Supplementary Information

Theoretical investigation on TfOH catalyzed cascade cyclization reaction with conjugated 1,5-enyne to construct benzo[b]-fluorenone and benzo[de]anthracen-7-one

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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 373 K by M06-2X/6-311++G(d,p)// M06-2X/6-31G(d) method and difference between absolute energy.

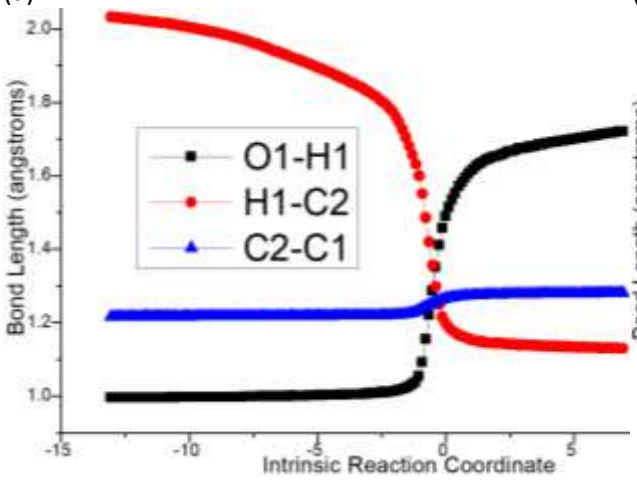
Species	ΔG_{gas}	$\Delta G_{sol(toluene)}$
1+tfoh	0.00	0.00
i1	-10.81	-1.03
ts-i1A	8.26	13.18
A	-13.20	-2.25
ts-AB	11.40	21.62
B	-22.67	-18.82
ts-Bi2	-7.41	-2.55
i2	-71.96	-58.24
1	0.00	0.00
C	-54.52	-53.00
1+h	0.00	0.00
D	-266.55	-211.57
ts-Di3	-243.28	-196.00
i3	-245.12	-200.25
ts-i34	-228.36	-188.70
i4	-284.35	-217.98
1-etoh	0.00	0.00
2	-38.55	-45.48
E	-34.93	-41.99
1-etoh+h	0.00	0.00
F	-237.88	-198.11
ts-FG	-232.57	-178.18
G	-238.36	-187.29
ts-Gi5	-230.85	-176.52
i5	-240.55	-205.65
1-etoh	0.00	0.00
3	-49.92	-57.00

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.

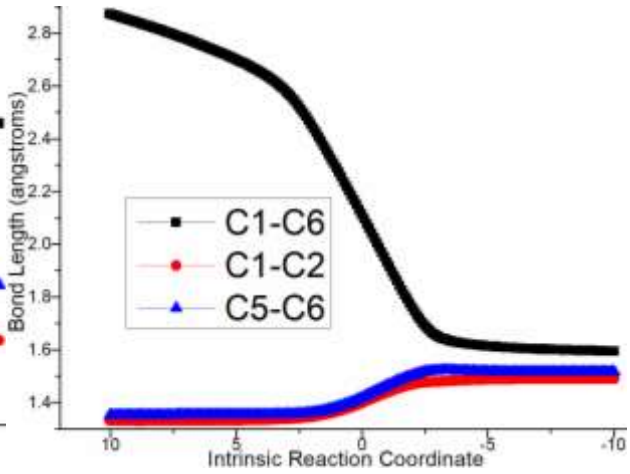
TS	$\Delta G^{\neq}_{gas}$	$\Delta G^{\neq}_{sol}$
ts-i1A (194i)	19.1	14.2
ts-AB (577i)	24.6	23.9
ts-Bi2 (685i)	15.3	16.3
ts-Di3 (270i)	23.3	15.6
ts-i34 (1391i)	16.8	11.6
ts-FG (145i)	5.3	19.9
ts-Gi5 (194i)	7.5	10.8

Figure S1. Evolution of bond lengths along the IRC for (a) **ts-i1A** (b) **ts-AB** (c) **ts-Di3** (d) **ts-i34** (e) **ts-Gi5** at M06-2X/6-311++G(d,p) level.

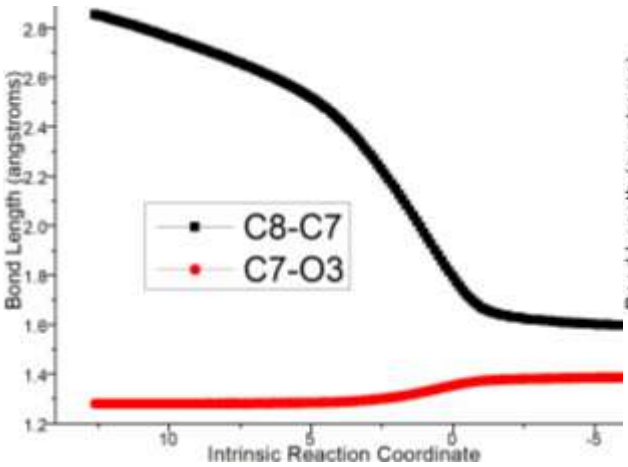
(a)



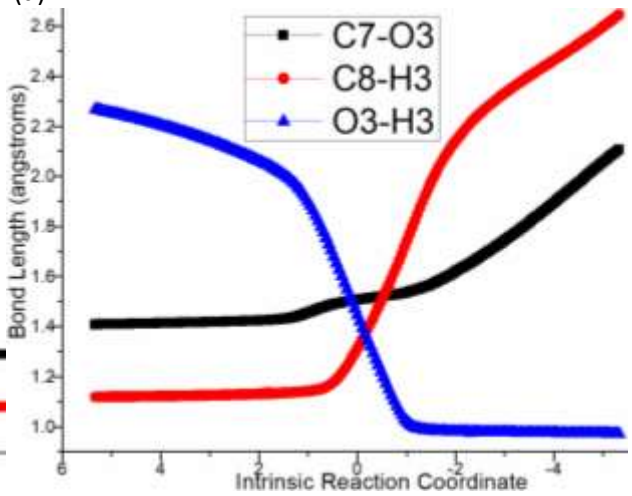
(b)



(c)



(d)



(e)