Supplemental Information

Experimental

Materials. The organic substrates were from commercial sources (Aldrich, Fluka) and were used without further purification. Na$_{12}$[WZn$_3$(H$_2$O)$_2$(ZnW$_9$O$_{34}$)$_2$] was prepared according to the published literature procedure (Tourné, C. M.; Tourné, G. F.; Zonnevijlle, F. J. Chem. Soc. Dalton Trans. 1991, 143-151).

Oximation reaction procedures. 5 mmol substrate, 14 mmol 30 % aqueous H$_2$O$_2$ and 1 mL of a 0.01 M solution of Na$_{12}$[WZn$_3$(H$_2$O)$_2$(ZnW$_9$O$_{34}$)$_2$] dissolved in water were placed in a 50 mL round bottomed flask at room temperature and vigorously stirred with a magnetic stirrer. An aqueous solution of 25 % NH$_4$OH was added dropwise at a rate of 0.3 mL/h by syringe pump (Aitecs, SEP-10S). The total amount of ammonia added was 16 mmol and the total reaction time was 6 h. After six hours the stirring was discontinued, effectively quenching the reaction. The organic phase was immediately analyzed by GLC (HP 6890) using a 30 m 5% phenylmethyl silicone capillary column with an ID of 0.32 mm and 0.25 μm coating (Restek 5MS); products were identified using reference standards or when necessary by GC-MS (HP 5973) with the same column and. The decomposition of hydrogen peroxide to molecular oxygen was measured using a gas burette. Reactions carried out using self-assembled Na$_{12}$[WZn$_3$(H$_2$O)$_2$(ZnW$_9$O$_{34}$)$_2$] were carried out in the same way except that instead of using purified Na$_{12}$[WZn$_3$(H$_2$O)$_2$(ZnW$_9$O$_{34}$)$_2$] a ~0.01 M solution of Na$_{12}$[WZn$_3$(H$_2$O)$_2$(ZnW$_9$O$_{34}$)$_2$] was prepared by mixing 0.019 mol (6.27 g) Na$_2$WO$_4$•2H$_2$O, 0.005 mol (1.49 g) Zn(NO$_3$)$_2$•6H$_2$O and 0.016 mol 70% HNO$_3$ in 100 mL H$_2$O.