Supplementary Information (SI) for Organic Chemistry Frontiers.
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Origin of Enantioselectivity in Copper-Catalyzed Aziridination of Enol Silyl Ethers: A Comprehensive DFT Study

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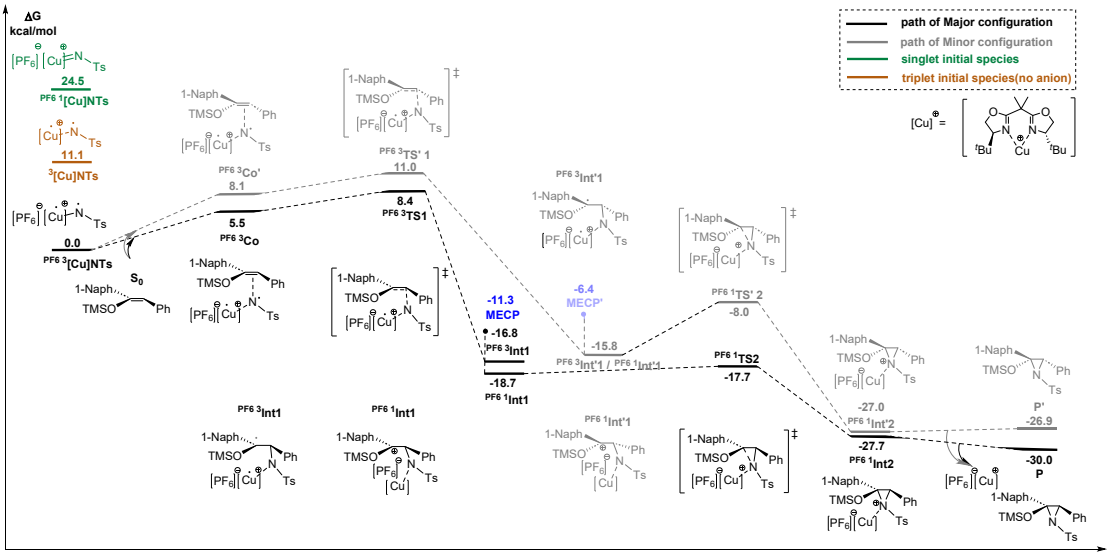


Fig. S1. Energy profiles of the asymmetric aziridination reaction between copper nitrenes and silyl enol ethers catalyzed by the chiral copper.

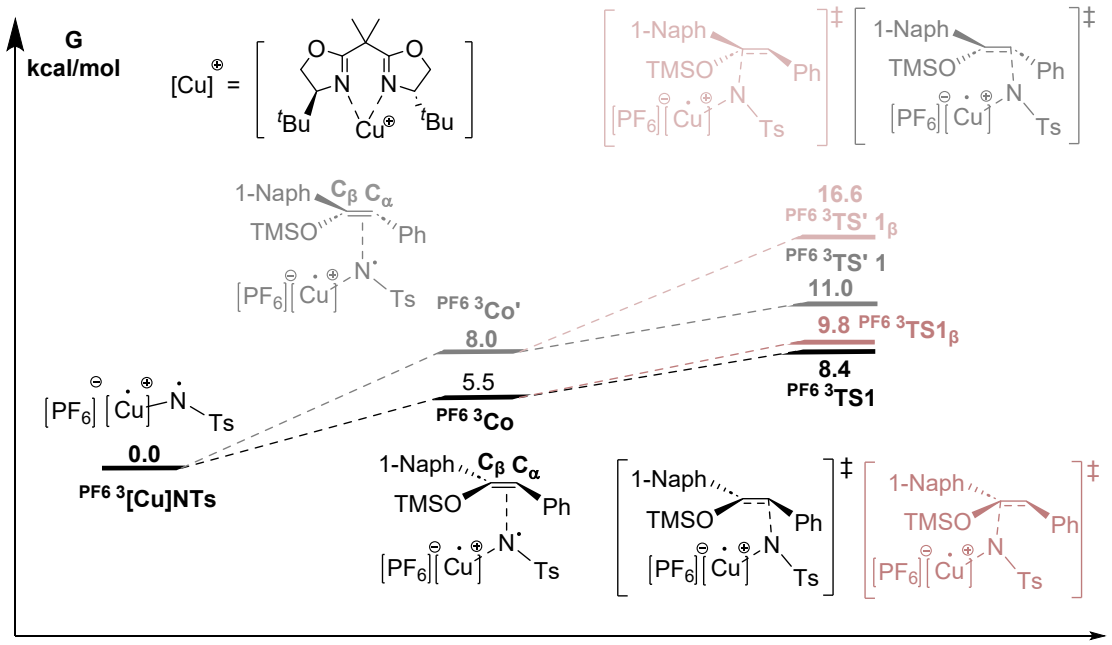


Fig. S2. Energy profiles of the attack of the nitrating species on the both carbon atom of the enol silyl ether double bond catalyzed by the chiral copper.

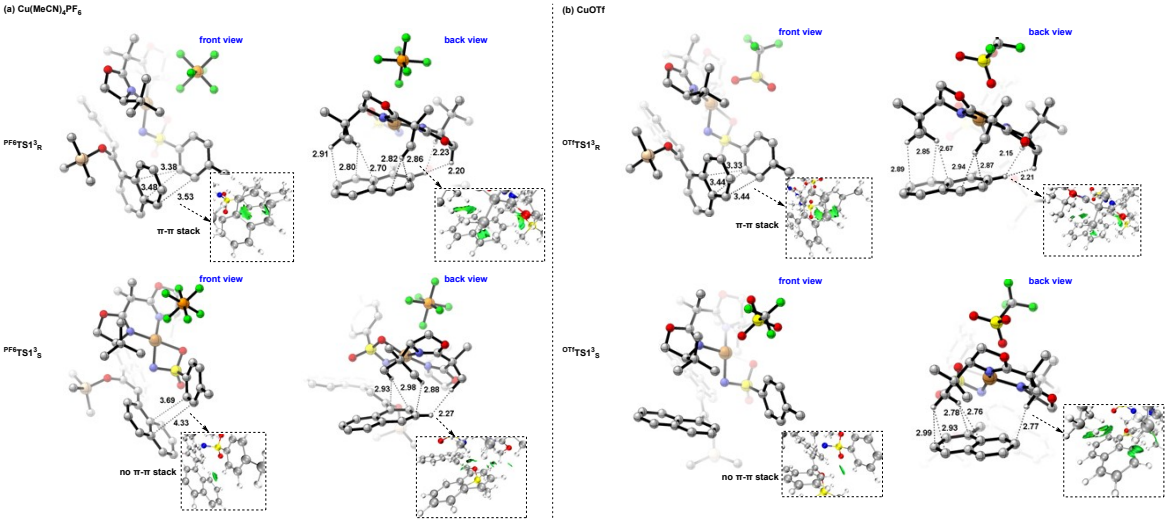


Fig. S3. Noncovalent interaction (NCI) analyses for $^{PF6}TS^{3}_{R}$, $^{PF6}TS^{3}_{S}$, $^{OTf}TS^{3}_{R}$ and $^{OTf}TS^{3}_{S}$. The green cloud represents the existence of weak interaction.

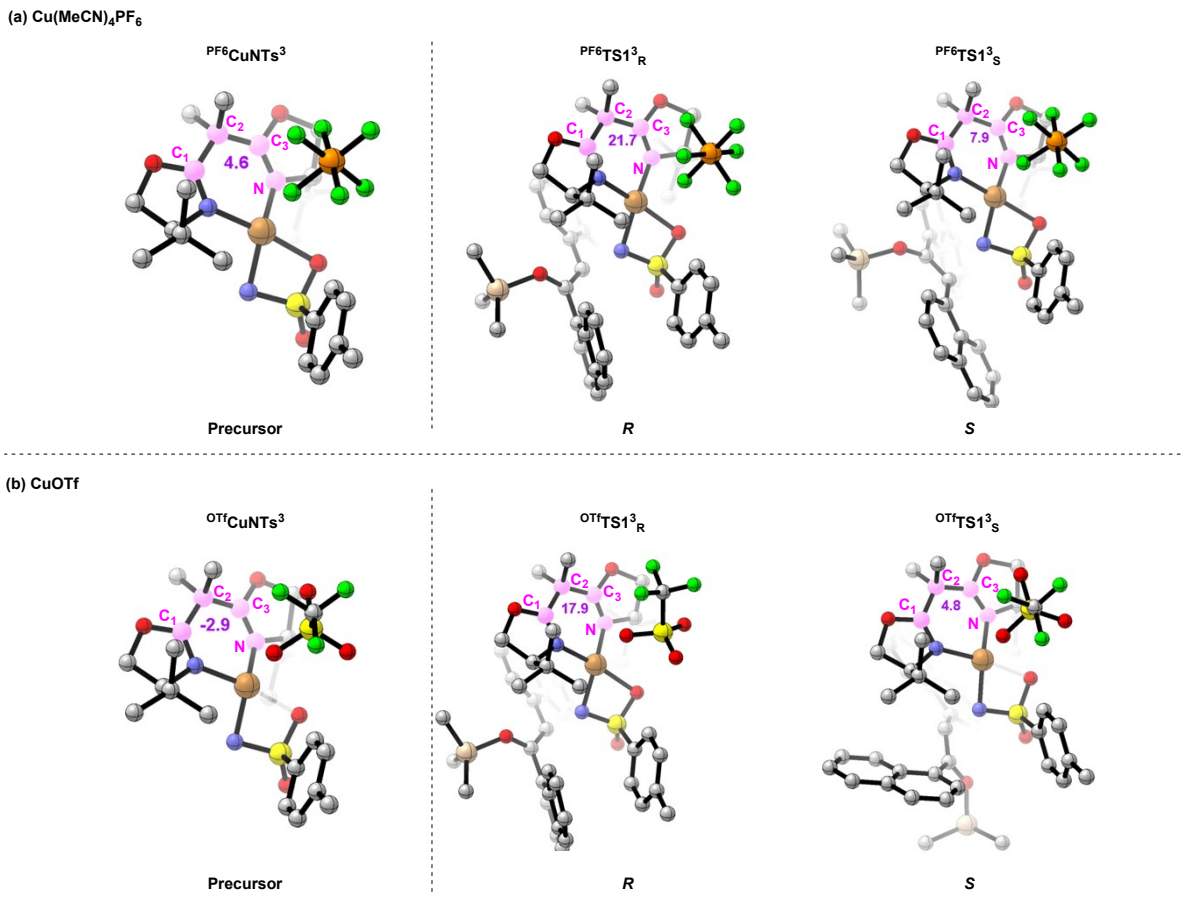


Fig. S4. Comparison diagram of dihedral angles between the intermediates and the transition states structure.

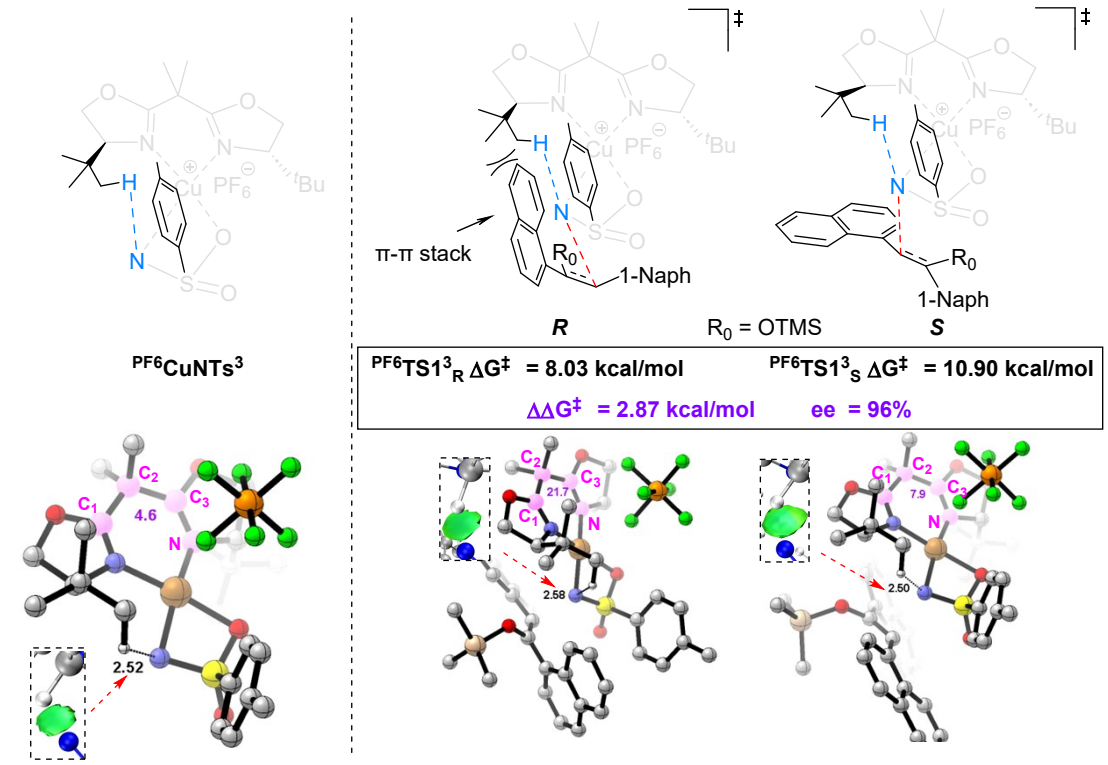


Fig. S5. The structures and NCI analysis of the intermediates and key transition states. The ligand substituent on the catalyst is -^{t}Bu.

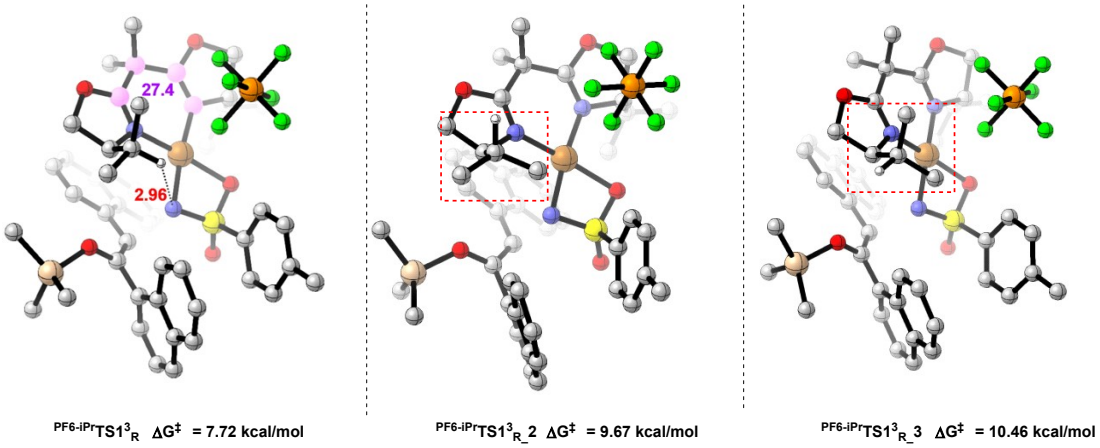


Fig. S6. Transition states of *R*- configuration with different conformations. The ligand substituent on the catalyst is -^{i}Pr.

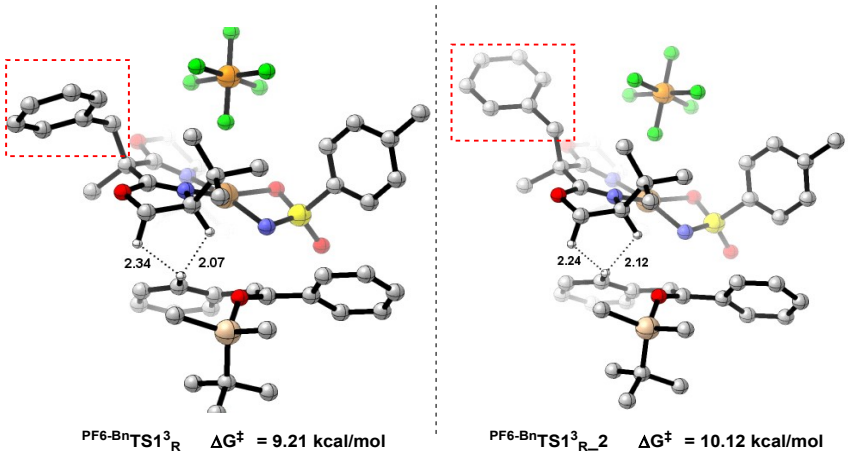
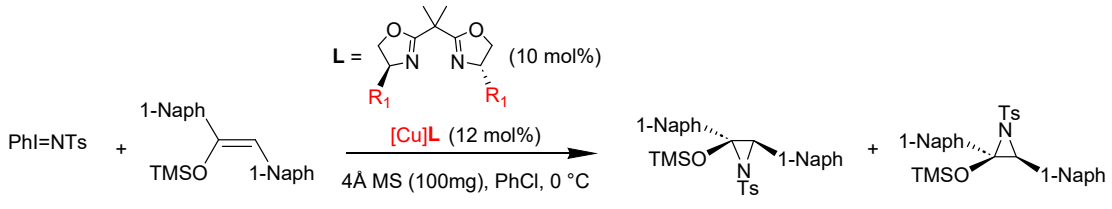


Fig. S7. Transition states of *R* configuration with different conformations. The side arms on the catalyst is -Bn.

Table S1. The experimental data mentioned in the main text.



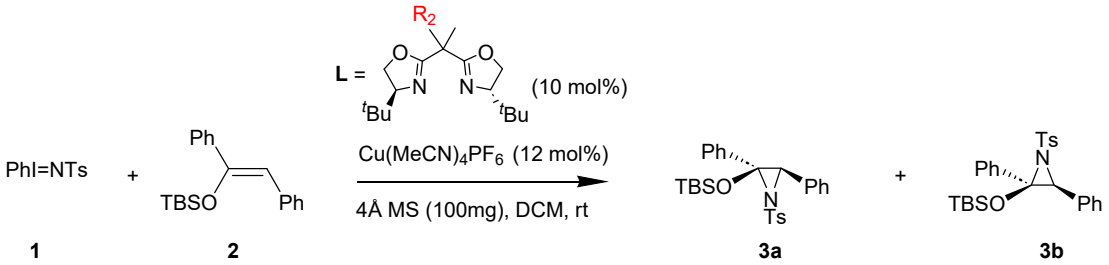
1 2 3a 3b

Entry	R_1	[Cu]	ee(%)[a]	Exp.$\Delta\Delta G^{\neq}$ (kcal/mol)	calc.$\Delta\Delta G^{\neq}$ (kcal/mol)
1	^{t}Bu	$Cu(MeCN)_4PF_6$	96	2.11	2.87

2	^{t}Bu	CuOTf	86	1.10	1.41
3	^{i}Pr	$Cu(MeCN)_4PF_6$	71	0.96	2.14

[a] Determined by chiral HPLC.

Table S2. The experimental data mentioned in the main text.



Entry	R_2	ee(%)[a]	Exp.$\Delta\Delta G^{\neq}$ (kcal/mol)	calc.$\Delta\Delta G^{\neq}$ (kcal/mol)
1	Me	41	0.47	1.19
2	Bn	19	0.21	-0.13

[a] Determined by chiral HPLC.