





897 8445 445 444

C2/s

C2/d





64.47 64.47 64.47

C3/d

TS-[C1-C3]/s

C3/s



**Fig S1**: Optimized geometrical parameters of reaction of  $\text{ReO}_4^-$  with ethylene. Bond distance in Å and angles in degrees.





Fig S2: Optimized geometrical parameters of reaction of  $ReO_3Cl$  with ethylene. Bond distance in Å and angles in degrees.



TS-[C8-C10]/s

C10/s









**Fig S3**: Optimized geometrical parameters of reaction of  $ReO_3NPH_3$  with ethylene. Bond distance in Å and angles in degrees











TS-[C13-C14]/s



C14/s



C14/d







TS-[C13-C14]/d







TS-[C15-C14]/d

TS-[C15-C14]/t



Fig S4: Optimized geometrical parameters of reaction of  $ReO_3CH_3$  with ethylene. Bond distance in Å and angles in degrees





B/d

Fig S5: Optimized geometrical parameters of reaction of  $TcO_3OCH_3$  with ethylene. Bond distance in Å and angles in degrees



Fig S6: Optimized geometrical parameters of reaction of  $ReO_3Cp$  with ethylene. Bond distance in Å and angles in degrees