Modulation of catalytic reactivity with pyridine ring substitutions of Fe-pyridinophane complexes

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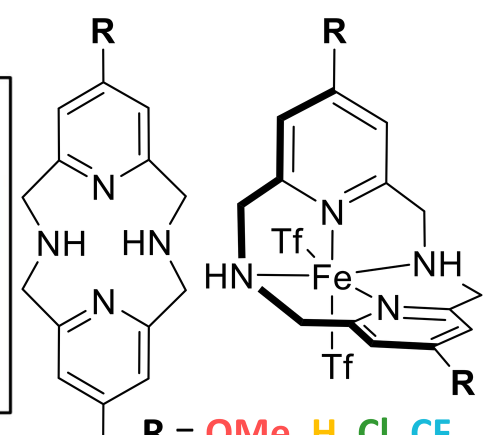
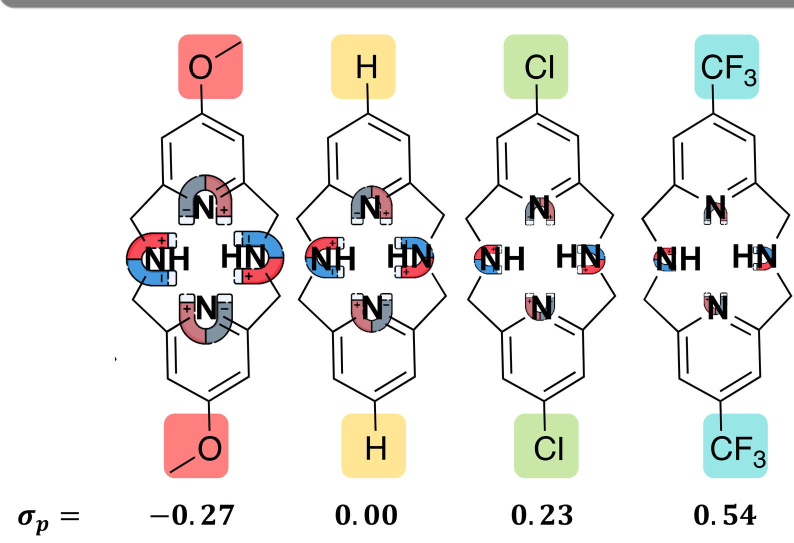
ABSTRACT

The inclusion of a pyridine moiety in the skeleton of tetra-aza macrocycles introduces a handle by which the electronics and basicity of the ligand can be tuned. Recent work has explored their potential for industrially relevant catalytic reactions. Previous studies of iron $^{R}PyN_3$ complexes showed moderate success for a direct Suzuki-Miyaura C-C coupling reaction. In that work, it became clear that the substitution on the 4-position of the pyridine ring offered significant influence over the efficacy of the catalyst: the electron donating groups offer a better handle of modification of the electronic properties of the iron center, but the electron withdrawing groups increased the catalytic activity of the complex. In this presentation we introduce a second pyridine ring to the macrocycle skeleton, which includes a second position for modification, and compare the activity of this new $^{R}Py_2N_2$ iron complex series to the previous $^{R}PyN_3$ series. The ultimate goal of this project is to develop an iron-based catalyst for direct Suzuki-Miyaura C-C coupling that rivals the catalytic activity of commonly used Palladium-based catalysts and is more environmentally friendly, less toxic, and significantly cheaper.

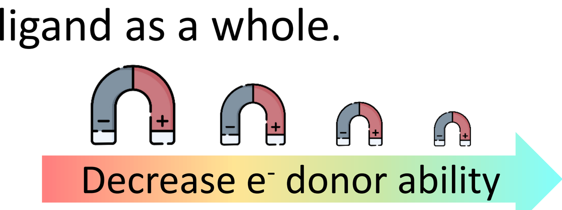
	Rare Earth Metals (Ex: Palladium)	Earth Abundant Metals (Ex: Iron)
Cost	\$1129.43 / ounce	\$114/metric ton
Terrestrial Availability	Scarce	Abundant
Toxicity	100 µg/day	No PDE limits
Global Warming Potential (kg CO_2-eq/kg element)	3,880 (high)	1.5 (low)

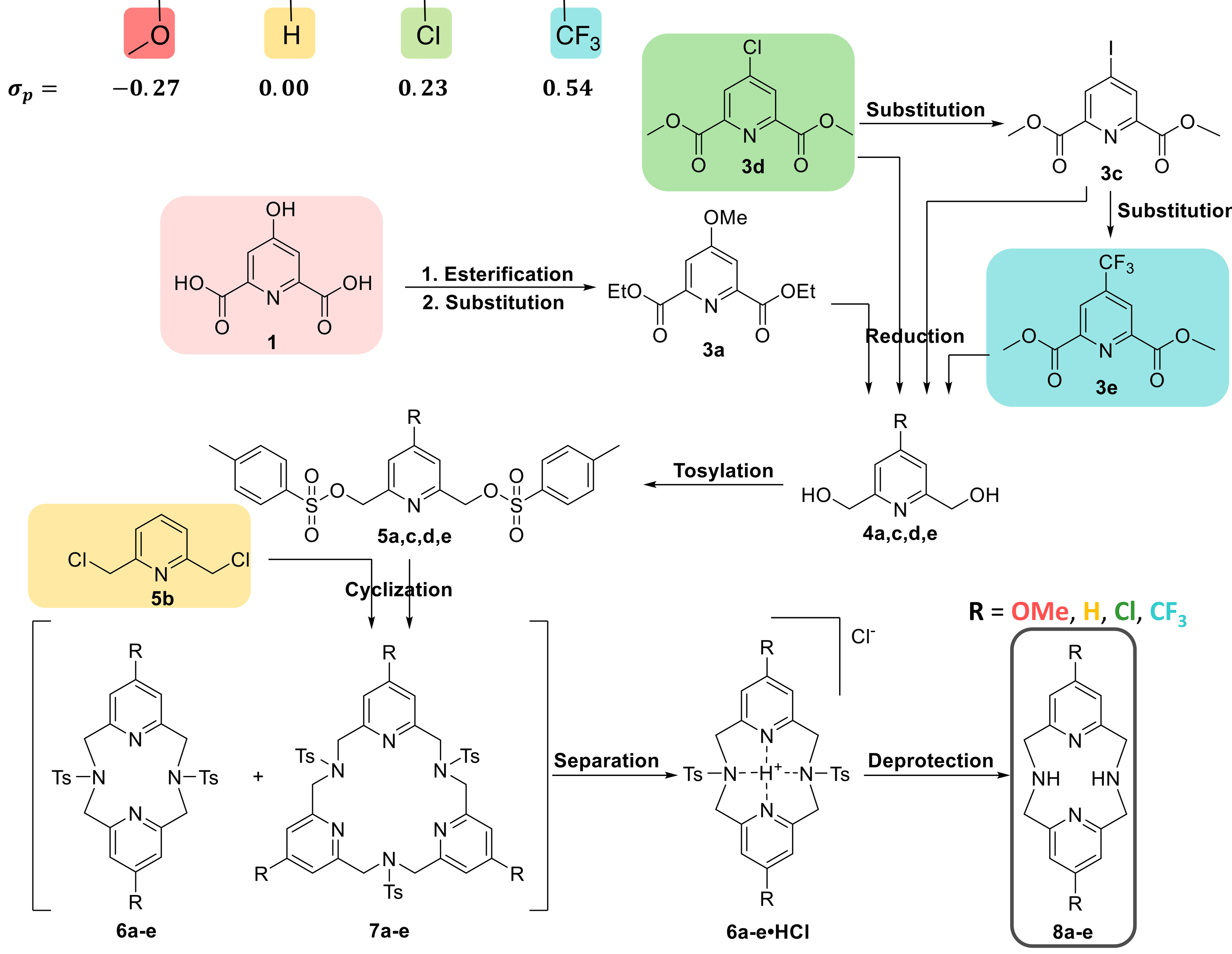


LIGAND RATIONAL AND SYNTHESIS

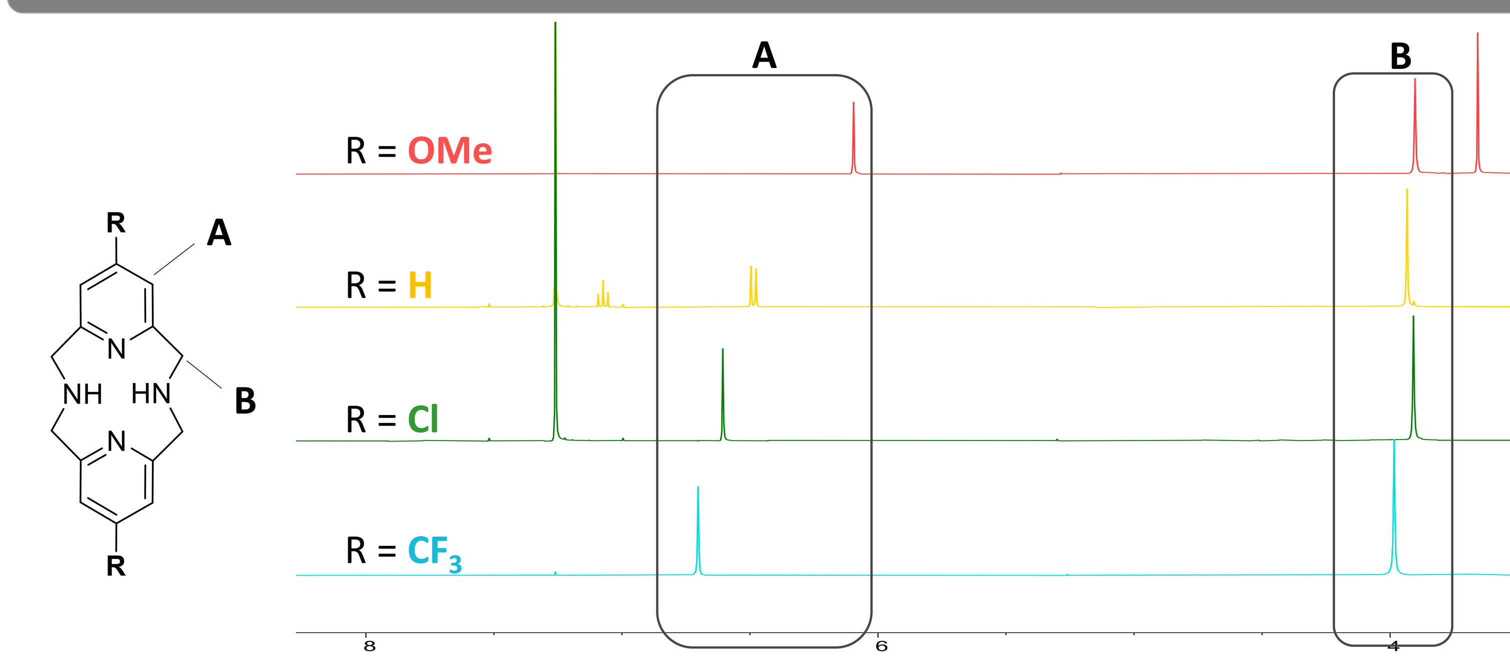


Substitution on 4 position modulates electronics of the ligand as a whole.



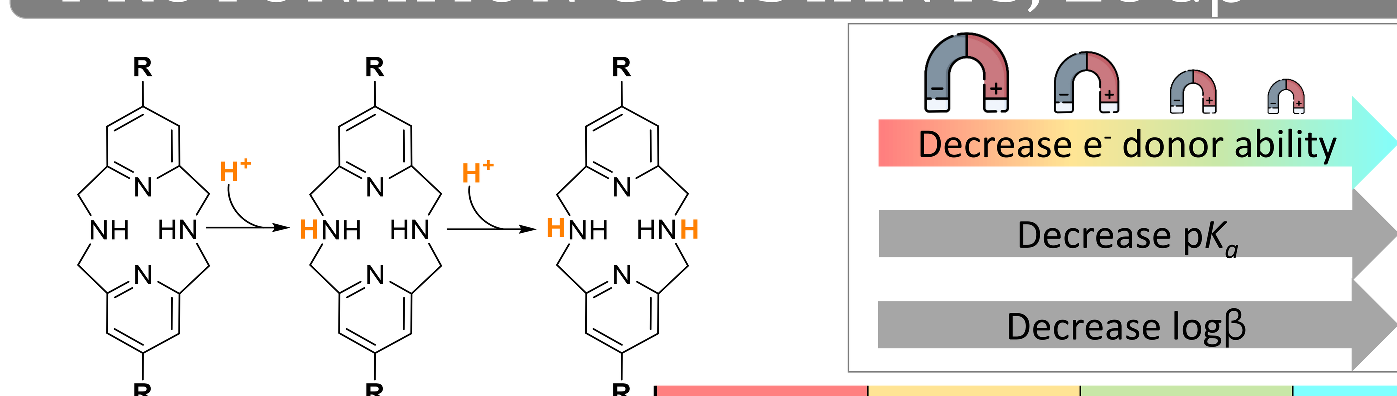


^{1}H NMR



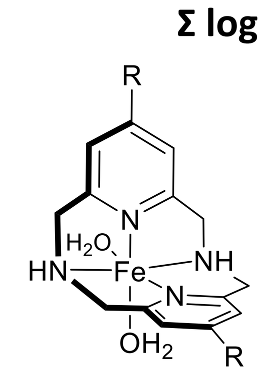
^{1}H NMRs with 400 MHz Bruker Avance spectrometer in $CDCl_3$

PROTONATION CONSTANTS, LOGβ



	$^{OMe}Py_2N_2$	$^{H}Py_2N_2$	$^{Cl}Py_2N_2$	$^{CF3}Py_2N_2$
log K_1^H	8.05(8)	8.35(2)	7.7(3)	7.5(2)
log K_2^H	7.01(7)	7.42(2)	6.2(3)	6.2(1)
Σ log $K_{N\text{-donors}}$	15.06	15.77	13.9	13.70

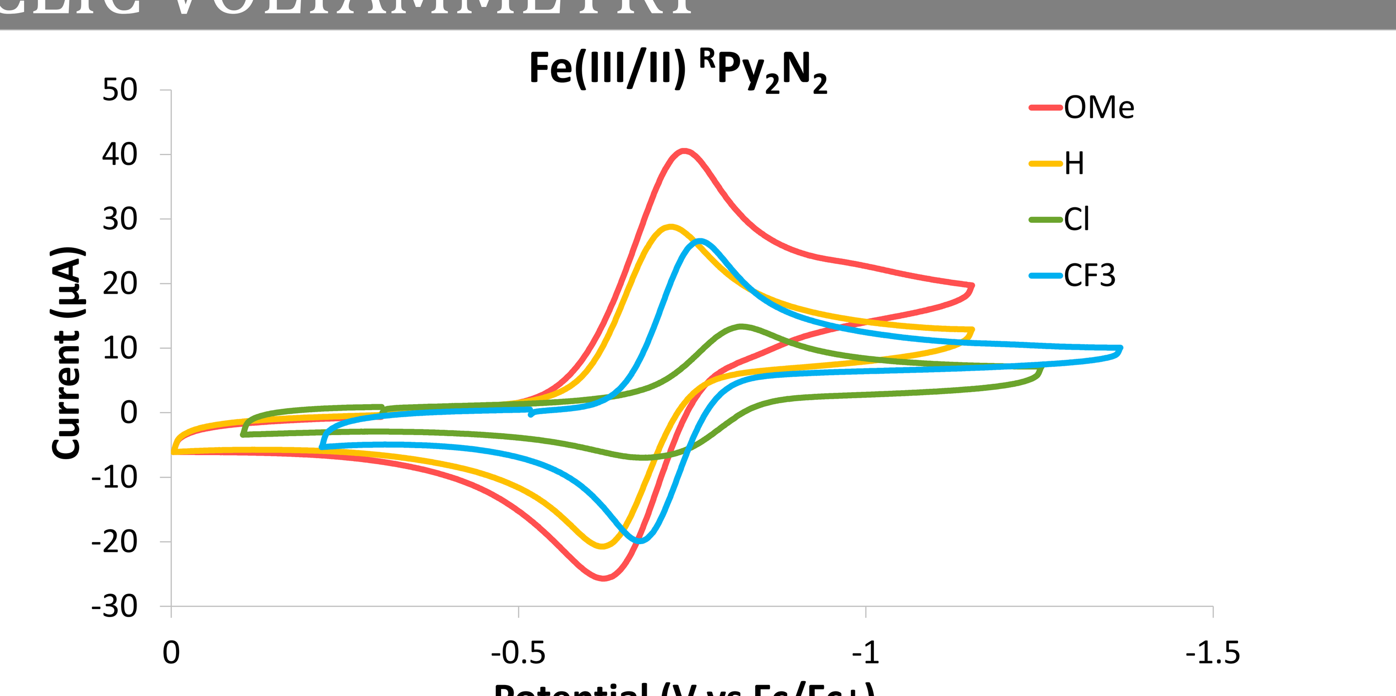
I = 0.15 M NaCl, T = 298 K



	$^{OMe}Py_2N_2$	$^{H}Py_2N_2$	$^{Cl}Py_2N_2$	$^{CF3}Py_2N_2$
Fe(III)	15.11	14.61	18.23	14.82
Fe(II)	11.05(3)	10.71(4)	12.97(9)	10.12(2)

$$\Delta E^{o\prime} = E^{o\prime}_{complex} - E^{o\prime}_{free} = -0.059 \log\left(\frac{\beta_{ox}}{\beta_{red}}\right)$$

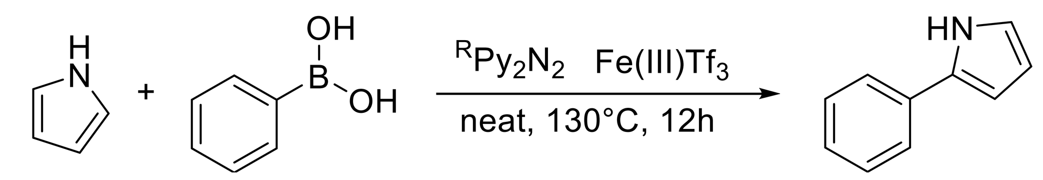
CYCLIC VOLTAMMETRY

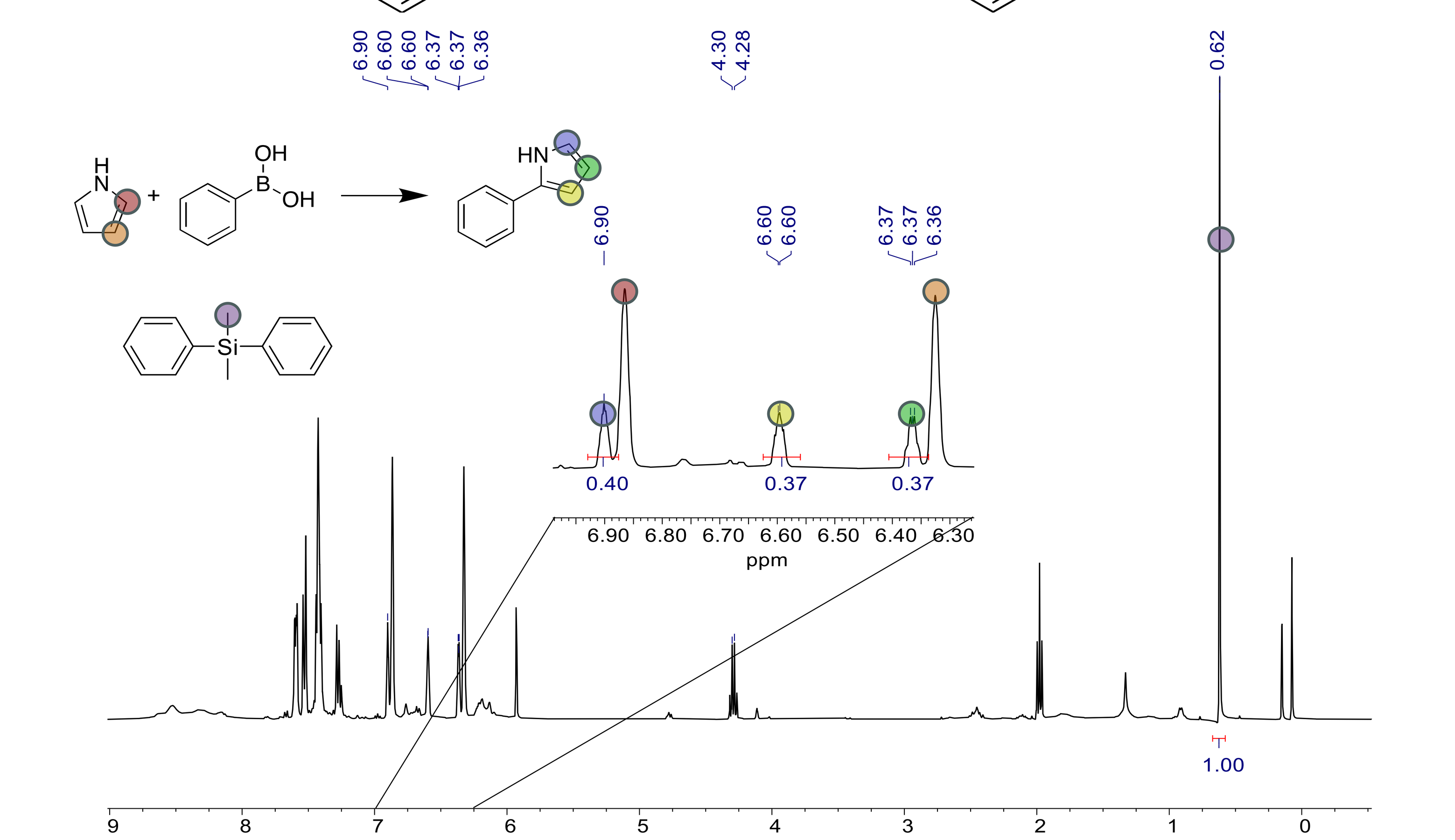


	E_{pc}	E_{pa}	$E_{1/2}$
Fe[$^{OMe}Py_2N_2$]	-736	-623	-854
Fe[$^{H}Py_2N_2$]	-720	-621	TBD
Fe[$^{Cl}Py_2N_2$]	-821	-678	TBD
Fe[$^{CF3}Py_2N_2$]	-760	-674	-733

	E_{pc}	E_{pa}	$E_{1/2}$
Fe[$^{OMe}PyN_3$]	-577	-461	-519
Fe[$^{H}PyN_3$]	-502	-404	-453
Fe[$^{Cl}PyN_3$]	-466	-365	-416
Fe[$^{CF3}PyN_3$]	-476	-377	-427

SUZUKI-MIYAURA C-C COUPLING

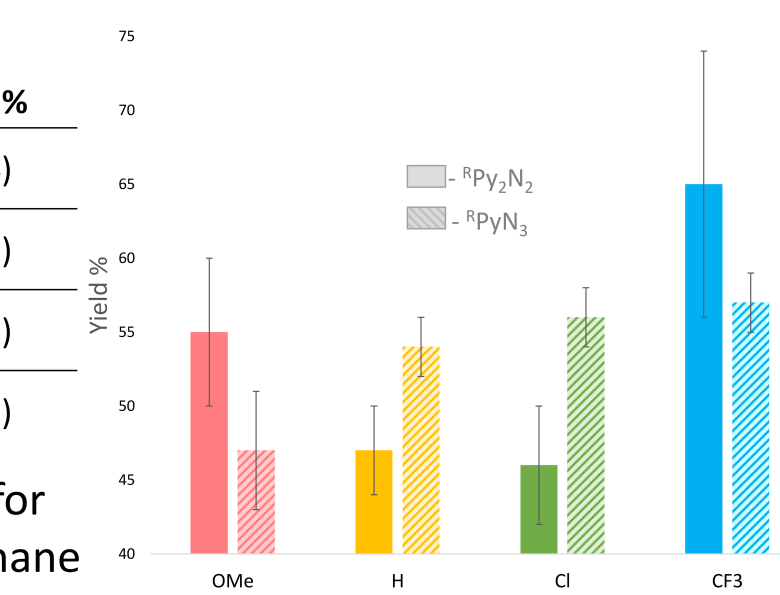




10 µL DMDPS	1 mL / 10^3 µL	0.985 g DMDPS / 1 mL DMDPS	1 mol DMDPS / 212.36 g DMDPS	6 mol H / 1 mol DMDPS	0.37 H / 1.00 H	1 mol prod / 1 H	143.19 g product / 1 mol product

Yield Comparison

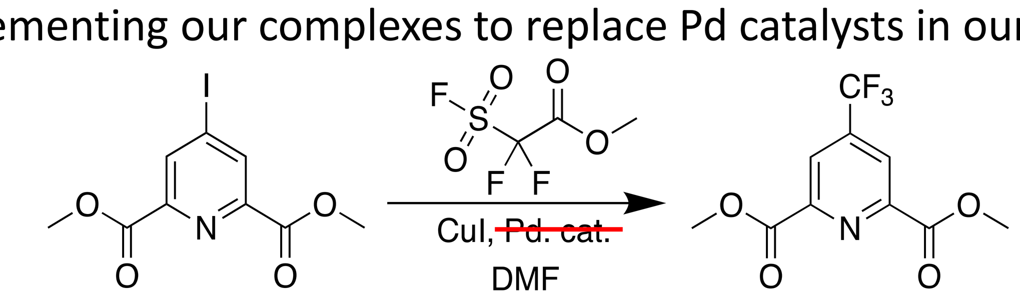
	Yield %		Yield %
Fe[$^{OMe}Py_2N_2$]	55(5)	Fe[$^{OMe}PyN_3$]	47(4)
Fe[$^{H}Py_2N_2$]	47(3)	Fe[$^{H}PyN_3$]	54(2)
Fe[$^{Cl}Py_2N_2$]	46(4)	Fe[$^{Cl}PyN_3$]	56(2)
Fe[$^{CF3}Py_2N_2$]	65(9)	Fe[$^{CF3}PyN_3$]	57(2)



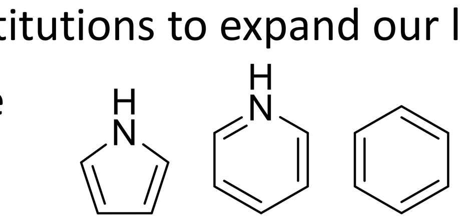
4-position substitution offers a handle for modulation of electronics of pyridinophane ligand, and the iron complex

ON GOING WORK

- Stop-flow experiments to determine rate limiting step
- Implementing our complexes to replace Pd catalysts in our own synthesis



- Introduction of more EDG substitutions to expand our library
- Pyrrole vs. Pyridine vs. Benzene



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