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2 Supporting Information

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4 **Oxidative hydroxylation of aryl boronic acid catalyzed**
5 **by Co-porphyrin complexes via blue-light irradiation**

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29 **Materials and preparations**

30 All of the chemicals used were purchased from TCI Company and used without further
31 purifications. The reactions followed by thin-layer chromatography (TLC) employed glass
32 0.25 mm silica gel plates with UV indicator. All of the products detected by using ^1H and
33 ^{13}C NMR data were obtained with a JEOL-GX (500 and 300 MHz). Infrared spectra by a
34 JASCO A-100 FTIR spectrophotometer, High-resolution mass spectra (HRMS) used by a
35 JEOL JMS-DX303. Kessil A160WE Tuna Blue used as source of visible light for the
36 hydroxylation reaction.

37 **Solvent and Reagents**

38 Phenyl boronic acid and acetonitrile, PdCl_2 and carboxy benzaldehyde were purchased
39 (Wako) and used without further purification. 1-Naphthalene boronic acid, 4-formyl
40 benzene boronic acid, 4-tolyl benzene boronic acid and 4-bromo benzene boronic acid
41 were purchased (Oakwood Chemical) and used without further purification. 3-amino
42 phenyl boronic acid, propionic acid, pyrrole and 2,4,6-trimethyl phenyl boronic acid
43 (Tokyo Kasei) were purchased and used without further purification. Triethylamine
44 (Nacalai) were purchased and used without further purification.

45 **Preparation of meso-Tetraphenylporphyrin H_2 (TPP)** ^[1]

46 Benzaldehyde (4 mL, 40 mmol) were added to 150 ml of propionic acid, and then heated to
47 80 °C in the three-neck round flask. Pyrrole (2.8 mL, 40 mmol) was added to the mixture
48 through 15 min before the temperature increased to 180 °C. After 1 h the reaction mixture
49 was cooled to room temperature and filtered. The solid residue was washed with hot water
50 and methanol. After drying under reduced pressure, the desired product was obtained in
51 50 % as a purple crystal.

52 ^1H NMR (500 MHz, CDCl_3) δ 8.85 (8 H, s), 8.22 (8 H, dd, $J=10, 5$ Hz), 7.75 (12 H, m). ^{13}C
53 NMR (500 MHz, CDCl_3) δ 142.15, 134.25, 132.00, 130.00, 127.61, 126.62, 120.1.
54 High-resolution MS, Calculated for $\text{C}_{44}\text{H}_{30}\text{N}_4$: 614.71, found m/e (relative intensity): 615

55 (M⁺). Elemental analysis: calculated for C₄₄H₃₀N₄: C, 85.97 H, 4.92; N, 9.11. Found: C,
56 85.55; H, 4.90; N, 9.01.

57 **Procedure for the preparation of**

58 **5,10,15,20-tetrakis(4-(methoxycarbonyl)phenyl)porphyrin H₂(TMCPP)** ^[2]

59 p-Methoxycarbonyl benzaldehyde (1.312 g, 8 mmol) was added to 100 mL of propionic
60 acid, and then stirred at 80 °C in the three-neck round flask. Pyrrole (0.56 mL, 8 mmol) was
61 added to the mixture through 15 min before the temperature increased to 140 °C. After 1 h ,
62 the reaction mixture was cooled to room temperature under the air atmosphere. The
63 reaction solution was filtered, and washed with hot water and methanol to remove adsorbed
64 acid. Purple crystal was obtained in 40 % after purification by thin-layer chromatography
65 with silica gel-coated glass plates using methylene chloride as eluent (**Scheme S1**).

66 UV-Vis (DMF) λ_{max}, 419 (a Soret band), 517, 550,591 and 647 (Q bands).

67 ¹H NMR (500 MHz, CDCl₃) δ 8.85 (8H, s), 8.43 (8H, d, *J*=8 Hz), 8.27 (8H, d, *J*=8 Hz),
68 4.00 (12H, s), -2.83 (2H, s). ¹³C NMR (500 MHz, CDCl₃) δ 52.46 (CO₂CH₃), 119.38
69 (C_{meso}), 127.97 (ArC_{meta}), 129.76 (C_β), 134.50 (ArC_{ortho}), 146.59 (C_α), 167.21 (C=O).

70 High-resolution MS, Calculated for C₅₂H₃₈N₄O₈: 846, found *m/e* (relative intensity): 847
71 (M⁺). Elemental analysis: calculated for C₅₂H₃₈N₄O₈: C 73.82, H 4.52, N 6.62. Found: C
72 73.25, H 4.25, N 6.55.

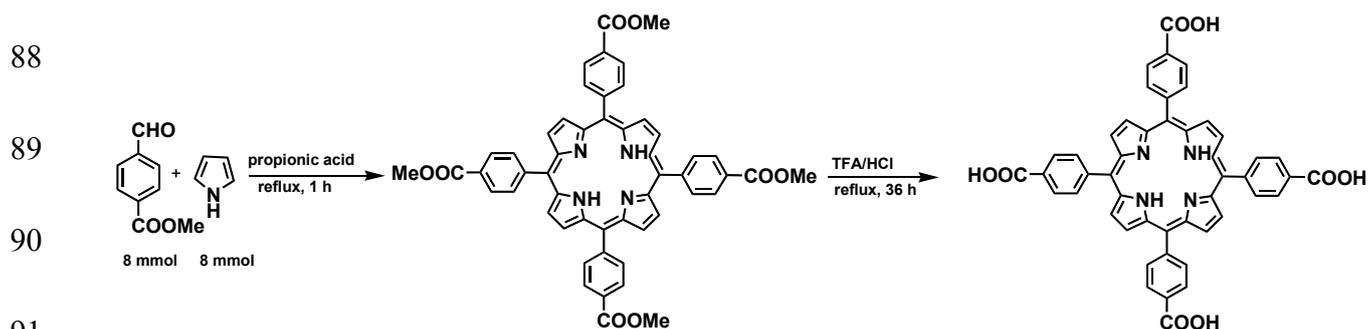
73 **Procedure for the preparation of 5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin**

74 **H₂(TCPP)** ^[2]

75 H₂(TMCPP) (0.12 mmol) was dissolved in 5 ml of trifluoroacetic acid, then 2.5 mL of HCl
76 (35%) was added to the solution, and the mixture was stirred at 85 °C for 36 h. The reaction
77 mixture was diluted with cold water to give green precipitate, filtered, and washed with
78 water and CH₂Cl₂ at three times to remove unreacted H₂(TMCPP). The green solid was
79 dissolved in 10 mL pyridine, filtered, and evaporated. After washing with water and
80 CH₂Cl₂ to afford H₂(TCPP) in 80% yield as purple powder (**Scheme S1**).

81 UV-Vis (DMF) λ_{max}, 422 (a Soret band), 515, 552,592 and 648 (Q bands).

82 ^1H NMR (500 MHz, DMSO) δ 13.3 (4H, br s.), 8.84 (8H, s), 8.37 (8H, d, $J=10$ Hz), 8.33
83 (8H, d, $J=10$ Hz). ^{13}C NMR (500 MHz, CDCl_3) δ 119.78 (Cmeso), 128.35 (ArCmeta),
84 131.00 (CB), 134.89 (ArCortho), 145.84 ($\text{C}\alpha$), 167.90 ($\text{C}=\text{O}$). High-resolution MS,
85 Calculated for $\text{C}_{48}\text{H}_{30}\text{N}_4\text{O}_8$: 790.77, found m/e (relative intensity): 791 (M^+). Elemental
86 analysis: calculated for $\text{C}_{48}\text{H}_{30}\text{N}_4\text{O}_8$: C 72.90, H 3.82, N 7.09. Found: C 72.11, H 3.67, N
87 6.75.



96 **Scheme S1** Preparation of the (H_2TMCPP and H_2TCPP)

96 **Metallation of Porphyrin**

97 Cobalt(II)TPP, Cobalt(II)TMCPP and Cobalt(II)TCPP were prepared by the reaction of
98 $\text{H}_2(\text{TPP})$, $\text{H}_2(\text{TMCPP})$ and $\text{H}_2(\text{TCPP})$ (1 mmol) with $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (6 mmol) on 150 mL of
99 dimethylformamide followed by refluxing for 6 hours under nitrogen atmosphere. After the
100 solution was cooled to room temperature, the solvent was evaporated in vacuum. The
101 residue was washed with water and dried under vacuum to give the corresponding
102 Cobalt(II)porphyrins (**Scheme S2**).

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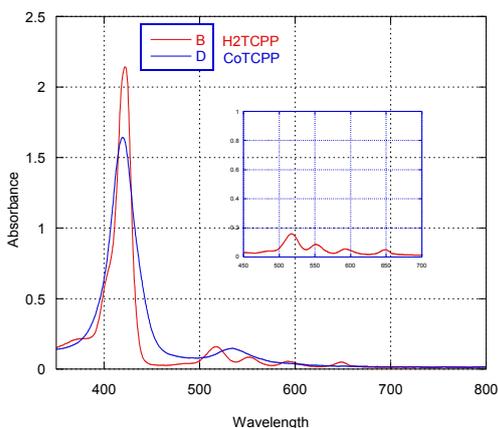


Figure S1 UV-Vis spectra of B) H₂TCPP and D)CoTCPP

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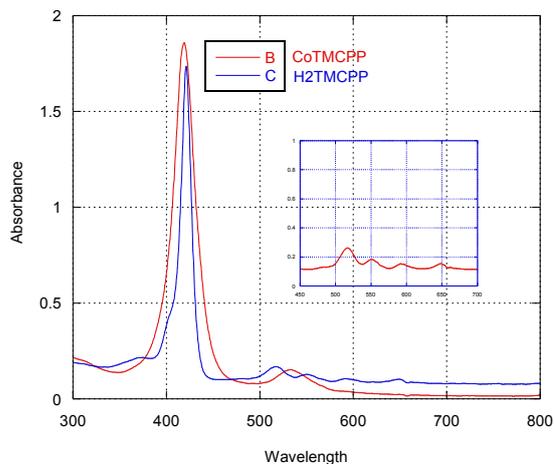


Figure S2 UV-Vis spectra of B) H₂TMCPP and D)CoTMCPP

114 **Figure 1 and 2** showed the UV-visible spectrum of H₂TMCPP and H₂TCPP before and
115 after metallation with cobalt, the appearance of a Soret peak at 422 nm and four Q peaks at
116 515, 552, 592 and 648 nm in case of H₂TCPP. However, it showed that CoTCPP, the Soret
117 peak is red-shifted and appeared at 435 nm and Q bands are reduced. Furthermore,
118 H₂TMCPP has a Soret peak at 419 nm and four Q peaks at 517, 550, 591, and 649 also, the
119 Soret band of CoTMCPP appears at 534 nm and Q bands are reduced.

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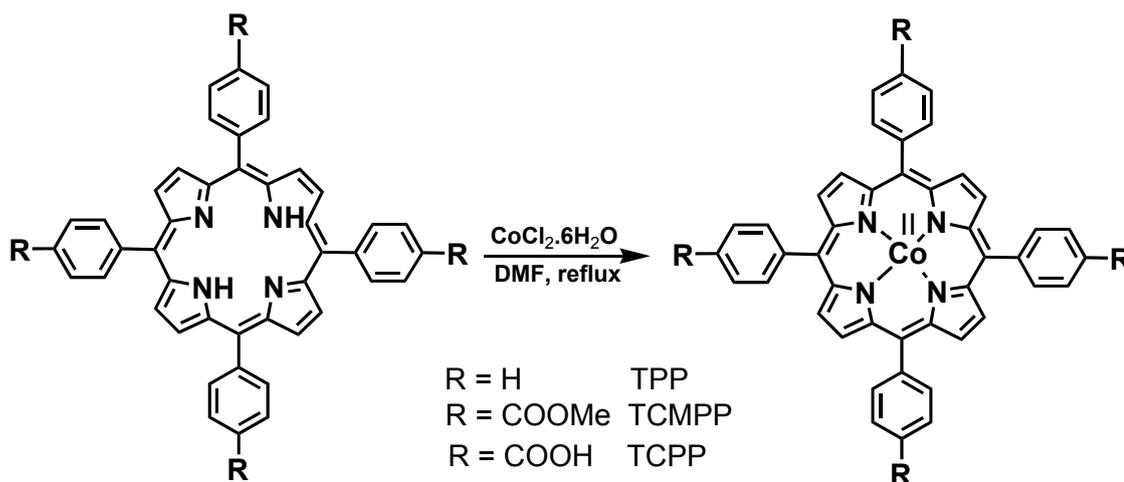
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Scheme S2 metallation of (H₂TPP, H₂TMCPP and H₂TCPP)

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128 **Procedure for the preparation of Co(II)TCPP immobilized on chitosan[3]**

129 In a three-neck flask, a mixture of CTS (0.1 g) and diluted acetic acid (5 mL) was stirred at
130 room temperature for 15 min. Then 10 mL of distilled water were added to form the
131 colloidal solution. Then $2.85 \text{ mol}\cdot\text{L}^{-1} \text{ NH}_3\cdot\text{H}_2\text{O}$ solution was added dropwise until the
132 colloidal solution became neutral. Moreover, Co-TCPP (0.05 g) was dissolved in ethanol
133 (100 mL) and slowly added into the reaction system. The solution was stirred for 24 h, then
134 the reaction was stopped, and filtered. Then saturated NH_4HCO_3 solution was added to the
135 obtained wheat-colored colloid, and stirred for 2 hours. The mixture was filtered, and dried
136 under vacuum to obtain Co-TCPP/p-CTS complex (**Scheme S3**).

137 FT-IR spectra of CoTCPP and CoTCPP-Chitosan complex between $4000\text{-}400 \text{ cm}^{-1}$
138 explained in (**Figure 3**). The appearance of a sharp band at 1700 cm^{-1} pointing to C=O
139 stretching vibration of CoTCPP and a broad absorption peak around 3000 cm^{-1} for OH
140 stretching vibration. The stretching vibration of C=O appears as strong peak at 1600 cm^{-1} .

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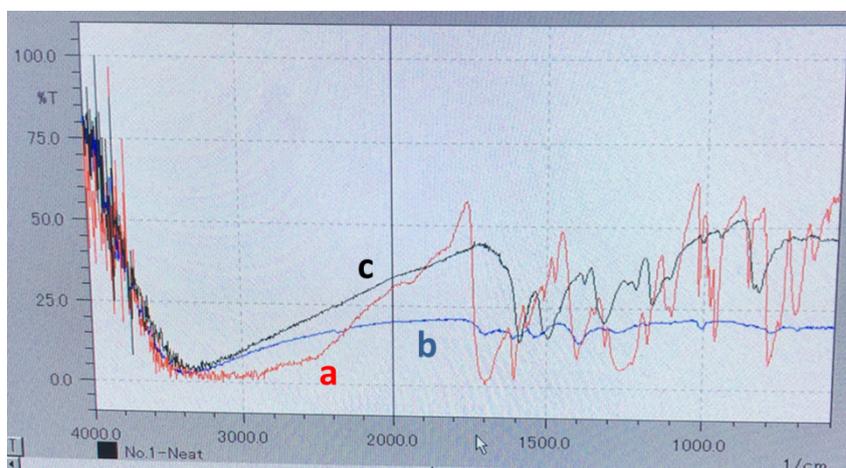
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148 **Figure S3** FT-IR spectra of, a) CoTCPP and c) CoTCPP-chitosan complex

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Scheme S3 Preparation of Co(II)TCPP-CTS

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160 Procedure for the preparation of polyaniline emeraldine hydrochloride

161 The polyaniline was prepared by the heterogeneous precipitation polymerization method [4–7]. In

162 this method, Aniline hydrochloride (2.29 g, 20 mmol) was dissolved in 50 mL distilled water.

163 Following that, ammonium peroxydisulfate (5.71 g, 25 mmol) was dissolved in distilled water (50

164 mL) and added dropwise to the aqueous solution of aniline hydrochloride at ambient temperature.

165 After cooling for 1h in an ice bath, the radical initiator was added very slowly and the

166 homogeneous solution turned into a heterogeneous system, the polymerization reaction was left for

167 24 h at ambient temperature. After 24 h, the reaction mixture was filtered and the precipitate was

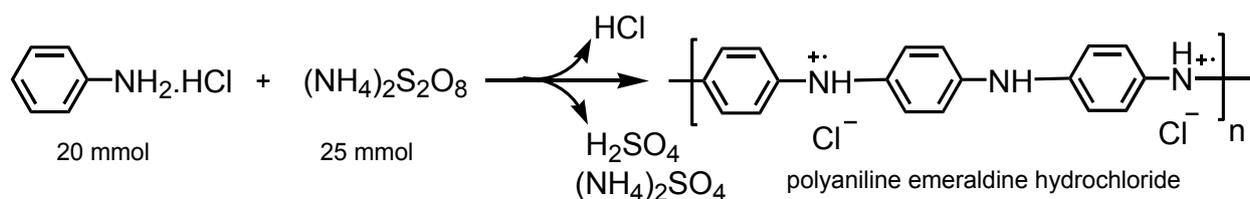
168 washed three times with aqueous HCl (0.2 M) and once with acetone. The green powder of

169 polyaniline emeraldine hydrochloride was obtained after drying under atmospheric air.

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Scheme S4 Oxidation of aniline hydrochloride with initiator yields poly aniline hydrochloride

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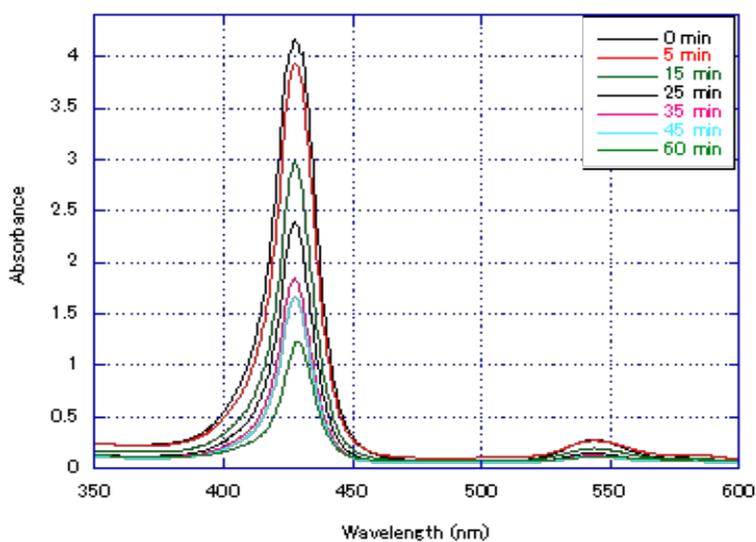
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Figure S4 UV-Vis spectra of adsorption of CoITCPP on the polyaniline

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185 **Figure S4** indicates to the adsorption of Co^{II} TCPP on the polyaniline hydrochloride
186 through 1h in basic medium and the results showed that the reaction was very fast at the
187 beginning and decreased gradually with time moreover, the expected structure of CoTCPP
188 and Polyaniline complex was showed in **Scheme S5** [8,9].

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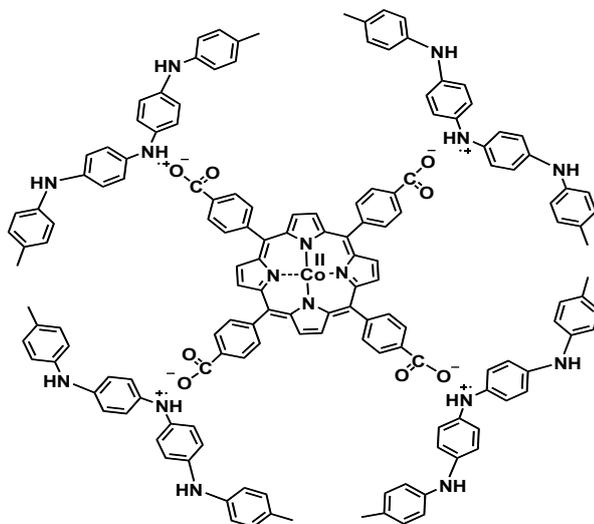
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206 **Scheme S5** Proposed possible structure of CoTCPP adsorbed on polyaniline through the oxidation reaction

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208 **General method for hydroxylation reaction**

209 All of oxidative hydroxylation reactions were performed under air atmosphere unless
210 otherwise noted.

211 **Hydroxylation reaction catalysed by Co(II)TPP, Co(II)TMCPP,Co(II)TCPP**

212 A mixture of arylboronic acid (1 mmol), (0.3 mol%) of catalyst in 5 mL of MeCN: H₂O
213 (4:1), TEA (0.64 mL, 5.0 mmol) were added to the reaction mixture, the mixture was
214 stirred at room temperature under blue light.

215 **Hydroxylation reaction catalysed by Co(II)TCPP supported on polyaniline**

216 A mixture of (0.3 mol%) of Co(II)TCPP and (0.3 mol%) of prepared polyaniline were
217 stirred for 15 min in 5 mL of MeCN: H₂O (4:1) at pH 9 using NaOH solution till
218 completely adsorption of catalyst on polyaniline surface, arylboronic acid (1 mmol) and
219 TEA (0.64 mL, 5.0 mmol) were added to the reaction mixture, the mixture was stirred at
220 room temperature under blue light.

221 **Hydroxylation reaction catalyzed by Co(II)TCPP supported on chitosan**

222 A mixture of arylboronic acid (1 mmol), Co-catalyst (0.3 mol%) dissolved in 5 mL of
223 MeCN: H₂O (4:1), TEA (0.64 mL, 5.0 mmol) were added and, the reaction mixture was
224 stirred at room temperature under blue light irradiation (24W, λ_{\max} = 525 nm).

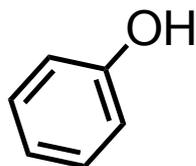
225 **Catalyst Re-use**

226 Re-use of the catalyst Co(II)TCPP supported on polyaniline was tested as the follows,
227 hydroxylation of phenylboronic acid was carried out under standard conditions of Table 1.
228 After completion of the first run, the solvent was removed by filtration and the product was
229 isolated and determined by NMR measurements. The precipitate (Co-porphyrin supported
230 on polyaniline) could be washed with water and used for the second time by added the initial
231 amount of phenylboronic acid, TEA and solvent. Then the reaction was carried out at room
232 temperature for 6 h to give 40 % of the product. After two runs, we found that the re-use of
233 the catalyst activity is less than the fresh catalyst. The deactivation of the catalyst could be
234 due to the accumulation of the reaction product and porphyrin in the polymer.

235 **Analytical data for products of hydroxylation products**

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239 **Phenol**

240 High-resolution MS, Calculated for C₆H₆O: 64 found 64(M⁺). ¹H NMR (500 MHz, CDCl₃)

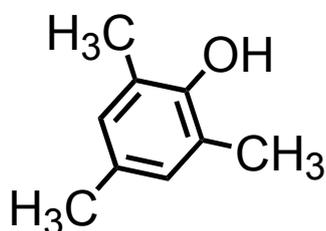
241 δ 7.24 (2H, t, *J*=10 Hz), 6.91 (1H, t, *J*=10 Hz), 6.82 (2H, d, *J*=10 Hz), 4.88 (1H, s). ¹³C

242 NMR (500 MHz, CDCl₃) δ 155.70, 129.59, 120.55, 115.26.

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247 **2,4,6-Trimethylphenol**

248 High-resolution MS, Calculated for C₉H₁₂O: 136.1 found 137 (M⁺). ¹H NMR (500 MHz,

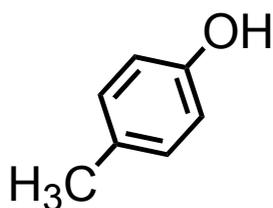
249 CDCl₃) δ 6.79 (2H, s), 4.43 (1H, s), 2.21 (9H, s). ¹³C NMR (500 MHz, CDCl₃) δ 149, 129.2,

250 122.7, 20.3, 15.8.

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255 **4-Methylphenol**

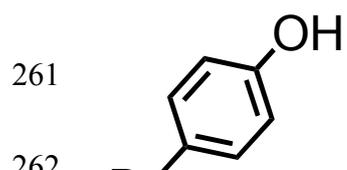
256 High-resolution MS, Calculated for C₇H₈O: 108.1 found 109 (M⁺). ¹H NMR (500 MHz,

257 CDCl₃) δ 7.03(2H, d, *J*=10 Hz), 6.73 (2H, d, *J*=10), 4.56 (1H, s), 2.27 (3H, s).

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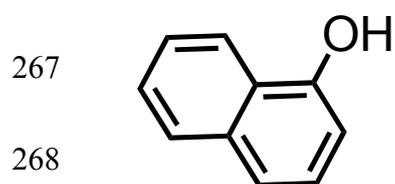
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263 **4-Bromophenol**

264 High-resolution MS, Calculated for C_6H_5OBr : 173.01 found 174 (M⁺). ¹H NMR (500 MHz,

265 $CDCl_3$) δ 7.03 (2H, d, $J=10$ Hz), 6.72 (2H, d, $J=10$ Hz), 4.77 (1H, s).

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269 **1-Hdroxynaphthalene**

270 High-resolution MS, Calculated for $C_{14}H_{10}O$: 144.17 found 145 (M⁺). ¹H NMR (500 MHz,

271 $CDCl_3$) δ 8.18 (1H, m), 7.81 (1H, m), 7.49 (2H, m), 7.44 (1H, d, $J=5$ Hz), 7.31 (1H, t, $J=10$

272 Hz), 6.62 (1H, d, $J=5$ Hz), 5.23 (1H, s).

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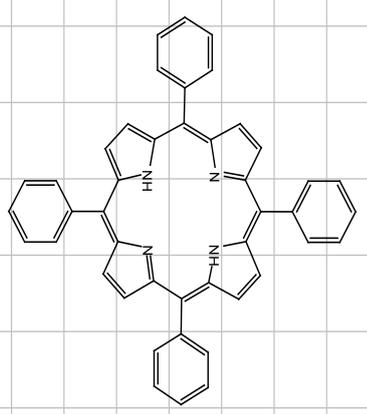
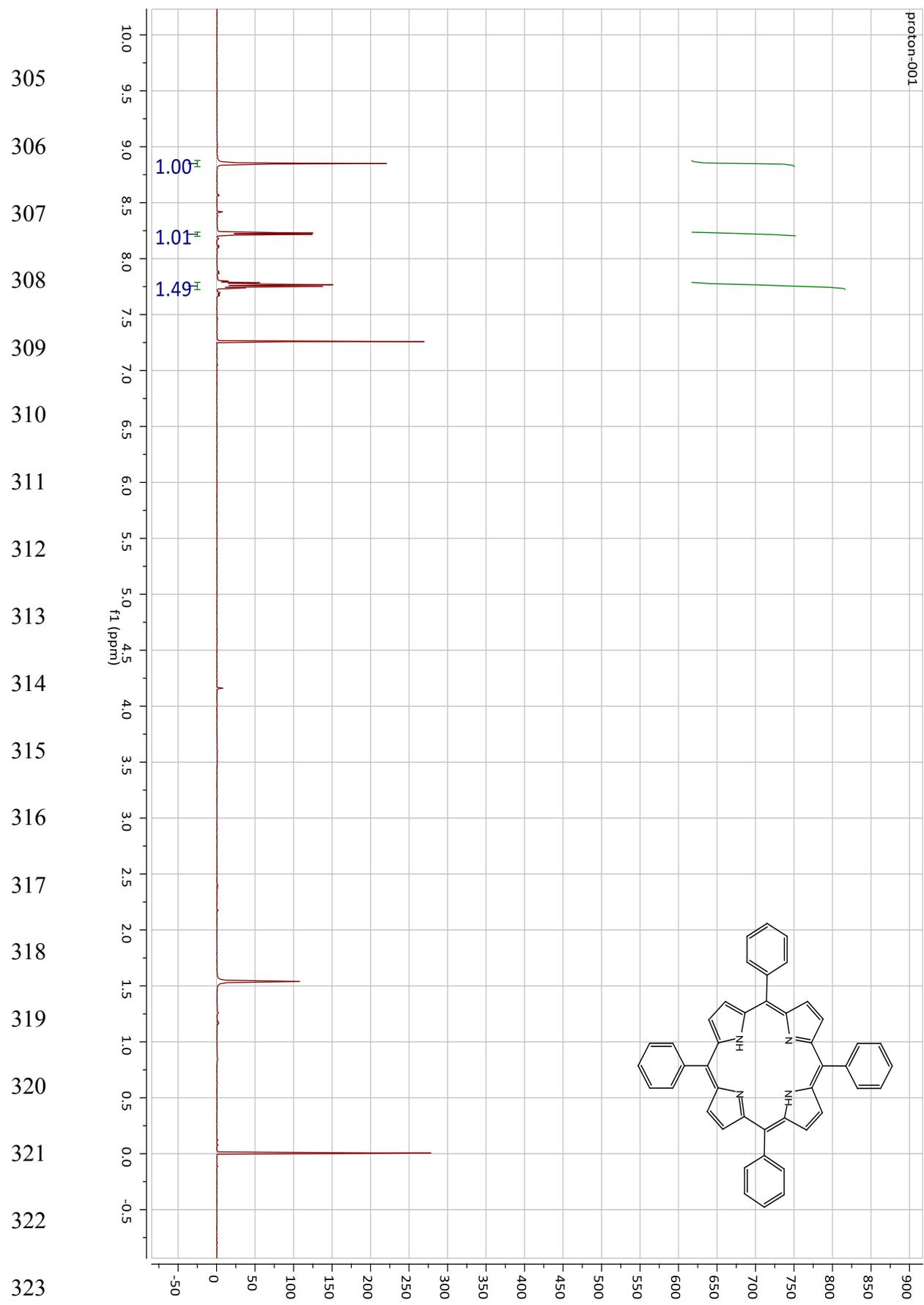
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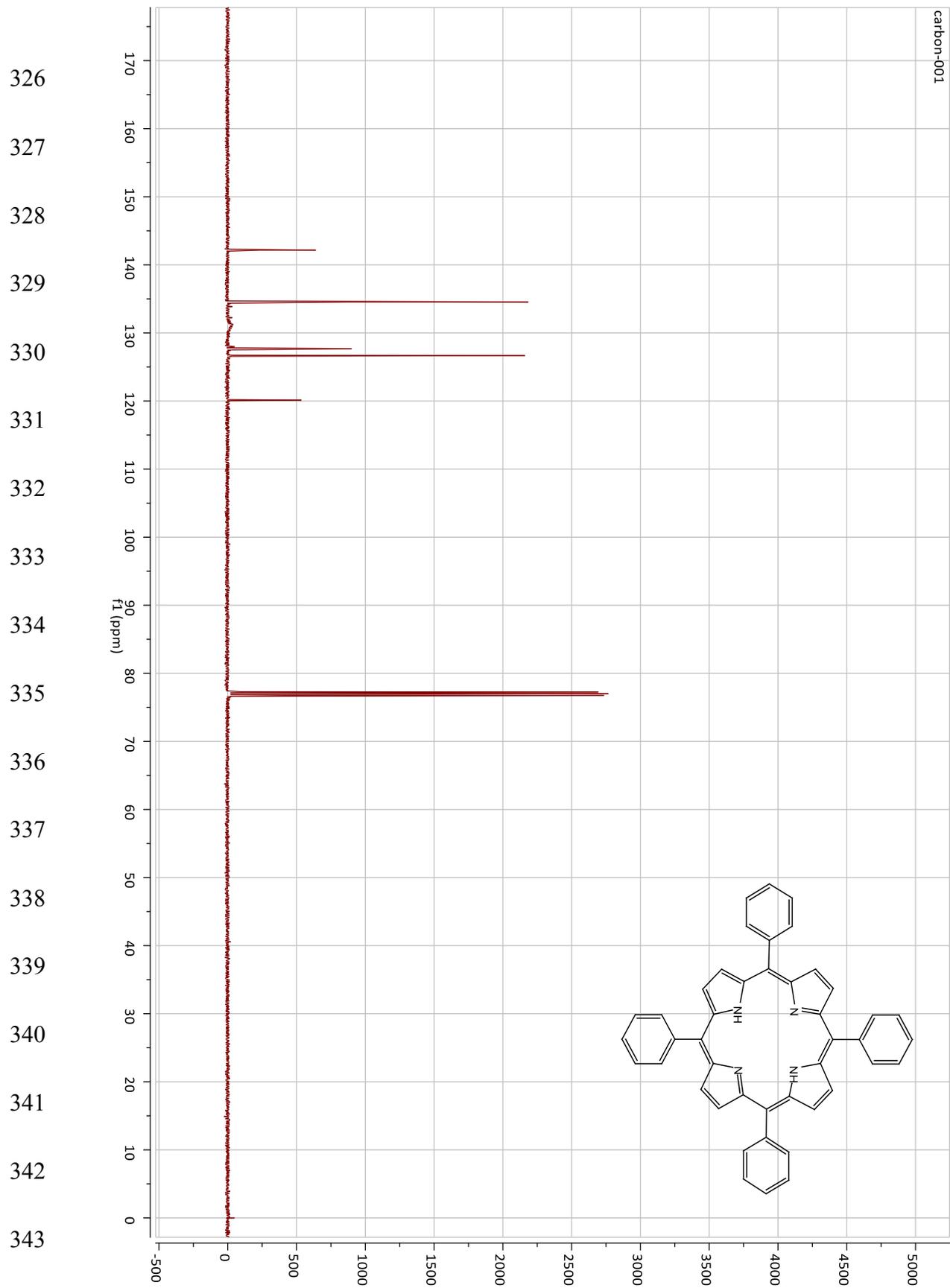
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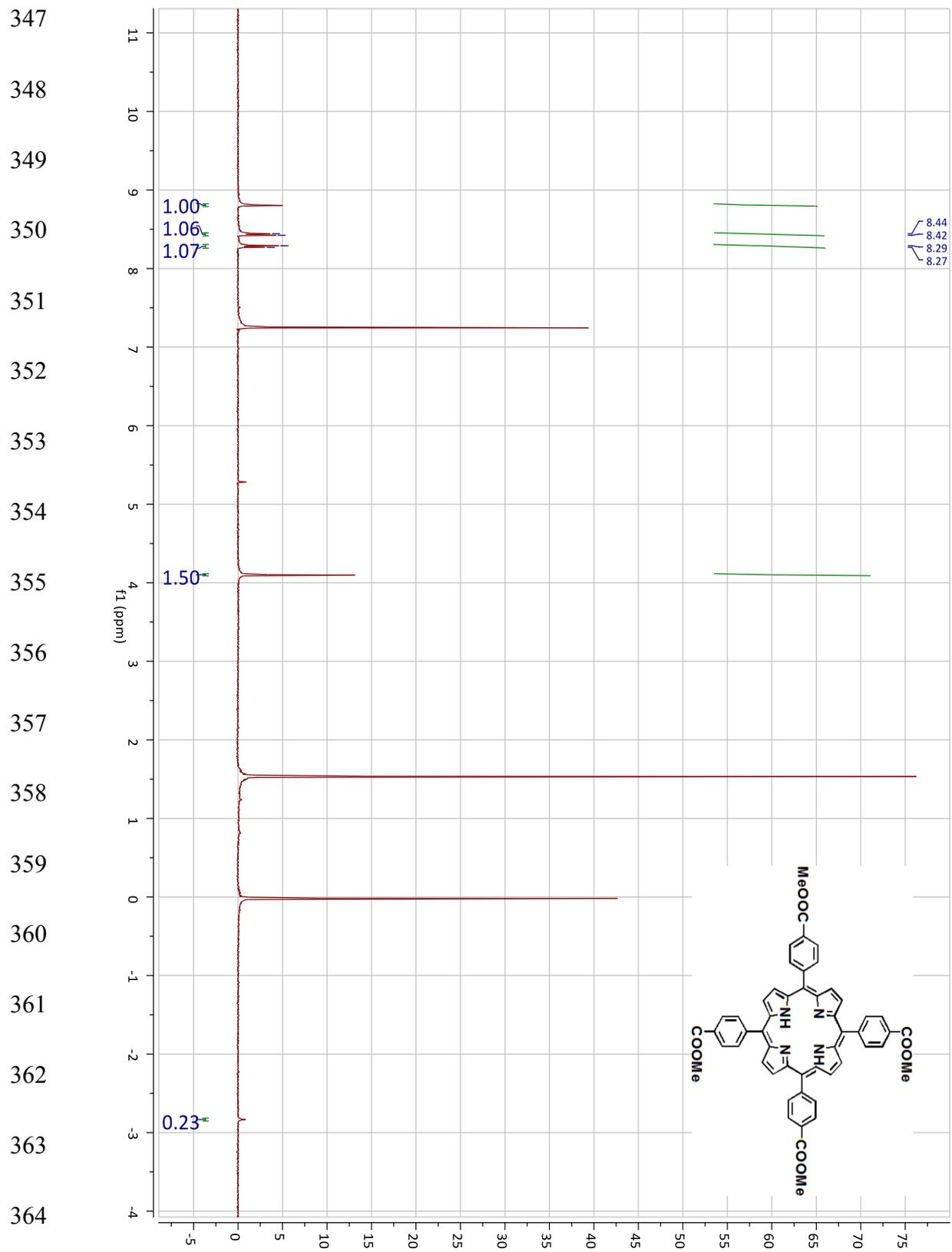
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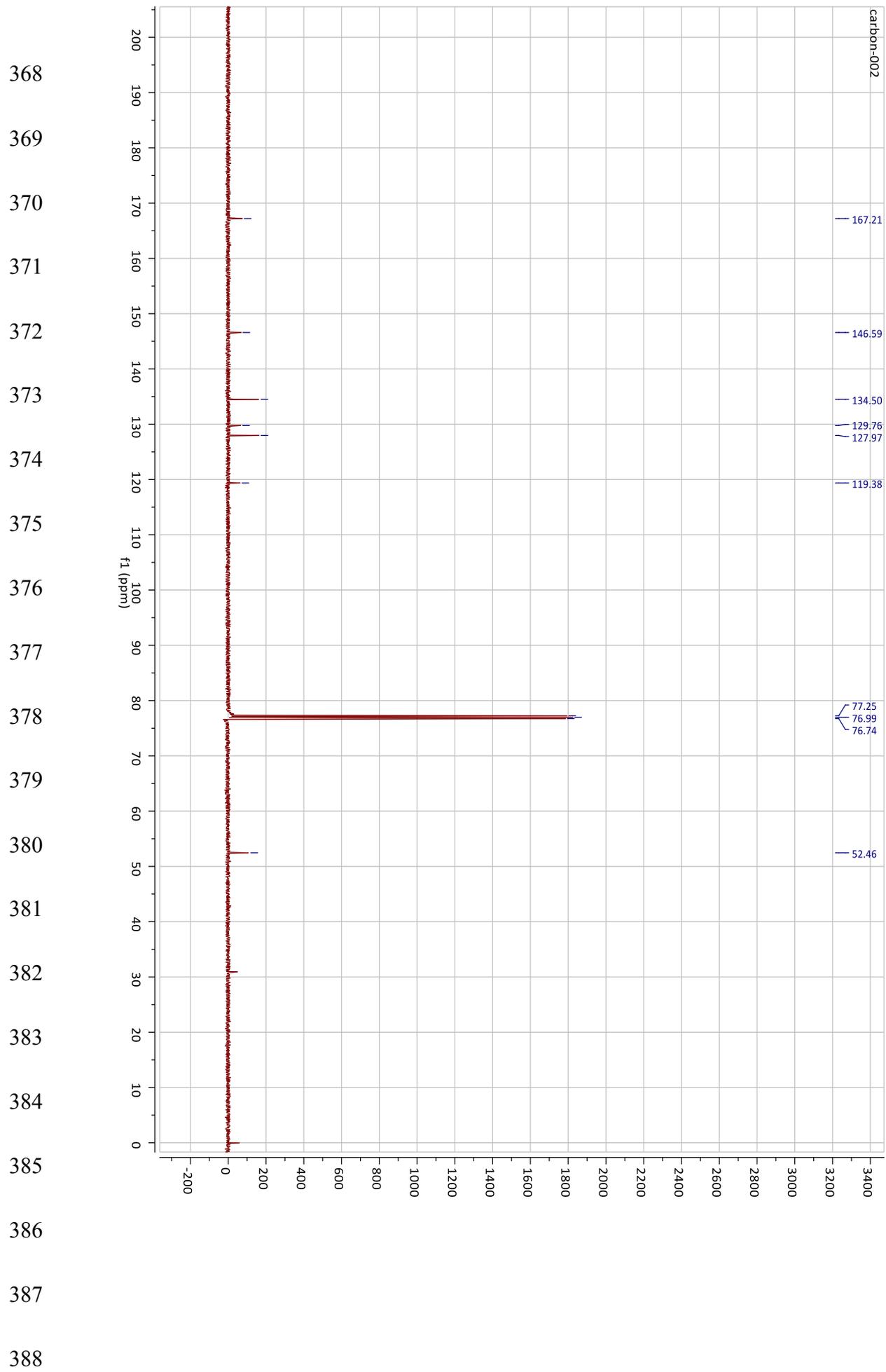
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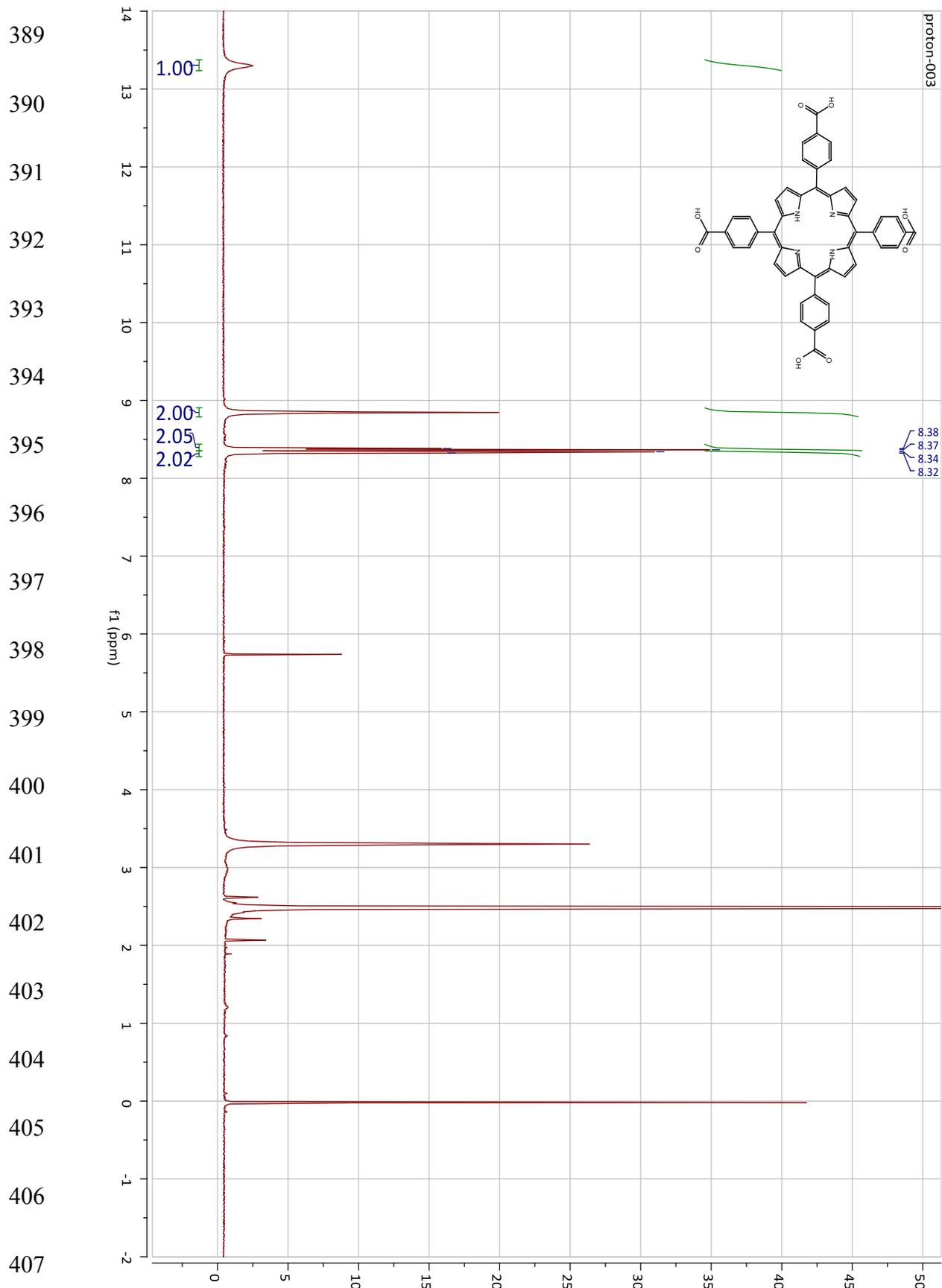
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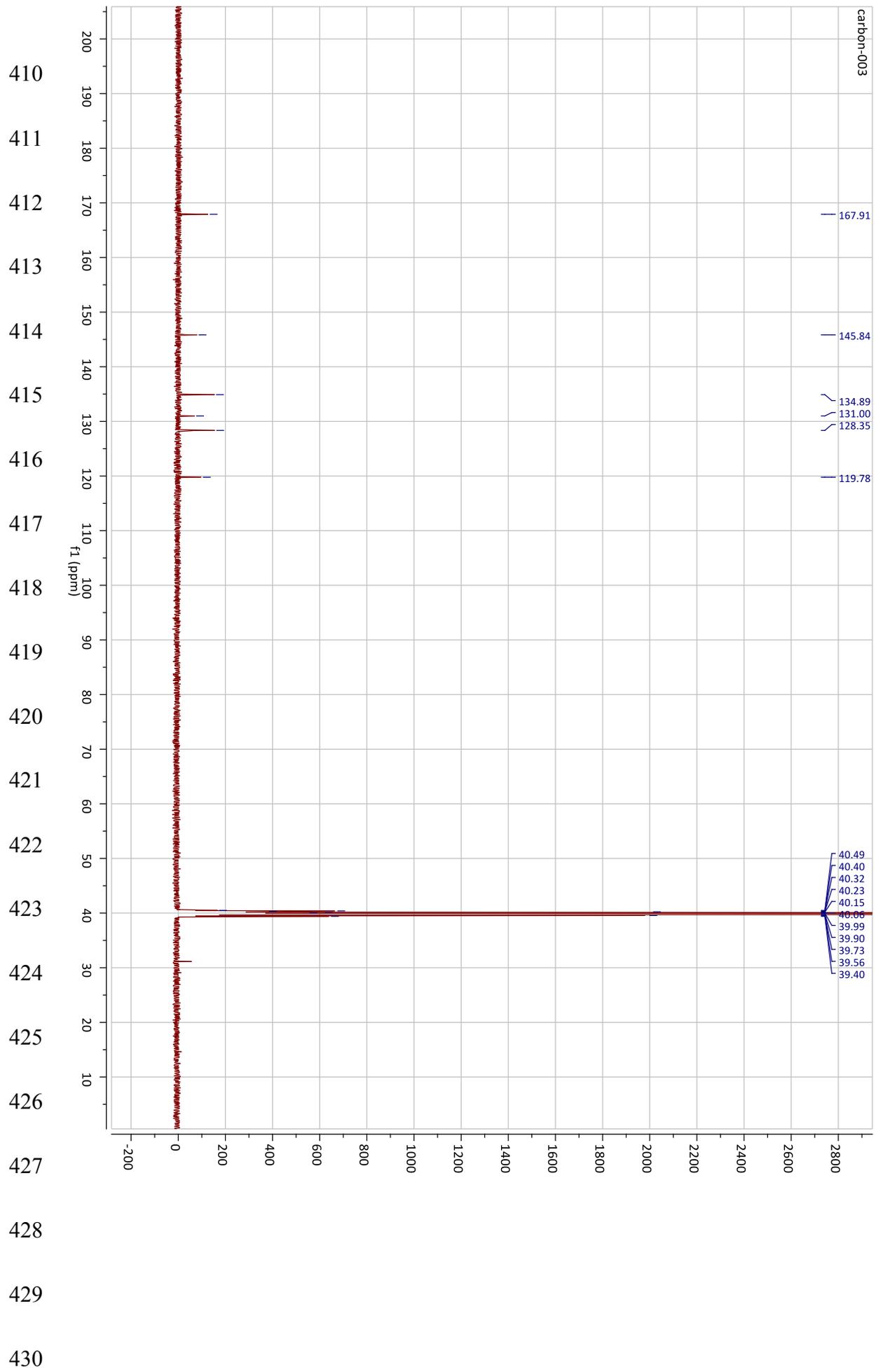


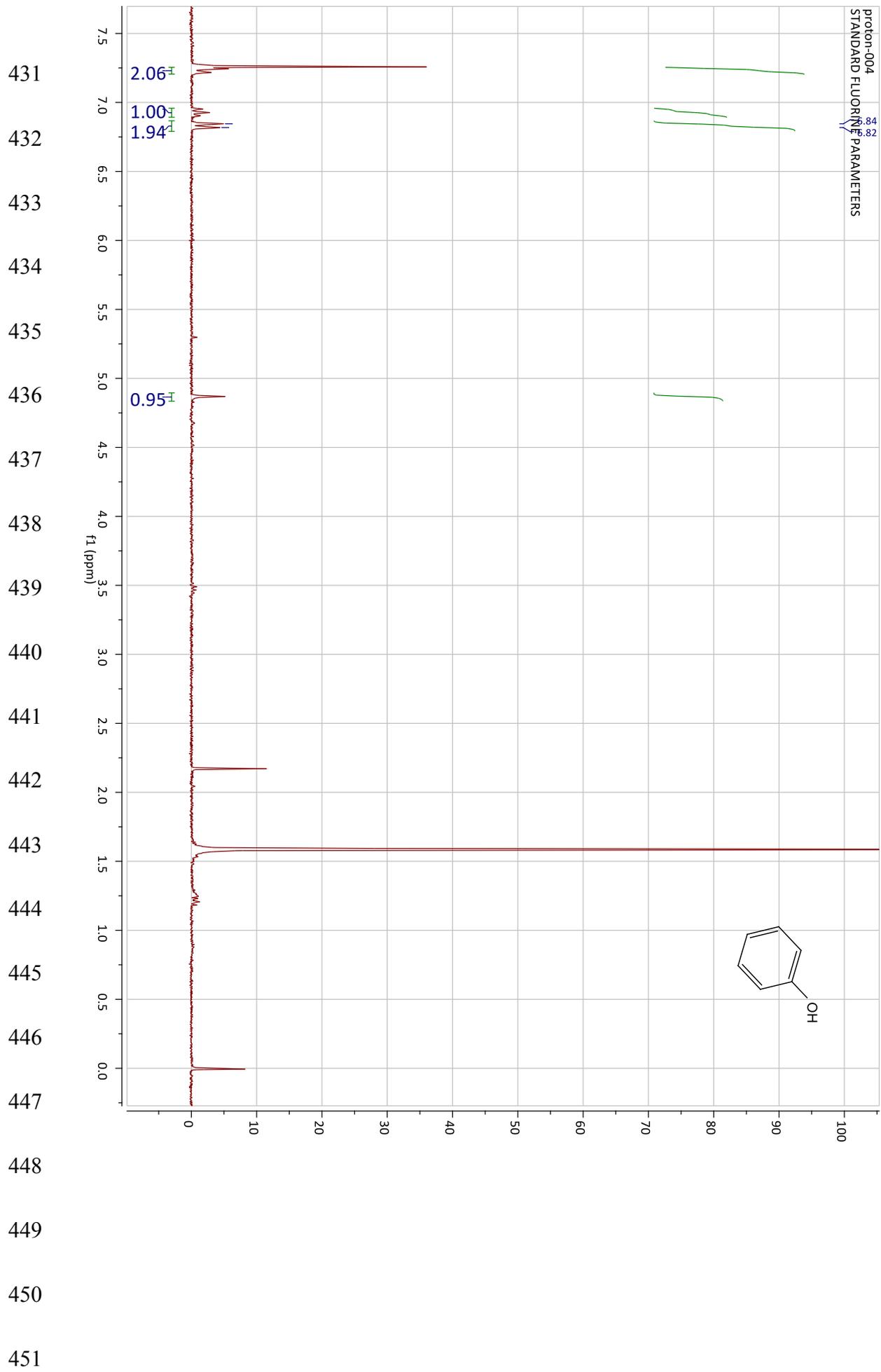


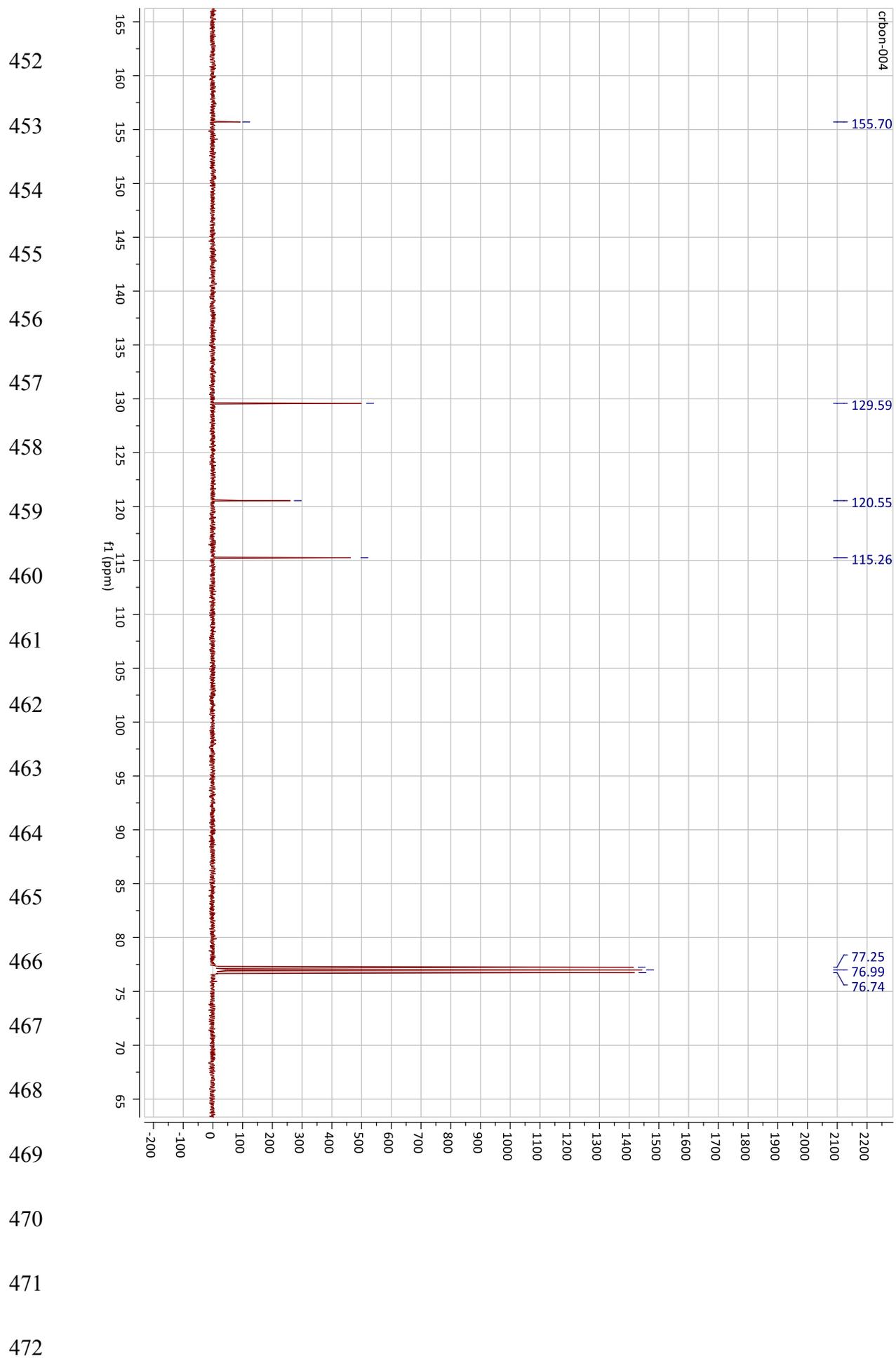


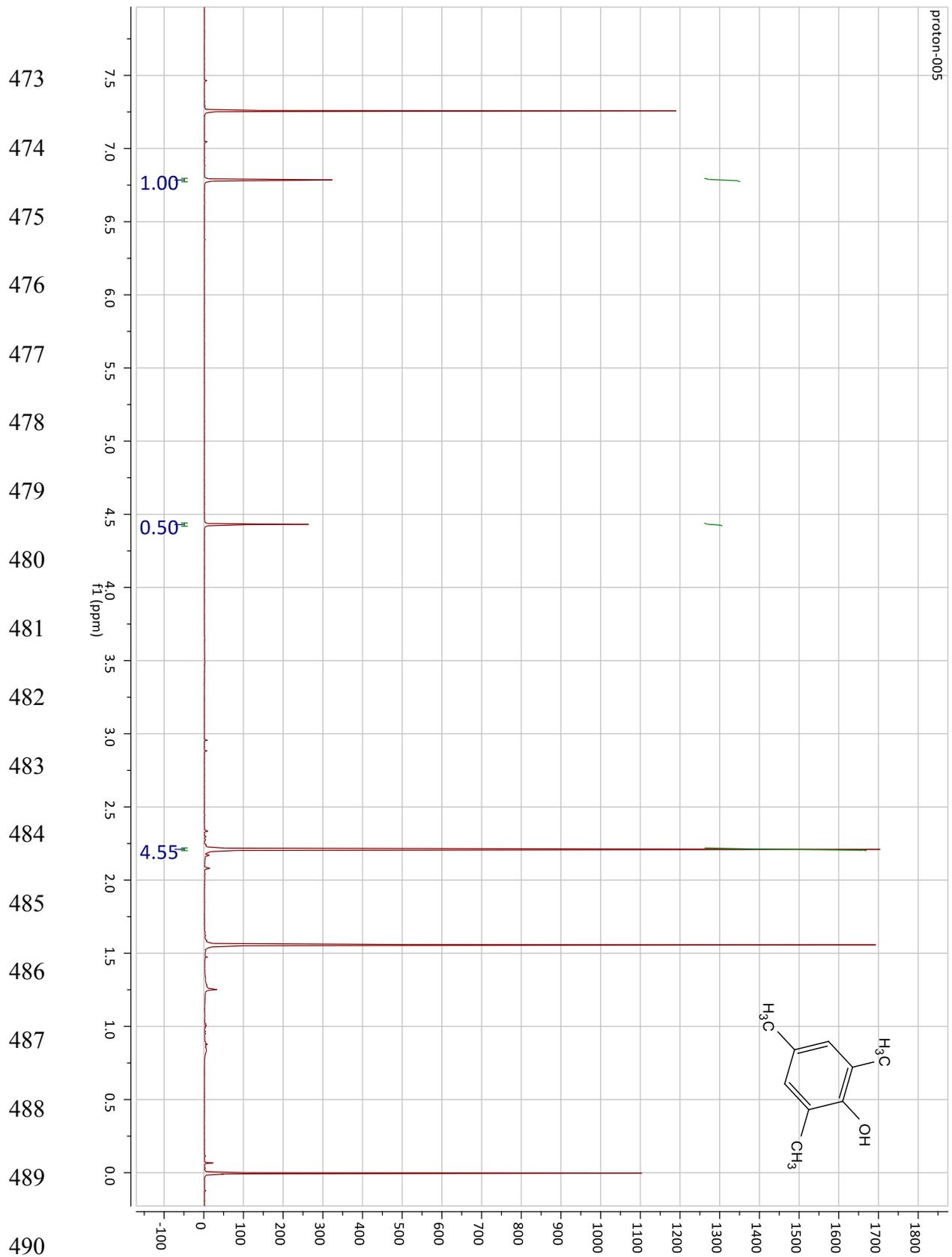
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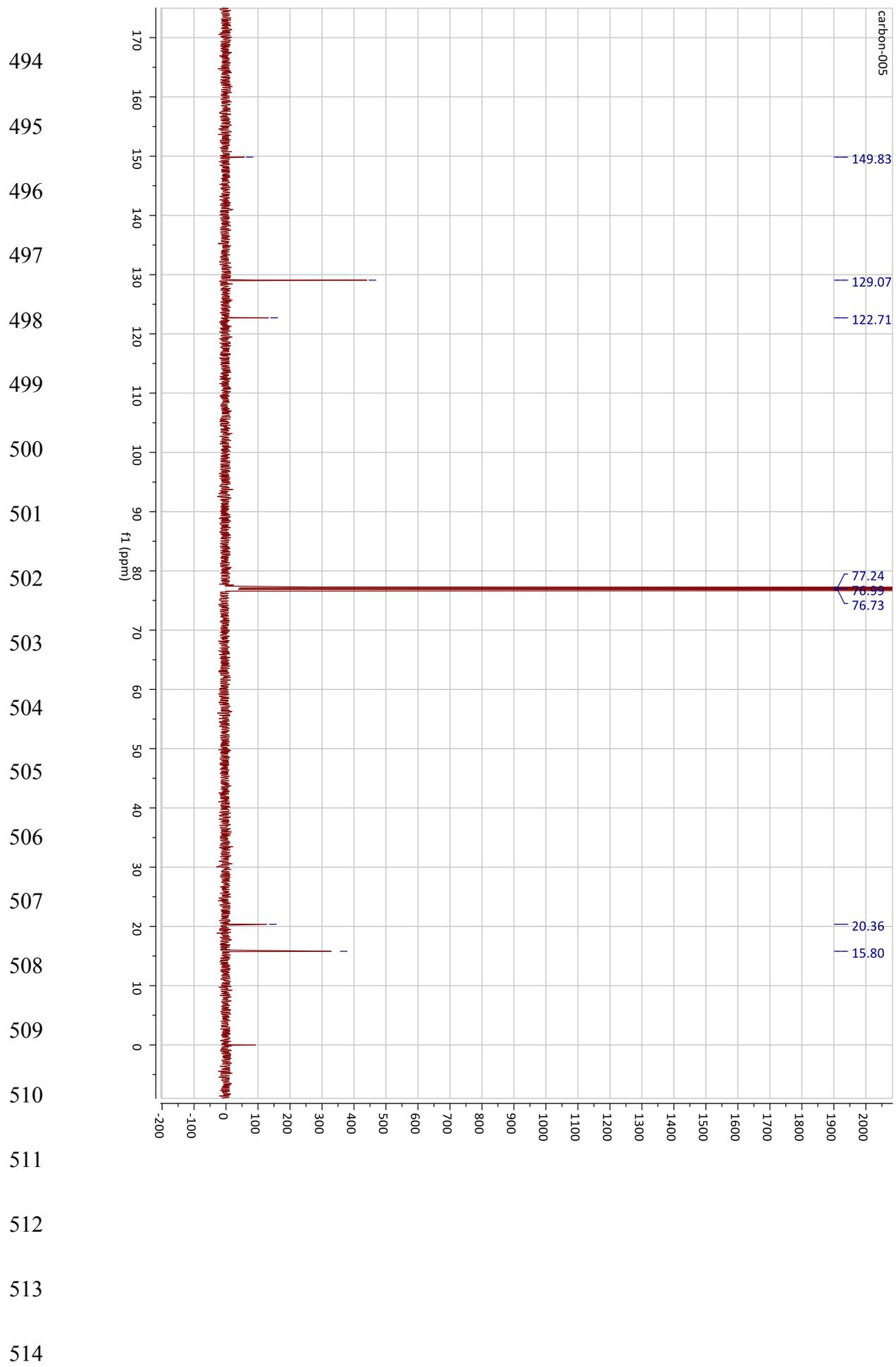


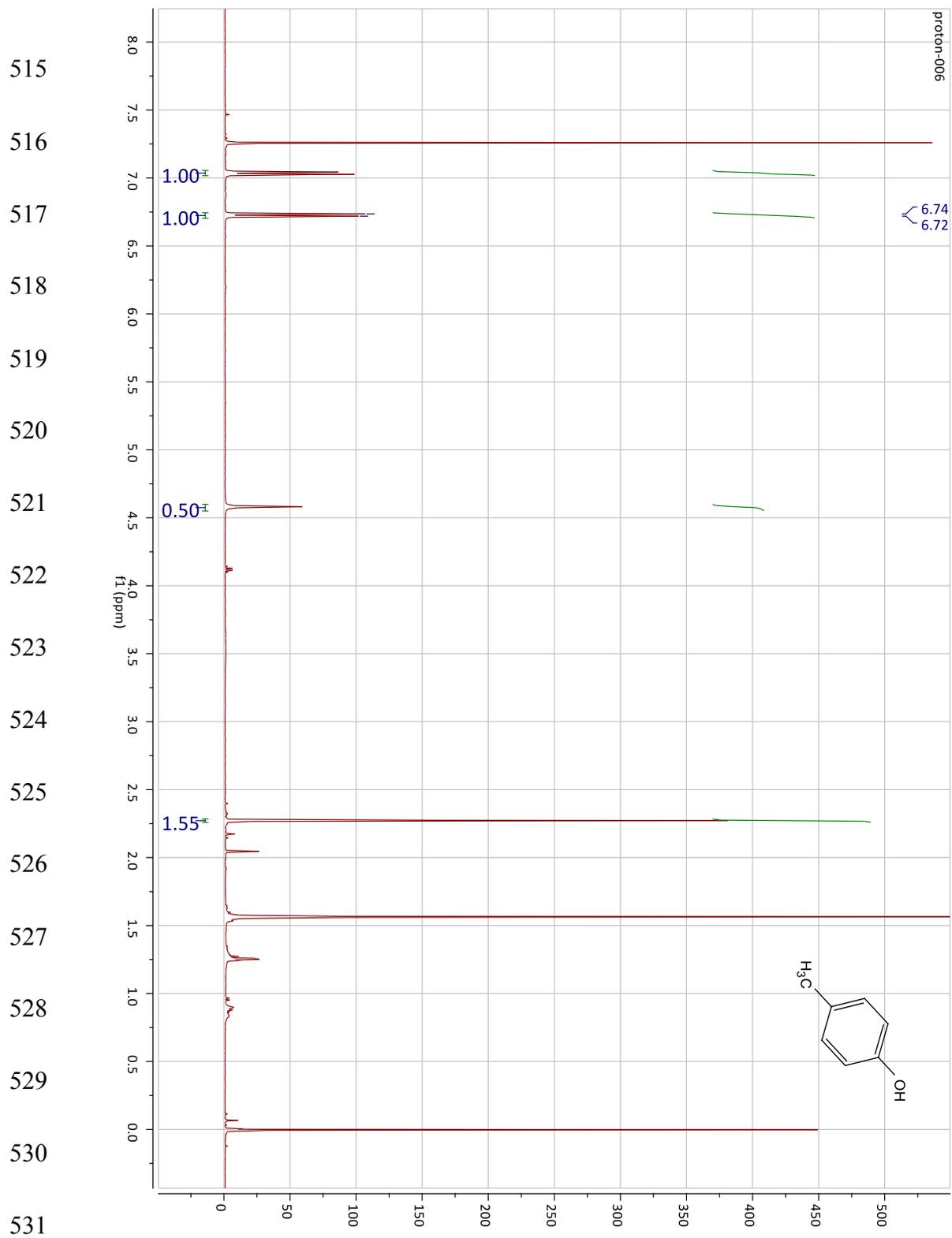


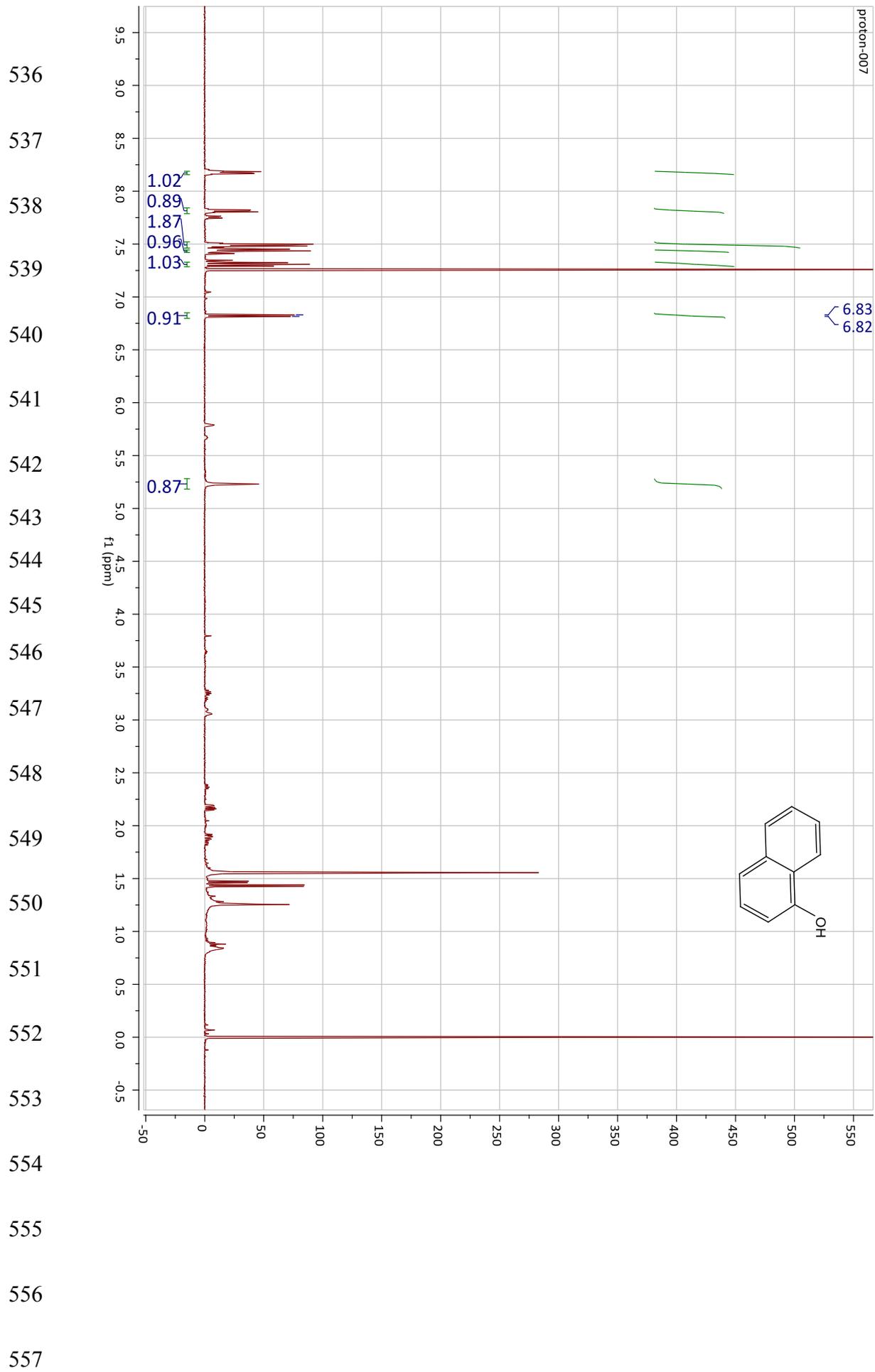




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