

SUPPORTING INFORMATION

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Ammonium Imidazoporphyrin – a Newborn in a Family of Porphyrins for Hybrid Materials

Vsevolod O. Nikulin,^a Kirill P. Birin,^{b@} Yulia G. Gorbunova,^{a,b} and Aslan Yu. Tsivadze^{a,b}

^a*N.S. Kurnakov Institute of General and Inorganic Chemistry RAS, Moscow, 119991, Russia.*

^b*A.N. Frumkin Institute of Physical Chemistry and Electrochemistry RAS, Moscow, 119071, Russia.*

@kirill.birin@gmail.com

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1. General methods

All the used reagent grade chemicals were purchased from commercial suppliers, unless otherwise stated. The solvents were purified according to conventional methods [1]. Chromatographic purification was performed with Macherey-Nagel Silica 60, 0.063–0.2 mm. Merck aluminum plates (TLC Silica 60 F254) were used for TLC analysis with hexane/dichloromethane mixtures as eluents. Gel-permeation chromatography was performed at Bio-Beads SX-1 sorbent (Bio-Rad) in CHCl_3 :MeOH (97.5:2.5) mixture

MALDI-TOF mass-spectra were recorded at Bruker Daltonics Ultraflex spectrometer in positive ions mode without matrix. UV-Vis spectra were recorded at Evolution 200 spectrophotometer (Thermo Scientific) in rectangular quartz cells with 0.1–10 mm optical path in 250–900 nm range. NMR spectra were recorded at Bruker Avance III spectrometer with 600 MHz proton frequency in CDCl_3 at ambient temperature with the use of the residual solvent resonance as internal reference.

2. Experimental procedures

4-butoxybenzaldehyde. 4-hydroxybenzaldehyde (5 g, 41 mmol) was dissolved in acetone (75 ml) and afterwards butyl bromide (7 ml, 64.9 mmol), dry K_2CO_3 (5.66 g, 41 mmol) and KI (6.80 g, 41 mmol) were added upon stirring. The resulting mixture was refluxed for 5 h. After cooling, the reaction mass was transferred to a separation funnel, diluted with ethyl acetate (100 ml) and subsequently washed once with 0.1N aqueous KOH (100 ml) and twice with water (2 x 100 ml). The organic layer was evaporated *in vacuo* to provide 5.5 g (75%) of the target compound as a yellow oil.

^1H NMR (CDCl_3 ; δ , ppm; J , Hz): 9.87 (s, 1H, CHO), 7.82 (d, 2H, $^3J = 7.8$, *o*- H_{Ar}), 6.98 (d, 2H, $^3J = 8.7$, *m*- H_{Ar}), 4.04 (t, 2H, $^3J = 6.5$, CH_2O), 1.82–1.77 (m, 2H, CH_2), 1.50 (sext, 2H, $^3J = 7.4$, CH_2), 0.99 (t, 3H, $^3J = 7.4$, CH_3).

5,10,15,20-tetrakis-(4-butoxyphenyl)-porphyrin 1. 4-butoxybenzaldehyde (5.5 g, 30.9 mmol) was dissolved in 230 ml of propionic acid and heated to 130°C upon stirring. Pyrrole (2.2 ml, 31.8 mmol) was added and the mixture was refluxed for 2 h, cooled to ambient temperature and diluted with MeOH (270 ml). The resulting mass was kept at *ca.* 5°C overnight, the formed precipitate was filtered, washed with MeOH and dried to provide 1 g (14%) of the target porphyrin **1** as violet crystals.

^1H NMR (CDCl_3 ; δ , ppm; J , Hz): 8.97 (s, 8H, H_β), 8.11 (d, 8H, $^3J = 8.1$, *o*- H_{Ar}), 7.27 (d, 8H, $^3J = 8.3$, *m*- H_{Ar}), 4.26 (t, 8H, $^3J = 6.5$, CH_2O), 2.01–1.95 (m, 8H, CH_2), 1.71–1.64 (m, 8H), 1.11 (t, 12H, $^3J = 7.3$, CH_3), -2.73 (s, 2H, H_{NH}).

Nickel(II) 5,10,15,20-tetrakis-(4-butoxyphenyl)-porphyrinate 2. **1** (150 mg, 0.17 mmol) and Ni(acac)₂ (85 mg, 0.33 mmol) were mixed in toluene (100 ml) and the mixture was refluxed for 2 h, that is, until complete conversion of the starting free-base porphyrin was detected by TLC. After cooling, the reaction mixture was filtered through a pad of silica with CHCl_3 as eluent CHCl_3 and the obtained solution was evaporated to provide 141 mg (89%) of **2** as red solid.

^1H NMR (CDCl_3 ; δ , ppm; J , Hz): 8.76 (s, 8H, H_β), 7.90 (d, 8H, $^3J = 8.2$, *o*- H_{Ar}), 7.20 (d, 8H, $^3J = 8.2$, *m*- H_{Ar}), 4.21 (t, 8H, $^3J = 6.5$, CH_2O), 1.97–1.90 (m, 8H, CH_2), 1.64 (sext, 8H, $^3J = 7.4$, CH_2), 1.08 (t, 8H, $^3J = 7.4$, CH_3).

Nickel(II) 2-nitro-5,10,15,20-tetrakis-(4-butoxyphenyl)-porphyrinate 3. **2** (339 mg, 0.35 mmol) was dissolved in CHCl_3 (63 ml) and the solution of LiNO_3 (390 mg, 5.65 mmol) in AcOH (3.26 ml) was added upon stirring. Afterwards succinic anhydride (1.76 g, 17.65 mmol) was added and the resulting mixture was refluxed for 5.5 h controlling the conversion by TLC. After complete consumption of the starting material the mixture was cooled to ambient temperature, water (50 ml) was added and the mixture was stirred overnight. The organic phase was separated, washed with water and evaporated with silica. Chromatographic separation at silica (hexane/ CH_2Cl_2 0 → 40% of CH_2Cl_2) and evaporation of the fractions provided 193 mg (54%) of **3** as green solid.

^1H NMR (CDCl_3 ; δ , ppm; J , Hz): 8.98 (s, 1H, H_β), 8.75–8.71 (2d, 2H, H_β), 8.69–8.67 (2d, 2H, H_β), 8.66–8.64 (2d, 2H, H_β), 7.89–7.85 (2d, 8H, *o*- H_{Ar}), 7.22–7.19 (2d, 6H, *m*- H_{Ar}), 7.13 (d, 4H, $^3J = 8.5$, *m*- H_{Ar}), 4.23–4.18 (2t, 6H, $\text{H}_{\text{CH}_2\text{O}}$), 4.16 (t, 2H, $^3J = 6.5$, $\text{H}_{\text{CH}_2\text{O}}$), 1.97–1.88 (m, 8H, H_{CH_2}), 1.68–1.58 (m, 8H, H_{CH_2}), 1.10–1.05 (m, 12H, H_{CH_3}).

Nickel(II) 2-amino-3-nitro-5,10,15,20-tetrakis-(4-butoxyphenyl)-porphyrinate 4. **3** (193 mg, 0.19 mmol) was dissolved in toluene (33 ml). The resulting mixture was heated to 75°C, a solution of 4-amino-4H-1,2,4-triazole (484 mg, 5.76 mmol) in ethanol (2.2 ml) was added upon stirring and the temperature was increased to 90°C. KOH (1.080 g, 19.29 mmol) was added and the reaction mixture was refluxed for 5 min. The mixture was cooled to ambient temperature and the solvents were evaporated under reduced pressure. The crude product was purified by flash-chromatography (hexane/ CH_2Cl_2 , 50 → 70% CH_2Cl_2) and evaporated to dryness to provide 190 mg (97%) of **4** as a green solid.

^1H NMR (CDCl_3 ; δ , ppm; J , Hz): 8.65 (d, 1H, $^3J = 4.8$, H_β), 8.62 (d, 1H, $^3J = 5.0$, H_β), 8.51 (d, 1H, $^3J = 5.0$, H_β), 8.50 (s, 2H, H_β), 8.44 (d, 1H, $^3J = 5.0$, H_β), 7.92 (d, 2H, $^3J = 8.4$, *o*- H_{Ar}), 7.88 (d, 2H, $^3J = 8.1$, *o*- H_{Ar}), 7.87 (d, 2H, $^3J = 8.2$, *o*- H_{Ar}), 7.84 (d, 2H, $^3J = 8.5$, *o*- H_{Ar}), 7.29 (d, 1H, $^3J = 8.4$, *m*- H_{Ar}), 7.22–7.18 (2d, 4H, *m*- H_{Ar}), 7.15 (d, 2H, $^3J = 8.4$, *m*- H_{Ar}), 6.57 (s, 2H, H_{NH_2}), 4.22–4.18 (3t, 6H, $\text{H}_{\text{CH}_2\text{O}}$), 4.14 (t, 2H, $^3J = 6.5$, $\text{H}_{\text{CH}_2\text{O}}$), 1.97–1.86 (m, 8H, H_{CH_2}), 1.67–1.57 (m, 8H, H_{CH_2}), 1.10–1.04 (m, 12H, H_{CH_3}).

Nickel(II) 2,3-diamino-5,10,15,20-tetrakis-(4-butoxyphenyl)-porphyrinate 5 and nickel(II) 2-(4-(2-hydroxyethoxy)-phenyl)-imidazo-5,10,15,20-tetrakis-(4-butoxyphenyl)-porphyrinate 6. **Step 1** A 100-ml two-necked flask containing **4** (190 mg, 0.19 mmol) was filled with argon through a rubber septum and charged with 95 mg of 10% Pd on activated charcoal, CH_2Cl_2 (56 ml) and MeOH (2 ml). NaBH_4 (106 mg, 2.79 mmol) was added portionwise upon stirring. After the completion of the reaction (*ca.* 15 min) the reaction mixture was filtered through a pad of Celite 545 in argon atmosphere and the solvents were evaporated *in vacuo*. The obtained **5** was used in the next step without purification.

Step 2. 4-(2-hydroxyethoxy)-benzaldehyde (308 mg, 1.86 mmol) was dissolved in 1,2-dichlorobenzene (30 ml) and added to the **5** under argon. The mixture was heated at 120°C for 19 h upon stirring. Afterwards the mixture was cooled to ambient temperature and the solvent was evaporated. The product was purified by column chromatography on silica (hexane/ CH_2Cl_2 , 50 → 100% CH_2Cl_2 , then CH_2Cl_2 /MeOH, 0 → 2% MeOH) followed by gel-permeation chromatography (CHCl_3 /MeOH, 2% MeOH) and finally by column chromatography on silica (hexane/ CH_2Cl_2 , 50 → 100% CH_2Cl_2 , CH_2Cl_2 /MeOH, 0 → 2% MeOH) to provide after evaporation 58 mg (27%) of **6** as a red solid.

^1H NMR (CDCl_3 ; δ , ppm; J , Hz): 8.81 (s, 2H, H_β), 8.79 (s, 2H, H_β), 8.76 (d, 1H, $^3J = 5.0$, H_β), 8.74 (d, 1H, $^3J = 5.0$, H_β), 8.60 (s, 1H, H_{NH}), 7.98 (d, 4H, $^3J = 8.8$, *o*- H_{Ar}), 7.97 (d, 4H, $^3J = 8.8$, *o*- H_{Ar}), 7.91 (d, 4H, $^3J = 8.0$, *o*- H_{Ar}), 7.73 (d, 2H, $^3J = 8.3$, *o*- H_{Ar}), 7.36 (d, 2H, $^3J = 8.0$, *m*- H_{Ar}), 7.27 (d, 2H, $^3J = 8.5$, *m*- H_{Ar}), 7.20 (d, 4H, $^3J = 8.1$, *m*- H_{Ar}), 7.00 (d, 2H, $^3J = 8.3$, *m*- H_{Ar}), 4.29 (t, 2H, $^3J = 6.53$, $\text{H}_{\text{CH}_2\text{O}}$).

4.25 (t, 2H, $^3J = 6.57$, H_{CH_2O}), 4.20 (t, 4H, $^3J = 6.5$, H_{CH_2O}), 4.16 (t, 2H, $^3J = 4.5$, H_{CH_2O}), 4.02 (q, 2H, $^3J = 5.0$, $H_{CH_2(OH)}$), 2.04-1.91 (m, 9H, H_{CH_2} , H_{OH}), 1.73-1.60 (m, 8H, H_{CH_2}), 1.15-1.06 (m, 12H, H_{CH_3}).

UV-Vis ($CHCl_3$, λ , nm (log ϵ)): 286 (4.50), 421 (5.37), 534 (4.26), 570 (4.00).

MALDI-TOF MS: calcd. for $C_{69}H_{68}N_6NiO_6 [M^+]$ 1134.46, found 1134.27.

Nickel(II) 2-(4-(2-tosyloxyethoxy)-phenyl)-imidazo-5,10,15,20-tetrakis-(4-butoxyphenyl)-porphyrinate 7b. 6 (25 mg, 0.022 mmol) was dissolved in CH_2Cl_2 (5 ml) under argon and the solution was cooled to $0^\circ C$. Pyridine (5.3 μ l, 0.066 mmol) and tosyl chloride (6 mg, 0.033 mmol) were added subsequently and the reaction mixture was warmed to room temperature and stirred for 4 d. Next, water (2 ml) and concentrated HCl (23 μ l) were added to the solution. The mixture was transferred to a separation funnel containing water (25 ml) and CH_2Cl_2 (18 ml), organic phase was separated and the aqueous phase was extracted with CH_2Cl_2 (25 ml). The organic phase was evaporated and the residue was purified by column chromatography on silica (hexane/ CH_2Cl_2 , 50 \rightarrow 100% CH_2Cl_2 , then CH_2Cl_2 /MeOH, 0 \rightarrow 1.2% MeOH), providing after evaporation 3 mg (11%) of **7b** as a red solid.

1H NMR ($CDCl_3$; δ , ppm; J , Hz): 8.81 (c, 2H, H_β), 8.78 (s, 2H, H_β), 8.76 (d, 1H, $^3J = 5.0$, H_β), 8.74 (d, 1H, $^3J = 4.9$, H_β), 8.59 (s, 1H, H_{NH}), 8.00-7.95 (2d, 4H, o- H_{Ar}), 7.90 (d, 4H, $^3J = 8.1$, o- H_{Ar}), 7.85 (d, 2H, $^3J = 8.0$, o- $H_{Ar(Ts)}$), 7.68 (d, 2H, $^3J = 8.3$, o- H_{Ar}), 7.39-7.35 (2d: 2H, m- $H_{Ar(Ts)}$; 2H, m- H_{Ar}), 7.28-7.24 (d, 2H, m- H_{Ar}), 7.20 (d, 4H, $^3J = 8.1$, m- H_{Ar}), 6.87 (d, 2H, $^3J = 8.3$, m- H_{Ar}), 4.42 (t, 2H, $^3J = 4.7$, $H_{CH_2O(Ts)}$), 4.29 (t, 2H, $^3J = 6.5$, H_{CH_2O}), 4.26 (t, 2H, $^3J = 6.6$, H_{CH_2O}), 4.24-4.21 (t, 2H, H_{CH_2O}), 4.20 (t, 4H, $^3J = 6.6$, H_{CH_2O}), 2.47 (s, 3H, $H_{CH_3(Ts)}$), 2.04-1.90 (m, 8H, H_{CH_2}), 1.73-1.60 (m, 8H, H_{CH_2}), 1.15-1.05 (m, 12H, H_{CH_3}).

UV-Vis ($CHCl_3$, λ , nm (log ϵ)): 286 (4.61), 422 (5.47), 534 (4.37), 571 (4.10).

MALDI-TOF MS: calcd. for $C_{76}H_{74}N_6NiO_8 [M^+]$ 1288.46, found 1288.31.

Nickel(II) 2-(4-(2-triethylammonium-ethoxy)-phenyl)-imidazo-5,10,15,20-tetrakis-(4-butoxyphenyl)-porphyrinate 8. Et_3N (1 ml, 7.19 mmol) was added to the solution of **7b** (3 mg, 2 μ mol) in $CHCl_3$ (3.5 ml) and the mixture was refluxed for 2 d. The solution was evaporated and the residue was purified by column chromatography on neutral alumina ($CHCl_3$ /MeOH, 0 \rightarrow 6% MeOH) to provide after evaporation 3.2 mg (95%) of **8** as red solid.

1H NMR ($CDCl_3$; δ , ppm; J , Hz): 8.78 (s, 2H, H_β), 8.79-8.77 (d, 1H, H_β), 8.76 (d, 1H, $^3J = 4.9$, H_β), 8.75-8.72 (2d, 2H, H_β), 8.64 (s, 1H, H_{NH}), 7.97 (d, 2H, $^3J = 8.1$, o- H_{Ar}), 7.93 (d, 2H, $^3J = 8.2$, o- H_{Ar}), 7.90 (d, 2H, $^3J = 8.3$, o- H_{Ar}), 7.87 (d, 2H, $^3J = 8.3$, o- H_{Ar}), 7.72 (d, 2H, $^3J = 8.3$, o- H_{Ar}), 7.34 (d, 2H, $^3J = 8.1$, m- H_{Ar}), 7.28-7.24 (d, 2H, m- H_{Ar}), 7.19 (d, 2H, $^3J = 8.4$, m- H_{Ar}), 7.17 (d, 2H, $^3J = 8.3$, m- H_{Ar}), 6.98 (d, 2H, $^3J = 8.3$, m- H_{Ar}), 4.58 (t, 2H, H_{CH_2N}), 4.27 (t, 2H, $^3J = 6.6$, H_{CH_2O}), 4.25 (t, 2H, $^3J = 6.6$, H_{CH_2O}), 4.23-16 (t, 2H, H_{CH_2O} ; m, 4H, H_{CH_2O}), 3.59 (q, 6H, $^3J = 7.3$, $H_{CH_2(NEt_3)}$), 2.03-1.89 (m, 8H, H_{CH_2}), 1.71-1.59 (m, 8H, H_{CH_2}), 1.47 (t, 9H, $^3J = 7.2$, $H_{CH_3(NEt_3)}$), 1.13-1.05 (m, 12H, H_{CH_3}).

UV-Vis ($CHCl_3$, λ , nm (log ϵ)): 284 (4.44), 422 (5.31), 534 (4.20), 568 (3.93).

MALDI-TOF MS: calcd. for $C_{75}H_{82}N_7NiO_5^+ [M^+]$ 1218.57, found 1218.50.

Preparation of the hybrid material. Chromatographic silica (22 mg) was added to the solution of nickel(II) 2-(4-(2-triethylammonium-ethoxy)-phenyl)-imidazo-5,10,15,20-tetrakis-(4-butoxyphenyl)-porphyrinate (3.2 mg, 2.3 μ mol) in dichloromethane (7.5 ml) under vigorous stirring. The fast decolourization of the liquid phase was observed along with the formation of coloured powder of the modified silica. The material was dried in the open air and proved to contain 3.19 mg of the cationic porphyrin, as determined by the UV-vis analysis of the remaining solution.

3. NMR spectra of the compounds

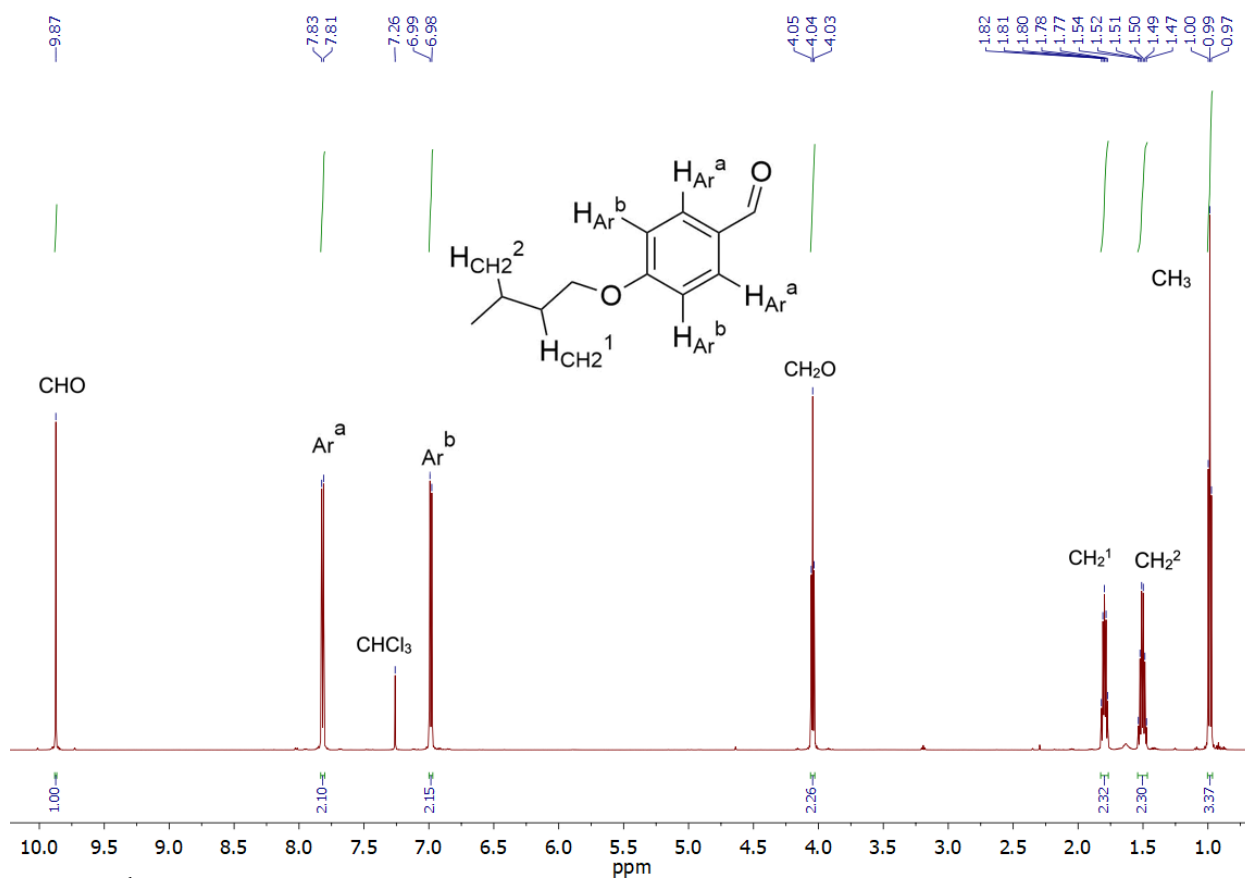


Figure S 1. 1H NMR spectrum of 4-butoxybenzaldehyde ($CDCl_3$).

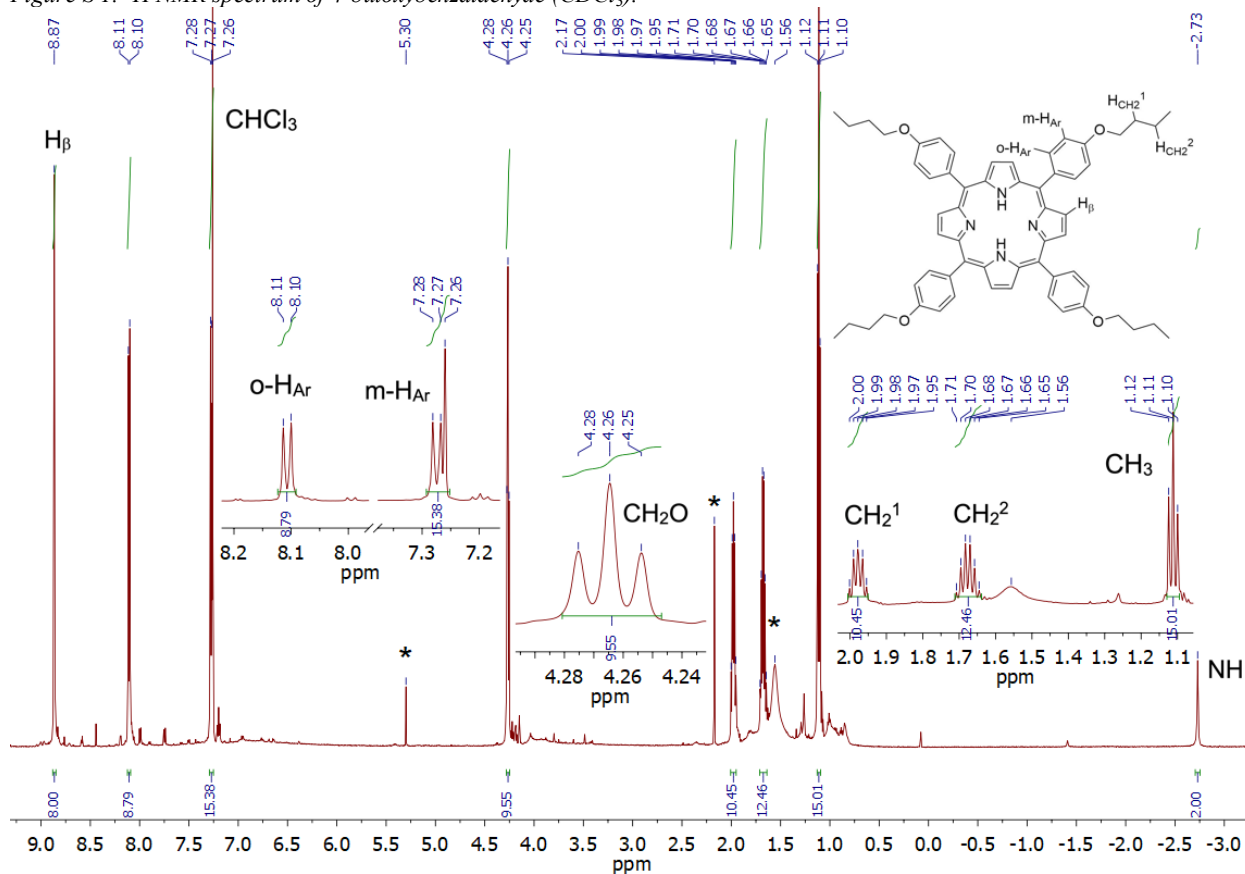


Figure S 2. 1H NMR spectrum of 1 ($CDCl_3$).

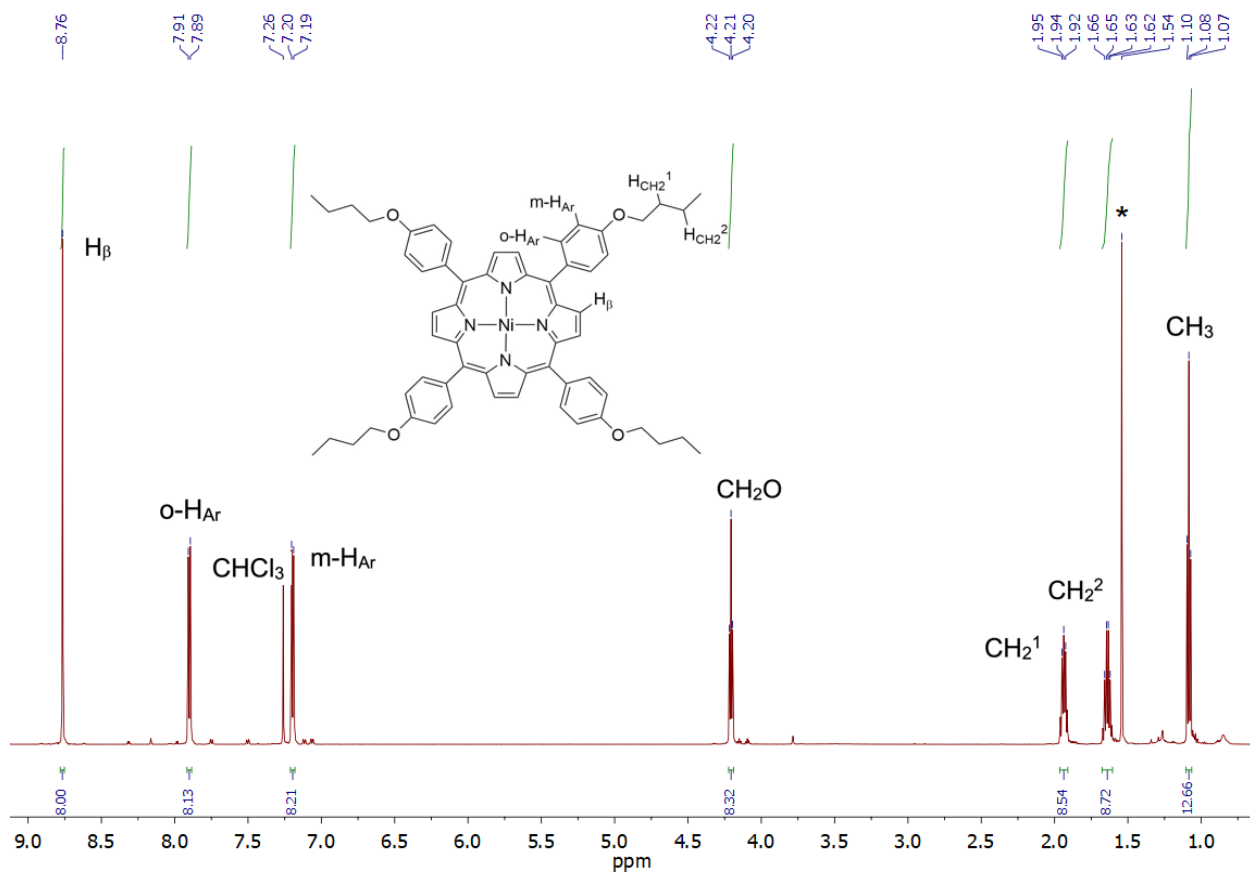


Figure S 3. ^1H NMR spectrum of **2** (CDCl_3).

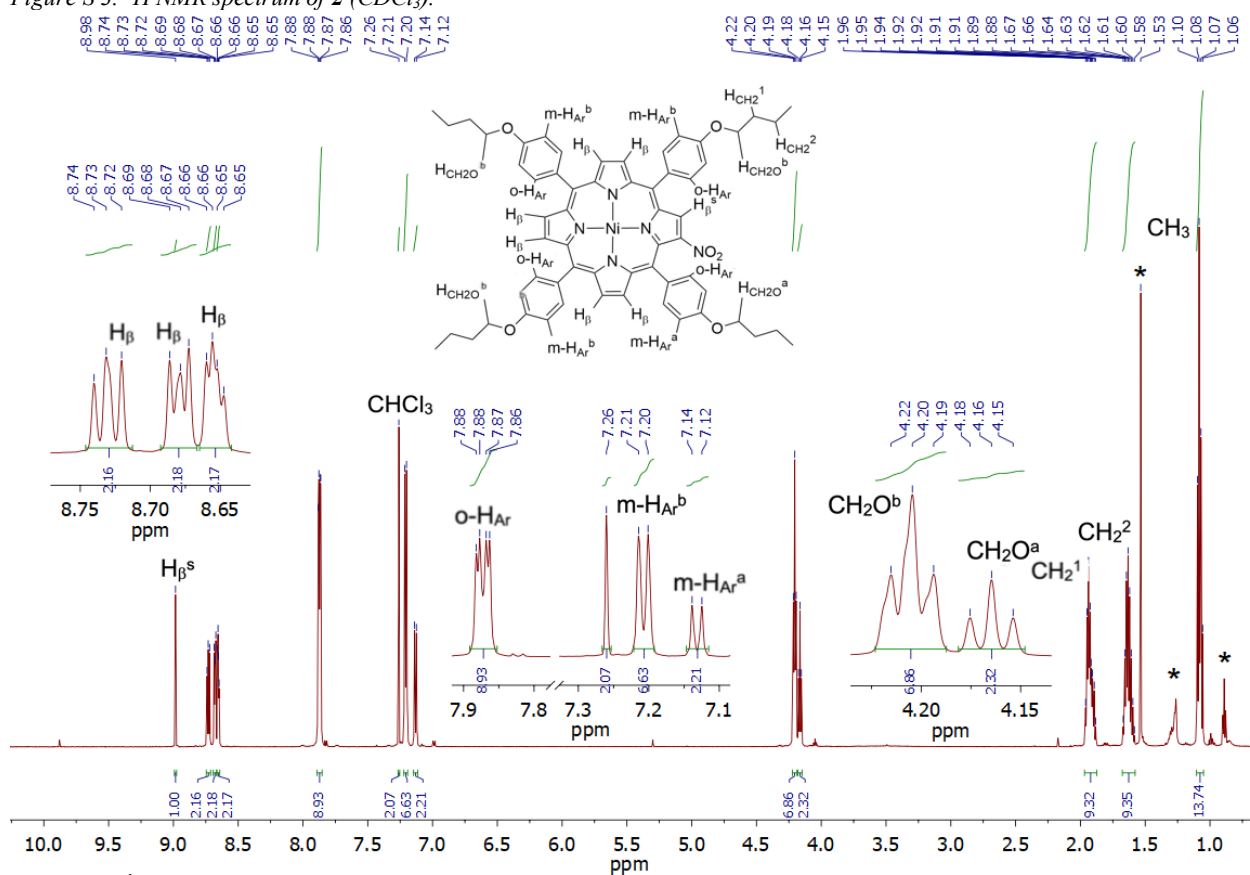


Figure S 4. ^1H NMR spectrum of **3** (CDCl_3).

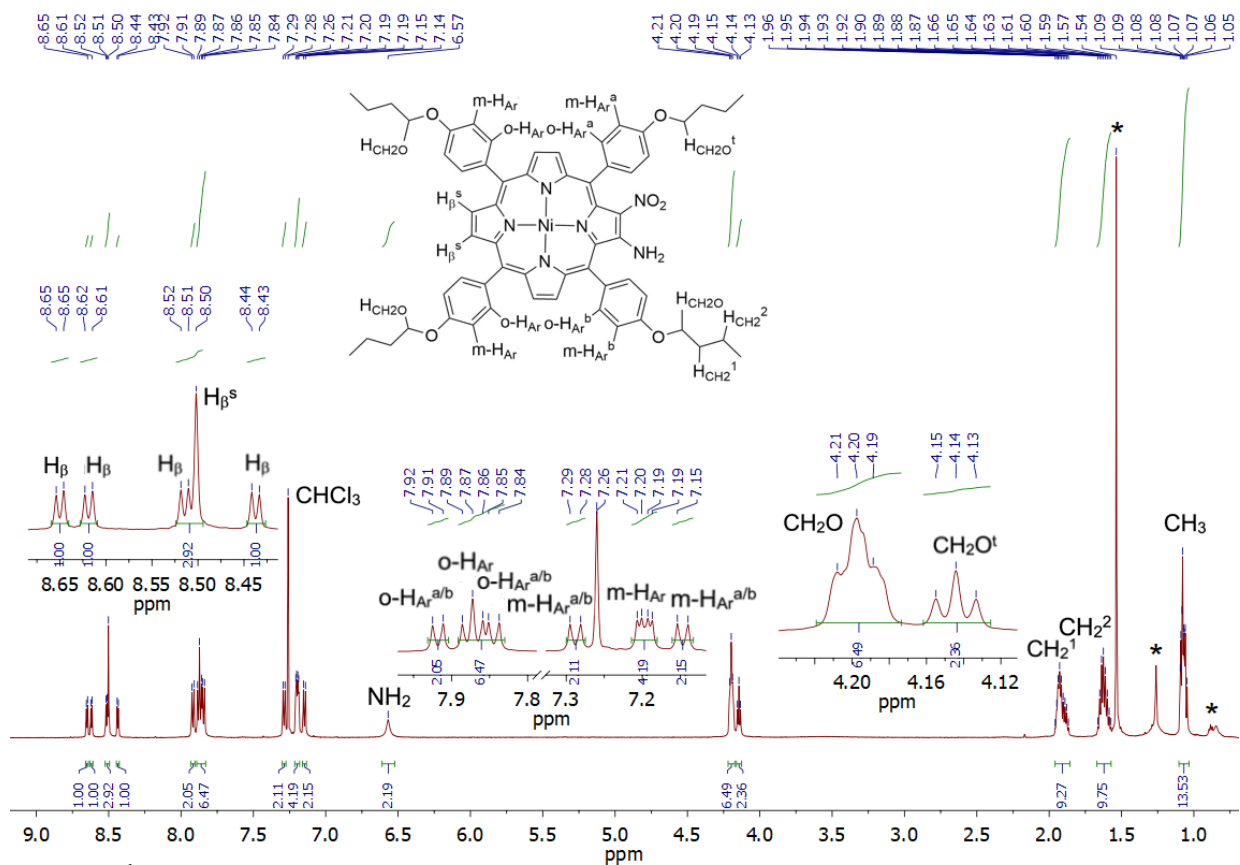


Figure S 5. ¹H NMR spectrum of 4 (CDCl₃).

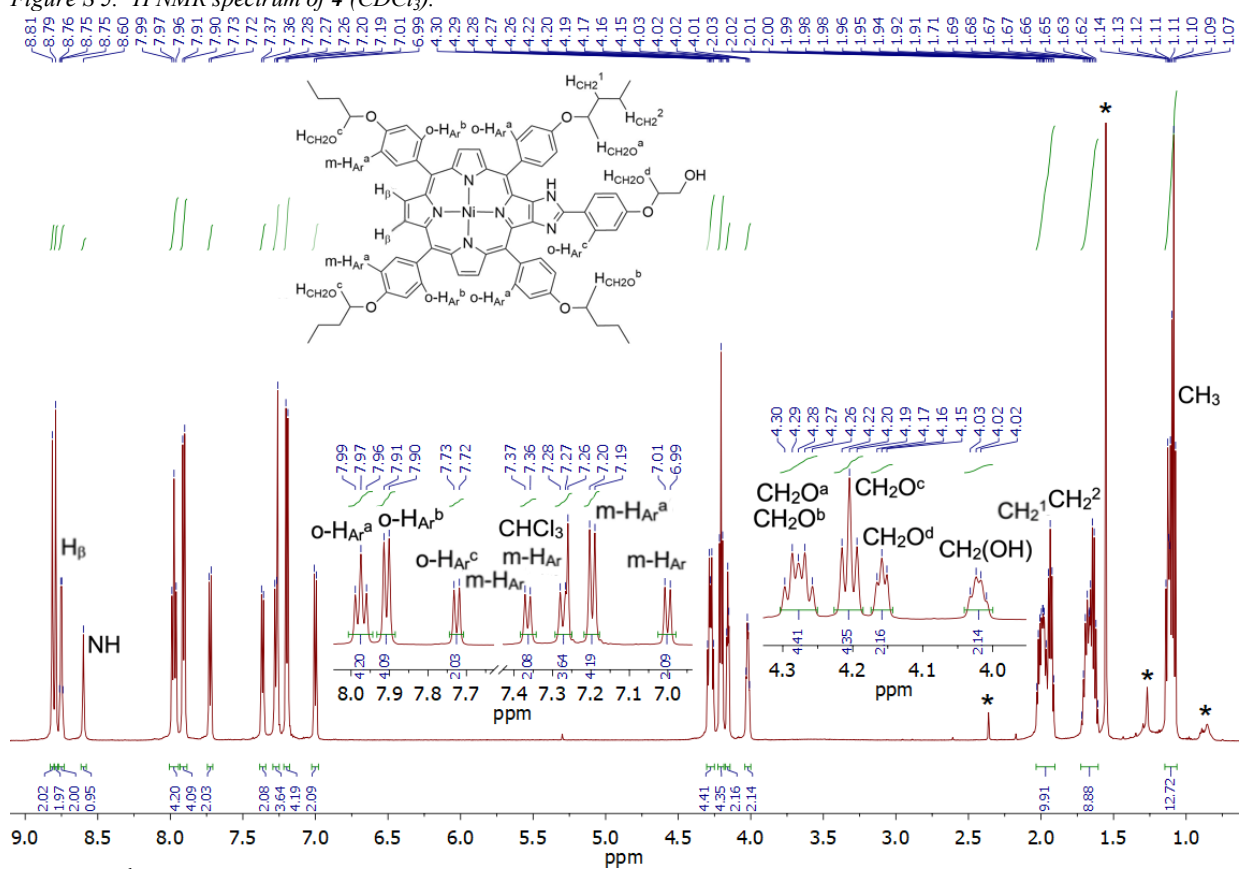
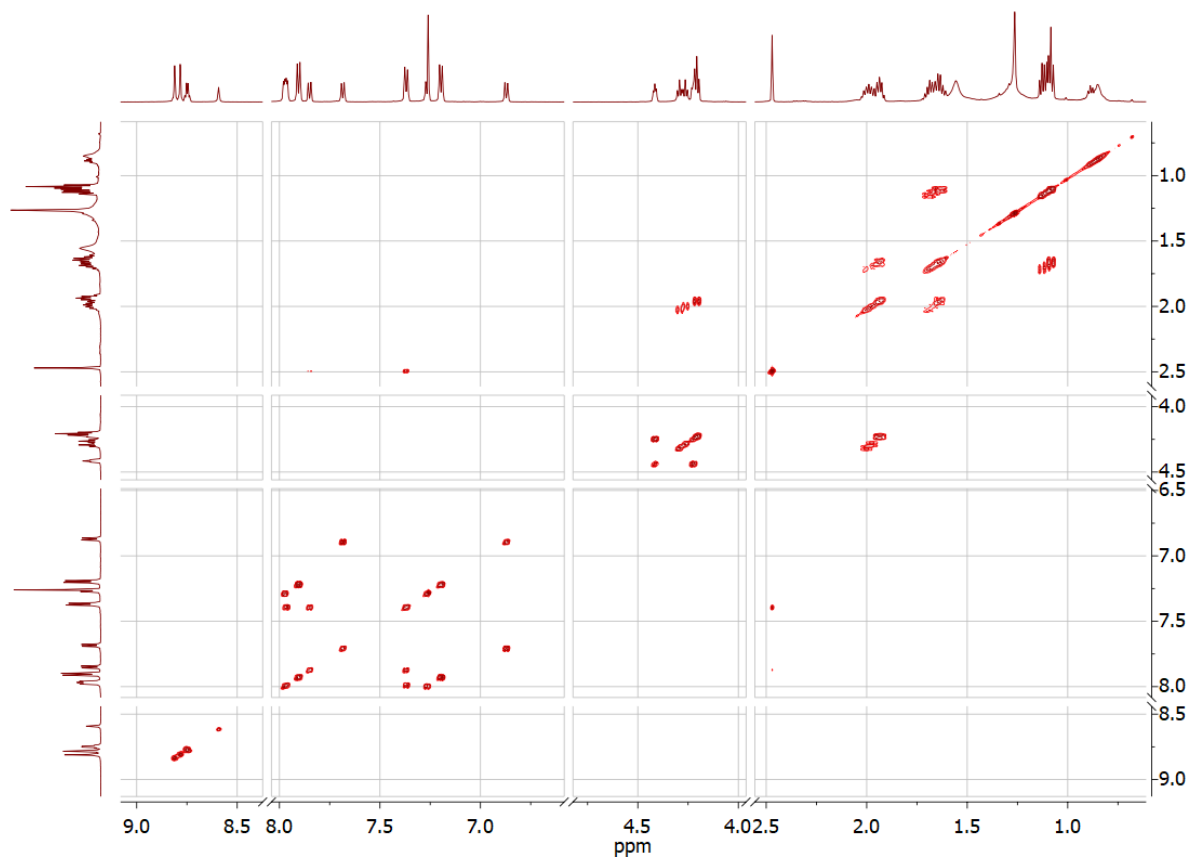
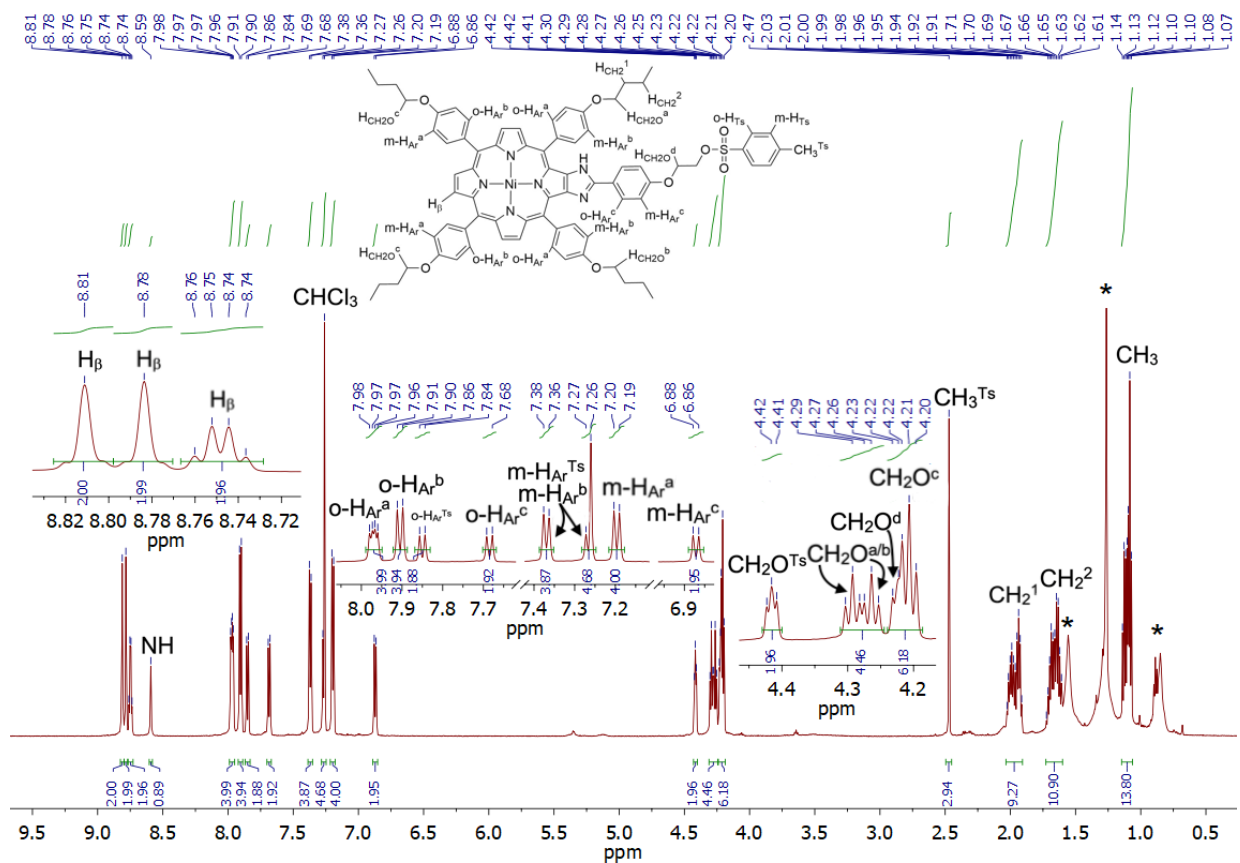


Figure S 6. ¹H NMR spectrum of 6 (CDCl₃).



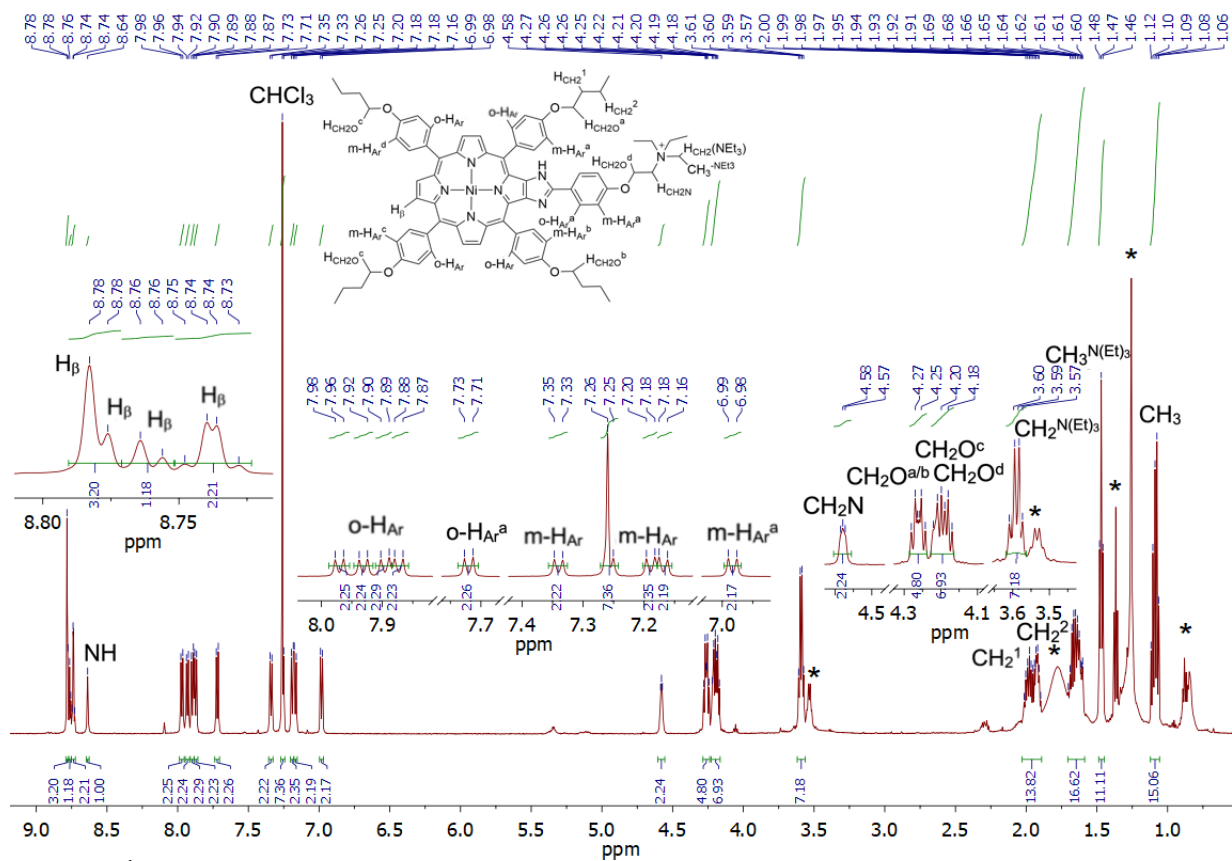


Figure S9. ^1H NMR spectrum of **8** (CDCl_3).

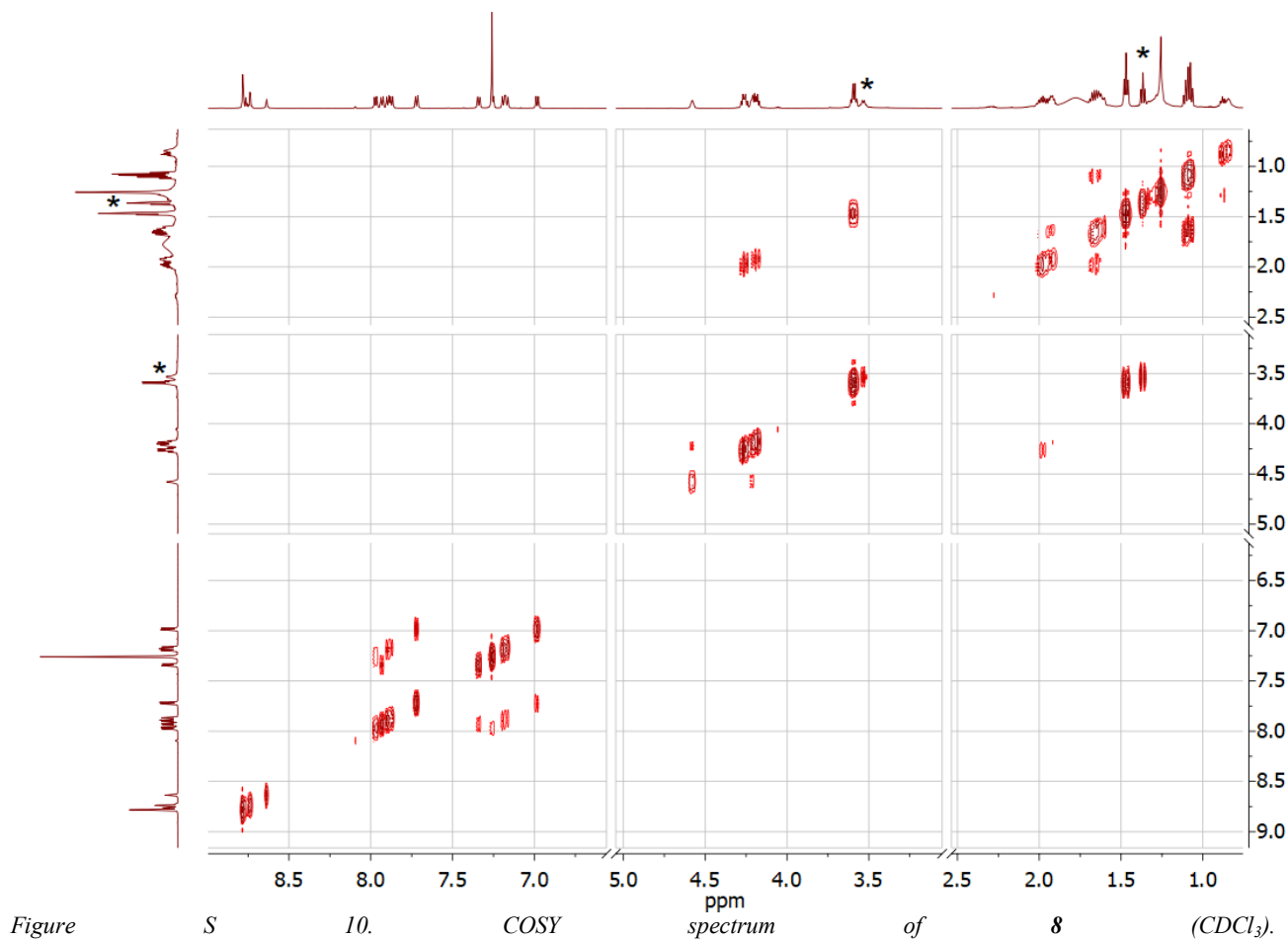


Figure 10. COSY spectrum of **8** (CDCl_3).

1. Armarego W.L.F., Chai C.L.L. Purification of laboratory chemicals. Elsevier/Butterworth-Heinemann, 2009. 743 p.