

ESI to:

Unexpected Hydroxylamine-induced Ring-closure Reactions of
meso-Tetraphenylsecochlorin Bisaldehyde

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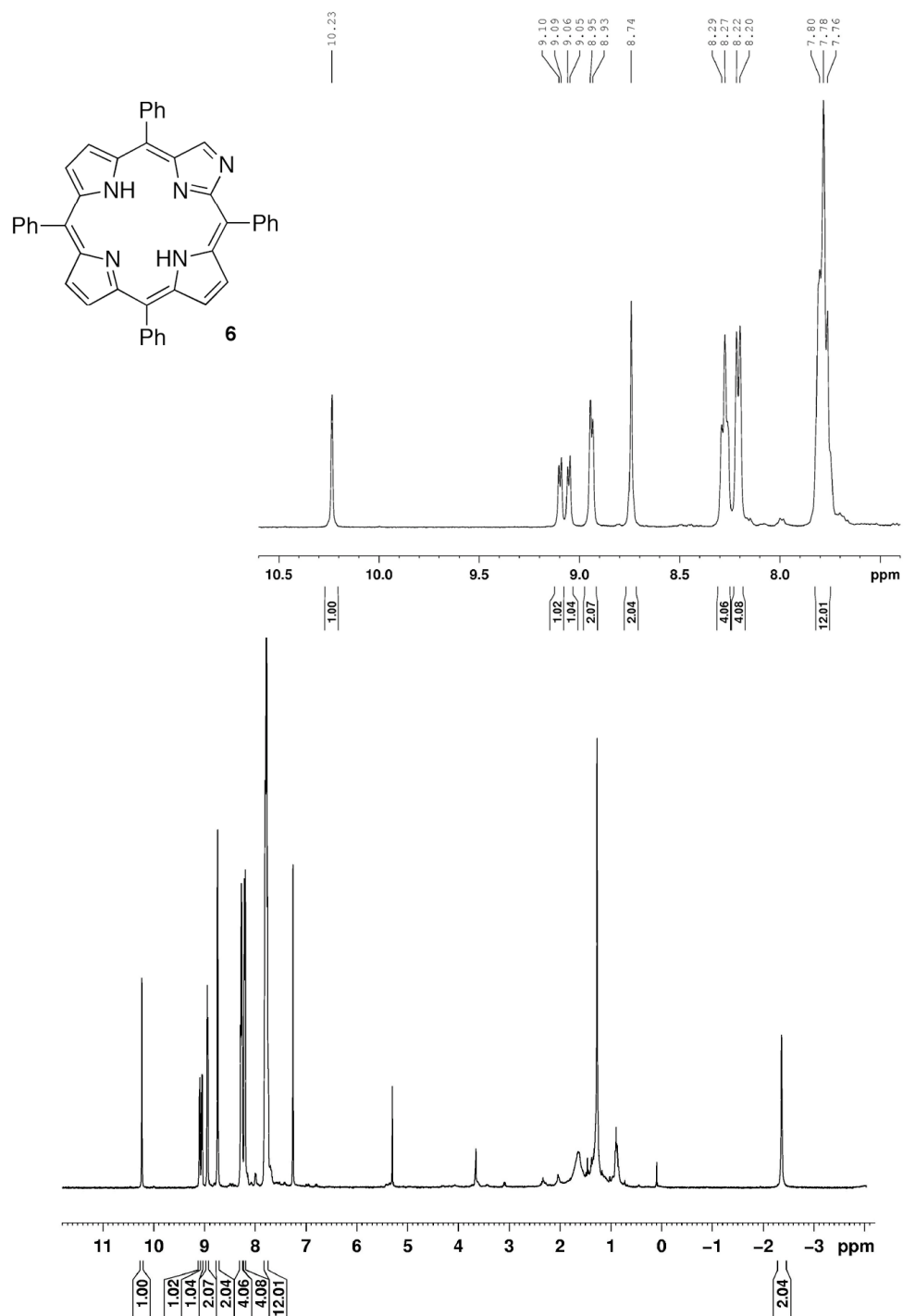


Figure ESI-1. ¹H NMR Spectrum (400 MHz, CDCl₃) of **6**

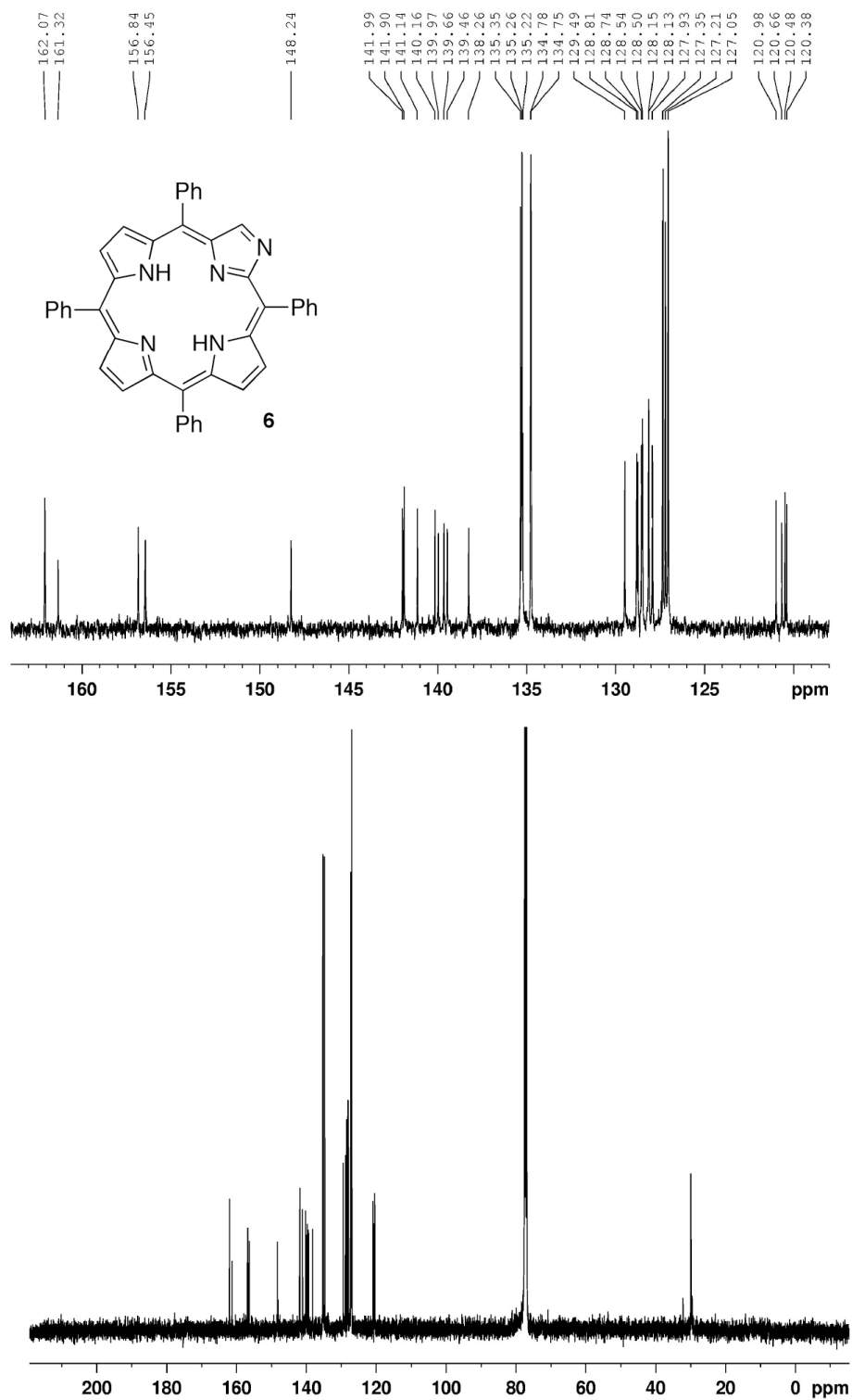


Figure ESI-2. ^{13}C NMR Spectrum (100 MHz, CDCl_3) of **6**

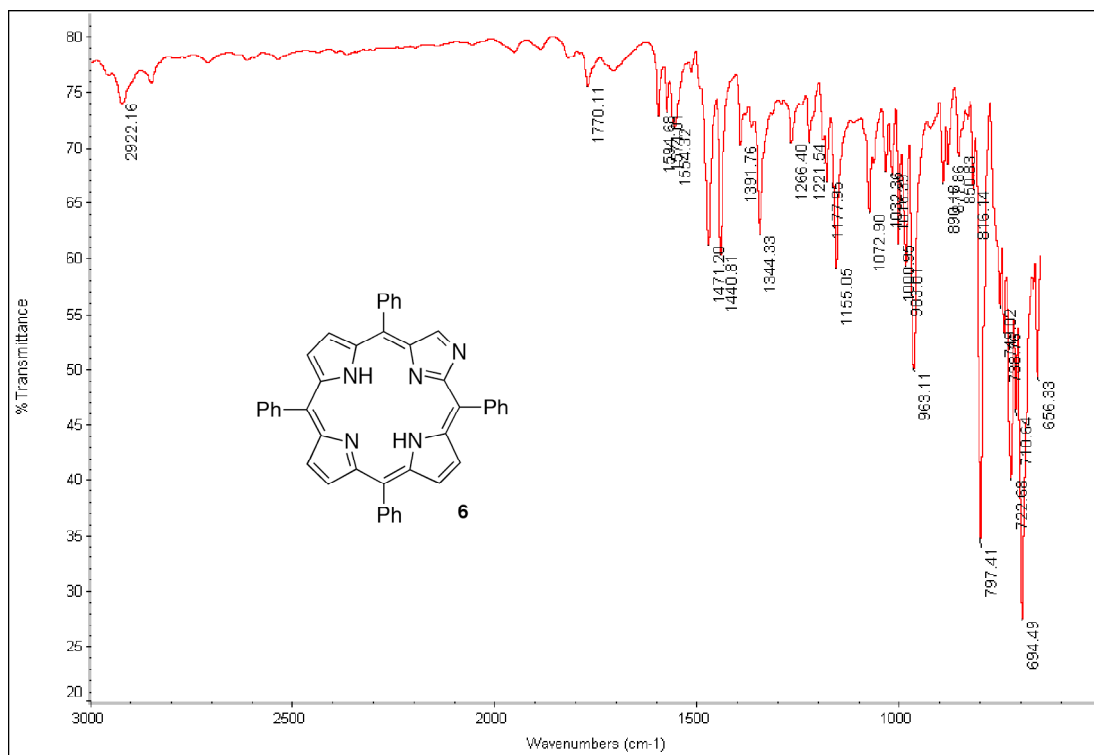


Figure ESI-3. FT-IR Spectrum (neat, diffuse reflectance) of **6**

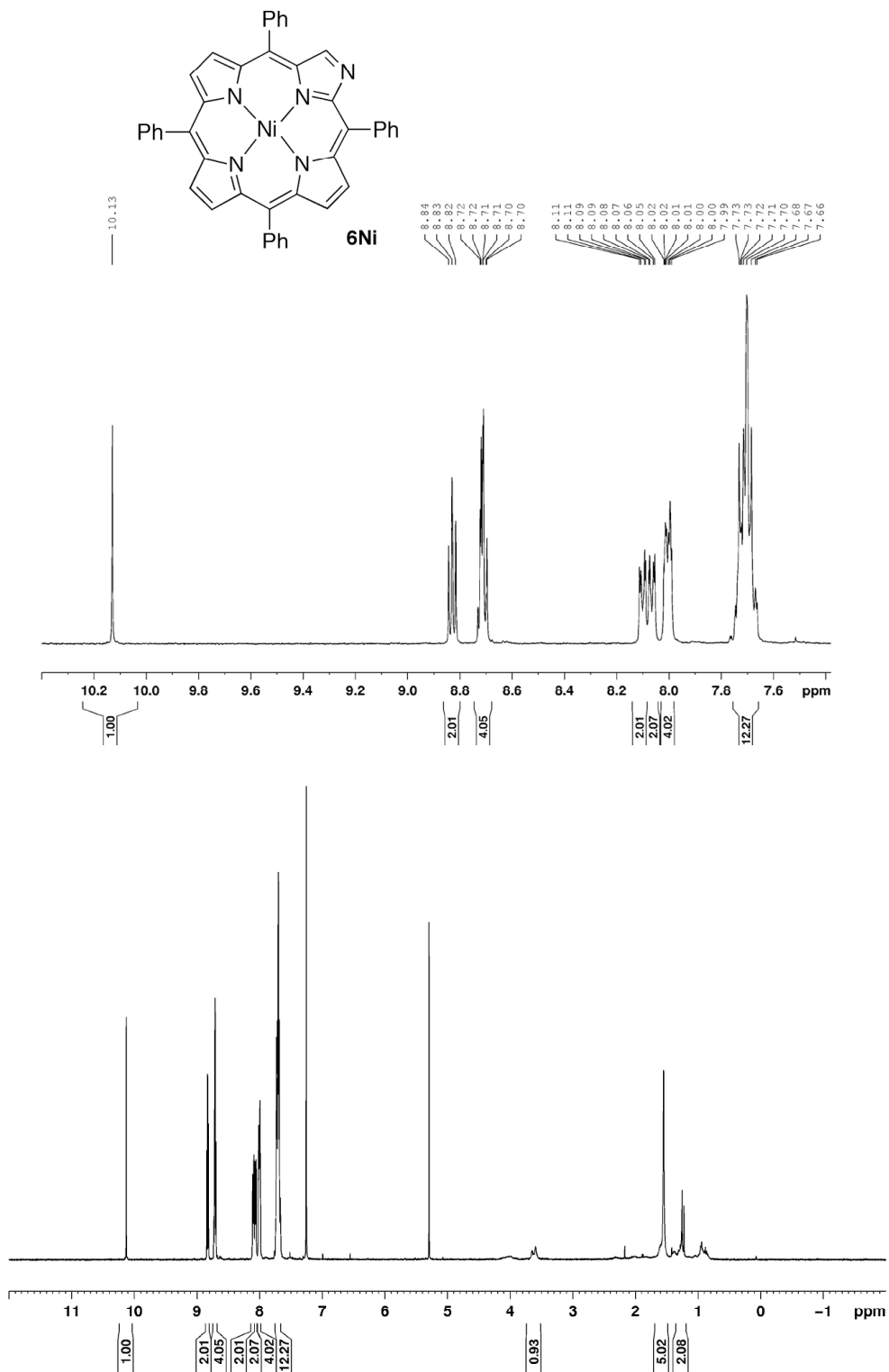


Figure ESI-4. ^1H NMR Spectrum (400 MHz, CDCl_3) of **6Ni**

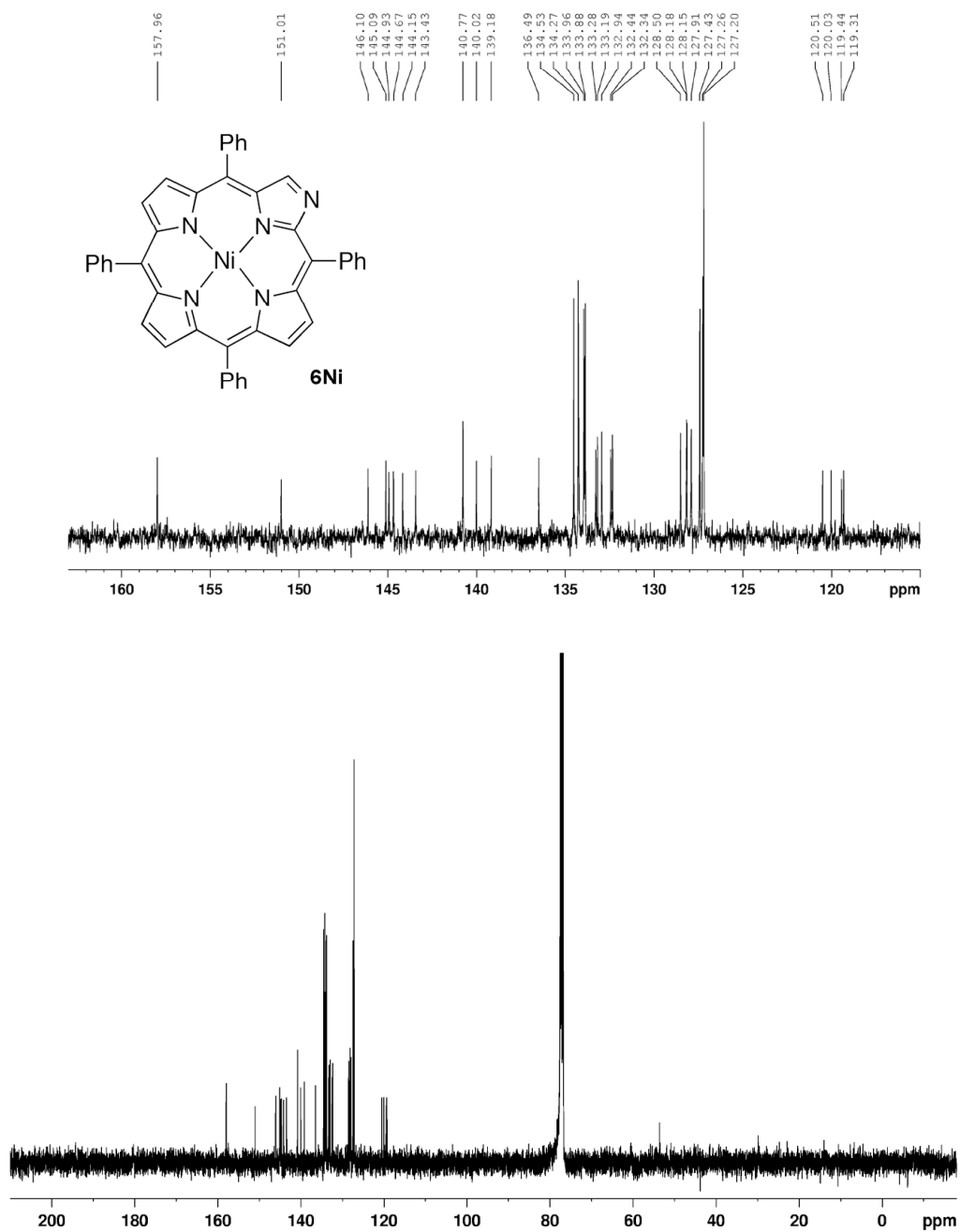


Figure ESI-5. ^{13}C NMR Spectrum (100 MHz, CDCl_3) of **6Ni**

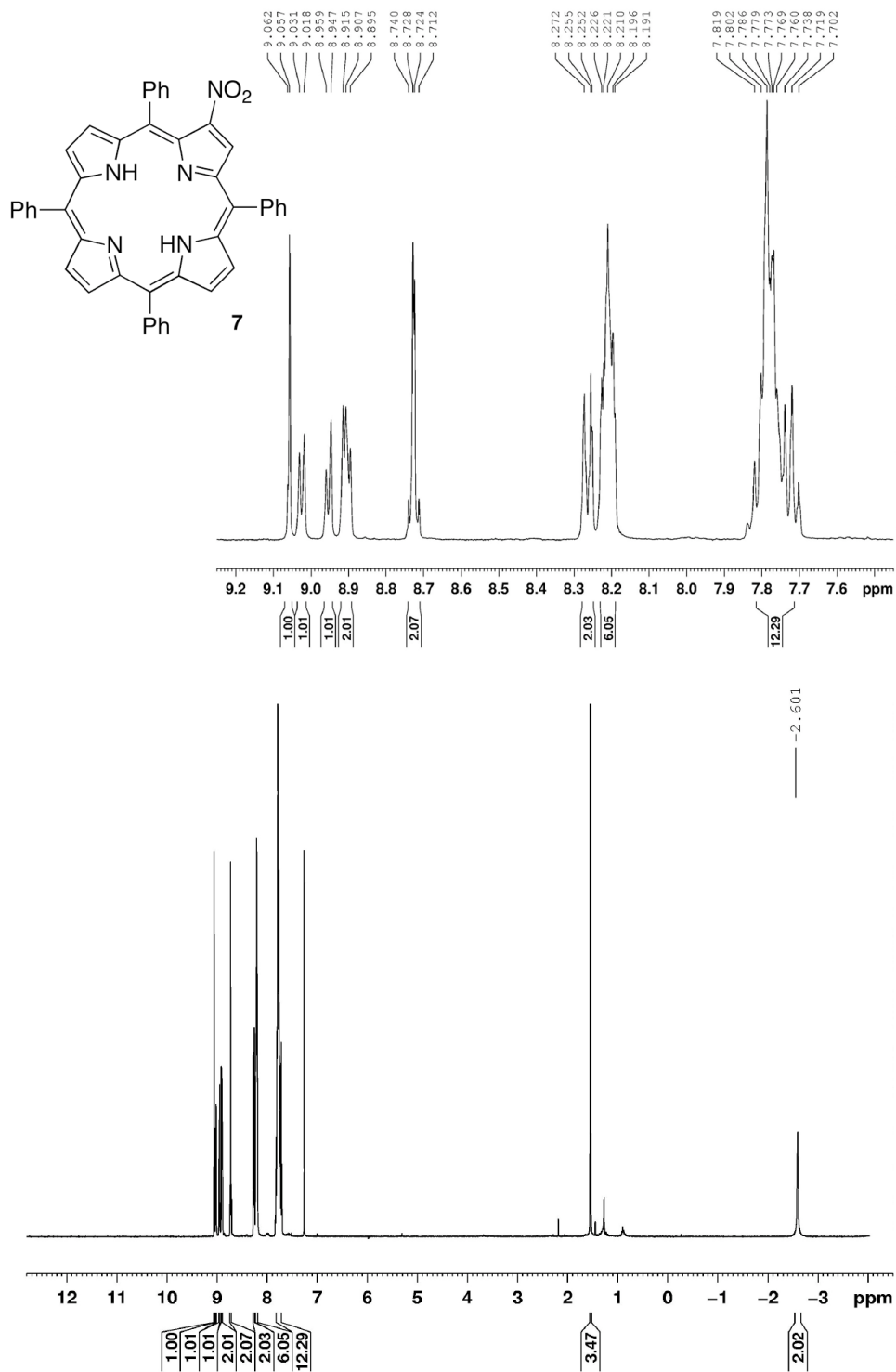
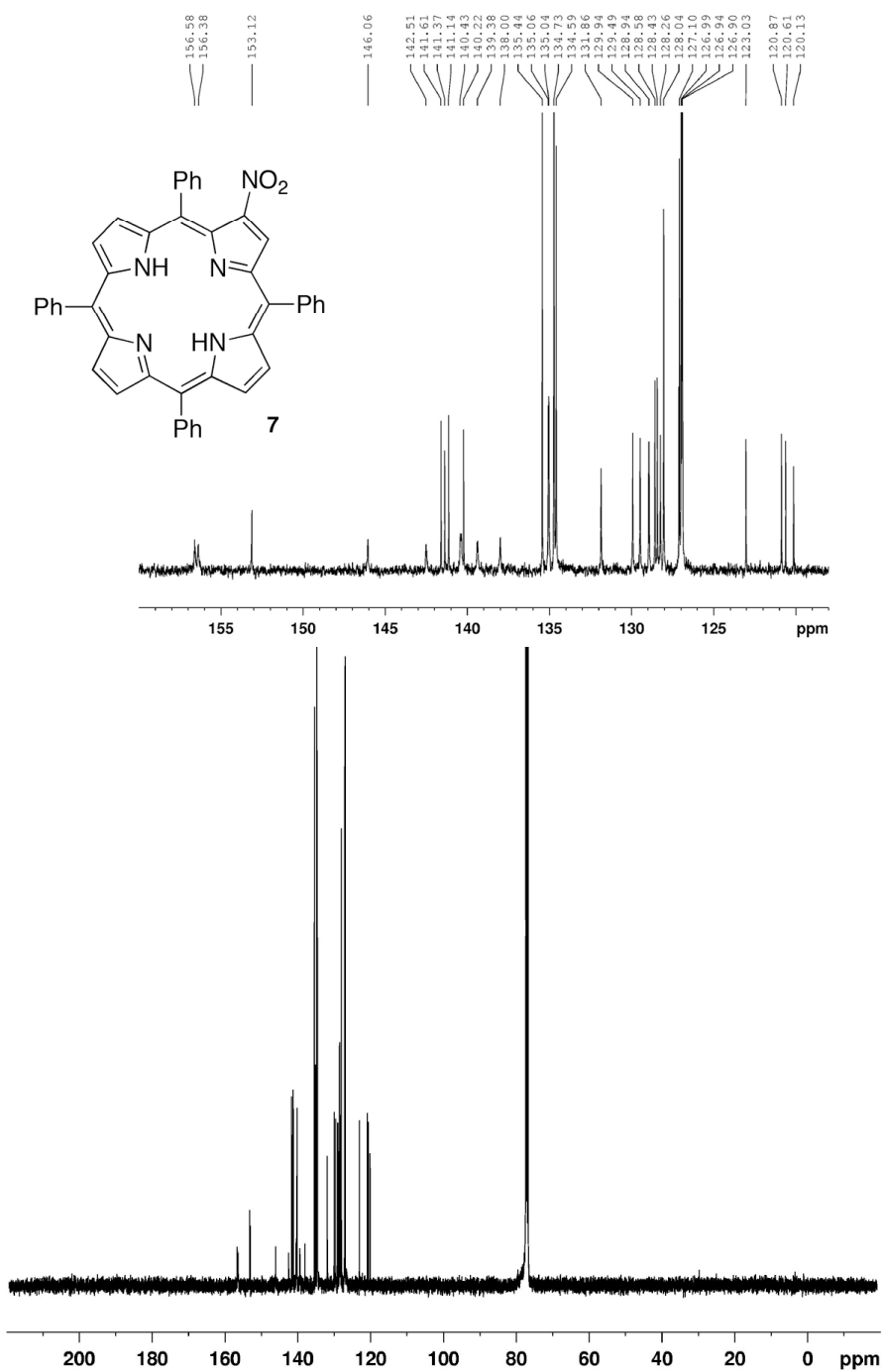


Figure ESI-6. ¹H NMR Spectrum (400 MHz, CDCl₃) of 7



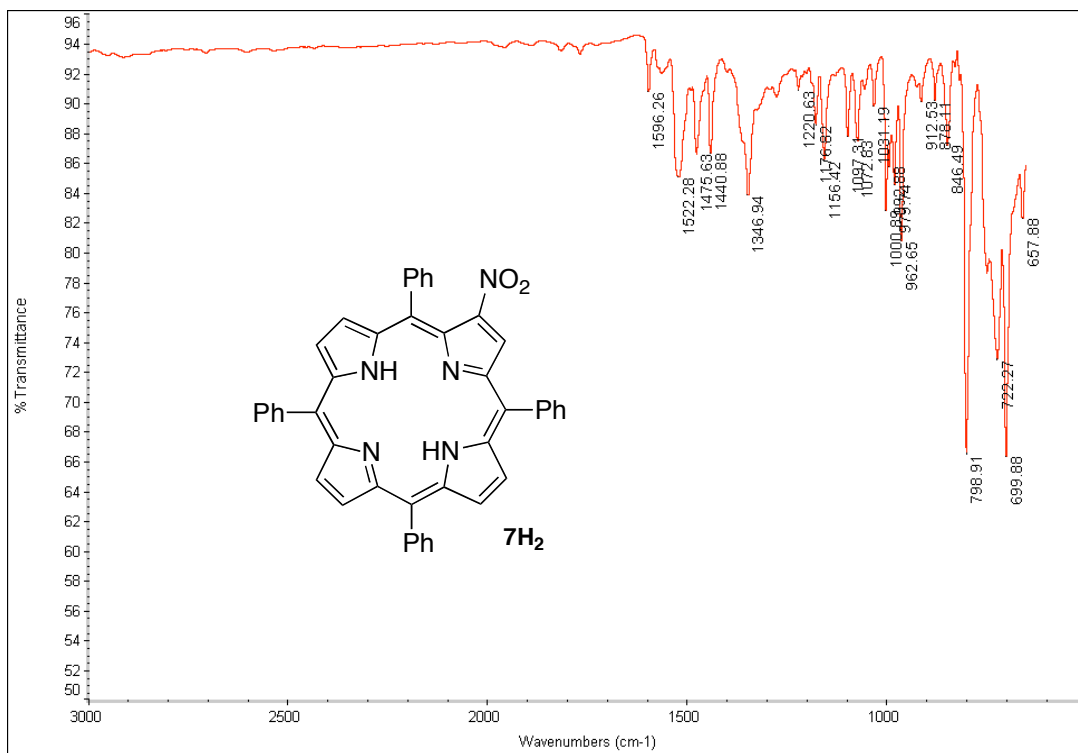


Figure ESI-8. FT-IR Spectrum (neat, diffuse reflectance) of **7**

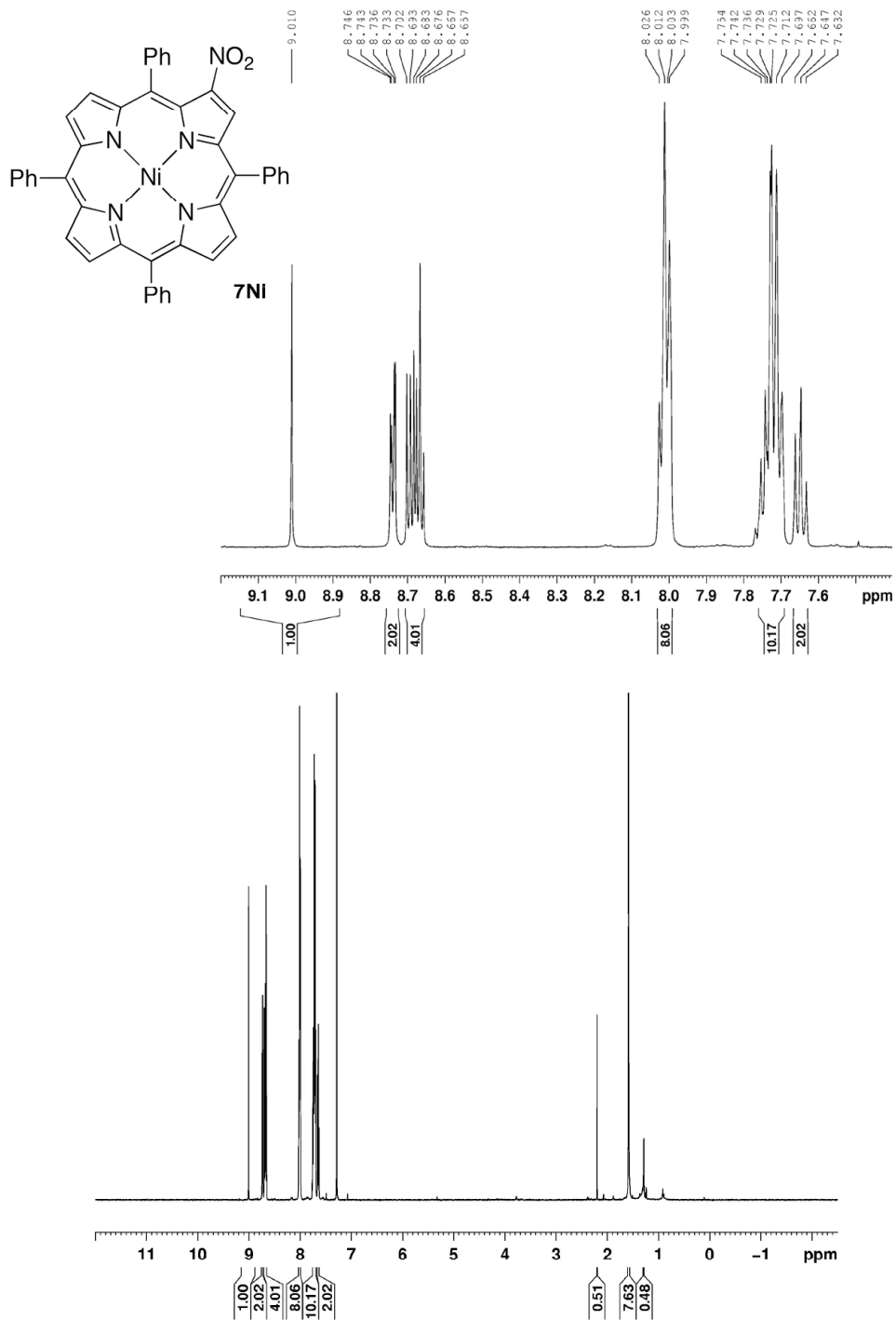


Figure ESI-9. ¹H NMR (500 MHz, CDCl₃) of **7Ni**

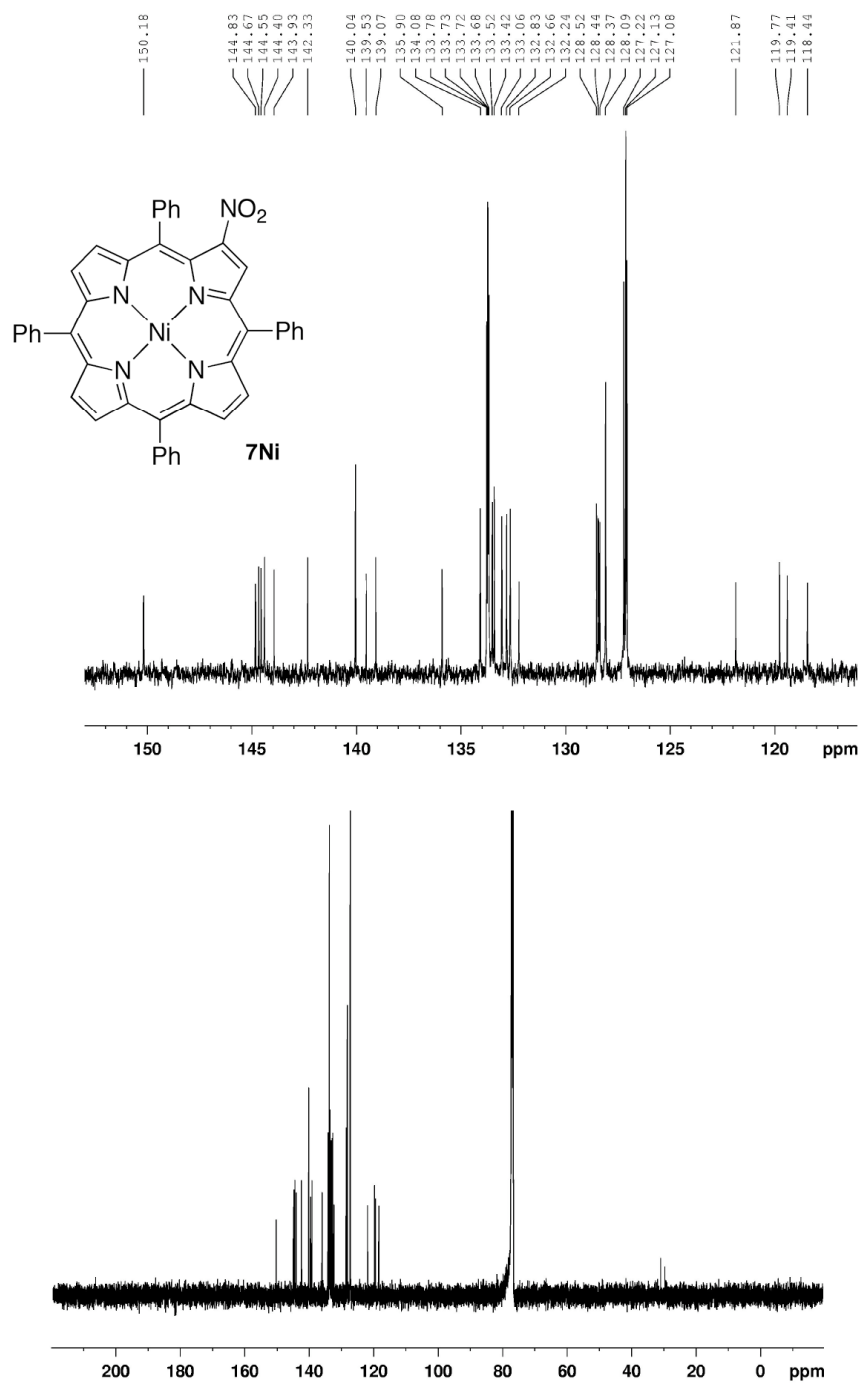


Figure ESI-10. ¹³C NMR Spectrum (125 MHz, CDCl₃) of **7Ni**

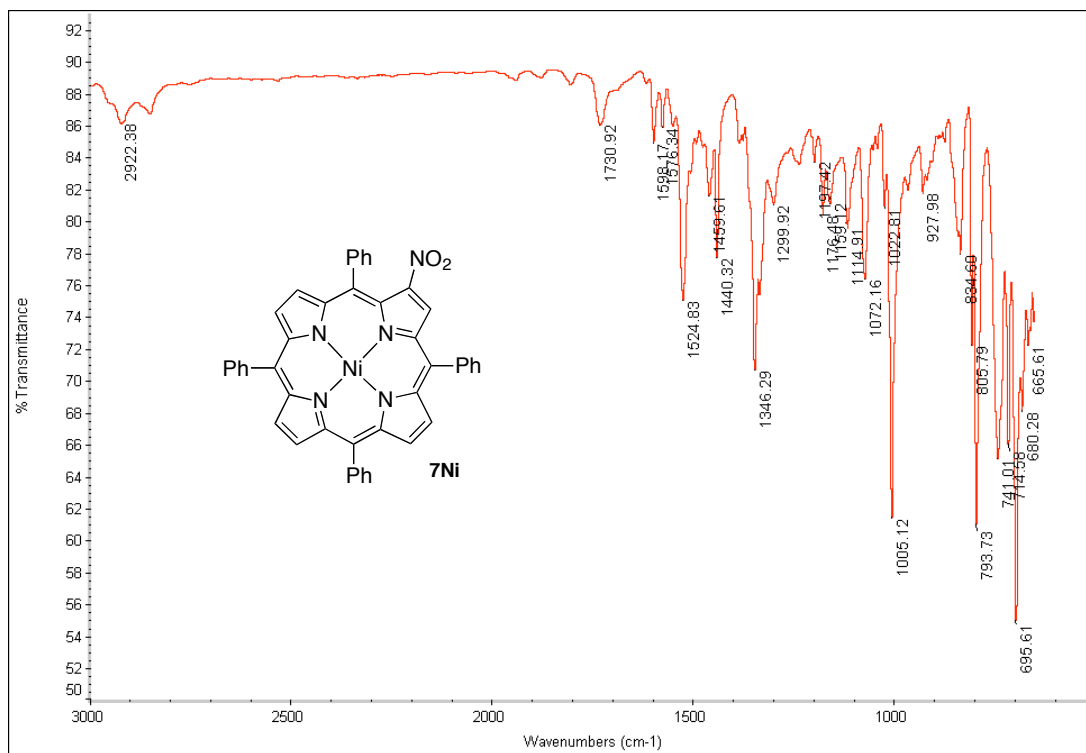


Figure ESI-11. FT-IR Spectrum (neat, diffuse reflectance) of **7Ni**

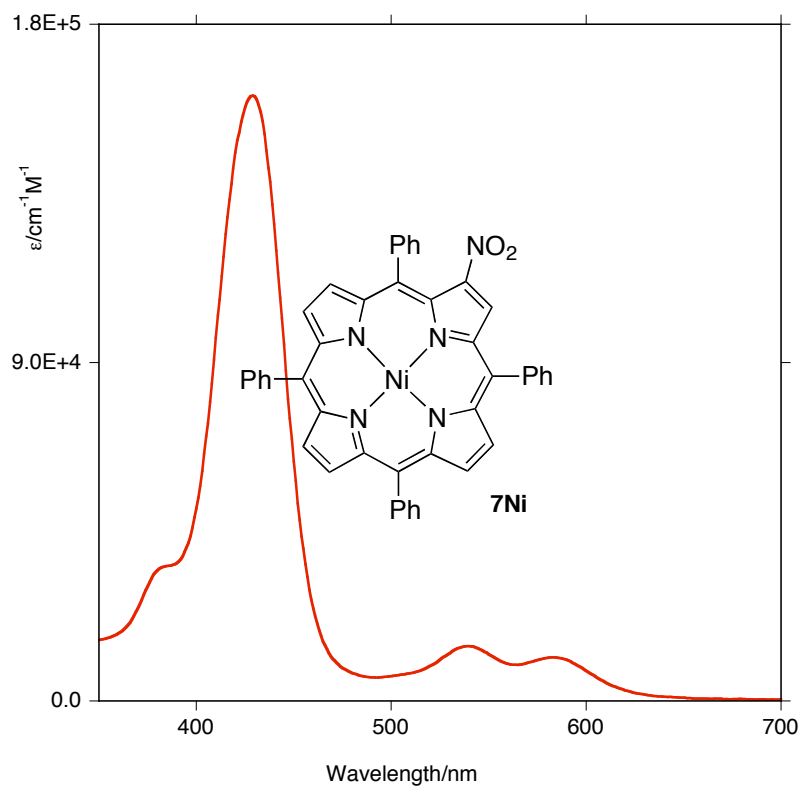


Figure ESI-12. UV-vis Spectrum (CH₂Cl₂) of **7Ni**

[*meso*-Tetraphenyl-2-nitroporphyrinato]Pd(II) 7Pd by insertion of Pd(II) into free base 7.

Free base **7** (14.0 mg, 2.12×10^{-5} mol) was dissolved in benzonitrile (5 mL) and added to a refluxing solution of benzonitrile (5 mL) and PdCl₂ (7.9 mg, 3.15×10^{-5} mol, 2.02 equiv) in a round-bottom flask equipped with a magnetic stirring bar and N₂ gas inlet. The mixture was heated to reflux for 3 h. When the starting material was consumed (reaction control by UV-vis and TLC), the reaction mixture was allowed to cool down, and was evaporated to dryness by rotary evaporation. The product **7Pd** was isolated and purified by flash column chromatography (CH₂Cl₂/40% petroleum ether 30-60) and recrystallized to provide a dark purple powdered of analytical purity in 93% yields. **7Pd**: R_f (silica-CH₂Cl₂) 0.89; ¹H NMR (400 MHz, CDCl₃): δ 9.11 (s, 1H), 8.85 (d, ³J = 4.0 Hz, 1H), 8.77 (overlapping d, 5H), 8.17 – 8.13 (m, 8H), 7.80 - 7.67 (m, 13H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 149.9, 143.6 143.5, 143.46, 143.42, 143.0, 141.8 141.3, 141.2, 140.8, 139.9, 134.9, 134.8, 134.4, 134.3, 134.2, 133.0, 132.4, 132.3, 132.1, 132.0, 131.8, 130.7, 128.8, 128.6, 128.3, 127.9, 127.2, 127.1, 124.8, 122.7, 122.4, 121.6 ppm; UV-vis (CHCl₂) λ_{max} (log ε) 426 (5.27), 531 (4.28), 572 (4.09) nm.

[*meso*-Tetraphenyl-2-nitroporphyrinato]Pt(II) 7Pt by insertion of Pt(II) into free base 7.

Prepared in near-quantitative yields (64 mg) as described for the Pd(II) complex **7Pd** from free base porphyrin **7** (50.0 mg, 7.58×10^{-5} mol) and PtCl₂ (45.8 mg, 1.72×10^{-4} mol, 2.3 equiv) as a brick-red powder of analytical purity. **7Pt**: R_f (silica-CH₂Cl₂) 0.85; ¹H NMR (400 MHz, CDCl₃): δ 9.08 (s, 1H), 8.82 (d, ³J = 8.0 Hz, 1H), 8.73, (overlapping d, 5H), 8.15 - 8.12 (m, 8H), 7.79 - 7.68 (m, 13H). ¹³C NMR (100 MHz, CDCl₃): δ 149.9, 143.0, 142.9, 142.8, 142.4, 142.3, 141.0 140.9, 140.8, 140.4, 139.6, 134.6, 134.1, 134.06, 134.02, 132.9, 132.7, 132.4, 132.0, 131.9, 131.6, 131.4, 129.8, 129.3, 128.9, 128.7, 128.4, 127.7, 127.3, 127.24, 127.22, 125.5, 123.22, 122.8, 122.3; UV-vis (CHCl₂) λ_{max} (log ε) 411 (5.32), 518 (4.37), 556 (4.20) nm.

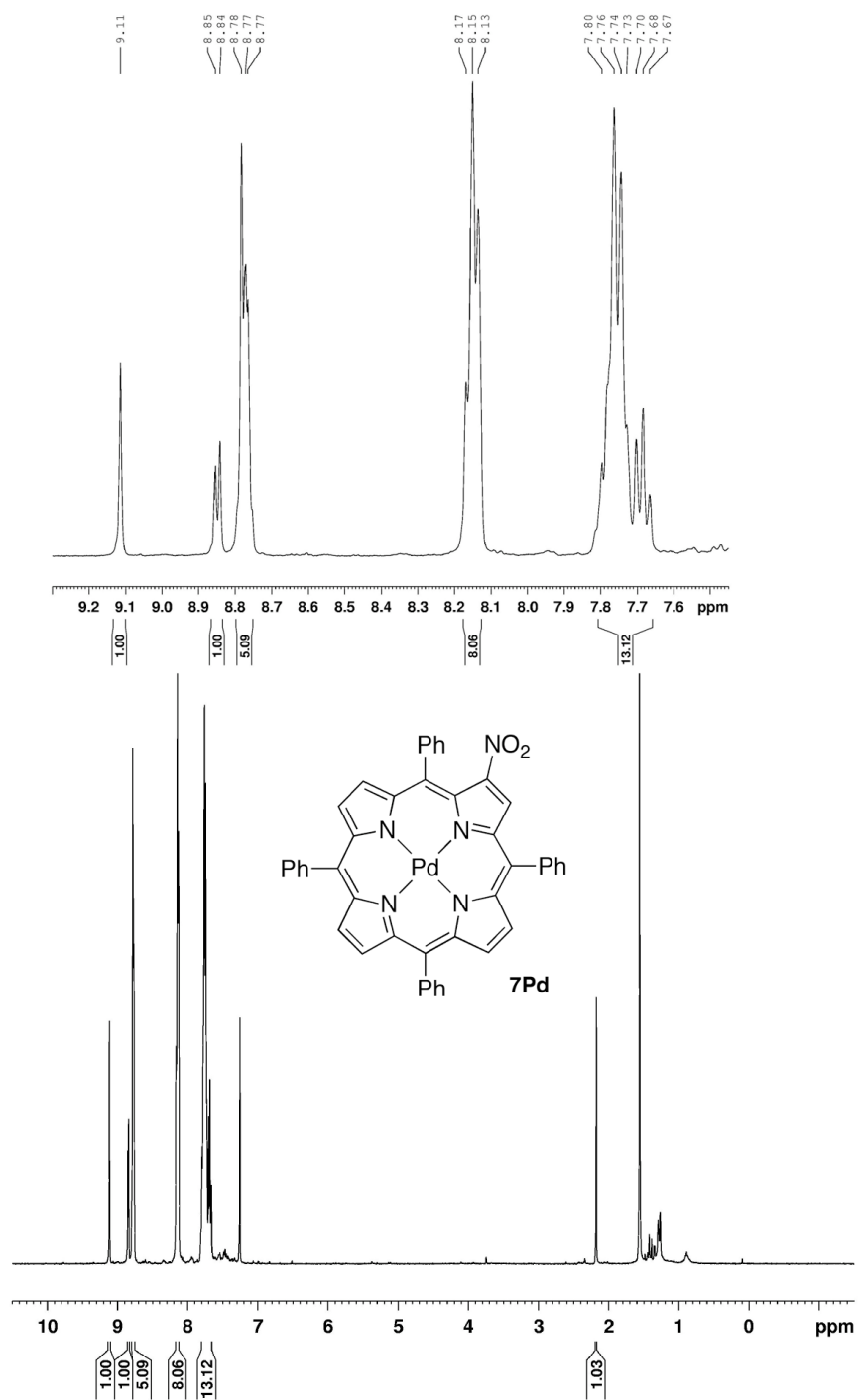


Figure ESI-13. ^1H NMR Spectrum (400 MHz, CDCl₃) of **7Pd**

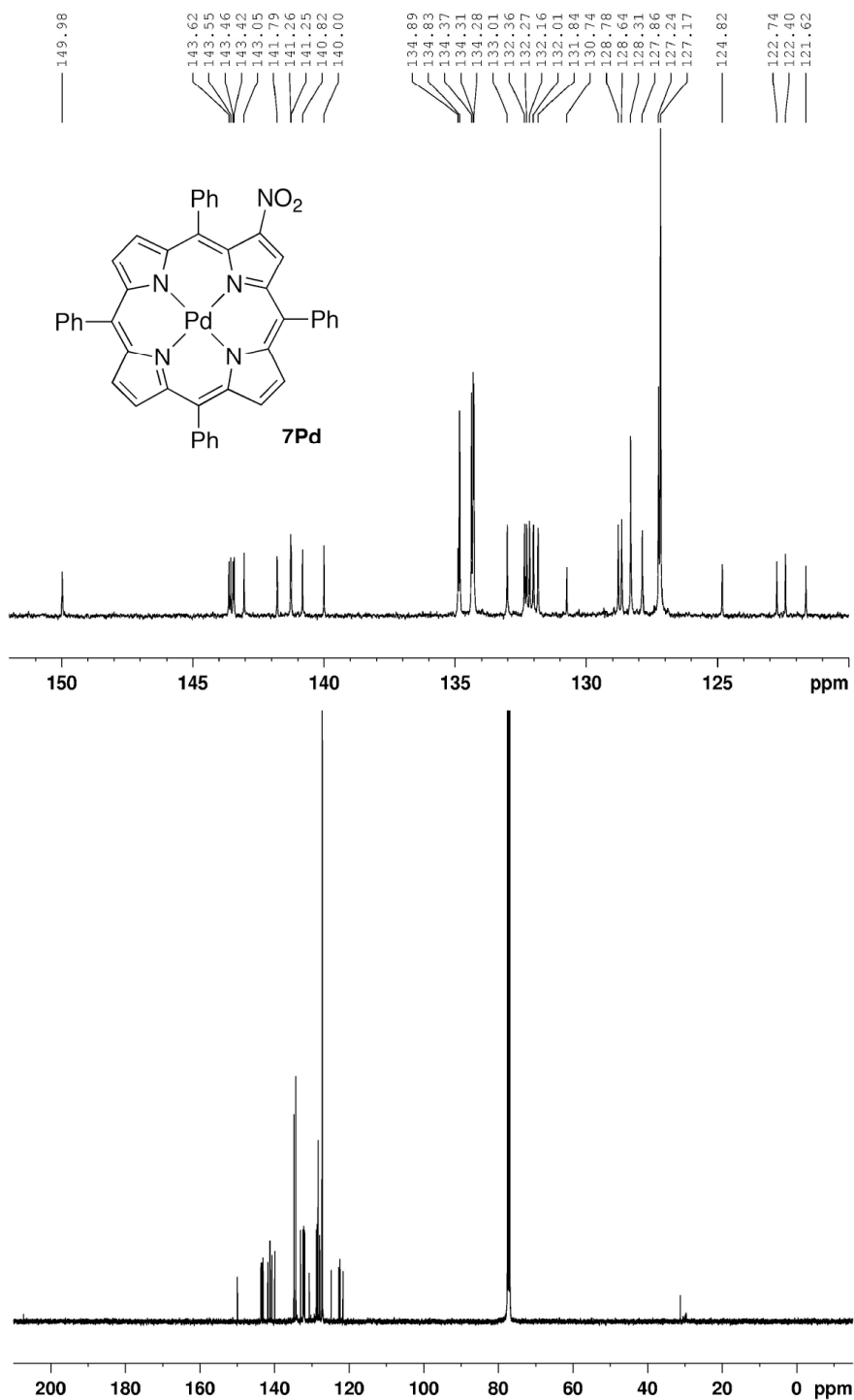


Figure ESI-14. ¹³C NMR Spectrum (100 MHz, CDCl₃) of **7Pd**

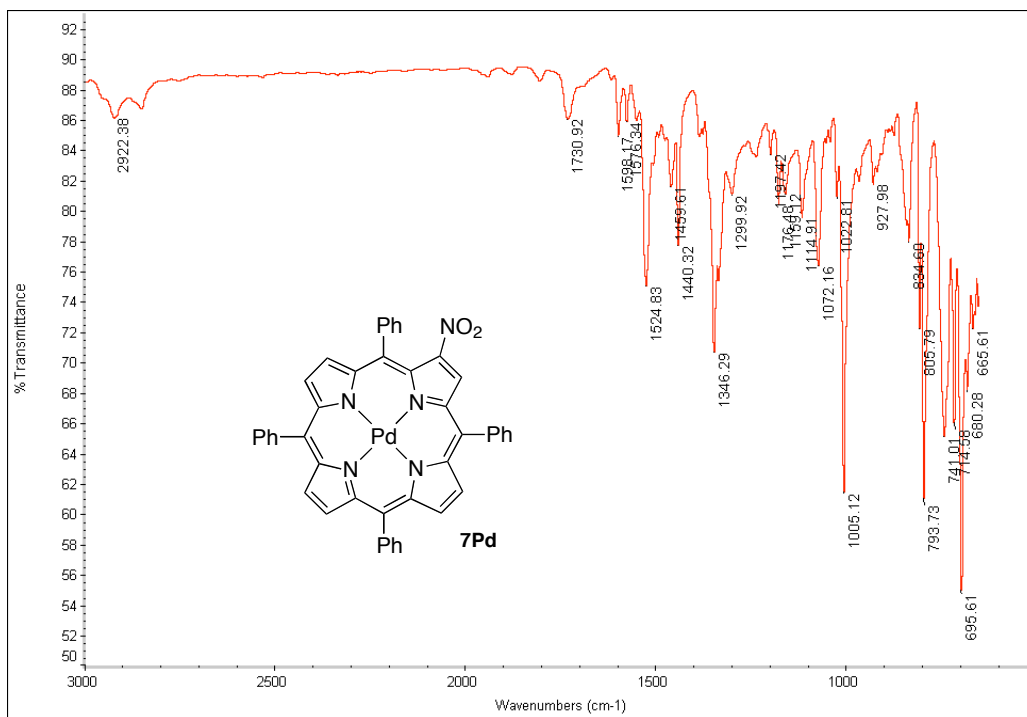


Figure ESI-15. FT-IR Spectrum (neat, diffuse reflectance) of **7Pd**

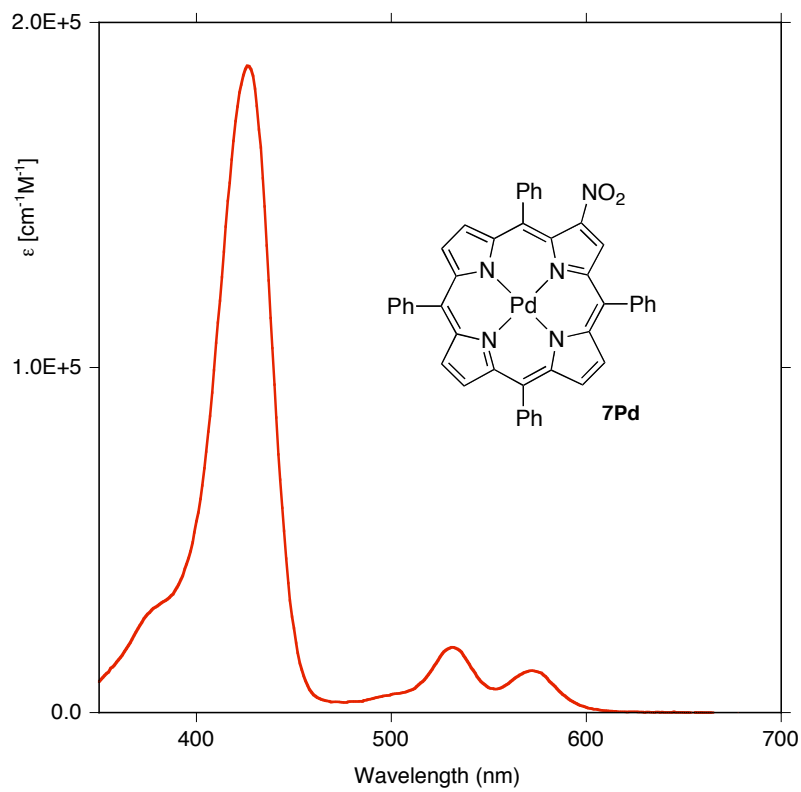


Figure ESI-16. UV-vis spectrum (CH₂Cl₂) of **7Pd**

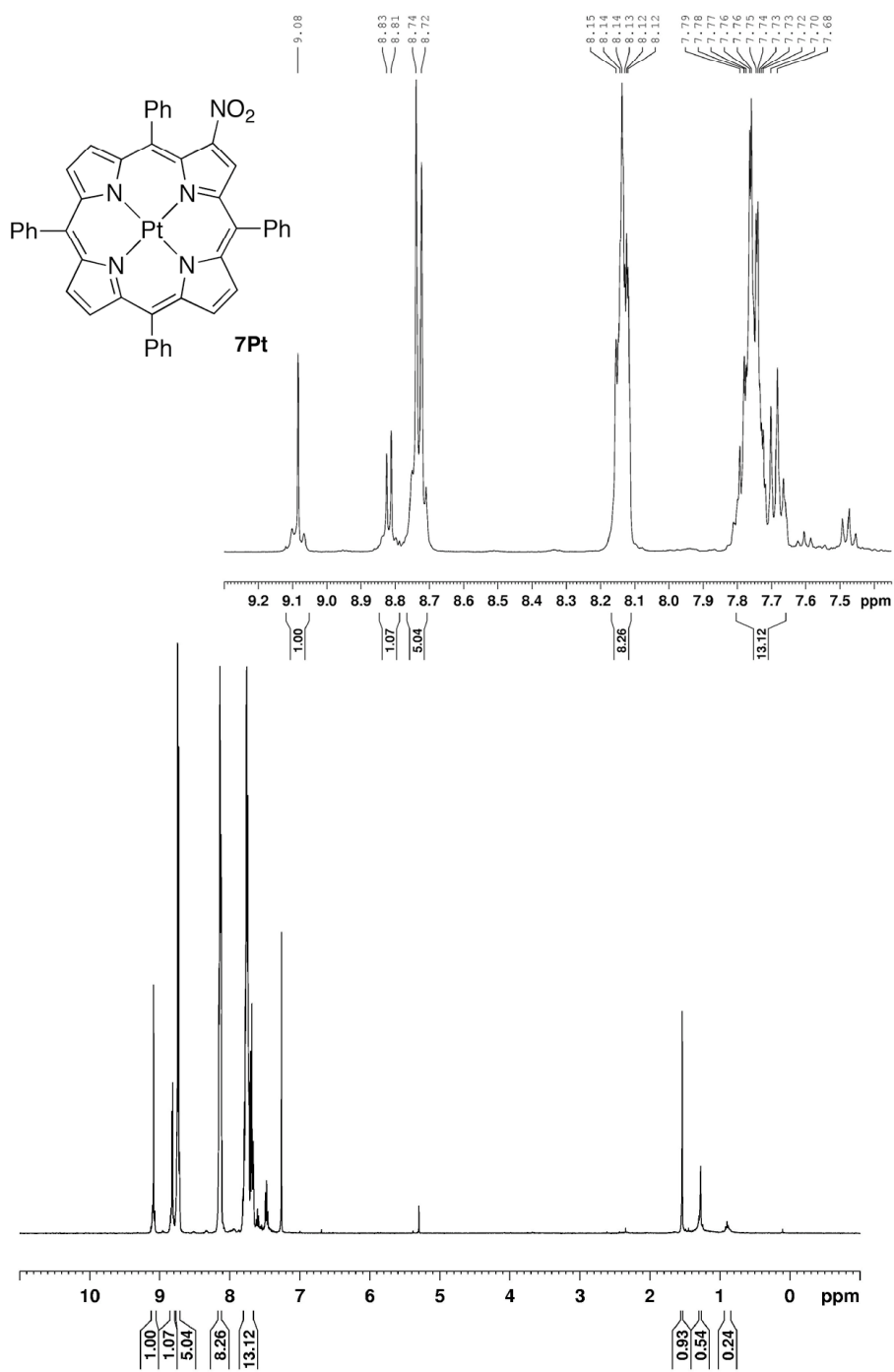


Figure ESI-17. ¹H NMR Spectrum (400 MHz, CDCl₃) of **7Pt**

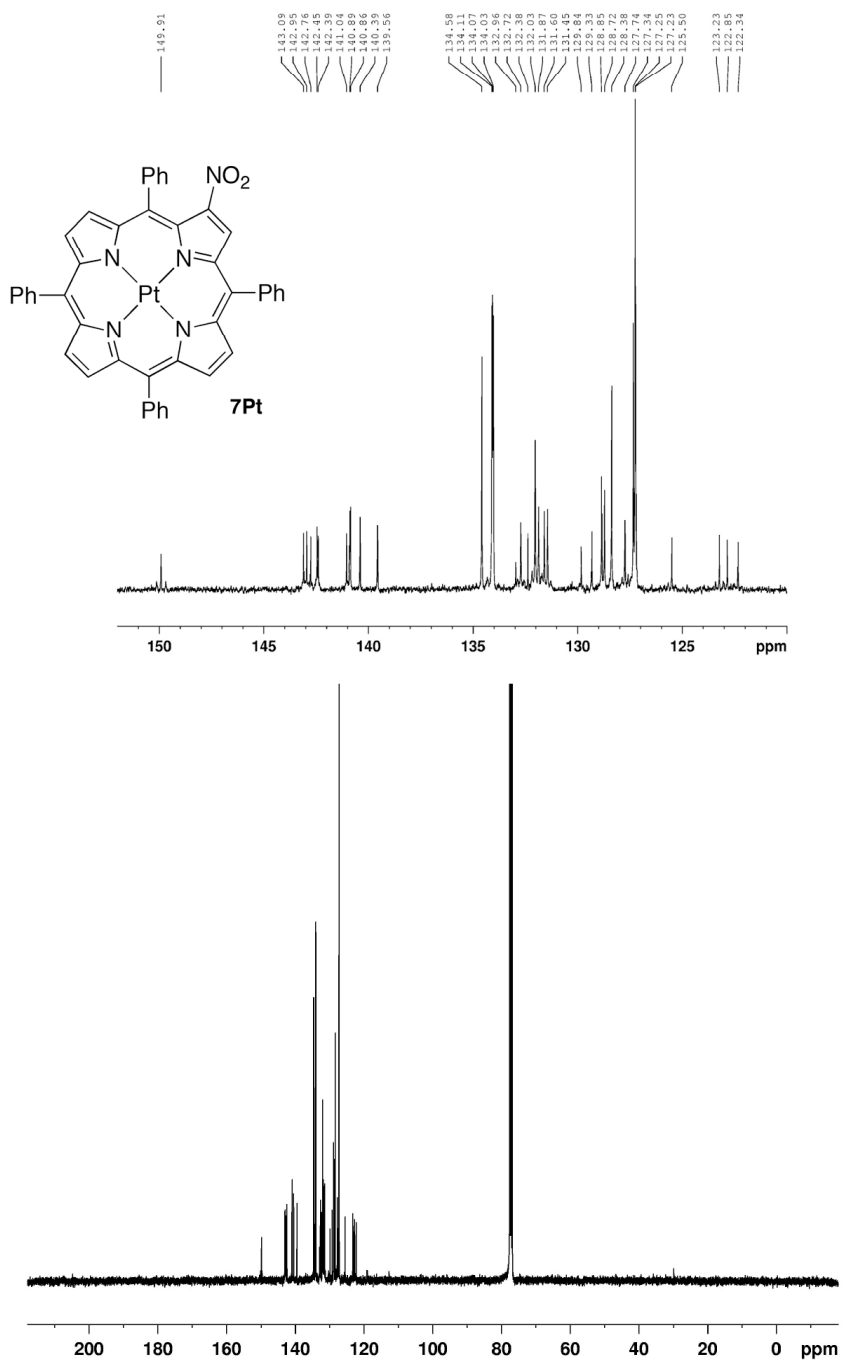


Figure ESI-18. ^{13}C NMR Spectrum (100 MHz, CDCl_3) of **7Pt**

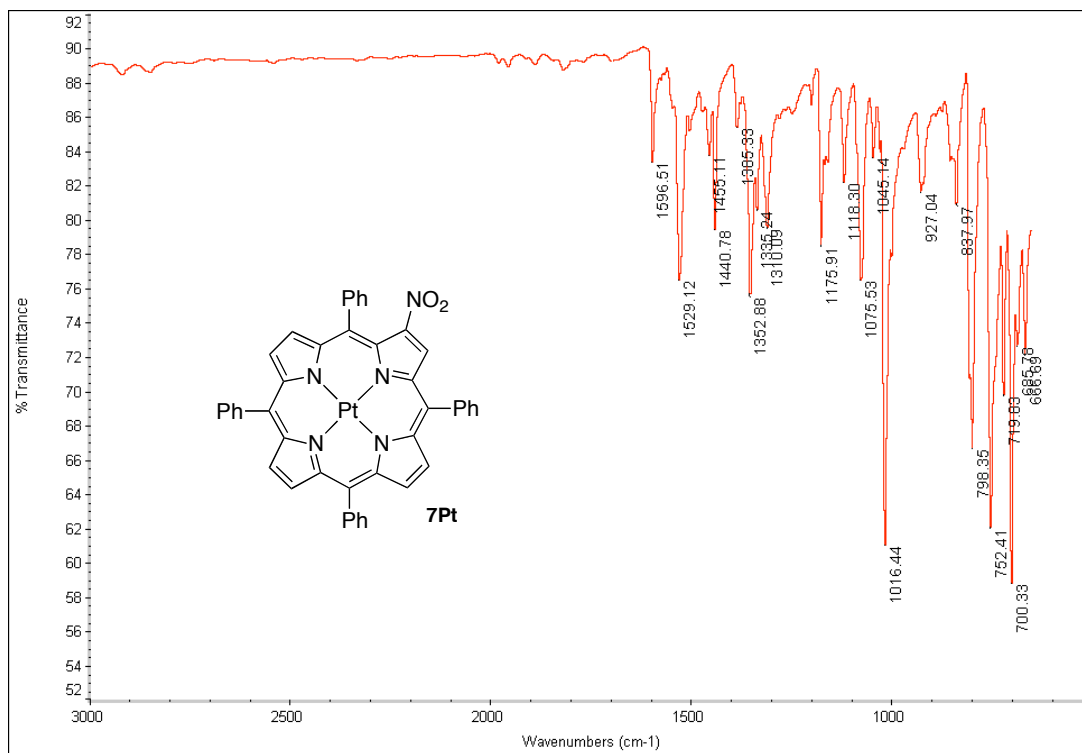


Figure ESI-19. FT-IR Spectrum (neat, diffuse reflectance) of **7Pt**

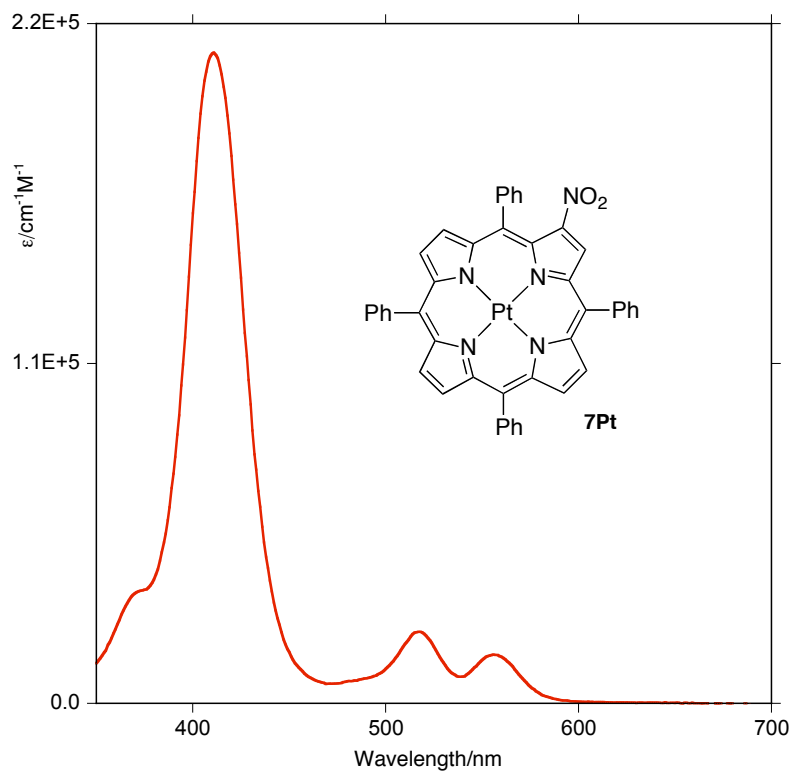


Figure ESI-20. UV-vis Spectrum (CH₂Cl₂) of **7Pt**

Details to the Single Crystal Diffractometry Studies

Experimental table

Compound	7	6
<i>Crystal data</i>		
Internal code	09mz434_0m	09mz366_0m
Chemical formula	C ₄₅ H ₃₃ N ₅ O ₃	C ₄₃ H ₂₉ N ₅
Moiety formula	C ₄₄ H ₂₉ N ₅ O ₂ · C ₁ H ₄ O ₁	---
<i>M_r</i>	691.76	615.71
Cell setting, space group	Monoclinic, <i>C2/c</i>	Triclinic, <i>P-1</i>
Temperature (K)	100 (2)	100 (2)
<i>a</i> , <i>b</i> , <i>c</i> (Å)	38.963 (16), 9.070 (4), 25.863 (11)	6.334 (2), 10.352 (3), 12.149 (4)
α , β , γ (°)	90.00, 130.953 (5), 90.00	94.288 (5), 99.895 (5), 101.107 (5)
<i>V</i> (Å ³)	6902 (5)	765.2 (4)
<i>Z</i>	8	1
<i>D_x</i> (Mg m ⁻³)	1.331	1.336
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α
μ (mm ⁻¹)	0.09	0.08
Crystal form, colour	Plate, black	Needle, black
Crystal size (mm)	0.24 × 0.22 × 0.08	0.42 × 0.09 × 0.07
Data collection		
Diffractometer	Bruker AXS SMART APEX CCD diffractometer	Bruker AXS SMART APEX CCD diffractometer
Data collection method	ω scans	ω scans
Absorption correction	Multi-scan (based on symmetry- related measurements)	Multi-scan (based on symmetry- related measurements)
<i>T_{min}</i>	0.614	0.529
<i>T_{max}</i>	0.746	0.746
No. of measured, independent and observed reflections	16363, 7040, 3065	7609, 3744, 2093
Criterion for observed reflections	<i>I</i> > 2σ(<i>I</i>)	<i>I</i> > 2σ(<i>I</i>)
<i>R_{int}</i>	0.089	0.059
θ_{\max} (°)	26.4	28.3

Refinement

Refinement on	F^2	F^2
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.086, 0.278, 0.96	0.062, 0.163, 1.09
No. of reflections	7040 reflections	3744 reflections
No. of parameters	480	223
H-atom treatment	Constrained to parent site	Constrained to parent site
Weighting scheme	Calculated $w = 1/[\sigma^2(F_o^2) + (0.1485P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$	Calculated $w = 1/[\sigma^2(F_o^2) + (0.0351P)^2 + 0.6297P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$	0.001	0.004
$\Delta\rho_{\max}, \Delta\rho_{\min}$ (e \AA^{-3})	1.32, -0.41	0.27, -0.38

Computer programs: *Apex2 v2009.7-0* (Bruker, 2009); *Apex2 v2009.7-0*; *SHELXTL 6.14* (Bruker, 2000-2003; Sheldrick, 2008); *SHELXTL 6.14*.

Comments:

Diffraction data were collected on a Bruker AXS SMART APEX CCD diffractometer at 100 K using monochromatic Mo K α radiation with the omega scan technique. Data for both structures were collected, their unit cells determined, and the data integrated and corrected for absorption and other systematic errors using the Apex2 suite of programs.¹ The structures were solved by direct methods and refined by full matrix least squares against F^2 with all reflections using SHELXTL.²

Crystals especially of the 7 (09mz434_0m) sample were very weakly diffracting, even at the 100 K data collection temperature, and data for this sample were thus collected with 1.5 minutes exposure time per frame. The resultant data set is still weak with quite high R values, but the data could be refined without any use of restraints or constraints and all quality indicators but the R values are in acceptable ranges.

¹ Apex2 v2009.7-0 (2009) Bruker Advanced X-ray Solutions, Bruker AXS Inc., Madison, Wisconsin, USA.

² SHELXTL (Version 6.14) (2000-2003) Bruker Advanced X-ray Solutions, Bruker AXS Inc., Madison, Wisconsin: USA.

Despite of the quite well diffracting crystals of the imidazole-TPP sample an unusually long exposure time of 60 seconds was chosen for this sample as well so as to allow for a reliable refinement of occupancy factors for superimposed disordered atoms.

For the imidazole TTP compound the nitrogen atom N3 is disordered over four chemically equivalent positions and across the inversion center of the molecule. It was thus refined as being disordered over the four positions with a combined occupancy of one half. The four partially occupied nitrogen atoms were constrained to have the same positions and thermal parameters as the carbon atoms it is sharing the site with. Occupancies of the N atoms refined to 0.090(4), 0.061(3), 0.171(3) and 0.171(3). The N-H hydrogen atoms were refined as disordered over the two alternative sites, the occupancy ratio refined to 0.663(4) to 0.337(4). The occupancies of N atom and H atom, while refined independently of each other, follow the same trend (the imidazole heterocycle seems to be not protonated).

The X-ray diffractometer was funded by NSF Grant 0087210, Ohio Board of Regents Grant CAP-491, and by Youngstown State University.

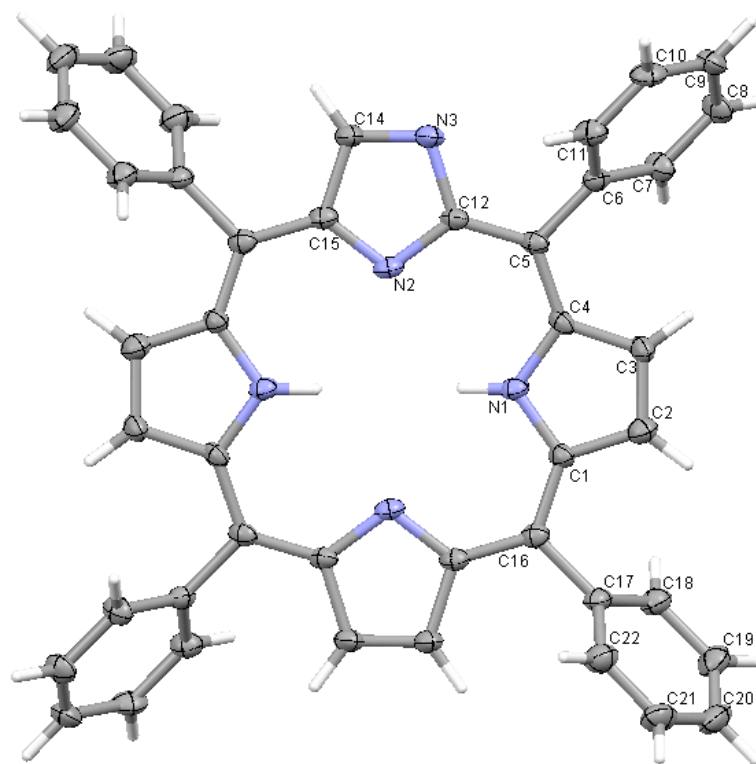


Figure ESI-21. ORTEP Representation of the crystal structure of **6** and the numbering system used.

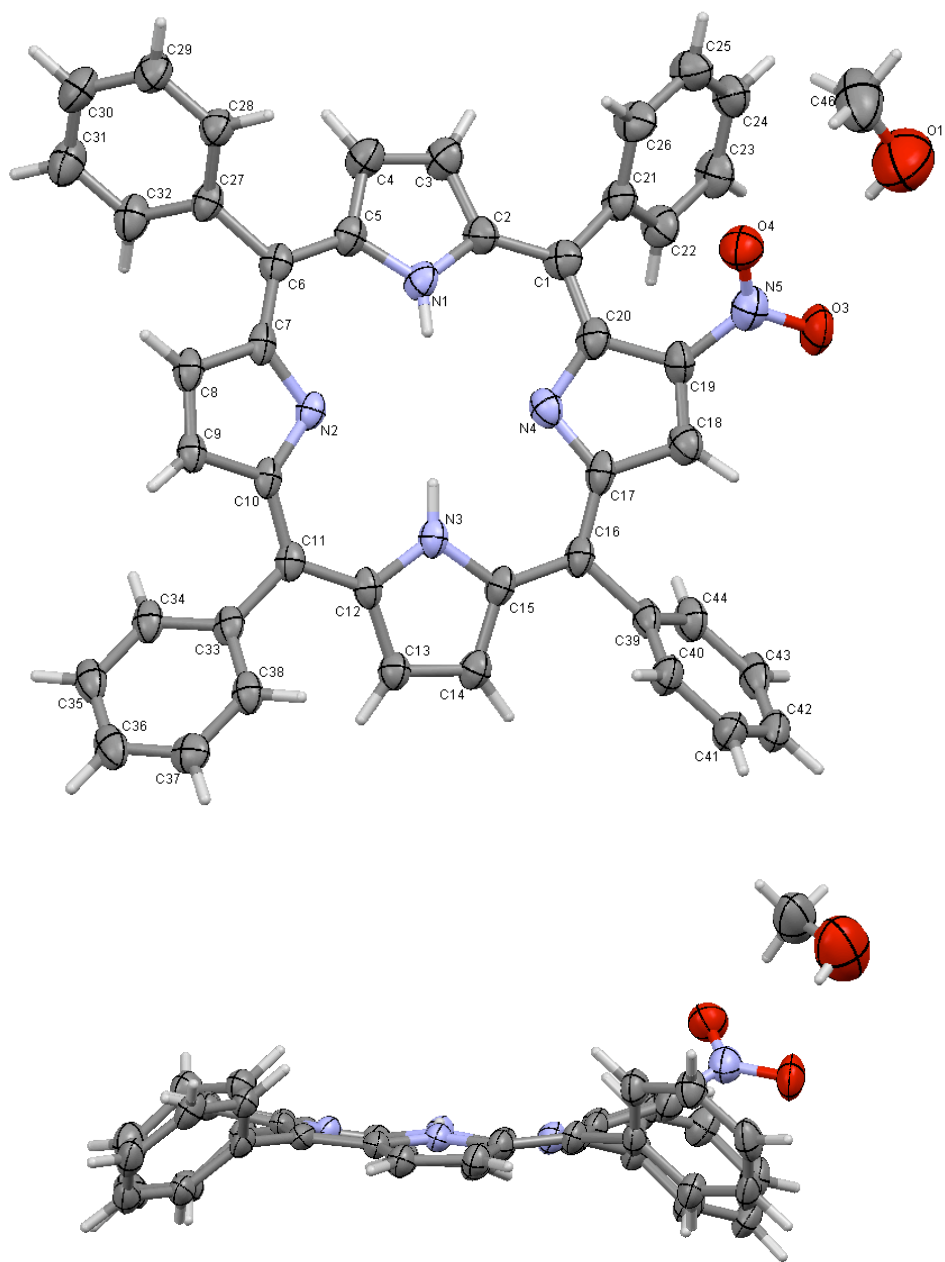


Figure ESI-22. ORTEP Representation (top and side view) of the crystal structure of 7·CH₃OH and the numbering system used.