Supporting Information for

A Ruthenium Porphyrin-Based Porous Organic Polymer for the Hydrosilylative Reduction of CO_2 to Formate

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A. Materials

Unless stated otherwise all reagents were purchased from commercial sources and used without further purification. dioxane, dichloromethane, acetonitrile, and dimethylformamide were purified by passage over activated alumina.

B. Instrumentation and Methods

Infrared spectra were recorded on a Thermo Scientific Nicolet iS5 with an iD7 diamond ATR attachment and are uncorrected.

UV-Vis absorbance spectra were recorded on a Cary 5000 UV-Vis/NIR spectrophotometer using an internal DRA with stock powder cell holder to record the % reflectance spectra. Emission spectra were recorded on a Cary Eclipse Fluorescence spectrophotometer equipped with a xenon flash lamp.

Surface area measurements were conducted on a Micromeritics ASAP 2020 Surface Area and Porosity Analyzer using ca. 15 mg samples. Nitrogen isotherms were generated by incremental exposure to ultra high purity nitrogen up to ca. 1 atm in a liquid nitrogen (77 K) bath. Carbon dioxide isotherms were generated incremental exposure to ultra-high purity carbon dioxide up to ca. 900 mmHg in a water bath at 295K. Surface parameters were determined using BET adsorption models in the instrument software. Pore size distributions were determined using the non-local density functional theory (NLDFT) model (slit pore, 2D-NLDFT, N2-carbon finite pores As=6) in the instrument software (Micromeritics ASAP 2020 V4.02).

^{1}H NMR spectra were recorded in deuterated solvents on a Bruker Avance DPX 400 (400 MHz). Chemical shits are reported in parts per million (ppm, δ) using the solvent as the internal standard. Quantitative ^{13}C NMR spectra were recorded on a Bruker Avance DPX 400 (100 MHz) using the solvent as an internal standard. ^{1}H NMR spectra were recorded in deuterated solvents on a Bruker Avance III HD Ascend 600 MHz using the solvent as an internal standard. Solid-state ^{13}C NMR spectra were recorded using a Bruker AVIII 600 MHz spectrometer with wide-bore magnet (600.3 MHz) using a 3.2 mm magic angle spinning (MAS) HXY solid-state NMR probe and running 32 k scans. Cross-polarization with MAS (CP-MAS) was used to acquire ^{13}C data at 150.9 MHz. The ^{13}C cross polarization time was 2 ms at 50 kHz for ^{13}C. ^{1}H decoupling was applied during data acquisition. The decoupling power corresponded to 100 kHz. The HXY sample spinning rate was 15 kHz.

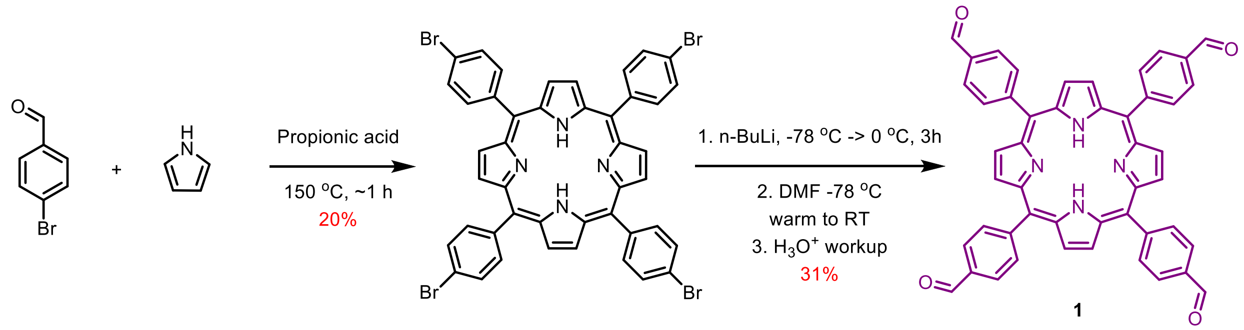
X-Ray photoelectron spectroscopy (XPS) was performed on a Kratos Axis Ultra XPS instrument. A monochromatic aluminum X-Ray (12kV, 10mA) source was used, with a charge neutralizer to minimize sample charging. The carbon 1s peak was subsequently calibrated to 284.4 eV with sample dwells ranging from 100-650 and 8 sweeps for each element.

Scanning electron microscopy (SEM) was performed on a FEI Sirion FE-SEM. Materials were deposited onto a film of wet colloidal silver paint on an aluminum sample stub and dried in a vacuum oven at 40 °C. The samples were coated with gold in a Leica EM ACE600 coater, using rotation, to a depth of approximately 20 nm. After coating the samples were imaged in the SEM at 5 keV, without tilting, using both the secondary electron (SE) detector and the through lens detector (TLD).

Elemental and ICP were performed by Galbraith Laboratories.

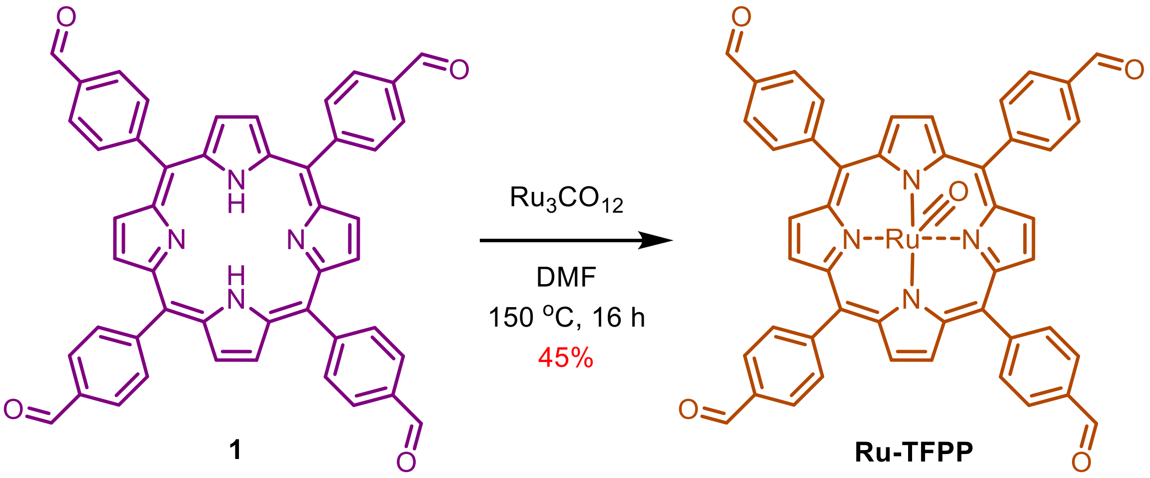
C. Synthetic Methods

C-1 Porphyrin & Polymer Synthesis



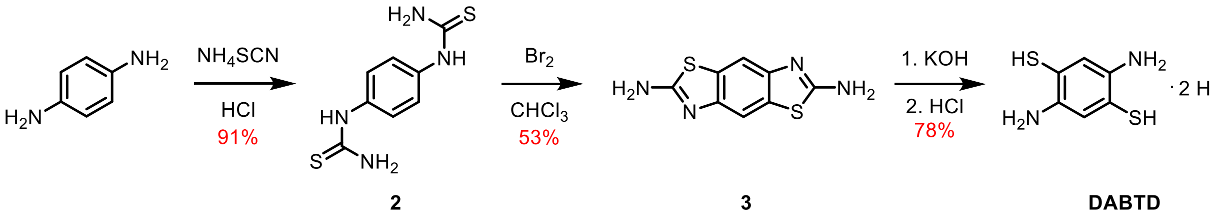
Scheme S1: Synthesis of meso-formylphenyl porphyrin **1**.

Synthesis of 1: Compound 1 was synthesized by a modified procedure from Hirel et. al.[1] To an oven-dried 100 mL flask with stirbar was added 4-bromophenylporphyrin (0.4 g, 0.42 mmol, 1 eq.). The flask was capped and degassed with N_2. Dry Et_2O (50 mL, 0.008 M) was added via syringe to the degassing mixture. The flask was cooled in a -78˚C bath before n-BuLi (2.5 M, 1.3 mL, 3.36 mmol, 8 eq.) was added via syringe. The mixture was allowed to warm to 0˚C for 3 h. After 3 h the mixture was cooled again to -78˚C and dry DMF (5 mL, 65 eq.) was added via syringe. The mixture was allowed to warm to RT over 3 h. After 3 h the mixture was opened to air and quenched by pouring into dilute HCl (1.65 M, 250 mL). Mixture stirred in air ~15 minutes before neutralizing with conc. NH_4OH solution (~30 mL). Product extracted into $CHCl_3$ and washed with water. Crude product purified by column chromatography on silica gel in 2% Et_2O in DCM, then washing with MeCN to afford the purified product in 31% yield as deep purple solids. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 10.40 (4 H, s), 8.83 (8 H, s), 8.43-8.29 (16 H, dd). ^{13}C-NMR (Acetone d-6, 175 MHz) δ 192.2, 143.6, 135.9, 134.8, 131.7, 127.8, 127.5.



Scheme S2: Synthesis of **Ru-TFPP**.

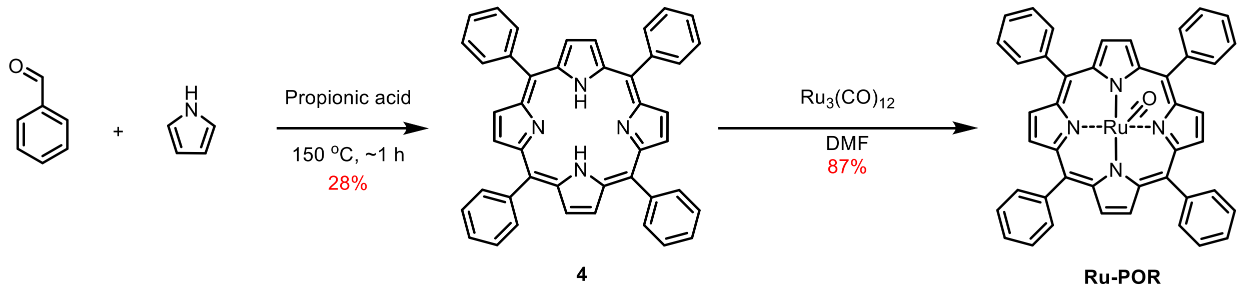
Synthesis of Ru-TFPP: To an oven-dried 25 mL flask with stir bar was added **1** (0.1 g, 0.13 mmol, 1 eq.) and Ru_3CO_{12} (0.04 g, 0.062 mmol, 1.4 eq.) where the Ru_3CO_{12} was added in an argon glovebox. The flask was capped with an oven-dried vigreux condenser, then degassed with N_2. Degassed DMF (8 mL, 0.016 M) was added to the mixture, and the flask was submerged in a 150 ˚C oil bath and allowed to react under positive pressure N_2 overnight (~18 h). After ~18 h mixture was allowed to cool before pouring into dilute HCl (100 mL, 1 M) and filtering to isolate solids. Crude solids are purified by column chromatography on silica gel in 1% Et_2O in DCM to afford pure **Ru-TFPP** in 45% yield. ^{1}H-NMR (acetone-d6, 400 MHz) δ 10.45 (4H, s), 8.71 (8H, d), 8.51 (4H, d), 8.41 (4H, d), 8.36 (8H, m). ^{13}C-NMR (acetone-d6, 175 MHz) δ 192.24, 143.53, 136.01, 134.68, 134.62, 131.76, 127.98, 127.46. HRMS (ESI): m/z calcd. For $C_{49}H_{28}N_4O_5Ru$ $[M+Na]^+$: 877.100, observed 877.101.



Scheme S3: Synthesis of **DABTD**.

Compounds **2**, **3**, and **DABTD** were synthesized using a procedure by Wolfe et. al.[2]

Synthesis of Ru-BBT-POP: To an oven dried 10 mL flask with stir bar was added (**4**) (0.0245 g, 0.1 mmol, 1 eq.) (which has been stored and weighed out in glovebox) the flask was then capped and degassed with N_2 while dry DMF:*o*-xylenes (1:1 v:v, 2.5 mL) was added. The mixture was cooled to -78˚C. A solution of **Ru-TFPP** (0.0427 g, 0.05 mmol, 0.5 eq.) in DMF:*o*-xylenes (1:1 v:v, 2.5 mL) was created and added to the salt via syringe under degassing conditions. The mixture was allowed to stir under N_2 at -78˚C for 5 hours. After stirring cold, the mixture was removed from the bath and allowed to warm to room temperature and stir under N_2 overnight (~16 h). After overnight stirring the mixture was degassed with air (1 balloon). The mixture was heated in a 130˚C bath open to air for 4d. After 4d the mixture was allowed to cool, then filtered to isolate solids, and washed with acetone. Unreacted starting materials were removed by soaking polymer solids in MeOH for 1d (changing MeOH 3x) and DCM for 1d (changing DCM 3x) then dried under high vacuum to give BBT-RuP POP (50 mg, 98% yield). ICP-AES analysis found 6.32 wt% of Ru in the COF. Elemental Analysis for $(C_{61}H_{40}N_8S_4O_4Ru)_n$: Calculated C (61.34%) H (3.38%) N (9.38%) S (10.74%). Observed C (60.07%), H (4.04%), N (9.49%), S (7.21%). ^{13}C CP-MAS NMR (75.5 MHz) δ 167.0, 151.1, 142.9, 132.0, 124.2, 119.9, 114.1 ppm. FT-IR (solid, ATR) 2917, 1934, 1701, 1685, 1600, 1522, 1483, 1425, 1399, 1346, 1309, 1205, 1106, 1071, 1005, 958, 853, 809, 789, 713, 688, 607 cm^{-1}.



Scheme S4: Synthesis of **Ru-POR**.

Compound **4** was synthesized using a procedure by Das et. al.[3]

Synthesis of Ru-POR: **4** (0.2064 g, 0.33 mmol, 1 eq.) and Ru_3CO_{12} (0.4035g. 0.63 mmol 1.91 eq.) were added to a flame dried flask equipped with a reflux condenser and placed under N_2 gas. Degassed DMF (6 mL) was added to the reaction flask and the solution was heated to 120 °C for 16 h. The reaction mixture was cooled before pouring into HCl (100 mL, 1M). Orange solids crashed out of solution and were filtered, rinsing with water. The solids were dissolved in 1:1 DCM:acetone and run through a plug of celite to remove insoluble byproducts. The filtrate was collected, removing the solvent under vacuum. The solids were washed with hexanes to leave **Ru-POR**. (0.2188 g, 0.29 mmol, 87%) ^{1}H-NMR (acetone-d6, 400 MHz) δ 8.65 (8 H, s), 8.24 (4 H, m), 8.11 (4 H, d), 7.96 (4 H, s) 7.81-7.76 (8H, m). ^{13}C-NMR (acetone d-6, 175 MHz) δ 143.9, 142.6, 133.9, 133.9, 131.4, 127.5, 126.6, 126.5.

D. FT-IR Spectra

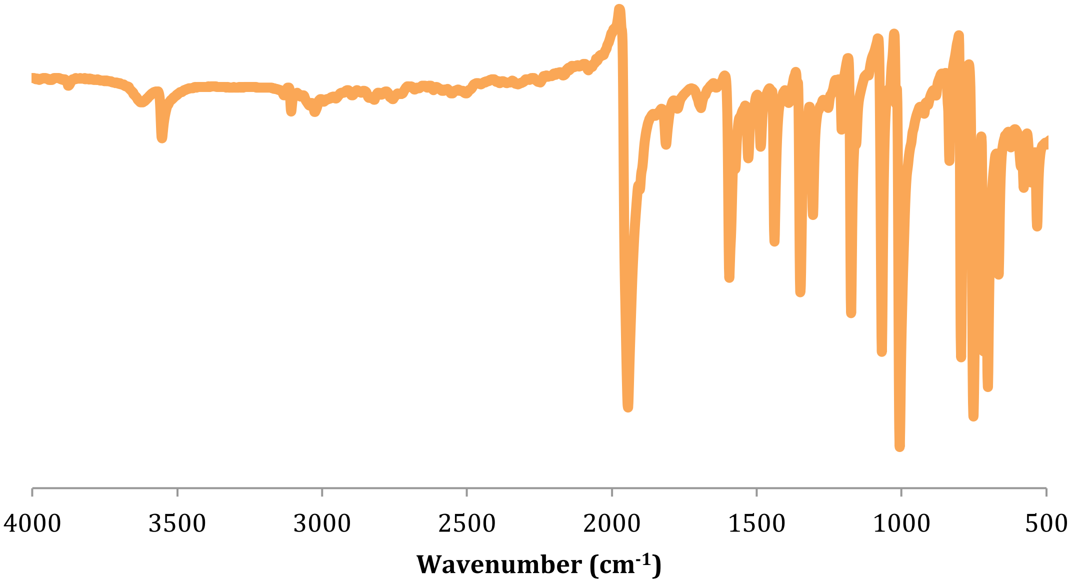


Figure S1. FT-IR spectrum of **Ru-POR**.

Table S1. FT-IR peak assignments for **Ru-POR**.

Peak (cm^{-1})	Assignment
1944	**C≡O stretch of carbon monoxide ligand**
1594	**C=C stretch of phenyls**
1573	**C=N stretch of porphyrin**
1006	**Ru-C stretching**

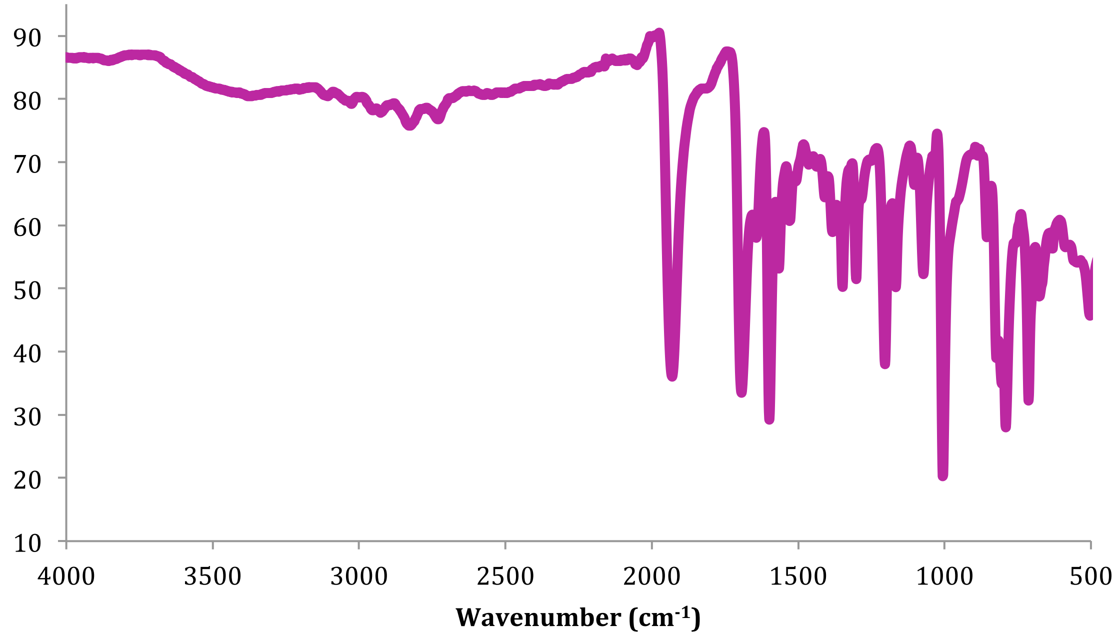


Figure S2. FT-IR spectrum of **Ru-TFPP**.

Table S2. FT-IR peak assignments **Ru-TFPP**.

Peak (cm^{-1})	Assignment
1938	**C≡O stretch of carbon monoxide ligand**
1698	**C=O stretch of aldehyde**
1598	**C=C stretch of phenyls**
1569	**C=N stretch of porphyrin**
1006	**Ru-C stretching**

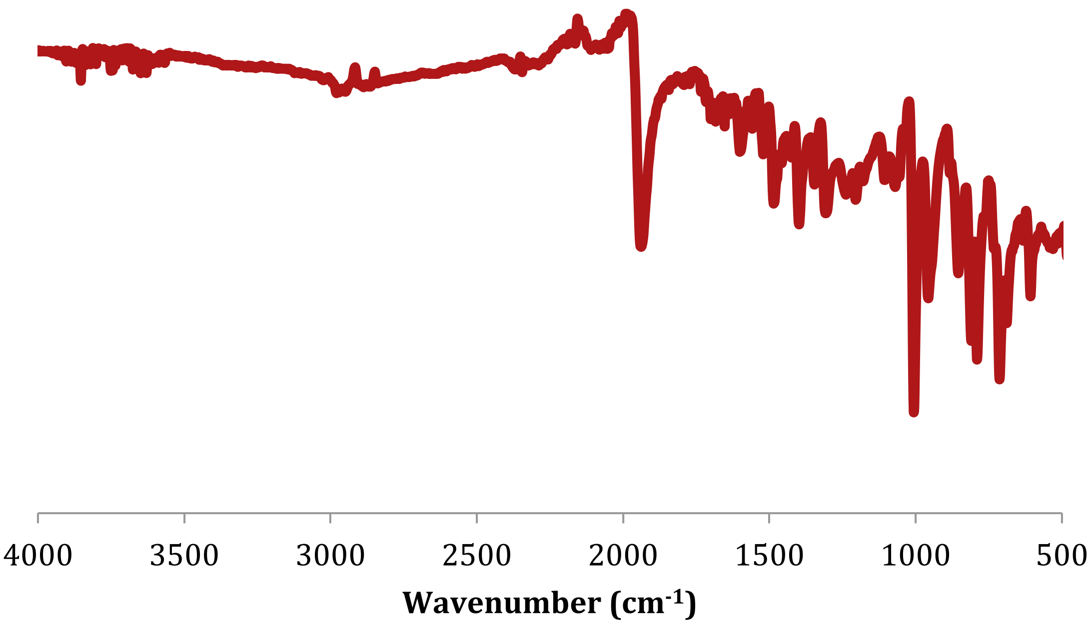


Figure S3. FT-IR spectrum of **Ru-BBT-POP**.

Table S3. FT-IR peak assignments for **Ru-BBT-POP**.

Peak (cm^{-1})	Assignment
1938	**C≡O stretch of carbon monoxide ligand**
1654	**C=N stretch of thiazole**
1600	**C=C stretch of phenyl**
1521	**C=N stretch of porphyrin**
1006	**Ru-C stretching**
713	**C-S stretch of thiazole**

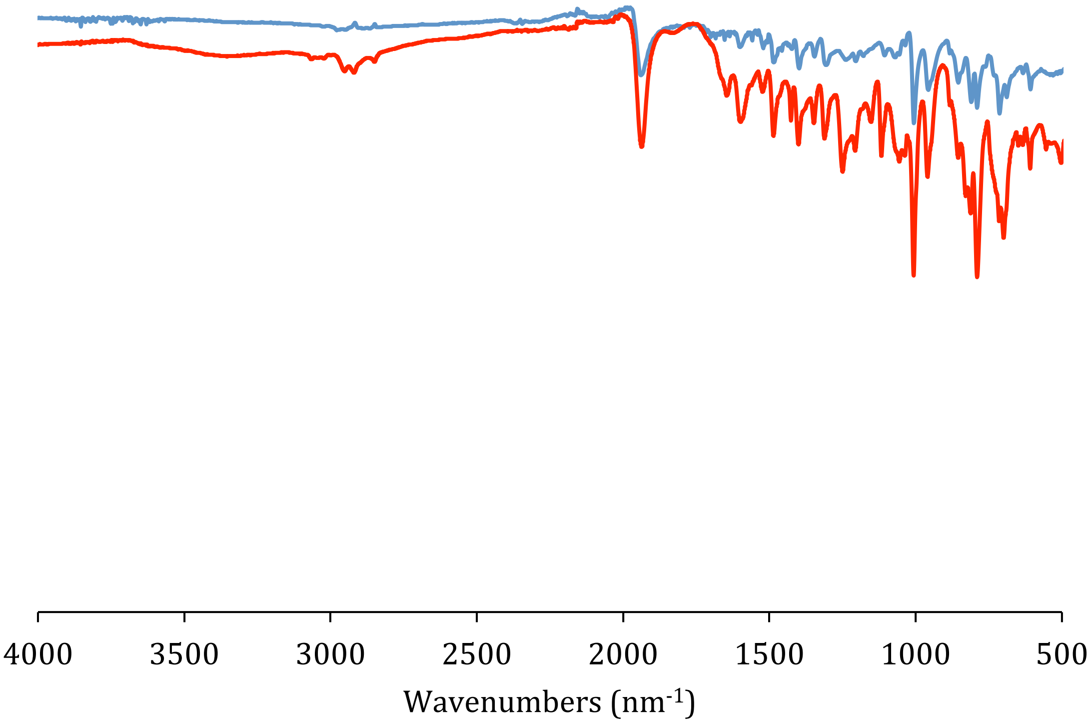


Figure S4. FT-IR spectrum of **Ru-BBT-POP** before (blue) and after (red) the hydrosilylative reduction of CO_2.

E. Experimental PXRD Profiles

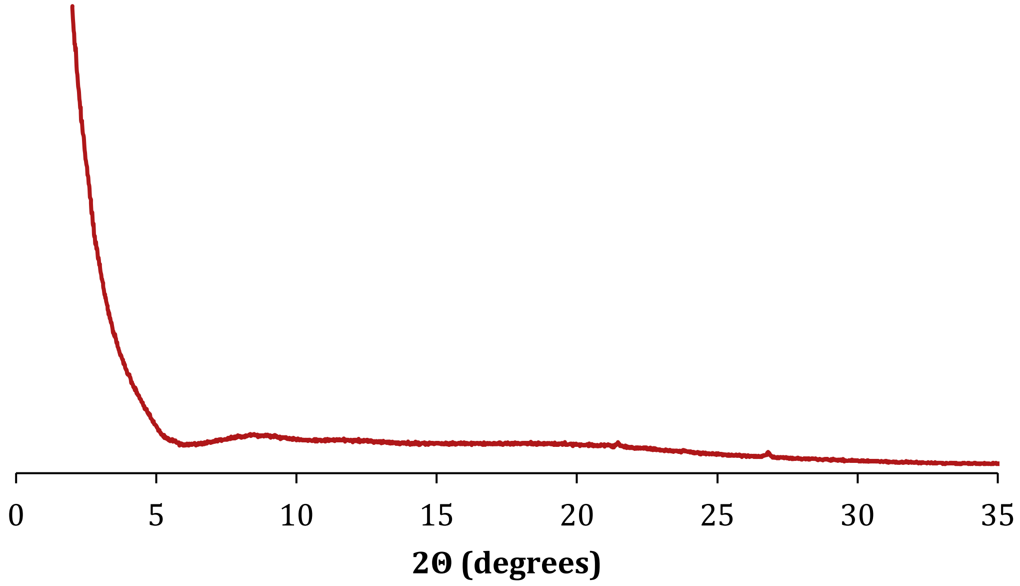


Figure S5. PXRD profile of **Ru-BBT-POP**.

F. Solid-State NMR Spectra

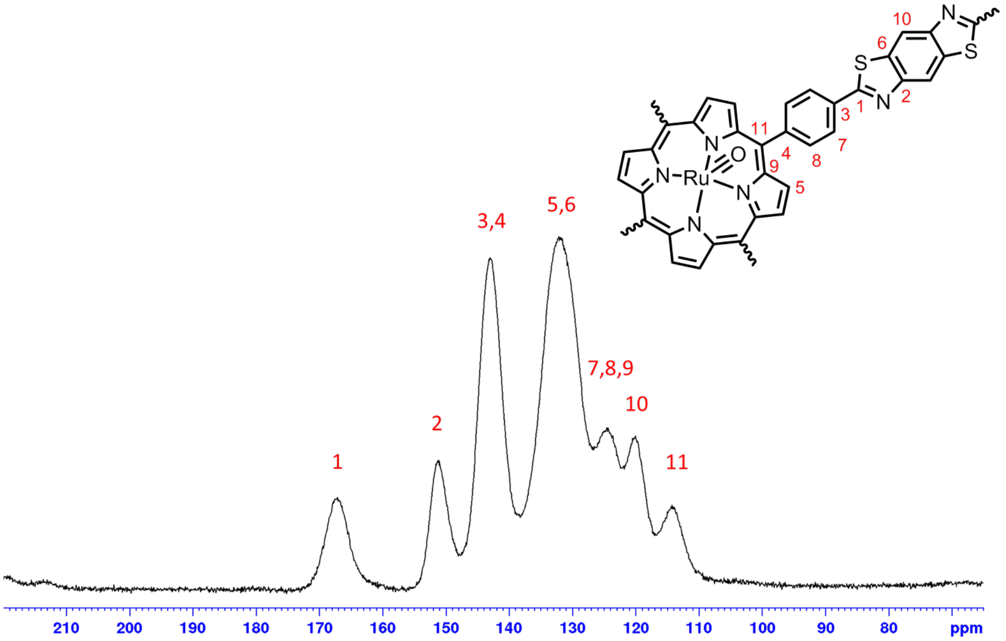


Figure S6. ^{13}C CP-MAS of **Ru-BBT-POP**.

G. TGA Profile

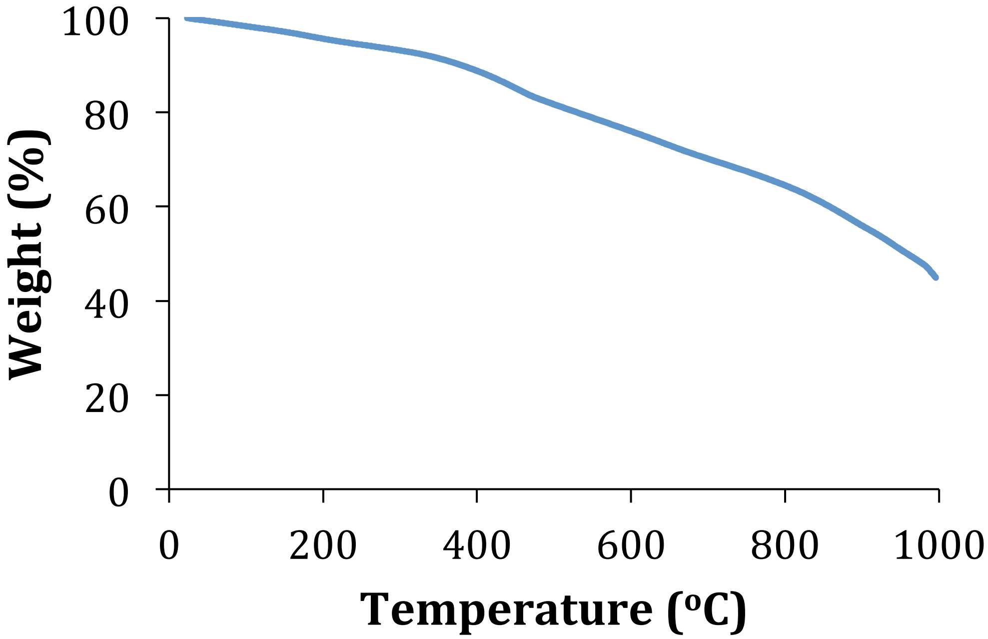


Figure S7. TGA profile of **Ru-BBT-POP**.

H. BET Surface Area Plots

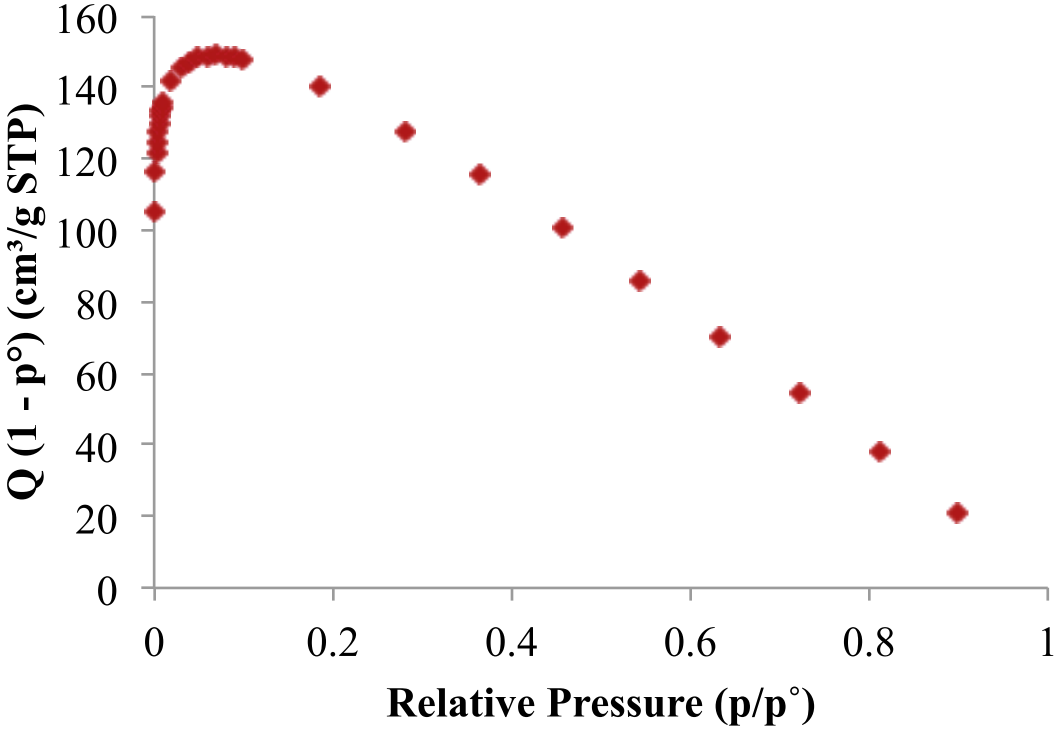


Figure S8. Roquerol BET analysis of **Ru-BBT-POP**.

Table S4. BET values derived from Roquerol BET analysis of **Ru-BBT-POP**.

Ru-BBT-POP			
(P/P_0)	BET (m^2/g)	Correlation coefficient	C
0.001001-0.069851	655	0.9999	1138.19
0.001001-0.060028	654	0.9999	1156.92
0.001001-0.049236	652	0.9999	1191.37

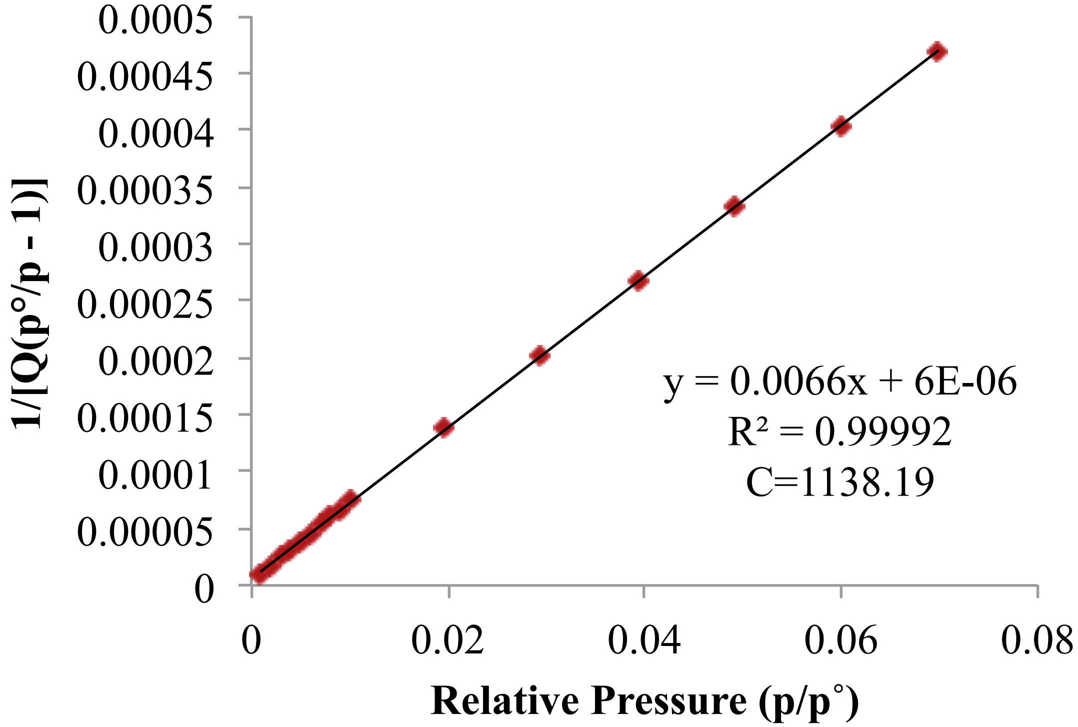


Figure S9. BET surface area plot for **Ru-BBT-POP**.

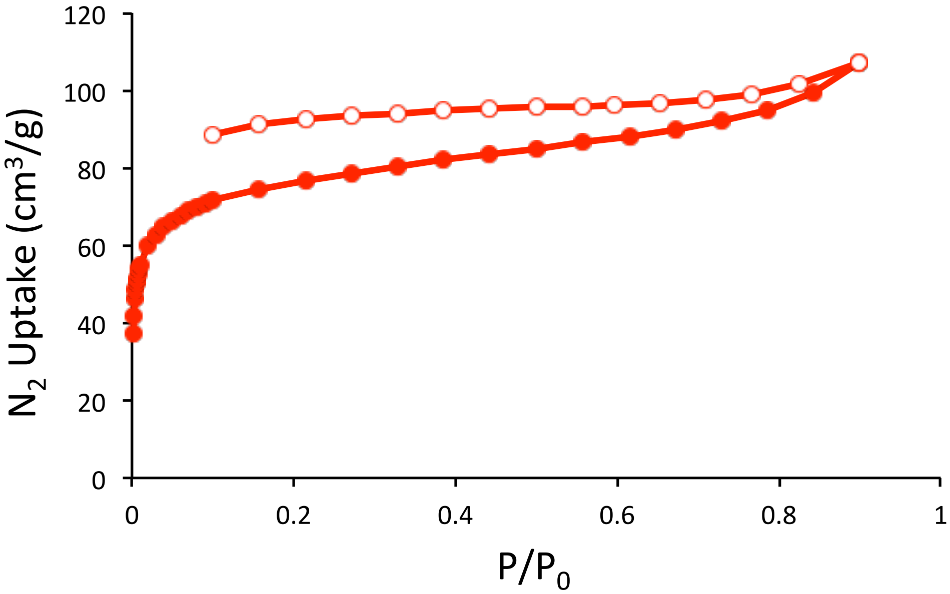


Figure S10. Nitrogen adsorption/desorption isotherm at 77 K of **Ru-BBT-POP** after catalysis.

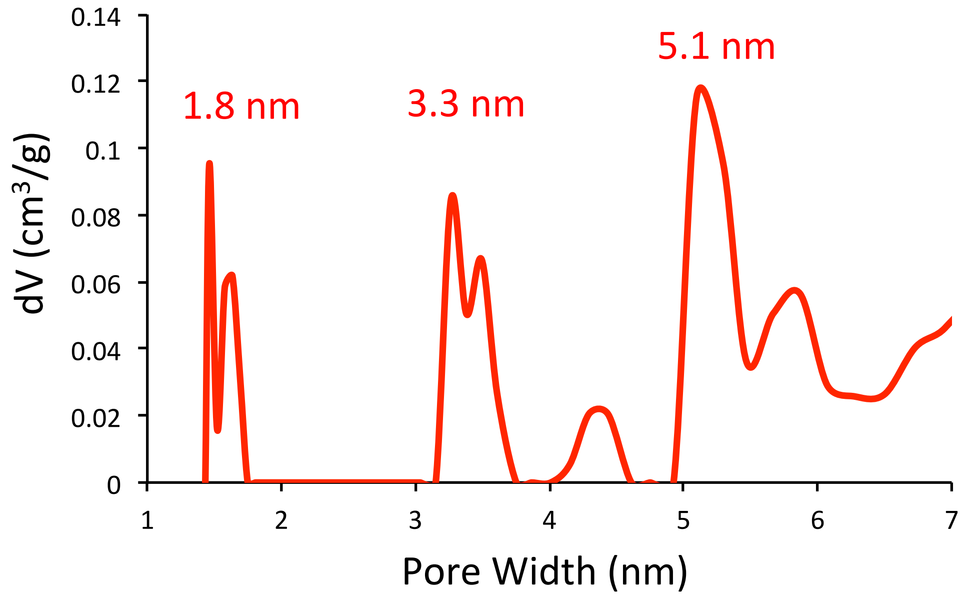


Figure S11. NLDFT pore size distribution of **Ru-BBT-POP** after catalysis.

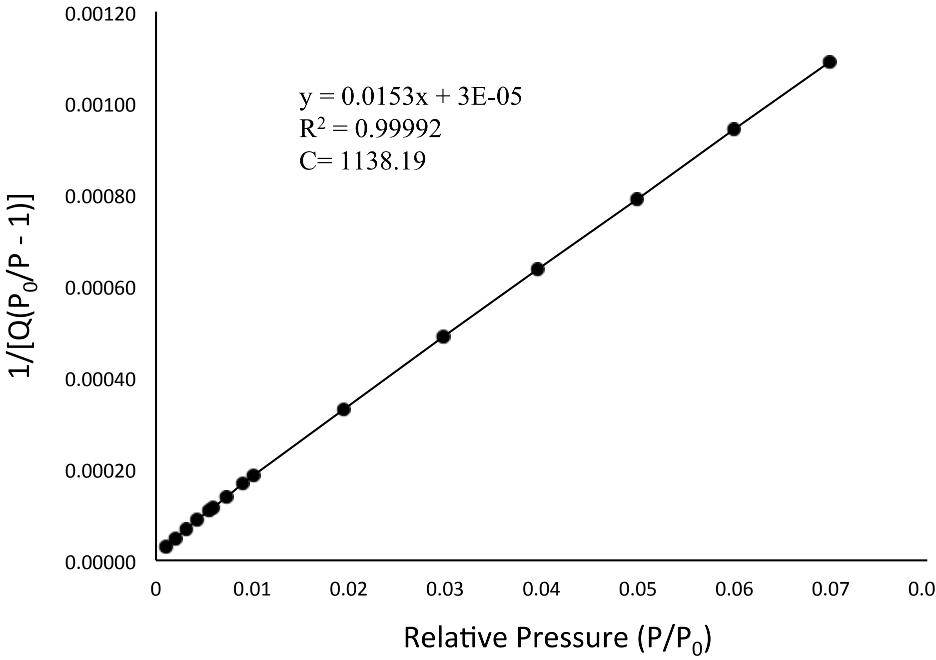


Figure S12. BET surface area plot for **Ru-BBT-POP** after catalysis.

Table S5. Physical parameters of Ru-BBT-POP before and after catalysis.

Sample	BET Surface (m^2 g^{-1})	Pore Width (nm)	Pore Volume (cm^3 g^{-1})
Ru-BBT-POP (Before)	655	1.8, 3.3, 5.1	0.312
Ru-BBT-POP (After)	284	1.4, 3.3, 5.3	0.126

I. CO_2 Isotherms

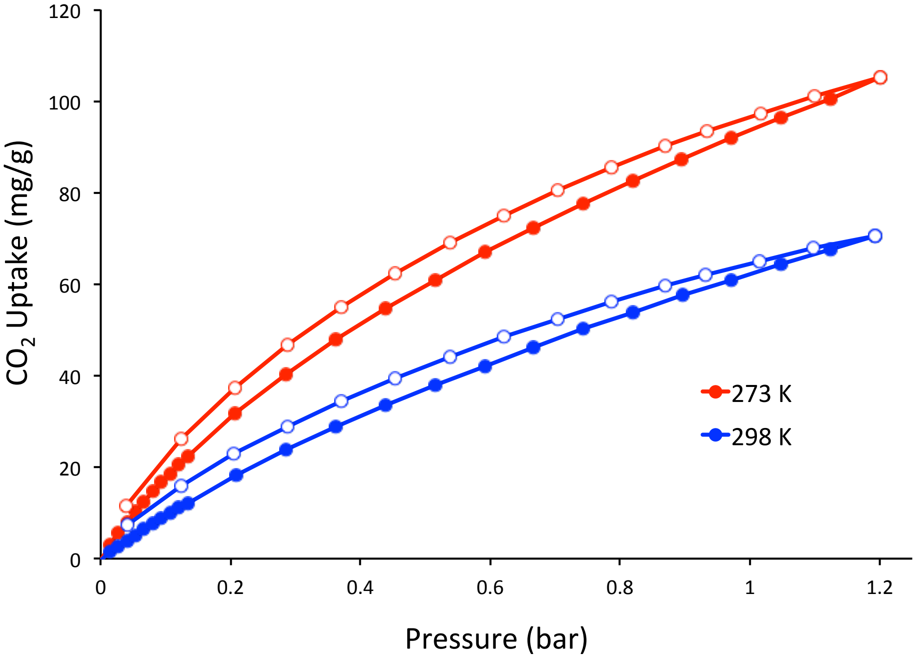


Figure S13. CO_2 adsorption (filled) and desorption (unfilled) isotherms for **Ru-BBT-POP** at 273 and 298 K.

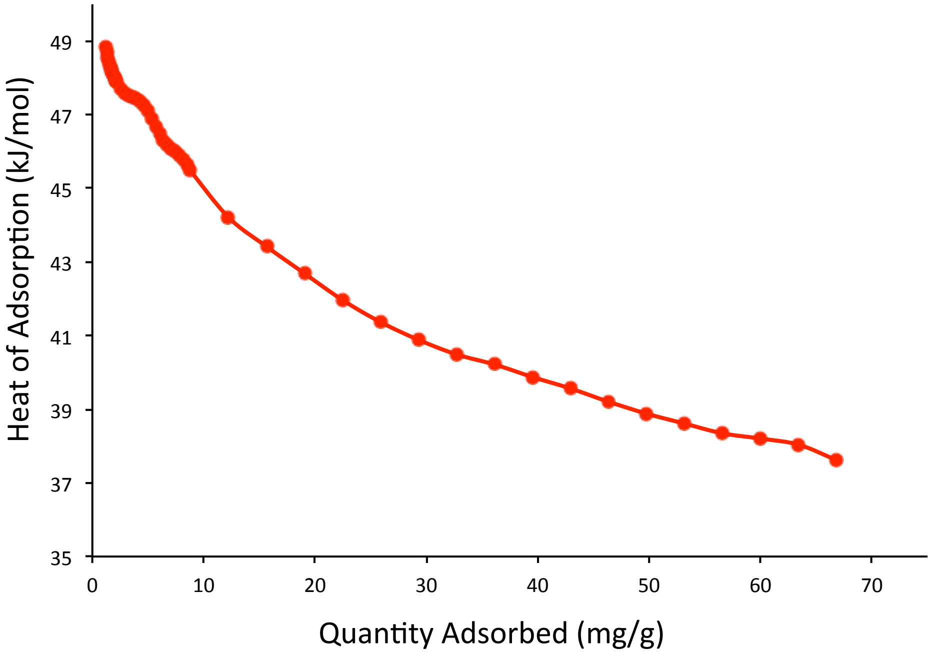


Figure S14. CO_2 isoteric heat of adsorption plot for **Ru-BBT-POP**.

J. SEM Micrographs

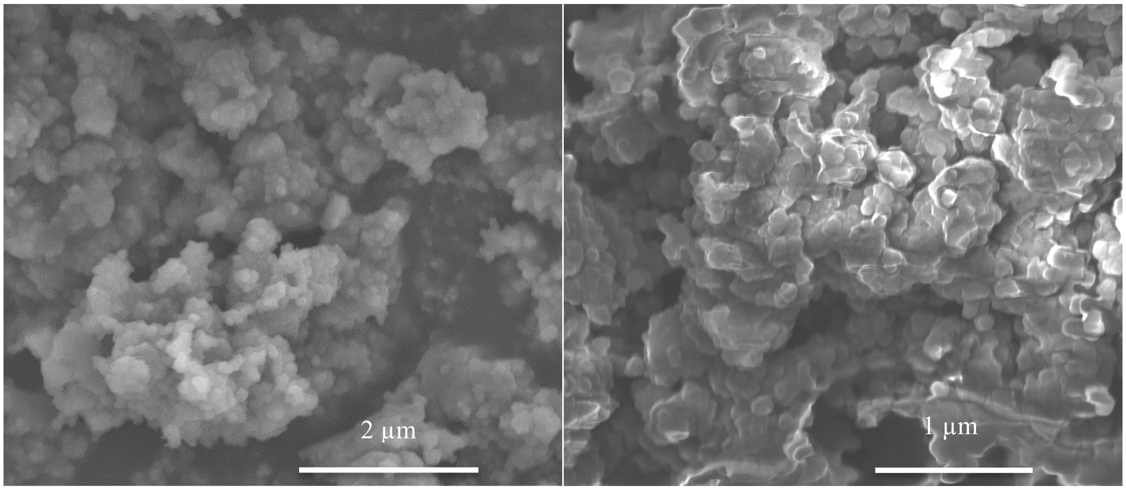


Figure S15. SEM images of **Ru-BBT-POP**.

K. UV-Vis and Emission Spectra

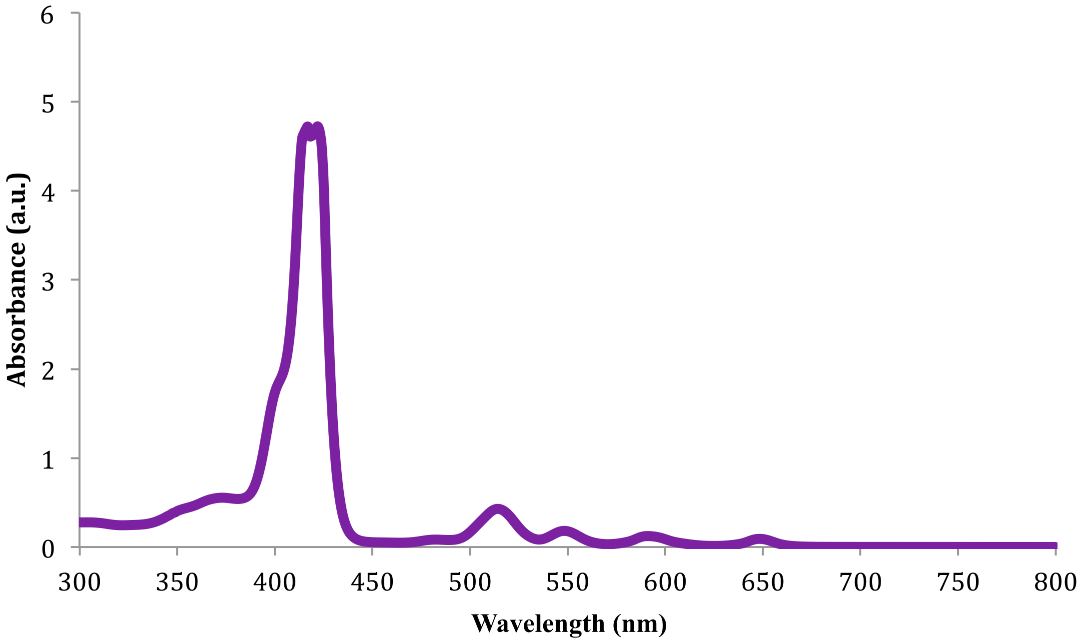


Figure S16. UV-Vis spectrum of **1** in toluene.

The UV-Vis absorbance of **1** shows the existence of several peaks corresponding to 379, 417, 423, 517, 551, 597, and 653 nm. The molecule contains Soret bands at 417 and 423 nm and Q bands at 517, 551, 597, and 653 which confirms formation of the porphyrin.

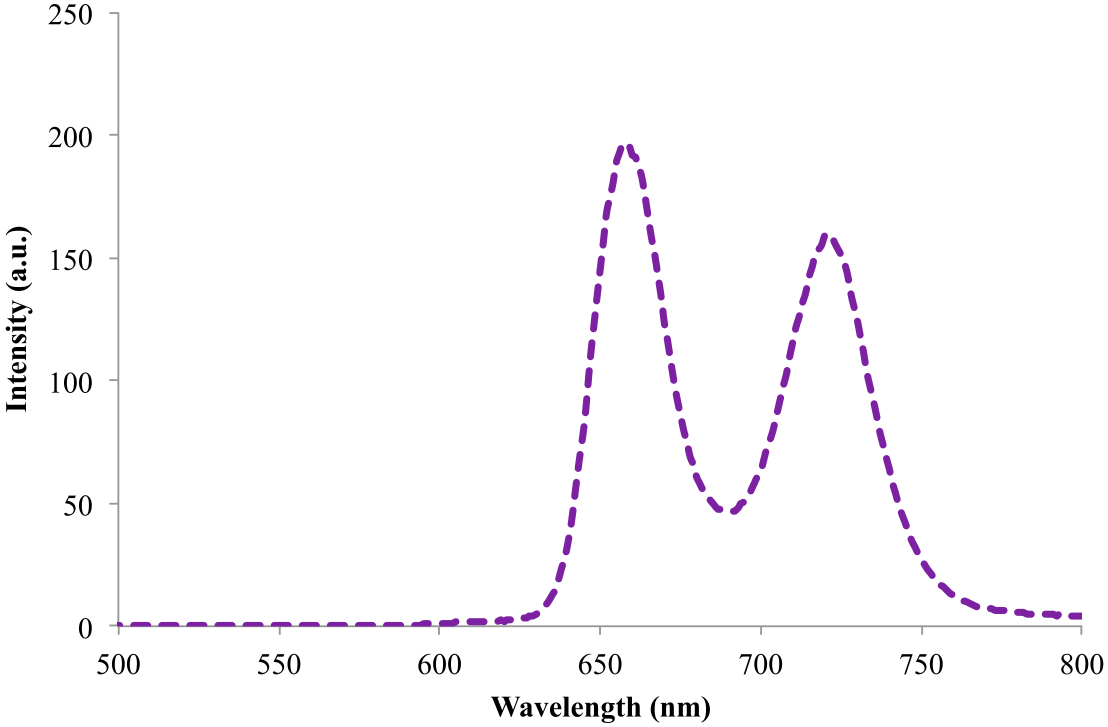


Figure S17. Fluorescence spectrum of **1** in toluene ($\lambda_{excitation}$= 430 nm).

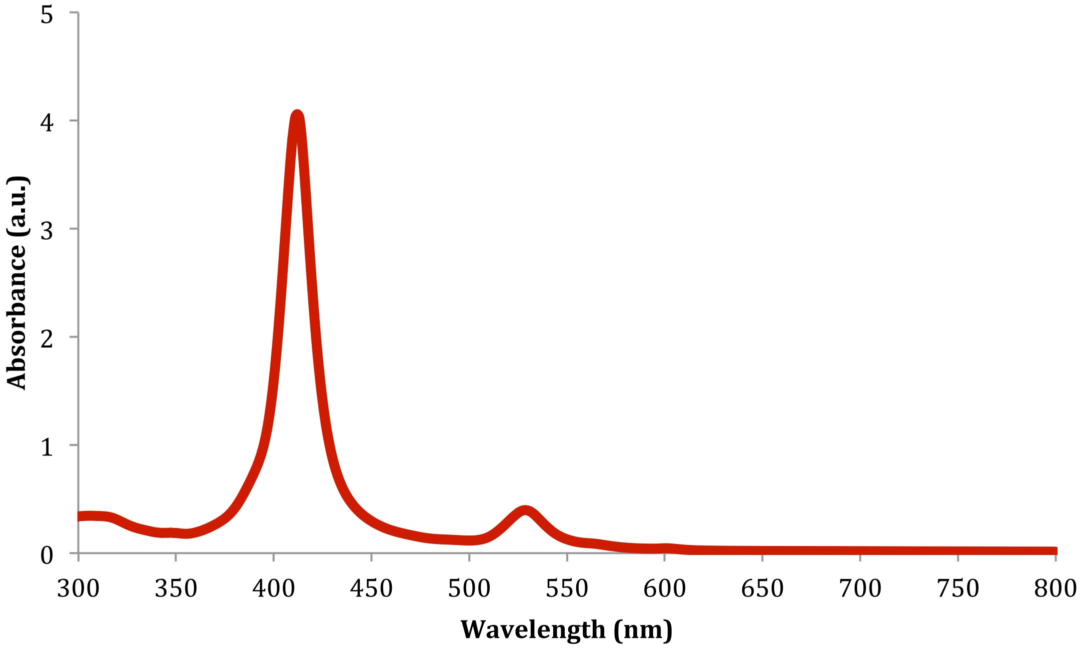


Figure S18. UV-Vis spectrum of **Ru-TFPP** in acetone.

The UV-Vis absorbance of **Ru-TFPP** shows the existence of several peaks corresponding to 318, 412, 531, and 571 nm. The molecule contains a Soret band at 423 nm and Q bands at 531 and 571.

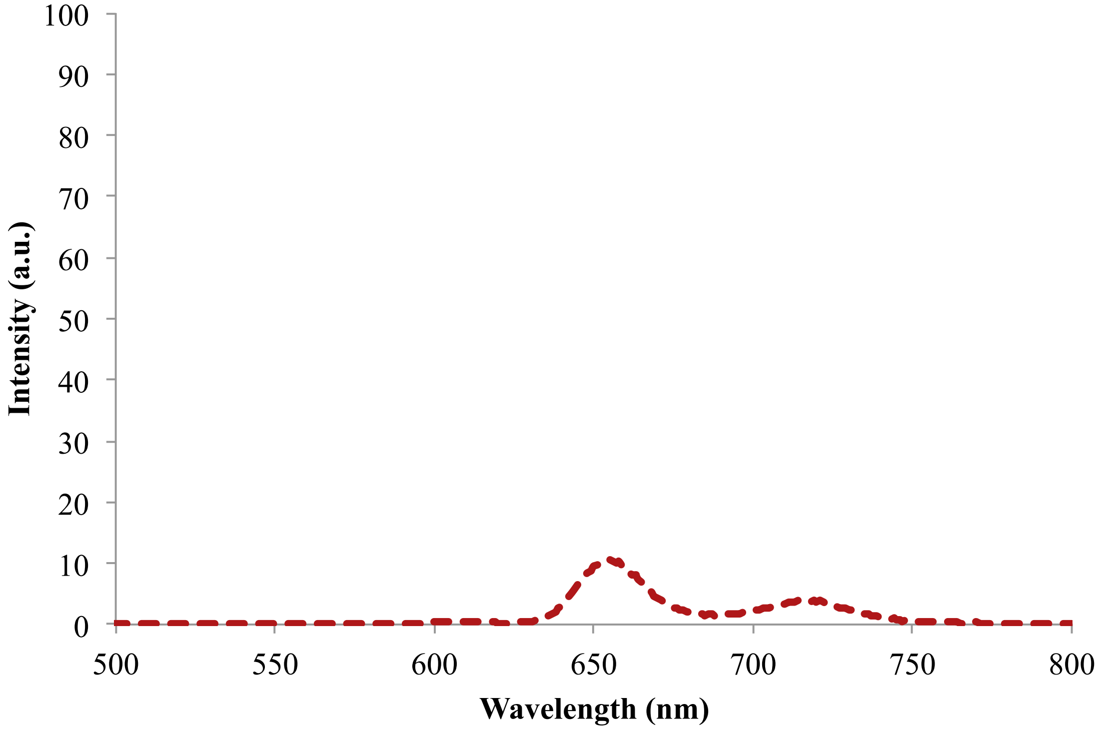


Figure S19. Fluorescence spectum of **Ru-TFPP** in acetone ($\lambda_{excitation}$= 415 nm).

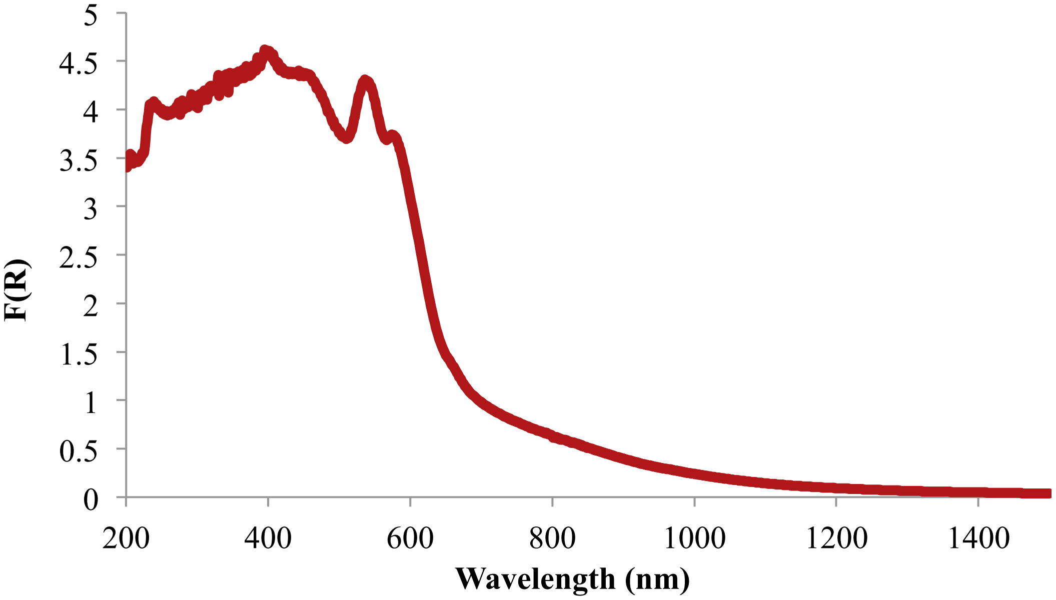


Figure S20. Kubelka-Munk function diffuse reflectance spectrum of **Ru-BBT-POP**.

The UV-Vis absorbance of **Ru-BBT-POP** shows the existence of several peaks corresponding to 243, 404, 466, 542, and 662 nm. The molecule contains a Soret band at 466 nm and Q bands at 542 and 662 nm. The bathochromic shift of the Soret band is due to extended conjugation in the polymer versus the small molecule **Ru-TFPP**.

L. XPS Spectra

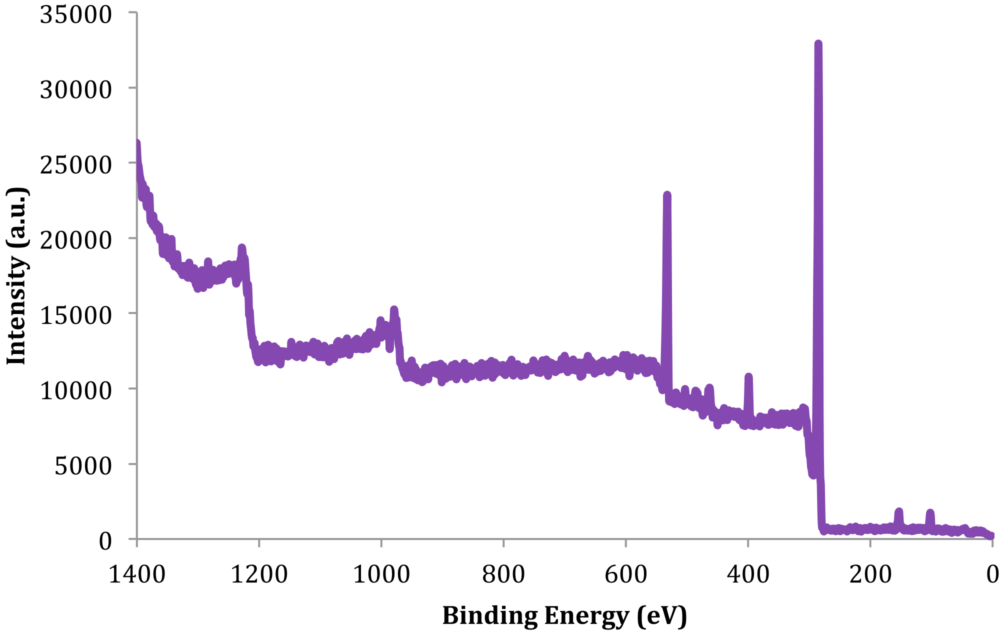


Figure S21. Full XPS spectrum of **Ru-TFPP**.

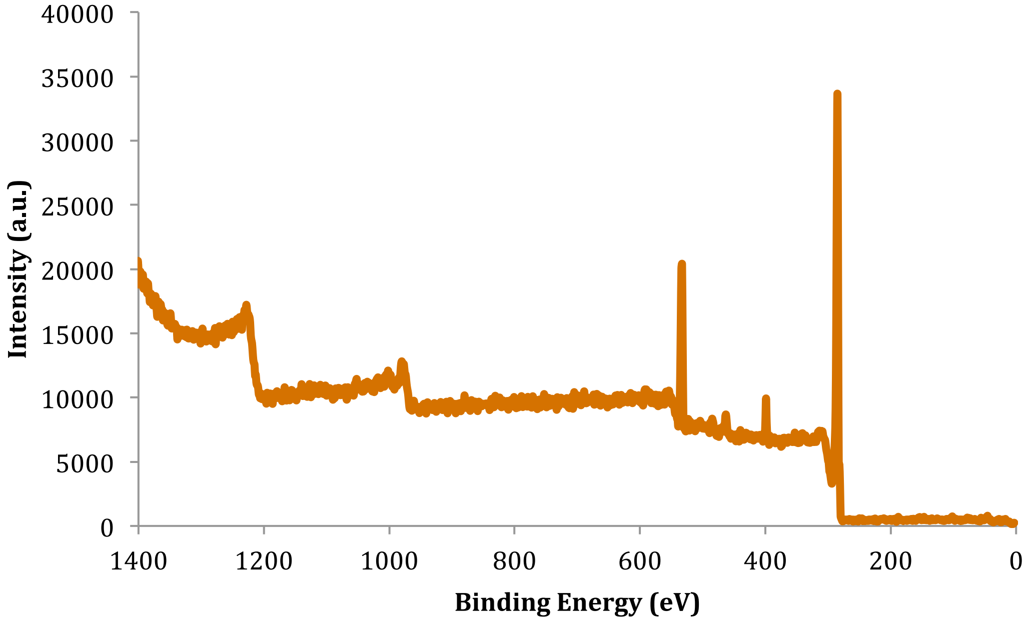


Figure S22. Full XPS spectrum of **Ru-POR**.

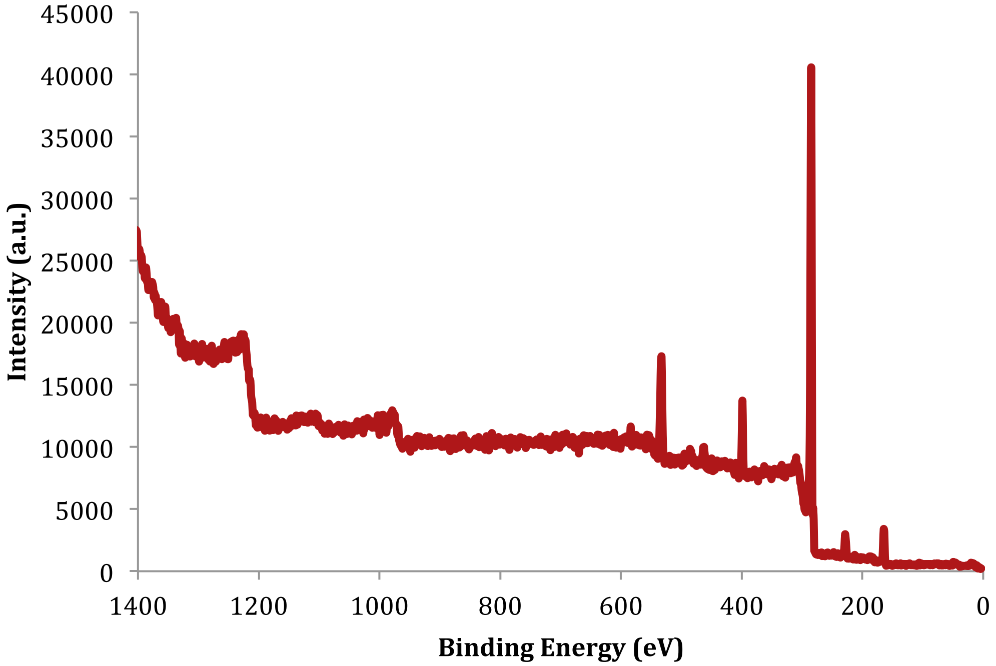


Figure S23. Full XPS spectrum of **Ru-BBT-POP**.

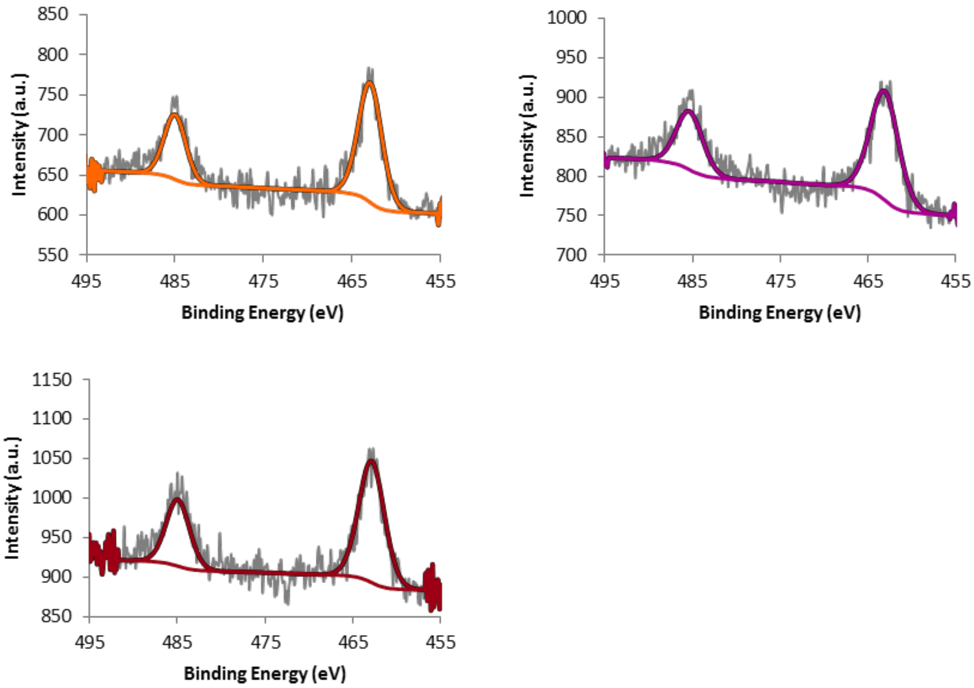


Figure S24. XPS spectra of the Ru 3P for **Ru-POR** (top left), **Ru-TFPP** (top right), and **Ru-BBT-POP** (bottom left).

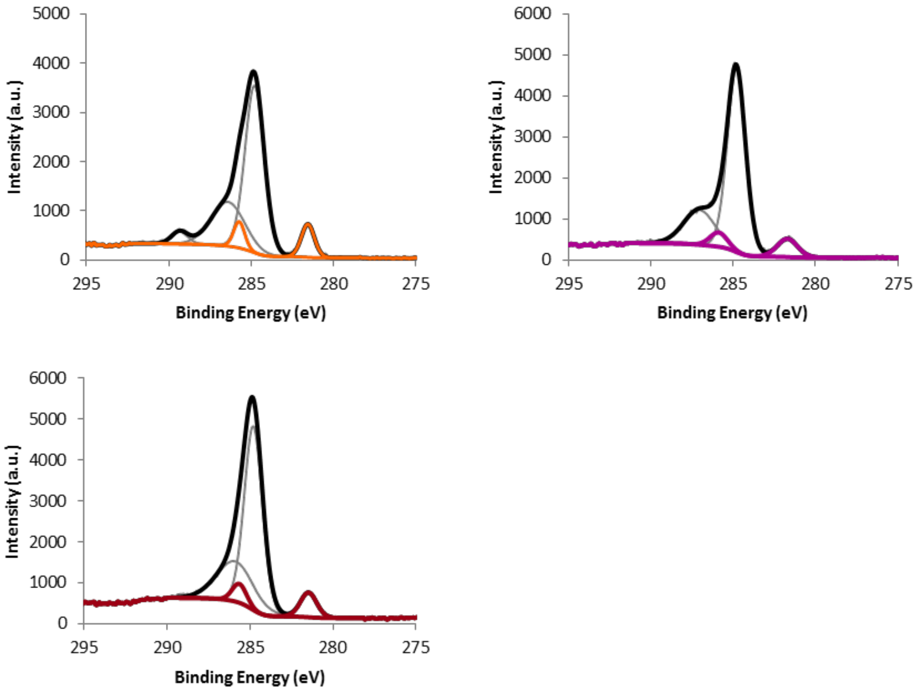


Figure S25. Full XPS Spectra of the Ru 3D and C 1S for **Ru-POR** (top left), **Ru-TFPP** top right), and **Ru-BBT-POP** (bottom left).

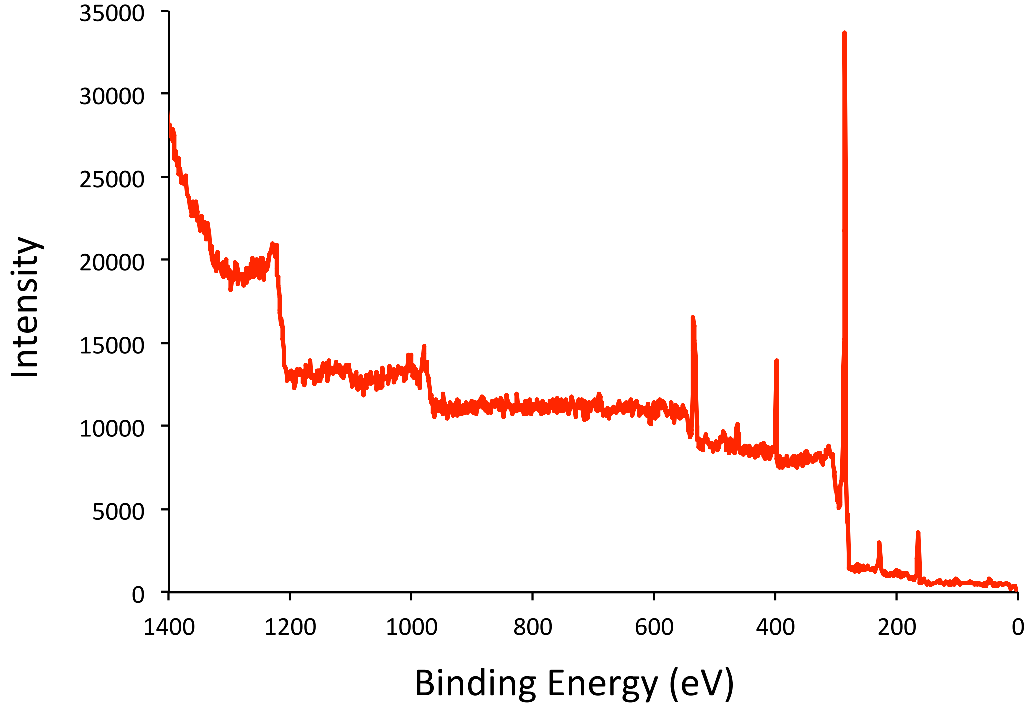


Figure S26. Full XPS spectrum of **Ru-BBT-POP** after catalysis.

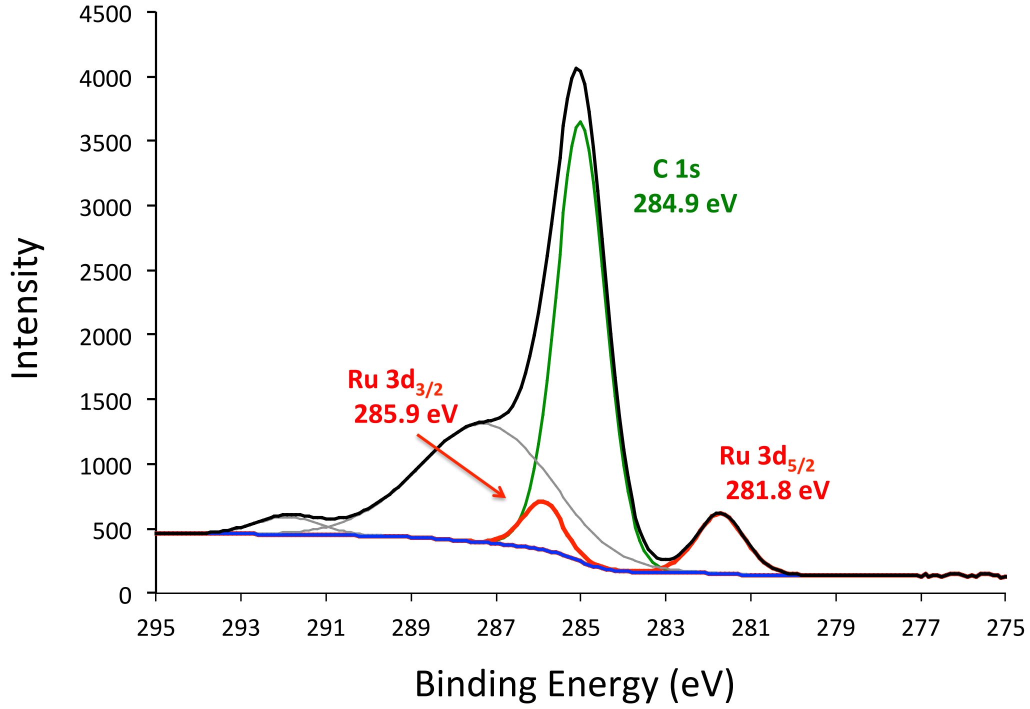


Figure S27. Full XPS spectrum of **Ru-BBT-POP** showing the Ru 3d$_{5/2}$ and Ru 3d$_{3/2}$ core energy levels remain intact after catalysis.

M. Catalytic Methods

Catalysis Conditions under 1 atm of CO_2 with Ru-POR: Ru-POR (0.0040 g, 0.005 mmol, 0.005 eq.) was added to a 4 mL vial, with KF (0.060 g, 1 mmol, 1 eq.) and dissolved in the chosen solvent (2 mL). A silane (1 mmol, 1 eq.) was added and the reaction was run under 1 atm of CO_2. The reaction was heated just below reflux while stirring for a number of hours. After, the reaction was cooled to room temperature and the solvent was removed under vacuum. The solids were dissolved in water and extracted with DCM (3 x 4 mL). The aqueous layer was separated and collected, before lyophilizing off the water to give potassium formate. The product was quantified using ^{1}H NMR in D_2O and using DMSO as an internal standard. Results found in Table S6.

Table S6. Summary of catalysis condition under 1 atm of CO_2 with **Ru-POR**.

Solvent	Time	Temperature	Silanes			
			Et_3SiH	PMHS	Me_2PhSiH	EtO_3SiH
Dioxane	4h	100 °C	0 %	0 %	0 %	1 %
THF	4h	60 °C	0 %	0 %	0 %	1 %
MeCN	4h	80 °C	22 %	3 %	19 %	3 %
MeCN	16h	80 °C	26 %	5 %	27 %	4 %
MeCN	24h	80 °C	16 %	5 %	22 %	5 %
MeCN	48h	80 °C	14 %	1 %	18 %	6 %

Catalysis Conditions Bubbling CO_2 with Ru-POR: Ru-POR (0.0040 g, 0.005 mmol, 0.005 eq) was added to a 50 mL two-necked round bottomed flask connected with a reflux condenser, with KF (0.060 g, 1 mmol, 1 eq) and dissolved in acetonitrile (10 mL). Me_2PhSiH (0.15 mL, 1 mmol, 1 eq) was added and 1 atm of CO_2 was bubbled through the solution. The reaction was heated at 60 °C while stirring for 4 h. After, the reaction was cooled to room temperature and the solvent was removed under vacuum. The solids were dissolved in water and extracted with DCM (3 x 4 mL). The aqueous layer was separated and collected, before lyophilizing off the water to give potassium formate. The product was quantified using ^{1}H NMR in D_2O and using DMSO as an internal standard. Results found in Table S7.

Table S7. Summary of catalysis condition bubbling CO_2 with **Ru-POR**.

Entry	Catalyst	Time	Temp.	Silane	Yield	TON	TOF
1	**Ru-POR 0.5%**	4 h	45 ^{o}C	Me_2PhSiH	33 %	66	17 h^{-1}
2	**Ru-POR 0.5%**	4 h	60 ^{o}C	Me_2PhSiH	55 %	110	28 h^{-1}
3	**Ru-POR 0.5%**	4 h	80 ^{o}C	Me_2PhSiH	28 %	57	14 h^{-1}
4	**Ru-POR 0.5%**	4 h	60 ^{o}C	Et_3SiH	18 %	36	9 h^{-1}
5^{a}	**Ru-POR 0.5%**	4 h	60 ^{o}C	Me_2PhSiH	0 %	0	0 h^{-1}

^{a}Trial was performed without KF present.

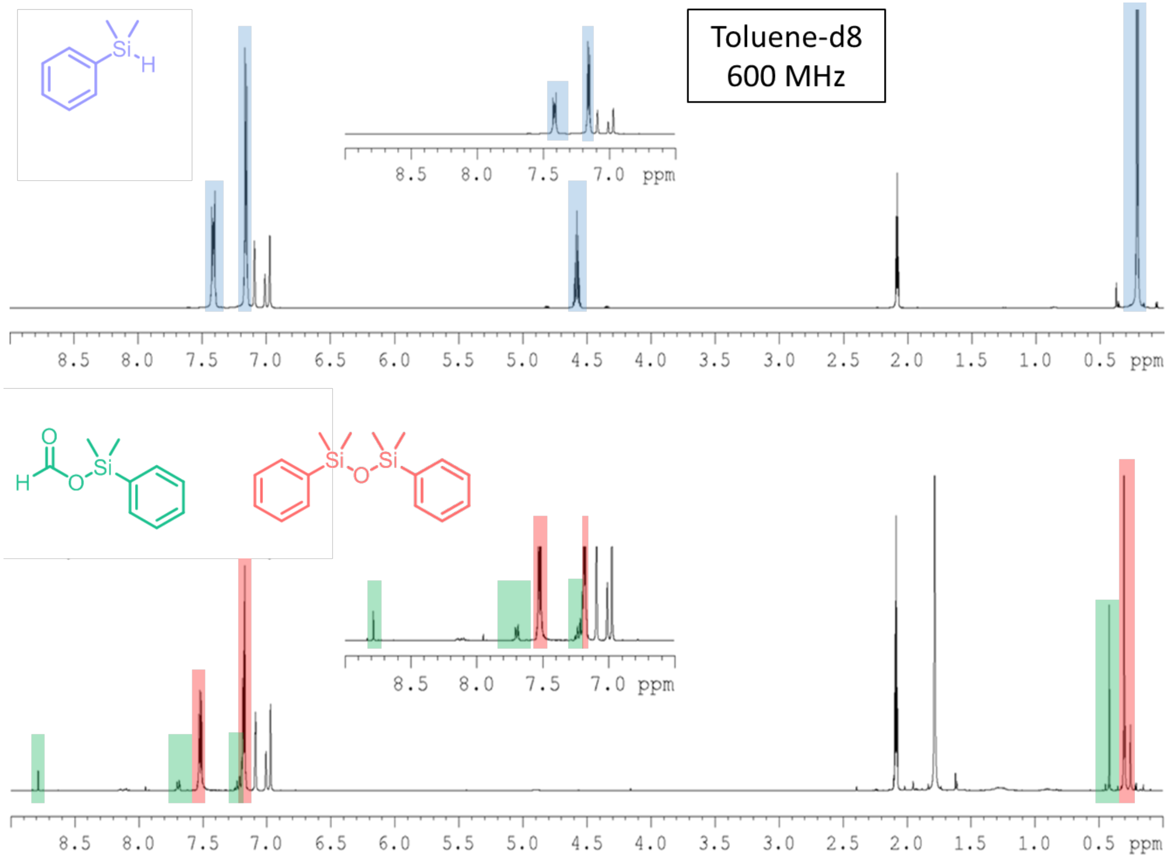


Figure S28. ^{1}H-NMR of dimeethylphenylsilane (top), compared with catalysis trial without KF (bottom) using 0.5% **Ru-POR** loading. The dimethylphenylsilane protons are labelled in blue, the dimethylphenyl siloxane protons are labelled in red, and the dimethylsilyl formate protons are labelled in green. The ratio of siloxane to silyl formate formed was 19:1.

The hydrosilylation pathway of this reaction is evident in the above ^{1}H-NMR data. The disappearance of the multiplet at 4.5 ppm in the bottom spectrum provides evidence of the complete consumption of the silane. The appearance of the singlet at ~8.7 ppm, the doublet at ~7.7 ppm, and the small multiplet at ~7.25 ppm is indicative of the formation of dimethylphenylsilyl formate. The overwhelming product is the further reduction to dimethylphenylsilyl ether.

Catalysis Conditions Bubbling CO_2 with 0.5% Ru-BBT-POP Loading: Ru-BBT-POP (0.0060 g, 0.005 mmol, 0.005 eq.) was added to a 50 mL two-necked round bottomed flask connected with a reflux condenser, with KF (0.060 g, 1 mmol, 1 eq.) and dissolved in acetonitrile (10 mL). Me_2PhSiH (0.15 mL, 1 mmol, 1 eq.) was added and 1 atm of CO_2 was bubbled through the solution. The reaction was heated at 60 ^oC while stirring for 4 h. After, the reaction was cooled to room temperature and the solvent was removed under vacuum. The solids were dissolved in water and extracted with DCM (3 x 4 mL). The aqueous layer was separated and collected, before lyophilizing off the water to give potassium formate. The product was quantified using ^1H NMR in D_2O and using DMSO as an internal standard. Results can be found in Table S8.

Table S8. Summary of recyclable catalysis condition bubbling CO_2 with **0.5% Ru-BBT-POP** loading.

Recycle Trial	Catalyst	Time	Temp.	Silane	Yield	TON	TOF
1	**Ru-BBT-POP 0.5%**	4 h	60 ^oC	Me_2PhSiH	25 %	67	17 h^{-1}
2	**Ru-BBT-POP 0.5%**	4 h	60 ^oC	Me_2PhSiH	23 %	61	15 h^{-1}
3	**Ru-BBT-POP 0.5%**	4 h	60 ^oC	Me_2PhSiH	22 %	58	14 h^{-1}

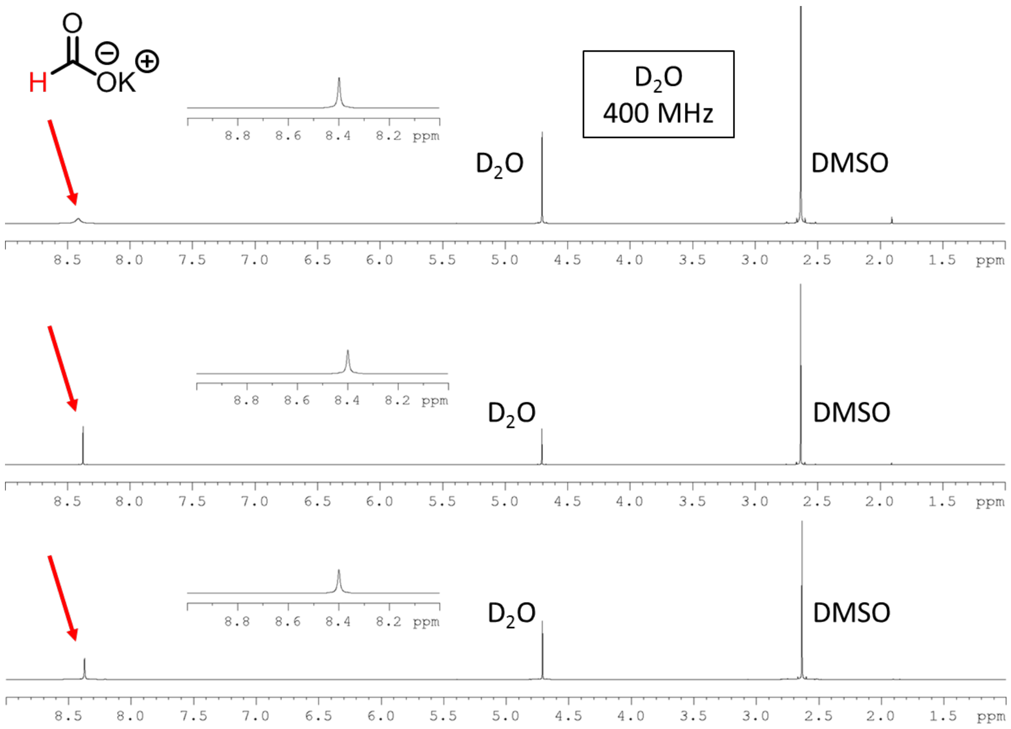


Figure S29. ^1H-NMR of recyclability trials 1 (top), 2 (middle), and 3 (bottom) with **0.5% Ru-BBT-POP** loading.

Catalysis Conditions Bubbling CO_2 with 1% Ru-BBT-POP Loading: Ru-BBT-POP (0.0090 g, 0.01 mmol, 0.01 eq.) was added to a 50 mL two-necked round bottomed flask connected with a reflux condenser, with KF (0.060 g, 1 mmol, 1 eq.) and dissolved in acetonitrile (10 mL). Me_2PhSiH (0.15 mL, 1 mmol, 1 eq.) was added and 1 atm of CO_2 was bubbled through the solution. The reaction was heated at 60 °C while stirring for 4 h. After, the reaction was cooled to room temperature and the solvent was removed under vacuum. The solids were dissolved in water and extracted with DCM (3 x 4 mL). The aqueous layer was separated and collected, before lyophilizing off the water to give potassium formate. The product was quantified using ^1H NMR in D_2O and using DMSO as an internal standard. Results can be found in Table S9.

Table S9. Summary of recyclable catalysis condition bubbling CO_2 with **1% Ru-BBT-POP** loading.

Recycle Trial	Catalyst	Time	Temp.	Silane	Yield	TON	TOF
1	**Ru-BBT-POP 1%**	4 h	60 °C	Me_2PhSiH	41 %	55	14 h^{-1}
2	**Ru-BBT-POP 1%**	4 h	60 °C	Me_2PhSiH	43 %	57	14 h^{-1}
3	**Ru-BBT-POP 1%**	4 h	60 °C	Me_2PhSiH	44 %	58	15 h^{-1}

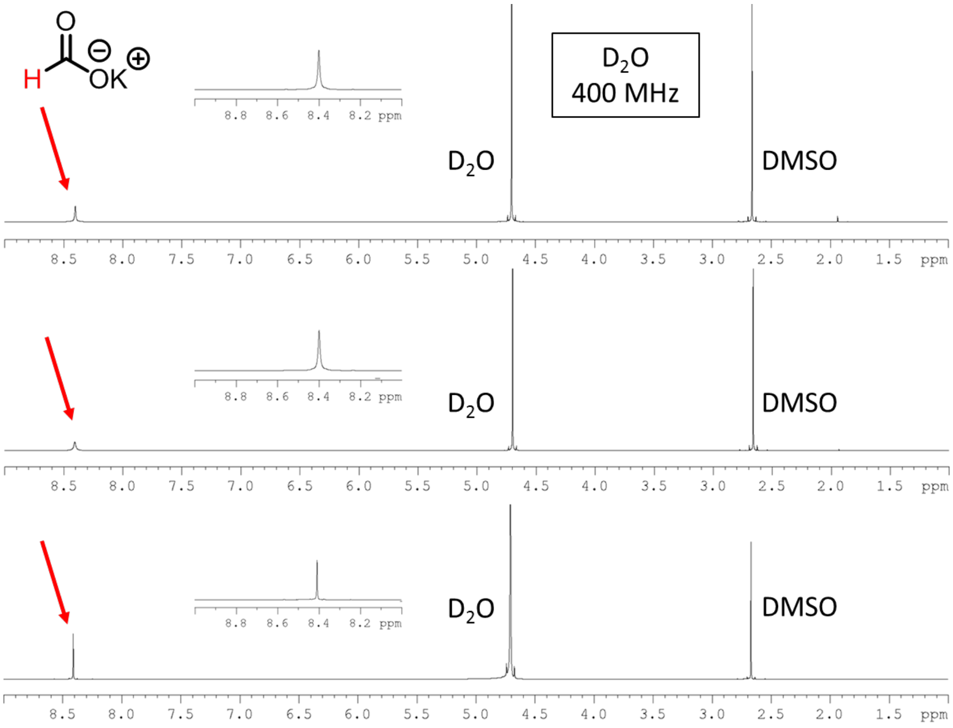


Figure S30. ^1H-NMR of recyclability trials 1 (top), 2 (middle), and 3 (bottom) with **1% Ru-BBT-POP** loading.

N. ^{1}H, ^{13}C NMR Spectra, and HRMS

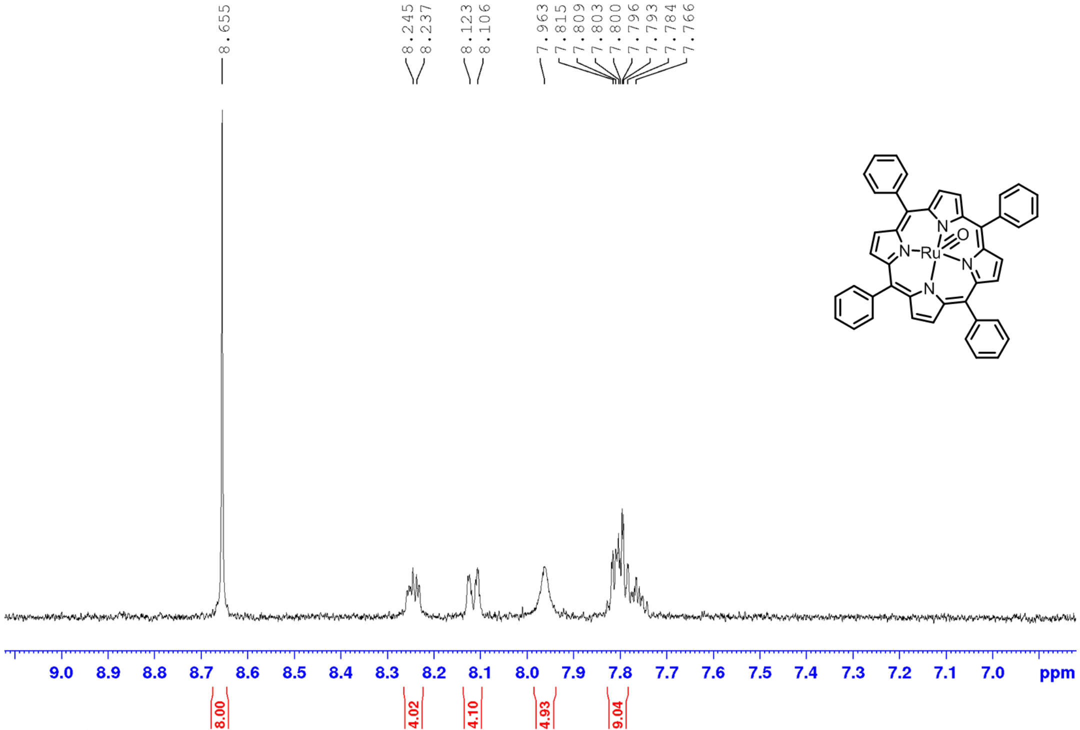


Figure S31. ^{1}H NMR spectra of **Ru-POR**.

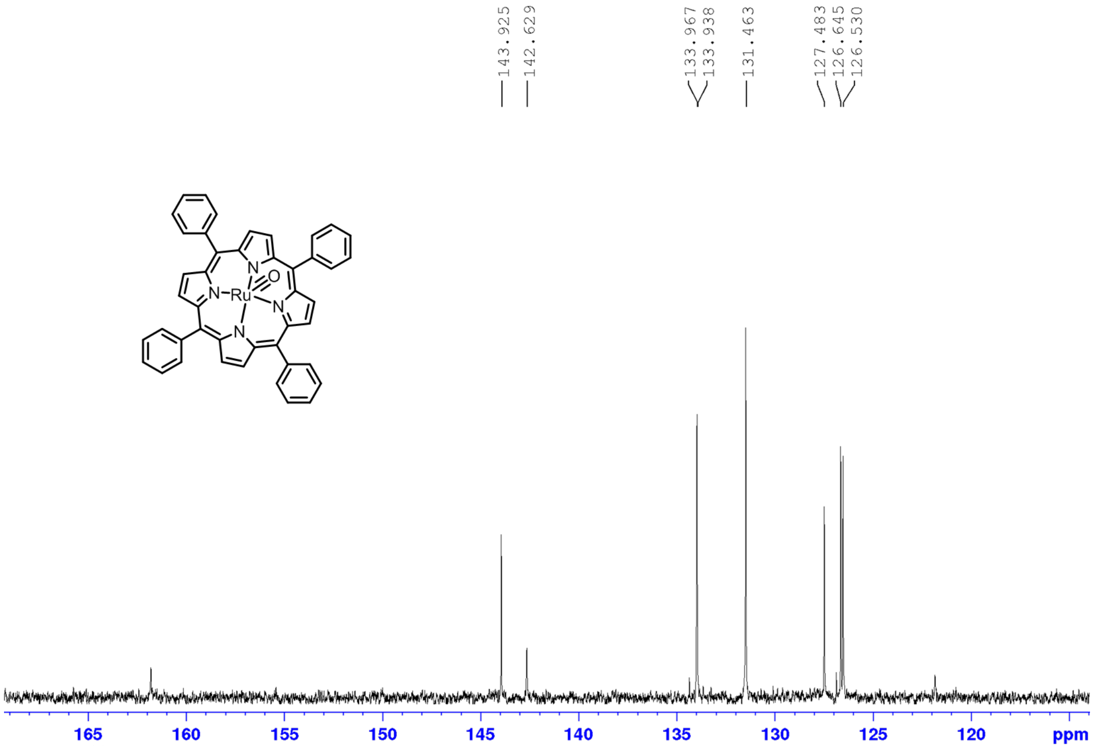
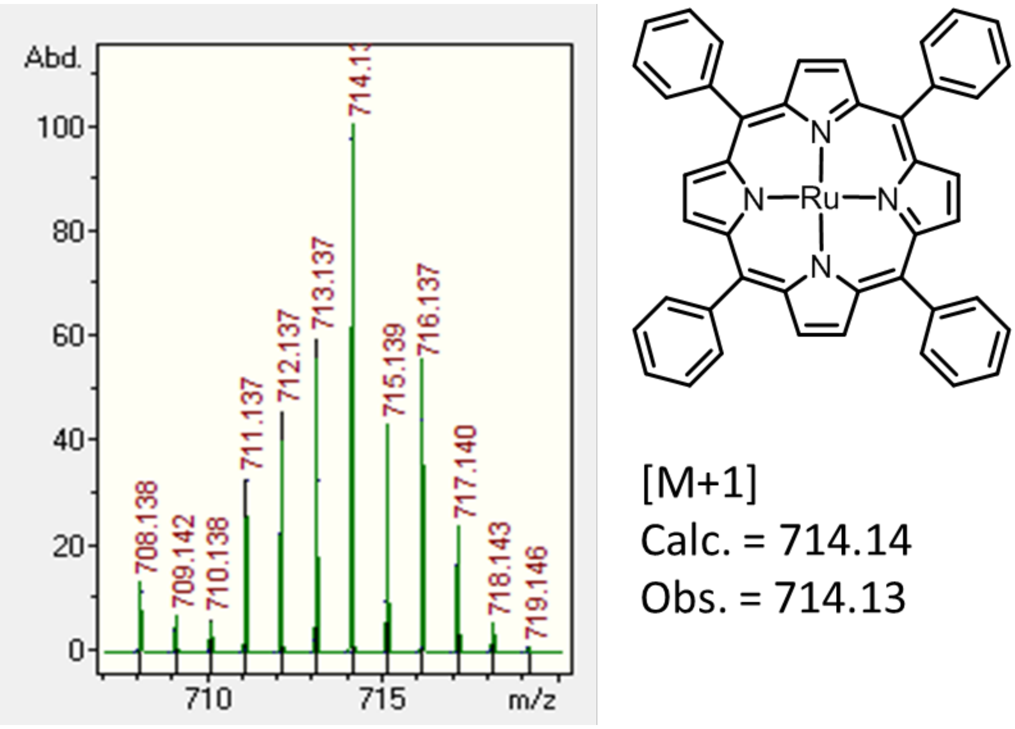


Figure S32. ^{13}C NMR spectra of **Ru-POR**.



[M+1]
Calc. = 714.14
Obs. = 714.13

Figure S33. High resolution mass spectrometry of **Ru-POR**, with loss of ligand.

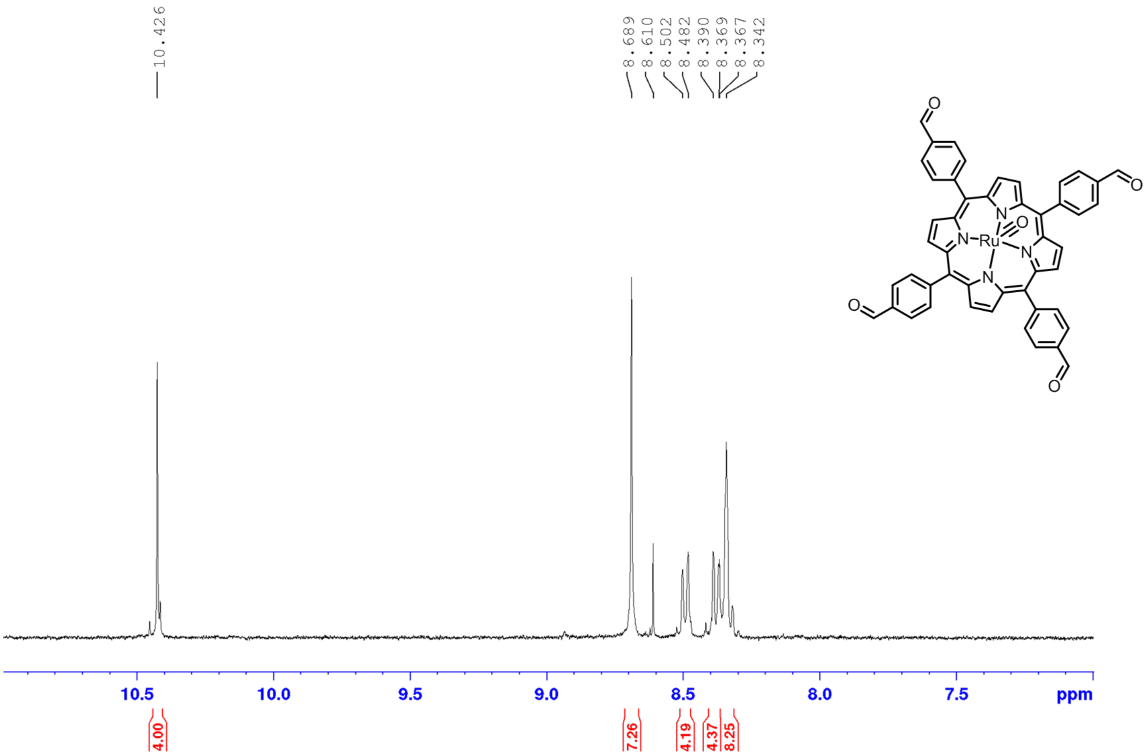


Figure S34. ^{1}H NMR spectra of **Ru-TFPP**.

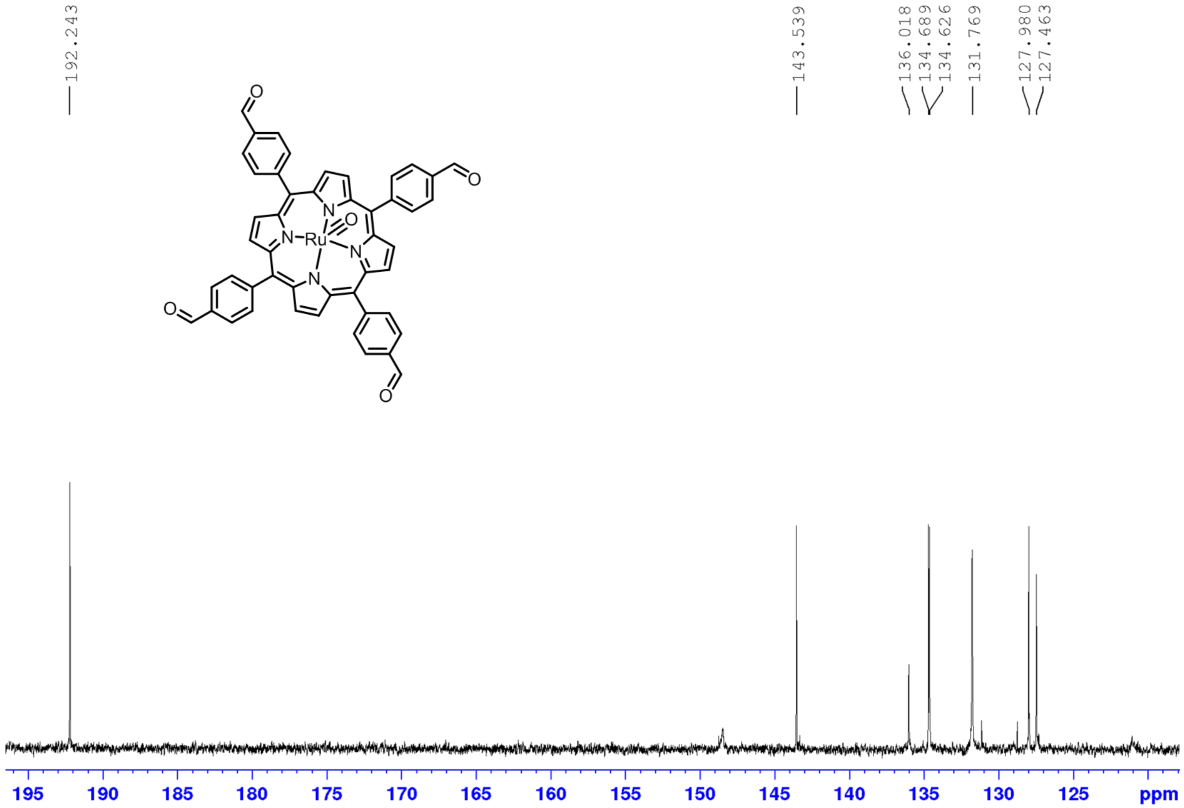


Figure S35. ^{13}C NMR spectra of **Ru-TFPP**.

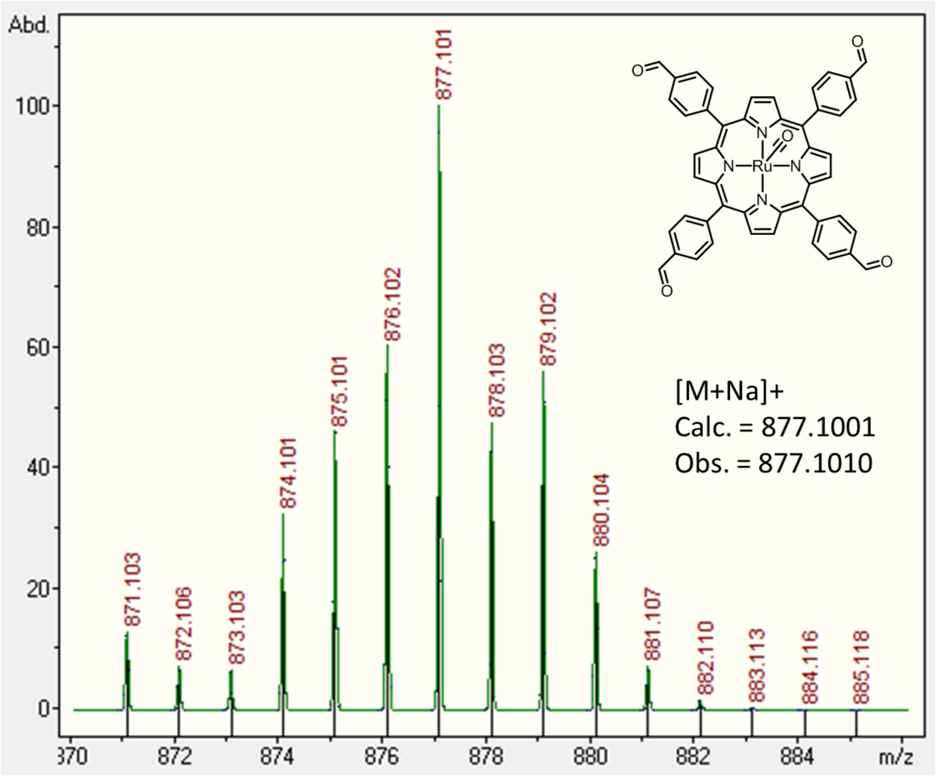


Figure S36. High resolution mass spectrometry spectra of **Ru-TFPP**.

References

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