Electronic Supplementary Material (ESI) for New Journal of Chemistry.

DFT investigation on

Lewis base-catalyzed Lewis acid-mediated reactions: Hypervalent silicon species as chiral organocatalysts in (direct) aldol reactions

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Supporting Information

1. Computational details

Preliminary energy structures related to intermediates of the (i) addition of trimethyl silylenol ether of 3-methyl-2-butanone to benzaldehyde; (ii) direct aldol reaction between cyclohexanone and benzaldehyde and (iii) Cross aldol reaction between isobutyraldehyde and benzaldehyde were obtained by MonteCarlo conformational analysis performed with Molecular Mechanics calculations using the OPLS_2005 force field of the Macromodel package in the Schrodinger suite.

Subsequently, the geometries obtained were fully optimized as minimum or transition state using PM6 semiempirical calculations and then with B3LYP-D3 functional with 6-31G(d,p) basis set, unless otherwise specified. Single point energies where performed using B3LYP-D3 / 6-311+G(2df,2pd) functional. All minima and transitions states were confirmed by frequency analysis using Gaussian G16 rev A3 package.ù

Geometries in XYZ file format

(i) Addition of trimethyl silylenol ether of 3-methyl-2-butanone to benzaldehyde

Complex (i)

131 atoms, 566 electrons, +1 charge, singlet. Calculated ad B3LYP / 6-31G(d) level.

```
C          7.59802        4.78764        0.16937
C          6.60128        4.62733       -0.76467
C          7.97363        3.69629        0.98607
N          3.20743       -2.66936       -0.42056
C          4.46547       -3.27378       -0.89067
C          7.37139        2.46614        0.83816
C          2.27606       -3.62893        0.19896
C         -7.54637        3.86072        0.88953
C          6.35563        2.25423       -0.13633
C         -6.47381        3.66698        1.72864
C          5.94943        3.37641       -0.92989
C         -7.86598        2.87883       -0.07719
C          4.87380        3.22377       -1.84153
C          4.20161        2.03429       -1.94062
N         -2.32647       -3.10284        0.08216
C          4.61185        0.90880       -1.18163
N          3.87812       -0.32257       -1.35793
P          3.09247       -1.04191       -0.08410
C          3.68691       -0.77458       -2.75204
C          5.71050        0.97763       -0.32953
C          6.18582       -0.21939        0.42176
C          5.31257       -0.89554        1.26449
C          5.75335       -1.95008        2.10425
C          7.06227       -2.35935        2.06937
C          7.97686       -1.77526        1.15208
C          7.53753       -0.70530        0.30234
N          3.91371       -0.55466        1.26995
C          3.38566        0.17130        2.43621
C          8.45701       -0.19057       -0.65319
C          9.74022       -0.68342       -0.74258
C         10.17912       -1.71424        0.12069
C          9.31181       -2.24857        1.04523
O          1.56451       -0.79148        0.15680
C         -3.49721       -3.93428        0.41152
C         -7.13348        1.71534       -0.16769
C         -1.21476       -3.84017       -0.54667
C         -6.03585        1.46593        0.70345
C         -5.68836        2.48614        1.64841
C         -4.54589        2.30430        2.46921
C         -3.75640        1.19034        2.33932
C         -4.10621        0.16234        1.42436
N         -3.27322       -1.01443        1.36680
P         -2.45735       -1.44490       -0.01502
C         -2.96267       -1.64992        2.66584
C         -5.26178        0.24931        0.65618
C         -5.67819       -0.87640       -0.22373
C         -4.80742       -1.35250       -1.19803
C         -5.22501       -2.32823       -2.14175
C         -6.48928       -2.85707       -2.08018
C         -7.38101       -2.48799       -1.03913
C         -6.96938       -1.50141       -0.08281
N         -3.45421       -0.85938       -1.23883
C         -2.89784       -0.56680       -2.57495
C         -7.85473       -1.20562        0.99118
C         -9.08207       -1.82302        1.09195
C         -9.49789       -2.76777        0.12498
C         -8.65981       -3.09379       -0.91598
O         -1.01389       -0.93853       -0.28009
C          1.73068       -4.64653       -0.81155
C          0.64999       -5.56571       -0.21708
C         -0.55155       -4.83804        0.41169
Si         0.23628        0.38783       -0.07919
Cl         1.54236        2.14693        0.14766
C         -4.31069        4.25595       -1.79211
C         -3.37527        3.32075       -1.37426
C         -4.34951        5.52237       -1.19301
C         -3.45575        5.86002       -0.17193
C         -2.51784        4.92723        0.25477
C         -2.47048        3.65274       -0.34500
C         -1.45468        2.73393        0.10101
O         -1.29330        1.59671       -0.39890
Cl        -0.22497        0.40779        2.08256
H          8.08641        5.75005        0.29192
H          6.28462        5.46220       -1.38487
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H	8.74155	3.82999	1.74280
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H	7.66900	1.64901	1.48441
H	2.78852	-4.15542	1.01942
H	1.45643	-3.06039	0.63744
H	-8.14230	4.76619	0.95996
H	-6.20404	4.42013	2.46483
H	-8.69929	3.04260	-0.75480
H	4.55681	4.07986	-2.43124
H	3.32929	1.95190	-2.57787
H	3.10895	-0.04961	-3.32668
H	3.14379	-1.71871	-2.75932
H	4.66726	-0.91611	-3.21807
H	5.03632	-2.42494	2.76797
H	7.40698	-3.15988	2.71878
H	3.74004	1.20686	2.43104
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H	10.42163	-0.27750	-1.48479
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H	-3.83253	-4.49184	-0.47113
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H	-0.48496	-3.10908	-0.89160
H	-4.28429	3.07716	3.18746
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H	-2.40334	-2.56946	2.49884
H	-3.90191	-1.88603	3.17464
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H	-4.53542	-2.65502	-2.91295
H	-6.80990	-3.59466	-2.81139
H	-3.67743	-0.06575	-3.15422
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H	-2.03951	0.09295	-2.48034
H	-7.55168	-0.49004	1.74654
H	-9.73609	-1.58494	1.92595
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H	-8.95886	-3.83128	-1.65657
H	2.54403	-5.27565	-1.19066
H	1.33710	-4.09891	-1.67712
H	1.09938	-6.21282	0.54736
H	0.29558	-6.23800	-1.00936
H	-0.24529	-4.30045	1.31773
H	-1.27608	-5.59447	0.73434
H	-5.01423	4.00807	-2.58045
H	-3.32685	2.33545	-1.82362
H	-5.08228	6.25130	-1.52739
H	-3.49184	6.84544	0.28173
H	-1.81150	5.17677	1.04236
H	-0.77906	3.05851	0.89757
Cl	0.47495	0.39785	-2.25440

Complex (ii)

131 atoms, 566 electrons, +1 charge, singlet. Calculated ad B3LYP / 6-31G(d) level.

C	8.09225	3.91655	2.41818
C	7.26491	4.28065	1.38189
C	8.17506	2.55807	2.80149
N	3.17485	-2.02769	-1.31034
C	4.40045	-2.44846	-2.00728
C	7.45639	1.59139	2.13306
C	2.28048	-3.13660	-0.93119
C	-7.83740	3.36656	1.74525
C	6.60671	1.92591	1.04020
C	-6.62035	3.33428	2.38684
C	6.49847	3.30964	0.68437
C	-8.18867	2.32250	0.85676
C	5.60046	3.68338	-0.34586
C	4.80431	2.75096	-0.95722
N	-2.03129	-2.89158	0.01460
C	4.90079	1.37513	-0.61953
N	4.03224	0.45423	-1.30939
P	3.05950	-0.60320	-0.46710
C	3.80205	0.68509	-2.75289
C	5.84484	0.93826	0.31164
C	6.05948	-0.50913	0.61254
C	5.00568	-1.28444	1.07797

C	5.19279	-2.61713	1.51997
C	6.43631	-3.19488	1.45356
C	7.53268	-2.48578	0.89282
C	7.34865	-1.13213	0.45175
N	3.66856	-0.74279	1.06749
C	3.20426	-0.01789	2.26345
C	8.44856	-0.47339	-0.16436
C	9.66374	-1.10500	-0.31057
C	9.85045	-2.42722	0.15621
C	8.80429	-3.10121	0.74230
O	1.53997	-0.28084	-0.30514
C	-2.96532	-3.84115	0.64485
C	-7.33725	1.25939	0.64774
C	-1.25063	-3.46949	-1.09999
C	-6.08231	1.17603	1.31586
C	-5.71456	2.25874	2.18073
C	-4.43335	2.24797	2.78925
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N	-2.93492	-0.90082	1.48851
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C	-5.58476	-1.11233	0.32915
C	-4.84550	-1.47448	-0.78998
C	-5.27630	-2.51758	-1.65194
C	-6.42293	-3.21687	-1.37433
C	-7.16399	-2.95449	-0.19120
C	-6.73336	-1.90629	0.68789
N	-3.59494	-0.80983	-1.05673
C	-3.41010	-0.21326	-2.38951
C	-7.44962	-1.71823	1.90228
C	-8.54319	-2.49746	2.21082
C	-8.98553	-3.50535	1.32297
C	-8.30484	-3.72888	0.14837
O	-1.03704	-0.59442	-0.50856
C	1.63969	-3.83710	-2.13425
C	0.71002	-4.99240	-1.71479
C	-0.34739	-4.62705	-0.65662
Si	0.14901	0.78510	-0.64088
Cl	1.38132	2.59744	-0.88472
C	-5.00391	4.24131	-1.15149
C	-3.88265	3.43588	-1.00903
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C	-3.88365	5.52025	-2.89741
C	-2.75639	4.71870	-2.76024
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C	-1.56150	2.86350	-1.71230
O	-1.46647	1.88338	-0.93879
Cl	-0.15126	1.23590	1.47577
H	8.66975	4.66679	2.95035
H	7.17238	5.32289	1.08700
H	8.80851	2.27283	3.63670
H	4.16344	-2.76949	-3.02649
H	4.87268	-3.28088	-1.47144
H	5.11420	-1.62864	-2.05791
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H	5.51850	4.73162	-0.62078
H	4.07923	3.06524	-1.69585
H	3.30707	-0.18474	-3.18460
H	4.76920	0.82932	-3.24258
H	3.16162	1.55250	-2.92532
H	4.33696	-3.16142	1.90813
H	6.59097	-4.21281	1.80185
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H	2.16928	0.29208	2.12737
H	8.32101	0.53919	-0.52919
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H	8.93179	-4.12275	1.09156
H	-2.40323	-4.58513	1.21792
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H	-3.64466	-3.32379	1.32048
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H	-1.93605	-3.81874	-1.88912
H	-0.64624	-2.66869	-1.52540
H	-4.15006	3.07121	3.43971
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H	-1.63740	-2.27221	2.42978
H	-2.95087	-1.64895	3.45395

H	-1.52820	-0.63150	3.07565
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H	-6.75784	-4.00769	-2.04055
H	-4.02839	0.68637	-2.47415
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H	-9.06911	-2.33840	3.14785
H	-9.85355	-4.10692	1.57621
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H	2.41596	-4.24580	-2.79132
H	1.09949	-3.08904	-2.72659
H	1.31439	-5.81938	-1.31992
H	0.21390	-5.38424	-2.61223
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H	-0.94826	-5.51830	-0.44143
H	-5.87683	4.06975	-0.52984
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H	-5.88313	5.90740	-2.20029
H	-3.89418	6.32894	-3.62126
H	-1.87728	4.89462	-3.37475
H	-0.70405	3.12339	-2.33992
Cl	0.21255	0.36247	-2.81262

TS(**1**)-*Re-ap*$_1$

162 atoms, 662 electrons, +1 charge, singlet. Calculated ad B3LYP / 6-31G(d) level.

C	-8.16179	3.73047	-2.24844
C	-7.30505	4.00687	-1.20885
C	-8.33023	2.39376	-2.67724
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C	-4.88467	-2.96086	1.94010
C	-7.66614	1.36277	-2.04959
C	-2.84410	-3.80851	0.83424
C	7.88397	1.64792	-1.86256
C	-6.78798	1.60627	-0.95509
C	6.66792	1.74613	-2.49811
C	-6.59296	2.96758	-0.55357
C	8.11323	0.59234	-0.94970
C	-5.66686	3.24806	0.48145
C	-4.92279	2.24781	1.04909
N	1.46585	-3.93670	-0.06528
C	-5.10191	0.89190	0.66373
N	-4.28662	-0.10011	1.31091
P	-3.39088	-1.20300	0.43031
C	-4.00844	0.08389	2.75238
C	-6.08369	0.54833	-0.26796
C	-6.40301	-0.87106	-0.60641
C	-5.41159	-1.70599	-1.10380
C	-5.70052	-3.00693	-1.58464
C	-6.98240	-3.49419	-1.52476
C	-8.01938	-2.72549	-0.93055
C	-7.73271	-1.40408	-0.44890
N	-4.04091	-1.26246	-1.09659
C	-3.53743	-0.56438	-2.29086
C	-8.77629	-0.68853	0.20103
C	-10.03332	-1.23425	0.34007
C	-10.32074	-2.52265	-0.16792
C	-9.33140	-3.25103	-0.78665
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C	2.33218	-4.95657	-0.68098
C	7.14328	-0.35814	-0.71490
C	0.60640	-4.45363	1.01935
C	5.88351	-0.30747	-1.37780
C	5.63953	0.79464	-2.26129
C	4.36032	0.92532	-2.86142
C	3.35839	0.03056	-2.58572
C	3.60151	-1.08647	-1.74404
N	2.53691	-2.03299	-1.53978
P	1.90904	-2.32516	-0.02916
C	1.77976	-2.45187	-2.74027
C	4.85595	-1.30120	-1.18206
C	5.13150	-2.50831	-0.35493
C	4.36181	-2.76630	0.77550
C	4.71098	-3.81075	1.67351
C	5.78631	-4.62180	1.41243
C	6.53137	-4.47784	0.21280
C	6.19225	-3.42182	-0.69614
N	3.18249	-1.97711	1.01846
C	2.88909	-1.61944	2.42217

C	6.91012	-3.34306	-1.92216
C	7.91834	-4.23506	-2.21480
C	8.27204	-5.25284	-1.29843
C	7.58796	-5.37010	-0.11070
O	0.64646	-1.56519	0.42515
C	-2.29570	-4.60951	2.02002
C	-1.47304	-5.83253	1.57223
C	-0.37443	-5.52872	0.53741
Si	-0.34452	-0.02687	0.58111
Cl	-1.57239	1.83280	0.76679
C	5.17337	1.68172	2.17593
C	3.94028	1.50407	1.55198
C	5.29817	2.56863	3.25038
C	4.18518	3.28652	3.69467
C	2.95147	3.11582	3.06749
C	2.81735	2.21620	1.99855
C	1.47464	2.01048	1.40117
O	1.24489	0.85289	0.83059
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Cl	-0.50168	-0.43112	2.74785
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H	-7.80601	0.34909	-2.40523
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H	-7.21389	-4.48666	-1.90291
H	-4.08692	0.36798	-2.46348
H	-3.66691	-1.22018	-3.15805
H	-2.47879	-0.34215	-2.16812
H	-8.57188	0.29893	0.59839
H	-10.81161	-0.67015	0.84610
H	-11.31891	-2.93684	-0.05901
H	-9.53587	-4.24881	-1.16680
H	1.72327	-5.65259	-1.26652
H	2.87599	-5.52231	0.08559
H	3.06169	-4.49355	-1.34338
H	7.34197	-1.15912	-0.01278
H	1.23556	-4.86587	1.82489
H	0.05895	-3.60734	1.43378
H	4.17338	1.76329	-3.52852
H	2.36824	0.17587	-2.99797
H	1.12456	-3.28394	-2.48217
H	2.49007	-2.78024	-3.50415
H	1.16127	-1.63979	-3.12773
H	4.12249	-3.96366	2.57171
H	6.05749	-5.41093	2.10912
H	3.80786	-1.23273	2.86770
H	2.53311	-2.47012	3.01625
H	2.12976	-0.84348	2.44618
H	6.64927	-2.57406	-2.64015
H	8.44513	-4.15847	-3.16176
H	9.07380	-5.94441	-1.54015
H	7.83720	-6.15791	0.59578
H	-3.11925	-4.96406	2.65001
H	-1.69718	-3.93772	2.64702
H	-2.14607	-6.58669	1.14391
H	-1.02552	-6.29742	2.46036
H	-0.82331	-5.19456	-0.40626
H	0.15975	-6.45888	0.31125
H	6.03905	1.13141	1.81839
H	3.83603	0.80398	0.73034
H	6.25916	2.69848	3.74045
H	4.27471	3.97034	4.53383
H	2.08239	3.66172	3.42671
H	0.64401	2.44713	1.95525
C	1.43368	3.33897	-0.14976
C	1.36131	4.61976	0.39803
O	2.39876	5.41791	0.53624
C	0.10385	5.16530	1.00887
C	-0.46627	6.40404	0.26129
C	-1.61461	7.01170	1.07787
C	-0.92517	6.04769	-1.15949
Si	3.79977	5.82917	-0.41490

C	3.21951	5.98125	-2.19577
C	5.14398	4.54196	-0.21592
C	4.30156	7.47345	0.32646
H	0.34772	5.46694	2.03733
H	-0.65536	4.37984	1.05214
H	0.33843	7.14904	0.19661
H	-2.01608	7.90053	0.57867
H	-2.43689	6.29446	1.19336
H	-1.28397	7.30939	2.07960
H	-1.32378	6.93180	-1.66929
H	-0.10572	5.65280	-1.77106
H	-1.71655	5.28839	-1.13669
H	0.50698	2.92572	-0.53232
H	2.33683	3.04086	-0.67483
H	4.05644	6.28912	-2.83473
H	2.83722	5.03267	-2.58890
H	2.43077	6.73419	-2.30242
H	4.89308	3.58281	-0.67924
H	6.06384	4.90487	-0.69245
H	5.36921	4.35365	0.83850
H	5.18711	7.87357	-0.18176
H	3.50132	8.21619	0.23747
H	4.54765	7.36971	1.38917

TS(**1**)-*Re-sc*$_1$

162 atoms, 662 electrons, +1 charge, singlet. Calculated ad B3LYP / 6-31G(d) level.

C	-8.26975	4.16876	-1.30628
C	-7.38454	4.27850	-0.25951
C	-8.44942	2.91764	-1.93993
N	-3.67019	-2.66108	0.99490
C	-4.90672	-3.08741	1.66692
C	-7.76821	1.80221	-1.50427
C	-2.91622	-3.75797	0.36563
C	7.97123	2.01228	-0.91662
C	-6.86082	1.87061	-0.40865
C	6.78076	2.25127	-1.56324
C	-6.65449	3.15068	0.20063
C	8.16755	0.78306	-0.24502
C	-5.69878	3.26608	1.24042
C	-4.93915	2.19104	1.61919
N	1.42775	-3.71394	-0.52838
C	-5.13040	0.91308	1.02786
N	-4.29855	-0.16624	1.48780
P	-3.43161	-1.11822	0.42109
C	-3.98872	-0.21290	2.93323
C	-6.13841	0.71904	0.08084
C	-6.46817	-0.62878	-0.47191
C	-5.49120	-1.37028	-1.12218
C	-5.79370	-2.57875	-1.79681
C	-7.07350	-3.07491	-1.77991
C	-8.09347	-2.41478	-1.04289
C	-7.79354	-1.18494	-0.36612
N	-4.11970	-0.92983	-1.07955
C	-3.65837	-0.02355	-2.14370
C	-8.81860	-0.58549	0.41709
C	-10.07110	-1.15205	0.50295
C	-10.37244	-2.34549	-0.19400
C	-9.40092	-2.96245	-0.94746
O	-1.90023	-0.90815	0.25673
C	2.31586	-4.62931	-1.26626
C	7.19073	-0.18929	-0.25544
C	0.52999	-4.39548	0.42662
C	5.95599	0.01029	-0.93740
C	5.74615	1.27680	-1.57579
C	4.49034	1.54479	-2.17919
C	3.47859	0.62066	-2.13750
C	3.68835	-0.65002	-1.54337
N	2.60991	-1.60428	-1.57767
P	1.89574	-2.14514	-0.18040
C	1.96487	-1.82589	-2.88918
C	4.91693	-0.98985	-0.98663
C	5.13771	-2.33437	-0.38631
C	4.30589	-2.77670	0.63879
C	4.59555	-3.97410	1.34643
C	5.67226	-4.74818	0.99432
C	6.48130	-4.40410	-0.12013
C	6.20429	-3.19228	-0.83495
N	3.12408	-2.02264	0.96576
C	2.78637	-1.88615	2.39694
C	6.98807	-2.90476	-1.98721
C	8.00019	-3.74901	-2.38796

C	8.29120	-4.92561	-1.65873
C	7.54267	-5.24456	-0.54947
O	0.63165	-1.44648	0.36211
C	-2.35734	-4.76472	1.37673
C	-1.53142	-5.87627	0.70256
C	-0.43219	-5.37631	-0.25254
Si	-0.39034	0.05950	0.65481
Cl	-1.65031	1.86483	1.01473
C	5.04252	1.33541	2.70306
C	3.83124	1.33217	2.01190
C	5.11550	1.86769	3.99328
C	3.97017	2.39499	4.59612
C	2.75974	2.39640	3.90560
C	2.68092	1.86736	2.60773
C	1.36528	1.87361	1.91555
O	1.16295	0.97349	0.98060
Cl	-0.16788	0.57279	-1.48932
Cl	-0.53669	-0.56828	2.77650
H	-8.81975	5.03802	-1.65507
H	-7.21862	5.23643	0.22731
H	-9.12902	2.83468	-2.78349
H	-4.66951	-3.60857	2.60005
H	-5.47727	-3.76283	1.01733
H	-5.53377	-2.22901	1.89829
H	-7.91760	0.85821	-2.01440
H	-3.57063	-4.27678	-0.35302
H	-2.09874	-3.31300	-0.20290
H	8.75552	2.76366	-0.91281
H	6.60970	3.19510	-2.07571
H	9.09919	0.60198	0.28359
H	-5.54467	4.23356	1.71134
H	-4.16986	2.31525	2.36939
H	-3.54591	-1.17841	3.17698
H	-4.91975	-0.09137	3.49448
H	-3.27320	0.56021	3.22011
H	-4.99484	-3.09424	-2.32160
H	-7.31566	-3.99527	-2.30510
H	-4.21017	0.92316	-2.12341
H	-3.82204	-0.51120	-3.11022
H	-2.59470	0.17331	-2.02244
H	-8.60302	0.32770	0.95958
H	-10.83504	-0.67857	1.11303
H	-11.36709	-2.77623	-0.12423
H	-9.61602	-3.88831	-1.47511
H	1.73331	-5.19945	-1.99674
H	2.80870	-5.33119	-0.58216
H	3.08847	-4.07555	-1.79675
H	7.36431	-1.12251	0.26659
H	1.13029	-4.93441	1.17807
H	-0.03329	-3.62375	0.95040
H	4.32484	2.51240	-2.64526
H	2.50200	0.85963	-2.53817
H	1.21882	-2.61515	-2.79824
H	2.72763	-2.13341	-3.61104
H	1.46018	-0.92497	-3.24235
H	3.95852	-4.27489	2.17125
H	5.89608	-5.65710	1.54696
H	3.68706	-1.56852	2.92600
H	2.41940	-2.81996	2.84089
H	2.01877	-1.12730	2.51802
H	6.77528	-2.01107	-2.56270
H	8.57862	-3.51081	-3.27608
H	9.09659	-5.57815	-1.98285
H	7.74476	-6.15387	0.01104
H	-3.17526	-5.23535	1.93417
H	-1.75602	-4.22093	2.11528
H	-2.20134	-6.53688	0.13697
H	-1.08266	-6.50121	1.48564
H	-0.87910	-4.88261	-1.12434
H	0.11567	-6.24410	-0.63770
H	5.93045	0.92683	2.22926
H	3.76760	0.90719	1.01664
H	6.06047	1.86861	4.52935
H	4.01858	2.79712	5.60399
H	1.86636	2.79686	4.38003
H	0.51448	2.07702	2.56777
C	1.19959	3.76984	1.20728
C	2.20231	4.08865	0.28191
O	2.02230	4.05431	-1.01734
C	3.60789	4.41264	0.69659
C	4.07285	5.84020	0.29884
C	5.57488	5.98688	0.57792
C	3.26792	6.92542	1.02747
Si	0.85221	4.61680	-2.18774
C	-0.89600	4.60191	-1.52138
C	1.09383	3.47395	-3.64898

C	1.40987	6.36749	-2.58610
H	4.26391	3.68029	0.20660
H	3.71605	4.27955	1.77616
H	3.91174	5.95064	-0.78133
H	5.93154	6.97564	0.26880
H	5.78951	5.87552	1.64806
H	6.15934	5.23157	0.03997
H	3.60157	7.92416	0.72548
H	2.19383	6.85657	0.81720
H	3.39919	6.84747	2.11431
H	1.33170	4.21613	2.18838
H	0.17780	3.70532	0.85209
H	-1.57221	4.93021	-2.32199
H	-1.21425	3.60545	-1.20141
H	-1.03007	5.29450	-0.68300
H	0.77306	2.45627	-3.40824
H	0.49506	3.82344	-4.49913
H	2.14041	3.44751	-3.97258
H	0.75978	6.79838	-3.35798
H	1.35851	7.02636	-1.71188
H	2.43629	6.39091	-2.96855

TS(**1**)-*Re-sc*$_2$

162 atoms, 662 electrons, +1 charge, singlet. Calculated ad B3LYP / 6-31G(d) level.

C	-8.31344	2.89663	-2.32064
C	-7.46220	3.30221	-1.31959
C	-8.36853	1.52988	-2.67854
N	-3.13111	-2.84380	1.34777
C	-4.32935	-3.25650	2.09349
C	-7.59896	0.59654	-2.01935
C	-2.25705	-3.95762	0.94125
C	7.82255	2.59074	-1.74497
C	-6.72237	0.97408	-0.96219
C	6.60017	2.57087	-2.37495
C	-6.64344	2.36640	-0.63375
C	8.18352	1.52821	-0.88397
C	-5.72194	2.78305	0.35872
C	-4.87716	1.88476	0.95507
N	2.03216	-3.69986	-0.08774
C	-4.94259	0.49988	0.64447
N	-4.02660	-0.38002	1.31944
P	-3.04916	-1.43433	0.46902
C	-3.74046	-0.10305	2.74392
C	-5.90842	0.02106	-0.24349
C	-6.09781	-1.43691	-0.50780
C	-5.04154	-2.19652	-0.99253
C	-5.21460	-3.53981	-1.40853
C	-6.44225	-4.14306	-1.29408
C	-7.53515	-3.44940	-0.70777
C	-7.36676	-2.08562	-0.29323
N	-3.71955	-1.62633	-1.03746
C	-3.29924	-0.95607	-2.27841
C	-8.45974	-1.44231	0.35083
C	-9.65507	-2.09791	0.54733
C	-9.82807	-3.43033	0.10534
C	-8.78713	-4.08990	-0.50599
O	-1.54990	-1.09115	0.25947
C	2.98743	-4.64171	-0.69573
C	7.33488	0.45964	-0.68955
C	1.24950	-4.27867	1.02489
C	6.07337	0.38971	-1.34731
C	5.69700	1.49116	-2.18421
C	4.41042	1.49228	-2.78283
C	3.52262	0.47379	-2.54679
C	3.89517	-0.63446	-1.74185
N	2.94328	-1.70103	-1.55736
P	2.33604	-2.05420	-0.05221
C	2.27264	-2.21084	-2.77265
C	5.16634	-0.72056	-1.18443
C	5.56805	-1.90572	-0.37794
C	4.82487	-2.25958	0.74439
C	5.27537	-3.27925	1.62518
C	6.42817	-3.97277	1.35527
C	7.16041	-3.73018	0.16368
C	6.71938	-2.69715	-0.72752
N	3.57123	-1.59878	0.99671
C	3.25921	-1.25645	2.39881
C	7.43273	-2.51851	-1.94565
C	8.53057	-3.29403	-2.24721
C	8.98167	-4.28866	-1.34827
C	8.30562	-4.50152	-0.16922

O	1.01158	-1.41047	0.41154
C	-1.59845	-4.67745	2.12244
C	-0.67957	-5.82699	1.66454
C	0.35249	-5.44244	0.58728
Si	-0.12822	0.02896	0.50554
Cl	-1.48664	1.78875	0.64528
C	5.22168	2.22143	2.16421
C	4.02398	1.98731	1.49245
C	5.21816	2.86460	3.40641
C	4.01131	3.27605	3.97595
C	2.81203	3.05605	3.29890
C	2.81019	2.40754	2.05453
C	1.50999	2.18029	1.37416
O	1.37143	1.07683	0.69676
Cl	0.04371	0.26116	-1.68780
Cl	-0.21631	-0.30053	2.69563
H	-8.93162	3.62021	-2.84410
H	-7.39194	4.35161	-1.04389
H	-9.02135	1.21158	-3.48649
H	-4.05836	-3.54918	3.11300
H	-4.81130	-4.10701	1.59544
H	-5.04866	-2.44164	2.14506
H	-7.65396	-0.44250	-2.32086
H	-2.84654	-4.67617	0.34942
H	-1.48593	-3.55224	0.28525
H	8.50526	3.42174	-1.89651
H	6.30007	3.38891	-3.02522
H	9.14038	1.55387	-0.37005
H	-5.66456	3.83767	0.61587
H	-4.13624	2.23097	1.66316
H	-3.20536	-0.94871	3.17541
H	-4.68863	0.03209	3.27246
H	-3.11204	0.78157	2.86561
H	-4.36001	-4.07175	-1.81596
H	-6.58568	-5.16944	-1.62188
H	-3.92985	-0.08469	-2.48856
H	-3.38786	-1.66750	-3.10596
H	-2.26110	-0.63983	-2.19160
H	-8.34204	-0.42231	0.69805
H	-10.47289	-1.58730	1.04777
H	-10.77915	-3.93197	0.25881
H	-8.90332	-5.11928	-0.83580
H	2.44379	-5.39710	-1.27211
H	3.58286	-5.14691	0.07487
H	3.67105	-4.12162	-1.36482
H	7.63138	-0.34129	-0.02300
H	1.93487	-4.62302	1.81659
H	0.64132	-3.47887	1.44623
H	4.12432	2.32967	-3.41457
H	2.52181	0.51546	-2.95706
H	1.65797	-3.07273	-2.51300
H	3.03617	-2.51851	-3.49319
H	1.62266	-1.45502	-3.21747
H	4.70196	-3.50759	2.51721
H	6.77499	-4.74355	2.03883
H	4.12676	-0.74494	2.82048
H	3.02773	-2.13618	3.01232
H	2.40487	-0.58644	2.42648
H	7.09764	-1.76588	-2.65019
H	9.05339	-3.14293	-3.18737
H	9.85282	-4.88784	-1.59654
H	8.63190	-5.27331	0.52346
H	-2.36435	-5.09404	2.78680
H	-1.04458	-3.94088	2.71649
H	-1.29319	-6.64804	1.27143
H	-0.16151	-6.23212	2.54353
H	-0.15563	-5.16263	-0.34381
H	0.95902	-6.32520	0.35339
H	6.15800	1.90481	1.71395
H	4.02311	1.48032	0.53390
H	6.15375	3.04414	3.92857
H	4.00289	3.76377	4.94648
H	1.87150	3.36565	3.74791
H	0.62620	2.55797	1.88802
C	1.69054	3.82481	0.04768
C	0.48292	4.31955	-0.44793
O	-0.22724	5.24027	0.17112
C	-0.11654	3.89098	-1.75213
C	-0.10723	5.02461	-2.81746
C	-0.90610	4.57492	-4.04806
C	1.31644	5.44505	-3.20806
Si	-0.16750	6.24885	1.57834
C	1.58923	6.81050	1.94926
C	-0.92322	5.26156	2.98470
C	-1.25101	7.69220	1.07871
H	-1.15189	3.58773	-1.56372

H	0.41565	3.01414	-2.12896
H	-0.61680	5.89199	-2.37671
H	-0.94212	5.37214	-4.79912
H	-0.44711	3.69548	-4.51699
H	-1.93659	4.31304	-3.78315
H	1.29207	6.24032	-3.96136
H	1.88855	5.81743	-2.35028
H	1.87030	4.59957	-3.63715
H	2.31336	3.28349	-0.65681
H	2.21879	4.44929	0.75682
H	1.54789	7.63449	2.67323
H	2.21619	6.02649	2.38692
H	2.09412	7.19334	1.05495
H	-0.31906	4.39062	3.26018
H	-1.02439	5.89094	3.87765
H	-1.92081	4.89844	2.71550
H	-1.37142	8.39444	1.91237
H	-0.82031	8.24652	0.23732
H	-2.24896	7.35223	0.78105

TS(**1**)-*Si-ap*$_2$

162 atoms, 662 electrons, +1 charge, singlet. Calculated ad B3LYP / 6-31G(d) level.

C	-7.85600	4.50100	-2.00500
C	-7.04300	4.63600	-0.90400
C	-8.09600	3.21600	-2.54200
N	-3.95300	-2.41100	1.21800
C	-5.25900	-2.72800	1.81400
C	-7.54700	2.09400	-1.96000
C	-3.17600	-3.59100	0.80400
C	7.53100	1.51300	-2.12100
C	-6.71900	2.19100	-0.80500
C	6.28800	1.64800	-2.69600
C	-6.44800	3.50100	-0.29200
C	7.78500	0.43000	-1.24700
C	-5.56400	3.63500	0.80700
C	-4.93000	2.54300	1.33800
N	1.07400	-3.94800	-0.06800
C	-5.18700	1.23600	0.84300
N	-4.48500	0.13700	1.45300
P	-3.60000	-0.93900	0.53300
C	-4.32200	0.16800	2.92400
C	-6.13300	1.03600	-0.16500
C	-6.52500	-0.32800	-0.63000
C	-5.56100	-1.19000	-1.13500
C	-5.90200	-2.43500	-1.71900
C	-7.21200	-2.84100	-1.75800
C	-8.23200	-2.04600	-1.16900
C	-7.89300	-0.78000	-0.58300
N	-4.16800	-0.83800	-1.02500
C	-3.56500	-0.06500	-2.12200
C	-8.92600	-0.04100	0.05700
C	-10.22000	-0.51100	0.09200
C	-10.55600	-1.74300	-0.51600
C	-9.58000	-2.49300	-1.12900
O	-2.05400	-0.80100	0.43000
C	1.85700	-4.98000	-0.76900
C	6.80800	-0.50500	-0.98300
C	0.22100	-4.46900	1.02100
C	5.51700	-0.41300	-1.57700
C	5.25500	0.70900	-2.43000
C	3.95300	0.86800	-2.97300
C	2.94500	-0.00500	-2.65100
C	3.19700	-1.12900	-1.81900
N	2.11800	-2.03900	-1.55000
P	1.60000	-2.36500	0.00300
C	1.17600	-2.30800	-2.66000
C	4.47800	-1.38500	-1.33900
C	4.78500	-2.63000	-0.58200
C	4.09700	-2.92500	0.59000
C	4.48500	-4.02400	1.40300
C	5.51300	-4.84700	1.01800
C	6.17000	-4.65900	-0.22500
C	5.79200	-3.54800	-1.05000
N	2.96400	-2.11800	0.96600
C	2.75600	-1.90100	2.41600
C	6.41900	-3.42300	-2.32200
C	7.37800	-4.32200	-2.73500
C	7.77100	-5.39500	-1.90100
C	7.17400	-5.55800	-0.67200
O	0.42800	-1.54600	0.56300
C	-2.70900	-4.44800	1.98600

C	-1.95500	-5.71300	1.53500
C	-0.83100	-5.46400	0.51400
Si	-0.52300	-0.00400	1.02200
Cl	-1.58500	1.84700	1.54300
C	5.63300	1.77400	2.13800
C	4.48100	1.68900	1.35400
C	5.53200	1.76100	3.53000
C	4.27600	1.65100	4.14000
C	3.12700	1.54800	3.36200
C	3.22200	1.56600	1.96100
C	2.02200	1.40600	1.11400
O	1.02500	0.76000	1.64200
Cl	-0.14700	0.71600	-1.06600
Cl	-0.78700	-0.89000	3.00900
H	-8.30200	5.37600	-2.47000
H	-6.83100	5.61800	-0.48900
H	-8.71700	3.11000	-3.42700
H	-5.12900	-3.13900	2.82000
H	-5.78600	-3.46400	1.19400
H	-5.87900	-1.83600	1.88100
H	-7.73900	1.12200	-2.39800
H	-3.79200	-4.19800	0.12000
H	-2.31300	-3.23900	0.23800
H	8.31500	2.23500	-2.33200
H	6.07400	2.48100	-3.36100
H	8.76000	0.33400	-0.77900
H	-5.36100	4.62700	1.20400
H	-4.21000	2.67300	2.13400
H	-3.91900	-0.78600	3.26300
H	-5.30200	0.33100	3.38200
H	-3.62700	0.94900	3.23700
H	-5.10700	-3.05200	-2.12700
H	-7.48300	-3.79000	-2.21300
H	-4.07100	0.89900	-2.24900
H	-3.65700	-0.64100	-3.04900
H	-2.51100	0.10800	-1.91200
H	-8.68300	0.90400	0.53100
H	-10.99000	0.06900	0.59300
H	-11.58200	-2.09800	-0.48700
H	-9.82400	-3.44900	-1.58600
H	1.18500	-5.62500	-1.34500
H	2.41500	-5.60000	-0.05700
H	2.56800	-4.52100	-1.45500
H	7.02100	-1.32200	-0.30500
H	0.85000	-4.95600	1.78300
H	-0.26300	-3.61600	1.49500
H	3.75600	1.70700	-3.63500
H	1.94500	0.16200	-3.03000
H	0.59400	-3.20100	-2.43100
H	1.75400	-2.48600	-3.57000
H	0.48400	-1.47500	-2.81500
H	3.96600	-4.21300	2.33700
H	5.81200	-5.67800	1.65200
H	3.70100	-1.55500	2.84000
H	2.43800	-2.80900	2.94200
H	1.99800	-1.13800	2.56400
H	6.12700	-2.61300	-2.98000
H	7.83400	-4.20900	-3.71400
H	8.53300	-6.09200	-2.23700
H	7.45300	-6.38700	-0.02700
H	-3.57000	-4.76300	2.58700
H	-2.08800	-3.82500	2.64000
H	-2.66600	-6.42200	1.09100
H	-1.54600	-6.21300	2.42300
H	-1.25300	-5.08100	-0.42300
H	-0.36100	-6.42400	0.26900
H	6.60500	1.83600	1.65700
H	4.56300	1.68400	0.27100
H	6.42800	1.82800	4.14200
H	4.19700	1.64000	5.22300
H	2.15100	1.44300	3.82600
H	2.17300	1.31500	0.03800
C	1.32900	3.42000	0.99200
C	2.26400	4.17200	0.30000
O	3.23700	4.73200	0.99600
C	2.28800	4.26500	-1.20900
C	0.92300	4.47200	-1.90700
C	0.26900	5.79700	-1.49100
C	1.11000	4.40400	-3.43000
Si	4.54500	5.84000	0.74700
C	5.32400	5.91500	2.44600
C	3.81200	7.49100	0.23000
C	5.74400	5.16600	-0.53700
H	0.15000	4.52100	-3.94300
H	1.53800	3.44300	-3.73900
H	1.77600	5.20100	-3.78700

H	0.10600	5.84800	-0.40800
H	0.89300	6.65400	-1.78100
H	-0.70400	5.91800	-1.97800
H	2.96600	5.07200	-1.50800
H	2.74100	3.33300	-1.58300
H	0.41200	3.14600	0.49000
H	4.61400	6.29500	3.19000
H	5.65200	4.92200	2.77200
H	6.19700	6.57900	2.44700
H	6.04700	4.13900	-0.30800
H	5.33500	5.17900	-1.55300
H	6.65100	5.78300	-0.54300
H	4.60200	8.25100	0.18000
H	3.33000	7.45500	-0.75300
H	3.06800	7.83800	0.95600
H	0.26200	3.64800	-1.61700
H	1.26900	3.55400	2.06600

TS(**1**)-*Si-sc*$_3$

162 atoms, 662 electrons, +1 charge, singlet. Calculated ad B3LYP / 6-31G(d) level.

C	-8.00853	2.64821	-2.88469
C	-7.28899	3.11073	-1.80775
C	-7.98335	1.27041	-3.20191
N	-3.05528	-2.78971	1.51379
C	-4.29594	-3.24383	2.15954
C	-7.26750	0.38224	-2.42960
C	-2.07244	-3.85900	1.27712
C	7.56642	2.59748	-2.58545
C	-6.52793	0.81958	-1.29384
C	6.29758	2.48675	-3.10551
C	-6.52653	2.22254	-1.00355
C	8.01647	1.65452	-1.63173
C	-5.73798	2.69550	0.07498
C	-4.94072	1.84155	0.79119
N	2.08567	-3.54346	0.27115
C	-4.92817	0.44748	0.51674
N	-4.06587	-0.38752	1.31012
P	-2.95594	-1.41034	0.59295
C	-3.97126	-0.09030	2.75700
C	-5.77488	-0.08545	-0.45775
C	-5.89677	-1.55606	-0.68758
C	-4.77369	-2.29796	-1.02663
C	-4.86163	-3.66411	-1.39155
C	-6.07597	-4.30379	-1.37557
C	-7.24554	-3.62204	-0.94374
C	-7.16260	-2.23596	-0.57972
N	-3.47393	-1.68244	-0.96249
C	-2.94259	-1.05738	-2.18251
C	-8.33769	-1.60148	-0.08984
C	-9.52791	-2.28771	0.00807
C	-9.61281	-3.64439	-0.38319
C	-8.49276	-4.29519	-0.84592
O	-1.46563	-0.99049	0.47429
C	3.01161	-4.51489	-0.33872
C	7.20677	0.61245	-1.23489
C	1.39810	-4.04897	1.47891
C	5.89796	0.44941	-1.77011
C	5.43489	1.43032	-2.70708
C	4.10731	1.33724	-3.19899
C	3.26084	0.35299	-2.75669
C	3.71378	-0.63326	-1.84007
N	2.79946	-1.67205	-1.44362
P	2.36890	-1.89960	0.14904
C	1.92941	-2.23291	-2.50118
C	5.03096	-0.64048	-1.39332
C	5.54335	-1.73524	-0.52394
C	4.93621	-2.00326	0.69920
C	5.51313	-2.92914	1.61041
C	6.65138	-3.61822	1.27721
C	7.24157	-3.47098	-0.00465
C	6.67354	-2.53350	-0.92870
N	3.69535	-1.35239	1.03108
C	3.47976	-1.00702	2.45344
C	7.24325	-2.45622	-2.23046
C	8.32408	-3.23469	-2.58214
C	8.90230	-4.13143	-1.65374
C	8.36656	-4.24645	-0.39204
O	1.10558	-1.20497	0.68366
C	-1.46588	-4.42345	2.56664
C	-0.48619	-5.58046	2.29362
C	0.55198	-5.29736	1.19333

Si	-0.11429	0.16427	0.95557
Cl	-1.54605	1.81700	1.20043
C	5.65670	3.01569	1.38829
C	4.43356	2.74438	0.77383
C	5.76638	2.96162	2.77853
C	4.65046	2.62711	3.55406
C	3.43146	2.34523	2.94307
C	3.31612	2.40127	1.54478
C	2.01666	2.13230	0.86777
O	1.22364	1.28831	1.47791
Cl	0.13515	0.67289	-1.21725
Cl	-0.26222	-0.49215	3.03926
H	-8.58473	3.33560	-3.49727
H	-7.28272	4.16936	-1.55965
H	-8.53154	0.90778	-4.06693
H	-4.12103	-3.44553	3.22142
H	-4.65403	-4.16245	1.67873
H	-5.07529	-2.48956	2.07174
H	-7.25744	-0.66700	-2.69952
H	-2.55870	-4.66636	0.70611
H	-1.28226	-3.44847	0.64748
H	8.21872	3.40841	-2.89639
H	5.93083	3.21218	-3.82770
H	9.01103	1.75337	-1.20575
H	-5.74478	3.75731	0.30828
H	-4.29902	2.23109	1.56976
H	-3.43016	-0.89334	3.25676
H	-4.98260	-0.02538	3.16900
H	-3.42730	0.83746	2.94341
H	-3.95284	-4.18517	-1.67826
H	-6.15292	-5.34894	-1.66405
H	-3.56718	-0.21362	-2.49935
H	-2.92641	-1.80550	-2.98217
H	-1.92842	-0.70532	-1.99996
H	-8.28888	-0.56311	0.21705
H	-10.41011	-1.78279	0.39115
H	-10.55995	-4.17072	-0.30821
H	-8.54230	-5.34186	-1.13553
H	2.44060	-5.33088	-0.79239
H	3.69047	-4.93589	0.41328
H	3.61312	-4.03935	-1.11192
H	7.56821	-0.09102	-0.49478
H	2.14045	-4.28237	2.25922
H	0.77090	-3.24246	1.85903
H	3.75638	2.07595	-3.91520
H	2.23590	0.32464	-3.10290
H	1.48671	-3.16530	-2.15044
H	2.54477	-2.44133	-3.38008
H	1.12229	-1.54554	-2.76797
H	5.05083	-3.08991	2.57775
H	7.09469	-4.31438	1.98465
H	4.35929	-0.46427	2.80357
H	3.32463	-1.88839	3.08807
H	2.60811	-0.36406	2.54032
H	6.81059	-1.78070	-2.95920
H	8.73448	-3.16171	-3.58533
H	9.75882	-4.73325	-1.94309
H	8.78970	-4.94341	0.32706
H	-2.25879	-4.79483	3.22600
H	-0.97522	-3.60538	3.10603
H	-1.05122	-6.47569	2.00272
H	0.02495	-5.83778	3.23038
H	0.04704	-5.16507	0.22836
H	1.19690	-6.17697	1.08332
H	6.52034	3.26129	0.77801
H	4.35258	2.78486	-0.30899
H	6.71606	3.18000	3.25885
H	4.73343	2.58672	4.63670
H	2.56264	2.08015	3.53813
H	2.04299	2.07313	-0.21981
C	1.43047	4.12874	0.84367
C	0.07250	4.49952	0.89285
O	-0.67445	4.73042	-0.14931
C	-0.59885	4.74671	2.21539
C	-0.25812	6.13416	2.83551
C	-0.70546	7.30265	1.94739
C	-0.89203	6.22796	4.23094
H	-0.63340	7.17876	4.70983
H	-0.55058	5.41689	4.88400
H	-1.98599	6.17232	4.16962
H	-0.21219	7.29244	0.96941
H	-1.78880	7.27341	1.77596
H	-0.47013	8.25966	2.42607
H	-1.68083	4.66281	2.08026
H	-0.28537	3.96157	2.91099
H	1.95882	4.39082	1.75263

H	0.83339	6.18976	2.95431
H	1.97021	4.36606	-0.06757
Si	-0.65063	4.81774	-1.88717
C	-0.97323	6.63497	-2.22812
H	-0.16247	7.27017	-1.85329
H	-1.05779	6.81123	-3.30756
H	-1.90641	6.96964	-1.76236
C	0.99347	4.27418	-2.61817
H	1.24517	3.24670	-2.33784
H	0.90949	4.30519	-3.71262
H	1.82098	4.93625	-2.34027
C	-2.06521	3.71314	-2.40763
H	-2.19821	3.74493	-3.49615
H	-1.87298	2.67680	-2.11250
H	-3.00584	4.02789	-1.94322

TS(**1**)-*Si-sc*$_4$

C	7.96182	3.19775	3.35776
C	7.15906	3.67887	2.35011
C	8.11894	1.80184	3.51927
N	3.62465	-2.31426	-1.55879
C	4.91074	-2.53124	-2.23834
C	7.49765	0.91881	2.66367
C	2.76959	-3.50979	-1.48765
C	-7.44267	1.34333	3.03371
C	6.67655	1.37897	1.59491
C	-6.18175	1.22532	3.57117
C	6.49147	2.79348	1.46293
C	-7.81149	0.53860	1.93006
C	5.61839	3.27738	0.45715
C	4.91336	2.41256	-0.33767
N	-1.47755	-3.84143	-0.63986
C	5.08333	1.00714	-0.22081
N	4.30955	0.16317	-1.09180
P	3.36314	-1.07348	-0.48579
C	4.12944	0.60918	-2.49095
C	6.01712	0.48190	0.67513
C	6.32587	-0.97800	0.73888
C	5.31352	-1.88945	1.00712
C	5.58098	-3.26442	1.21873
C	6.86495	-3.73948	1.11807
C	7.92823	-2.87242	0.74834
C	7.66289	-1.47697	0.54029
N	3.94448	-1.44172	1.02669
C	3.39409	-0.96899	2.30747
C	8.73570	-0.64989	0.10573
C	9.99879	-1.16508	-0.08406
C	10.26336	-2.53391	0.15537
C	9.24660	-3.36736	0.55995
O	1.83035	-0.87773	-0.32519
C	-2.32440	-4.98165	-0.24866
C	-6.92958	-0.37889	1.40121
C	-0.67124	-4.07665	-1.85669
C	-5.62444	-0.54637	1.94485
C	-5.24510	0.29835	3.03923
C	-3.92523	0.20634	3.55139
C	-3.00709	-0.63891	2.98287
C	-3.37324	-1.48558	1.90152
N	-2.38056	-2.37200	1.35424
P	-1.90743	-2.27712	-0.24263
C	-1.46073	-3.01848	2.31743
C	-4.67955	-1.50340	1.42340
C	-5.10042	-2.47163	0.37447
C	-4.45802	-2.49013	-0.85916
C	-4.94656	-3.29799	-1.92168
C	-6.03265	-4.11462	-1.73365
C	-6.65377	-4.21822	-0.46208
C	-6.17348	-3.40307	0.61514
N	-3.27112	-1.69575	-1.04942
C	-3.07545	-1.10631	-2.39250
C	-6.76980	-3.57574	1.89562
C	-7.79548	-4.47513	2.08777
C	-8.28850	-5.25082	1.01269
C	-7.72358	-5.12428	-0.23513
O	-0.70222	-1.39488	-0.60195
C	2.24931	-3.96122	-2.85734
C	1.41242	-5.25141	-2.77133
C	0.31625	-5.23927	-1.69062
Si	0.34380	0.15296	-0.61366
Cl	1.53055	2.00892	-0.59902
C	-5.68763	2.59304	-1.02490
C	-4.54484	2.20425	-0.32487

C	-5.60375	2.90440	-2.38431
C	-4.37211	2.82293	-3.04230
C	-3.22810	2.43009	-2.34814
C	-3.30859	2.11623	-0.98151
C	-2.11108	1.65721	-0.23621
O	-1.14617	1.16582	-0.95802
Cl	0.04184	0.25413	1.59054
Cl	0.53930	-0.12959	-2.78219
H	8.46345	3.88234	4.03559
H	7.01060	4.74845	2.22343
H	8.73236	1.42013	4.33064
H	4.76070	-2.62257	-3.31906
H	5.38146	-3.44949	-1.86638
H	5.58976	-1.70192	-2.05158
H	7.62614	-0.14612	2.81608
H	3.34003	-4.32539	-1.01491
H	1.92822	-3.27969	-0.83279
H	-8.15172	2.05452	3.44761
H	-5.87851	1.84502	4.41161
H	-8.80120	0.64429	1.49443
H	5.48166	4.35025	0.34859
H	4.20321	2.79867	-1.05619
H	3.71066	-0.20748	-3.07857
H	5.10629	0.88360	-2.89959
H	3.44030	1.45302	-2.56054
H	4.75170	-3.92340	1.45863
H	7.07948	-4.79111	1.29015
H	3.95267	-0.10335	2.68090
H	3.46354	-1.78040	3.03957
H	2.34919	-0.69218	2.17720
H	8.54909	0.40051	-0.08528
H	10.79998	-0.51424	-0.42248
H	11.26636	-2.92452	0.00978
H	9.43411	-4.42423	0.73246
H	-1.69295	-5.81243	0.08112
H	-2.94120	-5.32016	-1.09046
H	-2.98676	-4.70547	0.57056
H	-7.23017	-0.97773	0.54991
H	-1.33851	-4.28220	-2.70898
H	-0.13642	-3.15316	-2.07873
H	-3.63754	0.83710	4.38868
H	-1.99029	-0.65602	3.35175
H	-0.93207	-3.83212	1.82085
H	-2.05302	-3.42882	3.13917
H	-0.72097	-2.31411	2.70733
H	-4.45857	-3.26717	-2.88930
H	-6.40871	-4.71983	-2.55460
H	-3.99712	-0.59070	-2.66933
H	-2.84029	-1.85539	-3.15868
H	-2.26143	-0.38751	-2.35793
H	-6.40143	-2.99681	2.73453
H	-8.22758	-4.59315	3.07746
H	-9.10224	-5.95077	1.17826
H	-8.08024	-5.72587	-1.06745
H	3.08828	-4.14404	-3.53855
H	1.67027	-3.14019	-3.29573
H	2.07552	-6.10302	-2.57061
H	0.96252	-5.44488	-3.75386
H	0.77201	-5.17178	-0.69492
H	-0.21528	-6.19761	-1.72043
H	-6.64231	2.63536	-0.50910
H	-4.61775	1.95104	0.72910
H	-6.49406	3.20267	-2.93077
H	-4.30691	3.05314	-4.10236
H	-2.27259	2.33813	-2.85437
H	-2.28468	1.21331	0.74484
C	-1.40939	3.35968	0.77911
C	-1.66805	4.47429	-0.01094
O	-0.86144	4.70117	-1.02290
C	-2.89117	5.34500	0.13128
C	-3.53073	5.46985	1.52957
C	-2.59348	6.17225	2.52296
C	-4.87026	6.21285	1.41612
Si	-0.54346	5.91876	-2.21478
C	0.69124	5.06614	-3.32995
C	0.20101	7.38487	-1.30533
C	-2.11549	6.37702	-3.14242
H	-5.35016	6.30039	2.39684
H	-5.56281	5.69041	0.74611
H	-4.72670	7.22887	1.02694
H	-1.63823	5.64675	2.62936
H	-2.37741	7.19713	2.19447
H	-3.05389	6.23519	3.51496
H	-2.64695	6.34899	-0.23730
H	-3.63285	4.93909	-0.57554
H	-1.96797	3.26452	1.70241

H	1.53824	4.68531	-2.75019
H	0.23957	4.21225	-3.84647
H	1.07526	5.75679	-4.09040
H	-2.67267	5.48569	-3.45148
H	-2.79110	7.01285	-2.56091
H	-1.84802	6.92947	-4.05211
H	0.51838	8.15092	-2.02375
H	-0.50636	7.85850	-0.61521
H	1.08356	7.08419	-0.72985
H	-3.74615	4.45980	1.90344
H	-0.39280	2.98452	0.78534

(ii) Direct aldol reaction between cyclohexanone and benzaldehyde

Species-(iii)

78 atoms, 390 electrons, +1 charge, singlet. Calculated ad B3LYP-D3 / 6-31G(d,p) level.

C	-1.99154	-1.06042	2.21522
C	-1.46476	-0.87762	0.94190
C	-0.41680	-1.84919	0.61474
C	-0.25423	-2.79132	1.60064
S	-1.27527	-2.44880	2.96611
C	0.25434	-2.79116	-1.60083
C	0.41685	-1.84911	-0.61485
C	1.46478	-0.87747	-0.94191
C	1.99165	-1.06018	-2.21520
S	1.27548	-2.44855	-2.96621
P	2.17587	0.24646	0.26841
C	0.61909	-4.00865	1.59712
C	-3.01164	-0.29171	3.00589
C	-0.61900	-4.00848	-1.59747
C	3.01179	-0.29141	-3.00575
O	-1.29874	1.52045	-0.58994
O	1.29867	1.52057	0.58997
C	2.71617	-1.80963	4.33884
C	2.00826	-0.61054	4.24861
C	1.81828	0.00544	3.01126
C	2.32802	-0.60284	1.85514
C	3.02454	-1.81811	1.94202
C	3.22584	-2.41206	3.18515
C	6.32435	1.82254	-0.92672
C	5.23841	2.69419	-0.84726
C	3.97734	2.21648	-0.49078
C	3.80590	0.85232	-0.21635
C	4.90304	-0.02249	-0.28245
C	6.15646	0.46431	-0.64122
C	-6.32437	1.82243	0.92682
C	-6.15650	0.46420	0.64135
C	-4.90309	-0.02262	0.28256
C	-3.80594	0.85217	0.21644
C	-3.97736	2.21634	0.49085
C	-5.23841	2.69407	0.84734
C	-2.71603	-1.80960	-4.33891
C	-2.00825	-0.61043	-4.24861
C	-1.81833	0.00549	-3.01122
C	-2.32801	-0.60291	-1.85513
C	-3.02438	-1.81826	-1.94208
C	-3.22563	-2.41215	-3.18525
Cl	0.83756	2.40770	-2.06168
Cl	-0.83779	2.40762	2.06171
Si	-0.00009	2.45994	0.00003
P	-2.17591	0.24633	-0.26836
H	0.02552	-4.90704	1.39308
H	1.37691	-3.92305	0.81649
H	1.12602	-4.14852	2.55404
H	-4.03113	-0.59237	2.74731
H	-2.87163	-0.46990	4.07488
H	-2.91562	0.77878	2.82695
H	-1.12591	-4.14823	-2.55441
H	-0.02545	-4.90691	-1.39351
H	-1.37685	-3.92294	-0.81685
H	2.91576	0.77907	-2.82674
H	4.03127	-0.59208	-2.74713
H	2.87185	-0.46952	-4.07477
H	2.87099	-2.27723	5.30612
H	1.60629	-0.14500	5.14255
H	1.27057	0.93774	2.94208
H	3.38535	-2.31620	1.04787
H	3.77036	-3.34852	3.25261
H	7.30326	2.19939	-1.20550
H	5.36685	3.74981	-1.06219
H	4.78912	-1.07781	-0.06324
H	7.00204	-0.21369	-0.69409
H	-7.30326	2.19930	1.20561
H	-7.00208	-0.21379	0.69423
H	-4.78918	-1.07795	0.06340
H	-3.13837	2.89761	0.44160
H	-5.36684	3.74969	1.06227
H	-2.87081	-2.27715	-5.30621
H	-1.60633	-0.14480	-5.14252
H	-1.27072	0.93784	-2.94198
H	-3.38509	-2.31647	-1.04796
H	-3.77003	-3.34868	-3.25276
H	3.13836	2.89777	-0.44154
Cl	-0.00020	4.54349	0.00003

TS-(iii)-pre-(iv)

95 atoms, 444 electrons, +1 charge, singlet. Calculated ad B3LYP-D3 / 6-31G(d,p) level.

C	3.45227	-0.37481	2.06266
C	2.70331	-0.14826	0.92131
C	2.58496	1.26486	0.57767
C	3.24339	2.07442	1.46794
S	3.99684	1.13473	2.72555
C	2.75725	2.07637	-1.75269
C	1.96362	1.80257	-0.66420
C	0.55697	2.10996	-0.91038
C	0.32242	2.56135	-2.20126
S	1.80791	2.64657	-3.09323
P	-0.78764	1.89185	0.27079
C	3.37728	3.56601	1.44457
C	3.83109	-1.63616	2.79025
C	4.24593	1.96467	-1.88465
C	-0.93672	2.96902	-2.91456
O	0.41866	-0.89809	-0.20992
O	-1.54133	0.53143	0.14838
C	0.79538	2.15109	4.58866
C	0.51658	0.91144	4.01018
C	0.03203	0.83922	2.70631
C	-0.16562	2.01521	1.96883
C	0.09513	3.26089	2.55775
C	0.57595	3.32466	3.86461
C	-4.01590	5.09188	-0.34764
C	-4.36134	3.74324	-0.25062
C	-3.37660	2.77118	-0.06909
C	-2.03321	3.16783	0.00985
C	-1.68067	4.52198	-0.10650
C	-2.67494	5.48162	-0.27907
C	2.02771	-5.52371	1.88148
C	2.85121	-5.26341	0.78481
C	2.81349	-4.01642	0.16204
C	1.95257	-3.02438	0.65345
C	1.11910	-3.28870	1.75195
C	1.15816	-4.53939	2.35992
C	3.93418	-1.60102	-4.19334
C	2.54085	-1.64571	-4.11110
C	1.90522	-1.57311	-2.87214
C	2.68063	-1.43240	-1.71252
C	4.08189	-1.38114	-1.79211
C	4.70555	-1.47504	-3.03445
Cl	-1.57983	-0.38743	-2.48279
Cl	-2.10808	-1.82991	1.34822
Si	-1.27917	-1.11653	-0.49903
P	1.89964	-1.39173	-0.09355
Cl	-1.09226	-3.16351	-1.24001
O	-4.00129	-0.56104	-0.65226
C	-5.51526	-3.51092	0.43040
C	-4.92448	-2.78332	-0.80043
C	-4.98728	-1.28705	-0.59976
C	-6.35520	-0.73682	-0.25415
C	-6.92389	-1.47850	0.97941
C	-6.92281	-2.99860	0.76536
H	4.42702	3.87488	1.40845
H	2.87451	3.96680	0.56187
H	2.92301	4.01553	2.33243
H	2.98502	-2.03411	3.35804
H	4.15570	-2.41908	2.10296
H	4.64582	-1.44417	3.49225
H	4.52559	1.38850	-2.77054
H	4.70857	2.95450	-1.96523
H	4.66452	1.46660	-1.00879
H	-0.83755	2.79043	-3.98814
H	-1.79760	2.40163	-2.56562
H	-1.14393	4.03337	-2.76578
H	1.16958	2.20396	5.60616
H	0.66650	-0.00155	4.57779
H	-0.20875	-0.11873	2.26708
H	-0.08656	4.18094	2.01439
H	0.76899	4.29093	4.31987
H	-4.78865	5.84124	-0.48806
H	-5.40175	3.44209	-0.32181
H	-0.63730	4.82425	-0.10003
H	-2.40513	6.52875	-0.37164
H	2.05471	-6.49867	2.35784
H	3.51376	-6.03407	0.40473
H	3.44091	-3.82436	-0.70125
H	0.42703	-2.53684	2.11227
H	0.50309	-4.74936	3.19896
H	4.42149	-1.66509	-5.16123
H	1.94330	-1.74321	-5.01142

H	0.82516	-1.62197	-2.81405
H	4.67926	-1.25434	-0.89368
H	5.78831	-1.43890	-3.09910
H	-3.63858	1.71801	-0.02559
H	-5.52745	-4.58843	0.23813
H	-4.84785	-3.34768	1.28547
H	-5.53355	-3.02459	-1.68296
H	-3.89725	-3.09129	-0.99912
H	-6.27754	0.34060	-0.08611
H	-7.02085	-0.90659	-1.11150
H	-6.30861	-1.23232	1.85449
H	-7.93448	-1.11269	1.18805
H	-7.60947	-3.25161	-0.05423
H	-7.30317	-3.50203	1.66076

TSpre(iv)-(iv) Ha

123 atoms, 518 electrons, +1 charge, singlet. Calculated ad B3LYP-D3 / 6-31G(d,p) level.

C	-2.75071	0.70183	2.65516
C	-2.76184	0.38528	1.30473
C	-3.22917	-0.97400	1.04742
C	-3.66331	-1.60990	2.18446
S	-3.42014	-0.60541	3.58447
C	-4.25017	-2.02870	-0.98935
C	-3.14605	-1.65247	-0.26608
C	-1.89216	-1.95415	-0.95397
C	-2.08743	-2.47535	-2.22452
S	-3.78407	-2.66721	-2.53926
P	-0.29025	-1.83208	-0.13355
C	-4.24195	-2.98461	2.32313
C	-2.25001	1.90589	3.40128
C	-5.69453	-1.93468	-0.60366
C	-1.12546	-2.86675	-3.30959
O	-1.11848	1.56059	-0.72159
O	0.32254	-0.41802	-0.01587
C	-0.55439	-3.25319	4.23975
C	-0.07347	-1.98034	3.93310
C	-0.02797	-1.54208	2.60884
C	-0.47357	-2.38879	1.58472
C	-0.98205	-3.65832	1.89526
C	-1.01433	-4.08997	3.21911
C	2.81686	-4.59516	-2.13085
C	3.02299	-3.21700	-2.07334
C	2.08012	-2.38441	-1.46859
C	0.91174	-2.93766	-0.92814
C	0.70498	-4.32504	-0.98633
C	1.65630	-5.14880	-1.58323
C	-3.30456	5.86067	1.48439
C	-4.24703	4.85632	1.72749
C	-4.00169	3.55496	1.30058
C	-2.80754	3.25306	0.62459
C	-1.86544	4.25908	0.37714
C	-2.11957	5.56032	0.81395
C	-5.51552	0.95125	-3.42910
C	-4.14413	0.90235	-3.67897
C	-3.22998	1.07548	-2.63894
C	-3.70027	1.28305	-1.33516
C	-5.07913	1.32728	-1.08169
C	-5.98228	1.16677	-2.12926
Cl	0.38282	0.36540	-2.79336
Cl	0.81541	1.94023	1.39918
Si	0.63209	1.21067	-0.72668
P	-2.49465	1.59174	-0.01515
Cl	1.06845	3.22243	-1.52536
O	2.37192	0.73440	-0.72134
C	4.56574	2.84777	-2.80896
C	3.80106	1.55809	-2.47338
C	3.41022	1.47734	-1.02366
C	4.17880	2.05142	0.00261
C	5.05896	3.25082	-0.36642
C	5.65750	3.14763	-1.77459
H	-5.32742	-2.94382	2.46791
H	-4.04651	-3.56079	1.41621
H	-3.80750	-3.52092	3.17029
H	-3.05522	2.61248	3.62253
H	-1.80631	1.59404	4.35121
H	-1.48241	2.42645	2.83054
H	-6.30578	-1.55040	-1.42325
H	-6.08971	-2.91497	-0.31396
H	-5.80527	-1.26086	0.24832
H	-1.60549	-2.78139	-4.28785
H	-0.25334	-2.21369	-3.30620
H	-0.78483	-3.89995	-3.19243

H	-0.58192	-3.59139	5.27093
H	0.26462	-1.31943	4.72532
H	0.33673	-0.55007	2.36830
H	-1.37991	-4.30171	1.11793
H	-1.40418	-5.07530	3.45476
H	3.55227	-5.23797	-2.60471
H	3.91575	-2.78082	-2.51070
H	-0.19976	-4.76979	-0.58798
H	1.48927	-6.22027	-1.62692
H	-3.49713	6.87481	1.82059
H	-5.16820	5.08695	2.25321
H	-4.72374	2.77626	1.52364
H	-0.94391	4.03000	-0.14301
H	-1.38506	6.33670	0.62607
H	-6.22192	0.82610	-4.24397
H	-3.77819	0.73690	-4.68725
H	-2.16459	1.04568	-2.83426
H	-5.45502	1.47598	-0.07534
H	-7.04892	1.20765	-1.93155
H	2.23740	-1.31500	-1.43365
H	4.98859	2.77191	-3.81559
H	3.84596	3.67382	-2.82344
H	4.41585	0.67364	-2.69277
H	2.89596	1.45039	-3.07389
H	3.58329	2.18402	0.90756
H	4.92596	0.98066	0.47797
H	4.42352	4.14455	-0.31869
H	5.84417	3.39838	0.37805
H	6.42445	2.36177	-1.80599
H	6.16877	4.08283	-2.02626
C	6.97266	0.03513	1.49985
N	5.53953	-0.16552	1.08423
C	4.68909	-0.49695	2.29599
C	5.41254	-1.17642	-0.02922
C	5.72251	-2.61875	0.39214
C	6.27256	-0.77595	-1.23471
C	3.26229	-0.92245	1.94667
C	4.64998	0.69004	3.26880
C	7.49311	1.45162	1.29179
H	7.60114	-0.66330	0.94642
H	7.07223	-0.24676	2.55083
H	5.18800	-1.33576	2.80069
H	4.36573	-1.11901	-0.33542
H	5.56524	-3.28008	-0.46420
H	6.76340	-2.73040	0.71040
H	5.07801	-2.97215	1.19857
H	5.93609	-1.32927	-2.11625
H	6.19527	0.28856	-1.45507
H	7.32939	-1.01650	-1.09134
H	2.72735	-1.10282	2.88190
H	2.72485	-0.14968	1.39843
H	3.21115	-1.84822	1.37054
H	4.14914	0.37473	4.18817
H	5.64238	1.05015	3.54794
H	4.08092	1.52504	2.85546
H	8.53369	1.51045	1.62475
H	7.45992	1.73684	0.23802
H	6.91332	2.17903	1.86449

TSpre(iv)-(iv) Hb

123 atoms, 518 electrons, +1 charge, singlet. Calculated ad B3LYP-D3 / 6-31G(d,p) level.

C	-3.01715	1.25963	2.36019
C	-2.88705	0.87000	1.03510
C	-3.62316	-0.35504	0.73308
C	-4.36936	-0.80244	1.79495
S	-4.11424	0.19996	3.19371
C	-4.54004	-1.23916	-1.43148
C	-3.50727	-1.10372	-0.53791
C	-2.27075	-1.72241	-1.00604
C	-2.37534	-2.22655	-2.29389
S	-3.99832	-2.03288	-2.88242
P	-0.84796	-1.96275	0.07739
C	-5.27890	-1.99085	1.86124
C	-2.38420	2.36776	3.15316
C	-5.96051	-0.78610	-1.28907
C	-1.36647	-2.85370	-3.21337
O	-0.67039	1.49638	-0.67153
O	0.05804	-0.73274	0.30888
C	-2.14092	-3.13326	4.34174
C	-1.30533	-2.03704	4.12761
C	-0.94580	-1.66617	2.83122

C	-1.43509	-2.39877	1.74032
C	-2.28773	-3.49112	1.95509
C	-2.63490	-3.85757	3.25322
C	1.71565	-5.53322	-1.30033
C	2.28787	-4.27078	-1.14531
C	1.50650	-3.18498	-0.74776
C	0.13846	-3.36730	-0.50693
C	-0.43697	-4.63823	-0.66484
C	0.35075	-5.71584	-1.06046
C	-2.12865	6.31378	0.99157
C	-3.31261	5.57342	1.06764
C	-3.31420	4.22634	0.71884
C	-2.12560	3.61310	0.28821
C	-0.94097	4.35531	0.20694
C	-0.94946	5.70452	0.56476
C	-4.50370	1.74383	-4.17068
C	-3.16465	1.35477	-4.14373
C	-2.44699	1.37414	-2.94709
C	-3.08573	1.77627	-1.76614
C	-4.43333	2.16441	-1.79155
C	-5.13714	2.15038	-2.99285
Cl	0.91295	-0.14417	-2.36475
Cl	0.84172	1.49171	1.79695
Si	0.91167	0.73871	-0.33471
P	-2.10673	1.88539	-0.24254
Cl	1.95598	2.55536	-1.02077
O	2.46419	-0.14508	-0.00705
C	4.10528	-1.13785	3.18036
C	3.18232	-1.25134	1.96040
C	3.27308	-0.09035	1.01394
C	4.23480	0.92480	1.14451
C	4.80066	1.20462	2.54960
C	4.16978	0.32323	3.63841
H	-6.33071	-1.68640	1.81679
H	-5.08452	-2.65143	1.01362
H	-5.12958	-2.56112	2.78112
H	-1.43726	2.67401	2.71222
H	-3.03623	3.24412	3.21558
H	-2.18238	2.02546	4.17218
H	-6.31940	-0.29321	-2.19554
H	-6.62467	-1.63112	-1.07497
H	-6.03882	-0.07826	-0.46121
H	-1.61106	-2.61900	-4.25281
H	-0.36688	-2.47141	-3.01038
H	-1.34715	-3.94297	-3.11132
H	-2.41305	-3.42143	5.35235
H	-0.93126	-1.46337	4.96981
H	-0.31107	-0.80385	2.66121
H	-2.70225	-4.04432	1.11919
H	-3.29315	-4.70544	3.41527
H	2.32753	-6.37452	-1.61074
H	3.34575	-4.12354	-1.33822
H	-1.49875	-4.78979	-0.50494
H	-0.09941	-6.69555	-1.18486
H	-2.12959	7.36377	1.26747
H	-4.23086	6.04445	1.40391
H	-4.23079	3.65344	0.81502
H	-0.02310	3.88596	-0.12450
H	-0.02836	6.27538	0.50700
H	-5.05437	1.73484	-5.10624
H	-2.66918	1.03943	-5.05647
H	-1.40482	1.07799	-2.92761
H	-4.94153	2.46763	-0.88283
H	-6.17851	2.45651	-3.01010
H	1.94503	-2.20196	-0.64292
H	3.73520	-1.78840	3.97889
H	5.11166	-1.49068	2.92978
H	2.12746	-1.28381	2.26162
H	3.34661	-2.17589	1.39115
H	5.19345	0.50909	0.30283
H	3.96350	1.81009	0.56682
H	5.88812	1.07627	2.56766
H	4.61601	2.25878	2.78107
H	3.15192	0.67784	3.84200
H	4.73998	0.41451	4.56831
C	7.48954	-0.28446	-0.22332
N	6.25480	0.40152	-0.73225
C	5.66655	-0.38123	-1.89250
C	6.50550	1.85099	-1.09202
C	7.45621	2.02870	-2.28405
C	6.99498	2.66958	0.10806
C	4.50540	0.33962	-2.57750
C	5.22118	-1.78228	-1.45079
C	7.29956	-1.04277	1.08801
H	8.27500	0.45814	-0.08258
H	7.85641	-0.96432	-0.99945

H	6.47890	-0.51052	-2.62140
H	5.52170	2.24253	-1.36124
H	7.56519	3.09488	-2.50118
H	8.45347	1.63538	-2.06314
H	7.09124	1.54503	-3.19224
H	6.99103	3.72695	-0.17049
H	6.35205	2.55655	0.97973
H	8.01898	2.42075	0.40131
H	4.06688	-0.32753	-3.32328
H	3.71459	0.58923	-1.87357
H	4.81058	1.24833	-3.09844
H	4.85339	-2.31941	-2.32930
H	6.03010	-2.37631	-1.02145
H	4.39915	-1.72867	-0.73492
H	8.21424	-1.59448	1.32540
H	7.09960	-0.35947	1.91499
H	6.47799	-1.76011	1.03443

TS-(iv)-(v) (TS from species (iv) to species (v) – expulsion Cl anion)

94 atoms, 444 electrons, neutral, singlet. Calculated ad B3LYP-D3 / 6-31G(d,p) level.

C	0.34198	1.98817	2.49999
C	-0.14509	1.81394	1.21184
C	-1.60360	1.68377	1.17136
C	-2.18230	1.87813	2.39995
S	-0.97273	2.09021	3.63175
C	-3.22414	2.21898	-0.65720
C	-2.40234	1.31931	-0.02427
C	-2.38563	0.00933	-0.67426
C	-3.11522	-0.00832	-1.85128
S	-3.90636	1.52325	-2.09695
P	-1.59524	-1.44776	0.07391
C	-3.63634	1.93487	2.75428
C	1.72995	2.07458	3.06762
C	-3.55230	3.62438	-0.25454
C	-3.28626	-1.05424	-2.91682
O	1.36341	0.71720	-1.01123
O	-0.05078	-1.27966	0.06305
C	-2.65810	-1.84131	4.51596
C	-1.36244	-2.10142	4.06865
C	-1.03119	-1.95381	2.72024
C	-2.02135	-1.51688	1.82693
C	-3.32516	-1.25718	2.26998
C	-3.64356	-1.42536	3.61555
C	-3.29060	-5.26060	-1.83464
C	-1.92832	-4.99219	-1.94752
C	-1.37835	-3.84300	-1.37597
C	-2.22002	-2.95129	-0.70136
C	-3.58933	-3.23481	-0.55929
C	-4.12425	-4.38433	-1.13209
C	4.64466	4.50794	0.50669
C	3.41657	4.95904	0.99901
C	2.26522	4.20249	0.79849
C	2.33941	2.98913	0.09758
C	3.56915	2.54153	-0.40196
C	4.71950	3.30125	-0.18924
C	-1.36884	4.31814	-3.55964
C	-1.00573	2.98603	-3.75707
C	-0.34735	2.27557	-2.75280
C	-0.06658	2.90909	-1.53441
C	-0.43104	4.24838	-1.33363
C	-1.07809	4.95014	-2.34743
Cl	0.40320	-1.28723	-2.71920
Cl	2.36352	-0.70370	1.24751
Si	1.43571	-1.01602	-0.72893
P	0.86882	2.00178	-0.27167
Cl	0.82923	-4.16159	0.87451
O	2.73688	-1.76117	-1.40735
C	6.27110	-1.67181	-0.12329
C	5.06421	-1.22690	-0.96337
C	3.93733	-2.21691	-0.85921
C	4.03342	-3.44834	-0.36172
C	5.34003	-4.00150	0.14357
C	6.54684	-3.16856	-0.31434
H	-4.23597	1.56645	1.92023
H	-3.86092	1.32690	3.63339
H	-3.94429	2.96639	2.96165
H	2.47404	1.71342	2.36384
H	1.98055	3.10047	3.35671
H	1.79704	1.44423	3.95903
H	-3.52742	4.30513	-1.10855
H	-4.54842	3.68254	0.19964

H	-2.82695	3.97602	0.48223
H	-3.54701	-0.58129	-3.86759
H	-2.35753	-1.60884	-3.05503
H	-4.07353	-1.76992	-2.66494
H	-2.90671	-1.97058	5.56549
H	-0.60165	-2.44239	4.76345
H	-0.04285	-2.22161	2.35375
H	-4.08275	-0.90389	1.57668
H	-4.65435	-1.22870	3.96085
H	-3.70573	-6.16025	-2.27985
H	-1.27337	-5.68560	-2.46434
H	-4.24240	-2.56304	-0.01162
H	-5.18262	-4.60011	-1.02293
H	5.54209	5.09645	0.67105
H	3.35852	5.89386	1.54777
H	1.32318	4.53803	1.22065
H	3.62317	1.60396	-0.94168
H	5.67227	2.94392	-0.56641
H	-1.87409	4.86709	-4.34862
H	-1.23017	2.49144	-4.69667
H	-0.06047	1.24133	-2.90985
H	-0.21263	4.74870	-0.39663
H	-1.35487	5.98839	-2.19170
H	-0.31435	-3.66850	-1.42267
H	7.15311	-1.07297	-0.38097
H	6.05009	-1.48308	0.93522
H	5.34473	-1.09318	-2.01881
H	4.70452	-0.25311	-0.60905
H	3.12933	-4.04285	-0.25740
H	5.30686	-4.04341	1.24288
H	5.45203	-5.04250	-0.18653
H	6.74079	-3.36348	-1.37792
H	7.44818	-3.46745	0.23397

TS(8)-(vi)-a(2S1'R)

107 atoms, 482 electrons, +1 charge, singlet. Calculated ad B3LYP-D3/6-311+G(2df,2pd) // B3LYP-D3/6-31G(d,p) level of theory

C	5.16440	3.94380	0.42498
C	3.66851	3.74299	0.15223
C	3.36968	2.46230	-0.57941
C	4.37493	1.64034	-1.08596
C	5.80590	2.12545	-1.20429
C	5.97858	3.60643	-0.82852
O	2.10499	2.13836	-0.61869
C	-1.81909	-2.22799	-2.30469
C	-1.78643	-1.76354	-0.99828
C	-3.04541	-1.14831	-0.58387
C	-4.02573	-1.25357	-1.53834
S	-3.40633	-2.00928	-2.97846
C	-4.03820	-0.87230	1.70261
C	-3.23111	-0.41708	0.69012
C	-2.51425	0.80520	1.04684
C	-2.72121	1.18411	2.36533
S	-3.86644	0.11949	3.12216
P	-1.65696	1.81570	-0.17826
C	-5.44997	-0.79571	-1.46574
C	-0.76243	-2.82508	-3.18996
C	-4.94642	-2.06338	1.70589
C	-2.12512	2.28051	3.20194
O	0.48488	-0.84548	0.45531
O	-0.22757	1.36507	-0.56904
C	-3.92196	1.84300	-4.18186
C	-2.59119	1.42839	-4.12561
C	-1.91294	1.39408	-2.90651
C	-2.58456	1.76884	-1.73457
C	-3.92439	2.17996	-1.78850
C	-4.58805	2.21968	-3.01198
C	-1.45481	6.23736	1.06147
C	-0.29997	5.55255	0.68385
C	-0.36282	4.20502	0.32709
C	-1.59594	3.54039	0.36061
C	-2.75968	4.23015	0.73629
C	-2.68615	5.57546	1.08569
C	2.20088	-5.65185	-0.93514
C	0.81064	-5.77593	-1.01884
C	-0.00511	-4.68619	-0.72662
C	0.57240	-3.46214	-0.35450
C	1.96516	-3.33989	-0.26121
C	2.77386	-4.43760	-0.55658
C	-2.00461	-3.24264	4.32142

C	-1.17664	-2.13001	4.17115
C	-0.72740	-1.74934	2.90592
C	-1.12357	-2.49069	1.78438
C	-1.95564	-3.60966	1.93306
C	-2.39354	-3.98300	3.20107
H	5.47649	3.29110	1.25133
H	5.34715	4.97164	0.75234
H	3.27537	4.56076	-0.46887
H	3.06876	3.73855	1.07019
H	4.05376	0.85049	-1.75680
H	6.45796	1.50563	-0.57553
H	6.14304	1.95307	-2.23227
H	5.63764	4.24114	-1.65653
H	7.03899	3.82887	-0.67544
H	-5.57024	-0.09748	-0.63476
H	-5.75826	-0.29059	-2.38389
H	-6.12716	-1.64079	-1.29781
H	-0.87780	-2.44705	-4.20976
H	0.23474	-2.55417	-2.84900
H	-0.83473	-3.91631	-3.22825
H	-4.84649	-2.64276	2.62664
H	-5.99495	-1.76116	1.60534
H	-4.70146	-2.71497	0.86443
H	-1.13656	2.55510	2.83650
H	-2.75403	3.17569	3.20768
H	-2.01633	1.94128	4.23581
H	-4.44163	1.87529	-5.13443
H	-2.07291	1.13330	-5.03239
H	-0.87779	1.07468	-2.86111
H	-4.45761	2.45573	-0.88487
H	-5.62378	2.54210	-3.05284
H	-1.39968	7.28578	1.33754
H	0.65633	6.06595	0.66616
H	0.53223	3.67034	0.03434
H	-3.71554	3.71882	0.78505
H	-3.58570	6.10631	1.38045
H	2.83332	-6.50415	-1.16345
H	0.36393	-6.72012	-1.31366
H	-1.08255	-4.78533	-0.81420
H	2.40747	-2.39703	0.03449
H	3.85220	-4.33655	-0.48311
H	-2.34520	-3.53732	5.30919
H	-0.87369	-1.55445	5.04005
H	-0.08095	-0.88691	2.78603
H	-2.26923	-4.18617	1.06888
H	-3.03524	-4.85099	3.31588
C	4.00120	0.33546	0.56953
O	2.85371	-0.19709	0.23194
C	7.43179	-2.18117	0.26823
C	7.40792	-1.14335	1.20055
C	6.28767	-0.31647	1.29343
C	5.18328	-0.53294	0.45784
C	5.21467	-1.57422	-0.48599
C	6.33453	-2.39284	-0.57630
H	3.99771	1.05099	1.39674
H	8.30423	-2.82282	0.19420
H	8.25748	-0.97855	1.85540
H	6.26194	0.48846	2.02301
H	4.36227	-1.71785	-1.14190
H	6.36175	-3.19268	-1.31020
Cl	1.20695	1.41348	1.97527
Cl	1.45112	-0.19883	-2.20950
Si	1.31081	0.61047	-0.13327
P	-0.43754	-2.05559	0.16398

TS(8)-(vi)-b(2R1'S)

107 atoms, 482 electrons, +1 charge, singlet. Calculated ad B3LYP-D3/6-311+G(2df,2pd) // B3LYP-D3/6-31G(d,p) level of theory

C	5.37445	3.12888	-1.99474
C	3.85043	3.09312	-1.82795
C	3.41143	2.41177	-0.56056
C	4.31813	2.01577	0.42413
C	5.74975	2.51166	0.42387
C	6.03973	3.54362	-0.67846
O	2.13444	2.13798	-0.50997
C	-1.90489	-1.97592	-2.47061
C	-1.83694	-1.63583	-1.12769
C	-3.07730	-1.04593	-0.62928
C	-4.07949	-1.04875	-1.56678
S	-3.50258	-1.67466	-3.08466

C	-4.01858	-0.96820	1.69403
C	-3.22503	-0.43303	0.71036
C	-2.48509	0.74377	1.16062
C	-2.66216	1.00535	2.51161
S	-3.80524	-0.11124	3.19339
P	-1.63222	1.84719	0.01463
C	-5.49439	-0.57988	-1.41973
C	-0.87667	-2.50280	-3.43078
C	-4.94683	-2.14059	1.60731
C	-2.04116	2.01863	3.43080
O	0.47268	-0.89306	0.36446
O	-0.21484	1.41600	-0.43779
C	-3.94967	2.25846	-3.93791
C	-2.62458	1.82248	-3.93709
C	-1.93139	1.67119	-2.73544
C	-2.58224	1.95007	-1.52565
C	-3.91648	2.38226	-1.52434
C	-4.59514	2.53891	-2.73009
C	-1.36233	6.13860	1.63874
C	-0.21959	5.47924	1.18646
C	-0.30149	4.16940	0.71204
C	-1.54117	3.51634	0.70268
C	-2.69242	4.18113	1.15458
C	-2.60032	5.48914	1.62102
C	2.09379	-5.53495	-1.59580
C	0.70067	-5.65432	-1.60491
C	-0.09142	-4.59790	-1.16435
C	0.51164	-3.41235	-0.71512
C	1.90789	-3.29608	-0.69630
C	2.69285	-4.35979	-1.14225
C	-1.98737	-3.62998	4.01796
C	-1.13647	-2.52582	3.96367
C	-0.70042	-2.02980	2.73431
C	-1.13362	-2.64515	1.55175
C	-1.99085	-3.75371	1.60420
C	-2.41393	-4.24428	2.83684
H	5.64223	3.81085	-2.80721
H	5.73411	2.13362	-2.28905
H	3.34455	2.58812	-2.65896
H	3.43943	4.11225	-1.80013
H	3.89768	1.70977	1.37603
H	5.96411	2.93894	1.40976
H	6.43248	1.65819	0.32192
H	7.12066	3.65623	-0.80624
H	5.65239	4.52583	-0.37821
H	-6.18152	-1.42733	-1.31670
H	-5.58601	0.03853	-0.52435
H	-5.81380	0.01374	-2.27930
H	-1.02581	-2.05335	-4.41660
H	0.13038	-2.25280	-3.10220
H	-0.94693	-3.58881	-3.54463
H	-4.84369	-2.80044	2.47177
H	-5.99127	-1.81371	1.55069
H	-4.72581	-2.71931	0.70796
H	-1.91799	1.58888	4.42875
H	-1.05673	2.31737	3.07358
H	-2.66196	2.91443	3.52627
H	-4.48104	2.38174	-4.87650
H	-2.12255	1.60126	-4.87360
H	-0.90069	1.33474	-2.73219
H	-4.43409	2.58381	-0.59250
H	-5.62649	2.87755	-2.72772
H	-1.29204	7.15753	2.00652
H	0.74182	5.98257	1.20277
H	0.58511	3.65554	0.36177
H	-3.65273	3.67617	1.17149
H	-3.49026	5.99996	1.97453
H	2.70858	-6.35996	-1.94197
H	0.23343	-6.56799	-1.95823
H	-1.17235	-4.69049	-1.19765
H	2.37024	-2.38456	-0.33994
H	3.77408	-4.26512	-1.13208
H	-2.31757	-4.01524	4.97768
H	-0.80576	-2.04672	4.87972
H	-0.03740	-1.17283	2.68867
H	-2.33799	-4.23010	0.69325
H	-3.07503	-5.10436	2.87648
C	4.02135	0.02630	-0.29288
O	2.85011	-0.24519	0.23519
C	7.40762	-1.95617	1.36842
C	7.46599	-1.44293	0.07117
C	6.35715	-0.79243	-0.46823
C	5.18395	-0.65533	0.28984
C	5.12992	-1.17243	1.59497
C	6.23889	-1.82104	2.12714
H	4.05529	0.18898	-1.37352

H	8.27071	-2.46264	1.78924
H	8.37040	-1.55158	-0.51882
H	6.39384	-0.39667	-1.47982
H	4.21472	-1.06023	2.16658
H	6.19750	-2.22359	3.13439
Cl	1.23259	1.19754	2.07386
Cl	1.41933	-0.00770	-2.24742
Si	1.31595	0.60531	-0.07694
P	-0.46868	-2.05760	-0.02919

TS(8)-(vi)-c(2S1'S)

107 atoms, 482 electrons, +1 charge, singlet. Calculated ad B3LYP-D3/6-311+G(2df,2pd) // B3LYP-D3/6-31G(d,p) level of theory

C	5.74880	3.17763	-0.48276
C	4.37532	2.75741	0.05745
C	3.64408	1.82371	-0.86156
C	4.30878	1.00658	-1.76944
C	5.77677	1.20773	-2.06982
C	6.53680	1.95240	-0.96117
O	2.35357	1.73792	-0.67981
C	-2.25784	-1.96795	-2.29537
C	-2.08851	-1.54656	-0.98468
C	-3.22223	-0.76928	-0.48896
C	-4.25730	-0.70975	-1.38816
S	-3.83049	-1.50751	-2.87454
C	-4.05118	-0.40230	1.84897
C	-3.23529	-0.04783	0.80381
C	-2.33911	1.05742	1.13707
C	-2.43522	1.44469	2.46604
S	-3.67992	0.53515	3.26684
P	-1.40037	1.95199	-0.11833
C	-5.59616	-0.05782	-1.22735
C	-1.35021	-2.68891	-3.25086
C	-5.11910	-1.45211	1.88283
C	-1.66749	2.44520	3.28240
O	0.37238	-1.03022	0.36787
O	-0.07620	1.29718	-0.59049
C	-3.82789	2.39107	-4.00218
C	-2.56386	1.80136	-4.02135
C	-1.84034	1.64291	-2.83863
C	-2.39960	2.07036	-1.62641
C	-3.67395	2.65564	-1.60468
C	-4.38237	2.81863	-2.79234
C	-0.49645	6.27381	1.16289
C	0.53273	5.42734	0.75170
C	0.25903	4.10994	0.38151
C	-1.05977	3.63982	0.43381
C	-2.09719	4.49301	0.84320
C	-1.81326	5.80600	1.20697
C	1.26557	-5.97040	-1.26818
C	-0.13007	-5.89134	-1.25470
C	-0.75676	-4.70723	-0.87627
C	0.01550	-3.59315	-0.51283
C	1.41414	-3.67572	-0.51563
C	2.03320	-4.86561	-0.89869
C	-2.29135	-3.13222	4.29696
C	-1.31596	-2.14850	4.13271
C	-0.86659	-1.80491	2.85697
C	-1.41291	-2.45052	1.73934
C	-2.39429	-3.43915	1.90188
C	-2.82960	-3.77853	3.18022
H	6.30136	3.71490	0.29411
H	5.61150	3.87782	-1.31656
H	3.72386	3.61151	0.26788
H	4.47937	2.22036	1.01358
H	3.69253	0.58243	-2.55498
H	6.25343	0.24199	-2.27309
H	5.84436	1.77256	-3.01049
H	7.52186	2.25174	-1.33276
H	6.70859	1.27975	-0.11462
H	-6.37551	-0.80299	-1.03166
H	-5.57083	0.63246	-0.38157
H	-5.88051	0.50467	-2.11951
H	-0.30804	-2.58800	-2.95593
H	-1.59386	-3.75381	-3.31544
H	-1.45408	-2.26146	-4.25228
H	-6.11695	-1.00197	1.83203
H	-5.00636	-2.11944	1.02583
H	-5.06355	-2.05343	2.79311
H	-2.16522	3.41929	3.30233

H	-1.57819	2.09366	4.31395
H	-0.66141	2.57917	2.88775
H	-4.38235	2.51920	-4.92665
H	-2.13297	1.46520	-4.95906
H	-0.85683	1.18708	-2.85140
H	-4.12499	2.96915	-0.66919
H	-5.36680	3.27572	-2.77394
H	-0.27686	7.29755	1.44950
H	1.55510	5.79066	0.71814
H	1.05770	3.45052	0.06568
H	-3.11890	4.13344	0.90556
H	-2.61577	6.46256	1.52757
H	1.75140	-6.89456	-1.56521
H	-0.72806	-6.75024	-1.54208
H	-1.84033	-4.64672	-0.89205
H	2.00298	-2.81686	-0.21933
H	3.11679	-4.92809	-0.90449
H	-2.63137	-3.39979	5.29261
H	-0.89724	-1.64560	4.99859
H	-0.10647	-1.04264	2.72639
H	-2.82587	-3.93976	1.04138
H	-3.58678	-4.54619	3.30568
C	3.94096	-0.76077	-0.53551
O	2.83012	-0.58594	0.13583
C	7.50969	-1.20783	1.74501
C	7.45792	-1.68583	0.43332
C	6.28517	-1.55563	-0.30757
C	5.15983	-0.93704	0.25951
C	5.20728	-0.48123	1.58984
C	6.38127	-0.61524	2.32362
H	3.86740	-1.30528	-1.47920
H	8.42443	-1.30767	2.32103
H	8.32746	-2.16242	-0.00780
H	6.23649	-1.93757	-1.32349
H	4.31622	-0.04074	2.02616
H	6.42018	-0.26248	3.34945
Cl	1.38287	1.06654	1.91338
Cl	1.26813	-0.46397	-2.31999
Si	1.35602	0.33282	-0.20847
P	-0.74340	-2.07055	0.09858

TS(8)-(vi)-d(2R1'R)

107 atoms, 482 electrons, +1 charge, singlet. Calculated ad B3LYP-D3/6-311+G(2df,2pd) // B3LYP-D3/6-31G(d,p) level of theory.

C	-5.82623	2.44791	1.40974
C	-4.30896	2.33027	1.61774
C	-3.53449	2.19566	0.34041
C	-4.13804	2.19957	-0.92161
C	-5.57034	2.67135	-1.09287
C	-6.13610	3.31572	0.18482
O	-2.25878	1.97984	0.47314
C	1.75692	-2.25208	2.30496
C	1.78384	-1.74973	1.01256
C	3.03551	-1.06465	0.69659
C	3.95507	-1.14675	1.71207
S	3.28236	-1.97165	3.08842
C	4.17073	-0.73046	-1.51040
C	3.28041	-0.30973	-0.55414
C	2.55599	0.89634	-0.95096
C	2.84644	1.29512	-2.24793
S	4.06890	0.26735	-2.93198
P	1.59168	1.87414	0.22021
C	5.35757	-0.62165	1.74411
C	0.68122	-2.93818	3.09789
C	5.12349	-1.88488	-1.45400
C	2.29441	2.39002	-3.11608
O	-0.36527	-0.84328	-0.60817
O	0.14220	1.39925	0.50186
C	3.56302	1.89046	4.37610
C	2.26125	1.41588	4.21386
C	1.67184	1.38778	2.94937
C	2.40495	1.82860	1.83897
C	3.71599	2.30053	1.99918
C	4.28973	2.33419	3.26750
C	1.36529	6.30698	-0.97292
C	0.20573	5.59285	-0.67119
C	0.27819	4.24169	-0.33055

C	1.52550	3.60333	-0.30265
C	2.69285	4.32290	-0.60331
C	2.60999	5.67147	-0.93749
C	-2.17943	-5.63185	0.80499
C	-0.79100	-5.79810	0.79820
C	0.03830	-4.71950	0.50425
C	-0.52126	-3.46388	0.21725
C	-1.91302	-3.30097	0.21134
C	-2.73570	-4.38725	0.51112
C	2.43904	-3.22242	-4.25860
C	1.53944	-2.15858	-4.18557
C	0.98123	-1.78863	-2.96135
C	1.34054	-2.48862	-1.80099
C	2.25149	-3.55239	-1.87163
C	2.79474	-3.91931	-3.10030
H	-6.28856	2.86212	2.31064
H	-6.25293	1.44954	1.26423
H	-4.03073	1.47538	2.24739
H	-3.90566	3.21381	2.13174
H	-3.45269	2.37238	-1.74474
H	-5.60736	3.38071	-1.92632
H	-6.21529	1.83205	-1.37905
H	-7.21550	3.46036	0.07766
H	-5.69342	4.31112	0.32143
H	6.08390	-1.43025	1.60404
H	5.49875	0.10156	0.93823
H	5.58056	-0.12501	2.69109
H	0.74200	-4.02666	3.00528
H	0.78052	-2.68680	4.15732
H	-0.30665	-2.61869	2.76939
H	6.14655	-1.54110	-1.26388
H	4.83901	-2.55878	-0.64325
H	5.12409	-2.45316	-2.38687
H	1.28964	2.66912	-2.80459
H	2.92647	3.28286	-3.09241
H	2.23839	2.04761	-4.15320
H	4.01275	1.91776	5.36380
H	1.69601	1.06865	5.07284
H	0.65924	1.02215	2.82190
H	4.29618	2.63133	1.14440
H	5.30274	2.70426	3.39081
H	1.30268	7.35804	-1.23697
H	-0.76065	6.08592	-0.70071
H	-0.62114	3.68462	-0.09754
H	3.66030	3.83139	-0.60733
H	3.51283	6.22512	-1.17465
H	-2.82295	-6.47454	1.03803
H	-0.35587	-6.76624	1.02474
H	1.11445	-4.85638	0.52345
H	-2.34961	-2.33785	-0.01576
H	-3.81263	-4.25032	0.51484
H	2.86433	-3.51016	-5.21506
H	1.26645	-1.61295	-5.08323
H	0.28269	-0.96130	-2.90067
H	2.55498	-4.08323	-0.97529
H	3.49734	-4.74506	-3.15379
C	-3.89878	0.11165	-1.13123
O	-2.77874	-0.25534	-0.54404
C	-7.42202	-1.76865	0.38086
C	-7.40543	-1.27049	-0.92278
C	-6.25440	-0.65827	-1.41927
C	-5.11543	-0.53643	-0.60969
C	-5.13074	-1.05434	0.69807
C	-6.28156	-1.66491	1.18673
H	-3.84682	0.26781	-2.21117
H	-8.31780	-2.24473	0.76748
H	-8.28317	-1.36450	-1.55411
H	-6.23153	-0.29135	-2.44179
H	-4.23699	-0.97376	1.30890
H	-6.29359	-2.06152	2.19733
Cl	-1.02663	1.40813	-2.14749
Cl	-1.52119	-0.31383	1.99758
Si	-1.30049	0.56525	-0.07590
P	0.52342	-2.05936	-0.24061

TS(**7**)-(**vi**)-**a -** (*2S,1'R*)

113 atoms, 498 electrons, +1 charge, singlet.

Calculated ad B3LYP-D3/6-311+G(2df,2pd) // B3LYP-D3/6-31G(d,p) level of theory

C	5.85710	3.39427	0.78036
C	4.34723	3.37723	0.51128
C	3.91579	2.22273	-0.35207
C	4.82952	1.36286	-0.96029

C	6.30177	1.71213	-1.04887
C	6.62638	3.11740	-0.51567
O	2.62497	2.03474	-0.40696
P	-1.13707	2.01117	0.10649
O	0.71573	-0.87324	0.35849
O	0.22758	1.49414	-0.41076
C	-3.39561	3.02205	-3.76073
C	-2.15087	2.39455	-3.81374
C	-1.47415	2.07090	-2.63861
C	-2.05803	2.38291	-1.40195
C	-3.30150	3.02844	-1.34690
C	-3.96888	3.34153	-2.52708
C	-0.48473	6.06740	2.16345
C	-1.73565	5.45192	2.25848
C	-1.94392	4.20425	1.67561
C	-0.89406	3.56786	0.99358
C	0.36069	4.18584	0.89669
C	0.55809	5.43382	1.48659
C	1.88732	-5.45484	-2.03531
C	0.50503	-5.35014	-2.20917
C	-0.18529	-4.26241	-1.67771
C	0.51403	-3.26955	-0.97370
C	1.90059	-3.37871	-0.79338
C	2.58094	-4.47113	-1.32849
C	-1.87366	-3.70894	3.81209
C	-0.98700	-2.63211	3.83052
C	-0.53516	-2.07085	2.63681
C	-0.98052	-2.60229	1.41781
C	-1.85652	-3.69673	1.39674
C	-2.30619	-4.24258	2.59501
C	4.33344	-0.07090	0.54459
O	3.13737	-0.44674	0.16634
C	7.49193	-2.86922	-0.07805
C	7.57937	-1.93836	0.95774
C	6.54828	-1.01938	1.15675
C	5.42148	-1.03614	0.32323
C	5.34062	-1.97034	-0.72398
C	6.37221	-2.88138	-0.91942
Cl	1.64986	1.11109	2.10470
Cl	1.71212	-0.03963	-2.23738
Si	1.68579	0.54802	-0.08022
P	-0.32576	-1.91564	-0.11854
H	6.10488	2.62578	1.52488
H	6.14564	4.35569	1.21565
H	4.03698	4.29462	-0.00947
H	3.75348	3.33132	1.43202
H	6.89123	0.96418	-0.50322
H	6.61369	1.62210	-2.09517
H	6.34769	3.87113	-1.26333
H	7.70475	3.21355	-0.35646
H	-0.50966	1.57731	-2.67636
H	-3.75528	3.28040	-0.39394
H	-2.91122	3.72220	1.77778
H	1.17124	3.68520	0.38068
H	-1.25683	-4.18202	-1.83213
H	2.43861	-2.61110	-0.25083
H	0.14839	-1.22913	2.64538
H	-2.19307	-4.11948	0.45523
H	4.40347	0.54487	1.44596
H	8.29513	-3.58251	-0.23448
H	8.44626	-1.92831	1.61055
H	6.60893	-0.29722	1.96651
H	4.47211	-1.96021	-1.37427
H	6.31306	-3.59868	-1.73253
H	-3.92042	3.26671	-4.67886
H	-1.70266	2.14939	-4.77130
H	-4.93720	3.82915	-2.48531
H	-0.32448	7.03862	2.62121
H	-2.54559	5.94010	2.79094
H	1.53173	5.90912	1.41984
H	2.42100	-6.30379	-2.45127
H	-0.03503	-6.11282	-2.76104
H	3.65470	-4.54821	-1.18851
H	-2.22661	-4.13793	4.74466
H	-0.64717	-2.22038	4.77549
H	-2.99531	-5.08048	2.58081
H	4.42570	0.68963	-1.70932
C	-1.64761	-1.26128	-1.20059
C	-2.77952	-0.60034	-0.70564
C	-2.53796	-1.18225	-3.45940
C	-1.51899	-1.50188	-2.59836
C	-3.86772	-0.30236	-1.59056
C	-3.74810	-0.62008	-2.98243
C	-4.83390	-0.34726	-3.85543
C	-5.99846	0.20671	-3.37781
C	-6.11690	0.53386	-2.00612

C	-5.07496	0.30193	-1.13892
C	-2.84768	-0.18288	0.73099
C	-2.05523	0.87079	1.20564
C	-1.99597	1.14164	2.60266
C	-2.78432	0.44666	3.48439
C	-3.70715	-0.88562	1.63862
C	-3.68734	-0.54622	3.03039
C	-4.55404	-1.22572	3.92630
C	-5.41529	-2.19650	3.47144
C	-5.42864	-2.54540	2.10002
C	-4.58694	-1.91972	1.21033
H	-2.42630	-1.36848	-4.52342
H	-0.60237	-1.92986	-2.98297
H	-4.72812	-0.58965	-4.90879
H	-6.82682	0.40149	-4.05163
H	-7.03503	0.98074	-1.63799
H	-5.17531	0.56987	-0.09435
H	-1.31459	1.89796	2.97044
H	-2.72750	0.66171	4.54731
H	-4.52591	-0.96044	4.97908
H	-6.08105	-2.70327	4.16286
H	-6.10299	-3.32046	1.74972
H	-4.59963	-2.20677	0.16615

TS(**7**)-(**vi**)-**b -** (*2R,1'S*)

113 atoms, 498 electrons, +1 charge, singlet.

Calculated ad B3LYP-D3/6-311+G(2df,2pd) // B3LYP-D3/6-31G(d,p) level of theory

C	-5.94424	2.97090	1.59792
C	-4.42389	3.04613	1.41155
C	-3.92969	2.22155	0.25422
C	-4.80082	1.59926	-0.64185
C	-6.27170	1.95936	-0.69113
C	-6.64954	3.11835	0.24589
O	-2.63378	2.05857	0.22274
P	1.13444	1.98373	-0.37195
O	-0.70761	-0.90803	-0.23256
O	-0.22903	1.54434	0.21643
C	3.42327	3.47045	3.31984
C	2.18175	2.85025	3.46152
C	1.49618	2.38145	2.34175
C	2.06781	2.54028	1.07076
C	3.30803	3.17768	0.92482
C	3.98447	3.63646	2.05099
C	0.48392	5.75150	-2.91840
C	-0.55588	5.21624	-2.15732
C	-0.35979	4.05124	-1.41639
C	0.89009	3.41682	-1.44634
C	1.93666	3.95443	-2.21337
C	1.73011	5.12005	-2.94695
C	-1.85551	-5.09800	2.81645
C	-2.56564	-4.19710	2.02159
C	-1.89376	-3.19890	1.31773
C	-0.49854	-3.10074	1.41788
C	0.21678	-4.00975	2.21395
C	-0.46472	-5.00419	2.91213
C	1.84064	-4.18308	-3.30394
C	0.95139	-3.11873	-3.45394
C	0.51074	-2.40630	-2.33943
C	0.96994	-2.77204	-1.06569
C	1.84964	-3.85268	-0.91104
C	2.28724	-4.55137	-2.03201
C	-4.31912	-0.22253	0.36106
O	-3.13336	-0.46535	-0.14760
C	-7.52939	-2.72143	-0.90720
C	-7.61959	-2.02838	0.30160
C	-6.56839	-1.20983	0.71230
C	-5.42097	-1.08414	-0.08595
C	-5.33484	-1.78240	-1.30189
C	-6.38630	-2.59792	-1.70586
Cl	-1.64593	0.82524	-2.21154
Cl	-1.69562	0.26250	2.24383
Si	-1.68399	0.55766	0.00277
P	0.33219	-1.88276	0.37150
H	-6.26974	3.74241	2.30203
H	-6.21091	2.00423	2.04614
H	-3.87099	2.72039	2.30023
H	-4.10735	4.08173	1.22281
H	-4.35771	1.19172	-1.54422
H	-6.52844	2.20928	-1.72656
H	-6.87347	1.07427	-0.44732
H	-7.73575	3.15281	0.37428
H	-6.35373	4.07334	-0.20737

H	0.53447	1.89252	2.44815
H	-1.16813	3.62760	-0.83219
H	2.89984	3.45607	-2.26291
H	-2.44321	-2.49531	0.70459
H	1.29522	-3.93214	2.31129
H	-0.17395	-1.57304	-2.45133
H	2.20010	-4.14658	0.07325
H	-4.35723	0.09807	1.40577
H	-8.34762	-3.35880	-1.22785
H	-8.50379	-2.12742	0.92310
H	-6.62951	-0.67284	1.65526
H	-4.44024	-1.67562	-1.90629
H	-6.31985	-3.14010	-2.64392
H	3.95498	3.82858	4.19580
H	1.74330	2.72367	4.44626
H	3.75184	3.31156	-0.05627
H	4.95034	4.11812	1.94029
H	0.32442	6.65808	-3.49385
H	-1.52594	5.70272	-2.14284
H	2.53738	5.53110	-3.54461
H	-2.38345	-5.87277	3.36374
H	-3.64644	-4.26594	1.94886
H	0.08822	-5.70135	3.53352
H	2.18526	-4.73019	-4.17584
H	0.60134	-2.83426	-4.44115
H	2.97910	-5.37894	-1.91516
C	1.66961	-1.09560	1.34141
C	2.79220	-0.50237	0.74945
C	2.59320	-0.72843	3.55809
C	1.56259	-1.15638	2.76022
C	3.79404	-0.22934	2.99531
C	3.89207	-0.09179	1.57267
C	5.09012	0.45238	1.02945
C	6.14366	0.79555	1.84418
C	6.04666	0.64589	3.24804
C	4.89148	0.15488	3.80990
C	2.04100	0.71058	-1.32596
C	2.83981	-0.27406	-0.72976
C	1.96495	0.79982	-2.74553
C	2.74226	-0.00411	-3.54007
C	3.65082	-0.93193	-2.97338
C	3.68825	-1.08906	-1.54989
C	4.57461	-2.05951	-1.00275
C	5.40607	-2.79503	-1.81463
C	5.37510	-2.62613	-3.21931
C	4.50699	-1.72188	-3.78484
H	2.49806	-0.77822	4.63873
H	0.65364	-1.53395	3.21026
H	5.17383	0.58499	-0.04220
H	7.05444	1.19386	1.40827
H	6.88398	0.92692	3.87895
H	4.80216	0.04866	4.88706
H	4.60035	-2.20945	0.06951
H	6.08578	-3.51854	-1.37565
H	6.03293	-3.21802	-3.84784
H	4.46565	-1.59447	-4.86261
H	1.27994	1.50435	-3.19929
H	2.67267	0.07305	-4.62104

(iii) Cross aldol reaction between isobutyraldehyde and benzaldehyde

TS(8)-Re

103 atoms, 468 electrons, +1 charge, singlet. Calculated ad B3LYP-D3/6-311+G(2df,2pd) // B3LYP-D3/6-31G(d,p) level of theory

C	3.06501	2.88512	-1.00993
C	4.06496	3.13914	-0.02351
O	1.85068	2.69832	-0.69942
C	-1.03443	-2.53507	-2.19568
C	-1.16149	-1.99720	-0.92351
C	-2.53742	-1.62788	-0.59801
C	-3.42691	-1.98381	-1.58070
S	-2.59612	-2.67512	-2.94445
C	-3.67722	-1.47213	1.62648
C	-2.93713	-0.89412	0.62537
C	-2.52827	0.47308	0.94539
C	-2.88741	0.85369	2.23079
S	-3.80420	-0.40748	2.99638
P	-1.86132	1.60185	-0.29501
C	-4.91749	-1.83662	-1.58768
C	0.16266	-2.96791	-2.99334
C	-4.31221	-2.82854	1.65209
C	-2.61123	2.09568	3.02981
O	0.72691	-0.51742	0.58697
O	-0.34338	1.48836	-0.60606
C	-3.88633	0.93903	-4.37215
C	-2.50054	0.83868	-4.24871
C	-1.88672	1.01555	-3.00797
C	-2.67680	1.27909	-1.88069
C	-4.07111	1.37317	-2.00189
C	-4.67132	1.20864	-3.24738
C	-2.71953	6.00395	0.71854
C	-1.42062	5.58188	0.43583
C	-1.16196	4.24134	0.14826
C	-2.21557	3.31749	0.15389
C	-3.52352	3.74344	0.43521
C	-3.77183	5.08362	0.71686
C	3.64327	-4.77830	-0.62375
C	2.33601	-5.27520	-0.60952
C	1.26895	-4.41844	-0.35640
C	1.50872	-3.05505	-0.11979
C	2.81915	-2.55862	-0.12345
C	3.88170	-3.42584	-0.38096
C	-1.32920	-3.31290	4.43130
C	-0.72410	-2.06498	4.27962
C	-0.29909	-1.63458	3.02213
C	-0.49610	-2.46331	1.90837
C	-1.10948	-3.71549	2.05831
C	-1.52099	-4.13834	3.31967
H	-5.40721	-2.79834	-1.39745
H	-5.22347	-1.14206	-0.80272
H	-5.28108	-1.45393	-2.54380
H	1.05179	-2.41604	-2.69278
H	0.36146	-4.03739	-2.87573
H	-0.00833	-2.77474	-4.05587
H	-3.88031	-3.45324	0.86757
H	-4.15694	-3.32826	2.61096
H	-5.39135	-2.76063	1.47401
H	-1.70736	2.59229	2.68194
H	-3.44117	2.80650	2.97309
H	-2.46558	1.83521	4.08185
H	-4.35682	0.80963	-5.34190
H	-1.88908	0.62707	-5.12006
H	-0.80958	0.94174	-2.91253
H	-4.69293	1.56010	-1.13296
H	-5.75003	1.28690	-3.34000
H	-2.91518	7.04819	0.94130
H	-0.60290	6.29540	0.43887
H	-0.15314	3.91291	-0.06677
H	-4.34333	3.03343	0.46443
H	-4.78286	5.40969	0.93900
H	4.47300	-5.44952	-0.82290
H	2.14951	-6.32776	-0.79740
H	0.25697	-4.80971	-0.36700
H	3.00884	-1.51002	0.06632
H	4.89289	-3.03181	-0.39143
H	-1.65098	-3.64505	5.41345
H	-0.57759	-1.42175	5.14145
H	0.17181	-0.66514	2.90076
H	-1.28409	-4.35466	1.19889

H	-1.99303	-5.10898	3.43523
C	4.00629	1.41367	0.68604
O	2.90062	0.68857	0.38613
C	7.58293	-0.65780	-0.48107
C	7.55208	0.06697	0.71057
C	6.38967	0.74345	1.08551
C	5.25195	0.69486	0.27310
C	5.28388	-0.03778	-0.92202
C	6.44620	-0.70856	-1.29591
H	4.01930	1.72789	1.73534
H	8.48690	-1.18220	-0.77503
H	8.42832	0.10340	1.35019
H	6.36331	1.30007	2.01878
H	4.39265	-0.08399	-1.54064
H	6.46749	-1.27171	-2.22422
Cl	0.84046	1.92974	1.96716
Cl	1.62306	0.17882	-2.10411
Si	1.26350	1.03405	-0.03034
P	0.15770	-1.93349	0.30343
H	3.36114	2.66657	-2.04624
C	3.65721	4.03976	1.14345
H	3.66004	5.08310	0.81141
H	2.66923	3.79001	1.52750
H	4.38543	3.95021	1.95457
C	5.44322	3.46864	-0.58150
H	6.21084	3.35374	0.18645
H	5.71688	2.82442	-1.42027
H	5.46151	4.51089	-0.91739

TS(8)-Si

103 atoms, 468 electrons, +1 charge, singlet. Calculated ad B3LYP-D3/6-311+G(2df,2pd) // B3LYP-D3/6-31G(d,p) level of theory

C	2.85197	3.00121	-1.32622
C	4.10242	3.00195	-0.66053
O	1.73921	2.79607	-0.72635
C	-1.19575	-2.39898	-2.32598
C	-1.22546	-1.94127	-1.01749
C	-2.57532	-1.62035	-0.55796
C	-3.53768	-1.93925	-1.48300
S	-2.81264	-2.53349	-2.94926
C	-3.52678	-1.60882	1.75899
C	-2.88249	-0.96251	0.73371
C	-2.46969	0.39350	1.09431
C	-2.72635	0.69672	2.42389
S	-3.55927	-0.62079	3.19061
P	-1.92514	1.60353	-0.13037
C	-5.02578	-1.82119	-1.35997
C	-0.06254	-2.74791	-3.24838
C	-4.12490	-2.98197	1.76536
C	-2.39725	1.89712	3.26583
O	0.75559	-0.50388	0.40659
O	-0.43775	1.54036	-0.57197
C	-4.28235	1.12710	-4.05140
C	-2.88954	1.04808	-4.05195
C	-2.17497	1.16592	-2.85911
C	-2.86955	1.34977	-1.65590
C	-4.27044	1.41969	-1.65241
C	-4.97241	1.31389	-2.85021
C	-2.76696	5.92166	1.20386
C	-1.48920	5.54363	0.79221
C	-1.23277	4.22725	0.40651
C	-2.26793	3.28332	0.44422
C	-3.55491	3.66477	0.85615
C	-3.80103	4.98125	1.23438
C	3.66038	-4.64798	-1.14037
C	2.35389	-5.14541	-1.17916
C	1.28368	-4.32204	-0.84044
C	1.52009	-2.99022	-0.46524
C	2.83051	-2.49608	-0.41205
C	3.89614	-3.32790	-0.75614
C	-0.92727	-3.52765	4.26295
C	-0.40059	-2.24339	4.12240
C	-0.09077	-1.74145	2.85783
C	-0.32419	-2.53634	1.72706
C	-0.85372	-3.82746	1.86575
C	-1.15230	-4.32029	3.13361
H	-5.48362	-2.80044	-1.17999
H	-5.27597	-1.17252	-0.51805
H	-5.47275	-1.39771	-2.26209
H	-0.29674	-2.41626	-4.26387
H	0.85837	-2.25474	-2.94406

H	0.11418	-3.82734	-3.28302
H	-3.77367	-3.54068	0.89547
H	-3.84566	-3.53715	2.66374
H	-5.21873	-2.93595	1.71900
H	-2.16623	1.58210	4.28721
H	-1.52757	2.42265	2.87507
H	-3.23393	2.60045	3.31338
H	-4.83216	1.04384	-4.98377
H	-2.35214	0.89824	-4.98292
H	-1.09285	1.10638	-2.85648
H	-4.81786	1.54033	-0.72368
H	-6.05630	1.37310	-2.84641
H	-2.96028	6.94722	1.50256
H	-0.68543	6.27248	0.77101
H	-0.23934	3.93374	0.09097
H	-4.35782	2.93709	0.91052
H	-4.79548	5.27304	1.55659
H	4.49139	-5.29343	-1.40738
H	2.17013	-6.17305	-1.47606
H	0.27176	-4.71110	-0.89358
H	3.01272	-1.47570	-0.10156
H	4.90820	-2.93664	-0.71963
H	-1.15990	-3.91448	5.25023
H	-0.22602	-1.62680	4.99839
H	0.31942	-0.74383	2.74463
H	-1.04322	-4.44663	0.99477
H	-1.55978	-5.32069	3.24089
C	3.98081	1.07391	-0.61364
O	2.91601	0.74533	0.13596
C	7.68562	-0.27238	1.07348
C	7.56914	-0.08799	-0.30604
C	6.36693	0.36393	-0.84890
C	5.27437	0.63798	-0.01387
C	5.39227	0.44183	1.37028
C	6.59499	-0.01091	1.90786
H	3.90349	0.80753	-1.67116
H	8.62077	-0.62623	1.49635
H	8.40991	-0.30155	-0.95853
H	6.27067	0.49521	-1.92307
H	4.53162	0.62778	2.00267
H	6.68124	-0.16561	2.97888
Cl	0.97197	1.83650	1.90871
Cl	1.40447	0.35661	-2.30773
Si	1.22592	1.09897	-0.16394
P	0.18568	-1.91287	0.10382
H	2.83193	3.01364	-2.42401
C	4.14852	3.44260	0.78979
H	4.11637	4.53690	0.82601
H	3.30759	3.05269	1.36122
H	5.08218	3.11978	1.25487
C	5.29917	3.40515	-1.50126
H	6.22552	3.03865	-1.05464
H	5.23628	3.02093	-2.52443
H	5.36516	4.49716	-1.55168