Supplementary Information

Theoretical investigation on TMSOTf-promoted cascade reaction of propargyl alcohol and protected tryptamine to construct hexahydropyrrolo-[2,3-b]indoline

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Table S1. Calculated relative energies (all in kcal mol^{-1}, relative to isolated species) for the ZPE-corrected Gibbs free energies (ΔG_{gas}), Gibbs free energies for all species in solution phase (ΔG_{sol}) at 333 K by M06-2X/6-311++G(d,p)//M06-2X/6-31G(d) method and difference between absolute energy.

Species	ΔG_{gas}	$\Delta G_{sol(toluene)}$
1	0.00	0.00
B	-2.73	0.84
1+tmsotf-hosime3	0.00	0.00
A	5.58	6.04
1+tmsotf	0.00	0.00
i1	-8.60	-3.42
ts-i12	14.06	12.48
i2	-10.84	-7.76
ts-i23	20.95	15.96
i3	-1.43	1.09
i3-1	18.78	10.75
ts-i34	26.66	16.19
i4	-8.25	-5.21
1+2	0.00	0.00
i5	-10.43	-5.13
ts-i56	19.68	20.12
i6	-27.36	-24.76
ts-i67	5.50	3.60
i7	-9.05	-11.37
ts-i78	9.01	0.77
i8	-15.86	-20.87
ts-i83	-6.34	-14.19
3	-30.13	-22.19

Table S2. The activation energy (local barrier) (in kcal mol^{-1}) of all reactions in the gas, solution phase calculated with M06-2X/6-311++G(d,p)//M06-2X/6-31G(d) method.

TS	$\Delta G^{\neq}_{gas}$	$\Delta G^{\neq}_{sol}$
ts-i12 (156i)	22.67	15.90
ts-i23 (143i)	31.79	23.72
ts-i34 (197i)	7.88	5.44
ts-i56 (421i)	30.11	25.25
ts-i67 (555i)	32.86	28.36
ts-i78 (1226i)	18.06	12.14
ts-i83 (581i)	9.52	6.68

Figure S1. Evolution of bond lengths along the IRC for (a) **ts-i23** (b) **ts-i34** (c) **ts-i56** (d) **ts-i67** at M06-2X/6-311++G(d,p) level.