Regioselective Alkene Carbon-Carbon Bond Cleavage to Aldehydes and Chemoselective Alcohol Oxidation of Allylic Alcohols with Hydrogen Peroxide Catalyzed by $[cis\text{-Ru(II)(dmp)}_2(\text{H}_2\text{O})_2]^{2+}$ (dmp=2,9-dimethylphenanthroline)

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Supplementary Information

Catalyst Preparation: The catalyst, $[cis\text{-Ru(II)(dmp)}_2(\text{H}_2\text{O})_2]^{2+}$, was prepared according to the procedures described in the literature (Collin, J. P.; Sauvage, J. P. *Inorg. Chem.* **1986**, *25*, 135 and Goldstein, A. S.; Beer, R. H.; Drago, R. S. *J. Am. Chem. Soc.* **1994**, *116*, 2424).

Oxidation Reactions: The typical procedure for oxidation of substrates presented was as follows: in 10ml volume vial, equipped with glass-covered stir-bar were dissolved 8 mg (0.01 mmol) of $[cis\text{-Ru(II)(dmp)}_2(\text{H}_2\text{O})_2]^{2+}$ in 3 mL of acetonitrile under agitation in a ultrasound bath, and 1 mmol of substrate and chlorobenzene (0.1mmol) as internal standard was added. The solution was placed in preheated, 55 °C, oil bath and stirred for half hour. Portions of 2 mmol 30% aqueous H_2O_2 were added in intervals of 1h combined with a monitoring of the reaction by GC (column was 5% phenyl methylsilicone 0.32 mm ID, 0.25- μm coating, 30-m-length column (Restek 5MS). Compounds were identified by use of reference compounds and/or GC/MS measurements. For experiment using 7-methyl-1,6-octadiene as substrate the by-product epoxide was identified by it MS and use of a authentic epoxide prepared by the MCPA oxidation of the substrate m/z = 140 (0.9), 125(4.7), 111(2.8), 97(6.6) ,85(9.8) , 81(14.2) , 71(12.3), 67(100) and 59(47.6).

Computational Methods: Calculations were carried out using Gaussian 03 revision B02 (Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R. ; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision B.02; Gaussian, Inc.: Pittsburgh PA, 2003. The density functional theory (DFT) B97-1 hybrid exchange-correlation functional, Handy et al.'s reparameterization (Singleton, J. T.; *Tetrahedron* **2003**, *59*, 1837-1857.) of Becke's B97 functional, (Becke, A. D. *J. Chem. Phys.* **1997**, *107*, 8554-8560.) was used throughout (Hamprecht, F. A.; Cohen, A. J.; Tozer, D. J.; Handy, N. C. *J. Chem. Phys.* **1998**, *109*, 6264-6271.). With this functional, the basis set-RECP (relativistic effective core potential) combination SDD was used. It is the combination of the Huzinaga-Dunning double- basis set on lighter elements with the Stuttgart-Dresden basis set-RECP combination on transition metals (Dolg, M. In *Modern Methods and Algorithms of Quantum Chemistry*; Grotendorst, J., Ed.; John von Neumann Institute for Computing: Jülich, 2000; Vol. 1, pp 479-508.).