Electronic Supplementary Information: Adding to the Confusion! Synthesis and Metalation of Pyrazole Analogues of the Porphyrins

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Experimental procedures

Barium manganate, nickel(II) acetate and palladium(II) acetate were obtained from Aldrich or Acros. Dialdehydes **5b**[1] and **5c**,[2] and tripyrrane **6**,[3,4] were prepared by literature procedures. Melting points were determined in open capillary tubes on a Mel-Temp apparatus and are uncorrected. UV-vis absorption spectra were run on a Varian Cary Spectrophotometer, and NMR data were obtained on a Varian Gemini 400 MHz FT-NMR spectrometer. Mass spectral determinations were conducted at the Mass Spectral Laboratory, School of Chemical Sciences, University of Illinois at Urbana-Champaign, and elemental analyses were obtained from the School of Chemical Sciences Microanalysis Laboratory at the University of Illinois.

1-Phenylpyrazole-3,5-dicarboxaldehyde (5b). Barium manganate (5.9 g; 23 mmol) was added to a solution of 920 mg (4.55 mmol) of 3-hydroxymethyl-1-phenyl-5-pyrazolecarbaldehyde[1] in 100 mL of 1,1,2-trichloroethane and the mixture was refluxed with vigorous stirring for 3 h. The mixture was filtered through Celite, washed thoroughly with dichloromethane, and concentrated under reduced pressure to leave a residue which was purified on a silica gel column by eluting with toluene. Evaporation of the product fraction afforded 1-phenylpyrazole-3,5-dicarbaldehyde

(469 mg; 2.35 mmol; 52%) as a syrup that gradually crystallized to give yellow crystals, mp 84-85 °C (lit. mp[1] 84-85 °C); ^{1}H NMR ($CDCl_3$): δ 7.53-7.60 (6H, m), 9.91 (1H, s), 10.10 (1H, s); ^{13}C NMR ($CDCl_3$): δ 111.7, 125.8, 129.8, 130.3, 138.5, 141.8, 151.6, 179.5, 185.8.

N-Phenyl-2,3-diaza-21-carbaphlorin 7a. Tripyrrane dicarboxylic acid **6**[3,4] (100 mg; 0.220 mmol) was stirred with TFA (1 mL) under nitrogen for 2 min. The mixture was diluted with dichloromethane (99 mL) and 1-phenylpyrazole-3,5-dicarbaldehyde (48.0 mg; 0.24 mmol) was immediately added in a single portion. The resulting solution was stirred overnight under nitrogen and then washed with water, 0.1% ferric chloride solution, water, and saturated sodium bicarbonate (the aqueous solutions were back-extracted with chloroform at each stage in the extractions). The solvent was removed under reduced pressure and the residue chromatographed on grade 3 basic alumina, eluting with dichloromethane. The solvent was removed under reduced pressure and recrystallized from chloroform-methanol to yield the pyrazole porphyrin analogue (47.5 mg; 0.090 mmol; 41%) as dark blue crystals, mp >300 °C; UV-vis (1% Et_3N-$CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) 377 (4.67), 528 (sh, 4.08), 578 (4.27), 627 (4.28);^{1}H NMR ($CDCl_3$): δ 1.16-1.25 (12H, m), 2.09 (3H, s), 2.15 (3H, s), 2.56-2.63 (4H, m), 2.64-2.74 (4H, m), 4.17 (2H, s), 5.84 (1H, s), 5.90 (1H, s), 6.34 (1H, s), 6.84 (1H, s), 7.35 (1H, t, J = 7.0 Hz), 7.44 (2H, t, J = 7.8 Hz), 7.51 (2H, d, J = 8.0 Hz), 9.17 (2H, br s); ^{13}C NMR ($CDCl_3$): δ 9.1, 9.5, 14.8, 16.0, 16.5, 17.3, 17.8, 18.27, 18.29, 18.4, 26.1, 87.2, 89.4, 104.7, 111.8, 116.7, 124.7, 127.6, 129.0, 129.2, 129.3, 132.1, 133.5, 136.2, 137.5, 140.5, 141.4, 146.0, 147.3, 147.8, 148.1, 165.1; HR MS (FAB): Calc. for $C_{35}H_{39}N_5$: 529.3205. Found: 529.3206. Anal. calcd for $C_{35}H_{39}N_5 \cdot 0.6CHCl_3$: C, 71.10; H, 6.30; N, 11.64. Found: C, 70.79; H, 6.70; N, 11.22.

8,12,13,17-Tetraethyl-2,7,18-trimethyl-2,3-diaza-21-carbaporphyrin (**8b**). Tripyrrane dicarboxylic acid **6**[3,4] (100 mg; 0.220 mmol) and 1-methylpyrazole-3,5-dicarbaldehyde (31.0 mg; 0.225 mmol) were reacted in the presence of TFA (1 mL) in dichloromethane (99 mL) under the foregoing conditions. The reaction solution was shaken vigorously with 0.2% aqueous ferric chloride solution (100 mL) for 7-8 min. The two layers were separated, the aqueous solution was extracted with chloroform, and the combined organic solutions were washed with water (100 mL) and saturated sodium bicarbonate solution (100 mL). The solvent was evaporated under reduced pressure and the dark colored residue was run through a grade 3 basic alumina column eluting with dichloromethane. A dark fraction was collected and rechromatographed on grade 3 basic alumina eluting initially with 50% dichloromethane-hexanes and then with 70% dichloromethane-hexanes. Unidentified green and blue colored fractions eluted initially followed by a turquoise fraction that corresponded to the pyrazole-containing porphyrin analogue. Evaporation of the solvent gave the title compound (21.6 mg; 0.0465 mmol; 21%) as blue-green crystals, mp >300 °C. A sample was recrystallized from chloroform-ligroin to give dark blue-green crystals, mp > 300 °C; UV-vis (1% Et_3N-$CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) 323 (4.65), 393 (4.77), 639 nm (3.82); UV-vis ($CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) 378 (4.58), 569 (4.10), 607 (4.13), 707 nm (3.77); UV-vis (5 eq TFA-$CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) 403 (4.67), 526 (3.65), 567 (3.85), 711 (4.22), 787 nm (3.97); UV-vis (5% TFA-$CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) 348 (4.60), 408 (4.80), 546 (3.58), 588 (3.62), 735 nm (3.84); ^{1}H NMR ($CDCl_3$): δ 1.31-1.35 (6H, 2 overlapping triplets), 1.39-1.43 (6H, 2 overlapping triplets), 2.49 (6H, s), 2.84-2.90 (2H, 2 overlapping quartets), 2.97-3.03 (4H, 2 overlapping quartets), 4.50 (3H, s), 5.34 (1H, s), 6.75 (1H, br s), 6.89 (1H, s), 6.95 (1H, s), 7.45

(1H, s), 7.82 (1H, s); ^{1}H NMR (trace TFA-CDCl$_3$): δ 0.3 (1H, br s), 1.48-1.56 (12H, m), 2.97 (H, s), 3.02 (3H, s), 3.14-3.34 (8H, m), 4.89 (3H, s), 7.85 (2H, s), 8.83 (1H, s), 9.10 (1H, s); ^{1}H NMR (TFA-CDCl$_3$): δ 1.37-1.43 (12H, s), 2.77 (1H, s), 2.79 (3H, s), 2.83 (3H, s), 3.06-3.14 (8H, m), 4.56 (3H, s), 7.47 (1H, s), 7.52 (1H, s), 8.27 (1H, s), 8.72 (1H, s); ^{13}C NMR (CDCl$_3$): δ 10.1, 15.6, 16.3, 18.4, 18.6, 18.7, 37.6, 92.7, 94.3, 104.3, 109.2, 114.9, 138.5, 139.4, 140.0, 140.5, 141.1, 141.6, 142.8, 146.2, 146.7, 147.5, 157.5, 158.0, 166.5, 167.5; ^{13}C NMR (TFA-CDCl$_3$): δ 10.7, 10.9, 14.6, 14.7, 15.4, 15.5, 18.46, 18.50, 18.80, 18.86, 39.9, 93.6, 94.9, 95.9, 109.2, 120.9, 137.5, 142.9, 143.9, 144.3, 145.2, 145.5, 146.8, 147.3, 147.7, 147.9, 153.3, 154.8, 159.1, 159.9; HR MS (EI): Calc. for $C_{30}H_{35}N_5$: 465.28925. Found: 465.28925.

[8,12,13,17-tetraethyl-7,18-dimethyl-2-phenyl-2,3-diaza-21-carbaporphyrinato]nickel(II) (**12a**). Two equivalents of nickel(II) acetate tetrahydrate (12.0 mg; 0.0480 mmol; 2 equiv) were added to a solution of phlorin analogue **7a** (12.7 mg; 0.0240 mmol) in DMF (13 mL), and the solution was stirred under reflux for 30 min. The solution was cooled, diluted with chloroform, and washed with water. The organic layer was separated, evaporated to dryness and chromatographed on grade 3 basic alumina, eluting with chloroform, to give a dark green band. The solvent was evaporated to dryness and the residue recrystallized from chloroform-methanol to yield the nickel(II) complex (6.0 mg; 0.0103 mmol; 43%) as dark purple crystals, mp >300 °C; (CHCl$_3$): λ_{max} (log$_{10}$ε) 343 (4.63), 394 (4.65), 441 (sh, 4.16), 500 (3.89), 535 (4.05), 621 (3.87), 774 (2.99), 866 (2.92); UV-vis (1% TFA-CHCl$_3$): λ_{max} (log$_{10}$ε) 302 (sh, 4.41), 329 (4.48), 375 (4.71), 681 (3.73), 845 (3.13); ^{1}H NMR (CDCl$_3$): δ 1.33-1.39 (6H, 2 overlapping triplets), 1.42-1.47 (6H, 2 overlapping triplets), 2.45 (3H, s), 2.56 (3H, s), 2.92-3.06 (8H, m), 7.38 (1H, s), 7.45 (1H, s), 7.56 (1H, t, *J* = 8.0 Hz), 7.58 (1H, s), 7.68 (2H, t, *J* = 7.8 Hz), 7.85 (2H, d, *J* = 7.6 Hz), 8.02 (1H, s); ^{1}H NMR (TFA-CDCl$_3$): δ 1.16-1.23 (6H, 2 overlapping triplets), 1.29 (6H, t, *J* = 7.6 Hz), 2.05 (3H, s), 2.17 (3H, s), 2.53-2.61 (4H, m), 2.67 (4H, q, *J* = 7.6 Hz), 6.42 (1H, s), 6.49 (2H, s), 6.90 (1H, s), 7.57-7.62 (2H, m), 7.66-7.70 (3H, m); ^{13}C NMR (CDCl$_3$): δ 10.4, 10.5, 15.4, 15.6, 16.6, 18.66, 18.71, 18.77, 95.5, 96.1, 104.1, 113.6, 126.5, 128.3, 129.6, 137.3, 139.3, 140.0, 140.4, 141.1, 141.5, 144.6, 144.9, 148.4, 149.7, 151.1, 154.0, 154.4, 158.9, 160.0; HR MS (EI): Calc. for $C_{35}H_{35}N_5Ni$: 583.2246. Found: 583.2248. Anal. calcd for $C_{35}H_{35}N_5Ni\cdot0.5H_2O$: C, 70.84; H, 6.11; N, 11.79. Found: C, 70.56; H, 6.11; N, 11.33.

[8,12,13,17-Tetraethyl-2,7,18-trimethyl-2,3-diaza-21-carbaporphyrinato]nickel(II) (12b). Porphyrin analogue **8b** (34 mg; 0.0731 mmol) and nickel(II) acetate tetrahydrate (36 mg; 0.145 mmol; 2 equiv) were reacted in DMF (37 mL) under the foregoing conditions. Recrystallization from chloroform-methanol gave the nickel complex (17.0 mg; 0.0326 mmol; 45%) as dark green crystals, mp >300 °C; UV-vis (CHCl$_3$): λ_{max} (log$_{10}$ε) 340 (4.64), 393 (4.62), 497 (3.72), 533 (3.91), 614 (3.85), 731 (2.86), 870 nm (2.83); UV-vis (1% TFA-CHCl$_3$): λ_{max} (log$_{10}$ε) 325 (4.44), 370 (4.70), 683 (3.69), 842 nm (3.08); ^{1}H NMR (CDCl$_3$): δ 1.34-1.39 (6H, 2 overlapping triplets), 1.42-1.47 (6H, 2 overlapping triplets), 2.54 (3H, s), 2.56 (3H, s), 2.93-3.07 (8H, m), 4.53 (3H, s), 7.43 (1H, s), 7.47 (1H, s), 7.56 (1H, s), 7.96 (1H, s); ^{1}H NMR (TFA-CDCl$_3$): δ 1.16-1.21 (6H, 2 overlapping triplets), 1.27 (6H, t, *J* = 7.5 Hz), 2.14 (3H, s), 2.16 (3H, s), 2.52-2.60 (4H, 2 overlapping quartets), 2.65 (4H, q, *J* = 7.6 Hz), 4.31 (3H, s), 6.47 (2H, s), 6.52 (1H, s), 6.78 (1H, s); ^{13}C NMR (CDCl$_3$): δ 10.4, 10.5, 15.5, 15.7, 16.64, 16.70, 18.65, 18.71, 18.79, 95.3, 96.2, 102.0, 109.7, 113.6, 137.8, 138.9, 139.9, 140.7, 141.5, 144.6, 146.8, 149.3, 149.9, 153.4, 154.1, 158.5, 159.2; HR MS (EI): Calc. for $C_{30}H_{33}N_5Ni$: 521.2089. Found: 521.2093.

[8,12,13,17-tetraethyl-7,18-dimethyl-2-phenyl-2,3-diaza-21-carbaporphyrinato]palladium(II) (13a). Palladium(II) acetate (5.4 mg; 0.024 mmol) was added to a solution of pyrazole phlorin **7a** (12.7 mg; 0.0240 mmol) in acetonitrile (40 mL), and the solution was stirred under reflux for 30 min. The solution was cooled, diluted with chloroform, washed with water, and the organic layer separated and then evaporated to dryness. The residue was chromatographed on grade 3 basic alumina, eluting with chloroform, and the product was collected as a reddish/brown band. The solvent was evaporated to dryness and the residue recrystallized from chloroform-methanol to yield the palladium(II) complex (8.9 mg; 0.0141 mmol; 59%) as dark purple crystals, mp >300 °C; UV-vis ($CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) 318 (4.42), 350 (sh, 4.35), 370 (sh, 4.38), 395 (sh, 4.48), 415 (4.58), 484 (sh, 3.69), 524 (3.93), 575 (3.81), 674 (3.26), 740 (3.36), 821 (3.19); UV-vis (5% TFA-$CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) 307 (4.47), 374 (sh, 4.59), 390 (4.69), 542 (sh, 3.56), 578 (3.61), 622 (sh, 3.49), 746 (3.34), 833 (3.41); ^1H NMR ($CDCl_3$): δ 1.36-1.42 (6H, 2 overlapping triplets), 1.46 (6H, t, *J* = 7.6 Hz), 2.53 (3H, s), 2.62 (3H, s), 2.96-3.05 (8H, m), 7.35 (1H, s), 7.40 (1H, s), 7.57 (1H, t, *J* = 7.6 Hz), 7.61 (1H, s), 7.69 (2H, t, *J* = 7.8 Hz), 7.89 (2H, d, *J* = 7.6 Hz), 8.02 (1H, s); ^1H NMR (5 drops TFA-$CDCl_3$): δ 1.08-1.20 (12H, m), 1.98 (3H, s), 2.08 (3H, s), 2.40-2.55 (8H, m), 6.18 (1H, br s), 6.21 (2H, br s), 6.60 (1H, br s), 7.45-7.50 (2H, m), 7.55-7.61 (3H, m); ^{13}C NMR ($CDCl_3$): δ 10.3, 10.4, 15.3, 15.5, 16.59, 16.66, 16.79, 18.6, 18.8, 18.9, 95.7, 96.7, 106.4, 115.6, 126.5, 129.6, 135.3, 138.2, 138.8, 140.5, 140.7, 143.9, 144.2, 146.0, 147.1, 148.7, 152.8, 155.8, 157.1; HR MS (EI): Calc. for $C_{35}H_{35}N_5Pd$: 631.1927. Found: 631.1930.

[8,12,13,17-Tetraethyl-2,7,18-trimethyl-2,3-diaza-21-carbaporphyrinato]palladium(II) (13b). Using the foregoing procedure, pyrazole porphyrin analogue **8b** (21.0 mg; 0.045 mmol) was reacted with palladium(II) acetate (10.0 mg; 0.045 mmol) in acetonitrile (65 mL). Following chromatography on grade 3 basic alumina, eluting with chloroform, the product was recrystallized from chloroform-methanol to give the palladium complex (15.7 mg; 0.0276 mmol; 61%) as dark purplish brown crystals, mp >300 °C; UV-vis ($CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) 320 (4.45), 347 (4.48), 368 (4.47), 414 (4.63), 533 (3.93), 570 (3.87), 674 (3.35), 738 (3.44), 816 nm (3.24);UV-vis (1% TFA-$CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) 304 (4.52), 370 (sh, 4.63), 387 (4.96), 576 (3.64), 817 nm (3.47); ^1H NMR ($CDCl_3$): δ 1.38-1.42 (6H, 2 overlapping triplets), 1.44-1.48 (6H, 2 overlapping triplets), 2.62 (3H, s), 2.63 (3H, s), 2.97-3.06 (8H, m), 4.58 (3H, s), 7.40 (1H, s), 7.44 (1H, s), 7.61 (1H, s), 7.97 (1H, s); ^1H NMR (TFA-$CDCl_3$): δ 1.16-1.27 (12H, m), 2.15 (3H, s), 2.16 (3H, s), 2.50-2.62 (8H, m), 4.26 (3H, s), 6.27 (1H, s), 6.28 (1H, s), 6.34 (1H, s), 6.63 (1H, s); ^{13}C NMR ($CDCl_3$): δ 10.3, 10.4, 15.5, 15.6, 16.7, 16.8, 18.6, 18.8, 18.9, 37.7, 95.6, 96.8, 104.3, 115.7, 121.9, 140.1, 140.7, 135.8, 137.8, 138.6, 143.9, 144.0, 144.3, 146.6, 147.5, 152.2, 152.6, 155.5, 156.3; HR MS (EI): Calc. for $C_{30}H_{33}N_5Pd$: 569.1771. Found: 569.1767.

Crystallographic Experimental Details of 13a.

X-ray quality crystals of **13a** were obtained by recrystallization from chloroform-methanol. The crystals were quickly suspended in mineral oil at ambient temperature and a suitable crystal was selected. A mineral oil coated red plate thereby obtained of approximate dimensions 0.20 x 0.20 x 0.06 mm^3 was mounted on a 50 mm MicroMesh MiTeGen Micromount and transferred to a Bruker AXS SMART APEX CCD diffractometer. The X-ray diffraction data were collected at -173ºC using Mo-K_α (λ = 0.71073 Å) radiation. Data collection and cell refinement were performed using SMART and SAINT+, respectively.[5] The unit cell parameters were obtained from a least-squares refinement of 3358 centered reflections. Compound **13a** was found to crystallize in the monoclinic crystal system with the following unit cell parameters: a = 11.922(2) Å, b = 16.776(3) Å, c = 14.465(3) Å, β = 102.546(3)°, Z = 4. The systematic absences indicated the space group to be $P2_1/n$ (no. 14).[6] A total of 27503 reflections were collected, of which 8558 were unique, and 5376 were observed $F_o^2 > 2\ \sigma(F_o^2)$. Limiting indicies were as follows: $-16 \leq h \leq 17$, $-23 \leq k \leq 23$, $-20 \leq l \leq 18$. Data reduction were accomplished using SAINT.[5] The data were corrected for absorption using the SADABS procedure.[5]

Solution and data analysis were performed using the WinGX software package.[7] The structure of **13a** was solved by direct methods using the program SIR2004[8] and the refinement was completed using the program SHELX-97.[9] All non-hydrogen atoms were refined anisotropically. All H atoms were initially identified through difference Fourier syntheses then removed and included in the refinement in the riding-model approximation (C–H = 0.95, 0.98, and 0.99 Å for Ar–H, CH_3 and CH_2; $U_{iso}(H) = 1.2Ueq(C)$ except for methyl groups, where $U_{iso}(H) = 1.5U_{eq}(C)$). Full-matrix least-squares refinement on F^2 led to convergence, $(\Delta/\sigma)_{max}$ = 0.000, $(\Delta/\sigma)_{mean}$ = 0.0000, with R_1 = 0.0721 for 5736 data with $F_o^2 > 2\sigma(F_o^2)$ and wR_2 = 0.1397 for all data using 0 restraints and 372 parameters. A final difference Fourier synthesis showed features in the range of $\Delta\rho_{max}$ = 0.913 $e^-/Å^3$ to $\Delta\rho_{min}$ = -1.313 $e^-/Å^3$ which were deemed of no chemical significance. The refinement validation program checkcif reported no significant errors. The structure validation program Mogul[10] indicated that most bond distance and angles were within expected norms. Those outside normal ranges may be explained by the nature of the bonding and coordination of the macrocycle.. Molecular diagrams were generated using RASTEP,[11] ORTEP-3[12] and POV-Ray.[13] X-ray structural data has been deposited with the CCDC.[14]

Acknowledgement. This material is based upon work supported by the National Science Foundation under Grant Nos. CHE-0616555 (to TDL), and CHE-0348158 and CHE-0725294 (to GMF), and the Petroleum Research Fund, administered by the American Chemical Society (to TDL). The authors also thank Youngstown State University Structure & Chemical Instrumentation Facility's Matthias Zeller for X-ray data collection. The diffractometer was funded by NSF grant 0087210, Ohio Board of Regents grant CAP-491, and YSU.

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14. Crystallographic data (excluding structure factors) for **13a** have been deposited with the Cambridge Crystallographic Data Center as supplementary publication number CCDC 701970. Copies of this data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 IEZ, UK [fax: +44 (0)12233 336033 or e-mail: deposit@ccdc.cam.ac.uk].

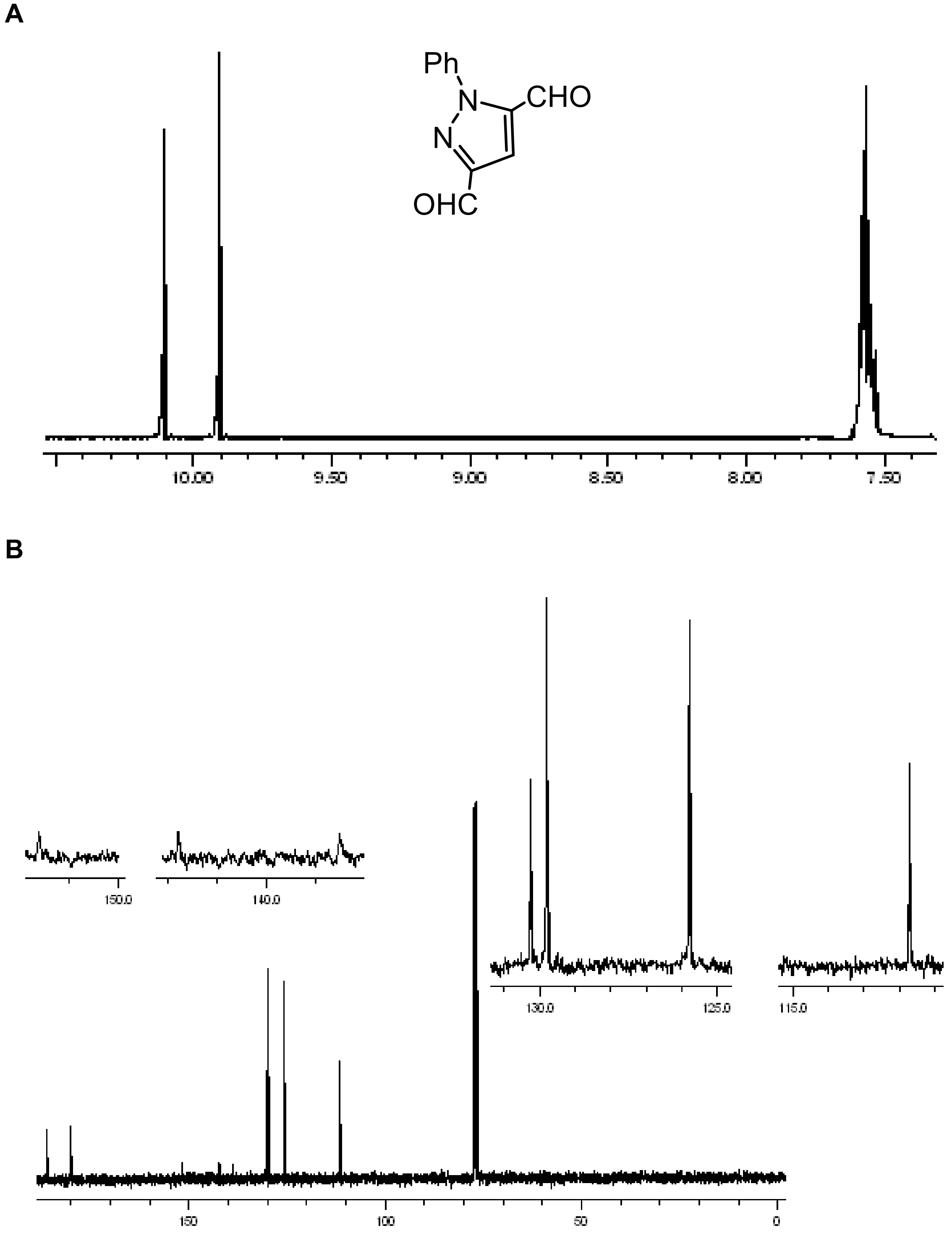


Figure S1: A. 400 MHz proton NMR spectrum of 1-phenyl-3,5-pyrazoledicarbaldehyde (**5b**) in $CDCl_3$. B. 100 MHz carbon-13 NMR spectrum of **5b** in $CDCl_3$.

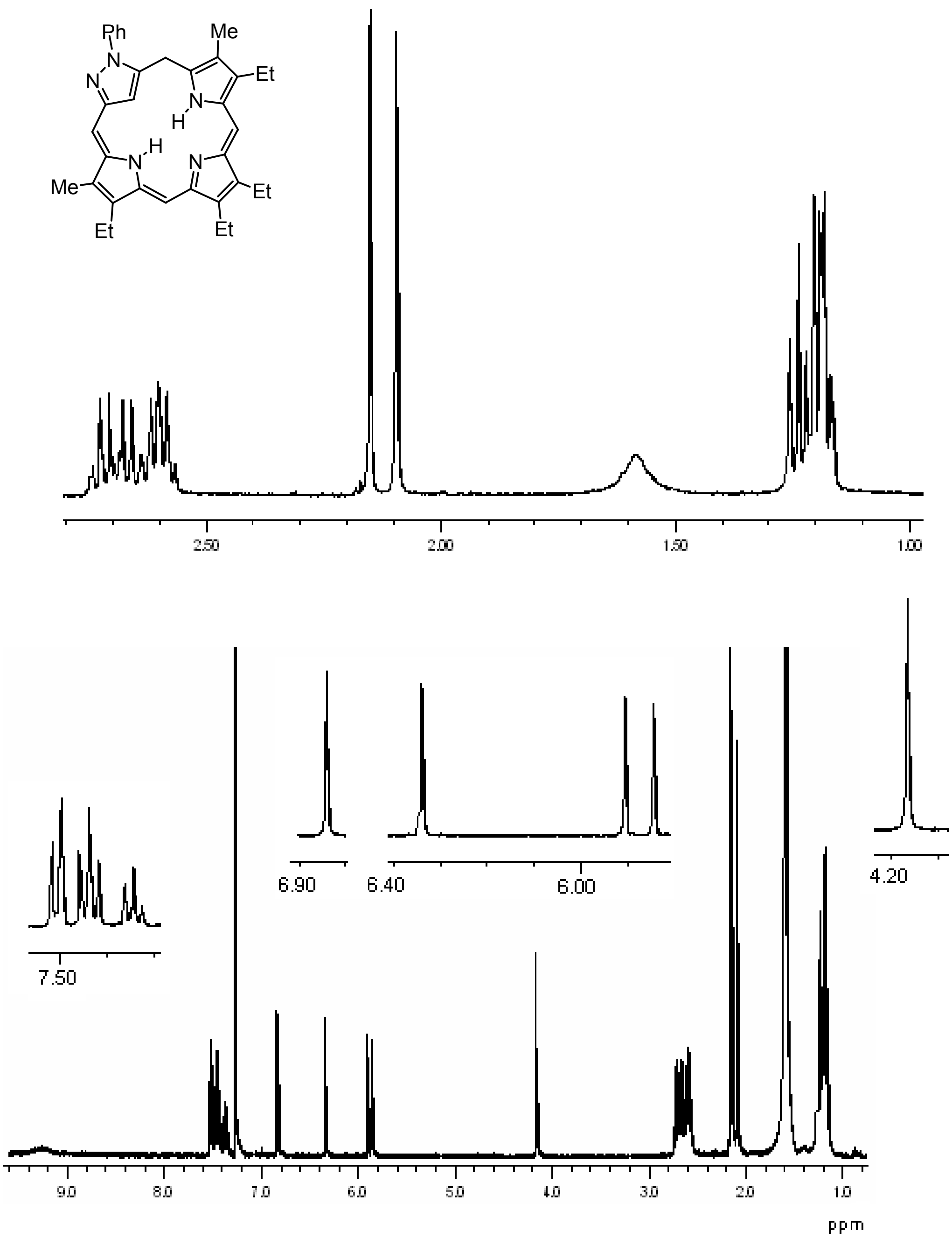


Figure S2: 400 MHz proton NMR spectrum of 2-phenyl-pyrazolephlorin **7a** in $CDCl_3$.

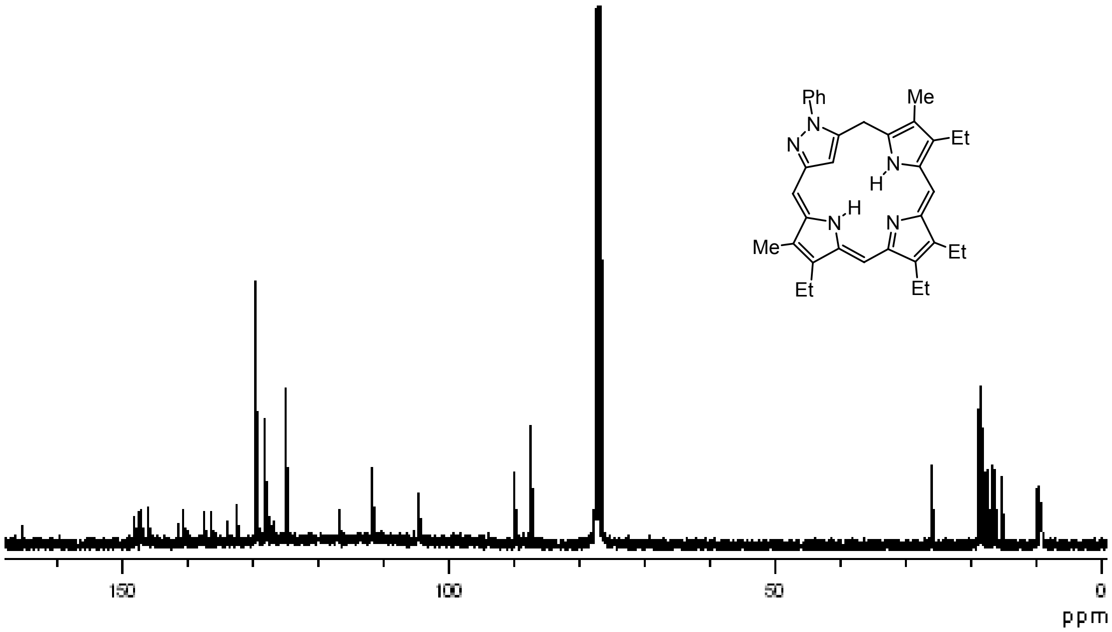


Figure S3: 100 MHz carbon-13 NMR spectrum of 2-phenyl-pyrazolephlorin **7a** in $CDCl_3$.

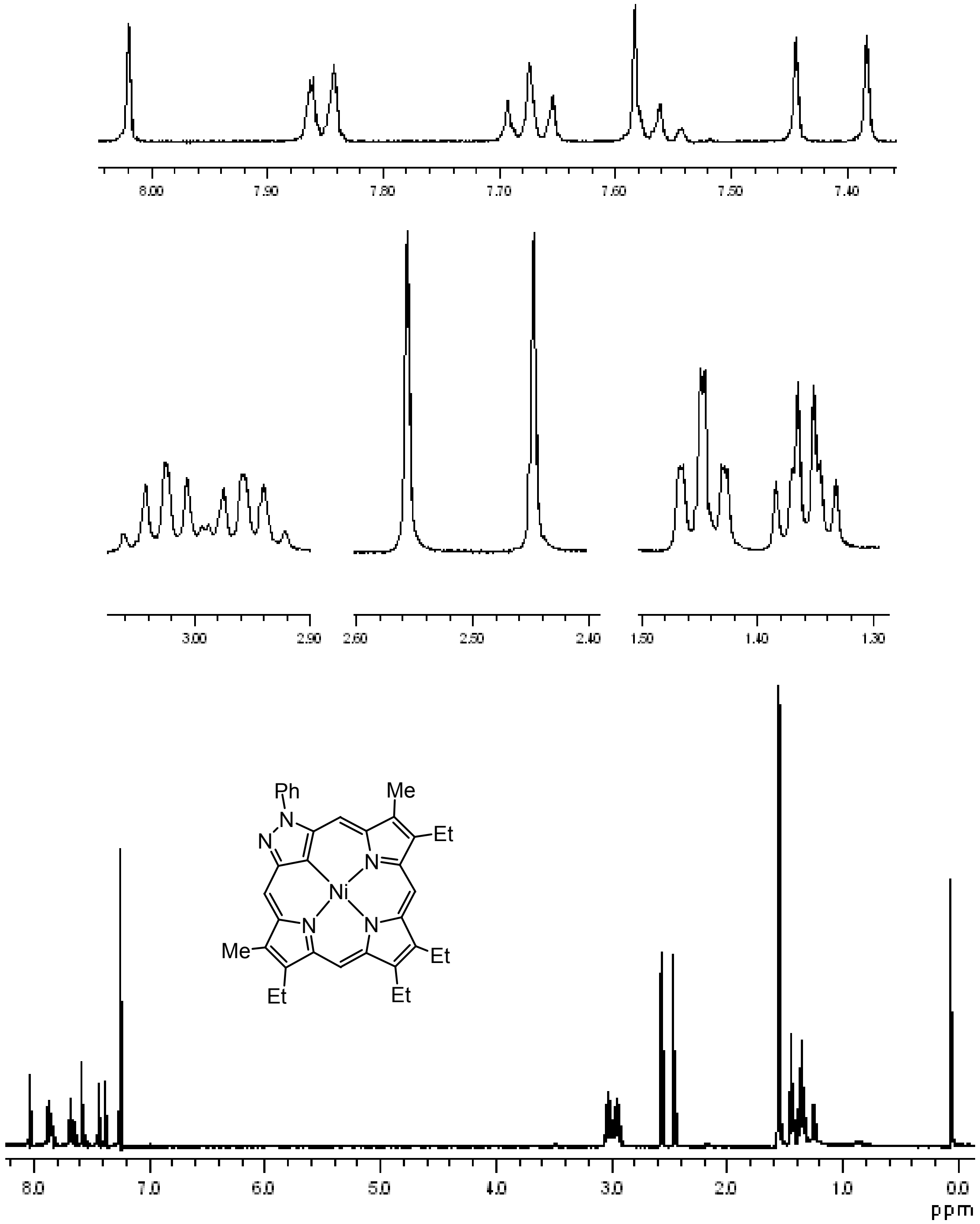


Figure S4: 400 MHz proton NMR spectrum of nickel complex **12a** in $CDCl_3$.

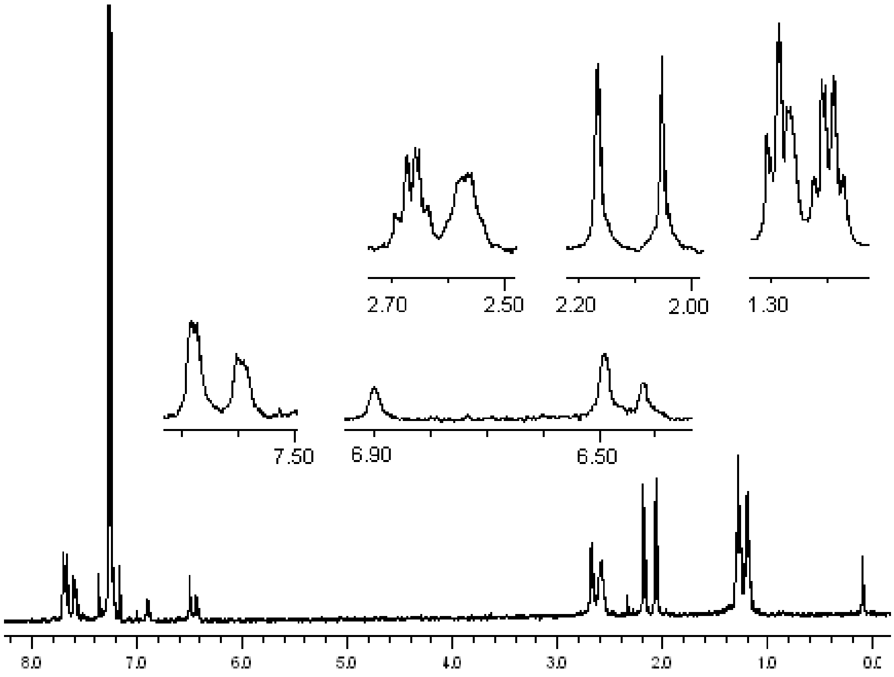


Figure S5: 400 MHz proton NMR spectrum of nickel complex **12a** in TFA-$CDCl_3$.

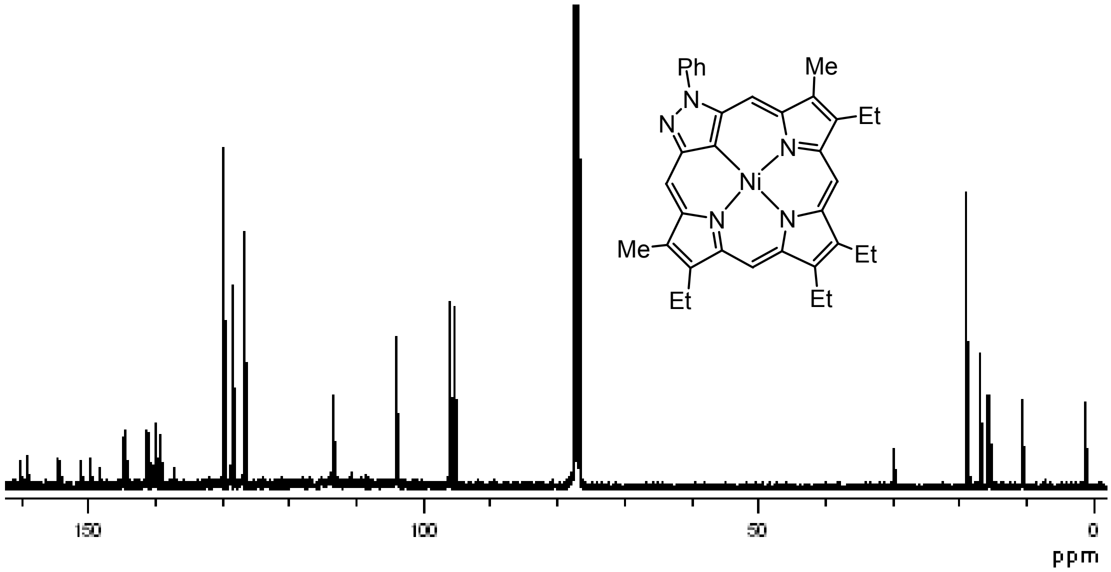


Figure S6: 100 MHz carbon-13 NMR spectrum of nickel complex **12a** in $CDCl_3$.

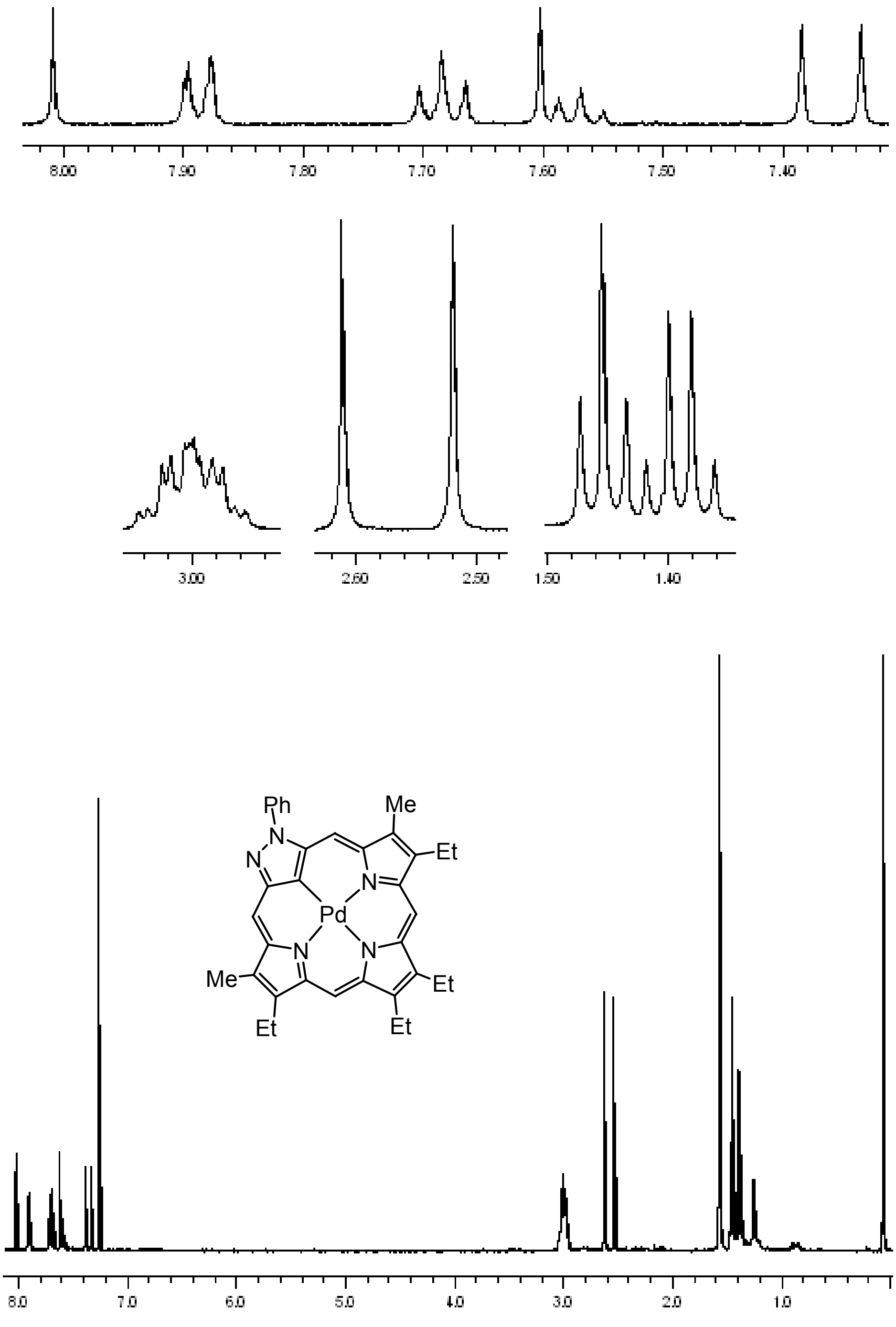


Figure S7: 400 MHz proton NMR spectrum of palladium complex **13a** in $CDCl_3$.

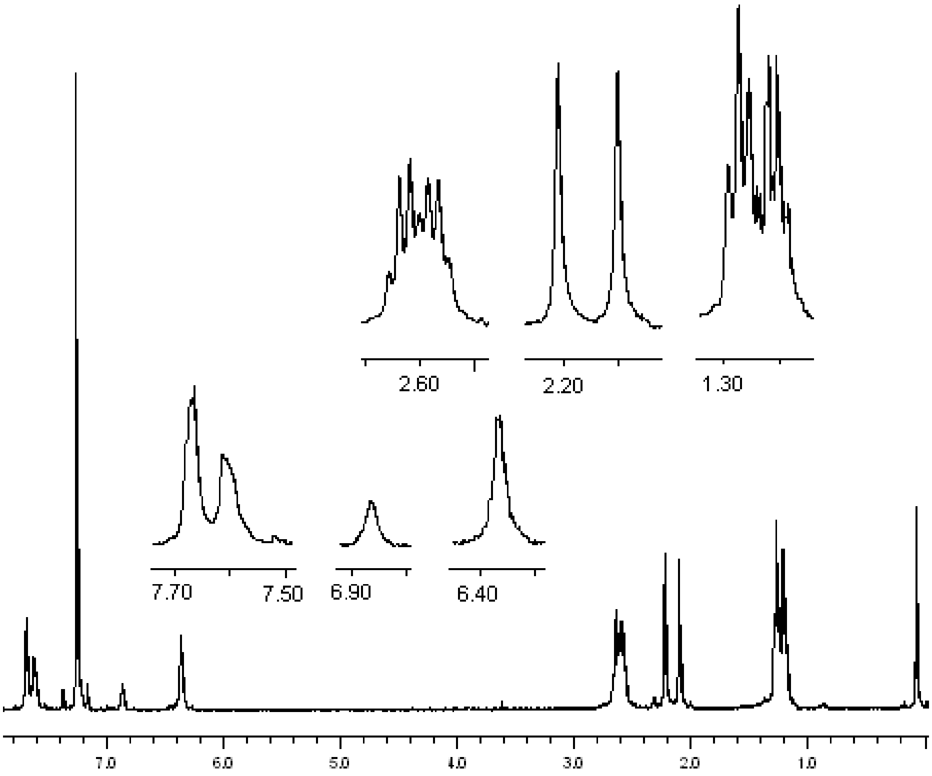


Figure S8: 400 MHz proton NMR spectrum of palladium complex **13a** with 2 drops of TFA in $CDCl_3$.

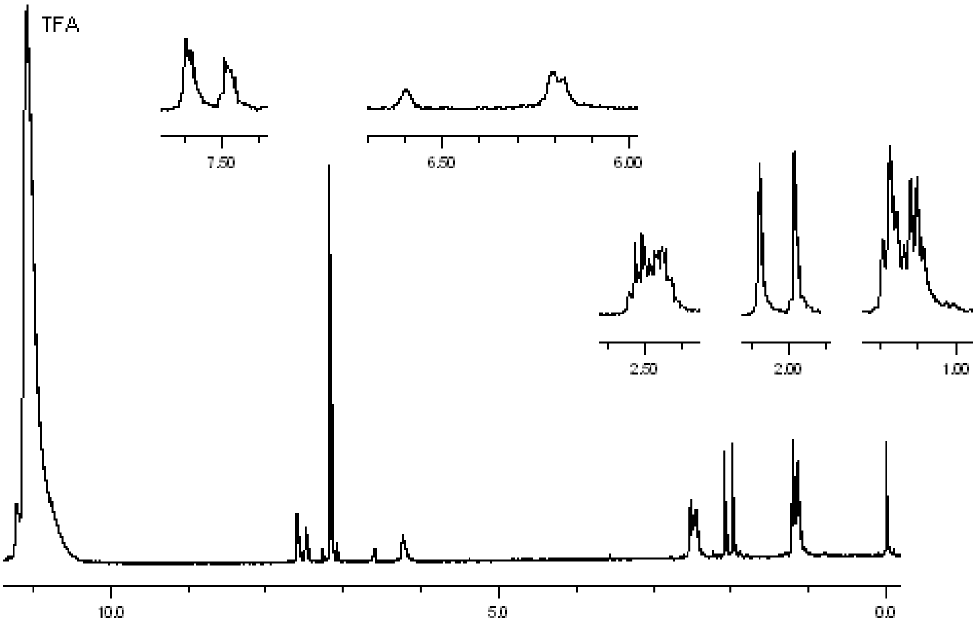


Figure S9: 400 MHz proton NMR spectrum of palladium complex **13a** with 5 drops of TFA in $CDCl_3$.

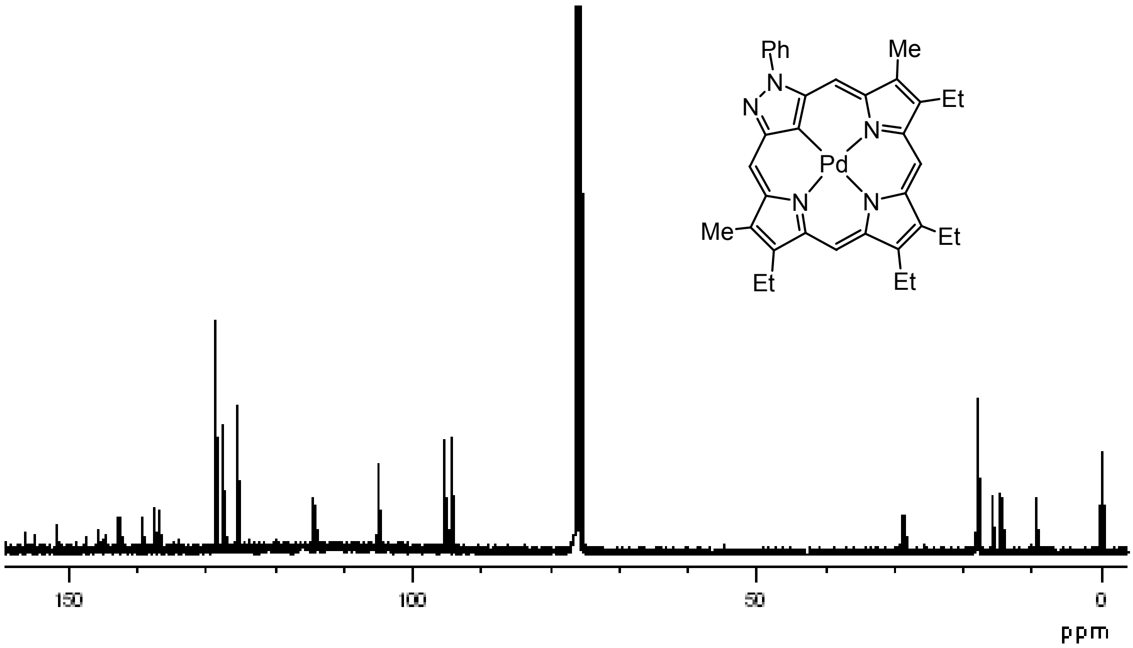


Figure S10: 100 MHz carbon-13 NMR spectrum of palladium complex **13a** in $CDCl_3$.

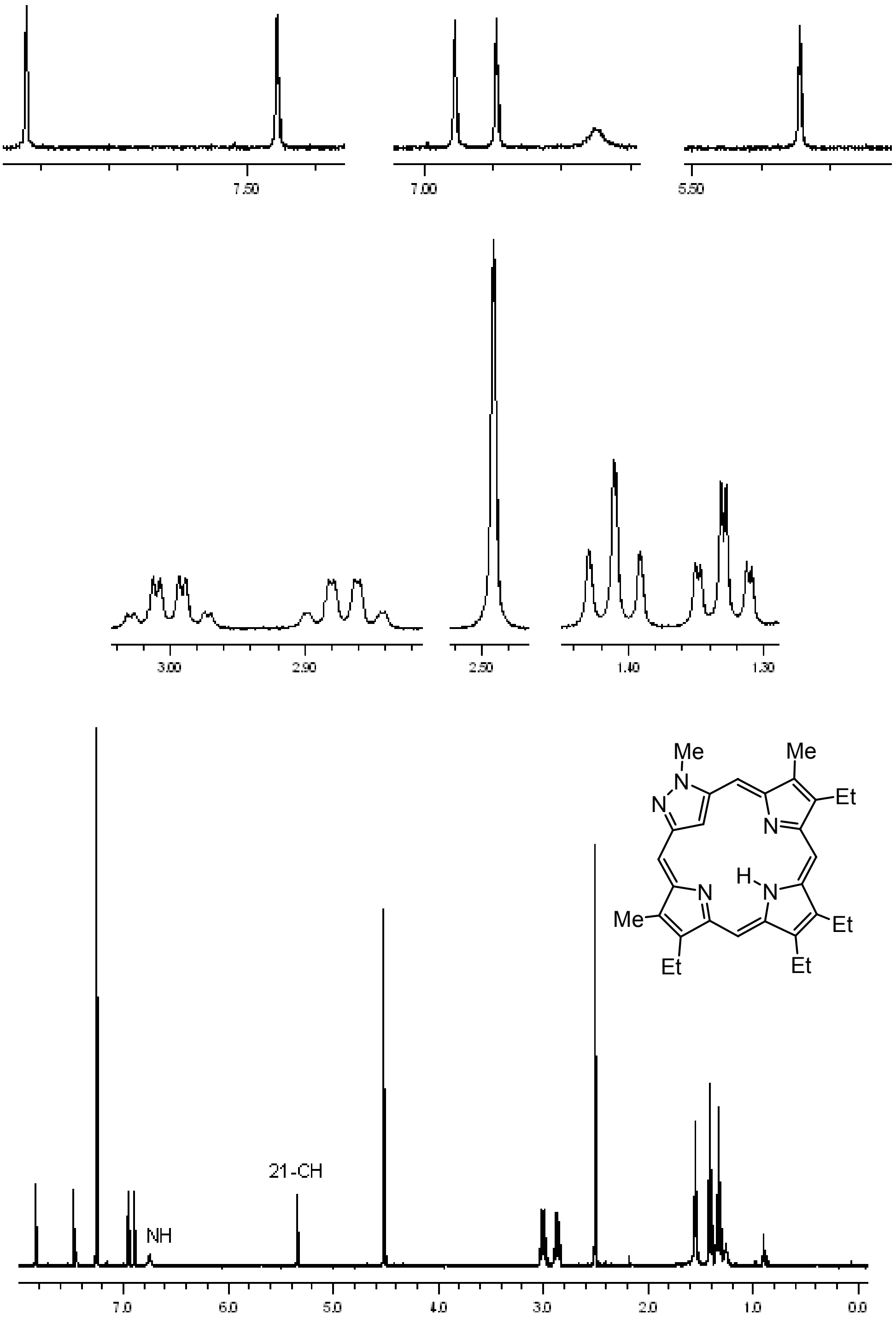
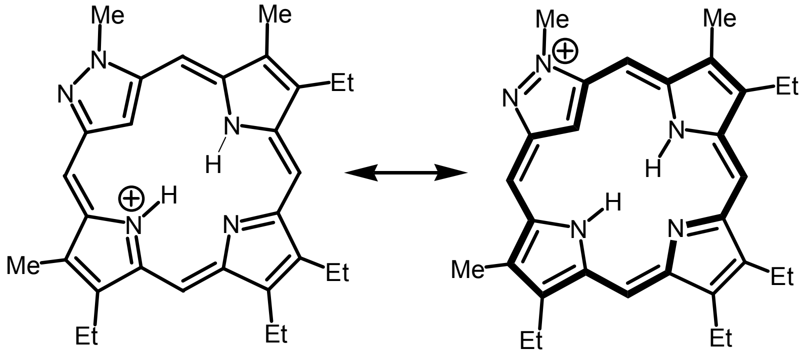


Figure S11: 400 MHz proton NMR spectrum of pyrazole porphyrin analogue **8b** in $CDCl_3$.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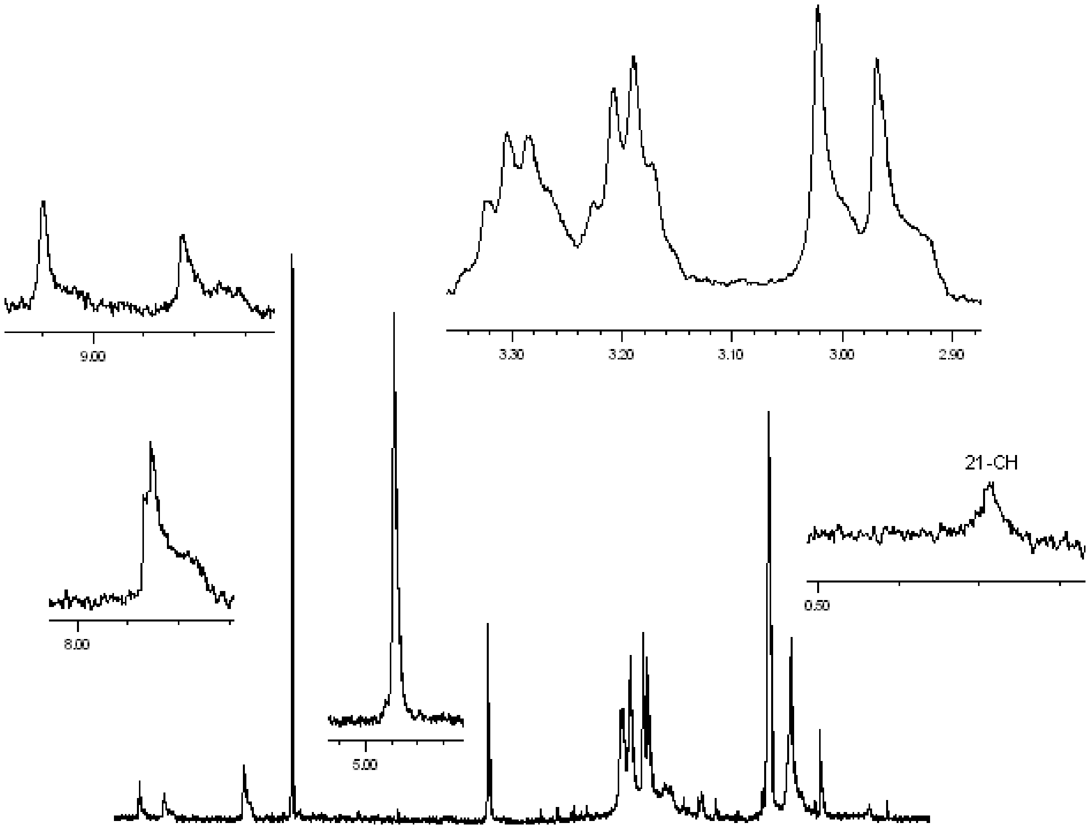
9.00
8.00
5.00
3.30
3.20
3.10
3.00
2.90
21-CH
0.50
5.0
0.0

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Figure S12: Poor quality 400 MHz proton NMR spectrum of pyrazole porphyrin analogue **8b** in trace TFA-$CDCl_3$ showing the presence of an intermediary protonated species with enhanced diatropic character.

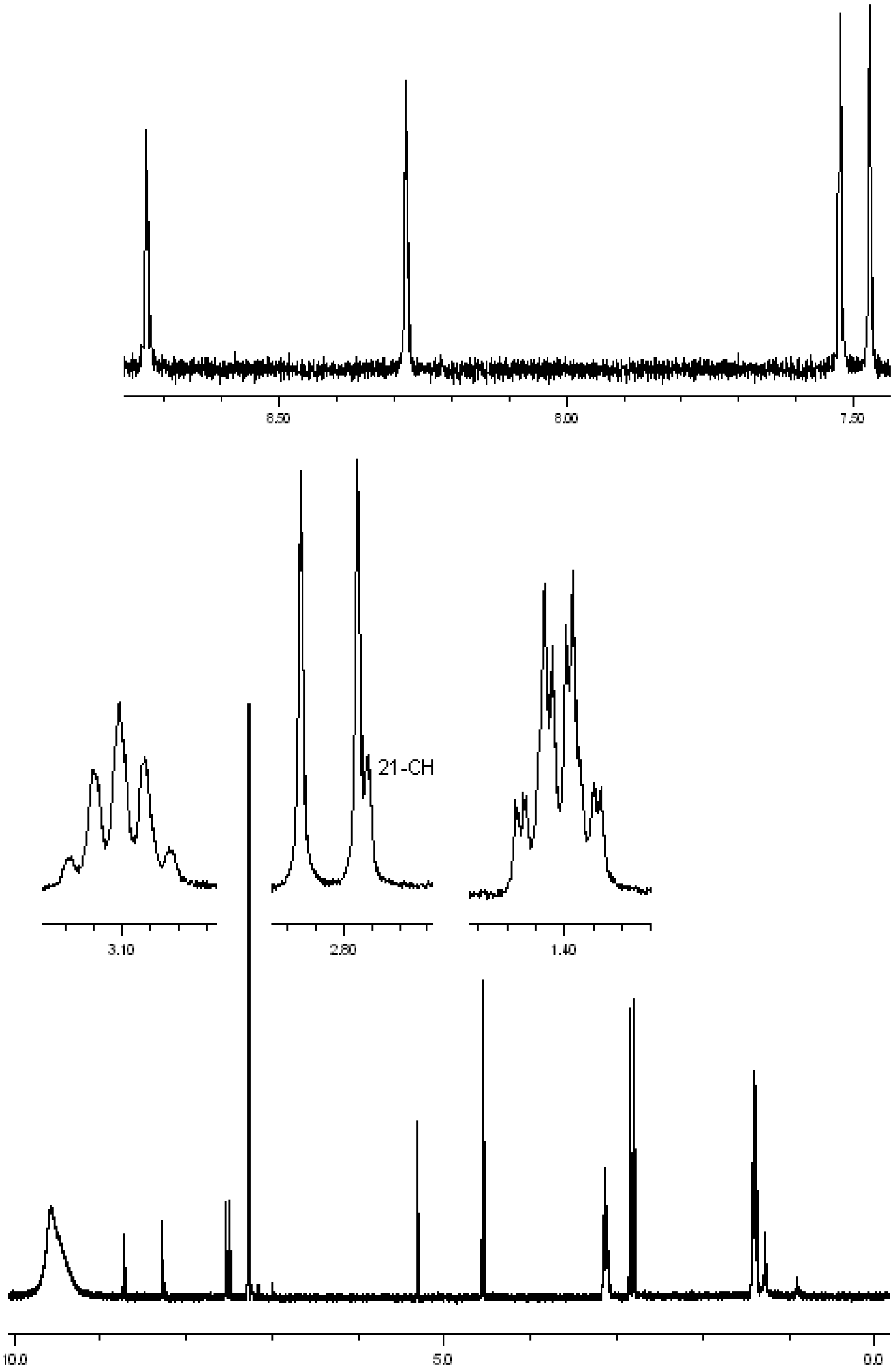


Figure S13: 400 MHz proton NMR spectrum of the fully protonated pyrazole porphyrin analogue **8b** in TFA-$CDCl_3$.

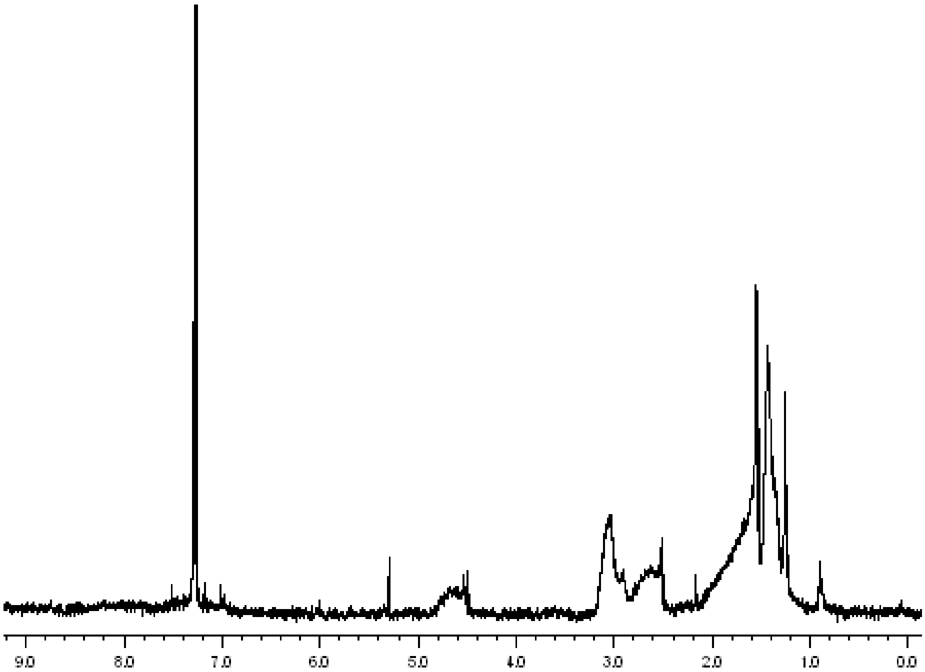


Figure S14: Broadened 400 MHz proton NMR spectrum of **8b** with 2 eq of TFA in $CDCl_3$.

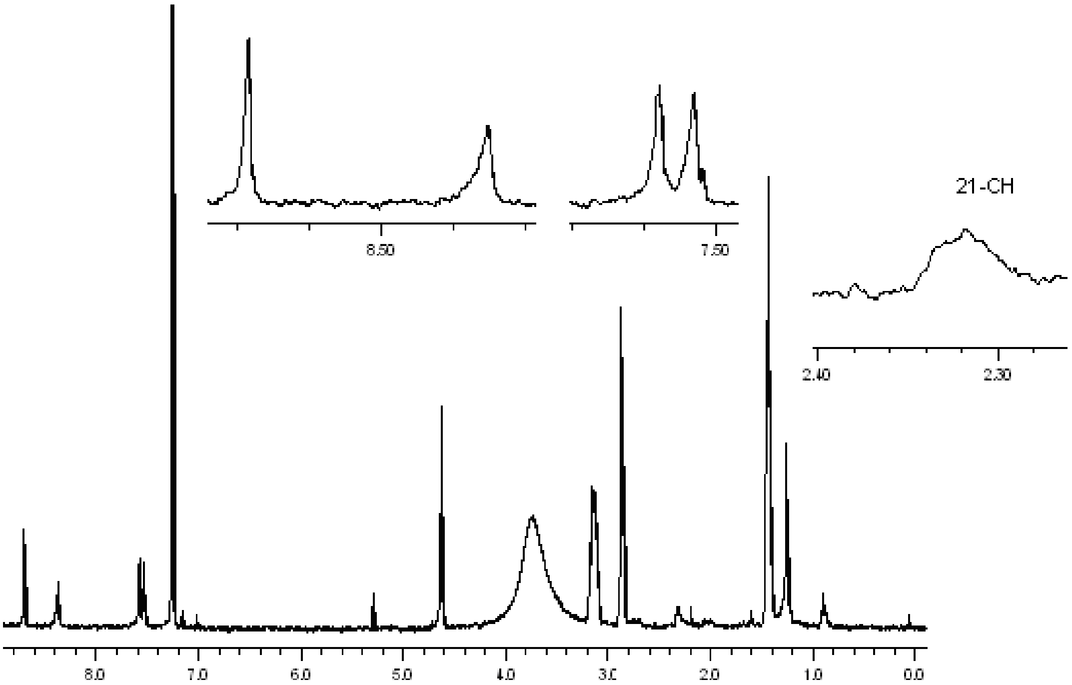


Figure S15: 400 MHz proton NMR spectrum of **8b** with 5 eq of TFA in $CDCl_3$.

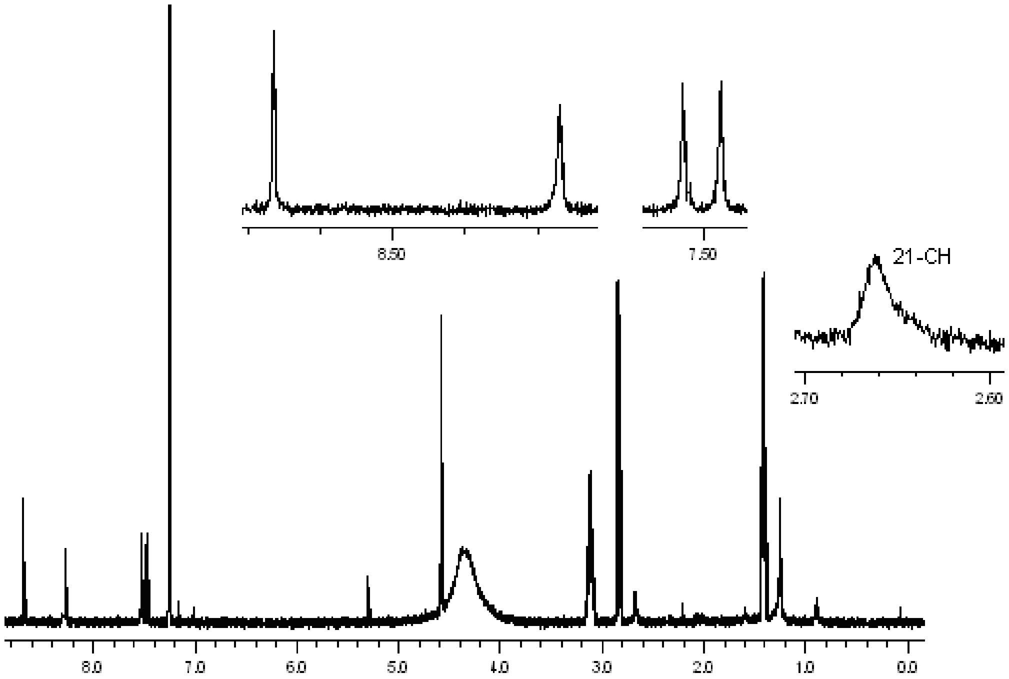


Figure S16: 400 MHz proton NMR spectrum of **8b** with 7.5 eq of TFA in $CDCl_3$.

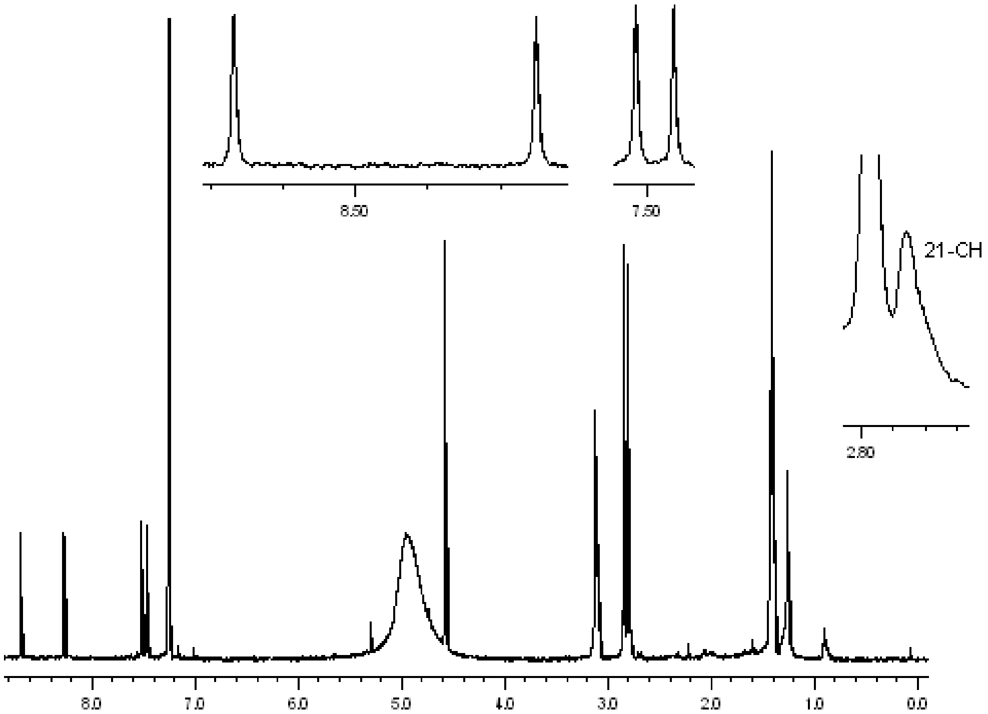
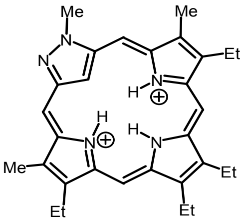


Figure S17: 400 MHz proton NMR spectrum of **8b** with 10 eq of TFA in $CDCl_3$.



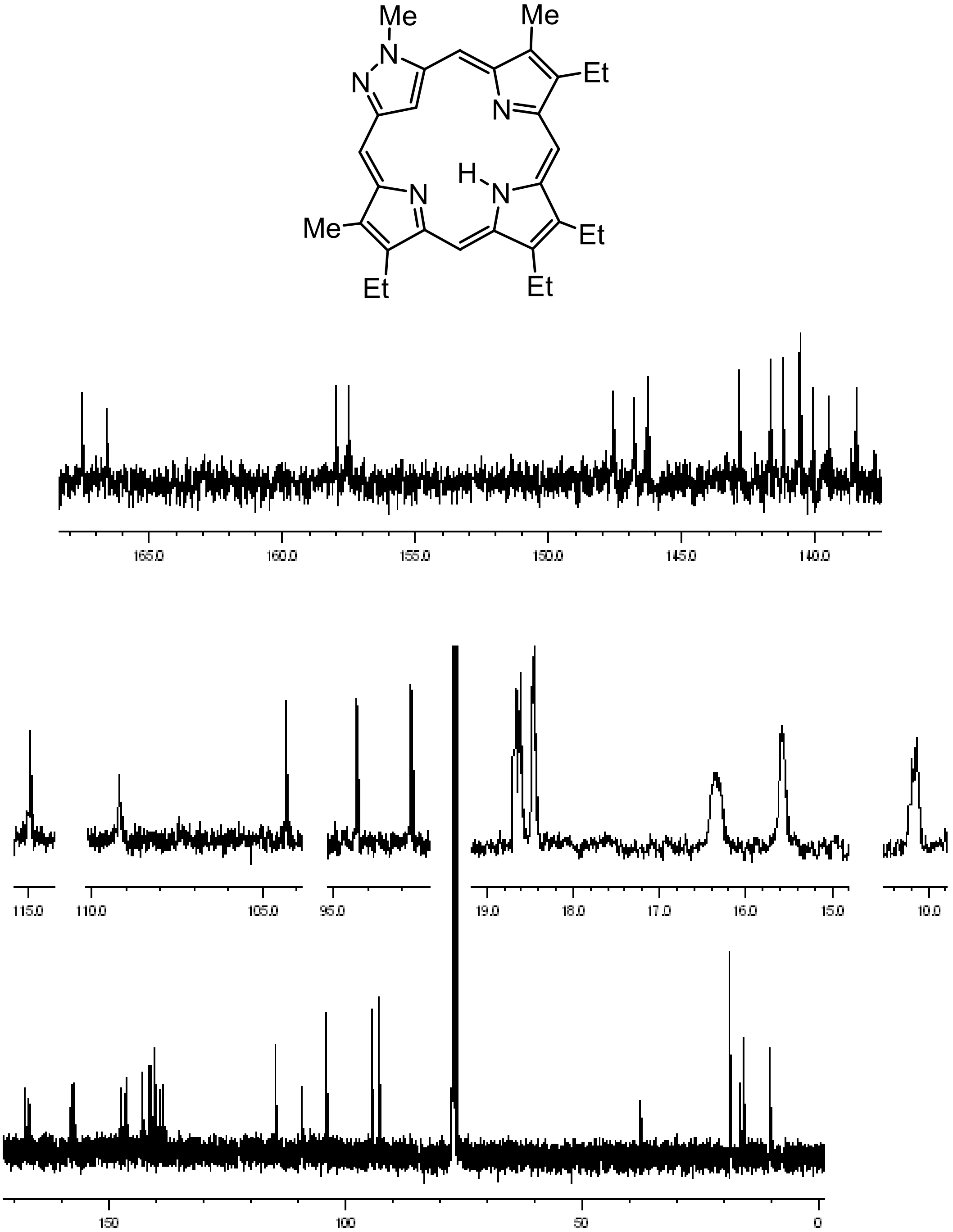


Figure S18: 100 MHz carbon-13 NMR spectrum of pyrazole porphyrin analogue **8b** in $CDCl_3$.

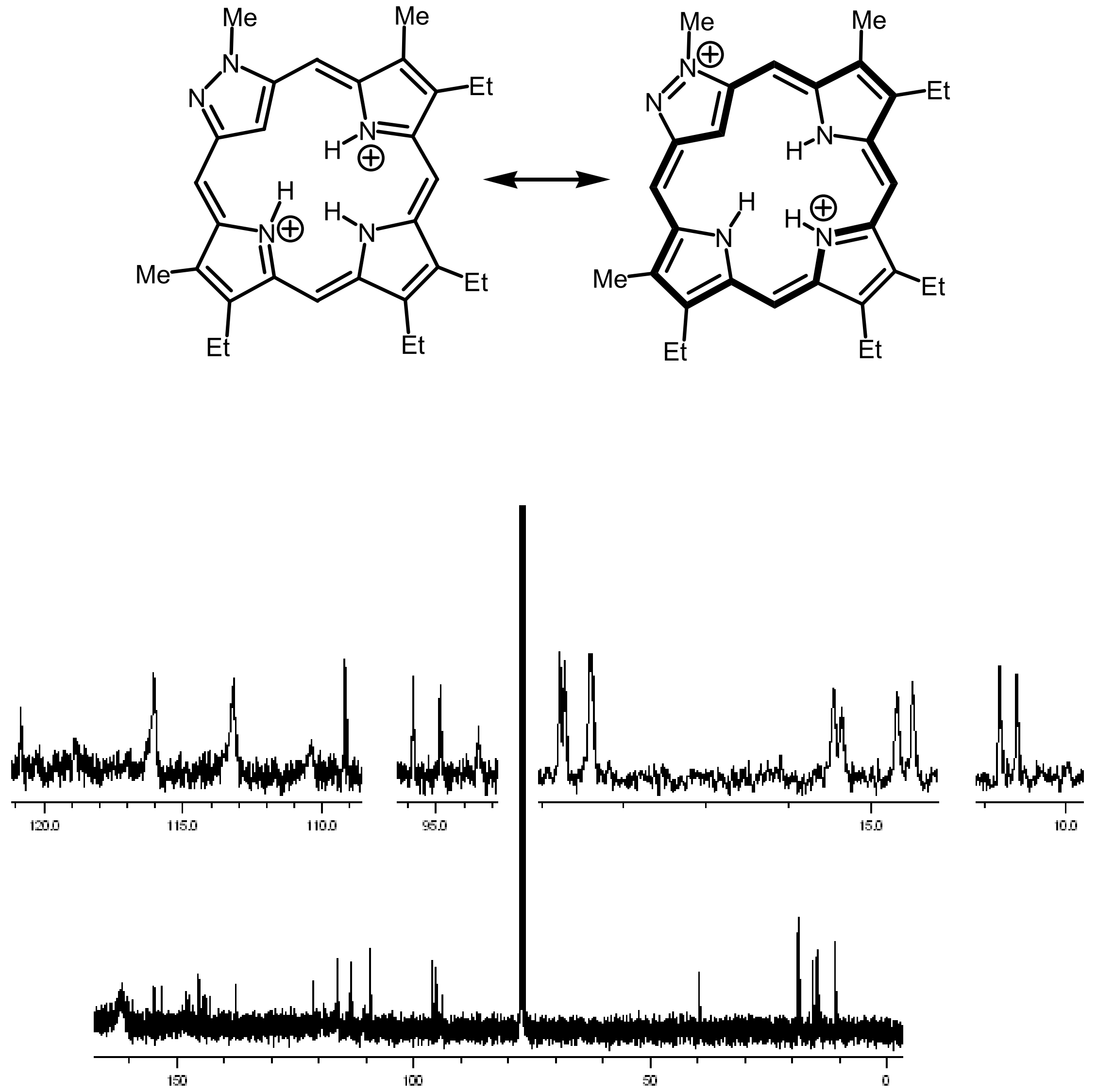


Figure S19: 100 MHz carbon-13 NMR spectrum of pyrazole porphyrin analogue **8b** in TFA-$CDCl_3$.

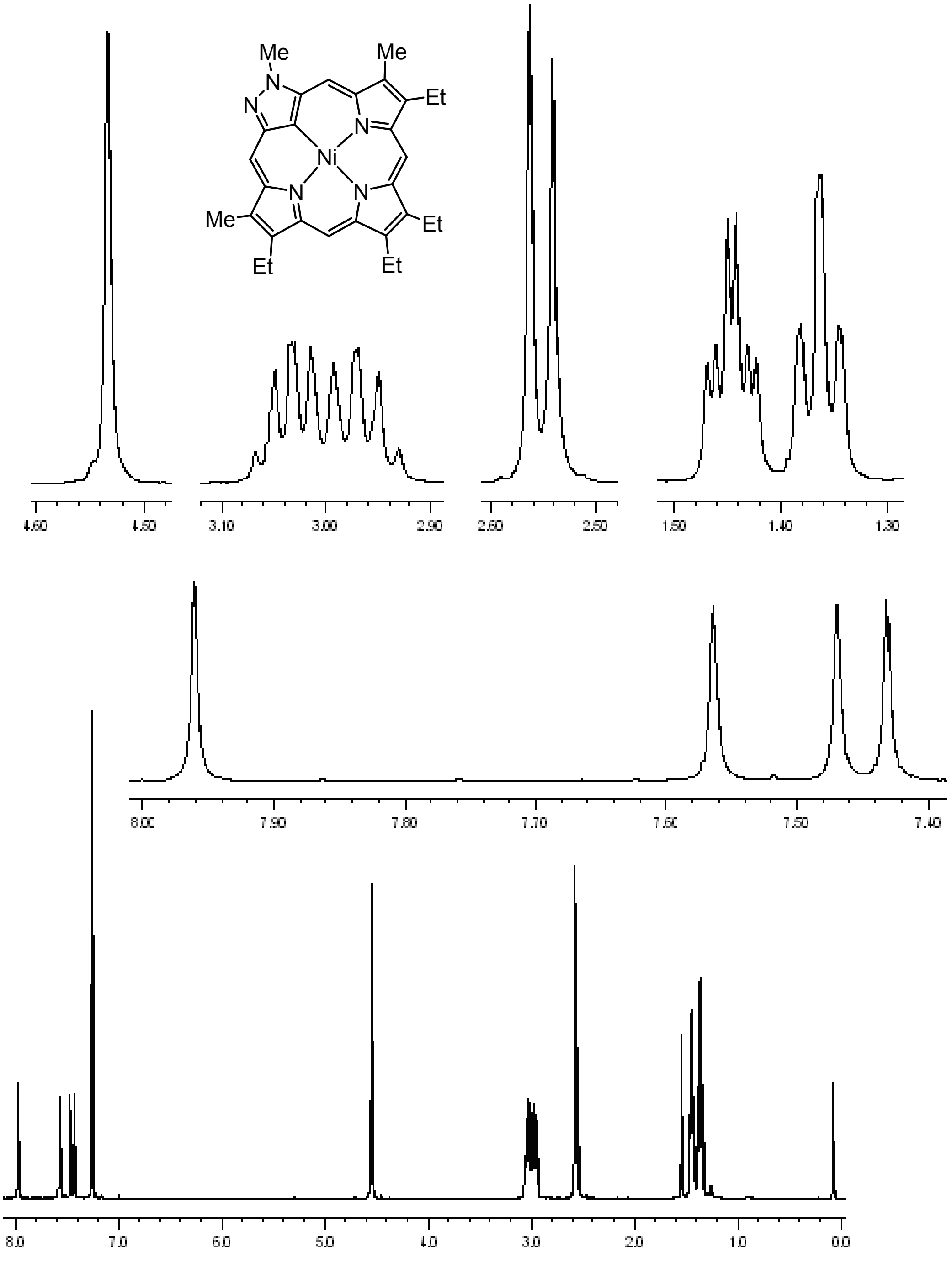


Figure S20: 400 MHz proton NMR spectrum of nickel complex **12b** in $CDCl_3$.

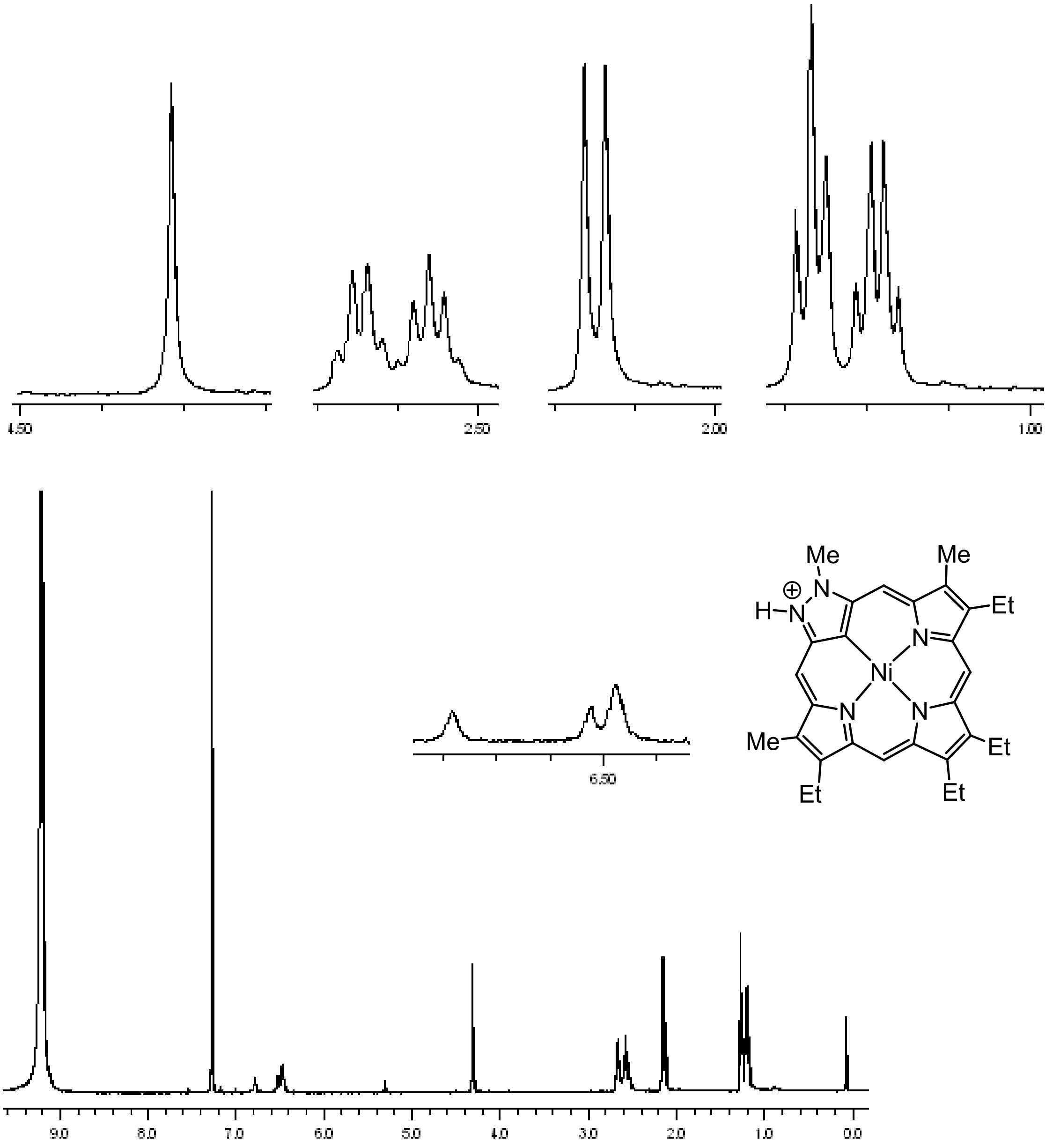
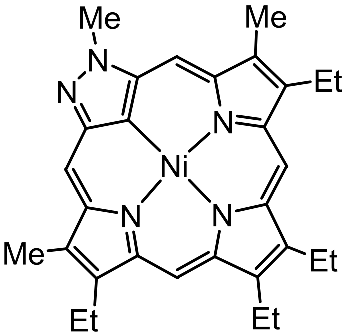


Figure S21: 400 MHz proton NMR spectrum of nickel complex **12b** in TFA-$CDCl_3$.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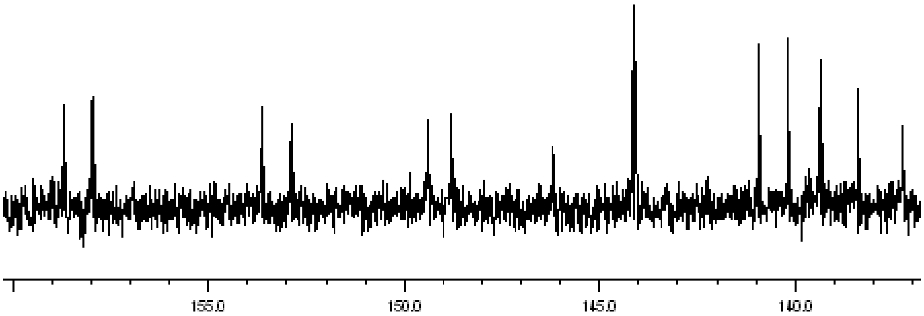
Me
Et
Et
Et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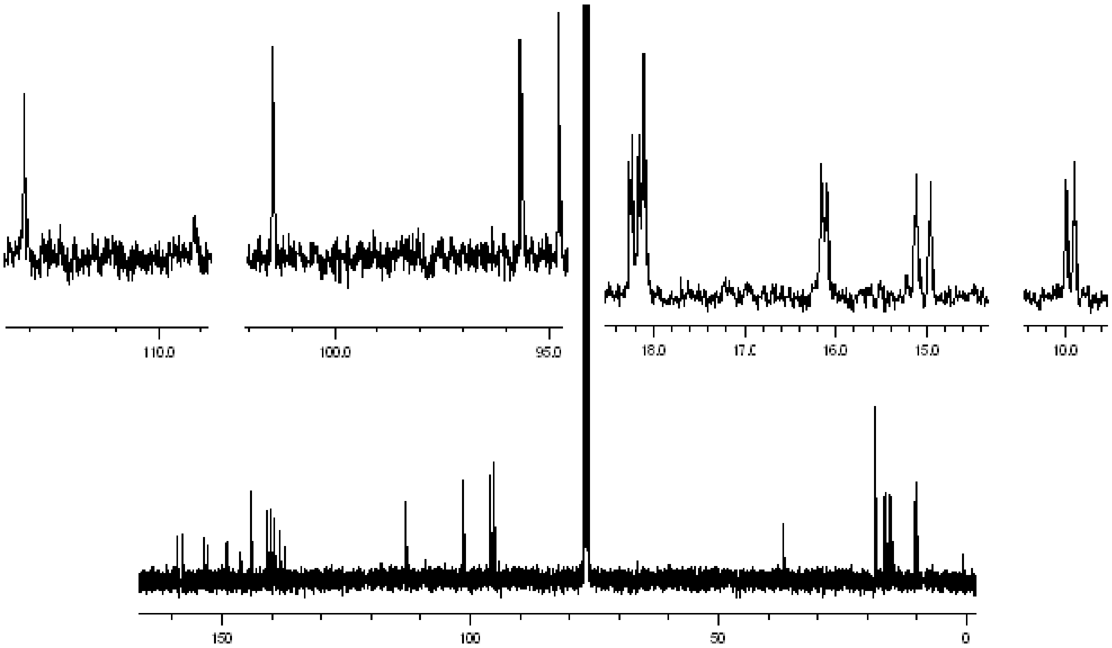
150.0
145.0
140.0


110.0
100.0
95.0
18.0
17.0
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15.0
10.0
150
100
50
0

Figure S22: 100 MHz carbon-13 NMR spectrum of nickel complex **12b** in $CDCl_3$.

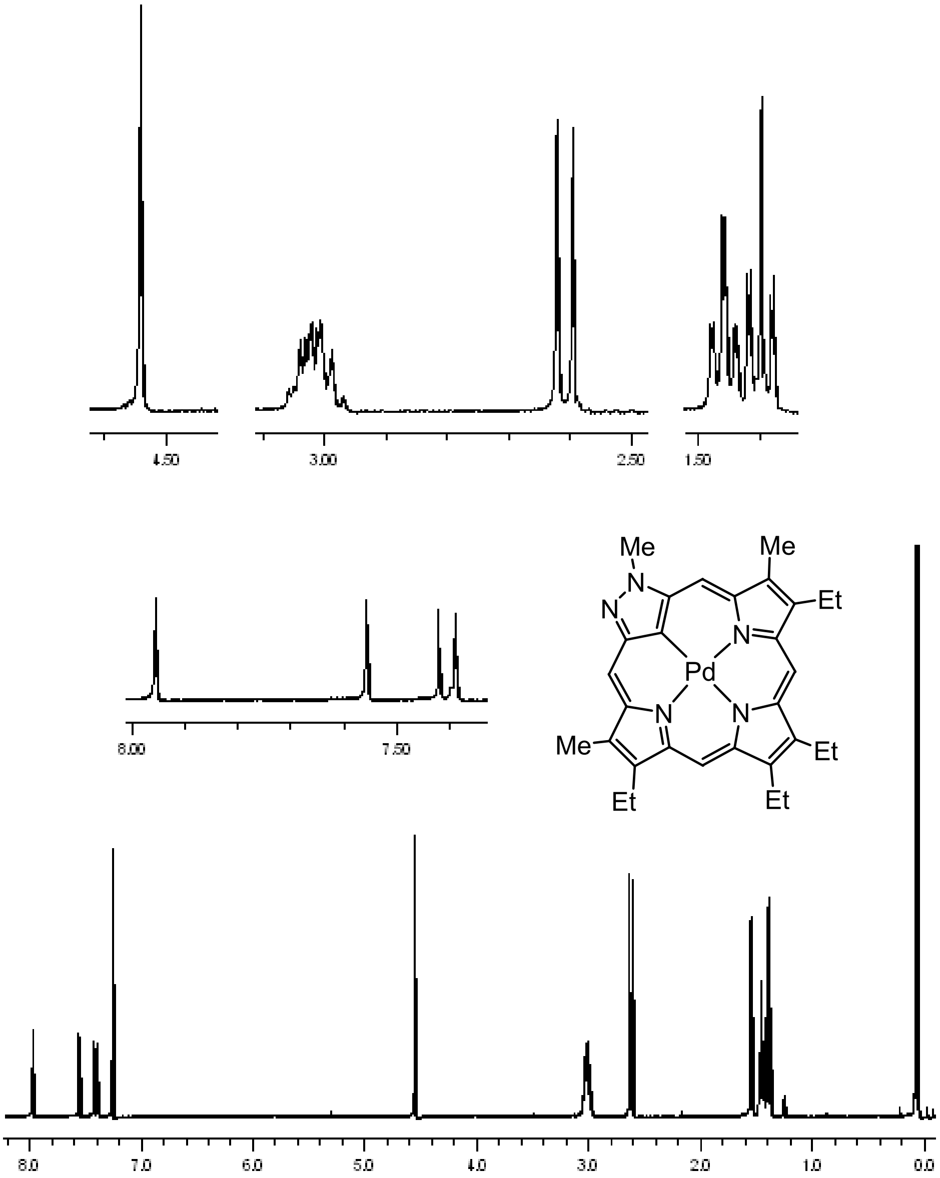


Figure S23: 400 MHz proton NMR spectrum of palladium complex **13b** in $CDCl_3$.

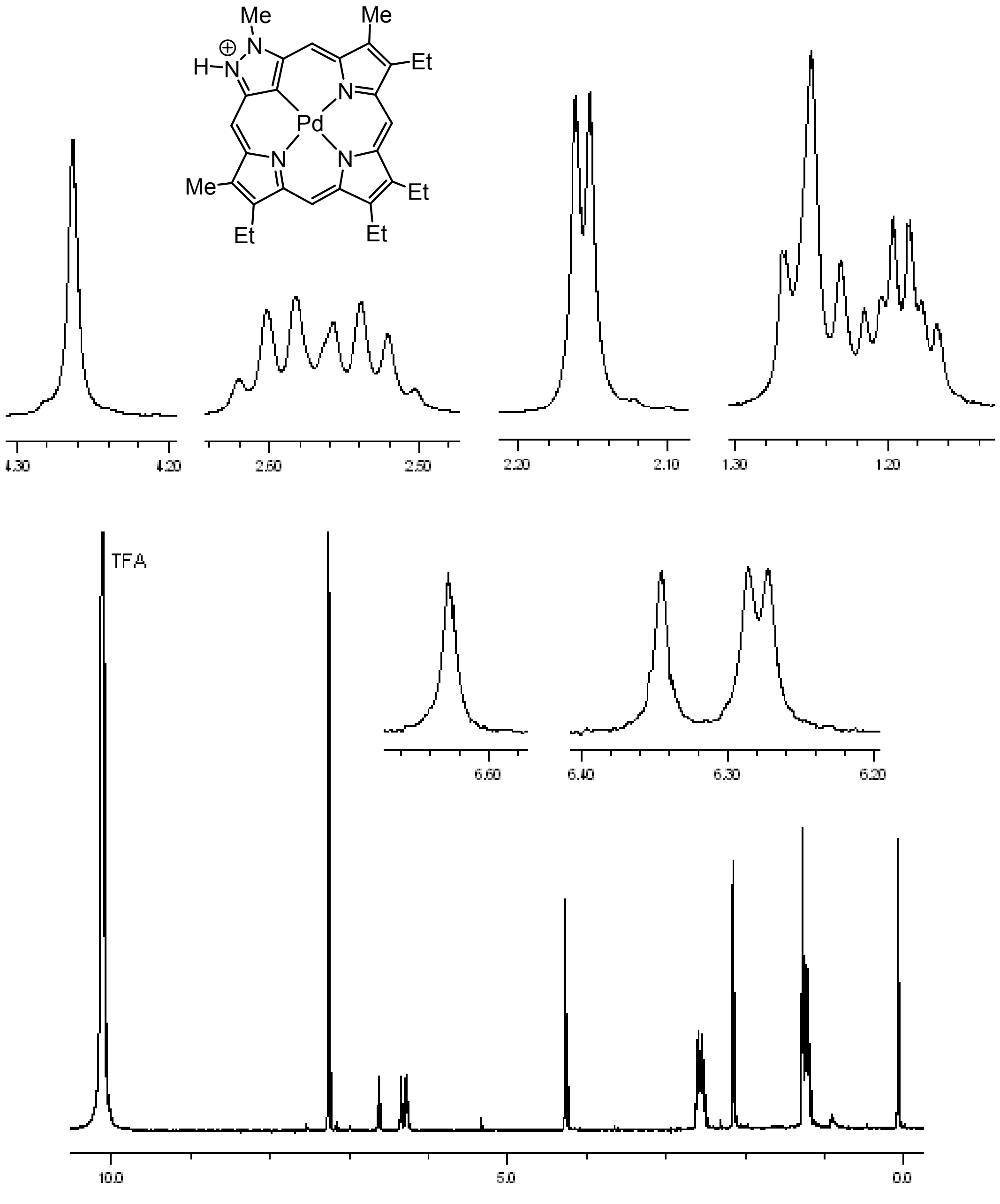
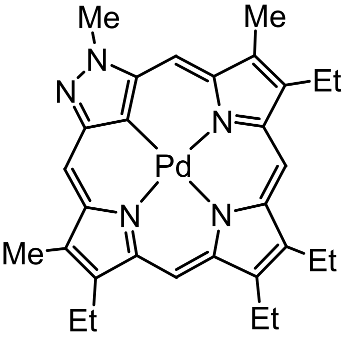


Figure S24: 400 MHz proton NMR spectrum of palladium complex **13b** in TFA-$CDCl_3$.



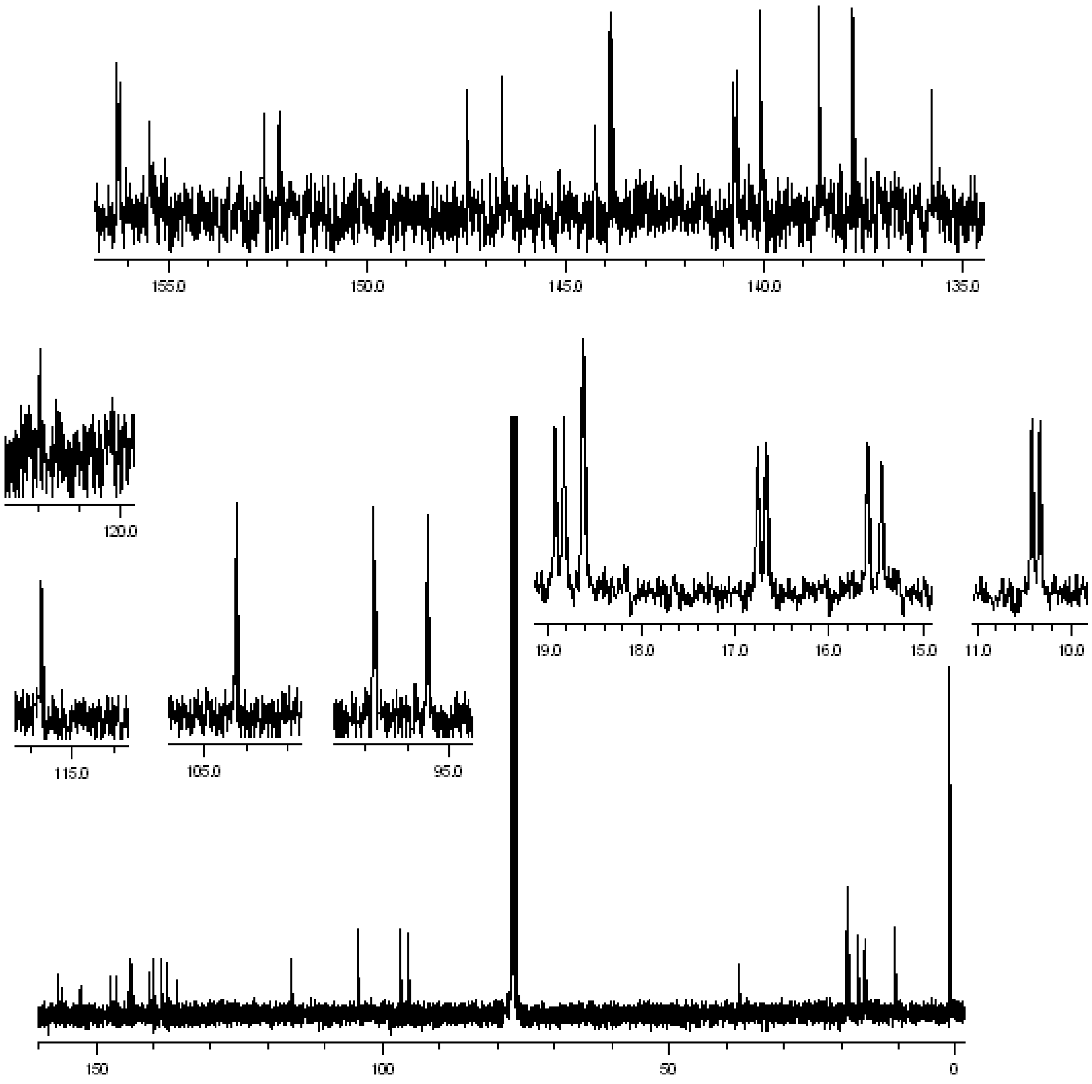


Figure S25: 100 MHz carbon-13 NMR spectrum of palladium complex **13b** in $CDCl_3$.

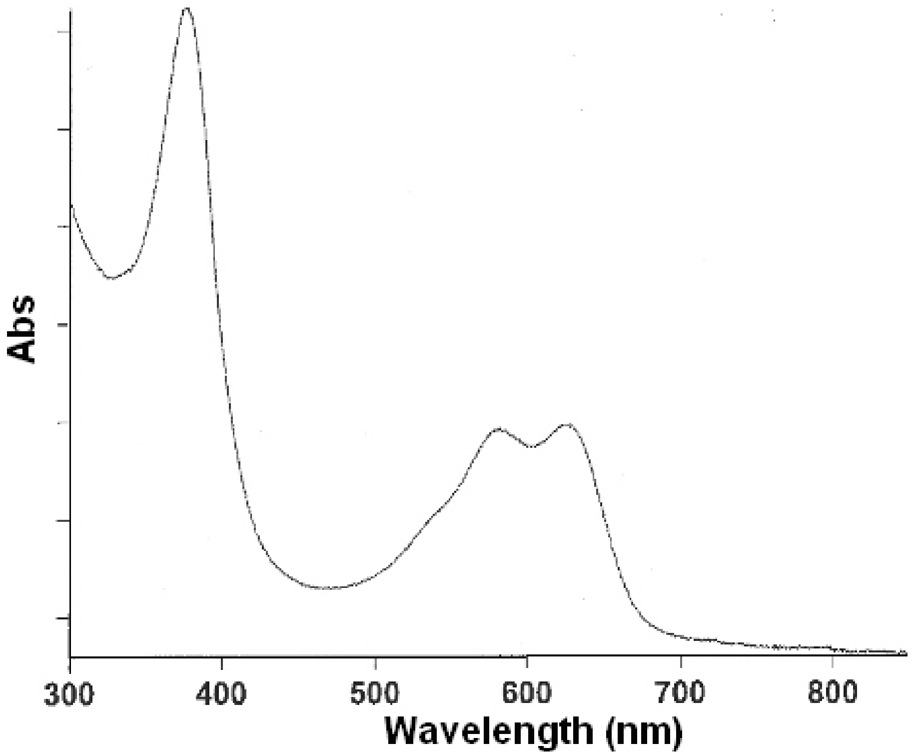


Figure S26: UV-vis spectrum of phlorin analogue **7a** in 1% Et_3N-chloroform.

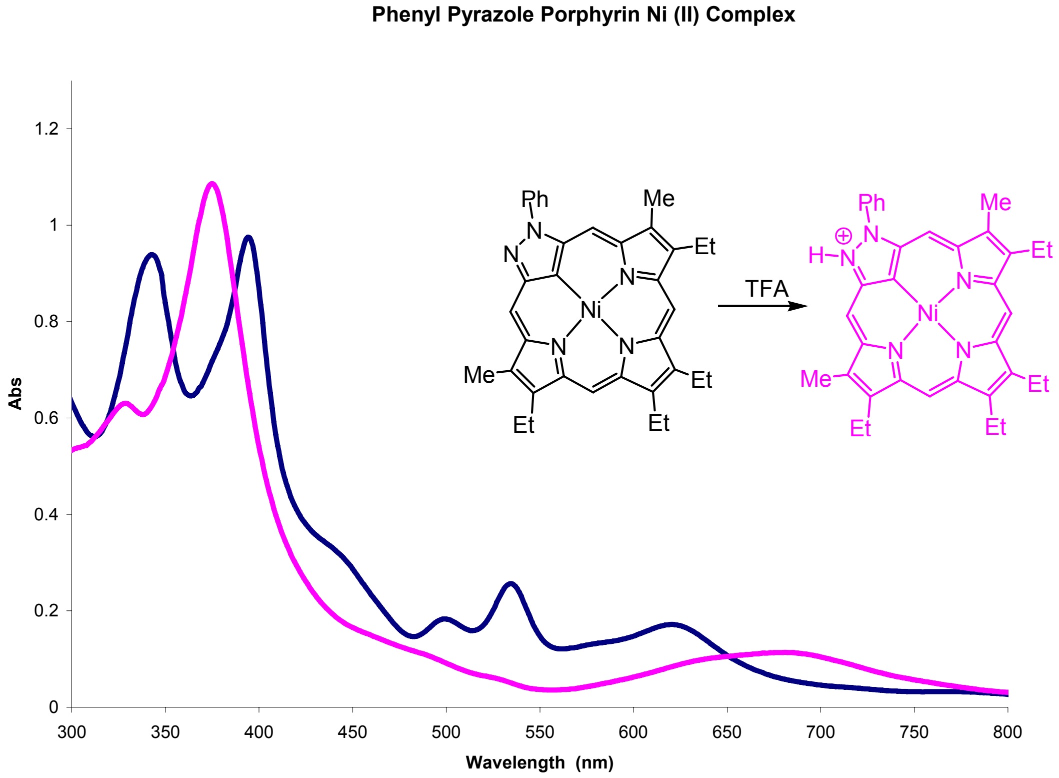


Figure S27: UV-vis spectra of nickel complex **12a.** Black line: in chloroform. Pink line: protonated species in 1% TFA-chloroform.

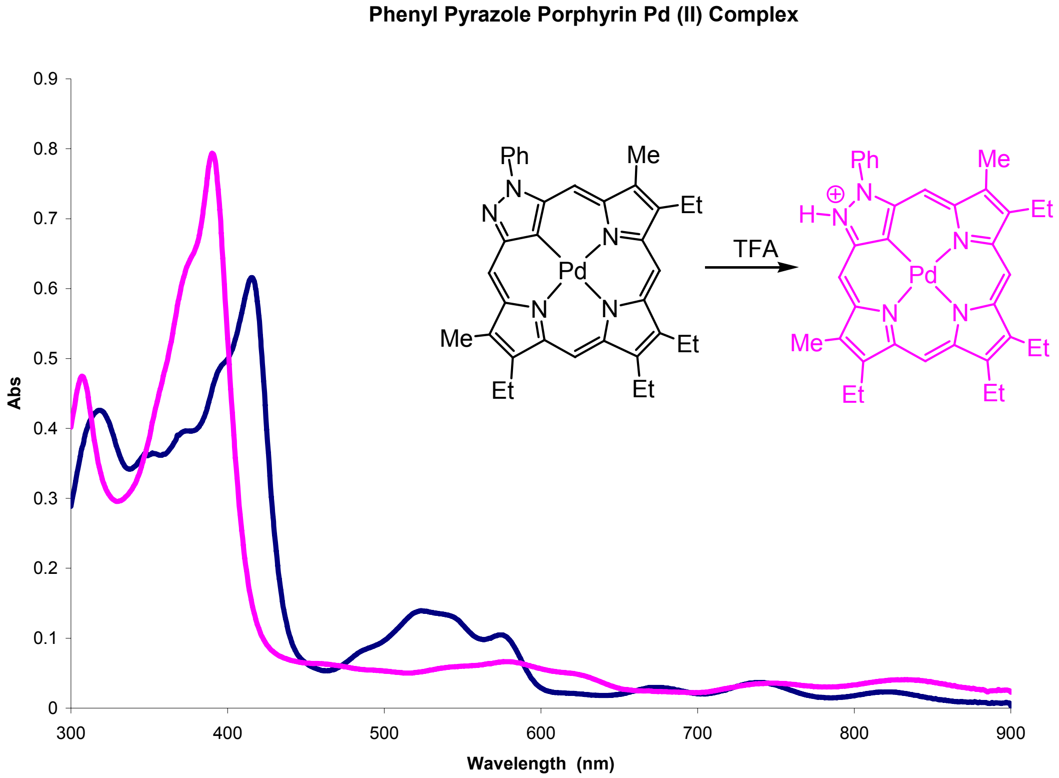


Figure S28: UV-vis spectra of palladium complex **13a.** Black line: in 1% Et_3N-chloroform. Pink line: protonated species in 1% TFA-chloroform.

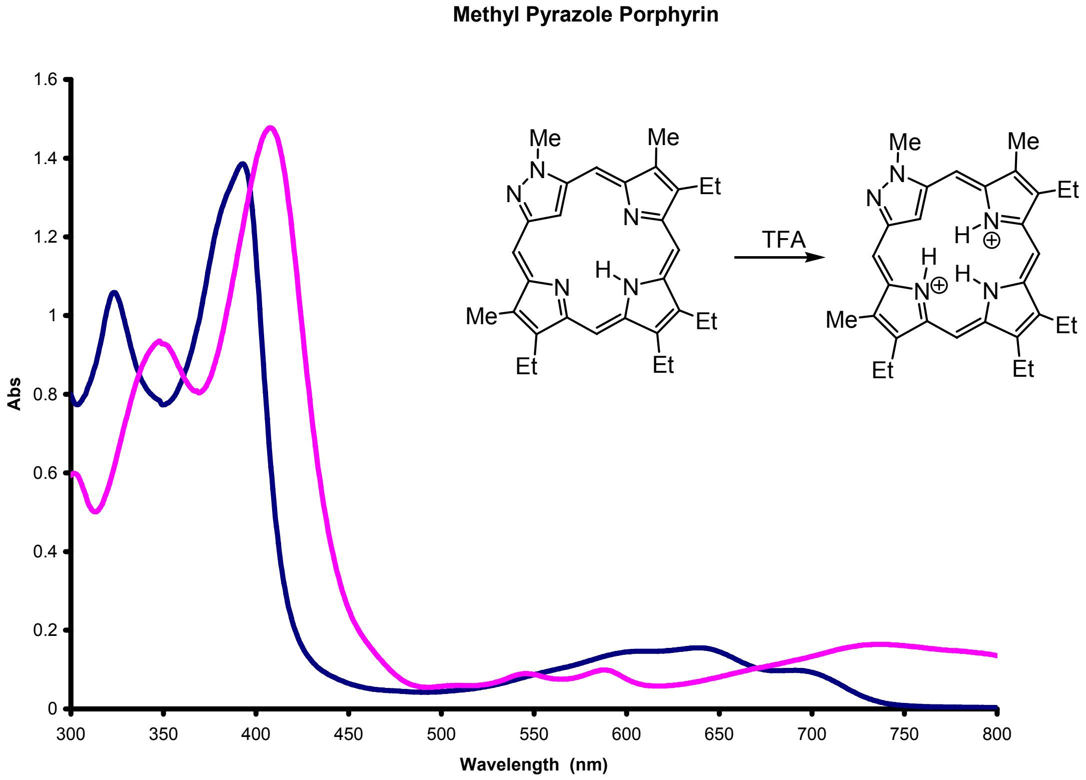


Figure S29: UV-vis spectra of the pyrazole-containing porphyrin analogue **8b.** Black line: free base in 1% Et_3N-chloroform. Pink line: fully protonated species in 1% TFA-chloroform.

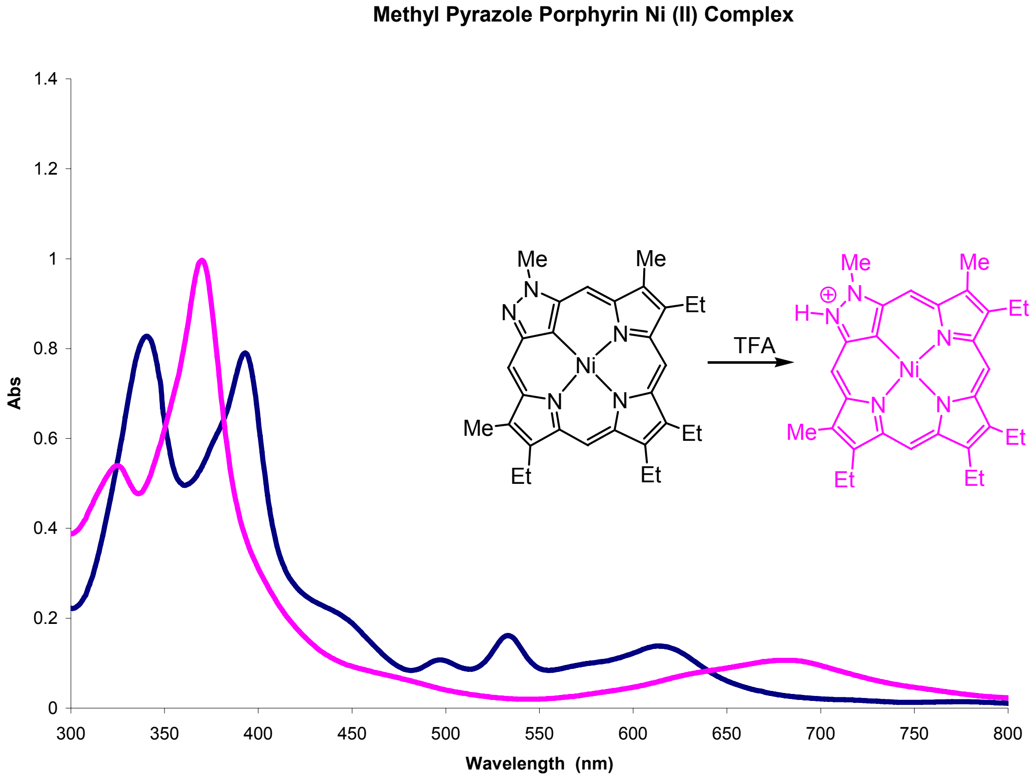


Figure S30: UV-vis spectra of nickel complex **12b.** Black line: in chloroform. Pink line: protonated species in 1% TFA-chloroform.

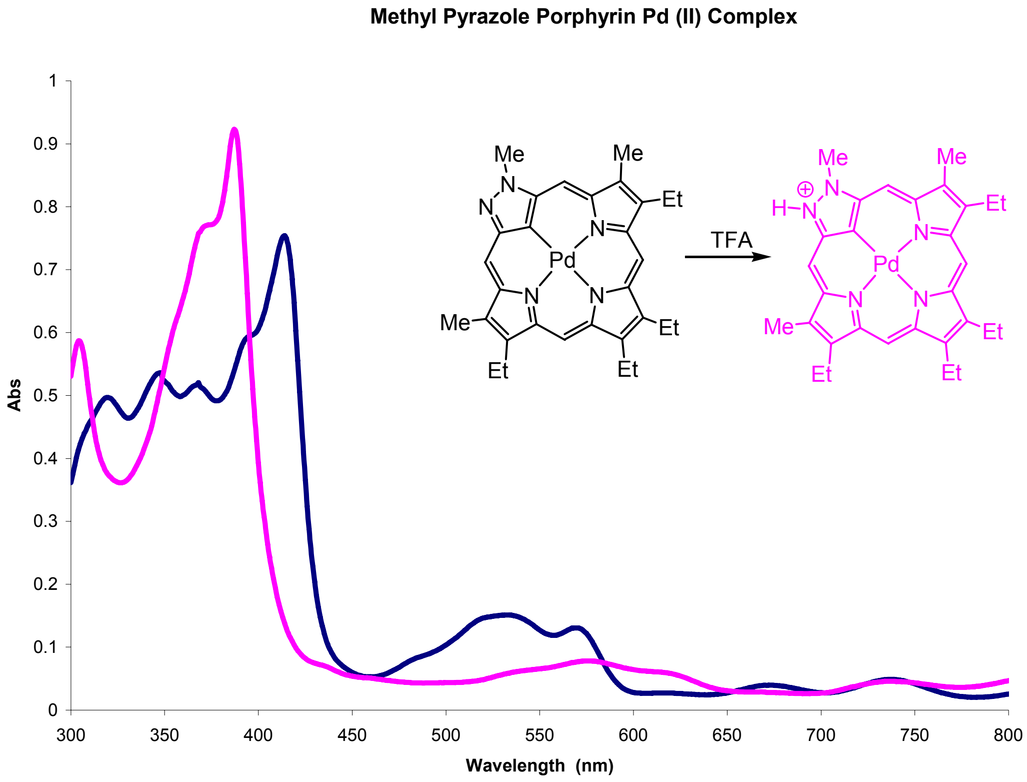
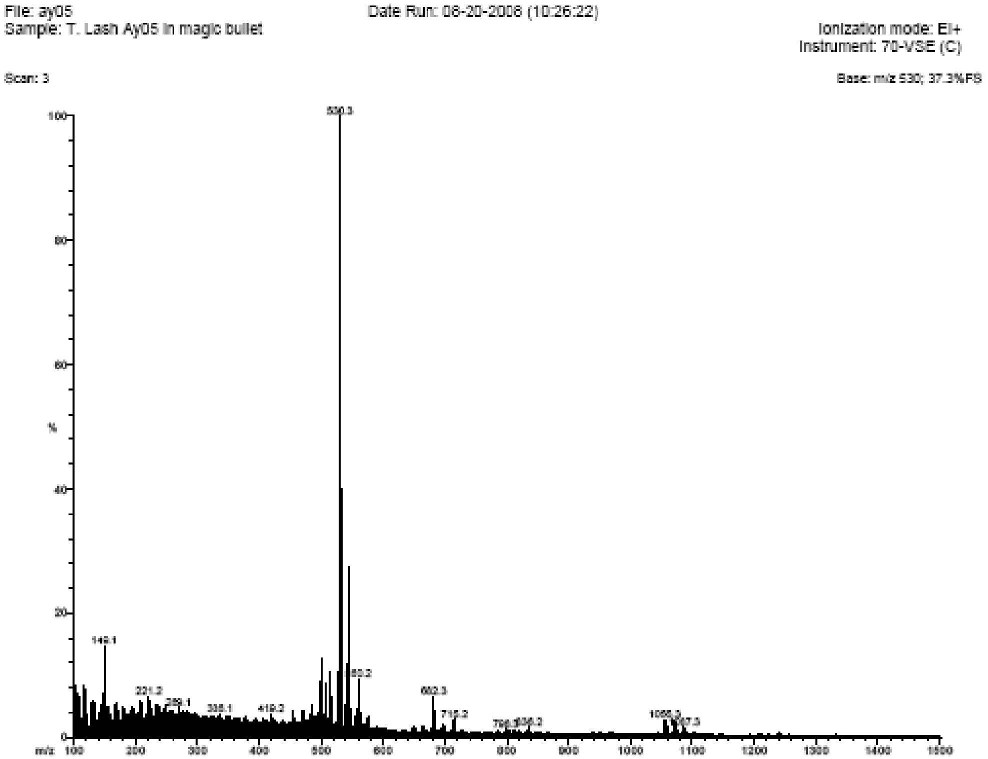


Figure S31: UV-vis spectra of palladium complex **13b.** Black line: in chloroform. Pink line: protonated species in 1% TFA-chloroform.



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Sample: T. Lash Ay05 in magic bullet
Date Run: 08-20-2008 (10:26:22)
Ionization mode: EI+
Instrument: 70-VSE (C)
Scan: 3
Base: m/z 530; 37.3%FS

Figure S32: FAB MS of 2-phenyl phlorin analogue **7a.**

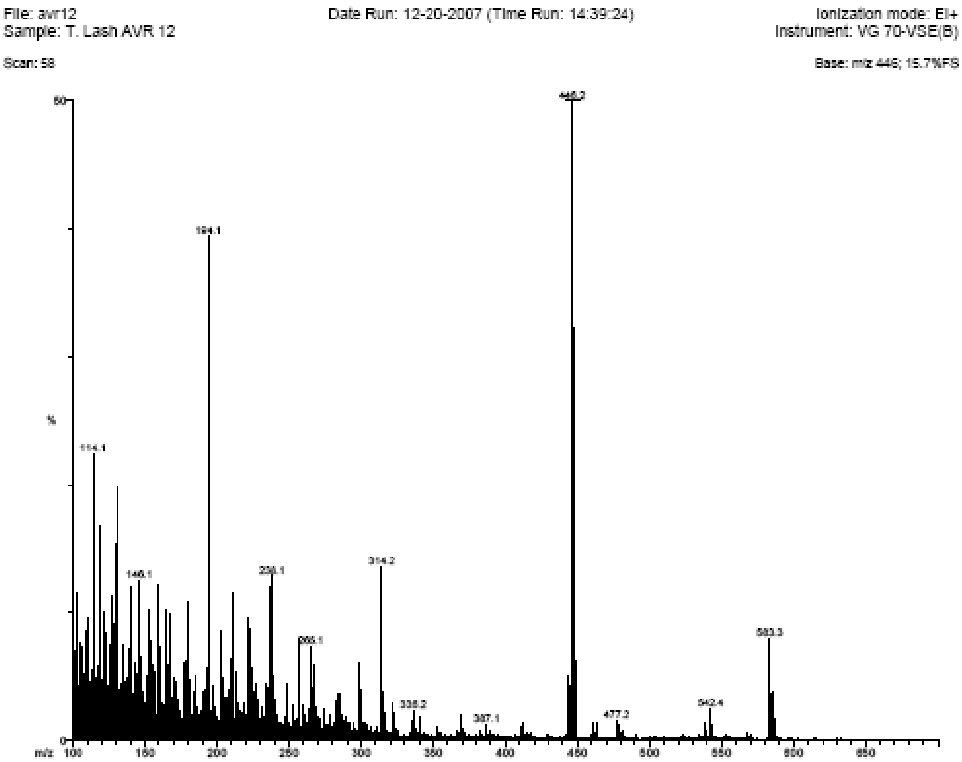


Figure S33: EI MS of 2-phenyl nickel complex **12a**. The peak at 446 is due to pump oil.

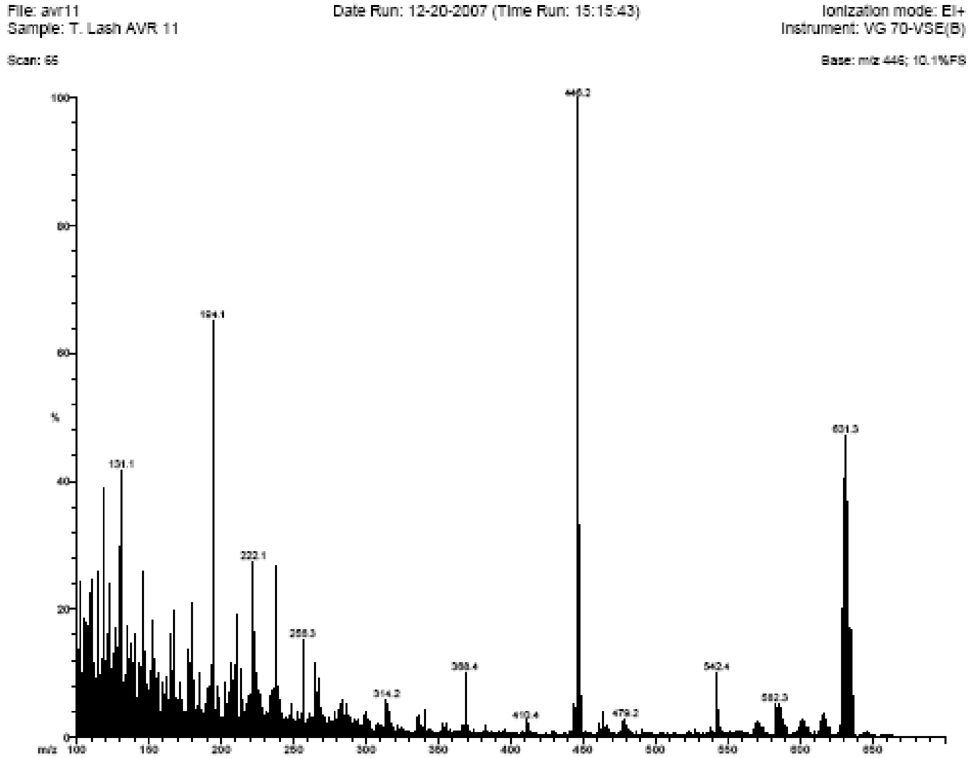
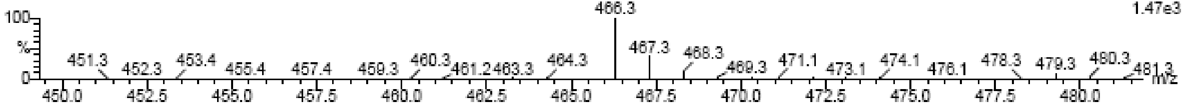


Figure S34: EI MS of 2-phenyl palladium complex **13a**. The peak at 446 is due to pump oil.

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -50.0, max = 200.0
Selected filters: None

Monoisotopic Mass, Even Electron Ions
50 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-70 H: 1-100 N: 3-5 O: 0-1

Timothy Lash, AY 02e Mass Spectrometry Center, SCS, University of Illinois QTOF
Qtof_21712 39 (2.794) AM (Cen,3, 80.00, Ar,14000.0,558.36,0.70,LS 3); Sm (SG, 2x3.00); Cm (39:42) 1: TOF MS ES+



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Minimum:                                      -50.0
Maximum:                    5.0      10.0     200.0

Mass       Calc. Mass       mDa      PPM      DBE      i-FIT     Formula

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Figure S35: ESI MS of 2-methyl pyrazole porphyrin analogue **8b.**

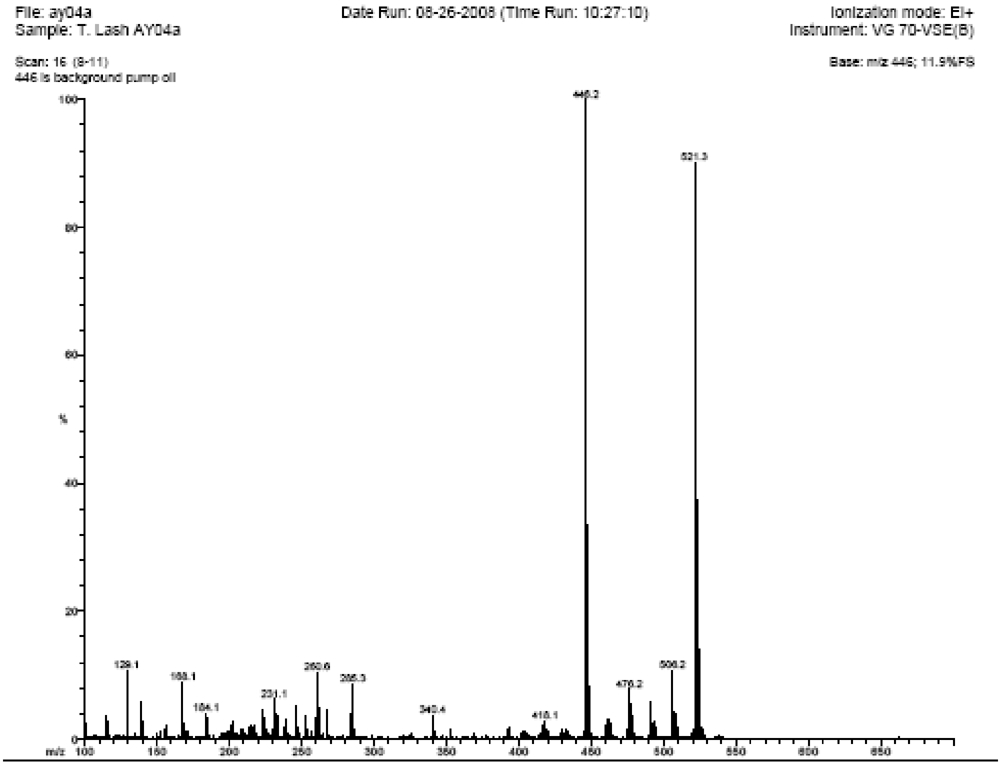

Figure S36: EI MS of 2-methyl-3-azaNCP nickel complex **12b**. The peak at 446 is due to pump oil.

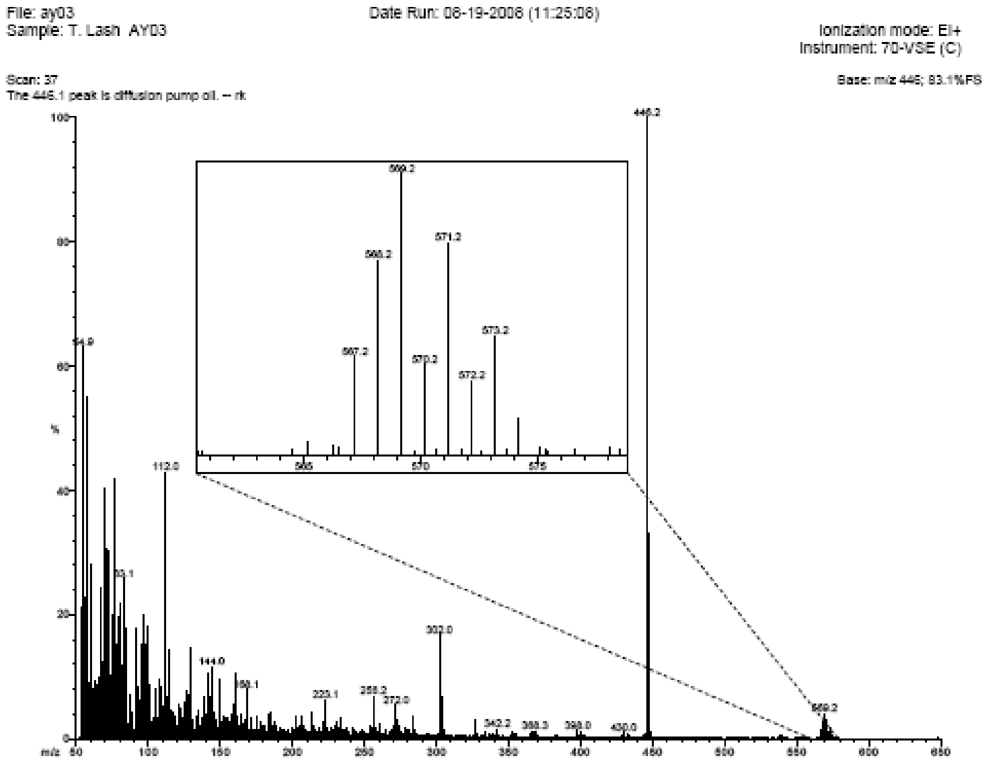

Figure S37: EI MS of 2-methyl-3-azaNCP palladium complex **13b**. The peak at 446 is due to pump oil.

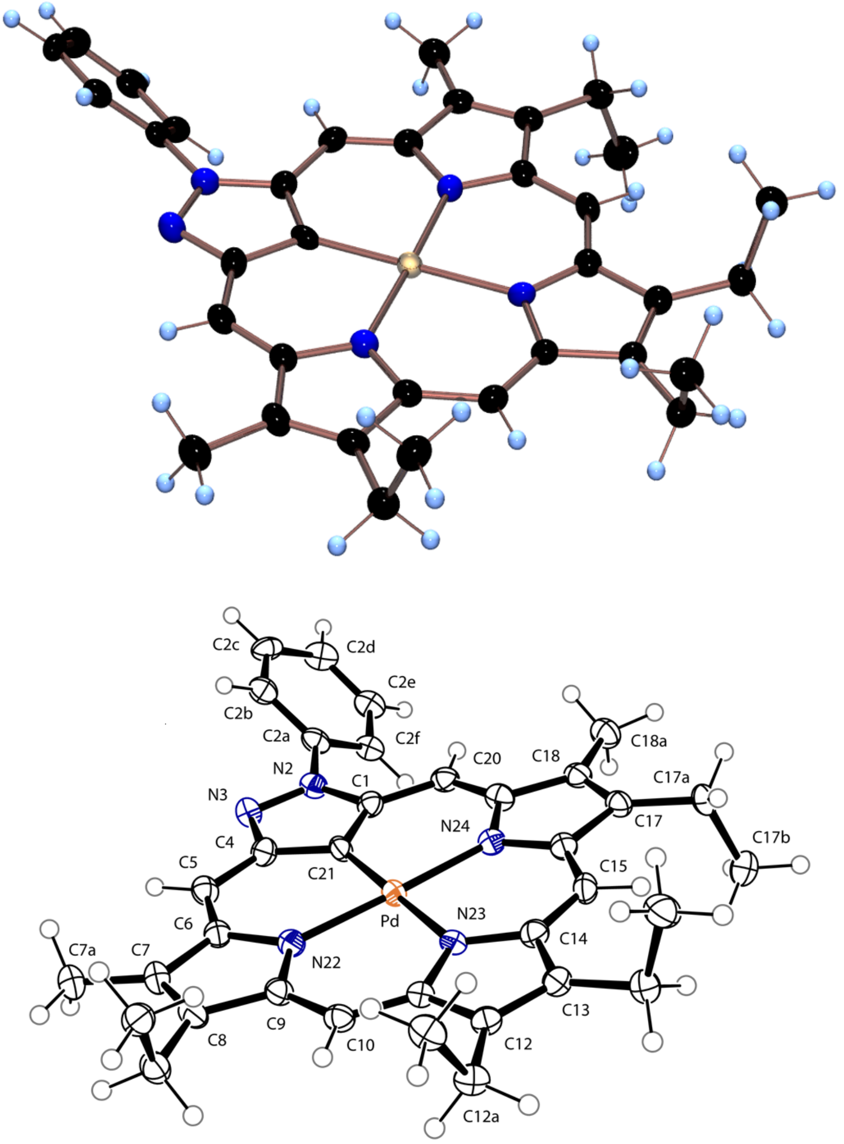

Figure S38: ORTEP III drawings (50% probability level, hydrogen atoms drawn arbitrarily small) of the palladium(II) 2-phenyl pyrazole porphyrin complex **13a**.

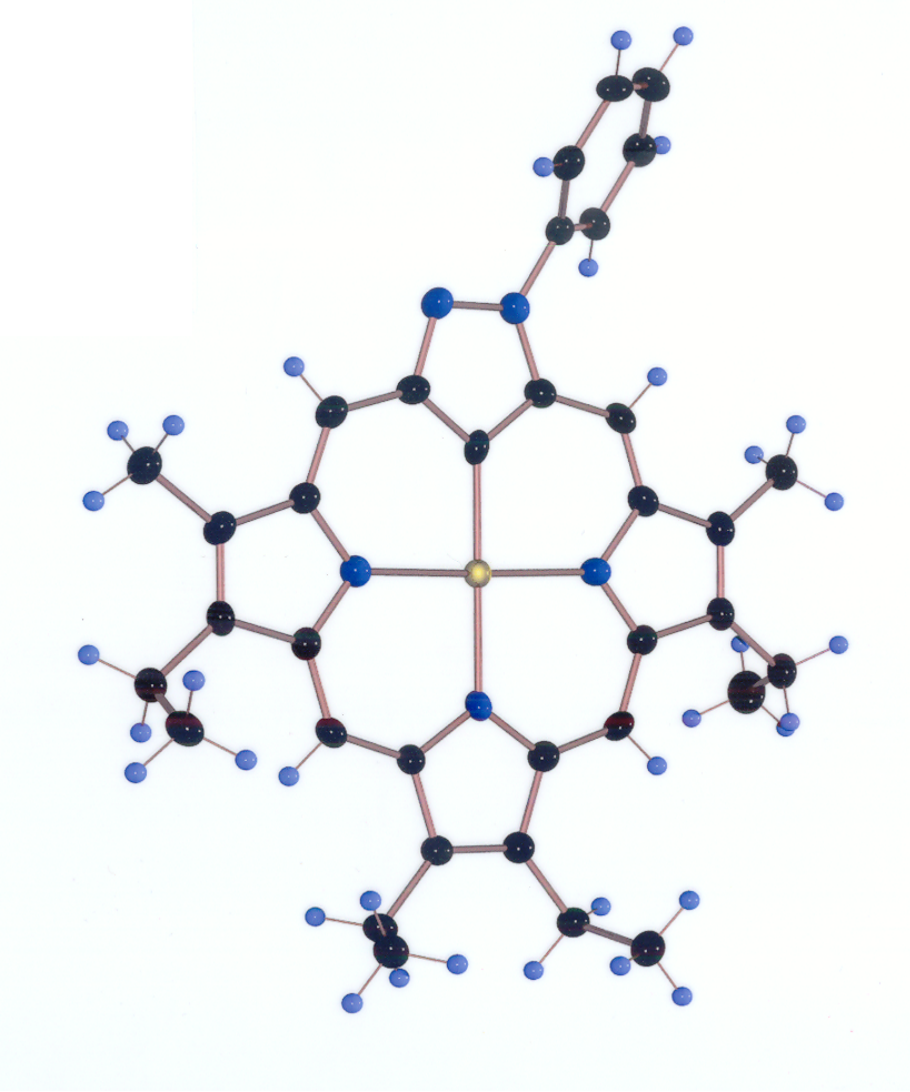

Figure S39: X-ray crystal structure of the 2-phenyl pyrazole porphyrin complex **13a** showing an arial view of the macrocycle.

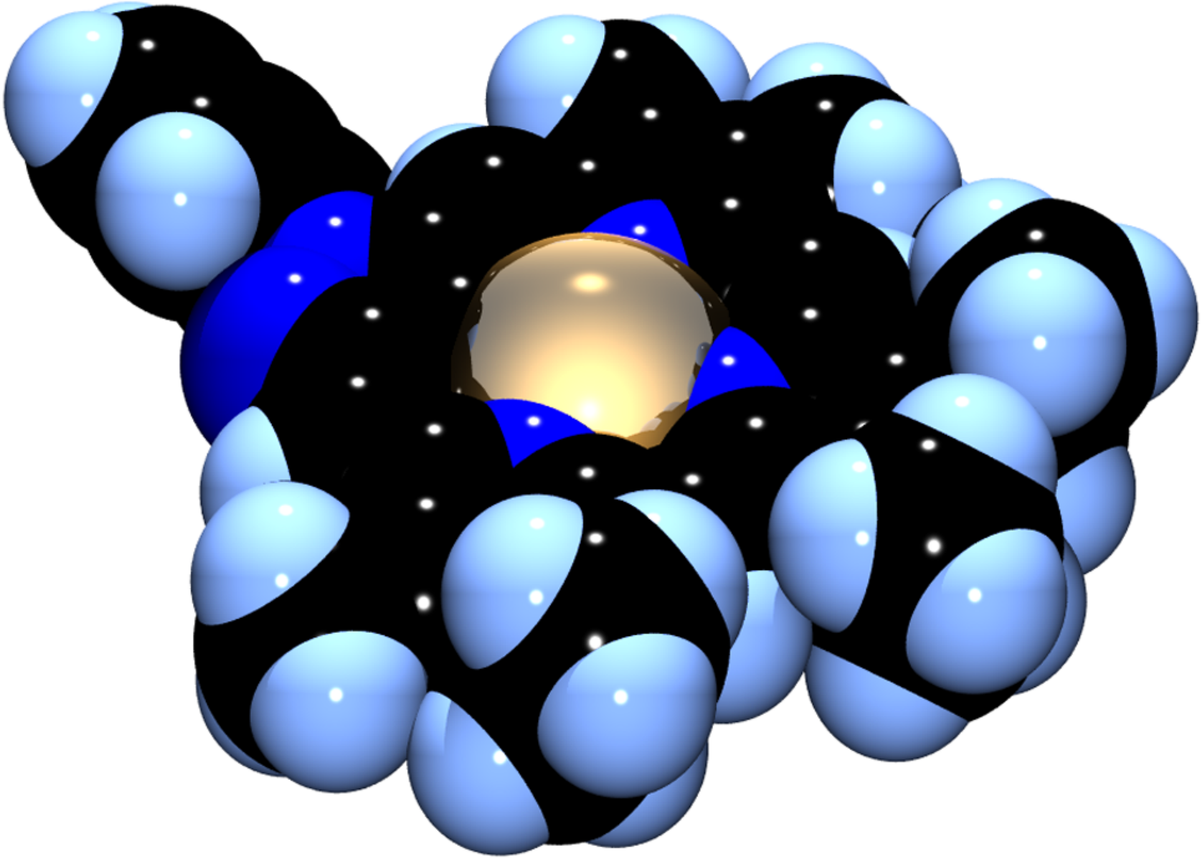

Figure S40. Space filling representation of the X-ray crystal structure for the palladium(II) 2-phenyl pyrazole porphyrin complex **13a** generated with POV-Ray.