

**A convenient synthesis of enantiopure  
(4a*S*,7a*R*)-1,4,4a,7a-tetrahydrocyclopenta[*c*]pyran-3,7-dione**

**Aidar Z. Al'mukhametov, Airat M. Gimazetdinov and Mansur S. Miftakhov**

**Experimental**

Solvents were purified and dried by standard procedures before use. Reagents were generally the best quality commercial grade and used without further purification unless otherwise indicated. All reactions were carried out in oven-dried glassware. TLC was performed using Sorbfil STC-1A 110  $\mu\text{m}$  layer, silica gel 5-17 percolated foil plates. Column chromatography was conducted using 210–280 mesh silica gel. Optical rotations were measured using the sodium D line at 589 nm on a Perkin–Elmer, Model 241 MC polarimeter at 20 °C. IR spectra were recorded on a Shimadzu IR Prestige-21 spectrometer as nujol mull or as neat thin films on KBr plates (film) and were reported in reciprocal centimeters ( $\text{cm}^{-1}$ ).  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were obtained using a Bruker AM-300 (300 MHz for  $^1\text{H}$  and 75.47 MHz for  $^{13}\text{C}$ ) or BrukerAvance III (500 MHz for  $^1\text{H}$  and 125.77 MHz for  $^{13}\text{C}$ ) as solutions in  $\text{CDCl}_3$  (Aldrich Chemical Company; spectra grade) or acetone- $d_6$  (Solvex-D; spectra grade). Chemical shifts are reported in  $\delta$  unit-parts per million (ppm) downfield from tetramethylsilane (TMS) as the internal reference. Splitting patterns are designated as s = singlet; br s = broad singlet; d = doublet, t = triplet; q = quartet; quin. = quintet; m = multiplet. Mass spectra were recorded on Shimadzu LCMS QP-2010EV (APCI) spectrometer. Elemental analyses were carried on a Euro EA 3000 CHNS-analyzer.

**[(1*R*,4*R*,5*S*)-5-(2-methoxyvinyl)-4-(trimethylsilyl)cyclopent-2-en-1-yl]methanol (3) and [(4*aR*,5*R*,7*aR*)-3-methoxy-1,3,4,4*a*,5,7*a*-hexahydrocyclopenta[*c*]pyran-5-yl]trimethylsilane (4)**

General procedure: To a stirred solution of (methoxymethyl)triphenylphosphonium chloride (0.87 g, 2.54 mmol) in dry toluene (20 ml), cooled to -78°C under argon atmosphere, was added 1.2 *M* solution of NaHMDS (1.85 mL, 2.22 mmol) and the temperature was raised to ambient. After being stirred at this temperature for 10 min, the mixture was cooled to -78°C and the solution of lactol **2** (0.2 g, 1.01 mmol) in dry toluene (5 mL) was added. Then, the reaction mixture was heated to room temperature and saturated solution of NH<sub>4</sub>Cl (3 mL) was added. The resulting mixture was filtered, the water layer extracted with EtOAc, the combined organic layers were dried with MgSO<sub>4</sub>, the solvent was evaporated. Purification by column chromatography on SiO<sub>2</sub> (petroleum ether/ethyl acetate, 1:1) gave poorly stable enol ether **3** (*E/Z*, 7:1).

**[(1*R*,4*R*,5*S*)-5-(2-methoxyvinyl)-4-(trimethylsilyl)cyclopent-2-en-1-yl]methanol (3)**

**For major *E*-isomer:**

Yield: 0.157 g (68%); colorless transparent oil.

*R<sub>f</sub>* = 0.4 (petroleum ether/ethyl acetate = 1:1).

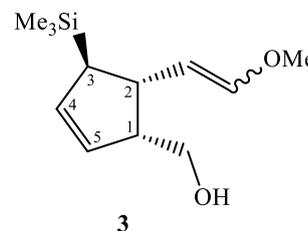
IR (liquid film): 3356, 3041, 2952, 2898, 1652, 1465, 1451, 1391, 1311, 1248, 1206, 1159, 1142, 1106, 1025, 949, 937, 868, 837, 793, 751, 719, 692 cm<sup>-1</sup>.

<sup>1</sup>H NMR (acetone-*d*<sub>6</sub>, 500 MHz): δ = 6.35 (d, *J* = 7.6 Hz, 1H, CH<sub>3</sub>OCH=CH), 5.70-5.75 (m, 1H, C<sup>3</sup>H), 5.60-5.65 (m, 1H, C<sup>2</sup>H), 4.82 (t, *J* = 11.7 Hz, 1H, CH<sub>3</sub>OCH=CH), 3.52-3.61 (m, 1H, CH<sub>α</sub>H<sub>β</sub>OH), 3.45 (s, 3H, CH<sub>3</sub>O), 3.36-3.45 (m, 1H, CH<sub>α</sub>H<sub>β</sub>OH), 2.05 (s, 1H, CHSi), 0.0 (s, 9H, (CH<sub>3</sub>)<sub>3</sub>Si).

<sup>13</sup>C NMR (acetone-*d*<sub>6</sub>, 125 MHz): δ = 146.74 (CH<sub>3</sub>OCH), 132.00, 129.20, 108.83, 62.93, 55.04, 52.43, 43.43, 41.13, -3.44.

MS (APCI): *m/z* (%) = 227 (100) [MH]<sup>+</sup>.

Anal. Calcd for C<sub>12</sub>H<sub>22</sub>O<sub>2</sub>Si: C, 63.67; H, 9.80. Found: C, 63.51; H, 9.77.

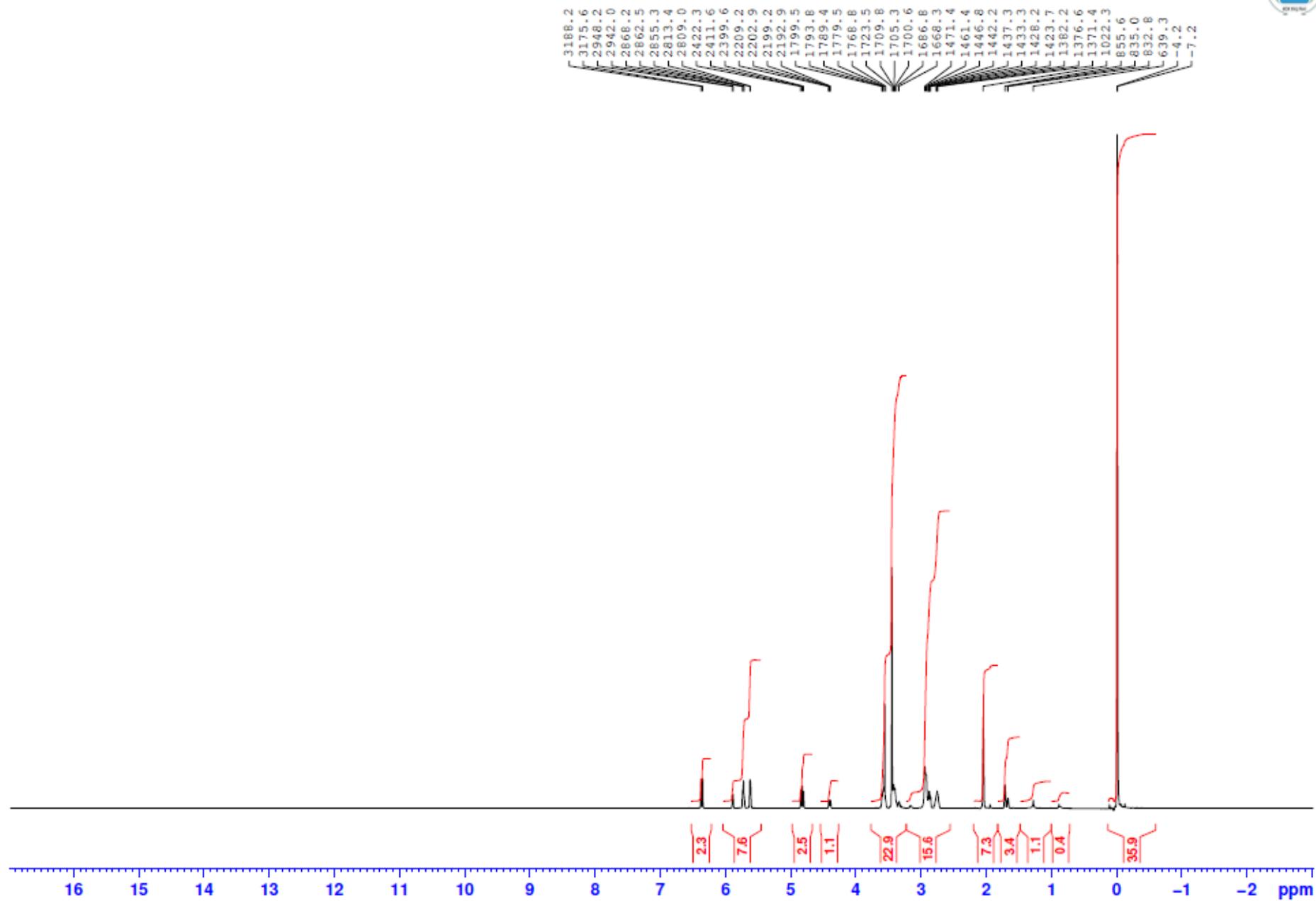


Sp-823 Al'mukhametov Pca-enol 30mg in Acetone, 1H AV500 22.05.2019 PAI

Ufa Institute of Chemistry of the Russian Academy of Sciences (UIC RAS). 2019



SW (1H) = 19.99ppm; O1 (1H) = 7.00ppm; Obs. Freq.: 500.13MHz; D1 = 2.0s; T = 295.7K; Probe: BBO; Exp. Time: 7 sec; TimesDate: 09:50:12 22 May 2019.

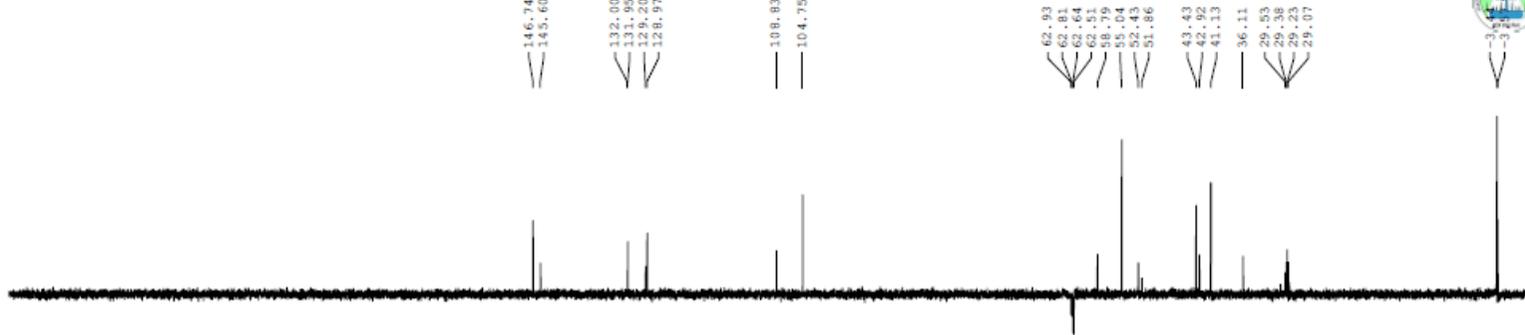


Sp-823 Al'mukhametov Pca-enol 30mg in Acetone,  $^{13}\text{C}\{^1\text{H}\}$  dept135 AV500 22.05.2019 PAI

Ufa Institute of Chemistry of the Russian Academy of Sciences (UIC RAS). 2019

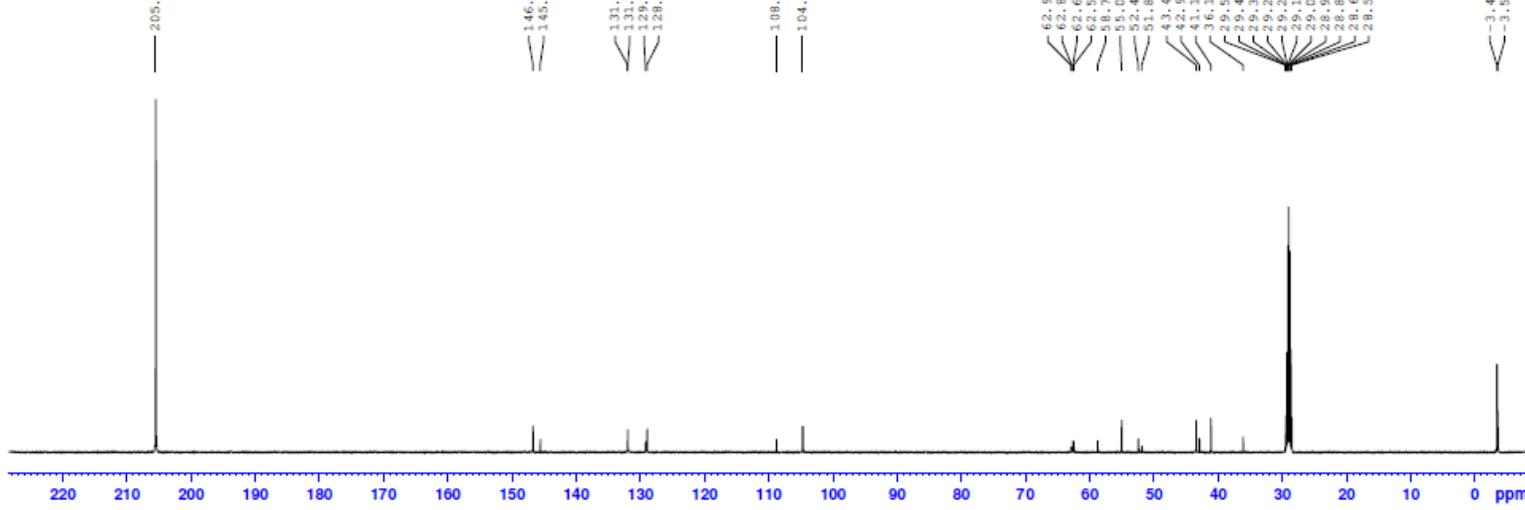


SW( $^{13}\text{C}$ )=236.63ppm O1( $^{13}\text{C}$ )=110.00ppm Obs.Freq.:125.76MHz DI=1.0s T=296.5K; Probe:BBQ Exp.Time: 2 min 27 sec TimesDate: 10:00:06 22 May 2019.



Sp-823 Al'mukhametov Pca-enol 30mg in Acetone,  $^{13}\text{C}\{^1\text{H}\}$  com AV500 22.05.2019 PAI

SW( $^{13}\text{C}$ )=236.63ppm O1( $^{13}\text{C}$ )=110.00ppm Obs.Freq.:125.76MHz DI=0.9s T=296.5K; Probe:BBQ Exp.Time: 7 min 11 sec TimesDate: 09:57:26 22 May 2019.



**[(4aR,5R,7aR)-3-methoxy-1,3,4,4a,5,7a-hexahydrocyclopenta[c]pyran-5-yl]trimethylsilane (4)**

Yield: Colorless transparent viscous oil.

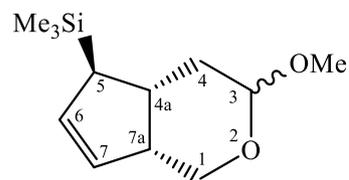
$R_f = 0.5$  (petroleum ether/ethyl acetate = 20:1).

IR (liquid film): 3046, 2953, 2836, 1404, 1248, 1139, 1060, 864, 800  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR (500 MHz, acetone- $d_6$ ):  $\delta = 5.71$ - $5.76$  (m, 1H,  $\text{C}^6\text{H}$ ,  $\text{C}^6\text{H}$ ), 5.52 (dt,  $J = 2.0, 5.6$  Hz, 1H,  $\text{C}^7\text{H}$ ), 5.35 (dt,  $J = 1.8, 5.7$  Hz, 1H,  $\text{C}^7\text{H}$ ), 4.62 (t,  $J = 3.5$  Hz, 1H,  $\text{C}^3\text{H}$ ), 4.49 (dd,  $J = 4.2, 8.7$  Hz, 1H,  $\text{C}^3\text{H}$ ), 3.90 (dd,  $J = 4.4, 11.8$  Hz, 1H,  $\text{C}^1\text{H}_\alpha$ ), 3.72 (dd,  $J = 6.6, 11.7$  Hz, 1H,  $\text{C}^1\text{H}_\alpha$ ), 3.68 (dd,  $J = 7.8, 11.7$  Hz, 1H,  $\text{C}^1\text{H}_\beta$ ), 3.58 (dd,  $J = 2.2, 11.8$  Hz, 1H,  $\text{C}^1\text{H}_\beta$ ), 3.37 (s, 3H,  $\text{C}^3\text{H}_3\text{O}$ ), 3.36 (s, 3H,  $\text{C}^3\text{H}_3\text{O}$ ), 2.75-2.81 (m, 1H,  $\text{C}^{7a}\text{H}$ ), 2.56-2.61 (br, 1H,  $\text{C}^{7a}\text{H}$ ), 2.51-2.56 (m, 1H,  $\text{C}^{4a}\text{H}$ ), 2.24-2.29 (m, 1H,  $\text{C}^{4a}\text{H}$ ), 1.50-1.72 (m, 6H,  $\text{C}^4\text{H}_2$ ,  $\text{C}^5\text{H}$ ,  $\text{C}^4\text{H}_2$ ,  $\text{C}^5\text{H}$ ), -0.02 (s, 9H,  $(\text{CH}_3)_3\text{Si}$ ), -0.03 (s, 9H,  $(\text{CH}_3)_3\text{Si}$ ).

$^{13}\text{C}$  NMR (125 MHz, acetone- $d_6$ ):  $\delta = -2.93, -2.60$  ( $(\text{CH}_3)_3$ ), 32.39, 34.83 ( $\text{C}^5$ ), 33.46, 34.22 ( $\text{C}^4$ ), 43.01, 43.15 ( $\text{C}^{4a}$ ), 44.00, 45.05 ( $\text{C}^{7a}$ ), 54.92, 55.14 ( $\text{CH}_3\text{O}$ ), 59.84, 62.83 ( $\text{C}^1$ ), 97.99, 99.84 ( $\text{C}^3$ ), 126.55, 129.37 ( $\text{C}^7$ ), 133.49, 133.66 ( $\text{C}^6$ ).

MS (APCI):  $m/z$  (%) = 227 (100)  $[\text{MH}]^+$ .

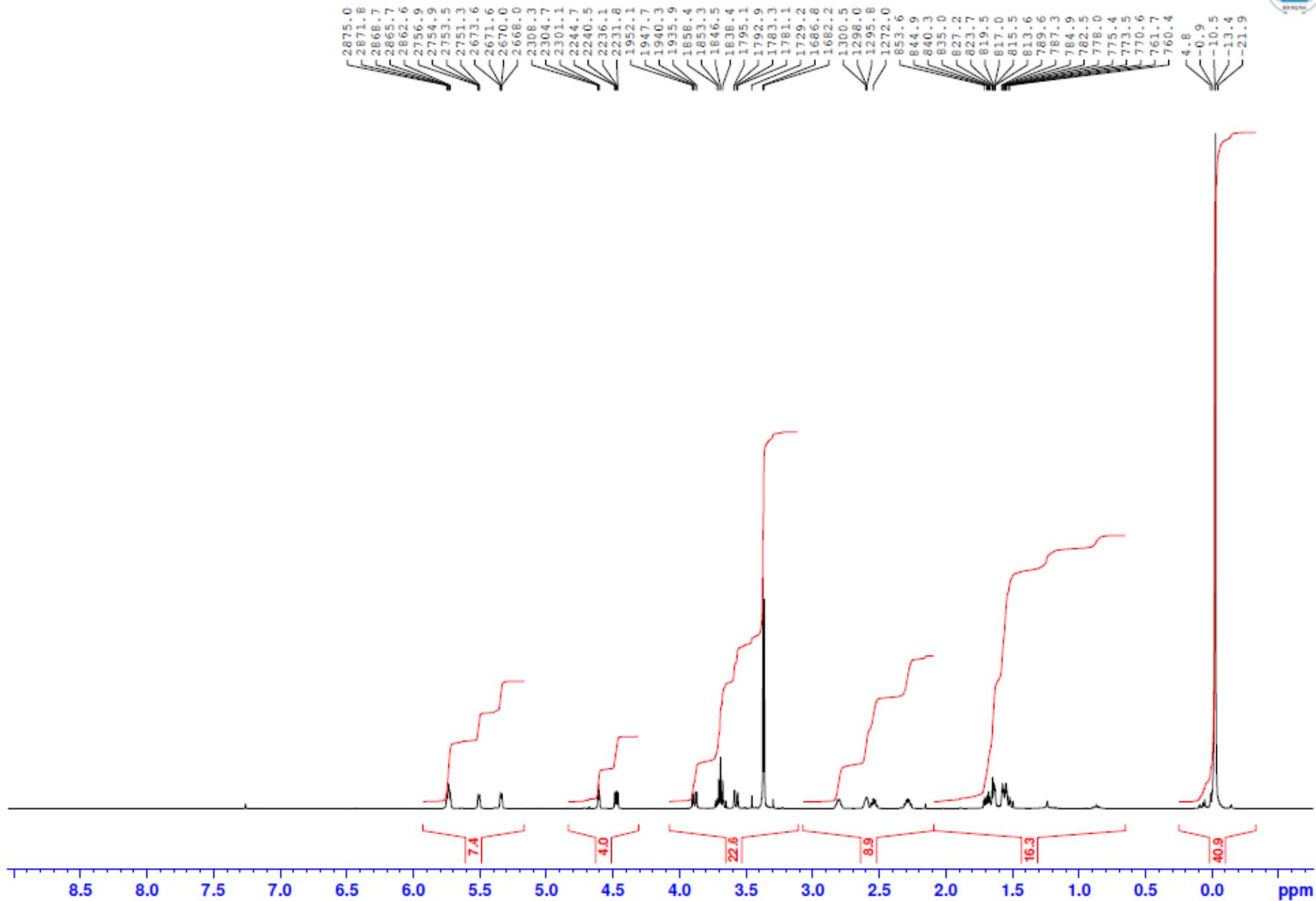


Anal. Calcd for  $\text{C}_{12}\text{H}_{22}\text{O}_2\text{Si}$ : C, 63.67; H, 9.80. Found: C, 63.49; H, 9.71.

4

Sp-421 Gimazetdinov Pc-471-dept 50mg in CDC13, 1H AV500 09.04.2019 SSH  
SW(H)=19.99ppm O1(H)=7.00ppm Obs.Freq.:500.13MHz; D1=2.0s; T=296.3K; Probe:BBO; Exp.Time: 7 sec; TimesDate: 11:41:27 09 Apr 2019.

Ufa Institute of Chemistry of the Russian Academy of Sciences (UIC RAS). 2019

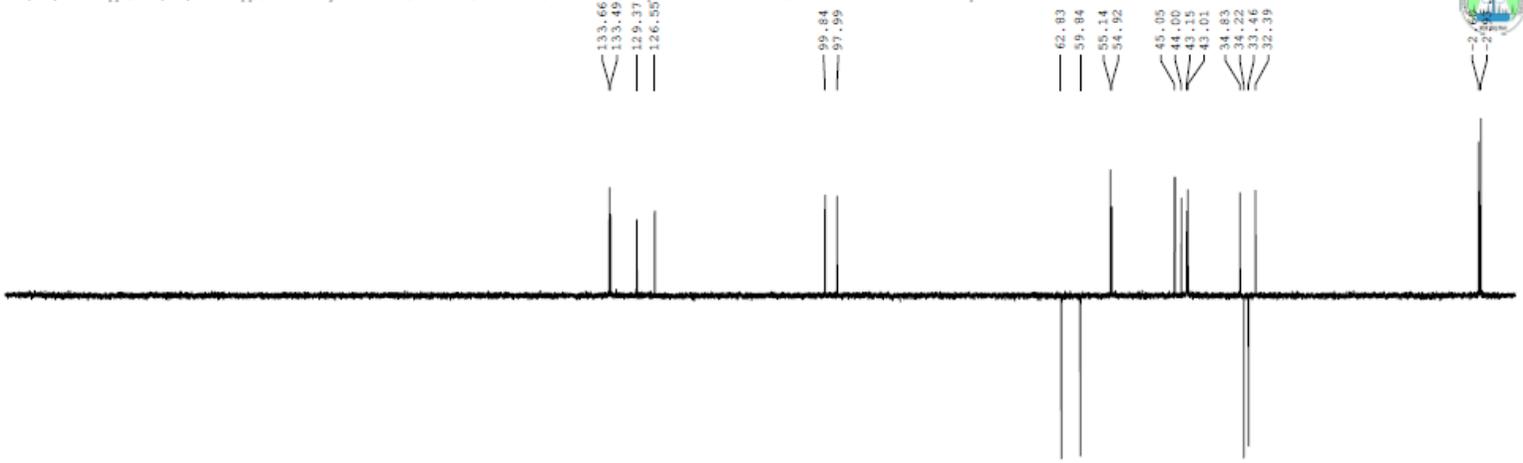


Sp-421 Gimazetdinov Pc-471-dept 50mg in CDCl3, 13C{1H} dept135 AV500 09.04.2019 SSH

Ufa Institute of Chemistry of the Russian Academy of Sciences (UIC RAS). 2019



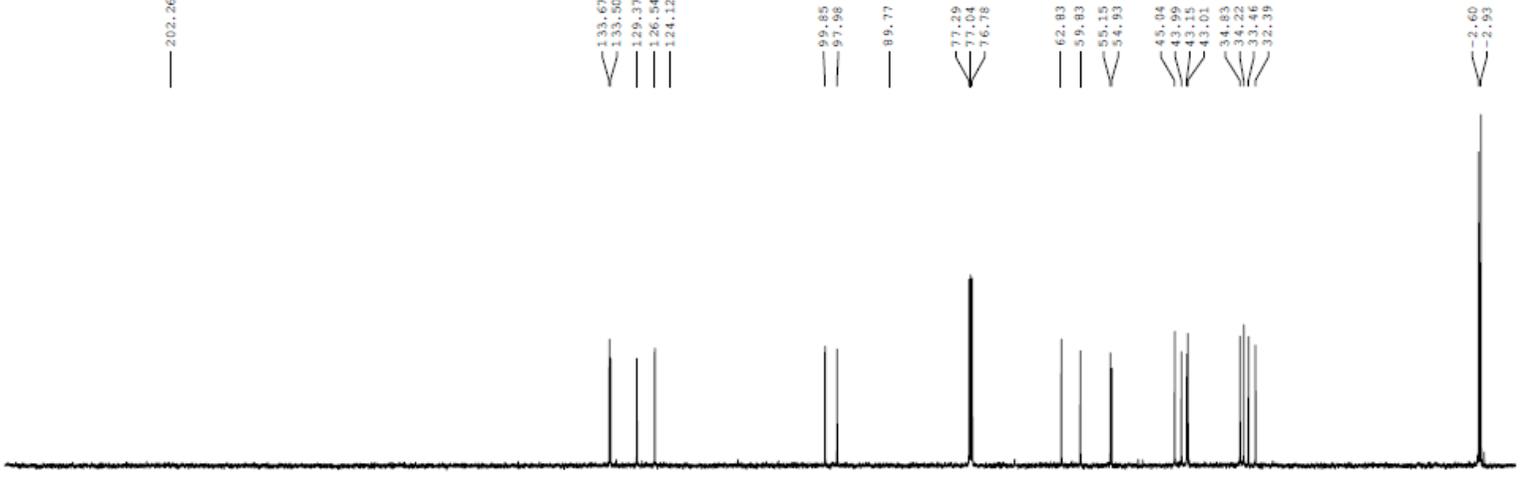
SW (13C)-236.63ppm D1 (13C)-110.00ppm Obs.Freq.:125.76MHz D1-1.0s T-296.Kr: Probe:BBG Exp.Time: 2 min 27 sec TimesDate: 11:50:48 09 Apr 2019.



Sp-421 Gimazetdinov Pc-471-dept 50mg in CDCl3, 13C{1H} com AV500 09.04.2019 SSH

Ufa Institute of Chemistry of the Russian Academy of Sciences (UIC RAS). 2019

SW (13C)-236.63ppm D1 (13C)-110.00ppm Obs.Freq.:125.76MHz D1-0.9s T-296.Kr: Probe:BBG Exp.Time: 6 min 38 sec TimesDate: 11:42:10 09 Apr 2019.



## [(1*S*,2*R*,5*R*)-5-trimethylsilylcyclopent-3-ene-1,2-diol](7)

**Method A.** To a stirred solution of compound **1** (2.1 g) in anhydrous THF (70 mL) at 0°C was added LiAlH<sub>4</sub> (1.2 g, 31.5 mmol). The reaction was monitored by TLC (petroleum ether/ethyl acetate, 1:1). After stirring for 1 h at 0°C, to the solution was added saturated NH<sub>4</sub>Cl (20 mL) and the resulting mixture was filtered, evaporated under reduced pressure and extracted with EtOAc (3x50 mL). The combined organic layers were dried over MgSO<sub>4</sub> and evaporated under reduced pressure. Purification by column chromatography (petroleum ether/ethyl acetate, 1:1) gave the title compound.

**Method B.** The monoprotected diol **8a** or **8b** (0.25 g, 0.8 mmol) was treated with Dowex (0.1 g) and Amberlyst (0.3 g) in wet methanol (100 mL). The reaction was controlled by TLC (petroleum ether/ethyl acetate = 20:1). Ion-exchange resins were separated on a Schott filter, the solvent was evaporated under reduced pressure. Product was purified by column chromatography (petroleum ether/ethyl acetate, 1:1).

Yield: 1.95 g (91%); light brown oil.

$R_f$  = 0.3 (petroleum ether/ethyl acetate, 1:1);  $[\alpha]_D^{20}$  : +103.4 (c 0.975, CH<sub>2</sub>Cl<sub>2</sub>).

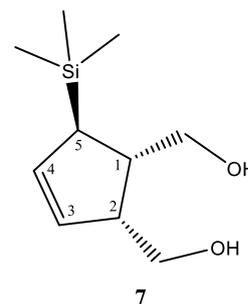
IR (liquid film): 3310, 1248, 1051, 837, 728 cm<sup>-1</sup>.

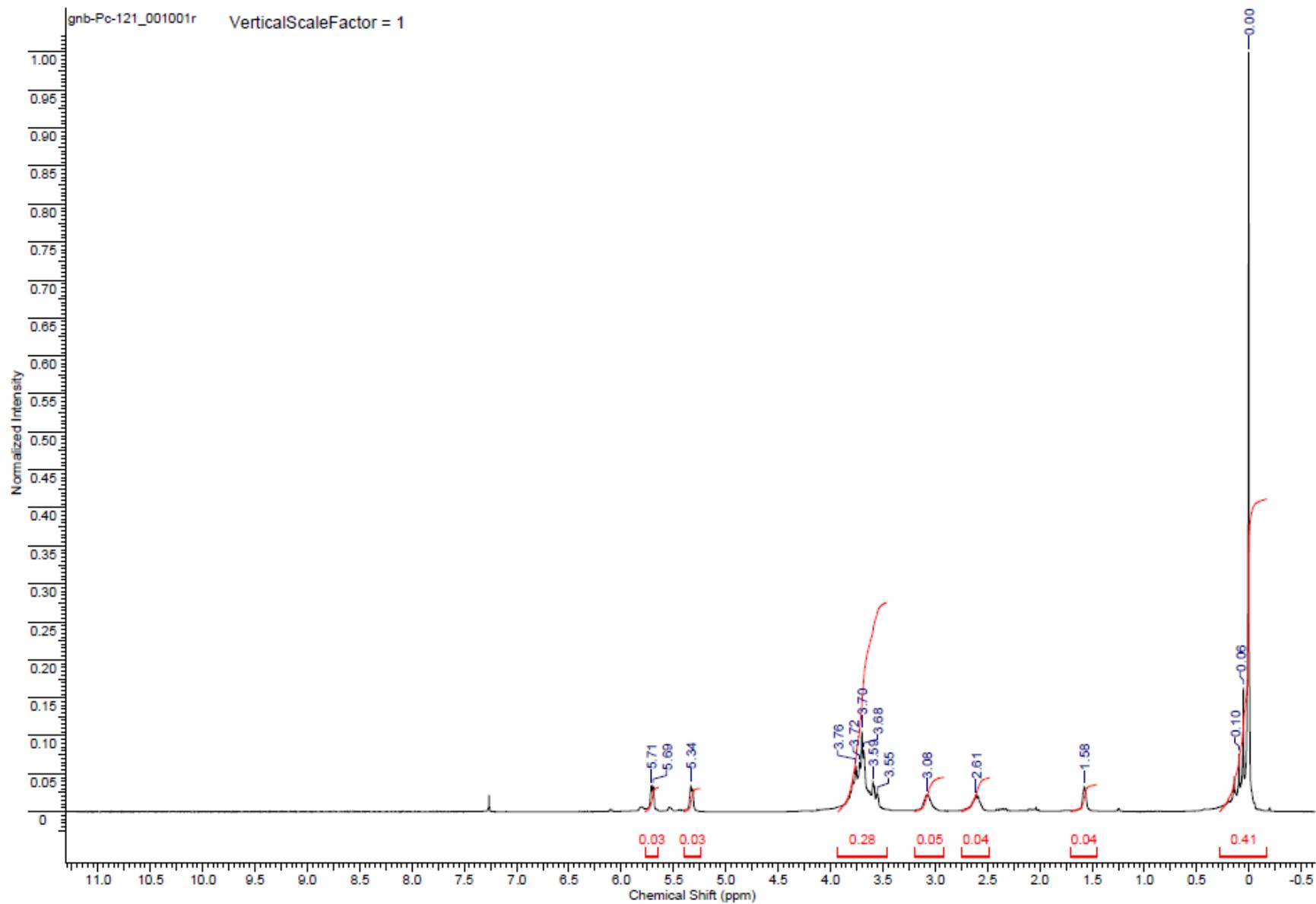
<sup>1</sup>H NMR (300MHz, CDCl<sub>3</sub>/CHCl<sub>3</sub>):  $\delta$  = 5.68-5.72 (m, 1H, C<sup>4</sup>H or C<sup>3</sup>H), 5.31-5.35 (m, 1H, C<sup>3</sup>H or C<sup>4</sup>H), 3.55-3.81 (m, 6H, 2CH<sub>2</sub>OH), 3.01-3.12 (m, 1H, C<sup>2</sup>H), 2.55-2.64 (m, 1H, C<sup>1</sup>H), 1.54-1.60 (m, 1H, C<sup>5</sup>H), 0.0 (s, 9H, (CH<sub>3</sub>)<sub>3</sub>Si).

<sup>13</sup>C (75.1 MHz, CDCl<sub>3</sub>/CHCl<sub>3</sub>):  $\delta$  = 133.35 (C<sup>3</sup>), 130.68 (C<sup>4</sup>), 62.93 (CH<sub>2</sub>O), 61.70 (CH<sub>2</sub>O), 49.38 (C<sup>2</sup>), 42.21 (C<sup>1</sup>), 34.31 (C<sup>5</sup>), 1.90 (Me<sub>3</sub>Si).

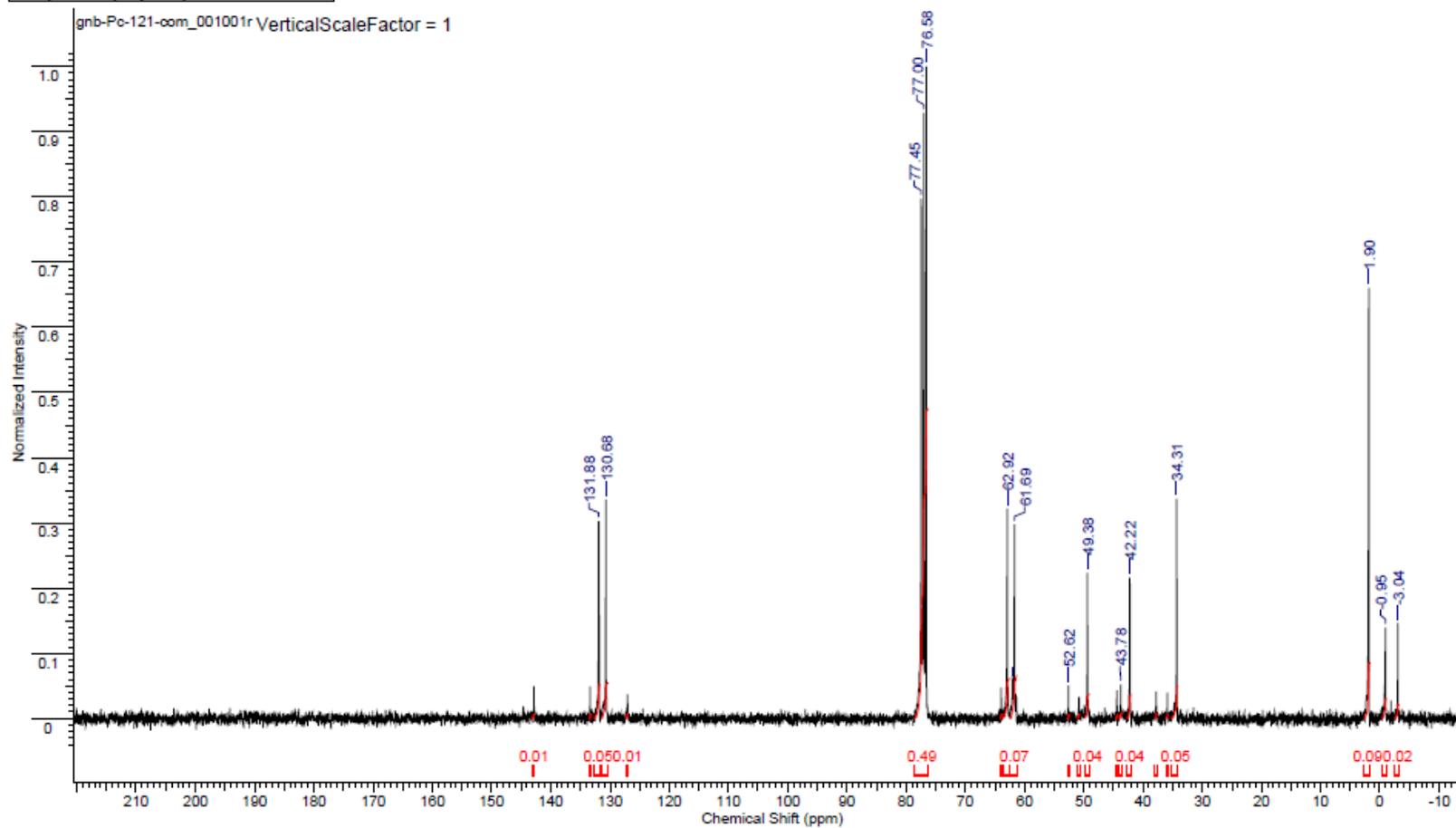
MS (APCI):  $m/z$  (%) = 201 (100) [MH]<sup>+</sup>.

Anal. Calcd for C<sub>10</sub>H<sub>20</sub>O<sub>2</sub>Si: C, 59.91; H, 9.98. Found: C, 59.74; H, 9.86.





Acquisition Time (sec)	0.4424	Comment	SP-1422 GIMAZETDINOV PC-121 IN CDCL3 13C COM 14.10.15 PAI		
Date	14 Oct 2015 09:12:32	Date Stamp	14 Oct 2015 09:12:32		
File Name	E:\документы Айрата\публикации\статья циклопропан\tetlet\suppl\8\gnb-Pc-121-com_001001r			Frequency (MHz)	75.46
Nucleus	<sup>1</sup> H	Number of Transients	3511	Origin	AM-300
Owner	spectr	Points Count	8192	Pulse Sequence	COM.AU
SW(cyclical) (Hz)	18518.52	Solvent	CHLOROFORM-d	Spectrum Offset (Hz)	8246.4141
Temperature (degree C)	27.000			Sweep Width (Hz)	18516.26



**[(1*S*,2*R*,5*R*)-5-({*tert*-Butyl(dimethylsilyl)oxy}methyl)-5-trimethylsilyl]cyclopent-3-en-1-yl]methanol (8a) and [(1*R*,4*R*,5*S*)-2-({*tert*-butyl(dimethylsilyl)oxy}methyl)-4-trimethylsilyl]cyclopent-2-en-1-yl]methanol (8b)**

A solution of diol **7** (1.5 g, 7.5 mmol) in dichloromethane (80 mL) was added under stirring to a mixture of *tert*-butyl(chloro)dimethylsilane (1.24 g, 8.25 mmol), imidazole (0.56 g, 8.25 mmol) and dichloromethane (30 mL) at 0°C. The mixture was stirred for 3 h at the same temperature (monitored by TLC) and evaporated under reduced pressure. Purification of the product by column chromatography (petroleum ether/ethyl acetate, 10:1) afforded individual compounds **8a** and **8b**.

**[(1*S*,2*R*,5*R*)-2-({*tert*-butyl(dimethylsilyl)oxy}methyl)-5-trimethylsilyl]cyclopent-3-en-1-yl]methanol (8a)**

Yield: 1.13 g (48%); transparent viscous oil.

$R_f = 0.4$  (petroleum ether/ethyl acetate, 10:1);  $[\alpha]_D^{20} : +106.4$  (c 1.03, CH<sub>2</sub>Cl<sub>2</sub>).

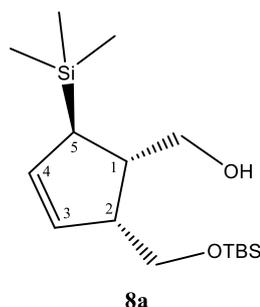
IR (liquid film): 3456, 2955, 2873, 1472, 1464, 1249, 1061, 841, 832, 778 cm<sup>-1</sup>.

<sup>1</sup>H NMR (500 MHz, *d*-acetone/acetone):  $\delta = 5.70$  (dt,  $J = 5.3, 2.3$  Hz, 1H, C<sup>4</sup>H), 5.48 (dt,  $J = 5.8, 2.3$  Hz, 1H, C<sup>4</sup>H), 4.09-4.12 (br. s, 1H, OH), 3.78 (dd,  $J = 10.3, 7.7$  Hz, 1H, CH <sub>$\alpha$</sub> H <sub>$\beta$</sub> OH), 3.67 (dd, 1H,  $J = 10.3, 5.8$  Hz, CH <sub>$\alpha$</sub> H <sub>$\beta$</sub> OH), 3.62-3.65 (m, 2H, CH<sub>2</sub>OSi), 2.92-3.01 (m, 1H, C<sup>2</sup>H), 2.46-2.53 (m, 1H, C<sup>1</sup>H), 1.78 (dt, 1H,  $J = 5.0, 2.3$  Hz, C<sup>5</sup>H), 0.91 (s, 9H, (CH<sub>3</sub>)<sub>3</sub>C), 0.10 (s, 6H, (CH<sub>3</sub>)<sub>2</sub>Si), 0.0 (s, 9H, (CH<sub>3</sub>)<sub>3</sub>Si).

<sup>13</sup>C (125.77 MHz, *d*-acetone/acetone):  $\delta = 132.42$  (C<sup>4</sup>), 127.17 (C<sup>3</sup>), 62.76 (CH<sub>2</sub>OH), 62.62 (CH<sub>2</sub>OSi), 50.63 (C<sup>2</sup>), 44.33 (C<sup>1</sup>), 37.63 (C<sup>5</sup>), 25.37 ((CH<sub>3</sub>)<sub>3</sub>C), 18.21 ((CH<sub>3</sub>)<sub>3</sub>C), -3.57 ((CH<sub>3</sub>)<sub>3</sub>Si), -6.12 ((CH<sub>3</sub>)<sub>2</sub>Si).

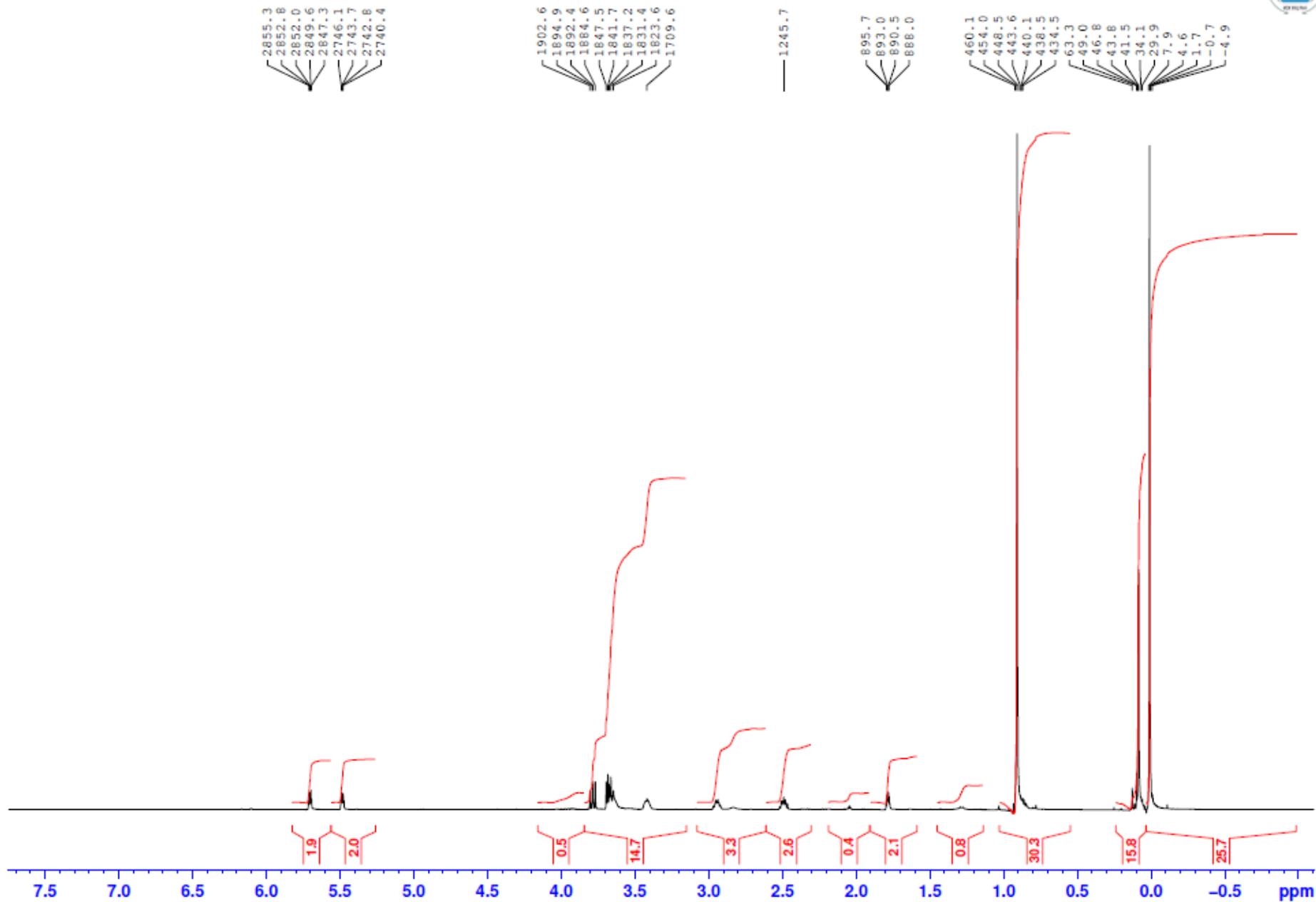
MS (APCI):  $m/z$  (%) = 315 (100) [MH]<sup>+</sup>.

Anal. Calcd for C<sub>16</sub>H<sub>34</sub>O<sub>2</sub>Si<sub>2</sub>: C, 61.03; H, 10.81. Found: C, 60.88; H, 10.56.



Sp-1260 Gimazetdinov Pc-213-1 70mg in Acetone, 1H AV500 26.05.2016 SSH  
 SW(H) $\approx$ 19.99ppm O1(H) $\approx$ 7.00ppm Obs.Freq.:500.13MHz; D1=2.0s; T=299.1K; Probe:BBO; Exp.Time: 7 sec; TimesDate: 12:52:39 26 May 2016.

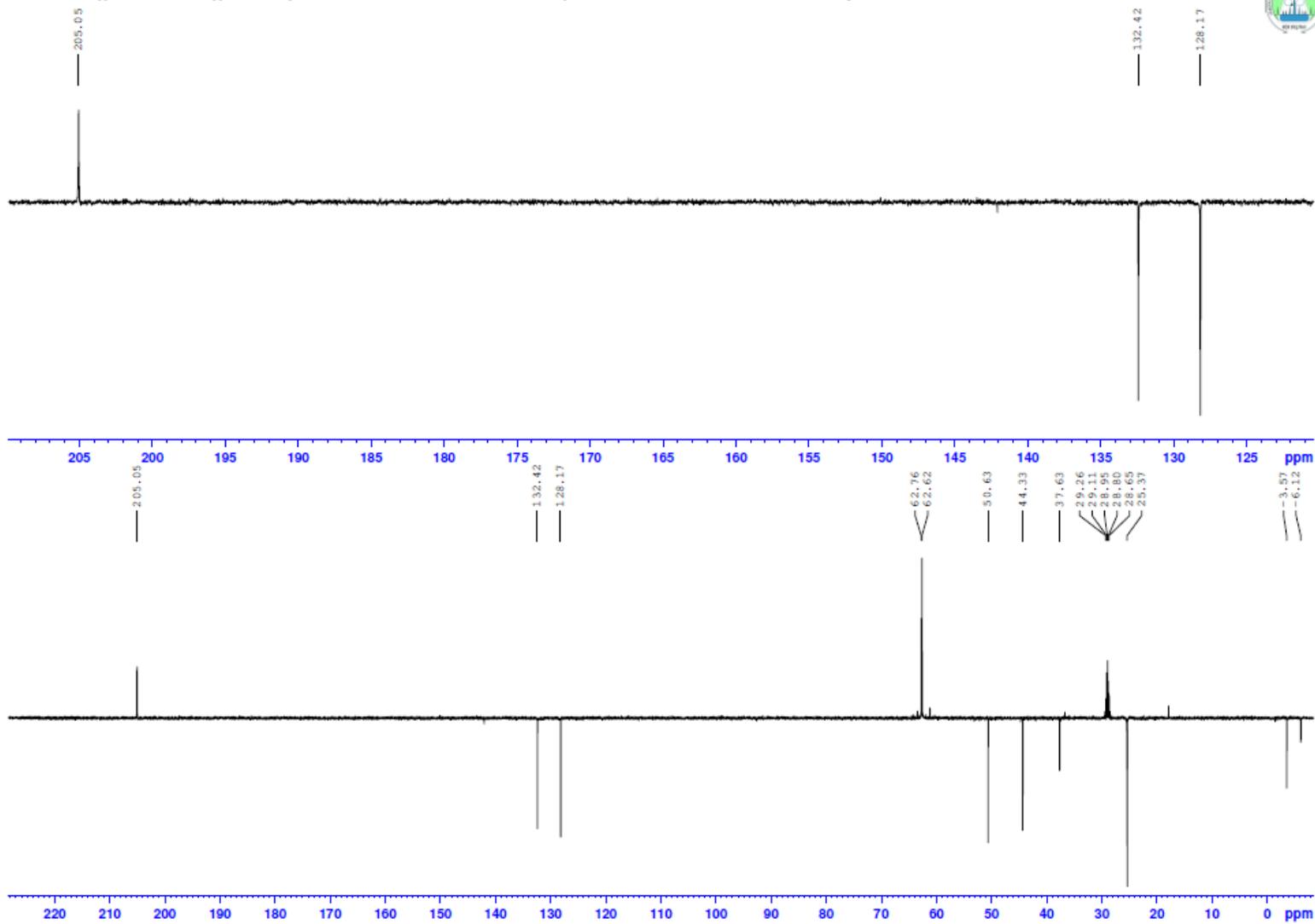
Ufa Institute of Chemistry of the Russian Academy of Sciences (UIC RAS). 2016



Sp-1260 Gimazetdinov Pc-213-1 70mg in Acetone,  $^{13}\text{C}\{^1\text{H}\}$  jmod AV500 26.05.2016 SSH

SN (13C)=236.63ppm; D1 (13C)=110.00ppm; Obs.Freq.:125.76MHz; D1=2.0s; T=299.5K; Probe:BBQ; Exp.Time: 2 min 9 sec; TimesDate: 12:53:49 26 May 2016.

Ufa Institute of Chemistry of the Russian Academy of Sciences (UIC RAS). 2016



**[(1*R*,4*R*,5*S*)-2-({[*tert*-Butyl(dimethylsilyl)]oxy}methyl)-4-trimethylsilyl]cyclopent-2-en-1-yl]methanol (**8b**)**

Yield: 1.11 g (47%); transparent viscous oil.

$R_f = 0.4$  (petroleum ether/ethyl acetate, 10:1);  $[\alpha]_D^{20} : +118.6$  (c 1.17, CH<sub>2</sub>Cl<sub>2</sub>).

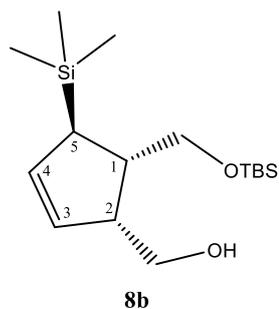
IR (liquid film): 3415, 2999, 2885, 1686, 1464, 1249, 836, 777 cm<sup>-1</sup>.

<sup>1</sup>H NMR (500 MHz, *d*-acetone/acetone):  $\delta = 5.69$  (ddd,  $J = 5.7, 3.6, 2.7$  Hz, 1H, C<sup>2</sup>H), 5.46 (dt,  $J = 5.7, 2.7$  Hz, 1H, C<sup>3</sup>H), 4.09-4.12 (br. s, 1H, OH), 3.80 (dd,  $J = 9.9, 7.8$  Hz, 1H, CH <sub>$\alpha$</sub> H <sub>$\beta$</sub> OH), 3.65 (dd,  $J = 10.1, 8.0$  Hz, 1H, CH <sub>$\alpha$</sub> H <sub>$\beta$</sub> OSi), 3.54 (dd,  $J = 10.1, 6.0$  Hz, 1H, CH <sub>$\alpha$</sub> H <sub>$\beta$</sub> OSi), 3.49 (dd,  $J = 9.9, 6.6$  Hz, 1H, CH <sub>$\alpha$</sub> H <sub>$\beta$</sub> OH), 2.94 (dddd,  $J = 7.8, 6.6, 6.0, 3.6$  Hz, 1H, C<sup>1</sup>H), 2.50 (dtd,  $J = 8.0, 6.0, 3.6$  Hz, 1H, C<sup>5</sup>H), 1.80 (dt,  $J = 5.6, 2.7$  Hz, 1H, C<sup>4</sup>H), 0.91 (s, 9H, (CH<sub>3</sub>)<sub>3</sub>C), 0.10 (s, 6H, (CH<sub>3</sub>)<sub>2</sub>Si), 0.0 (s, 9H, (CH<sub>3</sub>)<sub>3</sub>Si).

<sup>13</sup>C (125.77 MHz, *d*-acetone/acetone):  $\delta = 131.84$  (C<sup>3</sup>), 128.17 (C<sup>2</sup>), 63.51 (CH<sub>2</sub>OH), 61.60 (CH<sub>2</sub>OSi), 51.12 (C<sup>5</sup>), 43.73 (C<sup>1</sup>), 38.44 (C<sup>4</sup>), 25.44 ((CH<sub>3</sub>)<sub>3</sub>C), 17.86 ((CH<sub>3</sub>)<sub>3</sub>C), -3.60 ((CH<sub>3</sub>)<sub>3</sub>Si), -4.11 ((CH<sub>3</sub>)<sub>2</sub>Si).

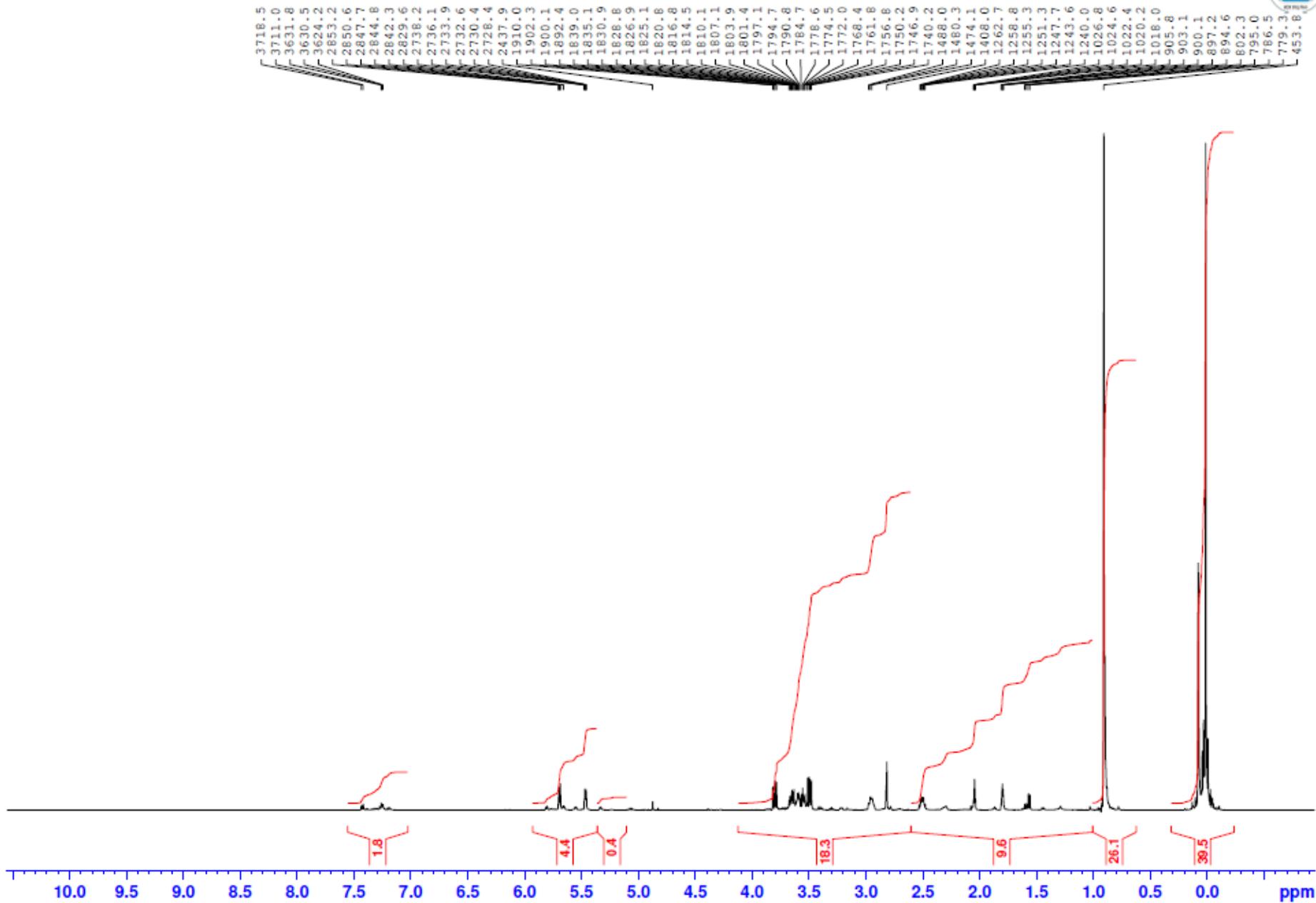
MS (APCI):  $m/z$  (%) = 315 (100) [MH]<sup>+</sup>.

Anal. Calcd for C<sub>16</sub>H<sub>34</sub>O<sub>2</sub>Si<sub>2</sub>: C, 61.03; H, 10.81. Found: C, 60.94; H, 10.65.



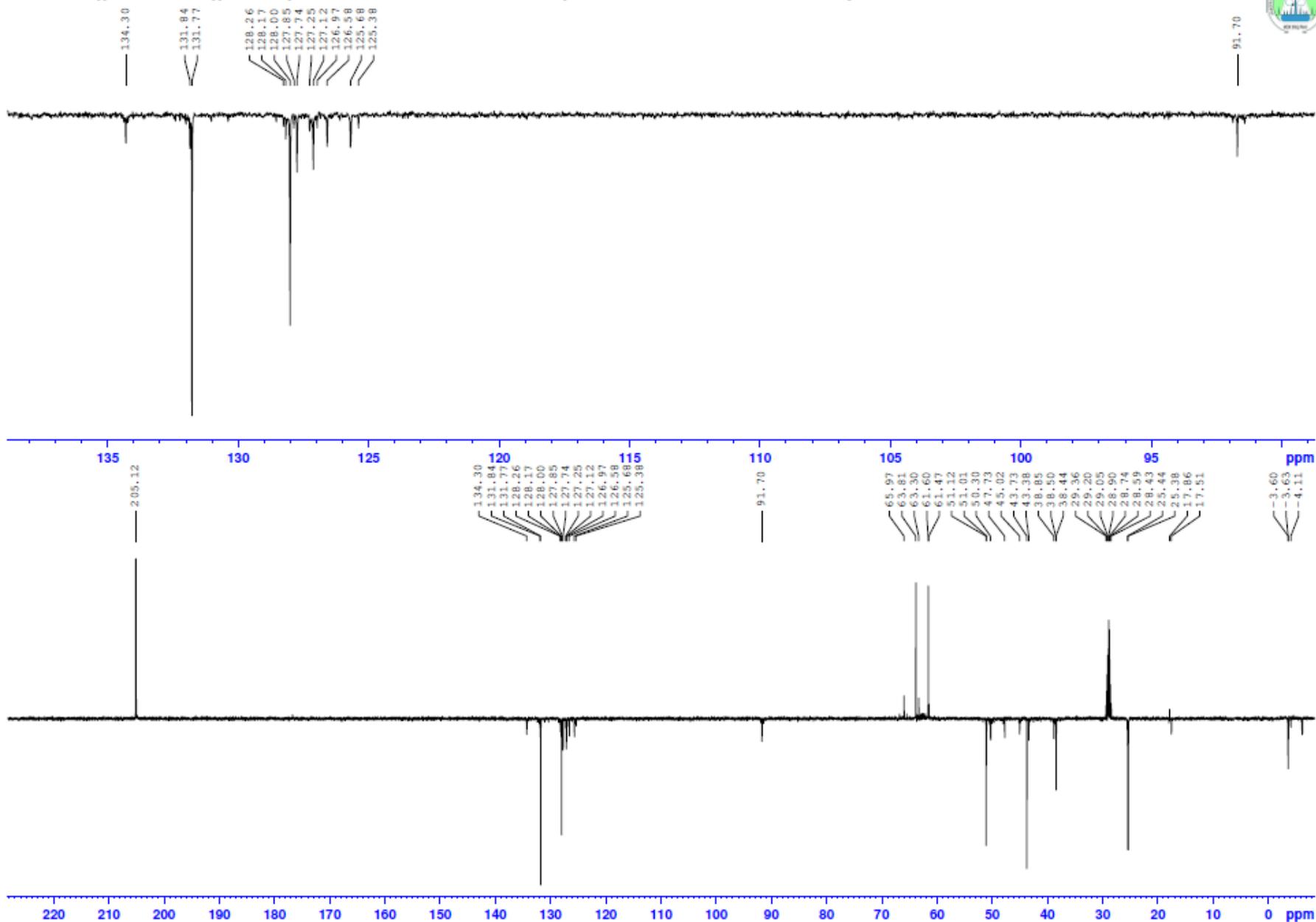
Sp-1261 Gimazetdinova Pc-213-2 50mg in Acetone, 1H AV500 26.05.2016 SSH  
SW (1H)=19.99ppm O1(1H)=7.00ppm Obs.Freq.:500.13MHz; D1=2.0s; T=299.3K; Probe:BBO; Exp.Time: 7 sec; TimesDate: 13:12:14 26 May 2016.

Ufa Institute of Chemistry of the Russian Academy of Sciences (UIC RAS). 2016



Sp-1261 Gimazetdinova Pc-213-2 50mg in Acetone,  $^{13}\text{C}\{^1\text{H}\}$  jmod AV500 26.05.2016 SSH  
SW(13C)=236.63ppm O1(13C)=110.00ppm Obs.Freq.:125.76MHz; D1=2.0s; T=300.1K; Probe:BB0; Exp.Time:22 min 11 sec; TimesDate: 13:34:35 26 May 2016.

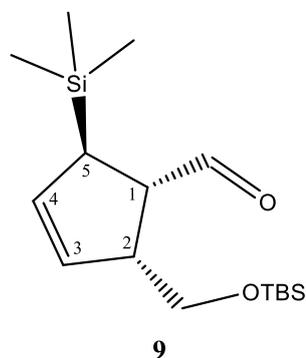
Ufa Institute of Chemistry of the Russian Academy of Sciences (IIC RAS), 2016



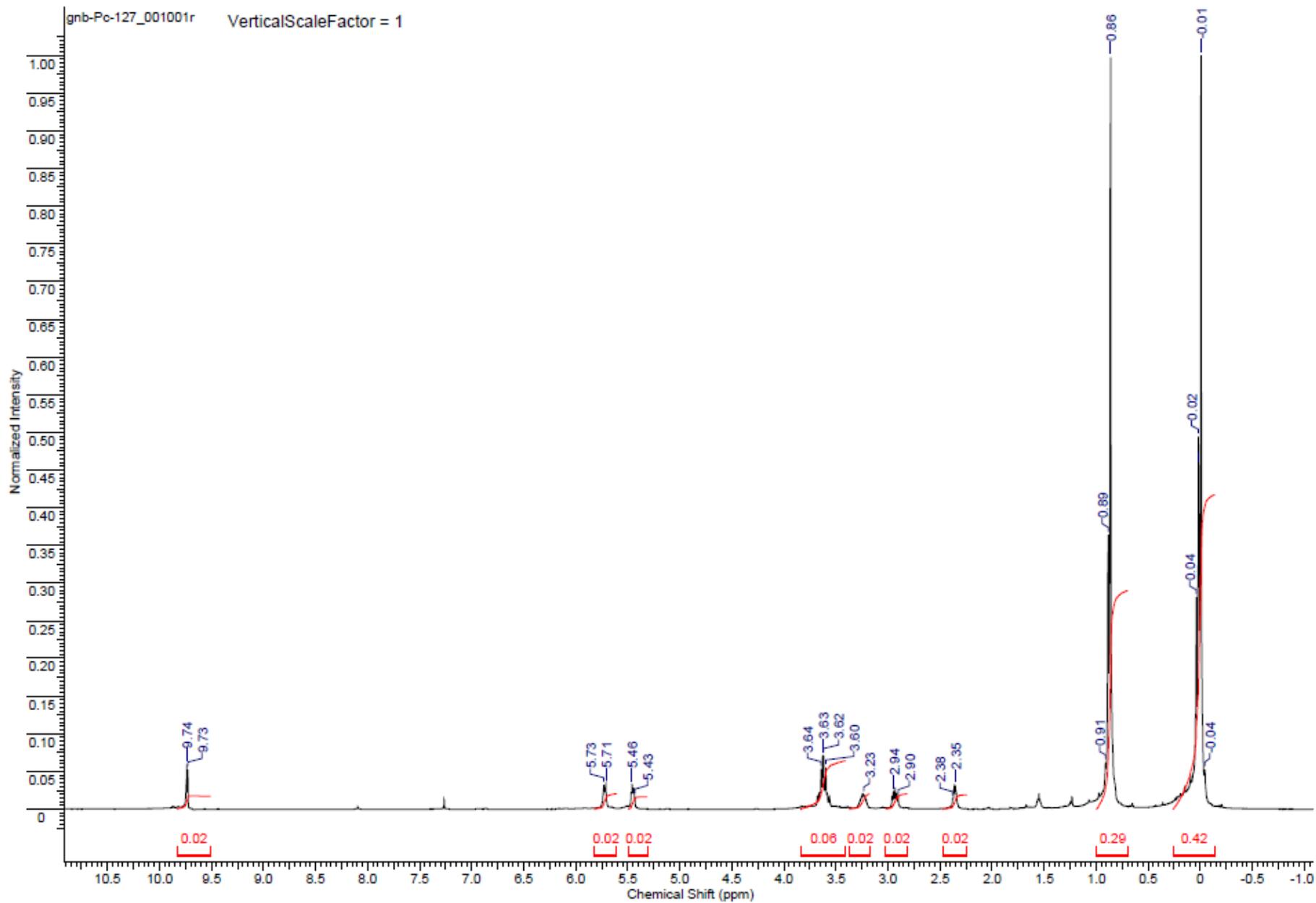
**(1*S*,2*R*,5*R*)-2-(((*tert*-butyldimethylsilyl)oxy)methyl)-5-(trimethylsilyl)cyclopent-3-ene-1-carbaldehyde (9) and *tert*-butyl(((1*R*,4*R*,5*S*)-5-(2-methoxyvinyl)-4-(trimethylsilyl)cyclopent-2-en-1-yl)methoxy)dimethylsilane (10)**

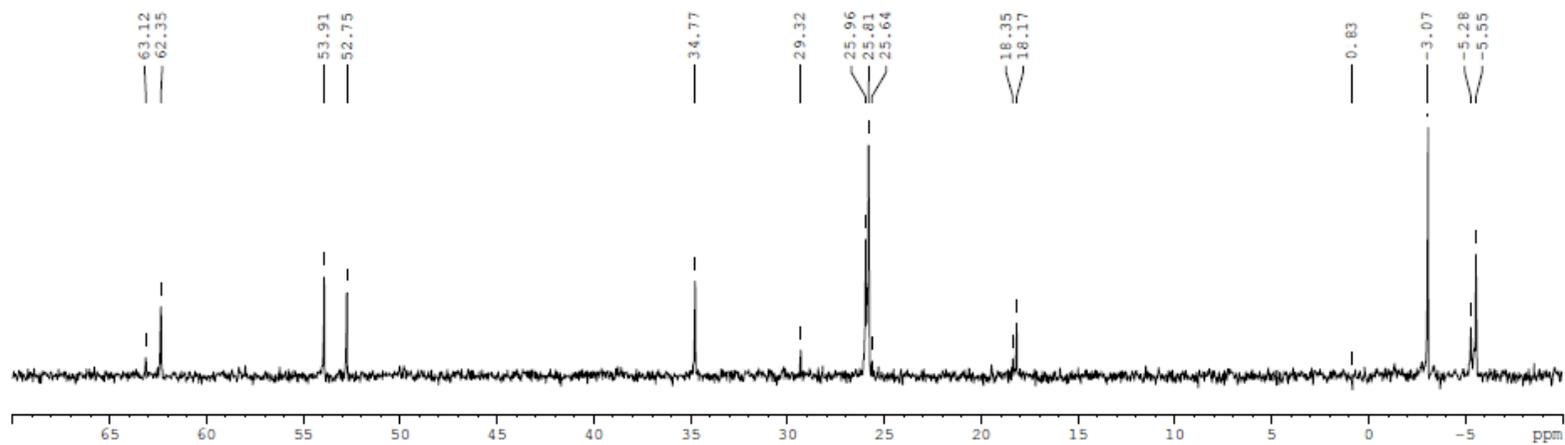
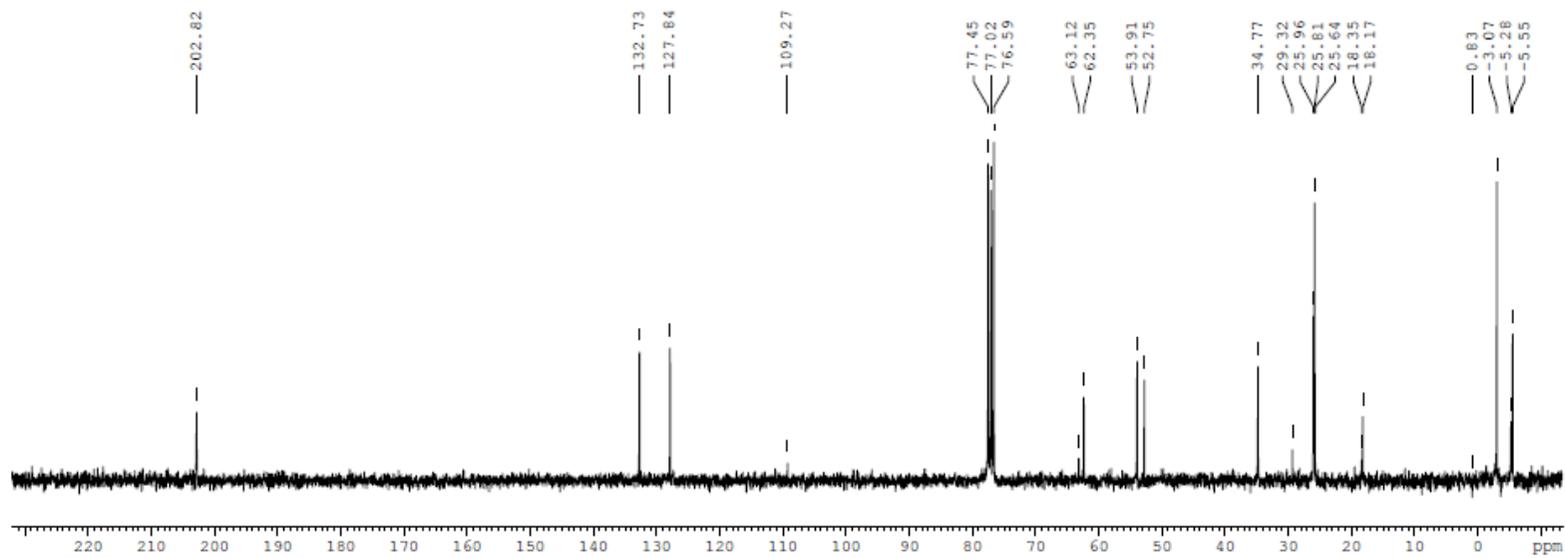
To the solution of oxalyl chloride (0.61 mL, 7.11 mmol) in dichloromethane (15 mL) cooled to  $-78^{\circ}\text{C}$  under argon atmosphere was added via dropping funnel solution of DMSO (0.63 mL, 8.88 mmol) in dichloromethane (5 mL). The mixture was stirred for 10 min. Then, alcohol **8a** (1.12 g, 3.55 mmol) in dichloromethane (20 mL) was added dropwise. The mixture was stirred under this temperature for 15 min (TLC control) and the solution of  $\text{Et}_3\text{N}$  in dichloromethane (10 mL) was added, and stirring was continued for 15 min. The mixture was warmed to room temperature and quenched with water (20 mL). The product was extracted with dichloromethane (30 mL). The combined organic layers were dried on  $\text{MgSO}_4$ , the solvent was evaporated and the residue was pumped. The residue containing aldehyde **9** was introduced into the Wittig reaction without purification. To this, ylide was prepared from the  $[\text{Ph}_3\text{P}^+\text{CH}_2\text{OCH}_3]\text{Cl}^-$  salt (3 g, 8.75 mmol) in dry toluene (30 mL) and 1.2 M NaHMDS (9.2 mL) (7.64 mmol) at  $0^{\circ}\text{C}$ . The resulting solution was stirred for 10 min under argon atmosphere at room temperature. Then, the reaction mixture was cooled to  $0^{\circ}\text{C}$  and the solution of crude aldehyde **9** in toluene (20 mL) was added dropwise. After being stirred at room temperature for 10 min (TLC controlled), saturated  $\text{NH}_4\text{Cl}$  solution was added. The resulting mixture was filtered, the water layer was extracted with EtOAc, the combined organic layers were dried with  $\text{MgSO}_4$ , the solvent was evaporated. Purification by column chromatography on  $\text{SiO}_2$  (petroleum ether/ethyl acetate, 40:1) gave enol ether **10** (*E/Z*, 5:1).

**(1*S*,2*R*,5*R*)-2-(((*tert*-butyldimethylsilyl)oxy)methyl)-5-(trimethylsilyl)cyclopent-3-ene-1-carbaldehyde (9)**



Colorless transparent viscous oil;  $R_f = 0.4$  (petroleum ether/ethyl acetate, 20:1);  $[\alpha]_D^{20} : + 80.0$  ( $c$  0.93,  $\text{CH}_2\text{Cl}_2$ ). IR (liquid film): 3049, 2955, 2857, 1718, 1472, 1250, 838, 776  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (300 MHz, *d*-chloroform/chloroform):  $\delta = 9.73$  (d,  $J = 3.5$  Hz, 1H, C=O), 5.72 (dt,  $J = 5.7, 2.2$  Hz, 1H,  $\text{C}^3\text{H}$ ), 5.44 (dt,  $J = 5.1, 2.3$  Hz, 1H,  $\text{C}^4\text{H}$ ), 3.65 (dd,  $J = 10.4, 5.0$  Hz, 1H,  $\text{CH}_\alpha\text{H}_\beta\text{O}$ ), 3.60 (dd,  $J = 10.4, 6.7$  Hz, 1H,  $\text{CH}_\alpha\text{H}_\beta\text{-O}$ ), 3.24 (dddd,  $J = 8.9, 6.7, 5.0, 2.2$  Hz, 1H,  $\text{C}^2\text{H}$ ), 2.94 (ddd,  $J = 8.9, 5.0, 3.6$  Hz, 1H,  $\text{C}^1\text{H}$ ), 2.36 (dt,  $J = 5.0, 2.2$  Hz, 1H,  $\text{C}^5\text{H}$ ), 0.87 (s, 9H,  $(\text{CH}_3)_3\text{C}$ ), 0.02 (s, 6H,  $(\text{CH}_3)_2\text{Si}$ ), 0.00 (s, 9H,  $(\text{CH}_3)_3\text{Si}$ ), -5.56 ( $(\text{CH}_3)_2\text{Si}$ ). MS (APCI):  $m/z$  (%) = 313 (100)  $[\text{MH}]^+$ . Anal. Calcd for  $\text{C}_{16}\text{H}_{32}\text{O}_2\text{Si}_2$ : C, 61.48; H, 10.32. Found: C, 61.33; H, 10.25.





***tert*-Butyl(((1*R*,4*R*,5*S*)-5-(2-methoxyvinyl)-4-(trimethylsilyl)cyclopent-2-en-1-yl)methoxy)dimethylsilane (10)**

For major *E*-isomer:

Yield: 0.98 g (81%); colorless transparent viscous oil.

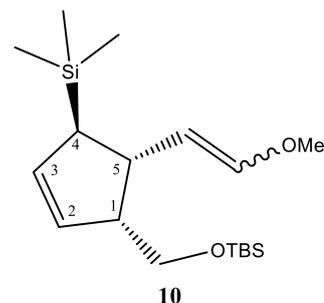
$R_f = 0.5$  (petroleum ether/ethyl acetate, 40:1).

IR (liquid film): 3057, 2955, 2856, 1436, 1248, 1193, 1119, 836, 720  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR (500 MHz, acetone- $d_6$ ):  $\delta = 6.36$  (d,  $J = 12.6$  Hz, 1H,  $\text{CH}=\underline{\text{C}}\text{HOMe}$ ), 5.73 (dt,  $J = 2.6, 5.8$  Hz, 1H,  $\text{C}^3\text{H}$ ), 5.59 (dt,  $J = 2.1, 5.6$  Hz, 1H,  $\text{C}^2\text{H}$ ), 4.83 (dd,  $J = 10.2, 12.6$  Hz, 1H,  $\text{CH}=\text{CHOMe}$ ), 3.66 (dd,  $J = 5.6, 9.8$  Hz, 1H,  $\text{CH}_\alpha\text{H}_\beta\text{O}$ ), 3.56 (dd,  $J = 2.2, 9.6$  Hz, 1H,  $\text{CH}_\alpha\text{H}_\beta\text{O}$ ), 3.46 (s, 3H,  $\text{CH}_3$ ), 2.85-2.89 (m, 1H,  $\text{C}^5\text{H}$ ), 2.71-2.77 (m, 1H,  $\text{C}^1\text{H}$ ), 1.90 (td,  $J = 2.5, 4.8$  Hz, 1H,  $\text{C}^4\text{H}$ ), 0.88 (s, 9H,  $(\text{CH}_3)_3\text{C}$ ), 0.03 (s, 6H,  $(\text{CH}_3)_2\text{Si}$ ), -0.01 (s, 9H,  $(\text{CH}_3)_3\text{Si}$ ).

$^{13}\text{C}$  NMR (125 MHz, acetone- $d_6$ ):  $\delta = 146.83$  ( $\text{CH}=\underline{\text{C}}\text{HOCH}_3$ ), 133.43 ( $\text{C}^2$ ), 131.78 ( $\text{C}^3$ ), 104.62 ( $\underline{\text{C}}\text{H}=\text{CHOCH}_3$ ), 63.65 ( $\text{CH}_2\text{OSi}$ ), 55.03 ( $\text{CH}_3\text{O}$ ), 52.31 ( $\text{C}^1$ ), 43.39 ( $\text{C}^5$ ), 41.12 ( $\text{CHSi}$ ), 25.39 ( $(\text{CH}_3)_3\text{C}$ ), 17.88 ( $(\text{CH}_3)_3\text{C}$ ), -3.59 ( $(\text{CH}_3)_3\text{Si}$ ), -6.0 ( $\text{OSi}(\text{CH}_3)_2$ ).

MS (APCI):  $m/z$  (%) = 341 (100)  $[\text{MH}]^+$ .



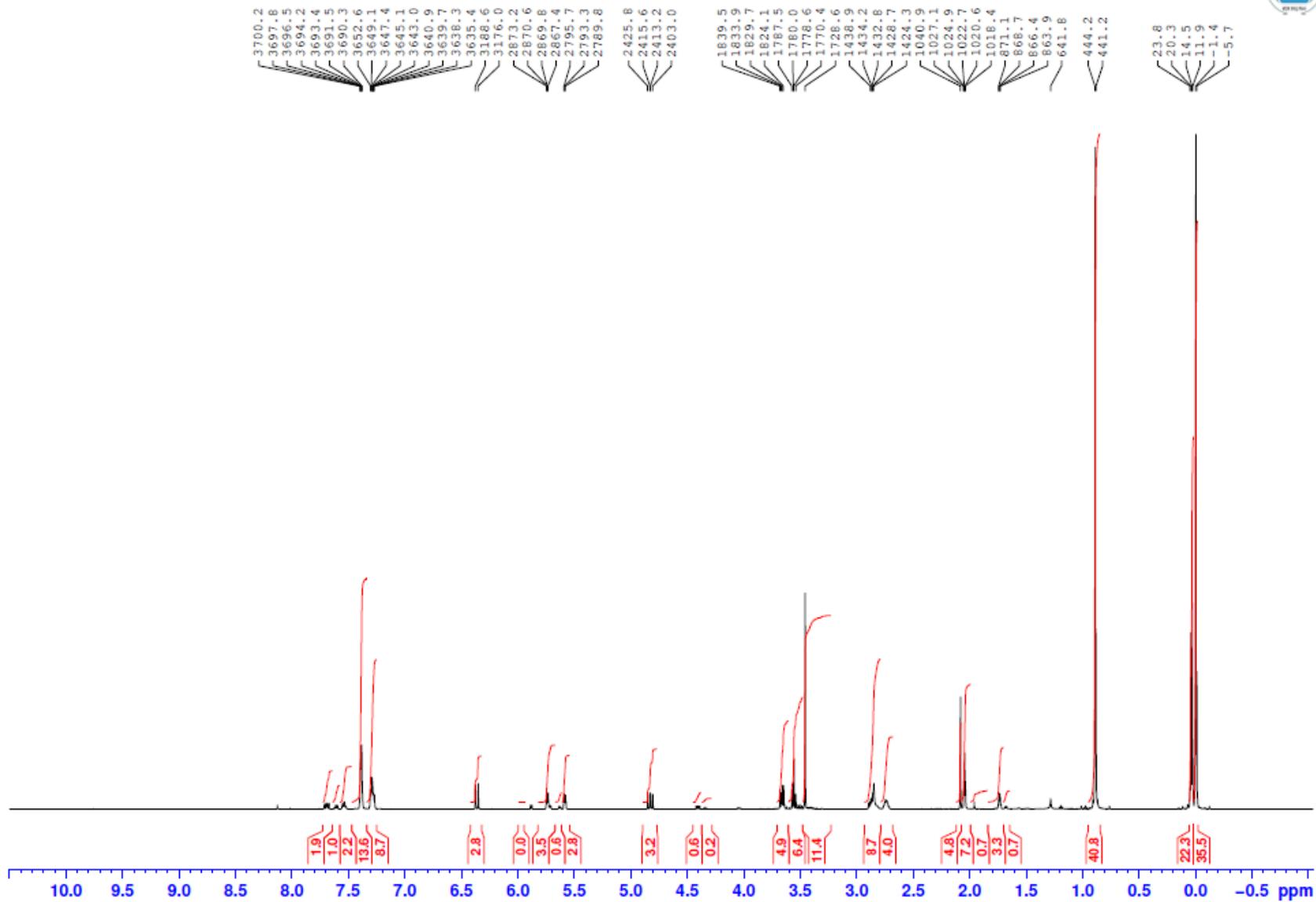
Anal. Calcd for  $\text{C}_{18}\text{H}_{36}\text{O}_2\text{Si}_2$ : C, 63.47; H, 10.65. Found: C, 63.26; H, 10.49.

Sp-117 Gimazetdinov Pc-247-2 23mg in Acetone, 1H AV500 06.02.2017 SSH

Ufa Institute of Chemistry of the Russian Academy of Sciences (IIC RAS) . 2017



SW (1H) -19.99ppm O1 (1H) -7.00ppm Obs. Freq.: 500.13MHz; D1 -2.0s; T -293.6K; Probe: BBO; Exp. Time: 7 sec; TimesDate: 16:14:54 06 Feb 2017.

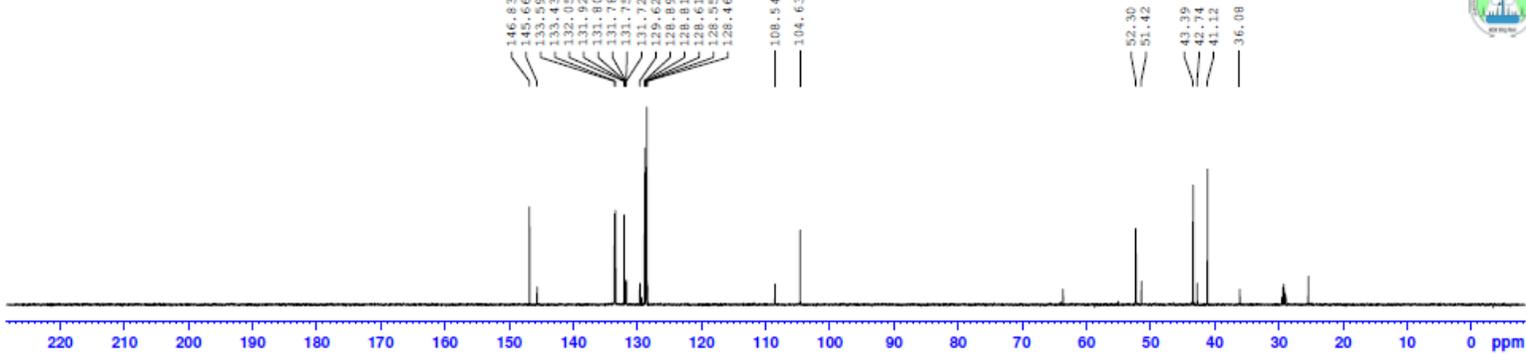


Sp-117 Gimazetidinov Pc-247-2 23mg in Acetone, 13C(1H) dept90 AV500 06.02.2017 SSH

Ufa Institute of Chemistry of the Russian Academy of Sciences (UIC RAS), 2017

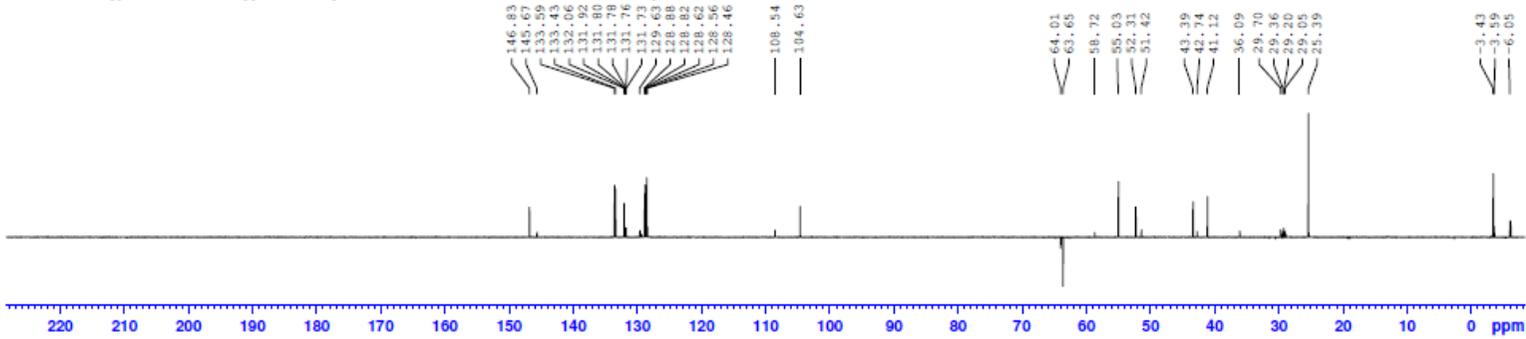


SW (13C)-236.63ppm O1 (13C)-110.00ppm Obs.Freq.:125.76MHz D1=2.0s T=296.5K Probe:BBQ Exp.Time: 1 h 47 min 51 sec TimesDate: 22:12:26 06 Feb 2017.



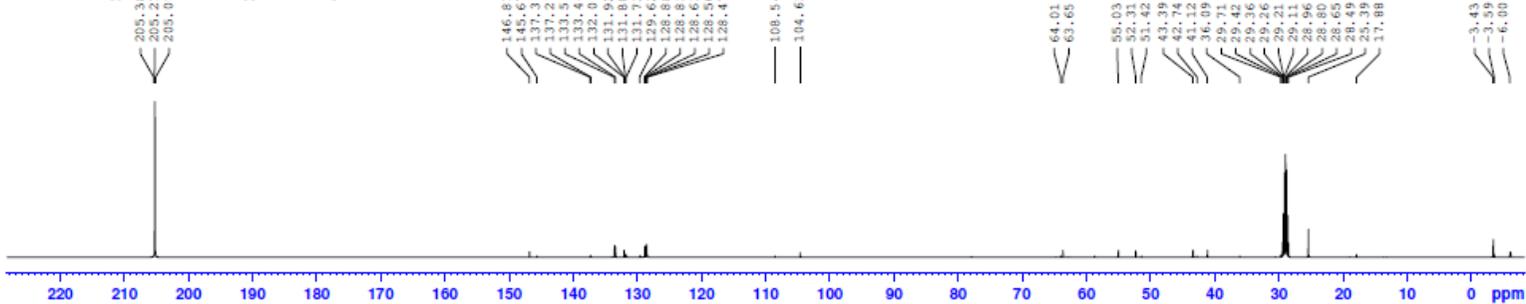
Sp-117 Gimazetidinov Pc-247-2 23mg in Acetone, 13C(1H) dept135 AV500 06.02.2017 SSH

SW (13C)-236.63ppm O1 (13C)-110.00ppm Obs.Freq.:125.76MHz D1=2.0s T=296.5K Probe:BBQ Exp.Time: 1 h 47 min 51 sec TimesDate: 20:24:33 06 Feb 2017.



Sp-117 Gimazetidinov Pc-247-2 23mg in Acetone, 13C(1H) com AV500 06.02.2017 SSH

SW (13C)-236.63ppm O1 (13C)-110.00ppm Obs.Freq.:125.76MHz D1=0.9s T=296.5K Probe:BBQ Exp.Time: 20 min 51 sec TimesDate: 18:36:39 06 Feb 2017.



**Methyl 2-((1R,2R,5R)-2-(((tert-butyl dimethylsilyl)oxy)methyl)-5-(trimethylsilyl)-cyclopent-3-en-1-yl)acetate (11)**

To a solution of enol ether **10** (0.89 g, 2.60 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> cooled to 0°C, were added SiO<sub>2</sub> (0.89 g), NaHCO<sub>3</sub> (0.17 g) and PCC (1.69 g, 7.83 mmol). The mixture was warmed to room temperature and stirred for 2 h (TLC control). The mixture was filtered throughout the Schott filter with SiO<sub>2</sub>, the solvent was evaporated. Purification of the product by column chromatography with SiO<sub>2</sub> gave product **11**.

Yield: 0.64 g (69%); colorless transparent viscous oil.

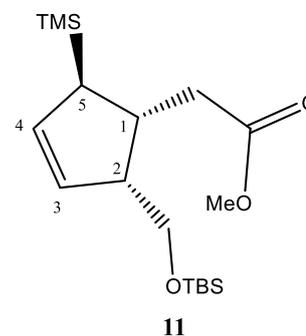
$R_f = 0.5$  (petroleum ether/ethyl acetate, 20:1);  $[\alpha]_D^{20} = +141.0$  ( $c$  1.0, CH<sub>2</sub>Cl<sub>2</sub>).

IR (liquid film): 2954, 2857, 1739, 1249, 1094, 837, 775 cm<sup>-1</sup>.

<sup>1</sup>H NMR (500 MHz, acetone-*d*<sub>6</sub>):  $\delta = 5.73$  (dt,  $J = 2.6, 5.7$  Hz, 1H, C<sup>4</sup>H), 5.45 (dt,  $J = 2.0, 5.7$  Hz, 1H, C<sup>3</sup>H), 3.70 (dd,  $J = 6.2, 10.2$  Hz, 1H, CH <sub>$\alpha$</sub> H <sub>$\beta$</sub> O), 3.63 (dd,  $J = 7.8, 10.3$  Hz, 1H, CH <sub>$\alpha$</sub> H <sub>$\beta$</sub> O), 3.60 (s, 3H, CH<sub>3</sub>), 2.88-2.94 (m, 1H, C<sup>2</sup>H), 2.73-2.79 (m, 1H, C<sup>1</sup>H), 2.59 (dd,  $J = 5.6, 15.0$  Hz, 1H CH <sub>$\alpha$</sub> H <sub>$\beta$</sub> CO<sub>2</sub>Me), 2.23 (dd,  $J = 9.5, 14.9$  Hz, 1H CH <sub>$\alpha$</sub> H <sub>$\beta$</sub> CO<sub>2</sub>Me), 1.70 (quint,  $J = 2.6$  Hz, 1H, C<sup>5</sup>H), 0.90 (s, 9H, (CH<sub>3</sub>)<sub>3</sub>C), 0.13 (s, 6H, OSi(CH<sub>3</sub>)<sub>2</sub>), 0.0 (s, 9H, (CH<sub>3</sub>)<sub>3</sub>Si).

<sup>13</sup>C NMR (125 MHz, acetone-*d*<sub>6</sub>):  $\delta = 173.12$  (C=O), 132.15 (C<sup>4</sup>), 127.38 (C<sup>3</sup>), 62.42 (CH<sub>2</sub>OSi), 50.62 (OCH<sub>3</sub>), 41.54 (C<sup>5</sup>), 37.99 (C<sup>1</sup>, C<sup>2</sup>), 35.29 (CH<sub>2</sub>C=O), 25.35 ((CH<sub>3</sub>)<sub>3</sub>C), 17.86 ((CH<sub>3</sub>)<sub>3</sub>C), -3.55 ((CH<sub>3</sub>)<sub>3</sub>Si), -6.11 (OSi(CH<sub>3</sub>)<sub>2</sub>).

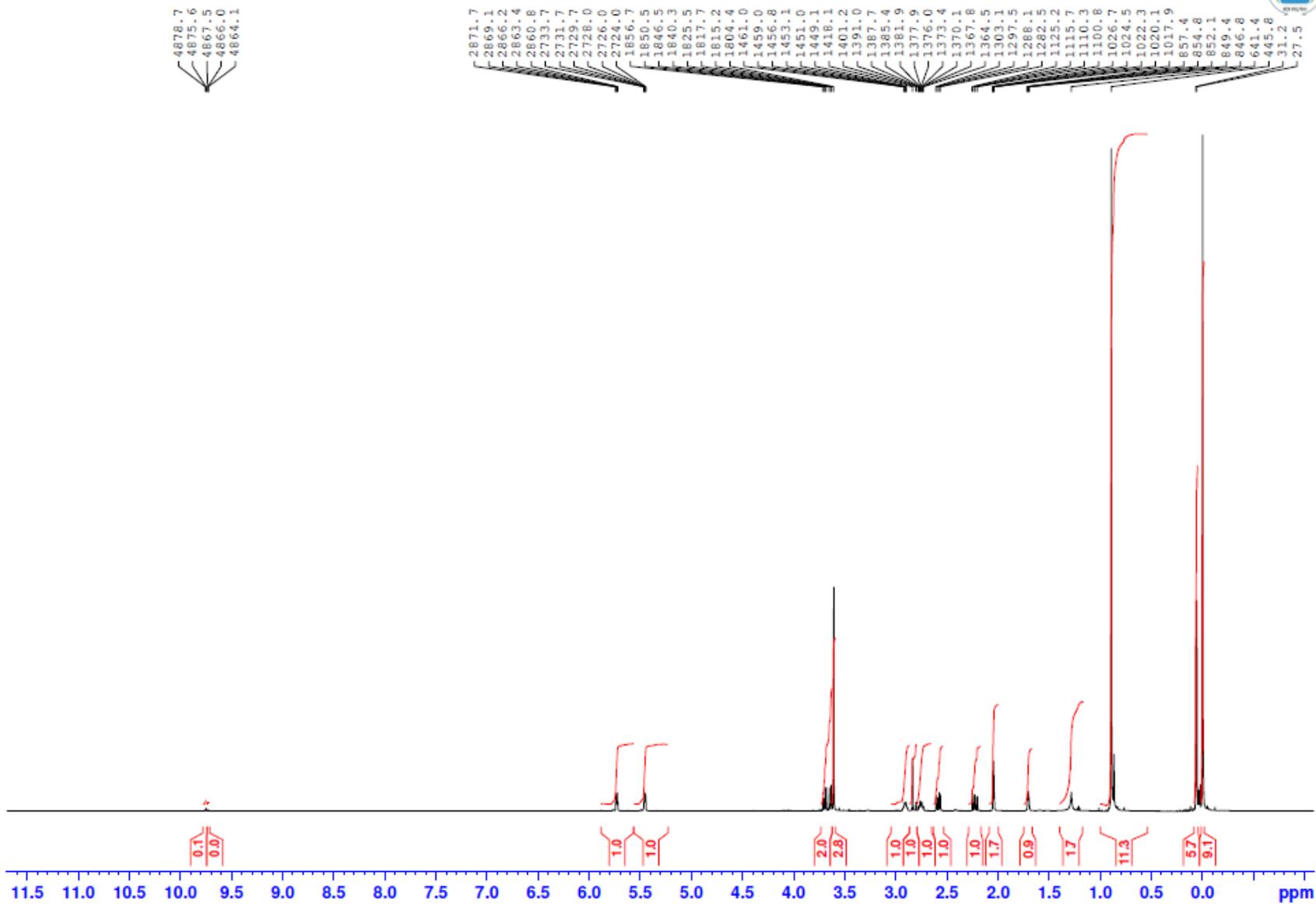
MS (APCI):  $m/z$  (%) = 357 (100%) [MH]<sup>+</sup>.



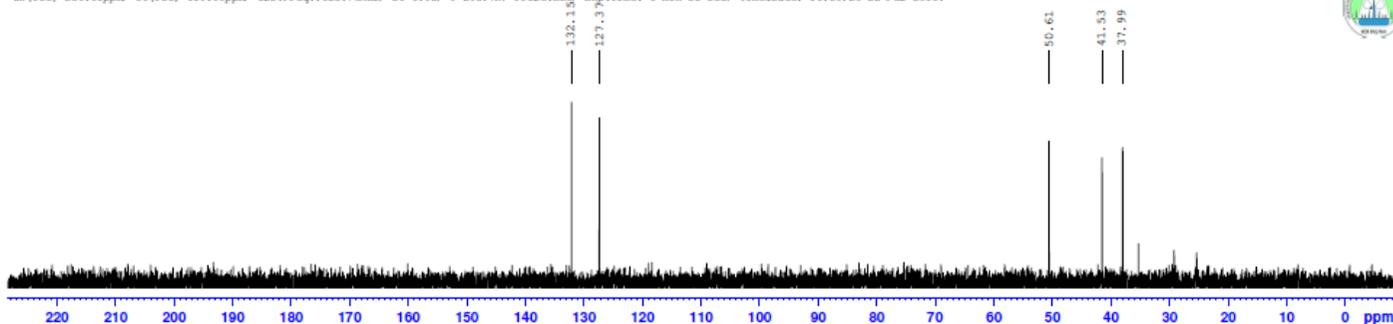
Anal. Calcd for C<sub>18</sub>H<sub>36</sub>O<sub>3</sub>Si<sub>2</sub>: C, 60.62; H, 10.17. Found: C, 60.49; H, 10.09.

Sp-1427 Gimazetdinov Pc-360 25mg in Acetone, 1H AV500 22.02.2018 LAN  
SW (1H)~19.99ppm O1 (1H)~7.00ppm Obs.Freq.:500.13MHz DI=5.0sr T=293.2K Probe:BB0V Exp.Time: 1 min 25 sec TimesDate: 11:28:08 22 Feb 2018.

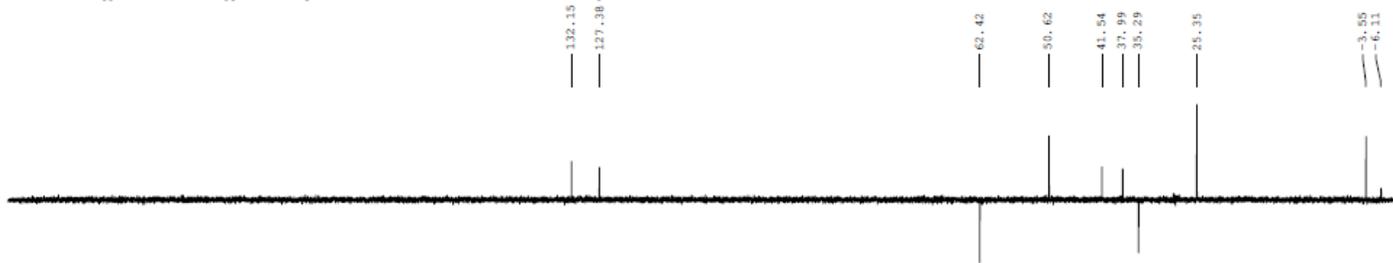
Ufa Institute of Chemistry of the Russian Academy of Sciences (UIC RAS). 2018



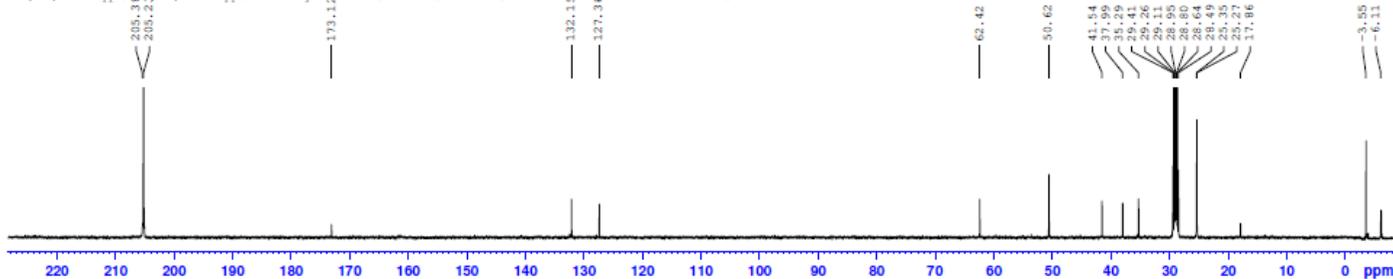
Sp-1427 Gimazetdinov Pc-360 25mg in Acetone, <sup>13</sup>C(1H) dept90 AV500 22.02.2018 LAN Ufa Institute of Chemistry of the Russian Academy of Sciences (UIC RAS). 2018  
 SW (13C)-236.63ppm O1 (13C)-110.00ppm Obs.Freq.:125.76MHz; D1-1.0s; T-293.7K; Proba:BBG; Exp.Time: 1 min 55 sec; TimesDate: 11:39:26 22 Feb 2018.



Sp-1427 Gimazetdinov Pc-360 25mg in Acetone, <sup>13</sup>C(1H) dept135 AV500 22.02.2018 LAN  
 SW (13C)-236.63ppm O1 (13C)-110.00ppm Obs.Freq.:125.76MHz; D1-1.0s; T-293.7K; Proba:BBG; Exp.Time: 1 min 32 sec; TimesDate: 11:38:42 22 Feb 2018.



Sp-1427 Gimazetdinov Pc-360 25mg in Acetone, <sup>13</sup>C(1H) com AV500 22.02.2018 LAN  
 SW (13C)-236.63ppm O1 (13C)-110.00ppm Obs.Freq.:125.76MHz; D1-0.9s; T-294.0K; Proba:BBG; Exp.Time: 8 min 50 sec; TimesDate: 11:37:08 22 Feb 2018.



**(4aR,5R,7aR)-5-trimethylsilyl-4,4a,5,7a-tetrahydrocyclopenta[c]pyran-3(1H)-one (12)**

Compound **11** (0.502 g, 1.4 mmol) was dissolved in wet methanol (25 ml), and Amberlyst (15 hydrogen form) and Dowex 50WX4 200-400 (0.25 g each) were added. The reaction proceeded within 16 h. The mixture was filtered through Schott funnel, the solvent was evaporated, and the residue was purified by column chromatography on SiO<sub>2</sub> (petroleum ether/ethyl acetate, 3:1).

Yield: 0.227 g (77%); colorless transparent viscous oil.

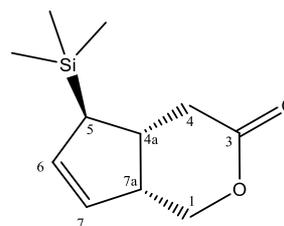
$R_f = 0.3$  (petroleum ether/ethyl acetate, 3:1);  $[\alpha]_D^{20} : +141$  (c 1.0, CH<sub>2</sub>Cl<sub>2</sub>).

IR (liquid film): 3471, 3048, 2954, 2900, 2850, 1749, 1478, 1434, 1358, 1350, 1248, 1140, 1076, 1034, 965, 906, 872, 838, 794, 694, 622 cm<sup>-1</sup>.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 5.77$  (dt,  $J = 2.2, 5.7$  Hz, 1H, C<sup>6</sup>H), 5.33 (dt,  $J = 2.2, 5.7$  Hz, 1H, C<sup>7</sup>H), 4.35 (dd,  $J = 4.6, 11.5$  Hz, 1H, C<sup>1</sup>H <sub>$\alpha$</sub> ), 4.12 (dd,  $J = 5.4, 11.5$  Hz, 1H, C<sup>1</sup>H <sub>$\beta$</sub> ), 3.18 (m, 1H, C<sup>7a</sup>H), 2.78 (m, 1H, C<sup>4a</sup>H), 2.61 (dd,  $J = 6.8, 14.6$  Hz, 1H, C<sup>4</sup>H <sub>$\alpha$</sub> ), 2.32 (dd,  $J = 5.9, 14.6$  Hz, 1H, C<sup>4</sup>H <sub>$\beta$</sub> ).

<sup>13</sup>C (125 MHz, CDCl<sub>3</sub>):  $\delta = 173.26$  (C=O), 134.83 (C<sup>6</sup>), 125.39 (C<sup>7</sup>), 69.39 (C<sup>1</sup>), 45.22 (C<sup>7a</sup>), 43.75 (C<sup>5</sup>), 36.51 (C<sup>4</sup>), 34.73 (C<sup>4a</sup>), -3.47 ((CH<sub>3</sub>)<sub>3</sub>Si).

MS (APCI):  $m/z$  (%) = 211 (100) [MH]<sup>+</sup>.



Anal. Calcd for C<sub>11</sub>H<sub>18</sub>O<sub>2</sub>Si: C, 62.81; H, 8.63. Found: C, 62.67; H, 8.51.

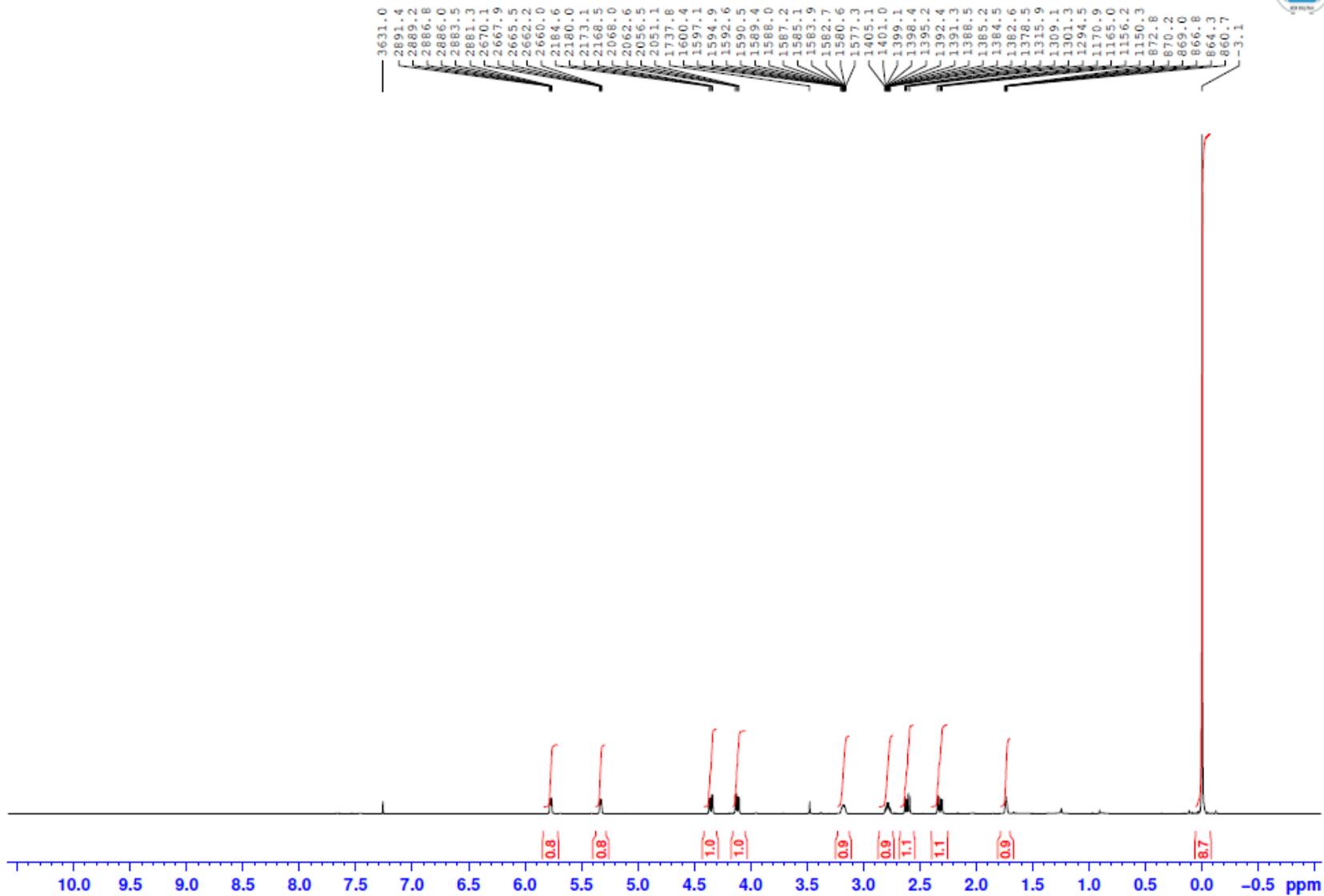
**12**

Sp-1412 Almukhametov Pca-121 21mg in CDCl3, 1H AV500 14.02.2019 LAN

Ufa Institute of Chemistry of the Russian Academy of Sciences (UIC RAS), 2019

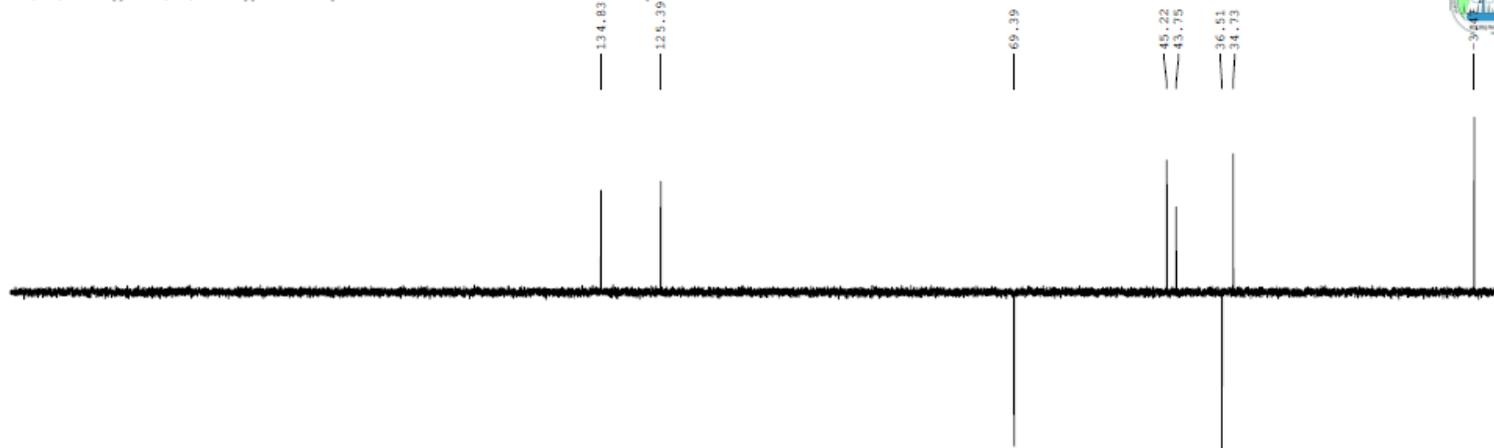


SN(1H)=19.99ppm O1(1H)=7.00ppm Obs.Freq.:500.13MHz DI=2.0s T=298.2K Proba:BBG Exp.Time: 7 sec TimeDate: 09:30:14 14 Feb 2019.

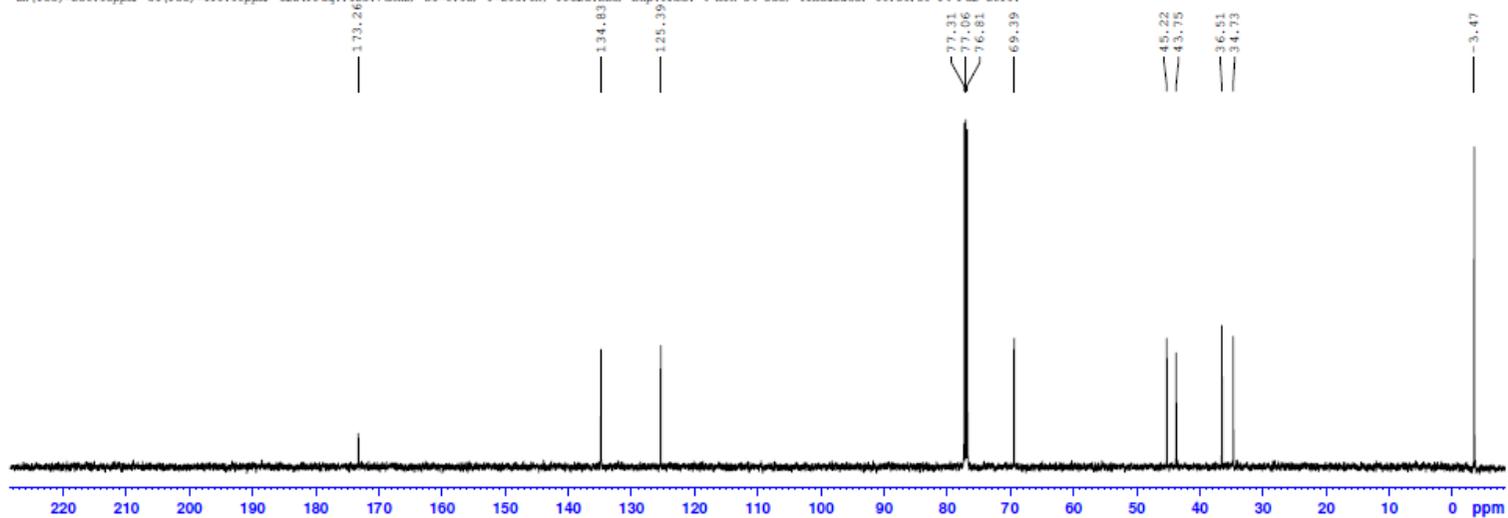


Sp-1412 Almukhametov Pca-121 21mg in CDCl3, 13C{1H} dept135 AV500 14.02.2019 LAN  
SW (13C)=-236.63ppm O1 (13C)=-110.00ppm Obs.Freq.:125.76MHz; D1=1.0s; T=298.7K; Proba:BB0; Exp.Time: 2 min 27 sec; TimesDate: 09:35:18 14 Feb 2019.

Ufa Institute of Chemistry of the Russian Academy of Sciences (UIC RAS), 2019



220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm  
Sp-1412 Almukhametov Pca-121 21mg in CDCl3, 13C{1H} com AV500 14.02.2019 LAN  
SW (13C)=-236.63ppm O1 (13C)=-110.00ppm Obs.Freq.:125.76MHz; D1=0.9s; T=298.9K; Proba:BB0; Exp.Time: 4 min 34 sec; TimesDate: 09:36:39 14 Feb 2019.



**(4a*S*,7*R*,7a*R*)-7-hydroxy-4,4a,7,7a-tetrahydrocyclopenta[*c*]pyran-3(1*H*)-one (13a) and (4a*S*,7*S*,7a*R*)-7-hydroxy-4,4a,7,7a-tetrahydrocyclopenta[*c*]pyran-3(1*H*)-one (13b)**

General procedure. Solid NaHCO<sub>3</sub> (1.4 g, 16.66 mmol) was placed in a round bottom flask, and H<sub>2</sub>O (5 mL) followed by acetone (15 mL) were added. The mixture was cooled to 0°C in an ice bath and stirred for 20 min. Oxone (1.33 g, 2.16 mmol) was added in one portion, and stirring was continued at 0°C for further 15 min. Then, compound **12** (0.227 g, 1.08 mmol) was added in one portion. The ice bath was removed, and the reaction mixture was stirred at room temperature for 1 h. The mixture was then diluted with water (15 mL) and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic layers were dried with MgSO<sub>4</sub>, solvent was evaporated *in vacuo*. Purification on SiO<sub>2</sub> using petroleum ether/ethyl acetate (3:1) as the solvent system, gave individual alcohols **13a** and **13b** with 88% overall yield.

**(4a*S*,7*R*,7a*R*)-7-hydroxy-4,4a,7,7a-tetrahydrocyclopenta[*c*]pyran-3(1*H*)-one (13a)**

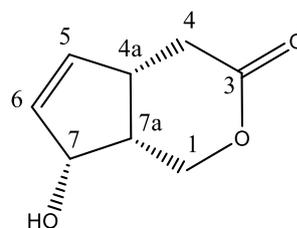
Yield: 0.097 g (75%); white solid; mp 127°C; *R*<sub>f</sub> = 0.4 (petroleum ether/ethyl acetate, 3:1); [ $\alpha$ ]<sub>D</sub><sup>20</sup>: +75 (*c* 0.9, CH<sub>2</sub>Cl<sub>2</sub>).

IR (liquid film): 3418, 2916, 1731, 1479, 1432, 1394, 1356, 1335, 1274, 1251, 1227, 1149, 1124, 1093, 1058, 1039, 1023, 950, 920, 843, 784, 734 cm<sup>-1</sup>.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 5.92 (dt, *J* = 1.9, 5.6, Hz, 1H, C<sup>6</sup>H), 5.79 (dd, *J* = 1.6, 5.6 Hz, 1H, C<sup>5</sup>H), 4.97 (d, *J* = 4.97 Hz, 1H, C<sup>7</sup>H), 4.62 (dd, *J* = 4.0, 11.9 Hz, 1H, C<sup>1</sup>H<sub>*a*</sub>), 4.27 (dd, *J* = 4.4, 11.9 Hz, 1H, C<sup>1</sup>H<sub>*b*</sub>), 3.31 (m, 1H, C<sup>4a</sup>H), 2.86 (sept, *J* = 4.4, 1H, C<sup>7a</sup>H), 2.72 (dd, *J* = 7.2, 15.2, 1H, C<sup>4</sup>H), 2.53 (dd, *J* = 4.2, 15.2, 1H, C<sup>4</sup>H).

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  = 172.41 (C=O), 135.47 (C<sup>6</sup>), 134.88 (C<sup>5</sup>), 77.94 (C<sup>7</sup>), 66.23 (C<sup>1</sup>), 41.48 (C<sup>7a</sup>), 38.27 (C<sup>4a</sup>), 34.62 (C<sup>4</sup>).

MS (APCI): *m/z* (%) = 155 (100) [MH]<sup>+</sup>.

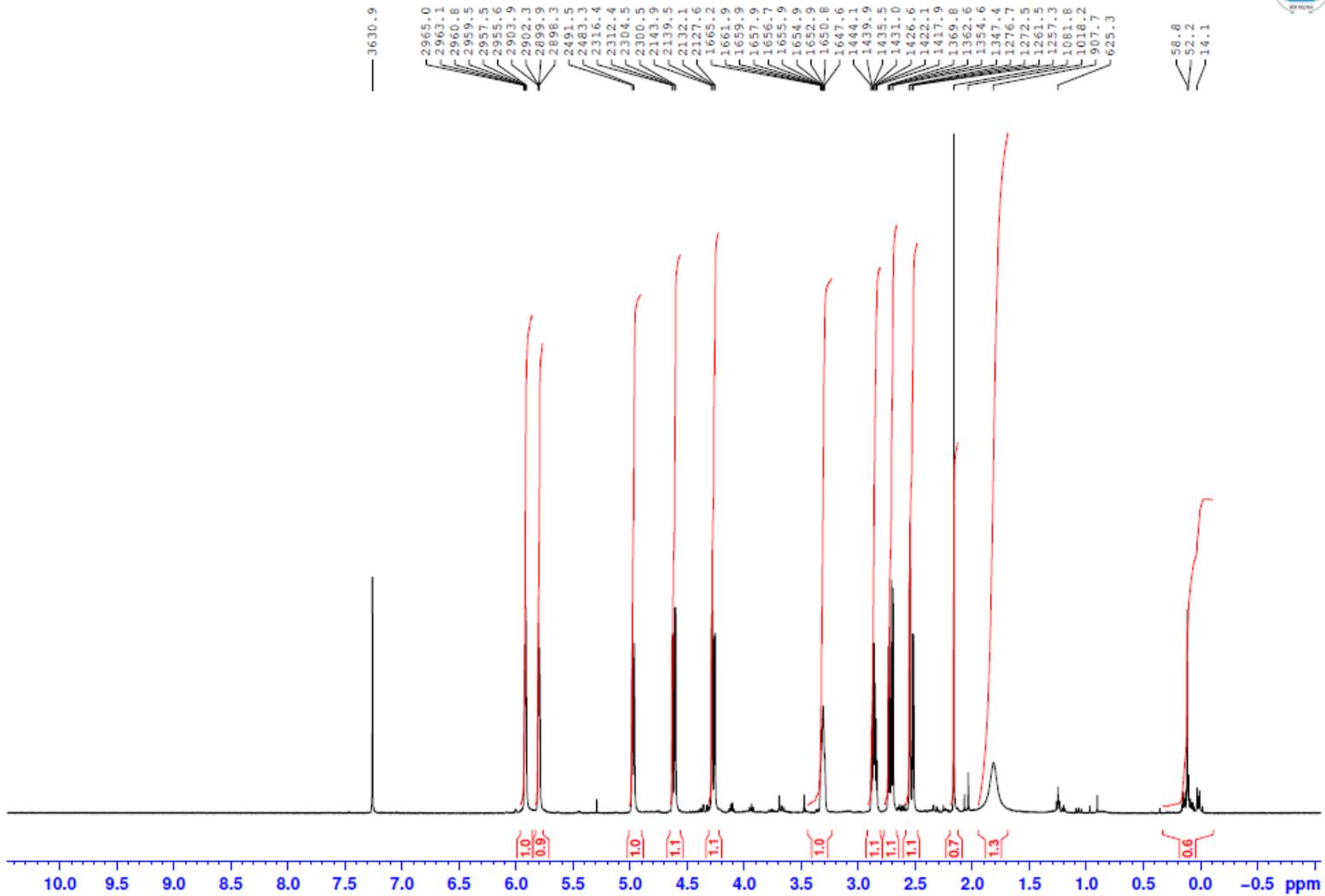


**13a**

Anal. Calcd for C<sub>8</sub>H<sub>10</sub>O<sub>3</sub>: C, 62.33; H, 6.54. Found: C, 62.12; H, 6.25.

Sp-127 Almukhametov Pca-124-1-1 40mg in CDCl3, 1H AV500 11.03.2019 LAN  
 SM (1H) = 19.99ppm; O1 (1H) = 7.00ppm; Obs. Freq.: 500.13MHz; D1 = 2.0s; T = 298.4K; Probe: BB0r; Exp. Time: 11 sec; TimesDate: 14:16:07 11 Mar 2019.

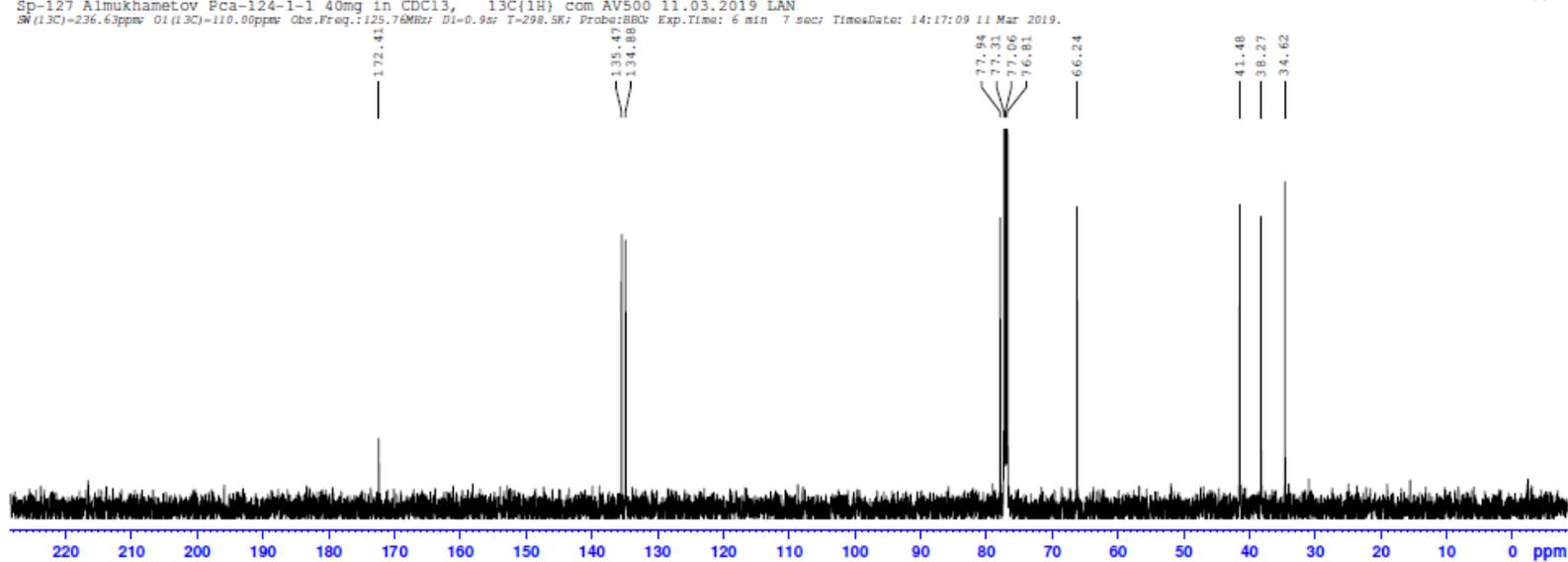
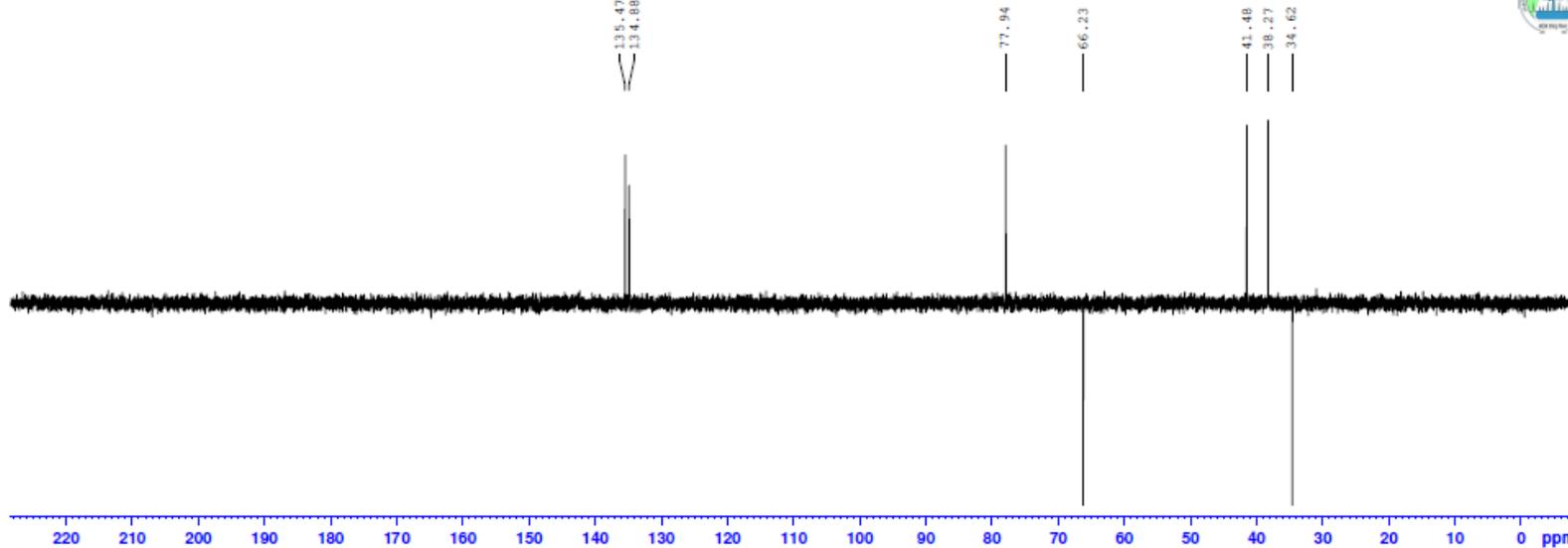
Ufa Institute of Chemistry of the Russian Academy of Sciences (UIC RAS). 2019



Sp-127 Almukhametov Pca-124-1-1 40mg in CDC13, 13C(1H) dept135 AV500 11.03.2019 LAN

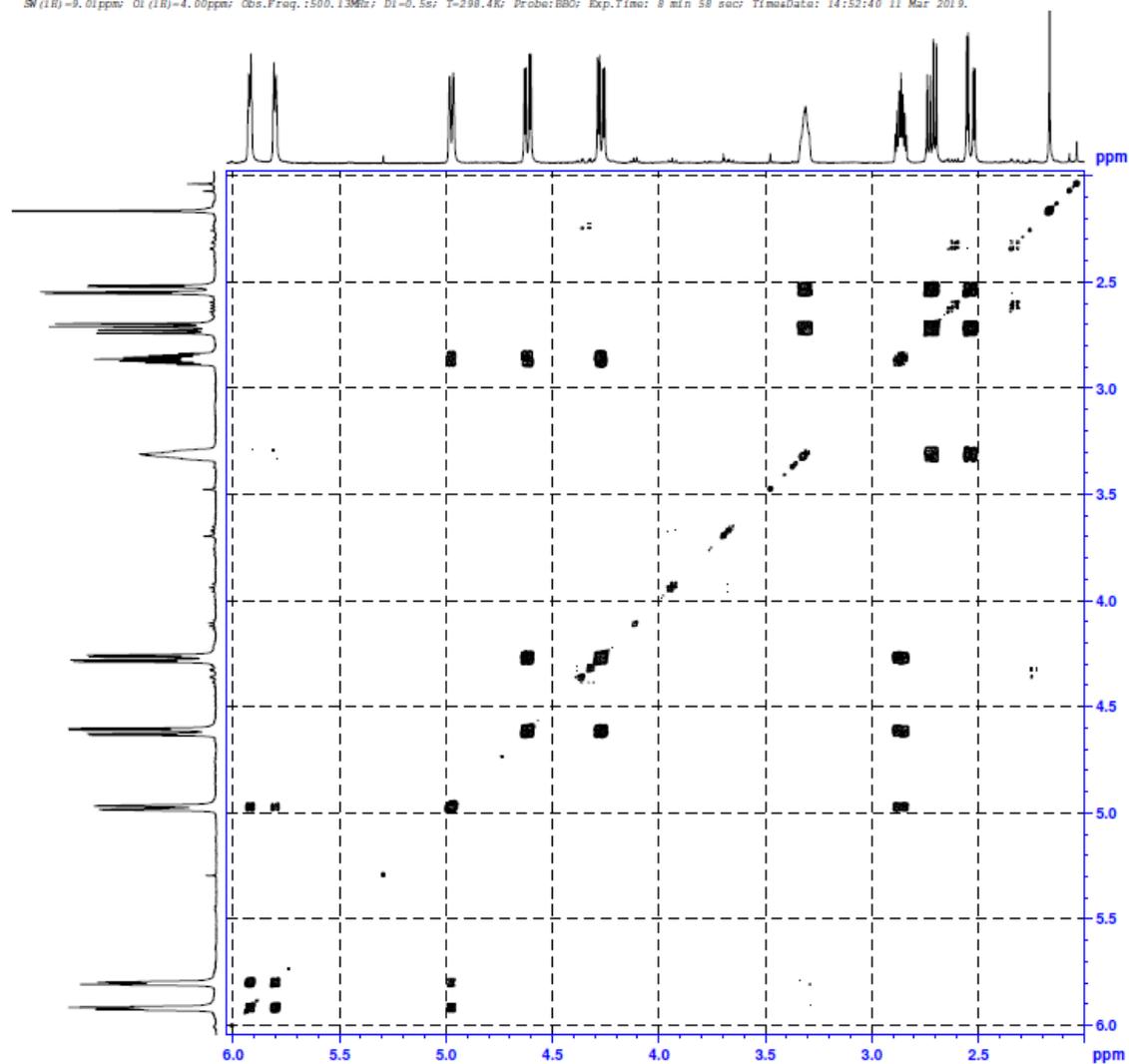
Ufa Institute of Chemistry of the Russian Academy of Sciences (UIC RAS) . 2019

SW(13C)=236.63ppm O1(13C)=110.00ppm Obs.Freq.:125.76MHz DI=1.5s T=298.5K Probe:BBQ Exp.Time: 3 min 12 sec TimesDate: 14:24:39 11 Mar 2019.



Sp-127 Almukhametov Pca-124-1-1 40mg in CDCl3, {1H, 1H} COSY AV500 11.03.2019 LAN  
 SW (1H)=9.01ppm; O1 (1H)=4.00ppm; Obs.Freq.:500.13MHz; D1=0.5s; T=298.4K; Probe:BB0; Exp.Time: 8 min 58 sec; TimesData: 14:52:40 11 Mar 2019.

Ufa Institute of Chemistry of the Russian Academy of Sciences (IUC RAS), 2019



```

Current Data Parameters
NAME      gnb-Pca-124-1-1-CDCl3
EXPNO     7
PROCNO    1

F2 - Acquisition Parameters
Date_     20190311
Time      14.52
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   cosyppgf
TD         4096
SOLVENT   CDCl3
NS         1
DS         16
SWH        4504.504 Hz
FIDRES     1.099733 Hz
AQ         0.4547060 sec
RG         49.8
DW         111.000 usec
DE         6.50 usec
TE         298.4 K
DO         0.00000300 sec
D1         0.50000000 sec
D13        0.00000400 sec
D16        0.00010000 sec
IN0        0.00022200 sec

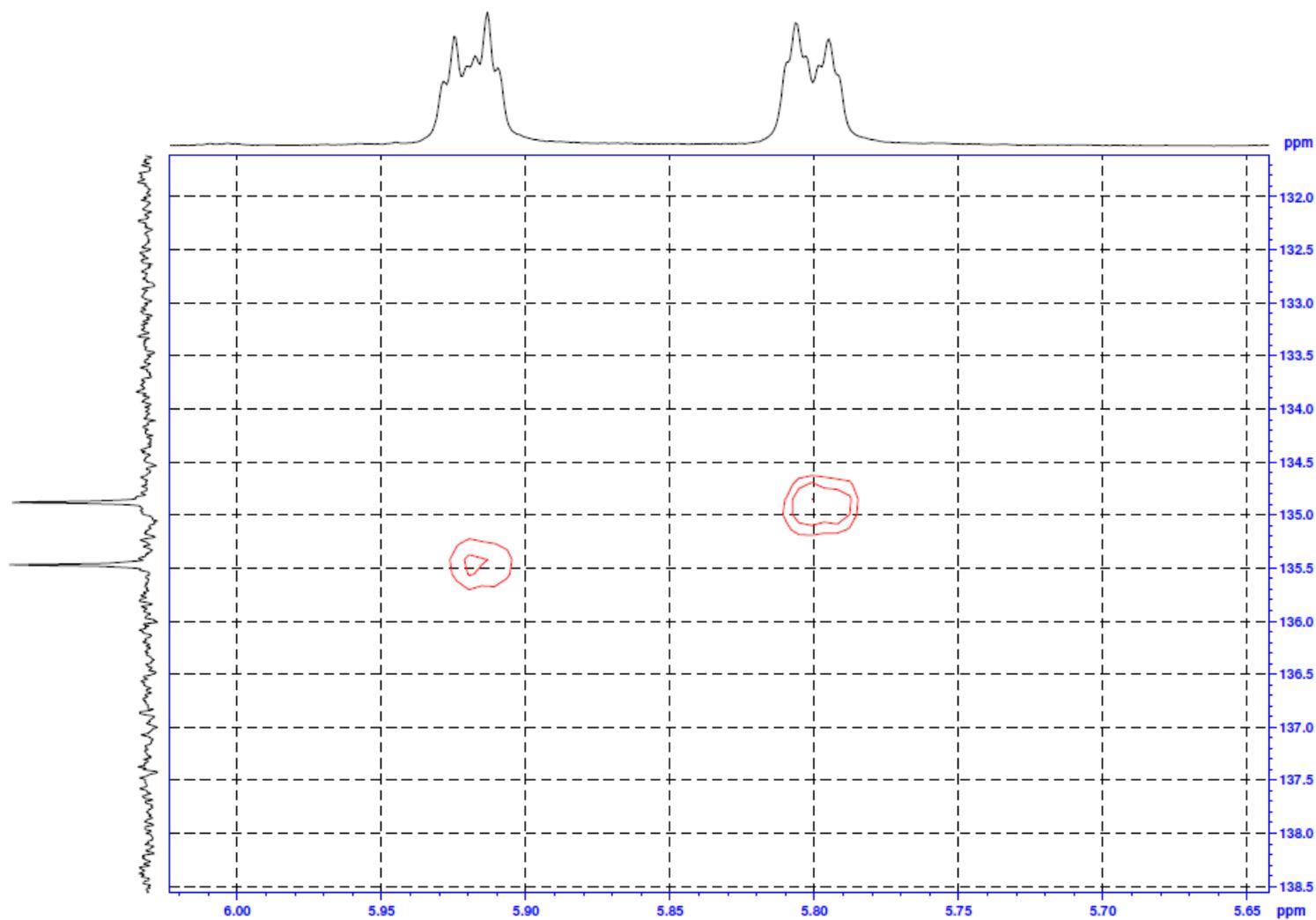
----- CHANNEL f1 -----
NUC1      1H
P0        11.50 usec
P1        11.50 usec
PLW1      15.84899998 W
SF01      500.1320005 MHz

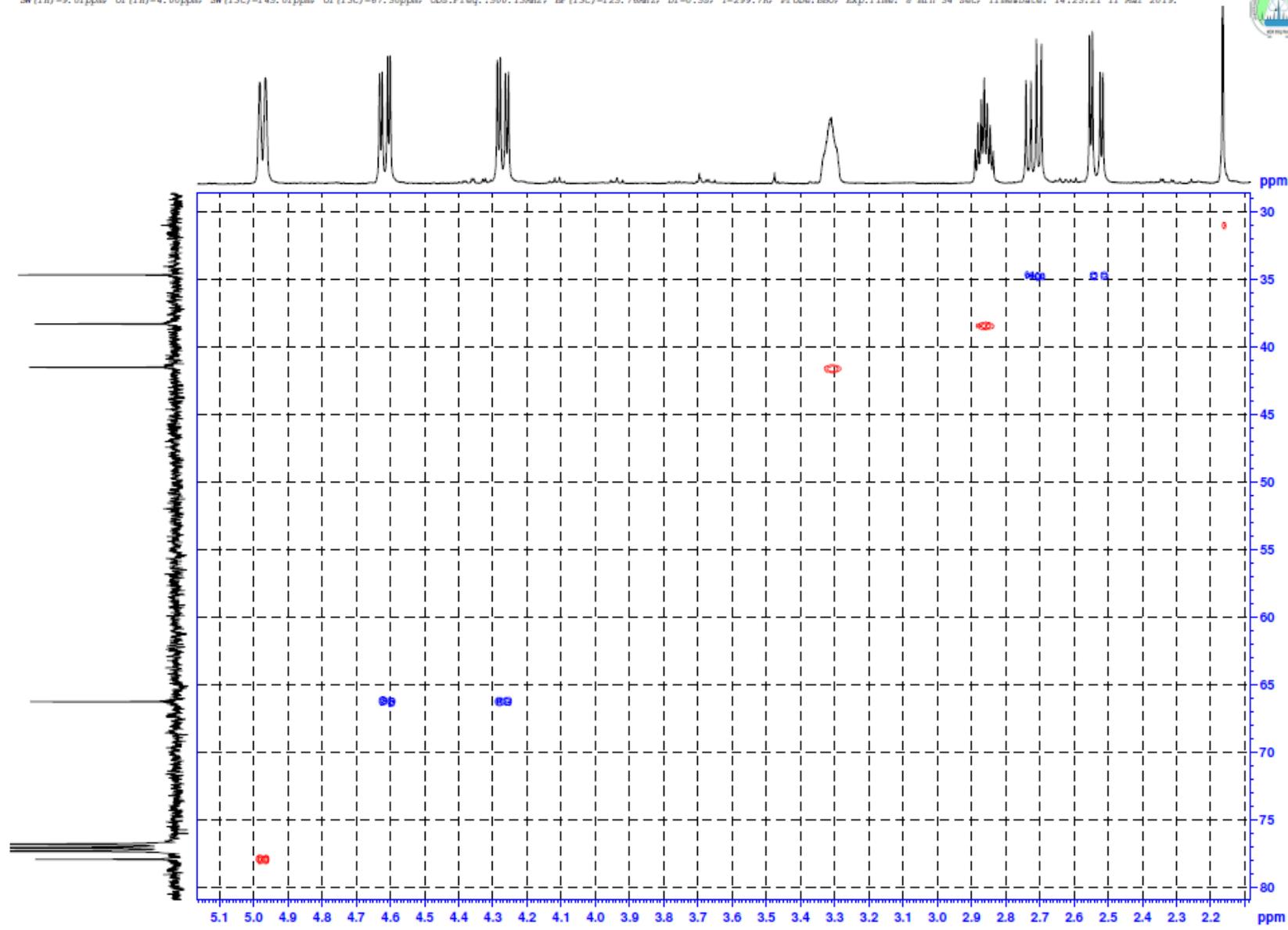
----- GRADIENT CHANNEL -----
GPMAM1    SMSQ10.100
GPZ1      10.00 %
P16       1000.00 usec

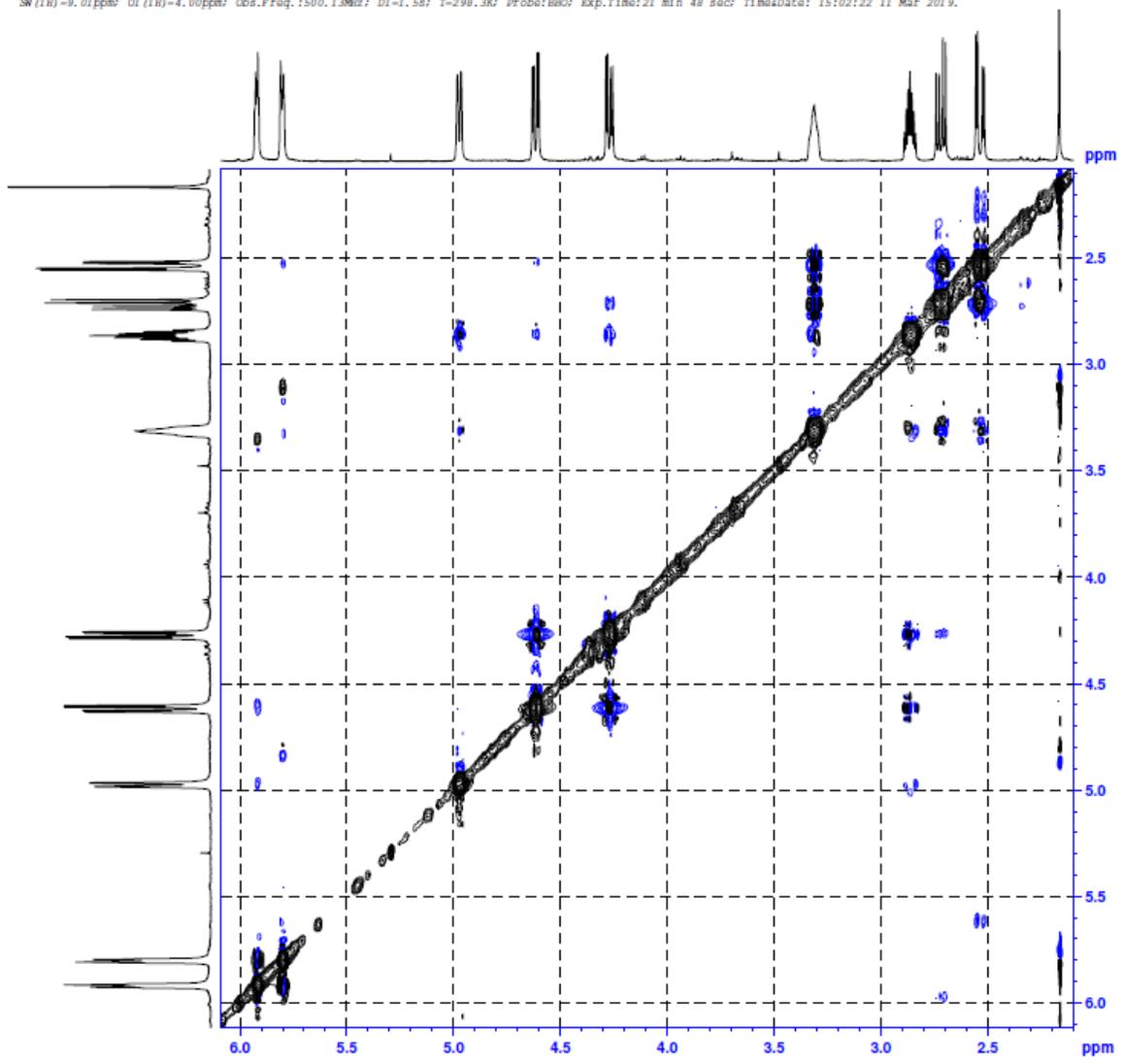
F1 - Acquisition parameters
TD         512
SF01       500.132 MHz
FIDRES     8.797859 Hz
SW         9.007 ppm
FnMODE     OF

F2 - Processing parameters
SI         2048
SF         500.1300132 MHz
WDW        QSIGN
SSB        0
LB         0 Hz
GB         0
PC         1.00

F1 - Processing parameters
SI         2048
MC2        OF
SF         500.1300132 MHz
WDW        TRAP
SSB        0
LB         0 Hz
GB         0
  
```







```

Current Data Parameters
NAME      gnb-Pca-124-1-1-CDC13
EXPNO     9
PROCNO    1

F2 - Acquisition Parameters
Data_     20190311
Time      15:02
INSTRUM   spect
PROBHD    5 mm PARBO BB-
PULPROG   noesyppgh
TD         4096
SOLVENT   CDC13
NS         2
DS         16
SWH        4504.504 Hz
FIDRES     1.099733 Hz
AQ         0.4547060 sec
RG         201.51
WDW        111.000 usec
DE         6.50 usec
TE         298.3 K
DQ         0.00009636 sec
D1         1.50000000 sec
DS         0.50000000 sec
D16        0.00010000 sec
IN0        0.00022200 sec

----- CHANNEL f1 -----
NUC1      1H
P1        11.50 usec
P2        23.00 usec
PLW1      15.84899998 W
SFO1      500.1320005 MHz

----- GRADIENT CHANNEL -----
GPNAM1    SINE.100
GPZ1      40.00 %
P16       1000.00 usec

F1 - Acquisition parameters
TD        217
SFO1      500.132 MHz
FIDRES    20.758083 Hz
SW        9.007 ppm
FMODER    StataS-TPPI

F2 - Processing parameters
SI         1024
SF         500.1300132 MHz
WDW        QSINE
SSB        2
LB         0 Hz
GB         0
PC         1.00

F1 - Processing parameters
SI         1024
MCZ        StataS-TPPI
SF         500.1300132 MHz
WDW        QSINE
SSB        2
LB         0 Hz
GB         0
    
```

**(4a*S*,7*S*,7a*R*)-7-hydroxy-4,4a,7,7a-tetrahydrocyclopenta[*c*]pyran-3(1*H*)-one (13b)**

Yield: 0.0325 g (25%); colorless transparent viscous oil;

$R_f = 0.3$  (petroleum ether/ethyl acetate, 3:1);  $[\alpha]_D^{20} : +193$  ( $c$  1.1,  $\text{CH}_2\text{Cl}_2$ ).

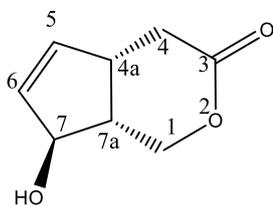
IR (liquid film): 3429, 1731, 1633, 1481, 1433, 1391, 1357, 1281, 1249, 1147, 1077, 1042, 1011, 963, 841, 780, 793  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta = 5.90$  (dt,  $J = 1.9, 5.7$  Hz, 1H,  $\text{C}^6\text{H}$ ), 5.84 (dd,  $J = 1.4, 5.5$  Hz, 1H,  $\text{C}^5\text{H}$ ), 4.8 (d,  $J = 2.1$  Hz, 1H,  $\text{C}^7\text{H}$ ), 4.39 (dd,  $J = 4.3, 11.7$  Hz, 1H,  $\text{C}^1\text{H}_\alpha$ ), 4.28 (dd,  $J = 4.8, 11.7$  Hz, 1H,  $\text{C}^1\text{H}_\beta$ ), 3.51 (m, 1H,  $\text{C}^{4a}\text{H}$ ), 2.72 (dd,  $J = 7.3, 15.1$ , 1H,  $\text{C}^4\text{H}_\alpha$ ), 2.52 (m, 1H,  $\text{C}^{7a}\text{H}$ ), 2.41 (dd,  $J = 4.8, 15.1$ , 1H,  $\text{C}^4\text{H}_\beta$ ).

$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta = 172.60$  (C=O), 137.00 ( $\text{C}^6$ ), 134.41 ( $\text{C}^5$ ), 81.07 ( $\text{C}^7$ ), 68.90 ( $\text{C}^1$ ), 45.02 ( $\text{C}^{7a}$ ), 41.15 ( $\text{C}^{4a}$ ), 40.66, 33.61 ( $\text{C}^4$ ).

MS (APCI):  $m/z$  (%) = 155 (100%)  $[\text{MH}]^+$ .

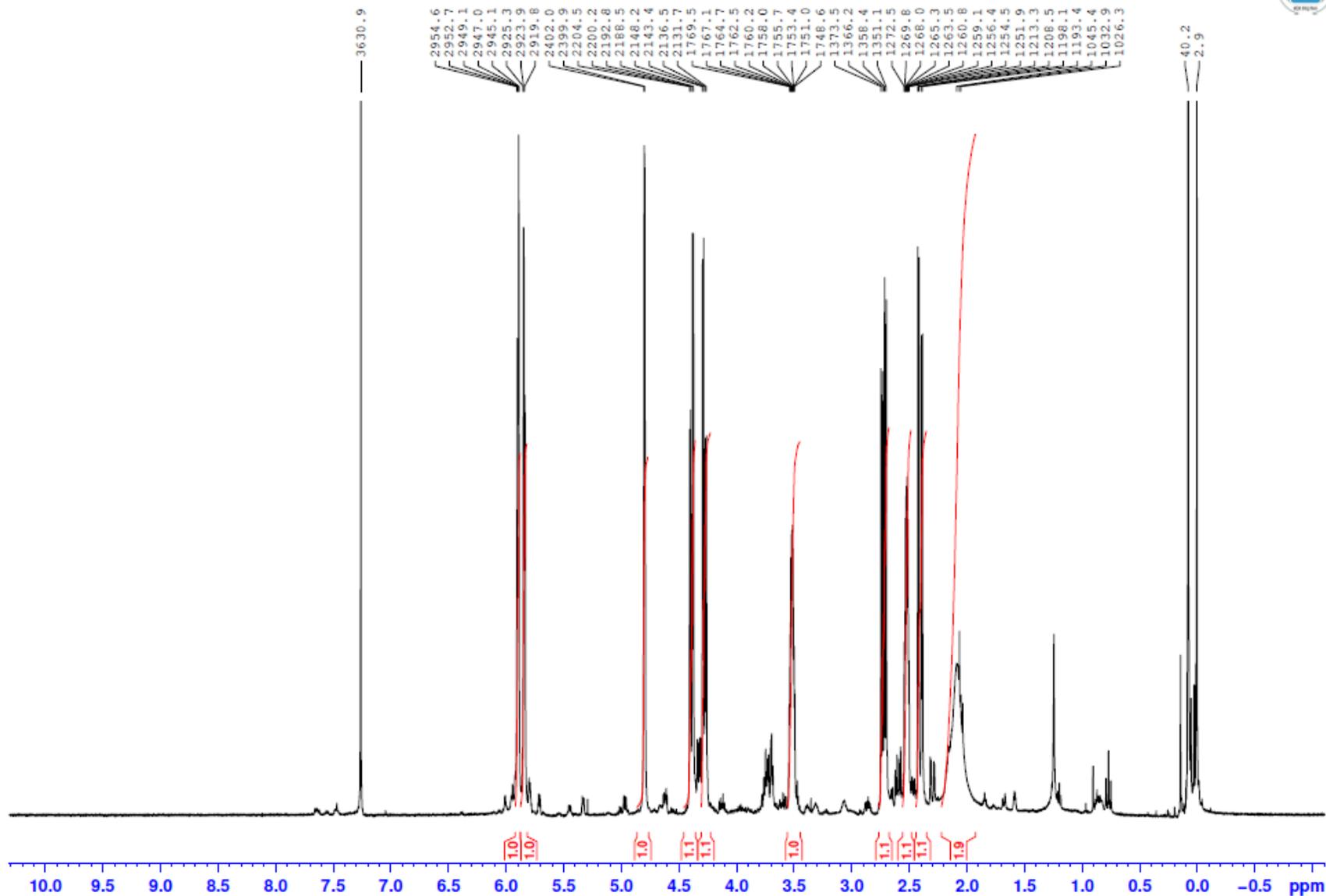
Anal. Calcd for  $\text{C}_8\text{H}_{10}\text{O}_3$ : C, 62.33; H, 6.54. Found: C, 62.09; H, 6.30.



13b

Sp-129 Almukhametov Pca-124-1-2 13mg in CDCl<sub>3</sub>, 1H AV500 11.03.2019 LAN  
SW(1H)=19.99ppm; O1(1H)=7.00ppm; Obs.Freq.:500.13MHz; D1=2.0s; T=298.3K; Probe:BBO; Exp.Time: 7 sec; TimesDate: 15:52:08 11 Mar 2019.

Ufa Institute of Chemistry of the Russian Academy of Sciences (IIC RAS). 2019

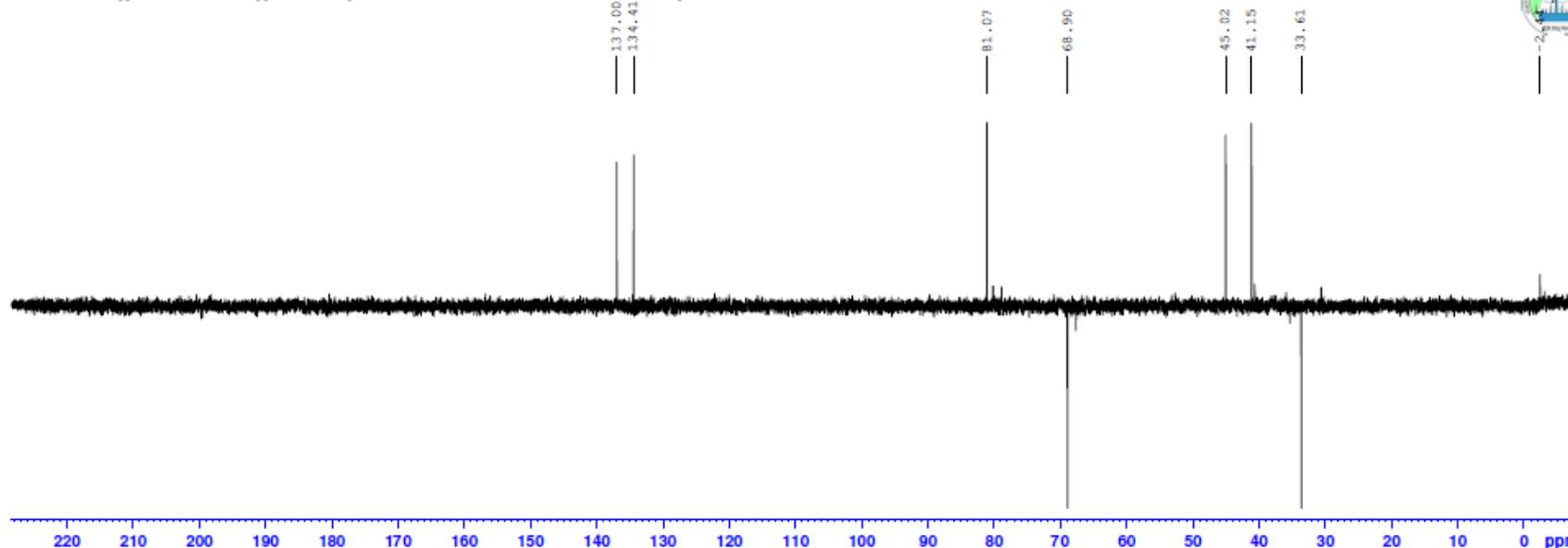


Sp-129 Almukhametov Pca-124-1-2 13mg in CDC13, 13C{1H} dept135 AV500 11.03.2019 LAN

Ufa Institute of Chemistry of the Russian Academy of Sciences (UIC RAS). 2019

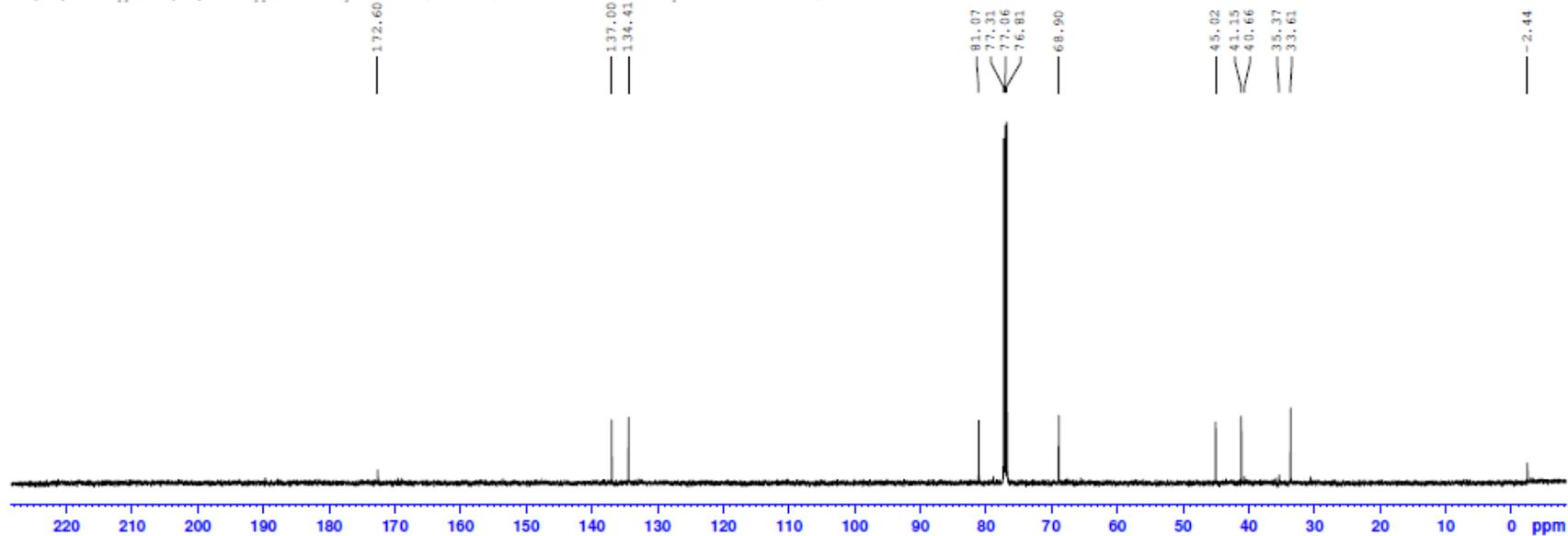


SW(13C)-236.63ppm O1(13C)-110.00ppm Obs.Freq.:125.76MHz DI=1.5s T=298.8K Probe:BB07 Exp.Time: 3 min 12 sec TimesDate: 16:04:39 11 Mar 2019.

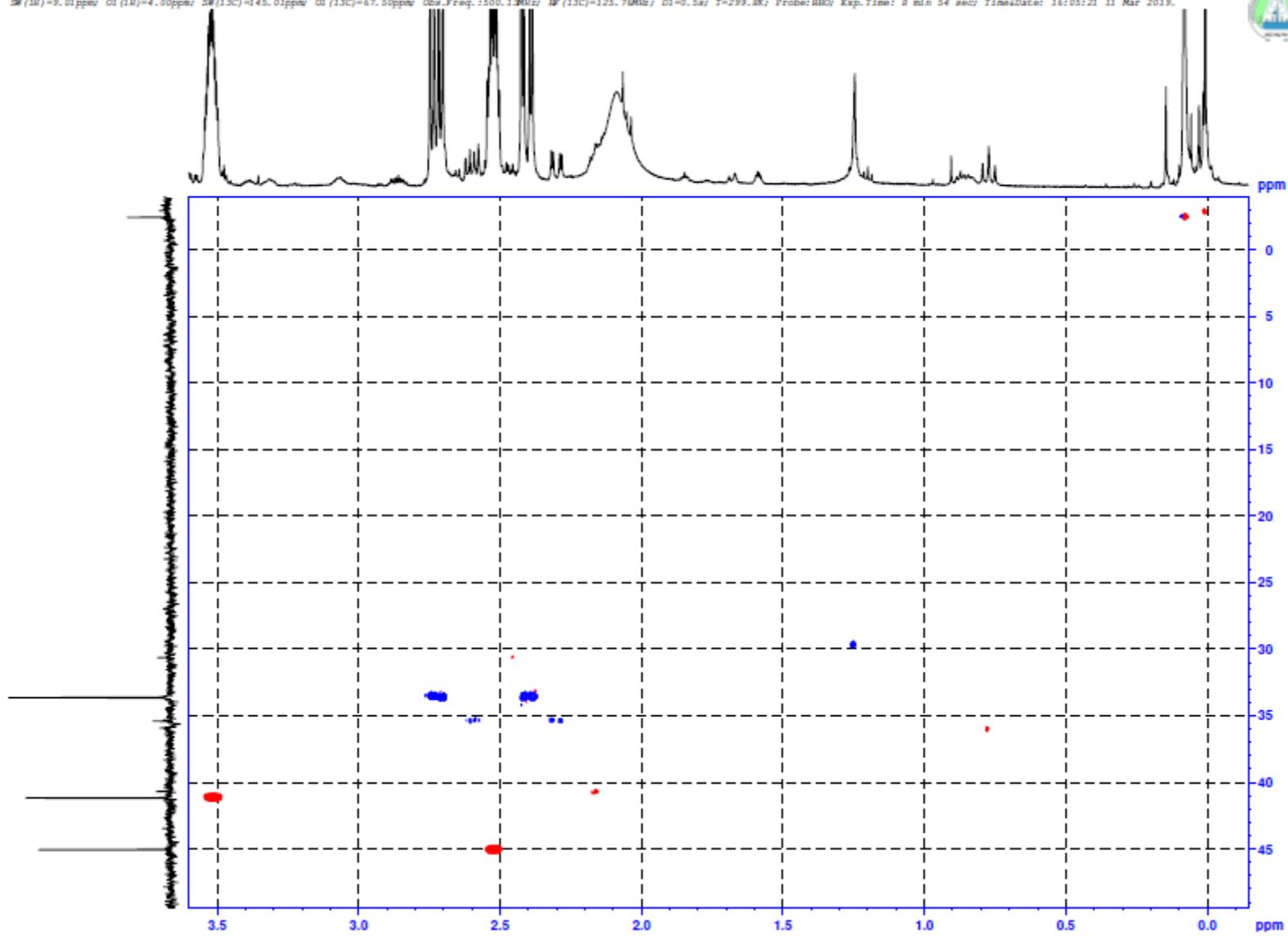


Sp-129 Almukhametov Pca-124-1-2 13mg in CDC13, 13C{1H} com AV500 11.03.2019 LAN

SW(13C)-236.63ppm O1(13C)-110.00ppm Obs.Freq.:125.76MHz DI=0.9s T=299.1K Probe:BB07 Exp.Time: 8 min 58 sec TimesDate: 15:58:24 11 Mar 2019.



Sp-129 Almukhametov Pca-124-1-2 13mg in CDCl<sub>3</sub>, (1H, 13C) HSQCED AV500 11.03.2019 IAN OIa Institute of Chemistry of the Russian Academy of Sciences (IC RAS). 2019  
SW(1H)=9.01ppm CI(1H)=4.00ppm SW(13C)=145.01ppm CI(13C)=67.50ppm Obs.Freq.:100.126MHz NF(13C)=125.76MHz Q1=0.5sx T=299.8K; Probe:BB0; Exp.Time: 8 min 54 sec; TimeDate: 16:05:21 11 Mar 2019.

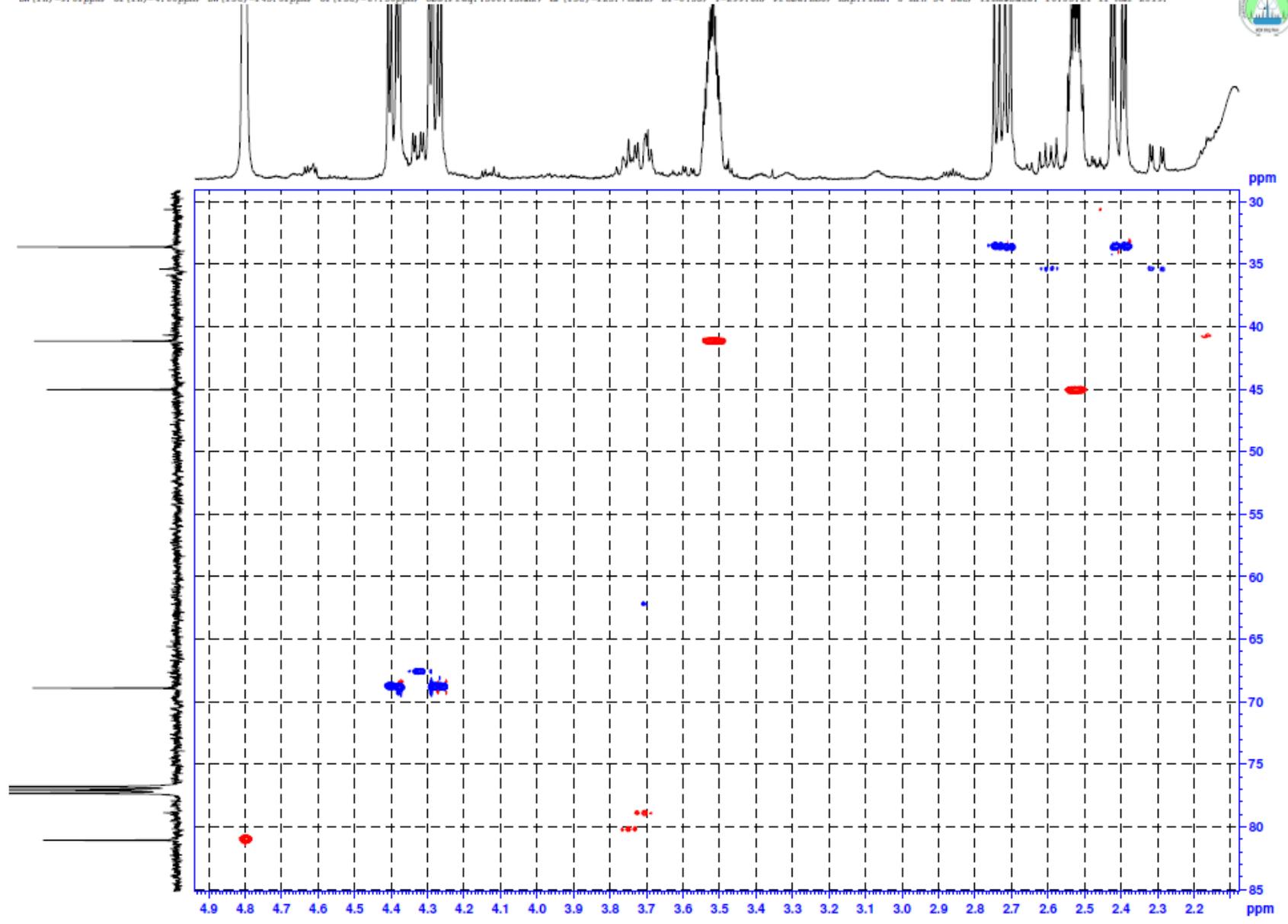


Sp-129 Almukhametov Pca-124-1-2 13mg in CDCl<sub>3</sub>, {1H, 13C} HSQCED AV500 11.03.2019 IAN

Ufa Institute of Chemistry of the Russian Academy of Sciences (IIC RAS), 2019

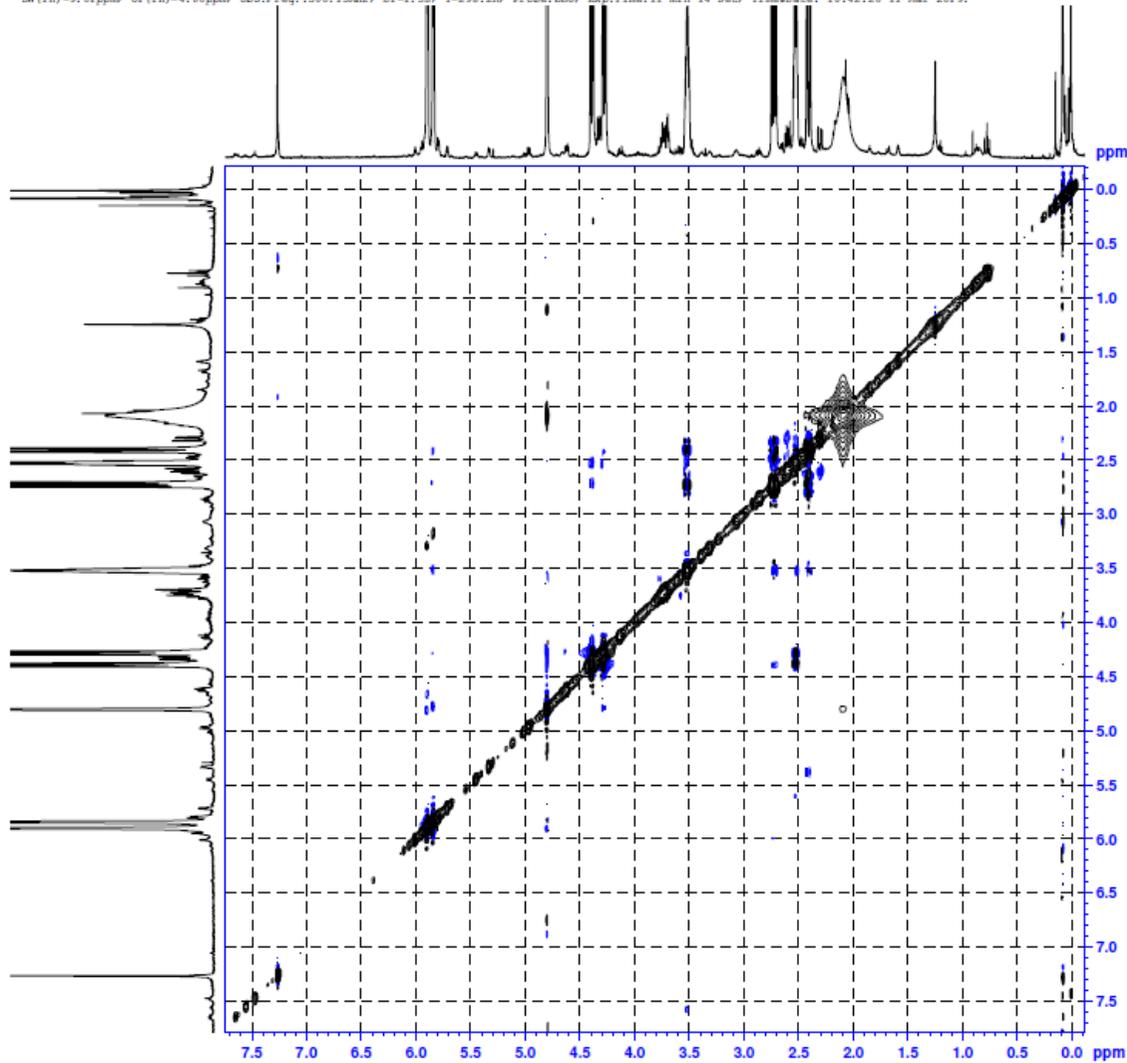


SN (1H)-9.01ppm; O1 (1H)-4.00ppm; SW (13C)-145.01ppm; O1 (13C)-67.50ppm; Obs.Freq.:500.13MHz; RF (13C)-125.76MHz; D1-0.5s; T-299.8K; Probe:BBO; Exp.Time: 8 min 54 sec; TimeDate: 16:05:21 11 Mar 2019.



Sp-129 Almkhametov Pca-124-1-2 13mg in CDCl3, {1H, 1H} NOESY AV500 11.03.2019 LAN  
 SW (1H) = 9.01 ppm; DI (1H) = 4.00 ppm; Obs. Freq. = 500.13 MHz; DI = 1.5 s; T = 298.2 K; Probe: BB0; Exp. Time: 11 min 14 sec; Time Date: 16:42:26 11 Mar 2019.

Ufa Institute of Chemistry of the Russian Academy of Sciences (IIC RAS), 2019



```

Current Data Parameters
NAME      gnb-Pca-124-1-2-CDCl3
EXPNO     9
PROCNO    1

F2 - Acquisition Parameters
Date_     20190311
Time      16.42
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   noesypph
TD         4096
SOLVENT   CDCl3
NS         2
DS         16
SWH        4504.504 Hz
FIDRES     1.099733 Hz
AQ         0.4547060 sec
RG         201.51
DW         111.000 usec
DE         6.50 usec
TE         298.2 K
D0         0.00009636 sec
D1         1.50000000 sec
D8         0.50000000 sec
D16        0.00010000 sec
IN0        0.00022200 sec

----- CHANNEL f1 -----
NUC1       1H
P1         11.50 usec
P2         23.00 usec
PLW1       15.84899998 W
SFO1       500.1320005 MHz

----- GRADIENT CHANNEL -----
CHANML     SINE 100
CP21       40.00 %
P16        1000.00 usec

F1 - Acquisition parameters
TD         128
SFO1       500.132 MHz
FIDRES     35.191437 Hz
SW         9.007 ppm
F2MODEX    States-TPPI

F2 - Processing parameters
SI         1024
SF         500.1300133 MHz
WDW        QSINE
SSB        2
LB         0 Hz
GB         0
PC         1.00

F1 - Processing parameters
SI         1024
MC2        States-TPPI
SF         500.1300133 MHz
WDW        14.6q
SSB        2
LB         0 Hz
GB         0
  
```

**(4a*S*,7a*R*)-1,4,4a,7a-tetrahydrocyclopenta[*c*]pyran-3,7-dione (6)**

A mixture of isomeric allylic alcohols **13a,b** (0.13 g, 0.844 mmol) in acetone (10 mL) was oxidized with Jones reagent. The resulting solution was treated with 2-propanol (1 mL) and saturated solution of NaHCO<sub>3</sub> (0.5 mL). Extraction of the product into EtOAc after removal acetone *in vacuo* and next purification on SiO<sub>2</sub> (chloroform/methanol, 10:1) gave product **6**.

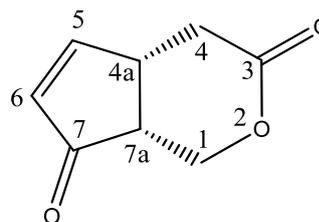
Yield: 0.1 g (79%); white solid; mp 104-108°C; *R*<sub>f</sub> = 0.6 (chloroform/methanol, 10:1); [α]<sub>D</sub><sup>20</sup>: +346.2 (*c* 1.0, CH<sub>2</sub>Cl<sub>2</sub>).

IR (liquid film): 1740, 1712, 1582, 1441, 1355, 1311, 1284, 1214, 1176, 1149, 1081, 1066, 1034, 959, 807, 793 cm<sup>-1</sup>.

<sup>1</sup>H NMR (500 MHz, acetone-*d*<sub>6</sub>): δ = 7.84 (dd, *J* = 2.6, 5.7 Hz, 1H, C<sup>5</sup>H), 6.31 (dd, *J* = 1.9, 5.7 Hz, 1H, C<sup>6</sup>H), 4.45 (dddd, *J* = 4.0, 2.4, 11.5 Hz, 2H, C<sup>1</sup>H<sub>2</sub>), 4.13 (dd, *J* = 2.4, 11.5 Hz, 1H, C<sup>1</sup>H<sub>β</sub>), 3.73 (m, 1H, C<sup>4a</sup>H), 3.11 (dd, *J* = 7.9, 15.4 Hz, 1H, C<sup>4</sup>H<sub>α</sub>), 2.79 (tdd, *J* = 1.6, 7.1, 6.8 Hz, 1H, C<sup>7a</sup>H), 2.65 (dd, *J* = 2.5, 5.4 Hz, 1H, C<sup>4</sup>H).

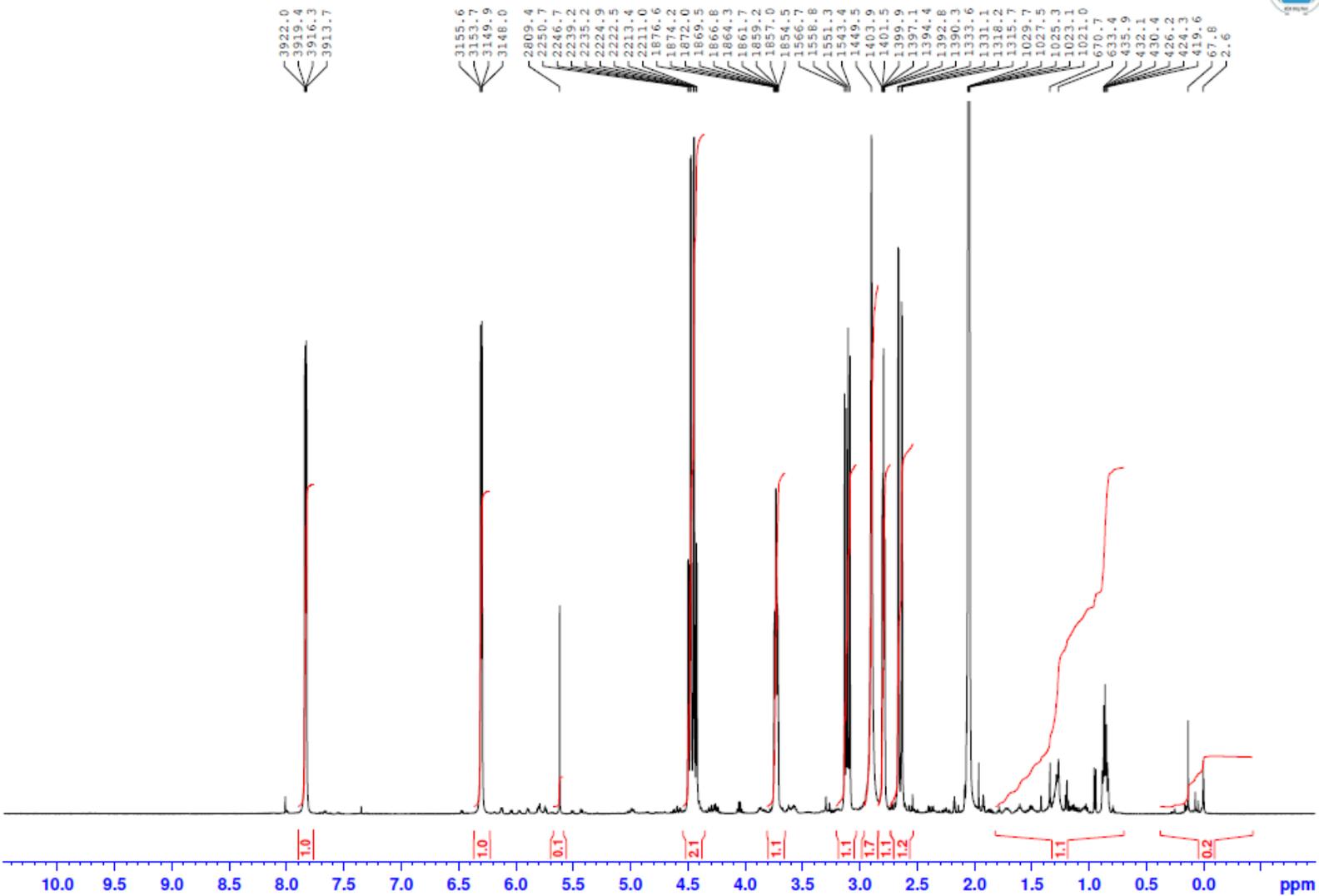
<sup>13</sup>C NMR (125 MHz, acetone-*d*<sub>6</sub>): δ = 208.28 (C<sup>7</sup>), 171.10 (C<sup>3</sup>), 167.89 (C<sup>5</sup>), 136.16 (C<sup>6</sup>), 66.97 (C<sup>1</sup>), 44.27 (C<sup>7a</sup>), 38.95 (C<sup>4a</sup>), 33.30 (C<sup>4</sup>).

MS (APCI): *m/z* (%) = 153 (100) [MH]<sup>+</sup>.



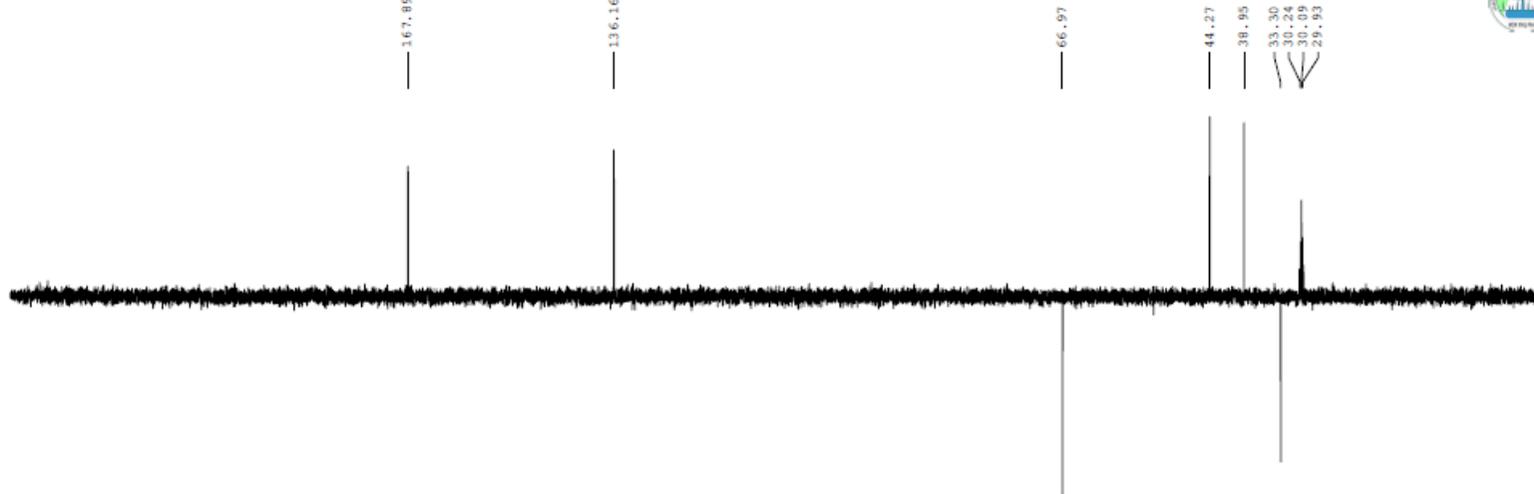
Anal. Calcd for C<sub>8</sub>H<sub>8</sub>O<sub>3</sub>: C, 63.15; H, 5.30. Found: C, 62.86; H, 5.05.

**6**

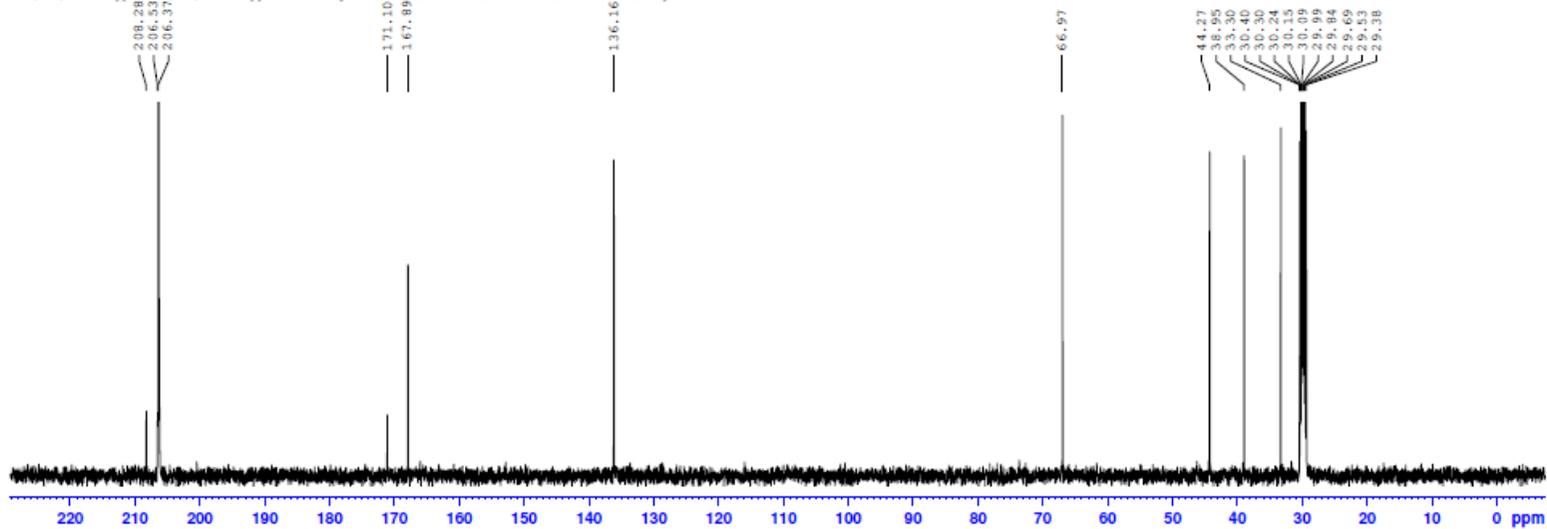


Sp-109 Almkhametov Pca-128 16mg in Acetone, 13C{1H} dept135 AV500 12.03.2019 IAN  
SW (13C)=-236.63ppm O1 (13C)=-110.00ppm Obs.Prog.:125.76MHz; D1=1.0s; T=298.0K; Probe:BBQ; Exp.Time: 2 min 27 sec; TimesDate: 09:21:16 12 Mar 2019.

Ufa Institute of Chemistry of the Russian Academy of Sciences (UIC RAS). 2019



Sp-109 Almkhametov Pca-128 16mg in Acetone, 13C{1H} com AV500 12.03.2019 IAN  
SW (13C)=-236.63ppm O1 (13C)=-110.00ppm Obs.Prog.:125.76MHz; D1=0.9s; T=298.2K; Probe:BBQ; Exp.Time: 5 min 44 sec; TimesDate: 09:18:19 12 Mar 2019.



### (4a*R*,7a*R*)-Hexahydrocyclopenta[*c*]pyran-3,7-dione (**14**)

Hydrogenation of enone **6** (0.036 g, 0.024 mmol) was carried out in methanol (3 mL) in the presence of Pd/C (0.036 g) for 5 h. The reaction was stopped when the gas absorption ceased. The product has  $R_f$  the same as the starting material. Filtration and evaporation of the solvent gave product **14**.

Yield: 0.035 g (95%); white amorphous mass;  $R_f = 0.6$  (chloroform/methanol, 10:1);  $[\alpha]_D^{20} : +150$  ( $c$  1.0, CH<sub>2</sub>Cl<sub>2</sub>).

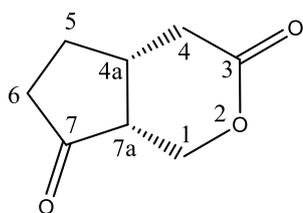
IR (liquid film): 2960, 2925, 1736, 1478, 1429, 1413, 1384, 1350, 1328, 1275, 1250, 1241, 1172, 1152, 1100, 1061, 1031, 949 cm<sup>-1</sup>.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 4.56$  (dd,  $J = 3.6, 11.7$  Hz, 1H, C<sup>1</sup>H <sub>$\alpha$</sub> ), 4.30 (dd,  $J = 5.6, 11.7$  Hz, 1H, C<sup>1</sup>H <sub>$\beta$</sub> ), 3.01-3.10 (m, 1H, C<sup>4a</sup>H), 2.76 (dd,  $J = 6.6, 15.5$  Hz, 1H, C<sup>6</sup>H <sub>$\alpha$</sub> ), 2.65-2.60 (m, 1H, C<sup>7a</sup>H), 2.53 (dd,  $J = 4.3, 15.6$  Hz, 1H, C<sup>6</sup>H <sub>$\beta$</sub> ), 2.41-2.30 (m, 2H, C<sup>4</sup>H<sub>2</sub>), 1.68-1.57 (m, 2H, C<sup>5</sup>H<sub>2</sub>).

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta = 216.02$  (C<sup>7</sup>), 171.85 (C<sup>3</sup>), 66.19 (C<sup>1</sup>), 44.75 (C<sup>7a</sup>), 37.92 (C<sup>6</sup>), 34.45 (C<sup>4</sup>), 31.13 (C<sup>4a</sup>), 27.84 (C<sup>5</sup>).

MS (APCI):  $m/z$  (%) = 155 (100) [MH]<sup>+</sup>.

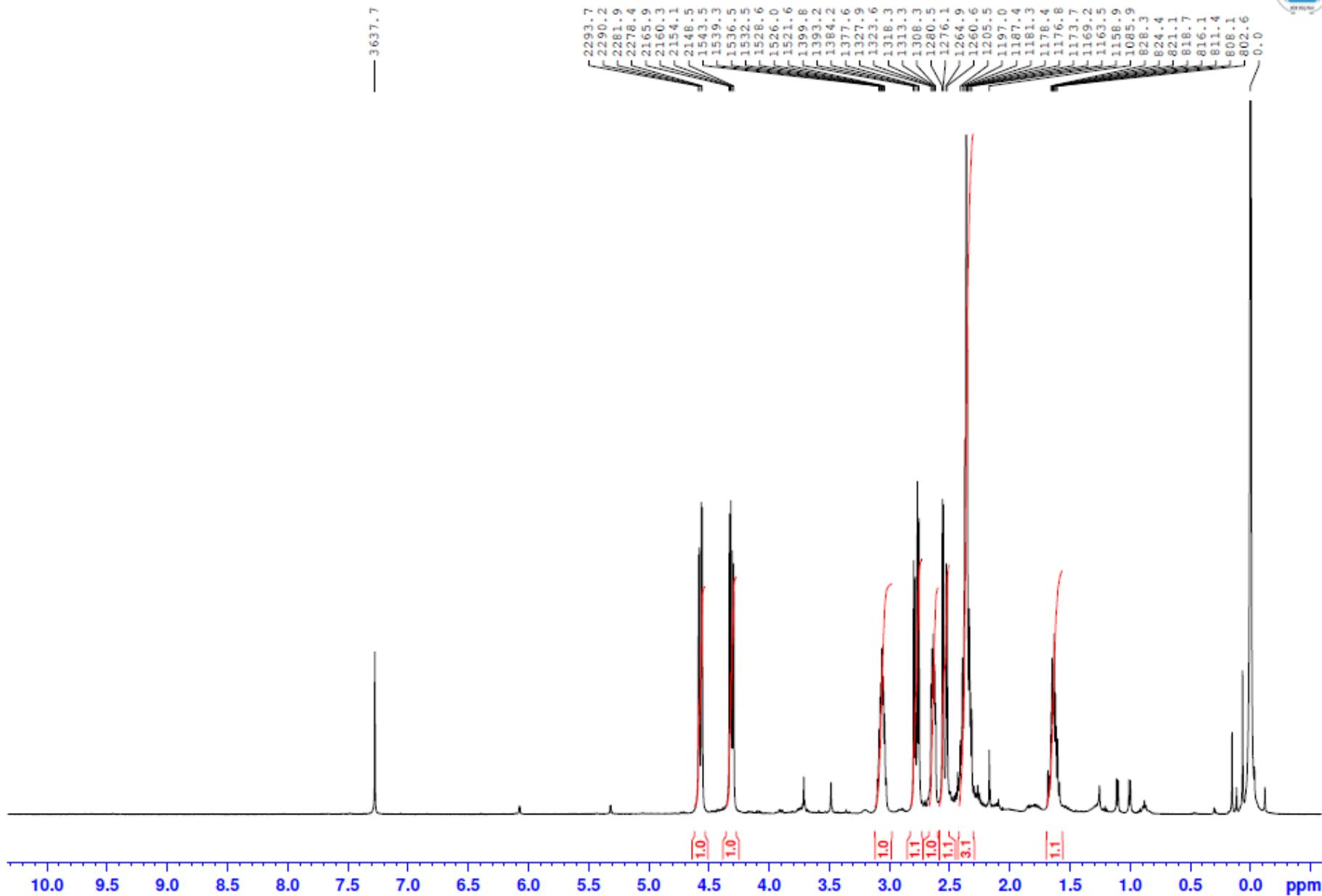
Anal. Calcd for C<sub>8</sub>H<sub>10</sub>O<sub>3</sub>: C, 62.33; H, 6.54. Found: C, 62.11; H, 6.38.



**14**

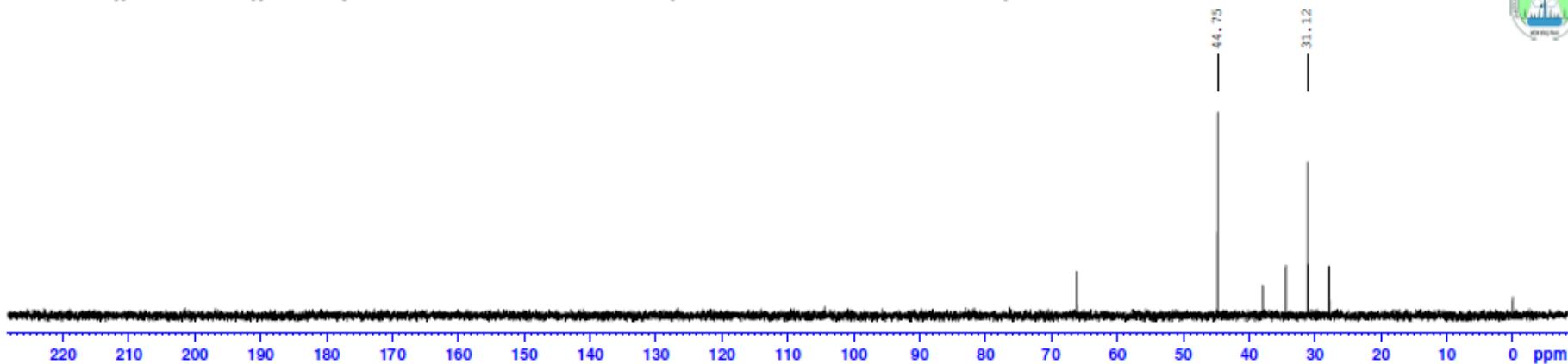
Sp-236 Almukhametov Pca-130 14mg in CDCl3, 1H AV500 27.04.2019 NTR  
SW (1H)=19.99ppm O1 (1H)=7.00ppm Obs. Freq.:500.13MHz; D1=2.0s; T=299.8K; Probe:BB0; Exp. Time: 1 min 32 sec; TimesDate: 12:52:02 27 Apr 2019.

Ufa Institute of Chemistry of the Russian Academy of Sciences (IIC RAS). 2019

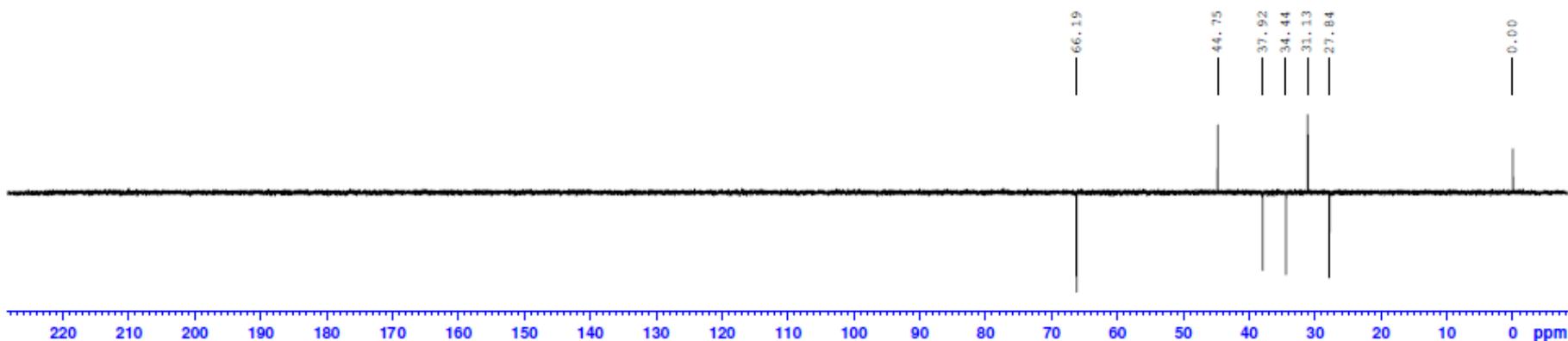


Sp-236 Almukhametov Pca-130 14mg in CDC13, <sup>13</sup>C{<sup>1</sup>H} dept90 AV500 27.04.2019 NTR  
SW (13C)-236.63ppm O1 (13C)-110.00ppm Obs.Freq.:125.76MHz DI=1.5s T=300.1K; Probe:BBO; Exp.Time: 5 min 51 sec; TimesDate: 12:57:33 27 Apr 2019.

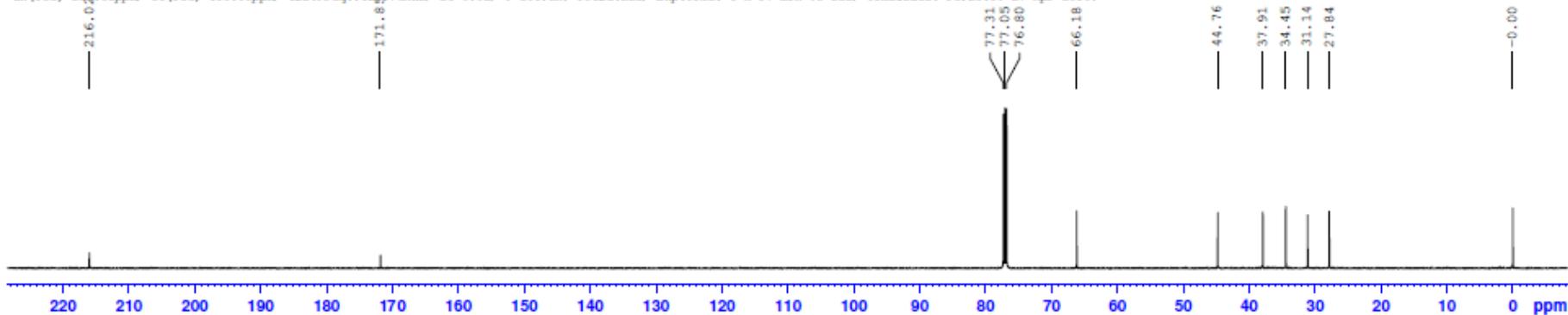
Ufa Institute of Chemistry of the Russian Academy of Sciences (UIC RAS). 2019



Sp-236 Almukhametov Pca-130 14mg in CDC13, <sup>13</sup>C{<sup>1</sup>H} dept135 AV500 27.04.2019 NTR  
SW (13C)-236.63ppm O1 (13C)-110.00ppm Obs.Freq.:125.76MHz DI=1.5s T=300.1K; Probe:BBO; Exp.Time: 4 min 47 sec; TimesDate: 12:54:53 27 Apr 2019.

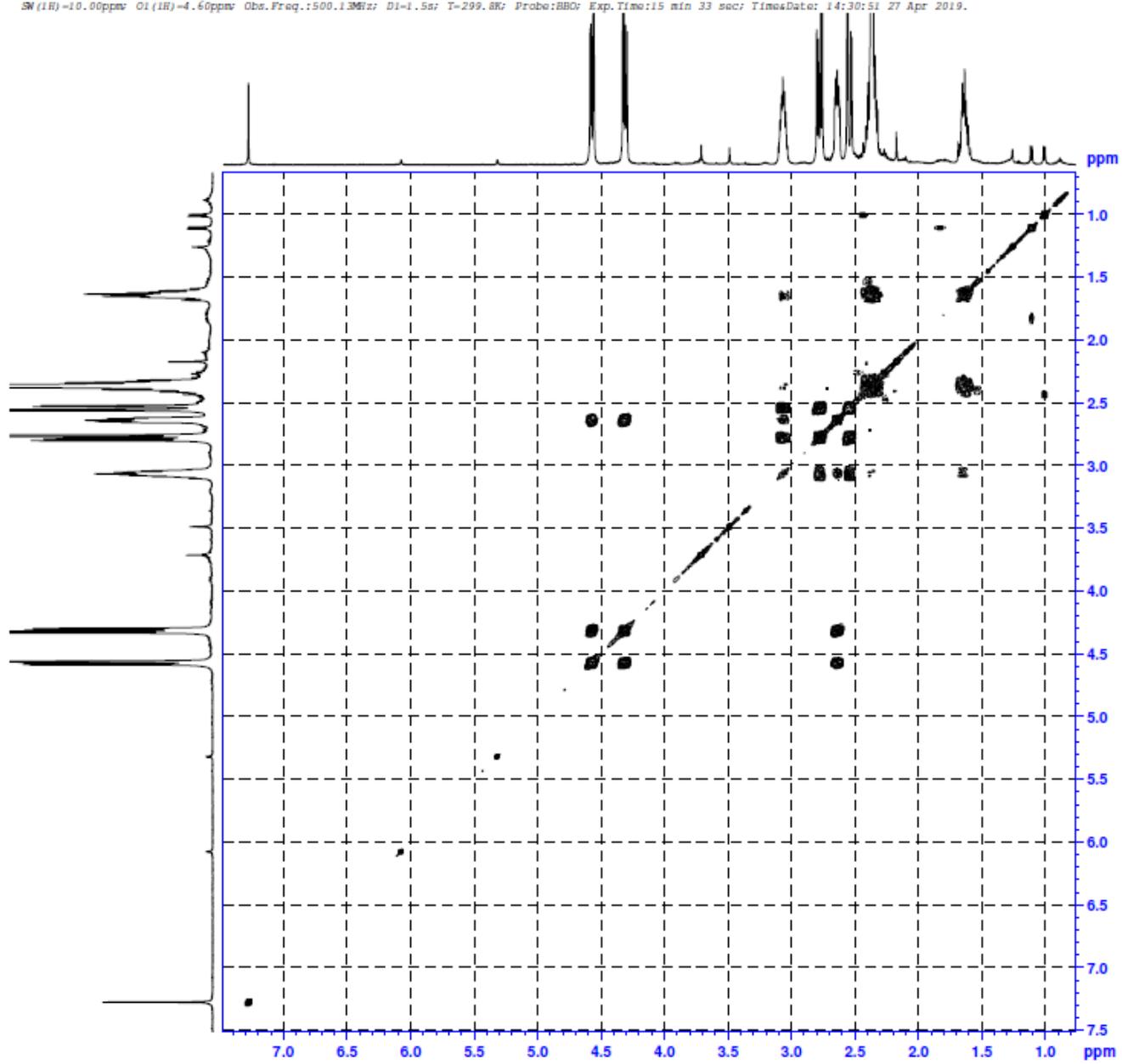


Sp-236 Almukhametov Pca-130 14mg in CDC13, <sup>13</sup>C{<sup>1</sup>H} com AV500 27.04.2019 NTR  
SW (13C)-236.63ppm O1 (13C)-110.00ppm Obs.Freq.:125.76MHz DI=0.9s T=301.3K; Probe:BBO; Exp.Time: 1 h 17 min 48 sec; TimesDate: 18:28:04 27 Apr 2019.



Sp-236 Almukhametov Pca-130 14mg in CDCl3, {1H, 1H} COSY AV500 27.04.2019 NTR  
 SW (1H) -10.00ppm O1 (1H) -4.60ppm Obs.Freq.:500.13MHz D1-1.5s; T-299.8K; Probe:BB0; Exp.Time:15 min 33 sec; TimesDate: 14:30:51 27 Apr 2019.

Ufa Institute of Chemistry of the Russian Academy of Sciences (UTC RAS). 2019



```

Current Data Parameters
NAME      gnb-Pca-130
EXPNO     7
PROCNO    1

F2 - Acquisition Parameters
Date_     20190427
Time      14:30
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   cosygpgf
TD         2048
SOLVENT   CDCl3
NS         1
DS         16
SWH        5000.000 Hz
FIDRES     2.441406 Hz
AQ         0.2048500 sec
RG         18.74
DW         100.000 usec
DE         6.50 usec
TE         299.8 K
D0         0.00000300 sec
D1         1.50000000 sec
D13        0.00000400 sec
D16        0.00010000 sec
IN0        0.00020000 sec

----- CHANNEL f1 -----
NUC1       1H
P0         11.50 usec
P1         11.50 usec
PLWL      15.84899998 W
SFO1       500.1323006 MHz

----- GRADIENT CHANNEL -----
CPN1M1     SMSQ10.100
CPE1       10.00 %
P16        1000.00 usec

F1 - Acquisition parameters
TD         512
SFO1       500.1323 MHz
FIDRES     9.765625 Hz
SW         9.997 ppm
FnMODE     QF

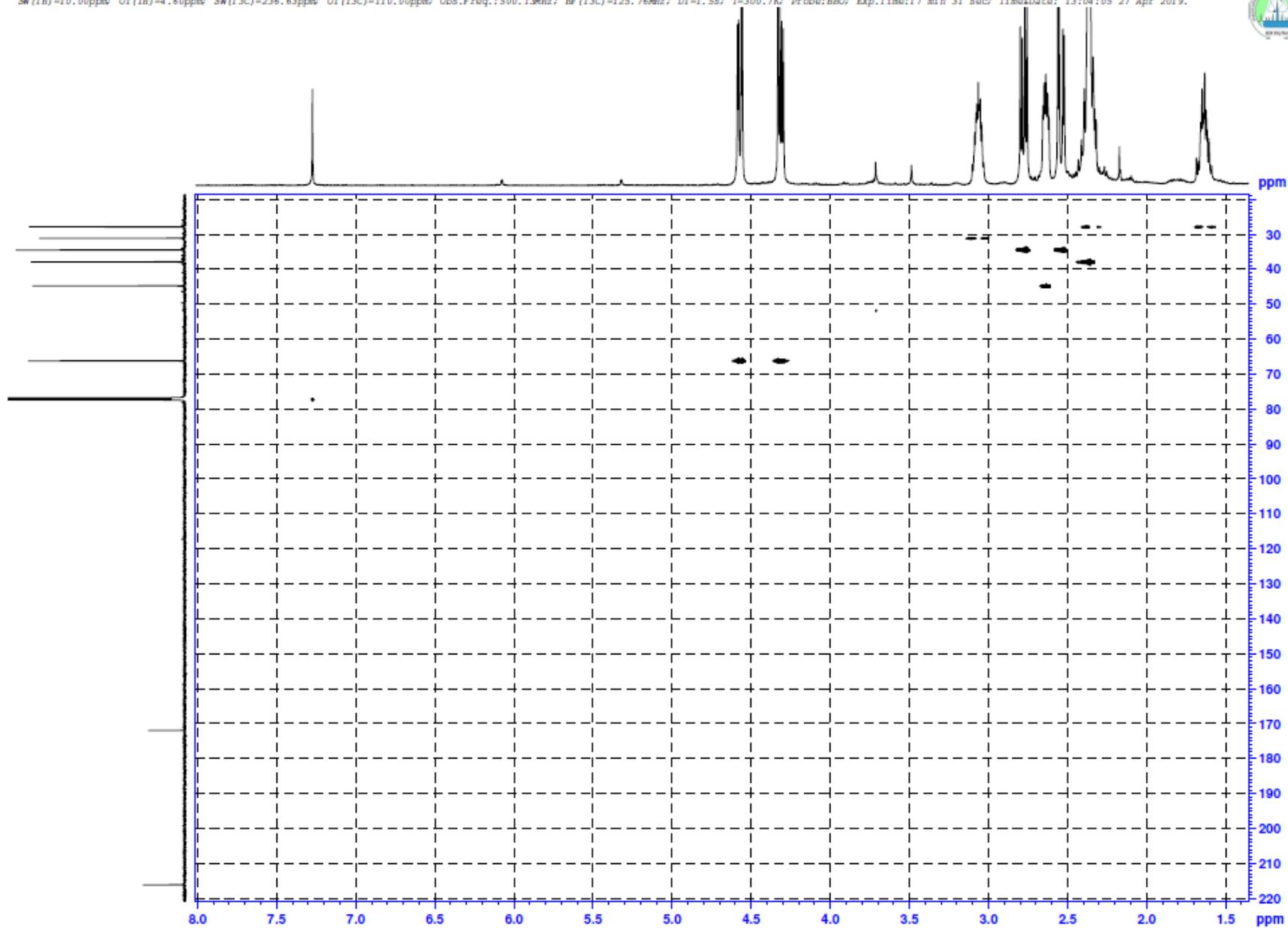
F2 - Processing parameters
SI         2048
SF         500.1300057 MHz
WDW        QSINE
SSB        0
LB         0 Hz
CB         0
PC         1.00

F1 - Processing parameters
SI         2048
MC2        QF
SF         500.1300057 MHz
WDW        USER
SSB        0
LB         0 Hz
CB         0
  
```

Sp-236 Almukhametov Pca-130 14mg in CDCl<sub>3</sub>, (1H, 13C) HSQC AV500 27.04.2019 NIR

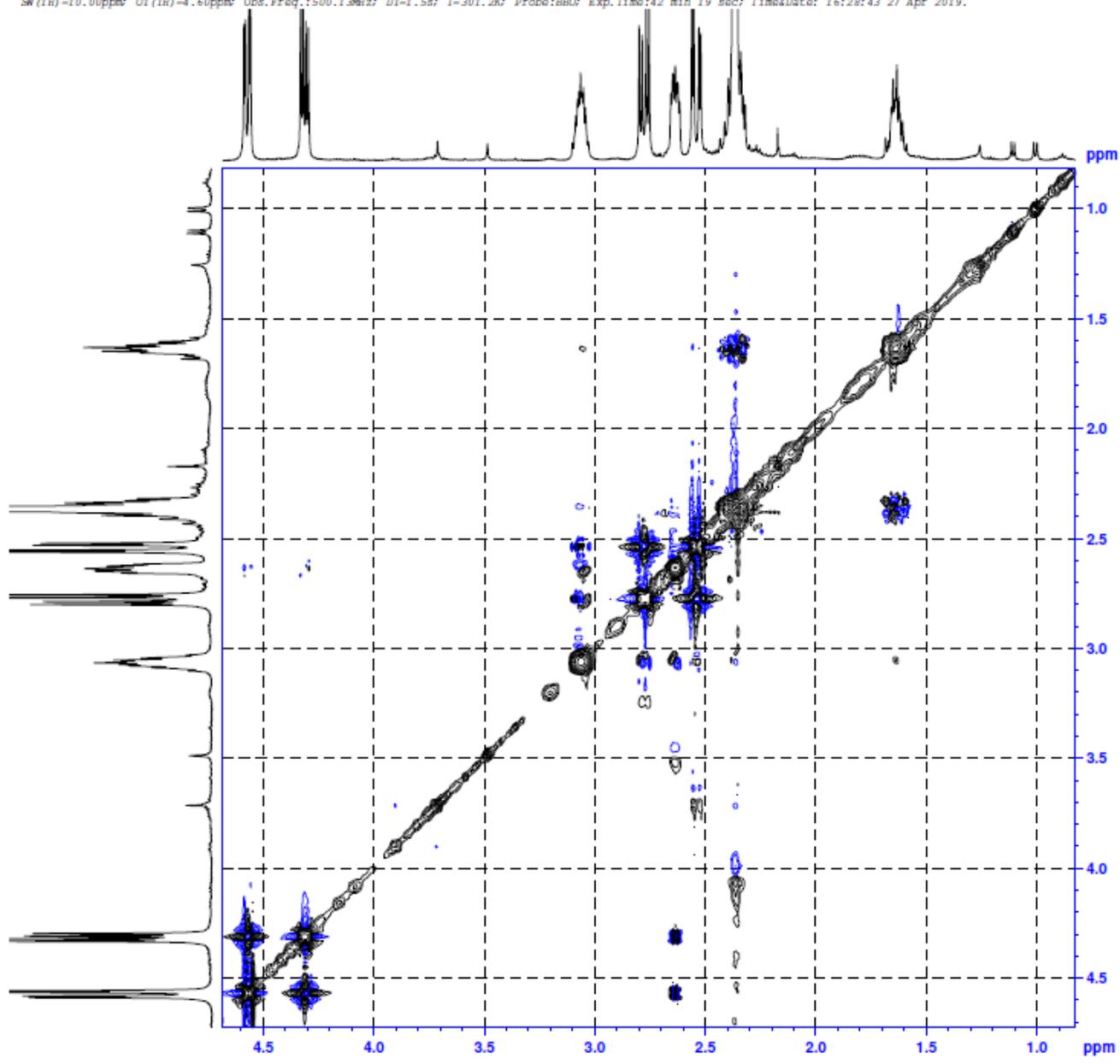
Ufa Institute of Chemistry of the Russian Academy of Sciences (UIC RAS), 2019

SW(1H)=10.00ppm O1(1H)=4.60ppm SW(13C)=236.63ppm O1(13C)=110.00ppm Obs.Freq.:500.13MHz; BF(13C)=125.76MHz; D1=1.5s; T=300.7K; Probe:BBO; Exp.Time:17 min 31 sec; TimesDate: 13:04:05 27 Apr 2019.



Sp-236 Almukhametov Pca-130 14mg in CDCl3, (1H, 1H) NOESY AV500 27.04.2019 NTR  
 SW (1H)=10.00ppm; O1 (1H)=4.60ppm; Obs.Freq.:500.13MHz; D1=1.5s; T=301.2K; Probe:BBQ; Exp.Time:42 min 19 sec; TimesDate: 16:28:43 27 Apr 2019.

Ufa Institute of Chemistry of the Russian Academy of Sciences (IUC RAS)



```

Current Data Parameters
NAME      gnb-Pca-130
EXPNO     9
PROCNO    1

F2 - Acquisition Parameters
Date_     20190427
Time      16.28
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   noesypph
TD         4096
SOLVENT   CDCl3
NS         2
DS         16
SWH        5000.000 Hz
FIDRES     1.220703 Hz
AQ         0.4096500 sec
RG         18.74
DW         100.000 usec
DE         6.50 usec
TE         301.2 K
DO         0.00008536 sec
D1         1.50000000 sec
DB         0.50000000 sec
D16        0.00010000 sec
IN0        0.00020000 sec

----- CHANNEL f1 -----
NUC1      1H
P1        11.50 usec
P2        23.00 usec
PLW1      15.84899998 W
SFO1      500.1323006 MHz

----- GRADIENT CHANNEL -----
GPNAM1    SINK.100
GPE1      40.00 %
P16       1000.00 usec

F1 - Acquisition parameters
TD         512
SFO1      500.1323 MHz
FIDRES     9.765625 Hz
SW         9.997 ppm
FnMODE     Status-TPPI

F2 - Processing parameters
SI         1024
SF         500.130057 MHz
WDW        QSINE
SSB        2
LB         0 Hz
GB         0
PC         1.00

F1 - Processing parameters
SI         1024
MC2        Status-TPPI
SF         500.130057 MHz
WDW        2
LB         0 Hz
GB         0
  
```