

Supporting information for the kinetics of the catalytic cleavage of HPNPP

Table 1S: The observed pseudo first order rate constants (k_{obs}) vs. [OTf] for the cleavage of HPNPP (0.04 mM) catalyzed by 0.5mM Zn-1 and 1.0mM Zn-2 at 25.0 ± 0.1 °C, and self-buffered conditions.

[OTf] (mM)	$10^3 k_{\text{obs}}$ (s^{-1}) [Zn-1]	[OTf] (mM)	$10^3 k_{\text{obs}}$ (s^{-1}) [Zn-2]
1.0	1.925	2.0	1.189
1.5	1.745	2.5	1.132
2.0	1.742	3.0	1.063
3.0	1.628	4.0	1.000
4.0	1.558	5.0	0.942
5.0	1.502	6.0	0.912
6.0	1.463	7.0	0.873

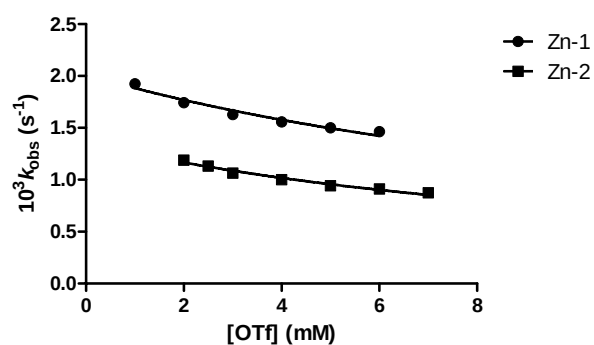


Figure 1S. OTf inhibition plots showing observed pseudo first order rate constants k_{obs} vs. [OTf] for the cleavage of HPNPP (0.04 mM) catalyzed by Zn-1 (0.5 mM) and Zn-2 (1.0 mM) at $\text{pH} = 10.0 \pm 0.1$, 25.0 ± 0.1 °C. Line through the data calculated on the basis of eq. (1) giving inhibition constants of $K_i = 14.5 \pm 1.8$ mM for Zn-1 and $K_i = 11.6 \pm 1.1$ mM for Zn-2, respectively.

Table 2S: The observed pseudo first order rate constants (k_{obs}) vs. $[\text{M(II)}]$ at $[\text{OCH}_3]/[\text{M(II)}] = 0.5$ for the catalyzed cleavage of HPNPP (0.04 mM) determined in anhydrous methanol at $\text{pH} = 10.0 \pm 0.1$ for Zn-1 and $\text{pH} = 8.9 \pm 0.1$ for Cu-1 at 25.0 ± 0.1 °C.

Zn-1 (mM)	$10^3 k_{\text{obs}}$	$10^3 k_{\text{obs}}^{\text{corr}} (\text{s}^{-1})$	Cu-1 (mM)	$10^3 k_{\text{obs}} (\text{s}^{-1})$
0.1	0.26	0.26	0.1	2.35
0.3	1.19	1.24	0.2	4.45
0.5	1.92	2.05	0.3	6.97
0.7	2.53	2.77	0.4	10.06
1.2	3.91	4.56	0.5	13.26
1.6	5.41	6.60	0.6	15.67
2.0	6.49	8.28		

Table 3S: The observed pseudo first order rate constants (k_{obs}) vs. $[\text{M(II)}]$ at $[\text{OCH}_3]/[\text{M(II)}] = 0.5$ for the catalyzed cleavage of HPNPP (0.04 mM) determined in anhydrous methanol at $\text{pH} = 10.0 \pm 0.1$ for Zn-2 and $\text{pH} = 8.9 \pm 0.1$ for Cu-2 at 25.0 ± 0.1 °C.

Zn-2 (mM)	$10^3 k_{\text{obs}}$	$10^3 k_{\text{obs}}^{\text{corr}} (\text{s}^{-1})$	Cu-2 (mM)	$10^3 k_{\text{obs}} (\text{s}^{-1})$
0.1	0.24	0.25	0.05	0.008
0.3	0.59	0.65	0.10	0.020
0.5	0.84	0.98	0.30	0.053
0.7	1.02	1.27	0.50	0.073
1.0	1.189	1.60	0.70	0.095
			0.90	0.118

Table 4S The observed pseudo first order rate constants k_{obs} vs. [OTf] for the cleavage of HPNPP (0.04 mM) catalyzed by 0.3 mM of Zn₂-**3a** and Zn₂-**3b**, 0.1 mM of Zn₂-**3c**, at 25.0 ± 0.1 °C and self-buffered conditions.

[OTf] (mM)	$10^3 k_{\text{obs}}$ (s ⁻¹) [Zn ₂ - 3a]	$10^3 k_{\text{obs}}$ (s ⁻¹) [Zn ₂ - 3b]	[OTf] (mM)	$10^3 k_{\text{obs}}$ (s ⁻¹) [Zn ₂ - 3c]
1.20	7.00	11.70	0.40	4.670
1.60	6.590	9.22	0.80	3.220
2.00	6.130	8.60	1.20	2.810
2.60	5.030	4.83	1.80	2.380
3.30	4.480	4.30	2.50	2.120
4.30	3.760	3.18	3.50	1.810
5.30	3.400	3.09	4.50	1.600

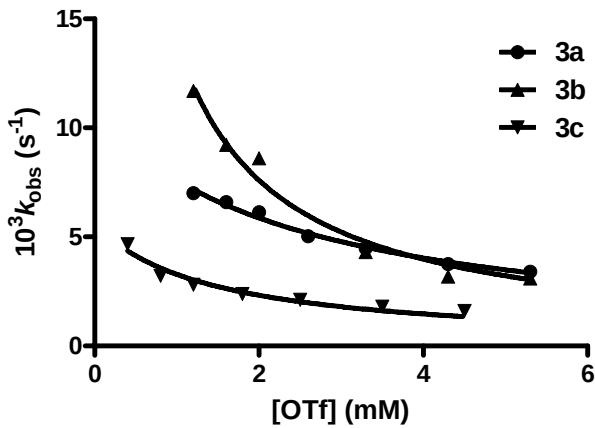


Figure 2S. OTf inhibition plots showing k_{obs} vs. [OTf] for the cleavage of HPNPP (0.04 mM) catalyzed by 0.3 mM of Zn₂-**3a** ($\text{s pH} = 9.8 \pm 0.1$), Zn₂-**3b** ($\text{s pH} = 9.7 \pm 0.1$), and 0.1 mM of Zn₂-**3c** ($\text{s pH} = 9.4 \pm 0.1$) at 25.0 ± 0.1 °C. Line through the data calculated on the basis of eq. (1) giving inhibition constants of $K_i = 2.4 \pm 0.3$ mM for Zn₂-**3a**, $K_i = 0.20 \pm 0.21$ mM for Zn₂-**3b**, and $K_i = 1.4 \pm 0.3$ mM for Zn₂-**3c**.

Table 5S: The observed pseudo first order rate constants (k_{obs}) vs. [Zn(II)] at [OCH₃]/[Zn(II)] = 0.5 for the catalyzed cleavage of HPNPP (0.04 mM) determined in anhydrous methanol at $\text{s pH} = 9.8 \pm 0.1$ for Zn₂-**3a**, $\text{s pH} = 10.1 \pm 0.1$ for Zn₂-**3b** and $\text{s pH} = 9.9 \pm 0.1$ for Zn₂-**3c** at 25.0 ± 0.1 °C.

Zn ₂ - 3a (mM)	$10^3 k_{\text{obs}}$ (s ⁻¹)	$10^3 k_{\text{obs}}^{\text{corr}}$ (s ⁻¹)	Zn ₂ - 3b (mM)	$10^3 k_{\text{obs}}$ (s ⁻¹)	$10^3 k_{\text{obs}}^{\text{corr}}$ (s ⁻¹)	Zn ₂ - 3c (mM)	$10^3 k_{\text{obs}}$ (s ⁻¹)	$10^3 k_{\text{obs}}^{\text{corr}}$ (s ⁻¹)
0.02	0.69	0.71	0.06	2.57	5.65	0.06	1.24	1.45
0.06	2.84	3.12	0.10	5.63	16.89	0.20	8.09	12.7
0.10	4.13	4.81	0.30	11.7	81.90	0.30	10.2	18.9
0.20	6.10	8.13	0.50	47.6	523.6	0.40	15.7	33.6
0.30	7.0	10.5	0.70	60.2	903.0	0.60	20.2	54.8
0.4	6.54	10.9	0.90	73.8	1402.2	1.00	25.4	98.0

Table 6S The observed pseudo first order rate constants k_{obs} vs. [OTf] for the cleavage of HPNPP (0.04 mM) catalyzed by 0.1 mM of Zn₂-**3d** and Zn₂-**3e** at 25.0 ± 0.1 °C and self-buffered conditions.

[OTf] (mM)	$10^3 k_{\text{obs}}$ (s ⁻¹) [Zn ₂ - 3d]	$10^3 k_{\text{obs}}$ (s ⁻¹) [Zn ₂ - 3e]
0.4	7.05	1.913
1.3	3.590	-
1.8	2.620	1.463
2.8	1.850	1.217
3.8	1.675	1.085
4.8	1.495	0.958
5.8	1.332	0.887
6.8	1.247	0.750

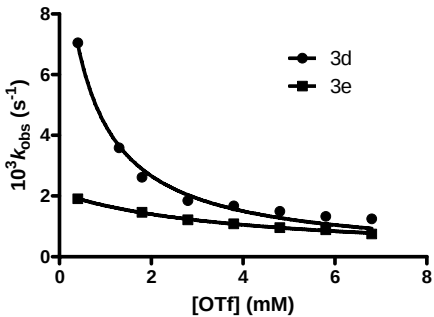


Figure 3S. OTf inhibition plots showing k_{obs} vs. [OTf] for the cleavage of HPNPP (0.04 mM) catalyzed by 0.1 mM of Zn₂-**3d** ($\text{s pH} = 9.2 \pm 0.1$) and Zn₂-**3e** ($\text{s pH} = 10.2 \pm 0.1$) at 25.0 ± 0.1 °C. Line through the data calculated on the basis of eq. (1) giving inhibition constants of $K_i = 0.59 \pm 0.08$ mM for Zn₂-**3d** and $K_i = 3.98 \pm 0.13$ mM for Zn₂-**3e**.

Table 7S: The observed pseudo first order rate constants (k_{obs}) vs. [Zn(II)] at [OCH₃]/[Zn(II)] = 0.5 for the catalyzed cleavage of HPNPP (0.04 mM) determined in anhydrous methanol at $\text{s pH} = 9.2 \pm 0.2$ for Zn₂-**3d** and $\text{s pH} = 10.1 \pm 0.2$ for Zn₂-**3e** at 25.0 ± 0.1 °C.

Zn ₂ - 3d (mM)	$10^3 k_{\text{obs}}$ (s ⁻¹)	$10^3 k_{\text{obs}}^{\text{corr}}$ (s ⁻¹)	Zn ₂ - 3e (mM)	$10^3 k_{\text{obs}}$ (s ⁻¹)	$10^3 k_{\text{obs}}^{\text{corr}}$ (s ⁻¹)
			0.02	0.495	0.505
0.05	3.980	5.32	0.04	1.108	1.152
0.10	7.055	11.83	0.06	1.510	1.601
0.20	9.678	22.80	0.10	1.913	2.105
0.30	10.630	32.25	0.30	2.887	3.757
0.40	11.000	40.83	0.50	3.185	4.786
0.50	11.625	51.03	0.70	3.257	5.548
			0.90	3.270	6.227

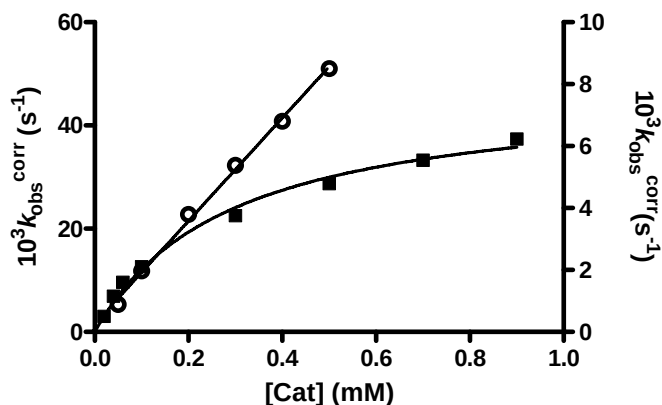


Figure 4S. Plots of k_{obs}^{corr} vs $[Zn_2]$ for the catalyzed cleavage of HPNPP (4.0×10^{-5} M) at $[OCH_3]/[Zn(II)] = 0.5$, $s_pH = 9.2 \pm 0.2$ for Zn_2-3d (○) and $s_pH = 10.1 \pm 0.2$ for Zn_2-3e (■), 25.0 ± 0.1 °C.

Table 8S The observed pseudo first order rate constants k_{obs} vs. $[OTf]$ for the cleavage of HPNPP (0.04 mM) catalyzed by 0.1 mM of Zn_2-4b and Zn_2-4d at 25.0 ± 0.1 °C and self-buffered pH conditions.

[OTf](mM)	$10^3 k_{obs} (s^{-1})$ [Zn_2-4b]	[OTf](mM)	$10^3 k_{obs} (s^{-1})$ [Zn_2-4d]
0.4	11.8	0.4	1.85
1.4	9.67	1.3	1.651
2.4	9.12	1.8	1.473
3.4	8.20	2.8	1.468
4.4	7.98	3.8	1.338
5.4	7.40	4.8	1.295
6.4	7.04	5.8	1.223
		6.8	1.167

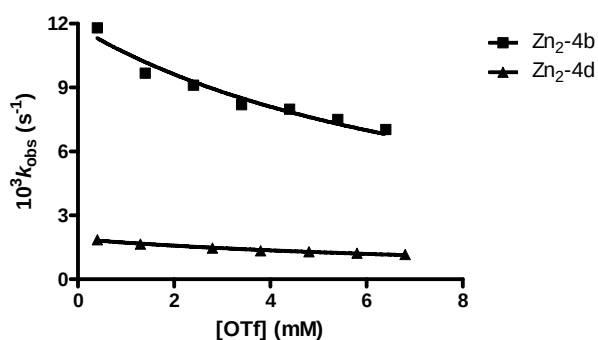


Figure 5S. OTf inhibition plots showing k_{obs} vs. $[OTf]$ for the cleavage of HPNPP (0.04 mM) catalyzed by 0.1 mM of Zn_2-4 ($4 = 4b, 4d$) at $s_pH = 9.6 \pm 0.1$ and $s_pH = 9.8 \pm 0.1$ for Zn_2-4b and Zn_2-4d , respectively, 25.0 ± 0.1 °C. Line through the data calculated on the basis of eq. (1) giving inhibition constants of $K_i = 8.7 \pm 1.1$ mM for Zn_2-4b and $K_i = 10.3 \pm 0.7$ mM for Zn_2-4d .

Table 9S: The observed pseudo first order rate constants k_{obs} vs. $[\text{Zn}_2]$ at $[\text{OCH}_3]/[\text{Zn(II)}] = 0.5$ for the catalyzed cleavage of HPNPP (0.04 mM) determined in anhydrous methanol at $^{\text{s}}\text{pH} = 10.0 \pm 0.1$ for $\text{Zn}_2\text{-4b}$, $^{\text{s}}\text{pH} = 9.9 \pm 0.1$ for $\text{Zn}_2\text{-5b}$ and $^{\text{s}}\text{pH} = 9.8 \pm 0.1$ for $\text{Zn}_2\text{-6b}$, 25.0 ± 0.1 °C.

$\text{Zn}_2\text{-4b}$ (mM)	$10^3 k_{\text{obs}}$ (s^{-1})	$10^3 k_{\text{obs}}^{\text{corr}}$ (s^{-1})	$\text{Zn}_2\text{-5b}$ (mM)	$10^3 k_{\text{obs}}(\text{s}^{-1})$	$\text{Zn}_2\text{-6b}$ (mM)	$10^3 k_{\text{obs}}$ (s^{-1})
0.02	1.65	1.66	0.1	1.72	0.10	1.10
0.06	7.19	7.39	0.2	3.63	0.30	1.80
0.10	11.8	12.3	0.4	6.40	0.50	2.38
0.20	33.0	36.0	0.6	7.48	0.60	2.45
0.30	48.7	55.4	0.8	8.13	0.80	2.66
0.50	91.4	112.4	1.0	9.45	1.40	3.18
			1.5	12.11	2.00	3.70
			2.0	13.50		

Table 10S: The observed pseudo first order rate constants k_{obs} vs. $[\text{Zn}_2]$ at $[\text{OCH}_3]/[\text{M(II)}] = 0.5$ for the catalyzed cleavage of HPNPP (0.04 mM) determined in anhydrous methanol at $^{\text{s}}\text{pH} = 9.6 \pm 0.2$ for $\text{Zn}_2\text{-4d}$ and $^{\text{s}}\text{pH} = 10.1 \pm 0.1$ for $\text{Zn}_2\text{-4g}$ at 25.0 ± 0.1 °C.

$\text{Zn}_2\text{-4d}(\text{mM})$	$10^3 k_{\text{obs}}(\text{s}^{-1})$	$10^3 k_{\text{obs}}^{\text{corr}}(\text{s}^{-1})$	$\text{Zn}_2\text{-4g}(\text{mM})$	$10^3 k_{\text{obs}}(\text{s}^{-1})$
0.05	1.05	1.07	0.1	1.97
0.10	1.85	1.92	0.2	3.72
0.20	3.30	3.56	0.3	4.93
0.30	4.38	4.89	0.4	5.35
0.40	5.16	5.96	0.6	5.31
0.50	5.58	6.66		
0.60	6.01	7.41		

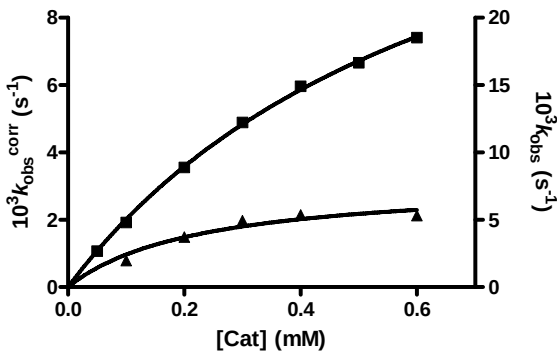


Figure 6S. Plots of k_{obs} vs $[\text{Zn}_2]$ for the cleavage of HPNPP (4.0×10^{-5} M) at $[\text{OCH}_3]/[\text{Zn(II)}] = 0.5$, $^{\text{s}}\text{pH} = 9.6 \pm 0.2$ for $\text{Zn}_2\text{-4d}$ (■ left axis), $^{\text{s}}\text{pH} = 10.1 \pm 0.1$ for $\text{Zn}_2\text{-4g}$ (▲ right axis), 25.0 ± 0.1 °C.

Table 11S: The observed pseudo first order rate constants (k_{obs}) vs. $[\text{OTf}^-]$ for the cleavage of HPNPP (0.04 mM) catalyzed by $\text{Cu}_2\text{-3d}$ (0.1 mM) and $\text{Cu}_2\text{-4d}$ (0.1 mM) at 25.0 ± 0.1 °C and self-buffered conditions.

$[\text{OTf}^-]$ (mM)	$10^3 k_{\text{obs}}$ (s^{-1}) $\text{Cu}_2\text{-3d}$	$[\text{OTf}^-]$ (mM)	$10^3 k_{\text{obs}}$ (s^{-1}) $\text{Cu}_2\text{-4d}$
0.4	0.567	0.4	1.228
1.7	0.507	1.4	1.130
2.1	0.498	2.4	1.095
2.6	0.485	3.4	1.007
3.6	0.432	4.4	0.967
4.6	0.371	5.4	0.922
5.6	0.371	6.4	0.852

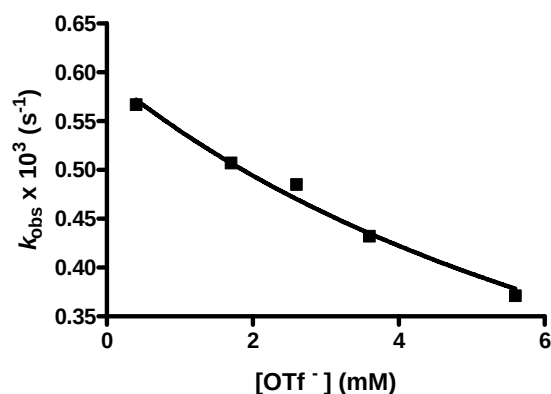


Figure 7S. OTf inhibition plot showing observed pseudo first order rate constants (k_{obs}) vs. $[\text{OTf}^-]$ for the cleavage of HPNPP (0.04 mM) catalyzed by $\text{Cu}_2\text{-3d}$ (0.1 mM) at $\text{pH} = 8.0 \pm 0.1$ and 25.0 ± 0.1 °C. Fitted by eq. (1) giving inhibition constant $K_i = 9.7 \pm 0.8$ mM.

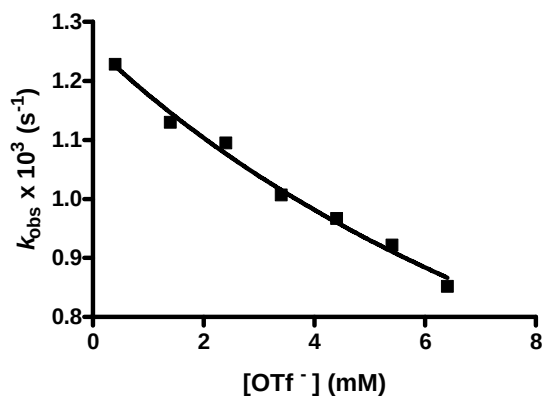


Figure 8S. OTf inhibition plot showing observed pseudo first order rate constants (k_{obs}) vs. $[\text{OTf}^-]$ for the cleavage of HPNPP (0.04 mM) catalyzed by $\text{Cu}_2\text{-4d}$ (0.1 mM) at $\text{pH} = 7.8 \pm 0.1$ and 25.0 ± 0.1 °C. Fitted by eq. (1) giving inhibition constant $K_i = 14.1 \pm 0.8$ mM.

Table 12S: The observed pseudo first order rate constants (k_{obs}) vs. $[\text{Cu}_2(\text{II})]$ at $[\text{OCH}_3]/[\text{Cu}(\text{II})] = 0.5$ for the catalyzed cleavage of HPNPP (0.04 mM) determined in anhydrous methanol at $^{\circ}\text{pH} = 7.9 \pm 0.2$ for $[\text{Cu}_2\text{-3d}]$ and $^{\circ}\text{pH} = 6.9 \pm 0.2$ for $[\text{Cu}_2\text{-4d}]$, 25.0 ± 0.1 °C.

$[\text{Cu}_2\text{-3d}]$ (mM)	$10^3 k_{\text{obs}}$ (s^{-1})	$10^3 k_{\text{obs}}^{\text{corr}}$ (s^{-1})	$[\text{Cu}_2\text{-4d}]$ (mM)	$10^3 k_{\text{obs}}$ (s^{-1})	$10^3 k_{\text{obs}}^{\text{corr}}$ (s^{-1})
0.1	0.567	0.590	0.10	1.228	1.067
0.2	0.695	0.752	0.20	1.898	2.006
0.4	0.803	0.935	0.30	2.765	3.000
0.6	0.830	1.035	0.40	3.025	3.368
0.8	0.853	1.134	0.50	3.260	3.722
			0.60	3.700	4.329
			0.70	4.323	5.181

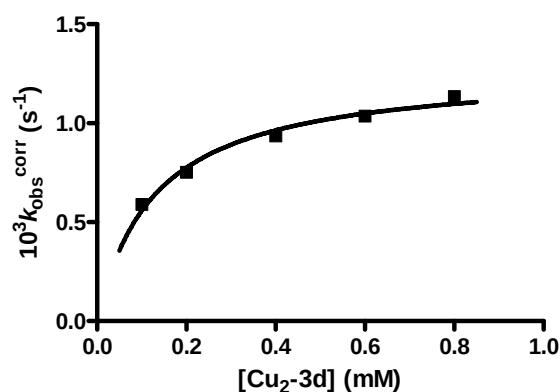


Figure 9S. A plot of k_{obs} vs $[\text{Cu}_2\text{-3d}]$ at $[\text{OCH}_3]/[\text{Cu}_2(\text{II})] = 0.5$ for the methanolysis of HPNPP (4×10^{-5} M), $^{\circ}\text{pH} = 7.9 \pm 0.2$ and 25 ± 0.1 °C. Line is fitted by Michaelis-Menten equation giving a binding constant of $K_m = (1.3 \pm 0.2) \times 10^{-4} \text{ M}^{-1}$, $k_{\text{max}} = (1.27 \pm 0.05) \times 10^{-3} \text{ s}^{-1}$.

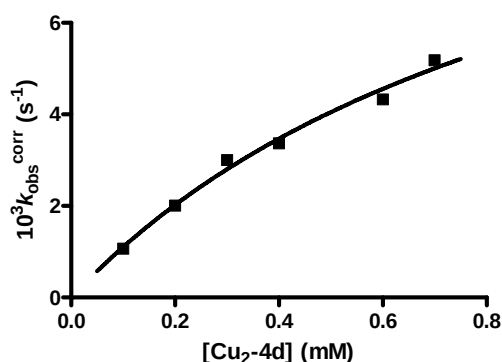


Figure 10S. A plot of k_{obs} vs $[\text{Cu}_2\text{-4d}]$ at $[\text{OCH}_3]/[\text{Cu}_2(\text{II})] = 0.5$ for the methanolysis of HPNPP (4×10^{-5} M), $^{\circ}\text{pH} 6.9 \pm 0.2$ and 25 ± 0.1 °C. Line is fitted by Michaelis-Menten equation giving a binding constant of $K_m = (1.01 \pm 0.26) \times 10^{-3} \text{ M}^{-1}$, $k_{\text{max}} = (1.22 \pm 0.25) \times 10^{-2} \text{ s}^{-1}$.

Table 13S: The observed pseudo first order rate constants k_{obs} vs. $[\text{Cu}_2\text{-4b}]$ for the catalyzed cleavage of HPNPP (0.04 mM) determined in anhydrous methanol at $^{\text{s}}\text{pH} = 9.2 \pm 0.1$ and 25.0 ± 0.1 °C.

$\text{Cu}_2\text{-4b}$ (mM)	$10^3 k_{\text{obs}} (\text{s}^{-1})$
0.02	2.07
0.06	12.09
0.10	21.39
0.20	41.56
0.30	61.31
0.40	82.50
0.50	106.90

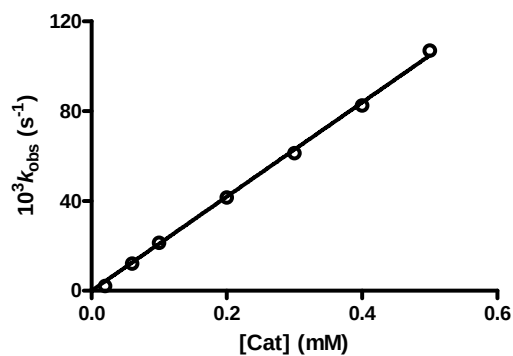


Figure 11S. Plot of k_{obs} vs $[\text{Cu}_2\text{-4b}]$ for the cleavage of HPNPP (4.0×10^{-5} M) at $[\text{OCH}_3]/[\text{Cu(II)}] = 0.5$, $^{\text{s}}\text{pH} = 9.2 \pm 0.1$, 25.0 ± 0.1 °C.