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The C–Br bond as a main reason for conformational isomerism

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Experimental details

The NMR spectra were recorded on a Bruker DPX-400 spectrometer (400.13 MHz - ^{1}H, 100.58 MHz - ^{13}C, 79.46 MHz - ^{29}Si) in $CDCl_3$ using TMS as a standard. Chemical shifts were measured with an accuracy of 0.01 ppm and were given in the δ scale.

The mass spectra were obtained using the Shimadzu GSMS-QP3050A gas chromatography mass spectrometer, Ultra-2 column d=0.2, l=50 m, layer thickness 0.33 μm.

The IR spectra were run on a Vertex-70 infrared Fourier spectrometer in thin layer.

N-Bromohexamethyldisilazane **1** was obtained as described [V. I. Rakhlin, S.V. Grigor'ev, R.G. Mirskov, T.A. Podgorbunskaya, M.G. Voronkov and D. V. Gendin, *Russ. J. Gen. Chem.*, 2003, **73,** 2063 *(Zh. Obshch. Chim.*, 2003, **73**, 1952).].

The reaction of N-bromohexamethyldisilazane with phenylacetylene. An equimolar mixture of phenylacetylene **2a** (2.13 g, 0.02 mol) and *N*-bromohexamethyldisilazane **1** (5 g, 0.02 mol) was placed in a dry glass ampule, degassed by "freeze-pump-thaw" method, sealed and irradiated with UV light (UV lamp DTP-400) for 10 h at room temperature. Vacuum distillation gave a fraction 5.7 g (yield 79%) with a boiling point of 138-144 °C (5 Torr).

Z-**3a**: ^{1}H NMR: 0.21 (s, 18 H, $SiMe_3$), 6.57 (s, 1 H, = CH), 7.27 (m, 1 H, H_p), 7.28(m, 2 H, H_m), 7.46 (m., 2 H, H_o). ^{13}C NMR: 1.78 ($SiMe_3$), 122.43 (= CPh), 127.84 (C_o), 128.21 (C_m), 127.96 (C_p), 135.38 (= CH), 139.08 (C_i). ^{29}Si NMR: 6.0

E-**3a**: ^{1}H NMR: 0.04 (s, 18 H, $SiMe_3$), 6.61 (s, 1 H, = CH), 7.21 (m, 1 H, H_p), 7.30 (m, 2 H, H_m), 7.56 (m, 2 H, H_o). ^{13}C NMR: 1.55 ($SiMe_3$), 117.44 (= CPh), 120.17 (C_o), 127.86 (C_m), 127.92 (C_p), 136.39 (= CH), 138.01 (C_i). ^{29}Si NMR: 6.9

Fraction mass spectra: *E*-**3a** (45%): 341[M]+, 326[M-Me], 262[3], 174[16], 146[18], 100[10], 73[100], 45[26]. *Z*-**3a** (55%): 343[M]+, 326[M-Me], 262[4], 174[18], 146[24], 100[10], 73[100], 45[30].

The assignment of isomers was made by a comparison of the CM/MS data with the data of NMR spectroscopy.

Elemental analysis. Found,%: C 48.94; H 6.88; N 3.91; Si 16.37. $C_{14}H_{24}NSi_2Br$. Calculated,%: C 49.11; H 7.06; N 4.09; Si 16.4.

The reaction of *N*-bromhexamethyldisilazane 1 with trimethylethynylsilane 2b. An equimolar mixture of trimethylethynylsilane **2b** (4.14 g, 0.042 mol) and *N*-bromohexamethyldisilazane **1** (10.18 g, 0.042 mol) was placed in the ampoule and degassed by the "freeze-pump-thaw" method. Then the ampule was sealed. The reaction mixture was irradiated with UV light (DTP-400 lamp) for 10 h at room temperature. Vacuum distillation gave a fraction 6.58 g (46% yield) with a boiling point of 98-104 °C (4 Torr).

The NMR spectra of the obtained fraction contain signals of two isomeric adducts of N-bromohexamethyldisilazane to the triple bond of ethynylsilane in a ratio of 1.6: 1.

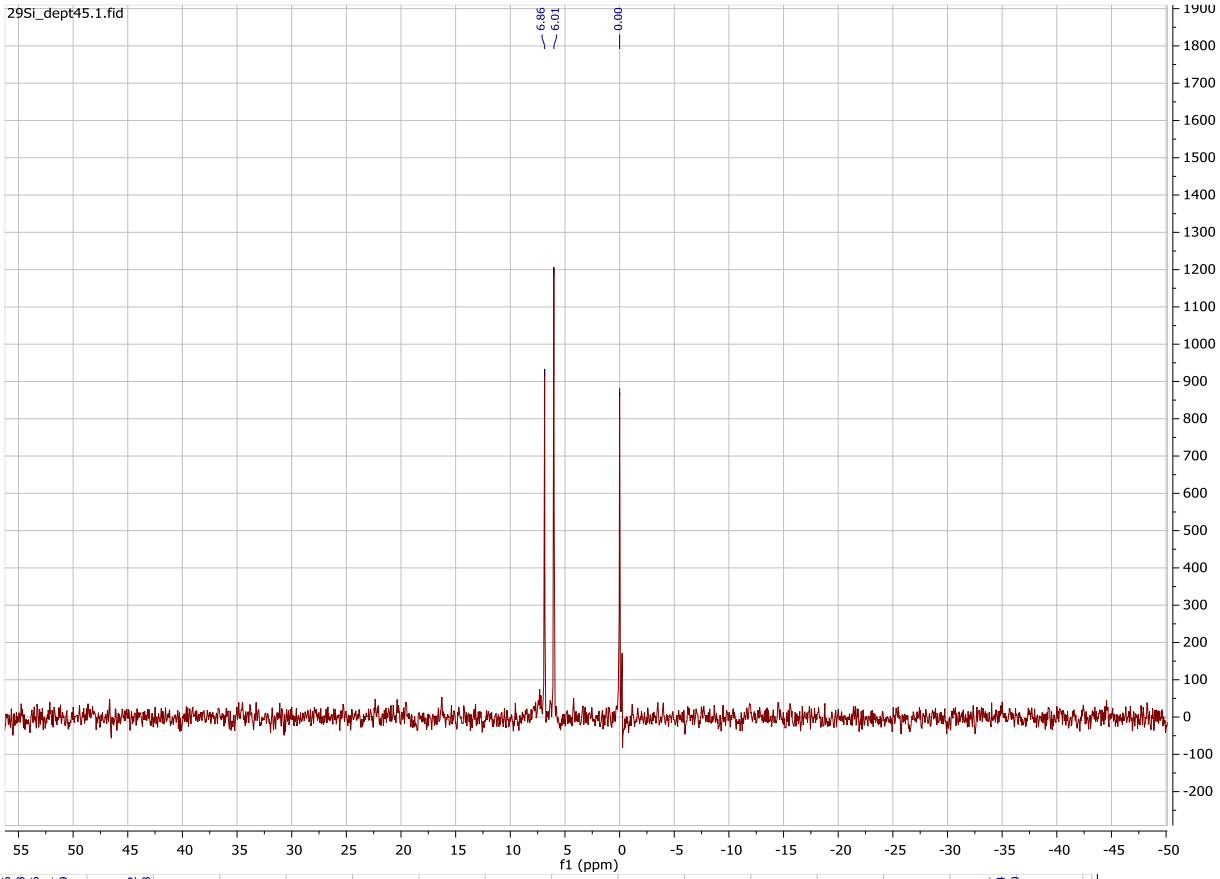
Z-**3b**: ^{1}H NMR: 0. 15 (s, 18 H, N($SiMe_3$)$_2$), 0.26 (s, 9 H, C$SiMe_3$), 6.47 (s, 1 H, =CH). ^{13}C NMR: -1.52 (C-$SiMe_3$), 1.71 (N-$SiMe_3$), 124. 13 (> C=), 142.69 (=CH). ^{29}Si NMR: -1.80, 4.178

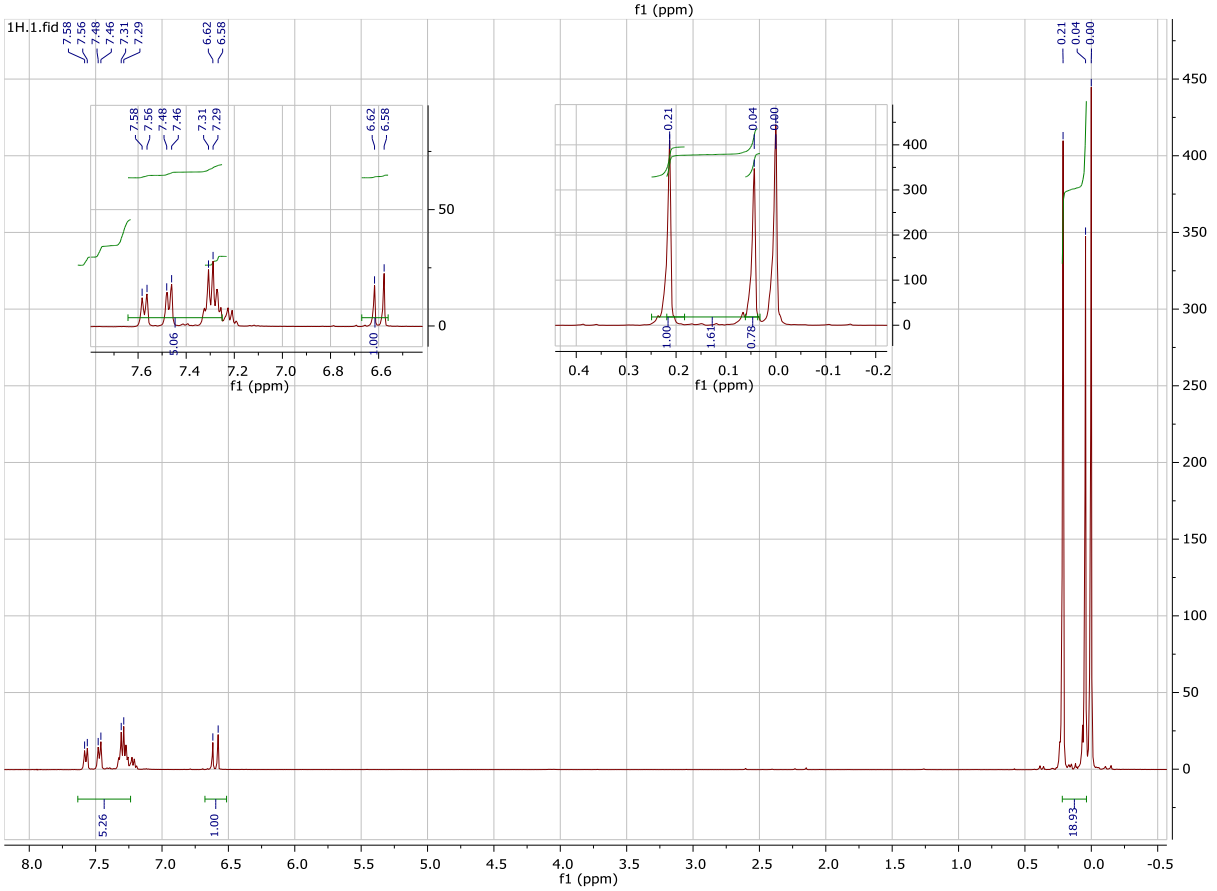
E-**3b**: ^{1}H NMR: 0.13 (s, 18 H, N($SiMe_3$)$_2$), 0. 17 (s, 9 H, C$SiMe_3$), 7.00 (s, 1 H, =CH). ^{13}C NMR: -1.52 (C-$SiMe_3$), 1.47 (N-$SiMe_3$), 128.97 (> C=), 147. 94 (=CH). ^{29}Si NMR: -3.66, 5.07

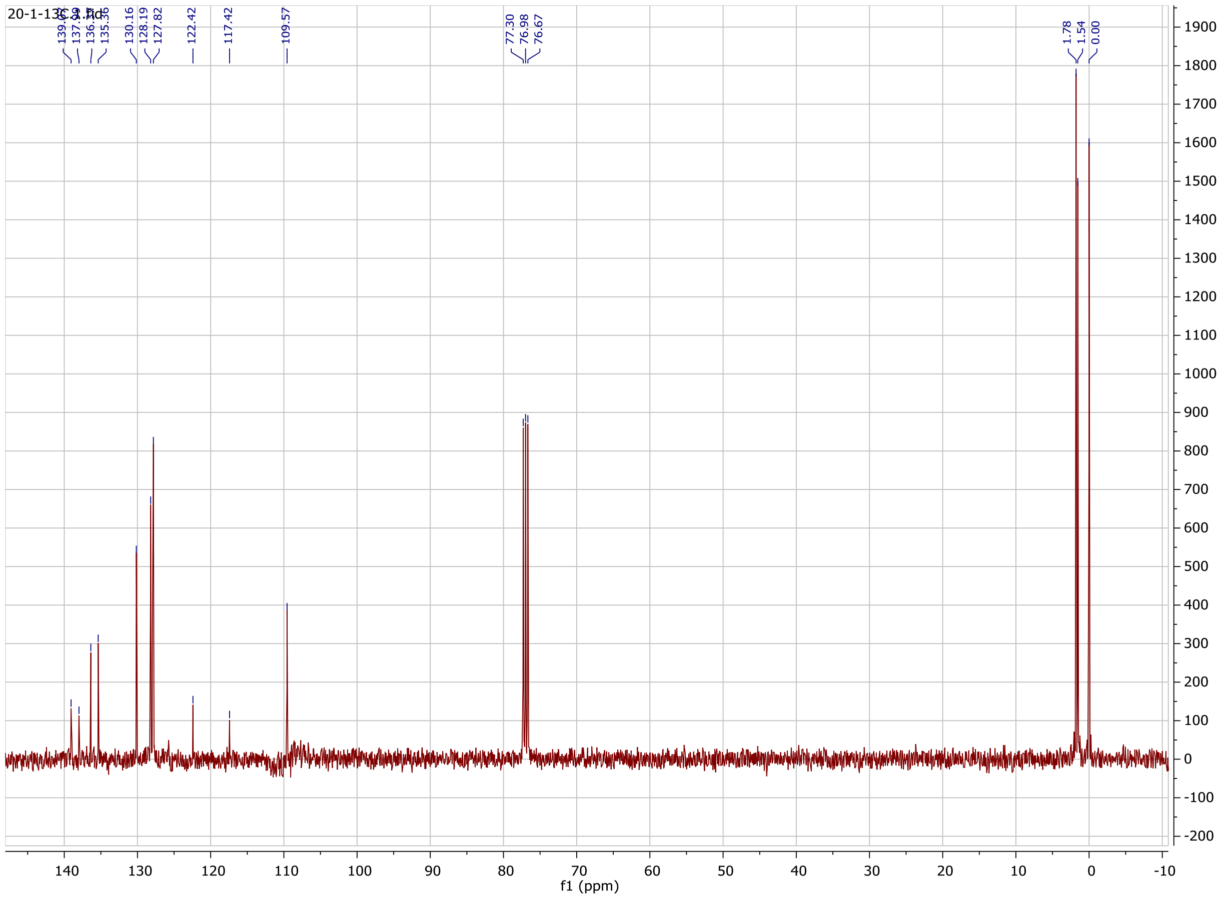
Elemental analysis. Found,%: C 35.58; H 5.16; N 4.28; Si 28.32. $C_{11}H_{28}NSi_3Br$. Calculated,%: C 35.75; H 5.33; N 4.63; Si 27.86.

The main results were obtained using the equipment of Baikal analytic center for collective use, Siberian Branch of the Russian Academy of Sciences.

The NMR and the CM/MS spectra *N*-(2-bromo-2-phenylethenyl)-*N*,*N*-bis(trimethylsilyl)amine **3a**:







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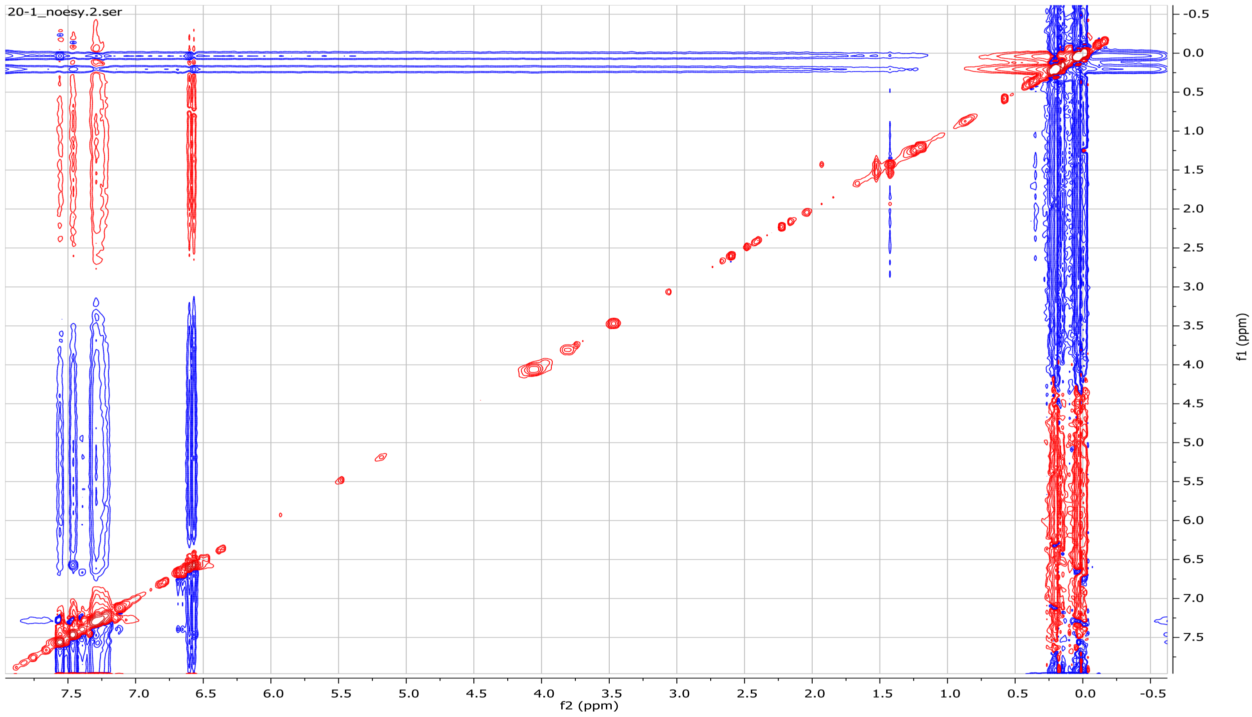
1.54
0.00
f1 (ppm)



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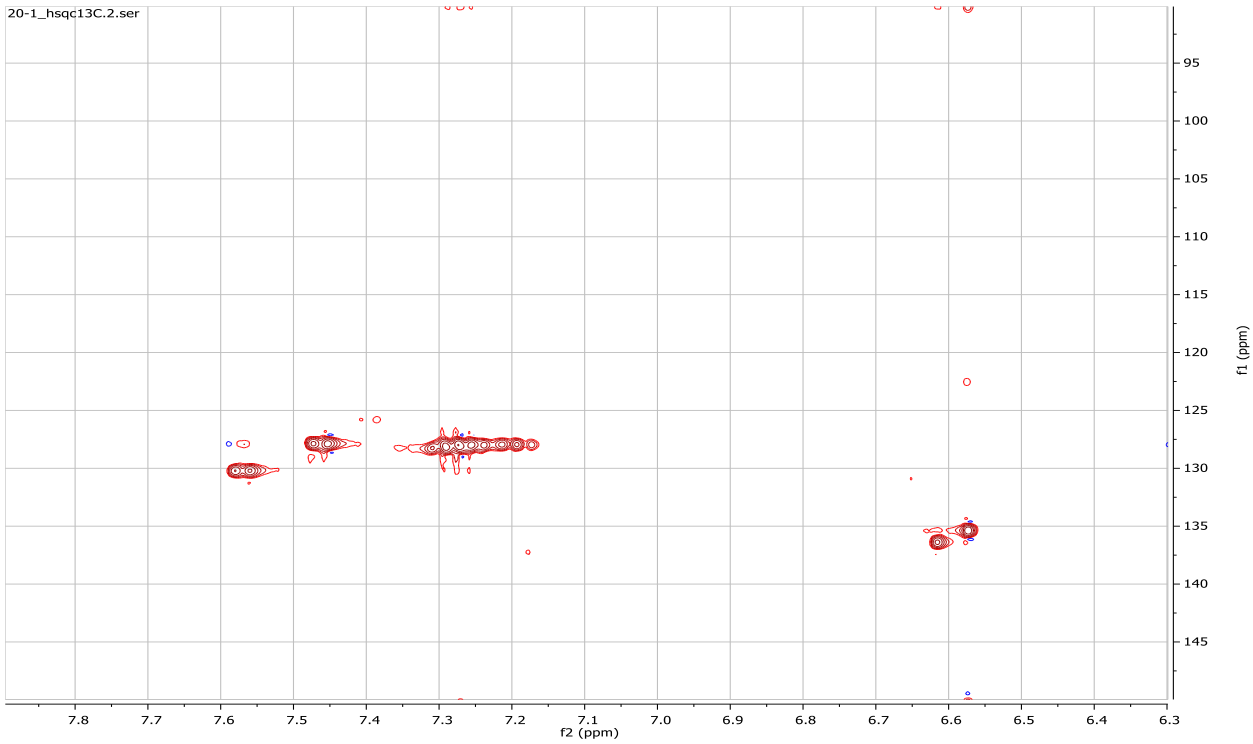
f2 (ppm)
f1 (ppm)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95
100
105
110
115
120
125
130
135
140
145
f1 (ppm)
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7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
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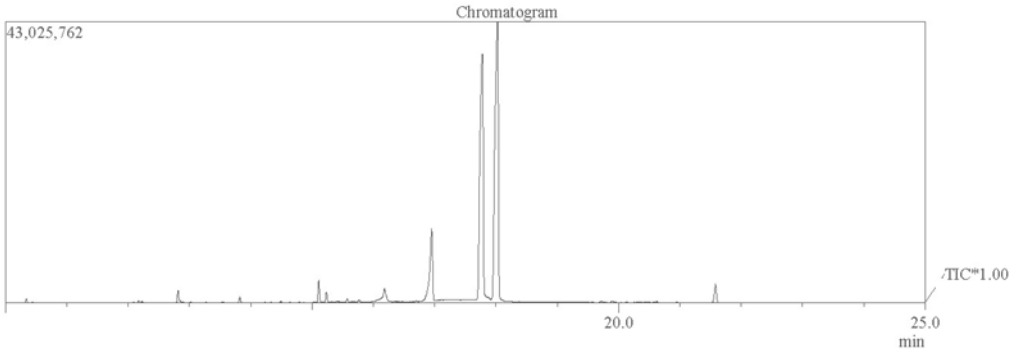
6.8
6.7
6.6
6.5
6.4
6.3
f2 (ppm)

PhCBrCHN(SiMe3)2



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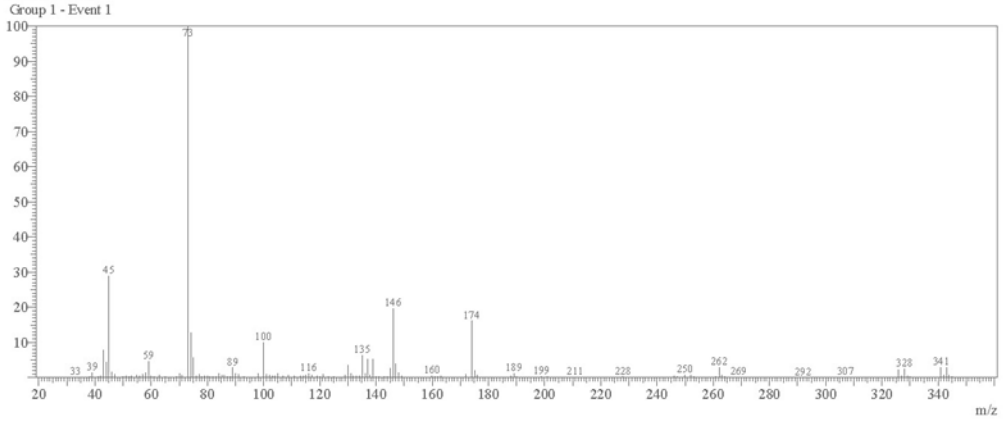

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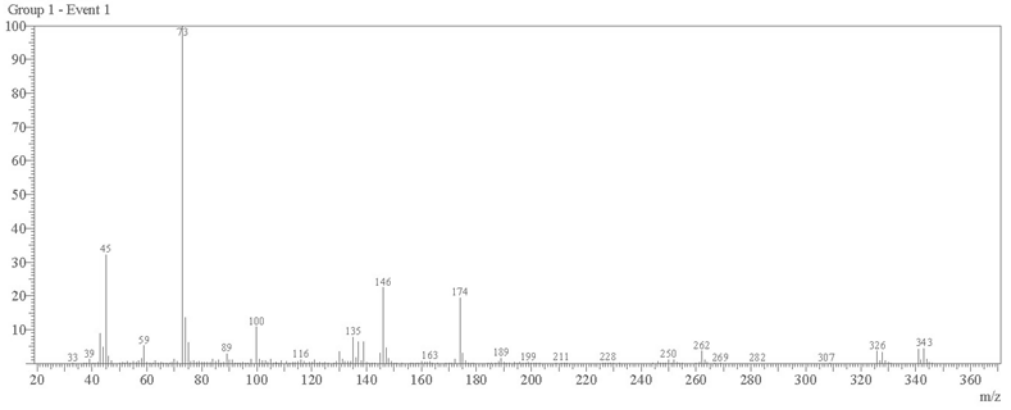
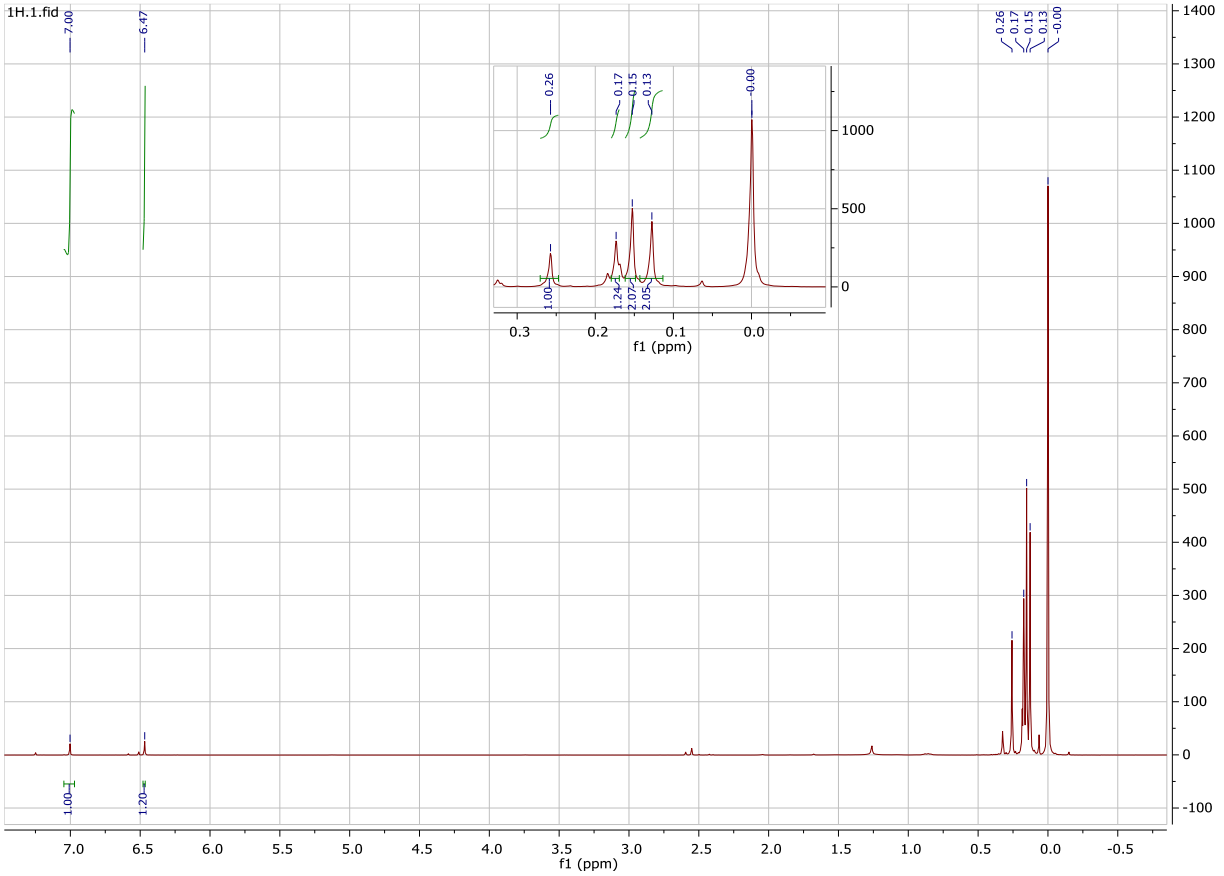
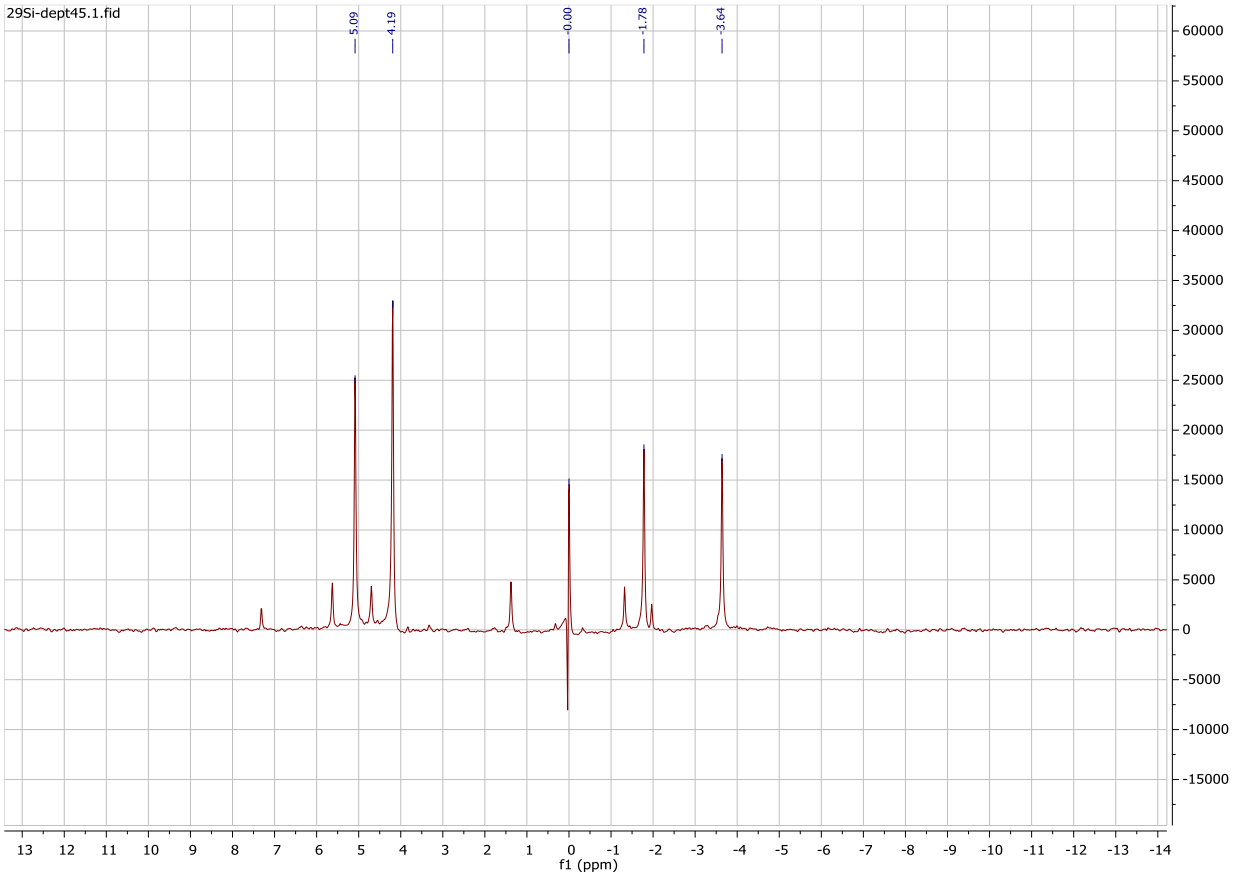
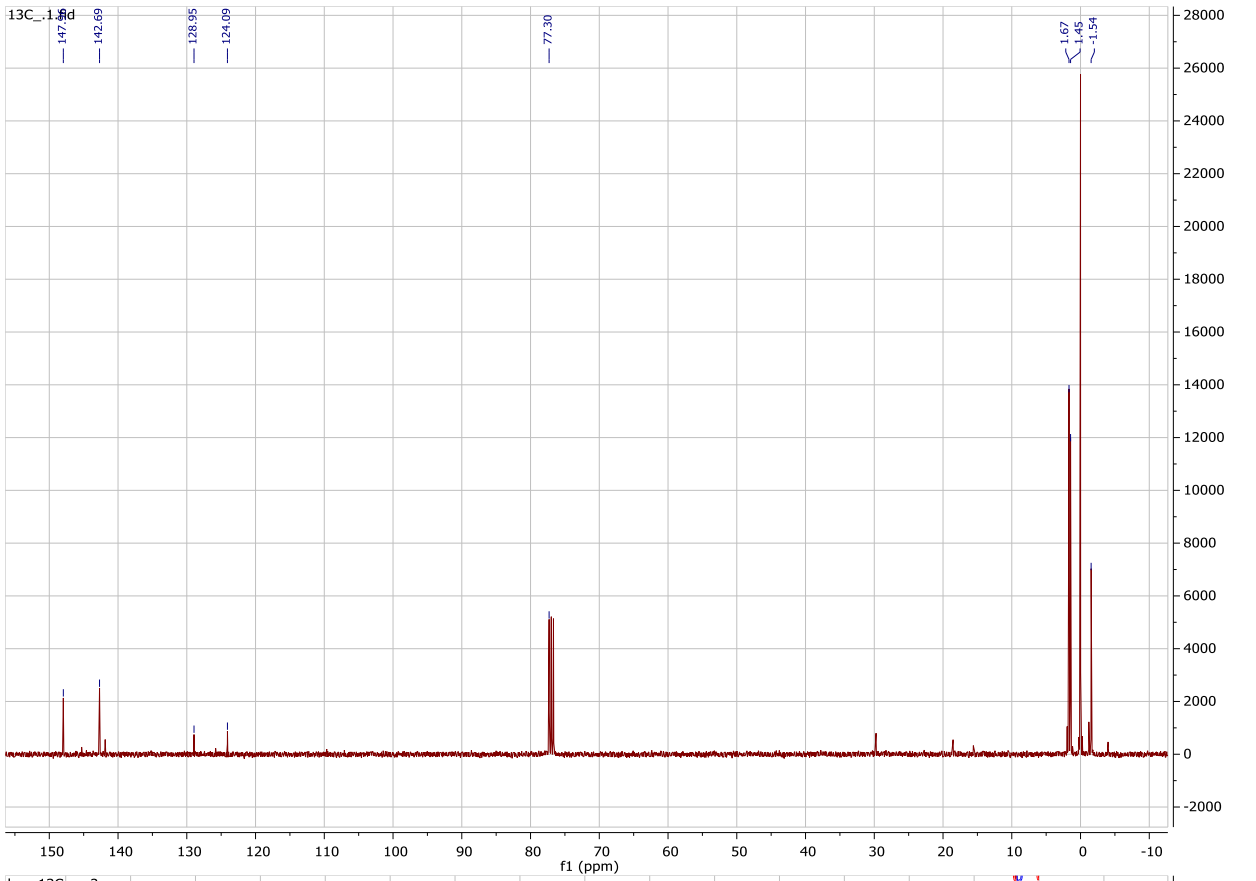


The NMR and the CM/MS spectra of *N*-(2-bromo-2-trimethylsilylethenyl)-*N*,*N*-bis(trimethylsilyl)amine **3b**:



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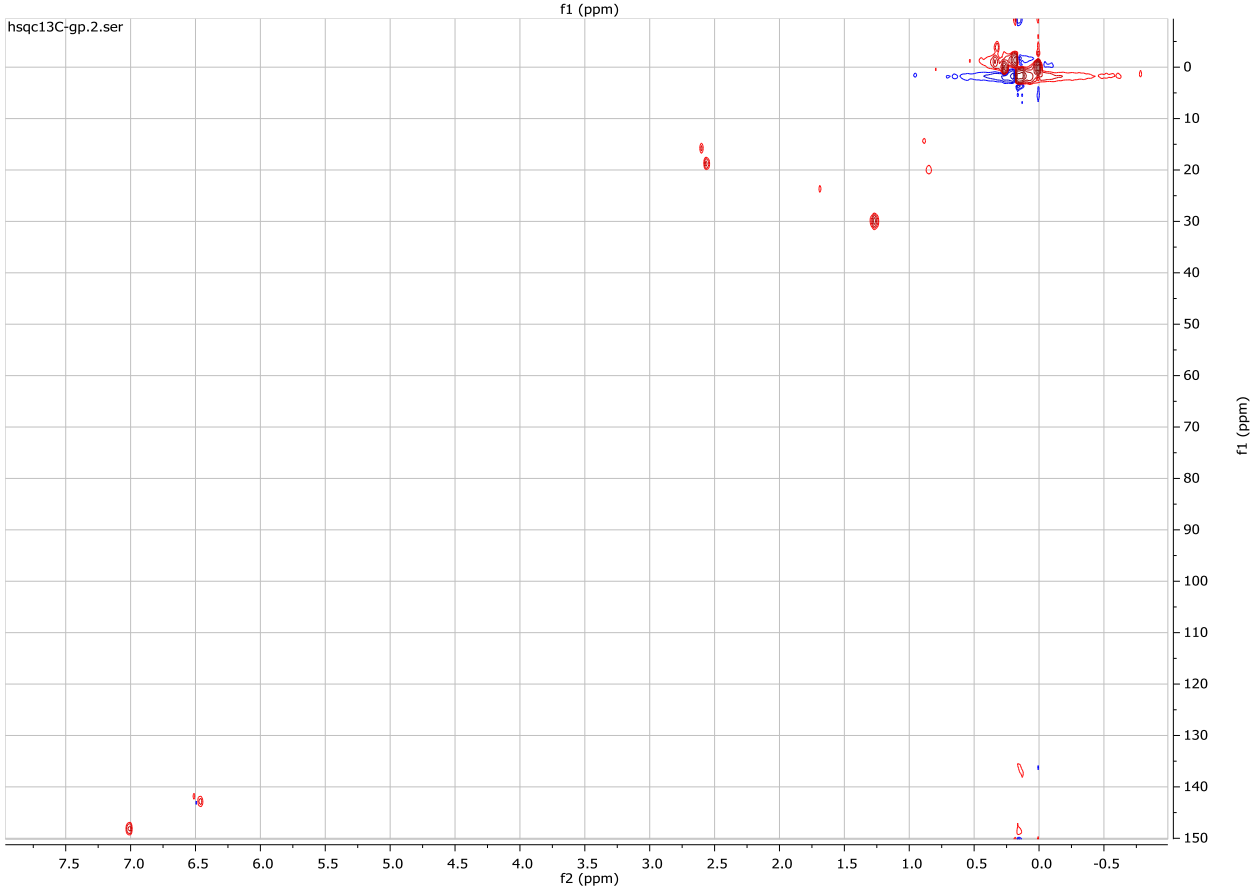
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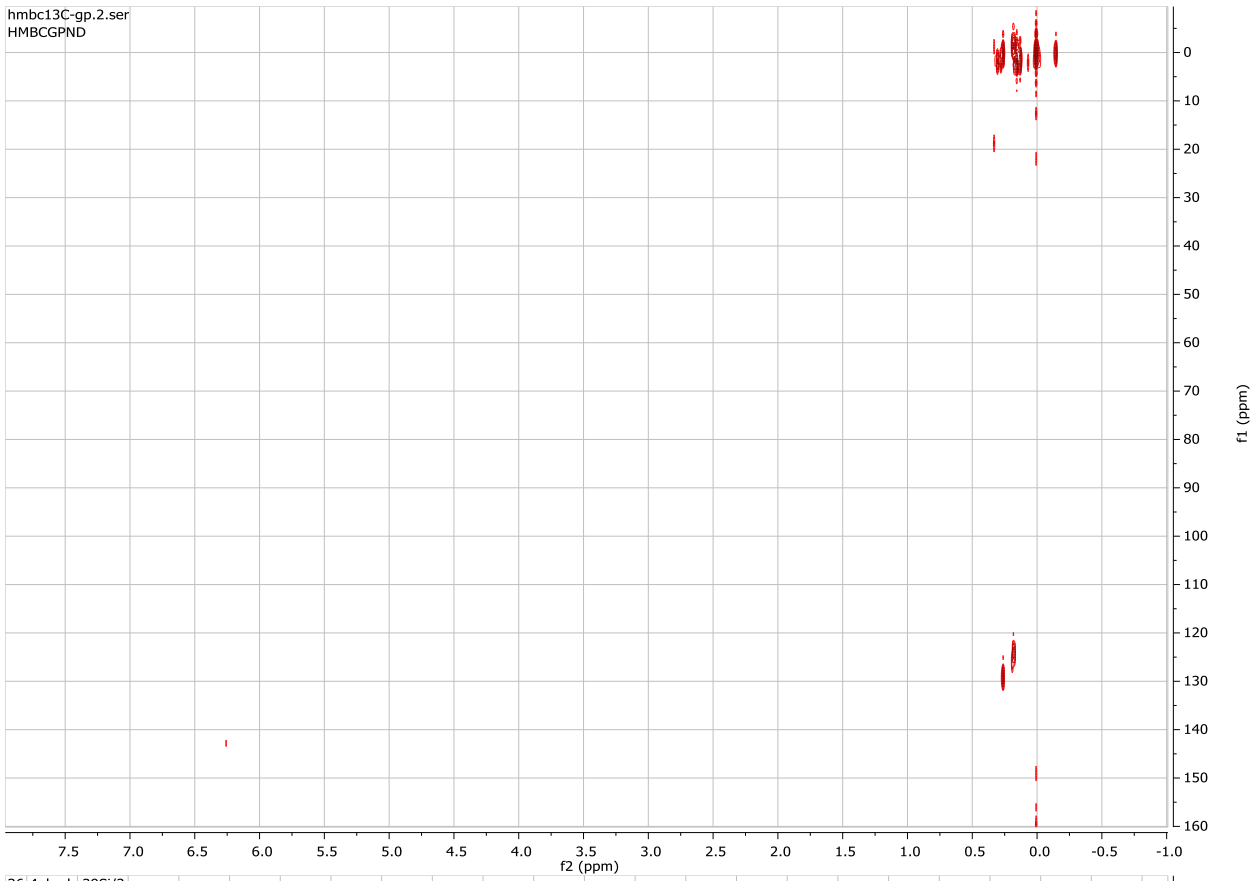
f1 (ppm)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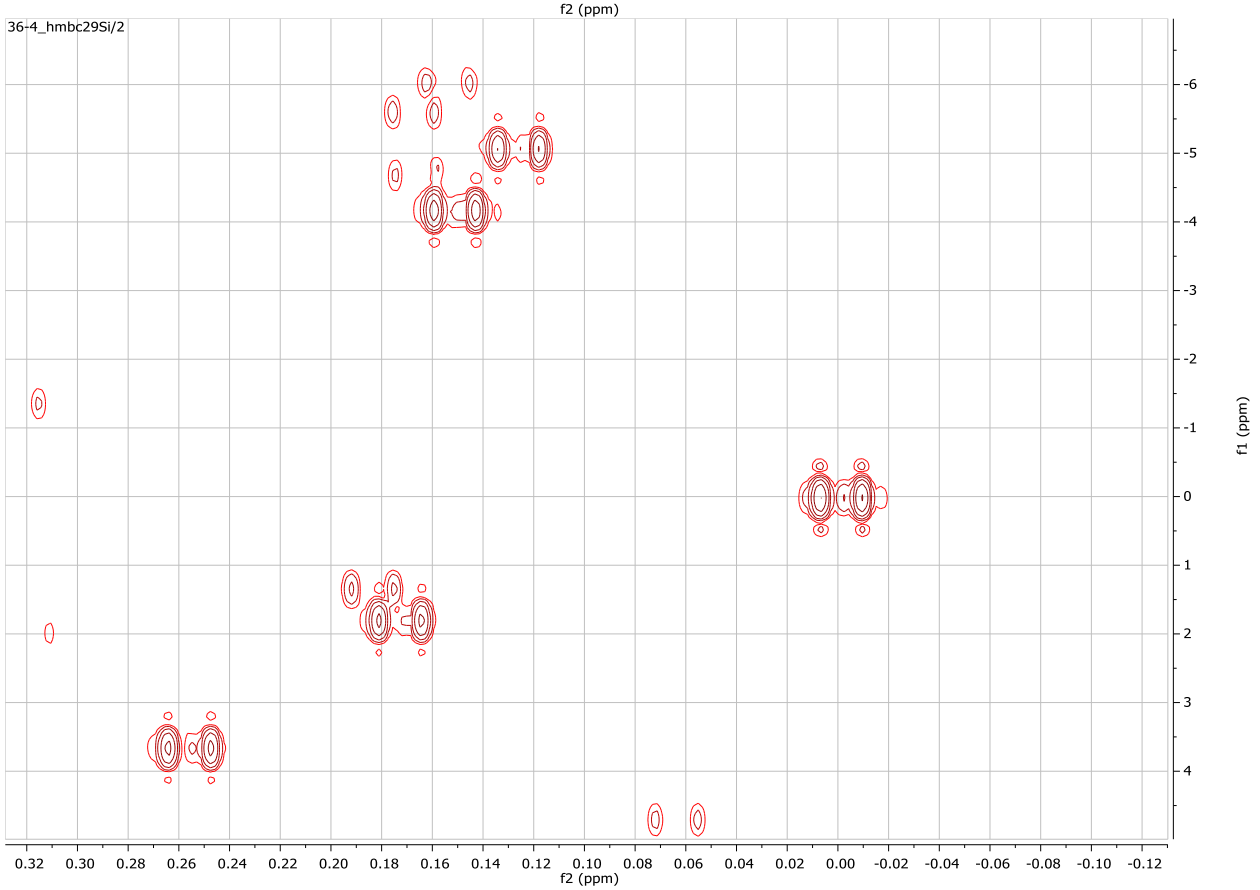
f2 (ppm)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f1 (ppm)
f2 (ppm)

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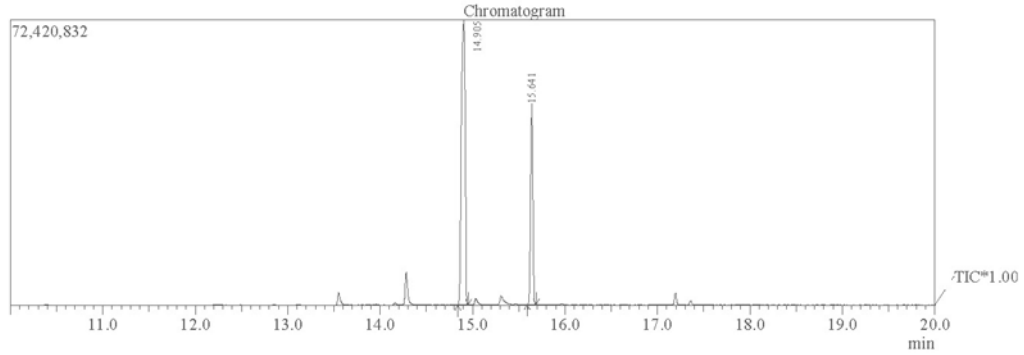

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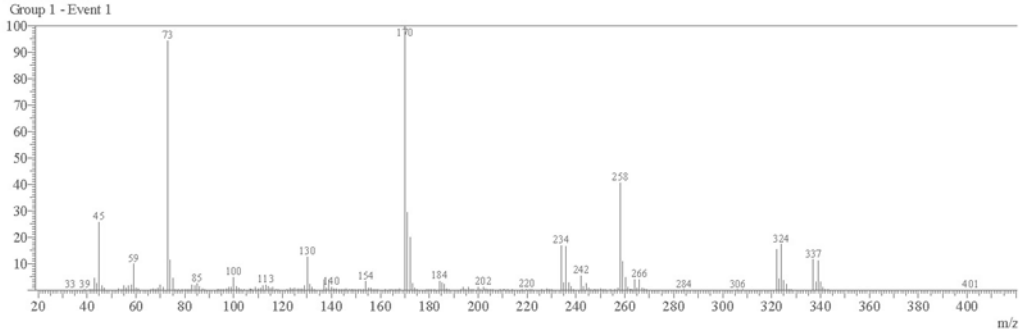

Spectrum

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