Electronic Supplementary Information for

Catalytic Coupling of CO_2 with Epoxide by the Ionic Liquid Modified Metal Macrocycles: Insight into Mechanism and Activity Regulation from Density functional Calculations

Ping Li and Zexing Cao*

State Key Laboratory of Physical Chemistry of Solid Surfaces, Fujian Provincial Key Laboratory of Theoretical and Computational Chemistry, and College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 360015, China

E−mail: zxcao@xmu.edu.cn; Fax: (+86) 592-218-3047; Tel:(+86) 592-218-6081

Table of Contents

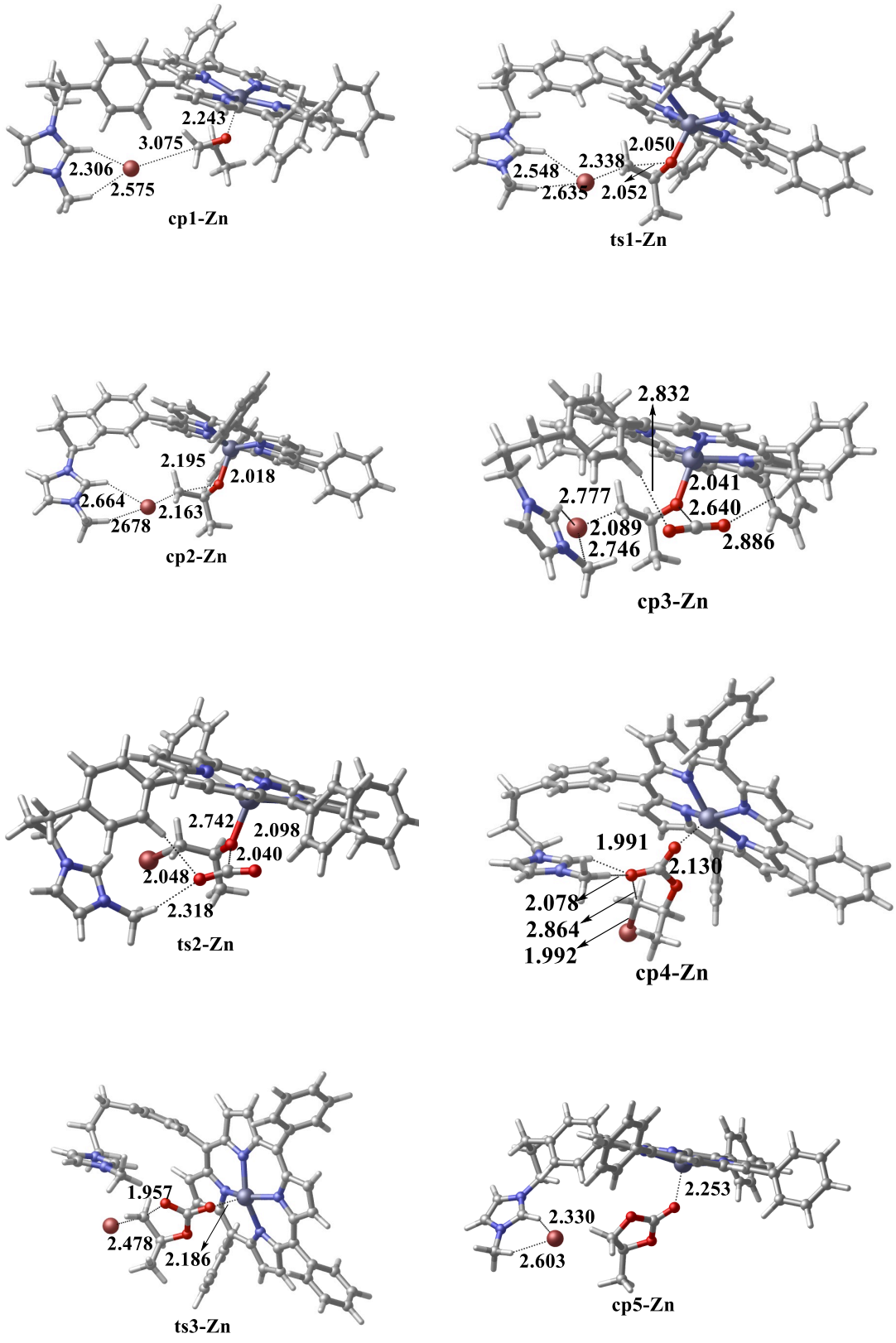


Fig. S1 Optimized structures (bonds in Å) of species for the cycloaddition reaction of CO_2 and PO catalyzed by IL-Zn(TPP) and the Zn as the catalytic center.

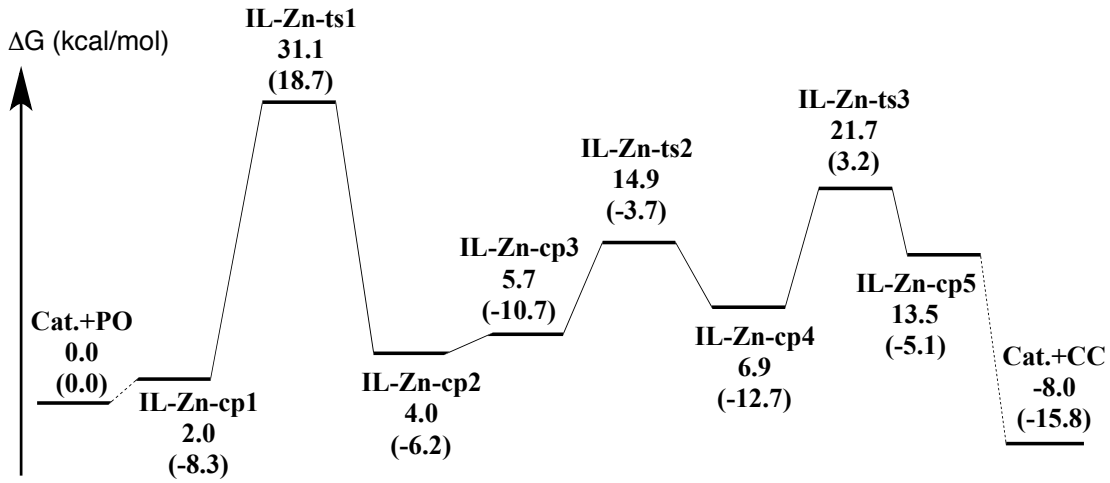
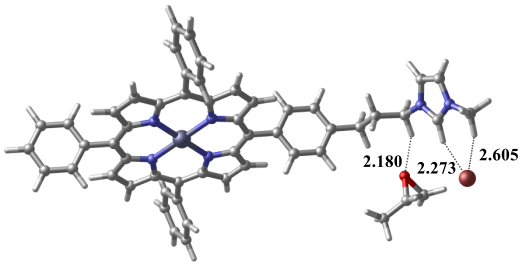
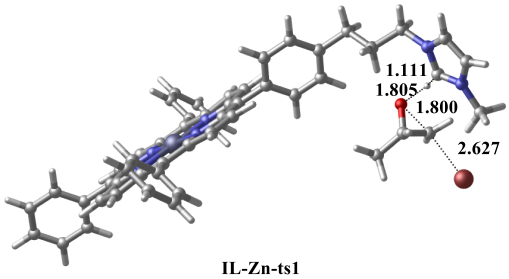


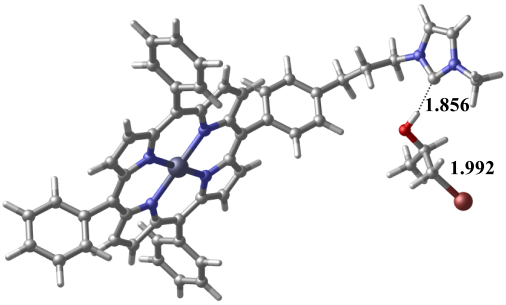
Fig. S2 Predicted relative free energy profile and electronic energies (in parentheses) for the cycloaddition reaction of CO_2 and PO catalyzed by IL-Zn(TPP) and the imidazole as the catalytic center.



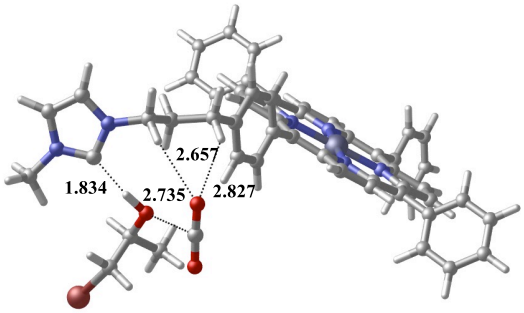
IL-Zn-cp1



IL-Zn-ts1



IL-Zn-cp2-N



IL-Zn-cp3

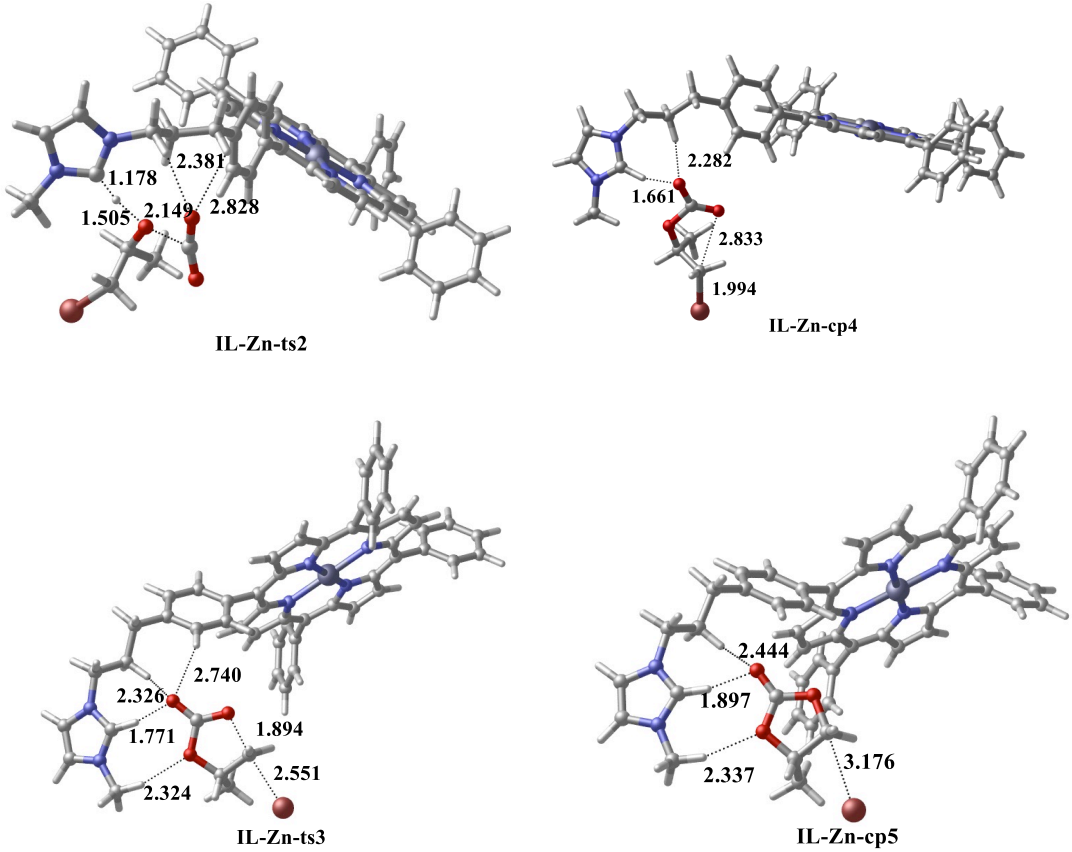
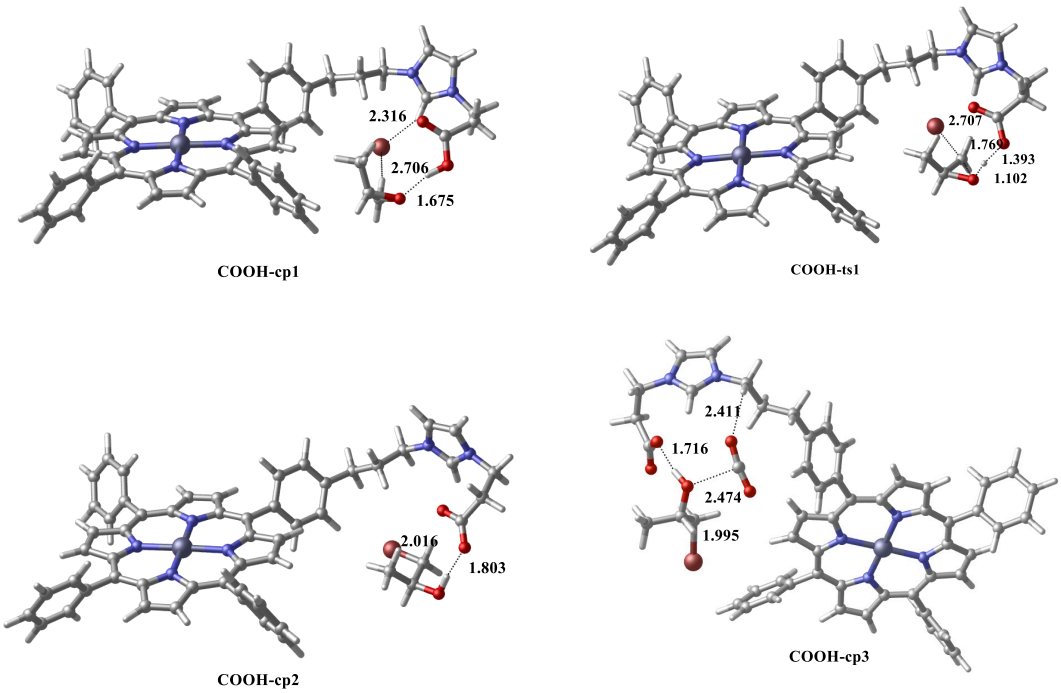


Fig. S3 Optimized structures (bonds in Å) of species for the cycloaddition reaction of CO_2 and PO catalyzed by IL-Zn(TPP) and the imidazole as the catalytic center.



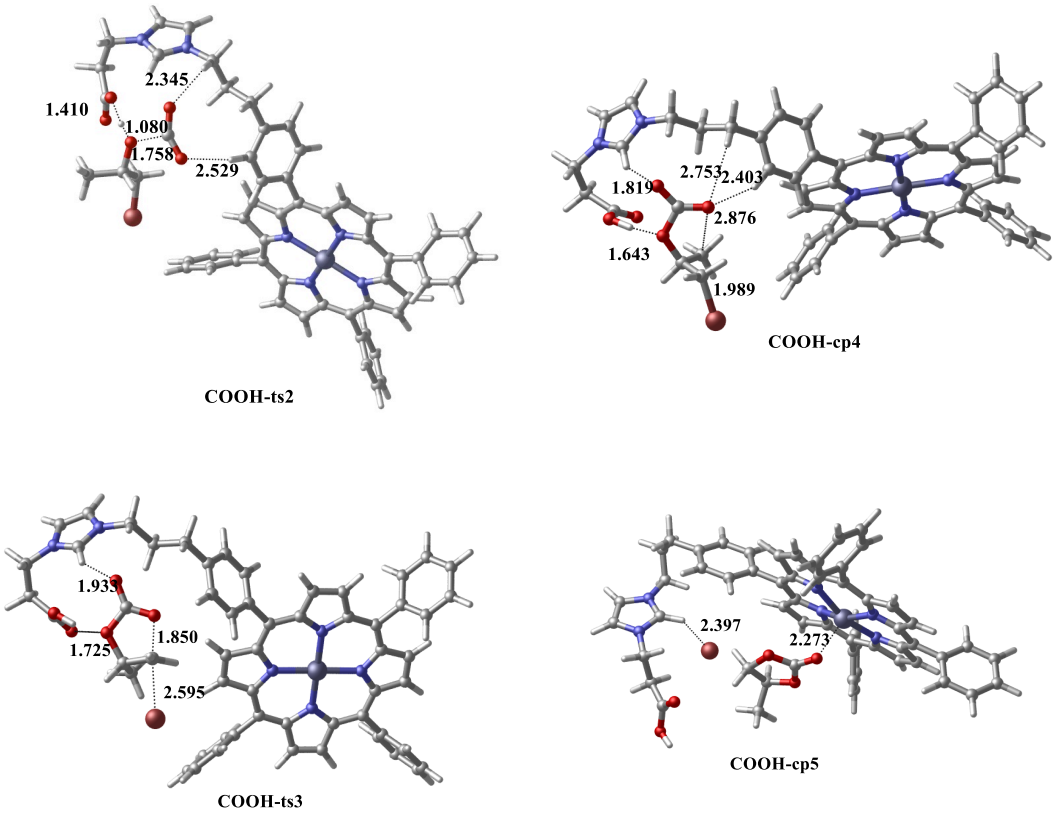


Fig. S4 Optimized structures (bonds in Å) of species for the cycloaddition reaction of CO_2 and PO catalyzed by IL-Zn(TPP) and the COOH group as the catalytic center.

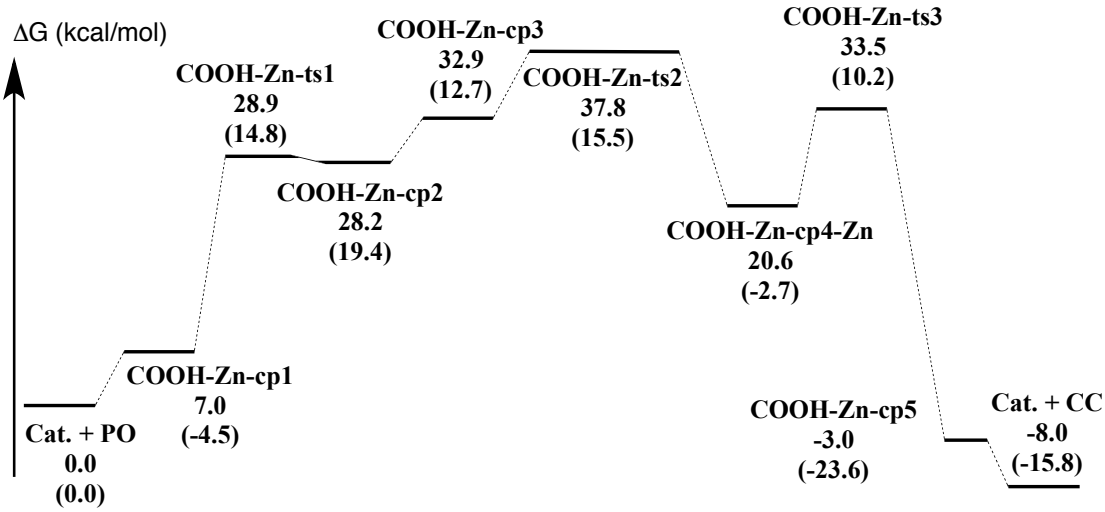
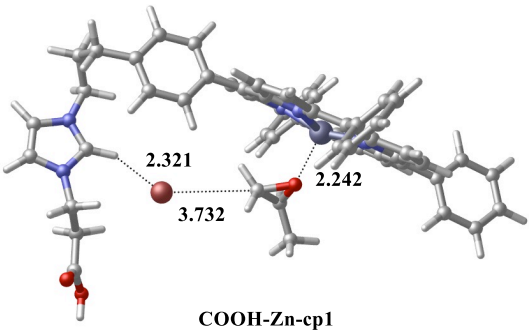
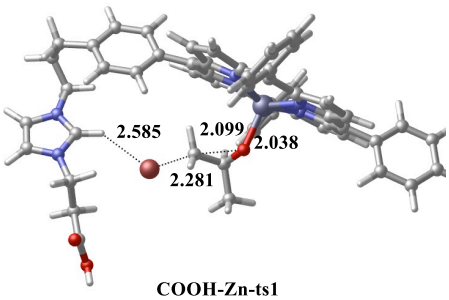


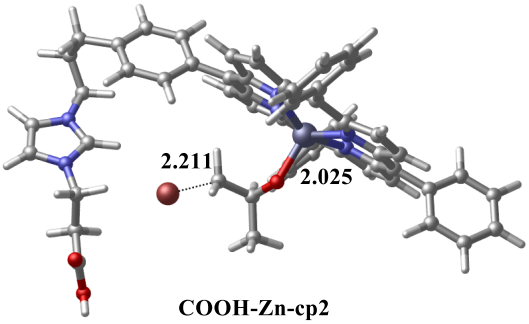
Fig. S5 Predicted relative free energy profile and electronic energies (in parentheses) for the cycloaddition reaction of CO_2 and PO catalyzed by the metalloporphyrin moiety of COOH-IL-Zn(TPP).



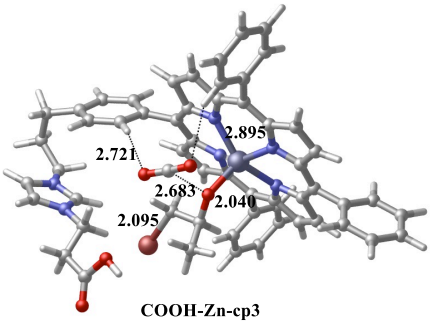
COOH-Zn-cp1



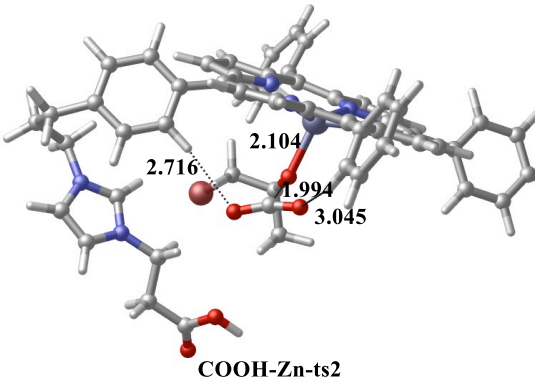
COOH-Zn-ts1



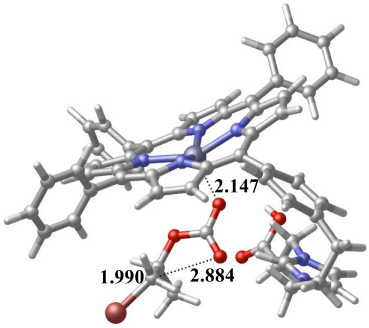
COOH-Zn-cp2



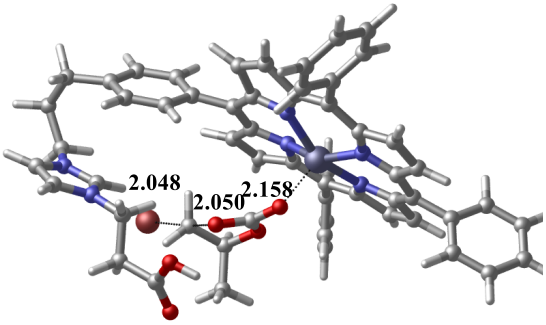
COOH-Zn-cp3



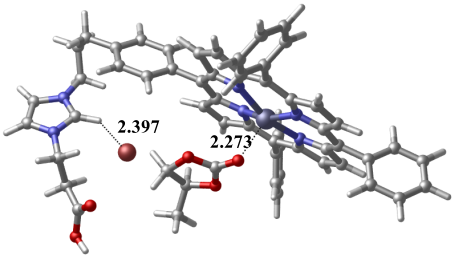
COOH-Zn-ts2



COOH-Zn-cp4



COOH-Zn-ts3



COOH-cp5

Fig. S6 Optimized structures (bonds in Å) of species for the catalytic cycloaddition reaction of CO_2 and PO by COOH-IL-Zn(TPP).

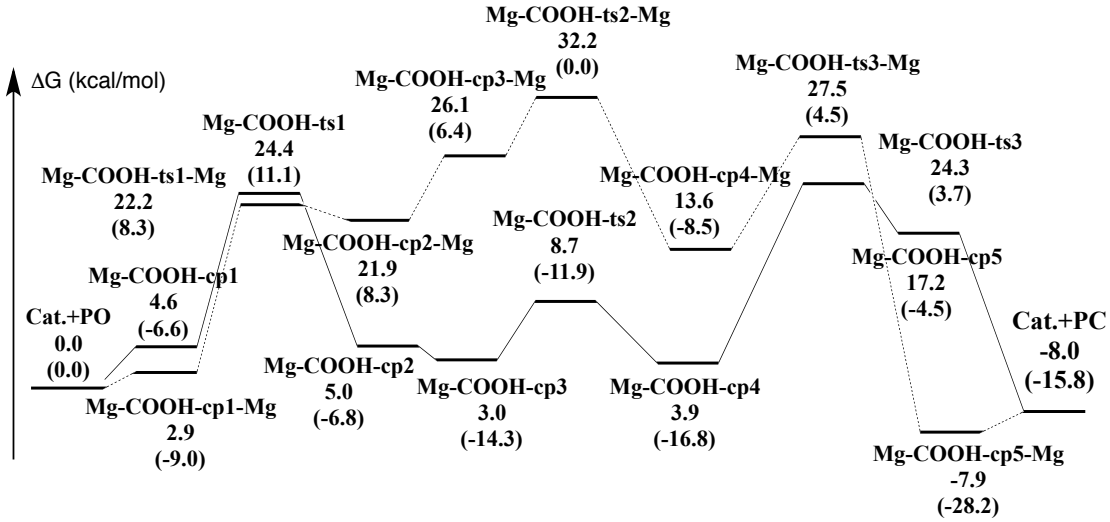
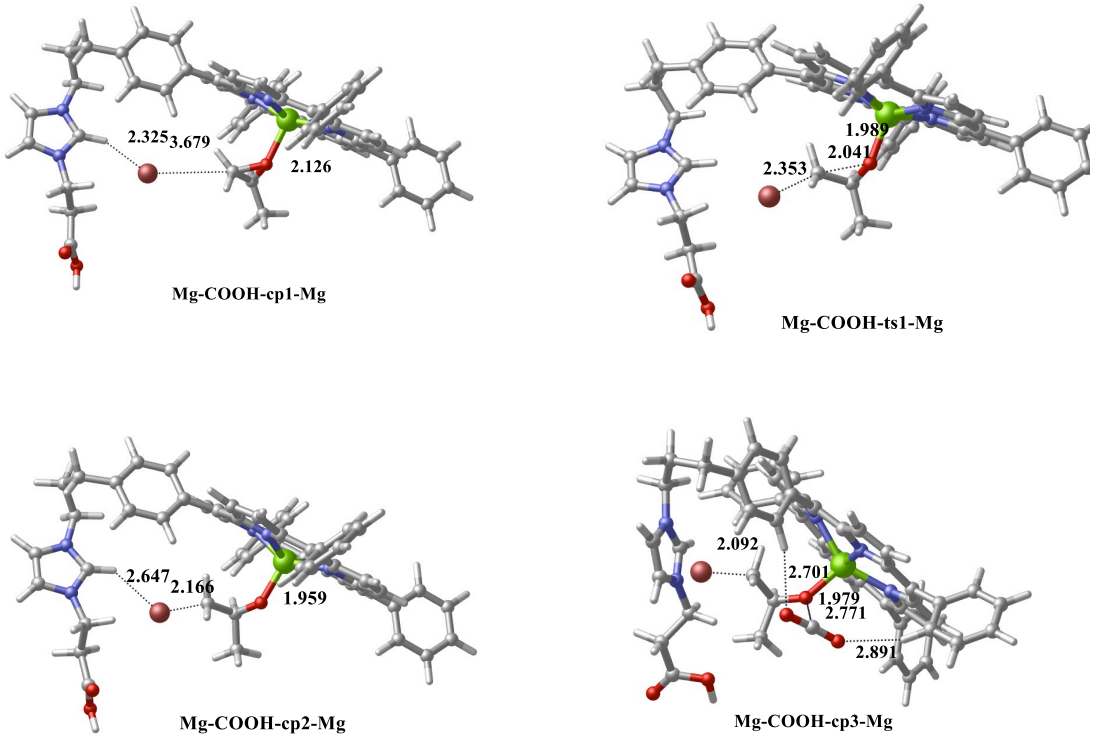
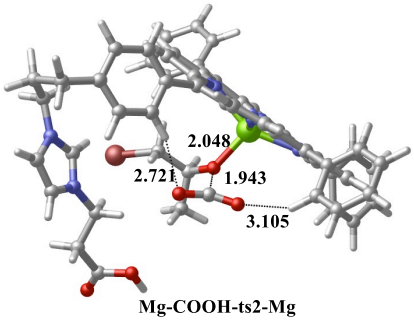
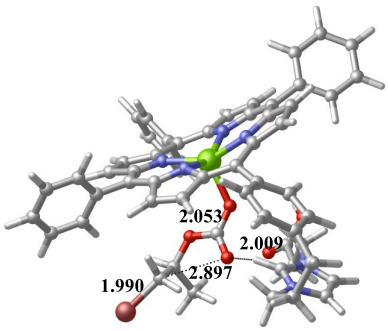


Fig. S7 Predicted relative free energy profile and electronic energies (in parentheses) for the catalytic cycloaddition reaction of CO_2 and PO by COOH-IL-Mg(TPP).

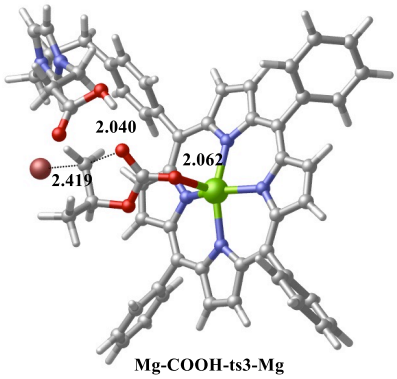




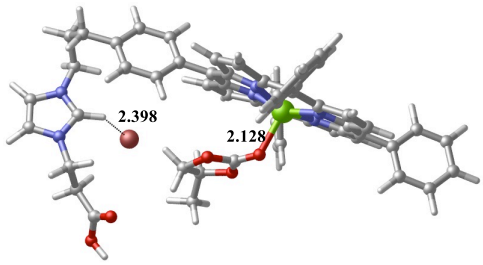
Mg-COOH-ts2-Mg



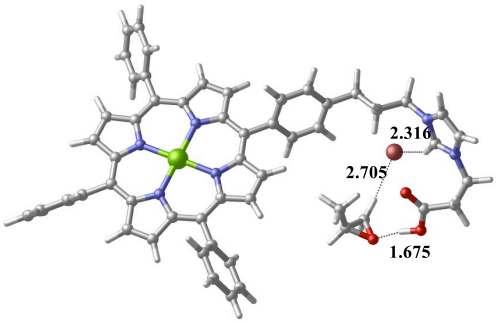
Mg-COOH-cp4-Mg



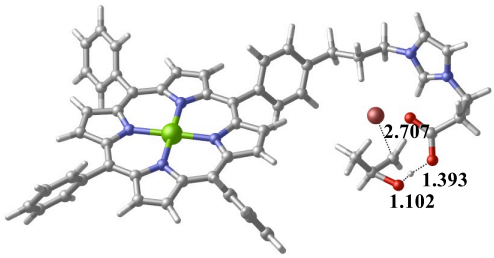
Mg-COOH-ts3-Mg



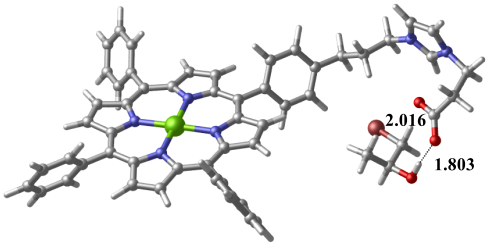
Mg-COOH-cp5-Mg



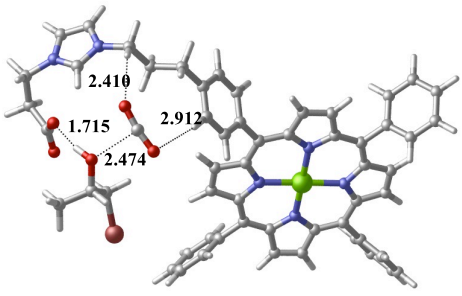
Mg-COOH-cp1



Mg-COOH-ts1



Mg-COOH-cp2



Mg-COOH-cp3

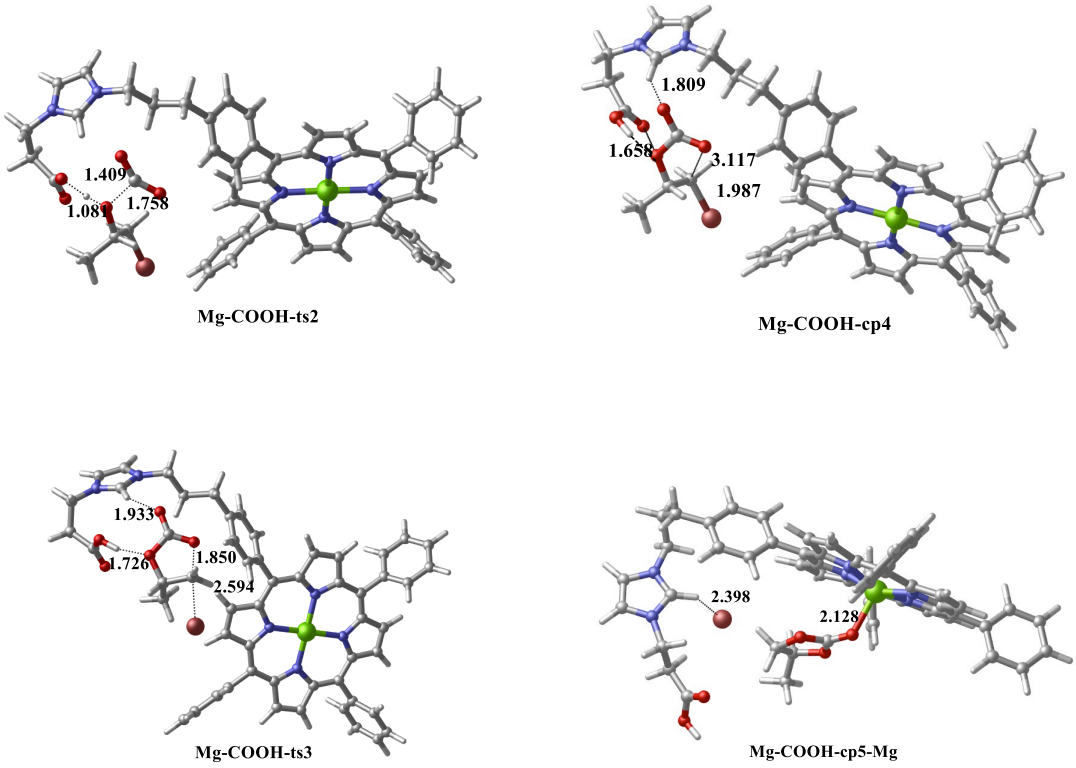
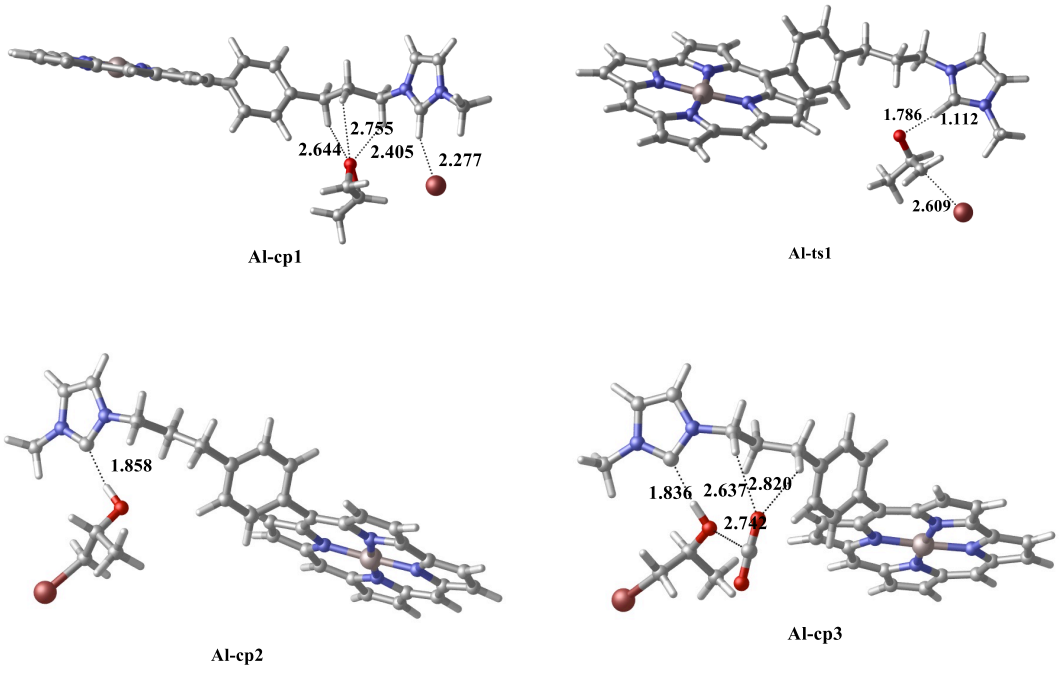


Fig. S8 Optimized structures (bonds in Å) of species for the catalytic cycloaddition reaction of CO_2 and PO by COOH-IL-Mg(TPP).



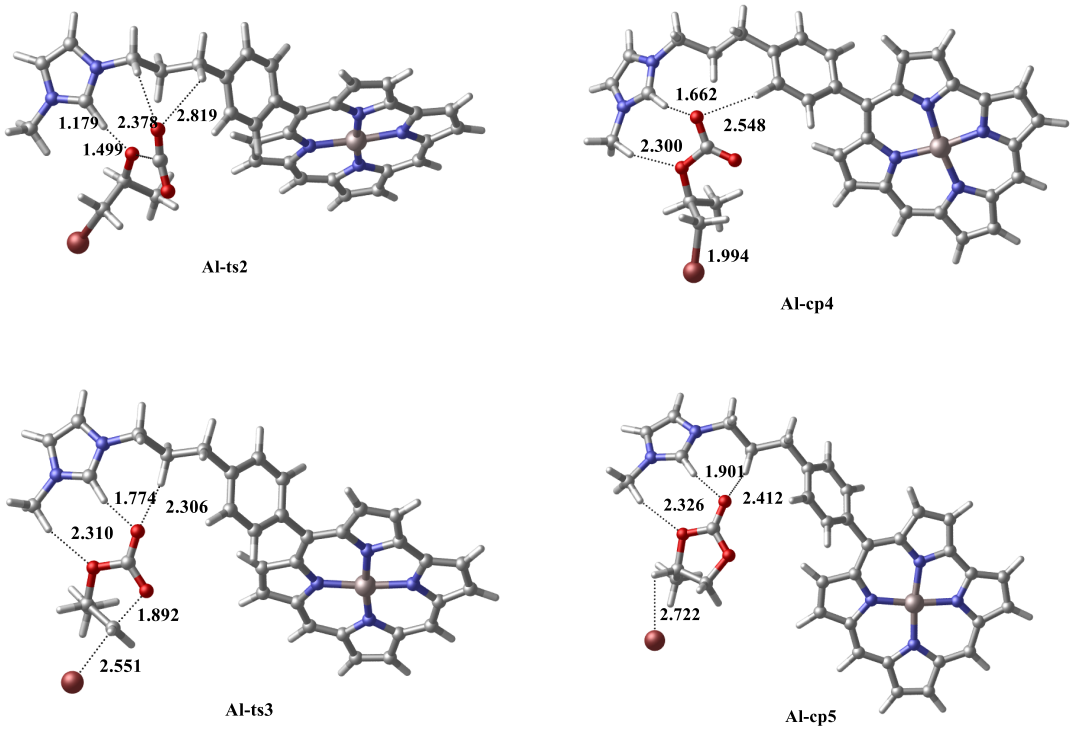
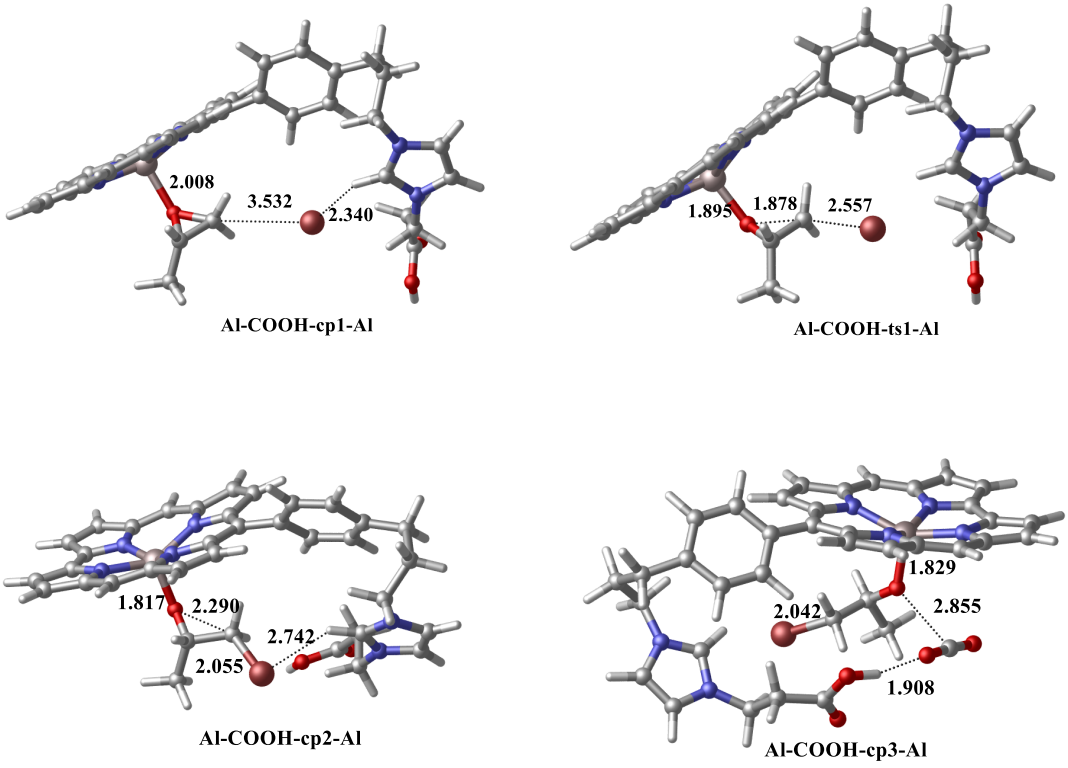
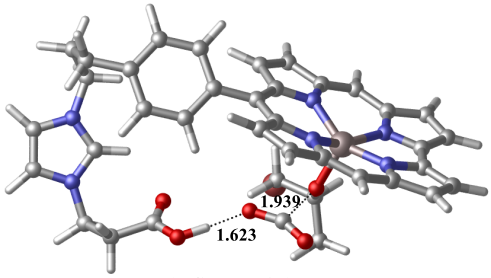
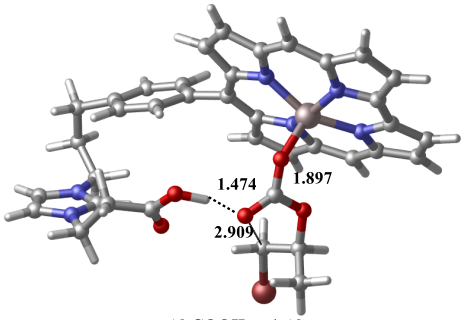


Fig. S9 Optimized structures (bonds in Å) of species involved in the catalytic cycloaddition reaction of CO_2 and PO by the IL moiety of IL-Al(Cor).

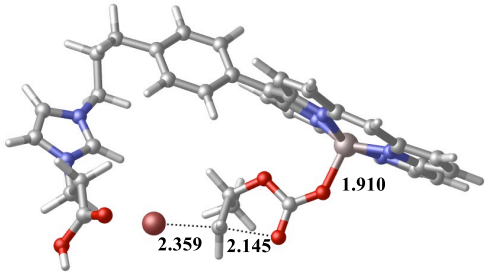




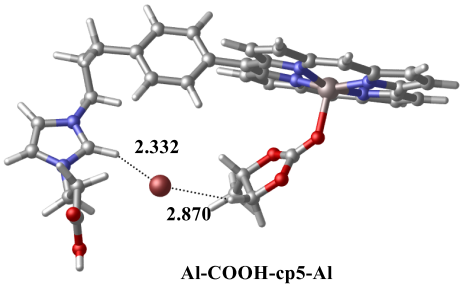
Al-COOH-ts2-Al



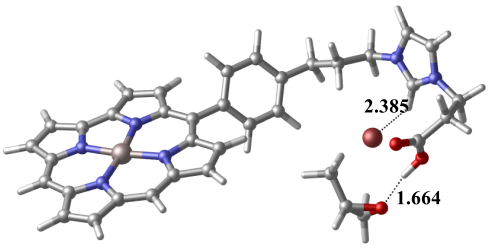
Al-COOH-cp4-Al



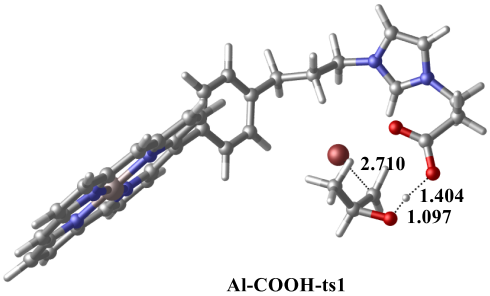
Al-COOH-ts3-Al



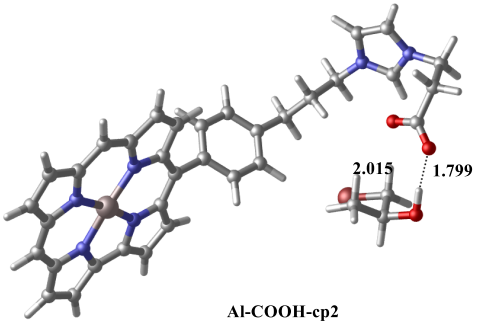
Al-COOH-cp5-Al



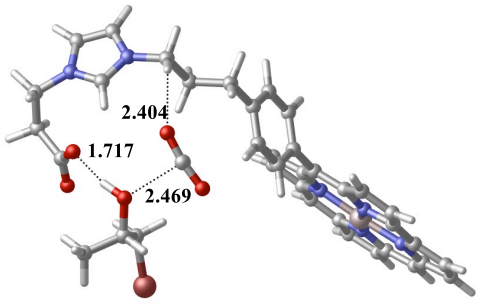
Al-COOH-cp1



Al-COOH-ts1



Al-COOH-cp2



Al-COOH-cp3

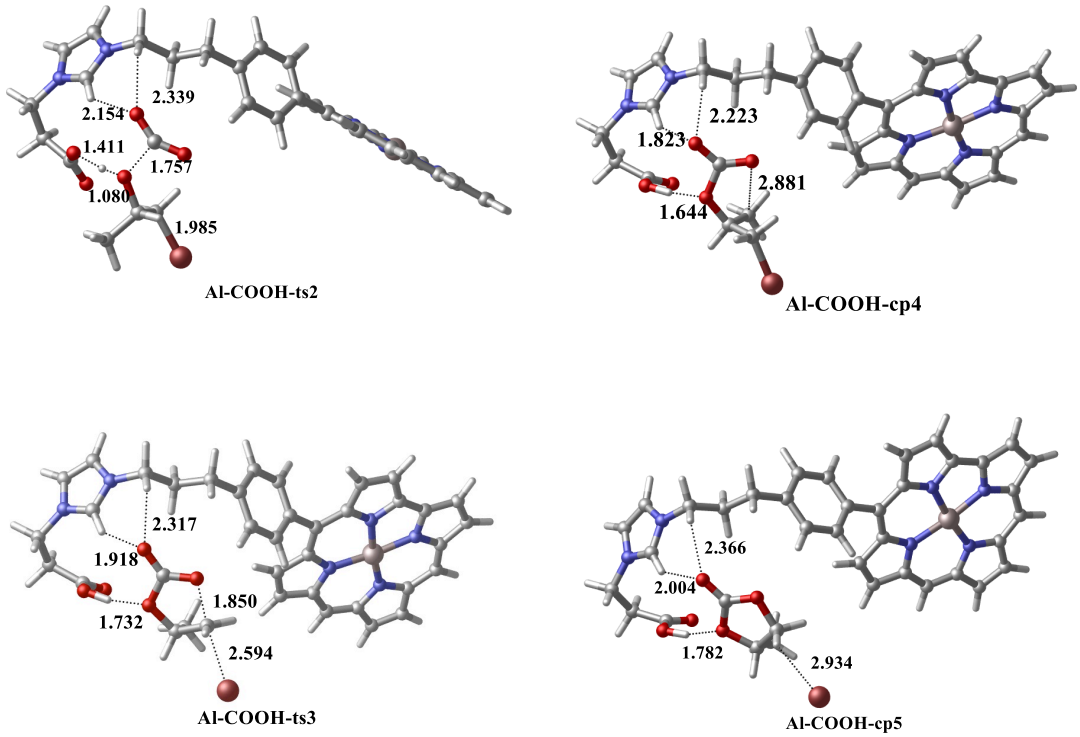


Fig. S10 Optimized structures (bonds in Å) of species for the catalytic cycloaddition reaction of CO_2 and PO by COOH- IL-Al(Cor).

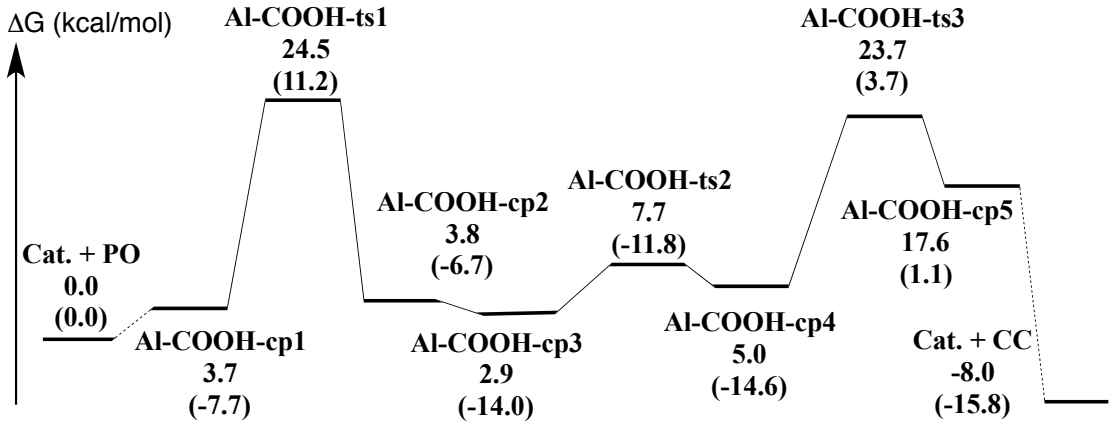


Fig. S11 Predicted relative free energy profile and electronic energies (in parentheses) for the catalytic cycloaddition reaction of CO_2 and PO by the IL moiety of COOH-IL-Al(Cor).

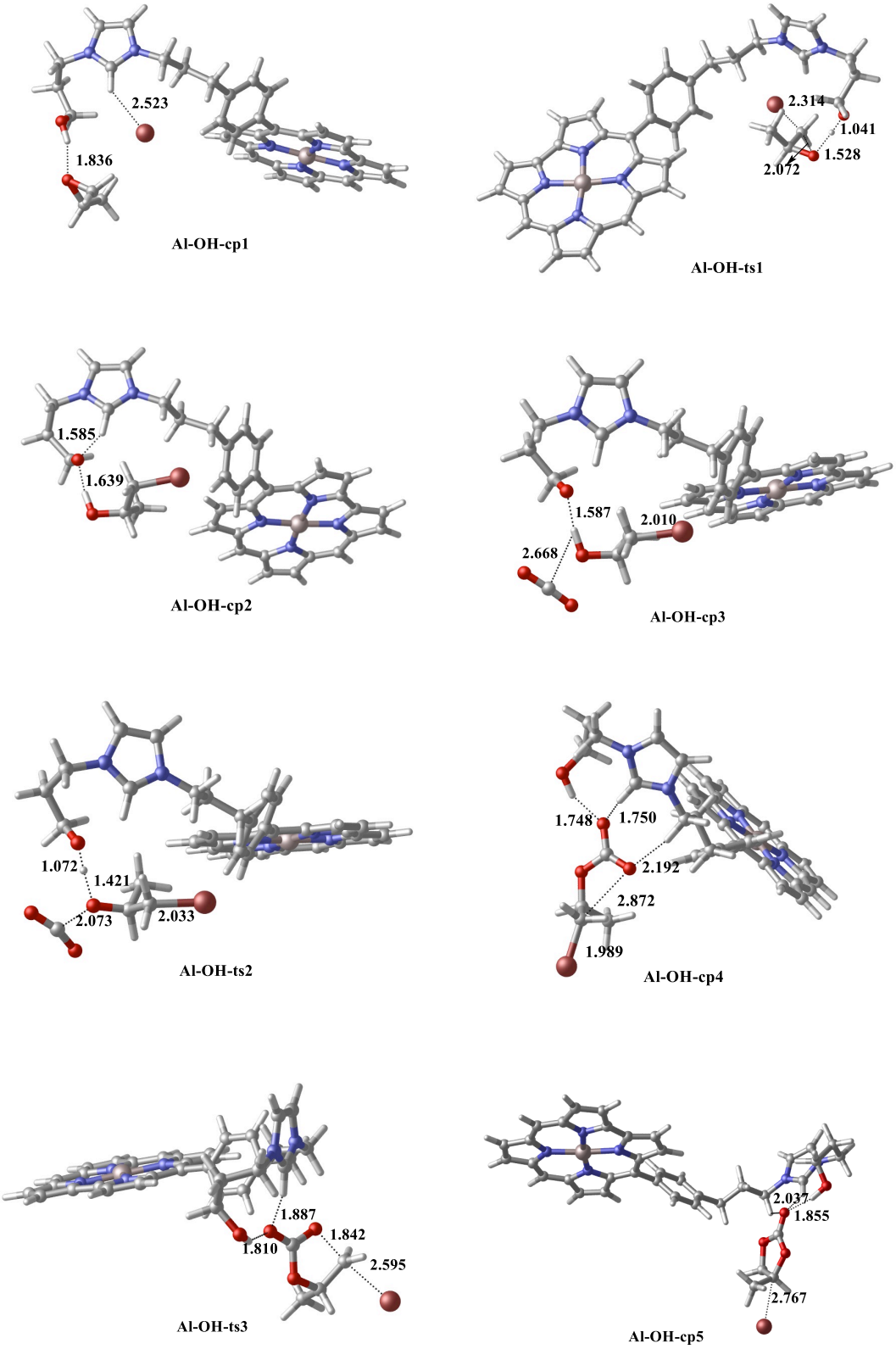


Fig. S12 Optimized structures (bonds in Å) of species for the catalytic cycloaddition reaction of CO_2 and PO by the IL moiety of OH- IL-Al(Cor).

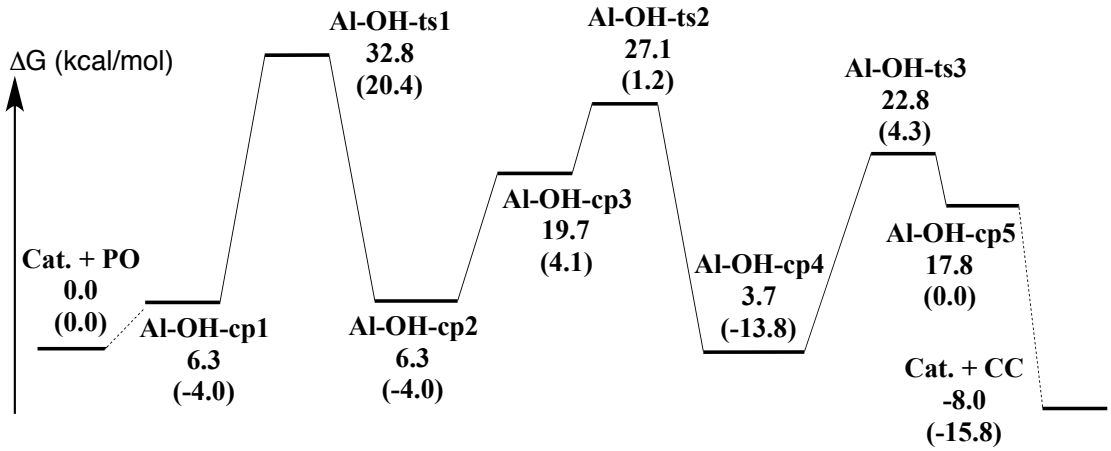


Fig. S13 Predicted relative free energy profile and electronic energies (in parentheses) for the catalytic cycloaddition reaction of CO_2 and PO by the IL moiety of OH-IL-Al(Cor).