Supporting Information for:

"Investigating the Ring Expansion Reaction of Pentaphenylborole and an Azide"

Shannon A. Couchman,[a] Trevor K. Thompson,[b] David J. D. Wilson,[a] Jason L. Dutton[a] and Caleb D. Martin[b*]

[a] La Trobe University, Department of Chemistry, La Trobe Institute for Molecular Science, Melbourne, Victoria, Australia

[b] Baylor University, Department of Chemistry and Biochemistry, One Bear Place #97348, Waco, TX, USA 76798

caleb_d_martin@baylor.edu

Table of Contents

General Considerations:

All manipulations were performed under an inert atmosphere in a nitrogen-filled MBraun glove box. Solvents were dried using a JC Meyer Solvent System. Borole **A** was prepared via the literature procedure.[1] Trimethylsilyl azide, 94% was purchased from Alfa Aesar and used as received. CD_2Cl_2 used for ^1H NMR spectroscopy was purchased from EMD Millipore and dried over CaH_2. Multinuclear NMR data are listed in ppm, relative to Me_4Si (^1H) and $BF_3 \bullet Et_2O$ (^{11}B) and all NMR spectra were recorded on a Bruker 360 MHz spectrometer. FT-IR spectra were recorded on a Bruker Alpha ATR FT-IR spectrometer on the solid sample. Single crystal X-ray diffraction data were collected on a Bruker Apex II-CCD detector using Mo-K_α radiation (λ = 0.71073 Å). Crystals were selected under oil, mounted on micromounts then immediately placed in a cold stream of N_2. Structures were solved and refined using SHELXTL. Melting points were measured with a Büchi melting point apparatus system.

CAUTION: Azides can be explosive and the proper safety procedures should be followed when handling.

2: Neat trimethylsilyl azide (0.0087 g, 0.076 mmol) was added to a toluene slurry of **A** (0.0673 g, 0.151 mmol in 3 mL toluene). The color changed from blue to red immediately following the addition. After 1 minute, the solvent was removed *in vacuo* to yield red solids. The solids were extracted with diethylether (3 mL) and red crystals were grown by vapour diffusion into hexanes at -35°C overnight. The crystals were washed with ditheylether (3 X 1 mL). Yield: 0.061 g, 8% (This crystallization was reproducible); d.p 108°C (turns black). ^1H (CD_2Cl_2) 7.74-7.69 (m, 2H), 7.62-7.47 (m, 3H), 7.33-7.20 (m, 6H), 7.18-7.12 (m, 3H), 7.07-6.96 (m, 6H), 6.93-6.65 (m, 26H), 6.62-6.56 (m, 2H), 6.09-5.94 (br, 2H), -0.22 (s, 9H). FT-IR (cm^{-1} (ranked intensity)) 507(10), 543(2), 594(14), 694(1), 744(5), 768(11), 801(4), 834(15), 1028(7), 1221(3), 1249(13), 1377(9), 1436(12), 1485(6), 1591(8). Elemental Anal.

Calc. for $C_{75}H_{69}B_2N_3OSi$: C 83.54, H 6.45, N 3.90; Found C 84.30, H 6.16, N 3.32. Attempts at obtaining a $^{11}B\{^1H\}$ NMR spectrum of **2** only led to the observation of decomposition products in low intensity presumably as they were formed (over the period of one hour).

Stability: Solutions of **2** converted to borole **A** and **1** over a period of 4 days (confirmed by ^1H and $^{11}B\{^1H\}$ NMR spectroscopy, see Fig S-3 and S-4). Solutions of **2** decomposed immediately upon exposure to air. Exposing crystals of **2** to air resulted in the fading of the red color to colorless slowly over a week.

References:

1. J. J. Eisch, N. H. Hota and S. Kozima, *J. Am. Chem. Soc.*, 1969, 91, 4575-4577.

Figure S-1: FT-IR spectrum of **2**.

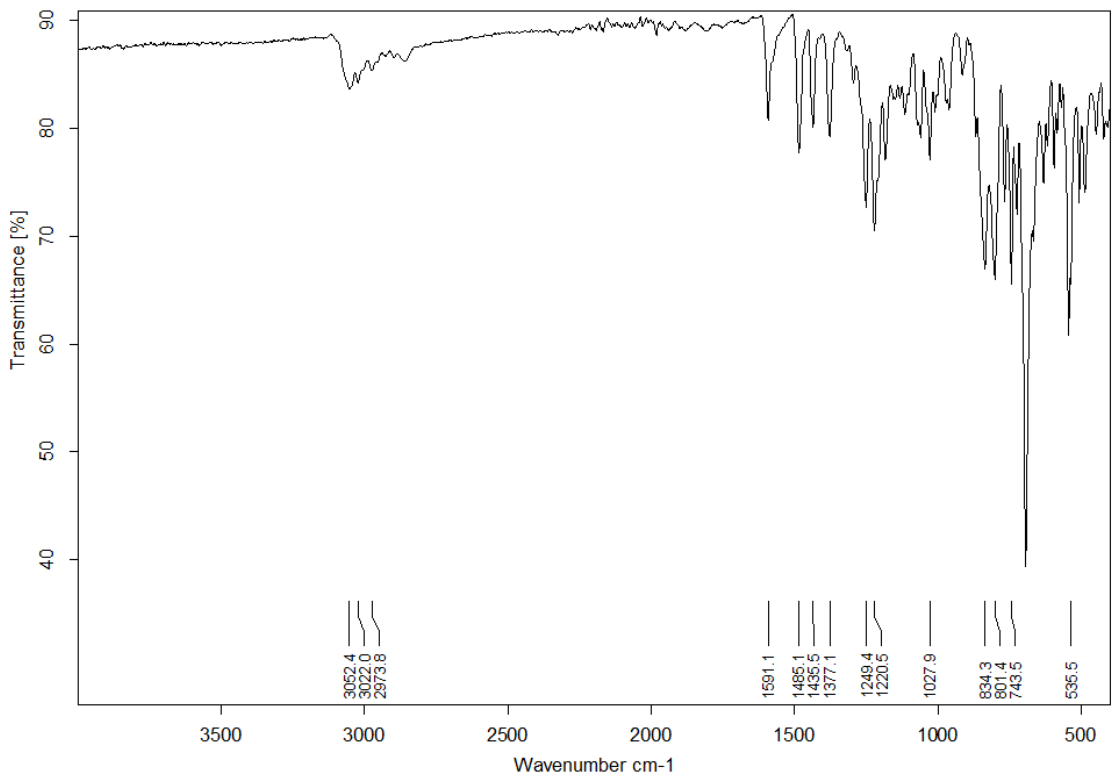
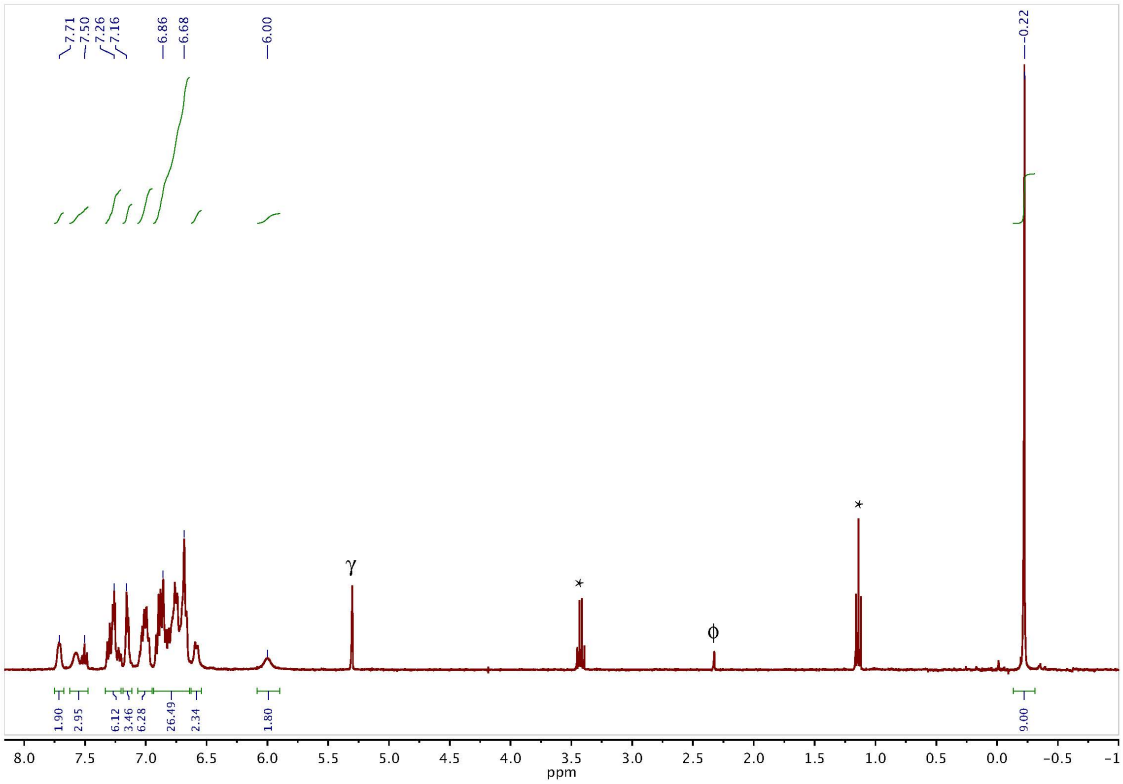


Figure S-2: ^{1}H NMR spectrum of **2**.



γ denotes $CHDCl_2$ residual from deuterated solvent, * denotes diethylether, ϕ is from a small amount of toluene remaining.

Fig. S-3: ^{1}H NMR spectrum of **2** after 4 days. This illustrates the conversion of **2** to **A** and **1** (δ_{TMS} = -0.16 ppm). Note this is the same sample used in to obtain the spectrum in Fig S-2 storing in an NMR tube with a Young's tap.

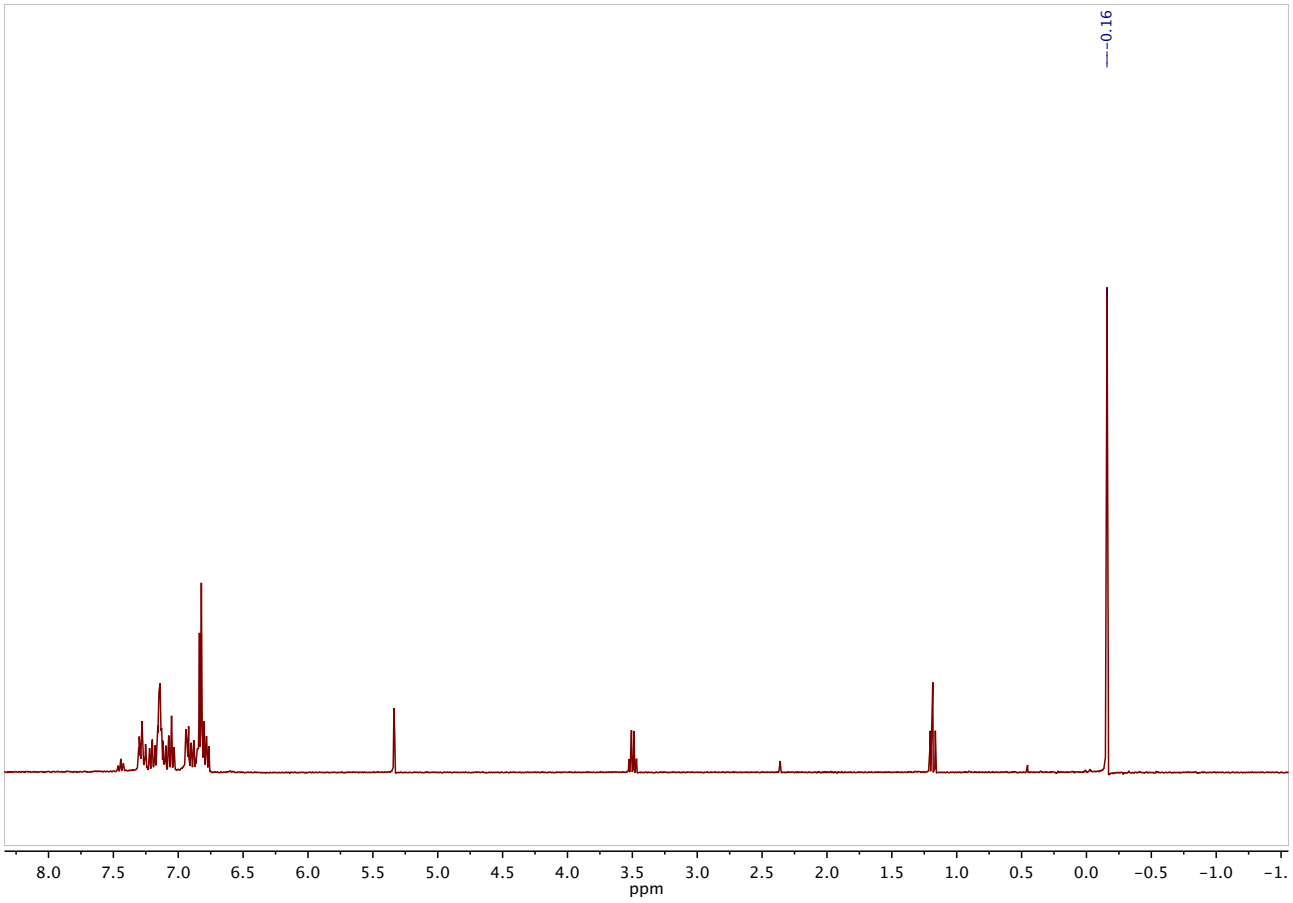


Fig. S-4: $^{11}B\{^{1}H\}$ NMR spectrum of **2** after 4 days. This illustrates the conversion of **2** to **A** (δ = 65 ppm) and **1** (δ = 40 ppm). Note this is the same sample used in to obtain the spectrum in Fig S-2 storing in an NMR tube with a Young's tap.

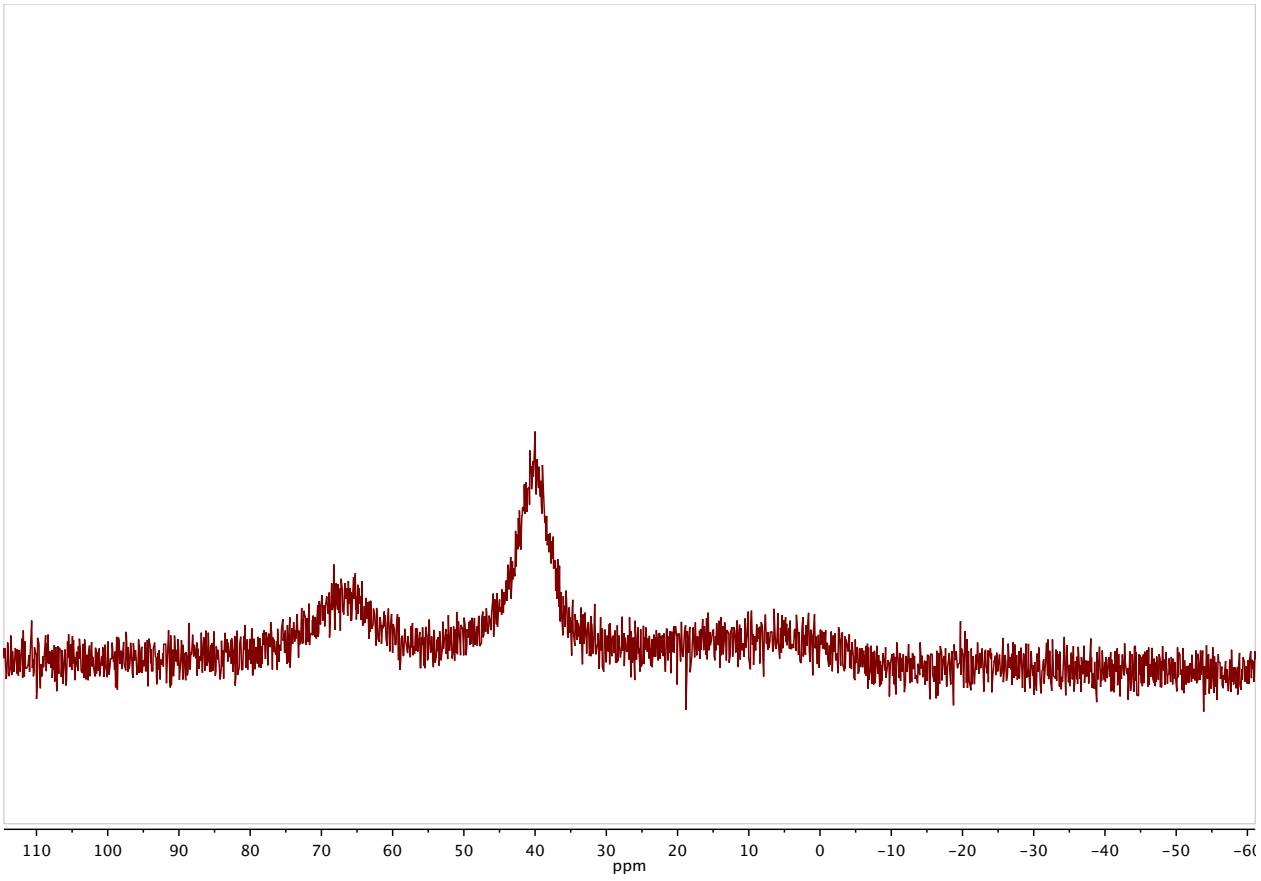


Table S1: X-ray details for **2•1.5Et$_2$O**.

Compound	**2•1.5Et$_2$O**
Empirical formula	$C_{154}H_{148}B_4N_6O_3Si_2$
CCDC	1010370
FW (g/mol)	2230.20
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	11.8934(8)
b (Å)	26.2175(18)
c (Å)	20.3647(15)
α (deg)	90
β (deg)	101.101(2)
γ (deg)	90
V (Å^3)	6231.2(8)
Z	2
D_c (Mg m^{-3})	1.189
radiation, λ (Å)	.71073
temp (K)	150(2)
$R1[I>2\sigma I]^a$	0.0608
$wR2(F^2)^a$	0.1538
GOF (S)^a	1.122

^{a} $R1(F[\mathrm{I} > 2(\mathrm{I})]) = \sum\|\|F_o| - |F_c\|\|/ \sum |F_o|$; $wR2(F^2$ [all data]) = $[w(F_o^2 - F_c^2)^2]^{1/2}$; S(all data) = $[w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = no. of data; p = no. of parameters varied; $w = 1/[^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$ and a and b are constants suggested by the refinement program.

Computational Methods

Fro computational efficiency model borole systems were employed, with methyl groups attached to the carbons on the rings (in place of phenyl groups). Two cases were considered for the B-substituent, with phenyl groups and methyl groups. Only results for B-phenyl groups are presented, as B-methyl systems yielded similar results. All calculations were carried out within Gaussian 09.[1] Geometries of all structures were optimized using the B3LYP[2, 3] density functional theory (DFT) method, inclusive of Grimme's D3 dispersion correction with Becke-Johnson damping (denoted B3LYP-D3BJ).[4, 5] All structures were optimized with the 6-31+G(d) basis set.[6, 7] Geometry optimization of transition states typically employed the quadratic synchronous transit (QST) approach.[8] Stationary points were characterised as minima or transition states by calculating the Hessian matrix analytically at the same level of theory. All structures labelled as minima exhibit no imaginary frequencies; transition states exhibit one imaginary frequency. Thermodynamic corrections were taken from these calculations (standard state of T = 298.15 K and p = 1 atm). Intrinsic reaction coordinate calculations were carried out to ensure transition states connected the appropriate local minima.

Single-point energies were calculated at the B3LYP-D3BJ and SCS-MP2[9] levels of theory inclusive of solvent effects with a polarizable continuum model (IEFPCM)[10-12] with dichloromethane solvent parameters using Truhlar's SMD solvation model.[13] Reported SCS-MP2 thermochemical data are SCS-MP2 electronic energies (inclusive of solvent effects) corrected by B3LYP-B3DJ/6-31+G(d) thermochemical corrections.

1. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian, Inc., Wallingford CT, Revision D.01, 2009.
2. A. D. Becke, *Phys. Rev. A*, 1988, 38, 3098-3100.
3. C. Lee, W. Yang and R. G. Parr, *Physical Review B*, 1988, 37, 785-789.
4. S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010, 132, 154104.
5. S. Grimme, S. Ehrlich and L. Goerigk, *J. Comp. Chem.*, 2011, 32, 1456-1465.
6. P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta*, 1973, 28, 213-222.
7. W. J. Hehre, R. Ditchfield and J. A. Pople, *J. Chem. Phys.*, 1972, 56, 2257.
8. C. Peng, P. Y. Ayala, H. B. Schlegel and M. J. Frisch, *J. Comp. Chem.*, 1996, 17, 49-56.
9. M. Gerenkamp and S. Grimme, *Chem. Phys. Letts.*, 2004, 392, 229-235.
10. C. Pomelli, J. Tomasi and V. Barone, *Theor. Chim. Acta*, 2001, 105, 446-451.
11. E. Cances, B. Mennucci and J. Tomasi, *J. Chem. Phys.*, 1997, 107, 3032-3041.
12. J. Tomasi, B. Mennucci and E. Cances, *J. Mol. Struct. (THEOCHEM)*, 1999, 464, 211-226.
13. A. V. Marenich, C. J. Cramer and D. G. Truhlar, *J. Phys. Chem. B*, 2009, 6378-6396.

Cartesian coordinates for
B3LYP-D3(BJ)/6-31+G(d) optimized geometries

Reactants

N_3-$SiMe_3$

B3LYP-D3BJ/6-31+G(d) optimized geometry (Å).
E_e = -573.532142671 (Hartrees)

0 1

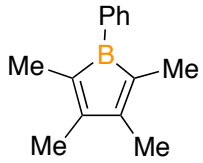
7	3.048149	0.000046	0.026705
7	1.976693	-0.000796	-0.373414
7	0.868021	-0.001906	-0.891424
6	-0.728161	-1.545218	1.092930
6	-0.728828	1.550694	1.085091
6	-1.986067	-0.003633	-1.306897
1	-0.669188	-2.453299	0.481660
1	0.101406	-1.567613	1.810421
1	-1.662914	-1.584879	1.666796
1	-0.668622	2.455599	0.469250
1	-1.664335	1.593764	1.657482
1	0.099792	1.576418	1.803566
1	-2.989291	-0.002384	-0.863248
1	-1.897866	0.880627	-1.948635
1	-1.897862	-0.891543	-1.943568
14	-0.667345	0.000060	0.021890

N_2

B3LYP-D3BJ/6-31+G(d) optimized geometry (Å).
E_e = -109.530531912 (Hartrees)

0 1

7	0.000000	0.000000	0.552564
7	0.000000	0.000000	-0.552564



For all compounds, (BR, CR) refers to the R substituent on the boron and carbon atoms of borole ring. For example, (BPh, CMe) has a phenyl group attached to B and methyl groups on all C atoms.

Compound A'
Reactant borole (BPh, CMe)

B3LYP-D3BJ/6-31+G(d) optimized geometry (Å).
E_e = -568.649967596 (Hartrees)

0 1

5	-0.107122	0.000011	-0.000121
6	-1.064760	1.261253	0.084910
6	-2.323215	0.761563	0.065533
6	-2.323188	-0.761566	-0.065570
6	-1.064713	-1.261258	-0.084901
6	1.443912	0.000026	-0.000081
6	2.181864	1.115972	-0.454086
1	1.653306	1.992817	-0.813471
6	3.576387	1.114163	-0.471345
1	4.117757	1.981265	-0.841162
6	4.277340	-0.000002	0.000037
1	5.364507	-0.000009	0.000088
6	3.576329	-1.114168	0.471331
1	4.117651	-1.981288	0.841174
6	2.181805	-1.115956	0.453931
1	1.653196	-1.992814	0.813219
6	-0.694339	2.710592	0.236858
1	0.104610	2.839980	0.978023
1	-0.316150	3.136522	-0.704500
1	-1.538715	3.334463	0.551149
6	-3.621185	1.506141	0.157224
1	-3.471784	2.580713	0.288466
1	-4.224428	1.362191	-0.750026
1	-4.231296	1.143395	0.995781
6	-3.621148	-1.506144	-0.157331
1	-3.471752	-2.580810	-0.287761
1	-4.224883	-1.361482	0.749461
1	-4.230746	-1.143916	-0.996501
6	-0.694326	-2.710623	-0.236511
1	0.104242	-2.840300	-0.978037
1	-0.315655	-3.136091	0.704855
1	-1.538822	-3.334659	-0.550129

Minimum 3'

Borole – N_3SiMe_3 adduct

BPh, CMe

B3LYP-D3BJ/6-31+G(d) optimized geometry (Å).

E_e = -1142.20275256 (Hartrees)

0 1

5	-0.383577	0.323560	-0.044550
6	0.240227	1.074978	1.235987
6	0.888503	2.169891	0.764134
6	0.891224	2.219145	-0.739128
6	0.200961	1.182524	-1.271330
6	-1.953639	0.036125	0.040831
6	-2.492328	-0.954412	0.884558
6	-2.870338	0.833176	-0.667761
6	-3.868977	-1.153575	1.006482
1	-1.819761	-1.582911	1.467139
6	-4.251031	0.654027	-0.544495
1	-2.492692	1.619021	-1.317223
6	-4.756715	-0.346148	0.289693
1	-4.249752	-1.932434	1.663376
1	-4.932309	1.291226	-1.103927
1	-5.829769	-0.494573	0.381701
7	0.405529	-1.221242	-0.173950
7	-0.206866	-2.066936	-0.856550
14	2.187667	-1.542610	0.182551
7	-0.833303	-2.798593	-1.454196
6	2.493502	-3.252627	-0.539373
6	3.220786	-0.248880	-0.680731
6	2.420823	-1.547371	2.037344
1	1.867099	-4.023469	-0.074680
1	2.327332	-3.286327	-1.622633
1	3.539762	-3.532593	-0.362709
1	3.079217	0.733404	-0.224950
1	4.280122	-0.527728	-0.600067
1	2.966741	-0.168517	-1.742460
1	3.430600	-1.911760	2.268652
1	2.314951	-0.543574	2.455696
1	1.703461	-2.208055	2.536402
6	-0.091082	0.783753	2.671610
1	-0.033439	-0.289092	2.894784
1	0.559033	1.305277	3.385177
1	-1.126520	1.079672	2.894453
6	1.503726	3.286099	1.563910
1	0.961447	4.230563	1.412826
1	1.498514	3.073146	2.636757
1	2.543624	3.474580	1.263196
6	1.633197	3.306515	-1.466156
1	1.308270	4.304694	-1.143504
1	2.714905	3.253841	-1.270622
1	1.491775	3.244548	-2.548932
6	0.056441	0.840404	-2.724054
1	0.470510	1.597668	-3.400507
1	0.565343	-0.109566	-2.960286
1	-0.997101	0.687356	-2.996893

Minimum 4'

bicyclic species with NNN attached to B,C

BPh, CMe

B3LYP-D3BJ/6-31+G(d) optimized geometry (Å).

E_e = -1142.21941305 (Hartrees)

0 1

6	-1.162409	-0.180487	1.270437
6	-2.511099	-0.406900	0.964404
6	-2.647965	-0.854537	-0.357812
6	-1.375098	-0.804941	-1.144410
5	-0.226051	-0.406625	-0.031364
7	-1.646017	0.504311	-1.868671
7	-0.894109	1.433688	-1.445432
7	0.003014	1.065285	-0.499800
6	0.174508	3.679074	0.939311
6	2.533693	1.669966	0.980915
6	1.800304	3.132292	-1.631463
1	0.805611	4.547970	1.166078
1	-0.691145	4.030092	0.365050
1	-0.191627	3.275931	1.890962
1	3.124871	0.950832	0.406065
1	3.196628	2.489036	1.290623
1	2.194602	1.158767	1.887112
1	2.351762	2.383174	-2.212316
1	0.985605	3.511111	-2.257704
1	2.484515	3.962631	-1.414185
14	1.128179	2.383710	-0.043097
6	-1.169645	-1.923373	-2.153277
1	-1.980324	-1.971411	-2.890505
1	-0.232036	-1.766032	-2.694807
1	-1.093495	-2.891710	-1.644067
6	-3.930782	-1.271043	-0.984784
1	-4.040158	-0.771623	-1.954514
1	-3.899848	-2.350583	-1.191403
1	-4.805855	-1.061097	-0.365640
6	-3.678387	-0.206030	1.899446
1	-3.346214	0.062727	2.905302
1	-4.338240	0.595672	1.544347
1	-4.286999	-1.114001	1.985483
6	-0.733256	0.325855	2.606945
1	-0.998076	-0.413397	3.377878
1	0.344390	0.485291	2.658016
1	-1.245923	1.256053	2.886159
6	1.085283	-1.300458	0.100935
6	1.316101	-2.166166	1.182372
6	2.067147	-1.266082	-0.906589
6	2.468666	-2.954444	1.265935
1	0.580699	-2.226590	1.983491
6	3.222949	-2.045226	-0.838287
1	1.924540	-0.602815	-1.758659
6	3.430002	-2.893941	0.254547
1	2.618408	-3.610625	2.120516
1	3.963679	-1.992010	-1.633152
1	4.330091	-3.500541	0.315610

Minimum 5'

8-membered ring

BPh, CMe

B3LYP-D3BJ/6-31+G(d) optimized geometry (Å).

E_e = -1142.22346866 (Hartrees)

0 1

6	-1.236384	1.273993	1.521018
6	-2.288116	0.960749	0.717305
6	-2.239197	1.367309	-0.713228
6	-1.115103	0.954191	-1.332627
5	-0.157527	0.101881	-0.406696
7	-0.286311	2.316953	1.224152
7	0.802382	2.085632	0.651944
7	1.001957	0.792788	0.166566
6	-0.293930	-1.448038	-0.273058
6	0.311964	-2.145072	0.789957
6	-1.078491	-2.189991	-1.174729
6	0.154942	-3.522006	0.942068
1	0.905715	-1.590058	1.511940
6	-1.231836	-3.571602	-1.040468
1	-1.575711	-1.672267	-1.991219
6	-0.613707	-4.240648	0.019498
1	0.626930	-4.036983	1.775218
1	-1.834679	-4.125397	-1.755871
1	-0.734387	-5.315300	0.130567
6	3.600960	0.181052	1.511195
6	2.888603	-1.037747	-1.256583
6	3.457763	1.975297	-1.003744
1	3.456487	1.043720	2.172794
1	3.207680	-0.706220	2.022021
1	4.680783	0.038410	1.376157
1	2.288851	-0.921883	-2.167233
1	3.936952	-1.151690	-1.562529
1	2.574966	-1.964953	-0.768941
1	4.526844	1.832124	-1.207082
1	2.952579	2.151449	-1.961261
1	3.338438	2.875409	-0.392721
14	2.741472	0.467707	-0.138542
6	-1.025559	0.800276	2.936504
1	-1.173514	1.622518	3.647152
1	-1.690279	-0.024031	3.199486
1	0.008233	0.452731	3.052958
6	-3.462140	0.126457	1.160881
1	-4.402334	0.606352	0.863872
1	-3.431830	-0.854573	0.666107
1	-3.500396	-0.033183	2.240131
6	-3.392186	2.139100	-1.300536
1	-4.318664	1.549833	-1.285497
1	-3.584381	3.053805	-0.724625
1	-3.204537	2.427336	-2.338088
6	-0.699182	1.260790	-2.747335
1	-1.435403	1.853940	-3.299206
1	0.247007	1.820103	-2.748741
1	-0.514926	0.339244	-3.317669

Minimum 2'

8-membered ring with borole adduct

BPh, CMe

B3LYP-D3BJ/6-31+G(d) optimized geometry (Å).

E_e = -1710.92085012 (Hartrees)

0 1

6	-0.181495	0.474680	1.308416
6	-0.468435	1.788897	1.111565
6	-0.519438	2.302379	-0.282177
6	-1.344708	1.549483	-1.041699
5	-1.988662	0.354949	-0.231612
7	0.547845	-0.308812	0.317917
7	-0.060826	-1.100873	-0.467260
7	-1.394110	-0.991939	-0.508206
6	-3.334418	0.454562	0.542553
6	-3.774293	-0.581165	1.389341
6	-4.132710	1.610091	0.453795
6	-4.960868	-0.474261	2.112899
1	-3.169416	-1.479438	1.484186
6	-5.327152	1.724270	1.167753
1	-3.806506	2.426900	-0.185316
6	-5.743075	0.680588	1.999164
1	-5.277939	-1.284424	2.764620
1	-5.931794	2.623089	1.078561
1	-6.671055	0.766288	2.558560
6	-2.070370	-3.888381	-0.428788
6	-3.883040	-1.823663	-1.910268
6	-1.085898	-2.515198	-3.032788
1	-1.039731	-4.098121	-0.118352
1	-2.683282	-3.785502	0.474540
1	-2.437692	-4.759569	-0.985610
1	-3.905921	-0.854327	-2.422594
1	-4.317479	-2.566804	-2.591451
1	-4.528682	-1.751664	-1.030387
1	-1.461925	-3.335554	-3.657148
1	-1.114834	-1.598259	-3.633339
1	-0.040231	-2.723179	-2.785586
14	-2.128514	-2.336624	-1.483181
5	2.163815	-0.241734	0.266918
6	2.779974	0.300529	1.665817
6	3.603577	-0.667846	2.137569
6	3.601069	-1.886829	1.267517
6	2.786141	-1.740075	0.194461
6	2.546831	0.671321	-1.022697
6	1.840076	0.608495	-2.235817
6	3.653792	1.538846	-0.984832
6	2.196675	1.377196	-3.346137
1	0.982942	-0.054497	-2.319171
6	4.026587	2.311537	-2.088900
1	4.237920	1.604669	-0.070658
6	3.292666	2.241774	-3.276114
1	1.619205	1.302587	-4.265667
1	4.887938	2.972671	-2.019859
1	3.573013	2.847394	-4.134571
6	2.628601	1.670976	2.274161

1	2.408974	2.420733	1.503818
1	1.804649	1.725327	3.002510
1	3.531072	2.005235	2.802634
6	4.479591	-0.605853	3.360869
1	4.213347	-1.390687	4.083422
1	5.537882	-0.764059	3.109846
1	4.398215	0.355652	3.876275
6	4.461490	-3.072674	1.617498
1	5.523474	-2.797000	1.684844
1	4.187423	-3.494237	2.595480
1	4.374034	-3.874342	0.878652
6	2.576947	-2.741259	-0.904194
1	2.629787	-2.251329	-1.886357
1	3.316041	-3.551924	-0.897372
1	1.581081	-3.204398	-0.847946
6	-1.602050	1.722221	-2.513130
1	-1.256650	0.836924	-3.064134
1	-2.676081	1.823487	-2.722430
1	-1.083212	2.586386	-2.937257
6	0.287635	3.503277	-0.686896
1	-0.077946	3.947474	-1.616198
1	0.273632	4.279453	0.086995
1	1.334096	3.213652	-0.842925
6	-0.932216	2.687502	2.225285
1	-0.537666	2.397874	3.201699
1	-0.630080	3.720107	2.028307
1	-2.030472	2.674666	2.273192
6	-0.308886	-0.294167	2.593396
1	-0.925142	0.237998	3.320528
1	-0.777989	-1.265146	2.396757
1	0.684477	-0.489600	3.014020

Minimum 1'

6-membered insertion product

BPh, CMe

B3LYP-D3BJ/6-31+G(d) optimized geometry (Å).

E_e = -1032.80391894 (Hartrees)

0 1

6	-2.803402	-0.396748	-0.224992
6	-2.271180	-1.700469	0.085674
6	-0.906485	-1.924562	0.103883
6	-1.973566	0.695139	-0.369042
7	-0.597755	0.595823	-0.153595
5	0.010022	-0.720474	-0.041782
6	1.576630	-0.862650	-0.152587
6	2.356563	-1.514870	0.819960
6	2.247118	-0.363186	-1.284079
6	3.741537	-1.627478	0.693416
1	1.871797	-1.921351	1.704905
6	3.632621	-0.477803	-1.427424
1	1.672032	0.122810	-2.069079
6	4.386773	-1.103113	-0.431612
1	4.319828	-2.121705	1.470429
1	4.122691	-0.080346	-2.313186
1	5.465537	-1.189391	-0.533933
6	-0.825911	3.151966	1.430904
6	1.756739	1.665318	1.542371
6	1.014166	3.043563	-1.084018
1	-1.416002	3.869524	0.854561
1	-1.519454	2.537713	2.017819
1	-0.214447	3.723551	2.139755
1	2.635093	1.254624	1.042175
1	2.047288	2.609877	2.022943
1	1.461601	0.968649	2.334492
1	1.414689	4.004096	-0.733460
1	1.835974	2.493779	-1.554796
1	0.265761	3.255673	-1.855368
14	0.329635	2.073932	0.383123
6	-2.523956	2.017115	-0.869494
1	-3.120194	1.856420	-1.773981
1	-3.166752	2.520043	-0.138481
1	-1.729657	2.708750	-1.146888
6	-4.299913	-0.264189	-0.422093
1	-4.681973	-1.011027	-1.129270
1	-4.842418	-0.417114	0.520841
1	-4.592924	0.716960	-0.795834
6	-3.253268	-2.831633	0.310710
1	-3.631379	-3.229106	-0.642699
1	-2.794143	-3.662111	0.850139
1	-4.125517	-2.503761	0.884481
6	-0.369026	-3.334527	0.256878
1	0.694119	-3.380910	0.010219
1	-0.478158	-3.715084	1.283772
1	-0.886754	-4.045232	-0.399926

TS1 (linking 3' and 4')
BPh, CMe

B3LYP-D3BJ/6-31+G(d) optimized geometry (Å).
E_e = -1142.19333245 (Hartrees)

0 1			
5	0.450274	0.369419	0.016671
6	1.561592	0.665404	1.138557
6	2.791776	0.599842	0.527128
6	2.683664	0.254800	-0.922011
6	1.387294	0.120735	-1.298059
7	1.808102	-1.838140	1.388571
7	0.749772	-1.866133	0.922508
7	-0.176397	-1.143831	0.398243
6	-2.784987	-2.102171	1.492455
6	-2.577902	-1.003359	-1.407246
6	-1.229483	-3.689457	-0.658168
1	-2.245647	-2.607927	2.302774
1	-3.081177	-1.109403	1.847083
1	-3.699346	-2.675334	1.291811
1	-1.912326	-0.819169	-2.255114
1	-3.433107	-1.589149	-1.770862
1	-2.947723	-0.038050	-1.052918
1	-2.116223	-4.269775	-0.942964
1	-0.575418	-3.624462	-1.535891
1	-0.697693	-4.255284	0.116070
14	-1.729695	-1.978981	-0.056975
6	1.301054	1.091371	2.551735
1	2.206489	1.161491	3.164592
1	0.806220	2.072903	2.568325
1	0.614566	0.398128	3.056688
6	4.128402	0.880760	1.144595
1	4.827797	0.056017	0.957269
1	4.580107	1.779807	0.701430
1	4.064530	1.033562	2.224405
6	3.922684	0.062673	-1.754699
1	4.573682	0.946636	-1.721004
1	4.523873	-0.783966	-1.394117
1	3.682546	-0.129171	-2.803914
6	0.911307	-0.327900	-2.646561
1	1.703968	-0.373993	-3.401908
1	0.467095	-1.333673	-2.585215
1	0.118066	0.326437	-3.031733
6	-0.777475	1.391589	-0.038596
6	-0.963808	2.272929	-1.116824
6	-1.708730	1.468756	1.014330
6	-2.036915	3.168322	-1.158586
1	-0.254933	2.260375	-1.940293
6	-2.790345	2.350702	0.982343
1	-1.588736	0.816564	1.876364
6	-2.962815	3.203361	-0.112834
1	-2.153891	3.834562	-2.010332
1	-3.496071	2.377573	1.809791
1	-3.804494	3.890521	-0.146650

TS2 (linking 4' and 5')
BPh, CMe

B3LYP-D3BJ/6-31+G(d) optimized geometry (Å).
E_e = -1142.21784915 (Hartrees)

0 1			
5	-0.277467	0.162192	-0.056376
6	-1.263039	0.741697	1.341533
6	-2.484616	0.900867	0.615765
6	-2.317288	1.335456	-0.740580
6	-1.055717	1.001520	-1.180956
7	-0.458051	1.995170	1.584083
7	0.713902	1.950574	1.133438
7	1.011044	0.864251	0.378298
6	3.732528	0.138305	1.374205
6	2.798766	-0.559020	-1.499867
6	3.327574	2.384780	-0.699278
1	3.600067	0.830487	2.214627
1	3.429189	-0.860952	1.708752
1	4.802923	0.101030	1.133964
1	2.178538	-0.260303	-2.352722
1	3.833516	-0.647046	-1.856033
1	2.464797	-1.549396	-1.176320
1	4.391579	2.343713	-0.965666
1	2.773465	2.724268	-1.582998
1	3.198390	3.139066	0.084485
14	2.718816	0.704073	-0.109184
6	-1.285462	-0.059988	2.630858
1	-0.264494	-0.221916	2.988040
1	-1.830308	0.473259	3.420363
1	-1.746325	-1.041488	2.480604
6	-3.807053	0.482470	1.170128
1	-4.641575	0.826993	0.554756
1	-3.852304	-0.616489	1.204529
1	-3.942913	0.834803	2.199286
6	-3.434160	1.964118	-1.535040
1	-4.179264	1.217318	-1.840040
1	-3.959033	2.732642	-0.956177
1	-3.056899	2.435630	-2.445974
6	-0.469676	1.363429	-2.504997
1	-0.239804	0.453530	-3.078118
1	-1.103036	2.009062	-3.121874
1	0.489702	1.874027	-2.352221
6	-0.269665	-1.421631	-0.166491
6	-1.025410	-2.116366	-1.127499
6	0.501607	-2.195408	0.720565
6	-1.016233	-3.512140	-1.202343
1	-1.629180	-1.554142	-1.836827
6	0.525881	-3.588970	0.653027
1	1.101103	-1.690736	1.474382
6	-0.236702	-4.254984	-0.311982
1	-1.608120	-4.019279	-1.960884
1	1.137224	-4.156571	1.350835
1	-0.219609	-5.340280	-0.371339

TS3 (linking 5' and 1')
BPh, CMe

B3LYP-D3BJ/6-31+G(d) optimized geometry (Å).
E_e = -1142.14903488 (Hartrees)

0 1

5	-0.001850	0.040712	-0.656545
6	-1.086956	1.205512	1.653502
6	-2.115296	1.228728	0.848633
6	-1.959382	1.741840	-0.536402
6	-0.918367	1.226834	-1.243053
7	0.447923	2.758322	1.022201
7	1.349959	2.610581	0.373502
7	1.307759	0.277033	-0.356160
6	3.372127	-0.237231	1.687735
6	3.217897	-1.993477	-0.843873
6	4.084866	0.930534	-1.061883
1	3.228211	0.759908	2.123513
1	2.762623	-0.949377	2.260319
1	4.423911	-0.514419	1.837914
1	2.960024	-2.030577	-1.909746
1	4.274098	-2.278443	-0.742934
1	2.610748	-2.749789	-0.333859
1	5.131402	0.616745	-0.951965
1	3.850796	0.956842	-2.133542
1	3.988934	1.951411	-0.674924
14	2.915845	-0.250635	-0.156553
6	-0.331901	0.785856	2.814843
1	-0.117246	1.606417	3.506646
1	-0.939795	0.023641	3.332190
1	0.603392	0.302853	2.511464
6	-3.437328	0.636004	1.324730
1	-4.214647	1.408000	1.315345
1	-3.721786	-0.167693	0.637148
1	-3.369755	0.227417	2.336420
6	-2.960624	2.780491	-0.978643
1	-3.989393	2.406603	-0.891827
1	-2.893031	3.684194	-0.356735
1	-2.808237	3.079900	-2.017085
6	-0.546115	1.685316	-2.629432
1	0.475827	2.085189	-2.603641
1	-0.520676	0.835776	-3.325553
1	-1.203683	2.452183	-3.049986
6	-0.712480	-1.374636	-0.454414
6	-1.876681	-1.735647	-1.156254
6	-0.217968	-2.299778	0.483106
6	-2.511803	-2.963188	-0.945925
1	-2.296030	-1.040059	-1.880379
6	-0.851073	-3.521895	0.716376
1	0.679565	-2.048064	1.042589
6	-2.002338	-3.860058	-0.002750
1	-3.403410	-3.219619	-1.514049
1	-0.447627	-4.212991	1.453343
1	-2.495758	-4.813513	0.169217

TS4 (linking 1' and 2')
BPh, CMe

B3LYP-D3BJ/6-31+G(d) optimized geometry (Å).
E_e = -1710.84617720 (Hartrees)

0 1

6	0.354048	-1.395686	0.754719
6	0.350627	-1.139181	2.184065
6	-0.407019	-0.106243	2.739940
6	-1.505627	0.508399	2.068802
5	-2.039203	0.001307	0.790975
7	0.745549	-0.247125	-0.107074
7	-0.351880	0.016910	-0.686971
7	-1.168819	-1.007793	-0.039471
6	-3.022286	-3.238563	0.081434
6	-3.144240	-1.300944	-2.423518
6	-0.909488	-3.277850	-2.168820
1	-3.541806	-4.057513	-0.431511
1	-2.341161	-3.683403	0.816783
1	-3.771082	-2.652109	0.620784
1	-2.615516	-0.441521	-2.848113
1	-3.355054	-2.001661	-3.242292
1	-4.090942	-0.944071	-2.015931
1	-1.525652	-3.761839	-2.938324
1	-0.140125	-2.701460	-2.693231
1	-0.424481	-4.070032	-1.594205
14	-2.083120	-2.200066	-1.165195
5	2.133547	0.457983	-0.383975
6	3.199429	0.135237	0.790227
6	4.139077	-0.701689	0.277229
6	3.841244	-1.066078	-1.141895
6	2.718031	-0.455389	-1.598307
6	3.231477	0.805765	2.129942
1	3.387833	1.886710	2.004425
1	2.273636	0.701650	2.652521
1	4.019349	0.429281	2.793365
6	5.387742	-1.208849	0.948830
1	5.435954	-2.306943	0.940193
1	6.292518	-0.854665	0.434642
1	5.452831	-0.882319	1.990473
6	4.755194	-1.981093	-1.911028
1	5.766271	-1.559797	-1.997454
1	4.866565	-2.952003	-1.407201
1	4.388148	-2.168188	-2.924363
6	2.087097	-0.573513	-2.948831
1	2.248315	0.338344	-3.542506
1	2.451951	-1.424455	-3.538286
1	0.992985	-0.667139	-2.863772
6	-2.244688	1.629745	2.776812
1	-3.100325	1.968893	2.189800
1	-2.621436	1.336063	3.766580
1	-1.596755	2.504735	2.934889
6	-0.117665	0.342590	4.160066
1	-0.178288	1.432321	4.228556
1	-0.858267	-0.058773	4.865469
1	0.874309	0.052458	4.506324

6	1.253290	-2.022421	3.021704
1	1.078101	-3.084191	2.815456
1	2.319582	-1.829758	2.831980
1	1.072836	-1.884577	4.087637
6	1.044384	-2.650629	0.276060
1	2.075035	-2.634191	0.640049
1	0.542759	-3.541348	0.665059
1	1.089107	-2.687573	-0.807224
6	1.902936	2.021138	-0.661843
6	2.692863	2.711239	-1.595914
6	0.972749	2.777305	0.075559
6	2.562418	4.088958	-1.793475
1	3.430454	2.158294	-2.173955
6	0.828408	4.153385	-0.118095
1	0.340295	2.282990	0.809566
6	1.623911	4.816865	-1.056697
1	3.189921	4.593698	-2.525005
1	0.095686	4.707958	0.464593
1	1.514441	5.887618	-1.211193
6	-3.388943	0.494226	0.149886
6	-4.645311	0.041007	0.587750
6	-3.366462	1.497283	-0.837834
6	-5.831327	0.531018	0.035019
1	-4.699433	-0.700994	1.381553
6	-4.546929	2.004646	-1.384024
1	-2.409398	1.881424	-1.181702
6	-5.784243	1.513005	-0.958605
1	-6.789685	0.156291	0.386187
1	-4.501225	2.780020	-2.144734
1	-6.704431	1.900194	-1.388481

TS5 (links 4' and 1')

BPh, CMe

B3LYP-D3BJ/6-31+G(d) optimized geometry (Å).

E_e = -1142.195552 (Hartrees)

0 1

6	-0.974872	0.081553	1.098264
6	-2.337027	-0.559910	0.971496
6	-2.381952	-1.520635	0.025178
6	-1.085176	-1.538398	-0.800478
5	-0.006258	-0.616194	0.067951
7	-1.509214	-0.594636	-1.924153
7	-1.475019	0.572896	-1.795075
7	-0.500469	0.804022	-0.185134
6	-1.037121	3.698440	-0.001500
6	1.756412	2.602099	0.820771
6	0.917651	2.526641	-2.110261
1	-0.642768	4.713168	-0.139810
1	-1.887212	3.570334	-0.682124
1	-1.413298	3.623732	1.025874
1	2.361685	1.689824	0.854734
1	2.394690	3.411796	0.442570
1	1.464235	2.862861	1.843097
1	1.650524	1.737917	-2.315765
1	0.110728	2.445420	-2.845096
1	1.419649	3.491443	-2.259848
14	0.285000	2.404201	-0.342486
6	-0.647652	-2.877006	-1.360711
1	-1.432085	-3.369158	-1.945919
1	0.241958	-2.766853	-1.988612
1	-0.379529	-3.532442	-0.524942
6	-3.553428	-2.358056	-0.395212
1	-3.835619	-2.156911	-1.437872
1	-3.312371	-3.427317	-0.332932
1	-4.433006	-2.182222	0.229681
6	-3.480082	-0.086367	1.821466
1	-4.402021	-0.642958	1.635134
1	-3.252398	-0.162836	2.892006
1	-3.683028	0.975128	1.619507
6	-0.644770	0.751600	2.410959
1	0.413971	1.007265	2.474786
1	-1.235301	1.659017	2.599202
1	-0.856295	0.051551	3.228846
6	1.524915	-0.982268	0.187624
6	2.091564	-1.371003	1.413450
6	2.384549	-0.917736	-0.924249
6	3.452934	-1.666397	1.533153
1	1.453529	-1.437876	2.292003
6	3.746204	-1.210665	-0.819721
1	1.980732	-0.626548	-1.892566
6	4.286601	-1.583648	0.414914
1	3.862997	-1.959631	2.496848
1	4.385844	-1.147439	-1.697047
1	5.346101	-1.810538	0.502965