

Supporting Information

Hydrogen Liberation from Gaseous 2-Bora-1,3-diazacycloalkanium Cations

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Figure S-1. Comparison of the IR absorption spectrum recorded for solid **4** ($n=1$) (upper panel) compared with the absorptions predicted by an anharmonic frequency calculation^a on the isolated molecule (lower panel) at B3LYP/aug-cc-pVTZ (using harmonic intensities with unscaled anharmonic frequencies).

Figure S-2. Collisionally Activated Dissociation (CAD) MS/MS spectrum of tetradeuterated ion **9** at 10V lab frame energy. The parent ion, m/z 77, gives m/z 74 (loss of HD) and m/z 57 (loss of ND₃).

Figure S-3. CAD MS/MS spectra of ion **4** at 10V lab frame energy, which shows the parent ion at m/z 87 and produces ions at m/z 85 (loss of H₂), m/z 70 (loss of ammonia), and m/z 68 (loss of H₂ and ammonia). Inset: CAD of ion **10** at 10V, which shows a parent ion at m/z 91 and daughter ions m/z 89 (loss of HD), a much smaller m/z 88 (loss of H₂), m/z 71 (loss of ND₃), and m/z 69 (loss of H₂ and ND₃ or of HD and NHD₂).

Figure S-4. CAD MS/MS spectra of ion **5** at 10V lab frame energy which shows the parent ion m/z 101 which produces m/z 99 (loss of H₂), m/z 84 (loss of ammonia), and lower mass ions. Inset: a CAD of ion **11** at 10V, which shows a parent ion at m/z 105 and daughter ions m/z 102 (loss of HD) and m/z 103 (loss of H₂), m/z 85 (loss of ND₃), and m/z 86 (loss of NHD₂).

Figure S-5. CAD MS/MS spectra of ion **6** at 10 V lab frame energy which shows the parent ion m/z 115 and daughter ions m/z 113 (loss of H₂), m/z 98 (loss of ammonia), m/z 96 (loss of H₂ and ammonia), and other daughter ions.

Figure S-6. CAD MS/MS spectra of ion **17** (m/z 157) and its d_4 analogue (m/z 161 from exchange with EtOD solvent) at 10V lab frame energy with argon collision gas.

Figure S-7. CAD spectra of ion **18** and its isotopomers (left inset a ¹⁰B & two ¹¹Bs at natural abundance; right inset the d_4 analogue from exchange in EtOD) at 10V lab frame energy with argon collision gas.

Figure S-8. Experimental IRMPD spectra (blue silhouette) vs. harmonic calculated normal modes (solid red line, scaled by 0.97 with 30 cm⁻¹ Gaussian line broadening)^a of **11**: without scrambling of the protons in the NBN branch (top) and shows a good fit except for a mismatch of peaks in the 1750 to 1950 cm⁻¹ region; with scrambling of the protons in the NBN branch (middle) which shows a matching peak in the 1750 to 1950 cm⁻¹ region but a poor fit for the rest; and a branched isomer which was found to be more stable than the two cyclic isomers on top(bottom) but shows a poor fit to the experimental peaks.

Figure S-9. Experimental IRMPD spectrum (blue silhouette) vs. harmonic calculated normal mode (solid red line, scaled by 0.97 with 30 cm⁻¹ Gaussian line broadening)^a of **8**: without scrambling of the protons in the NBN branch (top), which shows a good fit to experimental band positions; with scrambling of the protons in the NBN branch (middle) which shows a poor fit compared to the unscrambled isomer; and a branched isomer which was found to be more stable than the two cyclic isomers on top (bottom) but also shows a poor fit to the experimental bands.

Figure S-10. A comparison of harmonic normal modes (solid red line, unscaled with 30 cm⁻¹ Gaussian line broadening) and anharmonic vibrations (blue silhouette, unscaled using harmonic intensities and 30

cm^{-1} gaussian line broadening)^a calculated for **11**, which shows the same peaks positions below 800 cm^{-1} with a shift of about 3% in the wavenumbers above 800 cm^{-1} .

Figure S-11. Comparison of the experimental IRMPD spectrum (blue silhouette) with the harmonic calculated normal mode (solid red line, scaled by 0.97 with 30 cm^{-1} Gaussian line broadening)^a of a ring-opened isomer of **11** which, gives a poor match to the experimental spectrum.

Figure S-12. Comparison of the experimental IRMPD spectrum (blue silhouette) with the harmonic calculated normal modes (solid red line, scaled by 0.97 with 30 cm^{-1} Gaussian line broadening)^a of a ring-opened isomer of **11**, which does not match the experimental spectrum.

Figure S-13. Experimental IRMPD (blue silhouette) vs. harmonic calculated normal mode (solid red line, scaled by 0.97 with 30 cm^{-1} Gaussian line broadening)^a of **12** without the scrambling of the protons in the NBN branch of the cyclic isomer (top) and a branched isomer (bottom) which was found to be more stable than the cyclic isomers but gives a poor match to the experimental spectrum.

Figure S-14. Comparison of the experimental IRMPD spectrum (blue silhouette) with harmonic calculated modes of **12** (solid red line, scaled by 0.97 with 30 cm^{-1} Gaussian line broadening)^a when scrambling of the protons in the NBN branch takes place, which shows a poor match to the experimental spectrum.

Figure S-15. Comparison of the experimental IRMPD spectrum (blue silhouette) with the harmonic calculated normal mode (solid red line, scaled by 0.97 with 30 cm^{-1} Gaussian line broadening)^a of a ring-opened isomer of **12**, which gives a poor match to the experimental spectrum.

Figure S-16. Comparison of the experimental IRMPD (blue silhouette) of the m/z 57 daughter ion of **5** (solid red lines, scaled by 0.97 with 30 cm^{-1} Gaussian line broadening)^a after a loss of H_2 and propene. The daughter ion in which the charge of the molecule is in the inner nitrogen (top panel) shows a better fit to the experimental spectrum than does the daughter ion in which the charge is in the outer nitrogen (bottom panel).

Figure S-17. Comparison of the experimental IRMPD (blue silhouette) with the harmonic calculated normal modes (solid red lines, scaled by 0.97 with 30 cm^{-1} Gaussian line broadening)^a of a branched isomer of **6**. The branched isomer was found to be more stable than the cyclic isomer, however, the comparison of

Figure S-18. Comparison of the experimental IRMPD spectrum (blue silhouette) with the harmonic calculated normal modes (red solid line, scaled by 0.97 with 30 cm^{-1} Gaussian line broadening)^a of a branched isomer of **16**, in which the charge of the molecule is on the exocyclic nitrogen, which gives a worse match to the experimental spectrum than does the structure in Chart 2.

Figure S-19. Comparison of the experimental IRMPD spectrum (blue silhouette) with the harmonic calculated normal modes (red solid line, scaled by 0.97 with 30 cm^{-1} Gaussian line broadening)^a of another branched isomer of **16**, in which the charge of the molecule is on the endocyclic nitrogen, which also gives a poor match to the experimental spectrum.

^a Gaussian 03, Revision C.02, Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Scuseria, G.E.; Robb, M.A.; Cheeseman, J.R.; Montgomery, Jr., J.A.; Vreven, T.; Kudin, K.N.; Burant, J.C.; Millam, J.M.; Iyengar, S.S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G.A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H.P.; Cross, J.B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R.E.; Yazyev, O.; Austin, A.J.; Cammi, R.; Pomelli, C.; Ochterski, J.W.; Ayala, P. Y.; Morokuma, K.; Voth, G.A.; Salvador, P.; Dannenberg, J.J.; Zakrzewski, V.G.; Dapprich, S.; Daniels, A. D.; Strain, M.C.; Farkas, O.; Malick, D.K.; Rabuck, A.D.; Raghavachari, K.; Foresman, J.B.; Ortiz, J.V.; Cui, Q.; Baboul, A.G.; Clifford, S.; Cioslowski, J.; Stefanov, B.B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R.L.; Fox, D.J.; Keith, T.; Al-Laham, M.A.; Peng, C.Y.; Nanayakkara, A.; Challacombe, M.; Gill, P.M.W.; Johnson, B.; Chen, W.; Wong, M.W.; Gonzalez, C.; Pople, J.A.; Gaussian, Inc., Wallingford CT, 2004.

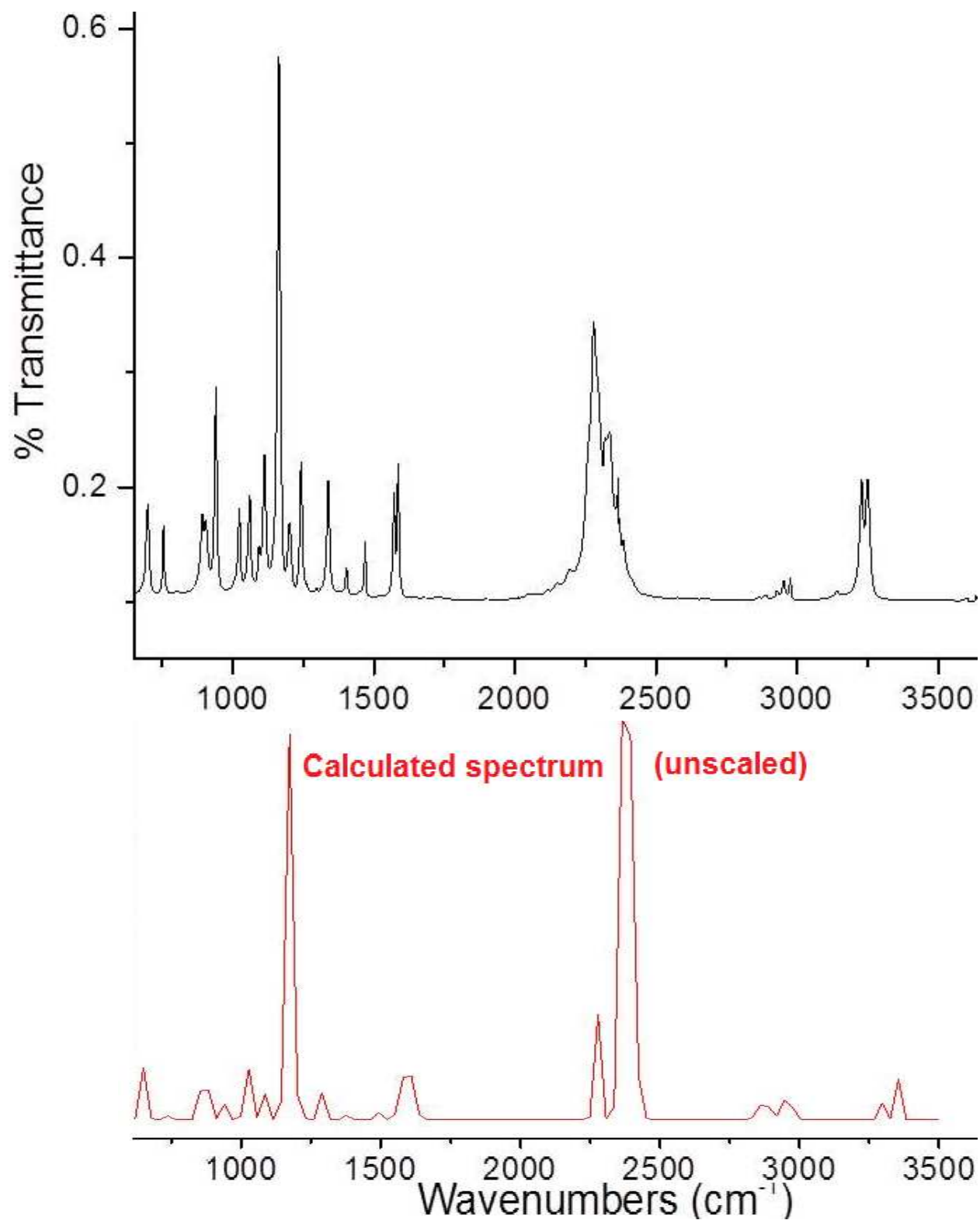


Figure S-1. Comparison of the IR absorption spectrum recorded for solid **4** ($n=1$) (upper panel) compared with the absorptions predicted by an anharmonic frequency calculation on the isolated molecule (lower panel) at B3LYP/aug-cc-pVTZ (using harmonic intensities with unscaled anharmonic frequencies).

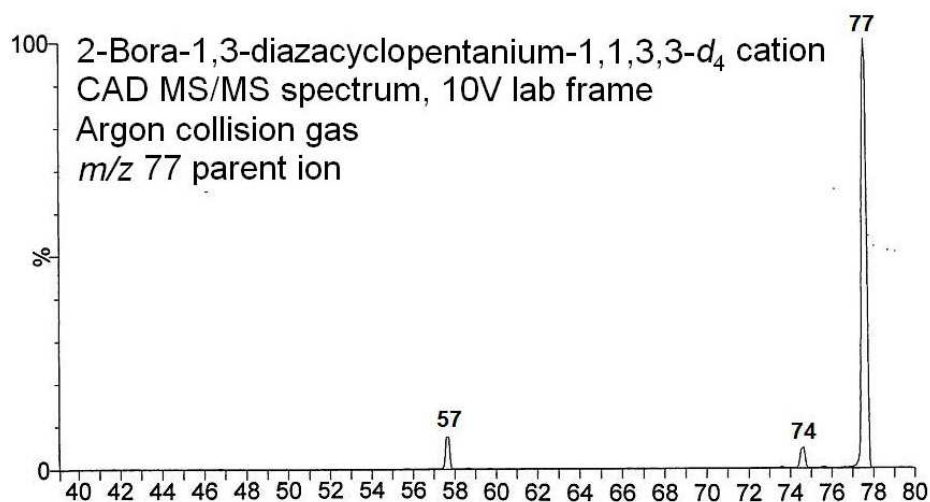


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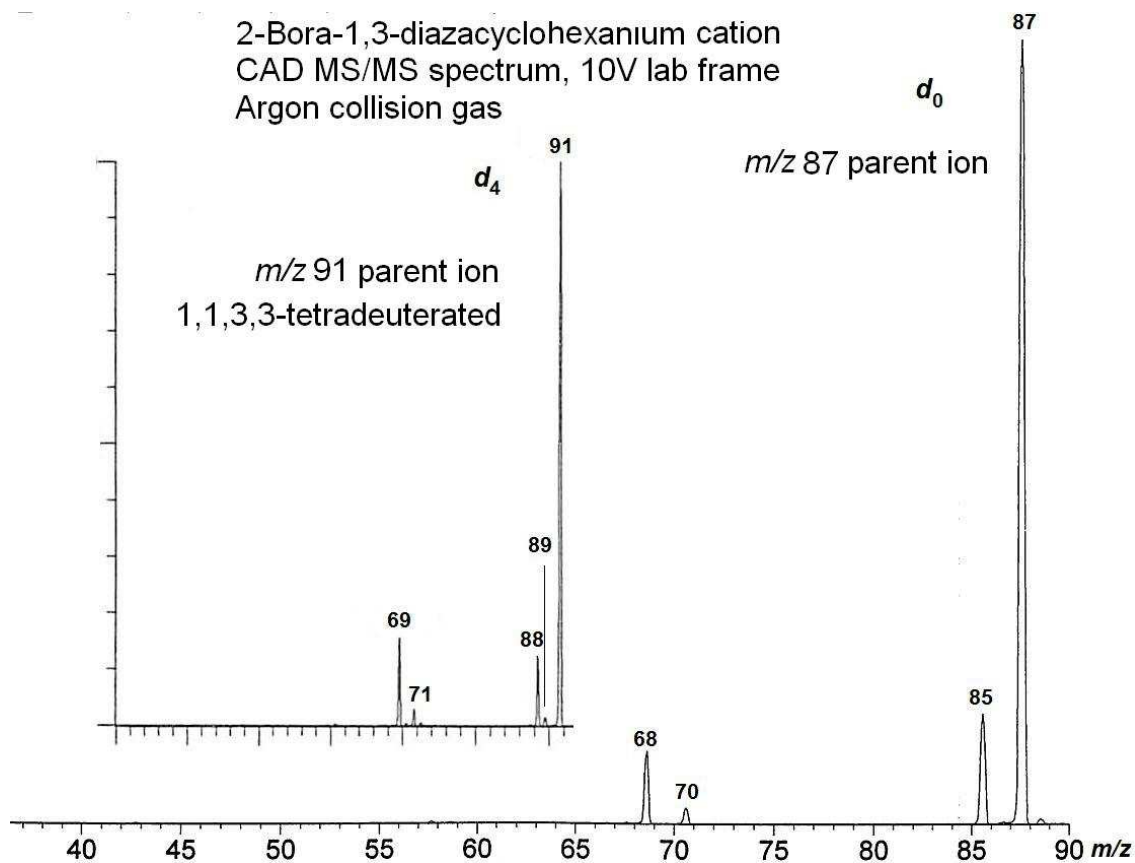


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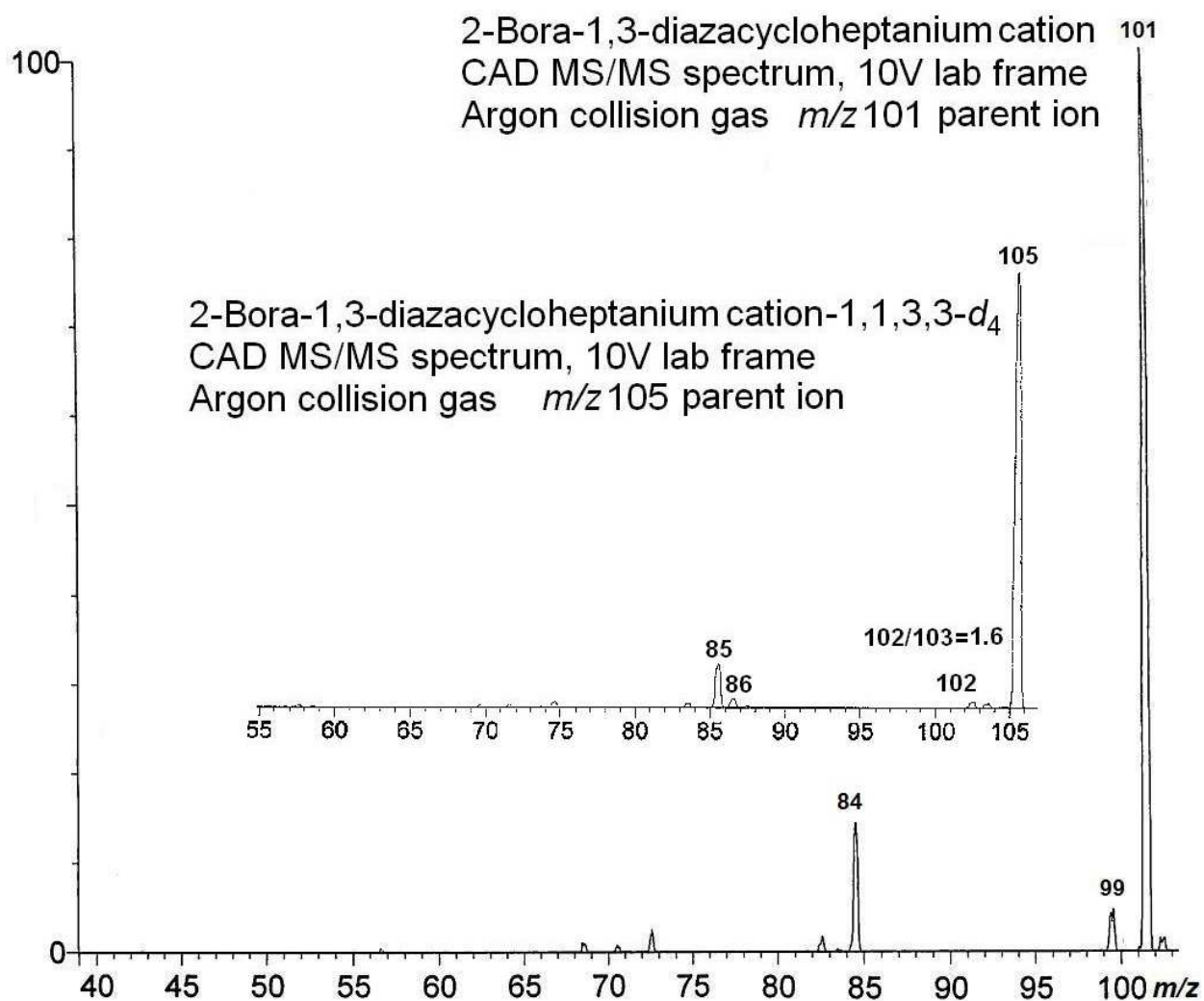


Figure S-4. CAD MS/MS spectra of ion **5** at 10V lab frame energy which shows the parent ion m/z 101 which produces m/z 99 (loss of H_2) and m/z 84 (loss of ammonia). Inset, a CAD of ion **11** at 10V, which shows a parent ion at m/z 105 and daughter ions m/z 102 (loss of HD) and m/z 103 (loss of H_2), m/z 85 (loss of ND_3), and m/z 86 (loss of NHD_2).

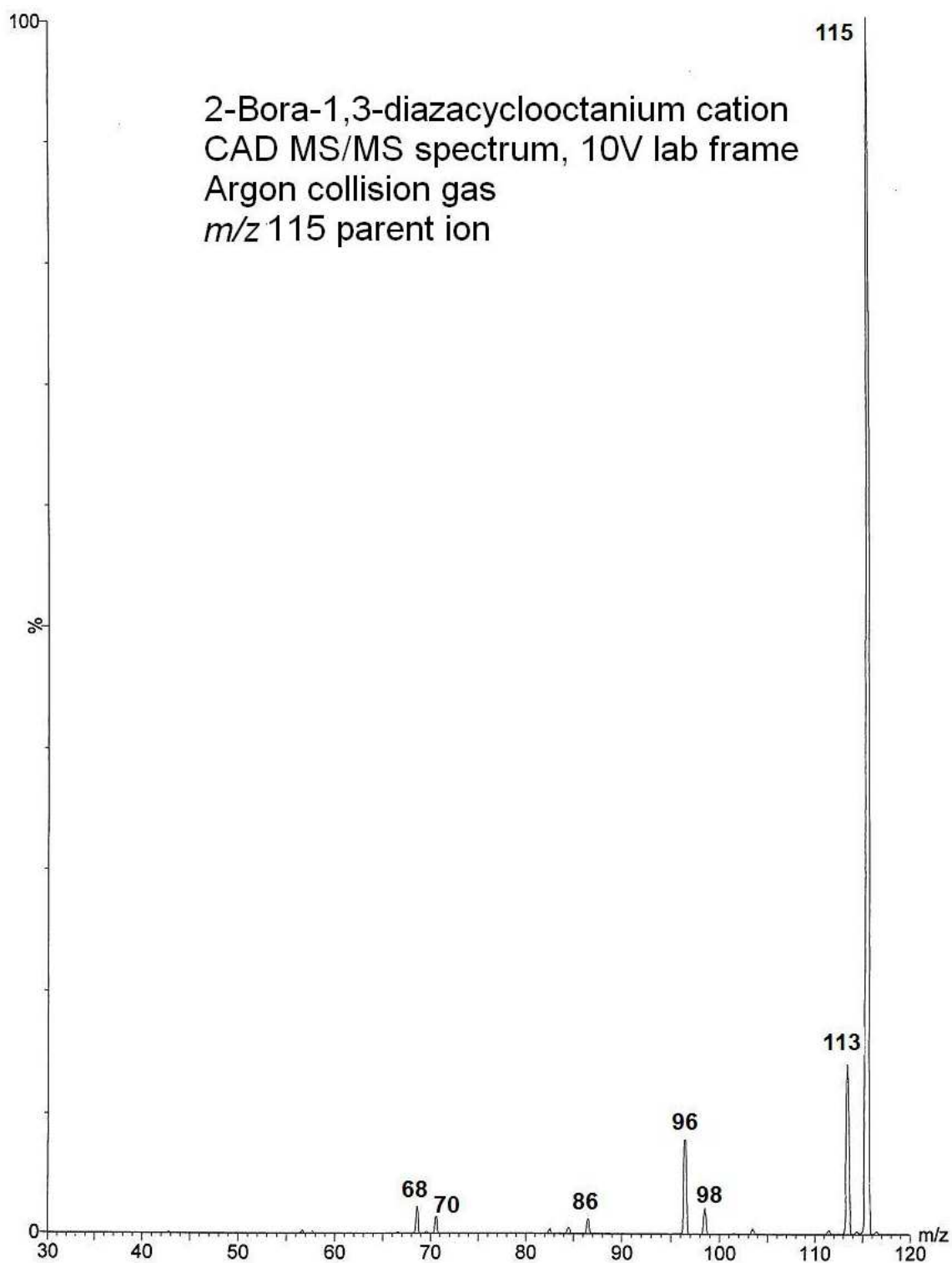


Figure S-5. CAD MS/MS spectra of ion **6** at 10 V lab frame energy which shows the parent ion m/z 115 and daughter ions m/z 113 (loss of H_2), m/z 98 (loss of ammonia), m/z 96 (loss of H_2 and ammonia), and other daughter ions.

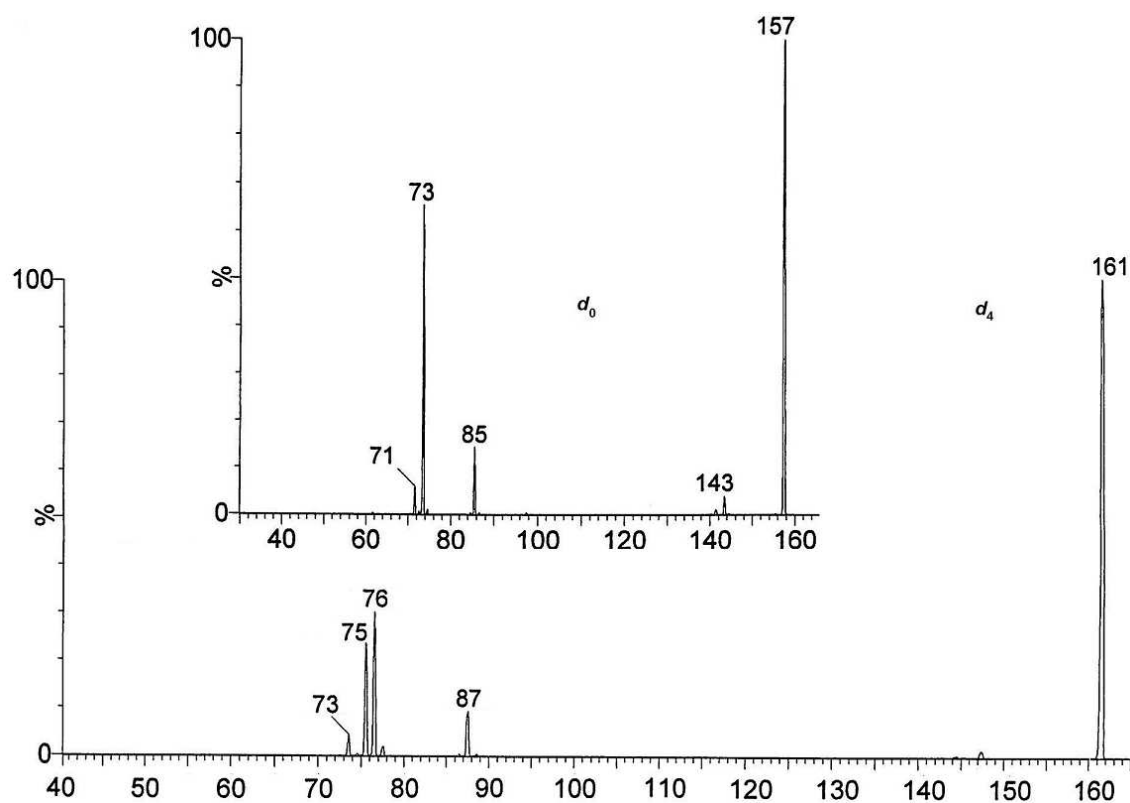


Figure S-6. CAD MS/MS spectra of ion **17** (m/z 157) and its d_4 analogue (m/z 161 from exchange with EtOD solvent) at 10V lab frame energy with argon collision gas.

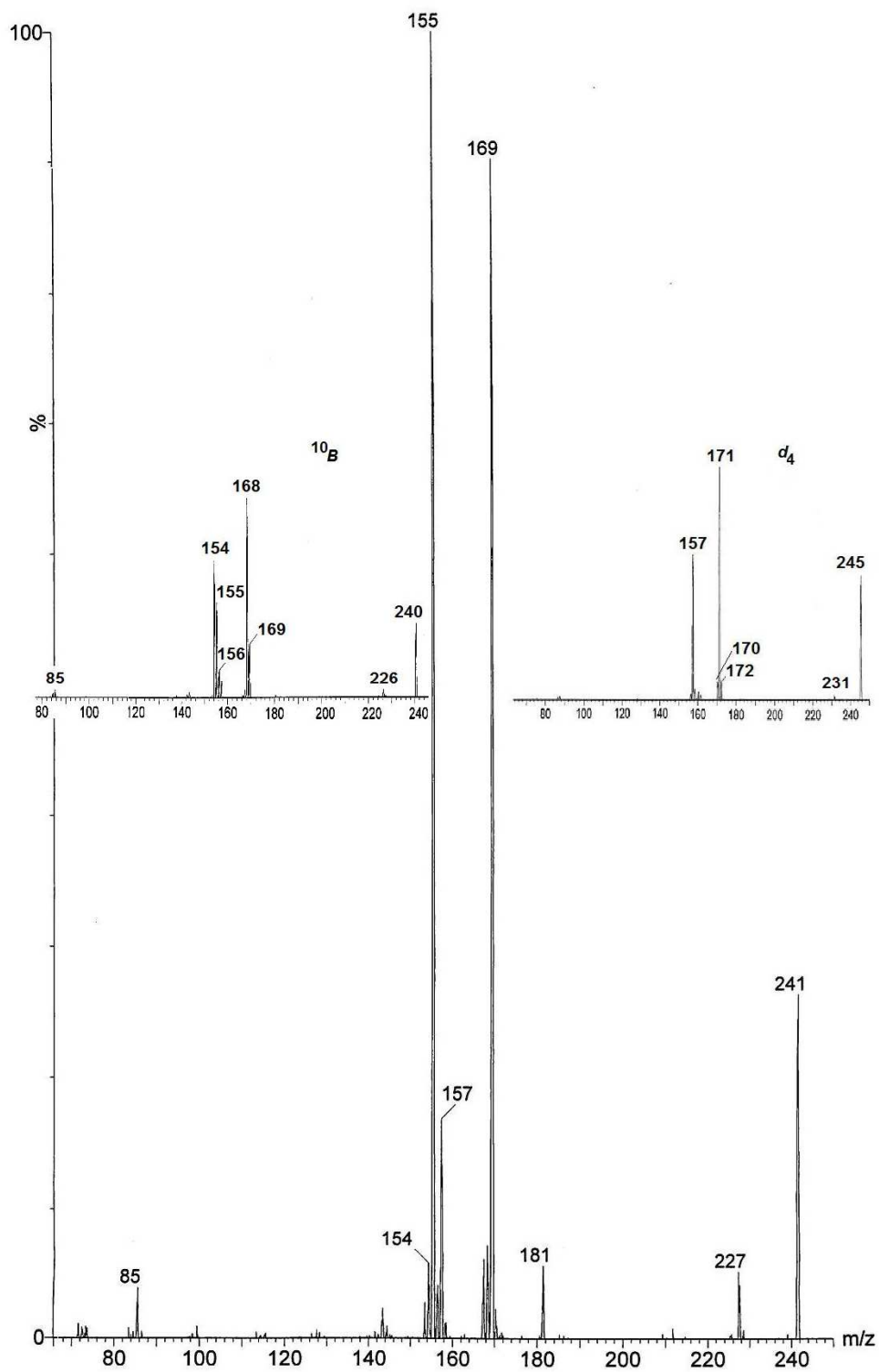


Figure S-7. CAD spectra of ion **18** and its isotopomers (left inset a ^{10}B & two ^{11}B s at natural abundance; right inset the d_4 analogue from exchange in EtOD) at 10V lab frame energy with argon collision gas.

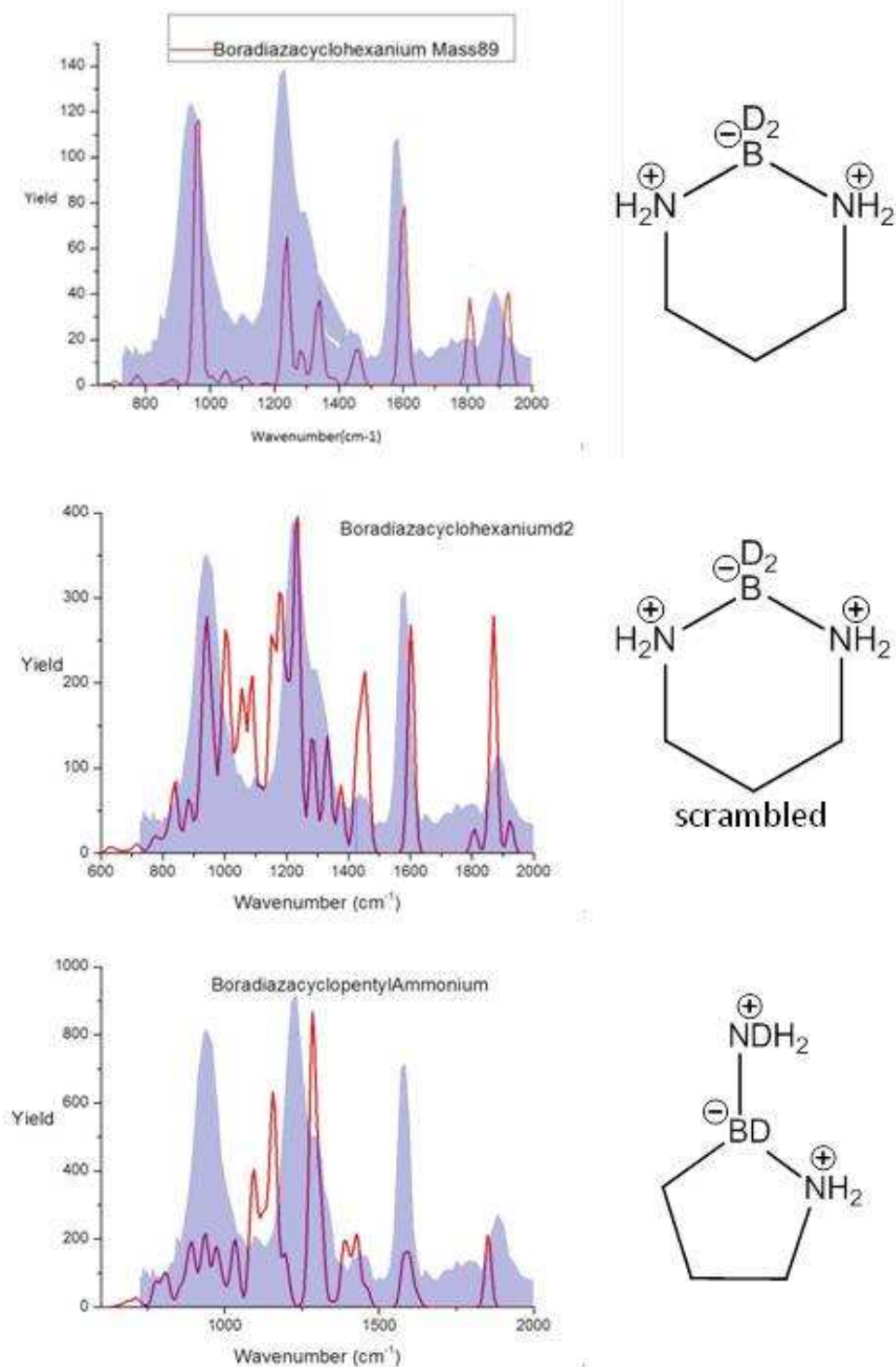


Figure S-8. Experimental IRMPD spectra (blue silhouette) vs. harmonic calculated normal modes (solid red line, scaled by 0.97 with 30 cm⁻¹ gaussian line broadening)^a of **7**: without scrambling of the protons in the NBN branch (top) and shows a good fit except for a mismatch of peaks in the 1750 to 1950 cm⁻¹ region; with scrambling of the protons in the NBN branch (middle) which shows a matching peak in the 1750 to 1950 cm⁻¹ region but a poor fit for the rest; and a branched isomer (bottom) which was found to be more stable than the two cyclic isomers on top but shows a poor fit to the experimental peaks.

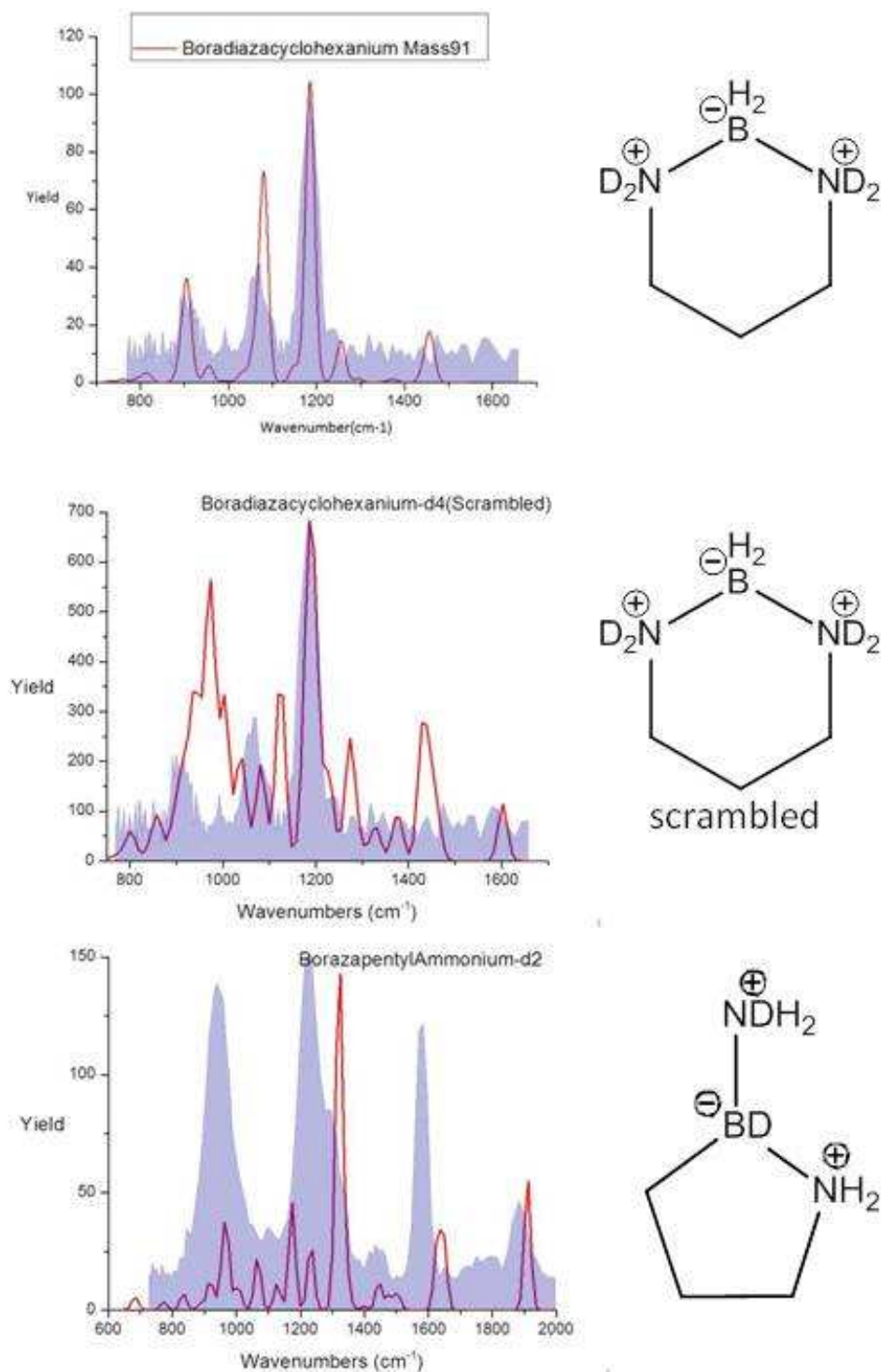


Figure S-9. Experimental IRMPD spectrum (blue silhouette) vs. harmonic calculated normal mode (solid red line, scaled by 0.97 with 30 cm^{-1} gaussian line broadening)^a of **10**: without scrambling of the protons in the NBN branch (top), which shows a good fit to experimental band positions; with scrambling of the protons in the NBN branch (middle) which shows a poor fit compared to the unscrambled isomer; and a branched isomer (bottom) which was found to be more stable than the two cyclic isomers on top but also shows a poor fit to the experimental bands.

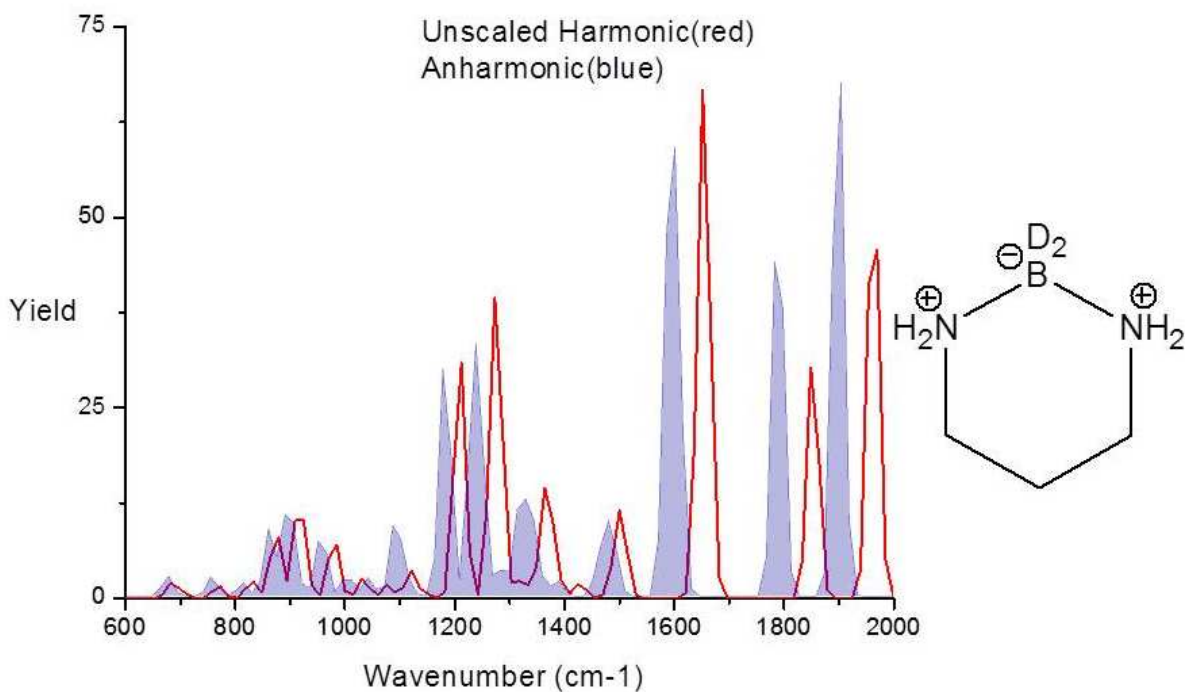


Figure S-10. A comparison of harmonic normal modes (solid red line, unscaled with 30 cm⁻¹ gaussian line broadening) and anharmonic vibrations (blue silhouette, unscaled using harmonic intensities and 30 cm⁻¹ gaussian line broadening)^a calculated for **7**, which shows the same peak positions below 800 cm⁻¹ with a shift of about 3% in the wavenumbers above 800 cm⁻¹.

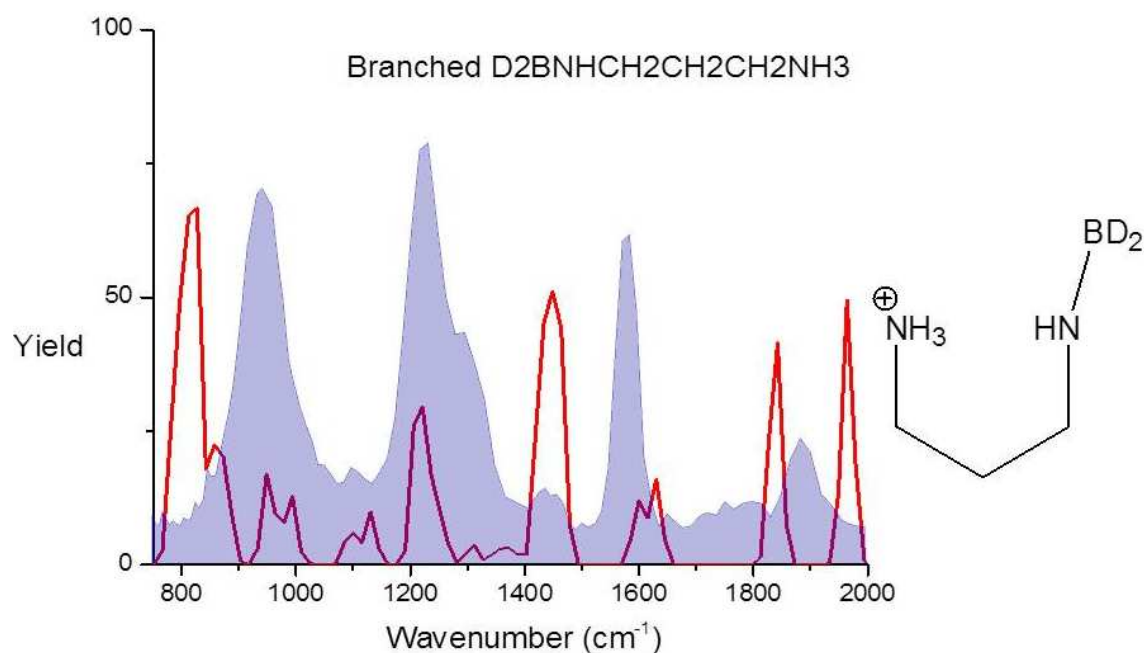


Figure S-11. Comparison of the experimental IRMPD spectrum (blue silhouette) with the harmonic calculated normal mode (solid red line, scaled by 0.97 with 30 cm⁻¹ gaussian line broadening)^a of a ring-opened isomer of **7** which, gives a poor match to the experimental spectrum.

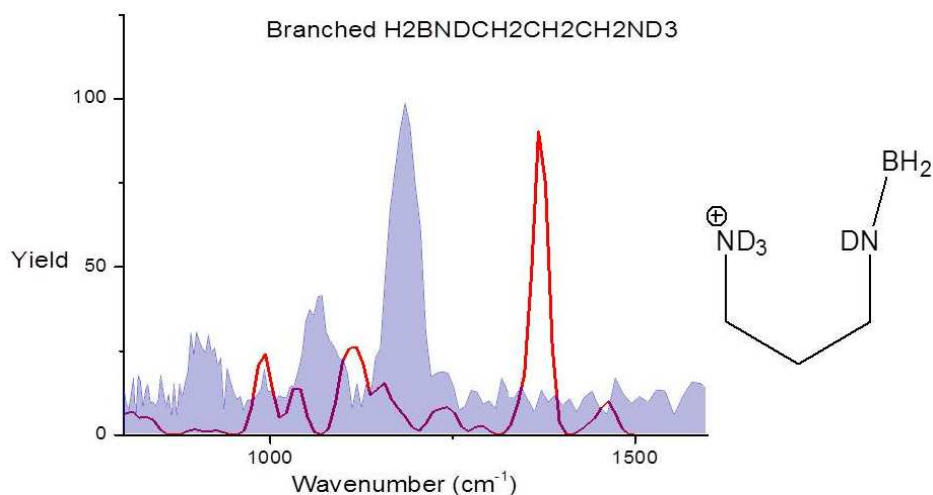


Figure S-12. Comparison of the experimental IRMPD spectrum (blue silhouette) with the harmonic calculated normal modes (solid red line, scaled by 0.97 with 30 cm⁻¹ gaussian line broadening)^a of a ring-opened isomer of **10**, which does not match the experimental spectrum.

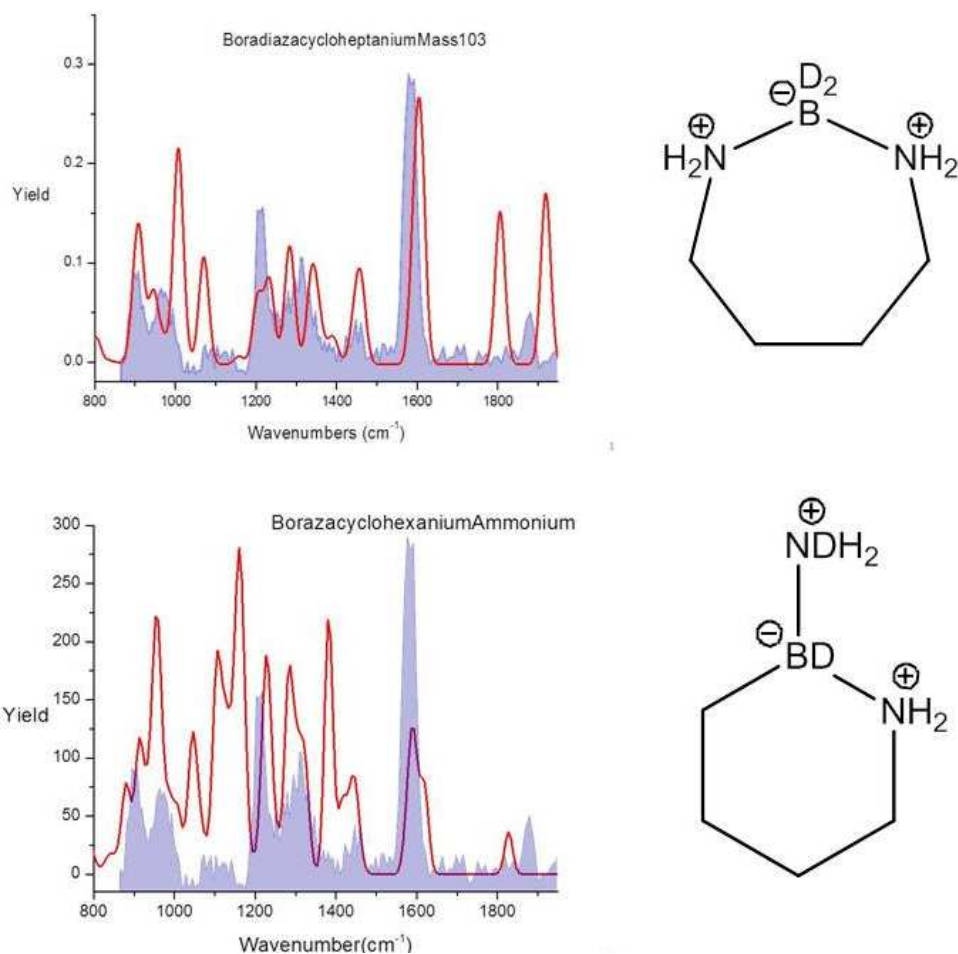


Figure S-13. Experimental IRMPD (blue silhouette) vs. harmonic calculated normal mode (solid red line, scaled by 0.97 with 30 cm⁻¹ gaussian line broadening)^a of **8** without the scrambling of the protons in the NBN branch of the cyclic isomer (top) and a branched isomer (bottom) which was found to be more stable than the cyclic isomers but gives a poor match to the experimental spectrum.

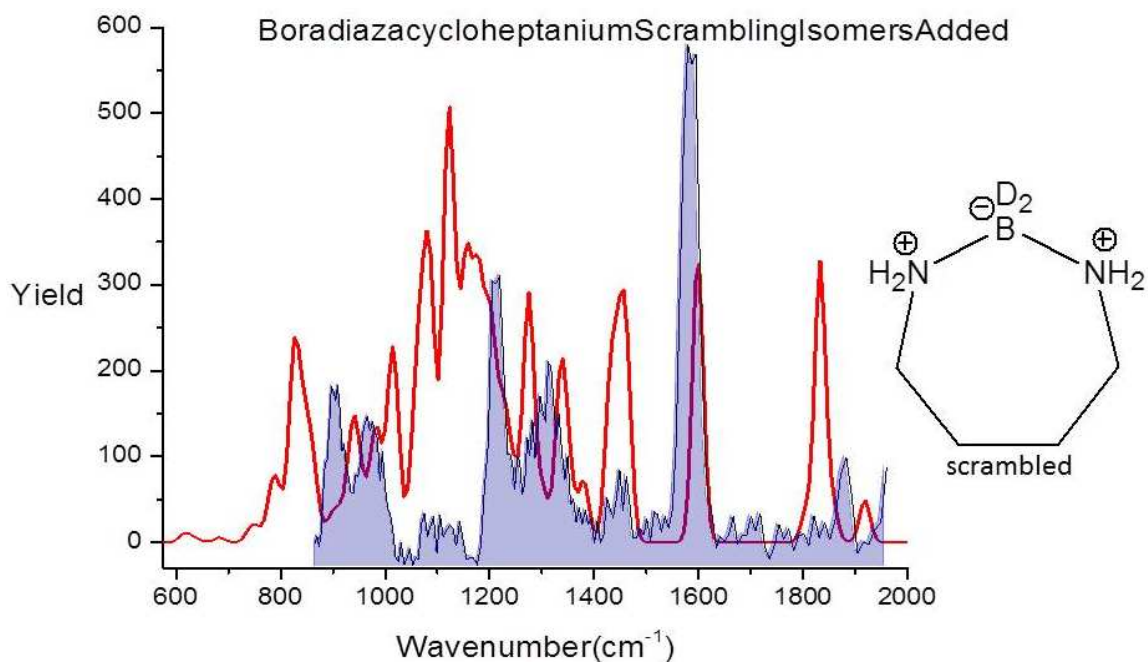


Figure S-14. Comparison of the experimental IRMPD spectrum (blue silhouette) with harmonic calculated modes of **8** (solid red line, scaled by 0.97 with 30 cm^{-1} gaussian line broadening)^a when scrambling of the protons in the NBN branch takes place, which shows a poor match to the experimental spectrum.

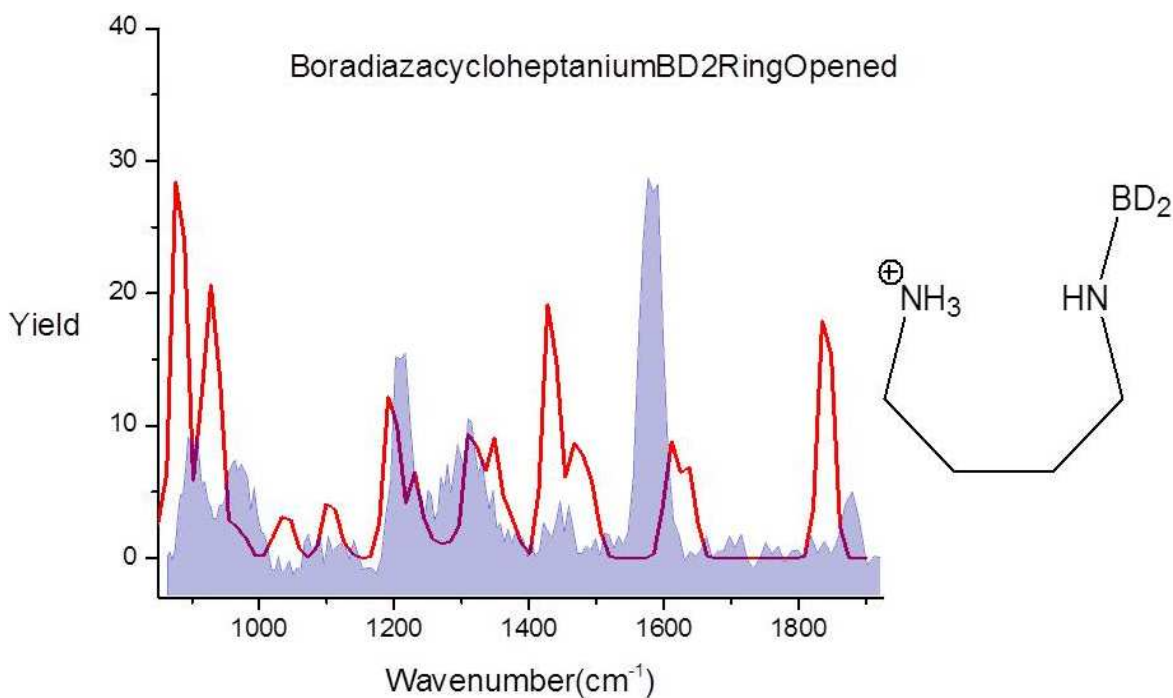


Figure S-15. Comparison of the experimental IRMPD spectrum (blue silhouette) with the harmonic calculated normal mode (solid red line, scaled by 0.97 with 30 cm^{-1} gaussian line broadening)^a of a ring-opened isomer of **8**, which gives a poor match to the experimental spectrum.

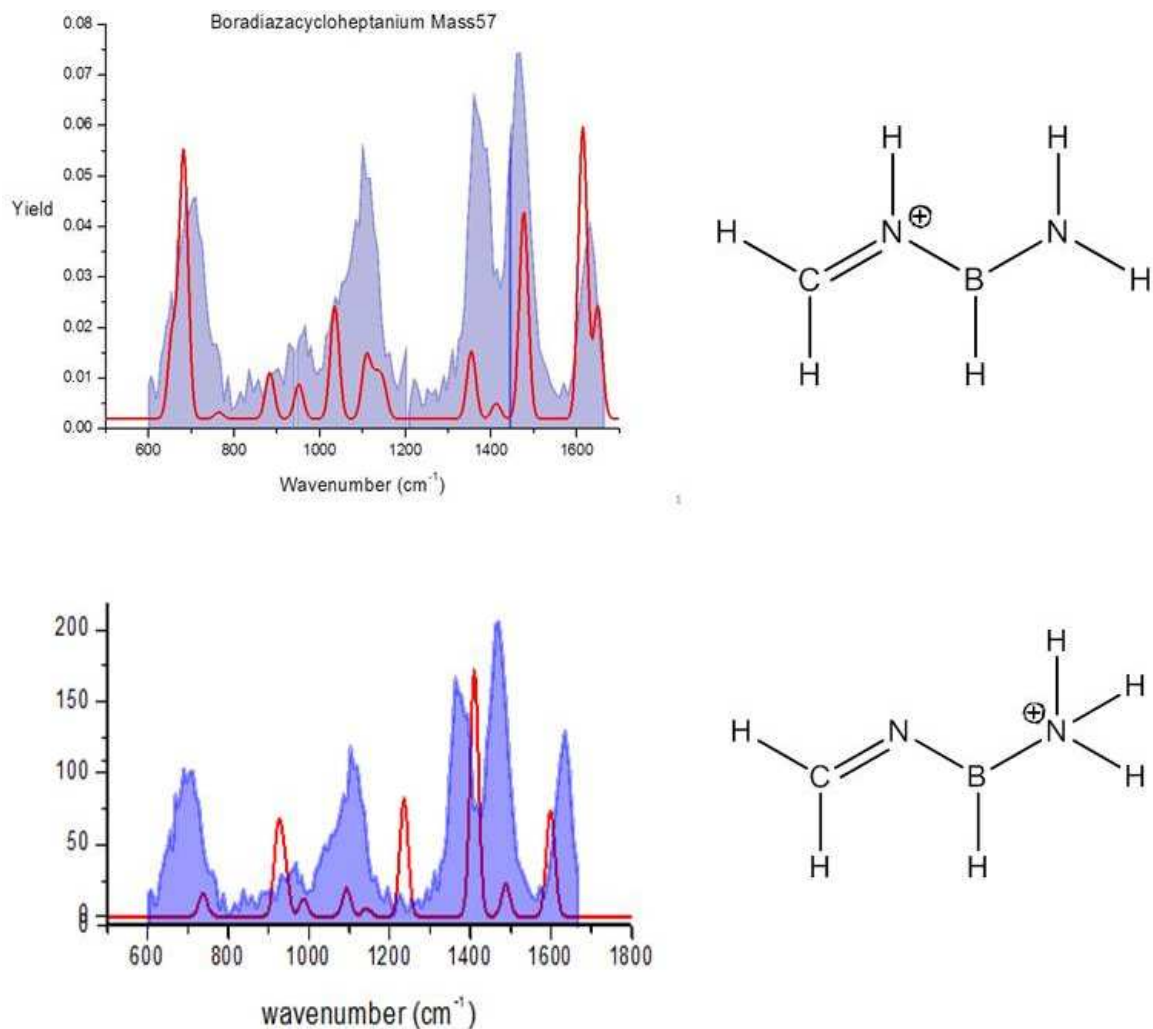


Figure S-16. Comparison of the experimental IRMPD (blue silhouette) of the m/z 57 daughter ion of **5** (solid red lines, scaled by 0.97 with 30 cm^{-1} gaussian line broadening)^a after a loss of H_2 and propene. The daughter ion in which the charge of the molecule is in the inner nitrogen (top panel) shows a better fit to the experimental spectrum than does the daughter ion in which the charge is in the outer nitrogen (bottom panel).

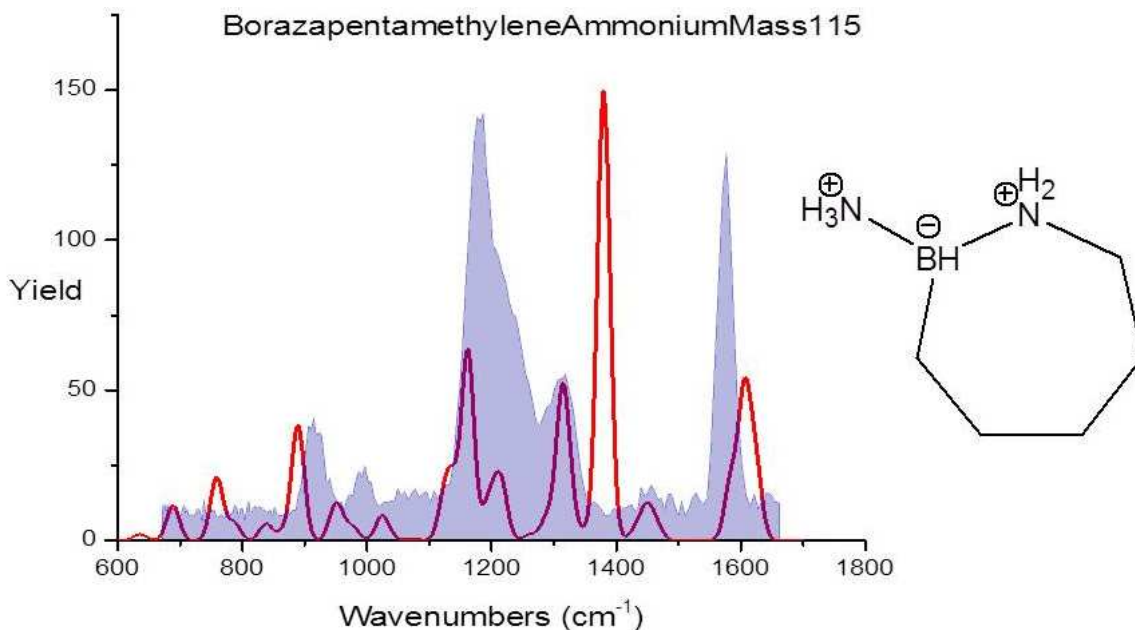


Figure S-17. Comparison of the experimental IRMPD (blue silhouette) with the harmonic calculated normal modes (solid red lines, scaled by 0.97 with 30 cm^{-1} gaussian line broadening)^a of a branched isomer of **6**. This branched isomer was found by calculation to be more stable than the cyclic isomer **6**; however, the comparison of the experimental spectrum with that calculated at the bottom of Figure 1 shows **6** to be the structure.

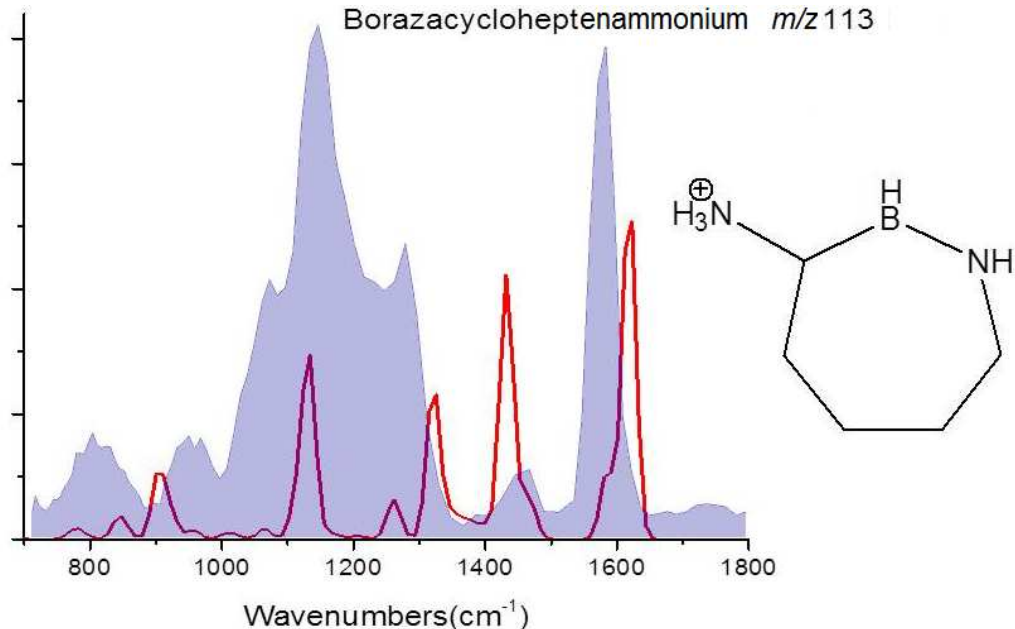


Figure S-18. Comparison of the experimental IRMPD spectrum (blue silhouette) with the harmonic calculated normal modes (red solid line, scaled by 0.97 with 30 cm^{-1} gaussian line broadening)^a of a branched isomer of **16**, in which the charge of the molecule is on the exocyclic nitrogen, which gives a worse match to the experimental spectrum than does the structure in Chart 2.

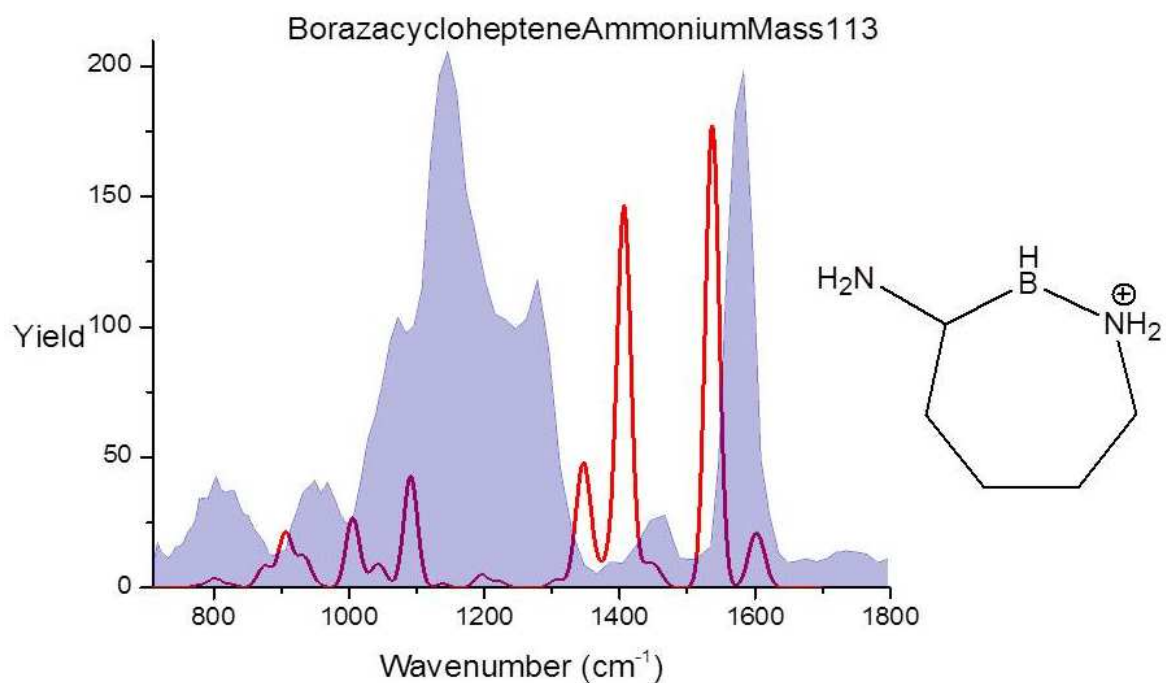


Figure S-19. Comparison of the experimental IRMPD spectrum (blue silhouette) with the harmonic calculated normal modes (red solid line, scaled by 0.97 with 30 cm⁻¹ gaussian line broadening)^a of another branched isomer of **16**, in which the charge of the molecule is on the endocyclic nitrogen, which also gives a poor match to the experimental spectrum.