

Supporting Information

Catalytic Dehydrogenation of Dimethylamine-Borane by Group 4 Metallocene Alkyne Complexes and Homoleptic Amido Compounds[‡]

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Table of Contents

S1	Experimental Details
S3	NMR of 2Ti catalysed dehydrogenation of 1
S4	NMR of 2Zr catalysed dehydrogenation of 1
S6	NMR of 8Ti catalysed dehydrogenation of 1
S7	NMR of 8Zr catalysed dehydrogenation of 1
S8	ESI-MS of 8Ti catalysed dehydrogenation of 1

Experimental Details

General Considerations: All operations were carried out under argon with standard Schlenk techniques or in a glovebox. Prior to use nonhalogenated solvents were freshly distilled from sodium tetraethylaluminate, stored under argon and degassed in an ultrasonic bath. Dimethylamine borane (**1**) was purchased from Sigma Aldrich and purified by sublimation. TiCl_4 , $\text{Ti}(\text{O}^i\text{Pr})_4$, $\text{Ti}(\text{NMe}_2)_4$ and $\text{Zr}(\text{NMe}_2)_4$ were purchased from Sigma Aldrich and used as received. Complexes **2Ti**, **2Zr**, **7Ti** and **7Zr** were synthesised according to published procedures.^{1,2} NMR spectra were recorded on a Bruker AV 300 (^1H : 300 MHz, ^{11}B : 96 MHz). Chemical shifts (^{11}B) are given in ppm relative to $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (external standard). Gas chromatography was performed using an Agilent Technologies 7890A, Column: 60/80 Carboxen 1000 (Supelco), Detection: TCD. ESI-MS was performed on a 6210 Time-of-Flight LC/MS (Agilent). Volumetric analyses were carried out in a double-walled thermostatically controlled reaction vessel using an automatically operating burette (MesSen Nord GmbH, Stäbelow, Germany).³

General procedure for the dehydrogenation of dimethylamine borane.

A solution of the catalyst (0.08 mmol, 2 mol%) in 3 mL of toluene was stirred at 24 °C. To this, a solution of dimethylamine borane (**1**) (0.240 g, 4.1 mmol) in 2 mL of toluene was added. The reaction vessel was closed, the flow of Argon was stopped and the excess pressure was released. The measurement was started and hydrogen evolution curves were recorded. Gas samples were taken at the end of the experiment and analysed by gas chromatography.

General procedure for NMR investigations of the dehydrogenation reactions.

Solutions of the catalyst (0.1 mL of a stock solution, 2 mol%) and dimethylamine borane (**1**) (0.005 g in 0.4 mL of toluene) were placed in a J. Young NMR tube. The progress of the reaction was monitored by $^{11}\text{B}\{^1\text{H}\}$ NMR spectroscopy. The ^{11}B NMR spectra were collected unlocked, however, the spectrometer was shimmed with a solution of the catalyst in toluene- d_8 and maintained with the same settings throughout. Proton coupled experiments were used to confirm the nature of the reaction intermediates.

NMR of 2Ti catalysed dehydrogenation of **1**

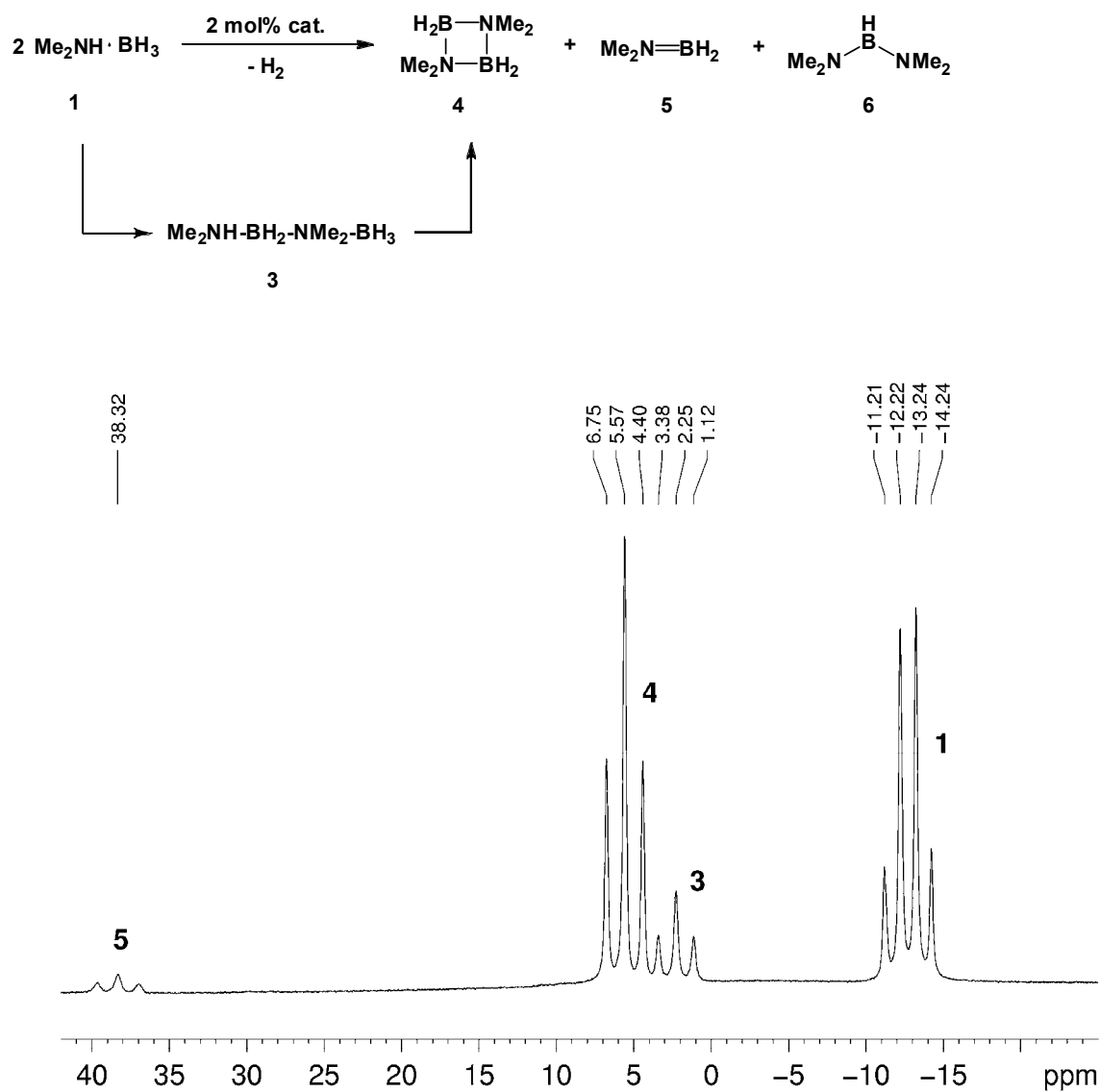


Figure S1. ^{11}B NMR spectrum (96 MHz, 297 K, toluene, unlocked) of the reaction of **1** with **2Ti** (2 mol%), recorded after a reaction time of 6 h.

NMR of 2Zr catalysed dehydrogenation of 1

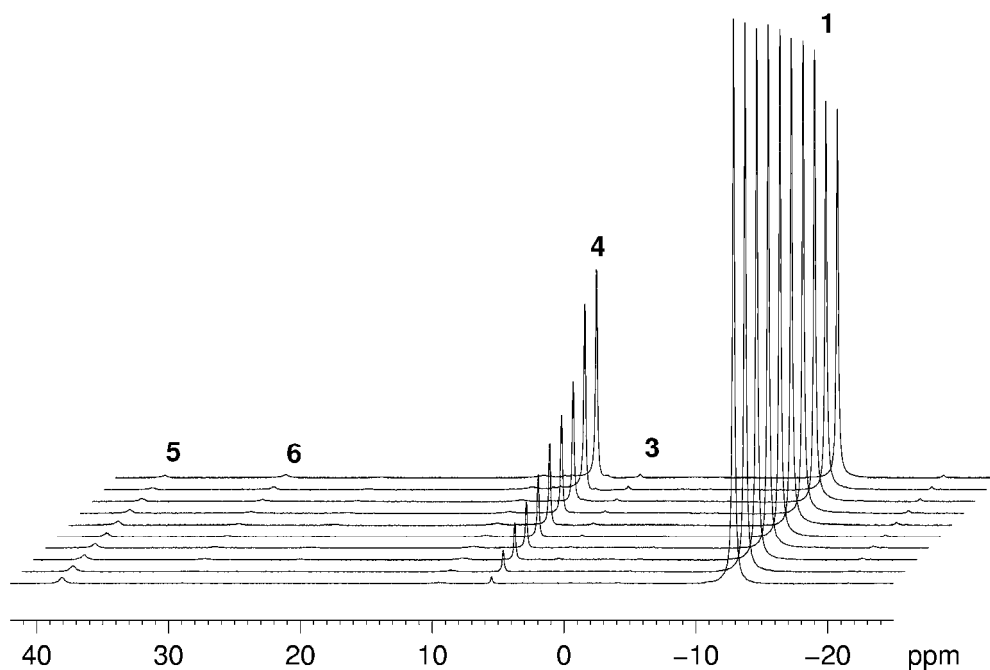
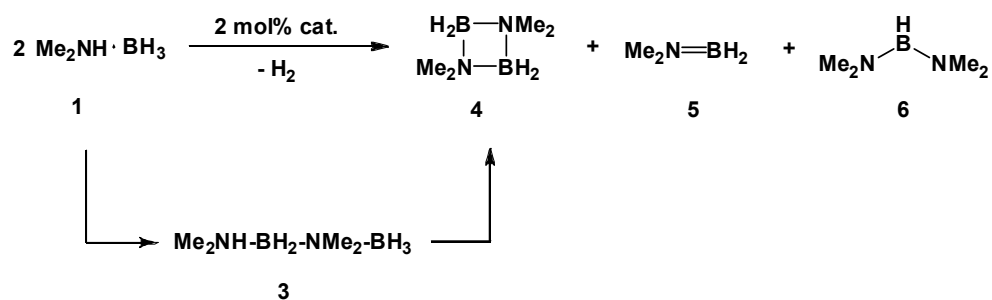


Figure S2. $^{11}\text{B}\{^1\text{H}\}$ NMR spectra (96 MHz, 297 K, toluene, unlocked) of the reaction of **1** with **2Zr** (2 mol%). Last spectrum recorded at $t = 30$ h.

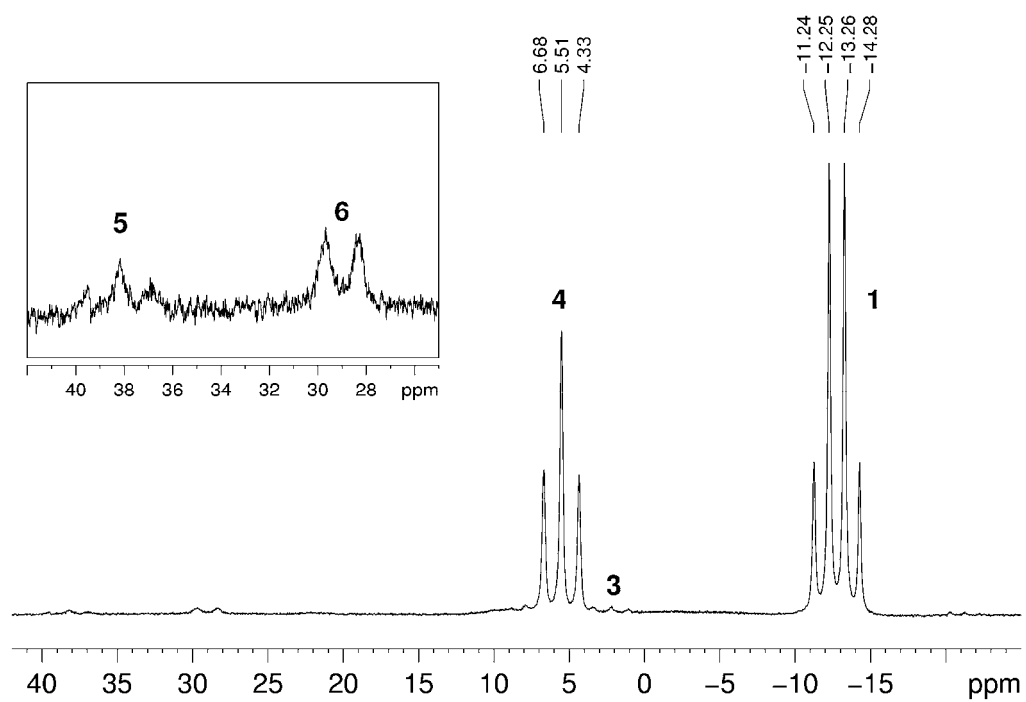


Figure S3. ^{11}B NMR spectrum (96 MHz, 297 K, toluene, unlocked) of the reaction of **1** with **2Zr** (2 mol%), recorded after a reaction time of 30 h.

NMR of 8Ti catalysed dehydrogenation of 1

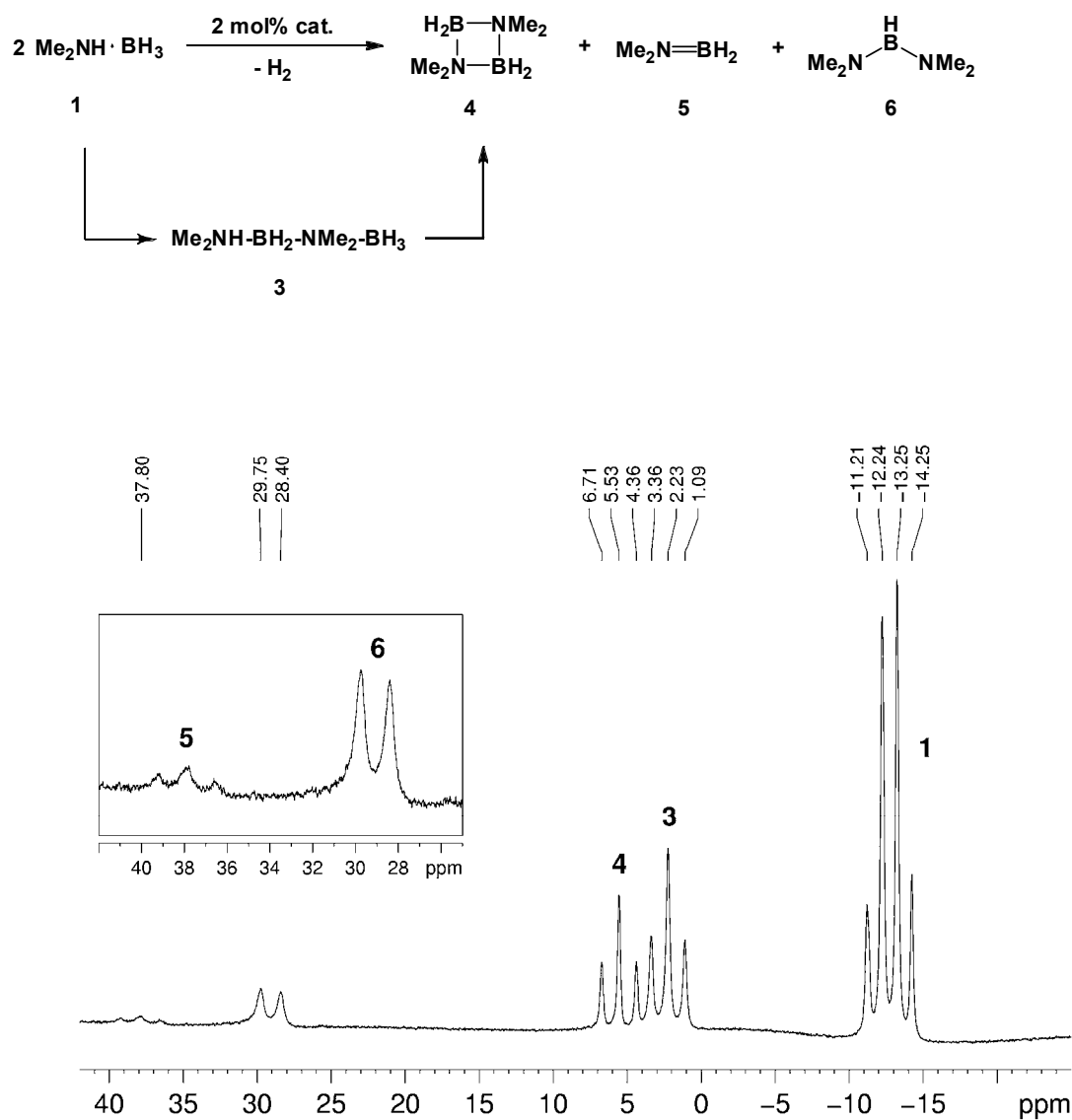


Figure S4. ^{11}B NMR spectrum (96 MHz, 297 K, toluene, unlocked) of the reaction of **1** with **8Ti** (2 mol%), recorded after a reaction time of 5.5 h.

NMR of 8Zr catalysed dehydrogenation of **1**

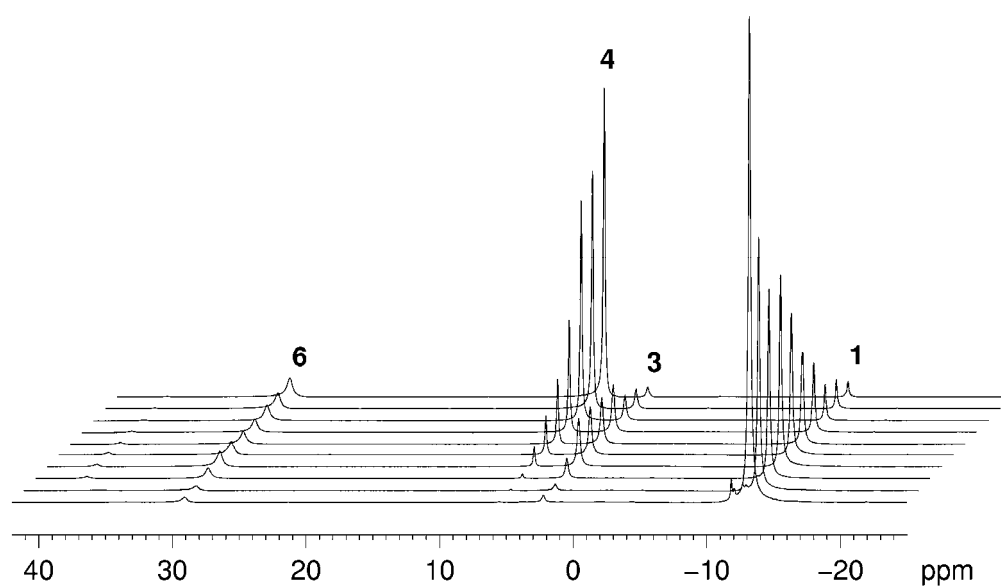
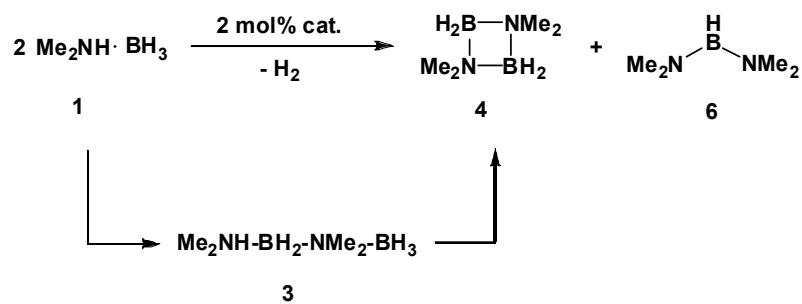


Figure S5. $^{11}\text{B}\{^1\text{H}\}$ NMR spectra (96 MHz, 297 K, toluene, unlocked) of the reaction of **1** with **8Zr** (2 mol%). Last spectrum recorded at $t = 24$ h.

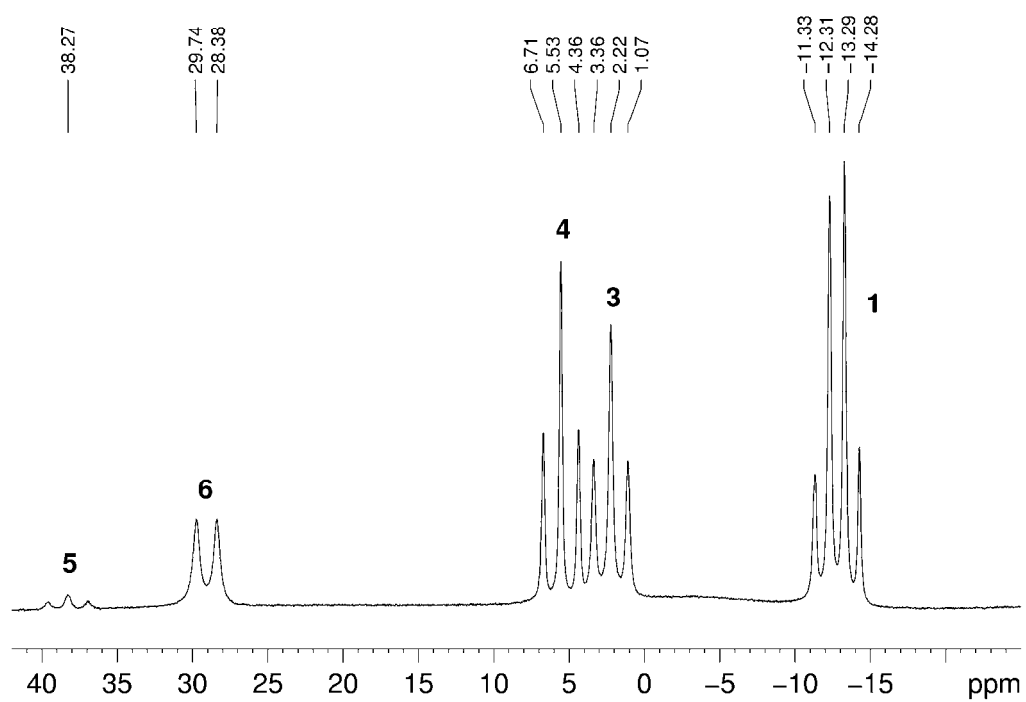


Figure S6. ^{11}B NMR spectrum (96 MHz, 297 K, toluene, unlocked) of the reaction of **1** with **8Zr** (2 mol%), recorded after a reaction time of 5 h.

ESI-MS of 8Ti catalysed dehydrogenation of 1.

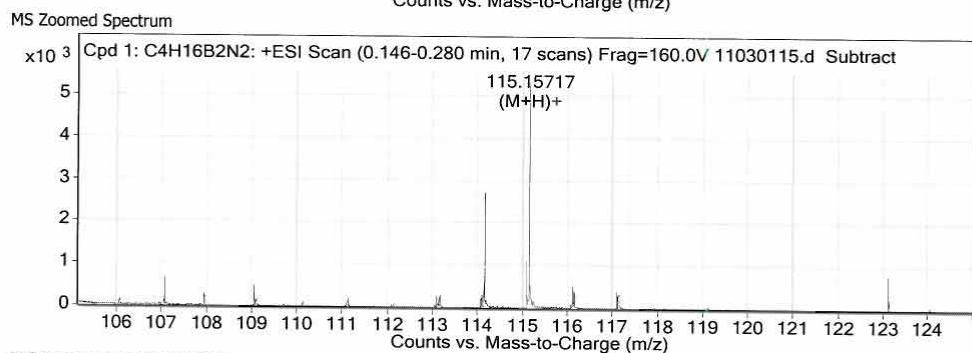
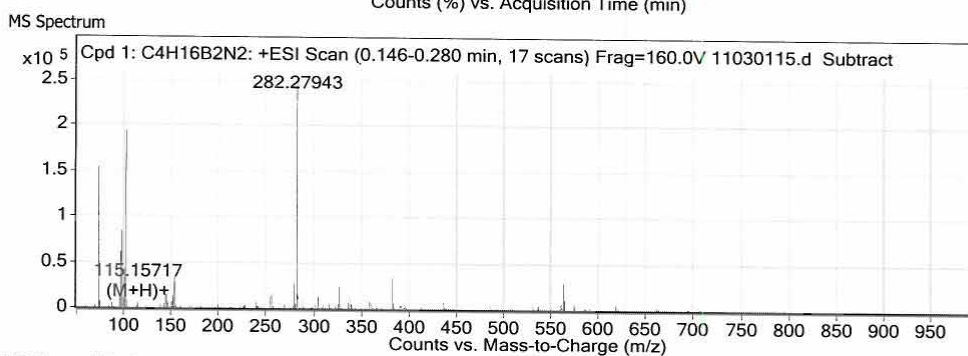
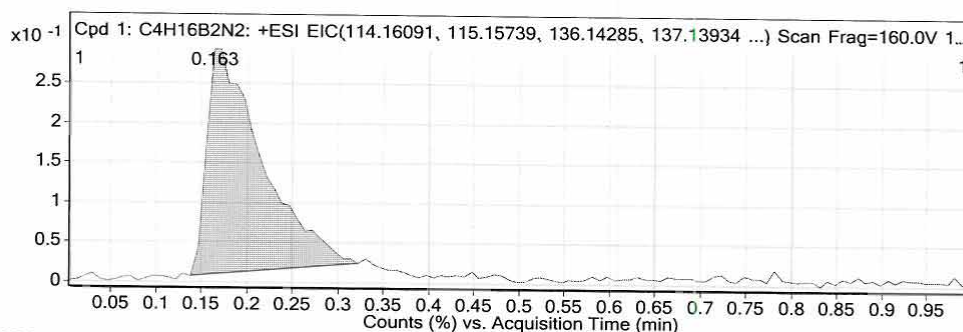
Compound 4 (C₄H₁₆B₂N₂)

Qualitative Compound Report

Instrument Name	ESI-TOF/MS	Date Filename	D:\MassHunter\Data\1103\11030115.d
Acq Method	HRMS Pos oS.m	Sample Name	TB 65
DA Method	HRMS.m	Position	Vial 2
User Name	Fischer	Comment	Acetonitril/0.1%HCOOH in H2O 90:10

Compound Table

Name	RT	Abund	Formula	Ion Mass	Ionization Mode
1	0.163	5305	C ₄ H ₁₆ B ₂ N ₂	112.15722	Positive



MS Spectrum Peak List

Ion	Abund	Formula	Calculated Mass	Measured Mass	Difference	Diff (ppm)
(M+H) ⁺	5416	C ₄ H ₁₇ B ₂ N ₂	115.15739	115.15717	-0.22	-1.95

--- End Of Report ---

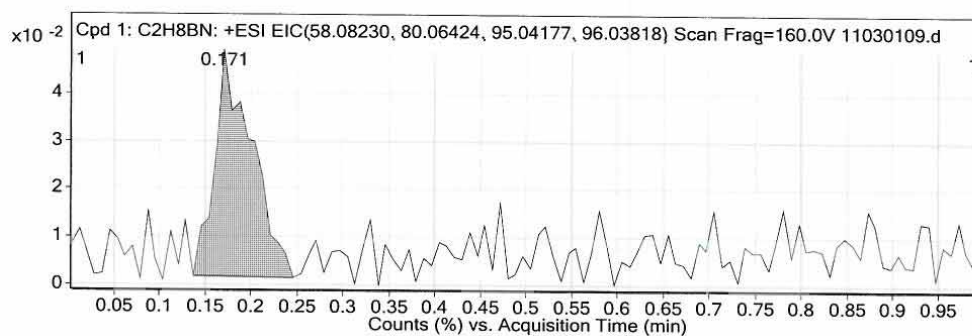
Compound 5 (C₂H₈BN)

Qualitative Compound Report

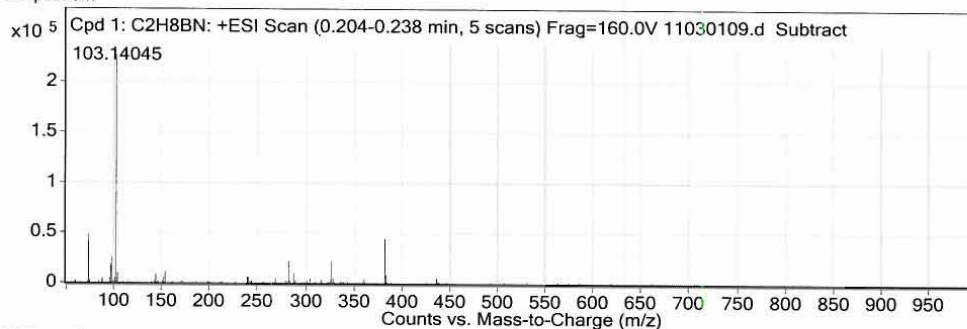
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Acq Method	HRMS Pos oS.m	Sample Name	TB 65
DA Method	HRMS.m	Position	Vial 2
User Name	Fischer	Comment	Acetonitril/0.1% <i>HCOOH</i> in H ₂ O 90:10

Compound Table

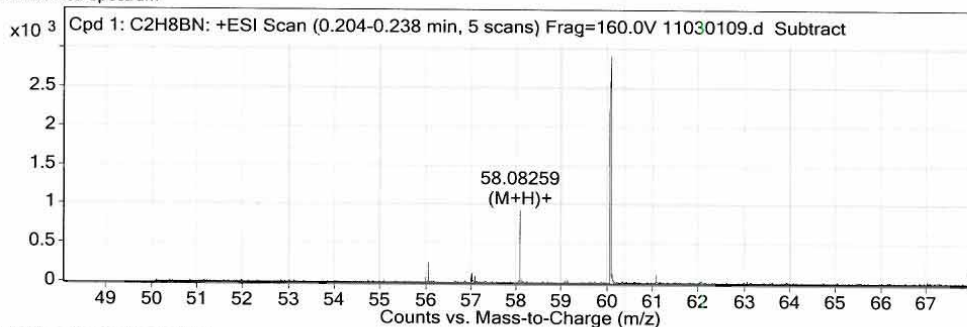
Name	RT	Abund	Formula	Ion Mass	Ionization Mode
1	0.171	930	C ₂ H ₈ BN	56.07861	Positive



MS Spectrum



MS Zoomed Spectrum



MS Spectrum Peak List

Ion	Abund	Formula	Calculated Mass	Measured Mass	Difference	Diff (ppm)
(M+H) ⁺	952	C ₂ H ₉ BN	58.0823	58.08259	0.29	4.97

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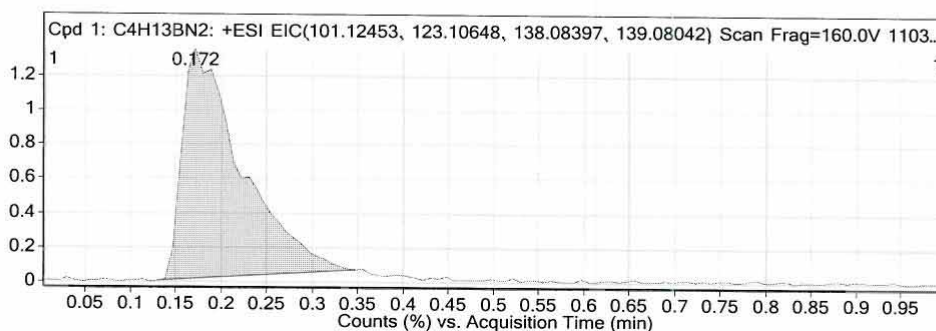
Compound 6 (C₄H₁₃BN₂)

Qualitative Compound Report

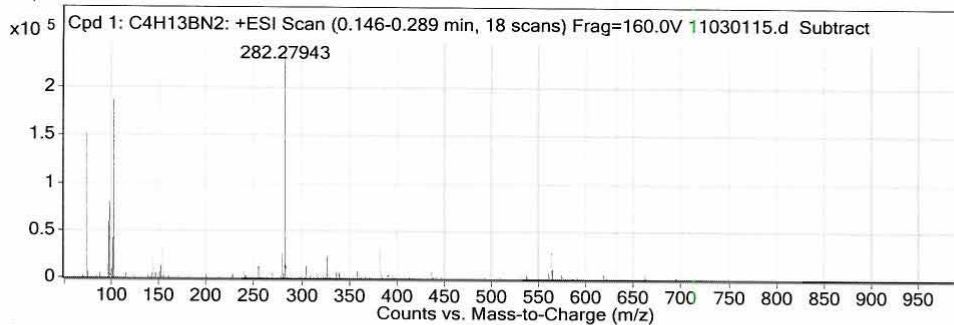
Instrument Name	ESI-TOF/MS	Date Filename	D:\MassHunter\Data\1103\11030115.d
Acq Method	HRMS Pos oS.m	Sample Name	TB 65
DA Method	HRMS.m	Position	Vial 2
User Name	Fischer	Comment	Acetonitril/0.1%HCOOH in H2O 90:10

Compound Table

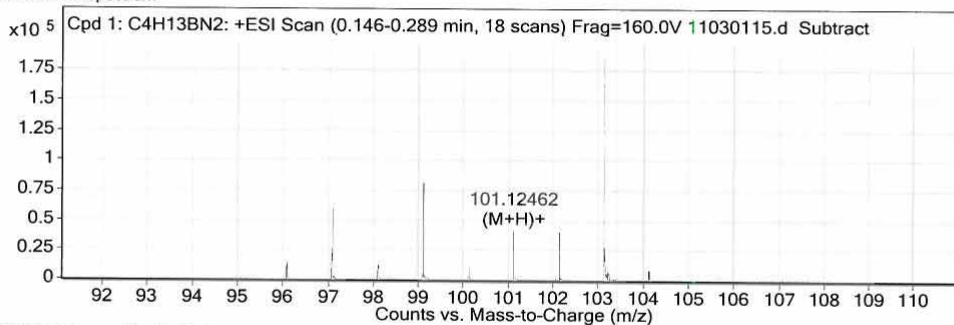
Name	RT	Abund	Formula	Ion Mass	Ionization Mode
1	0.172	41735	C ₄ H ₁₃ BN ₂	99.12081	Positive



MS Spectrum



MS Zoomed Spectrum



MS Spectrum Peak List

Ion	Abund	Formula	Calculated Mass	Measured Mass	Difference	Diff (ppm)
(M+H) ⁺	41800	C ₄ H ₁₄ B N ₂	101.12453	101.12462	0.09	0.88

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References

- [1] a) V. V. Burlakov, U. Rosenthal, P. V. Petrovskii, V. B. Shur, M. E. Vol'pin, *Organomet. Chem. USSR* 1988, **1**, 526; b) U. Rosenthal, A. Ohff, M. Michalik, H. Görls, V. V. Burlakov, V. B. Shur, *Angew. Chem. Int. Ed. Engl.* 1993, **32**, 1193.
- [2] a) V. V. Burlakov, A. V. Polyakov, A. I. Yanovsky, Y. T. Struchkov, V. B. Shur, M. E. Vol'pin, U. Rosenthal, H. Görls, *J. Organomet. Chem.* 1994, **476**, 197; b) J. Hiller, U. Thewalt, M. Polasek, L. Petrusova, V. Varga, P. Sedmera, K. Mach, *Organometallics* 1996, **15**, 3752.
- [3] Analogous equipment is used for the measurement of gas consumption in hydrogenation reactions. This equipment has been developed at the LIKAT Rostock together with MesSen Nord (Stäbelow) and has been described in: H.-J. Drexler, A. Preetz, T. Schmidt, D. Heller, in *The Handbook of Homogeneous Hydrogenation*, Vol. 1 (Eds.: J. G. De Vries, C. J. Elsevier), Wiley-VCH, Weinheim, 2007, pp. 257–293.