

Ring expansion reactions of electron-rich boron-containing heterocycles

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Supporting Information

Contents

1. Experimental details	S2
2. NMR spectroscopy	S3
3. MALDI-TOF Spectroscopy	S5
4. X-ray crystallographic analysis	S7
5. Quantum chemical calculations	S8
6. References	S8

1. Experimental Procedures

General Details. Toluene, hexane and tetrahydrofuran (THF) solvents were dried and purified using the Grubbs/Dow purification system¹ and stored in 500 mL thick-walled glass vessels under vacuum over sodium/benzophenone ketal. Pentanes were dried over CaH₂ and stored over sodium/benzophenone ketal in thick-walled glass vessels under vacuum. Dichloromethane was dried over CaH₂ and stored over molecular sieves (4A) in thick-walled glass vessels under vacuum. Unless otherwise noted, solvents were introduced into the reaction vessels *via* vacuum distillation with condensation at -78 °C. Carbon monoxide was purchased from Sigma-Aldrich and used as received. Carbon dioxide, bone-dry grade 3.0, was obtained from Praxair and used as received. Nuclear magnetic resonance spectroscopy (¹H, ¹¹B, ¹³C{¹H}, HSQC, HMBC, and COSY experiments) was performed on Bruker 400 MHz (¹H: 400 MHz; ¹¹B: 128 MHz, ¹³C: 100 MHz) or Bruker 600 MHz (¹H: 600 MHz; ¹¹B: 192 MHz, ¹³C: 150 MHz) spectrometers. All 2D NMR experiments were performed using Bruker 400 MHz or Bruker 600 MHz spectrometers. All ¹H NMR spectra were referenced to SiMe₄ through residual ¹H resonance(s) of the employed solvent: CD₂Cl₂ (5.32 ppm) or THF-*d*₈ (3.58 ppm). ¹¹B NMR spectra were referenced to an external standard of boron trifluoride diethyl etherate (0.0 ppm) in C₆D₆ prior to spectrum acquisition. ¹³C{¹H} NMR spectra were referenced relative to SiMe₄ through the resonance(s) of the employed solvent: CD₂Cl₂ (54.0 ppm) or THF-*d*₈ (25.31 ppm). High-resolution mass spectra were obtained on a Bruker Autoflex III using MALDI-TOF with a Smartbeam laser system; note that, due to the sensitivity of these compounds, satisfactory elemental analyses for were not obtained despite duplicate attempts. Thus, bulk purity has been established using high resolution mass spectrometry and NMR spectroscopy. UV-visible spectra were obtained on a Varian Cary 5000 UV-vis-NIR spectrophotometer operating in single-beam mode. Fluorescence spectra were obtained on a Horiba Jobin Yvon FluoroMax-4. X-Ray crystallography was carried out on either a Nonius Kappa CCD diffractometer using graphite-monochromated Mo K α radiation or a Bruker Smart APEX II three-circle diffractometer using Cu K α radiation. Supplementary crystallographic data for CCDC-1063731, (**3**) and CCDC-1063732 (**4**) can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, UK, CB21EZ; fax: (+44) 1223-336-03; or deposit@ccdc.cam.ac.uk).

2. NMR spectroscopy

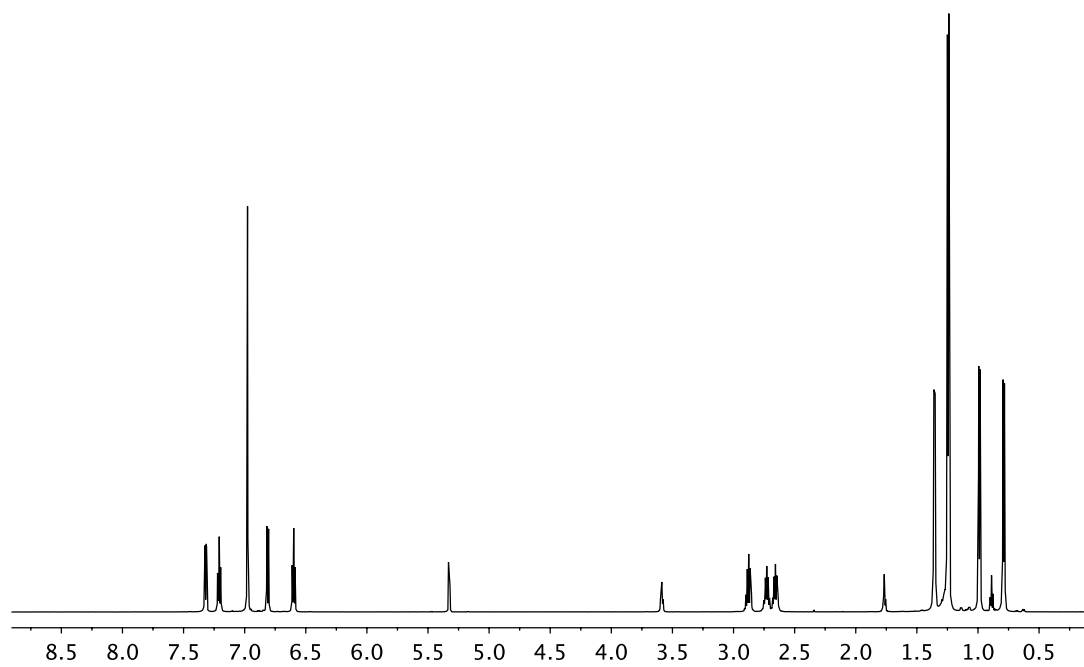


Figure S1. ^1H NMR spectrum of **3** in CD_2Cl_2 .

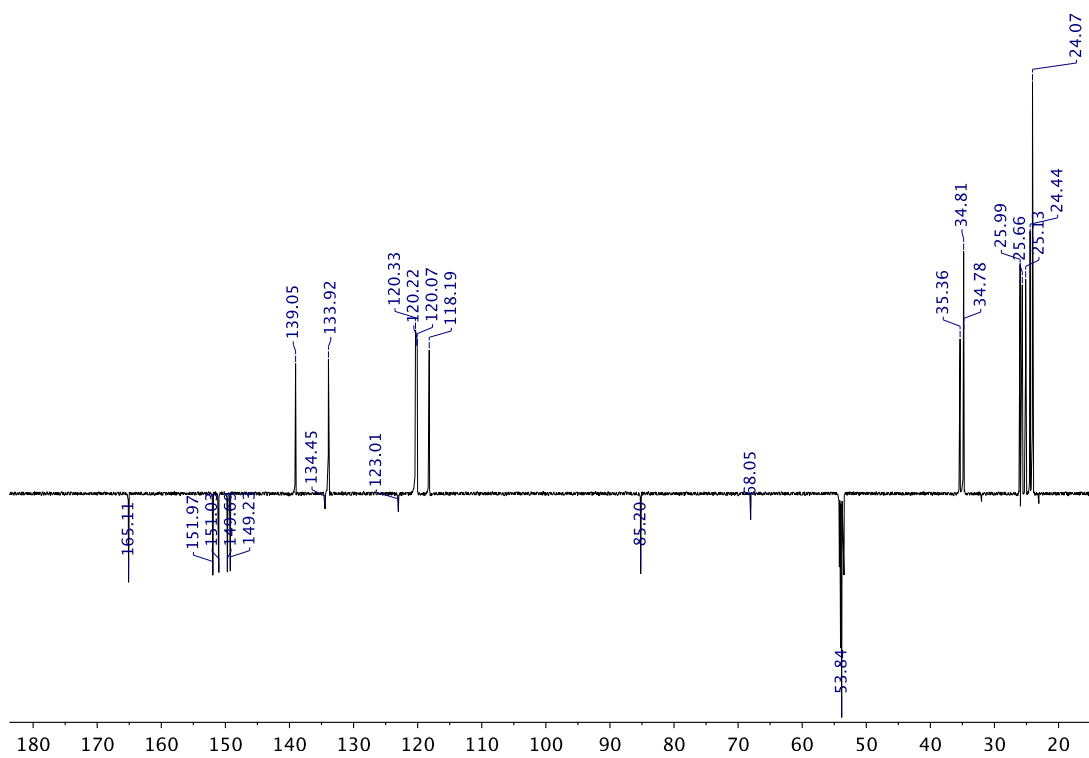


Figure S2. DEPTQ spectrum of **3** in CD₂Cl₂

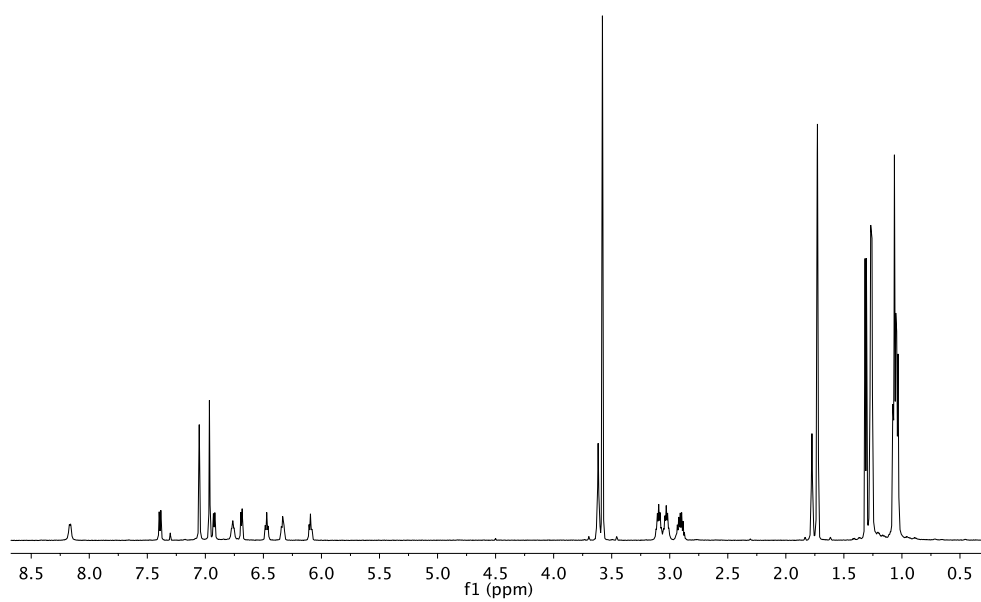


Figure S3. ¹H NMR spectrum of **4** in THF-d₈

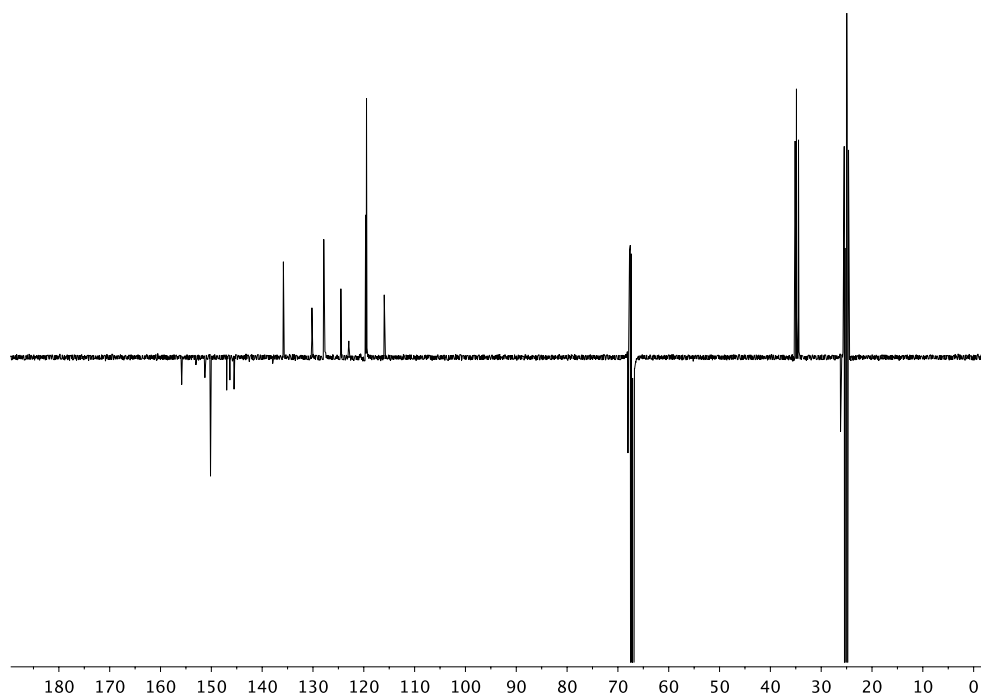


Figure S4. DEPTQ spectrum of **4** in THF- d_8

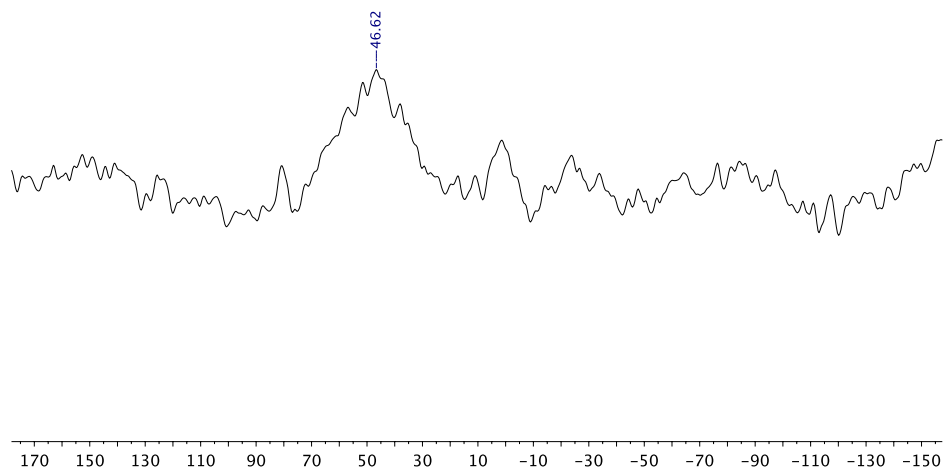


Figure S5. ^{11}B spectrum of **4** in THF- d_8

3. MALDI-TOF Spectroscopy

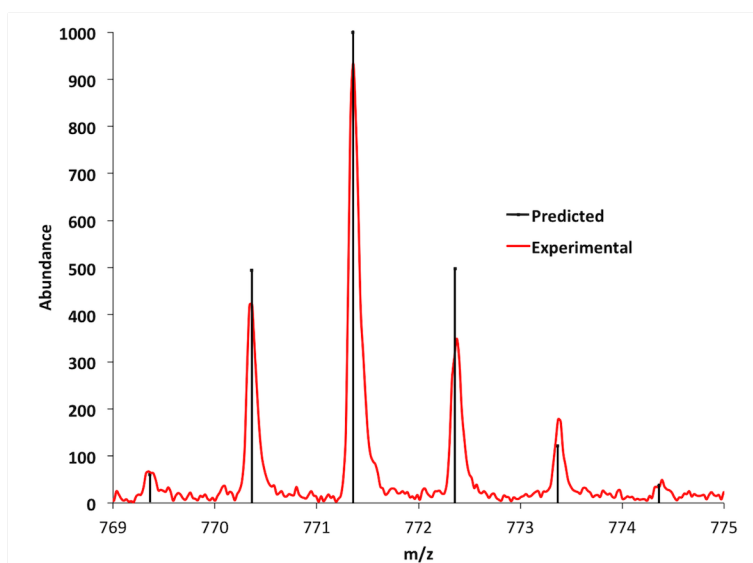


Figure S6. Truncated predicted isotopic distribution and MALDI-TOF spectrum of **3**

4. X-ray crystallography

Table S1: Data Collection and Structure Refinement Details for **3** and **4**.

	3	4
Empirical formula	C ₁₃₈ H ₁₆₂ B ₆ K ₆ O ₁₂ , 2(C ₄ H ₈ O)	C ₁₂₂ H ₁₇₂ B ₄ K ₄ O ₁₀
Crystal system	Hexagonal	Triclinic
<i>F</i> _w	2456.33	1998.23
<i>F</i> (000)	7860	1080
<i>T</i> (K)	173(2)	173(2)
Wavelength (Å)	0.71073	1.54178
Space group	R-3c	P-1
<i>a</i> (Å)	24.60(1)	14.3390(7)
<i>b</i> (Å)	24.60(1)	15.3414(7)
<i>c</i> (Å)	40.17 (1)	16.5198(9)
α (deg)	90	88.390(3)
β (deg)	90	78.224(3)
γ (deg)	120	64.155(3)
<i>Z</i>	6	1
<i>V</i> (Å ³)	21046(23)	3194.1(3)
ρ _{calcd} (g·cm ⁻³)	1.163	1.039
μ (mm ⁻¹)	0.245	1.624
θ range (deg)	2.242 – 25.382	2.74 – 68.50
Completeness	0.998	0.969
Collected reflections; R _σ	27816; 0.0477	37367; 0.0245
Unique reflections; R _{int}	27816; 0.0895	37367; 0.0245
R ₁ ; wR ₂ [I > 2σ(I)]	0.1158; 0.2259	0.0550; 0.1672
R ₁ ; wR ₂ [all data]	0.1580; 0.2476	0.0621; 0.1762
GOF	1.203	1.084
largest diff peak and hole	0.429 and -0.400	0.419 and -0.320

5. Quantum Chemical Calculations

XYZ-coordinates of optimized structures

See the submitted .mol file.

All calculations were carried out using Gaussian 09, Revision A.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. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, 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, 2009.

6. References

- (1) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.
- (2) Araneda, J. F.; Neue, B.; Piers, W. E.; Parvez, M. *Angewandte Chemie International Edition* **2012**, *51*, 8546.