First Asymmetric Cascade Reaction Catalysed by Chiral Primary Amino alcohols

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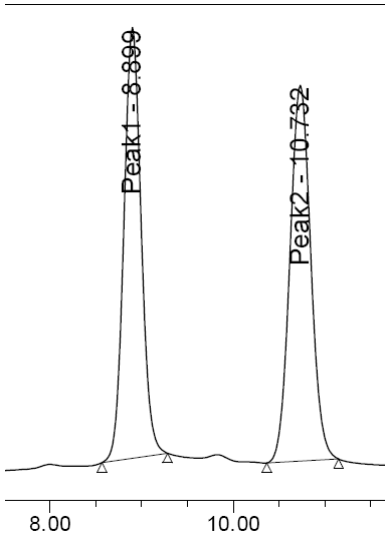
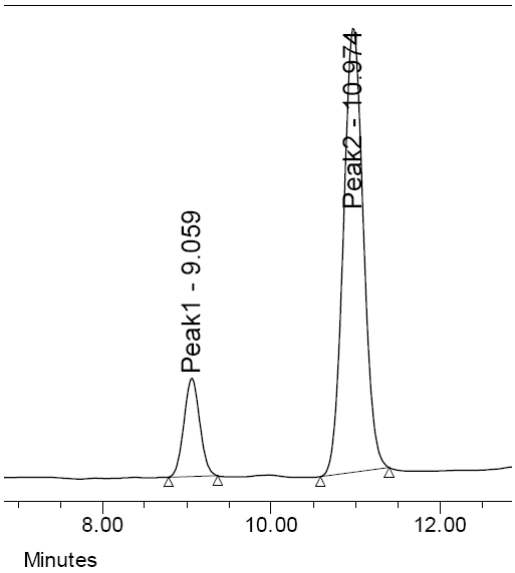
1. Copies of the HPLC chromatograms

Racemic mixture



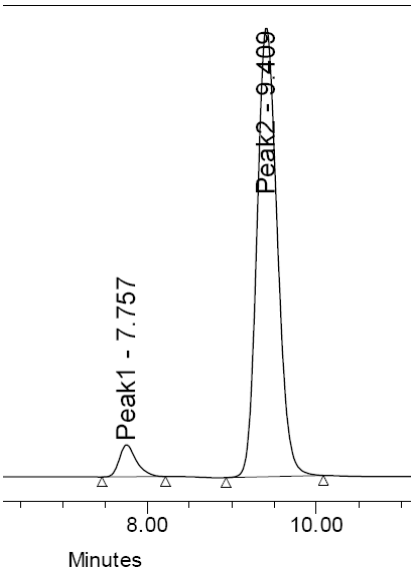
	Peak Name	RT	Area	% Area	Height
1	Peak1	8.899	4466346	48.79	341324
2	Peak2	10.732	4688225	51.21	297927

Table 1, entry 1



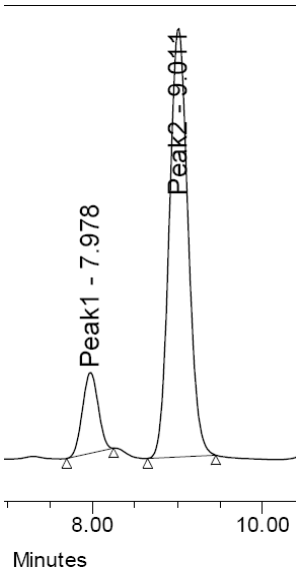
	Peak Name	RT	Area	% Area	Height
1	Peak1	9.059	1897025	14.91	145208
2	Peak2	10.974	10822917	85.09	657358

Table 1, entry 2



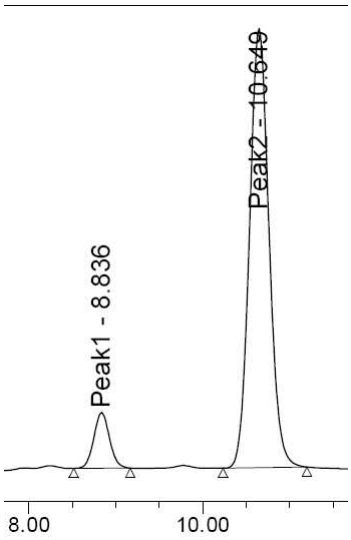
	Peak Name	RT	Area	% Area	Height
1	Peak1	7.757	347593	5.68	24663
2	Peak2	9.409	5771354	94.32	346792

Table 1, entry 3



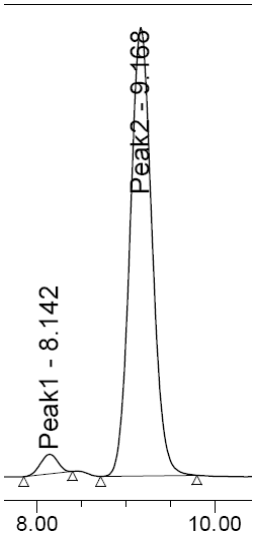
	Peak Name	RT	Area	% Area	Height
1	Peak1	7.978	687308	13.66	53806
2	Peak2	9.011	4345565	86.34	285319

Table 1, entry 4



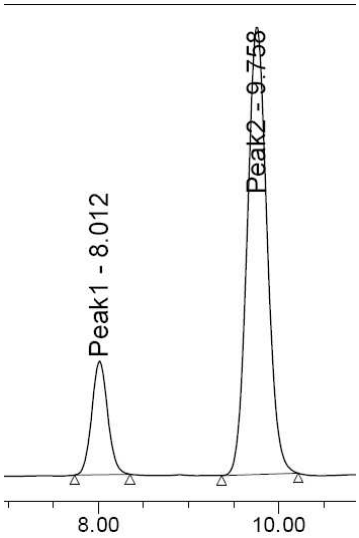
	Peak Name	RT	Area	% Area	Height
1	Peak1	8.836	1312815	9.27	104851
2	Peak2	10.649	12856759	90.73	826949

Table 1, entry 5



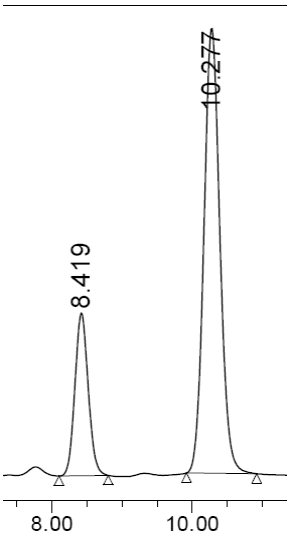
	Peak Name	RT	Area	% Area	Height
1	Peak1	8.142	172946	3.34	12756
2	Peak2	9.168	5006513	96.66	292317

Table 1, entry 6



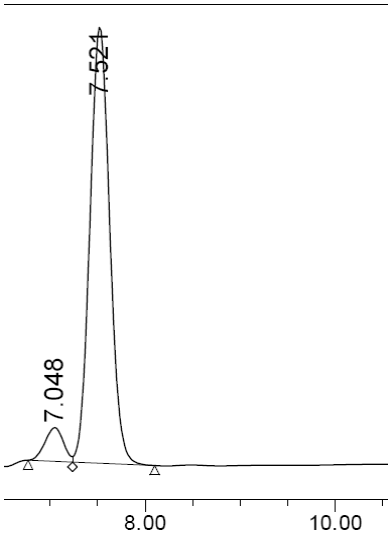
	Peak Name	RT	Area	% Area	Height
1	Peak1	8.012	2407876	16.95	195559
2	Peak2	9.758	11795644	83.05	772116

Table 1, entry 7



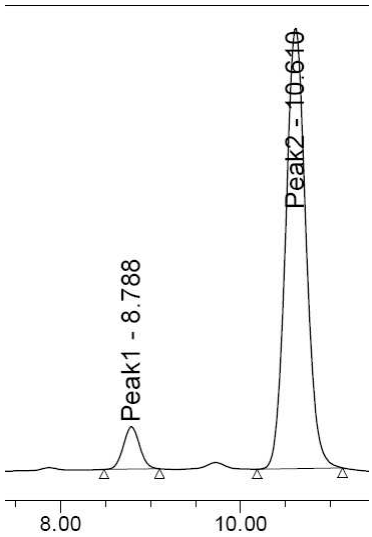
	RT	Area	% Area	Height
1	8.419	3820179	23.34	290239
2	10.277	12545204	76.66	793775

Table 1, entry 8



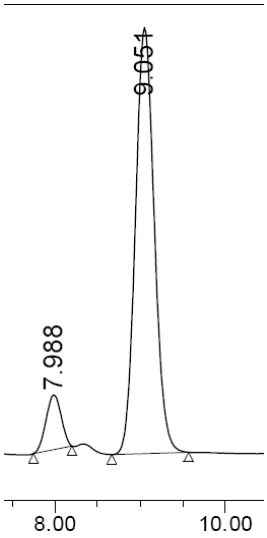
	RT	Area	% Area	Height
1	7.048	417380	6.71	30983
2	7.521	5800060	93.29	400751

Table 1, entry 9



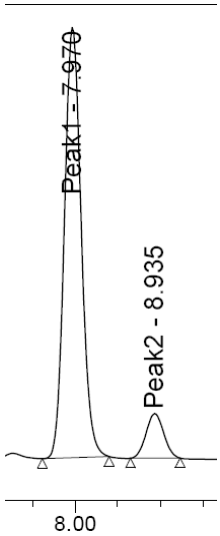
	Peak Name	RT	Area	% Area	Height
1	Peak1	8.788	1039925	7.19	82610
2	Peak2	10.610	13427700	92.81	859048

Table 1, entry 10



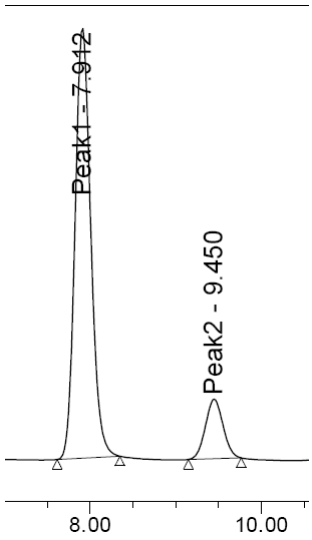
	RT	Area	% Area	Height
1	7.988	575178	9.34	46716
2	9.051	5582628	90.66	363571

Table 2, entry 2



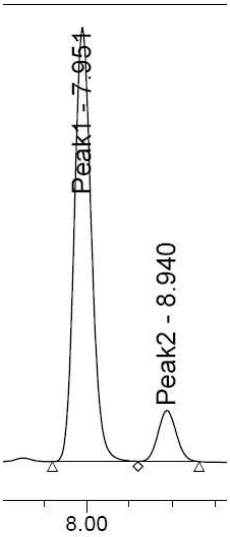
	Peak Name	RT	Area	% Area	Height
1	Peak1	7.970	5976486	90.14	438582
2	Peak2	8.935	654001	9.86	45347

Table 2, entry 3



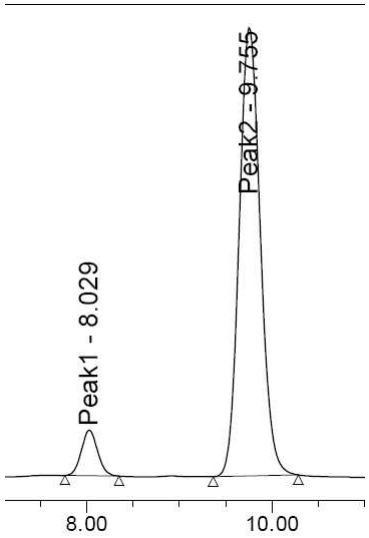
	Peak Name	RT	Area	% Area	Height
1	Peak1	7.912	8607832	86.55	676033
2	Peak2	9.450	1337364	13.45	93469

Table 2, entry 5



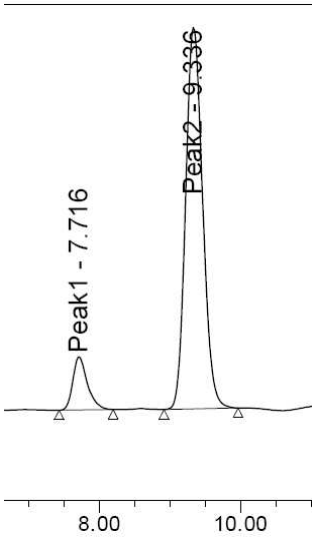
	Peak Name	RT	Area	% Area	Height
1	Peak1	7.951	8842418	88.72	638566
2	Peak2	8.940	1124124	11.28	75133

Table 2, entry 7



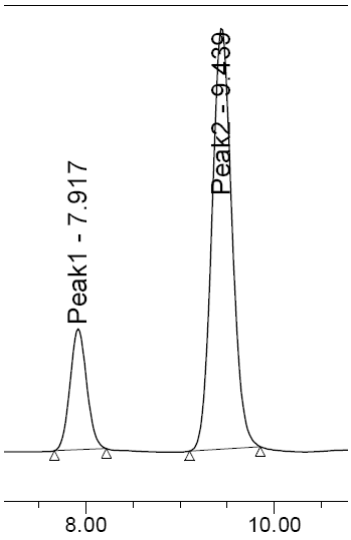
	Peak Name	RT	Area	% Area	Height
1	Peak1	8.029	2068753	7.25	170442
2	Peak2	9.755	26448707	92.75	1675175

Table 2, entry 9

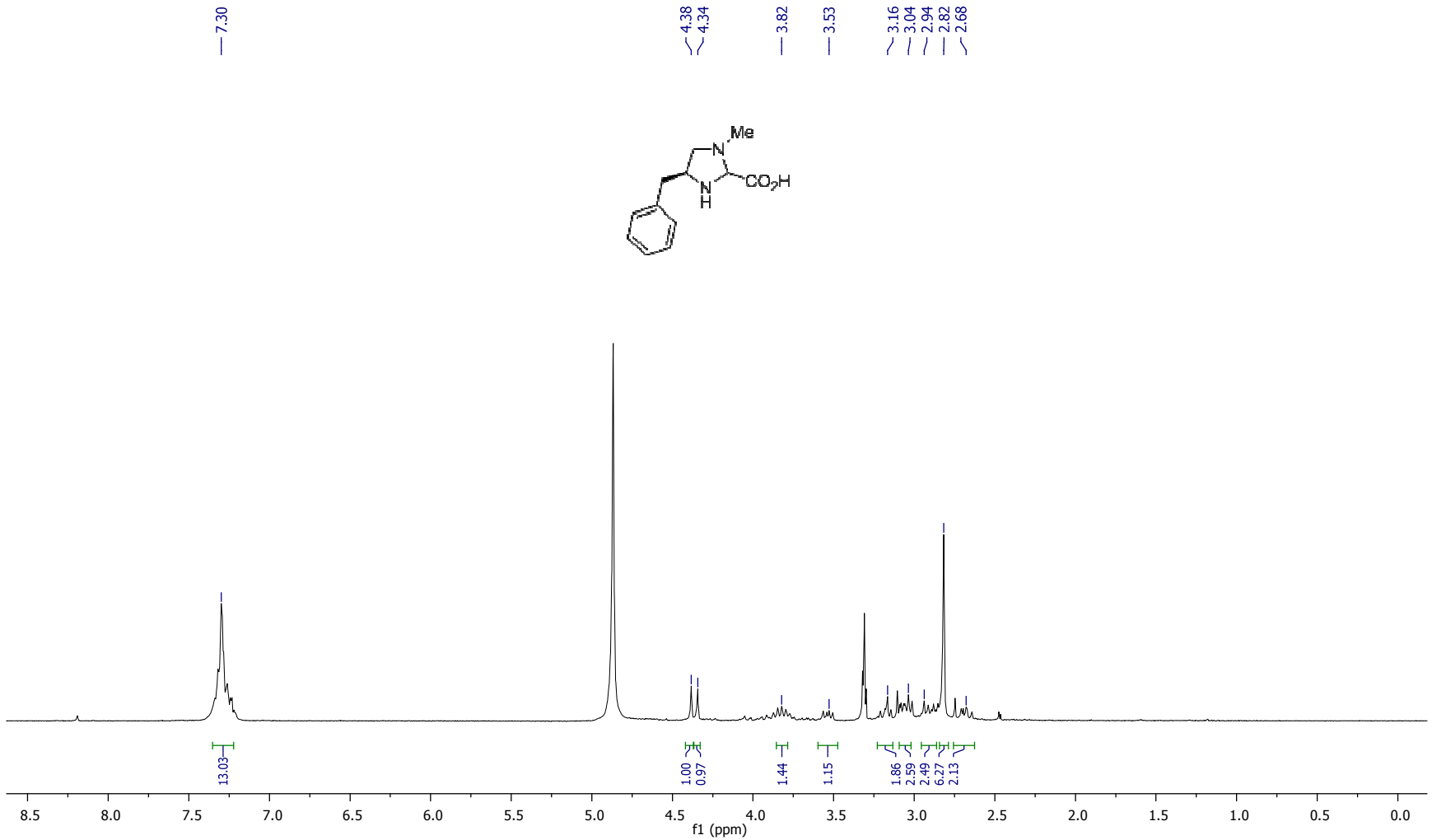


	Peak Name	RT	Area	% Area	Height
1	Peak1	7.716	395160	10.64	27650
2	Peak2	9.336	3317305	89.36	198704

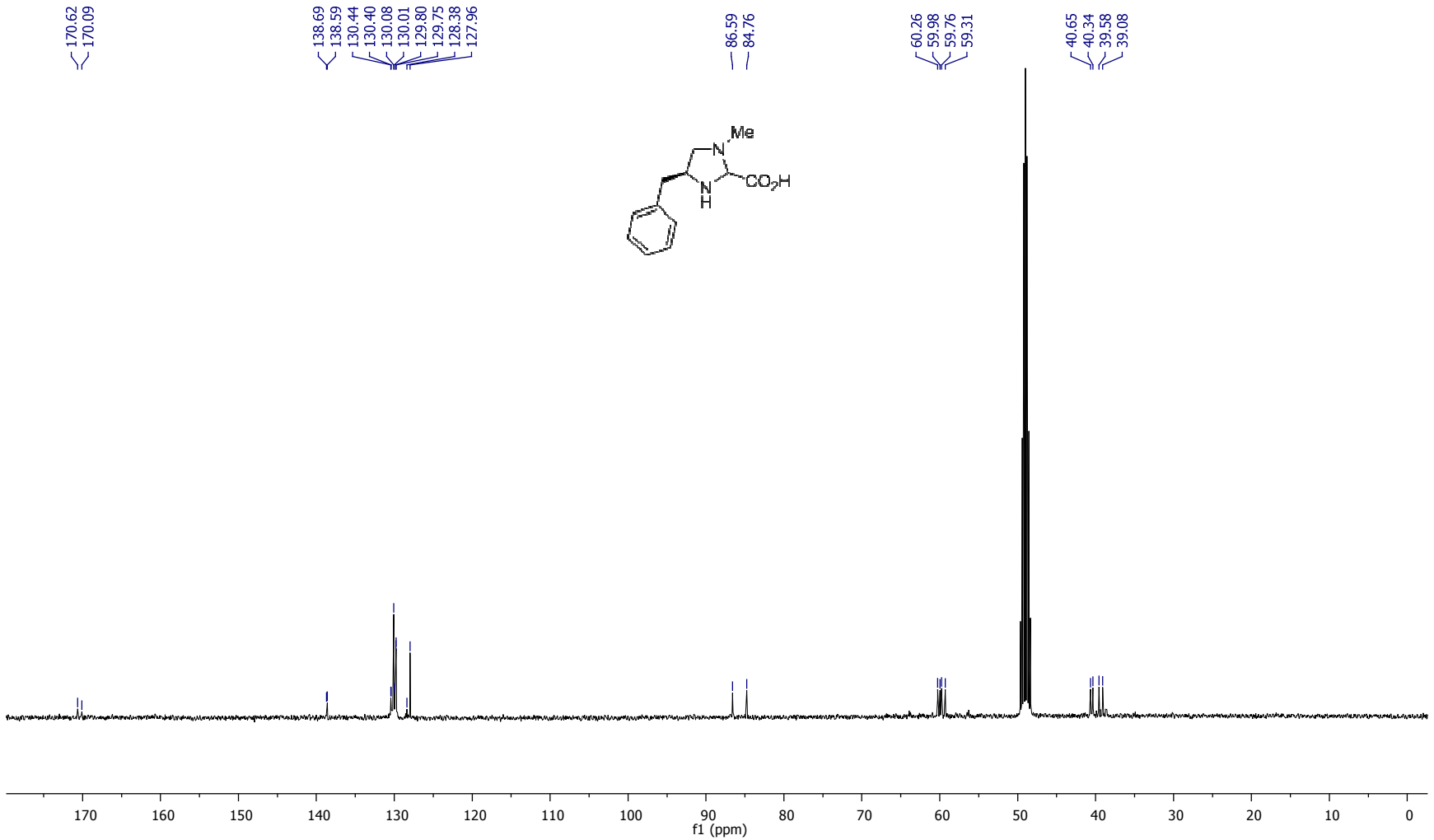
Table 2, entry 10



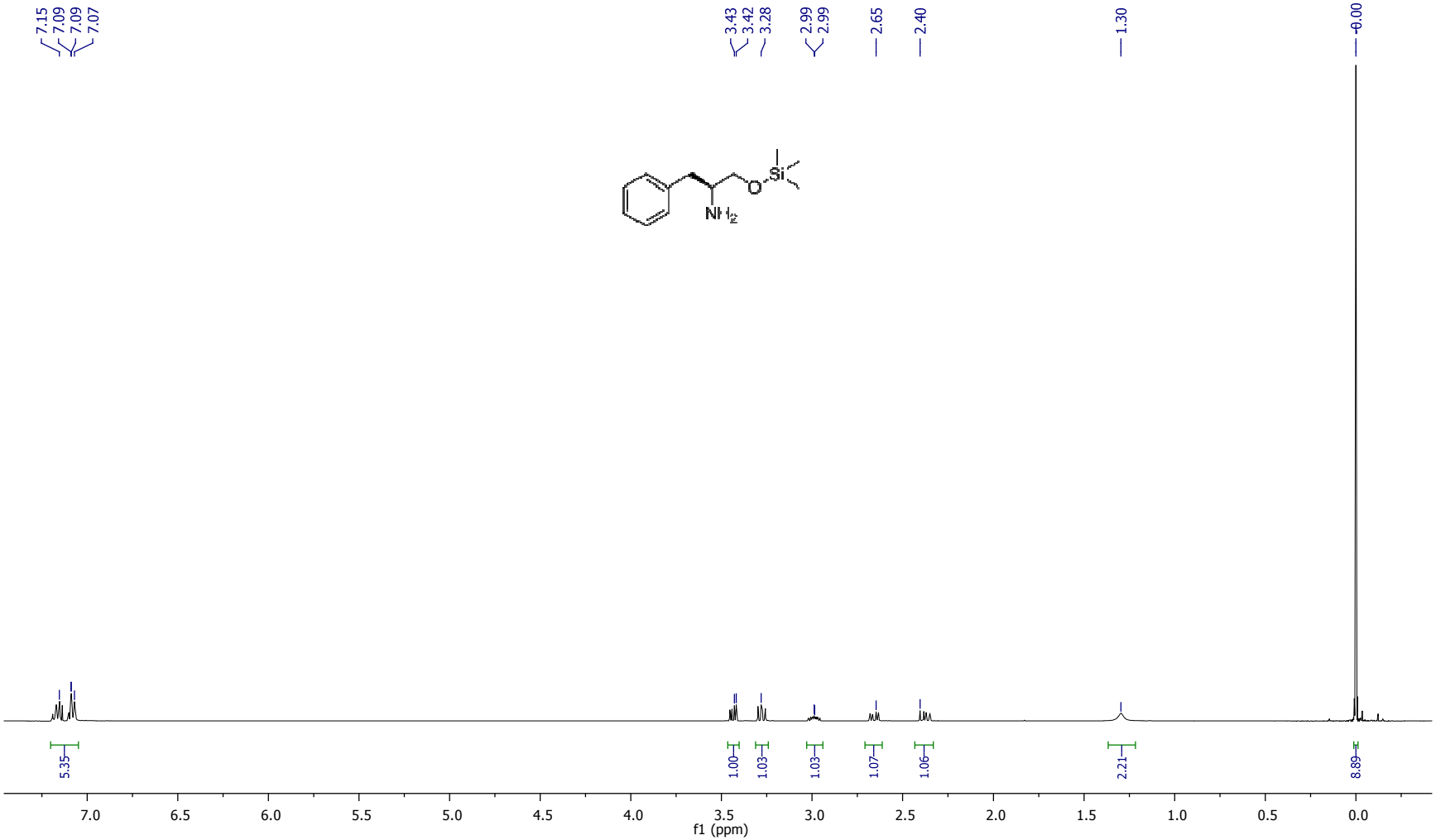
	Peak Name	RT	Area	% Area	Height
1	Peak1	7.917	1372558	19.40	111421
2	Peak2	9.439	5703367	80.60	388327



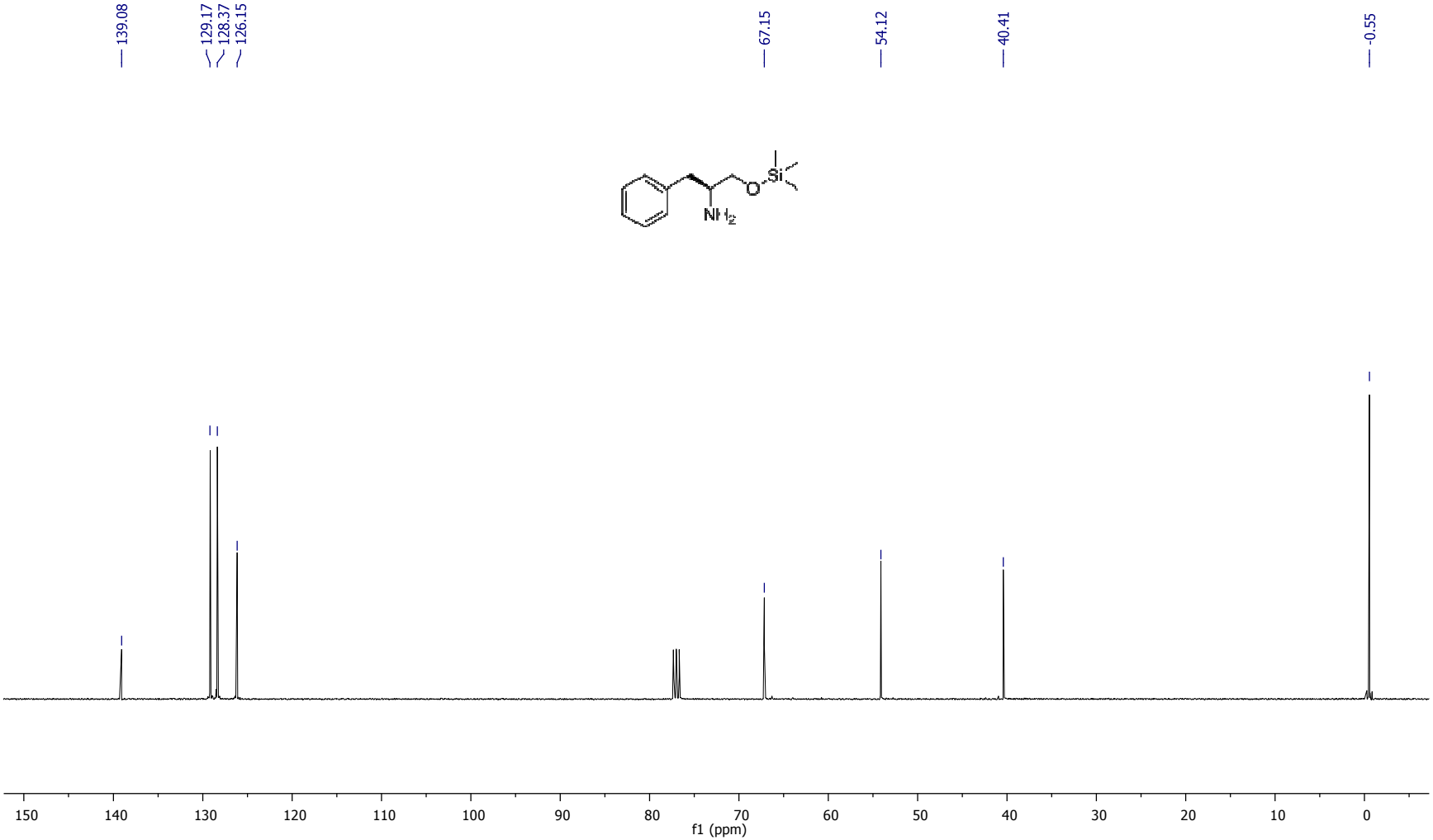
(4*S*)-4-Benzyl-1-methylimidazolidine-2-carboxylic acid (1)



(4*S*)-4-Benzyl-1-methylimidazolidine-2-carboxylic acid (1)

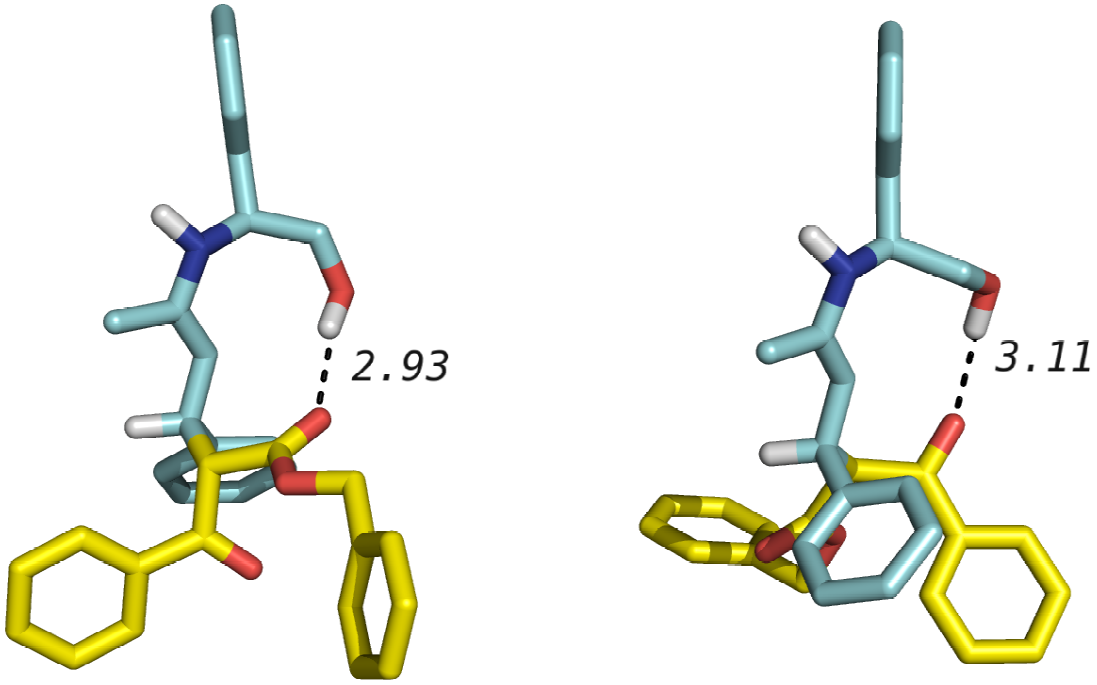


(*S*)-1-Phenyl-3-(trimethylsilyloxy)propan-2-amine (13)



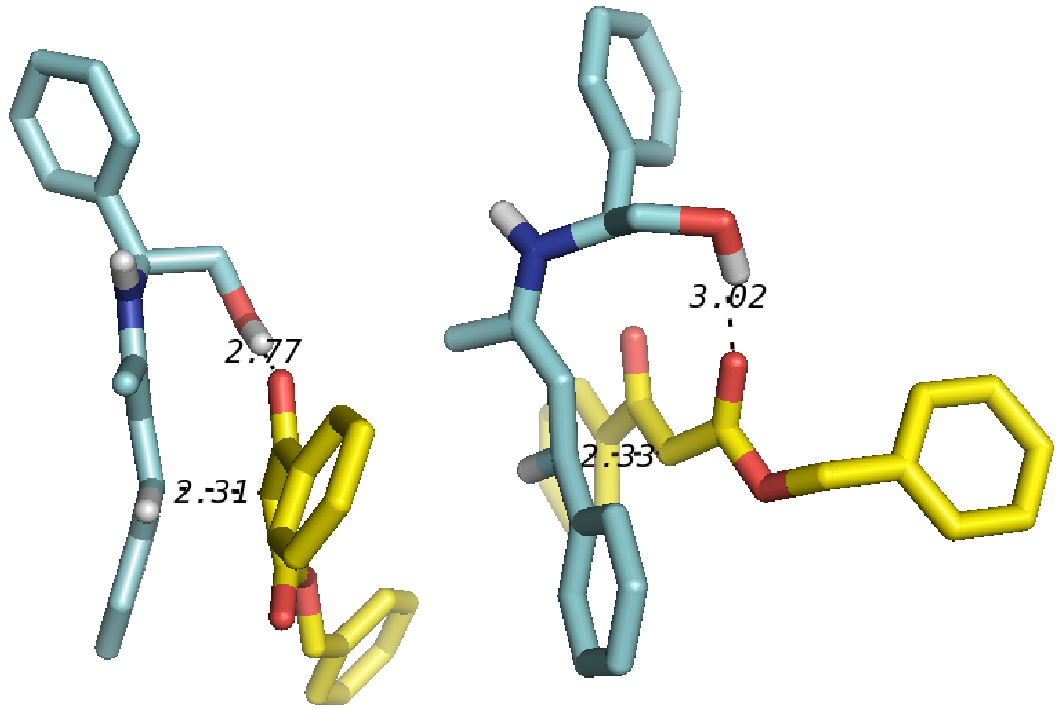
(*S*)-1-Phenyl-3-(trimethylsilyloxy)propan-2-amine (13)

Figure S1. Representation of the alternative products formed upon nucleophilic attack of the benzylbenzoylacetate (shown in yellow) to the *Si* / *Re* faces of the iminium intermediate *trans-im***2** (shown in blue). Compared to the structures shown in Figure 5, the intramolecular hydrogen-bond involves the hydroxyl unit and the alternative carbonyl moiety of the benzylbenzoylacetate reagent. The relative energy (kcal/mol; in bold), and selected intramolecular distances (Å; in italics) determined from geometry optimizations at the B3LYP/6-31G(d) level are shown.



Si face (**2.9**) *Re* face (**3.6**)

Figure S2. Representation of the transition states leading to the most stable products with R and S configuration (shown in Figure 5) formed upon nucleophilic attack of the benzylbenzoylacetate (shown in yellow) to the *Si* / *Re* faces of the iminium intermediate *trans-im***2** (shown in blue). The relative energy (kcal/mol; in bold), and selected intramolecular distances (Å; in italics) determined from geometry optimizations at the B3LYP/6-31G(d) level are shown.



Si face (**0.0**) *Re* face (**3.6**)

Optimized geometries and energies of the iminium derivatives (Figure 4)

*trans-im***2** (relative energy: 0.0 kcal/mol)

1	6	0	1.793966	2.437672	1.762878
2	6	0	1.422144	3.462743	0.889586
3	6	0	1.367128	3.220009	-0.483650
4	6	0	1.678472	1.953244	-0.982141
5	6	0	2.053153	0.921929	-0.111575
6	6	0	2.113257	1.174580	1.265571
7	6	0	2.461412	-0.422872	-0.687155
8	6	0	3.993611	-0.576344	-0.676475
9	8	0	4.279636	-1.924277	-1.029690
10	1	0	5.237709	-2.069378	-0.989590
11	7	0	1.929539	-1.604294	0.035594
12	1	0	2.646705	-2.318926	0.158554
13	6	0	0.682531	-1.938183	0.313550
14	6	0	0.490528	-3.281027	0.971403
15	6	0	-0.412331	-1.078066	0.002071
16	6	0	-1.711376	-1.408857	0.277610
17	6	0	-4.021544	1.370954	-0.798294
18	6	0	-2.847560	0.672456	-0.559422
19	6	0	-2.891317	-0.623784	0.005874
20	6	0	-4.149568	-1.183638	0.323782
21	6	0	-5.323419	-0.480724	0.080824
22	6	0	-5.260611	0.796946	-0.481372
23	1	0	1.840364	2.623045	2.831935
24	1	0	1.179002	4.446911	1.278809
25	1	0	1.084846	4.014184	-1.168520
26	1	0	1.638100	1.769602	-2.053786
27	1	0	2.403567	0.384115	1.953358
28	1	0	2.117400	-0.503368	-1.725607
29	1	0	4.379751	-0.331954	0.323520
30	1	0	4.413173	0.141547	-1.391789
31	1	0	-0.143453	-3.924489	0.353261
32	1	0	0.004210	-3.167089	1.945309
33	1	0	1.444181	-3.791278	1.126725
34	1	0	-0.182752	-0.130855	-0.468135
35	1	0	-1.908117	-2.368832	0.751369
36	1	0	-3.980834	2.366038	-1.230311
37	1	0	-1.895124	1.133778	-0.801351
38	1	0	-4.194516	-2.178100	0.760531
39	1	0	-6.283362	-0.922974	0.327682
40	1	0	-6.175579	1.350068	-0.671997

E(RB+HF-LYP) = -827.711346060

*trans-im***2** (relative energy: 1.2 kcal/mol)

1	6	0	5.488031	0.250020	-0.054415
2	6	0	5.708423	-0.417860	-1.260538
3	6	0	4.650483	-1.065413	-1.900620
4	6	0	3.373770	-1.041937	-1.338786
5	6	0	3.144188	-0.379068	-0.127282
6	6	0	4.213080	0.267998	0.511972
7	6	0	1.748591	-0.358975	0.470932
8	6	0	1.706800	-0.915899	1.900424
9	8	0	0.349500	-0.963152	2.306025
10	1	0	0.305860	-1.296944	3.215404
11	7	0	1.233075	1.037198	0.421786
12	1	0	1.966820	1.738294	0.462584
13	6	0	0.003511	1.481409	0.224666
14	6	0	-0.142647	2.975369	0.082895
15	6	0	-1.113879	0.597611	0.142266
16	6	0	-2.369894	1.032210	-0.180636
17	6	0	-4.803744	-1.848029	-0.084294
18	6	0	-3.613990	-1.143588	0.024738

19	6	0	-3.572658	0.238505	-0.273047
20	6	0	-4.764262	0.880768	-0.678497
21	6	0	-5.953744	0.170605	-0.789078
22	6	0	-5.974748	-1.194684	-0.492545
23	1	0	6.308808	0.751059	0.450026
24	1	0	6.701803	-0.434426	-1.698688
25	1	0	4.816761	-1.586850	-2.838448
26	1	0	2.552889	-1.545141	-1.844068
27	1	0	4.065219	0.780197	1.460959
28	1	0	1.083277	-0.967108	-0.146747
29	1	0	2.307820	-0.283784	2.569693
30	1	0	2.166030	-1.914129	1.875260
31	1	0	-0.847337	3.366142	0.822609
32	1	0	-0.524527	3.228658	-0.911645
33	1	0	0.812793	3.489605	0.214542
34	1	0	-0.944152	-0.440552	0.392649
35	1	0	-2.509775	2.088166	-0.404204
36	1	0	-4.828068	-2.908126	0.148386
37	1	0	-2.716549	-1.660817	0.349254
38	1	0	-4.744932	1.943305	-0.907472
39	1	0	-6.861571	0.675867	-1.103195
40	1	0	-6.902565	-1.752834	-0.576533

E(RB+HF-LYP) = -827.709389783

*trans-im***1** (relative energy: 0.7 kcal/mol)

1	6	0	-3.855605	-1.627363	1.664417
2	6	0	-4.832896	-2.147187	0.811935
3	6	0	-4.997784	-1.610436	-0.465571
4	6	0	-4.182974	-0.560691	-0.892740
5	6	0	-3.202694	-0.034261	-0.043734
6	6	0	-3.047795	-0.571518	1.242089
7	6	0	-2.379755	1.155582	-0.504042
8	6	0	-2.856728	2.448632	0.182311
9	8	0	-1.910232	3.462799	-0.133467
10	1	0	-2.165343	4.286861	0.309658
11	7	0	-0.927168	1.055784	-0.223095
12	1	0	-0.555442	1.930342	0.150603
13	6	0	-0.059014	0.119910	-0.564124
14	6	0	-0.542122	-1.111540	-1.270582
15	6	0	1.311122	0.345852	-0.215273
16	6	0	2.331072	-0.530242	-0.456073
17	6	0	5.598340	0.873644	0.809530
18	6	0	4.245996	0.784423	0.515280
19	6	0	3.726459	-0.368161	-0.118527
20	6	0	4.612571	-1.419924	-0.442941
21	6	0	5.966918	-1.327805	-0.144739
22	6	0	6.461390	-0.181030	0.481699
23	1	0	-3.726018	-2.039843	2.660690
24	1	0	-5.463354	-2.966665	1.143725
25	1	0	-5.756612	-2.009181	-1.132127
26	1	0	-4.314169	-0.148037	-1.890738
27	1	0	-2.293798	-0.169777	1.915242
28	1	0	-2.489775	1.288237	-1.587686
29	1	0	-2.924104	2.285690	1.267522
30	1	0	-3.860625	2.681630	-0.192795
31	1	0	0.270588	-1.629206	-1.777982
32	1	0	-1.306378	-0.861610	-2.010208
33	1	0	-1.002835	-1.799261	-0.552428
34	1	0	1.522216	1.285439	0.290202
35	1	0	2.097332	-1.469536	-0.951765
36	1	0	5.988926	1.762819	1.294522
37	1	0	3.591754	1.611092	0.773909
38	1	0	4.225325	-2.310714	-0.931009
39	1	0	6.636161	-2.143643	-0.398844
40	1	0	7.519188	-0.104812	0.715410

E(RB+HF-LYP) = -827.710297235

*trans-im***1** (relative energy: 1.1 kcal/mol)

1	7	0	1.001685	0.465990	-0.192271
2	6	0	4.434351	-2.159553	-0.835285
3	6	0	5.101171	-2.366699	0.373742
4	6	0	4.890584	-1.494042	1.442506
5	6	0	4.012178	-0.419157	1.304560
6	6	0	3.342489	-0.200494	0.094776
7	6	0	3.561421	-1.080474	-0.976146
8	6	0	2.389259	0.973941	-0.038456
9	6	0	2.745356	1.905921	-1.206774
10	6	0	-0.124681	0.943537	0.309453
11	6	0	-0.068210	2.161608	1.183809
12	6	0	-1.329947	0.236732	-0.002096
13	6	0	-2.575068	0.581899	0.440616
14	6	0	-5.158742	-1.854715	-0.839978
15	6	0	-3.925019	-1.259707	-0.622231
16	6	0	-3.823845	-0.092066	0.168953
17	6	0	-5.002383	0.450159	0.729017
18	6	0	-6.237083	-0.148647	0.508567
19	6	0	-6.316740	-1.301763	-0.276132
20	8	0	1.815686	2.976617	-1.201653
21	1	0	2.053125	3.602878	-1.902672
22	1	0	0.932431	-0.380403	-0.751919
23	1	0	4.598898	-2.832417	-1.671573
24	1	0	5.783913	-3.204205	0.481077
25	1	0	5.408032	-1.649397	2.384409
26	1	0	3.852115	0.256097	2.141674
27	1	0	3.065014	-0.926464	-1.932603
28	1	0	2.413384	1.566086	0.878090
29	1	0	2.715310	1.352313	-2.156466
30	1	0	3.776997	2.249238	-1.048208
31	1	0	-1.059898	2.521885	1.449383
32	1	0	0.472832	2.958697	0.667681
33	1	0	0.464719	1.928292	2.113823
34	1	0	-1.216626	-0.636791	-0.640555
35	1	0	-2.671575	1.460378	1.073472
36	1	0	-5.227071	-2.751197	-1.448316
37	1	0	-3.038243	-1.702042	-1.065366
38	1	0	-4.937458	1.347372	1.339338
39	1	0	-7.134212	0.278879	0.944949
40	1	0	-7.279521	-1.772945	-0.450511

E(RB+HF-LYP) = -827.709660367

Optimized geometries and energies of the products (Figure 5)

R configuration (*Si* face; relative energy: 0.0 kcal/mol)

1	7	0	3.603536	-0.527007	0.278010
2	6	0	7.548970	-1.201554	-1.208478
3	6	0	8.300928	-0.046568	-1.429949
4	6	0	7.660910	1.193058	-1.477806
5	6	0	6.278813	1.275405	-1.303337
6	6	0	5.512922	0.124343	-1.079565
7	6	0	6.166331	-1.117355	-1.037433
8	6	0	4.002764	0.217261	-0.928071
9	6	0	3.330486	-0.306489	-2.231803
10	6	0	2.456601	-0.227854	1.028649
11	6	0	2.454640	-0.959968	2.350281
12	6	0	1.471543	0.576149	0.579814
13	8	0	2.002871	0.129211	-2.453729
14	1	0	1.375217	-0.473499	-2.013974
15	1	0	4.401572	-0.727622	0.869990
16	1	0	8.038157	-2.171590	-1.172080
17	1	0	9.377487	-0.111949	-1.563217
18	1	0	8.237833	2.098749	-1.645852
19	1	0	5.786745	2.244538	-1.337746
20	1	0	5.587911	-2.022120	-0.868548
21	1	0	3.727095	1.278872	-0.829790
22	1	0	3.409419	-1.403428	-2.244327
23	1	0	3.916511	0.079645	-3.073756
24	1	0	1.579158	-0.729602	2.957880
25	1	0	3.343491	-0.691523	2.938720
26	1	0	2.485878	-2.044751	2.191919
27	1	0	1.597263	1.026930	-0.398522
28	6	0	-2.400309	0.352682	0.820405
29	6	0	-0.986063	0.176226	0.272964
30	6	0	-0.650355	-1.284501	-0.104381
31	6	0	-0.714615	-3.728847	0.289253
32	6	0	-0.921076	-4.853043	1.079927
33	6	0	-1.323867	-4.705896	2.411391
34	6	0	-1.521840	-3.430766	2.941410
35	6	0	-4.694655	0.414347	0.212330
36	6	0	-5.545866	0.262255	-1.017940
37	6	0	-6.209891	1.364482	-1.565860
38	6	0	-7.002121	1.221784	-2.706649
39	6	0	-7.131231	-0.027473	-3.313826
40	6	0	-6.468255	-1.133814	-2.775658
41	6	0	-5.683675	-0.989305	-1.633236
42	6	0	-0.919363	-2.437434	0.810312
43	6	0	-1.326417	-2.299234	2.148356
44	6	0	0.114991	0.816031	1.197893
45	6	0	-0.155340	2.309319	1.390854
46	6	0	-0.445539	2.818322	2.662152
47	6	0	-0.668870	4.182221	2.856386
48	6	0	-0.611993	5.062766	1.775620
49	6	0	-0.329882	4.567244	0.501110
50	6	0	-0.102504	3.203945	0.311801
51	8	0	-0.117509	-1.490936	-1.189350
52	8	0	-2.702727	0.526624	1.983474
53	8	0	-3.298624	0.285100	-0.180973
54	1	0	0.040685	0.339784	2.178068
55	1	0	-0.958380	0.692504	-0.690082
56	1	0	-0.392655	-3.821244	-0.742258
57	1	0	-0.766450	-5.844607	0.663350
58	1	0	-1.482739	-5.583855	3.032122
59	1	0	-1.833264	-3.312334	3.975499
60	1	0	-4.832404	1.389617	0.687192
61	1	0	-4.906875	-0.355472	0.961004
62	1	0	-6.106025	2.340114	-1.096741
63	1	0	-7.514642	2.085890	-3.120747

```
    64          1             0       -7.746188   -0.140743   -4.202631
    65          1             0       -6.566060   -2.108895   -3.245243
    66          1             0       -5.167236   -1.850452   -1.215969
    67          1             0       -1.502033   -1.319530    2.575106
    68          1             0       -0.507715    2.136963    3.506558
    69          1             0       -0.891974    4.554601    3.853046
    70          1             0       -0.787037    6.125145    1.923951
    71          1             0       -0.282659    5.243119   -0.348981
    72          1             0        0.126047    2.839365   -0.686880
E(RB+HF-LYP) =  -1671.12085604
```

S configuration (*Re* face; relative energy: 2.0 kcal/mol)

```
1           7             0       -3.590410    0.570387   -0.017789
    2           6             0       -7.105790   -1.829949   -0.235497
    3           6             0       -7.039684   -3.086643    0.369464
    4           6             0       -5.798992   -3.606908    0.740793
    5           6             0       -4.633826   -2.872242    0.515478
    6           6             0       -4.687475   -1.610606   -0.088938
    7           6             0       -5.939130   -1.100555   -0.466938
    8           6             0       -3.409306   -0.841938   -0.366446
    9           6             0       -2.955975   -0.975904   -1.864865
   10           6             0       -2.484801    1.400947    0.193695
   11           6             0       -2.868360    2.792815    0.631727
   12           6             0       -1.219620    0.995086   -0.048321
   13           6             0        0.615326    4.674770   -3.254978
   14           1             0       -4.346374    0.727502    0.639660
   15           6             0        1.308908    0.958764    0.164172
   16           8             0        2.915754   -0.205253   -1.084402
   17           1             0        7.491169   -3.413975   -1.727405
   18           6             0       -0.158841    2.515041   -2.474753
   19           6             0        0.780544    4.090357   -0.916289
   20           8             0       -1.931657   -1.935224   -2.043303
   21           1             0       -1.072974   -1.499129   -1.903584
   22           1             0       -8.066920   -1.417934   -0.532724
   23           1             0       -3.429699    3.304900   -0.159098
   24           1             0       -7.947874   -3.656237    0.548224
   25           1             0       -5.736548   -4.585016    1.210835
   26           1             0       -3.669598   -3.281717    0.805632
   27           1             0       -5.996069   -0.127854   -0.949490
   28           1             0       -2.607583   -1.290216    0.240576
   29           1             0        0.007344    2.464675    0.912203
   30           1             0       -2.658550    0.015600   -2.228297
   31           1             0       -3.806488   -1.307492   -2.468892
   32           1             0       -1.996780    3.402901    0.874509
   33           1             0       -3.514852    2.759239    1.519712
   34           1             0       -1.058954   -0.026347   -0.355033
   35           6             0        1.591238    0.014755   -1.004132
   36           6             0        1.230272    0.100246    1.442396
   37           6             0        0.963880    0.022983    3.907846
   38           6             0        1.058124    0.573642    5.181537
   39           6             0        1.547308    1.872996    5.347213
   40           6             0        1.941050    2.616927    4.233892
   41           6             0        3.386315   -1.199196   -2.035718
   42           6             0        4.356130   -2.128722   -1.352545
   43           6             0        5.624000   -2.352775   -1.897354
   44           6             0        6.509221   -3.247739   -1.292364
   45           6             0        6.134602   -3.917761   -0.128043
   46           6             0        4.871772   -3.691161    0.426907
   47           6             0        3.984776   -2.805329   -0.181939
   48           6             0        1.346258    0.766337    2.778536
   49           6             0        1.838250    2.069099    2.955392
   50           6             0        0.027393    1.851145    0.002684
   51           8             0        0.772832   -0.494649   -1.743815
   52           8             0        1.055332   -1.107112    1.363546
   53           1             0        3.006501   -2.625634    0.256246
   54           1             0        2.175415    1.622889    0.241068
   55           1             0        0.594618   -0.985947    3.757643
   56           1             0        0.753117   -0.007894    6.047121
```

57	1	0	5.921972	-1.825261	-2.800908
58	1	0	1.624111	2.302883	6.342326
59	1	0	2.514494	-1.726639	-2.430151
60	1	0	6.822765	-4.611516	0.347672
61	6	0	0.982678	5.005817	-1.950229
62	1	0	2.160940	2.657870	2.102715
63	6	0	0.044077	3.426643	-3.511420
64	1	0	4.575970	-4.208605	1.335674
65	6	0	0.210993	2.832808	-1.160911
66	1	0	2.330969	3.623049	4.359956
67	1	0	3.865844	-0.655562	-2.855117
68	1	0	1.419214	5.977747	-1.734349
69	1	0	0.766719	5.384903	-4.063625
70	1	0	-0.249944	3.160868	-4.523656
71	1	0	-0.605050	1.548512	-2.682134
72	1	0	1.059994	4.362123	0.100698

E(RB+HF-LYP) = -1671.11774119

Optimized geometries and energies of the products (Figure S1)

R configuration (*Si* face; relative energy: 2.9 kcal/mol)

1	7	0	3.380064	0.327096	-1.098089
2	6	0	7.339323	1.855533	-1.516000
3	6	0	8.338093	1.072557	-0.934695
4	6	0	7.988674	0.080381	-0.017051
5	6	0	6.649196	-0.127983	0.314378
6	6	0	5.637584	0.649914	-0.262674
7	6	0	6.000425	1.647866	-1.180910
8	6	0	4.183475	0.444816	0.131789
9	6	0	3.736319	1.616463	1.057104
10	6	0	2.178572	-0.393266	-1.171260
11	6	0	1.740715	-0.602498	-2.603072
12	6	0	1.475615	-0.791151	-0.090783
13	8	0	2.675829	1.326771	1.945591
14	1	0	1.818692	1.391674	1.490851
15	1	0	3.969564	0.158510	-1.905302
16	1	0	7.601954	2.632765	-2.229110
17	1	0	9.380709	1.234160	-1.195075
18	1	0	8.758742	-0.536516	0.438746
19	1	0	6.383316	-0.904449	1.027688
20	1	0	5.228608	2.264535	-1.634603
21	1	0	4.106860	-0.477747	0.727456
22	1	0	3.522698	2.491987	0.424989
23	1	0	4.588162	1.869335	1.697398
24	1	0	0.890564	-1.283037	-2.681500
25	1	0	2.556882	-1.032565	-3.200139
26	1	0	1.465899	0.348896	-3.076377
27	1	0	1.876329	-0.578478	0.891385
28	6	0	-0.940732	0.937684	0.383184
29	6	0	-1.048758	-0.387118	-0.366972
30	6	0	-2.440923	-0.987086	-0.106235
31	6	0	-4.136918	-2.707501	-0.674704
32	6	0	-4.725577	-3.630313	-1.532578
33	6	0	-4.201065	-3.828847	-2.813584
34	6	0	-3.085669	-3.100741	-3.230076
35	6	0	-1.969257	3.086835	0.541974
36	6	0	-3.376923	3.583546	0.340644
37	6	0	-3.610007	4.889486	-0.100285
38	6	0	-4.914197	5.370094	-0.237637
39	6	0	-5.996481	4.540575	0.054816
40	6	0	-5.769795	3.230609	0.487001
41	6	0	-4.468522	2.753878	0.633884
42	6	0	-3.009103	-1.973717	-1.079632
43	6	0	-2.490598	-2.180326	-2.367312
44	6	0	0.106246	-1.439165	-0.099158
45	6	0	-0.116745	-2.305496	1.140066
46	6	0	-0.403094	-3.667979	0.981901
47	6	0	-0.595275	-4.499103	2.087177
48	6	0	-0.504510	-3.975815	3.376421
49	6	0	-0.220021	-2.619467	3.547524
50	6	0	-0.027476	-1.790739	2.442427
51	8	0	-3.056174	-0.688584	0.906645
52	8	0	-0.180502	1.217110	1.288918
53	8	0	-1.824096	1.810087	-0.133401
54	1	0	0.034045	-2.120463	-0.954581
55	1	0	-0.978913	-0.112472	-1.425713
56	1	0	-4.529547	-2.534336	0.321583
57	1	0	-5.593865	-4.196125	-1.206249
58	1	0	-4.662097	-4.547956	-3.485407
59	1	0	-2.679739	-3.246712	-4.227215
60	1	0	-1.233773	3.783043	0.125586
61	1	0	-1.730896	2.937569	1.598877
62	1	0	-2.767646	5.536001	-0.336893
63	1	0	-5.081925	6.387970	-0.579580
64	1	0	-7.012527	4.910281	-0.055597

65	1	0	-6.610065	2.579426	0.713056
66	1	0	-4.291592	1.733470	0.963194
67	1	0	-1.631387	-1.614869	-2.714097
68	1	0	-0.473400	-4.086872	-0.019677
69	1	0	-0.813101	-5.553625	1.937582
70	1	0	-0.652733	-4.618168	4.240652
71	1	0	-0.146718	-2.200760	4.547926
72	1	0	0.190455	-0.738769	2.590731

E(RB+HF-LYP) = -1671.11627579

S configuration (*Re* face; relative energy: 3.6 kcal/mol)

1	7	0	-3.751337	0.004124	-1.170769
2	6	0	-7.728060	1.172113	-0.165528
3	6	0	-7.880861	2.343105	0.578796
4	6	0	-6.765046	2.923841	1.183889
5	6	0	-5.504983	2.342755	1.036744
6	6	0	-5.338382	1.171097	0.288406
7	6	0	-6.468392	0.587611	-0.304322
8	6	0	-3.967420	0.531251	0.179098
9	6	0	-3.771570	-0.598240	1.247915
10	6	0	-2.450656	-0.213245	-1.645115
11	6	0	-2.404899	-0.571235	-3.109277
12	6	0	-1.369983	-0.159475	-0.838090
13	6	0	0.832118	-4.626622	-2.231752
14	1	0	-4.359515	0.428100	-1.862746
15	6	0	0.973817	0.088083	-0.038138
16	8	0	3.078500	0.930918	0.581295
17	1	0	4.513238	4.866343	-2.748621
18	6	0	-0.310893	-2.977667	-0.877992
19	6	0	1.230641	-2.265061	-2.584970
20	8	0	-3.172377	-0.114128	2.435573
21	1	0	-2.206233	-0.128965	2.319079
22	1	0	-8.591660	0.708244	-0.635480
23	1	0	-1.381589	-0.675620	-3.473071
24	1	0	-8.861907	2.797769	0.688213
25	1	0	-6.873569	3.833845	1.768349
26	1	0	-4.639237	2.795935	1.512449
27	1	0	-6.360879	-0.333827	-0.871369
28	1	0	-3.216604	1.304596	0.407506
29	1	0	0.376298	0.123783	-2.075459
30	1	0	-3.191695	-1.414055	0.798960
31	1	0	-4.749104	-1.003094	1.527839
32	1	0	-2.904060	0.197497	-3.715612
33	1	0	-2.926240	-1.518858	-3.291470
34	1	0	-1.521732	0.106966	0.197538
35	6	0	2.397056	0.424273	-0.465557
36	6	0	0.846859	-0.701052	1.286499
37	6	0	1.777132	-2.176178	3.043828
38	6	0	2.659155	-3.145541	3.509163
39	6	0	3.601515	-3.705912	2.641707
40	6	0	3.655694	-3.291532	1.309778
41	6	0	4.454192	1.355068	0.343714
42	6	0	4.530797	2.814410	-0.026761
43	6	0	4.486542	3.214100	-1.369363
44	6	0	4.545721	4.566951	-1.704412
45	6	0	4.648477	5.534034	-0.702209
46	6	0	4.692160	5.144363	0.637832
47	6	0	4.634139	3.791165	0.971544
48	6	0	1.832494	-1.741736	1.707884
49	6	0	2.781053	-2.311147	0.843908
50	6	0	0.072364	-0.466522	-1.202792
51	8	0	2.848221	0.319446	-1.588345
52	8	0	-0.114001	-0.449984	2.008313
53	1	0	4.670381	3.488458	2.015707
54	1	0	0.542796	1.063096	0.223006
55	1	0	1.033967	-1.735960	3.699920
56	1	0	2.612485	-3.467446	4.545853
57	1	0	4.395233	2.459664	-2.145227

58	1	0	4.289173	-4.466185	3.002842
59	1	0	4.953985	1.159488	1.294502
60	1	0	4.696638	6.587579	-0.964621
61	6	0	1.475901	-3.598470	-2.921156
62	1	0	2.823327	-2.021860	-0.199775
63	6	0	-0.062452	-4.310088	-1.207346
64	1	0	4.774362	5.892570	1.421613
65	6	0	0.337156	-1.934871	-1.555515
66	1	0	4.376668	-3.734682	0.628732
67	1	0	4.879728	0.718854	-0.434200
68	1	0	2.167903	-3.831127	-3.726831
69	1	0	1.019480	-5.664616	-2.494184
70	1	0	-0.574005	-5.101931	-0.666091
71	1	0	-1.024765	-2.741800	-0.094018
72	1	0	1.745449	-1.469405	-3.115108

E(RB+HF-LYP) = -1671.11504066

Optimized geometries and energies of the transition states (Figure S2)

R configuration (*Si* face; relative energy: 0.0 kcal/mol)

1	7	0	-3.567190	-0.156159	0.421693
2	6	0	-7.519045	-1.288369	-0.962777
3	6	0	-7.945792	-2.477120	-0.368838
4	6	0	-7.012950	-3.317592	0.240583
5	6	0	-5.662284	-2.967770	0.259403
6	6	0	-5.220929	-1.777770	-0.331613
7	6	0	-6.166784	-0.943779	-0.947699
8	6	0	-3.746260	-1.412857	-0.322734
9	6	0	-3.168464	-1.329150	-1.764070
10	6	0	-2.437685	0.344845	0.971330
11	6	0	-2.621034	1.723636	1.557072
12	6	0	-1.270844	-0.404254	1.092556
13	8	0	-1.770984	-1.220338	-1.806518
14	1	0	-1.515827	-0.277348	-1.655685
15	1	0	-4.369455	0.459260	0.413971
16	1	0	-8.237333	-0.630529	-1.444592
17	1	0	-8.998135	-2.747145	-0.382393
18	1	0	-7.336045	-4.245120	0.705449
19	1	0	-4.941304	-3.624684	0.740036
20	1	0	-5.849923	-0.021506	-1.430172
21	1	0	-3.195852	-2.198408	0.205182
22	1	0	-3.663040	-0.500597	-2.295253
23	1	0	-3.444845	-2.259262	-2.276691
24	1	0	-1.676273	2.204227	1.803863
25	1	0	-3.223928	1.663261	2.472482
26	1	0	-3.137244	2.373883	0.844481
27	1	0	-1.288534	-1.407567	0.687493
28	6	0	-0.030668	0.083959	1.533217
29	6	0	1.060458	-0.817830	1.948374
30	6	0	1.958791	-0.384478	2.939377
31	6	0	2.979052	-1.218214	3.395312
32	6	0	3.130170	-2.497100	2.857148
33	6	0	2.255810	-2.933572	1.857057
34	6	0	1.232336	-2.105502	1.407202
35	1	0	0.003895	1.055936	2.014116
36	1	0	1.852660	0.614545	3.353313
37	1	0	3.655464	-0.866923	4.169985
38	1	0	3.926518	-3.148049	3.207655
39	1	0	2.378838	-3.920823	1.420458
40	1	0	0.579666	-2.450062	0.610475
41	6	0	2.310360	1.163272	-0.026183
42	6	0	0.914164	0.935010	-0.395348
43	6	0	-0.115516	1.880543	-0.729809
44	6	0	-0.929808	4.151021	-1.284974
45	6	0	-1.027342	5.525343	-1.092249
46	6	0	-0.315560	6.139005	-0.057136
47	6	0	0.497650	5.365689	0.770428
48	6	0	4.467931	0.176557	-0.147147
49	6	0	5.198255	-0.912069	-0.894043
50	6	0	6.216150	-1.631322	-0.258537
51	6	0	6.944409	-2.600380	-0.951262
52	6	0	6.653299	-2.869066	-2.288965
53	6	0	5.632110	-2.161825	-2.928307
54	6	0	4.912343	-1.187653	-2.237411
55	6	0	-0.100822	3.361966	-0.465421
56	6	0	0.613368	3.988369	0.567805
57	8	0	-1.171637	1.429119	-1.253306
58	8	0	2.797540	2.049943	0.663185
59	8	0	3.077548	0.140693	-0.511869
60	1	0	0.772039	-0.006400	-0.914094
61	1	0	-1.492914	3.660889	-2.071760
62	1	0	-1.660502	6.119709	-1.746316
63	1	0	-0.393921	7.212014	0.099428

64	1	0	1.053841	5.833808	1.578657
65	1	0	4.562803	0.046175	0.935889
66	1	0	4.868500	1.168139	-0.389747
67	1	0	6.439055	-1.433189	0.787645
68	1	0	7.732268	-3.150216	-0.442650
69	1	0	7.214695	-3.626923	-2.829202
70	1	0	5.395637	-2.369185	-3.968844
71	1	0	4.112856	-0.644600	-2.732165
72	1	0	1.277714	3.405194	1.191165

E(RB+HF-LYP) = -1671.09662570
Imaginary frequency: -189.2318

S configuration (*Re* face; relative energy: 3.6 kcal/mol)

1	7	0	-2.944775	0.287297	-1.739016
2	6	0	-6.150126	-2.450118	-0.496012
3	6	0	-6.130024	-2.499292	0.899096
4	6	0	-4.985137	-2.096347	1.589015
5	6	0	-3.864662	-1.646794	0.889023
6	6	0	-3.869647	-1.607824	-0.511547
7	6	0	-5.026093	-2.009004	-1.195772
8	6	0	-2.647825	-1.086479	-1.247379
9	6	0	-2.116419	-2.031387	-2.351520
10	6	0	-2.026883	1.282471	-1.690834
11	6	0	-2.588426	2.664880	-1.474013
12	6	0	-0.674654	1.020059	-1.902629
13	1	0	-3.907004	0.573537	-1.605471
14	6	0	2.137723	0.806030	-3.019817
15	6	0	2.623761	2.873451	-1.873998
16	8	0	-1.330037	-3.059330	-1.786103
17	6	0	3.889378	2.902955	-2.452101
18	6	0	3.405238	0.834108	-3.597452
19	6	0	1.725224	1.824146	-2.141499
20	6	0	0.384291	1.860070	-1.530087
21	6	0	4.287327	1.879765	-3.315967
22	1	0	-0.638824	-2.628028	-1.249413
23	1	0	-7.037749	-2.761815	-1.040534
24	1	0	-3.482565	2.809560	-2.093097
25	1	0	-7.002479	-2.849381	1.444669
26	1	0	-4.964231	-2.128854	2.675255
27	1	0	-2.979778	-1.309416	1.421319
28	1	0	-5.050896	-1.985814	-2.283091
29	1	0	-1.838971	-0.959623	-0.522618
30	1	0	0.132290	2.822586	-1.092309
31	1	0	-1.556076	-1.442886	-3.095636
32	1	0	-2.933044	-2.522513	-2.890132
33	1	0	-1.873752	3.445329	-1.738690
34	1	0	-2.879341	2.792406	-0.425917
35	1	0	-0.417686	0.024637	-2.239492
36	1	0	4.564833	3.725225	-2.231930
37	1	0	5.273702	1.900700	-3.771139
38	1	0	3.702047	0.039973	-4.277388
39	1	0	1.461165	-0.005824	-3.265783
40	1	0	2.318533	3.671522	-1.200731
41	6	0	1.236602	-0.360608	0.151820
42	6	0	-0.283774	1.385876	1.201845
43	6	0	-1.548649	3.021739	2.593608
44	6	0	-1.677956	4.186019	3.345876
45	6	0	-0.577903	5.028040	3.528424
46	6	0	0.649302	4.690142	2.956409
47	6	0	3.062891	-1.833124	-0.393919
48	6	0	3.455841	-2.717214	0.765697
49	6	0	4.797323	-2.828765	1.148550
50	6	0	5.167784	-3.641943	2.220848
51	6	0	4.194499	-4.352304	2.924768
52	6	0	2.852365	-4.246006	2.551495
53	6	0	2.484732	-3.435149	1.478324

54	6	0	-0.321688	2.670047	2.007654
55	6	0	0.777944	3.520199	2.206487
56	8	0	0.435462	-1.252264	-0.126809
57	8	0	-1.347302	0.756895	1.054080
58	6	0	0.950541	1.003646	0.564648
59	8	0	2.587137	-0.540839	0.050774
60	1	0	6.214012	-3.720930	2.504822
61	1	0	1.441623	-3.348237	1.188454
62	1	0	1.843769	1.573020	0.783554
63	1	0	-2.389474	2.352200	2.445735
64	1	0	-2.636111	4.437341	3.793773
65	1	0	5.557458	-2.275600	0.600957
66	1	0	-0.675154	5.937390	4.115746
67	1	0	2.287512	-2.302127	-1.003066
68	1	0	4.479841	-4.987836	3.759113
69	1	0	1.747735	3.278825	1.784069
70	1	0	2.090767	-4.799256	3.094808
71	1	0	1.512527	5.335444	3.097499
72	1	0	3.929264	-1.606054	-1.020017

E(RB+HF-LYP) = -1671.09093104
Imaginary frequency: -198.4592