Comparison of the barriers for CO_2 insertion facilitated by NEt_3, TMP, pyridine and DBU into the hydroxyl group of 2,2-dimethyl-1,3-propanediol via a ternary Lewis base-CO_2-diol mechanism is shown.

Table S4. Computed free Gibbs energies at the rωb97xD/6-31+g(d)/cpcm=acetonitrile/298K level of theory

Structure	*G (Hartree)*	*ΔG (kcal/mol)*
2,2-dimethyl-1,3-propanediol	-347.961854	-
CO_2	-188.536520	-
NEt_3	-292.159794	-
2,2-dimethyl 1-3 propanediol ($+NEt_3+CO_2$)	-828.658168	0 (NEt_3 reference)
I_a	-828.658929	-0.5
$TS1_a$	-828.646307	+7.4
II_a	-828.677571	-12.2
TMP	-347.961854	-
2,2-dimethyl-1,3-propanediol ($+TMP+CO_2$)	-945.324505	+7.9
I_b	-945.344464	-12.8
$TS1_b$	-945.311465	-1.4
Pyridine	-248.147221	-
2,2-dimethyl-1,3-propanediol ($+pyridine+CO_2$)	-784.645595	0 (pyridine reference)
I_c	-784.644178	+0.9
$TS_{I\text{-}IIc}$	-784.627340	+11.5
II_c	-784.644624	+0.6
DBU	-461.756771	-
2,2-dimethyl-1,3-propanediol ($+DBU+CO_2$)	-998.255145	0 (DBU reference)
I_d	-998.251133	-11.2
$TS_{I\text{-}IId}$	-998.272909	+2.5
II_d	-998.283852	-19.5

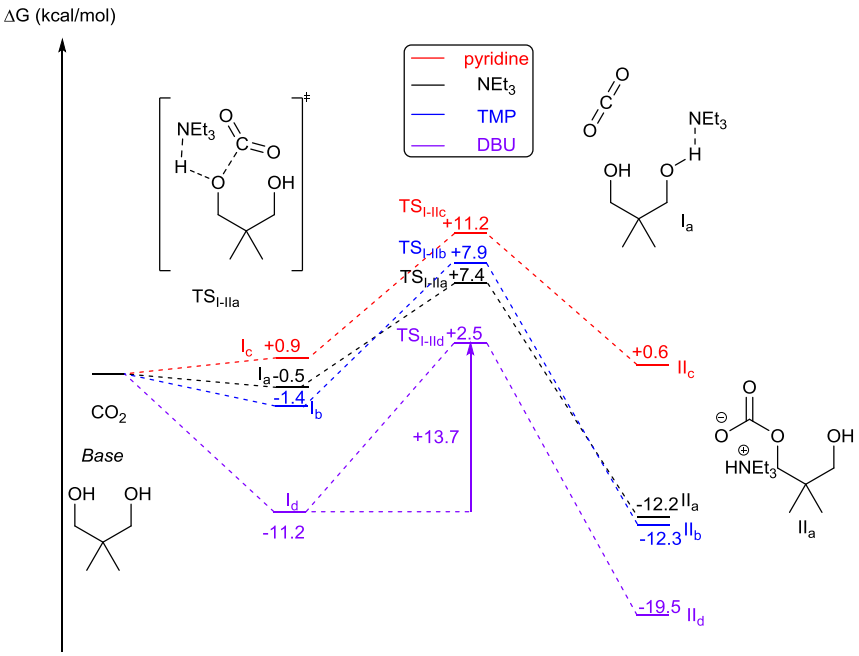

Fig. S4. Computed energy diagram for pyridine (black), NEt_3 (red) and DBU (blue) facilitated CO_2 insertion. Computed at the rωb97xD/6-31+g(d)/cpcm=acetonitrile/298K level of theory. Enthalpies given in kcal/mol.