

Supporting information for

Olefin Epoxidation by the Hydrogen Peroxide Adduct of a Novel Non-heme Manganese(IV) Complex: Demonstration of Oxygen Transfer by Multiple Mechanisms

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Properties of hydrogen peroxide in acetone. The reaction between H₂O₂ and acetone to form 2-hydroxy-2-hydroperoxypropane is well documented, and the equilibrium constant for formation of this acetone adduct was found to be $K=0.086 \text{ M}^{-1}$ at 25°C.¹ According to this equilibrium constant, under our reaction conditions (0.25 mL of 30% H₂O₂ in 5 mL of acetone/water (ratio 4:1)), ~50% of H₂O₂ exists as the acetone adduct (eq1). However, this 2-hydroxy-2-hydroperoxypropane compound is not capable of direct epoxidation of olefins since the baseline experiment, treating olefin with H₂O₂ in acetone/water (ratio 4:1) without catalyst, produces no conversion of olefin to epoxide. Furthermore, Que's work demonstrated that oxidation of cyclooctene with Fe^{II}(tpa) catalyst by H₂O₂ in acetone or acetonitrile provided similar product distributions, and the complexation reaction between 2-hydroxy-2-hydroperoxypropane and Que's catalyst formed an adduct that is not active in oxidation, indicating that 2-hydroxy-2-hydroperoxypropane was not involved in the epoxidation reactions.² In addition, dimethyl dioxirane, a known active intermediate in ketone catalyzed epoxidation reactions,³ is also not involved in epoxidation under our reaction condition (see parallel experiment without catalyst).



References

1. Sauer, M.C. V., Edwards, J. O. *J. Phys. Chem.* **1971**, 75, 3004.
2. Payeras, A. M., Ho, R. Y. N., Fujita, M., Que, Jr. L. *Chem. Eur. J.* **2004**, 10, 4944.
3. Wang, Z., Tu, Y., Frohn, M., Zhang, J., Shi, Y. *J. Am. Chem. Soc.* **1997**, 119, 11224.

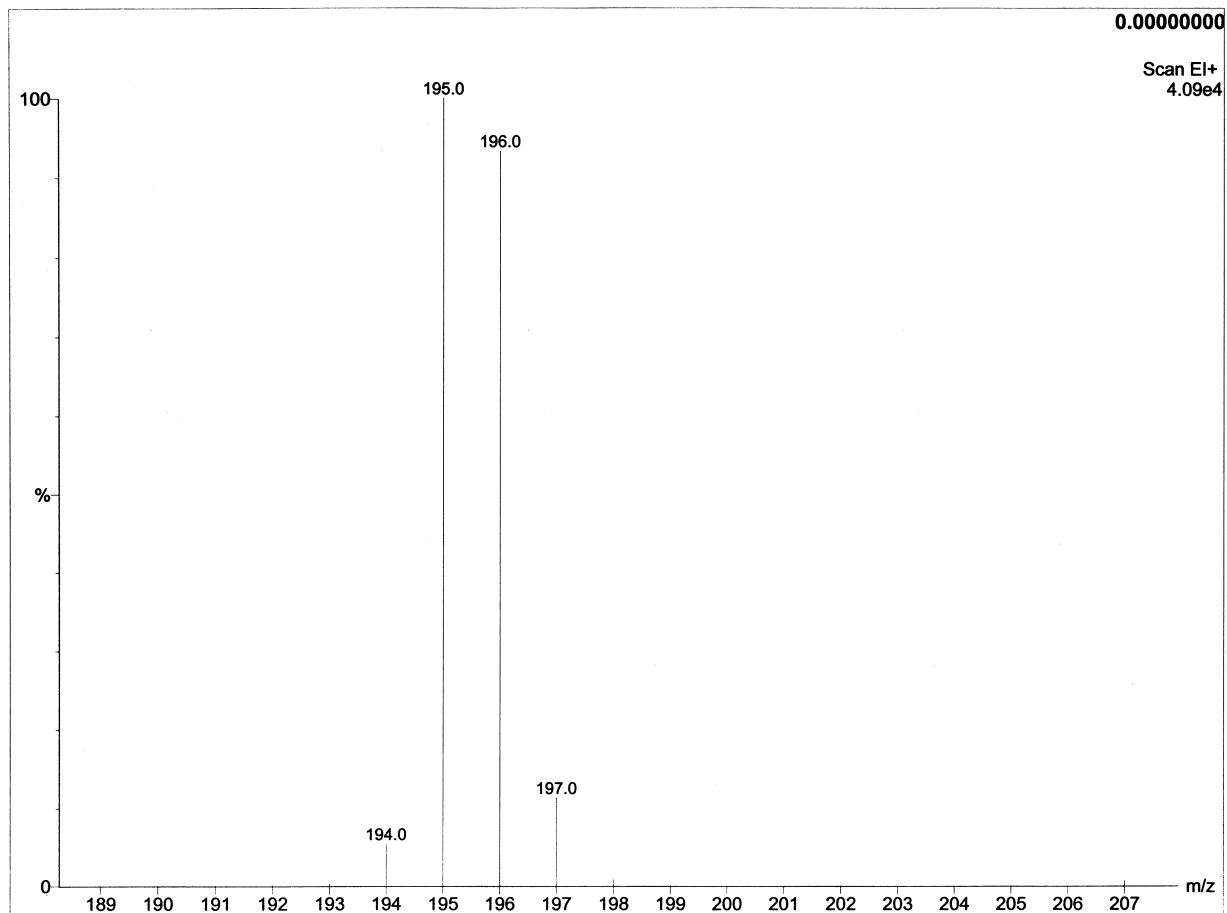


Figure S1 GC/MS graph of *cis*-stilbene oxide from epoxidation of *cis*-stilbene with $\text{Mn}(\text{Me}_2\text{EBC})\text{Cl}_2/\text{H}_2\text{O}_2/\text{H}_2\text{O}$ under air.

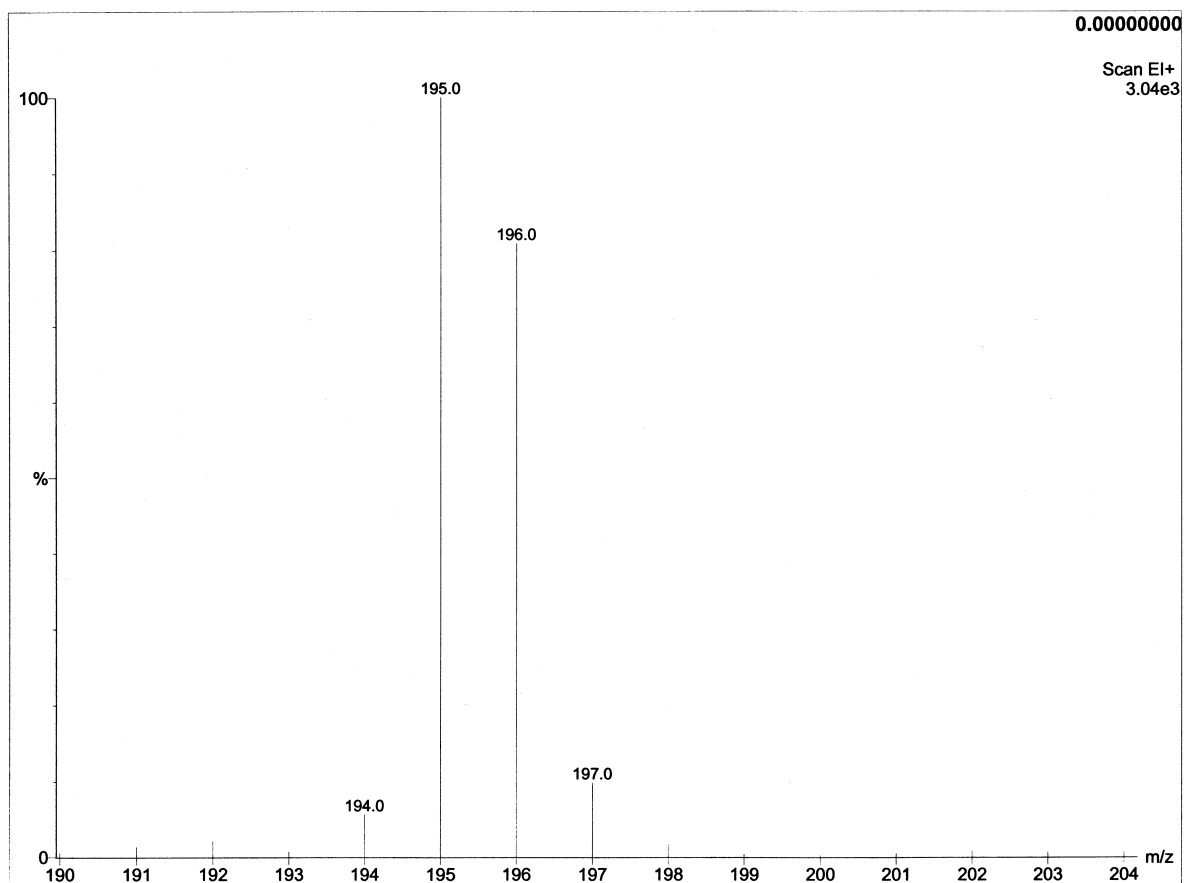


Figure S2 GC/MS graph of *trans*-stilbene oxide from epoxidation of *cis*-stilbene with Mn(Me₂EBC)Cl₂/H₂O₂/H₂O under air.

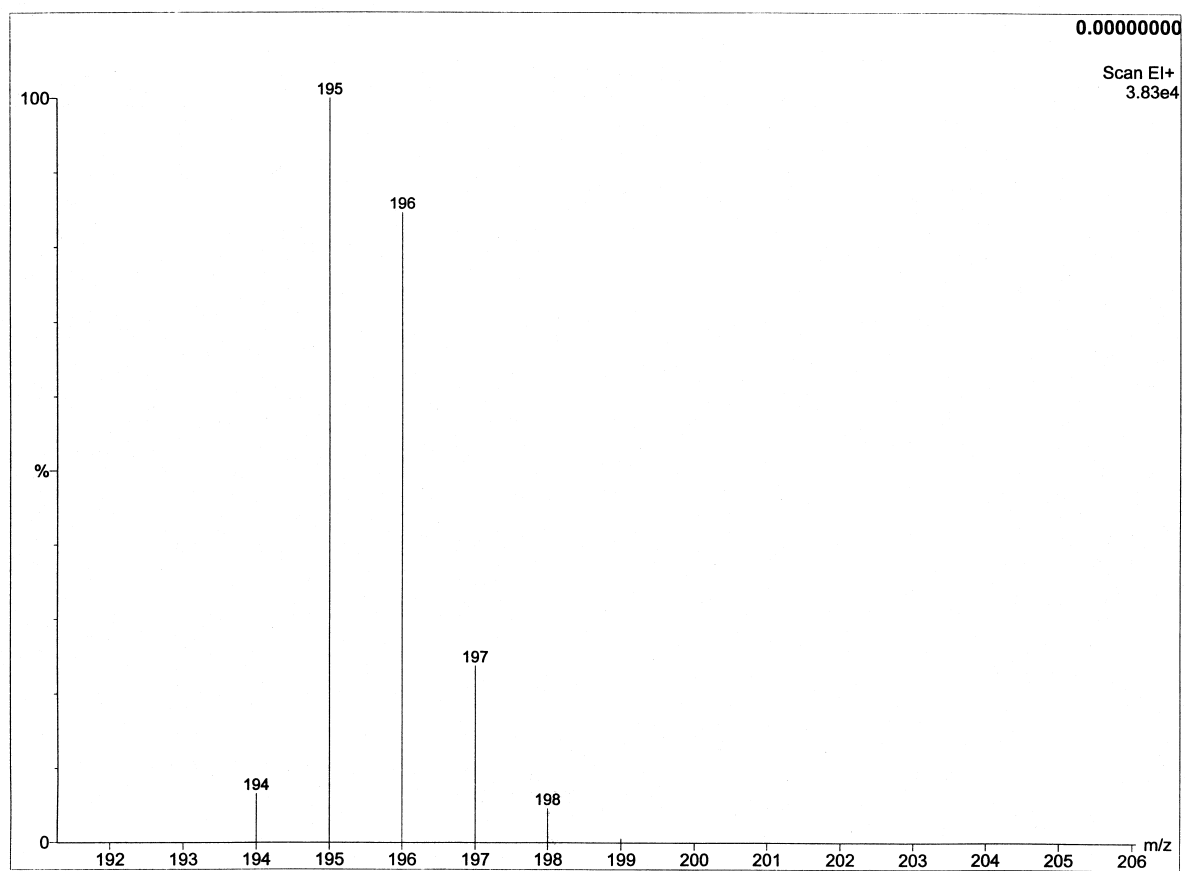


Figure S3 GC/MS graph of *cis*-stilbene oxide from epoxidation of *cis*-stilbene with $\text{Mn}(\text{Me}_2\text{EBC})\text{Cl}_2/\text{H}_2\text{O}_2/\text{H}_2^{18}\text{O}$ under air.

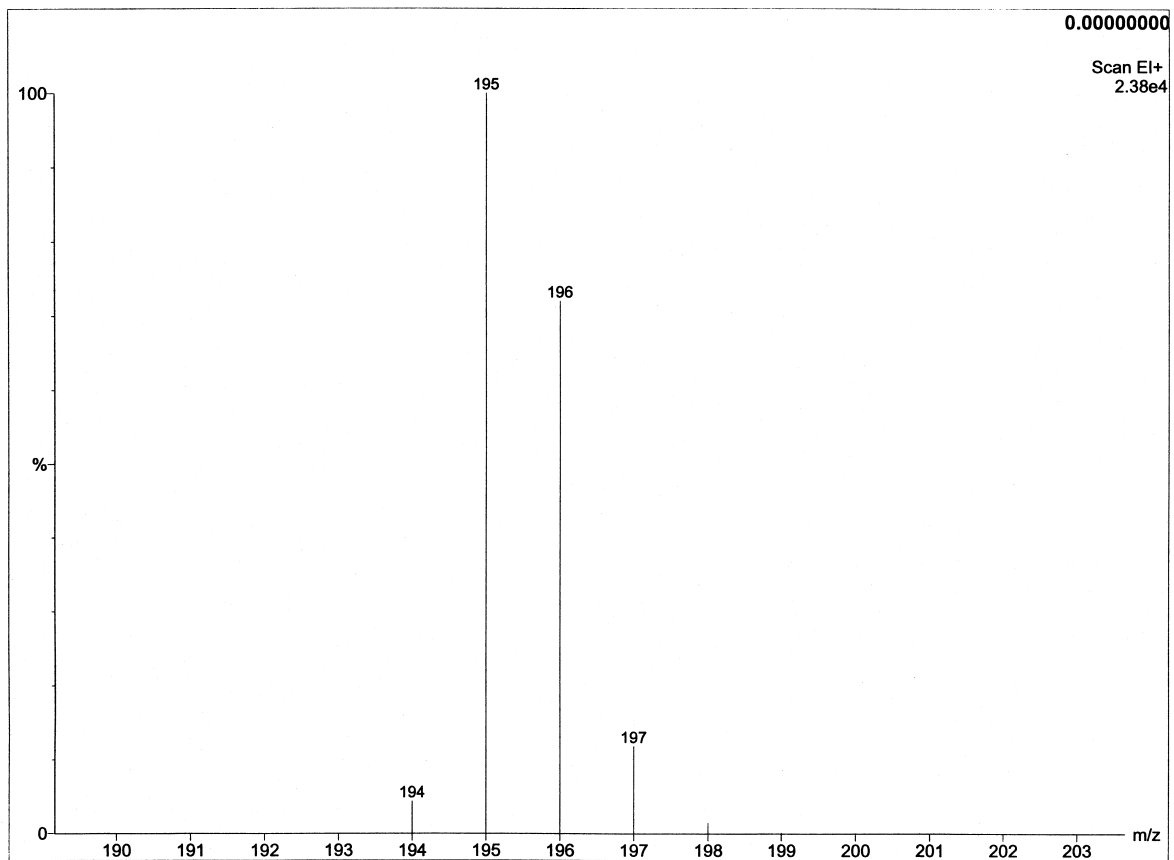


Figure S4 GC/MS graph of *trans*-stilbene oxide from epoxidation of *cis*-stilbene with $\text{Mn}(\text{Me}_2\text{EBC})\text{Cl}_2/\text{H}_2\text{O}_2/\text{H}_2^{18}\text{O}$ under air.

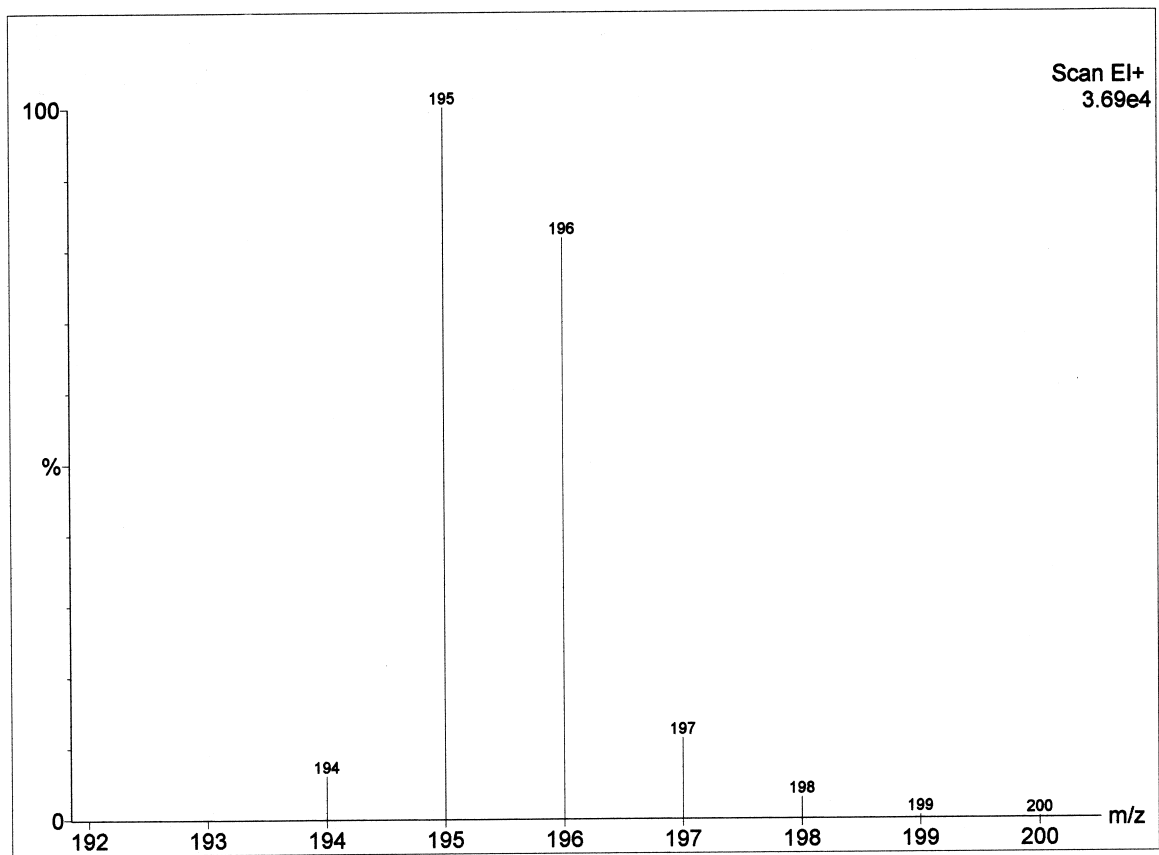


Figure S5 GC/MS graph of *cis*-stilbene oxide from epoxidation of *cis*-stilbene with $\text{Mn}(\text{Me}_2\text{EBC})\text{Cl}_2/\text{H}_2\text{O}_2/\text{H}_2\text{O}$ under $^{18}\text{O}_2$.

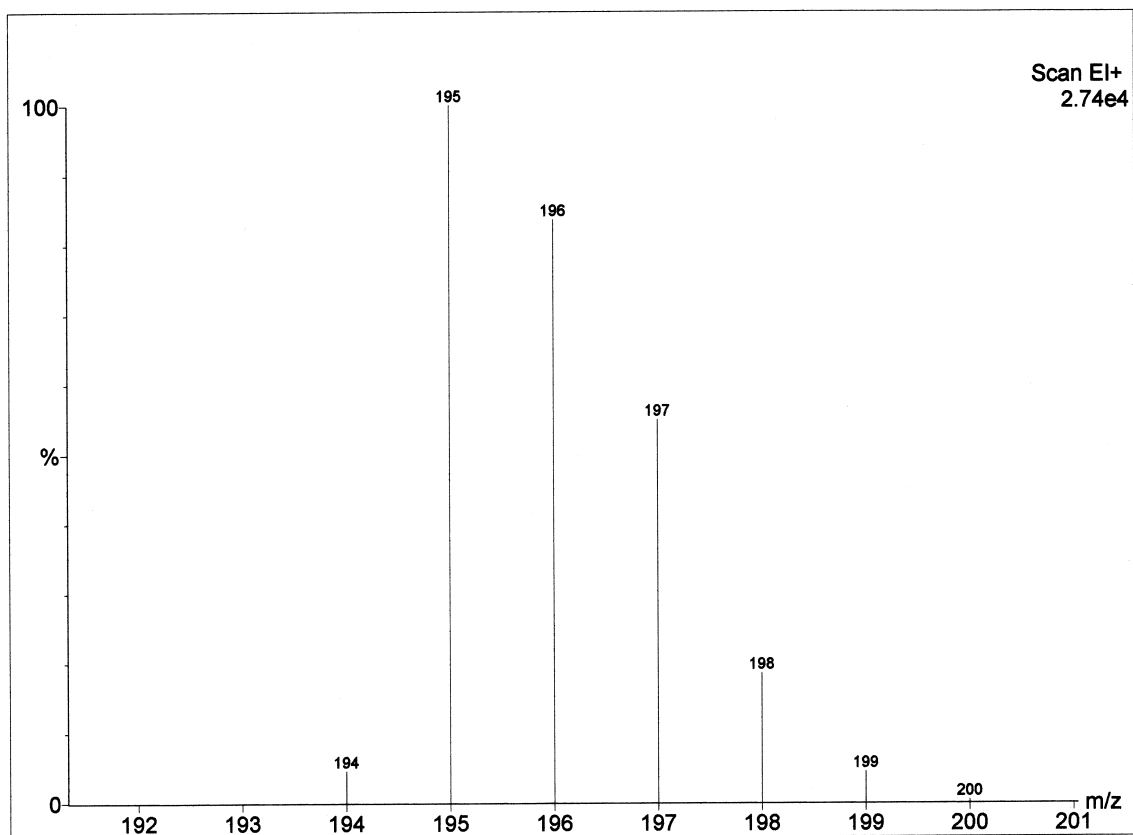


Figure S6 GC/MS graph of *trans*-stilbene oxide from epoxidation of *cis*-stilbene with $\text{Mn}(\text{Me}_2\text{EBC})\text{Cl}_2/\text{H}_2\text{O}_2/\text{H}_2\text{O}$ under $^{18}\text{O}_2$.

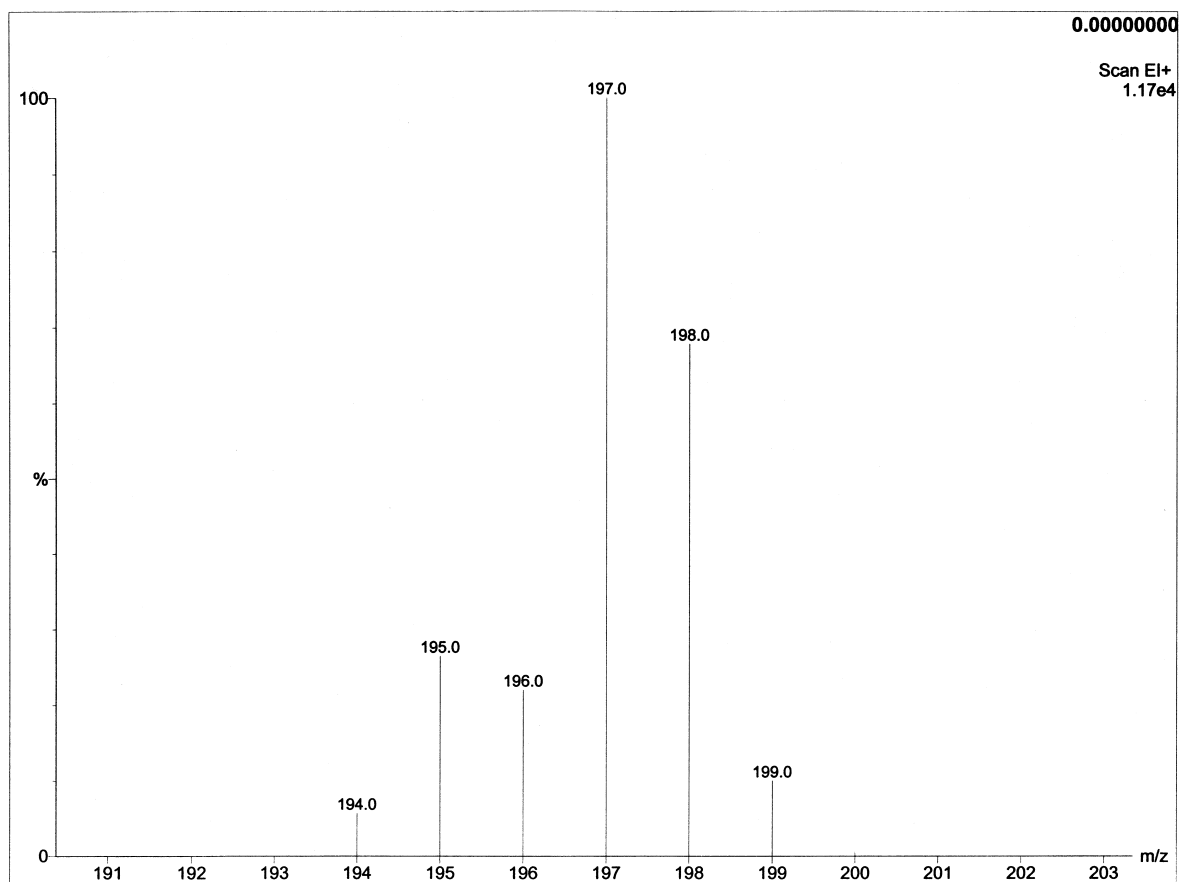


Figure S7 GC/MS graph of *cis*-stilbene oxide from epoxidation of *cis*-stilbene with $\text{Mn}(\text{Me}_2\text{EBC})\text{Cl}_2/\text{H}_2^{18}\text{O}_2/\text{H}_2\text{O}$ under air.

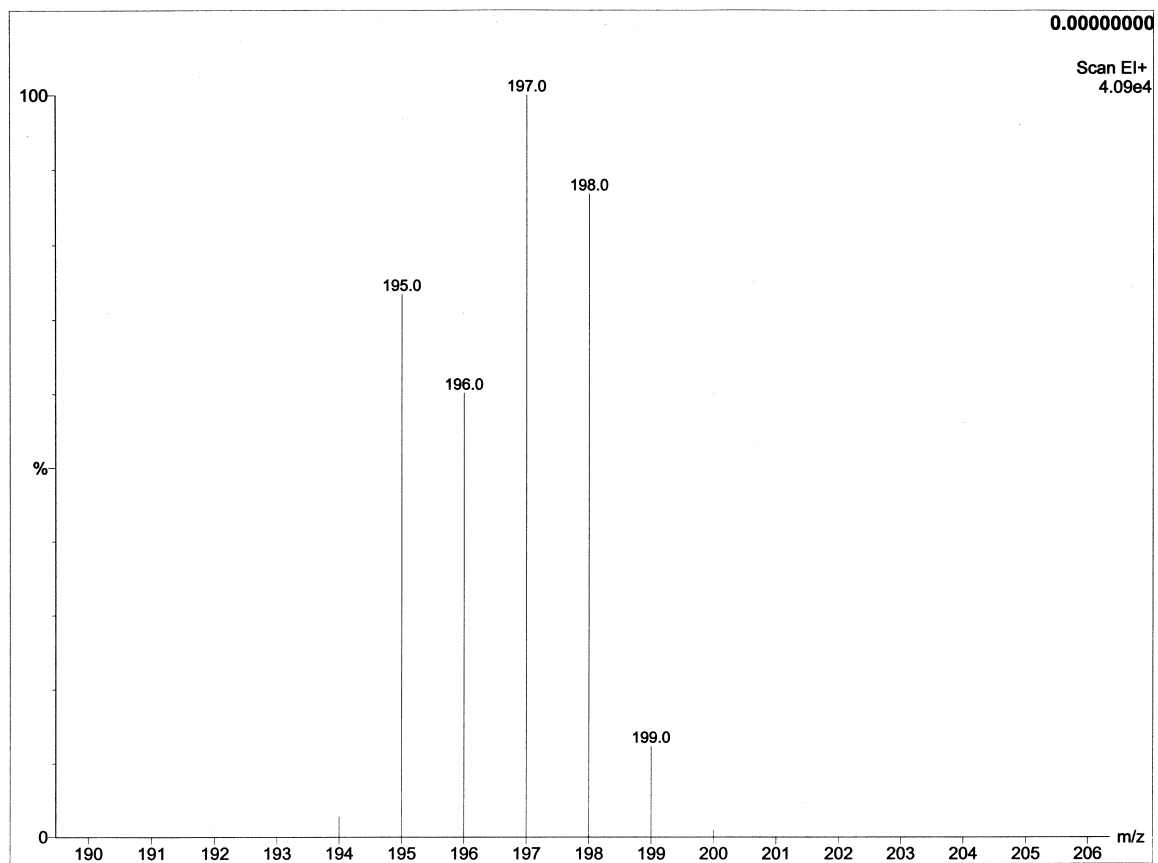


Figure S8 GC/MS graph of *trans*-stilbene oxide from epoxidation of *cis*-stilbene with $\text{Mn}(\text{Me}_2\text{EBC})\text{Cl}_2/\text{H}_2^{18}\text{O}_2/\text{H}_2\text{O}$ under air.