Electronic Supplementary Information (ESI) for

Oxidative Decarboxylation of α-Hydroxy Acids by a Functional Model of the Nonheme Iron Oxygenase, CloR

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Experimental Section:

All reagents and solvents were purchased from commercial sources and were used without further purification, unless otherwise noted. Solvents were purified and dried prior to use. Preparation and handling of air-sensitive materials were carried out under an inert atmosphere by using standard Schlenk techniques or a glove box. *Although no problems were encountered during the synthesis of these complexes from $Fe(ClO_4)_2$, perchlorate salts are potentially explosive and should be handled with care.*[1] Mandelic α -d acid,[2] ligand 6-Me_3-TPA[3] and complex **2-BPh_4** [4] were prepared according to literature procedures.

Synthesis:

1-BPh_4: Equimolar amounts (0.25 mmol) of 6-Me_3-TPA, $Fe(ClO_4)_2 \cdot 6H_2O$, mandelic acid, and triethylamine in 5 mL of methanol were stirred under nitrogen for 1 h. The resulting solution was then treated with a methanolic solution of $NaBPh_4$ (0.25 mmol) to precipitate a yellow microcrystalline solid, which was isolated by filtration, washed with methanol and dried. X-ray quality crystals were grown by vapor diffusion of ether into an acetonitrile solution of **1**-BPh_4. Yield: 0.17 g (79%). Anal. Calcd for **1**-$BPh_4 \cdot CH_3CN$, $C_{55}H_{54}BFeN_5O_3$ (899.7 g/mol): C, 73.42; H, 6.05; N, 7.78. Found: C, 73.1; H, 6.0; N, 7.5.

4-BPh_4: **4** was prepared similarly except that lactic acid was used instead of mandelic acid. Yield: 0.14 g (70%). Anal. Calcd for **4**-BPh_4, $C_{48}H_{49}BFeN_4O_3$ (796.58 g/mol): C, 72.37; H, 6.20; N, 7.03. Found: C, 72.1; H, 6.2; N, 7.0.

Analysis and quantification of organic products: A solution of 0.1 mmol (0.085 g) of **1-BPh_4** in 15 mL of dry acetonitrile under nitrogen atmosphere was saturated with O_2 and allowed to stir at room temperature for 6 h, during which time the initial light yellow color slowly turned to light orange. To this solution was added 1,4-benzoquinone as an internal standard (0.1 mmol, 0.010 g) and the solvent was removed under vacuum. To the residue was added 10 mL 3M HCl to decompose the metal complex, and the organic products were then extracted into diethyl ether (3 × 20mL), which was dried over sodium sulfate and evaporated under reduced pressure. The products were analyzed and quantified by ^{1}H-NMR spectroscopy with respect to the internal standard (δ 6.60(s) ppm) by comparing the integration of peaks for benzoic acid (δ 7.95 (d) ppm) and mandelic acid (δ 5.15 (s) ppm).

X-ray crystallographic data collection and refinement and solution of the structures of 1-BPh_4: A crystal (approximate dimensions 0.45 x 0.20 x 0.10 mm^3) was placed onto the tip of a 0.1 mm diameter glass capillary and mounted on a Siemens SMART Platform CCD diffractometer for a data collection at 173(2) K.[5] A preliminary set of cell constants was calculated from reflections harvested from three sets of 20 frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced initial orientation matrices determined from 191 reflections. The data collection was carried out using MoKα radiation (graphite monochromator) with a frame time of 20 seconds and a detector distance of 4.91 cm. A randomly oriented region of reciprocal space was surveyed to the extent of one sphere and to a resolution of 0.84 Å. Four major sections of frames were collected with 0.30º steps in ω at four different φ settings and a detector position of -28º in 2θ. The intensity data were corrected for absorption and decay (SADABS).[6] Final cell constants were calculated from the xyz centroids of 4028 strong reflections from the actual data collection after integration (SAINT).[7] The structure was solved using SIR97[8] and refined using SHELXL-97.[9] The space group *P*-1 was determined based on the lack of systematic absences and intensity statistics. There are four molecules in the asymmetric unit. The search for a higher symmetry space group

(using the program PLATON[10]) was unsuccessful. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydroxide hydrogen atoms were found from and refined from the difference map. All remaining hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to $R1$ = 0.0607 and $wR2$ = 0.1286 (F^2, all data).

Table S1. Crystallographic data for complex **1-BPh$_4$**

	1-BPh$_4$
Empirical formula	$C_{53}H_{51}BFeN_4O_3$
Formula weight	858.64
Crystal system	triclinic
Space group	*P*-1
a, Å	18.3459(17)
b, Å	20.4138(19)
c, Å	26.054(2)
α, deg	78.286(2)
β, deg	76.716(2)
γ, deg	74.207(2)
Volume, Å^3	9034.6(14)
Z	8
Density (calc.) Mg/m^3	1.263
μ Mo-Kα, mm^{-1}	0.382
F(000)	3616
θ range data collection, deg	0.81-25.03
Reflections collected	87092
Reflns unique	31797
R(int)	0.0447
Data (I>2σ(I)])	31797
parameters	2251
Goodness-of-fit on F^2	1.048
$R1$ [I>2σ(I)]	0.0607
$wR2$	0.1286
Residuals e.Å^{-3}	0.705, –0.315

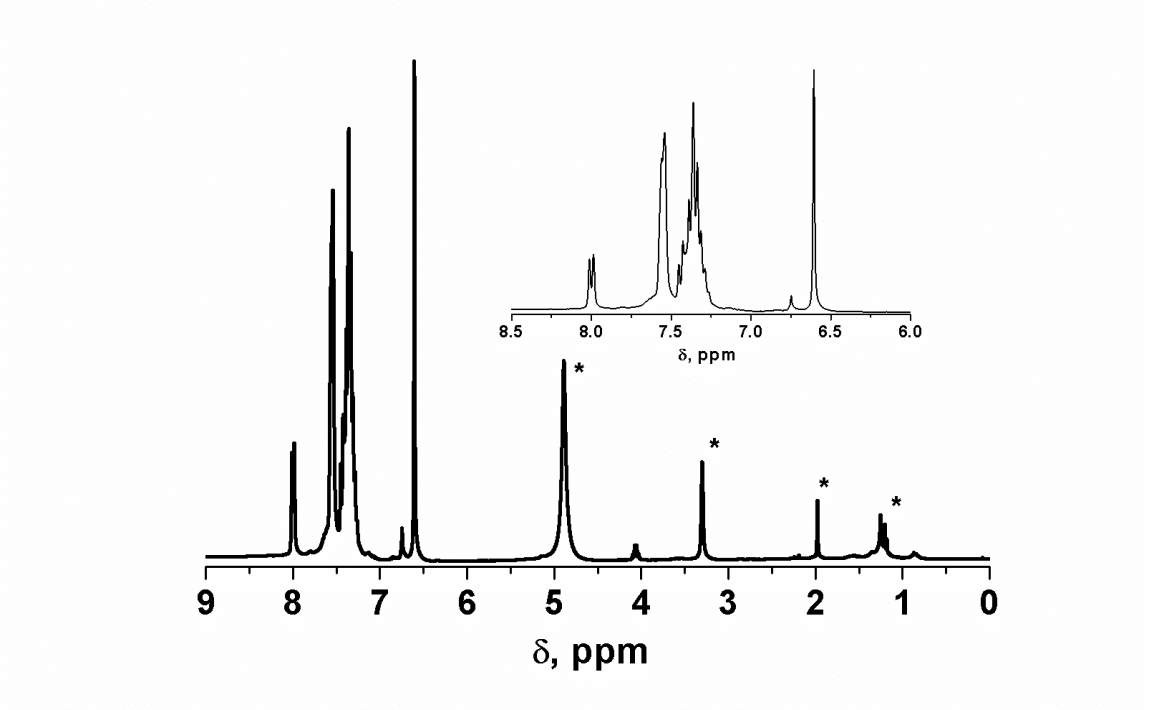

Fig. S1 ^{1}H NMR spectrum (300MHz, CD_3OD at 25°C) of the organic product after reaction of **1** with O_2 (* marked peaks derive from contamination from solvents used in the extraction).

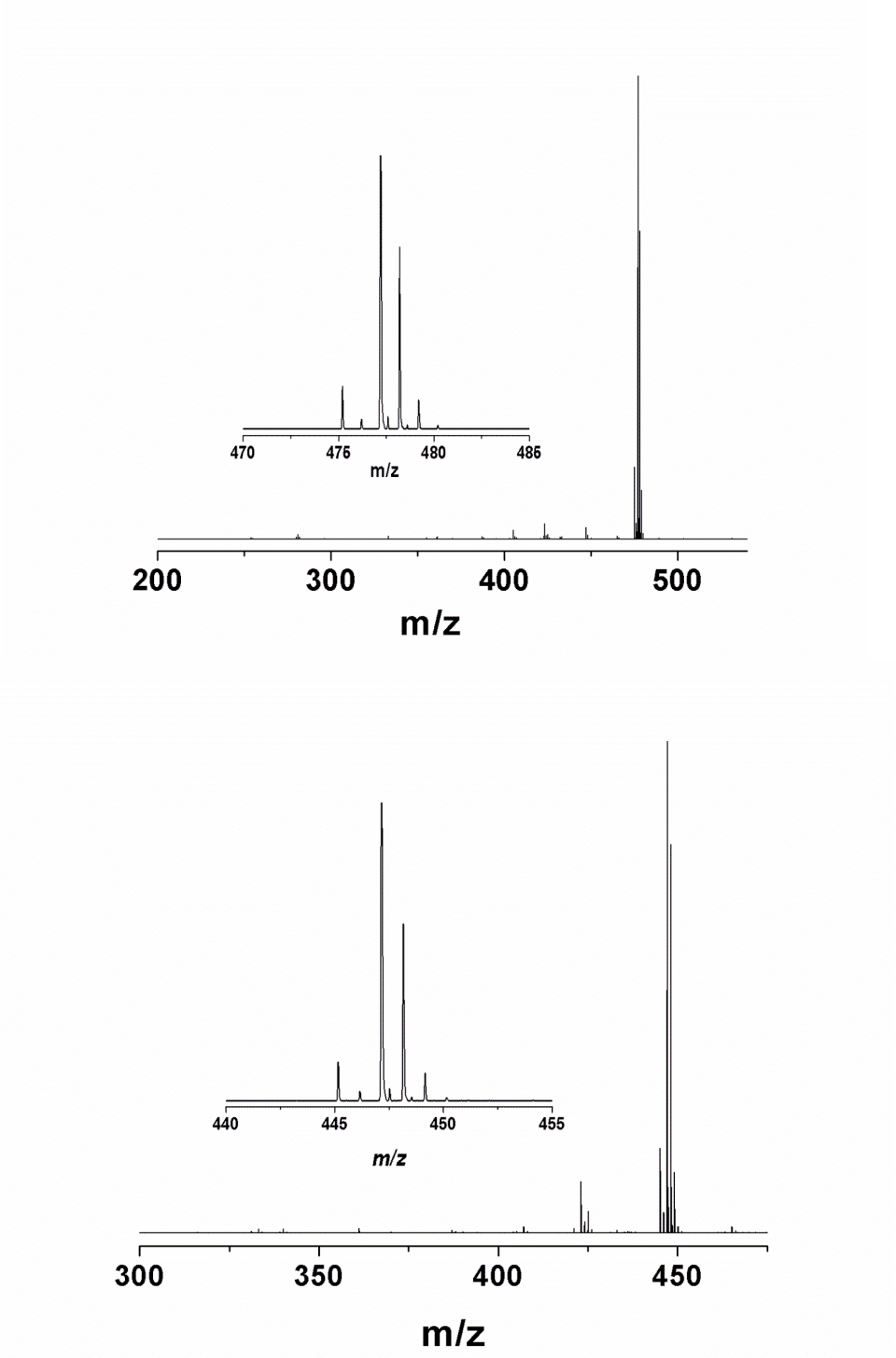

Fig. S2 ESI-MS of **4** in acetonitrile (top) and the solution after reaction with O_2 (bottom**),** demonstrating the oxidative decarboxylation of bound lactate.

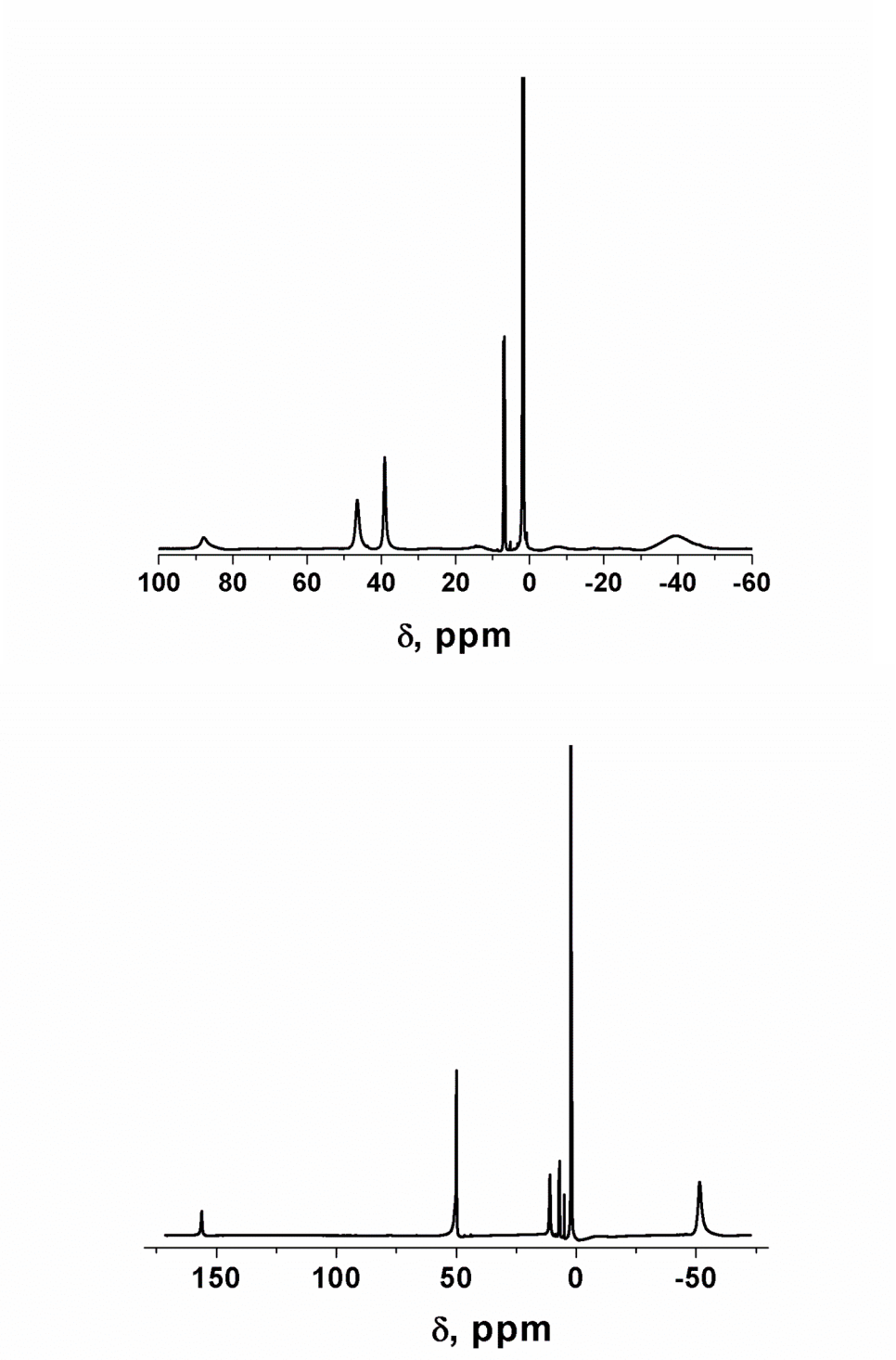

Fig. S3 ^{1}H NMR spectra of **4** (top) and its oxidation product, lactate (bottom) in CD_3CN at 25°C.

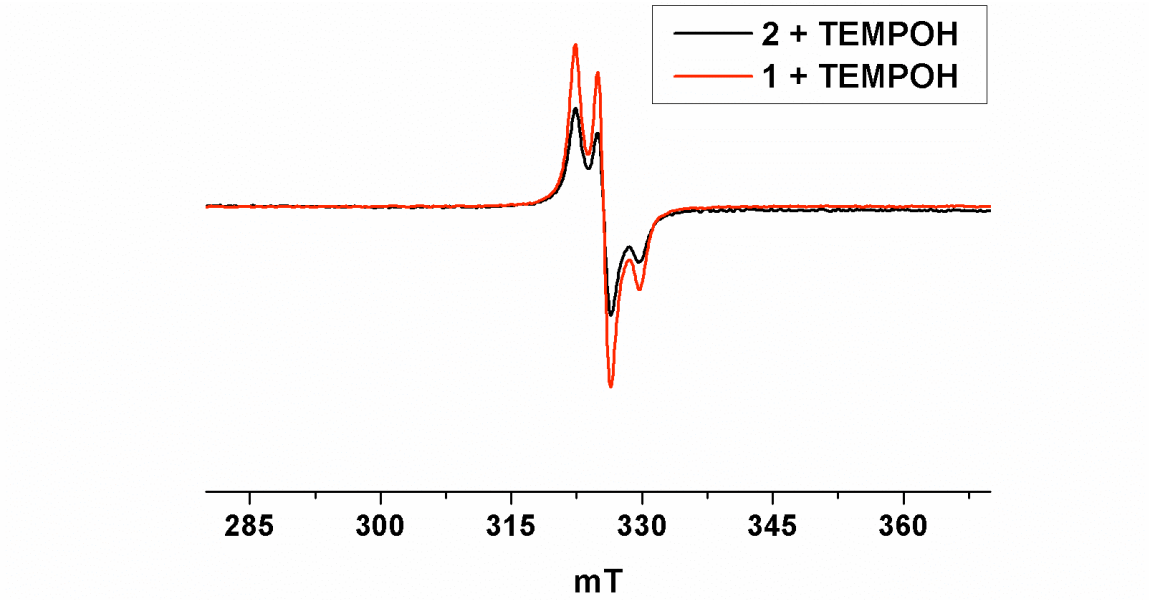

Fig. S4 X-band EPR spectrum (77 K, acetonitrile) of the solution after 1.5 h reaction of **1** with O_2 in the presence of one equivalent of TEMPOH. In a control experiment, **2** is oxygenated in the presence of one equivalent of TEMPOH for the same time to determine the amount of TEMPO radical formed. *Experimental condition: temperature = 77K, microwave frequency = 9.13 GHz, microwave power = 0.998 mW, modulation amplitude = 20 kHz, modulation width = 0.10 mT*

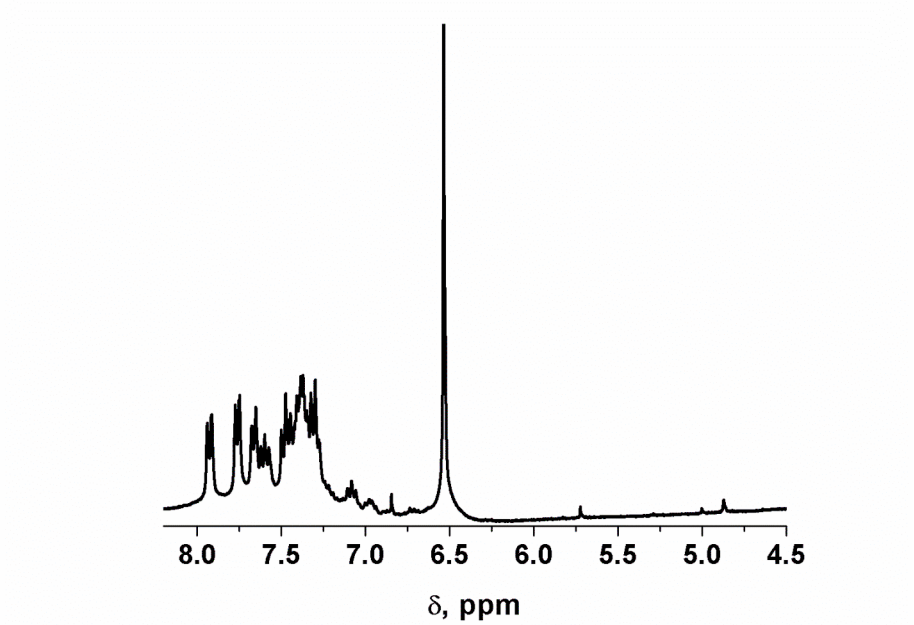

Fig. S5 ^{1}H NMR spectrum (300MHz,DMSO-d_6 at 25°C) of the organic products after reaction of **1** with O_2 in the presence of one equivalent of TEMPOH. Mandelate-to-benzoate ratio determined by monitoring the intensity of the mandelate resonance at 5.15 ppm related to that of the benzoate resonance at 8.00 ppm with the benzoquinone resonance at 6.60 ppm as internal standard.

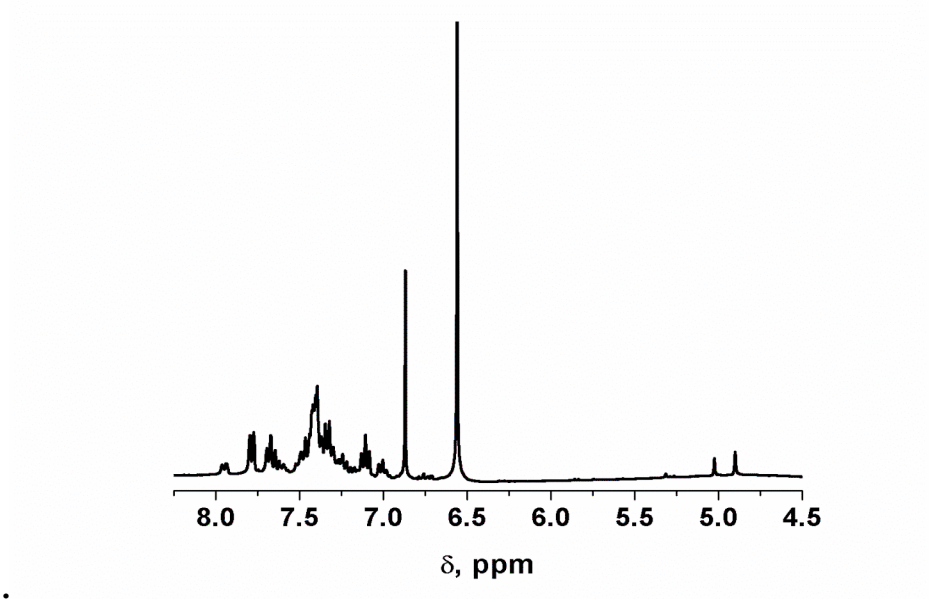

Fig. S6 ^{1}H NMR spectrum (300MHz,DMSO-d_6 at 25°C) of organic product after reaction of **1** with O_2 in the presence of 20 equivalents of TEMPOH. Mandelate-to-benzoate ratio determined by monitoring the intensity of the mandelate resonance at 5.15 ppm related to that of the benzoate resonance at 8.00 ppm with the benzoquinone resonance at 6.60 ppm as internal standard.

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