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Supporting information

Insight into the mechanism and site-selectivity of $Rh_2^{II,II}(esp)_2$-catalyzed intermolecular C−H amination

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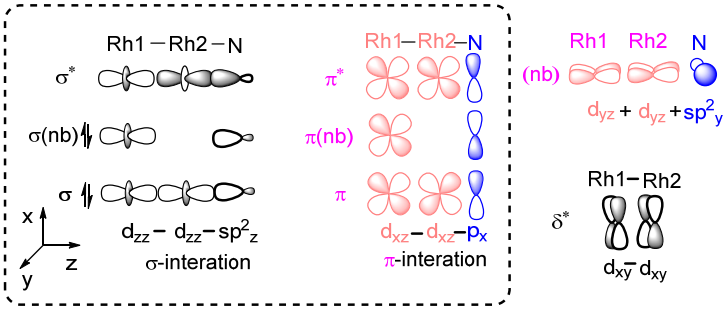

Fig. S1 Three-center Rh1-Rh2-N σ and π orbital interaction

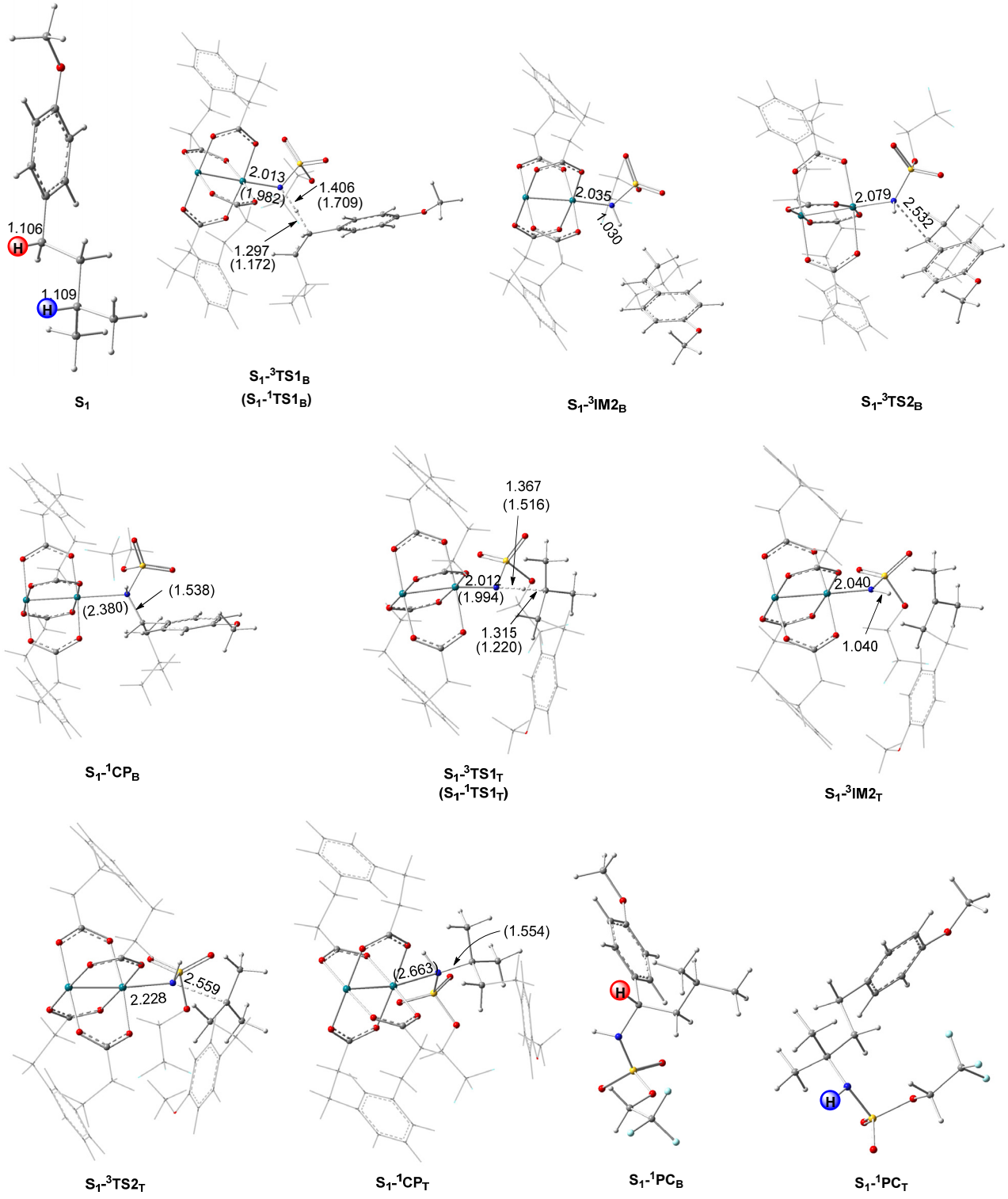

Fig. S2 Optimized structures and important geometrical parameters of the species in the benzylic and tertiary C-H amination pathways for $\mathbf{S_1}$. For clarity, the structure of species is visualized in different layers. Values without and with parentheses are for triplet and singlet states, respectively.

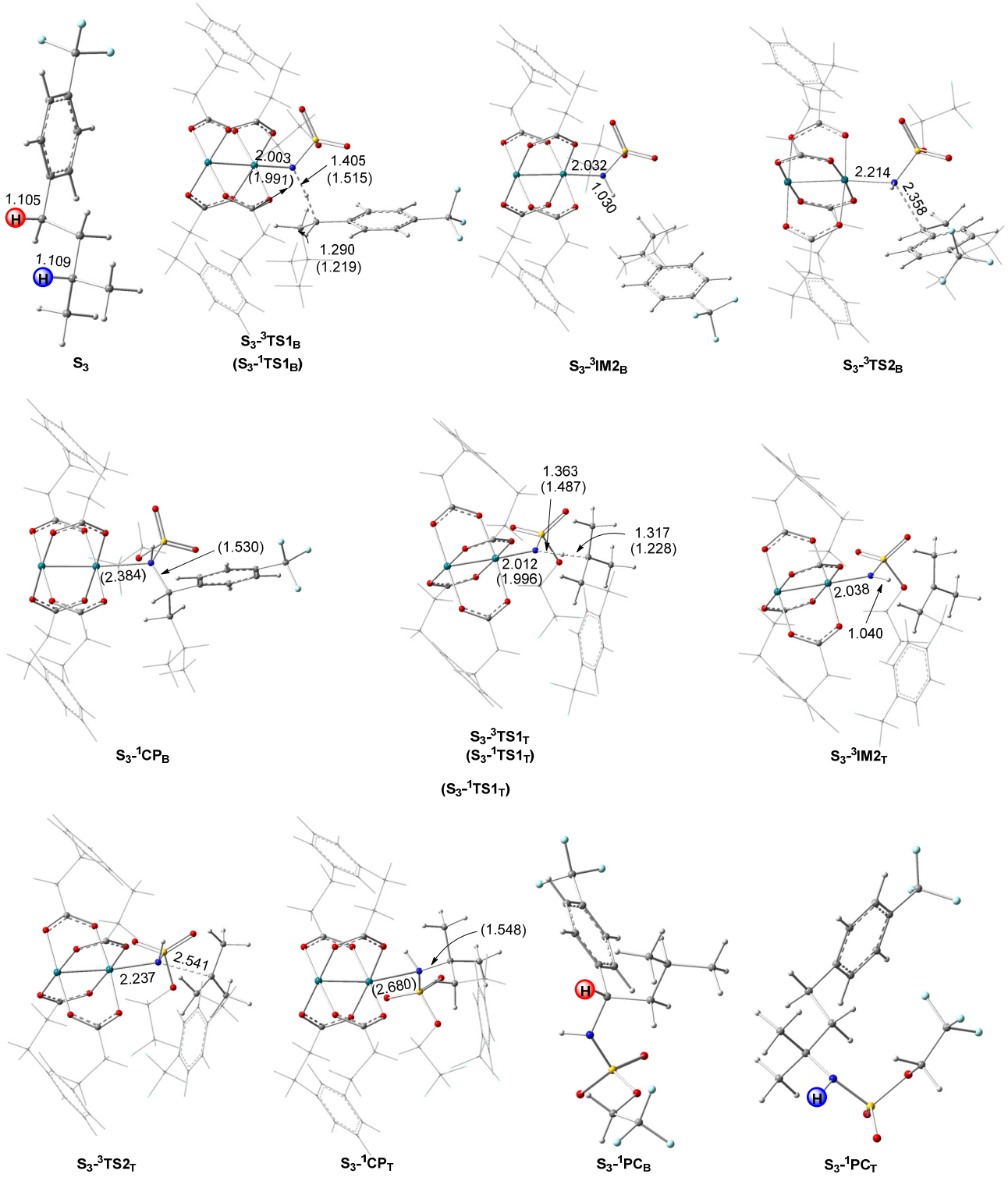

Fig. S3 Optimized structures and important geometrical parameters of the species in the benzylic and tertiary C-H amination pathways for **S_3**. For clarity, the structure of species is Visualized in different layers. Values without and with parentheses are for triplet and singlet states, respectively.

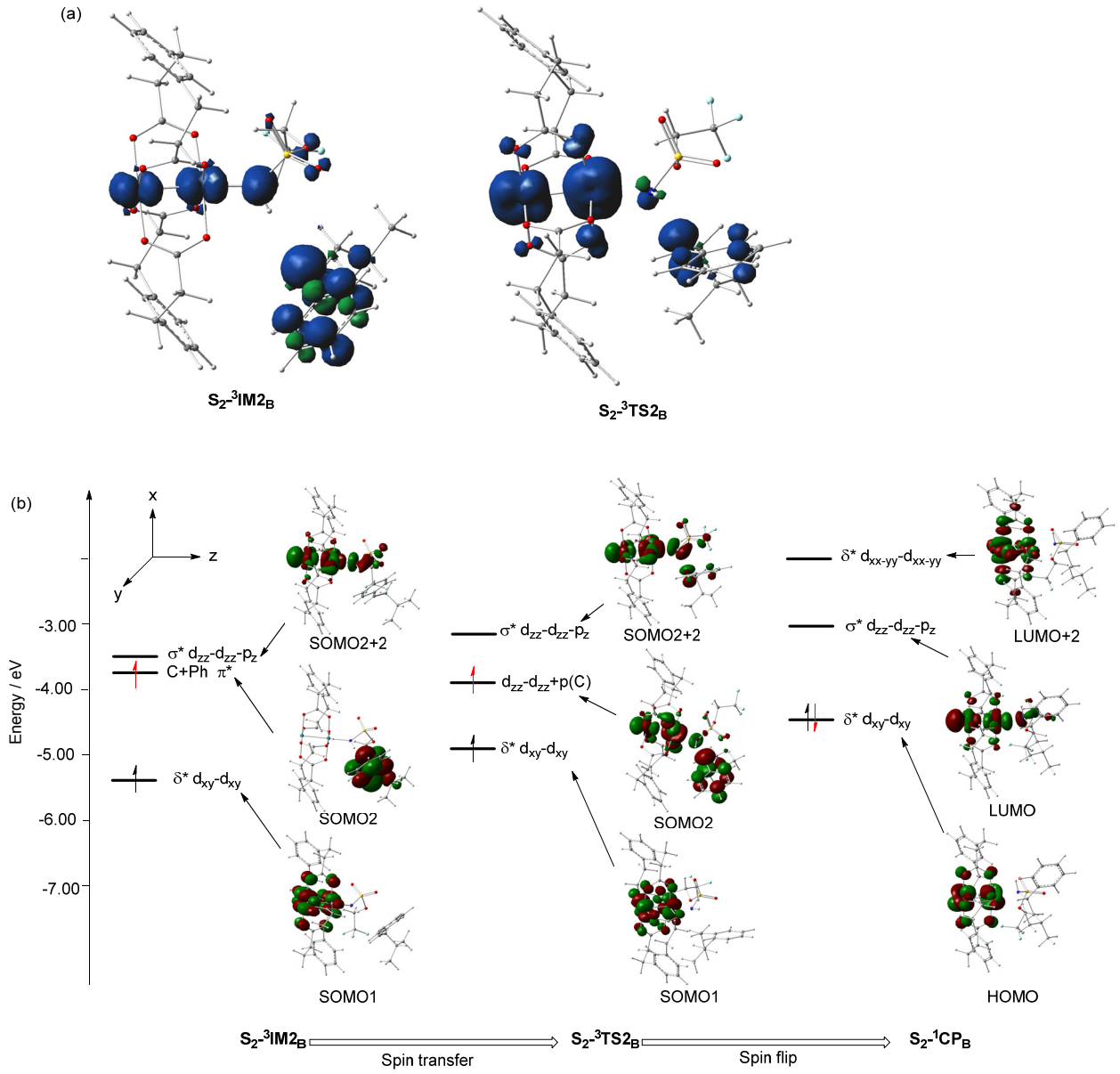

Fig. S4 (a) Surface plots of the spin denzylic distribution of **S_2-^{3}IM2** and **S_2-^{3}TS2**. **(b)** Frontier molecular orbitals of **S_2-^{3}IM2**, **S_2-^{3}TS2** and **S_2-^{1}CP**.

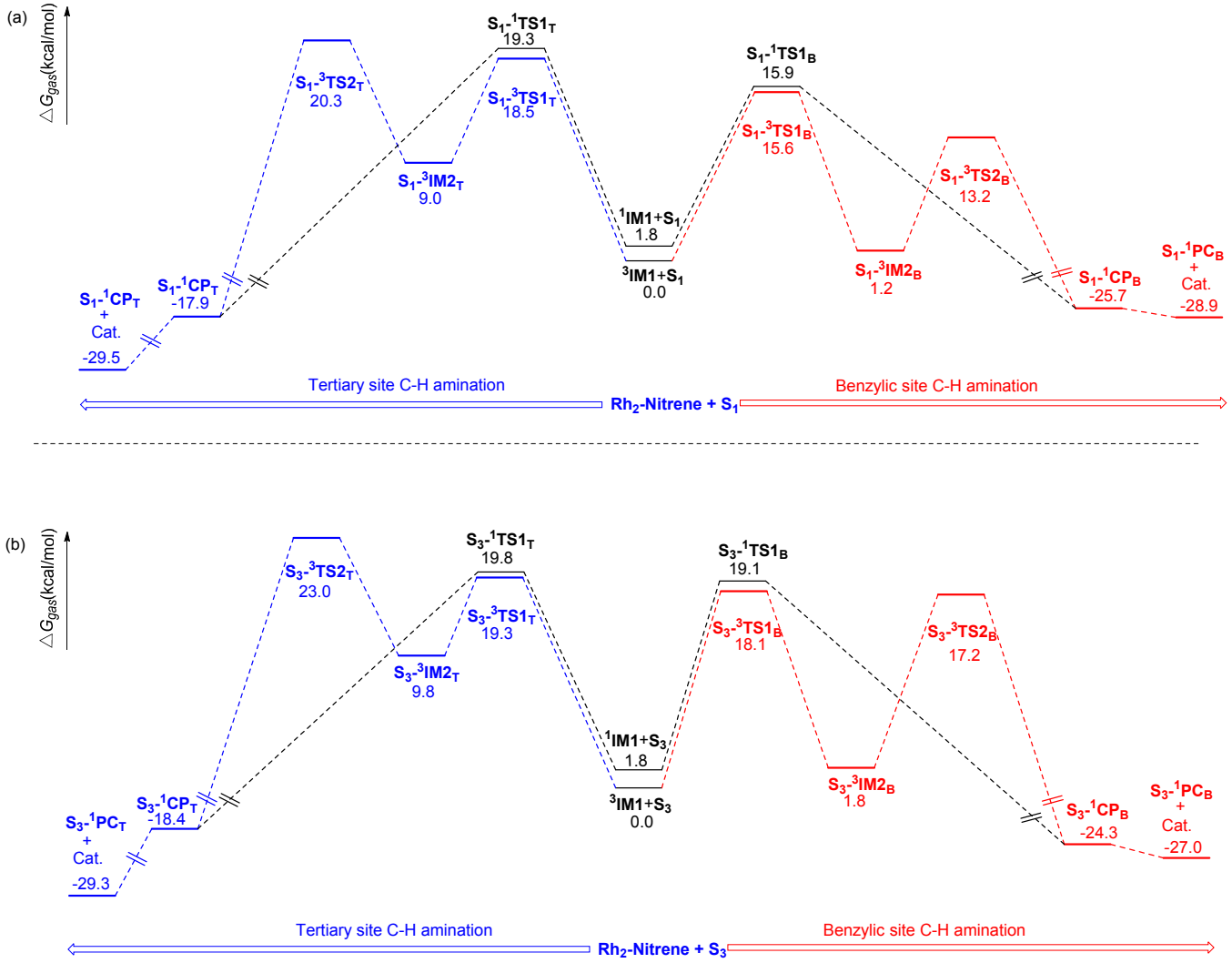

Fig. S5 (a) (b) Free energy profiles of intermolecular C-H aminations for the isoamylbenzene-derived substrate **S_1** and **S_3**, respectively.

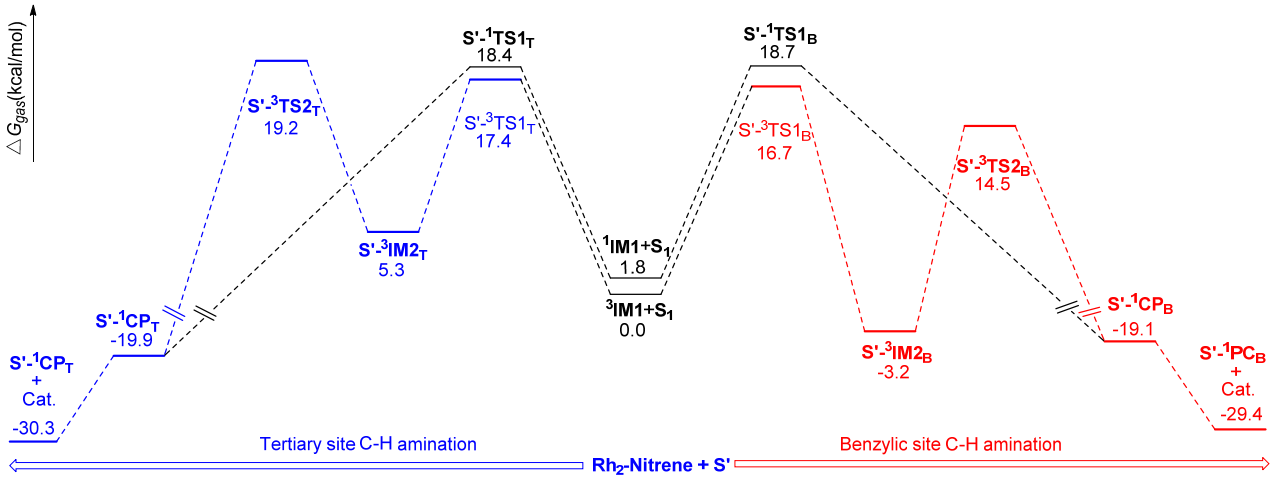

Fig. S6 Free energy profiles of intermolecular C-H aminations for the substrate **S'**.

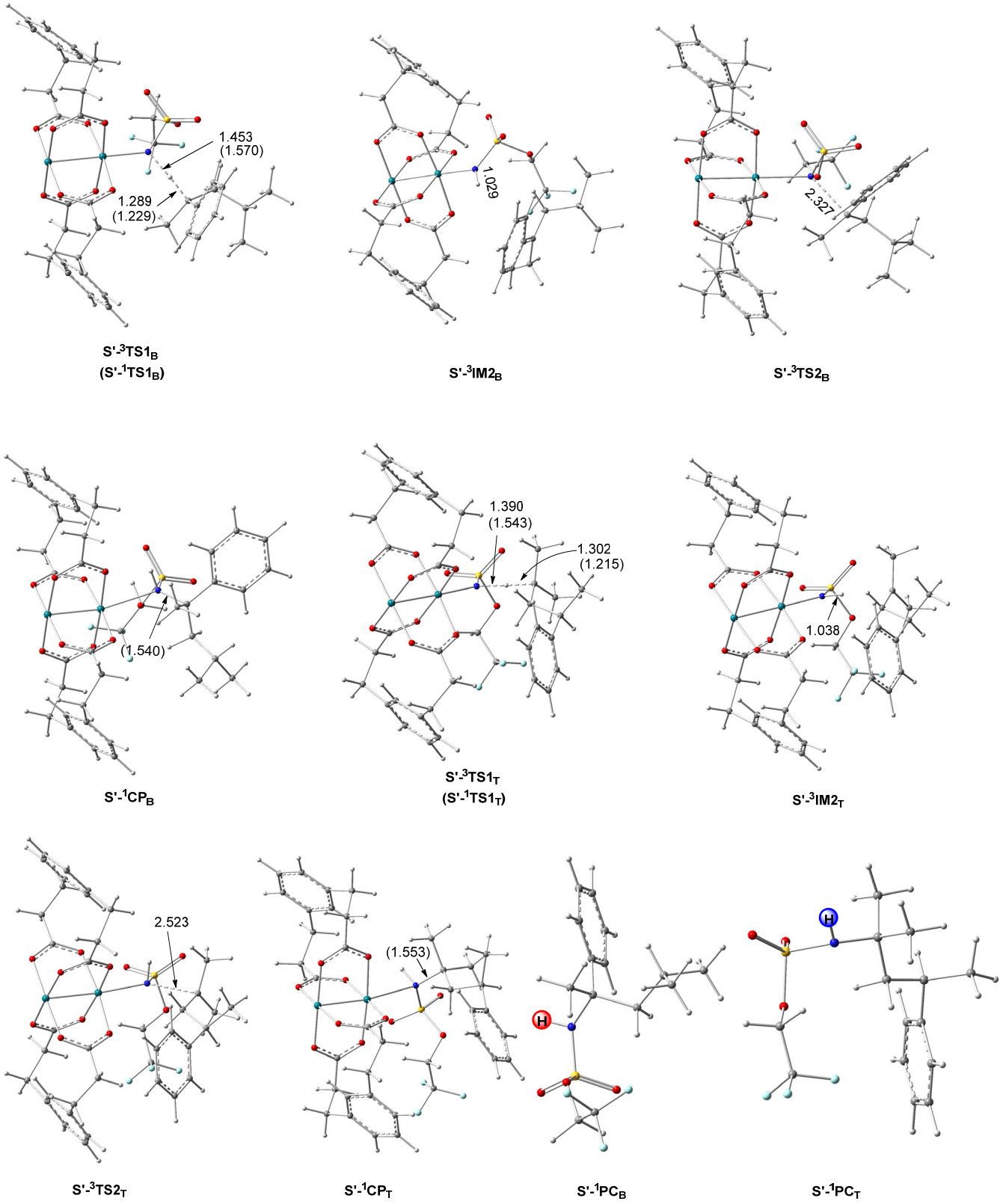

Fig. S7 Optimized structures and important geometrical parameters of the species in the benzylic and tertiary C-H amination pathways for **S'**. Values without and with parentheses are for triplet and singlet states, respectively.

Table S1 Thermal free energies in gas phase, solvation energy (G_{sol}) in benzene, relative free energies and activation free energies in solution of the species in the benzylic and tertiary C-H amination pathways for **S_2**.

species	G_{gas} (a.u.)	G_{sol} (kcal/mol)	ΔG^{rel}_{sol} (kcal/mol)	$\Delta G^{\neq}_{sol}$ (kcal/mol)
^{3}IM1	-2804.376613	-26.2	0	
^{1}IM1	-2804.373791	-25.89	2.1	
S_2-^{3}TS1$_B$	-3232.885064	-30.97	20.4	20.4
S_2-^{1}TS1$_B$	-3232.883138	-31.42	21.2	21.2
S_2-^{3}TS1$_T$	-3232.882532	-31.34	21.7	21.7
S_2-^{1}TS1$_T$	-3232.880346	-31.47	22.9	22.9
S_2-^{3}IM2$_B$	-3232.908056	-32.61	4.4	
S_2-^{3}IM2$_T$	-3232.898384	-32.21	10.8	
S_2-^{3}TS2$_B$	-3232.885563	-30.8	20.3	20.3
S_2-^{3}TS2$_T$	-3232.879339	-31.74	23.3	23.3
S_2-^{1}CP$_B$	-3232.953992	-29.98	-21.8	
S_2-^{1}CP$_T$	-3232.943083	-30.96	-16.0	
S_2-^{1}PC$_B$	-1483.902637	-11.2	-29.1	
S_2-^{1}PC$_T$	-1483.905213	-12.35	-31.9	

Table S2 Detailed spin density distribution of all species in the benzylic and tertiary C-H amination pathways for $\mathbf{S_1}$, $\mathbf{S_2}$, $\mathbf{S_3}$.

Species	Rh1	Rh2	N	C3/C5[a]	H4/H6[b]	Ph group
^{3}**IM1**	0.353	0.475	0.933	—	—	—
$\mathbf{S_1}$-^{3}**TS1**$_\mathbf{B}$	0.249	0.372	0.638	0.291	-0.004	0.229
$\mathbf{S_1}$-^{3}**TS1**$_\mathbf{T}$	0.295	0.384	0.653	0.413	-0.007	0.026
$\mathbf{S_1}$-^{3}**IM2**$_\mathbf{B}$	0.283	0.475	0.261	0.610	-0.005	0.247
$\mathbf{S_1}$-^{3}**IM2**$_\mathbf{T}$	0.291	0.392	0.289	0.838	0.025	0.017
$\mathbf{S_1}$-^{3}**TS2**$_\mathbf{B}$	0.358	1.058	0.074	0.195	-0.001	0.077
$\mathbf{S_1}$-^{3}**TS2**$_\mathbf{T}$	0.699	0.679	0.004	0.471	0.001	0.010
$\mathbf{S_2}$-^{3}**TS1**$_\mathbf{B}$	0.274	0.386	0.663	0.318	-0.010	0.189
$\mathbf{S_2}$-^{3}**TS1**$_\mathbf{T}$	0.299	0.386	0.658	0.416	-0.009	0.019
$\mathbf{S_2}$-^{3}**IM2**$_\mathbf{B}$	0.275	0.376	0.277	0.702	-0.005	0.321
$\mathbf{S_2}$-^{3}**IM2**$_\mathbf{T}$	0.289	0.391	0.289	0.846	0.022	0.019
$\mathbf{S_2}$-^{3}**TS2**$_\mathbf{B}$	0.613	0.814	0.001	0.285	0.002	0.134
$\mathbf{S_2}$-^{3}**TS2**$_\mathbf{T}$	0.706	0.672	-0.001	0.477	0.001	0.010
$\mathbf{S_3}$-^{3}**TS1**$_\mathbf{B}$	0.271	0.393	0.673	0.317	-0.015	0.170
$\mathbf{S_3}$-^{3}**TS1**$_\mathbf{T}$	0.298	0.387	0.661	0.421	-0.011	0.015
$\mathbf{S_3}$-^{3}**IM2**$_\mathbf{B}$	0.270	0.370	0.281	0.695	-0.007	0.318
$\mathbf{S_3}$-^{3}**IM2**$_\mathbf{T}$	0.282	0.383	0.290	0.855	0.023	0.022
$\mathbf{S_3}$-^{3}**TS2**$_\mathbf{B}$	0.712	0.648	0.014	0.337	0.002	0.175
$\mathbf{S_3}$-^{3}**TS2**$_\mathbf{T}$	0.708	0.660	-0.005	0.491	0.001	0.012

[a] In C3/C5 column, the value is corresponding to C3 atom for the species $\mathbf{S_m}$-^{3}**TS1**$_\mathbf{B}$, $\mathbf{S_m}$-^{3}**IM2**$_\mathbf{B}$ and $\mathbf{S_m}$-^{3}**TS2**$_\mathbf{B}$ while the value is corresponding to C5 atom for the species $\mathbf{S_m}$-^{3}**TS1**$_\mathbf{T}$, $\mathbf{S_m}$-^{3}**IM2**$_\mathbf{T}$ and $\mathbf{S_m}$-^{3}**TS2**$_\mathbf{T}$.

[b] In H4/H6 column, the value is corresponding to H4 atom for the species $\mathbf{S_m}$-^{3}**TS1**$_\mathbf{B}$, $\mathbf{S_m}$-^{3}**IM2**$_\mathbf{B}$ and $\mathbf{S_m}$-^{3}**TS2**$_\mathbf{B}$ while the value is corresponding to H6 atom for the species $\mathbf{S_m}$-^{3}**TS1**$_\mathbf{T}$, $\mathbf{S_m}$-^{3}**IM2**$_\mathbf{T}$ and $\mathbf{S_m}$-^{3}**TS2**$_\mathbf{T}$.

Table S3. Detailed NBO charge analysis of all species in the benzylicand tertiary C-H amination pathways for $\mathbf{S_1}$, $\mathbf{S_2}$, $\mathbf{S_3}$.

	Rh1	Rh2	N	C3/C5[a]	H4/H6[b]	Ph group	R
$Rh_2(esp)_2$	0.593	0.593	—	—	—	—	—
^{3}**IM1**	0.586	0.528	-0.557	—	—	—	—
^{1}**IM1**	0.565	0.520	-0.557	—	—	—	—
$\mathbf{S_1}$-^{3}**TS1**$_B$	0.552	0.517	-0.744	-0.404	0.347	0.322	-0.153
$\mathbf{S_1}$-^{1}**TS1**$_B$	0.539	0.501	-0.664	-0.442	0.306	0.342	-0.148
$\mathbf{S_1}$-^{3}**TS1**$_T$	0.562	0.518	-0.746	-0.124	0.347	0.182	-0.183
$\mathbf{S_1}$-^{1}**TS1**$_T$	0.551	0.503	-0.705	-0.154	0.319	0.206	-0.175
$\mathbf{S_1}$-^{3}**IM2**$_B$	0.582	0.529	-0.930	-0.135	0.436	0.181	-0.167
$\mathbf{S_1}$-^{3}**IM2**$_T$	0.580	0.528	-0.911	0.067	0.428	0.165	-0.188
$\mathbf{S_1}$-^{3}**TS2**$_B$	0.575	0.543	-0.971	-0.006	0.431	0.322	-0.134
$\mathbf{S_1}$-^{3}**TS2**$_T$	0.597	0.521	-0.982	0.207	0.414	0.177	-0.182
$\mathbf{S_1}$-^{1}**CP**$_B$	0.550	0.429	-0.832	-0.090	0.465	-0.056	-0.177
$\mathbf{S_1}$-^{1}**CP**$_T$	0.568	0.460	-0.869	0.129	0.447	0.174	-0.189
$\mathbf{S_2}$-^{3}**TS1**$_B$	0.561	0.521	-0.730	-0.389	0.343	0.087	0.244
$\mathbf{S_2}$-^{1}**TS1**$_B$	0.546	0.504	-0.678	-0.409	0.314	0.115	0.245
$\mathbf{S_2}$-^{3}**TS1**$_T$	0.565	0.520	-0.742	-0.123	0.346	-0.018	0.244
$\mathbf{S_2}$-^{1}**TS1**$_T$	0.556	0.504	-0.703	-0.148	0.317	-0.006	0.244
$\mathbf{S_2}$-^{3}**IM2**$_B$	0.590	0.528	-0.917	-0.142	0.440	-0.318	0.240
$\mathbf{S_2}$-^{3}**IM2**$_T$	0.583	0.529	-0.912	0.071	0.429	-0.033	0.243
$\mathbf{S_2}$-^{3}**TS2**$_B$	0.593	0.543	-0.965	-0.026	0.429	0.053	0.247
$\mathbf{S_2}$-^{3}**TS2**$_T$	0.601	0.520	-0.979	0.205	0.414	-0.017	0.245
$\mathbf{S_2}$-^{1}**CP**$_B$	0.554	0.434	-0.837	-0.090	0.468	0.004	0.246
$\mathbf{S_2}$-^{1}**CP**$_T$	0.567	0.464	-0.853	0.127	0.441	-0.019	0.243
$\mathbf{S_3}$-^{3}**TS1**$_B$	0.565	0.522	-0.729	-0.392	0.344	0.009	0.043
$\mathbf{S_3}$-^{1}**TS1**$_B$	0.551	0.505	-0.688	-0.399	0.319	0.031	0.046
$\mathbf{S_3}$-^{3}**TS1**$_T$	0.569	0.520	-0.746	-0.122	0.346	-0.075	0.040
$\mathbf{S_3}$-^{1}**TS1**$_T$	0.559	0.506	-0.707	-0.143	0.319	-0.066	0.041
$\mathbf{S_3}$-^{3}**IM2**$_B$	0.591	0.527	-0.916	-0.124	0.438	-0.147	0.030
$\mathbf{S_3}$-^{3}**IM2**$_T$	0.585	0.529	-0.912	0.064	0.428	-0.088	0.039
$\mathbf{S_3}$-^{3}**TS2**$_B$	0.615	0.521	-0.952	-0.047	0.425	-0.075	0.041
$\mathbf{S_3}$-^{3}**TS2**$_T$	0.605	0.519	-0.978	0.199	0.414	-0.076	0.042
$\mathbf{S_3}$-^{1}**CP**$_B$	0.554	0.428	-0.833	-0.093	0.466	-0.055	0.046
$\mathbf{S_3}$-^{1}**CP**$_T$	0.571	0.458	-0.875	0.128	0.451	-0.069	0.038

[a] In C3/C5 column, the value is corresponding to C3 atom for the species $\mathbf{S_m}$-^{n}**TS1**$_B$, $\mathbf{S_m}$-^{n}**IM2**$_B$ and $\mathbf{S_m}$-^{n}**TS2**$_B$ while the value is corresponding to C5 atom for the species $\mathbf{S_m}$-^{n}**TS1**$_T$, $\mathbf{S_m}$-^{n}**IM2**$_T$ and $\mathbf{S_m}$-^{n}**TS2**$_T$.

[b] In H4/H6 column, the value is corresponding to H4 atom for the species $\mathbf{S_m}$-^{n}**TS1**$_B$, $\mathbf{S_m}$-^{n}**IM2**$_B$ and $\mathbf{S_m}$-^{n}**TS2**$_B$ while the value is corresponding to H6 atom for the species $\mathbf{S_m}$-^{n}**TS1**$_T$, $\mathbf{S_m}$-^{n}**IM2**$_T$ and $\mathbf{S_m}$-^{n}**TS2**$_T$.