

## Supporting Information

### Spectroscopic characterization of two boron heterocyclic radicals in the solid neon matrix

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**Table S1.** Calculated vibrational frequencies (unscaled,  $\text{cm}^{-1}$ ) and intensities (in parentheses in  $\text{km/mol}$ ) of species **A** at the B3LYP/aug-ccpVTZ level. The experimentally observed values for  $^{10}\text{B}(\text{C}_5\text{H}_8)$  are also listed for comparison.

$^{10}\text{B}$	$^{11}\text{B}$		
$\text{C}_5\text{H}_8$	$\text{C}_5\text{H}_8$	$^{10}\text{B}/^{11}\text{B}$	Exptl.
3242.1 (0)	3242.1 (0)	1.0000	
3241.0 (1)	3241.0 (1)	1.0000	
3061.0 (36)	3061.0 (36)	1.0000	
3036.3 (51)	3036.3 (51)	1.0000	
3028.6 (33)	3028.6 (33)	1.0000	
3016.8 (3)	3016.8 (3)	1.0000	
2972.7 (19)	2972.7 (19)	1.0000	
2971.1 (44)	2971.1 (44)	1.0000	
<b>1508.6 (25)</b>	<b>1481.5 (7)</b>	<b>1.0183</b>	<b>1469.1</b>
1486.3 (2)	1486.3 (2)	1.0000	
1478.9 (5)	1478.9 (5)	1.0000	
<b>1462.4 (10)</b>	<b>1448.5 (27)</b>	<b>1.0096</b>	<b>1423.2</b>
1376.5 (1)	1376.2 (1)	1.0002	
1361.4 (1)	1361.0 (1)	1.0003	
<b>1332.8 (15)</b>	<b>1332.0 (14)</b>	<b>1.0006</b>	<b>1326.1</b>
<b>1263.9 (9)</b>	<b>1263.8 (8)</b>	<b>1.0001</b>	<b>1236.9</b>
1245.7 (0)	1240.7 (0)	1.0040	
<b>1223.2 (28)</b>	<b>1220.8 (27)</b>	<b>1.0020</b>	<b>1198.8</b>
1141.4 (5)	1141.2 (5)	1.0002	
<b>1084.7 (11)</b>	<b>1084.4 (12)</b>	<b>1.0003</b>	<b>1066.7</b>
1047.0 (0)	1046.8 (0)	1.0002	
1024.6 (0)	1024.5 (0)	1.0001	
994.1 (0)	994.0 (0)	1.0001	
<b>920.7 (18)</b>	<b>919.7 (20)</b>	<b>1.0011</b>	<b>868.3</b>
<b>887.8 (16)</b>	<b>882.1 (13)</b>	<b>1.0065</b>	<b>864.9</b>
870.3 (7)	870.1 (7)	1.0002	
849.6 (2)	849.6 (2)	1.0000	
791.1 (0)	789.8 (0)	1.0017	
<b>657.5 (12)</b>	<b>647.1 (14)</b>	<b>1.0161</b>	<b>637.6</b>
<b>566.0 (70)</b>	<b>561.3 (70)</b>	<b>1.0084</b>	<b>549.2 (s)</b>
512.0 (1)	512.0 (1)	1.0000	
467.3 (5)	462.5 (5)	1.0104	
365.4 (0)	364.2 (0)	1.0033	
346.1 (8)	337.9 (7)	1.0243	
271.8 (0)	271.2 (0)	1.0022	
117.7 (0)	117.7 (0)	1.0000	

**Table S2.** Calculated vibrational frequencies (unscaled,  $\text{cm}^{-1}$ ) and intensities (in parentheses in  $\text{km/mol}$ ) of species **B** at the B3LYP/aug-ccpVTZ level. The experimentally observed values for  $^{10}\text{B}(\text{C}_5\text{H}_8)$  are also listed for comparison.

$^{10}\text{B}$	$^{11}\text{B}$		
$\text{C}_5\text{H}_8$	$\text{C}_5\text{H}_8$	$^{10}\text{B}/^{11}\text{B}$	Exptl.
3181.0 (19)	3181.0 (19)	1.0000	
3169.5 (27)	3169.5 (27)	1.0000	
3149.6 (9)	3149.6 (9)	1.0000	
3082.7 (25)	3082.7 (25)	1.0000	
3042.2 (18)	3042.2 (18)	1.0000	
3015.0 (9)	3015.0 (9)	1.0000	
2999.8 (15)	2999.8 (15)	1.0000	
2997.2 (3)	2997.2 (3)	1.0000	
1471.2 (6)	1470.4 (4)	1.0005	
<b>1465.1 (24)</b>	<b>1464.5 (18)</b>	<b>1.0004</b>	<b>1431.2</b>
1459.4 (12)	1457.9 (10)	1.0010	
<b>1419.3 (16)</b>	<b>1417.7 (9)</b>	<b>1.0011</b>	<b>1408.1</b>
<b>1399.4 (20)</b>	<b>1398.5 (18)</b>	<b>1.0006</b>	<b>1367.6</b>
<b>1369.4 (174)</b>	<b>1355.9 (152)</b>	<b>1.0100</b>	<b>1342.1(s)</b>
1319.9 (7)	1316.7 (12)	1.0024	
<b>1257.7 (38)</b>	<b>1248.2 (44)</b>	<b>1.0076</b>	<b>1240.6</b>
<b>1165.6 (47)</b>	<b>1142.0 (55)</b>	<b>1.0207</b>	<b>1149.4</b>
1128.7 (4)	1110.7 (7)	1.0162	
1110.1 (6)	1107.6 (5)	1.0023	
1098.2 (3)	1097.9 (4)	1.0003	
1061.5 (1)	1057.9 (2)	1.0034	
990.2 (1)	990.1 (1)	1.0001	
<b>936.7 (12)</b>	<b>936.5 (12)</b>	<b>1.0002</b>	<b>929.0</b>
<b>923.4 (15)</b>	<b>909.5 (16)</b>	<b>1.0153</b>	<b>918.8</b>
837.2 (0)	836.4 (0)	1.0010	
785.6 (0)	783.3 (0)	1.0029	
777.8 (6)	777.2 (6)	1.0008	
753.5 (1)	751.1 (1)	1.0032	
<b>732.1 (17)</b>	<b>732.0 (17)</b>	<b>1.0001</b>	<b>719.8</b>
<b>635.7 (28)</b>	<b>634.6 (28)</b>	<b>1.0017</b>	--
527.4 (0)	525.5 (0)	1.0036	
461.1 (0)	458.7 (0)	1.0052	
302.9 (2)	299.4 (2)	1.0117	
272.7 (0)	271.1 (0)	1.0059	
135.3 (0)	135.1 (0)	1.0015	
29.0 (1)	29.0 (1)	1.0000	

**Table S3.** The computed electronic transition energies ( $\Delta E$ ), and the oscillator strengths ( $f$ ) of species **A** by the B3LYP-TD/ aug-cc-pVTZ level of theory.

States	Transition Energy (nm)	Oscillator strength ( $f$ )
S <sub>1</sub> ( 2-A'' )	534.9	0.0000
<b>S<sub>2</sub> ( 2-A'' )</b>	<b>427.7</b>	<b>0.0679</b>
S <sub>3</sub> ( 1-A' )	401.1	0.0024
S <sub>4</sub> ( 2-A'' )	317.9	0.0002
S <sub>5</sub> ( 2-A' )	289.4	0.0042
S <sub>6</sub> ( 2-A' )	281.3	0.0052
S <sub>7</sub> ( 2-A'' )	275.1	0.0000
S <sub>8</sub> ( 2-A'' )	270.5	0.0007
S <sub>9</sub> ( 2-A' )	248.7	0.0069
S <sub>10</sub> ( 2-A'' )	242.3	0.0134
S <sub>11</sub> ( 3-A' )	241.7	0.0096
S <sub>12</sub> ( 2-A' )	238.1	0.0001
S <sub>13</sub> ( 2-A'' )	238.1	0.0002
S <sub>14</sub> ( 2-A' )	235.2	0.0090
S <sub>15</sub> ( 2-A'' )	231.5	0.0008
S <sub>16</sub> ( 3-A'' )	219.1	0.0000
S <sub>17</sub> ( 3-A' )	216.6	0.0169
<b>S<sub>18</sub> ( 2-A'' )</b>	<b>215.0</b>	<b>0.0606</b>
S <sub>19</sub> ( 3-A' )	214.4	0.0038
S <sub>20</sub> ( 2-A'' )	213.2	0.0143
S <sub>21</sub> ( 2-A'' )	211.4	0.0000
S <sub>22</sub> ( 3-A'' )	209.9	0.0043
S <sub>23</sub> ( 2-A'' )	207.1	0.0107
S <sub>24</sub> ( 2-A' )	206.4	0.0072
S <sub>25</sub> ( 3-A' )	205.3	0.0015

**Table S4.** Calculated vibrational frequencies (unscaled,  $\text{cm}^{-1}$ ) and intensities (in parentheses in  $\text{km/mol}$ ) of the species **A** isomers 2,3,4-trihydroborinine and 2,3,6-trihydroborinine at the B3LYP/aug-ccpVTZ level.

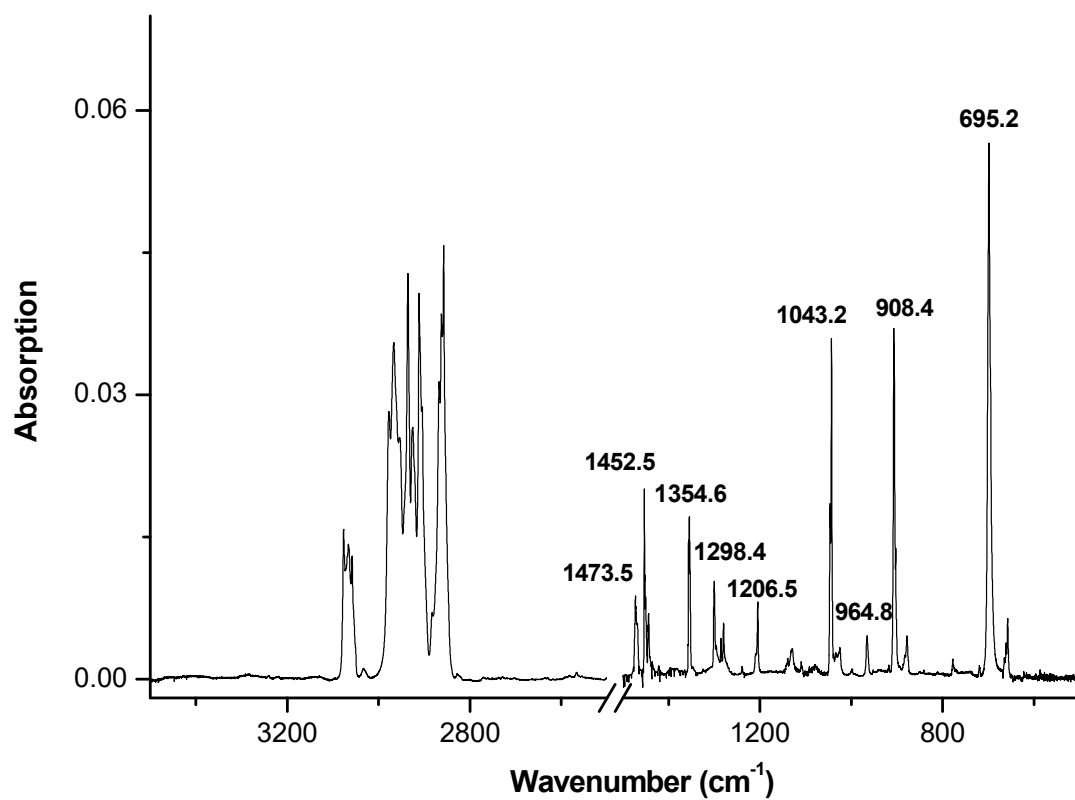
2,3,4-trihydroborinine	2,3,6-trihydroborinine
3145.3 (18)	3147.8 (34)
3095.0 (27)	3119.9 (13)
3052.8 (34)	3061.7 (17)
3045.7 (19)	3032.8 (31)
3036.2 (34)	3014.3 (8)
3015.8 (30)	2995.1 (35)
2974.6 (12)	2965.9 (9)
2970.4 (13)	2941.2 (6)
<b>1578.7 (31)</b>	<b>1697.6 (11)</b>
1494.7 (3)	1488.8 (3)
<b>1466.4 (14)</b>	1422.7 (5)
1424.4 (4)	<b>1406.9 (17)</b>
<b>1411.3 (31)</b>	1405.0 (3)
1374.7 (1)	<b>1366.4 (16)</b>
1361.4 (5)	<b>1301.2 (26)</b>
<b>1320.5 (15)</b>	1277.1 (3)
1256.6 (3)	<b>1245.1 (12)</b>
<b>1225.6 (11)</b>	<b>1176.8 (27)</b>
<b>1166.2 (29)</b>	1157.0 (4)
1152.3 (4)	1130.2 (5)
1134.6 (4)	1083.8 (6)
1044.3 (1)	1021.9 (4)
1025.9 (0)	1001.6 (0)
984.6 (8)	<b>939.8 (11)</b>
949.5 (6)	904.9 (6)
923.2 (8)	872.8 (3)
842.3 (2)	844.6 (1)
819.2 (3)	<b>784.6 (12)</b>
766.1 (1)	774.8 (8)
<b>704.9 (20)</b>	<b>653.0 (23)</b>
661.3 (8)	589.1 (3)
504.8 (0)	490.8 (1)
428.5 (1)	448.0 (0)
288.6 (3)	371.3 (0)
225.4 (1)	178.9 (5)
174.6 (15)	82.3 (4)

**Table S5.** Calculated vibrational frequencies (unscaled,  $\text{cm}^{-1}$ ) and intensities (in parentheses in  $\text{km/mol}$ ) of the species **B** isomer 1-methylene-2,3-dihydro-*1H*-borole radical at the B3LYP/aug-ccpVTZ level.

$^{10}\text{B}$	$^{11}\text{B}$	
$\text{C}_5\text{H}_8$	$\text{C}_5\text{H}_8$	$^{10}\text{B}/^{11}\text{B}$
3180.8 (14)	3180.8 (14)	1.0000
3160.3 (27)	3160.3 (27)	1.0000
3125.8 (24)	3125.8 (24)	1.0000
3108.0 (16)	3108.0 (16)	1.0000
3042.4 (22)	3042.4 (22)	1.0000
3018.9 (15)	3018.9 (15)	1.0000
3017.1 (6)	3017.1 (6)	1.0000
3002.4 (28)	3002.4 (28)	1.0000
<b>1583.2 (107)</b>	<b>1581.8 (99)</b>	<b>1.0009</b>
<b>1476.6 (44)</b>	<b>1472.2 (37)</b>	<b>1.0030</b>
1465.7 (13)	1465.4 (10)	1.0002
1430.4 (9)	1430.3 (10)	1.0001
<b>1406.6 (59)</b>	<b>1397.6 (55)</b>	<b>1.0064</b>
1323.1 (5)	1320.7 (3)	1.0018
<b>1282.5 (32)</b>	<b>1259.2 (40)</b>	<b>1.019</b>
1219.3 (2)	1219.2 (2)	1.0001
<b>1197.5 (38)</b>	<b>1179.5 (28)</b>	<b>1.0153</b>
1155.9 (7)	1138.4 (17)	1.0154
1129.4 (0)	1128.6 (1)	1.0007
1102.1 (5)	1098.3 (7)	1.0035
1024.8 (0)	1024.8 (0)	1.0000
988.4 (2)	987.9 (3)	1.0005
<b>937.8 (25)</b>	<b>932.7 (23)</b>	<b>1.0055</b>
902.1 (11)	902.1 (11)	1.0000
819.6 (2)	819.3 (2)	1.0004
<b>816.6 (16)</b>	<b>810.9 (18)</b>	<b>1.0070</b>
763.7 (1)	762.9 (1)	1.0011
<b>750.0 (31)</b>	<b>749.7 (30)</b>	<b>1.0004</b>
748.3 (3)	745.7 (3)	1.0035
690.2 (3)	686.8 (4)	1.0050
545.9 (1)	543.1 (1)	1.0052
437.6 (2)	432.9 (2)	1.0109
270.7 (0)	269.2 (0)	1.0056
253.2 (1)	251.2 (1)	1.0080
198.4 (0)	198.2 (0)	1.0010
99.9 (0)	99.8 (0)	1.0010

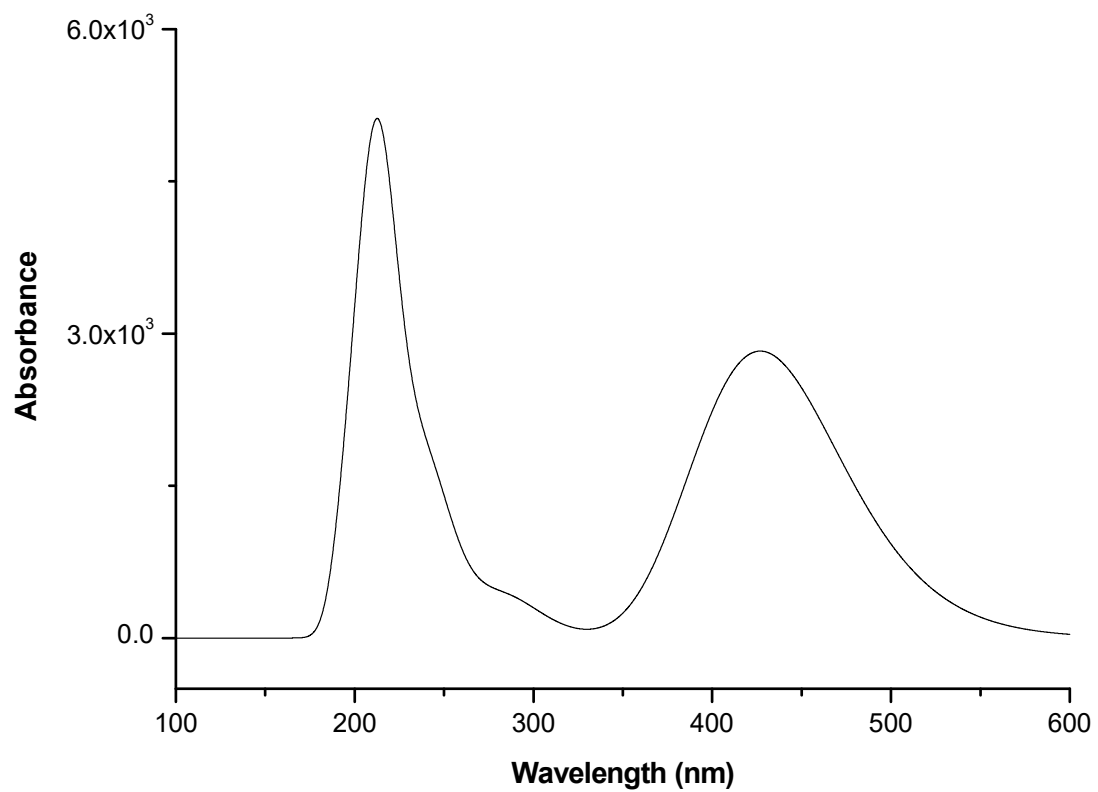
**Table S6.** Calculated vibrational frequencies (unscaled,  $\text{cm}^{-1}$ ) and intensities (in parentheses in  $\text{km/mol}$ ) of the species **B** isomer 1-methylene-2,5-dihydro-*1H*-borole radical at the B3LYP/aug-ccpVTZ level.

$^{10}\text{B}$	$^{11}\text{B}$	
$\text{C}_5\text{H}_8$	$\text{C}_5\text{H}_8$	$^{10}\text{B}/^{11}\text{B}$
3180.1 (12)	3180.1 (12)	1.0000
3171.3 (40)	3171.3 (40)	1.0000
3146.6 (9)	3146.6 (9)	1.0000
3107.0 (14)	3107.0 (14)	1.0000
2988.1 (0)	2988.1 (0)	1.0000
2987.4 (24)	2987.4 (24)	1.0000
2980.6 (32)	2980.6 (32)	1.0000
2976.4 (28)	2976.4 (28)	1.0000
1658.3 (2)	1658.3 (2)	1.0000
<b>1476.9 (35)</b>	<b>1472.7 (26)</b>	<b>1.0029</b>
1414.2 (9)	1413.7 (7)	1.0004
<b>1408.9 (23)</b>	<b>1408.9 (24)</b>	<b>1.0000</b>
1376.8 (1)	1375.4 (0)	1.0010
<b>1342.9 (69)</b>	<b>1317.1 (66)</b>	<b>1.0196</b>
<b>1243.5 (50)</b>	<b>1238.7 (43)</b>	<b>1.0039</b>
1181.0 (9)	1170.4 (15)	1.0091
<b>1137.3 (16)</b>	<b>1128.5 (12)</b>	<b>1.0078</b>
<b>1131.0 (13)</b>	<b>1110.7 (19)</b>	<b>1.0183</b>
1106.2 (1)	1105.8 (0)	1.0004
1105.8 (0)	1101.9 (2)	1.0035
979.4 (0)	979.4 (0)	1.0000
946.3 (0)	946.1 (0)	1.0002
<b>941.1 (15)</b>	<b>941.1 (15)</b>	<b>1.0000</b>
917.5 (2)	905.7 (2)	1.0130
809.6 (0)	809.2 (0)	1.0005
773.7 (5)	769.6 (6)	1.0053
<b>760.9 (47)</b>	<b>760.9 (47)</b>	<b>1.0000</b>
725.9 (3)	725.9 (3)	1.0000
<b>683.9 (26)</b>	<b>680.9 (27)</b>	<b>1.0044</b>
626.8 (0)	626.8 (0)	1.0000
538.1 (0)	535.3 (0)	1.0052
348.6 (0)	348.6 (0)	1.0000
335.4 (4)	329.4 (3)	1.0182
271.3 (0)	269.9 (0)	1.0052
117.9 (0)	117.7 (0)	1.0017
116.7 (0)	116.7 (0)	1.0000

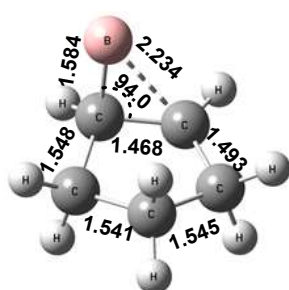


**Figure S1.** Infrared spectra in the 3500-2500 and 1500-500 cm<sup>-1</sup> region from 15 minutes deposition of net 0.05 % cyclopentene in solid argon.

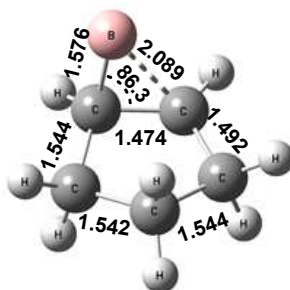




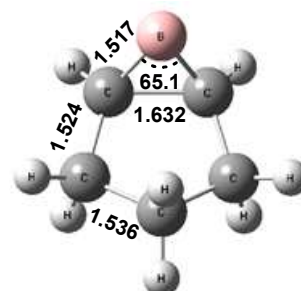
**Figure S2.** The calculated electronic absorptions spectrum of species **A** at the B3LYP-TD/aug-cc-pVTZ level of theory.



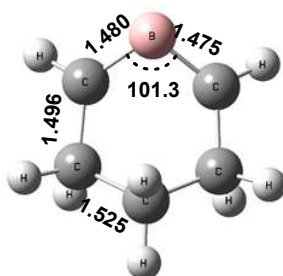
II,  $C_1, ^2A$



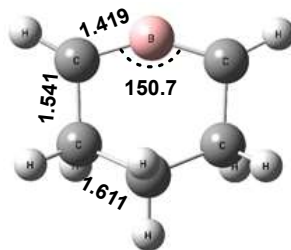
TS1,  $C_1, ^2A$



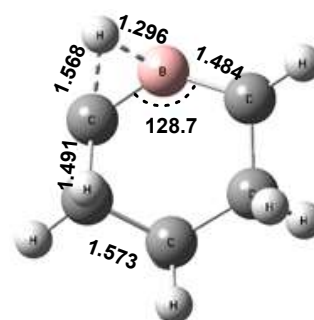
I2,  $C_s, ^2A'$



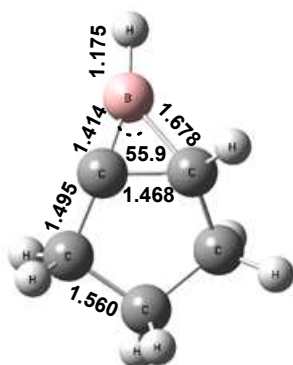
TS2,  $C_1, ^2A$



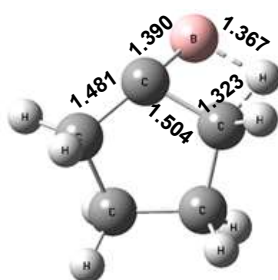
A,  $C_s, ^2A'$



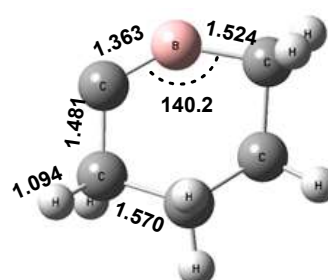
TS3,  $C_1, ^2A$



I3,  $C_1, ^2A$

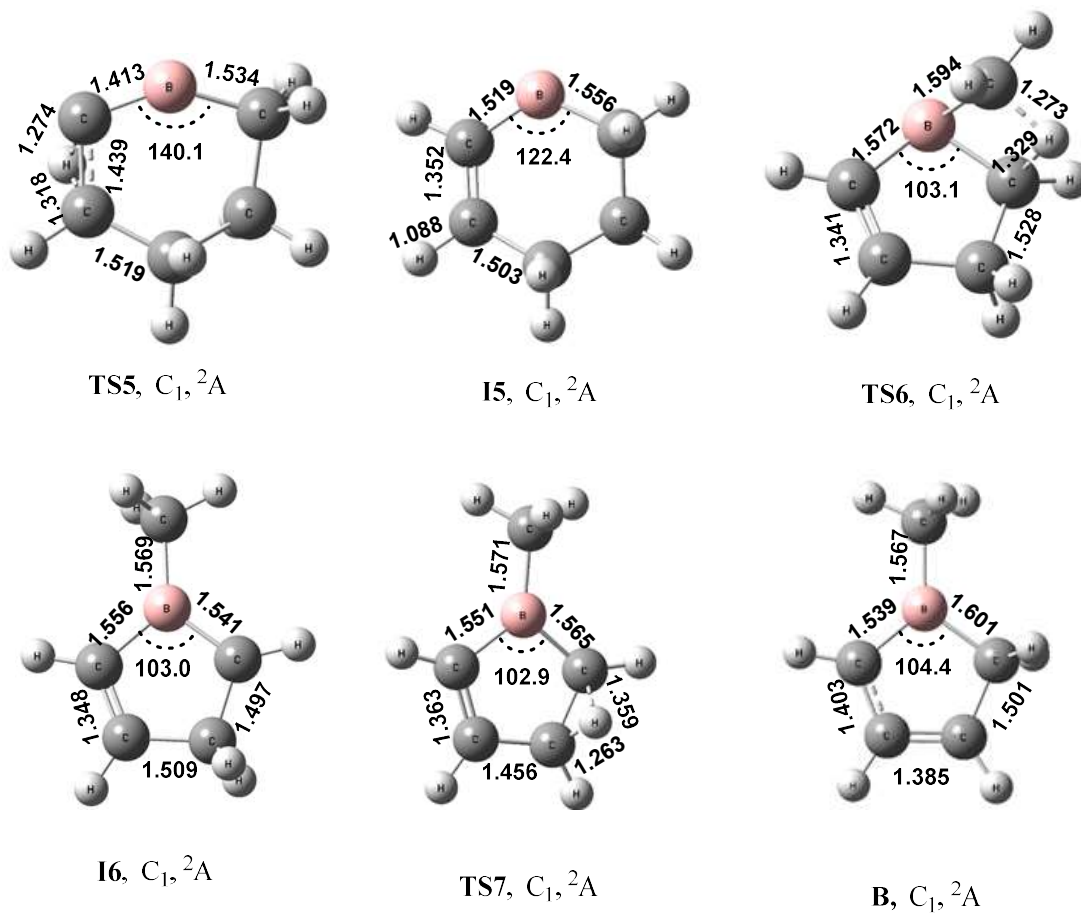


TS4,  $C_1, ^2A$

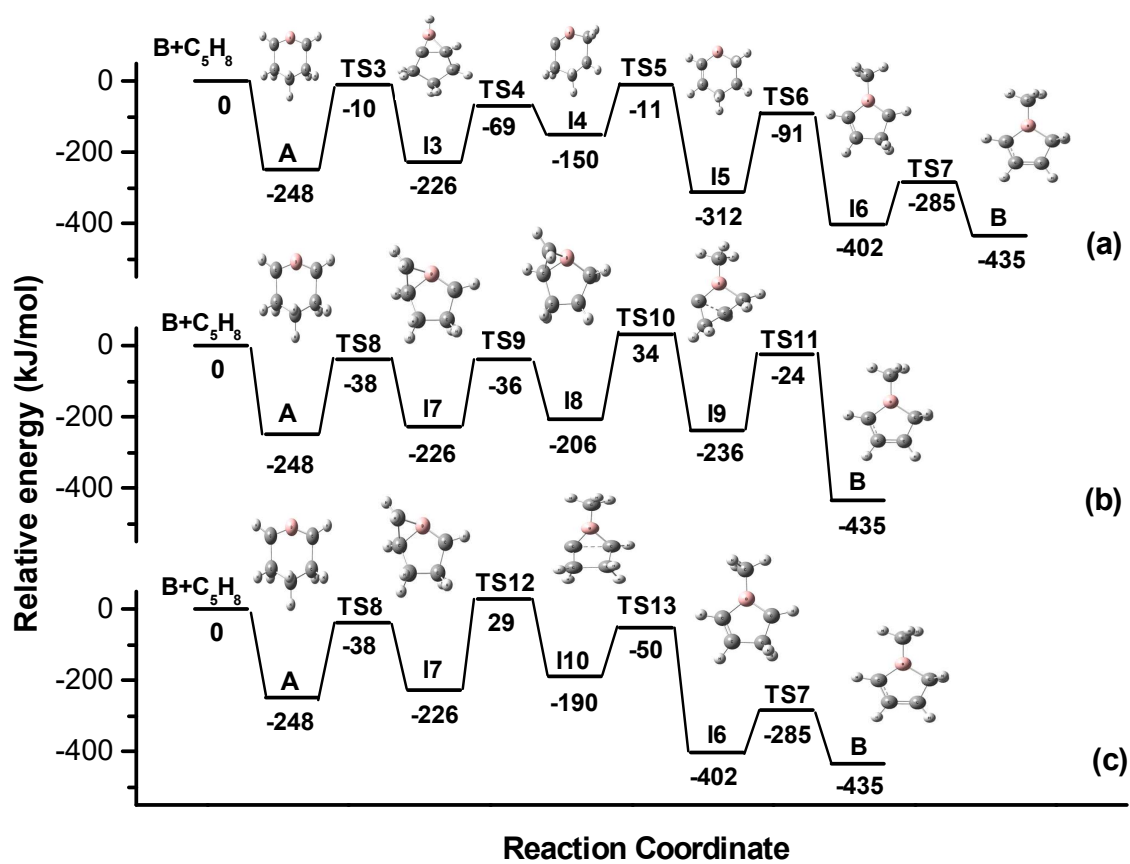


I4,  $C_1, ^2A$

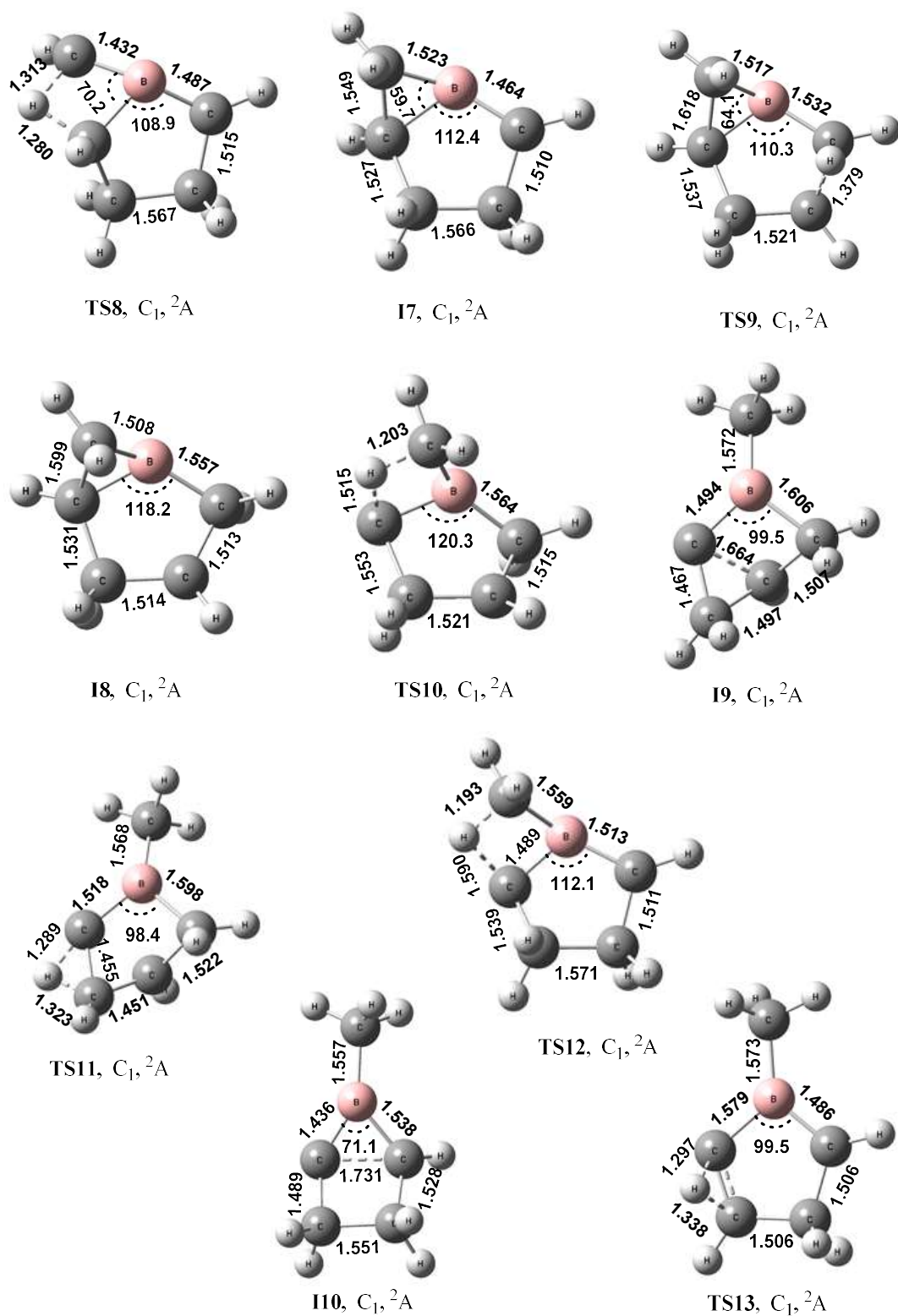
**Figure S3.** Optimized structures of the intermediates and transition states involved in the reaction pathways as shown in figure 7 at the B3LYP/aug-ccpVTZ level. Bond lengths in angstroms and bond angles in degrees.



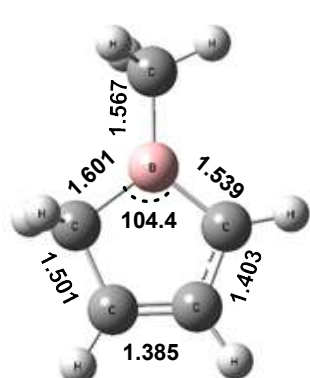
**Figure S4.** Optimized structures of the intermediates and transition states involved in the reaction pathways as shown in figure 7 at the B3LYP/aug-ccpVTZ level. Bond lengths in angstroms and bond angles in degrees.



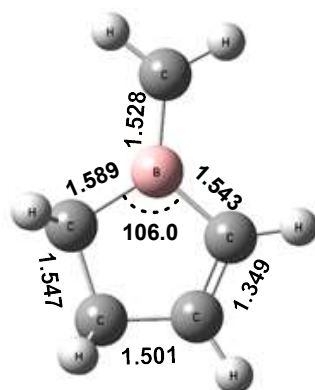
**Figure S5.** Three potential reaction pathways for the isomerization reactions from **A** to **B** were calculated at the CCSD(T)/cc-pVTZ //B3LYP/aug-cc-pVTZ level of theory. The energies are given in kJ/mol after zero-point energy corrections.



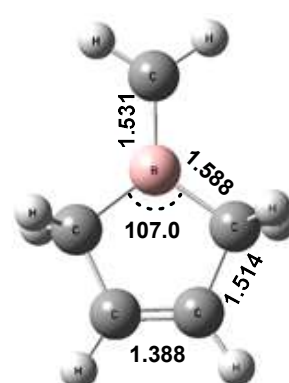
**Figure S6.** Optimized structures of the corresponding intermediates and transition states involved in the reaction pathways from A to B in Figure S4 at the B3LYP/aug-ccpVTZ level. (bond lengths in angstroms and bond angles in degrees).



**B**,  $C_1$ ,  $^2A$   
 $E = 0$  kJ/mol



**B-isomer1**,  $C_s$ ,  $^2A''$   
 $E = 49$  kJ/mol



**B-isomer2**,  $C_{2v}$ ,  $^2B_1$   
 $E = 71$  kJ/mol

**Figure S7.** Optimized structures of species **B** and two isomers (1-methylene-2,3-dihydro-*1H*-borole radical and 1-methylene-2,5-dihydro-*1H*-borole radical) at the B3LYP/aug-ccpVTZ level (bond lengths in angstrom and bond angles in degrees). The energy values shown are relative energy calculated at the CCSD(T)/cc-pVTZ //B3LYP/aug-cc-pVTZ level.

**Table S7.** Calculated atomic coordinates (in Angstroms) of species **A** and **B** at the B3LYP/aug-cc-pVTZ level.

(a) **A**, ( $C_s$ ,  $^2A''$ )

C	-0.10756600	-0.58836500	1.31053500
C	-0.10756600	0.95014800	1.36041600
C	-0.10756600	0.95014800	-1.36041600
C	-0.10756600	-0.58836500	-1.31053500
C	0.47385300	-1.16208300	0.00000000
H	-0.18010800	1.45114700	2.30990600
H	1.54955100	-0.97103900	0.00000000
H	-1.13303400	-0.95119500	1.45375700
H	-0.18010800	1.45114700	-2.30990600
H	0.47548800	-0.97817900	-2.14908100
H	-1.13303400	-0.95119500	-1.45375700
H	0.34262200	-2.24653200	0.00000000
H	0.47548800	-0.97817900	2.14908100
B	-0.09567800	1.36102400	0.00000000

(b) **B**, ( $C_1$ ,  $^2A$ )

C	-0.21674200	1.24493100	-0.00012900
C	-1.52731600	0.74301100	0.00009100
C	-1.56603800	-0.64091000	0.00012500
H	-0.01729100	2.30920800	-0.00019500
H	-2.42132700	1.35566500	0.00022600
H	-2.48099100	-1.21905500	0.00030700
B	0.75950900	0.05500300	-0.00027200
C	2.32666900	0.05342600	0.00003900
H	2.77596200	1.04711600	-0.00290400
H	2.71313700	-0.48599100	0.87170500
H	2.71427000	-0.49203900	-0.86728500
C	-0.18746500	-1.23643100	-0.00013000
H	-0.02782700	-1.88713900	0.86814900
H	-0.02812800	-1.88694200	-0.86861600