Electronic Supplementary Information (ESI)

Experimental section

General. All experiments were performed under anhydrous conditions using argon as protective gas. All NMR spectra were recorded on Bruker DRX 250 and Avance II 400 spectrometers. The NMR spectra were measured at room temperature in C_6D_6 that was purchased from Deutero GmbH. The spectra were referenced to residual benzene signals (^1H, ^{13}C, ^{29}Si: $SiMe_4$)[1] and externally (^{11}B: $BF_3 \bullet OEt_2$). For silicon-29 NMR a DEPT45 puls sequence with a J coupling constant of 8 Hz was employed. Mass spectrometry was done on a Finnigan MAT TSQ70 and high resolution mass spectrometry on a Finnigan MAT MAT95 (HRMS EI). GC-MS measurements were performed on a HP GC-MS system (GC: HP6890; MS-D: HP5973) using helium as carrier gas and a Macherey-Nagel OPTIMA-5-AMIN-1,0µm (30m x 0.25 mm ID) column. Tetramethylsilane (Acros) was distilled after drying over lithium aluminum hydride, pinacol boron azide was synthesized according to literature procedures[2] and distilled under vacuum and trimethylsilylmethylamine was bought from ABCR. $h_{1/2}$ is the Full Width at Half Maximum which is determined by a Lorentzian fit with TopSpin 2.1 (Bruker) and given in Hertz (Hz). TopSpin 2.1 was also used for the deconvolution of ^{11}B spectra. Starred peaks result from impurities of $O(BPin)_2$,[3] **2** (square) or **4** (filled square).

*Caution: Boron azides are potentially **explosive** and have to be handled with care, although no incidents were encountered during the research project.*

N-[pinacolatoboryl](trimethylsilyl)methylamine, 2

a) In a quartz tube fitted with a reflux condenser, 246 mg (1.456 mmol) of pinacol boron azide **1** was dissolved in 15 mL of tetramethylsilane. Then the solution was subjected to UV irradiation for 10 h at room temperature using a low pressure mercury vapor lamp. The solvent of the colorless photoproduct reaction mixture was removed. By adding 125 mg (1.472 mmol) dichloromethane to the crude reaction mixture, it was also possible to determine an amount of 80 % on the basis of the methylene (2.51 ppm) and dichloromethane signal (4.29 ppm) in hydrogen NMR spectra. Ca. 2 % hydrolysis product (PinBOBPin) and bisborylated aminoborane **4** (9%) can still be found in the sample.
   After the evaporation of the solvents a slightly turbid, colorless oil remained (247 mg, 57 %).
b) In a second reaction, the irradiation (12.5 h) was carried out in 25 mL of tetramethylsilane using 274 mg (1.621 mmol) of pinacol boron azide **1**. Distillation at 120 °C / 0.5 mbar yielded 43 mg (12 %) of almost pure **2** (a trace amount of hydrolysis product still present). After 7 days at room temperature, **2** is still persistent and there are no indications for the presence of **4**.

δ_H(250 MHz; C_6D_6) -0.08 (9 H, s, J_{HSi} 6.5, $(CH_3)_3Si$), 1.14 (12 H, s, Me), 1.87 (1 H, br s, NH), 2.49 (2 H, d, J_{HH} 7.1, CH_2); δ_C(101 MHz; C_6D_6) -3.2 ($(CH_3)_3Si$), 25.0 (Me), 31.2 (CH_2), 82.0 (CO); δ_B(80 MHz; C_6D_6) 25.0 ($h_{1/2}$ 107); δ_{Si}(50 MHz; C_6D_6) 0.1; EI-MS (70 eV, sector field) m/z: 229 (M^+, 100 %), 214 (50, M – Me), 172 (25), 156 (98, M – TMS), 132 (47), 114 (45), 84 (43), 73 (64, TMS^+); EI-HRMS (M^+, 70 eV, sector field) found: 229.16955, calc. for $C_{10}H_{24}NO_2SiB$: 229.16694.

N,N-[bispinacolatoboryl](trimethylsilyl)methylamine, 4

Separation of **4** from **2** (reaction a)) by crystallization from pentane afforded a few crystals that were suitable for X-ray structure, NMR and mass analysis (ca. 10 mg, 2 %). Due to measurement requirements it was necessary to acquire the high resolution mass (EI) from the [M – Me] peak.
An experiment on NMR scale was also carried out with 20 mg (0.087 mmol) of distilled **2** (from reaction b)) and an increasing amount of $pinBN_3$ (**1**). As standard 0.67 eq. tetrachloroethane ($C_2H_2Cl_4$) were added, followed by the addition of 0.56 eq. **1**. After 6 d, another 0.81 eq. of **1** were added and finally, after 14 d, a large excess of 10.90 eq. of **1** was added in addition. NMR spectra were recorded to show the slow conversion of **2** to **4** although the reaction cannot be driven to completion. It has to be mentioned that the peaks of **4** and **2** show slight upfield shifts of around 0.1 ppm compared to the isolated molecules when the $pinBN_3$ (**1**) amount increases. A high excess of **1** also causes a few more nmr signals in hydrogen nmr spectra.

δ_H(250 MHz; C_6D_6) 0.21 (9 H, s, J_{HSi} 6.5, $(CH_3)_3Si$), 1.09 (24 H, s, Me), 3.05 (2 H, s, CH_2); δ_C(101 MHz; C_6D_6) -1.9 ($(CH_3)_3Si$), 24.9 (Me), 34.3 (CH_2), 82.4 (CO); δ_B(80 MHz; C_6D_6) 26.4 ($h_{1/2}$ 236); δ_{Si}(50 MHz; C_6D_6) 1.2; EI-MS (70 eV, quadrupole) *m/z* 355 (M^+, 8 %), 340 (15, M – Me), 282 (27, M – TMS), 272 (56), 240 (45), 171 (30), 156 (43), 112 (100), 83 (83), 73 (35, TMS^+), 55 (45); EI-HRMS (M – Me!) (70 eV, sector field) found: 340.22948, calc. for $C_{15}H_{32}NO_4SiB_2$: 340.22867.

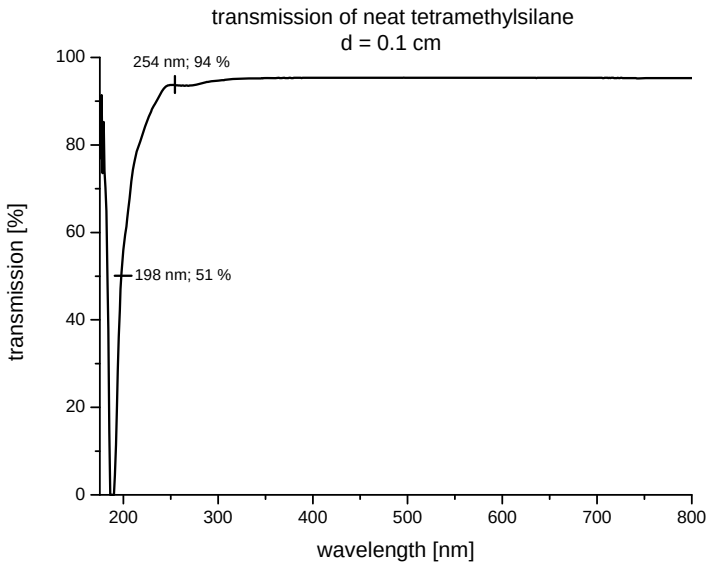
N-Isopropylidene-trimethylsilylmethylamine[4]

Reference compound for the reaction of **2a** and acetone, see S. 3

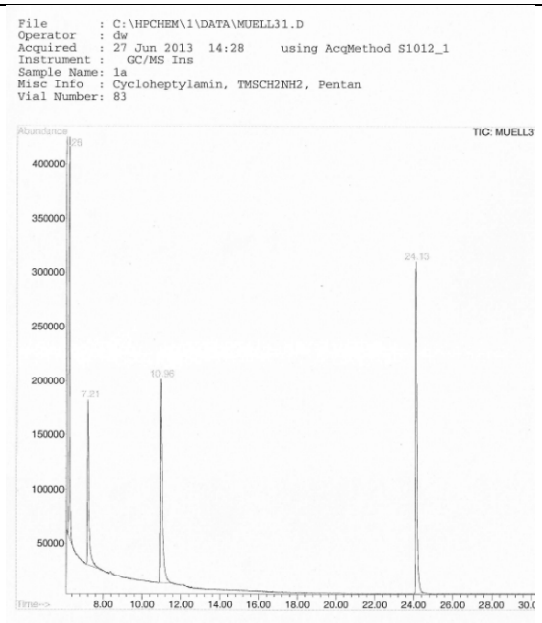
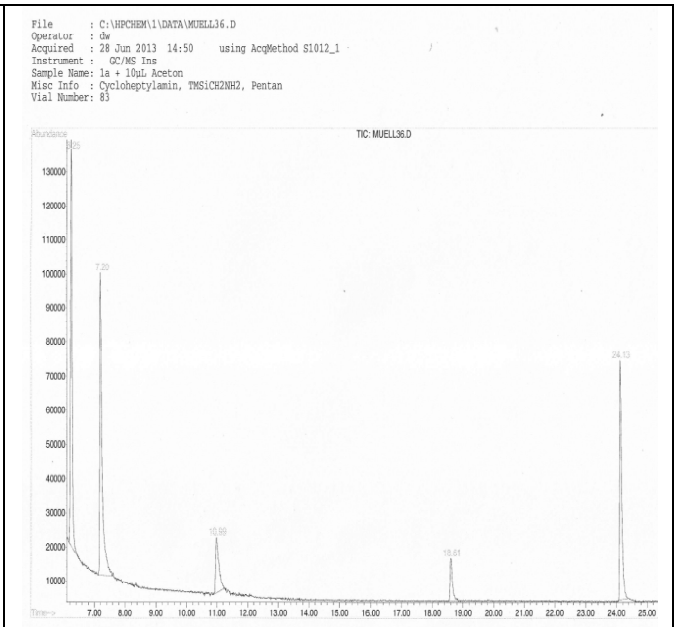
At room temperature, 1 mL (7.5 mmol) of **2a** were charged with 10 perls of molsieve (4 Å), 74 mg (0.07 mmol) of Na_2SO_4 and 0.56 ml (1.02 mmol) of acetone. The mixture was stirred for 65 h at room temperature and filtered afterwards. The yield of the title compound is nearly quantitative, only traces of acetone are left.

δ_H(400 MHz; C_6D_6): 0.06 (s, 9 H), 1.39 (s, 3 H), 1.87 (s, 3 H), 3.08 (s, 2 H); δ_C(101 MHz; C_6D_6): -2.2, 17.1, 29.0, 45.1, 161.3; EI-MS (70 eV, quadrupole) *m/z* 213, 144 ($M+H^+$, 100 %), 143 (55, M), 128 (70, M – Me); GC-MS: ret. time 18.61 min

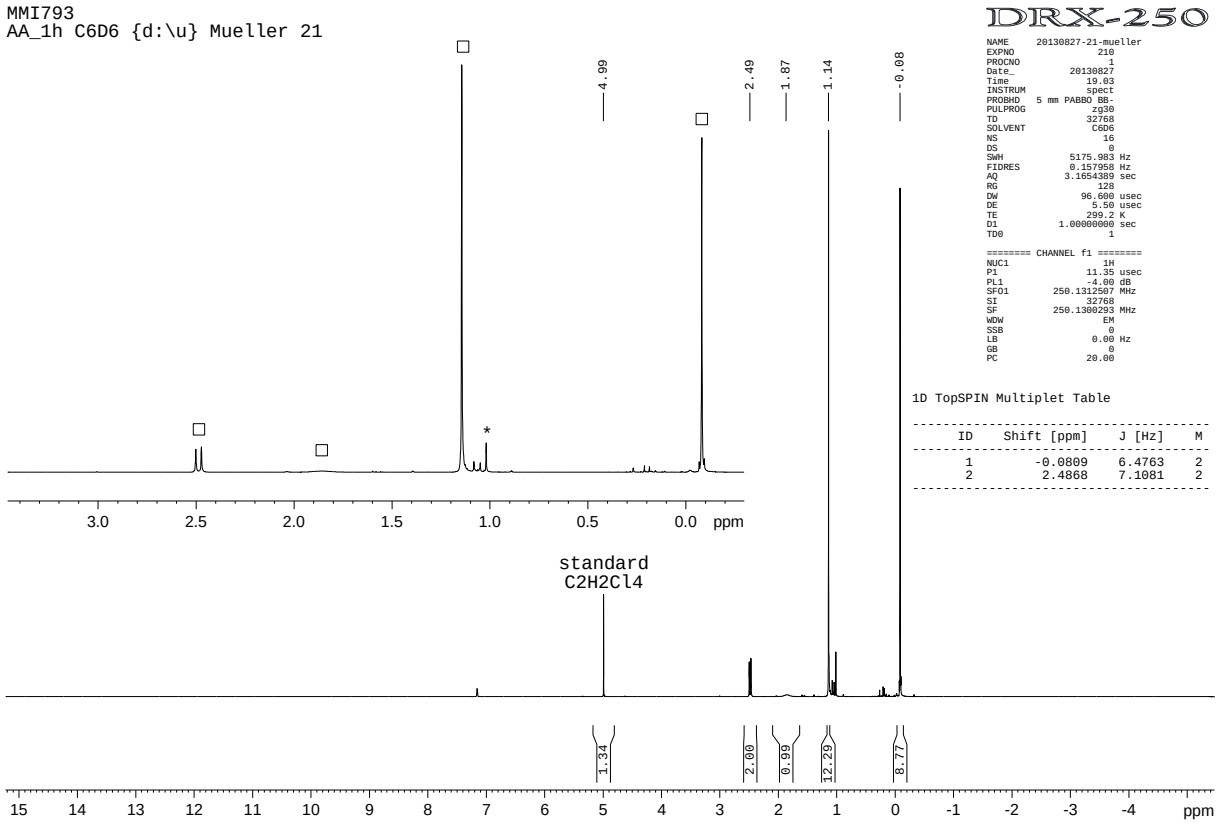
UV spectrum of neat tetramethylsilane



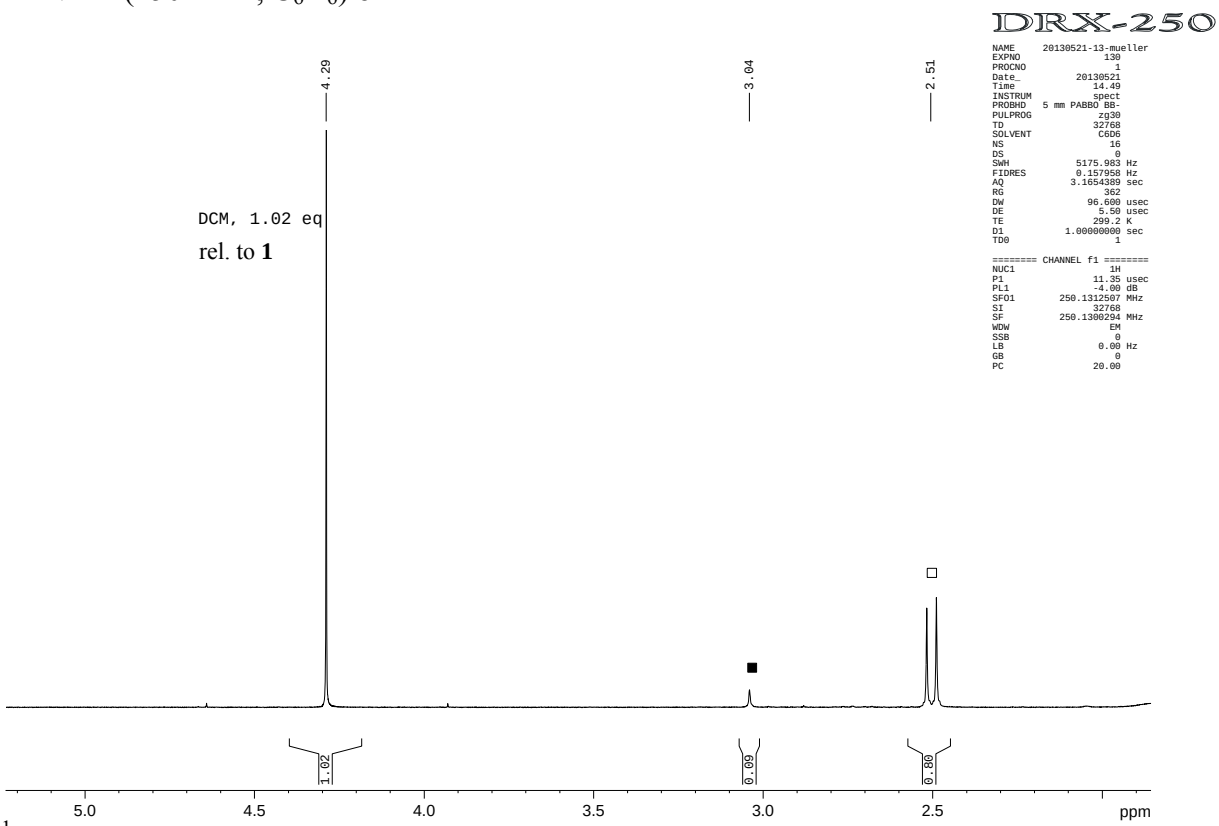
GC-MS measurement of 2a, Cy7NH2 and N-isopropylidene-trimethylsilylmethylamine

	
GC-MS of the mixture of **2a** (ret. time 10.96 min) and cycloheptylamine (Cy7NH2, ret. time 24.15) before the addition of acetone	GC-MS of the mixture of **2a** (ret. time 10.96 min) and cycloheptylamine (Cy7NH2, ret. time 24.13) after the addition of 10 µL of acetone (injection directly after a few seconds mixing time) with the occurrence of a peak at 18.61 min. This can be identified as N-isopropylidene-trimethylsilylmethylamine (by mass spec and ret. time). There are no indications for a similar reaction product with Cy7NH2 in this competition reaction.

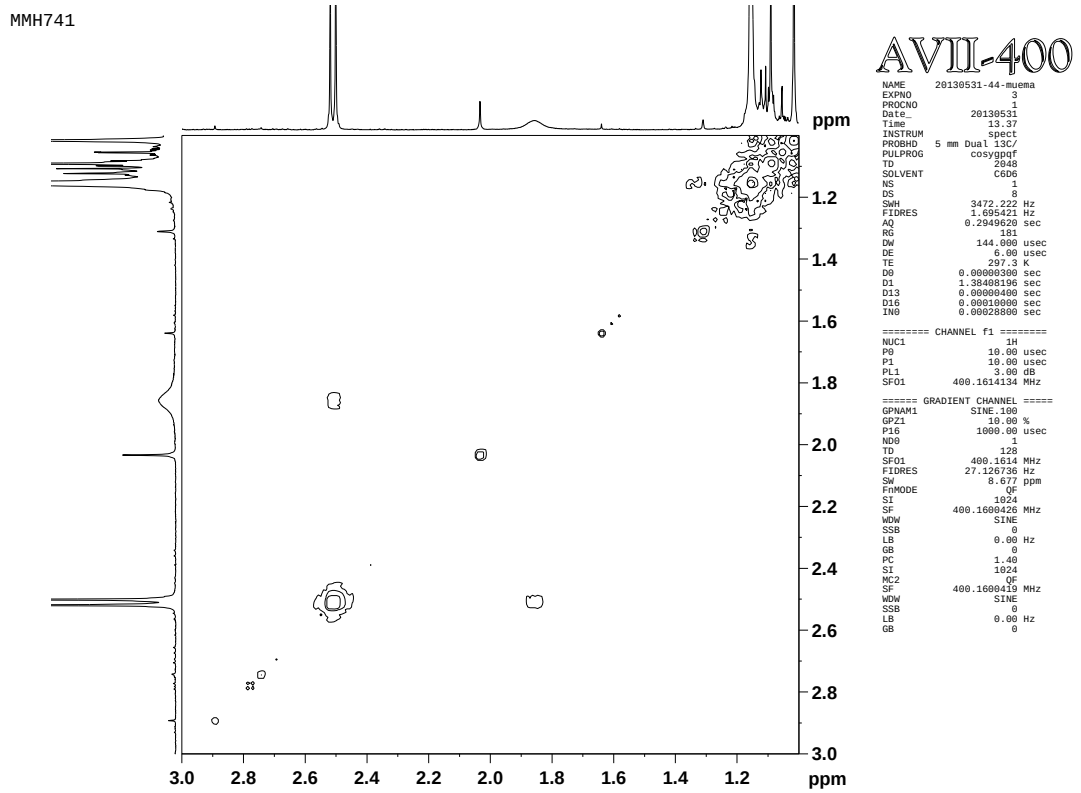
NMR/mass spectra of 2



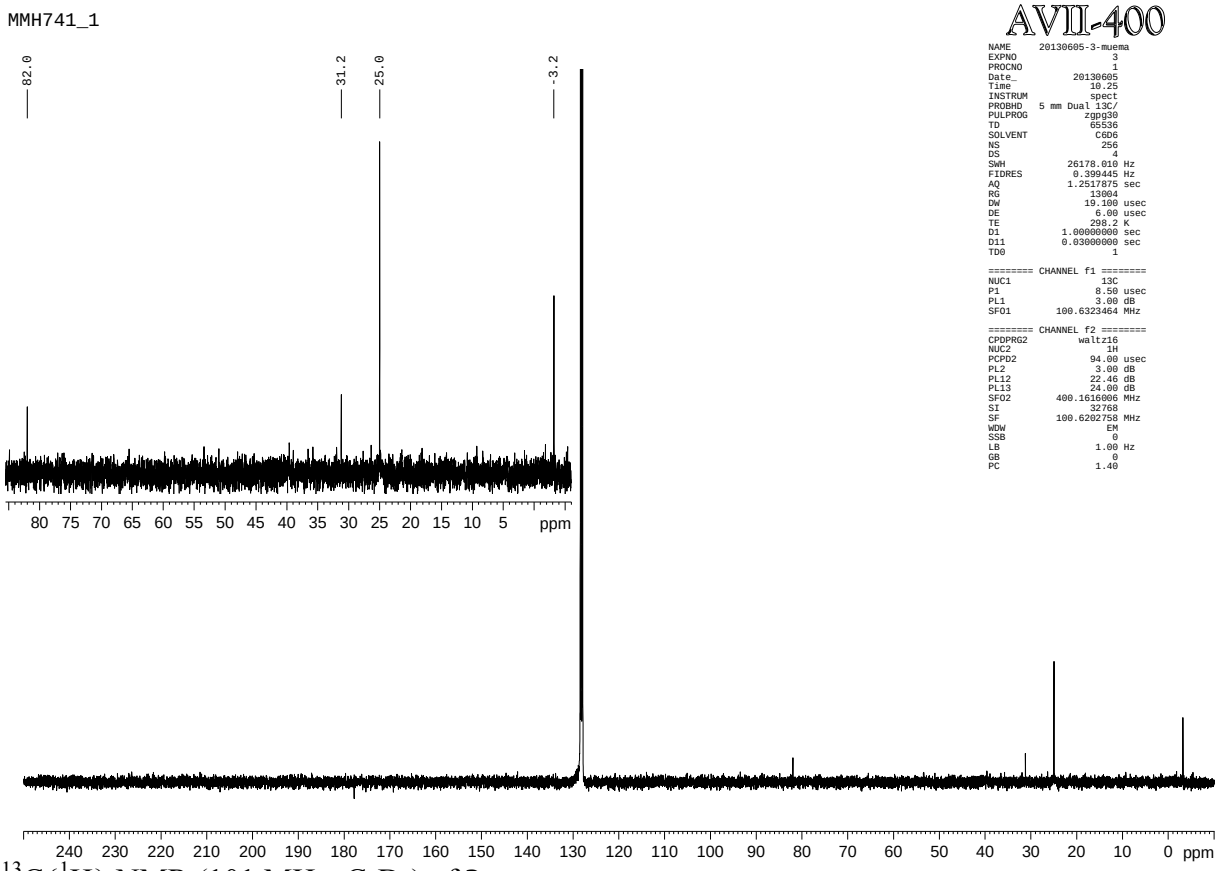
^{1}H NMR (250 MHz, C_6D_6) of **2**



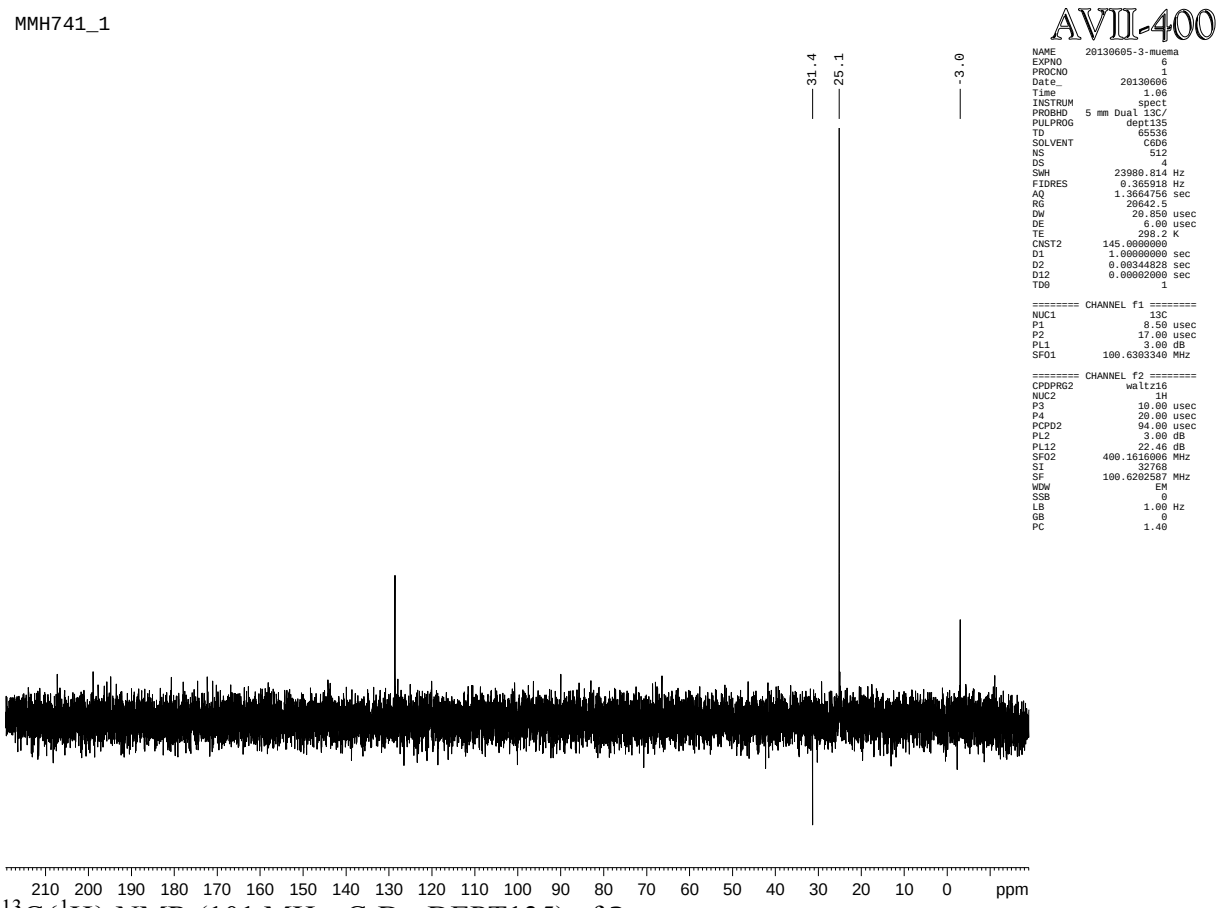
^{1}H NMR (250 MHz, C_6D_6), determination of the amount of **2** and **4** in the crude oil after irradiation



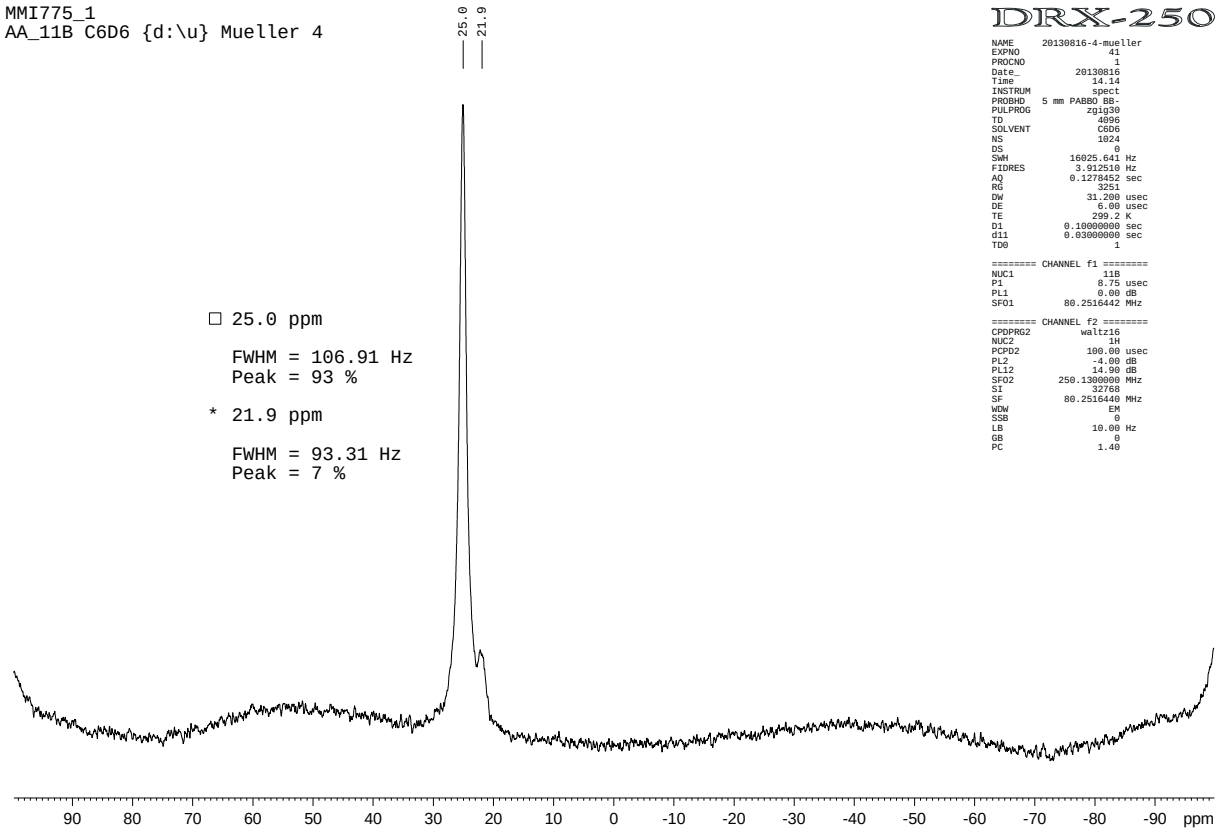
HHCosy (400 MHz, C_6D_6) of **2**



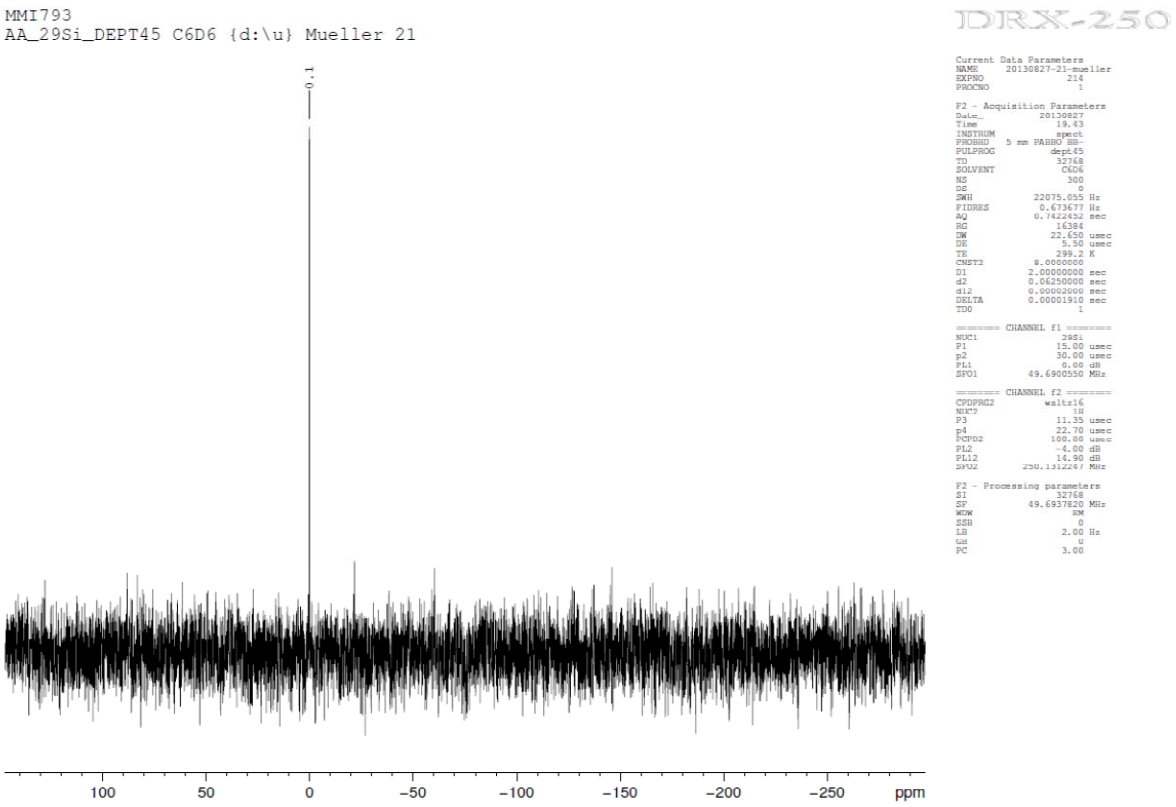
$^{13}C\{^{1}H\}$ NMR (101 MHz, C_6D_6) of **2**



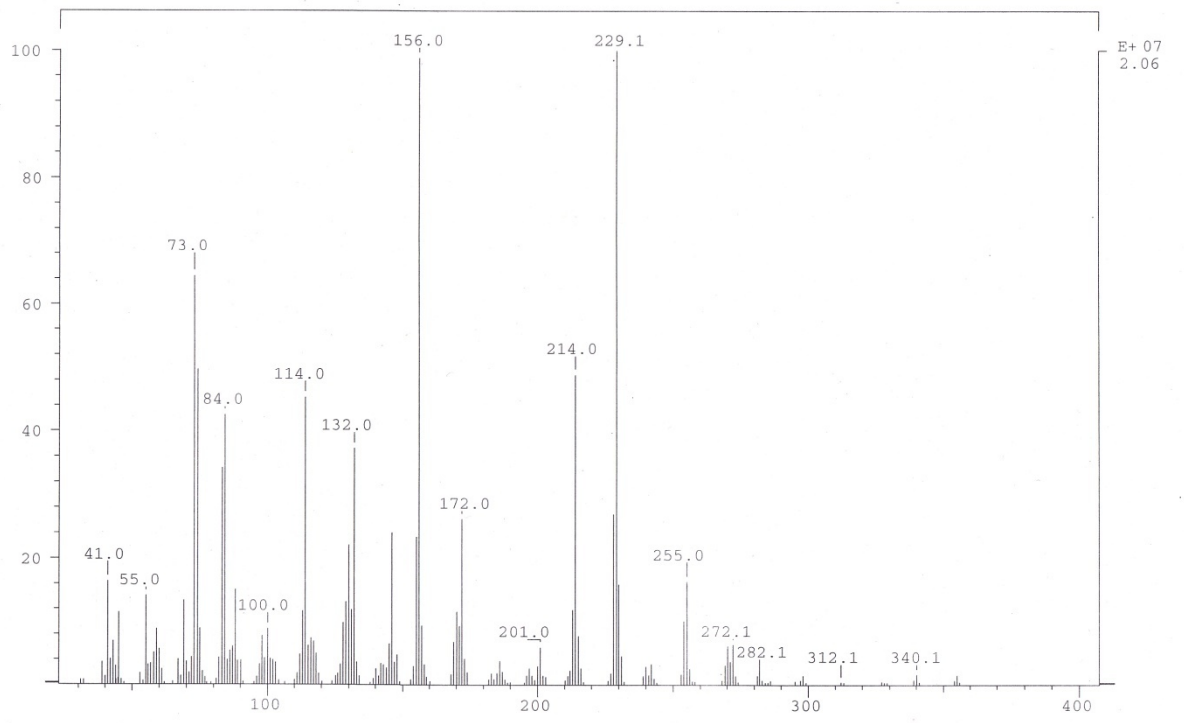
$^{13}C\{^{1}H\}$ NMR (101 MHz, C_6D_6, DEPT135) of **2**



$^{11}B\{^{1}H\}$ NMR (80 MHz, C_6D_6) of **2**



$^{29}Si\{^{1}H\}$ NMR (50 MHz, C_6D_6, DEPT45) of **2**



EI-MS (70 eV, sector field) of **2**

M a s s e n f e i n b e s t i m m u n g

Name: Müller Probenbezeichnung: **MMH741_1**

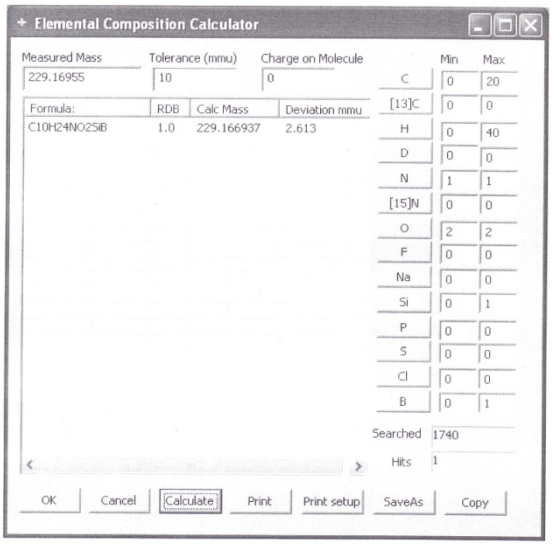
Ionisierungsmethode: **EI** ..X... **FAB** .....

Referenz - Ion und seine **exakte Masse:**

C_5F_9 231 230,98562

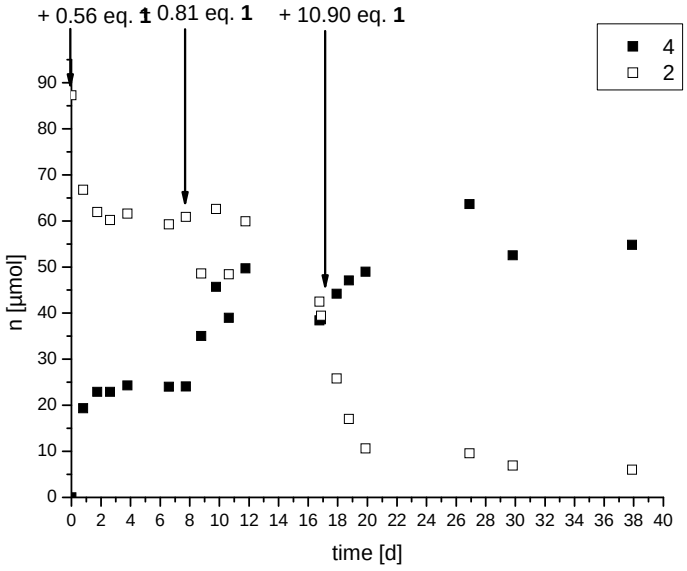
die **gefundene exakte Masse** erhält man zu: **229,16955**

damit ergibt/ergeben sich folgende **Elementkombination(en)** :



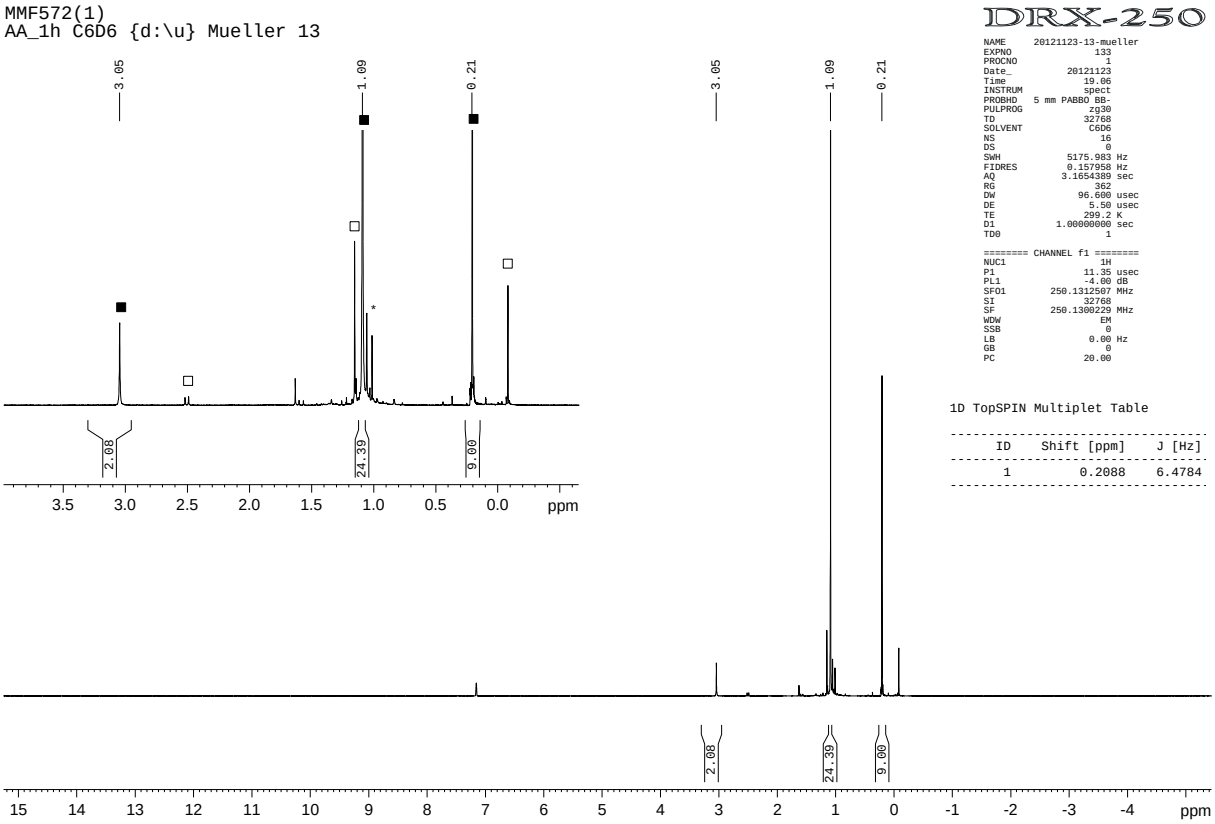
EI-MS (high resolution, 70 eV, sector field) of **2**

NMR experiment: transformation of 2 into 4 by the addition of 1

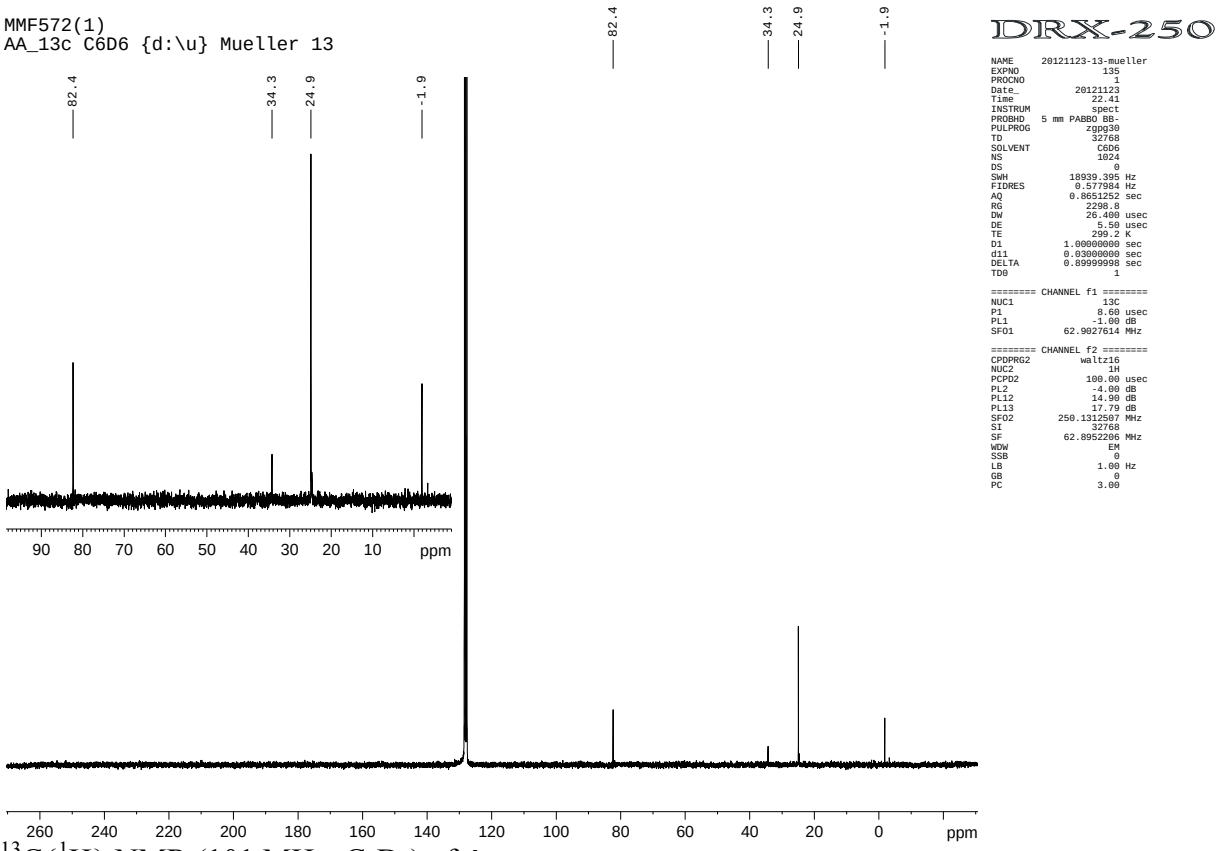


The amount of substance n in µmol was calculated from the peak of the standard compound ($C_2H_2Cl_4$) in the hydrogen NMR spectrum. The arrows point to measurements recorded directly after the addition of the given amount of **1**.

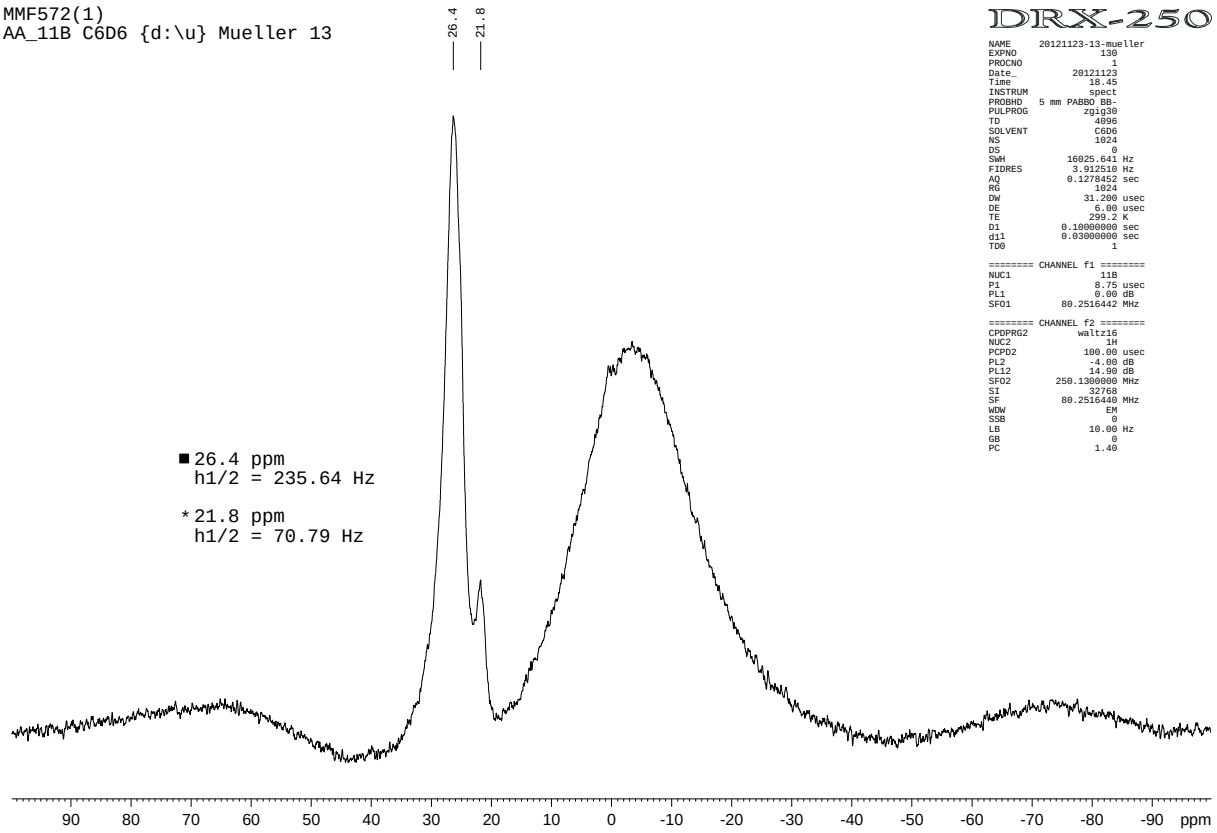
NMR/mass spectra of 4



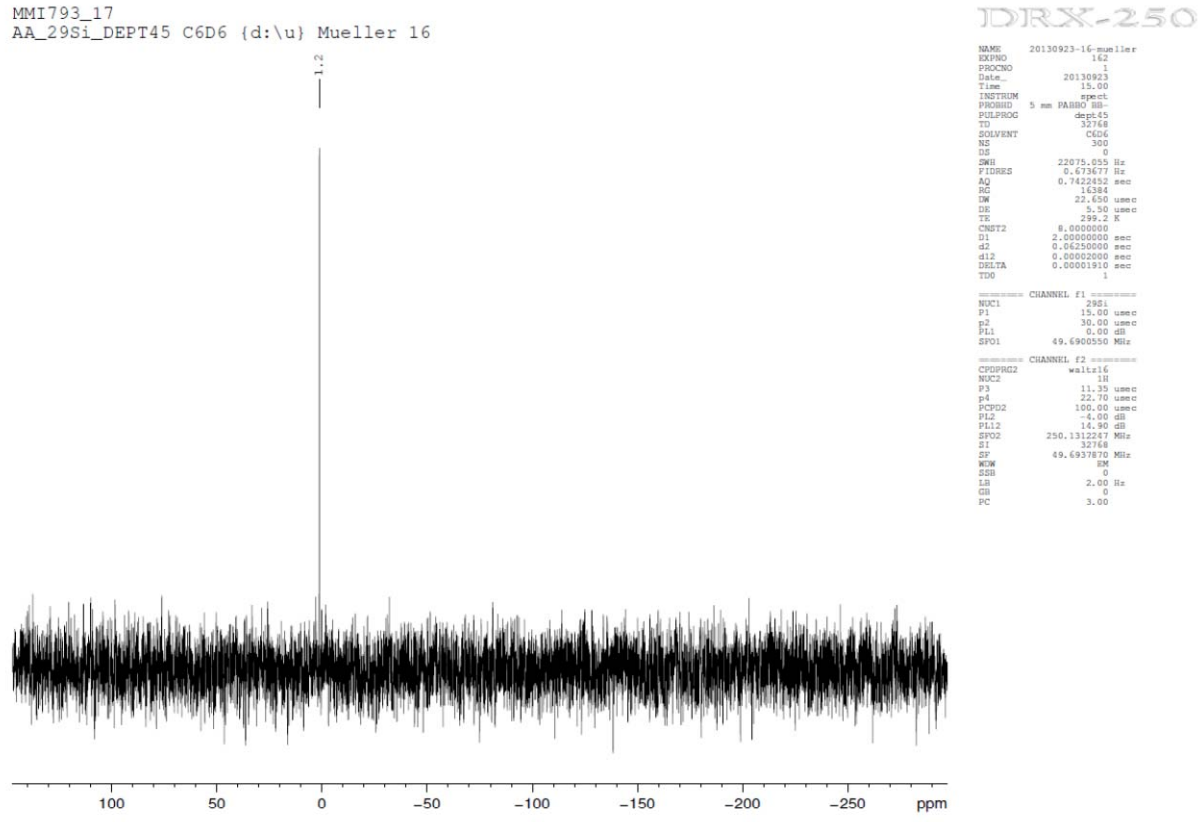
^{1}H NMR (250 MHz, C_6D_6) of **4**



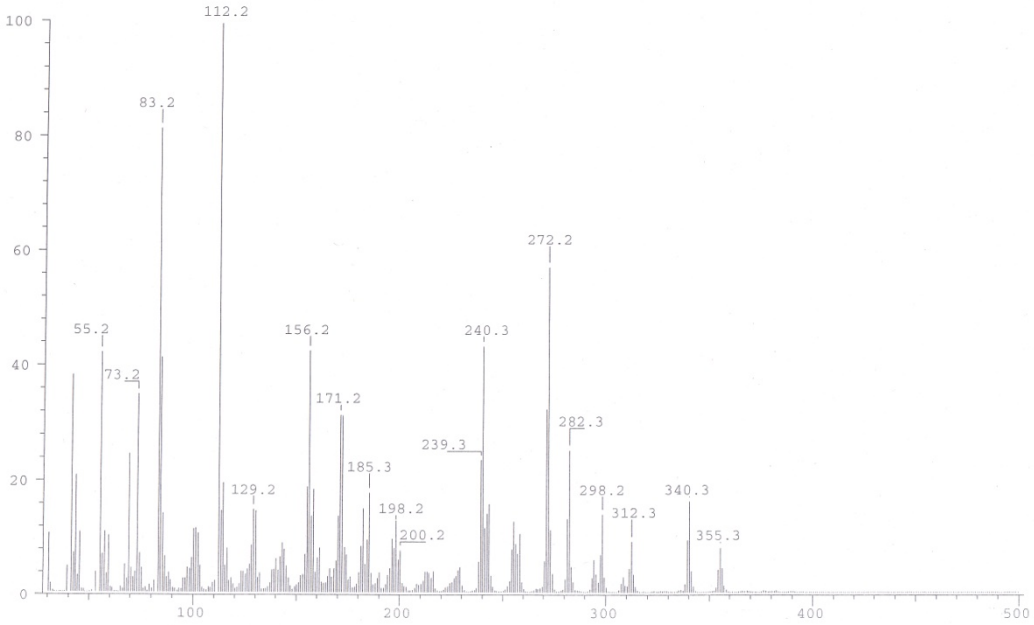
^{13}C{^{1}H} NMR (101 MHz, C_6D_6) of **4**



$^{11}B\{^{1}H\}$ NMR (80 MHz, C_6D_6) of **4**, due to background, integration is impossible



$^{29}Si\{^{1}H\}$ NMR (50 MHz, C_6D_6) of **4**



EI-MS (70 eV, quadrupole) of **4**

M a s s e n f e i n b e s t i m m u n g

Name: Müller Probenbezeichnung: **MMF572(1)**

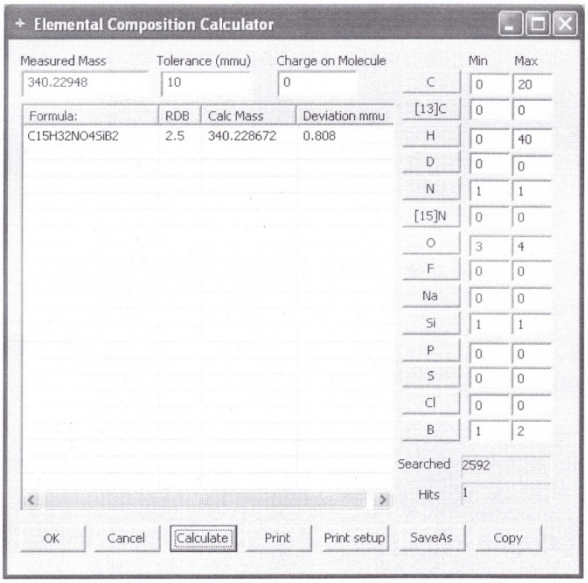
Ionisierungsmethode: **EI** ..X... **FAB** .....

Referenz - Ion und seine **exakte Masse:**

C_7F_{13} 331 330,97924

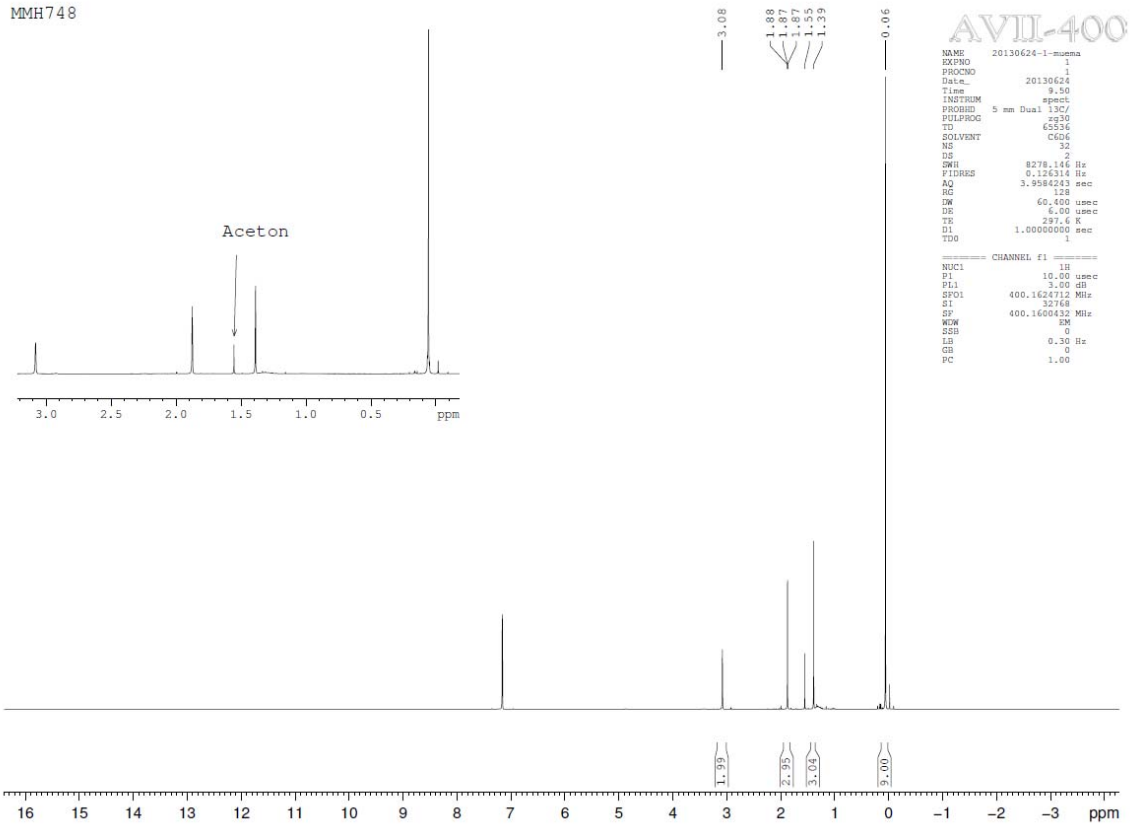
die **gefundene exakte Masse** erhält man zu: **340,22948**

damit ergibt/ergeben sich folgende **Elementkombination(en)** :

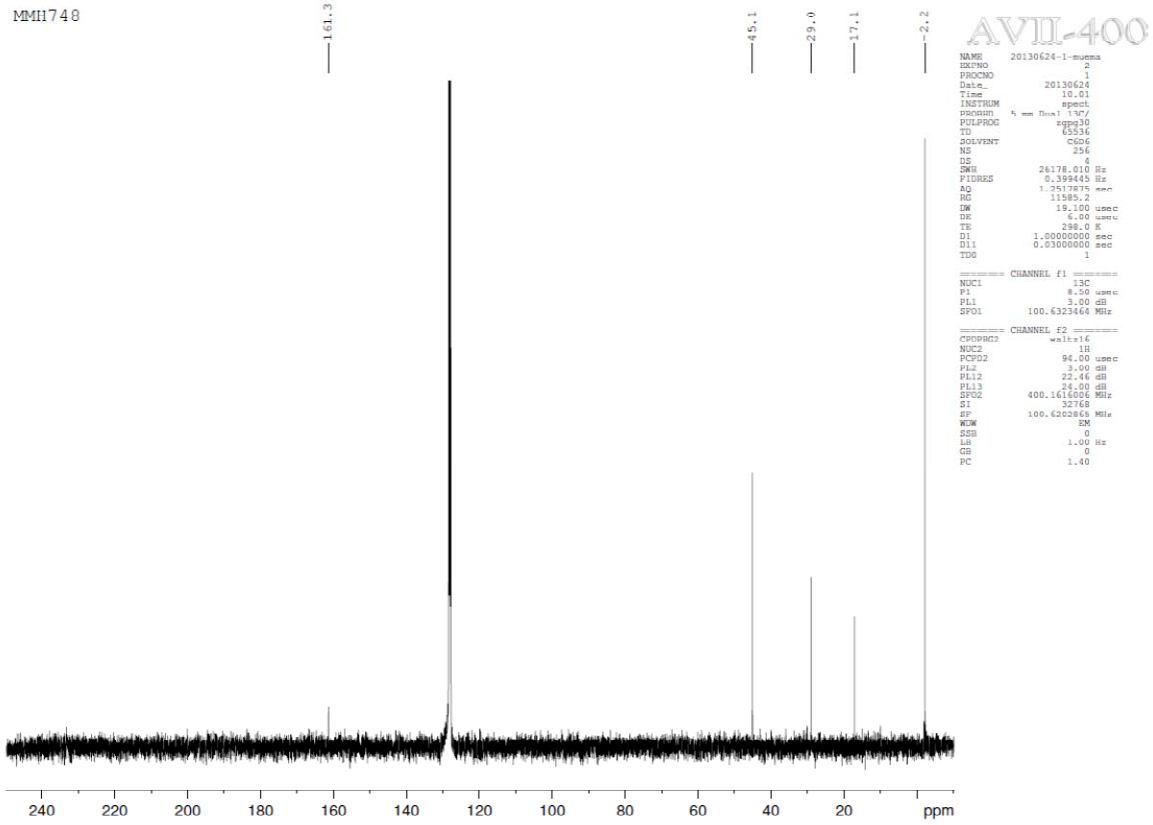


high resolution EI-MS (70 eV, sector field) of **4**

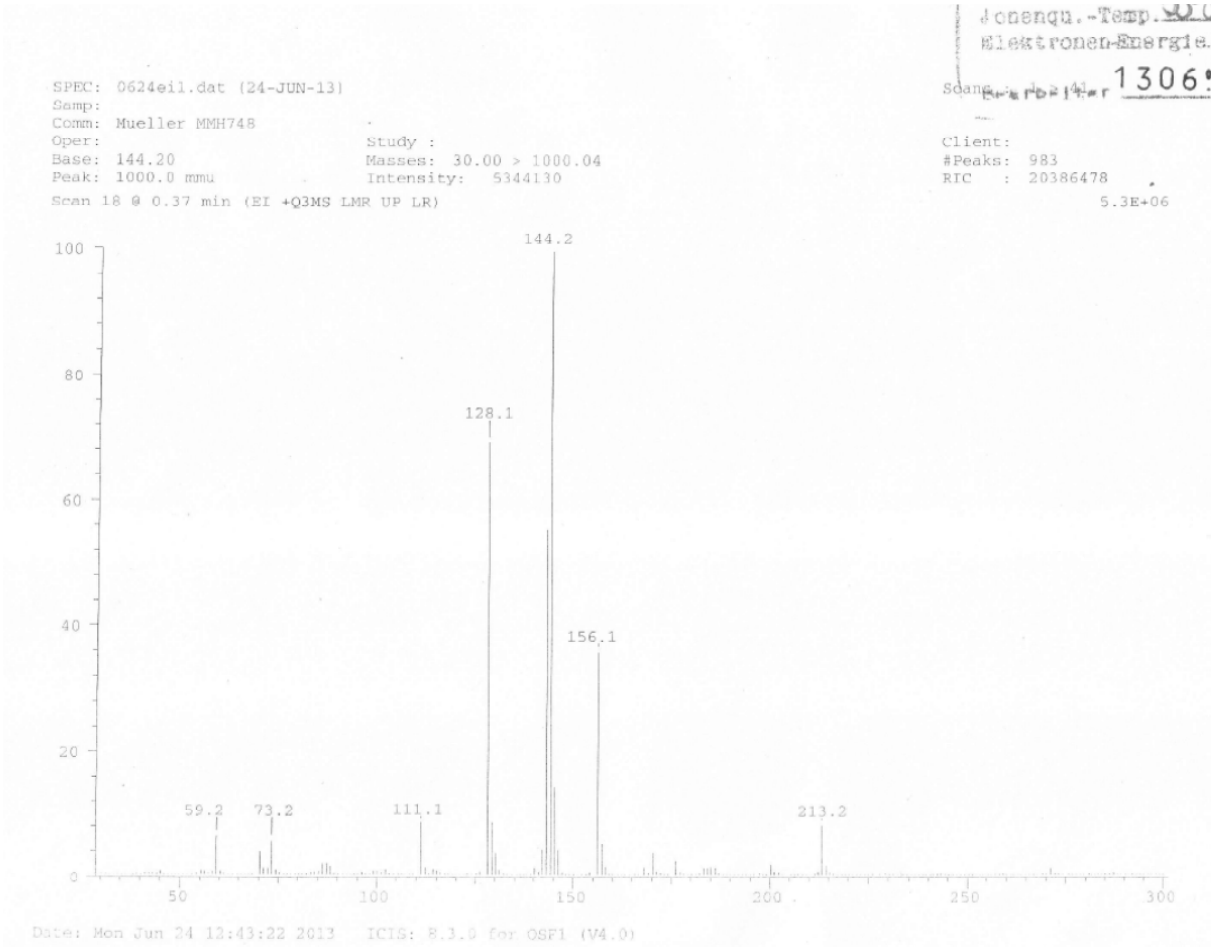
NMR/mass spectra of N-isopropylidene-trimethylsilylmethylamine



^{1}H NMR (400 MHz, C_6D_6) of N-isopropylidene-trimethylsilylmethylamine



^{13}C{^{1}H} NMR (101 MHz, C_6D_6) of N-isopropylidene-trimethylsilylmethylamine



EI-MS (70 eV, quadrupole) of N-isopropylidene-trimethylsilylmethylamine

X-ray crystallography and crystal structure determination

Crystals were grown by standard techniques from saturated solutions using pentane at room temperature. Suitable crystals for diffraction experiments were selected in a glovebox and mounted in Paratone-N (Hampton Research) on a fibre. Data collection was done on a Stoe IPSD II, using MoK_α radiation (λ= 0.71073 Å) performing ω scans in two φ-positions. Structure solution and final model refinement was done using X-Area software and SHELXS97 and SHELXL-97.[5] Further details of the refinement and crystallographic data are listed in the table below and in the CIF file; CCDC reference number is 945713.

Crystal data and structure refinement for 4

Identification code	mmf572_0m
Empirical formula	C16 H35 B2 N O4 Si
Formula weight	355.16
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 6.6093(14) Å α = 107.567(4)°
	b = 10.898(2) Å β = 97.679(5)°
	c = 15.669(3) Å γ = 102.186(4)°

Volume	1027.8(4) $Å^3$
Z, Calculated density	2, 1.148 Mg/m^3
Absorption coefficient	0.132 mm^{-1}
F(000)	388
Crystal size	0.45 x 0.13 x 0.11 mm
Theta range for data collection	1.39 to 28.41 deg.
Index ranges	-8<=h<=8, -14<=k<=14, -20<=l<=20
Reflections collected / unique	19057 / 5139 [R(int) = 0.0349]
Completeness to 2Θ= 28.41°	99.5%
Absorption correction	Numerical
Max. and min. transmission	0.9799 and 0.9209
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5139 / 0 / 228
Goodness-of-fit on F^2	1.017
Final R indices [I>2σ (I)]	R_1 = 0.0373, wR_2 = 0.0964
R indices (all data)	R_1 = 0.0416, wR_2 = 0.0993
Largest diff. peak and hole	0.475 and -0.382 $e.A^{-3}$

References

1 G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw and K. I. Goldberg, *Organometallics*, 2010, **29**, 2176.

2 H. F. Bettinger, M. Filthaus, H. Bornemann and I. M. Oppel, *Angew. Chem. Int. Ed.*, 2008, **47**, 4744.

3 S. Hawkeswood and D. W. Stephan, *Dalton Trans.*, 2005, 2182.

4 M. Letellier, D. J. McPhee and D. Griller, *Synth. Commun.*, 1988, **18**, 1975.

5 G. Sheldrick, *Acta Crystallographica Section A*, 2008, **64**, 112.