

Supporting Information

to

Radical Pathways for the Formation of Non-Canonical Nucleobases in Prebiotic Environment

Sarabjeet Kaur^a and Purshotam Sharma*^a

^a*Computational Biochemistry Laboratory, Department of Chemistry and Centre for Advanced Studies in Chemistry, Panjab University, Chandigarh, 160014, India.*

E-mail: psharma@pu.ac.in

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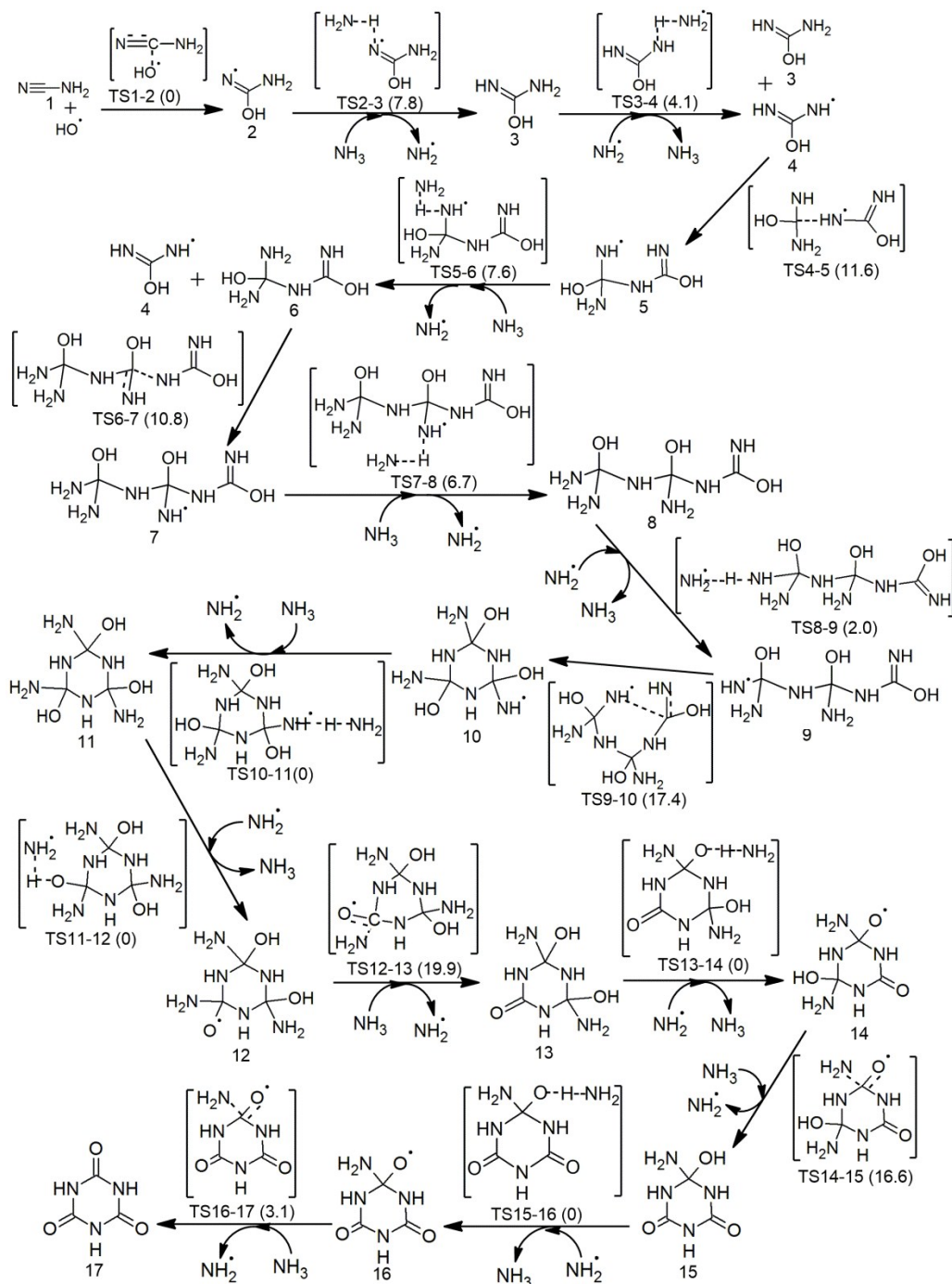


Figure S1. Proposed radical mechanism along with corresponding transition states (TSs) for the formation of cyanuric acid (**17**) from cyanamide (**1**). Gas phase B3LYP/6-311G(d,p) relative electronic energies (kcal mol⁻¹) of the TSs (barriers) with respect to reactants of each step are provided in parenthesis.

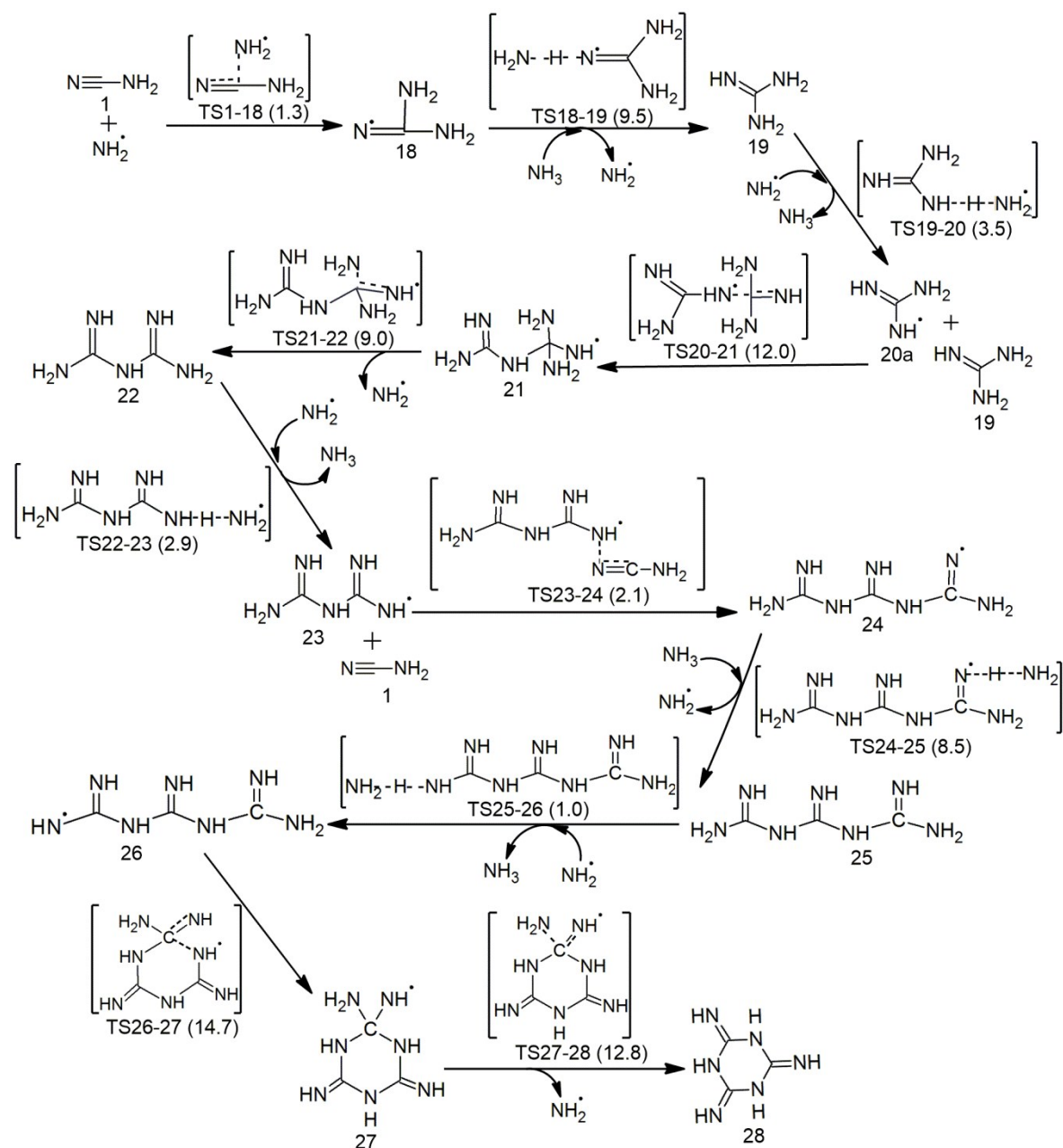


Figure S2. Proposed radical mechanism along with corresponding transition states (TSs) for the formation of melamine (**28**) from cyanamide (**1**). Gas phase B3LYP/6–311G(d,p) relative electronic energies (kcal mol⁻¹) of the TSs (barriers) with respect to reactants of each step are provided in parenthesis.

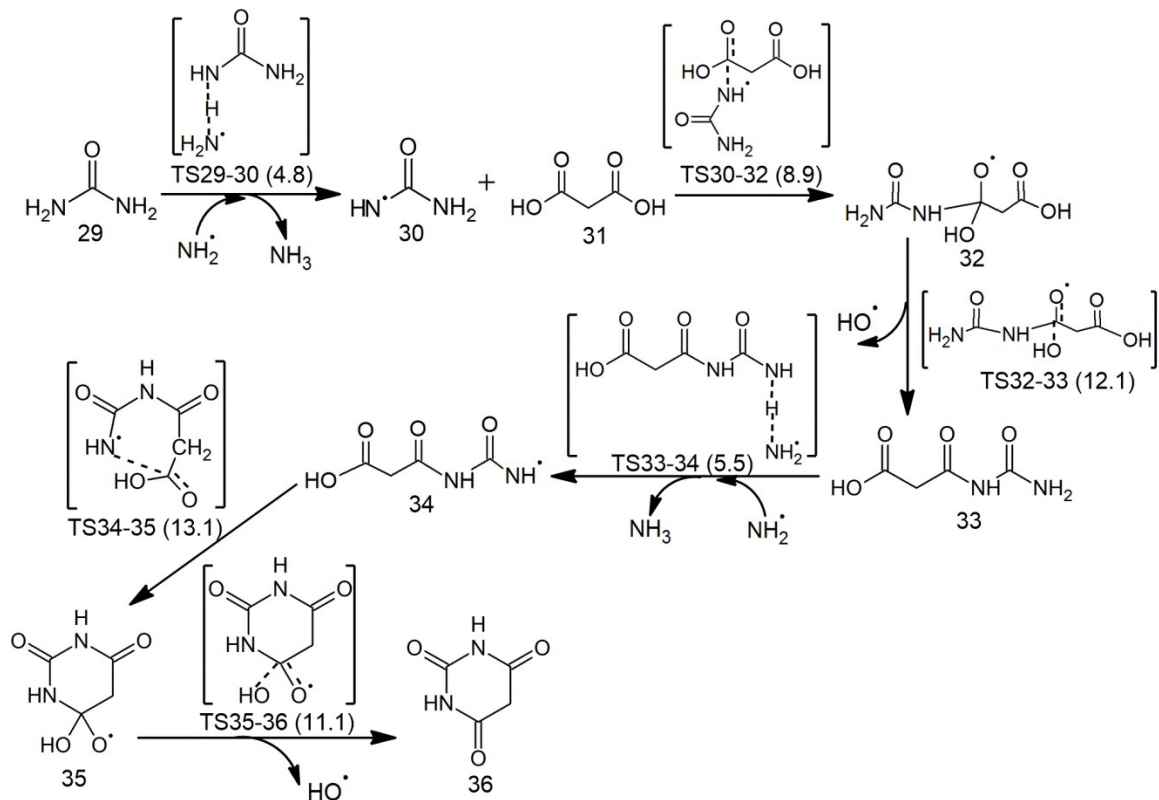


Figure S3. Proposed radical mechanism along with corresponding transition states (TSs) for the formation of barbituric acid (**30**) from urea (**23**) and malonic acid (**25**). Gas phase B3LYP/6-311G(d,p) relative electronic energies (kcal mol⁻¹) of the TSs (barriers) with respect to reactants of each step are provided in parenthesis.

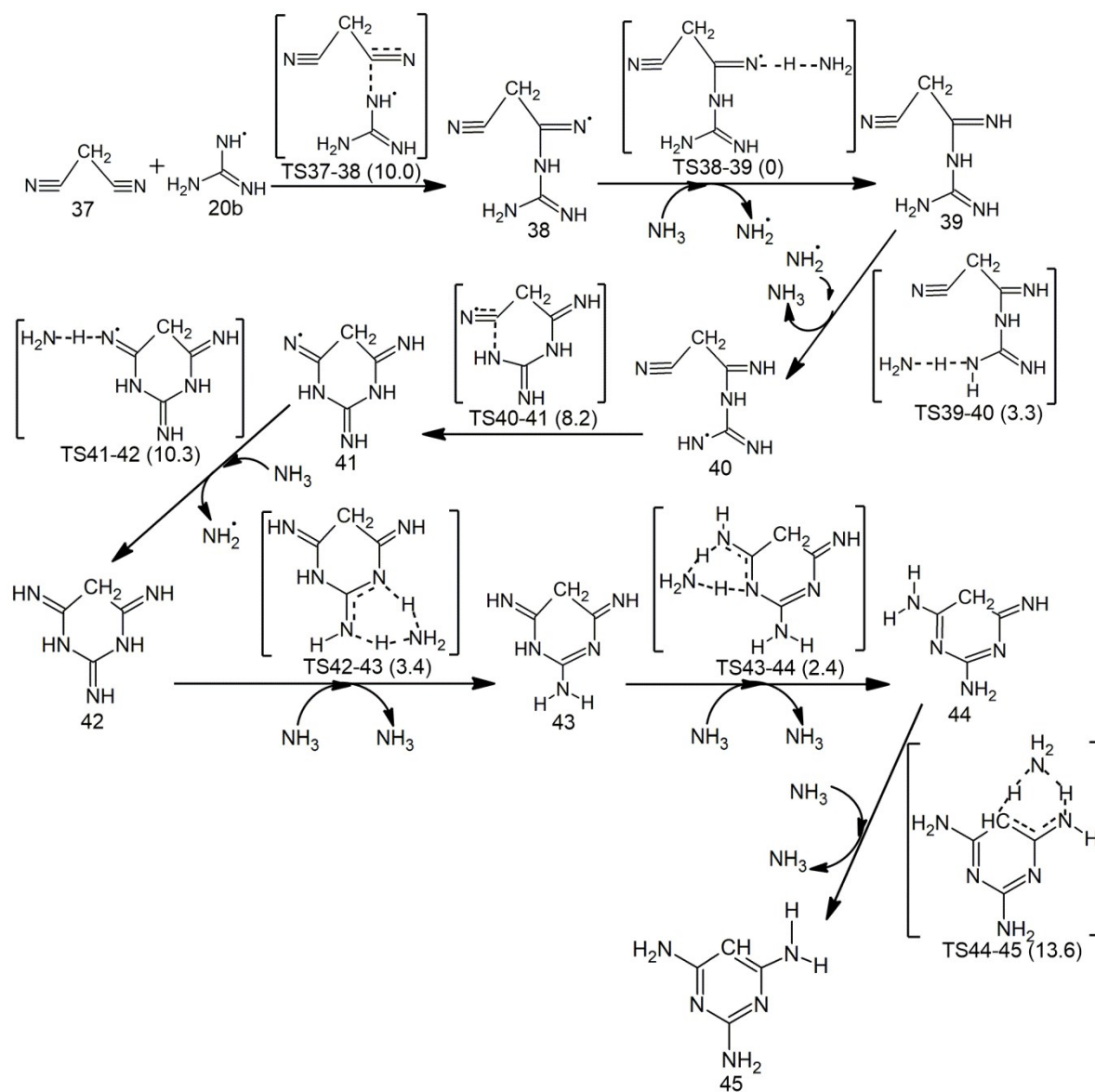


Figure S4. Proposed radical mechanism along with corresponding transition states (TSs) for the formation of 2,4,6-triaminopyrimidine (**45**) from malononitrile (**37**) and **20b**. Gas phase B3LYP/6-311G(d,p) relative electronic energies (kcal mol⁻¹) of the TSs (barriers) with respect to reactants of each step are provided in parenthesis.

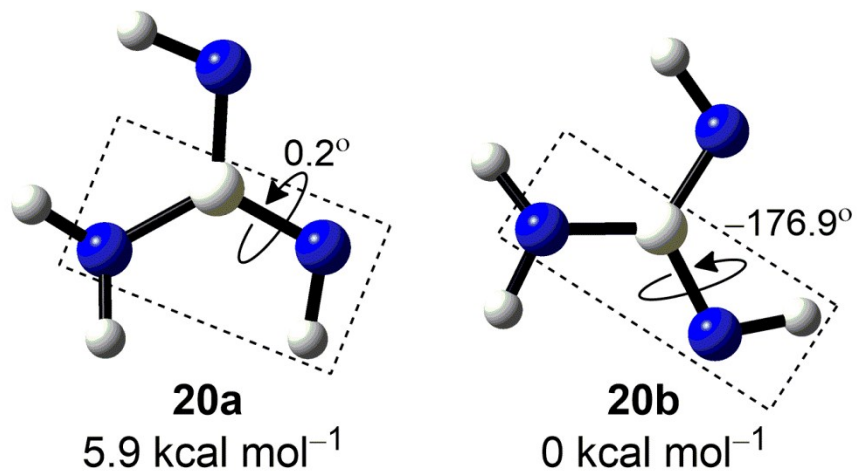


Figure S5. Structures of the two conformers of **20** (**a** and **b**) optimized at B3LYP/6-311G(d,p) and used in the formation pathways of MM (**20a**) and TAP (**20b**). The atoms used to define the dihedral angle are shown within the box.

Table S1. Relative electronic energies (in kcal mol⁻¹) of the various transition states (TS) and the corresponding products (P) associated with proposed mechanisms obtained using different functionals and 6-311G(d,p) basis set.^a

Conversion	Relative energy (kcal mol ⁻¹)							
	B3LYP		ω B97XD		M06-2X		B2PLYP	
	TS	P	TS	P	TS	P	TS	P
1+•OH→2	0	-31.8	0	-34.9	0.5	-32.9	4.2	-27.7
2→3	7.8	7.5	9.6	7.4	10.2	6.6	9.7	6.6
3→4	4.1	-2.4	6.3	-5.5	7.9	-6.2	8.1	-0.1
4+3→5	11.6	-0.5	7.5	-3.6	14.2	-4.5	12.8	-2.7
5→6	7.6	3.7	7.4	2.7	8.0	2.2	9.8	2.3
6+4→7	10.8	6.4	11.8	0.9	12.5	-0.5	8.4	5.4
7→8	6.7	3.8	6.5	2.7	7.6	2.6	10.4	8.0
8→9	2.0	-5.2	3.4	-3.7	4.6	-6.6	8.2	-8.7
9→10	17.4	5.9	19.0	-0.3	13.3	0.6	22.1	-1.0
10→11	0	3.6	1.3	5.5	4.1	6.9	4.2	5.8
11→12	0	-8.5	1.5	-5.9	0	-2.6	0.9	-1.9
12→13	19.9	-14.2	14.9	-10.3	18.4	-9.8	15.6	-20.2
13→14	0	-9.8	0	-7.3	2.8	-3.9	0	-3.1
14→15	16.6	-10.2	15.2	-6.9	14.0	-6.1	21.6	-15.5
15→16	0	-10.7	0	-7.9	0	-4.9	2.3	-4.3
16→17	3.1	-11.8	4.9	-8.3	4.4	-8.8	5.3	-17.0
1+•NH₂→18	1.2	-23.4	1.3	-27.6	2.3	-25.5	7.5	-21.8
18→19	9.5	9.3	11.1	9.0	11.8	8.3	16.4	8.1
19→20a	3.4	-2.4	7.8	-2.5	6.6	-5.5	9.7	0.0
20a+19→21	12.0	1.0	9.6	-6.2	12.7	-4.8	17.7	-1.1
21→22	10.4	-1.5	15.1	3.7	16.7	5.7	16.9	-0.7
22→23	2.8	1.2	4.0	2.8	6.8	-3.6	9.1	-3.0
23→24	2.1	-13.8	0	-19.2	9.2	-11.3	8.7	-6.8
24→25	8.5	8.2	10.0	7.9	10.7	7.1	12.5	7.1
25→26	1.0	-4.1	1.7	-2.8	2.2	-1.9	6.9	-1.8
26→27	14.7	-6.0	15.6	-10.5	15.7	-11.2	20.3	-8.8
27→28	12.8	1.2	16.9	7.2	17.7	7.6	18.1	-0.4

	Relative energy (kcal mol ⁻¹)							
	B3LYP		ωB97XD		M06-2X		B2PLYP	
Conversion	TS	P	TS	P	TS	P	TS	P
29→30	4.8	2.4	6.9	0.8	8.0	1.8	6.6	2.3
30+31→32	8.9	5.8	9.0	2.9	8.3	-0.9	12.8	7.4
32→33	12.1	7.7	14.3	9.5	18.2	12.8	18.7	10.9
33→34	5.5	2.1	8.9	3.4	7.0	3.3	5.1	4.6
34→35	13.1	1.5	16.6	-0.7	16.8	-1.1	19.0	0.2
35→36	11.1	5.2	13.7	7.3	15.9	8.8	15.3	0.1
37+20b→38	10.0	-9.6	7.5	-13.6	6.1	-14.5	16.5	-9.0
38→39	0	10.8	6.7	7.2	6.9	8.8	6.4	9.9
39→40	3.3	-8.3	5.0	-6.9	6.0	-5.3	8.4	-6.4
40→41	8.2	-13.3	10.0	-16.3	10.3	-14.8	14.0	-13.4
41→42	10.3	9.5	11.5	9.1	12.4	8.6	13.0	8.3
42→43	3.4	-2.7	2.5	-2.5	1.4	-2.8	9.1	-2.9
43→44	2.4	-6.2	1.5	-5.9	0.8	-5.5	8.4	-6.0
44→45	13.6	-20.2	12.2	-20.8	11.6	-21.0	19.4	-21.9

^aEach reactant is considered in its free optimized state while calculating the electronic energies.

Table S2. Absolute differences of the gas phase B3LYP/6–311G(d,p) and M06-2X/6–311G(d,p) relative electronic energies of transition states (TS) and the corresponding products (P) energies associated with the steps of the proposed mechanisms of CA, MM, BA and TAP.

Conversion	B3LYP/6–311G(d,p)		M06–2X/6–311G(d,p)		Abs[TS(B3LYP)–TS(M06–2X)]	Abs[P(B3LYP)–P(M06–2X)]
	TS	P	TS	P		
1+•OH→2	0	-31.8	0.5	-32.9	0.5	1.1
2→3	7.8	7.5	10.2	6.6	2.4	0.9
3→4	4.1	-2.4	7.9	-6.2	3.8	3.8
4+3→5	11.6	-0.5	14.2	-4.5	2.6	4.0
5→6	7.6	3.7	8.0	2.2	0.4	1.5
6+4→7	10.8	6.4	12.5	-0.5	1.7	6.9
7→8	6.7	3.8	7.6	2.6	0.9	1.2
8→9	2.0	-5.2	4.6	-6.6	2.6	1.4
9→10	17.4	5.9	13.3	0.6	4.1	5.3
10→11	0	3.6	4.1	6.9	4.1	3.3
11→12	0	-8.5	0	-2.6	0	5.9
12→13	19.9	-14.2	18.4	-9.8	1.5	4.4
13→14	0	-9.8	2.8	-3.9	2.8	5.9
14→15	16.6	-10.2	14.0	-6.1	2.6	4.1
15→16	0	-10.7	0	-4.9	0	5.8
16→17	3.1	-11.8	4.4	-8.8	1.3	3.0
1+•NH₂→18	1.2	-23.4	2.3	-25.5	1.1	2.1
18→19	9.5	9.3	11.8	8.3	2.3	1.0
19→20a	3.4	-2.4	6.6	-5.5	3.2	3.1
20a+19→21	12.0	1.0	12.7	-4.8	0.7	5.8
21→22	10.4	-1.5	16.7	5.7	6.3	7.2
22→23	2.8	1.2	6.8	-3.6	4.0	4.8
23→24	2.1	-13.8	9.2	-11.3	7.1	2.5
24→25	8.5	8.2	10.7	7.1	2.2	1.1
25→26	1.0	-4.1	2.2	-1.9	1.2	2.2
26→27	14.7	-6.0	15.7	-11.2	1.0	5.2
27→28	12.8	1.2	17.7	7.6	4.9	6.4
29→30	4.8	2.4	8.0	1.8	3.2	0.6
30+31→32	8.9	5.8	8.3	-0.9	0.6	6.7
32→33	12.1	7.7	18.2	12.8	6.1	5.1
33→34	5.5	2.1	7.0	3.3	1.5	1.2
34→35	13.1	1.5	16.8	-1.1	3.7	2.6
35→36	11.1	5.2	15.9	8.8	4.8	3.6
37+20b→38	10.0	-9.6	6.1	-14.5	3.9	4.9

38→39	0	10.8	6.9	8.8	6.9	2.0
39→40	3.3	-8.3	6.0	-5.3	2.7	3.0
40→41	8.2	-13.3	10.3	-14.8	2.1	1.5
41→42	10.3	9.5	12.4	8.6	2.1	0.9
42→43	3.4	-2.7	1.4	-2.8	2.0	0.1
43→44	2.4	-6.2	0.8	-5.5	1.6	0.7
44→45	13.6	-20.2	11.6	-21.0	2.0	0.8

Table S3. B3LYP/6–311G(d,p) cartesian coordinates for the optimized structures of CA mechanism.

Cartesian coordinates for 1 (cyanamide)			
C	0.22085300	-0.00006000	-0.00201100
N	1.37784600	0.00002100	0.01343800
N	-1.11864400	0.00000600	-0.08096000
H	-1.56987200	-0.84484800	0.24238400
H	-1.56965800	0.84501300	0.24233800
Cartesian coordinates for 2			
C	-0.03601600	0.15252100	-0.00656700
N	-0.41098300	1.36449200	0.02125300
N	1.26588700	-0.29809100	-0.07922100
H	1.96227400	0.41109600	0.09435300
H	1.43216400	-1.16831600	0.40721000
O	-0.91949700	-0.88840200	-0.01528600
H	-1.80669700	-0.51550300	0.06590000
Cartesian coordinates for 3			
C	-0.05101600	-0.10005300	-0.00477800
N	-0.69794300	-1.19456600	0.01688800
N	1.31996600	-0.05580300	-0.07266200
H	1.77215200	-0.92990200	0.14054700
H	1.75920800	0.77189600	0.29686900
O	-0.54614000	1.17893100	-0.00646700
H	-1.50586400	1.13370000	0.04923000
H	-1.70444500	-1.05424200	-0.01582800
Cartesian coordinates for 4			
C	0.01802900	-0.10375100	-0.00058500
N	-0.96508700	-0.97785300	0.00019300
N	1.27216100	-0.55190500	0.00011200
H	1.90039700	0.25717900	0.00010800
O	-0.14951300	1.26203000	0.00003800
H	-1.08644200	1.48769200	0.00045700
H	-1.87554400	-0.51029700	0.00050900
Cartesian coordinates for 5			
C	1.08912600	-0.02805400	-0.01490600
N	1.19506900	0.98528500	-1.03509900
N	1.40654300	0.57529700	1.25417900
H	2.39947400	0.77755100	1.29252000
H	1.16660900	-0.06193000	2.00623200
O	1.96711300	-1.09476600	-0.35018900
H	2.33416500	-0.85948400	-1.21079400
H	0.37942200	1.59678200	-0.88439900
C	-1.43849100	0.00691900	0.00571000
N	-0.23812200	-0.65053800	0.05935400
N	-1.54950900	1.27205000	-0.09560300
H	-2.51279100	1.59009700	-0.05028100

O	-2.44700200	-0.91710300	0.08230500
H	-3.28587900	-0.46555800	-0.05844700
H	-0.24356400	-1.63034700	-0.17640100

Cartesian coordinates for **6**

C	1.05472900	-0.05201800	0.01241500
N	1.25777100	1.04508900	-0.90124000
N	1.33372600	0.44047200	1.33314700
H	2.23190200	0.90909200	1.35377100
H	1.31424000	-0.31750300	2.00470500
O	1.87136700	-1.14756000	-0.41169500
H	2.73958700	-0.76921000	-0.58922900
H	0.58320000	1.77177400	-0.66842000
C	-1.45014600	0.01206700	0.00650600
N	-0.27216100	-0.67615000	0.01523500
N	-1.53563500	1.28471300	-0.01523600
H	-2.49560200	1.60856100	0.06220500
O	-2.48684300	-0.88961600	0.02329300
H	-3.30996100	-0.40483600	-0.09625500
H	-0.30237300	-1.64625400	-0.25392400
H	1.04940800	0.72663100	-1.84251200

Cartesian coordinates for **7**

C	1.61599800	-0.49033000	-0.07131100
C	-1.86513000	-0.62444300	0.02700700
C	-0.19508700	1.27384600	-0.01803700
N	-1.33248300	0.48864400	-0.57510100
N	1.11933800	0.83990700	-0.38437700
N	0.92007200	-1.52599400	-0.84202600
H	1.39891600	1.17679800	-1.29557000
H	1.24141200	-2.43574600	-0.52136100
H	-1.26970700	0.38598700	-1.57978800
N	-1.69859000	-0.91168900	1.25985700
H	-2.24224500	-1.71854200	1.55294500
N	-0.30077800	1.43436400	1.41449600
H	-1.30074400	1.48181700	1.63627500
N	1.50473500	-0.86101800	1.31643600
H	1.79367100	-0.06923800	1.88222600
H	0.52978000	-1.04885200	1.54768900
O	-2.62574400	-1.30063500	-0.88244700
H	-2.92428300	-2.12363600	-0.48161500
O	2.99369600	-0.39633800	-0.42070300
H	3.41978700	-1.12623500	0.04292800
O	-0.29735000	2.55967900	-0.61625500
H	-1.22778400	2.80851600	-0.56365300
H	1.19563500	-1.43645300	-1.81579400

Cartesian coordinates for **8**

C	1.58601500	-0.53793600	-0.08411700
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C	-1.85050800	-0.65493600	0.06148400
C	-0.18160600	1.30089800	-0.01390100
N	-1.34664800	0.51057300	-0.47042700
N	1.14382700	0.83106900	-0.33697200
N	0.86767800	-1.49883000	-0.92221100
H	1.43203500	1.15777900	-1.25005200
H	1.15233200	-2.43706200	-0.65564200
H	-1.40085100	0.51392600	-1.47881100
N	-1.67411800	-1.06332500	1.25576600
H	-2.18964900	-1.92066300	1.43822600
N	-0.28083700	1.49963800	1.39782400
H	-1.22692400	1.67034800	1.71267900
N	1.45695200	-0.99402000	1.27402700
H	1.84177000	-0.27934800	1.88249200
H	0.46791300	-1.08314600	1.51462800
O	-2.63012800	-1.24601300	-0.89943500
H	-2.95760100	-2.08188900	-0.55262500
O	2.97321000	-0.46359600	-0.41483300
H	3.35934200	-1.26550800	-0.04436500
O	-0.26042300	2.50028600	-0.79880000
H	-1.12834200	2.87949800	-0.62158600
H	1.14100000	-1.35548400	-1.88972200
H	0.35631900	2.23224000	1.68246900

Cartesian coordinates for **9**

C	1.70893000	-0.54416700	-0.16366900
C	-1.93117400	-0.68258500	0.01313000
C	-0.18958300	1.22728100	0.06117100
N	-1.40907300	0.51475900	-0.39868400
N	1.10056300	0.78191600	-0.39313100
N	1.06820400	-1.50888400	-1.02281500
H	1.29166100	1.10045200	-1.33445200
H	0.29776800	-1.89978600	-0.46889400
H	-1.68331400	0.78440400	-1.33171100
N	-1.43781600	-1.42597800	0.92509900
H	-2.03402100	-2.22091400	1.13982000
N	-0.20946200	1.27287800	1.48902400
H	0.52523600	1.88371700	1.82240500
H	-1.11348700	1.54077200	1.85701500
N	1.72784500	-1.00772400	1.19616000
H	2.29958700	-0.38472700	1.75630300
H	0.78429800	-1.03755400	1.57712900
O	-3.06627400	-0.92323100	-0.71878500
H	-3.35217300	-1.82795800	-0.55327400
O	3.03271600	-0.33279600	-0.60830600
H	3.34431900	-1.19937700	-0.89370200
O	-0.29915000	2.50097000	-0.59030100

H	-1.10906800	2.90948700	-0.26487000
Cartesian coordinates for 10			
C	-1.30111400	-0.61746200	-0.05479300
C	0.19094700	1.46406400	0.00293800
C	1.18184200	-0.81114900	-0.05735600
N	1.30628500	0.61554900	-0.37913800
N	-0.11848000	-1.40378200	-0.36448800
N	-1.09985000	0.82455000	-0.34049500
H	-0.14065600	-1.66866400	-1.34131200
H	-1.86206700	1.35153600	0.07932800
H	1.43423000	0.68880100	-1.38190900
N	0.26234900	1.77507900	1.40276200
H	-0.31613100	2.61717700	1.51425000
N	1.46226600	-0.98737800	1.32302900
H	1.55681100	-1.95923900	1.58074700
H	2.19985300	-0.39037600	1.66661000
N	-1.70436700	-0.85295400	1.30456600
H	-2.69649000	-0.66107800	1.40160200
H	-1.53827000	-1.82598000	1.53140300
O	0.25734600	2.66534600	-0.74347500
H	-0.23341300	2.49850900	-1.55790400
O	-2.35130000	-1.02482900	-0.92765300
H	-2.24516800	-0.51596500	-1.74060200
O	2.05660800	-1.50073600	-0.95710600
H	2.95259500	-1.26313500	-0.69472300
Cartesian coordinates for 11			
C	-0.28410800	1.41049600	-0.04990600
C	1.36517200	-0.45632000	-0.03565100
C	-1.06124000	-0.97365100	-0.03890200
N	0.29948000	-1.41512100	-0.30997900
N	-1.35114900	0.43996100	-0.35450200
N	1.06997600	0.95211000	-0.34648500
H	-1.47488200	0.47538800	-1.36120200
H	1.21468400	1.07263600	-1.34306500
H	0.35983100	-1.69823800	-1.28119400
N	1.73973700	-0.54672700	1.33546600
H	2.04260700	-1.48021500	1.57826800
H	2.39955000	0.16923800	1.60610800
N	-1.37966700	-1.20456900	1.33053600
H	-2.30179000	-0.86766800	1.57313500
H	-1.24017600	-2.17385500	1.58272200
N	-0.37738000	1.79143000	1.32017300
H	0.26864300	2.54055000	1.53214200
H	-1.32589400	2.01772500	1.58781300
O	2.38505500	-0.85602500	-0.96495100
H	3.19214100	-0.40849800	-0.69041100

O	-0.45597600	2.48891400	-0.98315700
H	-1.29691900	2.90520100	-0.76522300
O	-1.83041200	-1.74643600	-0.97448700
H	-2.75305300	-1.64661600	-0.71804100

Cartesian coordinates for **12**

C	-0.13702400	-1.42581000	-0.03229000
C	-1.16490700	0.83387200	-0.02639600
C	1.32153400	0.61687500	-0.18582500
N	0.12203700	1.42999400	-0.36327700
N	1.15775500	-0.82920700	-0.38841300
N	-1.30879900	-0.60033500	-0.31180300
H	1.31484400	-0.99457700	-1.37720000
H	-1.50752400	-0.68991700	-1.30267100
H	0.10450600	1.76372600	-1.32002800
N	-1.41416700	1.04642200	1.36508700
H	-1.44822000	2.03516300	1.57789500
H	-2.23881300	0.55526600	1.68443000
N	1.86947500	0.85098400	1.15049100
H	2.72607400	0.32918200	1.29995800
H	1.95919600	1.84184600	1.34564600
N	-0.10365800	-1.75340800	1.35803200
H	-0.93309100	-2.26535900	1.63077700
H	0.74450000	-2.24638800	1.60492000
O	-2.06984800	1.50859500	-0.90843100
H	-2.95861900	1.26958200	-0.62414000
O	-0.32476700	-2.54444700	-0.90786200
H	0.36116200	-3.18385500	-0.68684200
O	2.33209900	1.08892200	-0.93826900

Cartesian coordinates for **13**

C	1.25674700	-0.43371100	-0.06068100
C	-1.21788300	-0.54864500	-0.05622600
C	-0.11610100	1.67808000	0.09973700
N	-1.23183300	0.89676200	-0.08642200
N	1.06877400	0.97268500	0.23322600
N	0.04518100	-1.06346200	-0.58384000
H	1.88890200	1.55603500	0.16065700
H	0.02804600	-0.87529800	-1.58133300
H	-2.10784100	1.38039000	-0.20155100
N	-1.40114500	-1.03896700	1.27795000
H	-2.30748700	-0.78642200	1.65141500
H	-1.22194100	-2.03161400	1.35621600
N	1.66954300	-1.14141100	1.12124200
H	1.81235500	-2.12707100	0.93271400
H	2.49594600	-0.72726200	1.53617500
O	-2.24959800	-0.91216300	-0.96923400
H	-2.42304800	-1.84970100	-0.83114400

O 2.23381900 -0.45090400 -1.10962700
H 2.61815900 -1.33394700 -1.12857300
O -0.15588500 2.89323000 0.13803100

Cartesian coordinates for **14**

C 1.16577400 -0.61486600 -0.03830400
C -1.29374100 -0.35011400 -0.17284300
C 0.21317800 1.67182300 0.08238200
N -1.01150600 1.02784000 0.20199000
N 1.28103100 0.82485500 -0.08648500
N -0.09854500 -1.06736100 -0.60495300
H 2.18907100 1.24634300 -0.19792900
H -0.04139900 -0.97691400 -1.61447100
H -1.79515600 1.65971600 0.11688900
N -1.89476600 -1.07421800 0.96050900
H -2.71892000 -0.60704600 1.32526900
H -2.08311300 -2.04122900 0.71537900
N 1.23078300 -1.08160800 1.32048300
H 1.05480300 -2.07652300 1.39085600
H 2.10785600 -0.82954500 1.75999300
O -2.29823900 -0.44224100 -1.05818700
O 2.21934300 -1.06593500 -0.87879000
H 2.30759000 -2.01447400 -0.73495900
O 0.31877400 2.88218300 0.12082100

Cartesian coordinates for **15**

C 1.18143300 0.03045700 0.01432000
C -1.00507200 1.22146500 0.01152900
C -0.91715700 -1.26139600 0.06767200
N -1.52425400 -0.04614100 -0.26216300
N 0.40690100 -1.12128300 0.41954700
N 0.36494000 1.22161100 0.16667000
H 0.90458700 -1.97556700 0.61839700
H 0.75542700 1.98149100 0.70143000
H -2.52250900 -0.08707800 -0.40816100
N 1.56879700 -0.07724700 -1.37202400
H 1.94601000 0.78520900 -1.74565200
H 2.17017700 -0.87081900 -1.56137000
O -1.69707000 2.21018100 0.09980500
O 2.26951900 0.10456200 0.91903300
H 3.04511600 0.35995600 0.41038100
O -1.51853900 -2.31161000 0.07611700

Cartesian coordinates for **16**

C 1.20461200 -0.00049000 0.12856400
C -0.96027700 1.24518500 0.02483400
C -0.96128500 -1.24464400 0.02448200
N -1.53502600 0.00060100 -0.23650200
N 0.38457700 -1.17130400 0.30673400

N	0.38524200	1.17040800	0.30883900
H	0.84910900	-2.03457800	0.54245900
H	0.85048800	2.03368100	0.54323100
H	-2.53217200	0.00099700	-0.39458500
N	1.81538700	0.00041600	-1.23560900
H	2.36540100	0.83711700	-1.41043900
H	2.36458800	-0.83651100	-1.41190500
O	-1.59339800	2.27588700	0.01222700
O	2.32060100	-0.00149900	0.85779300
O	-1.59557500	-2.27461900	0.01244500

Cartesian coordinates for **17**

C	-0.35830100	1.39224900	-0.00005400
C	-1.02657500	-1.00642800	-0.00004300
C	1.38488100	-0.38581500	-0.00005600
N	0.33374600	-1.29683500	-0.00063900
N	0.95619700	0.93745100	0.00048900
N	-1.28993700	0.35938300	0.00001700
H	1.67761200	1.64472900	0.00019200
H	-2.26316100	0.63052600	0.00003700
H	0.58555600	-2.27524100	-0.00001100
O	-1.88678600	-1.84972400	0.00031400
O	-0.65855500	2.55882600	-0.00020400
O	2.54533000	-0.70910700	0.00009300

Cartesian coordinates for **ammonia**

N	0.00000000	0.00000000	0.11583300
H	0.00000000	0.93957100	-0.27027600
H	-0.81369200	-0.46978600	-0.27027600
H	0.81369200	-0.46978600	-0.27027600

Cartesian coordinates for **amino radical**

N	0.00000000	0.00000000	0.14394600
H	0.00000000	0.80205900	-0.50381200
H	0.00000000	-0.80205900	-0.50381200

Cartesian coordinates for **hydroxyl radical**

O	0.00000000	0.00000000	0.10835700
H	0.00000000	0.00000000	-0.86685200

Table S4. B3LYP/6-311G(d,p) cartesian coordinates of the optimized transition states for CA mechanism.

Cartesian coordinates for **TS1-2**

C	0.36889400	0.37962900	-0.00757500
N	-0.08857600	1.46206100	0.01879300
N	1.20571700	-0.66209700	-0.08957200
H	0.77081900	-1.55694100	0.08165800
H	2.11426500	-0.52399300	0.32959200
O	-1.36421900	-0.71393100	0.05553100
H	-2.00467900	-0.08515000	-0.31459600

Cartesian coordinates for **TS2-3**

C	0.75605700	-0.08269400	-0.07222700
N	1.79146700	-0.63392000	0.44881700
N	-0.27899200	-0.81264000	-0.58170500
H	-0.18004700	-1.77973400	-0.28479600
O	0.53378700	1.25829200	-0.24279700
H	1.27840900	1.74362900	0.12712900
H	2.53574100	0.03607400	0.63943300
N	-2.41007600	0.07489000	0.22641500
H	-2.63307700	-0.55215000	1.00236300
H	-2.09616600	0.94832400	0.65529800
H	-1.42828700	-0.36462400	-0.41837800

Cartesian coordinates for **TS3-4**

C	-0.66063700	0.06844200	-0.09887700
N	-0.42927200	1.32276800	-0.18725700
N	0.27434000	-0.87785700	-0.44571900
H	1.50257600	-0.49429300	-0.37818000
H	0.09280000	-1.75843000	0.03099200
O	-1.83381200	-0.52796600	0.29963400
H	-2.49464000	0.15512200	0.45853200
H	-1.23949800	1.88452700	0.06509000
N	2.44487200	0.04253900	0.15096200
H	2.10113800	0.98909800	0.33188700
H	2.64236700	-0.37509000	1.06196900

Cartesian coordinates for **TS4-5**

C	-1.31392900	0.00652000	0.15163300
N	-0.97312200	-0.53653800	1.35510600
N	-1.35819200	1.37632900	0.06655700
H	-1.51419700	1.67911500	-0.88667200
H	-0.50376400	1.79073700	0.43263700
O	-2.25520800	-0.54447500	-0.67642000
H	-2.22055100	-1.50332800	-0.60879000
C	1.46317300	0.03713400	-0.19265500
N	0.30726600	-0.56165000	-0.62813600
N	1.55690300	1.30656100	-0.03746300
H	2.46028800	1.58204000	0.34098400
O	2.46643600	-0.87972500	0.01161000
H	3.28564700	-0.41346200	0.21425600
H	0.41854000	-1.57316900	-0.58728600
H	-1.24123700	-1.52316800	1.36703200

Cartesian coordinates for **TS5-6**

C	0.82155200	-0.68733800	-0.00224200
N	1.42541900	0.19669500	-0.96772400
N	1.23891500	-0.29939900	1.32832300
H	2.25487400	-0.27757700	1.35683300
H	0.92774400	-1.00865100	1.98452300
O	1.24225800	-2.02469100	-0.34256600

H	2.03879900	-1.90301700	-0.87254300
H	1.66640800	1.38697200	-0.56655200
C	-1.60472000	0.11521400	-0.01263100
N	-0.63220700	-0.83974500	-0.04049300
N	-1.41367400	1.37535400	-0.08192900
H	-2.28392400	1.89185600	0.01450700
O	-2.81921300	-0.52180400	0.07875000
H	-3.51572900	0.12968800	-0.05242000
H	-0.94248500	-1.78743200	-0.18155200
H	0.77385100	0.32705200	-1.74013000
N	1.45067400	2.45700600	-0.02552100
H	0.45166400	2.61200900	-0.19884700
H	1.45955800	2.20442700	0.96736300

Cartesian coordinates for **TS6-7**

C	1.88535900	-0.47562100	0.01722900
C	-2.40575300	-0.53066200	-0.20481900
C	-0.00865300	1.07924700	-0.02971000
N	-1.84979100	0.67220200	-0.55486700
N	0.67284400	0.00578200	-0.66761300
N	2.45966400	-1.45517500	-0.87336800
H	0.04349100	-0.77973900	-0.84180100
H	3.31958500	-1.81091500	-0.46910900
H	-2.39430900	1.44130600	-0.16713000
N	-1.82020400	-1.62744400	-0.52509300
H	-2.30078400	-2.45268300	-0.17353600
N	-0.30062000	1.06373200	1.27262300
H	-0.53180500	2.01730500	1.56078900
N	1.73397600	-1.11358700	1.31324500
H	1.09695700	-0.55131500	1.87365400
H	1.31132300	-2.02687600	1.18221200
O	-3.59917800	-0.40140000	0.45305600
H	-3.99583800	-1.27144300	0.57814100
O	2.66734700	0.69966500	0.21211100
H	3.23520200	0.50371100	0.96573500
O	0.16714600	2.27654600	-0.62894500
H	0.56410100	2.08737900	-1.48967100
H	2.67275000	-1.01156900	-1.75974900

Cartesian coordinates for **TS7-8**

C	-0.30631900	1.70780600	-0.04844800
C	1.97200400	-0.87556800	0.24146900
C	-0.49303700	-0.80158700	-0.44411900
N	0.94344400	-1.12907100	-0.63917800
N	-0.92169300	0.55007300	-0.69544200
N	1.07423900	1.89931000	-0.49675800
H	-1.06838200	0.70556000	-1.68454600
H	1.48922200	2.64853100	0.04999700

H	1.22280700	-0.96281500	-1.59657400
N	1.83486400	-0.70493500	1.49622700
H	2.72962500	-0.59410400	1.96616300
N	-0.89305800	-1.19425300	0.87898800
H	-2.13521600	-1.18871700	1.00951300
H	-0.51415400	-2.11585600	1.09437300
N	-0.27677300	1.67238600	1.38841900
H	-1.20213700	1.41924000	1.71923300
H	0.35986200	0.93880200	1.70214100
O	3.14716200	-0.91692200	-0.46075500
H	3.86839700	-0.70118200	0.13906400
O	-1.16156400	2.76905500	-0.46843100
H	-0.95367100	3.50455900	0.11921100
O	-1.14330500	-1.51884200	-1.50506500
H	-0.81837900	-2.42496500	-1.45361200
H	1.06180200	2.19742200	-1.46758200
N	-3.32451100	-1.46913900	0.76206000
H	-3.45364300	-1.15980600	-0.20433600
H	-3.41595100	-2.48749700	0.72733500

Cartesian coordinates for **TS8-9**

C	-1.39348400	-0.49972200	-0.03010300
C	1.73725400	1.36601200	0.05533900
C	1.11799900	-1.14608800	-0.04859400
N	1.80300200	0.10610600	-0.47153500
N	-0.25659700	-1.35178700	-0.40682200
N	-1.34377000	0.76109900	-0.78633900
H	-0.33976800	-1.61851100	-1.37974100
H	-0.80423500	1.42362600	-0.22311400
H	2.08794900	0.07917300	-1.43926900
N	1.02437300	1.71187500	1.05718600
H	1.21076400	2.66820000	1.34780400
N	1.28134100	-1.28800900	1.36515800
H	0.97432600	-2.20999800	1.64858800
H	2.23157300	-1.10767000	1.66421800
N	-1.52099900	-0.23585100	1.38707000
H	-1.60471500	-1.12376200	1.87230800
H	-0.68273400	0.23342100	1.72707700
O	2.57086000	2.17639900	-0.67380500
H	2.40416100	3.09144800	-0.42367000
O	-2.48945400	-1.25547400	-0.47413500
H	-3.25015300	-0.65273200	-0.49561600
O	1.77627900	-2.14737200	-0.83696300
H	2.70860300	-2.12128400	-0.59444200
H	-2.48145300	1.13504200	-0.78155800
N	-3.66899300	1.42029200	-0.29512600
H	-3.49492400	1.43118500	0.71362100

H -3.81999300 2.39614000 -0.56398000

Cartesian coordinates for **TS9-10**

C 1.47523800 -0.32796900 -0.03873600
C -1.36236800 -0.98264600 0.06890400
C -0.43320100 1.33433300 -0.05803000
N -1.45739600 0.33073200 -0.41365000
N 0.93520400 0.98038100 -0.39391200
N 0.51813400 -1.41766700 -0.23300400
H 1.10519300 1.16361500 -1.37385900
H 0.72877400 -2.14483600 0.45275100
H -1.57367500 0.32993600 -1.41848300
N -1.41914400 -1.20818800 1.37364300
H -1.52784800 -2.21654000 1.49747900
N -0.53288200 1.61455900 1.32479500
H 0.03722300 2.39786600 1.60718000
H -1.47524000 1.62806100 1.68429900
N 2.02299100 -0.28277700 1.28605200
H 2.69197400 -1.03794600 1.40094600
H 2.50884200 0.59789100 1.40890000
O -1.90123400 -1.90850500 -0.80912400
H -1.19492000 -2.10453900 -1.43954300
O 2.52954500 -0.60255100 -0.98177400
H 2.12144500 -1.07312300 -1.71975400
O -0.68214000 2.43618400 -0.94120300
H -1.53750500 2.79700000 -0.68341200

Cartesian coordinates for **TS10-11**

C 0.40656300 1.44780700 -0.02852000
C -0.86472400 -0.73920400 0.06999700
C 1.54443100 -0.72369600 -0.30276300
N 0.26603200 -1.32420800 -0.61091600
N 1.45352800 0.67332600 -0.71119100
N -0.84599600 0.69127100 -0.13239200
H 2.34292300 1.12619600 -0.52034000
H -1.49951600 1.12913200 0.50807600
H 0.31116100 -2.32625600 -0.46477600
N -2.06354000 -1.38732900 -0.43397000
H -2.00042000 -1.35390400 -1.45146600
N 2.57043100 -1.44652200 -1.00213100
H 2.64808800 -1.11347700 -1.95616400
H 3.45379500 -1.34716100 -0.51705900
N 0.15323400 2.72706100 -0.63819000
H 0.89803600 3.37325500 -0.40421600
H 0.09016100 2.61658500 -1.64304100
O -0.84177200 -1.02339100 1.50261500
H -1.41251000 -1.79179300 1.62834900
O 0.77549700 1.77042800 1.30449800

H	1.22467400	0.98943000	1.65932300
O	1.88379000	-0.82818700	1.10725600
H	1.09731800	-1.17183400	1.56161600
H	-3.07793500	-0.71680300	-0.12139400
N	-3.96848600	0.14803500	-0.24118100
H	-3.51702900	0.96969400	-0.65199500
H	-4.57290700	-0.21475800	-0.98435400

Cartesian coordinates for **TS11-12**

C	1.60077200	0.70653400	-0.16506400
C	0.34957300	-1.43694500	-0.00768200
C	-0.88934600	0.73846200	0.12867600
N	-0.91383500	-0.71229600	-0.16975400
N	0.32966700	1.43440000	-0.32550400
N	1.54840000	-0.72360100	-0.46702600
H	0.21438800	1.61023500	-1.31799500
H	1.58235800	-0.81735200	-1.47673200
H	-1.17357700	-0.79614700	-1.14747800
N	0.51852900	-1.80469900	1.35654200
H	-0.19892100	-2.44973900	1.65916400
H	1.45260000	-2.13625100	1.55185200
N	-1.02787900	0.93016700	1.54241600
H	-1.19489100	1.91127000	1.73252400
H	-1.78037400	0.36563900	1.91499500
N	2.08339100	0.89884900	1.16130400
H	3.04415900	0.59531900	1.25006100
H	1.93918200	1.84403000	1.48757100
O	0.17917300	-2.54415500	-0.90776300
H	0.93939300	-3.12027300	-0.77094700
O	2.46814600	1.20684800	-1.19271100
H	2.62104500	2.13542200	-0.98553600
O	-1.89298200	1.33029200	-0.66537000
H	-3.00721400	0.91470400	-0.28890700
N	-3.85739500	0.09299900	-0.25267100
H	-4.16651700	-0.08012800	-1.21051400
H	-3.43846400	-0.77964900	0.07595300

Cartesian coordinates for **TS12-13**

C	-0.74481400	-1.23899100	-0.02247600
C	-0.74480100	1.23899700	-0.02248400
C	1.42117200	-0.00001400	-0.33479000
N	0.68323700	1.20186500	-0.27958300
N	0.68324100	-1.20191800	-0.27956100
N	-1.44955300	0.00000800	-0.36610900
H	0.98290000	-1.84727200	-0.99519600
H	-1.54468900	0.00000700	-1.37670100
H	0.98300800	1.84736500	-0.99503600
N	-0.98082000	1.53212900	1.35517800

H	-0.51159900	2.37910900	1.64666800
H	-1.96239100	1.52157400	1.59955300
N	2.39090900	-0.00001500	1.22538900
H	3.00171700	-0.82095200	1.20116900
H	3.00158500	0.82102400	1.20126600
N	-0.98083300	-1.53210100	1.35518200
H	-1.96239300	-1.52151600	1.59958800
H	-0.51158000	-2.37904500	1.64671800
O	-1.20813500	2.24363600	-0.93545100
H	-2.06405100	2.54049800	-0.61030800
O	-1.20818600	-2.24361800	-0.93544400
H	-2.06404900	-2.54054100	-0.61022000
O	2.49618800	-0.00001600	-1.01691400

Cartesian coordinates for **TS13-14**

C	-0.97319400	1.13384600	-0.04271700
C	0.86417500	-0.48643900	0.26297500
C	-1.50463000	-1.26213600	-0.22912500
N	-0.22303400	-1.45719100	0.27522900
N	-1.80562300	0.04503200	-0.53592200
N	0.42767500	0.79828300	-0.29631400
H	-2.78048400	0.23026000	-0.71943600
H	0.50160900	0.70907500	-1.30580900
H	0.04579400	-2.42987100	0.31791300
N	1.33134200	-0.26301800	1.61922900
H	1.41682900	-1.14914100	2.10589400
H	2.24666500	0.17731200	1.59953900
N	-1.16541900	1.37085300	1.35730900
H	-0.33709800	1.70760800	1.82697300
H	-1.99424200	1.91618700	1.55033400
O	1.81395600	-1.04061700	-0.60553000
H	2.85841500	-0.46614500	-0.45048500
O	-1.33381100	2.22516500	-0.87174200
H	-0.89139600	2.99832500	-0.50346500
O	-2.27849900	-2.18755400	-0.38096200
N	3.68742400	0.41809300	-0.61155400
H	4.04027700	0.31960200	-1.56633300
H	3.19579500	1.31485800	-0.59189500

Cartesian coordinates for **TS14-15**

C	1.09809500	-0.73570000	-0.03138500
C	-1.27824700	-0.12956500	-0.37091900
C	0.45310700	1.63319600	0.04645700
N	-0.85199500	1.14794600	0.05763000
N	1.40091800	0.66884400	-0.21015300
N	-0.21408100	-1.04877400	-0.58099100
H	2.36146900	0.96557100	-0.12731500
H	-0.14846000	-1.27406600	-1.56612200

H	-1.56130800	1.86536600	0.08585500
N	-2.16941000	-0.84921000	1.10270100
H	-3.00277600	-0.27967600	1.27818300
H	-2.51391200	-1.76034300	0.78743100
N	1.08373500	-1.08597300	1.36207600
H	0.66891300	-1.99288300	1.53234000
H	1.99189600	-0.98947300	1.79926000
O	-2.32583600	-0.23509200	-1.06546200
O	2.08162300	-1.40555400	-0.80378200
H	2.11891700	-2.31283900	-0.48241800
O	0.70713300	2.80826100	0.20787200

Cartesian coordinates for **TS14-15**

C	-0.61915800	-0.63033200	0.36841200
C	0.70095800	1.48435800	0.24679500
C	1.78246500	-0.69847000	-0.27417800
N	1.71428600	0.69117000	-0.28846600
N	0.66124300	-1.29927200	0.27116400
N	-0.33697100	0.74925400	0.78117100
H	0.60657500	-2.30069800	0.14626800
H	-1.13547400	1.30635100	1.04932000
H	2.52401100	1.17635800	-0.64568800
N	-1.43910100	-1.33190700	1.32132400
H	-1.17503900	-1.10627800	2.27372400
H	-2.42120900	-1.12844600	1.17322500
O	0.76004700	2.69446600	0.26401900
O	-1.18195600	-0.70729100	-0.90401300
H	-2.28117300	-0.22958900	-0.83801400
O	2.74725400	-1.31301100	-0.66892500
N	-3.31838400	0.41430700	-0.91572100
H	-3.06433700	1.36552100	-1.19438700
H	-3.80922000	0.02527800	-1.72557500

Cartesian coordinates for **TS16-17**

C	1.16523200	0.00003200	0.31584400
C	-0.95763700	1.24546300	0.03761100
C	-0.95762100	-1.24545900	0.03767700
N	-1.53192300	-0.00004300	-0.20635800
N	0.36886800	-1.16263400	0.41957700
N	0.36890000	1.16274400	0.41911600
H	0.85162000	-2.03681700	0.56342900
H	0.85160000	2.03684400	0.56362900
H	-2.51171500	-0.00005100	-0.45031100
N	1.77882400	-0.00022600	-1.38919500
H	2.38069400	0.81856700	-1.51028600
H	2.38205000	-0.81812000	-1.50962600
O	-1.56630000	2.28407800	-0.06173400
O	2.33915700	0.00013400	0.78534700

O -1.56620300 -2.28415100 -0.06181500

Table S5. B3LYP/6-311G(d,p) cartesian coordinates for the optimized structures of MM mechanism.

Cartesian coordinates for **18**

C 0.00010100 0.17324500 0.00009200
N -1.16736400 -0.60000700 0.07537000
H -1.19940700 -1.32813700 -0.62900100
N 0.00063800 1.44143900 0.00010000
N 1.16662800 -0.60088900 -0.07539800
H 2.00503300 -0.03467300 -0.07116700
H 1.19973200 -1.32729000 0.63082500
H -2.00528300 -0.03316600 0.06829000

Cartesian coordinates for **19**

C 0.01743800 0.12423000 0.00056900
N -1.27078900 -0.40519100 0.08508900
H -1.44050700 -1.18681900 -0.53404700
N 0.19335500 1.38890200 -0.01111800
H 1.18129600 1.62780300 0.04756700
N 0.99057200 -0.87788800 -0.07844600
H 1.93735800 -0.55071100 0.04487800
H 0.79261100 -1.69693700 0.48084300
H -1.96735200 0.32051600 -0.01132700

Cartesian coordinates for **20**

C 0.11181300 0.00021200 0.00428300
N 0.81627400 1.13252100 0.01127000
H 0.18323100 1.93576500 -0.05237300
N 0.82221300 -1.12825400 0.01125900
H 0.19345100 -1.93490800 -0.05192200
N -1.28657700 -0.00325800 -0.07656300
H -1.75338900 -0.84461800 0.22791600
H -1.75754100 0.83542300 0.22891800

Cartesian coordinates for **21**

C 1.42452800 0.03196200 0.00134600
N 0.26093800 -0.70831700 0.04514900
H 0.28890800 -1.63064300 -0.36504400
N 1.40018100 1.31666900 0.01635800
H 2.33800300 1.70578000 0.06490800
N 2.56339500 -0.77548600 -0.09073800
H 3.43299700 -0.28697300 0.06358300
H 2.51538600 -1.64350700 0.42564900
C -1.09090300 -0.10943200 -0.00987100
N -1.95794300 -1.24446000 -0.28829800
H -2.89109100 -0.82368500 -0.35176000
N -1.29182700 0.93223400 -1.00308400
H -1.25918200 0.52119800 -1.93237400
N -1.46767600 0.39893200 1.29664500

H	-0.75336600	0.22932600	1.98948200
H	-1.71803800	1.37712500	1.24805000
H	-0.50484500	1.57919600	-0.92356700

Cartesian coordinates for **22**

C	1.20291200	0.04126100	-0.03469900
N	0.00569400	-0.64542800	0.05695800
H	0.02232400	-1.63870100	-0.12068300
N	1.25152200	1.31387100	-0.19150200
H	2.20453500	1.66263300	-0.16603200
N	2.29592300	-0.82553400	0.01403200
H	3.18882600	-0.36675300	0.11363400
H	2.19793600	-1.61648200	0.63583200
C	-1.31694400	-0.15457200	0.01782700
N	-2.22243000	-1.04451700	-0.15473400
H	-3.15088400	-0.62910000	-0.13793200
N	-1.44940700	1.19175300	0.23801900
H	-0.61198200	1.74725000	0.06357000
H	-2.33567900	1.59000500	-0.02656300

Cartesian coordinates for **23**

C	1.16796800	0.06054500	-0.08873200
N	0.00524500	-0.69155400	0.12669900
H	0.03173200	-1.65466000	-0.17915000
N	1.09704700	1.25676200	-0.52025400
H	2.00258300	1.72029100	-0.51396800
N	2.30756300	-0.69981000	0.16355900
H	3.17831500	-0.19196700	0.12243500
H	2.24504200	-1.31921000	0.95996800
C	-1.26692500	-0.12104300	0.04795300
N	-2.22614200	-0.87389100	-0.40943600
H	-3.10884100	-0.36297200	-0.41438000
N	-1.40856100	1.09114800	0.64872600
H	-2.18116100	1.59292400	0.20471200

Cartesian coordinates for **24**

C	1.74285000	-0.46407900	-0.06710000
N	0.99659400	0.56851300	0.51030300
H	1.53892500	1.21316700	1.06829700
N	1.19464000	-1.51171300	-0.55415200
H	1.87280500	-2.11979000	-1.00451200
N	3.10726600	-0.23477400	0.06946300
H	3.71181200	-0.94398700	-0.31651200
H	3.43046600	0.70778700	-0.09784800
C	-0.13218300	1.23465200	0.00527600
N	-0.13134300	2.50570300	0.12847100
H	-1.03480400	2.90209400	-0.12137400
N	-1.12401700	0.47314000	-0.63597300
H	-1.70268400	1.05897300	-1.22484900

C	-1.95361100	-0.50490600	-0.00389700
N	-3.21047700	-0.41738800	-0.18567600
N	-1.31534200	-1.45005400	0.75886300
H	-1.93859700	-2.16012000	1.11570000
H	-0.44150000	-1.78610800	0.33633800

Cartesian coordinates for **25**

C	1.78886500	-0.49936900	-0.06372200
N	1.06269300	0.53910400	0.52508800
H	1.62563000	1.18350600	1.06286700
N	1.21796200	-1.54489000	-0.52926000
H	1.87563100	-2.16496100	-0.99312900
N	3.15858000	-0.28333100	0.03758600
H	3.74624200	-0.99850000	-0.36323300
H	3.48473100	0.65616500	-0.14087500
C	-0.05040100	1.23673500	0.01498800
N	0.00772500	2.50917600	0.12535200
H	-0.87956700	2.94013900	-0.12538200
N	-1.07989500	0.52075700	-0.60391500
H	-1.67648400	1.13857700	-1.14019900
C	-1.93927200	-0.44825500	-0.00563100
N	-3.18668100	-0.27893900	-0.23965400
N	-1.31123600	-1.40273600	0.74955800
H	-1.91627700	-2.14535200	1.06585600
H	-0.40303200	-1.70518200	0.37855900
H	-3.73606400	-1.05305600	0.12844300

Cartesian coordinates for **26**

C	1.57846400	-0.57382000	-0.15836300
N	1.11431900	0.64620100	0.31904900
H	1.79048000	1.24126600	0.77269100
N	0.81177100	-1.43073600	-0.71540800
H	1.33485300	-2.24561100	-1.02570600
N	2.93775700	-0.73756700	0.12708300
H	3.35175000	-1.55725600	-0.29069800
H	3.51866800	0.08240200	0.01453700
C	-0.02358400	1.38388600	-0.01785700
N	0.10223200	2.65714600	0.01192900
H	-0.79943800	3.11492600	-0.10079500
N	-1.18094200	0.70653300	-0.38294900
H	-1.81759400	1.22182600	-0.97178800
C	-1.72981300	-0.47691800	0.11069300
N	-2.87680200	-0.81905700	-0.43049300
N	-1.14814400	-1.04066800	1.18567400
H	-1.47723500	-2.00452300	1.25932600
H	-3.17321000	-1.72488500	-0.06858200

Cartesian coordinates for **27**

C	1.23891000	0.04155200	0.05513300
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N	0.40796700	1.20020400	-0.26137800
H	0.90772700	2.07605000	-0.23981000
N	1.56482800	-0.10341400	1.45340300
H	0.68128000	-0.02639200	1.96844800
N	2.47630300	0.19953000	-0.65260400
H	3.21001300	-0.33981800	-0.21117000
H	2.38113600	-0.03313900	-1.63386000
C	-0.95872100	1.22912800	-0.06284700
N	-1.73819900	2.23949100	-0.02845600
H	-1.22520600	3.11296200	-0.11879600
N	-1.52009600	-0.04037500	0.10008800
H	-2.52418000	-0.02882600	0.19599600
C	-0.88813600	-1.26105200	-0.11193100
N	-1.42323500	-2.41928300	-0.09155600
N	0.47329600	-1.13742800	-0.37491600
H	-2.43060700	-2.36971200	0.04165800
H	0.96147100	-2.01996000	-0.29666300

Cartesian coordinates for **28**

C	0.55484000	-1.32241100	0.00038300
N	1.32903100	-0.17314600	-0.00058200
H	2.33355000	-0.25987700	-0.00133800
N	0.94857300	-2.53280900	-0.00115000
H	1.96231100	-2.60556600	-0.00242700
C	0.86778700	1.14171700	0.00016700
N	1.71958400	2.08752600	-0.00068900
H	1.27670600	3.00241000	-0.00004300
N	-0.51468400	1.23768900	0.00218200
H	-0.94179100	2.15100100	-0.00178400
C	-1.42284500	0.18071300	0.00034600
N	-2.66790400	0.44505200	-0.00240600
N	-0.81452000	-1.06441500	0.00286200
H	-3.23827100	-0.39626300	-0.00316400
H	-1.39175400	-1.89109400	0.00187100

Table S6. B3LYP/6-311G(d,p) cartesian coordinates of the optimized transition states for MM mechanism.

Cartesian coordinates for **TS1-18**

C	-0.38607600	0.33039200	-0.00368600
N	-0.10162800	1.47459500	0.00364300
N	-1.16241000	-0.76703800	-0.07104800
H	-0.69280100	-1.62012300	0.19186000
H	-2.11207700	-0.65087500	0.25257300
N	1.45395000	-0.61857300	0.01993300
H	1.86466400	-0.25132600	-0.84496700
H	1.92728600	-0.08291400	0.75496000

Cartesian coordinates for **TS18-19**

C	-0.63891000	-0.07773500	0.01303100
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N	-0.37716800	1.29006800	0.09630000
H	-0.97449400	1.86264800	-0.48531500
N	0.19958000	-1.03663200	0.06283100
N	-2.00608900	-0.34732900	-0.12192300
H	-2.19475000	-1.33864200	-0.05890100
H	-2.58844500	0.19033300	0.50838100
H	0.60097600	1.51938600	0.00554500
N	2.54806200	-0.17403900	-0.03225100
H	2.57783900	0.47982200	0.75680200
H	1.33189100	-0.78722300	0.03132900
H	2.52975000	0.41560700	-0.87072500

Cartesian coordinates for **TS19-20**

C	-0.63938200	0.09176300	-0.05102400
N	0.23115600	-0.97547900	-0.27610000
H	0.08204300	-1.71184100	0.41335700
N	-0.23217200	1.30724900	-0.10059000
H	-1.00903400	1.96143600	-0.02651800
N	-1.94683300	-0.32936300	0.22975800
H	-2.64710000	0.39505300	0.15371700
H	-2.22652500	-1.17884700	-0.24196000
H	1.48861600	-0.62372900	-0.33917900
N	2.43896000	-0.01178800	0.04145300
H	2.06845500	0.94364600	0.07588900
H	2.64206500	-0.27063600	1.00919700

Cartesian coordinates for **TS20-21**

C	-1.45238300	0.03423900	-0.16313400
N	-0.35201200	-0.71379900	-0.50499000
H	-0.45165100	-1.67598800	-0.18666900
N	-1.37919300	1.32950500	-0.16178000
H	-2.27186900	1.74950700	0.08842100
N	-2.60313000	-0.68962700	0.18714100
H	-3.46394400	-0.16412100	0.11924600
H	-2.68752500	-1.59774500	-0.24896200
C	1.32012600	-0.04525700	0.11051800
N	1.69086100	-1.26089700	0.66702300
H	2.10538500	-1.82232100	-0.08328700
N	1.12126400	0.96239100	1.03948600
H	0.92419100	0.56947700	1.95133400
N	1.93648100	0.39498400	-1.07805300
H	1.59273100	-0.12405600	-1.87639500
H	1.77870600	1.38435200	-1.22760900
H	0.36762600	1.58910800	0.73782700

Cartesian coordinates for **TS21-22**

C	-1.43423500	0.00364800	0.06350700
N	-0.26054500	-0.72104200	0.03505800
H	-0.32347900	-1.72252800	0.12866900

N	-1.43583200	1.26159600	0.31588400
H	-2.36817500	1.65676200	0.22887300
N	-2.55200900	-0.80491600	-0.16325600
H	-3.41354300	-0.29384400	-0.28616100
H	-2.43026400	-1.52110500	-0.86670700
C	1.04958400	-0.20822100	0.27480200
N	1.34564100	0.78875200	1.08486400
H	0.49104400	1.31711900	1.27323100
N	1.30210200	0.90165200	-1.35376700
H	2.15227300	1.43291300	-1.14161000
N	1.98531100	-1.25119900	0.11984200
H	2.87940800	-0.94830800	0.48631500
H	2.07845100	-1.51097700	-0.85565000
H	0.54951200	1.59350000	-1.26718200

Cartesian coordinates for **TS22-23**

C	1.62887900	0.28390700	-0.01309700
N	0.73257500	-0.76727500	-0.05647700
H	1.08706400	-1.69057700	-0.25495700
N	1.28210100	1.45427800	0.38326900
H	2.04847500	2.11742400	0.32403000
N	2.91405300	-0.10831900	-0.38798800
H	3.55193700	0.65557500	-0.55271100
H	2.97310800	-0.81953300	-1.10364500
C	-0.64617400	-0.79182400	0.24979400
N	-1.22709200	-1.92316200	0.02939000
H	-2.19837800	-1.86694800	0.33047700
N	-1.22999200	0.33199200	0.76792000
H	-2.32460900	0.60294000	0.28869600
N	-3.13041600	1.04551700	-0.59559800
H	-2.97833700	2.05185900	-0.69719600
H	-2.86666100	0.64061600	-1.49662700
H	-0.57742700	1.12492700	0.75814500

Cartesian coordinates for **TS23-24**

C	1.73831700	-0.42626200	0.02106800
N	1.01624000	0.69849500	0.40152300
H	1.53658700	1.41007700	0.89313000
N	1.19761000	-1.45339500	-0.52557300
H	1.90171100	-2.13216800	-0.80247500
N	3.09556500	-0.30507600	0.28646500
H	3.59537800	-1.16357800	0.45414200
H	3.42334200	0.47672400	0.83145300
C	-0.11998400	1.29707300	-0.18827000
N	-0.16369300	2.58463000	-0.05446100
H	-1.06255400	2.94379000	-0.37083600
N	-0.99904700	0.48646600	-0.85555000
H	-1.74896200	1.06350200	-1.23173700

C	-2.10741400	-0.71299000	0.23693700
N	-2.92202600	0.02997500	0.69234700
N	-1.55886400	-1.90606600	-0.01960300
H	-1.80492800	-2.62543900	0.64665500
H	-0.56659000	-1.86503100	-0.31478300

Cartesian coordinates for **TS24-25**

C	2.12851200	0.82939400	0.03367400
N	1.64054300	-0.33092000	-0.57484300
H	2.29705000	-0.77820800	-1.19958100
N	1.35495500	1.66740600	0.61273500
H	1.87298500	2.41077000	1.07225100
N	3.49334900	0.97821600	-0.18001600
H	3.91496900	1.80109300	0.22310000
H	4.06162100	0.14722600	-0.09483000
C	0.78260800	-1.31196000	-0.04347100
N	1.13544300	-2.52207400	-0.25029800
H	0.40370900	-3.17286500	0.02689900
N	-0.33576600	-0.90248800	0.69879700
H	-0.70489500	-1.67694000	1.23684900
C	-1.45999100	-0.17756000	0.18325100
N	-2.59546600	-0.71975600	0.40807700
N	-1.15586700	0.97136300	-0.48843500
H	-1.95883900	1.53097900	-0.72769900
H	-0.33185700	1.47106800	-0.13208600
H	-3.55373400	-0.11988900	0.12732500
N	-4.43940200	0.81393200	-0.29406700
H	-4.17686400	1.68163600	0.18469100
H	-4.21543400	0.97612500	-1.28129300

Cartesian coordinates for **TS25-26**

C	2.04360900	0.01087500	0.26865000
N	1.07793400	0.97662300	-0.08468000
H	1.28818300	1.86367800	0.34951900
N	2.86526200	0.37038800	1.17970300
H	3.57703400	-0.33963200	1.33516900
N	2.05422300	-1.14984700	-0.47225800
H	2.54154300	-1.92558700	-0.05400000
H	1.22135300	-1.39237100	-0.98960700
C	-0.06133600	0.92757800	-0.86580100
N	-0.62921100	1.93450200	-1.41895200
H	-0.04917500	2.76935000	-1.34454500
N	-0.62446600	-0.34485900	-1.07377100
H	-1.13622000	-0.40433100	-1.94284400
C	-1.15931200	-1.19312200	-0.07313600
N	-1.52896800	-2.36278700	-0.47233900
N	-1.15110800	-0.68592000	1.19775800
H	-1.54859300	0.48545900	1.39273300

H	-2.00708000	-2.86253400	0.27551900
N	-2.30256000	1.48875100	1.32730000
H	-2.26627200	1.82961200	0.36035600
H	-3.27500400	1.23701100	1.51491900
H	-1.61127900	-1.32059400	1.84517900

Cartesian coordinates for **TS26–27**

C	-1.43529200	0.04691400	-0.04052000
N	-0.59050900	1.09901600	-0.44573800
H	-0.91256800	1.65239100	-1.22381200
N	-2.24876900	-0.40855300	-1.00961400
H	-3.00720600	-0.93890500	-0.57377800
N	-1.82913100	0.11148800	1.30054800
H	-2.08565700	-0.79477400	1.67143600
H	-1.13727300	0.54933700	1.89571100
C	0.72544100	1.30888400	-0.06042100
N	1.25850400	2.44985700	-0.25072000
H	2.25433600	2.43781800	-0.04283800
N	1.33739800	0.17648300	0.50586400
H	2.31956500	0.30581900	0.71117500
C	1.10065700	-1.12837000	0.01972200
N	2.12318600	-1.88891200	-0.14585200
N	-0.22391700	-1.48789400	-0.05018900
H	1.85193000	-2.82229200	-0.45101100
H	-0.41529600	-2.11435400	-0.82966800

Cartesian coordinates for **TS27–28**

C	-1.15942000	-0.06128000	-0.34889900
N	-0.43916600	1.12251900	-0.54994500
H	-0.95431200	1.99036400	-0.54476300
N	-2.43142000	-0.23651200	-0.70263300
H	-2.89313700	0.66629300	-0.80828400
N	-1.57802400	-0.01443300	1.54021000
H	-2.18710100	0.79394300	1.70376200
H	-2.17936100	-0.82650600	1.70540600
C	0.87200700	1.27666400	-0.09575700
N	1.33635300	2.45274400	0.05676000
H	2.31132900	2.44289900	0.34518300
N	1.52196100	0.07128200	0.11363100
H	2.48558000	0.08137300	0.40959100
C	0.99273900	-1.20425500	-0.06494500
N	1.75026800	-2.21266500	0.11266100
N	-0.33697900	-1.19117700	-0.45832500
H	1.25432500	-3.08896000	-0.02765900
H	-0.83024200	-2.06848600	-0.51214000

Table S7. B3LYP/6–311G(d,p) cartesian coordinates for the optimized structures of BA mechanism.

Cartesian coordinates for **29**

C	0.00000000	0.00000000	0.14633200
N	0.00000000	1.16210500	-0.61336800
H	0.20664700	1.98663400	-0.07038200
H	0.44978200	1.13290600	-1.51633700
N	0.00000000	-1.16210500	-0.61336800
H	-0.20664700	-1.98663400	-0.07038200
H	-0.44978200	-1.13290600	-1.51633700
O	0.00000000	0.00000000	1.36032500

Cartesian coordinates for **30**

C	0.05356900	0.07936500	0.01555300
N	-1.26937400	-0.23785200	0.05611900
H	-1.93991600	0.50713500	-0.04273200
H	-1.55395000	-1.18089700	-0.15119300
N	0.90474700	-1.02311100	-0.06954200
H	1.77175500	-0.75912000	0.40707500
O	0.49413600	1.22292900	-0.02656200

Cartesian coordinates for **31**

C	-1.27124200	-0.03304600	-0.13589700
C	0.00011600	-0.00060900	-0.96454200
C	1.27130400	0.03287600	-0.13582600
H	0.04477600	-0.88936200	-1.59490400
H	-0.04448400	0.88741600	-1.59593300
O	-2.21284700	0.69833400	-0.27608800
O	2.21314900	-0.69827900	-0.27532700
O	1.22913600	1.02750600	0.77946100
H	2.06359700	0.99336700	1.27077700
O	-1.22956200	-1.02690300	0.78021000
H	-2.06396500	-0.99202500	1.27160000

Cartesian coordinates for **32**

C	2.39558800	-0.01130100	-0.30733800
N	2.10399300	-1.34672500	-0.48735900
H	2.88609000	-1.87835300	-0.83777600
H	1.52699400	-1.78992700	0.21518700
N	1.43573800	0.71872000	0.39716400
O	3.39411700	0.52974600	-0.73806700
C	0.05895300	0.37188300	0.65676100
C	-0.76785200	0.25969000	-0.73076400
C	-2.24451100	-0.01964400	-0.59568800
H	-0.64131900	1.17798300	-1.29650500
H	-0.27000100	-0.56857400	-1.24489600
O	0.04628200	-0.85625300	1.34082900
O	-3.11580100	0.55125500	-1.18778400
O	-2.50124400	-1.04187900	0.27370900
H	-3.46420600	-1.14270500	0.32058000
H	1.62631300	1.70979300	0.41345000
O	-0.60063500	1.37051000	1.25115700

H -0.87680700 -1.14297800 1.40474200

Cartesian coordinates for **33**

C -2.06620200 -0.32998500 0.02803400
N -1.39086400 -1.50548100 0.23405000
H -2.00247800 -2.30151900 0.33541100
H -0.52491100 -1.66615300 -0.26490500
N -1.26606100 0.80347400 -0.26171100
O -3.27031500 -0.21581900 0.07679100
C 0.03443800 1.20129200 0.02369600
C 0.92742100 0.32056900 0.90253700
C 1.97494600 -0.42085200 0.09835700
H 1.45793300 0.99179800 1.57423700
H 0.35155800 -0.40447100 1.47920600
O 0.44000100 2.26804200 -0.38036800
O 3.16051300 -0.36378700 0.24838500
O 1.39442700 -1.21729100 -0.85049700
H 2.11037200 -1.65487300 -1.33583500
H -1.81462700 1.55396200 -0.66472100

Cartesian coordinates for **34**

C -1.86729100 -0.41300700 0.06733300
N -1.22576000 -1.35138900 0.84799400
H -1.48776700 -2.27423300 0.49320900
N -1.25603000 0.81226100 -0.14409200
O -3.01456200 -0.61795500 -0.31016100
C 0.02896300 1.31402200 0.10613800
C 1.04452300 0.45657100 0.84376500
C 1.82537200 -0.49704900 -0.04319500
H 1.76327800 1.13244000 1.30194500
H 0.56303400 -0.14806200 1.61585300
O 0.29665800 2.43183500 -0.26651700
O 2.97854000 -0.78569800 0.11146600
O 1.05849500 -1.02149700 -1.03261100
H 1.62749600 -1.61894500 -1.54181400
H -1.83596500 1.46599600 -0.65816900

Cartesian coordinates for **35**

C -0.77337100 -1.33076800 -0.10412500
N 0.58764500 -1.09712500 -0.28909800
H 1.15826200 -1.92890600 -0.19548600
N -1.54293100 -0.17900500 0.00119300
O -1.24327400 -2.44335400 -0.07529600
C -1.11718500 1.14720100 -0.05366900
C 0.34719300 1.34069900 -0.39080600
C 1.24242500 0.18559400 0.04463800
H 0.43656200 1.46015400 -1.47466600
H 0.68907300 2.26180200 0.07930800
O -1.89212000 2.05718600 0.11077600

O	1.36639700	0.02119500	1.38522900
H	-2.52899800	-0.33082100	0.17151500
O	2.46925200	0.29891300	-0.61204300
H	3.13569800	-0.05720100	-0.01088900

Cartesian coordinates for **36**

C	0.00021900	-1.42792300	0.00000400
N	1.17155700	-0.67544400	0.00003100
H	2.02887600	-1.21401800	0.00000600
N	-1.17136800	-0.67578500	-0.00006300
O	0.00043300	-2.63362800	-0.00000600
C	-1.30166300	0.70717800	-0.00001200
C	-0.00022200	1.48591000	-0.00012600
C	1.30143700	0.70753100	0.00000300
H	-0.00029600	2.14661700	-0.87108300
H	-0.00030200	2.14686400	0.87064600
O	-2.38489300	1.23880100	0.00010700
O	2.38450100	1.23951900	0.00006900
H	-2.02855000	-1.21457800	0.00007900

Table S8. B3LYP/6-311G(d,p) cartesian coordinates of the optimized transition states for BA mechanism.

Cartesian coordinates for **TS29-30**

N	-1.93367300	-0.25793200	0.26111100
H	-2.27120500	-1.14815000	-0.07319200
C	-0.63521900	0.11155400	-0.06219300
N	0.21798400	-0.96270400	-0.31993100
H	0.05446200	-1.74557900	0.31129400
O	-0.29474000	1.28039500	-0.12869100
H	-2.59694100	0.50031300	0.19477600
H	1.49106100	-0.60567600	-0.35441600
N	2.40722300	-0.00238400	0.07941300
H	2.04348300	0.95229500	0.14578600
H	2.60763700	-0.30454400	1.03428700

Cartesian coordinates for **TS30-32**

C	2.50603400	-0.39185700	-0.08590900
N	2.08498500	-1.24909600	0.88086500
H	2.79210000	-1.86058700	1.25776900
H	1.34781800	-0.92377500	1.49431300
N	1.53987800	0.50305300	-0.58905100
O	3.59768800	-0.40999300	-0.62994100
C	-0.14072500	0.77237900	0.06450700
C	-0.91150700	-0.39117300	-0.53918500
C	-2.34563300	-0.42735500	-0.04852900
H	-0.90944700	-0.30918100	-1.62699400
H	-0.42635000	-1.33358300	-0.28082000
O	0.20241600	0.79779000	1.28259500
O	-2.84945600	0.31034800	0.75439500

O	-3.01606800	-1.44012400	-0.64667800
H	-3.91939900	-1.41967100	-0.29642100
H	1.95843900	1.40911800	-0.79536200
O	-0.49927000	1.94752800	-0.54198500
H	-0.34869400	2.64363000	0.11242200

Cartesian coordinates for **TS32-33**

C	-2.40364300	-0.32508900	-0.02558600
N	-2.00153100	-0.53393800	-1.32665300
H	-2.75835100	-0.81293300	-1.93340400
H	-1.35771600	0.14802900	-1.70939800
N	-1.40716800	0.21676600	0.81255400
O	-3.50540100	-0.57775400	0.40466300
C	-0.04134100	0.39297200	0.59564100
C	0.72483900	-0.83652200	0.09305100
C	2.21555300	-0.61378700	-0.03918200
H	0.59046000	-1.61924100	0.84169400
H	0.31104400	-1.20054700	-0.84715200
O	0.03434800	1.59992600	-0.82616400
O	3.06208800	-1.22843900	0.54483700
O	2.52190700	0.35708700	-0.94862200
H	3.48713000	0.44749300	-0.94695600
H	-1.77412800	0.76945300	1.57600500
O	0.56151400	1.24479500	1.30934900
H	0.99434900	1.61759200	-0.99815000

Cartesian coordinates for **TS33-34**

C	1.45320900	-0.21596600	-0.81416200
N	1.11724600	1.08839000	-0.51548400
H	1.66500900	1.69981700	-1.11736200
N	0.88265100	-1.19948100	0.01229600
O	2.18329900	-0.54335800	-1.73264400
C	-0.30547600	-1.27746300	0.75049500
C	-1.16131900	-0.03852900	0.96999200
C	-1.77243000	0.61810800	-0.25459700
H	-1.98961400	-0.37597200	1.59690000
H	-0.62686500	0.73214000	1.52521800
O	-0.62023500	-2.34716500	1.22276000
O	-2.28007000	1.70611300	-0.25524400
O	-1.74443400	-0.18959300	-1.33866000
H	-2.17616500	0.29265000	-2.05979500
H	1.25902600	-2.12081000	-0.17845100
H	1.21382400	1.43888500	0.71369300
N	1.76151700	1.71758400	1.76003600
H	2.43182800	0.98608200	2.00323100
H	2.30068400	2.57688900	1.63857100

Cartesian coordinates for **TS34-35**

C	0.93994100	-1.22657600	-0.09520000
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N	-0.32609200	-1.26867900	-0.61996000
H	-0.79169300	-2.14806900	-0.40706700
N	1.49484800	0.03441600	0.06575600
O	1.58269800	-2.24628600	0.09976000
C	0.88078900	1.27227900	-0.10771000
C	-0.56461900	1.25394400	-0.57211300
C	-1.40290100	0.11252100	0.01863800
H	-1.01434500	2.20162600	-0.27378900
H	-0.60033800	1.16467400	-1.65842900
O	1.48901500	2.29766600	0.07959200
O	-1.24171700	0.06975300	1.38603900
H	2.45551200	0.05808600	0.38362500
O	-2.49878600	-0.20790100	-0.48637200
H	-1.99936200	-0.41533500	1.74124100

Cartesian coordinates for **TS35–36**

C	0.88353300	1.29451000	0.03953200
N	-0.46226500	1.17709200	0.37356500
H	-0.97737000	2.04726700	0.39549500
N	1.54598000	0.07947800	-0.10617000
O	1.42914900	2.36043300	-0.10974800
C	1.03369700	-1.20178300	0.07779100
C	-0.38728900	-1.24837400	0.60342100
C	-1.20392100	-0.00267200	0.33549500
H	-0.89512500	-2.11684600	0.19243400
H	-0.33412200	-1.36993200	1.69160500
O	1.70219400	-2.18405700	-0.12823100
O	-2.43902600	0.05403700	0.59893400
H	2.51235600	0.14662700	-0.39949000
O	-1.64328600	-0.34766400	-1.41649000
H	-2.24011300	0.38481600	-1.64497100

Table S9. B3LYP/6–311G(d,p) cartesian coordinates of the optimized transition states for TAP mechanism.

Cartesian coordinates for **37**

C	1.22216800	0.02458000	0.00000000
C	-0.00000600	0.83197900	0.00000000
H	-0.00004000	1.48247300	0.88073600
H	-0.00003900	1.48247300	-0.88073700
C	-1.22215200	0.02455900	0.00000000
N	2.19534800	-0.58940400	0.00000000
N	-2.19534500	-0.58940400	0.00000000

Cartesian coordinates for **20b**

C	0.11181300	0.00021200	0.00428300
N	0.81627400	1.13252100	0.01127000
N	0.82221300	-1.12825400	0.01125900
H	0.19345100	-1.93490800	-0.05192200
N	-1.28657700	-0.00325800	-0.07656300

H	-1.75338900	-0.84461800	0.22791600
H	-1.75754100	0.83542300	0.22891800
H	1.81386770	1.10037021	0.07269585

Cartesian coordinates for **38**

C	0.41824800	1.20984600	0.02927700
C	1.39463300	0.31820100	0.80201300
H	2.18874700	0.96066400	1.18608700
H	0.88033900	-0.14528200	1.64718600
C	1.97446900	-0.73664700	-0.02322800
N	0.71461700	2.43122900	-0.07826400
N	2.39918600	-1.58595600	-0.67677400
N	-0.72979900	0.67524500	-0.57264800
H	-1.29010200	1.39914500	-1.00824300
C	-1.59284300	-0.32473500	-0.05435400
N	-2.83572800	-0.05401600	-0.02785300
H	-3.39578100	-0.86768400	0.21920900
N	-0.94582800	-1.48245800	0.35850300
H	-1.56554000	-2.22157700	0.65650900
H	-0.20185200	-1.81355700	-0.24372900

Cartesian coordinates for **39**

C	0.47890400	1.15515100	0.04537300
C	1.31378900	0.15317800	0.85179800
H	2.10790200	0.70480300	1.35834300
H	0.70158000	-0.34000000	1.60993500
C	1.91539900	-0.88318900	0.01683500
N	0.85137800	2.34422600	-0.21471400
N	2.36293000	-1.70684300	-0.65433700
N	-0.75850300	0.75199300	-0.44996100
H	-1.26529600	1.53836100	-0.83856200
C	-1.64301300	-0.27041200	-0.05341200
N	-2.87915600	0.03073700	0.02167600
H	-3.45551300	-0.79373500	0.17874600
N	-1.04086000	-1.49767100	0.21115100
H	-1.69249300	-2.23937800	0.42185400
H	-0.31957300	-1.78805800	-0.43760400
H	1.78239600	2.53255400	0.14701800

Cartesian coordinates for **40**

C	0.70913700	1.09373200	0.07371900
C	1.46516200	-0.07936900	0.69922500
H	2.47949200	0.25498500	0.92624200
H	0.97747300	-0.38573800	1.62627100
C	1.53720900	-1.24730900	-0.17623200
N	1.21738700	2.23147000	-0.18284600
N	1.60780200	-2.16150500	-0.87413600
N	-0.62370100	0.90785600	-0.28077900
H	-1.01170700	1.68417600	-0.80008200

C	-1.53963400	-0.08039200	0.05092500
N	-2.74510000	0.09465600	-0.51700900
H	-3.32238400	-0.72983100	-0.34358300
N	-1.23063300	-0.99709900	0.95364000
H	2.20629400	2.25702600	0.05190500
H	-1.94069500	-1.72824100	0.96133400

Cartesian coordinates for **41**

C	-1.27343100	0.65543100	-0.00089000
C	-1.22006600	-0.80986300	-0.39012500
H	-2.05719600	-1.34984500	0.04841400
H	-1.30599900	-0.87385900	-1.48103200
C	0.07993600	-1.48684800	0.00343400
N	-2.31975600	1.34029800	0.23134500
N	0.12120900	-2.69807500	0.34681000
N	-0.04277200	1.28825700	0.01696100
H	-0.04774700	2.28760300	0.17046100
C	1.21703700	0.71140300	-0.02440600
N	2.24297600	1.46347200	0.02333800
H	3.11121300	0.93549400	-0.00667900
N	1.21752300	-0.68608400	-0.11662100
H	2.10134600	-1.14064600	0.06136600
H	-3.15674100	0.76544700	0.16655800

Cartesian coordinates for **42**

C	-1.46133400	-0.10134400	0.00342700
C	-0.61288600	-1.29908000	-0.36799000
H	-1.00551400	-2.20578400	0.08812000
H	-0.67587700	-1.42298400	-1.45641600
C	0.85047800	-1.18324800	-0.01156800
N	-2.71090700	-0.09330900	0.24396600
N	1.52441900	-2.23325300	0.23218400
N	-0.78001000	1.10509100	-0.00762800
H	-1.32967800	1.94263100	0.12746300
C	0.58975800	1.29943600	-0.02409100
N	1.04941300	2.48791700	0.00403800
H	2.06594400	2.50598800	-0.00864800
N	1.34550000	0.12006500	-0.05183400
H	2.33838900	0.24050200	0.08676700
H	-3.09407300	-1.03471400	0.19149700
H	2.50580700	-2.02580700	0.42747200

Cartesian coordinates for **43**

C	-1.45868100	-0.10450800	-0.00357700
C	-0.59219000	-1.30226900	0.32566800
H	-0.68334800	-1.49404200	1.40219000
H	-0.95252600	-2.19303300	-0.18766000
C	0.88001900	-1.10719700	0.01905400
N	-2.71332700	-0.08828400	-0.20851100

N	1.60856300	-2.15859500	-0.20253000
N	-0.76373100	1.09535700	-0.01017600
H	-1.30443300	1.94204500	-0.12442700
C	0.61318500	1.22493000	0.01374700
N	1.10532600	2.44007900	0.03479000
H	2.12228600	2.35386200	0.00750800
N	1.43282900	0.14054800	-0.00492300
H	-3.10055000	-1.02831400	-0.15466500
H	2.57695700	-1.84999300	-0.33284500

Cartesian coordinates for **44**

C	1.02894600	-1.03992500	0.01676000
C	1.39185900	0.35524600	0.46723300
H	1.40676200	0.35415600	1.56534300
H	2.38590200	0.63134300	0.12015000
C	0.38192200	1.40249900	0.01966400
N	1.79107700	-2.00886800	-0.28908200
N	0.80397300	2.56155800	-0.29492900
N	-0.35104100	-1.25625200	-0.01033300
H	-0.63699200	-2.16897000	-0.33878600
C	-1.26396300	-0.21604300	0.01606500
N	-2.57758100	-0.61012700	-0.05242000
H	-3.22866400	0.14736400	0.09100000
N	-0.96613300	1.04035900	0.04663900
H	2.76815300	-1.73088600	-0.22039800
H	-0.00001500	3.15131000	-0.52380200
H	-2.82979300	-1.48167500	0.38902900

Cartesian coordinates for **45**

C	1.32277400	-0.14113500	-0.00789400
C	0.74132200	1.19926400	-0.37194100
H	1.27805500	2.02851600	0.09062800
H	0.83756200	1.31537400	-1.45958400
C	-0.73547800	1.27591000	-0.00986600
N	2.66094700	-0.22350700	0.14107100
N	-1.22611700	2.42706800	0.24245000
N	0.59967900	-1.20816400	0.12043000
C	-0.77765400	-1.02427300	-0.00668100
N	-1.45156400	-2.19962900	-0.08681300
H	-2.45501400	-2.17127700	-0.01989800
N	-1.45322600	0.09239600	-0.02801800
H	3.24243800	0.59530200	0.11129200
H	-2.22825200	2.31614000	0.41614100
H	-0.95648300	-3.04651000	0.13307700
H	3.06788500	-1.11328600	0.38280200

Cartesian coordinates for **46**

C	1.18796900	-0.65263700	0.00000000
C	0.00070000	-1.39459200	0.00000000

H	0.00101200	-2.47729600	0.00000000
C	-1.18740200	-0.65346700	0.00000000
N	2.41199000	-1.25469100	0.00000000
N	-2.41066900	-1.25702600	0.00000000
N	1.20194600	0.68993200	0.00000000
C	-0.00056300	1.28131800	0.00000000
N	-0.00132300	2.64327000	0.00000100
H	-0.87702700	3.13300600	-0.00000100
N	-1.20265500	0.68908400	0.00000000
H	2.51108400	-2.25273700	-0.00000100
H	-3.22744800	-0.67186400	0.00000000
H	0.87353500	3.13448000	-0.00000100
H	3.22772700	-0.66807800	0.00000000
H	-2.50813100	-2.25522700	0.00000000

Table S10. B3LYP/6-311G(d,p) cartesian coordinates of the optimized transition states for TAP mechanism.

Cartesian coordinates for **TS37-38**

C	0.64170700	1.34965100	0.14301200
C	1.58756700	0.39036400	0.77568700
H	2.43750200	0.95846100	1.16234800
H	1.07663100	-0.07634300	1.62383300
C	2.06764500	-0.67270500	-0.10313500
N	0.30297300	2.47094800	0.01633600
N	2.46035200	-1.54612900	-0.74260900
N	-0.64159200	0.24374400	-0.85723900
H	-1.09779600	0.97557200	-1.40306200
C	-1.61473600	-0.37753000	-0.09993500
N	-2.84668400	0.00764700	-0.20198300
H	-3.47961600	-0.61898100	0.29891100
N	-1.11322000	-1.38812300	0.72203100
H	-1.80831600	-1.97675800	1.15745400
H	-0.35430600	-1.91723900	0.31099300

Cartesian coordinates for **TS38-39**

C	-0.49268900	-0.63281500	-0.12961500
C	-0.82958100	0.61440800	0.69343200
H	-1.86855300	0.52523700	1.02052300
H	-0.17643900	0.66667900	1.56767500
C	-0.66740000	1.84677900	-0.06935900
N	-1.35578400	-1.51285200	-0.44571200
N	-0.50780300	2.81486500	-0.67550700
N	0.81383100	-0.82459300	-0.58839900
H	0.90614400	-1.72239200	-1.05016500
C	2.04694800	-0.47246100	0.01211200
N	2.93287600	-1.38569500	0.07570500
H	3.82925500	-1.01828100	0.38933100
N	2.12867300	0.84019200	0.45661100

H	3.03825700	1.10568200	0.80440000
H	1.71550100	1.54373100	-0.14319300
H	-2.43295400	-1.20344300	-0.05458500
N	-3.61787500	-0.76406700	0.36373500
H	-4.07518600	-0.55263200	-0.52962400
H	-4.03711500	-1.65499700	0.65118700

Cartesian coordinates for **TS39-40**

C	-0.49268900	-0.63281500	-0.12961500
C	-0.82958100	0.61440800	0.69343200
H	-1.86855300	0.52523700	1.02052300
H	-0.17643900	0.66667900	1.56767500
C	-0.66740000	1.84677900	-0.06935900
N	-1.35578400	-1.51285200	-0.44571200
N	-0.50780300	2.81486500	-0.67550700
N	0.81383100	-0.82459300	-0.58839900
H	0.90614400	-1.72239200	-1.05016500
C	2.04694800	-0.47246100	0.01211200
N	2.93287600	-1.38569500	0.07570500
H	3.82925500	-1.01828100	0.38933100
N	2.12867300	0.84019200	0.45661100
H	3.03825700	1.10568200	0.80440000
H	1.71550100	1.54373100	-0.14319300
H	-2.43295400	-1.20344300	-0.05458500
N	-3.61787500	-0.76406700	0.36373500
H	-4.07518600	-0.55263200	-0.52962400
H	-4.03711500	-1.65499700	0.65118700

Cartesian coordinates for **TS40-41**

C	-1.22229500	-0.70776900	0.01531000
C	-1.35203900	0.75030500	0.45633900
H	-2.32364500	1.12580000	0.13168000
H	-1.30188500	0.79579900	1.54770000
C	-0.29511700	1.63150300	-0.07792600
N	-2.20537300	-1.48315300	-0.21227700
N	0.11989500	2.53930700	-0.70068500
N	0.05722200	-1.21829100	-0.13177600
H	0.10080100	-2.17261100	-0.46389900
C	1.28326700	-0.59732300	0.06007600
N	2.34968300	-1.27497000	-0.22804600
H	3.18655800	-0.70327100	-0.12718600
N	1.23393600	0.62477000	0.67630000
H	-3.09338300	-1.00083800	-0.09871500
H	2.06112000	1.18118600	0.46301300

Cartesian coordinates for **TS41-42**

C	-1.25500500	-0.65273100	0.02426900
C	-1.32963300	0.80570000	0.45926800
H	-2.29609400	1.18740700	0.13336700

H	-1.27513400	0.85617200	1.55004000
C	-0.24257400	1.64193000	-0.08422800
N	-2.35891700	-1.24975900	-0.18269800
N	0.21543100	2.52697600	-0.71094500
N	0.00743900	-1.22136900	-0.10185100
H	0.05669000	-2.17026000	-0.44723100
C	1.26149700	-0.63335200	0.06714300
N	2.29296200	-1.35263500	-0.23506900
H	3.15556900	-0.81923500	-0.14340700
N	1.25494400	0.59467000	0.67232000
H	2.09767400	1.12285400	0.44860700
H	-2.22742400	-2.23141600	-0.43238000

Cartesian coordinates for **TS42-43**

C	-0.58751400	1.45307800	0.02274800
C	0.68124600	0.74282400	0.43836000
H	1.53055300	1.28151500	0.02983800
H	0.74684800	0.79455100	1.53240000
C	0.74377900	-0.72189600	0.05581300
N	-0.54864600	2.70428200	-0.20426000
N	1.76960600	-1.41685600	-0.20176700
N	-1.71264100	0.64297100	-0.00958000
H	-2.62073300	1.05903900	-0.16343700
C	-1.74716900	-0.74984400	0.00203300
N	-2.88126200	-1.32567700	-0.07236000
H	-2.79886600	-2.33896500	-0.06311200
N	-0.50069100	-1.36201900	0.08255700
H	-0.47020900	-2.35821500	-0.08277300
H	-1.46885900	3.07940900	-0.44148100
H	2.83464500	-0.90723800	-0.17094400
N	3.89052500	-0.09833400	-0.11517800
H	3.76406000	0.59174600	-0.86227000
H	3.82228000	0.44261300	0.75217300

Cartesian coordinates for **TS43-44**

C	0.17090900	1.40226100	0.01532300
C	1.58187700	0.97403100	0.39166600
H	2.29557500	1.67758200	-0.03377500
H	1.66565800	1.03831600	1.48434400
C	1.91873300	-0.44132800	-0.00342700
N	-0.01440800	2.64853100	-0.21784700
N	3.05979600	-0.93461100	-0.28186200
N	-0.81219800	0.43626300	0.01894200
H	-2.37287900	0.52102000	-0.02978400
C	-0.51083700	-0.88149000	0.03575500
N	-1.48140200	-1.77081900	0.04499200
H	-1.15359200	-2.72882900	0.06438400
N	0.82047600	-1.29075900	0.01558800

H	1.02726500	-2.25986300	-0.18211700
N	-3.36103800	-0.01395200	-0.03485500
H	-3.92733900	0.18066700	0.78494500
H	-3.89666400	0.13259700	-0.88478300
H	-2.85415100	-1.00397900	0.00226400
H	3.77677600	-0.21309600	-0.23539900
H	-1.00330500	2.81217700	-0.42068700

Cartesian coordinates for **TS44-45**

C	-0.52527000	-0.94634000	-0.20931400
C	0.90389400	-1.37736100	-0.45526400
H	1.10244300	-2.37109800	-0.05474500
H	1.04451000	-1.42445700	-1.54364900
C	1.91105200	-0.38313800	0.09898700
N	-1.51372100	-1.79269400	-0.09330800
N	3.02921500	-0.82873500	0.52799100
N	-0.77864700	0.38782600	-0.15065200
H	-2.27796100	0.53399900	0.19999500
C	0.29496100	1.24150300	-0.10023300
N	-0.05282000	2.57590900	-0.12217500
H	0.72873900	3.19599300	-0.27101300
N	1.56298500	0.95610900	0.03813500
H	-1.20422300	-2.75608000	-0.15441400
H	3.59881600	-0.02825000	0.81526300
H	-0.89780900	2.80694800	-0.62035100
H	-2.84334400	-0.96911900	0.24712600
N	-3.27037300	0.03735400	0.41056900
H	-3.99685100	0.27406900	-0.25836100
H	-3.59861300	0.17963100	1.36117300

Cartesian coordinates for **TS45-46**

C	-0.39865600	1.32534000	0.15388200
C	0.78887900	0.58970100	0.46481300
H	1.92049800	0.56388100	-0.53626200
H	1.43067700	1.01571600	1.23542900
C	0.63664100	-0.87794500	0.49623500
N	-0.38379000	2.69421500	0.17923000
N	1.70636400	-1.60715100	0.70210800
N	-1.53462700	0.76024800	-0.22201600
C	-1.55070800	-0.60309300	-0.15099400
N	-2.74209600	-1.16343100	-0.51649400
H	-2.87724000	-2.13122000	-0.27523600
N	-0.58129600	-1.43060700	0.19738600
H	0.33839400	3.15871700	0.70451000
H	1.44610100	-2.59112800	0.65011200
H	-3.54125500	-0.55286000	-0.54689500
H	-1.28855000	3.13865700	0.15258800
H	2.85041400	-0.79130900	-0.29820500

N	2.97701600	0.05882400	-0.94349000
H	3.79886100	0.61114700	-0.72493700
H	2.97416700	-0.21030900	-1.92179500