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Supporting Information

Development of a new approach for synthesis of (+)-15-deoxy- $\Delta^{12,14}$ -prostaglandin J₂ methyl ester based on [2+2]-cycloadduct of 5-trimethylsilylcyclopentadiene and dichloroketene

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

* Corresponding author. Tel.: +7-347-235-58-47; e-mail: airopet@yandex.ru

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1. General Information

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. Air- and moisture-sensitive liquids and solutions were transferred by syringe. Reactions were stirred using Teflon-coated magnetic stir bars. Elevated temperatures were maintained using thermostat-controlled heating block. Organic solutions were concentrated using a rotary evaporator with a diaphragm vacuum pump. TLC was performed using Sorbfil STC-1A 110 μm layer, silica gel 5-17 pre-coated foil plates. The TLC plates were visualized by phosphomolybdic acid or anisaldehyde. Column chromatography was conducted using 210–280 mesh silica gel.

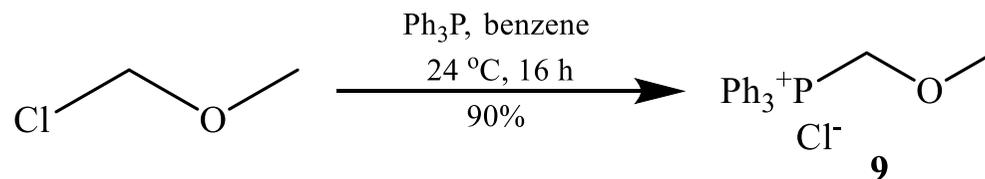
Analytical. Optical rotations were measured using the sodium D line at 589 nm on a Perkin–Elmer, Model 241 MC polarimeter at 20 °C. IR (infrared spectra) were recorded on a Shimadzu IR Prestige-21 spectrometer as nujol mull or as neat thin films on KBr plates (film) and were reported in reciprocal centimeters (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). DEPT135 spectra accompanied with the normal ^{13}C NMR were obtained using a Bruker Avance III (500 MHz for ^1H and 125.77 MHz for ^{13}C) as solutions in *d*-acetone (Aldrich Chemical Company; spectra grade) or *d*-chloroform (Aldrich Chemical Company; spectra grade). Chemical shifts are reported in δ unit-parts per million (ppm) downfield from tetramethylsilane (TMS), chloroform 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.

Abbreviations. DIBAL-H = diisobutyl aluminium hydride, DCM = dichloromethane, Et_2O = ethyl ether, DIPEA = *N,N*-diisopropylethylamine, Ac_2O = acetic anhydride, THF = tetrahydrofuran, EA = ethyl acetate, PE = petroleum ether, PPh_3 = triphenylphosphine, TBAF = tetrabutylammonium fluoride, MeOH = methanol, DMSO = dimethyl sulfoxide, DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene, TBS = *tert*-butyldimethylsilyl, MOM = methoxymethyl, Oxone® = the triple salt $2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$, *n*-BuLi = *n*-butyllithium, TFA = trifluoroacetic acid, Py = pyridine, MeCN = acetonitrile.

2. Experimental Procedures

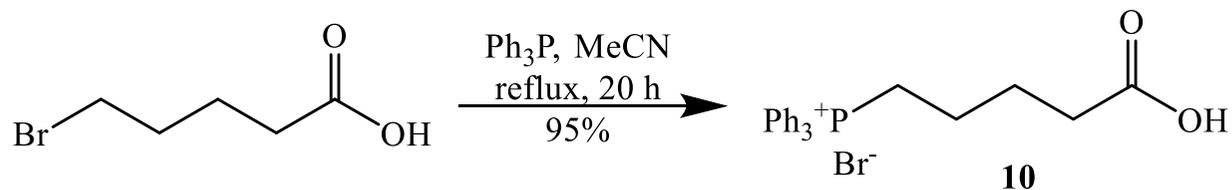
Total Synthesis of (+)-15-Deoxy- $\Delta^{12,14}$ -Prostaglandin J₂ Methyl Ester

Compound 9



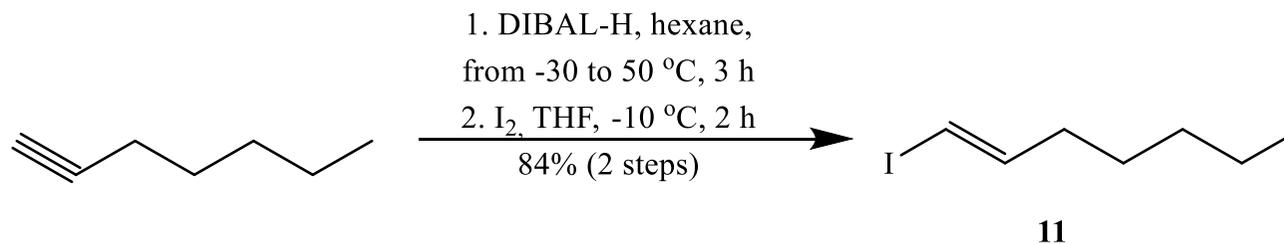
A solution of MOM chloride (3 mL, 0.04 mmol) in benzene (15 mL) was added dropwise in period over 15 min to a 250 mL round-bottom flask containing PPh_3 (10.74 g, 0.04 mmol) and benzene (100 mL) at rt under an argon atmosphere. The reaction mixture was stirred at the same temperature for 24 h and filtered on Schott® funnel. The residue on the filter was washed with three 10-ml. portions of benzene and evaporated under vacuum to afford *title compound* as a white crystalline solid (11.3 g, 90% yield). M.p.=200-202 °C; δ_{H} (300 MHz, *d*-chloroform/chloroform): 7.95-7.61 (m, 15H, 3Ph), 5.96 (d, *J* 3.9 Hz, 2H, CH_2), 3.68 (s, 3H, CH_3).

Compound 10



A solution of 5-bromopentanoic acid (6 g, 0.03 mmol) in MeCN (15 mL) was added to a 250 mL round-bottom flask containing PPh₃ (8.9 g, 0.03 mmol) and MeCN (100 mL) at rt under an argon atmosphere. The reaction mixture was stirred at reflux, cooled to rt and most of the solvent was evaporated under reducer pressure. The light beige crystalline residue was filtered on Schott® funnel, washed with three 10-ml. portions of Et₂O and evaporated under vacuum to afford *title compound* as a light-beige crystalline solid (12.9 g, 95% yield). M.p.=205-207 °C; δ_{H} (300 MHz, *d*-chloroform/chloroform): 11.87 (br.s, 1H, CO₂H), 7.98-7.65 (m, 15H, 3Ph), 3.71-3.58 (m, 2H, C¹H), 2.74 (t, *J* 6.8 Hz, 2H, C⁴H), 1.96 (quint, *J* 6.7 Hz, 2H, C³H), 1.85-1.64 (m, 2H, C²H).

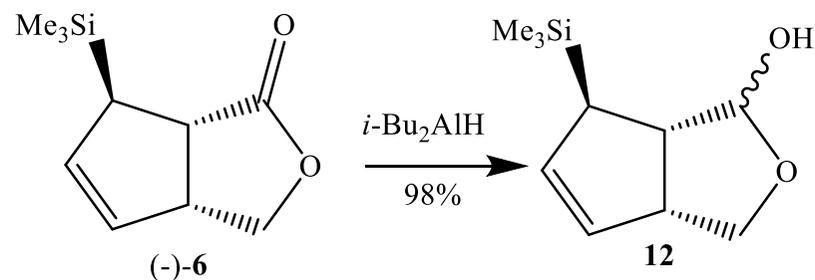
Compound 11



Step 1: To a solution of 1-heptyne (3g, 0.03 mole) in *n*-hexane (20 mL) was added *via* syringe DIBAL-H (8.7 mL, 0.1 mole) while maintaining the temperature below 40°. When the initial exothermic reaction had subsided, the reaction mixture was heated for 2 hr at 50 °C. Then the heptane was removed under reduced pressure (0.5 mm).

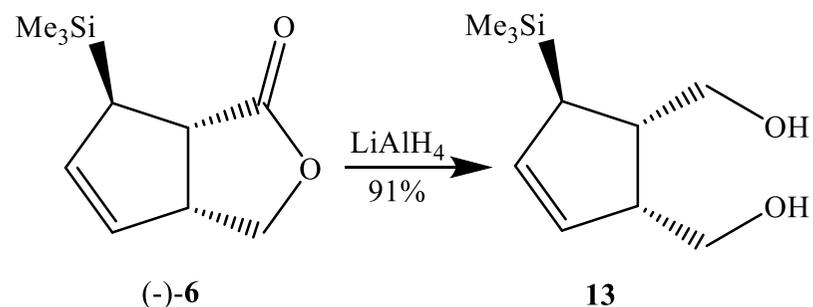
Step 2: The aforementioned residue was diluted with 40 ml of THF. To this vinylalane solution at -50 °C was added iodine (2.54 g, 0.1 mole) in THF (40 mL). After allowing the reaction mixture to warm up to rt, the diisobutylalane (-Al(C₄H₈)₂) was decomposed at 20-30 °C by dropwise addition of 20% sulfuric acid (exothermic reaction). When the isobutane evolution had diminished, the reaction mixture was poured into ice-20 % H₂SO₄. The vinyl iodide was extracted into hexane (3x20 mL) and the combined extracts were washed first with sodium thiosulfate, then with sodium bicarbonate. The residue was purified by column chromatography (100:1 PE/EA as eluent) to afford *title compound* as a transparent yellowish liquid (5.6 g, 84% yield over two steps). R_f (petroleum ether/ethyl acetate = 100:1) 0.7; δ_{H} (300 MHz, *d*-chloroform/chloroform): 6.56-6.47 (m, 1H, C²H), 6.0 (d, *J* 14.2 Hz, 1H, C¹H), 2.06 (q, *J* 7.0 Hz, 2H, C³H), 1.47-1.24 (m, 6H, C⁴H, C⁵H and C⁶H), 0.91 (t, *J* 6.9 Hz, 3H, CH₃).

Compound 12



To a stirred solution of 0.5 g (2.5 mmol) (-)-**6** in absolute CH_2Cl_2 (30 mL) at $-78\text{ }^\circ\text{C}$ was added dropwise 0.9 g (6.3 mmol) DIBAL-H in absolute CH_2Cl_2 (10 mL). The reaction was monitored by TLC (petroleum ether/ethyl acetate, 1:1). After stirring for 1 h at the same temperature the reaction mixture was warmed up to $0\text{ }^\circ\text{C}$ and 10 mL sat. NH_4Cl was added. The resulting mixture was filtered, evaporated under reduced pressure and extracted 3x30 mL EtOAc. The combined organic layers dried over MgSO_4 and evaporated. Purification of products by column chromatography (petroleum ether/ethyl acetate, 1:1) afforded of *title compound* (0.48 g, 98%) as a white crystalline solid; m.p. $54\text{--}56\text{ }^\circ\text{C}$; [Found: C, 60.44; H, 8.86. $\text{C}_{10}\text{H}_{18}\text{O}_2\text{Si}$ requires C, 60.60; H, 9.09%]; R_f (petroleum ether/ethyl acetate, 3:1) 0.3; IR (liquid film) ν_{max} , cm^{-1} : 3390, 2953, 2921, 1246, 964, 841; δ_{H} (300 MHz, *d*-chloroform/chloroform): 5.61-5.64 (m, 1H, C^5H), 5.39-5.42 (m, 1H, C^4H), 5.09 (s, 1H, C^1H), 3.89 (dd, J 8.2, 6.6 Hz, 1H, C^3H), 3.71 (dd, J 13.0, 9.4 Hz, 1H, C^3H), 3.35-3.39 (m, 1H, C^{3a}H), 2.62 (dd, J 8.1, 3.2 Hz, 1H, C^{6a}H), 1.91 (t, J 2.5 Hz, 1H, C^6H), 1.67-1.74 (br s, 1H, OH), -0.03 (s, 9H, $(\text{CH}_3)_3\text{Si}$); δ_{C} (75.1 MHz, *d*-chloroform/chloroform): 132.58 (C^5), 128.49 (C^4), 107.74 (C^1), 70.32 (C^3), 50.73 (C^{3a}), 49.86 (C^{6a}), 40.47 (C^6), -3.45 ($(\text{CH}_3)_3\text{Si}$); m/z (APCI): 199 (100%, $[\text{MH}]^+$).

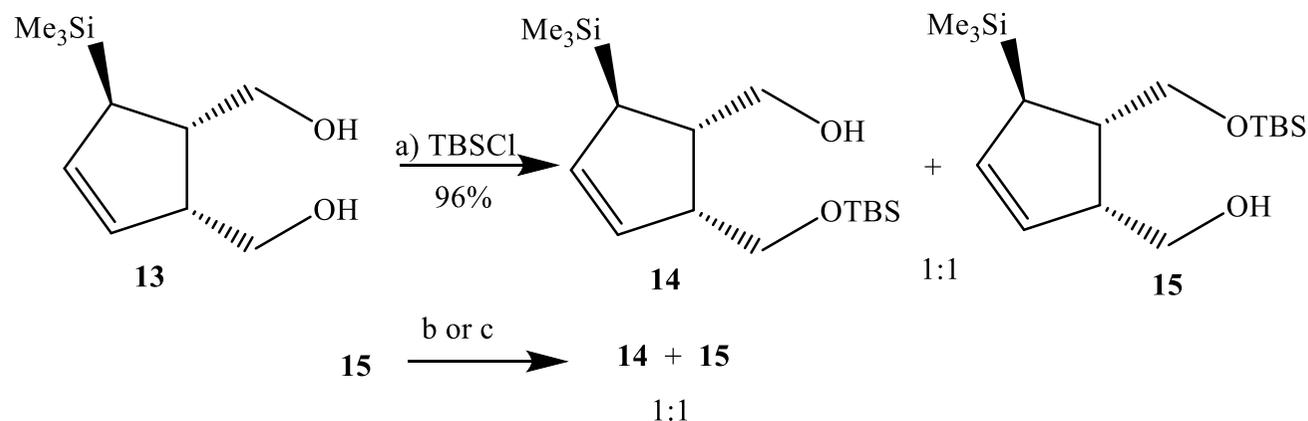
Compound 13



a. To a stirred solution of 2.1 g (10.7 mmol) (-)-6 in anhydrous THF (70 mL) at 0°C was added 1.2 g (31.5 mmol) LiAlH_4 . 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 20 mL sat. NH_4Cl and resulting mixture was filtered, evaporated under reduced pressure and extracted 3x50 mL EtOAc. The combined organic layers dried over MgSO_4 and evaporated under reduced pressure. Purification of products by column chromatography (petroleum ether/ethyl acetate, 1:1) afforded of *title compound* (1.95 g, 91%) as a light brown oil.

b. To a stirred solution of 0.25 g (0.8 mmol) **14** (or **15**) in CH_3OH (25 mL) at rt was added 0.9 g Dowex®. The reaction was monitored by TLC (petroleum ether/ethyl acetate, 1:1) and after 3 h stirring the ion-exchanged resin was removed by filtration through a short pad of Celite and washed with EtOAc (3x15 ml). The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate, 1:1) to furnish *title compound* (0.16 g, 98%) as a light brown oil. [Found: C, 59.74; H, 9.86. $\text{C}_{10}\text{H}_{20}\text{O}_2\text{Si}$ requires C, 59.91; H, 9.98%]; R_f (petroleum ether/ethyl acetate, 1:1) 0.3; $[\alpha]_D^{20} -103.4$ (c 0.98, CH_2Cl_2); IR (liquid film) ν_{max} , cm^{-1} : 3310, 1248, 1051, 837, 728; δ_{H} (300MHz, d -chloroform/chloroform): 5.68-5.72 (m, 1H, C^4H or C^3H), 5.31-5.35 (m, 1H, C^3H or C^4H), 3.55-3.81 (m, 6H, $2\text{CH}_2\text{OH}$), 3.01-3.12 (m, 1H, C^2H), 2.55-2.64 (m, 1H, C^1H), 1.54-1.60 (m, 1H, C^5H), 0.0 (s, 9H, $(\text{CH}_3)_3\text{Si}$); δ_{C} (75.1 MHz, d -chloroform/chloroform): 133.35 (C^3), 130.68 (C^4), 62.93 (CH_2O), 61.70 (CH_2O), 49.38 (C^2), 42.21 (C^1), 34.31 (C^5), 1.90 ($(\text{CH}_3)_3\text{Si}$); m/z (APCI) 201 (100%, $[\text{MH}]^+$).

Compounds 14 and 15



b) CHCl_3 , rt, 30 h, quant; c) NaH, THF, 0 °C, 30 min, 95%.

a. A solution of 1.5 g (7.5 mmol) of diol **13** in methylene chloride (80 mL) was added under stirring to a mixture of 1.24 g (8.25 mmol) of *tert*-butyl(chloro)dimethylsilane, 0.56 g (8.25 mmol) of imidazole and 30 mL of methylene chloride 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 *title compounds*.

Compound 14. Yield 1.13 g (48%), transparent viscous oil; [Found: C, 60.88; H, 10.56. $\text{C}_{16}\text{H}_{34}\text{O}_2\text{Si}_2$ requires C, 61.03; H, 10.81%]; R_f (petroleum ether/ethyl acetate, 10:1) 0.4; $[\alpha]_D^{20}$ -106.4 (*c* 1.03, CH_2Cl_2); IR (liquid film) ν_{max} , cm^{-1} : 3456, 2955, 2873, 1472, 1464, 1249, 1061, 841, 832, 778; δ_{H} (500 MHz, $(\text{CD}_3)_2\text{CO}$): 5.70 (dt, *J* 5.3, 2.3 Hz, 1H, C^3H), 5.48 (dt, *J* 5.8, 2.3 Hz, 1H, C^4H), 4.09-4.12 (br. s, 1H, OH), 3.78 (dd, *J* 10.3, 7.7 Hz, 1H, $\text{CH}_2\text{-OH}$), 3.67 (dd, *J* 10.3, 5.8 Hz, 1H, $\text{CH}_2\text{-OH}$), 3.62-3.65 (m, 2H, $\text{CH}_2\text{-OSi}$), 2.92-3.01 (m, 1H, C^2H), 2.46-2.53 (m, 1H, C^1H), 1.78 (dt, *J* 5.0, 2.3 Hz, 1H, C^5H), 0.91 (s, 9H, $(\text{CH}_3)_3\text{C}$), 0.10 (s, 6H, $(\text{CH}_3)_2\text{Si}$), 0.0 (s, 9H, $(\text{CH}_3)_3\text{Si}$); δ_{C} (125.77 MHz, $(\text{CD}_3)_2\text{CO}$): 132.42 (C^4), 127.17 (C^3), 62.76 (CH_2OH), 62.62 (CH_2OSi), 50.63 (C^2), 44.33 (C^1), 37.63 (C^5), 25.37 ($(\text{CH}_3)_3\text{C}$), 18.21 ($(\text{CH}_3)_3\text{C}$), -3.57 ($(\text{CH}_3)_3\text{Si}$), -6.12 ($(\text{CH}_3)_2\text{Si}$); *m/z* (APCI): 315 (100%, $[\text{MH}]^+$).

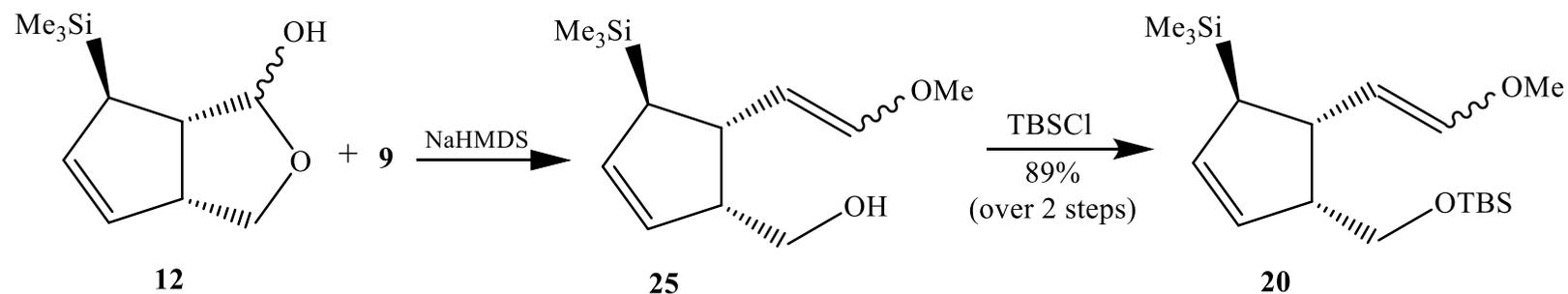
Compound 15. Yield 1.11 g (47%), transparent viscous oil; [Found: C, 60.94; H, 10.65. $\text{C}_{16}\text{H}_{34}\text{O}_2\text{Si}_2$ requires C, 61.03; H, 10.81%]; R_f (petroleum ether/ethyl acetate, 10:1) 0.3; $[\alpha]_D^{20}$ -118.6 (*c* 1.17, CH_2Cl_2); IR (liquid film) ν_{max} , cm^{-1} : 3415, 2999, 2885, 1686, 1464, 1249, 836, 777; δ_{H} (500 MHz,

(CD₃)₂CO): 5.69 (ddd, *J* 5.7, 3.6, 2.7 Hz, 1H, C²H), 5.46 (dt, *J* 5.7, 2.7 Hz, 1H, C³H), 4.09-4.12 (br. s, 1H, OH), 3.80 (dd, *J* 9.9, 7.8 Hz, 1H, CH₂-OH), 3.65 (dd, *J* 10.1, 8.0 Hz, 1H, CH₂-OSi), 3.54 (dd, *J* 10.1, 6.0 Hz, 1H, CH₂-OSi), 3.49 (dd, *J* 9.9, 6.6 Hz, 1H, CH₂-OH), 2.94 (dddd, *J* 7.8, 6.6, 6.0, 3.6 Hz, 1H, C¹H), 2.50 (dtd, *J* 8.0, 6.0, 3.6 Hz, 1H, C⁵H), 1.80 (dt, *J* 5.6, 2.7 Hz, 1H, C⁴H), 0.91 (s, 9H, (CH₃)₃C), 0.10 (s, 6H, (CH₃)₂Si), 0.0 (9H, s, (CH₃)₃Si); δ_C (125.77 MHz, (CD₃)₂CO): 131.84 (C³), 128.17 (C²), 63.51 (CH₂OH), 61.60 (CH₂OSi), 51.12 (C⁵), 43.73 (C¹), 38.44 (C⁴), 25.44 ((CH₃)₃C), 17.86 ((CH₃)₃C), -3.60 ((CH₃)₃Si), -4.11 ((CH₃)₂Si); m/z (APCI): 315 (100%, [MH]⁺).

b. Compound **15** (0.2 g, 0.67 mmol) was dissolved in 15 ml of commercially available crude chloroform and resulting mixture was stirred for 30 min at rt. Organic solvent was evaporated under reduced pressure and purification of the product by column chromatography (petroleum ether/ethyl acetate, 10:1) afforded individual compounds **14** and **15** in 95% overall yield.

c. To a stirred under argon atmosphere suspension of NaH (34 mg, 1.2 mmol, 65% in oil) in dry THF (5 mL) at 0 °C was added compound **15** (0.3 g, 1 mmol) in dry THF (10 mL). The resulting mixture was stirred for 30 min at the same temperature 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 (MgSO₄), and evaporated under reduced pressure. Purification of the product by column chromatography (petroleum ether/ethyl acetate, 10:1) afforded individual *title compounds* in quantitative yield.

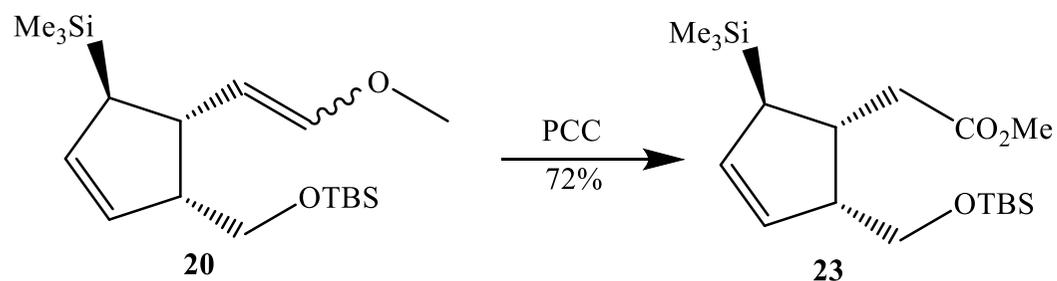
Compounds 25 and 20.



Step 1: To a stirred solution of methoxymethylidenetriphenylphosphonium chloride **9** (0.87 g, 2.54 mmol) in 20 ml of dry toluene, cooled to -78°C under argon atmosphere, was added 1.2M solution of NaHMDS (1.85 mL, 2.22 mmol) and the temperature was heated to rt. After being stirred at rt for 10 min, the reaction solution was cooled at -78°C and the solution of the lactole **12** (0.2 g, 1.01 mmol) in 5 mL of dry toluene was added. Then, the reaction mixture was heated to room temperature and 3 mL of saturated solution of NH_4Cl was added. The resulting mixture was filtered, water layer extracted with EtOAc, combined organic layers dried by MgSO_4 , solvent evaporated. The crude enolether **25** was used further without purification.

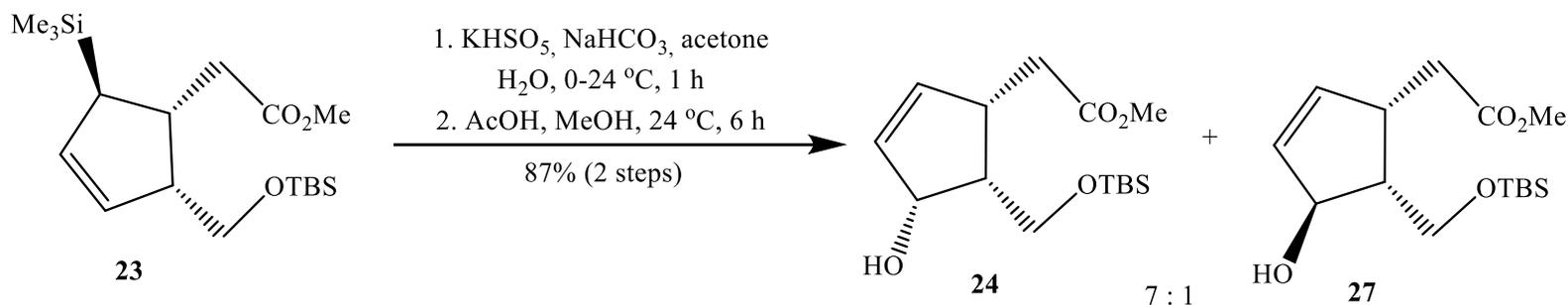
Step 2: The aforementioned residue was diluted with 20 ml of CH_2Cl_2 and the resulting mixture was added under stirring to a mixture of 0.22 g (1.5 mmol) of *tert*-butyl(chloro)dimethylsilane, 0.14 g (2.0 mmol) of imidazole and 15 mL of methylene chloride at rt. The mixture was stirred for 4 h at the same temperature (monitored by TLC) and evaporated under reduced pressure. Purification of the product by column chromatography (petroleum ether/ethyl acetate, 40:1) afforded individual *title compound* (0.30 g, 89%) as a colorless oily liquid. [Found: C, 63.26; H, 10.49. $\text{C}_{18}\text{H}_{36}\text{O}_2\text{Si}_2$ requires C, 63.47; H, 10.65%]; R_f (petroleum ether/ethyl acetate, 40:1) 0.5; IR (liquid film) ν_{max} , cm^{-1} : 3057, 2955, 2856, 1436, 1248, 1193, 1119, 836, 720; δ_{H} (500 MHz, $(\text{CD}_3)_2\text{CO}$): 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, C^3H), 5.59 (dt, J 2.1, 5.6 Hz, 1H, C^2H), 4.83 (dd, J 10.2, 12.6 Hz, 1H, $\underline{\text{C}}\text{H}=\text{CHOMe}$), 3.66 (dd, J 5.6, 9.8 Hz, 1H, $\underline{\text{C}}\text{H}_2\text{O}$), 3.56 (dd, J 2.2, 9.6 Hz, 1H, $\underline{\text{C}}\text{H}_2\text{O}$), 3.46 (s, 3H, CH_3), 2.85-2.89 (m, 1H, C^5H), 2.71-2.77 (m, 1H, C^1H), 1.90 (td, J 2.5, 4.8 Hz, 1H, C^4H), 0.88 (s, 9H, $(\text{CH}_3)_3\text{C}$), 0.03 (s, 6H, $(\text{CH}_3)_2\text{Si}$), -0.01 (s, 9H, $(\text{CH}_3)_3\text{Si}$); δ_{C} (125.77 MHz, $(\text{CD}_3)_2\text{CO}$): 146.83 ($\text{CH}=\underline{\text{C}}\text{HOMe}$), 133.43 (C^2), 131.78 (C^3), 104.62 ($\underline{\text{C}}\text{H}=\text{CHOMe}$), 63.65 (CH_2O), 55.03 (CH_3), 52.31 (C^1), 43.39 (C^5), 41.12 (C^4), 25.39 ($(\underline{\text{C}}\text{H}_3)_3\text{C}$), 17.88 ($(\text{CH}_3)_3\text{C}$), -3.59 ($(\text{CH}_3)_3\text{Si}$), -6.0 ($(\text{CH}_3)_2\text{Si}$); m/z (APCI): 341 (100%, $[\text{MH}]^+$).

Compound 23.



To the solution of enoether **20** (0.89 g, 2.60 mmol) in dry CH_2Cl_2 at 0°C , were added SiO_2 (0.89 g), NaHCO_3 (0.17 g, 10 %mass of PCC) and PCC (1.69 g, 7.83 mmol). Then, reaction mass warmed to room temperature and stirred for 2 h (control by TLC). The mixture was filtered throughout the Schott filter with SiO_2 , the solvent evaporated. Purification of the product by column chromatography with SiO_2 gave *title compound* (0.64 g, 69%) as a transparent viscous oil; [Found: C, 60.49; H, 10.09. $\text{C}_{18}\text{H}_{36}\text{O}_3\text{Si}_2$ requires C, 60.62; H, 10.17%]; R_f (petroleum ether/ethyl acetate, 20:1) 0.5; $[\alpha]_D^{20}$: +141.0 (c 1.0, CH_2Cl_2); IR (liquid film) ν_{max} , cm^{-1} : 2954, 2857, 1739, 1249, 1094, 837, 775; δ_{H} (500 MHz, $(\text{CD}_3)_2\text{CO}$): 5.73 (dt, J 2.6, 5.7 Hz, 1H, C^4H), 5.45 (dt, J 2.0, 5.7 Hz, 1H, C^3H), 3.70 (dd, J 6.2, 10.2 Hz, 1H, CH_2O), 3.63 (dd, J 7.8, 10.3 Hz, 1H, CH_2O), 3.60 (s, 3H, CH_3), 2.88-2.94 (m, 1H, C^2H), 2.73-2.79 (m, 1H, C^1H), 2.59 (dd, J 5.6, 15.0 Hz, 1H $\text{CH}_2\text{CO}_2\text{Me}$), 2.23 (dd, J 9.5, 14.9 Hz, 1H $\text{CH}_2\text{CO}_2\text{Me}$), 1.70 (quint, J 2.6 Hz, 1H, C^5H), 0.90 (s, 9H, $(\text{CH}_3)_3\text{C}$), 0.13 (s, 6H, $(\text{CH}_3)_2\text{Si}$), 0.0 (s, 9H, $(\text{CH}_3)_3\text{Si}$); δ_{C} (125.77 MHz, $(\text{CD}_3)_2\text{CO}$): 173.12 (C=O), 132.15 (C^4), 127.38 (C^3), 62.42 (CH_2O), 50.62 (CH_3), 41.54 (C^5 and C^2), 37.99 (C^1), 35.29 ($\text{CH}_2\text{CO}_2\text{Me}$), 25.35 ($(\text{CH}_3)_3\text{C}$), 17.86 ($(\text{CH}_3)_3\text{C}$), -3.55 ($(\text{CH}_3)_3\text{Si}$), -6.11 ($(\text{CH}_3)_2\text{Si}$); m/z (APCI): 357 (100%, $[\text{MH}]^+$).

Compounds 24 and 27



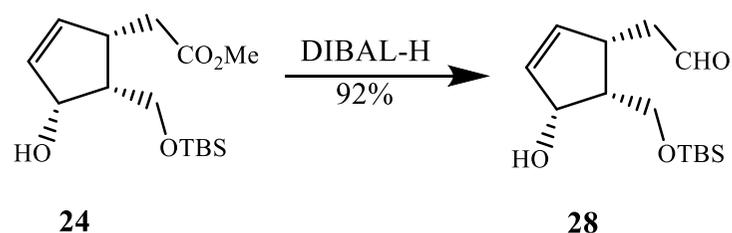
1 Step: Solid NaHCO₃ (1.74 g, 20.7 mmol) was placed in a round-bottom flask and water (24 mL) followed by acetone (38 mL) were added. The resulting mixture was cooled to 0 °C and stirred for 20 min. Oxone® (1.74 g, 3.55 mmol) was added in one portion and stirring was continued at 0 °C for 15 min. Then, silane **23** (0.62 g, 1.74 mmol) was added in one portion. Cooling was removed and the reaction mixture was stirred for 1 h (monitored by TLC) at rt. The resulting mixture was diluted with water (20 mL) and extracted with EA (3×30 mL). The combined organic layers were dried (MgSO₄) and the solvent was evaporated under reduced pressure.

Step 2: The aforementioned residue was diluted with 9:1-mixture of MeOH-CH₃COOH (10 mL) and resulting mixture was stirred for 6 h (monitored by TLC). The solvent was removed under reduced pressure and the residue was purified by column chromatography (5:1 PE/EA as eluent) to afford *title compounds*.

Compound 24. Yield 0.39 g (76%), transparent colorless liquid; [Found: C, 59.74; H, 9.12. C₁₅H₂₈O₄Si requires C, 59.96; H, 9.39%]; [α]_D²⁰ +48.4 (c 1.05, CH₂Cl₂); R_f (petroleum ether/ethyl acetate, 5:1) 0.4; IR (liquid film) ν_{max} , cm⁻¹: 3377, 2857, 1739, 1471, 1252, 1085, 838, 773; δ_H (500 MHz, (CD₃)₂CO): 6.04-6.00 (m, 1H, C³H), 5.90-5.86 (m, 1H, C²H), 4.61-4.57 (m, 1H, C⁴H), 3.96 (dd, *J* 10.4, 6.7 Hz, 1H, CH₂OSi), 3.79 (dd, *J* 10.3, 5.8 Hz, 1H, CH₂OSi), 3.62 (s, 3H, CH₃), 3.51 (d, *J* 5.3 Hz, 1H, OH), 3.02-2.95 (m, 1H, C¹H), 2.70 (dd, *J* 15.7, 5.3 Hz, 1H, CH₂CO₂), 2.32 (quint, *J* 7.0 Hz, 1H, C⁵H), 2.30 (dd, *J* 15.7, 10.1 Hz, 1H, CH₂CO₂), 0.90 (s, 9H, (CH₃)₃Si), 0.08 (s, 6H, (CH₃)₂Si); δ_C (125.77 MHz, (CD₃)₂CO): 172.90 (C=O), 137.89 (C³), 133.76 (C²), 74.91 (C⁴), 59.95 (CH₂OSi), 50.65 (CH₃O), 47.26 (C⁵), 41.68 (C¹), 36.03 (CH₂CO₂), 25.38 ((CH₃)₃C), 17.86 ((CH₃)₃C), -6.08 ((CH₃)₂Si); m/z (APCI): 283 (100%, [M-OH]⁺).

Compound 27. Yield 62 mg (11%), transparent colorless liquid; [Found: C, 59.81; H, 9.16. C₁₅H₂₈O₄Si requires C, 59.96; H, 9.39%]; $[\alpha]_D^{20} +88.7$ (*c* 1.13, CH₂Cl₂); R_f (petroleum ether/ethyl acetate, 5:1) 0.4; IR (liquid film) ν_{max} , cm⁻¹: 3377, 2857, 1739, 1471, 1252, 1085, 838, 773; δ_H (500 MHz, (CD₃)₂CO): .85-5.81 (m, 1H, C³H), 5.76-5.72 (m, 1H, C²H), 4.61-4.55 (m, 1H, C⁴H), 3.85 (dd, *J* 10.4, 5.2 Hz, 2H, CH₂OSi, OH), 3.77 (dd, *J* 10.5, 8.4 Hz, 1H, CH₂OSi), 3.61 (s, 3H, CH₃), 3.25-3.16 (m, 1H, C¹H), 2.71 (dd, *J* 15.7, 5.7 Hz, 1H, CH₂CO₂), 2.22-2.18 (m, 1H, C⁵H), 2.14 (dd, *J* 15.6, 10.1 Hz, 1H, CH₂CO₂), 0.90 (s, 9H, (CH₃)₃Si), 0.08 (s, 6H, (CH₃)₂Si); δ_C (125.77 MHz, (CD₃)₂CO): 172.85 (C=O), 135.45 (C³), 135.02 (C²), 77.40 (C⁴), 61.28 (CH₂OSi), 52.47 (C⁵), 50.67 (CH₃O), 41.89 (C¹), 34.72 (CH₂CO₂), 25.36 ((CH₃)₃C), 17.85 ((CH₃)₃C), -6.14 ((CH₃)₂Si); m/z (APCI): 301 (100%, [MH]⁺).

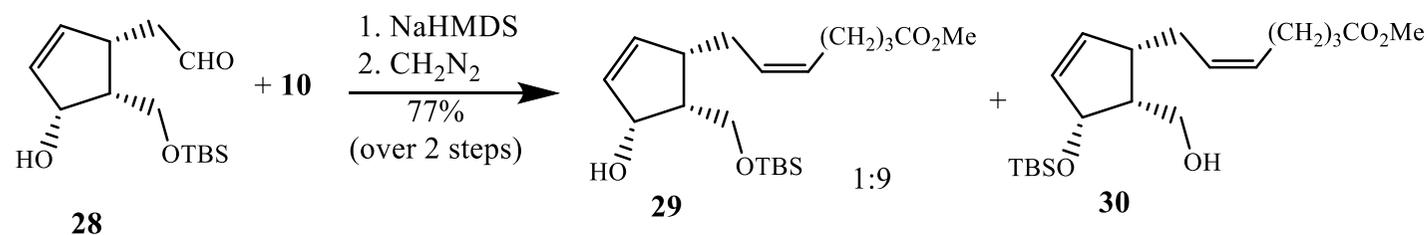
Compound 28



To a stirred solution of 0.74 g (2.5 mmol) **24** in absolute CH₂Cl₂ (50 mL) at -78 °C was added dropwise 0.71 g (5.0 mmol) DIBAL-H in absolute CH₂Cl₂ (20 mL). The reaction was monitored by TLC (petroleum ether/ethyl acetate, 1:1). After stirring for 30 min at the same temperature was added 20 mL sat. NH₄Cl and the reaction mixture was warmed up to rt. The resulting mixture was filtered, evaporated under reduced pressure and extracted 3x30 mL CH₂Cl₂. The combined organic layers dried over MgSO₄ and evaporated. Purification of products by column chromatography (petroleum ether/ethyl acetate, 3:1) afforded *title compound* (0.61 g, 92%) as a transparent viscous oil; [Found: C, 61.97; H, 9.41. C₁₄H₂₆O₃Si requires C, 62.18; H, 9.69%]; R_f (petroleum ether/ethyl acetate = 5:1) 0.3; $[\alpha]_D^{20} +22.0$ (*c* 1.0, CH₂Cl₂); IR (liquid film) ν_{max} , cm⁻¹: 3415, 2954, 2929, 2896, 2856, 1725, 1471, 1253, 1085, 837, 776; δ_H (500 MHz, (CD₃)₂CO): 9.79 (s, 1H, CHO), 6.02 (dd, *J* 5.5, 2.5 Hz, 1H, C²H), 5.87 (dd, *J* 4.1, 2.2 Hz, 1H, C³H), 4.62 (td, *J* 6.0, 2.3 Hz, 1H, C¹H), 3.96 (dd, *J* 10.5, 6.5 Hz, 1H, CH₂CHO), 3.78 (t, *J* 10.4 Hz, 1H, CH₂CHO), 3.12-3.09 (m, 1H, C⁴H), 2.85 (br s, 1H, OH) 2.75 (dd, *J* 5.8, 1.5 Hz, 1H, CH₂OSi), 2.47 (dd, *J* 8.4, 1.5 Hz, 1H, CH₂OSi), 2.33 (quint, *J* 7.9 Hz, 1H, C⁵H), 0.89 (s, 9H, (CH₃)₃C), 0.07 (s, 6H,

(CH₃)₂Si); δ_C (125.77 MHz, (CD₃)₂CO): 201.80 (C=O), 137.87 (C²), 133.44 (C³), 74.87 (C¹), 60.02 (CH₂OSi), 47.33 (C⁵), 46.09 (CH₂CHO), 39.62 (C⁴), 25.38 ((CH₃)₃C), 17.84 ((CH₃)₃C), -6.10 ((CH₃)₂Si); m/z (APCI): 301 (100%, [M-TBS]⁺).

Compounds 29 and 30



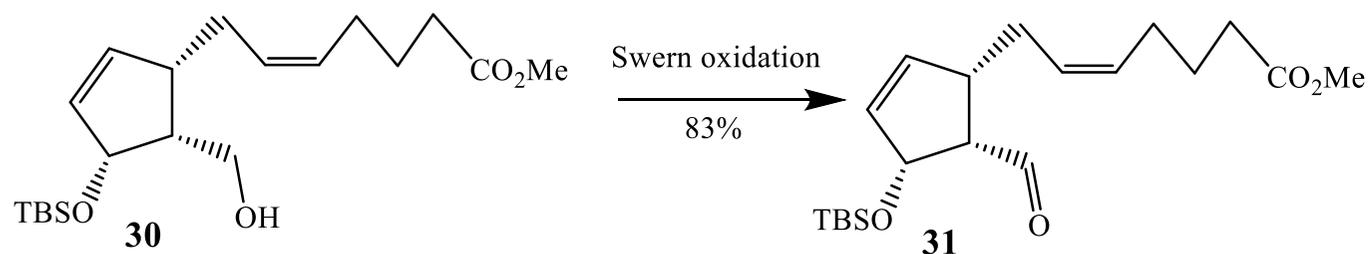
A solution of 2.69 g (6.1 mmol) of triphenylphosphonium salt of 5-bromopentanoate **10** in 80 mL of anhydrous THF was cooled under argon atmosphere to $-78\text{ }^\circ\text{C}$ and 8.54 mL of a 1.6 M solution of hexamethyldisilazane sodium in THF was added with stirring. The mixture was warmed up to $0\text{ }^\circ\text{C}$ and stirred for 30 min, then cooled to $-78\text{ }^\circ\text{C}$ and a solution of 0.41 g (1.51 mmol) of aldehyde **28** in 15 mL of anhydrous THF was added to the resulting bright orange solution. The resulting mixture was warmed up to rt and stirred for 1 h 30 min (TLC monitoring), and 10 mL of a saturated solution of ammonium chloride was added. The mixture was filtered, the organic phase was separated, and the aqueous phase was extracted with ethyl acetate ($3 \times 50\text{ mL}$). The extracts were combined with the organic phase, dried over MgSO₄, and evaporated under reduced pressure. The crude residue without purification was treated with excess of ether solution of diazomethane in 3 h at $0\text{ }^\circ\text{C}$, 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 *title compounds*.

Compound 29. Yield 42 mg (7.7%), transparent viscous oil; [Found: C, 64.91; H, 9.54. C₂₀H₃₆O₄Si requires C, 65.17; H, 9.85%]; R_f (petroleum ether/ethyl acetate = 5:1) 0.45; $[\alpha]_D^{20} +46.3$ (c 0.6, CH₂Cl₂); IR (liquid film) ν_{max} , cm⁻¹: 3477, 2953, 2856, 1741, 1463, 1255, 1081, 837, 776; δ_H (500 MHz, (CD₃)₂CO): 6.03 (dd, *J* 5.7, 2.6 Hz, 1H, C²H), 5.87-5.83 (m, 1H, C³H), 5.52-5.45 (m, 1H, C⁶H), 5.39-5.33 (m, 1H, C⁵H), 4.60 (dd, *J* 6.3, 2.3 Hz, 1H, C⁴H), 3.98 (dd, *J* 10.3, 6.9 Hz, 1H, CH₂O), 3.87 (dd, *J* 10.2, 8.3 Hz, 1H, CH₂O), 3.60 (s, 3H, CH₃O), 2.84 (s, 1H, OH), 2.61-2.55 (m, 1H, C¹H), 2.42-2.36 (m, 1H, C⁷H), 2.29 (t, *J* 7.5 Hz, 2H, C²H), 2.29-2.22 (m, 1H, C⁵H), 2.09-2.01 (m, 3H, C⁴H₂ and C⁷H), 1.63 (quint, *J* 7.4 Hz, 2H,

C³'H), 0.91 (s, 9H, (CH₃)₃C), 0.09 (s, 6H, (CH₃)₂Si); δ_C (125.77 MHz, (CD₃)₂CO): 173.16 (C=O), 138.96 (C²), 132.88 (C³), 129.45 (C^{6'}), 129.07 (C^{5'}), 75.0 (C⁴), 60.15 (CH₂O), 50.62 (CH₃O), 47.80 (C⁵), 45.62 (C¹), 32.91 (C^{2'}), 29.89 (C^{7'}), 26.43 (C^{4'}), 25.41 ((CH₃)₃C), 24.74 (C^{3'}), 17.87 ((CH₃)₃C), -6.04 ((CH₃)₂Si); m/z (APCI): 351.2 (100%, [M-OH]⁺).

Compound 30. Yield 0.38 g (69%), transparent viscous oil; [Found: C, 64.97; H, 9.63. C₂₀H₃₆O₄Si requires C, 65.17; H, 9.85%]; R_f (petroleum ether/ethyl acetate = 5:1) 0.4; $[\alpha]_D^{20} +12.2$ (c 1.07, CH₂Cl₂); IR (liquid film) ν_{max} , cm⁻¹: 3467, 2953, 2856, 1739, 1472, 1250, 1065, 836, 775; δ_H (500 MHz, (CD₃)₂CO): 6.07 (dd, *J* 8.2, 5.5 Hz, 1H, C²H), 5.89-5.84 (m, 1H, C³H), 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, C⁴H), 3.88 (dd, *J* 10.1, 7.4 Hz, 1H, CH₂O), 3.80 (dd, *J* 10.1, 7.9 Hz, 1H, CH₂O), 3.61 (s, 3H, CH₃O), 2.86 (br s, 1H, OH), 2.60-2.55 (m, 1H, C¹H), 2.36-2.30 (m, 1H, C⁷H), 2.28 (t, *J* 7.6 Hz, 2H, C²H), 2.21-2.15 (m, 1H, C⁵H), 2.09-2.02 (m, 3H, C^{4'}H₂ and C⁷H), 1.63 (quint, *J* 7.6 Hz, 2H, C³H), 0.89 (s, 9H, (CH₃)₃C), 0.09 (s, 6H, (CH₃)₂Si); δ_C (125.77 MHz, (CD₃)₂CO): 173.93 (C=O), 140.56 (C²), 133.45 (C³), 129.86 (C^{6'}), 129.83 (C^{5'}), 76.49 (C⁴), 60.31 (CH₂O), 51.50 (CH₃O), 49.29 (C⁵), 46.15 (C¹), 33.88 (C^{2'}), 30.79 (C^{7'}), 27.36 (C^{4'}), 26.23 ((CH₃)₃C), 25.64 (C^{3'}), 18.32 ((CH₃)₃C), -5.77 ((CH₃)₂Si); m/z (APCI): 367 (100%, [M-H]⁺).

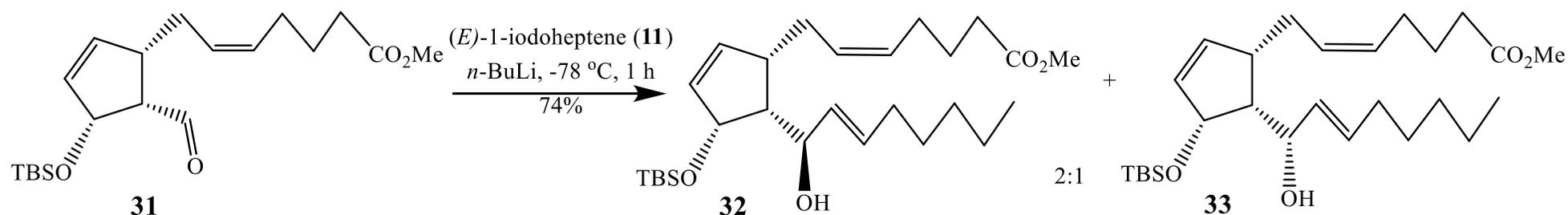
Compound 31



To a solution of 0.29 mL (3.4 mmol) of oxalyl chloride in DCM (15 mL) cooled at -70°C under argon atmosphere was added neat 0.53 mL (7.6 mmol) DMSO dropwise and stirred for 5 min. To the above, a solution of 0.74 g (2.0 mmol) **8** in DCM (20 mL) was added dropwise. The reaction mixture was stirred for 15 minutes at this temperature and 1.6 mL (11.5 mmol) Et₃N was added dropwise at -70 °C. The reaction mixture was allowed to warm to rt, water (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with CH₂Cl₂ (30 mLx3). The combined organic layers were dried over anhydrous Na₂SO₄, filtered und evaporated under reduced pressure. Purification of products by column chromatography

(petroleum ether/ethyl acetate, 10:1) afforded *title compound* (0.6 g, 83%) as a yellowish transparent oil; [Found: C, 65.36; H, 9.22. C₂₀H₃₄O₄Si requires C, 65.53; H, 9.35%]; R_f (petroleum ether/ethyl acetate = 10:1) 0.5; [α]_D²⁰: +21.6 (c 0.65, CH₂Cl₂); IR (liquid film) ν_{max}, cm⁻¹: 2953, 2930, 2857, 1738, 1472, 1251, 1059, 838, 777; δ_H (500 MHz, (CD₃)₂CO): 9.76 (d, *J* 4.6 Hz, 1H, CHO), 6.0 (d, *J* 5.5 Hz, 1H, C²H), 5.91 (td, *J* 5.5, 1.8 Hz, 1H, C³H), 5.45 (dd, *J* 11.0, 6.4 Hz, 1H, C⁶H), 5.40 (dd, *J* 11.0, 6.4 Hz, 1H, C⁵H), 5.16 (dd, *J* 6.7, 1.2 Hz, 1H, C⁴H), 3.60 (s, 3H, CH₃), 2.95 (dd, *J* 6.7, 4.9 Hz, 1H, C¹H), 2.91 (td, *J* 7.0, 1.5 Hz, 1H, C⁵H), 2.31-2.26 (m, 3H, C⁷H and C²H₂), 2.08-2.01 (m, 3H, C⁴H₂ and C⁷H), 1.63 (quint, *J* 7.5 Hz, 2H, C³H₂), 0.86 (s, 9H, (CH₃)₃Si), 0.1 (s, 6H, (CH₃)₂Si); δ_C (125.77 MHz, (CD₃)₂CO): 203.11 (CHO), 173.07 (CO₂Me), 136.53 (C²), 133.32 (C³), 130.07 (C⁶), 128.15 (C⁵), 78.38 (C⁴), 58.14 (C⁵), 50.61 (CH₃O), 46.29 (C¹), 32.85 (C²), 28.61 (C⁷), 26.43 (C⁴), 25.22 ((CH₃)₃C), 24.59 (C³), 17.67 ((CH₃)₃C), -5.34 (CH₃Si), -5.87 (CH₃Si); m/z (APCI): 219.1 (100%, [M-O-OTBS]⁺).

Compounds 32 and 33

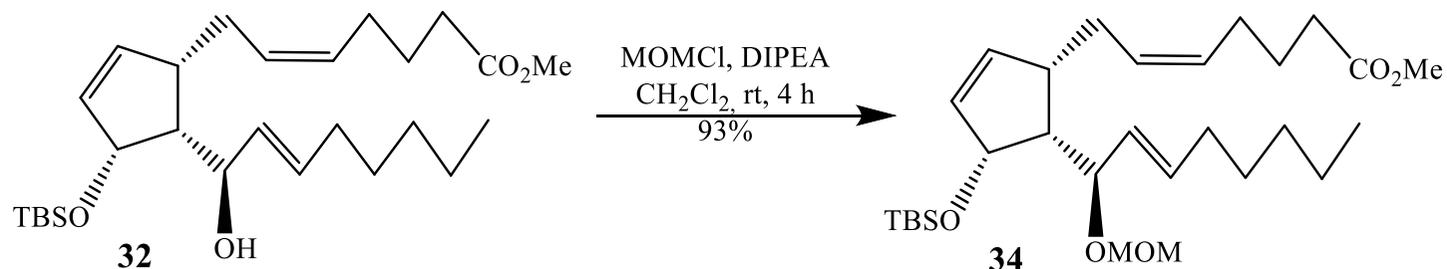


To a stirred solution of *trans*-1-iodoheptene (107 mg, 0.48 mmol) in anhydrous THF (10 mL) under argon atmosphere was added 1.93 M solution of *n*-butyllithium in hexane (0.28 mL) at -78 °C. The mixture was stirred for 30 min at the same temperature and then a solution of aldehyde **31** (117 mg, 0.32 mmol) in anhydrous THF (10 mL) was added dropwise. The resulting mixture was stirred for 30 min at -78 °C (monitored by TLC) and a saturated solution of ammonium chloride (10 mL) was added. The organic phase was separated and the aqueous phase was extracted with EA (3×20 mL). The combined organic extracts were dried (MgSO₄) and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography (10:1 PE/EA as eluent) to afford *title compounds*.

Compound 32. Yield 73 mg (50%), transparent light-yellow liquid; [Found: C, 69.57; H, 10.14. $C_{27}H_{48}O_4Si$ requires C, 69.78; H, 10.41%]; R_f (petroleum ether/ethyl acetate = 10:1) 0.55; $[\alpha]_D^{20} +20$ (c 1.2, CH_2Cl_2); IR (liquid film) ν_{max} , cm^{-1} : 3459, 2954, 2855, 1740, 1635, 1471, 1249, 1058, 835, 776; δ_H (500 MHz, $(CD_3)_2CO$): 6.11 (dd, J 5.7, 2.4 Hz, 1H, C^2H), 5.93 (dd, J 5.7, 2.3 Hz, 1H, C^3H), 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, $C^{6''}H$ and $C^{5''}H$), 4.70 (dd, J 5.3, 2.5 Hz, 1H, C^4H), 4.27 (dd, J 10.1, 7.7 Hz, 1H, $C^{1''}H$), 3.60 (s, 3H, CH_3O), 2.91 (br.s, 1H, OH), 2.42-2.32 (m, 2H, C^1H and C^7H), 2.27 (t, J 7.6 Hz, 2H, C^2H_2), 2.17-2.10 (m, 1H, C^7H), 2.09-2.02 (m, 4H, C^4H_2 and $C^{4''}H_2$), 1.94-1.88 (m, 1H, C^5H), 1.62 (quint, J 7.5 Hz, 2H, C^3H_2), 1.43-1.36 (m, 2H, $C^{5''}H_2$), 1.33-1.25 (m, 4H, $C^{6''}H_2$ and $C^{7''}H_2$), 0.92-0.85 (m, 12H, $C^{8''}H_3$ and $(CH_3)_3Si$), 0.14 (s, 3H, CH_3Si'), 0.09 (s, 3H, CH_3Si); δ_C (125.77 MHz, $(CD_3)_2CO$): 173.06 (C=O), 140.36 (C^2), 133.27 (C^3), 132.85 ($C^{3''}$), 131.82 ($C^{2''}$), 129.30 ($C^{5''}$), 128.87 ($C^{6''}$), 75.44 (C^4), 68.84 ($C^{1''}$), 52.76 (C^5), 50.64 (CH_3O), 44.95 (C^1), 32.99 ($C^{2'}$), 32.18 ($C^{7'}$), 31.17 ($C^{5''}$), 30.52 ($C^{4''}$), 28.88 ($C^{6''}$), 26.54 ($C^{4'}$), 25.42 ($(CH_3)_3C$), 24.75 ($C^{7''}$), 22.32 ($C^{3'}$), 17.71 ($(CH_3)_3C$), 13.47 ($C^{8''}$), -4.88 (CH_3Si'), -5.70 (CH_3Si); m/z (APCI): 447.4 (100%, $[M-OH]^+$).

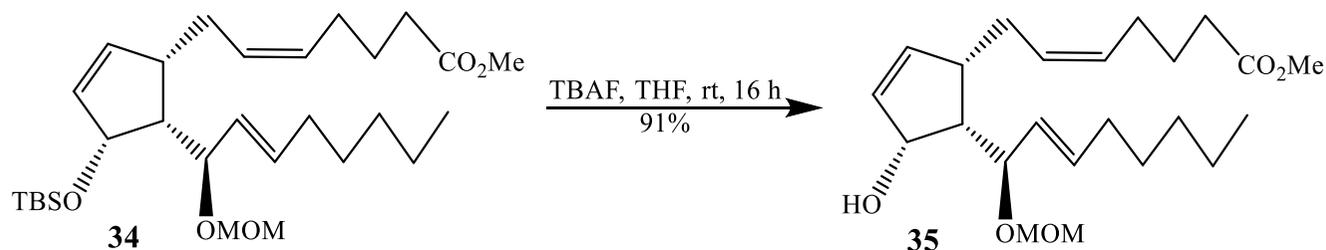
Compound 33. Yield 36 mg (24%), transparent light-yellow liquid; [Found: C, 69.53; H, 10.23. $C_{27}H_{48}O_4Si$ requires C, 69.78; H, 10.41%]; R_f (petroleum ether/ethyl acetate = 10:1) 0.45; $[\alpha]_D^{20} +16$ (c 0.76, CH_2Cl_2); IR (liquid film) ν_{max} , cm^{-1} : 3451, 2955, 2856, 1740, 1471, 1255, 1055, 836, 775; δ_H (500 MHz, $(CD_3)_2CO$): 6.14 (dd, J 5.7, 2.8 Hz, 1H, C^2H), 5.91 (dd, J 5.5, 1.5 Hz, 1H, C^3H), 5.78 (dt, J 15.6, 5.8 Hz, 1H, $C^{2''}H$), 5.72 (dd, J 15.6, 4.9 Hz, 1H, $C^{3''}H$), 5.54-5.45 (m, 1H, $C^{5''}H$), 5.42-5.33 (m, 1H, $C^{6''}H$), 4.50 (dd, J 5.4, 2.4 Hz, 1H, C^4H), 4.31 (dd, J 10.2, 4.9 Hz, 1H, $C^{1''}H$), 3.60 (s, 3H, CH_3O), 2.80 (br.s, 1H, OH), 2.78-2.72 (m, 1H, C^7H), 2.64-2.57 (m, 1H, C^1H), 2.28 (t, J 7.6 Hz, 2H, C^2H_2), 2.21-2.13 (m, 1H, C^7H), 2.09-2.02 (m, 4H, C^4H_2 and $C^{4''}H_2$), 1.95-1.88 (m, 1H, C^5H), 1.63 (quint, J 7.5 Hz, 2H, C^3H_2), 1.43-1.37 (m, 2H, $C^{5''}H_2$), 1.34-1.25 (m, 4H, $C^{6''}H_2$ and $C^{7''}H_2$), 0.90-0.85 (m, 12H, $C^{8''}H_3$ and $(CH_3)_3Si$), 0.09 (s, 3H, CH_3Si'), 0.07 (s, 3H, CH_3Si); δ_C (125.77 MHz, $(CD_3)_2CO$): 173.08 (C=O), 140.71 (C^2), 133.58 (C^3), 132.52 ($C^{3''}$), 129.80 ($C^{2''}$), 129.76 ($C^{5''}$), 128.78 ($C^{6''}$), 75.73 (C^4), 68.19 ($C^{1''}$), 53.72 (C^5), 50.60 (CH_3O), 45.71 (C^1), 33.04 ($C^{2'}$), 32.11 ($C^{7'}$), 31.22 ($C^{5''}$), 30.31 ($C^{4''}$), 28.48 ($C^{6''}$), 26.55 ($C^{4'}$), 25.45 ($(CH_3)_3C$), 24.84 ($C^{7''}$), 22.31 ($C^{3'}$), 17.59 ($(CH_3)_3C$), 13.43 ($C^{8''}$), -4.00 (CH_3Si'), -5.67 (CH_3Si); m/z (APCI): 447.4 (100%, $[M-OH]^+$).

Compound 34



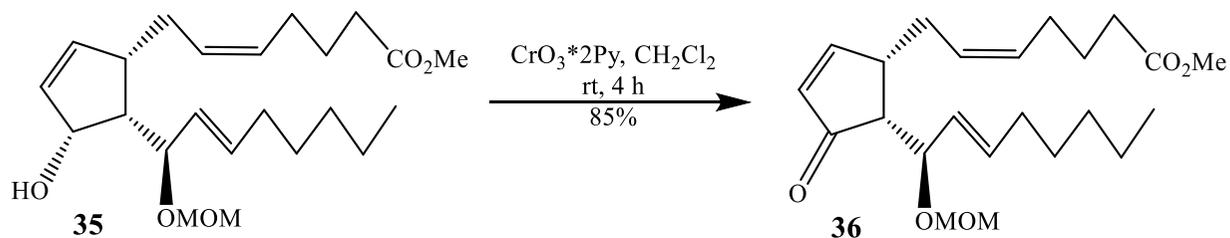
A solution of 0.06 mL (0.81 mmol) of chloromethyl methyl ether in methylene chloride (10 mL) was added under stirring to a mixture of 0.12 g (0.27 mmol) of monoprotected diol **32**, 0.28 mL (1.6 mmol) of *N,N*-diisopropylethylamine and 10 mL of methylene chloride at 0°C. The mixture was stirred for 4 h at rt (monitored by TLC) and evaporated under reduced pressure. Purification of the product by column chromatography (petroleum ether/ethyl acetate, 60:1) afforded *title compound* (0.13 g, 93%) as a transparent viscous oil; [Found: C, 68.32; H, 10.15. C₂₉H₅₂O₅Si requires C, 68.46; H, 10.30%]; R_f (petroleum ether/ethyl acetate = 20:1) 0.5; [α]_D²⁰: +34 (c 0.7, CH₂Cl₂); IR (liquid film) ν_{max}, cm⁻¹: 3057, 2955, 2928, 2856, 1743 (C=O), 1465, 1437, 1360, 1256, 1158, 1057, 1040, 967, 939, 897, 835, 799, 777, 751, 664; δ_H (500 MHz, (CD₃)₂CO): 6.15 (dd, *J* 5.8, 1.8 Hz, 1H, C²H), 5.98 (dd, *J* 5.8, 1.9 Hz, 1H, C³H), 5.81 (dt, *J* 15.5, 6.8 Hz, 1H, C^{2''}H), 5.46 (dd, *J* 15.5, 9.0 Hz, 1H, C^{3''}H), 5.42-5.29 (m, 2H, C^{6'}H and C^{5'}H), 4.65 (s, 2H, OCH₂O), 4.68-4.63 (m, 1H, C⁴H), 4.13 (dd, *J* 10.5, 9.2 Hz, 1H, C^{1''}H), 3.61 (s, 3H, CO₂CH₃), 3.29 (s, 1H, CH₃O), 2.83 (s, 1H, C¹H), 2.43-2.37 (m, 1H, C^{7'}H), 2.36-2.30 (m, 1H, C^{7''}H), 2.27 (t, *J* 7.7 Hz, 2H, C^{2'}H₂), 2.15-2.08 (m, 2H, C^{4''}H₂), 2.08-1.98 (m, 3H, C⁵H, C^{4'}H₂), 1.61 (quint, *J* 7.5 Hz, 2H, C^{3'}H₂), 1.48-1.40 (m, 2H, C^{5''}H₂), 1.35-1.27 (m, 4H, C^{6''}H₂ and C^{7''}H₂), 0.93-0.87 (m, 12H, C^{8''}H₃ and (CH₃)₃Si), 0.10 (d, *J* 2.6 Hz, 6H, (CH₃)₂Si); δ_C (125.77 MHz, (CD₃)₂CO): 173.02 (C=O), 140.37 (C²), 135.13 (C³), 133.22 (C^{3''}), 129.99 (C^{2''}), 129.17 (C^{5'}), 129.03 (C^{6'}), 94.86 (OCH₂O), 75.79 (C⁴), 74.82 (C^{1''}), 54.77 (C⁵), 50.62 (CH₃O), 52.02 (CO₂CH₃), 44.77 (C¹), 32.97 (C^{7'}), 32.19 (C^{2'}), 31.17 (C^{5''}), 30.23 (C^{4''}), 29.09 (C^{6''}), 26.59 (C^{4'}), 25.58 ((CH₃)₃C), 24.74 (C^{3'}), 22.30 (C^{7''}), 17.70 ((CH₃)₃C), 13.45 (C^{8''}), -4.20 (CH₃Si), -5.51 (CH₃Si); m/z (APCI): 315.2 (100%, [M-MOM-TBSOH]⁺).

Compound 35



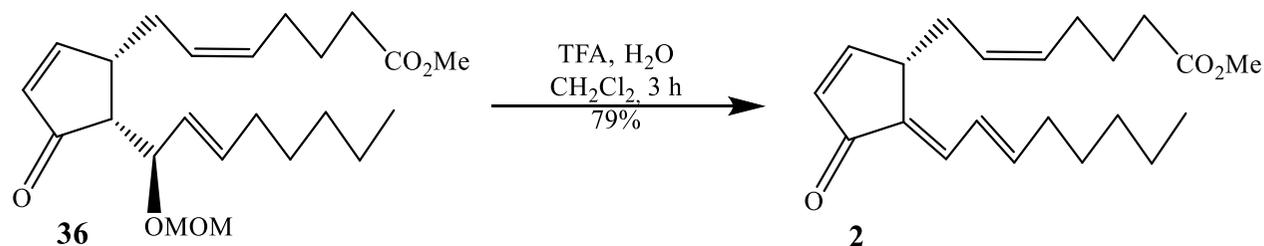
To a stirred solution of 0.13 g (0.26 mmol) of compound **34** in THF (25 mL) at rt was added 0.26 mL (0.26 mmol) 1M solution TBAF in THF. The reaction was monitored by TLC (petroleum ether/ethyl acetate, 1:1) and after stirring for 3 h at rt the solution was evaporated under reduced pressure. Purification of products by column chromatography (petroleum ether/ethyl acetate, 3:1) afforded *title compound* (90 mg, 91%) as a colorless oily liquid; [Found: C, 69.88; H, 9.53. C₂₃H₃₈O₅ requires C, 70.02; H, 9.71%]; R_f (petroleum ether/ethyl acetate = 3:1) 0.5; [α]_D²⁰: +9 (c 0.9, CH₂Cl₂); IR (liquid film) ν_{max} , cm⁻¹: 3483, 3055, 2955, 2858, 1731, 1669, 1459, 1376, 1315, 1259, 1213, 1157, 1094, 1047, 977, 934, 856, 807, 749, 700; δ_H (500 MHz, (CD₃)₂CO): 6.13 (dd, *J* 5.7, 2.7 Hz, 1H, C²H), 5.93 (dd, *J* 5.8, 1.9 Hz, 1H, C³H), 5.84 (dt, *J* 15.5, 7.0 Hz, 1H, C^{2''}H), 5.47-5.32 (m, 3H, C^{6'}H, C⁵H, C^{3''}H), 4.71 (d, *J* 6.3 Hz, 1H, OCH₂O), 4.64-4.59 (m, 1H, C⁴H), 4.55 (d, *J* 6.3 Hz, 1H, OCH₂O), 4.24 (dd, *J* 10.9, 8.9 Hz, 1H, C^{1''}H), 3.61 (s, 3H, CO₂CH₃), 3.36 (s, 3H, CH₃O), 3.22 (d, *J* 4.2 Hz, 1H, C¹H), 2.82 (br.s, 1H, OH), 2.39-2.46 (m, 1H, C⁷H), 2.34 (t, *J* 7.1 Hz, 3H, C^{2'}H₂ and C⁷H), 2.28 (t, *J* 7.5 Hz, 1H, C^{4''}H), 2.12 (q, *J* 7.1 Hz, 1H, C^{4''}H) 2.08-1.98 (m, 3H, C⁵H and C^{4'}H₂), 1.62 (quint, *J* 7.4 Hz, 2H, C^{3'}H₂), 1.46-1.35 (m, 3H, C^{7''}H and C^{5''}H₂), 1.33-1.27 (m, 3H, C^{6''}H₂ and C^{7''}H), 0.87 (t, *J* 7.2 Hz, 3H, C^{8''}H₃); δ_C (125.77 MHz, (CD₃)₂CO): 175.82 (C=O), 140.06 (C²), 135.73 (C³), 133.71 (C^{3''}), 129.39 (C^{2''}), 129.18 (C⁵), 129.06 (C^{6'}), 93.56 (OCH₂O), 74.97 (C⁴), 74.14 (C^{1''}), 54.82 (C⁵), 50.92 (CH₃O), 50.61 (CO₂CH₃), 44.80 (C¹), 32.88 (C^{7'}), 32.15 (C^{2'}), 31.17 (C^{5''}), 30.62 (C^{4''}), 28.46 (C^{6''}), 26.45 (C^{4'}), 24.69 (C^{3'}), 22.26 (C^{7''}), 13.44 (C^{8''}); m/z (APCI): 393.1 (100%, [M-H]⁺).

Compound 36



To a stirred solution of compound **35** (90 mg, 0.23 mmol) in DCM (10 mL) was added CrO₃·2Py (110 mg, 0.46 mmol) at rt. The reaction was stirred for 4 h at the same temperature (monitored by TLC) and evaporated under reduced pressure. The residue was purified by column chromatography (5:1 petroleum ether/ethyl acetate as eluent) to afford *title compound* (76 mg, 85% yield) as a transparent colorless liquid; [Found: C, 70.12; H, 9.09. C₂₃H₃₆O₅ requires C, 70.38; H, 9.24%]; R_f (petroleum ether/ethyl acetate = 5:1) 0.5; [α]_D²⁰: +60 (c 0.9, CH₂Cl₂); IR (liquid film) ν_{max} , cm⁻¹: 2928, 2855, 1738, 1709, 1623, 1438, 1366, 1349, 1205, 1149, 1035, 978, 920, 811; δ_H (500 MHz, (CD₃)₂CO): 7.71 (dd, *J* 5.8, 2.4 Hz, 1H, C²H), 6.08 (dd, *J* 5.7, 2.2 Hz, 1H, C³H), 5.89 (dd, *J* 15.5, 8.6 Hz, 1H, C^{2''}H), 5.70-5.49 (m, 3H, C^{6'}H, C^{5'}H and C^{3''}H), 4.64 (d, *J* 8.6 Hz, 1H, OCH₂O), 4.47 (d, *J* 8.6 Hz, 1H, OCH₂O), 4.42 (dd, *J* 8.7, 2.5 Hz, 1H, C^{1''}H), 3.61 (s, 3H, CO₂CH₃), 3.29 (s, 3H, CH₃O), 3.13-3.07 (m, 1H, C¹H), 2.59-2.52 (m, 2H, C^{7'}H and C⁵H), 2.31 (t, *J* 7.7 Hz, 3H, C^{2'}H₂ and C^{7'}H), 2.12 (q, *J* 7.4 Hz, 1H, C^{4''}H), 2.08-2.03 (m, 3H, C^{4''}H and C^{4'}H₂), 1.67 (quint, *J* 7.5 Hz, 2H, C^{3'}H₂), 1.39 (quint, *J* 7.3 Hz, 2H, C^{5''}H₂), 1.36-1.25 (m, 4H, C^{6''}H₂ and C^{7''}H₂), 0.88 (t, *J* 7.0 Hz, 3H, C^{8''}H₃); δ_C (125.77 MHz, (CD₃)₂CO): 207.51 (C⁴), 173.05 (C=O), 166.44 (C²), 134.28 (C^{3''}), 133.25 (C³), 130.56 (C^{5'}), 128.62 (C^{2''}), 128.55 (C^{6'}), 93.62 (OCH₂O), 76.46 (C^{1''}), 55.26 (C⁵), 52.50 (CH₃O), 50.62 (CO₂CH₃), 44.78 (C¹), 32.88 (C^{7'}), 31.89 (C^{2'}), 31.13 (C^{5''}), 28.66 (C^{4''}), 27.42 (C^{6''}), 26.57 (C^{4'}), 24.65 (C^{3'}), 22.23 (C^{7''}), 13.41 (C^{8''}); m/z (APCI): 331.2 (100%, [M-MOMO]⁺).

Compound 2



To a stirred solution of compound **36** (76 mg, 0.19 mmol) in DCM (10 mL) was added 9:1-mixture of TFA-H₂O (0.1 mL) at rt. The reaction was stirred for 3 h at the same temperature (monitored by TLC), then cooled to 0 °C and neutralized by addition of saturated solution of NaHCO₃. The resulting mixture was extracted with DCM (3×30 mL), the combined organic layers were dried (MgSO₄) and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography (5:1 petroleum ether/ethyl acetate as eluent) to afford *title compound* (50 mg, 79% yield) as a transparent colorless liquid; [Found: C, 76.19; H, 8.99. C₂₁H₃₀O₃ requires C, 76.33; H, 9.15%]; R_f (petroleum ether/ethyl acetate = 5:1) 0.3; [α]_D²⁰: +138.7 (c 0.75, CH₂Cl₂); IR (liquid film) ν_{max}, cm⁻¹: 2955, 2926, 2858, 1739, 1692, 1631, 1437, 1362, 1349, 1151, 1035, 978, 809; δ_H (500 MHz, (CD₃)₂CO): 7.61 (dd, *J* 5.9, 1.9 Hz, 1H, C²H), 6.82 (d, *J* 11.7 Hz, 1H, C^{1''}H), 6.50 (t, *J* 14.6 Hz, 1H, C³H), 6.31 (t, *J* 7.1 Hz, 1H, C^{2''}H), 6.29-6.25 (m, 1H, C^{3''}H), 5.48-5.39 (m, 1H, C⁵H) 5.38-5.32 (m, 1H, C⁶H) 3.70 (br.s, 1H, C¹H), 3.60 (s, 3H, CO₂CH₃), 2.65 (dt, *J* 14.5, 5.1 Hz, 1H, C⁷H), 2.39 (dt, *J* 14.5, 8.2 Hz, 1H, C^{7'}H), 2.28 (t, *J* 7.3 Hz, 2H, C^{2'}H₂), 2.25 (q, *J* 7.4 Hz, 2H, C^{4''}H₂), 2.09-1.98 (m, 2H, C^{4'}H₂), 1.61 (quint, *J* 7.3 Hz, 2H, C³H₂), 1.48 (quint, *J* 7.0 Hz, 2H, C^{5''}H₂), 1.39-1.25 (m, 4H, C^{6''}H₂ and C^{7''}H₂), 0.89 (t, *J* 6.6 Hz, 3H, C^{8''}H₃); δ_C (125.77 MHz, (CD₃)₂CO): 195.79 (C⁴), 173.03 (C=O), 160.79 (C²), 145.70 (C⁵), 135.61 (C^{3''}), 134.73 (C^{1''}), 131.25 (C³), 130.26 (C^{5'}), 126.07 (C^{6'}), 125.87 (C^{2''}), 50.59 (CH₃O), 43.21 (C¹), 33.00 (C^{7'}), 32.85 (C^{2'}), 31.24 (C^{5''}), 30.36 (C^{4''}), 28.39 (C^{6''}), 26.40 (C^{4'}), 24.66 (C^{3'}), 22.23 (C^{7''}), 13.37 (C^{8''}); m/z (APCI): 331.2 (100%, [MH]⁺).

3. NMR Spectra of New Compounds

Sp-1172 Gimazetdinov Pc-397(2) 36mg in Acetone, ¹H AV500 21.06.2018 LAN
SW (1H)=19.99ppm; *O1* (1H)=7.00ppm; *Obs.Freq.*:500.13MHz; *D1*=2.0s; *T*=295.5K; *Probe*:BB0; *Exp.Time*: 7 sec; *TimesDate*: 11:57:40 21 Jun 2018.

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

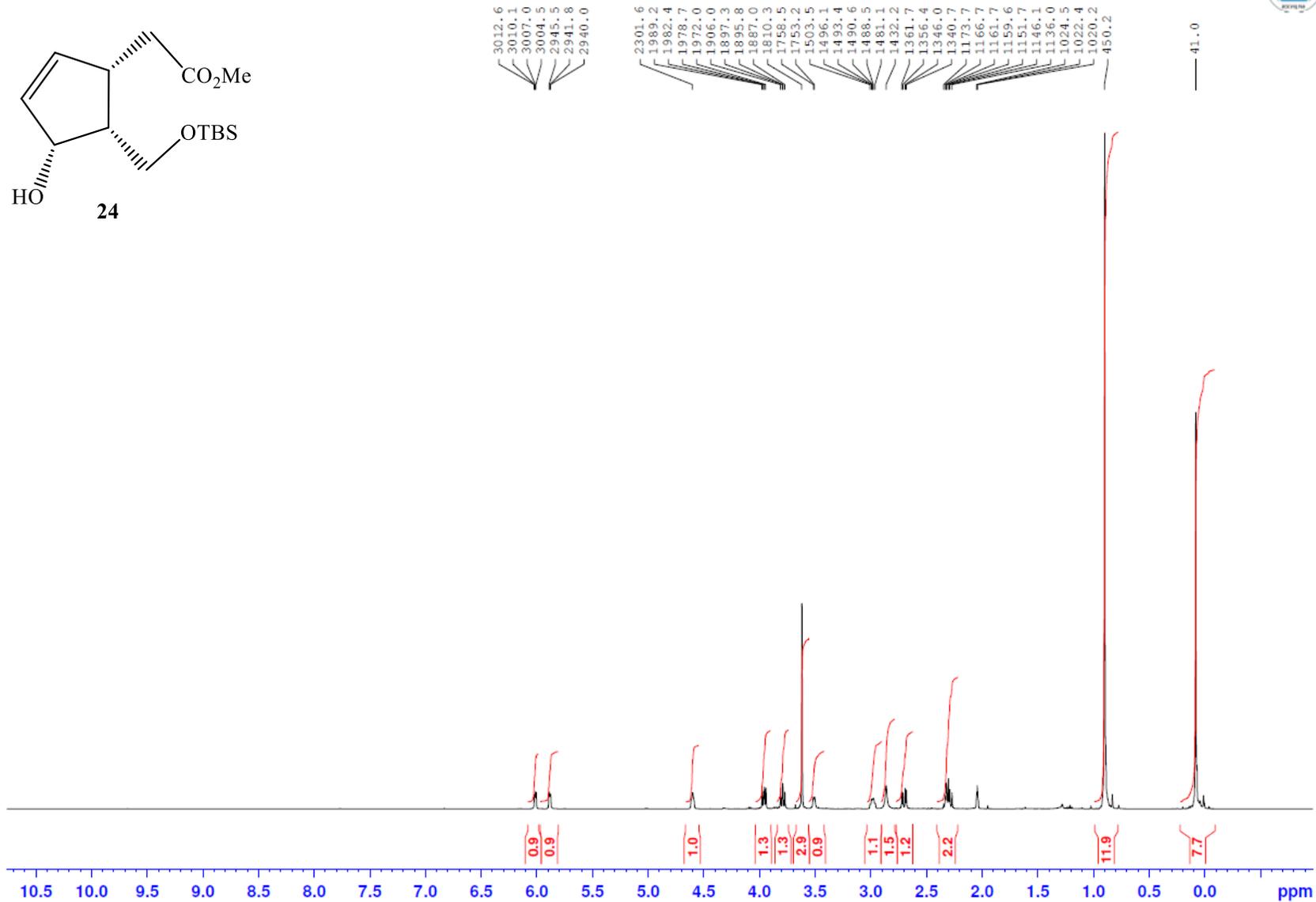


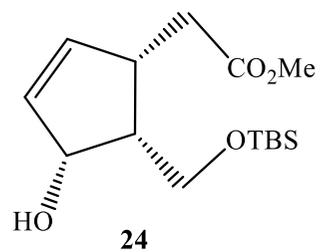
Figure. S1 ¹H NMR spectrum of **24** (*d*-acetone, 500 MHz)

Sp-1172 Gimazetdinov Pc-397(2) 36mg in Acetone, $^{13}\text{C}\{^1\text{H}\}$ dept135 AV500 21.06.2018 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=296.1K; Probe:BB0; Exp.Time: 2 min 36 sec; TimesDate: 12:07:23 21 Jun 2018.



137.89
133.76
74.91
59.95
50.65
47.26
41.68
36.03
25.37

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-1172 Gimazetdinov Pc-397(2) 36mg in Acetone, $^{13}\text{C}\{^1\text{H}\}$ com AV500 21.06.2018 LAN

SW(13C)=236.63ppm; O1(13C)=110.00ppm; Obs.Freq.:125.76MHz; D1=0.9s; T=296.1K; Probe:BB0; Exp.Time: 6 min 52 sec; TimesDate: 11:59:38 21 Jun 2018.

205.41
205.23
205.13
172.98
137.89
133.77
74.91
59.95
50.65
47.27
41.68
36.04
29.41
29.26
29.11
28.95
28.80
28.65
28.49
25.38
17.86
-6.08

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

Figure. S2 ^{13}C NMR spectrum of **24** (*d*-acetone, 125.77 MHz)

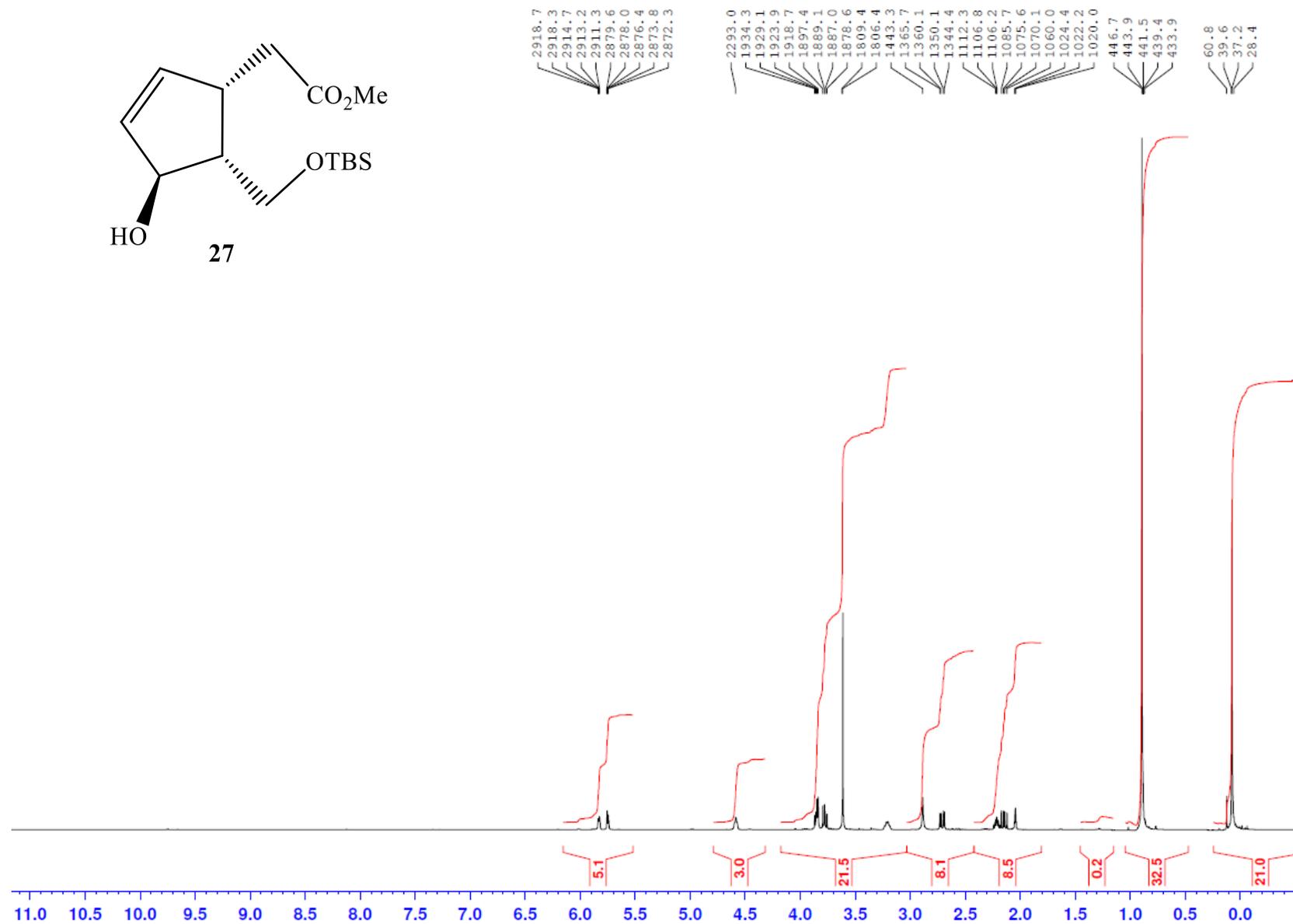
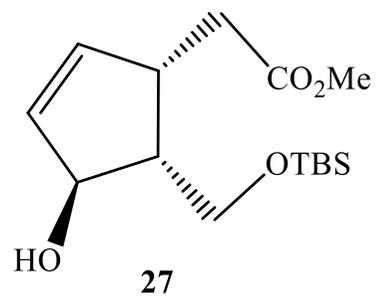
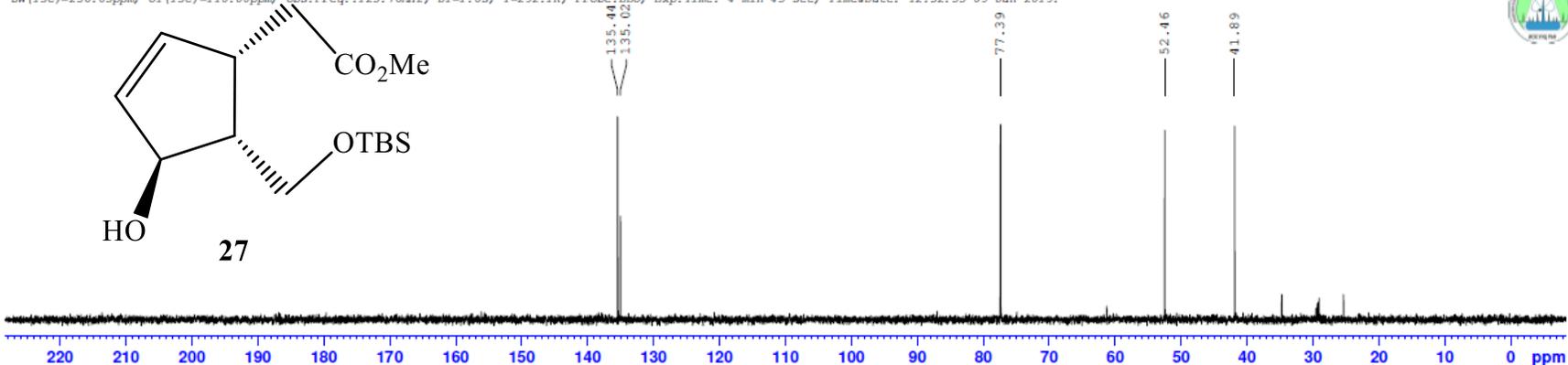
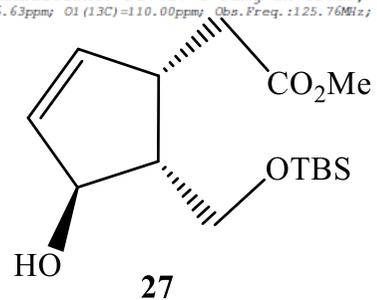


Figure. S3 ¹H NMR spectrum of **27** (*d*-acetone, 500 MHz)

Sp-283 Gimazetdinov Pc-437-1 25mg in CDC13, 13C(1H) dept90 AV500 09.01.2019 PAI

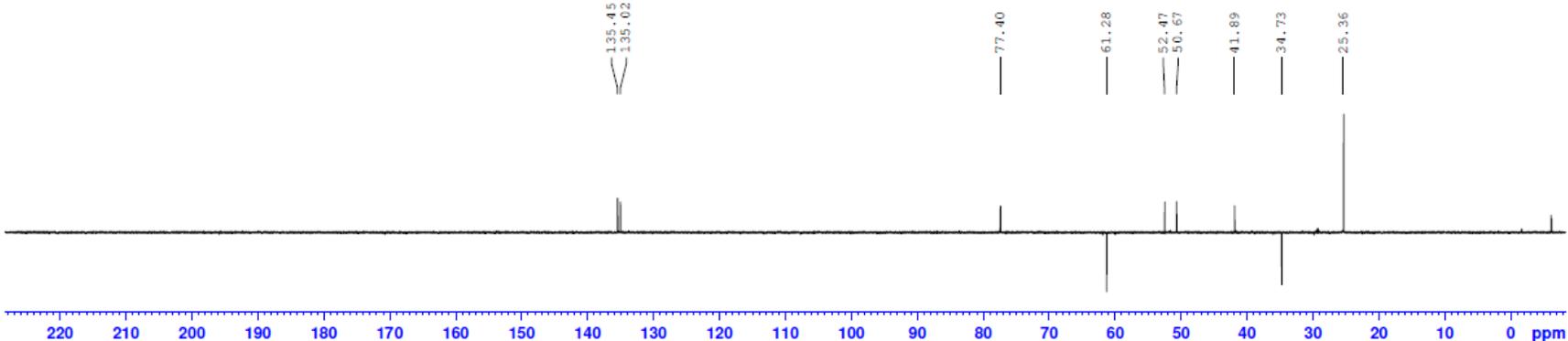
Ufa Institute of Chemistry of the Russian Academy of Sciences (UIC RAS), 2019

SW(13C)=236.63ppm; O1(13C)=110.00ppm; Obs.Freq.:125.76MHz; D1=1.0s; T=292.1K; Probe:BBO; Exp.Time: 4 min 45 sec; TimesDate: 12:32:55 09 Jan 2019.



Sp-283 Gimazetdinov Pc-437-1 25mg in Acetone, 13C(1H) dept135 AV500 09.01.2019 PAI

SW(13C)=236.63ppm; O1(13C)=110.00ppm; Obs.Freq.:125.76MHz; D1=1.0s; T=292.2K; Probe:BBO; Exp.Time: 4 min 45 sec; TimesDate: 12:28:07 09 Jan 2019.



Sp-283 Gimazetdinov Pc-437-1 25mg in Acetone, 13C(1H) com AV500 09.01.2019 PAI

SW(13C)=236.63ppm; O1(13C)=110.00ppm; Obs.Freq.:125.76MHz; D1=0.9s; T=292.3K; Probe:BBO; Exp.Time:17 min 46 sec; TimesDate: 12:10:06 09 Jan 2019.

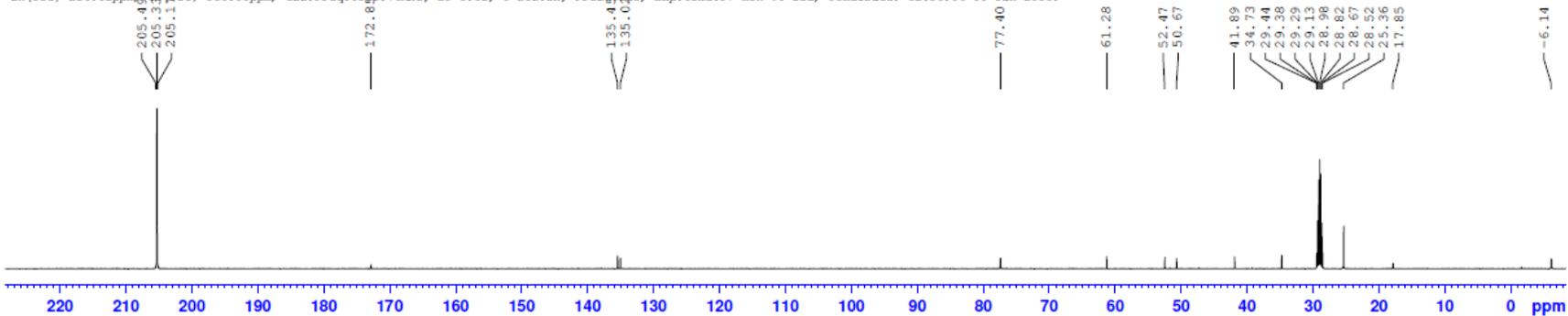


Figure. S4 ¹³C NMR spectrum of **27** (*d*-acetone, 125.77 MHz)

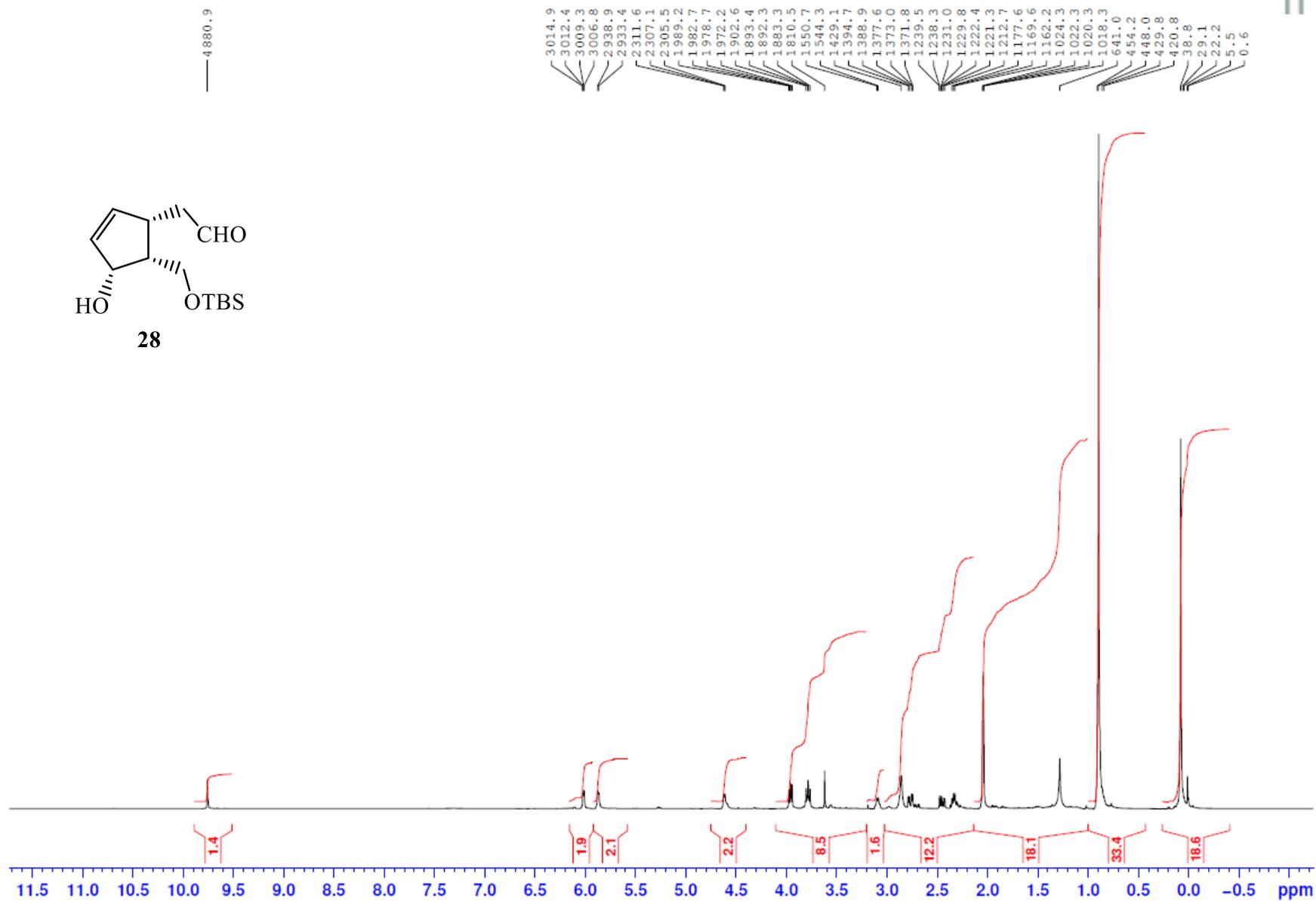
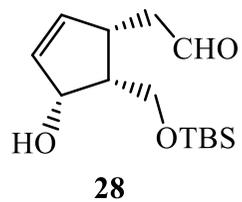


Figure. S5 ¹H NMR spectrum of **28** (*d*-acetone, 500 MHz)

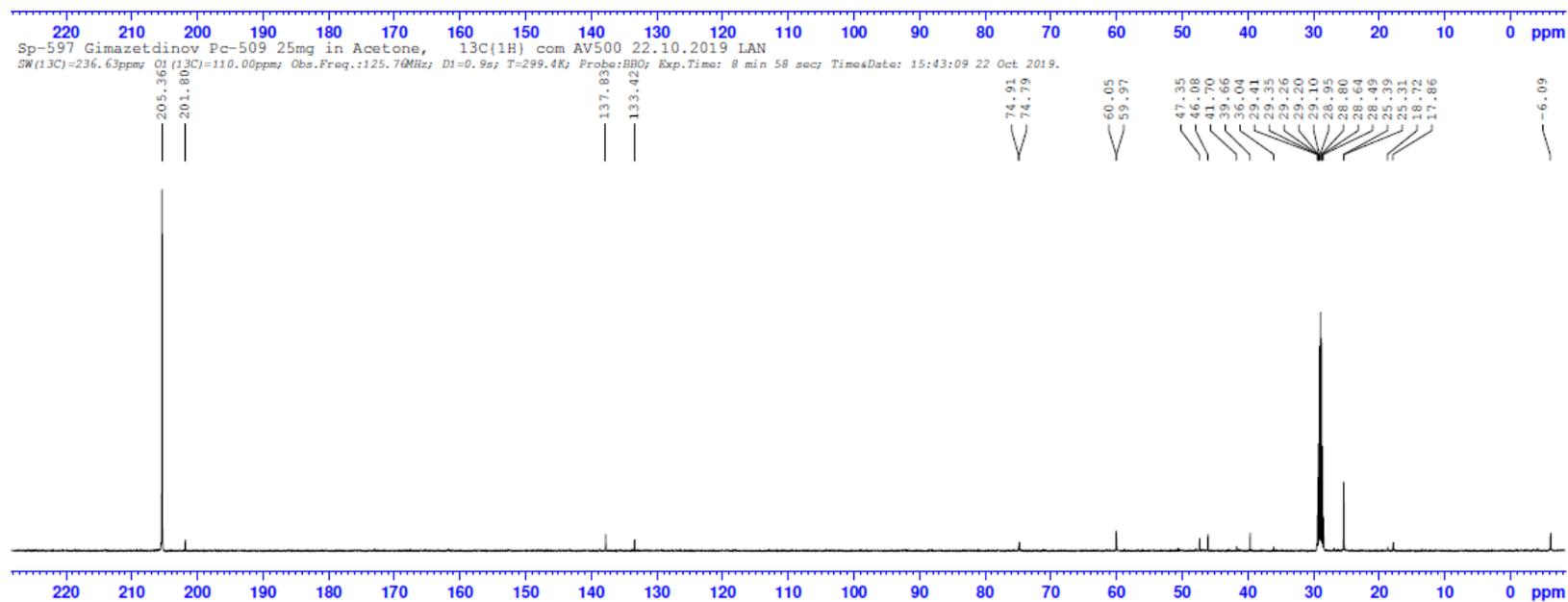
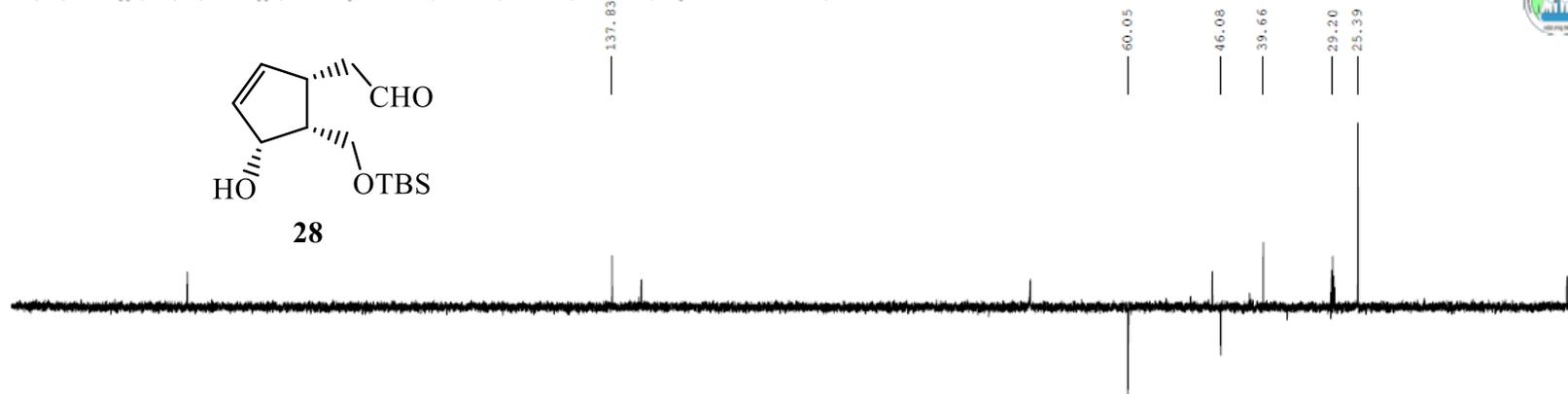
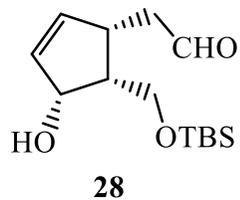


Figure. S6 ^{13}C NMR spectrum of **28** (*d*-acetone, 125.77 MHz)

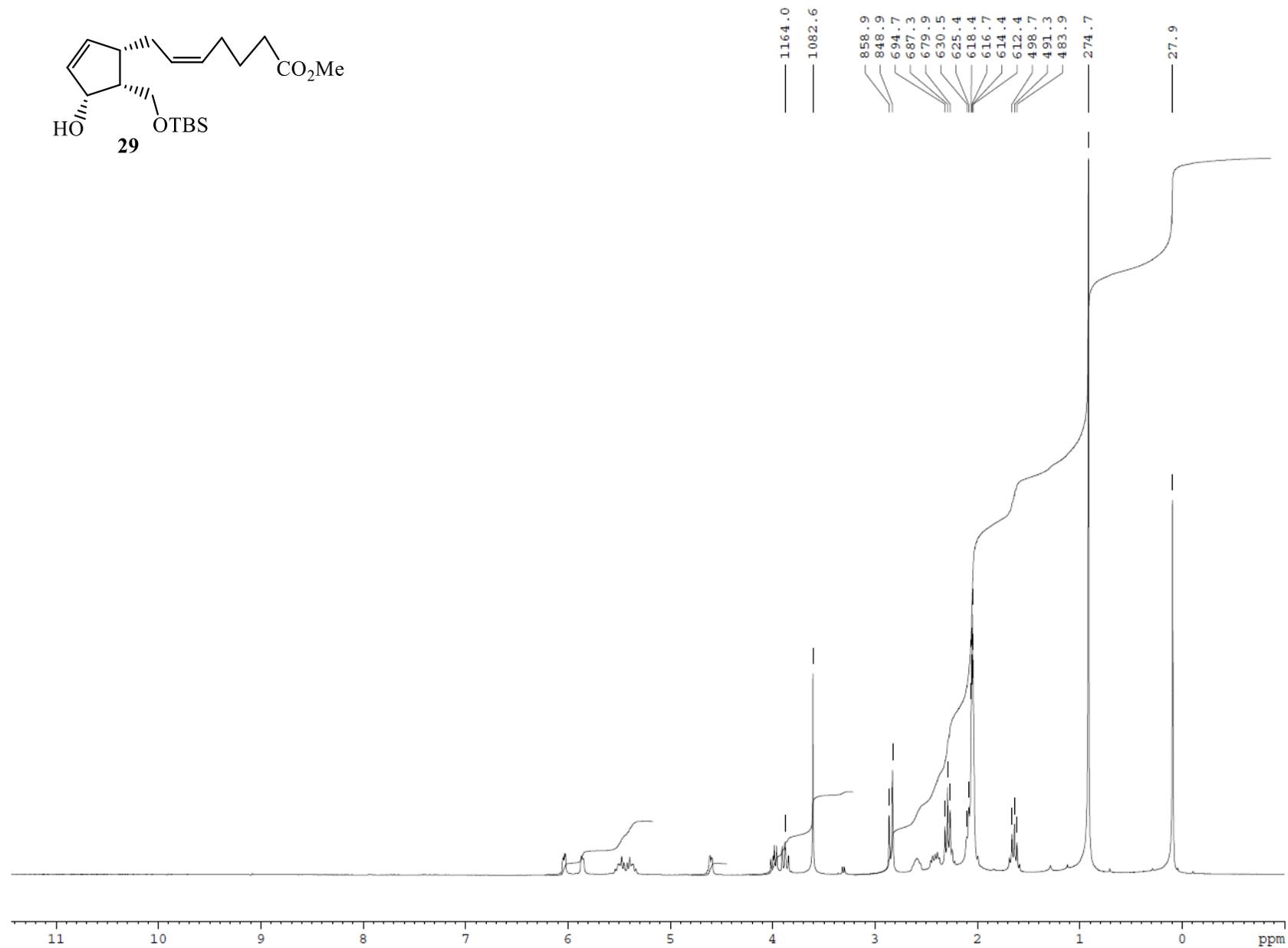
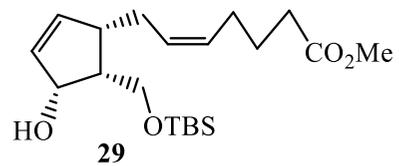


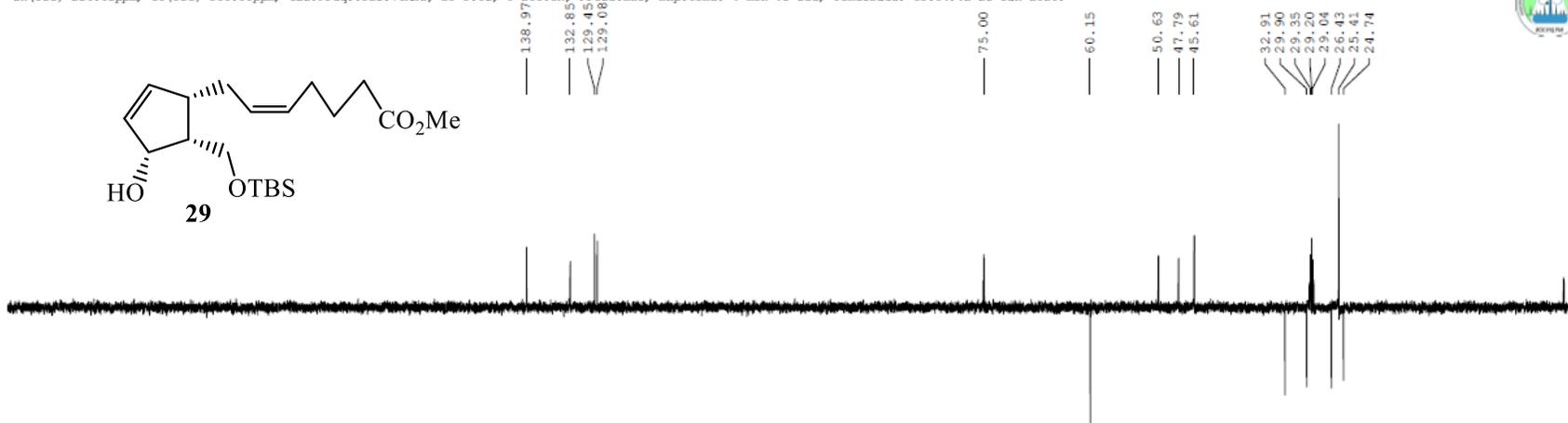
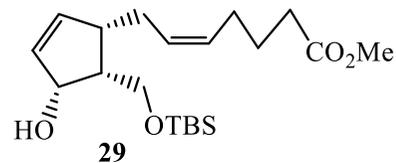
Figure. S7 ^1H NMR spectrum of **29** (*d*-acetone, 500 MHz)

Sp-714 Almuhametov Pca-148-3-dept 13mg in Acetone, ¹³C(1H) dept135 AV500 23.01.2020 BIP

Ufa Institute of Chemistry of the Russian Academy of Sciences (UIC RAS). 2020



SW(13C)=236.63ppm; O1(13C)=110.00ppm; Obs.Freq.:125.76MHz; D1=1.0s; T=298.8K; Probe:BBO; Exp.Time: 4 min 45 sec; Time&Date: 11:04:42 23 Jan 2020.



Sp-714 Almuhametov Pca-148-3-dept 13mg in Acetone, ¹³C(1H) com AV500 23.01.2020 BIP

SW(13C)=236.63ppm; O1(13C)=110.00ppm; Obs.Freq.:125.76MHz; D1=0.9s; T=298.8K; Probe:BBO; Exp.Time:17 min 46 sec; Time&Date: 10:31:26 23 Jan 2020.

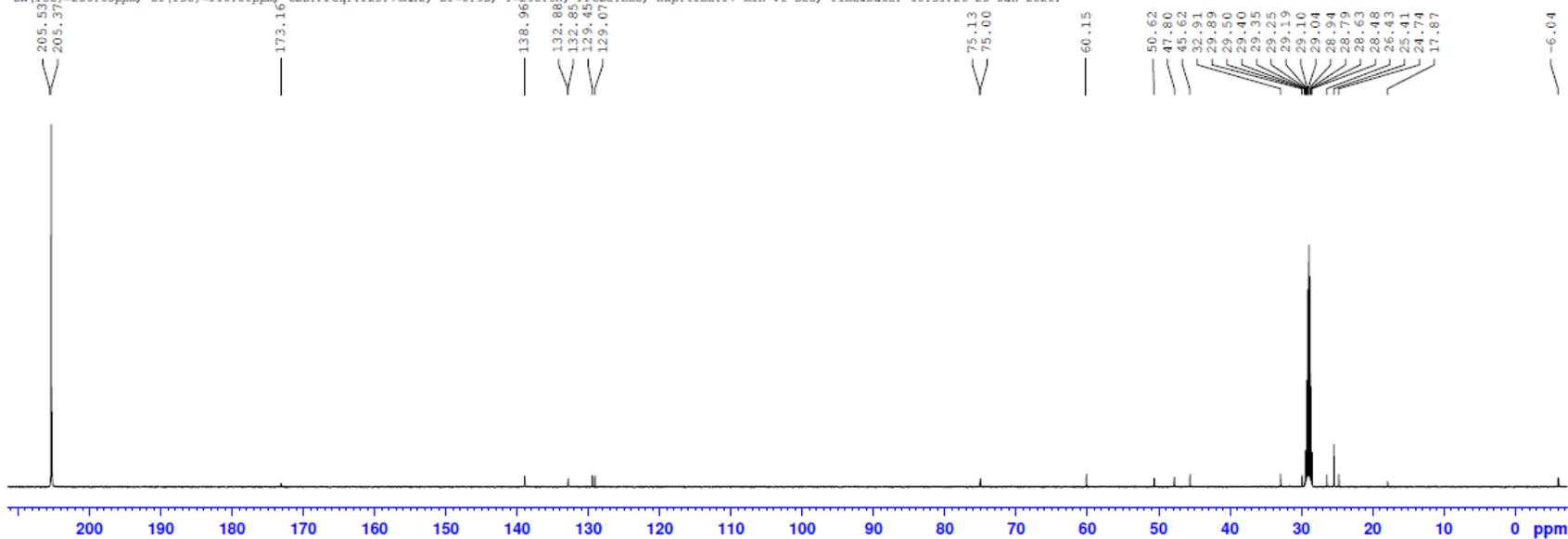


Figure. S8 ¹³C NMR spectrum of **29** (*d*-acetone, 125.77 MHz)

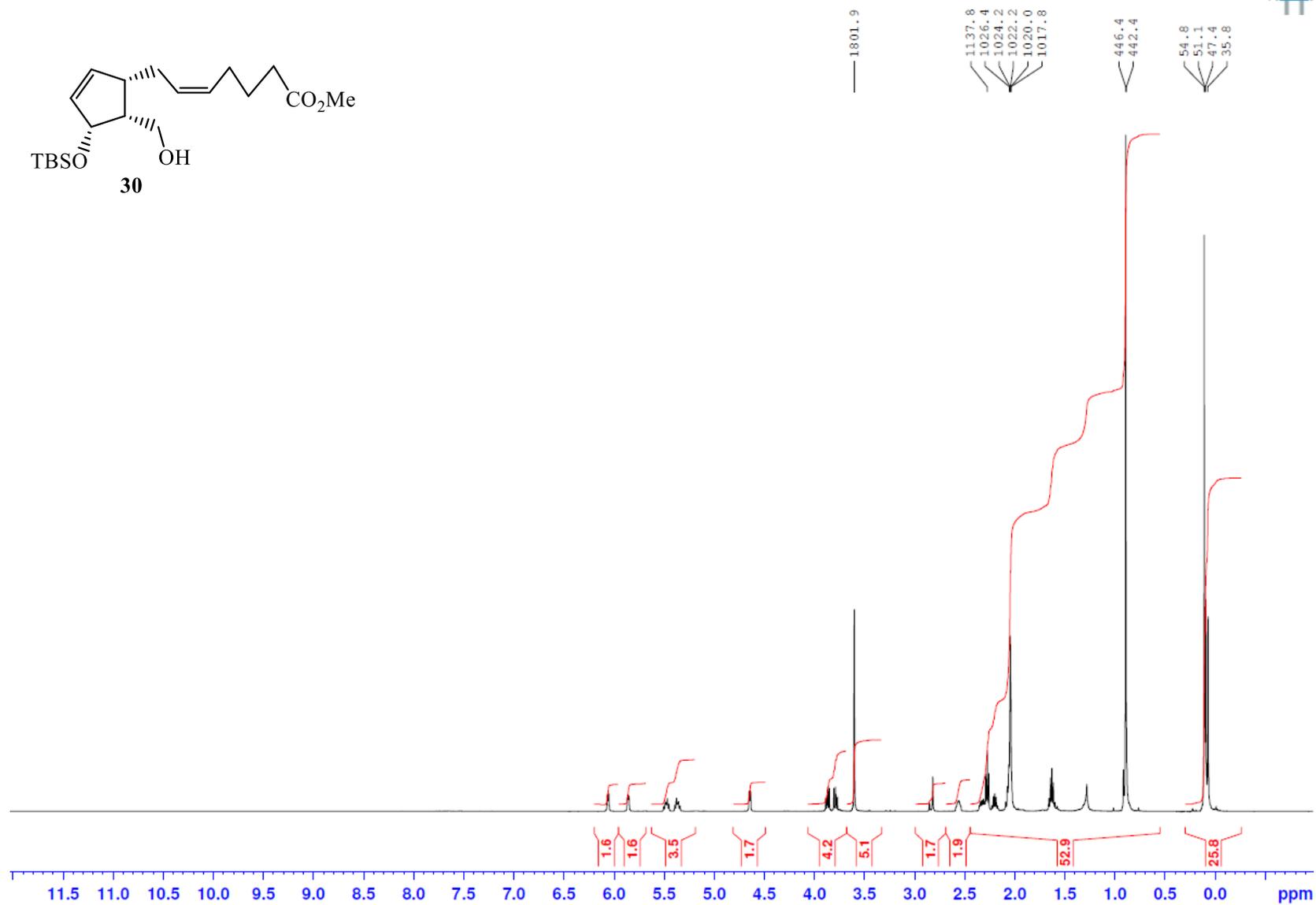


Figure. S9 ¹H NMR spectrum of **30** (*d*-acetone, 500 MHz)

Sp-680 Gimazetdinov Pc-476_1_0 25mg in Acetone, $^{13}\text{C}\{^1\text{H}\}$ dept135 AV500 26.04.2019 NTR

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

SW (^{13}C)=236.63ppm; O1 (^{13}C)=110.00ppm; Obs.Freq.:125.76MHz; D1=1.0s; T=299.5K; Probe:BBQ; Exp.Time: 2 min 27 sec; Time&Date: 11:00:33 26 Apr 2019.

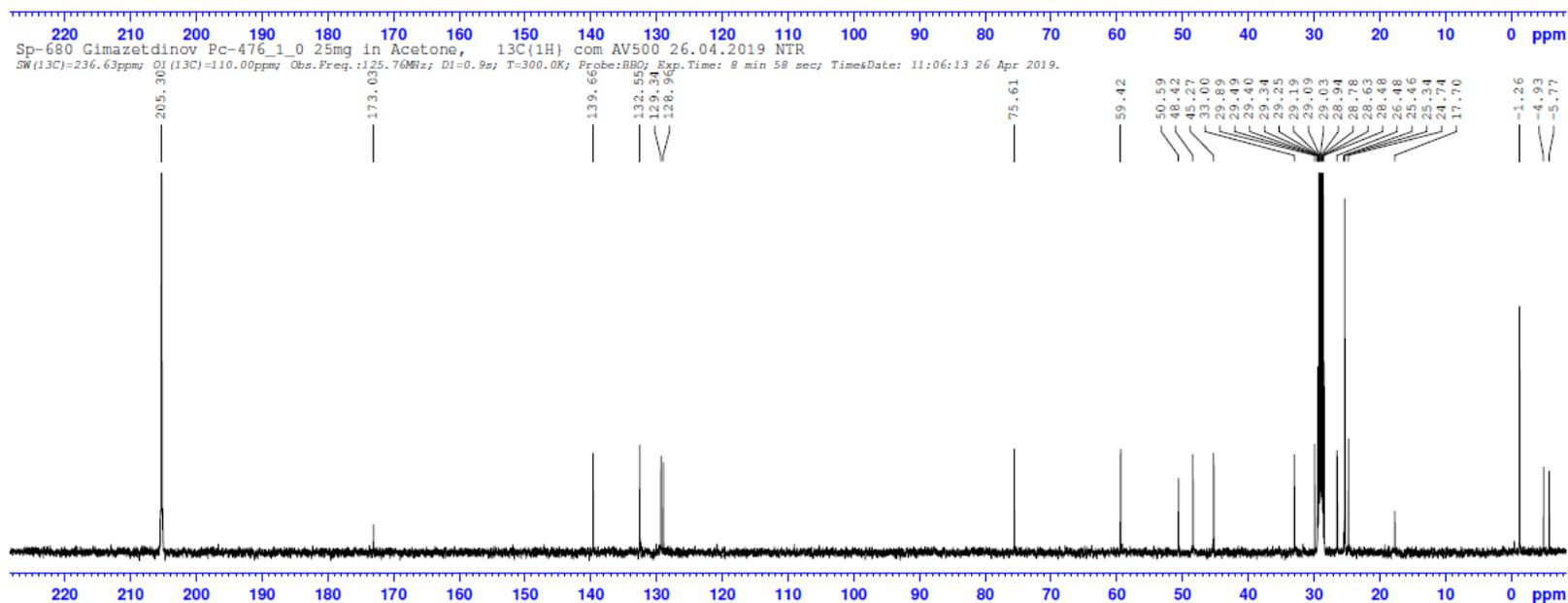
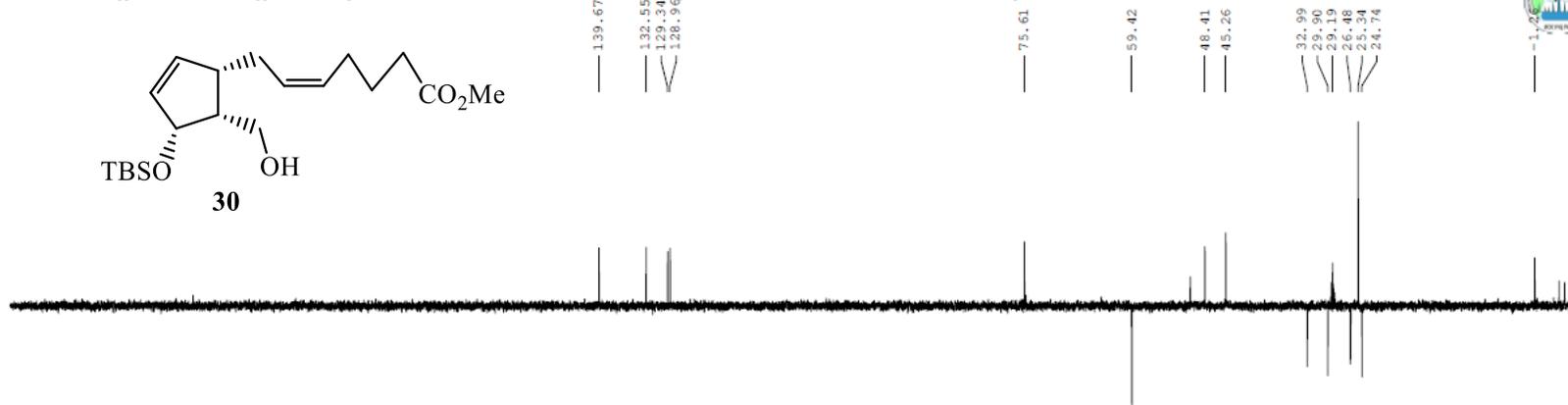
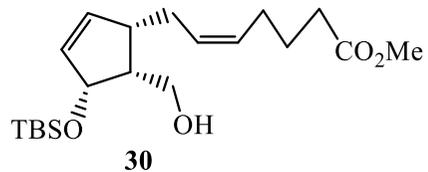


Figure. S10 ^{13}C NMR spectrum of **30** (*d*-acetone, 125.77 MHz)

Pc-515

04.03.2020 12:33:20

Acquisition Time (sec)	3.2768	Comment	Sp-145 Gimazetdinov Pc-515-dept 15mq in Acetone, 1H, AV500 29.10.2019 SSH		
Date	29 Oct 2019 08:27:44	Date Stamp	29 Oct 2019 08:27:44		
File Name	E:\текучее\gnb-Pc-515-dept\gnb-Pc-515-dept_001000fid	Frequency (MHz)	500.13	Nucleus	1H
Number of Transients	1	Origin	spect	Original Points Count	32768
Points Count	32768	Pulse Sequence	zg	Receiver Gain	52.29
Solvent	Acetone	Spectrum Offset (Hz)	3488.4607	Sweep Width (Hz)	9999.70
				SW(cyclical) (Hz)	10000.00
				Temperature (degree C)	25.629

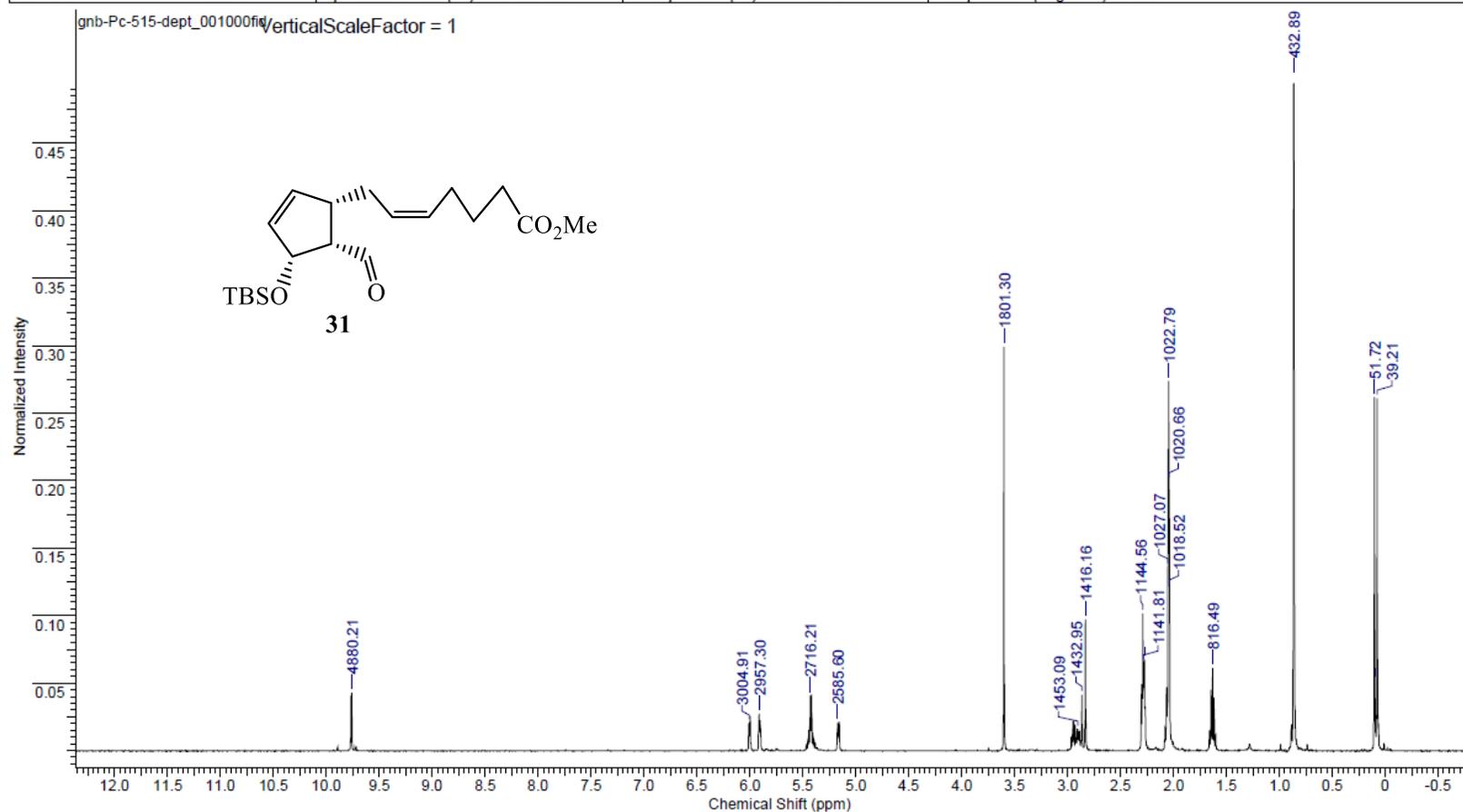


Figure. S11 ¹H NMR spectrum of **31** (*d*-acetone, 500 MHz)

Sp-145 Gimazetdinov Pc-515-dept 15mg in Acetone, ¹³C(1H) dept135 AV500 29.10.2019 SSH

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



SW(13C)=236.63ppm; OI(13C)=110.00ppm; Obs.Freq.:125.76MHz; D1=1.0s; T=299.2K; Probe:BB0; Exp.Time: 9 min 20 sec; TimesDate: 14:07:35 29 Oct 2019.

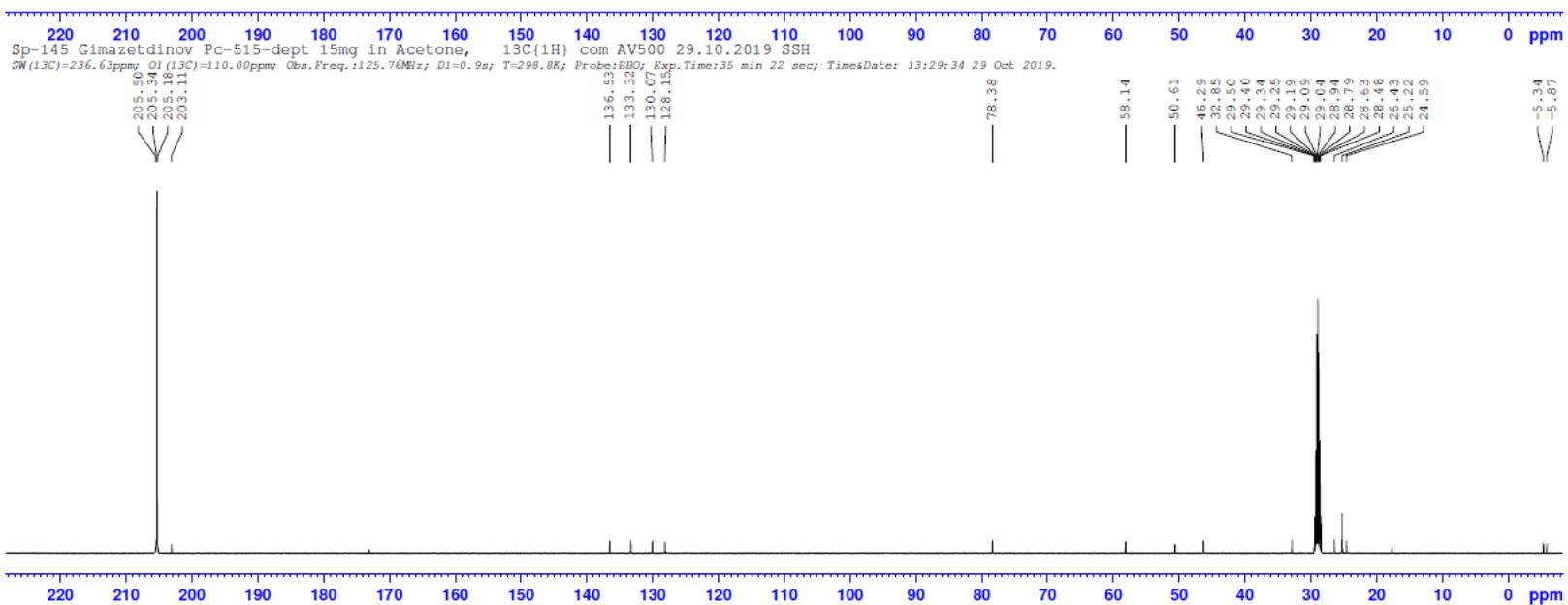
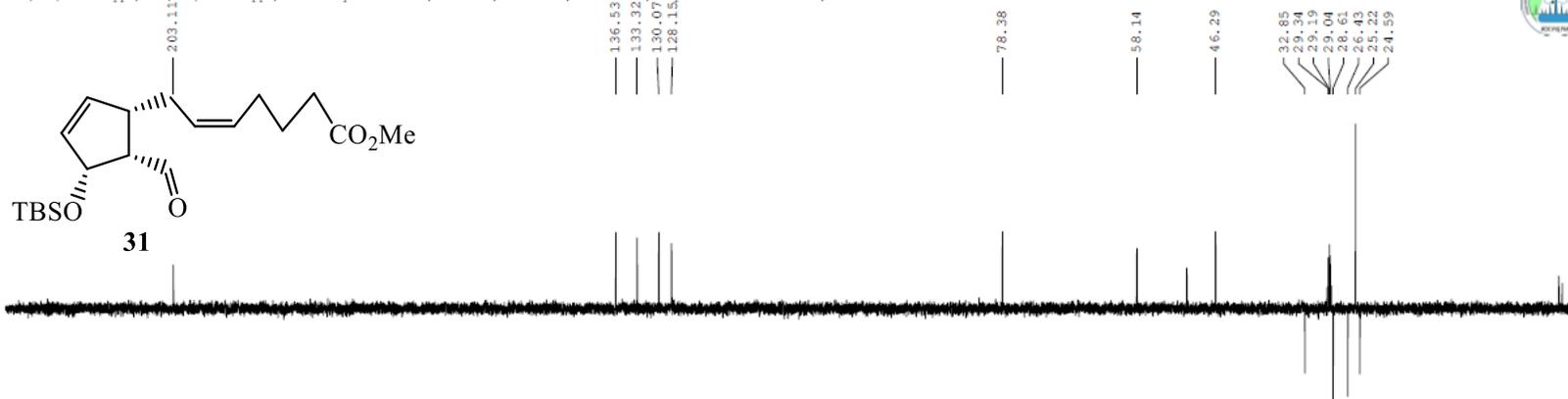


Figure. S12 ¹³C NMR spectrum of **31** (*d*-acetone, 125.77 MHz)

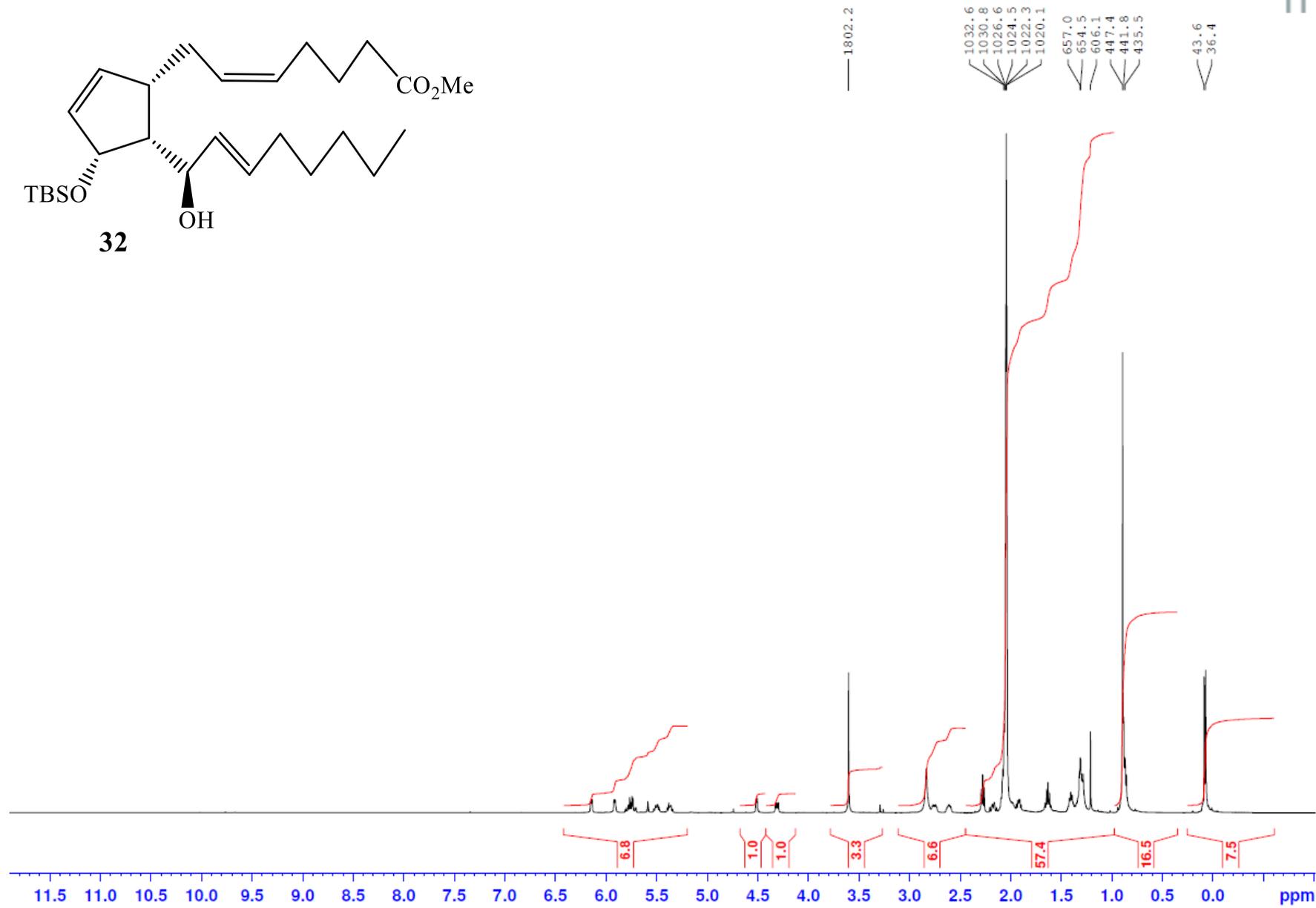


Figure. S13 ¹H NMR spectrum of **32** (d-acetone, 500 MHz)

Sp-32 Gimazetdinov Pc-406-1-com 15mg in Acetone, 13C(1H) dept135 AV500 14.10.2019 BIP

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; D1=1.0s; T=295.2K; Probe:BB0; Exp.Time: 7 min 2 sec; TimesDate: 10:25:33 14 Oct 2019.

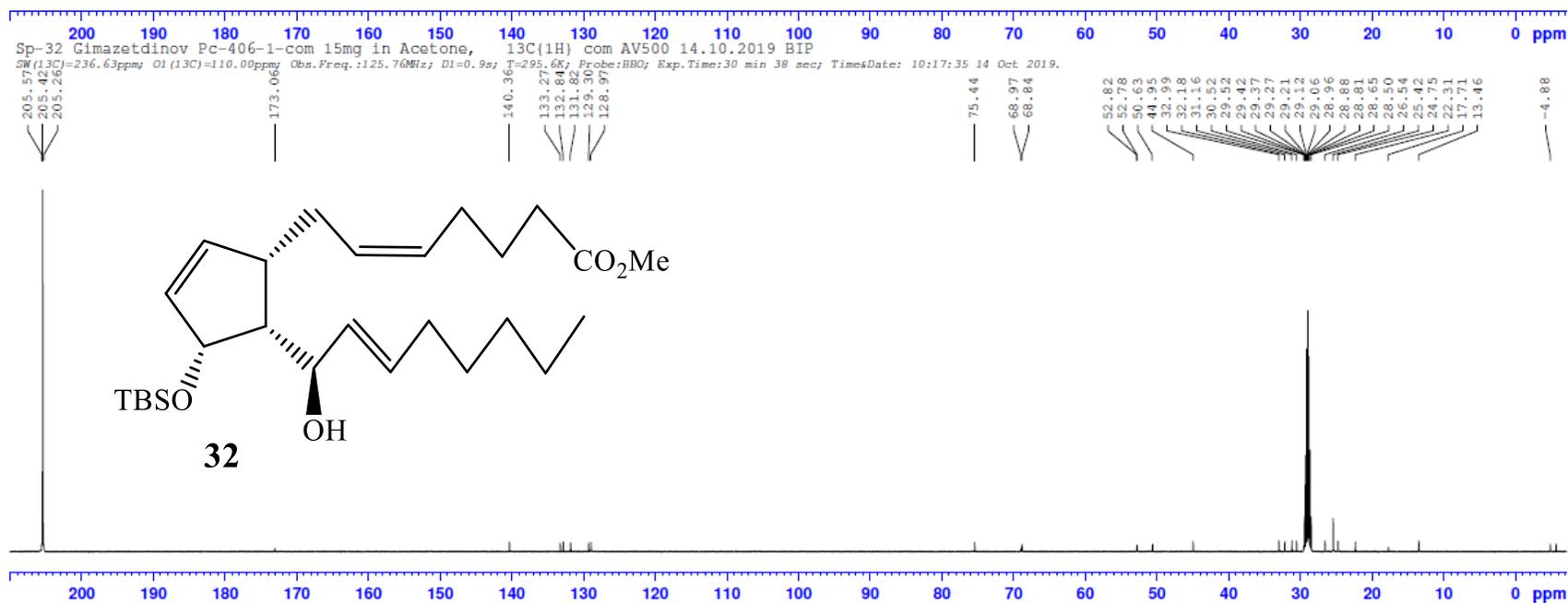
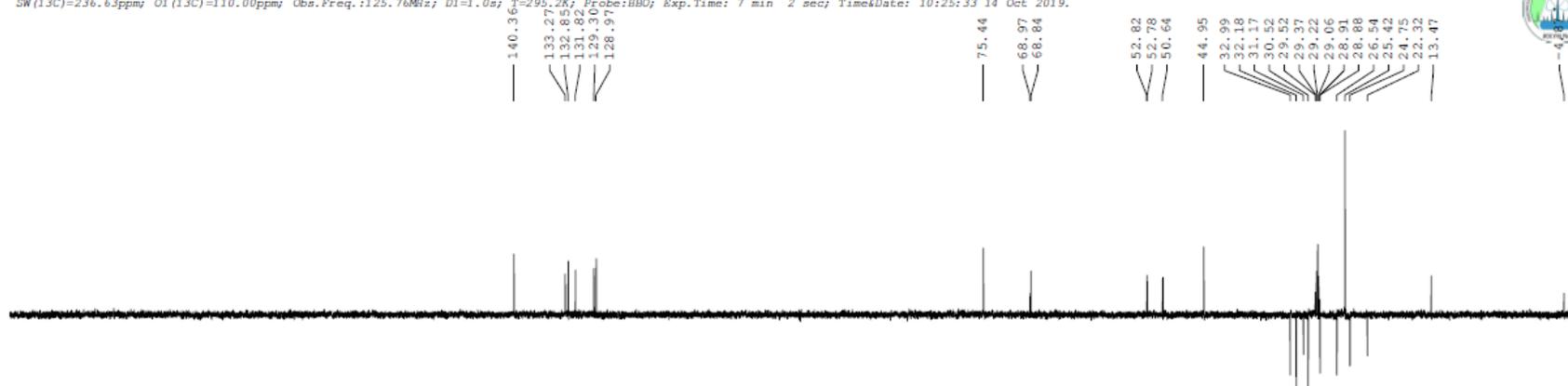


Figure. S14 ¹³C NMR spectrum of **32** (*d*-acetone, 500 MHz)

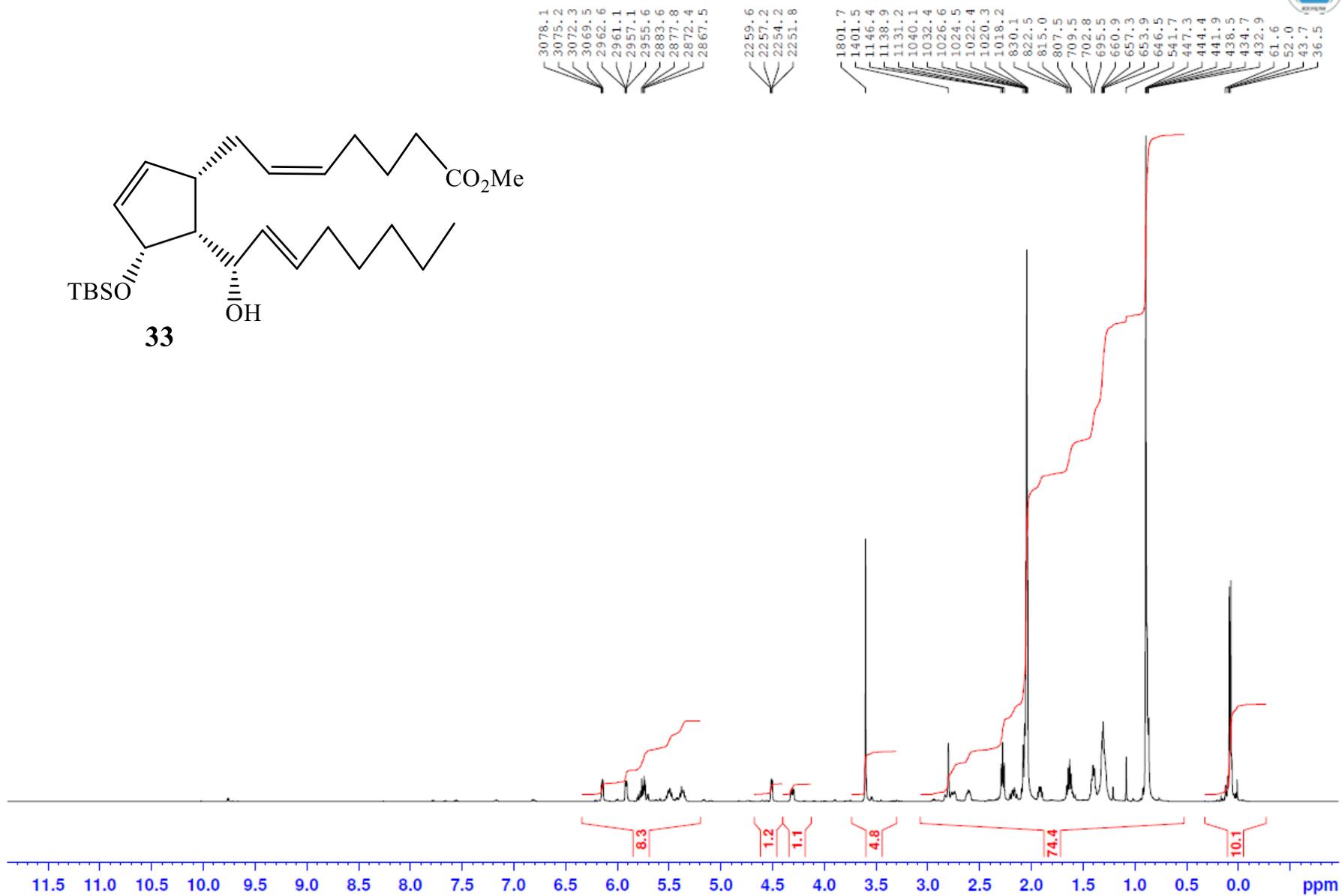


Figure. S15 ¹H NMR spectrum of **33** (*d*-acetone, 500 MHz)

Sp-3 Gimazetdinov Pc-603-2 10mg in Acetone, $^{13}\text{C}\{^1\text{H}\}$ dept135 AV500 16.10.2020 NTR

Ufa Institute of Chemistry of the Russian Academy of Sciences (IIC RAS). 2020



SW(^{13}C)=236.63ppm; O1(^{13}C)=110.00ppm; Obs.Freq.:125.76MHz; D1=1.0s; T=296.7K; Probe:BBQ; Exp.Time: 3 min 45 sec; TimesDate: 13:34:41 16 Oct 2020.

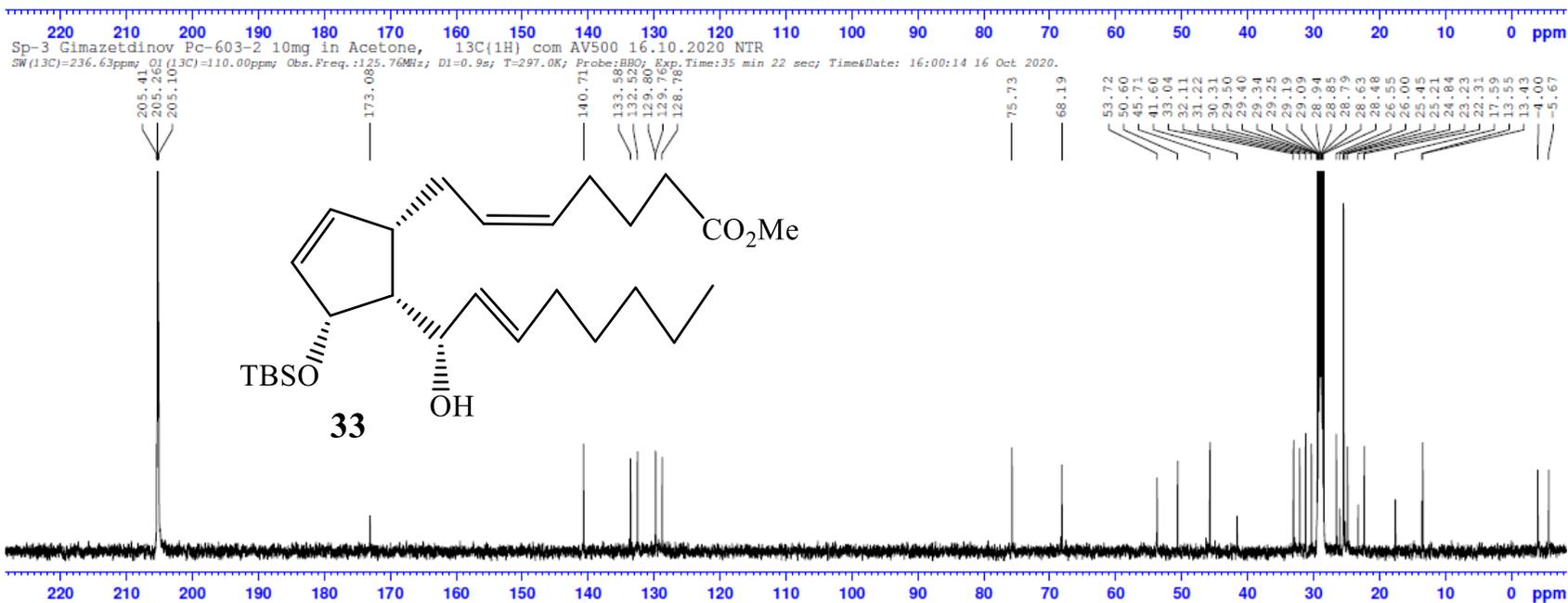
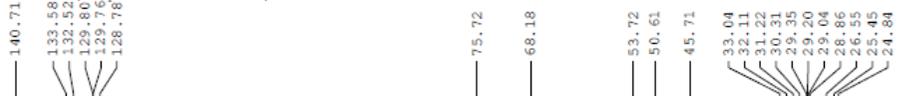


Figure. S16 ^{13}C NMR spectrum of **33** (*d*-acetone, 125.77 MHz)

Sp-3 Gimazetdinov Pc-603-2 10mg in Acetone (1H, 1H) NOESY AV500 16.10.2020 NTR
SW (1H)-10.39ppm; (1H)-4.86ppm; Obs. Freq.: 500.13MHz; D1-1.5s; T-296.2K; Probe:BBO; Exp.Time: 1 h 24 min 12 sec; Time&Date: 13:49:11 16 Oct 2020.

Ufa Institute of Chemistry of the Russian Academy of Sciences (UIC RAS). 2021

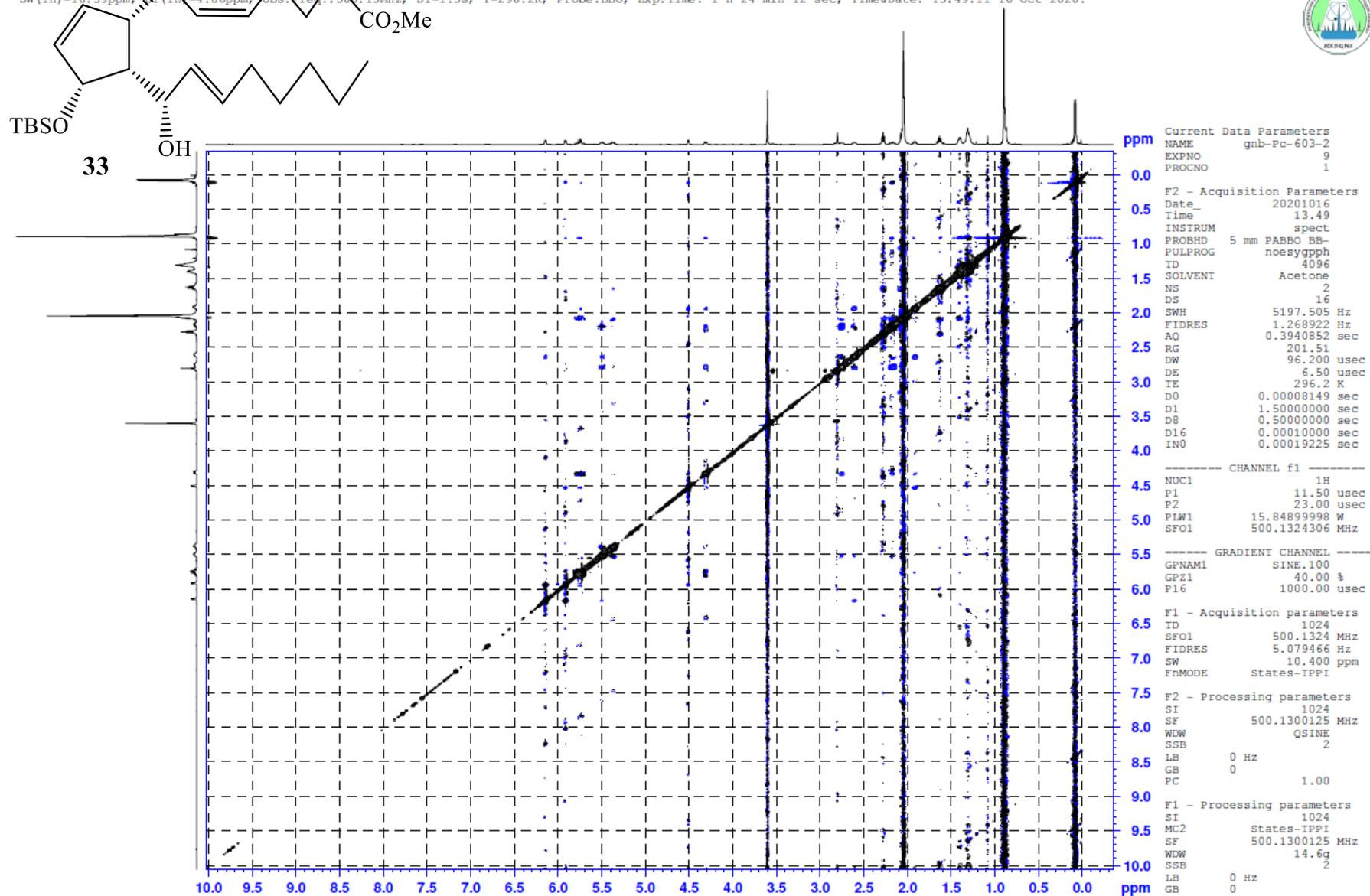
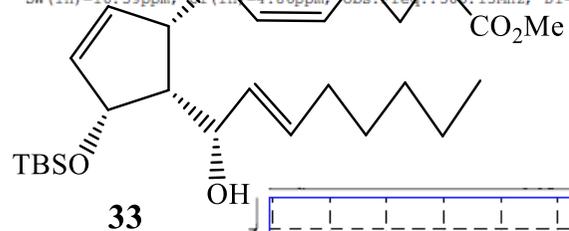


Figure. S17 $\{^1\text{H}, ^1\text{H}\}$ NOESY spectrum of **33** (*d*-acetone, 125.77 MHz)

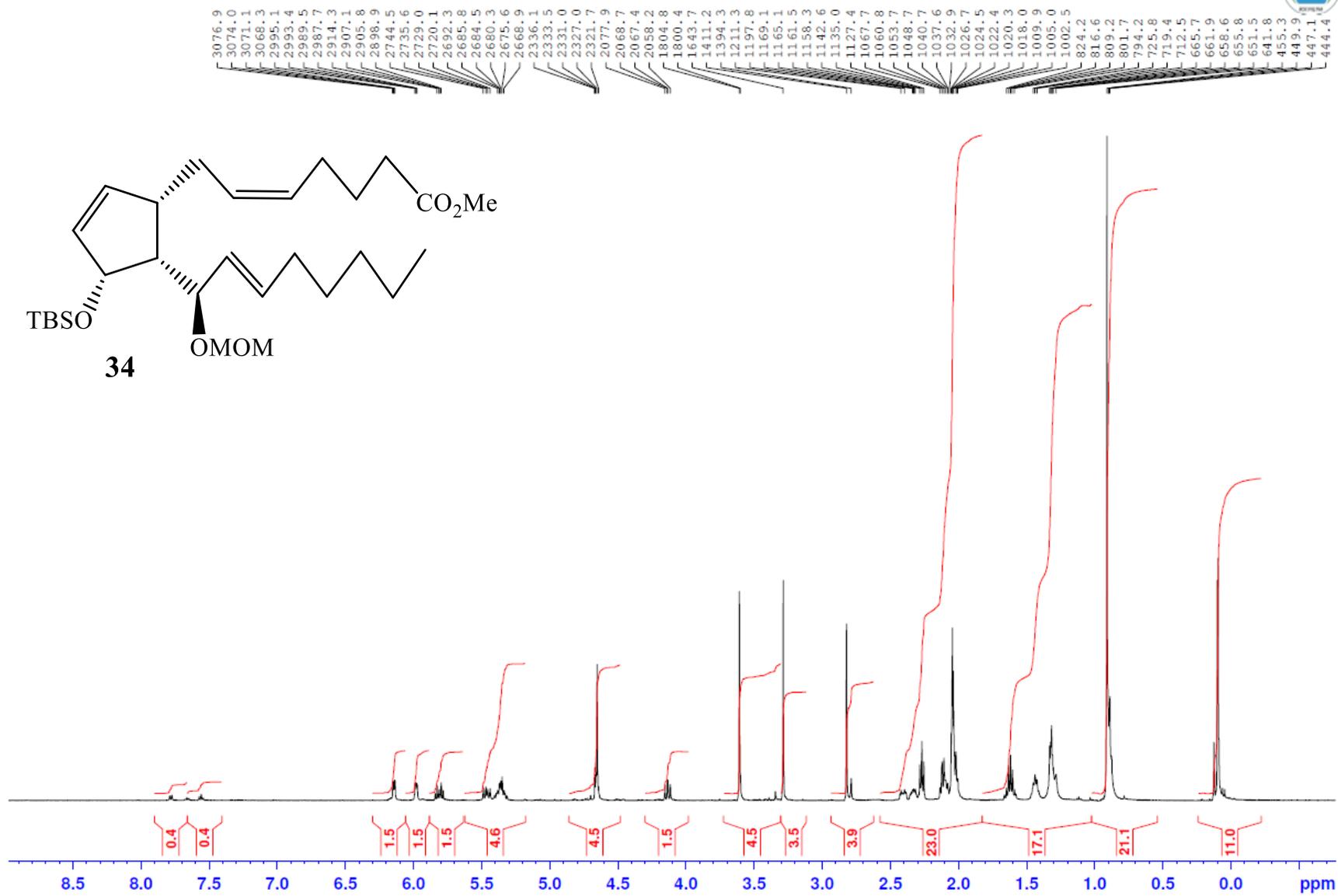


Figure. S18 ¹H NMR spectrum of **34** (d-acetone, 500 MHz)

Sp-800 Gimazetdinov Pc-604-com 10mg in Acetone, $^{13}\text{C}\{^1\text{H}\}$ com AV500 15.10.2020 SSH
SW (^{13}C)=236.63ppm; O1 (^{13}C)=110.00ppm; Obs.Freq.:125.76MHz; D1=0.9s; T=295.8K; Probe:BB0; Exp.Time:48 min 28 sec; Time&Date: 13:21:23 15 Oct 2020.

Ufa Institute of Chemistry of the Russian Academy of Sciences (UIC RAS). 2020

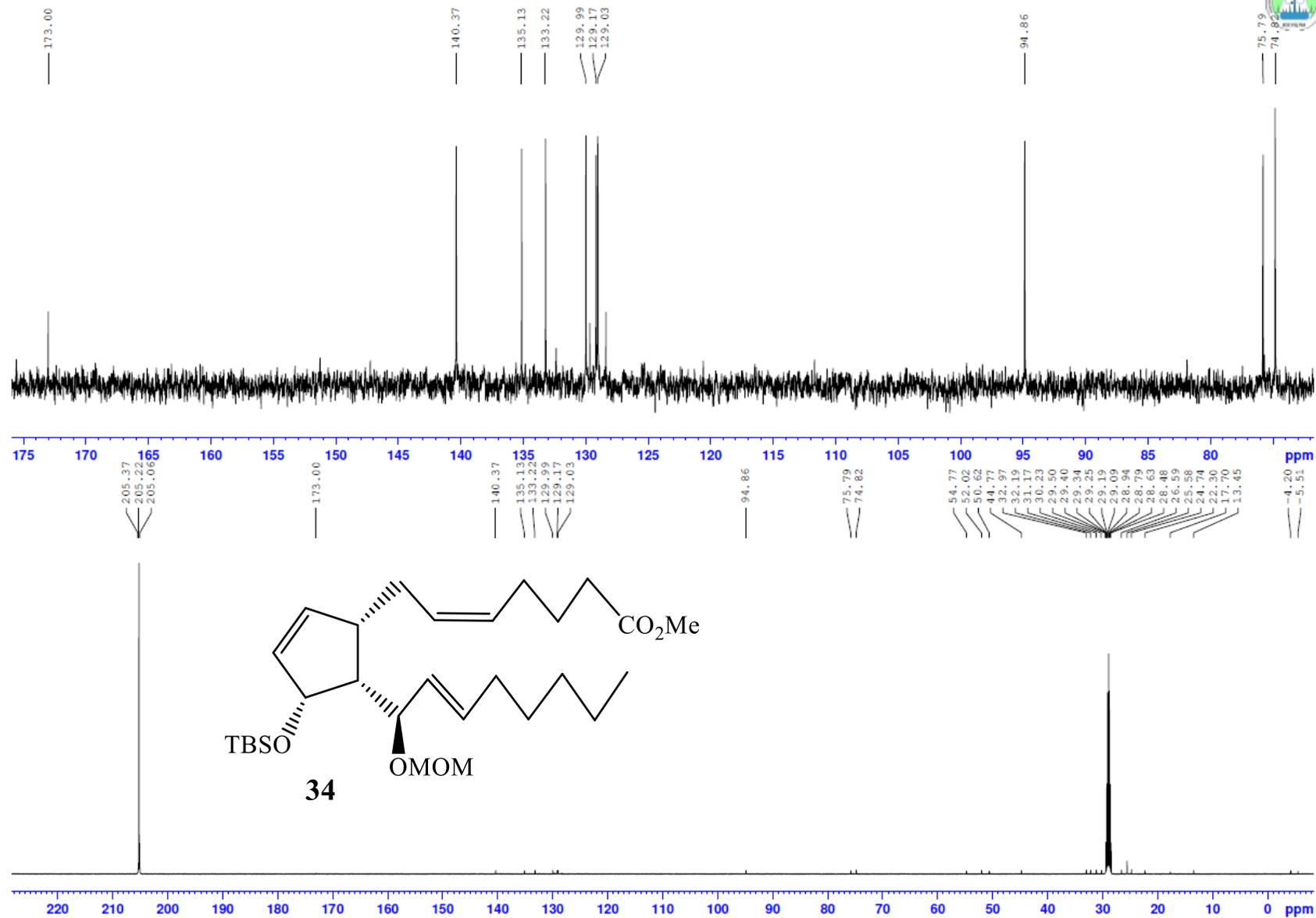


Figure. S19 ^{13}C NMR spectrum of **34** (*d*-acetone, 125.77 MHz)

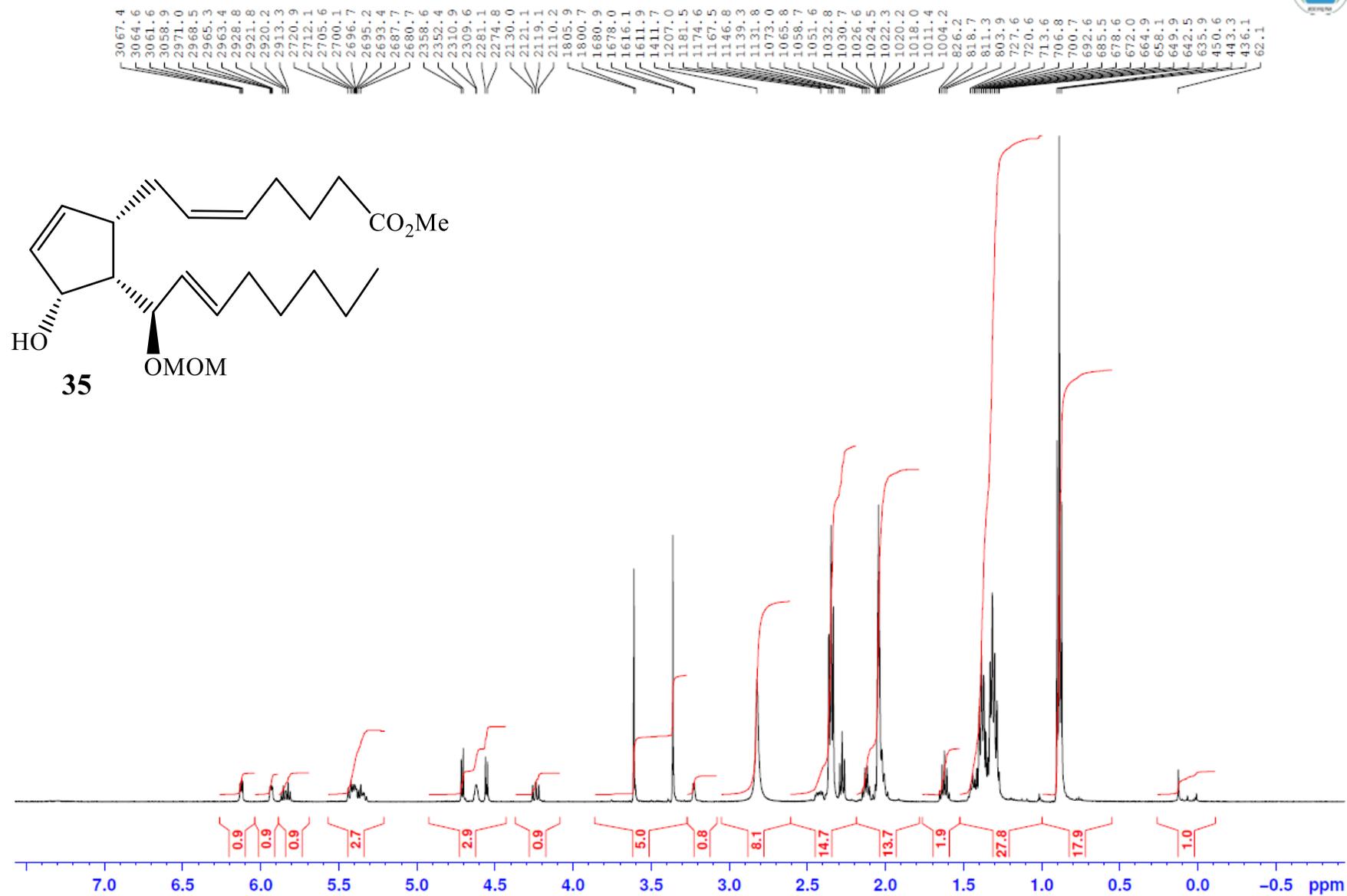


Figure. S20 ¹H NMR spectrum of **35** (*d*-acetone, 500 MHz)

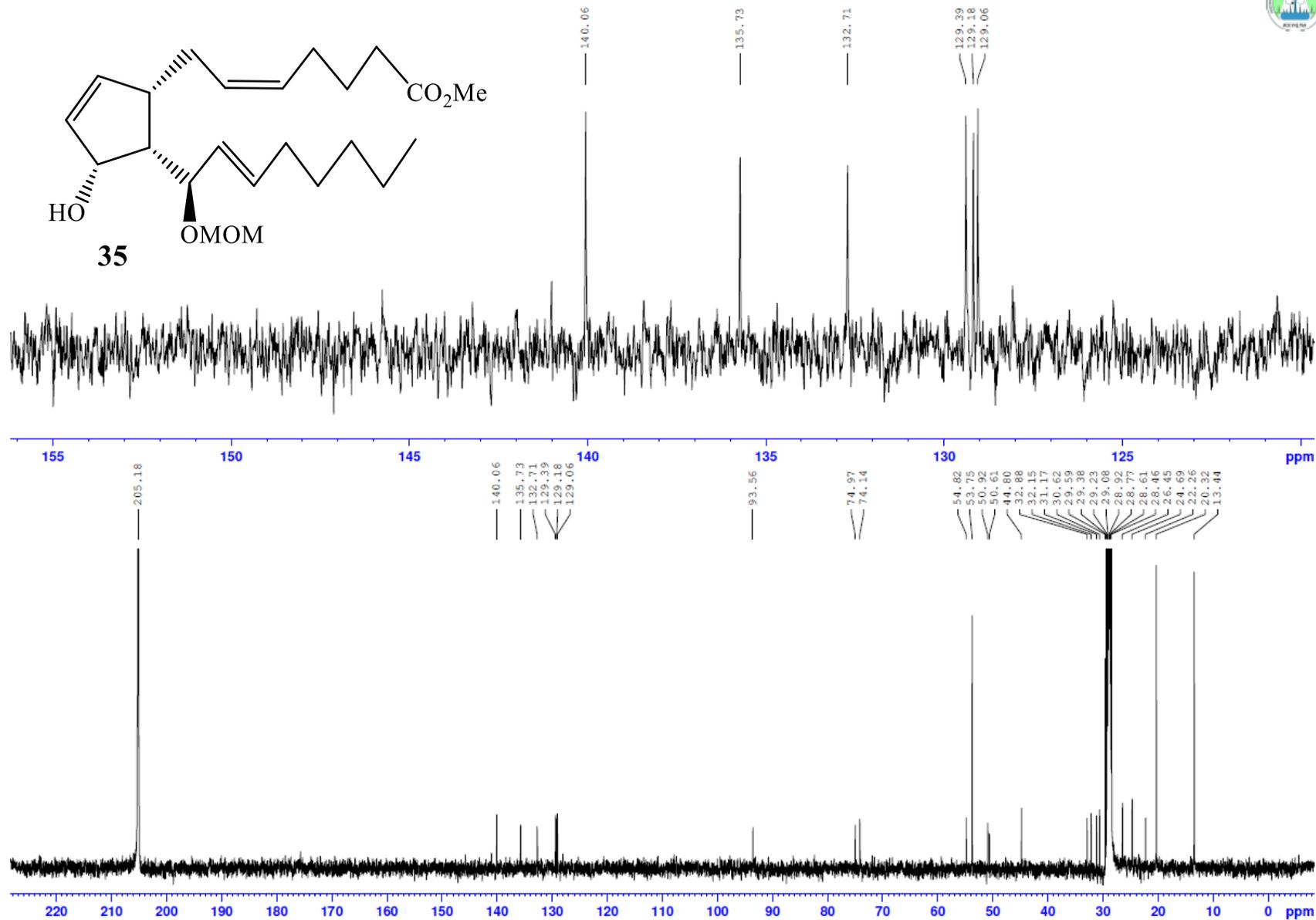


Figure. S21 ¹³C NMR spectrum of **35** (*d*-acetone, 125.77 MHz)

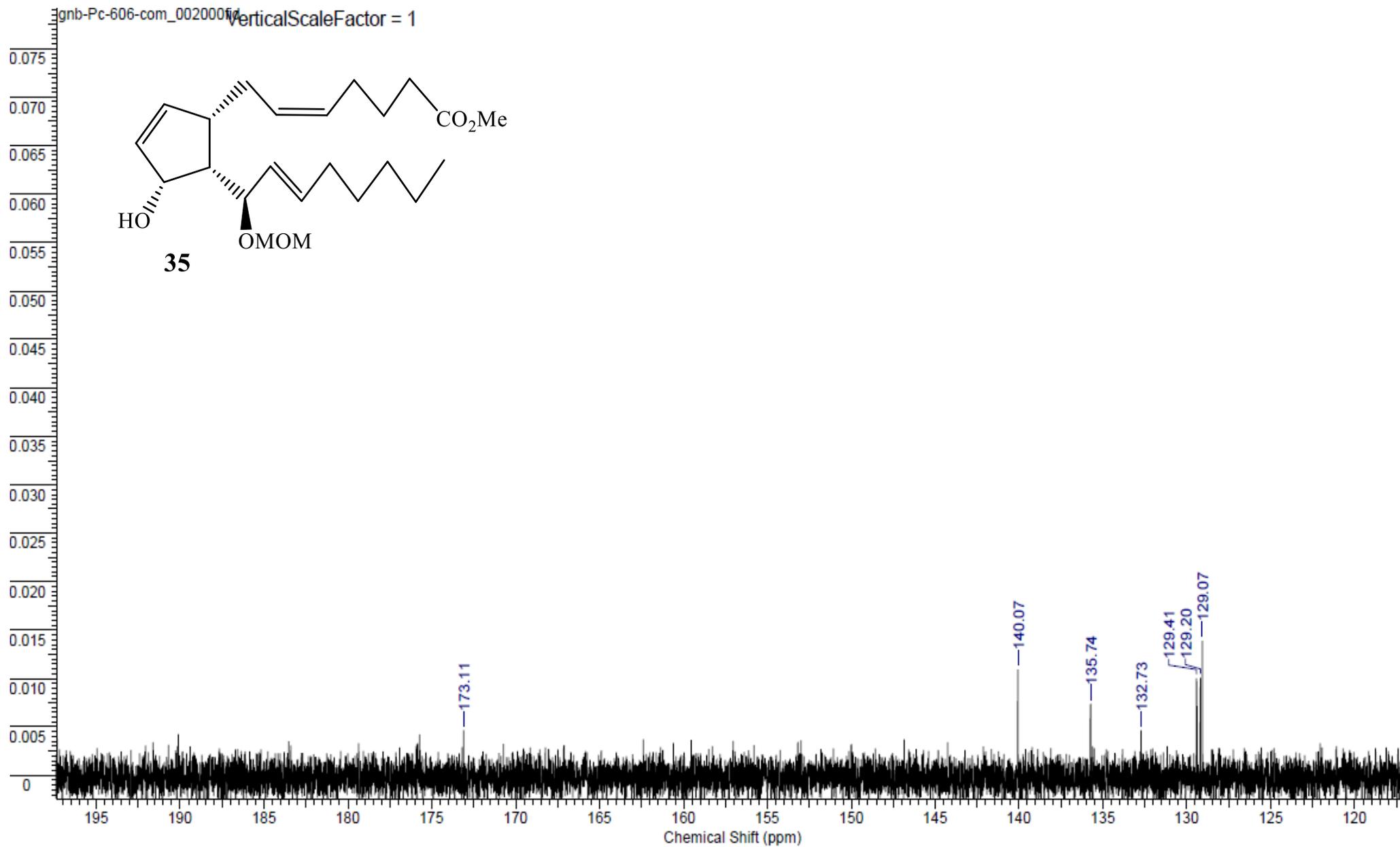


Figure. S22 ^{13}C NMR spectrum of **35** (*d*-acetone, 125.77 MHz)

Sp-924 Gimazetdinov Pc-608-com 10mg in Acetone, 1H AV500 02.11.2020 BIP

Ufa Institute of Chemistry of the Russian Academy of Sciences (ICh RAS), 2020

SW (1H)=19.99ppm; O1 (1H)=7.00ppm; Obs. Freq.: 500.13MHz; D1=2.0s; T=298.1K; Probe:BB0; Exp. Time: 7 sec; Time&Date: 16:11:13 02 Nov 2020.

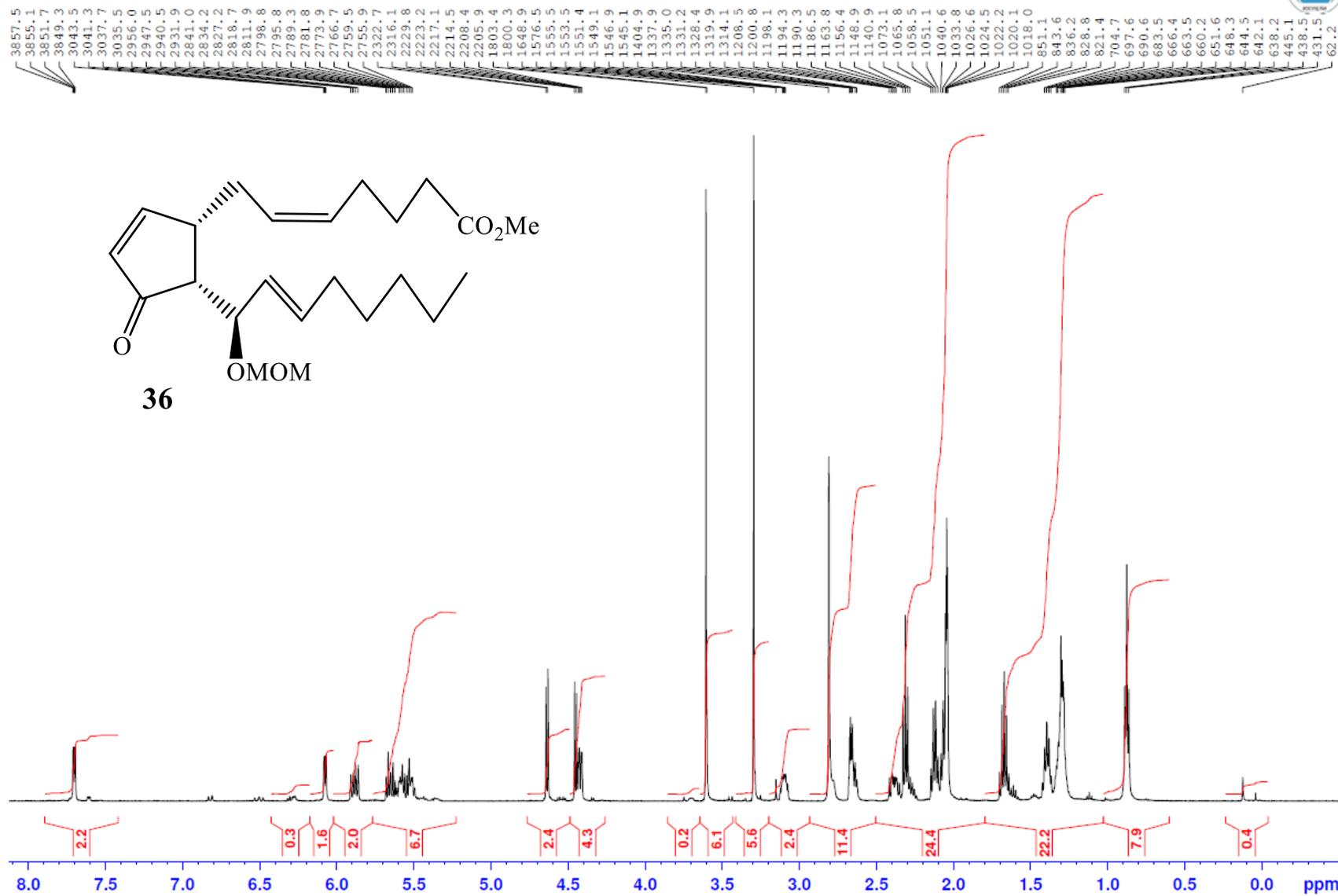


Figure. S23 ¹H NMR spectrum of **36** (d-acetone, 500 MHz)

Acquisition Time (sec)	1.1010	Comment	Sp-924 Gimazetdinov Pc-608-com 10mg in Acetone. 13C{1H} com AV500 02.11.2020 BIP		
Date	02 Nov 2020 11:14:08	Date Stamp	02 Nov 2020 11:14:08		
File Name	E:\текущие\gnb-Pc-608-com\gnb-Pc-608-com_002001r	Frequency (MHz)	125.76	Nucleus	13C
Number of Transients	398	Origin	spect	Original Points Count	32768
Points Count	32768	Pulse Sequence	zgpg30	Receiver Gain	201.51
Solvent	Acetone	Spectrum Offset (Hz)	13833.3623	Sweep Width (Hz)	29761.00
				Temperature (degree C)	25.534

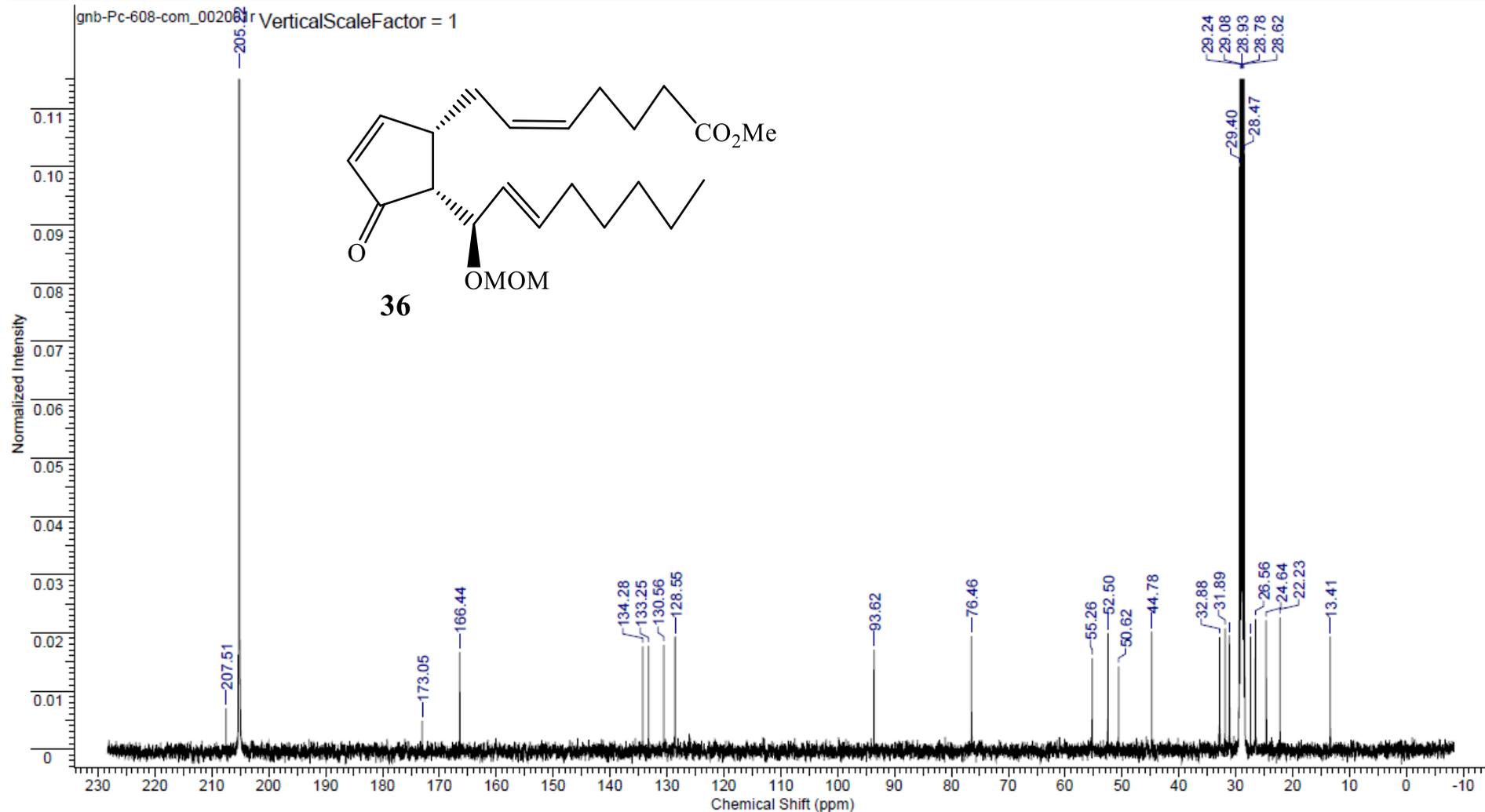


Figure. S24 ¹³C NMR spectrum of **36** (*d*-acetone, 125.77 MHz)

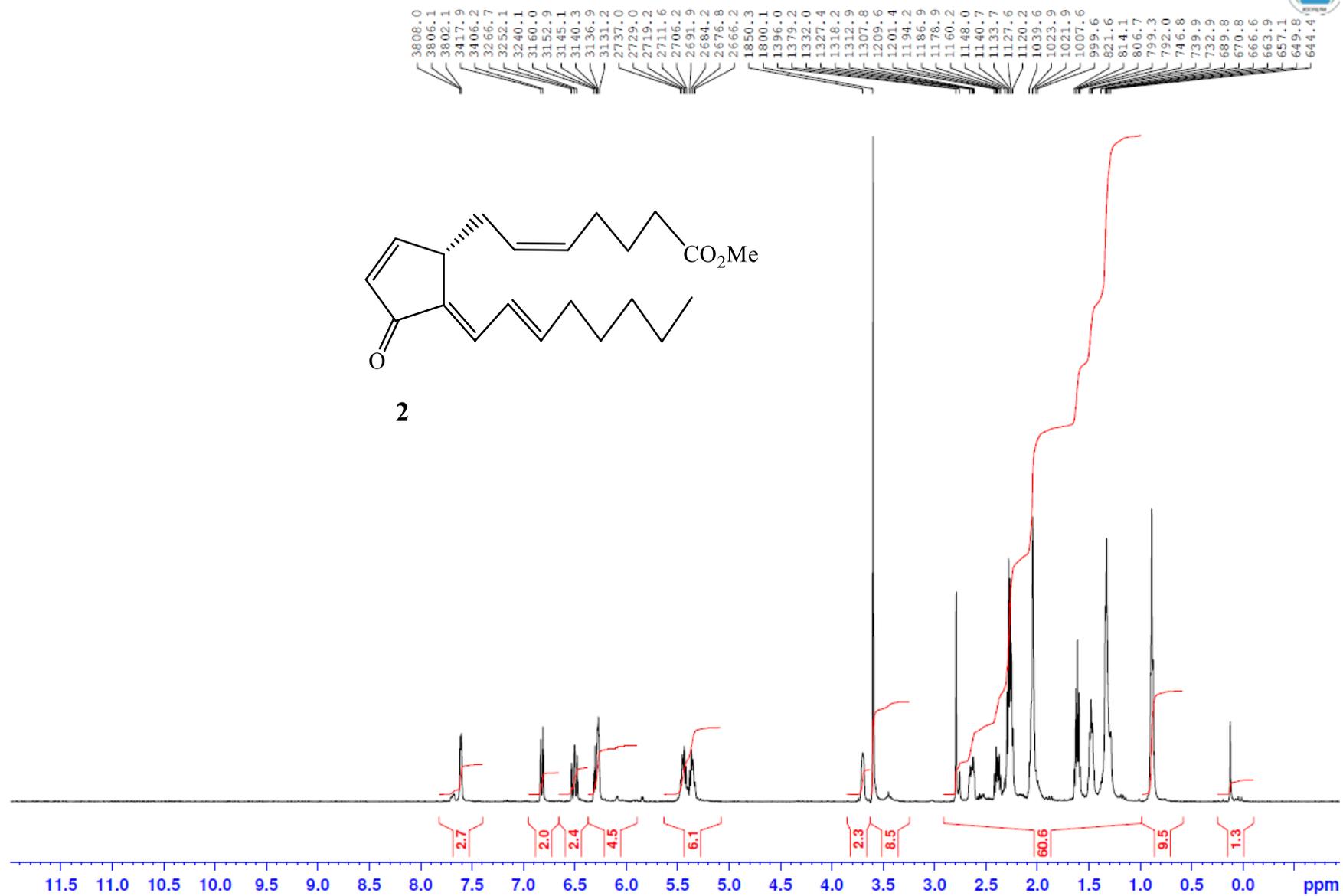


Figure. S25 ¹H NMR spectrum of **2** (*d*-acetone, 500 MHz)

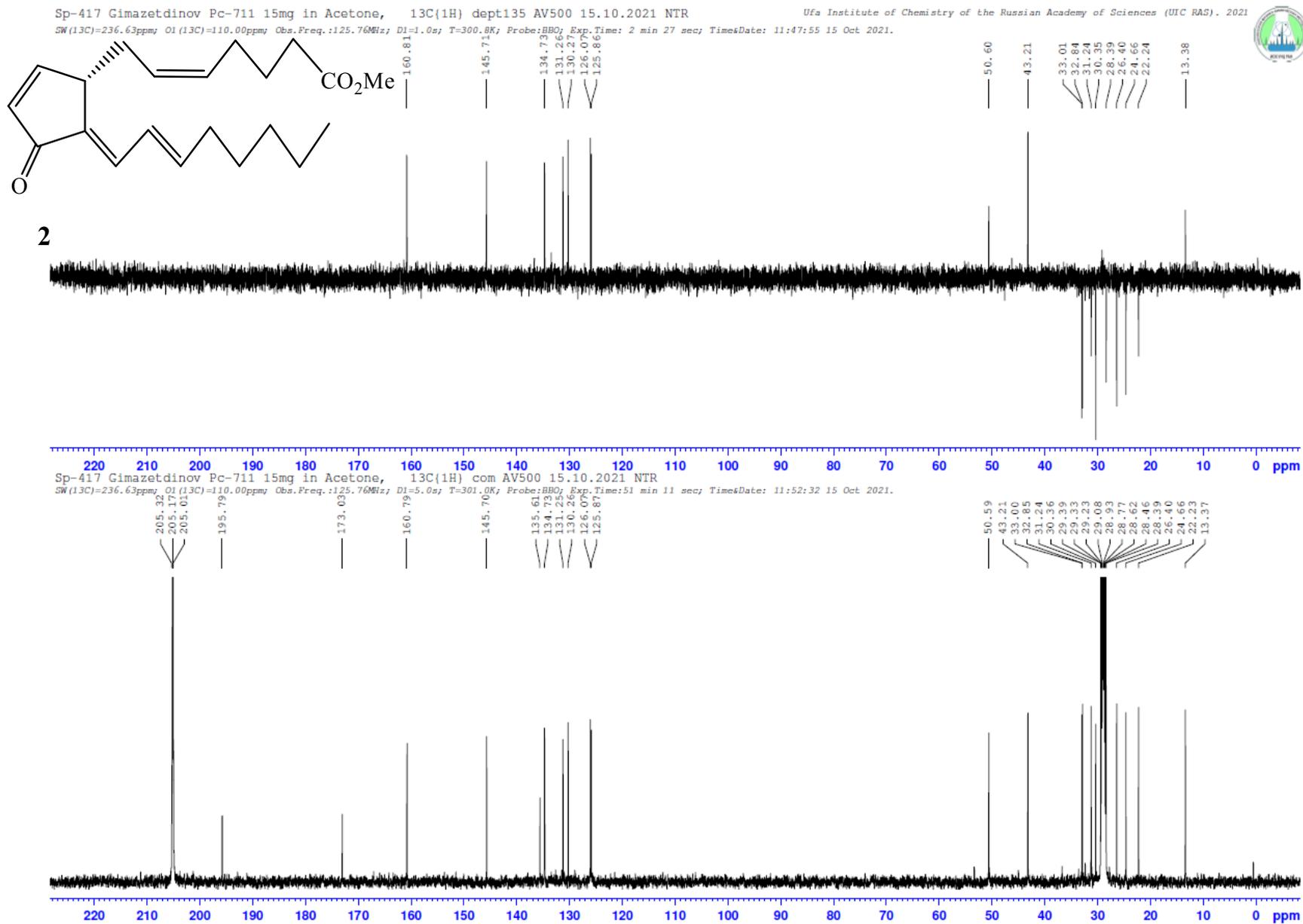


Figure. S26 ^{13}C NMR spectrum of **2** (*d*-acetone, 125.77 MHz)