Supporting Information

N-Heterocyclic Carbene (NHC) Ligands Annulated to Free–Base Porphyrins: Modulation of the Electronic Properties of the NHC Upon Protonation or Metallation of the Porphyrin

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I. EXPERIMENTAL DETAILS

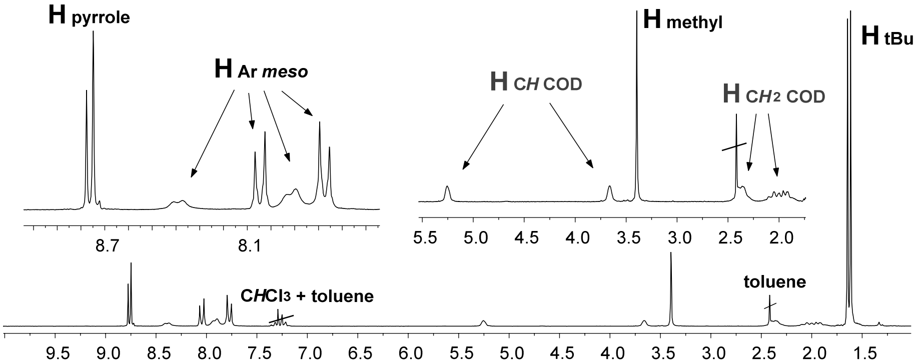
^{1}H NMR spectra were recorded on a Brücker DPX-200 spectrometer and reported downfield to $SiMe_4$ and referenced to chloroform peak (δ = 7.29 ppm) or dichloromethane peak (δ= 5.32 ppm). Abbreviations for ^{1}H NMR spectra used are as follows: s, singlet; d, doublet; m, multiplet. UV-visible spectra were recorded on a Perkin Elmer Lambda 35 spectrophotometer in quartz cells and CH_2Cl_2 or $CHCl_3$ was used as solvent. IR spectra were recorded on an Avatar 320 FT-IR spectrometer in solution in a CaF_2 cell. ESI mass spectra were recorded on a Q-Tof Waters 2001 MS instrument. EDX microanalyses were performed on a FEI Quanta DEG 200 environmental microscope. All reagents and solvents were of the commercial reagent grade and were used without further purification except where noted. Dry CH_2Cl_2 was obtained by distilling over CaH_2. Dry toluene was obtained by distilling over Na. Dry THF was obtained by distilling over CaH_2, then Na/benzophenone. Preparative separations were performed by silica gel flash column chromatography (Baeckeroot-Labo 60M).

II. SYNTHESES OF THE COMPOUNDS

Synthesis of the rhodium(I) complex **2-Ni**.

Imidazolium salt **1-Ni** (80 mg, 7.33×10^{-5} mol) was dissolved in toluene (7 mL). Then, rhodium(I) complex $[Rh(COD)Cl]_2$ (20 mg, 4.06×10^{-5} mol) and K_2CO_3 (60 mg, 4.34×10^{-4} mol) were added and the mixture was stirred at room temperature under an atmosphere of argon for 20 hours. After evaporation of toluene, the rhodium(I) complex **2-Ni** was purified by column chromatography on silica gel (eluent: dichloromethane). After evaporation of the solvent, complex **2-Ni** was obtained in 92% yield (88 mg) as a purple solid.

^{1}H NMR (200 MHz, 25°C, CDCl$_3$) : δ 8.78 (s, 2H, pyrrole), 8.75 (s, 4H, pyrrole), 8.39 (d broad, *J* = 8.2 Hz, 4H, Ar *meso*), 8.05 (d, *J* = 8.2 Hz, 4H, Ar *meso*), 7.92 (d broad, *J* = 8.2 Hz, 4H, Ar *meso*), 7.77 (2d, *J* = 8.2 Hz, 8H, Ar *meso*), 5.26 (s broad, 2H, C*H* COD), 3.66 (s broad, 2H, C*H* COD), 3.39 (s, 6H, N-C*H*$_3$), 2.49 – 2.23 (m, 4H, C*H*$_2$ COD), 2.15 – 1.81 (m, 4H C*H*$_2$ COD), 1.65 (s, 18H, *t*Bu), 1.61 (s, 18H, *t*Bu) ppm.



UV-visible (CH$_2$Cl$_2$) : λ_{max} (ε): 426 (211700), 539 (18000), 576 nm (sh 5470 L.mol^{-1}.cm^{-1}).

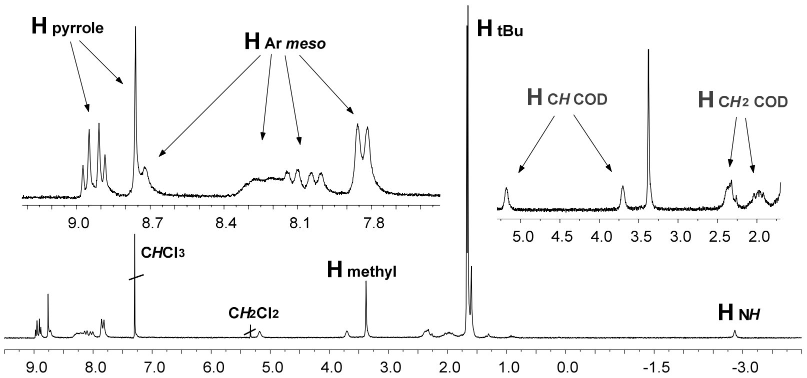
ESI$^+$ MS : calculated for $C_{63}H_{64}IN_6NaNiRh^+$: 1215.25, found: 1215.5 ([M-COD+Na]$^+$).

ESI$^-$ MS : calculated for I$^-$: 126.9, found: 126.9

Synthesis of the rhodium(I) complex **2-2H**.

Rhodium(I) complex **2-2H** was obtained in 90% yield from **1-2H** following the same procedure as described for **2-Ni**.

^{1}H NMR (200 MHz, 25°C, CDCl$_3$) : δ 8.78 (d, *J* = 5.1 Hz, 2H, pyrrole), 8.78 (d, *J* = 5.1 Hz, 2H, pyrrole), 8.77 (s, 2H, pyrrole), 8.74 (d broad, *J* = 8.1 Hz, 2H, Ar *meso*), 8.25 (m, 4H, Ar *meso*), 8.13 (d broad, *J* = 8.1 Hz, 4H, Ar *meso*), 8.03 (d broad, *J* = 8.1 Hz, 6H, Ar *meso*), 7.77 (d broad, *J* = 8.1 Hz, 8H, Ar *meso*), 5.19 (s broad, 2H, C*H* COD), 3.71 (s broad, 2H, C*H* COD), 3.39 (s, 6H, N-C*H*$_3$), 2.51 – 2.21 (m, 4H, C*H*$_2$ COD), 2.17 – 1.83 (m, 4H, C*H*$_2$ COD), 1.68 (s, 18H, *t*Bu), 1.66 (s, 18H, *t*Bu), -2.85 (s, 2H, N*H*) ppm.



UV-visible (CH_2Cl_2) : λ_{max} (ε): 427 (346200), 526 (17850), 564 (11620), 600 (5810), 660 nm (sh 3740 $L.mol^{-1}.cm^{-1}$).

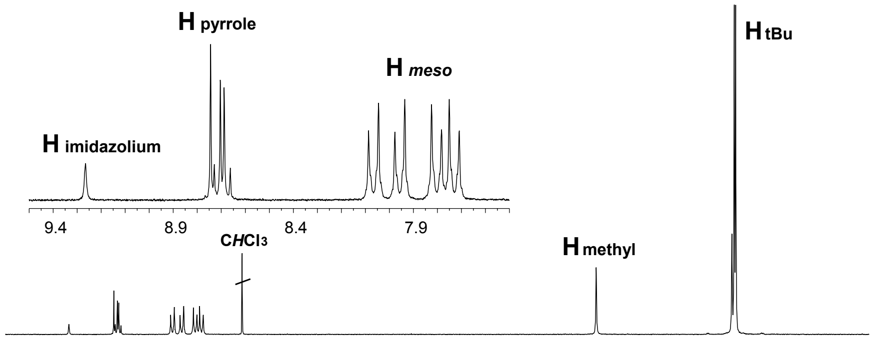
ESI^+ MS : calculated for $C_{71}H_{79}IN_6Rh^+$: 1245.45, found: 1245.6 ($[M+H]^+$).

ESI^- MS : calculated for I^-: 126.9, found: 126.9

Synthesis of the imidazolium salt **4-Ni**

Imidazolium salt **1-Ni** (84 mg, 7.69×10^{-5} mol) was dissolved in acetone (20 mL). Then, a solution of silver tetrafluoroborate $AgBF_4$ (16 mg, $8.22.\times10^{-5}$ mol) in acetone (1 mL) was slowly added and the reaction mixture was stirred in the dark for one hour. After evaporation of solvent, the imidazolium salt **4-Ni** was purified by column chromatography on silica gel (eluent: from dichloromethane → dichloromethane/ethanol 95:5). Evaporation of the solvent afforded the imidazolium salt 4-Ni as a purple solid in 92% yield (74 mg).

^{1}H NMR (200 MHz, 25°C, $CDCl_3$) : δ 9.29 (s, 1H, C*H* iminium), 8.77 (s, 2H, pyrrole), 8.75 (d, *J* = 5.0 Hz, 2H, pyrrole), 8.71 (d, *J* = 5.0 Hz, 2H, pyrrole), 8.10 (d, *J* = 8.3 Hz, 4H, Ar *meso*), 7.99 (d, *J* = 8.3 Hz, 4H, Ar *meso*), 7.83 (d, *J* = 8.3 Hz, 4H, Ar *meso*), 7.76 (d, *J* = 8.3 Hz, 4H, Ar *meso*), 3.19 (s, 6H, N-CH_3), 1.59 (s, 18H, *t*Bu), 1.57 (s, 18H, *t*Bu) ppm.



UV-visible (CH_2Cl_2): λ_{max} (ε): 426 (221800), 537 (16300), 575 nm (sh 4020 $L.mol^{-1}.cm^{-1}$).

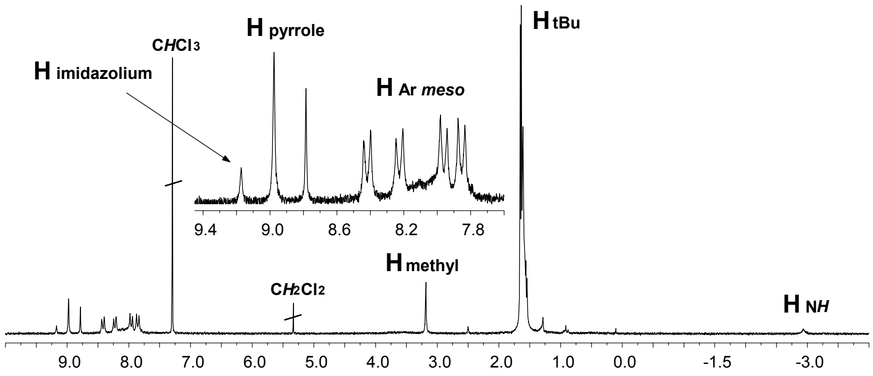
ESI$^+$ MS : calculated for $C_{63}H_{65}N_6Ni^+$: 963.46, found : 963.3 (M^+).

ESI$^-$ MS : calculated for BF_4^- : 87.0, found : 87.0 (M^-).

Synthesis of the imidazolium salt **4-2H**

The imidazolium salt **4-2H** was obtained in 90% yield from **1-2H** following the same procedure as described for **4-Ni**.

^{1}H NMR (200 MHz, 25°C, $CDCl_3$) : δ 9.29 (s, 1H, C*H* iminium), 8.98 (s, 4H, pyrrole), 8.79 (s, 2H, pyrrole), 8.42 (d, *J* = 8,1 Hz, 4H, Ar *meso*), 8.23 (d, *J* = 8,1 Hz, 4H, Ar *meso*), 7.96 (d, *J* = 8,1 Hz, 4H, Ar *meso*), 7.86 (d, *J* = 8,1 Hz, 4H, Ar *meso*), 3.20 (s, 6H, N-C*H*$_3$), 1.66 (s, 18H, *t*Bu), 1.64 (s, 18H, *t*Bu), -2.97 (s, 2H, N*H*) ppm.



UV-visible (CH_2Cl_2) : λ_{max} (ε): 428 (352500), 528 (12500), 567 (8300), 597 (5000), 657 nm (6800 $L.mol^{-1}.cm^{-1}$).

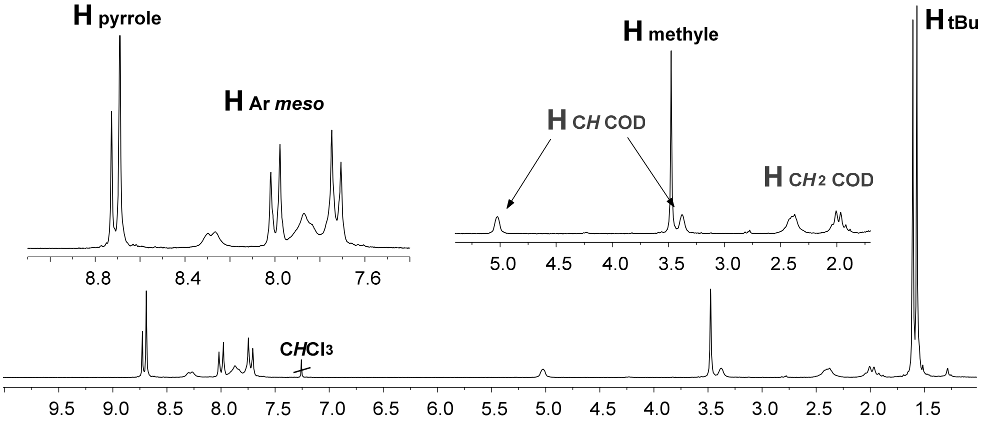
ESI$^+$ MS : calculated for $C_{63}H_{67}N_6^+$: 907.54, found : 907.5 (M^+).

ESI$^-$ MS : calculated for BF_4^- : 87.0, found : 87.0 (M^-).

Synthesis of the rhodium(I) complex **5-Ni.**

A 25 mL flask was charged with imidazolium salt **4-Ni** (35 mg, 3.33×10^{-5} mol), $[RhCl(COD)Cl]_2$ (3,5 mg, 1.99×10^{-5} mol) and sodium *tert*-butoxyde (3,5 mg, 3.64×10^{-5} mol) in THF (10 mL). The reaction mixture was stirred under an atmosphere of argon for 2 hours at ambient temperature. Completion of the reaction was verified by TLC analysis. THF was removed under reduced pressure leaving crude product that was purified by a silica gel column chromatography with dichloromethane as eluent. Evaporation of solvent afforded rhodium(I) complex **5-Ni** in 94% yield (37.7 mg) as purple solid.

^{1}H NMR (200 MHz, 25°C, $CDCl_3$) : δ 8.75 (s, 2H, pyrrole), 8.72 (s, 4H, pyrrole), 8.31 (d broad, 2H, Ar *meso*), 8.03 (d, *J* = 8.2 Hz, 4H, Ar *meso*), 7.90 (s broad, 4H, Ar *meso*), 7.76 (d, *J* = 8.2 Hz, 6H, Ar *meso*), 5.05 (s broad, 2H, C*H* COD), 3.50 (s, 6H, N-CH_3), 3.40 (s broad, 2H, C*H* COD), 2.46 - 2.34 (m broad, 4H, CH_2 COD), 2.08 - 1.91 (m broad, 4H, CH_2 COD), 1.64 (m, 18H, *t*Bu), 1.60 (m, 18H, *t*Bu) ppm.



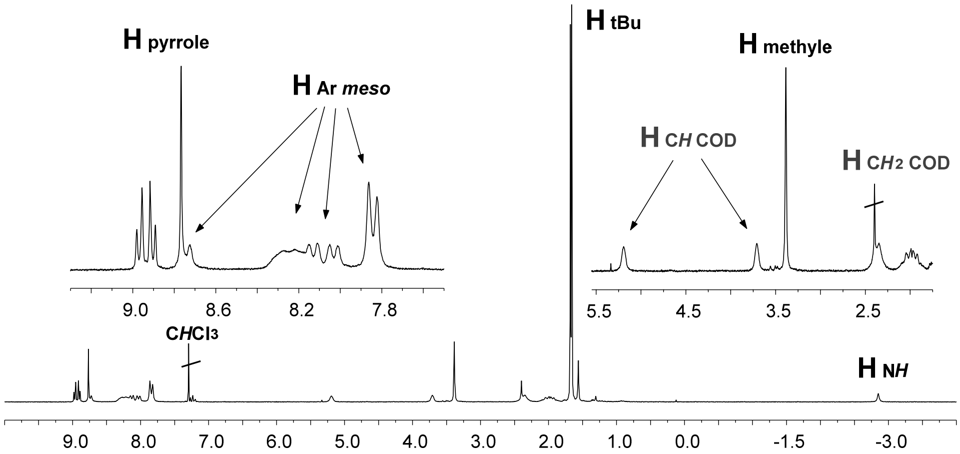
UV-visible (CH_2Cl_2): λ_{max} (ε): 426 (295700), 538 (21900), 572 nm (sh 7260 $L.mol^{-1}.cm^{-1}$).

ESI$^+$ MS : calculated for $C_{71}H_{76}ClLiN_6NiRh^+$: 1215.44, found: 1215.3 ($[M+Li]^+$).

Synthesis of the rhodium(I) complex **5-2H**.

Rhodium(I) complex **5-2H** was obtained in 92% yield from **4-2H** following the same procedure as described for **5-Ni**.

^{1}H NMR (200 MHz, 25°C, $CDCl_3$) : δ 8.95 (d, *J* = 5.1 Hz, 2H, pyrrole), 8.89 (d, *J* = 5.1 Hz, 2H, pyrrole), 8.76 (s, 2H, pyrrole), 8.68 (d broad, 2H, Ar *meso*), 8.33 - 8.15 (m broad, 4H, Ar *meso*), 8.15 (d broad, 2H, Ar *meso*), 8.02 (d broad, 2H, Ar *meso*), 7.83 (d broad, 6H, Ar *meso*), 5.00 (s broad, 2H, C*H* COD), 3.50 (s, 6H, N-CH_3), 3.49 (s broad, 2H, C*H* COD), 2.50 – 2.38 (m broad, 4H, CH_2 COD), 2.04 – 1.88 (m broad, 4H, CH_2 COD), 1.68 (s, 18H, *t*Bu), 1.65 (s, 18H, *t*Bu), -2.94 (s, 2H, N*H*) ppm.



UV-visible (CH_2Cl_2): λ_{max} (ε): 430 (322000), 528 (15700), 564 (10570), 599 (5430), 661 nm (4000 $L.mol^{-1}.cm^{-1}$).

ESI$^+$ MS : calculated for $C_{71}H_{78}ClLiN_6Rh^+$: 1159.52, found: 1159.7 ($[M+Li]^+$).

III. PREPARATION OF CARBONYL RHODIUM(I) COMPLEXES

Typical procedure for preparation of carbonyl rhodium(I) complexes **3-M** (M = Ni or 2H)

Rhodium(I) complex **2-M** (20 mg) was dissolved and stirred in dichloromethane (20 mL). Then, carbon monoxide was bubbled for one hour and the carbonyl rhodium(I) complex **3-M** was obtained. Aliquots of the reaction mixture were sampled for IR spectroscopy analyses. Carbonyl rhodium(I) complex **3-M** (M = Ni or 2H) were stable for hours in solution but decomposed upon evaporation of dichloromethane.

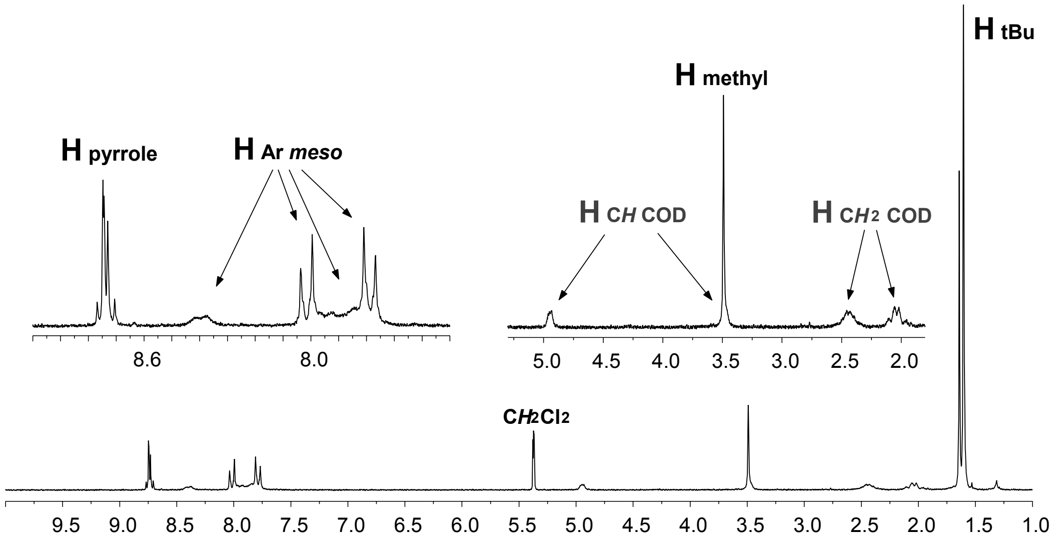
IR (CH_2Cl_2) : **3-2H**: $\bar{\upsilon}$ (CO) = 2001 (sym), 2073 cm^{-1} (asym)
3-Ni: $\bar{\upsilon}$ (CO) = 2002 (sym), 2074 cm^{-1} (asym)

Typical procedure for preparation of carbonyl rhodium(I) complexes **6-M** (M = Ni or 2H)

Carbonyl rhodium(I) complexes **6-M** were obtained from **5-M** following the same procedure as described for **3-M**.

IR (CH_2Cl_2) : **6-2H**: $\bar{\upsilon}$ (CO) = 2002 (sym), 2080 cm^{-1} (asym)
6-Ni: $\bar{\upsilon}$ (CO) = 2002 (sym), 2081 cm^{-1} (asym)

Preparation of carbonyl rhodium(I) complexes **6-Ni** (Fig. 1) and **6-2H** (Fig. 2) in CD_2Cl_2 and monitored by ^1H NMR spectroscopy



a.

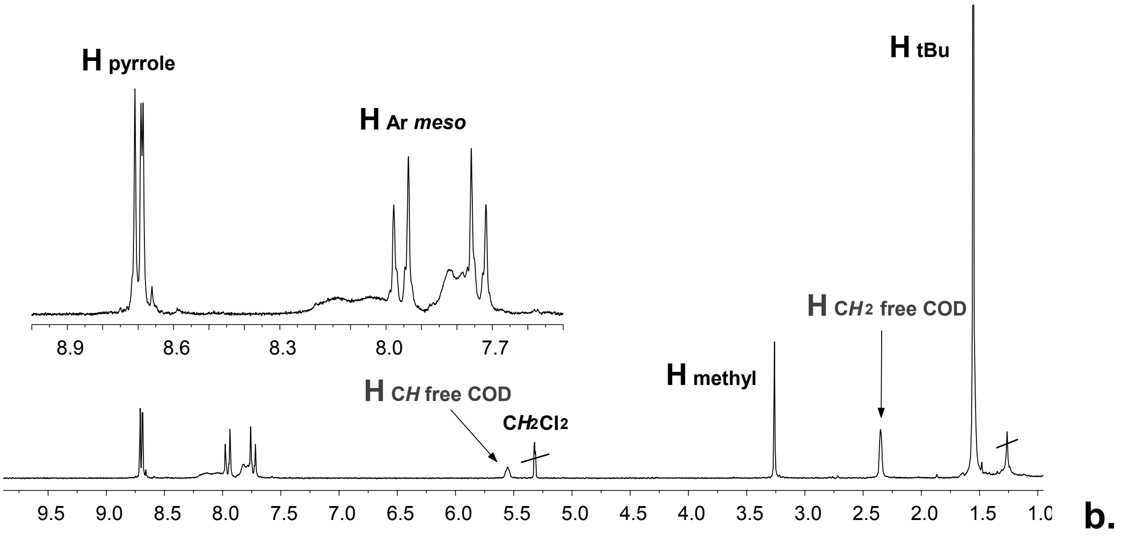


Fig. 1 (a) ^{1}H NMR (200 MHz, 25°C) spectra of **5-2H** in CD_2Cl_2. (b) After bubbling CO for one hour

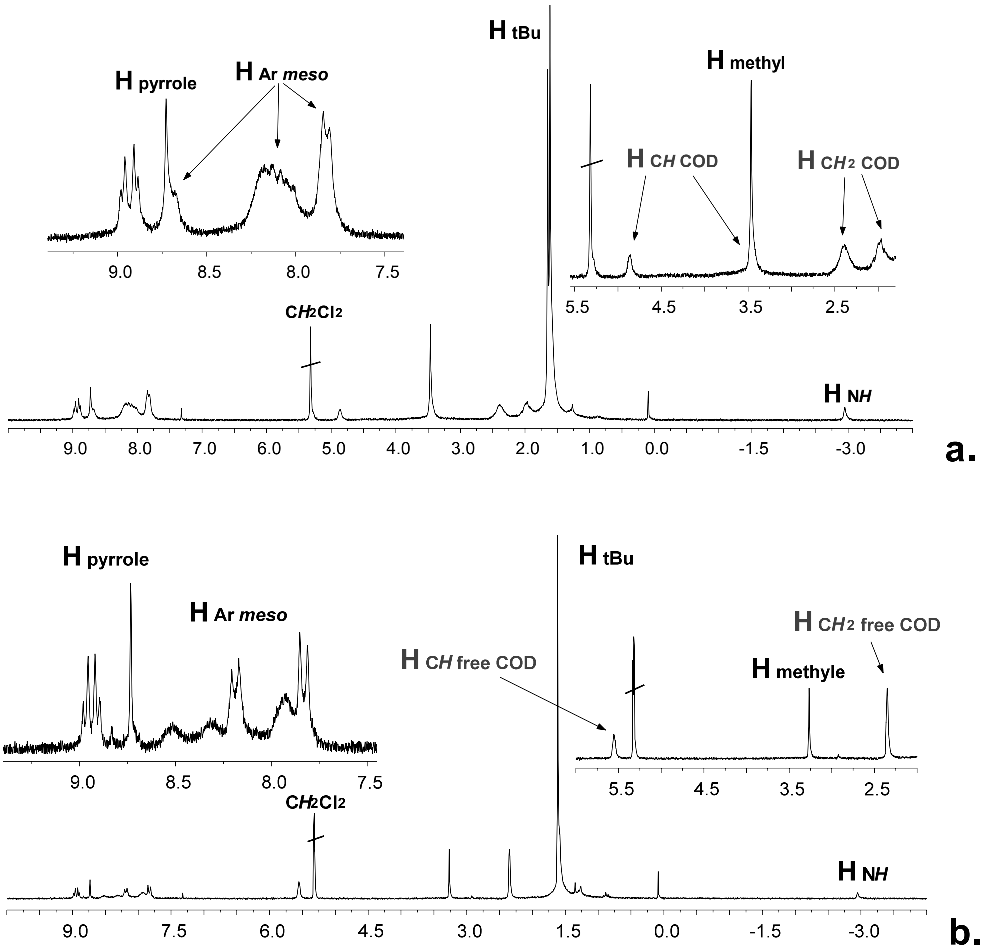


Fig. 2 (a) ^{1}H NMR (200 MHz, 25°C) spectra of **5-2H** in CD_2Cl_2. (b) After bubbling CO for one hour.

IV. PROTONATION / DEPROTONATION FREE-BASE PORPHYRIN

Protonation reaction with trifluoroacetic acid (TFA)

Rhodium(I) complex **2-2H** or **5-2H** (20 mg) was dissolved and stirred in dichloromethane (20 mL) and carbon monoxide was bubbled for one hour and the carbonyl rhodium(I) complexes **3-2H** or **6-2H** . Then, TFA was slowly added until the colour of the reaction mixture turned green. Aliquot of the reaction mixture was sampled for IR spectroscopy analyses.

IR (CH_2Cl_2) : **3-4H^{2+}**: ū (CO) = 2009 (sym), 2079 cm^{-1} (asym)
6-4H^{2+}: ū (CO) = 2010 (sym), 2089 cm^{-1} (asym)

Deprotonation reaction with diisopropylethylamine (DIPEA)

To the reaction mixture containing the protonated porphyrins **3-4H^{2+}** or **6-4H^{2+}** in dichloromethane, DIPEA was slowly added until the reaction mixture turned back to purple. Aliquot of the reaction mixture was sampled for IR spectroscopy analyses and the CO-stretching frequencies observed were identical to the data obtained for **3-2H** or **6-2H**.

IR (CH_2Cl_2) : **3-2H**: ū (CO) = 2001 (sym), 2073 cm^{-1} (asym)
6-2H: ū (CO) = 2002 (sym), 2080 cm^{-1} (asym)