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SUPPORTING INFORMATION

Title: Bis(oxazoline)titanium Complexes as Chiral Catalysts for Enantioselective Hydrosilylation of Ketones – A Combined Experimental and Theoretical Investigation

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Ref. No.: O02675

General Information: ^{1}H NMR spectra were recorded by means of Varian Gemini-200 (200 MHz) or Varian Gemini-300 (300 MHz) spectrometers. Chemical shifts are given in δ ppm with respect to TMS and coupling constants J are measured in Hz. Data are reported as follows: chemical shifts, multiplicity (s = singlet, d = douplet, t = triplet, q = quartet, br = broad, m = multiplet). ^{13}C NMR spectra were recorded on a Varian Gemini 200 (50 MHz) or Varian Gemini 300 (75 MHz) spectrometers with complete proton decoupling. Chemical shifts are reported in ppm from TMS with the solvent as the internal standard (deuterochloroform: δ = 77.0 ppm, deuterodimethyl sulfoxide: δ = 39.0 ppm).

GC-MS spectra were taken by EI ionization at 70 eV on a Hewlett-Packard 5971 with GC injection. They are reported as: m/z (rel. intense).

Column flash chromatographies were run over 270-400 mesh silica gel. All the organic phases were dried over sodium sulphate.

Elemental analyses were carried out by using a EACE 1110 CHNOS analyzer.

Analytical high performance liquid chromatograph (HPLC) was performed on a HP 1090 liquid chromatograph equipped with a variable wave-length UV detector (deuterium lamp 190-600 nm), using a Daicel Chiralcel^{TM} OD or OF column (0.46 cm I.D. x 25 cm) (Daicel Inc.). HPLC grade isopropanol and hexane were used as the eluting solvents. Optical rotations were determined in a 1 ml cell with a path length of 10 mm using a Na_D line.

The bis-oxazolines **2-5** are commercially available (Aldrich). $(EtO)_3SiH$ and catecholborane (Aldrich) were used as received.

TiF_4 was transferred and handled under nitrogen in vials which were sealed by flame. The contents of the vial were used for the catalytic enantioselective reactions. TiF_4 solutions were prepared by dissolving the desired amount of titanium salt in dry CH_3CN and stored in Schlenk flasks under nitrogen.

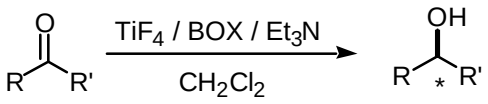
Anhydrous CH_3CN, CH_2Cl_2 and THF were purchased from the Fluka Co CD_2Cl_2 was dried over activated molecular sieves. THF-d^8 was dried over sodium. All the deuterated solvents were vacuum transferred into reaction flasks. All the other chemicals were commercially available and used as received.

Synthesis of the BOX 1: (*S*)-(-)-2-Amino-3-phenyl propanol (6.0 g, 39.7 mmol) and dimethylmalonate (2.26 ml, 19.8 mmol) were refluxed in xilene (12 mL) under nitrogen for 24 h. Xilene was evaporated under reduced pressure and the amide was precipitated by adding AcOEt. The crude amide was re-crystallized from ethyl acetate (70% yield). ^{1}H-NMR ($CDCl_3$, 200 MHz): δ 7.55-7.40 (m, 10H); 4.69 (d, 2H, J = 9.7 Hz); 3.90 (d, 2H, J = 9.7 Hz); 3.11 (s, 2H); 2.80 (d, 2H, J = 13.7 Hz); 2.62 (d, 2H, J = 13.7 Hz).

The (*S*,*S*)-*N*,*N*'-bis-(1-benzyl-2-hydroxy-ethyl)-malonamide (1.15 g, 3.11 mmol) was dissolved in CH_2Cl_2 (6 mL) then Et_3N (1.90 ml, 13.7 mmol) and mesylchloride (0.53 mL, 6.84 mmol) were added at 0°C. The mixture was allowed to warm to room temperature and stirred 2 h, then was cooled to 0°C. Other 0.1 mL of mesylchloride were added and the reaction mixture was allowed to warm to room temperature and stirred 24 h. The reaction mixture was quenched with H_2O and diluted with diethyl ether (30 mL). The organic phase was separated and the aqueous phase extracted with Et_2O (2 x 10 mL). The combined organic phases were dried over sodium sulphate and evaporated under reduced pressure to a viscous yellow oil. The oil was dissolved in dry MeOH (6 mL) and solid NaOH (0.24 g, 10 mmol) was added. The mixture was refluxed under nitrogen for two h then cooled to room temperature and quenched with H_2O (10 mL). The MeOH was evaporated under reduced pressure then the residue was extracted with CH_2Cl_2 (2 x 8 mL). The combined organic phases were dried over sodium sulphate then evaporated to reduced pressure to give an oil purified by flash chromatography (CH_2Cl_2 : MeOH 95:5, yield 60%).

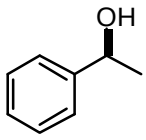
^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.41-7.25 (m, 10H), 4.45-4.39 (m, 2H); 4.31 (dd, 2H, J = 9.7 Hz); 4.15 (dd, 2H, J = 9.7 Hz); 3.46 (s, 2H); 3.23 (dd, 2H, J = 13.5, 5.4 Hz); 2.78 (dd, 2H, J = 8.1, 13.5, Hz). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 41.46, 67.36, 72.21, 126.40, 128.62, 129.11, 137.60, 161.97.

General procedure for the reduction of the ketones using the Ti(BOX)F_2 complex prepared from Et_3N (route B).



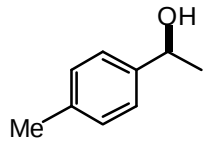
In a flamed dried flask BOX ligand (**1-5**) (0.12 mmol.) was dissolved in CH_2Cl_2 (2 mL). The solvent was degassed by freezing-pump cycle. Solid TiF_4 (0.06 mmol) was added, followed by Et_3N (0.06 mmol) and the reaction mixture vigorously stirred. The solution color turned pale orange and it was stirred during one hour at room temperature. The ketones (1 mmol) and triethoxysilane (WARNING its vapours can cause blindness!) (2 mmol) were added and the reaction mixture was stirred for the 24-48 h. The reaction was diluted with Et_2O then NaOH 2 M was carefully added. The reaction mixture was stirred for 30 min at room temperature then the organic phase was separated. The aqueous phase was extracted with Et_2O. The combined organic phases were dried over sodium sulphate then evaporated to reduced pressure to give an oil purified by flash chromatography. (cyclohexane: Et_2O, 8:2-9:1).

(*S*)-1-Phenylethanol



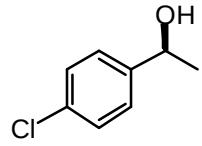
Ee = 61%, yield = 90%; ^{1}H-NMR ($CDCl_3$, 200 MHz): 7.36-7.23 (m, 5H, Ph); 4.87 (q, 1H, J = 6.3 Hz, C<u>H</u>OH); 1.48 (d, 3H, J = 6.4 Hz, C<u>H$_3$</u>). ^{13}C-NMR ($CDCl_3$, 50 MHz): 25.08, 70.23, 125.26, 127.25, 128.30, 145.68. IR (neat): 606, 699, 761, 899, 997, 1011, 1029, 1078, 1099, 1204, 1303, 1369, 1451, 1493, 2875, 2927, 2973, 3028, 3062, 3085, 3356 (cm^{-1}). $[\alpha]_D$= -23.7 (*c* = 0.97, $CHCl_3$). (lit $[\alpha]_D$ = + 48.6 (*c* = 1.0, CH_2Cl_2) e.e.= 96% (*R*)). Chiral GC analysis: isotherm: 100°C : t_r (*R*: 10.1 min; t_r (*S*): 11.3 min.

(*S*)-1-(4'-Methylphenyl) ethanol



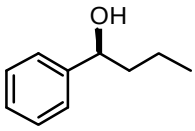
Ee = 43%; yield = 50%. ^{1}H-NMR ($CDCl_3$, 300 MHz) 7.22 (AA'BB', 4H, J = 7.9 Hz, Ph); 4.88 (dq, 1H, J = 6.4, 2.3 Hz, C<u>H</u>OH); 2.35 (s, 3H, C<u>H</u>$_3$); 1.80 (br, 1H, O<u>H</u>); 1.48 (d, 3H, J = 6.4, C<u>H</u>$_3$). ^{13}C-NMR ($CDCl_3$, 75 MHz): 21.04, 15.03, 125.23, 128.98, 136.89, 142.78. IR (neat): 819, 899, 1010, 1089, 1117, 1202, 1368, 1415, 1451, 1514, 2868, 2924, 2972, 3021, 3356 (cm^{-1}). $[\alpha]_D$ = -22.0 (*c* = 0.97, $CHCl_3$). (lit$^{25}[\alpha]_D$ = -54.1 (*c* = 0.053, $CHCl_3$), e.e.= 96% (*S*)). Chiral GC analysis: isotherm 105 °C: t_r (*R*): 10.2 min; t_r (*S*): 11.2 min.

(*S*)-1-(4'-Chlorophenyl)-ethanol



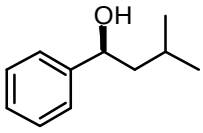
Ee = 34%, yield = 81%; ^{1}H-NMR ($CDCl_3$, 300 MHz); 7.32 (s, 4H, Ph); 4.85 (br, q, 1H, C<u>H</u>OH); 1.84 (br,1H, O<u>H</u>) 1.45 (d, 3H, J = 6.9 Hz, C<u>H</u>$_3$). ^{13}C-NMR ($CDCl_3$, 50 MHz): 25.25, 69.68, 126.70, 128.50, 132.94, 144.14. IR (neat): 778, 829, 898, 1013, 1089, 1112, 1201, 1272, 1295, 1338, 1371, 1408, 1453, 1493, 2886, 2928, 2973, 3346 (cm^{-1}). $[\alpha]_D$= -12.0 (*c* = 0.80, Et_2O). (lit$[\alpha]_D$ = - 48.9 (*c* = 0.061, Et_2O) e.e.= 94 % (*S*)). Chiral GC analysis: isotherm: 120 °C: t_r (*R*): 10.3 min; t_r (*S*): 11.1 min

(*S*)-1-Buthylphenylethanol



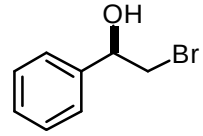
Ee = 75%; yield = 58%. ^{1}H-NMR ($CDCl_3$, 200 MHz): 7.44-7.21 (m, 5H, Ph); 4.69 (t, 1H, J = 7.2 Hz, C<u>H</u>OH); 1.95-1.63 (m, 3H, C<u>H</u>$_2$,O); 1.55-1.26 (m, 2H, $CH_3C\underline{H}_2$); 0.95 (t, 3H, J = 7.2 Hz, CH_3). ^{13}C-NMR ($CDCl_3$, 75 MHz): 13.89, 18.94, 41.13, 74.25, 125.83, 127.31, 128.27, 144.88. $[\alpha]_D$= -28.4 (*c* = 0.88, $CHCl_3$). (lit$^{25}[\alpha]_D$= - 41.3 (*c* = 0.053, $CHCl_3$), e.e.= 91% (*S*)). Chiral GC analysis: isotherm 110°C (*O*-silyl ether): t_r (*R*): 25.3 min; t_r (*S*): 25.7 min.

(*S*)-3-Methyl-1-phenylbutanol



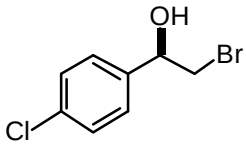
Ee = 85%; yield = 61%. ^{1}H-NMR ($CDCl_3$, 200 MHz): 7.33-7.20 (m, 5H, Ph); 4.74-4.68 (m, 1H, C<u>H</u>OH); 1.73 (d,1H, J = 3.1 Hz, O<u>H</u>); 1.75-1.62 (m, 2H, $C\underline{H}_2CH(CH_3)_2$); 1.53-1.45 (m, 1H, C<u>H</u>$(CH_3)_2$); 0.91 (d, 6H, J = 6.3 Hz, C<u>H</u>$_3$). ^{13}C-NMR ($CDCl_3$, 75 MHz): 22.22, 2305, 24.70, 48.25, 72.64, 125.82, 127.37, 128.37, 145.16. IR (neat): 1047, 1368, 1385, 1454, 1467, 1493, 2870, 2928, 2959, 3605 (cm^{-1}). $[\alpha]_D$= -25.8 (*c* = 1.2, $CHCl_3$). (lit^{25} $[\alpha]_D$= -39.9 (*c* = 0.050, eptane), e.e.= 94% (*S*)). Chiral GC analysis: isotherm 120°C: t_r (*S*): 13.8 min; t_r (*R*): 14.8 min.

(*R*)-2-Bromo-1-phenylethanol



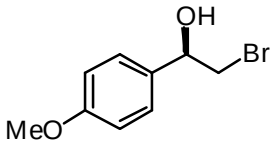
Ee = 84%; yield = 60%. ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.44-7.23 (m, 5H, Ph); 4.97-4.92 (ddd, 1H, J = 3.1; 3.3; 10.4 Hz, C<u>H</u>OH); 3.68-3.63 (dd, 1H, J = 3.3, 10.4 Hz, C<u>H</u>H'Br); 3.56 (t, 1H, J = 10.4 Hz, CH<u>H</u>'Br); 2.65 (d, 1H, J = 3.1 Hz, O<u>H</u>). ^{13}C-NMR ($CDCl_3$, 50 MHz): 41.29, 74.87, 127.02, 129.53, 129.75, 141.34. $[\alpha]_D$= - 42.3 (*c* = 1.11, $CHCl_3$). (lit $[\alpha]_D$= + 32.4, ee= 83% (*S*)). Chiral GC analysis: isotherm 110°C: t_r (*R*): 18.5 min; t_r (*S*): 19.1 min.

(*R*)-2-Bromo-(4'-chlorophenyl)ethanol



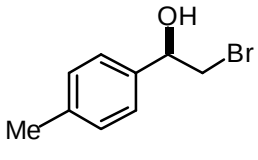
Ee = 63%; yield = 49%. ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.44-7.32 (m, 4H, Ph); 4.91 (ddd, 1H, J = 3.0, 3.3, 9.1, Hz, C<u>H</u>OH), 3.62 (dd, 1H, J = 3.0, 9.8 Hz, C<u>H</u>H'Br) 3.50 (dd, 1H, J = 9.1, 9.8 Hz, CH<u>H</u>'Br); 2.68 (d, 1H, J = 3.3 Hz, O<u>H</u>). ^{13}C-NMR ($CDCl_3$, 75 MHz): 39.73, 73.01, 127.31, 128.76, 134.14, 138.73. $[\alpha]_D$= - 18.4 (*c* = + 1.25, $CHCl_3$). Chiral GC analysis: isotherm 160°C: t_r (*S*): 15.6 min; t_r (*R*): 16.3 min.

(*R*)-2-Bromo-(4'-methoxyphenyl)ethanol



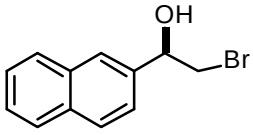
Ee = 79%; yield = 53%. ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.46-7.40 (dd, 1H, J = 1.5, 8.5 Hz, Ph); 7.37-7.28 (dt, 1H, J = 1.5, 8.5 Hz, Ph); 7.02-6.95 (t, 1H, J = 8.5 Hz, Ph); 6.90-6.86 (d, 1H, J = 8.5, Ph), 5.18-5.13 (ddd, 1H, J = 3.6, 5.4, 8.5 Hz, C<u>H</u>OH); 3.87 (s, 3H, C<u>H</u>$_3$O); 3.79-3.74 (dd, 1H, J = 3.6, 10.2 Hz, C<u>H</u>H'Br); 3.58-3.52 (dd, 1H, J = 8.5, 10.2 Hz, CH<u>H</u>'Br); 2.90 (d, 1H, J = 5.4 Hz, O<u>H</u>). ^{13}C-NMR ($CDCl_3$, 75 MHz): 55.30, 70.02, 110.43, 120.82, 127.09, 129.17, 156.17. $[\alpha]_D$= -23.6 (*c* = 1.2, $CHCl_3$). Chiral GC analysis: isotherm 150°C: t_r (*R*): 21.1 min; t_r (*S*): 22.8 min.

(*R*)-2-Bromo-(4'-methylphenyl)-ethanol



Ee = 83%; yield = 61%.^{1}H-NMR: ($CDCl_3$, 300 MHz) 7.32-7.18 (d, 4H, J = 8.0 Hz, Ph); 4.90 (ddd, 1H, J = 3.2, 3.5, 8.9 Hz, C<u>H</u>OH); 3.64 (dd, 1H, J = 3.5; 10.4 Hz, C<u>H</u>H'Br); 3.54 (dd, 1H, J = 8.9, 10.4 Hz, CH<u>H</u>'Br); 2.64 (d, 1H, J = 3.2 Hz, O<u>H</u>). ^{13}C-NMR ($CDCl_3$, 75 MHz): 22.24, 41.21, 74.76, 126.98, 130.41, 139.31. $[\alpha]_D$= - 36.4 (*c* = 1.07, $CHCl_3$). Chiral GC analysis: isotherm 110°C: t_r (*R*): 12.4 min; t_r (*S)*: 13.3 min.

(*R*)-2-Bromo-2-naphthylethanol



Ee = 59%; yield = 64%; ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.9-7.8 (m, 4H, Ph); 7.55-7.45 (m, 3H, Ph); 5.12 (ddd, 1H, J = 3.2, 3.4, 8.9 Hz, C<u>H</u>OH); 3.74 (dd, 1H, J = 3.4, 10.5 Hz, C<u>H</u>H'Br); 3.64 (dd, 1H, J = 8.9, 10.5 Hz, CH<u>H</u>'Br); 2.75 (d, 1H, J = 3.2, OH). ^{13}C-NMR ($CDCl_3$, 75 MHz): 40.01, 73.89, 123.54, 125.15, 126.27, 126.38, 127.61, 128.03, 128.51, 133.29, 137.62. $[\alpha]_D$= -25.6 (*c* = 0.82, $CHCl_3$). Chiral HPLC (Chiralcel-OD) analysis: n-Hex:IPA 90:10, flow 0.5 mL/min: t_r (*S*): 27.2 min; t_r (*R*) 29.0 min.

Computational Information.

Table S1. Cartesian Coordinates (Å) of the Critical Points Computed for Model-Reaction A.

M_1^A, E = -2006.536117			
c	0.044560	0.179763	-0.015599
n	-0.008698	0.116870	1.502647
ti	1.738144	0.130996	2.594167
n	0.509741	0.682104	4.199317
c	1.100270	1.376692	5.407314
c	-1.192250	-0.389678	2.009412
c	-1.553498	-0.398348	3.377691
c	-0.751793	0.188292	4.395463
o	-1.196650	0.348147	5.719750
o	-2.036874	-0.863744	0.993318
n	2.637579	1.973453	2.685764
c	2.019735	2.918780	1.678045
f	2.553447	-0.400008	1.043832
n	3.418146	-0.512598	3.684546
c	3.698069	-2.007679	3.692127
c	3.738286	2.435516	3.356805
o	4.029725	3.778088	3.054103
c	4.477675	1.655083	4.272677
c	4.317434	0.243214	4.384521
o	5.136494	-0.536703	5.225261
c	-3.327904	-1.412202	1.451280
c	-2.574216	-0.112054	5.980078
c	6.201327	0.196823	5.934236
c	5.261502	4.297073	3.679615
h	1.324975	-1.430953	3.168823
h	-2.511030	-0.828270	3.657204
h	5.248782	2.139474	4.864398
h	-0.832065	0.727835	-0.401708
h	0.965067	0.708371	-0.295066
h	0.069675	-0.834270	-0.447709
h	3.175973	-2.489657	4.535197
h	3.308878	-2.408125	2.746655
h	4.782858	-2.193862	3.766366
h	0.414616	2.156916	5.781295
h	1.296421	0.645673	6.210716
h	2.042598	1.835110	5.089619
h	2.723039	3.126300	0.852265
h	1.119227	2.424146	1.279033
h	1.719972	3.863918	2.161977
h	-3.843528	-1.740333	0.529210
h	-3.189983	-2.284785	2.121654
h	-3.945413	-0.644178	1.960548
h	-2.760270	0.124996	7.044595
h	-3.315852	0.422743	5.352415
h	-2.679640	-1.205813	5.829206
h	6.747824	-0.575410	6.507913
h	6.903573	0.692422	5.233106
h	5.790902	0.947545	6.640227
h	5.388858	5.315693	3.267252
h	5.168573	4.363231	4.783275
h	6.147127	3.682826	3.419247

M_2^A, E = -2121.096752			
c	0.535153	2.373363	0.898331
n	0.512544	1.393544	2.055886
ti	2.233590	1.094710	3.110867
n	0.945768	0.549204	4.668192
c	1.396788	0.690670	6.107655
c	-0.541511	0.513547	2.109003
c	-0.882934	-0.275246	3.224033
c	-0.207370	-0.156249	4.481750
o	-0.690210	-0.733593	5.664816
o	-1.286326	0.508233	0.894654
n	2.589575	2.890369	4.083382
c	1.495303	3.812373	4.562435
f	3.225154	1.580199	1.662719
n	3.865951	0.365076	4.121136
c	4.039915	-1.092484	4.475528
c	3.875686	3.374392	4.085387
o	3.928125	4.762898	4.271086
c	5.028205	2.552175	3.941042
c	5.005955	1.125726	4.047914
o	6.169279	0.349029	4.128997
c	0.933123	-1.065379	-0.409741
o	0.818377	-1.811066	-1.373186
c	-2.472667	-0.380806	0.884820
c	-1.963525	-1.471284	5.532916
c	7.439029	1.101727	4.093144
c	5.287609	5.337734	4.317039
h	2.133426	-0.593351	2.606869
h	-1.729976	-0.952490	3.150373
h	5.995064	3.038648	3.840624
h	-0.462526	2.824703	0.762124
h	1.263939	3.156951	1.154365
h	0.851314	1.878686	-0.036281
h	3.040885	-1.475899	4.720634
h	4.437089	-1.649283	3.609798
h	4.716957	-1.206127	5.340406
h	1.635218	-0.297393	6.537312
h	2.298720	1.315495	6.090238
h	0.610673	1.173971	6.713613
h	1.382730	4.674018	3.881707
h	0.567856	3.221044	4.563260
h	1.703048	4.178082	5.583473
h	0.089714	-0.444482	-0.049268
h	1.884029	-0.987547	0.153485
h	-2.205193	-1.811899	6.557292
h	-2.780452	-0.820260	5.161113
h	-1.858698	-2.355000	4.871152
h	-2.914297	-0.253892	-0.120994
h	-2.187072	-1.442005	1.029308
h	-3.206316	-0.073104	1.656895
h	5.138464	6.417879	4.503153
h	5.889457	4.903394	5.141112
h	5.821669	5.204859	3.354105
h	8.229869	0.333580	4.183811
h	7.566923	1.644392	3.134581
h	7.520116	1.812210	4.941071

TS_1^A, E = -2121.089654			
c	0.360558	2.614605	0.896643
n	0.347805	1.671899	2.087432
ti	2.105838	1.349386	3.039207
n	0.902479	0.600814	4.587451
c	1.400467	0.639154	6.017891
c	-0.571902	0.639923	2.035408
c	-0.918080	-0.186305	3.122000
c	-0.259937	-0.085997	4.391074
o	-0.736933	-0.706274	5.552354
o	-1.096980	0.476768	0.731510
n	2.568276	2.971776	4.184798
c	1.521411	3.878248	4.782952
f	3.047179	1.990754	1.622978
n	3.739404	0.416656	3.849436
c	3.851706	-1.087209	3.955880
c	3.876043	3.404731	4.183132
o	3.985923	4.763143	4.498790
c	4.985363	2.562836	3.906585
c	4.907383	1.133665	3.822089
o	6.036920	0.312016	3.739496
c	1.369595	-1.472852	1.007330
o	2.283669	-1.915217	0.302462
c	-2.182358	-0.527239	0.610412
c	-2.028789	-1.408567	5.400889
c	7.336807	1.013928	3.725447
c	5.365599	5.285923	4.548177
h	1.963929	-0.275097	2.272570
h	-1.711214	-0.919716	2.998912
h	5.968191	3.021029	3.830501
h	-0.665884	2.954054	0.675657
h	0.980741	3.479001	1.178319
h	0.797848	2.124299	0.009890
h	2.870758	-1.451464	4.291070
h	4.078248	-1.517808	2.965191
h	4.632363	-1.369330	4.683671
h	1.642078	-0.379266	6.368344
h	2.308076	1.255581	6.014809
h	0.638948	1.084211	6.681822
h	1.427145	4.808144	4.196167
h	0.571182	3.325413	4.746622
h	1.766807	4.126233	5.830804
h	0.648510	-0.715559	0.643672
h	1.029571	-2.030970	1.907166
h	-2.292981	-1.748573	6.419868
h	-2.821333	-0.733482	5.020046
h	-1.937494	-2.291327	4.735590
h	-2.471178	-0.505198	-0.456825
h	-1.827837	-1.544088	0.872741
h	-3.053928	-0.252296	1.238507
h	5.262630	6.347310	4.842014
h	5.977549	4.752985	5.304328
h	5.859925	5.228114	3.556970
h	8.093809	0.210233	3.657334
h	7.431791	1.679950	2.844086
h	7.500930	1.593786	4.656647

M_3^A, E = -2121.104318			
c	0.464606	2.828236	0.973924
n	0.390555	1.975214	2.230588
ti	2.096527	1.725447	3.239130
n	0.960658	1.066952	4.762536
c	1.454922	1.171700	6.189075
c	-0.675554	1.086758	2.266779
c	-0.948487	0.253325	3.411521
c	-0.174760	0.270350	4.582510
o	-0.467627	-0.476363	5.732986
o	-1.553154	1.253511	1.208274
n	2.634709	3.406467	4.108065
c	1.655779	4.435406	4.621127
f	3.099797	1.997125	1.735031
n	3.686959	0.742198	4.083320
c	3.711107	-0.739104	4.379312
c	3.975784	3.756009	3.997410
o	4.151298	5.139202	4.041937
c	5.028799	2.819893	3.872193
c	4.886123	1.389822	3.996626
o	5.976696	0.521416	4.079742
c	1.316535	-1.032899	1.795255
o	0.327705	-0.728934	0.982862
c	-2.552974	0.169572	1.066778
c	-1.645310	-1.358991	5.608151
c	7.310181	1.158446	4.034662
c	5.553102	5.598080	3.962900
h	1.701056	-0.122157	2.455813
h	-1.788526	-0.433452	3.339135
h	6.033006	3.207725	3.713703
h	-0.478660	3.385006	0.843703
h	1.297485	3.538261	1.097399
h	0.651497	2.174948	0.104658
h	2.673883	-1.035331	4.590644
h	4.079303	-1.295068	3.499770
h	4.352875	-0.952605	5.251930
h	1.870745	0.211175	6.540284
h	2.245074	1.935410	6.197531
h	0.630075	1.477706	6.856179
h	1.511985	5.242058	3.882035
h	0.703937	3.906709	4.781050
h	2.011412	4.861366	5.576107
h	1.103853	-1.780474	2.610249
h	2.268081	-1.349017	1.306232
h	-1.718981	-1.881769	6.580166
h	-2.574144	-0.778838	5.432014
h	-1.511565	-2.103903	4.797272
h	-3.049672	0.367647	0.098985
h	-2.024535	-0.803010	1.036300
h	-3.304419	0.206005	1.882558
h	5.500907	6.700260	4.038381
h	6.158192	5.198816	4.802472
h	6.016689	5.318161	2.995008
h	8.027919	0.323533	4.141351
h	7.484948	1.668187	3.065538
h	7.451191	1.873396	4.870510

TS_2^A, E = -2121.094703			
c	0.563266	3.099710	1.312178
n	0.420007	2.127470	2.462674
ti	2.134294	1.443100	3.280488
n	1.010720	0.727478	4.778643
c	1.495660	0.745993	6.212152
c	-0.583243	1.181652	2.325080
c	-0.981590	0.292568	3.390999
c	-0.243415	0.137588	4.573318
o	-0.666934	-0.591630	5.693654
o	-1.298247	1.320873	1.146731
n	2.631155	3.151640	4.090792
c	1.615104	4.092211	4.695487
f	3.065434	1.690725	1.735742
n	3.879540	0.675417	4.162255
c	4.046502	-0.751911	4.634190
c	3.913437	3.634183	3.845960
o	3.930885	5.029063	3.785684
c	5.043897	2.806728	3.699529
c	5.022143	1.389156	3.967799
o	6.181905	0.619588	4.091561
c	1.495857	-1.232347	2.178626
o	0.828233	-0.496098	1.286793
c	-2.133245	0.147979	0.799880
c	-1.992470	-1.223465	5.538666
c	7.454577	1.350724	3.913952
c	5.265046	5.623676	3.567276
h	2.313026	-0.657822	2.758522
h	-1.874302	-0.310256	3.237203
h	5.995671	3.265380	3.440044
h	-0.378845	3.651131	1.153462
h	1.364156	3.804831	1.584931
h	0.848658	2.555343	0.394962
h	3.042095	-1.129235	4.868904
h	4.489588	-1.367433	3.832549
h	4.685857	-0.794195	5.533185
h	1.634318	-0.278179	6.600078
h	2.458386	1.275996	6.216926
h	0.769278	1.279968	6.849856
h	1.279397	4.838125	3.955441
h	0.760731	3.474058	5.002909
h	2.049425	4.602281	5.573665
h	0.883712	-1.664517	3.018379
h	2.098831	-2.076260	1.762013
h	-2.191579	-1.722170	6.505701
h	-2.783387	-0.471270	5.341551
h	-1.989465	-1.981446	4.728686
h	-2.459872	0.330173	-0.240726
h	-1.507473	-0.765123	0.853350
h	-3.024041	0.075159	1.457600
h	5.099223	6.717103	3.568949
h	5.966530	5.355103	4.383540
h	5.688949	5.318049	2.589008
h	8.244040	0.591754	4.069790
h	7.545847	1.766672	2.890139
h	7.570507	2.160188	4.662912

M_4^A, E = -2121.176406			
c	0.683387	3.105795	1.097026
n	0.550581	2.011541	2.128690
ti	2.250377	1.237355	3.065352
n	0.972262	0.849132	4.646284
c	1.445322	0.817552	6.076620
c	-0.627881	1.337512	2.171184
c	-0.962917	0.373184	3.182862
c	-0.190759	0.188040	4.353395
o	-0.492934	-0.804691	5.326737
o	-1.495831	1.678371	1.123863
n	2.592308	3.067334	3.955953
c	1.480755	3.961704	4.445292
f	3.227398	1.753451	1.598697
n	3.982999	0.673828	4.029652
c	4.221705	-0.765444	4.413071
c	3.838457	3.629033	3.847439
o	3.800261	5.030698	3.910601
c	5.041694	2.882799	3.720114
c	5.090794	1.470698	3.898827
o	6.287546	0.744491	3.984425
c	1.358111	-1.737106	2.904661
o	1.912804	-0.520966	2.509621
c	-2.826818	1.041017	1.177292
c	-1.826055	-1.436013	5.187035
c	7.519572	1.551048	3.883389
c	5.117726	5.694319	3.874939
h	0.848651	-1.682752	3.882167
h	-1.860058	-0.225965	3.050993
h	5.973039	3.418171	3.557726
h	-0.214266	3.747099	1.087292
h	1.568029	3.698560	1.371693
h	0.841130	2.669344	0.095805
h	3.265409	-1.168349	4.775887
h	4.552173	-1.346164	3.535188
h	4.977443	-0.838182	5.214681
h	1.812804	-0.185056	6.357384
h	2.271731	1.538916	6.141272
h	0.632642	1.112434	6.764289
h	1.174714	4.678110	3.664119
h	0.640656	3.297172	4.683462
h	1.793654	4.516971	5.346803
h	0.623130	-2.085731	2.159998
h	2.142809	-2.507175	2.964357
h	-1.918712	-2.108736	6.060236
h	-2.637822	-0.681352	5.215133
h	-1.902485	-2.035351	4.257715
h	-3.391352	1.481022	0.333781
h	-2.761493	-0.057027	1.035448
h	-3.353099	1.264318	2.127486
h	4.901105	6.774436	3.975341
h	5.763864	5.370756	4.716471
h	5.641332	5.516889	2.913412
h	8.348106	0.825881	3.989937
h	7.600742	2.053950	2.898349
h	7.586563	2.304612	4.694560

Table S2. Cartesian Coordinates (Å) of the Critical Points Computed for Model-Reaction B.

M_1^B, E = -1907.151282			
c	-0.008620	0.041404	0.001893
n	-0.012352	0.002425	1.513729
ti	1.817569	-0.010744	2.493625
n	0.840428	0.392663	4.234695
c	1.560103	1.055747	5.390527
c	-1.167802	-0.421419	2.104129
c	-1.368551	-0.505582	3.516860
c	-0.445162	-0.047571	4.489030
o	-0.751349	0.028075	5.862063
o	-2.167769	-0.751264	1.171514
n	2.597246	1.682262	1.675026
c	1.711049	2.858950	1.326314
n	3.684680	-0.431555	3.298778
c	3.780398	-1.503614	4.360973
c	3.909894	1.756312	1.247189
o	4.104056	2.842353	0.371172
c	4.955218	0.881699	1.634435
c	4.845408	-0.113384	2.655236
o	5.946557	-0.857257	3.116104
c	-3.452167	-1.189460	1.748661
c	-2.116253	-0.393515	6.228548
c	7.237161	-0.541747	2.476037
c	5.484567	3.019926	-0.116311
h	1.980029	-1.662286	1.761726
h	-2.325458	-0.879818	3.868353
h	5.928786	1.026809	1.175561
h	-0.188375	-0.963254	-0.416624
h	-0.769199	0.744135	-0.381924
h	0.993582	0.384570	-0.300767
h	4.450473	-1.194428	5.182548
h	2.761354	-1.648550	4.753725
h	4.139383	-2.452540	3.927962
h	1.718746	0.350791	6.224901
h	2.534867	1.386493	5.001175
h	0.990516	1.928746	5.755508
h	1.589757	2.963609	0.234204
h	0.731202	2.657038	1.784988
h	2.127048	3.795725	1.737675
h	5.450365	3.921075	-0.757252
h	6.199533	3.190997	0.714360
h	5.824006	2.156006	-0.723988
h	-2.182764	-0.236569	7.321712
h	-2.890467	0.220857	5.725005
h	-2.292660	-1.465875	6.005479
h	7.972390	-1.207721	2.965873
h	7.223558	-0.756134	1.387745
h	7.536331	0.513564	2.642204
h	-4.105026	-1.392098	0.878763
h	-3.343582	-2.119142	2.343977
h	-3.916673	-0.400409	2.375079

M_2^B, E = -2021.715420			
c	-0.009957	-0.608895	0.320701
n	0.244954	-0.530411	1.810832
c	1.542972	-0.692095	2.210470
o	2.413852	-0.936591	1.136505
c	3.827254	-1.152304	1.500382
ti	-1.185880	0.378846	2.985785
n	-2.473485	1.767330	3.883175
c	-3.799650	1.817385	3.637275
o	-4.478987	3.034845	4.125789
c	-5.353983	2.718427	5.292470
n	-0.244495	-0.318875	4.639385
c	1.123540	-0.526071	4.690903
o	1.574275	-0.629646	6.019207
c	3.020016	-0.877742	6.178251
n	-2.806156	-0.772734	2.485236
c	-4.115101	-0.340853	2.407656
c	-4.599171	0.890161	2.944920
o	-6.738430	3.242467	2.705561
c	-0.991117	-0.448089	5.950001
c	1.981474	-0.640438	3.569773
c	-2.576571	-2.209657	2.048146
c	-1.837497	2.938201	4.603457
o	-4.948879	-1.265699	1.770677
c	-6.361430	-0.846946	1.628091
h	-0.655281	1.852630	2.105429
h	3.044248	-0.759179	3.760491
h	-5.659565	1.130515	2.862517
h	0.247491	-1.606756	-0.076295
h	-1.085961	-0.421362	0.173469
h	0.566954	0.164108	-0.214252
h	-2.264231	3.066801	5.613794
h	-0.763385	2.706884	4.684969
h	-1.960515	3.865981	4.020610
h	-0.808988	-1.436234	6.408315
h	-0.695437	0.343570	6.660437
h	-2.062100	-0.345979	5.714531
h	-2.810555	-2.339801	0.977567
h	-1.511883	-2.424674	2.222717
h	-3.200259	-2.898372	2.644602
h	4.345811	-1.338751	0.541096
h	4.270614	-0.258024	1.983974
h	3.954644	-2.034851	2.160147
h	3.180861	-0.950272	7.270403
h	3.331806	-1.828687	5.700098
h	3.629208	-0.042372	5.776426
h	-5.679465	3.692867	5.700952
h	-6.238706	2.136203	4.972124
h	-4.763101	2.158779	6.045373
h	-6.843637	-1.662244	1.056806
h	-6.857767	-0.745641	2.614372
h	-6.453976	0.105489	1.067823
c	-5.632713	3.798647	2.704421
h	-4.855383	3.532345	1.964169
h	-5.516549	4.816278	3.128265

TS_1^B, E = -2021.682247			
c	-0.469163	-0.237167	0.358396
n	-0.084105	-0.180961	1.818665
c	1.243198	-0.263633	2.108282
o	2.057094	-0.343295	0.965333
c	3.500032	-0.502984	1.227677
ti	-1.394894	0.473187	3.291547
n	-2.718213	1.505945	4.508251
c	-4.043866	1.644270	4.196941
o	-4.639624	2.738137	4.856076
c	-6.087211	2.901665	4.628163
n	-0.380048	-0.587354	4.656640
c	1.000064	-0.459187	4.615360
o	1.561983	-0.570459	5.897957
c	3.030090	-0.450563	5.956947
n	-2.932676	-0.792035	2.771479
c	-4.247867	-0.396058	2.730487
c	-4.769161	0.789091	3.318033
o	-2.994988	1.954193	1.289010
c	-0.993925	-1.128072	5.924834
c	1.773448	-0.272333	3.442121
c	-2.643207	-2.192446	2.276547
c	-2.179045	2.420913	5.583744
o	-5.054187	-1.323150	2.042429
c	-6.490164	-0.991551	1.985347
h	-0.635962	2.128159	3.004650
h	2.850659	-0.183255	3.556317
h	-5.811444	1.028297	3.127328
h	-0.155004	-1.190904	-0.100998
h	-1.565367	-0.149051	0.319679
h	-0.016050	0.601931	-0.196524
h	-2.713325	2.268216	6.538495
h	-1.115846	2.162849	5.707292
h	-2.255331	3.480000	5.284509
h	-0.553959	-2.107545	6.184422
h	-0.862270	-0.432088	6.771532
h	-2.067666	-1.249871	5.718800
h	-2.878243	-2.295932	1.203023
h	-1.567203	-2.360191	2.433012
h	-3.223827	-2.939021	2.847328
h	3.964210	-0.620071	0.230229
h	3.930904	0.391158	1.723181
h	3.713077	-1.404413	1.837658
h	3.285882	-0.548920	7.028664
h	3.532206	-1.259399	5.387231
h	3.378121	0.536120	5.588561
h	-6.379185	3.774942	5.241582
h	-6.320465	3.113382	3.564573
h	-6.662713	2.014330	4.962697
h	-6.960727	-1.839731	1.453073
h	-6.936843	-0.903618	2.996772
h	-6.677146	-0.058563	1.415222
c	-2.710177	3.133359	1.408377
h	-1.932198	3.447036	2.125551
h	-3.219753	3.905355	0.789604

M_3^B, E = -2021.695335			
c	-0.630751	-0.278253	0.201765
n	-0.238149	-0.112712	1.654456
c	1.103877	-0.029692	1.921414
o	1.881148	0.012249	0.756024
c	3.339091	0.096626	0.971087
ti	-1.622377	0.560910	3.014482
n	-2.890652	1.426328	4.409406
c	-4.219775	1.523696	4.105170
o	-4.840580	2.607886	4.746628
c	-6.286985	2.751319	4.493577
n	-0.479651	-0.326410	4.440125
c	0.898600	-0.257942	4.405581
o	1.467136	-0.477543	5.668655
c	2.941764	-0.449499	5.707550
n	-3.043035	-0.925611	2.846166
c	-4.380652	-0.607347	2.780228
c	-4.933361	0.603556	3.270386
o	-2.605005	1.516905	1.576711
c	-1.092861	-0.881585	5.707370
c	1.664360	-0.029091	3.234403
c	-2.658856	-2.361126	2.574491
c	-2.368319	2.363932	5.471330
o	-5.146031	-1.634030	2.200317
c	-6.598630	-1.377568	2.150114
h	-0.747603	2.124966	3.156761
h	2.740532	0.083216	3.333920
h	-5.985386	0.799971	3.080923
h	-0.106784	-1.139559	-0.247883
h	-1.716655	-0.448019	0.185728
h	-0.400904	0.638112	-0.367579
h	-2.974474	2.296374	6.392328
h	-1.332252	2.059790	5.673338
h	-2.366743	3.403201	5.100444
h	-0.715866	-1.901223	5.902085
h	-0.871342	-0.238470	6.575793
h	-2.177576	-0.911189	5.538392
h	-2.867071	-2.636395	1.525890
h	-1.576163	-2.434067	2.761659
h	-3.199952	-3.051287	3.245313
h	3.778382	0.123164	-0.043814
h	3.620640	1.021529	1.514288
h	3.727370	-0.789342	1.513856
h	3.207271	-0.660304	6.760537
h	3.385264	-1.229326	5.055306
h	3.341054	0.545643	5.423770
h	-6.593271	3.642555	5.073027
h	-6.502189	2.925057	3.419671
h	-6.858588	1.870521	4.851492
h	-7.039575	-2.292318	1.711269
h	-7.024430	-1.215241	3.161311
h	-6.841240	-0.510841	1.501891
c	-2.778286	2.756674	1.270007
h	-2.229573	3.539080	1.800246
h	-3.407876	3.000647	0.406745

TS_2^B, E = -2021.683032			
c	-0.582331	-0.155906	0.115433
n	-0.240950	0.034516	1.578567
c	1.095612	0.059455	1.900146
o	1.914556	0.129081	0.763717
c	3.366083	0.136377	1.032106
ti	-1.630402	0.662997	2.948766
n	-2.871149	1.563989	4.317239
c	-4.225783	1.568771	4.089717
o	-4.858643	2.666358	4.696913
c	-6.326921	2.706599	4.559196
n	-0.576065	-0.403511	4.339553
c	0.796083	-0.319587	4.359284
o	1.325156	-0.604917	5.626881
c	2.797644	-0.577769	5.716708
n	-3.008698	-0.905480	2.918388
c	-4.350902	-0.638486	2.888984
c	-4.936395	0.573722	3.358619
o	-2.752091	1.404934	1.442421
c	-1.232065	-1.007904	5.559857
c	1.604892	-0.020488	3.227430
c	-2.582921	-2.324472	2.628298
c	-2.353484	2.540084	5.348272
o	-5.103070	-1.710451	2.379716
c	-6.564417	-1.503552	2.367509
h	-0.556803	2.058956	3.278466
h	2.676951	0.081654	3.373240
h	-6.002426	0.718118	3.204490
h	-0.049414	-1.031835	-0.293863
h	-1.668325	-0.313979	0.061303
h	-0.318574	0.742593	-0.468389
h	-2.986440	2.527180	6.253149
h	-1.330087	2.224915	5.593440
h	-2.320666	3.560725	4.929709
h	-0.793683	-1.993445	5.794340
h	-1.124801	-0.342968	6.433622
h	-2.294524	-1.119094	5.309930
h	-2.770560	-2.583160	1.571076
h	-1.502150	-2.368706	2.829608
h	-3.114430	-3.043880	3.275848
h	3.843295	0.177965	0.034975
h	3.670048	1.027222	1.618632
h	3.692823	-0.785192	1.555693
h	3.027758	-0.842736	6.765789
h	3.264901	-1.322832	5.040760
h	3.204218	0.430831	5.498762
h	-6.644387	3.606400	5.119062
h	-6.639193	2.809779	3.500012
h	-6.807993	1.811476	5.003923
h	-6.986471	-2.446561	1.971980
h	-6.964560	-1.323509	3.386166
h	-6.856324	-0.667447	1.699917
c	-2.437605	2.662468	1.283021
h	-1.399672	2.982076	1.180574
h	-3.240873	3.405206	1.211727

M_4^B, E = -2021.785018			
c	-0.483991	-0.669268	0.214791
n	-0.249108	-0.494029	1.694947
c	0.928217	0.078659	2.068068
o	1.658370	0.592472	0.959636
ti	-1.819291	0.093418	2.957970
n	-3.381642	0.776299	4.157889
c	-4.612781	0.856090	3.578181
o	-5.404090	1.888188	4.109421
n	-0.685924	-0.577250	4.525152
c	0.653460	-0.268067	4.542174
o	1.221903	-0.432813	5.815548
n	-3.040451	-1.433922	2.366634
c	-4.370527	-1.175281	2.104822
c	-5.082744	-0.033119	2.555411
c	-1.263050	-1.226380	5.761437
c	1.388346	0.199093	3.412284
c	-2.538356	-2.825553	2.055511
c	-3.088146	1.767812	5.256965
o	-4.956981	-2.189127	1.325498
c	-0.698957	2.601352	1.530165
o	-1.660254	1.860710	2.229714
c	2.959281	1.216940	1.290626
c	2.677416	-0.195752	5.886146
c	-6.746040	2.032030	3.514175
c	-6.394923	-2.015245	1.047180
h	-0.235055	3.356401	2.192829
h	2.382929	0.603132	3.581290
h	-6.089501	0.118396	2.176528
h	-0.540026	0.305457	-0.301882
h	0.314339	-1.277747	-0.245669
h	-1.447718	-1.188293	0.111090
h	-3.812206	1.679577	6.086009
h	-2.077821	1.536703	5.626443
h	-3.102204	2.798384	4.861781
h	-1.148059	-0.579986	6.648827
h	-2.333683	-1.379880	5.556118
h	-0.775483	-2.198012	5.953636
h	-2.665730	-3.078622	0.988877
h	-1.467935	-2.829910	2.309498
h	-3.069598	-3.573734	2.670347
h	-1.172667	3.162526	0.706209
h	0.119239	1.998509	1.103191
h	-6.694063	-2.923737	0.491172
h	-6.991056	-1.944492	1.979659
h	-6.588705	-1.124343	0.415004
h	-7.199738	2.897741	4.032450
h	-6.694852	2.245638	2.427196
h	-7.374598	1.134702	3.688793
h	2.966229	-0.472793	6.917538
h	3.233810	-0.828874	5.165801
h	2.928783	0.871077	5.714601
h	3.354644	1.583832	0.325038
h	2.839108	2.071550	1.985821
h	3.665932	0.477150	1.718776

Table S3. Cartesian Coordinates (Å) of the Critical Points M_2^{A*}, TS_1^{A*}, M_2^{B*} and TS_1^{B*}.

M_2^{A*}, E = -2199.76031270			
c	-1.366477	-0.013333	-3.063000
n	-1.405651	0.087626	-1.541098
ti	0.431363	0.235386	-0.573316
n	-0.682474	0.413500	1.221692
c	0.090372	0.764291	2.482299
c	-2.541373	-0.418463	-0.965048
c	-2.886573	-0.348532	0.404667
c	-1.954727	0.002030	1.417344
o	-2.292247	-0.220674	2.793720
o	-3.356801	-1.146637	-1.880216
n	1.004733	2.204582	-0.239389
c	-0.000133	3.313266	-0.047803
f	1.247826	0.202552	-2.193801
n	2.154837	-0.295009	0.403346
c	2.328496	-1.624801	1.112511
c	2.293102	2.563031	-0.543424
o	2.414276	3.923956	-0.854946
c	3.388949	1.657415	-0.524137
c	3.311762	0.333720	0.004461
o	4.441934	-0.473269	0.196614
c	-1.605930	-3.552272	0.897259
o	-0.522873	-3.930838	1.323296
c	-4.772980	-1.320053	-1.464982
c	-3.722338	0.035462	3.117317
c	5.733632	0.145608	-0.161967
c	3.785988	4.378440	-1.155983
h	0.231076	-1.469743	-0.382809
h	-3.873042	-0.683540	0.713859
h	4.358223	2.017920	-0.857081
h	-2.362829	0.210483	-3.478327
h	-0.635021	0.723823	-3.419765
h	-1.049589	-1.024559	-3.369937
h	1.368538	-1.867522	1.586219
h	2.569376	-2.413122	0.379044
h	3.128162	-1.555520	1.870648
h	0.361755	-0.154288	3.028890
h	0.997830	1.284409	2.153637
h	-0.514712	1.418655	3.132672
h	-0.189920	3.839978	-0.999672
h	-0.929279	2.835900	0.296462
h	0.345999	4.038355	0.709524
c	-1.937771	-3.625915	-0.585404
c	-2.674751	-3.094765	1.882343
h	-3.762037	0.072499	4.222364
h	-4.057981	1.004003	2.695950
h	-4.385795	-0.778579	2.762706
h	-5.273382	-1.760750	-2.347609
h	-4.871635	-2.016244	-0.607945
h	-5.239427	-0.345085	-1.218249
h	3.695300	5.463939	-1.348539
h	4.470047	4.214574	-0.298382
h	4.193630	3.881329	-2.059709
h	6.494200	-0.620413	0.079837
h	5.788757	0.383986	-1.243599
h	5.932392	1.059507	0.434256
h	-2.534615	-4.539163	-0.734540
h	-2.510233	-2.789661	-1.001422
h	-1.005813	-3.731550	-1.144453
h	-2.723265	-3.842636	2.679393

TS_1^{A*}, E = -2199.75021067			
c	-1.53442	0.54148	-2.81342
n	-1.57892	0.35716	-1.30895
ti	0.20832	0.25828	-0.31703
n	-0.90714	0.72634	1.3674
c	-0.23491	1.34214	2.5759
c	-2.71011	-0.21839	-0.79298
c	-3.00927	-0.3231	0.58823
c	-2.09128	0.08434	1.59479
o	-2.2688	-0.26435	2.95384
o	-3.51461	-0.80592	-1.79575
n	0.89632	2.15264	-0.39052
c	0.05096	3.39794	-0.31562
f	1.03485	-0.29664	-1.8422
n	1.81377	-0.24415	0.83919
c	1.82934	-1.34212	1.88282
c	2.21734	2.27339	-0.7828
o	2.46056	3.47647	-1.44904
c	3.20689	1.28931	-0.53022
c	3.02017	0.14649	0.32588
o	4.07304	-0.66818	0.74738
c	-0.68962	-3.04902	0.15307
o	0.39849	-3.64123	0.3248
c	-4.83435	-1.30464	-1.33622
c	-3.64962	-0.65757	3.33569
c	5.41393	-0.28829	0.25521
c	3.86006	3.69173	-1.86652
h	-0.36702	-1.41817	0.10365
h	-3.92044	-0.8304	0.89311
h	4.19382	1.4349	-0.96399
h	-2.48305	0.97674	-3.17102
h	-0.70577	1.23362	-3.02899
h	-1.34566	-0.42111	-3.31902
h	0.82021	-1.38063	2.31519
h	2.04342	-2.31251	1.40754
h	2.57389	-1.11447	2.66599
h	0.18781	0.56925	3.23925
h	0.57817	1.97266	2.18934
h	-0.9561	1.95846	3.14079
h	-0.14021	3.80629	-1.3225
h	-0.90021	3.09453	0.145
h	0.54041	4.16633	0.30895
c	-1.31135	-3.07144	-1.25722
c	-1.6877	-3.02568	1.34622
h	-3.62311	-0.75349	4.43739
h	-4.38329	0.12117	3.04516
h	-3.93605	-1.63288	2.89373
h	-5.33793	-1.66066	-2.25424
h	-4.72369	-2.15025	-0.62832
h	-5.43111	-0.49295	-0.87338
h	3.87145	4.69183	-2.33863
h	4.54832	3.68725	-0.99651
h	4.18454	2.93365	-2.60826
h	6.1023	-1.02708	0.70674
h	5.47694	-0.35901	-0.84965
h	5.69904	0.73086	0.5868
h	-1.66022	-4.10058	-1.43402
h	-2.14672	-2.38893	-1.44186
h	-0.51816	-2.8668	-1.98097
h	-1.47186	-3.92831	1.9253

h	-2.405237	-2.134744	2.350058
h	-3.660945	-3.006885	1.415889

M_2^{B*}, E = -2100.38100724

c	-0.062453	-0.614914	0.335771
n	0.206149	-0.520829	1.822487
c	1.517166	-0.600567	2.206198
o	2.389048	-0.781434	1.120985
c	3.818242	-0.902791	1.466719
ti	-1.241062	0.323673	3.023482
n	-2.559298	1.659903	3.963581
c	-3.889100	1.688721	3.740120
o	-4.607586	2.870811	4.212930
c	-5.639509	2.546546	5.236830
n	-0.260083	-0.358133	4.661638
c	1.117853	-0.483497	4.694250
o	1.591691	-0.577198	6.014816
c	3.051729	-0.739280	6.152580
n	-2.830557	-0.870656	2.540794
c	-4.151092	-0.469581	2.473650
c	-4.662078	0.742411	3.021353
o	-6.705187	4.092114	2.838825
c	-0.985762	-0.553172	5.975586
c	1.967201	-0.528322	3.560738
c	-2.565435	-2.297407	2.091827
c	-1.935421	2.809066	4.724859
o	-4.958752	-1.411711	1.823081
c	-6.381283	-1.034376	1.685765
h	-0.782746	1.826925	2.147509
h	3.037692	-0.579808	3.737957
h	-5.726348	0.961147	2.931691
h	0.256198	-1.592882	-0.066310
h	-1.150458	-0.500374	0.202970
h	0.454219	0.195527	-0.205429
h	-2.466178	3.002103	5.673248
h	-0.893541	2.516120	4.935055
h	-1.926251	3.722099	4.104848
h	-0.748924	-1.540355	6.410341
h	-0.723981	0.236995	6.700752
h	-2.062845	-0.500696	5.751733
h	-2.803680	-2.428223	1.022185
h	-1.493496	-2.483115	2.256409
h	-3.163843	-3.007815	2.688775
h	4.336426	-1.048396	0.500201
h	4.205577	0.016977	1.950569
h	4.012874	-1.778286	2.119421
h	3.230718	-0.818642	7.241418
h	3.414411	-1.661968	5.655332
h	3.603553	0.137947	5.757109
h	-6.380593	3.365021	5.194448
h	-6.136923	1.583344	5.017871
h	-5.155309	2.507172	6.234951
h	-6.845138	-1.866754	1.123904
h	-6.877766	-0.937309	2.672616
h	-6.502391	-0.091525	1.113974
c	-5.494345	4.185808	2.629463
c	-4.864210	3.515258	1.419979
c	-4.665212	5.262846	3.309547
h	-3.850237	3.152953	1.598094
h	-5.499099	2.702024	1.067056
h	-4.812954	4.280969	0.636526

h	-1.61174	-2.16593	2.02314
h	-2.72475	-3.08577	0.99553

TS_1^{B*}, E = -2100.36157023

c	-0.992076	-0.298988	0.158099
n	-0.482160	-0.092630	1.566564
c	0.861457	-0.210227	1.759377
o	1.581720	-0.395711	0.567919
c	3.033727	-0.597042	0.734169
ti	-1.651049	0.578011	3.148887
n	-2.837857	1.615635	4.489230
c	-4.138458	1.861469	4.147081
o	-4.564796	3.155613	4.583087
c	-5.967478	3.505407	4.258473
n	-0.556494	-0.501170	4.425283
c	0.812323	-0.329168	4.283020
o	1.467331	-0.383946	5.523063
c	2.929870	-0.204000	5.473572
n	-3.257019	-0.676514	2.806907
c	-4.564701	-0.278244	2.919234
c	-4.992255	0.974286	3.451088
o	-3.181844	2.097687	1.245134
c	-1.068404	-1.048486	5.733913
c	1.492182	-0.159654	3.049233
c	-3.030800	-2.100642	2.346380
c	-2.199275	2.555954	5.484974
o	-5.461639	-1.245597	2.433484
c	-6.890018	-0.914538	2.600998
h	-0.895044	2.244675	2.876467
h	2.573433	-0.049002	3.078163
h	-6.025385	1.270391	3.290573
h	-0.862126	-1.349774	-0.156917
h	-2.060931	-0.038752	0.170362
h	-0.459366	0.355789	-0.554543
h	-2.808071	2.630610	6.403989
h	-1.214385	2.126420	5.727189
h	-2.048970	3.561604	5.057040
h	-0.600892	-2.023777	5.957142
h	-0.882683	-0.352727	6.570047
h	-2.153498	-1.179975	5.606925
h	-3.400269	-2.249858	1.316865
h	-1.943144	-2.266756	2.374660
h	-3.534229	-2.817432	3.019430
h	3.414643	-0.811861	-0.282083
h	3.534592	0.313732	1.122076
h	3.258170	-1.455987	1.398691
h	3.263542	-0.252103	6.527101
h	3.423852	-1.013704	4.897908
h	3.208525	0.781192	5.046905
h	-6.096359	4.540849	4.624905
h	-6.158354	3.473373	3.167284
h	-6.677176	2.836179	4.786381
h	-7.437263	-1.816051	2.266624
h	-7.144137	-0.702220	3.659233
h	-7.189917	-0.054399	1.967774
c	-2.515286	3.127895	1.375064
c	-2.991737	4.263914	2.268741
c	-1.365601	3.436834	0.431874
h	-2.204220	5.001669	2.440533
h	-3.812540	4.757256	1.725386
h	-3.405166	3.916231	3.221169

h	-3.596564	5.043894	3.305963	h	-0.496150	3.802619	0.980770
h	-4.824423	6.211321	2.785236	h	-1.101190	2.539300	-0.128239
h	-4.994740	5.394999	4.341760	h	-1.689314	4.220053	-0.26983