Supplementary Information

Theoretical investigation of Cp*Co(III)-mediated regioselective [4 + 2]-annulation of N-chlorobenzamide with vinyl acetate for the synthesis of isoquinolone

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Software: GAUSSIAN09

Level of Theory: B3LYP

Basis Set: 6-31G(d)

Geometry [Cartesian coordinates]:

Optimized Cartesian coordinates for **ts-i12**

Sum of electronic and zero-point Energies= -1852.202223
Sum of electronic and thermal Energies= -1852.168619
Sum of electronic and thermal Enthalpies= -1852.167675
Sum of electronic and thermal Free Energies= -1852.269264

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.064723	-0.999977	-1.098283
2	6	0	3.224615	0.446171	-0.996132
3	6	0	3.411679	0.777689	0.364691
4	6	0	3.351275	-0.452510	1.132048
5	6	0	3.223186	-1.551885	0.199712
6	6	0	2.875702	-1.765067	-2.374610
7	1	0	3.849137	-2.015313	-2.817115
8	1	0	2.330676	-2.698140	-2.210802
9	1	0	2.321451	-1.182421	-3.115565
10	6	0	3.144228	-2.996674	0.583180
11	1	0	4.092412	-3.322173	1.029004
12	1	0	2.347697	-3.161549	1.315920
13	1	0	2.940509	-3.632427	-0.280956
14	6	0	3.533529	-0.578248	2.612977
15	1	0	4.601393	-0.568161	2.870026
16	1	0	3.051403	0.247696	3.142195
17	1	0	3.109183	-1.514126	2.986420
18	6	0	3.530023	2.169233	0.900533
19	1	0	4.450122	2.644438	0.536146
20	1	0	2.669829	2.751161	0.552184
21	1	0	3.550610	2.183130	1.992705
22	6	0	3.167655	1.429255	-2.119516
23	1	0	2.312588	2.097515	-1.960524
24	1	0	4.083054	2.034106	-2.136101
25	1	0	3.066988	0.937579	-3.089783
26	27	0	1.555068	-0.271834	0.222404
27	8	0	0.377090	-1.557766	1.107608
28	8	0	0.737785	2.149392	-0.553641
29	6	0	-0.075002	-0.616125	1.851204
30	8	0	0.510689	0.505664	1.725655
31	6	0	-0.317468	2.835778	-0.441697
32	8	0	-1.503899	2.398930	-0.517698

33	6	0	-1.240949	-0.820561	2.766577
34	1	0	-1.161495	-0.161143	3.634211
35	1	0	-2.156704	-0.565406	2.220792
36	1	0	-1.303566	-1.866017	3.077497
37	6	0	-0.158712	4.334192	-0.168125
38	1	0	-1.074621	4.877319	-0.412567
39	1	0	0.057180	4.480343	0.897987
40	1	0	0.683688	4.743274	-0.734826
41	6	0	-6.295665	-1.046467	0.197745
42	6	0	-6.434167	0.204073	0.805964
43	6	0	-5.359180	1.094565	0.810683
44	6	0	-4.143722	0.745767	0.217223
45	6	0	-4.001996	-0.512284	-0.391095
46	6	0	-5.087809	-1.400997	-0.397663
47	6	0	-2.742857	-1.009166	-1.062676
48	7	0	-1.650938	-0.182447	-0.916389
49	17	0	-0.217239	-0.673625	-1.749846
50	8	0	-2.704862	-2.091247	-1.635117
51	1	0	-7.129347	-1.743828	0.186087
52	1	0	-7.376696	0.484090	1.269754
53	1	0	-5.463771	2.072321	1.273588
54	1	0	-3.331537	1.465893	0.217868
55	1	0	-4.956495	-2.363855	-0.879400
56	1	0	-1.626611	0.891293	-0.762785

Optimized Cartesian coordinates for **ts-i23**

Sum of electronic and zero-point Energies= -1852.199347

Sum of electronic and thermal Energies= -1852.166445

Sum of electronic and thermal Enthalpies= -1852.165501

Sum of electronic and thermal Free Energies= -1852.263282

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.852621	0.495667	0.031425
2	6	0	2.974122	-0.082373	-1.313746
3	6	0	2.029045	0.506539	-2.137006
4	6	0	1.300464	1.478793	-1.351548
5	6	0	1.860678	1.542165	-0.049268
6	6	0	3.952464	0.409757	1.055874
7	1	0	4.824298	1.002629	0.743557
8	1	0	3.624754	0.790234	2.026109
9	1	0	4.290685	-0.622627	1.193328
10	6	0	1.668365	2.649469	0.948215
11	1	0	0.689595	3.124402	0.846689
12	1	0	1.755846	2.283882	1.973905
13	1	0	2.433726	3.425083	0.800609
14	6	0	0.244951	2.370190	-1.920667

15	1	0	-0.504680	1.802814	-2.482920
16	1	0	-0.272433	2.950606	-1.156053
17	1	0	0.705816	3.074676	-2.628892
18	6	0	1.698435	0.177873	-3.561180
19	1	0	1.759663	1.066247	-4.203531
20	1	0	2.378303	-0.572630	-3.973199
21	1	0	0.677243	-0.214164	-3.653724
22	6	0	3.921577	-1.190281	-1.642152
23	1	0	3.871706	-1.474508	-2.696504
24	1	0	4.958042	-0.905977	-1.417329
25	1	0	3.690368	-2.078346	-1.040995
26	27	0	1.016172	-0.409131	0.439299
27	8	0	1.668368	-1.955333	1.532785
28	8	0	0.798702	-1.893148	-1.327640
29	6	0	1.509303	-1.220214	2.551658
30	8	0	1.158788	-0.006830	2.312593
31	6	0	0.206040	-2.701761	-2.044498
32	8	0	-1.080687	-2.698244	-2.309854
33	6	0	1.666511	-1.725440	3.952915
34	1	0	0.709971	-2.153215	4.275608
35	1	0	2.422509	-2.513633	3.985616
36	1	0	1.929808	-0.909320	4.629806
37	6	0	0.932809	-3.847047	-2.712958
38	1	0	0.520741	-4.042200	-3.706264
39	1	0	2.001884	-3.638010	-2.771378
40	1	0	0.784291	-4.749242	-2.107623
41	6	0	-3.365524	3.110353	-0.543369
42	6	0	-2.954597	3.766496	0.620706
43	6	0	-2.172178	3.090060	1.561143
44	6	0	-2.187183	1.109274	0.162293
45	6	0	-2.985401	1.788885	-0.770491
46	6	0	-1.876222	-0.340129	-0.091994
47	7	0	-0.967666	-0.881185	0.771933
48	17	0	-1.223185	-2.640535	0.933663
49	8	0	-2.501881	-0.937338	-0.994986
50	1	0	-3.987008	3.627480	-1.269743
51	1	0	-3.255412	4.795344	0.801367
52	1	0	-1.868567	3.590244	2.477190
53	1	0	-1.604970	-2.031428	-1.744668
54	1	0	-3.310241	1.256314	-1.657978
55	6	0	-1.795917	1.764295	1.340015
56	1	0	-1.208482	1.223230	2.073480

Optimized Cartesian coordinates for **ts-i4B**

Sum of electronic and zero-point Energies= -1623.178853

Sum of electronic and thermal Energies= -1623.151351

Sum of electronic and thermal Enthalpies= -1623.150407

Sum of electronic and thermal Free Energies= -1623.235492

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.690530	0.268380	-0.052463
2	6	0	-1.941111	0.902953	-1.095622
3	6	0	-1.137380	-0.091435	-1.728520
4	6	0	-1.477994	-1.378839	-1.147896
5	6	0	-2.436957	-1.154270	-0.133916
6	6	0	-3.681855	0.908352	0.872094
7	1	0	-4.706950	0.774234	0.499572
8	1	0	-3.626724	0.464472	1.870648
9	1	0	-3.497702	1.979499	0.977423
10	6	0	-3.083323	-2.180996	0.743902
11	1	0	-4.156407	-2.250389	0.522982
12	1	0	-2.647194	-3.172910	0.598901
13	1	0	-2.974302	-1.910657	1.798749
14	6	0	-1.005106	-2.714027	-1.643592
15	1	0	-1.721315	-3.121321	-2.370569
16	1	0	-0.037082	-2.638789	-2.142803
17	1	0	-0.911359	-3.443272	-0.833207
18	6	0	-0.241295	0.118863	-2.912800
19	1	0	-0.780185	-0.101645	-3.844702
20	1	0	0.109764	1.152040	-2.972247
21	1	0	0.639737	-0.527214	-2.874494
22	6	0	-1.968700	2.359802	-1.442034
23	1	0	-1.004932	2.704260	-1.824997
24	1	0	-2.723704	2.543261	-2.218928
25	1	0	-2.217621	2.976008	-0.575943
26	27	0	-0.637878	-0.043321	0.372595
27	8	0	-0.934807	-0.554143	2.230506
28	6	0	0.036484	-0.848020	2.993992
29	8	0	1.232810	-0.972185	2.594852
30	6	0	-0.250737	-1.032662	4.465932
31	1	0	-1.283719	-1.350565	4.621743
32	1	0	0.446681	-1.750409	4.902962
33	1	0	-0.107702	-0.067421	4.965823
34	6	0	3.668385	-0.203156	-1.625961
35	6	0	3.123931	-1.470659	-1.379864
36	6	0	2.001815	-1.599862	-0.559676
37	6	0	1.401298	-0.470836	0.034316
38	6	0	1.979800	0.791436	-0.227116
39	6	0	3.103509	0.931300	-1.041597
40	6	0	1.358257	2.000022	0.421616
41	7	0	0.139325	1.627344	0.908141
42	17	0	-0.714665	2.822531	1.841642
43	8	0	1.907484	3.095093	0.490182
44	1	0	4.544335	-0.105968	-2.262601

45	1	0	3.587850	-2.353071	-1.814142
46	1	0	1.620837	-2.593843	-0.335419
47	1	0	1.203202	-0.716301	1.329205
48	1	0	3.517168	1.923237	-1.198316

Optimized Cartesian coordinates for **ts-i012**

Sum of electronic and zero-point Energies= -1251.192566
Sum of electronic and thermal Energies= -1251.176887
Sum of electronic and thermal Enthalpies= -1251.175943
Sum of electronic and thermal Free Energies= -1251.239001

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.055949	-0.938595	0.118247
2	6	0	-3.574013	-2.202779	-0.229889
3	6	0	-2.208593	-2.385148	-0.454461
4	6	0	-1.321660	-1.315488	-0.321755
5	6	0	-1.800111	-0.045929	0.035116
6	6	0	-3.175569	0.132782	0.245572
7	6	0	-0.937470	1.185074	0.209762
8	7	0	0.417021	0.907255	0.355289
9	17	0	1.405057	2.387130	0.513530
10	8	0	-1.436413	2.297944	0.290362
11	1	0	-5.118904	-0.786834	0.286180
12	1	0	-4.260139	-3.039387	-0.333266
13	1	0	-1.829490	-3.362339	-0.741847
14	1	0	-0.269168	-1.472855	-0.530012
15	1	0	-3.529761	1.125428	0.501907
16	1	0	1.122944	0.084429	-0.317891
17	6	0	3.674620	-2.231829	-0.944648
18	6	0	2.731396	-1.322696	-0.181382
19	8	0	1.874503	-0.691879	-0.911527
20	8	0	2.826328	-1.225745	1.064597
21	11	0	1.628341	0.165464	2.195240
22	1	0	4.305123	-2.799236	-0.258369
23	1	0	4.303768	-1.626416	-1.606461
24	1	0	3.101281	-2.912413	-1.581913

Optimized Cartesian coordinates for **ts-i034**

Sum of electronic and zero-point Energies= -1851.565321
Sum of electronic and thermal Energies= -1851.531212
Sum of electronic and thermal Enthalpies= -1851.530267
Sum of electronic and thermal Free Energies= -1851.632840

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

1	6	0	3.115670	0.705370	0.196360
2	6	0	2.708087	0.175993	-1.085261
3	6	0	1.653732	0.978244	-1.540769
4	6	0	1.430661	2.068869	-0.551166
5	6	0	2.308842	1.884214	0.506026
6	6	0	4.310589	0.278463	0.980516
7	1	0	5.183083	0.873779	0.671890
8	1	0	4.161846	0.445460	2.050913
9	1	0	4.546272	-0.774581	0.815768
10	6	0	2.472748	2.711938	1.745210
11	1	0	1.729087	3.511756	1.794070
12	1	0	2.358035	2.088313	2.638519
13	1	0	3.465678	3.179314	1.784350
14	6	0	0.532368	3.237985	-0.791418
15	1	0	-0.406843	2.950095	-1.266485
16	1	0	0.295173	3.767333	0.134039
17	1	0	1.030757	3.951714	-1.464411
18	6	0	0.972054	0.885976	-2.867310
19	1	0	1.565704	1.406144	-3.633692
20	1	0	0.855211	-0.157297	-3.167375
21	1	0	-0.017723	1.348853	-2.847109
22	6	0	3.351648	-0.979358	-1.793990
23	1	0	2.640242	-1.460920	-2.466526
24	1	0	4.225020	-0.649652	-2.373559
25	1	0	3.683739	-1.737142	-1.078878
26	27	0	1.066109	-0.232172	0.490416
27	8	0	2.094580	-1.910514	1.225254
28	8	0	0.337788	-1.934876	-1.745548
29	6	0	1.972630	-1.453679	2.406358
30	8	0	1.467616	-0.297673	2.572726
31	6	0	-0.247090	-3.021898	-1.795521
32	8	0	-1.450531	-3.289869	-1.417909
33	6	0	2.382731	-2.287476	3.594622
34	1	0	1.520052	-2.890078	3.902378
35	1	0	3.196006	-2.966630	3.328075
36	1	0	2.670318	-1.649369	4.433596
37	6	0	0.454594	-4.274378	-2.340698
38	1	0	-0.228982	-5.115477	-2.472185
39	1	0	0.923322	-4.019714	-3.296067
40	1	0	1.239944	-4.552041	-1.629869
41	6	0	-3.198535	2.503732	-2.013778
42	6	0	-3.270405	3.440503	-0.976478
43	6	0	-2.826119	3.099769	0.303090
44	6	0	-2.227356	0.888335	-0.489379
45	6	0	-2.695780	1.226786	-1.768517
46	6	0	-1.854278	-0.537876	-0.197432
47	7	0	-0.891722	-0.701111	0.747983
48	17	0	-1.015049	-2.282936	1.529259

49	8	0	-2.534158	-1.419536	-0.759552
50	1	0	-3.554932	2.763291	-3.007084
51	1	0	-3.683525	4.428051	-1.164515
52	1	0	-2.899152	3.819234	1.114433
53	1	0	-2.680402	0.471948	-2.548147
54	6	0	-2.299312	1.829768	0.547717
55	1	0	-1.968643	1.545165	1.541352

Optimized Cartesian coordinates for **ts-C1D**

Sum of electronic and zero-point Energies= -1700.510640

Sum of electronic and thermal Energies= -1700.481813

Sum of electronic and thermal Enthalpies= -1700.480868

Sum of electronic and thermal Free Energies= -1700.568329

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	9.948776	12.678878	5.245390
2	6	0	8.601456	12.693979	4.704774
3	6	0	7.774592	13.396925	5.632806
4	6	0	8.568909	13.719917	6.776264
5	6	0	9.931981	13.321352	6.507109
6	6	0	11.153320	12.128560	4.543356
7	1	0	11.569444	12.882276	3.860400
8	1	0	11.941604	11.848130	5.247034
9	1	0	10.904289	11.243381	3.953930
10	6	0	11.121432	13.595782	7.377624
11	1	0	11.531172	14.592786	7.164870
12	1	0	10.867324	13.558648	8.439963
13	1	0	11.919725	12.867890	7.208585
14	6	0	8.106601	14.548445	7.941930
15	1	0	8.030350	15.606306	7.655255
16	1	0	7.117511	14.243110	8.301175
17	1	0	8.802495	14.489665	8.781911
18	6	0	6.344537	13.794522	5.414871
19	1	0	5.819584	13.960942	6.361792
20	1	0	6.301823	14.739857	4.856272
21	1	0	5.794442	13.041624	4.844930
22	6	0	8.209428	12.292097	3.312850
23	1	0	8.836408	11.480321	2.939698
24	1	0	7.169952	11.959210	3.268962
25	1	0	8.324134	13.145518	2.629024
26	27	0	8.583948	11.557423	6.507992
27	6	0	11.211539	10.294961	10.277722
28	6	0	10.303604	11.331566	10.515529
29	6	0	9.325464	11.644859	9.568561
30	6	0	9.250698	10.942128	8.355902
31	6	0	10.170953	9.902035	8.129970

32	6	0	11.140100	9.580250	9.082729
33	6	0	10.135313	9.158024	6.828267
34	7	0	9.314049	9.838443	5.981325
35	17	0	9.131625	9.096125	4.411328
36	8	0	10.763728	8.122715	6.622425
37	1	0	11.962029	10.043900	11.022266
38	1	0	10.344202	11.889646	11.447932
39	1	0	8.602713	12.423170	9.798896
40	1	0	11.823372	8.767167	8.855071
41	6	0	6.751892	10.771558	6.704131
42	6	0	7.314468	10.626473	8.007314
43	1	0	6.023581	11.548699	6.508286
44	1	0	6.961333	11.327436	8.756301
45	1	0	7.425315	9.606346	8.361976
46	8	0	6.454382	9.573208	6.044756
47	6	0	5.724271	9.635881	4.901835
48	8	0	5.332566	10.674213	4.409905
49	6	0	5.467397	8.253563	4.360890
50	1	0	6.420774	7.790569	4.087171
51	1	0	5.004896	7.624203	5.127997
52	1	0	4.817510	8.320070	3.487659

Optimized Cartesian coordinates for **ts-DE**

Sum of electronic and zero-point Energies= -1700.498398

Sum of electronic and thermal Energies= -1700.469190

Sum of electronic and thermal Enthalpies= -1700.468246

Sum of electronic and thermal Free Energies= -1700.557229

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.390800	-7.105493	0.355487
2	6	0	1.346152	-7.045882	1.335781
3	6	0	0.306859	-6.182381	0.826873
4	6	0	0.710199	-5.727639	-0.468780
5	6	0	2.009443	-6.265992	-0.747124
6	6	0	3.668328	-7.869462	0.516765
7	1	0	4.353706	-7.695518	-0.316968
8	1	0	4.174195	-7.581710	1.446321
9	1	0	3.463060	-8.947408	0.562080
10	6	0	2.812872	-6.042286	-1.995719
11	1	0	2.574324	-6.801919	-2.752424
12	1	0	2.608745	-5.064504	-2.442601
13	1	0	3.887376	-6.101735	-1.799453
14	6	0	-0.101541	-4.844492	-1.370085
15	1	0	-0.914591	-5.421732	-1.830189
16	1	0	-0.546473	-4.013897	-0.816703
17	1	0	0.501203	-4.431642	-2.184897

18	6	0	-0.991495	-5.859469	1.503201
19	1	0	-1.778618	-6.550478	1.170158
20	1	0	-0.909160	-5.951489	2.589541
21	1	0	-1.312210	-4.840086	1.277339
22	6	0	1.374841	-7.753444	2.654817
23	1	0	1.353960	-8.840825	2.502059
24	1	0	2.288676	-7.503574	3.206896
25	1	0	0.516339	-7.485257	3.275248
26	27	0	2.111935	-5.140650	1.042499
27	6	0	6.612565	-1.451404	3.459496
28	6	0	6.821277	-1.055651	2.135642
29	6	0	5.916284	-1.431049	1.144089
30	6	0	4.803880	-2.229391	1.438952
31	6	0	4.610918	-2.631474	2.772763
32	6	0	5.500800	-2.224593	3.775576
33	6	0	3.423043	-3.436162	3.180829
34	7	0	2.995575	-4.390643	2.206779
35	17	0	4.449837	-5.920141	3.508509
36	8	0	2.776704	-3.235756	4.188949
37	1	0	7.309797	-1.155276	4.237999
38	1	0	7.681592	-0.444187	1.876788
39	1	0	6.070494	-1.093675	0.121240
40	1	0	5.309794	-2.544419	4.794547
41	6	0	2.439851	-2.980774	0.697722
42	6	0	3.849652	-2.586879	0.309358
43	1	0	1.801009	-3.165639	-0.167479
44	1	0	4.264307	-3.415140	-0.280149
45	1	0	3.788208	-1.724150	-0.371921
46	8	0	1.871317	-1.995253	1.522361
47	6	0	0.521193	-1.960532	1.695760
48	8	0	-0.246656	-2.644444	1.054480
49	6	0	0.157307	-0.991261	2.786816
50	1	0	0.523389	-1.387760	3.740742
51	1	0	0.647316	-0.026508	2.623990
52	1	0	-0.925461	-0.867082	2.823274

Optimized Cartesian coordinates for **a-ts-i56**

Sum of electronic and zero-point Energies= -1929.650518

Sum of electronic and thermal Energies= -1929.616302

Sum of electronic and thermal Enthalpies= -1929.615358

Sum of electronic and thermal Free Energies= -1929.717202

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-5.473456	4.895041	1.827344
2	6	0	-6.003448	3.968922	0.915153
3	6	0	-5.361990	2.670381	1.149756

4	6	0	-4.496647	2.801644	2.259409
5	6	0	-4.480040	4.204624	2.631366
6	6	0	-5.782072	6.355420	1.949451
7	1	0	-6.258424	6.568300	2.914750
8	1	0	-4.861792	6.945291	1.891850
9	1	0	-6.454279	6.697217	1.159049
10	6	0	-3.766076	4.826221	3.786638
11	1	0	-4.485553	4.995893	4.601720
12	1	0	-2.951116	4.201580	4.145525
13	1	0	-3.337329	5.791724	3.505633
14	6	0	-3.686329	1.732138	2.919181
15	1	0	-4.200368	1.387570	3.826955
16	1	0	-3.545678	0.869089	2.264927
17	1	0	-2.704544	2.116268	3.203841
18	6	0	-5.674100	1.421198	0.382494
19	1	0	-6.641169	1.008437	0.700812
20	1	0	-5.734066	1.617699	-0.692129
21	1	0	-4.915115	0.652008	0.545272
22	6	0	-7.056954	4.217734	-0.116567
23	1	0	-6.790075	3.782112	-1.082749
24	1	0	-7.999853	3.755582	0.207702
25	1	0	-7.238318	5.284521	-0.264452
26	27	0	-3.814925	4.073900	0.711741
27	6	0	2.615143	2.912256	1.447478
28	6	0	2.813540	1.983112	0.421344
29	6	0	1.728160	1.517342	-0.322842
30	6	0	0.437228	1.977592	-0.050602
31	6	0	0.242511	2.913381	0.975561
32	6	0	1.330230	3.372879	1.726311
33	6	0	-1.136919	3.409722	1.303202
34	7	0	-2.148523	3.142779	0.427218
35	17	0	-4.928885	3.396518	-2.895551
36	8	0	-1.335826	4.004064	2.373516
37	1	0	3.460813	3.274241	2.026196
38	1	0	3.814881	1.623487	0.198463
39	1	0	1.883138	0.795388	-1.121350
40	1	0	1.142927	4.087603	2.520758
41	6	0	-1.849808	2.587306	-0.862836
42	6	0	-0.778629	1.494168	-0.793114
43	1	0	-2.757104	2.185570	-1.320495
44	1	0	-1.226578	0.637523	-0.267131
45	1	0	-0.542956	1.161567	-1.805843
46	6	0	-2.418889	7.600648	-0.985109
47	1	0	-2.305380	8.143456	-0.043990
48	1	0	-2.924345	8.218483	-1.730564
49	1	0	-1.416217	7.359344	-1.357663
50	6	0	-3.173483	6.300048	-0.779466
51	8	0	-3.024316	5.759518	0.374873

52	8	0	-3.862043	5.842140	-1.721009
53	1	0	-4.424201	4.503003	-2.282957
54	8	0	-1.410861	3.693574	-1.731562
55	6	0	-1.355200	3.467412	-3.066261
56	8	0	-1.521652	2.382117	-3.581884
57	6	0	-1.074789	4.751831	-3.811637
58	1	0	-0.951808	4.536988	-4.873906
59	1	0	-1.914433	5.439490	-3.664093
60	1	0	-0.173807	5.233887	-3.418053

Optimized Cartesian coordinates for **a-ts-i67**

Sum of electronic and zero-point Energies= -1929.648119

Sum of electronic and thermal Energies= -1929.613267

Sum of electronic and thermal Enthalpies= -1929.612323

Sum of electronic and thermal Free Energies= -1929.717105

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-5.683335	4.821210	1.492249
2	6	0	-6.044255	3.827954	0.550337
3	6	0	-5.599639	2.536637	1.052004
4	6	0	-4.987826	2.754639	2.320579
5	6	0	-4.949491	4.171258	2.560751
6	6	0	-6.021091	6.278035	1.439664
7	1	0	-6.904278	6.468510	2.065204
8	1	0	-5.204378	6.892179	1.827116
9	1	0	-6.235114	6.611964	0.424427
10	6	0	-4.367256	4.830835	3.773969
11	1	0	-4.985190	4.628309	4.659266
12	1	0	-3.353808	4.464559	3.962012
13	1	0	-4.310825	5.913961	3.644705
14	6	0	-4.411598	1.727140	3.243730
15	1	0	-5.118893	1.530775	4.061254
16	1	0	-4.216780	0.781003	2.733952
17	1	0	-3.473929	2.080627	3.679083
18	6	0	-5.887501	1.214672	0.403203
19	1	0	-6.962079	0.993893	0.452911
20	1	0	-5.587941	1.207501	-0.649154
21	1	0	-5.363138	0.399549	0.909926
22	6	0	-6.779893	4.047245	-0.735915
23	1	0	-6.523034	3.284888	-1.476426
24	1	0	-7.864100	3.990833	-0.566855
25	1	0	-6.555422	5.029769	-1.158633
26	27	0	-3.893096	3.812108	0.818576
27	6	0	2.364310	4.239532	0.871431
28	6	0	2.516380	3.612868	-0.370993
29	6	0	1.477643	2.851794	-0.905679

30	6	0	0.274051	2.712237	-0.207839
31	6	0	0.118914	3.351788	1.031501
32	6	0	1.169120	4.108224	1.570242
33	6	0	-1.174457	3.286227	1.771802
34	7	0	-2.281091	2.714118	1.122688
35	17	0	-4.501497	8.705240	-2.481274
36	8	0	-1.289086	3.709339	2.914705
37	1	0	3.176147	4.830079	1.286504
38	1	0	3.446465	3.718121	-0.922974
39	1	0	1.601835	2.360598	-1.868002
40	1	0	1.017052	4.587728	2.531385
41	6	0	-2.168791	2.110430	-0.066255
42	6	0	-0.841123	1.839482	-0.715838
43	1	0	-2.960744	1.425834	-0.348344
44	1	0	-0.613730	0.779887	-0.508757
45	1	0	-0.960330	1.899526	-1.803101
46	6	0	-1.905299	7.388647	-0.057435
47	1	0	-1.419188	7.477101	0.916248
48	1	0	-2.319570	8.349884	-0.371148
49	1	0	-1.146667	7.092909	-0.792299
50	6	0	-2.985996	6.321791	-0.027615
51	8	0	-2.810116	5.395763	0.846862
52	8	0	-3.954566	6.364485	-0.821955
53	1	0	-4.193806	7.618631	-1.707245
54	8	0	-3.095224	3.490107	-1.074747
55	6	0	-3.742836	3.063270	-2.166556
56	8	0	-4.178777	1.925217	-2.291212
57	6	0	-3.829982	4.108072	-3.259166
58	1	0	-4.477641	3.758018	-4.065294
59	1	0	-4.185241	5.054706	-2.845332
60	1	0	-2.824891	4.293791	-3.656938

Optimized Cartesian coordinates for **ts-C2G**

Sum of electronic and zero-point Energies= -1625.283549

Sum of electronic and thermal Energies= -1625.255801

Sum of electronic and thermal Enthalpies= -1625.254857

Sum of electronic and thermal Free Energies= -1625.339091

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.908663	-1.004397	-1.712019
2	6	0	2.056614	-0.733908	-0.868150
3	6	0	2.002090	-1.638219	0.233863
4	6	0	0.787974	-2.389361	0.138216
5	6	0	0.142316	-2.032874	-1.104555
6	6	0	0.627579	-0.360938	-3.035840
7	1	0	1.182536	-0.877508	-3.831318

8	1	0	-0.434589	-0.406833	-3.291003
9	1	0	0.927480	0.689228	-3.044155
10	6	0	-1.086174	-2.664284	-1.687733
11	1	0	-0.808716	-3.414755	-2.440326
12	1	0	-1.689217	-3.161790	-0.925697
13	1	0	-1.725274	-1.923082	-2.176203
14	6	0	0.386617	-3.504927	1.061762
15	1	0	0.976263	-4.409315	0.858995
16	1	0	0.548728	-3.244613	2.113505
17	1	0	-0.666443	-3.770632	0.942286
18	6	0	3.080984	-1.793848	1.264169
19	1	0	3.464069	-0.821843	1.589282
20	1	0	2.732949	-2.342437	2.144992
21	1	0	3.917161	-2.364398	0.836561
22	6	0	3.219427	0.161609	-1.179756
23	1	0	2.992096	0.845739	-1.998238
24	1	0	3.505547	0.760556	-0.309513
25	1	0	4.089013	-0.442506	-1.474747
26	27	0	0.279675	-0.277032	0.221859
27	6	0	-4.458936	-0.513897	-0.121405
28	6	0	-3.882569	-1.482623	0.707531
29	6	0	-2.539037	-1.386656	1.074945
30	6	0	-1.740207	-0.331044	0.607182
31	6	0	-2.333729	0.634323	-0.226680
32	6	0	-3.680912	0.544821	-0.587084
33	6	0	-1.491502	1.743467	-0.784113
34	7	0	-0.188232	1.492725	-0.458820
35	17	0	0.938379	2.671338	-1.090389
36	8	0	-1.953264	2.692239	-1.411886
37	1	0	-5.508167	-0.583650	-0.395084
38	1	0	-4.483831	-2.307549	1.082145
39	1	0	-2.126413	-2.127755	1.755587
40	1	0	-4.085765	1.316675	-1.235197
41	6	0	0.791631	0.382285	2.076282
42	6	0	-0.630949	0.300498	2.170234
43	1	0	1.347339	-0.451377	2.494448
44	1	0	-1.028277	-0.475071	2.815907
45	1	0	-1.190304	1.229230	2.202720
46	6	0	1.599467	1.634680	2.097078
47	8	0	2.823887	1.553620	2.060776
48	6	0	0.911300	2.972357	2.289304
49	1	0	1.636168	3.773408	2.135625
50	1	0	0.067275	3.103416	1.608860
51	1	0	0.529257	3.031339	3.318141

Optimized Cartesian coordinates for **ts-GH**

Sum of electronic and zero-point Energies= -1625.263781

Sum of electronic and thermal Energies= -1625.235196

Sum of electronic and thermal Enthalpies= -1625.234252
Sum of electronic and thermal Free Energies= -1625.322337

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.073957	2.492997	4.032467
2	6	0	-1.926144	3.451988	3.395609
3	6	0	-3.131234	2.771991	2.980485
4	6	0	-3.016143	1.401218	3.365235
5	6	0	-1.730742	1.216923	3.980447
6	6	0	0.286250	2.792122	4.582036
7	1	0	0.788208	1.888967	4.938463
8	1	0	0.915697	3.259309	3.815437
9	1	0	0.208617	3.488768	5.427192
10	6	0	-1.197940	-0.072263	4.535810
11	1	0	-1.500188	-0.197268	5.584437
12	1	0	-1.573134	-0.940740	3.985321
13	1	0	-0.105328	-0.104048	4.503270
14	6	0	-4.061509	0.338715	3.182936
15	1	0	-4.714281	0.293445	4.064997
16	1	0	-4.700080	0.533655	2.316550
17	1	0	-3.622430	-0.656436	3.059335
18	6	0	-4.312550	3.424566	2.325555
19	1	0	-4.937347	3.925851	3.077310
20	1	0	-4.003516	4.179939	1.597285
21	1	0	-4.945074	2.699716	1.806008
22	6	0	-1.611285	4.905382	3.222164
23	1	0	-1.567546	5.402704	4.200455
24	1	0	-0.642354	5.034654	2.727551
25	1	0	-2.370496	5.412915	2.621847
26	27	0	-1.449479	1.958478	2.018572
27	6	0	3.143550	0.828786	-2.143902
28	6	0	3.116388	-0.465443	-1.616435
29	6	0	2.085674	-0.851285	-0.761482
30	6	0	1.074822	0.043191	-0.389719
31	6	0	1.123564	1.347164	-0.912670
32	6	0	2.138865	1.726263	-1.802013
33	6	0	0.070502	2.349503	-0.599838
34	7	0	-0.456057	2.272544	0.735770
35	17	0	1.240993	3.912797	1.249819
36	8	0	-0.416753	3.117680	-1.402338
37	1	0	3.939278	1.131650	-2.818291
38	1	0	3.890605	-1.179966	-1.883281
39	1	0	2.054087	-1.871256	-0.384475
40	1	0	2.130024	2.736915	-2.196581
41	6	0	-1.326141	0.352613	0.533390
42	6	0	-0.033219	-0.447665	0.528689

43	1	0	-2.012645	-0.028214	1.301431
44	1	0	0.347197	-0.491202	1.557659
45	1	0	-0.272378	-1.481105	0.241305
46	6	0	-2.083797	0.410699	-0.769982
47	8	0	-1.694415	-0.238473	-1.726833
48	6	0	-3.326127	1.275295	-0.850074
49	1	0	-3.018906	2.306630	-1.060880
50	1	0	-3.958358	0.923107	-1.668597
51	1	0	-3.887977	1.281493	0.089265

Optimized Cartesian coordinates for **b-ts-i56**

Sum of electronic and zero-point Energies= -2083.413018

Sum of electronic and thermal Energies= -2083.373417

Sum of electronic and thermal Enthalpies= -2083.372472

Sum of electronic and thermal Free Energies= -2083.486529

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.886008	5.406094	1.483292
2	6	0	0.984080	6.431581	1.395327
3	6	0	-0.219065	6.025103	2.119382
4	6	0	0.004508	4.794304	2.768420
5	6	0	1.273373	4.297596	2.288539
6	6	0	3.234103	5.292771	0.854294
7	1	0	3.271197	4.401308	0.219479
8	1	0	3.479119	6.170309	0.250066
9	1	0	4.016417	5.175447	1.617711
10	6	0	2.129596	3.306331	3.030101
11	1	0	2.699028	3.820393	3.820316
12	1	0	1.535320	2.526289	3.513235
13	1	0	2.840468	2.823597	2.357190
14	6	0	-0.843382	4.175362	3.854143
15	1	0	-1.837402	4.629954	3.891928
16	1	0	-0.998342	3.098777	3.727725
17	1	0	-0.374063	4.322355	4.837633
18	6	0	-1.452889	6.867722	2.188812
19	1	0	-1.250499	7.798675	2.736756
20	1	0	-1.781530	7.163164	1.184478
21	1	0	-2.280756	6.356629	2.686109
22	6	0	1.083611	7.698851	0.599590
23	1	0	0.804940	8.579264	1.193413
24	1	0	2.100953	7.859551	0.232573
25	1	0	0.422776	7.673888	-0.278159
26	27	0	-0.227021	3.625194	0.961697
27	6	0	3.158208	-1.594885	-1.414751
28	6	0	2.114823	-2.524236	-1.472151
29	6	0	0.837560	-2.169539	-1.037079

30	6	0	0.587215	-0.886229	-0.540043
31	6	0	1.635267	0.045773	-0.487013
32	6	0	2.916857	-0.314937	-0.923821
33	6	0	1.428266	1.444335	0.032853
34	7	0	0.149099	1.816999	0.423771
35	17	0	0.178200	4.512123	-1.055506
36	8	0	2.399126	2.191900	0.149865
37	1	0	4.152908	-1.868698	-1.755451
38	1	0	2.294917	-3.523378	-1.860279
39	1	0	0.025995	-2.892233	-1.085239
40	1	0	3.703899	0.429335	-0.869469
41	6	0	-0.999533	1.052901	-0.112186
42	6	0	-0.768886	-0.474843	-0.031336
43	1	0	-1.860595	1.283494	0.514553
44	1	0	-0.875166	-0.777717	1.017752
45	1	0	-1.569710	-0.988584	-0.577630
46	6	0	-0.671648	-0.677440	4.927235
47	1	0	0.034822	-0.239724	5.641009
48	1	0	-0.275856	-1.656860	4.640144
49	1	0	-1.649478	-0.789139	5.396584
50	6	0	-0.787818	0.213495	3.713742
51	8	0	-1.803001	0.781014	3.356708
52	8	0	0.383835	0.320719	3.057612
53	1	0	0.254682	0.911280	2.271690
54	6	0	-1.446529	1.441644	-1.546707
55	8	0	-2.623352	1.711735	-1.728233
56	6	0	-0.466953	1.413347	-2.700499
57	1	0	-0.099609	0.393802	-2.865116
58	1	0	-0.975997	1.767298	-3.599669
59	1	0	0.399496	2.048080	-2.495279
60	8	0	-2.869539	4.790454	-1.038468
61	6	0	-3.159111	4.018337	-0.012318
62	8	0	-2.308863	3.563046	0.764193
63	6	0	-4.617981	3.703818	0.137311
64	1	0	-5.237776	4.519373	-0.241469
65	1	0	-4.810816	2.807954	-0.464269
66	1	0	-4.850169	3.483744	1.180628
67	1	0	-1.877205	4.830613	-1.144038

Optimized Cartesian coordinates for **b-ts-i67**

Sum of electronic and zero-point Energies= -2083.443257

Sum of electronic and thermal Energies= -2083.405427

Sum of electronic and thermal Enthalpies= -2083.404482

Sum of electronic and thermal Free Energies= -2083.511665

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

1	6	0	2.091031	4.137508	1.818806
2	6	0	1.239210	4.888898	0.922668
3	6	0	0.102338	5.341780	1.688359
4	6	0	0.133572	4.692188	2.952959
5	6	0	1.385686	3.961908	3.035985
6	6	0	3.532038	3.771990	1.632489
7	1	0	3.866320	3.945740	0.613039
8	1	0	4.130311	4.389928	2.318333
9	1	0	3.731658	2.724419	1.872411
10	6	0	1.919557	3.278947	4.257792
11	1	0	2.538517	3.979850	4.835042
12	1	0	1.115944	2.939237	4.916383
13	1	0	2.549651	2.422118	4.002387
14	6	0	-0.863725	4.822461	4.064519
15	1	0	-1.819103	5.210526	3.702773
16	1	0	-1.053191	3.854439	4.537621
17	1	0	-0.497828	5.510336	4.838380
18	6	0	-0.927248	6.297963	1.196581
19	1	0	-0.505316	7.312396	1.245482
20	1	0	-1.204413	6.118885	0.149494
21	1	0	-1.830997	6.288106	1.811233
22	6	0	1.567853	5.343896	-0.464818
23	1	0	0.659041	5.469232	-1.064210
24	1	0	2.081699	6.315628	-0.430806
25	1	0	2.217965	4.621731	-0.960372
26	27	0	0.122374	3.153042	1.504421
27	6	0	3.112063	-0.805992	-3.187911
28	6	0	2.235351	-1.893673	-3.127777
29	6	0	1.167677	-1.884372	-2.229762
30	6	0	0.961719	-0.790879	-1.383790
31	6	0	1.843620	0.300034	-1.445240
32	6	0	2.915975	0.286387	-2.348020
33	6	0	1.688243	1.493026	-0.540290
34	7	0	0.581831	1.545863	0.306153
35	17	0	-1.999291	5.628363	-2.123670
36	8	0	2.571691	2.346831	-0.518581
37	1	0	3.941066	-0.810697	-3.889975
38	1	0	2.379132	-2.746324	-3.786141
39	1	0	0.482064	-2.727503	-2.189754
40	1	0	3.579889	1.143614	-2.372955
41	6	0	-0.586207	0.717486	-0.091817
42	6	0	-0.166826	-0.741264	-0.387334
43	1	0	-1.266286	0.693632	0.760567
44	1	0	0.147726	-1.216977	0.552497
45	1	0	-1.041238	-1.295132	-0.745000
46	6	0	-0.440511	0.000646	4.423190
47	1	0	-0.941078	-0.916108	4.091018
48	1	0	-1.122713	0.577203	5.048947

49	1	0	0.443520	-0.299989	4.993038
50	6	0	-0.024898	0.796669	3.215571
51	8	0	-0.619429	1.855628	2.907845
52	8	0	0.955941	0.310312	2.519921
53	1	0	0.968854	0.843630	1.565531
54	6	0	-1.484103	1.215376	-1.257865
55	8	0	-2.648284	0.846108	-1.219313
56	6	0	-0.960357	2.059970	-2.390311
57	1	0	0.077162	1.840487	-2.650064
58	1	0	-1.604137	1.910267	-3.260483
59	1	0	-1.027292	3.123705	-2.118622
60	8	0	-3.512233	4.122526	-0.212597
61	6	0	-2.784511	3.432473	0.592884
62	8	0	-1.531902	3.419944	0.491605
63	6	0	-3.541323	2.599781	1.592708
64	1	0	-3.761180	1.642598	1.102887
65	1	0	-2.939279	2.408294	2.481681
66	1	0	-4.489236	3.077591	1.848478
67	1	0	-2.930866	4.672082	-0.942309

Table S1. Calculated relative energies (all in kcal mol^{-1}, relative to isolated species) for the ZPE-corrected Gibbs free energies (ΔG_{gas}), Gibbs free energies for all species in solution phase (ΔG_{sol}) at 298 K by B3LYP/6-311++G(d,p)//B3LYP/6-31G(d) method and difference between absolute energy.

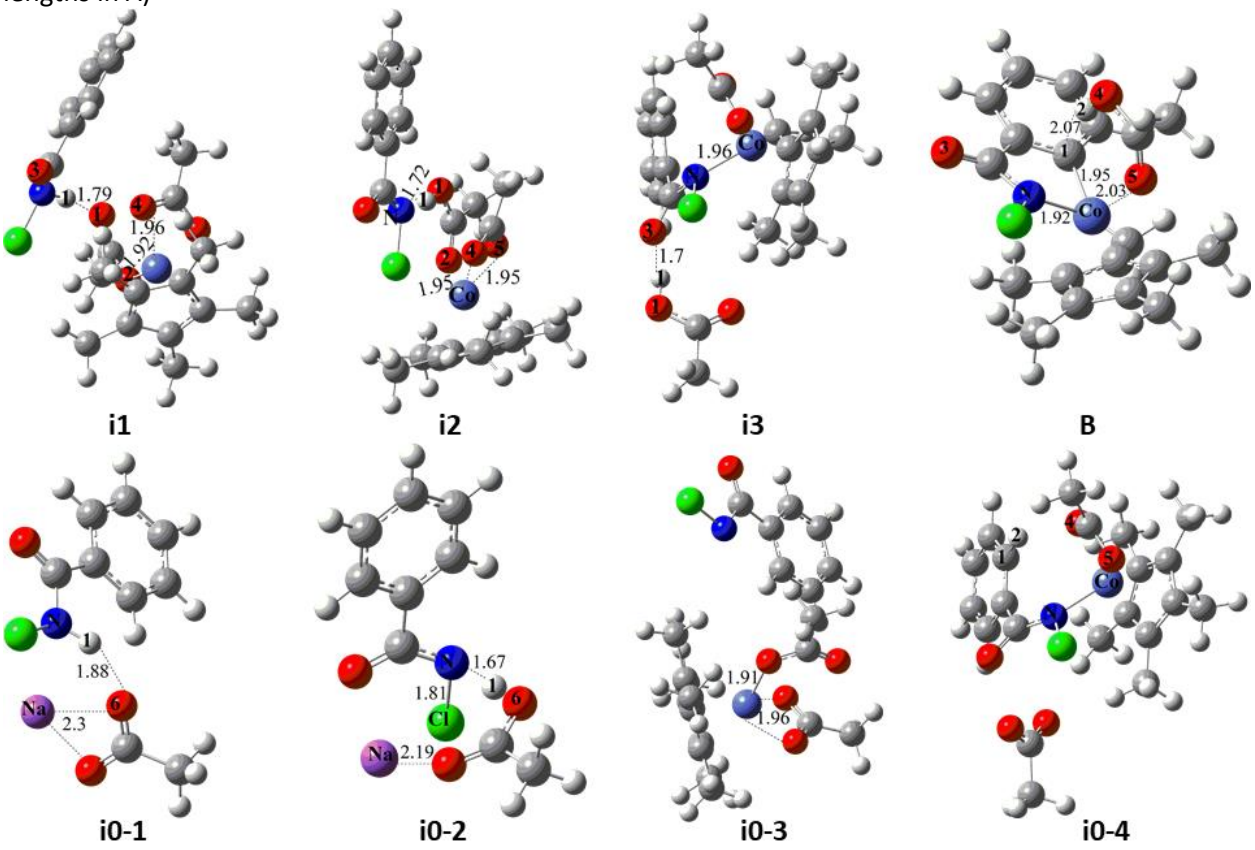
Species	ΔG_{gas}	ΔG_{sol}	$\Delta\Delta G_{sol-gas}$
1+A			
i1	0.00	0.00	0.00
ts-i12	30.13	26.12	-4.01
i2	19.96	15.37	-4.60
ts-i23	35.09	36.67	1.58
i3	0.55	2.21	1.66
1+A-hoac			
i4	0.00	0.00	0.00
ts-i4B	17.62	18.89	1.27
B	6.30	8.46	2.16
1+naoac			
i0-1	0.00	0.00	0.00
ts-i012	1.50	1.86	0.37
i0-2	-9.43	-3.59	5.84
1-h+A			
i0-3	0.00	0.00	0.00
ts-i034	23.97	21.67	-2.30
i0-4	17.92	14.73	-3.19
B+2a-hoac			
C1	0.00	0.00	0.00
ts-C1D	9.02	9.65	0.63
D	-10.74	-11.71	-0.97
ts-DE	19.09	13.14	-5.96
E	-81.84	-82.99	-1.15
E+hoac			
a-i5	0.00	0.00	0.00
a-ts-i56	22.13	20.03	-2.10
a-i6	7.09	10.41	3.31
a-ts-i67	24.06	25.81	1.75
a-i7	10.62	8.69	-1.93
a-i7-1	-0.58	3.74	4.32
B+2a-A-hcl	0.00	0.00	0.00
F	16.40	2.15	-14.25
3a	-6.43	-19.07	-12.64
F+oac			
i8	0.00	0.00	0.00
ts-i89	9.31	6.81	-2.50
i9	-41.83	-39.36	2.48
ts-i910	-25.02	-31.15	-6.13

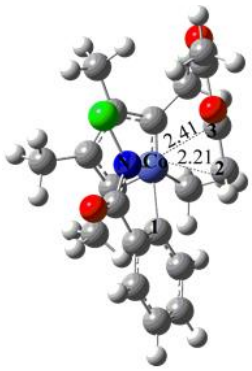
i10	-42.82	-55.37	-12.55
B+2b-hoac			
C2	0.00	0.00	0.00
ts-C2G	5.75	5.80	0.04
G	-17.27	-16.34	0.94
ts-GH	20.30	12.06	-8.24
H	-79.76	-78.80	0.96
B+2b+hoac			
b-i5	0.00	0.00	0.00
b-ts-i56	42.43	40.08	-2.35
b-i6	22.41	15.12	-7.29
b-ts-i67	25.58	18.03	-7.54
b-i7	19.03	15.54	-3.49
b-i7-1	-2.24	-6.33	-4.10
B+2b+hoac-A-hcl	0.00	0.00	0.00
I	-7.50	-19.74	-12.24
I-2h	0.00	0.00	0.00
3b	-76.35	-85.71	-9.36

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

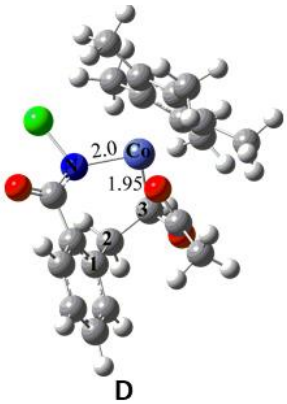
TS	energy level (global barrier)		activation energy (local barrier)	
	$\Delta G^{\neq}_{gas}$	$\Delta G^{\neq}_{sol}$	$\Delta G^{\neq}_{gas}$	$\Delta G^{\neq}_{sol}$
ts-i12 (105i)	30.14	26.12	30.14	26.12
ts-i23 (87i)	35.09	36.67	15.13	21.31
ts-i4B (1116i)	17.61	18.88	17.61	18.88
ts-i012 (859i)	1.49	1.87	1.49	1.87
ts-i034 (75i)	23.97	21.67	23.97	21.67
ts-C1D (296i)	9.02	9.65	9.02	9.65
ts-DE (296i)	19.09	13.14	29.83	24.84
a-ts-i56 (82i)	22.13	20.02	22.13	20.02
a-ts-i67 (234i)	24.06	25.81	16.97	15.40
ts-i89 (273i)	9.30	6.81	9.30	6.81
ts-i910 (527i)	-25.02	-31.15	16.81	8.21
ts-C2G (268i)	5.76	5.80	5.76	5.80
ts-GH (322i)	20.30	12.06	37.57	28.39
b-ts-i56 (131i)	42.43	40.08	42.43	40.08
b-ts-i67 (86i)	25.58	18.03	3.17	2.91

Figure S1 Optimized structures of substrates, catalysts, and intermediates proposed in Scheme 2. (Bond lengths in Å)





C1



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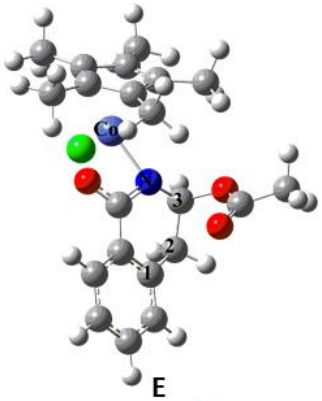

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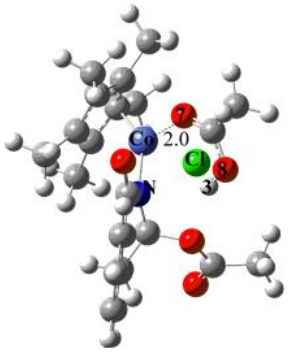
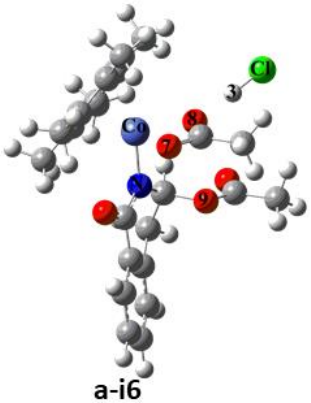


a-i5



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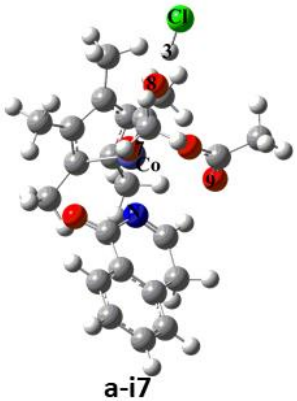
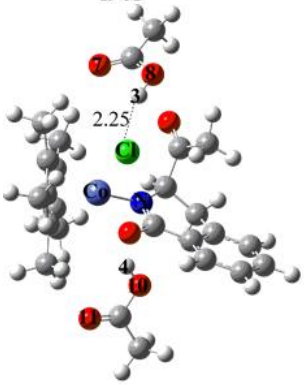
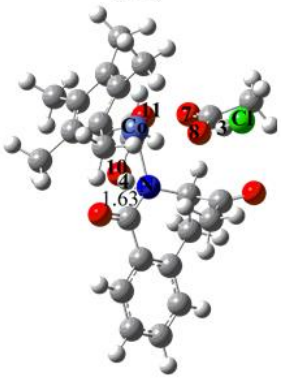


a-i7



b-i5



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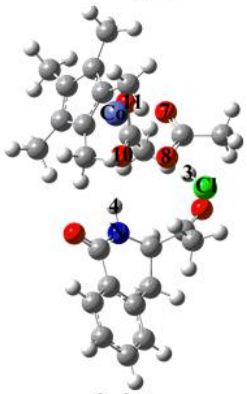
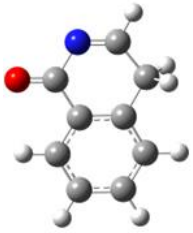


b-i7



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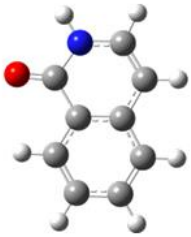
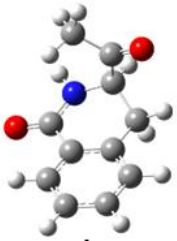


3a



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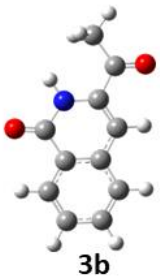

3b

Figure S2 Mechanism of pathway from **i1** to **i4**.

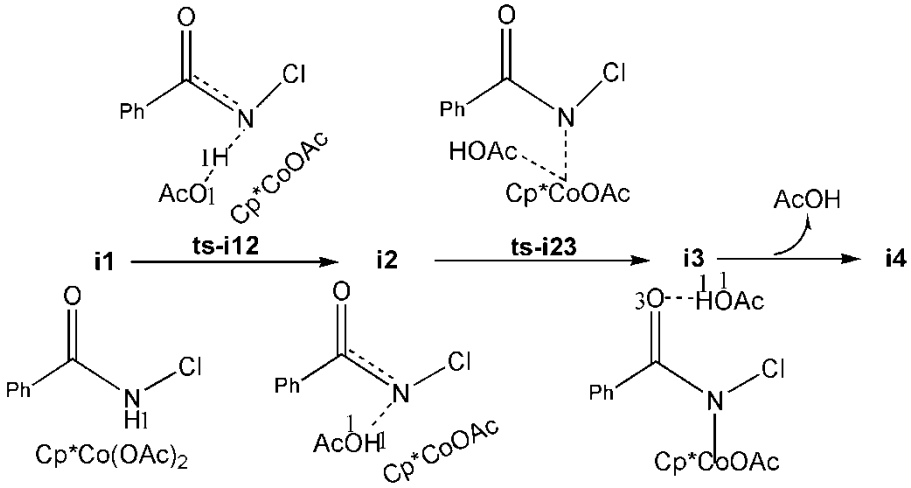

Figure S3 Evolution of bond lengths along the IRC for (a) **ts-i4B** (b) **ts-C1D** (c) **ts-DE** (d) **a-ts-i56** (e) **a-ts-i67** (f) **b-ts-i67** at the B3LYP/6-311++G(d,p) level.

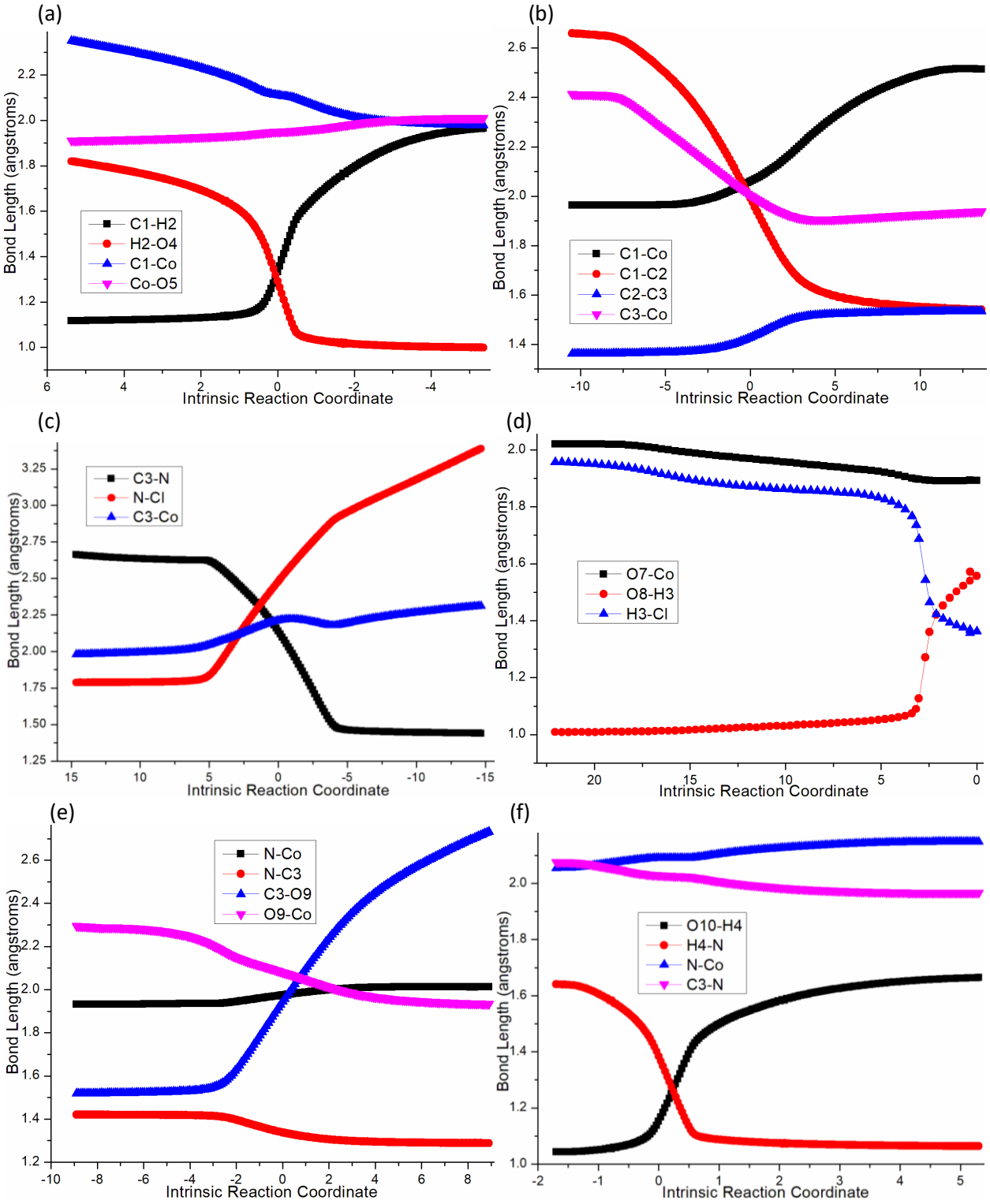

Figure S4 Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) of typical transition states **ts-i23**, **ts-i4B**, **ts-C1D**, **ts-DE**, **a-ts-i67**, and **b-ts-i67**. Different colors are used to identify the phase of the wave functions.