Solvent induced enhancement of enantiomeric excess: a case study of the Henry reaction with cinchona thiourea catalyst

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Electronic Supplementary Information

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[Figure 1 about here.]

[Figure 2 about here.]

Coordinates of the transition states of conformers β, (C-C coupling step)

TS_{S1}

1.H	-3.442115	-0.740005	7.941369
2.H	-5.678691	-0.063151	5.817320
3.O	-3.233845	-0.418405	5.074308
4.H	-7.612472	1.345837	6.567182
5.C	-4.203876	1.385303	6.391033
6.C	-3.977424	2.655441	6.943395
7.C	-5.047774	3.450289	7.362403
8.C	-6.359219	2.977815	7.234335
9.C	-3.039171	0.523338	5.933695
10.H	-2.205217	0.636125	8.174793
11.H	-2.108558	1.134241	5.828335
12.H	-2.953263	3.028710	7.034222
13.H	-4.861449	4.440045	7.783042
14.C	-5.518975	0.921224	6.259767
15.N	-1.530305	-1.098627	7.267843
16.C	-6.590832	1.712878	6.679313
17.O	-1.799139	-2.292143	6.985770
18.C	-2.553715	-0.215639	7.592946
19.O	-0.341426	-0.615520	7.047313
20.H	-7.197516	3.596701	7.559139
21.C	3.060981	-3.594285	5.305016
22.C	2.391111	-3.836540	3.937447
23.C	2.158288	-2.466737	3.261001
24.C	1.002601	-1.746909	3.992759
25.C	2.241802	-2.520038	6.056273
26.C	1.028125	-4.521966	4.176380
27.C	0.246781	-3.715864	5.243207
28.C	1.044130	-0.206698	4.013674
29.C	2.113424	1.548850	5.217863
30.C	0.944014	0.309825	2.579704

31.C	-0.304049	0.327289	1.876347
32.C	-0.263720	0.710194	0.487858
33.C	1.995863	1.112990	0.552608
34.C	2.081542	0.719274	1.907901
35.C	-1.547875	-0.007529	2.461212
36.C	-2.731631	0.013056	1.719099
37.C	-2.673181	0.331597	0.330298
38.C	-1.474521	0.676227	-0.251086
39.C	-5.220789	-0.277548	2.014660
40.C	-5.870541	-2.112678	3.630208
41.C	-4.808772	-3.014741	3.435766
42.C	-4.725813	-4.170795	4.212713
43.C	-5.688260	-4.457519	5.186204
44.C	-6.751654	-3.567646	5.370683
45.C	-6.844730	-2.406604	4.604166
46.H	0.171112	0.137532	4.594641
47.C	-9.246276	0.388876	1.951820
48.C	-11.581061	0.415117	2.687702
49.C	-10.884165	1.624183	0.616098
50.H	3.069409	1.780489	5.701868
51.H	-11.304317	2.585826	0.949738
52.H	0.304320	-1.726486	6.034365
53.H	-11.629838	1.117603	-0.016064
54.H	-8.536398	0.734055	1.173079
55.H	-11.137714	-0.217422	3.463518
56.H	-12.372086	-0.143204	2.163641
57.N	0.894500	-2.360174	5.387068
58.N	0.877099	1.097053	-0.156171
59.N	-3.904678	-0.334663	2.401271
60.N	-6.081290	-0.960104	2.839580
61.H	-12.028216	1.308793	3.150425
62.N	-10.526108	0.794110	1.757312
63.O	2.238366	0.221966	4.679241

64.H	3.104028	-4.532633	5.879698
65.H	-7.518346	-3.776657	6.118284
66.O	-8.860978	-0.310462	2.904920
67.H	-9.988657	1.821858	0.015285
68.S	-5.850194	0.594715	0.707523
69.H	1.918982	2.287799	4.424089
70.H	-0.805627	-3.547291	4.990871
71.H	2.713006	-1.532508	6.027966
72.H	3.029705	-4.467807	3.305424
73.H	0.460606	-4.570815	3.234878
74.H	4.094988	-3.243892	5.173519
75.H	1.303891	1.589059	5.965180
76.H	0.045391	-2.000535	3.514193
77.H	1.893251	-2.584083	2.201297
78.H	3.077671	-1.862513	3.306665
79.H	0.274744	-4.181645	6.236194
80.H	1.168965	-5.556196	4.523232
81.H	-3.593788	0.331722	-0.246724
82.H	-1.425097	0.943742	-1.306503
83.H	-1.634688	-0.263032	3.520519
84.H	2.898246	1.441723	0.029624
85.H	3.042588	0.732920	2.422730
86.H	-3.755017	-0.474977	3.431413
87.H	-7.075357	-0.677383	2.754059
88.H	-4.059678	-2.818849	2.670446
89.H	-7.682529	-1.721481	4.735302
90.H	2.035080	-2.786749	7.100938
91.H	-5.613584	-5.363499	5.788535
92.H	-3.899565	-4.863552	4.044265

TS$_{S2}$

1.H	-3.500575	1.920336	7.163009
2.H	-3.380173	-2.344880	6.621584
3.O	-3.107832	-0.583624	4.789243
4.H	-4.480132	-3.435592	8.589226
5.C	-4.510408	-0.533535	6.786877
6.C	-5.543909	0.124275	7.475794
7.C	-6.179215	-0.480022	8.561153
8.C	-5.789134	-1.760618	8.974332
9.C	-3.863819	0.123074	5.582055
10.H	-2.775828	2.243638	5.480494
11.H	-4.598663	0.801080	5.089752
12.H	-5.863639	1.117499	7.147224
13.H	-6.983325	0.042257	9.082479
14.C	-4.142796	-1.820357	7.194732
15.N	-1.683944	1.027969	6.733100
16.C	-4.773344	-2.429355	8.283906
17.O	-1.541130	0.470668	7.843805
18.C	-2.909563	1.564712	6.320623
19.O	-0.765422	0.966285	5.821699
20.H	-6.284448	-2.237207	9.822105
21.C	2.234274	-2.923134	6.466608
22.C	1.658721	-3.587098	5.197716
23.C	1.859072	-2.620288	4.007519
24.C	0.874807	-1.441196	4.171339
25.C	1.653016	-1.493101	6.572181
26.C	0.147139	-3.825985	5.411802
27.C	-0.496443	-2.507859	5.906919
28.C	1.326544	-0.068392	3.633691
29.C	2.899051	1.638218	4.187655
30.C	1.252940	-0.045351	2.109159
31.C	-0.013915	0.003400	1.443371
32.C	0.000978	-0.001264	0.004379
33.C	2.295904	-0.057343	-0.073200

34.C	2.399417	-0.078089	1.337076
35.C	-1.259348	0.028141	2.117892
36.C	-2.464326	-0.005446	1.419110
37.C	-2.442731	-0.011365	-0.007335
38.C	-1.244199	0.001860	-0.681842
39.C	-4.924346	0.160598	1.802839
40.C	-5.878518	-1.809661	3.060688
41.C	-4.926164	-2.791637	2.731161
42.C	-5.042351	-4.079399	3.257624
43.C	-6.098118	-4.417913	4.110518
44.C	-7.049868	-3.443925	4.430275
45.C	-6.943929	-2.152969	3.914698
46.H	0.616308	0.683298	4.017600
47.C	-8.758889	1.512342	1.896642
48.C	-10.975313	1.983697	2.822623
49.C	-10.143286	3.219101	0.817043
50.H	3.911864	1.752628	4.591361
51.H	-10.313069	4.208484	1.269721
52.H	-0.032524	-0.443141	5.824037
53.H	-11.020193	2.961018	0.203149
54.H	-8.030569	1.778215	1.103546
55.H	-10.637073	1.201544	3.509877
56.H	-11.900017	1.659319	2.320647
57.N	0.470694	-1.379892	5.642592
58.N	1.148659	-0.023879	-0.735708
59.N	-3.637625	-0.152298	2.163839
60.N	-5.892117	-0.502858	2.513714
61.H	-11.185713	2.905785	3.386644
62.N	-9.919146	2.213404	1.845534
63.O	2.635033	0.226904	4.141138
64.H	1.977195	-3.518747	7.356212
65.H	-7.883307	-3.686700	5.090601
66.O	-8.492521	0.645478	2.747074

67.H	-9.262454	3.276825	0.166726
68.S	-5.352827	1.330392	0.656616
69.H	2.854316	2.090831	3.184372
70.H	-1.435968	-2.241521	5.401244
71.H	2.369642	-0.728120	6.254801
72.H	2.170326	-4.538824	5.001656
73.H	-0.320564	-4.156871	4.472604
74.H	3.331333	-2.872602	6.412791
75.H	2.180480	2.150965	4.848781
76.H	-0.066612	-1.667812	3.653445
77.H	1.663402	-3.121523	3.049224
78.H	2.897133	-2.254888	3.988260
79.H	-0.682246	-2.505304	6.988921
80.H	-0.017591	-4.621266	6.153240
81.H	-3.384627	-0.026627	-0.550295
82.H	-1.215833	-0.006419	-1.771271
83.H	-1.317159	0.063151	3.206348
84.H	3.205909	-0.074474	-0.679311
85.H	3.378664	-0.115401	1.815252
86.H	-3.482855	-0.398206	3.192971
87.H	-6.827729	-0.055518	2.494535
88.H	-4.105467	-2.555758	2.056862
89.H	-7.691883	-1.397791	4.157534
90.H	1.283578	-1.246548	7.575939
91.H	-6.181470	-5.427367	4.515183
92.H	-4.299375	-4.830272	2.983109

TS$_{S3}$

1.H	-1.378766	1.060134	5.278003
2.H	-4.910598	2.242844	5.467868
3.H	-3.792477	6.383331	5.667137

4.H	-1.409586	5.720520	5.764017
5.O	-3.291840	0.341571	5.066986
6.C	-2.450692	1.179665	5.526077
7.C	-2.113980	0.659919	7.406748
8.N	-0.912409	1.239349	7.765676
9.O	-0.857812	2.315146	8.369730
10.C	-2.817132	2.632966	5.616358
11.H	-5.550253	4.644116	5.524085
12.C	-4.159057	3.014832	5.557663
13.C	-4.508454	4.357010	5.581575
14.H	-2.055204	-0.405730	7.260946
15.C	-3.519786	5.336368	5.659171
16.C	-2.181638	4.964788	5.711671
17.C	-1.832700	3.619052	5.690716
18.H	-0.788867	3.336325	5.724416
19.O	0.169167	0.691541	7.303285
20.H	-2.954963	1.049198	7.960487
21.H	-0.763916	-3.888323	4.269560
22.H	-0.306967	-4.694150	5.761942
23.H	-3.230682	0.979247	-0.412761
24.H	-1.023150	0.969372	-1.509529
25.H	-1.375718	0.390540	3.374518
26.H	3.227944	-3.409246	5.822237
27.H	3.294190	0.450512	-0.264536
28.H	3.340590	0.127190	2.195229
29.H	-3.553948	0.307651	3.254547
30.H	-6.802554	0.022743	2.304754
31.H	2.257342	1.992369	5.545342
32.H	-0.285137	-1.352438	3.877334
33.H	1.158915	-2.781622	2.776987
34.H	-0.601550	-2.746445	7.041172
35.H	2.581011	-2.264952	3.674825
36.H	-3.914576	-1.992830	1.783727

37.H	-7.168216	-1.175343	4.445384
38.H	1.582977	-1.867178	7.557128
39.H	-5.111365	-4.933064	4.661814
40.H	-3.634259	-4.206783	2.804908
41.C	2.158694	-3.360429	6.030956
42.C	1.345384	-3.682169	4.765803
43.C	1.523478	-2.517985	3.769770
44.C	0.722561	-1.307290	4.285670
45.C	1.788687	-1.936539	6.490592
46.C	-0.140416	-3.800084	5.160317
47.C	-0.542316	-2.546772	5.972012
48.C	1.264308	0.085380	3.926768
49.C	2.905467	1.596264	4.759463
50.C	1.228412	0.293137	2.414326
51.C	0.003637	0.496476	1.707796
52.C	0.091651	0.663059	0.289799
53.C	2.365603	0.461069	0.296097
54.C	2.395955	0.275327	1.692705
55.C	-1.271130	0.513762	2.309935
56.C	-2.434827	0.663349	1.571867
57.C	-2.332590	0.838297	0.165385
58.C	-1.107777	0.840029	-0.439767
59.C	-4.933335	0.633556	1.797907
60.C	-5.547814	-1.421777	3.067304
61.C	-4.551005	-2.287401	2.605554
62.C	-4.396233	-3.539282	3.186201
63.C	-5.229460	-3.952085	4.221556
64.C	-6.229678	-3.095549	4.669572
65.C	-6.388191	-1.839752	4.100457
66.H	3.935915	1.593027	5.108064
67.C	-8.848893	0.162373	0.771851
68.C	-11.143235	-0.670805	0.726186
69.C	-10.111297	0.318362	-1.309936

70.H	-10.916091	1.044058	-1.453361
71.H	0.225467	-0.601783	6.270526
72.H	-10.324695	-0.558987	-1.926442
73.H	-8.056349	0.633652	0.173087
74.H	-10.883461	-0.891201	1.757285
75.H	-11.411402	-1.597210	0.211484
76.H	-12.003226	0.003574	0.701899
77.N	0.523991	-1.497528	5.786481
78.N	1.264925	0.647526	-0.392453
79.N	-3.642760	0.535344	2.250520
80.N	-5.808916	-0.167392	2.465743
81.H	1.945204	-4.091940	6.813257
82.N	-9.993591	-0.051658	0.088449
83.O	2.568207	0.233776	4.470357
84.H	-6.891693	-3.403855	5.467264
85.H	0.603280	0.823010	4.393271
86.O	-8.662481	-0.124787	1.954875
87.H	-9.177863	0.762708	-1.649190
88.S	-5.474438	1.684115	0.602464
89.H	2.829366	2.221068	3.866017
90.H	-1.489378	-2.120359	5.642864
91.H	2.545759	-1.204583	6.231000
92.H	1.690020	-4.614733	4.319702

TS$_{R1}$

1.H	-4.592732	2.033114	4.320905
2.H	-2.653063	2.537994	6.706600
3.H	-6.805637	3.157976	4.541962
4.H	-8.221260	2.744093	6.553176
5.H	-7.419929	1.191182	8.333595
6.C	-5.218073	1.853332	5.196446

7.C	-6.456914	2.484868	5.326349
8.C	-7.252676	2.251546	6.454841
9.C	-6.802309	1.381248	7.454232
10.O	-0.584814	1.727300	5.663588
11.C	-3.424871	0.282047	6.067821
12.C	-4.760857	0.977677	6.192129
13.C	-5.562474	0.750976	7.321869
14.C	-2.357885	1.562052	7.086421
15.O	-2.890367	0.062549	4.918553
16.N	-1.076558	1.215256	6.702473
17.H	-2.581172	1.321246	8.123743
18.O	-0.502602	0.209262	7.289985
19.H	-5.213554	0.063550	8.097268
20.H	-3.300701	-0.510386	6.840413
21.C	1.996514	-3.570618	5.990240
22.C	1.243982	-3.885845	4.681248
23.C	1.510168	-2.736474	3.682411
24.C	0.711597	-1.495880	4.139908
25.C	1.657635	-2.118998	6.398490
26.C	-0.268263	-3.951013	4.991434
27.C	-0.669338	-2.679805	5.778857
28.C	1.290849	-0.116723	3.780216
29.C	2.985980	1.357862	4.583182
30.C	1.253337	0.076171	2.265029
31.C	0.009064	0.222006	1.568526
32.C	0.063432	0.288851	0.132301
33.C	2.356574	0.199864	0.113444
34.C	2.418152	0.068383	1.520839
35.C	-1.251785	0.246080	2.210049
36.C	-2.439874	0.240660	1.479124
37.C	-2.380663	0.294435	0.056109
38.C	-1.161991	0.335034	-0.583155
39.C	-4.934329	0.053057	1.804379

40.C	-5.474257	-1.747882	3.478285
41.C	-4.407245	-2.633335	3.234809
42.C	-4.242032	-3.763698	4.037742
43.C	-5.125975	-4.037545	5.087519
44.C	-6.193934	-3.163522	5.320142
45.C	-6.368946	-2.029450	4.527118
46.H	1.705418	-4.282357	6.778705
47.C	-8.825566	-0.655453	1.178385
48.C	-11.068203	-1.572319	1.530029
49.C	-10.163787	-1.263831	-0.778943
50.H	-6.900322	-3.363340	6.127129
51.H	-8.072137	-0.368868	0.414883
52.H	-10.760943	-1.397724	2.566129
53.H	-11.268846	-2.645028	1.380843
54.H	-11.989007	-1.008072	1.316158
55.H	-9.266768	-0.895223	-1.290931
56.H	-11.031623	-0.679177	-1.121111
57.N	0.436915	-1.660155	5.633542
58.N	1.231059	0.293252	-0.578091
59.N	-3.624784	0.097255	2.214305
60.N	-5.763287	-0.631271	2.657335
61.H	0.643696	0.637983	4.259315
62.N	-9.986129	-1.130742	0.659593
63.O	2.614528	-0.007897	4.324455
64.H	3.989661	1.328278	5.023668
65.H	0.098544	-0.757569	6.112657
66.O	-8.587368	-0.533564	2.391926
67.H	-10.320822	-2.317932	-1.057831
68.S	-5.575913	0.831148	0.445709
69.H	3.015261	1.948595	3.653546
70.H	-1.589880	-2.205282	5.410861
71.H	2.454901	-1.412756	6.144008
72.H	1.587846	-4.841392	4.263497

73.H	-0.843407	-4.020449	4.056651
74.H	3.082216	-3.668235	5.846071
75.H	2.282902	1.827693	5.288811
76.H	-0.288797	-1.519683	3.688825
77.H	1.191779	-3.007884	2.666085
78.H	2.587066	-2.509867	3.643334
79.H	-0.780879	-2.865762	6.855073
80.H	-0.504705	-4.845934	5.585289
81.H	-3.309273	0.321814	-0.508376
82.H	-1.105945	0.388470	-1.670309
83.H	-1.330379	0.262669	3.297639
84.H	3.284131	0.210614	-0.465789
85.H	3.380887	-0.047418	2.018985
86.H	-3.473696	-0.004645	3.246493
87.H	-6.776847	-0.435910	2.544255
88.H	-3.723866	-2.450414	2.406542
89.H	-7.203706	-1.351264	4.705483
90.H	1.413637	-2.013960	7.463570
91.H	-4.993730	-4.927119	5.705109
92.H	-3.424121	-4.453069	3.821009

TS$_{R2}$

1.H	-2.485843	1.480575	5.278235
2.H	-3.604889	-2.234936	7.470118
3.H	-2.251465	3.431949	6.844066
4.H	-3.581911	3.490338	8.951181
5.H	-5.134575	1.613673	9.488591
6.C	-3.032606	1.515893	6.220579
7.C	-2.918154	2.603317	7.090918
8.C	-3.666735	2.639738	8.272868
9.C	-4.537392	1.585146	8.575552

10.O	-1.244190	-1.392047	7.438478
11.C	-4.058584	-0.700385	5.560452
12.C	-3.891392	0.451584	6.520945
13.C	-4.647559	0.501295	7.703526
14.C	-3.190760	-2.198311	6.464505
15.O	-3.605344	-0.614641	4.361749
16.N	-1.837630	-1.928141	6.463370
17.H	-3.470818	-2.972115	5.754301
18.O	-1.219595	-2.124351	5.330038
19.H	-5.337934	-0.315041	7.933274
20.H	-5.039517	-1.204623	5.707986
21.C	3.113877	0.094189	6.264862
22.C	3.752813	-0.862875	5.235765
23.C	3.108887	-0.620379	3.853732
24.C	1.613543	-1.041751	3.899140
25.C	1.573986	-0.072389	6.216612
26.C	3.481546	-2.315792	5.671711
27.C	1.956839	-2.481198	5.876344
28.C	0.613247	-0.091271	3.192201
29.C	0.002202	2.213671	3.082260
30.C	0.529028	-0.416845	1.701293
31.C	-0.652082	-0.975056	1.113923
32.C	-0.587233	-1.320955	-0.285997
33.C	1.566887	-0.550768	-0.485510
34.C	1.618771	-0.183178	0.877156
35.C	-1.873598	-1.159478	1.806710
36.C	-3.005509	-1.649115	1.161542
37.C	-2.912145	-2.063395	-0.199395
38.C	-1.735459	-1.896013	-0.892236
39.C	-5.479416	-1.762944	1.499120
40.C	-6.264840	-2.923041	3.596159
41.C	-5.275727	-3.919163	3.714767
42.C	-5.283030	-4.784381	4.810512

43.C	-6.260495	-4.681141	5.806597
44.C	-7.244804	-3.693540	5.688405
45.C	-7.249094	-2.821318	4.600297
46.H	3.499129	-0.126077	7.272428
47.C	-9.397197	-0.751697	1.136922
48.C	-11.680165	-0.178842	1.810243
49.C	-10.871070	0.315416	-0.500279
50.H	-8.021600	-3.599903	6.448803
51.H	-8.664910	-0.733464	0.304607
52.H	-11.312047	-0.634329	2.734991
53.H	-12.559012	-0.734803	1.448771
54.H	-11.977889	0.863250	2.005246
55.H	-9.973870	0.209955	-1.121341
56.H	-11.133772	1.383033	-0.438564
57.N	1.240540	-1.262237	5.357178
58.N	0.517922	-1.120413	-1.061749
59.N	-4.176472	-1.770094	1.926351
60.N	-6.394885	-2.076533	2.477420
61.H	-0.374868	-0.258266	3.649027
62.N	-10.608234	-0.227676	0.824793
63.O	1.017989	1.265370	3.445957
64.H	0.392047	3.203043	3.348663
65.H	0.166454	-1.510632	5.419104
66.O	-9.092632	-1.221291	2.247590
67.H	-11.701715	-0.221389	-0.984130
68.S	-6.022021	-1.332115	-0.043079
69.H	-0.211296	2.181827	2.002536
70.H	1.541846	-3.346296	5.343588
71.H	1.083971	0.792289	5.757425
72.H	4.835118	-0.683585	5.175678
73.H	3.848445	-3.015130	4.905223
74.H	3.381703	1.134711	6.032939
75.H	-0.932140	2.024563	3.636714

76.H	1.474596	-2.029416	3.435725
77.H	3.631169	-1.196638	3.077106
78.H	3.183067	0.445049	3.596199
79.H	1.673081	-2.569933	6.933135
80.H	4.014999	-2.547145	6.605376
81.H	-3.785725	-2.486549	-0.687102
82.H	-1.656450	-2.187671	-1.939201
83.H	-1.976638	-0.893420	2.858903
84.H	2.436070	-0.373733	-1.125084
85.H	2.518670	0.291313	1.269767
86.H	-4.046974	-1.501824	2.941147
87.H	-7.365247	-1.760471	2.284139
88.H	-4.515531	-4.026417	2.943317
89.H	-8.024741	-2.061546	4.501251
90.H	1.112703	-0.259854	7.193877
91.H	-6.259879	-5.365202	6.655596
92.H	-4.516578	-5.557950	4.876263

TS$_{R3}$

1 H	-0.731466	4.073909	7.566997
2 H	-2.042622	2.005679	7.805346
3 H	-0.375594	5.073774	5.326364
4 H	-2.981140	-1.502070	6.871342
5 H	-1.354946	3.980994	3.326413
6 C	-2.218015	2.367482	4.441169
7 C	-2.412445	1.788397	5.696813
8 C	-1.484655	3.540679	4.306496
9 C	-1.878405	2.425065	6.821316
10 O	-0.059758	-0.265093	7.176259
11 O	-3.822919	0.029889	4.818430
12 C	-3.282558	0.561642	5.837500

13	C	-2.175014	-0.880431	6.514177
14	H	-1.697665	-1.176215	5.593574
15	H	-2.677275	1.912506	3.576436
16	N	-1.271824	-0.553075	7.509665
17	O	-1.648290	-0.413422	8.685829
18	H	-3.870438	0.609299	6.768479
19	C	-0.938969	4.155394	5.428838
20	C	-1.140896	3.594892	6.687532
21	H	0.613298	-3.583412	6.935153
22	H	0.682420	-4.693567	4.140036
23	H	1.461678	-5.314940	5.587124
24	H	-3.237181	-0.272238	-0.596311
25	H	-1.027690	-0.119014	-1.669579
26	H	-1.401683	-0.204227	3.256628
27	H	3.272851	0.293331	-0.344954
28	H	3.316748	0.168139	2.132685
29	H	-3.640337	-0.358183	3.108870
30	H	4.358157	-2.913861	5.510102
31	H	-6.876601	-0.550743	2.083044
32	H	-4.141962	-2.869912	2.054658
33	H	-7.413258	-1.321779	4.339206
34	H	1.478587	1.985165	5.251527
35	H	2.380317	-2.045463	7.369774
36	H	0.257954	-2.094943	3.787099
37	H	2.026233	-2.993102	2.591405
38	H	3.250558	-2.045271	3.422404
39	H	-5.648200	-5.083936	5.401324
40	H	-4.059439	-4.848557	3.510532
41	C	3.348462	-3.230613	5.773811
42	C	2.620789	-3.794185	4.541085
43	C	2.340906	-2.629550	3.569443
44	C	1.221956	-1.745973	4.160480
45	C	2.546356	-2.020471	6.294043

46	C	1.286424	-4.410214	5.003891
47	C	0.540433	-3.370006	5.869423
48	C	1.268112	-0.239996	3.830487
49	C	2.319227	1.749896	4.593271
50	C	1.207220	-0.064076	2.316310
51	C	-0.019443	-0.112978	1.589695
52	C	0.074798	-0.051039	0.162451
53	C	2.345977	0.170584	0.204825
54	C	2.374394	0.097527	1.609473
55	C	-1.299504	-0.202963	2.181721
56	C	-2.458027	-0.228898	1.419262
57	C	-2.342568	-0.229976	0.001733
58	C	-1.118429	-0.137573	-0.592806
59	C	-4.954533	-0.156334	1.581365
60	C	-5.771603	-1.951180	3.117816
61	C	-4.829198	-2.955899	2.883682
62	C	-4.786888	-4.072304	3.708738
63	C	-5.682882	-4.210335	4.764608
64	C	-6.633435	-3.218562	4.982727
65	C	-6.679147	-2.096427	4.168019
66	H	3.438794	-4.000600	6.543139
67	C	-8.913646	-0.321088	0.542295
68	C	-11.281657	-0.908447	0.608652
69	C	-10.200440	-0.235015	-1.529854
70	H	-7.340754	-3.313180	5.795473
71	H	-8.090922	0.009806	-0.107969
72	H	-11.028130	-1.027694	1.658328
73	H	-11.637600	-1.862242	0.209571
74	H	-12.078922	-0.167801	0.506247
75	H	-9.236251	0.082107	-1.921993
76	H	-10.936491	0.545545	-1.738815
77	N	1.175091	-2.021620	5.656301
78	N	1.246933	0.082268	-0.506760

79	N	-3.680013	-0.323275	2.074196
80	N	-5.907928	-0.820572	2.279299
81	H	0.393157	0.230547	4.289276
82	N	-10.091040	-0.471839	-0.101775
83	O	2.435138	0.331784	4.401554
84	H	3.250145	2.073749	5.053593
85	H	0.599123	-1.279808	6.171772
86	O	-8.731081	-0.521408	1.743600
87	H	-10.506924	-1.145736	-2.051793
88	S	-5.381193	0.844004	0.295052
89	H	2.187682	2.265808	3.638783
90	H	-0.513883	-3.286385	5.613193
91	H	3.000929	-1.072373	6.029115
92	H	3.233100	-4.551040	4.051415

TS_{S1}- CF_3

1.H	-3.285658	-0.380273	8.051666
2.H	-5.645665	-0.272631	6.091240
3.O	-3.210843	-0.385060	5.092245
4.H	-7.664901	0.982859	6.880796
5.C	-4.316274	1.392774	6.355029
6.C	-4.202888	2.734618	6.749427
7.C	-5.323750	3.444285	7.189051
8.C	-6.572026	2.813676	7.241599
9.C	-3.090885	0.631853	5.886907
10.H	-2.002515	0.966605	8.013582
11.H	-2.250156	1.336206	5.675882
12.H	-3.228926	3.229666	6.698671
13.H	-5.225818	4.489948	7.485230
14.C	-5.570232	0.769187	6.405820
15.N	-1.465807	-0.879088	7.236220

16.C	-6.691841	1.475293	6.846678
17.O	-1.800465	-2.069884	7.049073
18.C	-2.429370	0.075452	7.556404
19.O	-0.271744	-0.461369	6.929846
20.H	-7.449457	3.364675	7.584386
21.C	3.107341	-3.588503	5.407281
22.C	2.438899	-3.882820	4.049109
23.C	2.230483	-2.541733	3.309432
24.C	1.087555	-1.768779	4.006427
25.C	2.295166	-2.477304	6.111907
26.C	1.066125	-4.539146	4.311391
27.C	0.287049	-3.673270	5.332088
28.C	1.165419	-0.229197	3.975151
29.C	2.302128	1.540236	5.097053
30.C	1.050043	0.251550	2.530411
31.C	-0.212053	0.297404	1.853789
32.C	-0.191213	0.656937	0.458943
33.C	2.081266	0.984194	0.466046
34.C	2.184672	0.610514	1.825614
35.C	-1.453835	0.009331	2.469452
36.C	-2.649811	0.050811	1.749265
37.C	-2.613221	0.351212	0.356749
38.C	-1.417513	0.651814	-0.254415
39.C	-5.134231	-0.164292	2.092529
40.C	-5.854027	-2.039916	3.622877
41.C	-4.791108	-2.941367	3.419460
42.C	-4.775176	-4.159839	4.097379
43.C	-5.794722	-4.523337	4.985558
44.C	-6.848776	-3.627269	5.178022
45.C	-6.886162	-2.403051	4.510115
46.H	0.312340	0.154128	4.561066
47.C	-9.192034	0.504050	2.103472
48.C	-11.517455	0.292363	2.835259

49.C	-10.936914	1.615573	0.797269
50.H	3.271323	1.761280	5.559203
51.H	-11.451011	2.521202	1.153850
52.H	0.368348	-1.648958	6.028192
53.H	-11.627302	1.052954	0.150309
54.H	-8.518270	0.927216	1.332127
55.H	-11.019221	-0.312600	3.599160
56.H	-12.246435	-0.327830	2.291684
57.N	0.957251	-2.323703	5.422874
58.N	0.946718	0.996241	-0.216755
59.N	-3.819608	-0.268332	2.457181
60.N	-6.007181	-0.828958	2.936539
61.H	-12.051705	1.126786	3.314800
62.N	-10.501000	0.796688	1.919931
63.O	2.381911	0.192055	4.604678
64.H	3.140849	-4.502248	6.020532
65.C	-7.997912	-3.997741	6.079440
66.O	-8.743602	-0.182276	3.039675
67.H	-10.064761	1.916355	0.205045
68.S	-5.774367	0.730299	0.812593
69.H	2.117291	2.256181	4.280139
70.H	-0.758458	-3.502793	5.055207
71.H	2.781392	-1.498458	6.054692
72.H	3.071700	-4.550473	3.449351
73.H	0.501422	-4.628250	3.371941
74.H	4.144533	-3.252297	5.264221
75.H	1.505154	1.630830	5.853298
76.H	0.127296	-2.019754	3.532813
77.H	1.963780	-2.704296	2.256071
78.H	3.160401	-1.952490	3.329024
79.H	0.295698	-4.094482	6.345217
80.H	1.191705	-5.556540	4.709126
81.H	-3.544125	0.370088	-0.202707

82.H	-1.381767	0.902827	-1.314296
83.H	-1.523587	-0.234990	3.532351
84.H	2.982048	1.272433	-0.082840
85.H	3.156827	0.602040	2.319018
86.H	-3.655984	-0.394547	3.497518
87.H	-6.991955	-0.498371	2.881396
88.H	-3.988754	-2.695152	2.729300
89.H	-7.722260	-1.720678	4.655396
90.H	2.074099	-2.705631	7.162779
91.H	-5.764695	-5.472868	5.515054
92.C	-3.675129	-5.151140	3.828358
93.F	-7.668289	-4.975271	6.973712
94.F	-9.076196	-4.466601	5.370077
95.F	-8.456066	-2.929807	6.804300
96.F	-2.574817	-4.579480	3.243343
97.F	-4.078435	-6.154911	2.987757
98.F	-3.237077	-5.767499	4.972153

TS_{S2}- CF_3

1.H	-3.588610	1.642963	7.231300
2.H	-3.171650	-2.603873	6.522380
3.O	-3.135859	-0.769263	4.767154
4.H	-4.059006	-3.849610	8.503958
5.C	-4.413917	-0.887273	6.838994
6.C	-5.441164	-0.333636	7.622449
7.C	-5.956123	-1.025086	8.719060
8.C	-5.450303	-2.289079	9.048695
9.C	-3.899574	-0.142725	5.623309
10.H	-2.992999	2.061648	5.519572
11.H	-4.714100	0.482568	5.192936
12.H	-5.853123	0.644940	7.359627

13.H	-6.759478	-0.585507	9.312192
14.C	-3.929077	-2.158900	7.165599
15.N	-1.734434	0.912871	6.674901
16.C	-4.439828	-2.854984	8.265360
17.O	-1.480838	0.359608	7.768204
18.C	-3.022705	1.354557	6.346942
19.O	-0.870693	0.932929	5.711968
20.H	-5.854953	-2.834841	9.902477
21.C	2.531096	-2.602662	6.512404
22.C	2.009733	-3.377153	5.283525
23.C	2.106743	-2.455457	4.045923
24.C	1.025833	-1.358097	4.171048
25.C	1.810190	-1.234644	6.567801
26.C	0.530744	-3.749805	5.527963
27.C	-0.235045	-2.474966	5.957999
28.C	1.362741	0.026405	3.580140
29.C	2.821428	1.862265	4.021166
30.C	1.259725	-0.016216	2.057923
31.C	-0.018395	-0.060673	1.414716
32.C	-0.026215	-0.133556	-0.022067
33.C	2.266902	-0.080625	-0.139743
34.C	2.393990	-0.026950	1.267385
35.C	-1.255381	-0.054125	2.109850
36.C	-2.464993	-0.155462	1.430673
37.C	-2.464874	-0.243363	0.007916
38.C	-1.279154	-0.221618	-0.687626
39.C	-4.895263	0.120154	1.838125
40.C	-6.066960	-1.721890	3.122791
41.C	-5.114783	-2.752800	3.015220
42.C	-5.396289	-4.014164	3.541982
43.C	-6.611252	-4.293932	4.176130
44.C	-7.553382	-3.266830	4.275626
45.C	-7.292126	-1.997684	3.761964

46.H	0.606758	0.738016	3.952177
47.C	-8.676927	1.723515	1.836127
48.C	-10.940144	2.153756	2.661494
49.C	-10.047731	3.389776	0.682033
50.H	3.829125	2.065185	4.401981
51.H	-10.260400	4.378298	1.117263
52.H	0.031633	-0.383340	5.781622
53.H	-10.891037	3.103874	0.034923
54.H	-7.923654	1.989165	1.067734
55.H	-10.619419	1.384708	3.371101
56.H	-11.832204	1.805650	2.118729
57.N	0.621603	-1.273879	5.640055
58.N	1.109368	-0.137573	-0.781427
59.N	-3.638722	-0.284728	2.191578
60.N	-5.919614	-0.429853	2.588941
61.H	-11.195689	3.075753	3.205872
62.N	-9.844959	2.399754	1.730927
63.O	2.654280	0.435665	4.048694
64.H	2.346645	-3.180798	7.430888
65.C	-8.897886	-3.548218	4.894821
66.O	-8.428652	0.869507	2.706929
67.H	-9.141674	3.462535	0.069180
68.S	-5.261711	1.271407	0.658119
69.H	2.732221	2.260083	2.997862
70.H	-1.189688	-2.326737	5.434956
71.H	2.447284	-0.414853	6.219333
72.H	2.608173	-4.284018	5.125079
73.H	0.091222	-4.176481	4.614760
74.H	3.616585	-2.444957	6.437484
75.H	2.078450	2.358112	4.668258
76.H	0.104964	-1.680993	3.666802
77.H	1.942563	-3.018693	3.116777
78.H	3.107974	-2.002094	3.991069

79.H	-0.431702	-2.435393	7.037027
80.H	0.449201	-4.514563	6.313701
81.H	-3.412258	-0.329476	-0.518301
82.H	-1.265836	-0.290266	-1.775035
83.H	-1.295719	0.029268	3.196472
84.H	3.166683	-0.082097	-0.761130
85.H	3.381232	0.009213	1.728807
86.H	-3.479409	-0.507707	3.238255
87.H	-6.811344	0.100246	2.525946
88.H	-4.162009	-2.574065	2.527486
89.H	-8.038302	-1.208231	3.840815
90.H	1.417562	-0.988871	7.562840
91.H	-6.812593	-5.278988	4.591823
92.C	-4.389166	-5.125446	3.406844
93.F	-3.148265	-4.681662	3.045696
94.F	-4.761136	-6.050219	2.465564
95.F	-4.230765	-5.823733	4.578657
96.F	-8.839790	-4.527916	5.846155
97.F	-9.810889	-3.975050	3.960054
98.F	-9.445616	-2.445007	5.486406

$\mathbf{TS}_{R1}$- $\mathbf{CF}_3$

1.H	-4.783715	1.386620	4.194781
2.H	-2.820198	2.033297	6.517479
3.H	-7.044876	2.398237	4.502800
4.H	-8.352214	1.919699	6.573204
5.H	-7.398009	0.421295	8.324525
6.C	-5.364079	1.184026	5.096465
7.C	-6.628442	1.748658	5.274645
8.C	-7.362997	1.480541	6.437130
9.C	-6.826300	0.642849	7.421771

10.O	-0.726151	1.397083	5.407777
11.C	-3.448512	-0.266984	5.903802
12.C	-4.819084	0.344587	6.079829
13.C	-5.559780	0.082035	7.243256
14.C	-2.435382	1.084519	6.884253
15.O	-2.945489	-0.445488	4.733386
16.N	-1.142378	0.845923	6.459925
17.H	-2.603185	0.827251	7.927444
18.O	-0.461223	-0.096228	7.035535
19.H	-5.143207	-0.578936	8.008262
20.H	-3.240991	-1.049804	6.666567
21.C	3.402228	-2.566188	5.920695
22.C	2.788091	-3.366289	4.753926
23.C	2.494901	-2.390310	3.593973
24.C	1.297105	-1.488989	3.981149
25.C	2.493749	-1.347163	6.203279
26.C	1.463617	-3.997458	5.231741
27.C	0.596263	-2.889593	5.875110
28.C	1.317113	-0.056044	3.415253
29.C	2.418854	2.024067	3.803808
30.C	1.165107	-0.121090	1.896515
31.C	-0.104025	-0.372820	1.281444
32.C	-0.115208	-0.533511	-0.149486
33.C	2.135941	-0.119121	-0.322053
34.C	2.272316	0.015822	1.078369
35.C	-1.323446	-0.480897	1.996769
36.C	-2.519004	-0.776912	1.343274
37.C	-2.511633	-0.992334	-0.065147
38.C	-1.344361	-0.858419	-0.780297
39.C	-4.986596	-0.950413	1.761580
40.C	-5.648719	-2.479438	3.666113
41.C	-4.512658	-3.308396	3.738481
42.C	-4.452564	-4.318849	4.699980

43.C	-5.499580	-4.541782	5.600650
44.C	-6.628487	-3.720148	5.516378
45.C	-6.709069	-2.701666	4.569051
46.H	3.495336	-3.204659	6.812978
47.C	-9.052425	-0.440842	1.514899
48.C	-11.363087	-0.394984	2.318585
49.C	-10.789450	0.449069	0.038347
50.C	-7.788268	-3.985179	6.441222
51.H	-8.381098	-0.203724	0.665727
52.H	-10.863063	-0.830692	3.189032
53.H	-12.120078	-1.097373	1.937910
54.H	-11.865262	0.540038	2.609831
55.H	-9.922059	0.587712	-0.617539
56.H	-11.265351	1.427525	0.205880
57.N	1.167215	-1.540593	5.502792
58.N	0.996182	-0.402724	-0.933899
59.N	-3.669144	-0.932284	2.137160
60.N	-5.847002	-1.481441	2.700532
61.H	0.463352	0.483815	3.855247
62.N	-10.354194	-0.133758	1.299641
63.O	2.532781	0.588912	3.821087
64.H	3.380929	2.415296	4.155369
65.H	0.494497	-0.804367	5.913540
66.O	-8.607708	-0.943952	2.561671
67.H	-11.513085	-0.209325	-0.466451
68.S	-5.627856	-0.312064	0.335709
69.H	2.226574	2.398279	2.785251
70.H	-0.445749	-2.904450	5.535735
71.H	2.907782	-0.413360	5.809437
72.H	3.483014	-4.149225	4.422117
73.H	0.934752	-4.457268	4.384605
74.H	4.412355	-2.218619	5.660094
75.H	1.612125	2.359070	4.474975

76.H	0.359268	-1.934924	3.620133
77.H	2.250937	-2.932754	2.670210
78.H	3.382284	-1.771482	3.391071
79.H	0.595734	-2.931719	6.972074
80.H	1.652461	-4.793808	5.965778
81.H	-3.441937	-1.239376	-0.568491
82.H	-1.331654	-1.003028	-1.860293
83.H	-1.360128	-0.315332	3.075016
84.H	3.015073	-0.002847	-0.962302
85.H	3.248668	0.223485	1.516684
86.H	-3.498887	-0.823666	3.171436
87.H	-6.845363	-1.224691	2.555523
88.H	-3.687700	-3.173456	3.045029
89.H	-7.594153	-2.070042	4.512522
90.H	2.261944	-1.215728	7.268256
91.H	-5.437974	-5.332374	6.346773
92.C	-3.246369	-5.213750	4.786489
93.F	-7.373352	-4.279619	7.714871
94.F	-8.533427	-5.061072	6.026961
95.F	-8.646756	-2.931392	6.533943
96.F	-2.286288	-4.913760	3.861864
97.F	-3.563898	-6.532948	4.614021
98.F	-2.635882	-5.135641	6.020601

TS_{R2}- CF_3

1.H	-2.545796	1.500909	5.194488
2.H	-3.532098	-2.173102	7.540958
3.H	-2.337591	3.515444	6.682304
4.H	-3.635620	3.619338	8.807622
5.H	-5.130307	1.725428	9.440655
6.C	-3.078091	1.557715	6.144037

7.C	-2.978155	2.679826	6.971205
8.C	-3.708803	2.741590	8.163221
9.C	-4.546822	1.677454	8.519875
10.O	-1.203851	-1.252617	7.456960
11.C	-4.050685	-0.707299	5.585252
12.C	-3.904300	0.483951	6.499072
13.C	-4.643098	0.558527	7.691268
14.C	-3.132307	-2.149473	6.529187
15.O	-3.607520	-0.649853	4.378281
16.N	-1.785208	-1.835379	6.503780
17.H	-3.381474	-2.961711	5.851120
18.O	-1.173814	-2.044692	5.372539
19.H	-5.309154	-0.264515	7.964268
20.H	-5.021325	-1.224277	5.757131
21.C	3.208822	0.130749	6.236701
22.C	3.821569	-0.855230	5.219364
23.C	3.165607	-0.629225	3.840251
24.C	1.666106	-1.030950	3.910079
25.C	1.666295	-0.012556	6.207588
26.C	3.534069	-2.295619	5.685885
27.C	2.010188	-2.434304	5.913975
28.C	0.670303	-0.083104	3.193069
29.C	0.084140	2.226989	3.047989
30.C	0.573026	-0.436027	1.709157
31.C	-0.610924	-1.005892	1.138878
32.C	-0.554343	-1.377163	-0.254528
33.C	1.597648	-0.609385	-0.481193
34.C	1.657373	-0.216713	0.873924
35.C	-1.829705	-1.178775	1.841000
36.C	-2.962651	-1.679662	1.207903
37.C	-2.877743	-2.118318	-0.144588
38.C	-1.704275	-1.964347	-0.845665
39.C	-5.431880	-1.734073	1.545300

40.C	-6.302832	-2.903775	3.597799
41.C	-5.338092	-3.925383	3.711284
42.C	-5.422148	-4.848961	4.754829
43.C	-6.444248	-4.789491	5.709431
44.C	-7.392999	-3.768622	5.595875
45.C	-7.331389	-2.836596	4.560417
46.H	3.601228	-0.076755	7.244159
47.C	-9.355018	-0.639499	1.223082
48.C	-11.638162	-0.153107	1.957247
49.C	-10.929179	0.303762	-0.394429
50.C	-8.535538	-3.696957	6.576808
51.H	-8.653537	-0.620509	0.365340
52.H	-11.221402	-0.560428	2.883543
53.H	-12.497755	-0.762648	1.639450
54.H	-11.980766	0.878671	2.129016
55.H	-10.049051	0.222854	-1.042981
56.H	-11.244540	1.357641	-0.356783
57.N	1.305851	-1.215256	5.376798
58.N	0.546089	-1.190213	-1.040464
59.N	-4.136152	-1.784167	1.977729
60.N	-6.363603	-1.995194	2.537980
61.H	-0.316023	-0.230328	3.660513
62.N	-10.595543	-0.180178	0.938281
63.O	1.092820	1.272727	3.416363
64.H	0.493665	3.216485	3.281481
65.H	0.232397	-1.442642	5.451905
66.O	-8.992865	-1.059282	2.337955
67.H	-11.746474	-0.290721	-0.830477
68.S	-5.972645	-1.312670	0.005434
69.H	-0.150547	2.171104	1.973292
70.H	1.575236	-3.304536	5.406528
71.H	1.184728	0.849806	5.735248
72.H	4.905374	-0.692898	5.143632

73.H	3.879716	-3.014442	4.927986
74.H	3.490088	1.162636	5.982515
75.H	-0.841572	2.067332	3.626028
76.H	1.510240	-2.026680	3.470278
77.H	3.671443	-1.226151	3.068701
78.H	3.250772	0.430362	3.562543
79.H	1.740208	-2.495266	6.976237
80.H	4.076171	-2.518268	6.616488
81.H	-3.752359	-2.552190	-0.620743
82.H	-1.628955	-2.275948	-1.887003
83.H	-1.927461	-0.895981	2.889324
84.H	2.462932	-0.443815	-1.129019
85.H	2.559029	0.265662	1.252326
86.H	-4.005610	-1.503337	2.996105
87.H	-7.317920	-1.621795	2.348267
88.H	-4.536477	-4.003779	2.980924
89.H	-8.083879	-2.053691	4.475317
90.H	1.213185	-0.172378	7.193552
91.H	-6.494212	-5.512127	6.520593
92.C	-4.435870	-5.988170	4.819248
93.F	-3.261577	-5.704833	4.185310
94.F	-4.931344	-7.125239	4.236724
95.F	-4.122891	-6.324794	6.110567
96.F	-8.230898	-4.284295	7.773951
97.F	-9.656710	-4.331380	6.108161
98.F	-8.907307	-2.408747	6.848003

List of Figures

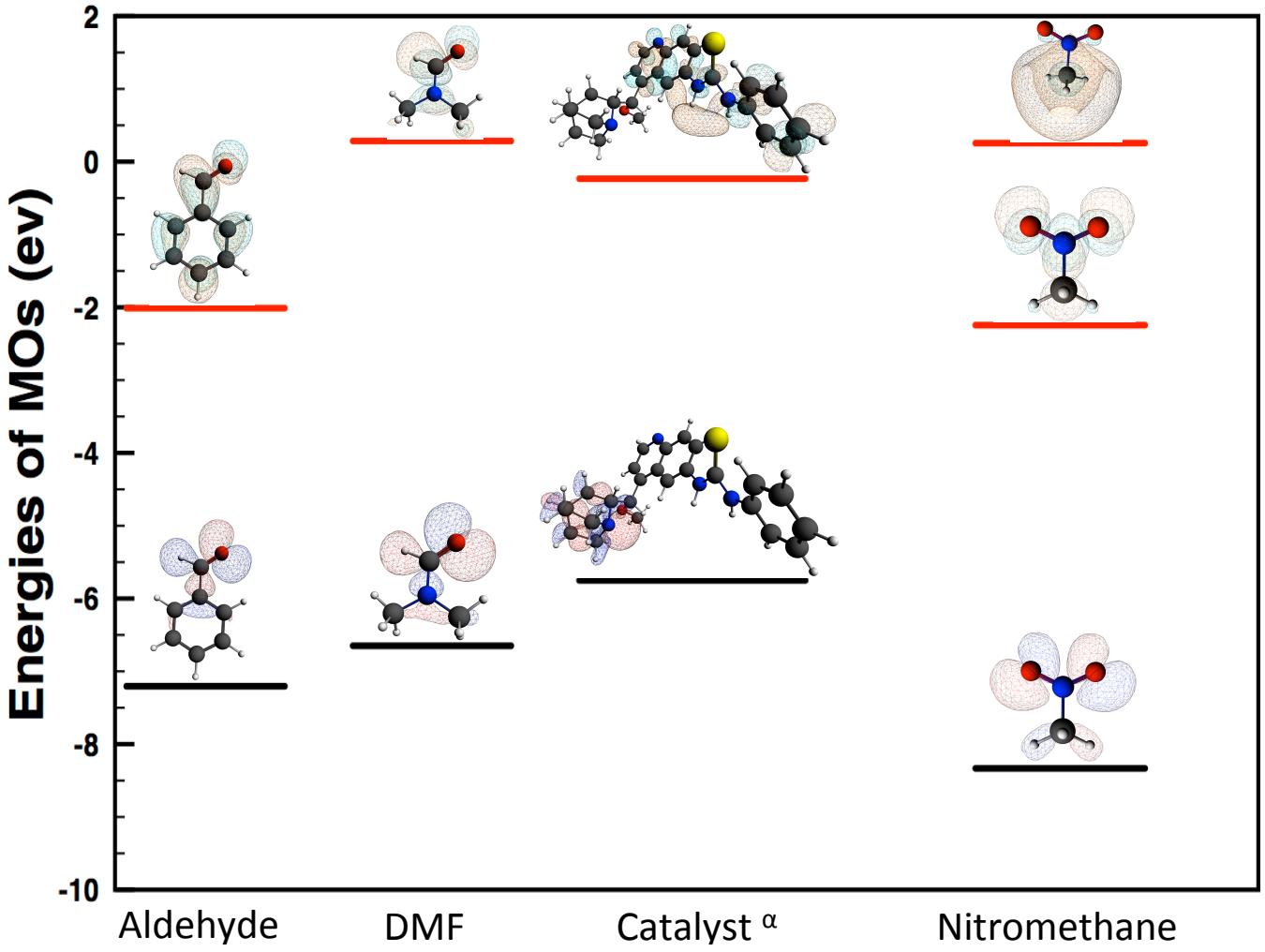

Figure 1: Frontier orbital energies (black: HOMO, red: LUMO) and shapes of the various interacting species.

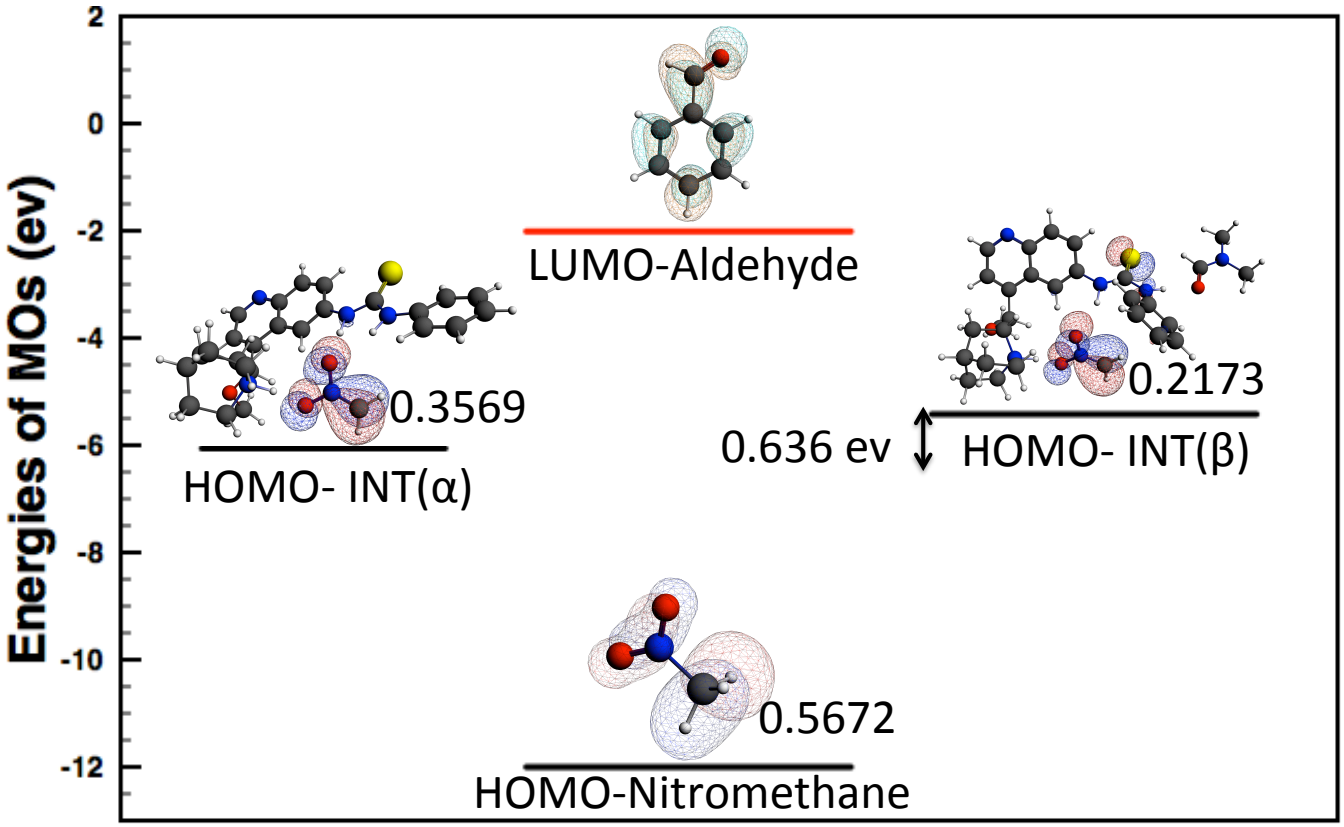

Figure 2: Comparison of the electronic charge and energy of the molecular orbital (HOMO) in the intermediate INT(α/β) after the proton transfer step. Most of its amplitude is on the carbon atom of nitromethide anion that will attack the aldehyde molecule. Levels of the HOMO in free nitromethane and LUMO of aldehyde are shown for comparison. The Mulliken atomic charges of the carbon atoms are shown in the figure.