Thermal Science and Engineering 2024, 7(1), 5949.
https://doi.org/10.24294/tse.v7i1.5949

Article

Theoretical investigation on diastereoselective [2+2] cycloaddition and Pd-catalyzed enantioselective [3+2] cycloaddition for synthesis of cis-β-lactam and exo-furobenzopyranone

Supplementary materials

Software: GAUSSIAN09
Level of Theory: B3LYP
Basis Set: 6-31G(d)
Geometry [Cartesian coordinates]:

Table S1. Optimized Cartesian coordinates for ts-1i1.

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	**Number**	**Type**	**X**	**Y**	**Z**
1	6	0	1.762035	–3.155761	0.183039
2	6	0	1.839284	–2.131029	1.315591
3	6	0	0.646570	–1.175029	1.245129
4	6	0	0.592238	–0.431941	–0.092488
5	6	0	0.638522	–1.407606	–1.274290
6	6	0	1.750541	–2.458927	–1.178228
7	6	0	1.904420	0.624187	–0.308101
8	6	0	1.260077	1.560966	0.458452
9	6	0	–0.158530	1.763137	0.105629
10	7	0	–0.545528	0.484173	–0.203198
11	8	0	–0.833961	2.768682	0.138013
12	8	0	2.908974	0.322404	–0.893227
13	7	0	1.970730	3.578186	0.086165
14	7	0	2.385357	4.581322	0.251416
15	6	0	–1.931872	0.083876	–0.303493
16	1	0	0.846288	–3.752309	0.303837
17	1	0	2.605179	–3.851981	0.238015
18	1	0	2.775011	–1.562415	1.235935
19	1	0	1.848802	–2.629820	2.290116
20	1	0	0.652601	–0.454756	2.067536
21	1	0	–0.279137	–1.765755	1.326516
22	1	0	0.707416	–0.844968	–2.210723
23	1	0	–0.337020	–1.918298	–1.271711
24	1	0	1.608110	–3.192181	–1.979366
25	1	0	2.715121	–1.974310	–1.347752
26	1	0	–2.530695	0.982402	–0.142304
27	1	0	–2.188136	–0.662810	0.456741
28	1	0	–2.158245	–0.319538	–1.294891

Table S2. Optimized Cartesian coordinates for ts-zi2i3.

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	**Number**	**Type**	**X**	**Y**	**Z**
1	7	0	–1.422153	–4.167029	3.158477
2	6	0	–1.732950	–3.147909	4.177746
3	6	0	–1.225950	–2.137336	3.125899
4	6	0	–0.891842	–3.288841	2.243841
5	6	0	–0.873103	–3.259616	5.434431
6	6	0	–1.145775	–2.098722	6.395856
7	6	0	–2.633077	–2.015011	6.747972
8	6	0	–3.489527	–1.899421	5.485126
9	6	0	–3.216580	–3.060063	4.523806
10	8	0	–0.365191	–3.489828	1.172671
11	6	0	–1.123053	–0.823331	3.205034
12	6	0	–0.472792	–0.813057	–0.144585
13	6	0	–0.090534	–0.232061	–1.462824
14	8	0	–1.149563	0.282672	3.587973
15	6	0	–1.284752	–5.593714	3.255202
16	6	0	1.244943	–0.041773	–1.805455
17	6	0	1.603599	0.533283	–3.024670
18	6	0	0.604009	0.929019	–3.914732
19	6	0	–0.741695	0.726838	–3.585903
20	6	0	–1.080918	0.141735	–2.379067
21	8	0	0.834758	1.507915	–5.120897
22	6	0	2.177254	1.716891	–5.499464
23	6	0	0.233388	1.098356	1.077017
24	6	0	–0.709941	2.136328	0.503980
25	6	0	–1.965687	2.330256	1.085799
26	6	0	–2.849936	3.266060	0.559096
27	6	0	–2.489005	4.021556	–0.555230
28	6	0	–1.239417	3.835026	–1.138758
29	6	0	–0.356116	2.896138	–0.611238
30	1	0	0.183069	–3.296859	5.145444
31	1	0	–1.114089	–4.209118	5.936425
32	1	0	–0.830964	–1.157331	5.925638
33	1	0	–0.541786	–2.215608	7.301871
34	1	0	–2.818344	–1.163585	7.411279
35	1	0	–2.924669	–2.919375	7.300700
36	1	0	–3.263344	–0.950731	4.979349
37	1	0	–4.553395	–1.871407	5.743125
38	1	0	–3.516008	–4.006302	4.999168
39	1	0	–3.792419	–2.957718	3.598399
40	1	0	–0.917180	–1.808904	–0.141772

Table S2. (*Continued*).

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	**Number**	**Type**	**X**	**Y**	**Z**
41	1	0	–0.901412	–5.945725	2.294701
42	1	0	–2.250095	–6.073146	3.448449
43	1	0	–0.579294	–5.883736	4.044141
44	1	0	2.024969	–0.353431	–1.115517
45	1	0	2.652585	0.661392	–3.264485
46	1	0	–1.497842	1.041229	–4.297444
47	1	0	–2.128127	0.001081	–2.125321
48	1	0	2.725792	0.769311	–5.564513
49	1	0	2.691093	2.384143	–4.796475
50	1	0	2.144313	2.184433	–6.483503
51	1	0	1.202537	1.159957	0.572272
52	1	0	0.398961	1.303008	2.139045
53	1	0	–2.241471	1.744166	1.958239
54	1	0	–3.822408	3.409155	1.021027
55	1	0	–3.180350	4.751050	–0.966368
56	1	0	–0.952525	4.413510	–2.011882
57	1	0	0.609474	2.733535	–1.085740
58	7	0	–0.316932	–0.264956	0.993195

Table S3. Optimized Cartesian coordinates for ts-zi3c3.

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	**Number**	**Type**	**X**	**Y**	**Z**
1	7	0	2.611161	–2.351340	–0.214033
2	6	0	3.221946	–1.052516	0.161315
3	6	0	1.873449	–0.439291	–0.224331
4	6	0	1.463080	–1.783876	–0.721168
5	6	0	4.411409	–0.676424	–0.727220
6	6	0	5.014526	0.682368	–0.355615
7	6	0	5.352019	0.753485	1.135018
8	6	0	4.120296	0.430673	1.983199
9	6	0	3.584370	–0.961324	1.642256
10	8	0	0.556039	–2.271425	–1.369003
11	6	0	1.463072	0.832056	–0.725173
12	6	0	–0.358582	0.070775	0.403128
13	6	0	–1.590162	–0.677178	0.451212
14	8	0	2.069918	1.831683	–1.098208
15	6	0	3.216925	–3.609647	–0.554014
16	6	0	–2.125433	–1.303790	–0.684553
17	6	0	–3.329734	–1.988246	–0.616519
18	6	0	–4.014051	–2.063818	0.603542

Table S3. (*Continued*).

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	**Number**	**Type**	**X**	**Y**	**Z**
19	6	0	–3.475725	–1.464767	1.754018
20	6	0	–2.275645	–0.792059	1.676708
21	8	0	–5.188926	–2.701666	0.776584
22	6	0	–5.765140	–3.348513	–0.341957
23	6	0	–0.805688	1.559093	–1.578295
24	6	0	–1.447195	2.702222	–0.829765
25	6	0	–0.645500	3.745614	–0.358548
26	6	0	–1.216097	4.789016	0.361372
27	6	0	–2.587362	4.795871	0.617938
28	6	0	–3.385407	3.753073	0.158327
29	6	0	–2.814427	2.704992	–0.561704
30	1	0	4.096293	–0.687756	–1.777373
31	1	0	5.176908	–1.458653	–0.605411
32	1	0	4.290256	1.465116	–0.604740
33	1	0	5.911999	0.859633	–0.958943
34	1	0	5.737907	1.747501	1.386124
35	1	0	6.148188	0.032454	1.371595
36	1	0	3.338251	1.175897	1.778036
37	1	0	4.355339	0.494101	3.051369
38	1	0	4.355443	–1.714807	1.862878
39	1	0	2.700326	–1.212316	2.238880
40	1	0	0.126279	0.295399	1.346545
41	1	0	2.425790	–4.256465	–0.940847
42	1	0	3.663520	–4.083068	0.326563
43	1	0	3.989442	–3.501512	–1.326768
44	1	0	–1.546621	–1.304805	–1.601239
45	1	0	–3.713319	–2.478564	–1.502837
46	1	0	–4.023972	–1.553458	2.685358
47	1	0	–1.858409	–0.327961	2.566498
48	1	0	–5.107932	–4.138380	–0.722664
49	1	0	–5.979940	–2.633168	–1.143883
50	1	0	–6.696473	–3.787480	0.013715
51	1	0	–1.559286	0.924505	–2.047981
52	1	0	–0.127203	1.930883	–2.350188
53	1	0	0.423972	3.715217	–0.558026
54	1	0	–0.591851	5.601198	0.721548
55	1	0	–3.031979	5.613449	1.177434
56	1	0	–4.452038	3.752128	0.361456
57	1	0	–3.432492	1.881662	–0.913559
58	7	0	0.043048	0.756900	–0.689792

Table S4. Optimized Cartesian coordinates for ts-ei2i3.

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	**Number**	**Type**	**X**	**Y**	**Z**
1	7	0	–0.745492	–2.156551	0.498384
2	6	0	0.654696	–2.277361	0.957712
3	6	0	0.378359	–0.972857	1.725231
4	6	0	–0.963960	–0.933012	1.088935
5	6	0	1.675517	–2.143562	–0.169216
6	6	0	3.100669	–2.115668	0.388630
7	6	0	3.378298	–3.356820	1.241923
8	6	0	2.346265	–3.497612	2.364166
9	6	0	0.918277	–3.514952	1.809322
10	8	0	–1.926814	–0.194582	1.018710
11	6	0	1.177191	–0.276232	2.528895
12	6	0	–1.391815	1.280057	3.234373
13	8	0	2.143470	–0.002565	3.138107
14	6	0	–1.393402	–2.718130	–0.655620
15	6	0	0.191589	2.585251	2.074009
16	6	0	0.777829	2.181776	0.738723
17	6	0	–0.061902	1.912831	–0.343160
18	6	0	0.470062	1.490884	–1.557935
19	6	0	1.847910	1.333724	–1.701656
20	6	0	2.690707	1.595354	–0.623911
21	6	0	2.155928	2.022114	0.589076
22	1	0	1.458395	–1.234337	–0.741356
23	1	0	1.566904	–3.005268	–0.846482
24	1	0	3.227492	–1.212369	1.000642
25	1	0	3.821674	–2.043567	–0.433333
26	1	0	4.388945	–3.310753	1.661766
27	1	0	3.339142	–4.249733	0.601476
28	1	0	2.451675	–2.654037	3.059013
29	1	0	2.533050	–4.408637	2.942947
30	1	0	0.778652	–4.407511	1.180619
31	1	0	0.178189	–3.555751	2.615606
32	1	0	–0.836489	–2.515153	–1.580111
33	1	0	–2.379445	–2.253963	–0.731342
34	1	0	–1.518936	–3.800214	–0.547860
35	1	0	0.942990	3.140433	2.647410
36	1	0	–0.676401	3.244281	1.924021
37	1	0	–1.137583	2.004189	–0.221064
38	1	0	–0.191911	1.283044	–2.393490
39	1	0	2.262454	1.004265	–2.650068
40	1	0	3.764543	1.470251	–0.727742

Table S4. (*Continued*).

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	**Number**	**Type**	**X**	**Y**	**Z**
41	1	0	2.811132	2.212584	1.435604
42	7	0	–0.183979	1.417790	2.863536
43	6	0	–1.854756	0.160520	4.062604
44	6	0	–3.205227	–0.179878	4.052694
45	6	0	–0.972013	–0.584510	4.859563
46	6	0	–3.685426	–1.252961	4.797717
47	1	0	–3.890548	0.386064	3.427236
48	6	0	–1.435127	–1.647893	5.609557
49	1	0	0.078123	–0.308902	4.892615
50	6	0	–2.794110	–1.992505	5.577835
51	1	0	–4.738956	–1.501995	4.759530
52	1	0	–0.772182	–2.233767	6.237244
53	1	0	–2.153605	2.014000	2.936696
54	8	0	–3.146507	–3.053694	6.343777
55	6	0	–4.502437	–3.444039	6.339465
56	1	0	–4.831261	–3.728006	5.332587
57	1	0	–4.569583	–4.307921	7.000433
58	1	0	–5.148866	–2.643395	6.718706

Table S5. Optimized Cartesian coordinates for ts-ei3t3.

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	**Number**	**Type**	**X**	**Y**	**Z**
1	7	0	0.918842	2.094394	1.583969
2	6	0	0.328643	2.033035	0.227466
3	6	0	0.485089	0.516162	0.358145
4	6	0	1.043300	0.740284	1.727793
5	6	0	1.171595	2.748500	–0.827866
6	6	0	0.566293	2.638046	–2.232079
7	6	0	–0.903255	3.065531	–2.248472
8	6	0	–1.709418	2.271655	–1.217758
9	6	0	–1.132526	2.480182	0.184085
10	8	0	1.449413	0.071726	2.667564
11	6	0	0.745417	–0.528558	–0.574658
12	6	0	–0.366082	–1.497758	1.070023
13	8	0	0.849323	–0.558055	–1.783021
14	6	0	0.972845	3.145058	2.562284
15	6	0	1.904084	–2.412122	0.772706
16	6	0	3.157128	–1.849097	0.147721
17	6	0	3.889289	–0.861335	0.809030
18	6	0	5.031888	–0.326329	0.219731

Table S5. (*Continued*).

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	**Number**	**Type**	**X**	**Y**	**Z**
19	6	0	5.446698	–0.771277	–1.032605
20	6	0	4.714283	–1.751025	–1.699096
21	6	0	3.573480	–2.286283	–1.110514
22	1	0	2.188560	2.340011	–0.806313
23	1	0	1.235017	3.808684	–0.537255
24	1	0	0.643116	1.597827	–2.564154
25	1	0	1.150602	3.250285	–2.927977
26	1	0	–1.323762	2.925524	–3.250144
27	1	0	–0.983178	4.137772	–2.015742
28	1	0	–1.666187	1.201135	–1.464819
29	1	0	–2.765012	2.564296	–1.237765
30	1	0	–1.190827	3.547013	0.449577
31	1	0	–1.701825	1.918400	0.935207
32	1	0	1.635368	3.954914	2.238842
33	1	0	1.367000	2.712002	3.484733
34	1	0	–0.022414	3.562435	2.761236
35	1	0	1.816875	–3.481089	0.550206
36	1	0	1.929217	–2.278835	1.860319
37	1	0	3.549467	–0.510998	1.779869
38	1	0	5.598399	0.439158	0.741409
39	1	0	6.338533	–0.353987	–1.490565
40	1	0	5.030469	–2.096021	–2.678598
41	1	0	2.991133	–3.039914	–1.634608
42	7	0	0.689987	–1.742708	0.272609
43	6	0	–1.735653	–1.416723	0.579552
44	6	0	–2.748794	–1.057038	1.472116
45	6	0	–2.075024	–1.690578	–0.760074
46	6	0	–4.068581	–0.931457	1.055462
47	1	0	–2.495823	–0.850399	2.509324
48	6	0	–3.383576	–1.570823	–1.181896
49	1	0	–1.298766	–1.987195	–1.459184
50	6	0	–4.388560	–1.183374	–0.282094
51	1	0	–4.829751	–0.642648	1.770152
52	1	0	–3.667267	–1.778990	–2.207980
53	1	0	–0.222853	–1.628136	2.145807
54	8	0	–5.634984	–1.094123	–0.799267
55	6	0	–6.682183	–0.716234	0.069626
56	1	0	–6.507187	0.280080	0.492501
57	1	0	–7.586420	–0.699344	–0.537848
58	1	0	–6.802564	–1.440829	0.883737

Table S6. Optimized Cartesian coordinates for ts-78.

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	**Number**	**Type**	**X**	**Y**	**Z**
1	6	0	1.910985	–0.234344	5.000065
2	6	0	3.247047	0.085213	5.700671
3	6	0	3.797583	1.433744	5.232765
4	6	0	4.122122	1.428093	3.713130
5	6	0	3.253054	0.414098	2.980555
6	6	0	1.865985	0.325376	3.562816
7	6	0	3.384204	0.623594	1.480665
8	8	0	3.422243	–0.737655	0.888877
9	6	0	3.738664	–1.576094	1.834715
10	7	0	4.007304	–2.833707	1.513148
11	8	0	3.712217	2.512689	3.033846
12	8	0	3.769840	–1.161105	3.031260
13	6	0	4.415922	–3.816406	2.519678
14	6	0	5.875748	–3.657816	2.924850
15	1	0	1.081896	0.202653	5.566921
16	1	0	1.745819	–1.317343	4.985238
17	1	0	3.979540	–0.698387	5.466828
18	1	0	3.105692	0.063802	6.786575
19	1	0	4.684451	1.717046	5.808635
20	1	0	3.049381	2.221785	5.378636
21	1	0	5.195117	1.119448	3.583547
22	1	0	1.526611	1.366096	3.557170
23	1	0	1.190314	–0.253796	2.920934
24	1	0	4.311461	1.129714	1.222369
25	1	0	2.529909	1.120261	1.028093
26	1	0	4.050659	–3.050674	0.526445
27	1	0	4.221807	–4.802939	2.093560
28	1	0	3.758196	–3.689171	3.383042
29	1	0	6.140451	–4.409594	3.673135
30	1	0	6.041659	–2.668067	3.358134
31	1	0	6.537590	–3.780819	2.063146

Table S7. Optimized Cartesian coordinates for ts-i01.

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	**Number**	**Type**	**X**	**Y**	**Z**
1	6	0	2.551119	–1.876264	–0.276614
2	6	0	3.556689	–0.827449	–0.798361
3	6	0	3.049087	0.611121	–0.588682
4	6	0	1.520499	0.709834	–0.698526
5	6	0	0.921759	–0.119616	0.496710

Table S7. (*Continued*).

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	**Number**	**Type**	**X**	**Y**	**Z**
6	6	0	1.770641	–1.317673	0.911515
7	6	0	0.511908	0.803184	1.655858
8	8	0	–0.940348	0.727472	1.698361
9	6	0	–1.326479	0.002773	0.687990
10	7	0	–2.603899	–0.307920	0.526191
11	8	0	1.073071	1.986567	–0.713024
12	8	0	–0.400093	–0.628954	0.048819
13	6	0	–3.038293	–0.807614	–0.788483
14	6	0	–4.545276	–0.994633	–0.785987
15	1	0	3.066769	–2.798035	0.009824
16	1	0	1.840124	–2.147522	–1.065680
17	1	0	3.736352	–1.007171	–1.863688
18	1	0	4.520786	–0.960207	–0.294484
19	1	0	3.472240	1.296572	–1.327033
20	1	0	3.352639	0.998499	0.394699
21	1	0	1.216804	0.122282	–1.595424
22	1	0	2.479278	–0.974709	1.677130
23	1	0	1.132564	–2.074173	1.383616
24	1	0	0.783557	1.830121	1.400263
25	1	0	0.871699	0.481143	2.634004
26	1	0	–3.226634	0.351813	0.978935
27	1	0	–2.528496	–1.758192	–0.961826
28	1	0	–2.707373	–0.082508	–1.539584
29	1	0	–4.872714	–1.383347	–1.752630
30	1	0	–5.058894	–0.041374	–0.622256
31	1	0	–4.856232	–1.697665	–0.008071
32	8	0	–1.341661	1.718357	–0.855134
33	1	0	–0.240008	1.904684	–0.882440
34	1	0	–1.712846	2.565725	–0.573389

Table S8. Optimized Cartesian coordinates for ts-i12.

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	**Number**	**Type**	**X**	**Y**	**Z**
1	6	0	–2.420592	1.990557	–0.267390
2	6	0	–3.573599	1.006772	–0.556244
3	6	0	–3.158063	–0.453941	–0.298506
4	6	0	–1.674987	–0.654470	–0.579008
5	6	0	–0.835116	0.158063	0.444536
6	6	0	–1.533933	1.454576	0.853959
7	6	0	–0.391096	–0.692081	1.639865

Table S8. (*Continued*).

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	**Number**	**Type**	**X**	**Y**	**Z**
8	8	0	0.840885	–1.261922	1.219104
9	6	0	1.218964	–0.676512	0.000803
10	7	0	2.708310	–0.304951	0.056854
11	8	0	–1.390635	–2.029289	–0.549642
12	8	0	0.439691	0.472415	–0.144383
13	6	0	3.078813	1.076491	–0.290294
14	6	0	4.590563	1.222618	–0.354503
15	1	0	–2.816200	2.976978	–0.006707
16	1	0	–1.804302	2.126900	–1.163885
17	1	0	–3.896983	1.123544	–1.596040
18	1	0	–4.438026	1.255675	0.068586
19	1	0	–3.727755	–1.147153	–0.922830
20	1	0	–3.356288	–0.740455	0.743096
21	1	0	–1.435497	–0.229531	–1.567525
22	1	0	–2.151776	1.253978	1.740178
23	1	0	–0.764894	2.174452	1.153163
24	1	0	–1.098275	–1.493698	1.863414
25	1	0	–0.224632	–0.067512	2.527104
26	1	0	3.114140	–0.611833	0.943164
27	1	0	2.634166	1.757392	0.441748
28	1	0	2.614735	1.287683	–1.256652
29	1	0	4.858836	2.244563	–0.633346
30	1	0	5.016707	0.540263	–1.094993
31	1	0	5.050627	1.008130	0.615765
32	8	0	1.301354	–1.505484	–1.036690
33	1	0	–0.470680	–2.147673	–0.867915
34	1	0	2.578372	–1.147918	–0.832238

Table S9. Optimized Cartesian coordinates for ts-i34.

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	**Number**	**Type**	**X**	**Y**	**Z**
1	6	0	2.954332	–2.247802	–0.874390
2	6	0	2.905749	–0.739384	–0.545518
3	6	0	1.543565	–0.259059	–0.198306
4	6	0	0.644141	–1.136250	0.552923
5	6	0	0.742410	–2.635196	0.297225
6	6	0	2.216060	–3.070920	0.186924
7	8	0	2.387316	1.463392	1.359832
8	6	0	2.626698	2.462368	0.726523
9	8	0	1.756740	2.021608	–1.018057

Table S9. (*Continued*).

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	**Number**	**Type**	**X**	**Y**	**Z**
10	6	0	1.015349	0.969874	–0.833943
11	6	0	0.029006	–0.593271	1.686860
12	8	0	3.085059	3.532037	0.556181
13	1	0	4.002088	–2.554247	–0.948178
14	1	0	2.504481	–2.420541	–1.860015
15	1	0	3.331204	–0.101071	–1.325547
16	1	0	3.502386	–0.552594	0.361136
17	1	0	0.227874	–2.872011	–0.641384
18	1	0	0.215994	–3.176011	1.085858
19	1	0	2.712884	–2.957611	1.158923
20	1	0	2.252280	–4.135555	–0.066128
21	1	0	–0.048307	1.195803	–0.388609
22	1	0	0.736181	0.432228	–1.798981
23	1	0	–0.450954	–1.260927	2.395096
24	1	0	0.278138	0.406873	2.026828
25	46	0	–1.411510	–0.191457	0.068241
26	17	0	–3.178317	0.832822	–0.957923
27	17	0	–2.721961	–2.007488	0.614367

Table S10. Optimized Cartesian coordinates for ts-i56.

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	**Number**	**Type**	**X**	**Y**	**Z**
1	6	0	0.046267	–2.579367	–0.452969
2	6	0	0.525972	–1.229342	–0.990943
3	6	0	–0.179508	–0.047330	–0.419556
4	6	0	–1.138207	–0.215904	0.652102
5	6	0	–1.069970	–1.473227	1.523477
6	6	0	–0.044263	–2.522744	1.075133
7	8	0	1.179633	1.420625	–1.773898
8	6	0	0.055166	1.245979	–1.087722
9	6	0	–2.051338	0.780223	1.029390
10	1	0	0.736118	–3.367205	–0.770177
11	1	0	–0.934712	–2.827421	–0.880726
12	1	0	0.447789	–1.151847	–2.085521
13	1	0	1.602706	–1.096873	–0.814697
14	1	0	–2.081369	–1.936534	1.552043
15	1	0	–0.882197	–1.153065	2.555567
16	1	0	0.932413	–2.255154	1.493862
17	1	0	–0.318272	–3.496565	1.491893
18	1	0	–0.284621	2.110215	–0.492394

Table S10. (*Continued*).

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	**Number**	**Type**	**X**	**Y**	**Z**
19	1	0	–0.824160	1.114142	–1.813511
20	1	0	–2.565971	0.706932	1.984485
21	1	0	–2.091197	1.747026	0.546271
22	46	0	–3.218495	–0.663798	–0.187521
23	17	0	–4.979132	–1.963831	–0.882549
24	17	0	–3.278447	0.793736	–1.968070
25	6	0	5.597212	–2.059529	–0.046248
26	6	0	5.979514	–1.321104	–1.178852
27	6	0	5.342798	–0.127781	–1.496670
28	6	0	4.313033	0.324856	–0.668652
29	6	0	3.910663	–0.394492	0.466713
30	6	0	4.572978	–1.597891	0.766800
31	8	0	3.729816	1.519264	–1.013735
32	6	0	2.663042	1.959198	–0.332419
33	6	0	2.256101	1.384299	0.874965
34	6	0	2.829108	0.117512	1.338748
35	8	0	2.445807	–0.480552	2.346126
36	6	0	1.259541	2.032814	1.650885
37	7	0	0.414750	2.558562	2.260448
38	1	0	6.106160	–2.988220	0.191286
39	1	0	6.780985	–1.682900	–1.815695
40	1	0	5.619466	0.459232	–2.365441
41	1	0	4.256443	–2.136209	1.654021
42	1	0	2.393423	2.966374	–0.614979

Table S11. Optimized Cartesian coordinates for ts-i67.

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	**Number**	**Type**	**X**	**Y**	**Z**
1	6	0	0.711675	1.201675	0.174203
2	6	0	1.013248	–0.160622	–0.464230
3	6	0	0.438643	–1.347982	0.285689
4	6	0	–0.418361	–1.136701	1.409640
5	6	0	–1.073435	0.228362	1.639554
6	6	0	–0.757609	1.292001	0.586372
7	8	0	1.175416	–2.951227	–1.354368
8	6	0	1.168982	–2.652870	0.033063
9	6	0	–0.948324	–2.215065	2.174011
10	1	0	0.967019	1.996887	–0.533024
11	1	0	1.352712	1.346306	1.055399
12	1	0	2.096243	–0.318736	–0.541848

Table S11. (*Continued*).

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	**Number**	**Type**	**X**	**Y**	**Z**
13	1	0	0.658238	–0.175355	–1.499570
14	1	0	–0.738980	0.624329	2.642405
15	1	0	–2.152420	0.089737	1.771275
16	1	0	–1.405522	1.124855	–0.280753
17	1	0	–0.994422	2.282638	0.986504
18	1	0	0.764246	–3.488435	0.613568
19	1	0	2.216962	–2.534419	0.325326
20	1	0	–1.685135	–2.007805	2.941075
21	1	0	–0.443551	–3.166184	2.258029
22	46	0	0.890450	–0.722526	3.165513
23	17	0	1.867130	0.440764	4.889196
24	17	0	2.360993	–2.470066	3.302020
25	6	0	–0.720541	0.063837	–5.463782
26	6	0	0.049158	–1.001635	–5.956671
27	6	0	0.280018	–2.134667	–5.183623
28	6	0	–0.260983	–2.207430	–3.897530
29	6	0	–1.038537	–1.150776	–3.386965
30	6	0	–1.263135	–0.018050	–4.190531
31	8	0	–0.058724	–3.371207	–3.206529
32	6	0	–0.122811	–3.338545	–1.804198
33	6	0	–1.192319	–2.405417	–1.248617
34	6	0	–1.666140	–1.259555	–2.057062
35	8	0	–2.498294	–0.455843	–1.636432
36	6	0	–1.942164	–2.831235	–0.174533
37	7	0	–2.399787	–3.108399	0.881197
38	1	0	–0.893330	0.941303	–6.078284
39	1	0	0.473945	–0.945008	–6.954605
40	1	0	0.870061	–2.967067	–5.550869
41	1	0	–1.879812	0.775100	–3.780498
42	1	0	–0.314203	–4.374470	–1.499500

Table S12. Optimized Cartesian coordinates for 4-ts-i34.

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	**Number**	**Type**	**X**	**Y**	**Z**
1	6	0	2.866648	–2.053999	–0.993229
2	6	0	2.908659	–0.556184	–0.626304
3	6	0	1.558751	–0.076690	–0.208109
4	6	0	0.749061	–0.943692	0.593785
5	6	0	1.070761	–2.254264	0.776065
6	6	0	2.255517	–2.897859	0.136710

Table S12. (*Continued*).

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	**Number**	**Type**	**X**	**Y**	**Z**
7	8	0	2.367544	1.541879	1.347209
8	6	0	2.552714	2.606392	0.823689
9	8	0	1.654418	2.205170	–1.034248
10	6	0	0.968530	1.117690	–0.879325
11	8	0	2.923304	3.711610	0.698953
12	1	0	3.877578	–2.401729	–1.222789
13	1	0	2.270620	–2.186882	–1.903553
14	1	0	3.290263	0.066892	–1.438996
15	1	0	3.574118	–0.399202	0.233840
16	1	0	0.444615	–2.861738	1.426644
17	1	0	2.990723	–3.068669	0.942156
18	1	0	1.981200	–3.900359	–0.212817
19	1	0	–0.123466	1.301249	–0.439630
20	1	0	0.723707	0.577418	–1.848747
21	46	0	–1.537255	0.023487	–0.165342
22	17	0	–3.111076	1.253293	–1.233706
23	17	0	–2.986475	–1.663501	0.379519
24	1	0	–0.062360	–0.505052	1.202386

Table S13. Optimized Cartesian coordinates for 4-ts-i56.

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	**Number**	**Type**	**X**	**Y**	**Z**
1	6	0	0.647343	–2.032607	0.434029
2	6	0	–0.181516	–0.910277	1.071894
3	6	0	0.201019	0.457064	0.614930
4	6	0	1.018836	0.645933	–0.545352
5	6	0	1.314177	–0.442981	–1.386454
6	6	0	0.801769	–1.824078	–1.082864
7	8	0	–1.332160	1.516887	2.166449
8	6	0	–0.229623	1.615460	1.431729
9	1	0	0.191914	–3.005329	0.641383
10	1	0	1.644283	–2.071475	0.908421
11	1	0	–0.154006	–0.930976	2.168947
12	1	0	–1.246573	–1.048495	0.840881
13	1	0	1.681133	–0.229975	–2.386117
14	1	0	–0.171586	–1.916648	–1.589091
15	1	0	1.463702	–2.576876	–1.522221
16	1	0	–0.073665	2.570244	0.889817
17	1	0	0.682445	1.582212	2.111787
18	46	0	3.054988	–0.158966	–0.013211

Table S13. (*Continued*).

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	**Number**	**Type**	**X**	**Y**	**Z**
19	17	0	4.958726	–0.789536	1.099077
20	17	0	4.100277	1.258350	–1.486148
21	6	0	–4.805500	–2.871725	0.241130
22	6	0	–5.309302	–2.361427	1.449498
23	6	0	–4.980698	–1.078710	1.870670
24	6	0	–4.139607	–0.303443	1.069183
25	6	0	–3.620660	–0.790203	–0.140440
26	6	0	–3.968817	–2.091917	–0.543086
27	8	0	–3.860543	0.963360	1.519797
28	6	0	–3.000082	1.735748	0.842485
29	6	0	–2.526983	1.396196	–0.427308
30	6	0	–2.739899	0.056082	–0.978539
31	8	0	–2.223675	–0.349409	–2.022305
32	6	0	–1.814362	2.371816	–1.175610
33	7	0	–1.215421	3.181211	–1.763159
34	1	0	–5.074743	–3.873751	–0.077169
35	1	0	–5.963547	–2.972171	2.064094
36	1	0	–5.356630	–0.663346	2.799152
37	1	0	–3.567527	–2.449364	–1.485686
38	1	0	–2.992613	2.750971	1.211696
39	1	0	1.198076	1.656889	–0.898533

Table S14. Optimized Cartesian coordinates for 4-ts-i67.

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	**Number**	**Type**	**X**	**Y**	**Z**
1	6	0	–0.150645	–2.120892	–0.441243
2	6	0	0.459834	–0.863595	–1.098594
3	6	0	–0.026174	0.463881	–0.589316
4	6	0	–0.865530	0.540955	0.562540
5	6	0	–1.050505	–0.577628	1.405209
6	6	0	–0.630538	–1.966245	1.020878
7	8	0	1.633323	1.721960	–1.782278
8	6	0	0.257505	1.664791	–1.449734
9	1	0	0.592680	–2.921093	–0.488257
10	1	0	–0.995001	–2.467721	–1.049848
11	1	0	0.276957	–0.890704	–2.181690
12	1	0	1.550013	–0.888282	–1.022494
13	1	0	–1.366422	–0.418208	2.431731
14	1	0	0.120479	–2.294365	1.749342
15	1	0	–1.494408	–2.627943	1.182140

Table S14. (*Continued*).

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	**Number**	**Type**	**X**	**Y**	**Z**
16	1	0	–0.105023	2.583320	–0.970501
17	1	0	–0.255859	1.564909	–2.415154
18	46	0	–2.948998	–0.389436	0.197201
19	17	0	–5.020853	–1.314652	–0.166095
20	17	0	–3.814830	1.358508	1.400470
21	6	0	5.004949	–2.278091	0.162499
22	6	0	5.646541	–1.563239	–0.861621
23	6	0	5.199197	–0.302538	–1.240035
24	6	0	4.093441	0.258279	–0.592180
25	6	0	3.434816	–0.445375	0.435247
26	6	0	3.911710	–1.716655	0.804292
27	8	0	3.744144	1.523965	–0.967301
28	6	0	2.463126	2.017500	–0.648497
29	6	0	1.889468	1.469156	0.639878
30	6	0	2.313133	0.178046	1.168383
31	8	0	1.756187	–0.360832	2.134901
32	6	0	1.181220	2.369126	1.466052
33	7	0	0.586841	3.143454	2.107212
34	1	0	5.368869	–3.257946	0.454059
35	1	0	6.505628	–1.995110	–1.366537
36	1	0	5.687150	0.265325	–2.024607
37	1	0	3.403067	–2.226532	1.616104
38	1	0	2.583484	3.104786	–0.591137
39	1	0	–1.131503	1.518013	0.947904

Table S15. 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 473 K, 363 K by B3LYP/6-311++G(d,p)//B3LYP/6-31G(d) method and difference between absolute energy.

Species	ΔG_{gas}	$\Delta G_{sol(ChloroBenzene)}$
1	0.00	0.00
ts-1i1	46.07	46.81
i1	–11.79	–8.64
i1-n2	0.00	0.00
A	1.59	0.45
A+z2	0.00	0.00
zi2	–5.97	–1.45
ts-zi2i3	–3.86	0.22
zi3	–17.23	–17.31
ts-zi3c3	–2.46	–2.84
c3	–46.45	–51.47

Table S15. (*Continued*).

Species	**ΔG_{gas}**	**$\Delta G_{sol(ChloroBenzene)}$**
A+e2	0.00	0.00
ei2	–13.48	–8.91
ts-ei2i3	–8.17	–3.72
ei3	–15.36	–16.96
ts-ei3t3	6.81	8.49
t3	–38.70	–44.61
Species	**ΔG_{gas}**	**$\Delta G_{sol(Chloroform)}$**
7	0.00	0.00
ts-i78	48.02	34.21
8	47.37	31.28
8+h2o	0.00	0.00
i0	–31.47	–15.56
ts-i01	–28.73	–11.37
i1	–62.83	–41.66
ts-i12	–28.12	–6.09
i2	–64.58	–43.46
6+pdcl2	0.00	0.00
i3	–148.00	–141.50
ts-i34	–118.21	–112.94
i4	–183.26	–173.22
6+pdcl2-co2+9	0.00	0.00
i5	–255.94	–245.04
ts-i56	–220.90	–211.36
i6	–264.39	–251.23
ts-i67	–241.00	–228.61
i7	–267.70	–255.07
6-co2+9	0.00	0.00
10	–16.08	–16.21
4+pdcl2	0.00	0.00
4-i3	–128.55	–122.23
4-ts-i34	–96.17	–93.03
4-i4	–173.69	–162.89
4+pdcl2-co2+9	0.00	0.00
4-i5	–255.08	–242.39
4-ts-i56	–215.25	–205.44
4-i6	–253.27	–238.74
4-ts-i67	–227.98	–216.88
4-i7	–269.23	–253.31
4-co2+9	0.00	0.00
11	–9.59	–9.50

Table S16. 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 and difference between the two.

TS	$\Delta G^{\neq}_{gas}$	$\Delta G^{\neq}_{sol}$
ts-1i1 (329i)	46.07	46.81
ts-zi2i3 (113i)	2.11	1.67
ts-zi3c3 (178i)	14.76	14.48
ts-ei2i3 (143i)	5.31	5.19
ts-ei3t3 (281i)	22.17	25.45
ts-i78 (251i)	48.02	34.21
ts-i01 (207i)	2.74	4.20
ts-i12 (1528i)	34.72	35.57
ts-i34 (319i)	29.79	28.56
ts-i56 (291i)	35.04	33.68
ts-i67 (360i)	23.39	22.61
4-ts-i34 (287i)	32.38	29.20
4-ts-i56 (279i)	39.83	36.95
4-ts-i67 (303i)	26.29	23.86

Table S17. Mayer bond order (MBO) of typical TSs.

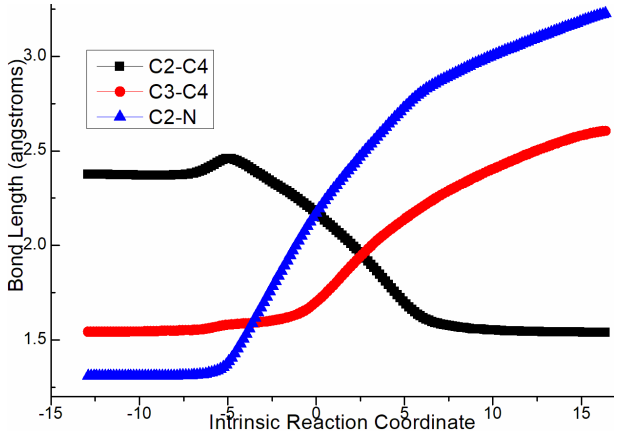
ts-1i1	C2⋯C4	C2⋯N	C3⋯C4	
	0.19	0.13	0.69	
ts-zi3c3	C2⋯C5	C2⋯C3	N⋯C5	
	0.37	1.14	1.23	
ts-78	C2⋯O3	C2⋯O1	C3⋯O1	
	0.48	0.18	1.15	
ts-i34	O2⋯C4	C2⋯O3	C1⋯H3	H3⋯C2
	0.32	0.11	0.77	0.15
ts-i56	O2⋯C4	C1⋯H3	H3⋯C2	
	0.29	0.73	0.10	
ts-i67	C2⋯C5	N2⋯C6		
	0.36	0.32		

Table S18. Contribution (%) of Natural Atomic Orbital (NAO) to Highest Occupied Molecular Orbital (HOMO) of typical TSs.

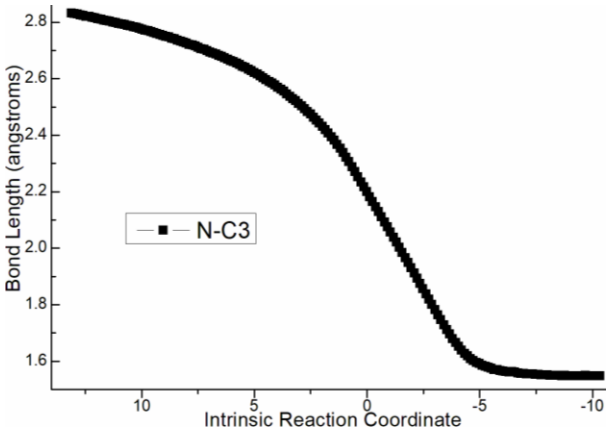
ts-1i1	C2	C3	C4	N	
	54.01	4.91	10.40	7.92	
ts-zi3c3	C2	C5	C3	N	
	39.61	6.63	3.50	2.24	
ts-78	C2	O3	O1	C3	
	2.50	0.30	77.10	2.30	
ts-i34	O2	C2	O3	C1	H3
	2.61	19.76	1.52	2.44	2.15

Table S18. (*Continued*).

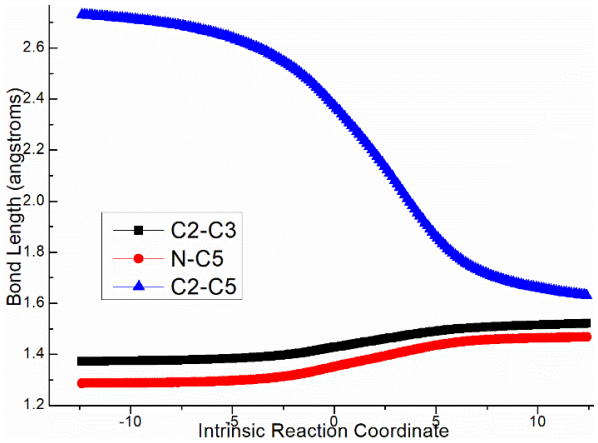
ts-i56	O2	C4	C1	H3	C2
	36.11	0.61	0.53	1.15	10.68
ts-i67	C2	C5	N2	C6	
	1.38	8.95	4.35	0.47	



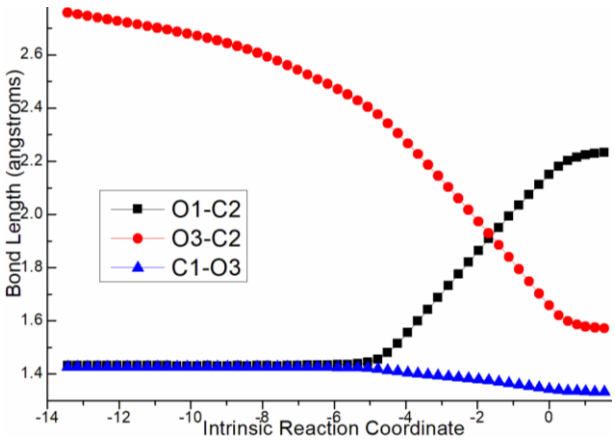
(a)



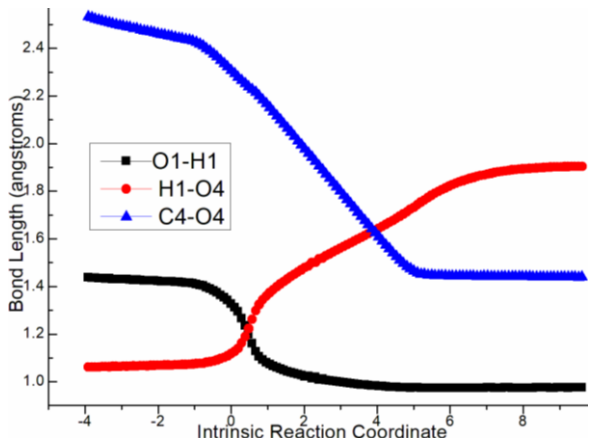
(b)



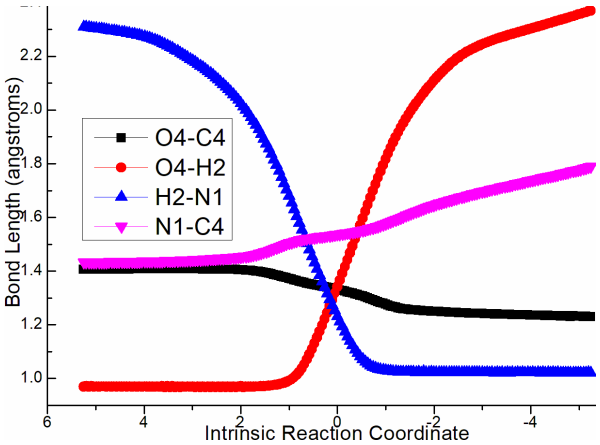
(c)



(d)



(e)



(f)

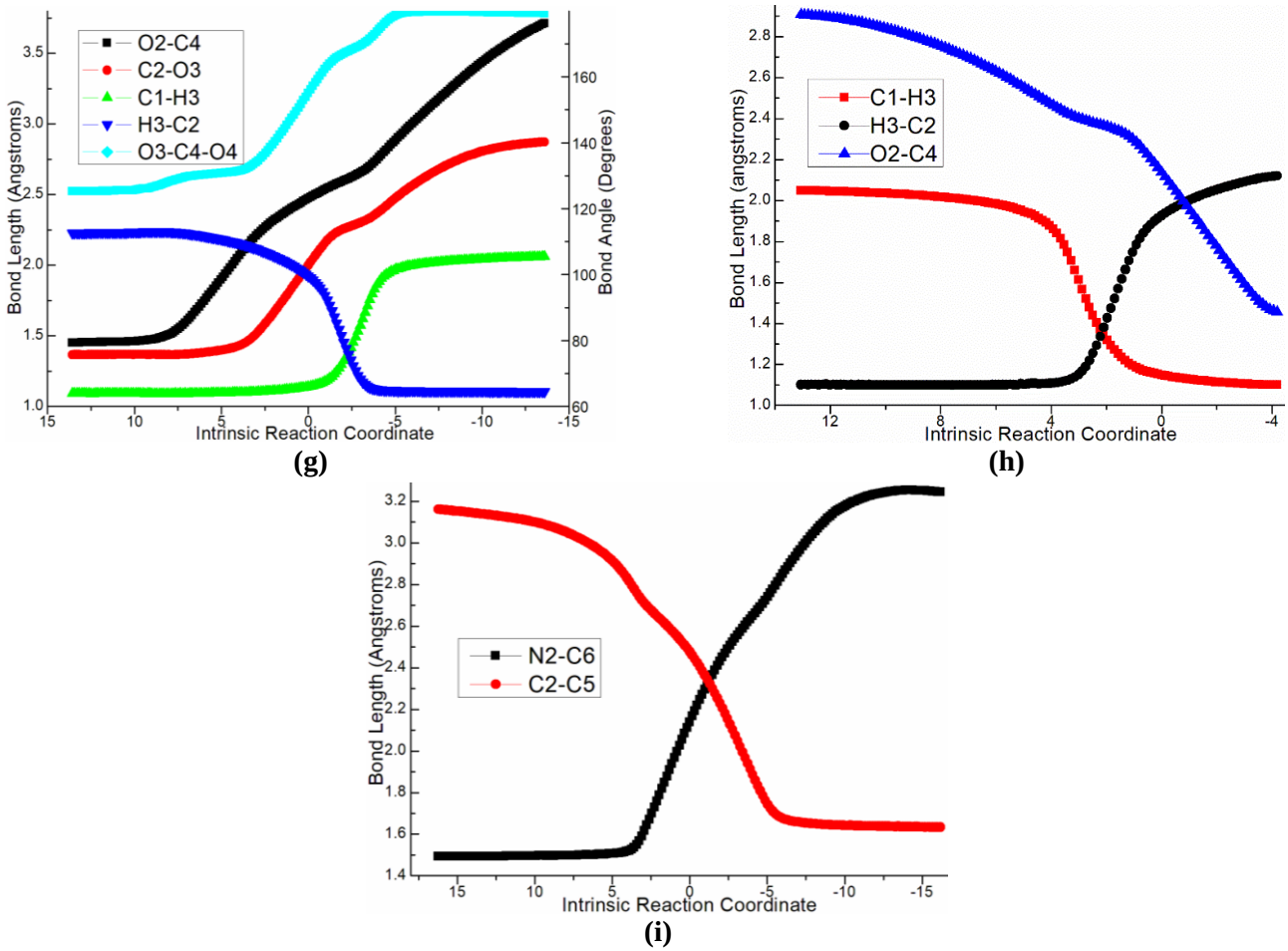


Figure S1. Evolution of bond lengths along the IRC. **(a)** ts-1i1; **(b)** ts-zi2i3; **(c)** ts-zi3c3; **(d)** ts-78; **(e)** ts-i01; **(f)** ts-i12; **(g)** ts-i34; **(h)** ts-i56; **(i)** ts-i67 at the B3LYP/6-311++G(d,p) level.

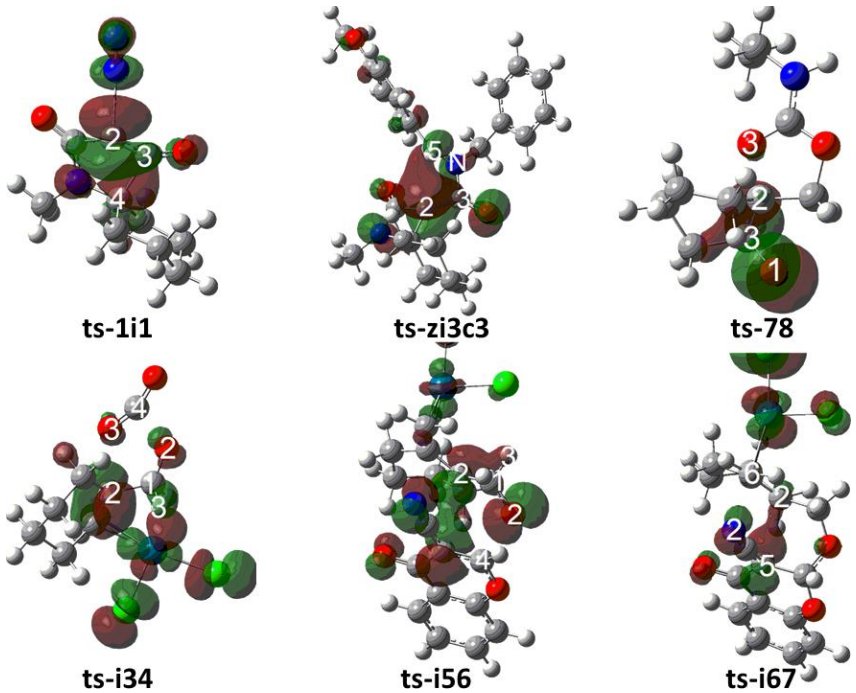


Figure S2. Highest Occupied Molecular Orbital (HOMO) of typical TSs.

Different colors are used to identify the phase of the wave functions.