Supplementary Information

Theoretical investigation on the mechanism and selectivity of catalyst-free annulation of ynediones and (iso)quinoline *N*-oxides

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Software: GAUSSIAN09

Level of Theory: M06-2X

Basis Set: 6-31G(d)

Geometry [Cartesian coordinates]:

Optimized Cartesian coordinates for **ts-ca**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.438503	2.668207	-0.714962
2	6	0	3.434155	3.599537	-0.982643
3	6	0	2.129762	3.340925	-0.586752
4	6	0	1.820480	2.154446	0.088086
5	6	0	2.827633	1.222707	0.354666
6	6	0	4.133239	1.483056	-0.052007
7	6	0	0.390405	1.914008	0.436638
8	8	0	-0.493020	2.670214	0.088929
9	6	0	0.016815	0.678654	1.284859
10	8	0	0.685826	0.387573	2.269526
11	6	0	1.002114	-1.957055	-2.032181
12	6	0	-0.148572	-2.161922	0.481053
13	7	0	-0.900833	-2.189749	-0.626786
14	6	0	-0.341414	-1.993154	-1.875662
15	6	0	-1.112034	-0.021174	0.797327
16	6	0	-2.236882	-0.322436	0.326738
17	8	0	-2.181062	-1.976297	-0.474816

18	6	0	-3.614844	0.092963	0.127274
19	6	0	-3.884623	1.468697	0.151958
20	6	0	-5.188783	1.921118	-0.004578
21	6	0	-6.229596	1.012155	-0.187059
22	6	0	-5.961494	-0.354580	-0.214405
23	6	0	-4.659702	-0.817793	-0.059768
24	1	0	5.459949	2.869250	-1.024937
25	1	0	3.672132	4.522664	-1.501937
26	1	0	1.327542	4.043042	-0.790583
27	1	0	2.596516	0.308187	0.889163
28	1	0	4.912885	0.755933	0.155228
29	1	0	1.421367	-1.836184	-3.025013
30	1	0	-0.662410	-2.373892	1.408696
31	1	0	-1.073119	-1.894675	-2.666229
32	1	0	-3.057265	2.160401	0.284919
33	1	0	-5.393043	2.987274	0.012301
34	1	0	-7.247669	1.369332	-0.309716
35	1	0	-6.770036	-1.065143	-0.356349
36	1	0	-4.444947	-1.879736	-0.082278
37	6	0	1.274075	-2.186496	0.381877
38	6	0	2.081269	-2.271182	1.535487
39	6	0	1.869559	-2.068082	-0.896609
40	6	0	3.454014	-2.265835	1.410433
41	1	0	1.607088	-2.315729	2.510638
42	6	0	3.274692	-2.058979	-0.997382

43	6	0	4.050721	-2.164019	0.137958
44	1	0	4.078681	-2.329470	2.295196
45	1	0	3.734652	-1.962955	-1.976631
46	1	0	5.133237	-2.160590	0.052904

Optimized Cartesian coordinates for **ts-ro**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-5.486269	-0.902789	-3.236522
2	6	0	-4.545255	-1.253775	-4.204044
3	6	0	-3.202466	-1.332399	-3.862511
4	6	0	-2.789400	-1.070894	-2.551117
5	6	0	-3.736356	-0.721537	-1.582145
6	6	0	-5.080467	-0.635440	-1.931506
7	6	0	-1.323124	-1.109956	-2.276543
8	8	0	-0.520467	-1.285391	-3.181644
9	6	0	-0.826591	-0.998683	-0.819986
10	8	0	-1.487276	-1.638904	0.004197
11	6	0	3.295921	2.247965	-2.059678
12	6	0	1.054007	0.602521	-1.647355
13	7	0	1.074389	1.970102	-1.232221
14	6	0	2.112350	2.736638	-1.504497
15	6	0	0.344388	-0.226499	-0.583238

16	6	0	0.922445	0.100018	0.679550
17	8	0	1.725696	1.056508	0.748341
18	6	0	0.664838	-0.648105	1.952723
19	6	0	0.478739	-2.030705	1.986818
20	6	0	0.340982	-2.681014	3.208091
21	6	0	0.375376	-1.955863	4.397378
22	6	0	0.566928	-0.576366	4.366390
23	6	0	0.728528	0.072721	3.148006
24	1	0	-6.537762	-0.838523	-3.501138
25	1	0	-4.860823	-1.462233	-5.221746
26	1	0	-2.448888	-1.592157	-4.599275
27	1	0	-3.420160	-0.535927	-0.562929
28	1	0	-5.814406	-0.363949	-1.179075
29	1	0	4.110834	2.937386	-2.272076
30	1	0	0.392703	0.612344	-2.535607
31	1	0	2.026026	3.786407	-1.236979
32	1	0	0.434104	-2.590071	1.060112
33	1	0	0.199282	-3.757116	3.231025
34	1	0	0.255750	-2.466375	5.348583
35	1	0	0.599151	-0.008658	5.291411
36	1	0	0.906611	1.141995	3.102449
37	6	0	2.357719	0.022391	-2.102132
38	6	0	2.494924	-1.343688	-2.367670
39	6	0	3.466584	0.877607	-2.324275
40	6	0	3.706112	-1.836478	-2.819490

41	1	0	1.640271	-1.993897	-2.220835
42	6	0	4.700349	0.354335	-2.793190
43	6	0	4.817234	-0.991500	-3.031249
44	1	0	3.806474	-2.899477	-3.017715
45	1	0	5.537066	1.029865	-2.947957
46	1	0	5.754101	-1.409290	-3.383977

Optimized Cartesian coordinates for **ts-IIdb**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-5.413658	-1.789067	0.960473
2	6	0	-5.239190	-1.510754	-0.397140
3	6	0	-3.967052	-1.274209	-0.891568
4	6	0	-2.866769	-1.311843	-0.019499
5	6	0	-3.043490	-1.590096	1.345276
6	6	0	-4.322489	-1.831121	1.827406
7	6	0	-1.548073	-1.017336	-0.530239
8	8	0	-1.342290	-0.823973	-1.758559
9	6	0	-0.210308	-0.978632	0.260609
10	8	0	-0.055820	-1.770455	1.173515
11	6	0	4.618879	-1.826667	-0.836939
12	6	0	2.129053	-0.694863	-0.533346
13	7	0	2.261955	-1.754538	-1.305236

14	6	0	3.492388	-2.310978	-1.443392
15	6	0	0.745786	-0.149053	-0.449621
16	6	0	0.516843	1.266239	-0.746162
17	8	0	1.345304	1.964944	-1.314262
18	6	0	-0.817300	1.877987	-0.380861
19	6	0	-1.457031	1.640255	0.838930
20	6	0	-2.686081	2.238567	1.116653
21	6	0	-3.282688	3.069936	0.175153
22	6	0	-2.637014	3.327859	-1.035656
23	6	0	-1.405167	2.746555	-1.304904
24	1	0	-6.411918	-1.975705	1.345265
25	1	0	-6.096286	-1.480114	-1.061236
26	1	0	-3.803961	-1.051665	-1.941084
27	1	0	-2.178403	-1.631233	1.997019
28	1	0	-4.471407	-2.053501	2.878613
29	1	0	5.584714	-2.298368	-0.992751
30	1	0	-0.250782	-0.559584	-1.702240
31	1	0	3.537601	-3.182981	-2.090696
32	1	0	-0.982293	1.012836	1.590365
33	1	0	-3.172339	2.054983	2.070064
34	1	0	-4.243901	3.528878	0.386149
35	1	0	-3.095547	3.988627	-1.765133
36	1	0	-0.875598	2.950644	-2.230411
37	6	0	3.224911	-0.121406	0.191063
38	6	0	3.081693	0.972402	1.081897

39	6	0	4.508584	-0.701286	0.016569
40	6	0	4.169639	1.475116	1.747796
41	1	0	2.099848	1.405886	1.237255
42	6	0	5.620285	-0.155808	0.709678
43	6	0	5.453704	0.910776	1.553616
44	1	0	4.050110	2.311668	2.429007
45	1	0	6.599670	-0.603378	0.563069
46	1	0	6.306513	1.325206	2.083075

Optimized Cartesian coordinates for **ts-IIba**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.962039	-2.516651	0.279169
2	6	0	-5.092584	-1.517828	-0.685551
3	6	0	-3.960338	-0.901676	-1.200725
4	6	0	-2.689633	-1.277534	-0.754437
5	6	0	-2.559851	-2.282334	0.209854
6	6	0	-3.697830	-2.898802	0.721864
7	6	0	-1.529438	-0.505607	-1.290865
8	8	0	-1.650821	0.294161	-2.195047
9	6	0	-0.112293	-0.751390	-0.730740
10	8	0	0.286565	-1.905431	-0.633049
11	6	0	4.826688	0.116982	-1.455693

12	6	0	2.205917	0.173204	-0.625411
13	7	0	2.547967	0.583674	-1.836517
14	6	0	3.836399	0.576028	-2.277813
15	6	0	0.739696	0.417832	-0.566502
16	6	0	0.361514	1.719712	0.025160
17	8	0	1.174065	2.629006	0.106634
18	6	0	-1.038012	1.924185	0.527173
19	6	0	-1.693647	0.947576	1.276682
20	6	0	-2.980829	1.173356	1.756836
21	6	0	-3.614598	2.382713	1.490312
22	6	0	-2.953006	3.373135	0.762780
23	6	0	-1.664786	3.150332	0.293558
24	1	0	-5.847225	-2.997102	0.685583
25	1	0	-6.077736	-1.218039	-1.029267
26	1	0	-4.034503	-0.111396	-1.940906
27	1	0	-1.574697	-2.587950	0.543305
28	1	0	-3.596030	-3.681650	1.467065
29	1	0	5.856857	0.105034	-1.797062
30	1	0	1.260054	0.807335	-1.929671
31	1	0	4.010861	0.942087	-3.281927
32	1	0	-1.196740	0.004569	1.494359
33	1	0	-3.488524	0.398187	2.323094
34	1	0	-4.623145	2.557943	1.852504
35	1	0	-3.445641	4.319846	0.563135
36	1	0	-1.128868	3.912614	-0.263195

37	6	0	3.159178	-0.331553	0.284594
38	6	0	2.805172	-0.803393	1.570170
39	6	0	4.512979	-0.355490	-0.149245
40	6	0	3.780901	-1.278187	2.407969
41	1	0	1.759396	-0.785886	1.861644
42	6	0	5.496801	-0.852073	0.741586
43	6	0	5.133848	-1.298801	1.987947
44	1	0	3.522781	-1.643142	3.396545
45	1	0	6.535340	-0.874281	0.424310
46	1	0	5.892323	-1.678194	2.665784

Optimized Cartesian coordinates for **ts-IIbc**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-6.217288	-1.174726	0.246836
2	6	0	-5.852939	0.102864	0.672167
3	6	0	-4.533602	0.515209	0.559926
4	6	0	-3.562998	-0.346917	0.032061
5	6	0	-3.932613	-1.627893	-0.396208
6	6	0	-5.260016	-2.032064	-0.288247
7	6	0	-2.180550	0.195071	-0.076979
8	8	0	-1.943782	1.371813	0.130088
9	6	0	-0.980390	-0.726876	-0.409130

10	8	0	-1.073331	-1.937494	-0.262045
11	6	0	4.030329	-1.811597	-1.379361
12	6	0	1.534314	-0.708125	-0.992214
13	7	0	2.205031	-0.427497	-2.093552
14	6	0	3.433672	-0.968705	-2.276588
15	6	0	0.194439	-0.045647	-0.908611
16	6	0	0.257344	1.430941	-1.036755
17	8	0	-0.162990	1.736490	-2.190169
18	6	0	0.851943	2.413262	-0.136560
19	6	0	1.266816	2.024684	1.140462
20	6	0	1.830274	2.962897	1.995034
21	6	0	1.975985	4.283935	1.574452
22	6	0	1.563755	4.672386	0.299422
23	6	0	1.002740	3.737983	-0.560178
24	1	0	-7.249825	-1.500717	0.331583
25	1	0	-6.598401	0.774262	1.086542
26	1	0	-4.227158	1.507440	0.874698
27	1	0	-3.186164	-2.299393	-0.799138
28	1	0	-5.546182	-3.024448	-0.621940
29	1	0	5.010010	-2.236988	-1.575948
30	1	0	-0.260178	0.488131	-2.237478
31	1	0	3.928338	-0.696961	-3.205393
32	1	0	1.143637	0.991587	1.452486
33	1	0	2.154337	2.667087	2.987246
34	1	0	2.415125	5.016523	2.244995

35	1	0	1.682638	5.702222	-0.021069
36	1	0	0.676883	4.013390	-1.557955
37	6	0	2.079604	-1.529455	0.052340
38	6	0	1.438422	-1.760517	1.298583
39	6	0	3.360246	-2.106095	-0.167620
40	6	0	2.032183	-2.539884	2.257863
41	1	0	0.464972	-1.327469	1.489877
42	6	0	3.943237	-2.924675	0.835300
43	6	0	3.292857	-3.138226	2.021451
44	1	0	1.529192	-2.706994	3.204960
45	1	0	4.917595	-3.367103	0.646326
46	1	0	3.744202	-3.761528	2.787408

Optimized Cartesian coordinates for **ts-IIa**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.602137	-2.971449	0.463101
2	6	0	-4.950222	-1.873379	-0.324042
3	6	0	-3.956887	-1.087783	-0.893006
4	6	0	-2.609993	-1.393691	-0.678057
5	6	0	-2.262040	-2.492961	0.111964
6	6	0	-3.261130	-3.279867	0.678236
7	6	0	-1.592642	-0.469360	-1.265876

8	8	0	-1.895637	0.394413	-2.062699
9	6	0	-0.109512	-0.684165	-0.933048
10	8	0	0.354510	-1.798064	-1.227590
11	6	0	4.844204	-0.107402	-1.309647
12	6	0	2.124633	0.198636	-0.664292
13	7	0	2.633594	0.479025	-1.862994
14	6	0	3.949813	0.344721	-2.222034
15	6	0	0.681013	0.406469	-0.485542
16	6	0	0.332237	1.755457	-0.110162
17	8	0	1.168033	2.664811	-0.169399
18	6	0	-1.042879	2.060239	0.409712
19	6	0	-1.767509	1.152861	1.183053
20	6	0	-3.034294	1.484848	1.656315
21	6	0	-3.577717	2.732692	1.365802
22	6	0	-2.846518	3.653110	0.614547
23	6	0	-1.581025	3.321369	0.147404
24	1	0	-5.378237	-3.587201	0.908519
25	1	0	-5.995938	-1.632146	-0.489168
26	1	0	-4.196905	-0.220141	-1.499569
27	1	0	-1.215322	-2.738949	0.255006
28	1	0	-2.991941	-4.139473	1.284402
29	1	0	5.888150	-0.218444	-1.580409
30	1	0	1.960643	0.833821	-2.538506
31	1	0	4.197626	0.617275	-3.239235
32	1	0	-1.340262	0.180284	1.415001

33	1	0	-3.595150	0.765377	2.245656
34	1	0	-4.568225	2.992168	1.727899
35	1	0	-3.267752	4.629576	0.394193
36	1	0	-0.988998	4.024008	-0.430423
37	6	0	3.028894	-0.278779	0.325593
38	6	0	2.560691	-0.601925	1.620324
39	6	0	4.404268	-0.435774	0.005799
40	6	0	3.441102	-1.061438	2.567951
41	1	0	1.503546	-0.473263	1.828193
42	6	0	5.287051	-0.913133	0.999707
43	6	0	4.810024	-1.217105	2.252847
44	1	0	3.089508	-1.309914	3.563622
45	1	0	6.339266	-1.034817	0.760472
46	1	0	5.493035	-1.583773	3.012918

Optimized Cartesian coordinates for **ts-IIa'e**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.735432	4.310819	0.701954
2	6	0	2.515898	3.083946	1.323806
3	6	0	1.477837	2.264091	0.894040
4	6	0	0.646430	2.673217	-0.150392
5	6	0	0.854124	3.916038	-0.752058

6	6	0	1.903346	4.726618	-0.336401
7	6	0	-4.053555	-1.845977	-0.971323
8	6	0	-1.729786	-0.386351	-0.561935
9	7	0	-1.745155	-1.399672	-1.422292
10	6	0	-2.879388	-2.126023	-1.606660
11	6	0	2.075210	-3.794843	-0.069840
12	6	0	1.994728	-2.405748	0.056923
13	6	0	2.706709	-1.753012	1.070260
14	6	0	3.487380	-2.491259	1.947991
15	6	0	3.566965	-3.878447	1.821719
16	6	0	2.863401	-4.527377	0.811775
17	6	0	-4.023599	1.212100	1.933314
18	6	0	-2.884842	0.936070	1.221213
19	6	0	-2.893955	-0.058895	0.211265
20	6	0	-4.085852	-0.792304	-0.021892
21	6	0	-5.253886	-0.476250	0.717515
22	6	0	-5.223003	0.509370	1.669551
23	6	0	1.088525	-1.682921	-0.854264
24	8	0	0.639081	-2.312800	-1.895458
25	6	0	0.694191	-0.288916	-0.666009
26	8	0	1.883263	-0.005619	-1.036100
27	6	0	-0.530321	1.858775	-0.599425
28	8	0	-1.517986	2.417206	-1.050322
29	6	0	-0.478741	0.387257	-0.459828
30	1	0	3.552151	4.946592	1.030616

31	1	0	3.153140	2.767390	2.143863
32	1	0	1.292308	1.312011	1.384390
33	1	0	0.180194	4.226631	-1.544250
34	1	0	2.070763	5.686076	-0.816034
35	1	0	-4.946715	-2.428695	-1.172388
36	1	0	-0.317597	-1.932391	-2.026046
37	1	0	-2.799599	-2.940443	-2.320355
38	1	0	1.516978	-4.288776	-0.857376
39	1	0	2.675080	-0.670890	1.134707
40	1	0	4.043546	-1.983223	2.729174
41	1	0	4.180931	-4.451553	2.509663
42	1	0	2.926156	-5.605934	0.708670
43	1	0	-4.007327	1.974367	2.705565
44	1	0	-1.966665	1.470693	1.436201
45	1	0	-6.165105	-1.033997	0.520327
46	1	0	-6.118483	0.747833	2.235230

Optimized Cartesian coordinates for **ts-eNnu**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	5.174628	-1.941989	0.805965
2	6	0	3.885390	-2.124130	1.299749
3	6	0	2.832488	-1.368437	0.794039

4	6	0	3.066068	-0.418114	-0.201030
5	6	0	4.365596	-0.224672	-0.676770
6	6	0	5.414342	-0.991482	-0.185680
7	6	0	-2.541163	2.957240	-1.001645
8	6	0	-0.472634	1.130169	-0.747753
9	7	0	-1.488832	0.874768	-1.560468
10	6	0	-2.511224	1.763357	-1.662345
11	6	0	-3.306133	-2.768799	-0.338394
12	6	0	-2.111957	-2.093828	-0.049317
13	6	0	-1.749100	-1.826181	1.277662
14	6	0	-2.577157	-2.240566	2.310989
15	6	0	-3.759393	-2.920927	2.021818
16	6	0	-4.124598	-3.184713	0.700921
17	6	0	0.508864	3.699350	1.815512
18	6	0	0.538397	2.553670	1.061127
19	6	0	-0.446824	2.316871	0.069511
20	6	0	-1.493715	3.260316	-0.091908
21	6	0	-1.490949	4.445548	0.686678
22	6	0	-0.505951	4.663240	1.615484
23	6	0	-1.257016	-1.613167	-1.118595
24	8	0	-1.648061	-1.852550	-2.331338
25	6	0	0.167124	-1.207492	-0.869232
26	8	0	0.717225	-2.332392	-0.920469
27	6	0	1.993793	0.499457	-0.713614
28	8	0	2.315099	1.594992	-1.155091

29	6	0	0.575651	0.100203	-0.667291
30	1	0	5.994100	-2.538894	1.195835
31	1	0	3.700063	-2.858744	2.077359
32	1	0	1.826686	-1.515225	1.173909
33	1	0	4.527885	0.540493	-1.429079
34	1	0	6.419836	-0.845906	-0.568785
35	1	0	-3.358794	3.656830	-1.144800
36	1	0	-1.116261	-1.306157	-2.942387
37	1	0	-3.312390	1.475072	-2.338437
38	1	0	-3.576461	-2.961017	-1.371136
39	1	0	-0.829506	-1.284818	1.482026
40	1	0	-2.304741	-2.033657	3.340307
41	1	0	-4.404279	-3.245833	2.832731
42	1	0	-5.047799	-3.712473	0.486487
43	1	0	1.268935	3.867945	2.571515
44	1	0	1.315342	1.818177	1.231760
45	1	0	-2.288646	5.168869	0.541106
46	1	0	-0.510287	5.570646	2.211814

Optimized Cartesian coordinates for **ts-bNhn**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.619629	-1.958785	1.613215

2	6	0	3.427890	-1.445289	2.118005
3	6	0	2.317765	-1.315599	1.288450
4	6	0	2.394598	-1.710881	-0.048348
5	6	0	3.585899	-2.247417	-0.543758
6	6	0	4.697918	-2.362083	0.280614
7	6	0	0.292275	3.015412	1.352546
8	6	0	0.243757	0.596129	-0.000678
9	7	0	-0.742661	0.914399	0.834655
10	6	0	-0.726723	2.113752	1.467292
11	6	0	-4.620836	0.447598	-0.952080
12	6	0	-3.648182	-0.320188	-0.293732
13	6	0	-3.951110	-0.994265	0.898018
14	6	0	-5.231699	-0.895696	1.425551
15	6	0	-6.197701	-0.134236	0.769672
16	6	0	-5.896129	0.536874	-0.417629
17	6	0	3.335776	2.177511	-1.452093
18	6	0	2.319475	1.274977	-1.254004
19	6	0	1.322829	1.514811	-0.275364
20	6	0	1.357204	2.730243	0.456143
21	6	0	2.423539	3.638585	0.241084
22	6	0	3.396151	3.363546	-0.686416
23	6	0	-2.309898	-0.400678	-0.830293
24	8	0	-1.955694	0.249135	-1.853574
25	6	0	-1.176885	-1.344699	-0.367162
26	8	0	-1.443547	-2.468313	0.003731

27	6	0	1.211436	-1.640063	-0.973330
28	8	0	1.155138	-2.385648	-1.935205
29	6	0	0.094263	-0.696603	-0.681116
30	1	0	5.487472	-2.049337	2.259937
31	1	0	3.362343	-1.144948	3.159219
32	1	0	1.385316	-0.925169	1.686398
33	1	0	3.613483	-2.573168	-1.579234
34	1	0	5.625195	-2.769708	-0.110496
35	1	0	0.287816	3.942442	1.916915
36	1	0	-0.866164	-0.030035	-1.851505
37	1	0	-1.578191	2.307475	2.115104
38	1	0	-4.358959	0.961265	-1.871587
39	1	0	-3.183736	-1.581795	1.388685
40	1	0	-5.478125	-1.411309	2.347469
41	1	0	-7.197506	-0.060117	1.187139
42	1	0	-6.657075	1.125954	-0.918423
43	1	0	4.093057	1.983834	-2.204843
44	1	0	2.273033	0.378528	-1.863328
45	1	0	2.447993	4.559910	0.816653
46	1	0	4.208048	4.066264	-0.847826

Optimized Cartesian coordinates for **ts-aNhn**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	6	0	0.718670	5.245913	0.705170
2	6	0	0.785058	4.101553	1.497856
3	6	0	0.348748	2.881584	0.993948
4	6	0	-0.166502	2.800066	-0.300907
5	6	0	-0.246575	3.952357	-1.084619
6	6	0	0.203488	5.170061	-0.587379
7	6	0	-3.558533	-2.643341	-0.233886
8	6	0	-1.521457	-0.753711	-0.138732
9	7	0	-1.240161	-2.036122	-0.360999
10	6	0	-2.237459	-2.954933	-0.384861
11	6	0	3.338691	-2.757421	1.322696
12	6	0	2.861319	-1.771610	0.434903
13	6	0	3.689710	-1.312946	-0.608053
14	6	0	4.965389	-1.841321	-0.749875
15	6	0	5.434186	-2.800476	0.145093
16	6	0	4.621600	-3.256725	1.185189
17	6	0	-4.502419	1.294190	0.933509
18	6	0	-3.201821	0.959776	0.649707
19	6	0	-2.871582	-0.337604	0.183573
20	6	0	-3.906532	-1.304701	0.084470
21	6	0	-5.245536	-0.927881	0.359938
22	6	0	-5.538763	0.347706	0.767072
23	6	0	1.484781	-1.331977	0.567389
24	8	0	0.784697	-2.014033	1.405616

25	6	0	0.955777	-0.059006	-0.094777
26	8	0	1.878792	0.732515	-0.379381
27	6	0	-0.734285	1.525228	-0.856601
28	8	0	-1.496516	1.573353	-1.806298
29	6	0	-0.422021	0.210421	-0.209079
30	1	0	1.067596	6.197243	1.096191
31	1	0	1.181511	4.161295	2.506906
32	1	0	0.397199	1.984390	1.604385
33	1	0	-0.667315	3.868584	-2.081478
34	1	0	0.150348	6.062038	-1.204341
35	1	0	-4.328833	-3.403566	-0.316681
36	1	0	-0.171254	-1.823753	1.258049
37	1	0	-1.918680	-3.977732	-0.569848
38	1	0	2.695624	-3.116000	2.118442
39	1	0	3.321068	-0.551315	-1.281175
40	1	0	5.599655	-1.496783	-1.559475
41	1	0	6.437801	-3.199719	0.032166
42	1	0	4.990609	-4.004366	1.879073
43	1	0	-4.736502	2.291802	1.290785
44	1	0	-2.420206	1.695444	0.804168
45	1	0	-6.027937	-1.674765	0.256627
46	1	0	-6.565115	0.629456	0.982162

Optimized Cartesian coordinates for **ts-cOhn**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.759951	-0.607641	-0.185295
2	6	0	3.175379	-0.636735	-0.281784
3	6	0	3.919321	0.096858	0.674638
4	6	0	3.245595	0.803086	1.634872
5	7	0	1.895982	0.809577	1.765761
6	6	0	1.173173	0.122162	0.903011
7	6	0	0.989234	-1.259100	-1.181631
8	6	0	1.601129	-1.940715	-2.201921
9	6	0	3.013980	-2.006282	-2.271631
10	6	0	3.784671	-1.363824	-1.338063
11	6	0	-2.401677	-1.165215	1.742435
12	6	0	-0.959726	-1.069270	1.307713
13	6	0	-0.291137	0.135176	1.124615
14	6	0	-1.042900	1.339329	1.400050
15	8	0	-2.145219	1.288126	1.978099
16	8	0	-0.603109	-2.263897	1.228404
17	6	0	-0.546349	2.680599	0.956223
18	6	0	-1.007886	3.803756	1.646282
19	6	0	-0.618197	5.078992	1.254948
20	6	0	0.218413	5.242219	0.152919
21	6	0	0.660866	4.127494	-0.555893
22	6	0	0.284914	2.850324	-0.153950

23	6	0	-3.434359	-1.684696	0.868424
24	6	0	-3.110760	-2.196337	-0.397881
25	6	0	-4.126577	-2.614957	-1.243152
26	6	0	-5.458246	-2.514887	-0.838112
27	6	0	-5.782440	-2.003631	0.417791
28	6	0	-4.773653	-1.590992	1.275974
29	8	0	-2.704045	-1.065303	2.994255
30	1	0	5.004397	0.105867	0.631495
31	1	0	3.785184	1.395612	2.369560
32	1	0	-0.091853	-1.184250	-1.135384
33	1	0	1.004807	-2.432687	-2.964009
34	1	0	3.485648	-2.556954	-3.080041
35	1	0	4.869449	-1.391444	-1.397084
36	1	0	-1.676494	3.653942	2.487766
37	1	0	-0.969383	5.946862	1.804966
38	1	0	0.521267	6.237917	-0.157402
39	1	0	1.300646	4.252357	-1.424154
40	1	0	0.624506	1.986112	-0.717168
41	1	0	-2.068252	-2.306797	-0.675134
42	1	0	-3.883969	-3.024465	-2.217921
43	1	0	-6.249582	-2.838207	-1.507690
44	1	0	-6.820238	-1.923711	0.723270
45	1	0	-5.005876	-1.172660	2.249260
46	1	0	-2.088969	-0.418955	3.401002

Table S1. Calculated relative energies (all in kcal mol^{-1}, relative to isolated species) for the ZPE-corrected Gibbs free energies (ΔG_{gas}), Gibbs free energies for all species in solution phase (ΔG_{sol}) at 298 K by M06-2X/6-311++G(d,p)//M06-2X/6-31G(d) method and difference between the two.

Species	ΔG_{gas}	$\Delta G_{sol(THF)}$	$\Delta\Delta G_{sol-gas}$
[3 + 2]cycloaddition/ring-opening			
1a+2a	0.00	0.00	0.00
im1	-13.33	-7.58	5.75
ts-ca	2.31	9.38	7.07
I	-38.57	-37.32	1.25
ts-ro	-18.04	-29.08	-11.04
IId	-54.91	-63.78	-8.87
tautomerization			
IId	-54.91	-63.78	-8.87
ts-IIdb	-52.15	-53.87	-1.72
IIb	-87.95	-91.20	-3.25
ts-IIba	-48.46	-56.10	-7.64
IIa	-94.60	-90.71	3.89
ts-IIa	-80.88	-82.91	-2.03
IIa'	-87.83	-85.00	2.84
ts-IIa'e	-64.56	-60.37	4.18
IIe	-67.71	-62.80	4.92
ts-IIbc	-38.83	-40.38	-1.54
IIc	-93.53	-86.88	6.66
N-nucleophilic addition			
IIe	-67.71	-62.80	4.92
ts-eNnu	-60.54	-57.57	2.97
IIb	-95.31	-97.21	-1.90
ts-bNhn	-53.79	-53.02	0.77
IIa'	-87.83	-85.00	2.84
ts-aNhn	-52.04	-53.34	-1.30
3aa	-103.35	-101.31	2.04
O-nucleophilic addition			
IIc	-84.05	-81.23	2.82
ts-cOhn	-62.93	-67.13	-4.20
4aa	-96.71	-97.05	-0.34
[3 + 2]cycloaddition/ring-opening/tautomerization			
1a+2e	0.00	0.00	0.00
eim1	-12.15	-7.27	4.88
ts-eca	4.05	7.62	3.57
eI	-35.05	-34.02	1.03
ts-ero	-12.44	-21.60	-9.16
eIId	-45.86	-53.11	-7.25
ts-eIIdb	-57.64	-56.23	1.41

eIIb	-91.38	-94.91	-3.54
ts-eIIba	-48.26	-59.71	-11.45
eIIa	-92.45	-89.28	3.17
ts-eIIa	-75.49	-83.70	-8.21
eIIa'	-89.48	-86.45	3.03
ts-eIIa'e	-63.99	-58.89	5.09
eIIe	-64.28	-65.10	-0.82
N-nucleophilic addition			
eIIe	-64.28	-65.10	-0.82
ts-eeNnu	-56.38	-61.28	-4.90
eIIb	-91.38	-94.91	-3.54
ts-ebNhn	-58.26	-56.72	1.53
eIIa'	-89.48	-86.45	3.03
ts-eaNhn	-61.89	-65.20	-3.31
3ae	-101.67	-104.45	-2.77

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

TS	$\Delta G^{\neq}_{gas}$	$\Delta G^{\neq}_{sol}$	$\Delta\Delta G^{\neq}_{sol-gas}$
ts-ca (299i)	15.64	16.96	1.32
ts-ro (151i)	20.53	8.25	-12.29
ts-IIdb (792i)	2.77	9.91	7.15
ts-IIba (1782i)	39.49	35.10	-4.40
ts-IIbc (1857i)	49.12	50.82	1.70
ts-IIa (59i)	13.72	7.80	-5.92
ts-IIa'e (266i)	23.27	24.62	1.35
ts-eNnu (122i)	7.18	5.22	-1.96
ts-bNhn (810i)	41.53	44.19	2.67
ts-aNhn (130i)	35.79	31.66	-4.13
ts-cOhn (127i)	21.13	14.10	-7.03
ts-eca (93i)	16.20	14.89	-1.31
ts-ero (135i)	22.62	12.43	-10.19
ts-eIIdb (1110i)	-11.77	-3.12	8.66
ts-eIIba (1763i)	43.12	35.21	-7.91
ts-eIIa (44i)	16.97	5.59	-11.38
ts-eIIa'e (274i)	25.49	27.55	2.06
ts-eeNnu (343i)	7.90	3.82	-4.08
ts-ebNhn (1438i)	33.12	38.19	5.07
ts-eaNhn (131i)	27.59	21.25	-6.34

Figure S1. Evolution of bond lengths along the IRC for (a) **ts-ca** (b) **ts-ro** (c) **ts-eNnu** (d) **ts-bNhn** (e) **ts-aNhn** (f) **ts-cOhn** at the M06-2X/6-31G(d) level.

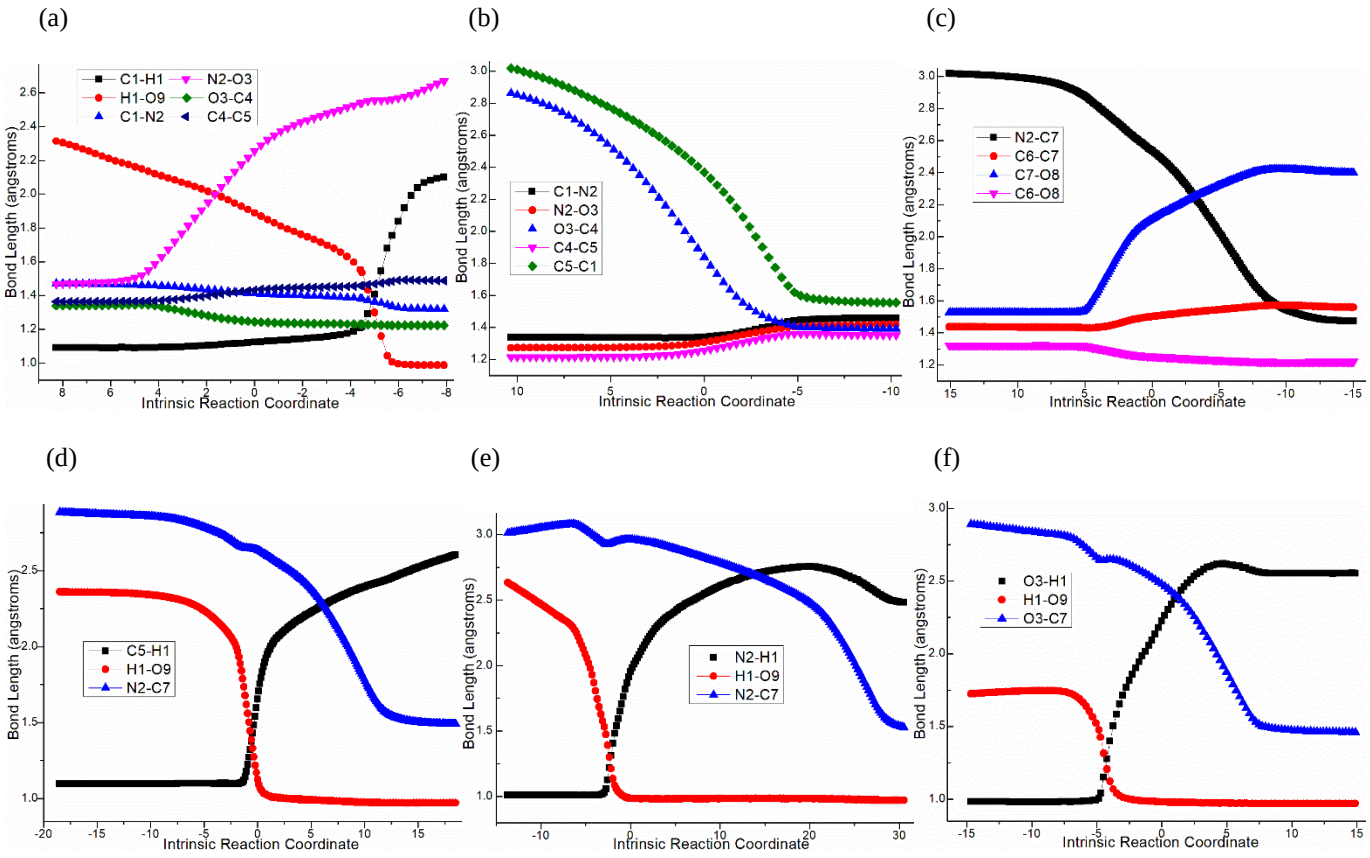

Figure S2. Optimized structures of typical stable compounds and intermediates proposed in **Scheme2** and **Figure 1, Figure 2, Figure 3**. Bond lengths are given in angstroms. Hydrogen atoms on methyl and benzene ring are removed for clarity.