Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Information for

Mechanistic insights into α-branched amines formation with pivalic acid assisted C−H bond activation catalysed by Cp*Rh complexes

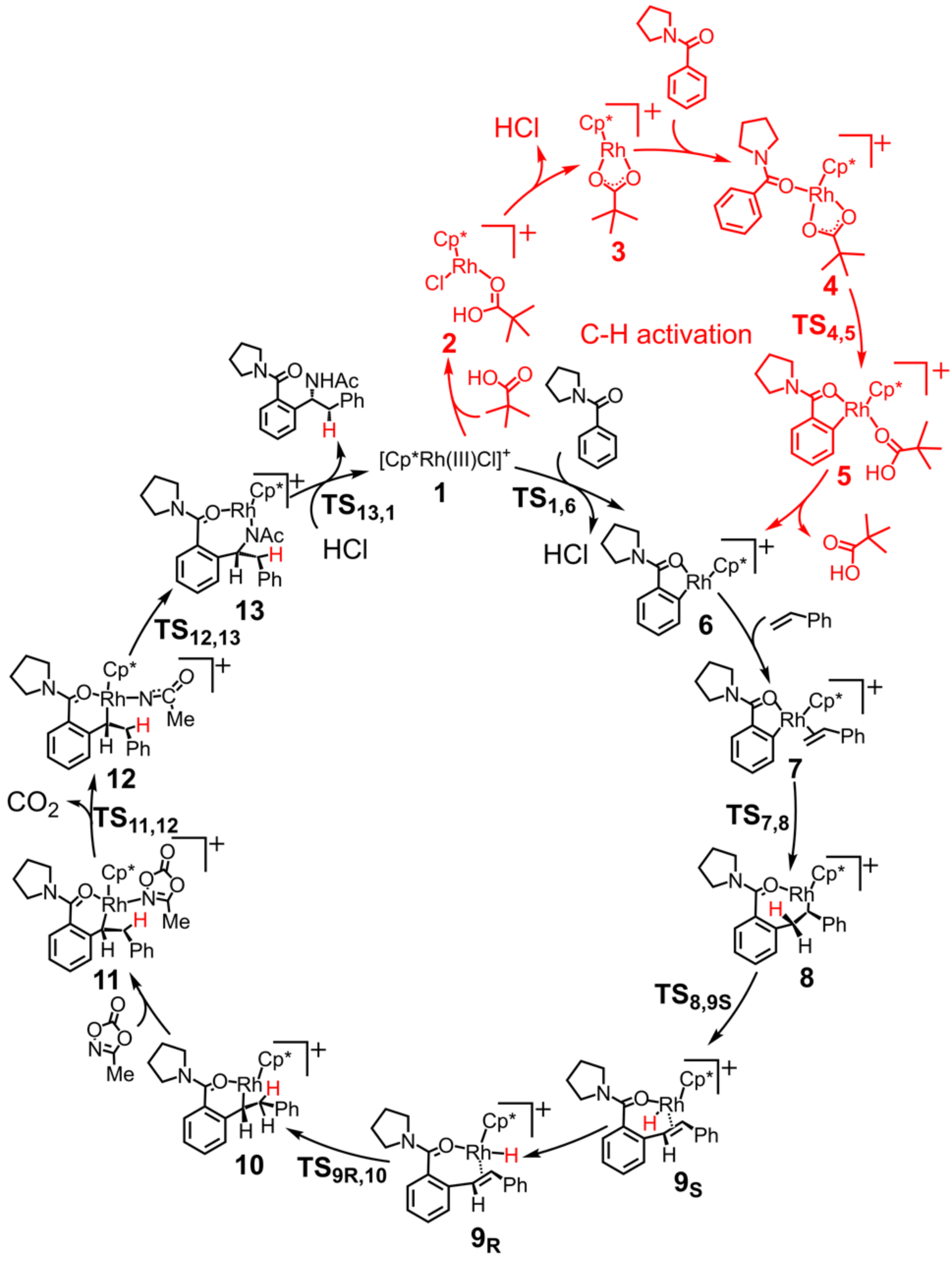
Contents

Evaluation of density functionals

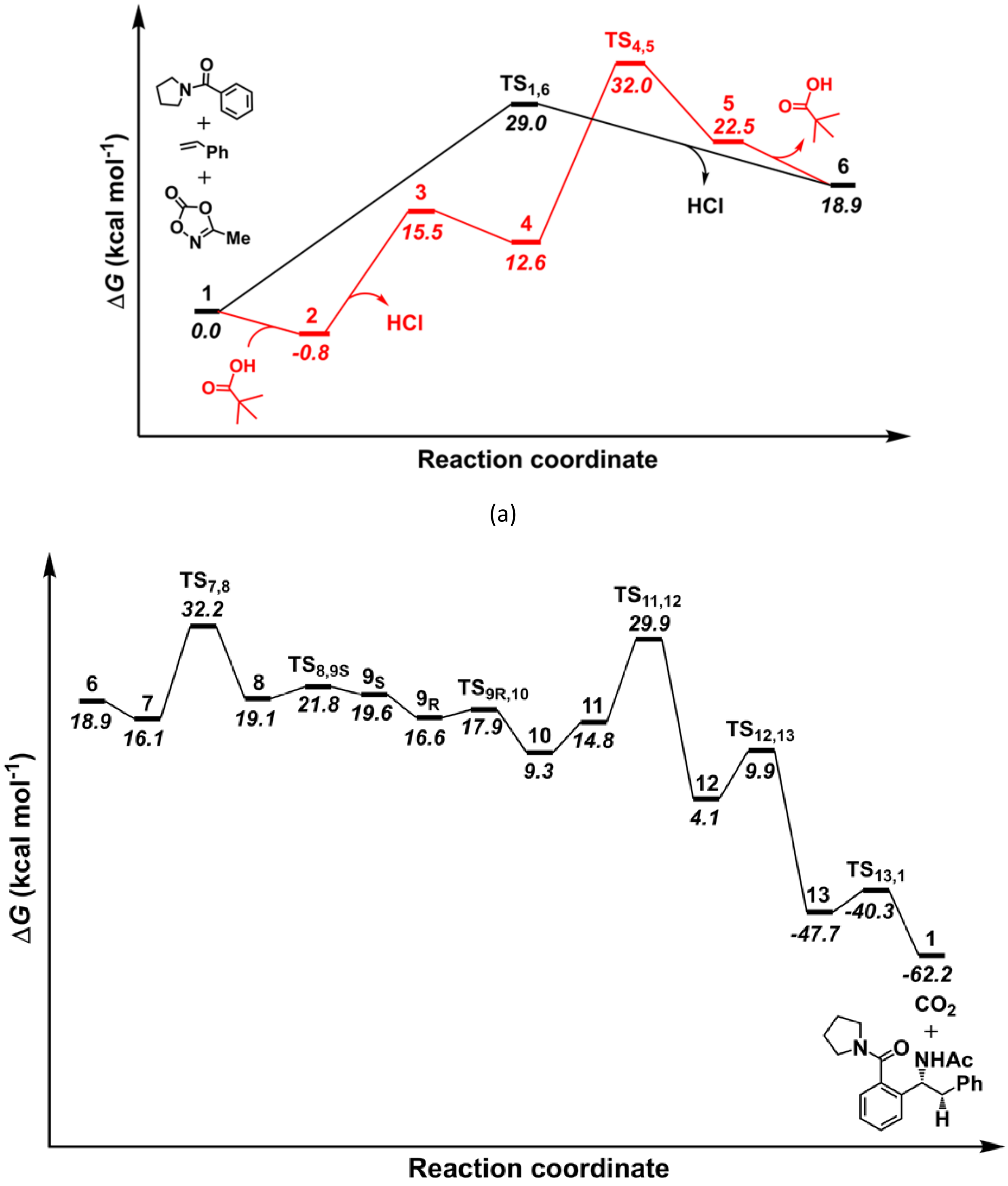
In order to examine the reliability of density functionals for this Rh system, we also calculated the single point electronic energies between **4** and **TS$_{4,5}$** using other six well recognized functionals with different Hartree-Fock exchanges and disperse corrections, including B3LYP-D3[1], B3LYP[1], *ω*B97X-D[2], BMK[3], *ω*B97X[4] and M06-L[5] on M06 optimized structures. The calculated absolute and relative electronic energies are listed in Table S1. All structures were calculated using above six functionals with the same basis set BS2 described in computation details. We can see that B3LYP-D3 and B3LYP functional has lower relative energy of 20.7 and 20.8 kcal mol^{-1}, while the ωB97X and M06-L functional has higher relative energy of 24.7 kcal mol^{-1}. Their difference is approximately less than 4 kcal/mol, which indicates that the calculated free energy barrier of the formation of α-branched amines catalyzed by rhodium complex has a rather weak dependence of density functionals. In addition, the *ω*B97X-D and M06 result of 22.4 kcal/mol and 22.5 kcal/mol, respectively, is in the middle and very close to each other. Therefore, M06 is a suitable functional for the computational study of this Rh system.

Table S1. Absolute and relative electronic energies of **4** and **TS$_{4,5}$** calculated by using different functionals.

Functionals	E_4(a.u.)	$E_{TS4,5}$(a.u.)	ΔE(kcal/mol)
B3LYP-D3	-1404.6330292	-1404.5999819	20.7
B3LYP	-1404.5416230	-1404.5084601	20.8
*ω*B97X-D	-1404.1484894	-1404.1127211	22.4
M06	-1403.5753183	-1403.5394159	22.5
BMK	-1403.1504535	-1403.1122414	24.0
ωB97X	-1404.1840674	-1404.1446623	24.7
M06-L	-1404.4319199	-1404.3925000	24.7



Scheme S1. Proposed mechanism for *ortho* C(sp^2)−H bond activation and the formation of α-branched amine with the presence of pivalic acid but without $NaHCO_3$.



(a)

(b)

Figure S1. Free energy profiles for the activation of C−H bond in phenyl(pyrrolidin-1-yl)methanone (a) and the formation of α-branched amine (b) with the presence of pivalic acid but without $NaHCO_3$.

References

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