

Electronic Supplementary Information (ESI)

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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 C₆D₆ that was purchased from Deutero GmbH. The spectra were referenced to residual benzene signals (¹H, ¹³C, ²⁹Si: SiMe₄)¹ and externally (¹¹B: BF₃•OEt₂). For silicon-29 NMR a DEPT45 pulse 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 procedures² 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 ¹¹B 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**

- 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 %).
- 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; C₆D₆) -0.08 (9 H, s, J_{HSi} 6.5, (CH₃)₃Si), 1.14 (12 H, s, Me), 1.87 (1 H, br s, NH), 2.49 (2 H, d, J_{HH} 7.1, CH₂); δ_C (101 MHz; C₆D₆) -3.2 ((CH₃)₃Si), 25.0 (Me), 31.2 (CH₂), 82.0 (CO); δ_B (80 MHz; C₆D₆) 25.0 ($h_{1/2}$ 107); δ_{Si} (50 MHz; C₆D₆) 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 C₁₀H₂₄NO₂SiB: 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 pinBN₃ (**1**). As standard 0.67 eq. tetrachloroethane (C₂H₂Cl₄) 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 pinBN₃ (**1**) amount increases. A high excess of **1** also causes a few more nmr signals in hydrogen nmr spectra.

δ_{H} (250 MHz; C₆D₆) 0.21 (9 H, s, J_{HSi} 6.5, (CH₃)₃Si), 1.09 (24 H, s, Me), 3.05 (2 H, s, CH₂); δ_{C} (101 MHz; C₆D₆) -1.9 ((CH₃)₃Si), 24.9 (Me), 34.3 (CH₂), 82.4 (CO); δ_{B} (80 MHz; C₆D₆) 26.4 ($h_{1/2}$ 236); δ_{Si} (50 MHz; C₆D₆) 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 C₁₅H₃₂NO₄SiB₂: 340.22867.

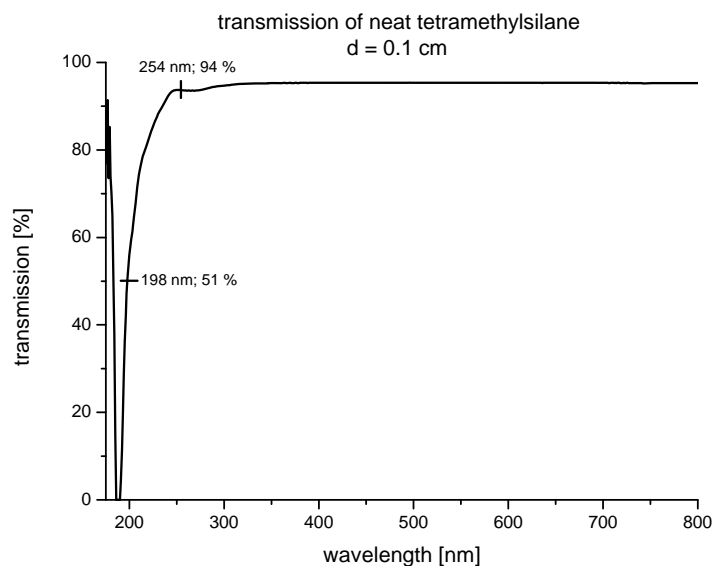
N-Isopropylidene-trimethylsilylmethylamine⁴

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 Na₂SO₄ 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; C₆D₆): 0.06 (s, 9 H), 1.39 (s, 3 H), 1.87 (s, 3 H), 3.08 (s, 2 H); δ_{C} (101 MHz; C₆D₆): -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

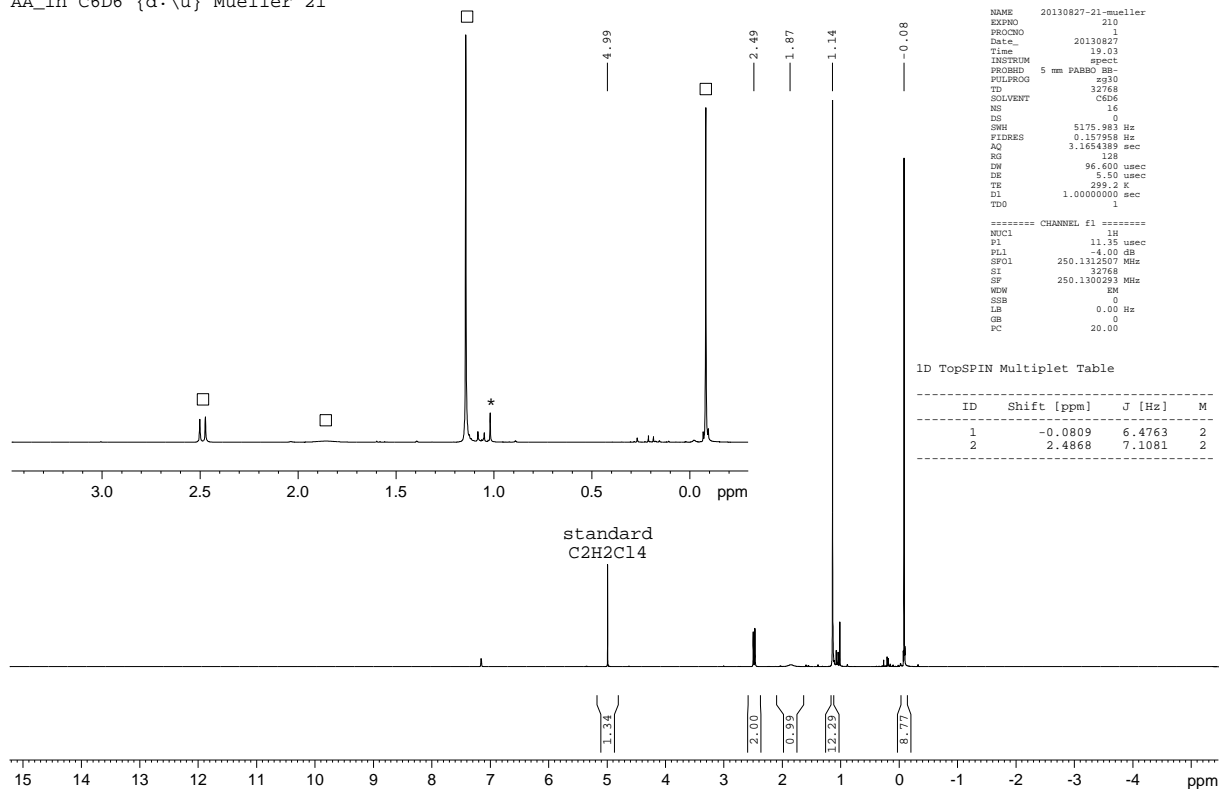


GC-MS measurement of **2a**, Cy7NH₂ and N-isopropylidene-trimethylsilylmethylamine

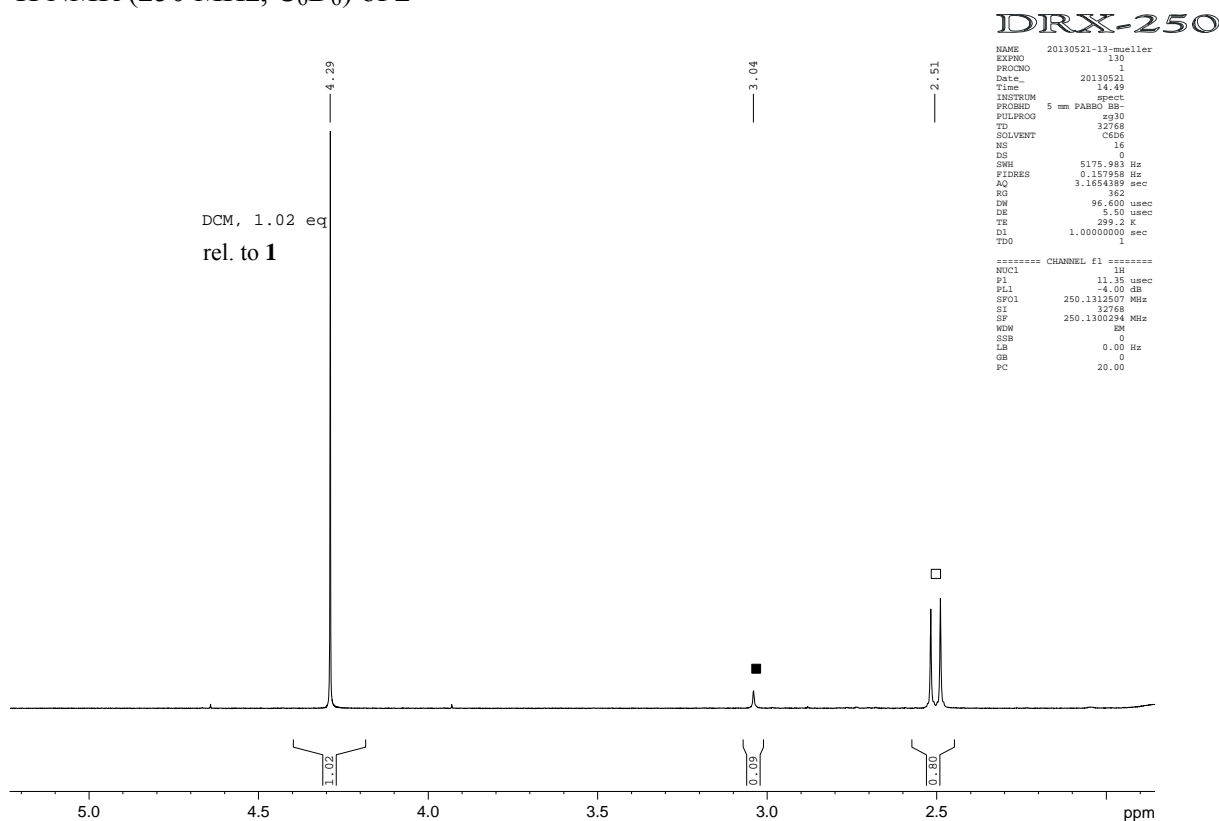
<p>File : C:\HPCHEM\1\DATA\MUELL31.D Operator : dw Acquired : 27 Jun 2013 14:28 using AcqMethod S1012_1 Instrument : GC/MS Ins Sample Name: 1a Misc Info : Cycloheptylamin, TMSCH₂NH₂, Pentan Vial Number: 83</p> <p>Abundance TIC: MUELL31</p>	<p>File : C:\HPCHEM\1\DATA\MUELL36.D Operator : dw Acquired : 28 Jun 2013 14:50 using AcqMethod S1012_1 Instrument : GC/MS Ins Sample Name: 1a + 10µL Aceton Misc Info : Cycloheptylamin, TMSCH₂NH₂, Pentan Vial Number: 83</p> <p>Abundance TIC: MUELL36</p>
<p>GC-MS of the mixture of 2a (ret. time 10.96 min) and cycloheptylamine (Cy7NH₂, ret. time 24.15) before the addition of acetone</p>	<p>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.</p>

NMR/mass spectra of 2

MMI793
AA_1h C6D6 {d:\u} Mueller 21

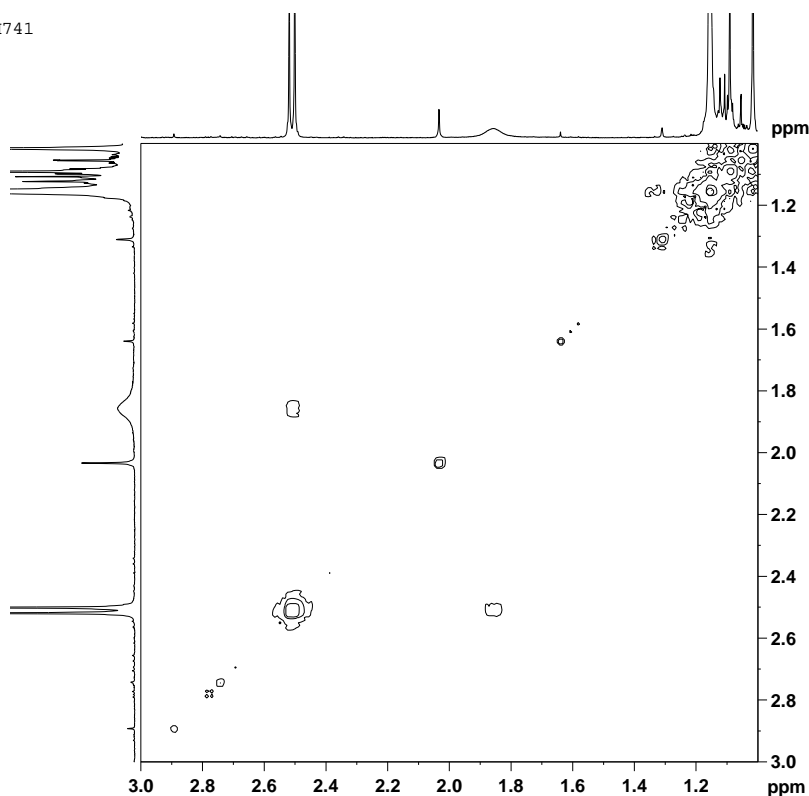


¹H NMR (250 MHz, C₆D₆) of 2



¹H NMR (250 MHz, C₆D₆), determination of the amount of 2 and 4 in the crude oil after irradiation

MMH741



AVII-400

```

NAME      20130531-44-mjema
EXPNO     3
PROCNO    1
Date_     20130531
Time      13.37
INSTRUM   spect
PROBHD    5 mm Dual 13C/
PULPROG   coesyppg
TD         2048
SOLVENT   C6D6
NS         1
DS         8
SWH        3472.222 Hz
FIDRES     1.595421 Hz
AQ         0.2949620 sec
RG         181
DW         144.000 usec
DE         6.00 usec
TE         297.3 K
D0         0.0000300 sec
D1         1.38408196 sec
D13        0.0000800 sec
D16        0.0001000 sec
IN0        0.0002800 sec

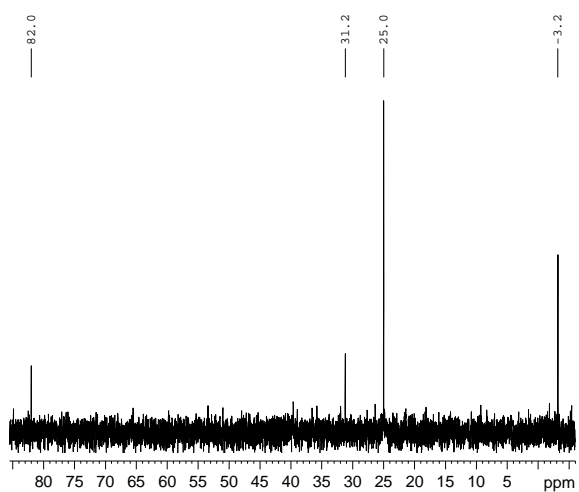
===== CHANNEL f1 =====
NUC1       1H
P0         10.00 usec
P1         10.00 usec
PL1        3.00 dB
SFO1       400.1614134 MHz

===== GRADIENT CHANNEL =====
GPNAM1     SINE.100
GP21       10.00 %
P16        1000.00 usec
NDD         1
TD         128
SFO1       400.1614 MHz
FIDRES     27.126736 Hz
SN          8.677 ppm
FHM0DE     QF
SI          1024
SF         400.1600426 MHz
W0W        SINE
SSB         0
LB          0.00 Hz
GB          0
PC          1.40
SI          1024
MC2        QF
SF         400.1600419 MHz
W0W        SINE
SSB         0
LB          0.00 Hz
GB          0

```

HHCosy (400 MHz, C₆D₆) of 2

MMH741_1



AVII-400

```

NAME      20130605-3-mjema
EXPNO     3
PROCNO    1
Date_     20130605
Time      10.25
INSTRUM   spect
PROBHD    5 mm Dual 13C/
PULPROG   zgpg30
TD         65536
SOLVENT   C6D6
NS         256
DS         8
SWH        26178.010 Hz
FIDRES     0.399445 Hz
AQ         1.2517875 sec
RG         13004
DW         19.100 usec
DE         6.00 usec
TE         298.2 K
D1         1.0000000 sec
D11        0.0300000 sec
TD0        1

===== CHANNEL f1 =====
NUC1       13C
P1         8.50 usec
PL1        3.00 dB
SFO1       100.6323464 MHz

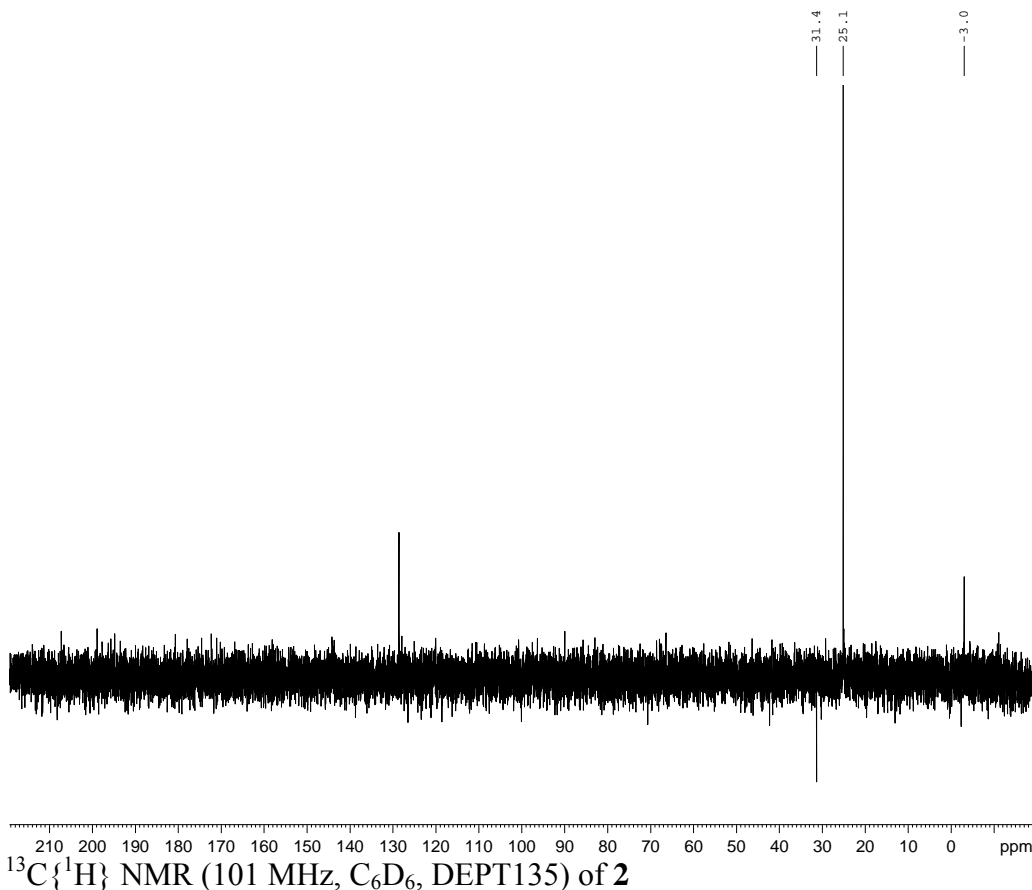
===== CHANNEL f2 =====
CPDPRG2   waltz16
NUC2       1H
PCPD2     94.00 usec
PL2        3.00 dB
PL12       22.46 dB
PL13       24.00 dB
SFO2       400.1616006 MHz
SI         32768
SF         100.6202758 MHz
W0W        EM
SSB         0
LB          1.00 Hz
GB          0
PC          1.40

```

13C{1H} NMR (101 MHz, C₆D₆) of 2

MMH741_1

AVII-400



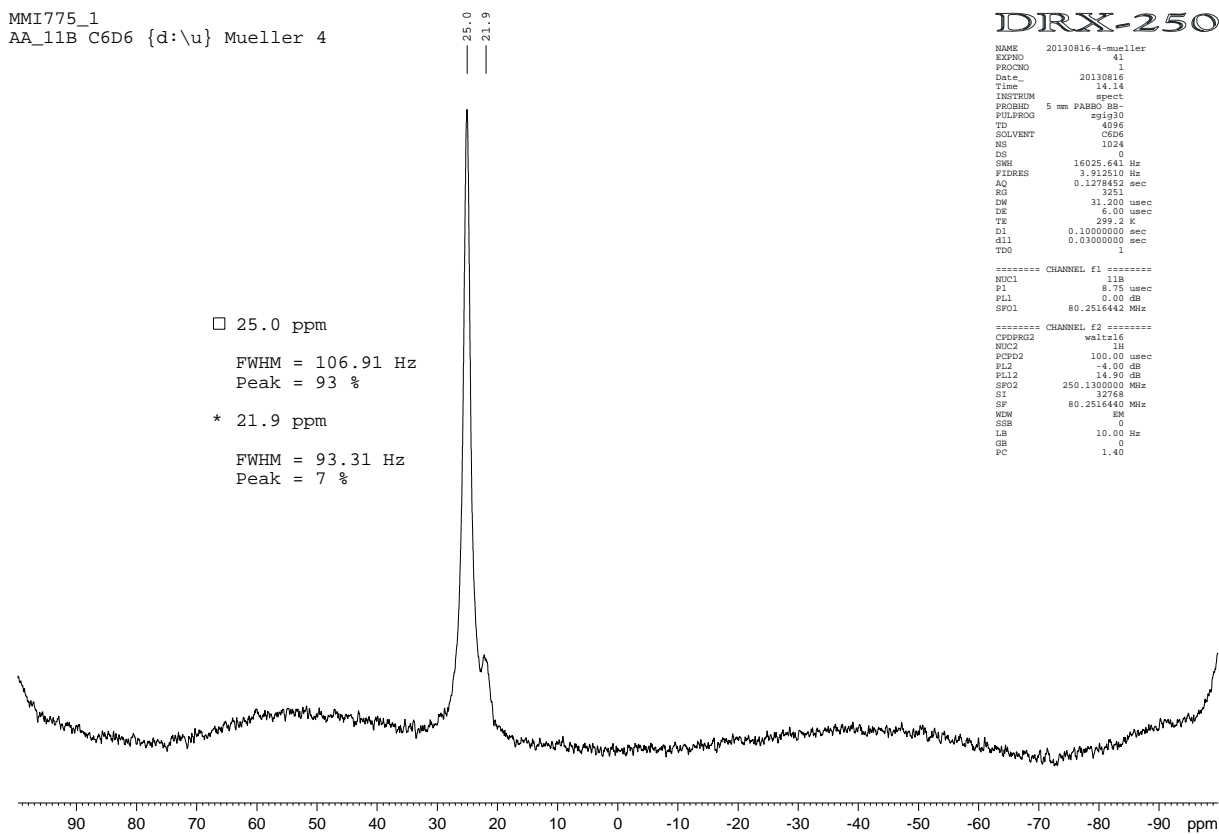
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NAME      20130605-3-muema
EXPNO     1
PROCNO    1
Date_     20130606
Time      1.06
INSTRUM   spect
PROBHD    5 mm Dual 13C/
PULPROG   dept135
TD         65536
SOLVENT   CDCl3
NS         512
DS         4
SWH        23980.814 Hz
FIDRES     0.365918 Hz
AQ         1.3664756 sec
RG         20642.5
DW         20.850 usec
DE         6.00 usec
TE         299.2 K
CNST2     145.0000000
D1         1.00000000 sec
D2         0.0034828 sec
D12        0.00002000 sec
TDO        1
===== CHANNEL f1 =====
NUC1       13C
P1         8.50 usec
P2         17.00 usec
PL1        3.00 dB
SFO1       100.6303340 MHz
===== CHANNEL f2 =====
CPDPRG2    waltz16
NUC2       1H
P3         10.00 usec
P4         20.00 usec
PCPD2      94.00 usec
PL2        3.00 dB
PL12       22.46 dB
SFO2       400.1614508 MHz
SI         32768
SF         100.6202587 MHz
WDW        EM
SSB        0
LB         10.00 Hz
GB         0
PC         1.40

```

MMI775_1
AA_11B C6D6 {d:\u} Mueller 4

DRX-250



```

NAME      20130816-4-mueller
EXPNO     41
PROCNO    1
Date_     20130816
Time      14.14
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   zgpg30
TD         4096
SOLVENT   CDCl3
NS         1024
DS         0
SWH        16025.641 Hz
FIDRES     3.912510 Hz
AQ         0.1278452 sec
RG         3251
DW         31.200 usec
DE         6.00 usec
TE         299.2 K
D1         0.10000000 sec
d11        0.03000000 sec
TDO        1
===== CHANNEL f1 =====
NUC1       11B
P1         8.75 usec
PL1        0.00 dB
SFO1       80.2516442 MHz
===== CHANNEL f2 =====
CPDPRG2    waltz16
NUC2       1H
P3         100.00 usec
PL2        4.00 dB
PL12       14.90 dB
SFO2       250.1300000 MHz
SI         32768
SF         80.2516440 MHz
WDW        EM
SSB        0
LB         10.00 Hz
GB         0
PC         1.40

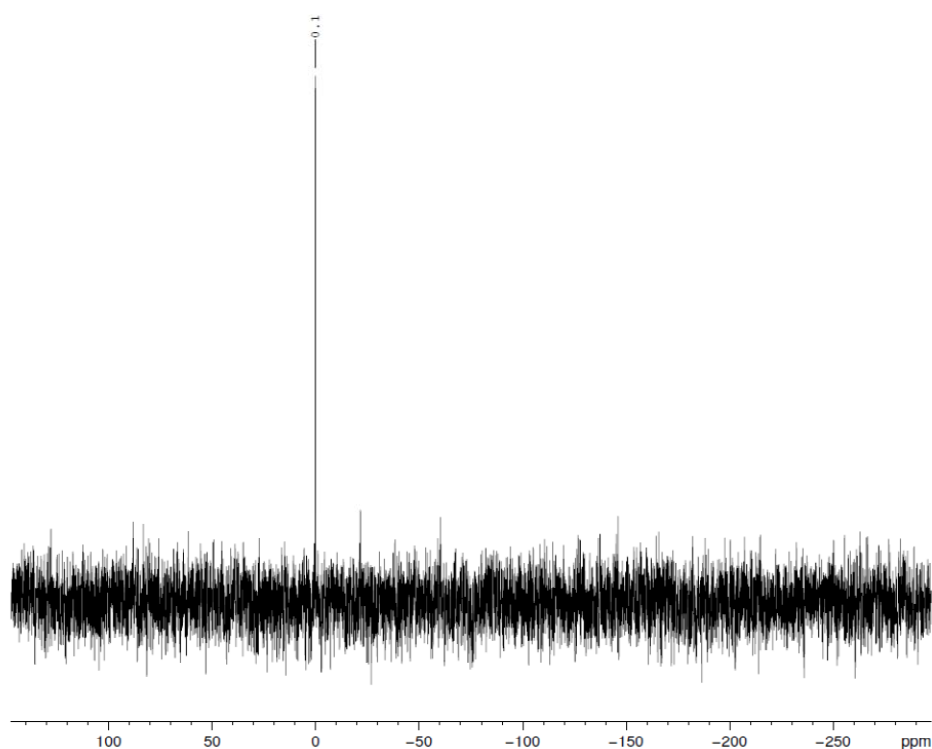
```

□ 25.0 ppm
FWHM = 106.91 Hz
Peak = 93 %

* 21.9 ppm
FWHM = 93.31 Hz
Peak = 7 %

MMI793
AA_29Si_DEPT45 C6D6 (d:\u) Mueller 21

DIRX-250



```
Current Data Parameters
NAME      20130827-21-mueller
EXPNO     214
PROCNO    1

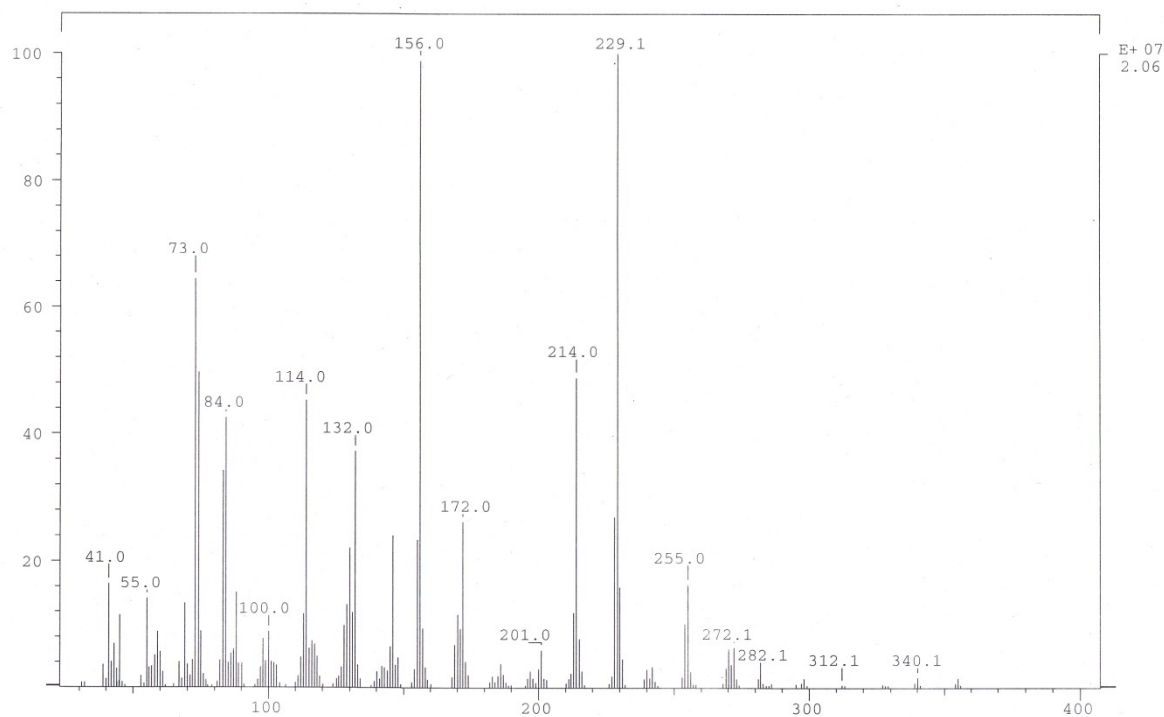
F2 - Acquisition Parameters
Date_     20130827
Time      19.43
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   zgpg30
TD         32768
SOLVENT   CDCl3
NS         300
DS         6
SWH        22075.055 Hz
FIDRES     0.673677 Hz
AQ         0.7422632 sec
RG         16384
DM         22.650 usec
DE         5.50 usec
TE         299.2 K
CHFT2     0.0000000
D1         2.0000000 sec
d2         0.0425000 sec
d12        0.0000200 sec
DELTA     0.00001910 sec
TDO        1

===== CHANNEL f1 =====
NUC1       29Si
P1         15.00 usec
P2         30.00 usec
PL1        0.00 dB
SFO1       49.690250 MHz

===== CHANNEL f2 =====
CPDPRG2   waltz16
NUC2       13C
P3         11.35 usec
P4         22.70 usec
PCTD2     100.00 usec
PL2        -4.00 dB
PL12       14.50 dB
SFO2       200.131224 MHz

F2 - Processing parameters
SI         32768
SF         49.6937800 MHz
WDW        DM
SSB         0
LB         2.00 Hz
GB         0
PC         3.00
```

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



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

Massenfeinbestimmung

Name: Müller Probenbezeichnung: MMH741_1

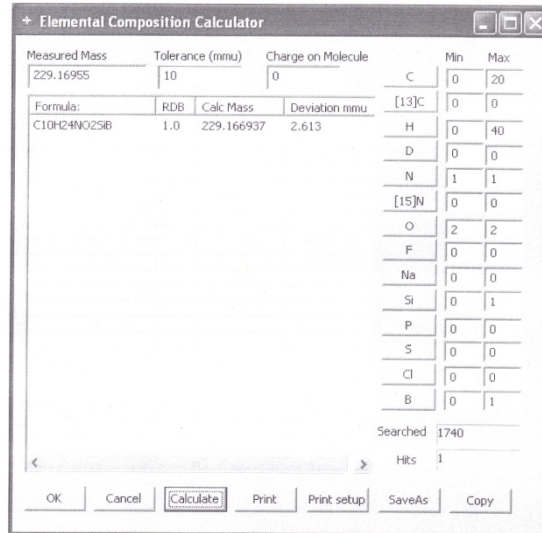
Ionisierungsmethode: EI ...X... FAB

Referenz - Ion und seine exakte Masse:

C₅F₉ 231 230,98562

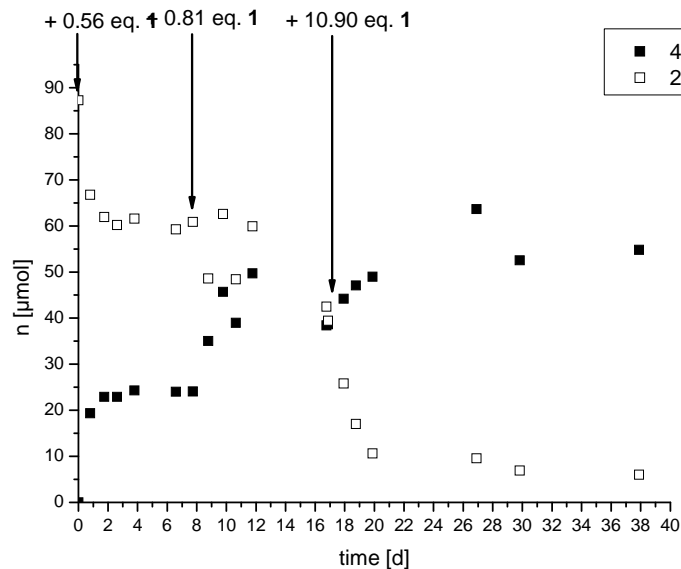
die gefundene exakte Masse erhält man zu: 229,16955

damit ergibt/ergeben sich folgende Elementkombination(en) :



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

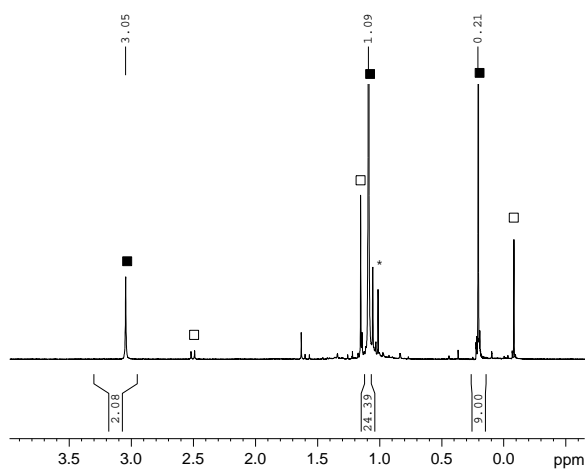
NMR experiment: transformation of 2 into 4 by the addition of 1



The amount of substance n in μmol was calculated from the peak of the standard compound ($\text{C}_2\text{H}_2\text{Cl}_4$) 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

MMF572(1)
AA_1h C6D6 {d:\u} Mueller 13



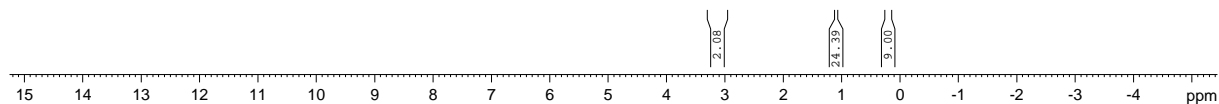
DRX-250

```

NAME      20121123-13-mueller
EXPNO    133
PROCNO   1
Date_    20121123
Time     19.06
INSTRUM  spect
PROBHD   5 mm PABBO BB-
PULPROG  zg30
TD        32768
SOLVENT  C6D6
NS        0
DS        0
SWH       5175.983 Hz
FIDRES   0.157958 Hz
AQ        3.1654389 sec
RG        362
RW        96.600 usec
DE        5.50 usec
TE        299.2 K
D1        1.00000000 sec
TDO       1
===== CHANNEL f1 =====
NUC1      1H
P1         11.35 usec
PL1        -4.00 dB
SFO1      250.1312507 MHz
SI         32768
SF         250.1300429 MHz
WDW        EM
SSB        0
LB         0.00 Hz
GB         0
PC         20.00
    
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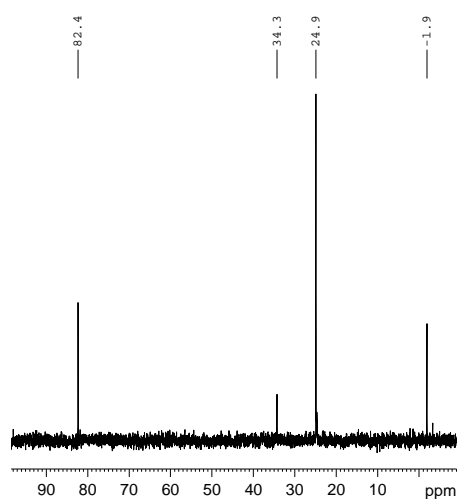
1D TopSPIN Multiplet Table

ID	Shift [ppm]	J [Hz]
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¹H NMR (250 MHz, C₆D₆) of 4

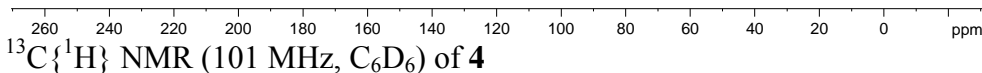
MMF572(1)
AA_13c C6D6 {d:\u} Mueller 13



DRX-250

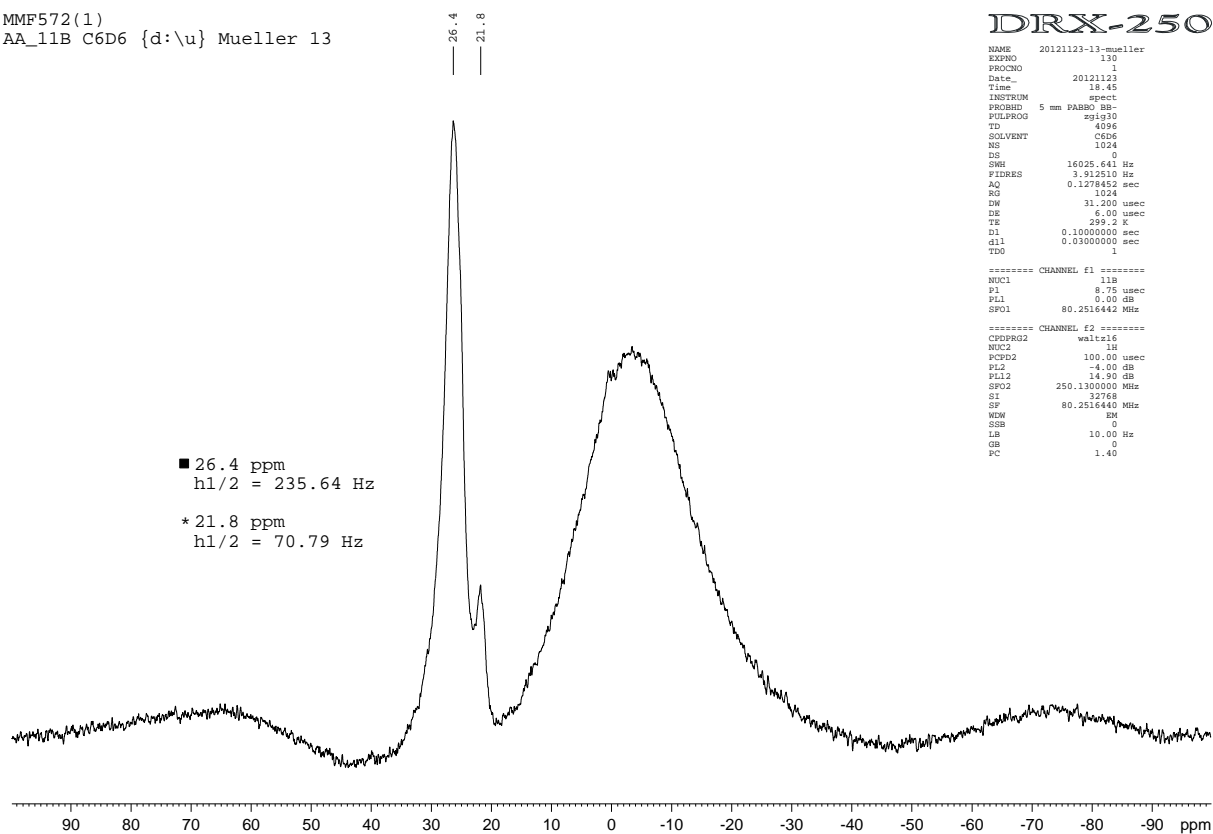
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EXPNO    135
PROCNO   1
Date_    20121123
Time     22.41
INSTRUM  spect
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PULPROG  zgpg30
TD        32768
SOLVENT  C6D6
NS        0
DS        0
SWH       18939.395 Hz
FIDRES   0.577984 Hz
AQ        0.8651252 sec
RG        2298.8
RW        26.400 usec
DE        5.50 usec
TE        299.2 K
D1        1.00000000 sec
d11       0.03000000 sec
DELTA    0.69999998 sec
TDO       1
===== CHANNEL f1 =====
NUC1      13C
P1         8.60 usec
PL1        -1.00 dB
SFO1      62.9027614 MHz
===== CHANNEL f2 =====
CHOPRO2  waltz16
NUC2      1H
PCPD2     100.00 usec
PL2        -4.00 dB
PL12       14.90 dB
PL13       17.79 dB
SFO2      250.1312507 MHz
SI         32768
SF         62.8952206 MHz
WDW        EM
SSB        0
LB         1.00 Hz
GB         0
PC         3.00
    
```



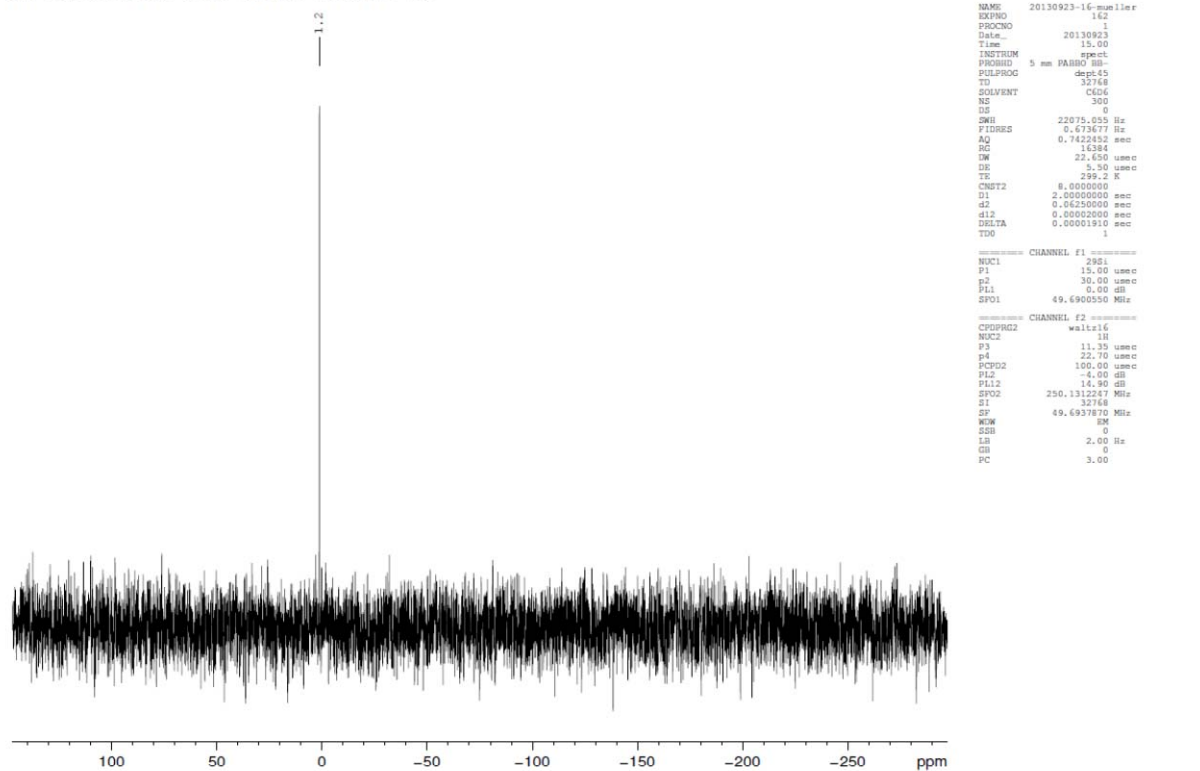
¹³C {¹H} NMR (101 MHz, C₆D₆) of 4

MMF572(1)
AA_11B C6D6 {d:\u} Mueller 13

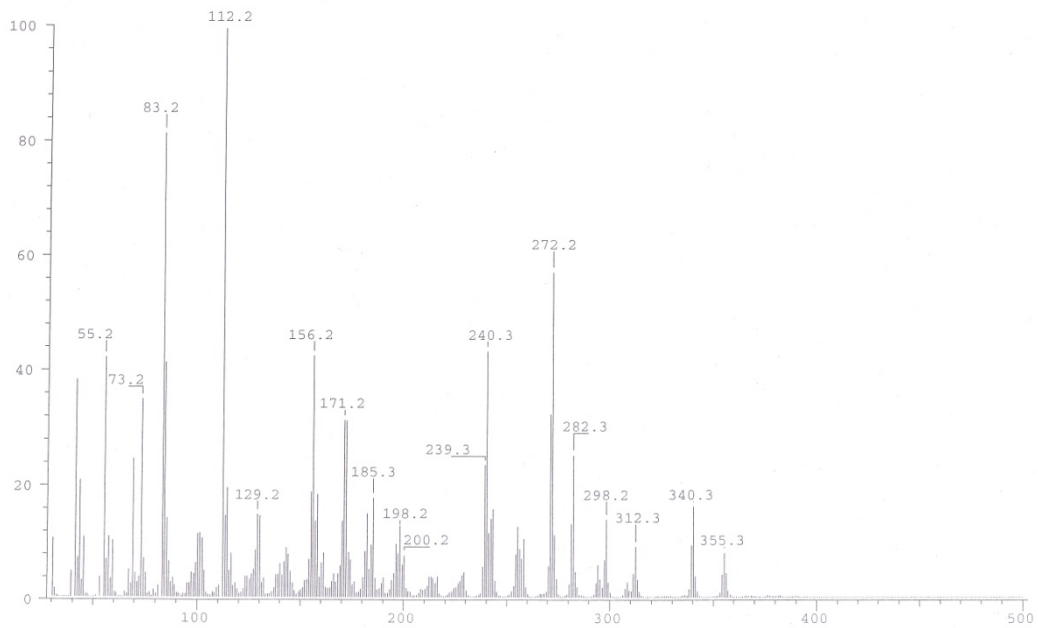


$^{11}\text{B}\{^1\text{H}\}$ NMR (80 MHz, C_6D_6) of **4**, due to background, integration is impossible

MMI793_17
AA_29Si_DEPT45 C6D6 {d:\u} Mueller 16



$^{29}\text{Si}\{^1\text{H}\}$ 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

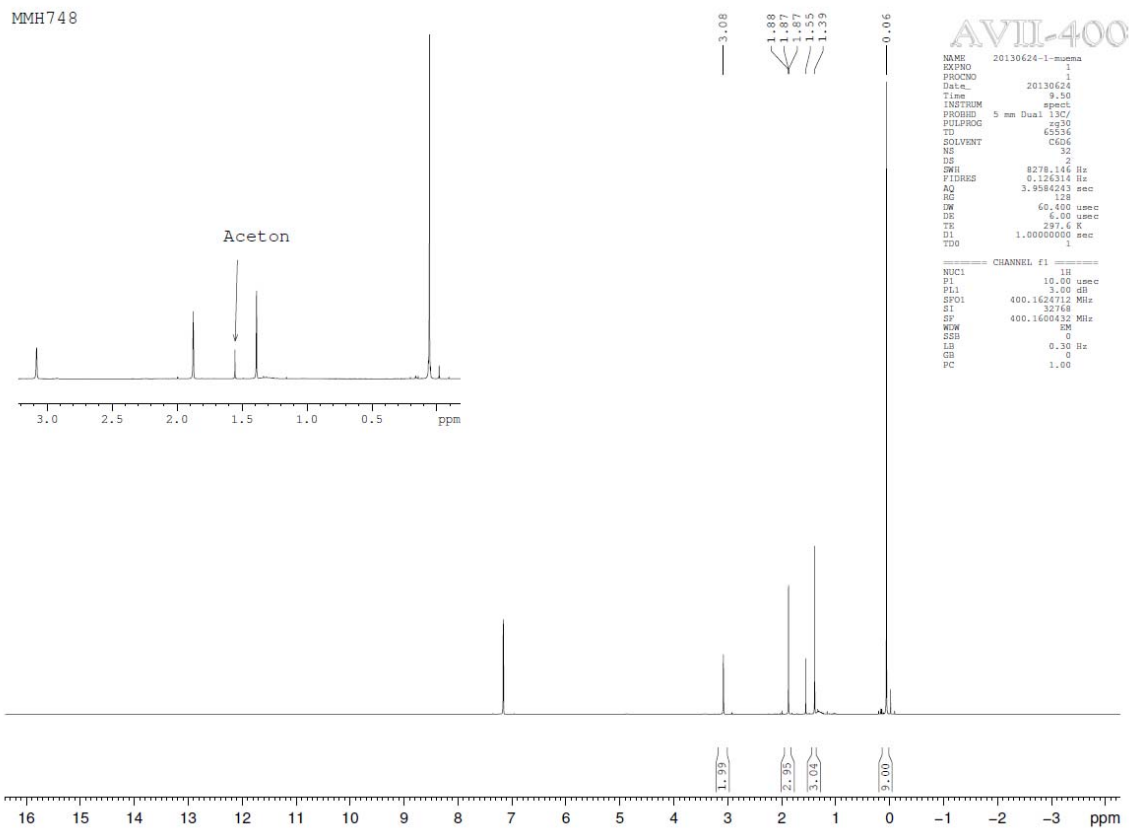
die **gefundene exakte Masse** erhält man zu: **340,22948**

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

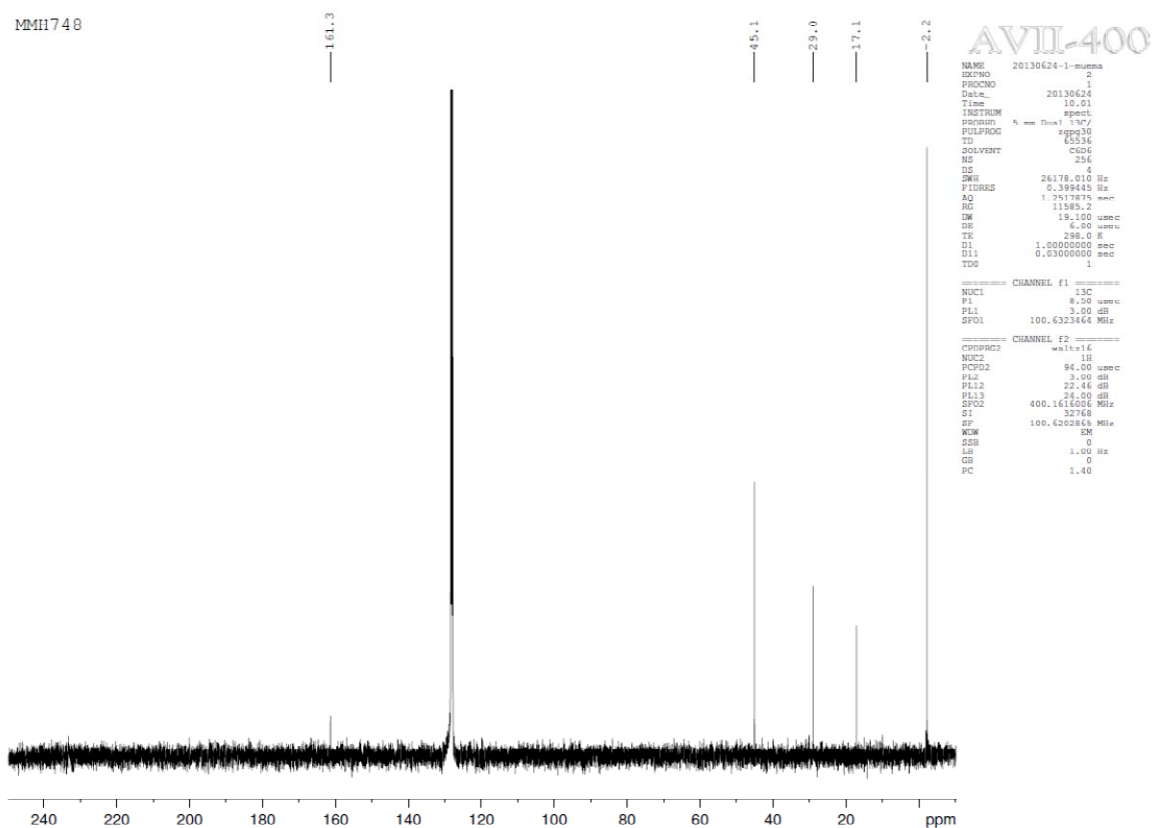
+ Elemental Composition Calculator				Min	Max
Measured Mass	Tolerance (mmu)	Charge on Molecule			
340.22948	10	0			
Formula:	RDB	Calc Mass	Deviation mmu		
C15H32NO4SiB2	2.5	340.228672	0.808		
				C	0 20
				[13]C	0 0
				H	0 40
				D	0 0
				N	1 1
				[15]N	0 0
				O	3 4
				F	0 0
				Na	0 0
				Si	1 1
				P	0 0
				S	0 0
				Cl	0 0
				B	1 2
				Searched	2592
				Hits	1
				OK	Cancel
				Calculate	Print
				Print setup	SaveAs
				Copy	

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

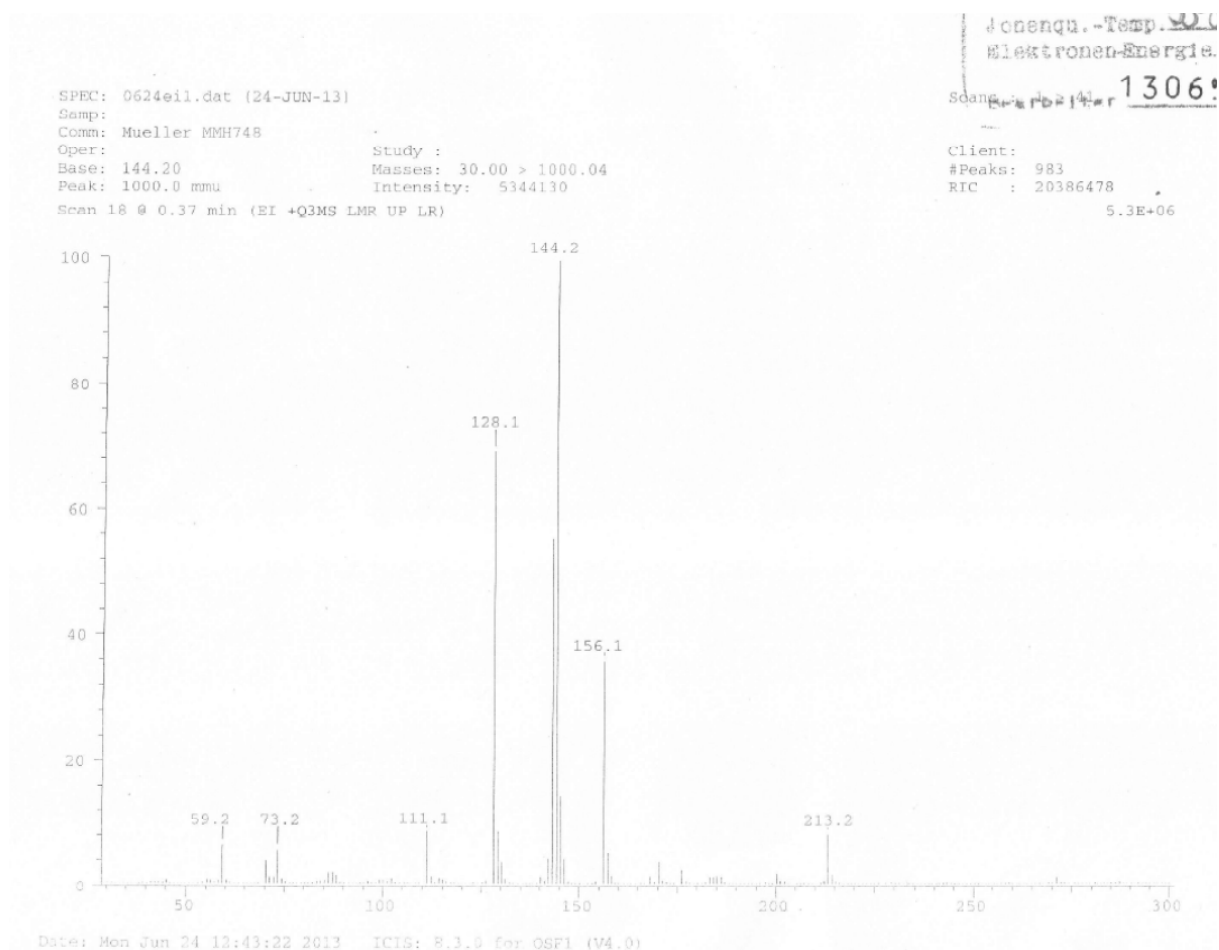
NMR/mass spectra of N-isopropylidene-trimethylsilylmethylamine



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



$^{13}\text{C}\{^1\text{H}\}$ 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 ($\lambda = 0.71073 \text{ \AA}$) 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	C ₁₆ H ₃₅ B ₂ N O ₄ Si
Formula weight	355.16
Temperature	100(2) K
Wavelength	0.71073 \AA
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 6.6093(14) \AA $\alpha = 107.567(4)^\circ$ b = 10.898(2) \AA $\beta = 97.679(5)^\circ$ c = 15.669(3) \AA $\gamma = 102.186(4)^\circ$

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.Å ⁻³

References

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