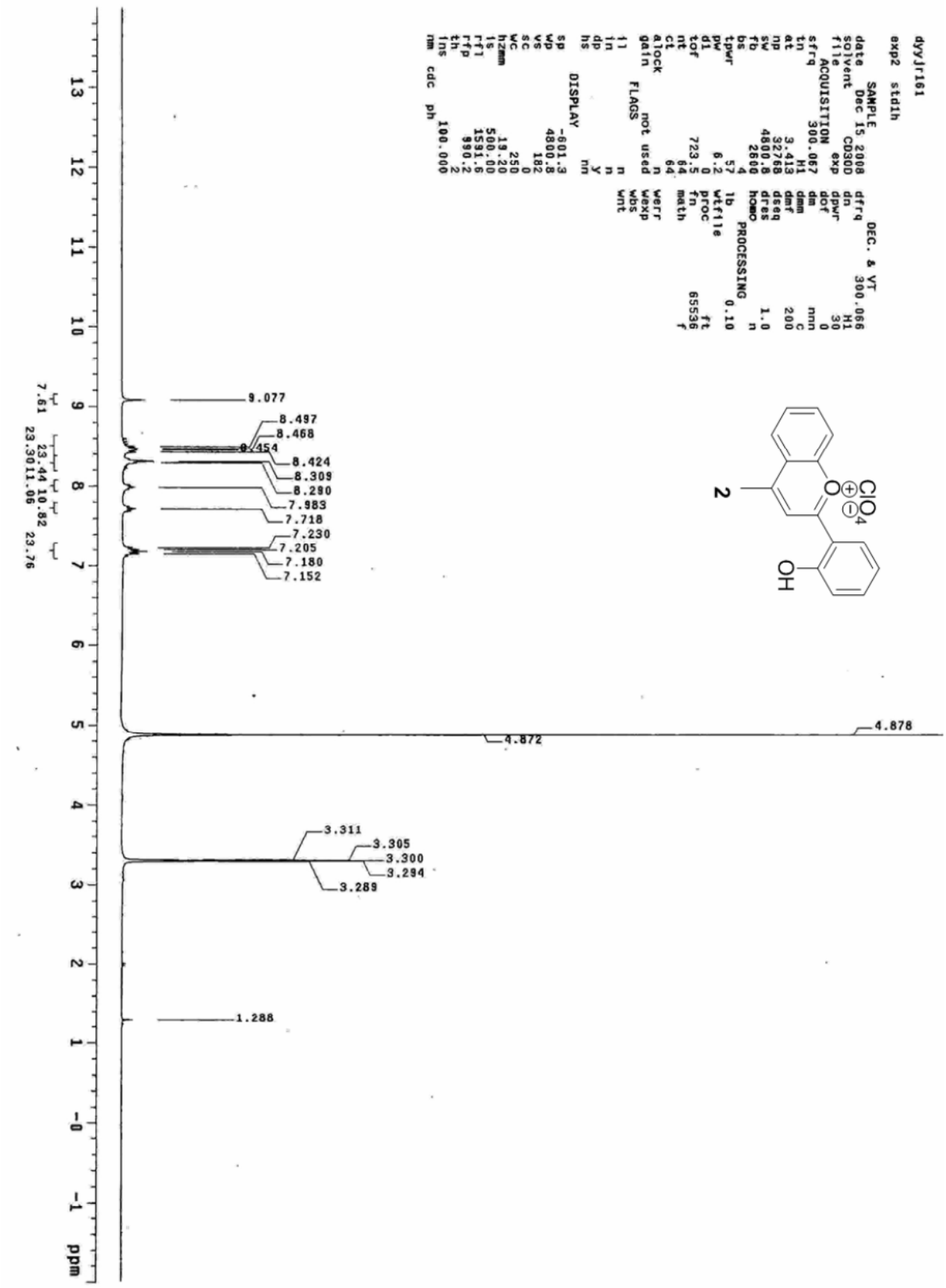


Figure S3. The partial proton NMR spectra of **1** in $CDCl_3$ obtained under temperature between 20 to 55 ^{o}C.

Reference

1. Dorofeenko, G. N.;Tkachenko, V. V. *J. Heterocycl. Chem*. **1974**, *10*, 154–157.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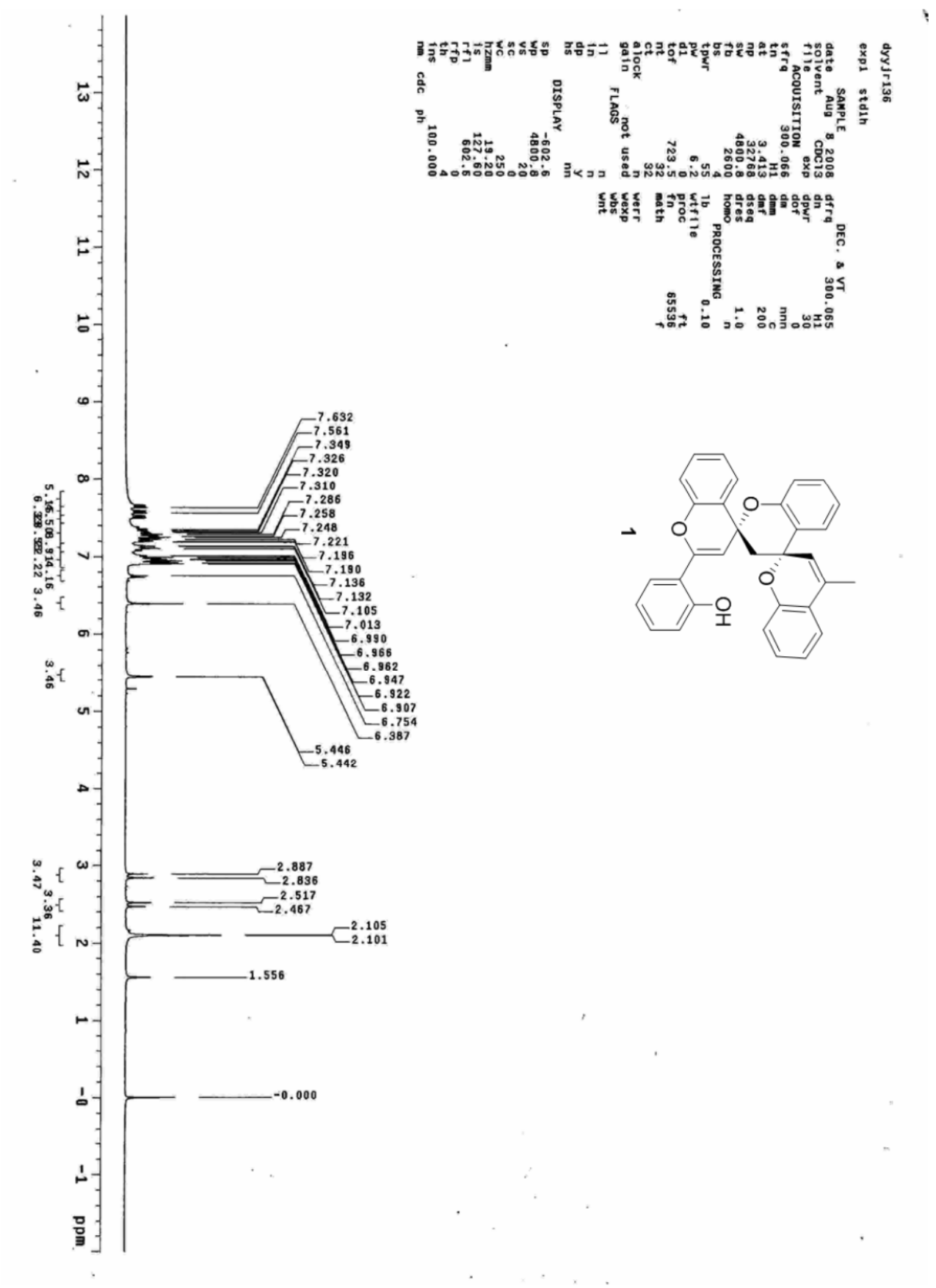
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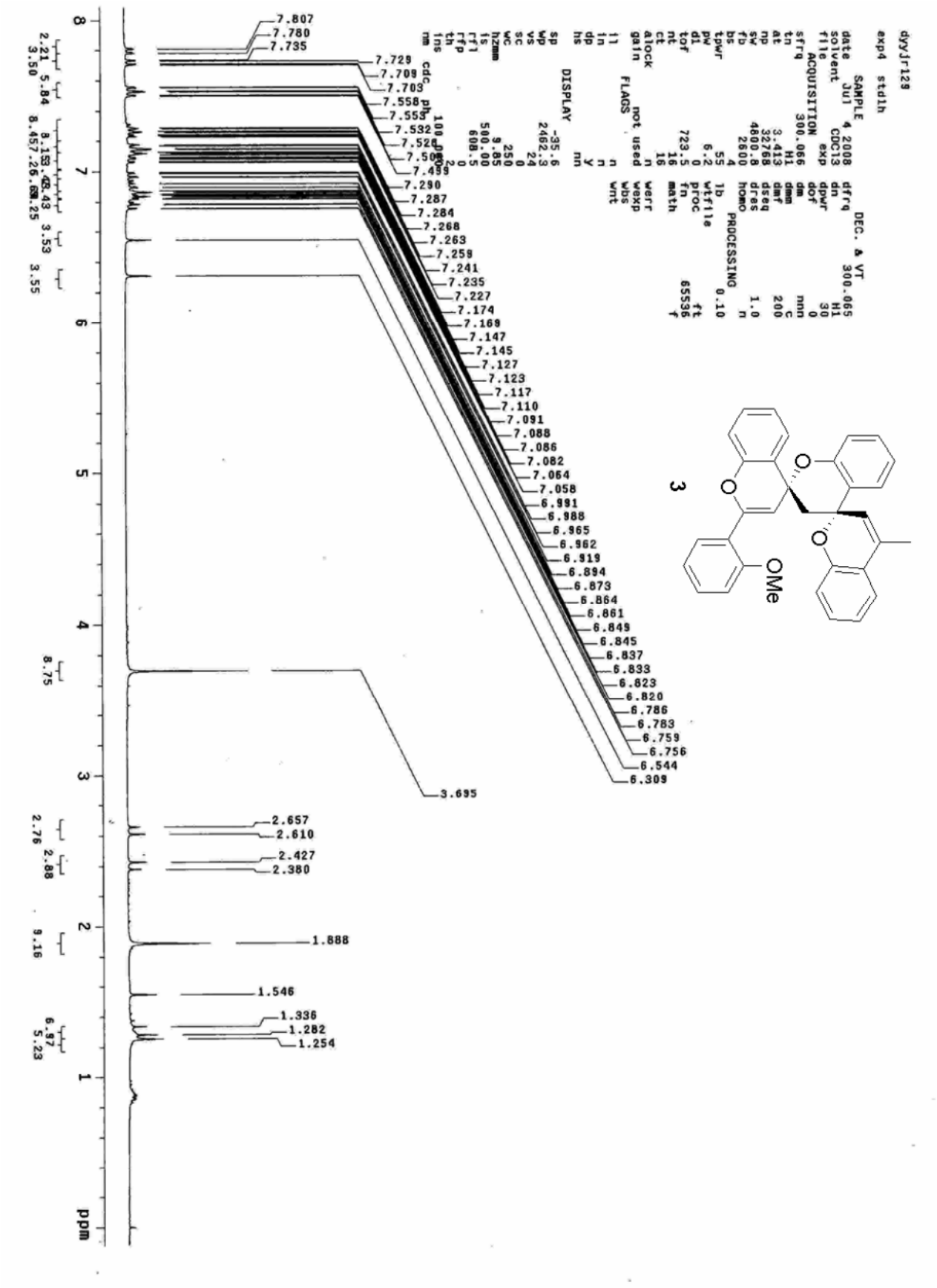
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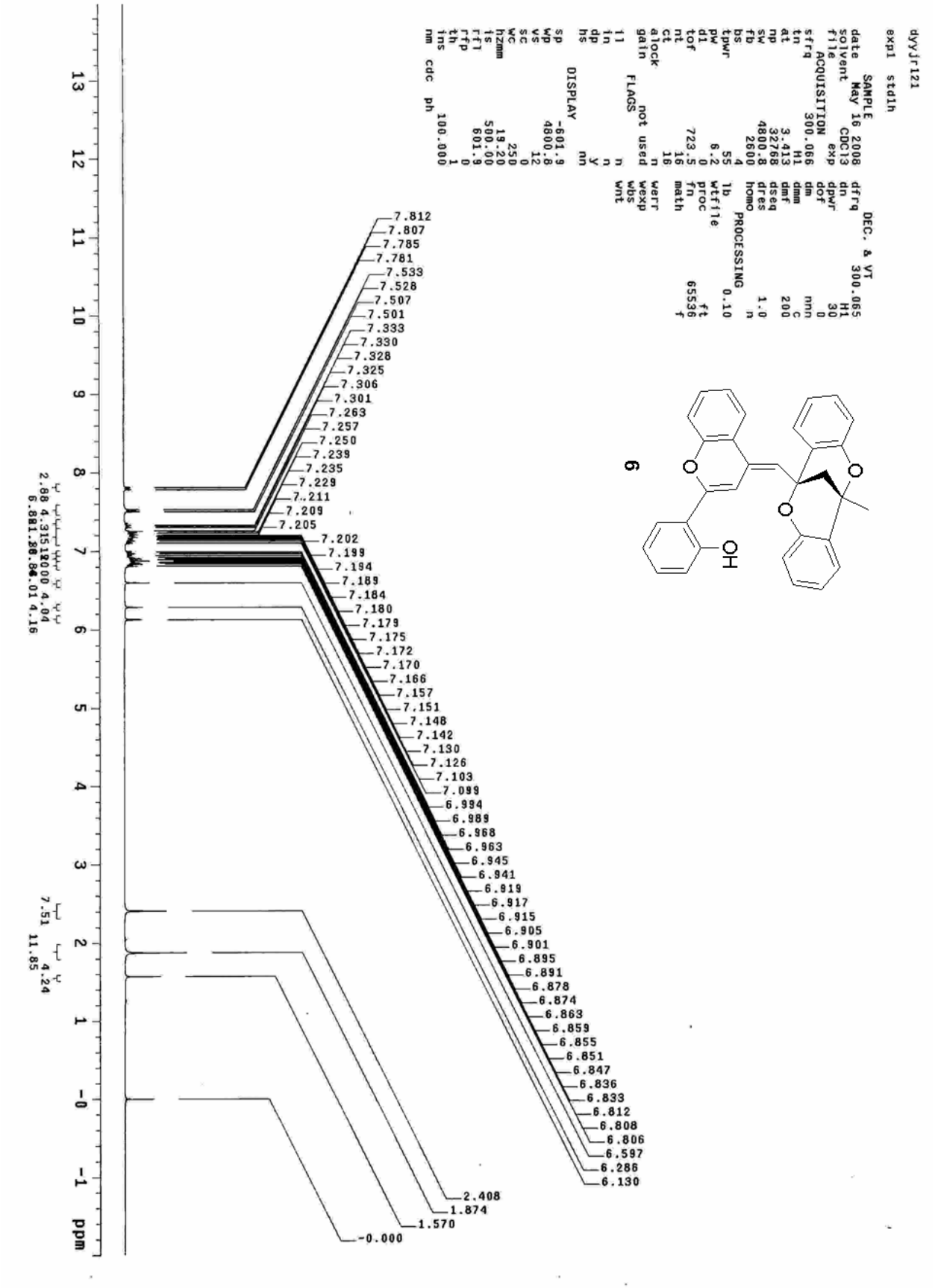
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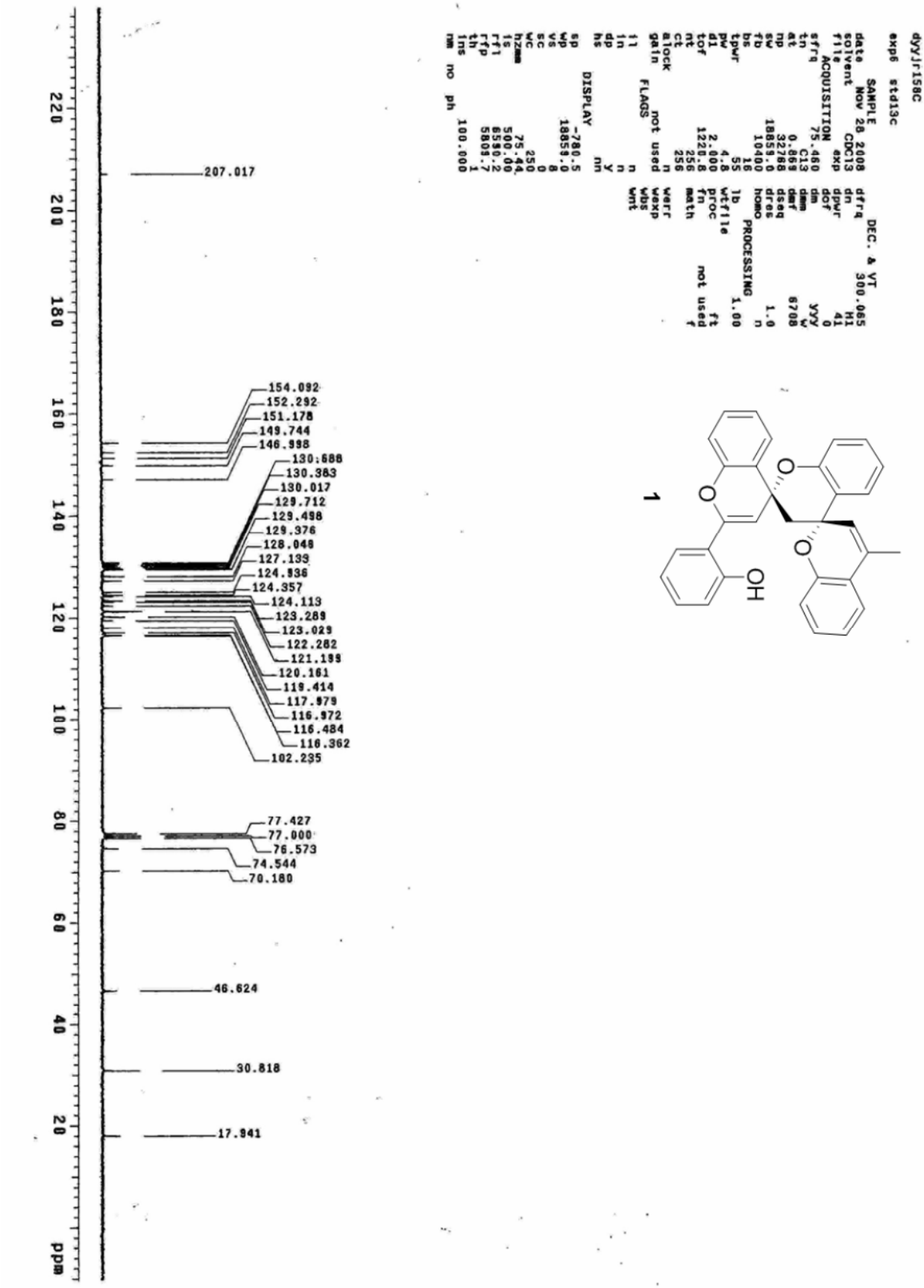
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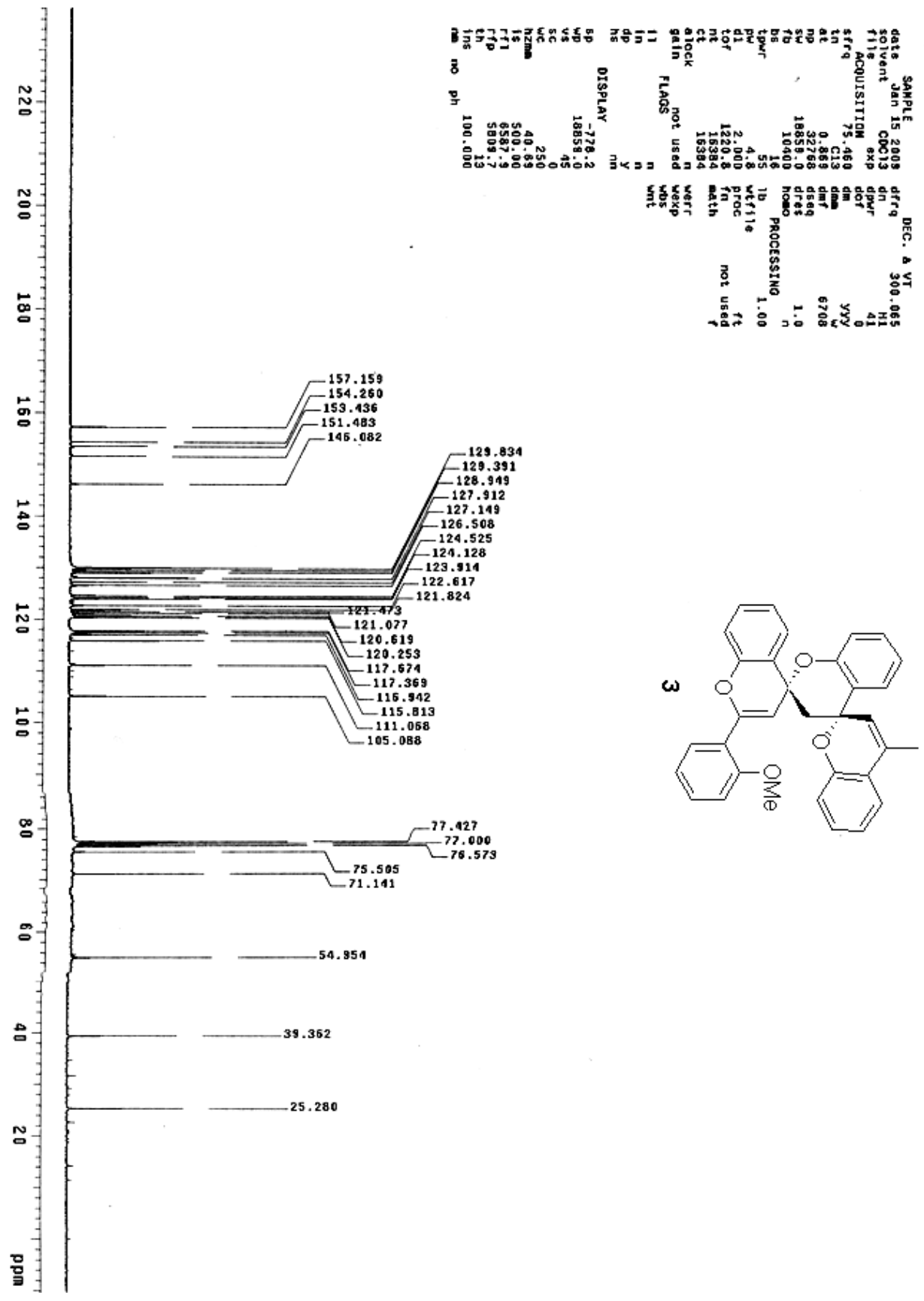
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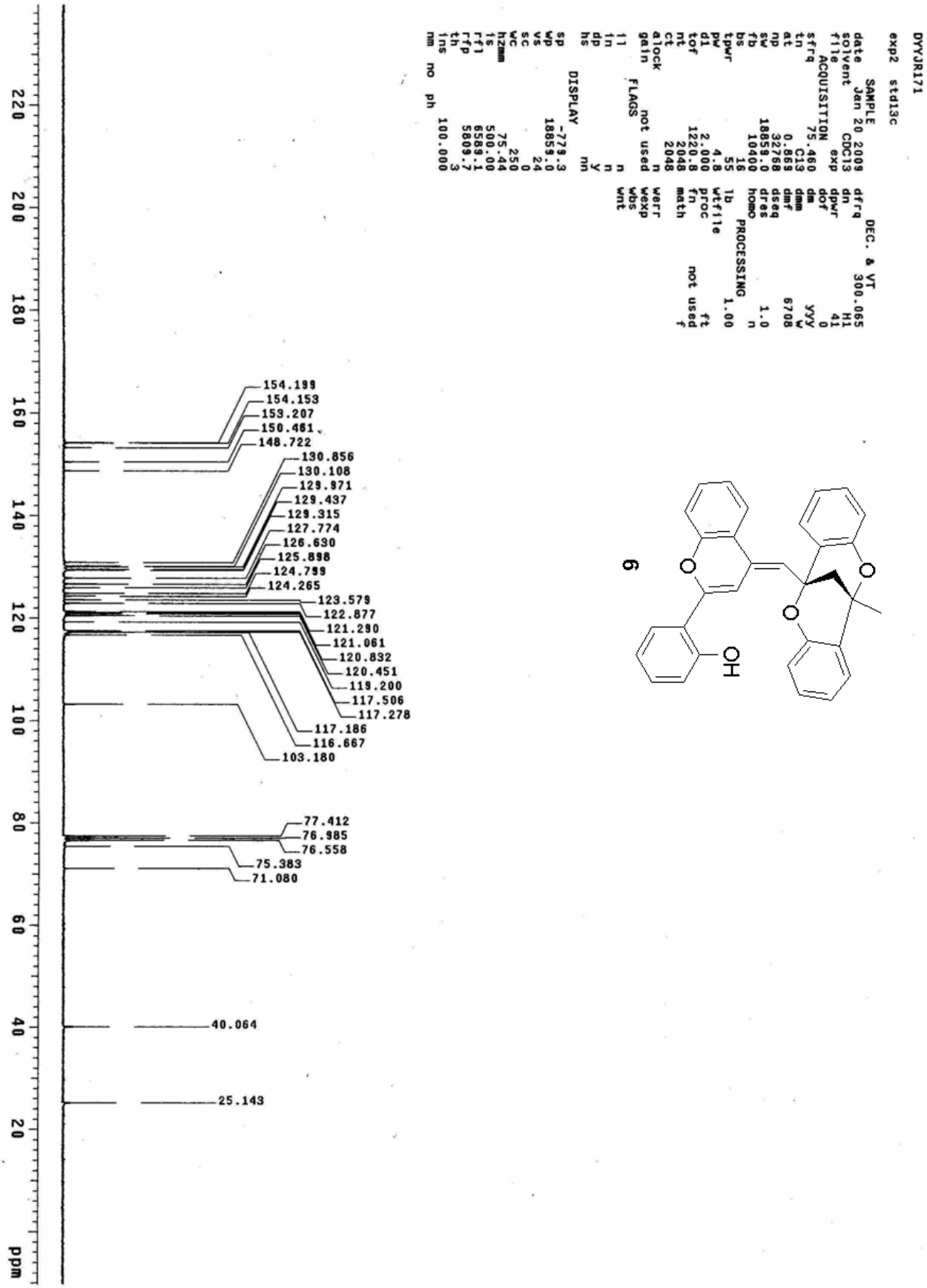
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127.774
126.630
125.898
124.799
124.265
123.579
122.877
121.290
121.061
120.832
120.451
119.200
117.506
117.278
117.186
116.667
103.180
77.412
76.985
76.558
75.383
71.080
40.064
25.143
ppm
6
OH