Synthesis, Characterisation, and Catalytic Evaluation of Ru-ONO Complexes featuring N-, and P-based ligands

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SUPPLEMENTARY INFORMATION

1. NMR spectra of complexes **C2**-**C10** (Figures S1-S20).
2. Mass spectra of complexes **C2**-**C10** (Figures S21-S29).
3. Crystallographic details of **C1**-**C10** (Tables S1-S5 and Figures S30 and S31).
4. Electrochemical details **C1**-**C10** (Table S6, Figures S32-S35)
5. Catalysis details (Table S7 and Figures S36-S37).

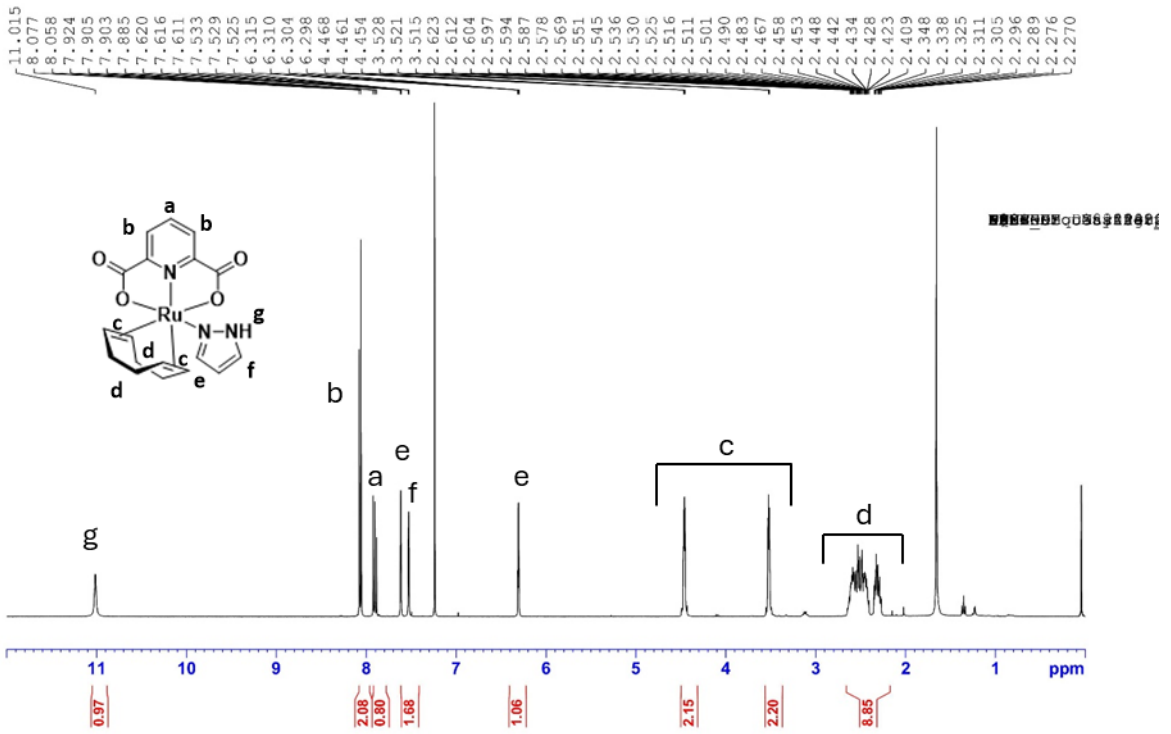


Figure S1 C2: ^{1}H NMR spectrum (300 MHz, $CDCl_3$).

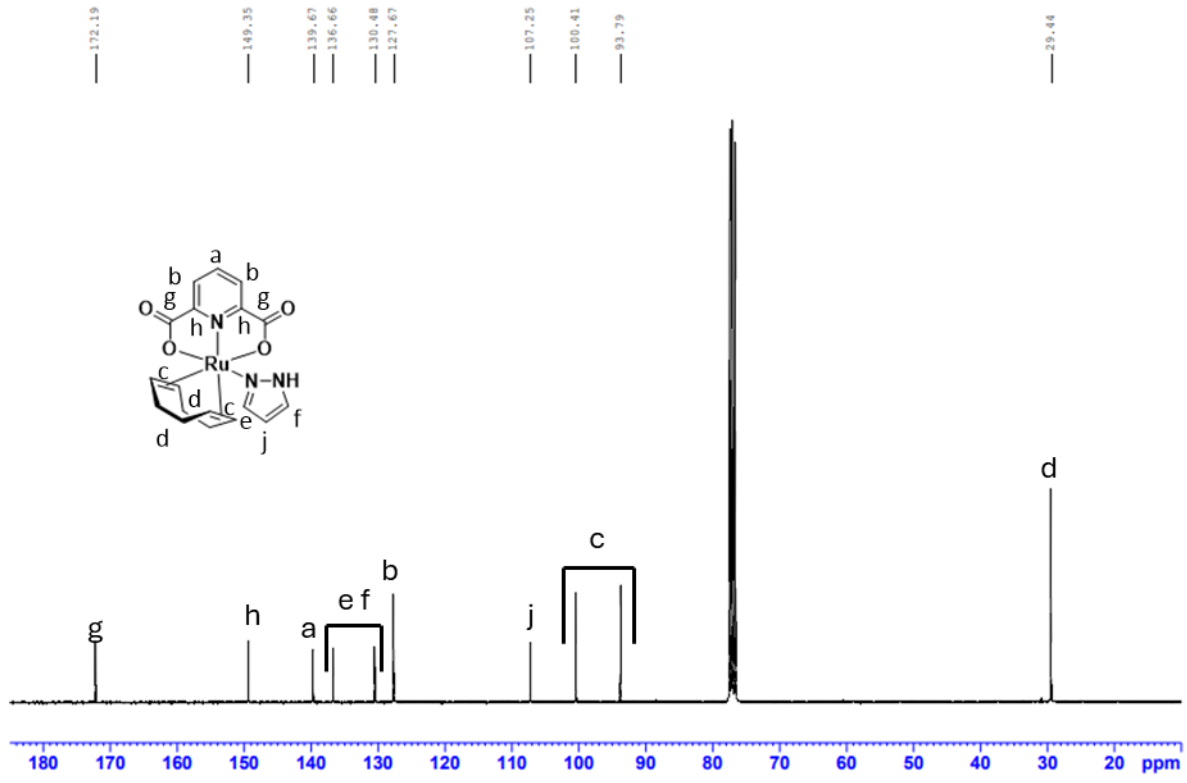


Figure S2 C2: ^{13}C NMR spectrum (75.4 MHz, $CDCl_3$).

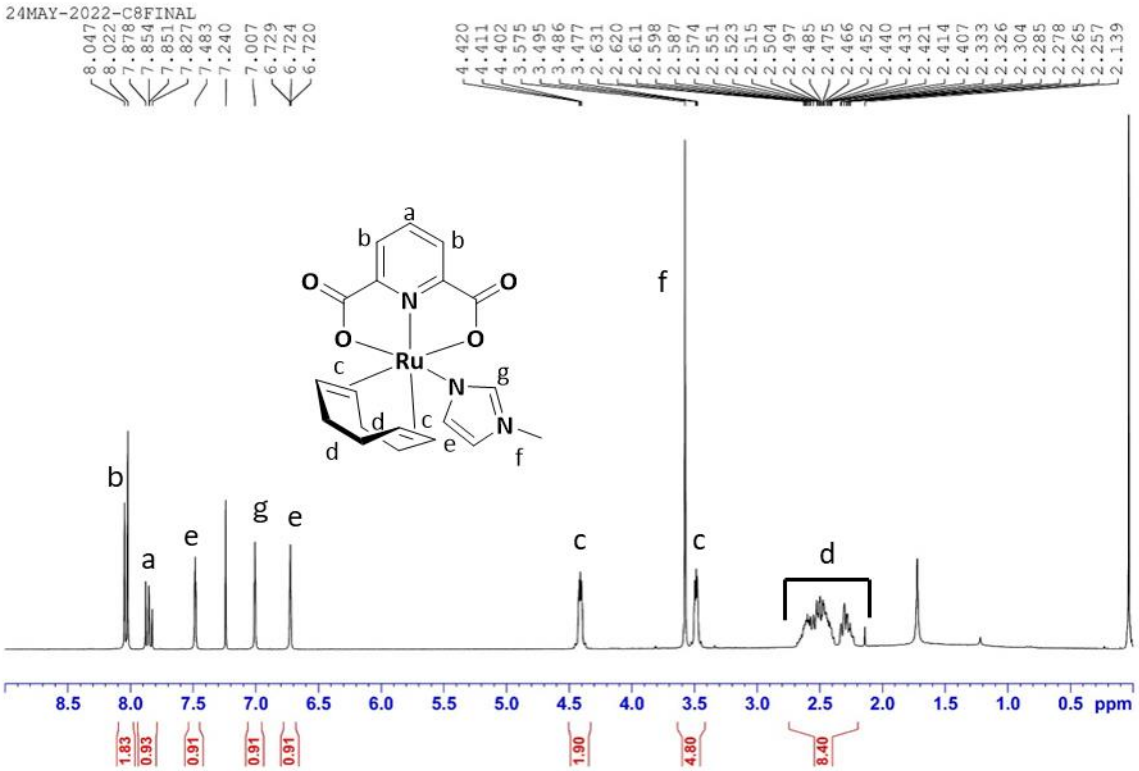


Figure S3 C3: ^{1}H NMR spectrum (300 MHz, $CDCl_3$).

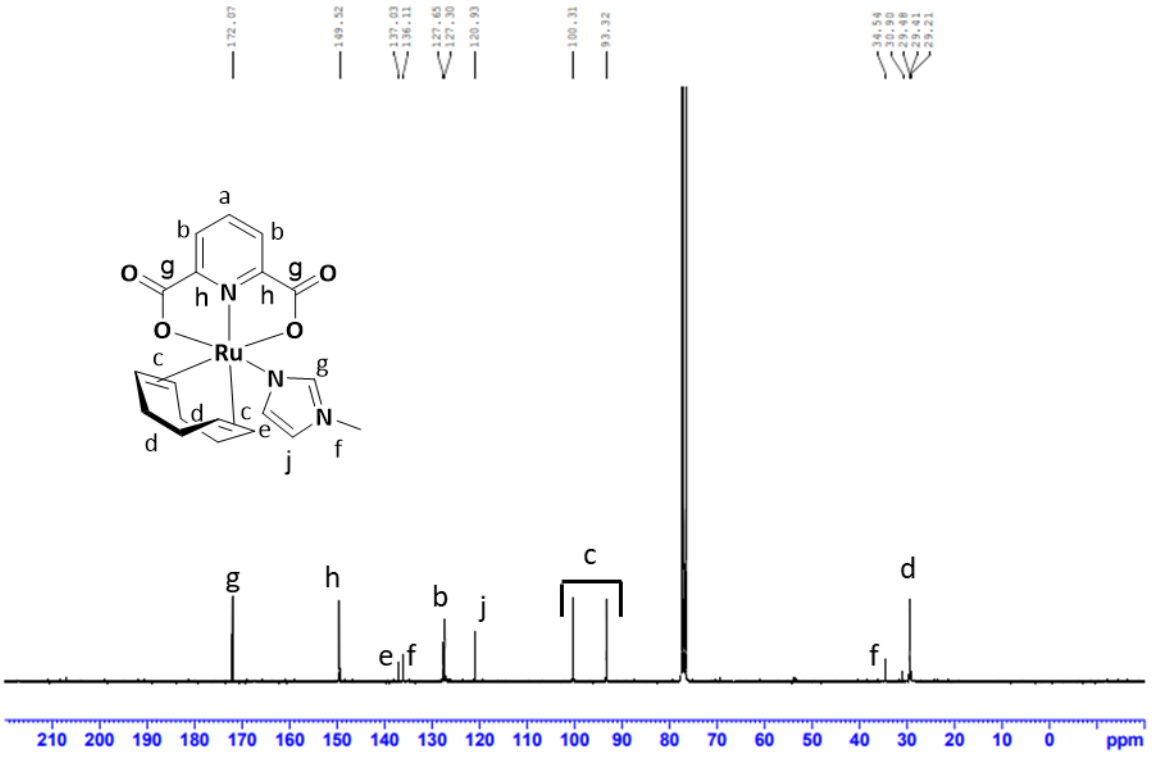


Figure S4 C3: ^{13}C NMR spectrum (75.4 MHz, $CDCl_3$).

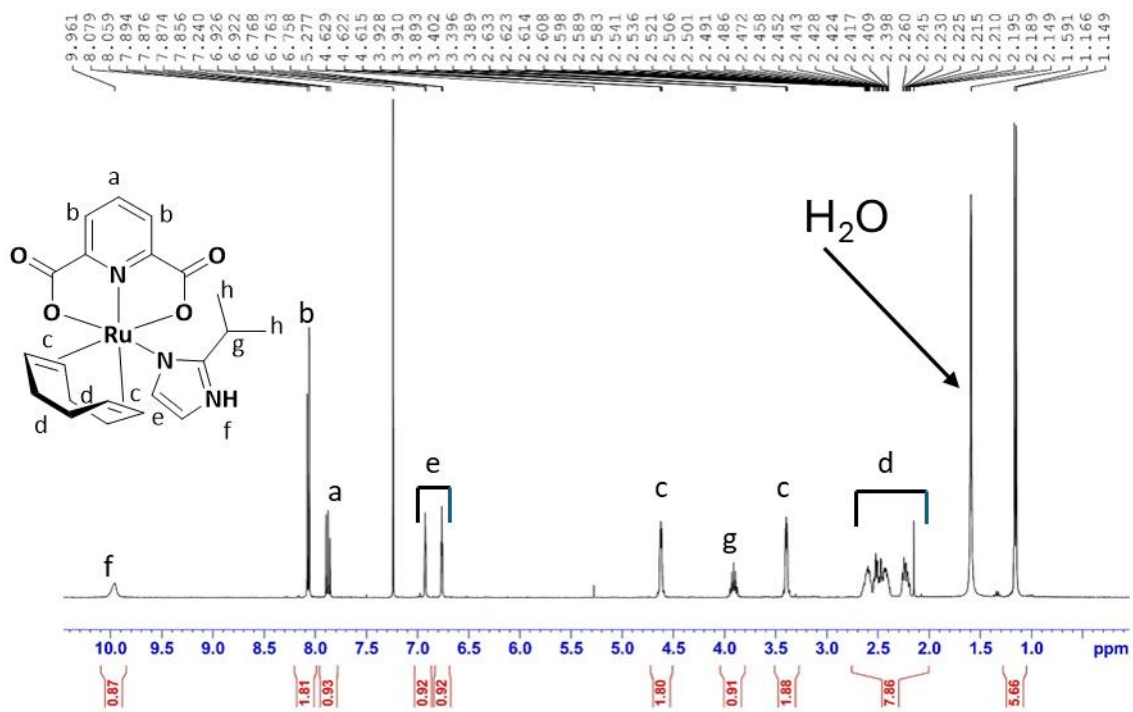


Figure S5 C4: ^{1}H NMR spectrum (400 MHz, $CDCl_3$).

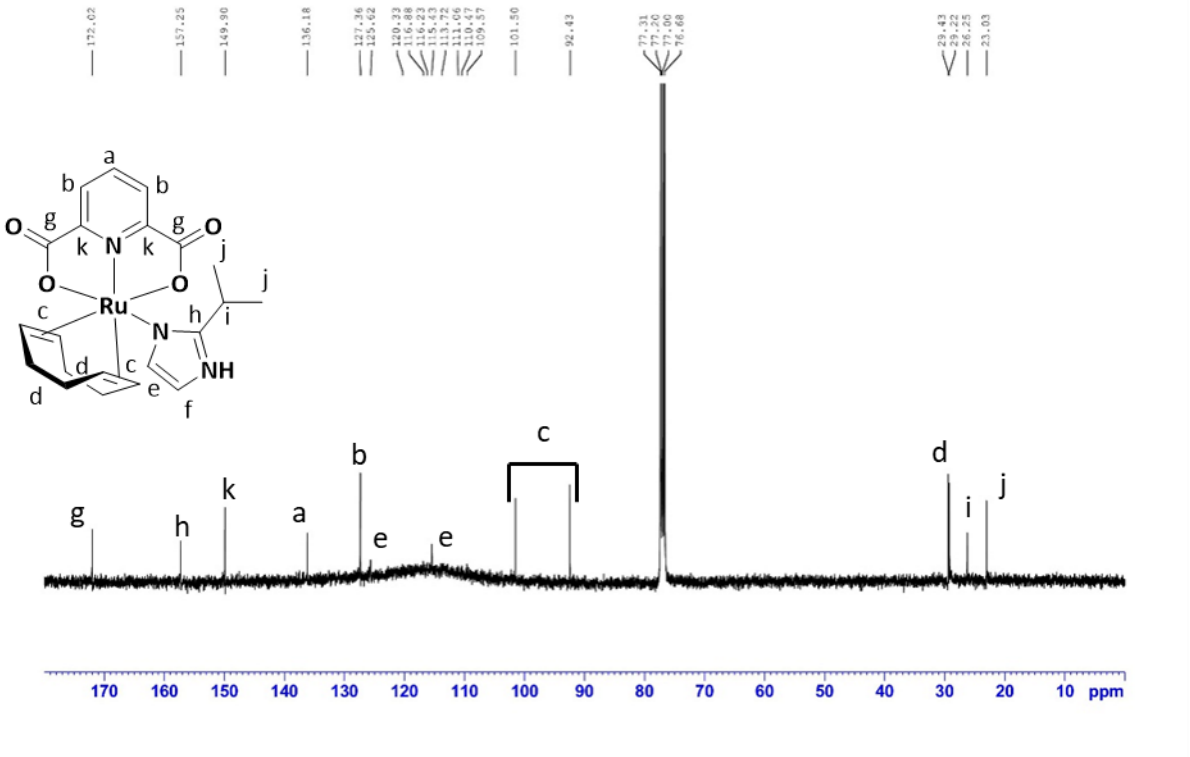


Figure S6 C4: ^{13}C NMR spectrum (100.6 MHz, $CDCl_3$).

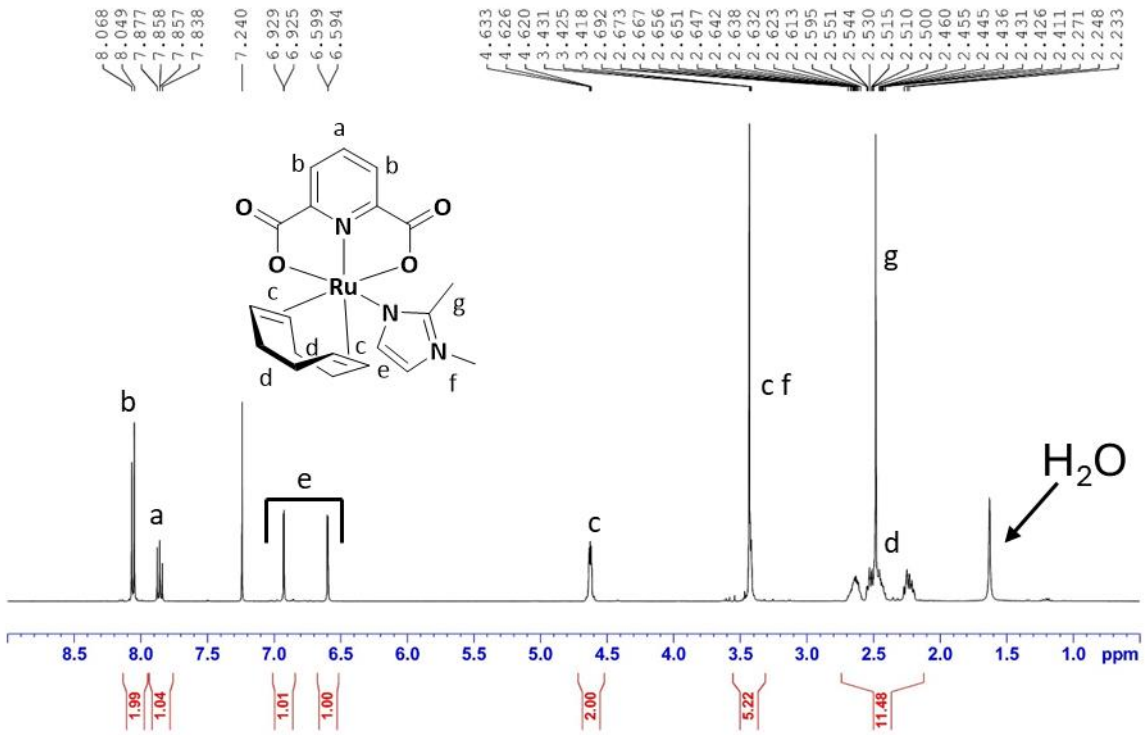


Figure S7 C5: ^{1}H NMR spectrum (400 MHz, $CDCl_3$).

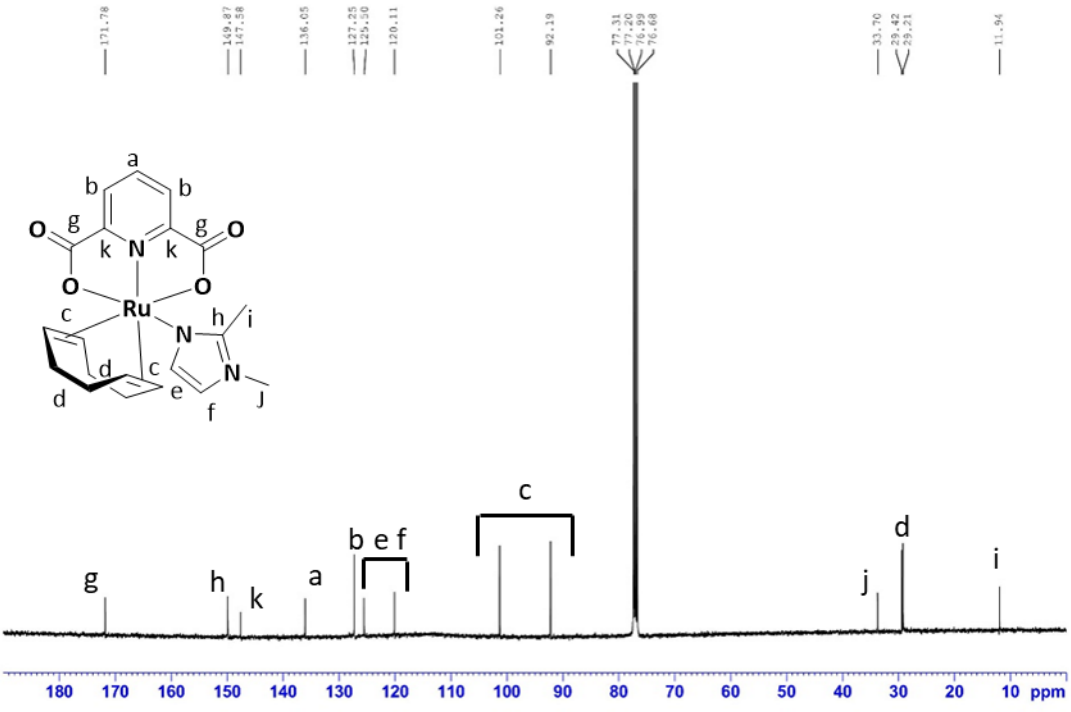


Figure S8 C5: ^{13}C NMR spectrum (100.6 MHz, $CDCl_3$).

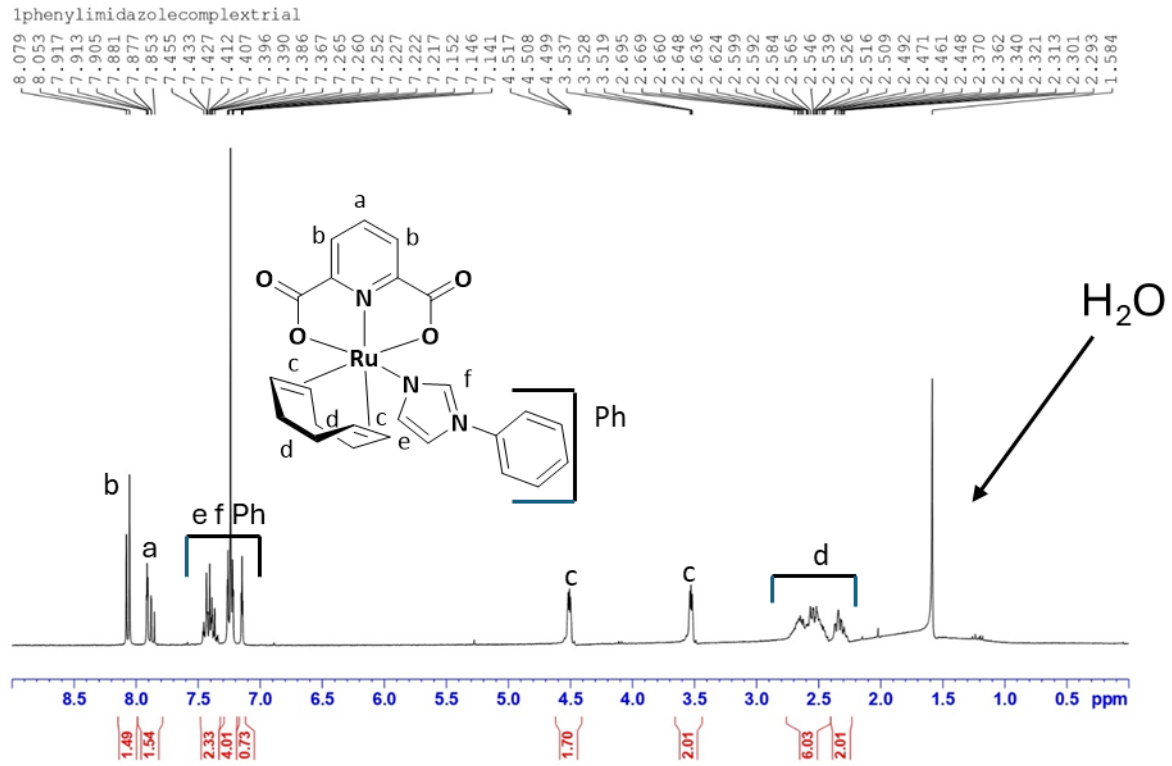


Figure S9 C6: ^{1}H NMR spectrum (300 MHz, $CDCl_3$).

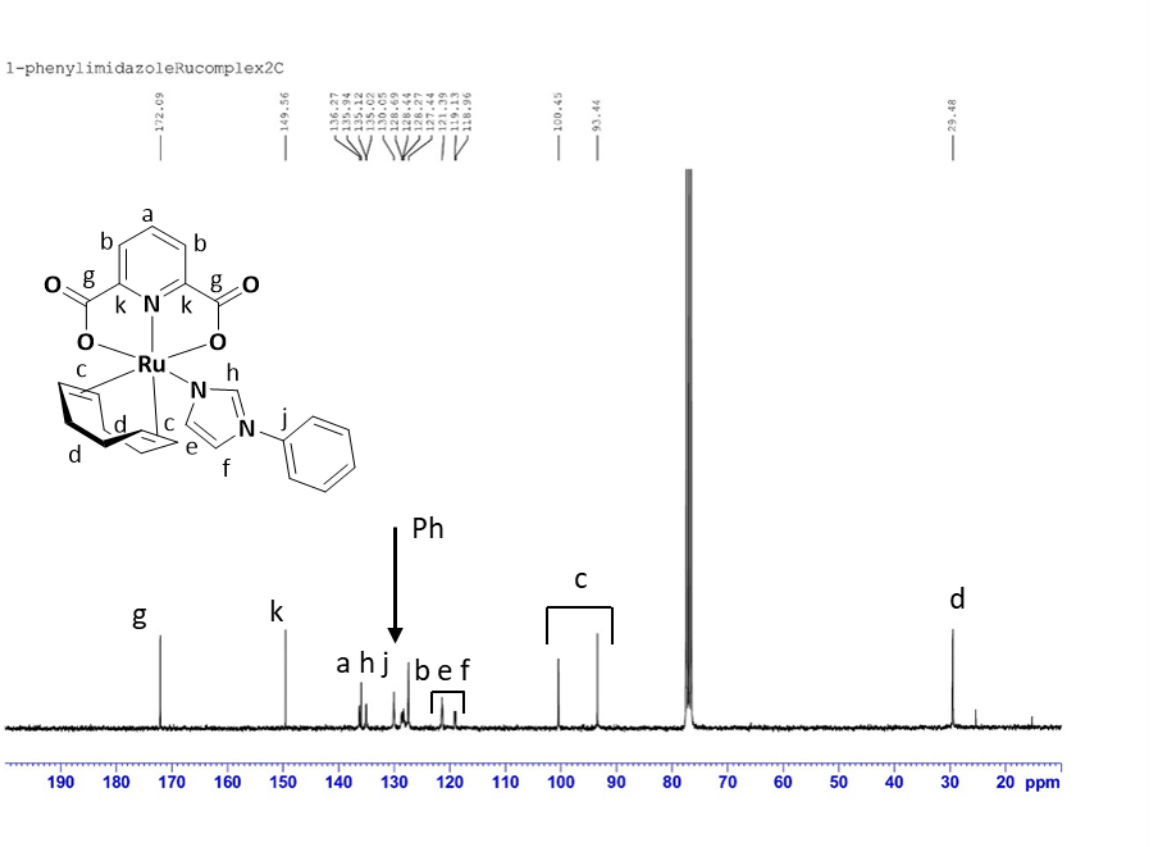


Figure S10 C6: ^{13}C NMR spectrum (75.4 MHz, $CDCl_3$).

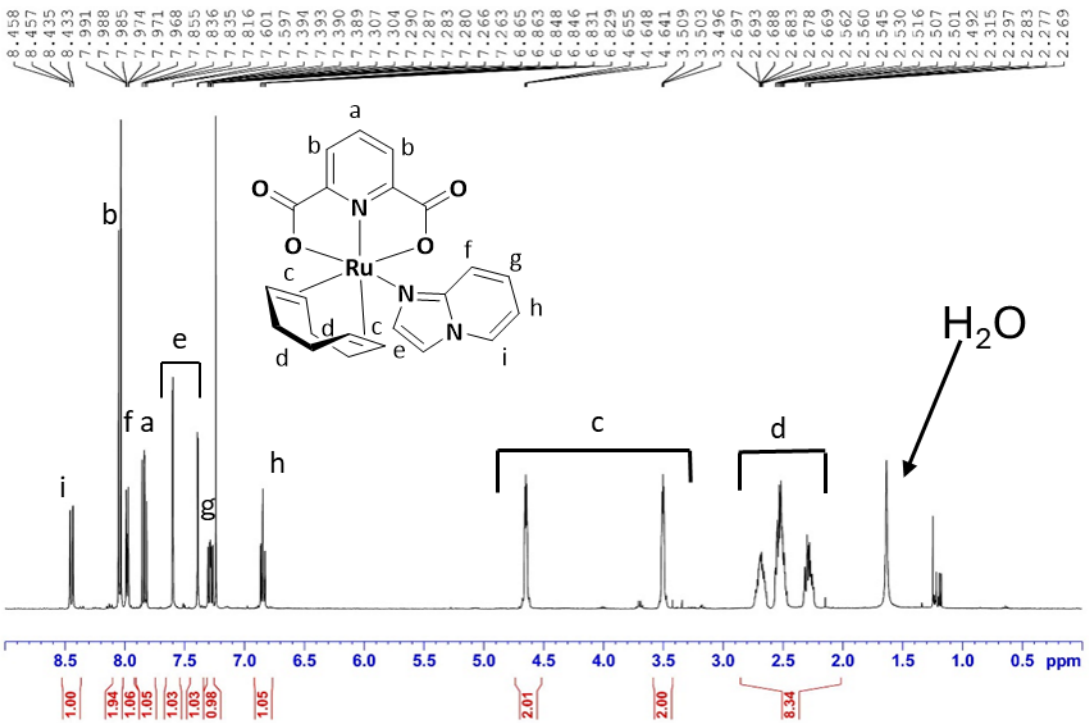


Figure S11 C7: ^{1}H NMR spectrum (400 MHz, $CDCl_3$).

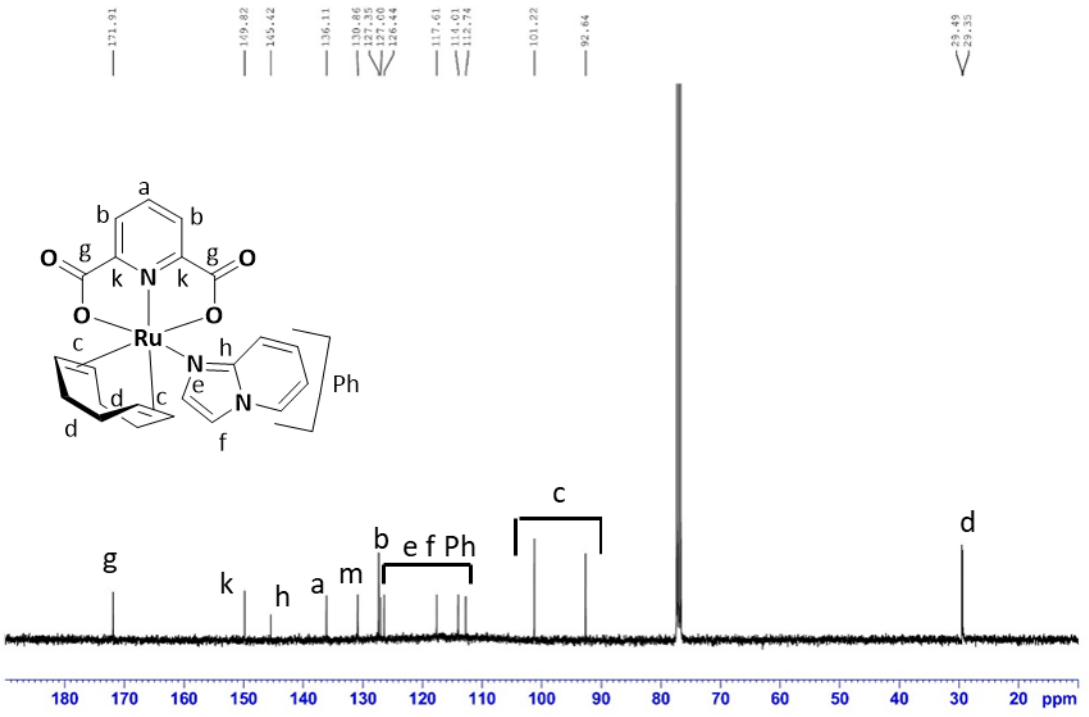


Figure S12 C7: ^{13}C NMR spectrum (100.6 MHz, $CDCl_3$).

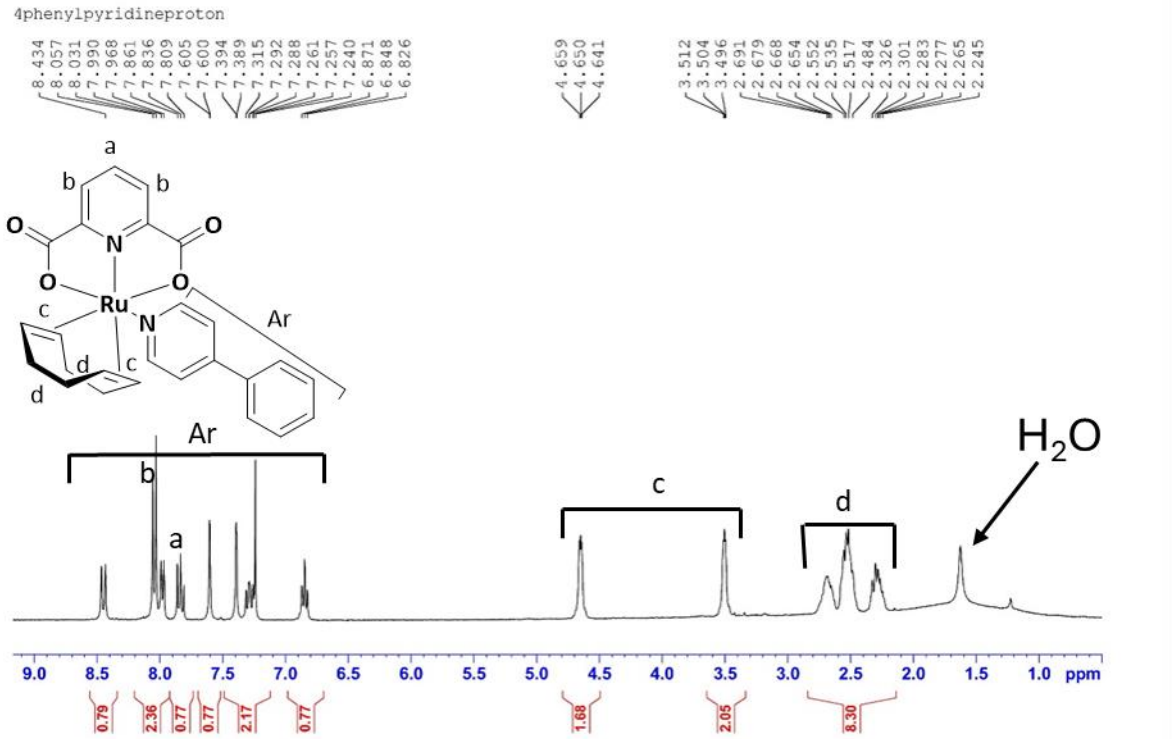


Figure S13 C8: ^{1}H NMR spectrum (300 MHz, $CDCl_3$).

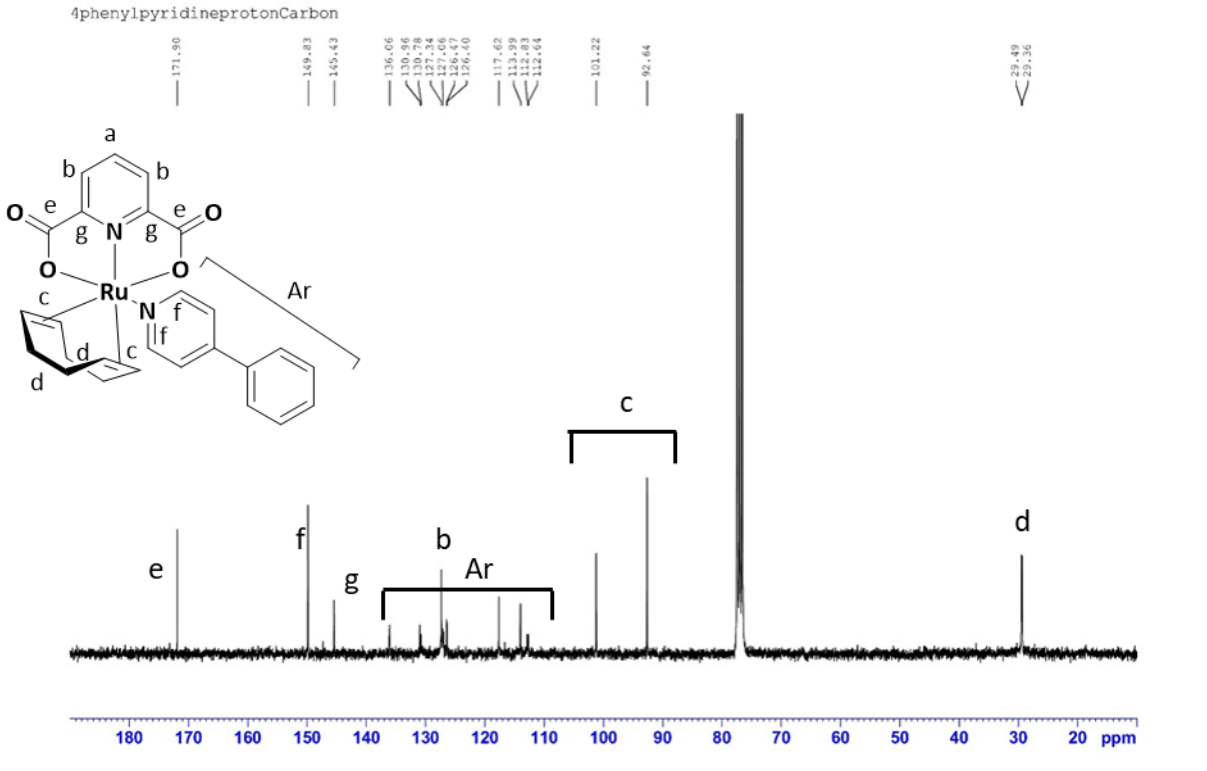


Figure S14 C8: ^{13}C NMR spectrum (100.6 MHz, $CDCl_3$).

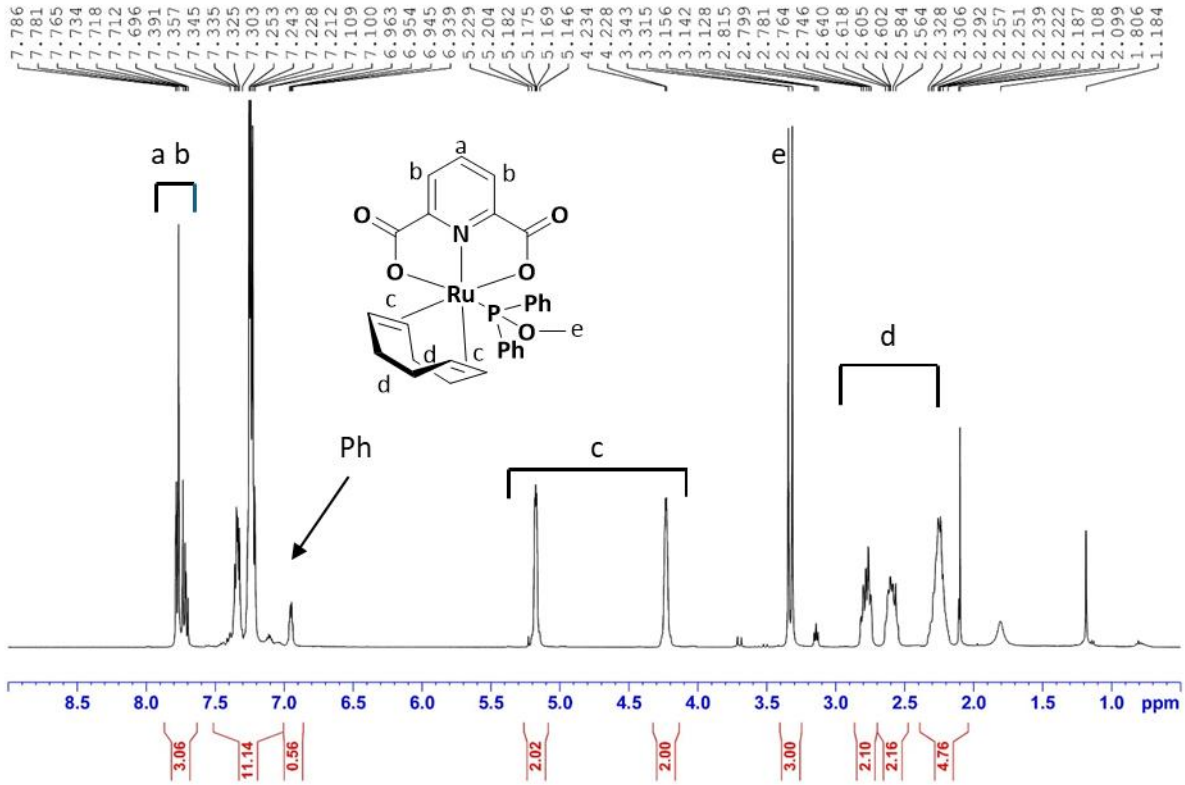


Figure S15 C9: ^{1}H NMR spectrum (400 MHz, $CDCl_3$).

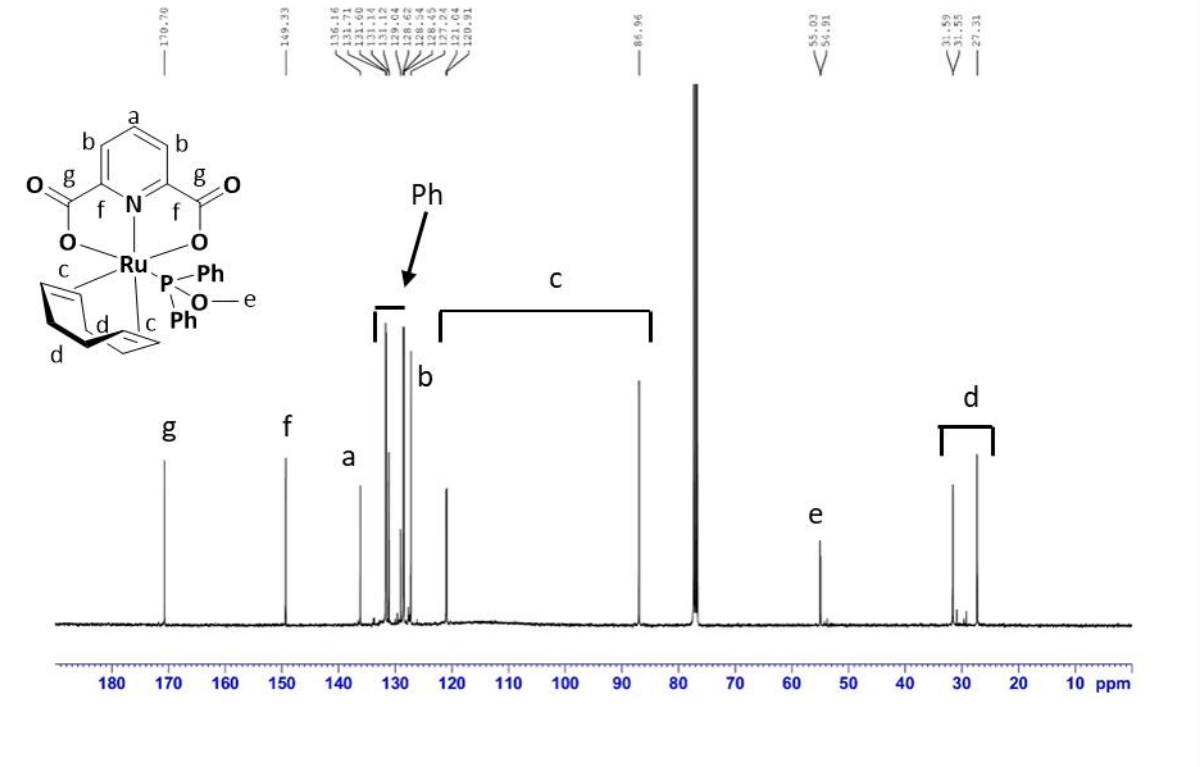


Figure S16 C9: ^{13}C NMR spectrum (100.6 MHz, $CDCl_3$).

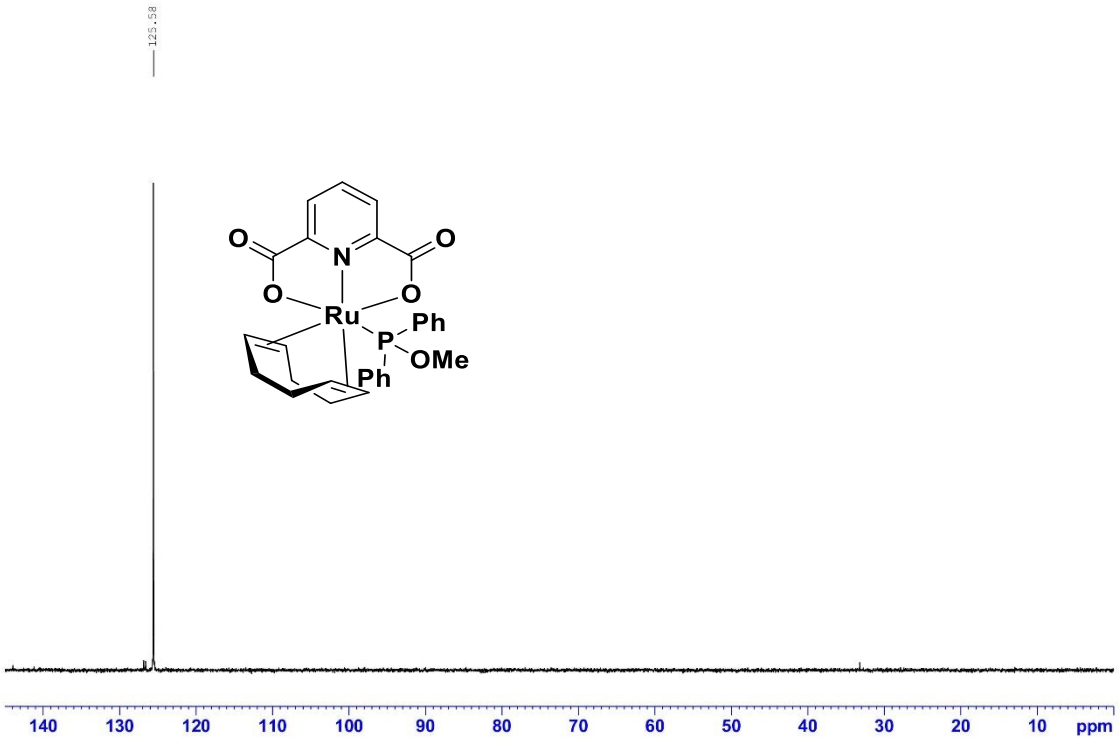


Figure S17 C9: ^{31}P NMR spectrum (161.9 MHz, $CDCl_3$).

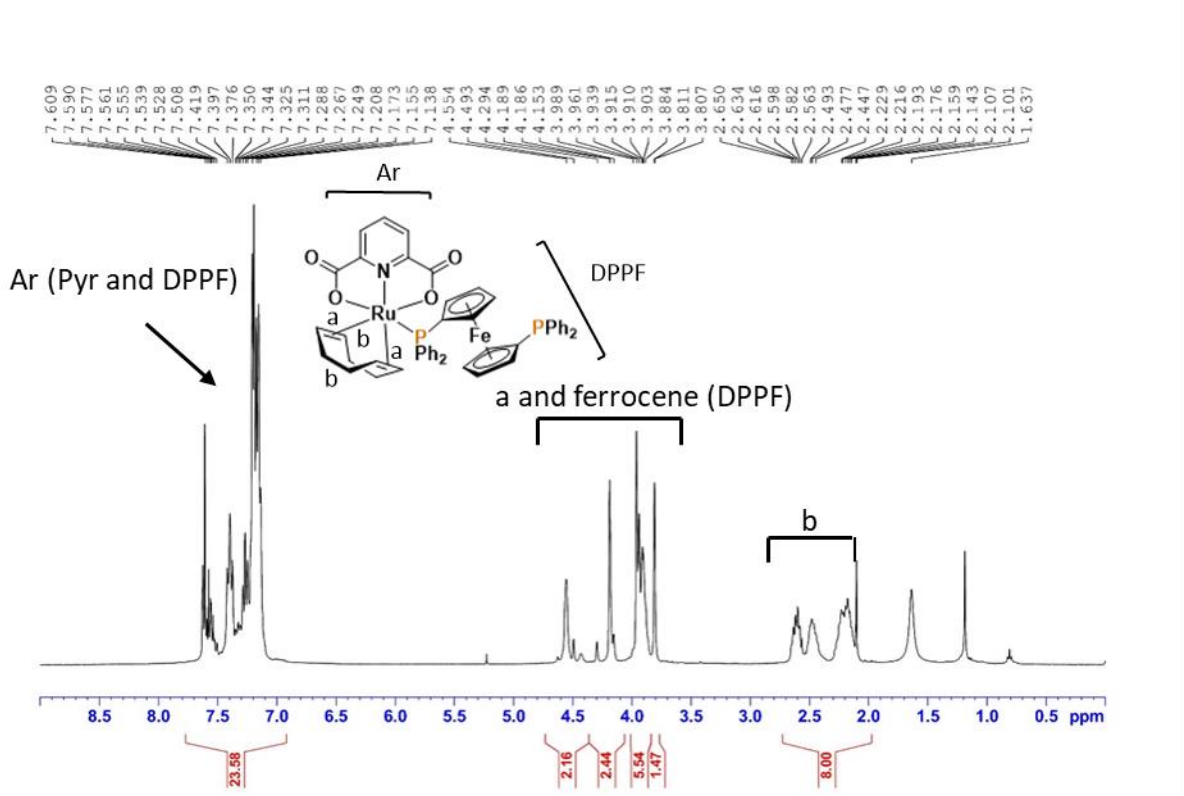


Figure S18 C10: ^{1}H NMR spectrum (300 MHz, $CDCl_3$).

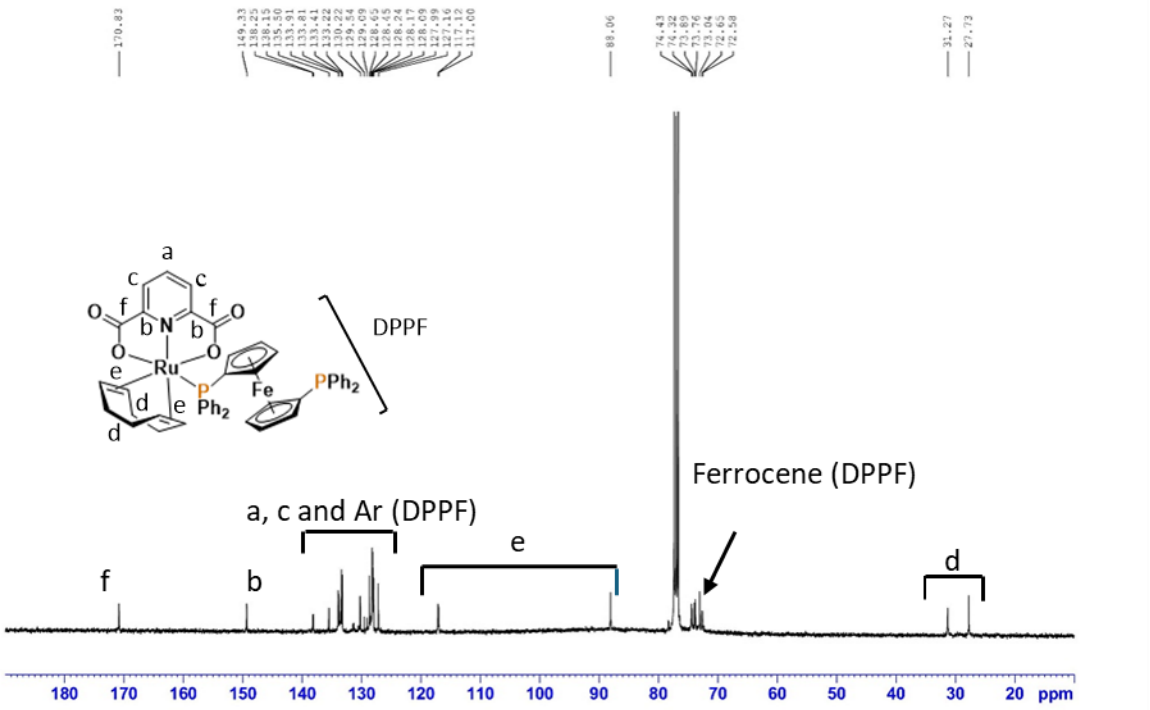


Figure S19 C10: ^{13}C NMR spectrum (75.4 MHz, $CDCl_3$).

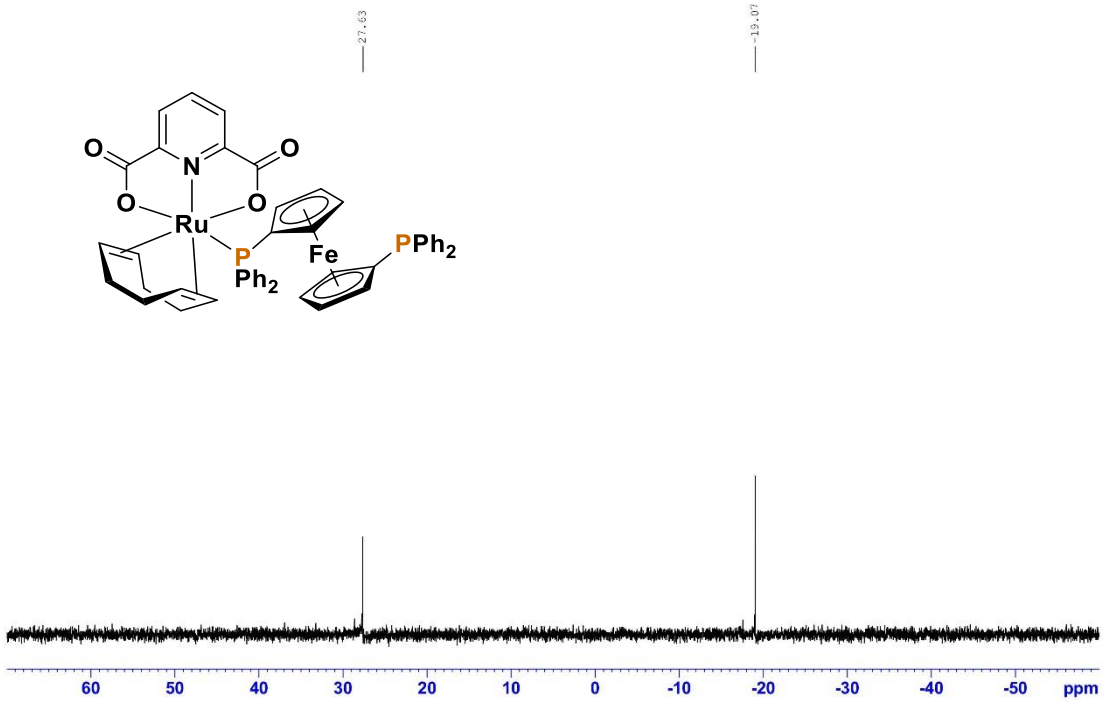


Figure S20 C10: ^{31}P NMR spectrum (161.9 MHz, $CDCl_3$).

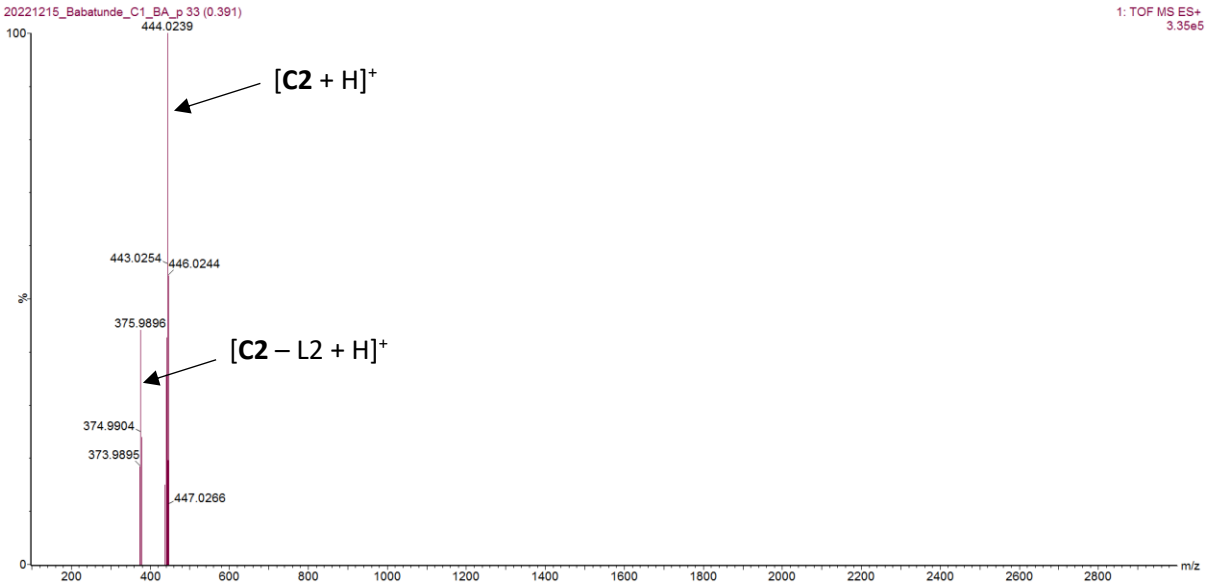


Figure S21 C2: Mass Spectrum. Positive ionization. Solvent: CH_3CN.

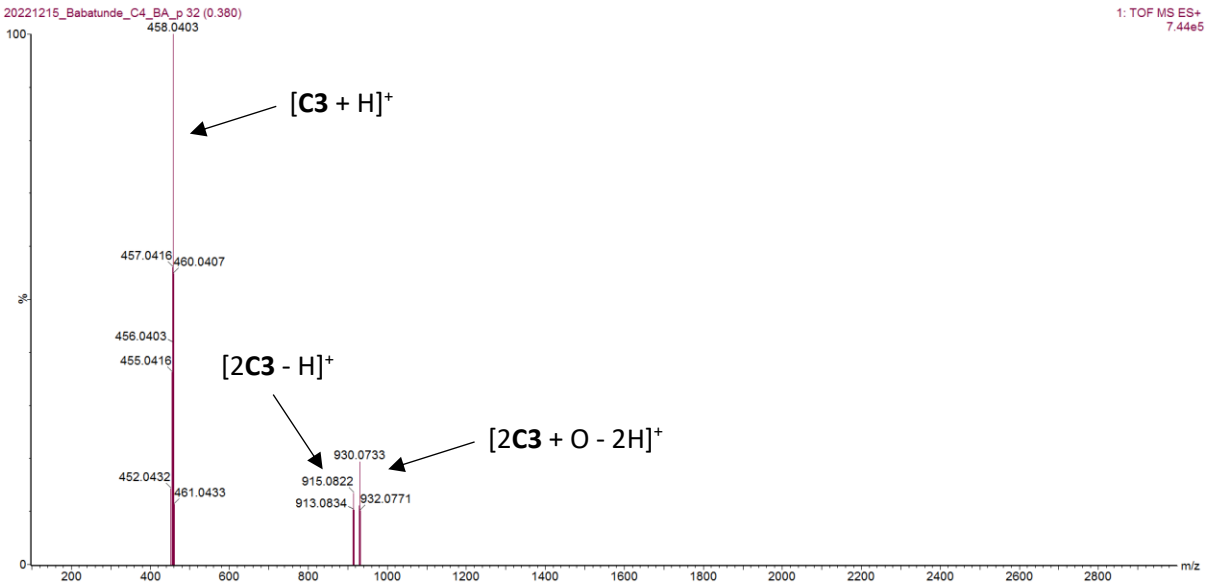


Figure S22 C3: Mass Spectrum. Positive ionization. Solvent: CH_3CN.

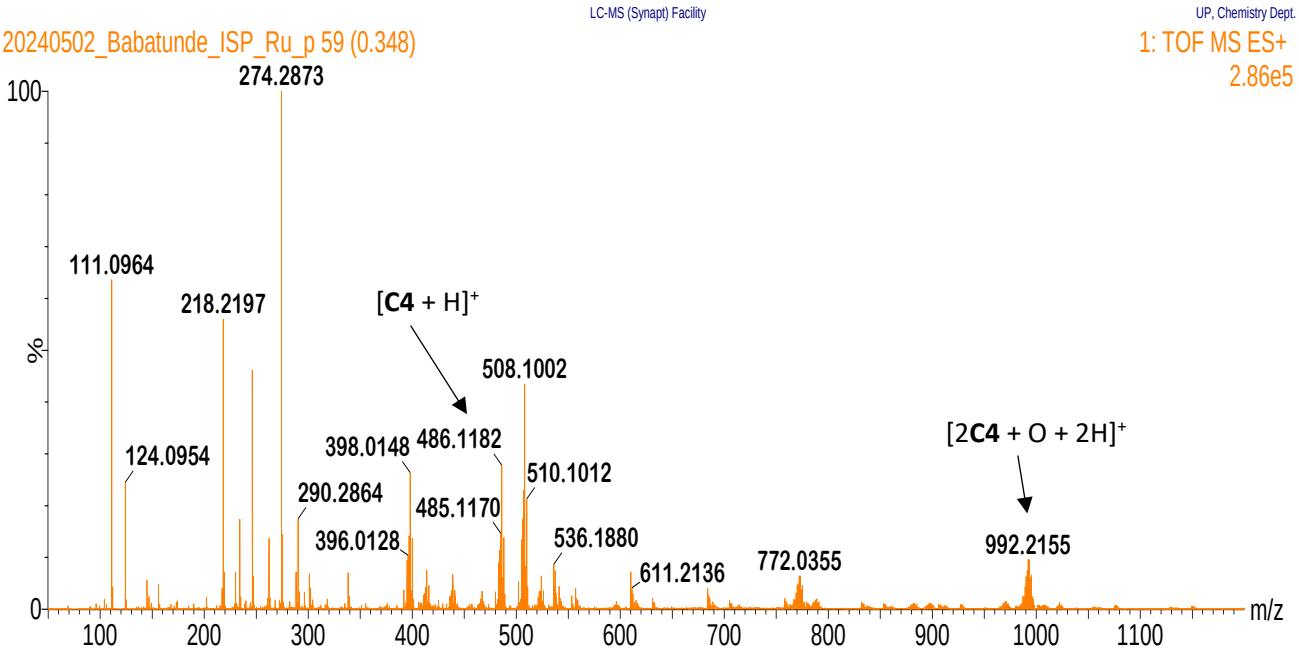


Figure S23 C4: Mass Spectrum. Positive ionization. Solvent: MeOH.

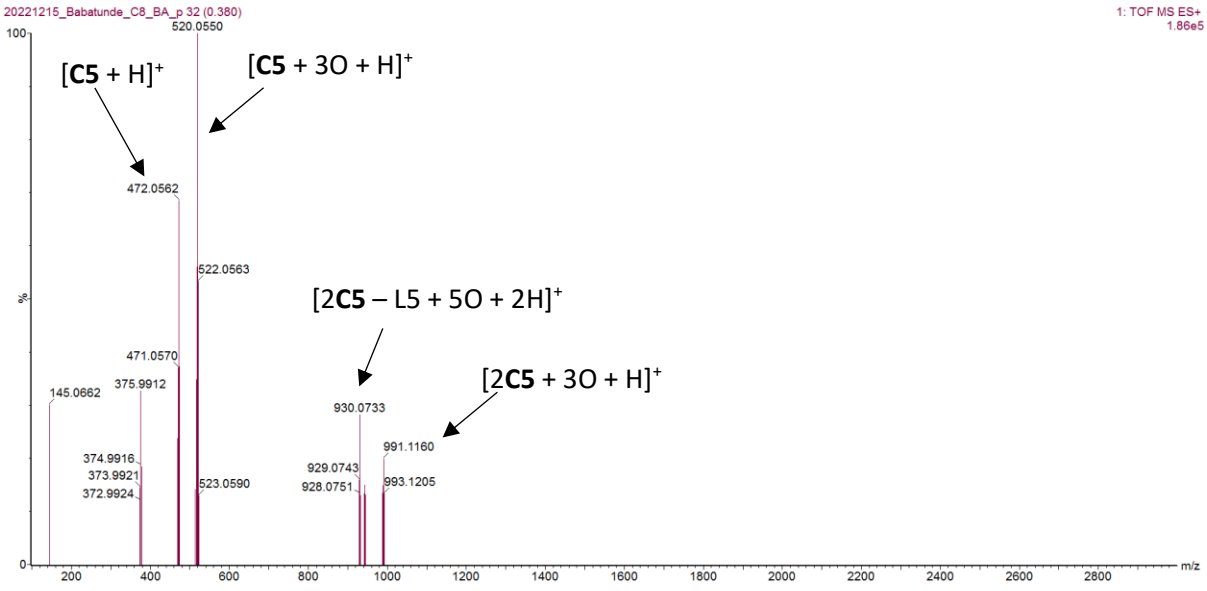


Figure S24 C5: Mass Spectrum. Positive ionization. Solvent: CH_3CN.

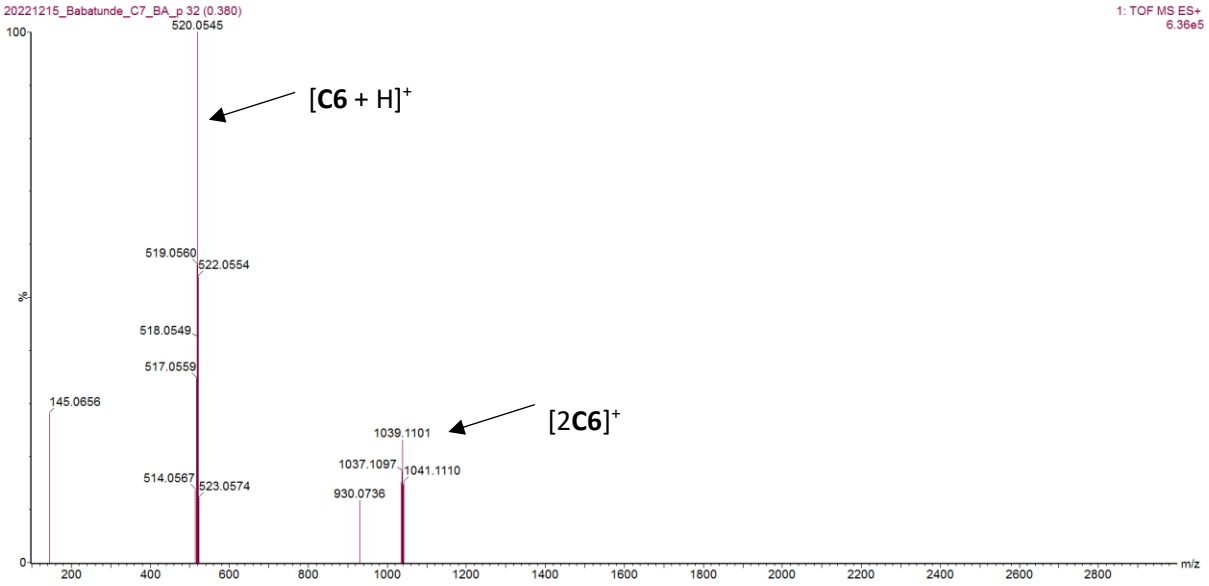


Figure S25 C6: Mass Spectrum. Positive ionization. Solvent: CH_3CN.

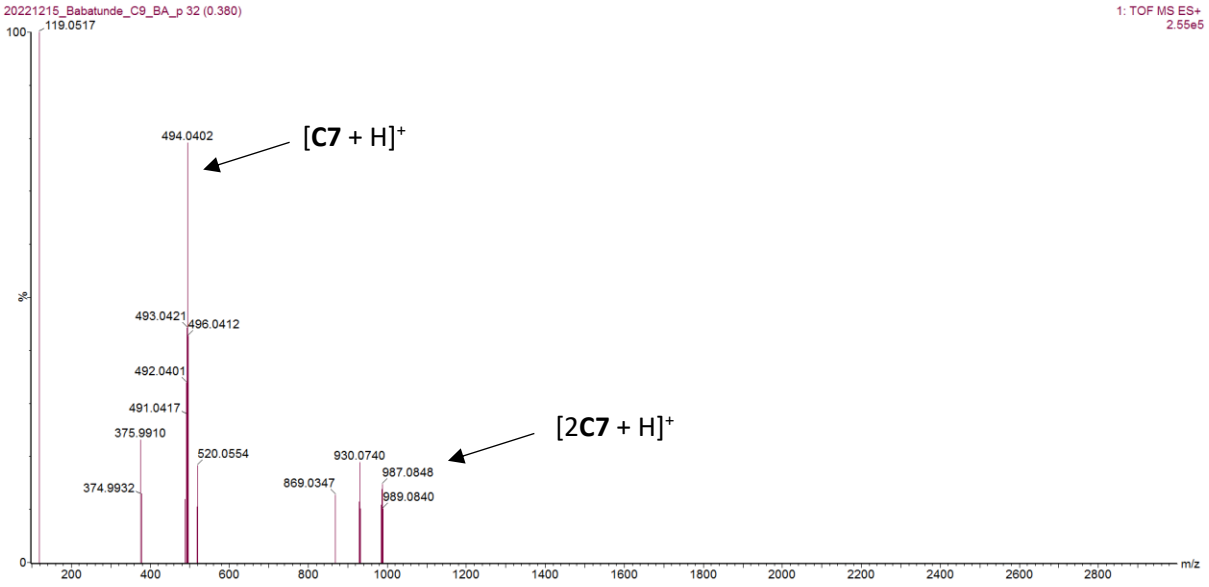


Figure S26 C7: Mass Spectrum. Positive ionization. Solvent: CH_3CN.

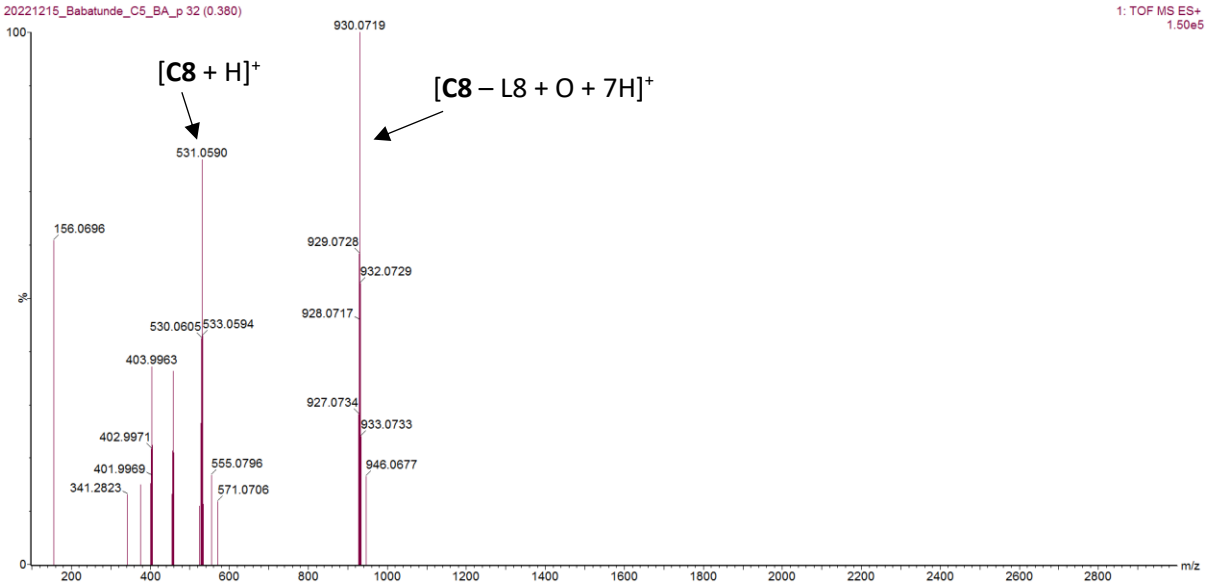


Figure S27 C8: Mass Spectrum. Positive ionization. Solvent: CH_3CN.

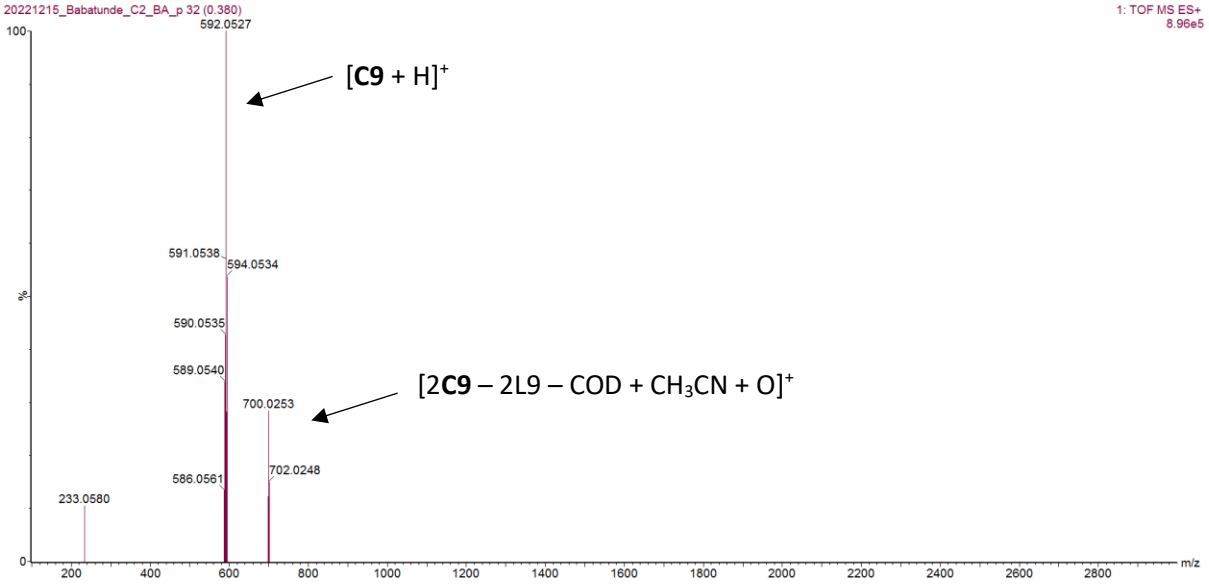


Figure S28 C9: Mass Spectrum. Positive ionization. Solvent: CH_3CN.

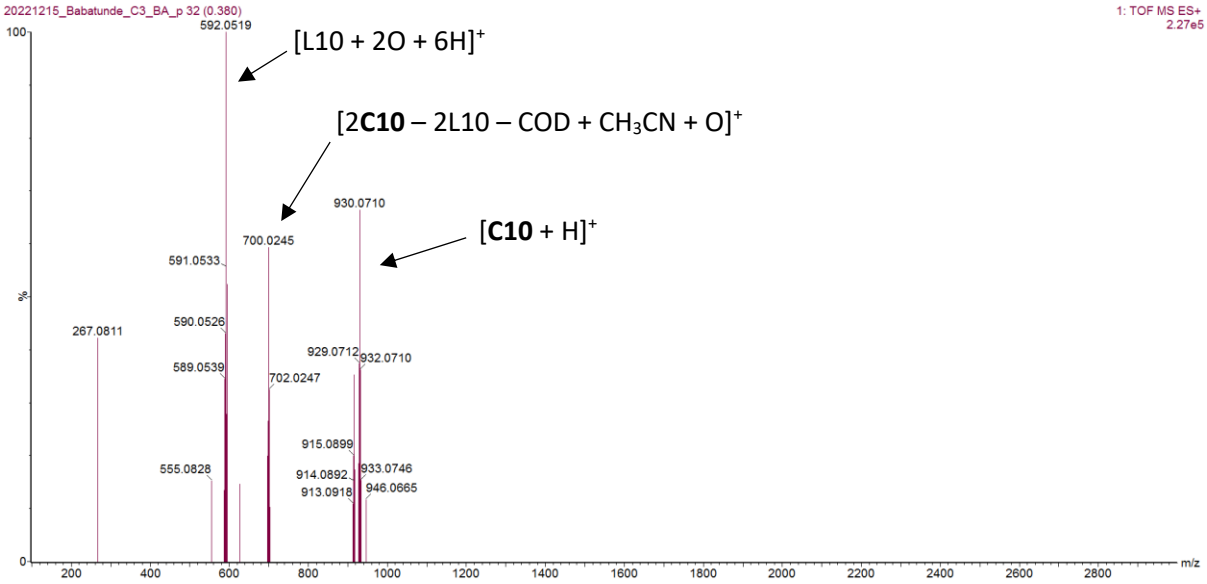
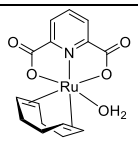
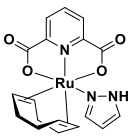
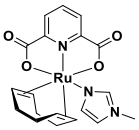
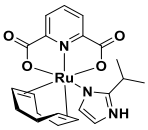
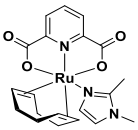


Figure S29 C10: Mass Spectrum. Positive ionization. Solvent: CH_3CN.

Table S1: Crystallographic parameters for **C1**-**C10**.

Description	C1b	C2	C3	C4	C5
Structure					
Empirical formula	$C_{15}H_{17}NO_5Ru$	$C_{18}H_{19}N_3O_4Ru$	$C_{19}H_{21}N_3O_4Ru$	$C_{21}H_{25}N_3O_4Ru$	$C_{20}H_{23}N_3O_4Ru$
Formula weight	392.36	442.43	456.46	484.51	470.48
Temperature (K)	150.00(10)	150.00(10)	150.00(2)	150.00(2)	150.00(2)
Crystal system	triclinic	monoclinic	triclinic	monoclinic	monoclinic
Space group	*P*-1	$P2_1/n$	*P*-1	I_2/a	$P2_1/c$
a (Å)	6.5303(5)	9.9830(2)	7.91810(10)	15.4522(2)	13.1979(2)
b (Å)	7.0283(6)	12.6440(2)	9.37670(10)	9.39410(10)	16.9554(2)
c (Å)	16.2104(11)	13.2138(2)	13.30400(10)	27.8369(3)	16.4943(3)
α (°)	90.128(6)	90	91.1050(10)	90	90
β (°)	99.266(6)	94.456(2)	102.6310(10)	102.0130(10)	96.1330(10)
γ (°)	106.746(7)	90	113.7950(10)	90	90
Volume (Å^3)	702.23(10)	1662.87(5)	875.508(17)	3952.30(8)	3669.90(10)
Z	2	4	2	8	8
ρ_{calc}g (cm^3)	1.856	1.767	1.731	1.629	1.703
μ (mm^{-1})	1.141	0.974	7.529	0.827	0.888
F(000)	396.0	896.0	464.0	1984.0	1920.0
Crystal size (mm^3)	0.21 × 0.155 × 0.058	0.174 × 0.155 × 0.1	0.3 × 0.233 × 0.154	0.333 × 0.27 × 0.101	0.213 × 0.199 × 0.152
Radiation (λ, Å)	0.71073	0.71073	1.54184	0.71073	0.71073
Reflections collected	9571	23347	27736	61393	59671
Independent reflections	2861	4471	3656	5691	9935
R_{int}	0.0501	0.0371	0.0683	0.0313	0.0373
Data/restraints/parameters	2861/0/205	4471/0/235	3656/0/245	5691/0/264	9935/0/509
Goodness-of-fit on F^2	1.125	1.063	1.052	1.065	1.029
Final R indexes [all data]	R_1 = 0.0534, wR_2 = 0.1355	R_1 = 0.0296, wR_2 = 0.0632	R_1 = 0.0275, wR_2 = 0.0691	R_1 = 0.0267, wR_2 = 0.0610	R_1 = 0.0316, wR_2 = 0.0598
Largest diff. peak/hole (e.Å^{-3})	2.47/-1.09	0.46/-0.68	0.78/-0.94	1.16/-0.56	0.44/-0.66

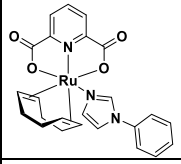
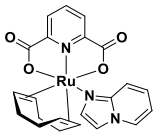
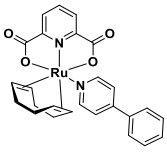
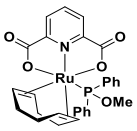
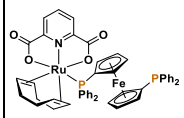
Description	C6	C7	C8	C9	C10
Structure					
Empirical formula	$C_{24}H_{23}N_3O_4Ru$	$C_{22}H_{21}N_3O_4Ru$	$C_{26}H_{24}N_2O_4Ru$	$C_{28}H_{28}NO_5PRu$	$C_{49}H_{45.9}FeNO_{5.4}{}_5P_2Ru$
Formula weight	518.52	492.49	529.54	590.55	954.78
Temperature (K)	150.00(2)	150.00(2)	149.98(10)	150.00(10)	150.00(10)
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a (Å)	8.97690(10)	9.3611(3)	10.0679(2)	16.85350(10)	25.0246(2)
b (Å)	19.1990(2)	15.0636(5)	12.1714(2)	10.51780(10)	10.64480(10)
c (Å)	12.18010(10)	13.6503(5)	17.3557(3)	14.57130(10)	15.8523(2)
α (°)	90	90	90	90	90
β (°)	102.1700(10)	102.8250(10)	90.3490(10)	111.0280(10)	90.8770(10)
γ (°)	90	90	90	90	90
Volume (Å^3)	2052.03(4)	1876.83(11)	2126.74(7)	2410.92(4)	4222.27(7)
Z	4	4	4	4	4
ρcalcg (cm^3)	1.678	1.743	1.654	1.627	1.502
μ (mm^{-1})	6.512	0.873	0.775	6.240	6.776
F(000)	1056.0	1000.0	1080.0	1208.0	1962.0
Crystal size (mm^3)	0.302 × 0.234 × 0.181	0.314 × 0.254 × 0.199	0.288 × 0.214 × 0.182	0.233 × 0.198 × 0.185	0.305 × 0.279 × 0.174
Radiation (λ, Å)	1.54184	0.71073	0.71073	1.54184	1.54184
Reflections collected	21225	86070	34434	40591	86017
Independent reflections	4282	3841	5746	5116	8309
R_{int}	0.0480	0.0467	0.0314	0.0375	0.0775
Data/restraints/parameters	4282/0/289	3841/0/271	5746/0/298	5116/0/326	8309/0/549
Goodness-of-fit on F^2	1.123	1.059	1.033	1.107	1.247
Final R indexes [all data]	R_1 = 0.0416, wR_2 = 0.1114	R_1 = 0.0211, wR_2 = 0.0521	R_1 = 0.0295, wR_2 = 0.0681	R_1 = 0.0285, wR_2 = 0.0741	R_1 = 0.0764, wR_2 = 0.1813
Largest diff. peak/hole (e Å^{-3})	0.68/-1.13	0.53/-0.61	0.58/-0.83	0.49/-1.11	2.47/-1.39

Table S2: Bond angles (°) for **C1**-**C10**, obtained from SC-XRD data.

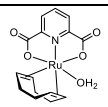
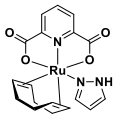
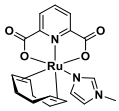
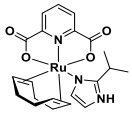
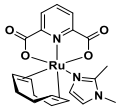
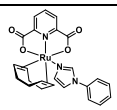
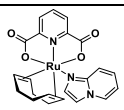
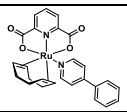
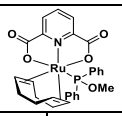
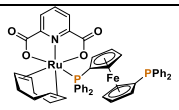
C1b		**C2**		**C3**		**C4**		**C5**	
									
Atoms	**Angle (˚)**	**Atoms**	**Angle (˚)**	**Atoms**	**Angle (˚)**	**Atoms**	**Angle (˚)**	**Atoms**	**Angle (˚)**
O5-Ru1-C9	91.4(2)	**N2-Ru1-C9**	161.04(6)	**N2-Ru1-C9**	161.42(9)	**N2-Ru1-C9**	158.27(5)	**N2-Ru1-C9**	161.34(6)
O5-Ru1-C8	95.2(2)	**N2-Ru1-C13**	93.64(6)	**N2-Ru1-C13**	90.28(9)	**N2-Ru1-C13**	92.26(5)	**N2-Ru1-C13**	93.58(6)
O5-Ru1-C12	162.5(2)	**N2-Ru1-O1**	83.98(5)	**N2-Ru1-O1**	84.53(7)	**N2-Ru1-O1**	89.84(4)	**N2-Ru1-O1**	85.56(5)
O5-Ru1-C13	160.3(2)	**N1-Ru1-C12**	161.77(7)	**N1-Ru1-C12**	160.38(9)	**N1-Ru1-C12**	162.25(5)	**N1-Ru1-C12**	162.68(6)
O3-Ru1-O5	84.63(17)	**N1-Ru1-C8**	91.96(6)	**N1-Ru1-C8**	92.12(9)	**N1-Ru1-C8**	90.31(5)	**N1-Ru1-C8**	91.84(6)
O3-Ru1-C9	82.0(2)	**N1-Ru1-C13**	161.30(7)	**N1-Ru1-C13**	162.63(9)	**N1-Ru1-C13**	160.43(5)	**N1-Ru1-C13**	160.33(6)
O3-Ru1-C8	118.9(2)	**N1-Ru1-C9**	97.14(6)	**N1-Ru1-C9**	95.86(9)	**N1-Ru1-C9**	94.19(5)	**N1-Ru1-C9**	96.92(6)
O3-Ru1-C12	78.7(2)	**N2-Ru1-C12**	89.30(6)	**N2-Ru1-C12**	86.19(9)	**N2-Ru1-C12**	87.14(5)	**N2-Ru1-C12**	89.34(6)
N1-Ru1-O5	87.90(19)	**N1-Ru1-N2**	88.12(6)	**N1-Ru1-N2**	92.01(8)	**N1-Ru1-N2**	92.34(5)	**N1-Ru1-N2**	88.32(5)
N1-Ru1-O3	78.19(19)	**N2-Ru1-O3**	84.92(5)	**N2-Ru1-O3**	86.48(7)	**N2-Ru1-O3**	84.41(4)	**N2-Ru1-O3**	86.21(5)
N1-Ru1-O1	77.66(19)	**N1-Ru1-O1**	78.34(6)	**N1-Ru1-O1**	77.73(8)	**N1-Ru1-O1**	77.62(4)	**N1-Ru1-O1**	77.74(5)
O1-Ru1-O3	151.60(5)	**O1-Ru1-O3**	154.11(5)	**O1-Ru1-O3**	153.34(7)	**O1-Ru1-O3**	154.26(4)	**O1-Ru1-O3**	154.44(5)
C6		**C7**		**C8**		**C9**		**C10**	
									
Atoms	**Angle (˚)**	**Atoms**	**Angle (˚)**	**Atoms**	**Angle (˚)**	**Atoms**	**Angle (˚)**	**Atoms**	**Angle (˚)**
N2-Ru1-C9	161.62(12)	**N2-Ru1-C9**	164.01(6)	**N2-Ru1-C9**	161.02(7)	**P1-Ru1-C9**	161.96(6)	**P1-Ru1-C9**	161.28(19)
N2-Ru1-C13	88.32(12)	**N2-Ru1-C13**	89.06(6)	**N2-Ru1-C13**	86.00(6)	**C12-Ru1-C13**	71.64(11)	**C12-Ru1-C13**	36.6(3)
N2-Ru1-O1	85.02(10)	**N2-Ru1-O1**	83.41(5)	**N2-Ru1-O1**	87.16(5)	**C8-Ru1-C9**	72.82(13)	**C8-Ru1-C9**	34.5(3)
N1-Ru1-C12	160.72(12)	**N1-Ru1-C12**	160.88(6)	**N1-Ru1-C12**	161.67(7)	**N1-Ru1-C12**	158.23(7)	**N1-Ru1-C12**	159.5(3)
N1-Ru1-C8	94.86(12)	**N1-Ru1-C8**	90.76(6)	**N1-Ru1-C8**	95.87(7)	**N1-Ru1-C8**	95.02(7)	**N1-Ru1-C8**	92.0(2)
N1-Ru1-C13	162.06(12)	**N1-Ru1-C13**	161.72(6)	**N1-Ru1-C13**	161.23(7)	**N1-Ru1-C13**	164.13(7)	**N1-Ru1-C13**	162.0(2)
N1-Ru1-C9	90.36(12)	**N1-Ru1-C9**	93.83(6)	**N1-Ru1-C9**	91.77(7)	**O3-Ru1-P1**	84.37(4)	**O3-Ru1-P1**	82.21(12)
N2-Ru1-C12	92.17(12)	**N2-Ru1-C12**	88.40(6)	**N2-Ru1-C12**	90.32(6)	**O1-Ru1-P1**	90.00(4)	**O1-Ru1-P1**	89.56(12)
N1-Ru1-N2	91.08(11)	**N1-Ru1-N2**	92.97(6)	**N1-Ru1-N2**	92.54(6)	**N1-Ru1-P1**	91.80(5)	**N1-Ru1-P1**	91.68(14)
N2-Ru1-O3	84.37(10)	**N2-Ru1-O3**	90.02(5)	**N2-Ru1-O3**	85.93(5)	**N1-Ru1-O3**	77.80(6)	**N1-Ru1-O3**	77.5(2)
N1-Ru1-O1	77.48(10)	**N1-Ru1-O1**	77.83(5)	**N1-Ru1-O1**	77.37(6)	**N1-Ru1-O1**	77.20(6)	**N1-Ru1-O1**	77.7(2)
O1-Ru1-O3	153.01(9)	**O1-Ru1-O3**	154.08(5)	**O1-Ru1-O3**	153.52(5)	**O1-Ru1-O3**	154.17(6)	**O1-Ru1-O3**	153.53(16)

Table S3: Bond lengths (Å) for **C1**-**C10**, obtained from SC-XRD data.

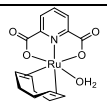
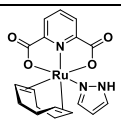
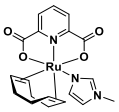
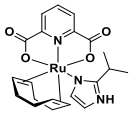
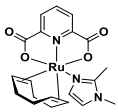
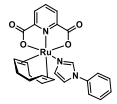
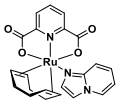
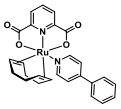
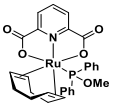
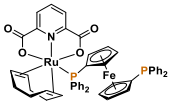
C1b		**C2**		**C3**		**C4**		**C5**	
									
Atoms	**Length (Å)**	**Atoms**	**Length (Å)**	**Atoms**	**Length (Å)**	**Atoms**	**Length (Å)**	**Atoms**	**Length (Å)**
Ru1-O1	2.098(4)	Ru1-O1	2.1129(12)	Ru1-O1	2.1162(16)	Ru1-O1	2.1176(10)	Ru1-O1	2.1263(12)
Ru1-O3	2.103(4)	Ru1-O3	2.1069(12)	Ru1-O3	2.1221(16)	Ru1-O3	2.1161(10)	Ru1-O3	2.1048(12)
Ru1-O5	2.163(5)	Ru1-N1	1.9887(15)	Ru1-N1	1.999(2)	Ru1-N1	1.9984(11)	Ru1-N1	1.9951(14)
Ru1-N1	1.985(5)	Ru1-N2	2.1074(14)	Ru1-N2	2.114(2)	Ru1-N2	2.1823(12)	Ru1-N2	2.1570(14)
Ru1-C13	2.182(6)	Ru1-C13	2.1890(18)	Ru1-C13	2.207(2)	Ru1-C13	2.1907(14)	Ru1-C13	2.1902(17)
Ru1-C9	2.196(6)	Ru1-C9	2.2184(17)	Ru1-C9	2.215(2)	Ru1-C9	2.2210(14)	Ru1-C9	2.2149(16)
Ru1-C12	2.185(6)	Ru1-C12	2.1917(17)	Ru1-C12	2.191(2)	Ru1-C12	2.1857(14)	Ru1-C12	2.1918(16)
Ru1-C8	2.213(6)	Ru1-C8	2.2050(18)	Ru1-C8	2.216(2)	Ru1-C8	2.2135(14)	Ru1-C8	2.2108(17)
Ru1-C_{alk}	2,1811(17)	Ru1-C_{alk}	2,2010(18)	Ru1-C_{alk}	2.2073(2)	Ru1-C_{alk}	2,2027(14)	Ru1-C_{alk}	2,2019(17)
C6		**C7**		**C8**		**C9**		**C10**	
									
Ru1-O1	2.127(2)	Ru1-O1	2.1128(12)	Ru1-O1	2.1178(12)	Ru1-P1	2.3122(5)	Ru1-P1	2.3426(15)
Ru1-O3	2.112(2)	Ru1-O3	2.1101(12)	Ru1-O3	2.1196(13)	Ru1-O3	2.1225(14)	Ru1-O3	2.118 (5)
Ru1-N1	1.994(3)	Ru1-N1	1.9970(14)	Ru1-N1	2.0066(15)	Ru1-O1	2.1318(15)	Ru1-O1	2.121(4)
Ru1-N2	2.104(3)	Ru1-N2	2.1577(14)	Ru1-N2	2.1363(15)	Ru1-N1	2.0071(17)	Ru1-N1	2.005(5)
Ru1-C13	2.193(3)	Ru1-C13	2.1887(16)	Ru1-C13	2.1863(17)	Ru1-C13	2.204(2)	Ru1-C13	2.206(6)
Ru1-C9	2.200(3)	Ru1-C9	2.2255(16)	Ru1-C9	2.2234(18)	Ru1-C12	2.2000(19)	Ru1-C12	2.231(5)
Ru1-C12	2.193(3)	Ru1-C12	2.1759(17)	Ru1-C12	2.1992(17)	Ru1-C9	2.324(2)	Ru1-C9	2.290(6)
Ru1-C8	2.214(3)	Ru1-C8	2.2025(16)	Ru1-C8	2.2201(18)	Ru1-C8	2.326(2)	Ru1-C8	2.295(6)
Ru1-C_{alk}	2.200(3)	Ru1-C_{alk}	2,198(16)	Ru1-C_{alk}	2,207(18)	Ru1-C_{alk}	2,264(6)	Ru1-C_{alk}	2,256(6)

Table S4: Crystallographic parameters for polymorph **C1c**.

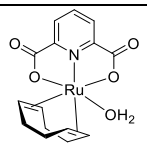
Description	C1c
Structure	
Empirical formula	$C_{15}H_{17}NO_5Ru$
Formula weight	392.36
Temperature (K)	150.00(10)
Crystal system	monoclinic
Space group	C2/c
a (Å)	18.7224(4)
b (Å)	10.4260(2)
c (Å)	14.4176(3)
α (°)	90
β (°)	92.908(2)
γ (°)	90
Volume ($Å^3$)	2810.69(10)
Z	8
ρ_{calc}g (cm^3)	1.854
μ (mm^{-1})	1.140
F(000)	1584.0
Crystal size (mm^3)	0.271 × 0.189 × 0.120
Radiation (λ, Å)	0.71073
Reflections collected	17475
Independent reflections	3606
R_{int}	0.0234
Data/restraints/parameters	3606/0/205
Goodness-of-fit on F^2	1.050
Final R indexes [all data]	R_1 = 0.0239, wR_2 = 0.0524
Largest diff. peak/hole ($e.Å^{-3}$)	0.72/-0.50

Table S5: Bond angles and bond lengths (SC-XRD) for polymorph **C1c**.

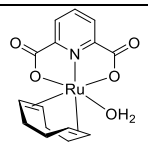
C1c			
			
Atoms	**Angle (˚)**	**Atoms**	**Length (Å)**
O5-Ru1-C9	162.62(7)	Ru1-O1	2.1075(12)
O5-Ru1-C8	159.15(6)	Ru1-O3	2.1104(12)
O5-Ru1-C12	91.65(7)	Ru1-O5	2.1296(13)
O5-Ru1-C13	87.60(6)	Ru1-N1	1.9984(14)
O3-Ru1-O5	84.48(5)	Ru1-C13	2.1908(16)
O3-Ru1-C9	79.15(6)	Ru1-C9	2.1676(18)
O3-Ru1-C8	116.32(6)	Ru1-C12	2.1982(17)
O3-Ru1-C12	84.45(6)	Ru1-C8	2.1676(18)
N1-Ru1-O5	91.55(6)		
N1-Ru1-O3	77.30(5)		
N1-Ru1-O1	77.69(5)		
O1-Ru1-O3	151.60(5)		

Figure S30. Packing diagram of the series of polymorphs **C1a**, **C1b**, and **C1c.**

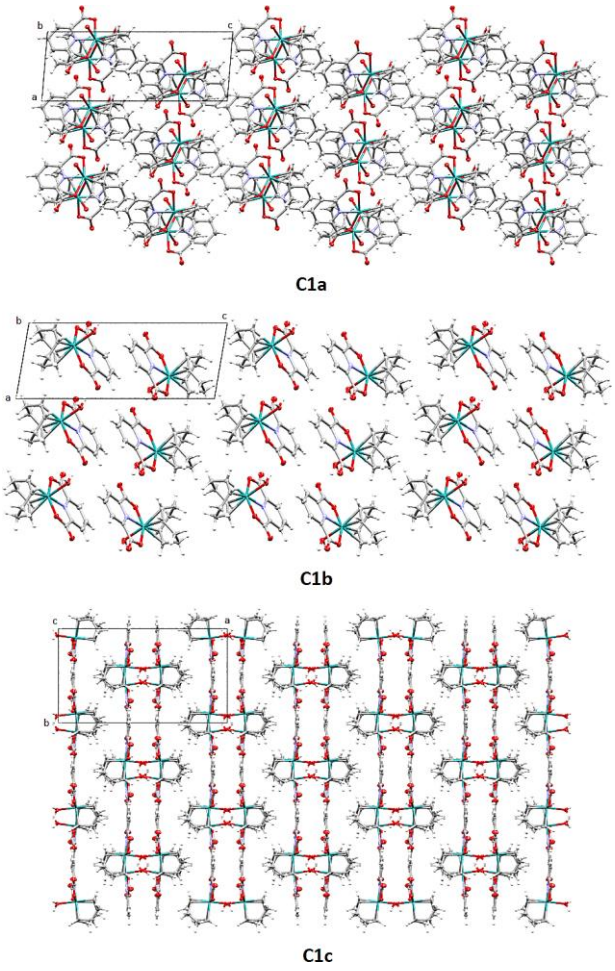


Figure S31. Hydrogen bonding network (indicated with dotted cyan lines) along the *b*-axis present in the structure of **C10**.

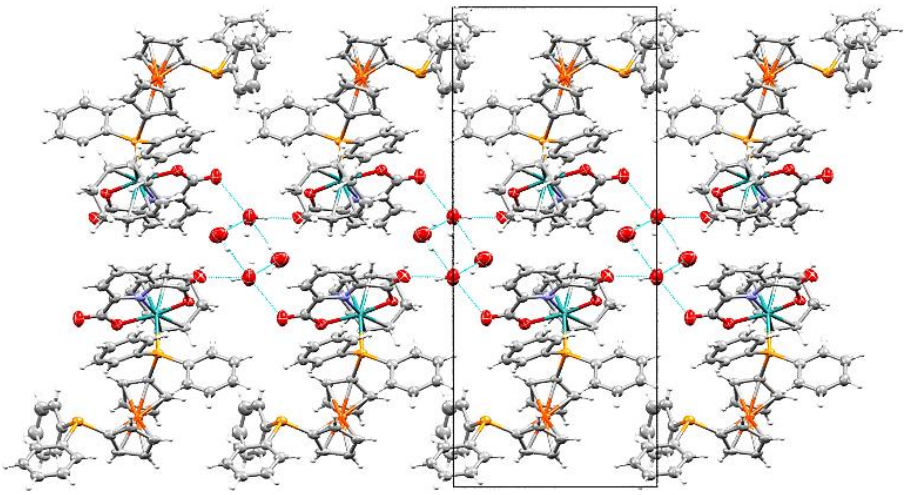


Figure S32. Cyclic voltammogram overlays of **C1** in the oxidation region (-0.5 V to +1.3 V *vs* $Ag/AgNO_3$) using scan rates 50, 100, 150, 200, 250, 300, 400, 500 and 1000 $mV.s^{-1}$. CVs were measured in 0.3 $mol.dm^{-3}$ $[NBu_4][PF_6]$/DCE on a glassy carbon working electrode at 70 °C. [Ru] = unknown (saturated solution, based on poor solubility in DCE, analyte mass = 0.485 mg). Scans were initiated in the positive direction. Internal standard: Decamethylferrocene (0.067 mM).

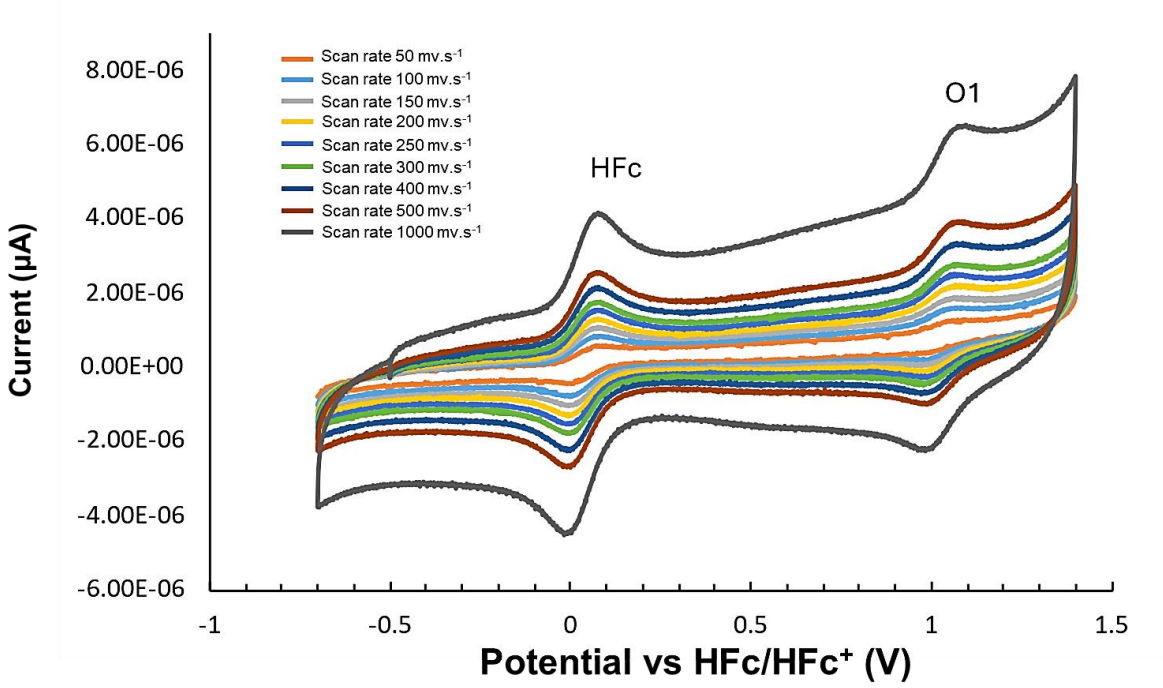
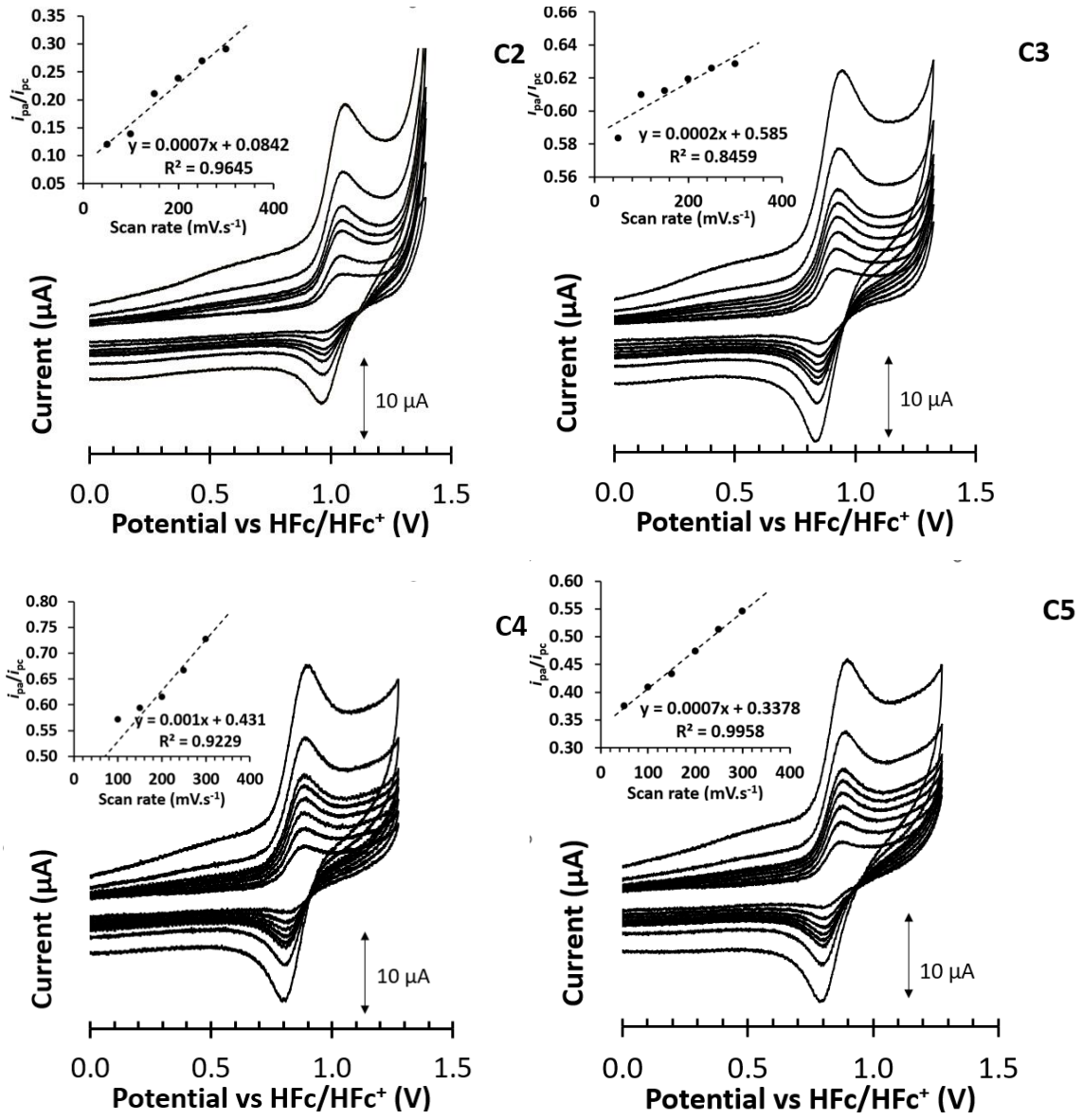
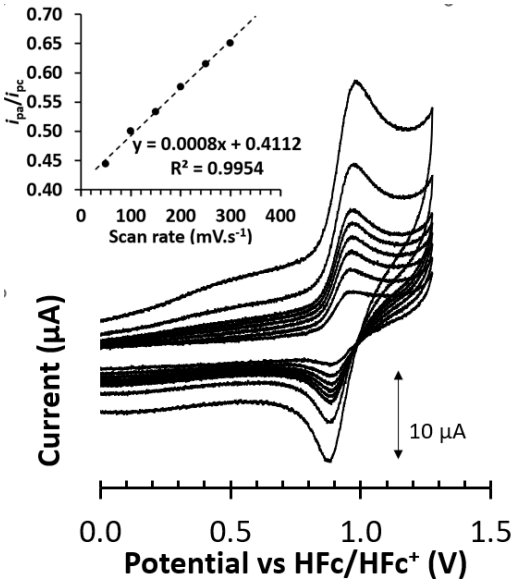
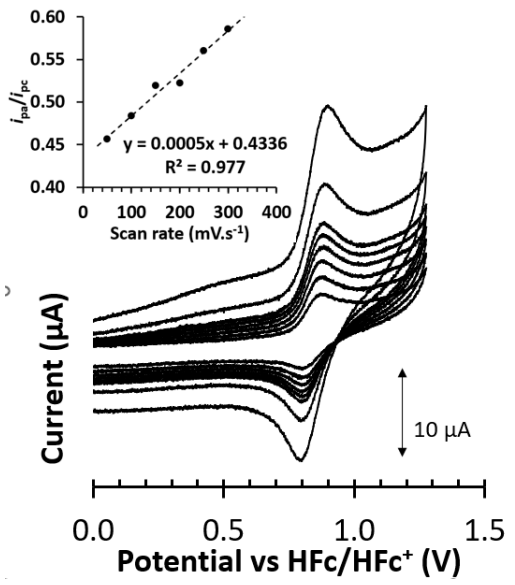


Figure S33. Cyclic voltammogram overlays of **C2**-**C10** in the oxidation region (*vs* ferrocene) using scan rates 50, 100, 150, 200, 250, 300, 500 and 1000 $mV.s^{-1}$. CVs were measured in 0.3 $mol.dm^{-3}$ $[NBu_4][PF_6]$/DCM on a glassy carbon working electrode at 25 °C. Scans were initiated in the positive direction.

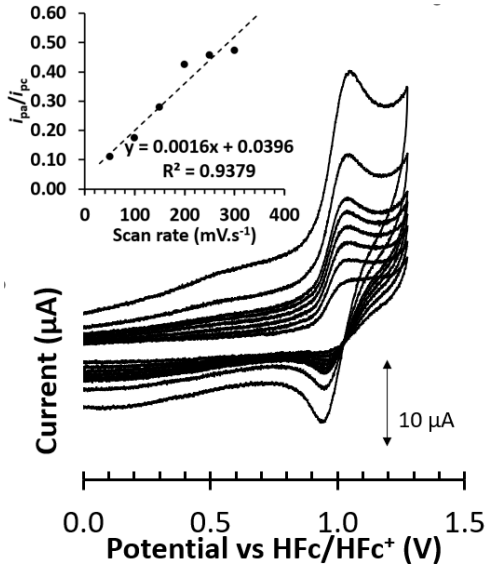




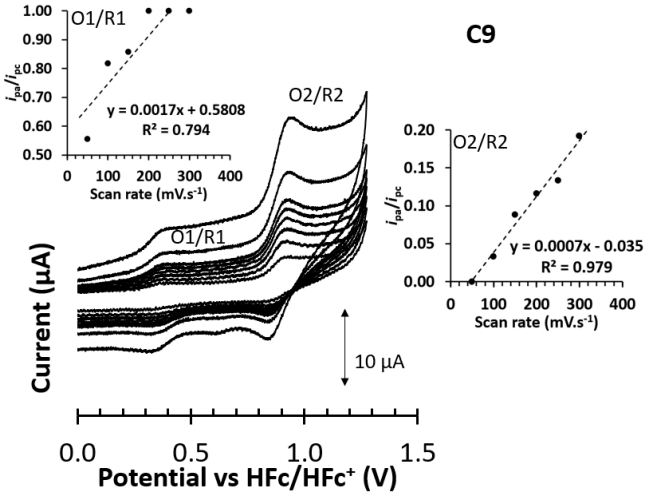
C6



C7



C8



C9

C10

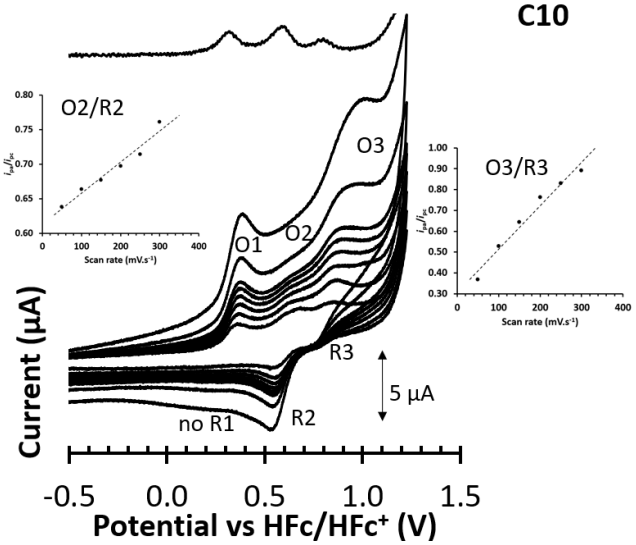


Figure S34. Left: Comparative cyclic voltammograms of **C2**-**C10** in the reduction region (-2.0 V to -0.3 V *vs* Ag/$AgNO_3$) using a scan rate of 0.1 $V.s^{-1}$. CVs were measured in 0.3 $mol.dm^{-3}$ [NBu_4][PF_6]/DCM on a glassy carbon working electrode at 25 °C. [Ru] = 0.001 $mol.dm^{-3}$ or saturated solution. Scans were initiated in the negative direction. **Right:** Cyclic voltammogram and Linear Sweep Voltammetry overlays of **C2** in the region -2.0 V to +1.5 V (vs Ag/$AgNO_3$) using scan rates 100 $mV.s^{-1}$ (CV) and 0.2 $mV.s^{-1}$ (LSVs). CV and LSVs were measured in 0.1 $mol.dm^{-3}$ [NBu_4][PF_6]/DCM on a glassy carbon working electrode at 25 °C. [Ru] = 0.001 $mol.dm^{-3}$ or saturated solution. The CV and oxidation LSV scans were initiated in the positive direction, and the reduction LSV in the negative.

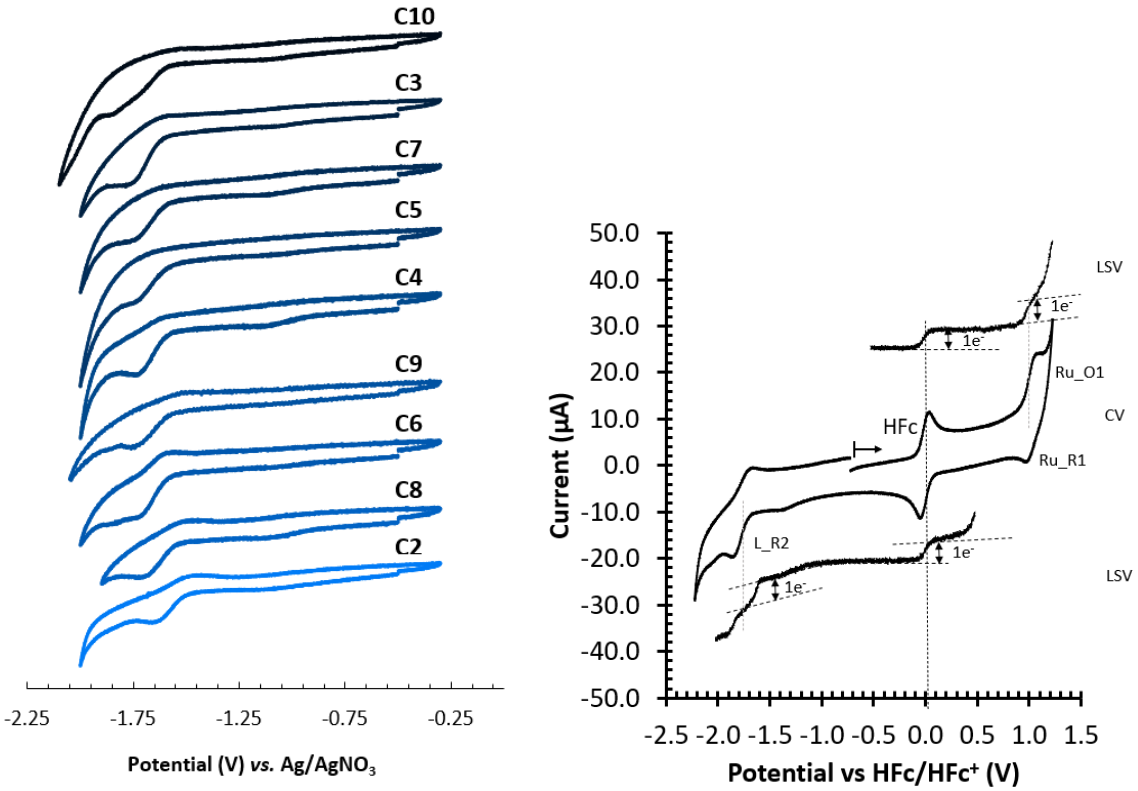


Table S6. The cyclic voltammetry data of 0.001 $mol.dm^{-3}$ C2-C10 in 0.3 $mol.dm^{-3}$ [NBu_4][PF_6]/DCM on a glassy carbon working electrode at 25 °C.

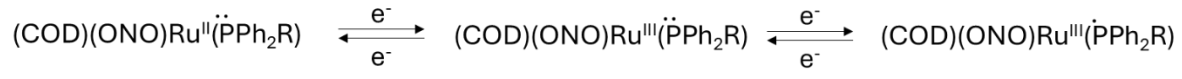
C2							
v ($mV.s^{-1}$)	$E_{pa\ O1}$ (V)	$E_{pc\ R1}$ (V)	$E°'$	ΔE	i_{pa} (µA)	i_{pc} (µA)	i_{pa}/i_{pc}
50	1.043	0.971	1.007	0.072	7.14	0.86	0.12
100	1.047	0.97	1.009	0.077	10.29	1.43	0.14
150	1.047	0.97	1.009	0.077	10.86	2.29	0.21
200	1.049	0.969	1.009	0.08	12.00	2.86	0.24
250	1.049	0.968	1.009	0.081	14.86	4.00	0.27
300	1.055	0.967	1.011	0.088	17.71	5.14	0.29
500	1.06	0.966	1.013	0.094	22.29	6.86	0.31
1000	1.064	0.965	1.014	0.099	27.71	10.00	0.36

C3							
v (mV.s^{-1})	$E_{pa\ O1}$ (V)	$E_{pc\ R1}$ (V)	$E°'$	ΔE	i_{pa} (µA)	i_{pc} (µA)	i_{pa}/i_{pc}
50	0.926	0.850	0.888	0.076	5.00	2.92	0.58
100	0.929	0.849	0.889	0.080	6.83	4.17	0.61
150	0.932	0.848	0.890	0.083	8.17	5.00	0.61
200	0.934	0.847	0.891	0.087	9.42	5.83	0.62
250	0.937	0.847	0.892	0.091	10.92	6.83	0.63
300	0.940	0.846	0.893	0.094	11.67	7.33	0.63
500	0.943	0.844	0.893	0.099	14.83	9.58	0.65
1000	0.949	0.839	0.894	0.110	14.83	10.33	0.70
C4							
v (mV.s^{-1})	$E_{pa\ O1}$ (V)	$E_{pc\ R1}$ (V)	$E°'$	ΔE	i_{pa} (µA)	i_{pc} (µA)	i_{pa}/i_{pc}
50	0.888	0.832	0.860	0.056	4.50	2.00	0.44
100	0.891	0.832	0.861	0.059	7.00	4.00	0.57
150	0.894	0.832	0.863	0.062	8.00	4.75	0.59
200	0.896	0.831	0.864	0.065	9.75	6.00	0.62
250	0.899	0.831	0.865	0.068	10.50	7.00	0.67
300	0.902	0.831	0.866	0.071	11.00	8.00	0.73
500	0.905	0.831	0.868	0.074	15.00	10.00	0.67
1000	0.910	0.830	0.870	0.080	20.00	15.00	0.75
C5							
v (mV.s^{-1})	$E_{pa\ O1}$ (V)	$E_{pc\ R1}$ (V)	$E°'$	ΔE	i_{pa} (µA)	i_{pc} (µA)	i_{pa}/i_{pc}
50	0.873	0.806	0.840	0.067	4.00	1.50	0.38
100	0.876	0.805	0.840	0.071	5.50	2.25	0.41
150	0.878	0.805	0.841	0.073	7.50	3.25	0.43
200	0.881	0.805	0.843	0.076	9.50	4.50	0.47
250	0.883	0.804	0.844	0.079	9.75	5.00	0.51
300	0.884	0.803	0.844	0.081	11.00	6.00	0.55
500	0.892	0.800	0.846	0.092	14.00	7.50	0.54
1000	0.903	0.799	0.851	0.104	19.00	11.00	0.58
C6							
v (mV.s^{-1})	$E_{pa\ O1}$ (V)	$E_{pc\ R1}$ (V)	$E°'$	ΔE	i_{pa} (µA)	i_{pc} (µA)	i_{pa}/i_{pc}
50	0.957	0.891	0.924	0.066	4.09	1.82	0.44
100	0.964	0.890	0.927	0.074	5.45	2.73	0.50
150	0.967	0.888	0.928	0.079	6.82	3.64	0.53
200	0.971	0.887	0.929	0.084	7.73	4.45	0.58
250	0.972	0.885	0.929	0.087	8.86	5.45	0.62
300	0.974	0.884	0.929	0.090	9.77	6.36	0.65
500	0.981	0.875	0.928	0.106	12.73	8.18	0.64
1000	0.983	0.872	0.928	0.111	17.73	10.91	0.62
C7							
v (mV.s^{-1})	$E_{pa\ O1}$ (V)	$E_{pc\ R1}$ (V)	$E°'$	ΔE	i_{pa} (µA)	i_{pc} (µA)	i_{pa}/i_{pc}
50	0.887	0.802	0.845	0.085	3.83	1.75	0.46
100	0.890	0.802	0.846	0.088	5.17	2.50	0.48

150	0.893	0.801	0.847	0.091	6.42	3.33	0.52
200	0.895	0.801	0.848	0.095	7.50	3.92	0.52
250	0.898	0.800	0.849	0.098	8.33	4.67	0.56
300	0.901	0.800	0.850	0.101	9.25	5.42	0.59
500	0.904	0.799	0.851	0.105	11.67	7.08	0.61
1000	0.909	0.798	0.854	0.111	16.33	11.25	0.69
C8							
v (mV.s^{-1})	$E_{pa\ O1}$ (V)	$E_{pc\ R1}$ (V)	$E°'$	ΔE	i_{pa} (µA)	i_{pc} (µA)	i_{pa}/i_{pc}
50	1.028	0.944	0.986	0.084	8.18	0.91	0.11
100	1.034	0.944	0.989	0.090	10.45	1.82	0.17
150	1.035	0.944	0.990	0.091	11.36	3.18	0.28
200	1.036	0.944	0.990	0.092	15.00	6.36	0.42
250	1.037	0.944	0.991	0.093	17.27	7.91	0.46
300	1.038	0.945	0.992	0.093	20.00	9.45	0.47
500	1.038	0.948	0.993	0.090	25.91	9.09	0.35
1000	1.048	0.945	0.997	0.103	34.09	15.91	0.47
C9 (O1/R1)							
v (mV.s^{-1})	$E_{pa\ O1}$ (V)	$E_{pc\ R1}$ (V)	$E°'$	ΔE	i_{pa} (µA)	i_{pc} (µA)	i_{pa}/i_{pc}
50	0.361	0.312	0.337	0.049	0.60	0.33	0.56
100	0.361	0.312	0.337	0.049	0.73	0.60	0.82
150	0.362	0.312	0.337	0.050	0.93	0.80	0.86
200	0.362	0.312	0.337	0.050	1.07	1.07	1.00
250	0.363	0.312	0.338	0.051	1.13	1.13	1.00
300	0.364	0.312	0.338	0.052	1.20	1.20	1.00
500	0.370	0.312	0.341	0.058	1.73	1.73	1.00
1000	0.402	0.312	0.357	0.090	2.27	2.27	1.00
C9 (O2/R2)							
v (mV.s^{-1})	$E_{pa\ O2}$ (V)	$E_{pc\ R2}$ (V)	$E°'$	ΔE	i_{pa} (µA)	i_{pc} (µA)	i_{pa}/i_{pc}
50	0.916				2.50		
100	0.919	0.856	0.888	0.063	3.75	0.13	0.03
150	0.921	0.856	0.889	0.065	4.38	0.39	0.09
200	0.923	0.855	0.889	0.068	5.38	0.63	0.12
250	0.925	0.855	0.890	0.070	6.00	0.80	0.13
300	0.927	0.852	0.890	0.075	6.50	1.25	0.19
500	0.932	0.843	0.888	0.089	8.50	2.00	0.24
1000	0.939	0.842	0.891	0.097	11.38	4.50	0.40
C10 (O1/R1)							
v (mV.s^{-1})	$E_{pa\ O1}$ (V)	$E_{pc\ R1}$ (V)	$E°'$	ΔE	i_{pa} (µA)	i_{pc} (µA)	i_{pa}/i_{pc}
50	0.362				1.85		
100	0.366				2.26		
150	0.369				2.70		
200	0.373				3.06		
250	0.377				3.47		
300	0.380				3.87		

500	0.385				5.24		
1000	0.395				6.94		
C10 (O2/R2)							
v (mV.s^{-1})	$E_{pa\ O2}$ (V)	$E_{pc\ R2}$ (V)	$E°'$	ΔE	i_{pa} (µA)	i_{pc} (µA)	i_{pa}/i_{pc}
50	0.64	0.548	0.594	0.092	3.92	2.50	0.64
100	0.643	0.547	0.595	0.096	4.33	2.88	0.66
150	0.643	0.546	0.595	0.097	5.42	3.67	0.68
200	0.644	0.549	0.597	0.095	6.33	4.42	0.70
250	0.645	0.539	0.592	0.106	7.00	5.00	0.71
300	0.646	0.538	0.592	0.108	7.67	5.83	0.76
500	0.647	0.537	0.592	0.110	9.25	7.00	0.76
1000	0.648	0.531	0.590	0.117	10.42	7.92	0.76
C10 (O3/R3)							
v (mV.s^{-1})	$E_{pa\ O3}$ (V)	$E_{pc\ R3}$ (V)	$E°'$	ΔE	i_{pa} (µA)	i_{pc} (µA)	i_{pa}/i_{pc}
50	0.852	0.727	0.790	0.125	1.69	0.63	0.37
100	0.870	0.727	0.799	0.143	1.90	1.00	0.53
150	0.873	0.727	0.800	0.146	2.14	1.38	0.64
200	0.874	0.727	0.801	0.147	2.46	1.88	0.76
250	0.875	0.727	0.801	0.148	2.86	2.38	0.83
300	0.883	0.727	0.805	0.156	3.23	2.88	0.89
500	0.936	0.727	0.832	0.209	4.23	3.00	0.71
1000	1.003	0.727	0.865	0.276	4.72	3.25	0.69

Figure S35: Schematic representation of electrochemical reactions C9 and C10.



ONO = dipicolinic acid
R = OMe (**C9**) or FcPPh$_2$ (**C10**)

Table S7. Transfer hydrogenation optimization processes

Complex	Base	Catalytic loading (mol%)	Time (Hr)	Conversion%[d]	Yields%[d]	TON	TOF (h^{-1})
C1	^{t}BuOK/10mol%	-	0.5	-	-	-	-
C1	^{t}BuOK/10mol %	-	0.75	-	-	-	-
C1	^{t}BuOK/10mol%	-	1	-	-	-	-
C1	-	-	0.5	-	-	-	-
C1	-	-	0.75	-	-	-	-
C1	-	-	1	-	-	-	-
C1	^{t}BuOK/10mol%[a]	1	1	-	-	-	-
C1	^{t}BuOK/10mol%[b]	1	1	88	88	88.00	88.00
C1	^{t}BuOK/10mol%[c]	1	1	91	91	91.00	91.00
C1	^{t}BuOK/10mol%	3	0.5	94	94	31,33	62.66
C1	^{t}BuOK/10mol%	3	0.75	96	96	32.00	43.67
C1	^{t}BuOK/10mol%	3	1	98	98	32.67	32.67
C1	^{t}BuOK/10mol%	2	0.5	92	92	46.00	92.00
C1	^{t}BuOK/10mol%	2	0.75	92	92	46.00	61.33
C1	^{t}BuOK/10mol%	2	1	94	94	47.00	47.00
C1	^{t}BuOK/10mol%	1	0.5	78	78	78.00	156.00
C1	^{t}BuOK/10mol%	1	0.75	87	87	87.00	116.00
C1	^{t}BuOK/10mol%	1	1	89	89	89.00	89.00
C1	KOH/10mol%	1	0.5	81	81	81.00	162.00
C1	KOH/10mol%	1	0.75	90	90	90.00	120.00
C1	KOH/10mol%	1	1	91	91	91.00	91.00
C1	^{t}BuOK/10mol%	5	0.5	99	99	19.80	39.60
C1	^{t}BuOK/10mol%	5	0.75	99	99	19.80	26.40
C1	^{t}BuOK/5mol%	5	0.5	25	25	5.00	10.00
C1	^{t}BuOK/5mol%	5	0.75	85	85	17.00	22.67
C1	^{t}BuOK/5mol%	5	1	94	94	18.80	18.80
C1	^{t}BuOK/0mol%	5	0.5	0	0	0.00	0.00
C1	^{t}BuOK/0mol%	5	0.75	1	1	0.20	0.27
C1	^{t}BuOK/0mol%	5	1	10	10	2.00	2.00
C1	^{t}BuOK/10mol%	5	0.25	99	99	19.80	79.20

General conditions: Ph_2CO (0.3 mmol; 0.6 mmol was used with 5 mol% catalytic loading), base (5/10 mol%), anisole (0.3 mmol), ^{i}PrOH (300 µL), 80^{o}C, times: 0.25, 0.30, 0.75, and 1 hour. [a] C_6D_6, ^{i}PrOH = 0 µL. [b] C_6D_6, ^{i}PrOH = 600 µL. [c] Pure ^{i}PrOH (1 mL), sample taken after 1 hour. [d] Based on the average of two runs.

Figure S36. Stacked NMR spectra of transfer hydrogenation of benzophenone (0.6mmol) at intervals of time 0, 15, 30, and 45 minutes.

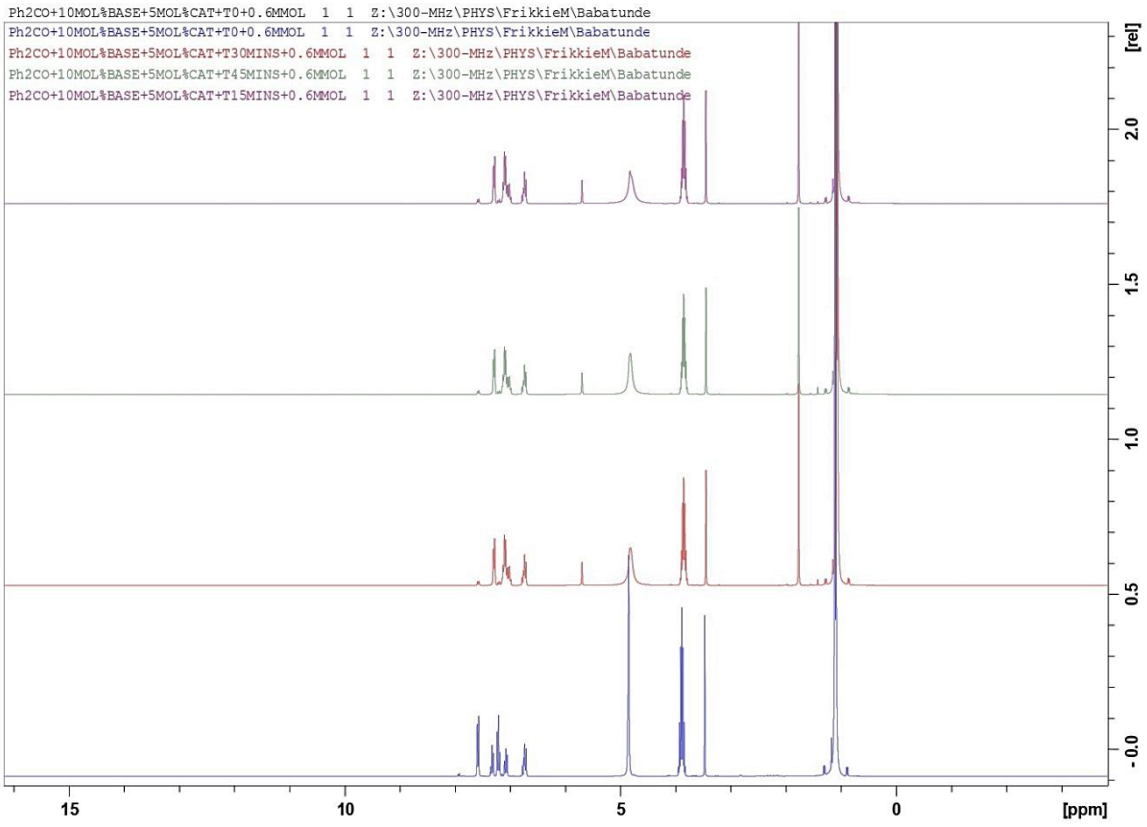


Figure S37(A). Stacked ^{1}H NMR spectra of transfer hydrogenation of benzophenone (0.6mmol) using C1 at 5 mol% concentration at intervals of time 0, 15, and 30 minutes.

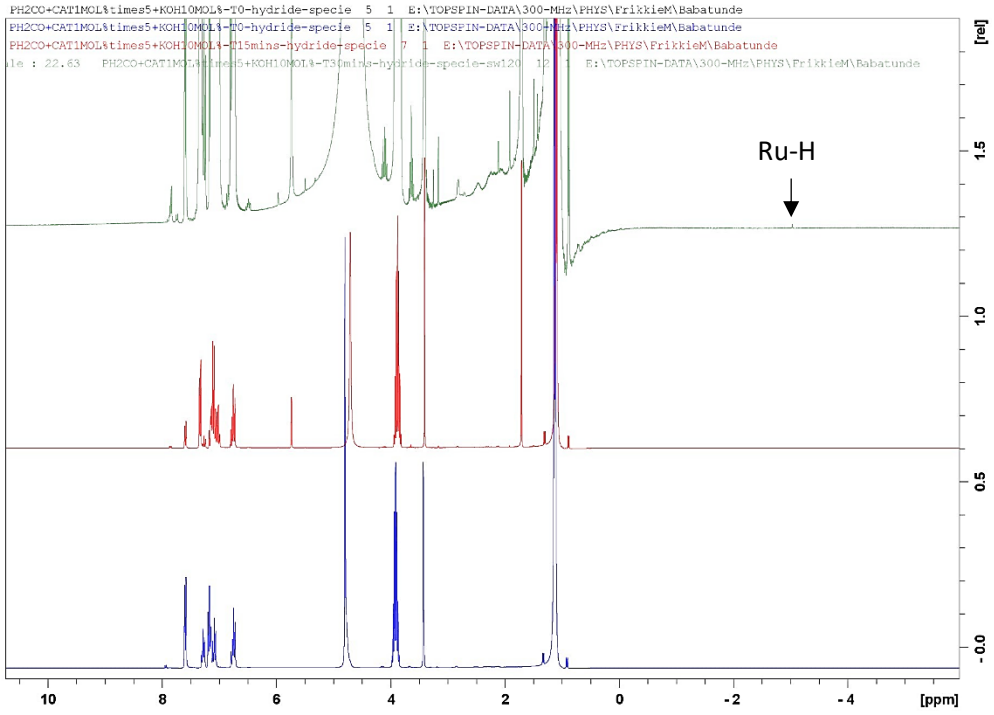


Figure S37(B). Enlarged ^{1}H NMR spectrum of transfer hydrogenation reaction in Figure S367 above after 30 minutes.

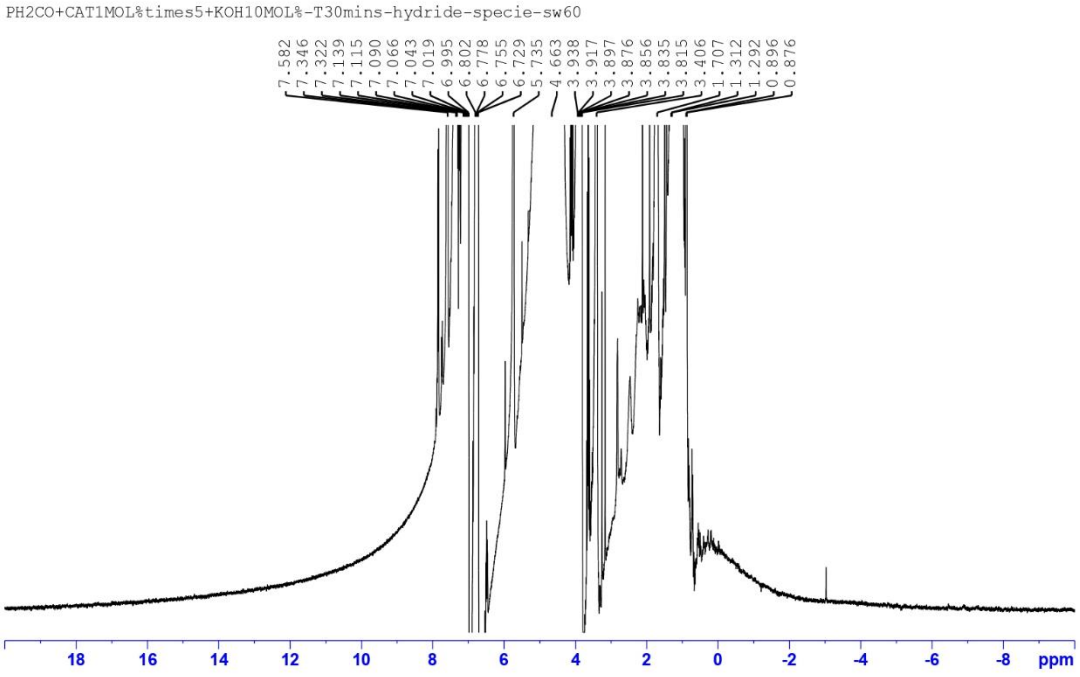


Figure S37(C). Hydride region of ^{1}H NMR spectrum of transfer hydrogenation reaction in Figure S37 above after 30 minutes.