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Facile reaction of bis(tri-*n*-butyltin) oxide with silica gel

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Results of semi-empirical method PM3 (program HyperChem 8.0) geometrical calculations of stannylated silica gel parameters

Interatomic distances		Various	
Atom pair	Length, Å	Item	Value
Sn-C	2.16	Area covered by rotated n-Bu_3Sn	118 $Å^2$
Sn-O	2.07	Bu_3Sn/nm^2	0.85
Si-O	1.63	Sn-Sn distance	10.86 Å
Sn-O-Si	3.00		
$Sn(CH_2)_4H$	6.6	$H(CH_2)_4Sn(CH_2)_4H$	10-11 Å

NMR spectroscopy

The NMR experiments were performed in accordance with target-oriented approach (see V. V. Kachala, L. L. Khemchyan, A. S. Kashin, N. V. Orlov, A. A. Grachev, S. S. Zalesskiy, V. P. Ananikov, *Russ. Chem. Rev.*, 2013, **82**, 648).

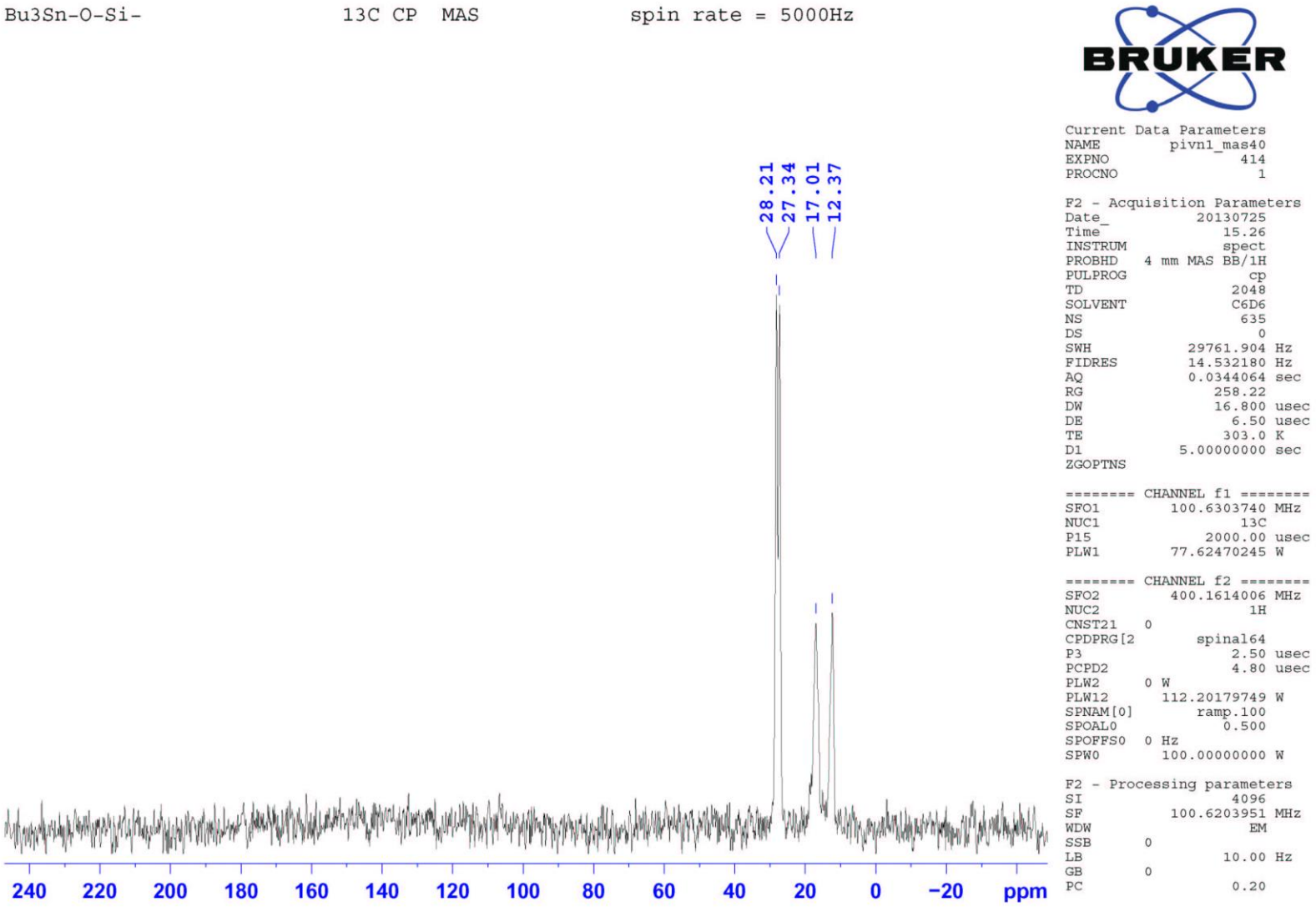
The ^{13}C cross polarization (CP) MAS NMR spectra (100.62 MHz) were recorded on a wide-bore Bruker spectrometer AVANCE III 400 using a double-resonance 4.0-mm MAS probe. The samples were packed in zirconium oxide rotors, the latter were spun at 5.0 kHz at Magic Angle. Room temperature was set for all experiments. Standard Bruker pulse program CP was used for cross-polarization with contact time of 2 ms and ^1H ramp pulse from 50 to 100% amplitude. ^{13}C pulse power corresponded to 4.0 μs 90-degree pulse length. Hartmann−Hann conditions (proton contact pulse power and proton decoupler frequency offset) were optimized for maximum signal intensity. ^1H decoupling performed with standard SPINAL64 pulse program, ^1H RF field strength was 100 kHz. The spectra widths were about 296 ppm, the acquisition time was 0.034 s (2048

points were collected) and the relaxation delay was 5 s. The spectra were acquired with 635 scans. Exponential multiplication was used for FID with LB=10 Hz. ^{13}C chemical shifts were referenced to the ^{13}C adamantane signal at 38.48 ppm (external rotor) on the TMS scale.

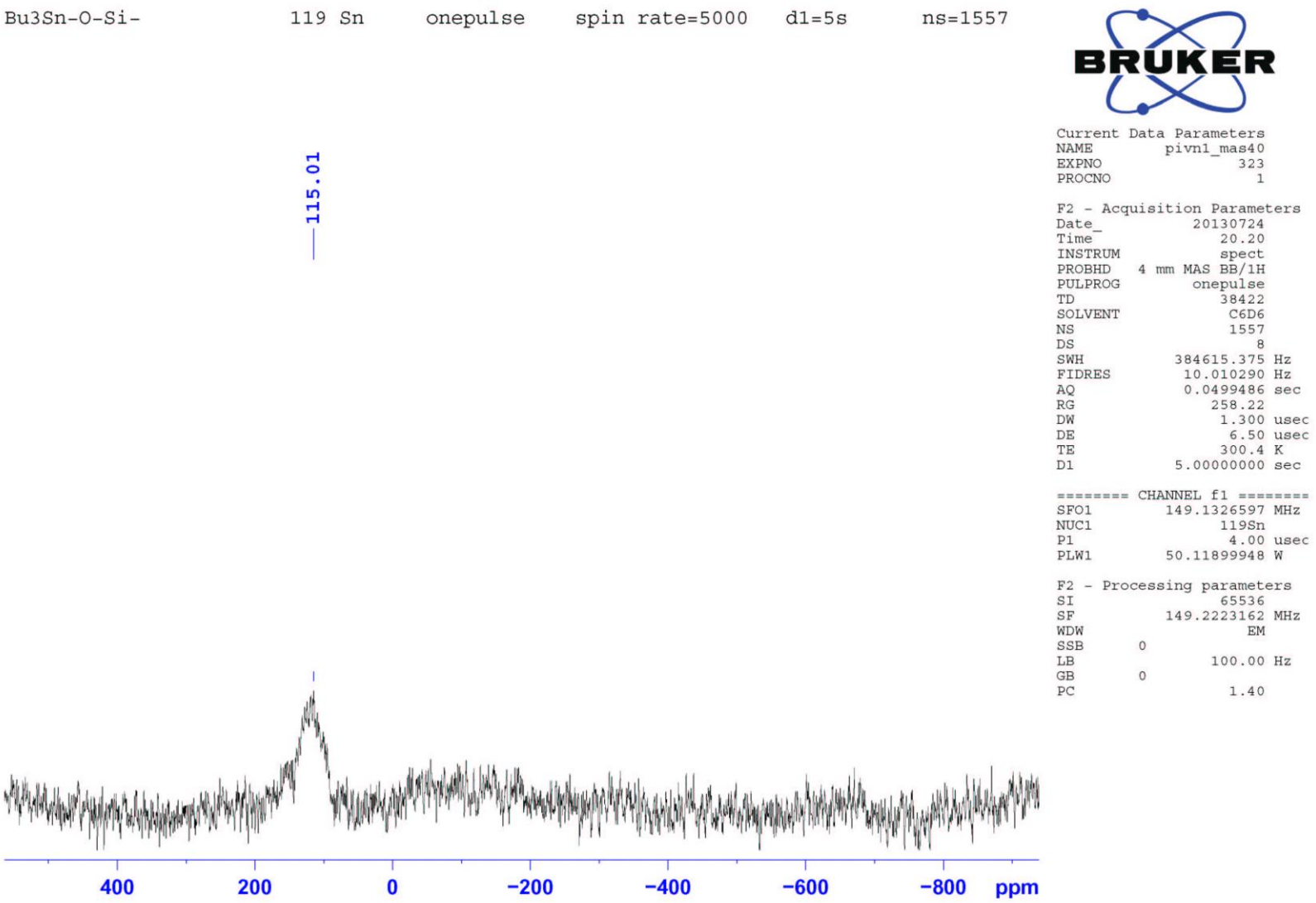
The ^{29}Si cross polarization (CP) MAS NMR spectra (79.49 MHz) were recorded at the same spectrometer. ^{29}Si pulse power corresponded to 5.2 μs 90-degree pulse length. Hartmann−Hann conditions were also optimized for maximum signal intensity. The spectra widths were about 983 ppm, the acquisition time was 0.035 s (5460 points were collected) and the relaxation delay was 5 s. The spectra were acquired with 5120 scans. Exponential multiplication was used for FID with LB=50 Hz. ^{29}Si chemical shifts were referenced to the ^{13}C adamantane signal at 38.48 ppm (external rotor) on the TMS scale. The obtained ^{29}Si chemical shift values of our sample of silica gel were very close to the silica gel values published in the work [S. H. Kim, O. H. Han, J. K. Kim, K. H. Lee, *Bull. Korean Chem. Soc.*, 2011, **32**, 3644]. All other parameters of ^{29}Si CP-experiment were the same as in the case of our ^{13}C CP-experiment.

The ^{119}Sn MAS NMR spectrum (149.22 MHz) was recorded with standard Bruker pulse program ONEPULSE. ^{119}Sn pulse was 4.0 μs. The spectra widths were about 2579 ppm, the acquisition time was 0.050 s (38422 points were collected) and the relaxation delay was 5 s. The spectrum were acquired with 1560 scans. Exponential multiplication was used for FID with LB=100 Hz. ^{119}Sn chemical shifts were referenced to the ^{119}Sn of neat liquid $(n\text{-}Bu_3Sn)_2O$ at 81.68 ppm. The sample was spun at 5.0 kHz at Magic Angle; room temperature was set for experiment.

Original NMR spectra



Picture 1. Spectrum ^{13}C CP MAS NMR (100.62 MHz) of tributylstannylated Kieselgel 60 (Fluka)

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Current Data Parameters
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EXPNO                323
PROCNO                 1

F2 - Acquisition Parameters
Date_           20130724
Time               20.20
INSTRUM            spect
PROBHD   4 mm MAS BB/1H
PULPROG         onepulse
TD                38422
SOLVENT            C6D6
NS                 1557
DS                    8
SWH          384615.375 Hz
FIDRES        10.010290 Hz
AQ            0.0499486 sec
RG               258.22
DW                1.300 usec
DE                6.50 usec
TE               300.4 K
D1           5.00000000 sec

======== CHANNEL f1 ========
SFO1         149.1326597 MHz
NUC1              119Sn
P1                4.00 usec
PLW1         50.11899948 W

F2 - Processing parameters
SI                65536
SF           149.2223162 MHz
WDW                  EM
SSB       0
LB                100.00 Hz
GB        0
PC                 1.40
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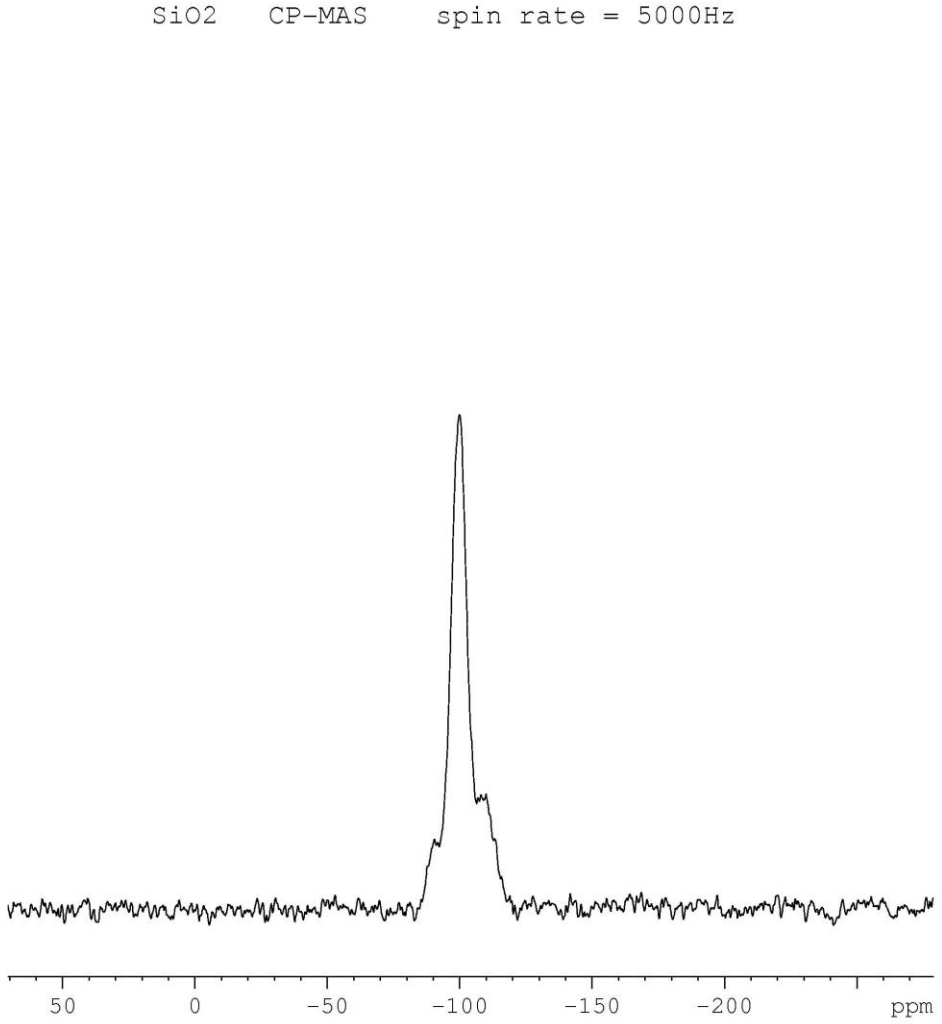
Picture 2. Spectrum ^{119}Sn MAS NMR (149.22 MHz) of tributylstannylated Kieselgel 60 (Fluka)

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Current Data Parameters
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EXPNO                146
PROCNO                 1

F2 - Acquisition Parameters
Date_           20131125
Time               22.48
INSTRUM            spect
PROBHD   4 mm MAS BB/1H
PULPROG               cp
TD                  5460
SOLVENT             DMSO
NS                  5120
DS                     0
SWH           78125.000 Hz
FIDRES        14.308608 Hz
AQ            0.0349440 sec
RG                 89.14
DW                 6.400 usec
DE                 6.50 usec
TE                303.0 K
D1           5.00000000 sec
ZGOPTNS

======== CHANNEL f1 ========
SFO1         79.4933800 MHz
NUC1                29Si
P15              2000.00 usec
PLW1        77.62500000 W

======== CHANNEL f2 ========
SFO2        400.1618800 MHz
NUC2                  1H
CNST21   0
CPDPRG[2        spinal64
P3                 2.50 usec
PCPD2              4.80 usec
PLW2     0 W
PLW12      112.20179749 W
SPNAM[0]        ramp.100
SPOAL0             0.500
SPOFFS0  0 Hz
SPW0        60.00000000 W

F2 - Processing parameters
SI                16384
SF           79.5005775 MHz
WDW                  EM
SSB      0
LB                55.00 Hz
GB       0
PC                 0.20
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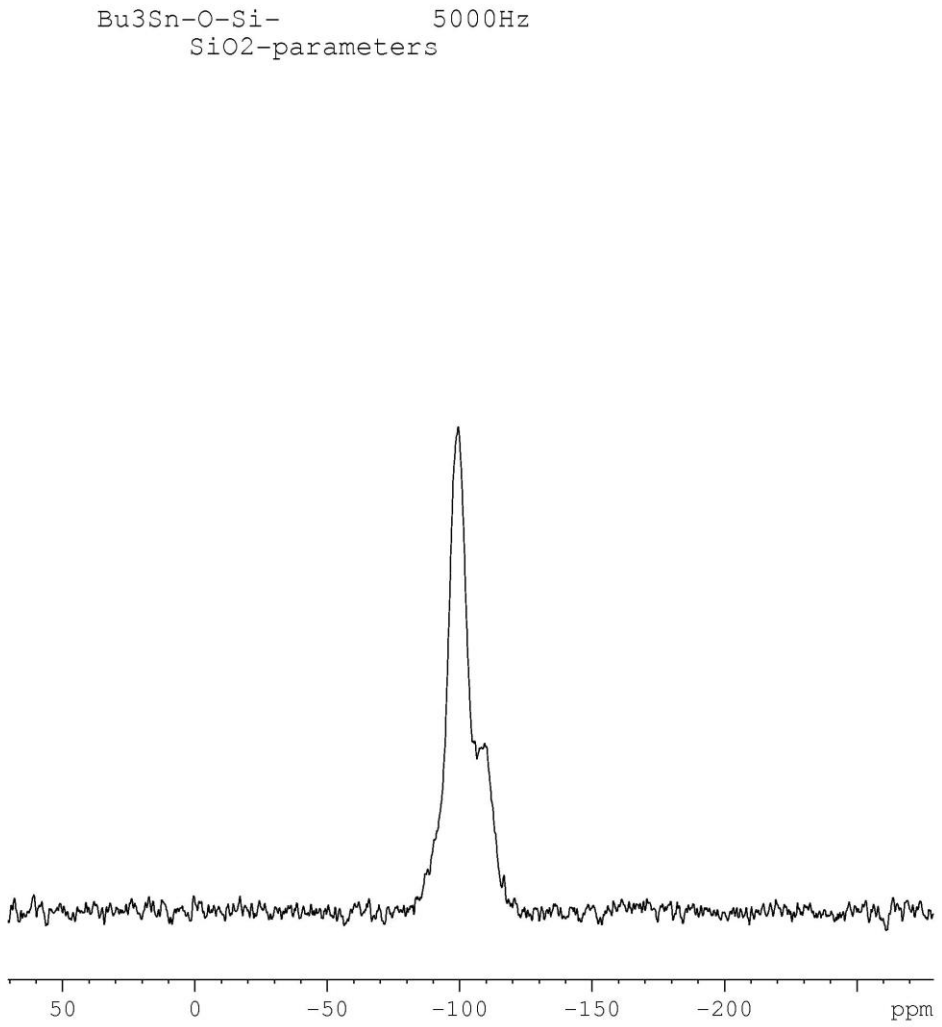
Picture 3. Spectrum ^{29}Si CP MAS NMR (79.49 MHz) of Kieselgel 60 (Fluka)

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EXPNO               929
PROCNO                1

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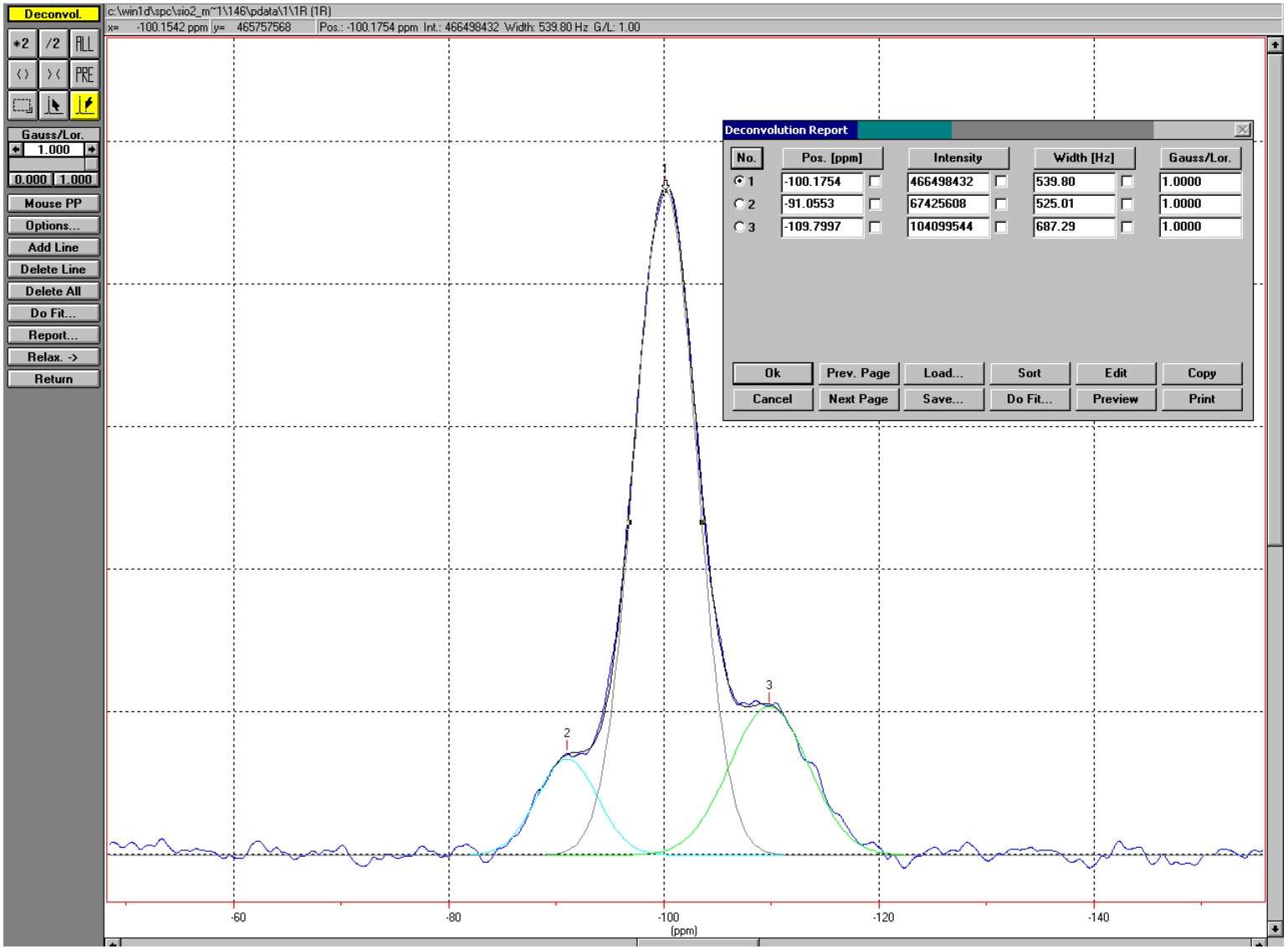
INSTRUM           spect
PROBHD   4 mm MAS BB/1H
PULPROG              cp
TD                 5460
SOLVENT            C6D6
NS                 5120
DS                    0
SWH           78125.000 Hz
FIDRES        14.308608 Hz
AQ            0.0349440 sec
RG                89.14
DW                6.400 usec
DE                 6.50 usec
TE                303.0 K
D1           5.00000000 sec
ZGOPTNS

======== CHANNEL f1 ========
SFO1         79.4933800 MHz
NUC1                29Si
P15              2000.00 usec
PLW1        77.62500000 W

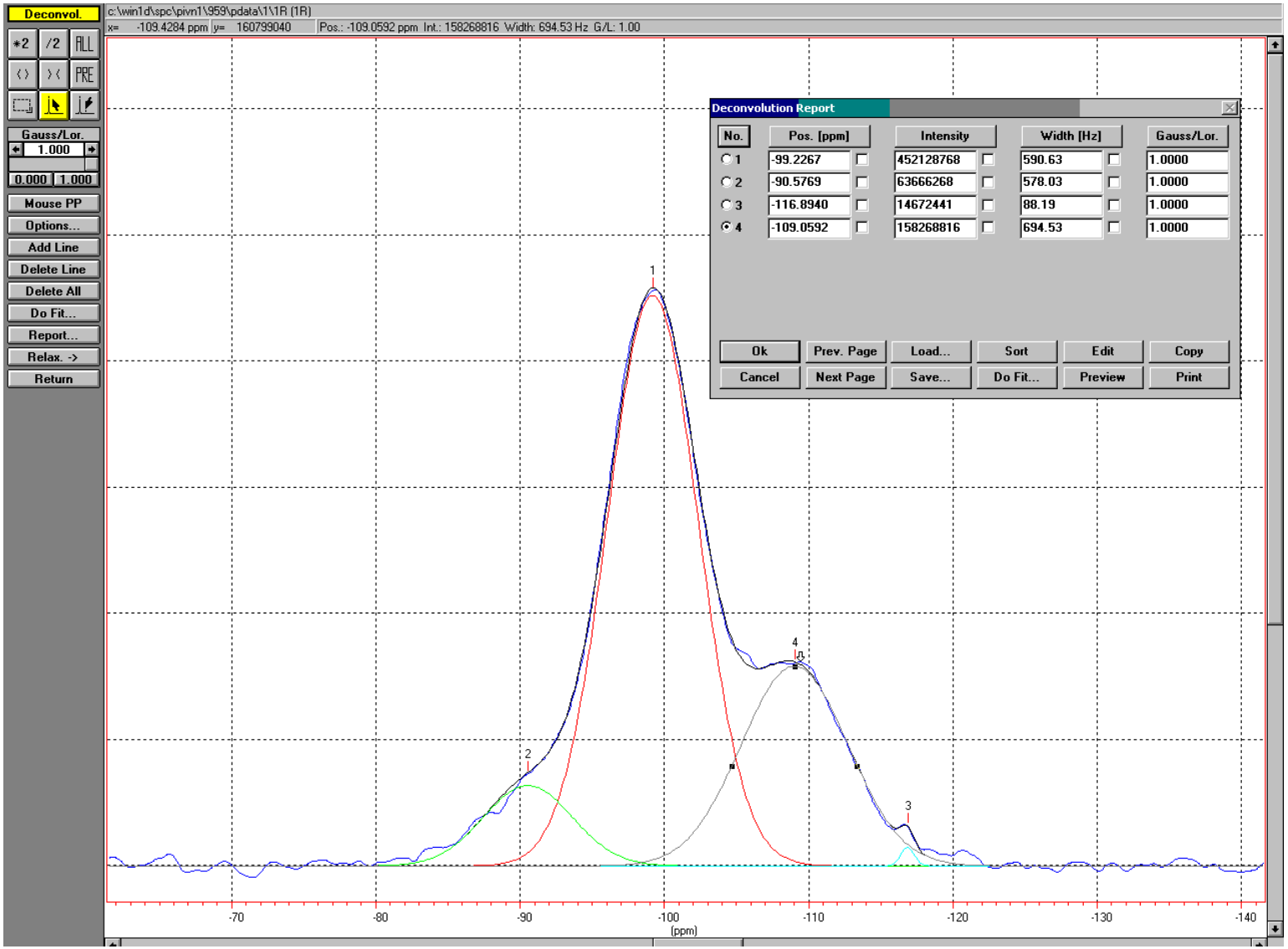
======== CHANNEL f2 ========
SFO2        400.1618800 MHz
NUC2                  1H
CNST21   0
CPDPRG[2        spinal64
P3                 2.50 usec
PCPD2              4.80 usec
PLW2     0 W
PLW12      112.20179749 W
SPNAM[0]        ramp.100
SPOAL0             0.500
SPOFFS0  0 Hz
SPW0        60.00000000 W

F2 - Processing parameters
SI                16384
SF           79.5005775 MHz
WDW                  EM
SSB      0
LB                50.00 Hz
GB       0
PC                 0.20
```

Picture 4. Spectrum ^{29}Si CP MAS NMR (79.49 MHz) of tributylstannylated Kieselgel 60



Picture 5. Deconvoluted spectrum ^{29}Si CP MAS NMR (79.49 MHz) of Kieselgel 60 (Fluka)



Picture 6. Deconvoluted spectrum ^{29}Si CP MAS NMR (79.49 MHz) of tributylstannylated Kieselgel 60