

Supporting Information
for
Oxidative phenylamination of 5-substituted 1-hydroxynaphthalenes to *N*-phenyl-1,4-naphthoquinone monoimines by air and light “on water”

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Experimental procedures, characterization data, copies of the NMR spectra of compounds 4a, 9, 10 and X-ray view of compound 6.

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Experimental:

General

All reagents were commercially available reagent grade and were used without further purification. Melting points were determined on a Stuart Scientific SMP3 apparatus and are uncorrected. ^1H -NMR spectra were recorded on Bruker AM-400 instrument. ^{13}C -NMR spectra were obtained at 100 MHz. Bidimensional NMR techniques and DEPT were used for signal assignment. Chemical shifts are expressed in ppm downfield relative to tetramethylsilane and the coupling constants (J) are reported in Hertz. HRMS data for all final compounds were obtained using a LTQ-Orbitrap mass spectrometer (Thermo-Fisher Scientific, MA 02454, USA) with the analysis performed using an APCI source operated in positive mode. Silica gel Merck 60 (70–230 mesh) was used for preparative column chromatography and TLC aluminum foil 60F₂₅₄ for analytical TLC.

Procedure for synthesis of compound 4a and 4b

A suspension of 1,5-dihydroxynaphthalene (**1**; 1.25 mmol), rose bengal (20 mg; 0.02 mmol) as sensitizer and water (150 mL), in a round bottom flask, was exposed to direct sunlight for 5 h while a gentle stream of air is bubbled through the solution. Then is added 4-hydroxyphenylamine (1.5 mmol), and the solution was stirred at rt for 4 h. Work up followed by column chromatography over silica gel (2.5:1.5 petroleum ether/ethyl acetate) yield pure compounds **4a** and **4b**.

Spectroscopic data

5-Hydroxy-3-((4-hydroxyphenyl)amino)naphthalene-1,4-dione (**4a**): Isolated yield 45%; brown solid, mp 247-249 °C; IR (KBr) ν_{max} cm^{-1} : 3384 (O-H), 3340 (O-H), 3286 (N-H), 1630 (C=O), 1619 (C=O). ^1H -NMR (400 MHz, DMSO- d_6): δ 5.82 (s, 1H, 2-H), 6.85 (d, 2H, J = 8.5 Hz, 3'-H + 5'-H), 7.16 (d, 2H, J = 8.5 Hz, 2'-H + 6'-H), 7.23 (d, 1H, J = 8.4 Hz, 6-H), 7.45 (d, 1H, J = 7.3 Hz, 8-H), 7.72 (dd, 2H, J = 7.8, 7.9 Hz, 7-H), 8.27 (s, 1H, 4'-OH), 9.0 (s, 1H, NH), 9.54 (s, 1H, 5-OH); ^{13}C -NMR (100 MHz, DMSO- d_6): δ 101.54, 114.67, 116.26 (2C), 117.94, 122.36, 126.25 (2C), 129.25, 133.60, 137.91, 147.45, 155.84, 160.90,

181.80,186.18. HRMS (APCI) calcd. for $C_{16}H_{11}NO_4$: 281.06881 $[M+H]^+$; found 281.07541.

5-Hydroxy-2-((4-hydroxyphenyl)amino)naphthalene-1,4-dione (4b): Isolated yield 16%; brown solid, mp 241-243 °C; IR (KBr) $\nu_{\max}$ cm^{-1} : 3383 (O-H), 3339 (O-H), 3286 (N-H), 1631 (C=O), 1619 (C=O). 1H -NMR (400 MHz, DMSO- d_6): δ 5.82 (s, 1H, 3-H), 6.85 (d, 2H, J = 8.6 Hz, 3'-H + 5'-H), 7.16 (d, 2H, J = 8.6 Hz, 2'-H + 6'-H), 7.22 (d, 1H, J = 8.3 Hz, 6-H), 7.45 (d, 1H, J = 7.3 Hz, 8-H), 7.72 (dd, 2H, J = 7.7, 8.1 Hz, 7-H), 9.0 (s, 1H, NH), 9.56 (s, 1H, 4'-OH), 11.45 (s, 1H, 5-OH); ^{13}C -NMR (100 MHz, DMSO- d_6): δ 101.56, 114.67, 116.27 (2C), 117.93, 122.36, 126.24 (2C), 129.26, 133.61, 137.89, 147.44, 155.85, 160.92, 181.80, 186.16; HRMS (APCI) calcd. for $C_{16}H_{11}NO_4$: 281.06881 $[M+H]^+$; found 281.07527.

General procedure for the synthesis of compounds 6-10

A suspension of 1,5-dihydroxynaphthalene (**1**) or 5-acetylamino-1-hydroxynaphthalene (**5**; 1.25 mmol), rose bengal (20 mg), the phenylamine required (1.25 mmol) and water (150 mL), into a round bottom flask, was vigorously stirred at room temperature. Then, the solution was irradiated by solar light or Light Emitting Diode lamps (LED: InGaN, 0.768 W, 42.24 lm, 530 nm) for 5 h at the same time a gently stream of air is bubbled through the solution. The reaction mixture was extracted with ethyl acetate (2 x 20 mL), the dry extract was evaporated under vacuum and the residue was chromatographed on silica gel (3:1 petroleum ether/ethyl acetate) to give pure the respective *N*-phenyl quinone imines.

Spectroscopic data

5-Hydroxy-4-((4-hydroxyphenyl)imino)naphthalen-1(4H)-one (6): Prepared from **1** and 4-hydroxyphenylamine, in 98 and 80% yield by using solar light and green LEDs respectively; brown solid, mp 149-151 °C; IR (KBr) $\nu_{\max}$ cm^{-1} : 3568 (O-H), 1647 (C=O), 1638 (C=N). 1H -NMR (400 MHz, $CDCl_3$): δ 5.16 (s, 1H, O-H), 6.72 (d, 1H, J = 10.4 Hz, 3-H), 6.95 (dd, 4H, J = 8.8, 8.8 Hz, 2'-H + 3'-H + 5'-

H + 6'-H), 7.31 (d, 1H, $J = 8.3$ Hz, 6-H), 7.37 (d, 1H, $J = 10.4$ Hz, 2-H), 7.53 (dd, 1H, $J = 7.8, 8.0$ Hz, 7-H), 7.71 (d, 1H, $J = 7.3$ Hz, 8-H), 14.20 (s, 1H, OH). ^{13}C -NMR (100 MHz, CDCl_3): δ 114.59, 116.11(2C), 118.28, 123.65, 124.28 (2C), 130.22, 131.53, 132.86, 135.09, 138.77, 154.70, 159.30, 160.72, 185.18; HRMS (APCI) calcd. for $\text{C}_{16}\text{H}_{11}\text{NO}_3$: 266.08172 $[\text{M}+\text{H}]^+$; found 266.08029.

5-Hydroxy-4-((4-methoxyphenyl)imino)naphthalen-1(4H)-one (7): Prepared from **1** and 4-methoxyphenylamine, in 47 and 34% yield with solar light green LEDs respectively; brown solid, mp 147-149 °C; IR (KBr) ν_{max} cm^{-1} : 3630 (O-H), 1640 (C=O), 1624 (C=N). ^1H -NMR (400 MHz, CDCl_3): δ 3.86 (s, 1H, OMe), 6.71 (d, 1H, $J = 10.5$ Hz, 3-H), 7.01 (dd, 4H, $J = 9.1, 9.0$ Hz, 2'-H + 3'-H + 5'-H + 6'-H), 7.30 (d, 1H, $J = 8.2$ Hz, 6-H), 7.37 (d, 1H, $J = 10.5$ Hz, 2-H), 7.53 (dd, 1H, $J = 7.9, 7.9$ Hz, 7-H), 7.70 (d, 1H, $J = 7.6$ Hz, 8-H), 14.21 (s, 1H, OH). ^{13}C -NMR (100 MHz, CDCl_3): δ 55.59, 114.56, 114.59, 116.02, 118.20, 123.56, 124.12 (2C), 130.20, 131.55, 132.78, 135.04, 138.69, 158.61, 159.20, 160.71, 185.10; HRMS (APCI) calcd. for $\text{C}_{17}\text{H}_{13}\text{NO}_3$: 280.09737 $[\text{M}+\text{H}]^+$; found 280.09625.

4-((2,5-Dimethoxyphenyl)imino)-5-hydroxynaphthalen-1(4H)-one (8): Prepared from **1** and 2,5-dimethoxyphenylamine, in 60 and 43% yield with solar light and green LEDs respectively; brown solid, mp 260-262 °C; IR (KBr) ν_{max} cm^{-1} : 3285 (O-H), 1645 (C=O), 1635 (C=N). ^1H -NMR (400 MHz, CDCl_3): δ 3.79 (s, 3H, OMe), 3.86 (s, 3H, OMe), 6.65 (m, 1H, 4'-H or 3'-H), 6.71 (s, 1H, Hz, 6'-H), 6.79 (m, 1H, 3'-H or 4'-H), 6.83 (d, 1H, $J = 8.9$ Hz, 3-H), 6.93 (d, 1H, $J = 8.9$ Hz, 2-H), 7.34 (d, 1H, $J = 8.3$ Hz, 6-H), 7.51 (dd, 1H, $J = 7.9, 8.0$ Hz, 7-H), 7.78 (d, 1H, $J = 7.6$ Hz, 8-H), 15.34 (s, 1H, OH). ^{13}C -NMR (100 MHz, CDCl_3): δ 55.71, 56.24, 97.21, 105.07, 109.39, 111.05, 113.31, 118.56, 125.13, 128.60, 131.92, 136.17, 140.04, 144.67, 153.89, 161.58, 161.82, 185.10; HRMS (APCI) calcd. for $\text{C}_{18}\text{H}_{15}\text{NO}_4$: 310.10794 $[\text{M}+\text{H}]^+$; found 310.10712.

5-Hydroxy-4-((3,4,5-trimethoxyphenyl)imino)naphthalen-1(4H)-one (9): This compound was prepared from **1** and 3,4,5-trimethoxyphenylamine, in 59 and 38% yield with solar light and green LEDs respectively; red solid, mp 148- 150 °C; IR (KBr) ν_{max} cm^{-1} : 3568 (O-H), 1689 (C=O), 1627 (C=N). ^1H -NMR (400

MHz, CDCl₃): δ 3.87 (s, 6H, OMe), 3.89 (s, 3H, OMe), 6.25 (s, 2H, 2'-H + 6'-H), 6.72 (d, 1H, J = 10.4 Hz, 3-H), 7.32 (d, 1H, J = 8.2 Hz, 6-H), 7.34 (d, 1H, J = 10.4 Hz, 2-H), 7.55 (dd, 1H, J = 7.9, 8.0 Hz, 7-H), 7.71 (d, 1H, J = 7.5 Hz, 8-H), 13.86 (s, 1H, OH). ¹³C-NMR (100 MHz, CDCl₃): δ 56.28 (2C), 61.09, 99.62 (2C), 114.56, 115.69, 118.43, 123.71, 130.39, 131.57, 133.14, 135.42, 136.36, 141.71, 153.69, 160.13, 160.64, 184.99; HRMS (APCI): calcd. for C₁₉H₁₇NO₅: 340.11850 [M+H]⁺; found 340.11746.

5-Hydroxy-4-((4-hydroxyphenyl)imino)naphthalen-1(4H)-one (**10**): Prepared from **5** and 4-hydroxyphenylamine, in 88 and 82% yield with solar light and green LEDs respectively; red solid, mp 258-259 °C; IR (KBr) ν_{max} cm⁻¹: 3244 (NH), 1691 (C=O), 1655 (C=O), 1643 (C=N). ¹H-NMR (400 MHz, DMSO-*d*₆): δ 2.15 (s, 3H, COMe), 6.75 (d, 1H, J = 10.5 Hz, 3-H), 6.92 (d, 2H, J = 8.6 Hz, 3'-H + 5'-H), 7.04 (d, 2H, J = 8.6 Hz, 2'-H + 6'-H), 7.42 (d, 1H, J = 10.5 Hz, 2-H), 7.66 (dd, 1H, J = 8.0, 8.0 Hz, 7-H), 7.77 (d, 1H, J = 7.4 Hz, 6-H), 8.94 (d, 1H, J = 8.2 Hz, 8-H), 9.88 (s, 1H, 4'-OH), 13.41 (s, 1H, 5-OH). ¹³C-NMR (400 MHz, DMSO-*d*₆): δ 26.13, 116.37 (2C), 118.17, 121.01, 124.59, 124.77 (2C), 131.96, 132.01, 132.30, 132.80, 138.76, 139.91, 157.26, 169.42, 184.99, 185.03; HRMS (APCI) calcd. for C₁₈H₁₄N₂O₃: 306.10044 [M+H]⁺; found 306.10189.

X-ray crystallography:

X-ray crystallographic data were collected at 293 K with Cu K α (1.5418 Å) using an Oxford diffraction CCD area-detector diffractometer equipped with graphite monochromator. The Cris Alis PRO software [1] was used for data collection data reduction and cell refinement. The structure was solved by direct methods and refined by full-matrix least-squares calculations using SHELXL [2] software. All the non-H atoms were refined in the anisotropic approximation against F² of all reflections. The H-atoms were placed at their calculated positions and refined isotropic approximation. The crystallographic parameters are given in Table S1.

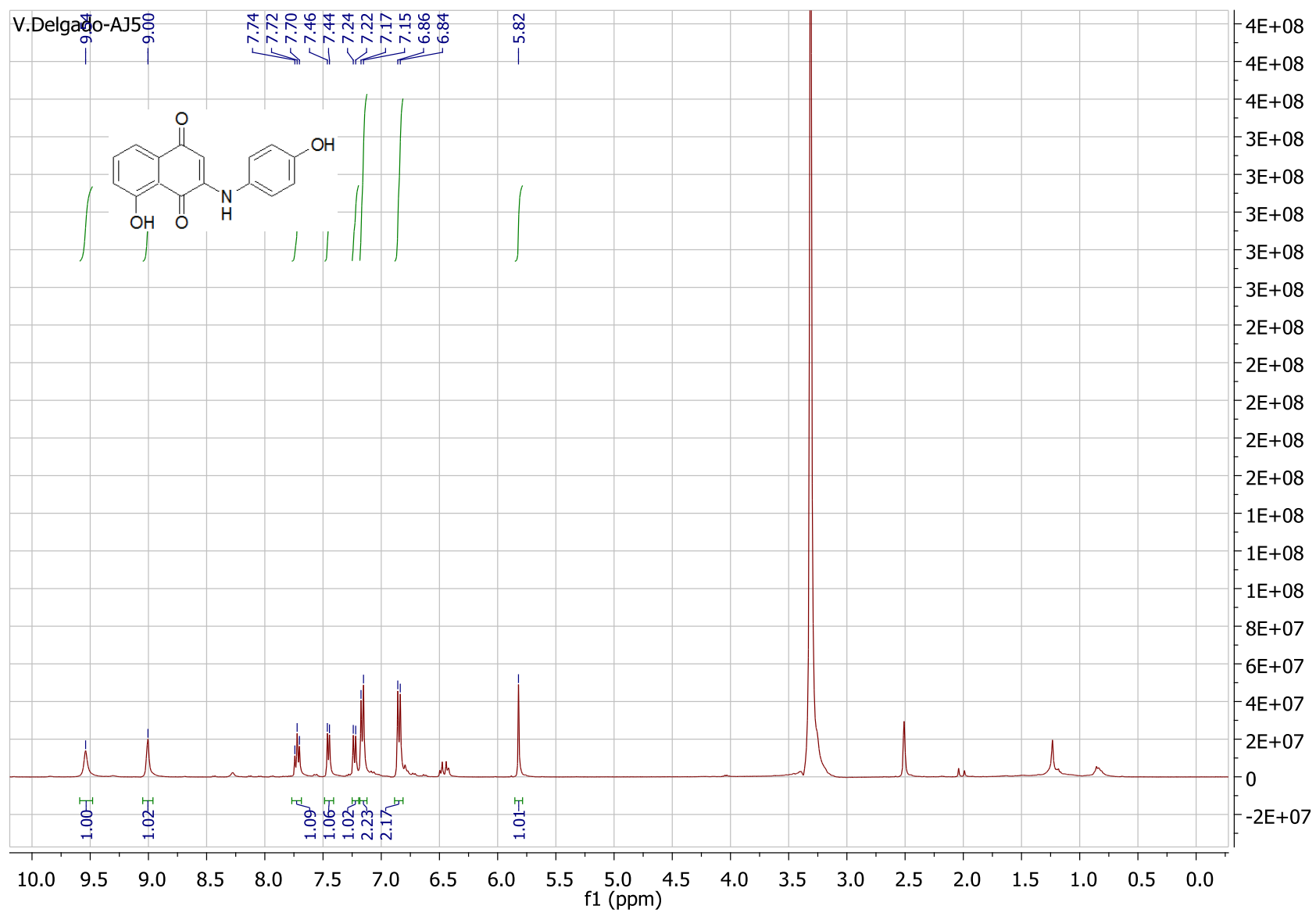
The crystallographic information of the compound is deposited to Cambridge Crystallographic Database and has the CCDC number 1015027

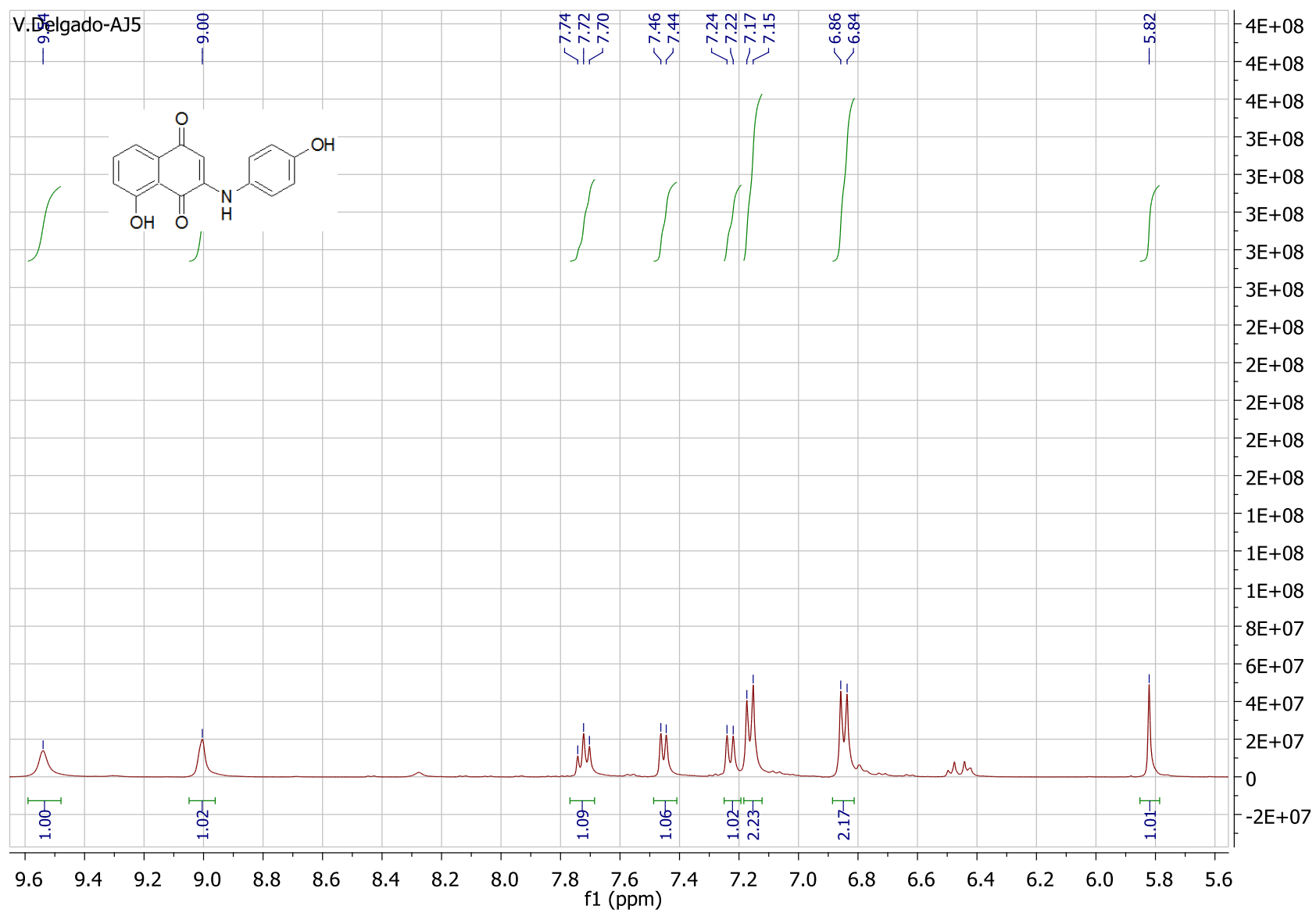
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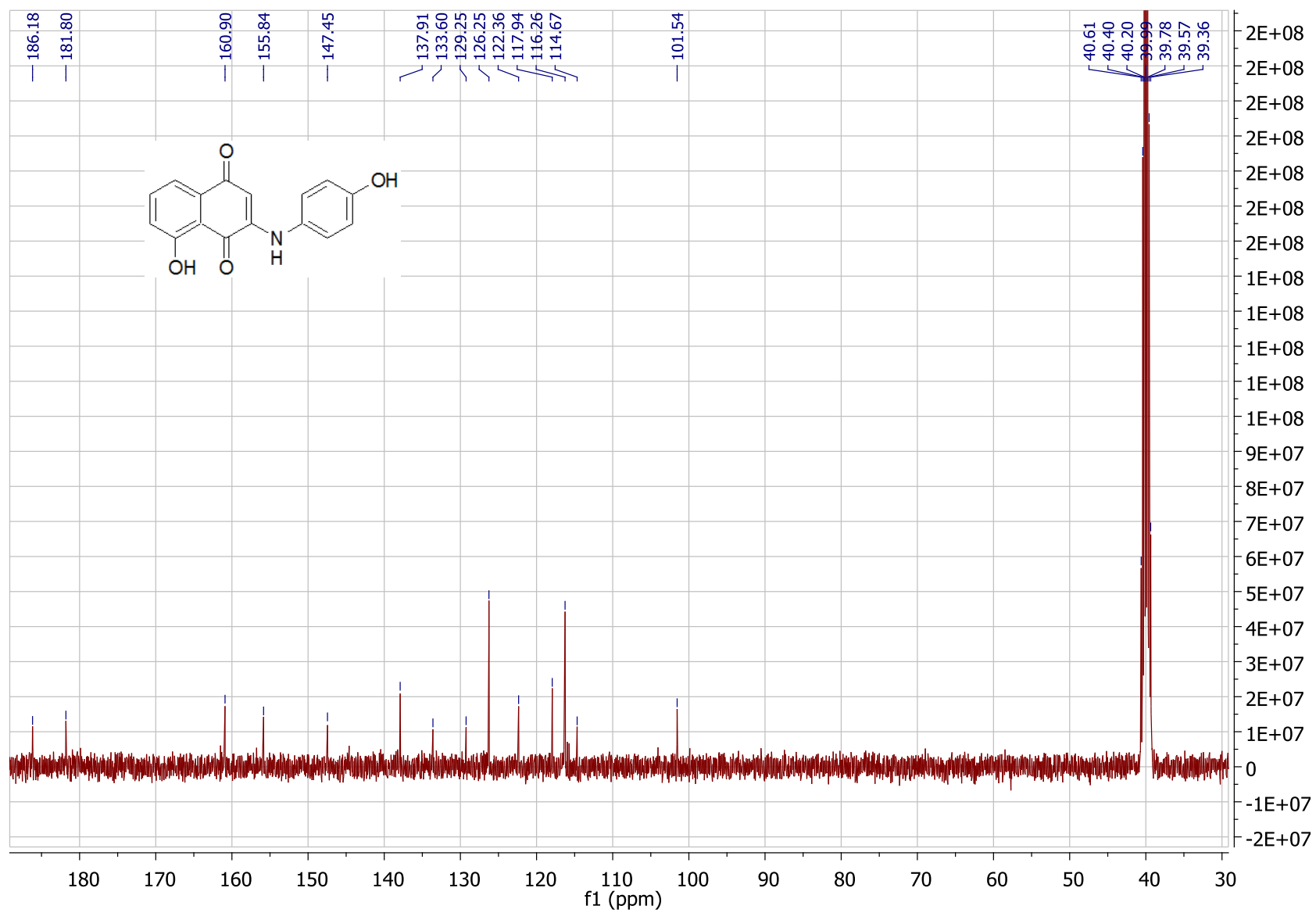
- [1] Agilent (2010). CrysAlis PRO. Agilent Technologies, Yarnton, England.
 [2] Sheldrick, G. M. (2008). Acta Cryst. A64, 112–122.

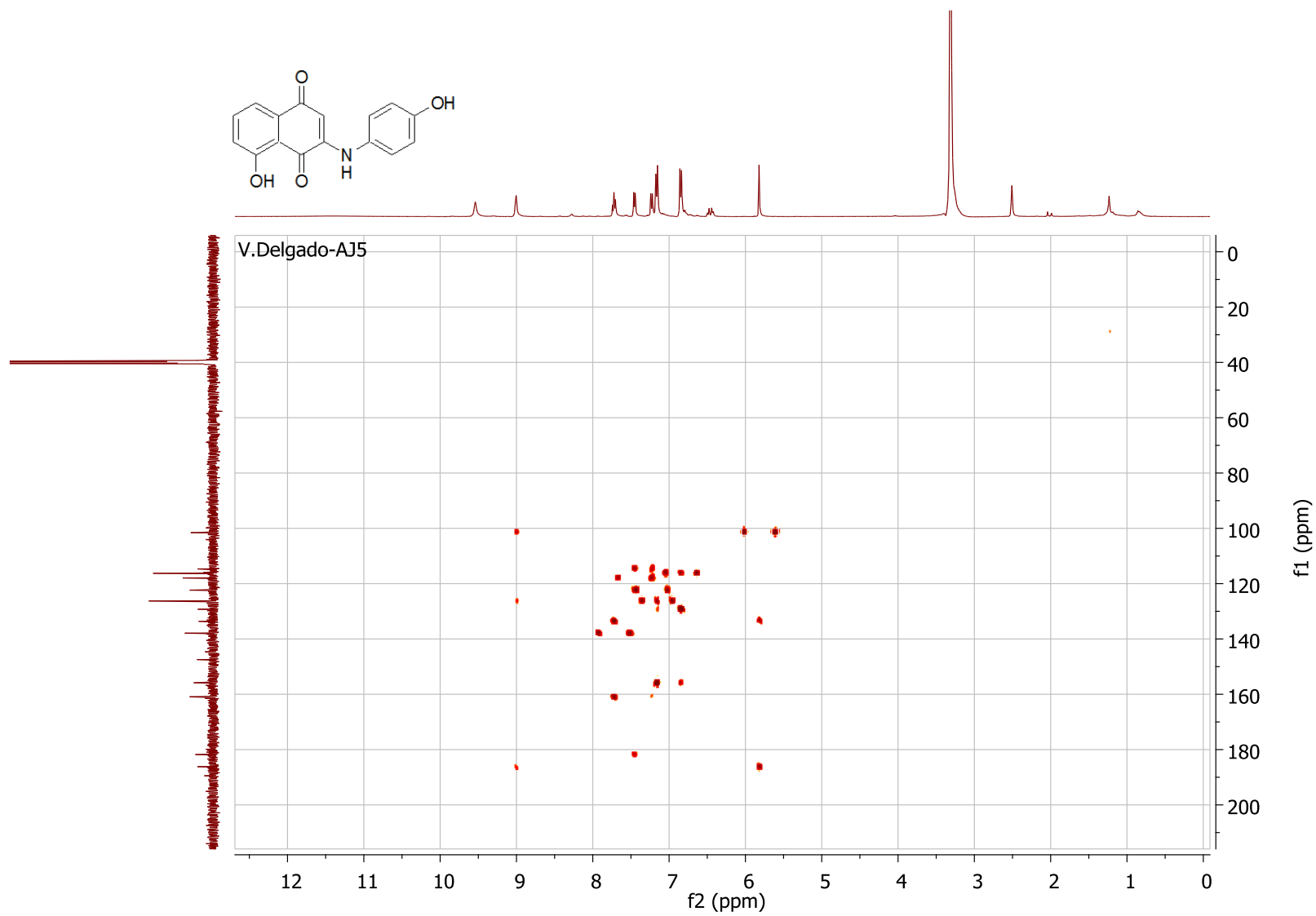
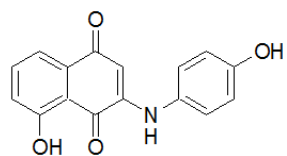
Table S1. Crystal data and structure refinement for compound 6.

Identification code	shelx
Empirical formula	C ₁₆ H ₁₁ NO ₃
Formula weight	266.08
Temperature	293(2) K
Wavelength	1.5418 $\approx$
Crystal system	Triclinic
Space group	P -1
Unit cell dimensions	a = 7.445(3) $\approx$ α = 109.945(3) $^\circ$. b = 13.785(4) $\approx$ β = 101.686(4) $^\circ$. c = 14.088(6) $\approx$ γ = 101.735(3) $^\circ$.
Volume	1271.3(8) $\approx$ 3
Z	2
Density (calculated)	1.433 Mg/m ³
Absorption coefficient	0.844 mm ⁻¹
F(000)	572
Theta range for data collection	3.493 to 61.581 $^\circ$.
Index ranges	-6 $\leq$ h $\leq$ 8, -15 $\leq$ k $\leq$ 15, -16 $\leq$ l $\leq$ 14
Reflections collected	6849
Independent reflections	3883 [R(int) = 0.0122]
Completeness to theta = 67.680 $^\circ$	84.7 %
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3883 / 0 / 388
Goodness-of-fit on F ²	1.045
Final R indices [I $\geq$ 2 σ (I)]	R1 = 0.0337, wR2 = 0.0872
R indices (all data)	R1 = 0.0392, wR2 = 0.0928
Extinction coefficient	n/a
Largest diff. peak and hole	0.300 and -0.160 e. $\approx$ ⁻³



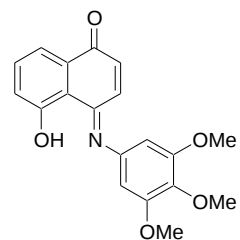








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JM4
CDCl3

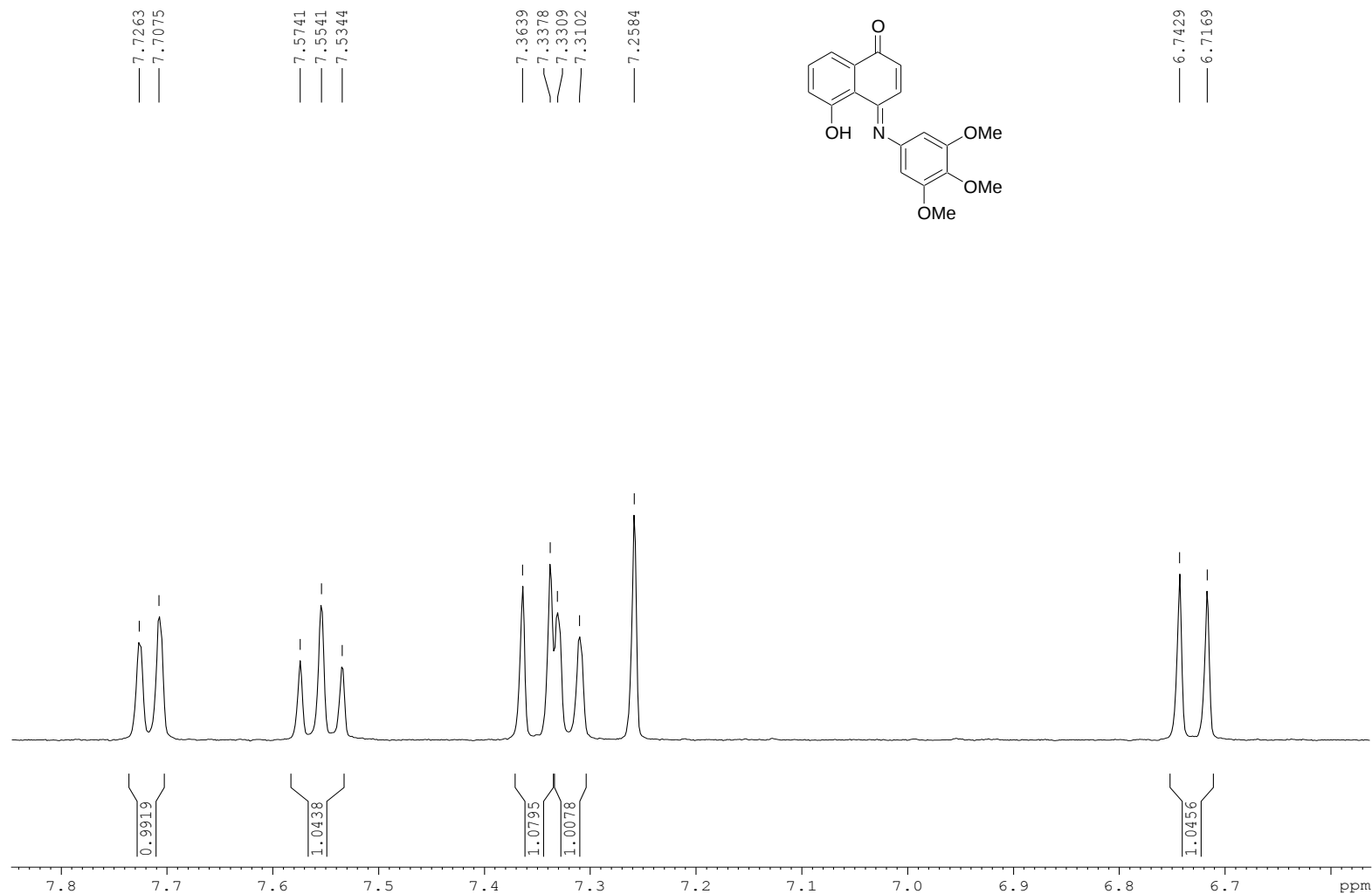


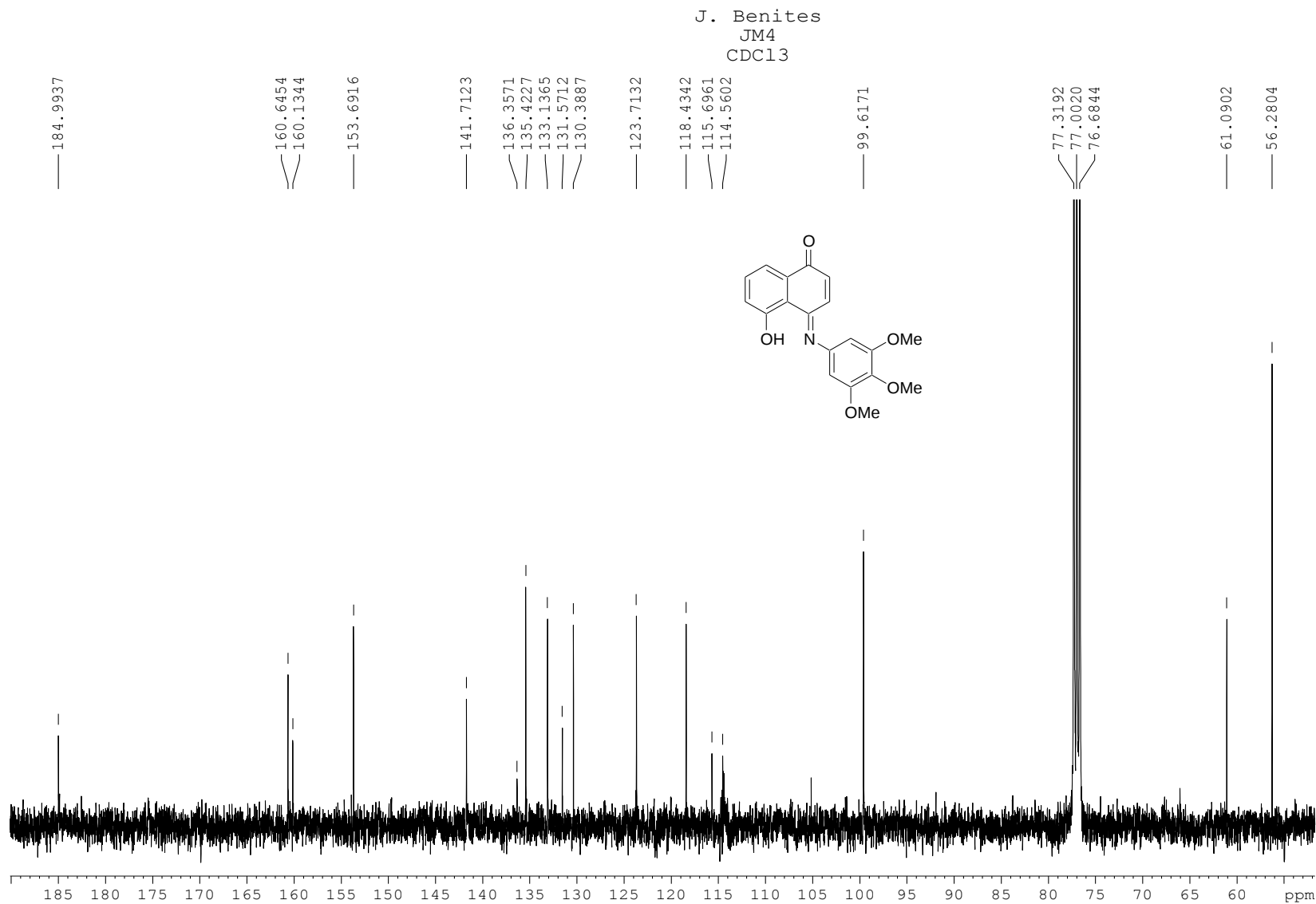
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RG         322.5
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DE         6.00 usec
TE         294.2 K
D1         1.00000000 sec
TD0        1

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LB         0.00 Hz
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TD0       1

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PL13      23.00 dB
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PC        1.40

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