Carbene spacers in bis-porphyrinic scaffolds

Julien Haumesser, Jean-Paul Gisselbrecht, Jean Weiss* and Romain Ruppert*

Institut de Chimie, UMR 7177 du CNRS, Université de Strasbourg
1 rue Blaise Pascal, F-67008 Strasbourg cedex, France.
Tel: ++(33) 368851700;
E-mail: rruppert@unistra.fr jweiss@unistra.fr

Summary

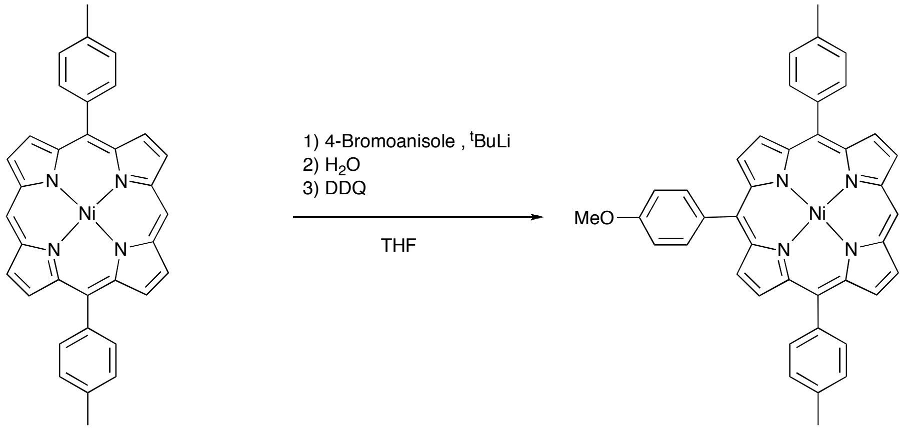
Experimental part

General

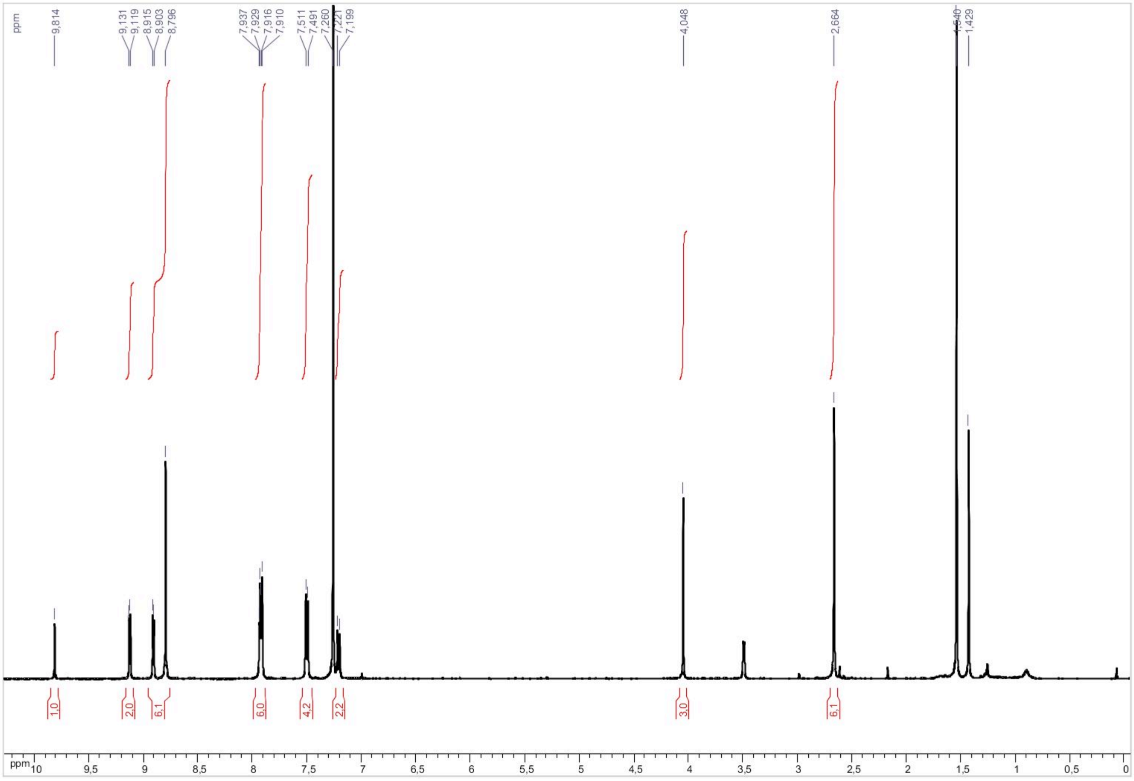
Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on Avance 300, 400, or 500 MHz Bruker instruments. ^{1}H NMR data are presented as followed: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (*J* in Hz), and integration. UV-visible spectra were recorded with an Agilent 8453 diode-array spectrophotometer in CH_2Cl_2 (1 cm path length quartz cell). Mass spectra were recorded by MALDI-TOF using a Bruker Ultrafex spectrometer with a dithranol matrix. Elemental analyses were performed at the Service de Microanalyse, Université de Strasbourg (France). Column chromatography was carried out on silica gel (40-63 µm, Merck) and aluminium oxide standardized (Merck). CH_2Cl_2 was distilled from CaH_2 and THF was distilled from sodium/benzophenone. All other solvents and reagents were used without further purification.

Synthetic procedures and spectral data

Preparation of the starting nickeltriarylporphyrin **1**

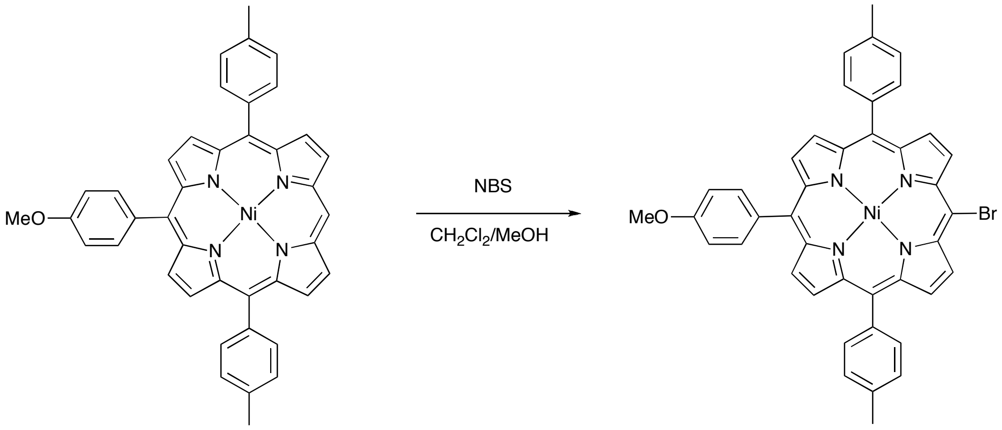


t-Butyllithium (3.7 mL of a 1.7 M solution in pentane, 12 eq.) was added under argon to a solution of 4-bromoanisole (0.4 mL, 6 eq.) in 120 mL of dry THF. The mixture was stirred at -78 °C for 1 h, at r.t. for 20 min and then at -78 °C for 40 min. The solution was transferred with a canula to a solution of nickelditolylporphyrin (292 mg, 0.53 mmol) in 180 mL of dry THF at 0 °C. The solution was stirred at this temperature for 20 min, and at r.t. for 20 min. A mixture of water (3 mL) diluted in THF (10 mL) was added for hydrolysis. After 30 min, DDQ (484 mg, 4 eq.) was added and the mixture was stirred for another 60 min at r.t. The mixture was filtered through alumina and the solution was dried under vacuum. The desired compound was purified by chromatography column (silica gel, CH_2Cl_2/cyclohexane: 3/7) and recrystallized from dichloromethane/methanol (313 mg, 0.48 mmol, 90%).

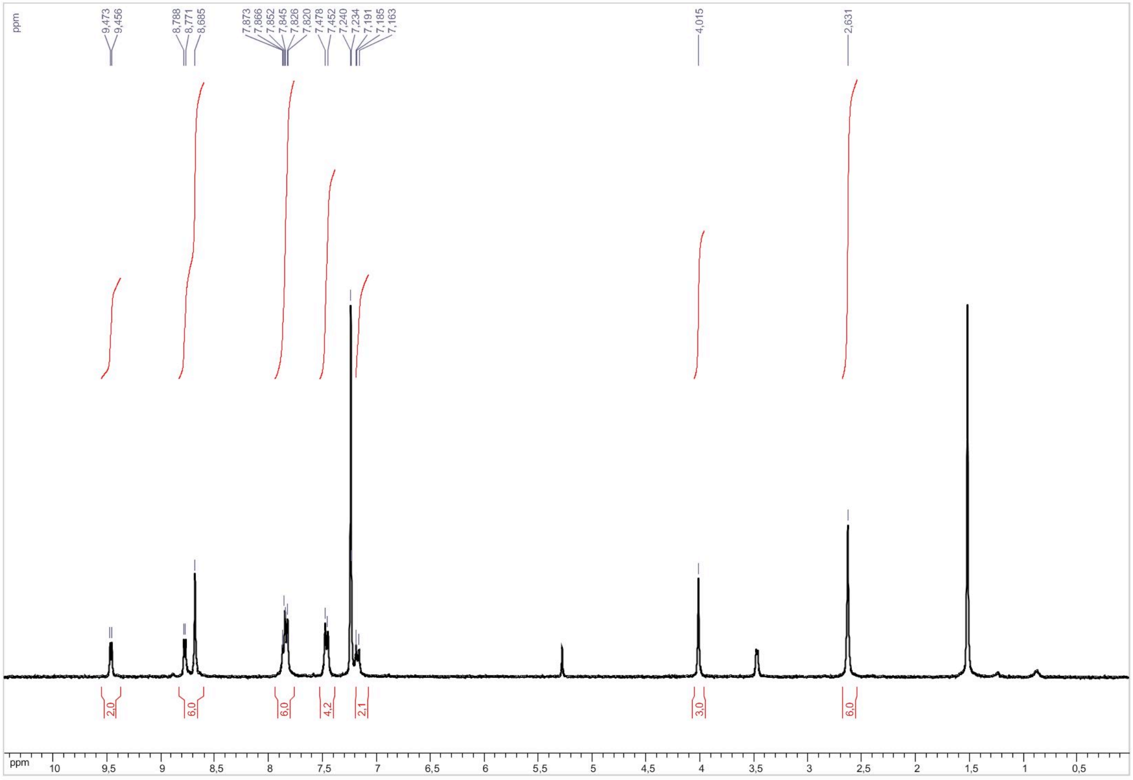


^{1}H NMR (300 MHz, CDCl$_3$, 25 °C) δ (ppm) = 9.81 (s, 1H, H *meso*), 9.12 (d, J = 4.8 Hz, 2H, pyrr), 8.91 (d, J = 4.8 Hz, 2H, pyrr), 8.80 (AB, J < 1 Hz, 4H, pyrr), 7.93 (d, J = 8.6 Hz, 2H, H$_{anis}$), 7.92 (d, J = 7.4 Hz, 4H, H$_{tolyl}$), 7.50 (d, J = 7.4 Hz, 4H, H$_{tolyl}$), 7.21 (d, J = 8.6 Hz, 2H, H$_{anis}$), 4.05 (s, 3H, OCH$_3$), 2.66 (s, 6H, CH$_3$).

Synthesis and characterization of **2**

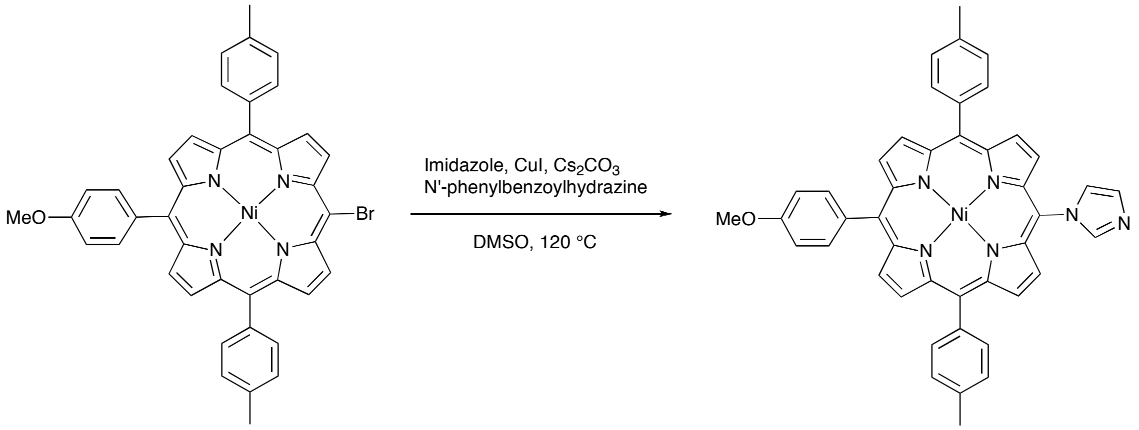


N-Bromosuccinimide (60 mg, 1.1 eq.) was added to a solution of **1** (200 mg, 0.31 mmol) in CH_2Cl_2/MeOH (5:1 v/v, 18 mL). The mixture was stirred under air at r.t. for 15 min and quenched with acetone (2 mL). The solvents were removed under vacuum, and the resulting solid was dissolved in CH_2Cl_2 (40 mL). The solution was then washed once with saturated $NaHCO_3$ (aq) (50 mL) and finally once with water (50 mL). The organic phase was dried over sodium sulfate and the desired compound was recrystallized from dichloromethane/methanol (213 mg, 0.29 mmol, 95%).

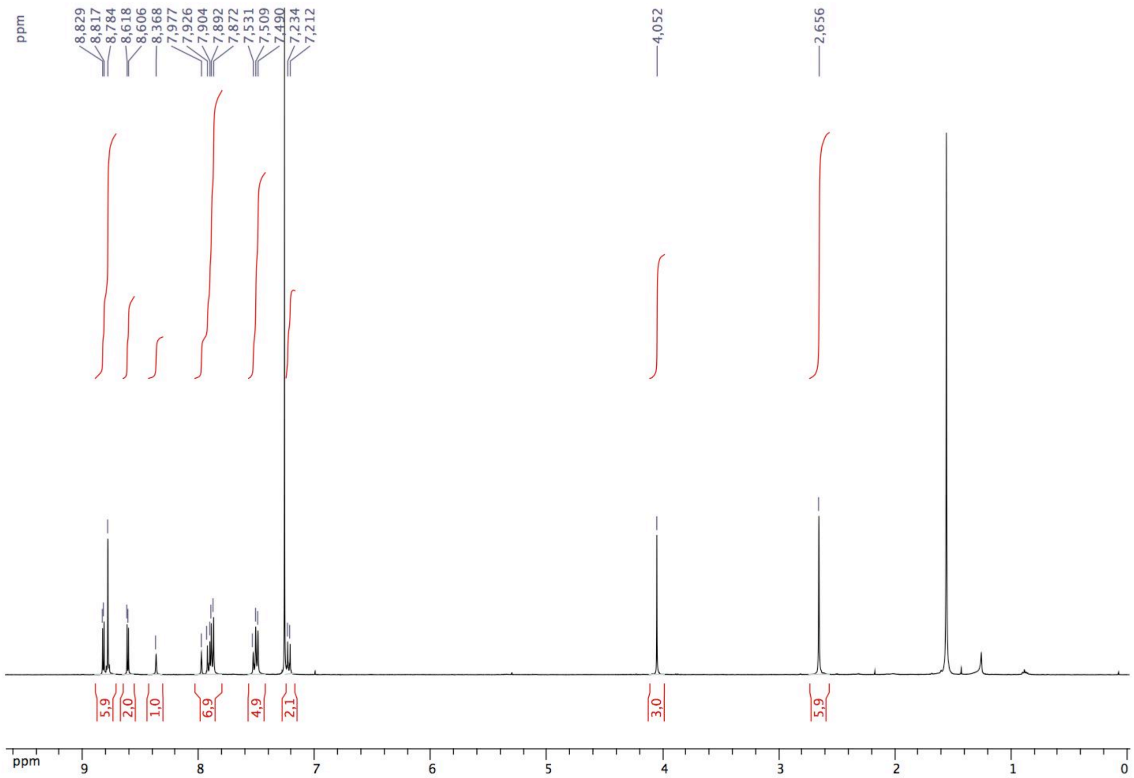


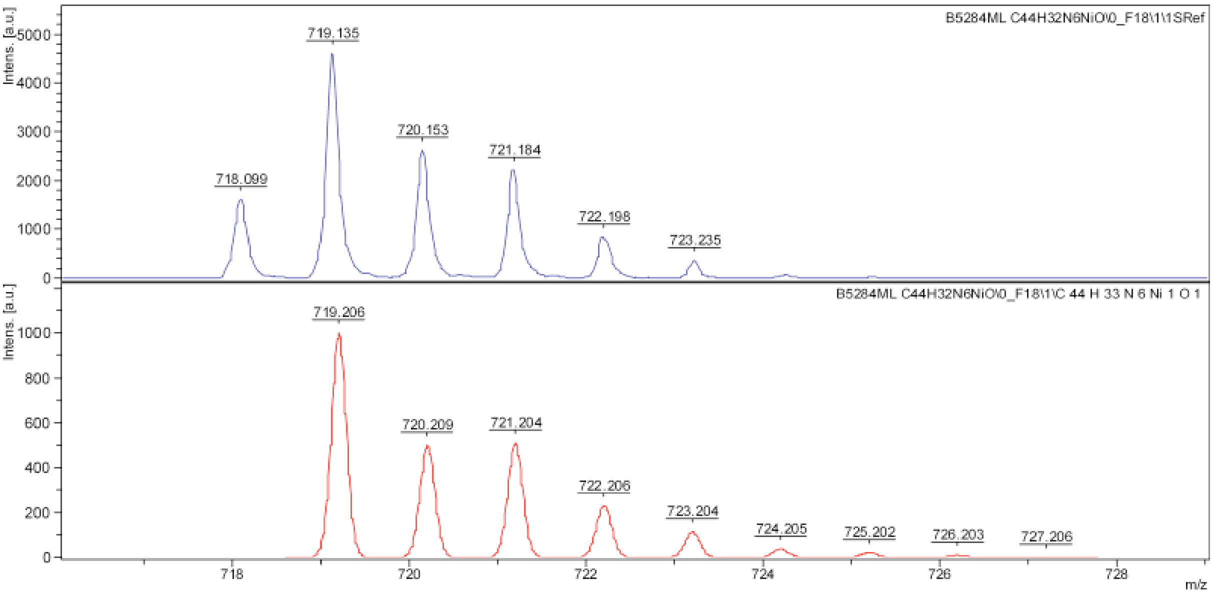
^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ (ppm) = 9.46 (d, J = 5.0 Hz, 2H, pyrr), 8.78 (d, J = 5.0 Hz, 2H, pyrr), 8.68 (AB, J < 1 Hz, 4H, pyrr), 7.86 (d, J = 8.7 Hz, 2H, H_{anis}), 7.84 (d, J = 7.9 Hz, 4H, H_{tolyl}), 7.46 (d, J = 7.9 Hz, 4H, H_{tolyl}), 7.18 (d, J = 8.7 Hz, 2H, H_{anis}), 4.01 (s, 3H, OCH_3), 2.63 (s, 6H, CH_3).

Synthesis and characterization of **3a**



A degassed mixture of **2** (210 mg, 0.29 mmol), imidazole (195 mg, 10 eq.), CuI (5 mg, 0.1 eq.), *N*'-phenylbenzoylhydrazine (12 mg, 0.2 eq.) and Cs_2CO_3 (187 mg, 2 eq.) in DMSO (5 mL) was heated under argon at 120 °C overnight. After cooling, the mixture was diluted in CH_2Cl_2 (100 mL), washed twice with a saturated $NaHCO_3$ (aq.) solution (50 mL) and finally twice with water (50 mL). The organic phase was dried over sodium sulfate, filtered and solvent was removed in vacuo. The desired compound was obtained after purification on a short chromatography column (silica gel, CH_2Cl_2 then $CHCl_3$) followed by recrystallization from dichloromethane/methanol (189 mg, 0.26 mmol, 92%).





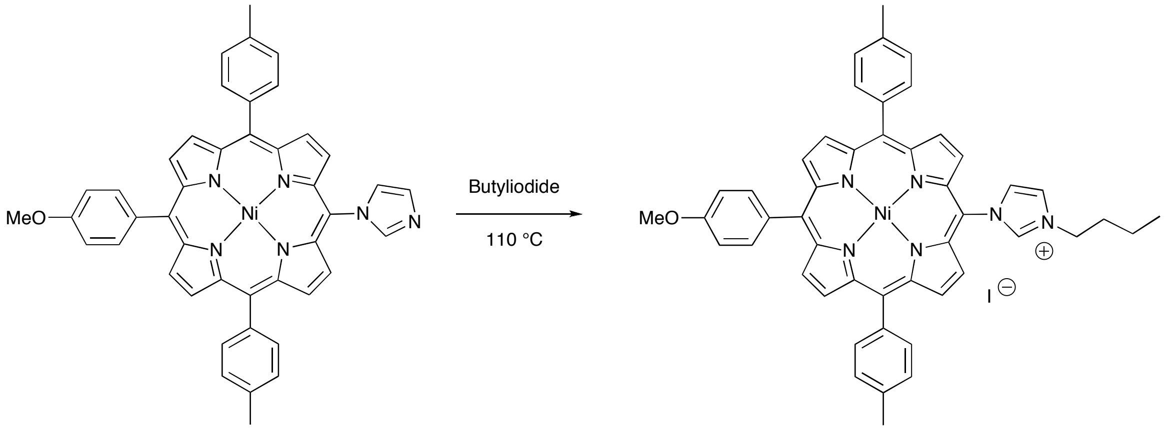
^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm) = 8.83 (d, J = 5.0 Hz, 2H, pyrr), 8.78 (AB, J < 1 Hz, 4H, pyrr), 8.61 (d, J = 5.0 Hz, 2H, pyrr), 8.37 (br s, 1H, NC*H*N imid), 7.98 (br s, 1H, NC*H* imid), 7.91 (d, J = 8.4 Hz, 2H, H_{anis}), 7.88 (d, J = 7.9 Hz, 4H, H_{tolyl}), 7.53 (br s, 1H, NC*H* imid), 7.50 (d, J = 7.9 Hz, 4H, H_{tolyl}), 7.22 (d, J = 8.4 Hz, 2H, H_{anis}), 4.05 (s, 3H, OCH_3), 2.66 (s, 6H, CH_3).

UV-visible (CH_2Cl_2): λ_{max} = 414 (ε = 272000), 527 (21300).

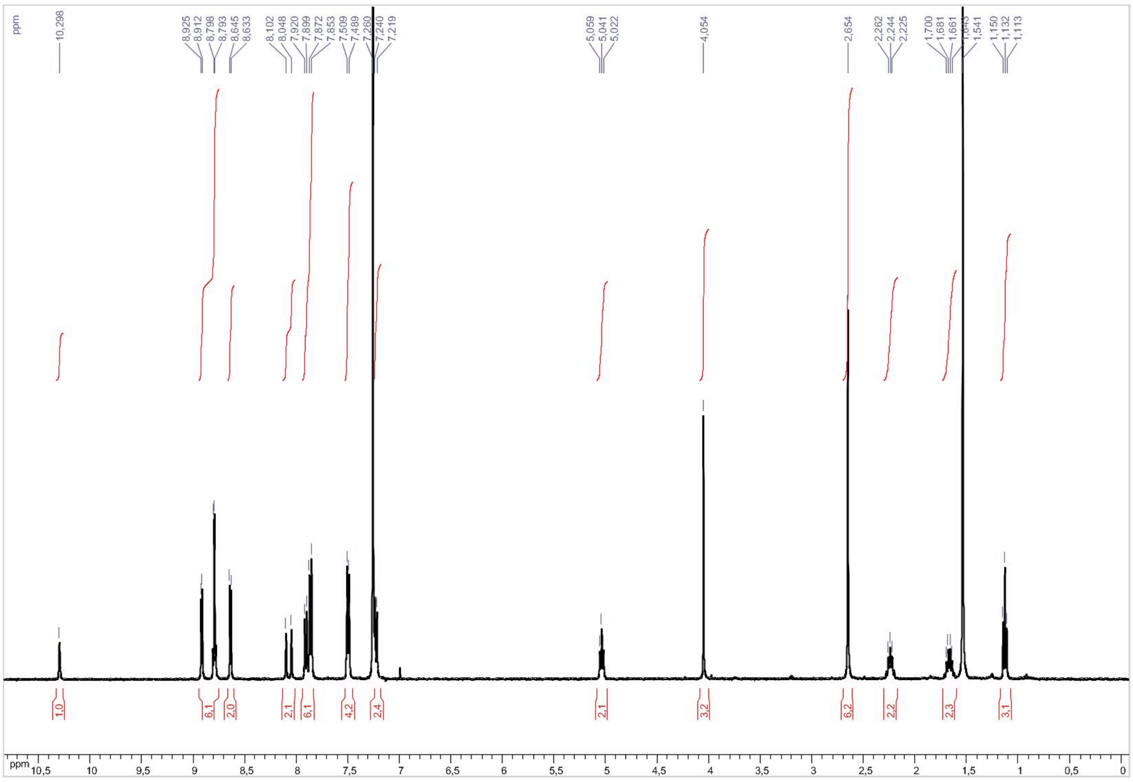
Maldi-TOF (m/z): Calcd for $C_{44}H_{33}N_6NiO^+$: 719.210; found: 719.135.

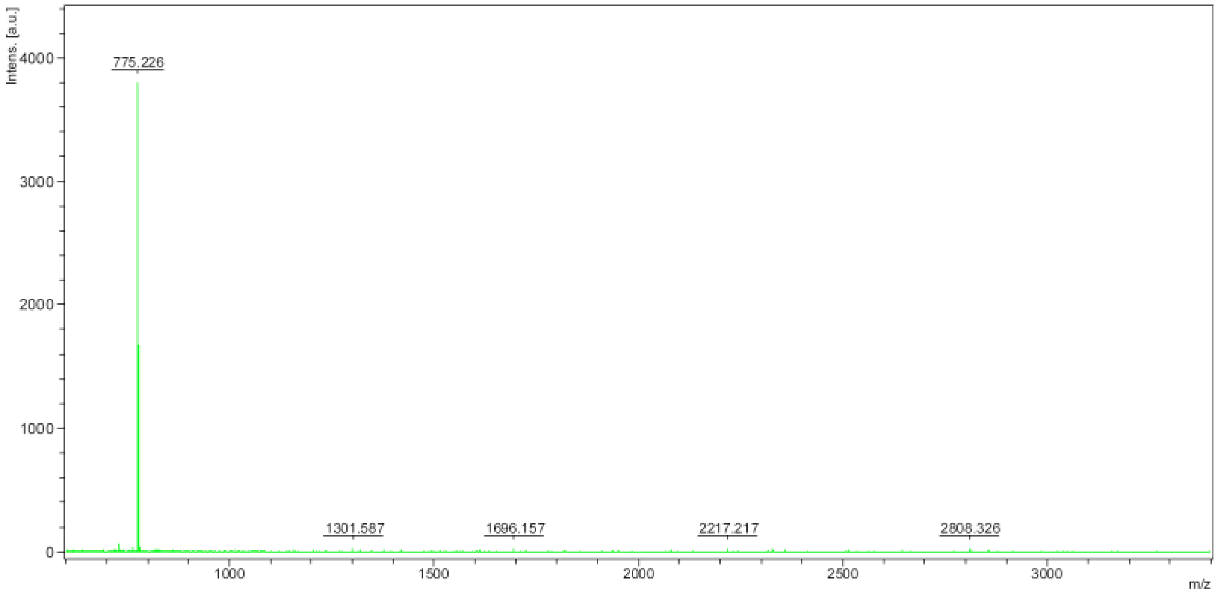
E.A. Calcd for $C_{44}H_{32}N_6NiO \bullet ½H_2O$: C 72.55, H 4.57, N 11.54; found: C 72.57, H 4.63, N 11.35.

Synthesis and characterization of **4a**



Porphyrin **3a** (84 mg, 0.12 mmol) was dissolved in butyliodide (5 mL) and heated at 110 °C overnight. When no more starting material was observed by TLC, n-hexane was added and the precipitate was filtered and washed with *n*-hexane to obtain **4a** as a red solid (103 mg, 0.11 mmol, 98%).





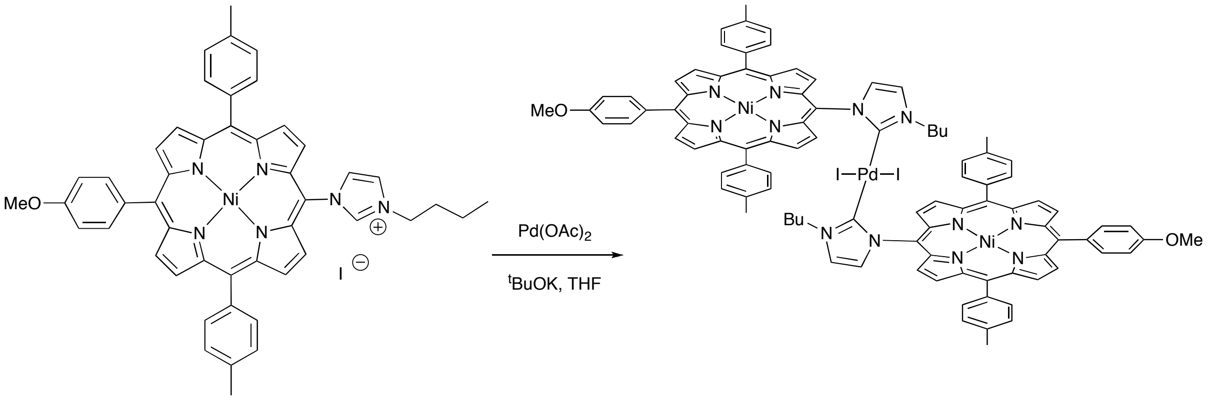
^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm) = 10.30 (s, 1H, NC*H*N imid), 8.92 (d, J = 5.1 Hz, 2H, pyrr), 8.79 (AB, J < 1 Hz, 4H, pyrr), 8.64 (d, J = 5.1 Hz, 2H, pyrr), 8.10 (s, 1H, NC*H* imid), 8.05 (s, 1H, NC*H* imid), 7.91 (d, J = 8.2 Hz, 2H, H_{anis}), 7.86 (d, J = 7.6 Hz, 4H, H_{tolyl}), 7.50 (d, J = 7.6 Hz, 4H, H_{tolyl}), 7.23 (d, J = 8.2 Hz, 2H, H_{anis}), 5.04 (t, J = 7.4 Hz, 2H, $\mathrm{NC}\mathit{H_2}\mathrm{CH_2CH_2CH_3}$), 4.05 (s, 3H, OCH_3), 2.65 (s, 6H, CH_{3tolyl}), 2.24 (tt, J = 7.4 Hz, J = 7.4 Hz, 2H, $\mathrm{NCH_2C}\mathit{H_2}\mathrm{CH_2CH_3}$), 1.67 (qt, J = 7.4 Hz, J = 7.4 Hz, 2H, $\mathrm{NCH_2CH_2C}\mathit{H_2}\mathrm{CH_3}$), 1.13 (t, J = 7.4 Hz, 3H, $\mathrm{NCH_2CH_2CH_2C}\mathit{H_3}$).

UV-visible (CH_2Cl_2): λ_{max} = 415 (ε = 183000), 529 (14000)**.**

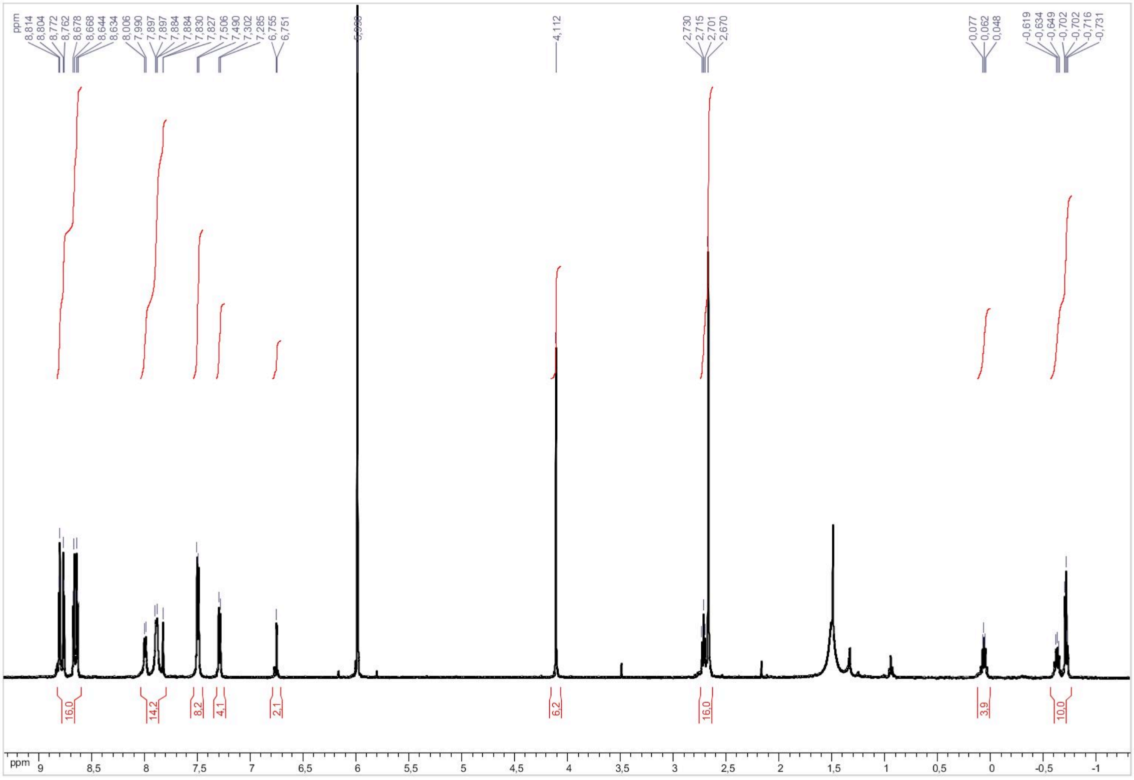
Maldi-TOF (m/z): Calcd for $C_{48}H_{41}N_6NiO^+$: 775.269; found: 775.226.

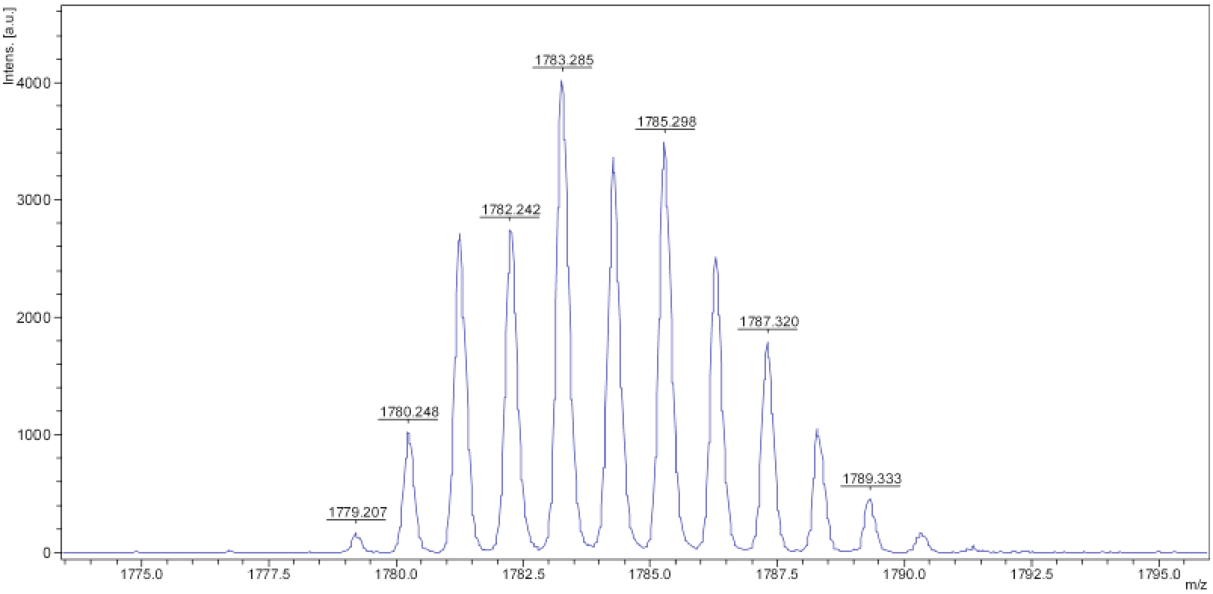
E.A. Calcd for $C_{48}H_{41}IN_6NiO{\bullet}2H_2O$: C 61.36, H 4.57, N 9.01; found C 61.65, H 4.54, N 9.01.

Synthesis and characterization of **5a**



To a solution of **4a** (80 mg, 0.09 mmol) in dry THF (3 mL), were added ^{t}BuOK (11 mg, 1.1 eq.) and $Pd(OAc)_2$ (8 mg, 0.4 eq.). The mixture was stirred at r.t. overnight under argon. The mixture was diluted in CH_2Cl_2 (100 mL), and the solution was washed twice with a saturated $NaHCO_3$ (aq.) solution (50 mL) and finally twice with water (50 mL). The organic phase was dried over sodium sulfate, filtered and solvent was removed in vacuo. The desired compound was obtained after purification by chromatography column (silica gel, eluant CH_2Cl_2/cyclohexane: 1/1) followed by recrystallization from dichloromethane/methanol (43 mg, 0.02 mmol, 64%).





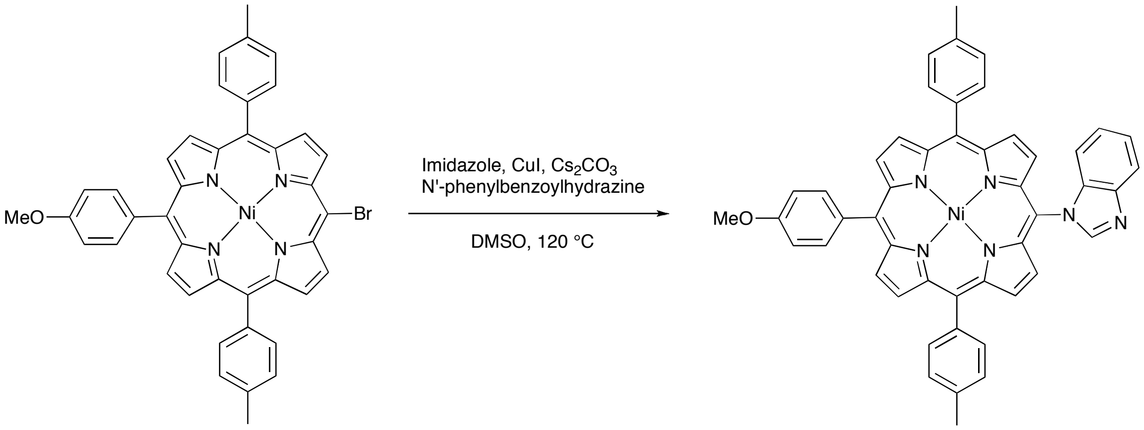
^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 85 °C) δ (ppm) = 8.81 (d, J = 4.9 Hz, 4H, pyrr), 8.77 (d, J = 4.9 Hz, 4H, pyrr), 8.67 (d, J = 4.9 Hz, 4H, pyrr), 8.64 (d, J = 4.9 Hz, 4H, pyrr), 8.00 (d, J = 8.7 Hz, 4H, H_{anis}), 7.89 (d, J = 8.0 Hz, 4H, H_{tolyl}), 7.83 (d, J = 1.8 Hz, 2H, NC*H* imid), 7.50 (d, J = 8.0 Hz, 8H, H_{tolyl}), 7.29 (d, J = 8.7 Hz, 4H, H_{anis}), 6.75 (d, J = 1.8 Hz, 2H, NC*H* imid), 4.11 (s, 6H, OCH_3), 2.72 (t, J = 7.1 Hz, 4H, $NC\mathit{H_2}CH_2CH_2CH_3$), 2.67 (s, 12H, CH_{3tolyl}), 0.07 (tt, J = 7.1 Hz, J = 7.1 Hz, 4H, $NCH_2C\mathit{H_2}CH_2CH_3$), -0.63 (m, 4H, $NCH_2CH_2C\mathit{H_2}CH_3$), -0.72 (m, 3H, $NCH_2CH_2CH_2C\mathit{H_3}$).

UV-visible (CH_2Cl_2): λ_{max} = 422 (ε = 375000), 532 (39000).

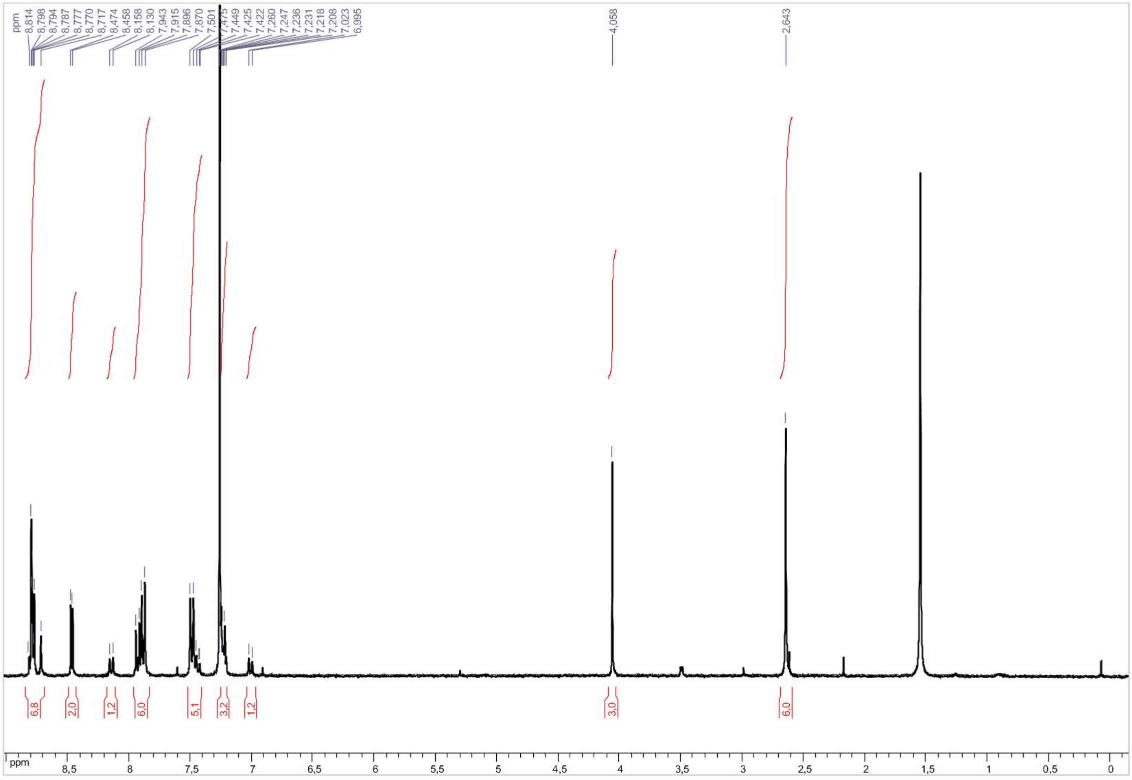
Maldi-TOF (m/z): Calcd for $C_{96}H_{80}IN_{12}NiO_2Pd^+$: 1783.33; found 1783.285.

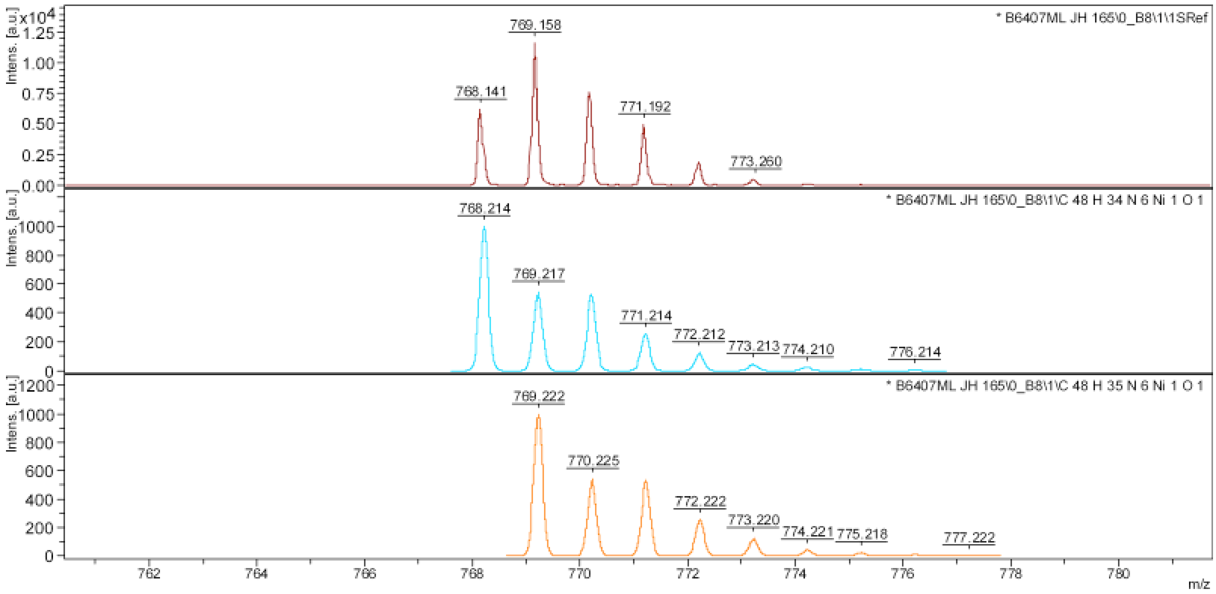
E.A.: Calcd for $C_{96}H_{80}I_2N_{12}NiO_2Pd$•2MeOH: C 59.52, H 4.59, N 8.50; found C 59.79, H 4.58, N 8.15.

Synthesis and characterization of **3b**



Compound **3b** was prepared according to the procedure described for the synthesis of **3a** using the following: **2** (100 mg, 0.14 mmol), benzimidazole (100 mg, 10 eq.), CuI (3 mg, 0.1 eq.), *N*'-phenylbenzoylhydrazine (6 mg, 0.2 eq.), Cs_2CO_3 (90 mg), and DMSO (2 mL). The desired compound **3b** was obtained as a purple solid (80 mg, 0.10 mmol, 76%).





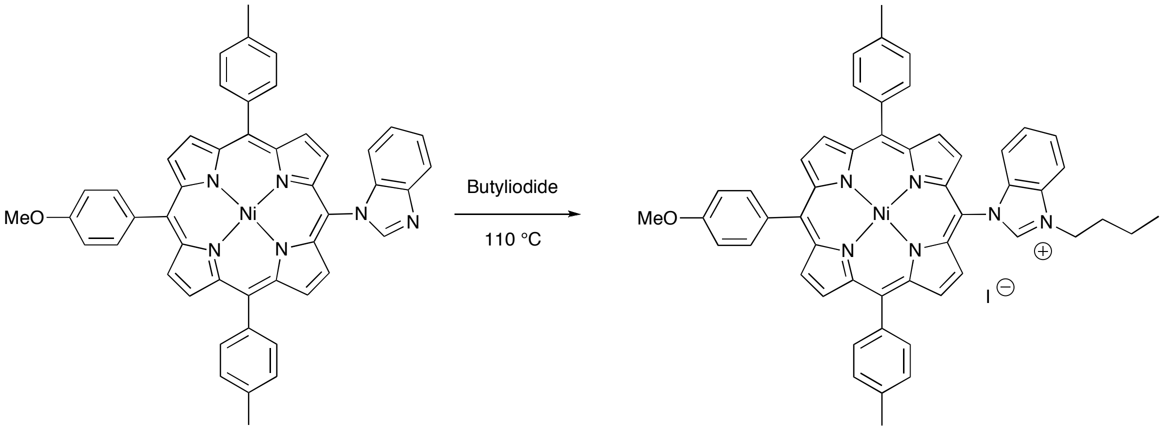
^{1}H NMR (400 MHz, CDCl$_3$, 25 °C) δ (ppm) = 8.79 (AB, J < 1 Hz, 6H, pyrr), 8.71 (s, 1H, NC*H*N benzimid), 8.46 (d, J = 5.9 Hz, 2H, pyrr), 8.15 (d, J = 8.4 Hz, 1H, H benzimid), 7.93 (d, J = 8.7 Hz, 2H, H$_{anis}$), 7.88 (d, J = 7.8 Hz, 4H, H$_{tolyl}$), 7.43 (m, 1H, H benzimid), 7.48 (d, J = 7.8 Hz, 4H, H$_{tolyl}$), 7.26 (m, 1H, H benzimid), 7.22 (d, J = 8.7 Hz, 2H, H$_{anis}$), 7.01 (d, J = 8,4 Hz, 1H, H benzimid), 4.06 (s, 3H, OCH$_3$), 2.64 (s, 6H, CH$_3$).

UV-visible (CH$_2$Cl$_2$): λ_{max} = 416 (ε = 273000), 528 (22000)**.**

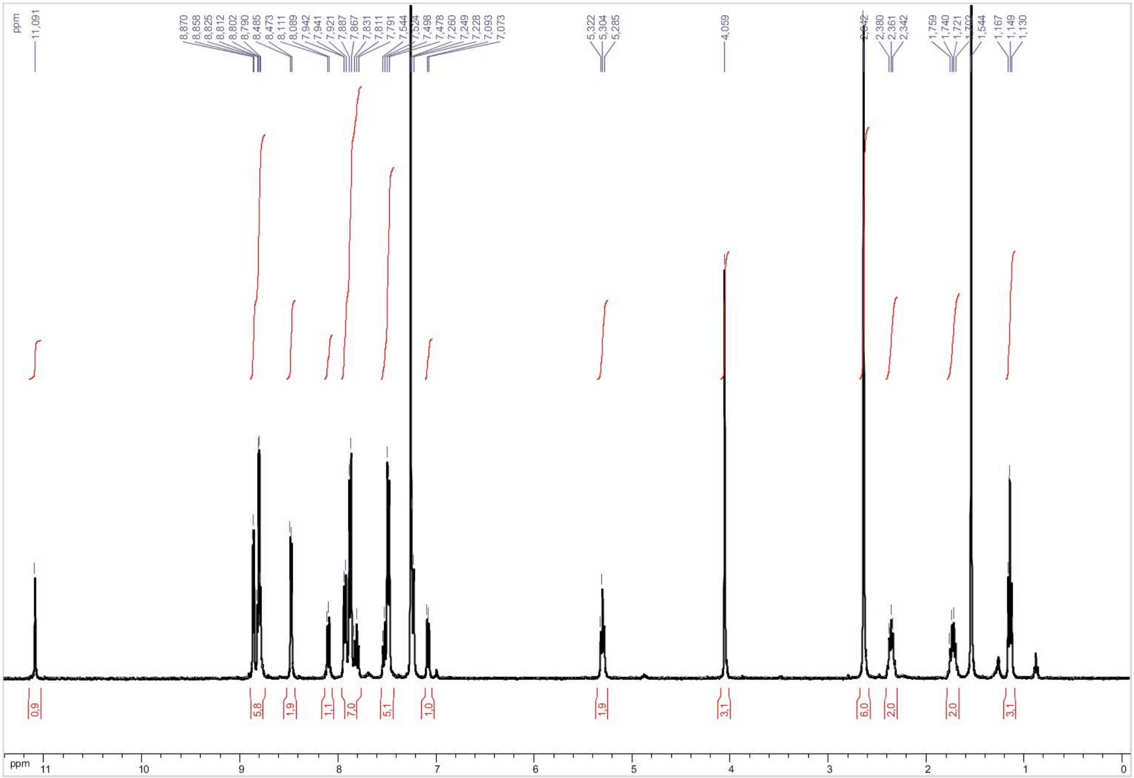
Maldi-TOF (m/z): Calcd for $C_{48}H_{35}N_6NiO^+$: 769.220; found 769.158.

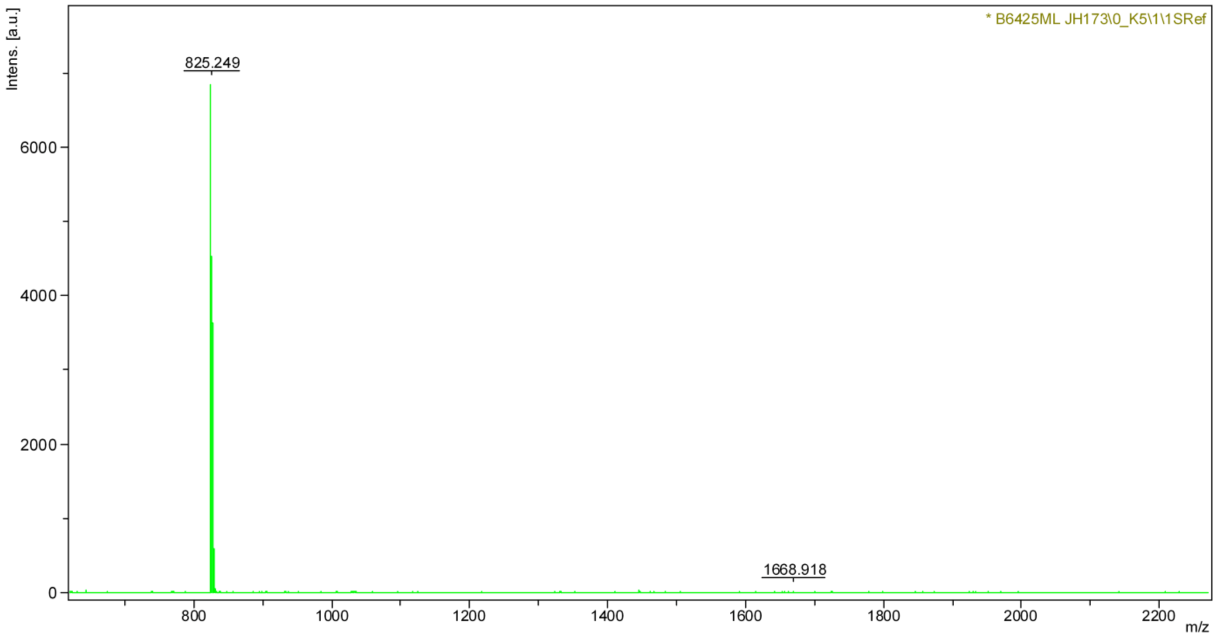
E.A.: Calcd for $C_{48}H_{34}N_6NiO \bullet H_2O$: C 73.21, H 4.61, N 10.67; found C 73.44, H 4.37, N 10.44.

Synthesis and characterization of **4b**



4b was prepared according to the procedure described for the synthesis of **4a** using the following: **3b** (139 mg, 0.18 mmol), butyliodide (5 mL). The desired compound **4b** was obtained as a red solid (164 mg, 0.17 mmol, 95%).





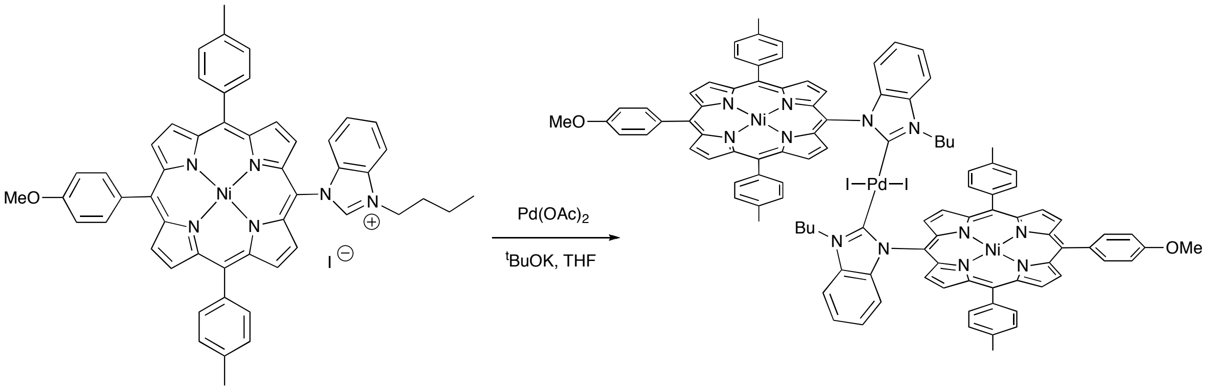
^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm) = 11.09 (s, 1H, NC*H*N benzimid), 8.86 (d, J = 5.0 Hz, 2H, pyrr), 8.80 (AB, J < 1 Hz, 4H, pyrr), 8.48 (d, J = 5.0 Hz, 2H, pyrr), 8.10 (d, J = 8.4 Hz, 1H, H benzimid), 7.93 (d, J = 8.4 Hz, 2H, H_{anis}), 7.88 (d, J = 7.9 Hz, 4H, H_{tolyl}), 7.82 (ddd, J = 8.1 Hz , J = 8.1 Hz, J = 0.5 Hz, 1H, H benzimid), 7.53 (ddd, J = 8.1 Hz , J = 8.1 Hz, J = 0.5 Hz, 1H, H benzimid), 7.49 (d, J = 7.9 Hz, 4H, H_{tolyl}), 7.24 (d, J = 8.4 Hz, 2H, H_{anis}), 7.08 (d, J = 8.4 Hz, 1H, H benzimid), 5.30 (t, J = 7.3 Hz, 2H, $NC\mathit{H_2}CH_2CH_2CH_3$), 4.06 (s, 3H, OCH_3), 2.64 (s, 6H, CH_3 tolyl), 2.36 (tt, J = 7.3 Hz, J = 7.3 Hz, 2H, $NCH_2C\mathit{H_2}CH_2CH_3$), 1.73 (qt, J = 7.3 Hz, J = 7.3 Hz, 2H, $NCH_2CH_2C\mathit{H_2}CH_3$), 1.15 (t, J = 7.3 Hz, 3H, $NCH_2CH_2CH_2C\mathit{H_3}$).

UV-visible (CH_2Cl_2): λ_{max} = 418 (ε = 167000), 530 (13000).

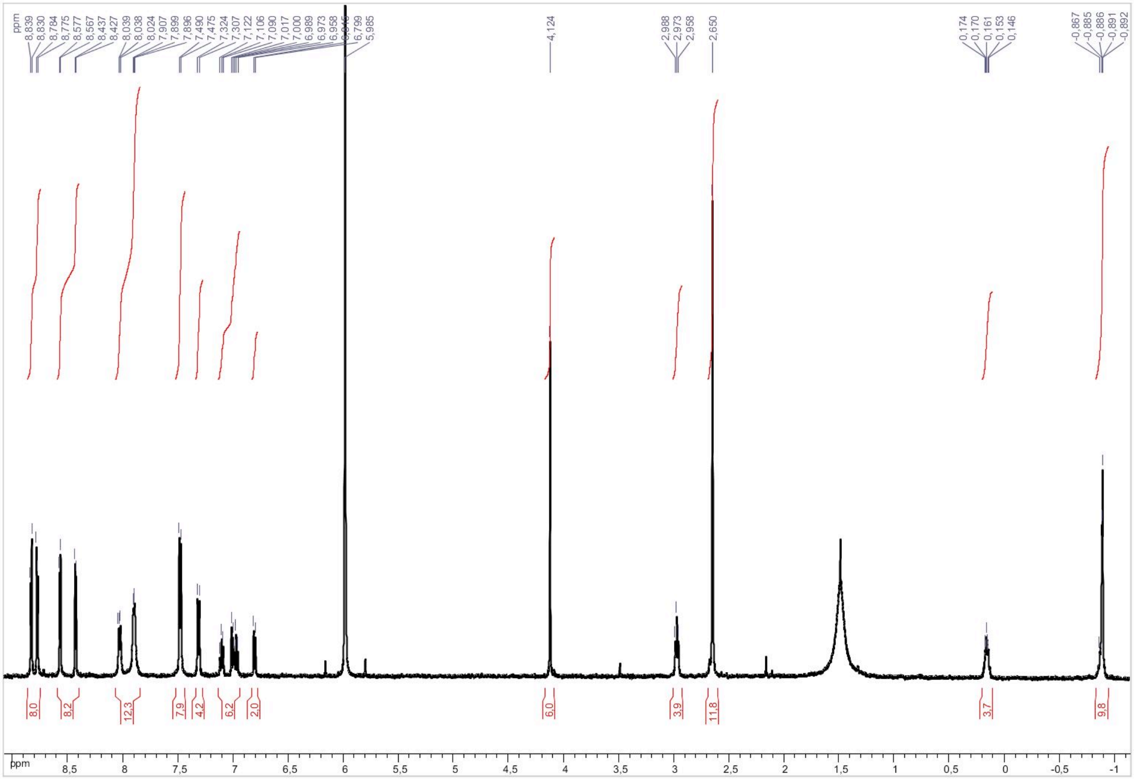
Maldi-TOF (m/z): Calcd for $C_{52}H_{43}N_6NiO^+$: 825.285; found 825.249.

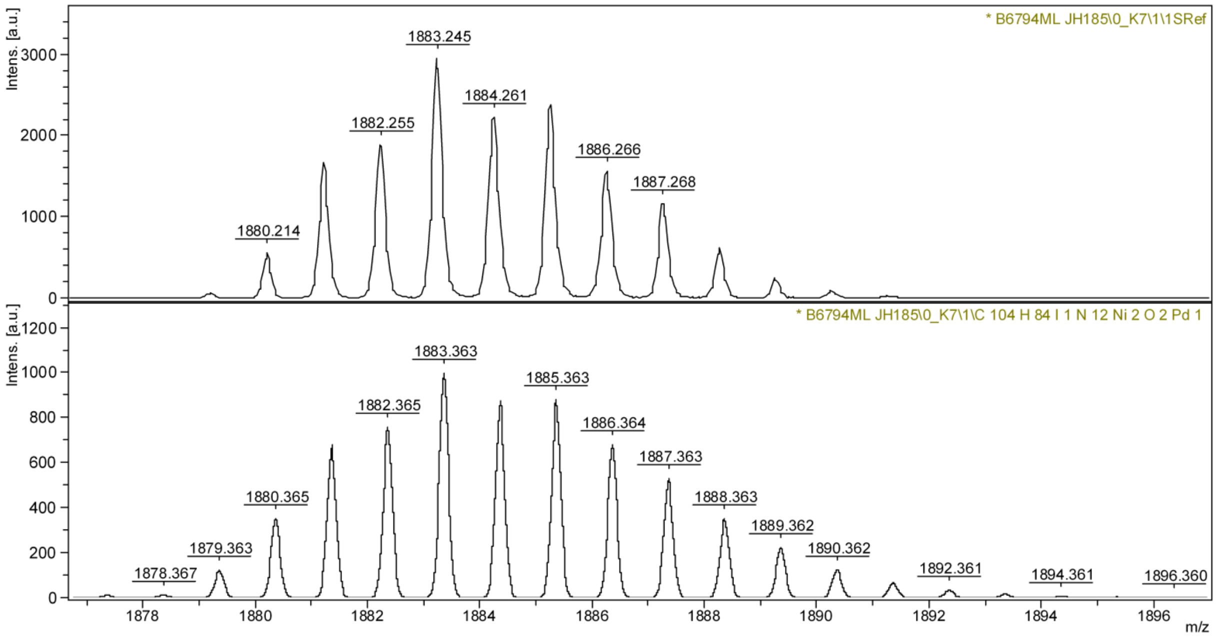
E.A. Calcd for $C_{52}H_{43}IN_6NiO{\bullet}CH_2Cl_2$: C 61.30, H 4.27, N 8.28; found C 61.24, H 4.42, N 7.82.

Synthesis and characterization of **5b**



Complex **5b** was prepared according to the procedure described for the synthesis of **5a** using the following: **4b** (80 mg, 0.08 mmol), Pd(OAc)$_2$ (8 mg, 0.4 eq), tBuOK (12 mg, 1.2 eq.), THF (5 mL). The desired compound **5b** was obtained as a red solid (40 mg, 0.02 mmol, 59%).





^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 85°C) δ (ppm) = 8.83 (d, J = 4.9 Hz, 4H, pyrr), 8.77 (d, J = 4.9 Hz, 4H, pyrr), 8.57 (d, J = 5.0 Hz, 4H, pyrr), 8.43 (d, J = 5.0 Hz, 4H, pyrr), 8.03 (d, J = 8.6 Hz, 4H, H_{anis}), 7.90 (d, J = 7.7 Hz, 4H, H_{tolyl}), 7.48 (d, J = 7.7 Hz, 8H, H_{tolyl}), 7.31 (d, J = 8.6 Hz, 4H, H_{anis}), 7.11 (dd, J = 8.0 Hz , J = 8.0 Hz, 2H, H benzimid), 7.01 (d, J = 8.0 Hz, 1H, H benzimid), 6.97 (dd, J = 8.0 Hz , J = 8.0 Hz, 2H, H benzimid), 6.81 (d, J = 8.0 Hz, 1H, H benzimid), 4.12 (s, 6H, OCH_3), 2.97 (t, J = 7.2 Hz, 4H, $\mathrm{NC}\mathit{H_2}\mathrm{CH_2CH_2CH_3}$), 2.67 (s, 12H, CH_3 tolyl), 0.16 (m, 4H, $\mathrm{NCH_2C}\mathit{H_2}\mathrm{CH_2CH_3}$), -0.89 (m, 10H, $\mathrm{NCH_2CH_2C}\mathit{H_2}\mathrm{CH_3}$ and $\mathrm{NCH_2CH_2CH_2C}\mathit{H_3}$).

UV-visible (CH_2Cl_2): λ_{max} = 422 (ε = 361000), 529 (37000).

Maldi-TOF (m/z): Calcd for $C_{104}H_{84}IN_{12}Ni_2O_2Pd^+$: 1883.363; found 1883.245.

E.A. Calcd for $C_{104}H_{84}I_2N_{12}Ni_2O_2Pd{\bullet}H_2O$: C 61.55, H 4.27, N 8.28; found C 61.35, H 4.38, N 7.95.

X-Ray :

X-Ray diffraction data collection was carried out on a Bruker APEX II DUO Kappa-CCD diffractometer equipped with an Oxford Cryosystem liquid N_2 device, using Mo-Kα radiation (λ = 0.71073 Å). The crystal-detector distance was 38 mm. The cell parameters were determined (APEX2 software) [1] from reflections taken from three sets of 12 frames, each at 10 s exposure. The structure was solved by Direct methods using the program SHELXS-97 [2]. The refinement and all further calculations were carried out using SHELXL-97 [3]. The H-atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F^2. A semi-empirical absorption correction was applied using SADABS in APEX2 [5]; transmission factors: $T_{min/}T_{max}$ = 0.6720/0.9480.

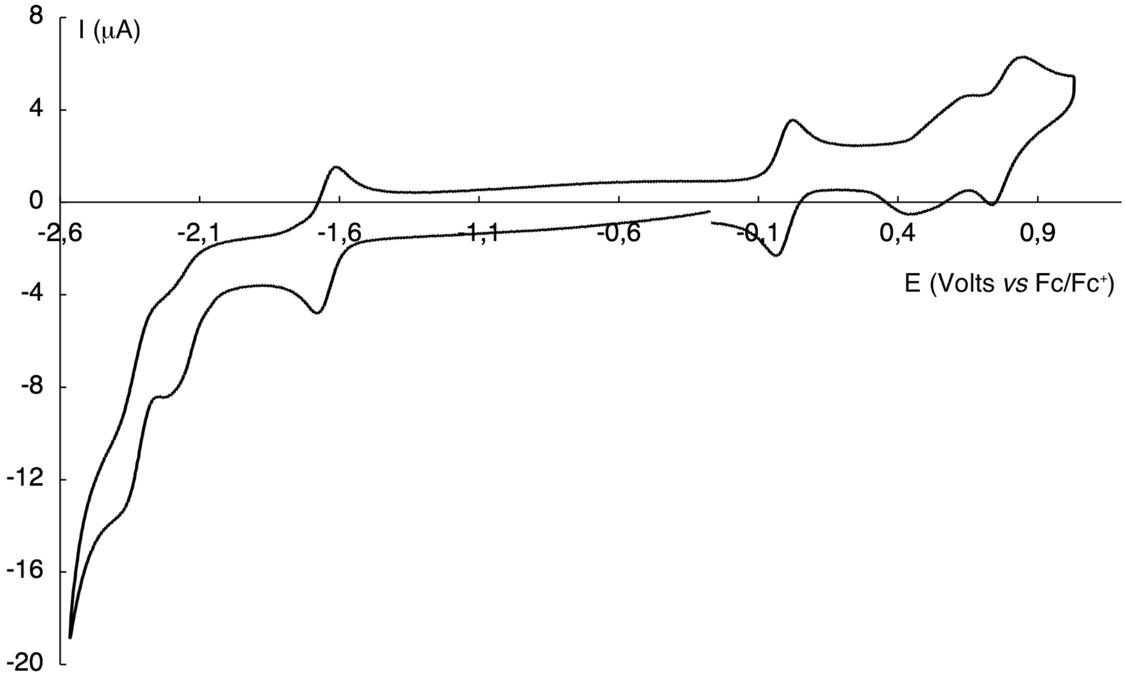
The SQUEEZE instruction in PLATON [4] was applied. The residual electron density was assigned to two molecules of ethanol.

[1] “M86-E01078 APEX2 User Manual”, Bruker AXS Inc., Madison, USA, 2006.
[2] G. M. Sheldrick, (1990) “SHELXS-97 Program for Crystal Structure Determination”, *Acta Crystallogr.,* **A46**, 467 473.
[3] G. Sheldrick, (1999) “SHELXL-97”, Universität Göttingen, Göttingen, Germany.
[4] Spek, A.L. (2003), J. Appl. Cryst. 36, 7-13.

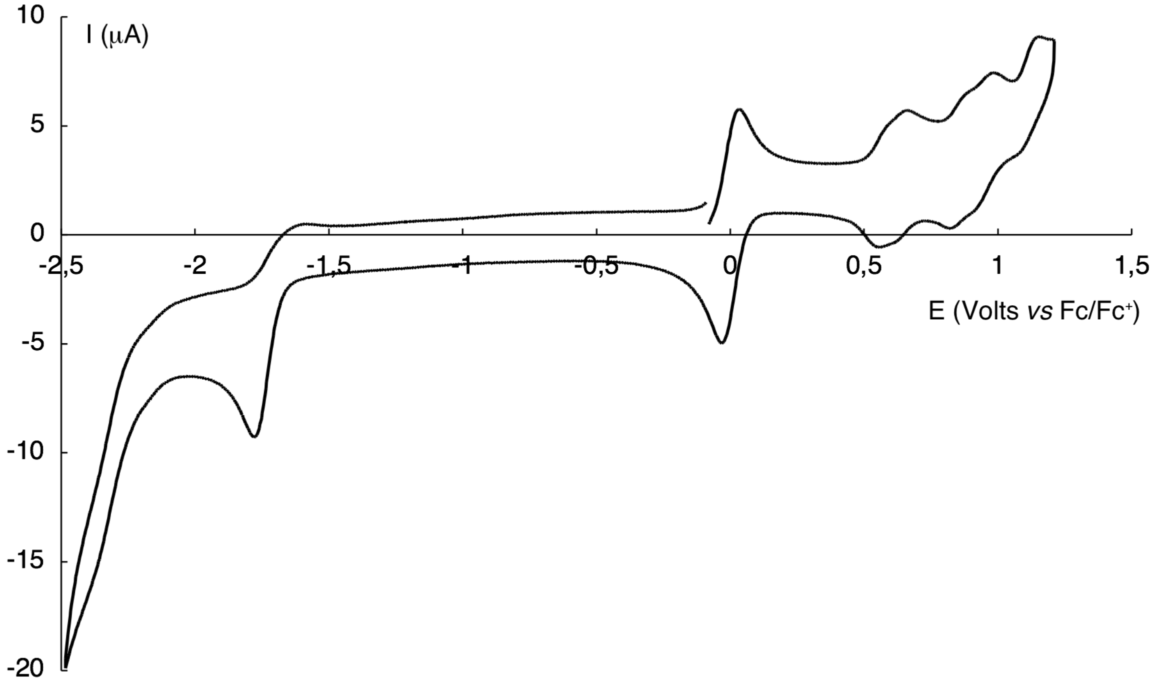
Electrochemistry

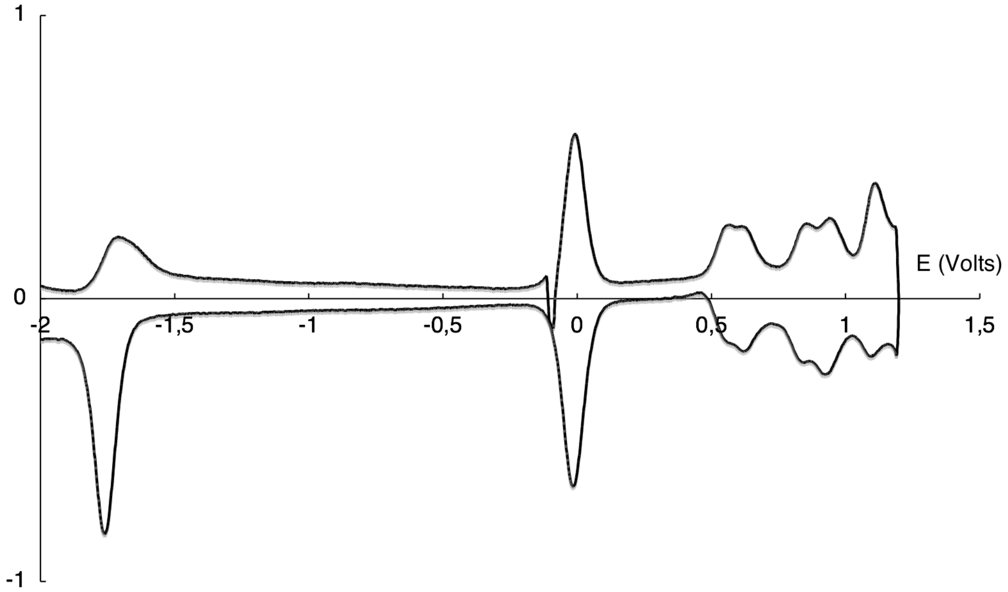
Experimental: Electrochemical measurements were carried out in CH_2Cl_2 containing 0.1 M Bu_4NPF_6 in a classical three-electrode cell by cyclic voltammetry (CV). The cell was connected to an Autolab PGSTAT30 potentiostat (Eco Chemie, Holland) driven by a GPSE software running on a personal computer. The working electrode was a glassy C disk (3 mm in diameter), the auxiliary electrode a Pt wire, and the reference electrode a Pt wire used as pseudo reference electrode. At the end of the studies, ferrocene, was added to the solution. All potentials are given *vs*. Fc^+/Fc used as internal standard and are uncorrected from ohmic drop.

Cyclic Voltammetry of compound **3a**.

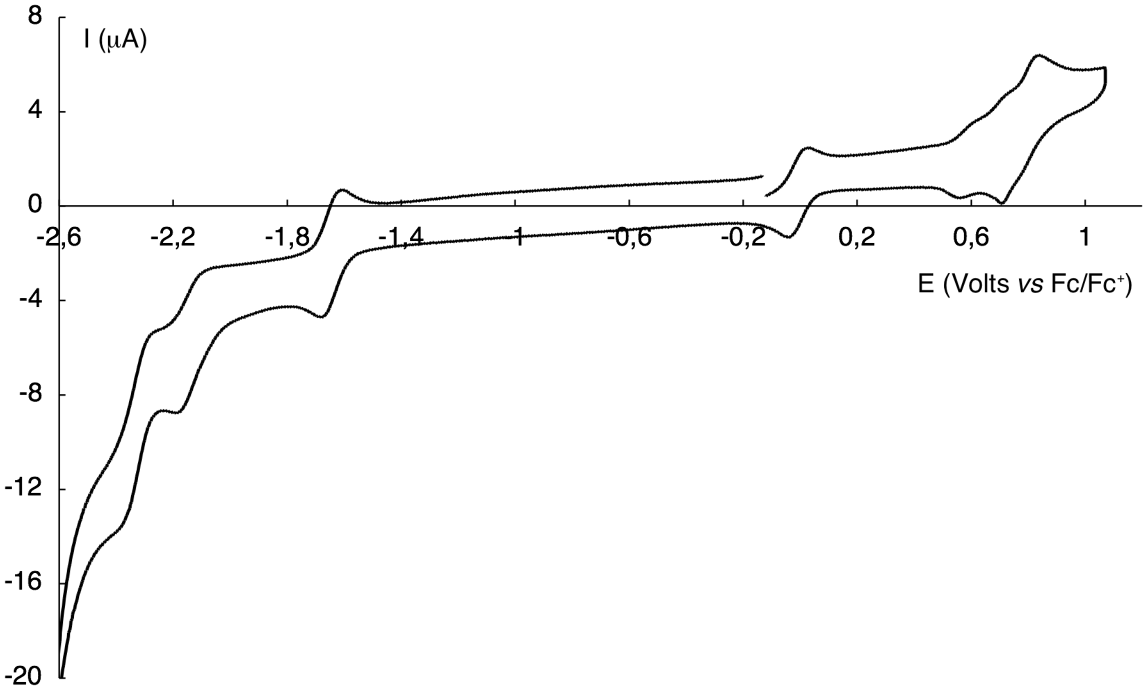


Cyclic Voltammetry (top) and deconvoluted voltammetry (bottom) of compound **5a**.





Cyclic Voltammetry of compound **3b**.



Cyclic Voltammetry of compound **5b**.