

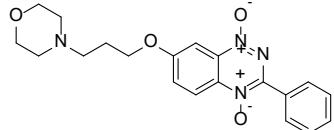
Supplementary Materials:

Spin Trapping Hydroxyl and Aryl Radicals of One-Electron Reduced Anticancer Benzotriazine 1,4-Dioxides

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A. One-electron reduction potential of compound **3**.



Redox equilibrium between methylviogen (MV²⁺) as the redox indicator ($E(MV^{2+}/MV^{\cdot-}) = -447 \pm 7$ mV) and compound **3** (A) were established in N₂-saturated solutions containing 2-methylpropan-2-ol (0.2 M), MV²⁺ (1-3 mM), compound **3** (0.1-0.5 mM) at pH 7 (phosphate, 2.5 mM). Following pulse radiolysis (2.5 Gy in 200 ns), MV²⁺ and A were reduced by e_{aq}⁻ and the equilibrium (1) observed at 600 nm to be established within 50 μs.



From the experimental equilibrium constant, $K = 14.24 \pm 1.45$, $\Delta E = 68 \pm 3$ mV is calculated using the Nernst equation, and making the calculated correction for ionic strength of 8 mV, yielded the value $E(A/A^{\cdot-}) = -387 \pm 7$ mV.

B. Reaction rate constant of one-electron reduced compound **3** with O₂.

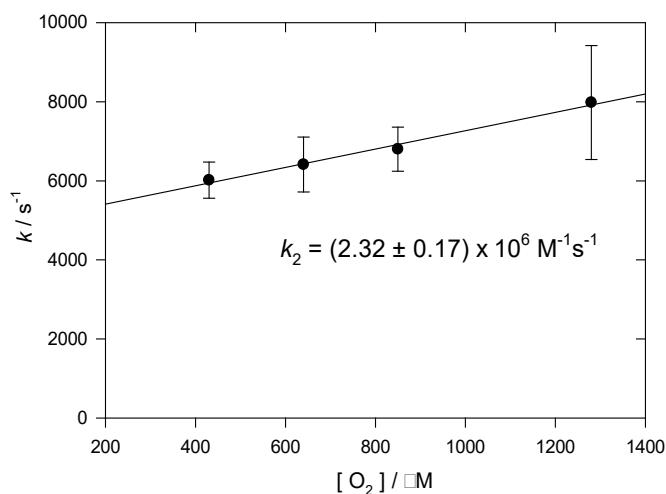


Figure S1. Dependence of the 1st-order rate constants for the decay of the radical anion of compound **3** on the concentration of O₂ following pulse radiolysis (ca. 10 Gy in 200 ns) of solutions saturated with O₂/N₂O mixtures, containing compound **3** (170 μM), sodium formate (0.1 M) and sodium phosphate (2.5 mM) at pH 4.5 (●), observed at 530 nm (The 2nd-order rate constant, k_2 , is derived from the slope of the graph).

C. EPR spectrum of PBN spin-trapped radicals of one-electron reduced compound **2**.

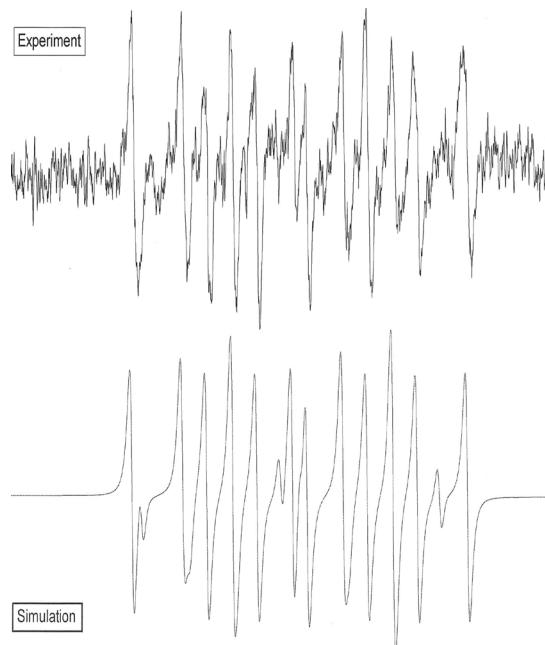


Figure S2. (a) EPR spectra (20 scans) obtained on reduction of compound **1** (17 mM) by POR (14 ng/mL) in anaerobic solutions at 37 °C containing phosphate buffer (50 mM, pH 7), DTPA (100 μM), SOD (300 units/mL), catalase (1500 units/mL), glucose-6-phosphate (10 mM), glucose-6-phosphate-

dehydrogenase (13 units/mL), and NADPH (1 mM) in presence of DEPMPO (105 mM); (b) simulated spectrum of DEPMPO-C centred species (0.90) and DEPMPO-OH centred species (0.10), $r = 0.88$.

D. G-loss determinations for compounds **2 – 4** upon stepwise steady-state radiolysis.

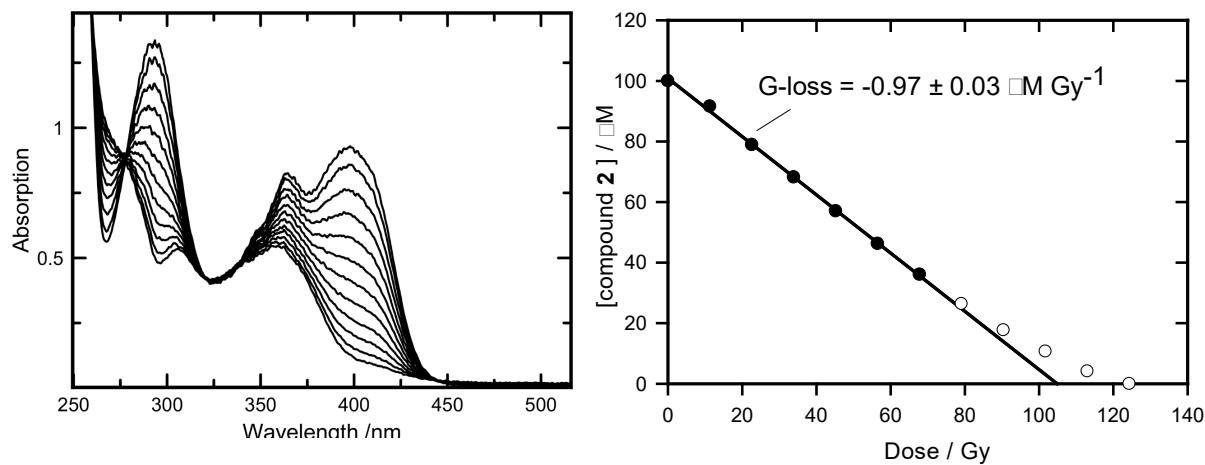


Figure S3. LHS Stepwise changes in absorption spectrum of compound **2** (SN30000) ($100 \mu\text{M}$) with accumulated radiation dose in N_2 -saturated solution containing sodium formate (0.1 M) and phosphate buffer (2.5 mM at pH 7). RHS Change in the concentration of **2** (measured at 300 nm) with accumulated radiation dose. The G-loss value is calculated from the linear regression fit to the initial points of the graph.

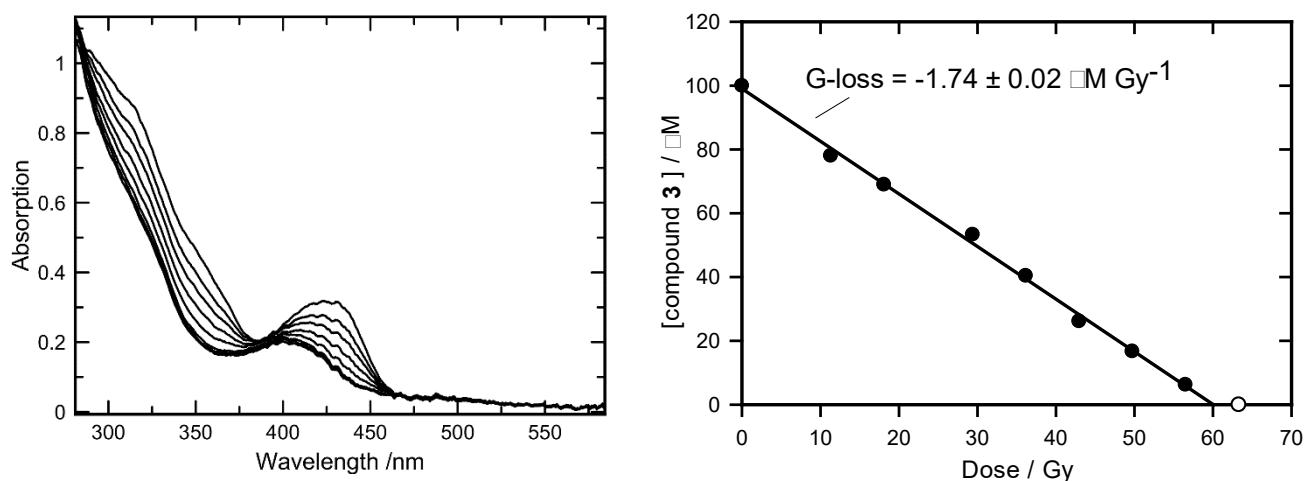
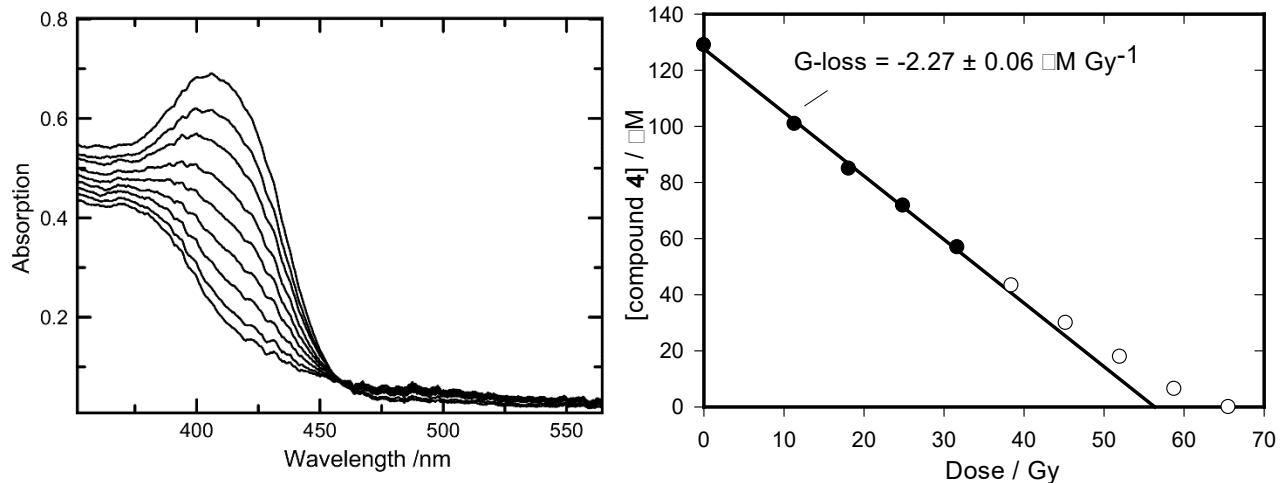


Figure S4. LHS Stepwise changes in absorption spectrum of compound **3** ($100 \mu\text{M}$) with accumulated radiation dose in N_2 -saturated solution containing sodium formate (0.1 M) and phosphate buffer (2.5 mM at pH 7). RHS Change in the concentration of compound **3** (measured at 350 nm) with accumulated radiation dose. The G-loss value is calculated from the linear regression fit to the graph.



E. Control EPR experiments.



Figure S6. EPR spectrum obtained in anaerobic solution at 310 K containing phosphate buffer (50 mM , pH 7), POR (14 ng/mL), DTPA ($100 \mu\text{M}$), SOD (300 units/mL), catalase (1500 units/mL), glucose-6-phosphate (10 mM), and glucose-6-phosphate-dehydrogenase (13 units/mL).



Figure S7. EPR spectrum obtained in anaerobic solution at 310 K containing phosphate buffer (50 mM, pH 7), POR (14 ng/mL), DTPA (100 μ M), SOD (300 units/mL), catalase (1500 units/mL), glucose-6-phosphate (10 mM), glucose-6-phosphate-dehydrogenase (13 units/mL), and NADPH (1 mM).



Figure S8. EPR spectrum obtained in anaerobic solution at 310 K containing phosphate buffer (55 mM, pH 7) and PBN (50 mM).



Figure S9. EPR spectrum obtained in anaerobic solution at 310 K containing phosphate buffer (50 mM, pH 7), POR (14 ng/mL), DTPA (100 μ M), SOD (300 units/mL), catalase (1500 units/mL), glucose-6-phosphate (10 mM), glucose-6-phosphate-dehydrogenase (13 units/mL), and NADPH (1 mM) in presence of PBN (50 mM).



Figure S10. EPR spectrum obtained in anaerobic solution at 310 K containing phosphate buffer (50 mM, pH 7) and POBN (33 mM).

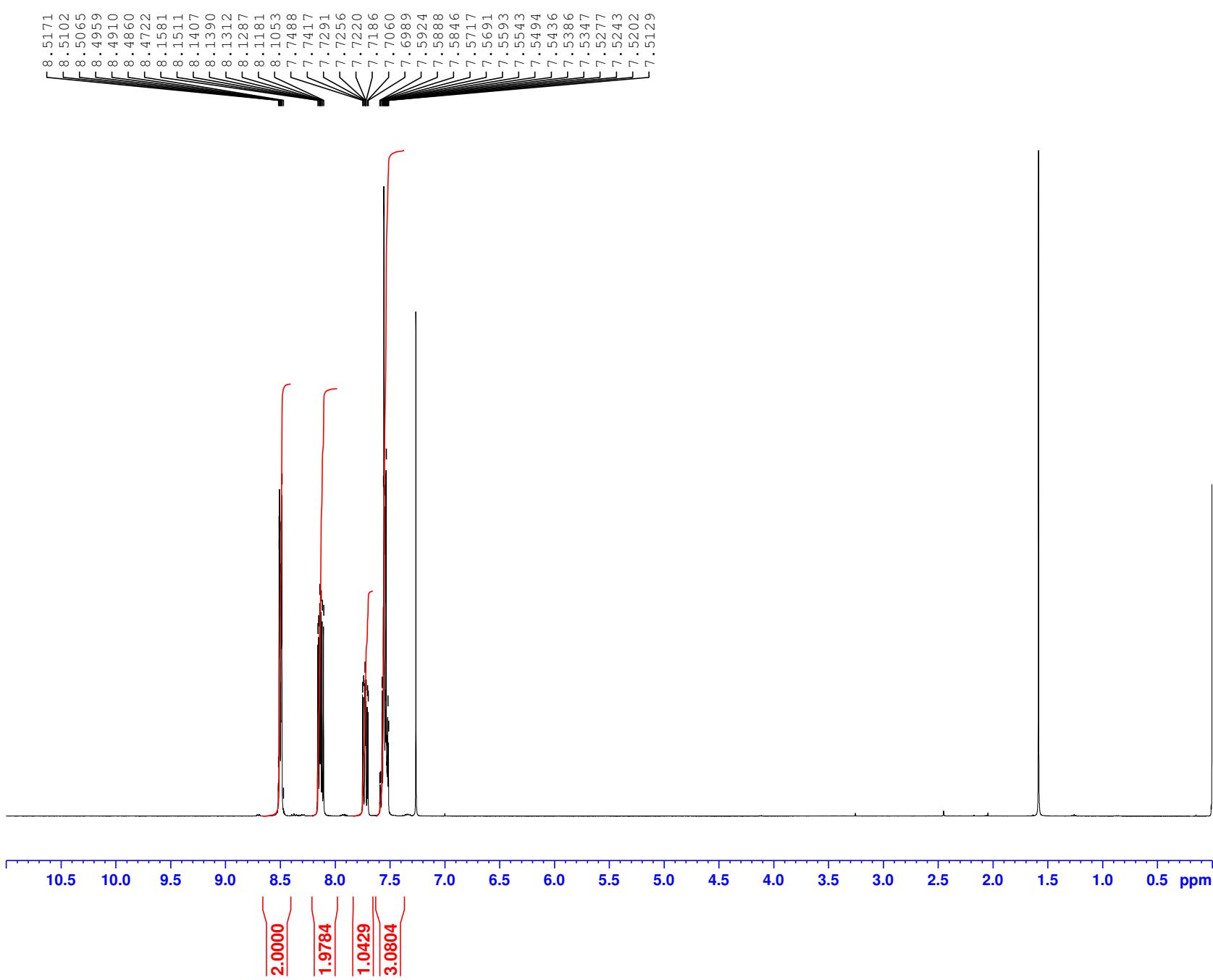


Figure S11. EPR spectrum obtained in anaerobic solution at 310 K containing phosphate buffer (50 mM, pH 7), POR (14 ng/mL), DTPA (100 μ M), SOD (300 units/mL), catalase (1500 units/mL), glucose-6-phosphate (10 mM), glucose-6-phosphate-dehydrogenase (13 units/mL), and NADPH (1 mM) in presence of POBN (30 mM)



Figure S12. EPR spectrum obtained in anaerobic solution at 310 K containing phosphate buffer (50 mM, pH 7), POR (14 ng/mL), DTPA (100 μ M), SOD (300 units/mL), catalase (1500 units/mL), glucose-6-phosphate (10 mM), glucose-6-phosphate-dehydrogenase (13 units/mL), and NADPH (1 mM) in presence of DEPMPO (25 mM).

Compound 8

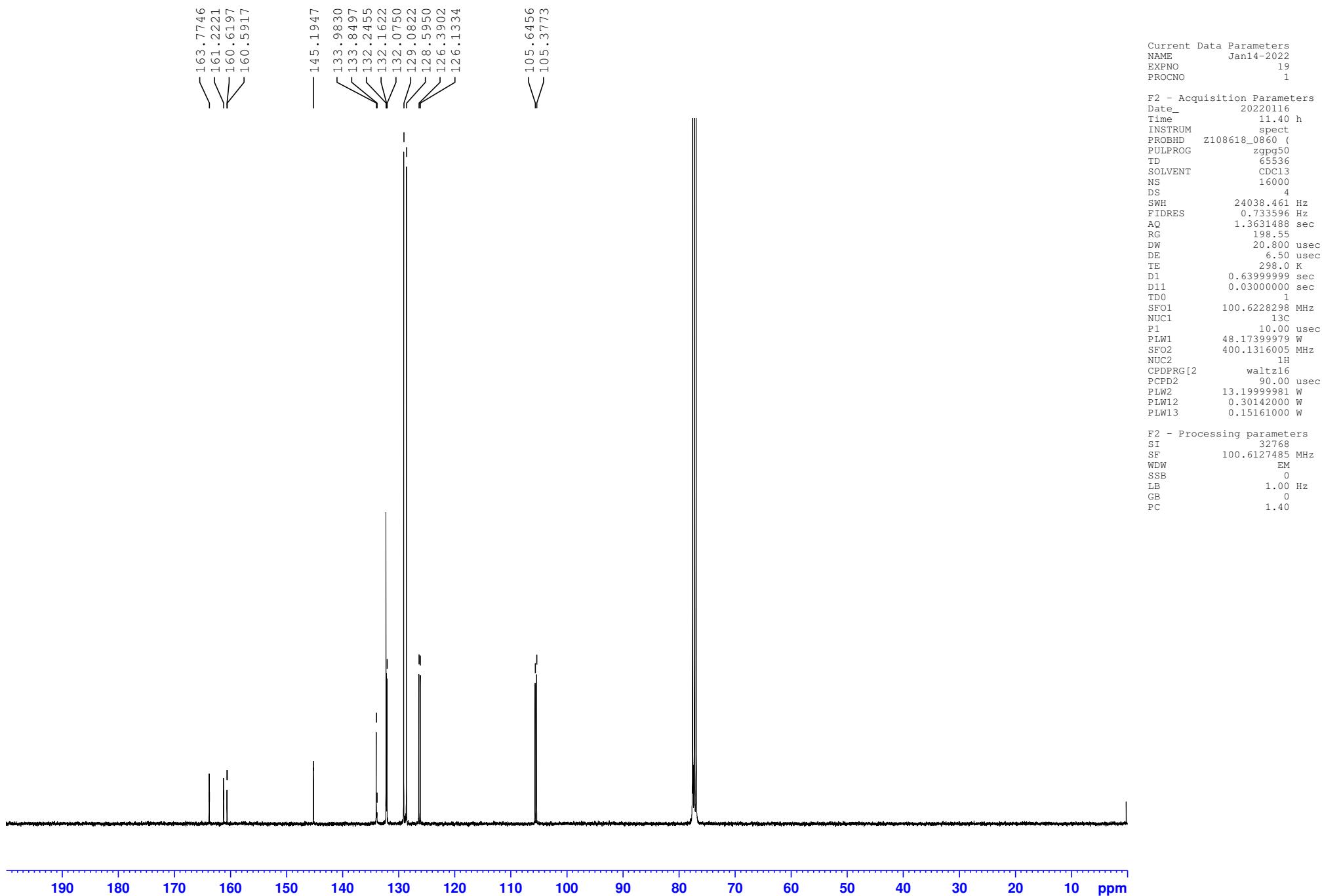


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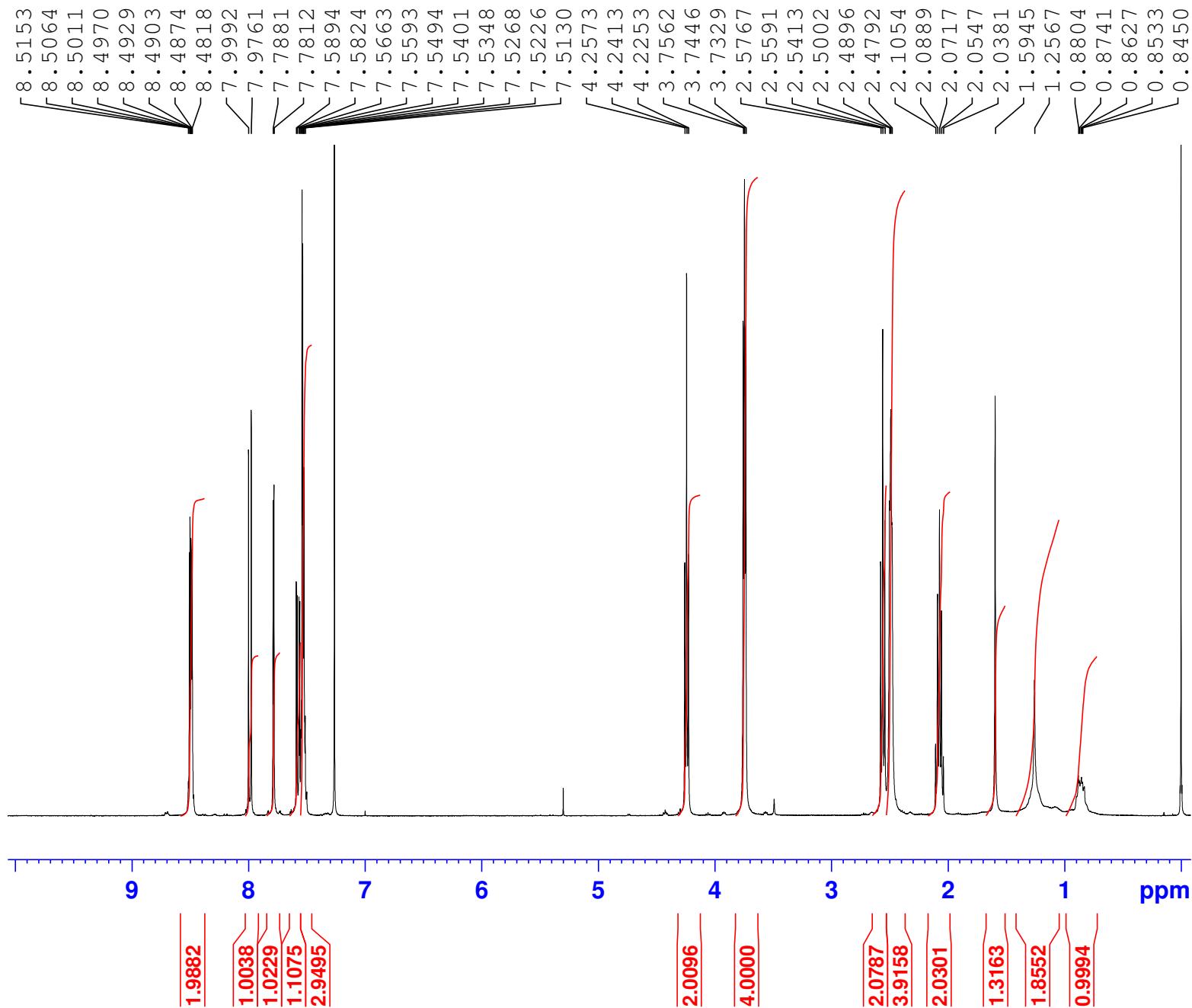
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Compound 8



Compound 9

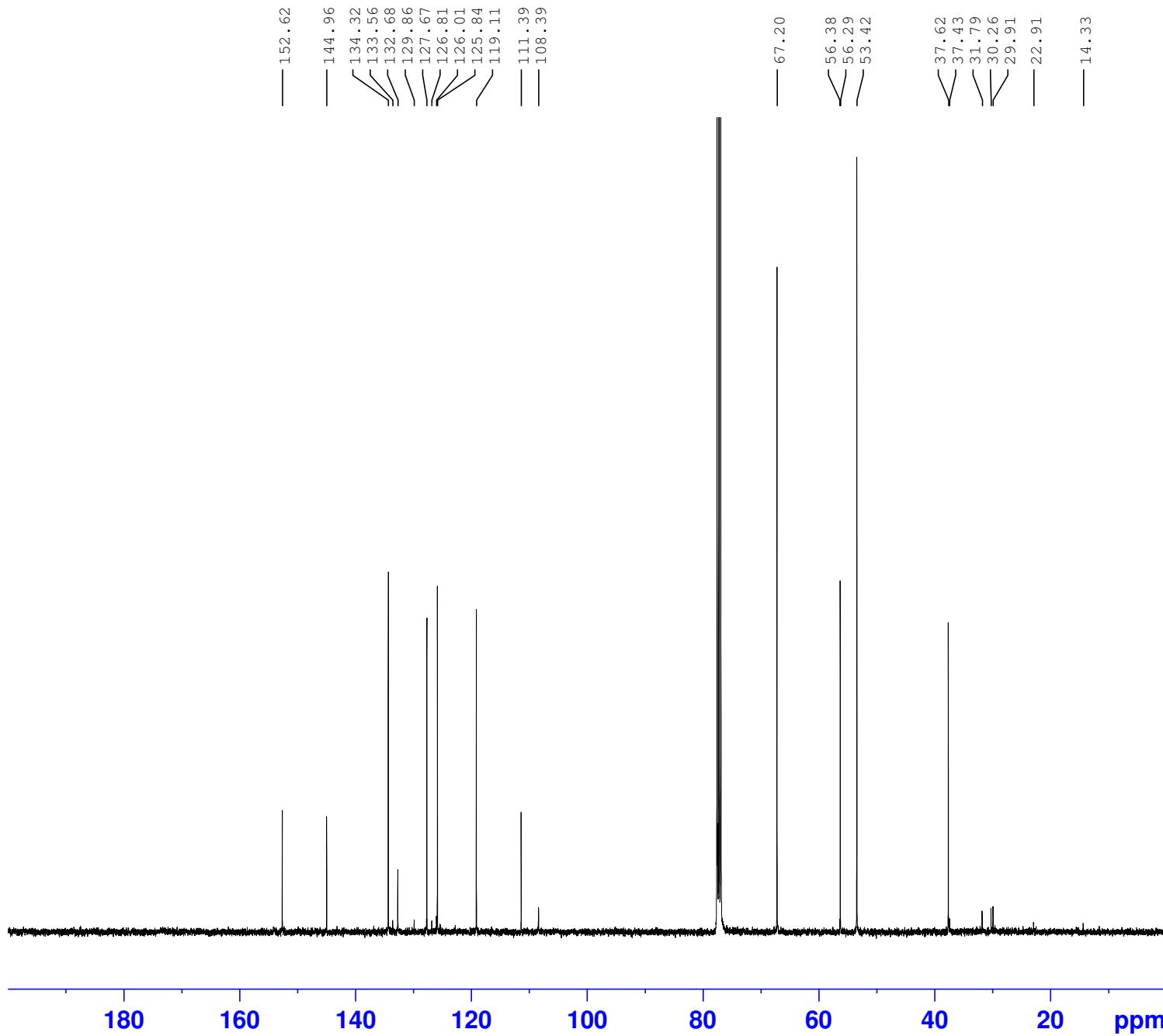


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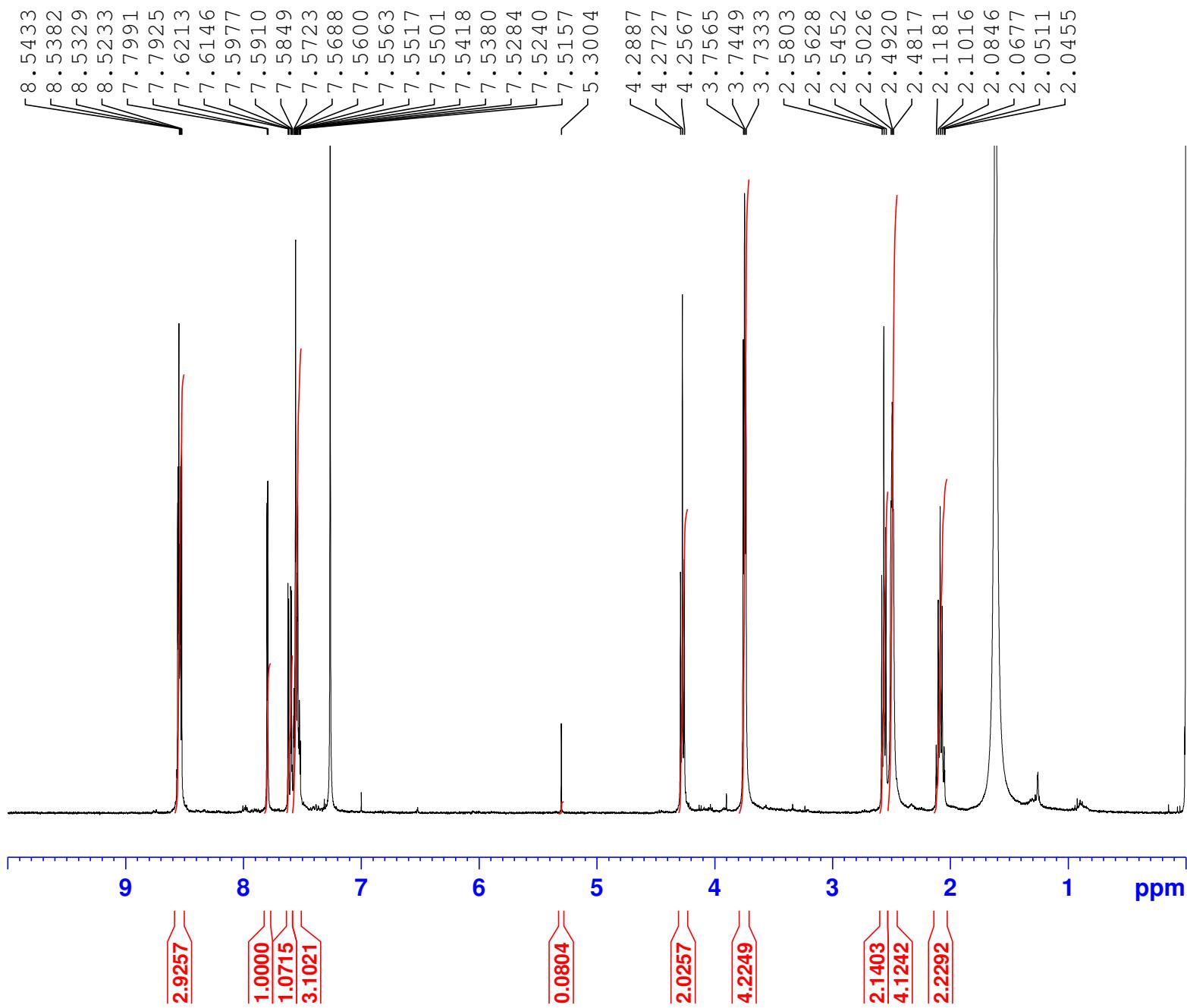


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Compound 3

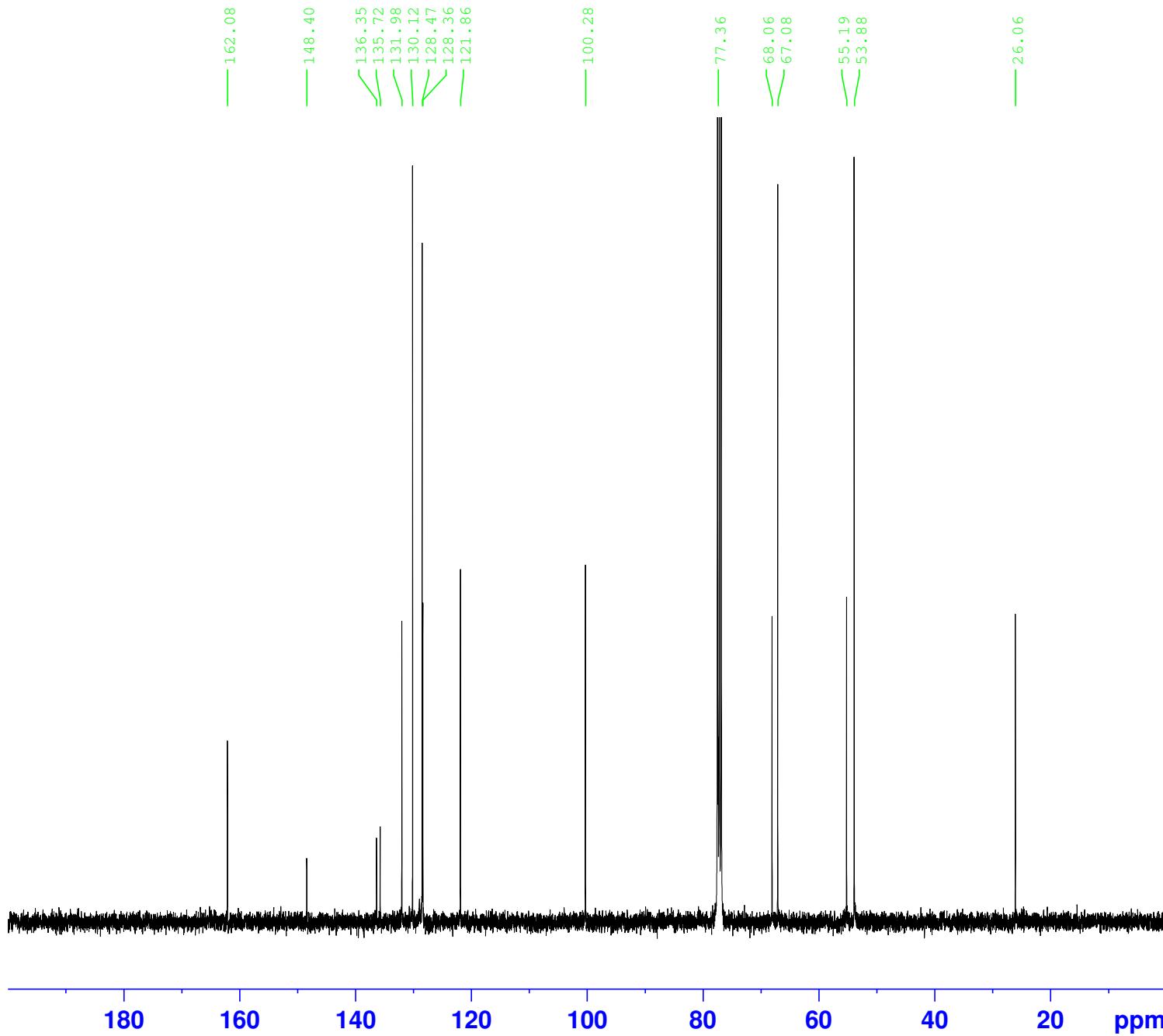


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Compound 3



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