[Supporting information to accompany]

Supramolecular Allosteric Cofacial Porphyrin Complexes

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Crystallographic data in CIF format can be found via the Internet at http://pubs.acs.org.

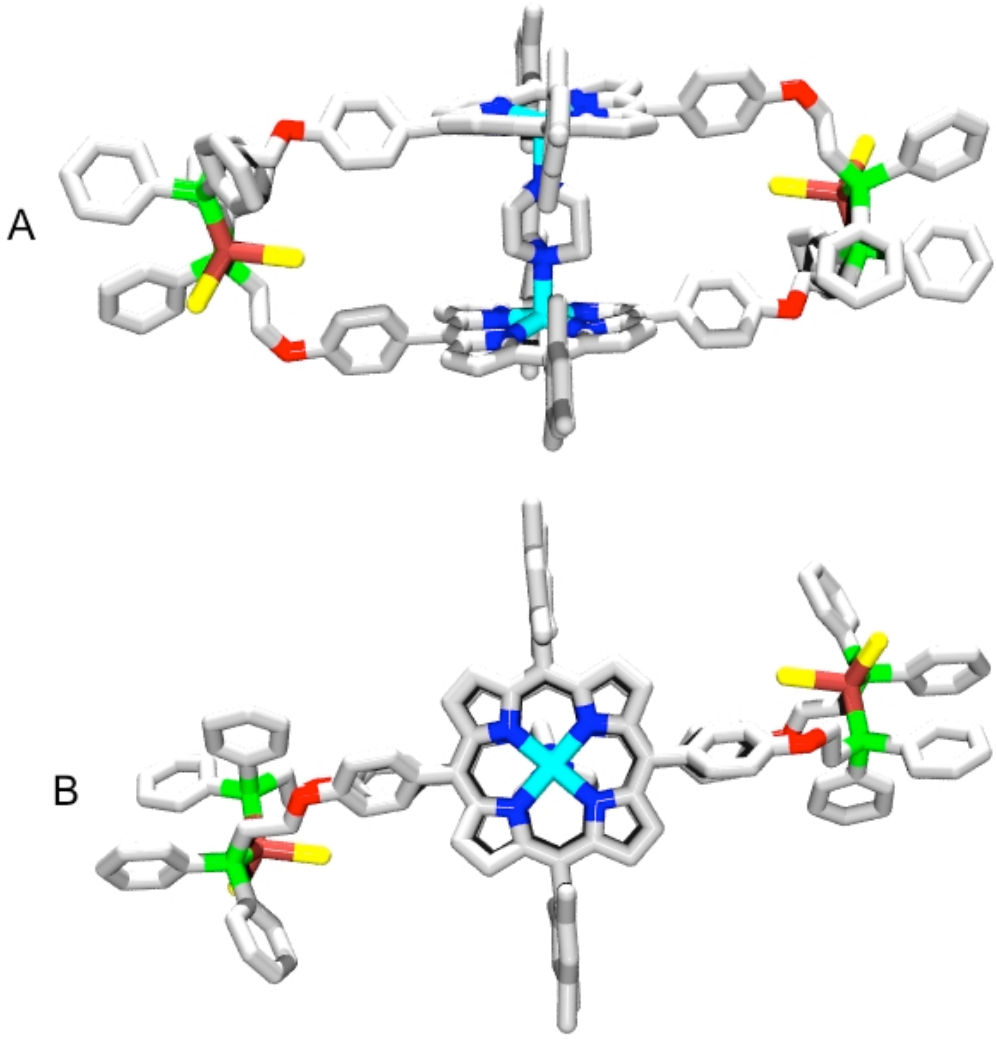


Figure S1. Graphic representations of the X-ray crystal structure of **8c⊂DABCO** as viewed from the side (A) and from the top (B) containing a molecule of DABCO bridging both Zn atoms. Hydrogen atoms, disordered DABCO carbon atoms, and solvent molecules have been omitted for clarity. Zn-Zn distance: 6.99 Å. Cu-Cu distance: 22.6 Å. Gray = Carbon, Brown = Cu, Red = O, Yellow = Cl, Green = P, Blue = N, Light Blue = Zn.

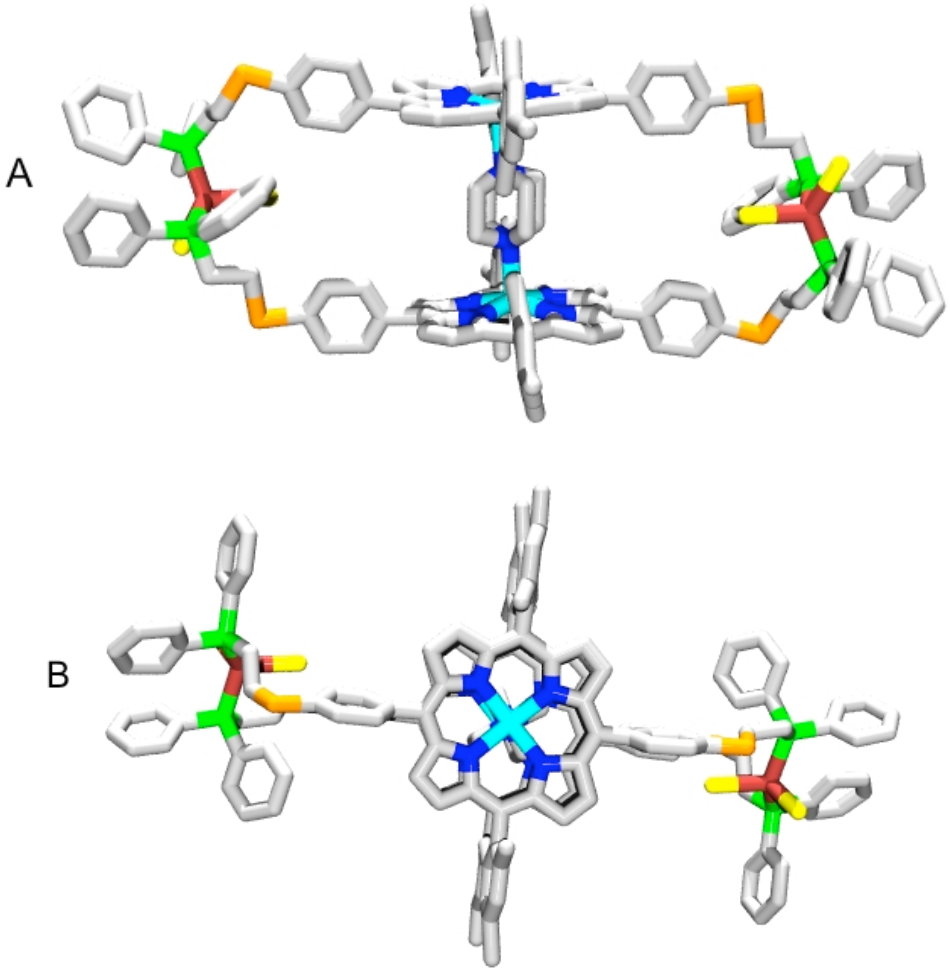
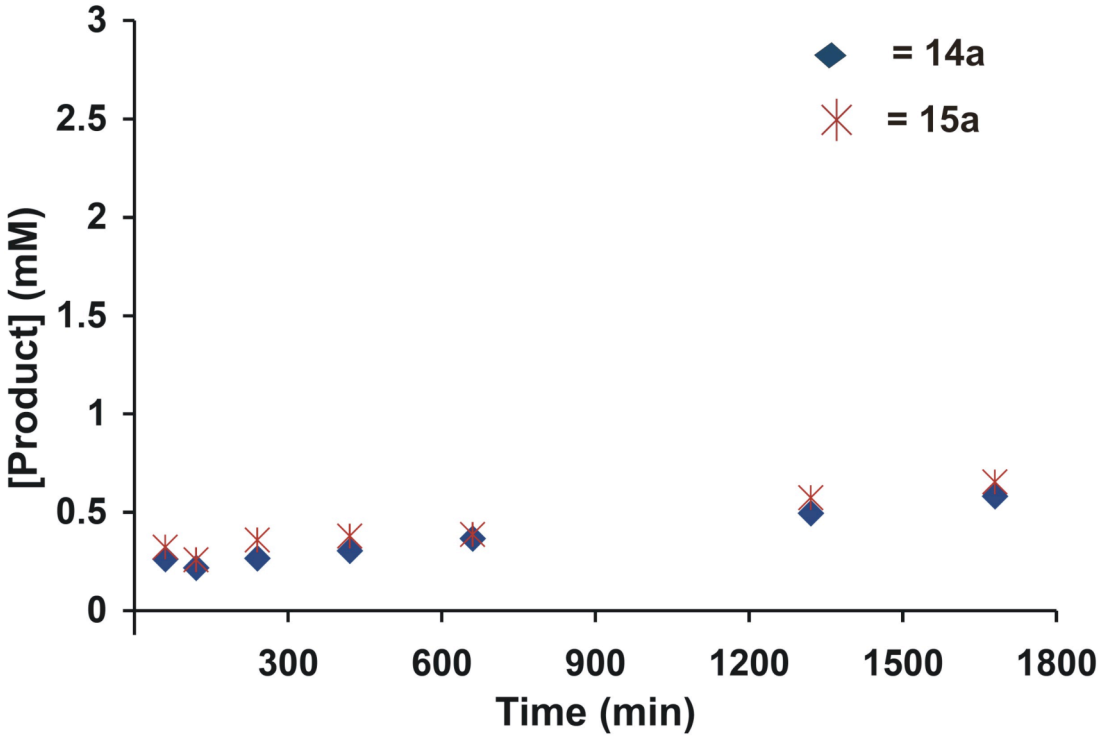


Figure S2. Graphic representations of the X-ray crystal structure of **15c⊂DABCO** as viewed from the side (A) and from the top (B) containing a molecule of DABCO bridging both Zn atoms. Hydrogen atoms, disordered DABCO carbon atoms, and solvent molecules have been omitted for clarity. Zn-Zn distance: 7.05 Å. Cu-Cu distance: 22.3 Å. Gray = C, Brown = Cu, Red = O, Orange = S, Yellow = Cl, Green = P, Dark Blue = N, Light Blue = Zn.

Table 1. X-ray Crystallographic Data for **8c⊂DABCO** and **15c⊂DABCO**.

	8c⊂DABCO	**15c⊂DABCO**
Empirical formula	$C_{174}H_{136}Cl_4Cu_2N_{14}O_4P_4Zn_2$	$C_{172}H_{156}Cl_4Cu_2N_{14}P_4S_4Zn_2$
Formula weight	3010.46	3094.86
Temperature	153(2) K	153(2) K
Wavelength	0.71000 Å	0.71073 Å
Crystal system, space group	Triclinic, P-1	Triclinic, P-1
Unit cell dimensions	a = 13.127(9) Å α = 97.501(6)º b = 16.349(8) Å β = 96.354(14)º c = 22.544(12) Å γ = 100.273(10)º	a = 13.283(3) Å α = 89.34(3) b = 17.340(4) Å β = 89.58(3) º c = 22.330(5) Å γ = 73.30(3)º
Volume	4675(5) $Å^3$	4926.0(17) $Å^3$
Z, Calculated density	1, 1.065 Mg/m^3	1, 1.043 Mg/m^3
Absorption coefficient	0.618 mm^{-1}	0.628 mm^{-1}
F(000)	1550	1608
Crystal size	0.080 x 0.040 x 0.010 mm	0.060 x 0.040 x 0.010 mm
Theta range for data collection	2.06 to 21.93 º	1.9 to 21.9 º
Reflections collected / unique	45189 / 10805 [R(int) = 0.0712]	33613 / 8598 [R(int) = 0.083]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	10756 / 0 / 887	10326 / 0 / 909
Goodness-of-fit on F^2	0.984	0.863
Final R indices [I>2sigma(I)]	R1 = 0.1117, wR2 = 0.2676	R1 = 0.0910, wR2 = 0.2107
R indices (all data)	R1 = 0.1591, wR2 = 0.2846	R1 = 0.1562, wR2 = 0.2311



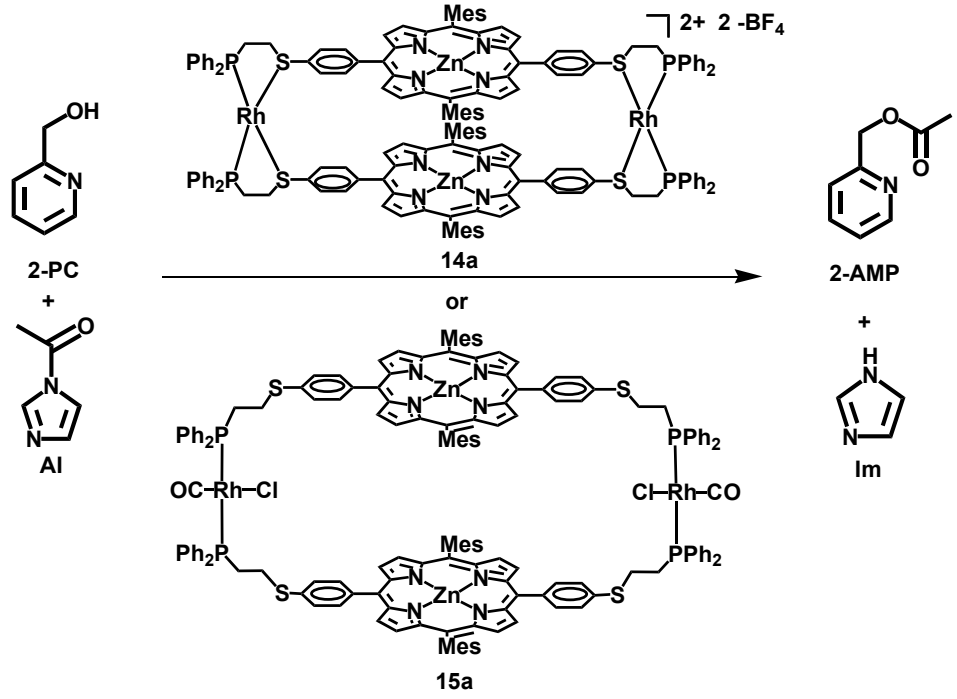


Figure S3. Formation of 2-(acetoxymethyl)pyridine (2-AMP) plotted as concentration vs. time for **14a** and **15a**. All data are uncorrected for background reactions. Conditions: CH_2Cl_2, rt, 9 mM 2-pyridylcarbinol (2-PC), 6 mM 1-acetylimidazole (AI), 2.5 mM biphenyl (GC reference standard), and 0.3 mM supramolecular catalyst (**14a** or **15a**). CO (1 atm) and appropriate amounts of benzyltriethylammonium chloride when indicated.

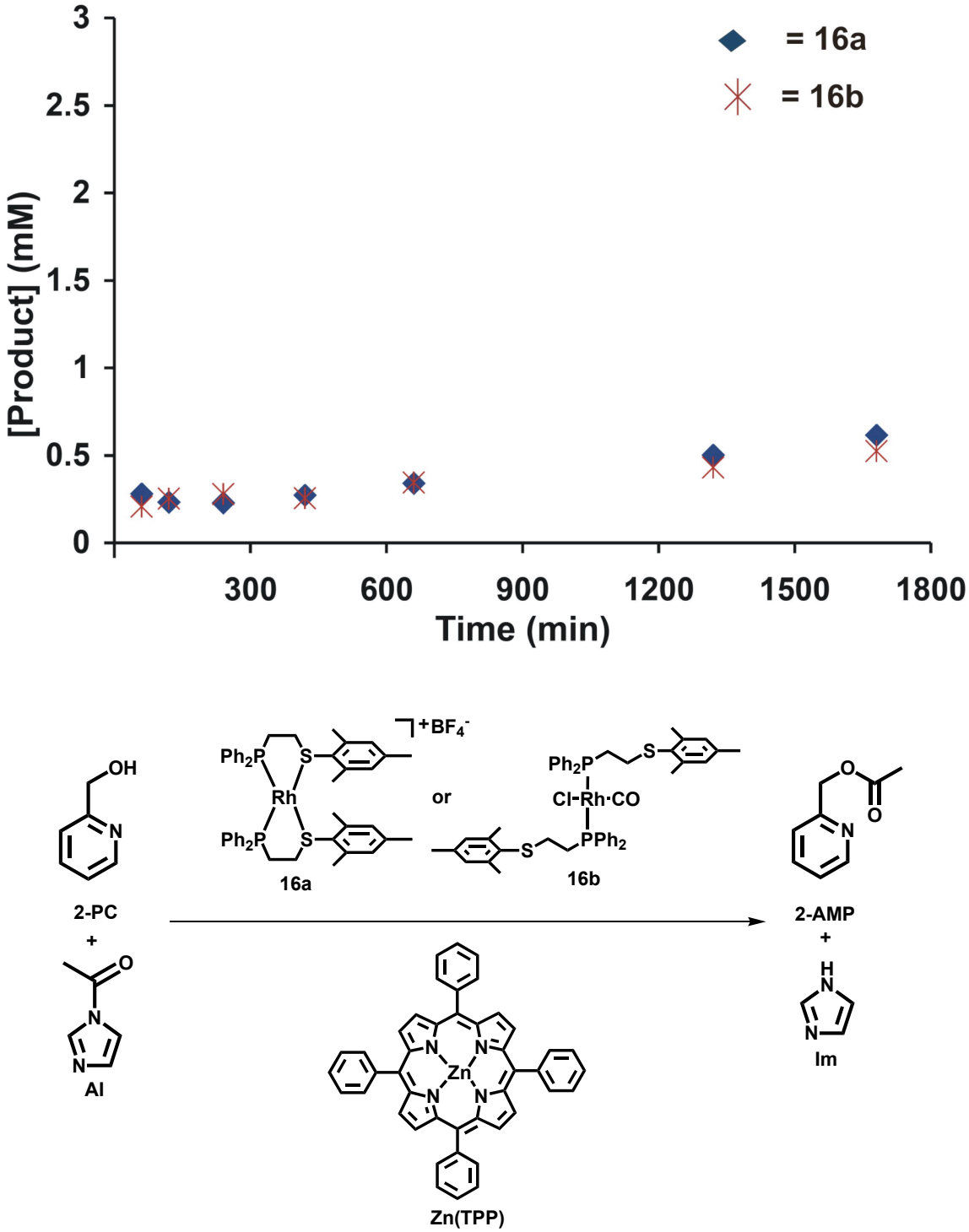
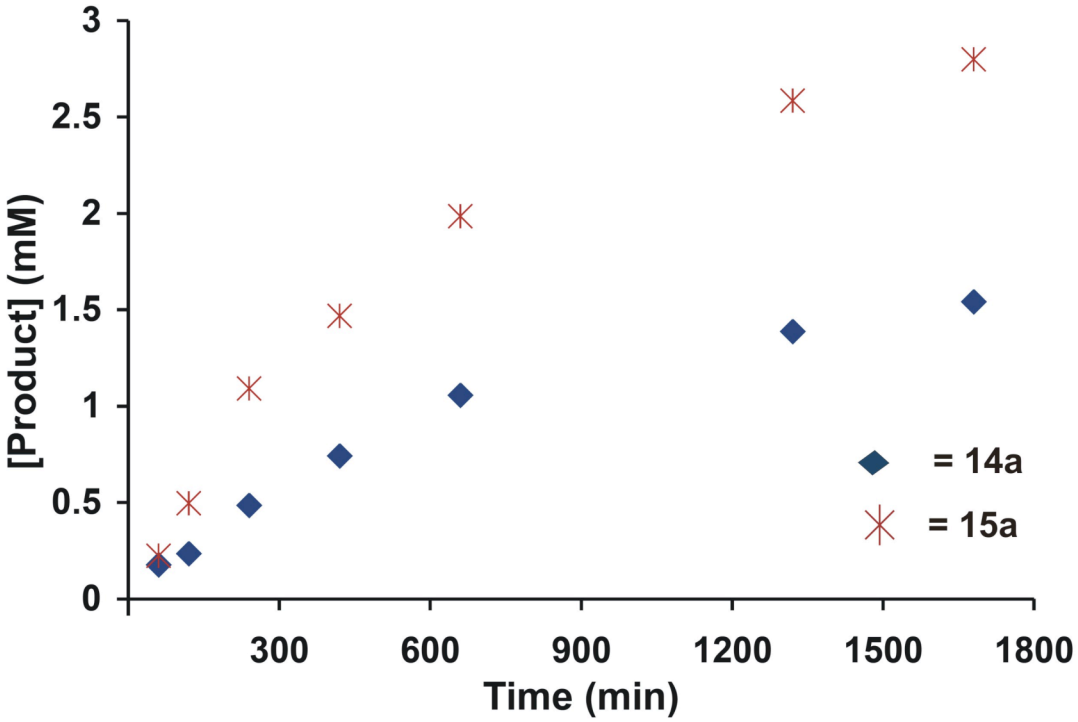


Figure S4. Formation 2-(acetoxymethyl)pyridine (2-AMP) plotted as concentration vs. time for **[Zn(TPP) + 16a]** and **[Zn(TPP) + 16b]**. Conditions: CH_2Cl_2, rt, 9 mM 2-pyridylcarbinol (2-PC), 6 mM 1-acetylimidazole (AI), 2.5 mM biphenyl (GC reference standard), 0.6 mM Rh^I-monomer (**16a** or **16b**), and 0.6 mM Zn(TPP). CO (1 atm) and appropriate amounts of benzyltriethylammonium chloride when indicated.



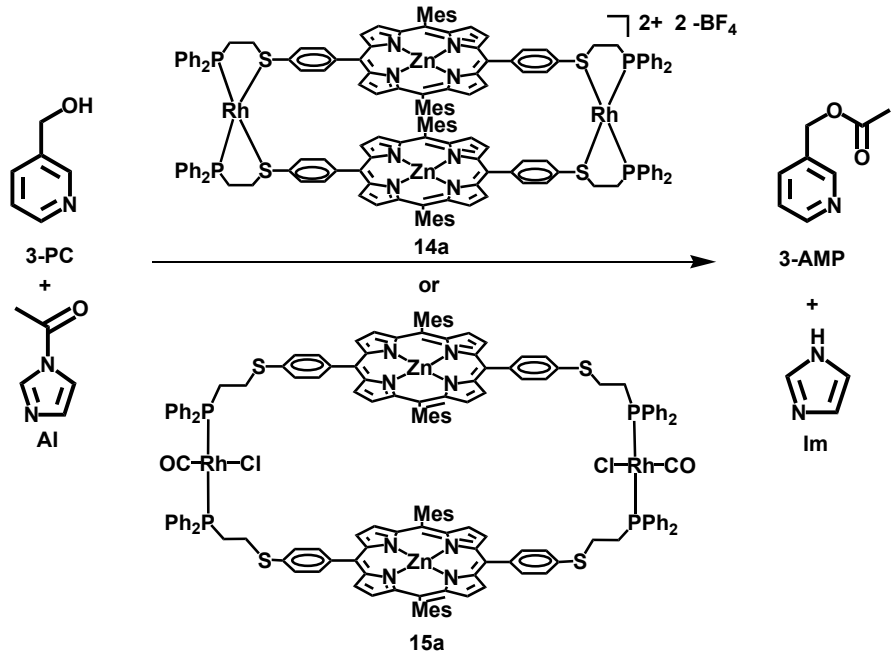


Figure S5. Formation of 3-(acetoxymethyl)pyridine (3-AMP) plotted as concentration vs. time for **14a** and **15a**. All data are uncorrected for background reactions. Conditions: CH_2Cl_2, rt, 9 mM 3-pyridylcarbinol (3-PC), 6 mM 1-acetylimidazole (AI), 2.5 mM biphenyl (GC reference standard), and 0.3 mM supramolecular catalyst (**14a** or **15a**). CO (1 atm) and appropriate amounts of benzyltriethylammonium chloride when indicated

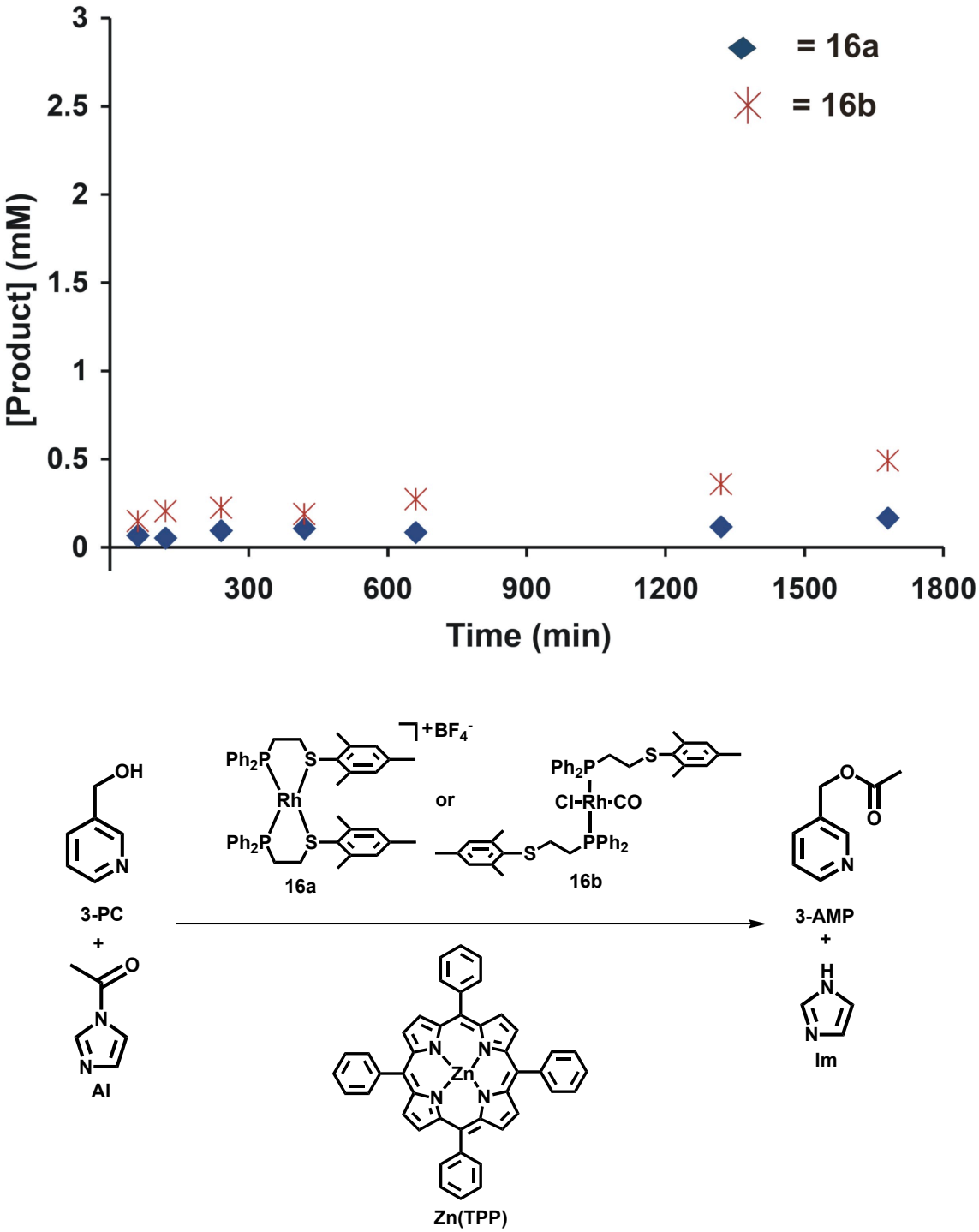
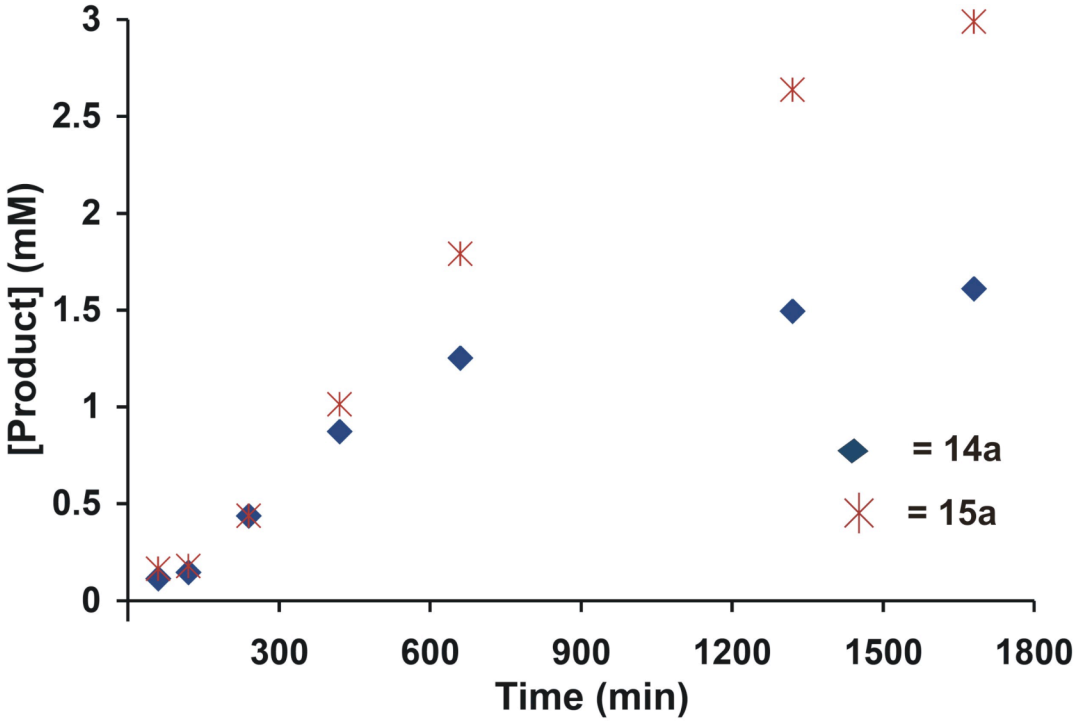


Figure S6. Formation 3-(acetoxymethyl)pyridine (3-AMP) plotted as concentration vs. time for **[Zn(TPP) + 16a]** and **[Zn(TPP) + 16b]**. Conditions: CH_2Cl_2, rt, 9 mM 3-pyridylcarbinol (3-PC), 6 mM 1-acetylimidazole (AI), 2.5 mM biphenyl (GC reference standard), 0.6 mM Rh^I-monomer (**16a** or **16b**), and 0.6 mM Zn(TPP). CO (1 atm) and appropriate amounts of benzyltriethylammonium chloride when indicated.



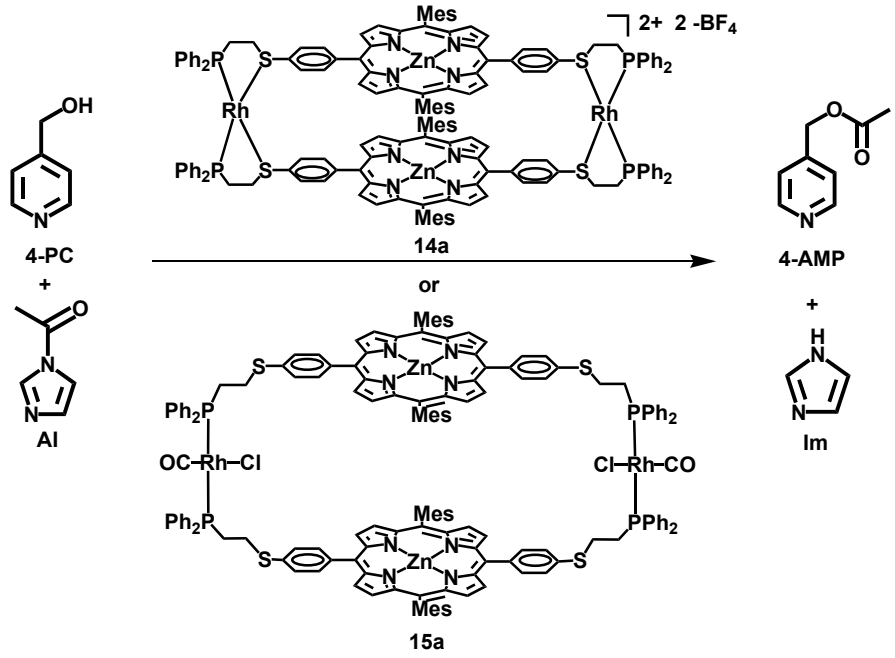


Figure S7. Formation of 4-(acetoxymethyl)pyridine (4-AMP) plotted as concentration vs. time for **14a** and **15a**. All data are uncorrected for background reactions. Conditions: CH_2Cl_2, rt, 9 mM 4-pyridylcarbinol (4-PC), 6 mM 1-acetylimidazole (AI), 2.5 mM biphenyl (GC reference standard), and 0.3 mM supramolecular catalyst (**14a** or **15a**). CO (1 atm) and appropriate amounts of benzyltriethylammonium chloride when indicated.

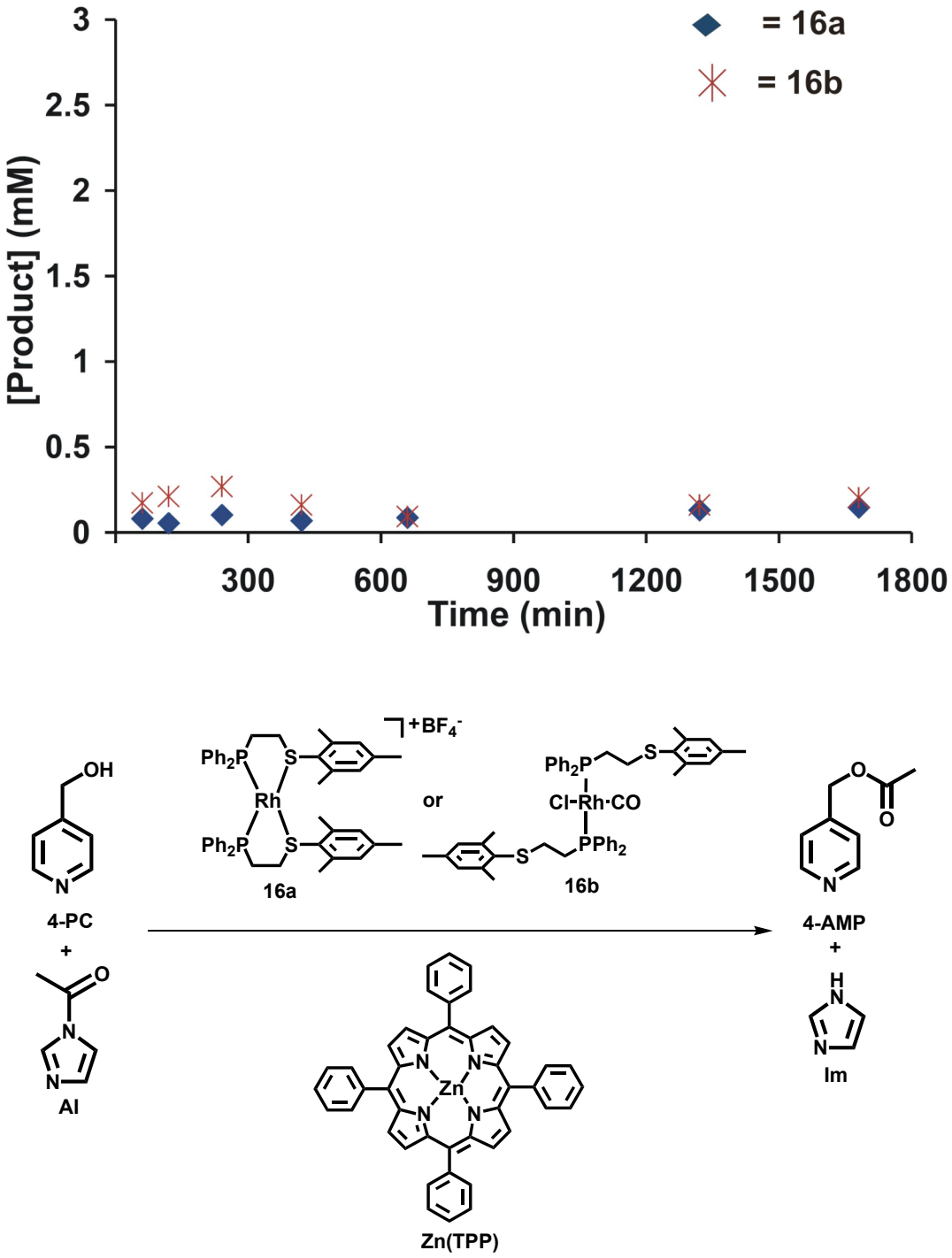


Figure S8. Formation 4-(acetoxymethyl)pyridine (4-AMP) plotted as concentration vs. time for **[Zn(TPP) + 16a]** and **[Zn(TPP) + 16b]**. Conditions: CH_2Cl_2, rt, 9 mM 4-pyridylcarbinol (4-PC), 6 mM 1-acetylimidazole (AI), 2.5 mM biphenyl (GC reference standard), 0.6 mM Rh^I-monomer (**16a** or **16b**), and 0.6 mM Zn(TPP). CO (1 atm) and appropriate amounts of benzyltriethylammonium chloride when indicated.