Supporting Information

A readily accessible ruthenium catalyst for the solvolytic dehydrogenation of amine–borane adducts.

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Fig. S1 .Solvents analysis. Reaction conditions: 1.38 mmol AB, 0.5 mol % [Ru(p-Cym)(bipy)Cl]Cl, 3 mL solvent, rt.

Fig.S2 Reaction profile (gas evolution) using different substrates in THF/H₂O 1/3. Unreactive substrates (TEAB and TMAB have not been represented since no gas evolution was detected).

Fig.S3 Reaction profile (gas evolution) using different substrates in iPrOH/H$_2$O = 1/1. Unreactive substrates (TEAB and TMAB have not been represented since no gas evolution was detected).
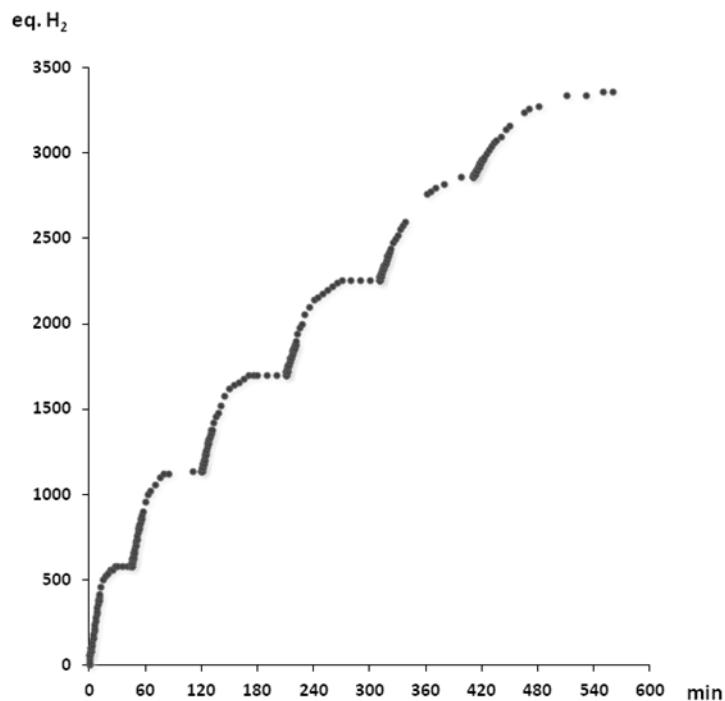
Fig. S4 Reaction profile (equivalents of H_2 evolved per mole of Ru vs time) in 6 successive cycles. Reaction conditions (first cycle): 1.38 mmol AB, 0.5 mol % [Ru(*p*-Cym)(bipy)Cl]Cl, 3 mL THF/H_2O 1/3, rt. Successive additions of 1.38 mmol AB in 0.5 mL of THF/H_2O 1/3.
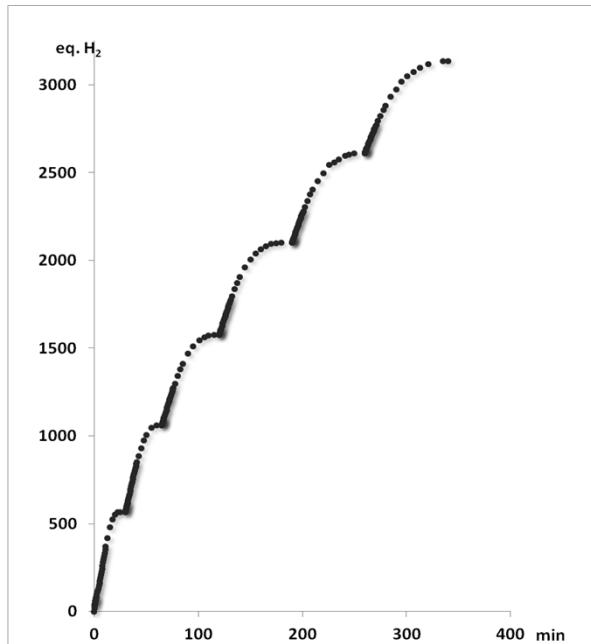
Fig. S5 Reaction profile (equivalents of H_2 per mole of Ru evolved vs time) in 6 successive cycles. Reaction conditions (first cycle): 1.38 mmol AB, 0.5 mol % [Ru(*p*-Cym)(bipy)Cl]Cl, 3 mL iPrOH/H_2O 1/1, rt. Successive additions of 1.38 mmol AB in 0.5 mL of THF/H_2O 1/3.
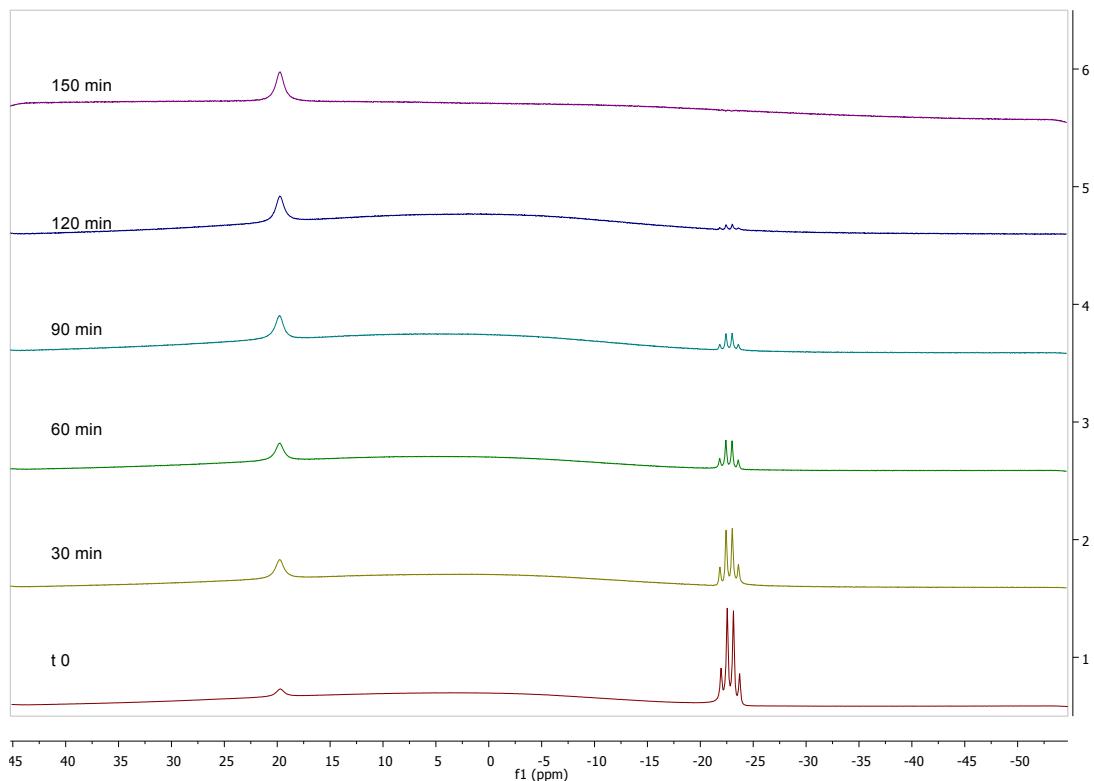
Fig. S6 ^{11}B-NMR spectra (160.46 MHz) at different reaction times. Reaction conditions: 0.46 mmol AB, 0.5 mol % [Ru(p-Cym)(bipy)Cl]Cl, 1 mL THF/H_2O 3/1, internal D_2O capillary, rt.
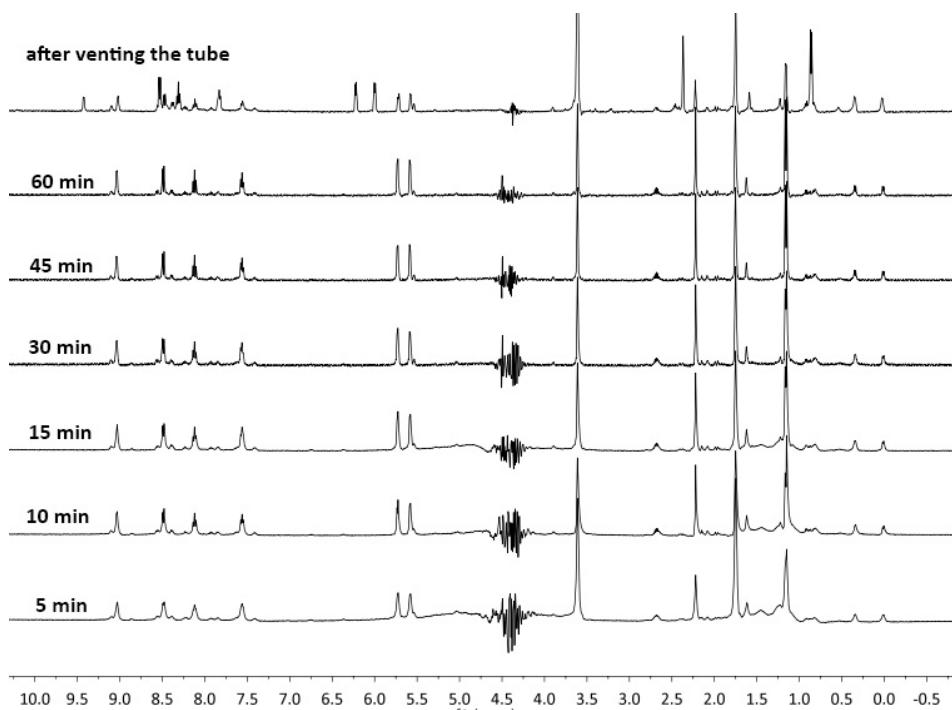
Fig. S7 ^{1}H-NMR spectra at different reaction times, and after venting the tube. Reaction conditions: 0.14 mmol AB, 0.014 mmol [Ru(p-Cym)(bipy)Cl]Cl, 1 mL THF-d_8/H_2O 3/1, 15 ºC.
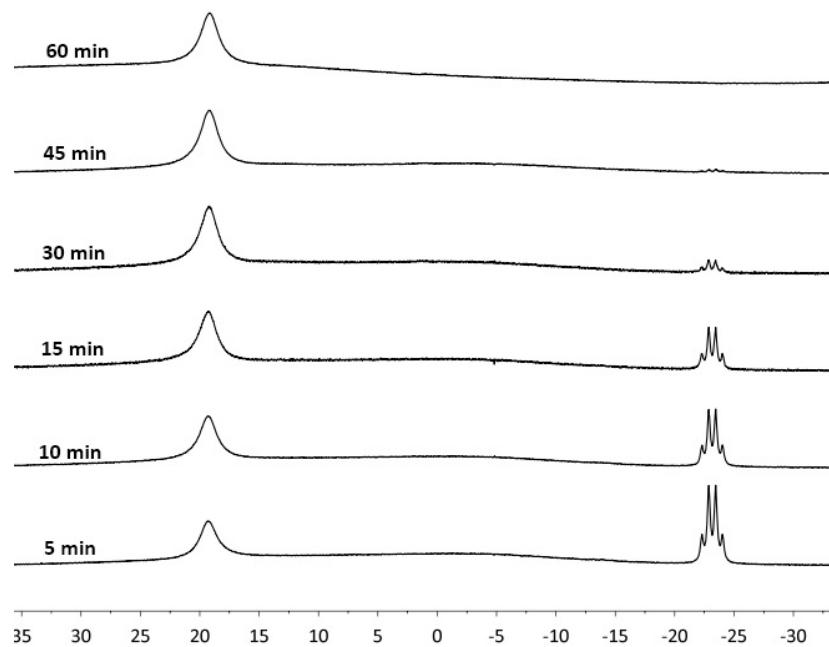
Fig. S8 ^{11}B-NMR spectra (160.46 MHz) at different reaction times. Reaction conditions: 0.14 mmol AB, 0.014 mmol [Ru(p-Cym)(bipy)Cl]Cl, 1 mL THF-d_8/H$_2$O 3/1, 15 ºC.
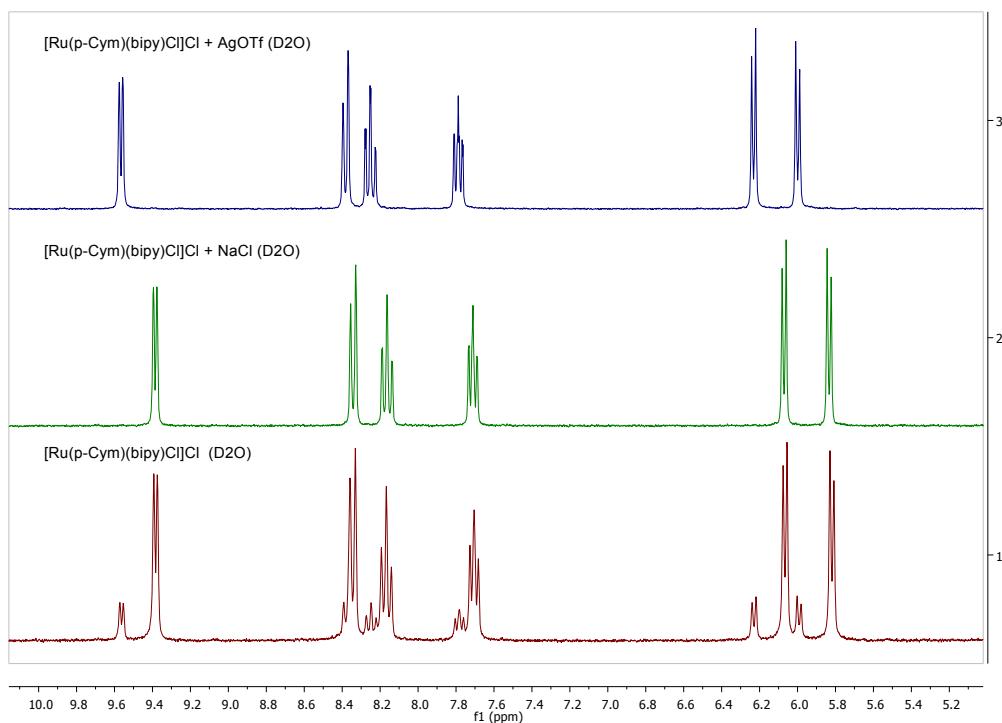
Fig. S9 ^{1}H-NMR spectra (D$_2$O), aromatic region, 300MHz. Top: [Ru(p-Cym)(bipy)Cl]Cl + AgOTf, middle [Ru(p-Cym)(bipy)Cl]Cl + NaCl, bottom [Ru(p-Cym)(bipy)Cl]Cl. The spectrum of the complex with excess of NaCl has been recalibrated to correct the shift in the spectra produced by the addition of salt.
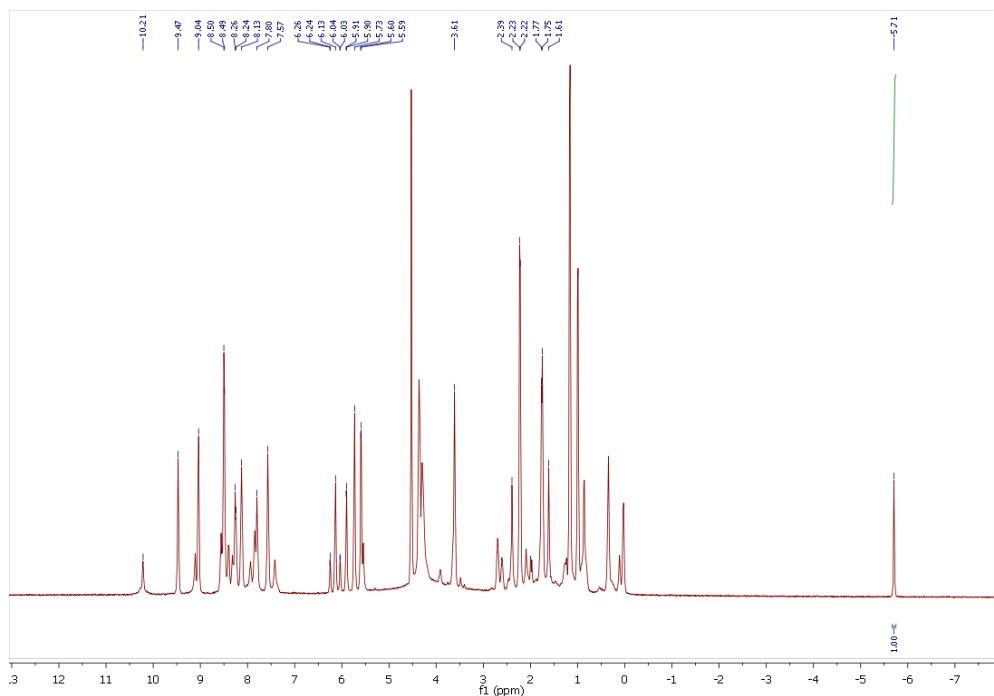
Fig. S10 ^{1}H-NMR spectra, 500MHz (THF-d_8/H$_2$O = 3/1). [Ru(p-Cym)(bipy)Cl]Cl + 1 eq. AB.
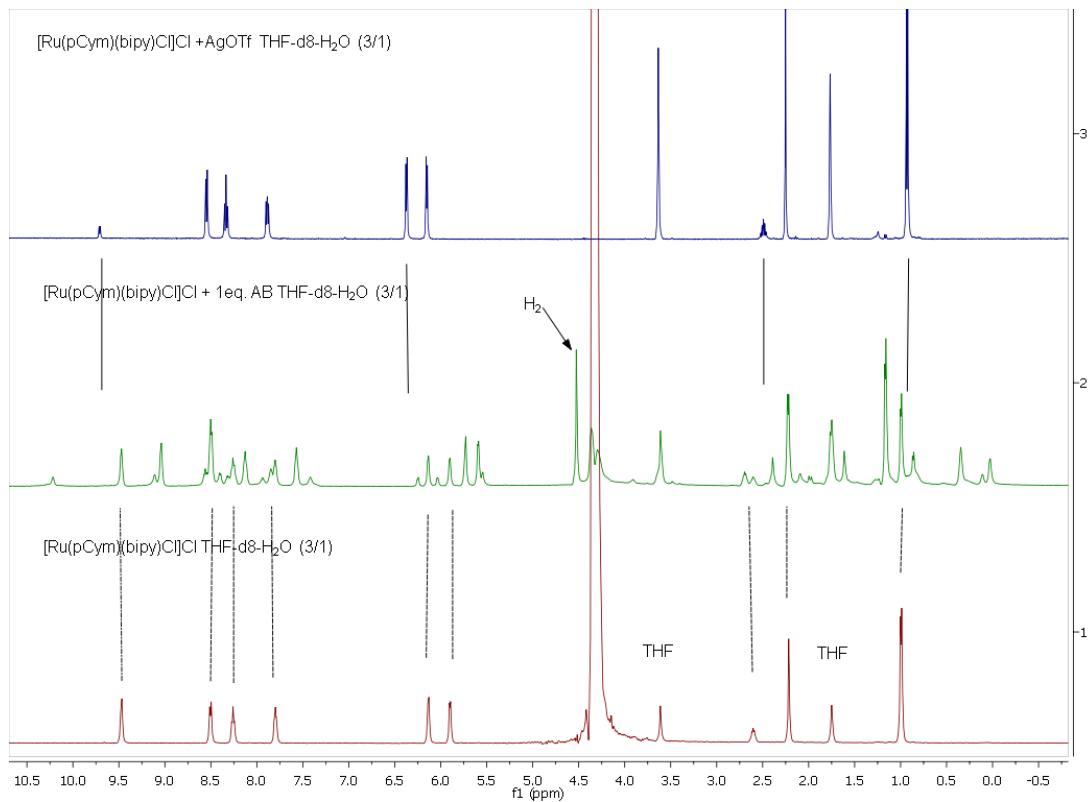
Fig. S11 ^{1}H-NMR spectra, 500MHz (THF-d_8/H$_2$O = 3/1). Top (blue): [Ru(p-Cym)(bipy)Cl]Cl + AgOTf = [Ru(p-Cym)(bipy)(H$_2$O)]$^{2+}$. Middle (green): [Ru(p-Cym)(bipy)Cl]Cl + 1 eq. AB, bottom (red) [Ru(p-Cym)(bipy)Cl]Cl. The top spectra has been recorded and introduced here only to show that this species is not present in the reaction mixture.
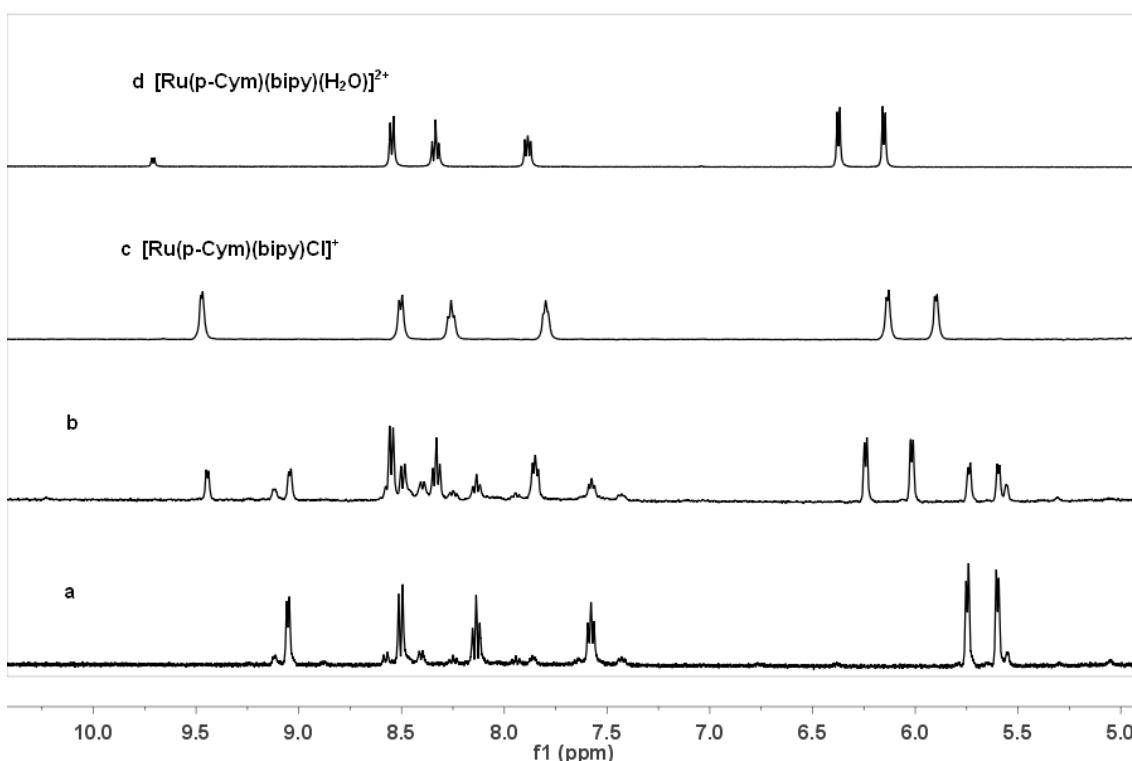
Fig S12. ^{1}H-NMR spectra (500MHz) in THF-d$_8$/H$_2$O = 3/1. a) *In situ* NMR experiment 60 min of reaction at 15 ºC. b) *In situ* NMR experiment after venting the tube. c) Ru(p-Cym)(bipy)Cl]Cl. d) Ru(p-Cym)(bipy)Cl]Cl + excess of AgOTf (in this spectra the intensity of the signal of the bipyridine at 9.7 ppm presents low intensity due to an artifact caused by the solvent suppression sequence used to acquire this spectra).
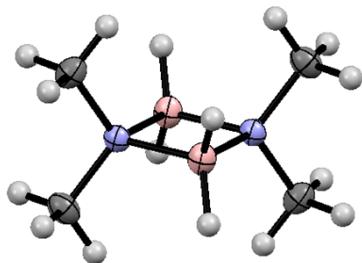
Fig.S13 ORTEP representation of [NMe$_2$BH$_2$]$_2$. Ellipsoids at 50% of probability.

Crystallographic data:

> Table S1 - Crystal Data and Details of the Structure Determination
>   for: a2014197_martin1   R = 0.04

> Table S2 - Final Coordinates and Equivalent Isotropic Displacement
>   Parameters of the non-Hydrogen atoms
>   for: a2014197_martin1   R = 0.04

> Table S3 - Hydrogen Atom Positions and Isotropic Displacement

Parameters
for: a2014197_martin1   R = 0.04

Table S4 - (An)isotropic Displacement Parameters
for: a2014197_martin1   R = 0.04

Table S5 - Bond Distances (Angstrom)
for: a2014197_martin1   R = 0.04

Table S6 - Bond Angles   (Degrees)
for: a2014197_martin1   R = 0.04

Table S7 - Torsion Angles (Degrees)
for: a2014197_martin1   R = 0.04

Table S8 - Contact Distances(Angstrom)
for: a2014197_martin1   R = 0.04

Table S1 - Crystal Data and Details of the Structure Determination
for: a2014197_martin1   R = 0.04

Crystal Data

Formula   C4 H16 B2 N2

Formula Weight   113.81

Crystal System   Triclinic

Space group   P-1   (No. 2)

a, b, c [Angstrom]   5.8241(12) 6.0130(13) 6.2338(13)

alpha, beta, gamma [deg]   80.299(18) 81.535(17)   65.94(2)

V [Ang**3]   195.74(8)

Z   1

D(calc) [g/cm**3]   0.965

Mu(CuKa) [/mm]   0.408

F(000)   64

Crystal Size [mm]   0.00 x 0.00 x 0.00

Data Collection

Temperature (K)   100

Radiation [Angstrom]   CuKa   1.54184

Theta Min-Max [Deg]   7.2, 62.4

Dataset   -5: 6 ; -6: 6 ; -7: 7

Tot., Uniq. Data, R(int)   969, 619, 0.027

Observed data [I > 2.0 sigma(I)]   513

             Refinement

Nref, Npar   619, 47

R, wR2, S   0.0387, 0.0905, 1.09

w = 1/[\s^2^(Fo^2^)+(0.0341P)^2^+0.0338P] where P=(Fo^2^+2Fc^2^)/3

Max. and Av. Shift/Error   0.00, 0.00

Min. and Max. Resd. Dens. [e/Ang^3]   -0.14, 0.13

Table S2 - Final Coordinates and Equivalent Isotropic Displacement
      Parameters of the non-Hydrogen atoms
      for: a2014197_martin1   R = 0.04

Atom	x	y	z	U(eq) [Ang^2]
N1	0.4753(2)	0.1413(2)	-0.15659(19)	0.0199(4)
C1	0.6823(3)	0.1647(3)	-0.3128(2)	0.0287(5)
C2	0.2326(3)	0.3265(3)	-0.2279(2)	0.0270(5)
B1	0.5140(3)	0.1324(3)	0.0947(3)	0.0238(5)

  U(eq) = 1/3 of the trace of the orthogonalized U Tensor

Table S3 - Hydrogen Atom Positions and Isotropic Displacement
      Parameters
      for: a2014197_martin1   R = 0.04

Atom	x	y	z	U(iso) [Ang^2]
H1A	0.65970	0.13930	-0.45820	0.0430
H1B	0.84400	0.04140	-0.26580	0.0430
H1C	0.68110	0.32910	-0.31820	0.0430
H1D	0.694(3)	0.137(3)	0.113(3)	0.025(4)
H1E	0.344(3)	0.267(3)	0.177(3)	0.026(4)
H2A	0.22940	0.49100	-0.22960	0.0400
H2B	0.09420	0.30810	-0.12660	0.0400

H2C   0.21270   0.30350   -0.37510   0.0400

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The Temperature Factor has the Form of Exp(-T) Where
T = 8*(Pi**2)*U*(Sin(Theta)/Lambda)**2 for Isotropic Atoms

Table S4 - (An)isotropic Displacement Parameters
      for: a2014197_martin1   R = 0.04

Atom	U(1,1) or U	U(2,2)	U(3,3)	U(2,3)	U(1,3)	U(1,2)
N1	0.0235(7)	0.0207(6)	0.0162(6)	-0.0038(4)	-0.0020(5)	-0.0086(5)
C1	0.0319(9)	0.0348(8)	0.0236(8)	-0.0070(6)	0.0016(6)	-0.0173(7)
C2	0.0309(9)	0.0231(8)	0.0259(8)	-0.0044(6)	-0.0074(6)	-0.0074(7)
B1	0.0336(10)	0.0220(9)	0.0179(9)	-0.0041(6)	-0.0053(7)	-0.0115(7)

==

The Temperature Factor has the Form of Exp(-T) Where
T = 8*(Pi**2)*U*(Sin(Theta)/Lambda)**2 for Isotropic Atoms
T = 2*(Pi**2)*Sumij(h(i)*h(j)*U(i,j)*Astar(i)*Astar(j)), for
Anisotropic Atoms. Astar(i) are Reciprocal Axial Lengths and
  h(i) are the Reflection Indices.

Table S5 - Bond Distances (Angstrom)
      for: a2014197_martin1   R = 0.04

N1	-C1	1.472(2)	C1	-H1C	0.9800
N1	-C2	1.473(2)	C2	-H2A	0.9800
N1	-B1	1.604(2)	C2	-H2B	0.9800
N1	-B1_a	1.603(2)	C2	-H2C	0.9800
C1	-H1A	0.9800	B1	-H1D	1.083(19)
C1	-H1B	0.9800	B1	-H1E	1.112(18)

Table S6 - Bond Angles   (Degrees)
      for: a2014197_martin1   R = 0.04

C1	-N1	-C2	109.32(11)	N1	-C2	-H2A	109.00
C1	-N1	-B1	114.59(12)	H2A	-C2	-H2B	109.00
C1	-N1	-B1_a	115.03(12)	N1	-C2	-H2B	109.00

C2	-N1	-B1	114.61(11)	N1	-C2	-H2C	109.00
C2	-N1	-B1_a	115.16(13)	H2A	-C2	-H2C	109.00
B1	-N1	-B1_a	86.81(11)	H2B	-C2	-H2C	109.00
N1	-C1	-H1C	109.00	N1	-B1	-N1_a	93.19(11)
N1	-C1	-H1A	109.00	N1	-B1	-H1D	111.8(10)
N1	-C1	-H1B	109.00	N1	-B1	-H1E	110.7(10)
H1B	-C1	-H1C	109.00	H1D	-B1	-H1E	116.8(13)
H1A	-C1	-H1B	110.00	N1_a	-B1	-H1D	110.5(9)
H1A	-C1	-H1C	109.00	N1_a	-B1	-H1E	111.5(9)

Table S7 - Torsion Angles (Degrees)
for: a2014197_martin1   R = 0.04

C1	-N1	-B1	-N1_a	-116.13(13)
C2	-N1	-B1	-N1_a	116.29(13)
B1_a	-N1	-B1	-N1_a	0.00(11)
C1_a	-N1_a	-B1	-N1	-115.72(13)
C2_a	-N1_a	-B1	-N1	115.76(12)
B1_a	-N1_a	-B1	-N1	0.00(10)

Table S8 - Contact Distances(Angstrom)
for: a2014197_martin1   R = 0.04

H1A	.H2C	2.3900	H1E	.H2B	2.4700
H1B	.H1D	2.4700	H1E	.H1B_a	2.4600
H1B	.H1E_a	2.4600	H2A	.H1C	2.4200
H1C	.H2A	2.4200	H2B	.H1E	2.4700
H1D	.H1B	2.4700	H2B	.H1D_a	2.4400
H1D	.H2B_a	2.4400	H2C	.H1A	2.3900

Translation of Symmetry Code to Equiv.Pos

a =[2655.00] = [2_655] =1-x,-y,-z