# *Appendix B*

# SUPPLEMENTARY DATA FOR CHAPTER 3

## B.1 General Considerations

**Chemicals.** All manipulations were carried out using standard Schlenk or glovebox techniques under an $N_2$ atmosphere. Solvents were deoxygenated and dried by thoroughly sparging with $N_2$ followed by passage through an activated alumina column in a solvent purification system by SG Water, USA LLC. Solvents were tested with sodium benzophenone ketyl in tetrahydrofuran (THF) in order to confirm the absence of oxygen and water. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc., degassed, and dried over activated 3 Å molecular sieves prior to use. $Cp^*{}_2Co$,[1] $NaBAr^F{}_4$,[2] $Ph_2NH_2OTf$,[3] 1-(4-bromobutyl)pyrene,[4] 3-iodo-4-bromophenol,[5] and diisopropylphosphine[6] were prepared according to literature procedures. All other reagents were purchased from commercial vendors and used without further purification unless otherwise stated.

**Infrared, EPR, and UV-Vis Spectroscopy.** UV-vis experiments were conducted with sealable 1-cm path length fused quartz cuvettes (Starna Cells) using a Cary 50 UV-vis spectrometer. X-band EPR measurements were made with a Bruker EMX spectrometer at 77 K. IR measurements were recorded on a Bruker ALPHA Diamond ATR.

**NMR Spectroscopy.** All NMR spectra were obtained at ambient temperature using Varian 400 and 500 MHz spectrometers unless otherwise noted. $^1H$ and $^{13}C$ NMR chemical shifts (δ) are reported in parts per million (ppm) relative to TMS. $^{31}P$ NMR spectra are reported relative to 85% aqueous $H_3PO_4$. Solution phase magnetic measurements were performed by the method of Evans.[7]

**Mass Spectrometry.** The ESI-MS data was collected using a Thermo LTQ ion trap mass spectrometer.

**X-ray Photoelectron Spectroscopy.** The surface composition of the carbon electrode surface before and after controlled potential electrolysis measurements was determined via XPS on a Kratos Axis Ultra spectrometer with DLD (Kratos Analytical; Manchester, UK). The excitation source for all analysis was monochromatic Al $K\alpha_{1,2}$ ($h\nu = 1486.6$ eV) operating at 10 mA and 15 kV. The X-ray source was directed at 54° with respect to the sample normal. A base pressure of $1 \times 10^{-9}$ Torr is maintained in the analytical chamber, which rises to $5 \times 10^{-9}$ Torr during spectral acquisition. All spectra were acquired using the hybrid lens magnification mode and slot aperture, resulting in an analyzed area of 700 μm × 400 μm. Survey scans were collected using 160 eV pass energy, while narrow region scans used 10 eV; charge compensation via the attached $e^{-}$-flood source was not necessary in this study.

**Gas Chromatography.** $H_2$ was quantified on an Agilent 7890A gas chromatograph (HP-PLOT U, 30 m, 0.32 mm ID; 30 °C isothermal; nitrogen carrier gas) equipped with a thermal conductivity detector. A 10 mL injection was used for all measurements and integration area was converted to percent $H_2$ using a calibration obtained from injection of mixtures of known amounts of $H_2$ and $N_2$.

**Combustion Analysis.** Combustion analysis measurements were collected using a PerkinElmer 2400 Series II CHN Elemental Analyzer by facility staff.

**Ammonia Quantification.** Reaction mixtures were transferred to a Schlenk tube and frozen at 77 K. The frozen reaction mixture was treated with a solution of [Na][O-*t*-Bu] (40 mg, 0.4 mmol) in THF (2 mL) over 1 minute, ensuring no thawing of the reaction mixture, and sealed. The resulting suspension was allowed to stir for 10 minutes before all volatiles were vacuum transferred into a Schlenk charged with HCl (3 mL of a 2.0 M solution in $Et_2O$, 6 mmol). After completion of the vacuum transfer, the collection flask was sealed and warmed to room temperature. Solvent was removed in vacuo and $[NH_4][Cl]$ was quantified by the Indophenol method.[8]

## B.2 Synthesis and Characterization

### Synthesis of 3-Iodo-4-Bromo-*O*-(1-pyrenyl-butyl)phenol

In a 250 mL flask, 1.6 g 4-bromobutyl-(1-pyrene) (4.7 mmol), 1.6 g 3-bromo-4-iodophenol (5.4 mmol, 1.2 equiv), and 1.6 g $K_2CO_3$ (11.6 mmol, 2.5 equiv) were added to 80 mL DMF. The reaction was heated to 80 ˚C and stirred for 16 h. After cooling, the reaction was diluted into 200 mL DCM and washed with water (2 x 200 mL). The organic layer was dried on a rotovap, and the resulting yellow solid was recrystallized from DCM/pentane to give white crystals (2.5 g, 95%). $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 9.3 Hz, 1H), 8.18 (d, *J* = 2.7 Hz, 1H), 8.16 (d, *J* = 3.0 Hz, 1H), 8.12 (d, *J* = 3.6 Hz, 1H), 8.10 (d, *J* = 5.1 Hz, 1H), 8.03 (s, 1H), 8.03 (s, 1H), 8.00 (t, *J* = 7.6 Hz, 1H), 7.88 (d, *J* = 7.8 Hz, 1H), 7.42 (d, *J* = 8.8 Hz, 1H), 7.37 (d, *J* = 2.9 Hz, 1H), 6.72 (dd, *J* = 8.9, 2.9 Hz, 1H), 3.94 (t, *J* = 6.2 Hz, 2H), 3.41(t, *J* = 7.5 Hz, 2H), 2.27-1.82 (M, 4H). $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 158.15, 136.29, 132.59, 131.43, 130.88, 129.89, 128.62, 127.51, 127.32, 127.26, 126.67, 125.99, 125.86, 125.11, 125.02, 124.94, 124.81, 124.75, 123.30, 120.09, 116.40, 101.05, 68.21, 33.11, 29.02, 28.07.

### Synthesis of 3-diisopropylphosphino-4-Bromo-*O*-(1-pyrenyl-butyl)phenol

1.67 g 3-Iodo-4-Bromo-*O*-(1-pyrenyl-butyl)phenol (3.0 mmol), 0.50 g $K_2CO_3$ (3.62 mmol, 1.2 equiv), 36 mg $Pd(OAc)_2$ (0.16 mmol, 5.3 mol %), and 80 mg 1,1′-bis(diisopropylphosphino)ferrocene (0.14 mmol, 4.8 mol %) were weighed into a 100 mL sealable Schlenk tube. 5 mL dioxane and 1 mL THF were then added, and the suspension was stirred at 25 ˚C (Note: solvents must be extremely dry to prevent ether cleavage). After 1 h, 590 µL $HPiPr_2$ (470 mg, 4.0 mmol) was added and the tube was sealed. The reaction was stirred 22 h at 85 ˚C. The reaction was cooled, 2 mL THF was added, and the resulting suspension was filtered over Celite. The filtrate was dried in vacuo, and the resulting residue was purified by silica gel column chromatography (2:1 hexane/DCM performed in air with solvents used as received, $R_f = 0.38$) to give a white solid (1.28 g, 77%). $^1$H NMR (300 MHz, $C_6D_6$) δ 8.15 (dd, *J* = 9.3, 0.8 Hz, 1H), 8.03 – 7.89 (m, 4H), 7.84 (d, *J* = 3.7 Hz, 1H), 7.79 (td, *J* = 7.6, 1.1 Hz, 1H), 7.67 (d, *J* = 7.8 Hz, 1H), 7.43 (ddd, *J* = 8.7, 3.3, 0.9 Hz, 1H), 7.08 (dd, *J* = 3.0, 1.2 Hz, 1H), 6.40 (ddd, *J* = 8.8, 3.0, 0.9 Hz, 1H), 3.52 (t, *J* = 6.3 Hz, 2H), 3.13 (t, *J* = 7.5 Hz, 2H), 1.97 – 1.61 (m, 6H), 1.07 (dd, *J* = 14.2, 7.0 Hz, 5H), 0.92 (dd, *J* = 12.0, 6.9 Hz, 4H). $^{31}$P NMR (121 MHz, $C_6D_6$) δ 9.83.

### Synthesis of Tris(2-diisopropylphosphino-4-(1-pyrenyl-butoxy)phenyl)borane ($^{Py}P_3^B$, 3.1)

550 mg 3-diisopropylphosphino-4-Bromo-*O*-(1-pyrenyl-butyl)phenol (1.0 mmol) was dissolved in a mixture of 75 mL toluene and 15 mL $Et_2O$. The resulting solution was cooled to –78 ˚C and 0.66 mL nBuLi (1.6 M in hexanes, 1.05 mmol, 1.05 equiv) was added. After stirring 20 min, the reaction was warmed to 25 ˚C and stirred for a further 30 min. The resulting yellow solution was cooled back to –78 ˚C and 45 µL $BF_3{\cdot}OEt_2$ (0.36 mmol, 0.36 equiv) was added. The reaction was then stirred 8 h at –78 ˚C and allowed to warm to 25 ˚C. After 16 h, 20 mL pentane was added and the resulting suspension was stirred 1 h and filtered over Celite. The reaction was then concentrated to 5 mL and layered with 20 mL pentane and allowed to crystallize at –40 ˚C. The resulting product was recrystallized two more times, giving **1** as a white solid (285 mg, 61%). $^1H$ NMR (400 MHz, $C_6D_6$) δ 8.11 (d, *J* = 8.6 Hz, 1H), 7.99 – 7.84 (m, 5H), 7.79 (q, *J* = 6.6 Hz, 2H), 7.74 (d, *J* = 9.2 Hz, 1H), 7.62 (d, *J* = 7.4 Hz, 1H), 7.29 (s, 1H), 6.80 (d, *J* = 7.9 Hz, 1H), 3.71 (t, *J* = 6.1 Hz, 2H), 3.10 (t, *J* = 7.6 Hz, 2H), 2.08 – 1.95 (m, 2H), 1.79 (p, 2H), 1.68 (p, *J* = 169.2 Hz, 2H), 1.19 – 0.81 (m, 12H). $^{31}P$ NMR (162 MHz, $C_6D_6$) δ 2.7. Anal. calcd for $C_{96}H_{102}O_3P_3B$: C 81.92, H 7.30, N 0.0; found: C 81.19, H7.48 N 0.0.

### Synthesis of $^{py}P_3^BFeBr$ (3.2)

In a vial, 70 mg $^{py}P_3^B$ (**3.1**) (0.050 mmol) and 11 mg $FeBr_2$ (0.050 mmol, 1 equiv) were suspended in 4 mL THF. The suspension was vigorously stirred for 2 h, giving a bright yellow solution. Excess 1% Na/Hg (3 mg Na, 0.13 mmol, 2.6 equiv) was added and the solution was stirred a further 2 h. The green-brown solution was decanted and dried in vacuo and extracted with benzene (2 x 2 mL) and lyophilized to give the product as a brown powder (55 mg, 71%). ES-MS (positive mode, m/z) calcd for $^{py}P_3^BFeBr$: 1543.6, found 1543.8. $^1H$

NMR (400 MHz, $C_6D_6$) δ 91.11, 33.68, 19.09, 7.99, 7.85, 7.79, 7.73, 7.50, 3.62, 3.28, 3.00, 2.64, 1.68, 1.32, 1.03, 0.90, 0.26, –1.54, –23.14. Evans, $\mu_{eff}$ ($C_6D_6$, Evans method, 20 °C): 3.7 $\mu_B$ Anal. calcd for $C_{96}H_{102}O_3P_3BFeBr$: C 74.71, H 6.66, N 0.0; found: C 75.64, H 6.90, N 0.2.

### Synthesis of $^{py}P_3^BFeMe$ (3.3)

15.4 mg $^{py}P_3^BFeBr$ (**3.2**) (0.010 mmol) was dissolved in a mixture of 1.5 mL THF and 1.5 mL $Et_2O$ and cooled to –78 ˚C. 13 µL methyllithium solution (1.6 M in $Et_2O$, 0.021 mmol, 2.1 equiv) was added, and the reaction was stirred 1 h at –78 ˚C then allowed to warm to room temperature. The solution was stirred 2 h at 25 ˚C, and the solvent was removed in vacuo. The residue was washed with pentane (2 x 3 mL) and extracted with 2 mL benzene and lyophilized to give the product as a red powder (14.2 mg, 96%). ES-MS (positive mode, m/z) calcd for $^{py}P_3^BFeMe$: 1478.7, found 1478.5. $^1H$ NMR (400 MHz, $C_6D_6$) δ 72.08, 33.15, 12.30, 9.95, 8.11, 7.89, 7.79, 7.62, 6.81, 5.10, 3.83, 3.71, 3.38, 3.11, 2.96, 2.58, 1.79, 1.67, 1.47, 1.31, 1.03, 0.27, –2.35, –2.86, –7.43, –16.22. $\mu_{eff}$ ($C_6D_6$, Evans method, 20 °C): 3.8 $\mu_B$. Anal. calcd for $C_{97}H_{105}O_3P_3BFe$: C 78.80, H 7.16, N 0.0; found: C 78.42, H 7.24 N 0.3. UV-vis (THF, nm {$cm^{-1}M^{-1}$}): 375 {4800}.

### Synthesis of $[^{py}P_3^BFeN_2][Na(THF)_n]$ (3.4)

6.0 mg $^{py}P_3^BFeBr$ (**3.2**) (3.9 µmol) was dissolved in 1 mL THF and cooled to –78 ˚C. 7.8 µL Na/naphthalene (1M in THF, 2.0 equiv) was added and the reaction was allowed to warm. 1 mL pentane was added and the reaction was filtered and solvent was removed in vacuo to give **3.4** as a red solid (4.8 mg, 60% assuming n = 6). ES-MS (negative mode, m/z) calcd for

$[^{py}P_3^BFe]^-$, $[^{py}P_3^BFe(THF)]^-$: 1462.6, 1535.7; found 1462.6, 1535.2. The $N_2$ adduct was not observed under electrospray conditions. $^1H$ NMR (400 MHz, THF-$d_8$) δ 18.65, 13.26, 12.87, 12.74, 12.54, 12.45, 12.34, 12.18, 10.49, 9.05, 8.77, 7.21, 6.92, 6.73, 6.32, 5.55, 5.41, 3.91. $\mu_{eff}$ (THF-$d_8$, Evans method, 20 °C): 1.7 $\mu_B$. IR (thin film) $\nu_{NN}$ = 1930, 1880 cm$^{-1}$.

## B.3 Chemical Ammonia Generation Experiments

Ammonia generation experiments were conducted based on a previously reported protocol. In a nitrogen-filled glovebox, the precatalyst (2.0 μmol) was weighed into a vial. The precatalyst was then transferred quantitatively into a 250 mL Schlenk tube with a Teflon valve using THF. The THF was then evaporated to provide a thin film of precatalyst at the bottom of tube. The tube is then charged with a stir bar, the acid (108 equiv), and $Cp^*_2Co$ (54 equiv) as solids. The tube is then chilled to 77 K and allowed to equilibrate for 10 minutes. To the chilled tube is added 1 mL of $Et_2O$. The temperature of the system is allowed to equilibrate for 5 minutes. This tube is sealed and is passed out of the box and transported to a fume hood. The tube is then transferred to a dry ice/acetone bath and is allowed to stir at −78 °C for 3 h. The tube is then allowed to warm to RT with stirring and then stirred at RT for a further ten minutes. At this point the previously described procedure for quantifying ammonia was employed. To ensure reproducibility, all experiments were conducted in 250 mL tubes using 25 mm stir bars and stirring was conducted at ~ 650 rpm.

## B.4 Electrochemistry

All electrochemical measurements were conducted in a nitrogen-filled glovebox with a CH Instruments 600B electrochemical analyzer. For all measurements at low temperature, the temperature was controlled by immersing the glovebox cold well in a well-stirred isopropanol bath cooled by an SP Scientific FTS Systems FC100 immersion cooler. For all measurements, a Ag/$AgPF_6$ reference electrode filled with 0.1 M $NaBar^F_4$ and isolated from the cell by a Coralpor frit was used. All potentials are reported relative to externally-referenced $Fc^{+/0}$.

**HOPG Electrode Preparation.** Highly-ordered pyrolytic graphite (HOPG) was obtained from graphitestore.com and cut into rectangular plates of 15 mm x 10 mm x 1 mm. These plates were then sonicated in deionized water for 30 minutes followed by acetonitrile for a further 30 minutes. The plates were dried in a dessicator overnight, followed by oven drying for 2 h. The plates were then brought into the glovebox and soaked in a 1 mM THF solution of analyte for 16 h, followed by washing with THF to remove any loosely-bound species. The electrodes were then dried in vacuo for 30 minutes to remove any remaining THF.

**Cyclic voltammetry of solution-phase species.** CV experiments were conducted in a 20 mL cell using a 3 mm glassy carbon disc as the working electrode and a 5 mm glassy carbon rod as the auxiliary electrode.

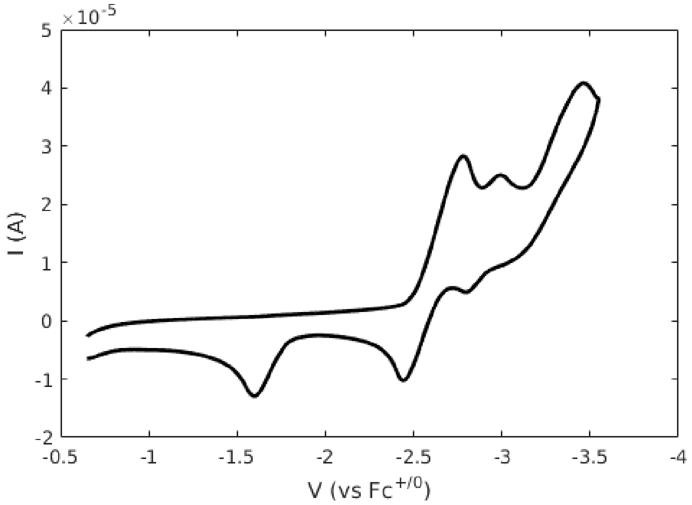

**Figure B.1:** Cyclic voltammogram of $^{py}P_3^B$ (**3.1**) in 0.1 M $NaBAr^F_4/Et_2O$ solution. Scan rate = 100 mv/s.

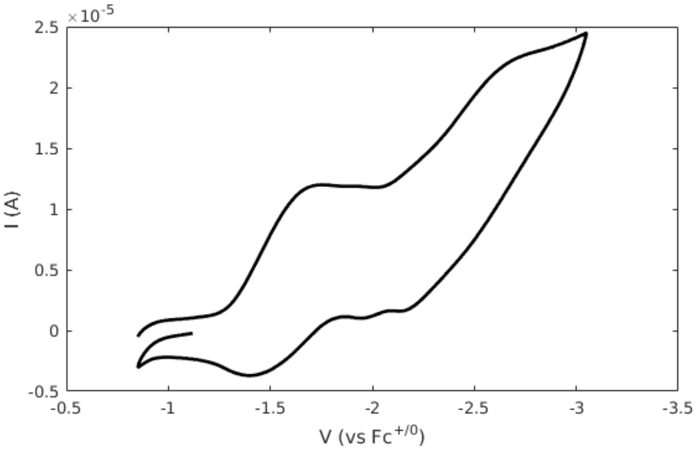

**Figure B.2:** Cyclic voltammogram of $^{py}P_3^BFeMe$ (**3.3**) in 0.1 M $NaBAr^F_4/Et_2O$ solution. Scan rate = 100 mv/s.

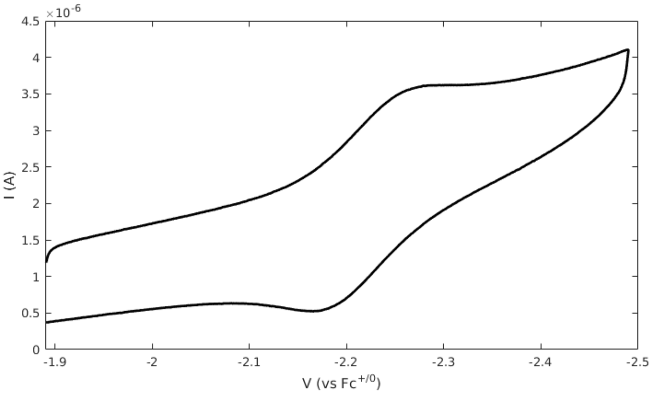

**Figure B.3:** Cyclic voltammogram of $[^{py}P_3{}^BFeN_2][Na(THF)_n]$ (**3.4**) in 0.1 M $NaBAr^F{}_4/Et_2O$ solution. Scan rate = 100 mv/s.

**CV of prepared electrodes.** In a 20 mL cell, a 0.1 M solution of $NaBar^F{}_4$ in $Et_2O$ was prepared and cooled to –35 ˚C. An HOPG working electrode presoaked in analyte, a clean HOPG auxiliary electrode, and a reference electrode were then placed into the pre-cooled solution. The cell was allowed to thermally equilibrate for 5 minutes before measurement. A freshly prepared electrode was used for every scan so electrochemical decomposition did not affect any subsequent measurements.

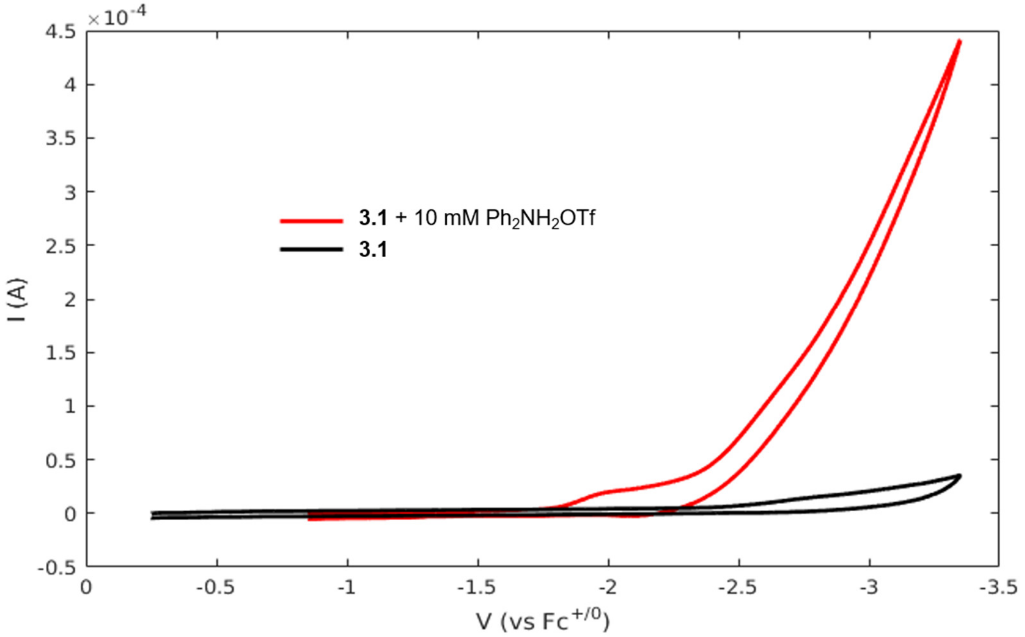

**Figure B.4:** Cyclic voltammograms of surface-attached ${}^{py}P_3{}^B$ (**3.1**) in the presence (red trace) and absence (black trace) of 10 mM $[Ph_2NH_2][OTf]$ on an HOPG electrode in 0.1 M $NaBAr^F{}_4/Et_2O$ solution. Scan rate = 50 mv/s, temperature = –35 ˚C.

## B.5 Electrochemical Ammonia Generation Experiments.

For CPE experiments, a sealable single-compartment cell was filled with 6 mL of 0.1 M $NaBAr^F{}_4$ in $Et_2O$ electrolyte, and 100 μmol of acid was added. The chamber is fitted with a Na metal auxiliary electrode inside a 7 mm diameter glass tube separated from the working electrode by a medium porosity sintered glass frit, an HOPG working electrode submerged to a solution depth of 10 mm, and a $Ag/AgPF_6$ in 0.1 M $NaBAr^F{}_4/Et_2O$ reference electrode isolated by a CoralPor frit and referenced externally to $Fc^{+/0}$. The temperature is maintained at –35 °C by a SP Scientific FTS Systems FC100 immersion cooler. All experiments were stirred with a stirring rate of ~300 rpm. The cell is held at a working potential of –2.4 V vs

$Fc^{+/0}$ for 6 h, after which an additional 100 μmol of acid in 2 mL 0.1 M $NaBAr^F_4/Et_2O$ is injected through a rubber septum to sequester $NH_3$ as $[NH_4][OTf]$. The cell was then stirred a further 10 minutes, and the contents were transferred to a Schlenk tube and washed with additional $Et_2O$. The resulting solution was analyzed for $NH_3$ as described above.

## B.6 Electrode Desorption Experiment

An electrode containing adsorbed $^{py}P_3^BFeMe$ (**3.3**) was prepared as above. The electrode was then soaked in 2 mL THF for 1 h. The THF was then transferred to another vial, and the soaking procedure was repeated a further two times. The THF extracts were combined and the solvent was removed in vacuo. The resulting residue was then dissolved in 300 μL THF, and this solution was analyzed by UV-visible spectroscopy in a 1 cm path length low-volume cuvette.

## B.7 Supplementary XPS data

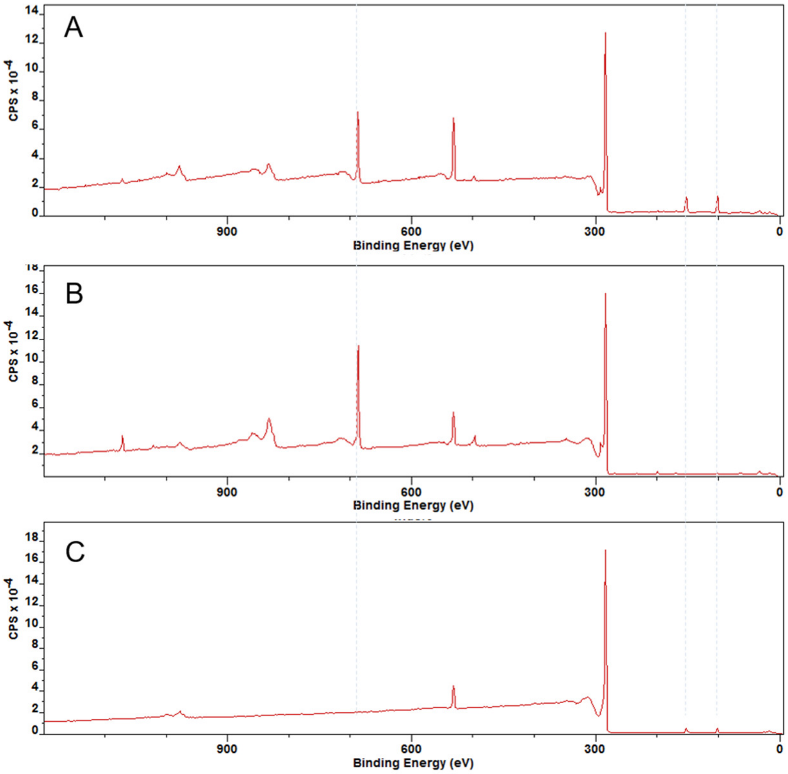

**Figure B.5:** Overview XPS spectra of (A) functionalized electrode pre-electrolysis, (B) functionalized electrode post-electrolysis, and (C) unfunctionalized electrode.

## B.8 NMR Spectra

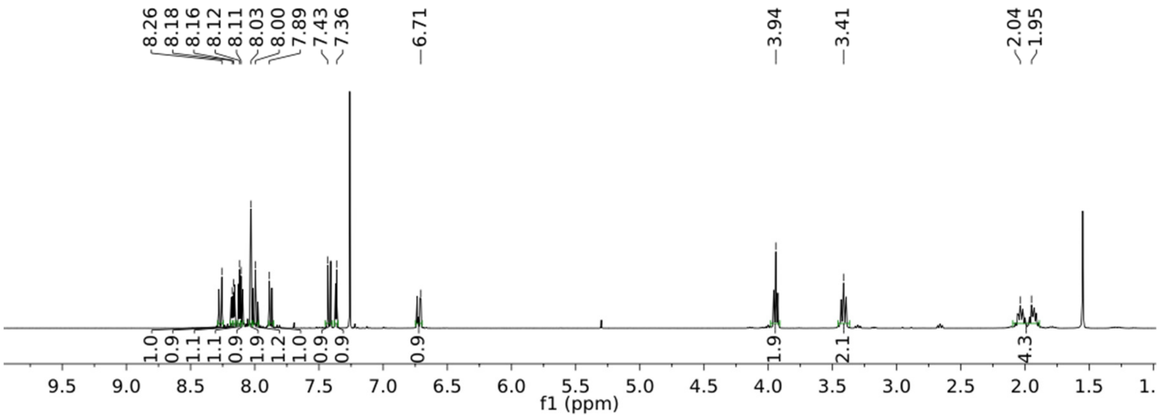

**Figure B.6:** $^1$H NMR of 3-Iodo-4-Bromo-*O*-(1-pyrenyl-butyl)phenol in $CDCl_3$.

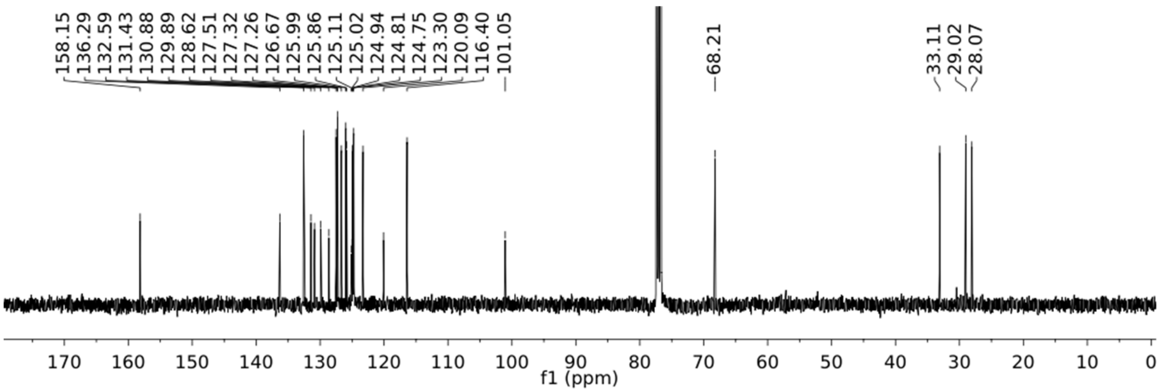

**Figure B.7:** $^{13}C\{^1H\}$ NMR of 3-Iodo-4-Bromo-*O*-(1-pyrenyl-butyl)phenol in $CDCl_3$.

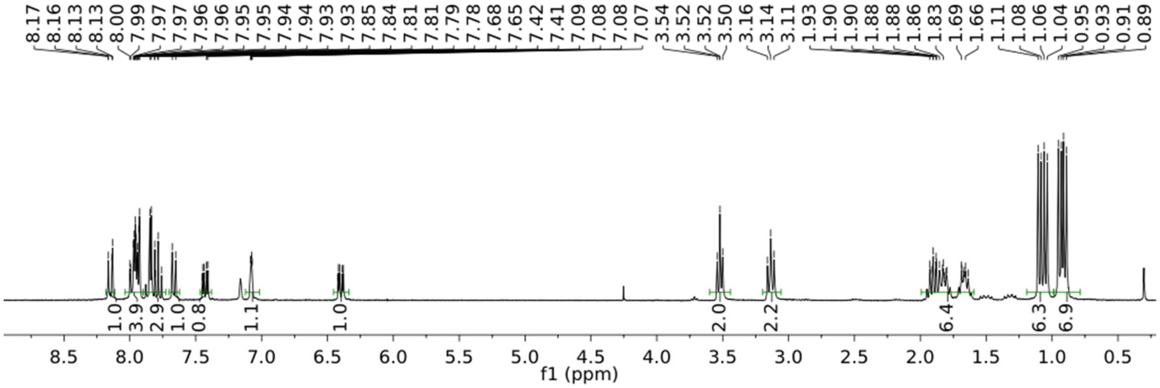

**Figure B.8:** $^1H$ NMR of 3-diisopropylphosphino-4-Bromo-*O*-(1-pyrenyl-butyl)phenol in $C_6D_6$.

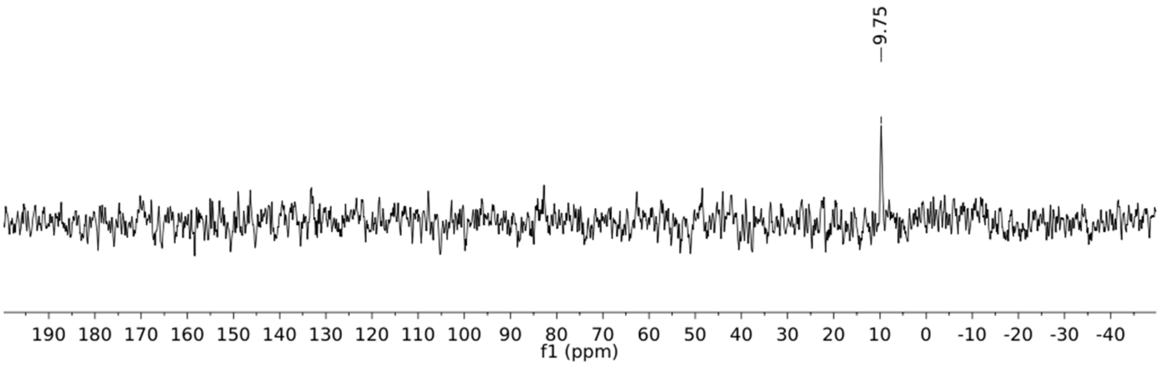

**Figure B.9:** $^{31}P\{^1H\}$ NMR of 3-diisopropylphosphino-4-Bromo-*O*-(1-pyrenyl-butyl)phenol in $C_6D_6$.

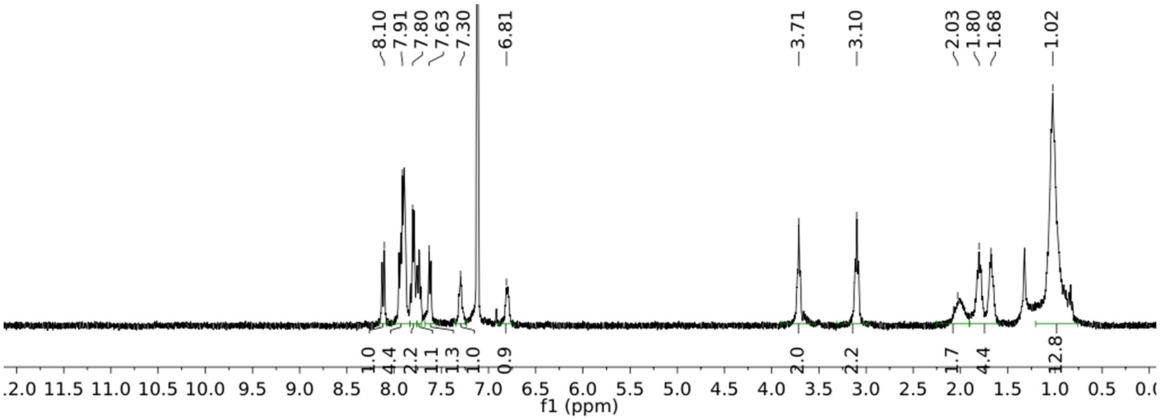

**Figure B.10:** $^1$H NMR of $^{py}P_3^B$ (**3.1**) in $C_6D_6$.

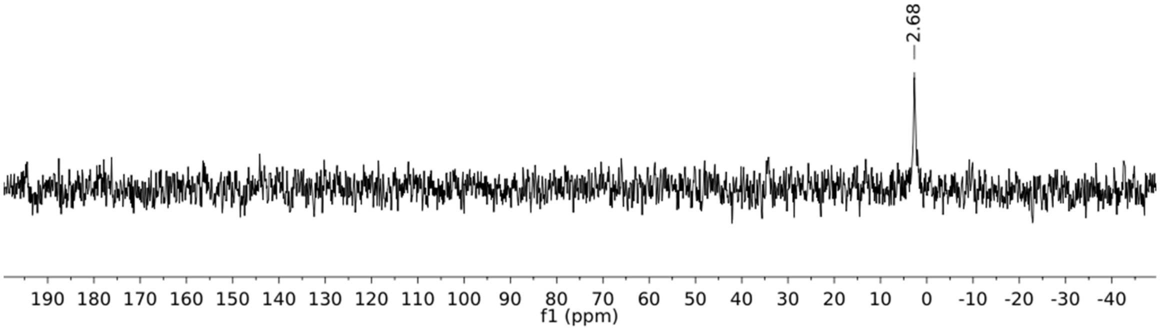

**Figure B.11:** $^{31}P\{^1H\}$ NMR of $^{py}P_3^B$ (**3.1**) in $C_6D_6$.

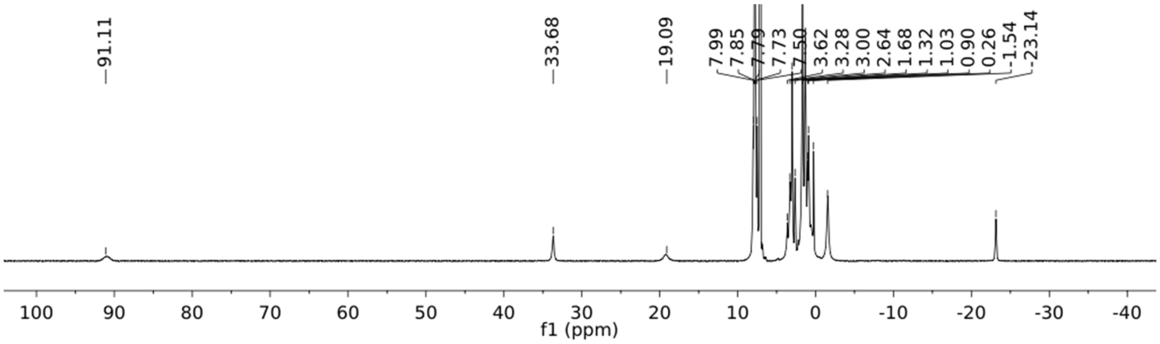

**Figure B.12:** $^1$H NMR of $^{py}P_3^B$FeBr (**3.2**) in $C_6D_6$.

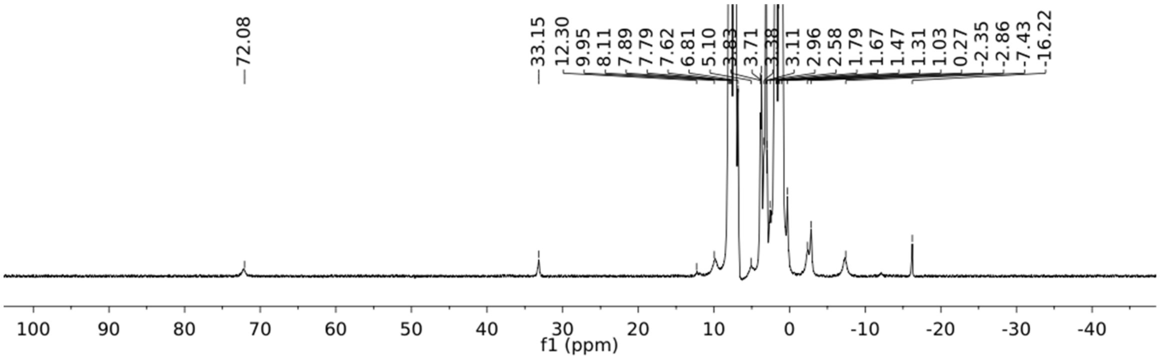

**Figure B.13:** $^1$H NMR of $^{py}P_3^BFeMe$ (**3.3**) in $C_6D_6$.

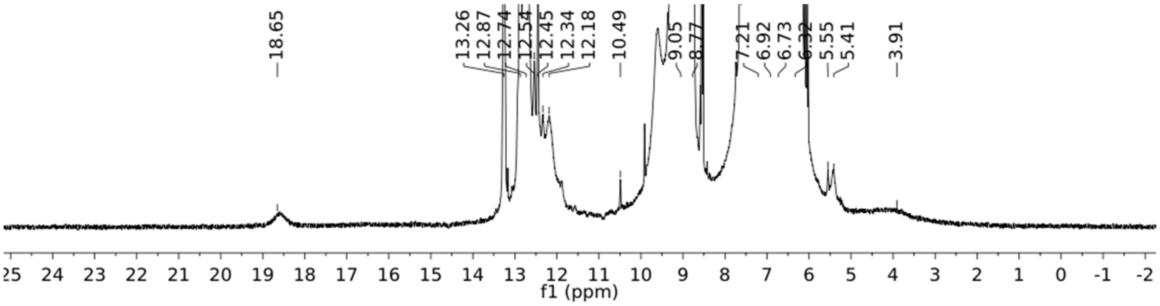

**Figure B.14:** $^1$H NMR of $[^{py}P_3^BFeN_2][Na(THF)_n]$ (**3.4**) in THF-$d_8$.

## B.9 References

(1) Robbins, J. L.; Edelstein, N.; Spencer, B.; Smart, J. C. Syntheses and Electronic Structures of Decamethylmetallocenes. *J. Am. Chem. Soc.* **1982**, *104* (7), 1882–1893.

(2) Del Castillo, T. J.; Thompson, N. B.; Peters, J. C. A Synthetic Single-Site Fe Nitrogenase: High Turnover, Freeze-Quench $^{57}$Fe Mössbauer Data, and a Hydride Resting State. *J. Am. Chem. Soc.* **2016**, *138* (16), 5341–5350.

(3) Vicente, J.; Chicote, M.-T.; Guerrero, R.; Jones, P. G. Synthesis of Complexes $[Au(PPh_3)L]^+$(L = Primary, Secondary or Tertiary Amine). Crystal Structure of $[Au(PPh_3)(NMe_3)][ClO_4]\cdot CH_2Cl_2$. *J. Chem. Soc. Dalton Trans.* **1995**, *0* (8), 1251–1254.

(4) Taher, A.; Lee, K. C.; Han, H. J.; Kim, D. W. Pyrene-Tagged Ionic Liquids: Separable Organic Catalysts for $S_N2$ Fluorination. *Org. Lett.* **2017**, *19* (13), 3342–3345.

(5) Yavari, K.; Retailleau, P.; Voituriez, A.; Marinetti, A. Heterohelicenes with Embedded P-Chiral 1H-Phosphindole or Dibenzophosphole Units: Diastereoselective Photochemical Synthesis and Structural Characterization. *Chem. – Eur. J.* **2013**, *19* (30), 9939–9947.

(6) Zhu, K.; Achord, P. D.; Zhang, X.; Krogh-Jespersen, K.; Goldman, A. S. Highly Effective Pincer-Ligated Iridium Catalysts for Alkane Dehydrogenation. DFT Calculations of Relevant Thermodynamic, Kinetic, and Spectroscopic Properties. *J. Am. Chem. Soc.* **2004**, *126* (40), 13044–13053.

(7) Sur, S. K. Measurement of Magnetic Susceptibility and Magnetic Moment of Paramagnetic Molecules in Solution by High-Field Fourier Transform NMR Spectroscopy. *J. Magn. Reson. (1969)* **1989**, *82* (1), 169–173.

(8) Weatherburn, M. W. Phenol-Hypochlorite Reaction for Determination of Ammonia. *Anal. Chem.* **1967**, *39* (8), 971–974.