Supporting Information

Synthesis and Structural Characterisation of the First N–Heterocyclic Carbene Ligand Fused to a Porphyrin

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I. EXPERIMENTAL DETAILS

^{1}H NMR spectra were recorded on a Brucker DPX-200 spectrometer and referenced to $SiMe_4$ in 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. IR spectra were recorded on an Avatar 320 FT-IR spectrometer as KBr discs. FAB$^+$ mass spectrometer were recorded on a Jeol DX300 MS instrument and NBA was used as matrix. X-Ray analysis was realized on the Oxford Xcalibur CCD (Mo-Kα, λ = 0.71073 Å) of the Institut Charles Gerhardt Montpellier.

II. SYNTHESES AND CHARACTERISATION OF THE COMPOUNDS

Preparation of the free base porphyrin 4

Pyrrole (12 g, 0.179 mmol) and 4-*tert*-butylbenzaldehyde (30 mL, 0.179 mmol) were stirred in refluxing propionic acid under air during 90 minutes. After cooling, the purple solid was filtered off and washed several times with methanol. The free base porphyrin **4** was obtained in 21% yield (7.90 g).
^{1}H NMR ($CDCl_3$, 200 MHz, 300K): δ 8.91 (s, 8H, $H_{pyrrole}$), 8.19 (d, J = 8.4Hz, 8H, $H_{Ar\,ortho}$), 7.80 (d, J = 8.4Hz, 8H ; $H_{Ar\,meta}$), 1.65 (s, 36H ; H_{tBu}), -2.71 (s ; 2H ; NH).
UV-visible : λ_{nm} (ε L.mol^{-1}.cm^{-1}): 421 (470200), 518 (16600), 554 (10100), 592 (5300), 650 (6200).

Preparation of the nickel (II) complex 4

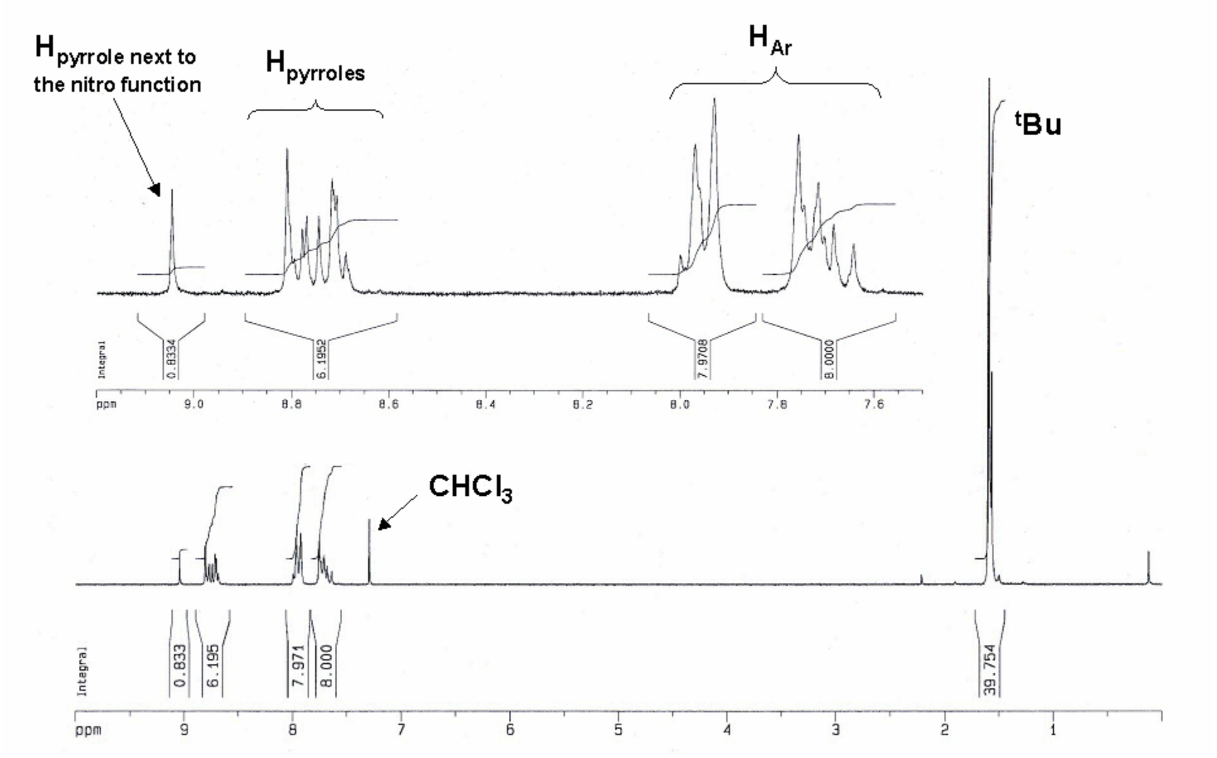
The free base porphyrin **4** (5 g, 5.96x10^{-3} mol) and $Ni(acac)_2$ (1.85 g, 7.21x10^{-3} mol) were stirred in refluxing toluene for 12 hours. After evaporation of the solvent, and crystallization from chloroform/methanol, the red nickel(II) complex **4** was obtained in 96% yield (5.12 g).
^{1}H NMR (200 MHz, 25°C, $CDCl_3$) : δ 8.81 (s, 8H, $H_{pyrrole}$), 7.97 (d, J = 8.4Hz, 8H, $H_{Ar\,ortho}$), 7.72 (d, J = 8.4Hz, 8H, $H_{Ar\,meta}$). 1.58 (s, 36H, H_{tBu}).
UV-visible : λ_{nm} (ε L.mol^{-1}.cm^{-1}): 418 (303100), 531 (15600), 619 (500).
FAB$^+$ MS : calculated for $C_{60}H_{61}N_4Ni^+$: 894.42, found: 894.

Preparation of the β-nitroporphyrin 5

To a warm chloroform solution (400 mL, 45°C) of the nickel complex **4** (2.46 g, 2.75×10^{-3} mol) were added a solution of lithium nitrate in acetic acid (1.72 g, 2.5×10^{-2} mol in 100 mL) and acetic anhydride (95 mL, 1 mol). The advancement of the reaction was carefully monitored by silica gel TLC, and after completion of the nitration (approximatively 1.5 h), the reaction mixture was neutralized with an aqueous $NaHCO_3$ solution, washed three times with water, and the solvent was evaporated. After crystallization (dichloromethane/methanol) the β-nitroporphyrin **5** was obtained in 78% yield (2.02 g).

^{1}H NMR (200 MHz, 25°C, $CDCl_3$) : δ 9.05 (s, 1H, $H_{pyrrole}$) ; 8.82-8.60 (m, 6H, $H_{pyrrole}$), 8.05-7.90 (m, 8H, $H_{Ar\ ortho}$), 7.80-7.60 (m, 8H ; $H_{Ar\ meta}$), 1,59 (s, 36H, H_{tBu}).
UV-visible : λ_{nm} (ε $L.mol^{-1}.cm^{-1}$) : 430 (138000), 540 (10500), 587 (7300).
FAB$^+$ MS : calculated for $C_{60}H_{60}N_5NiO_2^+$: 939.40, found: 940.

^{1}H NMR spectrum (200 MHz, 25°C, $CDCl_3$) of the β-nitroporphyrin 5



Preparation of the 2-amino-3-nitroporphyrin 6

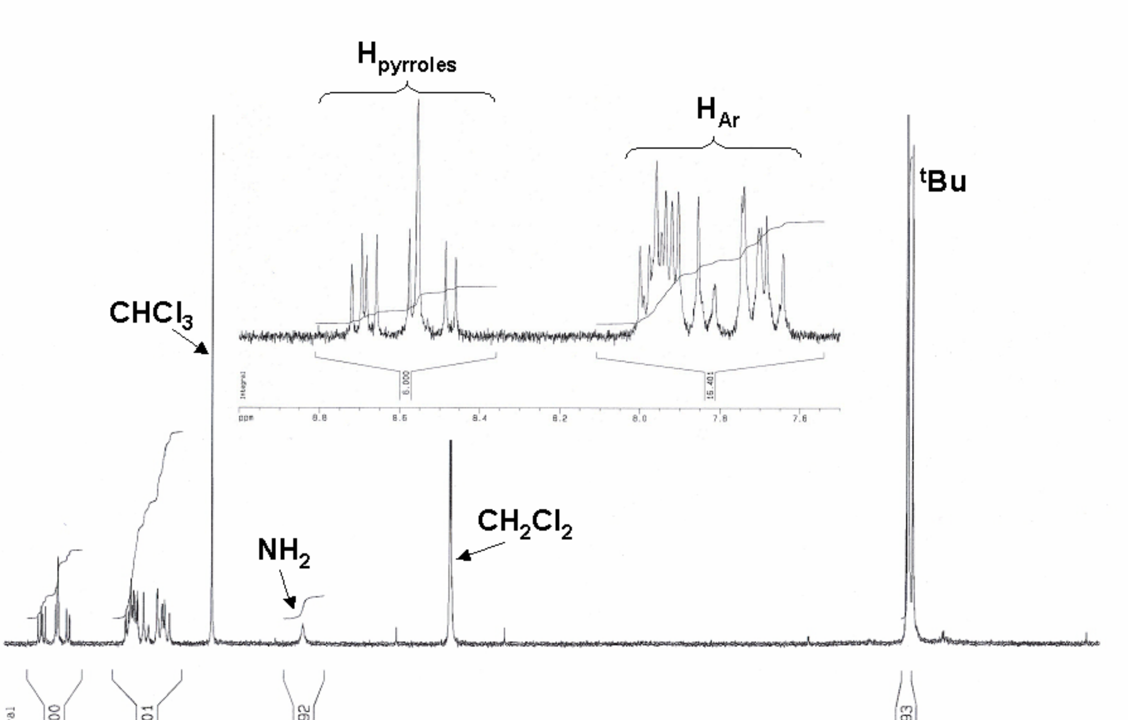
A solution of the β-nitroporphyrin **5** (1 g, 1.06×10^{-3} mol), sodium hydroxide (0.2 g, 5×10^{-3} mol) and 4-amino-4*H*-1,2,4-triazole (0.943 g, 1.12×10^{-2} mol) in a mixture of toluene and ethanol (200 and 10 mL) was heated under reflux for 1 hour. After cooling and evaporation, dichloromethane was added and the organic phase was then washed three times with water and dried with sodium sulfate. Chromatography on silica gel (eluent: dichloromethane/pentane 7:3) and crystallization from dichloromethane/methanol afforded the 2-amino-3-nitroporphyrin **6** in 82% yield (0.83 g).

^{1}H NMR (200 MHz, 25°C, $CDCl_3$) : δ 8.71 (d, *J* = 5.0Hz, 1H, $H_{pyrrole}$), 8.67 (d, *J* = 5.0Hz, 1H, $H_{pyrrole}$), 8.57 (d, *J* = 5,0Hz, 1H, $H_{pyrrole}$), 8.56 (s, 2H, $H_{pyrrole}$), 8.47 (d, *J* = 5.0Hz, 1H, $H_{pyrrole}$), 8.01-7.89 (m, 8H, $H_{Ar\ ortho}$), 7.87-7.63 (m, 8H, $H_{Ar\ meta}$), 6.55 (s broad, 2H, H_{NH2}), 1.58 (s, 36H, H_{tBu}).

UV-visible : λ_{nm} (ε $L.mol^{-1}.cm^{-1}$): 444 (131600), 558 (12600), 601 (8900).

FAB$^+$ MS : calculated for $C_{60}H_{61}N_6NiO_2^+$: 954.41, found: 954.

^{1}H NMR spectrum (200 MHz, 25°C, $CDCl_3$) of the 2-amino-3-nitroporphyrin 6



Preparation of the β,β'-fused imidazole porphyrin 1

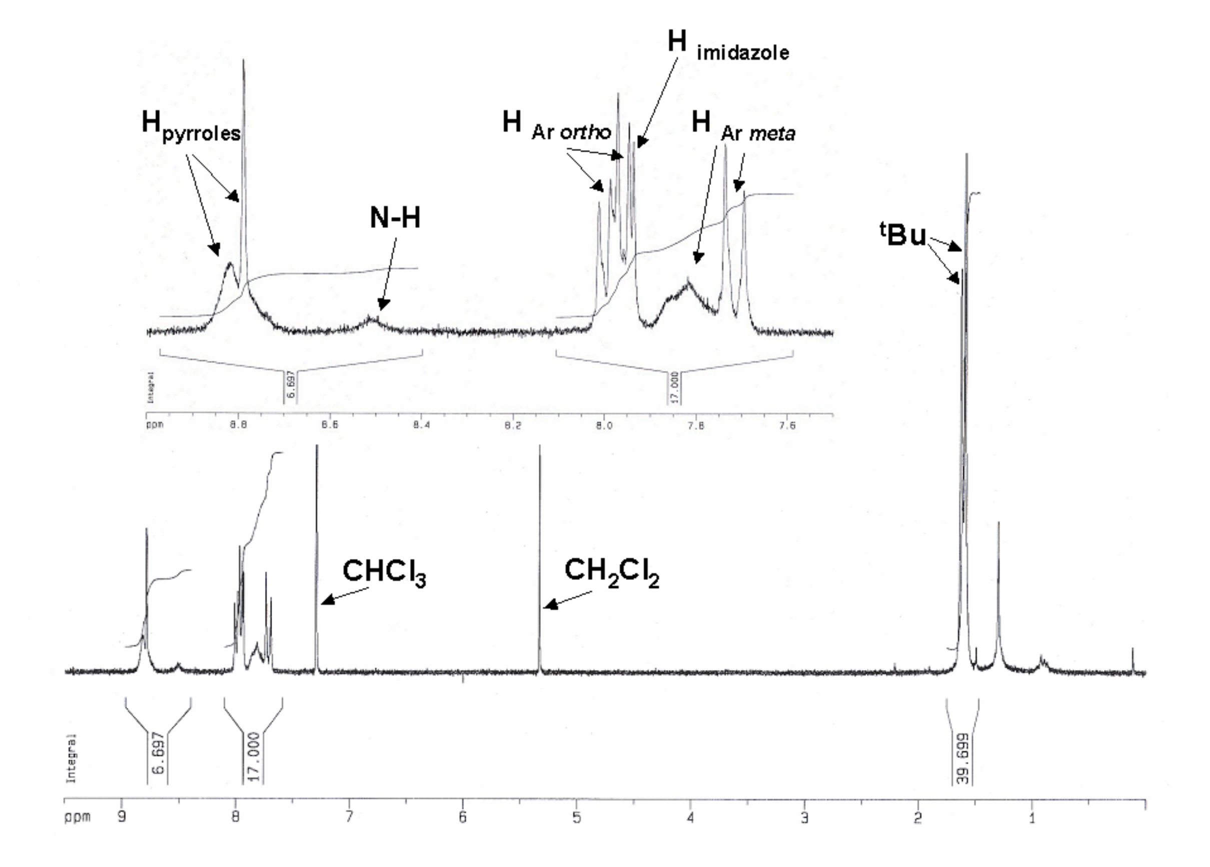
A solution of the porphyrin **6** (0.6 g, 6.28×10^{-4} mol) and palladium on activated carbon 10% (0.54 g, 5.02×10^{-3} mol) in a mixture of dichloromethane and methanol (300 and 30 mL) was prepared and degassed. Sodium borohydride (0.615 g, 1.61×10^{-2} mol) was added and the solution was stirred under argon for two hours. The completion of the reduction was verified by silica gel TLC and the reaction mixture was filtered through a pad of celite. After the evaporation of the solvent, formic acid (25 mL) and toluene (25 mL) were added and the reaction mixture was heated under argon at reflux for 10 minutes. After cooling, dichloromethane (200 mL) and water (200 mL) were added. The mixture was neutralized with K_2CO_3, washed three times with water, and the solvent evaporated. Toluene (200 mL) and TFA (10 mL) were added to the residue and the reaction mixture was heated under argon at reflux for 3 hours. After cooling, dichloromethane (200 mL) and water (200 mL) were added. The mixture was neutralized with K_2CO_3, washed three times with water, and the solvent evaporated. Chromatography on silica gel (eluent: dichloromethane/ethanol 98:2) and crystallization from dichloromethane/methanol afforded the β,β'-fused imidazole porphyrin **1** in 48% yield. (0.28 g).

^{1}H NMR (200 MHz, 25°C, $CDCl_3$) : δ 8.90-8.70 (s broad, 4H, $H_{pyrrole}$), 8.79 (s, 2H, $H_{pyrrole}$), 8.52 (s broad, 1H, $NH_{imidazole}$), 8.10-7.90 (m, 8H, $H_{Ar\ ortho}$), 7.94 (s, 1H, $CH_{imidazole}$), 7.90-7.75 (s broad, 4H, $H_{Ar\ meta}$), 7.72 (d, J = 8.2 Hz, 4H, $H_{Ar\ meta}$), 1.62 (s broad, 18H, H_{tBu}), 1.59 (s, 18H, H_{tBu}).

UV-visible : λ_{nm} (ε $L.mol^{-1}.cm^{-1}$) : 419 (248600), 531 (14500), 568 (7700).

FAB$^+$ MS : calculated for $C_{61}H_{61}N_6Ni^+$: 934.42, found: 935.

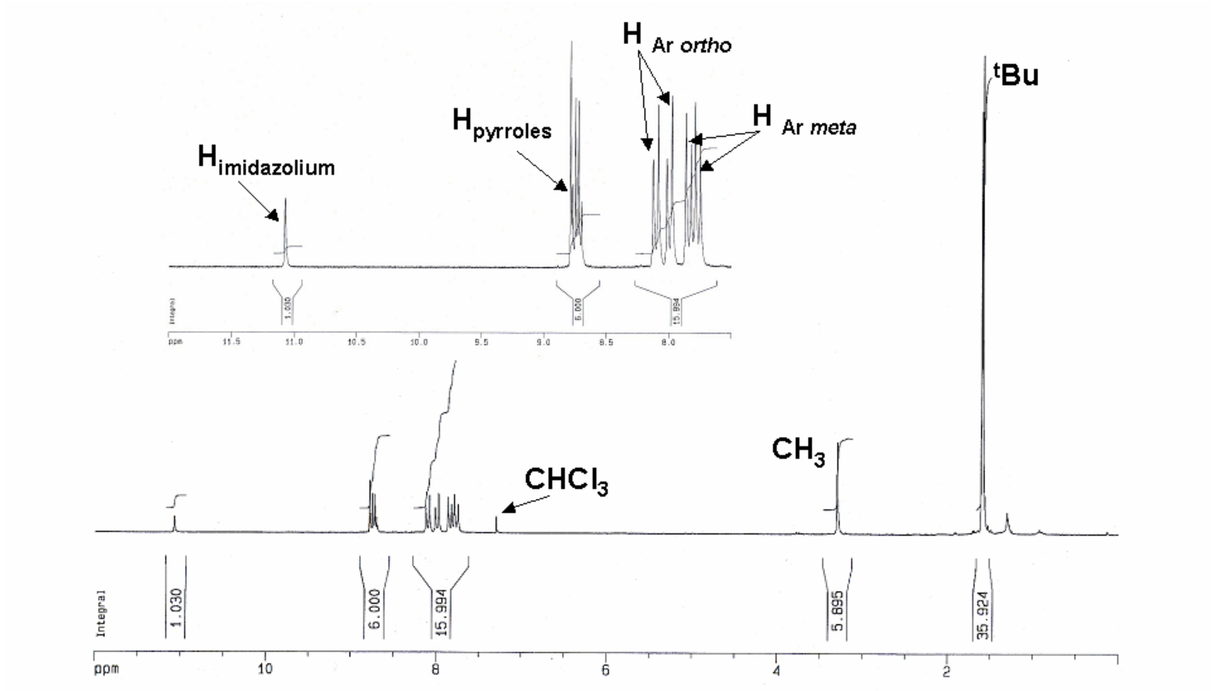
^{1}H NMR spectrum (200 MHz, 25°C, $CDCl_3$) of the β,β'-fused imidazole porphyrin 1



Preparation of the β,β'-fused imidazolium salt 2

The β,β'-fused imidazole porphyrin **1** (0.125 g, 1.33x10^{-4} mole) was dissolved in acetone (30 mL). Iodomethane (5 mL) and K_2CO_3 (0.5 g) were added and the solution was stirred at 40°C under argon for 24 hours. The completion of the alkylation was verified by silica gel TLC and the solvent was evaporated. Chromatography on silica gel (eluent: dichloromethane to dichloromethane ethanol 95:5) and crystallization from pentane afforded the imidazololium salt **2** in 81% yield (0.118 g).
^{1}H NMR (200 MHz, 25°C, $CDCl_3$) : δ 11.07 (s, 1H, $C_{2'}$-$H_{imidazolium}$), 8.78 (s, 2H, $H_{pyrrole}$), 8.75 (d, *J* = 5.0 Hz, 2H, $H_{pyrrole}$), 8.70 (d, *J* = 5.0 Hz, 2H, $H_{pyrrole}$), 8.09 (d, *J* = 8.3 Hz, 4H, $H_{Ar\ ortho}$), 7.99 (d, *J* = 8.3 Hz, 4H, $H_{Ar\ ortho}$), 7.84 (d, *J* = 8.3 Hz, 4H, $H_{Ar\ meta}$), 7.76 (d, *J* = 8.3 Hz, 4H, $H_{Ar\ meta}$), 3.30 (s, 6H, H_{methyl}), 1.60 (s, 18H, H_{tBu}), 1.59 (s, 18H, H_{tBu}).
UV-visible : λ_{nm} (ε $L.mol^{-1}.cm^{-1}$) : 425 (276100), 537 (18000), 575 (3800 sh).
FAB$^+$ MS : calculated for $C_{63}H_{65}N_6Ni^+$: 963.46, found: 963.

^{1}H NMR spectrum (200 MHz, 25°C, $CDCl_3$) of the β,β'-fused imidazolium salt 2



Preparation of the complex 10

The imidazolium salt **2** (40 mg, 3.7×10^{-5} mol) and $Pd(OAc)_2$ (5.3 mg, 2.3×10^{-5} mol) were dissolved in toluene (20 mL), and the mixture was refluxed under argon for 1h30. After the evaporation of the toluene, chromatography on silica gel (eluent: dichloromethane) and crystallization from dichloromethane/methanol afforded the complex **10** in 76% yield (32 mg).

^{1}H NMR (200 MHz, 25°C, $CDCl_3$) : δ 8.72 (s, 4H, $H_{pyrrole}$), 8.68 (s, 8H, $H_{pyrrole}$), 8.11 (d, J = 8.2 Hz, 8H, $H_{Ar\ ortho}$), 8.98 (d, J = 8.2 Hz, 8H, $H_{Ar\ ortho}$), 7.80 (d, J = 8.2 Hz, 8H, $H_{Ar\ meta}$), 7.73 (d, J = 8.2 Hz, 8H, $H_{Ar\ meta}$), 3.26 (s, 12H, H_{methyl}), 1.59 (s, 36H, H_{tBu}), 1.58 (s, 36H, H_{tBu}).

UV-visible : λ_{nm} (ε L.mol^{-1}.cm^{-1}) : 429 (370300), 539 (29500), 580 (8200 sh).

FAB$^+$ MS : calculated for $C_{126}H_{129}I_2N_{12}Ni_2Pd^+$: 2289.07, found: 2289.

^{1}H NMR spectrum (200 MHz, 25°C, $CDCl_3$) of the complex 10