Supporting Information

Two-Photon Oxygen Sensing with Quantum Dot-Porphyrin Conjugates

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Synthetic Procedures for Porphyrin Precursors

5-(3-Pyridyl)dipyrromethane (S1). A solution of 20 mL pyrrole (19 g, 290 mmol) and 2 mL 3-pyridinecarboxaldehyde (2.3 g, 21 mmol) was heated at 85 °C for 24 h. Solvent was removed by rotary evaporation. The crude reaction mixture was loaded onto a silica gel column packed with ethyl acetate. The product was eluted with 100% ethyl acetate as the second band (orange). Solvent was removed by rotary evaporation to afford 2.41 g (51.4% yield) of the title compound as a tan solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.49 (s, 1H), 5.88 (m, 2H), 6.16 (m, 2H), 6.74 (m, 2H), 7.24 (m, 1H), 7.51 (m, 1H), 8.07 (bs, 2H), 8.50 (overlapping m, 2H).

***S*-2-Pyridyl nicotinothioate (S2).** In an oven-dried flask, 5.54 g (49.8 mmol) 2-mercaptopyridine and 9.02 g (50.7 mmol) nicotinoyl chloride hydrochloride were dissolved in 40 mL of anhydrous THF and stirred at room temperature under a nitrogen atmosphere for 2 h. The yellow solid was collected on a Büchner funnel and washed with hexanes until the filtrate was clear. The solid was slowly added to a biphasic mixture of 200 mL saturated $NaHCO_3$ and 200 mL ethyl acetate; the mixture was stirred until bubbling subsided. The product was extracted with ethyl acetate (~1.5 L) and the organics were dried over Na_2SO_4. Solvent was removed by rotary evaporation to afford a yellow oil, which was isolated as a solid with the addition of a large excess of hexanes. The yellow solid was collected on a frit and washed with hexanes until the filtrate was clear to afford 4.05 g (37.6% yield) of the title compound. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (m, 1H), 7.45 (m, 1H), 7.73 (m, 1H), 7.81 (m, 1H), 8.26 (m, 1H), 8.69 (m, 1H), 8.83 (m, 1H), 9.23 (m, 1H).

5-Phenyldipyrromethane (S3). A solution of 40 mL pyrrole (38 g, 580 mmol) and 1.3 mL benzaldehyde (1.4 g, 13 mmol) were bubbled with N_2 for 10 min to degas the solution. Then, 280 mg $InCl_3$ (1.3 mmol) was added and the tan suspension was stirred at room temperature for 1.5 h. Sodium hydroxide beads (2.5 g, 63 mmol) were added and the suspension was stirred for an additional 45 min at room temperature. The crude reaction mixture was then filtered using a Büchner funnel. The flask and solids were rinsed with acetone and the filtrated was brought to dryness. The crude reaction mixture was purified on a silica gel column packed with hexanes and the product was eluted using 3:1 CH_2Cl_2:hexanes. Solvent was removed to afford 2.57 g (88.9% yield) of the title compound as a yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.49 (s, 1H), 5.92 (m, 2H), 6.16 (m, 2H), 6.70 (m, 2H), 7.21–7.28 (m, 3H), 7.30–7.34 (m, 2H), 7.94 (bs, 2H).

***S*-2-Pyridyl benzoylthioate (S4).** In an oven-dried flask, 5.52 g (49.7 mmol) 2-mercaptopyridine was dissolved in 40 mL anhydrous THF under a nitrogen atmosphere. Then 7.6 mL benzoyl chloride (9.2 g, 65 mmol) was added and the solution was stirred at room temperature for 2 h. The yellow solid was collected on a Büchner funnel and washed with hexanes until the filtrate was clear. The solid was slowly added to a biphasic mixture

of 200 mL saturated $NaHCO_3$ and 200 mL Et_2O; the mixture was stirred until bubbling subsided. The product was extracted with Et_2O (~1.5 L) and the organics were dried over Na_2SO_4. Solvent was removed by rotary evaporation to afford a yellow oil, which was isolated as a solid with the addition of a large excess of hexanes. The yellow solid was collected on a frit and washed with hexanes until the filtrate was clear to afford 6.06 g (56.6% yield) of the title compound. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (m, 1H), 7.49 (m, 2H), 7.62 (m, 1H), 7.73 (m, 1H), 7.79 (m, 1H), 8.02 (m, 2H), 8.68 (m, 1H).

5-(4-Methoxycarbonylphenyl)dipyrromethane (4) A solution of 2.1 g methyl 4-formylbenzoate (13 mmol) in 45 mL pyrrole (44 g, 650 mmol) was bubbled with argon for 10 minutes. Then 285 mg $InCl_3$ (1.3 mmol) was added and the mixture was stirred at room temperature for 1.5 hours. Sodium hydroxide beads (1.5 g, 38 mmol) were added and the suspension was stirred for an additional 45 minutes. The crude reaction mixture was then filtered using a Büchner funnel. The flask and solids were rinsed with acetone; the filtrated was brought to dryness and residual pyrrole was removed by triturating with hexanes to afford a tan solid. The residue was dissolved in MeOH using a hot water bath to fully dissolve the material and the product was allowed to crystallize overnight at room temperature. Solid material was collected on a frit, washed with hexanes and a minimal amount of EtOH, and dried under vacuum to afford 2.30 g (63% yield) of the title compound as a tan solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.91 (s, 3H), 5.53 (s, 1H), 5.89 (m, 2H), 6.16 (m, 2H), 6.72 (m, 2H), 7.29 (m, 2H), 7.96 (overlapping bs, 2H), 7.98 (overlapping m, 2H).

***S*-2-Pyridyl isonicotinothioate (5).** In an oven-dried flask, 11.15 g (100.3 mmol) 2-mercaptopyridine and 17.86 g isonicotinoyl chloride hydrochloride (100.3 mmol) were dissolved in 100 mL anhydrous THF and stirred at room temperature under an argon atmosphere for 2.5 h. The yellow solid was collected on a Büchner funnel and washed with hexanes until the filtrate was clear. The solid was slowly added to a biphasic mixture of 200 mL saturated $NaHCO_3$ and 200 mL Et_2O; the mixture was stirred until bubbling subsided. The product was extracted with Et_2O and the organics were dried over Na_2SO_4. Solvent was removed by rotary evaporation to afford a pale yellow solid; the solid was collected on a frit and washed with hexanes until the filtrate was clear to afford 13.00 g (59.93% yield) of the title compound. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (m, 1H), 7.72 (m, 1H), 7.80 (m, 2H), 7.82 (m, 1H), 8.69 (m, 1H), 8.84 (m, 2H).

1-Isonicotinoyl-5-(4-pyridyl)dipyrromethane (7). In an oven-dried flask, 1.51 g 5-(4-pyridyl)dipyrromethane (**12**) (6.76 mmol) was dissolved in 15 mL anhydrous THF under an argon atmosphere to afford a tan solution. Then 17 mL EtMgBr (1 M solution in THF) was slowly added and the resultant dark brown solution was stirred at room temperature for 10 min. The solution was then cooled to –78 °C in a dry ice/acetone bath and 1.48 g *S*-2-pyridyl isonicotinothioate (**5**) (6.84 mmol) was added as a solid in one portion; the

resultant mixture was stirred at –78 °C for 10 min. The solution was then warmed to room temperature and stirred for an additional 3 h. Saturated NH_4Cl was added and the product was extracted with EtOAc; the combined organics were washed with water and brine then dried over Na_2SO_4. Solvent was removed by rotary evaporation to afford a brown oil. The crude reaction mixture was loaded onto a silica gel column packed with EtOAc. The product (second band, turns yellow-orange upon Br_2 staining on TLC) was eluted with 100% EtOAc. After solvent removal, the oily brown residue was dissolved in a minimal amount of EtOAc and subsequently precipitated with a large excess of hexanes and the resultant solid was collected on a frit and washed with hexanes to afford 0.66 g (30% yield) of the title compound as a tan solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.53 (s, 1H), 5.98 (m, 1H), 6.08 (m, 1H), 6.21 (m, 1H), 6.78 (m, 1H), 6.82 (m, 1H), 7.15 (m, 2H), 7.64 (m, 2H), 8.09 (bs, 1H), 8.59 (m, 2H), 8.78 (m, 2H), 9.45 (bs, 1H).

1-Nicotinoyl-5-(3-pyridyl)dipyrromethane (8). In an oven-dried flask, 0.65 g 5-(3-pyridyl)dipyrromethane (**S1**) (2.9 mmol) was dissolved in 10 mL anhydrous THF under a nitrogen atmosphere to afford a tan solution. Then 8 mL EtMgBr (1 M solution in THF) was slowly added and the resultant dark brown solution was stirred at room temperature for 10 min. The solution was then cooled to –78 °C in a dry ice/acetone bath, 0.69 g *S*-2-pyridyl nicotinothioate (**S2**) (3.2 mmol) was added as a solid in one portion, and the resultant mixture was stirred at –78 °C for 30 min. The solution was then warmed to room temperature and stirred for an additional 2 h. Saturated $(NH_4)_2SO_4$ was added and the product was extracted with EtOAc (x3); the combined organics were washed with water and brine then dried over Na_2SO_4. Solvent was removed by rotary evaporation to afford a brown oil. The crude reaction mixture was loaded onto a silica gel column packed with EtOAc. The product (second fraction, turns yellow-orange upon Br_2 staining on TLC) was eluted with 100% EtOAc. After solvent removal, the oily brown residue was dissolved in a minimal amount of EtOAc and subsequently precipitated with a large excess of hexanes and the resultant solid was collected on a frit and washed with hexanes to afford 0.58 g (61% yield) of the title compound as a tan solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.57 (s, 1H), 5.96 (m, 1H), 6.09 (m, 1H), 6.19 (m, 1H), 6.77 (m, 1H), 6.83 (m, 1H), 7.27 (m, 1H), 7.43 (m, 1H), 7.53 (m, 1H), 8.10 (m, 1H), 8.34 (bs, 1H), 8.50 (m, 1H), 8.53 (m, 1H), 8.78 (m, 1H), 9.06 (m, 1H), 9.71 (bs, 1H).

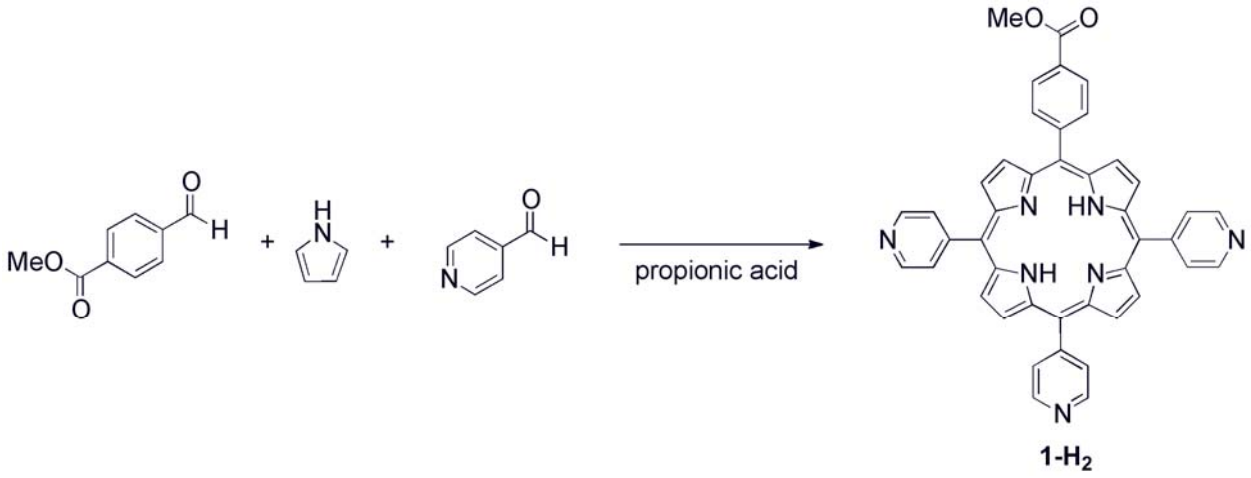
1-Benzoyl-5-phenyldipyrromethane (9). In an oven-dried flask, 0.80 g 5-phenyldipyrromethane (**S3**) (3.6 mmol) was dissolved in 10 mL anhydrous THF under a nitrogen atmosphere to afford a tan solution. Then 8 mL EtMgBr (1 M solution in THF) was slowly added and the resultant dark brown solution was stirred at room temperature for 10 min. The solution was then cooled to –78 °C in a dry ice/acetone bath, 0.82 g *S*-2-pyridyl benzoylthioate (**S4**) (3.8 mmol) was added as a solid in one portion, and the resultant mixture was stirred at –78 °C for 40 min. The solution was then warmed to room temperature and stirred for an additional 3.5 h. Saturated $(NH_4)SO_4$ was added and the

product was extracted with EtOAc (x3); the combined organics were washed with water and brine then dried over Na_2SO_4. Solvent was removed by rotary evaporation to afford a brown oil. The crude reaction mixture was loaded onto a silica gel column packed with CH_2Cl_2, which was also used as the initial eluent to remove unreacted dipyrromethane (first spot by TLC in 100% CH_2Cl_2, turns pink upon Br_2 staining). The eluent was then switched to 2:3 ethyl acetate:CH_2Cl_2 to elute the product (turns yellow-orange upon Br_2 staining). After solvent removal, the oily residue was dissolved in a minimal amount of CH_2Cl_2 and subsequently precipitated with a large excess of hexanes and the resultant solid was collected on a frit and washed with hexanes to afford 0.13 g (11% yield) of the title compound as a brown solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.56 (s, 1H), 5.99 (m, 1H), 6.09 (m, 1H), 6.17 (m, 1H), 6.69 (m, 1H), 6.81 (m, 1H), 7.20–7.23 (m, 2H), 7.28–7.34 (m, 3H), 7.43–7.48 (m, 3H), 7.80–7.83 (m, 2H), 8.19 (bs, 1H), 9.74 (bs, 1H).

1,9-Dibenzoyl-5-phenyldipyrromethane (10). In an oven-dried flask, 0.41 g 5-phenyldipyrromethane (**S3**) (1.8 mmol) was dissolved in 40 mL toluene under a nitrogen atmosphere to afford a tan solution. Then 9 mL EtMgBr (1 M solution in THF) was slowly added and the resultant amber solution was stirred at room temperature for 20 min. Then 0.7 mL benzoyl chloride (0.85 g, 6 mmol) was added and the resultant mixture was stirred for an additional 1 h at room temperature. Saturated $(NH_4)SO_4$ was added and the product was extracted with EtOAc (x3); the combined organics were washed with water and brine then dried over Na_2SO_4. Solvent was removed by rotary evaporation to afford a brown oil. After the addition of a large excess of hexanes, a brown solid was obtained, collected on a frit, and washed with hexanes, affording 0.16 g (20% yield) of the title product. The compound used without further purification as only one spot was visible by TLC (100% CH_2Cl_2) and the ^{1}H NMR spectrum indicated a nearly pure product. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.66 (s, 1H), 6.04 (m, 2H), 6.68 (m, 2H), 7.40–7.47 (m, 9H), 7.78–7.44 (m, 6H), 10.63 (bs, 2H).

5-(4-Pyridyl)dipyrromethane (12). A solution of 21 mL pyrrole (20 g, 300 mmol) and 1.9 mL 4-pyridinecarboxaldehyde (2.2 g, 20 mmol) were heated at 85 °C for 15 h. Solvent was removed by rotary evaporation. The crude reaction mixture was loaded onto a silica gel column packed with ethyl acetate. The product was eluted with 100% EtOAc as the second band (orange-red). After solvent removal, the residue was dissolved in a minimal amount of EtOAc and the product was precipitated with a large excess of hexanes and collected on a frit. The collected orange-red solid was rinsed with hexanes and dried under vacuum to afford 2.27 g (51% yield) of the title compound. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.46 (s, 1H), 5.90 (m, 2H), 6.17 (m, 2H), 6.74 (m, 2H), 7.13 (m, 2H), 8.06 (bs, 2H), 8.52 (m, 2H).

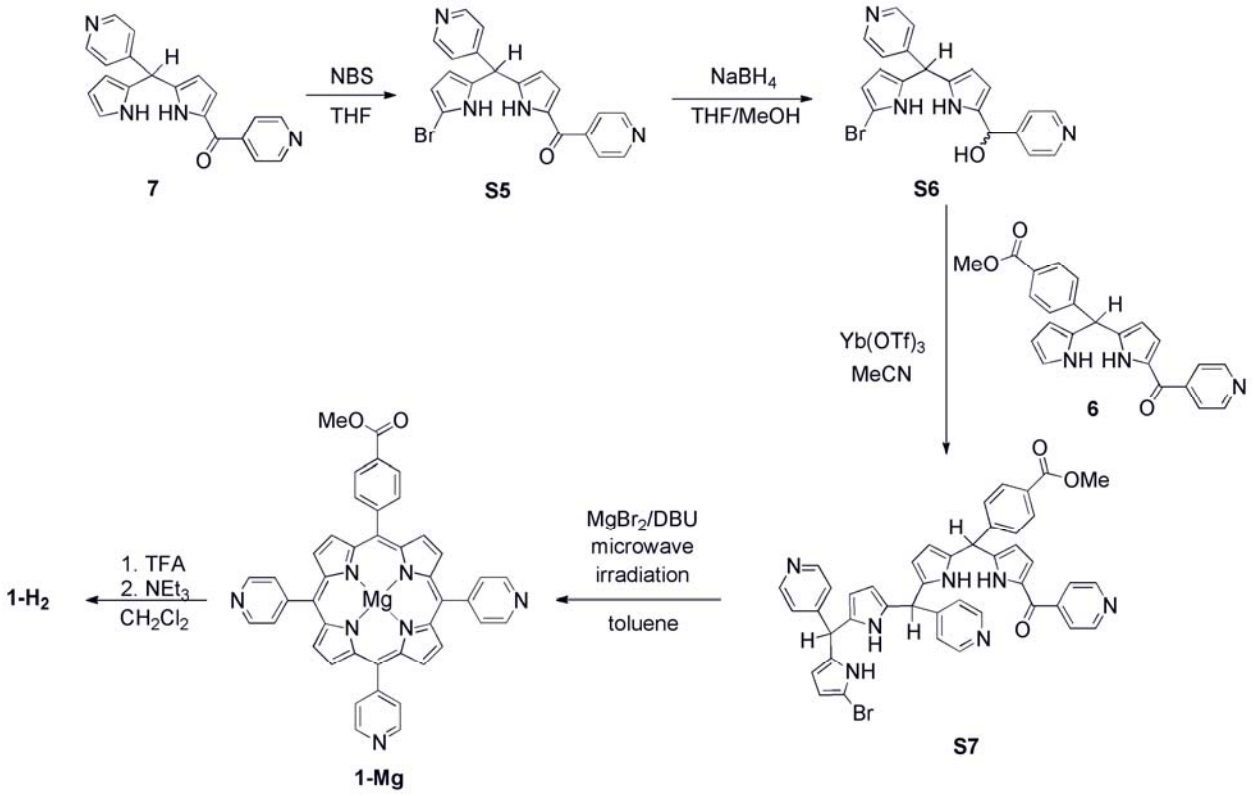
Statistical Synthesis of 1-H_2



Scheme S1. Adler-Longo Synthesis of **1-H_2**.

In a 500 mL round bottom flask, 1.60 g methyl 4-formylbenzoate (9.75 mmol) and 2.7 mL 4-pyridinecarboxaldehyde (29 mmol) were dissolved 160 mL propionic acid and brought to reflux. Pyrrole (2.6 mL, 37 mmol) was added and the solution was refluxed for 1.5 h. Solvent was removed by rotary evaporation. The residue was dissolved in $CHCl_3$ and the organics were washed with saturated $NaHCO_3$ and dried over Na_2SO_4. Solvent was removed by rotary evaporation. The residue was purified on a silica column using CH_2Cl_2 → 1:1 CH_2Cl_2:EtOAc → EtOAc → 10% MeOH in EtOAc → 20% MeOH in EtOAc. The product was identified as the porphyrin that eluted with 20% MeOH in EtOAc; this material was further purified on a silica gel column using EtOAc → 5% MeOH in EtOAc → 10% MeOH in EtOAc as the eluent. The product was then filtered through a short (~ 3 inch) plug of silica gel with EtOAc. After removing the solvent, the residue was dissolved in a minimal amount of CH_2Cl_2 and subsequently precipitated with a large excess of hexanes. The purple solid was collected on a frit, washed with EtOH, and dried under vacuum to afford 225 mg (3.9%) of the product.

Rational Synthesis of 1-H_2



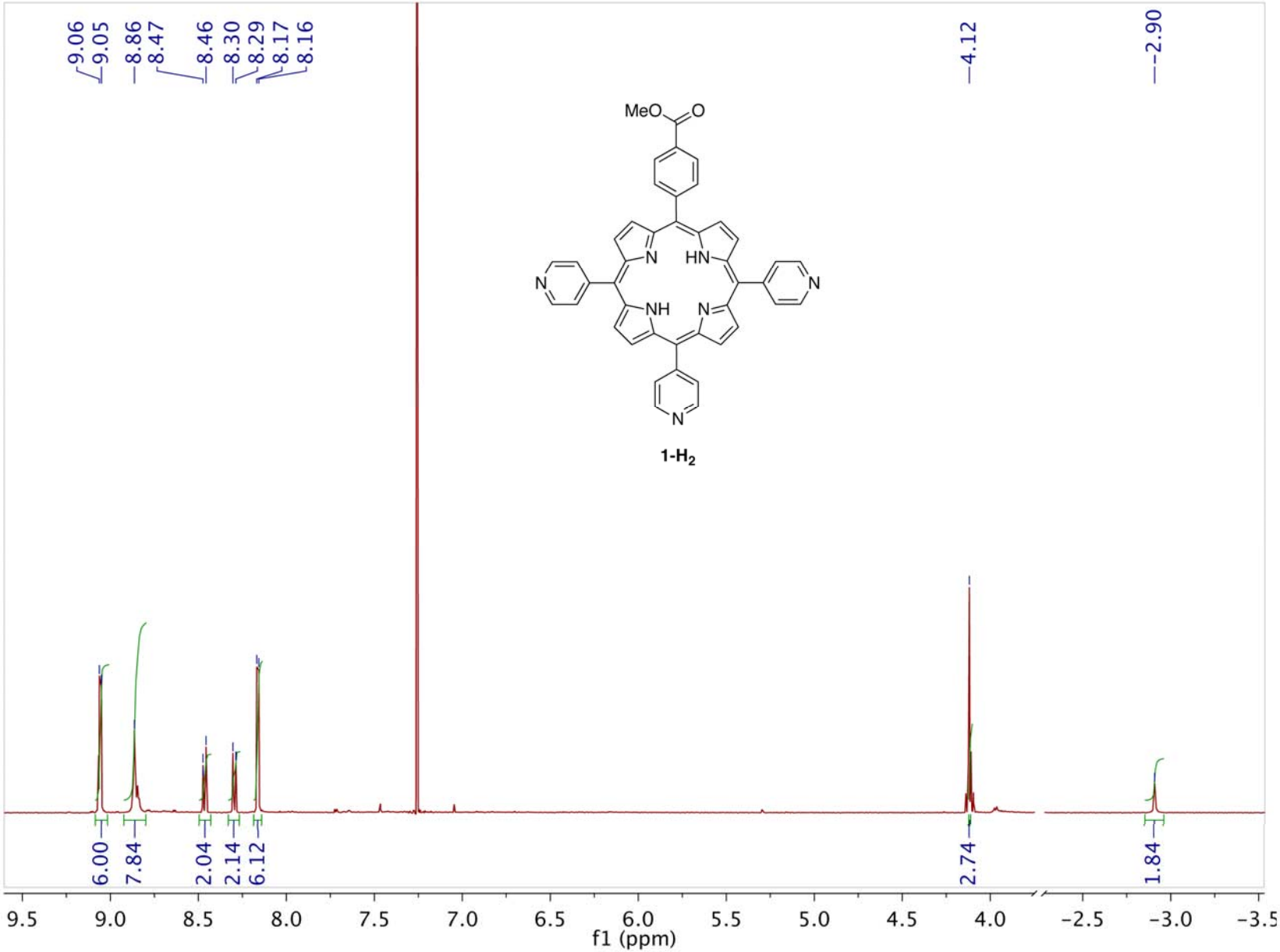
Scheme S2. Rational Synthesis of **1-H_2**.

1-Bromo-9-isonicotinoyl-5-(4-pyridyl)dipyrromethane (S5). In an oven-dried flask, 125 mg 1-isonicotinoyl-5-(4-pyridyl)dipyrromethane (**7**) (0.38 mmol) was dissolved in 8 mL anhydrous THF under argon. The mixture was briefly heated with a heat gun to ensure that all of the solid material had dissolved. The solution was cooled to –78 °C in a dry ice/acetone bath and 70 mg *N*-bromosuccinimide (0.39 mmol) was added as a solid in several small portions. The resultant mixture was stirred at –78 °C for 1 h. After removing the bath, water (20 mL) and hexanes (20 mL) were added and the biphasic solution was stirred and allowed to warm to room temperature. The product was extracted with EtOAc and the combined organics were washed with water and brine then dried over K_2CO_3. Solvent was removed by rotary evaporation without heating. The crude material was filtered over a plug of silica with EtOAc to afford 134 mg (87% yield) of the title compound as a yellow solid. The product was stored at 4 °C protected from light. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.47 (s, 1H), 5.90 (m, 1H), 6.10 (m, 1H), 6.13 (m, 1H), 6.83 (m, 1H), 7.14 (m, 2H), 7.64 (m, 2H), 8.05 (bs, 1H), 8.61 (m, 2H), 8.79 (m, 2H), 9.43 (bs, 1H).

1-Bromo-15-(4-methoxycarbonylphenyl)-19-(isonicotinoyl)-5,10-bis(4-pyridyl)-bilane (S7). In an oven-dried flask, 50 mg 1-bromo-9-isonicotinoyl-5-(4-pyridyl)dipyrro-

methane (**S5**) (0.12 mmol) was dissolved in 7 mL anhydrous THF and 3 mL anhydrous MeOH under argon. Then, 166 mg $NaBH_4$ (4.4 mmol) was added as a solid in one portion and the resulting solution was stirred at room temperature for 45 min, protected from light. Saturated NH_4Cl was added to quench the excess $NaBH_4$ and the product was extracted with Et_2O; the combined organics were then washed with water and brine then dried over K_2CO_3 to afford a solution of the carbinol (**S6**). Since the carbinol is not very robust, the solution was concentrated to near-dryness without heating. The residue was dissolved in 2 mL anhydrous MeCN and 47 mg 1-isonicotinoyl-5-(4-methoxycarbonyl-phenyl)dipyrromethane (**6**) (0.12 mmol) and 39 mg $Yb(OTf)_3$ (0.06 mmol) were added; the mixture was stirred at room temperature for 30 min, protected from light. Over the course of the next 3.5 h, 666 mg $Yb(OTf)_3$ (1.07 mmol) was added in several portions. After 4 h of total reaction time, 700 mg $Yb(OTf)_3$ (1.13 mmol) was added in one portion and the mixture was stirred at room temperature overnight. The reaction mixture was neutralized with 0.8 mL NEt_3 (0.58 g, 5.7 mmol) and the product was extracted with EtOAc. The combined organics were washed with water and brine then dried over K_2CO_3. Solvent was removed by rotary evaporation without heating to afford the crude bilane **S7**. Due to the relatively clean conversion (as observed by TLC) to the bilane, the instability of the compound, and the high polarity of this species, the crude residue was used without further purification.

Bilane cyclization The crude bilane **S7** was dissolved in 3 mL anhydrous toluene and 0.2 mL DBU (0.2 g, 1.3 mmol) and the mixture was transferred to a 10 mL microwave tube and stirred for 5 min. Then 79 mg $MgBr_2$ (0.43 mmol) was added and the resultant suspension was placed in a microwave reactor and irradiated at 115 °C for 2 h. The reaction mixture was transferred to a flask, the black tar was dissolved in THF, and the solvent was removed by rotary evaporation. The residue was dissolved in a minimal amount of EtOAc and filtered through a plug of silica, using EtOAc to elute the fluorescent porphyrin material. The porphyrin was demetallated by dissolving the residue in 10 mL CH_2Cl_2 and adding 0.2 mL TFA (0.30 g, 2.6 mmol); the resulting green solution was stirred at room temperature for 30 min. Then 0.4 mL NEt_3 (0.29 g, 2.9 mmol) was added and the reaction mixture was washed with water and brine, dried over Na_2SO_4, and brought to dryness. The product was then purified on a silica gel column using EtOAc then 10% MeOH in EtOAc to afford 12 mg (15% yield based on the amount of **S5** used in the bilane synthesis) of**1-H$_2$**.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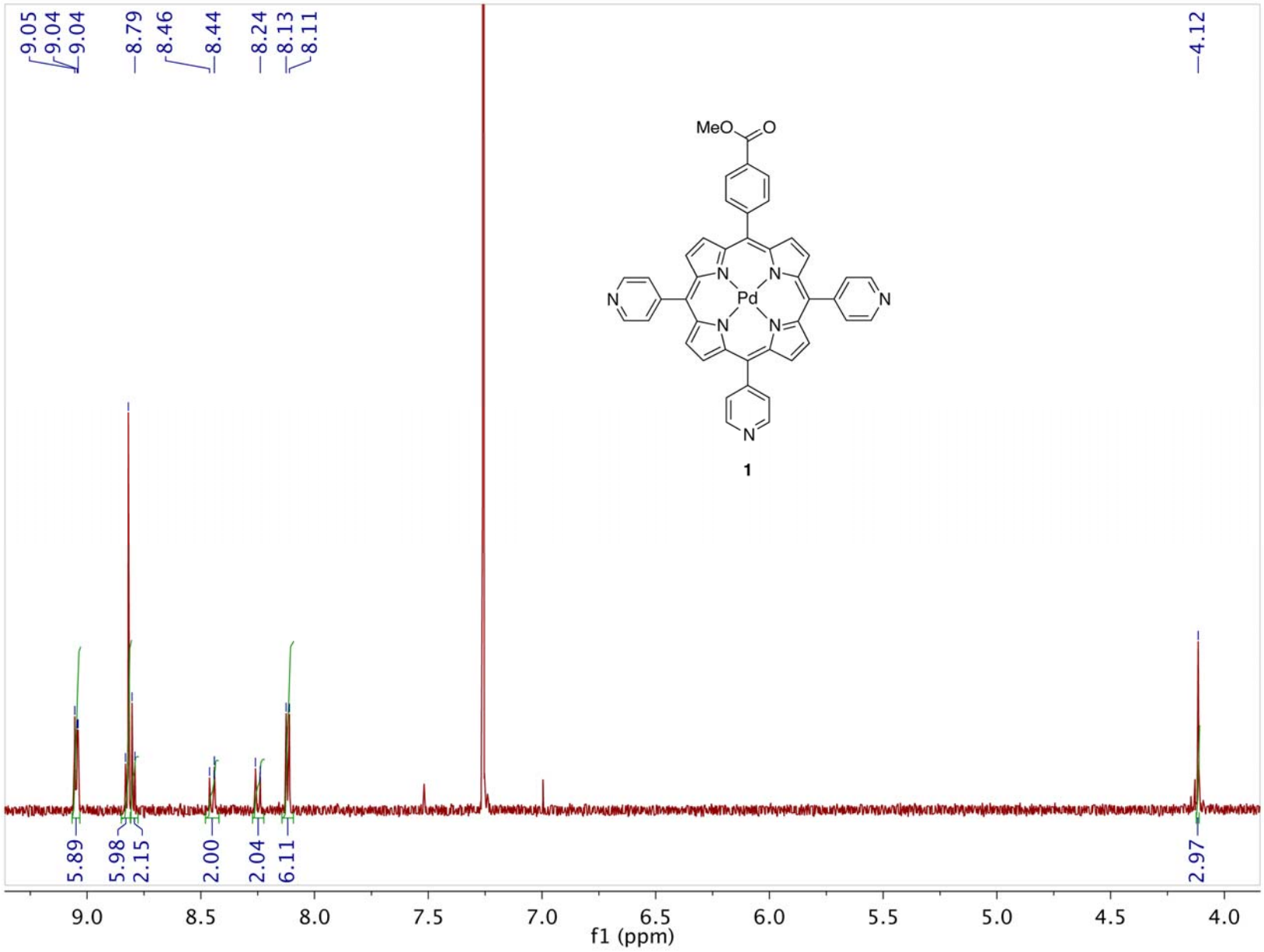
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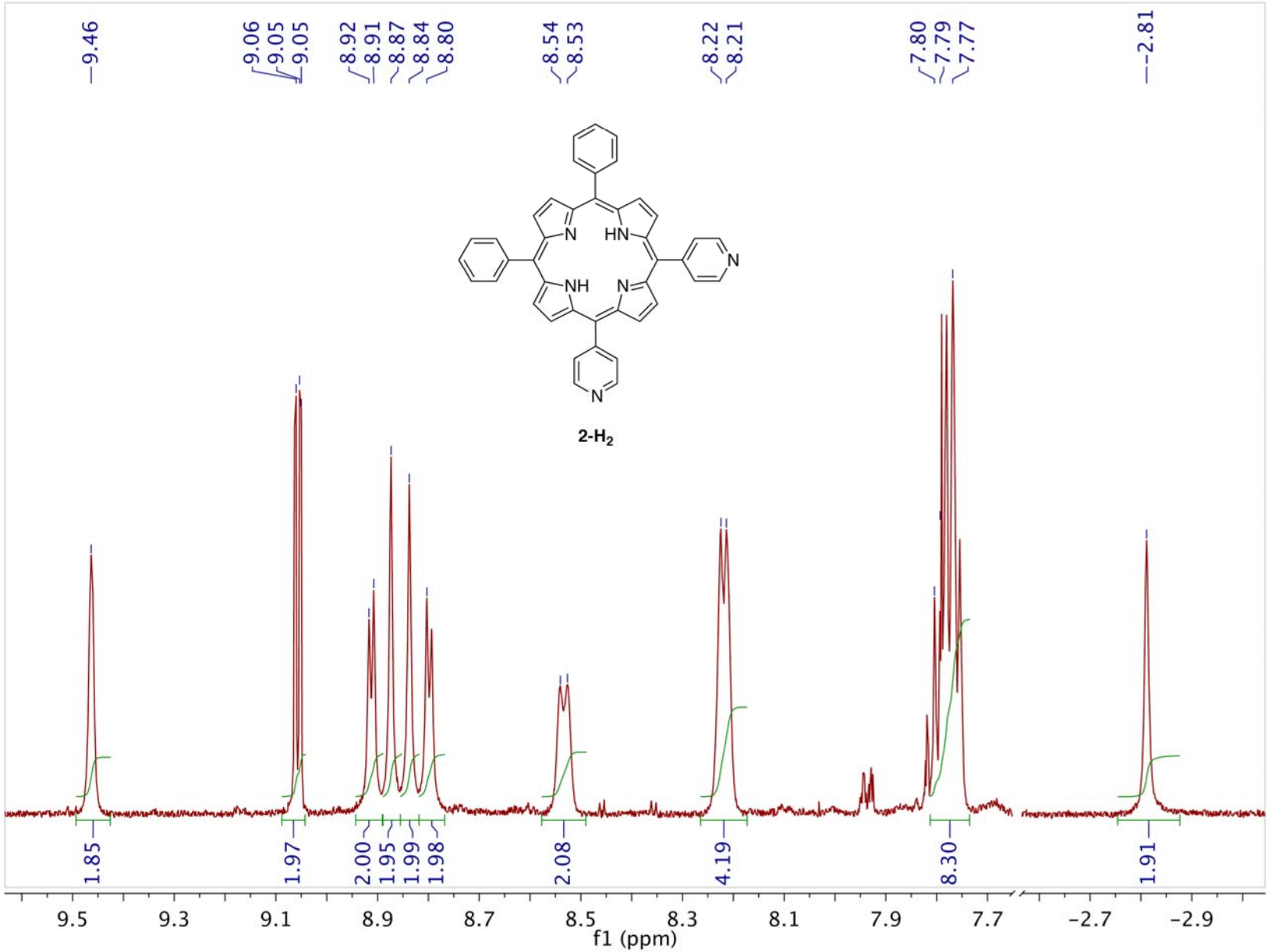
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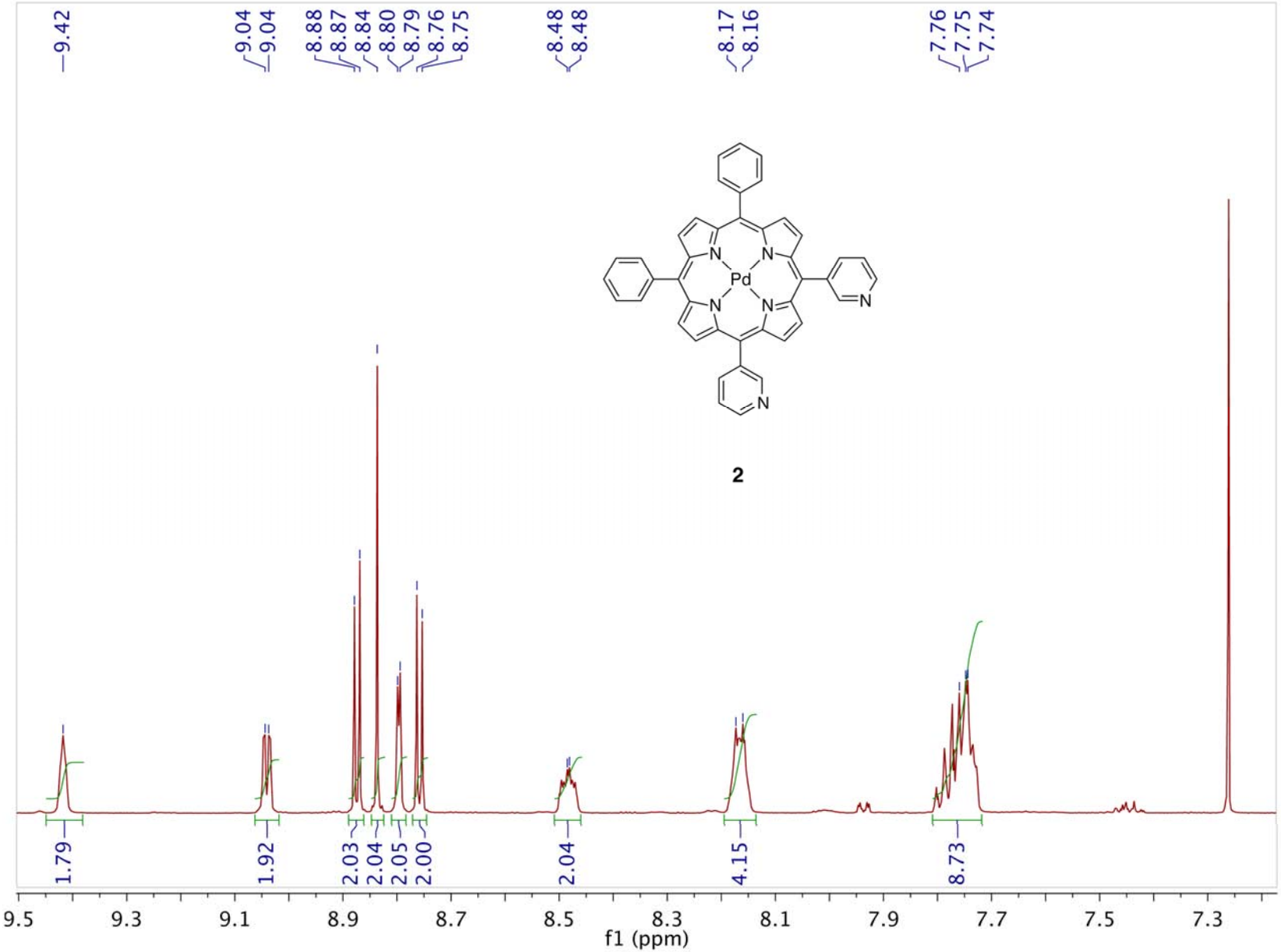
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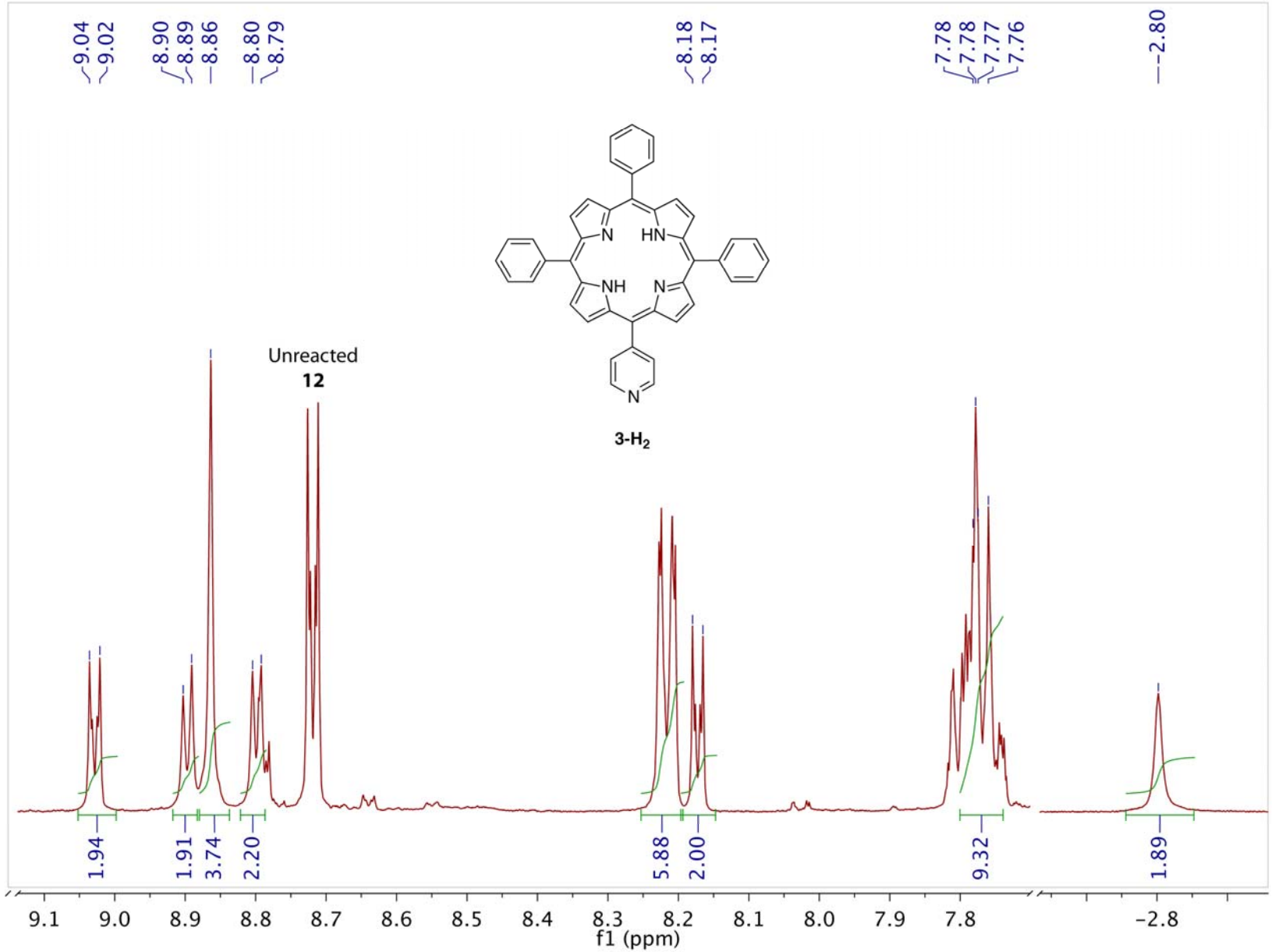
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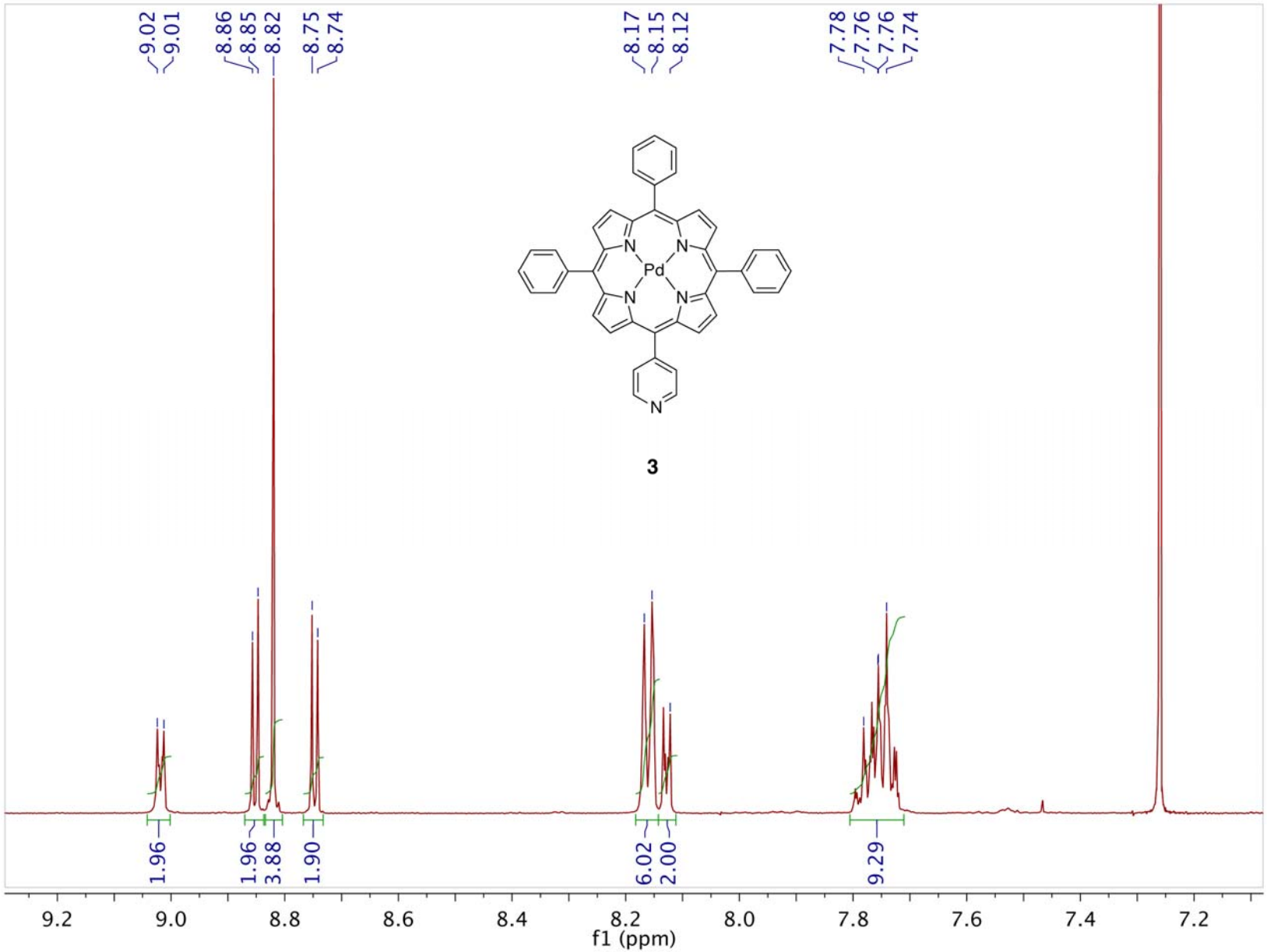
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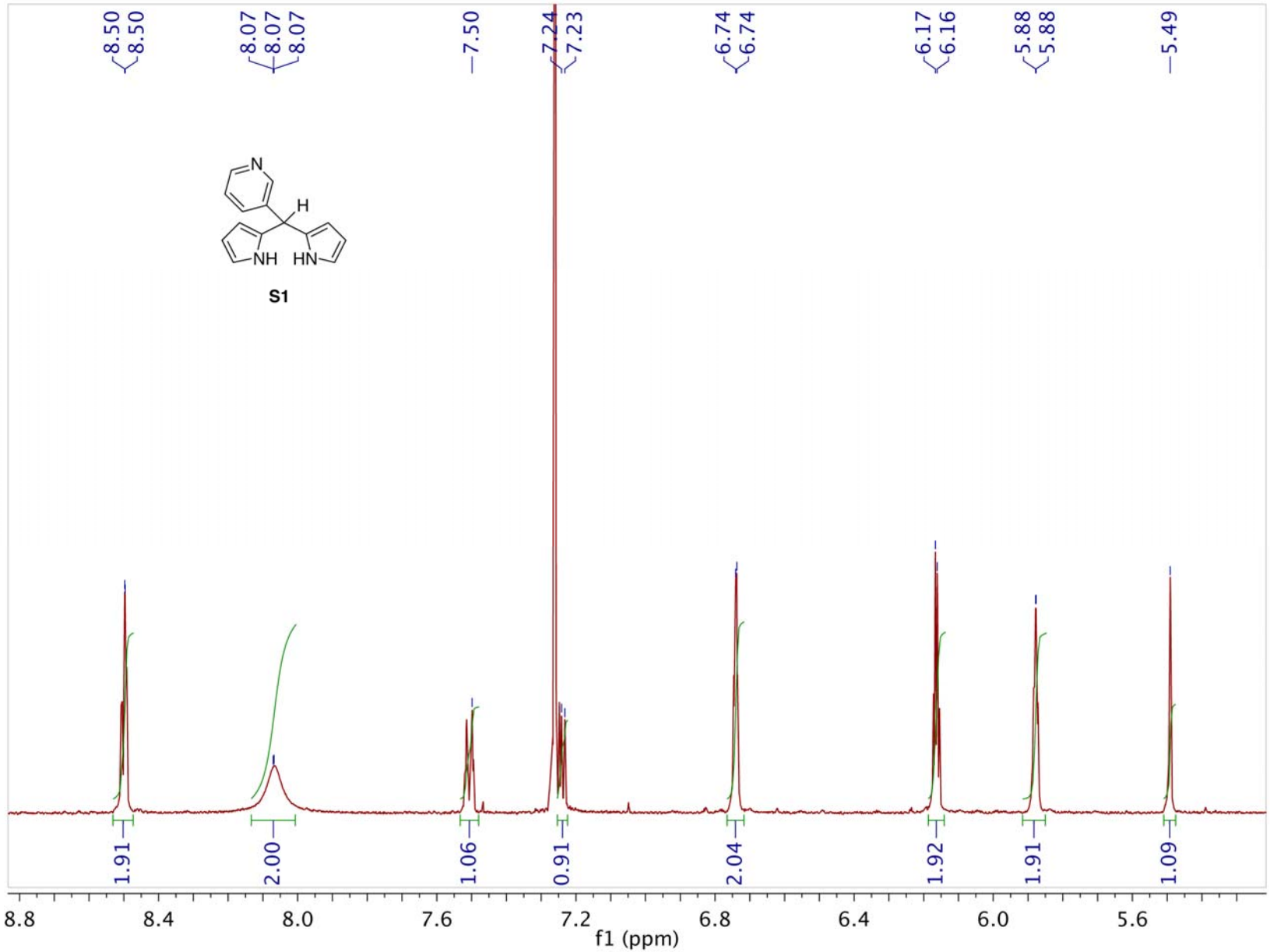
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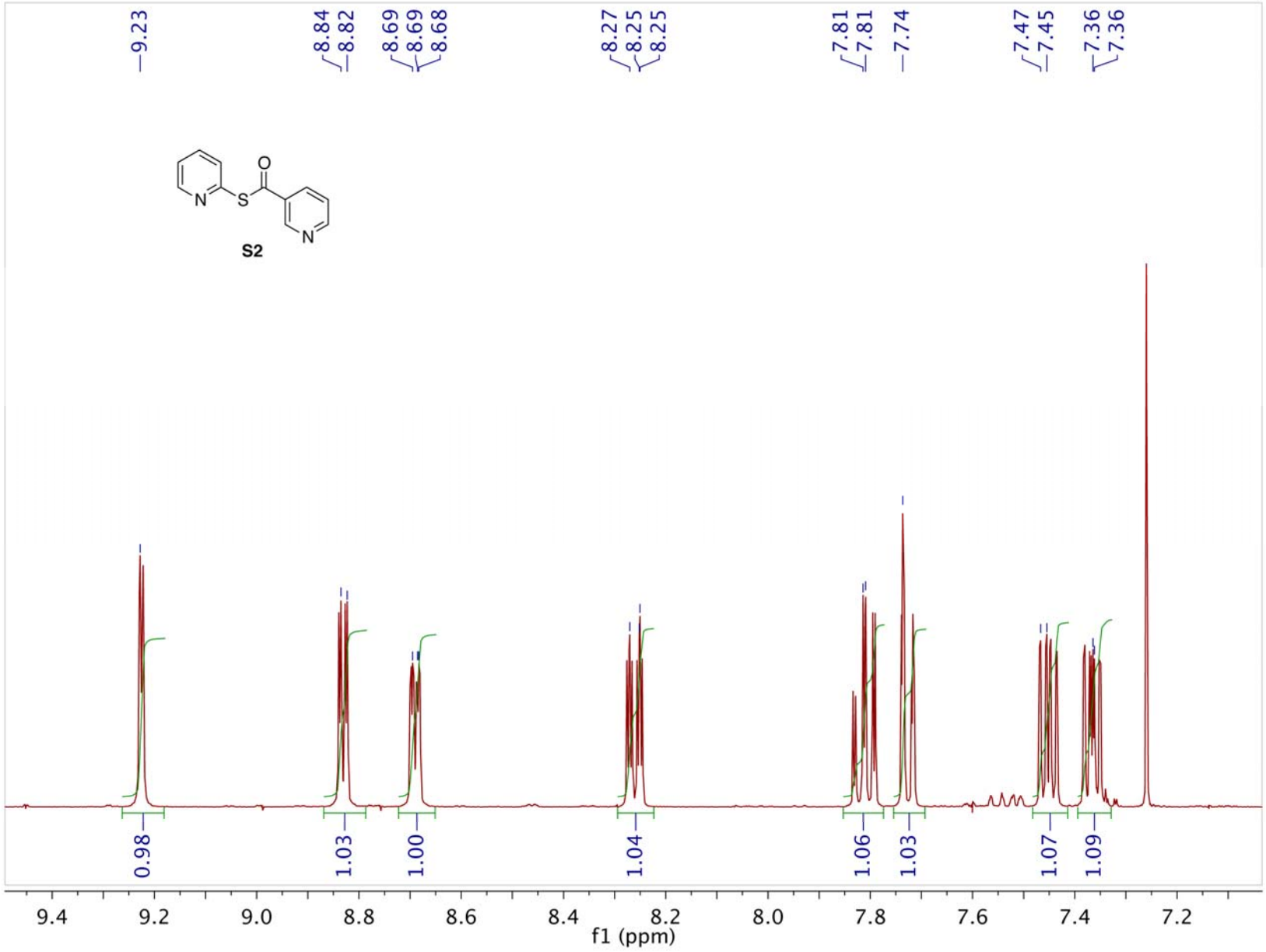
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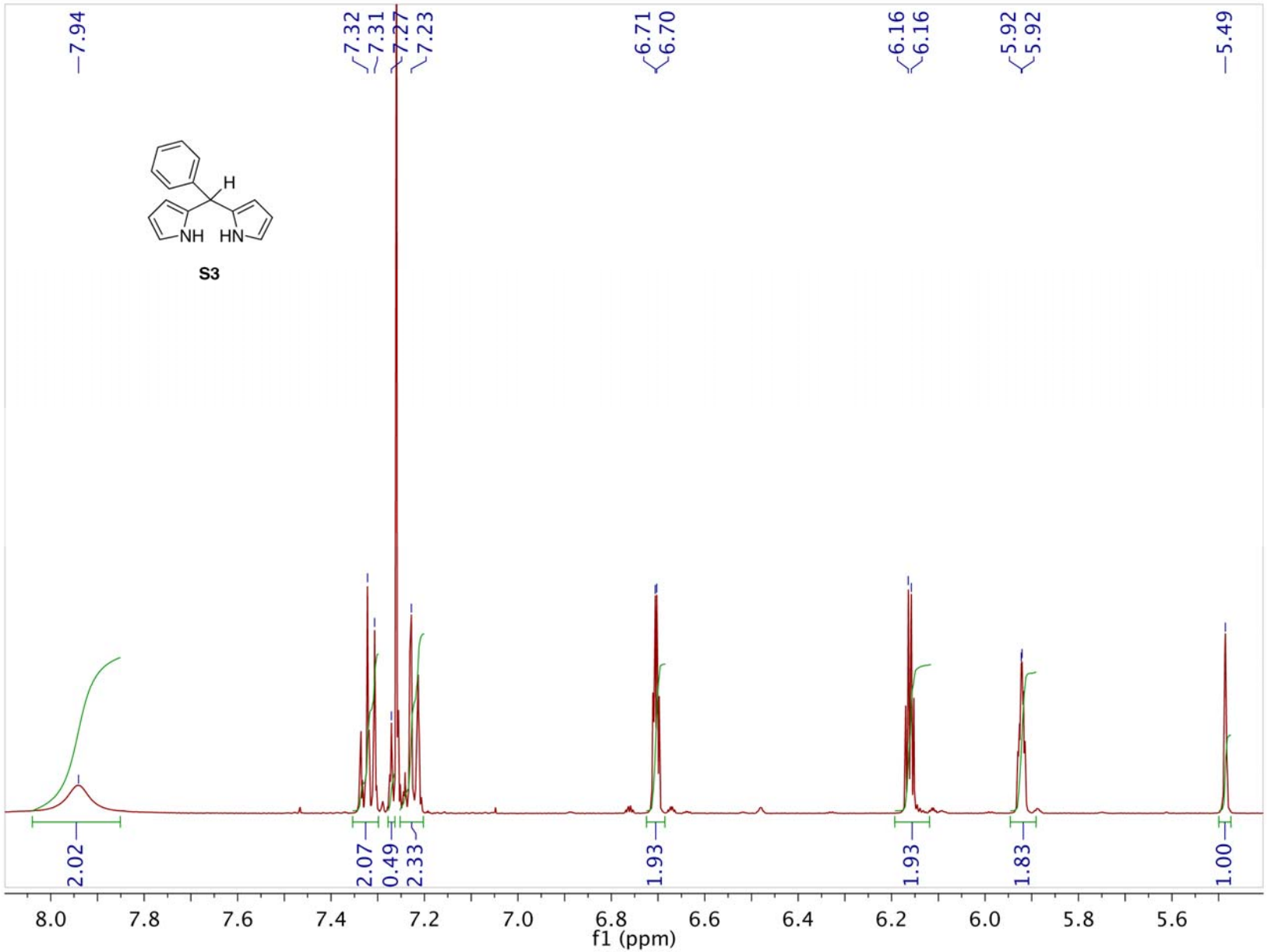
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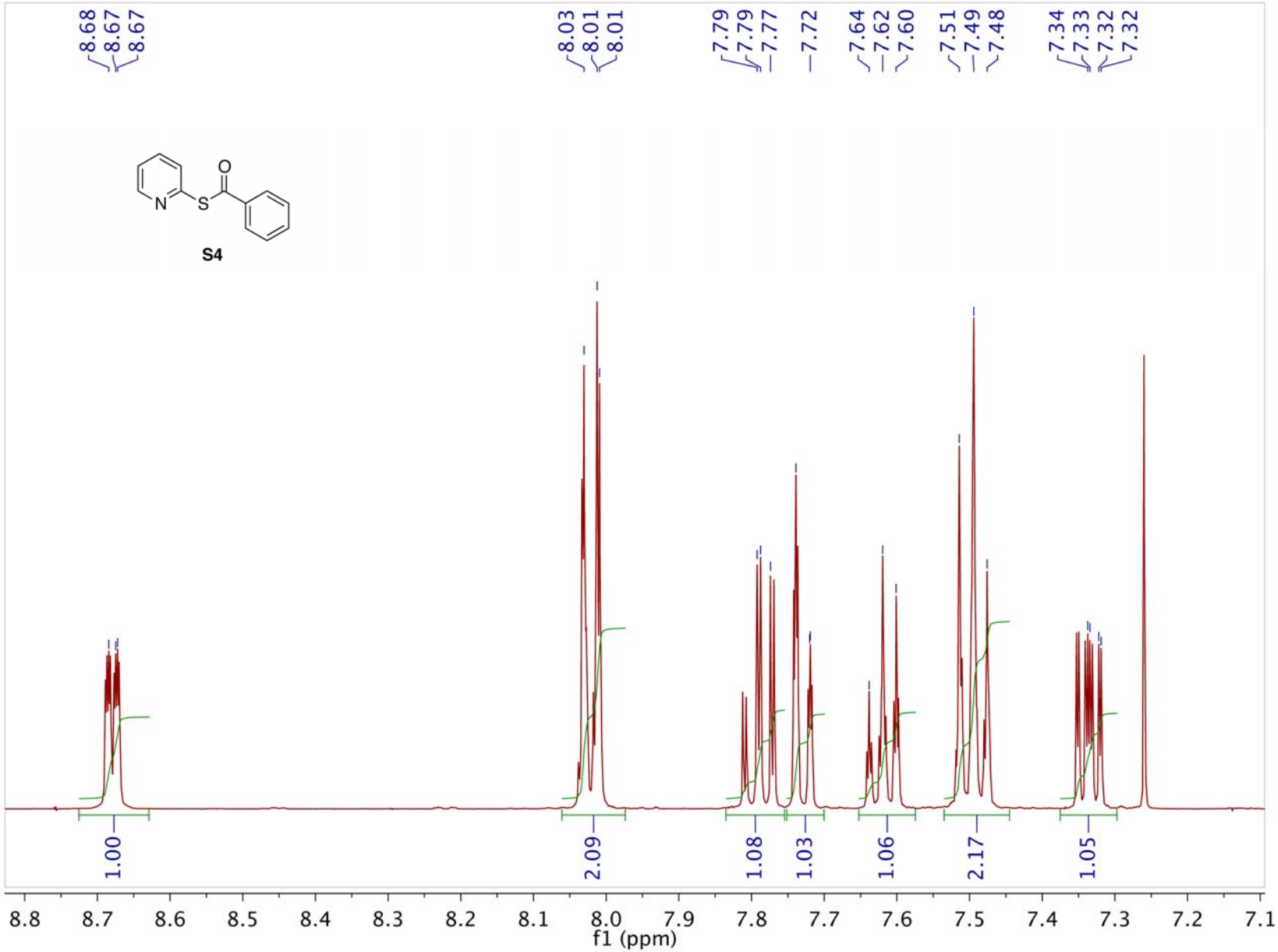
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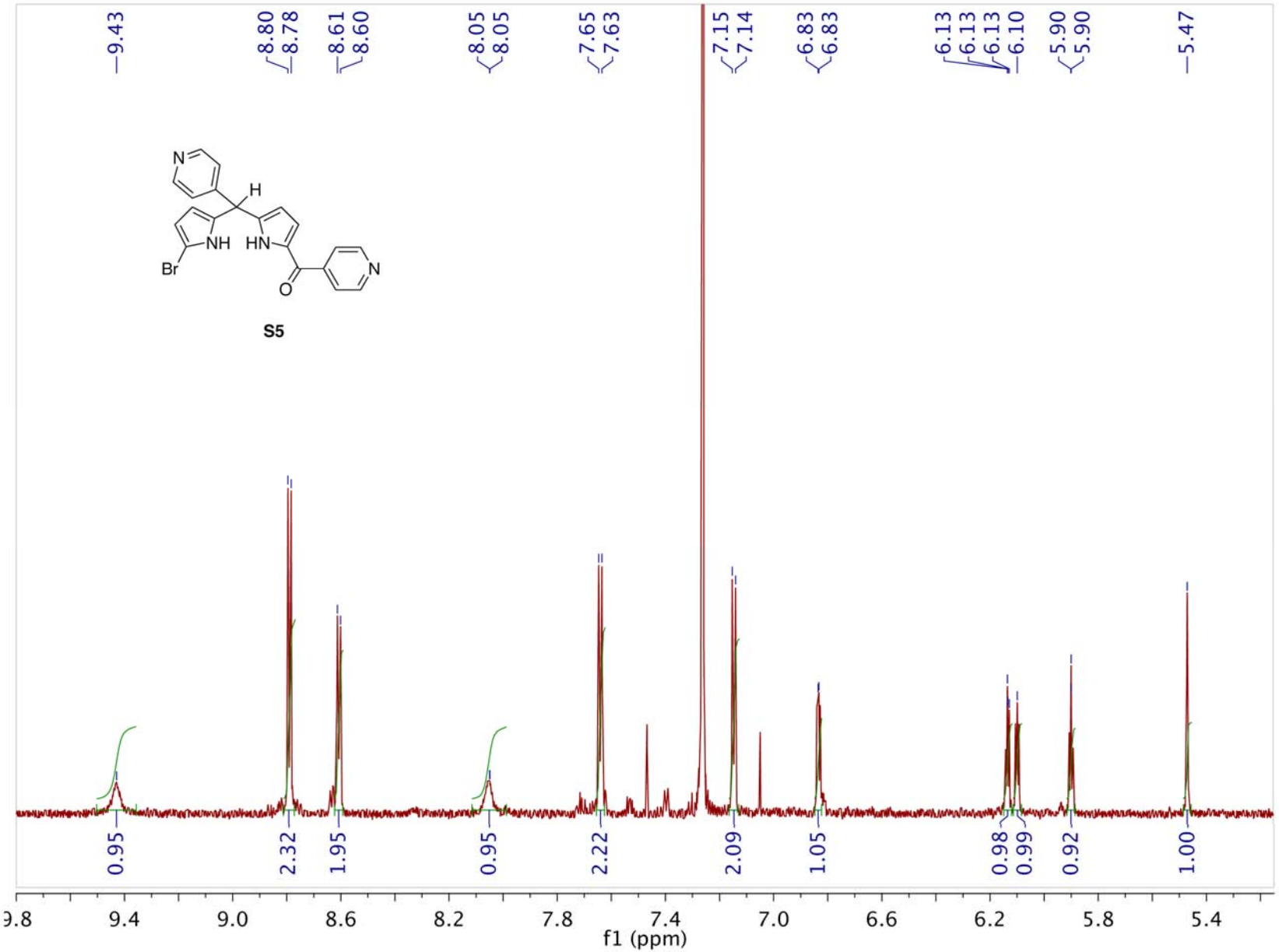
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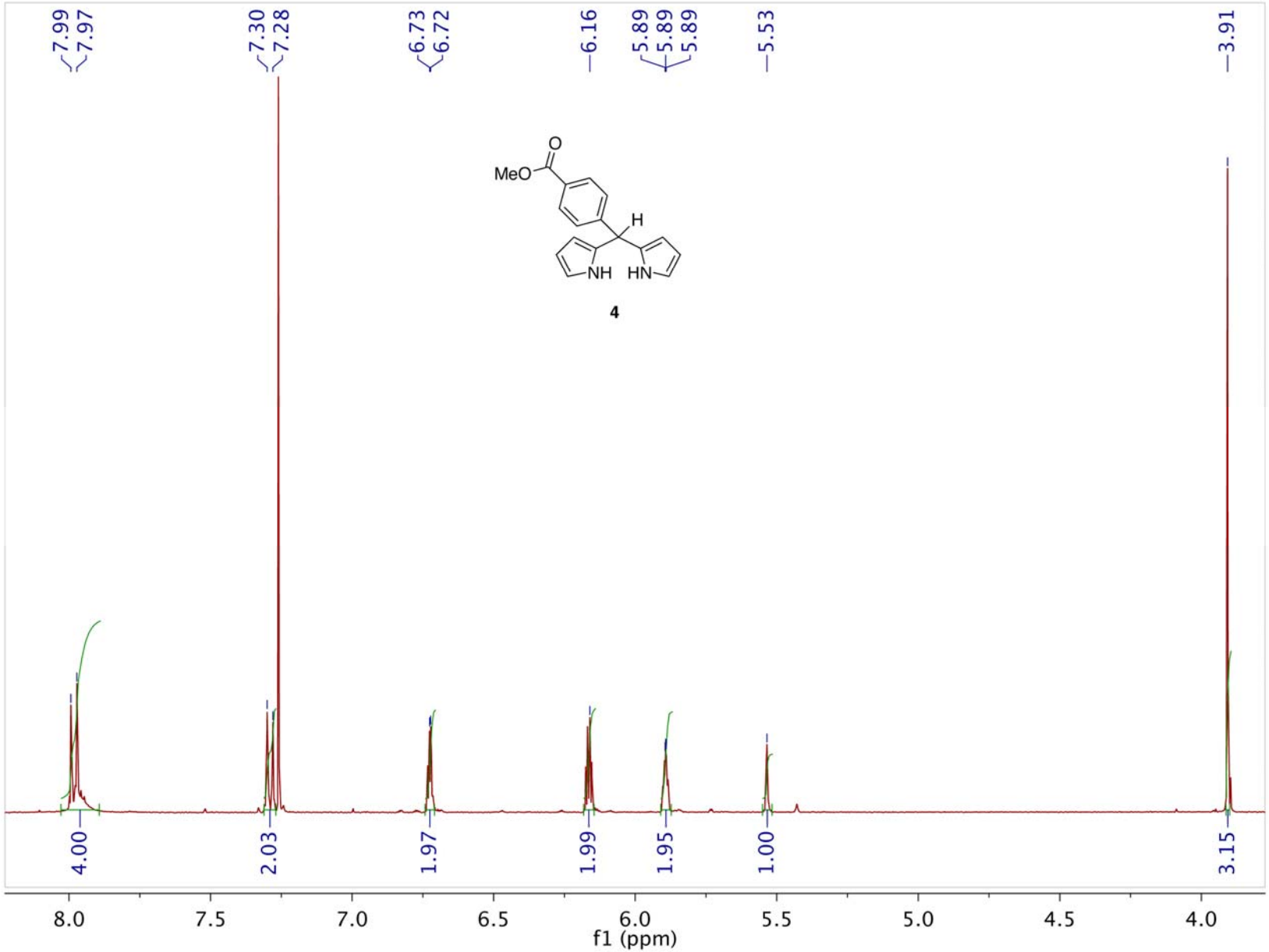
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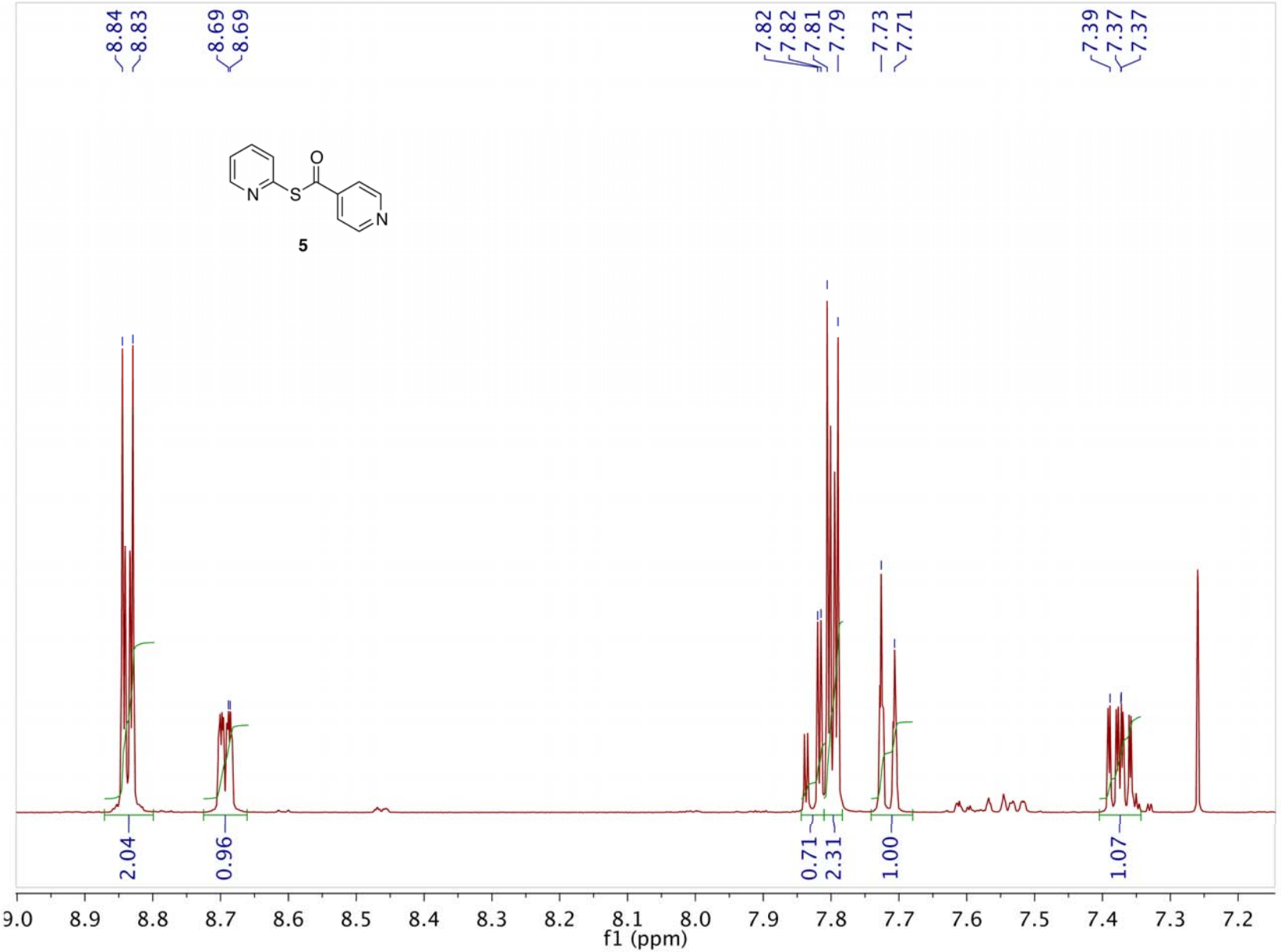
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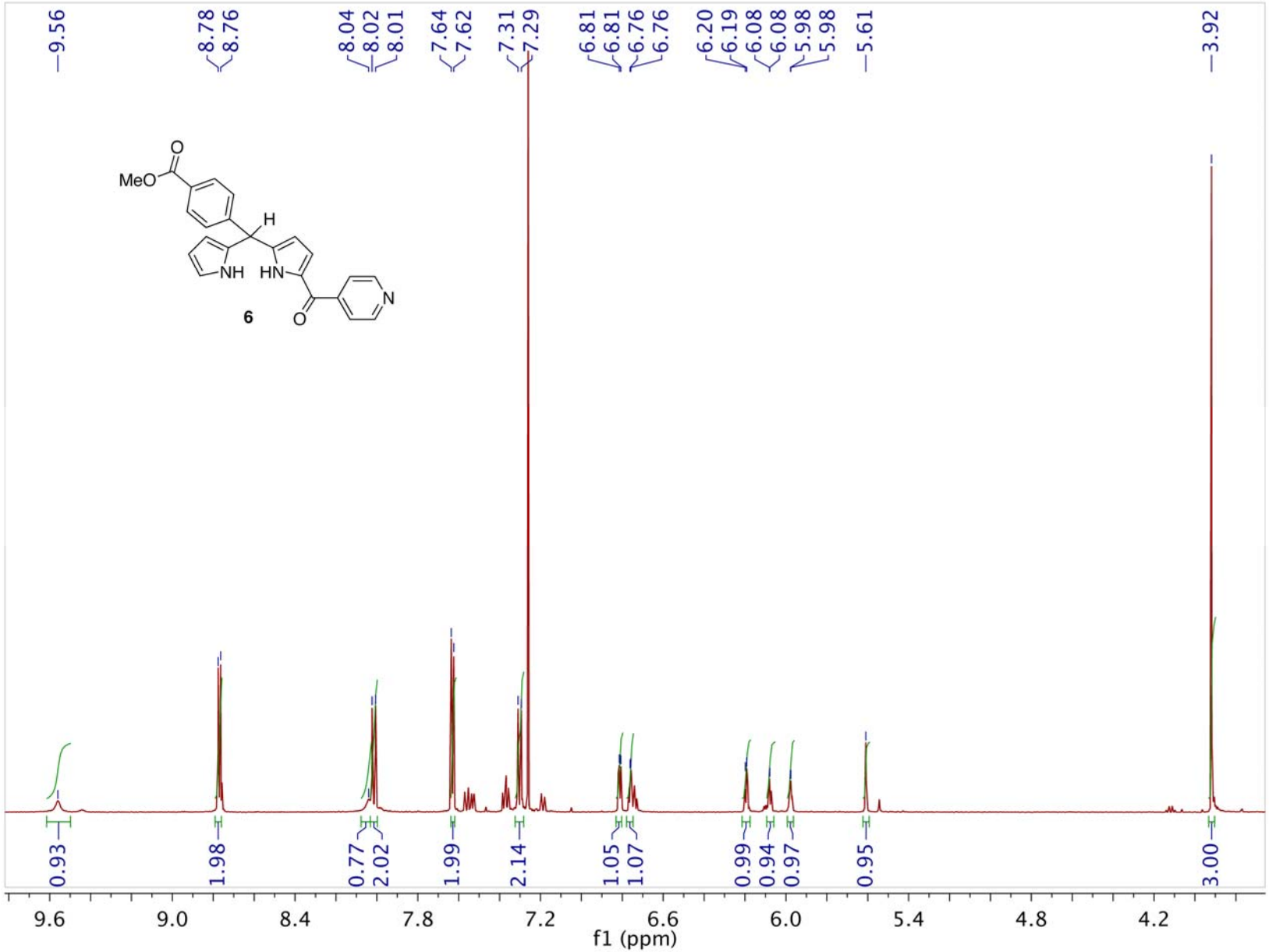
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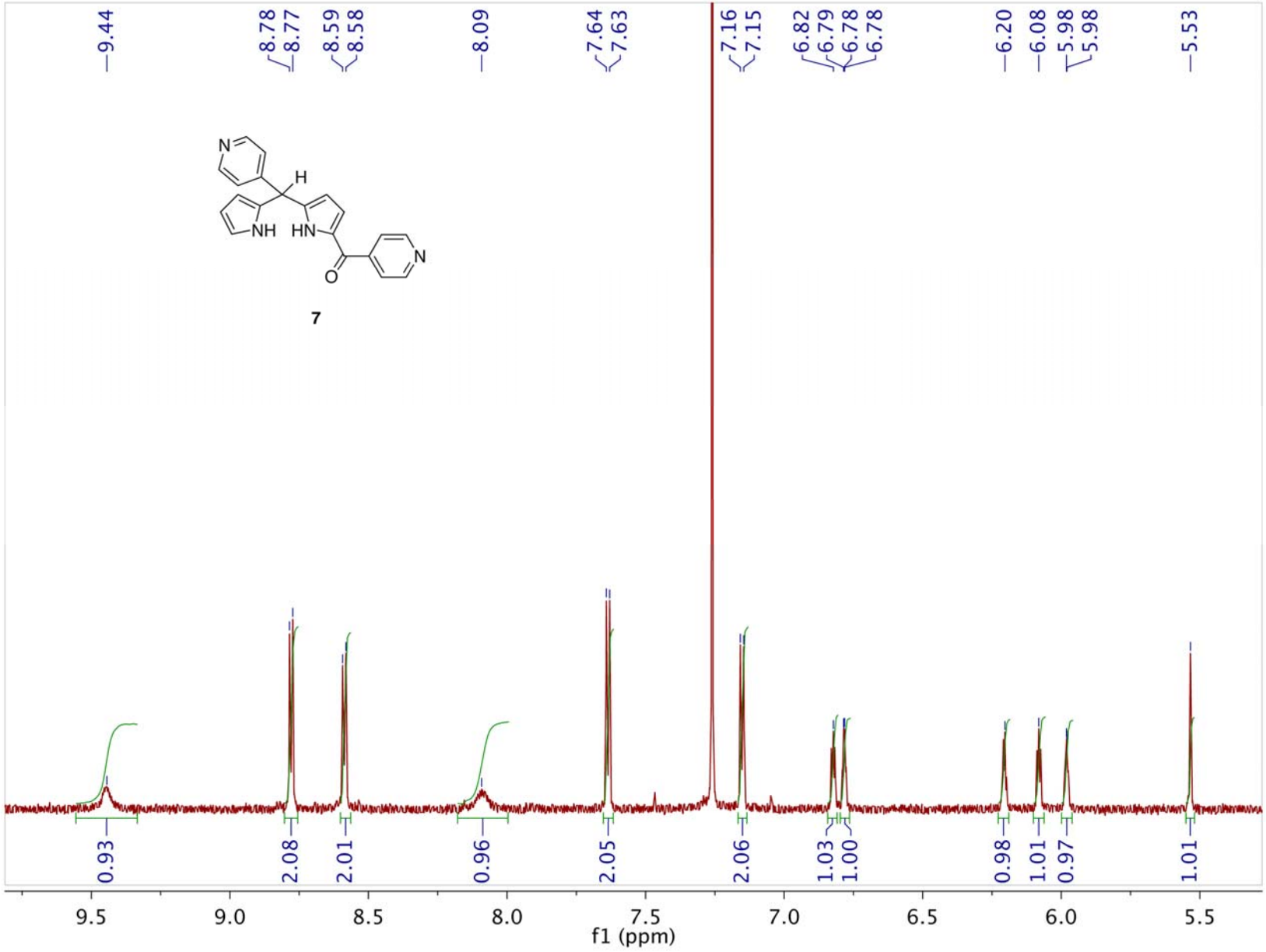
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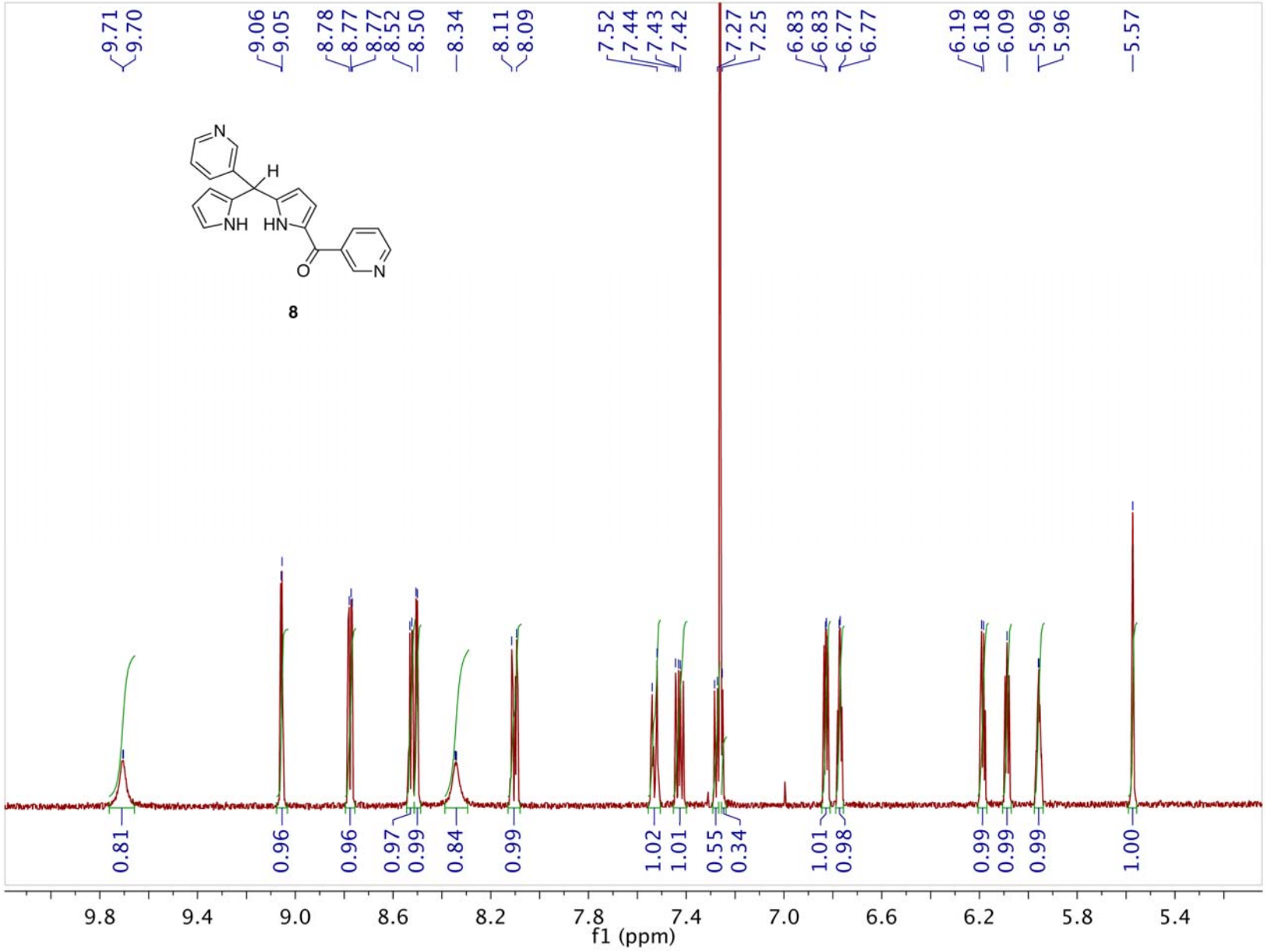
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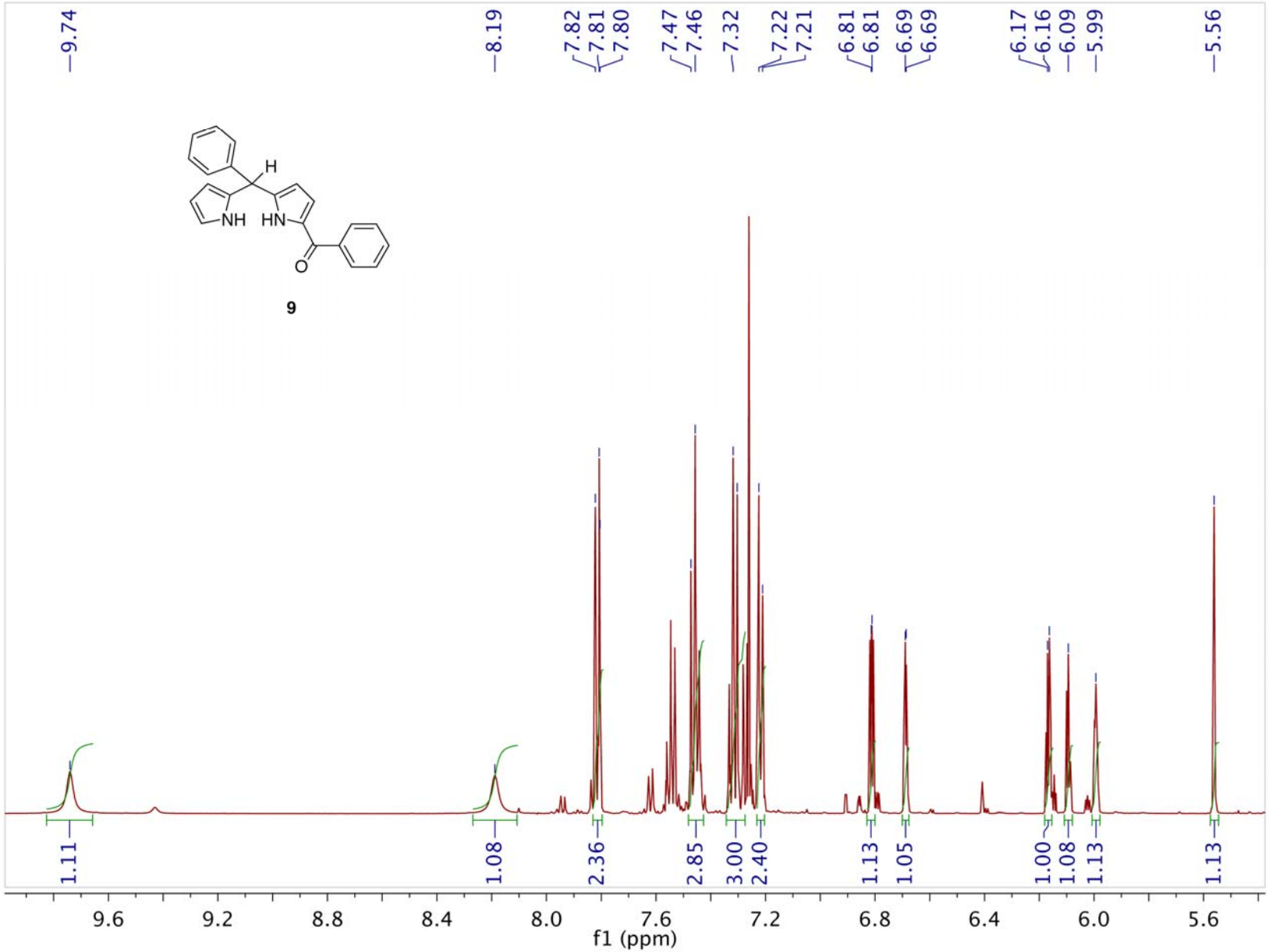
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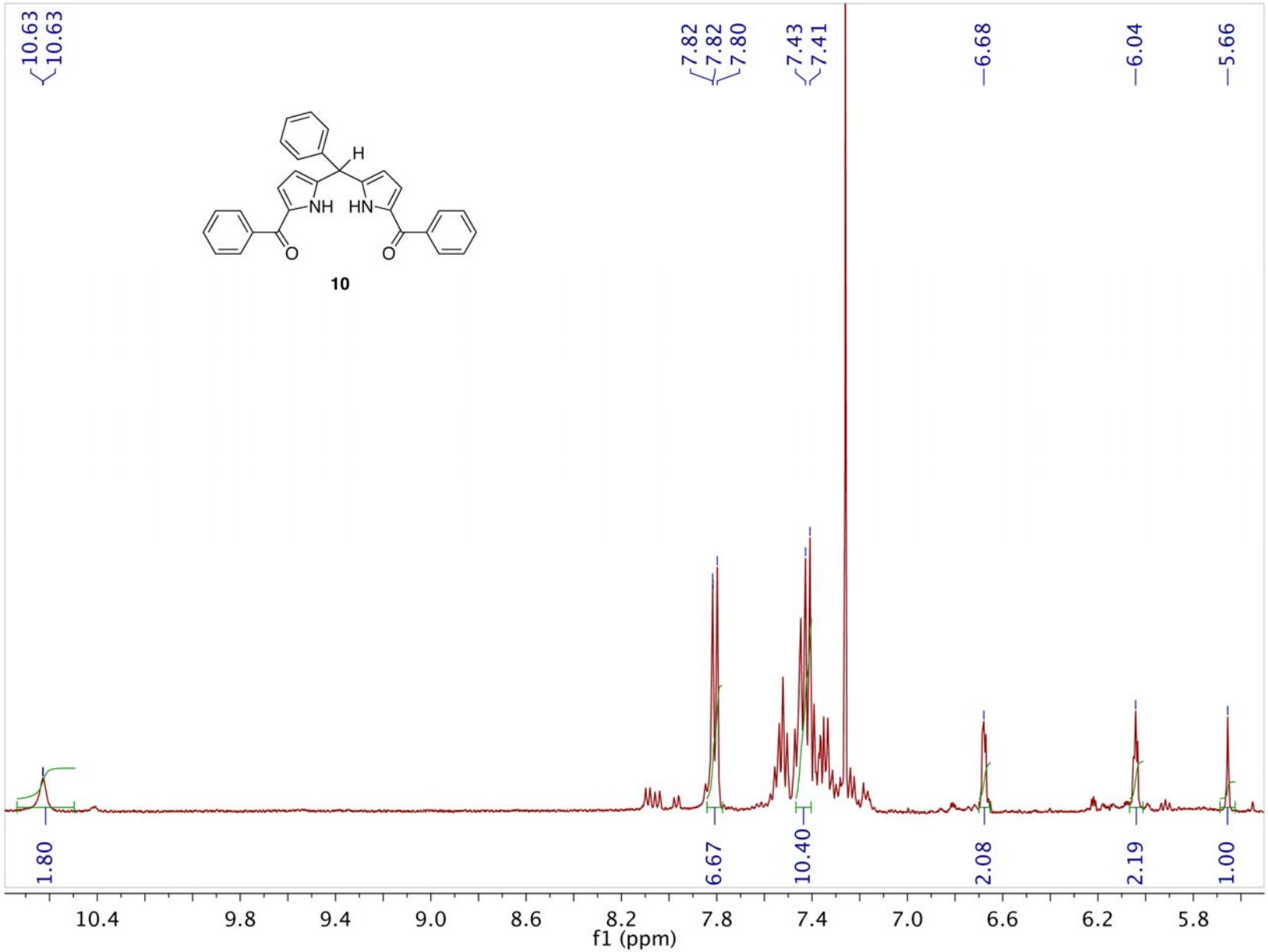
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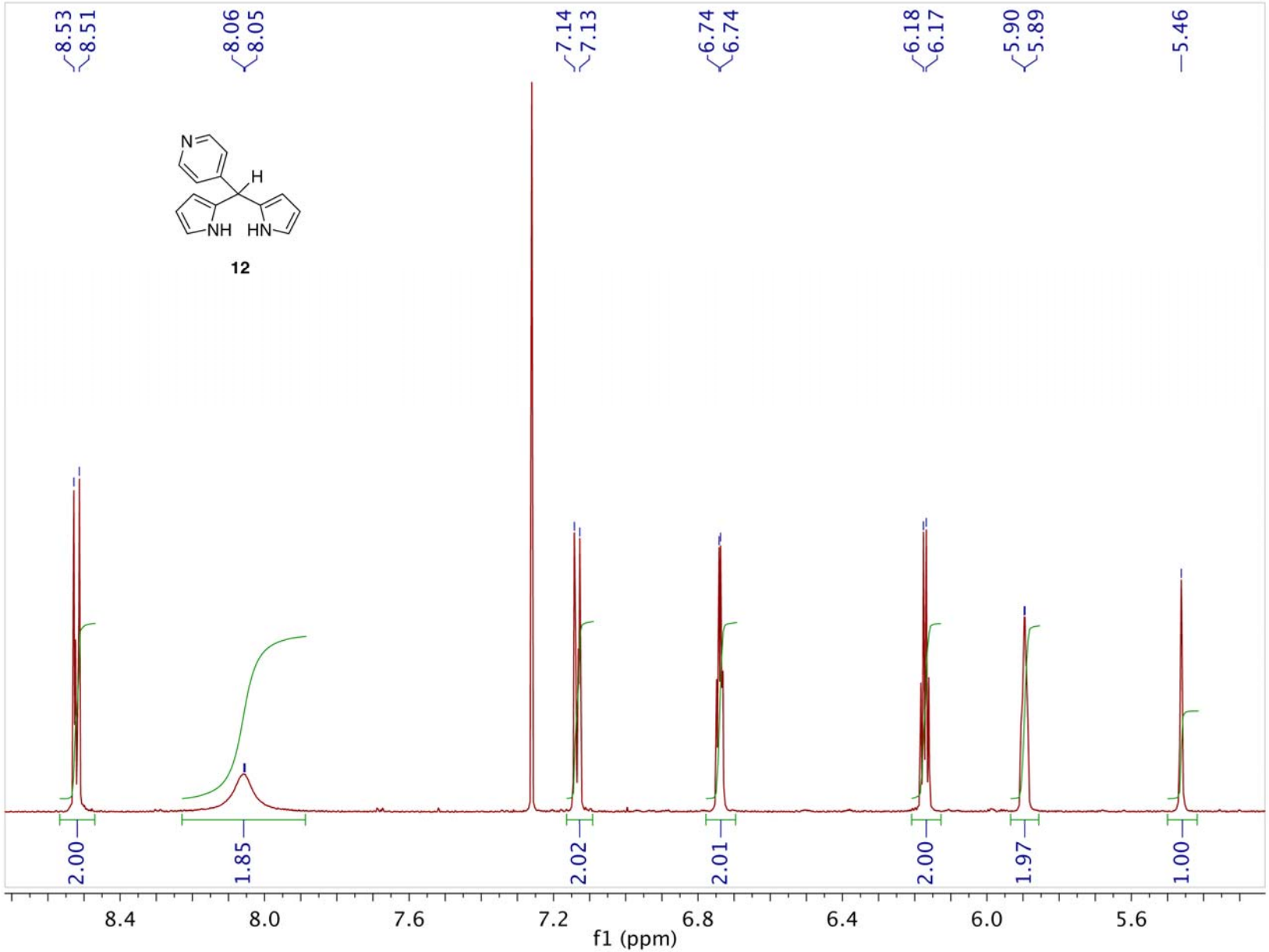
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5.6
f1 (ppm)

Table S1. Summary of Crystallographic Data for Compound **3**

	3
Formula	$C_{43}H_{27}N_5Pd$
Formula weight (g/mol)	720.10
Temperature (K)	100(2)
Crystal System	Monoclinic
Space Group	Cc
Color	Orange
a (Å)	13.736(3)
b (Å)	21.167(3)
c (Å)	12.464(2)
α (°)	90
β (°)	121.980(4)
γ (°)	90
V (Å^3)	3074.1(10)
Z	4
No. Reflections	27676
No. Unique Reflections	7607
R_{int}	0.0602
$R1^a$ (all data)	0.0518
$wR2^b$ (all data)	0.1087
$R1$ [(I > 2σ)]	0.0425
$wR2$ [(I > 2σ)]	0.1021
GOF^c	1.127

^{a} $R1 = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|$. ^{b} $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^2]^{1/2}$. ^{c} GOF = $[\Sigma w(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$ where n is the number of independent reflections and p is the number of refined parameters

Table S2. QD Luminescence Lifetime Data for QD Titration with Pd Porphyrins

Compound[a]	Equiv.	τ_1 (ns)	A_1 (%)[b]	τ_2 (ns)	A_2 (%)[b]
QD	–	16.93 ± 0.36[c]	53	5.07 ± 0.95	47
1	1	16.93	12	2.05 ± 0.29	88
1	2	16.93	6	0.98 ± 0.16	94
1	5	16.93	3	0.47 ± 0.05	97
1	10	16.93	4	0.30 ± 0.02	96
2	1	16.93	2	0.89 ± 0.16	98
2	2	16.93	3	0.57 ± 0.06	97
2	5	16.93	7	0.39 ± 0.03	93
2	10	16.93	6	0.32 ± 0.02	94
3	1	16.93	25	2.81 ± 0.40	75
3	2	16.93	18	2.61 ± 0.21	82
3	5	16.93	6	1.98 ± 0.23	94
3	10	16.93	3	1.67 ± 0.25	97

[a] Toluene solution, λ_{ex} = 450 nm. [b] Relative contribution to the biexponential fit. [c] 95% confidence interval.

Table S3. Summary of K_A as Determined from the Linear Region of the Data

Compound	Data	K_A (M^{-1})[a]
1	Intensity	3.26×10^7
1	Lifetime	1.74×10^7
2	Intensity	3.52×10^7
2	Lifetime	2.14×10^7
3	Intensity	1.42×10^6
3	Lifetime	1.30×10^6

[a] Fit to Eq. 7

Table S4. Summary of Binding Parameters Obtained from the Hill Equation

Compound	Data	y_{max}	n	K_D (M)[a]
1	Intensity	29.3	2.2	3.81×10^{-7}
1	Lifetime	19.5	1.4	4.83×10^{-7}
2	Intensity	55.3	0.8	1.19×10^{-6}
2	Lifetime	20.4	0.8	3.22×10^{-7}

[a] Fit to Eq. 8

Table S5. Summary of Förster Energy Transfer Parameters

Compound	m	J^a (M^{-1} cm^3)	r^b (nm)	$R_0{}^a$ (nm)	E^c
QD1	10	7.96×10^{-14}	3.81	4.11	0.94
QD2	10	8.54×10^{-14}	3.85	4.15	0.94
QD3	10	7.89×10^{-14}	5.35	4.10	0.67

[a] Calculated using Eq. 4. [b] Calculated using Eq. 2. [c] Calculated using Eq. 3.

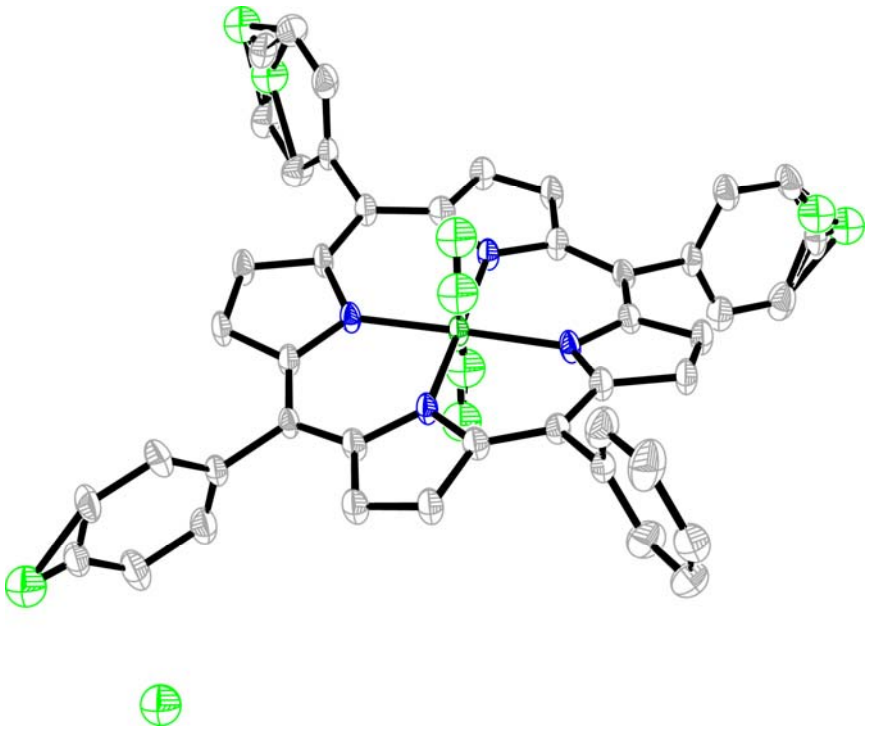

Figure S1. Illustration of **3** where the 4 position of each *meso* ring has been refined as a carbon atom. The ten largest residual density peaks (Q peaks) are shown as green spheres. Three of the *meso* substituents have a Q peak corresponding to a hydrogen atom, while the fourth does not, thus delineating the 4-pyridyl group. Thermal ellipsoids are drawn at the 50% probability level.

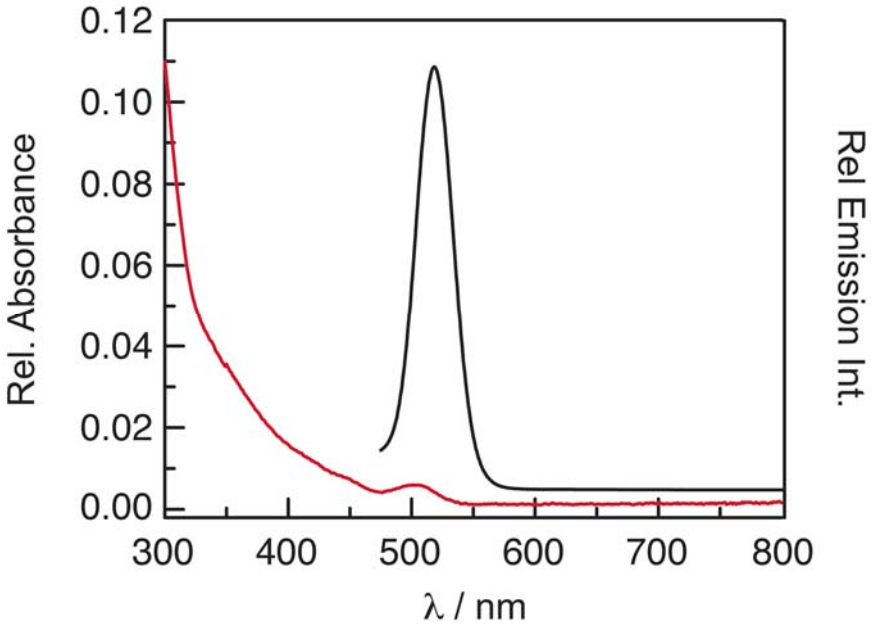

Figure S2. Comparison of the steady state absorption (—) and emission spectra (—) of QD (λ_{exc} = 450 nm) in toluene.

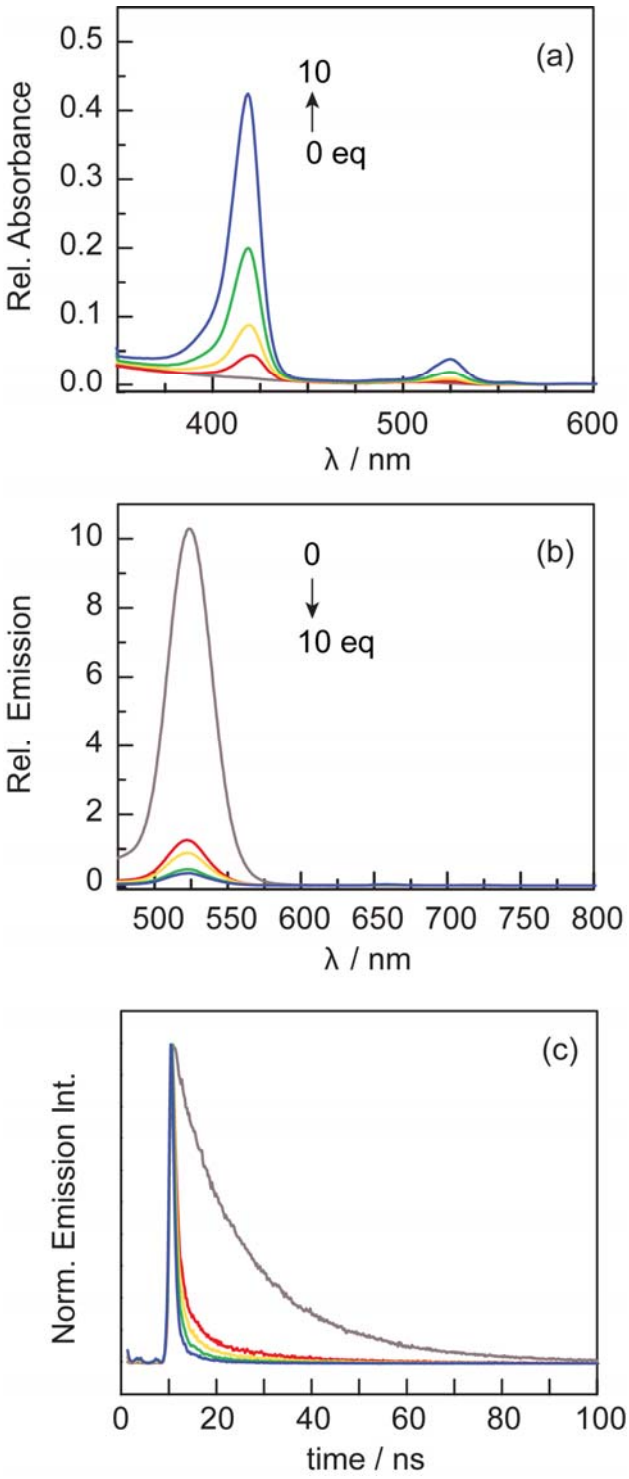

Figure S3. Spectral changes associated with titration of a toluene solution of QD (—) with 1 (—), 2 (—), 5 (—) and 10 (—) equiv of **2**. (a) The intensity of the Soret and Q band absorption profiles increases. (b) The QD emission (λ_{exc} = 450 nm) intensity is quenched and (c) the decay profiles of the QD emission (λ_{exc} = 450 nm) decreases with increasing equivalents of porphyrin.

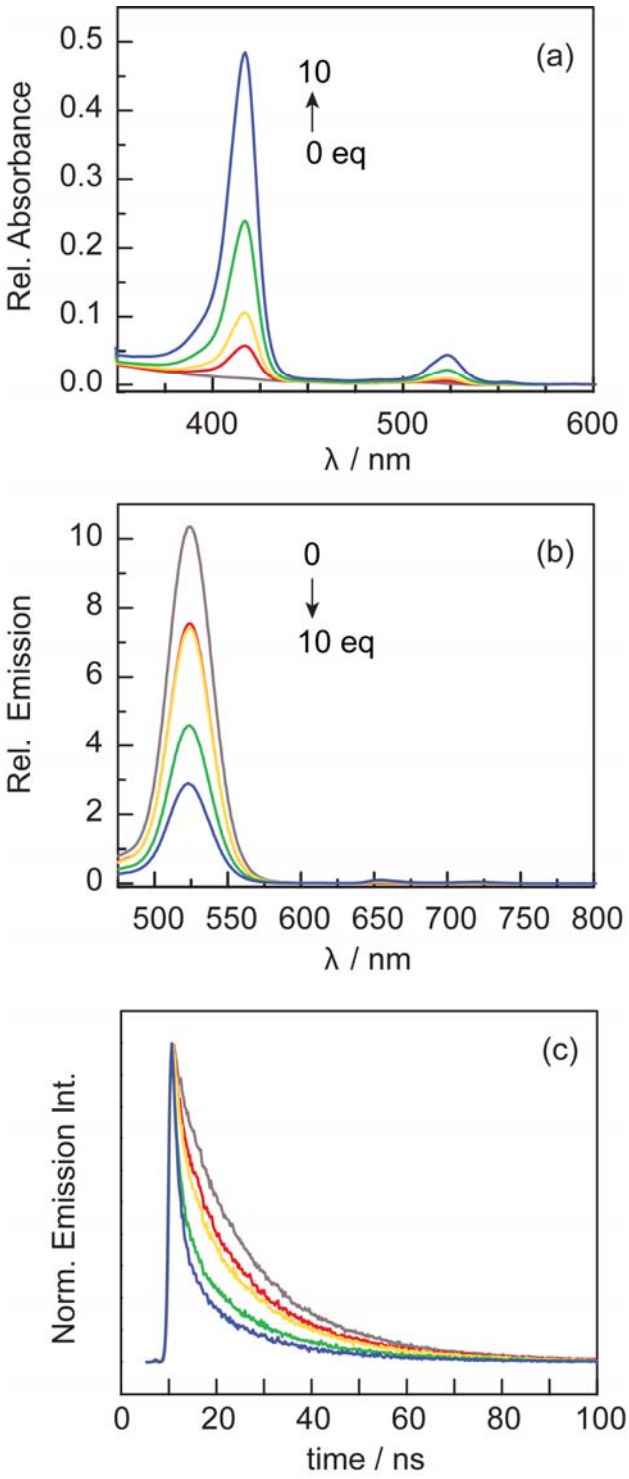

Figure S4. Spectral changes associated with titration of a toluene solution of QD (—) with 1 (—), 2 (—), 5 (—) and 10 (—) equiv of **3**. (a) The intensity of the Soret and Q band absorption profiles increases. (b) The QD emission (λ_{exc} = 450 nm) intensity is quenched and (c) the decay profiles of the QD emission (λ_{exc} = 450 nm) decreases with increasing equivalents of porphyrin.

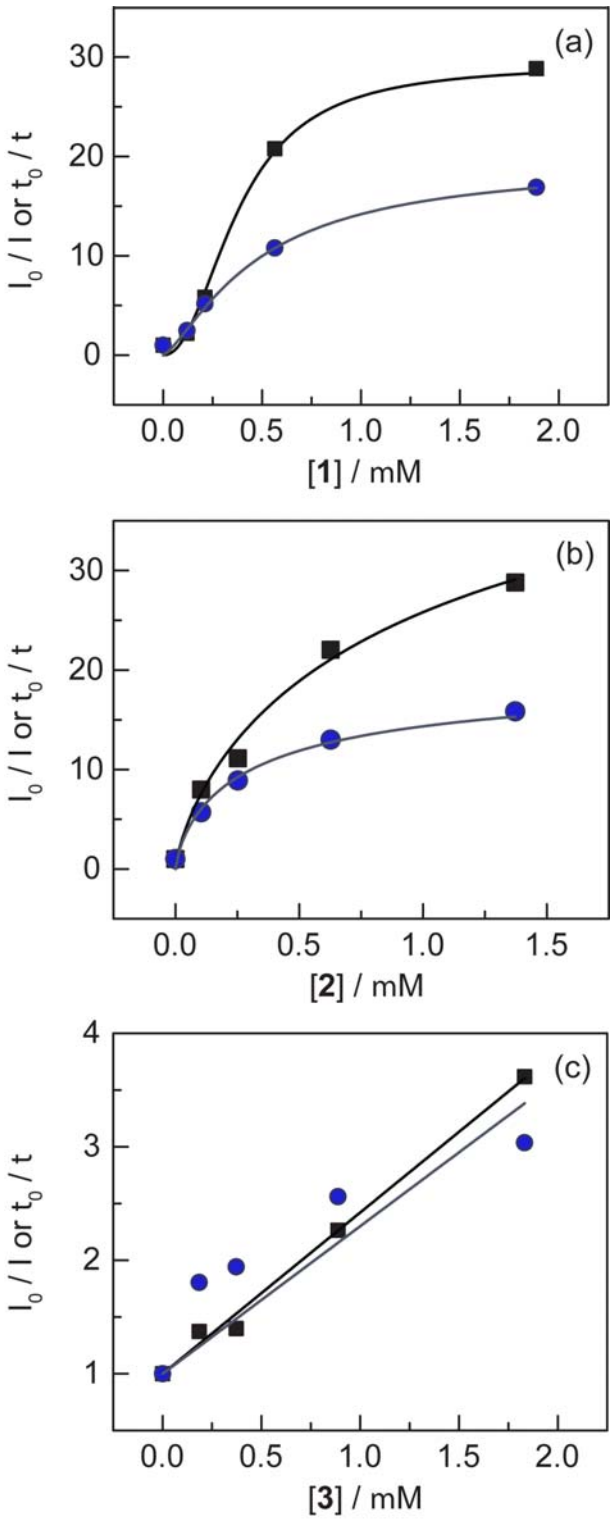

Figure S5. Plot of intensity (●) and lifetime (■) quenching data obtained from titration experiments (Figures 5, S3, S4, and Table S2) to determinate binding constants for **1** (a), **2** (b), and **3** (c). The black traces represent the curves of best fit to Eq. 7 for (a) and (b) or Eq. 6 for (c).

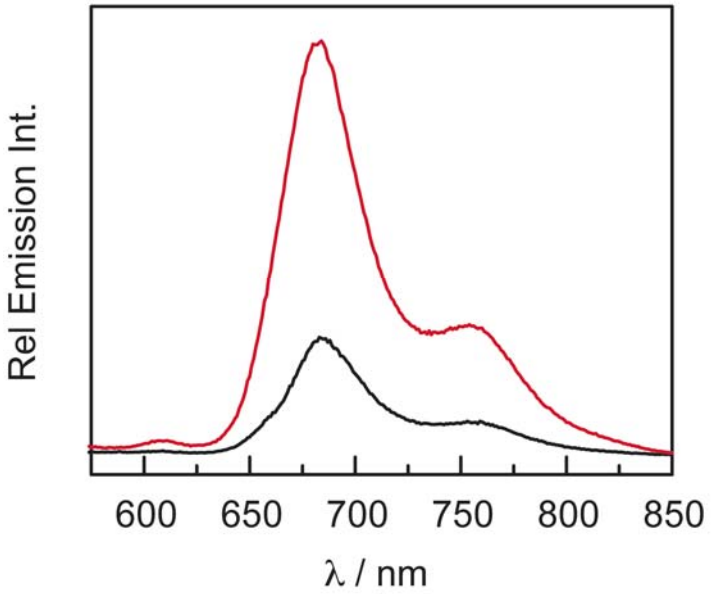

Figure S6. Emission spectra (λ_{exc} = 450 nm) of concentration-matched toluene solutions of **1** (—) and **QD1** (—) under vacuum. The enhancement of the emission intensity of **QD1** is attributed to FRET excitation of the porphyrin, as the QD has a greater absorbance at 450 nm relative to **1**.

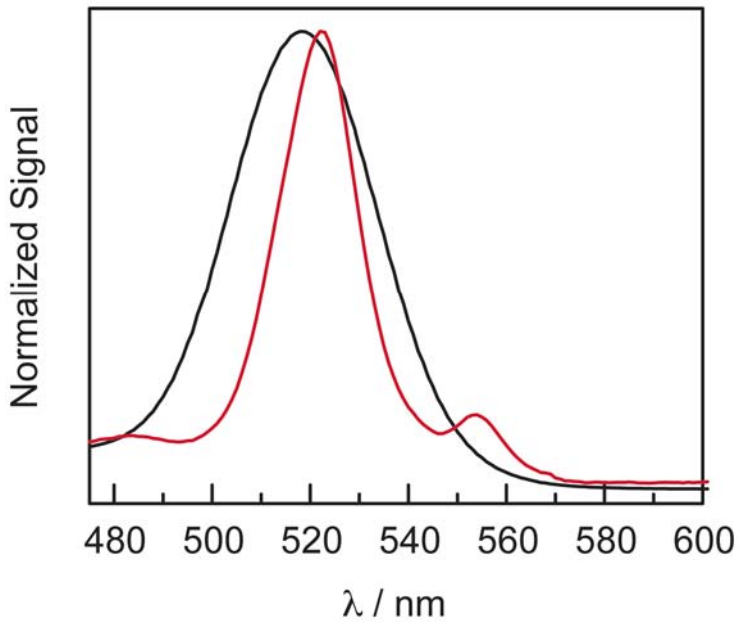

Figure S7. Normalized QD emission (—) (λ_{exc} = 450 nm) and absorption of **1** (—), illustrating spectral overlap that accounts for the high FRET efficiency in **QD1**.