

Interplay between the gentlest ascent dynamics method and conjugate directions to locate transition states

Supporting Information

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1. Sets of internal coordinates

Table S1.1. Set of internal coordinates employed in the location of the TS configuration of the *sn2* reaction.

Variable number	Type of variable	Atoms involved in the definition of the internal variable ^a				
1	distance	2	1			
2	distance	3	2			
3	angle ^b	3	1	2		
4	distance	4	2			
5	angle	4	3	2		
6	dihedral	4	2	3	1	
7	distance	5	2			
8	angle	5	1	2		
9	dihedral	5	2	1	3	
10	distance	6	2			
11	angle	6	1	2		
12	dihedral	6	2	1	3	

^a See Figure 2 in the main text for the atom numbering

^b In the definition of angles, the third atom number refers to the atom in the apex.

Table S1.2. Set of internal coordinates employed in the location of the TS configuration of the *sn2b* reaction.

Variable number	Type of variable	Atoms involved in the definition of the internal variable ^a				
1	distance	2	1			
2	distance	3	2			
3	angle ^b	2	1	3		
4	distance	4	2			
5	angle	4	3	2		
6	dihedral	4	2	3	1	
7	distance	5	4			
8	angle	5	2	4		
9	dihedral	5	4	3	2	
10	distance	6	2			
11	angle	6	3	2		
12	dihedral	6	2	3	1	
13	distance	7	2			
14	angle	7	3	2		
15	dihedral	7	2	3	1	
16	distance	8	4			
17	angle	8	5	4		
18	dihedral	8	4	5	2	
19	distance	9	4			
20	angle	9	5	4		
21	dihedral	9	4	5	2	

^a See Figure 3 in the main text for the atom numbering

^b In the definition of angles, the third atom number refers to the atom in the apex.

Table S1.3. Set of internal coordinates employed in the location of the TS configuration of the *sig* reaction.

Variable number	Type of variable	Atoms involved in the definition of the internal variable ^a				
1	distance	2	1			
2	distance	3	2			
3	angle ^b	3	1	2		
4	distance	4	3			
5	angle	4	2	3		
6	dihedral	4	3	2	1	
7	distance	5	1			
8	angle	5	2	1		
9	dihedral	5	1	2	3	
10	distance	6	2			
11	angle	6	3	2		
12	dihedral	6	2	3	4	
13	distance	7	3			
14	angle	7	4	3		
15	dihedral	7	3	2	4	
16	distance	8	4			
17	angle	8	3	4		
18	dihedral	8	4	3	2	
19	distance	9	1			
20	angle	9	2	1		
21	dihedral	9	1	2	3	
22	distance	10	9			
23	angle	10	4	9		
24	dihedral	10	9	4	3	
25	distance	11	1			
26	angle	11	1	9		
27	dihedral	11	9	1	3	

^a See Figure 4 in the main text for the atom numbering

^b In the definition of angles, the third atom number refers to the atom in the apex.

Table S1.4. Set of internal coordinates employed in the location of the TS configuration of the *dcc* reaction.

Variable number	Type of variable	Atoms involved in the definition of the internal variable ^a				
1	distance	2	1			
2	distance	3	1			
3	angle ^b	3	2	1		
4	distance	4	3			
5	angle	4	1	3		
6	dihedral	4	3	1		2
7	distance	5	2			
8	angle	5	1	2		
9	dihedral	5	2	1		3
10	distance	6	1			
11	angle	6	2	1		
12	dihedral	6	1	2		3
13	distance	7	1			
14	angle	7	3	1		
15	dihedral	7	1	3		2
16	distance	8	2			
17	angle	8	1	2		
18	dihedral	8	2	1		3
19	distance	9	3			
20	angle	9	1	3		
21	dihedral	9	3	1		2
22	distance	10	4			
23	angle	10	3	4		
24	dihedral	10	4	3		1
25	distance	11	4			
26	angle	11	3	4		
27	dihedral	11	4	3		10
28	distance	12	4			
29	angle	12	3	4		
30	dihedral	12	4	3		10
31	distance	13	5			
32	angle	13	2	5		
33	dihedral	13	5	2		1
34	distance	14	5			
35	angle	14	2	5		
36	dihedral	14	5	2		13
37	distance	15	5			
38	angle	15	2	5		
39	dihedral	15	5	2		13

^a See Figure 5 in the main text for the atom numbering

^b In the definition of angles, the third atom number refers to the atom in the apex.

Table S1.5. Set of internal coordinates employed in the location of the TS configuration of the *bcb* reaction.

Variable number	Type of variable	Atoms involved in the definition of the internal variable ^a				
1	distance	2	1			
2	distance	3	1			
3	angle ^b	3	2	1		
4	distance	4	2			
5	angle	4	1	2		
6	dihedral	4	2	1		3
7	distance	5	3			
8	angle	5	1	3		
9	dihedral	5	3	1		2
10	distance	6	4			
11	angle	6	2	4		
12	dihedral	6	4	2		1
13	distance	7	4			
14	angle	7	2	4		
15	dihedral	7	4	2		8
16	distance	8	2			
17	angle	8	1	2		
18	dihedral	8	2	1		3
19	distance	9	1			
20	angle	9	2	1		
21	dihedral	9	1	2		4
22	distance	10	3			
23	angle	10	1	3		
24	dihedral	10	3	1		2
25	distance	11	5			
26	angle	11	3	5		
27	dihedral	11	5	3		1
28	distance	12	6			
29	angle	12	4	6		
30	dihedral	12	6	4		2
31	distance	13	11			
32	angle	13	5	11		
33	dihedral	13	11	5		6
34	distance	14	12			
35	angle	14	6	12		
36	dihedral	14	12	6		4
37	distance	15	11			
38	angle	15	5	11		

39	dihedral	15	11	5	3
40	distance	16	12		
41	angle	16	6	12	
42	dihedral	16	12	6	5
43	distance	17	15		
44	angle	17	11	15	
45	dihedral	17	15	11	5
46	distance	18	15		
47	angle	18	11	15	
48	dihedral	18	15	11	7
49	distance	19	15		
50	angle	19	11	15	
51	dihedral	19	15	11	17
52	distance	20	16		
53	angle	20	12	16	
54	dihedral	20	16	12	6
55	distance	21	16		
56	angle	21	12	16	
57	dihedral	21	16	12	20
58	distance	22	16		
59	angle	22	12	16	
60	dihedral	22	16	12	20

^a See Figure 6 in the main text for the atom numbering

^b In the definition of angles, the third atom number refers to the atom in the apex.

2. Initial configurations

2.1. Initial configurations for the *sn2* reactions

Initial configuration (in cartesian coordinates) for the *sn2.1.n* reactions (*n*=1,15)

F -2.4672660 0.0007512 -0.0001717
C -0.6731430 0.0005964 -0.0014634
H -0.5364968 -0.8920896 -0.5943660
Cl 1.8526759 0.0004861 -0.0002772
H -0.5335207 -0.0701768 1.0929060
H -0.5360983 0.9622929 -0.4741287

Initial configuration (in internal coordinates) for the *sn2.1.n* reactions (*n*=1,15)

(distances in atomic units; angles and dihedrals in degree)

1	distance	2	1				3.39040
2	distance	3	2				2.04151
3	angle	3	1	2			97.29355
4	distance	4	2				4.77311
5	angle	4	3	2			82.74619
6	dihedral	4	2	3	1		179.94412
7	distance	5	2				2.08911
8	angle	5	1	2			97.21481
9	dihedral	5	2	1	3		240.11201
10	distance	6	2				2.04148
11	angle	6	1	2			97.30180
12	dihedral	6	2	1	3		120.24410

Initial configuration (in cartesian coordinates) for the *sn2.2.n* reactions (*n*=1,2)

F -2.4279870 0.0007465 -0.0002054
C -0.7557393 0.0005718 -0.0009818
H -0.5447866 -0.8847321 -0.5895375
Cl 1.8602496 0.0004868 -0.0002907
H -0.5410869 -0.0692703 1.0795792
H -0.5442577 0.9543927 -0.4701656

Initial configuration (in internal coordinates) for the *sn2.2.n* reactions (*n*=1,2)

(distances in atomic units; angles and dihedrals in degree)

1	distance	2	1			3.16009
2	distance	3	2			2.04812
3	angle	3	1	2		101.24332
4	distance	4	2			4.94350
5	angle	4	3	2		78.78323
6	dihedral	4	2	3	1	179.96689
7	distance	5	2			2.08604
8	angle	5	1	2		101.18652
9	dihedral	5	2	1	3	240.08418
10	distance	6	2			2.04809
11	angle	6	1	2		101.25862
12	dihedral	6	2	1	3	120.20026

Initial configuration (in cartesian coordinates) for the *sn2.3.n* reactions (*n*=1,6)

F -2.3894780 0.0007449 -0.0002117
C -0.8413690 0.0005793 -0.0010560
H -0.5604436 -0.8743733 -0.5825627
Cl 1.8698667 0.0004884 -0.0003033
H -0.5553969 -0.0686303 1.0684808
H -0.5598854 0.9432155 -0.4644695

Initial configuration (in internal coordinates) for the *sn2.3.n* reactions (*n*=1,6)

(distances in atomic units; angles and dihedrals in degree)

1	distance	2	1			2.92550
2	distance	3	2			2.05504
3	angle	3	1	2		104.99322
4	distance	4	2			5.12349
5	angle	4	3	2		75.03638
6	dihedral	4	2	3	1	179.96176
7	distance	5	2			2.09622
8	angle	5	1	2		104.90890
9	dihedral	5	2	1	3	240.09772
10	distance	6	2			2.05498
11	angle	6	1	2		105.00996
12	dihedral	6	2	1	3	120.22629

2.2. Initial configuration for the *sn2b* reaction

Initial configuration (in cartesian coordinates) for the *sn2b.1.n* reactions ($n=1,4$)

Br -1.0636208 -0.0000441 -0.0001072
C 1.7787006 0.0006178 0.0015304
H 1.4630861 -0.9966441 0.3143327
N 3.4098239 -0.0003301 -0.0008114
H 3.7830058 -0.7045887 -0.6500730
H 1.4612773 0.2290434 -1.0178036
H 1.4644553 0.7699130 0.7096108
H 3.7846509 0.9130553 -0.2870653
H 3.7863063 -0.2100547 0.9325308

Initial configuration (in internal coordinates) for the *sn2b.1.n* reactions ($n=1,4$)

1	distance	2	1			5.37121
2	distance	3	2			2.06317
3	angle	2	1	3		84.33338
4	distance	4	2			3.08238
5	angle	4	3	2		106.79582
6	dihedral	4	2	3	1	180.12947
7	distance	5	4			1.94264
8	angle	5	2	4		111.36584
9	dihedral	5	4	3	2	60.04631
10	distance	6	2			2.06316
11	angle	6	3	2		111.99699
12	dihedral	6	2	3	1	-63.24883
13	distance	7	2			2.06313
14	angle	7	3	2		112.00005
15	dihedral	7	2	3	1	63.53118
16	distance	8	4			1.94257
17	angle	8	5	4		107.48619
18	dihedral	8	4	5	2	237.74951
19	distance	9	4			1.94270
20	angle	9	5	4		107.49972
21	dihedral	9	4	5	2	122.29893

2.3. Initial configurations for the *sig* reactions

Initial configuration (in cartesian coordinates) for the *sig.1.n* reactions ($n=1,2$)

C -0.9439243 -0.7589479 -0.0483523
C 0.3858443 -1.1540546 -0.0098707
C 1.2012554 0.0113897 -0.0035884
C 0.4105539 1.1486558 -0.0084393
H -1.8411883 -1.3729454 -0.1257973
H 0.7415728 -2.1838222 0.0381117
H 2.3253662 0.0038012 0.0602227
H 0.7495869 2.1835349 0.0264660
C -0.9669535 0.7320307 0.0003400
H -1.8378151 1.3510140 -0.2291739
H -1.1778655 0.2671743 1.0667453

Initial configuration (in internal coordinates) for the *sig.1.n* reactions ($n=1,2$)

1	distance	2	1			2.62248
2	distance	3	2			2.68793
3	angle	3	1	2		108.43072
4	distance	4	3			2.61753
5	angle	4	2	3		110.21035
6	dihedral	4	3	2	1	1.28357
7	distance	5	1			2.05978
8	angle	5	2	1		129.07822
9	dihedral	5	1	2	3	175.77855
10	distance	6	2			2.06081
11	angle	6	3	2		125.90953
12	dihedral	6	2	3	4	182.99062
13	distance	7	3			2.12773
14	angle	7	4	3		125.14506
15	dihedral	7	3	2	4	176.53619
16	distance	8	4			2.05897
17	angle	8	3	4		127.02081
18	dihedral	8	4	3	2	177.89248
19	distance	9	1			2.81938
20	angle	9	2	1		107.36204
21	dihedral	9	1	2	3	-2.72046
22	distance	10	9			2.06510
23	angle	10	4	9		126.69201
24	dihedral	10	9	4	3	195.12999
25	distance	11	1			2.89757
26	angle	11	1	9		68.85452
27	dihedral	11	9	1	3	259.14340

Initial configuration (in cartesian coordinates) for the *sig.2.n* reactions ($n=1,4$)

C -0.9342752 -0.7759210 -0.0786104
C 0.3698478 -1.1596542 -0.0156359
C 1.2056588 0.0274456 -0.0028656
C 0.4290301 1.1457096 -0.0103722
H -1.8242523 -1.4063528 -0.0872598
H 0.7392685 -2.1852146 0.0386752
H 2.3321572 0.0099758 0.0526422
H 0.7630856 2.1829416 0.0225020
C -0.9861406 0.7141360 0.0421940
H -1.8004730 1.3178177 -0.3822355
H -1.2186614 0.6543064 1.1372637

Initial configuration (in internal coordinates) for the *sig.2.n* reactions ($n=1,4$)

1	distance	2	1			2.57166
2	distance	3	2			2.74365
3	angle	3	1	2		108.75526
4	distance	4	3			2.57289
5	angle	4	2	3		110.06759
6	dihedral	4	3	2	1	2.10953
7	distance	5	1			2.06108
8	angle	5	2	1		128.26804
9	dihedral	5	1	2	3	181.14613
10	distance	6	2			2.06248
11	angle	6	3	2		124.95984
12	dihedral	6	2	3	4	183.31382
13	distance	7	3			2.13161
14	angle	7	4	3		125.63695
15	dihedral	7	3	2	4	177.45126
16	distance	8	4			2.06017
17	angle	8	3	4		127.33577
18	dihedral	8	4	3	2	178.23726
19	distance	9	1			2.82674
20	angle	9	2	1		108.08191
21	dihedral	9	1	2	3	-6.11754
22	distance	10	9			2.07673
23	angle	10	4	9		122.30878
24	dihedral	10	9	4	3	207.68121
25	distance	11	1			3.58788
26	angle	11	1	9		91.88631
27	dihedral	11	9	1	5	75.42335

Initial configuration (in cartesian coordinates) for the *sig.3.n* reactions ($n=1,6$)

C -0.9320234 -0.7863220 -0.0331547
C 0.3673617 -1.1638013 -0.0527704
C 1.2164020 0.0335404 -0.0160395
C 0.4387754 1.1379411 0.0272826
H -1.8039778 -1.4421811 -0.0510860
H 0.7409614 -2.1893208 -0.0927854
H 2.3603997 0.0156048 -0.0261657
H 0.7744463 2.1757911 0.0619081
C -1.0050492 0.7141450 0.0609271
H -1.6166523 1.1751886 -0.7377528
H -1.4807859 1.0227942 1.0141455

Initial configuration (in internal coordinates) for the *sig.3.n* reactions ($n=1,6$)

1	distance	2	1			2.55727
2	distance	3	2			2.77465
3	angle	3	1	2		109.11142
4	distance	4	3			2.55378
5	angle	4	2	3		109.54134
6	dihedral	4	3	2	1	0.06470
7	distance	5	1			2.06212
8	angle	5	2	1		126.82430
9	dihedral	5	1	2	3	180.00669
10	distance	6	2			2.06393
11	angle	6	3	2		124.66742
12	dihedral	6	2	3	4	179.87918
13	distance	7	3			2.16219
14	angle	7	4	3		126.04525
15	dihedral	7	3	2	4	180.15638
16	distance	8	4			2.06232
17	angle	8	3	4		126.95638
18	dihedral	8	4	3	2	179.97599
19	distance	9	1			2.84439
20	angle	9	2	1		108.99951
21	dihedral	9	1	2	3	-1.69902
22	distance	10	9			2.09112
23	angle	10	4	9		113.37489
24	dihedral	10	9	4	3	234.26860
25	distance	11	1			4.08412
26	angle	11	1	9		110.60541
27	dihedral	11	9	1	3	242.96632

2.4. Initial configurations for the *dcc* reactions

Initial configuration (in cartesian coordinates) for the *dcc.1.n* reactions ($n=1,5$)

C 0.0501798 0.1804853 -0.1292330
C -1.1066651 0.1016331 -1.0077937
C 0.7177559 -0.7175706 -1.0408016
C 1.6412108 -1.8283596 -0.6078733
C -2.5463769 -0.0303780 -0.5673896
Cl -0.3053665 -0.6150558 1.4553818
Cl 0.9859143 1.8796327 0.1203746
H -0.9638291 0.6107239 -1.9670141
H 0.9718964 -0.2491656 -1.9948637
H 1.2197783 -2.4670395 0.1802190
H 1.9685466 -2.4511880 -1.4528529
H 2.5371788 -1.3345950 -0.1803985
H -2.8718124 0.9682959 -0.2131112
H -3.2043400 -0.3155868 -1.4018481
H -2.6839228 -0.7318124 0.2655242

Initial configuration (in internal coordinates) for the *dcc.1.n* reactions ($n=1,5$)

1	distance	2	1			2.74913
2	distance	3	1			2.72744
3	angle	3	2	1		87.28657
4	distance	4	3			2.84970
5	angle	4	1	3		124.07322
6	dihedral	4	3	1	2	218.56552
7	distance	5	2			2.85602
8	angle	5	1	2		125.89275
9	dihedral	5	2	1	3	137.65226
10	distance	6	1			3.41738
11	angle	6	2	1		110.42578
12	dihedral	6	1	2	3	247.77135
13	distance	7	1			3.69585
14	angle	7	3	1		113.57127
15	dihedral	7	1	3	2	237.96010
16	distance	8	2			2.06981
17	angle	8	1	2		113.57759
18	dihedral	8	2	1	3	-70.52016
19	distance	9	3			2.06510
20	angle	9	1	3		113.09542
21	dihedral	9	3	1	2	70.90974
22	distance	10	4			2.07578
23	angle	10	3	4		113.53537

24	dihedral	10	4	3	1	49.56721
25	distance	11	4			2.07789
26	angle	11	3	4		112.26645
27	dihedral	11	4	3	10	125.07139
28	distance	12	4			2.09521
29	angle	12	3	4		106.11149
30	dihedral	12	4	3	10	242.75953
31	distance	13	5			2.09476
32	angle	13	2	5		107.10397
33	dihedral	13	5	2	1	76.49553
34	distance	14	5			2.07920
35	angle	14	2	5		111.79596
36	dihedral	14	5	2	13	117.48467
37	distance	15	5			2.07412
38	angle	15	2	5		113.34913
39	dihedral	15	5	2	13	241.92346

Initial configuration (in cartesian coordinates) for the *dcc.2.n* reactions ($n=1,8$)

C 0.1041371 0.2710712 -0.0698725
C -0.9814904 0.0457930 -1.0400369
C 0.5962197 -0.6810691 -1.0683612
C 1.4996951 -1.8485435 -0.6598501
C -2.4444812 -0.1184447 -0.6194347
Cl -0.2800434 -0.5742462 1.4796551
Cl 0.9554914 1.8568574 0.1387620
H -0.9004352 0.7080936 -1.9115574
H 1.0165965 -0.1636718 -1.9371749
H 1.0805328 -2.4892782 0.1265274
H 1.7848592 -2.4728324 -1.5199218
H 2.4209624 -1.3873338 -0.2581493
H -2.7833869 0.8724957 -0.2651300
H -3.0838781 -0.4045833 -1.4684900
H -2.5937071 -0.8335382 0.1987803

Initial configuration (in internal coordinates) for the *dcc.2.n* reactions ($n=1,8$)

1	distance	2	1			2.78410
2	distance	3	1			2.76811
3	angle	3	2	1		72.49928
4	distance	4	3			2.89452
5	angle	4	1	3		120.78300

6	dihedral	4	3	1	2	217.77546
7	distance	5	2			2.89333
8	angle	5	1	2		122.65711
9	dihedral	5	2	1	3	138.43780
10	distance	6	1			3.41366
11	angle	6	2	1		109.66912
12	dihedral	6	1	2	3	253.78605
13	distance	7	1			3.42403
14	angle	7	3	1		119.30958
15	dihedral	7	1	3	2	240.56651
16	distance	8	2			2.07419
17	angle	8	1	2		112.09731
18	dihedral	8	2	1	3	-86.06076
19	distance	9	3			2.06945
20	angle	9	1	3		111.26257
21	dihedral	9	3	1	2	86.24083
22	distance	10	4			2.07408
23	angle	10	3	4		114.25398
24	dihedral	10	4	3	1	55.16226
25	distance	11	4			2.07937
26	angle	11	3	4		112.13790
27	dihedral	11	4	3	10	124.85004
28	distance	12	4			2.08967
29	angle	12	3	4		105.68781
30	dihedral	12	4	3	10	241.97271
31	distance	13	5			2.08928
32	angle	13	2	5		106.54644
33	dihedral	13	5	2	1	70.01142
34	distance	14	5			2.08007
35	angle	14	2	5		111.77963
36	dihedral	14	5	2	13	117.26531
37	distance	15	5			2.07277
38	angle	15	2	5		113.88190
39	dihedral	15	5	2	13	241.45253

Initial configuration (in cartesian coordinates) for the *dcc.3.n* reactions ($n=1,6$)

C 0.1474413 0.3203373 0.0113191
C -0.8462702 0.0737190 -1.0818081
C 0.5617195 -0.5878190 -1.1015437
C 1.0731100 -1.9894105 -0.8385490
C -2.2383492 -0.4541721 -0.7977997
Cl -0.2146868 -0.4661391 1.5721114
Cl 0.9373385 1.9009045 0.1945968
H -0.8682168 0.9069161 -1.8091960
H 1.1932406 -0.0622822 -1.8278294
H 0.4612341 -2.5447608 -0.1149487
H 1.1346200 -2.5751747 -1.7693977
H 2.0926641 -1.9126846 -0.4238110
H -2.8449752 0.3643220 -0.3742850
H -2.7317001 -0.7915401 -1.7233693
H -2.2464239 -1.2817609 -0.0764872

Initial configuration (in internal coordinates) for the *dcc.3.n* reactions ($n=1,6$)

1	distance	2	1			2.83031
2	distance	3	1			2.82502
3	angle	3	2	1		62.64614
4	distance	4	3			2.86289
5	angle	4	1	3		121.75835
6	dihedral	4	3	1	2	234.34889
7	distance	5	2			2.86418
8	angle	5	1	2		122.00331
9	dihedral	5	2	1	3	124.43833
10	distance	6	1			3.37291
11	angle	6	2	1		115.53482
12	dihedral	6	1	2	3	252.46638
13	distance	7	1			3.35698
14	angle	7	3	1		119.60959
15	dihedral	7	1	3	2	247.95792
16	distance	8	2			2.09051
17	angle	8	1	2		111.65652
18	dihedral	8	2	1	3	260.01488
19	distance	9	3			2.07225
20	angle	9	1	3		111.19219
21	dihedral	9	3	1	2	99.99406
22	distance	10	4			2.07561
23	angle	10	3	4		113.20949
24	dihedral	10	4	3	1	45.77298

25	distance	11	4			2.08160
26	angle	11	3	4		111.35368
27	dihedral	11	4	3	10	122.70134
28	distance	12	4			2.08503
29	angle	12	3	4		108.23041
30	dihedral	12	4	3	10	240.82168
31	distance	13	5			2.08495
32	angle	13	2	5		108.57474
33	dihedral	13	5	2	1	75.12640
34	distance	14	5			2.08204
35	angle	14	2	5		111.13121
36	dihedral	14	5	2	13	118.23317
37	distance	15	5			2.07462
38	angle	15	2	5		113.10545
39	dihedral	15	5	2	13	240.60138

2.5. Initial configurations for the *bcb* reactions

Initial configuration (in cartesian coordinates) for the *bcb.1.n* reactions ($n=1,14$)

```

C  2.2775993 -1.0294153  0.3945519
C  2.6247237  0.2790740  0.0005532
C  0.9565349 -1.4813882  0.3303552
C  1.6485087  1.2177177 -0.3543473
C  0.0058725 -0.5686427 -0.1374678
C  0.3158738  0.7944940 -0.2928589
H  1.9238978  2.2503393 -0.5951831
H  3.6776927  0.5751542  0.0154238
H  3.0677398 -1.7151586  0.7118063
H  0.7061383 -2.5206600  0.5588773
C -1.3605770 -0.6721625 -0.6490454
C -1.0082747  1.4269168 -0.3707194
H -1.4240714 -0.5326814 -1.7363040
H -1.1584949  2.2011698 -1.1458856
C -2.3722056 -1.6563686 -0.0852217
C -1.8520006  1.6761159  0.8591584
H -3.2479061 -1.1325731  0.3414219
H -2.7607963 -2.3410212 -0.8580190
H -1.9390635 -2.2575520  0.7308583
H -1.7131435  0.8850256  1.6119050
H -1.6152060  2.6436037  1.3444186
H -2.9212773  1.7105553  0.5883382

```

Initial configuration (in internal coordinates) for the *bcb.1.n* reactions ($n=1,14$)

1	distance	2	1			2.66436
2	distance	3	1			2.64130
3	angle	3	2	1		121.33001
4	distance	4	2			2.64562
5	angle	4	1	2		121.42559
6	dihedral	4	2	1	3	5.92321
7	distance	5	3			2.64273
8	angle	5	1	3		116.53980
9	dihedral	5	3	1	2	-0.25268
10	distance	6	4			2.64482
11	angle	6	2	4		116.74781
12	dihedral	6	4	2	1	0.26314
13	distance	7	4			2.07022
14	angle	7	2	4		120.82470
15	dihedral	7	4	2	8	-1.39324
16	distance	8	2			2.06718

17	angle	8	1	2		118.97193
18	dihedral	8	2	1	3	183.26962
19	distance	9	1			2.06596
20	angle	9	2	1		119.03056
21	dihedral	9	1	2	4	183.05004
22	distance	10	3			2.06578
23	angle	10	1	3		120.95183
24	dihedral	10	3	1	2	174.93572
25	distance	11	5			2.76418
26	angle	11	3	5		134.89765
27	dihedral	11	5	3	1	163.14611
28	distance	12	6			2.77693
29	angle	12	4	6		136.51275
30	dihedral	12	6	4	2	169.25271
31	distance	13	11			2.07493
32	angle	13	5	11		113.03826
33	dihedral	13	11	5	6	69.57733
34	distance	14	12			2.08976
35	angle	14	6	12		117.44294
36	dihedral	14	12	6	4	42.88077
37	distance	15	11			2.87210
38	angle	15	5	11		122.53932
39	dihedral	15	11	5	3	37.47374
40	distance	16	12			2.85753
41	angle	16	6	12		122.04684
42	dihedral	16	12	6	5	77.97038
43	distance	17	15			2.09004
44	angle	17	11	15		111.31107
45	dihedral	17	15	11	5	118.58210
46	distance	18	15			2.08468
47	angle	18	11	15		112.11597
48	dihedral	18	15	11	7	119.27757
49	distance	19	15			2.08301
50	angle	19	11	15		111.48656
51	dihedral	19	15	11	17	241.25062
52	distance	20	16			2.08019
53	angle	20	12	16		111.55298
54	dihedral	20	16	12	6	-33.92907
55	distance	21	16			2.09375
56	angle	21	12	16		112.38794
57	dihedral	21	16	12	20	120.85114
58	distance	22	16			2.08546
59	angle	22	12	16		110.25347
60	dihedral	22	16	12	20	239.74588

Initial configuration (in cartesian coordinates) for the *bcb.2.n* reactions ($n=1,5$)

C 2.2911304 -1.0283543 0.3922468
C 2.6305240 0.2793658 0.0083299
C 0.9687822 -1.4910568 0.3134198
C 1.6463761 1.2260449 -0.3306864
C 0.0302169 -0.5738212 -0.1379185
C 0.3268431 0.7859266 -0.2827026
H 1.9216774 2.2588442 -0.5641759
H 3.6825177 0.5780943 0.0178251
H 3.0833701 -1.7108707 0.7127625
H 0.7205324 -2.5333666 0.5333455
C -1.3646099 -0.5740557 -0.6475986
C -1.0804571 1.2872230 -0.3948771
H -1.3583148 -0.6095333 -1.7476596
H -1.2985564 1.9739564 -1.2334930
C -2.3764798 -1.5981570 -0.0821617
C -1.8423114 1.6806975 0.8635892
H -3.2722022 -1.1180779 0.3478438
H -2.7281265 -2.2887216 -0.8660223
H -1.9216541 -2.1998685 0.7217882
H -1.6987657 0.9287700 1.6559527
H -1.5435290 2.6614756 1.2754573
H -2.9198654 1.7342164 0.6348338

Initial configuration (in internal coordinates) for the *bcb.2.n* reactions ($n=1,5$)

1	distance	2	1			2.65418
2	distance	3	1			2.65162
3	angle	3	2	1		121.29132
4	distance	4	2			2.65887
5	angle	4	1	2		121.55353
6	dihedral	4	2	1	3	7.08886
7	distance	5	3			2.62252
8	angle	5	1	3		115.95545
9	dihedral	5	3	1	2	-1.20154
10	distance	6	4			2.63017
11	angle	6	2	4		116.23559
12	dihedral	6	4	2	1	-0.93584
13	distance	7	4			2.06749
14	angle	7	2	4		120.70162
15	dihedral	7	4	2	8	-1.23412
16	distance	8	2			2.06666
17	angle	8	1	2		118.97286
18	dihedral	8	2	1	3	184.29745

19	distance	9	1			2.06681
20	angle	9	2	1		119.08402
21	dihedral	9	1	2	4	184.12498
22	distance	10	3			2.06699
23	angle	10	1	3		121.11917
24	dihedral	10	3	1	2	174.84941
25	distance	11	5			2.80630
26	angle	11	3	5		138.30903
27	dihedral	11	5	3	1	165.00261
28	distance	12	6			2.83104
29	angle	12	4	6		141.46167
30	dihedral	12	6	4	2	172.80804
31	distance	13	11			2.07993
32	angle	13	5	11		109.73443
33	dihedral	13	11	5	6	82.03927
34	distance	14	12			2.08936
35	angle	14	6	12		116.73919
36	dihedral	14	12	6	4	45.86287
37	distance	15	11			2.92290
38	angle	15	5	11		119.28131
39	dihedral	15	11	5	3	34.29142
40	distance	16	12			2.87771
41	angle	16	6	12		119.63962
42	dihedral	16	12	6	5	89.55859
43	distance	17	15			2.08530
44	angle	17	11	15		112.67007
45	dihedral	17	15	11	5	123.14798
46	distance	18	15			2.08297
47	angle	18	11	15		111.31799
48	dihedral	18	15	11	7	120.07979
49	distance	19	15			2.08321
50	angle	19	11	15		110.98269
51	dihedral	19	15	11	17	240.35121
52	distance	20	16			2.08199
53	angle	20	12	16		110.65956
54	dihedral	20	16	12	6	-44.59679
55	distance	21	16			2.08798
56	angle	21	12	16		113.71093
57	dihedral	21	16	12	20	121.24469
58	distance	22	16			2.08412
59	angle	22	12	16		109.26487
60	dihedral	22	16	12	20	241.16550

Initial configuration (in cartesian coordinates) for the *bcb.3.n* reactions ($n=1,20$)

C 2.3646289 -1.0178083 0.3348790
C 2.6288333 0.3411663 0.1052319
C 1.0720146 -1.5515026 0.1778588
C 1.6012701 1.2578548 -0.1935271
C 0.0850732 -0.6473700 -0.1890537
C 0.3185330 0.7280700 -0.2795061
H 1.8241887 2.3224794 -0.3264513
H 3.6682257 0.7034686 0.1912483
H 3.1904295 -1.6794174 0.6149283
H 0.8834730 -2.6204062 0.3147572
C -1.3613830 -0.5287487 -0.6391148
C -1.1663013 1.0512264 -0.4469009
H -1.3971040 -0.7068897 -1.7286600
H -1.4365531 1.6449876 -1.3387014
C -2.4708268 -1.3505375 0.0207533
C -1.8253804 1.6512260 0.7975510
H -3.4021819 -0.7715938 0.1335346
H -2.7138536 -2.2351731 -0.5896008
H -2.1801535 -1.7082957 1.0212078
H -1.6001816 1.0527970 1.6950514
H -1.4611519 2.6756300 0.9804987
H -2.9212318 1.7025213 0.6854411

Initial configuration (in internal coordinates) for the *bcb.3.n* reactions ($n=1,20$)

1	distance	2	1			2.65192
2	distance	3	1			2.65931
3	angle	3	2	1		121.46198
4	distance	4	2			2.66274
5	angle	4	1	2		121.83005
6	dihedral	4	2	1	3	4.91180
7	distance	5	3			2.62266
8	angle	5	1	3		115.82574
9	dihedral	5	3	1	2	-1.21615
10	distance	6	4			2.62766
11	angle	6	2	4		115.97506
12	dihedral	6	4	2	1	-1.55416
13	distance	7	4			2.07077
14	angle	7	2	4		120.62539
15	dihedral	7	4	2	8	-0.83557
16	distance	8	2			2.08641
17	angle	8	1	2		118.83331
18	dihedral	8	2	1	3	183.08325

19	distance	9	1			2.06845
20	angle	9	2	1		119.02325
21	dihedral	9	1	2	4	183.17685
22	distance	10	3			2.06737
23	angle	10	1	3		120.98987
24	dihedral	10	3	1	2	177.20171
25	distance	11	5			2.87143
26	angle	11	3	5		143.71753
27	dihedral	11	5	3	1	171.39287
28	distance	12	6			2.88899
29	angle	12	4	6		145.30722
30	dihedral	12	6	4	2	174.03124
31	distance	13	11			2.08737
32	angle	13	5	11		108.08042
33	dihedral	13	11	5	6	94.87936
34	distance	14	12			2.08804
35	angle	14	6	12		116.07304
36	dihedral	14	12	6	4	55.36334
37	distance	15	11			2.89173
38	angle	15	5	11		114.33257
39	dihedral	15	11	5	3	43.27588
40	distance	16	12			2.89261
41	angle	16	6	12		114.33257
42	dihedral	16	12	6	5	105.25182
43	distance	17	15			2.08326
44	angle	17	11	15		111.99972
45	dihedral	17	15	11	5	141.54166
46	distance	18	15			2.08228
47	angle	18	11	15		110.62152
48	dihedral	18	15	11	7	119.24005
49	distance	19	15			2.08161
50	angle	19	11	15		112.00880
51	dihedral	19	15	11	17	239.13795
52	distance	20	16			2.08242
53	angle	20	12	16		111.17929
54	dihedral	20	16	12	6	-49.54163
55	distance	21	16			2.08345
56	angle	21	12	16		110.90795
57	dihedral	21	16	12	20	119.64541
58	distance	22	16			2.08392
59	angle	22	12	16		111.31258
60	dihedral	22	16	12	20	239.38056

3. Transition state configurations

3.1. TS configuration for the *sn2* reaction

Cartesian coordinates

F -2.6318067 -0.0000242 0.0000595
C -0.4599682 0.0000377 -0.0001588
H -0.6404202 0.5663719 -0.9041343
Cl 1.6207714 -0.0000067 0.0000342
H -0.6400560 -1.0660802 -0.0384852
H -0.6405552 0.4999510 0.9421885

Internal coordinates

1	distance	2	1				4.10774
2	distance	3	2				2.04458
3	angle	3	1	2			80.35772
4	distance	4	2				3.92891
5	angle	4	3	2			99.65339
6	dihedral	4	2	3	1		179.99600
7	distance	5	2				2.04437
8	angle	5	1	2			80.31107
9	dihedral	5	2	1	3		239.98503
10	distance	6	2				2.04459
11	angle	6	1	2			80.33776
12	dihedral	6	2	1	3		119.98246

3.2. TS configuration for the *sn2b* reaction

Cartesian coordinates

```
Br -1.0538771  0.0000011  0.0000186
C  1.7111907 -0.0000226 -0.0002853
H  1.4463561 -1.0430044  0.1695814
N  3.4155720  0.0000062  0.0001362
H  3.7856908 -0.6077663 -0.7394539
H  1.4466281  0.3743758 -0.9883772
H  1.4461737  0.6685919  0.8179942
H  3.7852178  0.9446136 -0.1562076
H  3.7848509 -0.3367163  0.8964969
```

Internal coordinates

1	distance	2	1			5.22626
2	distance	3	2			2.05859
3	angle	2	1	3		81.20361
4	distance	4	2			3.22051
5	angle	4	3	2		104.08484
6	dihedral	4	2	3	1	180.03760
7	distance	5	4			1.93947
8	angle	5	2	4		111.10536
9	dihedral	5	4	3	2	59.88672
10	distance	6	2			2.05871
11	angle	6	3	2		114.26399
12	dihedral	6	2	3	1	-67.11382
13	distance	7	2			2.05872
14	angle	7	3	2		114.29643
15	dihedral	7	2	3	1	67.20039
16	distance	8	4			1.93948
17	angle	8	5	4		107.78620
18	dihedral	8	4	5	2	238.06408
19	distance	9	4			1.93947
20	angle	9	5	4		107.78626
21	dihedral	9	4	5	2	121.97009

3.3. TS configuration for the *sig* reaction

Cartesian coordinates

C -0.9548335 -0.7453027 -0.0241861
C 0.3980492 -1.1508283 -0.0086476
C 1.2031930 -0.0002091 -0.0036150
C 0.3984363 1.1506887 -0.0086441
H -1.8437599 -1.3603633 -0.1670599
H 0.7436499 -2.1836223 0.0315322
H 2.2932808 -0.0004238 0.0588786
H 0.7444470 2.1833348 0.0315928
C -0.9545634 0.7456397 -0.0242114
H -1.8432519 1.3610540 -0.1669850
H -1.1701761 0.0001597 1.0378822

Internal coordinates

1	distance	2	1			2.66910
2	distance	3	2			2.65383
3	angle	3	1	2		108.29746
4	distance	4	3			2.65383
5	angle	4	2	3		110.05449
6	dihedral	4	3	2	1	0.30287
7	distance	5	1			2.06050
8	angle	5	2	1		128.34174
9	dihedral	5	1	2	3	170.89704
10	distance	6	2			2.05945
11	angle	6	3	2		126.47471
12	dihedral	6	2	3	4	182.48759
13	distance	7	3			2.06334
14	angle	7	4	3		124.92070
15	dihedral	7	3	2	4	176.43502
16	distance	8	4			2.05945
17	angle	8	3	4		126.47466
18	dihedral	8	4	3	2	177.51235
19	distance	9	1			2.81749
20	angle	9	2	1		106.67480
21	dihedral	9	1	2	3	-0.18120
22	distance	10	9			2.06050
23	angle	10	4	9		128.34178
24	dihedral	10	9	4	3	189.10285
25	distance	11	1			2.48569
26	angle	11	1	9		55.47657
27	dihedral	11	9	1	3	259.07740

3.4. TS configuration for the *dcc* reaction

Cartesian coordinates

```
C -0.1793308 -0.0678738 -0.2681056
C -1.0965801 0.6492242 -1.0621722
C 0.4282588 -1.0342060 -1.0919926
C 0.7633947 -2.4230114 -0.7122408
C -2.4230530 1.1569878 -0.6395954
Cl -0.6836043 -0.5506372 1.3471619
Cl 1.6928890 1.2492621 0.1437098
H -0.7256267 0.9306212 -2.0507384
H 0.7313596 -0.6687183 -2.0756162
H 0.0573574 -2.8321662 0.0255715
H 0.8414696 -3.0847371 -1.5867528
H 1.7561576 -2.3979723 -0.2182169
H -2.2962542 2.1817781 -0.2320757
H -3.1191427 1.2323066 -1.4888147
H -2.8670032 0.5488571 0.1616258
```

Internal coordinates

1	distance	2	1			2.66342
2	distance	3	1			2.66023
3	angle	3	2	1		107.47335
4	distance	4	3			2.79314
5	angle	4	1	3		126.33194
6	dihedral	4	3	1	2	219.64650
7	distance	5	2			2.80074
8	angle	5	1	2		126.59774
9	dihedral	5	2	1	3	142.69519
10	distance	6	1			3.32534
11	angle	6	2	1		118.03896
12	dihedral	6	1	2	3	223.20882
13	distance	7	1			4.39424
14	angle	7	3	1		98.25828
15	dihedral	7	1	3	2	246.22580
16	distance	8	2			2.06513
17	angle	8	1	2		114.83001
18	dihedral	8	2	1	3	-43.79701
19	distance	9	3			2.06385
20	angle	9	1	3		114.64966
21	dihedral	9	3	1	2	44.15490
22	distance	10	4			2.07881
23	angle	10	3	4		112.10047

24	dihedral	10	4	3	1	31.34152
25	distance	11	4			2.07754
26	angle	11	3	4		112.16682
27	dihedral	11	4	3	10	125.39967
28	distance	12	4			2.09587
29	angle	12	3	4		107.21993
30	dihedral	12	4	3	10	243.44605
31	distance	13	5			2.09790
32	angle	13	2	5		108.59936
33	dihedral	13	5	2	1	89.84550
34	distance	14	5			2.07996
35	angle	14	2	5		111.67827
36	dihedral	14	5	2	13	117.75691
37	distance	15	5			2.07779
38	angle	15	2	5		112.31303
39	dihedral	15	5	2	13	242.10017

3.5. TS configuration for the *bcb* reaction

Cartesian coordinates

```
C 2.2186974 -1.0139515 0.3964655
C 2.5601381 0.3061585 -0.0037797
C 0.9078988 -1.4695644 0.3490866
C 1.5840154 1.2257940 -0.3671827
C -0.0741968 -0.5690749 -0.1307104
C 0.2358871 0.8077246 -0.2916076
H 1.8471799 2.2599006 -0.6103635
H 3.6106622 0.6096379 0.0165038
H 3.0166651 -1.6944415 0.7073186
H 0.6673618 -2.5099627 0.5871057
C -1.4065885 -0.7589156 -0.6185802
C -1.0021386 1.5378429 -0.3130044
H -1.6065382 -0.3613130 -1.6150599
H -1.0688345 2.4114824 -0.9849937
C -2.4126162 -1.7139881 -0.0604597
C -1.9271443 1.6514397 0.8735908
H -3.2651616 -1.1557814 0.3763480
H -2.8422709 -2.3803233 -0.8290254
H -1.9909050 -2.3276561 0.7519711
H -1.7820356 0.8349133 1.5959762
H -1.7445661 2.6067844 1.4066458
H -2.9916547 1.6654665 0.5778237
```

Internal coordinates

1	distance	2	1			2.68545
2	distance	3	1			2.62394
3	angle	3	2	1		121.46710
4	distance	4	2			2.62572
5	angle	4	1	2		121.31322
6	dihedral	4	2	1	3	4.70958
7	distance	5	3			2.67621
8	angle	5	1	3		117.23130
9	dihedral	5	3	1	2	0.76252
10	distance	6	4			2.67111
11	angle	6	2	4		117.40595
12	dihedral	6	4	2	1	1.52565
13	distance	7	4			2.06818
14	angle	7	2	4		120.96882
15	dihedral	7	4	2	8	-1.54578
16	distance	8	2			2.06674

17	angle	8	1	2		118.90422
18	dihedral	8	2	1	3	182.17279
19	distance	9	1			2.06702
20	angle	9	2	1		118.86104
21	dihedral	9	1	2	4	182.08519
22	distance	10	3			2.06744
23	angle	10	1	3		120.80879
24	dihedral	10	3	1	2	175.32959
25	distance	11	5			2.70518
26	angle	11	3	5		132.57488
27	dihedral	11	5	3	1	162.43004
28	distance	12	6			2.71642
29	angle	12	4	6		132.09909
30	dihedral	12	6	4	2	165.09742
31	distance	13	11			2.06233
32	angle	13	5	11		115.68264
33	dihedral	13	11	5	6	50.89174
34	distance	14	12			2.08669
35	angle	14	6	12		117.57372
36	dihedral	14	12	6	4	37.85730
37	distance	15	11			2.82558
38	angle	15	5	11		125.71241
39	dihedral	15	11	5	3	39.53494
40	distance	16	12			2.85132
41	angle	16	6	12		123.68323
42	dihedral	16	12	6	5	66.21895
43	distance	17	15			2.09511
44	angle	17	11	15		110.05162
45	dihedral	17	15	11	5	114.54725
46	distance	18	15			2.08671
47	angle	18	11	15		112.78979
48	dihedral	18	15	11	7	118.37321
49	distance	19	15			2.08250
50	angle	19	11	15		111.92901
51	dihedral	19	15	11	17	241.75895
52	distance	20	16			2.07836
53	angle	20	12	16		112.31997
54	dihedral	20	16	12	6	-22.53577
55	distance	21	16			2.09597
56	angle	21	12	16		109.99281
57	dihedral	21	16	12	20	119.79604
58	distance	22	16			2.08801
59	angle	22	12	16		112.39856
60	dihedral	22	16	12	20	237.69745

4. Initial v_1 vectors

sn2.1.1

0.739151 -0.011375 -0.183260 -0.543787 0.147278 0.026465 -0.010066 -0.252423
0.001575 -0.010454 -0.194667 0.004509

sn2.1.2

0.739151 -0.011375 -0.183260 -0.543787 0.147278 0.026465 -0.010066 -0.252423
0.001575 -0.010454 -0.194667 0.004509

sn2.1.3

-0.653836 0.000000 0.181062 0.653836 -0.160944 0.000000 0.000000 0.231357
0.000000 0.000000 0.181062 0.000000

sn2.1.4

-0.666667 0.000000 0.166667 0.666667 -0.166667 0.000000 0.000000 0.166667
0.000000 0.000000 0.166667 0.000000

sn2.1.5

-0.680414 0.000000 0.136083 0.680414 -0.136083 0.000000 0.000000 0.136083
0.000000 0.000000 0.136083 0.000000

sn2.1.6

-0.688247 0.000000 0.114708 0.688247 -0.114708 0.000000 0.000000 0.114708
0.000000 0.000000 0.114708 0.000000

sn2.1.7

-0.693103 0.000000 0.099015 0.693103 -0.099015 0.000000 0.000000 0.099015
0.000000 0.000000 0.099015 0.000000

sn2.1.8

-0.707107 0.000000 0.000000 0.707107 0.000000 0.000000 0.000000 0.000000
0.000000 0.000000 0.000000 0.000000

sn2.1.9

-0.639602 0.000000 0.213201 0.639602 -0.213201 0.000000 0.000000 0.213201
0.000000 0.000000 0.213201 0.000000

sn2.1.10

-0.577350 0.000000 0.288675 0.577350 -0.288675 0.000000 0.000000 0.288675
0.000000 0.000000 0.288675 0.000000

sn2.1.11

-0.549972 0.000000 0.314270 0.549972 -0.314270 0.000000 0.000000 0.314270
0.000000 0.000000 0.314270 0.000000

sn2.1.12

-0.514496 0.000000 0.342997 0.514496 -0.342997 0.000000 0.000000 0.342997
0.000000 0.000000 0.342997 0.000000

sn2.1.13

-0.737865 0.000000 0.210819 0.527046 -0.210819 0.000000 0.000000 0.210819
0.000000 0.000000 0.210819 0.000000

sn2.1.14

-0.527046 0.000000 0.210819 0.737865 -0.210819 0.000000 0.000000 0.210819
0.000000 0.000000 0.210819 0.000000

sn2.1.15

0.693582 0.011854 -0.205179 -0.588039 0.197100 -0.000043 0.012272 -0.214266
0.000419 0.012269 -0.214137 -0.000777

sn2.2.1

-0.648346 0.017198 0.188205 0.649794 -0.166694 -0.035063 0.016684 0.237323
-0.002697 0.017085 0.189073 -0.005778

sn2.2.2

-0.648346 0.017198 0.188205 0.649794 -0.166694 -0.035063 0.016684 0.237323
-0.002697 0.017085 0.189073 -0.005778

sn2.3.1

-0.351205 0.019090 0.146423 0.882329 -0.150704 -0.069432 0.019284 0.176189
-0.004156 0.020967 0.130005 -0.006385

sn2.3.2

0.693690 0.011900 -0.204824 -0.588030 0.197068 -0.000208 0.012286 -0.214363
0.000678 0.012301 -0.214078 -0.000875

sn2.3.3

-0.351205 0.019090 0.146423 0.882329 -0.150704 -0.069432 0.019284 0.176189
-0.004156 0.020967 0.130005 -0.006385

sn2.3.4

-0.351205 0.019090 0.146423 0.882329 -0.150704 -0.069432 0.019284 0.176189
-0.004156 0.020967 0.130005 -0.006385

sn2.3.5

0.693690 0.011900 -0.204824 -0.588030 0.197068 -0.000208 0.012286 -0.214363
0.000678 0.012301 -0.214078 -0.000875

sn2.3.6

-0.351205 0.019090 0.146423 0.882329 -0.150704 -0.069432 0.019284 0.176189
-0.004156 0.020967 0.130005 -0.006385

sn2b.1.1

0.682593 0.016569 0.271637 -0.523295 0.185401 0.011263 0.010719 0.016313
-0.008679 0.017408 -0.154767 0.236908 0.017147 -0.152238 -0.213232 0.011259
-0.018805 -0.024179 0.010860 -0.020414 0.017072

sn2b.1.2

0.682593 0.016569 0.271637 -0.523295 0.185401 0.011263 0.010719 0.016313
-0.008679 0.017408 -0.154767 0.236908 0.017147 -0.152238 -0.213232 0.011259
-0.018805 -0.024179 0.010860 -0.020414 0.017072

sn2b.1.3

0.555879 0.015939 0.176629 -0.670693 0.170498 -0.001192 0.011917 0.015259
-0.000835 0.015073 -0.141069 0.261840 0.014936 -0.140454 -0.264821 0.011774
-0.016772 -0.017913 0.011903 -0.016144 0.018946

sn2b.1.4

0.601102 0.000000 0.185795 -0.601102 0.185795 -0.000000 0.000000 0.000000
0.000000 0.000000 -0.153008 0.284157 0.000000 -0.153008 -0.284157 0.000000
0.000000 0.000000 0.000000 0.000000 0.000000

sig.1.1

-0.082207 0.086863 0.010976 -0.070034 -0.005809 -0.000318 0.001452 -0.019233
0.110330 0.003081 -0.025965 0.006801 0.000594 0.006450 0.031093 0.000568
0.012457 0.016119 -0.002926 0.018226 -0.061989 0.010107 -0.071857 0.318262
0.799190 0.463233 -0.043705

sig.1.2

-0.082207 0.086863 0.010976 -0.070034 -0.005809 -0.000318 0.001452 -0.019233
0.110330 0.003081 -0.025965 0.006801 0.000594 0.006450 0.031093 0.000568
0.012457 0.016119 -0.002926 0.018226 -0.061989 0.010107 -0.071857 0.318262
0.799190 0.463233 -0.043705

sig.2.1

0.079667 -0.127467 0.000000 0.079667 0.000000 0.000000 0.000000 0.000000
0.000000 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000
0.000000 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000
-0.478000 -0.717001 -0.478000 0.000000

sig.2.2

0.000000 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000
0.000000 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000
0.000000 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000 -0.346844
-0.780399 -0.520266 0.000000

sig.2.3

0.196740 -0.149740 -0.036699 0.158465 -0.003594 0.007403 0.009388 -0.045975
-0.203198 -0.002208 0.016376 -0.017683 0.000838 -0.002319 -0.007854 0.001893
-0.019516 -0.012855 -0.016594 -0.049317 0.133500 -0.002622 0.020489
-0.192692 -0.671761 -0.591522 0.091671

sig.2.4

0.079667 -0.127467 0.000000 0.079667 0.000000 0.000000 0.000000 0.000000
0.000000 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000
0.000000 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000 -0.478000
-0.717001 -0.478000 0.000000

sig.3.1

0.006675 -0.012321 0.003362 0.004639 -0.006718 -0.088993 -0.003424 -0.000926
0.089647 -0.002674 0.005628 -0.069315 0.001529 0.006149 0.106813 0.002215
0.006934 -0.030790 -0.094285 0.005039 -0.098074 -0.035901 0.132625 -0.410401
-0.615602 -0.615602 0.051872

sig.3.2

0.006675 -0.012321 0.003362 0.004639 -0.006718 -0.088993 -0.003424 -0.000926
0.089647 -0.002674 0.005628 -0.069315 0.001529 0.006149 0.106813 0.002215
0.006934 -0.030790 -0.094285 0.005039 -0.098074 -0.035901 0.132625 -0.410401
-0.615602 -0.615602 0.051872

sig.3.3

0.198257 -0.147638 -0.035054 0.156772 -0.004412 -0.007756 0.008547 -0.050964
-0.245192 -0.002073 0.015469 -0.018867 0.000662 -0.002110 -0.008525 0.001939
-0.019427 -0.013559 -0.018721 -0.049946 0.144965 -0.003240 0.023344
-0.203918 -0.663003 -0.584727 -0.038783

sig.3.4

0.006675 -0.012321 0.003362 0.004639 -0.006718 -0.088993 -0.003424 -0.000926
0.089647 -0.002674 0.005628 -0.069315 0.001529 0.006149 0.106813 0.002215
0.006934 -0.030790 -0.094285 0.005039 -0.098074 -0.035901 0.132625 -0.410401
-0.615602 -0.615602 0.051872

sig.3.5

0.006675 -0.012321 0.003362 0.004639 -0.006718 -0.088993 -0.003424 -0.000926
0.089647 -0.002674 0.005628 -0.069315 0.001529 0.006149 0.106813 0.002215
0.006934 -0.030790 -0.094285 0.005039 -0.098074 -0.035901 0.132625 -0.410401
-0.615602 -0.615602 0.051872

sig.3.6

0.198257 -0.147638 -0.035054 0.156772 -0.004412 -0.007756 0.008547 -0.050964
-0.245192 -0.002073 0.015469 -0.018867 0.000662 -0.002110 -0.008525 0.001939
-0.019427 -0.013559 -0.018721 -0.049946 0.144965 -0.003240 0.023344
-0.203918 -0.663003 -0.584727 -0.038783

dcc.1.1

-0.032483 -0.027418 0.582014 -0.029426 -0.036112 -0.144038 -0.044062
-0.003425 0.193511 0.057281 -0.036247 -0.150531 0.313388 -0.207633 -0.203075
0.004656 -0.003446 0.432737 0.000938 0.045825 -0.431801 0.004076 -0.004208
0.075042 -0.001780 0.025853 0.027695 0.009620 -0.006976 0.044535 0.009620 -
0.012243 -0.031241 -0.001837 0.015404 0.002948 0.002932 -0.009107 0.026149

dcc.1.2

-0.032483 -0.027418 0.582014 -0.029426 -0.036112 -0.144038 -0.044062

-0.003425 0.193511 0.057281 -0.036247 -0.150531 0.313388 -0.207633 -0.203075
0.004656 -0.003446 0.432737 0.000938 0.045825 -0.431801 0.004076 -0.004208
0.075042 -0.001780 0.025853 0.027695 0.009620 -0.006976 0.044535 0.009620 -
0.012243 -0.031241 -0.001837 0.015404 0.002948 0.002932 -0.009107 0.026149

dcc.1.3

0.048183 0.049164 -0.323162 0.011839 -0.010178 0.105983 -0.011552 -0.005011
-0.250609 0.006130 0.002114 0.300314 -0.444274 0.631441 0.079721 -0.007644
0.000539 -0.236637 -0.004590 0.013547 0.248249 -0.001022 0.014478 -0.013447
0.001920 0.009900 -0.009667 0.010443 0.012899 -0.011246 -0.002091 -0.059267
-0.015399 -0.001152 0.018717 -0.011555 -0.001143 0.004910 0.023758

dcc.1.4

-0.032483 -0.027418 0.582014 -0.029426 -0.036112 -0.144038 -0.044062
-0.003425 0.193511 0.057281 -0.036247 -0.150531 0.313388 -0.207633 -0.203075
0.004656 -0.003446 0.432737 0.000938 0.045825 -0.431801 0.004076 -0.004208
0.075042 -0.001780 0.025853 0.027695 0.009620 -0.006976 0.044535 0.009620 -
0.012243 -0.031241 -0.001837 0.015404 0.002948 0.002932 -0.009107 0.026149

dcc.1.5

-0.032483 -0.027418 0.582014 -0.029426 -0.036112 -0.144038 -0.044062
-0.003425 0.193511 0.057281 -0.036247 -0.150531 0.313388 -0.207633 -0.203075
0.004656 -0.003446 0.432737 0.000938 0.045825 -0.431801 0.004076 -0.004208
0.075042 -0.001780 0.025853 0.027695 0.009620 -0.006976 0.044535 0.009620 -
0.012243 -0.031241 -0.001837 0.015404 0.002948 0.002932 -0.009107 0.026149

dcc.2.1

-0.041922 -0.041922 0.838444 0.000000 0.000000 0.000000 0.000000 0.000000
0.000000 0.000000 0.000000 -0.041922 0.251533 -0.041922 0.041922 0.000000
0.000000 0.335377 0.000000 0.000000 -0.335377 0.000000 0.000000 0.000000
0.000000 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000
0.000000 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000

dcc.2.2

-0.041922 -0.041922 0.838444 0.000000 0.000000 0.000000 0.000000 0.000000
0.000000 0.000000 0.000000 -0.041922 0.251533 -0.041922 0.041922 0.000000

dcc.3.5

-0.041922 -0.041922 0.838444 0.000000 0.000000 0.000000 0.000000 0.000000
0.000000 0.000000 0.000000 -0.041922 0.251533 -0.041922 0.041922 0.000000
0.000000 0.335377 0.000000 0.000000 -0.335377 0.000000 0.000000 0.000000
0.000000 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000
0.000000 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000

dcc.3.6

0.000000 0.000000 1.000000 0.000000 0.000000 0.000000 0.000000 0.000000
0.000000 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000
0.000000 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000
0.000000 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000
0.000000 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000

bcb.1.1

-0.052277 -0.046441 -0.023822 -0.067894 -0.034278 0.056020 0.062263 0.162993
0.041703 0.063472 0.175220 0.042005 0.003642 -0.019996 0.001999 0.000216
0.009152 -0.016736 0.000879 0.012399 0.007741 0.002642 -0.023594 0.004103
-0.156916 -0.535400 -0.063645 -0.173493 -0.551865 0.013921 -0.015922
0.058348 -0.325768 -0.001454 -0.020005 -0.123526 -0.040384 -0.046767 -0.139376
-0.059453 0.090933 -0.317482 0.001607 -0.011886 0.015141 0.008353 0.005723
-0.008226 0.002262 0.003911 0.012728 -0.001455 0.013091 0.008956 0.007630
-0.046969 0.007036 0.002300 0.023548 -0.007276

bcb.1.2

-0.052277 -0.046441 -0.023822 -0.067894 -0.034278 0.056020 0.062263 0.162993
0.041703 0.063472 0.175220 0.042005 0.003642 -0.019996 0.001999 0.000216
0.009152 -0.016736 0.000879 0.012399 0.007741 0.002642 -0.023594 0.004103
-0.156916 -0.535400 -0.063645 -0.173493 -0.551865 0.013921 -0.015922
0.058348 -0.325768 -0.001454 -0.020005 -0.123526 -0.040384 -0.046767 -0.139376
-0.059453 0.090933 -0.317482 0.001607 -0.011886 0.015141 0.008353 0.005723
-0.008226 0.002262 0.003911 0.012728 -0.001455 0.013091 0.008956 0.007630
-0.046969 0.007036 0.002300 0.023548 -0.007276

bcb.1.3

-0.052277 -0.046441 -0.023822 -0.067894 -0.034278 0.056020 0.062263 0.162993

0.041703 0.063472 0.175220 0.042005 0.003642 -0.019996 0.001999 0.000216
0.009152 -0.016736 0.000879 0.012399 0.007741 0.002642 -0.023594 0.004103
-0.156916 -0.535400 -0.063645 -0.173493 -0.551865 0.013921 -0.015922
0.058348 -0.325768 -0.001454 -0.020005 -0.123526 -0.040384 -0.046767 -0.139376
-0.059453 0.090933 -0.317482 0.001607 -0.011886 0.015141 0.008353 0.005723
-0.008226 0.002262 0.003911 0.012728 -0.001455 0.013091 0.008956 0.007630
-0.046969 0.007036 0.002300 0.023548 -0.007276

bcb.1.4

-0.014277 0.077887 0.017164 0.075703 0.014726 -0.019625 -0.090326 -0.121424
-0.051635 -0.087900 -0.130771 -0.032700 -0.003001 0.012111 -0.009859
0.000500 -0.008153 0.005019 0.000526 -0.008132 0.010683 -0.001282 0.017234
-0.004146 0.170472 0.383960 -0.039170 0.164856 0.426228 -0.009138 -0.000642
-0.036277 0.471289 0.006089 0.064517 0.254617 0.021112 0.018789 0.215351
0.037169 -0.103971 0.436294 0.000903 0.024908 -0.000590 -0.007622 -0.019323
0.015255 0.000665 -0.010476 -0.004086 0.001275 -0.012213 -0.017522 -0.000034
0.049996 -0.009626 -0.000787 -0.034085 0.006404

bcb.1.5

0.000000 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000
0.000000 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000
0.000000 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000
0.000000 0.364474 0.000000 0.000000 0.364474 0.000000 0.000000 0.000000
0.546711 0.000000 0.000000 0.364474 0.000000 0.000000 0.060746 0.000000
0.000000 0.546711 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000
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0.000000 0.000000 0.000000 0.000000

bcb.1.6

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0.000000 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000
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bcb.1.7

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bcb.2.1

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0.000000 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000
0.000000 0.354713 0.000000 0.000000 0.390184 0.000000 0.000000 0.000000
0.532070 0.000000 0.000000 0.390184 0.000000 0.000000 0.059119 0.000000
0.000000 0.532070 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000
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0.000000 0.000000 0.000000 0.000000

bcb.2.2

-0.014245 0.077916 0.017186 0.075670 0.014749 -0.019457 -0.090399
-0.121556 -0.051432 -0.087913 -0.130867 -0.032807 -0.002996 0.012137
-0.009875 0.00049 -0.008152 0.005025 0.000520 -0.008138 0.010738 -0.001278
0.017268 -0.004150 0.170468 0.384091 -0.039214 0.164759 0.426228 -0.009441
-0.000632 -0.036433 0.471376 0.006089 0.064497 0.254535 0.021168 0.018945
0.215469 0.037183 -0.103889 0.436052 0.000882 0.024704 -0.000794 -0.007615
-0.019244 0.015184 0.000663 -0.010541 -0.004134 0.001281 -0.012168 -0.017514
-0.000036 0.050013 -0.009609 -0.000778 -0.034087 0.006394

bcb.2.3

0.000000 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000
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0.000000 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000
0.000000 0.378717 0.000000 0.000000 0.378717 0.000000 0.000000 0.000000
0.568075 0.000000 0.000000 0.252478 0.000000 0.000000 0.063119 0.000000
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bcb.2.4

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0.568075 0.000000 0.000000 0.252478 0.000000 0.000000 0.063119 0.000000

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bcb.3.8

-0.014277 0.077887 0.017164 0.075703 0.014726 -0.019625 -0.090326 -0.121424
-0.051635 -0.087900 -0.130771 -0.032700 -0.003001 0.012111 -0.009859 0.000500
-0.008153 0.005019 0.000526 -0.008132 0.010683 -0.001282 0.017234 -0.004146
0.170472 0.383960 -0.039170 0.164856 0.426228 -0.009138 -0.000642 -0.036277
0.471289 0.006089 0.064517 0.254617 0.021112 0.018789 0.215351 0.037169
-0.103971 0.436294 0.000903 0.024908 -0.000590 -0.007622 -0.019323 0.015255
0.000665 -0.010476 -0.004086 0.001275 -0.012213 -0.017522 -0.000034 0.049996
-0.009626 -0.000787 -0.034085 0.006404

bcb.3.9

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0.568075 0.000000 0.000000 0.252478 0.000000 0.000000 0.063119 0.000000
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bcb.3.10

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0.632456 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000
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bcb.3.19

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0.000000 0.653410 0.000000 0.000000 0.653410 0.000000 0.000000 0.000000
0.261364 0.000000 0.000000 0.087121 0.000000 0.000000 0.043561 0.000000
0.000000 0.261364 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000
0.000000 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000
0.000000 0.000000 0.000000 0.000000

bcb.3.20

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0.000000 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000
0.000000 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000
0.000000 0.171499 0.000000 0.000000 0.171499 0.000000 0.000000 0.000000
0.685994 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000
0.000000 0.685994 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000
0.000000 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000
0.000000 0.000000 0.000000 0.000000

5. TS eigenvectors

TS eigenvector at the TS configuration for the *sn2* reaction

0.692729 0.011749 -0.205353 -0.588689 0.197221 -0.000006 0.012196
-0.214723 0.000744 0.012200 -0.214390 -0.000542

TS eigenvector at the TS configuration for the *sn2b* reaction

0.556081 0.015955 0.177469 -0.670210 0.170722 -0.001969 0.011922
0.014780 0.001220 0.015055 -0.141272 0.260197 0.014970 -0.140552
-0.266386 0.011791 -0.016754 -0.018049 0.011876 -0.016196 0.018811

TS eigenvector at the TS configuration for the *sig* reaction

-0.198318 0.147666 0.035068 -0.156812 0.004416 0.007746 -0.008556
0.051025 0.245191 0.002071 -0.015459 0.018850 -0.000663 0.002104
0.008518 -0.001940 0.019438 0.013552 0.018676 0.049962 -0.144970 0.003235
-0.023311 0.203875 0.662863 0.584857 0.038770

TS eigenvector at the TS configuration for the *dcc* reaction

0.047894 0.048986 -0.323207 0.011664 -0.010667 0.106250 -0.011684
-0.005056 -0.250039 0.005908 0.002456 0.299933 -0.443695 0.631986
0.080513 -0.007649 0.000500 -0.236783 -0.004593 0.013545 0.248535
-0.000973 0.014176 -0.011025 0.001828 0.010073 -0.009355 0.010423
0.012676 -0.010459 -0.002056 -0.059614 -0.015174 -0.001164 0.018748
-0.011674 -0.001189 0.005020 0.023888

TS eigenvector at the TS configuration for the *bcb* reaction

-0.014277 0.077887 0.017164 0.075703 0.014726 -0.019625 -0.090326
-0.121424 -0.051635 -0.087900 -0.130771 -0.032700 -0.003001 0.012111
-0.009859 0.000500 -0.008153 0.005019 0.000526 -0.008132 0.010683
-0.001282 0.017234 -0.004146 0.170472 0.383960 -0.039170 0.164856
0.426228 -0.009138 -0.000642 -0.036277 0.471289 0.006089 0.064517
0.254617 0.021112 0.018789 0.215351 0.037169 -0.103971 0.436294
0.000903 0.024908 -0.000590 -0.007622 -0.019323 0.015255 0.000665
-0.010476 -0.004086 0.001275 -0.012213 -0.017522 -0.000034 0.049996
-0.009626 -0.000787 -0.034085 0.006404

5. Performance of GAD-CD as a function of the initial \mathbf{v}_1 vector

Table S5.1. Assessment of the performance of the GAD-CD method for the S_N2 reaction as a function of the initial \mathbf{v}_1 vector.^a

Reaction ^b	\mathbf{v}_1 relevant components ^c						Angle ^d	#steps ^e
	\mathbf{v}_1 (1)	\mathbf{v}_1 (3)	\mathbf{v}_1 (4)	\mathbf{v}_1 (5)	\mathbf{v}_1 (8)	\mathbf{v}_1 (11)		
sn2.1.1	0.74	-0.18	-0.54	0.14	-0.25	-0.19	6.1	7
sn2.1.3	0.65	-0.18	-0.65	0.16	-0.23	-0.18	5.6	7
sn2.1.4	0.66	-0.16	-0.66	0.16	-0.16	-0.16	6.8	8
sn2.1.5	0.68	-0.14	-0.68	0.14	-0.14	-0.14	9.9	9
sn2.1.6	0.69	-0.11	-0.69	0.11	-0.11	-0.11	12.2	11
sn2.1.7	0.69	-0.09	-0.69	0.09	-0.09	-0.09	14.0	15
sn2.1.8	0.71	0.00	-0.71	0.00	0.00	0.00	25.1	–
sn2.1.9	0.64	-0.21	-0.64	0.21	-0.21	-0.21	4.5	7
sn2.1.10	0.58	-0.29	-0.58	0.29	-0.29	-0.29	11.5	9
sn2.1.11	0.55	-0.31	-0.55	0.31	-0.31	-0.31	15.0	15
sn2.1.12	0.51	-0.34	-0.51	0.34	-0.34	-0.34	19.2	–
sn2.1.13	0.74	-0.21	-0.53	0.21	-0.21	-0.21	4.7	8
sn2.1.14	0.53	-0.21	-0.74	0.21	-0.21	-0.21	12.9	8
sn2.1.15	0.69	-0.21	-0.59	0.19	-0.21	-0.21	0.0	8

a) The starting configuration was the same for all the calculations and was taken from the IRC (the arc length along the IRC associated with the starting configuration is 0.58). In all the calculations, the Hessian was analytically evaluated at every point of the optimization and the \mathbf{v}_1 vector was updated according to Eq. 17 in the main text.

b) Labels used to identify the reactions studied and the initial conditions employed to locate the TS configurations.

c) The components of the initial \mathbf{v}_1 vector with a non-negligible weight are (see Figure 2 for the atom numbering):

$\mathbf{v}_1(1)$ = bond length {2 1} (ie., the bond length between atoms 1 and 2)

$\mathbf{v}_1(3)$ = angle {3 2 1} (ie, the angle formed between atoms 3, 2 and 1, atom 2 being the apex atom)

$\mathbf{v}_1(4)$ = bond length {4 2}

$\mathbf{v}_1(5)$ = angle {4 2 3}

$\mathbf{v}_1(8)$ = angle {5 2 1}

$\mathbf{v}_1(11)$ = angle {6 2 1}

d) Angle between the initial \mathbf{v}_1 vector and the eigenvector associated with the imaginary frequency at the TS configuration

e) Number of steps needed to reach convergence. If the entry is “–”, it means that convergence was not achieved due to any of the following reasons: i) the maximum number of steps (150) was reached; ii) the algorithm failed to progress after reaching a specific configuration (i.e., the molecular structure barely changed from a certain point on); iii) the optimization led to a high-energy configuration for which the SCF calculation did not converge.

Table S5.2. Assessment of the performance of the GAD-CD method for the *bc*b reaction as a function of the initial \mathbf{v}_1 vector.^a

Reaction ^b	\mathbf{v}_1 relevant components ^c						Angle ^d	#steps ^e
	\mathbf{v}_1 (26)	\mathbf{v}_1 (29)	\mathbf{v}_1 (33)	\mathbf{v}_1 (36)	\mathbf{v}_1 (39)	\mathbf{v}_1 (42)		
bc b.1.3 ^f	0.54	0.55	0.33	0.12	0.14	0.32	20.4	14
bc b.1.4 ^f	0.38	0.42	0.47	0.25	0.21	0.44	0.00	78
bc b.1.5	0.36	0.36	0.55	0.36	0.06	0.55	26.2	8
bc b.1.6	0.50	0.50	0.50	0.00	0.00	0.50	30.8	16
bc b.1.7	0.39	0.39	0.59	0.00	0.00	0.59	31.6	10
bc b.1.8	0.32	0.32	0.63	0.00	0.00	0.63	33.9	19
bc b.1.9	0.22	0.22	0.67	0.00	0.00	0.67	37.8	–
bc b.1.10	0.59	0.59	0.39	0.00	0.00	0.39	33.6	23
bc b.1.11	0.63	0.63	0.32	0.00	0.00	0.32	36.9	16
bc b.1.12	0.67	0.67	0.22	0.00	0.00	0.22	41.7	32
bc b.1.13	0.69	0.69	0.17	0.00	0.00	0.17	44.6	89
bc b.1.14	0.71	0.71	0.00	0.00	0.00	0.00	55.0	–

a) The starting configuration was the same for all the calculations and was taken from the IRC (the arc length along the IRC associated with the starting configuration is 0.75). In all the calculations, the Hessian was analytically evaluated every 5 steps of the optimization. The Hessian was updated via Eq. 18 in between the steps in which an analytical evaluation was carried out. The \mathbf{v}_1 vector was updated according to Eq. 17 in all calculations.

b) Labels used to identify the reactions studied and the initial conditions employed to locate the TS configurations.

c) The components of the initial \mathbf{v}_1 vector with a non-negligible weight are (see Figure 6 for the atom numbering):

$\mathbf{v}_1(26)$ = angle {11 5 3} (ie., the angle formed between atoms 11, 5 and 3, atom 5 being the apex atom)

$\mathbf{v}_1(29)$ = angle {12 6 4}

$\mathbf{v}_1(33)$ = dihedral {13 11 5 6} (ie., the dihedral angle formed between atoms 13, 11, 5 and 6)

$\mathbf{v}_1(36)$ = dihedral {14 12 6 4}

$\mathbf{v}_1(39)$ = dihedral {15 11 5 3}

$\mathbf{v}_1(42)$ = dihedral {16 12 6 5}

d) Angle between the initial \mathbf{v}_1 vector and the eigenvector associated with the imaginary frequency at the TS configuration

e) Number of steps needed to reach convergence. If the entry is “–”, it means that convergence was not achieved due to any of the reasons mentioned in footnote g) of Table S5.1.

f) In this particular case, the \mathbf{v}_1 vector has other components with a non-negligible weight. The full list of components is given in Section 4 of the Supp. Info.