Supplementary Information

Theoretical investigation on Lewis/Brønsted acid catalyzed modulation of BCB reactive site in synthesis of spirocyclic and bicyclic framework

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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 298 K by B3LYP/6-311++G(d,p)//B3LYP/6-31G(d) method and difference between absolute energy.

Species	ΔG_{gas}	$\Delta G_{sol(toluene)}$
1+ni2+	0.00	0.00
A	-103.05	-101.45
1+ni2+2	0.00	0.00
i1	-262.30	-255.51
ts-i1B	-237.79	-235.11
B	-242.60	-237.52
ts-BC	-237.86	-234.38
C	-284.89	-277.76
1+2	0.00	0.00
3	-47.27	-47.16
1+dtbp	0.00	0.00
D	-7.66	-3.85
ts-DE	8.08	11.06
E	-12.69	-7.07
1+dtbp+2	0.00	0.00
i2	47.40	47.09
ts-i2F	52.18	51.66
F	-37.47	-40.82
ts-Fi3	-17.20	-22.60
i3	-36.50	-37.78
G	-57.39	-53.87
ts-Gi4	-26.81	-25.11
i4	-63.97	-59.62
1+2-ch4	0.00	0.00
4	-47.72	-48.81

Table S2. The activation energy (local barrier) (in kcal mol^{-1}) of all reactions in the gas, solution phase calculated with B3LYP/6-311++G(d,p)//B3LYP/6-31G(d) method.

TS	$\Delta G^{\neq}_{gas}$	$\Delta G^{\neq}_{sol}$
ts-i1B (389i)	24.5	20.4
ts-BC (462i)	4.7	3.1
ts-DE (1018i)	15.7	14.9
ts-i2F (236i)	4.8	4.6
ts-Fi3 (1301i)	20.3	18.2
ts-Gi4 (1372i)	30.6	28.8

Figure S1. Evolution of bond lengths along the IRC for (a) **ts-i1B** (b) **ts-i2F** (c) **ts-Fi3** (d) **ts-Gi4** at B3LYP/6-311++G(d,p) level.