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Supporting Information for

B-Methyl Amine Borane Derivatives: Synthesis, Characterization and Hydrogen Release

Patrick G. Campbell, Jacob S. A. Ishibashi, Lev N. Zakharov, and Shih-Yuan Liu*

Department of Chemistry and Biochemistry, University of Oregon, Eugene, Oregon 97403

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Supporting Information

General

All oxygen- and moisture-sensitive manipulations were carried out under an inert atmosphere using either standard Schlenk techniques or a glove box. THF, Et_2O, CH_2Cl_2, and pentane were purified by passing through a neutral alumina column under argon. Ammonia borane was purchased from GFS Chemicals and used as received, BN heterocycle **2**,[1] and $Li[MeBH_3]$[2] were prepared according to literature methods. All other chemicals and solvents were purchased (Aldrich or Strem) and used as received.

^{11}B NMR spectra were recorded on a Varian Unity/Inova 600 spectrometer or Varian Unity/Inova 300 spectrometer at ambient temperature. ^{1}H NMR spectra were recorded on a Varian Unity/Inova 300 or Varian Unity/Inova 600 spectrometer. ^{13}C NMR spectra were recorded on a Varian Unity/Inova 600 spectrometer. All chemical shifts are externally referenced: ^{11}B NMR to $BF_3 \bullet Et_2O$ (δ 0). IR spectra were recorded on a Nicolet Magna 550 FT-IR instrument with OMNIC software.

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[1] W. Luo, P. G. Campbell, L. N. Zakharov, S.-Y. Liu, *J. Am. Chem. Soc.* **2011,** *133,* 19326-19329.

[2] B. Singaram, T. E. Cole, H. C. Brown, *Organometallics* **1984,** *3,* 774-777.

Synthesis of 3 and 4

Compound 3. To a stirring solution of $Li[MeBH_3]$ (0.135 g, 3.77 mmol) in Et_2O (10 mL) was added $MeNH_3Cl$ (0.255 g, 3.77 mmol). The slurry was allowed to stir for 1 hour, and then filtered through an Acrodisc. The majority of the solvent (75%) was removed under reduced pressure, and pentane was added to cause precipitation of the product. The solvent layer was removed by pipet and the solid residue was washed two times with pentane to give **3** as a white crystalline solid (0.191 g, 88% yield).

$MeH_2N–BH_2Me$
3

Melting point: 47 °C. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 3.35 (m (br), 2H, N–H), 2.54 (t, $^3J_{HH}$ = 4.0 Hz, 3H, N–Me), 1.82 (q (br), J_{BH} = 90 Hz, 2H, B–H), 0.20 (s (br), 3H, B–Me). ^{13}C NMR (125 MHz, CD_2Cl_2): δ 32.01, 0.83 (br). ^{11}B NMR (96.27 MHz, CD_2Cl_2): δ –11.17 (t, $^3J_{BH}$ = 95 Hz). HRMS (EI+) calcd. for C_2H_8NB ($–H_2$) 57.074980 found 57.074987.

Compound 4. To a stirring solution of $Li[MeBH_3]$ (0.075 g, 2.10 mmol) in Et_2O (10 mL) was added NH_4Cl (0.112 g, 2.10 mmol). The slurry was allowed to stir for 1 hour, and then filtered through an Acrodisc. The majority of the solvent (75%) was removed under reduced pressure and pentane was added to cause precipitation of the product. The solvent layer was removed by pipet and the solid residue was washed two times with pentane to give **4** as a white crystalline solid (0.072 g, 75% yield).

$H_3N–BH_2Me$
4

Melting point: 58 °C (with decomposition, loss of H_2). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 3.37 (br, 3H, N–H), 2.93 (q (br), J_{BH} = 90 Hz, 2H, B–H), –0.17 (s (br), 3H, B–Me). ^{13}C NMR (125 MHz, CD_2Cl_2): δ 3.10 (br). ^{11}B NMR (96.27 MHz, CD_2Cl_2): δ –14.56 (t, $^3J_{BH}$ = 93 Hz).

Dehydrogenation Experiments on the Automated Burette Apparatus

General Procedure. The automated gas burette used was based on a reported design.[3] The burette system was purged of air by repeated evacuation/nitrogen cycles (3x). In a glovevox, a 100 mL two-neck flask was charged with ca. 0.075 g BN material, 5 mol% $CoCl_2$ catalyst and diglyme solvent (3 mL). The flask was attached to the burette apparatus under flowing N_2. Once the system pressure equalized, the data collection program was started and the flask was immersed into a preheated oil bath (80 °C). Agitation was provided for each run using the same type of Teflon coated magnetic stir bar, and care was taken to insure that the rate of agitation was comparable in each experiment.

60 °C Dehyrogenation, Compound 4

Using the same general procedure described above, the burette flask was immersed in a 60 °C oil bath and allowed to react. Complete release of 2 equiv. H_2 required ca. 90 minutes (Figure S1).

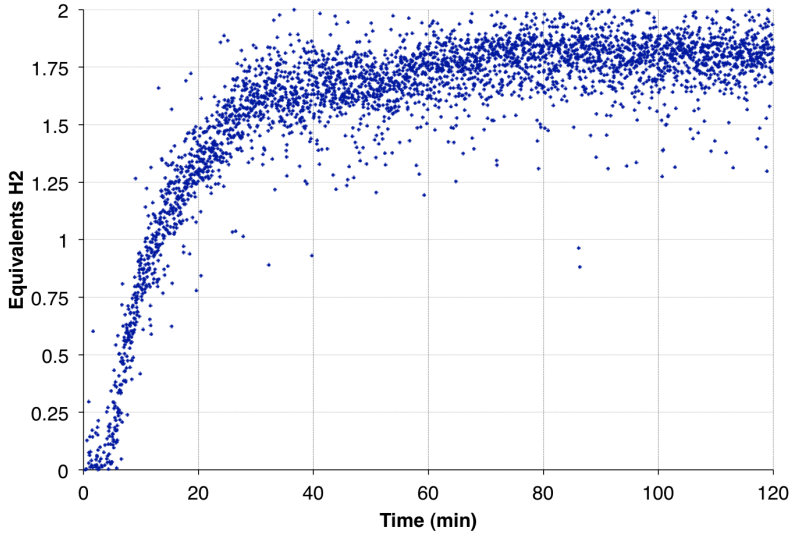


Figure S1. Burette measurement of H_2 release from **4** at 60 °C.

[3] F. Zheng, S. D. Rassat, D. J. Helderandt, D. D. Caldwell, C. L. Aardahl, T. Autrey, J. C. Linehan, K. G. Rappé, *Rev. Sci. Instrum.* **2008,** *79,* 084103.

"Qualitative" 2 Equiv Experiment

The general procedure described above was modified to separate the catalyst from the substrate before initiating data collection. Compound **4** was dissolved in diglyme (2 mL) and added to the burette flask. $CoCl_2$ (ca. 10 mol%) was made into a slurry in diglyme (1 mL) and added to a pressure equalizing addition funnel connected to the burette flask via a ground glass joint. Data collection was initiated, and the addition funnel stopcock was opened to drain the catalyst slurry into the burette flask. As can be seen from Figure S2, the reaction proceeds with a ca. 3-minute induction period in which the rate of H_2 release is slower than the subsequent 4-8 minutes. We consider this a qualitative experiment because we are unable to accurately determine the precise amount of the heterogeneous catalyst introduced into the reaction flask and thus make repeatable burette runs to evaluate the rate of reaction.

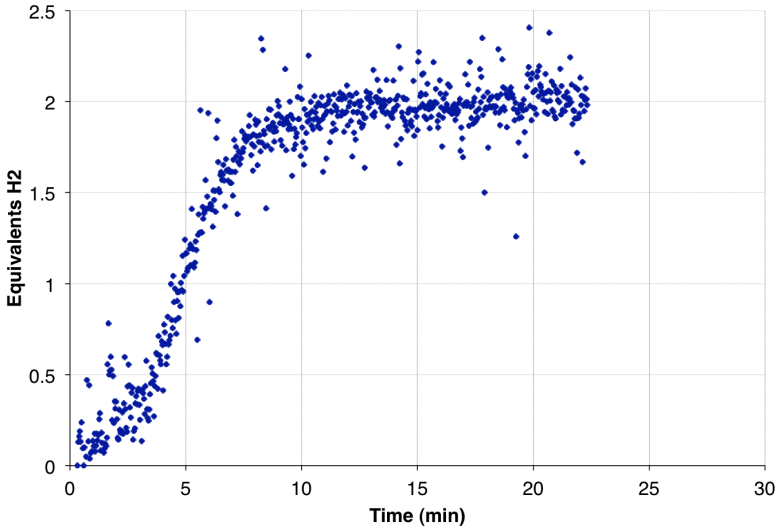


Figure S2. Burette measurement of H_2 release from **4** using an addition funnel to introduce the catalyst.

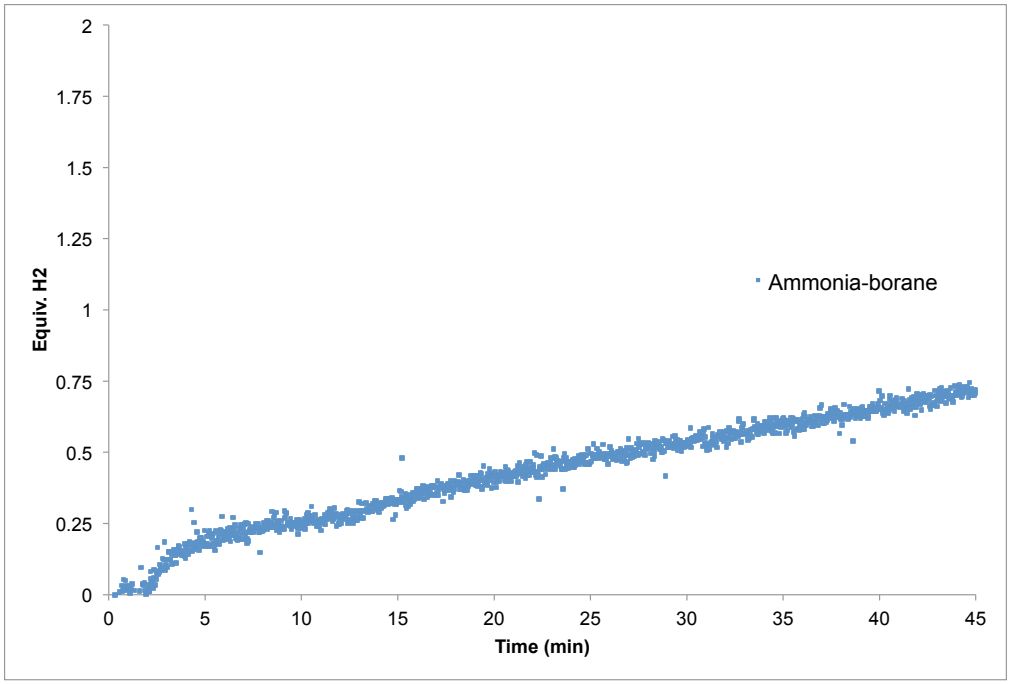
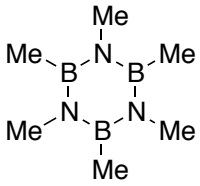


Figure S3. Burette measurement of H_2 release from AB (5 mol% $CoCl_2$, diglyme, 80 °C)

Isolation of Dehydrogenation Product of 3, Hexamethylborazine

Compound 5. A round-bottom flask equipped with a reflux condenser was charged with **3** (0.035 g, 0.61 mmol), $CoCl_2$ (0.004 g, 0.03 mmol) and THF (5 mL). The reaction was stirred at reflux for 24 hours. The crude mixture was filtered through an Acrodisc and the solvent was removed under reduced pressure. The residue was dissolved in Et_2O and passed through a short (ca. 5 cm) column of neutral alumnia. Hexamethylborazine was recovered (0.024 g, 71% yield). ^{1}H and ^{11}B spectra are consistent with spectra collected from authentic hexamethylborazine, prepared by literature method.[4]

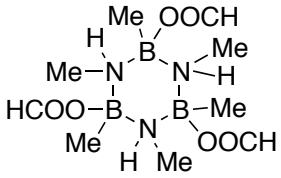


5

[4] M. A. Forgeron, D. L. Bryce, R. E. Wasylishen, R. Rösler, *J. Phys. Chem. A* **2003,** *107,* 726-735.

Regeneration of Spent Material

Compound 7. A round bottom flask was charged with hexamethylborazine **5** (0.085 g, 0.52 mmol), formic acid (0.071 g, 1.55 mmol) and CH_2Cl_2 (10 mL).



7

The reaction mixture was stirred for 1 hour and the solvent was removed under reduced pressure. The residue was washed with cold Et_2O and compound **7** as a mixture of diastereomers was recovered (0.142 g, 91% yield). X-ray quality crystals (of a single diastereomer) were grown from slow evaporation of Et_2O (see below).

^{1}H NMR (300 MHz, C_6D_6): δ 7.78 (s, 3H, OOC–H), 5.32 (s (br), 3H, N–H), 1.86 (m, 9H, N–Me), 0.06 (s, 9H B–Me).). ^{13}C NMR (125 MHz, C_6D_6): δ 164.38, 28.06. B-Me not detected. ^{11}B NMR (96.27 MHz, CD_2Cl_2): δ 4.7 (s). HRMS (ES+) calcd. for $C_9H_{24}B_3N_3O_6Na$ 326.1842 found 326.1839.

Compound 3 from 7. A round bottom flask was charged with **7** (0.071 g, 0.24 mmol) and Et_2O (10 mL). $LiAlH_4$ (0.013 g, 0.35 mmol) was added and the mixture was stirred for 20 minutes, at which time the reaction flask was opened to the air and wet THF (5 mL, 5 drops H_2O) was added. The crude mixture was filtered through an Acrodisc, the solvent was removed under reduced pressure, and the residue was washed with cold pentane to give compound **3** (0.020g, 46% yield). ^{1}H and ^{11}B NMR spectra are consistent with authentic **3** prepared as above. No other products were isolated or identified. The low yield is presumably due to losses associated with difficulty separating the product from the Li/Al salt slurry.

Crystallographic Data for 7 (liu153)

Procedure

Diffraction intensity data for **7** (aka. liu153) were collected with a Bruker Smart Apex CCD diffractometer at 173(2) K using MoKα - radiation (0.71073 Å). The structures were solved using direct methods, completed by subsequent difference Fourier syntheses, and refined by full matrix least-squares procedures on F^2. All non-H atoms were refined with anisotropic thermal parameters. H atoms were found on the residual density map and refined with isotropic thermal parameters All software and sources scattering factors are contained in the SHELXTL (6.10) program package (G.Sheldrick, Bruker XRD, Madison, WI). Crystallographic data and some details of data collection and crystal structure refinement for **7** are given in the following tables.

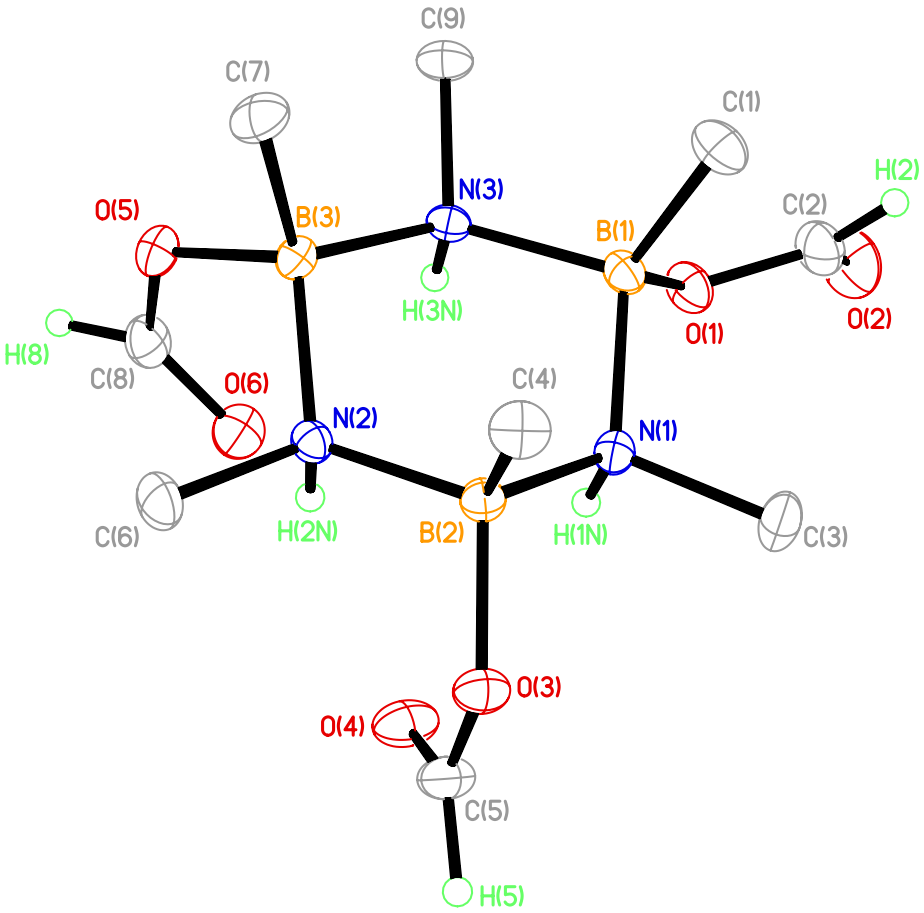


Table 1. Crystal data and structure refinement for liu153.

Identification code	liu153	
Empirical formula	C9 H24 B3 N3 O6	
Formula weight	302.74	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 7.5759(14) Å	a= 90°.
	b = 24.347(4) Å	b= 96.923(3)°.
	c = 8.4374(15) Å	g = 90°.
Volume	1544.9(5) $Å^3$	
Z	4	
Density (calculated)	1.302 Mg/m^3	
Absorption coefficient	0.102 mm^{-1}	
F(000)	648	
Crystal size	0.32 x 0.26 x 0.14 mm^3	
Theta range for data collection	1.67 to 27.00°.	
Index ranges	-9<=h<=9, -31<=k<=31, -10<=l<=10	
Reflections collected	17175	
Independent reflections	3378 [R(int) = 0.0385]	
Completeness to theta = 27.00°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9859 and 0.9682	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3378 / 0 / 286	
Goodness-of-fit on F^2	1.062	
Final R indices [I>2sigma(I)]	R1 = 0.0394, wR2 = 0.1065	
R indices (all data)	R1 = 0.0437, wR2 = 0.1103	
Largest diff. peak and hole	0.356 and -0.187 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for liu153. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	1410(1)	1424(1)	718(1)	32(1)
O(2)	3450(2)	1540(1)	2785(1)	57(1)
O(3)	-3786(1)	303(1)	-1139(1)	29(1)
O(4)	-1301(1)	-174(1)	-1356(1)	39(1)
O(5)	59(1)	1150(1)	-4859(1)	30(1)
O(6)	1457(1)	451(1)	-3494(1)	38(1)
N(1)	-1498(1)	999(1)	-122(1)	22(1)
N(2)	-2152(1)	824(1)	-3094(1)	21(1)
N(3)	294(1)	1500(1)	-2050(1)	21(1)
B(1)	-329(2)	1535(1)	-303(2)	24(1)
B(2)	-3063(2)	865(1)	-1495(2)	22(1)
B(3)	-1057(2)	1341(1)	-3578(2)	22(1)
C(1)	-1288(2)	2094(1)	71(2)	34(1)
C(2)	2028(2)	1652(1)	2067(2)	39(1)
C(3)	-2135(2)	968(1)	1489(2)	35(1)
C(4)	-4723(2)	1271(1)	-1614(2)	30(1)
C(5)	-2822(2)	-143(1)	-1069(2)	33(1)
C(6)	-3424(2)	619(1)	-4461(2)	33(1)
C(7)	-2210(2)	1846(1)	-4335(2)	33(1)
C(8)	1138(2)	728(1)	-4681(2)	33(1)
C(9)	1354(2)	1998(1)	-2387(2)	31(1)

Table 3. Bond lengths [Å] and angles [°] for liu153.

O(1)-C(2)	1.3023(16)
O(1)-B(1)	1.5096(15)
O(2)-C(2)	1.2018(19)
O(3)-C(5)	1.3065(15)
O(3)-B(2)	1.5169(14)
O(4)-C(5)	1.2081(17)
O(5)-C(8)	1.3096(16)
O(5)-B(3)	1.5228(15)
O(6)-C(8)	1.2078(17)
N(1)-C(3)	1.4980(15)
N(1)-B(2)	1.5884(15)
N(1)-B(1)	1.5939(16)
N(1)-H(1N)	0.845(16)
N(2)-C(6)	1.4972(15)
N(2)-B(3)	1.5870(15)
N(2)-B(2)	1.5908(15)
N(2)-H(2N)	0.879(15)
N(3)-C(9)	1.4987(15)
N(3)-B(3)	1.5944(16)
N(3)-B(1)	1.6037(16)
N(3)-H(3N)	0.849(15)
B(1)-C(1)	1.5921(17)
B(2)-C(4)	1.5927(17)
B(3)-C(7)	1.5974(17)
C(1)-H(1A)	0.97(2)
C(1)-H(1B)	0.939(18)
C(1)-H(1C)	1.01(2)
C(2)-H(2)	1.004(18)
C(3)-H(3A)	0.948(18)
C(3)-H(3B)	0.937(18)
C(3)-H(3C)	0.931(18)
C(4)-H(4A)	0.943(19)
C(4)-H(4B)	0.94(2)
C(4)-H(4C)	0.97(2)

C(5)-H(5)	0.939(17)
C(6)-H(6A)	0.939(18)
C(6)-H(6B)	0.945(18)
C(6)-H(6C)	0.942(17)
C(7)-H(7A)	0.964(18)
C(7)-H(7B)	0.995(19)
C(7)-H(7C)	0.97(2)
C(8)-H(8)	0.950(19)
C(9)-H(9A)	0.954(17)
C(9)-H(9B)	0.972(17)
C(9)-H(9C)	0.938(16)

C(2)-O(1)-B(1)	128.26(11)
C(5)-O(3)-B(2)	123.07(9)
C(8)-O(5)-B(3)	123.36(10)
C(3)-N(1)-B(2)	110.97(9)
C(3)-N(1)-B(1)	111.83(10)
B(2)-N(1)-B(1)	118.20(9)
C(3)-N(1)-H(1N)	103.5(10)
B(2)-N(1)-H(1N)	105.8(10)
B(1)-N(1)-H(1N)	105.1(10)
C(6)-N(2)-B(3)	111.98(9)
C(6)-N(2)-B(2)	111.72(9)
B(3)-N(2)-B(2)	117.51(8)
C(6)-N(2)-H(2N)	104.9(9)
B(3)-N(2)-H(2N)	106.3(9)
B(2)-N(2)-H(2N)	103.1(9)
C(9)-N(3)-B(3)	110.50(9)
C(9)-N(3)-B(1)	110.83(9)
B(3)-N(3)-B(1)	121.61(9)
C(9)-N(3)-H(3N)	104.4(10)
B(3)-N(3)-H(3N)	105.3(10)
B(1)-N(3)-H(3N)	102.3(10)
O(1)-B(1)-C(1)	115.36(10)
O(1)-B(1)-N(1)	104.79(9)
C(1)-B(1)-N(1)	114.10(10)

O(1)-B(1)-N(3)	100.45(9)
C(1)-B(1)-N(3)	114.77(10)
N(1)-B(1)-N(3)	105.91(8)
O(3)-B(2)-N(1)	107.26(9)
O(3)-B(2)-N(2)	108.36(9)
N(1)-B(2)-N(2)	105.65(9)
O(3)-B(2)-C(4)	105.71(9)
N(1)-B(2)-C(4)	115.63(10)
N(2)-B(2)-C(4)	113.90(10)
O(5)-B(3)-N(2)	107.06(9)
O(5)-B(3)-N(3)	106.89(9)
N(2)-B(3)-N(3)	106.85(9)
O(5)-B(3)-C(7)	105.92(10)
N(2)-B(3)-C(7)	115.86(10)
N(3)-B(3)-C(7)	113.73(10)
B(1)-C(1)-H(1A)	115.9(12)
B(1)-C(1)-H(1B)	112.9(10)
H(1A)-C(1)-H(1B)	103.7(15)
B(1)-C(1)-H(1C)	115.3(11)
H(1A)-C(1)-H(1C)	100.6(16)
H(1B)-C(1)-H(1C)	107.1(15)
O(2)-C(2)-O(1)	123.37(15)
O(2)-C(2)-H(2)	121.5(10)
O(1)-C(2)-H(2)	115.1(10)
N(1)-C(3)-H(3A)	108.3(10)
N(1)-C(3)-H(3B)	110.4(10)
H(3A)-C(3)-H(3B)	110.4(14)
N(1)-C(3)-H(3C)	109.6(10)
H(3A)-C(3)-H(3C)	110.9(15)
H(3B)-C(3)-H(3C)	107.3(14)
B(2)-C(4)-H(4A)	115.1(12)
B(2)-C(4)-H(4B)	109.9(12)
H(4A)-C(4)-H(4B)	108.3(17)
B(2)-C(4)-H(4C)	112.9(11)
H(4A)-C(4)-H(4C)	110.6(16)
H(4B)-C(4)-H(4C)	98.7(16)

O(4)-C(5)-O(3)	125.77(12)
O(4)-C(5)-H(5)	122.7(10)
O(3)-C(5)-H(5)	111.5(10)
N(2)-C(6)-H(6A)	108.5(11)
N(2)-C(6)-H(6B)	108.6(10)
H(6A)-C(6)-H(6B)	110.3(15)
N(2)-C(6)-H(6C)	107.8(10)
H(6A)-C(6)-H(6C)	110.9(14)
H(6B)-C(6)-H(6C)	110.7(14)
B(3)-C(7)-H(7A)	110.6(10)
B(3)-C(7)-H(7B)	115.3(10)
H(7A)-C(7)-H(7B)	105.0(15)
B(3)-C(7)-H(7C)	112.1(11)
H(7A)-C(7)-H(7C)	106.4(15)
H(7B)-C(7)-H(7C)	106.8(15)
O(6)-C(8)-O(5)	126.33(12)
O(6)-C(8)-H(8)	122.0(11)
O(5)-C(8)-H(8)	111.6(11)
N(3)-C(9)-H(9A)	109.0(9)
N(3)-C(9)-H(9B)	109.4(10)
H(9A)-C(9)-H(9B)	110.6(13)
N(3)-C(9)-H(9C)	107.8(10)
H(9A)-C(9)-H(9C)	109.3(13)
H(9B)-C(9)-H(9C)	110.7(14)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$)for liu153. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	30(1)	32(1)	30(1)	-5(1)	-6(1)	2(1)
O(2)	48(1)	71(1)	47(1)	-8(1)	-20(1)	-2(1)
O(3)	26(1)	27(1)	36(1)	2(1)	7(1)	-4(1)
O(4)	38(1)	27(1)	56(1)	9(1)	15(1)	6(1)
O(5)	33(1)	36(1)	22(1)	1(1)	7(1)	1(1)
O(6)	37(1)	37(1)	39(1)	0(1)	9(1)	10(1)
N(1)	23(1)	23(1)	20(1)	0(1)	3(1)	3(1)
N(2)	21(1)	21(1)	20(1)	-1(1)	0(1)	0(1)
N(3)	20(1)	17(1)	26(1)	1(1)	2(1)	1(1)
B(1)	24(1)	22(1)	23(1)	-3(1)	-1(1)	1(1)
B(2)	20(1)	22(1)	23(1)	1(1)	3(1)	-1(1)
B(3)	24(1)	24(1)	20(1)	2(1)	2(1)	1(1)
C(1)	35(1)	27(1)	41(1)	-7(1)	3(1)	5(1)
C(2)	42(1)	40(1)	33(1)	-6(1)	-5(1)	-4(1)
C(3)	39(1)	46(1)	21(1)	0(1)	7(1)	-2(1)
C(4)	21(1)	32(1)	37(1)	1(1)	4(1)	3(1)
C(5)	35(1)	24(1)	40(1)	4(1)	10(1)	-3(1)
C(6)	33(1)	39(1)	25(1)	-6(1)	-3(1)	-7(1)
C(7)	33(1)	30(1)	34(1)	10(1)	-2(1)	4(1)
C(8)	32(1)	38(1)	32(1)	-7(1)	11(1)	1(1)
C(9)	28(1)	24(1)	41(1)	4(1)	4(1)	-6(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for liu153.

	x	y	z	U(eq)
H(1A)	-560(30)	2423(8)	90(20)	63(6)
H(1B)	-2270(20)	2176(7)	-680(20)	44(4)
H(1C)	-1710(30)	2116(8)	1150(30)	63(5)
H(1N)	-780(20)	734(6)	-114(17)	28(4)
H(2)	1220(20)	1931(7)	2480(20)	48(5)
H(2N)	-1380(20)	557(6)	-2888(17)	28(4)
H(3A)	-2500(20)	603(7)	1660(20)	44(4)
H(3B)	-1230(20)	1071(7)	2290(20)	41(4)
H(3C)	-3070(20)	1213(7)	1530(20)	42(4)
H(3N)	1050(20)	1242(6)	-1945(17)	26(3)
H(4A)	-4490(30)	1633(8)	-1930(20)	55(5)
H(4B)	-5650(30)	1130(8)	-2330(30)	63(6)
H(4C)	-5320(20)	1272(7)	-650(20)	51(5)
H(5)	-3460(20)	-449(7)	-773(19)	38(4)
H(6A)	-4030(20)	314(7)	-4110(20)	44(4)
H(6B)	-2770(20)	517(7)	-5300(20)	43(4)
H(6C)	-4220(20)	906(7)	-4784(19)	40(4)
H(7A)	-1470(20)	2100(7)	-4840(20)	48(5)
H(7B)	-2790(20)	2072(8)	-3560(20)	52(5)
H(7C)	-3140(30)	1730(8)	-5160(20)	55(5)
H(8)	1690(20)	662(7)	-5620(20)	49(5)
H(9A)	2270(20)	2053(6)	-1520(20)	36(4)
H(9B)	1860(20)	1945(7)	-3380(20)	40(4)
H(9C)	580(20)	2301(7)	-2462(19)	36(4)

Table 6. Torsion angles [°] for liu153.

C(2)-O(1)-B(1)-C(1)	16.87(19)
C(2)-O(1)-B(1)-N(1)	-109.47(14)
C(2)-O(1)-B(1)-N(3)	140.84(13)
C(3)-N(1)-B(1)-O(1)	72.68(12)
B(2)-N(1)-B(1)-O(1)	-156.61(9)
C(3)-N(1)-B(1)-C(1)	-54.44(14)
B(2)-N(1)-B(1)-C(1)	76.28(13)
C(3)-N(1)-B(1)-N(3)	178.36(10)
B(2)-N(1)-B(1)-N(3)	-50.93(12)
C(9)-N(3)-B(1)-O(1)	-73.44(11)
B(3)-N(3)-B(1)-O(1)	154.16(9)
C(9)-N(3)-B(1)-C(1)	50.94(13)
B(3)-N(3)-B(1)-C(1)	-81.45(13)
C(9)-N(3)-B(1)-N(1)	177.75(9)
B(3)-N(3)-B(1)-N(1)	45.35(12)
C(5)-O(3)-B(2)-N(1)	-61.00(14)
C(5)-O(3)-B(2)-N(2)	52.63(14)
C(5)-O(3)-B(2)-C(4)	175.09(11)
C(3)-N(1)-B(2)-O(3)	-56.30(12)
B(1)-N(1)-B(2)-O(3)	172.59(9)
C(3)-N(1)-B(2)-N(2)	-171.74(10)
B(1)-N(1)-B(2)-N(2)	57.16(12)
C(3)-N(1)-B(2)-C(4)	61.31(13)
B(1)-N(1)-B(2)-C(4)	-69.79(13)
C(6)-N(2)-B(2)-O(3)	57.04(12)
B(3)-N(2)-B(2)-O(3)	-171.52(9)
C(6)-N(2)-B(2)-N(1)	171.73(9)
B(3)-N(2)-B(2)-N(1)	-56.84(12)
C(6)-N(2)-B(2)-C(4)	-60.28(13)
B(3)-N(2)-B(2)-C(4)	71.15(12)
C(8)-O(5)-B(3)-N(2)	-53.58(14)
C(8)-O(5)-B(3)-N(3)	60.64(14)
C(8)-O(5)-B(3)-C(7)	-177.77(11)
C(6)-N(2)-B(3)-O(5)	-63.33(12)

B(2)-N(2)-B(3)-O(5)	165.36(9)
C(6)-N(2)-B(3)-N(3)	-177.57(9)
B(2)-N(2)-B(3)-N(3)	51.12(12)
C(6)-N(2)-B(3)-C(7)	54.55(14)
B(2)-N(2)-B(3)-C(7)	-76.76(13)
C(9)-N(3)-B(3)-O(5)	67.29(11)
B(1)-N(3)-B(3)-O(5)	-160.18(9)
C(9)-N(3)-B(3)-N(2)	-178.36(9)
B(1)-N(3)-B(3)-N(2)	-45.82(12)
C(9)-N(3)-B(3)-C(7)	-49.24(13)
B(1)-N(3)-B(3)-C(7)	83.29(13)
B(1)-O(1)-C(2)-O(2)	-178.92(14)
B(2)-O(3)-C(5)-O(4)	-4.3(2)
B(3)-O(5)-C(8)-O(6)	-3.3(2)

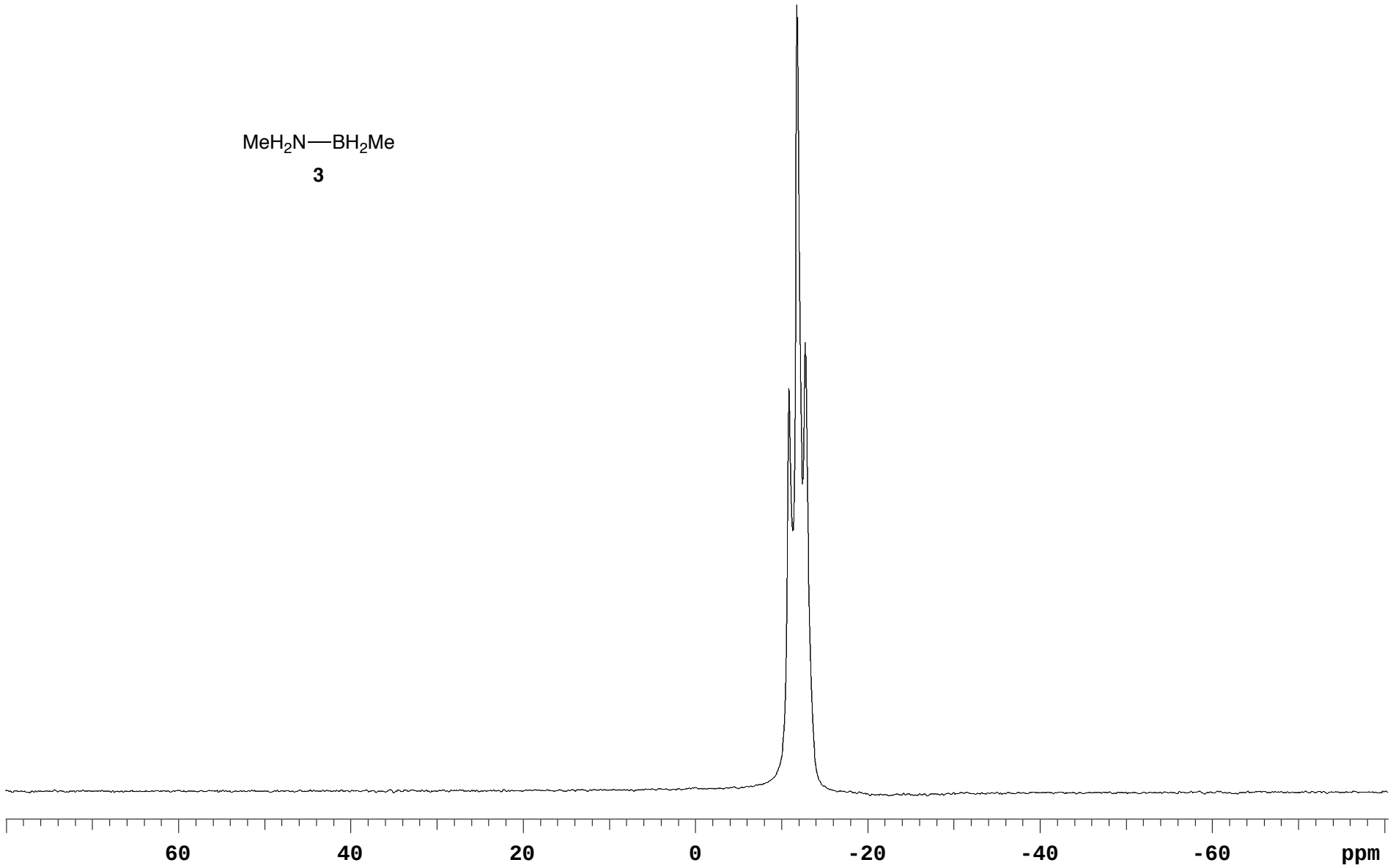
Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for liu153 [Å and °].

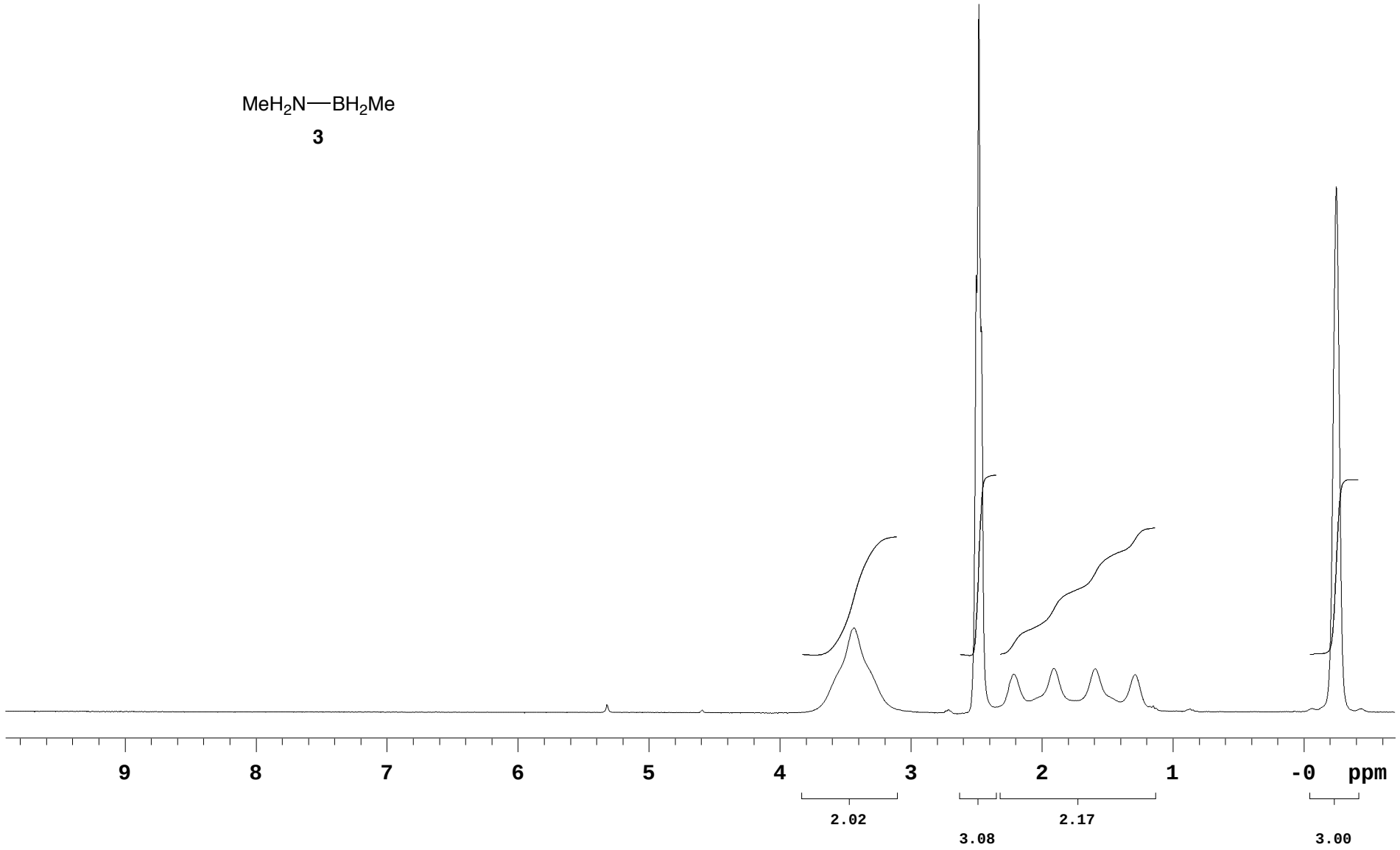
D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1N)...O(4)#1	0.845(16)	2.326(15)	3.0747(14)	147.9(13)
N(1)-H(1N)...O(4)	0.845(16)	2.458(15)	3.0505(15)	127.9(12)
N(2)-H(2N)...O(4)	0.879(15)	2.196(15)	2.8709(14)	133.3(12)
N(2)-H(2N)...O(6)	0.879(15)	2.282(15)	2.9385(14)	131.5(12)
N(3)-H(3N)...O(6)	0.849(15)	2.367(15)	3.0066(14)	132.5(12)

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y,-z



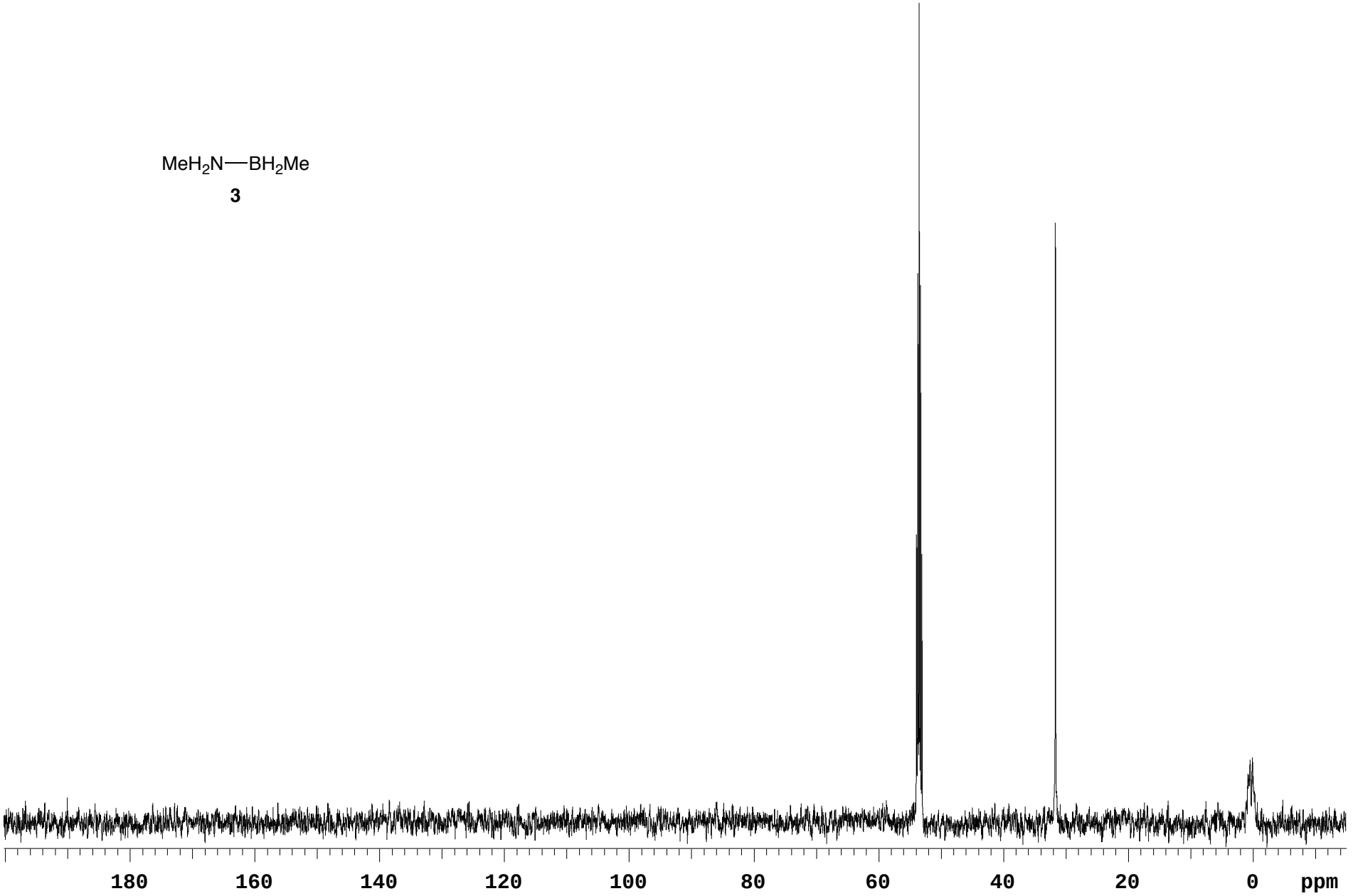
PULSE SEQUENCE Relax. delay 0.200 sec Pulse 90.0 degrees Acq. time 0.200 sec Width 40000.0 Hz 48 repetitions	OBSERVE B11, 96.2682868	DATA PROCESSING Line broadening 10.0 Hz FT size 16384 Total time 1 minute		UO Inova-300-North Boron-11 Solvent: cd2cl2 Temp. 25.0 C / 298.1 K Operator: ishibash File: ji-III-B077_B INOVA-500 "sunofnmr.uoregon.edu"



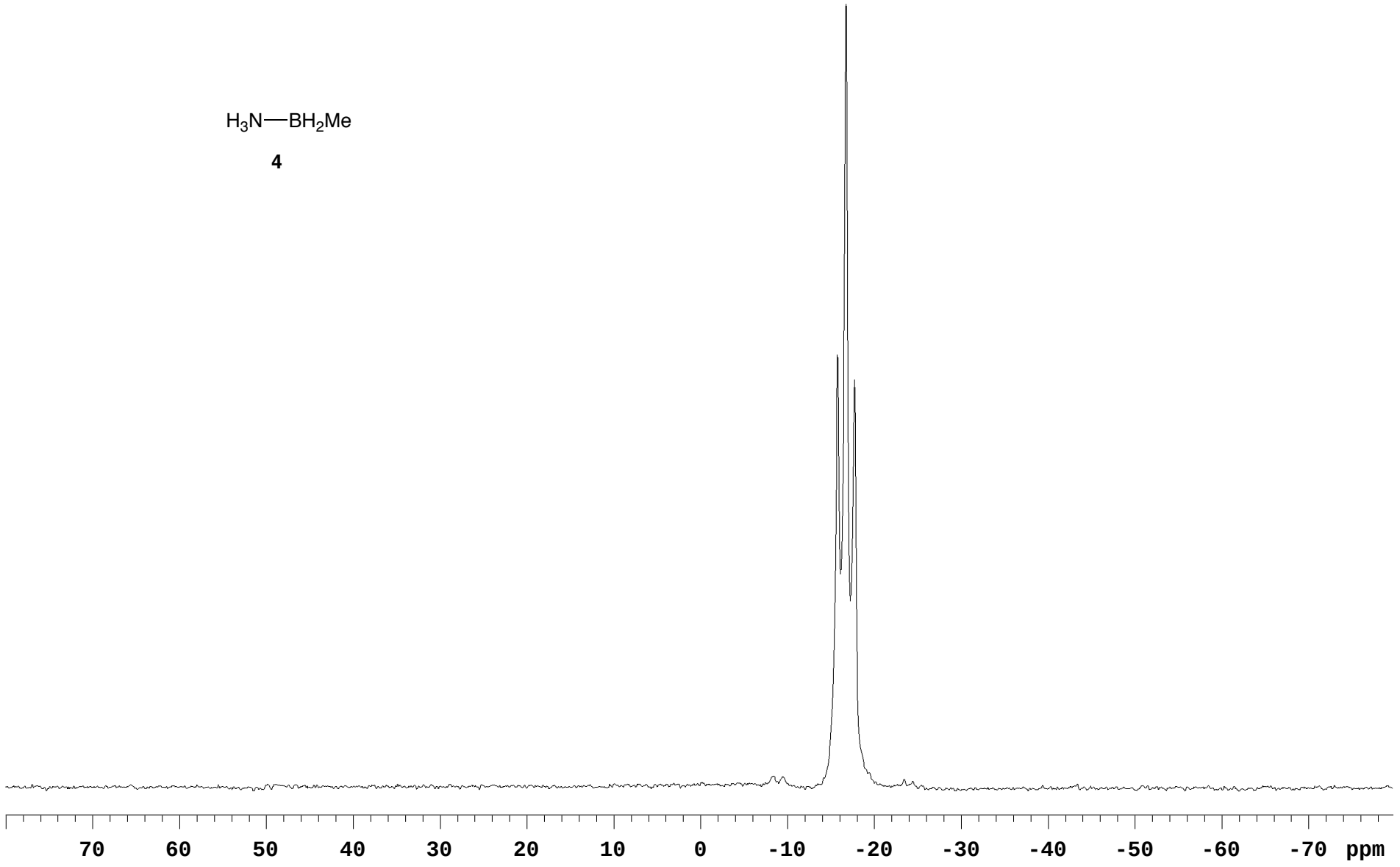
PULSE SEQUENCE Relax. delay 1.000 sec Pulse 45.0 degrees Acq. time 3.000 sec Width 4800.8 Hz 16 repetitions	OBSERVE H1, 300.0510213	DATA PROCESSING FT size 32768 Total time 1 minute		UO Inova-300-North standard 1H Solvent: cd2cl2 Temp. 25.0 C / 298.1 K Operator: ishibash File: ji-III-H077_B INOVA-500 "sunofnmr.uoregon.edu"

$MeH_2N—BH_2Me$

3



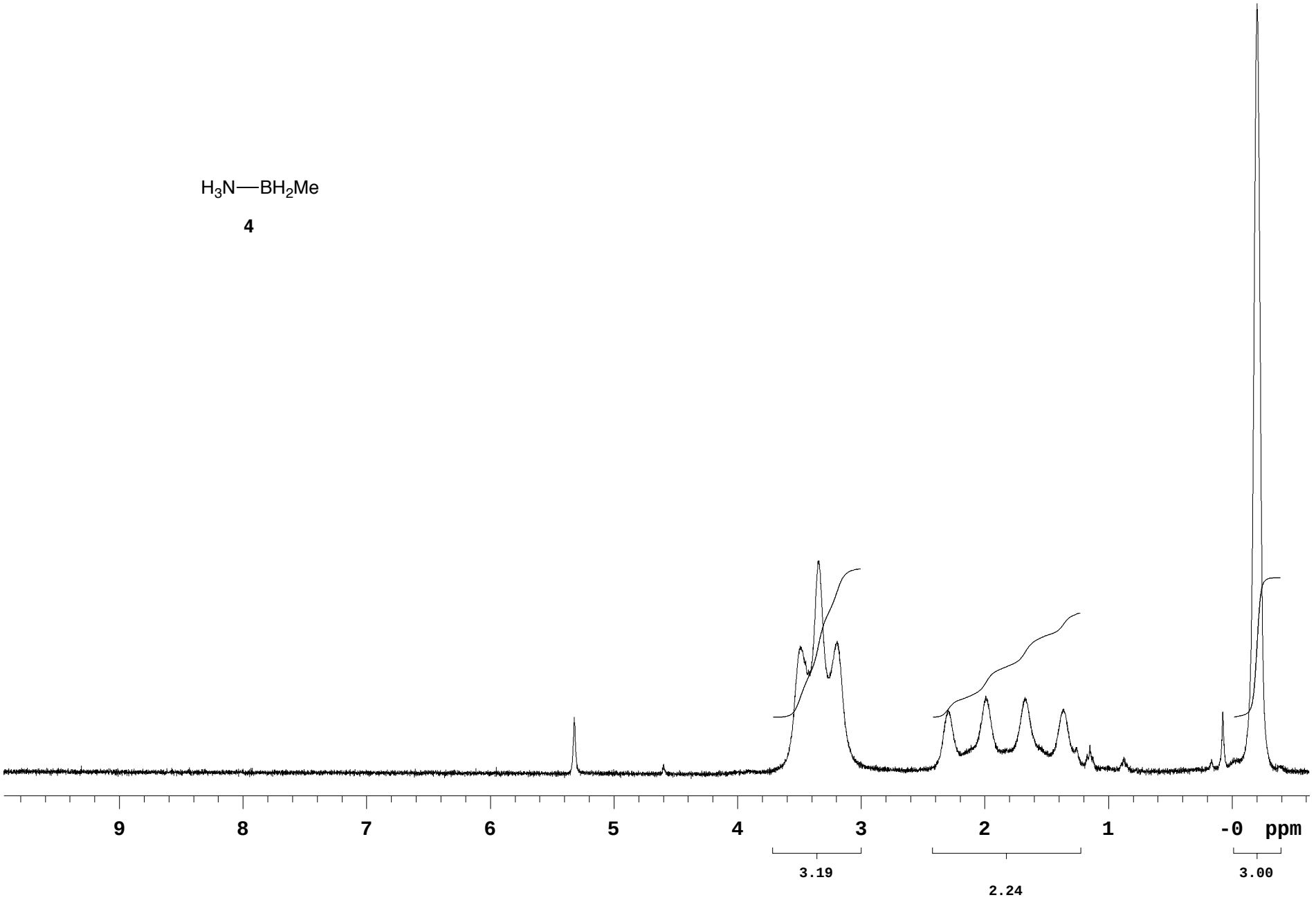
PULSE SEQUENCE Relax. delay 1.000 sec Pulse 45.0 degrees Acq. time 1.000 sec Width 31434.2 Hz 68 repetitions	OBSERVE C13, 125.7515527 DECOUPLE H1, 500.1077051 Power 39 dB continuously on WALTZ-16 modulated	DATA PROCESSING Line broadening 5.0 Hz FT size 65536 Total time 2 minutes		UO Inova-500 Carbon-13 Solvent: cd2cl2 Temp. 25.0 C / 298.1 K Operator: ishibash File: ji-III-C077_B INOVA-500 "sunofnmr.uoregon.edu"



PULSE SEQUENCE Relax. delay 0.200 sec Pulse 90.0 degrees Acq. time 0.200 sec Width 40000.0 Hz 40 repetitions	OBSERVE B11, 96.2682868	DATA PROCESSING Line broadening 10.0 Hz FT size 16384 Total time 1 minute		UO Inova-300-North Boron-11 Solvent: cd2cl2 Temp. 25.0 C / 298.1 K Operator: ishibash File: ji-III-B078_A INOVA-500 "sunofnmr.uoregon.edu"

$H_3N—BH_2Me$

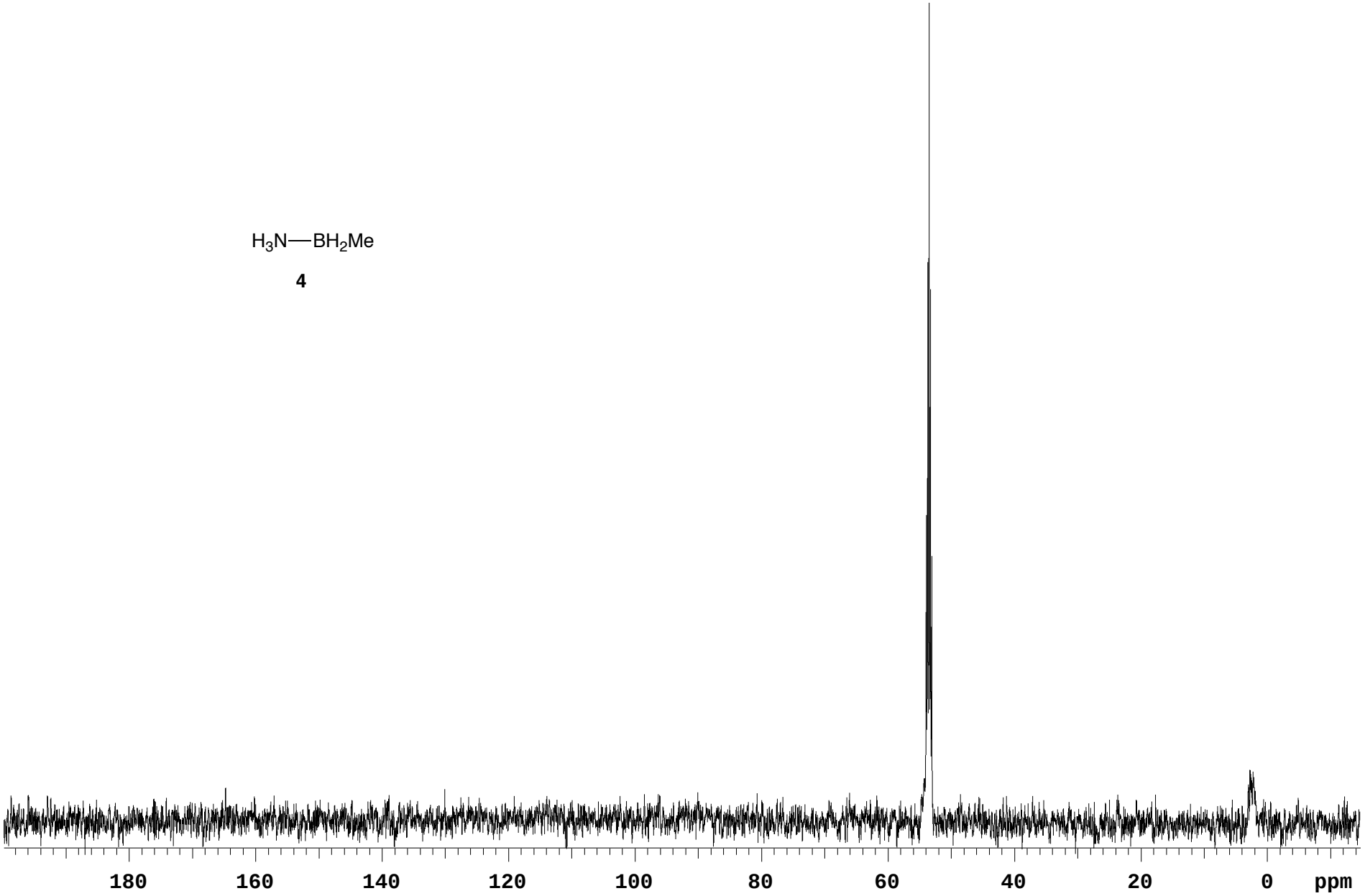
4



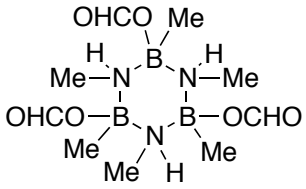
PULSE SEQUENCE Relax. delay 1.000 sec Pulse 45.0 degrees Acq. time 3.000 sec Width 4800.8 Hz 4 repetitions	OBSERVE H1, 300.0510210	DATA PROCESSING FT size 32768 Total time 1 minute		STANDARD 1H OBSERVE - profile Solvent: cd2cl2 Temp. 25.0 C / 298.1 K Operator: ishibash File: ji-III-H078_A INOVA-500 "sunofnmr.uoregon.edu"

$H_3N—BH_2Me$

4

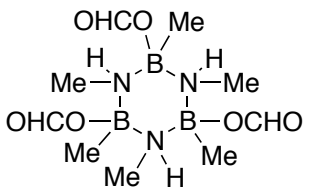


PULSE SEQUENCE Relax. delay 1.000 sec Pulse 45.0 degrees Acq. time 1.000 sec Width 31434.2 Hz 236 repetitions	**OBSERVE C13, 125.7515499** **DECOUPLE H1, 500.1077051** Power 39 dB continuously on WALTZ-16 modulated	**DATA PROCESSING** Line broadening 5.0 Hz FT size 65536 Total time 7 minutes		**UO Inova-500 Carbon-13** Solvent: cd2cl2 Temp. 25.0 C / 298.1 K Operator: ishibash File: ji-III-C078_A INOVA-500 "sunofnmr.uoregon.edu"



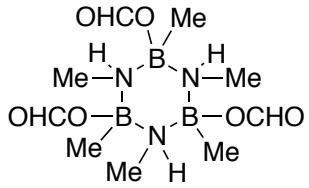
7

PULSE SEQUENCE Relax. delay 0.200 sec Pulse 90.0 degrees Acq. time 0.200 sec Width 40000.0 Hz 40 repetitions	OBSERVE B11, 96.2682868	DATA PROCESSING Line broadening 10.0 Hz FT size 16384 Total time 1 minute		UO Inova-300-North Boron-11 Solvent: cd2cl2 Temp. 25.0 C / 298.1 K Operator: ishibash File: ji-III-B076_B INOVA-500 "sunofnmr.uoregon.edu"



7

PULSE SEQUENCE Relax. delay 1.000 sec Pulse 45.0 degrees Acq. time 2.048 sec Width 8001.6 Hz 16 repetitions	OBSERVE H1, 500.1042894	DATA PROCESSING FT size 32768 Total time 1 minute		UO Inova-500 standard 1H Solvent: c6d6 Temp. 25.0 C / 298.1 K Operator: ishibash File: ji-III-H079_C INOVA-500 "sunofnmr.uoregon.edu"



7

PULSE SEQUENCE Relax. delay 1.000 sec Pulse 45.0 degrees Acq. time 1.000 sec Width 31434.2 Hz 1120 repetitions	OBSERVE C13, 125.7515470 DECOUPLE H1, 500.1077051 Power 39 dB continuously on WALTZ-16 modulated	DATA PROCESSING Line broadening 5.0 Hz FT size 65536 Total time 37 minutes		UO Inova-500 Carbon-13 Solvent: cd2cl2 Temp. 25.0 C / 298.1 K Operator: ishibash File: ji-III-C076_B-2 INOVA-500 "sunofnmr.uoregon.edu"