Supporting Information

Structural, Electronic and Catalytic Modulation of Chelating Pyridylideneamide Ruthenium(II) Complexes

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1. Transfer Hydrogenation of Complex 3a–e

Table S1. Transfer hydrogenation of benzophenone with Ru-PYA iridium complexes **3a–e.**[a]

entry	time/h	conversion /% [b]				
		3a	**3b**	**3c**	**3d**	**3e**[c]
1	0.5	15	9	5	12	9
2	1	40	13	11	22	14
3	2	71	15	20	35	25
4	4	99	19	39	49	43
5	6	n.d.[d]	24	55	56	n.d.
6	8	n.d.	30	67	61	65
7	24	n.d.	45	96	97	88

[a] General conditions: benzophenone (1.0 mmol), KOH (50 μL, 2M in H_2O, 0.1 mmol), hexamethylbenzene (0.16 mmol), ruthenium complex (0.01 mmol), ^{i}PrOH (5 mL), reflux temperature. [b] determined by ^{1}H NMR spectroscopy (error ±3%) with hexamethylbenzene as internal standard; n.d. = not determined. [c] data from reference S1. [d] not determined.

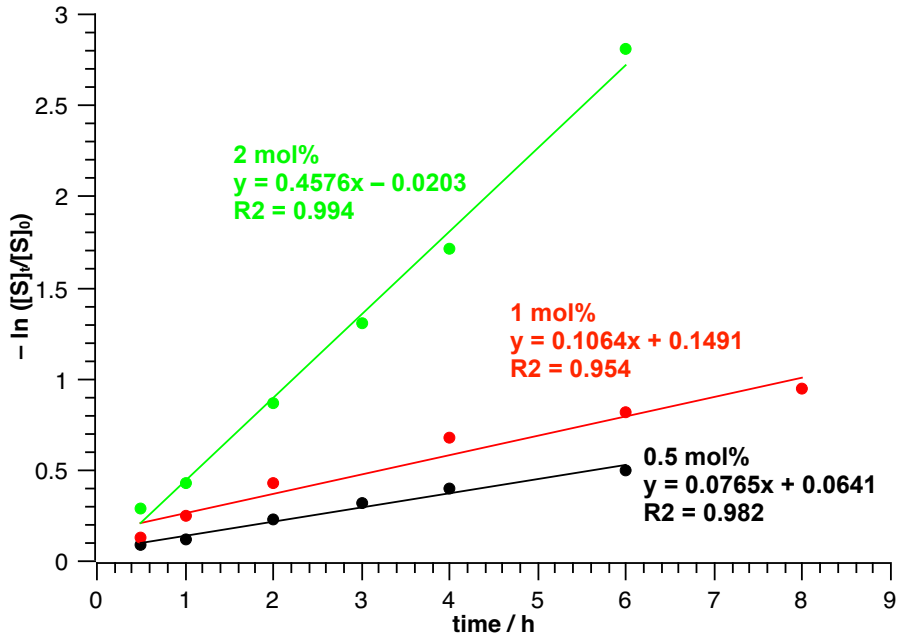

Figure S1. First-order fit of transfer hydrogenation with different concentrations of complex **3d** (2 mol% green; 1 mol% red; 0.5 mol% black; [S] = substrate concentration).

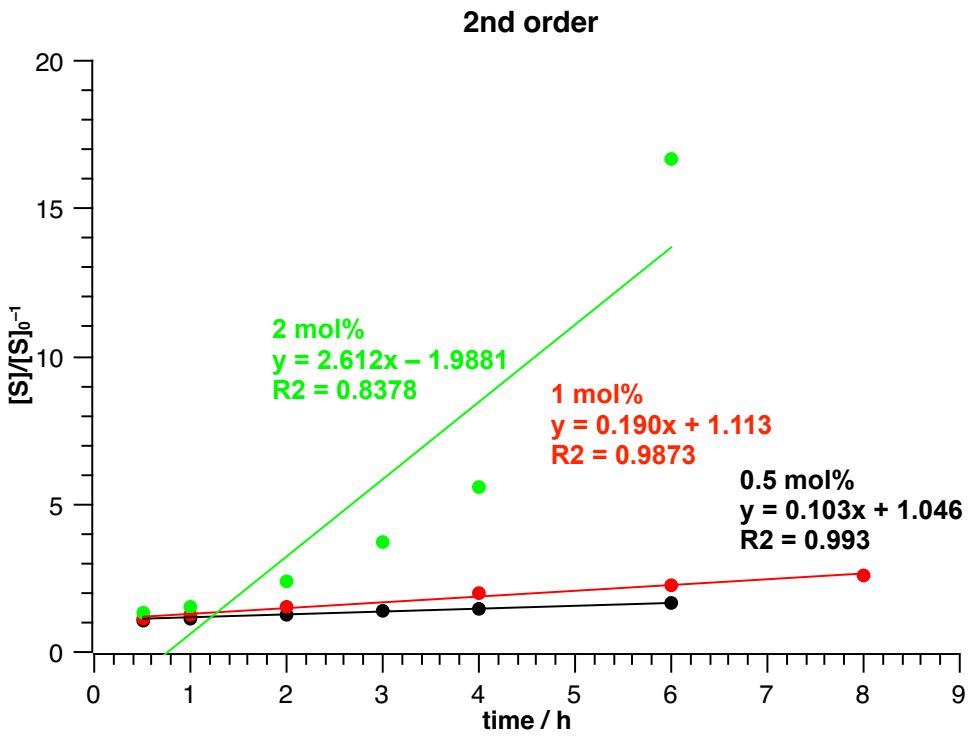

Figure S2. Second-order fit of transfer hydrogenation with different concentrations of complex **3d** (2 mol% green; 1 mol% red; 0.5 mol% black; [S] = substrate concentration).

2. Crystal structure determinations

Table S2. Selected bond lengths (Å) and dihedral angles (°) pertaining to the PYA ligands environment of the Ru-PYA complexes **3a–e**.[a]

	3a	**3b**	**3c**	**3d**[a]	**3e**[b]
Cα–Cβ	1.366(4)	1.366(3)	1.368(4)	1.370(4)	1.3669(18)
	1.365(4)	1.372(3)	1.373(4)	1.371(5)	1.3756(17)
				1.368(5)	
				1.375(5)	
Cβ–Cγ	1.411(4)	1.404(3)	1.411(4)	1.401(4)	1.4046(18)
	1.411(4)	1.410(3)	1.412(4)	1.409(4)	1.4057(16
				1.406(4)	
				1.404(5)	
N_{PYA}–Cγ	1.382(3)	1.389(2)	1.385(4)	1.391(4)	1.3900(15)
				1.388(4)	
O–C–N–Ru	177.237	178.504	177.906	171.642	176.194
				–169.940	
Ru–N–Cγ–Cβ	–30.710	40.236	–32.961	148.226	41.331
	146.877	–142.799	143.963	–30.622	–137.336
				51.079	
				–126.265	
C–N–Cγ–Cβ	–29.292	39.548	–35.865	41.003	39.380
	152.484	–137.416	147.211	–141.654	–141.954
				–23.023	
				158.129	

[a] Data from reference S2;[b] Data from data from reference S1.

Table S3. Crystal data and structure refinement for compound **3a**.

CCDC No.	1989987	
Empirical formula	$C_{23}H_{27}ClN_2O_2Ru$	
Formula weight	499.98	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 16.0919(3) Å	α= 90°
	b = 11.5737(2) Å	β = 107.795(2)°.
	c = 12.0498(3) Å	γ= 90°
Volume	2136.82(8) $Å^3$	
Z	4	
Density (calculated)	1.554Mg/m^3	
Absorption coefficient	0.880mm^{-1}	
F(000)	1024	
Crystal size	0.275 x 0.2207 x 0.1383 mm^3	
Theta range for data collection	2.205 to 28.116°.	
Index ranges	–21<=h<=21, –15<=k<=14, –15<=l<=15	
Reflections collected	18220	
Independent reflections	4797 [R(int) = 0.0272]	
Completeness to theta = 25.000°	100.0 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.902 and 0.824	
Refinement method	Full–matrix least–squares on F^2	
Data / restraints / parameters	4797 / 6 / 285	
Goodness–of–fit on F^2	1.094	
Final R indices [I>2sigma(I)]	R1 = 0.0322, wR2 = 0.0817	
R indices (all data)	R1 = 0.0392, wR2 = 0.0867	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.324 and -0.601 e.$Å^{-3}$	

Table S4. Crystal data and structure refinement for compound **3b**.

CCDC No.	1989988	
Empirical formula	$C_{24}H_{26}Cl_4F_3N_3O_4RuS$	
Formula weight	752.41	
Temperature	123(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 2/c	
Unit cell dimensions	a = 27.8894(6) Å	α= 90°
	b = 11.15180(10) Å	β = 122.960(2)°
	c = 22.0852(5) Å	γ= 90°
Volume	5763.3(2) $Å^3$	
Z	8	
Density (calculated)	1.734 Mg/m^3	
Absorption coefficient	1.044 mm^{-1}	
F(000)	3024	
Crystal size	0.238 x 0.183 x 0.069 mm^3	
Theta range for data collection	1.74 to 28.185°	
Index ranges	–36<=h<=35, –14<=k<=14, –29<=l<=29	
Reflections collected	59980	
Independent reflections	6749 [R(int) = 0.0332]	
Completeness to theta = 25.242°	100 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1 and 0.90948	
Refinement method	Full–matrix least–squares on F^2	
Data / restraints / parameters	6749 / 114 / 402	
Goodness–of–fit on F^2	1.038	
Final R indices [I>2sigma(I)]	R1 = 0.0258, wR2 = 0.0589	
R indices (all data)	R1 = 0.0299, wR2 = 0.0611	
Largest diff. peak and hole	1.168 and -0.68 e.$Å^{-3}$	

Table S5. Crystal data and structure refinement for compound **3c**.

CCDC No.	1989989	
Empirical formula	$C_{25}H_{29}Cl_3F_3N_3O_4RuS$	
Formula weight	731.99	
Temperature	123(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 2/c	
Unit cell dimensions	a = 30.2627(14) Å	α = 90°.
	b = 10.8172(2) Å	β = 134.002(8)°.
	c = 24.6497(12) Å	γ = 90°.
Volume	5804.3(7) $Å^3$	
Z	8	
Density (calculated)	1.675 Mg/m^3	
Absorption coefficient	0.945 mm^{-1}	
F(000)	2960	
Crystal size	0.1393 x 0.0877 x 0.0519 mm^3	
Theta range for data collection	1.675 to 27.257°.	
Index ranges	–36<=h<=37, –13<=k<=13, –30<=l<=31	
Reflections collected	28334	
Independent reflections	5969 [R(int) = 0.0399]	
Completeness to theta = 25.000°	100.0 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.955 and 0.9	
Refinement method	Full–matrix least–squares on F^2	
Data / restraints / parameters	5969 / 0 / 366	
Goodness–of–fit on F^2	1.063	
Final R indices [I>2sigma(I)]	R1 = 0.0359, wR2 = 0.0819	
R indices (all data)	R1 = 0.0443, wR2 = 0.0860	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.539 and -0.934 e.$Å^{-3}$	

3. NMR spectra of all new compounds

In some NMR spectra residual solvents from synthetic or purification procedures are present. In all cases, such residual signals were assigned according literature: Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stolts, B. M.; Bercaw, J. E.; Goldberg, K. I.; Organometallics 2010, 29, 2176.

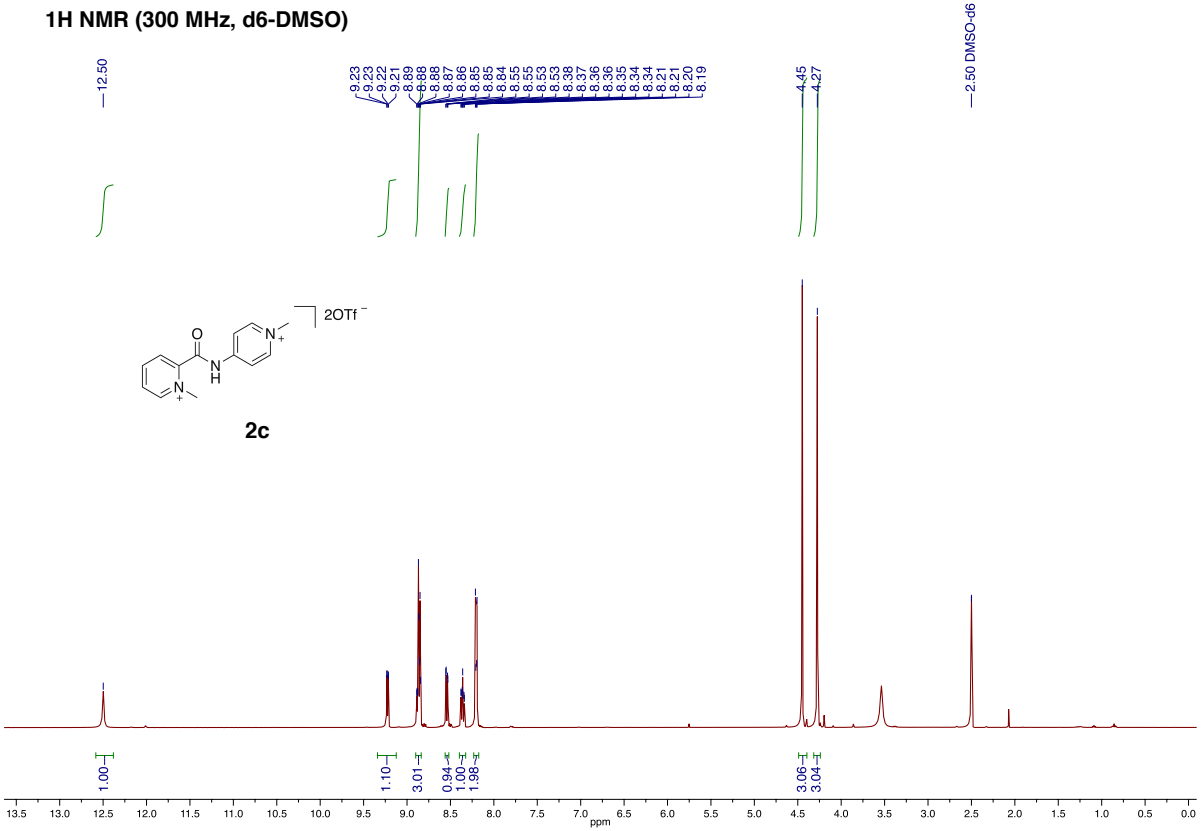

Figure S3. ^{1}H NMR spectrum of compound **2b**.

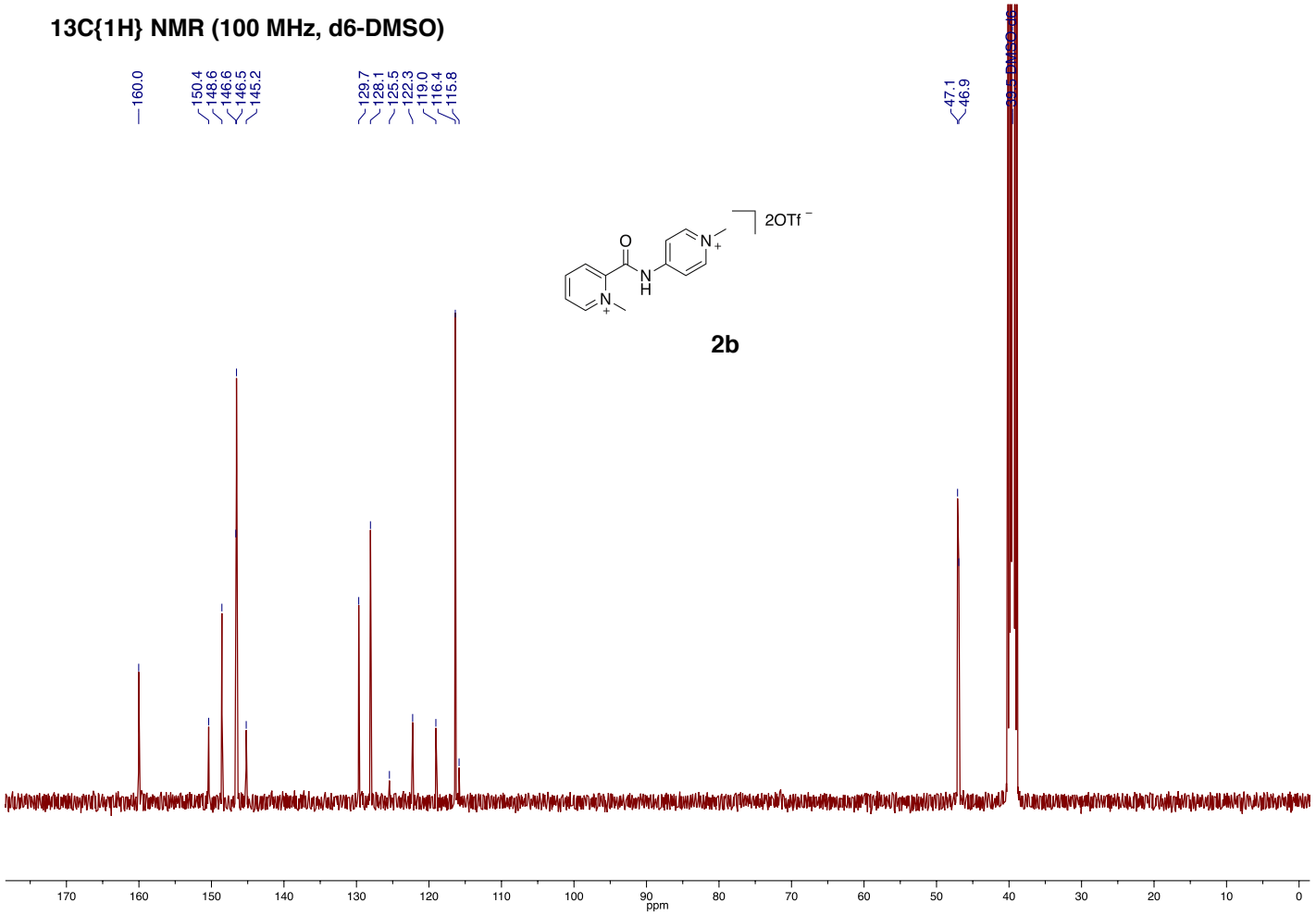

Figure S4. $^{13}C\{^{1}H\}$ NMR spectrum of compound **2b**.

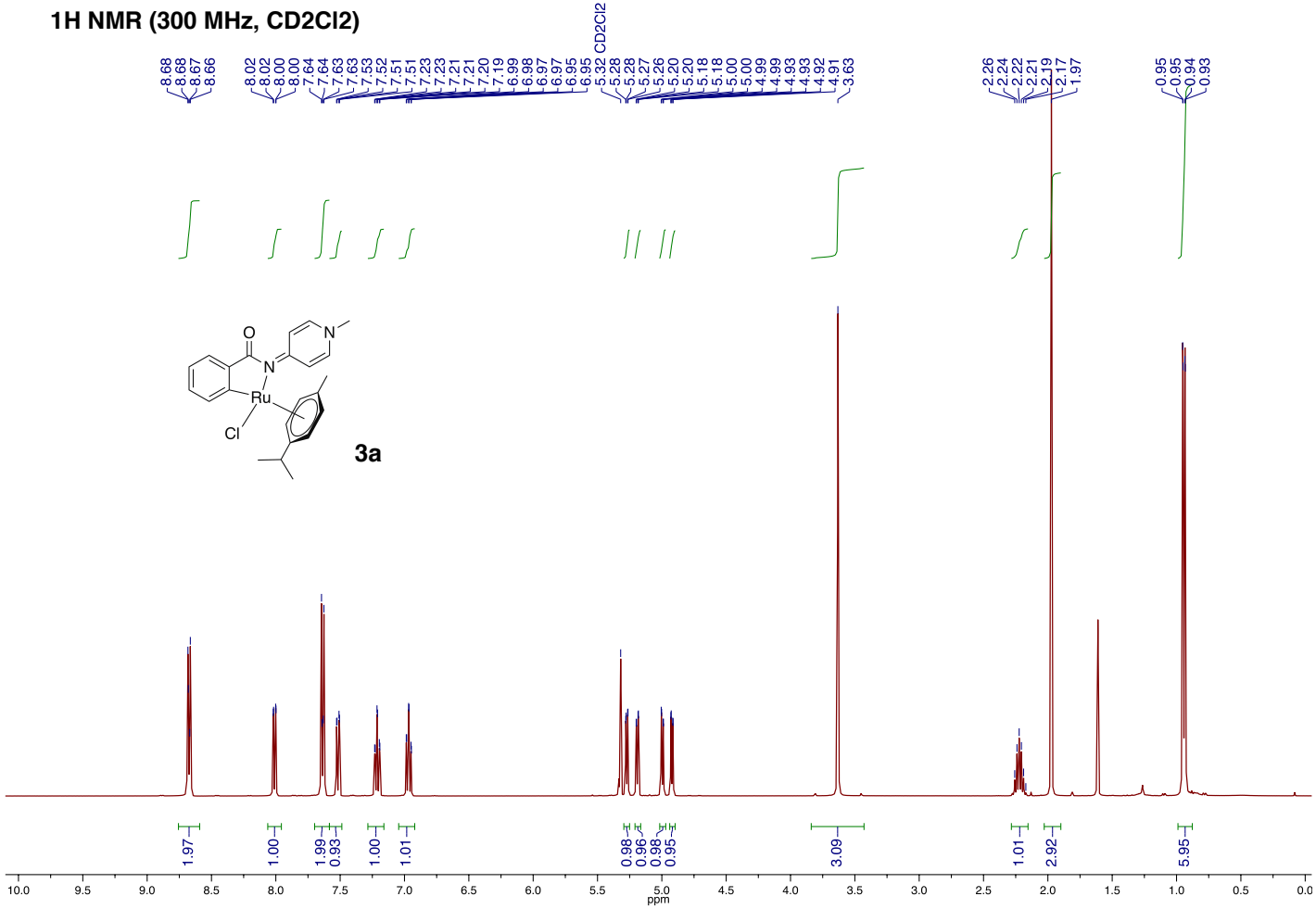

Figure S5. ^{1}H NMR spectrum of compound **3a**.

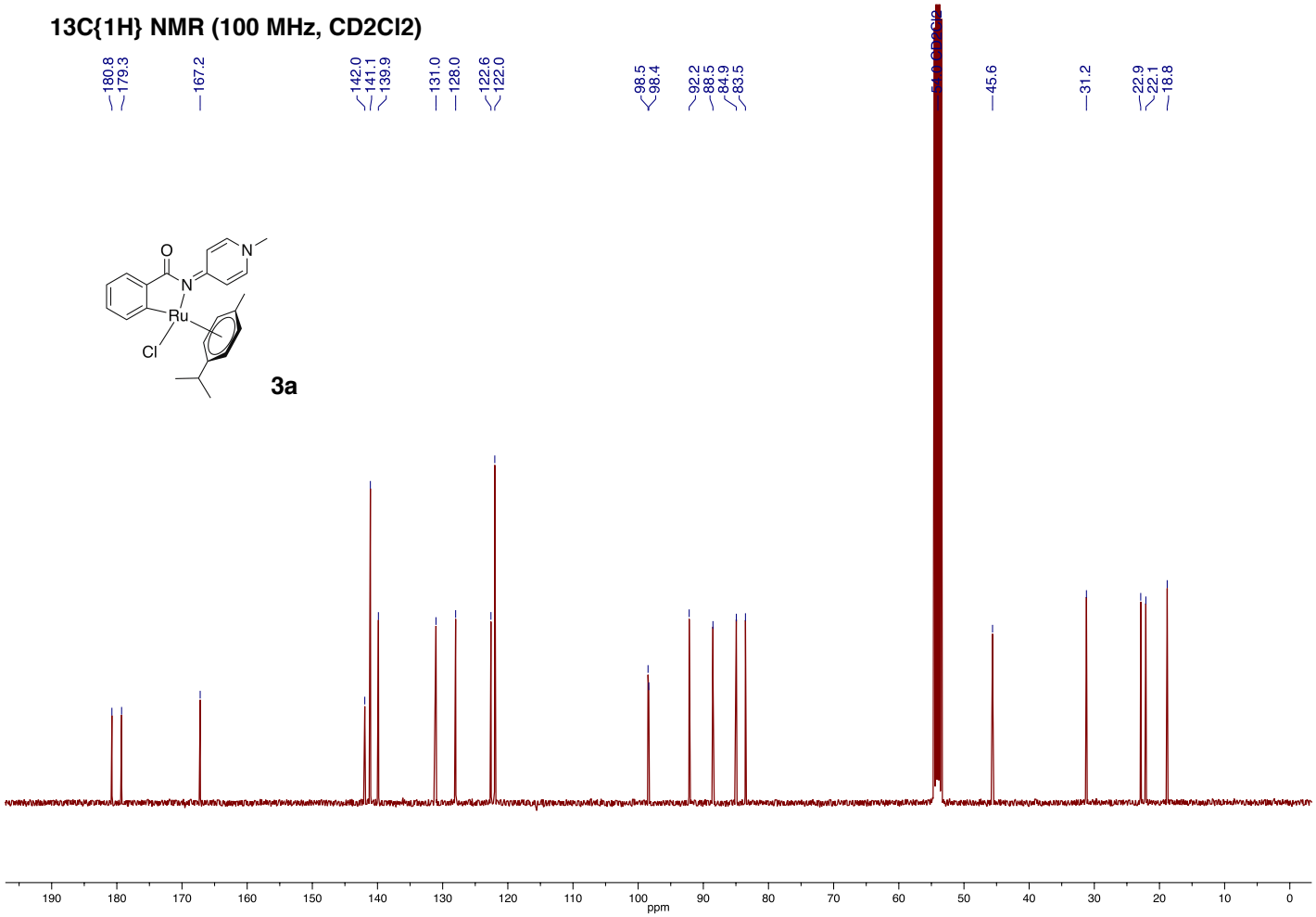

Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum of compound **3a**.

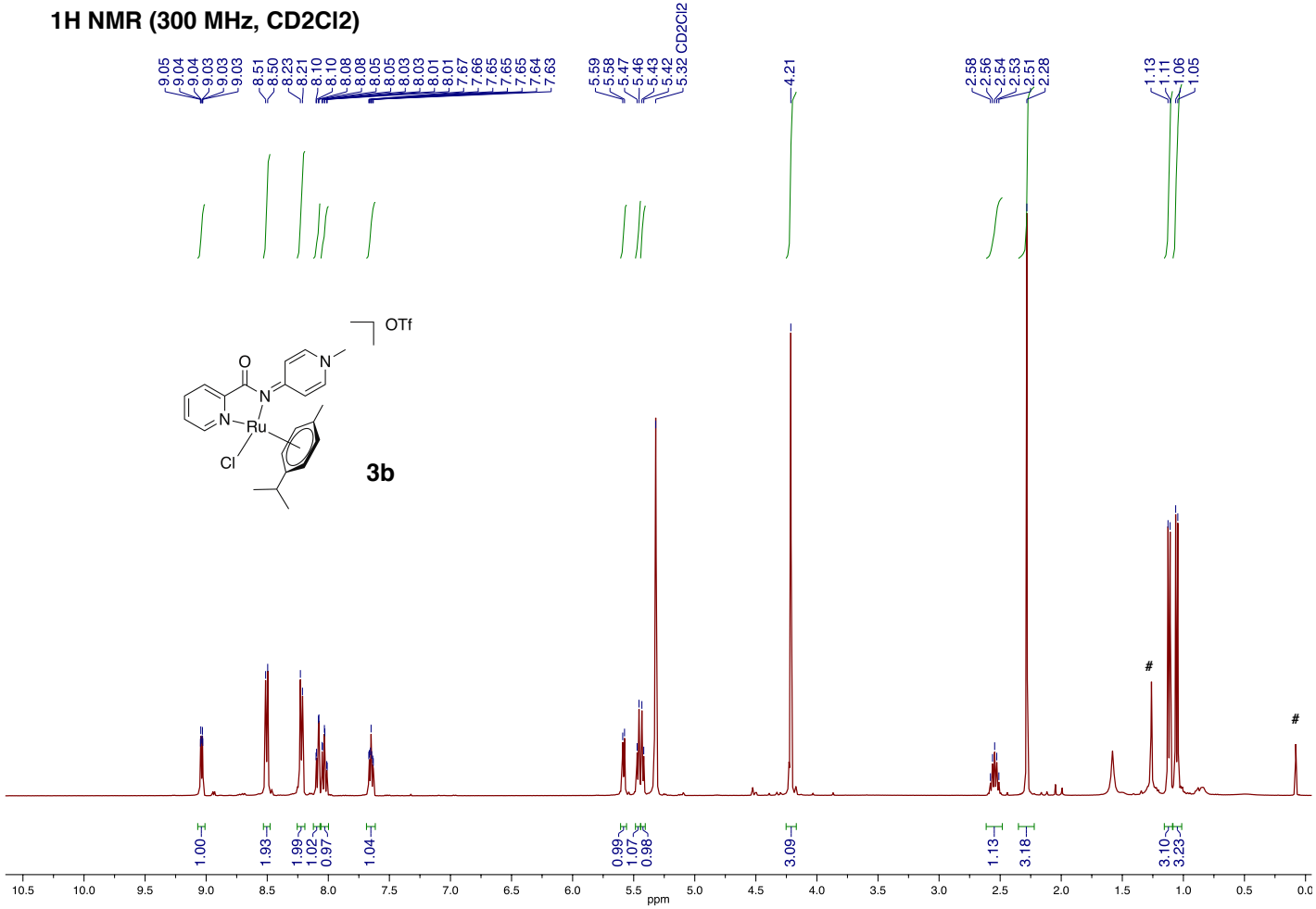

Figure S7. ^{1}H NMR spectrum of compound **3b**.

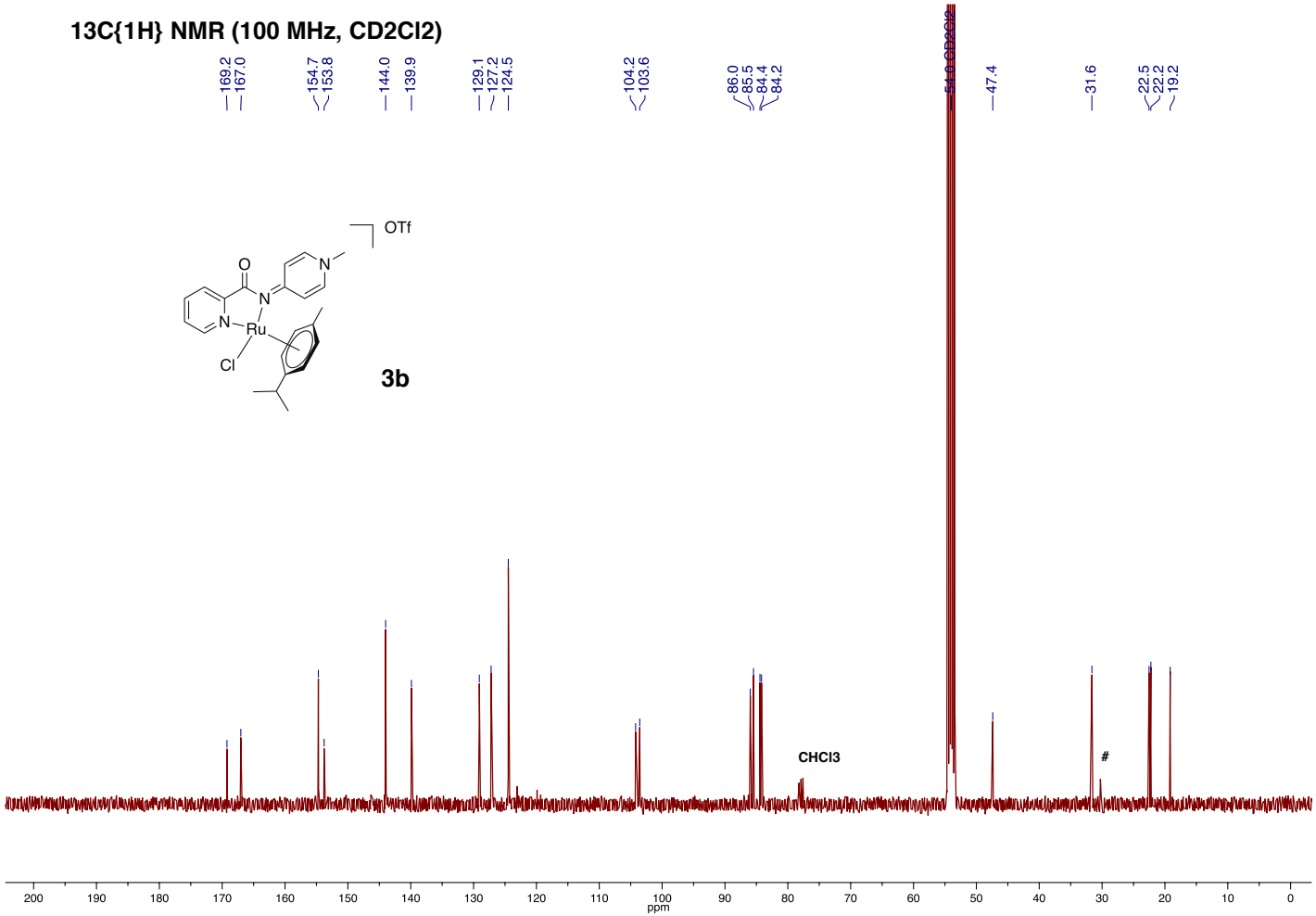

Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum of compound **3b**.

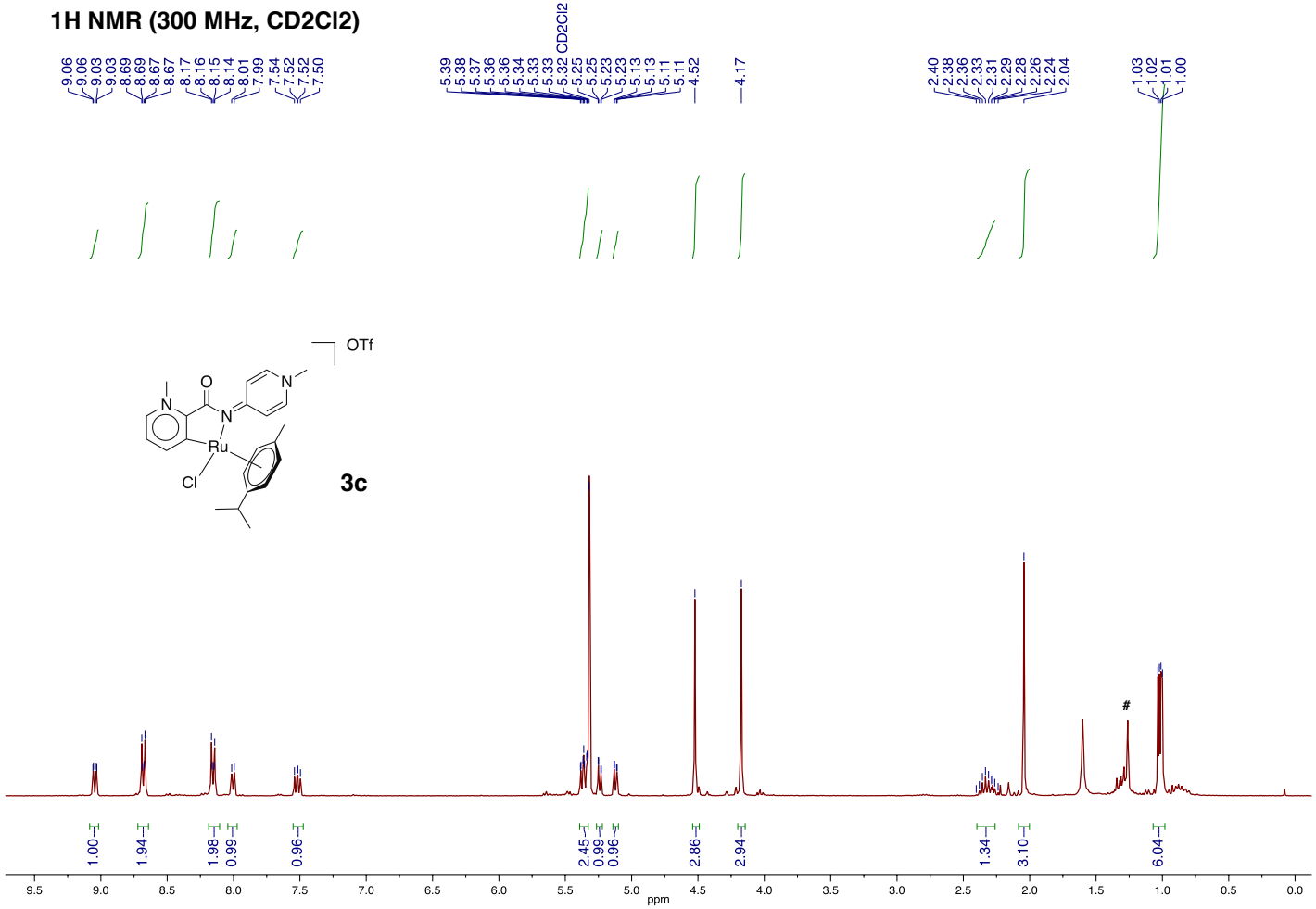

Figure S9. ^{1}H NMR spectrum of compound **3c**.

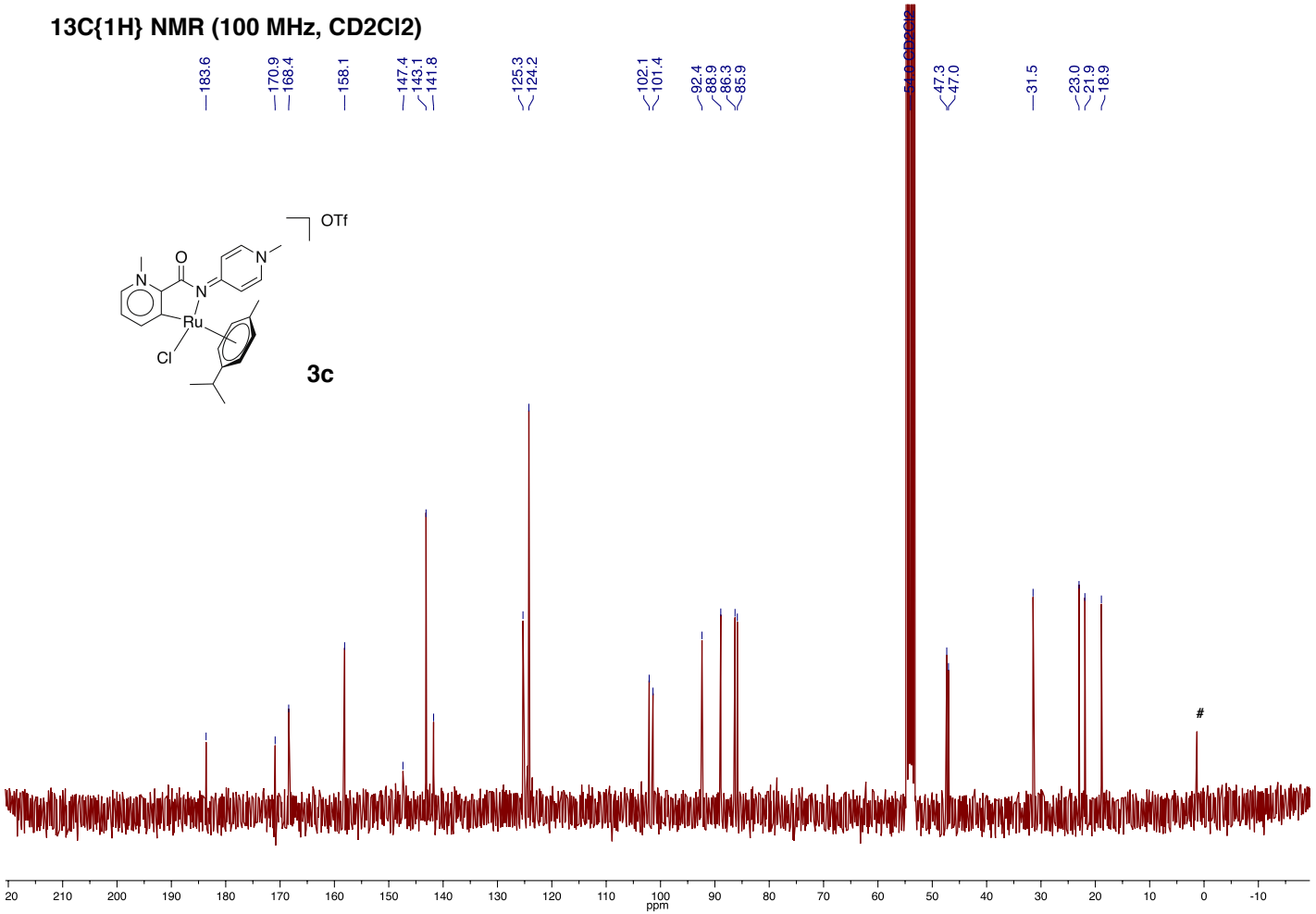

Figure S10. $^{13}C\{^{1}H\}$ NMR spectrum of compound **3c**.

4. CV plots

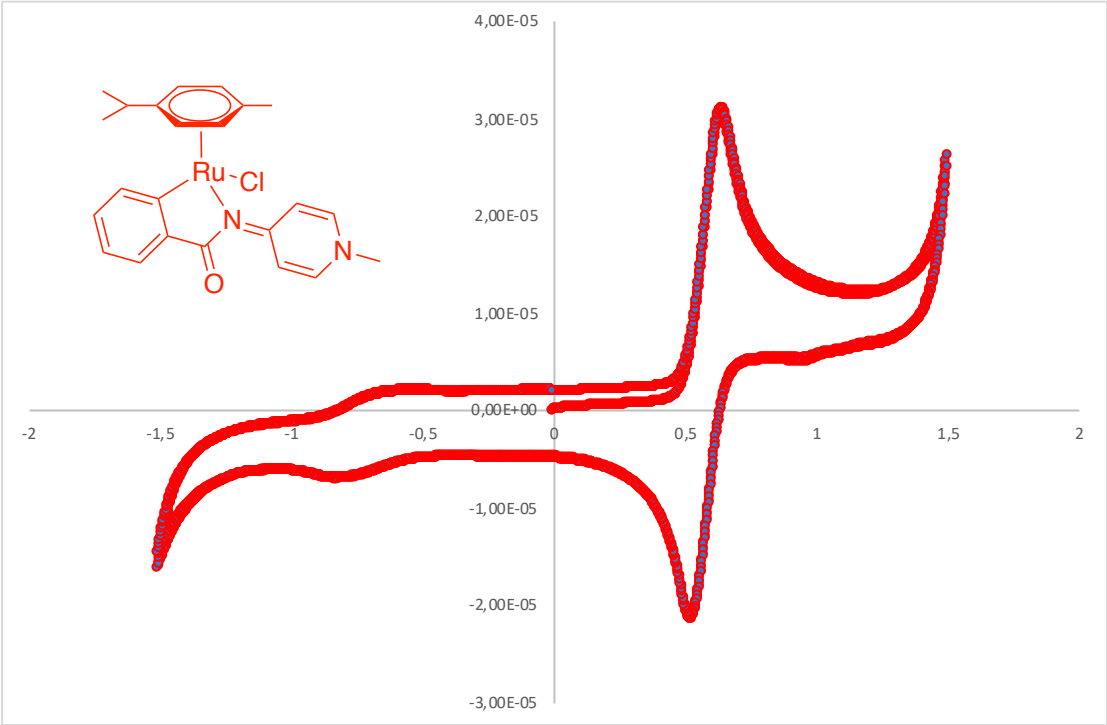

Figure S11. CV plot (potential *V vs* SCE) of Ru-PYA complexes **3a** in dry CH_2Cl_2.

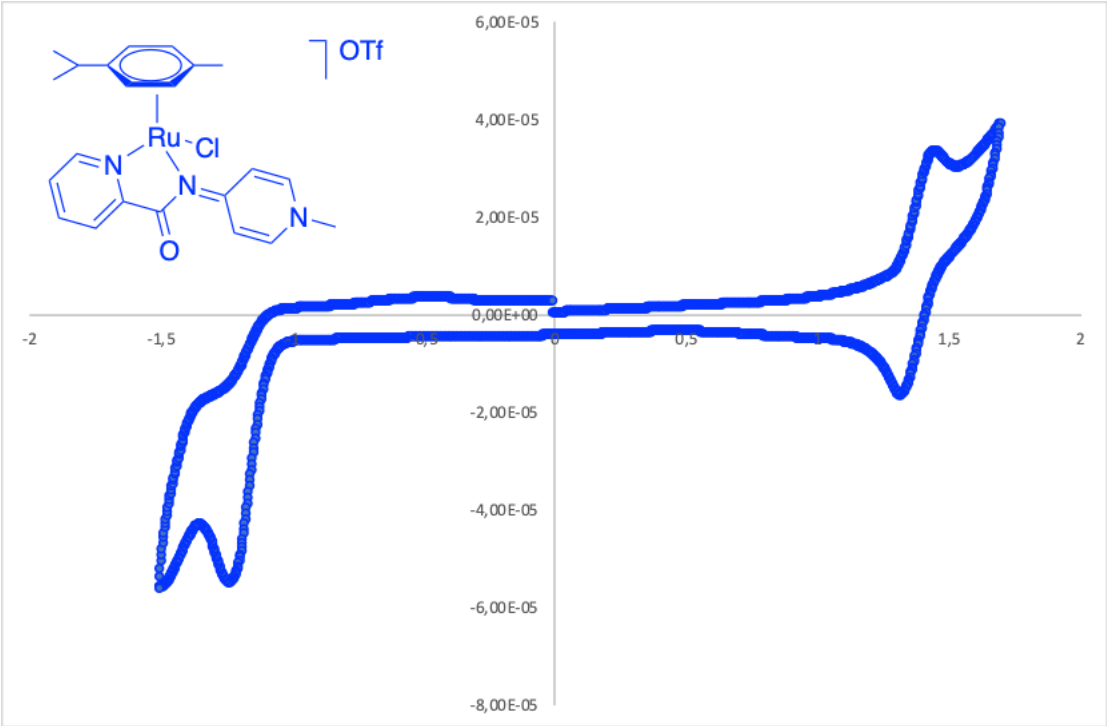

Figure S12. CV plot (potential *V vs* SCE) of Ru-PYA complexes **3b** in dry CH_2Cl_2.

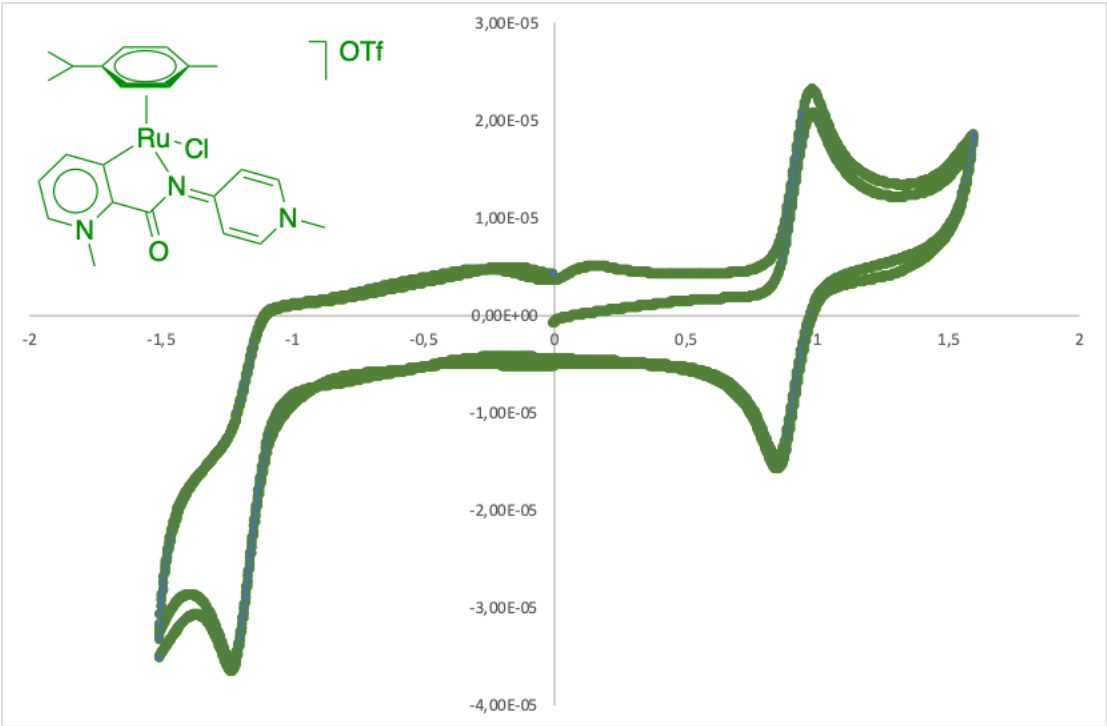

Figure S13. CV plot (potential *V vs* SCE) of Ru-PYA complexes **3c** in dry CH_2Cl_2.

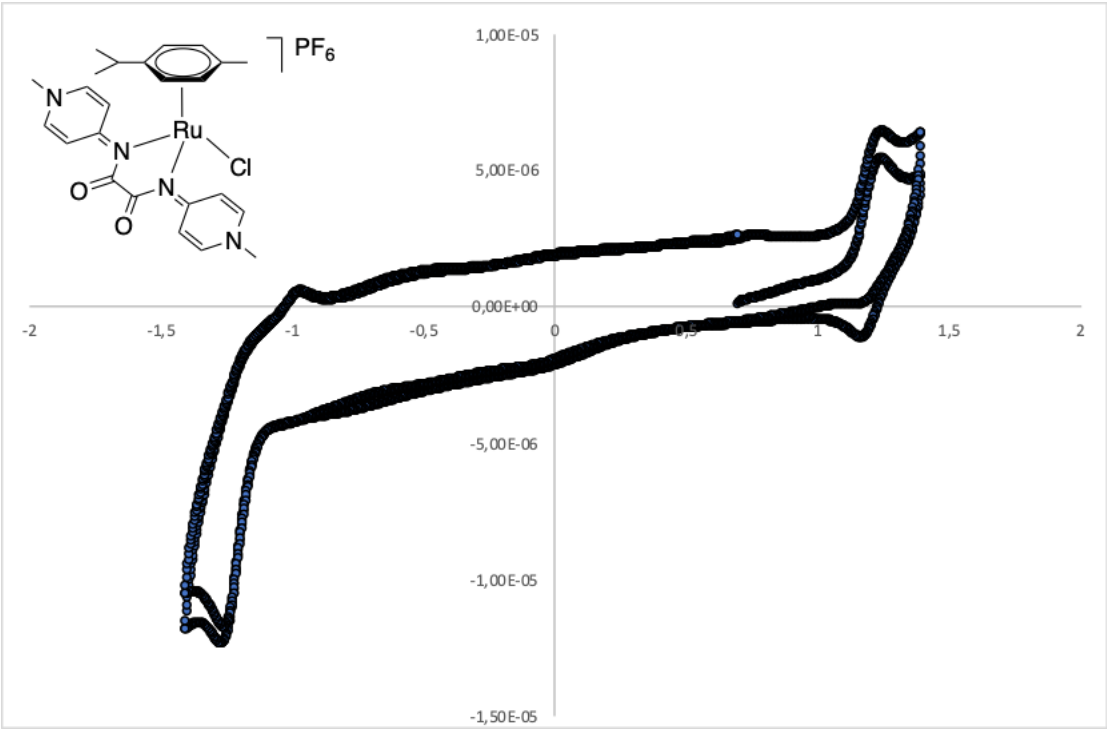

Figure S14. CV plot (potential *V vs* SCE) of Ru-PYA complexes **3d** in dry CH_2Cl_2.

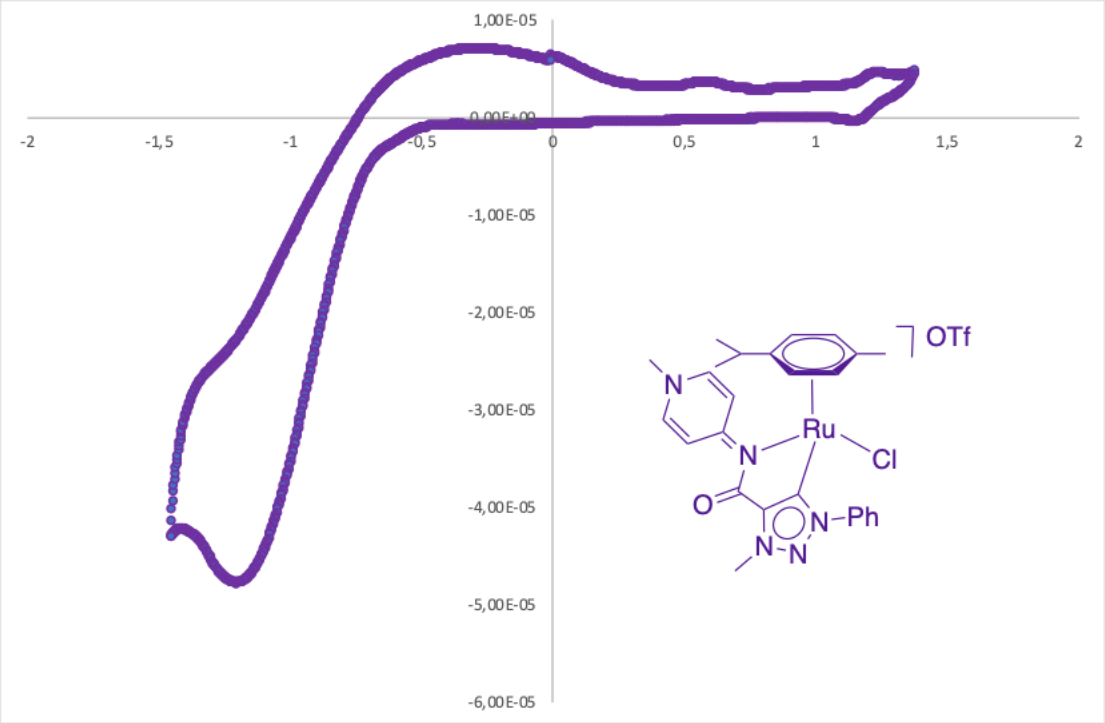

Figure S15. CV plot (potential *V vs* SCE) of Ru-PYA complexes **3e** in dry CH_2Cl_2.

5. References

[S1] Donnelly, K. F.; Segarra, C.; Shao, L-X.; Suen, Rachelle, Müller-Bunz, H.; Albrecht, M. *Organometallics* **2015**, *34*, 4076–4068.

[S2] Salzmann, K.; Segarra, C.; Albrecht, M. *Angew. Chem. Int. Ed.* **2020**, DOI: 10.1002/anie.202002014.