Electronic supplementary materials *Mendeleev Commun.*, 2021, **31**, 239–241

Formal synthesis of J-type prostaglandins based on enantiopure polyfunctional cyclopentenol derivative

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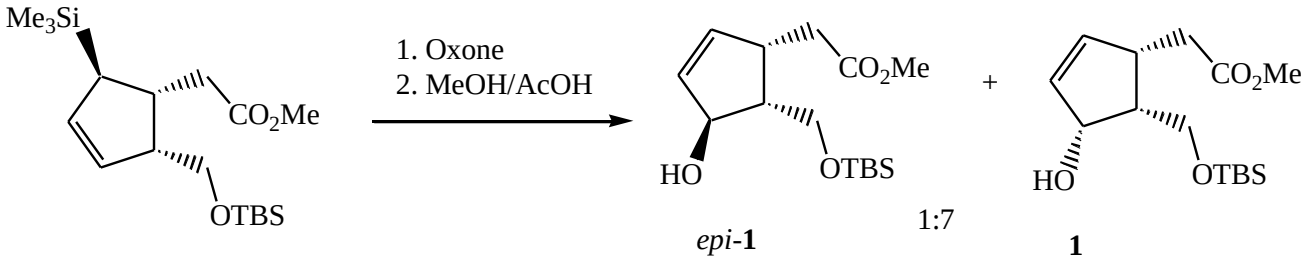
General Information

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 μm layer, silica gel 5-17 precoated 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 (infrared 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 (cm^{-1}). ^1H NMR spectra were obtained using a Bruker AM-300 (300 MHz for ^1H and 75.47 MHz for ^{13}C) as solutions in *d*-acetone (Aldrich Chemical Company; spectra grade). DEPT 135 spectra accompanied with the normal ^{13}C NMR were obtained using a BrukerAvance III (500 MHz for ^1H and 125.77 MHz for ^{13}C) as solutions in *d*-acetone (Aldrich Chemical Company; spectra grade). Chemical shifts are reported in δ unit-parts per million (ppm) downfield from tetramethylsilane (TMS) or acetone as the internal reference. Splitting patterns are designated as s, singlet; br s, broad singlet; d, doublet, t, triplet; q, quartet; quint., quintet.

Mass spectra were recorded on Shimadzu LCMS QP-2010EV (APCI) spectrometer. Elemental analyses were carried on a Euro EA 3000 CHNS-analyzer.

Preparation of dimsyl sodium. The required amount of sodium hydride under argon atmosphere was dissolved with stirring in excess dimethyl sulfoxide and kept at 70 ° C for 1 hour. The resulting solution was used immediately after cooling.

Methyl 2-((1*S*,4*R*,5*R*)-5-((*tert*-butyldimethylsilyloxy)methyl)-4-hydroxycyclopent-2-en-1-yl)acetate (1) and methyl 2-((1*S*,4*S*,5*R*)-5-(*tert*-butyldimethylsilyloxy)-4-(hydroxymethyl)cyclopent-2-en-1-yl)acetate (*epi*-1).



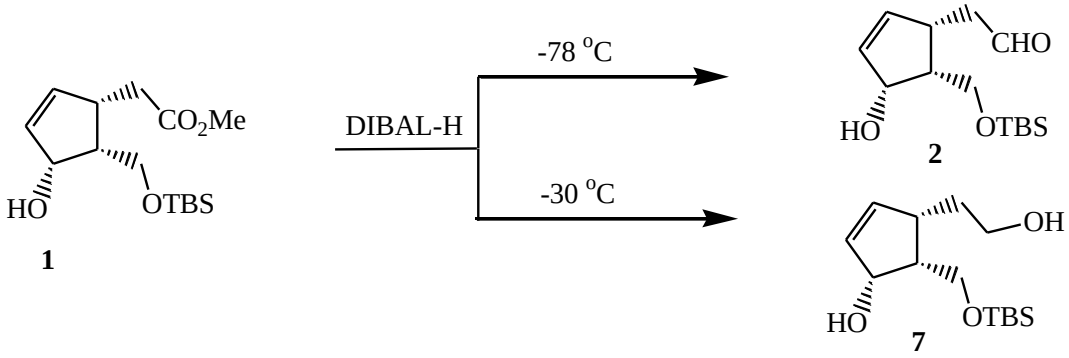
Solid $NaHCO_3$ (1.74 g, 20.7 mmol) was placed in a round-bottom flask and water (24 mL) followed by acetone (38 mL) were added. The resulting mixture was cooled to 0 °C and stirred for 20 min. Oxone (1.74 g, 3.55 mmol) was added in one portion, and stirring was continued at 0 °C for 15 min. Then, allylsilane derivative (0.62 g, 1.74 mmol) was added in one portion. Cooling was removed and the reaction mixture was stirred at r.t. for 1 h (TLC control). The resulting mixture was diluted with water (20 mL) and extracted with EtOAc (3×30 mL). The combined organic layers were dried ($MgSO_4$) and the solvent was evaporated in vacuo. The treatment with AcOH (1 mL) in MeOH (9 mL) was carried out in 3 h without purification due to instability of the product during column chromatography, affording alcohols **1** and *epi*-**1** as a mixture of isomers (*syn*:*anti* = 7:1). These isomers were separated by column chromatography on SiO_2 (petroleum ether/ethyl acetate, 5:1).

Major isomer 1: Yield: 0.39 g (76%); colorless transparent oil; R_f = 0.4 (petroleum ether/ethyl acetate = 5:1); $[\alpha]_D^{20}$: + 48.4 (*c* 1.05, CH_2Cl_2).

IR (liquid film): 3377, 2857, 1739, 1471, 1252, 1085, 838, 773 cm^{-1}.

^{1}H NMR (acetone-d_6, 500 MHz): δ = 6.04-6.00 (m, 1H, C^{3}H), 5.90-5.86 (m, 1H, C^{2}H), 4.61-4.57 (m, 1H, C^{4}H), 3.96 (dd, *J* = 10.4, 6.7 Hz, 1H, CH_αH$_\beta$OSi), 3.79 (dd, *J* = 10.3, 5.8 Hz, 1H, CH$_\alpha H_\beta$OSi), 3.62 (s, 3H, CH$_3$), 3.51 (d, *J* = 5.3 Hz, 1H, OH), 3.02-2.95 (m, 1H, C^{1}H), 2.70 (dd, *J* = 15.7, 5.3 Hz, 1H, CH_αH$_\beta$CO$_2$Me), 2.32 (quint, *J* = 7.0 Hz, 1H, C^{5}H), 2.30 (dd, *J* = 15.7, 10.1 Hz, 1H, CH$_\alpha H_\beta$CO$_2$Me), 0.90 (s, 9H, (CH$_3$)$_3$Si), 0.08 (s, 6H, (CH$_3$)$_2$Si).
^{13}C NMR (acetone-d_6, 125.77 MHz): δ = 172.90, 137.89, 133.76, 74.91, 59.95, 50.65, 47.26, 41.68, 36.03, 25.38, 17.86, -6.08.
MS (APCI): *m*/z (%) = 283.1 (100) [M-OH]$^+$.
Anal. Calcd for C$_{15}$H$_{28}$O$_4$Si: C, 59.96; H, 9.39. Found: C, 59.74; H, 9.12.
Minor isomer *epi*-1: Yield: 0.06 g (11%); colorless transparent oil; R_f = 0.35 (petroleum ether/ethyl acetate = 5:1); $[\alpha]_D^{20}$: + 88.7 (*c* 1.125, CH$_2$Cl$_2$).
IR (liquid film): 3424, 2857, 1741, 1471, 1254, 1085, 838, 776 cm^{-1}.
^{1}H NMR (acetone-d_6, 500 MHz): δ = 5.85-5.81 (m, 1H, C^{3}H), 5.76-5.72 (m, 1H, C^{2}H), 4.61-4.55 (m, 1H, C^{4}H), 3.85 (dd, *J* = 10.4, 5.2 Hz, 2H, CH_αH$_\beta$OSi, OH), 3.77 (dd, *J* = 10.5, 8.4 Hz, 1H, CH$_\alpha H_\beta$OSi), 3.61 (s, 3H, CH$_3$), 3.25-3.16 (m, 1H, C^{1}H), 2.71 (dd, *J* = 15.7, 5.7 Hz, 1H, CH_αH$_\beta$CO$_2$Me), 2.22-2.18 (m, 1H, C^{5}H), 2.14 (dd, *J* = 15.6, 10.1 Hz, 1H, CH$_\alpha H_\beta$CO$_2$Me), 0.90 (s, 9H, (CH$_3$)$_3$Si), 0.08 (s, 6H, (CH$_3$)$_2$Si).
^{13}C NMR (acetone-d_6, 125.77 MHz): δ = 172.85, 135.45, 135.02, 77.40, 61.28, 52.47, 50.67, 41.89, 34.72, 25.36, 17.85, -6.14.
MS (APCI): *m*/z (%) = 301.1 (100) [MH]$^+$.
Anal. Calcd for C$_{15}$H$_{28}$O$_4$Si: C, 59.96; H, 9.39. Found: C, 59.81; H, 9.16.

Representative procedure for the DIBAL-H reduction of compound 1.

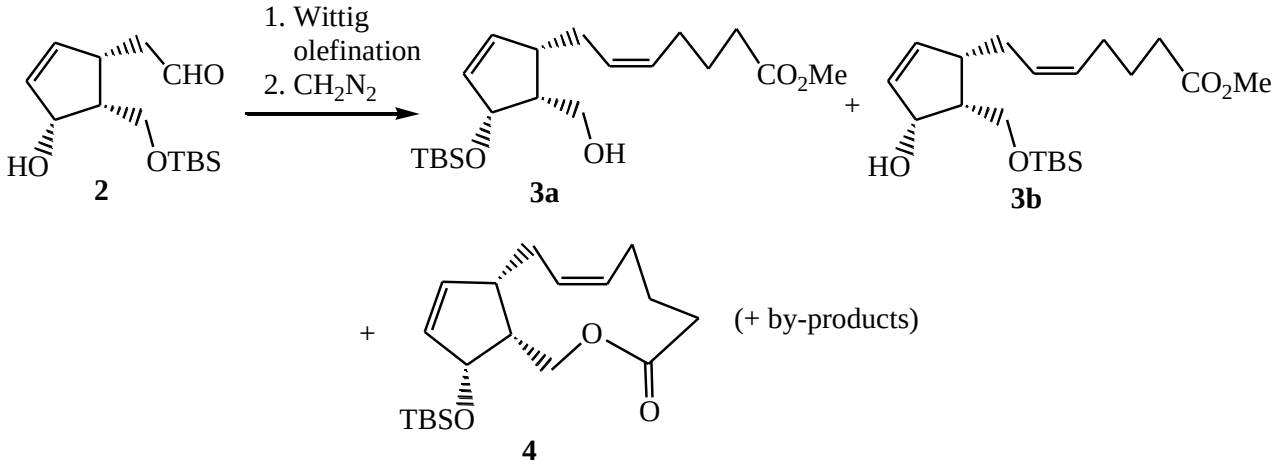


To a stirred solution of compound **1** (0.74 g, 2.5 mmol) in absolute CH$_2$Cl$_2$ (50 mL) at -78 °C was added dropwise DIBAL-H (0.71 g, 5.0 mmol) in absolute CH$_2$Cl$_2$ (20 mL). The reaction was monitored by TLC (petroleum ether/ethyl acetate, 1:1). After stirring for 30 min at the same temperature, sat. NH$_4$Cl (20 mL) was added, and the reaction mixture was warmed up to rt. The resulting mixture was filtered, evaporated under reduced pressure and extracted with CH$_2$Cl$_2$ (3x30 mL). The combined organic layers were dried (MgSO$_4$) and evaporated. Purification of products by column chromatography (petroleum ether/ethyl acetate, 3:1) afforded compound **2**.
2-((1*S*,4*R*,5*R*)-5-((*tert*-Butyldimethylsilyloxy)methyl)-4-hydroxycyclopent-2-en-1-yl)acetaldehyde (2). Yield: 0.61 g (92%); colorless transparent oil; R_f = 0.3 (petroleum ether/ethyl acetate = 5:1); $[\alpha]_D^{20}$: + 22.0 (*c* 1.0, CH$_2$Cl$_2$).
IR (liquid film): 3415, 2954, 2929, 2896, 2856, 1725, 1471, 1253, 1085, 837, 776 cm^{-1}.

^{1}H NMR (500 MHz, acetone-d_6): δ = 9.79 (s, 1H, CHO), 6.02 (dd, *J* = 5.5, 2.5 Hz, 1H, C^{2}H), 5.87 (dd, *J* = 4.1, 2.2 Hz, 1H, C^{3}H), 4.62 (td, *J* = 6.0, 2.3 Hz, 1H, C^{4}H), 3.96 (dd, *J* = 10.5, 6.5 Hz, 1H, CH_αH$_\beta$OSi), 3.78 (t, *J* = 10.4 Hz, 1H, CH$_\alpha H_\beta$OSi), 3.12-3.05 (m, 1H, C^{1}H), 2.85 (br s, 1H, OH), 2.75 (dd, *J* = 5.8, 1.5 Hz, 1H, CH_αH$_\beta$CHO), 2.45 (dd, *J* = 8.4, 1.5 Hz, 1H, CH$_\alpha H_\beta$CHO), 2.33 (quint, *J* = 7.9 Hz, 1H, C^{5}H), 0.89 (s, 9H, (CH$_3$)$_3$Si), 0.07 (s, 6H, (CH$_3$)$_2$Si).
^{13}C NMR (125.77 MHz, acetone-d_6): δ = 201.80, 137.87, 133.44, 74.87, 60.02, 47.33, 46.09, 39.62, 25.38, 17.84, -6.10.
MS (APCI): *m*/z (%) = 156.1 (100) [M-TBS]$^+$.
Anal. Calcd for $C_{14}H_{26}O_3Si$: C, 62.18; H, 9.69. Found: C, 61.97; H, 9.41.

(1*R*,4*S*,5*R*)-5-((*tert*-Butyldimethylsilyloxy)methyl)-4-(2-hydroxyethyl)cyclopent-2-en-1-ol (7).
Compound **1** (0.3 g, 1.0 mmol) was treated as described in the synthesis of **2** with DIBAL-H (0.43 g, 3.0 mmol) at -30 °C to afford the title compound.
Yield: 0.24 g (90%); yellowish transparent crystalline solid; mp 57-59 °C; R_f = 0.3 (petroleum ether/ethyl acetate = 1:1); $[\alpha]_D^{20}$: + 26.3 (*c* 1.15, CH_2Cl_2).
IR (nujol mull): 3320, 2954, 2929, 1471, 1255, 1085, 838, 776 cm^{-1}.
^{1}H NMR (500 MHz, acetone-d_6): δ = 6.09 (dd, *J* = 5.8, 2.7 Hz, 1H, C^{2}H), 5.85 (td, *J* = 5.6, 1.5 Hz, 1H, C^{3}H), 4.58 (dd, *J* = 6.0, 1.9 Hz, 1H, C^{1}H), 3.98 (dd, *J* = 10.2, 7.1 Hz, 1H, CH_αH$_\beta$OSi), 3.86 (dd, *J* = 10.3, 7.9 Hz, 1H, CH$_\alpha H_\beta$OSi), 3.62-3.54 (m, 2H, CH_2OH), 2.88 (br s, 2H, OH), 2.74-2.65 (m, 1H, C^{4}H), 2.25 (quint, *J* = 7.1 Hz, 1H, C^{5}H), 1.88-1.84 (m, 1H, C$H\alpha$HβCH$_2$OH), 1.54-1.49 (m, 1H, CH$\alpha H\beta$CH$_2$OH), 0.89 (s, 9H, (CH$_3$)$_3$Si), 0.08 (s, 6H, (CH$_3$)$_2$Si).
^{13}C NMR (125.77 MHz, acetone-d_6): δ = 138.83, 132.73, 74.95, 60.23 (2C), 47.91, 42.18, 34.76, 25.43, 17.89, -6.02.
MS (APCI): *m*/z (%) = 255.1 (100) [M-OH]$^+$.
Anal. Calcd for $C_{14}H_{28}O_3Si$: C, 61.72; H, 10.36. Found: C, 61.54; H, 10.21.

Representative procedure for Wittig olefination of aldehyde 2.



A solution of (5-hydroxy-5-oxopentyl)triphenylphosphonium bromide (2.69 g, 6.1 mmol) of in anhydrous THF (80 mL) was cooled under argon atmosphere to – 78 °C, and a solution of sodim hexamethyldisilazanide in THF (8.54 mL, 1.6 M) was added with stirring. The mixture was warmed up to 0 °C and stirred for 30 min, then cooled to –78 °C, and a solution of aldehyde **2** (0.41 g,1.51 mmol) in anhydrous THF (15 mL) was added to the resulting bright orange solution. The resulting

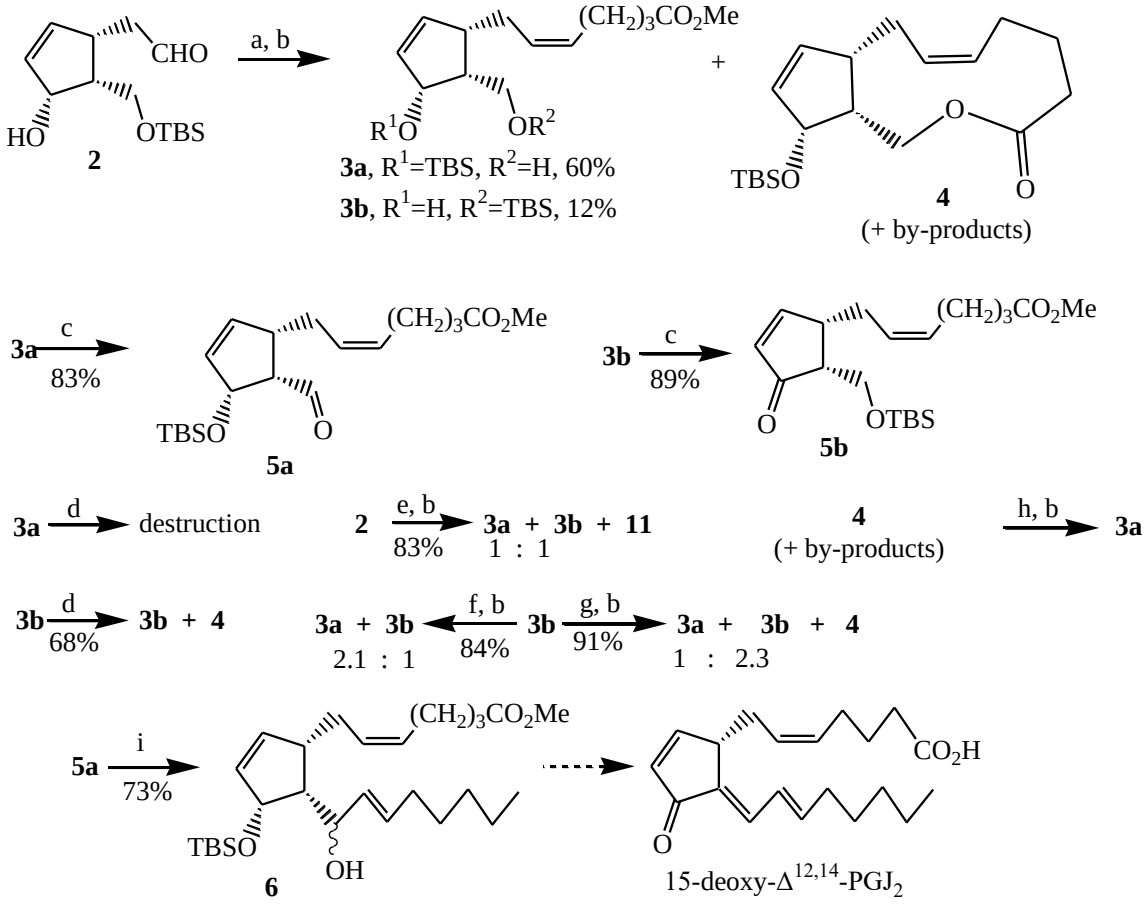
mixture was warmed up to 0 °C and stirred for 30 min (monitored by TLC). Then saturated solution of ammonium chloride (10 mL) was added. The mixture was filtered, the organic phase was separated, and the aqueous phase was extracted with ethyl acetate (3 × 50 mL). The extracts were combined with the organic phase, dried ($MgSO_4$), and evaporated under reduced pressure. The crude residue without purification was treated with excess of ether solution of diazomethane in 3 h at 0 °C, then filtered, washed with ether, evaporated under reduced pressure and purified by column chromatography using petroleum ether–ethyl acetate (gradient elution from 40:1 to 5:1) as eluent with obtaining of compounds **3a,b** and **4** (see Table S1, entry 1).

Methyl (*Z*)-7-((1*S*,4*R*,5*R*)-4-(*tert*-butyldimethylsilyloxy)-5-(hydroxymethyl)cyclopent-2-en-1-yl)hept-5-enoate (3a). Yield: 0.33 g (60%); colorless transparent oil; R_f = 0.4 (petroleum ether/ethyl acetate = 5:1); $[\alpha]_D^{20}$: + 12.2 (*c* 1.07, CH_2Cl_2).
IR (liquid film): 3467, 2953, 2856, 1739, 1472, 1250, 1065, 836, 775 cm^{-1}.
^1H NMR (500 MHz, acetone-d_6): δ = 6.07 (dd, *J* = 8.2, 5.5 Hz, 1H, C^2H), 5.89-5.84 (m, 1H, C^3H), 5.53-5.45 (m, 1H, $C^{6'}H$), 5.41-5.33 (m, 1H, $C^{5'}H$), 4.65 (dd, *J* = 5.8, 2.4 Hz, 1H, C^4H), 3.88 (dd, *J* = 10.1, 7.4 Hz, 1H, $CH_\alpha H_\beta OH$), 3.80 (dd, *J* = 10.1, 7.9 Hz, 1H, $CH_\alpha H_\beta OH$), 3.61 (s, 3H, CH_3), 2.86 (br s, 1H, OH), 2.60-2.55 (m, 1H, C^1H), 2.36-2.30 (m, 1H, $C^{7'}H$), 2.28 (t, *J* = 7.6 Hz, 2H, $C^{2'}H_2$), 2.21-2.15 (m, 1H, C^5H), 2.09-2.02 (m, 3H, $C^{4'}H_2$, $C^{7'}H$), 1.63 (quint, *J* = 7.6 Hz, 2H, $C^{3'}H_2$), 0.89 (s, 9H, $(CH_3)_3Si$), 0.09 (s, 6H, $(CH_3)_2Si$).
^{13}C NMR (125.77 MHz, acetone-d_6): δ = 173.93 (C=O), 140.56 (C^2), 133.45 (C^3), 129.86 ($C^{6'}$), 129.83 ($C^{5'}$), 76.49 (C^4), 60.31 (CH_2OH), 51.50 (CH_3O), 49.29 (C^5), 46.15 (C^1), 33.88 ($C^{2'}$), 30.79 ($C^{7'}$), 27.36 ($C^{4'}$), 26.23 [($\underline{C}H_3)_3C$], 25.64 ($C^{3'}$), 18.32 [$(CH_3)_3\underline{C}$], -5.77 [$(CH_3)_2Si$].
MS (APCI): *m*/z (%) = 367.1 (100) $[M-H]^+$.
Anal. Calcd for $C_{20}H_{36}O_4Si$: C, 65.17; H, 9.85. Found: C, 64.97; H, 9.63.

Methyl (*Z*)-7-((1*S*,4*R*,5*R*)-5-((*tert*-butyldimethylsilyloxy)methyl)-4-hydroxycyclopent-2-en-1-yl)hept-5-enoate (3b). Yield: 0.07 g (12%); colorless transparent oil; R_f = 0.45 (petroleum ether/ethyl acetate = 5:1); $[\alpha]_D^{20}$: + 46.3 (*c* 0.6, CH_2Cl_2).
IR (liquid film): 3477, 2953, 2856, 1741, 1463, 1255, 1081, 837, 776 cm^{-1}.
^1H NMR (500 MHz, acetone-d_6): δ = 6.03 (dd, *J* = 5.7, 2.6 Hz, 1H, C^2H), 5.87-5.83 (m, 1H, C^3H), 5.52-5.45 (m, 1H, $C^{6'}H$), 5.39-5.33 (m, 1H, $C^{5'}H$), 4.60 (dd, *J* = 6.3, 2.3 Hz, 1H, C^4H), 3.98 (dd, *J* = 10.3, 6.9 Hz, 1H, $CH_\alpha H_\beta OSi$), 3.87 (dd, *J* = 10.2, 8.3 Hz, 1H, $CH_\alpha H_\beta OSi$), 3.60 (s, 3H, CH_3), 2.84 (br s, 1H, OH), 2.61-2.55 (m, 1H, C^1H), 2.42-2.36 (m, 1H, $C^{7'}H$), 2.29 (t, *J* = 7.5 Hz, 2H, $C^{2'}H_2$), 2.29-2.22 (m, 1H, C^5H), 2.09-2.01 (m, 3H, $C^{4'}H_2$, $C^{7'}H$), 1.63 (quint, *J* = 7.4 Hz, 2H, $C^{3'}H_2$), 0.91 (s, 9H, $(CH_3)_3Si$), 0.09 (s, 6H, $(CH_3)_2Si$).
^{13}C NMR (125.77 MHz, acetone-d_6): δ = 173.16, 138.96, 132.88, 129.45, 129.07, 75.0, 60.15, 50.62, 47.80, 45.62, 32.91, 29.89, 26.43, 25.41, 24.74, 17.87, -6.04.
MS (APCI): *m*/z (%) = 351.2 (100) $[M-OH]^+$.
Anal. Calcd for $C_{20}H_{36}O_4Si$: C, 65.17; H, 9.85. Found: C, 64.91; H, 9.54.

(9a*S*,12*R*,12a*R*,*Z*)-12-(*tert*-butyldimetylsilyloxy)-1,4,5,6,9,9a,12,12a-octahydro-3*H*-cyclopenta[*c*][1]oxacycloundecin-3-one (4). Yield: 0.08 g; inseparable mixture with unidentified minor by-products and/or isomers; colorless transparent oil; R_f = 0.55 (petroleum ether/EtOAc = 20:1).
IR (liquid film): 2956, 2928, 2855, 1733, 1471, 1257, 1080, 1070, 836, 775 cm^{-1}.

^{1}H NMR (500 MHz, acetone-d_6): δ = 6.15-6.11 (m, 1H, C^{10}H), 5.93-5.83 (m, 1H, C^{11}H), 5.58-5.47 (m, 1H, C^{8}H), 5.42-5.31 (m, 1H, C^{7}H), 4.72-4.64 (m, 1H, C^{12}H), 4.35-4.30 (m, 1H, C$^{1}H_{\alpha}H_{\beta}$), 4.21-4.15 (m, 1H, C$^{1}H_{\alpha}H_{\beta}$), 2.54-2.44 (m, 1H, C^{9a}H), 2.35 (t, J = 6.9 Hz, 2H, C^{4}H$_2$), 2.35-2.30 (m, 1H, C^{6} $H_{\alpha}H_{\beta}$), 2.25-2.12 (m, 1H, C^{12a}H), 2.08-1.98 (m, 3H, C^{9}H$_2$, C$^{6}H_{\alpha}H_{\beta}$), 1.65-1.55 (m, 2H, C^{5}H$_2$), 0.86 (s, 9H, $(CH_3)_3$Si), 0.07 (s, 6H, $(CH_3)_2$Si).
^{13}C NMR (125.77 MHz, acetone-d_6): δ = 172.65, 139.08, 132.62, 129.50, 128.88, 75.73, 61.76, 46.34, 44.68, 32.86, 29.95, 26.21, 25.31, 24.47, 17.64, -5.81.
MS (APCI): m/z (%) = 337.2 (100) $[M+H]^+$.
Anal. Calcd for $C_{19}H_{32}O_3Si$: C, 67.81; H, 9.58. Found: C, 67.74; H, 9.32.



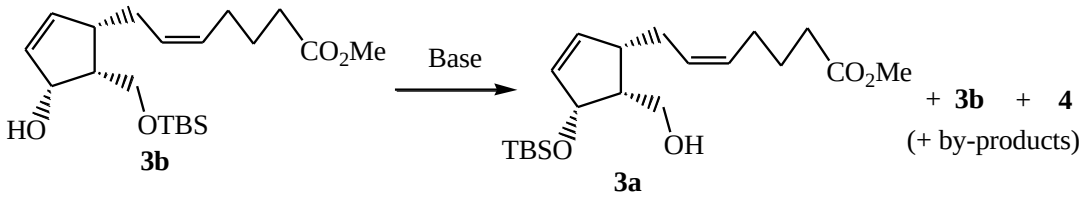
Scheme S1 *Reagents and contions:* (a) $Ph_3P^+[(CH_2)_4CO_2H]Br^-$ (4 equiv.), NaHMDS (9 equiv.), THF, -78→20 °C, 1 h; (b) CH_2N_2, Et_2O, ice/water bath, 3 h; (c) Collins reagent, CH_2Cl_2, rt, 3 h; (d) NaHMDS (ex.), THF, ice/water bath; (e) Bu^{t}OK (9 equiv.), $Ph_3P^+[(CH_2)_4CO_2H]Br^-$ (4 equiv.), THF, 0→20 °C, 1 h; (f) NaDMSO (3 equiv.), DMSO, 1 h; (g) Bu^{t}OK (9 equiv.), THF, rt, 10 h; (h) LiOH (10 equiv.), THF, H_2O, rt, 3 h; (i) BuLi (1.7 equiv.), *E*-1-iodoheptene (1.5 equiv.), THF, -78 °C, 30 min.

Table S1 Transformation of compounds **2**, **3a** and **3b** under basic conditions

Entry	Substrate	Base, equiv.[a]	Time, min	T, °C	Products[b]	
					Yield **3a**, %	Yield **3b**, %
1	**2**	1[c]	30	-78→20	60	12
2	**2**	2[c]	60	-78→20	9	32
3	**2**	1[c]	60[d]	-78	-	28
4	**2**	1[e]	60	0→20	24	28
5	**3a**	2[c]	5	0	traces	-
6	**3b**	1[c]	5	0	-	17
7	**3b**	9[e]	600	20	26	61
8	**3b**	2[f]	60	20	57	27

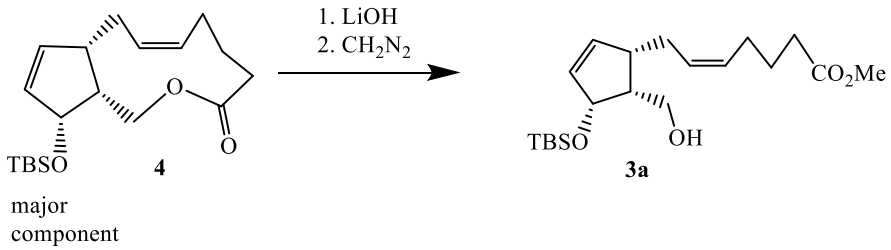
[a] Excess relative to substrate. [b] After methylation. [c] NaHMDS solution in THF.
[d] 50% conversion of **2**. [e] Bu^{t}OK solution in THF. [f] NaDMSO solution in DMSO

Representative procedure for the treatment of compounds 3a and 3b with bases.



A solution of ester **3b** (40 mg, 0.1 mmol) in anhydrous THF (5 mL) was cooled under argon to 0 °C, and solution of sodium hexamethyldisilazanide in THF (0.07 mL, 1.6 M) was added with stirring. The resulting mixture was stirred for 5 min (monitored by TLC), and saturated solution of ammonium chloride (5 mL) was added. The mixture was filtered, the organic phase was separated, and the aqueous phase was extracted with ethyl acetate (3 × 10 mL). The extracts were combined with the organic phase, dried ($MgSO_4$), and evaporated under reduced pressure. The crude residue without purification was treated with excess of ether solution of diazomethane in 3 h at 0 °C, then filtered, washed with ether, evaporated under reduced pressure and purified by column chromatography using petroleum ether–ethyl acetate (gradient elution from 40:1 to 5:1) as eluent with obtaining of mixture **4** (24 mg) and starting ester **3b (**7 mg, 17%) (see Table S1, entry 6).

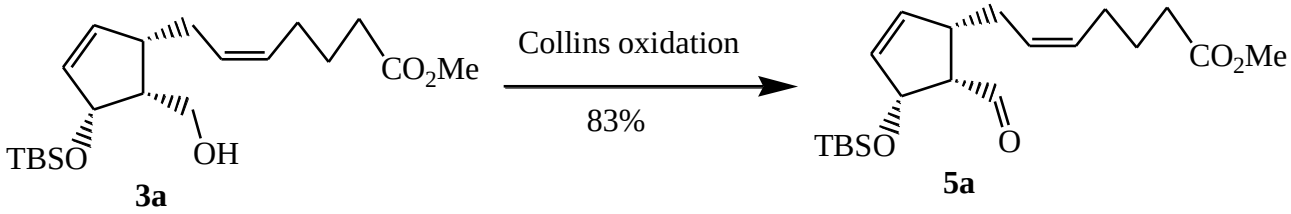
Preparation of ester 3a from compound 4 and impurities.



To a stirred solution of compund **4** with impurities (110 mg) in 2:1 mixture of THF and water (15 mL) at rt was added LiOH (8 mg, 3.3 mmol), and the resulting mixture was stirred for 3 h (TLC control).

Saturated NH_4Cl solution was then added (pH = 7-8), the organic phase was separated, and the aqueous phase was extracted with ethyl acetate (3 × 15 mL). The extracts were combined with the organic phase, dried ($MgSO_4$), and evaporated under reduced pressure. The crude residue without purification was treated with excess of ether solution of diazomethane in 3 h at 0 °C, then filtered, washed with ether, evaporated under reduced pressure and purified by column chromatography using petroleum ether–ethyl acetate (5:1) as eluent with obtaining of compounds **3a** (95 mg).

Representative procedure for oxidation by Collins reagent of alcohols 3a and 3b.



3a **5a**

To a stirred solution of compound **3a** (0.37 g,1.0 mmol) in absolute CH_2Cl_2 (50 mL) at rt was added CrO_3•2Py (0.9 g, 3.5 mmol). The reaction was monitored by TLC (petroleum ether/ethyl acetate, 5:1). After stirring for 3 h at the same temperature, the resulting mixture was filtered through thin layer of SiO_2, washed with ether and evaporated under reduced pressure. Purification of products by column chromatography (petroleum ether/ethyl acetate, 10:1) afforded aldehyde **5a**.

Methyl (*Z*)-7-((1*S*,4*R*,5*S*)-4-(*tert*-buryldimethylsilyloxy)-5-formylcyclopent-2-en-1-yl)hept-5-enoate (5a). Yield: 0.3 g (83%); yellowish transparent oil; R_f = 0.5 (petroleum ether/ethyl acetate = 10:1); $[\alpha]_D^{20}$: + 21.6 (*c* 0.65, CH_2Cl_2).

IR (liquid film): 2953, 2930, 2857, 1738, 1472, 1251, 1059, 838, 777 cm^{-1}.

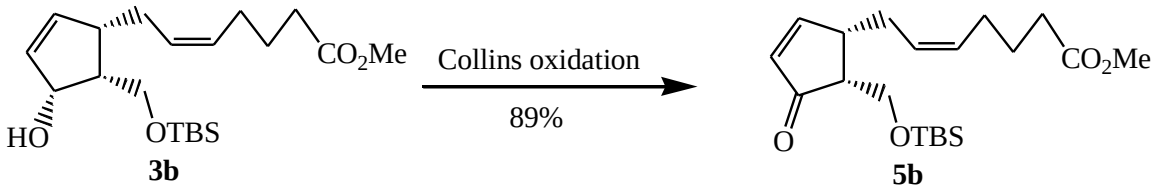
^1H NMR (500 MHz, acetone-d_6): δ = 9.76 (d, *J* = 4.6 Hz, 1H, CHO), 6.0 (d, *J* = 5.5 Hz, 1H, C^2H), 5.91 (td, *J* = 5.5, 1.8, Hz 1H, C^3H), 5.45 (dd, *J* = 11.0, 6.4 Hz, 1H, $C^{6'}H$), 5.40 (dd, *J* = 11.0, 6.4 Hz, 1H, $C^{5'}H$), 5.16 (dd, *J* = 6.7, 1.2 Hz, 1H, C^4H), 3.60 (s, 3H, CH_3), 2.95 (dd, *J* = 6.7, 4.9 Hz, 1H, C^1H), 2.91 (td, *J* = 7.0, 1.5 Hz, 1H, C^5H), 2.31-2.26 (m, 3H, $C^{7'}H$, $C^{2'}H_2$), 2.08-2.01 (m, 3H, $C^{4'}H_2$, $C^{7'}H$), 1.63 (quint, *J* = 7.5 Hz, 2H, $C^{3'}H_2$), 0.86 (s, 9H, $(CH_3)_3Si$), 0.1 (s, 6H, $(CH_3)_2Si$).

^{13}C NMR (125.77 MHz, acetone-d_6): δ = 203.11, 173.07, 136.53, 133.32, 130.07, 128.15, 78.38, 58.14, 50.61, 46.29, 32.85, 28.61, 26.43, 25.22, 24.59, 17.67, -5.34, -5.87.

MS (APCI): *m*/z (%) = 219.1 (100) $[M\text{-}O\text{-}OTBS]^+$.

Anal. Calcd for $C_{20}H_{34}O_4Si$: C, 65.53; H, 9.35. Found: C, 65.36; H, 9.22.

Methyl (*Z*)-7-((1*S*,5*R*)-5-((*tert*-butyldimethylsilyloxy)methyl)-4-oxocyclopent-2-en-1-yl)hept-5-enoate (5b).



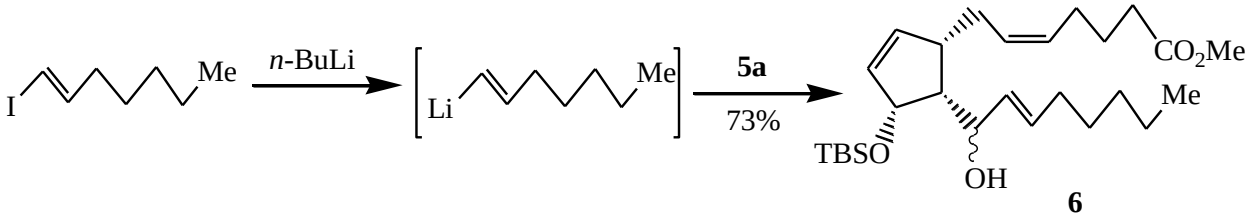
3b **5b**

Alcohol **3b** (0.13 g, 0.35 mmol) was treated as described in the synthesis of **5a** with Collins reagent (0.31 g, 1.22 mmol) at rt, afforded the title compound. Yield: 0.32 g (89%); colorless transparent oil; R_f = 0.5 (petroleum ether/ethyl acetate = 5:1); $[\alpha]_D^{20}$: + 122.5 (*c* 1.2, CH_2Cl_2).

IR (liquid film): 2953, 2930, 2856, 1740, 1712, 1472, 1250, 1109, 837, 778 cm^{-1}.

^{1}H NMR (500 MHz, acetone-d_6): δ = 7.77 (dd, *J* = 5.8, 2.4 Hz, 1H, C^{2}H), 6.12 (dd, *J* = 5.8, 2.0 Hz, 1H, C^{3}H), 5.62-5.56 (m, 1H, C$^{6'}$H), 5.54-5.48 (m, 1H, C$^{5'}$H), 3.98-3.92 (m, 2H, CH_2OSi), 3.60 (s, 3H, CH_3), 3.12-3.06 (m, 1H, C^{1}H), 2.64 (dt, *J* = 13.4, 5.8 Hz, 1H, C$^{7'}H_\alpha H_\beta$), 2.53 (td, *J* = 5.8, 3.5 Hz, 1H, C$^{7'}H_\alpha H_\beta$), 2.39-2.32 (m, 1H, C^{5}H), 2.30 (t, *J* = 7.3 Hz, 2H, C$^{2'}H_2$), 2.10 (q, 2H, C$^{4'}H_2$), 1.66 (quint, *J* = 7.4 Hz, 2H, C$^{3'}H_2$), 0.86 (s, 9H, $(CH_3)_3Si$), 0.03 (s, 6H, $(CH_3)_2Si$).
^{13}C NMR (125.77 MHz, acetone-d_6): δ = 208.33, 173.02, 132.94, 130.47, 128.40, 60.49, 50.78, 45.17, 32.94, 27.23, 26.59, 25.30, 24.65, 17.76, -6.25, -6.40.
MS (APCI): *m*/z (%) = 367.2 (100) $[MH]^+$.
Anal. Calcd for $C_{20}H_{34}O_4Si$: C, 65.53; H, 9.35. Found: C, 65.31; H, 9.24.

Representative procedure for coupling reaction of (hept-1-en-1-yl)lithium with aldehyde 5a.

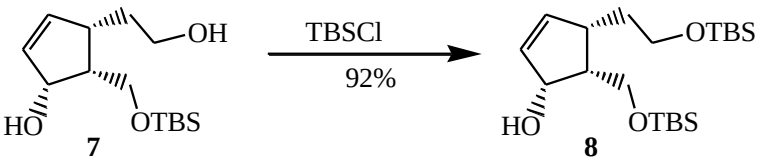


6

A solution of *trans*-1-iodoheptene (107 mg, 0.48 mmol) in anhydrous THF (10 mL) was cooled under argon atmosphere to – 78 °C, and solution of *n*-butyllithium in hexane (0.28 mL, 1.93 M) was added with stirring. The mixture was stirred for 30 min at the same temperature, then a solution of aldehyde **5a** (117 mg, 0.32 mmol) in anhydrous THF (10 mL) was added dropwise. The resulting mixture was stirred for 30 min at – 78 °C (monitored by TLC), and saturated solution of ammonium chloride (10 mL) was added. The organic phase was separated, and the aqueous phase was extracted with ethyl acetate (3 × 20 mL). The extracts were combined with the organic phase, dried ($MgSO_4$), and evaporated under reduced pressure. The crude residue was purified by column chromatography using petroleum ether–ethyl acetate (10:1) as eluent to afford product **6**.

Methyl (*Z*)-7-((1*S*,4*R*,5*R*)-4-(*tert*-betyldimethylsilyloxy)-5-((*E*)-1-hydroxyoct-2-en-1-yl)cyclopent-2-en-1-yl)hept-5-enoate (6). Yield: 108 mg (73%); yellowish transparent oil; R_f = 0.5 (petroleum ether/ethyl acetate = 5:1).
IR (liquid film): 3459, 2954, 2855, 1740, 1635, 1471, 1249, 1058, 835, 776 cm^{-1}.
^{1}H NMR (500 MHz, acetone-d_6): δ = 6.11 (dd, *J* = 5.7, 2.4 Hz, 1H, C^{2}H), 5.93 (dd, *J* = 5.7, 2.3 Hz, 1H, C^{3}H), 5.75 (dt, *J* = 15.4, 7.1 Hz, 1H, C$^{2''}$H), 5.61 (dd, *J* = 15.3, 7.5 Hz, 1H, C$^{3''}$H), 5.45-5.31 (m, 2H, C$^{6'}$H, C$^{5'}$H), 4.70 (dd, *J* = 5.3, 2.5 Hz, 1H, C^{4}H), 4.27 (dd, *J* = 10.1, 7.7 Hz, 1H, C$^{1''}$H), 3.60 (s, 3H, CH_3), 2.91 (br s, 1H, OH), 2.42-2.32 (m, 2H, C^{1}H, C$^{7'}$H), 2.27 (t, *J* = 7.6 Hz, 2H, C$^{2'}H_2$), 2.17-2.10 (m, 1H, C^{5}H), 2.09-2.02 (m, 4H, C$^{4'}H_2$, C$^{4''}H_2$), 1.94-1.88 (m, 1H, C$^{7'}$H), 1.62 (quint, *J* = 7.5 Hz, 2H, C$^{3'}H_2$), 1.43-1.36 (m, 2H, C$^{5''}H_2$), 1.33-1.25 (m, 4H, C$^{6''}H_2$, C$^{7''}H_2$), 0.92-0.85 (m, 12H, C$^{8''}H_3$, $(CH_3)_3Si$), 0.14 (s, 3H, CH_3Si), 0.09 (s, 3H, CH_3Si).
^{13}C NMR (125.77 MHz, acetone-d_6): δ = 173.06, 140.36, 133.27, 132.85, 131.82, 129.30, 128.87, 75.44, 68.84, 52.76, 50.64, 44.95, 32.99, 32.18, 31.17, 30.52, 28.88, 26.54, 25.42, 24.75 (2C), 22.32, 13.47, -4.88, -5.70.
MS (APCI): *m*/z (%) = 447.4 (100) $[M\text{-}OH]^+$.
Anal. Calcd for $C_{27}H_{48}O_4Si$: C, 69.78; H, 10.41. Found: C, 69.57; H, 10.14.

(1*R*,4*S*,5*R*)-4-(2-((*tert*-Butyldimethylsilyl)oxy)ethyl)-5-((*tert*-butyldimethylsilyloxy)methyl)-cyclopent-2-en-1-ol (8).



To a stirred solution of diol **7** (0.14 g, 0.5 mmol) in CH_2Cl_2 (20 mL) at rt was added *tert*-butyl(chloro)dimethylsilane (0.15 g,1.0 mmol) and imidazole (0.07 g, 1.0 mmol). The mixture was stirred at rt for 3 h (monitored by TLC), water (10 mL) was added, and the mixture was extracted with CH_2Cl_2 (3 × 20 mL). The combined extracts were dried ($MgSO_4$) and evaporated under reduced pressure, and the residue was dried under reduced pressure and subjected to column chromatography using petroleum ether–ethyl acetate (10:1) as eluent to isolate of compound **8**.

Yield: 0.2 g (92%); colorless transparent oil; R_f = 0.4 (petroleum ether/ethyl acetate = 10:1); $[\alpha]_D^{20}$: + 15.4 (*c* 0.7, CH_2Cl_2).

IR (liquid film): 3432, 2954, 2857, 1471, 1255, 1092, 836, 774 cm^{-1}.

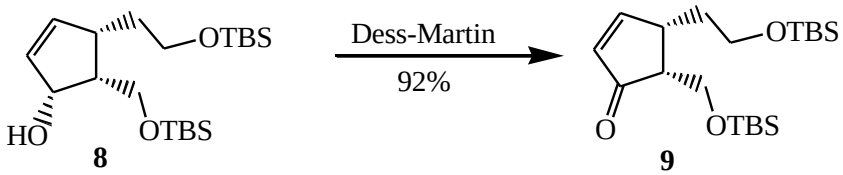
^1H NMR (500 MHz, acetone-d_6): δ = 6.11 (dd, *J* = 5.7, 2.6 Hz, 1H, C^2H), 5.85 (td, *J* = 5.7, 1.2 Hz, 1H, C^3H), 4.58 (dd, *J* = 6.2, 2.1 Hz, 1H, C^1H), 3.98 (dd, *J* = 10.3, 6.6 Hz, 1H, $CH_\alpha H_\beta OSi$), 3.84 (dd, *J* = 10.2, 8.4 Hz, 1H, $CH_\alpha H_\beta OSi$), 3.76-3.70 (m, 1H, $CH_2CH_\alpha H_\beta OSi$), 3.70-3.65 (m, 1H, $CH_2CH_\alpha H_\beta OSi$), 2.89 (s, 1H, OH), 2.76-2.65 (m, 1H, C^4H), 2.26 (quint, *J* = 7.2 Hz, 1H, C^5H), 1.94 (qd, *J* = 20.5, 5.0 Hz, 1H, $CH_\alpha H_\beta CH_2OSi$), 1.48 (qd, *J* = 18.3, 5.8 Hz, 1H, $CH_\alpha H_\beta CH_2OSi$), 0.91 (s, 9H, $(CH_3)_3Si$), 0.89 (s, 9H, $(CH_3)_3Si$'), 0.08 (s, 6H, $(CH_3)_2Si$), 0.05 (s, 6H, $(CH_3)_2Si$').

^{13}C NMR (125.77 MHz, acetone-d_6): δ = 138.84, 132.81, 74.91, 61.72, 60.22, 47.92, 42.86, 35.14, 25.43, 25.42, 17.94, -5.96, -6.05.

MS (APCI): *m*/z (%) = 358.2 (100) $[M-H]^+$.

Anal. Calcd for $C_{20}H_{42}O_3Si_2$: C, 62.12; H, 10.95. Found: C, 61.88; H, 10.76.

(4*S*,5*R*)-4-(2-(*tert*-Butyldimethylsilyloxy)ethyl)-5-((*tert*-butyldimethylsilyloxy)methyl)cyclopent-2-en-1-one (9).



To a solution of alcohol **8** (0.2 g, 0.5 mmol) in CH_2Cl_2 (30 mL) was added Dess–Martin periodinane (0.5 g, 1.25 mmol) at 0 °C. The mixture was stirred at rt for 8 h (monitored by TLC) before treatment with sat aq $NaHCO_3$ (5 mL) and sat aq $Na_2S_2O_3$ (5 mL). The resulting mixture was stirred for 1 h, extracted with CH_2Cl_2 (3×20 mL), the combined organic layers were dried ($MgSO_4$) and evaporated under reduced pressure. The residue was dried under reduced pressure and subjected to column chromatography using petroleum ether–ethyl acetate (20:1) as eluent to isolate of compound **9**.

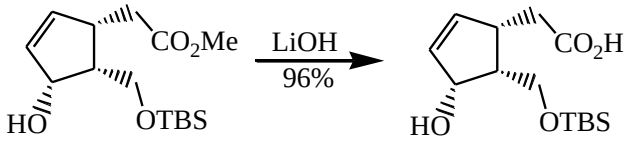
Yield: 0.18 g (92%); colorless transparent oil; R_f = 0.5 (petroleum ether/ethyl acetate = 20:1); $[\alpha]_D^{20}$: + 92.6 (*c* 0.95, CH_2Cl_2).

IR (liquid film): 2954, 2857, 1471, 1255, 1715, 1472, 1256, 1102, 836, 776 cm^{-1}.

^1H NMR (500 MHz, acetone-d_6): δ = 7.91 (dd, *J* = 5.9, 2.6 Hz, 1H, C^3H), 6.09 (dd, *J* = 5.9, 2.2 Hz, 1H, C^2H), 3.96 (dd, *J* = 10.5, 3.2 Hz, 1H, $CH_\alpha H_\beta OSi$), 3.93 (dd, *J* = 10.4, 6.0 Hz, 1H, $CH_\alpha H_\beta OSi$),

3.87 (t, 2H, CH_2CH_2OSi), 3.24-3.18 (m, 1H, C^4H), 2.51 (td, *J* = 6.3, 3.2 Hz, 1H, C^5H), 2.18 (sextet, *J* = 5.6 Hz, 1H, $CH_\alpha H_\beta CH_2OSi$), 1.75-1.65 (m, 1H, $CH_\alpha H_\beta CH_2OSi$), 0.91 (s, 9H, $(CH_3)_3Si$), 0.85 (s, 9H, $(CH_3)_3Si$'), 0.09 (s, 6H, $(CH_3)_2Si$), 0.05 (s, 3H, CH_3Si'), 0.02 (s, 3H, CH_3Si').
^{13}C NMR (125.77 MHz, acetone-d_6): δ = 208.36, 168.26, 132.52, 61.61, 60.61, 50.96, 41.15, 32.55, 25.42, 25.33, 17.90, 17.79, -6.02, -6.05.
MS (APCI): *m*/z (%) = 385.2 (100) $[MH]^+$.
Anal. Calcd for $C_{20}H_{40}O_3Si_2$: C, 62.44; H, 10.48. Found: C, 62.27; H, 10.28.

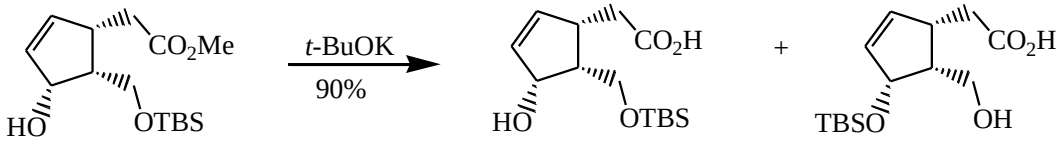
2-((1*S*,4*R*,5*R*)-5-((*tert*-Butyldimethylsilyloxy)methyl)-4-hydroxycyclopent-2-en-1-yl)acetic acid (10a). Counter synthesis for identification acids 10a and 10b.



1 **10a**

To a stirred solution of ester **1** (0.23 g, 0.77 mmol) in 2:1-mixture of THF and water (15 mL) at rt was added LiOH (0.06 g, 2.5 mmol), and the resulting mixture was stirred for 18 h (monitored by TLC). Saturated NH_4Cl solution was then added (pH = 7-8), the organic phase was separated, and the aqueous one was extracted with EtOAc (3×15 mL). The extracts were combined with the organic phase, dried ($MgSO_4$), and evaporated under reduced pressure. Purification by column chromatography (petroleum ether/EtOAc, 1:1) afforded the title compound (see Table S2, entry 11).
Yield: 0.21 g (96%); white crystalline solid; mp 78-80 °C; R_f = 0.3 (petroleum ether/ethyl acetate = 1:1); $[\alpha]_D^{20}$: + 12.6 (*c* 0.65, CH_2Cl_2).
IR (liquid film): 3372, 2955, 2929, 2857, 1709, 1471, 1256, 1085, 837, 776 cm^{-1}.
^1H NMR (acetone-d_6, 500 MHz): δ = 6.06 (dd, *J* = 5.7, 2.6 Hz, 1H, C^3H), 5.92-5.86 (m, 1H, C^2H), 4.60 (dd, *J* = 6.1, 2.1 Hz, 1H, C^4H), 3.98 (dd, *J* = 10.4, 6.7 Hz, 1H, $CH_\alpha H_\beta OSi$), 3.82 (dd, *J* = 10.3, 8.6 Hz, 1H, $CH_\alpha H_\beta OSi$), 3.01-2.93 (m, 1H, C^1H), 2.87 (br s, 2H, OH, COOH), 2.71 (dd, *J* = 16.0, 5.2 Hz, 1H, $CH_\alpha H_\beta CO_2H$), 2.33 (dd, *J* = 15.7, 7.9 Hz, 1H, C^5H), 2.30 (dd, *J* = 15.9, 10.1 Hz, 1H, $CH_\alpha H_\beta CO_2Me$), 0.90 (s, 9H, $(CH_3)_3Si$), 0.09 (s, 6H, $(CH_3)_2Si$).
^{13}C NMR (acetone-d_6, 125.77 MHz): δ = 173.56, 138.05, 133.58, 74.90, 60.04, 47.20, 41.63, 35.69, 25.38, 17.85, -6.08.
MS (APCI): *m*/z (%) = 269.1 (100) $[M-OH]^+$.
Anal. Calcd for $C_{14}H_{26}O_4Si$: C, 58.70; H, 9.15. Found: C, 58.61; H, 9.02.

2-((1*S*,4*R*,5*R*)-5- ((*tert*-Butyldimethylsilyloxy)methyl)-4-hydroxycyclopent-2-en-1-yl)acetic acid (10a) and 2-((1*S*,4*R*,5*R*)-5-((*tert*-butyldimethylsilyloxy)-5-(hydroxymethyl)cyclopent-2-en-1-yl)acetic acid (10b).



1 **10a** **10b**

To a stirred under argon solution of ester **1** (0.29 g, 0.77 mmol) in THF (15 mL) at rt was added potassium *tert*-butoxide (0.33 g, 2.91 mmol), and the resulting mixture was stirred for 12 h (monitored by TLC). Saturated NH_4Cl solution was then added (pH = 7-8), the organic phase was separated, and

the aqueous phase was extracted with ethyl acetate (3 × 15 mL). The extracts were combined with the organic phase, dried ($MgSO_4$), and evaporated under reduced pressure. Purification of products by column chromatography (petroleum ether/ethyl acetate, 1:1) afforded of inseparable 1:2.5-mixture (by NMR ^1H) of compounds **9a**+**9b** (see Table S2, entry 9).

Yield: 0.25 g (90%); transparent viscous oil; R_f = 0.3 (petroleum ether/ethyl acetate = 1:1).

IR (liquid film): 3455, 2954, 2929, 2856, 1739, 1735, 1472, 1252, 1073, 837, 776 cm^{-1}.

MS (APCI): *m*/z (%) = 269.1 (100) $[M\text{-}OH]^+$.

Anal. Calcd for $C_{14}H_{26}O_4Si$: C, 58.70; H, 9.15. Found: C, 58.55; H, 8.91.

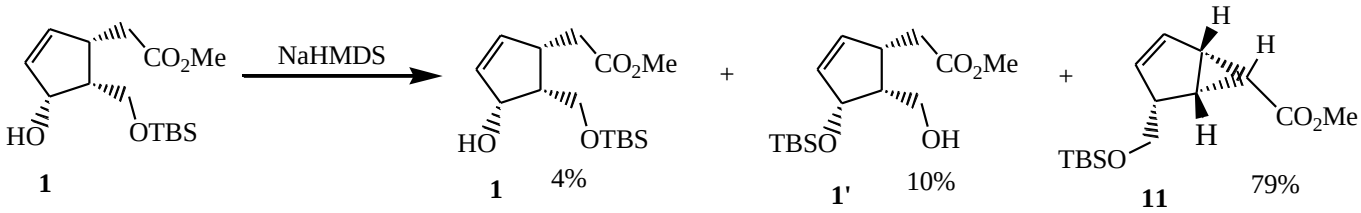
For minor isomer 10a: the spectral data as above.

For major isomer 10b:

^1H NMR (acetone-d_6, 500 MHz): δ = 6.11 (dd, *J* = 5.7, 2.7 Hz, 1H, C^3H), 5.88 (dd, *J* = 5.4, 1.3 Hz, 1H, C^2H), 4.71 (dd, *J* = 5.9, 2.3 Hz, 1H, C^4H), 3.80 (dd, *J* = 10.8, 6.4 Hz, 1H, $CH_\alpha H_\beta OSi$), 3.70 (dd, *J* = 10.8, 7.9 Hz, 1H, $CH_\alpha H_\beta OSi$), 3.02-2.94 (m, 3H, C^1H, OH, COOH), 2.71 (dd, *J* = 16.2, 5.8 Hz, 1H, $CH_\alpha H_\beta CO_2H$), 2.34-2.29 (m, 1H, C^5H), 2.26 (dd, *J* = 16.5, 9.8 Hz, 1H, $CH_\alpha H_\beta CO_2Me$), 0.88 (s, 9H, $(CH_3)_3Si$), 0.07 (s, 6H, $(CH_3)_2Si$).

^{13}C NMR (acetone-d_6, 125.77 MHz): δ = 173.66, 138.93, 133.14, 76.31, 58.72, 47.90, 41.42, 36.05, 25.31, 17.66, -5.83.

Representative procedure for treatment ester 1 with NaHMDS.

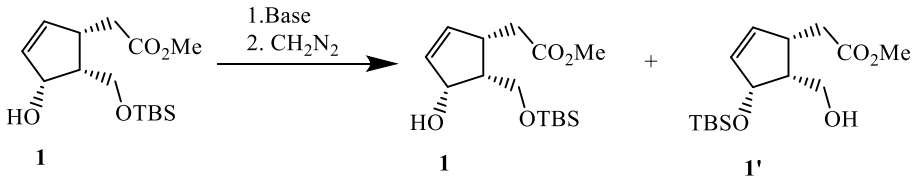


A solution of ester **1** (0.31 g, 1.0 mmol) in anhydrous THF (20 mL) was cooled under argon atmosphere to 0 °C, and solution of sodium hexamethyldisilazanide in THF (1.9 mL, 1.6 M) was added with stirring. The mixture was stirred for 30 min (monitored by TLC) and saturated solution of ammonium chloride (10 mL) was added. The mixture was filtered, the organic phase was separated, and the aqueous phase was extracted with ethyl acetate (3 × 20 mL). The extracts were combined with the organic phase, dried ($MgSO_4$), and evaporated under reduced pressure. The crude residue without purification was treated with excess of ether solution of diazomethane in 3 h at 0 ºC, then filtered, washed with ether, evaporated under reduced pressure and purified by column chromatography using petroleum ether–ethyl acetate (gradient elution from 40:1 to 5:1) as eluent with obtaining of compounds **1**, **1'** and **11** (see Table S2, entry 3).

For compound 1: Yield: 12 mg (4%); transparent viscous oil. The analytical data as previously described.

Methyl 2-((1*S*,4*R*,5*R*)-4-((*tert*-butyldimethylsilyloxy)methyl)-5-hydroxycyclopent-2-en-1-yl)acetate (1'). Yield: 30 mg (10%); colorless transparent oil; R_f = 0.45 (petroleum ether/ethyl acetate = 5:1); $[\alpha]_D^{20}$: + 20.7 (*c* 0.44, CH_2Cl_2).
IR (liquid film): 3451, 2954, 2929, 2856, 1738, 1472, 1252, 1073, 1029, 836, 776 cm^{-1}.
^1H NMR (acetone-d_6, 500 MHz): δ = 6.08 (dd, *J* = 5.7, 2.7 Hz, 1H, C^3H), 5.89 (td, *J* = 5.7, 1.4 Hz, 1H, C^2H), 4.71 (dd, *J* = 5.9, 2.4 Hz, 1H, C^4H), 3.78 (dd, *J* = 10.8, 6.6 Hz, 1H, $CH_\alpha H_\beta OSi$), 3.67 (dd, *J* = 10.7, 8.1 Hz, 1H, $CH_\alpha H_\beta OSi$), 3.63 (s, 3H, CH_3), 3.03-2.96 (m, 1H, C^1H), 2.88 (s, 1H, OH), 2.72 (dd, *J* = 15.8, 5.6 Hz, 1H, $CH_\alpha H_\beta CO_2Me$), 2.31 (quint, *J* = 6.8 Hz, 1H, C^5H), 2.26 (dd, *J* = 15.8, 9.9 Hz, 1H, $CH_\alpha H_\beta CO_2Me$), 0.88 (s, 9H, $(CH_3)_3Si$), 0.09 (s, 6H, $(CH_3)_2Si$).
^{13}C NMR (acetone-d_6, 125.77 MHz): δ = 173.01, 138.71, 133.29, 76.23, 58.61, 50.66, 47.83, 41.54, 36.27, 25.29, 17.56, -5.06, -5.85.
MS (APCI): *m*/z (%) = 269.1 (100) $[M\text{-}MeOH]^+$.
Anal. Calcd for $C_{15}H_{28}O_4Si$: C, 59.96; H, 9.39. Found: C, 59.82; H, 9.08.

Methyl (1*S*,4*R*,5*S*,6*S*)-4-((*tert*-butyldimethylsilyloxy)methyl)bicyclo[3.1.0]hex-2-ene-6-carboxylate (11). Yield: 0.22 g (79%); colorless transparent oil; R_f = 0.45 (petroleum ether/ethyl acetate = 20:1); $[\alpha]_D^{20}$: + 162.3 (*c* 1.4, CH_2Cl_2).
IR (liquid film): 2954, 2927, 2855, 1739, 1257, 1147, 1076, 837, 776 cm^{-1}.
^1H NMR (acetone-d_6, 500 MHz): δ = 5.64 (dt, *J* = 7.6, 5.3 Hz, 1H, C^3H), 5.58 (d, *J* = 5.8 Hz, 1H, C^2H), 3.92 (dd, *J* = 9.4, 7.3 Hz, 1H, $CH_\alpha H_\beta OSi$), 3.67 (t, *J* = 9.4 Hz, 1H, $CH_\alpha H_\beta OSi$), 3.53 (s, 3H, CH_3), 3.34-3.27 (m, 1H, C^4H), 2.41 (dd, *J* = 7.4, 6.5 Hz, 1H, C^1H), 1.94 (q, *J* = 7.2 Hz, 1H, C^5H), 1.78 (t, *J* = 8.0 Hz, 1H, C^6H), 0.90 (s, 9H, $(CH_3)_3Si$), 0.06 (s, 3H, CH_3Si), 0.05 (s, 3H, CH_3Si).
^{13}C NMR (acetone-d_6, 125.77 MHz): δ = 171.01 (C=O), 133.63 (C^2), 128.59 (C^3), 64.02 (CH_2OSi), 51.80 (C^5), 51.35 (Me), 30.76 (C^1), 26.30 ($(\underline{C}H_3)_3C$), 24.16 (C^6), 23.88 (C^5), 18.82 ($(CH_3)_3\underline{C}$), -5.06 (CH_3ˈSi), -5.11 (CH_3Si).
MS (APCI): *m*/z (%) = 283.1 (100) $[MH]^+$.
Anal. Calcd for $C_{15}H_{26}O_3Si$: C, 63.79; H, 9.28. Found: C, 63.61; H, 9.11.



Representative procedure for treatment ester 1 with dimsyl sodium.
To a freshly prepared dimsyl sodium (see General Information) from NaH (25 mg, 0.66 mmol, 65% dispersion in mineral oil) solution of with stirring under argon atmosphere at rt was added compound **1** (67 mg, 0.22 mmol) of in dry DMSO (5 mL). The resulting mixture was stirred for 30 min, and saturated solution of ammonium chloride (10 mL) was added. The mixture was extracted with ethyl acetate (3 × 20 mL), the extracts were dried ($MgSO_4$), and evaporated under reduced pressure. The crude residue without purification was treated with excess of ether solution of diazomethane in 3 h at 0 °C, then filtered, washed with ether, evaporated under reduced pressure and purified by column chromatography using petroleum ether–ethyl acetate (5:1) as eluent with obtaining of 40 mg (59%) of compound **1'** and 14 mg (21%) of starting **1** (see Table S2, entry 5).

Representative procedure for treatment ester 1 with *t*-BuOK.

Compound **1** (150 mg, 0.5 mmol) was treated as described in the synthesis of 1:2.5-mixture of acids **10a+10b** with *t*-BuOK (112 mg, 1.0 mmol) to afford the corresponding 3:1-mixture. The crude residue without purification was treated with excess of ether solution of diazomethane in 3 h at 0 °C, then filtered, washed with ether, evaporated under reduced pressure and purified by column chromatography using petroleum ether–ethyl acetate (5:1) as eluent with obtaining of compound **1'** (30 mg, 23%) and starting **1** (102 mg, 68%) (see Table S2, entry 8).

Representative procedure for treatment ester 1 with sodium hydride.

To a stirred under argon atmosphere suspension of NaH (34 mg, 1.2 mmol, 65% dispersion in mineral oil) in dry THF (5 mL) at rt was added compound **1** (92 mg, 0.3 mmol) in dry THF (5 mL). The resulting mixture was stirred for 14 h and saturated solution of ammonium chloride (10 mL) was added. The reaction solution was extracted with ethyl acetate (3×20 mL), the extracts were dried ($MgSO_4$), and evaporated under reduced pressure. The crude residue without purification was treated with excess of ether solution of diazomethane in 3 h at 0 °C, then filtered, washed with ether, evaporated under reduced pressure and purified by column chromatography using petroleum ether–ethyl acetate (5:1) as eluent with obtaining of compound **1'** (30 mg, 23%) and starting **1** (102 mg, 68%) (see Table S2, entry 10).

Representative procedure for treatment ester 1 with LiOH.

Ester **1** (78 mg, 0.26 mmol) was hydrolyzed as described in the synthesis of acid **10a** with LiOH (19 mg, 0.78 mmol). The crude acid was treated with excess of ether solution of diazomethane in 3 h at 0 °C, then filtered, washed with ether, evaporated under reduced pressure and purified by column chromatography using petroleum ether–ethyl acetate (5:1) as eluent with obtaining of starting **1** (75 mg, 96%) (see Table S2, entry 11).

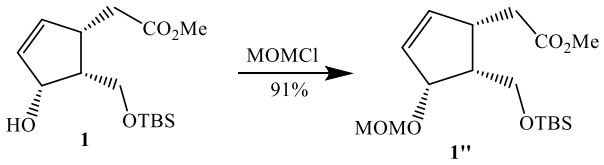
Table S2 Transformation of ester **1** under basic conditions

Entry	Base	Equiv.	Solvent	Time[a], h	T, °C	Product composition, %[b]		
						1	**1'**	**10**
1	NaHMDS	1	THF	0.5	0	89	-	-
2	NaHMDS	2	THF	0.5	0	25	9	61
3	NaHMDS	3	THF	0.5	0	4	10	79
4	NaDMSO	2	DMSO	1	25	12	28	-
5	NaHMDS	3	DMSO	0.5	25	21	59	-
6	NaHMDS	4	DMSO	0.5	25	24	51	-
7	NaHMDS	4	DMSO	12	25	-	traces	-
8	*t*-BuOK	2	THF	12	25	68	23	-
9	*t*-BuOK	3	THF	12	25	26	64	-
10	NaH	3	THF	14	25	71	18	-
11	LiOH	3	THF/H_2O	18	25	96	-	-
12	DBU/DMAP/ Et_3N	10	CH_2Cl_2/ toluene	24	25/100	100[c]	-	-

[a] Treatment with base. [b] After treatment with diazomethane. [c] No reaction

Methyl 2-{(1*S*,4*R*,5*R*)-5-[(*tert*-butyldimethylsilyloxy)methyl]-4-(methoxymethoxy)cyclopent-2-en-1-yl}acetate (1").

Method A.



A solution of chloromethyl methyl ether (0.29 mL, 3.9 mmol)in CH_2Cl_2 (10 mL) was added under stirring to a mixture of monoprotected diol **1** (0.78 g, 2.6 mmol), N,N-diisopropylethylamine (1.0 mL, 5.7 mmol) and CH_2Cl_2 (50 mL) at 0 °C. The mixture was stirred for 3 h at rt (monitored by TLC) and evaporated under reduced pressure. Purification of the product by column chromatography (petroleum ether/ethyl acetate, 3:1) afforded the title compound. Yield: 0.81 g (91%); colorless transparent oil; R_f = 0.6 (petroleum ether/ethyl acetate = 10:1); $[\alpha]_D^{20}$: + 30.7 (*c* 0.95, CH_2Cl_2).

IR (liquid film): 2953, 2857, 1740, 1472, 1255, 1096, 1040, 838, 775 cm^{-1}.

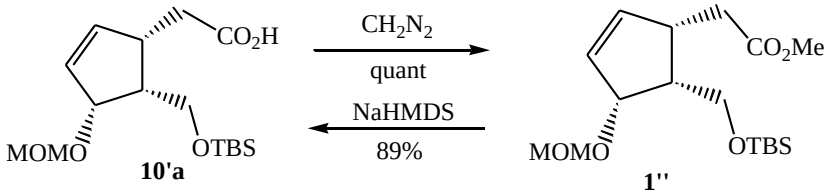
^1H NMR (acetone-d_6, 500 MHz): δ = 6.17 (dd, *J* = 5.8, 2.7 Hz, 1H, C^3H), 6.07-6.02 (m, 1H, C^2H), 4.67 (d, *J* = 6.6 Hz, 1H, $OCH_\alpha H_\beta O$), 4.63 (d, *J* = 6.6 Hz, 1H, $OCH_\alpha H_\beta O$), 4.48 (dd, *J* = 6.1, 2.4 Hz, 1H, C^4H), 3.94 (dd, *J* = 10.1, 7.7 Hz, 1H, $CH_\alpha H_\beta OSi$), 3.81 (dd, *J* = 10.1, 7.9 Hz, 1H, $CH_\alpha H_\beta OSi$), 3.67 (s, 3H, CO_2CH_3), 3.31 (s, 3H, CH_2OCH_3), 3.06-3.00 (m, 1H, C^1H), 2.68 (dd, *J* = 15.5, 5.4 Hz, 1H, $CH_\alpha H_\beta CO_2Me$), 2.42 (quint, *J* = 7.6 Hz, 1H, C^5H), 2.24 (dd, *J* = 15.7, 10.1 Hz, 1H, $CH_\alpha H_\beta CO_2Me$), 0.95 (s, 9H, $(CH_3)_3Si$), 0.13 (s, 3H, CH_3Si), 0.12 (s, 3H, CH_3Si).

^{13}C NMR (acetone-d_6, 125.77 MHz): δ = 173.50, 140.35, 133.03, 96.82, 81.72, 60.29, 55.17, 51.57, 48.18, 42.40, 37.06, 26.26, 18.74, -5.22, -5.28.

MS (APCI): *m*/z (%) = 345.1 (100) $[MH]^+$.

Anal. Calcd for $C_{17}H_{32}O_5Si$: C, 59.27; H, 9.36. Found: C, 59.01; H, 9.11.

Method B



Treatment of acid **10'a** with excess diazomethane at 0 °C for 3 h gave ester **1"** in quantitative yield.

2-[(1*S*,4*R*,5*R*)-5-((*tert*-Butyldimethylsilyloxy)methyl)-4-(methoxymethoxy)cyclopent-2-en-1-yl]acetic acid (10'a).

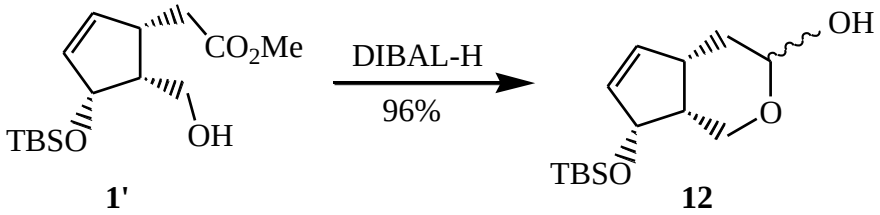
Ester **1"** (110 mg, 0.3 mmol) was treated as described in the synthesis of compounds **1**+**1'**+**11** with 1.6 M solution NaHMDS (0.3 mL, 0.45 mmol) in THF without methylation. Purification by column chromatography afforded the title compound. Yield: 93 mg (89%); colorless transparent oil; R_f = 0.4 (petroleum ether/ethyl acetate = 3:1); $[\alpha]_D^{20}$: + 36.3 (*c* 0.75, CH_2Cl_2).

IR (liquid film): 2953, 2857, 1740, 1472, 1255, 1096, 1040, 838, 775 cm^{-1}.

^1H NMR (acetone-d_6, 500 MHz): δ = 6.17 (dd, *J* = 5.8, 2.7 Hz, 1H, C^3H), 5.96-6.00 (m, 1H, C^2H), 4.62 (d, *J* = 6.6 Hz, 1H, $OCH_\alpha H_\beta O$), 4.59 (d, *J* = 6.6 Hz, 1H, $OCH_\alpha H_\beta O$), 4.42 (dd, *J* = 6.1, 2.4 Hz, 1H, C^4H), 3.90 (dd, *J* = 10.1, 7.8 Hz, 1H, $CH_\alpha H_\beta OSi$), 3.79 (dd, *J* = 10.1, 7.7 Hz, 1H, $CH_\alpha H_\beta OSi$), 3.28 (s,

3H, CH_3), 3.01-2.94 (m, 1H, C^1H), 2.93-2.82 (br s, 1H, COOH), 2.62 (dd, *J* = 15.8, 5.2 Hz, 1H, $CH_\alpha H_\beta CO_2Me$), 2.37 (quint, *J* = 7.2 Hz, 1H, C^5H), 2.17 (dd, *J* = 15.8, 10.5 Hz, 1H, $CH_\alpha H_\beta CO_2Me$), 0.90 (s, 9H, $(CH_3)_3Si$), 0.08 (s, 6H, $(CH_3)_2Si$).
^{13}C NMR (acetone-d_6, 125.77 MHz): δ = 173.14, 139.72, 131.96, 95.93, 80.90, 59.44, 54.27, 47.26, 41.44, 35.95, 25.37, 17.83, -6.11.
MS (APCI): *m*/z (%) = 329.2 (100) $[M-H]^-$.
Anal. Calcd for $C_{16}H_{30}O_5Si$: C, 58.15; H, 9.15. Found: C, 57.94; H, 9.00.

(4a*S*,7*R*,7a*R*)-7-((*Tert*-butyldimethylsilyl)oxy)-1,3,4,4a,7,7a-hexahydrocyclopenta[*c*]pyran-3-ol (12).



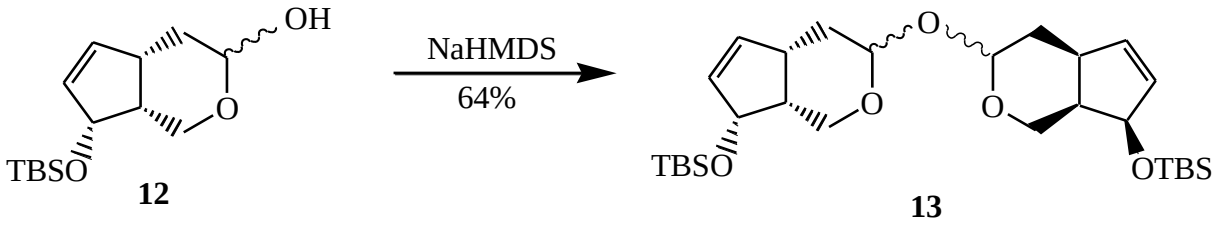
1' **12**

The compound **1'** (0.12 g, 0.4 mmol), treated as described in the synthesis of **2** with DIBAL-H (0.11 g, 0.8 mmol) at -78 °C, afforded the title compound as a 2:1 mixture of epimers.
Yield: 0.1 g (96%); colorless transparent oil; R_f = 0.4 (petroleum ether/ethyl acetate = 3:1).
IR (liquid film): 2954, 2857, 1727, 1471, 1250, 1092, 836, 776 cm^{-1}.
MS (APCI): *m*/z (%) = 269.1 (100) $[M-H]^+$.
Anal. Calcd for $C_{14}H_{26}O_3Si$: C, 62.18; H, 9.69. Found: C, 61.97; H, 9.41.

For major isomer:
^1H NMR (acetone-d_6, 500 MHz): δ = 5.76-5.72 (m, 1H, C^6H), 5.68-5.64 (m, 1H, C^5H), 4.94-4.88 (m, 1H, C^3H), 4.65 (dd, *J* = 7.8, 2.5 Hz, 1H, C^7H), 3.78 (dd, *J* = 12.0, 6.1 Hz, 1H, $C^1H_\alpha H_\beta$), 3.58 (dd, *J* = 12.2, 9.7 Hz, 1H, $C^1H_\alpha H_\beta$), 2.86 (s, 1H, OH), 2.50-2.35 (m, 2H, $C^{7a}H$, $C^{4a}H$), 1.81 (dt, *J* = 13.6, 3.0 Hz, 1H, $C^4H_\alpha H_\beta$), 1.65-1.57 (m, 1H, $C^1H_\alpha H_\beta$), 0.89 (s, 9H, $(CH_3)_3Si$), 0.08 (s, 6H, $(CH_3)_2Si$).
^{13}C NMR (acetone-d_6, 125.77 MHz): δ = 134.76, 134.62, 93.06, 78.84, 62.00, 41.09, 40.10, 33.67, 25.29, 17.79, -5.58, -5.75.

For minor isomer:
^1H NMR (acetone-d_6, 500 MHz): δ = 5.91-5.84 (m, 1H, C^6H), 5.72-5.69 (m, 1H, C^5H), 5.03 (dd, *J* = 5.4, 4.7 Hz, 1H, C^3H), 4.85 (d, *J* = 6.9 Hz, 1H, C^7H), 4.05 (t, *J* = 11.5 Hz, 1H, $C^1H_\alpha H_\beta$), 3.51 (dd, *J* = 11.9, 6.9 Hz, 1H, $C^1H_\alpha H_\beta$), 2.89 (s, 1H, OH), 2.60-2.53 (m, 1H, $C^{4a}H$), 2.36-2.31 (m, 1H, $C^{7a}H$), 1.94 (dt, *J* = 13.8, 5.4 Hz, 1H, $C^4H_\alpha H_\beta$), 1.47 (ddd, *J* = 13.6, 9.6, 6.6 Hz, 1H, $C^1H_\alpha H_\beta$), 0.87 (s, 9H, $(CH_3)_3Si$), 0.09 (s, 6H, $(CH_3)_2Si$).
^{13}C NMR (acetone-d_6, 125.77 MHz): δ = 136.64, 132.98, 91.21, 77.50, 56.77, 40.59, 39.54, 33.39, 25.32, 17.79, -5.34, -5.78.

(((4a*S*,4a'*S*,7*R*,7a*R*,7'*R*,7a'*R*)-Oxybis(1,3,4,4a,7,7a-hexahydrocyclopenta[*c*]pyran-3,7-diyl))bis(oxy))bis(*tert*-butyldimethylsilane) (13).



Compound **12** (170 mg, 0.63 mmol) was treated as described in the synthesis of compounds **3a**+**3b**+**4** with 1.6 M solution NaHMDS (3.54 mL, 5.67 mmol) in THF and (5-hydroxy-5-oxopentyl)triphenylphosphonium bromide (1.12 g, 5.04 mmol) for 5 h by reflux. Final purification by column chromatography afforded title compound.
Yield: 0.1 g (64%); colorless transparent oil; R_f = 0.4 (petroleum ether/ethyl acetate = 40:1).
IR (liquid film): 2956, 2929, 2856, 1472, 1249, 1117, 1073, 839, 774 cm^{-1}.
MS (APCI): *m*/z (%) = 156.1 (100) $[C_8H_{12}O_3]^+$.
Anal. Calcd for $C_{28}H_{50}O_5Si_2$: C, 64.32; H, 9.64. Found: C, 64.17; H, 9.51.

For major epimer:
^{1}H NMR (acetone-d_6, 500 MHz): δ = 5.76-5.72 (m, 1H, C^{6}H), 5.69-5.65 (m, 1H, C^{5}H), 4.92 (dd, *J* = 4.7, 2.3 Hz, 1H, C^{3}H), 4.79 (dd, *J* = 7.6, 2.6 Hz, 1H, C^{7}H), 3.79 (dd, *J* = 12.0, 6.3 Hz, 1H, C$^1H_\alpha H_\beta$), 3.63 (dd, *J* = 12.0, 9.6 Hz, 1H, C$^1H_\alpha H_\beta$), 2.94-2.87 (m, 1H, C^{4a}H), 2.53-2.45 (m, 1H, C^{7a}H), 1.78 (dt, *J* = 7.2, 3.0 Hz, 1H, C$^4H_\alpha H_\beta$), 1.71-1.64 (m, 1H, C$^1H_\alpha H_\beta$), 0.89 (s, 9H, $(CH_3)_3Si$), 0.10 (s, 6H, $(CH_3)_2Si$).
^{13}C NMR (acetone-d_6, 125.77 MHz): δ = 134.79, 134.51, 93.79, 78.75, 61.90, 40.83, 39.57, 34.68, 25.30, 17.79, -5.56, -5.76.

For minor epimer:
^{1}H NMR (acetone-d_6, 500 MHz): δ = 5.88 (d, *J* = 5.5 Hz, 1H, C^{6}H), 5.71 (dt, *J* = 5.5, 1.9 Hz, 1H, C^{5}H), 5.11 (dd, *J* = 6.4, 4.7 Hz, 1H, C^{3}H), 4.73 (d, *J* = 6.9 Hz, 1H, C^{7}H), 4.02 (dd, *J* = 11.5, 10.6 Hz, 1H, C$^1H_\alpha H_\beta$), 3.54 (dd, *J* = 11.8, 7.2 Hz, 1H, C$^1H_\alpha H_\beta$), 2.57-2.52 (m, 1H, C^{4a}H), 2.45-2.39 (m, 1H, C^{7a}H), 1.97 (dt, *J* = 13.7, 5.4 Hz, 1H, C$^4H_\alpha H_\beta$), 1.46 (ddd, *J* = 13.6, 9.7, 6.4 Hz, 1H, C$^1H_\alpha H_\beta$), 0.87 (s, 9H, $(CH_3)_3Si$), 0.09 (s, 6H, $(CH_3)_2Si$).
^{13}C NMR (acetone-d_6, 125.77 MHz): δ = 136.74, 132.85, 92.21, 77.09, 57.12, 40.05, 39.05, 34.98, 25.30, 17.79, -5.15, -5.78.

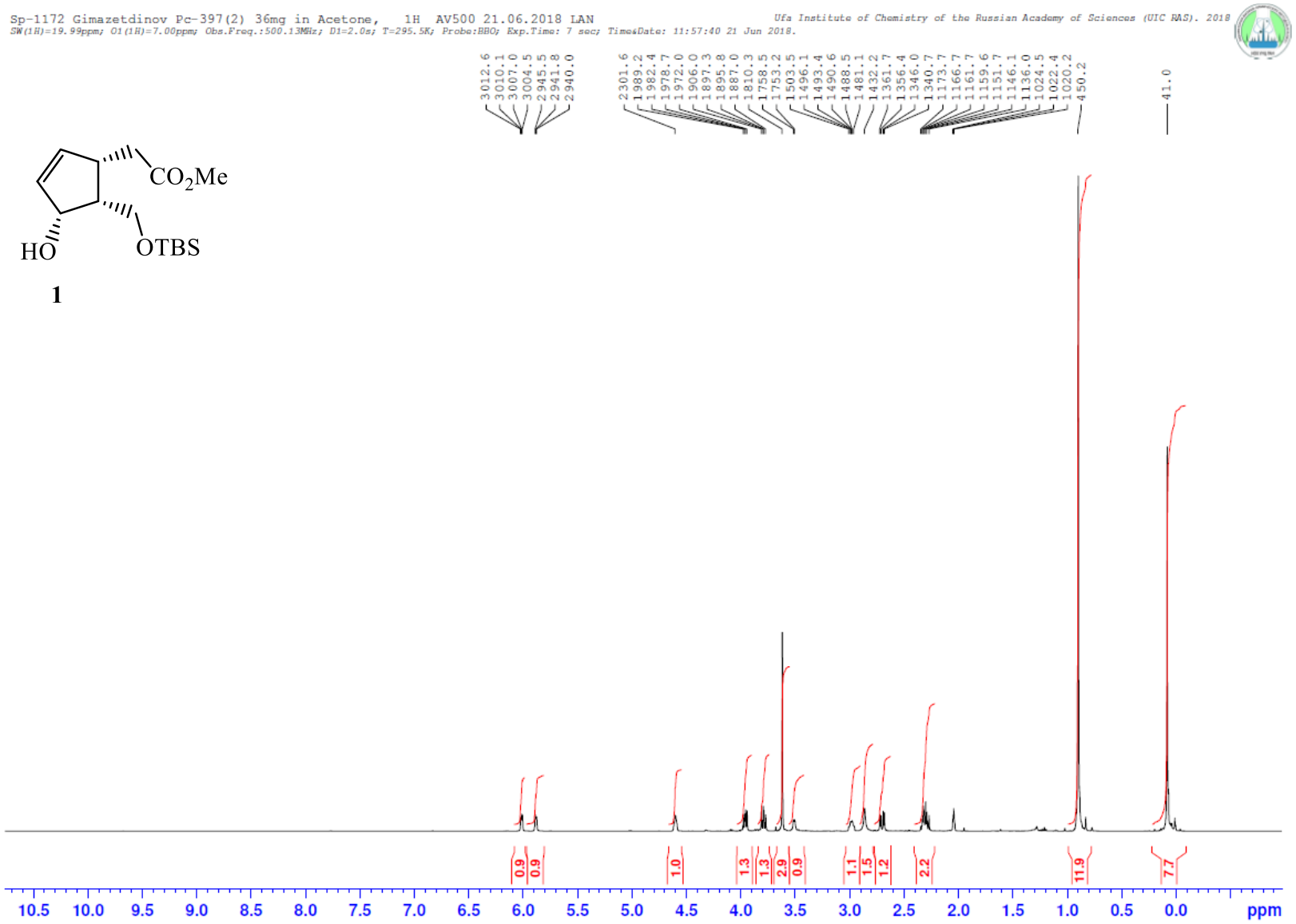


Figure S1 ^{1}H NMR spectrum of **1** (*d*-acetone, 500 MHz)

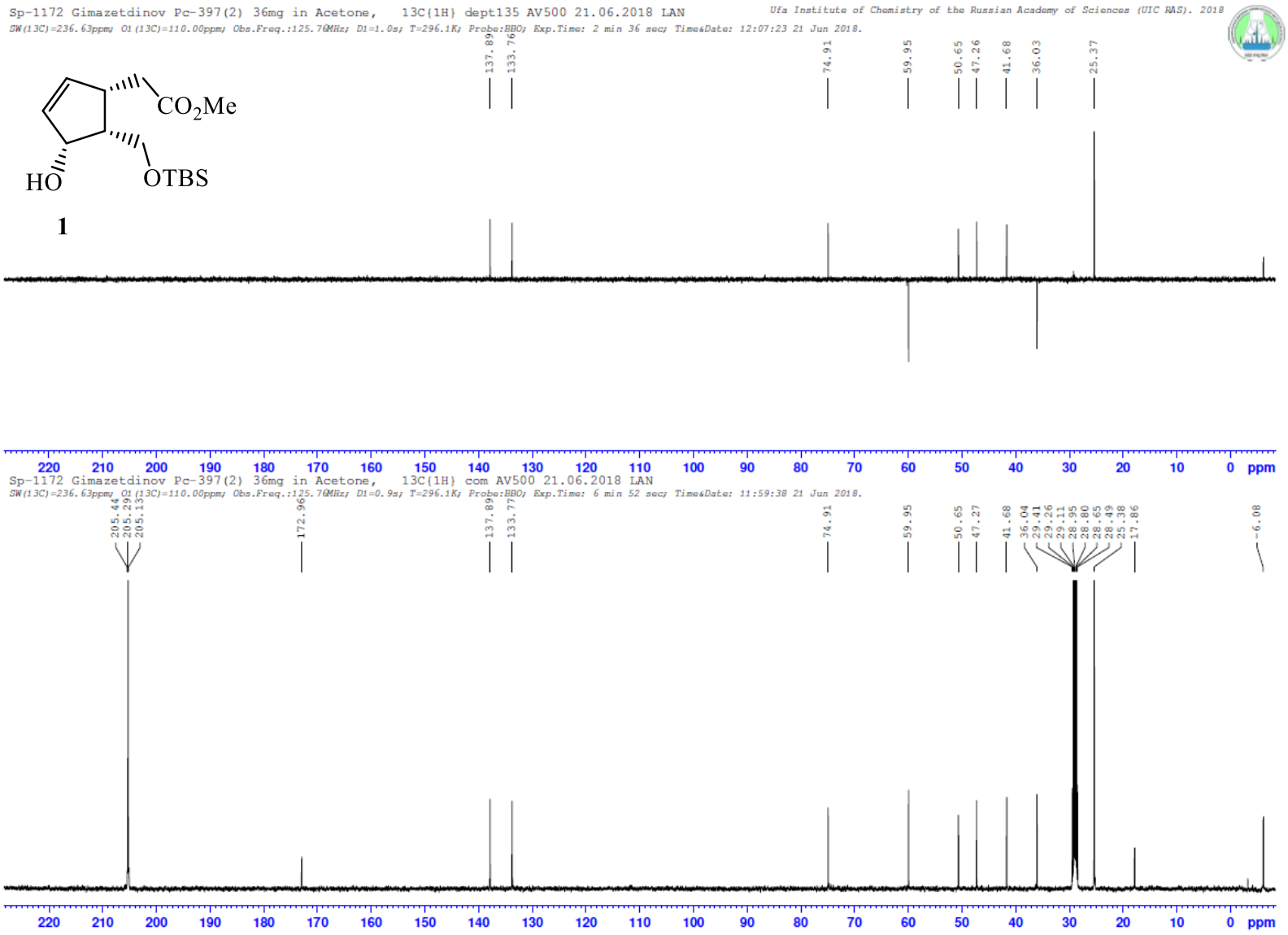


Figure S2 ^{13}C NMR spectrum of **1** (*d*-acetone, 125.77 MHz)

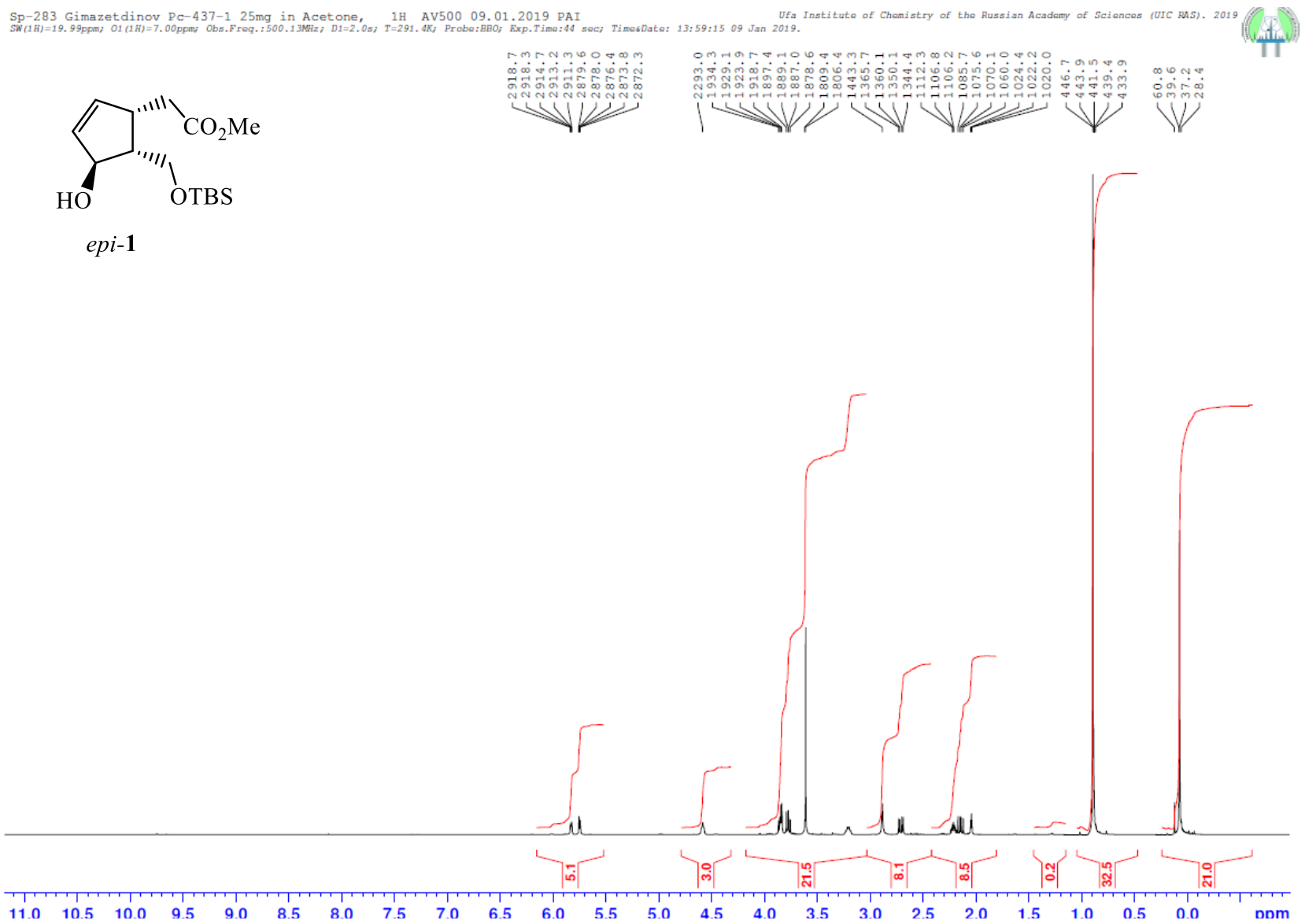
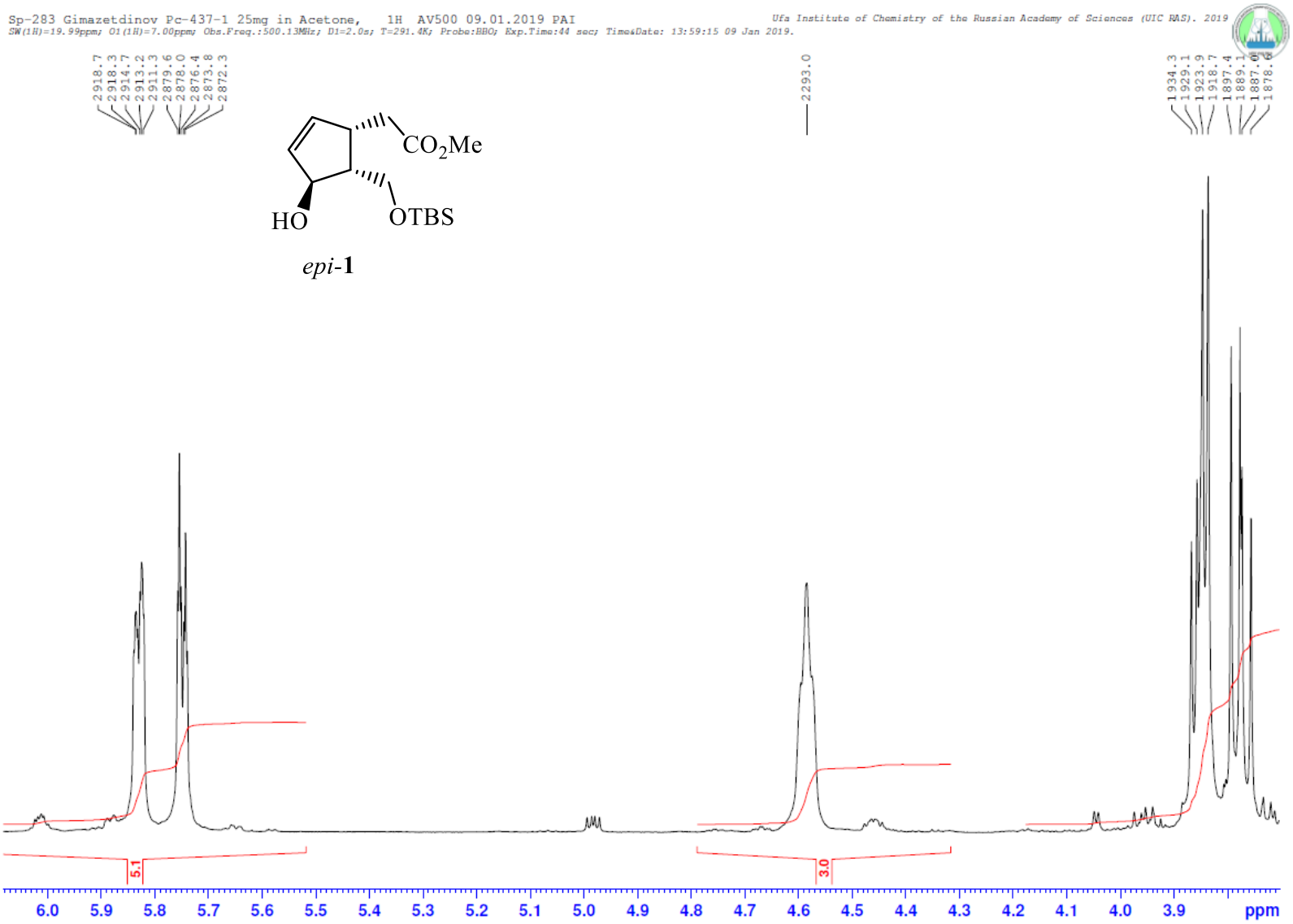


Figure S3 ^{1}H NMR spectrum of *epi*-**1** (*d*-acetone, 500 MHz)



epi-**1**

Figure S4 ^{1}H NMR spectrum of *epi*-**1** (*d*-acetone, 500 MHz)

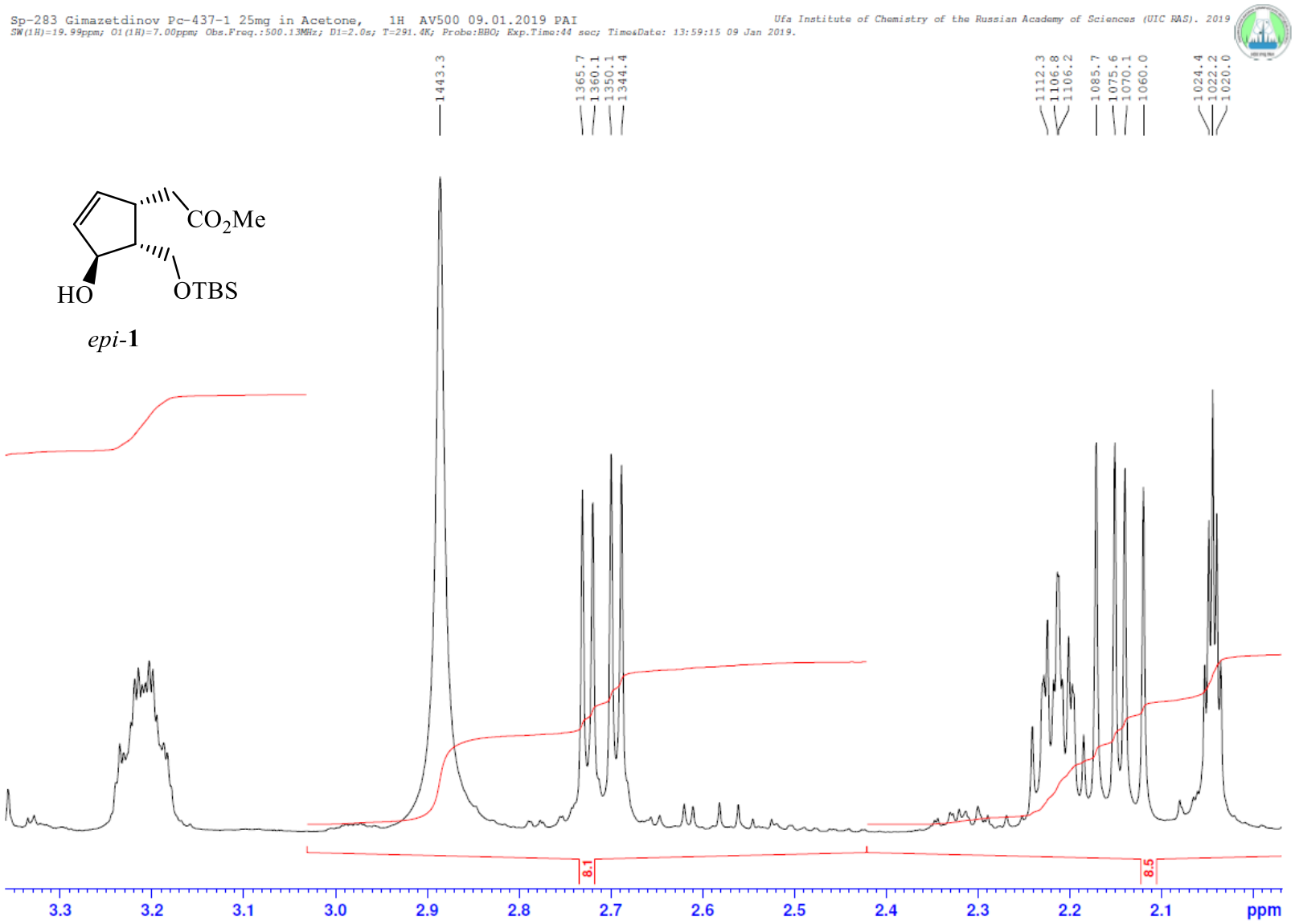


Figure S5 ^{1}H NMR spectrum of *epi*-**1** (*d*-acetone, 500 MHz)

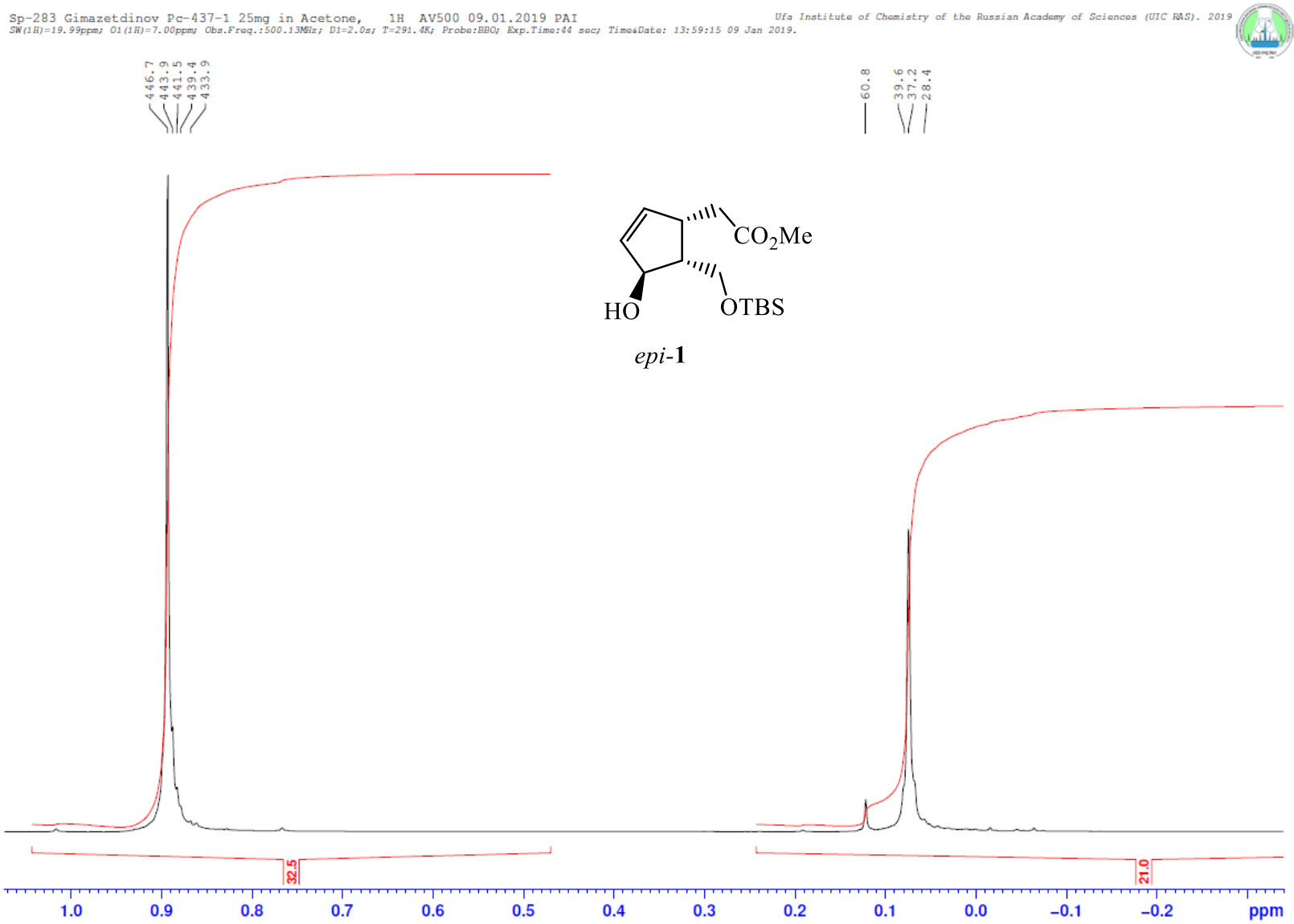


Figure S6 ^{1}H NMR spectrum of *epi*-**1** (*d*-acetone, 500 MHz)

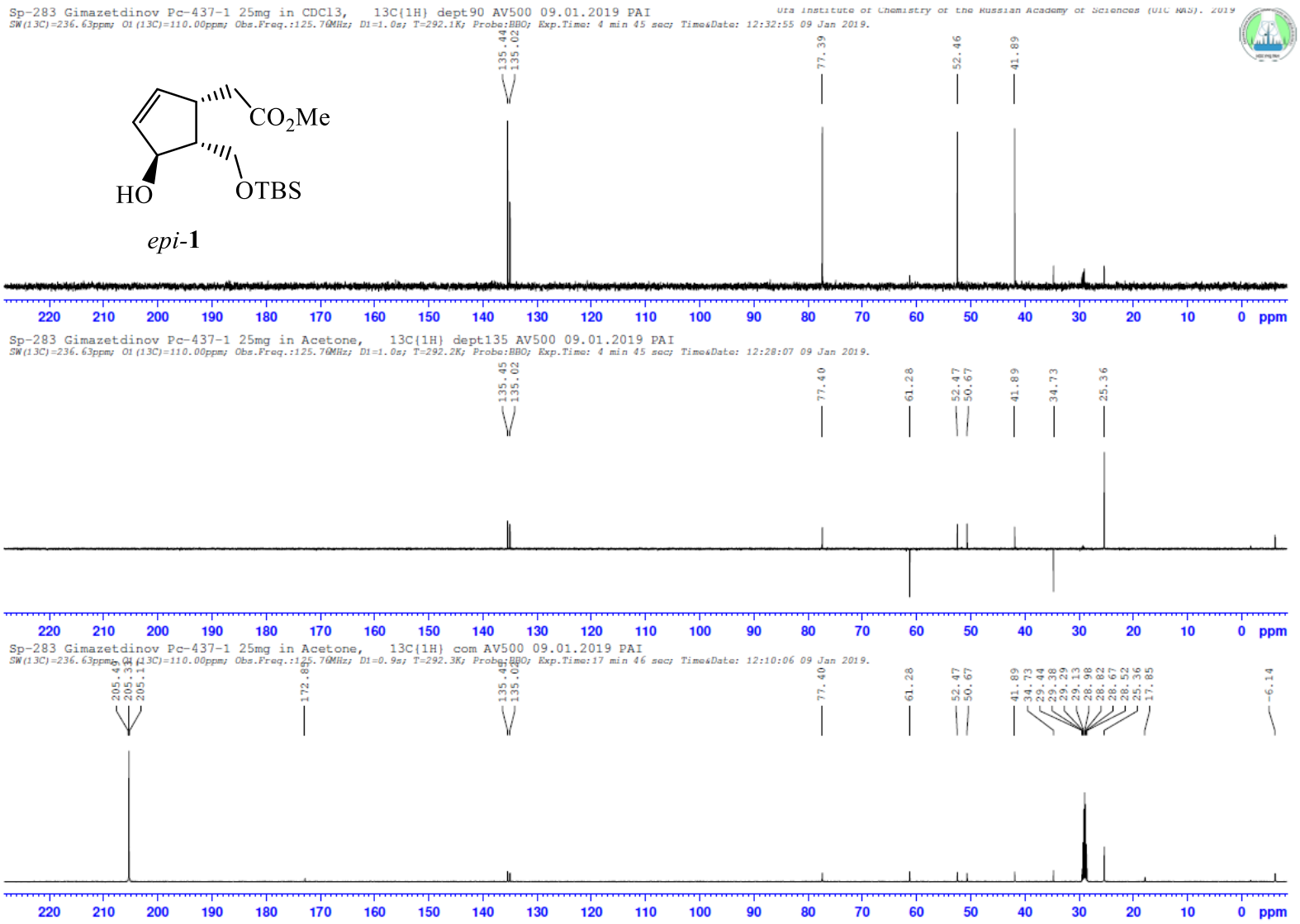


Figure S7 ^{13}C NMR spectrum of *epi*-**1** (*d*-acetone, 125.77 MHz)

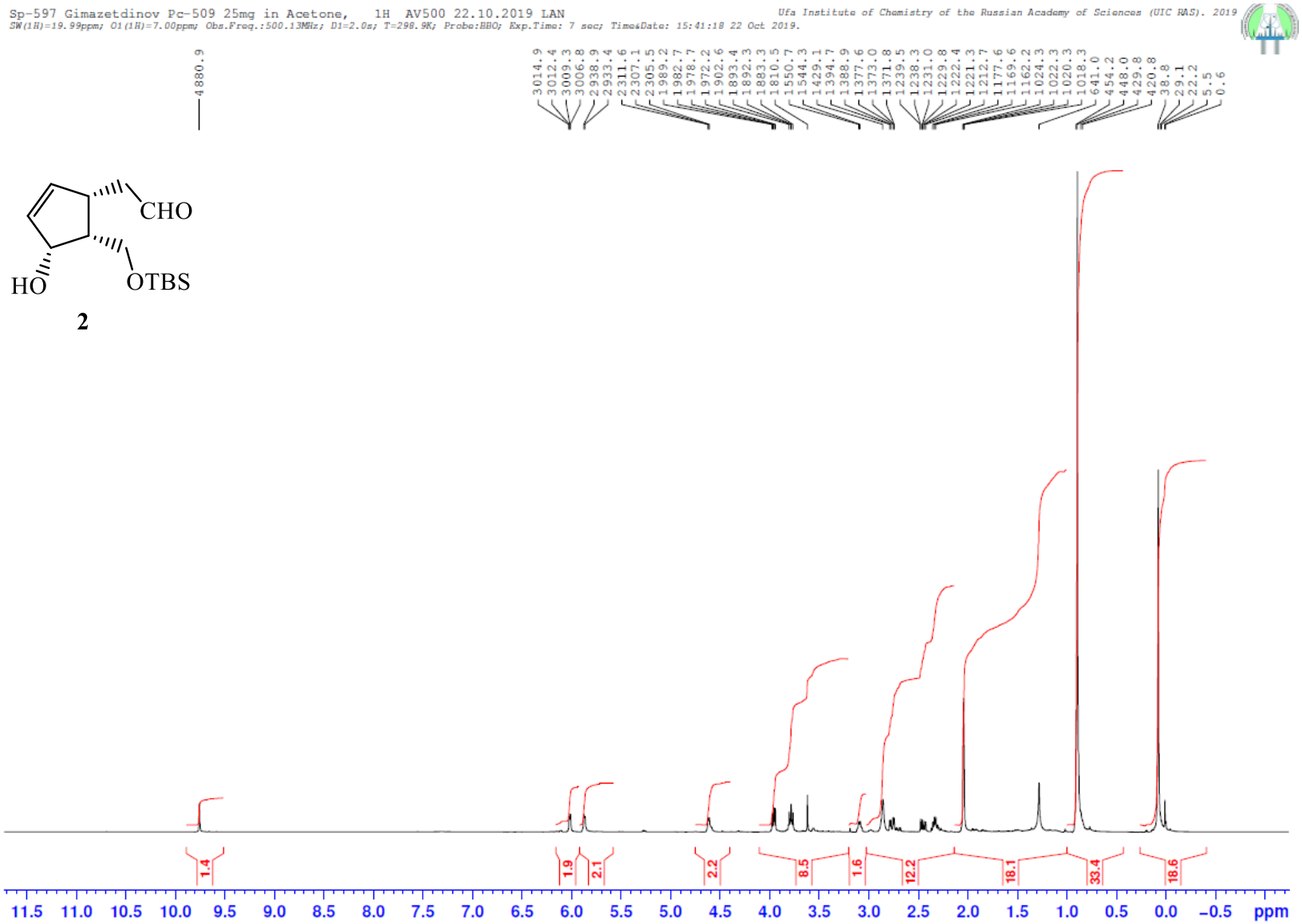


Figure S8 ^{1}H NMR spectrum of **2** (*d*-acetone, 500 MHz)

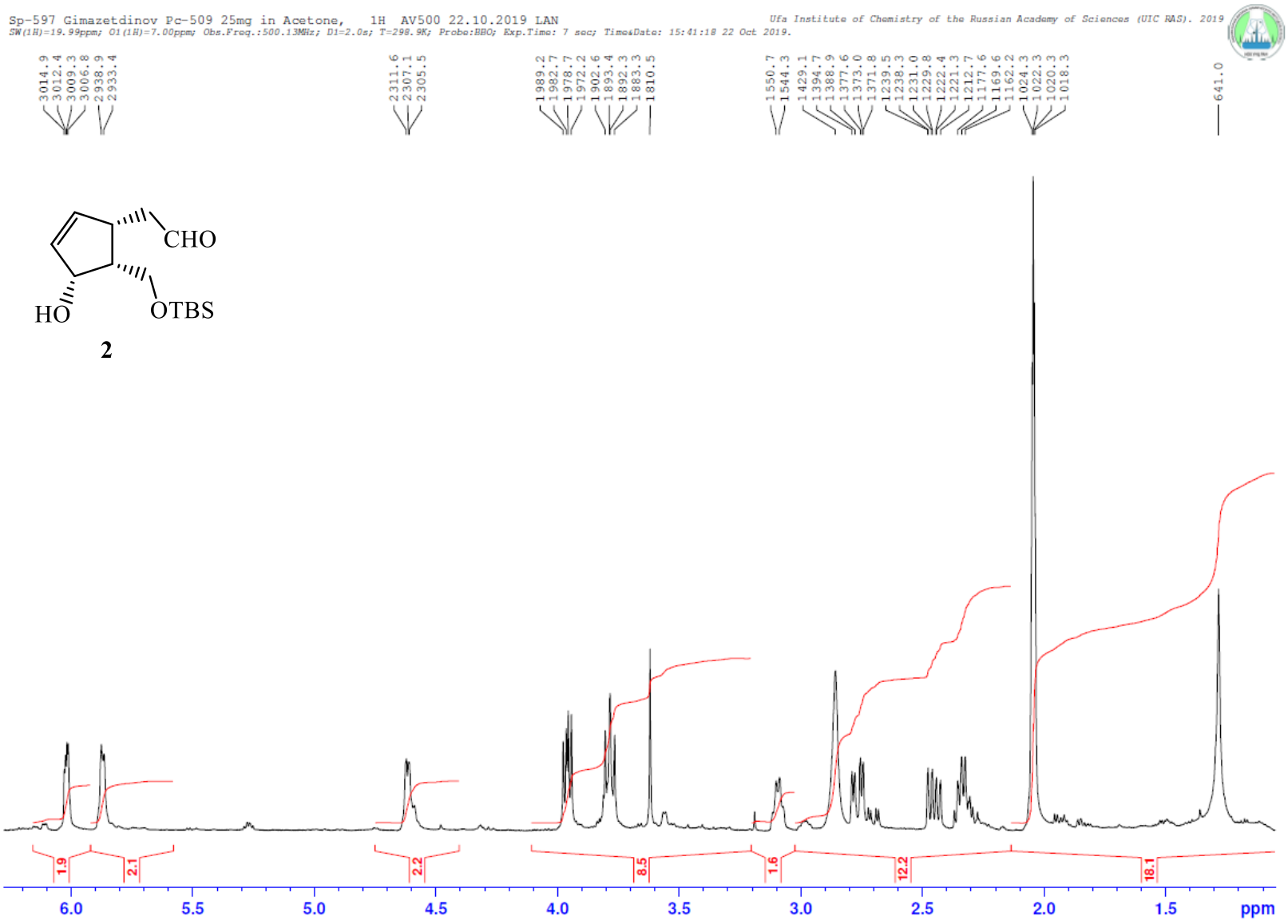


Figure S9 ^{1}H NMR spectrum of **2** (*d*-acetone, 500 MHz)

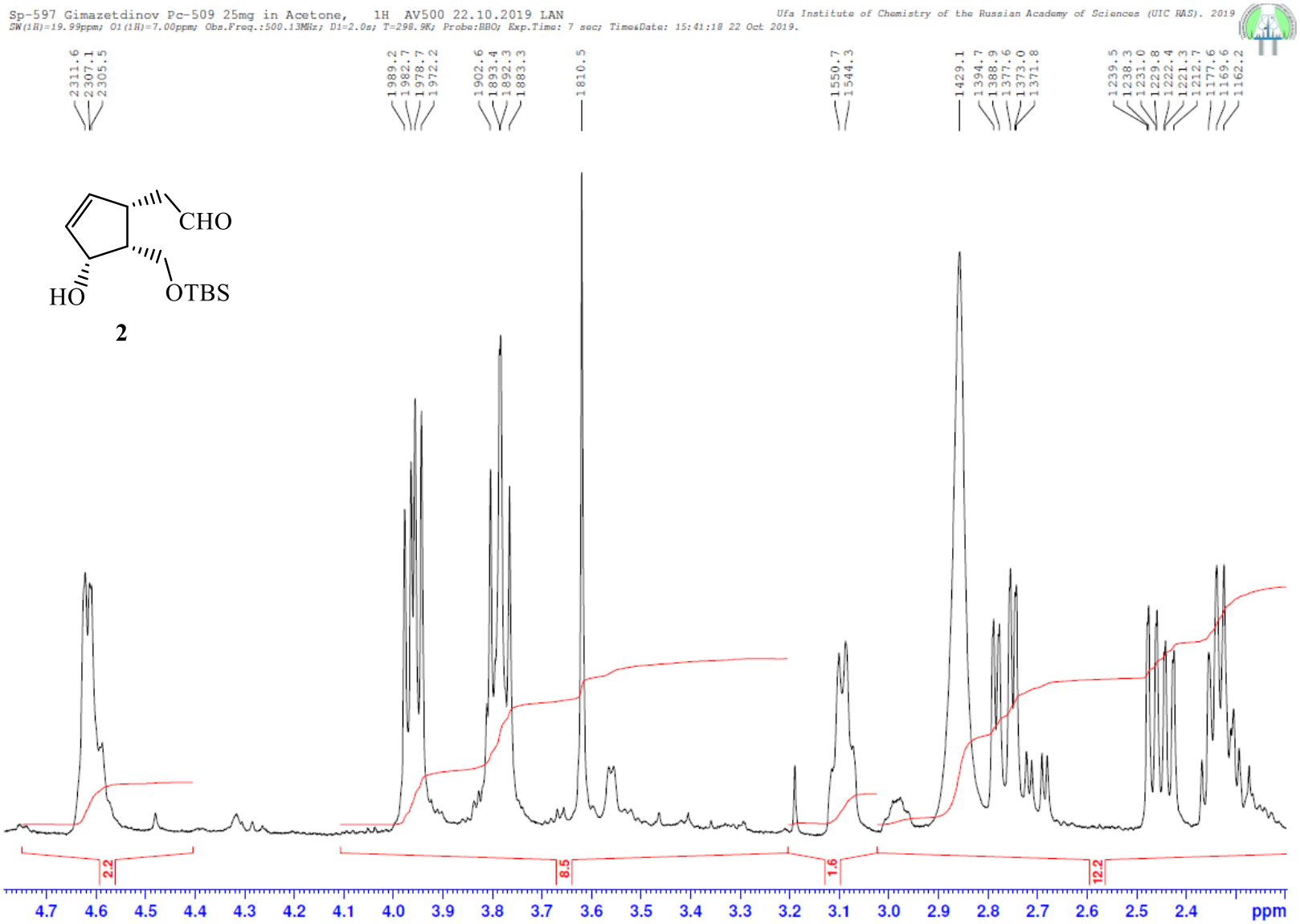


Figure S10 ^{1}H NMR spectrum of **2** (*d*-acetone, 500 MHz)

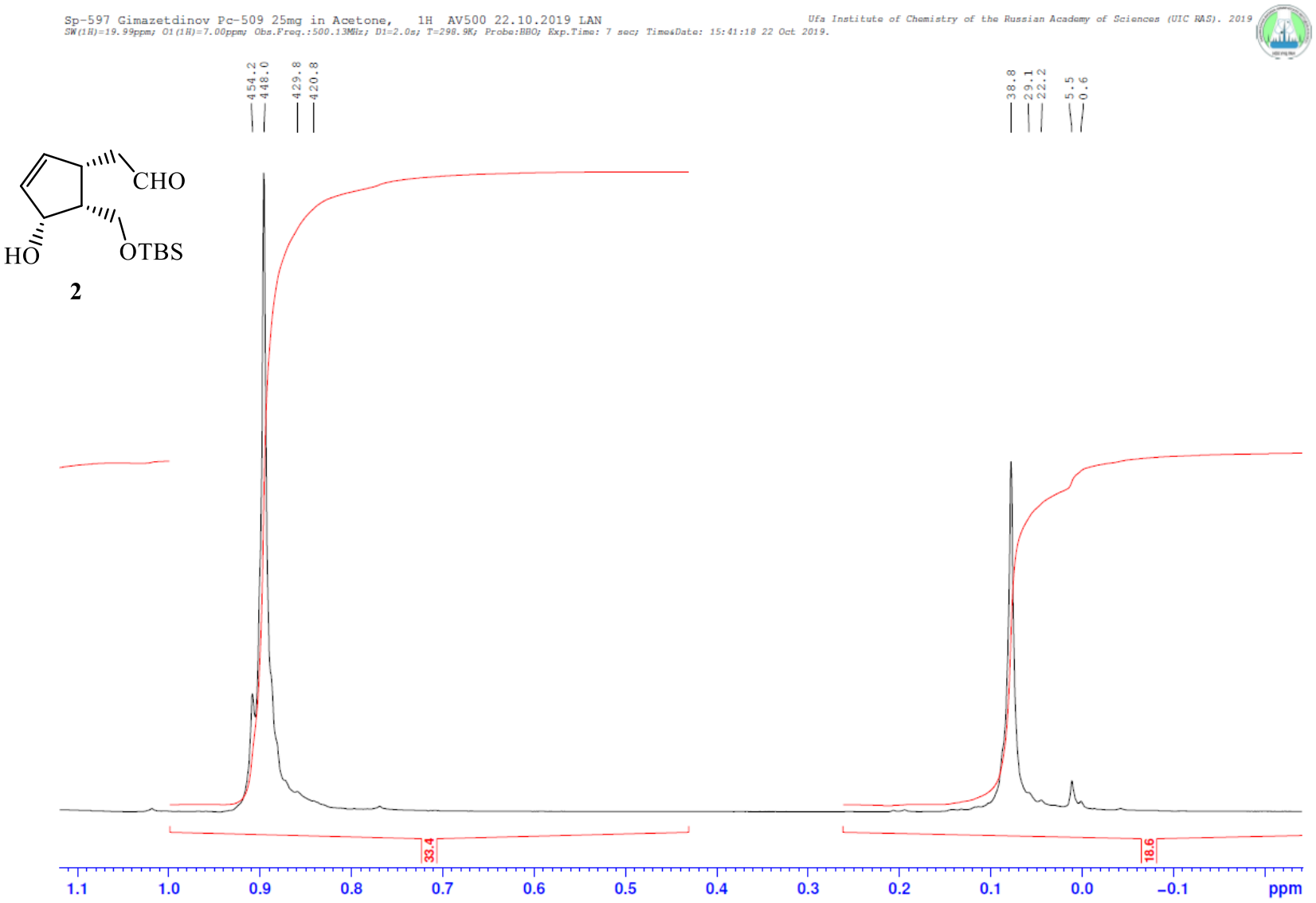


Figure S11 ^{1}H NMR spectrum of **2** (*d*-acetone, 500 MHz)

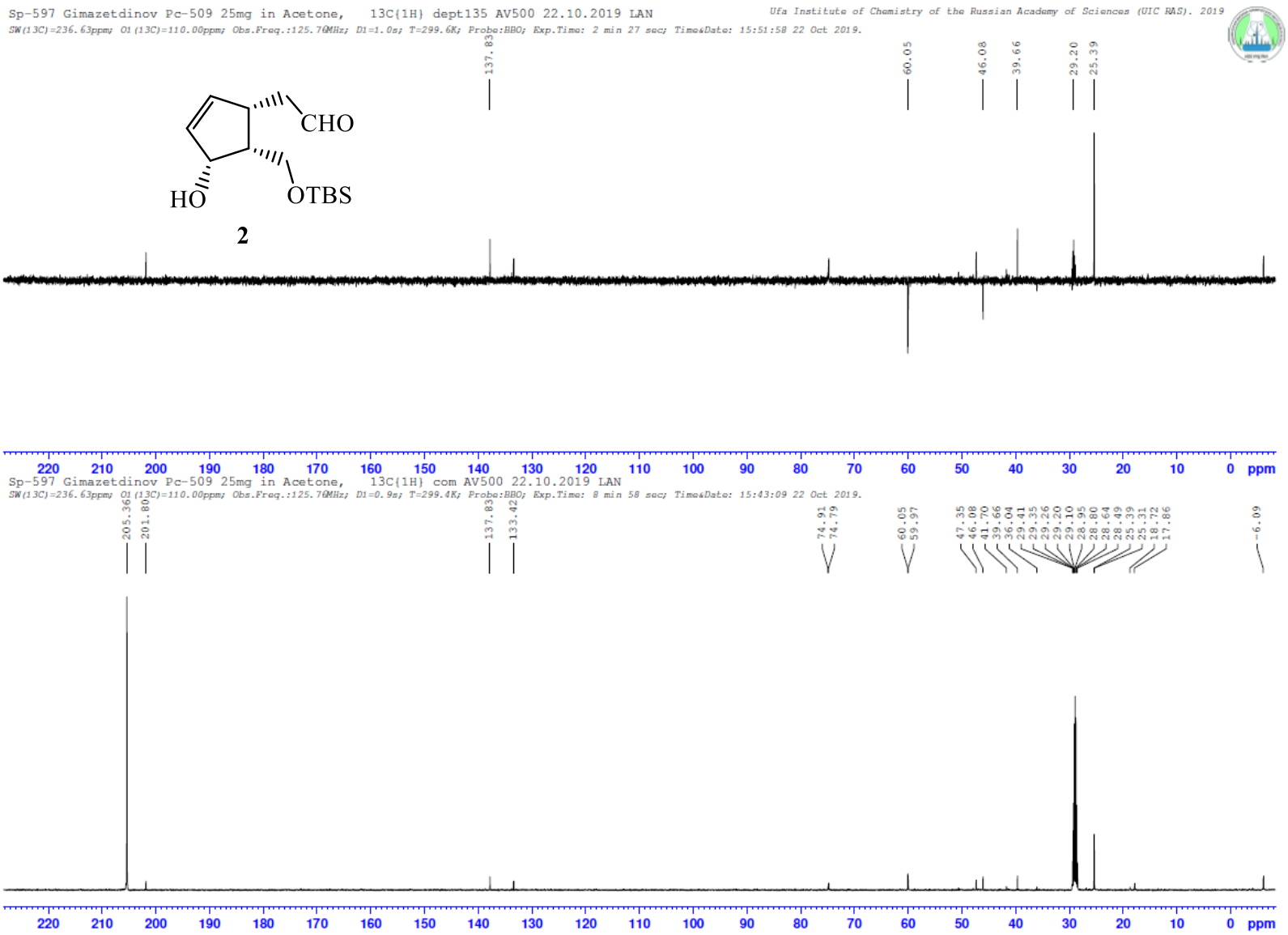


Figure S12 ^{13}C NMR spectrum of **2** (*d*-acetone, 125.77 MHz)

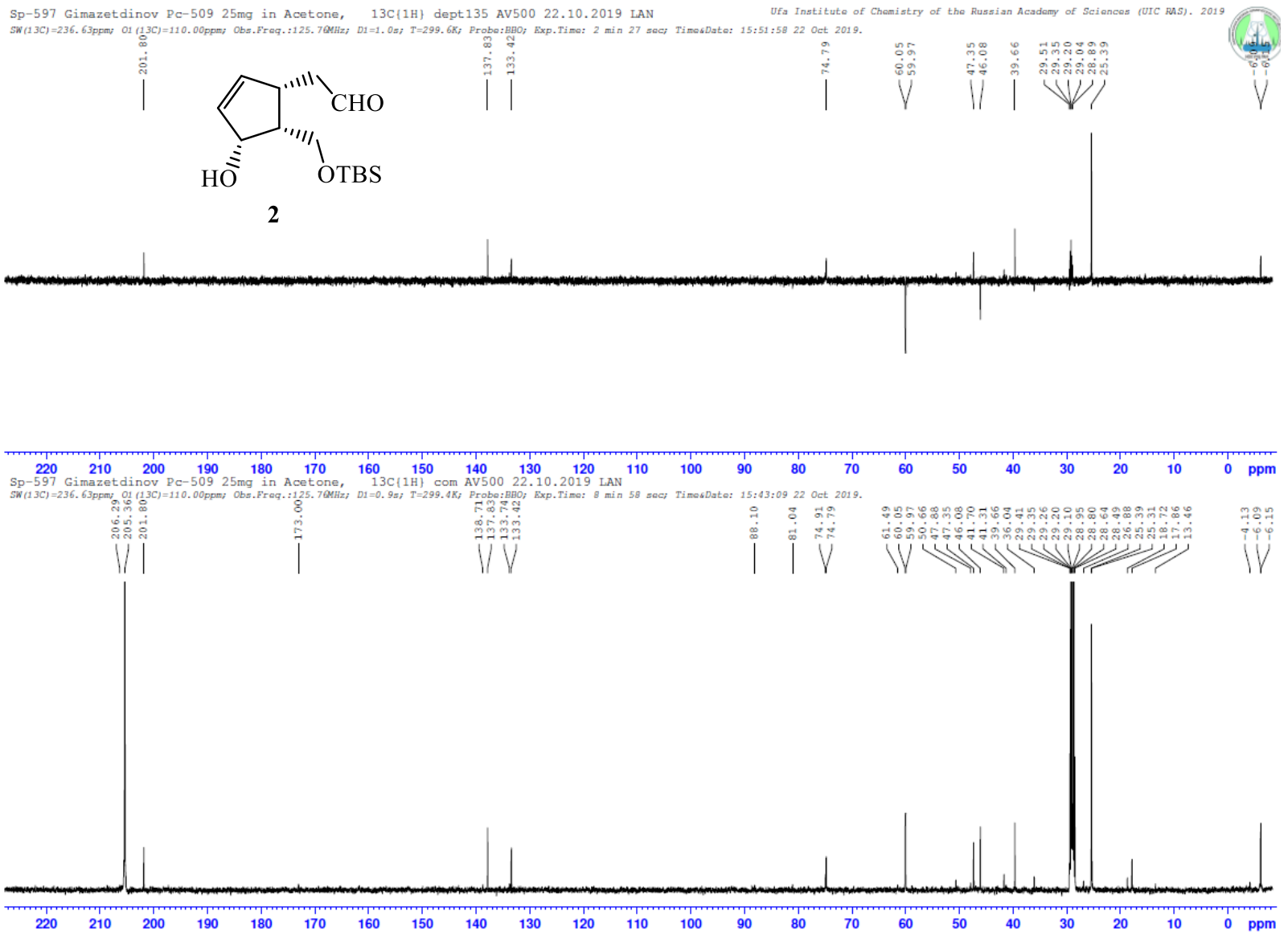


Figure S13 ^{13}C NMR spectrum of **2** (*d*-acetone, 125.77 MHz)

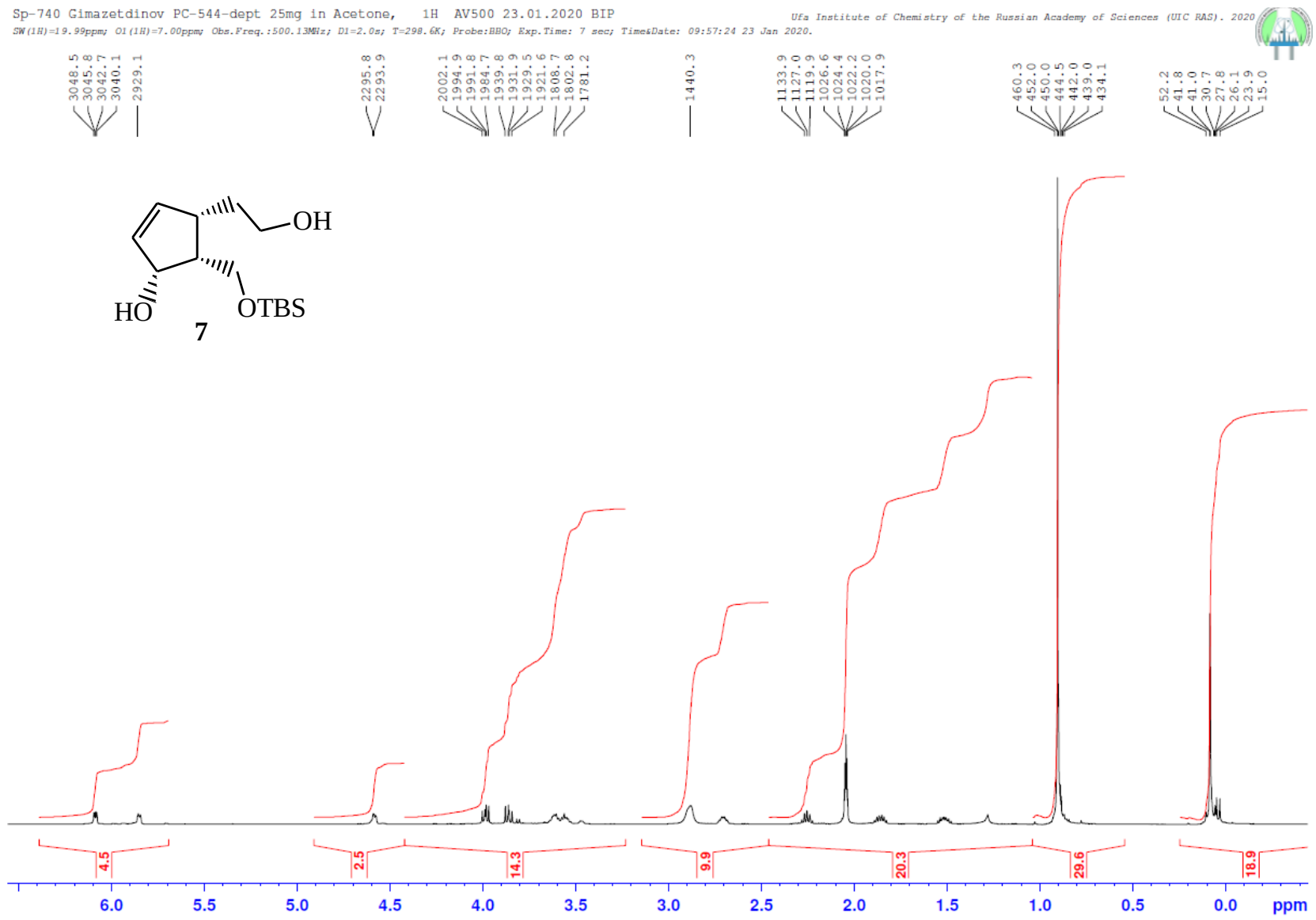


Figure S14 ^{1}H NMR spectrum of **7** (*d*-acetone, 500 MHz)

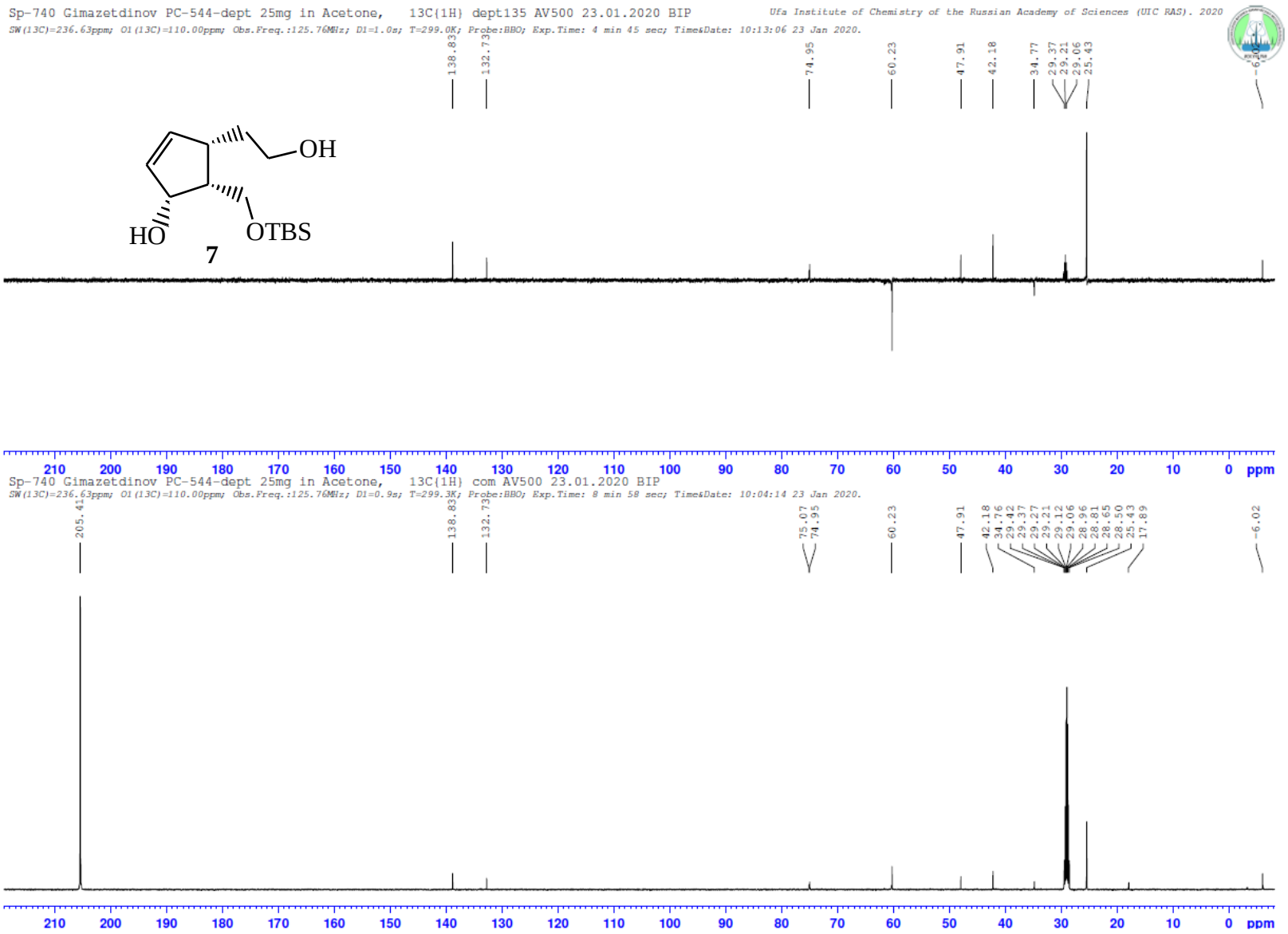


Figure S15 ^{13}C NMR spectrum of **7** (*d*-acetone, 125.77 MHz)

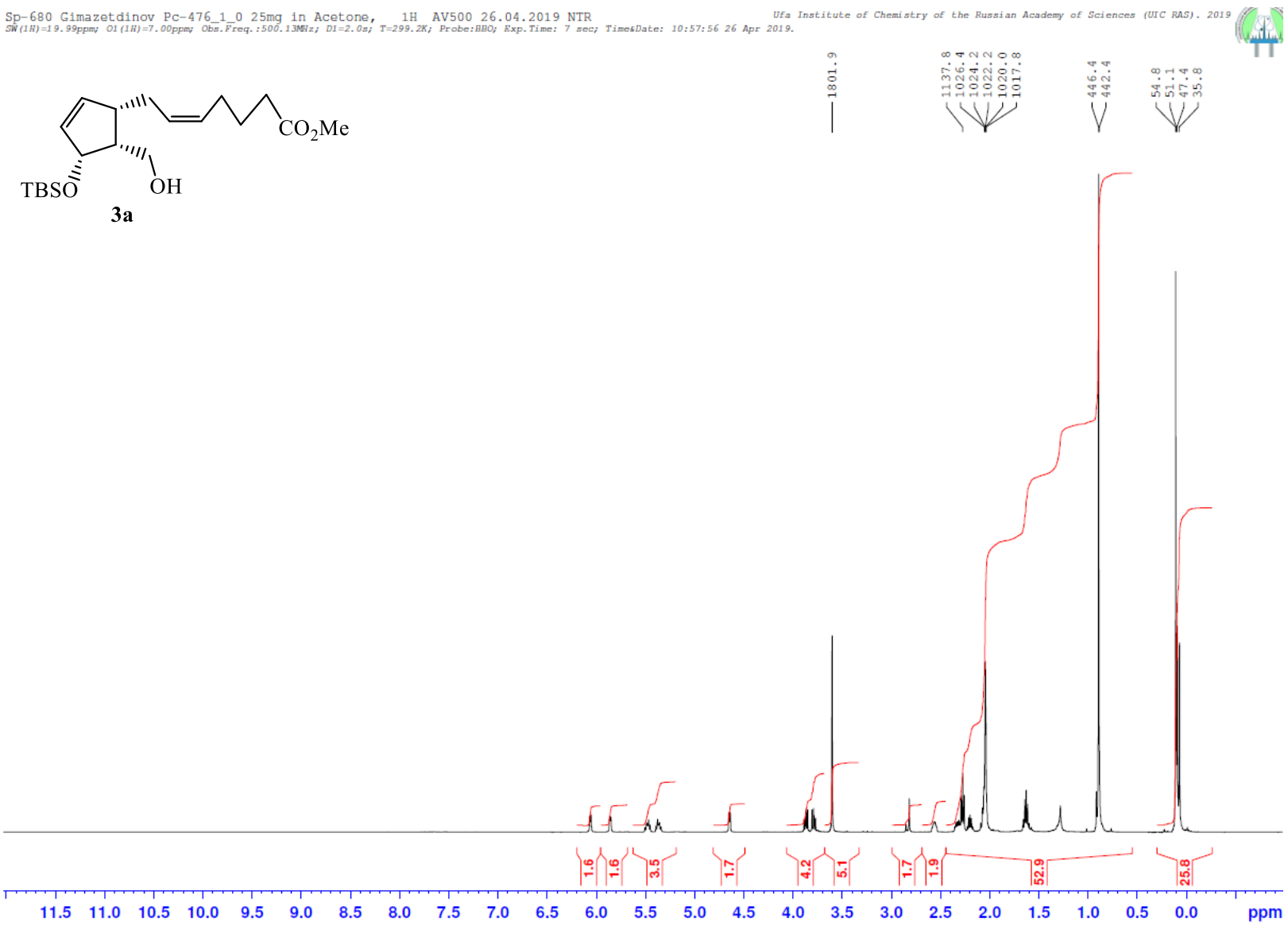


Figure S16 ^{1}H NMR spectrum of **3a** (*d*-acetone, 500 MHz)

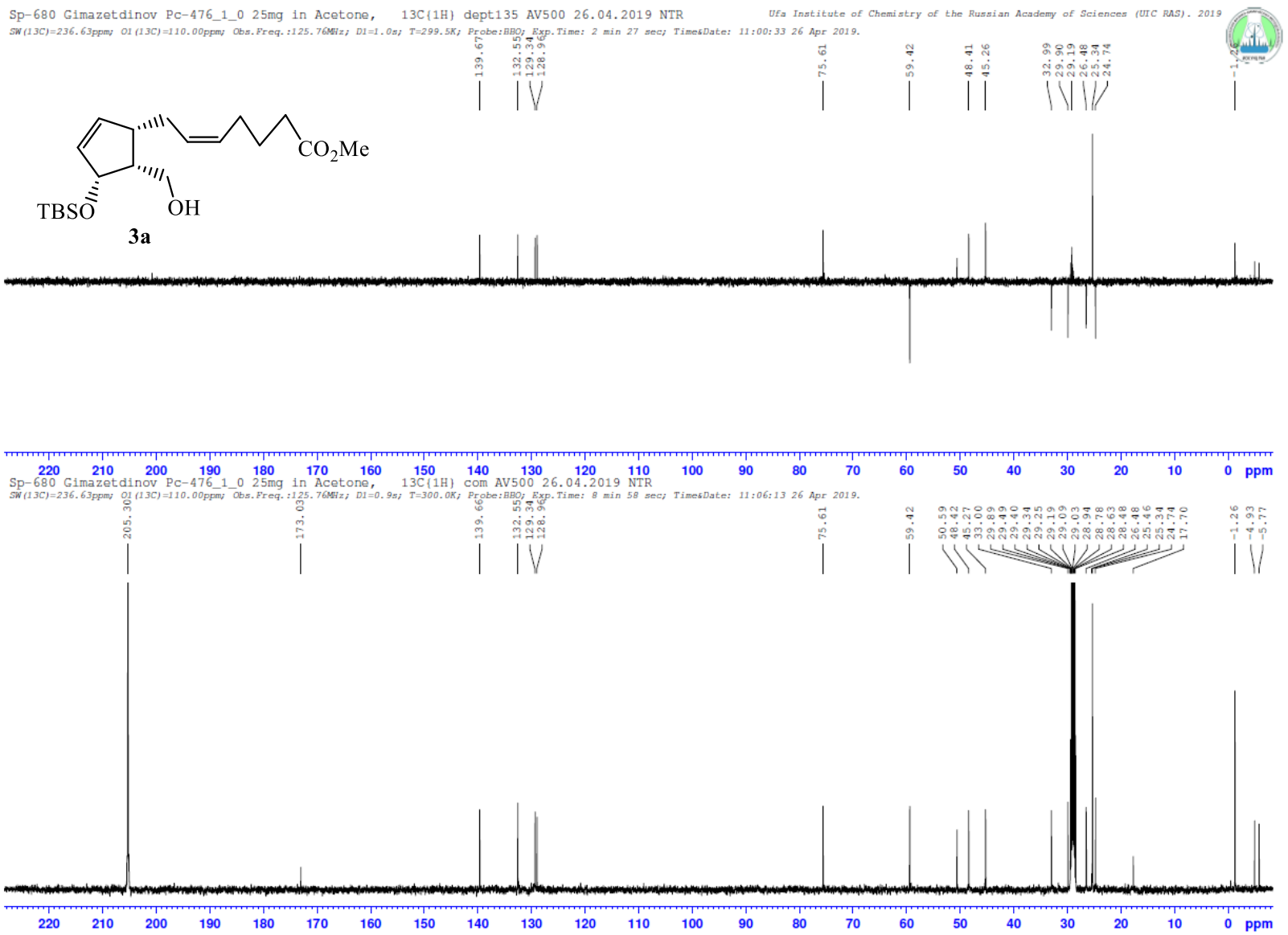


Figure S17 ^{13}C NMR spectrum of **3a** (*d*-acetone, 125.77 MHz)

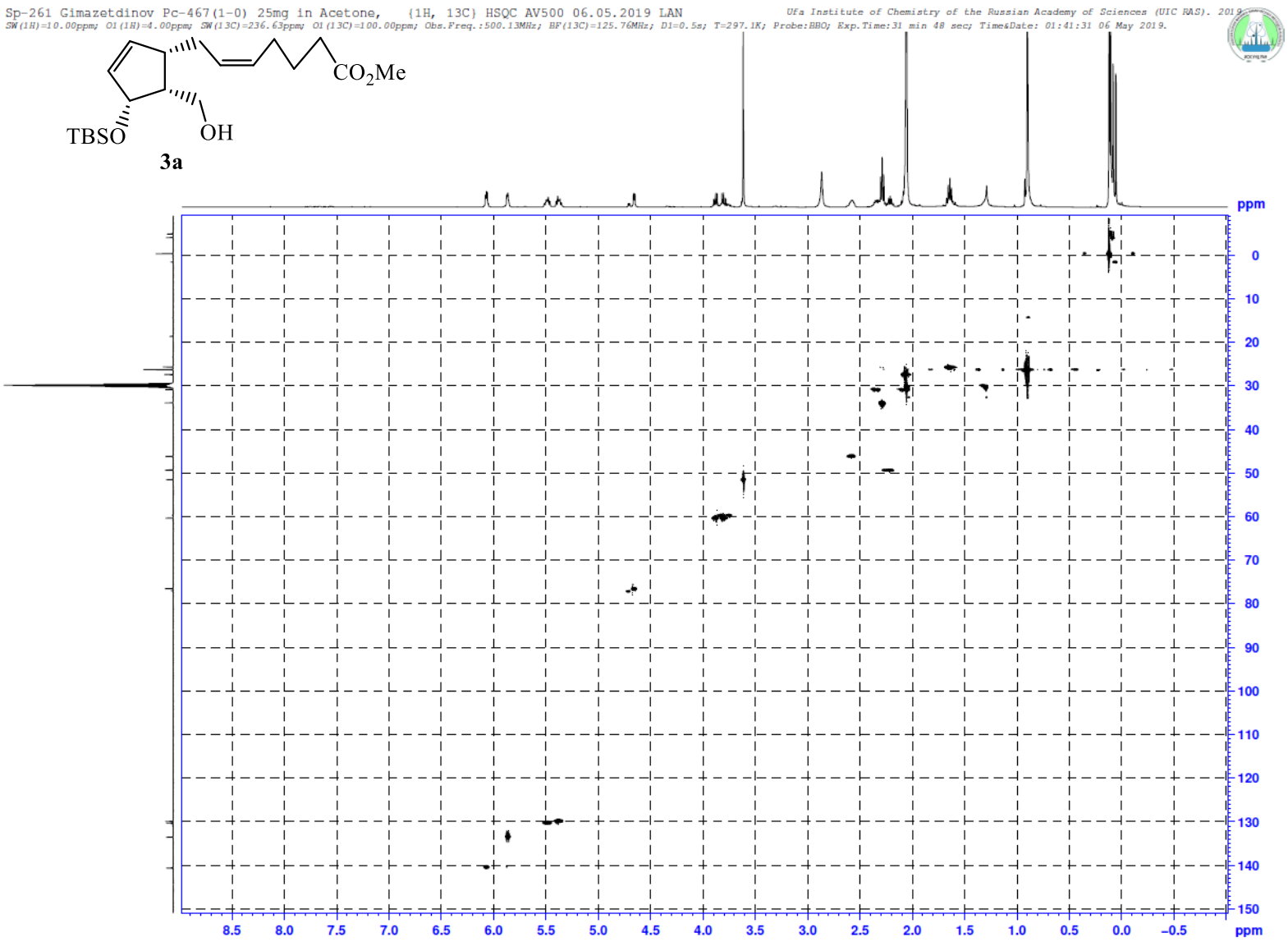


Figure S18 {^{1}H, ^{13}C} HSQC NMR spectrum of **3a** (*d*-acetone, 125.77 MHz)

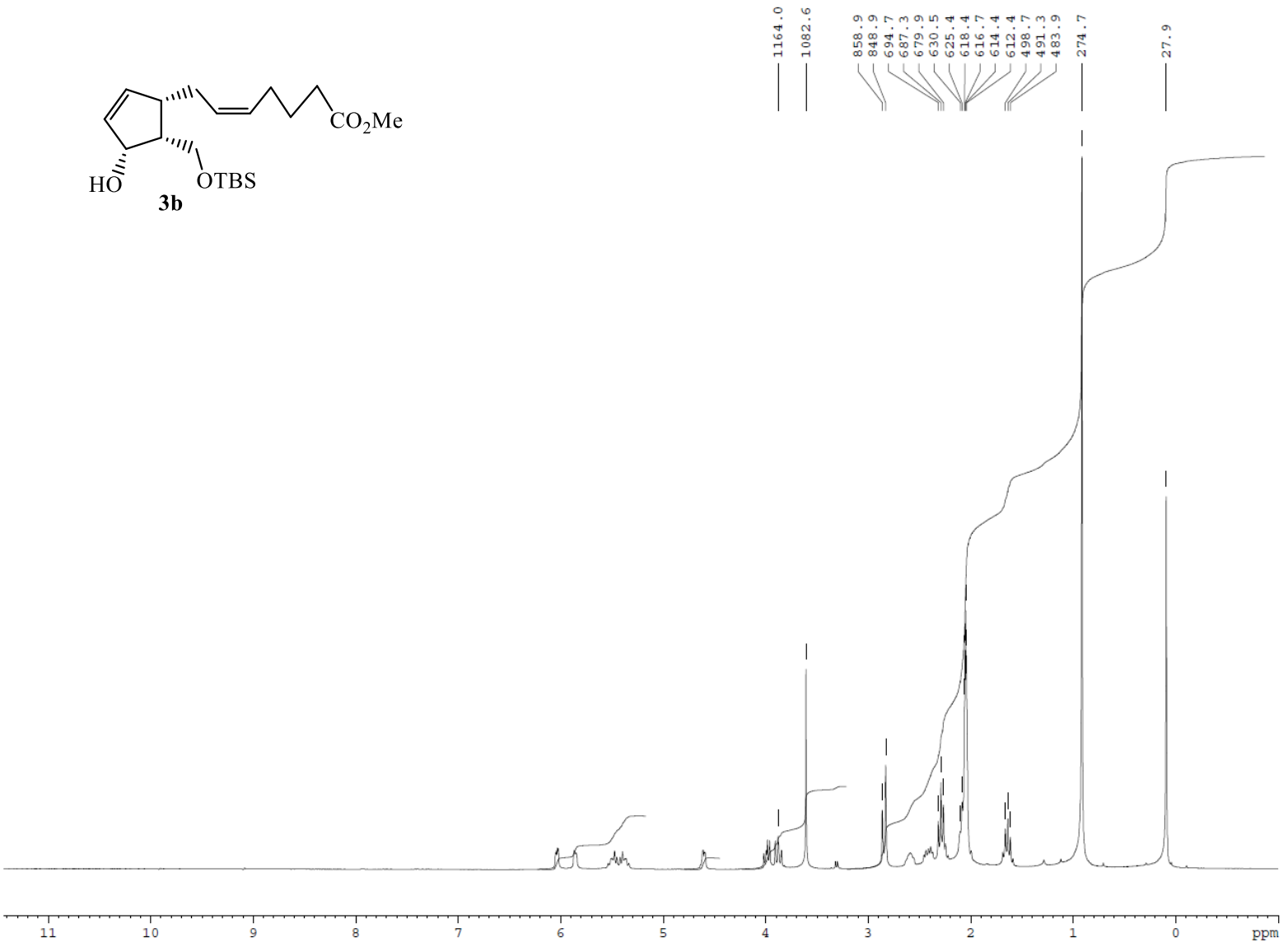


Figure S19 ^{1}H NMR spectrum of **3b** (*d*-acetone, 500 MHz)

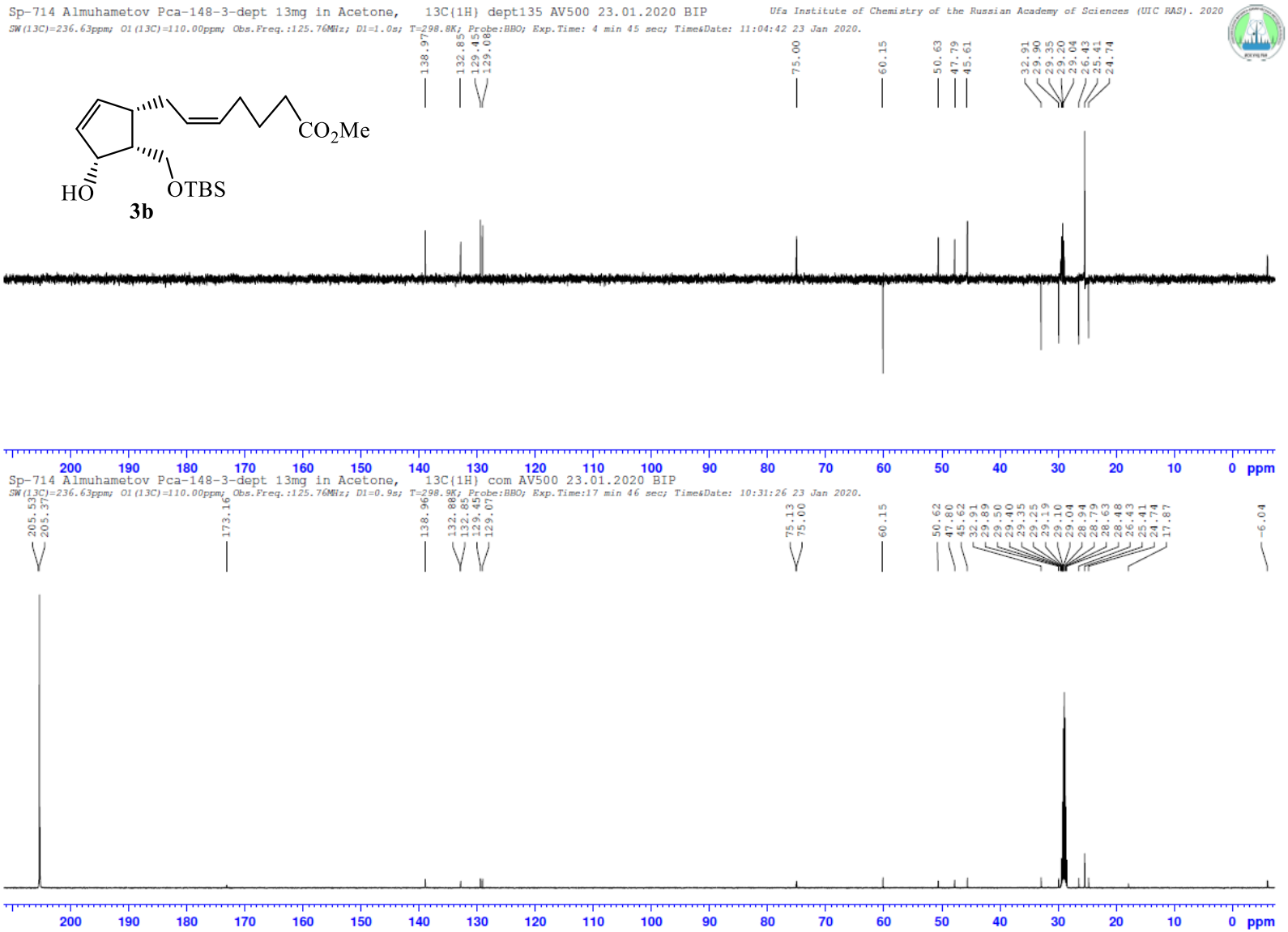


Figure S20 ^{13}C NMR spectrum of **3b** (*d*-acetone, 125.77 MHz)

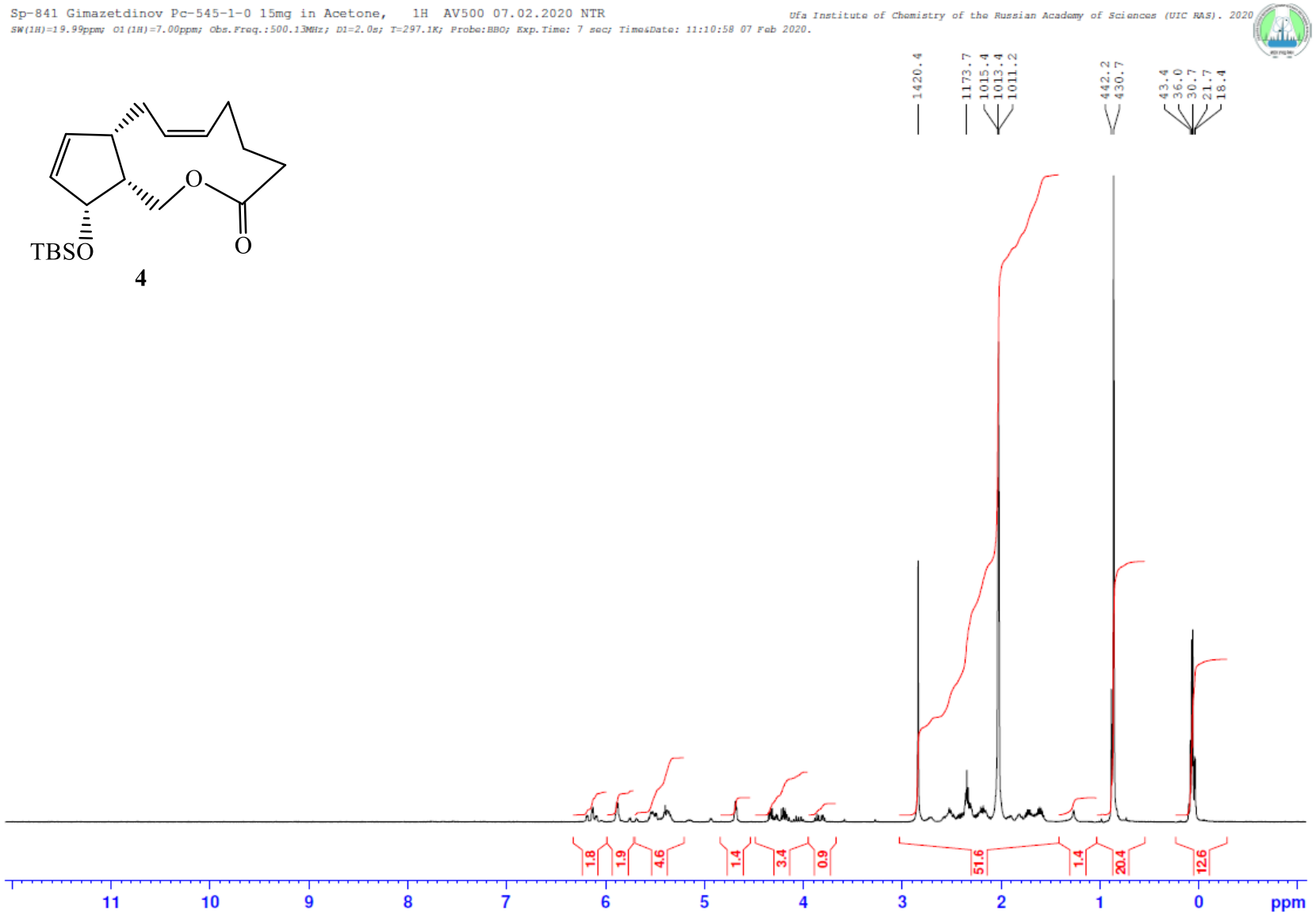


Figure S21 ^{1}H NMR spectrum of **4** (*d*-acetone, 500 MHz)

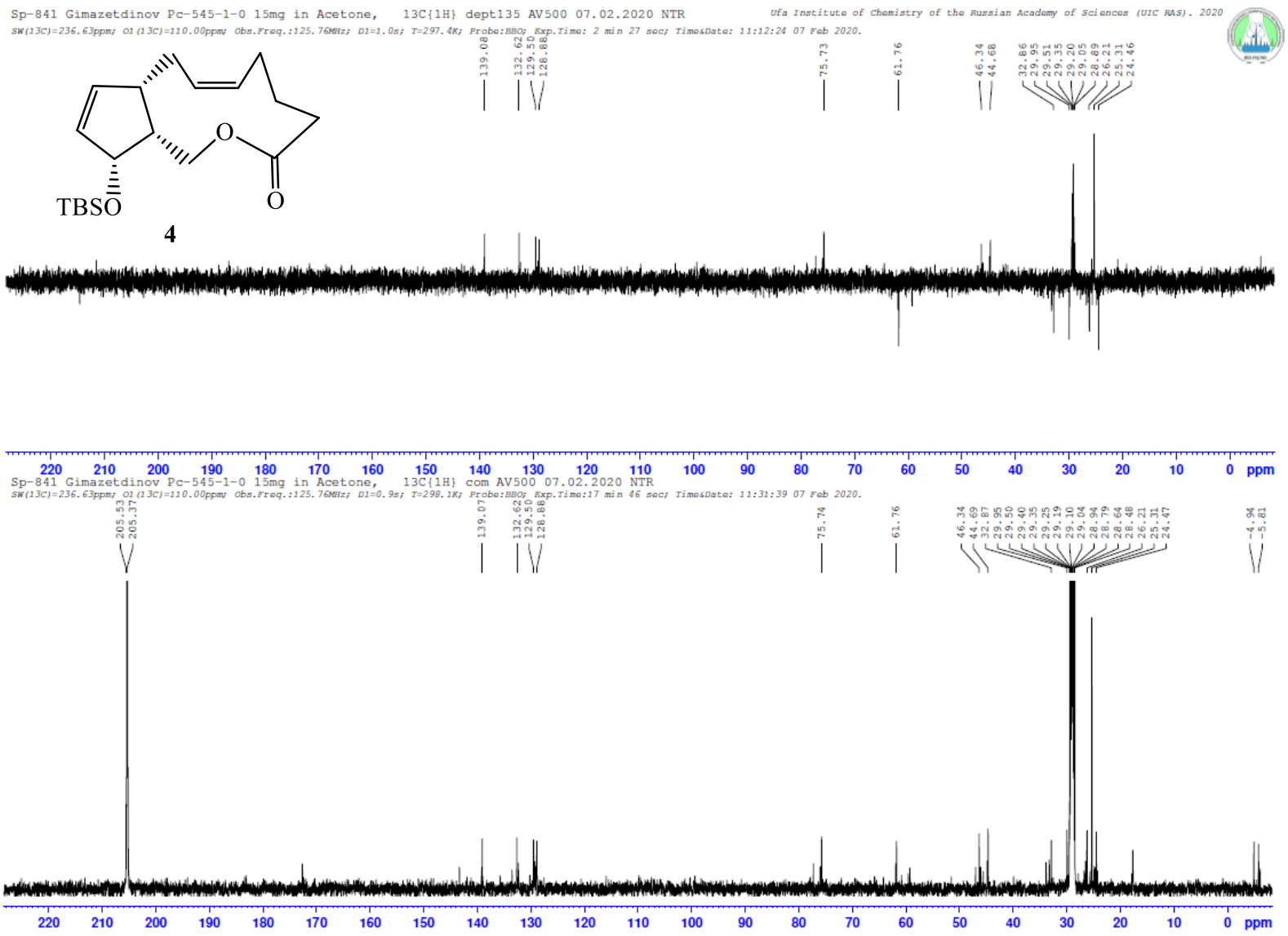


Figure S22 ^{13}C NMR spectrum of **4** (*d*-acetone, 125.77 MHz)

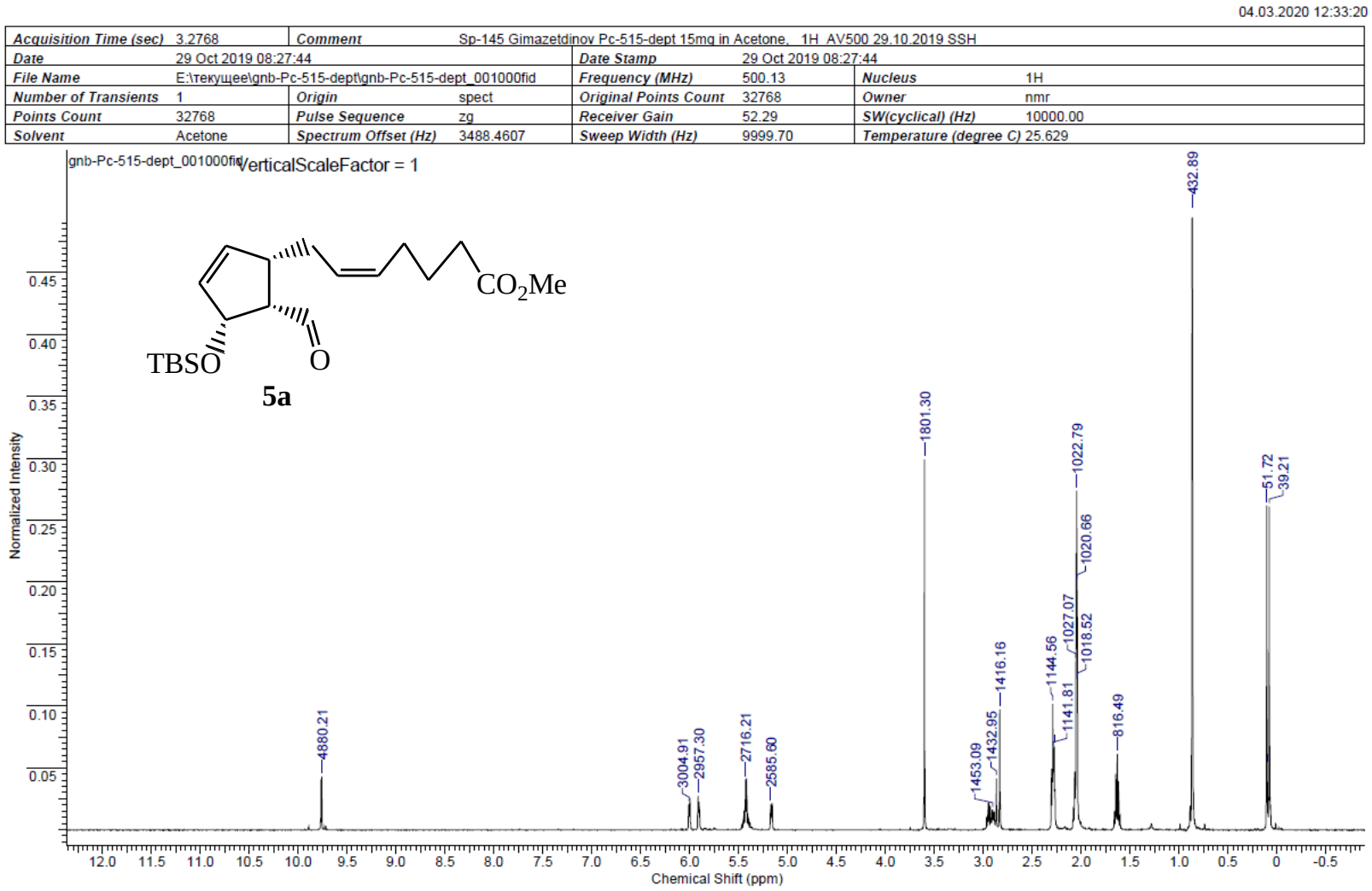


Figure S23 ^{1}H NMR spectrum of **5a** (*d*-acetone, 500 MHz)

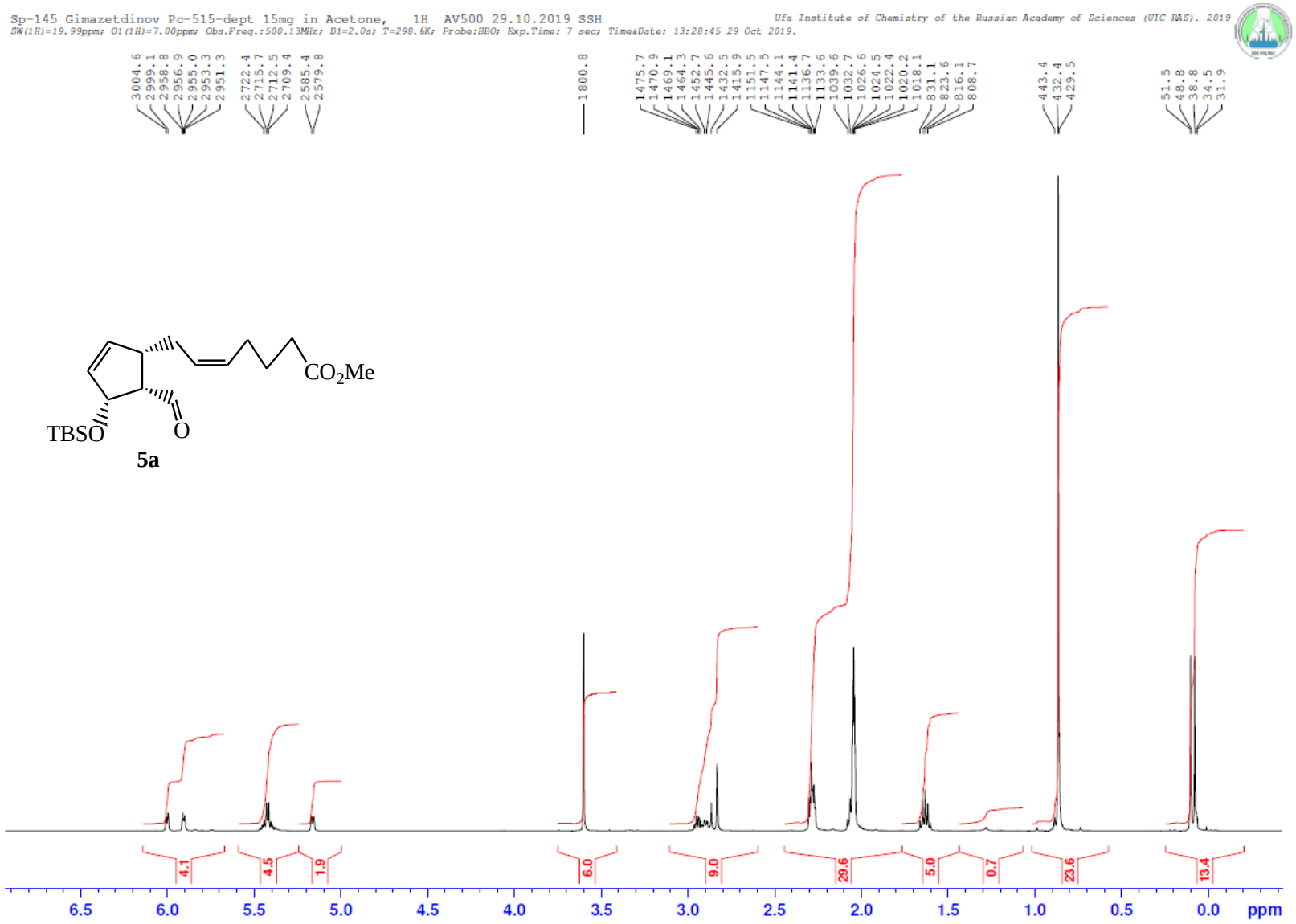


Figure S24 ^{1}H NMR spectrum of **5a** (*d*-acetone, 500 MHz)

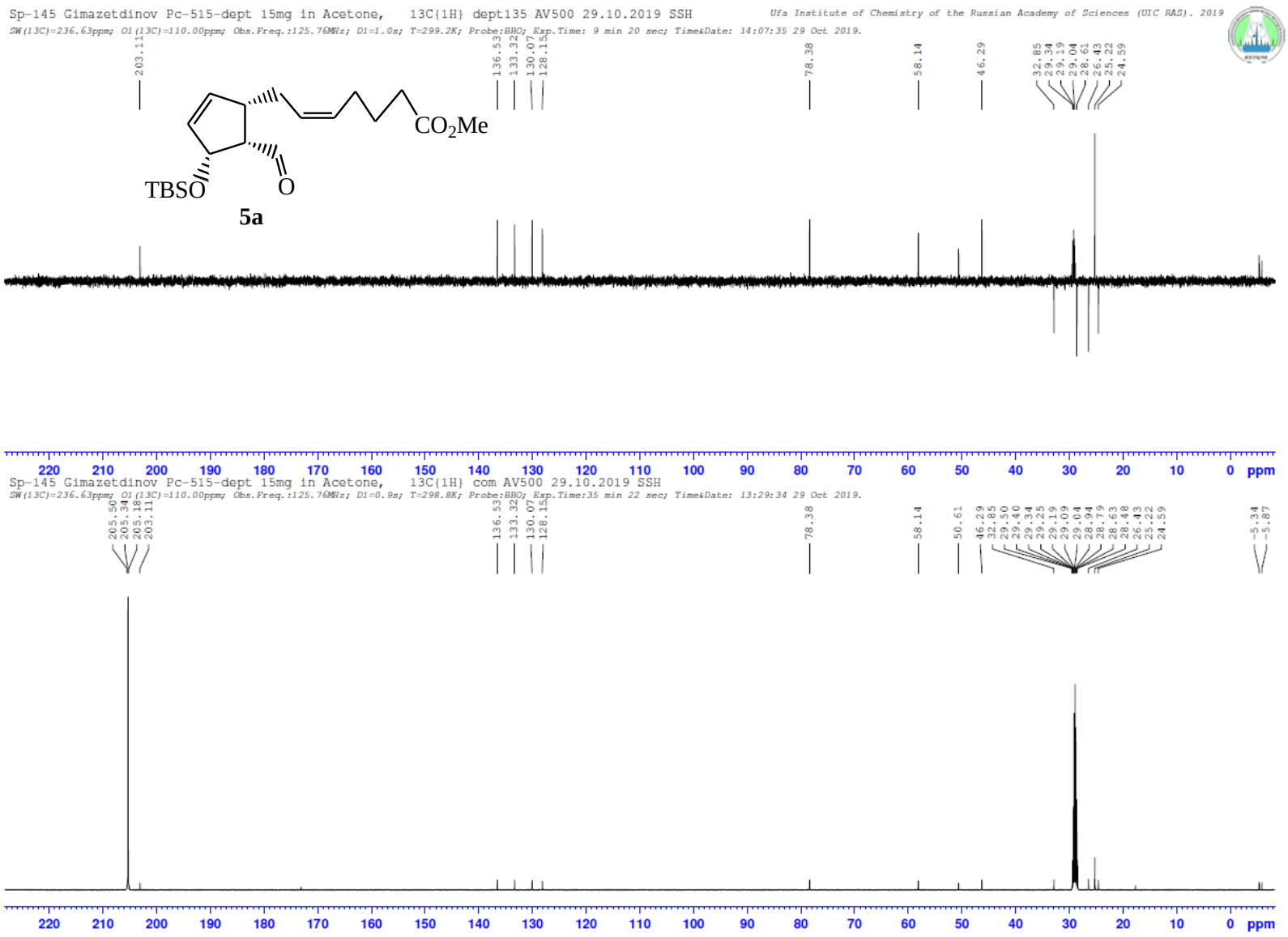


Figure S25 ^{13}C NMR spectrum of **5a** (*d*-acetone, 125.77 MHz)

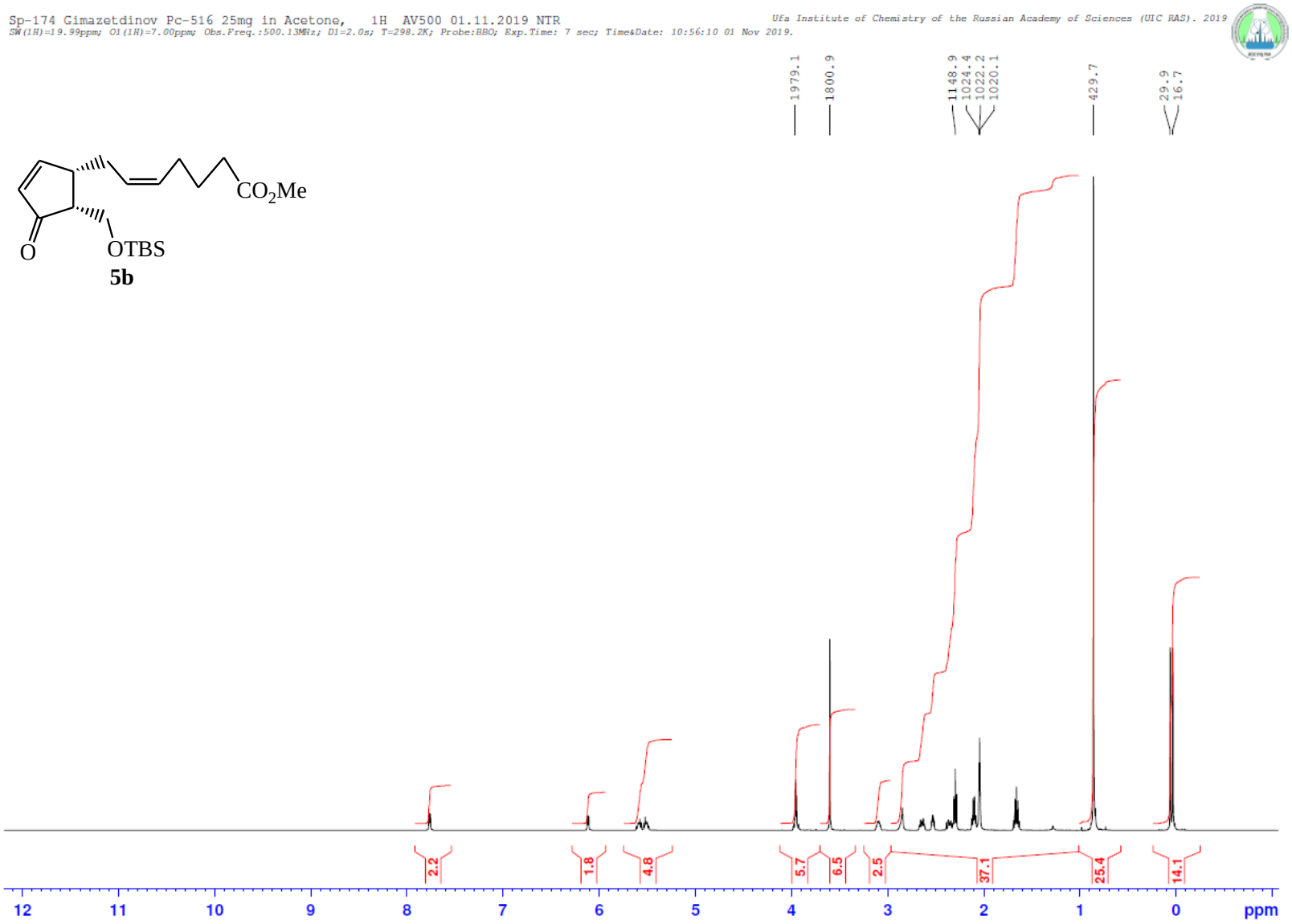


Figure S26 ^{1}H NMR spectrum of **5b** (*d*-acetone, 500 MHz)

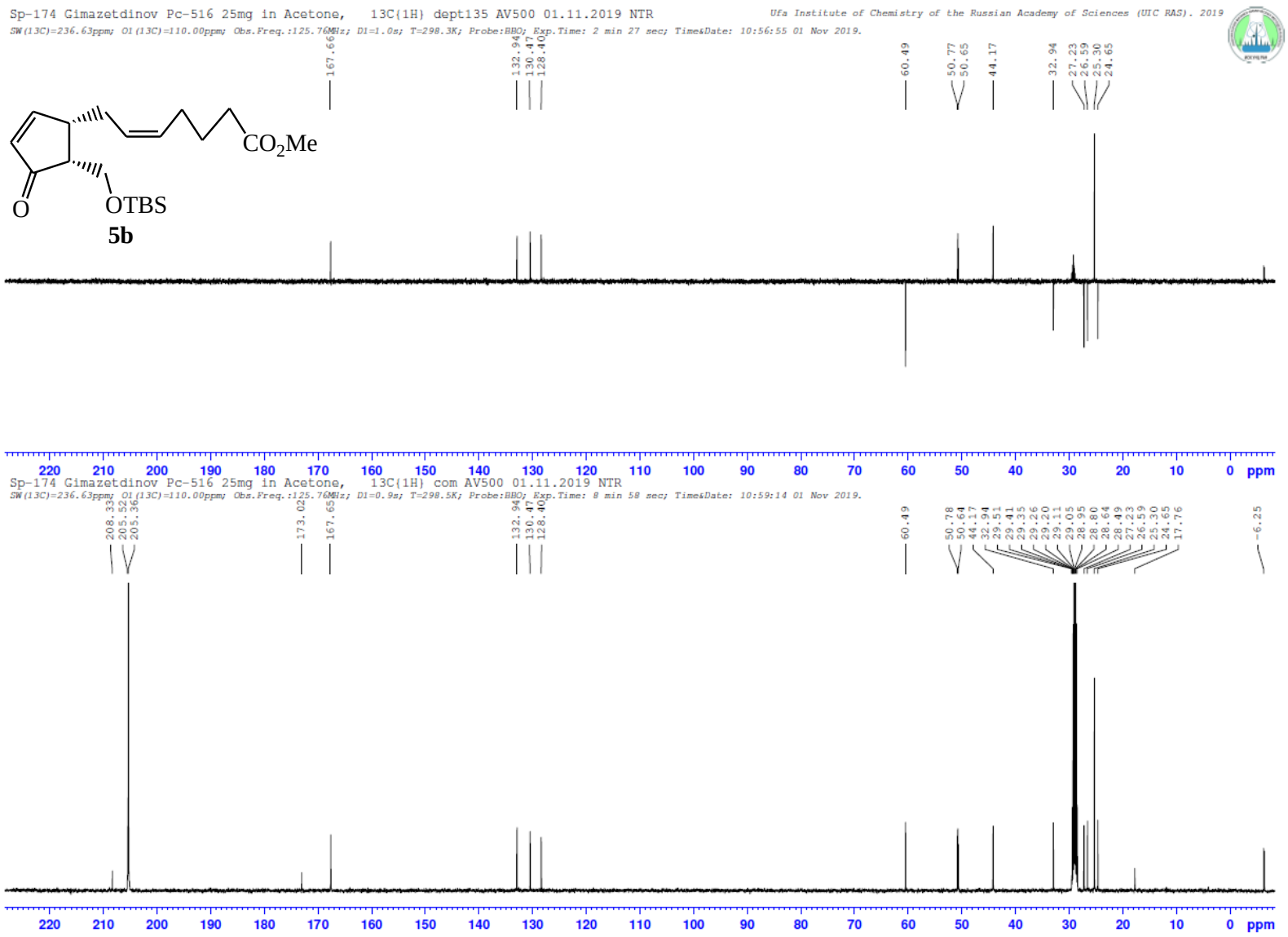


Figure S27 ^{13}C NMR spectrum of **5b** (*d*-acetone, 75.1 MHz)

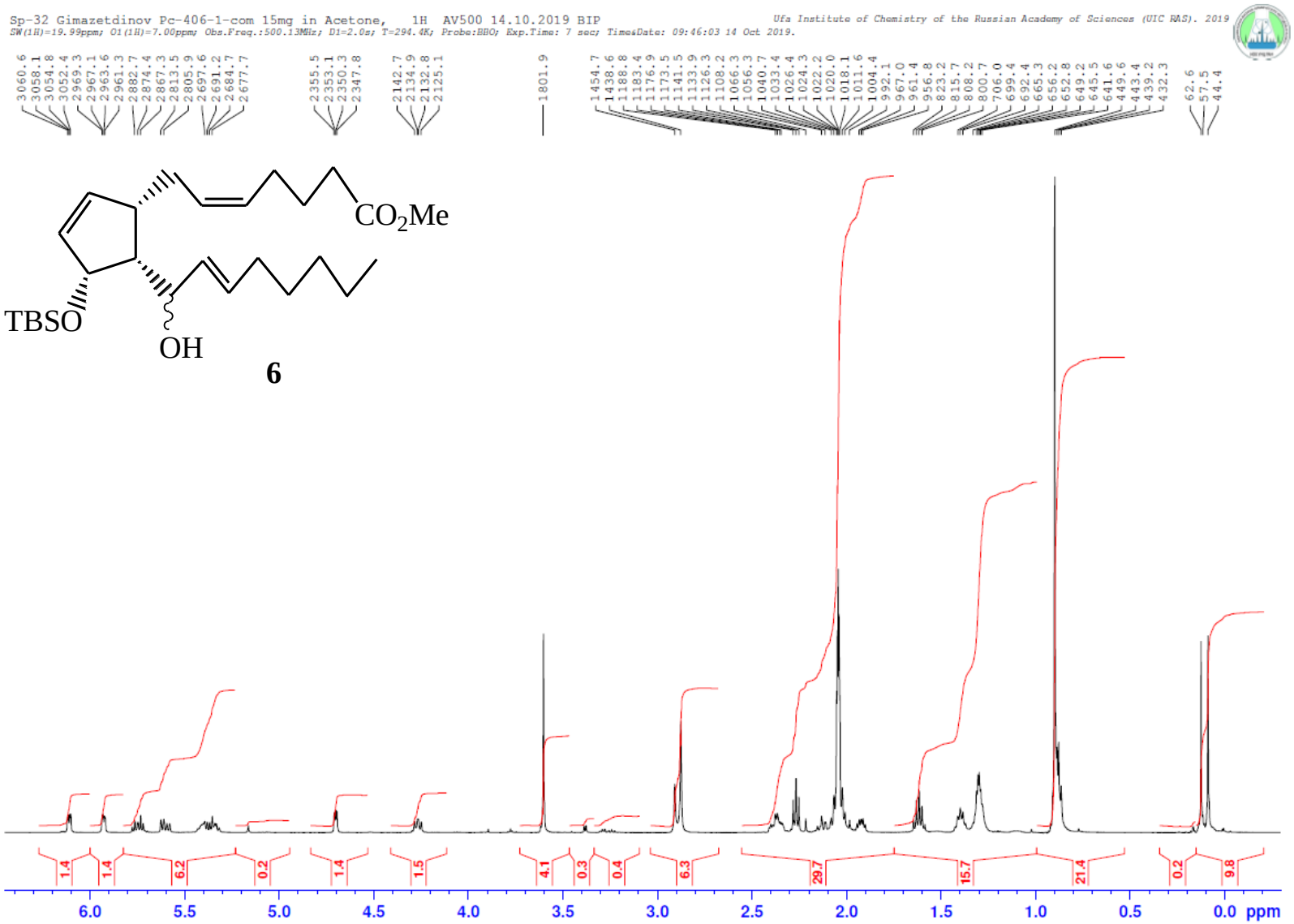


Figure S28 ^{1}H NMR spectrum of **6** (*d*-acetone, 500 MHz)

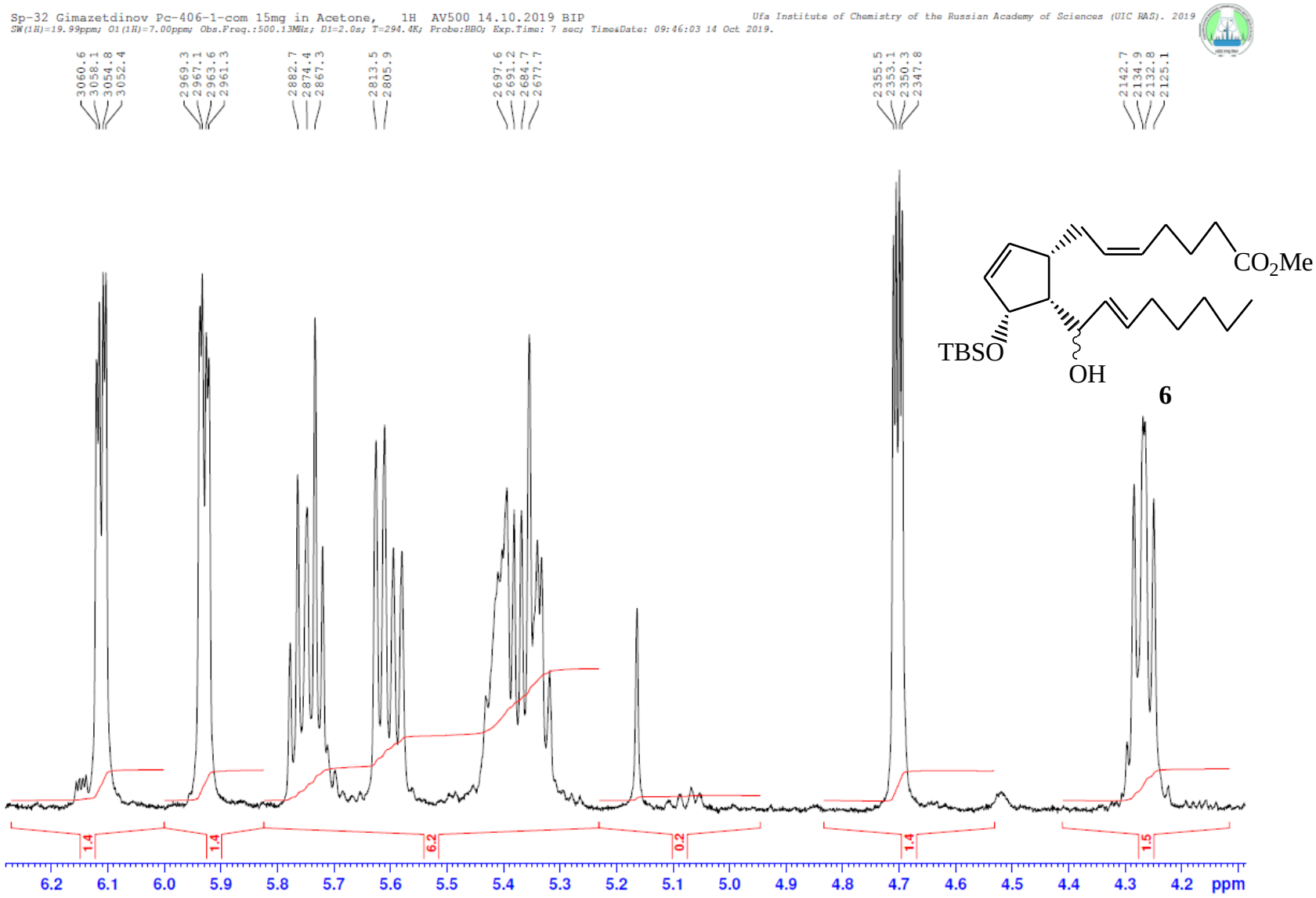


Figure S29 ^{1}H NMR spectrum of **6** (*d*-acetone, 500 MHz)

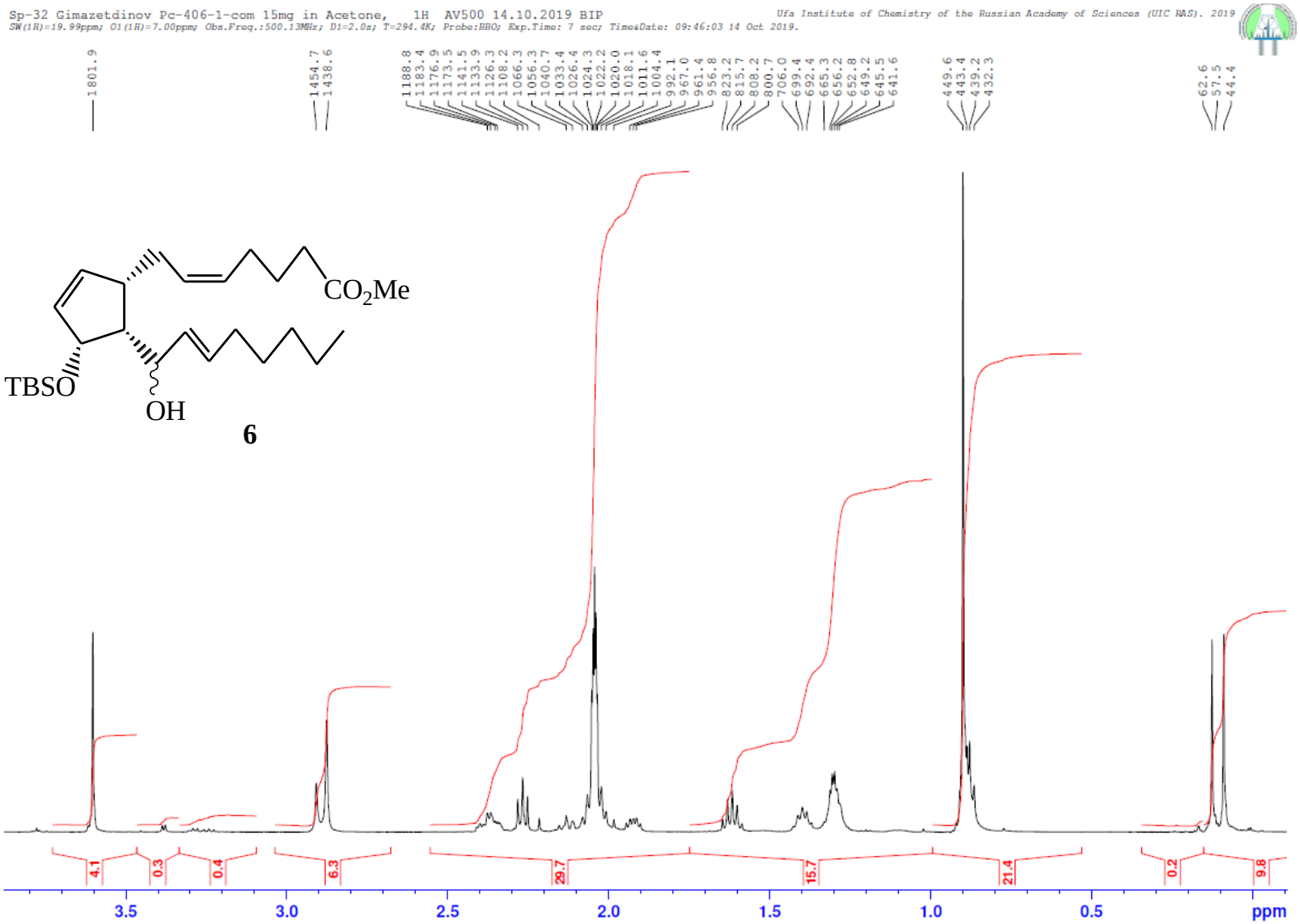


Figure S30 ^{1}H NMR spectrum of **6** (*d*-acetone, 500 MHz)

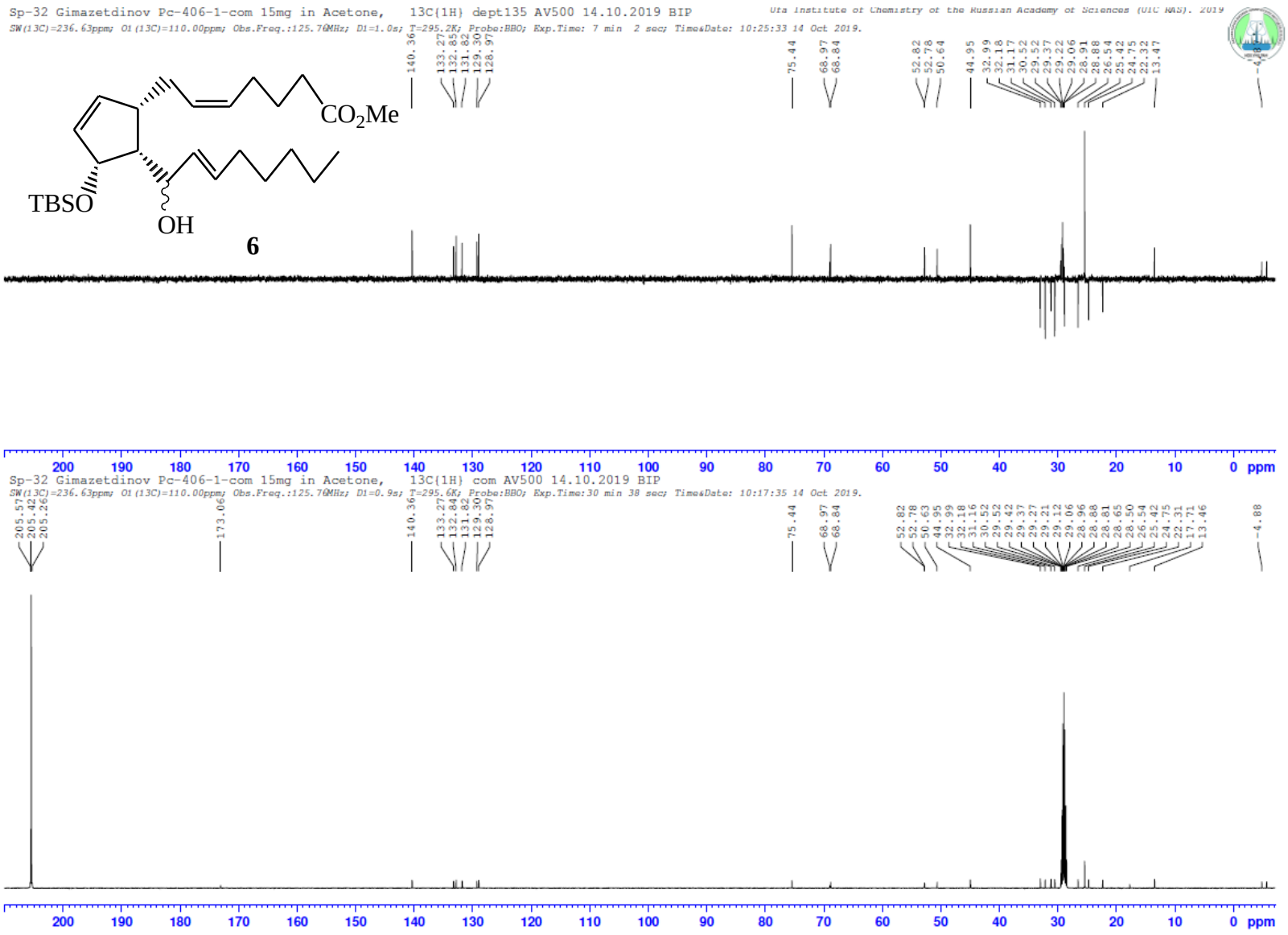


Figure S31 ^{13}C NMR spectrum of **6** (*d*-acetone, 75.1 MHz)

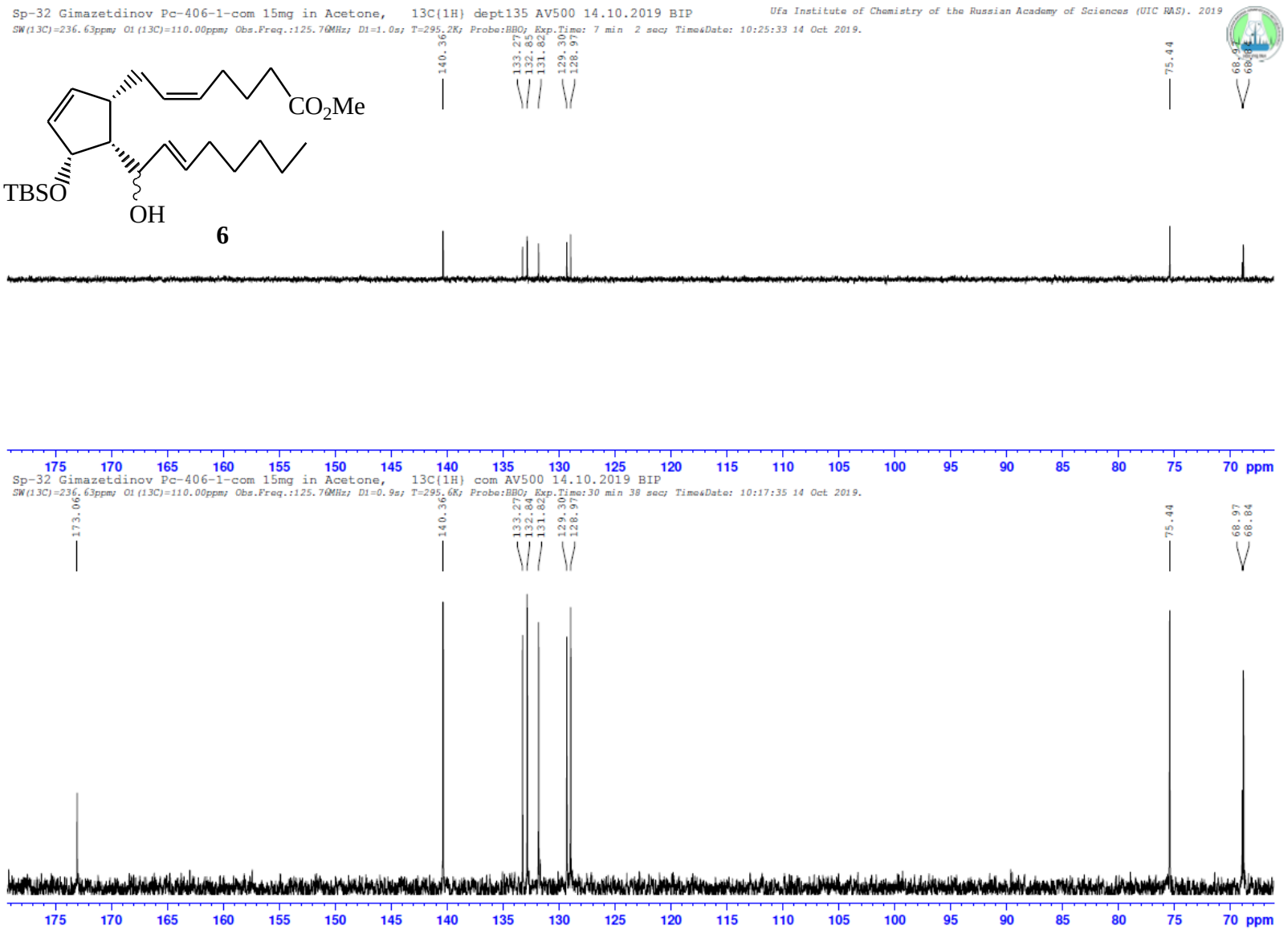


Figure S32 ^{13}C NMR spectrum of **6** (*d*-acetone, 75.1 MHz)

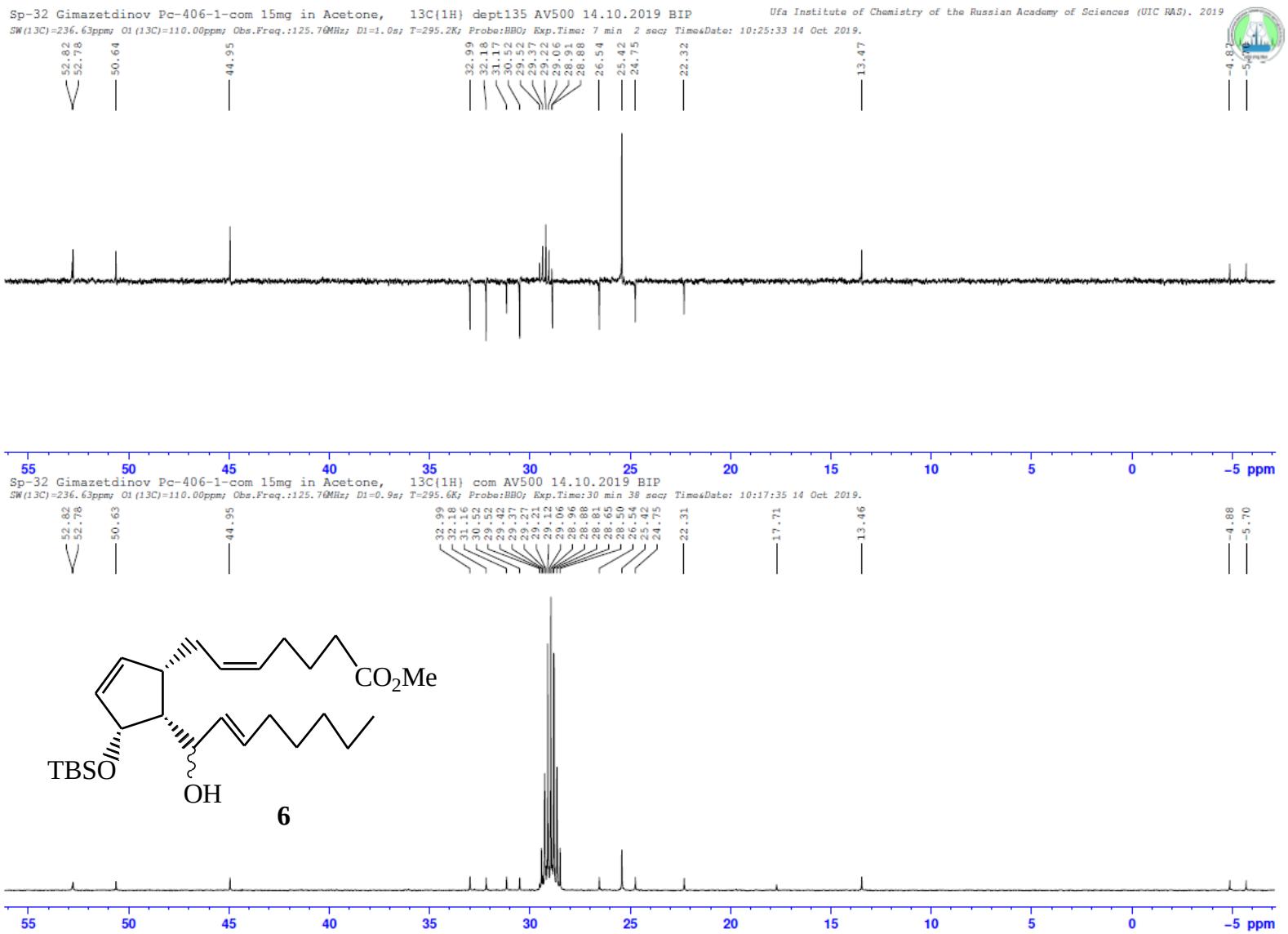


Figure S33 ^{13}C NMR spectrum of **6** (*d*-acetone, 75.1 MHz)

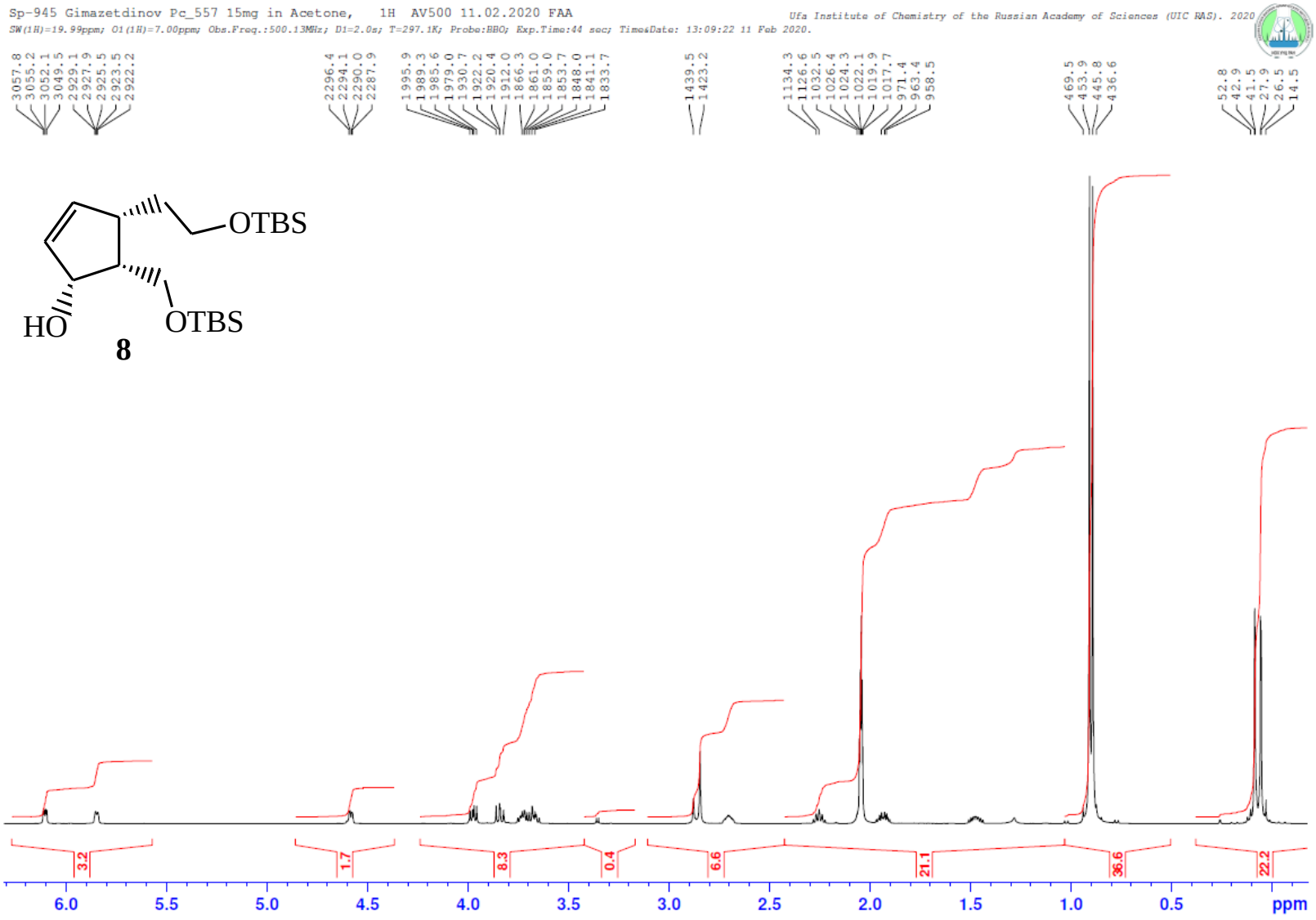


Figure S34 ^{1}H NMR spectrum of **8** (*d*-acetone, 500 MHz)

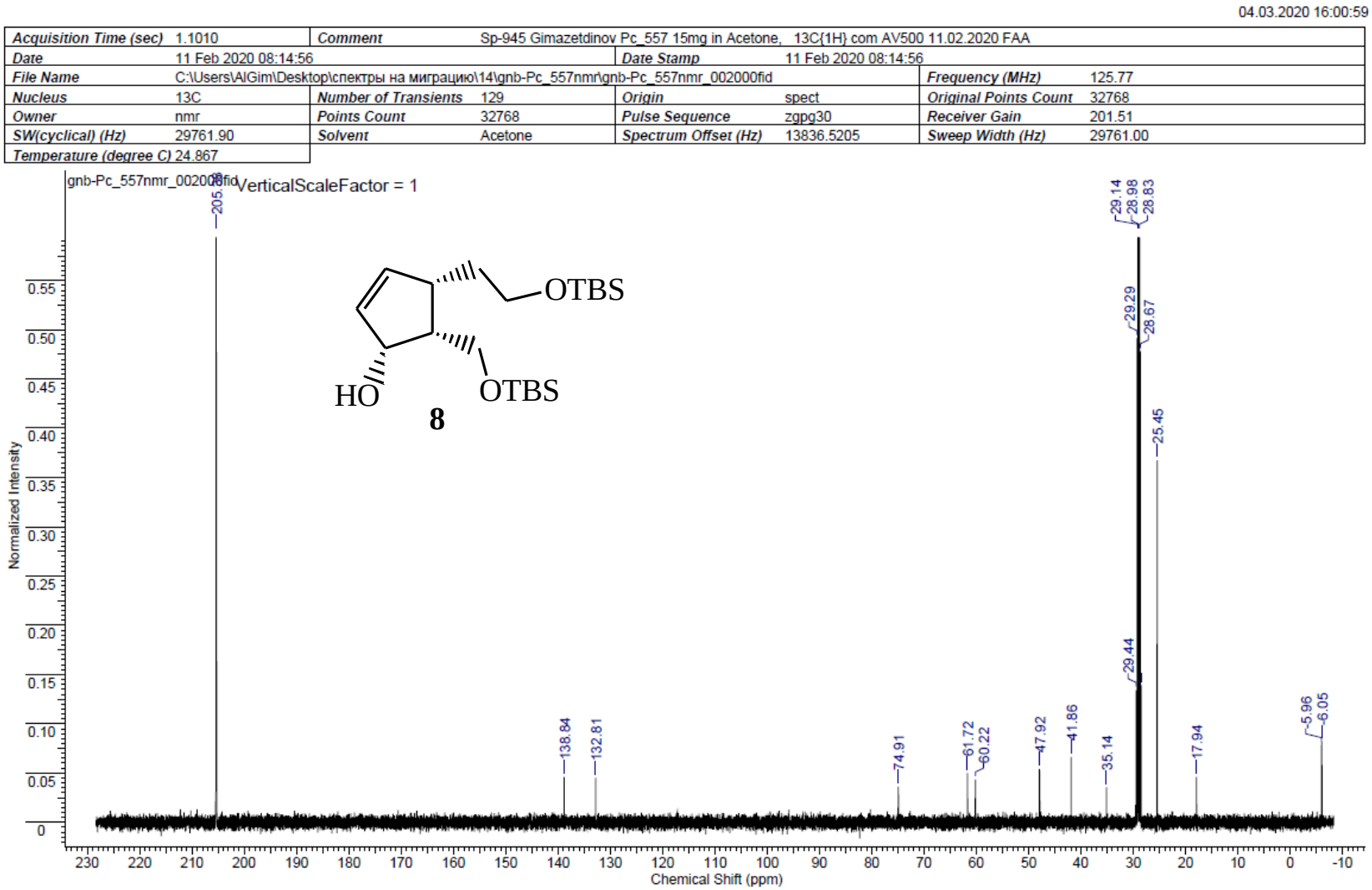


Figure S35 ^{13}C NMR spectrum of **8** (*d*-acetone, 125.77 MHz)

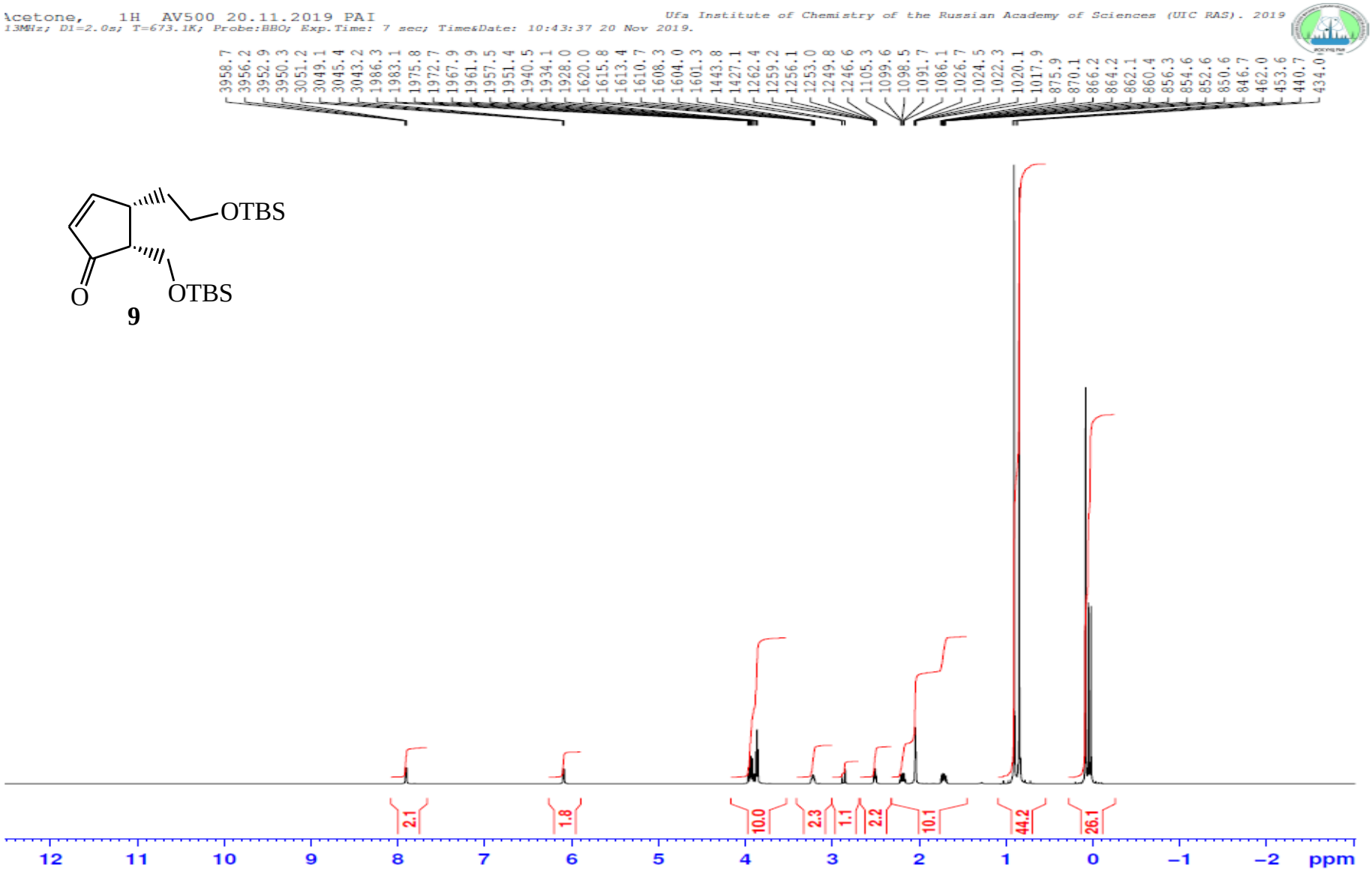


Figure S36 ^{1}H NMR spectrum of **9** (*d*-acetone, 500 MHz)

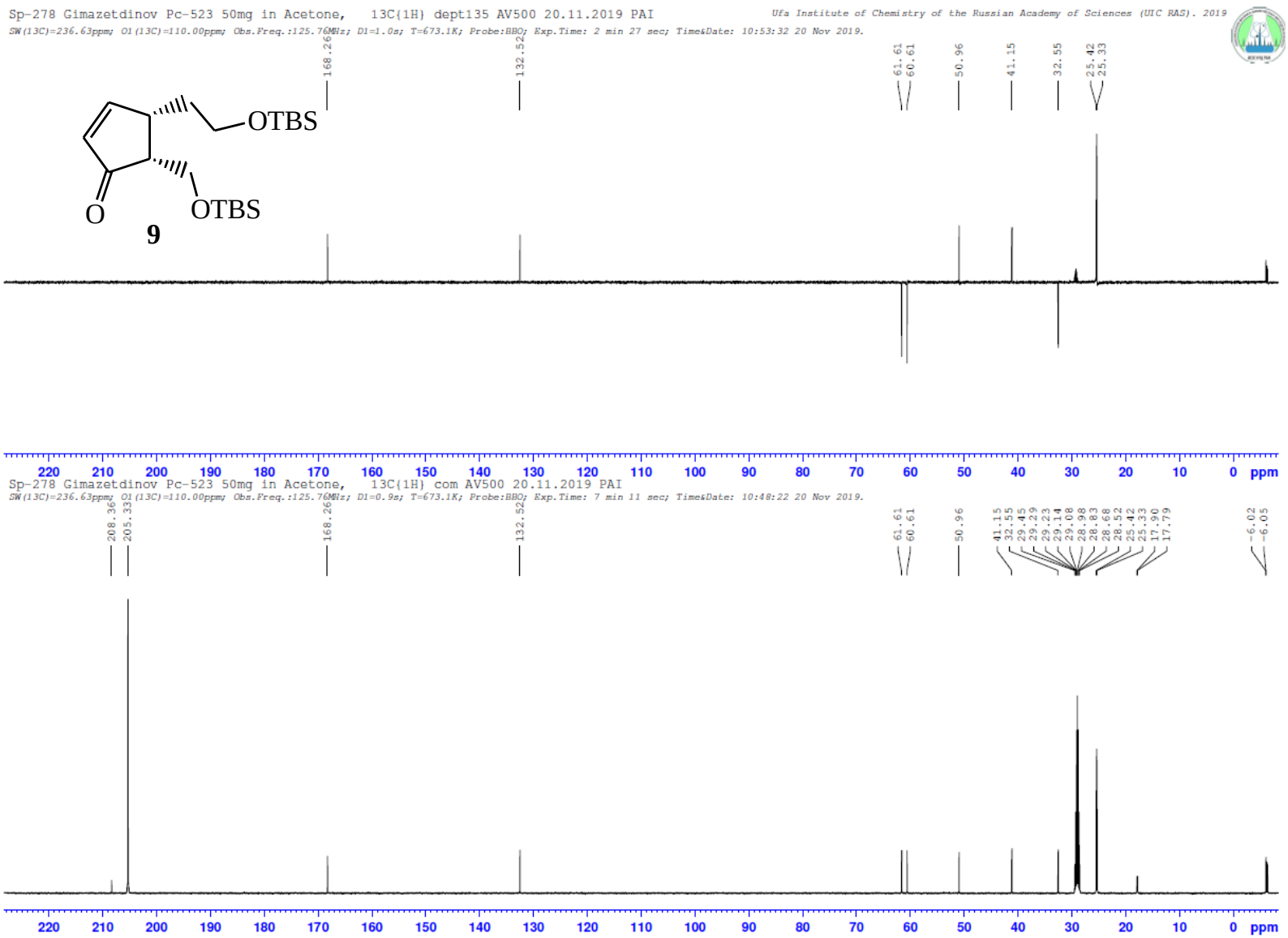


Figure S37 ^{13}C NMR spectrum of **9** (*d*-acetone, 125.77 MHz)

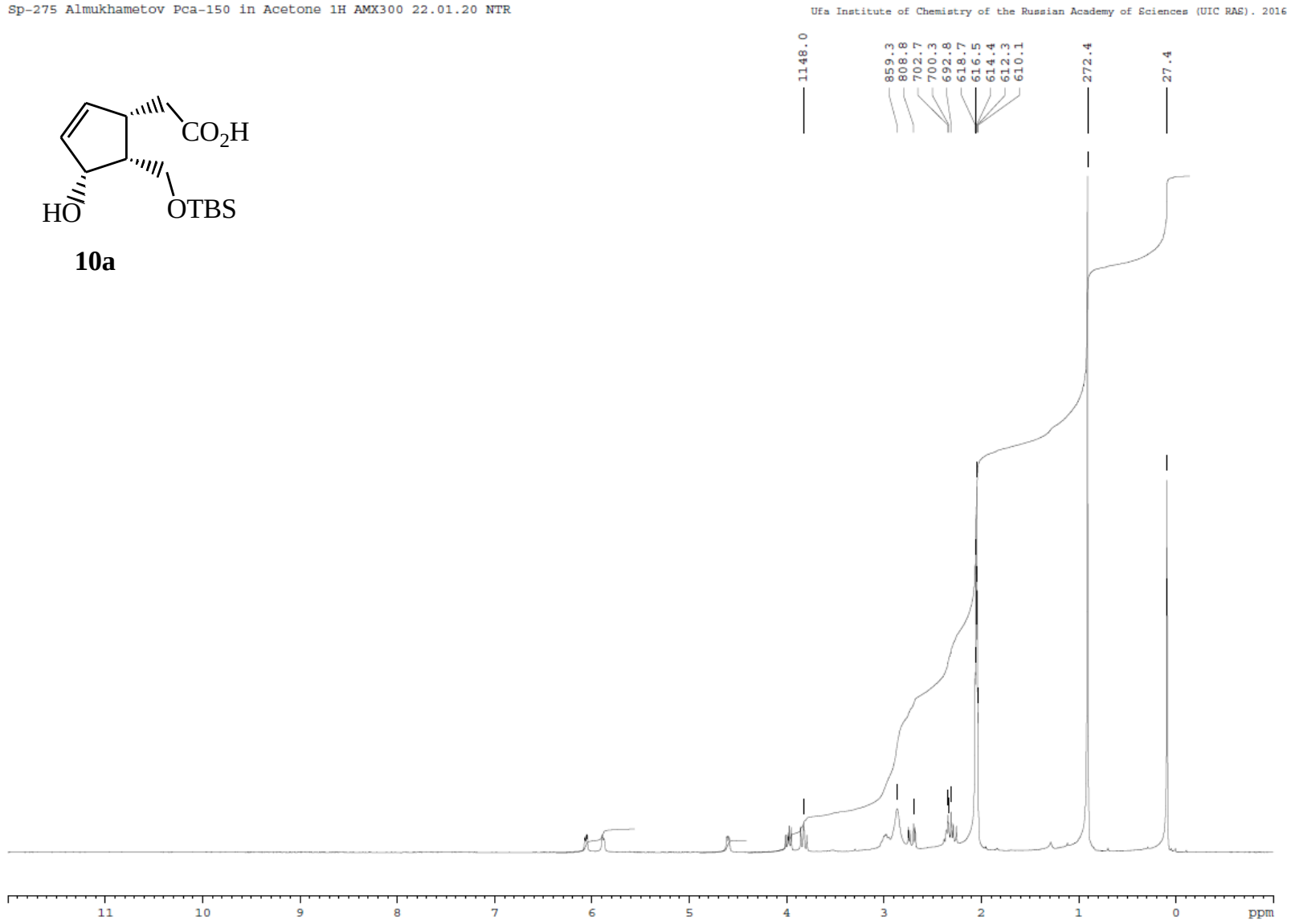


Figure S38 ^{1}H NMR spectrum of **10a** (*d*-acetone, 300 MHz)

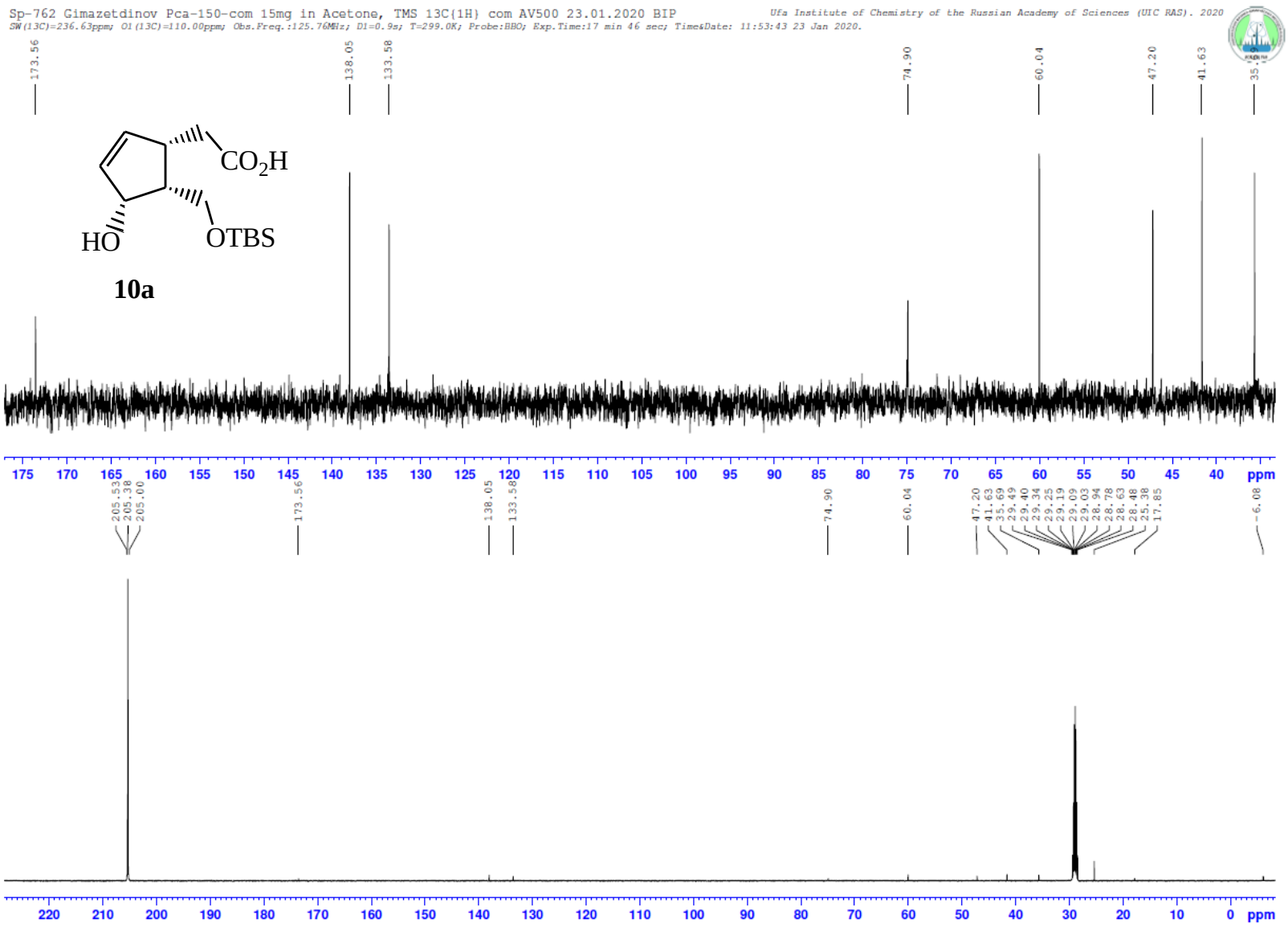


Figure S39 ^{13}C NMR spectrum of **10a** (*d*-acetone, 125.77 MHz)

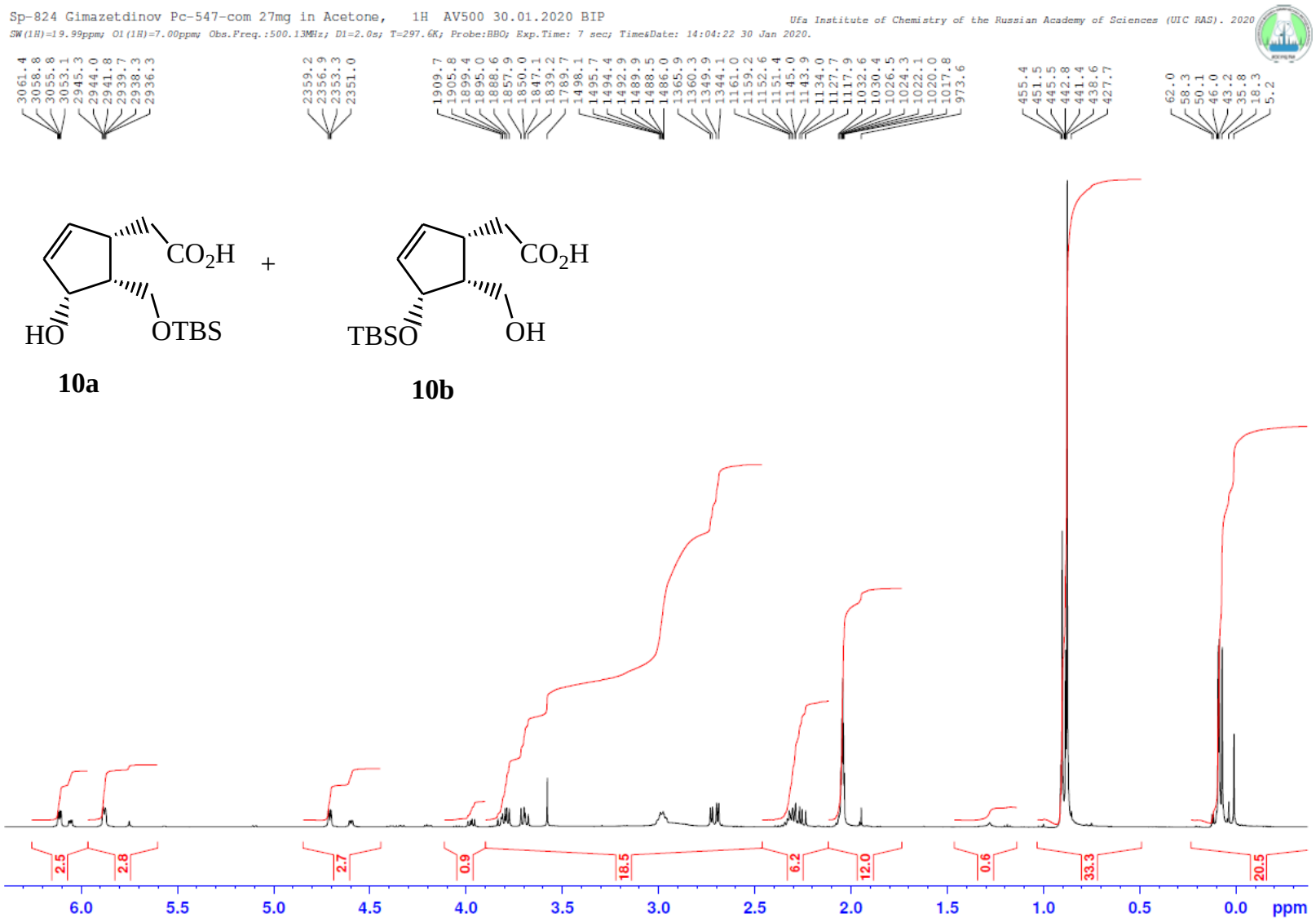


Figure S40 ^{1}H NMR spectrum of **10a**+**10b** (*d*-acetone, 500 MHz)

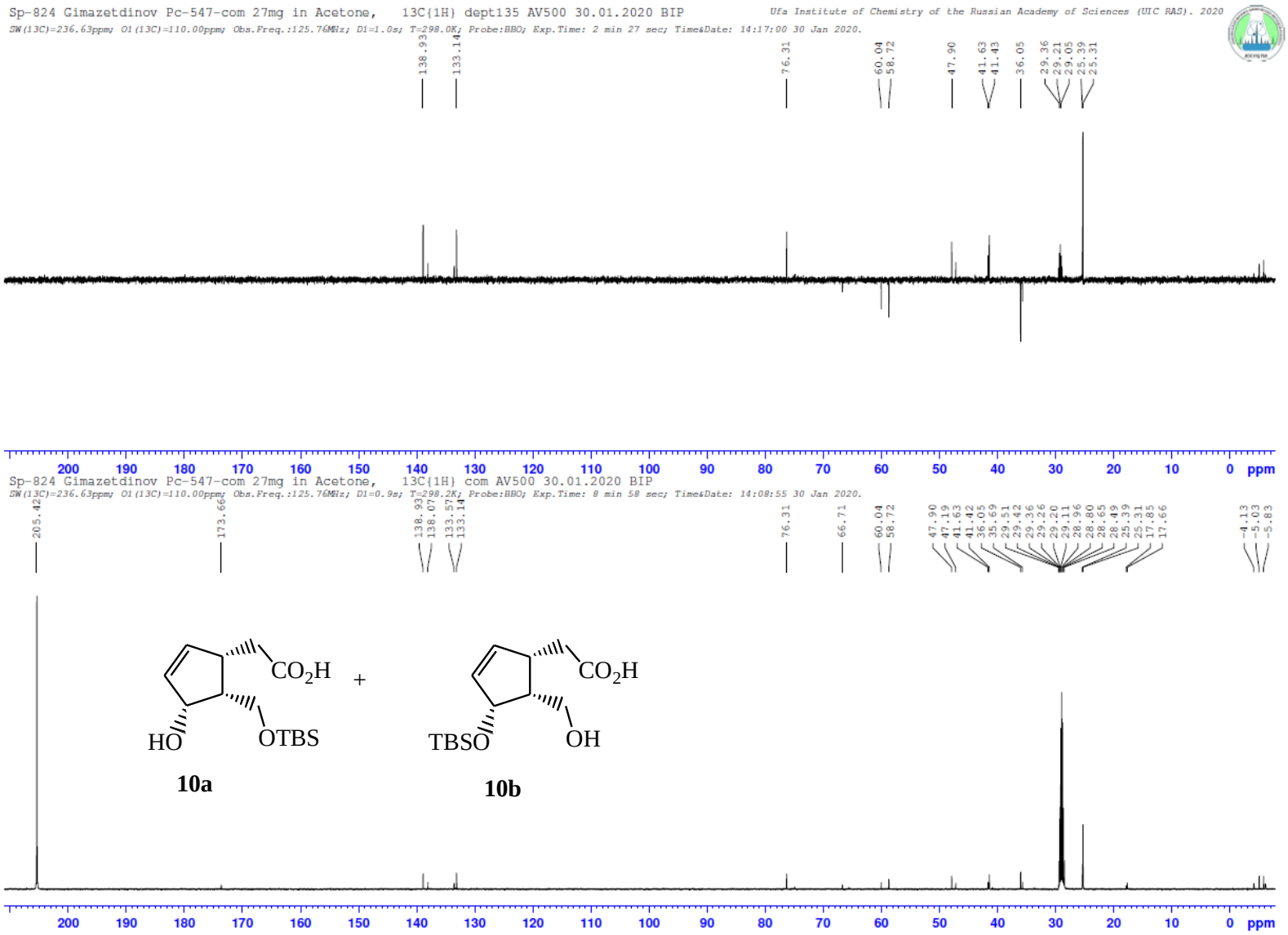


Figure S41 ^{13}C NMR spectrum of **10a**+**10b** (*d*-acetone, 125.77 MHz)

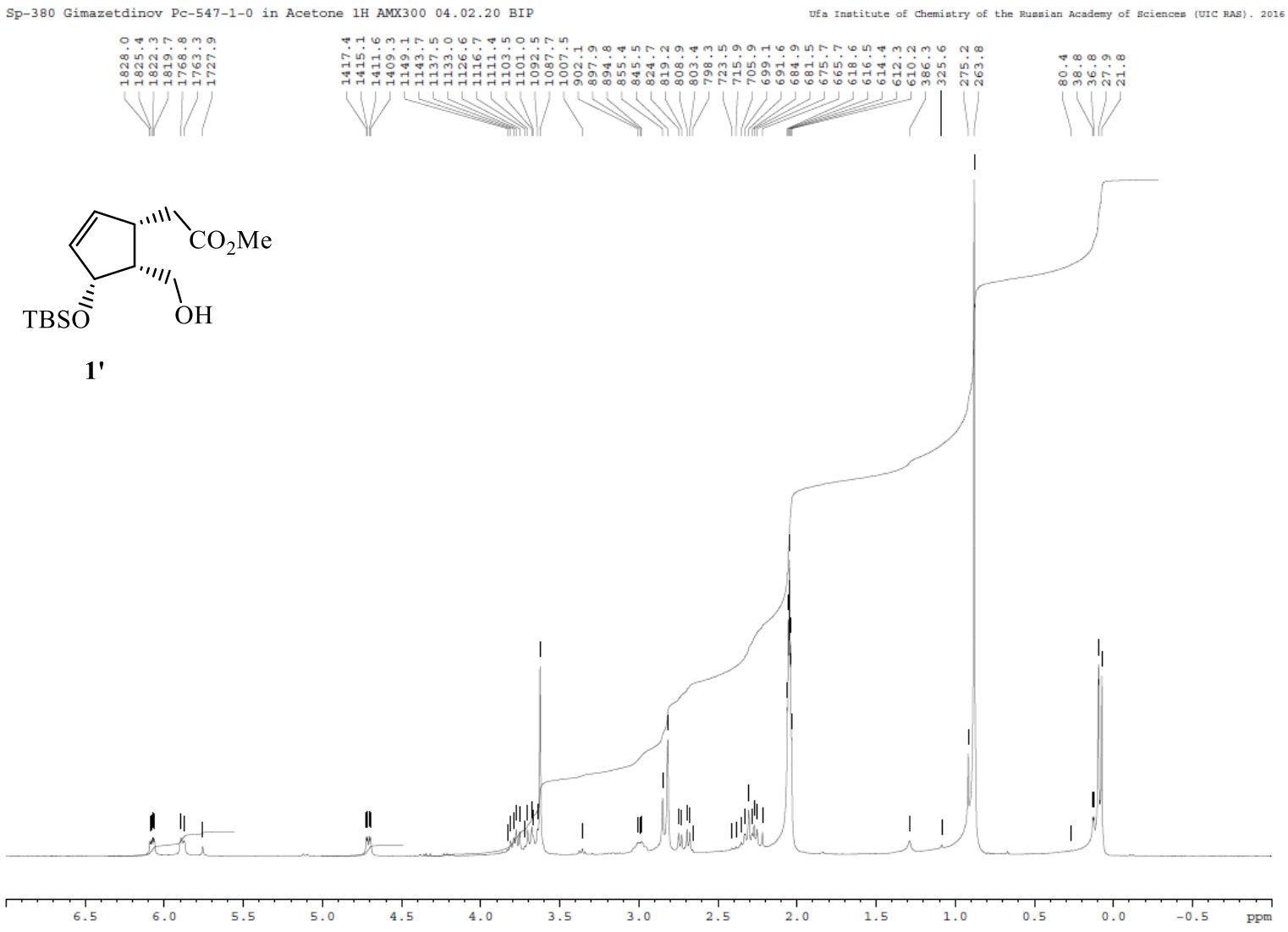


Figure S42 ^{1}H NMR spectrum of **1'** (*d*-acetone, 300 MHz)

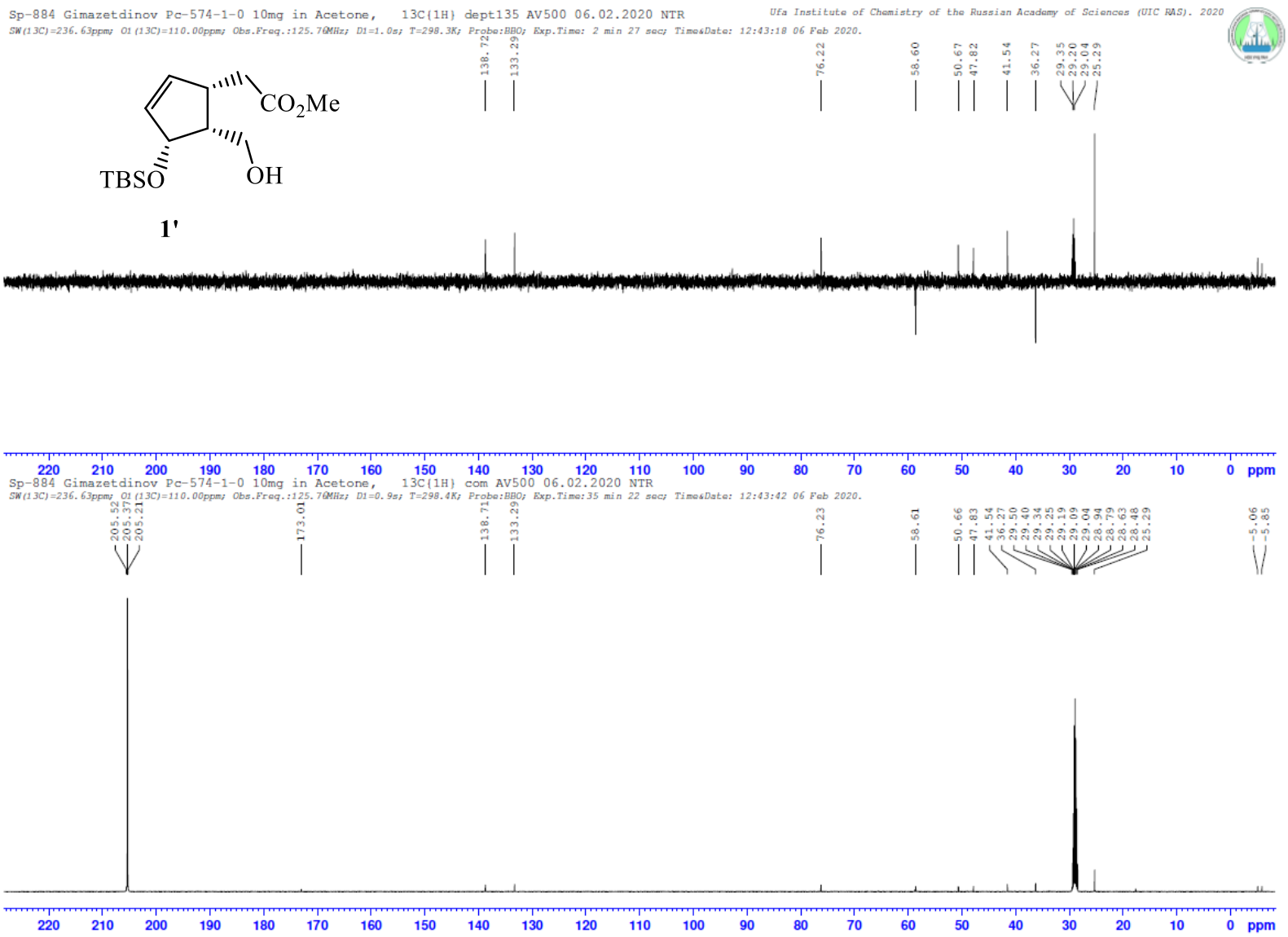


Figure S43 ^{13}C NMR spectrum of **1'** (*d*-acetone, 125.77 MHz)

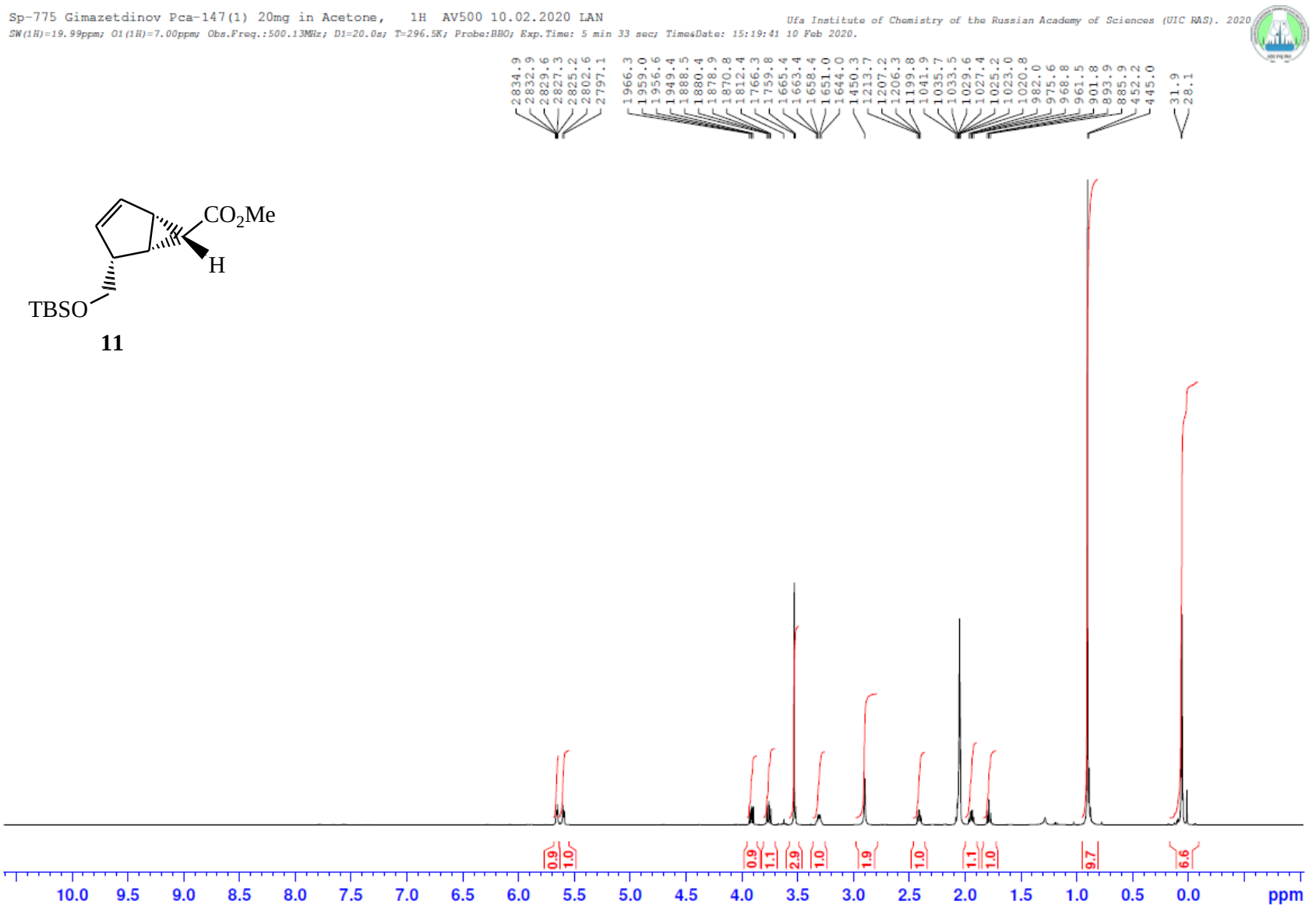


Figure S44 ^{1}H NMR spectrum of **11** (*d*-acetone, 500 MHz)

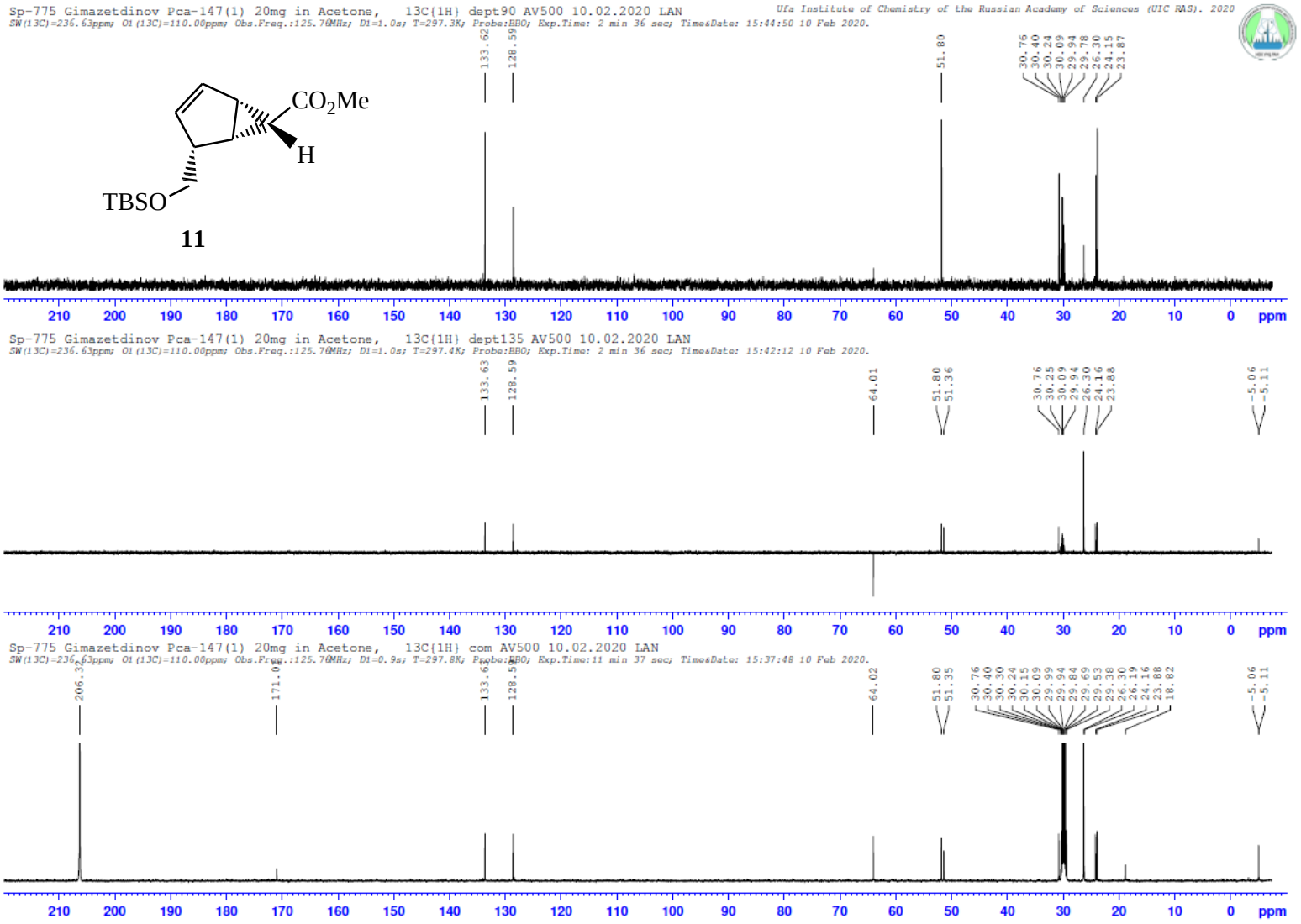


Figure S45 ^{13}C NMR spectrum of **11** (*d*-acetone, 125.77 MHz)

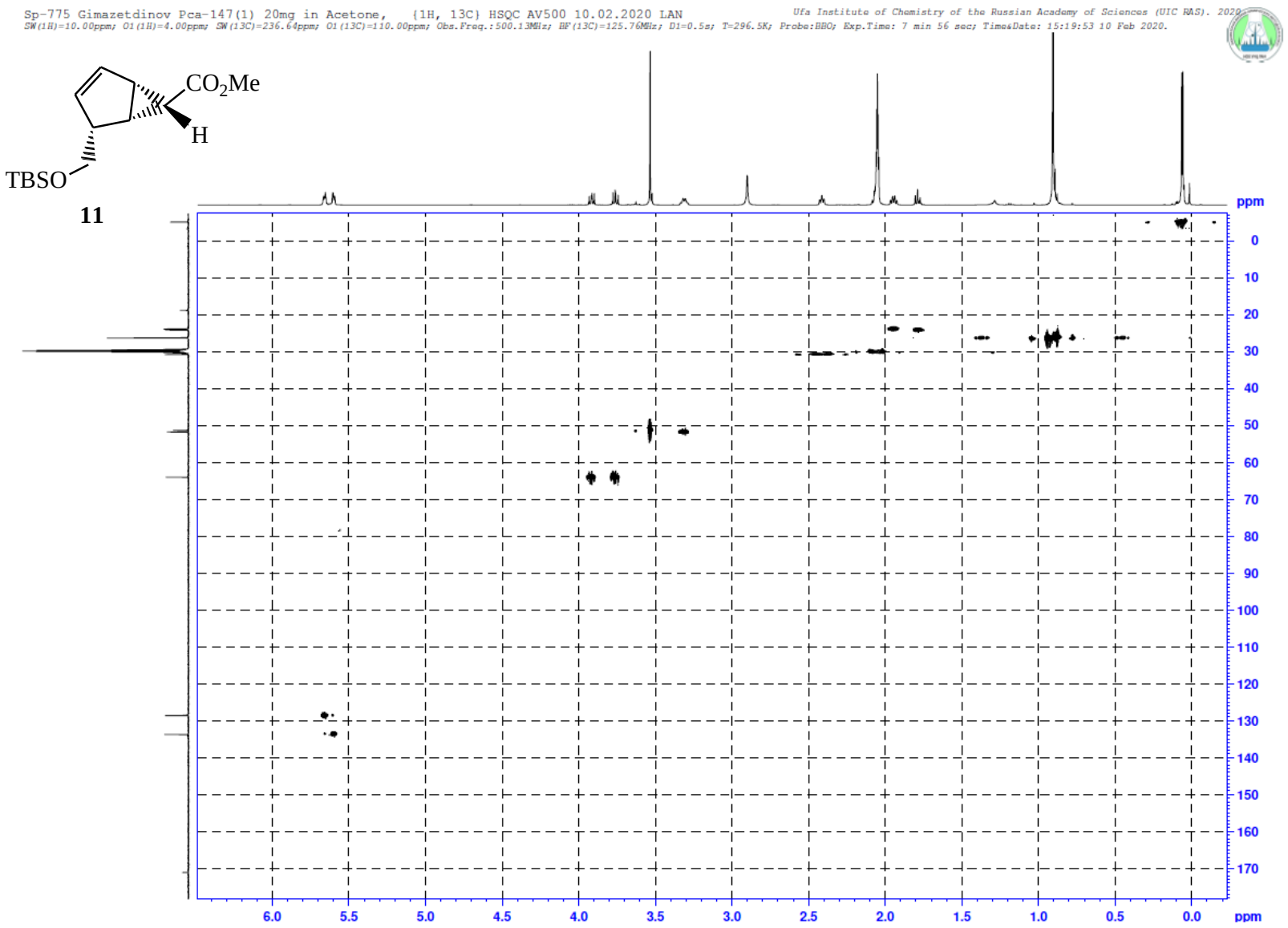


Figure S46 {^{1}H, ^{13}C} HSQC spectrum of **11** (*d*-acetone, 300 MHz)

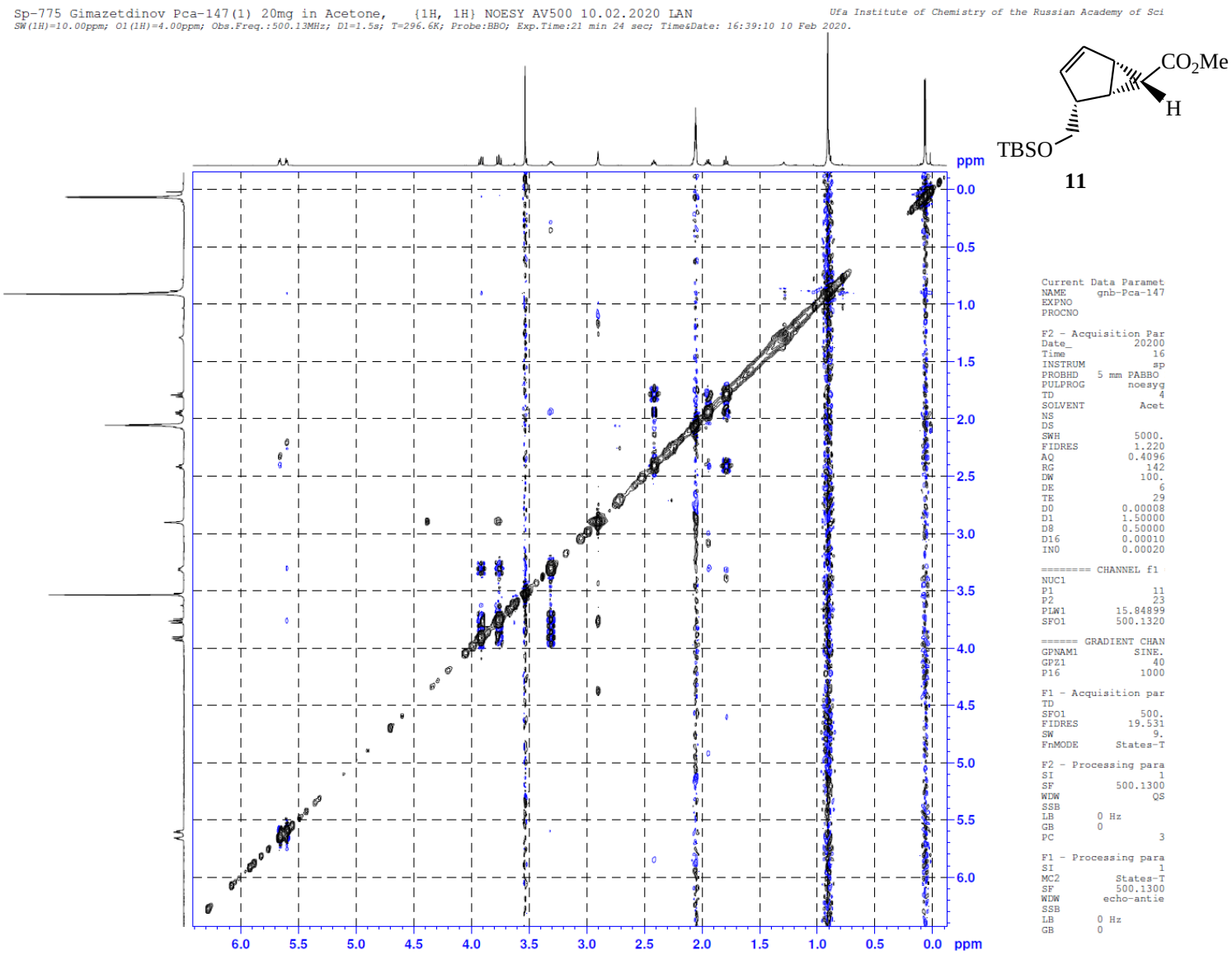


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Figure S47 {^{1}H, ^{1}H} NOESY spectrum of **11** (*d*-acetone, 125.77 MHz)

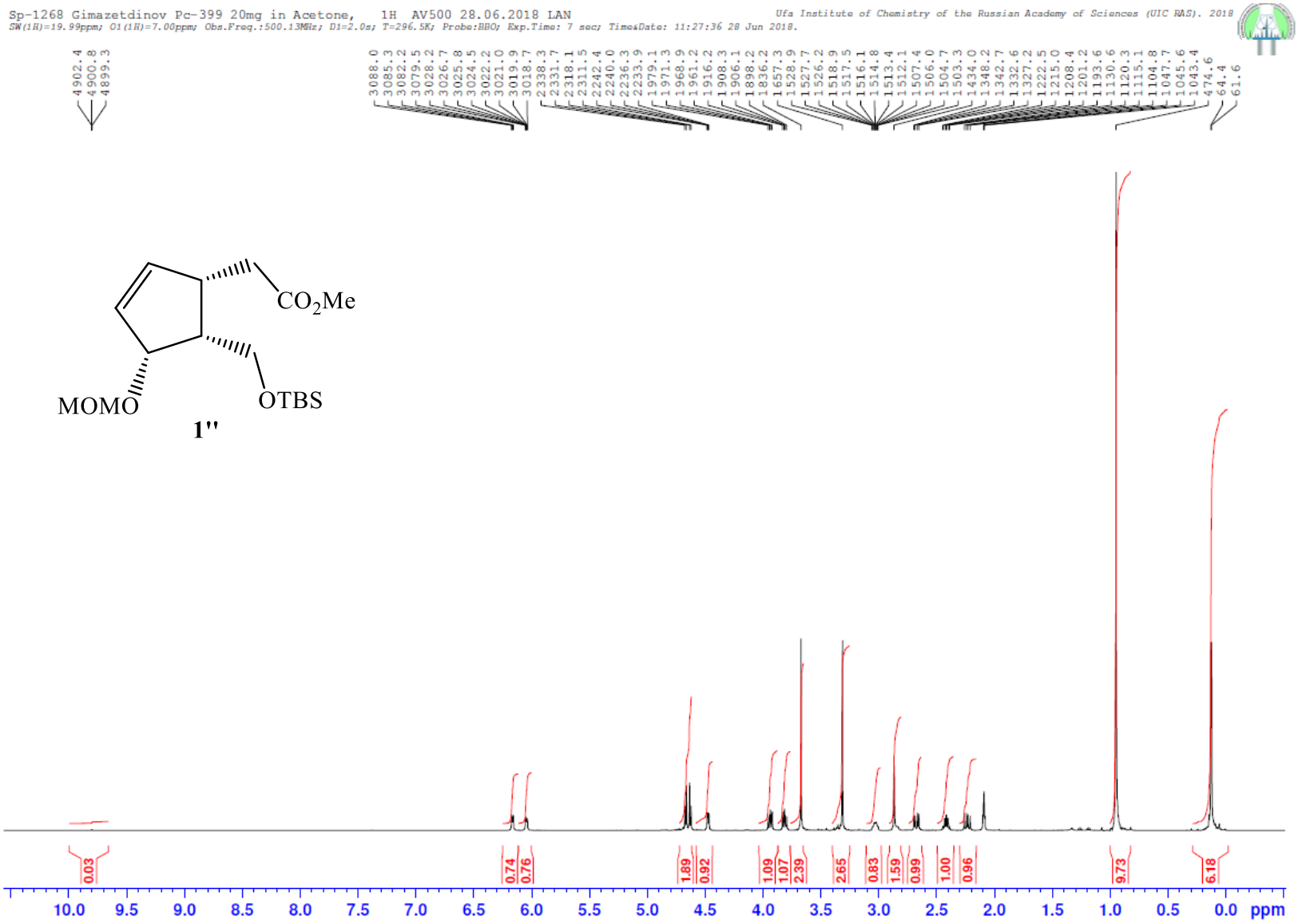

Figure S48 ^{1}H NMR spectrum of **1"** (*d*-acetone, 500 MHz)

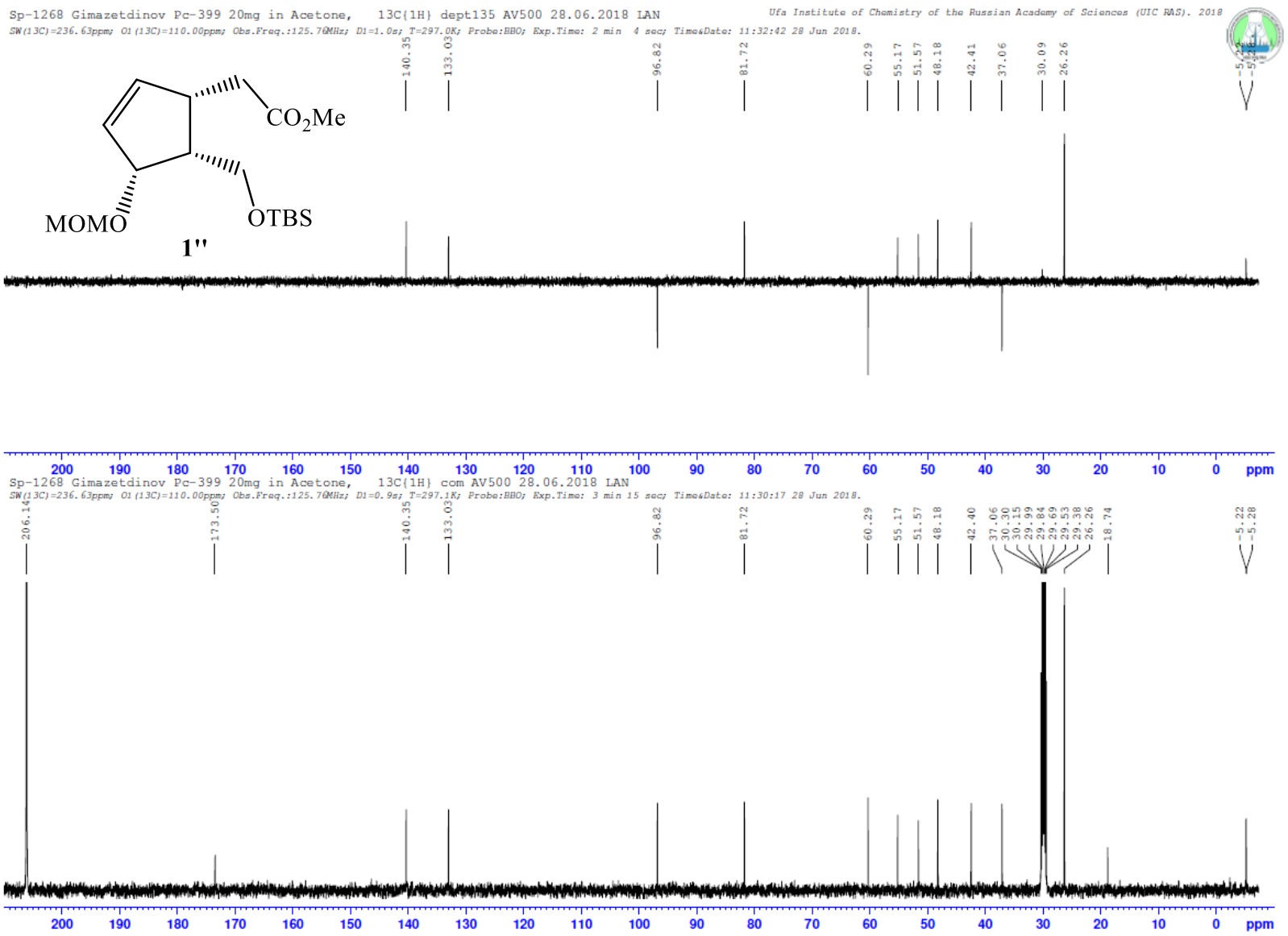

Figure S49 ^{13}C NMR spectrum of **1"** (*d*-acetone, 125.77 MHz)

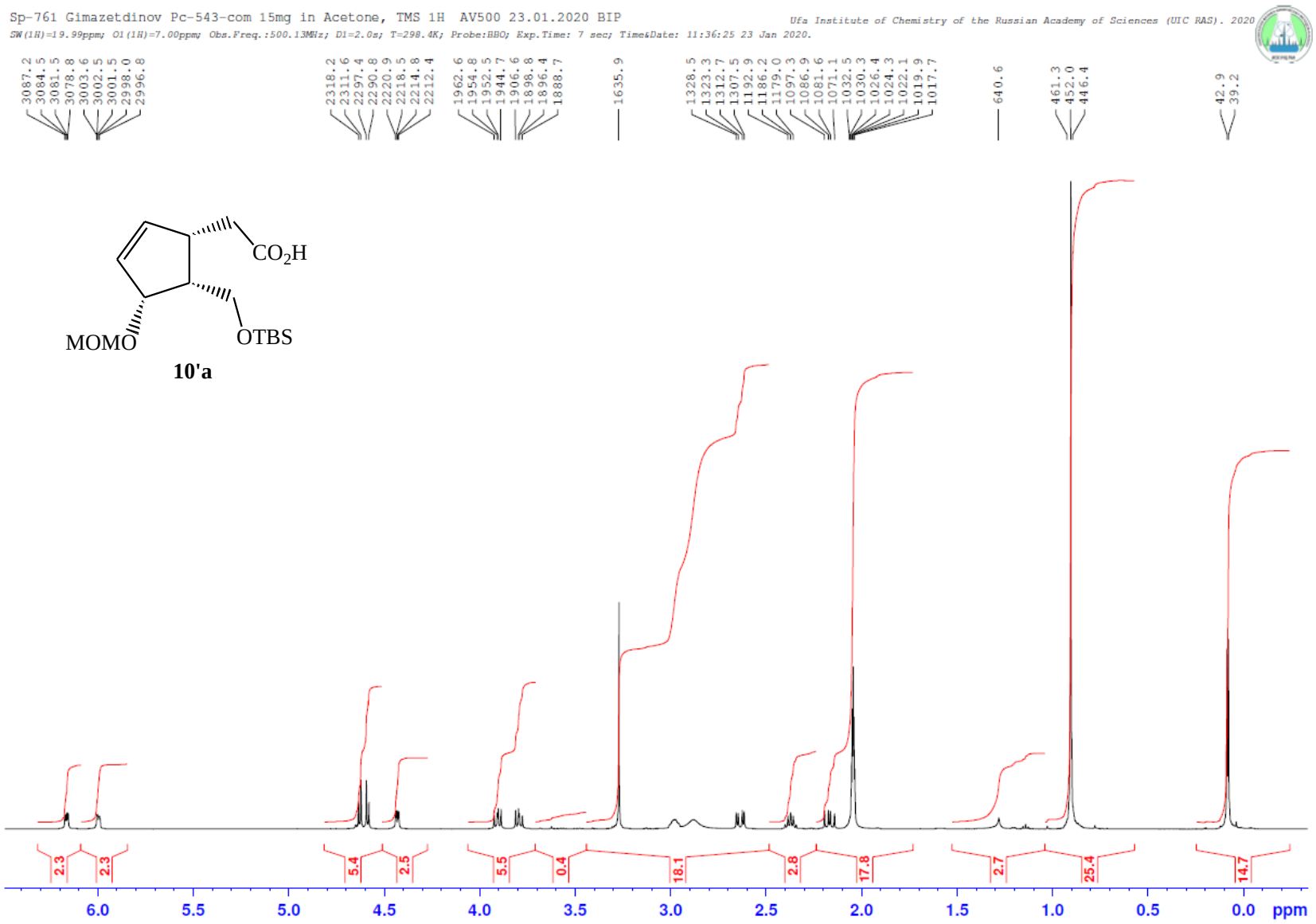

Figure S50 ^{1}H NMR spectrum of **10'a** (*d*-acetone, 500 MHz)

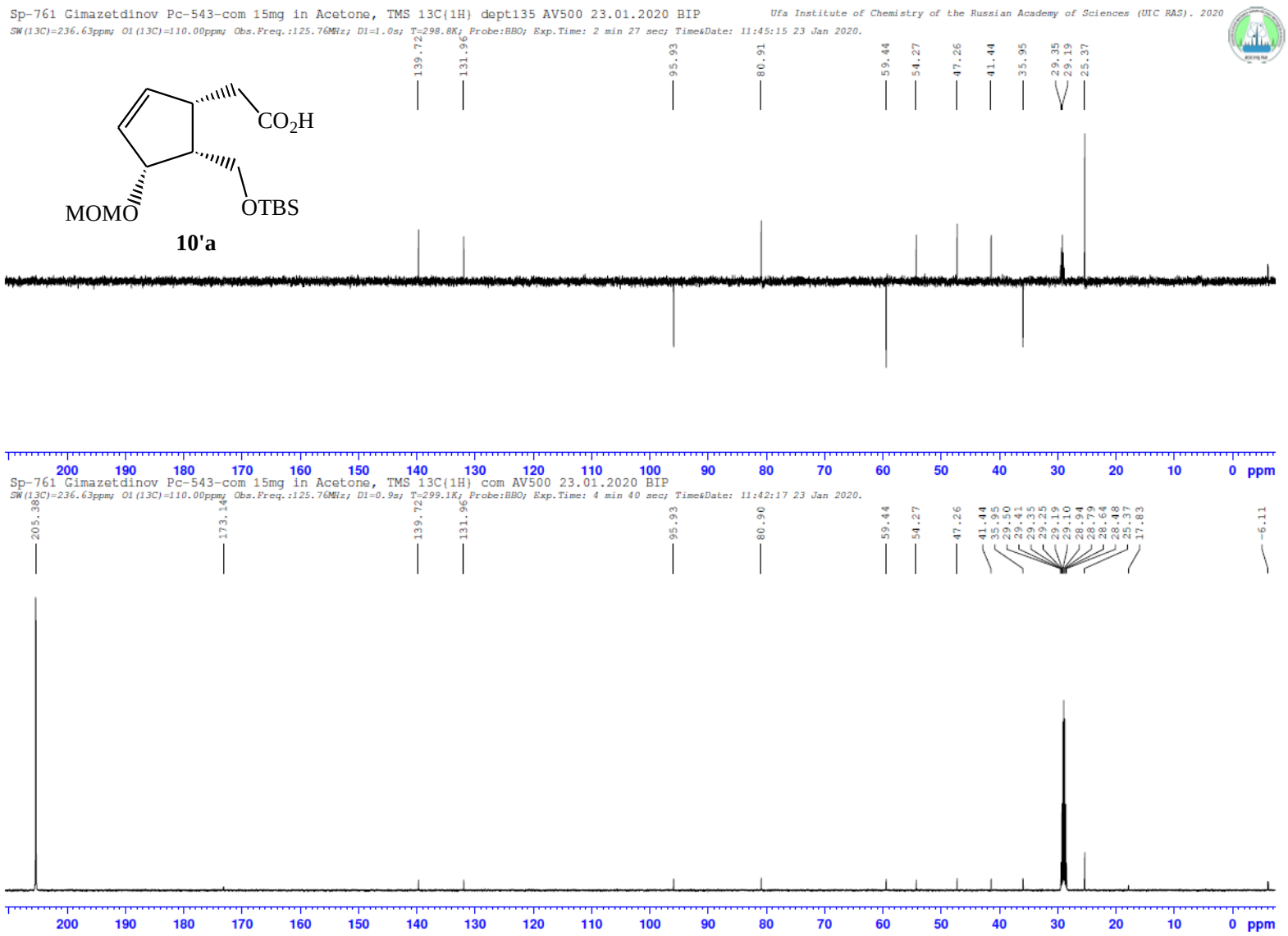

Figure S51 ^{13}C NMR spectrum of **10'a** (*d*-acetone, 125.77 MHz)

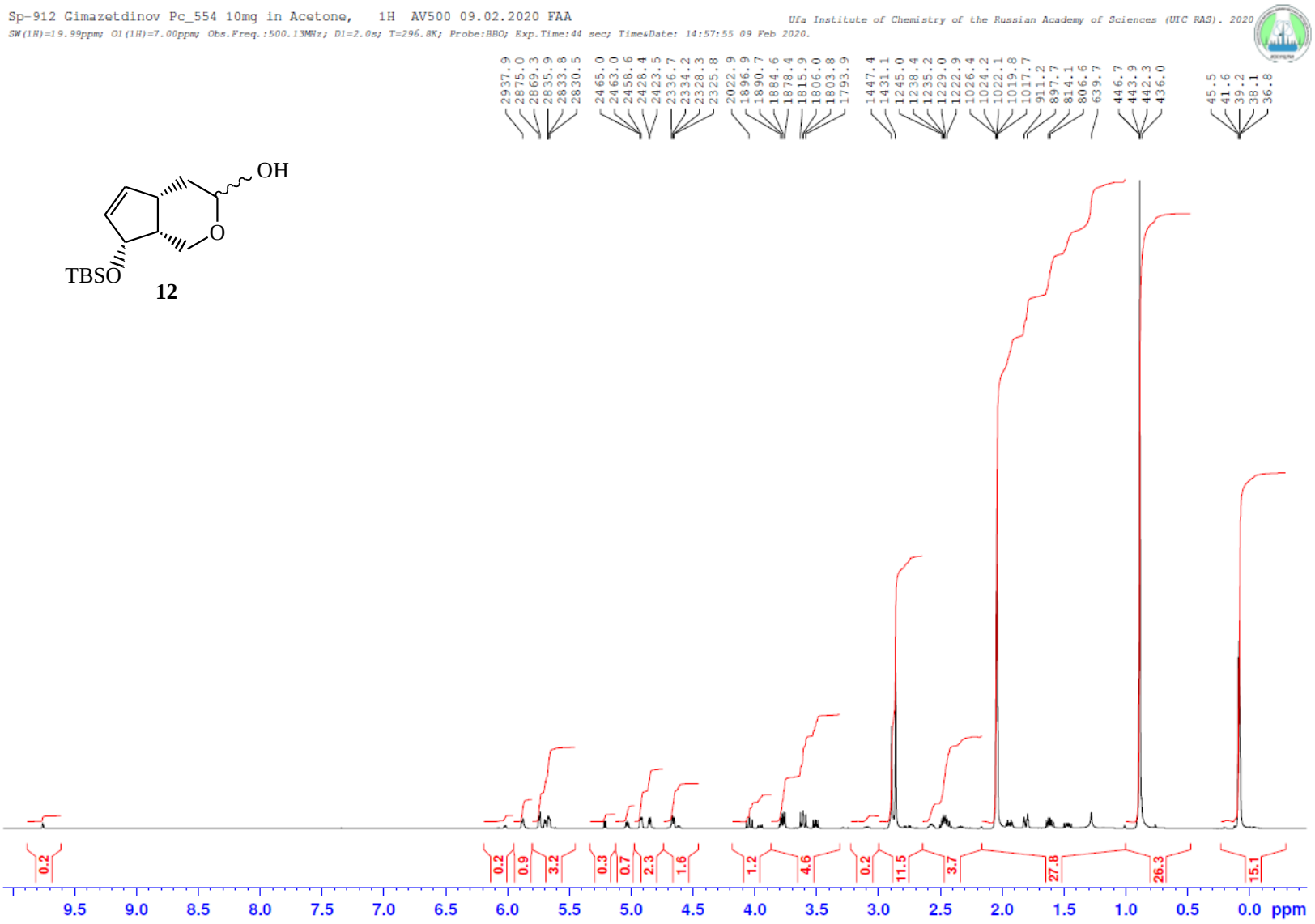

Figure S52 ^{1}H NMR spectrum of **12** (*d*-acetone, 500 MHz)

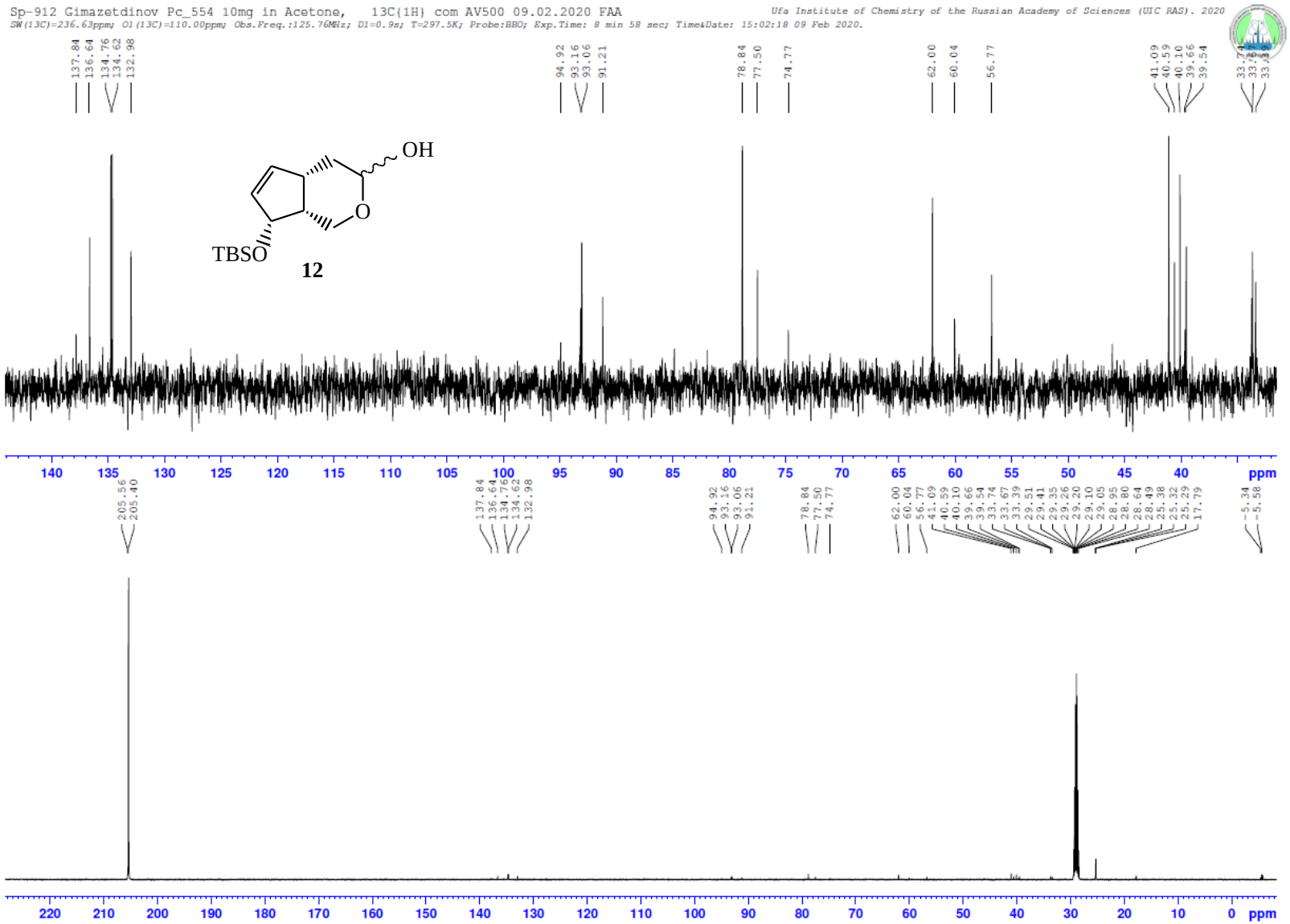

Figure S53 ^{13}C NMR spectrum of **12** (*d*-acetone, 125.77 MHz)

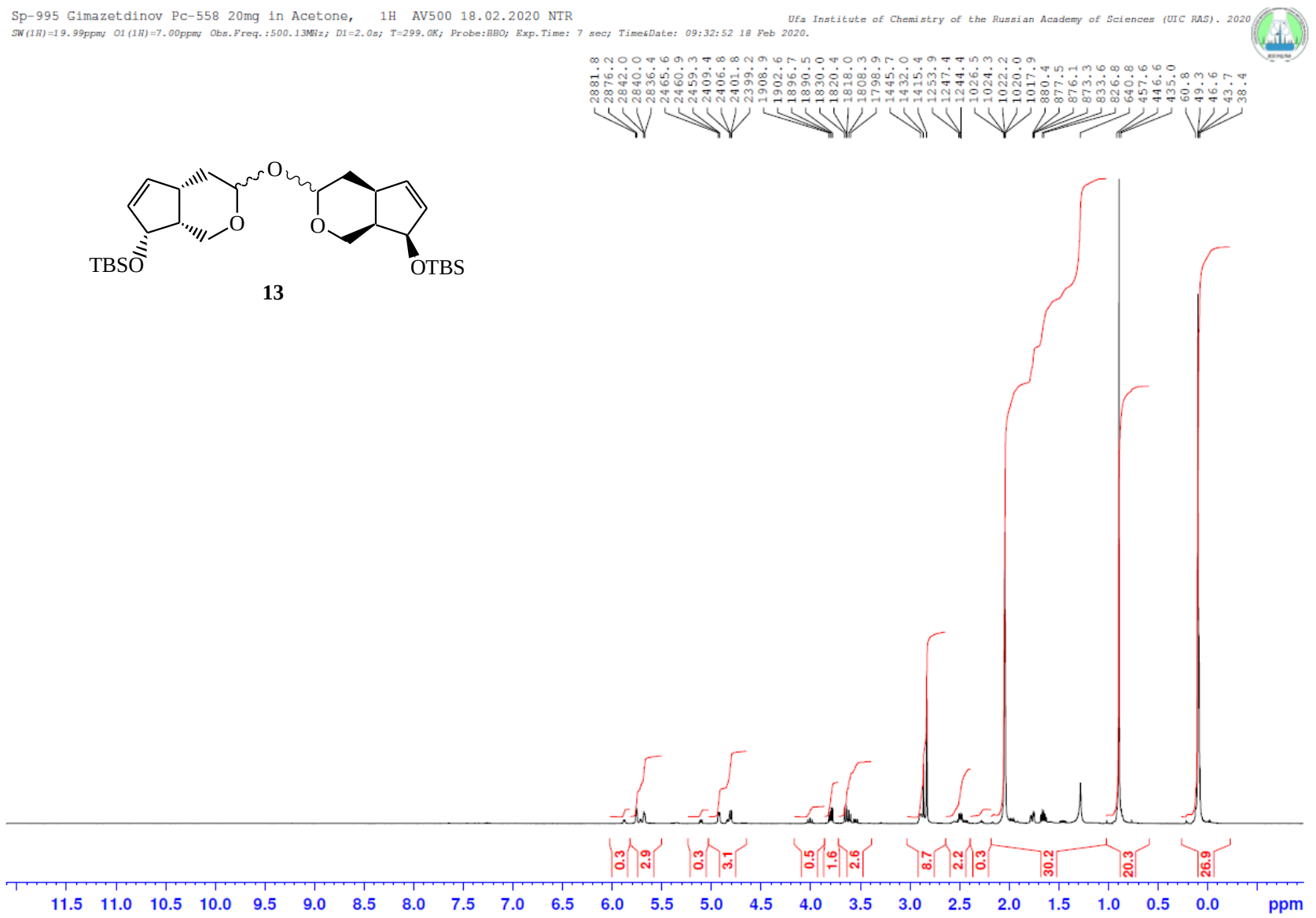

Figure S54 ^{1}H NMR spectrum of **13** (*d*-acetone, 500 MHz)

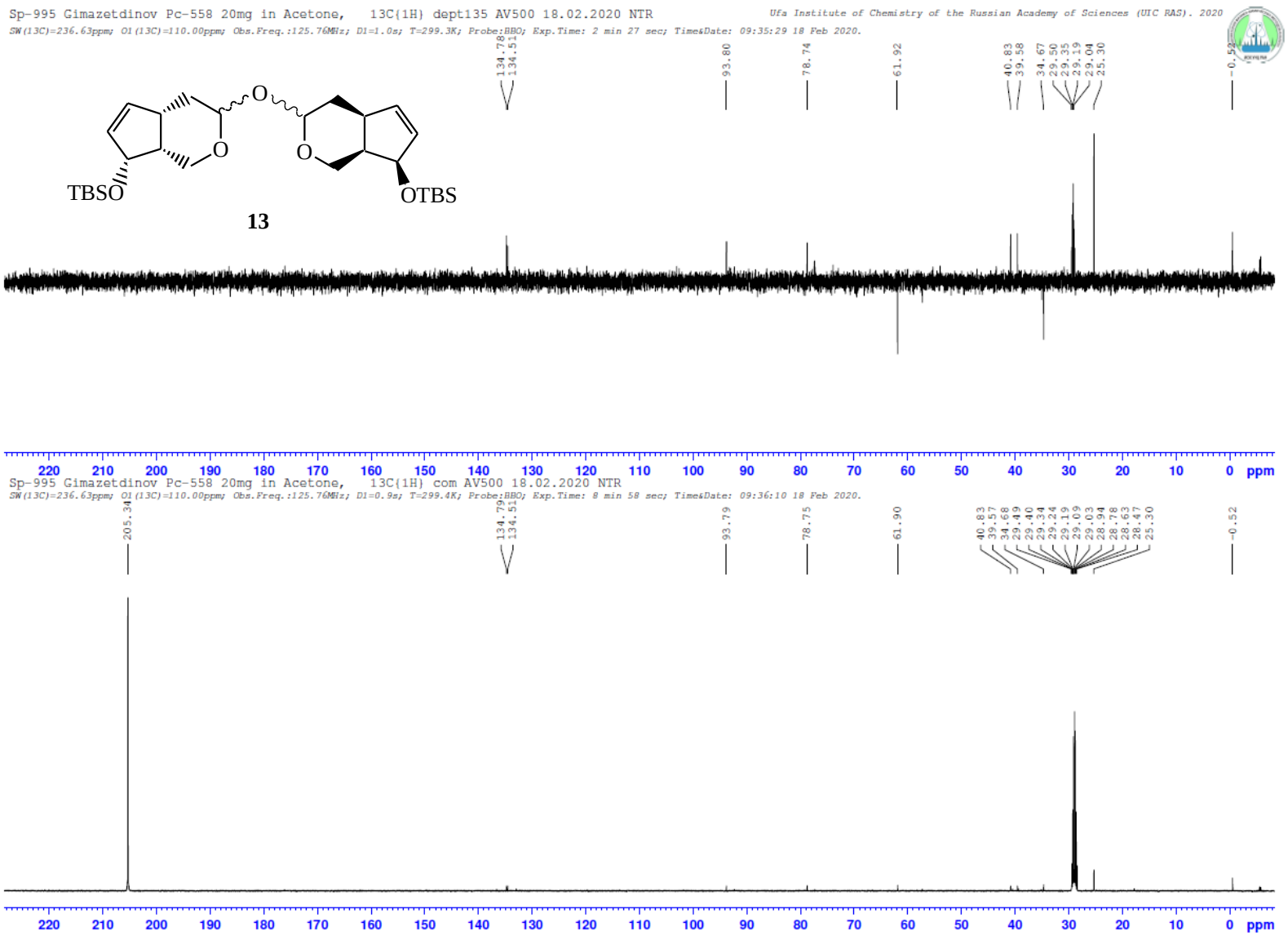

Figure S55 ^{13}C NMR spectrum of **13** (*d*-acetone, 125.77 MHz)

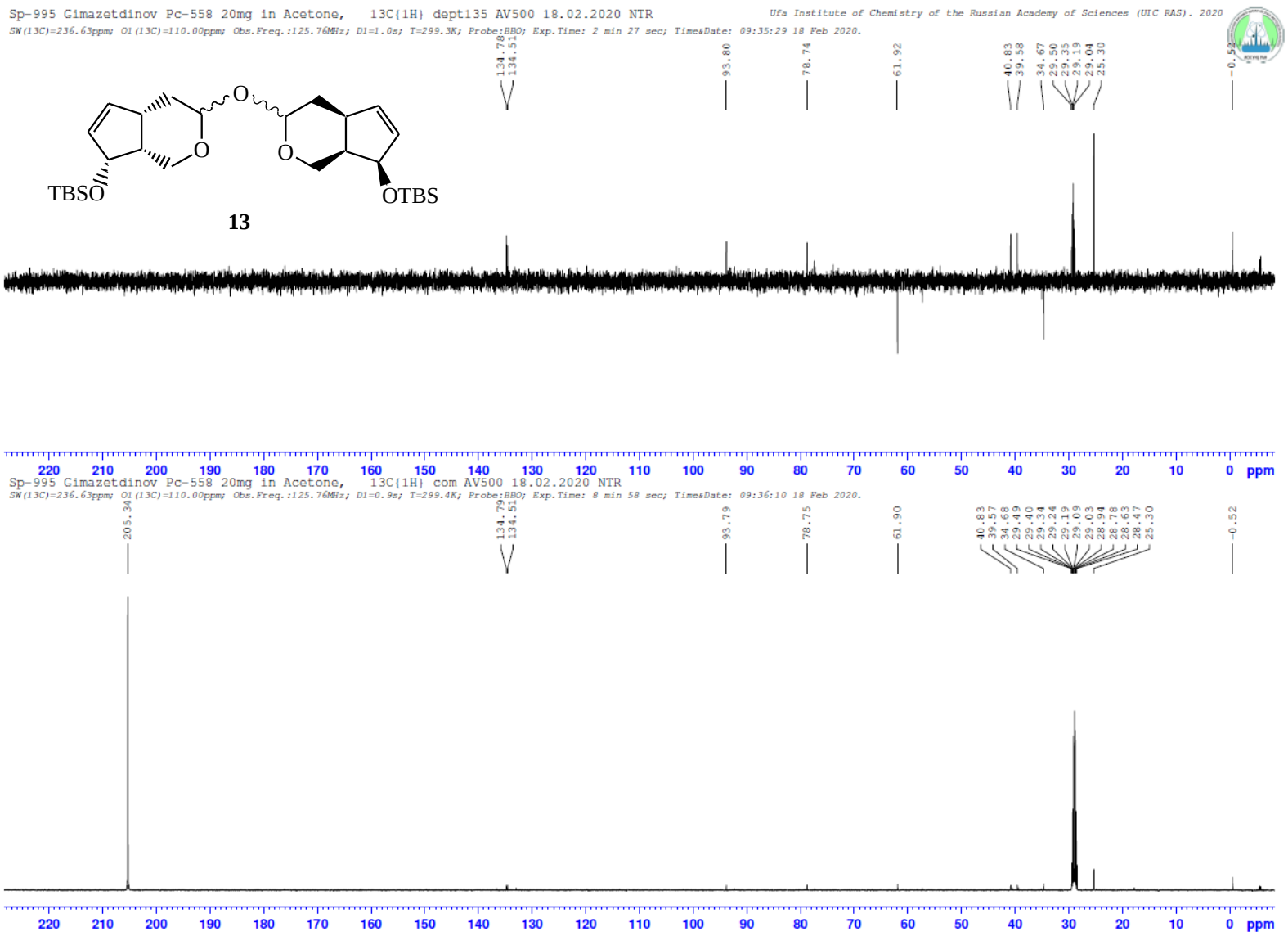

Figure S56 ^{13}C NMR spectrum of **13** (*d*-acetone, 125.77 MHz)

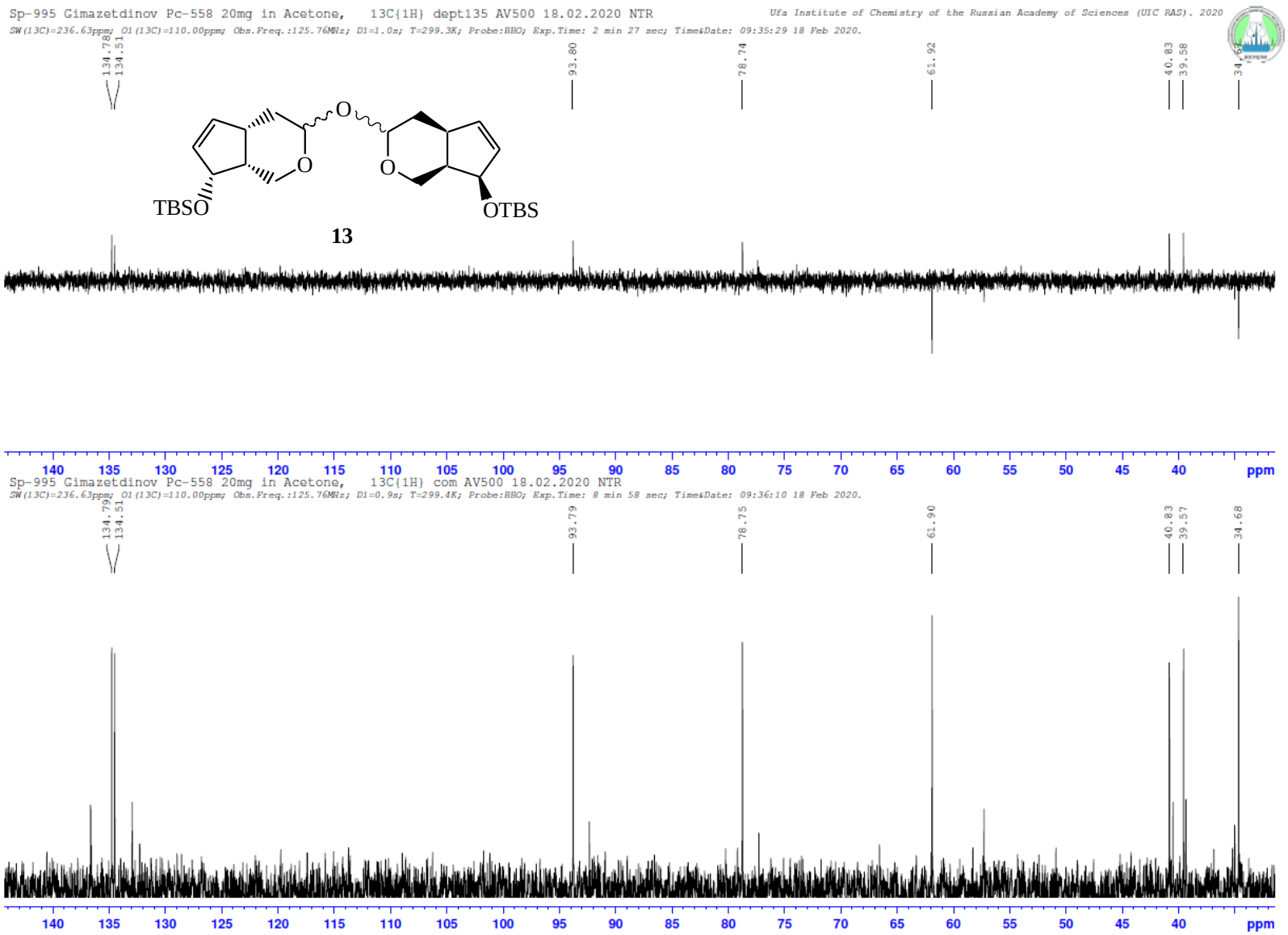

Figure S57 ^{13}C NMR spectrum (2) of **13** (*d*-acetone, 125.77 MHz)