



Supporting Information

for

Convenient access to pyrrolidin-3-ylphosphonic acids and tetrahydro-2H-pyran-3-ylphosphonates with multiple contiguous stereocenters from nonracemic adducts of a Ni(II)-catalyzed Michael reaction

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Experimental procedures, copies of NMR, FTIR, and mass spectra, HPLC and X-ray diffraction data

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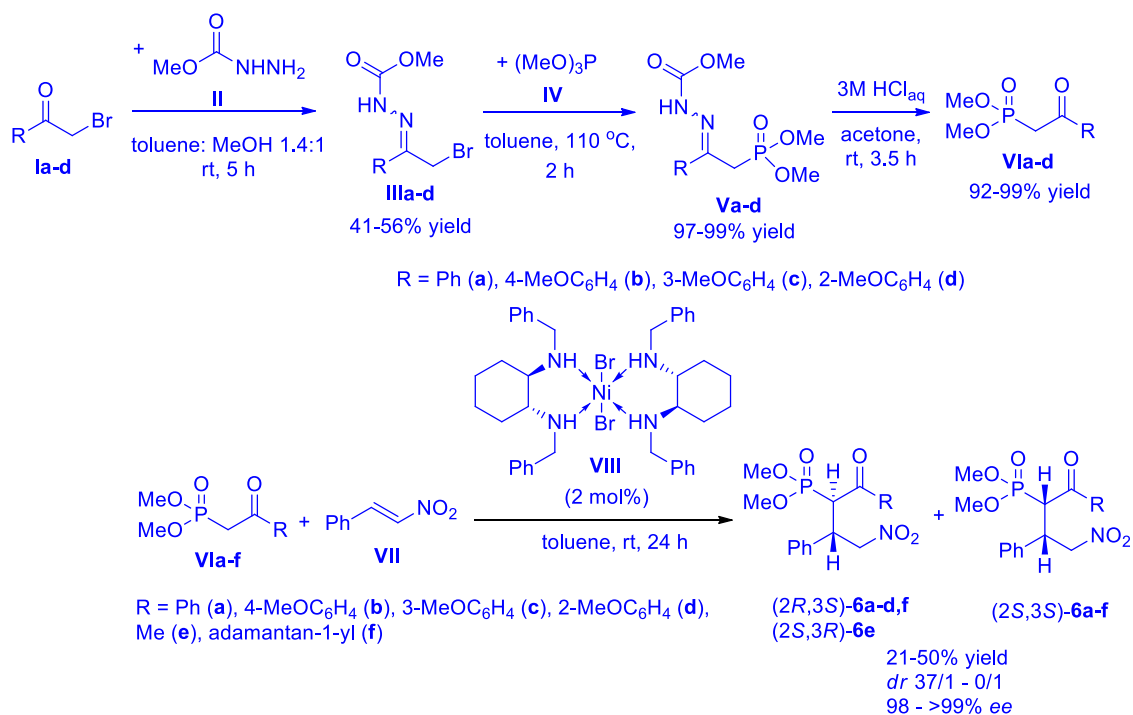
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1. General information

All commercially obtained reagents were used without further purification. All solvents were distilled prior to use. Dimethyl 2-oxopropylphosphonate **Vle** [1] and dimethyl 2-(adamantan-1-yl)-2-oxoethyl phosphonate **Vlf** [2] were obtained according to reported procedures. Other β -keto phosphonates **Via–d** were synthesized following the modified Corbel's procedures [3] (see below). Bis[(1*R*,2*R*)-*N,N*-dibenzylcyclohexane-1,2-diamine- κ^2N,N'](dibromo)nickel **VIII** was obtained according to a reported procedure [4]. Melting points were measured with an OptiMelt automated melting point system. All the reactions were monitored by TLC, performed on precoated silica gel plates (Sorbfil); compounds were made visible with I₂. ¹H, ¹³C and ³¹P NMR spectra were recorded with a JEOL JNM-ECX400 spectrometer at 399.78, 100.53 and 161.83 MHz, respectively, in CDCl₃, DMSO-*d*₆ and D₂O solution. FTIR spectra were recorded with a Shimadzu IR Affinity-1 spectrophotometer with Specac® Quest ATR. Elemental analysis was performed with an EuroVector EA-3000 analyzer. High-resolution mass spectrometry was recorded with an Agilent AccuTOF 6230 mass-spectrometer. Optical rotations were measured with Rudolph Research Analytical (Autopol V Plus Automatic Polarimeter). The enantiomeric purity of the products was determined by HPLC analysis on Shimadzu Prominence LC-20AD (Spd-20auv vis detector, Cto-20a column over, Dgu-20a degasing unit) equipped with a chiral stationary phase column (ChiralPAK AD-3) with hexane/2-propanol as eluent and with a chiral stationary phase column ChiralPAK AD-3R with water/acetonitrile as eluent. Column chromatography was performed on Silica gel 60, Merck (230–400 mesh). X-ray crystallographic data were collected using a Enraf-Nonius CAD-4 diffractometer.

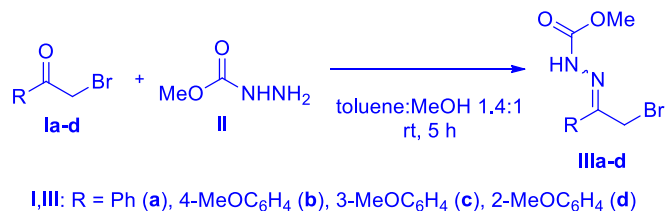
2. Synthesis of initial compounds

The initial 4-nitro-2-oxophosphonates were synthesized according to scheme S1:



Scheme S1: General scheme for the synthesis of initial compounds.

General procedure for the synthesis of methyl 2-(2-bromo-1-arylethylidene)-hydrazine-1-carboxylates IIIa-d.

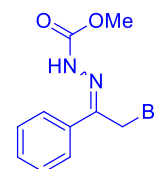


Scheme S2: Synthesis of methyl 2-(2-bromo-1-arylethylidene)hydrazine-1-carboxylates IIIa-d.

A solution of α -bromoketone **la-d** (93.8 mmol) and methylhydrazine carboxylate **II** (85.3 mmol) in toluene (84 mL) and methanol (59 mL) was stirred for 10 h at 25 °C. Then it was kept at -10 °C for 2 h. The precipitate was filtered off and recrystallized from acetone.

Methyl 2-(2-bromo-1-phenylethylidene)hydrazine-1-carboxylate (IIIa).

Mixture of isomers 2.2:1. Yield: 10.4 g (45%), white crystals,
m.p. 130-131 °C (acetone).



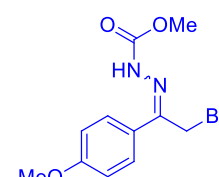
^1H NMR (400 MHz, CDCl_3 , 298 K) δ [ppm] 8.63 (br s, 1H, NH, minor isomer), 7.87 (br s, 1H, NH, major isomer), 7.72-7.71 (m, 1H, aromatic, major isomer), 7.50-7.42 (m, 2H, aromatic, major isomer, 2H, aromatic, minor isomer), 7.35-7.34 (m, 1H, aromatic, major isomer, 1H, aromatic, minor isomer), 7.27-7.25 (m, 1H, aromatic, major isomer, 2H, aromatic, minor isomer), 4.29 (s, 2H, CH_2 , major isomer), 4.25 (s, 2H, CH_2 , minor isomer), 3.83 (s, 3H, Me, minor isomer), 3.74 (s, 3H, Me, major isomer).

^{13}C NMR (101 MHz, CDCl_3 , 298 K) δ [ppm] 154.5 (s, $\text{C}=\text{O}$, minor isomer), 153.8 (s, $\text{C}=\text{O}$, major isomer), 149.1 (s, $\text{C}=\text{N}$, major isomer), 145.7 (s, $\text{C}=\text{N}$, minor isomer), 135.4 (s, aromatic, C, major isomer), 134.0 (s, aromatic, C, minor isomer), 130.7 (s, aromatic, CH, minor isomer), 130.4 (s, aromatic, CH, major isomer), 129.8 (s, aromatic, 2CH, major isomer), 128.8 (s, aromatic, 2CH, minor isomer), 127.7 (s, aromatic, 2CH, major isomer), 126.3 (s, aromatic, 2CH, minor isomer), 53.4 (s, Me, major isomer), 53.2 (s, Me, minor isomer), 34.9 (s, CH_2 , major isomer), 19.1 (s, CH_2 , minor isomer).

Anal. Calcd. for $\text{C}_{10}\text{H}_{11}\text{BrN}_2\text{O}_2$: C, 44.30; H, 4.09; N 10.33. Found: C, 44.25; H, 4.14; N 10.37.

Methyl 2-[2-bromo-1-(4-methoxyphenyl)ethylidene]hydrazine-1-carboxylate (IIIb).

Mixture of isomers 2.0:1. Yield: 14.4 g (56%), white crystals,
m.p. 128-129 °C (acetone).



^1H NMR (400 MHz, CDCl_3 , 298 K) δ [ppm] 8.25 (br.s, 1H, NH, minor

isomer), 7.91 (br.s, 1H, NH, major isomer), 7.70-7.68 (m, 2H, aromatic, minor isomer), 7.25-7.22 (m, 2H, aromatic, major isomer), 7.01-6.99 (m, 2H, aromatic, major isomer), 6.90-6.87 (m, 2H, aromatic, minor isomer), 4.30 (s, 2H, CH₂, major isomer), 4.20 (s, 2H, CH₂, minor isomer), 3.86-3.78 (m, 6H, 2Me, minor isomer, 6H, 2Me, major isomer).

¹³C NMR (101 MHz, CDCl₃, 298 K) δ [ppm] 161.1 (s, aromatic, C(OMe), minor isomer), 160.9 (s, aromatic, C(OMe), major isomer), 154.4 (s, C=O, minor isomer), 153.8 (s, C=O, major isomer), 149.1 (s, C=N, major isomer), 145.9 (s, C=N, minor isomer), 129.2 (s, aromatic, 2CH, major isomer), 127.8 (s, aromatic, 2CH, minor isomer), 122.5 (s, aromatic, C, minor isomer, C, major isomer), 115.3 (s, aromatic, 2CH, major isomer), 114.2 (s, aromatic, 2CH, minor isomer), 55.5 (s, 2Me, major isomer), 53.4 (s, 2Me, minor isomer), 35.2 (s, CH₂, major isomer), 18.9 (s, CH₂, minor isomer).

IR (ATR) ν [cm⁻¹] 3226 (w), 3170 (w), 3128 (w), 2956 (w), 2831 (w), 1707 (vs), 1604 (s), 1591 (s), 1514 (s), 1494 (s), 1469 (vs), 1413 (s), 1363 (vs), 1303 (vs), 1251 (vs), 1201 (s), 1178 (s), 1149 (s), 1066 (vs), 833 (vs), 812 (s), 796 (s), 686 (s), 607 (s), 555 (s), 534 (vs).

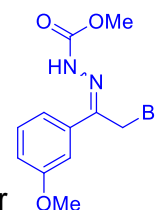
Anal. Calcd for C₁₁H₁₃BrN₂O₃: C, 43.87; H, 4.35; N 9.30. Found: C, 43.81; H, 4.39; N 9.39.

Methyl 2-[2-bromo-1-(3-methoxyphenyl)ethylidene]hydrazine-1-carboxylate (IIIc).

Mixture of isomers 1.9:1. Yield: 10.5 g (41%); white crystals;

m.p. 129-130 °C (acetone).

¹H NMR (400 MHz, CDCl₃, 298 K) δ [ppm] 8.63 (br.s, 1H, NH, minor isomer), 7.93 (br.s, 1H, NH, major isomer), 7.41-7.25 (m, 2H, aromatic, minor isomer, 2H, major isomer), 6.97-6.77 (m, 2H, aromatic, minor isomer, 2H, major isomer), 4.28 (s, 2H, CH₂, major isomer), 4.23 (s, 2H, CH₂, minor isomer), 3.83 (s, 6H, 2Me, minor isomer), 3.79 (s, 6H, 2Me, major isomer).



^{13}C NMR (101 MHz, CDCl_3 , 298 K) δ [ppm] 160.5 (s, aromatic, C(OMe), major isomer), 159.9 (s, aromatic, C(OMe), minor isomer), 154.5 (s, C=O, minor isomer), 153.8 (s, C=O, major isomer), 148.9 (s, C=N, major isomer), 145.6 (s, C=N, minor isomer), 136.9 (s, aromatic, C, minor isomer), 131.9 (s, aromatic, C, major isomer), 131.1 (s, aromatic, CH, major isomer), 129.7 (s, aromatic, CH, minor isomer), 119.6 (s, aromatic, CH, major isomer), 118.7 (s, aromatic, CH, minor isomer), 115.8 (s, aromatic, CH, major isomer), 115.6 (s, aromatic, CH, minor isomer), 113.2 (s, aromatic, CH, major isomer), 111.7 (s, aromatic, CH, minor isomer), 55.5 (s, 2Me, major isomer), 53.4 (s, 2Me, minor isomer), 34.8 (s, CH_2 , major isomer), 19.2 (s, CH_2 , minor isomer).

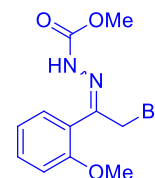
IR (ATR) ν [cm^{-1}] 3226 (w), 3124 (w), 2956 (w), 2831 (w), 1714 (vs), 1608 (s), 1591 (s), 1570 (s), 1469 (vs), 1429 (s), 1367 (vs), 1321 (s), 1292 (vs), 1222 (vs), 1155 (s), 1068 (vs), 1053 (vs), 1020 (vs), 856 (vs), 781 (vs), 682 (vs), 623 (s), 507 (s), 478 (s).

Anal. Calcd for $\text{C}_{11}\text{H}_{13}\text{BrN}_2\text{O}_3$: C, 43.87; H, 4.35; N 9.30. Found: C, 43.80; H, 4.43; N 9.36.

Methyl 2-[2-bromo-1-(2-methoxyphenyl)ethylidene]hydrazine-1-carboxylate (IIId).

Yield: 11.8 g (46%), white crystals, m.p. 135-137 °C (acetone).

^1H NMR (400 MHz, CDCl_3 , 298 K) δ [ppm] 7.74 (br.s, 1H, NH), 7.44-7.40 (m, 1H, aromatic), 7.16-7.14 (m, 1H, aromatic), 7.05-6.97 (m, 2H, aromatic), 4.33 (s, 2H, CH_2), 3.78 (s, 6H, 2Me).

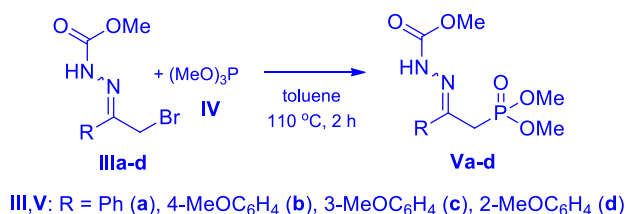


^{13}C NMR (101 MHz, CDCl_3 , 298 K) δ [ppm] 156.2 (s, aromatic, C(OMe)), 153.9 (s, C=O), 147.5 (s, C=N), 132.1 (s, aromatic, CH), 129.9 (s, aromatic, CH), 121.4 (s, aromatic, CH), 118.8 (s, aromatic, C), 111.9 (s, aromatic, CH), 55.8 (s, 2Me), 34.9 (s, CH_2).

IR (ATR) ν [cm^{-1}] 3226 (w), 3124 (w), 3026 (w), 2958 (w), 2837 (w), 1693 (vs), 1616 (m), 1597 (m), 1579 (m), 1471 (s), 1452 (s), 1367 (s), 1290 (m), 1273 (m), 1246 (vs), 1220 (s), 1132 (m), 1076 (vs), 1056 (s), 1024 (vs), 750 (vs), 690 (s), 559 (s), 518 (s).

Anal. Calcd for C₁₁H₁₃BrN₂O₃: C, 43.87; H, 4.35; N 9.30. Found: C, 43.81; H, 4.41; N 9.38.

General procedure for the synthesis of methyl 2-[2-(dimethoxyphosphoryl)-1-arylethylidene]hydrazinecarboxylates Va–d.

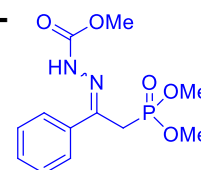


Scheme S3: Synthesis of methyl 2-[2-(dimethoxyphosphoryl)-1-arylethylidene]hydrazinecarboxylates **Va–d**

The resulting hydrazone **IIIa–d** (25.0 mmol) was added with stirring in an argon atmosphere for 1 h to a boiling solution of trimethyl phosphite **IV** (26.1 mmol) in toluene (25 mL). The mixture was stirred for 3 h, cooled and washed with water. The mixture was extracted with CHCl₃ (3 × 50 mL). The combined organic extracts were dried over Na₂SO₄, filtered, and evaporated in vacuo.

Methyl 2-[2-(dimethoxyphosphoryl)-1-phenylethylidene]hydrazine-1-carboxylate (Va).

Yield: 7.28 g (97%), yellow solid, m.p. 107-108 °C (toluene).



¹H NMR (400 MHz, CDCl₃, 298 K) δ [ppm] 9.85 (br s, 1H, NH), 7.70-7.68 (m, 2H, aromatic), 7.32-7.20 (m, 3H, aromatic), 3.73 (s, 3H, Me), 3.62 (d, ³J_{HP} = 11.2 Hz, 6H, 2MeO), 3.26 (d, ²J_{HP} = 23.2 Hz, 2H, CH₂).

¹³C NMR (101 MHz, CDCl₃, 298 K) δ [ppm] 155.5 (s, C=O), 143.8 (d, ²J_{CP} = 10.5 Hz, C=N), 137.0 (d, ³J_{CP} = 3.8 Hz, C), 129.6 (s, aromatic, CH), 128.5 (s, aromatic, 2CH),

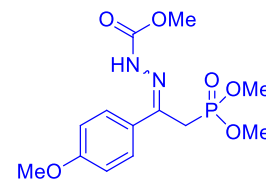
126.6 (s, aromatic, 2CH), 53.6 (d, $^2J_{CP}$ = 6.7 Hz, MeO), 52.8 (s, Me), 27.2 (d, $^1J_{CP}$ = 137.1 Hz, CH₂).

^{31}P NMR (162 MHz, CDCl₃, 298 K) δ [ppm] 26.64.

Anal. Calcd for C₁₂H₁₇N₂O₅P: C, 48.00; H, 5.71; N 9.33. Found: C, 47.91; H, 5.79; N 9.36.

Methyl 2-(2-(dimethoxyphosphoryl)-1-(4-methoxyphenyl)ethylidene)hydrazine-1-carboxylate (Vb).

Mixture of isomers 8.0:1. Yield: 8.17 g (99%), yellow solid, m.p. 92-94 °C (toluene).



^1H NMR (400 MHz, CDCl₃, 298 K) δ [ppm] 9.75 (br.s, 1H, NH, major isomer, 1H, NH, minor isomer), 7.68-7.66 (m, 2H, aromatic, minor isomer, 2H, aromatic, major isomer), 6.82-6.80 (m, 2H, aromatic, minor isomer, 2H, aromatic, major isomer), 3.75 (s, 3H, Me, minor isomer, 3H, Me, major isomer), 3.74 (s, 3H, Me, minor isomer, 3H, Me, major isomer), 3.64 (d, $^3J_{HP}$ = 9.2 Hz, 6H, 2MeO, minor isomer, $^3J_{HP}$ = 9.2 Hz, 6H, 2MeO, major isomer), 3.24 (d, $^2J_{HP}$ = 22.7 Hz, 2H, CH₂, major isomer, $^2J_{HP}$ = 22.7 Hz, 2H, CH₂, minor isomer).

^{13}C NMR (101 MHz, CDCl₃, 298 K) δ [ppm] 160.9 (s, aromatic, C(OMe), major isomer), 160.6 (s, aromatic, C(OMe), minor isomer), 155.6 (s, C=O, minor isomer, C=O, major isomer), 144.0 (d, $^2J_{CP}$ = 10.5 Hz, C=N), 129.5 (d, $^3J_{CP}$ = 3.8 Hz, C, aromatic), 128.1 (s, aromatic, 2CH, minor isomer), 127.7 (s, aromatic, 2CH, major isomer), 115.0 (s, aromatic, 2CH, minor isomer), 113.9 (s, aromatic, 2CH, major isomer), 55.4 (s, Me, minor isomer, Me, major isomer), 53.6 (d, $^2J_{CP}$ = 4.7 Hz, MeO, major isomer, $^2J_{CP}$ = 4.7 Hz, MeO, minor isomer), 52.8 (s, Me, minor isomer, Me, major isomer), 35.8 (d, $^1J_{CP}$ = 138.0 Hz, CH₂, minor isomer), 27.1 (d, $^1J_{CP}$ = 136.0 Hz, CH₂, major isomer).

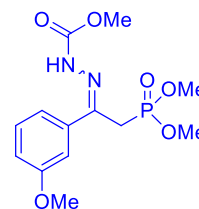
^{31}P NMR (162 MHz, CDCl₃, 298 K) δ [ppm] 26.80 (major isomer), 26.63 (minor isomer).

IR (ATR) ν [cm⁻¹] 3174 (w), 2958 (w), 2908 (w), 2852 (w), 2837 (w), 1737 (vs), 1610 (s), 1544 (s), 1510 (s), 1442 (s), 1398 (s), 1325 (s), 1240 (vs), 1174 (vs), 1018 (vs), 966 (s), 879 (s), 831 (s), 802 (s), 775 (s), 756 (s), 738 (s), 630 (s), 582 (s), 532 (s).

Anal. Calcd for C₁₃H₁₉N₂O₆P: C, 47.28; H, 5.80; N 8.48. Found: C, 47.21; H, 5.89; N 8.48.

Methyl 2-(2-(dimethoxyphosphoryl)-1-(3-methoxyphenyl)ethylidene)hydrazine-1-carboxylate (Vc).

Mixture of isomers 7.1:1. Yield: 8.18 g (99%), yellow solid,
m.p. 96-98 °C (toluene).



¹H NMR (400 MHz, CDCl₃, 298 K) δ [ppm] 9.89 (br.s, 1H, NH, major isomer), 7.88 (br.s, 1H, NH, minor isomer), 7.35-7.11 (m, 3H, aromatic, minor isomer, 3H, aromatic, major isomer), 6.96-6.76 (m, 1H, aromatic, minor isomer, 1H, aromatic, major isomer), 3.77 (s, 6H, 2Me, minor isomer, 6H, 2Me, major isomer), 3.68 (d, ³J_{HP} = 11.2 Hz, 6H, 2MeO, minor isomer, ³J_{HP} = 11.2 Hz, 6H, 2MeO, major isomer), 3.27 (d, ²J_{HP} = 22.0 Hz, 2H, CH₂, major isomer, ²J_{HP} = 22.0 Hz, 2H, CH₂, minor isomer).

¹³C NMR (101 MHz, CDCl₃, 298 K) δ [ppm] 160.5 (s, aromatic, C(OMe), minor isomer), 159.8 (s, aromatic, C(OMe), major isomer), 155.5 (s, C=O, minor isomer, C=O, major isomer), 143.7 (d, ²J_{CP} = 10.5 Hz, C=N, minor isomer, ²J_{CP} = 10.5 Hz, C=N, major isomer), 138.5 (d, ³J_{CP} = 3.8 Hz, C, minor isomer, ³J_{CP} = 3.8 Hz, C, major isomer), 129.5 (s, aromatic, CH, major isomer), 129.1 (s, aromatic, CH, minor isomer), 119.1 (s, aromatic, CH, major isomer), 119.0 (s, aromatic, CH, minor isomer), 115.6 (s, aromatic, CH, major isomer, aromatic, CH, minor isomer), 111.9 (s, aromatic, CH, major isomer, aromatic, CH, minor isomer), 55.4 (s, Me, minor isomer, Me, major isomer), 53.7 (d, ²J_{CP} = 5.7 Hz, MeO), 52.9 (s, Me), 35.6 (d, ¹J_{CP} = 138.0 Hz, CH₂, minor isomer), 27.5 (d, ¹J_{CP} = 137.1 Hz, CH₂, major isomer).

³¹P NMR (162 MHz, CDCl₃, 298 K) δ [ppm] 26.65 (major isomer), 26.45 (minor isomer).

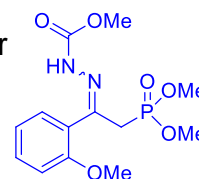
IR (ATR) ν [cm⁻¹] 3217 (w), 3003 (w), 2954 (w), 2852 (w), 1743 (s), 1720 (s), 1598 (m), 1575 (m), 1531 (s), 1487 (s), 1448 (s), 1431 (s), 1359 (m), 1220 (vs), 1182 (s), 1024 (vs), 974 (s), 910 (s), 860 (s), 806 (s), 786 (s), 727 (vs), 688 (s).

Anal. Calcd for C₁₃H₁₉N₂O₆P: C, 47.28; H, 5.80; N 8.48. Found: C, 47.28; H, 5.80; N 8.48.

Methyl 2-(2-(dimethoxyphosphoryl)-1-(2-methoxyphenyl)ethylidene)hydrazine-1-carboxylate (Vd).

Mixture of isomers 2.7:1. Yield: 8.17 g (99%), yellow solid, m.p. 89-91 °C (toluene).

¹H NMR (400 MHz, CDCl₃, 298 K) δ [ppm] 9.92 (br.s, 1H, NH, major isomer), 7.73 (br.s, 1H, NH, minor isomer), 7.38-6.81 (m, 4H, aromatic, minor isomer, 4H, aromatic, major isomer), 3.76 (s, 6H, 2Me, minor isomer, 6H, 2Me, major isomer), 3.60 (d, ³J_{HP} = 11.1 Hz, 6H, 2MeO, minor isomer, ³J_{HP} = 11.1 Hz, 6H, 2MeO, major isomer), 3.39 (d, ²J_{HP} = 22.4 Hz, 2H, CH₂, major isomer, ²J_{HP} = 22.4 Hz, 1H, CH₂, minor isomer), 3.22 (d, ²J_{HP} = 22.4 Hz, 1H, CH₂, minor isomer).

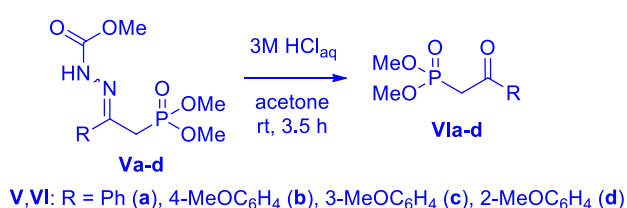


¹³C NMR (101 MHz, CDCl₃, 298 K) δ [ppm] 157.1 (s, aromatic, C(OMe), major isomer), 156.2 (s, C=O, minor isomer), 155.9 (s, aromatic, C(OMe), minor isomer), 155.5 (s, C=O, major isomer), 145.7 (d, ²J_{CP} = 10.5 Hz, C=N), 131.7 (s, aromatic, CH, minor isomer), 131.1 (s, aromatic, CH, major isomer), 130.9 (s, aromatic, CH, major isomer), 129.0 (s, aromatic, CH, minor isomer), 127.6 (s, aromatic, C, major isomer), 121.3 (s, aromatic, CH, minor isomer), 120.9 (s, aromatic, CH, major isomer), 120.7 (s, aromatic, C, minor isomer), 111.9 (s, aromatic, CH, minor isomer), 110.9 (s, aromatic, CH, major isomer), 55.7 (s, Me, minor isomer), 55.5 (s, Me, major isomer), 53.2 (d, ²J_{CP} = 5.7 Hz, MeO, major isomer), 52.8 (s, Me, minor isomer, major isomer), 52.7 (d, ²J_{CP} = 5.7 Hz, MeO, minor isomer), 34.9 (d, ¹J_{CP} = 138.0 Hz, CH₂, minor isomer), 29.5 (d, ¹J_{CP} = 134.2 Hz, CH₂, major isomer).

^{31}P NMR (162 MHz, CDCl_3 , 298 K) δ [ppm] 27.55 (major isomer), 27.00 (minor isomer).
 IR (ATR) ν [cm^{-1}] 3211 (w), 2999 (w), 2953 (w), 1747 (s), 1720 (s), 1598 (m), 1579 (w), 1490 (s), 1458 (s), 1436 (s), 1359 (m), 1303 (m), 1236 (vs), 1220 (vs), 1020 (vs), 968 (s), 879 (s), 842 (s), 802 (s), 752 (vs).

Anal. Calcd for $\text{C}_{13}\text{H}_{19}\text{N}_2\text{O}_6\text{P}$: C, 47.28; H, 5.80; N 8.48. Found: C, 47.28; H, 5.80; N 8.48.

General procedure for the synthesis of β -keto phosphonates **Via-d**.

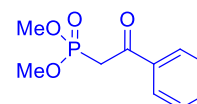


Scheme S4: Synthesis of β -keto phosphonates **Via-d**

Hydrochloric acid (3M, 12 mL) was added to a solution of methyl 2-[2-(dimethoxyphosphoryl)-1-arylethylidene]hydrazinecarboxylate **Va-d** (20 mmol) in acetone (12 mL). The resulting mixture was stirred for 3.5 h at rt, then the acetone was removed in vacuo and the residue was extracted with CHCl_3 (3 \times 50 mL). The combined organic layers were dried (Na_2SO_4) and evaporated to give the β -keto phosphonates.

Dimethyl (2-oxo-2-phenylethyl)phosphonate (**Vla**).

Yield: 2.26 g (99%); pale yellow oil.



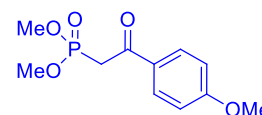
^1H NMR (400 MHz, CDCl_3 , 298 K) δ [ppm] 7.93-7.90 (m, 2H, Ph), 7.53-7.48 (m, 1H, Ph), 7.41-7.36 (m, 2H, Ph), 3.68 (d, $^3J_{\text{HP}}$ = 11.2 Hz, 6H, CH_3O), 3.57 (d, $^2J_{\text{HP}}$ = 22.7 Hz, 2H, CH_2).

^{13}C NMR (101 MHz, CDCl_3 , 298 K) δ [ppm] 191.8 (s, C=O), 136.4 (s, C, Ph), 133.8 (s, CH, Ph), 129.0 (s, CH, Ph), 128.7 (s, CH, Ph), 53.2 (d, CH_3O , $^2J_{\text{CP}} = 1.9$ Hz), 37.5 (d, CH_2 , $^1J_{\text{CP}} = 130.6$ Hz).

^{31}P NMR (162 MHz, CDCl_3 , 298 K) δ [ppm] 23.44.

Anal. Calcd for $\text{C}_{10}\text{H}_{13}\text{O}_4\text{P}$: C, 52.64; H, 5.74. Found: C, 52.58; H, 5.81.

Dimethyl [2-(4-methoxyphenyl)-2-oxoethyl]phosphonate (VIb).



Yield: 2.45 g (95%); pale yellow oil.

^1H NMR (400 MHz, CDCl_3 , 298 K) δ [ppm] 7.75 (d, $^3J_{\text{HH}} = 9.0$ Hz, 2H, aromatic), 6.71 (d, $^3J_{\text{HH}} = 9.0$ Hz, 2H, aromatic), 3.63 (s, 3H, CH_3O), 3.54 (d, $^3J_{\text{HP}} = 11.2$ Hz, 6H, CH_3O), 3.39 (d, $^2J_{\text{HP}} = 22.7$ Hz, 2H, CH_2).

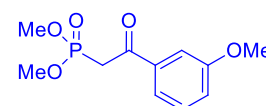
^{13}C NMR (101 MHz, CDCl_3 , 298 K) δ [ppm] 190.0 (d, $^2J_{\text{CP}} = 5.7$ Hz, C=O), 164.0 (s, C, aromatic), 131.3 (s, CH, aromatic), 129.3 (d, $^3J_{\text{CP}} = 2.9$ Hz, C, aromatic), 113.8 (s, CH, aromatic), 54.4 (s, CH_3O), 53.5 (d, $^2J_{\text{CP}} = 5.7$ Hz, CH_3O), 36.5 (d, $^1J_{\text{CP}} = 129.6$ Hz, CH_2).

^{31}P NMR (162 MHz, CDCl_3 , 298 K) δ [ppm] 23.87.

IR (ATR) ν [cm^{-1}] 3007 (w), 2955 (w), 2845 (w), 1667 (s), 1597 (s), 1574 (m), 1512 (m), 1460 (m), 1421 (m), 1315 (m), 1283 (m), 1250 (vs), 1173 (s), 1134 (m), 1113 (m), 1053 (s), 1020 (vs), 989 (vs), 878 (m), 829 (s), 799 (vs), 721 (m), 644 (w), 631 (w), 567 (s), 517 (s).

Anal. Calcd for $\text{C}_{11}\text{H}_{15}\text{O}_5\text{P}$: C, 51.17; H, 5.86. Found: C, 51.07; H, 5.89.

Dimethyl [2-(3-methoxyphenyl)-2-oxoethyl]phosphonate (VIc).



Yield: 2.45 g (95%); pale yellow oil.

^1H NMR (400 MHz, CDCl_3 , 298 K) δ [ppm] 7.55-7.44 (m, 1H, CH), 7.38-7.31 (m, 2H, CH), 7.02-6.95 (m, 1H, CH), 3.67 (s, 3H, CH_3O), 3.52 (d, $^3J_{\text{HP}} = 11.2$ Hz, 6H, CH_3O), 3.36 (d, $^2J_{\text{HP}} = 22.7$ Hz, 2H, CH_2).

^{13}C NMR (101 MHz, CDCl_3 , 298 K) δ [ppm] 192.5 (d, $^2J_{\text{CP}} = 5.8$ Hz, C=O), 161.2 (s, C, aromatic), 137.1 (s, C, aromatic), 133.1 (s, CH, aromatic), 123.6 (s, CH, aromatic),

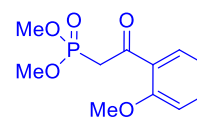
121.3 (s, CH, aromatic), 113.0 (s, CH, aromatic), 54.3 (s, CH₃O), 53.3 (d, ²J_{CP} = 5.7 Hz, CH₃O), 36.2 (d, ¹J_{CP} = 129.6 Hz, CH₂).

³¹P NMR (162 MHz, CDCl₃, 298 K) δ [ppm] 23.87.

IR (ATR) ν [cm⁻¹] 2999 (w), 2954 (w), 2853 (w), 1678 (s), 1597 (m), 1584 (m), 1487 (m), 1450 (m), 1429 (m), 1252 (vs), 1182 (s), 1128 (w), 1022 (vs), 864 (s), 841 (s), 791 (vs), 746 (vs), 685 (m), 665 (m), 596 (w), 542 (m), 517 (s).

Anal. Calcd for C₁₁H₁₅O₅P: C, 51.17; H, 5.86. Found: C, 51.11; H, 5.93.

Dimethyl [2-(2-methoxyphenyl)-2-oxoethyl]phosphonate (VId).



Yield: 2.38 g (92%), pale yellow oil.

¹H NMR (400 MHz, CDCl₃, 298 K) δ [ppm] 7.69 (dd, ³J_{HH} = 7.3 Hz, ⁴J_{HH} = 1.6 Hz, 1H, aromatic), 7.45 (dt, ³J_{HH} = 7.9 Hz, ⁴J_{HH} = 1.8 Hz, 1H, aromatic), 6.98-6.92 (m, 2H, aromatic), 3.89 (s, 3H, CH₃O), 3.78 (d, ²J_{HP} = 21.5 Hz, 2H, CH₂), 3.70 (d, ³J_{HP} = 11.2 Hz, 6H, CH₃O).

¹³C NMR (101 MHz, CDCl₃, 298 K) δ [ppm] 193.4 (d, ²J_{CP} = 6.7 Hz, C=O), 158.8 (s, C, aromatic), 134.6 (s, CH, aromatic), 131.0 (s, CH, aromatic), 127.4 (d, ³J_{CP} = 3.4 Hz, C, aromatic), 120.9 (s, CH, aromatic), 111.7 (s, CH, aromatic), 55.7 (s, CH₃O), 52.9 (d, ²J_{CP} = 1.9 Hz, CH₃O), 41.2 (d, ¹J_{CP} = 131.6 Hz, CH₂).

³¹P NMR (162 MHz, CDCl₃, 298 K) δ [ppm] 24.79.

IR (ATR) ν [cm⁻¹] 3003 (w), 2953 (w), 2851 (w), 1667 (m), 1597 (m), 1578 (w), 1485 (m), 1464 (m), 1437 (m), 1395 (w), 1296 (s), 1242 (vs), 1182 (m), 1163 (m), 1144 (w), 1101 (w), 1018 (vs), 1001 (vs), 876 (m), 843 (m), 800 (s), 756 (vs), 731 (s), 700 (m), 662 (w), 586 (m), 513 (m).

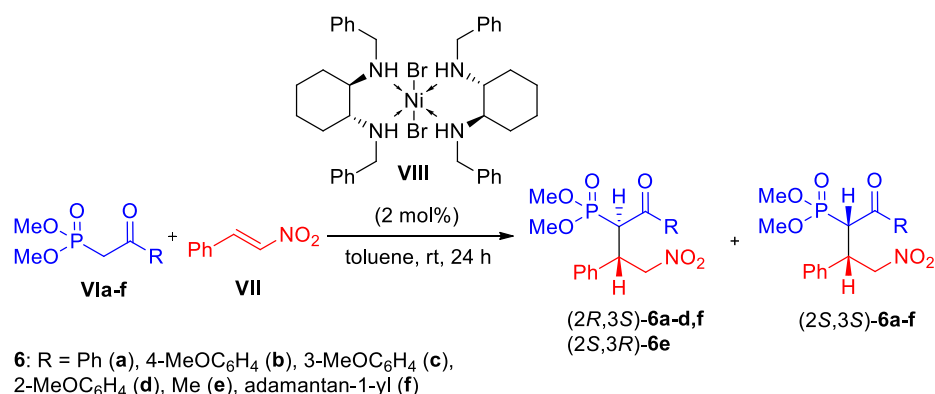
Anal. Calcd for C₁₁H₁₅O₅P: C, 51.17; H, 5.86. Found: C, 51.09; H, 5.92.

3. Catalysis

General procedure for catalytic asymmetric Michael addition of β -keto phosphonates to ω -nitrostyrene in the presence of a Ni(II) complex.

A mixture of β -keto phosphonate **Vla–f** (8.10 mmol), ω -nitrostyrene **VII** (8.90 mmol) and bis[(1*R*,2*R*)-*N,N*-dibenzylcyclohexane-1,2-diamine- κ^2N,N'](dibromo)nickel **VIII** (0.16 mmol) in 10 mL of toluene was stirred at rt for 24 h. The formed crystalline product was filtered and recrystallized from appropriate solvent (MeOH for **6a,d,e,f**; EtOH for **6c**; toluene for **6b**) to give an individual diastereomer.

Table S1: Asymmetric Michael addition of β -keto phosphonates to ω -nitrostyrene in the presence of bis[(1*R*,2*R*)-*N,N*-dibenzylcyclohexane-1,2-diamine- κ^2N,N'](dibromo)nickel



Entry	R	Compd.	Conv., %	dr ^a	ee ^a , %	Yield ^b , %	dr ^c	ee ^c , %
1 ^d	Ph	6a	90	37/1	>99	45	37/1	>99
2	4-MeOC ₆ H ₄	6b	92	13/1	97	46	1/–	98
3	3-MeOC ₆ H ₄	6c	87	12/1	86	45	14/1	>99
4	2-MeOC ₆ H ₄	6d	82	1/2	83	50	–/1	98
5	Me	6e	86	1.2/1	ND ^e	46	11/1	>99 ^f
6 ^d	1-Ad	6f	81	1/1.8	85	21	1/25	>99

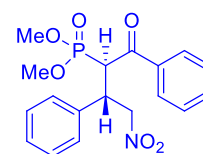
^adr (by ³¹P NMR) and ee (by chiral HPLC) in reaction mixture; ^bisolated yield; ^cdr (by ³¹P NMR) and ee (by chiral HPLC) after crystallization; ^dpreviously reported data [2,5]; ^enot determined; ^fThe enantiomeric excess for compound **6e** could not be determined by HPLC due to overlapping peaks of the corresponding enantiomers in the chromatograms. For this reason, the value of the ee was determined on the basis of HPLC analysis of its derivative - compound **13b** (see below).

The absolute (2*R*,3*S*)-configuration of compound **6a** was determined earlier by X-ray diffraction analysis [5]. The absolute configurations of other Michael adducts **6b–f** were assumed by analogy and is additionally confirmed by X-ray diffraction data for **13b** (see below), since the absolute configuration of the stereo center at C-2 in **6e** does not change during the transformation of **6e** to **13b**. The relative configurations of **6b–f** were also confirmed by comparing the NMR spectra of these compounds and **6a**. For (2*R*,3*S*)-isomers the values of ³J_{HH} for proton at 2-C were 6.6–6.9 Hz, while for (2*S*,3*S*)-isomers these values were 11 Hz. A characteristic difference in the values of the spin – spin coupling constants was previously observed for structurally similar phosphonates [5] and sulfones [6].

Dimethyl [(2*R*,3*S*)-4-nitro-1-oxo-1,3-diphenylbutan-2-yl]phosphonate (**6a**) [5]

Yield: 1.13 g (45%), white crystals, m.p. 160–162 °C (methanol).

[α]_D²⁰ -40.0 (c 2.5, CHCl₃), dr 1:-, > 99% ee.



¹H NMR (400 MHz, CDCl₃, 298 K) δ [ppm] 7.79-7.77 (m, 2H, aromatic), 7.56-7.52 (m, 1H, aromatic), 7.42-7.38 (m, 2H, aromatic), 7.27-7.18 (m, 5H, aromatic), 5.14-5.01 (m, 2H, H-4), 4.63 (dd, ²J_{HP} = 23.6 Hz, ³J_{HH} = 7.2 Hz, 1H, H-2), 4.42-4.30 (m, 1H, H-3), 3.55 (d, ³J_{HP} = 10.4 Hz, 3H, MeO), 3.52 (d, ³J_{HP} = 10.0 Hz, 3H, MeO).

¹³C NMR (101 MHz, CDCl₃, 298 K) δ [ppm] 195.5 (d, ²J_{CP} = 4.8 Hz, C-1), 137.43 (d, ³J_{CP} = 9.5 Hz, aromatic, C), 137.27 (s, aromatic, C), 134.1 (s, aromatic, CH), 129.1 (s,

aromatic, 2CH), 128.9 (s, aromatic, 2CH), 128.7 (s, aromatic, 2CH), 128.4 (s, aromatic, CH), 128.0 (s, aromatic, 2CH), 77.4 (s, C-4), 53.7 (d, $^2J_{CP}$ = 6.6 Hz, MeO), 53.5 (d, $^2J_{CP}$ = 7.6 Hz, MeO), 50.3 (d, $^1J_{CP}$ = 128.5 Hz, C-2), 43.0 (d, $^2J_{CP}$ = 2.9 Hz, C-3).

^{31}P NMR (162 MHz, CDCl_3 , 298 K) δ [ppm] 22.48.

IR (ATR) ν [cm^{-1}] 3063 (w), 2949 (w), 2853 (w), 1674 (s), 1597 (w), 1545 (s), 1449 (w), 1383 (w), 1250 (s), 1045 (s), 968 (m), 858 (w), 849 (w), 783 (m), 706 (m), 519 (m).

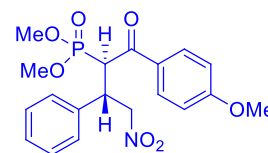
HRMS (APPI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{20}\text{NO}_6\text{P}\cdot\text{H}^+$: 378.1101; found: 378.1101.

HPLC analysis (CHIRALPAK AD-3 column; hexane/2-propanol, 80:20; flow rate 1.0 mL/min; wavelength 230 nm): t_R = 9.7 (2*R*,3*S*), 22.3 (2*S*,3*R*) min.

Dimethyl [(2*R*,3*S*)-1-(4-methoxyphenyl)-4-nitro-1-oxo-3-phenylbutan-2-yl]-phosphonate (6b).

Yield: 1.51 g (46%), white crystals, m.p. 136–138 °C (toluene).

$[\alpha]_D^{20}$ -75.8 (c 1.0, CHCl_3), 98% ee.



^1H NMR (400 MHz, CDCl_3 , 298 K) δ [ppm] 7.79 (d, $^3J_{HH}$ = 9.0 Hz, 2H, aromatic), 7.29–7.19 (m, 5H, aromatic), 6.87 (d, $^3J_{HH}$ = 9.0 Hz, 2H, aromatic), 5.16–5.01 (m, 2H, H-4), 4.56 (dd, $^2J_{HP}$ = 23.2 Hz, $^3J_{HH}$ = 6.4 Hz, 1H, H-2), 4.39–4.31 (m, 1H, H-3), 3.84 (s, 3H, MeO), 3.58 (d, $^3J_{HP}$ = 11.2 Hz, 3H, MeO), 3.55 (d, $^3J_{HP}$ = 11.2 Hz, 3H, MeO).

^{13}C NMR (101 MHz, CDCl_3 , 298 K) δ [ppm] 193.5 (d, $^2J_{CP}$ = 4.8 Hz, C-1), 164.4 (s, aromatic, C), 137.6 (d, $^3J_{CP}$ = 10.5 Hz, aromatic, C), 131.3 (s, aromatic, 2CH), 130.3 (d, $^3J_{CP}$ = 1.9 Hz, aromatic, C), 129.1 (s, aromatic, 2CH), 128.3 (s, aromatic, CH), 128.0 (s, aromatic, 2CH), 114.1 (s, aromatic, 2CH), 77.3 (s, C-4), 55.7 (s, MeO), 53.7 (d, $^2J_{CP}$ = 6.7 Hz, MeO), 53.5 (d, $^2J_{CP}$ = 5.7 Hz, MeO), 49.9 (d, $^1J_{CP}$ = 129.4 Hz, C-2); 43.0 (d, $^2J_{CP}$ = 3.8 Hz, C-3).

^{31}P NMR (162 MHz, CDCl_3 , 298 K) δ [ppm] 23.87.

IR (ATR) ν [cm^{-1}] 3063 (w), 3008 (w), 2955 (w), 2843 (w), 1667 (vs), 1597 (vs), 1551 (vs), 1516 (m), 1458 (m), 1435 (m), 1381 (m), 1334 (m), 1311 (m), 1269 (vs), 1242 (vs), 1172 (vs), 1061 (vs), 1018 (vs), 972 (m), 837 (m), 818 (m), 702 (m).

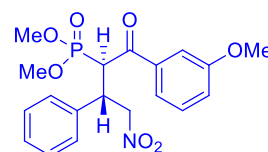
HRMS (APPI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{22}\text{NO}_7\text{P}\cdot\text{H}^+$: 408.1207; found: 408.1212.

HPLC analysis (CHIRALPAK AD-3R column; water/acetonitrile, gradient: 0.1 min 30% acetonitrile to 50 min 100% acetonitrile; flow rate 0.2 mL/min; wavelength 230 nm): t_R = 13.3 (2*R*,3*S*), 16.3 (2*S*,3*R*) min.

Dimethyl [(2*R*,3*S*)-1-(3-methoxyphenyl)-4-nitro-1-oxo-3-phenylbutan-2-yl]phosphonate (6c).

Yield: 1.49 g (45%), white crystals, m.p. 120–121 °C (EtOH).

$[\alpha]_D^{20}$ -54.6 (c 1.0, CHCl_3), dr 14:1, >99% ee.



^1H NMR (400 MHz, CDCl_3 , 298 K) δ [ppm] 7.32-7.20 (m, 8H, aromatic), 7.09-7.05 (m, 1H, aromatic), 5.14-5.00 (m, 2H, H-4), 4.58 (dd, $^2J_{\text{HP}}$ = 23.2 Hz, $^3J_{\text{HH}}$ = 6.8 Hz, 1H, H-2), 4.44-4.32 (m, 1H, H-3), 3.79 (s, 3H, MeO), 3.57 (d, $^3J_{\text{HP}}$ = 9.0 Hz, 3H, MeO), 3.54 (d, $^3J_{\text{HP}}$ = 9.0 Hz, 3H, MeO).

^{13}C NMR (101 MHz, CDCl_3 , 298 K) δ [ppm] 195.3 (d, $^2J_{\text{CP}}$ = 4.7 Hz, C-1), 159.9 (s, aromatic), 138.7 (s, aromatic), 137.5 (d, $^3J_{\text{CP}}$ = 10.6 Hz, aromatic), 129.8 (s, aromatic), 129.1 (s, aromatic), 128.4 (s, aromatic), 128.0 (s, aromatic), 121.4 (s, aromatic), 120.6 (s, aromatic), 112.8 (s, aromatic), 77.3 (s, C-4), 55.5 (s, MeO), 53.7 (d, $^2J_{\text{CP}}$ = 7.2 Hz, MeO), 53.5 (d, $^2J_{\text{CP}}$ = 7.2 Hz, MeO), 50.6 (d, $^1J_{\text{CP}}$ = 128.5 Hz, C-2), 43.0 (d, $^2J_{\text{CP}}$ = 2.8 Hz, C-3).

^{31}P NMR (162 MHz, CDCl_3 , 298 K) δ [ppm] 22.47.

IR (ATR) ν [cm^{-1}] 3049 (w), 3022 (w), 2961 (w), 2839 (w), 1710 (m), 1670 (s), 1597 (m), 1549 (vs), 1454 (m), 1429 (m), 1381 (m), 1269 (s), 1250 (s), 1234 (s), 1217 (s), 1167 (s), 1057 (s), 1043 (vs), 1030 (vs), 1009 (vs), 878 (m), 851 (m), 826 (m), 795 (vs), 758 (s), 698 (vs), 679 (s), 638 (m), 553 (m), 513 (vs).

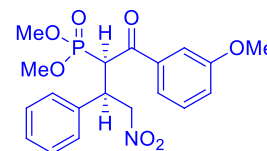
HRMS (APPI): m/z $[M+H]^+$ calcd for $C_{19}H_{22}NO_7P \cdot H^+$: 408.1207; found: 408.1213.

HPLC analysis (CHIRALPAK AD-3 column; hexane/2-propanol, 80:20; flow rate 1.2 mL/min; wavelength 210 nm): t_R = 11.7 (2*R*,3*S*), 22.3 (2*S*,3*R*) min.

For (2*R*,3*R*)-isomer:

Yield: 1.19 g (36%), white crystals, m.p. 124–125 °C (MeOH).

$[\alpha]_D^{20}$ +51.3 (c 1.0, $CHCl_3$), dr 8:1, >99% ee.



1H NMR (400 MHz, $CDCl_3$, 298 K) δ [ppm] 7.31-6.99 (m, 9H, aromatic), 5.24 (dd, $^2J_{HH}$ = 13.2 Hz, $^3J_{HH}$ = 4.0 Hz, 1H, H-4), 4.92 (dd, $^2J_{HH}$ = 12.8 Hz, $^3J_{HH}$ = 10.4 Hz, 1H, H-4), 4.64 (dd, $^2J_{HP}$ = 20.4 Hz, $^3J_{HH}$ = 11.6 Hz, 1H, H-2), 4.44-4.36 (m, 1H, H-3), 3.82 (d, $^3J_{HP}$ = 10.8 Hz, 3H, MeO), 3.76 (s, 3H, MeO), 3.72 (d, $^3J_{HP}$ = 11.2 Hz, 3H, MeO).

^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ [ppm] 194.0 (d, $^2J_{CP}$ = 5.8 Hz, C-1), 159.8 (s, aromatic, C(OMe)), 138.6 (s, aromatic, C), 136.9 (d, $^3J_{CP}$ = 15.3 Hz, aromatic, C), 129.7 (s, aromatic, CH), 129.0 (s, aromatic, 2CH), 128.2 (s, aromatic, CH), 128.0 (s, aromatic, 2CH), 120.9 (s, aromatic, CH), 120.2 (s, aromatic, CH), 112.6 (s, aromatic, CH), 78.8 (s, C-4), 55.5 (s, MeO), 54.0 (d, $^2J_{CP}$ = 6.7 Hz, MeO), 53.8 (d, $^2J_{CP}$ = 7.6 Hz, MeO), 49.6 (d, $^1J_{CP}$ = 125.5 Hz, C-2), 43.3 (d, $^2J_{CP}$ = 3.9 Hz, C-3).

^{31}P NMR (162 MHz, $CDCl_3$, 298 K) δ [ppm] 22.62.

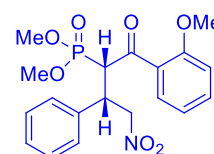
IR (ATR) ν [cm^{-1}] 3047 (w), 2960 (w), 1670 (vs), 1597 (vs), 1548 (vs), 1489 (s), 1454 (s), 1429 (s), 1381 (s), 1269 (s), 1234 (vs), 1217 (vs), 1029 (vs), 1008 (vs), 875 (s), 850 (s), 825 (s), 794 (vs), 758 (vs), 698 (vs), 677 (s).

HPLC analysis (CHIRALPAK AD-3 column; hexane/2-propanol, 80:20; flow rate 1.2 mL/min; wavelength 210 nm): t_R = 9.3 (2*S*,3*S*), 12.8 (2*R*,3*R*) min.

Dimethyl [(2*S*,3*S*)-1-(2-methoxyphenyl)-4-nitro-1-oxo-3-phenylbutan-2-yl]phosphonate (6d).

Yield: 1.65 g (50%), white crystals, m.p. 138–139 °C (MeOH).

$[\alpha]_D^{20}$ -88.7 (c 1.0, $CHCl_3$), dr 1:-, 98% ee.



^1H NMR (400 MHz, CDCl_3 , 298 K) δ [ppm] 7.40-7.33 (m, 2H, aromatic), 7.20-7.05 (m, 5H, aromatic), 6.92-6.80 (m, 2H, aromatic), 5.22 (dd, $^2J_{\text{HH}} = 13.6$ Hz, $^3J_{\text{HH}} = 4.4$ Hz, 1H, H-4), 5.18 (dd, $^2J_{\text{HH}} = 21.6$ Hz, $^3J_{\text{HH}} = 10.8$ Hz, 1H, H-4), 4.93 (dd, $^2J_{\text{HP}} = 13.6$ Hz, $^3J_{\text{HH}} = 10.8$ Hz, 1H, H-2), 4.41-4.32 (m, 1H, H-3), 3.92 (s, 3H, MeO), 3.79 (d, $^3J_{\text{HP}} = 11.0$ Hz, 3H, MeO), 3.65 (d, $^3J_{\text{HP}} = 11.0$ Hz, 3H, MeO).

^{13}C NMR (101 MHz, CDCl_3 , 298 K) δ [ppm] 195.0 (d, $^2J_{\text{CP}} = 5.7$ Hz, C-1), 158.1 (s, aromatic), 137.4 (d, $^3J_{\text{CP}} = 14.3$ Hz, aromatic), 134.5 (s, aromatic), 131.3 (s, aromatic), 128.6 (s, aromatic), 128.3 (s, aromatic), 127.9 (s, aromatic), 127.6 (s, aromatic), 121.0 (s, aromatic), 111.7 (s, aromatic), 78.9 (s, C-4), 55.8 (d, $^2J_{\text{CP}} = 2.9$ Hz, MeO), 53.6 (s), 53.4 (s), 53.3 (d, $^1J_{\text{CP}} = 125.6$ Hz, C-2), 43.4 (d, C-3, $^2J_{\text{CP}} = 3.8$ Hz, C-3).

^{31}P NMR (162 MHz, CDCl_3 , 298 K) δ [ppm] 23.82.

IR (ATR) ν [cm^{-1}] 3050 (w), 3021 (w), 2959 (w), 2851 (w), 1674 (vs), 1597 (m), 1543 (vs), 1485 (m), 1443 (m), 1385 (m), 1323 (m), 1300 (m), 1242 (vs), 1196 (m), 1061 (s), 1026 (vs), 841 (w), 814 (m), 764 (s), 702 (m).

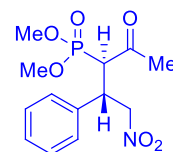
HRMS (APPI): m/z [$\text{M}+\text{H}$] $^+$ calcd for $\text{C}_{19}\text{H}_{22}\text{NO}_7\text{P}\cdot\text{H}^+$: 408.1207; found: 408.1214.

HPLC analysis (CHIRALPAK AD-3 column; hexane/2-propanol, 85:15; flow rate 1.2 mL/min; wavelength 210 nm): $t_R = 15.1$ (2*S*,3*S*), 17.5 (2*R*,3*R*) min.

Dimethyl [(2*S*,3*R*)-1-nitro-4-oxo-2-phenylpentan-3-yl]phosphonate (6e).

Yield: 1.17 g (46%), white crystals, m.p. 130–132 °C (MeOH).

$[\alpha]_D^{20} +70.7$ (c 1.0, CHCl_3), dr 11:1.



^1H NMR (400 MHz, CDCl_3 , 298 K) δ [ppm] 7.32-7.19 (m, 5H, Ph) 5.02 (dd, $^2J_{\text{HH}} = 13.4$ Hz, $^3J_{\text{HH}} = 9.5$ Hz, 1H, H-1), 4.88 (dd, $^2J_{\text{HH}} = 13.4$ Hz, $^3J_{\text{HH}} = 3.4$ Hz, 1H, H-1), 4.12-4.05 (m, 1H, H-2), 3.85-3.75 (m, 1H, H-3), 3.59 (d, $^3J_{\text{HP}} = 4.0$ Hz, 3H, MeO), 3.56 (d, $^3J_{\text{HP}} = 4.0$ Hz, 3H, MeO), 2.23 (s, 3H, H-5).

^{13}C NMR (101 MHz, CDCl_3 , 298 K) δ [ppm] 203.4 (d, $^2J_{\text{CP}} = 3.8$ Hz, C-4), 137.4 (d, $^3J_{\text{CP}} = 9.5$ Hz, Ph), 129.2 (s, Ph), 128.4 (s, Ph), 127.9 (s, Ph), 127.8 (s, Ph), 77.1 (d, $^3J_{\text{CP}} =$

7.6 Hz, C-1), 55.7 (d, $^1J_{CP}$ = 125.6 Hz, C-3), 53.9 (d, $^2J_{CP}$ = 6.6 Hz, MeO), 53.1 (d, $^2J_{CP}$ = 6.6 Hz, MeO), 42.2 (d, $^2J_{CP}$ = 2.8 Hz, C-2), 33.1 (s, C-5).

^{31}P NMR (162 MHz, CDCl_3 , 298 K) δ [ppm] 21.95.

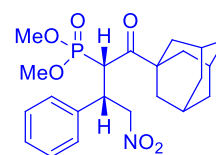
IR (ATR) ν [cm^{-1}] 3050 (w), 3025 (w), 2959 (m), 2840 (w), 1713 (vs), 1547 (vs), 1458 (m), 1439 (m), 1381 (m), 1362 (m), 1250 (vs), 1181 (m), 1157 (m), 1038 (vs), 880 (m), 826 (s), 764 (m), 706 (s), 606 (s).

HRMS (APPI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{13}\text{H}_{19}\text{NO}_6\text{P}\cdot\text{H}^+$ 316.0945; found 316.0944.

Dimethyl [(2S,3S)-1-(adamantan-1-yl)-4-nitro-1-oxo-3-phenylbutan-2-yl]phosphonate (6f) [2]

Yield: 0.74 g (21%), white crystals, m.p. 179–180 °C (MeOH).

$[\alpha]_D^{20}$ -18.6 (c 1.0, CHCl_3), dr 25:1, >99% ee.



^1H NMR (400 MHz, CDCl_3 , 298 K) δ [ppm] 7.32-7.16 (m, 5H, aromatic), 5.16 (dd, $^2J_{HH}$ = 13.2 Hz, $^3J_{HH}$ = 4.4 Hz, 1H, H-4), 4.85 (dd, $^2J_{HH}$ = 13.2 Hz, $^3J_{HH}$ = 11.6 Hz, 1H, H-4), 4.19-4.13 (m, 1H, H-3), 4.02 (dd, $^2J_{HP}$ = 18.4 Hz, $^3J_{HH}$ = 10.8 Hz, 1H, H-2), 3.82 (d, $^3J_{HP}$ = 10.8 Hz, 3H, MeO), 3.79 (d, $^3J_{HP}$ = 11.9 Hz, 3H, MeO), 1.84 (br s, 3H, Ad), 1.66-1.37 (m, 12H, Ad).

^{13}C NMR (101 MHz, CDCl_3 , 298 K) δ [ppm] 209.7 (d, $^2J_{CP}$ = 5.7 Hz, C-1), 137.3 (d, $^3J_{CP}$ = 15.3 Hz, aromatic, C), 129.0 (s, aromatic, 2CH), 128.7 (s, aromatic, 2CH), 128.4 (s, aromatic, CH), 77.0 (s, C-4), 54.0 (d, $^2J_{CP}$ = 6.7 Hz, MeO), 53.4 (d, $^2J_{CP}$ = 6.7 Hz, MeO), 49.5 (d, $^1J_{CP}$ = 124.5 Hz, C-2), 47.4 (s, C-3), 43.7 (d, $^3J_{CP}$ = 4.7 Hz, C, Ad), 37.8 (s, CH_2 , Ad), 36.2 (s, CH_2 , Ad), 27.8 (s, CH, Ad).

^{31}P NMR (162 MHz, CDCl_3 , 298 K) δ [ppm] 23.39.

IR (ATR) ν [cm^{-1}] 3032 (w), 2916 (vs), 2854 (s), 1689 (vs), 1546 (vs), 1496 (m), 1452 (s), 1381 (s), 1344 (m), 1307 (m), 1232 (vs), 1176 (s), 1058 (vs), 1016 (vs), 999 (vs), 867 (s), 821 (s), 812 (s), 775 (s), 759 (s), 744 (s), 702 (s), 555 (s), 528 (s).

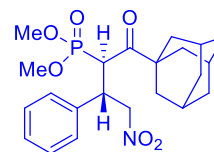
HRMS (APPI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{22}\text{H}_{30}\text{NO}_6\text{P}\cdot\text{H}^+$: 436.1883; found: 436.1892.

HPLC analysis (CHIRALPAK AD-3 column; hexane/2-propanol, 90:10; flow rate 1.2 mL/min; wavelength 210 nm): t_R = 7.8 (2*S*,3*S*), 8.7 (2*R*,3*R*) min.

For (2*R*,3*S*)-isomer:

Yield: 176 mg (5%), white crystals, m.p. 91–93 °C (benzene).

$[\alpha]_D^{20}$ +12.2 (c 1.0, CHCl₃), dr 30:1.



¹H NMR (400 MHz, CDCl₃, 298 K) δ [ppm] 7.31-7.18 (m, 5H, aromatic), 5.05 (d, ² J_{HH} = 7.2 Hz, 2H, H-4), 4.23-4.17 (m, 1H, H-3), 4.15 (dd, ² J_{HP} = 28.4 Hz, ³ J_{HH} = 6.4 Hz, 1H, H-2), 3.66 (d, ³ J_{HP} = 11.2 Hz, 3H, MeO), 3.62 (d, ³ J_{HP} = 11.2 Hz, 3H, MeO), 1.92 (br s, 3H, Ad), 1.65-1.52 (m, 12H, Ad).

¹³C NMR (101 MHz, CDCl₃, 298 K) δ [ppm] 211.2 (d, ² J_{CP} = 4.8 Hz, C-1), 137.5 (d, ³ J_{CP} = 10.5 Hz, aromatic, C), 129.0 (s, aromatic, 2CH), 128.4 (s, aromatic, CH), 128.0 (s, aromatic, 2CH), 77.0 (s, C-4), 54.0 (d, ² J_{CP} = 6.7 Hz, MeO), 53.1 (d, ² J_{CP} = 7.6 Hz, MeO), 49.6 (d, ¹ J_{CP} = 126.5 Hz, C-2), 47.9 (s, C-3), 43.0 (d, ³ J_{CP} = 3.8 Hz, C, Ad), 37.9 (s, CH₂, Ad), 36.2 (s, CH₂, Ad), 27.8 (s, CH, Ad).

³¹P NMR (162 MHz, CDCl₃, 298 K) δ [ppm] 22.78.

IR (ATR) ν [cm⁻¹] 3032 (w), 2904 (vs), 2852 (s), 1687 (vs), 1544 (vs), 1496 (m), 1452 (s), 1381 (s), 1342 (m), 1325 (m), 1249 (vs), 1211 (s), 1145 (m), 1056 (vs), 1016 (vs), 935 (m), 916 (m), 871 (s), 844 (s), 829 (s), 812 (s), 775 (s), 698 (s), 559 (s), 532 (s).

4. Synthesis of pyrrolidin-3-ylphosphonic acids

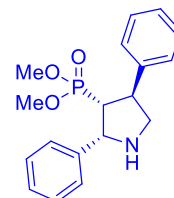
The study of the hydrogenation of phosphonate **6a** under various conditions

A solution of phosphonate **6a** (2.65 mmol) in various solvents (MeOH, EtOH, iPrOH, THF, EtOAc, 9 mL) was transferred in a 100 mL steel autoclave under argon and 10% Pd/C (0.3 g) was added. Argon was replaced with hydrogen with 3 cycles of pressurization (10 bar)/depressurization. The reactor was finally charged with a

pressure of H₂ (30 bar), then left stirring with magnetic stirrer for 36 h at 25 °C. Then the reactor was depressurized. The reaction mixture was diluted by chloroform (30 mL), filtered and evaporated in vacuo. The components of the reaction mixture were separated by column liquid chromatography (eluent – chloroform/ethanol 0–5%) and analyzed by NMR ¹H, ¹³C and ³¹P spectroscopy.

Dimethyl [(2*R*,3*R*,4*S*)-2,4-diphenylpyrrolidin-3-yl]phosphonate (7).

¹H NMR (400 MHz, CDCl₃, 298 K) δ [ppm] 7.52-7.22 (m, 10H, Ph), 4.70 (dd, ³J_{HH} = 8.0 Hz, ³J_{HP} = 25.2 Hz, 1H, H-2), 3.85-3.72 (m, 1H, H-4, 1H, H-5), 3.27 (d, ³J_{HP} = 10.8 Hz, 3H, CH₃O), 3.11-3.03 (m, 1H, H-5), 2.96 (d, ³J_{HP} = 10.4 Hz, 3H, CH₃O), 2.88-2.80 (m, 1H, H-3).

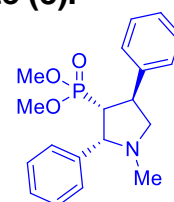


¹³C NMR (101 MHz, CDCl₃, 298 K) δ [ppm] 142.6 (d, ³J_{CP} = 5.8 Hz, C, aromatic), 139.4 (d, ³J_{CP} = 5.7 Hz, C, aromatic), 128.8 (s, 2CH, aromatic), 128.1 (s, 2CH, aromatic), 128.0 (s, 2CH, aromatic), 127.6 (s, 2CH, aromatic), 127.5 (s, CH, aromatic), 127.0 (s, CH, aromatic), 65.4 (s, C-2), 56.2 (d, ³J_{CP} = 8.6 Hz, C-5), 51.88 (d, ²J_{CP} = 6.7 Hz, CH₃O), 51.86 (d, ²J_{CP} = 7.6 Hz, CH₃O), 50.1 (d, ¹J_{CP} = 144.7 Hz, C-3), 47.8 (s, C-4).

³¹P NMR (162 MHz, CDCl₃, 298 K) δ [ppm] 31.49.

Dimethyl [(2*R*,3*R*,4*S*)-1-methyl-2,4-diphenylpyrrolidin-3-yl]phosphonate (8).

¹H NMR (400 MHz, DMSO-*d*₆, 298 K) δ [ppm] 7.44-7.38 (m, 4H, aromatic), 7.31-7.27 (m, 4H, aromatic), 7.22-7.20 (m, 2H, aromatic), 3.77 (dd, ³J_{HH} = 10.0 Hz, ³J_{HP} = 24.0 Hz, 1H, H-2), 3.65-3.53 (m, 1H, H-4), 3.43-3.38 (m, 1H, H-5), 3.03 (d, ³J_{HP} = 10.8 Hz, 3H, MeO), 2.76 (d, ³J_{HP} = 10.8 Hz, 3H, MeO), 2.47-2.46 (m, 1H, H-5, 1H, H-3), 2.04 (s, 3H, Me).



¹³C NMR (101 MHz, DMSO-*d*₆, 298 K) δ [ppm] 142.6 (d, ³J_{HP} = 2.8 Hz, aromatic, C), 139.5 (d, ³J_{HP} = 6.6 Hz, aromatic, C), 130.0 (s, aromatic, 2CH), 128.8 (s, aromatic, 2CH), 128.5 (s, aromatic, 2CH), 127.9 (s, aromatic, 2CH), 127.7 (s, aromatic, CH), 127.2 (s, aromatic, CH), 72.2 (s, C-2), 65.7 (d, ³J_{CP} = 9.6 Hz, C-5), 51.8 (d, ²J_{CP} = 7.6

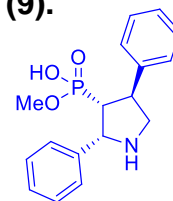
Hz, MeO), 51.7 (d, $^2J_{CP}$ = 6.7 Hz, MeO), 48.4 (d, $^1J_{CP}$ = 146.6 Hz, C-3), 45.0 (d, $^2J_{CP}$ = 1.9 Hz, C-4), 40.3 (s, Me-N).

^{31}P NMR (162 MHz, DMSO- d_6 , 298 K) δ [ppm] 31.52.

IR (ATR) ν [cm^{-1}] 3062 (w), 3028 (w), 2947 (w), 2914 (w), 2850 (w), 2789 (w), 1494 (m), 1452 (m), 1253 (m), 1234 (s), 1215 (s), 1182 (m), 1147 (m), 1066 (vs), 1051 (vs), 1020 (vs), 997 (s), 914 (m), 842 (s), 817 (s), 777 (vs), 761 (s), 754 (s), 698 (vs), 690 (vs).

Methyl hydrogen [(2*R*,3*R*,4*S*)-2,4-diphenylpyrrolidin-3-yl]phosphonate (9).

^1H NMR (400 MHz, D_2O , 298 K) δ [ppm] 7.16-6.96 (m, 10H, aromatic), 4.98 (t, $^3J_{HH}$ = 8.4 Hz, $^3J_{HP}$ = 8.4 Hz, 1H, H-2), 3.80-3.71 (m, 2H, H-5), 3.23-3.16 (m, 1H, H-4), 3.03-2.93 (m, 1H, H-3), 2.74 (d, $^3J_{HP}$ = 11.2 Hz, 3H, MeO).



^{13}C NMR (101 MHz, D_2O , 298 K) δ [ppm] 136.8 (s, aromatic, C), 132.5 (d, $^3J_{CP}$ = 3.8 Hz, aromatic, C), 129.6 (s, aromatic, CH), 129.0 (s, aromatic, CH), 129.0 (s, aromatic, 2CH), 128.7 (s, aromatic, 2CH), 128.1 (s, aromatic, 2CH), 127.7 (s, aromatic, 2CH), 64.2 (d, $^2J_{CP}$ = 13.5 Hz, C-2), 51.8 (s, C-5), 51.8 (d, $^2J_{CP}$ = 14.4 Hz, MeO), 47.0 (d, $^1J_{CP}$ = 150.5 Hz, C-3), 44.4 (s, C-4).

^{31}P NMR (162 MHz, D_2O , 298 K) δ [ppm] 22.67.

IR (ATR) ν [cm^{-1}] 3412 (w), 3062 (w), 2968 (w), 1602 (m), 1587 (m), 1496 (m), 1456 (s), 1203 (vs), 1172 (vs), 1051 (vs), 756 (vs), 696 (vs).

General procedure for the synthesis of 1-formylpyrrolidin-3-ylphosphonates (10a–d).

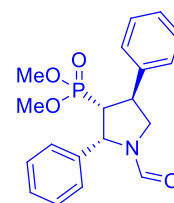
A solution of phosphonate **6a–c, e** (2.65 mmol) in AcOH (9 mL) was transferred in a 100 mL steel autoclave under argon and 10% Pd/C (0.3 g) was added. Argon was replaced with hydrogen with 3 cycles of pressurization (10 bar)/depressurization. The reactor was finally charged with a pressure of H_2 (30 bar), then left stirring with magnetic stirrer for 36 h at 25 °C. Then the reactor was depressurized. The reaction mixture was diluted by chloroform (30 mL), filtered and evaporated in vacuo. The residue was treated by

NaHCO₃ and water. The mixture was extracted with CH₂Cl₂ (3 × 10 mL). The combined organic extracts were dried over Na₂SO₄, filtered, and evaporated in vacuo. Ethyl formate (16 mL) was added to a residue and the reaction mixture was refluxed for 3 h. The excess of ethyl formate was evaporated in vacuo. The crude product was purified by flash chromatography on silica gel and eluted with a mixture of chloroform/ethanol (0–5%) to give a mixture – a yellow oil. From this mixture, a product is precipitated in cyclohexane and recrystallized from CCl₄ to give a white solid.

Dimethyl [(2*R*,3*R*,4*S*)-1-formyl-2,4-diphenylpyrrolidin-3-yl]phosphonate (10a).

Mixture of rotamers 4.8:1. Yield: 0.50 g (52%), white crystals,

m.p. 126–129 °C (cyclohexane); [α]_D²⁰ +45.4 (c 1.0, CHCl₃).



¹H NMR (400 MHz, CDCl₃, 298 K) δ [ppm] 8.30 (s, 1H, CHO, minor rotamer), 8.15 (s, 1H, CHO, major rotamer), 7.40–7.24 (m, 10H, aromatic, major rotamer, 10H, aromatic, minor rotamer), 5.56 (dd, ³J_{HH} = 2.8 Hz, ³J_{PH} = 8.0 Hz, 1H, H-2, minor rotamer), 5.40 (dd, ³J_{HH} = 2.0 Hz, ³J_{PH} = 7.6 Hz, 1H, H-2, major rotamer), 4.37–4.32 (m, 1H, H-4, minor rotamer), 4.29–4.24 (m, 1H, H-4, major rotamer), 4.03–3.95 (m, 1H, H-5, minor rotamer), 3.90–3.80 (m, 1H, H-5, major rotamer), 3.79–3.67 (m, 1H, H-5, minor rotamer, 1H, H-5, major rotamer), 3.14 (d, ³J_{HP} = 11.2 Hz, 3H, MeO, minor rotamer), 3.13 (d, ³J_{HP} = 11.2 Hz, 3H, MeO, major rotamer), 3.10–3.02 (m, 1H, H-3, minor rotamer, 1H, H-3, major rotamer), 2.91 (d, ³J_{HP} = 10.8 Hz, 3H, MeO, minor rotamer), 2.90 (d, ³J_{HP} = 10.8 Hz, 3H, MeO, major rotamer).

¹³C NMR (101 MHz, CDCl₃, 298 K) δ [ppm] 161.6 (s, CHO, major rotamer), 160.3 (s, CHO, minor rotamer), 139.7 (d, ³J_{CP} = 2.8 Hz, aromatic, minor rotamer), 138.3 (s, aromatic, major rotamer), 128.9 (s, aromatic, minor rotamer), 128.8 (s, aromatic, major rotamer), 128.7 (s, aromatic, minor rotamer), 128.5 (s, aromatic, major rotamer), 128.4 (s, aromatic, major rotamer), 128.2 (s, aromatic, major rotamer), 128.1 (s, aromatic, minor rotamer), 128.0 (s, aromatic, minor rotamer), 127.9 (s, aromatic, minor rotamer),

127.9 (s, aromatic, major rotamer), 127.8 (s, aromatic, minor rotamer), 127.7 (s, aromatic, major rotamer), 62.8 (d, $^2J_{CP} = 5.7$ Hz, C-2, major rotamer), 60.8 (d, $^2J_{CP} = 4.7$ Hz, C-2, minor rotamer), 54.3 (d, $^3J_{CP} = 14.4$ Hz, C-5, minor rotamer), 52.4 (d, $^3J_{CP} = 14.4$ Hz, C-5, major rotamer), 52.2 (d, $^2J_{CP} = 6.7$ Hz, MeO, minor rotamer, MeO, major rotamer), 51.6 (d, $^2J_{CP} = 6.7$ Hz, MeO, minor rotamer, MeO, major rotamer), 49.4 (d, $^1J_{CP} = 154.3$ Hz, C-3, major rotamer), 48.6 (d, $^1J_{CP} = 155.3$ Hz, C-3, minor rotamer), 43.5 (s, C-4, minor rotamer), 42.8 (d, $^2J_{CP} = 1.9$ Hz, C-4, major rotamer).

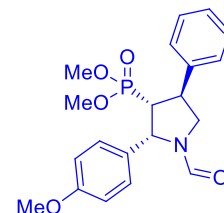
^{31}P NMR (162 MHz, CDCl_3 , 298 K) δ [ppm] 26.02 (minor rotamer), 25.44 (major rotamer).

IR (ATR) ν [cm^{-1}] 3061 (w), 3032 (w), 2951 (w), 2920 (w), 2891 (w), 2852 (w), 1658 (vs), 1604 (m), 1494 (m), 1469 (m), 1454 (m), 1413 (m), 1388 (s), 1247 (vs), 1184 (s), 1041 (vs), 1020 (vs), 1006 (vs), 823 (vs), 781 (s), 734 (vs), 696 (vs), 671 (s), 569 (s), 524 (s), 426 (s).

HRMS (APPI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{22}\text{NO}_4\text{P}\cdot\text{H}^+$, 360.1359, found 360.1361.

Dimethyl [(2*R*,3*R*,4*S*)-1-formyl-2-(4-methoxyphenyl)-4-phenylpyrrolidin-3-yl]-phosphonate (10b).

Mixture of rotamers 4.8:1. Yield: 0.52 g (50%), white crystals, m.p. 120–122 °C (CCl_4). $[\alpha]_D^{20} +47.5$ (c 1.0, CHCl_3).



^1H NMR (400 MHz, CDCl_3 , 298 K) δ [ppm] 8.28 (s, 1H, CHO, minor rotamer), 8.14 (s, 1H, CHO, major rotamer), 7.35-7.23 (m, 7H, aromatic, minor rotamer, 7H, aromatic, major rotamer), 6.91 (s, 1H, aromatic, major rotamer), 6.88 (s, 1H, aromatic, major rotamer, 1 H, aromatic, minor rotamer), 6.86 (s, 1H, aromatic, minor rotamer), 5.52 (dd, $^3J_{HP} = 8.0$ Hz, $^3J_{HH} = 2.5$ Hz, 1H, H-2, minor rotamer), 5.34 (dd, $^3J_{HP} = 7.8$ Hz, $^3J_{HH} = 1.8$ Hz, 1H, H-2 major rotamer), 4.34-4.29 (m, 1H, H-4, minor rotamer), 4.27-4.21 (m, 1H, H-4, major rotamer), 4.01-3.95 (m, 1H, H-5, minor rotamer), 3.86-3.81 (m, 1H, H-5, major rotamer, 1H, H-5, minor rotamer), 3.79 (s, 3H, MeO, major rotamer), 3.76 (s, 3H,

MeO, minor rotamer), 3.69-3.63 (m, 1H, H-5, major rotamer), 3.17 (d, $^3J_{HP} = 10.9$ Hz, 3H, MeO, minor rotamer), 3.15 (d, $^3J_{HP} = 10.9$ Hz, 3H, MeO, major rotamer), 3.08-2.98 (m, 1H, H-3, minor rotamer, 1H, H-3, major rotamer), 2.95 (d, $^3J_{HP} = 10.7$ Hz, 3H, MeO, minor rotamer), 2.94 (d, $^3J_{HP} = 10.7$ Hz, 3H, MeO, major rotamer).

^{13}C NMR (101 MHz, CDCl_3 , 298 K) δ [ppm] 161.6 (s, CHO, major rotamer), 160.2 (s, CHO, minor rotamer), 159.7 (s, aromatic, major rotamer), 159.3 (s, aromatic, minor rotamer), 138.5 (s, aromatic, minor rotamer), 138.4 (s, aromatic, major rotamer), 131.8 (d, $^3J_{CP} = 2.8$ Hz, aromatic, major rotamer), 130.7 (d, $^3J_{CP} = 2.8$ Hz, aromatic, minor rotamer), 129.6 (s, aromatic, major rotamer), 129.4 (s, aromatic, minor rotamer), 128.9 (s, aromatic, minor rotamer), 128.8 (s, aromatic, major rotamer), 127.9 (s, aromatic, major rotamer), 127.78 (s, aromatic, minor rotamer), 127.75 (s, aromatic, minor rotamer, aromatic, major rotamer), 113.8 (s, aromatic, major rotamer), 113.6 (s, aromatic, minor rotamer), 62.3 (d, $^2J_{CP} = 4.8$ Hz, C-2, major rotamer), 60.3 (d, $^2J_{CP} = 4.8$ Hz, C-2, minor rotamer), 55.4 (s, MeO, major rotamer), 55.3 (s, MeO, minor rotamer), 54.2 (d, $^3J_{CP} = 13.4$ Hz, C-5, minor rotamer), 52.3 (d, $^2J_{CP} = 6.7$ Hz, MeO, minor rotamer, MeO, major rotamer), 52.2 (d, $^3J_{CP} = 14.3$ Hz, C-5, major rotamer), 51.5 (d, $^2J_{CP} = 6.7$ Hz, MeO, minor rotamer, MeO, major rotamer), 49.4 (d, $^1J_{CP} = 155.3$ Hz, C-3, major rotamer), 48.7 (d, $^1J_{CP} = 155.3$ Hz, C-3, minor rotamer), 43.6 (s, C-4, minor rotamer), 42.8 (s, C-4, major rotamer).

^{31}P NMR (162 MHz, CDCl_3 , 298 K) δ [ppm] 25.76 (major rotamer), 26.30 (minor rotamer).

IR (ATR) ν [cm^{-1}] 3066 (w), 3001 (w), 2949 (w), 2843 (w), 1654 (vs), 1612 (m), 1512 (s), 1382 (s), 1244 (vs), 1176 (s), 1043 (vs), 1022 (vs), 821 (s), 781 (s), 756 (vs), 702 (s), 661 (m), 569 (s), 532 (s).

HRMS (APPI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{20}\text{H}_{24}\text{NO}_5\text{P}\cdot\text{H}^+$, 390.1464, found 390.1463.

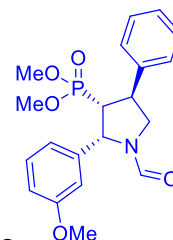
Dimethyl [(2*R*,3*R*,4*S*)-1-formyl-2-(3-methoxyphenyl)-4-phenylpyrrolidin-3-yl]-phosphonate (10c).

Mixture of rotamers 4.1:1. Yield: 0.49 g (48%), white crystals, m.p. 158–159 °C (CCl₄).

$[\alpha]_D^{20} +41.9$ (c 1.0, CHCl₃).

¹H NMR (400 MHz, CDCl₃, 298 K) δ [ppm] 8.29 (s, 1H, CHO, minor rotamer), 8.15 (s, 1H, CHO, major rotamer), 7.29-7.26 (m, 6H, aromatic, minor rotamer, 6H, aromatic, major rotamer), 6.96-6.92 (m, 2H, aromatic, minor rotamer, 2H, aromatic, major rotamer), 6.85-6.78 (m, 1H, aromatic, minor rotamer, 1H, aromatic, major rotamer), 5.54 (d, ³J_{HP} = 8.0 Hz, 1H, H-2, minor rotamer), 5.36 (d, ³J_{HP} = 7.5 Hz, 1H, H-2, major rotamer), 4.31 (t, ³J_{HH} = 10.0 Hz, 1H, H-4, minor rotamer), 4.23 (t, ³J_{HH} = 11.1 Hz, 1H, H-4, major rotamer), 3.98-3.91 (m, 1H, H-5, minor rotamer), 3.87-3.75 (m, 1H, H-5, minor rotamer, 1H, H-5, major rotamer), 3.71-3.65 (m, 1H, H-5, major rotamer), 3.81 (s, 3H, MeO, major rotamer), 3.79 (s, 3H, MeO, minor rotamer), 3.14 (d, ³J_{HP} = 11.2 Hz, 3H, MeO, minor rotamer), 3.13 (d, ³J_{HP} = 10.9 Hz, 3H, MeO, major rotamer), 3.09-2.98 (m, 1H, H-3, minor rotamer, 1H, H-3, major rotamer), 2.95 (d, ³J_{HP} = 10.7 Hz, 3H, MeO, minor rotamer), 2.94 (d, ³J_{HP} = 10.9 Hz, 3H, MeO, major rotamer).

¹³C NMR (101 MHz, CDCl₃, 298 K) δ [ppm] 161.6 (s, CHO, major rotamer), 160.3 (s, CHO, minor rotamer), 159.6 (s, aromatic, major rotamer), 159.4 (s, aromatic, minor rotamer), 141.2 (d, ³J_{CP} = 3.8 Hz, aromatic, major rotamer), 140.0 (d, ³J_{CP} = 3.8 Hz, aromatic, minor rotamer), 138.4 (s, aromatic), 129.5 (s, aromatic, major rotamer), 129.2 (s, aromatic, minor rotamer), 128.9 (s, aromatic, minor rotamer), 128.8 (s, aromatic, major rotamer), 127.9 (s, aromatic, major rotamer), 127.79 (s, aromatic, minor rotamer), 127.76 (s, aromatic), 120.5 (s, aromatic, major rotamer), 120.3 (s, aromatic, minor rotamer), 114.5 (s, aromatic, major rotamer), 114.3 (s, aromatic, minor rotamer), 113.7 (s, aromatic, major rotamer), 113.3 (s, aromatic, minor rotamer), 62.7 (d, ²J_{CP} = 5.7 Hz,



C-2, major rotamer), 60.6 (d, $^2J_{CP}$ = 4.8 Hz, C-2, minor rotamer), 55.4 (s, MeO, major rotamer), 55.3 (s, MeO, minor rotamer), 54.2 (d, $^3J_{CP}$ = 14.3 Hz, C-5, minor rotamer), 52.3 (d, $^3J_{CP}$ = 14.3 Hz, C-5, major rotamer), 52.2 (d, $^2J_{CP}$ = 6.7 Hz, MeO, minor rotamer, MeO, major rotamer), 51.6 (d, $^2J_{CP}$ = 6.7 Hz, MeO, minor and major rotamer), 49.4 (d, $^1J_{CP}$ = 154.3 Hz, C-3, major rotamer), 48.6 (d, $^1J_{CP}$ = 155.2 Hz, C-3, minor rotamer), 43.5 (s, C-4, minor rotamer), 42.9 (s, C-4, major rotamer).

^{31}P NMR (162 MHz, CDCl_3 , 298 K) δ [ppm] 25.50 (major rotamer), 25.97 (minor rotamer).

IR (ATR) ν [cm^{-1}] 3055 (w), 3012 (w), 2953 (w), 2908 (w), 1654 (vs), 1600 (m), 1463 (m), 1386 (s), 1246 (vs), 1043 (vs), 1024 (vs), 817 (vs), 792 (vs), 754 (vs), 721 (vs), 700 (vs), 570 (s), 524 (vs).

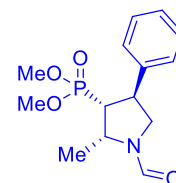
HRMS (APPI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{20}\text{H}_{24}\text{NO}_5\text{P}\cdot\text{H}^+$, 390.1464, found 390.1464.

Dimethyl [(2*R*,3*R*,4*S*)-1-formyl-2-methyl-4-phenylpyrrolidin-3-yl]phosphonate

(10d).

Mixture of rotamers 2.1:1. Yield: 0.39 g (49%), white crystals,

m.p. 79–80 °C. $[\alpha]_D^{20}$ +5.8 (c 1.0, CHCl_3).



^1H NMR (400 MHz, CDCl_3 , 298 K) δ [ppm] 8.26 (s, 1H, CHO, major rotamer), 8.16 (s, 1H, CHO, minor rotamer), 7.34-7.21 (m, 5H, aromatic, minor rotamer, 5H, aromatic, major rotamer), 4.67-4.60 (m, 1H, H-2, minor rotamer), 4.40-4.33 (m, 1H, H-2, major rotamer), 4.03-3.98 (m, 1H, H-4, minor rotamer), 3.92-3.86 (m, 1H, H-4, major rotamer), 3.85-3.69 (m, 1H, H-5, minor rotamer, 1H, H-5, major rotamer), 3.55-3.48 (m, 1H, H-5, minor rotamer, 1H, H-5, major rotamer), 3.54 (d, $^3J_{HP}$ = 10.9 Hz, 3H, MeO, minor rotamer), 3.49 (d, $^3J_{HP}$ = 10.9 Hz, 3H, MeO, major rotamer), 3.20 (d, $^3J_{HP}$ = 10.7 Hz, 3H, MeO, major rotamer), 3.15 (d, $^3J_{HP}$ = 10.9 Hz, 3H, MeO, minor rotamer), 2.76-2.65 (m, 1H, H-3, minor rotamer, 1H, H-3, major rotamer), 1.45 (d, $^3J_{HH}$ = 6.6 Hz, 3H, Me, major rotamer), 1.42 (d, $^3J_{HH}$ = 6.6 Hz, 3H, Me, minor rotamer).

^{13}C NMR (101 MHz, CDCl_3 , 298 K) δ [ppm] 160.2 (s, CHO, minor rotamer), 160.1 (s, CHO, major rotamer), 138.8 (s, aromatic, major rotamer), 138.6 (s, aromatic, minor rotamer), 129.0 (s, aromatic, minor rotamer), 128.9 (s, aromatic, major rotamer), 127.9 (s, aromatic, minor rotamer, aromatic, major rotamer), 127.8 (s, aromatic, minor rotamer, aromatic, major rotamer), 55.3 (d, $^2J_{\text{CP}} = 4.7$ Hz, C-2, major rotamer), 53.1 (d, $^2J_{\text{CP}} = 2.8$ Hz, C-2, minor rotamer), 52.5 (d, $^2J_{\text{CP}} = 6.7$ Hz, MeO, major rotamer), 52.4 (d, $^2J_{\text{CP}} = 6.7$ Hz, MeO, minor rotamer), 51.79 (d, $^2J_{\text{CP}} = 6.7$ Hz, MeO, major rotamer), 51.77 (d, $^2J_{\text{CP}} = 6.7$ Hz, MeO, minor rotamer), 50.9 (d, $^3J_{\text{CP}} = 14.3$ Hz, C-5, major rotamer, C-5, minor rotamer), 47.3 (d, $^1J_{\text{CP}} = 151.4$ Hz, C-3, major rotamer), 46.6 (d, $^1J_{\text{CP}} = 151.4$ Hz, C-3, minor rotamer), 43.1 (s, C-4, minor rotamer), 42.6 (s, C-4, major rotamer), 20.4 (d, $^3J_{\text{CP}} = 1.9$ Hz, Me, major rotamer), 16.5 (d, $^3J_{\text{CP}} = 2.8$ Hz, Me, minor rotamer).

^{31}P NMR (162 MHz, CDCl_3 , 298 K) δ [ppm] 28.03 (major rotamer), 28.44 (minor rotamer).

IR (ATR) ν [cm^{-1}] 3061 (w), 2989 (w), 2953 (w), 2881 (w), 2852 (w), 1662 (vs), 1606 (m), 1498 (m), 1467 (m), 1456 (m), 1413 (m), 1381 (s), 1232 (vs), 1182 (s), 1022 (vs), 1002 (vs), 821 (vs), 781 (s), 748 (vs), 702 (vs), 650 (m), 596 (s), 565 (s), 526 (vs).

HRMS (APPI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{20}\text{NO}_4\text{P}\cdot\text{H}^+$, 298.1202, found 298.1201.

General procedure for the synthesis of pyrrolidin-3-ylphosphonic acids (**11a–d**)

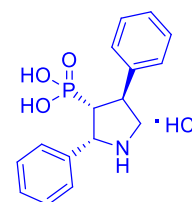
The mixture of 1-formylpyrrolidin-3-ylphosphonate **10a–d** (1.30 mmol) and 5% hydrochloric acid (5 mL) was refluxed for 33 h and resulting colorless solution was evaporated at reduced pressure. The residue was dried in vacuo to a constant weight.

(**2R,3R,4S**)-2,4-Diphenylpyrrolidin-3-ylphosphonic acid hydrochloride (**11a**).

Yield: 398 mg (90%), white crystals, m.p. 179–180 °C (decomp.).

$[\alpha]_D^{20} +81.0$ (c 1.0, H_2O).

^1H NMR (400 MHz, D_2O , 298 K) δ [ppm] 7.54–7.27 (m, 10H, aromatic),



5.22 (dd, $^3J_{\text{HH}}$ 8.4 Hz, $^3J_{\text{HP}}$ 16.8 Hz, 1H, H-2), 4.21-4.04 (m, 1H, H-5, 1H, H-4), 3.53-3.48 (m, 1H, H-5), 3.12-3.04 (m, 1H, H-3).

^{13}C NMR (101 MHz, D_2O , 298 K) δ [ppm] 138.6 (d, $^3J_{\text{CP}}$ 1.9 Hz, aromatic, C), 133.2 (d, $^3J_{\text{CP}}$ 3.8 Hz, aromatic, C), 129.4 (s, aromatic, CH), 129.1 (s, aromatic, 2CH), 128.8 (s, aromatic, 2CH), 128.2 (s, aromatic, 2CH), 128.0 (s, aromatic, CH), 127.8 (s, aromatic, 2CH), 64.9 (d, $^2J_{\text{CP}}$ 1.9 Hz, C-2), 51.8 (d, $^3J_{\text{CP}}$ 12.4 Hz, C-5), 48.9 (d, $^1J_{\text{CP}}$ 143.8 Hz, C-3), 44.7 (s, C-4).

^{31}P NMR (162 MHz, D_2O , 298 K) δ [ppm] 17.01.

IR (ATR) ν [cm^{-1}] 2891 (s), 2727 (s), 1602 (m), 1496 (m), 1456 (m), 1159 (s), 983 (s), 916 (s), 756 (s), 694 (s).

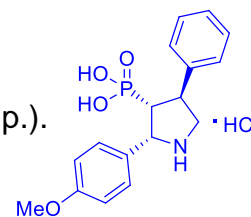
HRMS (APPI): m/z $[\text{M}-\text{Cl}]^+$ calcd for $\text{C}_{16}\text{H}_{19}\text{ClNO}_3\text{P}\cdot\text{H}^+$, 304.1097, found 304.1099.

(2R,3R,4S)-2-(4-methoxyphenyl)-4-phenylpyrrolidin-3-ylphosphonic acid

hydrochloride (11b).

Yield: 356 mg (74%), white crystals, m.p. 205–208 °C (decomp.).

$[\alpha]_{\text{D}}^{20} +75.1$ (c 1.0, H_2O).



^1H NMR (400 MHz, $\text{DMSO}-d_6$, 298 K) δ [ppm] 11.00 (br s, 1H, NH), 9.02 (br s., 1H, OH), 7.48-7.46 (m, 2H, aromatic), 7.43-7.41 (m, 2H, aromatic), 7.32-7.29 (m, 2H, aromatic), 7.24-7.20 (m, 1H, aromatic), 6.89-6.87 (m, 2H, aromatic), 5.07-4.97 (m, 1H, H-2), 4.03-3.90 (m, 1H, H-5, 1H, H-4), 3.73 (s, 3H, MeO), 3.36-3.21 (br s, 1H, H-5), 2.95-2.86 (m, 1H, H-3).

^{13}C NMR (101 MHz, $\text{DMSO}-d_6$, 298 K) δ [ppm] 159.7 (s, aromatic, $\text{C}(\text{OMe})$), 141.0 (d, $^3J_{\text{CP}}$ = 2.8 Hz, aromatic, C), 130.8 (s, aromatic, 2CH), 129.0 (s, aromatic, 2CH), 128.6 (s, aromatic, 2CH), 127.6 (s, aromatic, CH), 126.4 (d, $^3J_{\text{CP}}$ = 2.8 Hz, aromatic, C), 113.8 (s, aromatic, 2CH), 64.0 (s, C-2), 55.7 (s, MeO), 51.4 (d, $^3J_{\text{CP}}$ = 10.5 Hz, C-5), 49.2 (d, $^1J_{\text{CP}}$ = 144.7 Hz, C-3), 44.5 (s, C-4).

^{31}P NMR (162 MHz, $\text{DMSO}-d_6$, 298 K) δ [ppm] 18.81.

IR (ATR) ν [cm⁻¹] 2899 (s), 2723 (s), 1612 (m), 1585 (m), 1517 (s), 1496 (m), 1456 (m), 1253 (s), 1182 (s), 989 (s), 923 (s), 827 (s), 700 (s), 520 (s).

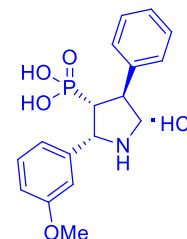
HRMS (APPI): m/z [M-Cl]⁺ calcd for C₁₇H₂₁ClNO₄P-HCl·H⁺, 334.1202, found 334.1204.

(2*R*,3*R*,4*S*)-2-(3-methoxyphenyl)-4-phenylpyrrolidin-3-ylphosphonic acid

hydrochloride (11c).

Yield: 481 mg (90%), white crystals, m.p. 172–173 °C (decomp.).

$[\alpha]_D^{20}$ +70.1 (c 1.0, H₂O).



¹H NMR (400 MHz, DMSO-*d*⁶, 298 K) δ [ppm] 11.09 (br s, 1H, NH), 9.08 (br s., 1H, OH), 7.49-7.47 (m, 2H, aromatic), 7.33-7.21 (m, 4H, aromatic), 7.09-7.04 (m, 2H, aromatic), 6.89-6.86 (m, 1H, aromatic), 5.06-5.01 (m, 1H, H-2), 4.00-3.95 (m, 1H, H-5, 1H, H-4), 3.74 (s, 3H, MeO), 3.30 (br s, 1H, H-5), 2.98-2.90 (m, 1H, H-3).

¹³C NMR (101 MHz, DMSO-*d*⁶, 298 K) δ [ppm] 159.2 (s, aromatic, C(OMe)), 141.1 (d, ³*J*_{CP} = 3.8 Hz, aromatic, C), 135.6 (d, ³*J*_{CP} = 3.8 Hz, aromatic, C), 129.6 (s, aromatic, CH), 129.0 (s, aromatic, 2CH), 128.5 (s, aromatic, 2CH), 127.6 (s, aromatic, CH), 121.3 (s, aromatic, CH), 115.3 (s, aromatic, CH), 114.3 (s, aromatic, CH), 64.1 (d, ²*J*_{CP} = 6.7 Hz, C-2), 55.6 (s, MeO), 51.4 (d, ³*J*_{CP} = 9.6 Hz, C-5), 49.1 (d, ¹*J*_{CP} = 144.7 Hz, C-3), 44.5 (s, C-4).

³¹P NMR (162 MHz, DMSO-*d*⁶, 298 K) δ [ppm] 18.89.

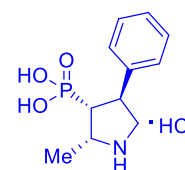
IR (ATR) ν [cm⁻¹] 3045 (s), 2139 (s), 1602 (m), 1587 (m), 1496 (m), 1456 (m), 1261 (m), 1201 (m), 1159 (s), 987 (vs), 925 (s), 779 (m), 758 (m), 696 (vs), 530 (m).

HRMS (APPI): m/z [M-Cl]⁺ calcd for C₁₇H₂₁ClNO₄P-HCl·H⁺, 334.1202, found 334.1204.

(2*R*,3*R*,4*S*)-2-methyl-4-phenylpyrrolidin-3-ylphosphonic acid hydrochloride (11d).

Yield: 339 mg (94%), white crystals, m.p. 214–215 °C (decomp.).

$[\alpha]_D^{20}$ +64.3 (c 1.0, H₂O).



^1H NMR (400 MHz, D_2O , 298 K) δ [ppm] 7.27-7.21 (m, 5H, aromatic), 4.17-4.12 (m, 1H, H-2), 3.81-3.64 (m, 1H, H-5, 1H, H-4), 3.19-3.13 (m, 1H, H-5), 2.62-2.54 (m, 1H, H-3), 1.43 (d, $^3J_{\text{HH}} = 6.4$ Hz, 3H, Me).

^{13}C NMR (101 MHz, D_2O , 298 K) δ [ppm] 139.4 (s, aromatic, C), 129.0 (s, aromatic, 2CH), 127.8 (s, aromatic, 2CH), 127.6 (s, aromatic, CH), 57.9 (s, $^2J_{\text{CP}} = 3.8$ Hz, C-2), 51.0 (d, $^3J_{\text{CP}} = 12.4$ Hz, C-5), 48.0 (d, $^1J_{\text{CP}} = 139.9$ Hz, C-3), 44.1 (s, C-4), 14.8 (d, $^3J_{\text{CP}} = 2.8$ Hz, Me).

^{31}P NMR (162 MHz, D_2O , 298 K) δ [ppm] 16.35.

IR (ATR) ν [cm^{-1}] 2964 (s), 2750 (s), 1544 (m), 1494 (m), 1460 (m), 1361 (m), 1274 (m), 1190 (vs), 1130 (s), 1062 (vs), 1026 (vs), 1012 (vs), 950 (vs), 771 (s), 756 (s), 702 (vs), 673 (s), 557 (vs), 495 (vs).

HRMS (APPI): m/z $[\text{M}-\text{Cl}]^+$ calcd for $\text{C}_{11}\text{H}_{17}\text{ClNO}_3\text{P}-\text{HCl}\cdot\text{H}^+$, 242.0940, found 242.0934.

5. Synthesis of tetrahydro-2*H*-pyran-3-ylphosphonates

General procedure for the synthesis of tetrahydro-2*H*-pyran-3-ylphosphonates

13a–f

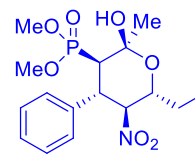
The aldehyde **12a–f** (15.9 mmol), K_2CO_3 (219 mg, 1.59 mmol), benzyltriethylammonium chloride (36 mg, 0.16 mmol) and water (2 mL) were added successively to a solution of phosphonate **6e** (0.50 g, 1.59 mmol) in THF (15 mL). The resulting mixture was stirred for 72 h at rt. Then, the mixture was extracted with CH_2Cl_2 (3 \times 10 mL). The combined extracts were dried (Na_2SO_4) and evaporated at reduced pressure. Purification by column chromatography on silica gel, eluting with $\text{CHCl}_3/\text{MeOH}$ (98:2), followed by recrystallization from methanol gave the desired compounds **13a–f**.

Dimethyl

[(2*S*,3*R*,4*S*,5*S*,6*R*)-6-ethyl-2-hydroxy-2-methyl-5-nitro-4-phenyltetrahydro-2*H*-pyran-3-yl]phosphonate (13a).

Yield: 206 mg (34%), white crystals, m.p. 173–174 °C (methanol).

$[\alpha]_D^{20} +42.4$ (c 1.0, CHCl₃). *dr* 1:-.



¹H NMR (400 MHz, CDCl₃, 298 K) δ [ppm] 7.29-7.16 (m, 5H, aromatic), 4.47 (td, ³*J*_{HH} = 10.8 Hz, ⁴*J*_{HP} = 0.8 Hz, 1H, H-5), 4.38-4.33 (m, 1H, H-6), 3.91 (s, 1H, OH), 3.93 (td, ³*J*_{HH} = 12.0 Hz, ³*J*_{HP} = 8.9 Hz, 1H, H-4), 3.56 (d, ³*J*_{HP} = 10.8 Hz, 3H, MeO), 3.19 (d, ³*J*_{HP} = 11.1 Hz, 3H, MeO), 2.50 (ddd, ²*J*_{HP} = 18.4, ³*J*_{HH} = 12.4 Hz, ⁴*J*_{HH} = 1.2 Hz, 1H, H-3), 1.82 (s, 3H, Me), 1.59-1.41 (m, 2H, CH₂), 0.95 (t, ³*J*_{HH} = 7.6 Hz, 3H, MeCH₂).

¹³C NMR (101 MHz, CDCl₃, 298 K) δ [ppm] 137.2 (s, aromatic), 128.6 (s, aromatic), 128.4 (s, aromatic), 128.0 (s, aromatic), 95.9 (s, C-2), 92.8 (d, ³*J*_{CP} = 14.3 Hz, C-5), 70.5 (s, C-6), 53.5 (d, ²*J*_{CP} = 6.7 Hz, MeO), 51.6 (d, ²*J*_{CP} = 6.7 Hz, MeO), 48.4 (d, ¹*J*_{CP} = 138.9 Hz, C-3), 44.3 (s, C-4), 29.4 (s, Me), 24.8 (s, CH₂), 8.9 (s, Me).

³¹P NMR (162 MHz, CDCl₃, 298 K) δ [ppm] 27.29.

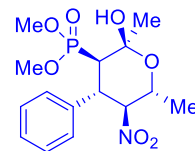
IR (ATR) ν [cm⁻¹] 3267 (m), 2962 (w), 2926 (w), 2856 (w), 1550 (vs), 1377 (m), 1240 (vs), 1028 (vs), 813 (s), 702 (s), 520 (s).

HRMS (APPI): *m/z* [M-H₂O+H]⁺ calcd for C₁₆H₂₄NO₇P-H₂O·H⁺ 356.1257; found 356.1258.

Dimethyl [(2*S*,3*R*,4*S*,5*S*,6*R*)-2-hydroxy-2,6-dimethyl-5-nitro-4-phenyltetrahydro-2*H*-pyran-3-yl]phosphonate (13b).

Yield: 202 mg (36%), white crystals, m.p. 193–194 °C (methanol).

$[\alpha]_D^{20} +34.1$ (c 1.0, CHCl₃). *dr* 14:1, > 99% *ee*.



¹H NMR (400 MHz, CDCl₃, 298 K) δ [ppm] 7.31-7.16 (m, 5H, aromatic), 4.59-4.52 (m, 1H, H-6), 4.39 (td, ³*J*_{HH} = 11.2 Hz, ⁴*J*_{HP} = 1.2 Hz, 1H, H-5), 4.00 (s, 1H, OH), 3.93 (td, ³*J*_{HH} = 12.0 Hz, ³*J*_{HP} = 8.8 Hz, 1H, H-4), 3.56 (d, ³*J*_{HP} = 10.7 Hz, 3H, MeO), 3.20 (d, ³*J*_{HP}

= 11.1 Hz, 3H, MeO), 2.50 (ddd, $^2J_{HP}$ = 18.7, $^3J_{HH}$ = 12.5 Hz, $^4J_{HH}$ = 1.3 Hz, 1H, H-3), 1.80 (s, 3H, Me), 1.20 (d, $^3J_{HH}$ = 6.4 Hz, 3H, Me).

^{13}C NMR (101 MHz, CDCl_3 , 298 K) δ [ppm] 137.1 (s, aromatic), 128.6 (s, aromatic), 128.3 (s, aromatic), 128.0 (s, aromatic), 96.0 (s, C-2), 94.6 (d, $^3J_{CP}$ = 14.3 Hz, C-5), 66.2 (s, C-6), 53.5 (d, $^2J_{CP}$ = 6.7 Hz, MeO), 51.7 (d, $^2J_{CP}$ = 6.7 Hz, MeO), 48.3 (d, $^1J_{CP}$ = 138.0 Hz, C-3), 44.0 (s, C-4), 29.5 (s, Me), 18.1 (s, Me).

^{31}P NMR (162 MHz, CDCl_3 , 298 K) δ [ppm] 27.32.

IR (ATR) ν [cm^{-1}] 3250 (m), 2958 (w), 2854 (w), 1544 (vs), 1379 (m), 1238 (vs), 1014 (vs), 740 (s), 700 (s), 545 (s).

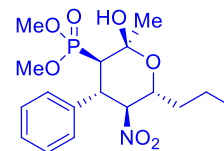
HRMS (APPI): m/z $[\text{M}-\text{H}_2\text{O}+\text{H}]^+$ calcd for $\text{C}_{15}\text{H}_{22}\text{NO}_7\text{P}-\text{H}_2\text{O}\cdot\text{H}^+$ 342.1101; found 342.1096.

HPLC analysis (Chiralpak AD-3 column; hexane/*i*-PrOH, 92:8; flow rate 1.2 mL/min; wavelength 230 nm): t_R = 7.0 (2*R*,3*S*,4*R*,5*R*,6*S*), 7.7 (2*S*,3*R*,4*S*,5*S*,6*R*) min.

Dimethyl [(2*S*,3*R*,4*S*,5*S*,6*R*)-2-hydroxy-2-methyl-5-nitro-4-phenyl-6-propyl-tetrahydro-2*H*-pyran-3-yl]phosphonate (13c).

Yield: 216 mg (35%), white crystals, m.p. 180–181 °C (methanol).

$[\alpha]_D^{20}$ +55.6 (c 1.0, CHCl_3). dr 10:1.



^1H NMR (300 MHz, CDCl_3 , 298 K) δ [ppm] 7.34-7.19 (m, 5H, aromatic), 4.48 (s, 1H, OH), 4.52-4.45 (m, 1H, H-5), 4.05-3.89 (m, 1H, H-4), 3.80-3.63 (m, 1H, H-6), 3.57 (d, $^3J_{HP}$ = 11.1 Hz, 3H, MeO), 3.24 (d, $^3J_{HP}$ = 11.1 Hz, 3H, MeO), 2.53 (dd, $^2J_{HP}$ = 18.3, $^3J_{HH}$ = 12.6 Hz, 1H, H-3), 1.84 (s, 3H, Me), 1.62-1.28 (m, 4H, 2CH₂), 0.91 (t, $^3J_{HH}$ = 6.6 Hz, 3H, MeCH₂).

^{13}C NMR (75 MHz, CDCl_3 , 298 K) δ [ppm] 137.2 (s, aromatic), 128.5 (s, aromatic), 128.2 (s, aromatic), 127.9 (s, aromatic), 95.8 (s, C-2), 93.1 (d, $^3J_{CP}$ = 14.3 Hz, C-5), 69.3 (s, C-6), 53.3 (d, $^2J_{CP}$ = 6.6 Hz, MeO), 51.5 (d, $^2J_{CP}$ = 6.7 Hz, MeO), 48.2 (d, $^1J_{CP}$ = 138.3 Hz, C-3), 44.2 (s, C-4), 33.6 (s, CH₂), 29.5 (s, Me), 17.8 (s, CH₂), 13.7 (s, Me).

^{31}P NMR (121 MHz, CDCl_3 , 298 K) δ [ppm] 26.67.

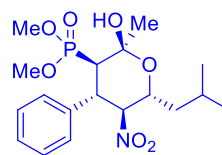
IR (ATR) ν [cm^{-1}] 3275 (m), 2954 (w), 2929 (w), 2872 (w), 1546 (vs), 1379 (m), 1238 (vs), 1024 (vs), 810 (s), 779 (s), 702 (s), 520 (vs).

HRMS (APPI): m/z $[\text{M}-\text{H}_2\text{O}+\text{H}]^+$ calcd for $\text{C}_{17}\text{H}_{26}\text{NO}_7\text{P}-\text{H}_2\text{O}\cdot\text{H}^+$ 370.1414; found 370.1418.

Dimethyl [(2*S*,3*R*,4*S*,5*S*,6*R*)-2-hydroxy-6-isobutyl-2-methyl-5-nitro-4-phenyl-tetrahydro 2*H*-pyran-3-yl]phosphonate (13d).

Yield: 191 mg (30%), white crystals, m.p. 153–154 °C (methanol).

$[\alpha]_D^{20} +51.5$ (c 1.0, CHCl_3). *dr* 9:1.



^1H NMR (400 MHz, CDCl_3 , 298 K) δ [ppm] 7.29-7.15 (m, 5H, aromatic), 4.48 (td, $^3J_{\text{HH}} = 9.9$ Hz, $^4J_{\text{HP}} = 1.6$ Hz, 1H, H-5), 4.41 (t, $^3J_{\text{HH}} = 9.9$ Hz, 1H, H-6), 4.13 (s, 1H, OH), 3.97-3.89 (m, 1H, H-4), 3.56 (d, $^3J_{\text{HP}} = 10.7$ Hz, 3H, MeO), 3.18 (d, $^3J_{\text{HP}} = 11.2$ Hz, 3H, MeO), 2.49 (dd, $^2J_{\text{HP}} = 18.5$, $^3J_{\text{HH}} = 12.3$ Hz, 1H, H-3), 1.81 (s, 3H, Me), 1.53-1.46 (m, 1H, CH_2), 1.13-1.06 (m, 1H, CH_2), 0.89-0.84 (m, 1H, CH, *i*-Bu), 0.88 (d, $^3J_{\text{HH}} = 6.8$ Hz, 3H, **MeCH**), 0.84 (d, $^3J_{\text{HH}} = 6.4$ Hz, 3H, **MeCH**).

^{13}C NMR (101 MHz, CDCl_3 , 298 K) δ [ppm] 137.2 (s, aromatic), 128.6 (s, aromatic), 128.3 (s, aromatic), 128.0 (s, aromatic), 95.8 (s, C-2), 93.7 (d, $^3J_{\text{CP}} = 14.3$ Hz, C-5), 67.9 (s, C-6), 53.5 (d, $^2J_{\text{CP}} = 6.7$ Hz, MeO), 51.6 (d, $^2J_{\text{CP}} = 6.7$ Hz, MeO), 48.5 (d, $^1J_{\text{CP}} = 138.0$ Hz, C-3), 44.4 (s, C-4), 40.4 (s, CH_2 , *i*-Bu), 29.4 (s, Me), 23.9 (s, CH, *i*-Bu), 23.6 (s, CH_3 , *i*-Bu), 21.2 (s, CH_3 , *i*-Bu).

^{31}P NMR (162 MHz, CDCl_3 , 298 K) δ [ppm] 27.37.

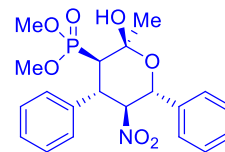
IR (ATR) ν [cm^{-1}] 3280 (m), 2954 (w), 2870 (w), 1548 (vs), 1369 (m), 1232 (vs), 1033 (vs), 761 (s), 698 (s).

HRMS (APPI): m/z $[\text{M}-\text{H}_2\text{O}+\text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{28}\text{NO}_7\text{P}-\text{H}_2\text{O}\cdot\text{H}^+$ 384.1570; found 384.1575.

Dimethyl [(2*S*,3*R*,4*S*,5*S*,6*R*)-2-hydroxy-2-methyl-5-nitro-4,6-diphenyltetrahydro-2*H*-pyran-3-yl]phosphonate (13e).

Yield: 214 mg (32%), white crystals, m.p. 197–198 °C (methanol).

$[\alpha]_D^{20} +66.0$ (c 0.5, CHCl₃). *dr* 1:-.



¹H NMR (400 MHz, CDCl₃, 298 K) δ [ppm] 7.33-7.21 (m, 10H, aromatic), 5.46 (d, ³*J*_{HH} = 9.8 Hz, 1H, H-6), 4.67 (td, ³*J*_{HH} = 9.8 Hz, ⁴*J*_{HP} = 1.1 Hz, 1H, H-5), 4.12 (td, ³*J*_{HH} = 11.6 Hz, ³*J*_{HP} = 8.7 Hz, 1H, H-4), 3.61 (d, ³*J*_{HP} = 10.9 Hz, 3H, MeO), 3.23 (d, ³*J*_{HP} = 10.9 Hz, 3H, MeO), 2.67 (dd, ²*J*_{HP} = 18.7, ³*J*_{HH} = 12.4 Hz, 1H, H-3), 1.92 (s, 3H, Me).

¹³C NMR (101 MHz, CDCl₃, 298 K) δ [ppm] 136.8 (s, aromatic), 135.9 (s, aromatic), 129.4 (s, aromatic), 128.9 (s, aromatic), 128.6 (s, aromatic), 128.1 (s, aromatic), 127.1 (s, aromatic), 97.1 (s, C-2), 94.6 (d, ³*J*_{CP} = 14.3 Hz, C-5), 72.8 (s, C-6), 53.6 (d, ²*J*_{CP} = 6.7 Hz, MeO), 51.7 (d, ²*J*_{CP} = 6.7 Hz, MeO), 48.2 (d, ¹*J*_{CP} = 138.0 Hz, C-3), 44.7 (s, C-4), 29.7 (s, Me).

³¹P NMR (162 MHz, CDCl₃, 298 K) δ [ppm] 26.85.

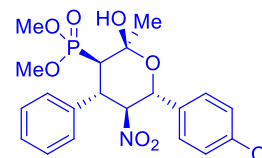
IR (ATR) ν [cm⁻¹] 3300 (m), 3188 (m), 2954 (w), 2856 (w), 1550 (vs), 1375 (m), 1238 (vs), 1041 (vs), 761 (s), 750 (s), 696 (vs), 528 (s), 520 (s).

HRMS (APPI): *m/z* [M-H₂O+H]⁺ calcd for C₂₀H₂₄NO₇P-H₂O·H⁺ 404.1257; found 404.1257.

Dimethyl [(2*S*,3*R*,4*S*,5*S*,6*R*)-6-(4-chlorophenyl)-2-hydroxy-2-methyl-5-nitro-4-phenyltetrahydro-2*H*-pyran-3-yl]phosphonate (13f).

Yield: 217 mg (30%), white crystals, m.p. 183–184 °C (methanol).

$[\alpha]_D^{20} +66.4$ (c 1.0, CHCl₃). *dr* 1:-.



¹H NMR (400 MHz, CDCl₃, 298 K) δ [ppm] 7.31-7.20 (m, 9H, aromatic), 5.44 (d, ³*J*_{HH} = 9.8 Hz, 1H, H-6), 4.60 (t, ³*J*_{HH} = 11.2 Hz, 1H, H-5), 4.10 (td, ³*J*_{HH} = 11.9 Hz, ³*J*_{HP} = 8.6 Hz, 1H, H-4), 3.59 (d, ³*J*_{HP} = 10.9 Hz, 3H, MeO), 3.47 (s, 1H, OH), 3.24 (d, ³*J*_{HP} = 11.2 Hz, 3H, MeO), 2.66 (dd, ²*J*_{HP} = 18.7, ³*J*_{HH} = 12.4 Hz, 1H, H-3), 1.91 (s, 3H, Me).

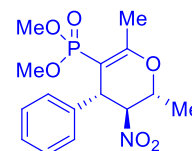
^{13}C NMR (101 MHz, CDCl_3 , 298 K) δ [ppm] 136.6 (s, aromatic), 135.3 (s, aromatic), 134.5 (s, aromatic), 129.1 (s, aromatic), 128.7 (s, aromatic), 128.4 (s, aromatic), 128.2 (s, aromatic), 97.1 (s, C-2), 94.5 (d, $^3J_{\text{CP}} = 15.3$ Hz, C-5), 72.2 (s, C-6), 53.6 (d, $^2J_{\text{CP}} = 6.7$ Hz, MeO), 51.7 (d, $^2J_{\text{CP}} = 6.7$ Hz, MeO), 48.2 (d, $^1J_{\text{CP}} = 138.0$ Hz, C-3), 44.6 (s, C-4), 29.6 (s, Me).

^{31}P NMR (162 MHz, CDCl_3 , 298 K) δ [ppm] 26.72.

IR (ATR) ν [cm^{-1}] 3321 (m), 2951 (w), 2916 (w), 2850 (w), 1548 (vs), 1373 (m), 1228 (vs), 1024 (vs), 900 (s), 752 (vs), 698 (s), 594 (s), 536 (s).

HRMS (APPI): m/z $[\text{M}-\text{H}_2\text{O}+\text{H}]^+$ calcd for $\text{C}_{20}\text{H}_{23}\text{ClNO}_7\text{P}-\text{H}_2\text{O}-\text{H}^+$ 438.0867; found 438.0873.

Dimethyl [(2*R*,3*S*,4*S*)-2,6-dimethyl-3-nitro-4-phenyl-3,4-dihydro-2*H*-pyran-5-yl]phosphonate (14).



TsOH (5 mg, 0.029 mmol) was added to a solution of **13b** (206 mg, 0.573 mmol) in 8 mL of toluene and the resulting mixture was refluxed for 2 h. Then the reaction mixture was evaporated at reduced pressure. The residue was dissolved in CHCl_3 and filtered through silica gel (1.0 g). The filtrate was evaporated in vacuo.

Yield: 168 mg (86%); yellow oil; $[\alpha]_D^{20} -24.0$ (c 1.0, CHCl_3).

^1H NMR (300 MHz, CDCl_3 , 298 K) δ [ppm] 7.33-7.15 (m, 5H, aromatic), 4.48 (t, $^3J_{\text{HH}} = 9.3$ Hz, 1H, H-5), 4.31-4.26 (m, 2H, H-4, H-6), 3.51 (d, $^3J_{\text{HP}} = 11.2$ Hz, 3H, MeO), 3.25 (d, $^3J_{\text{HP}} = 11.1$ Hz, 3H, MeO), 2.25 (s, 3H, Me), 1.35 (d, $^3J_{\text{HH}} = 6.2$ Hz, 3H, Me).

^{13}C NMR (75 MHz, CDCl_3 , 298 K) δ [ppm] 165.3 (d, $^2J_{\text{CP}} = 24.1$ Hz, C-2), 139.1 (s, aromatic), 128.8 (s, aromatic), 127.9 (s, aromatic), 99.1 (d, $^1J_{\text{CP}} = 203.3$ Hz, C-3), 93.4 (d, $^3J_{\text{CP}} = 11.8$ Hz, C-5), 72.7 (s, C-6), 52.02 (d, $^2J_{\text{CP}} = 6.0$ Hz, MeO), 51.95 (d, $^2J_{\text{CP}} = 6.0$ Hz, MeO), 46.4 (d, $^2J_{\text{CP}} = 9.1$ Hz, C-4), 20.1 (d, $^3J_{\text{CP}} = 2.2$ Hz, Me), 17.2 (s, Me).

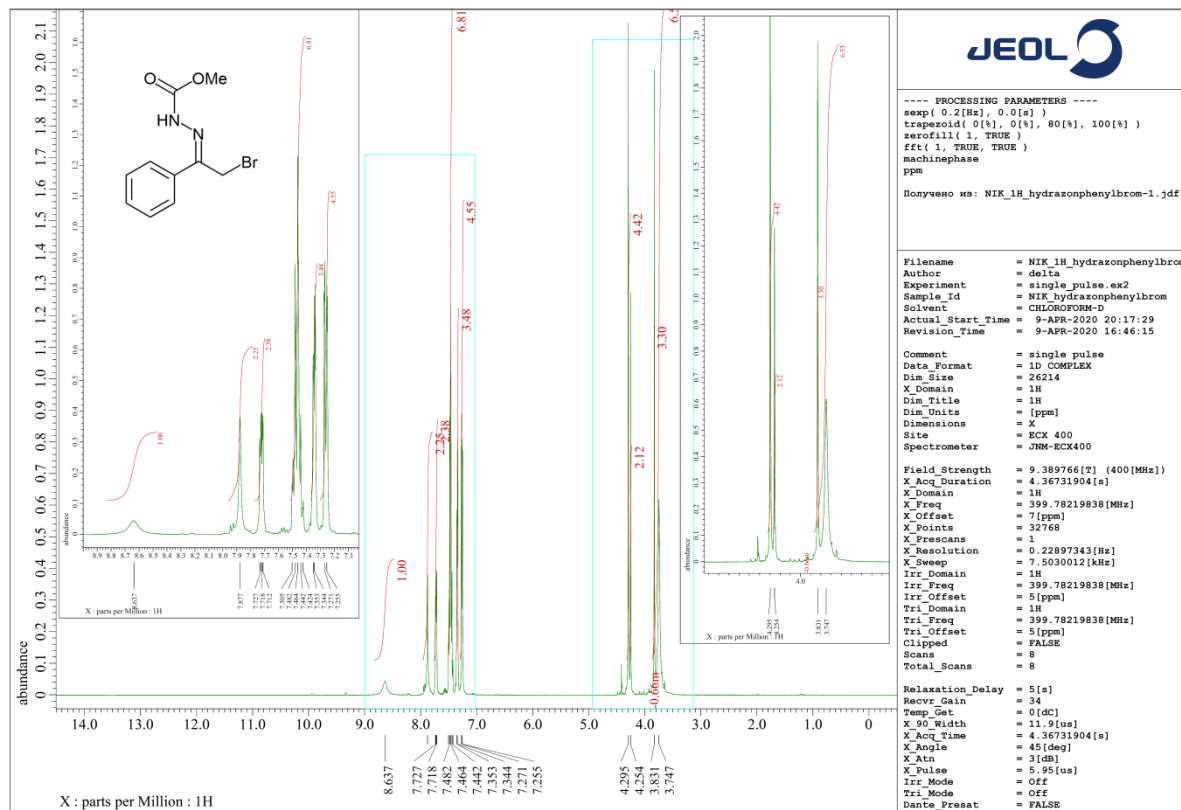
^{31}P NMR (121 MHz, CDCl_3 , 298 K) δ [ppm] 21.79.

IR (ATR) ν [cm^{-1}] 2987 (w), 2953 (w), 2848 (w), 1620 (s), 1550 (vs) 1456 (m), 1249 (s), 1020 (vs), 754 (s), 700 (s), 596 (s).

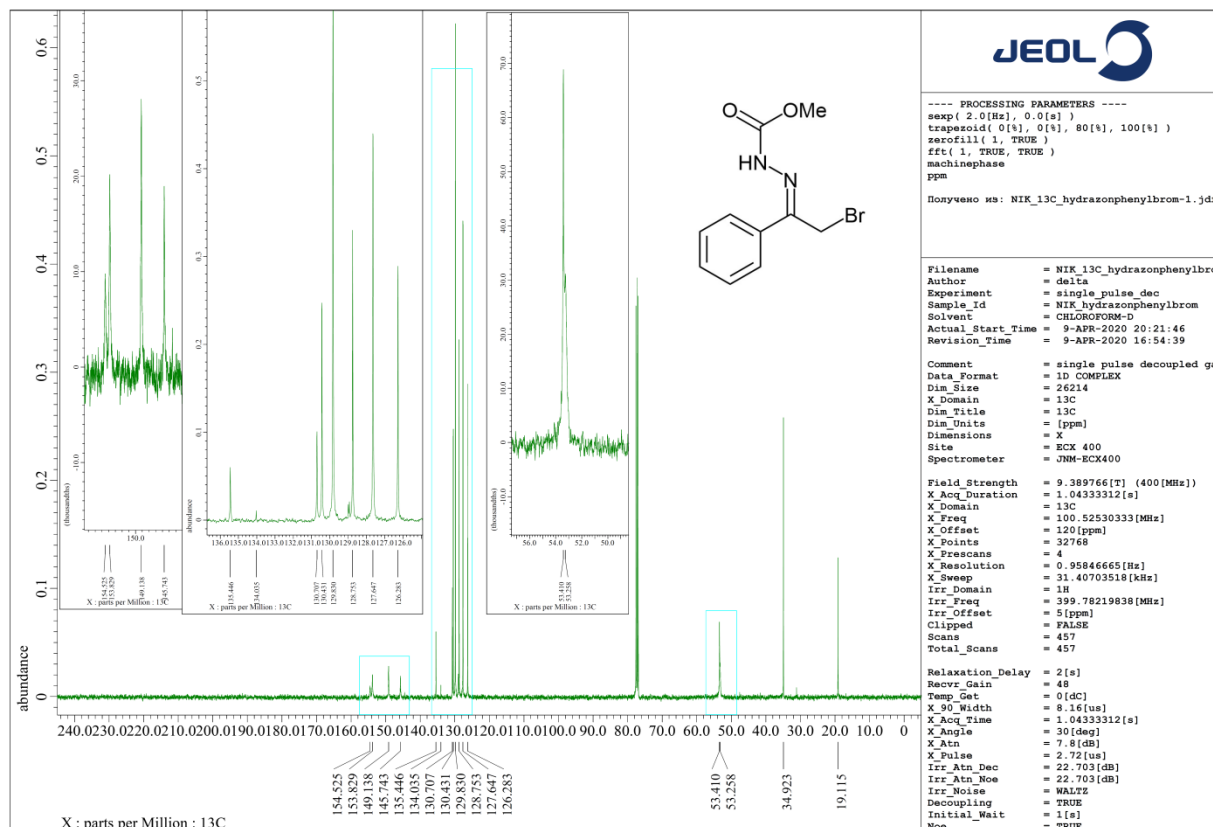
HRMS (APPI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{15}\text{H}_{20}\text{NO}_6\text{P}\cdot\text{H}^+$ 342.1101; found 342.1106.

6. Copies of NMR, FTIR and mass spectra for initial compounds

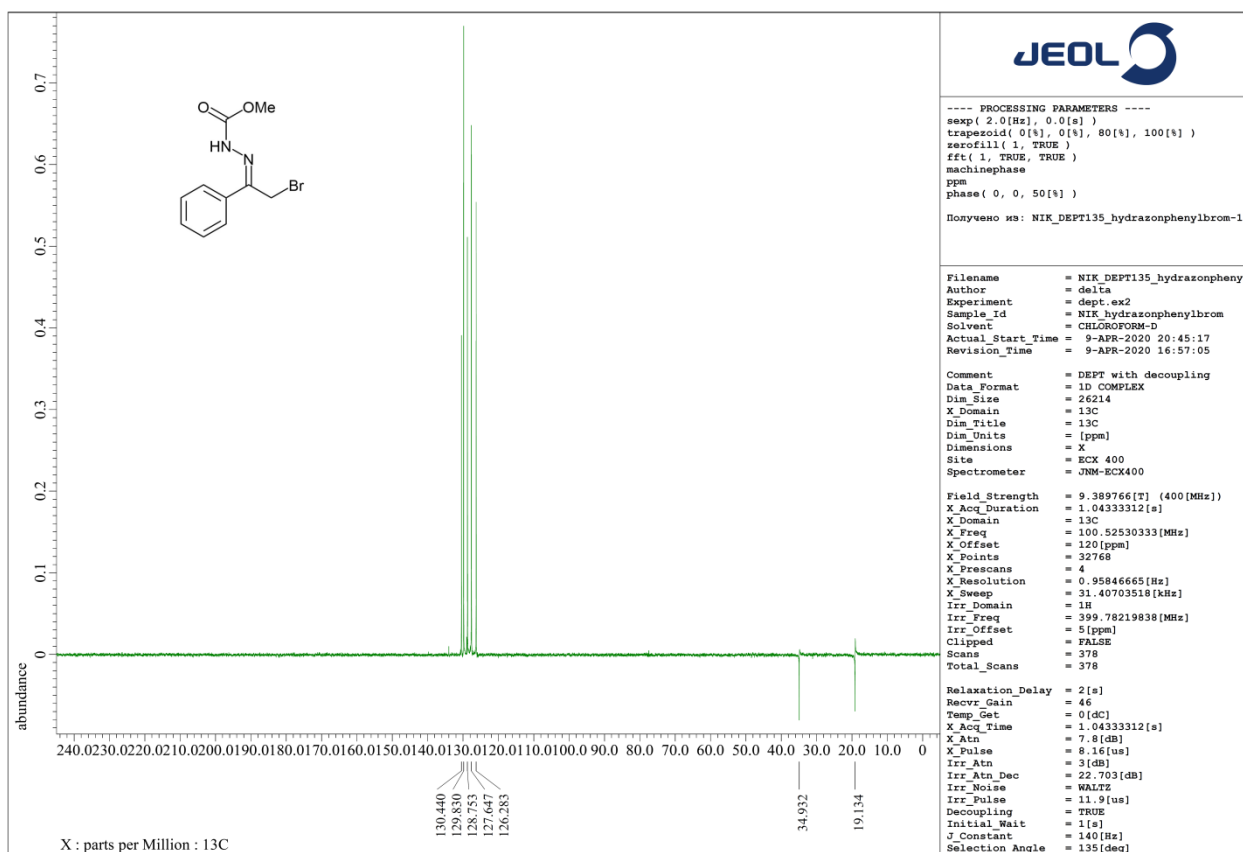
¹H NMR spectra of methyl 2-(2-bromo-1-phenylethylidene)hydrazine-1-carboxylate **IIIa** in CDCl₃



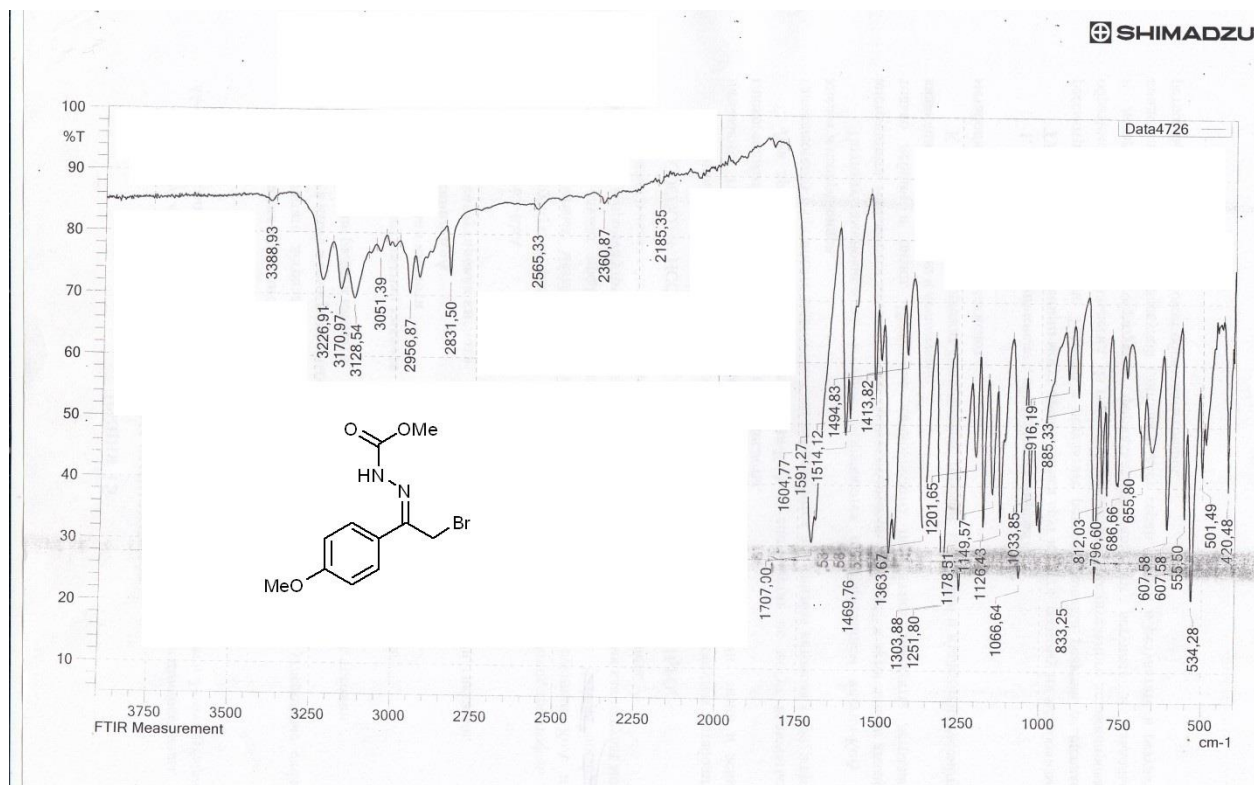
¹³C NMR spectra of methyl 2-(2-bromo-1-phenylethylidene)hydrazine-1-carboxylate **IIIa** in CDCl₃



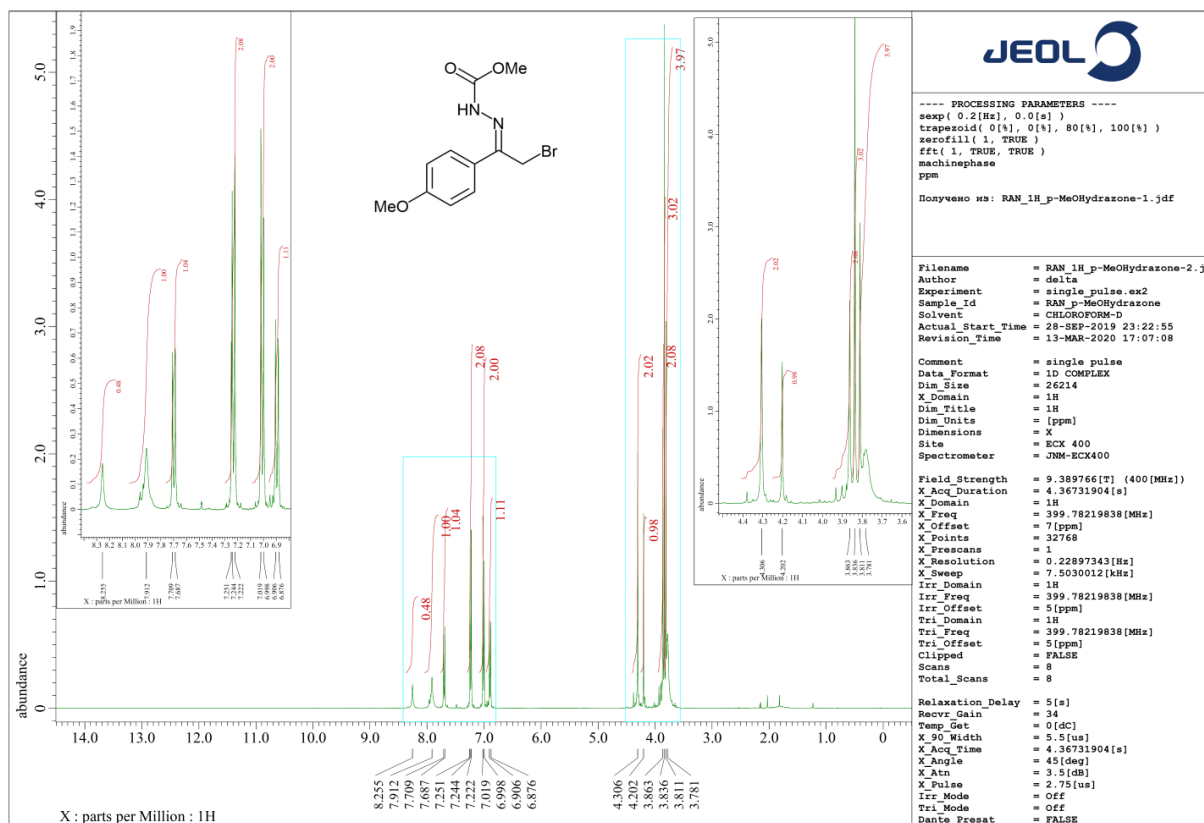
DEPT NMR spectra of methyl 2-(2-bromo-1-phenylethylidene)hydrazine-1-carboxylate **IIIa** in CDCl₃



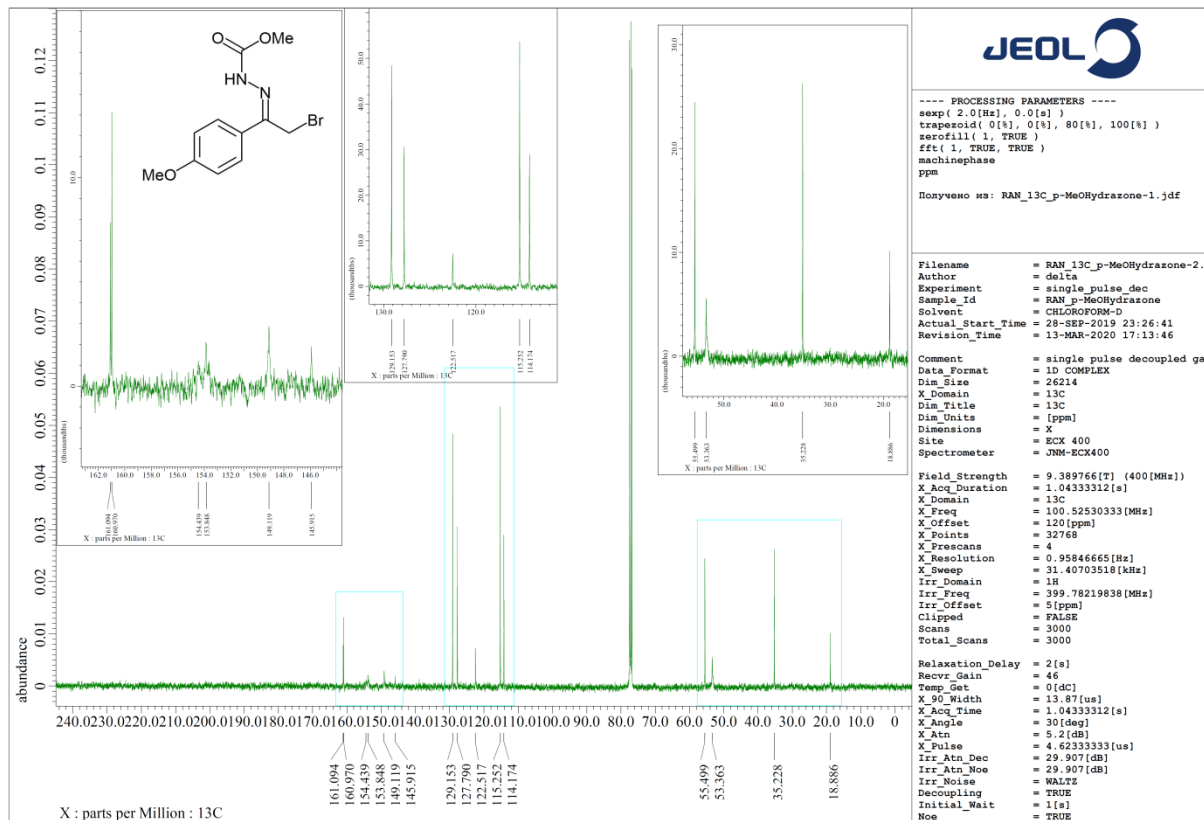
FTIR spectra of methyl 2-[2-bromo-1-(4-methoxyphenyl)ethylidene]hydrazine-1-carboxylate **IIIb**



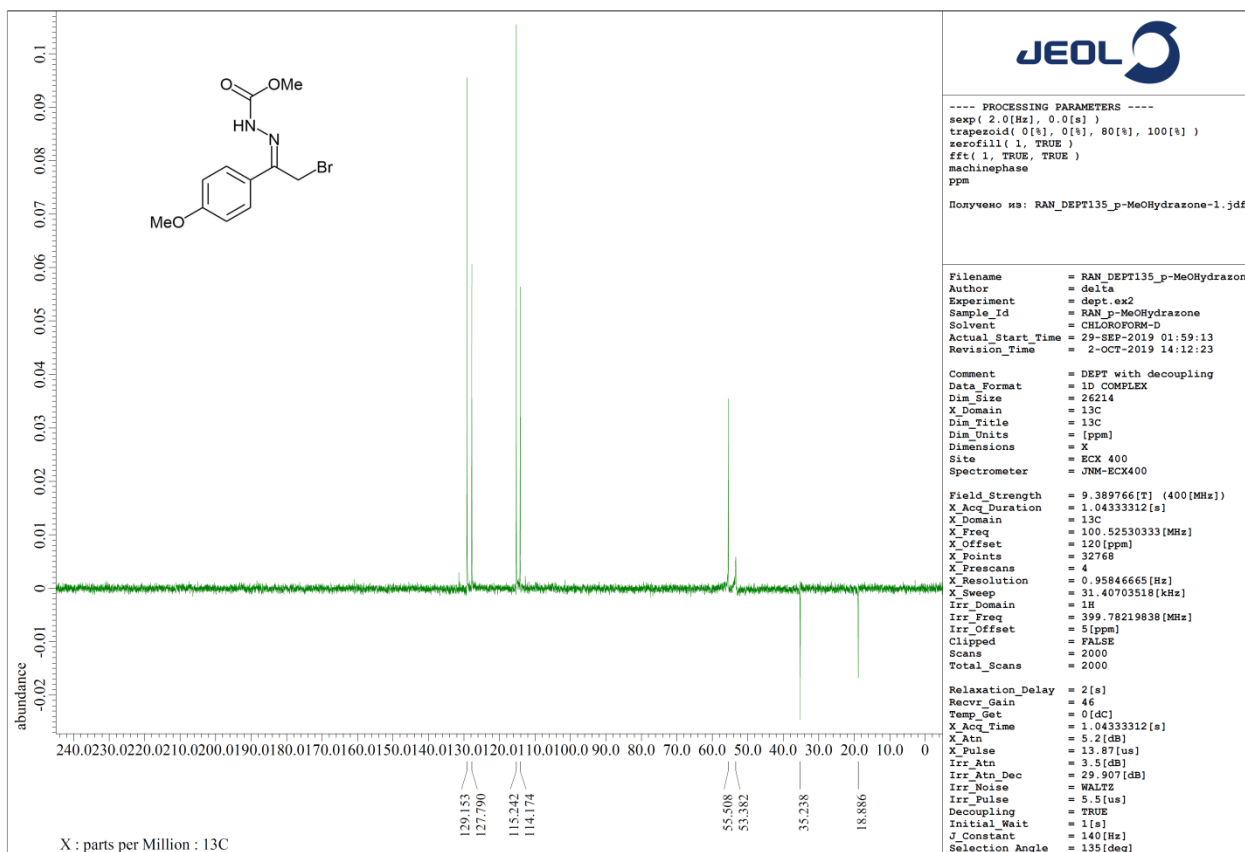
¹H NMR spectra of methyl 2-[2-bromo-1-(4-methoxyphenyl)ethylidene]hydrazine-1-carboxylate **IIIb**
in CDCl₃



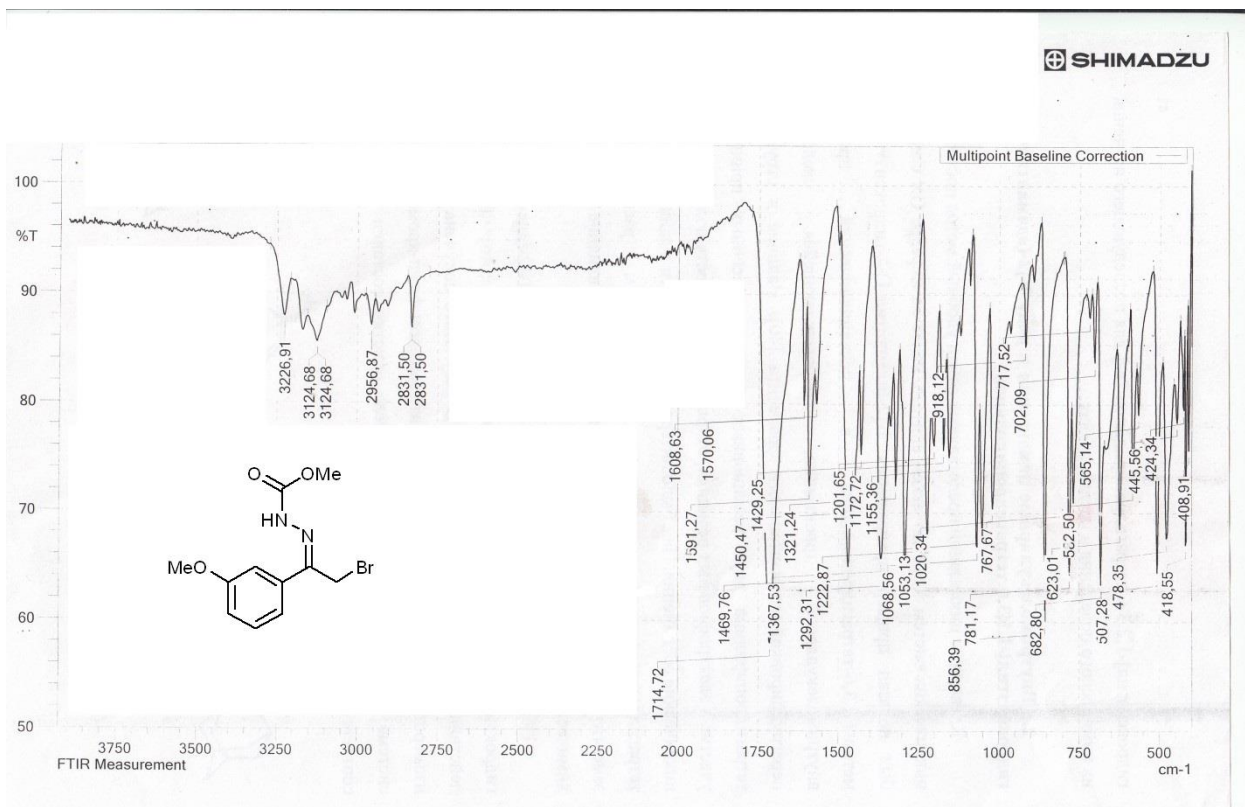
¹³C NMR spectra of methyl 2-[2-bromo-1-(4-methoxyphenyl)ethylidene]hydrazine-1-carboxylate **IIIb**
in CDCl₃



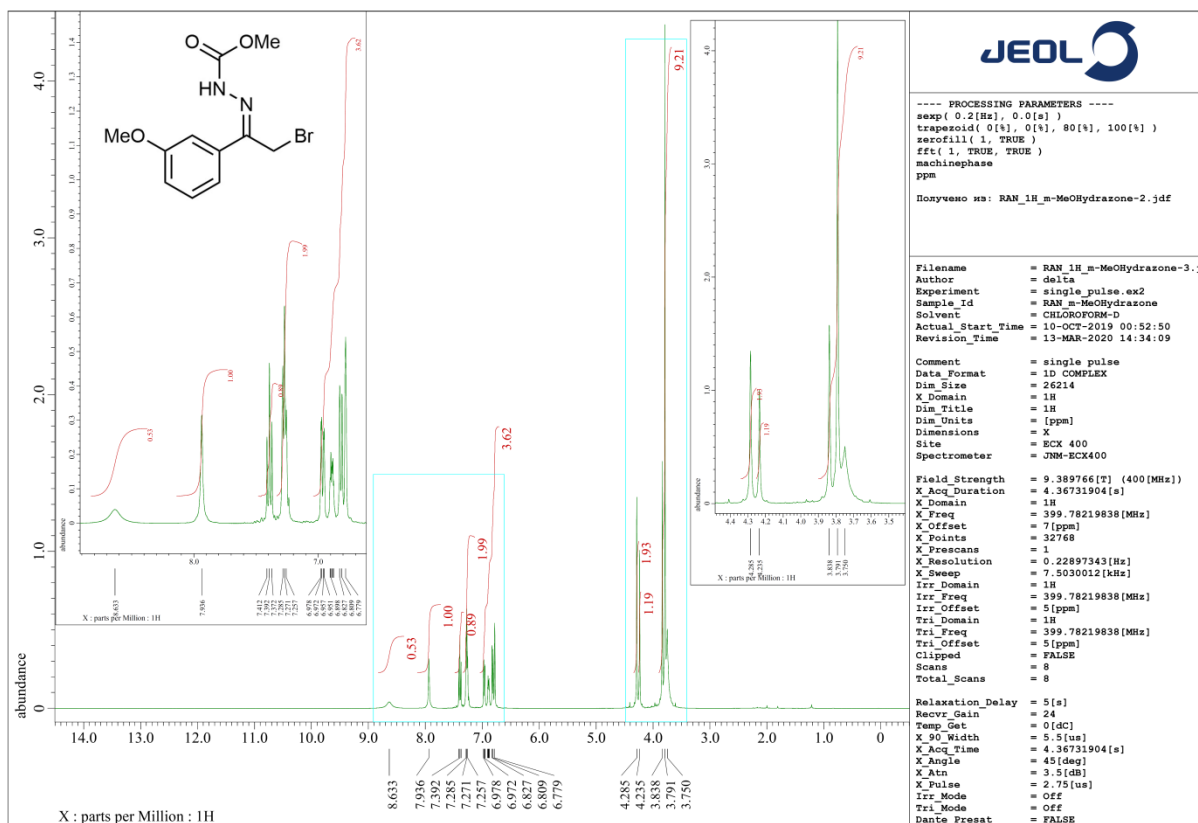
DEPT NMR spectra of methyl 2-[2-bromo-1-(4-methoxyphenyl)ethylidene]hydrazine-1-carboxylate **IIIb**
in CDCl₃



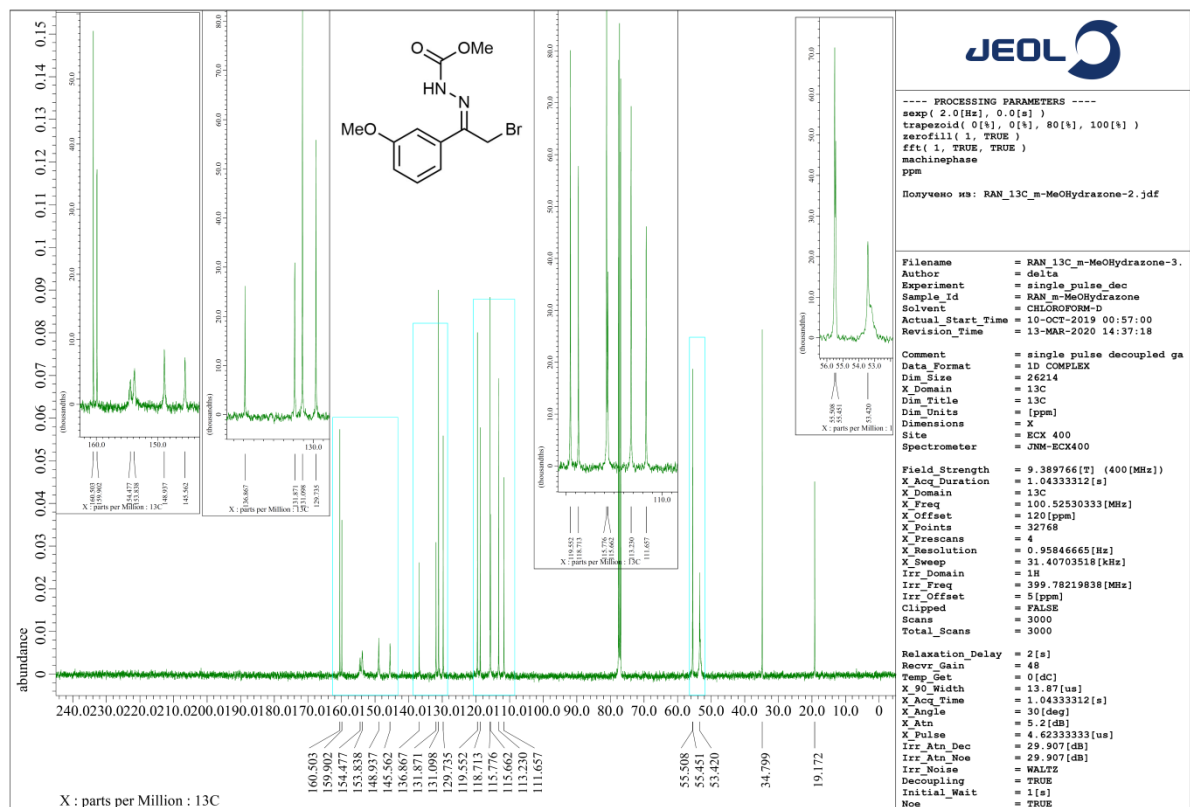
FTIR spectra of methyl 2-[2-bromo-1-(3-methoxyphenyl)ethylidene]hydrazine-1-carboxylate **IIIc**



¹H NMR spectra of methyl 2-[2-bromo-1-(3-methoxyphenyl)ethylidene]hydrazine-1-carboxylate **IIIc**
in CDCl₃

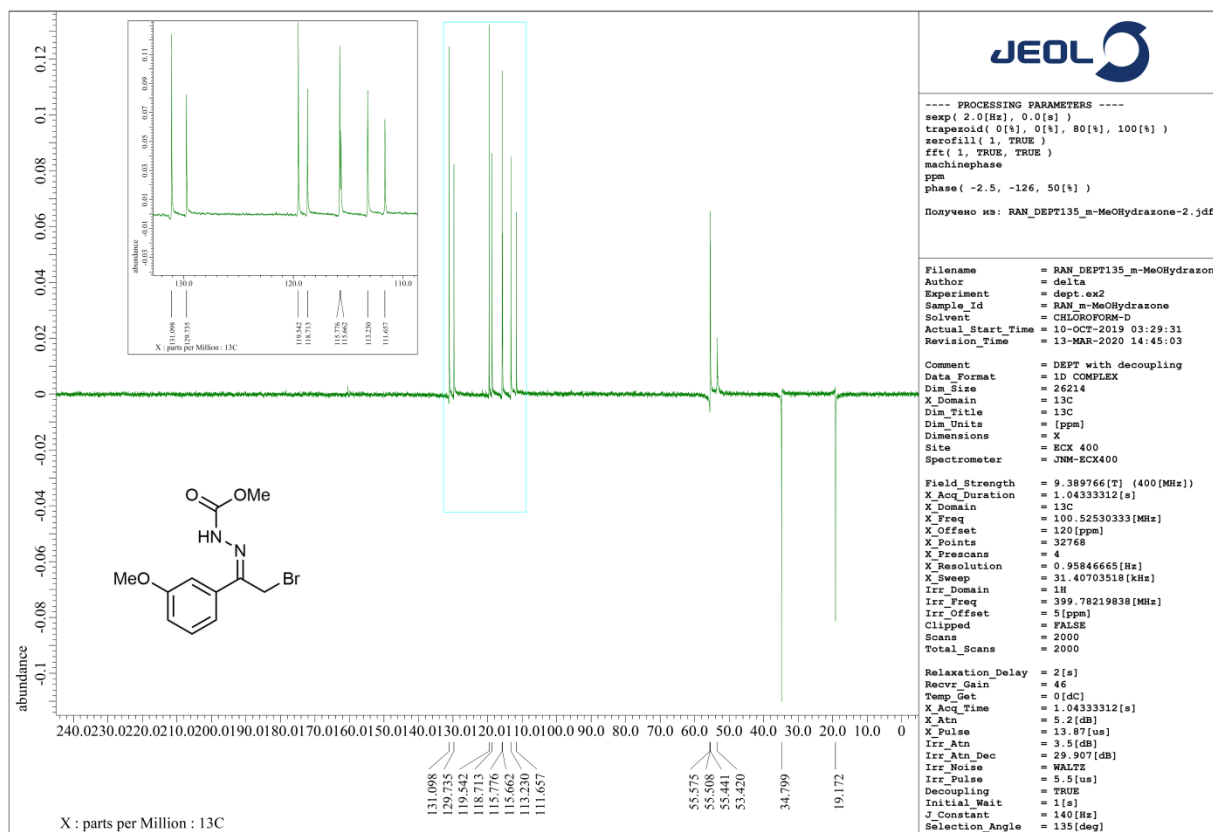


¹³C NMR spectra of methyl 2-[2-bromo-1-(3-methoxyphenyl)ethylidene]hydrazine-1-carboxylate **IIIc** in
CDCl₃

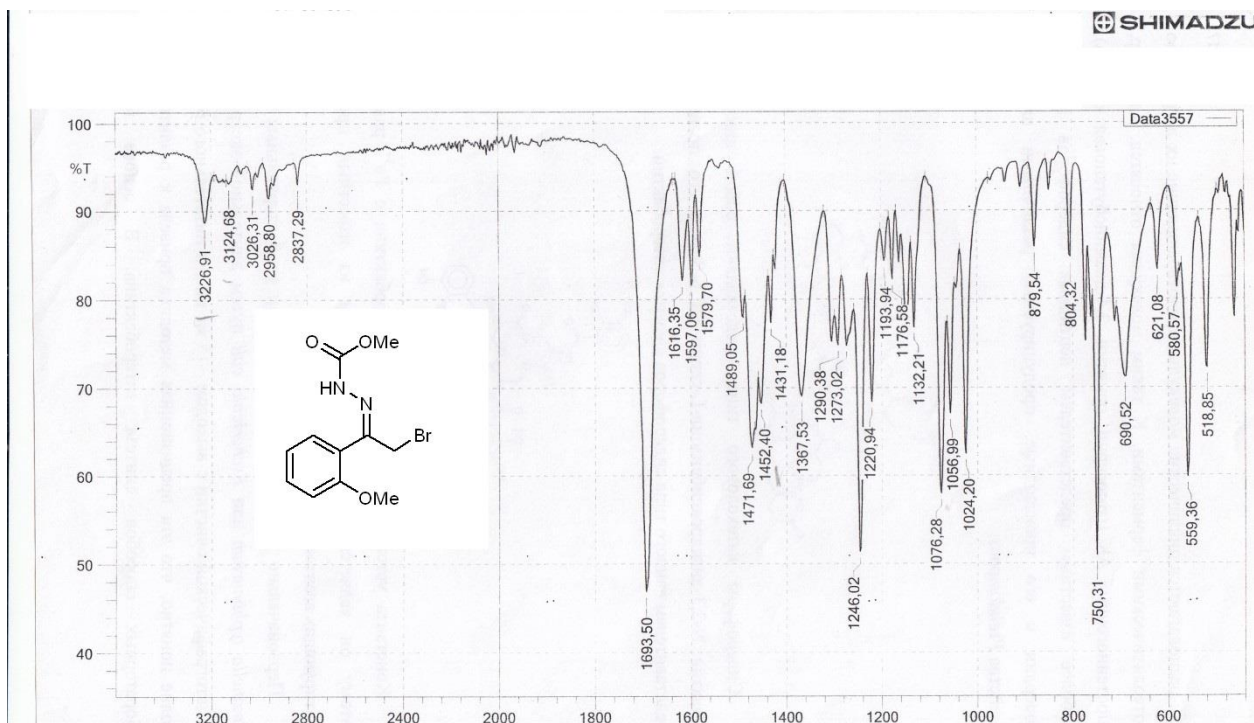


DEPT NMR spectra of methyl 2-[2-bromo-1-(3-methoxyphenyl)ethylidene]hydrazine-1-carboxylate **IIIc** in

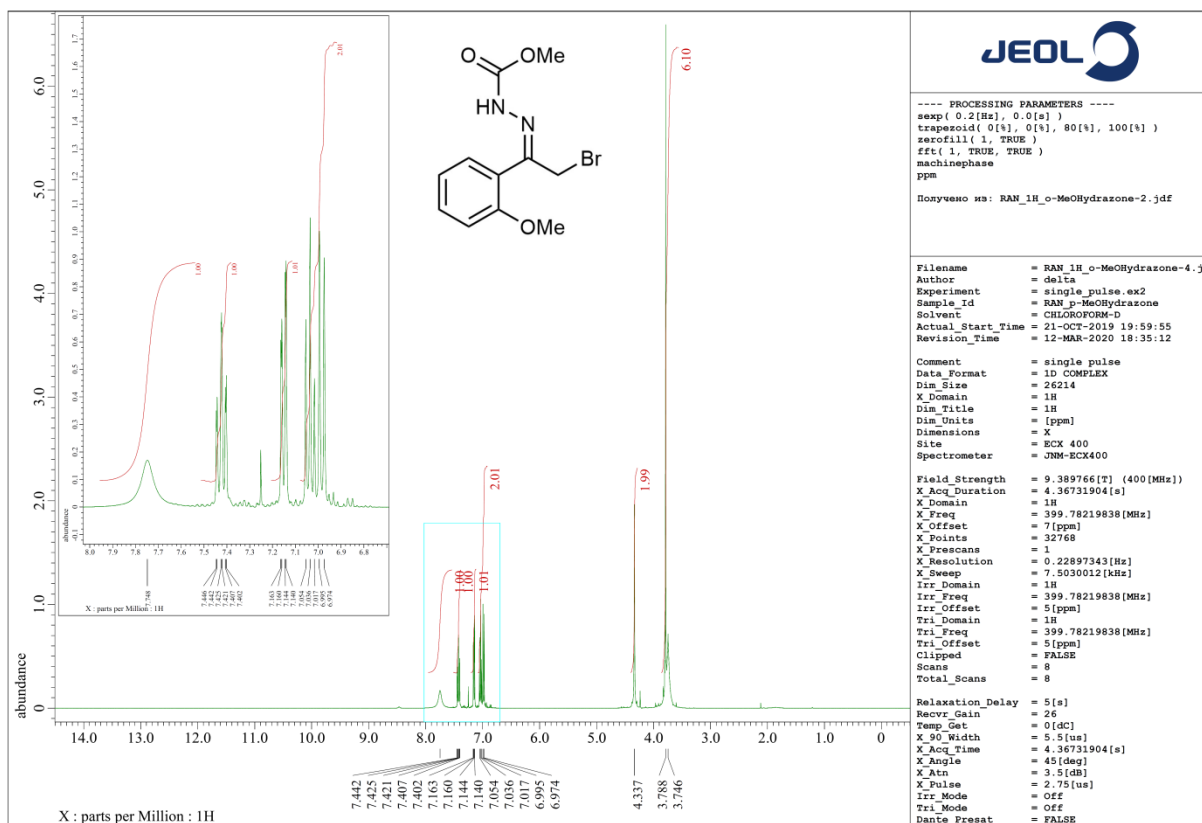
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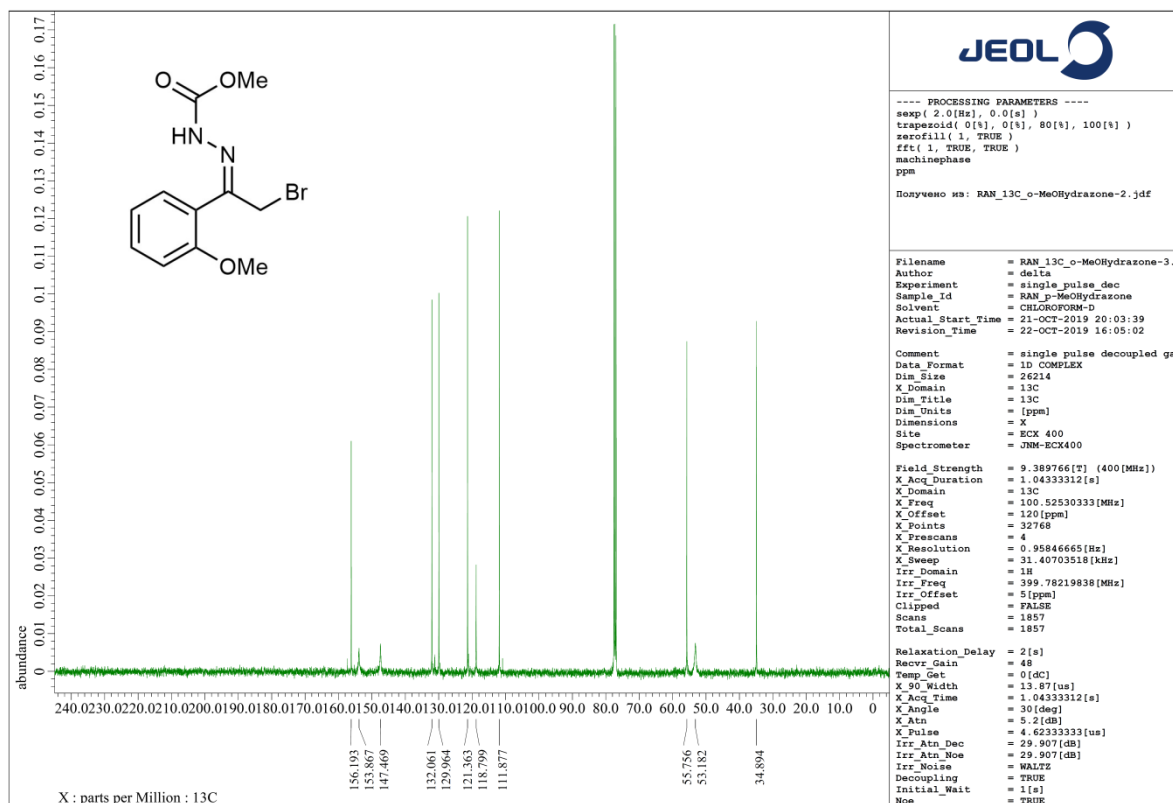
FTIR spectra of methyl 2-[2-bromo-1-(2-methoxyphenyl)ethylidene]hydrazine-1-carboxylate **IIId**



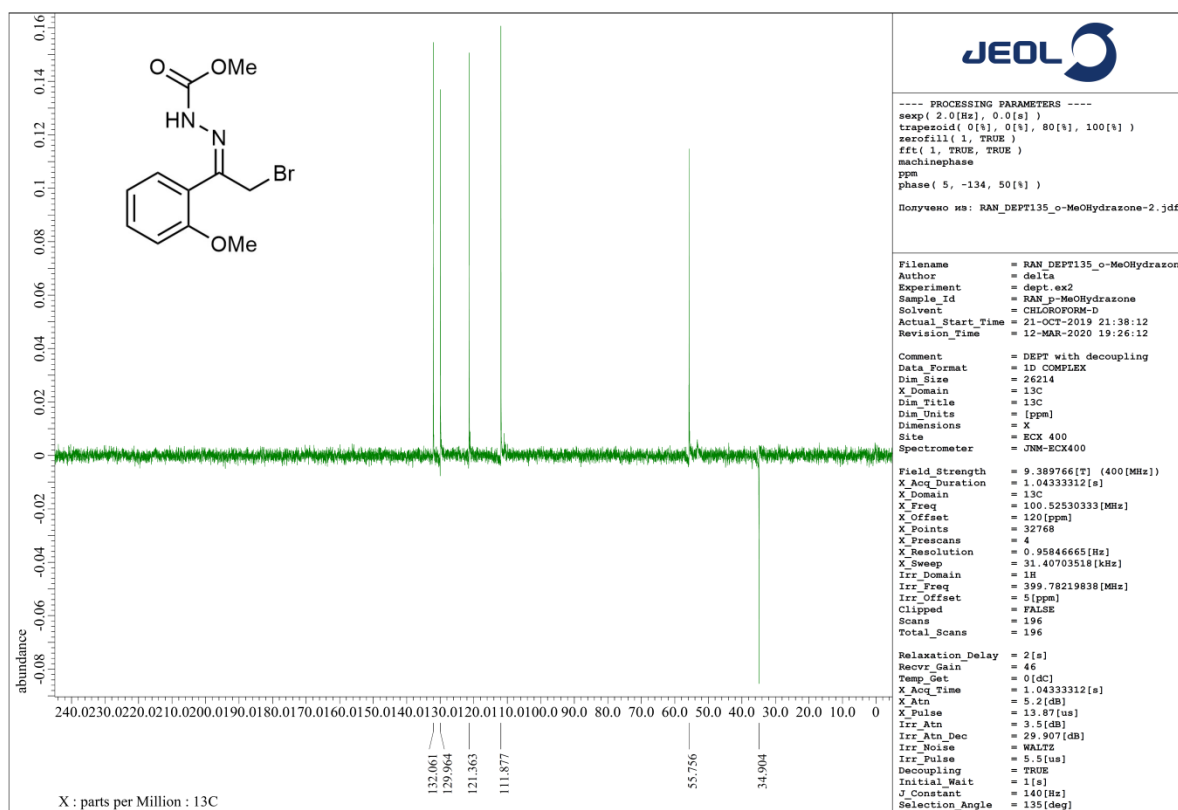
¹H NMR spectra of methyl 2-[2-bromo-1-(2-methoxyphenyl)ethylidene]hydrazine-1-carboxylate **IIId**
in CDCl₃



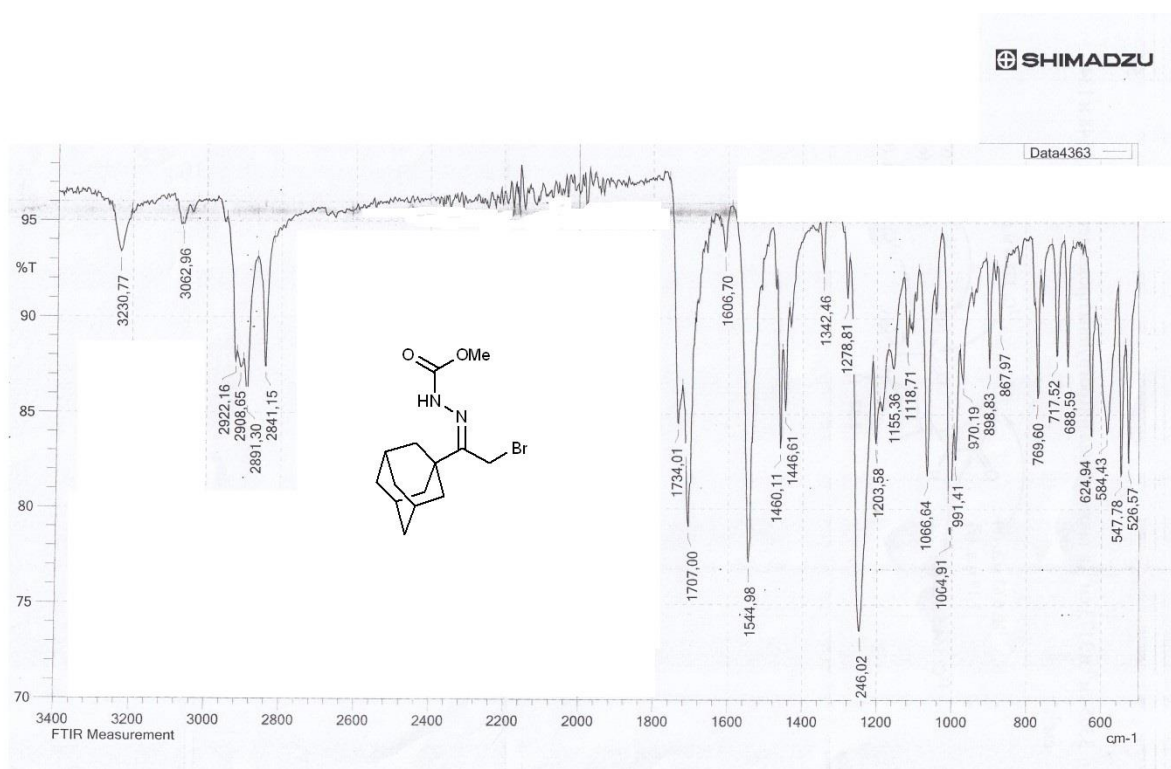
¹³C NMR spectra of methyl 2-[2-bromo-1-(2-methoxyphenyl)ethylidene]hydrazine-1-carboxylate **IIId**
in CDCl₃



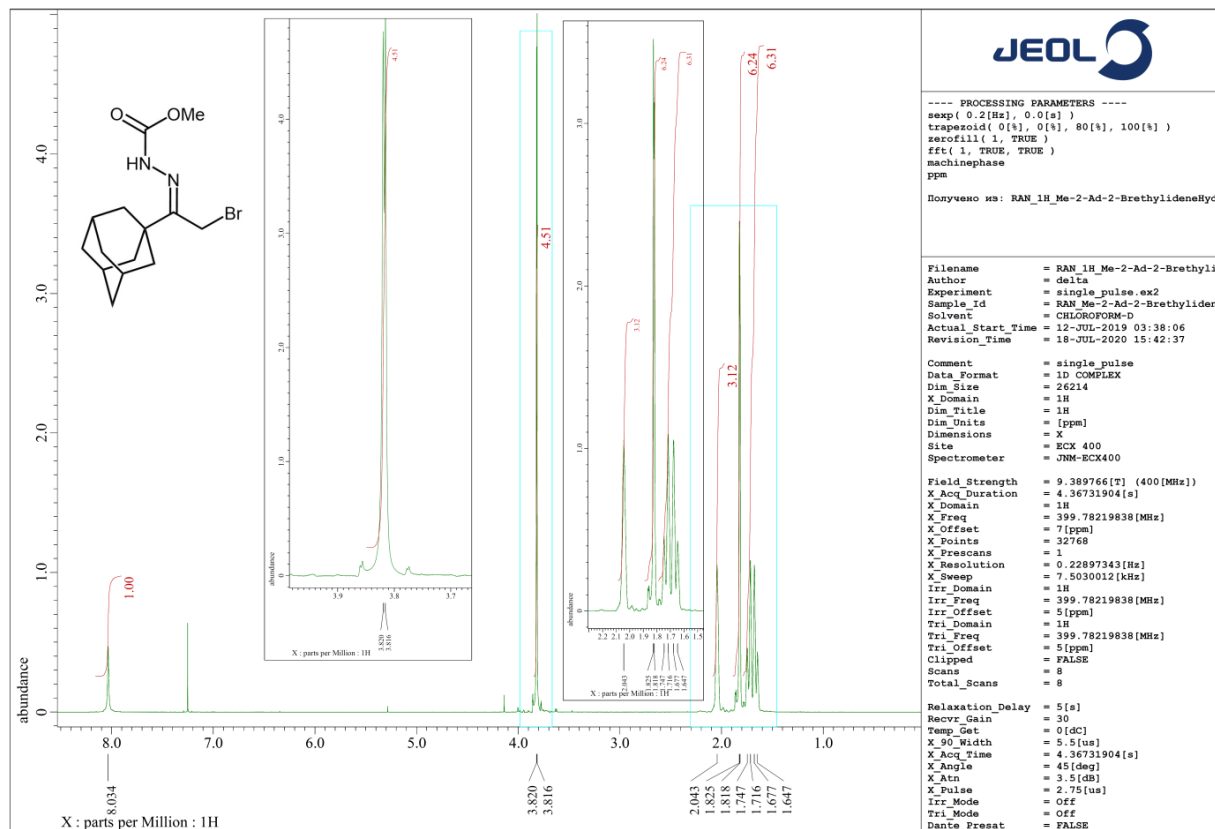
DEPT NMR spectra of methyl 2-[2-bromo-1-(2-methoxyphenyl)ethylidene]hydrazine-1-carboxylate **IIIId**
in CDCl₃



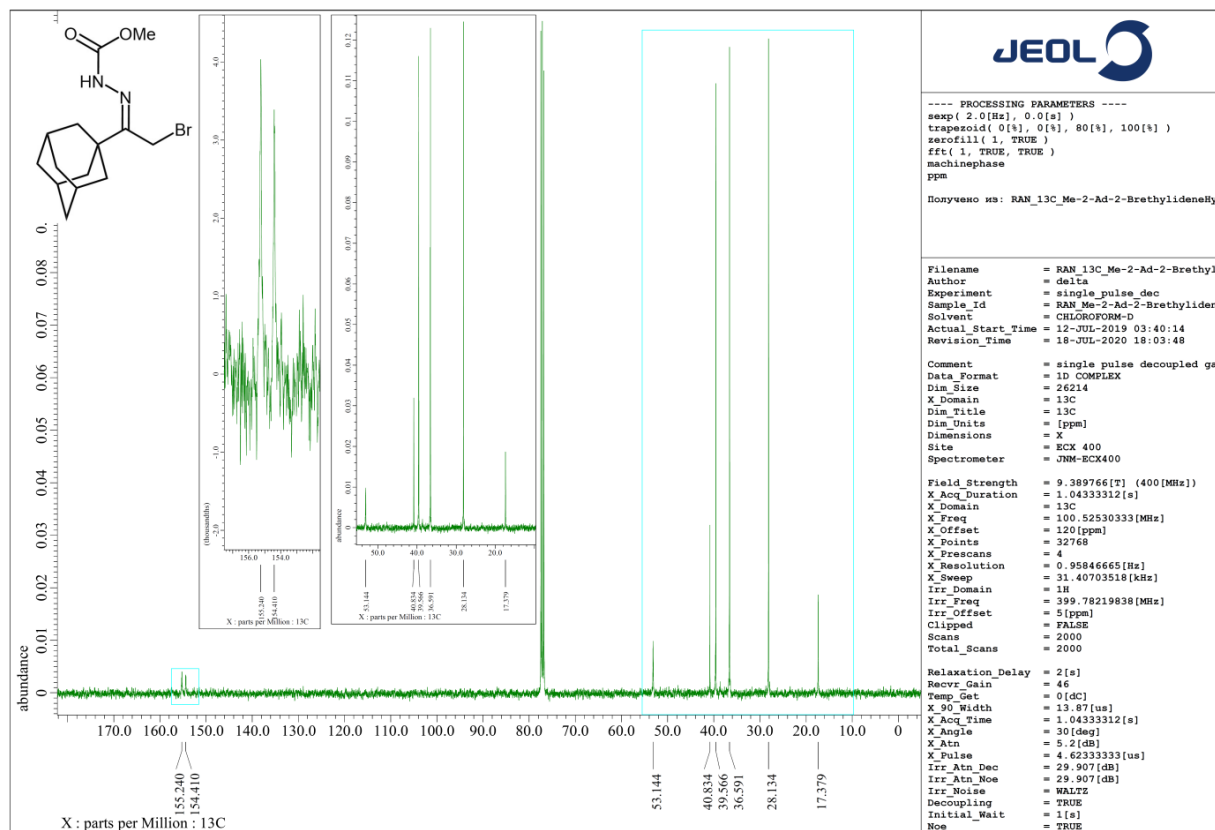
FTIR spectra of methyl 2-(1-(adamantan-1-yl)-2-bromoethylidene)hydrazine-1-carboxylate



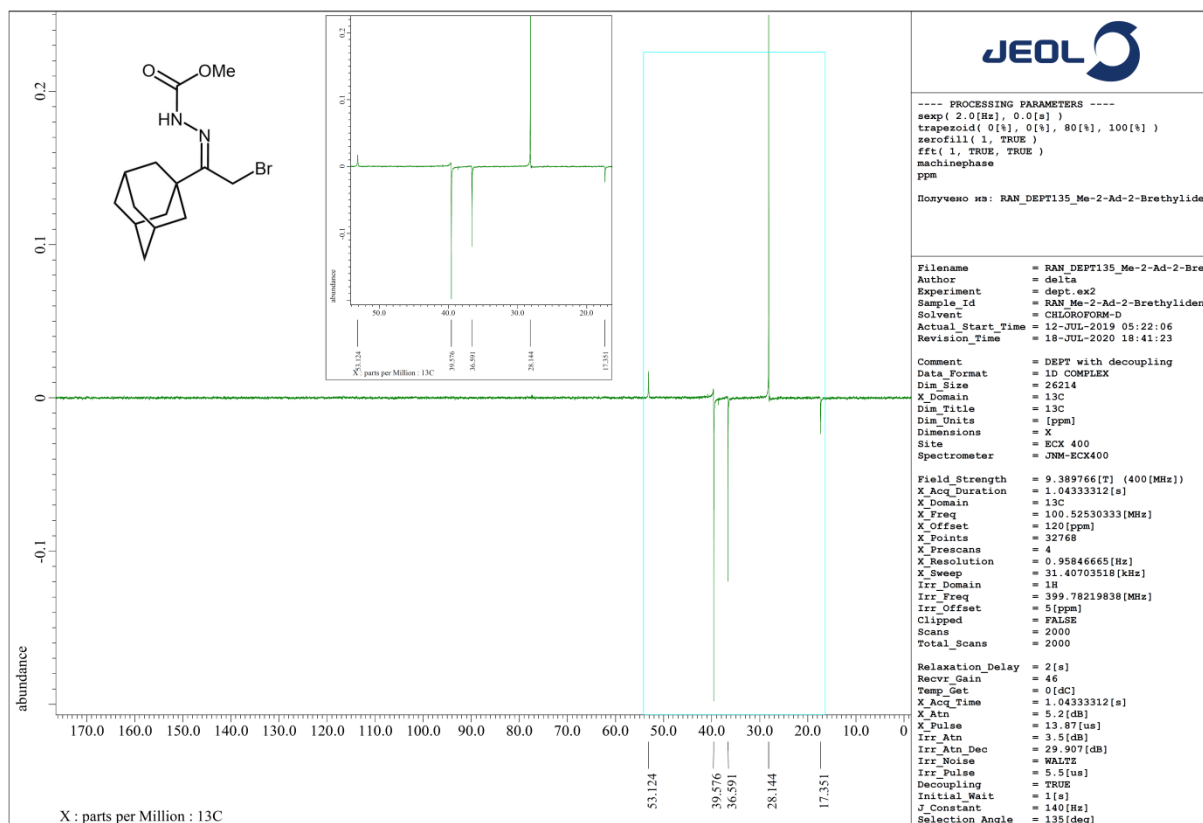
¹H NMR spectra of methyl 2-(1-(adamantan-1-yl)-2-bromoethylidene)hydrazine-1-carboxylate in CDCl₃



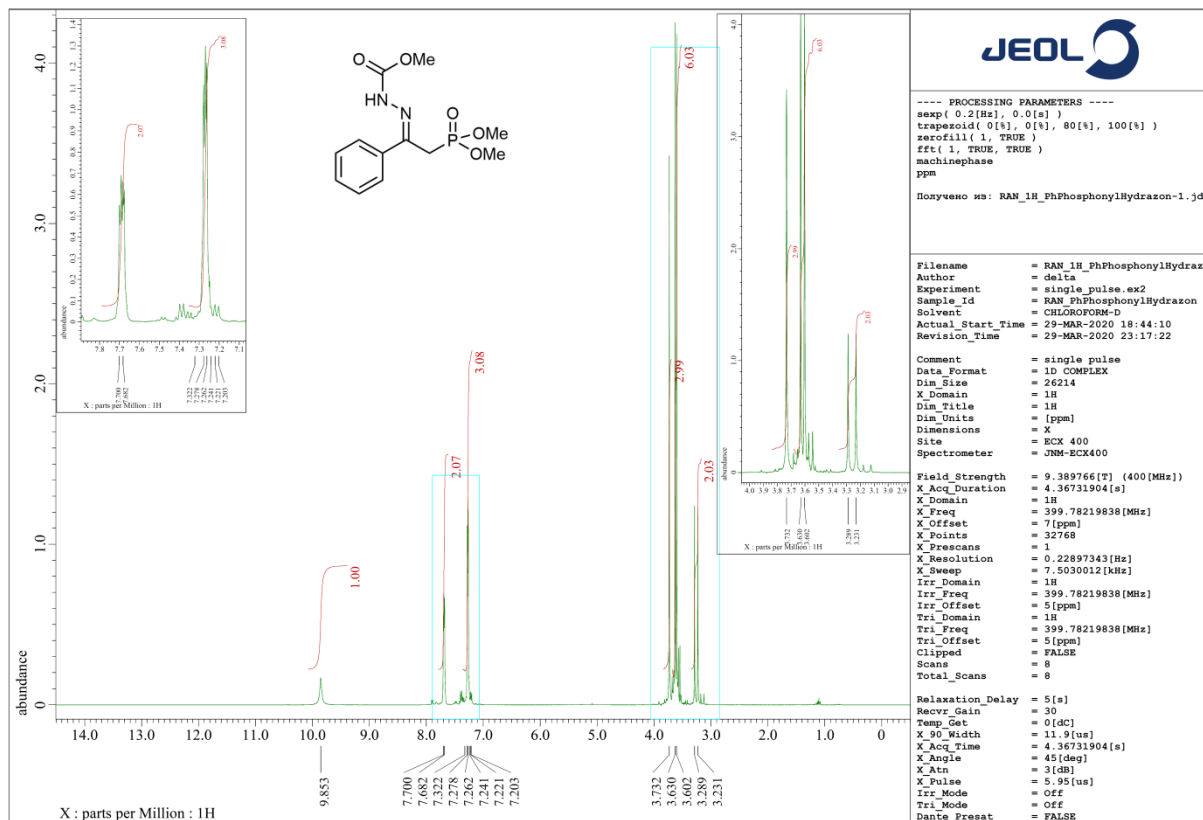
¹³C NMR spectra of methyl 2-(1-(adamantan-1-yl)-2-bromoethylidene)hydrazine-1-carboxylate in CDCl₃



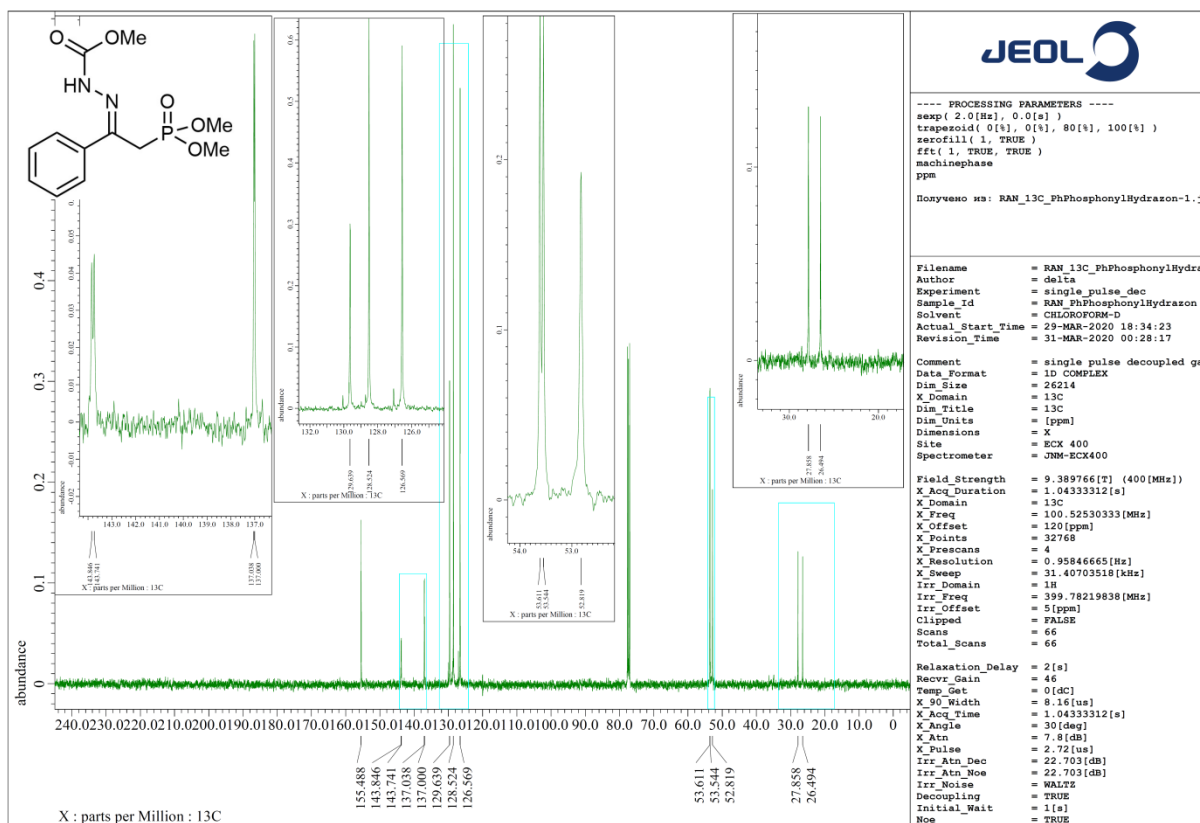
DEPT NMR spectra of methyl 2-(1-(adamantan-1-yl)-2-bromoethylidene)hydrazine-1-carboxylate in CDCl_3



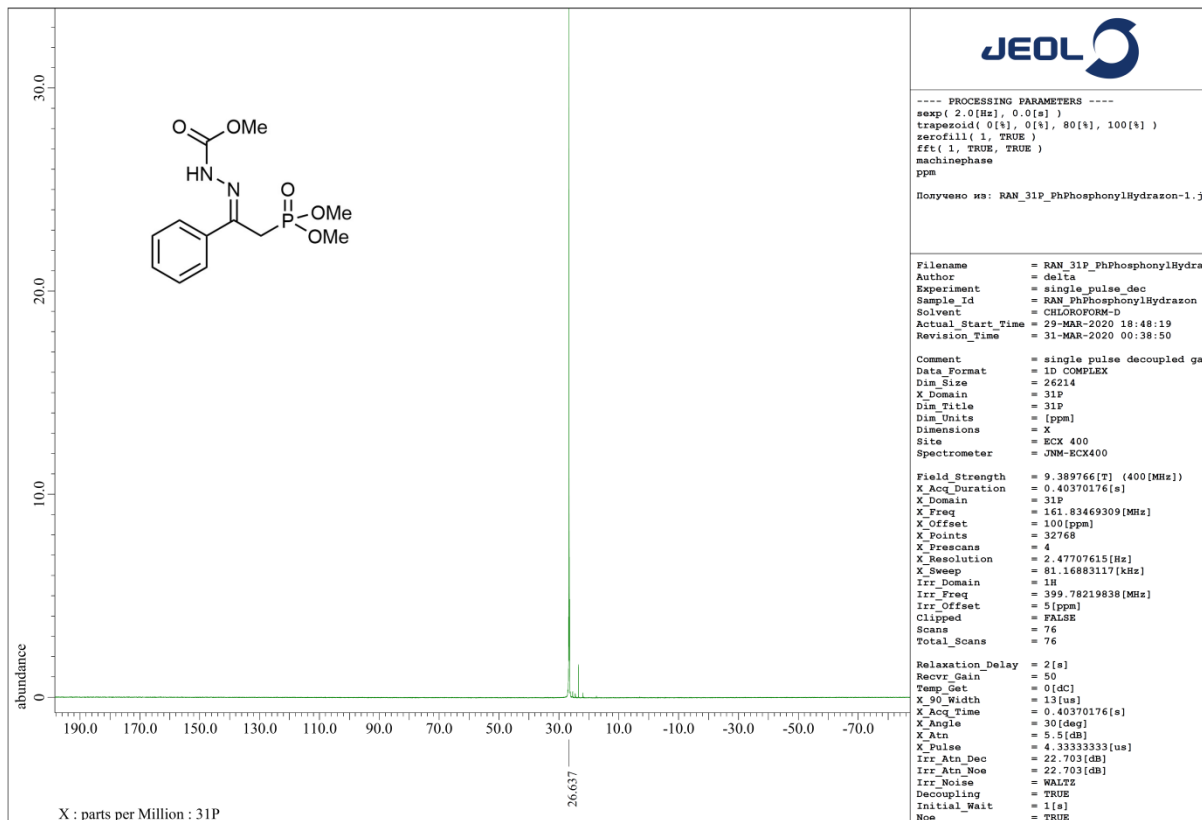
^1H NMR spectra of methyl 2-[2-(dimethoxyphosphoryl)-1-phenylethylidene]hydrazine-1-carboxylate **Va** in CDCl_3



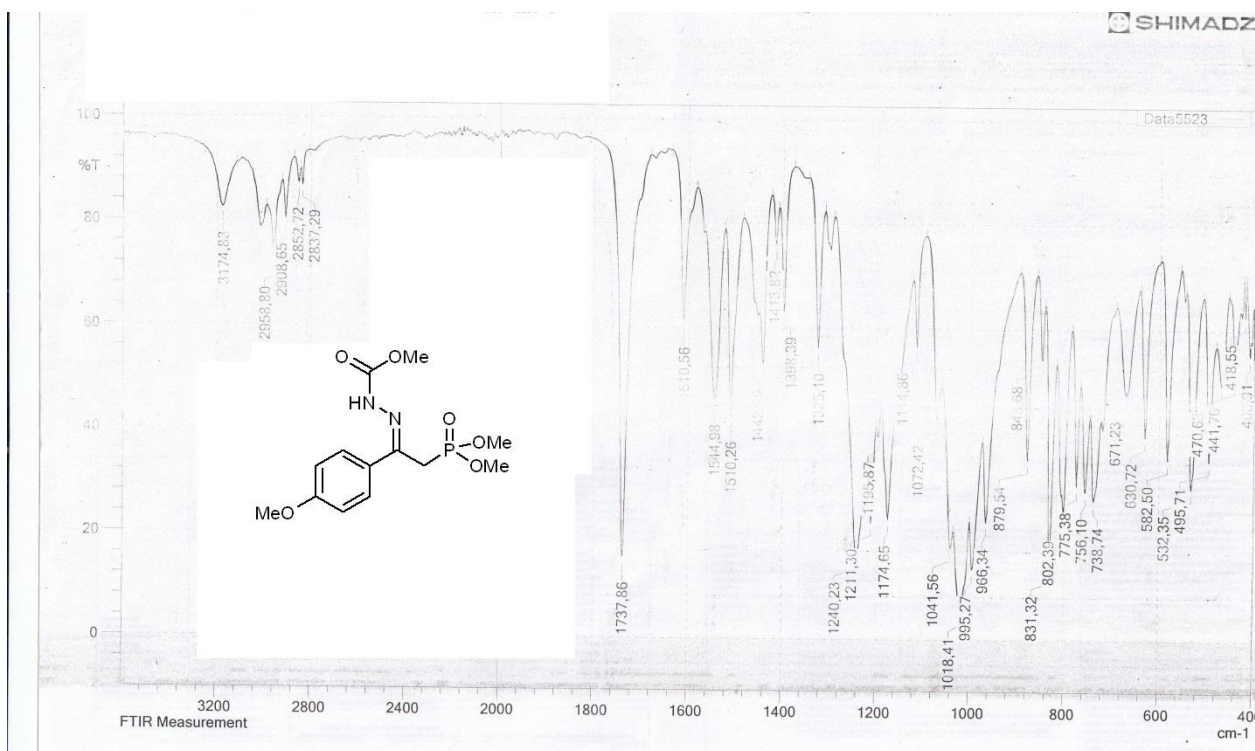
¹³C NMR spectra of methyl 2-[2-(dimethoxyphosphoryl)-1-phenylethylidene]hydrazine-1-carboxylate **Va**
in CDCl₃



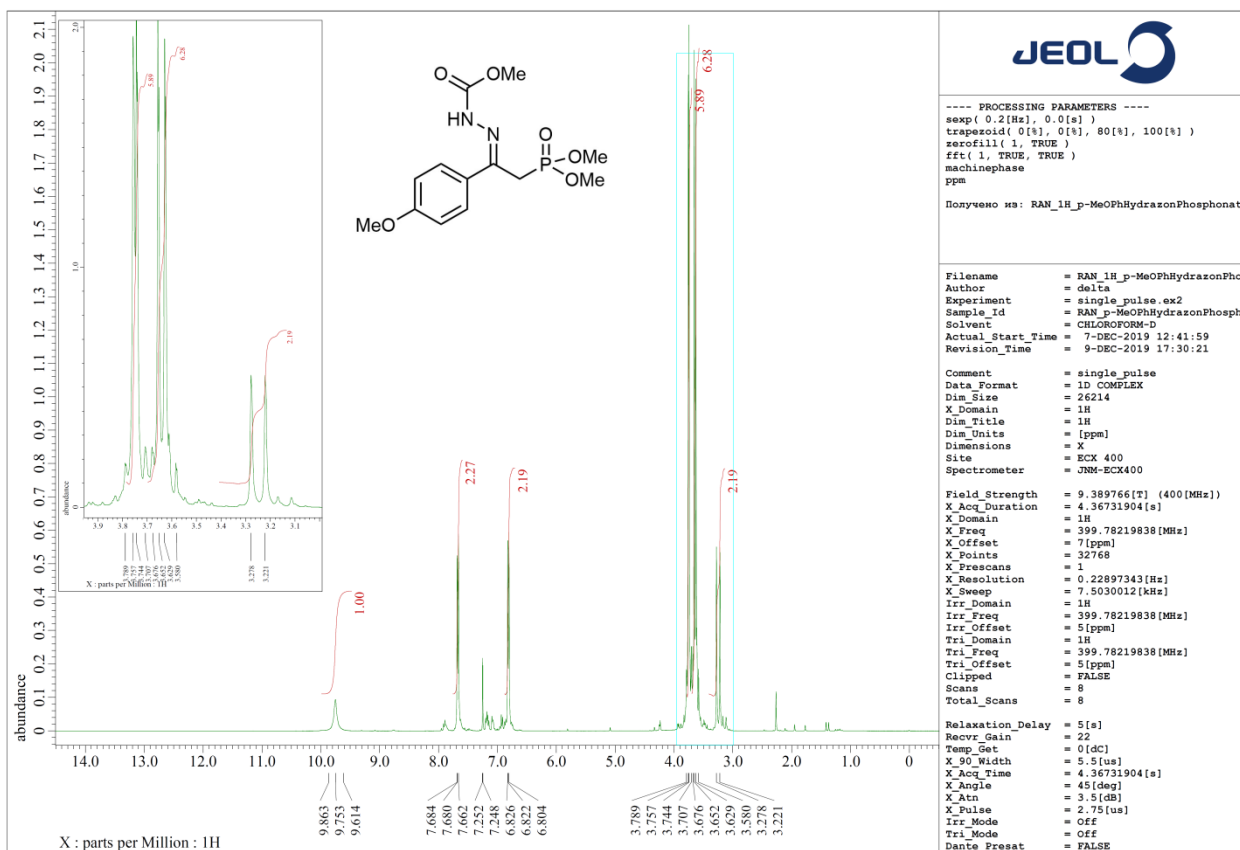
³¹P NMR spectra of methyl 2-[2-(dimethoxyphosphoryl)-1-phenylethylidene]hydrazine-1-carboxylate **Va** in
CDCl₃



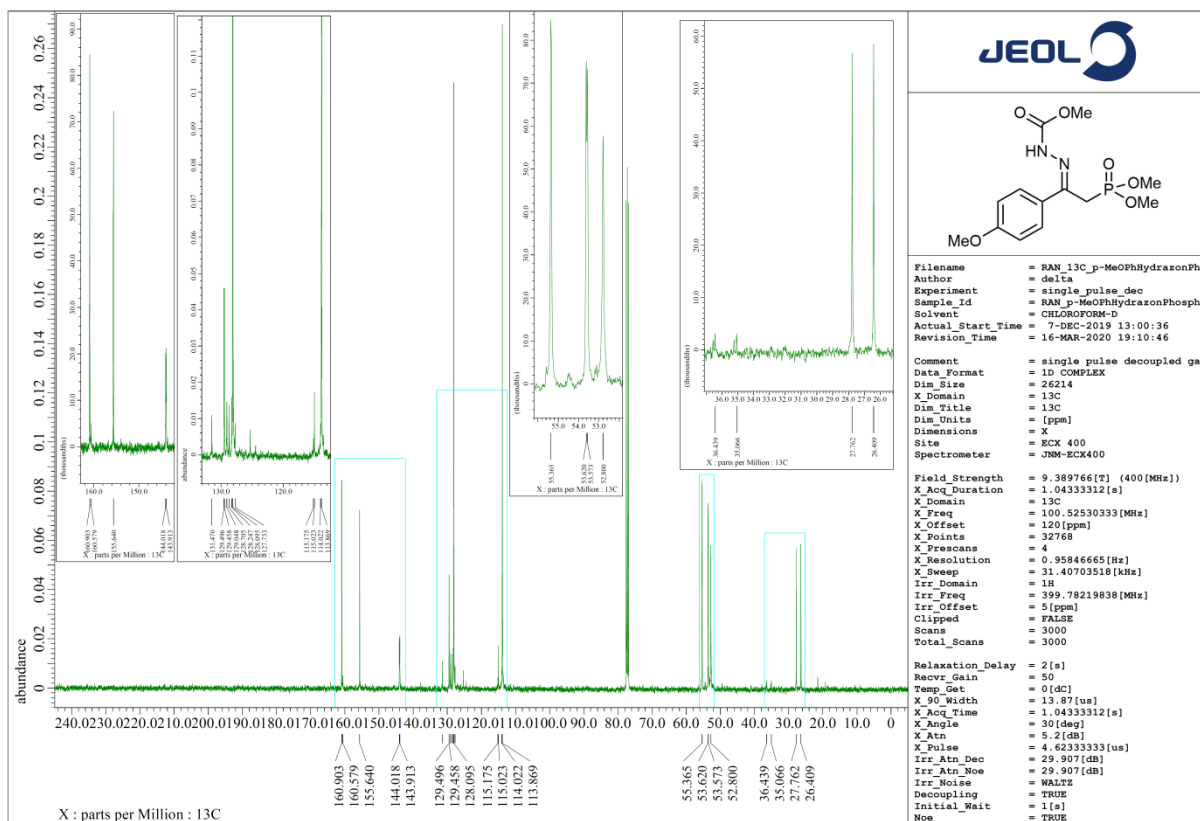
FTIR spectra of methyl 2-(2-(dimethoxyphosphoryl)-1-(4-methoxyphenyl)ethylidene)hydrazine-1-carboxylate **Vb**



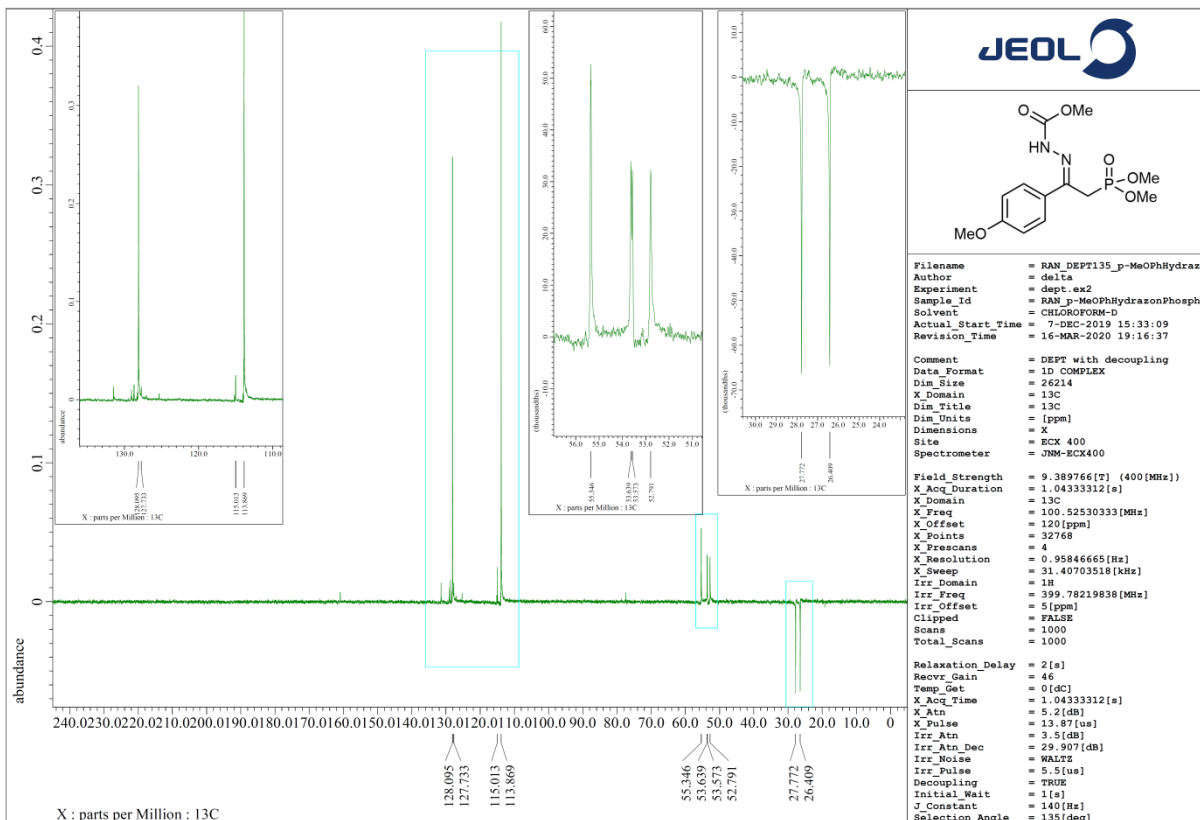
¹H NMR spectra of methyl 2-(2-(dimethoxyphosphoryl)-1-(4-methoxyphenyl)ethylidene)hydrazine-1-carboxylate **Vb** in CDCl₃



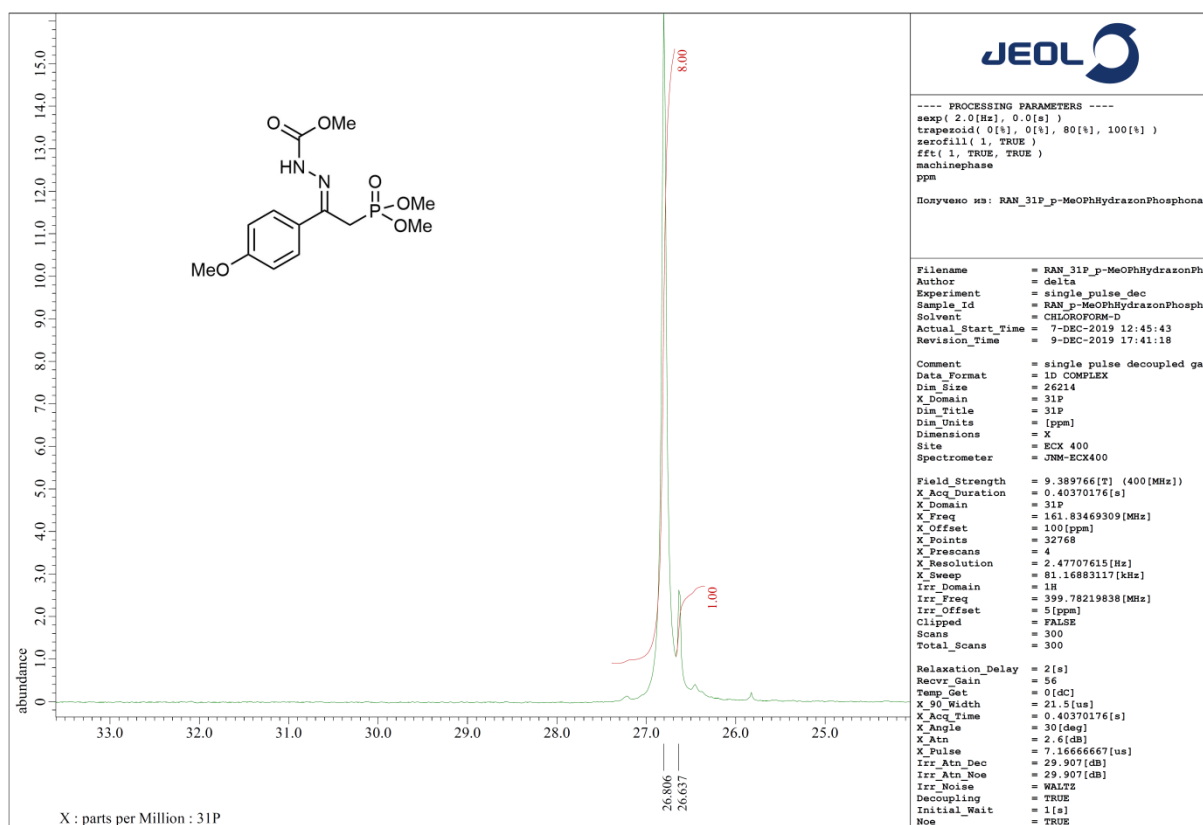
¹³C NMR spectra of methyl 2-(2-(dimethoxyphosphoryl)-1-(4-methoxyphenyl)ethylidene)hydrazine-1-carboxylate **Vb** in CDCl₃



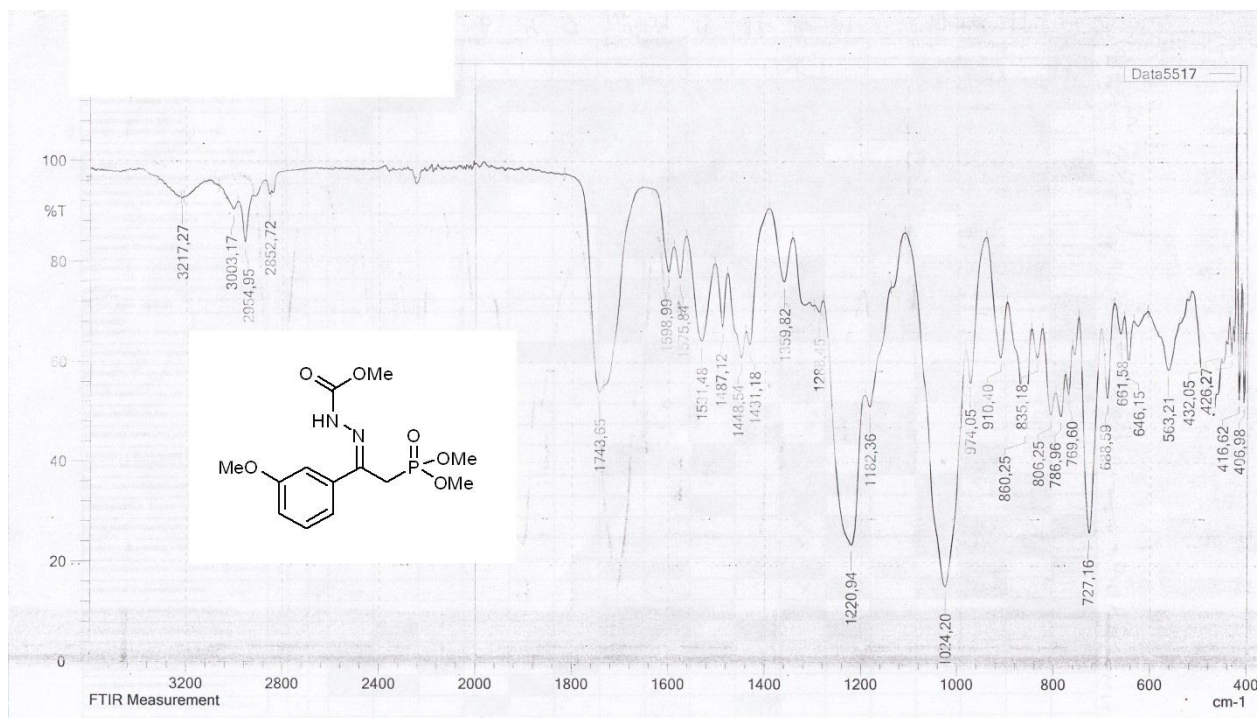
DEPT NMR spectra of methyl 2-(2-(dimethoxyphosphoryl)-1-(4-methoxyphenyl)ethylidene)hydrazine-1-carboxylate **Vb** in CDCl₃



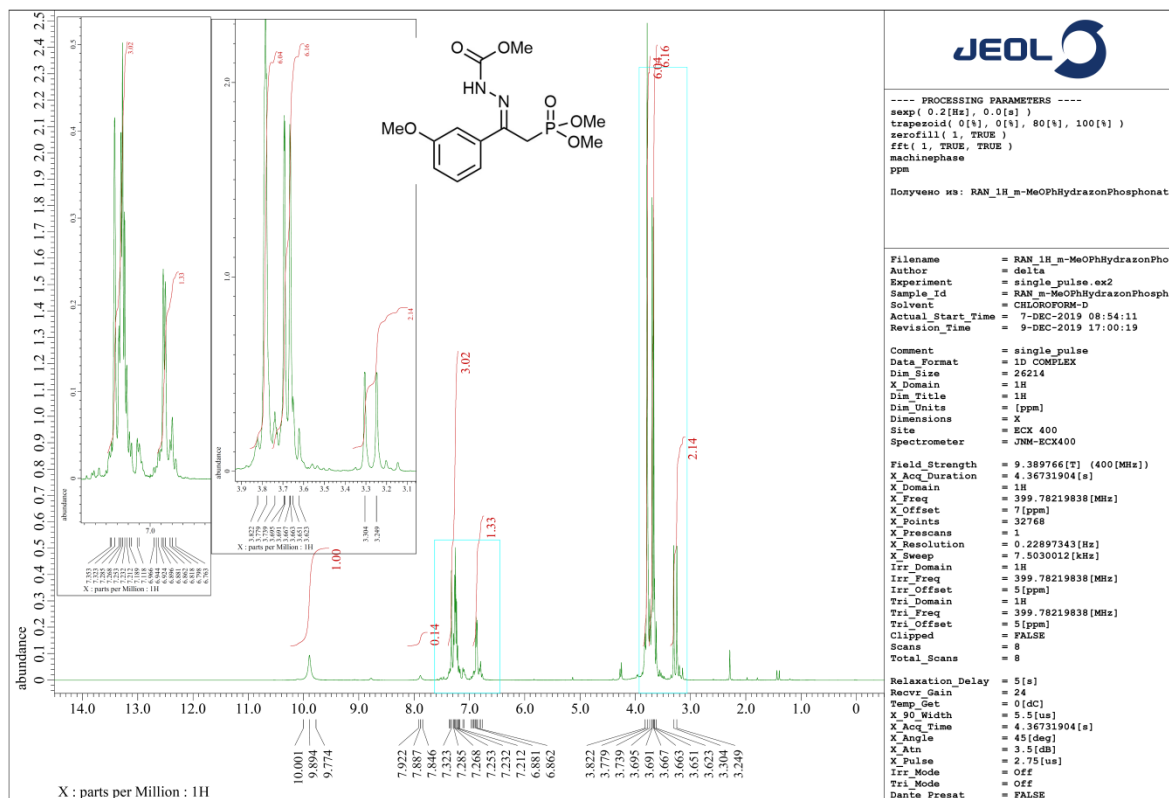
³¹P NMR spectra of methyl 2-(2-(dimethoxyphosphoryl)-1-(4-methoxyphenyl)ethylidene)hydrazine-1-carboxylate **Vb** in CDCl₃



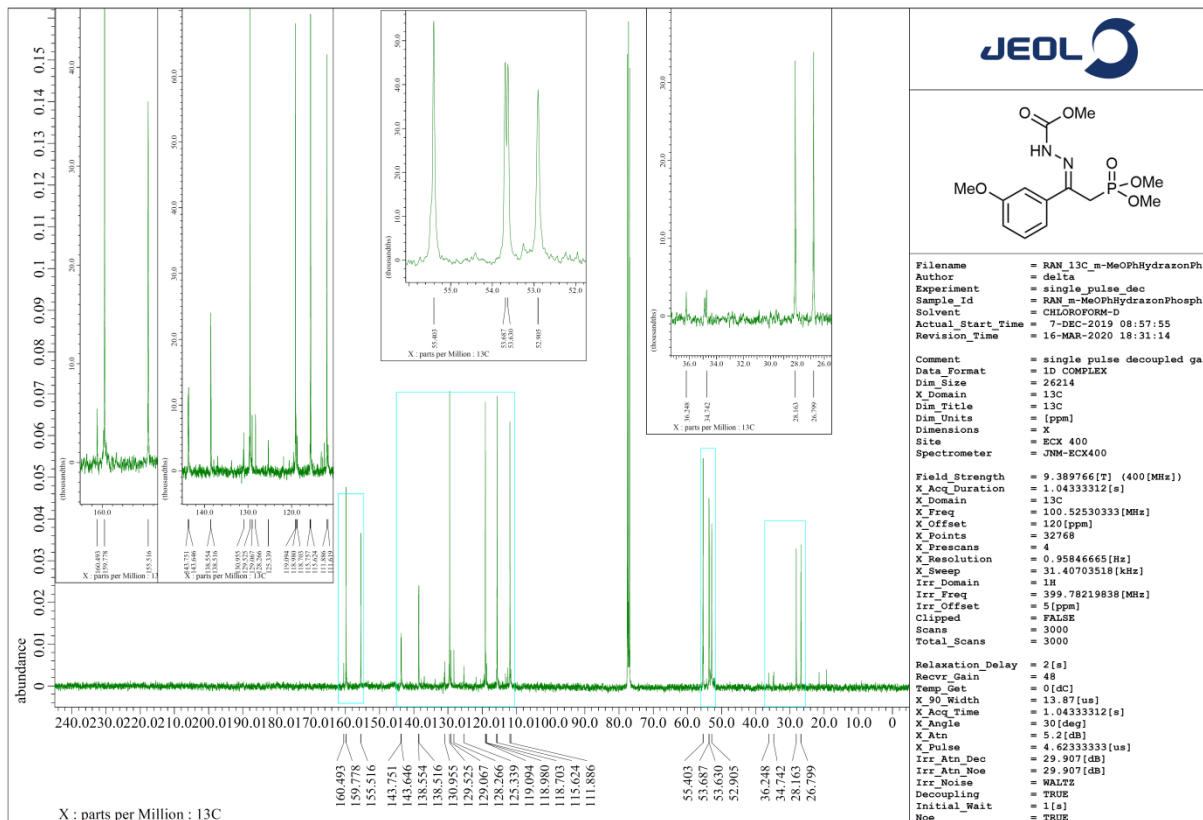
FTIR spectra of methyl 2-(2-(dimethoxyphosphoryl)-1-(3-methoxyphenyl)ethylidene)hydrazine-1-carboxylate **Vc**



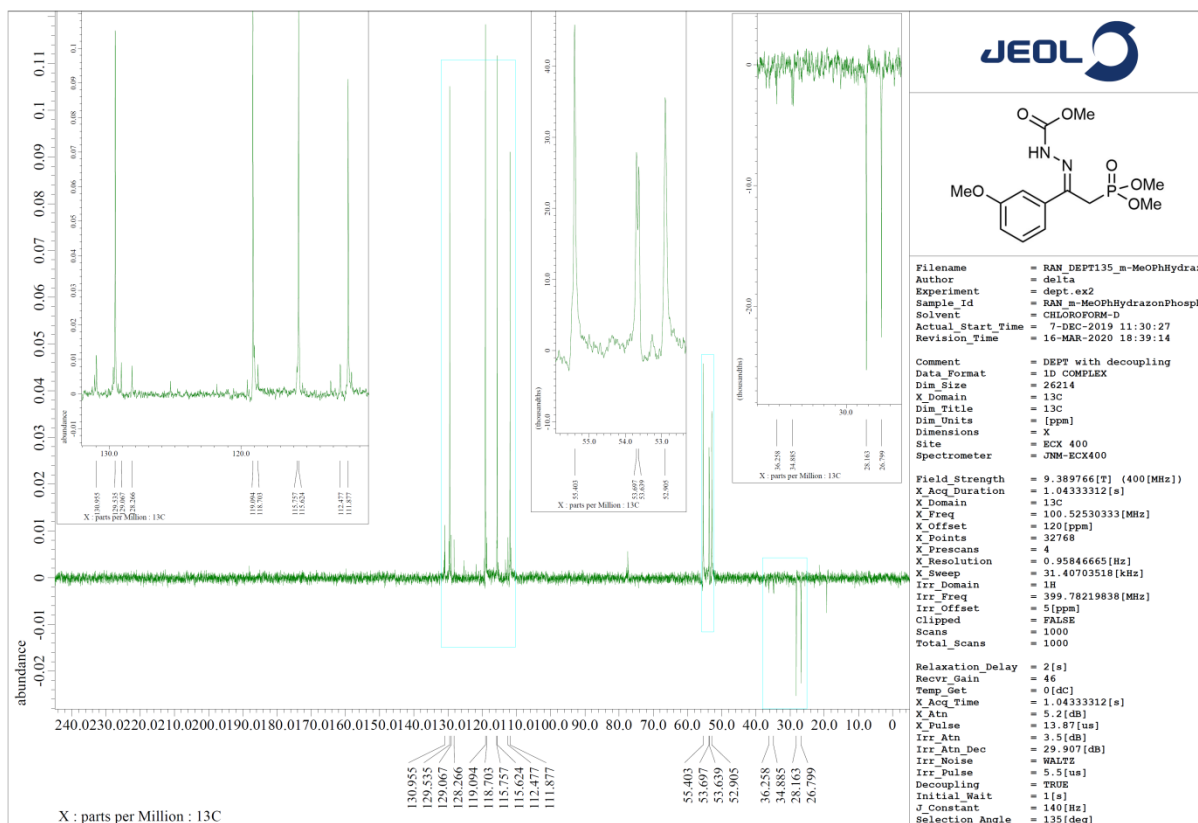
¹H NMR spectra of methyl 2-(2-(dimethoxyphosphoryl)-1-(3-methoxyphenyl)ethylidene)hydrazine-1-carboxylate **Vc** in CDCl₃



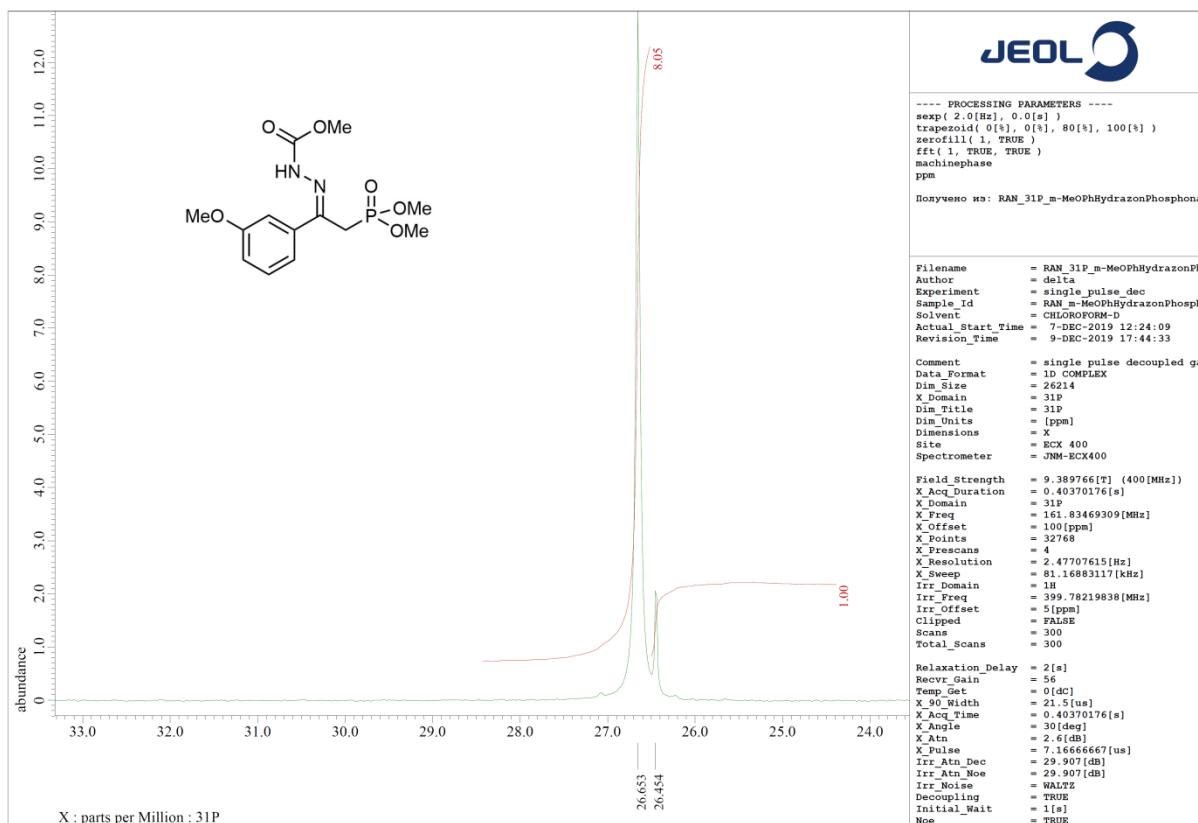
¹³C NMR spectra of methyl 2-(2-(dimethoxyphosphoryl)-1-(3-methoxyphenyl)ethylidene)hydrazine-1-carboxylate **Vc** in CDCl₃



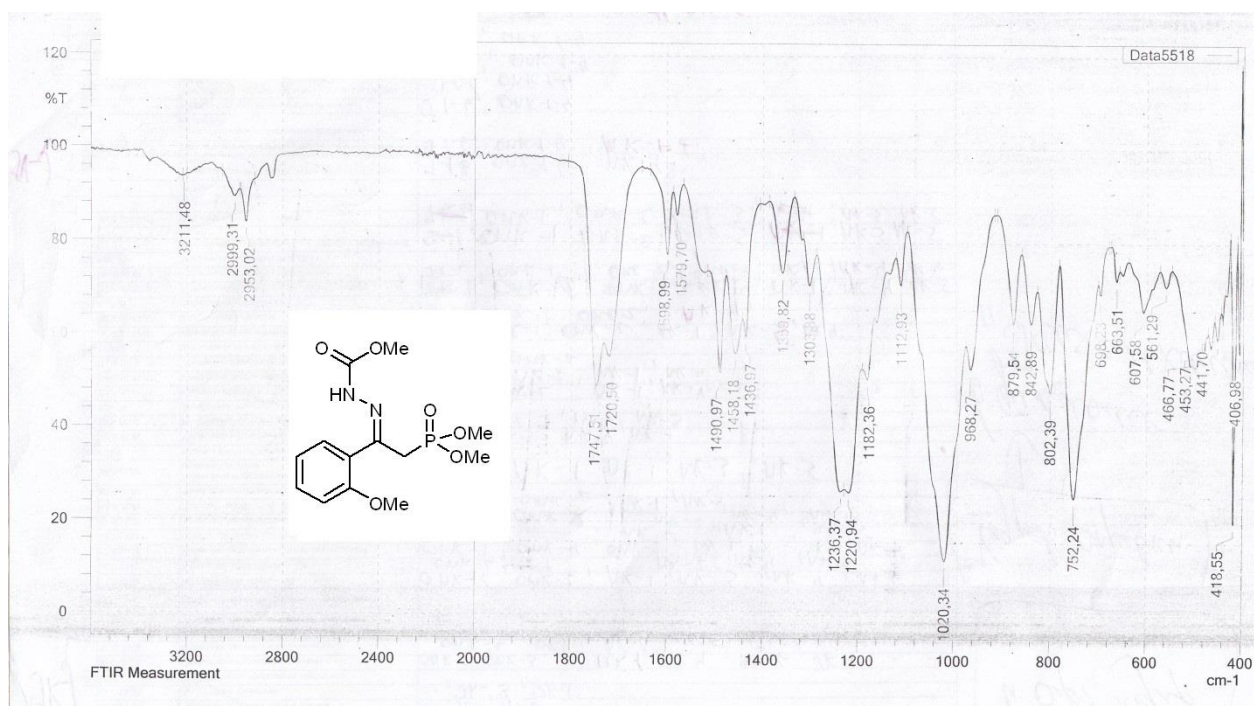
DEPT NMR spectra of methyl 2-(2-(dimethoxyphosphoryl)-1-(3-methoxyphenyl)ethylidene)hydrazine-1-carboxylate **Vc** in CDCl₃



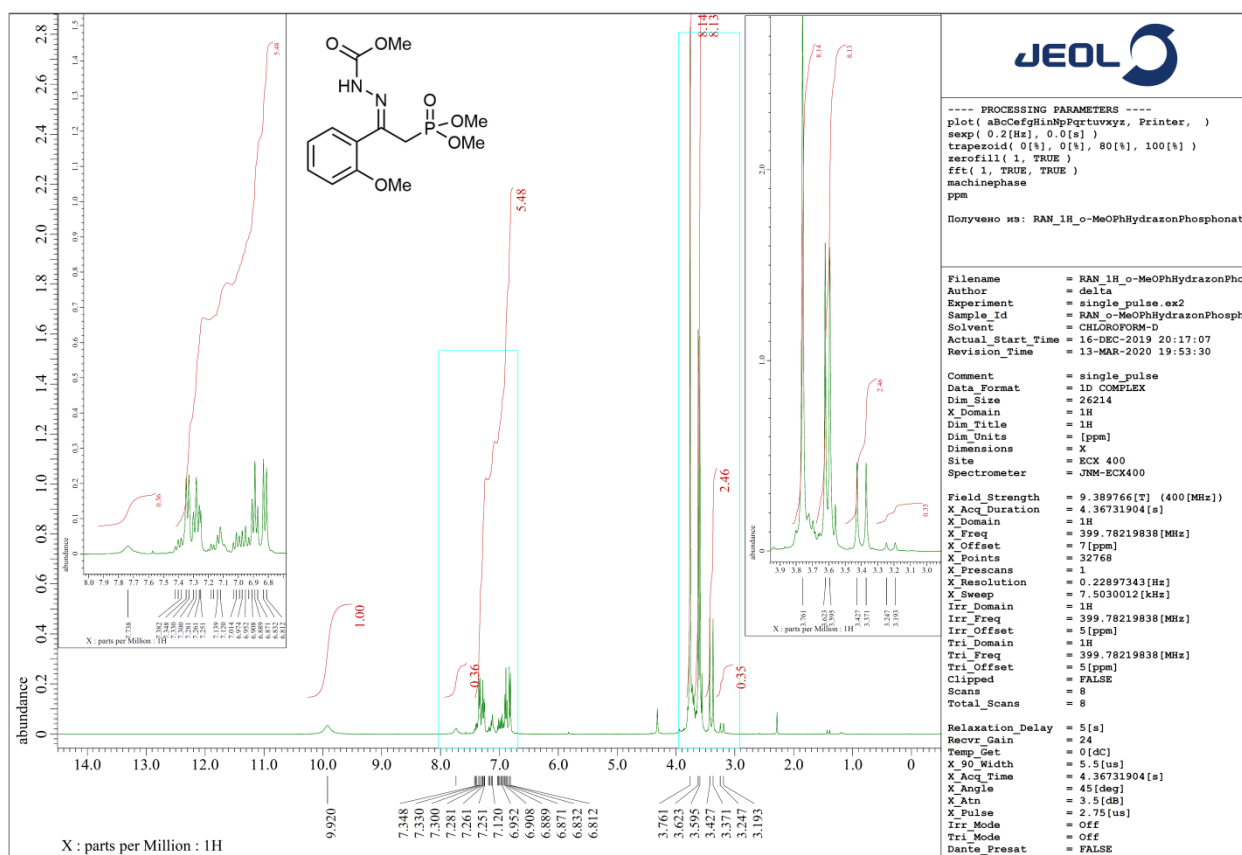
³¹P NMR spectra of methyl 2-(2-(dimethoxyphosphoryl)-1-(3-methoxyphenyl)ethylidene)hydrazine-1-carboxylate **Vc** in CDCl₃



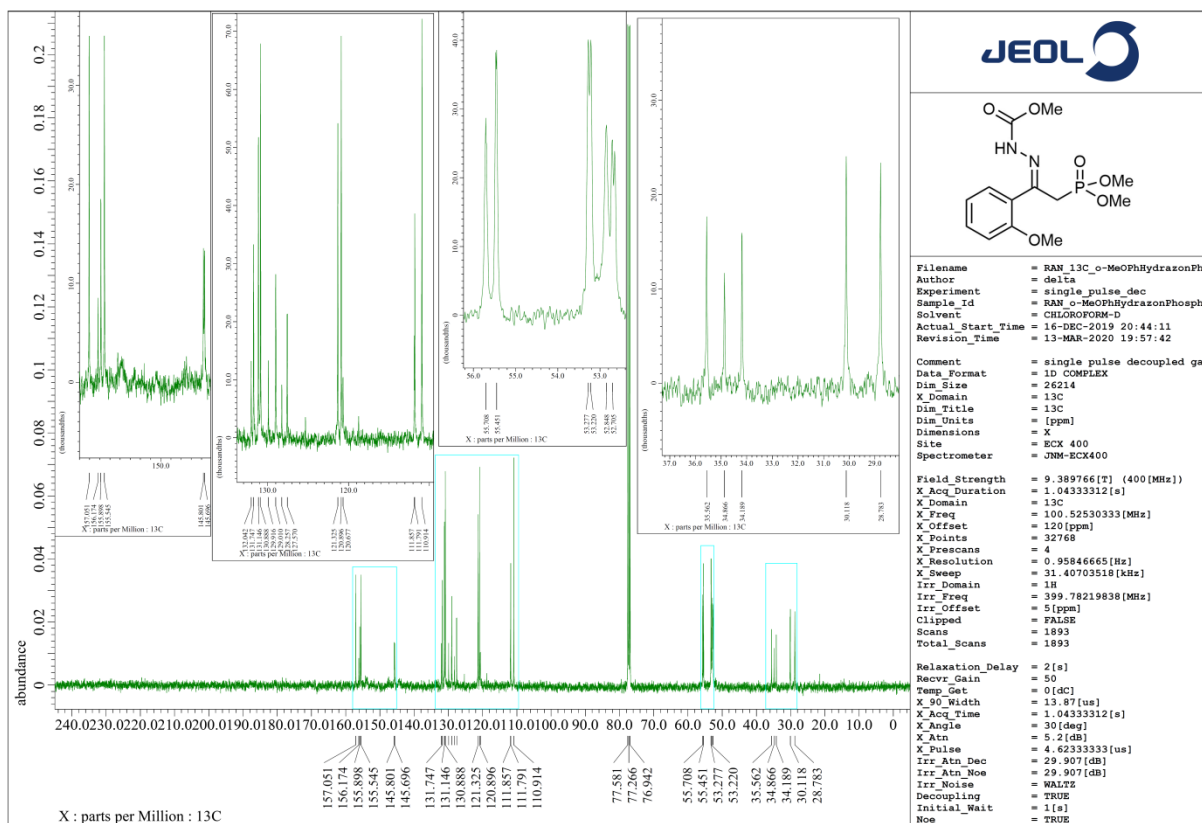
FTIR spectra of methyl 2-(2-(dimethoxyphosphoryl)-1-(2-methoxyphenyl)ethylidene)hydrazine-1-carboxylate **Vd**



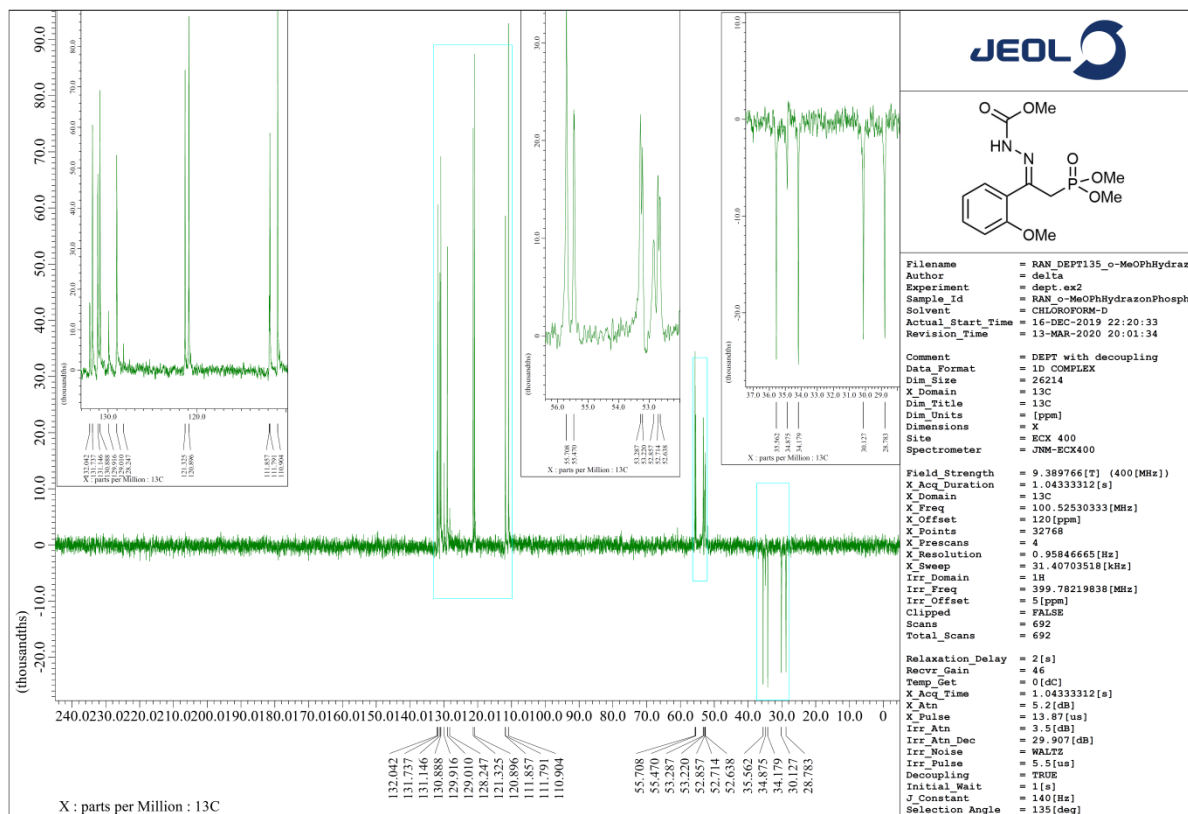
¹H NMR spectra of methyl 2-(2-(dimethoxyphosphoryl)-1-(2-methoxyphenyl)ethylidene)hydrazine-1-carboxylate **Vd** in CDCl₃



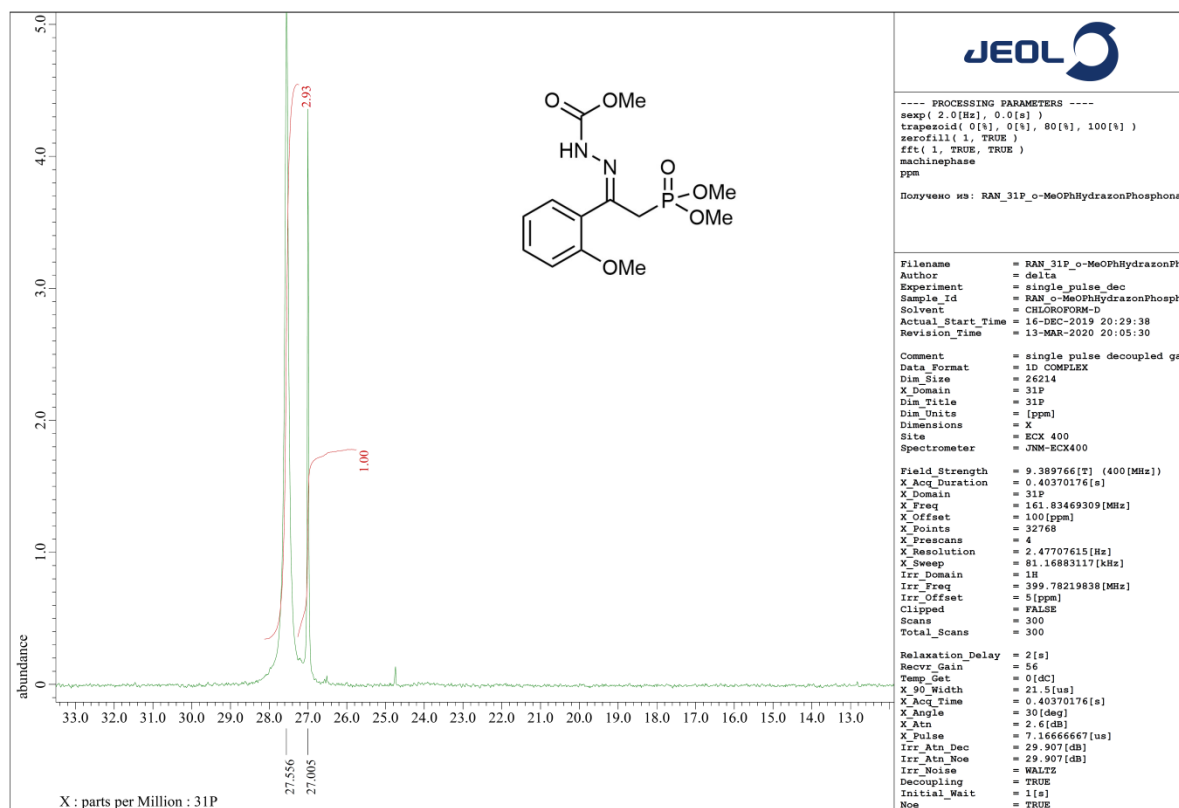
¹³C NMR spectra of methyl 2-(2-(dimethoxyphosphoryl)-1-(2-methoxyphenyl)ethylidene)hydrazine-1-carboxylate **Vd** in CDCl₃



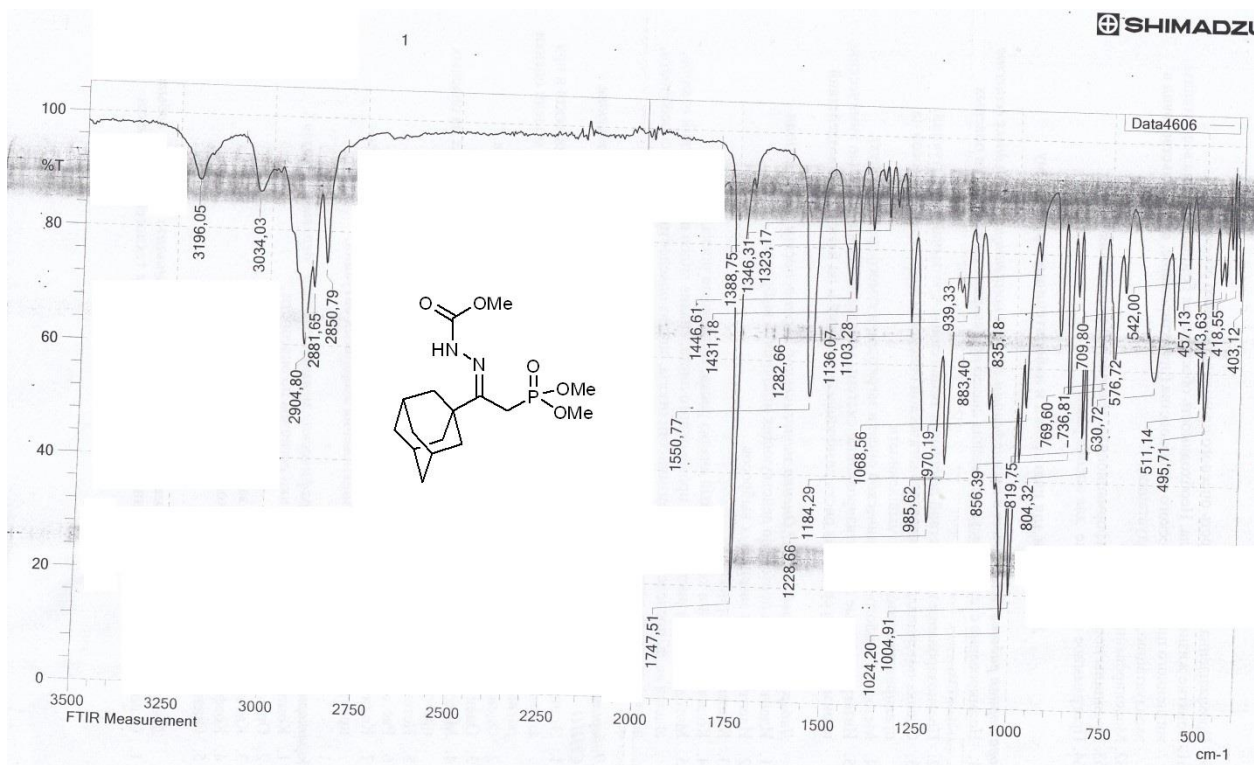
DEPT NMR spectra of methyl 2-(2-(dimethoxyphosphoryl)-1-(2-methoxyphenyl)ethylidene)hydrazine-1-carboxylate **Vd** in CDCl₃



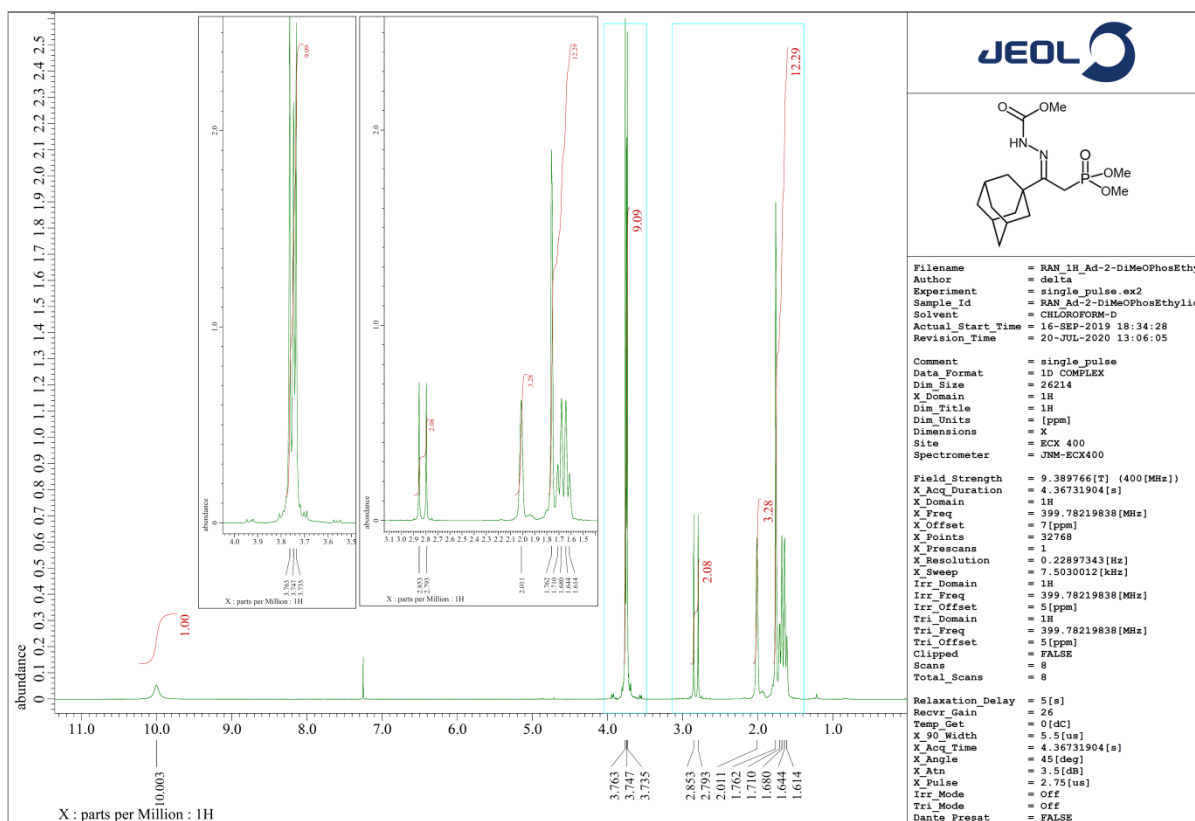
³¹P NMR spectra of methyl 2-(2-(dimethoxyphosphoryl)-1-(2-methoxyphenyl)ethylidene)hydrazine-1-carboxylate **Vd** in CDCl₃



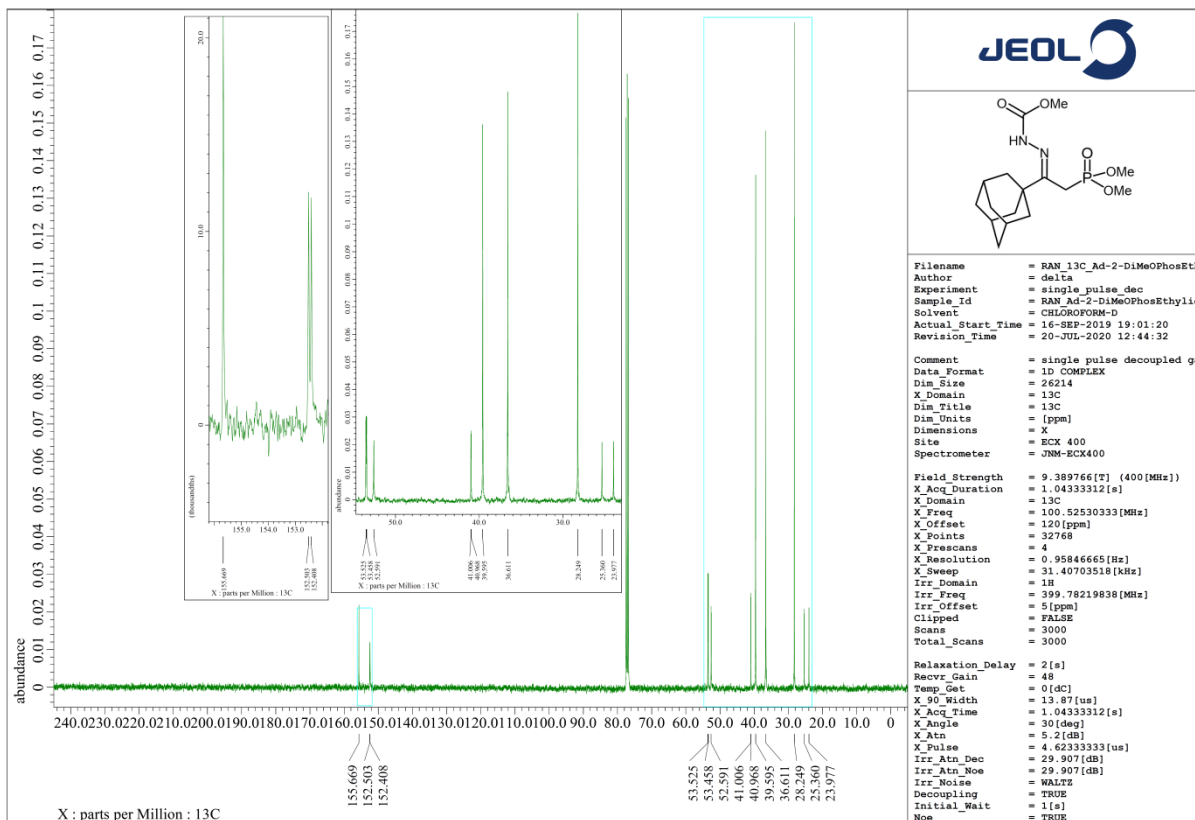
FTIR spectra of methyl 2-(1-(adamantan-1-yl)-2-(dimethoxyphosphoryl)ethylidene)hydrazine-1-carboxylate



¹H NMR spectra of methyl 2-(1-(adamantan-1-yl)-2-(dimethoxyphosphoryl)ethylidene)hydrazine-1-carboxylate in CDCl₃



¹³C NMR spectra of methyl 2-(1-(adamantan-1-yl)-2-(dimethoxyphosphoryl)ethylidene)hydrazine-1-carboxylate in CDCl₃



JEOL

Chemical structure of RAN_DEPT135_Ad-2-DiMeOPhosEthylidene:

COC(=O)N=C(C1C2CC3CCC(CC2)C1C3)CP(=O)(OC)OC

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trapezoid(0[%], 0[%], 80[%], 100[%])
zerofill(1, TRUE)
fft(1, TRUE, TRUE)
machinephase
ppm

Получено из: RAN_DEPT135_Ad-2-DiMeOPhosEthylidene

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Author = delta
Experiment = dept.ex2
Sample_Id = RAN_Ad-2-DiMeOPhosEthylid
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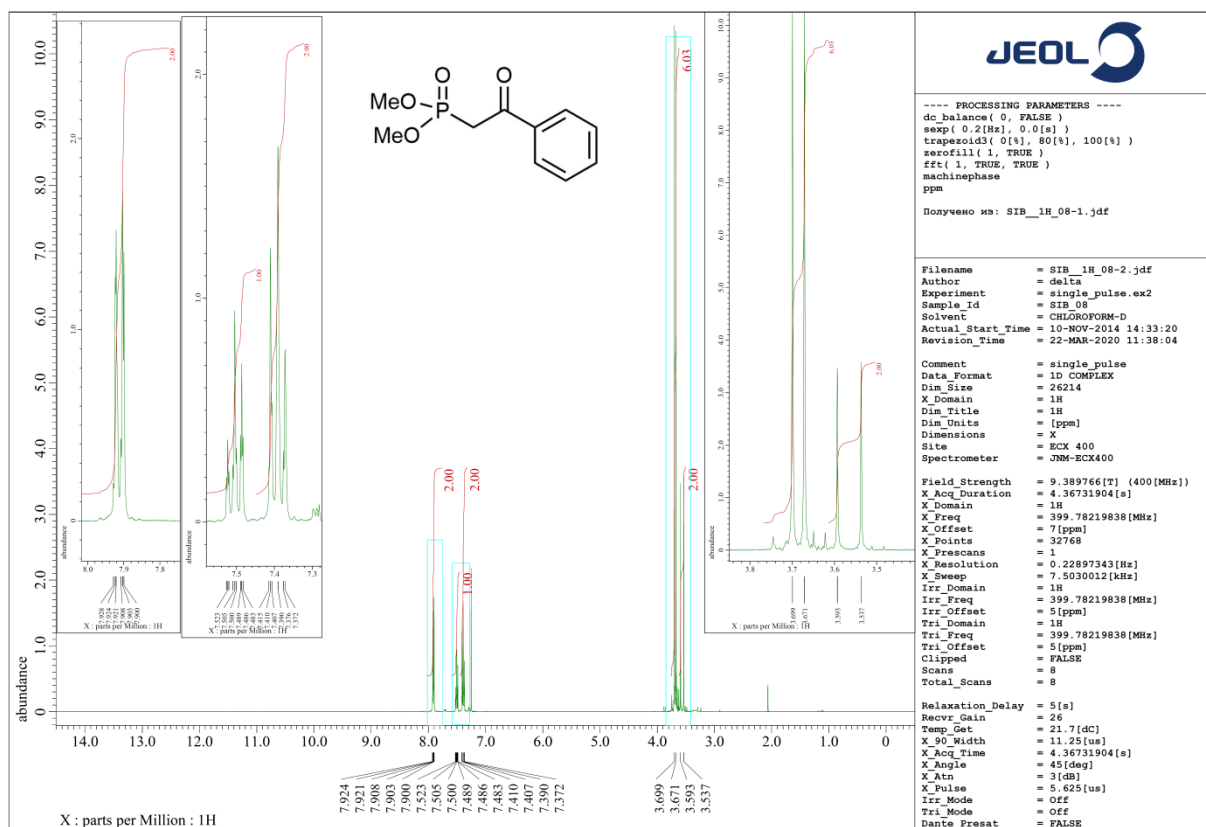
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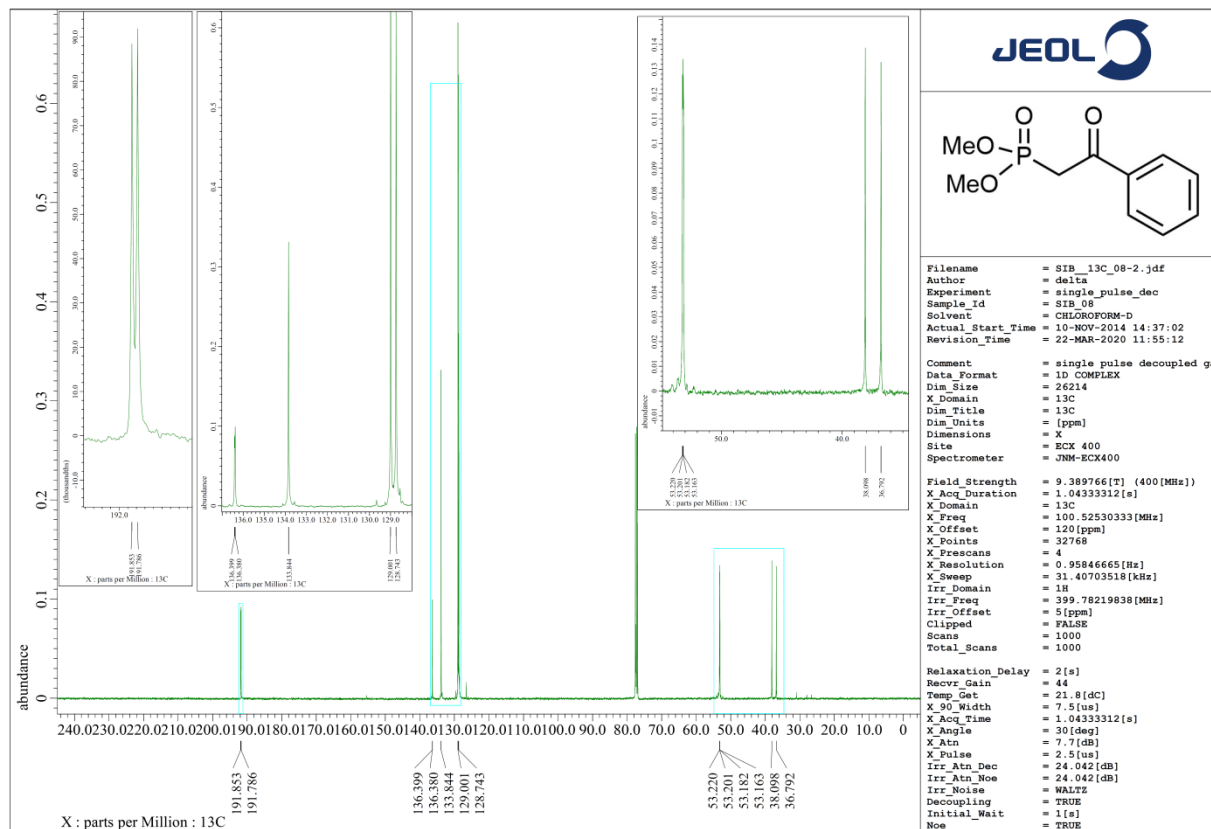
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Chemical structure: COC(=O)N=C(C12CC3CC4CC5CC6CC7CC8CC9CC10CC11CC12CC13CC14CC15CC16CC17CC18CC19CC20CC21CC22CC23CC24CC25CC26CC27CC28CC29CC30CC31CC32CC33CC34CC35CC36CC37CC38CC39CC40CC41CC42CC43CC44CC45CC46CC47CC48CC49CC50CC51CC52CC53CC54CC55CC56CC57CC58CC59CC60CC61CC62CC63CC64CC65CC66CC67CC68CC69CC70CC71CC72CC73CC74CC75CC76CC77CC78CC79CC80CC81CC82CC83CC84CC85CC86CC87CC88CC89CC90CC91CC92CC93CC94CC95CC96CC97CC98CC99CC100CC101CC102CC103CC104CC105CC106CC107CC108CC109CC110CC111CC112CC113CC114CC115CC116CC117CC118CC119CC120CC121CC122CC123CC124CC125CC126CC127CC128CC129CC130CC131CC132CC133CC134CC135CC136CC137CC138CC139CC140CC141CC142CC143CC144CC145CC146CC147CC148CC149CC150CC151CC152CC153CC154CC155CC156CC157CC158CC159CC160CC161CC162CC163CC164CC165CC166CC167CC168CC169CC170CC171CC172CC173CC174CC175CC176CC177CC178CC179CC180CC181CC182CC183CC184CC185CC186CC187CC188CC189CC190CC191CC192CC193CC194CC195CC196CC197CC198CC199CC200CC201CC202CC203CC204CC205CC206CC207CC208CC209CC210CC211CC212CC213CC214CC215CC216CC217CC218CC219CC220CC221CC222CC223CC224CC225CC226CC227CC228CC229CC230CC231CC232CC233CC234CC235CC236CC237CC238CC239CC240CC241CC242CC243CC244CC245CC246CC247CC248CC249CC250CC251CC252CC253CC254CC255CC256CC257CC258CC259CC260CC261CC262CC263CC264CC265CC266CC267CC268CC269CC270CC271CC272CC273CC274CC275CC276CC277CC278CC279CC280CC281CC282CC283CC284CC285CC286CC287CC288CC289CC290CC291CC292CC293CC294CC295CC296CC297CC298CC299CC300CC301CC302CC303CC304CC305CC306CC307CC308CC309CC310CC311CC312CC313CC314CC315CC316CC317CC318CC319CC320CC321CC322CC323CC324CC325CC326CC327CC328CC329CC330CC331CC332CC333CC334CC335CC336CC337CC338CC339CC340CC341CC342CC343CC344CC345CC346CC347CC348CC349CC350CC351CC352CC353CC354CC355CC356CC357CC358CC359CC360CC361CC362CC363CC364CC365CC366CC367CC368CC369CC370CC371CC372CC373CC374CC375CC376CC377CC378CC379CC380CC381CC382CC383CC384CC385CC386CC387CC388CC389CC390CC391CC392CC393CC394CC395CC396CC397CC398CC399CC400CC401CC402CC403CC404CC405CC406CC407CC408CC409CC410CC411CC412CC413CC414CC415CC416CC417CC418CC419CC420CC421CC422CC423CC424CC425CC426CC427CC428CC429CC430CC431CC432CC433CC434CC435CC436CC437CC438CC439CC440CC441CC442CC443CC444CC445CC446CC447CC448CC449CC450CC451CC452CC453CC454CC455CC456CC457CC458CC459CC460CC461CC462CC463CC464CC465CC466CC467CC468CC469CC470CC471CC472CC473CC474CC475CC476CC477CC478CC479CC480CC481CC482CC483CC484CC485CC486CC487CC488CC489CC490CC491CC492CC493CC494CC495CC496CC497CC498CC499CC500CC501CC502CC503CC504CC505CC506CC507CC508CC509CC510CC511CC512CC513CC514CC515CC516CC517CC518CC519CC520CC521CC522CC523CC524CC525CC526CC527CC528CC529CC530CC531CC532CC533CC534CC535CC536CC537CC538CC539CC540CC541CC542CC543CC544CC545CC546CC547CC548CC549CC550CC551CC552CC553CC554CC555CC556CC557CC558CC559CC560CC561CC562CC563CC564CC565CC566CC567CC568CC569CC570CC571CC572CC573CC574CC575CC576CC577CC578CC579CC580CC581CC582CC583CC584CC585CC586CC587CC588CC589CC590CC591CC592CC593CC594CC595CC596CC597CC598CC599CC600CC601CC602CC603CC604CC605CC606CC607CC608CC609CC610CC611CC612CC613CC614CC615CC616CC617CC618CC619CC620CC621CC622CC623CC624CC625CC626CC627CC628CC629CC630CC631CC632CC633CC634CC635CC636CC637CC638CC639CC640CC641CC642CC643CC644CC645CC646CC647CC648CC649CC650CC651CC652CC653CC654CC655CC656CC657CC658CC659CC660CC661CC662CC663CC664CC665CC666CC667CC668CC669CC670CC671CC672CC673CC674CC675CC676CC677CC678CC679CC680CC681CC682CC683CC684CC685CC686CC687CC688CC689CC690CC691CC692CC693CC694CC695CC696CC697CC698CC699CC700CC701CC702CC703CC704CC705CC706CC707CC708CC709CC710CC711CC712CC713CC714CC715CC716CC717CC718CC719CC720CC721CC722CC723CC724CC725CC726CC727CC728CC729CC730CC731CC732CC733CC734CC735CC736CC737CC738CC739CC740CC741CC742CC743CC744CC745CC746CC747CC748CC749CC750CC751CC752CC753CC754CC755CC756CC757CC758CC759CC760CC761CC762CC763CC764CC765CC766CC767CC768CC769CC770CC771CC772CC773CC774CC775CC776CC777CC778CC779CC780CC781CC782CC783CC784CC785CC786CC787CC788CC789CC790CC791CC792CC793CC794CC795CC796CC797CC798CC799CC800CC801CC802CC803CC804CC805CC806CC807CC808CC809CC810CC811CC812CC813CC814CC815CC816CC817CC818CC819CC820CC821CC822CC823CC824CC825CC826CC827CC828CC829CC830CC831CC832CC833CC834CC835CC836CC837CC838CC839CC840CC841CC842CC843CC844CC845CC846CC847CC848CC849CC850CC851CC852CC853CC854CC855CC856CC857CC858CC859CC860CC861CC862CC863CC864CC865CC866CC867CC868CC869CC870CC871CC872CC873CC874CC875CC876CC877CC878CC879CC880CC881CC882CC883CC884CC885CC886CC887CC888CC889CC890CC891CC892CC893CC894CC895CC896CC897CC898CC899CC900CC901CC902CC903CC904CC905CC906CC907CC908CC909CC910CC911CC912CC913CC914CC915CC916CC917CC918CC919CC920CC921CC922CC923CC924CC925CC926CC927CC928CC929CC930CC931CC932CC933CC934CC935CC936CC937CC938CC939CC940CC941CC942CC943CC944CC945CC946CC947CC948CC949CC950CC951CC952CC953CC954CC955CC956CC957CC958CC959CC960CC961CC962CC963CC964CC965CC966CC967CC968CC969CC970CC971CC972CC973CC974CC975CC976CC977CC978CC979CC980CC981CC982CC983CC984CC985CC986CC987CC988CC989CC990CC991CC992CC993CC994CC995CC996CC997CC998CC999CC1000CC1001CC1002CC1003CC1004CC1005CC1006CC1007CC10

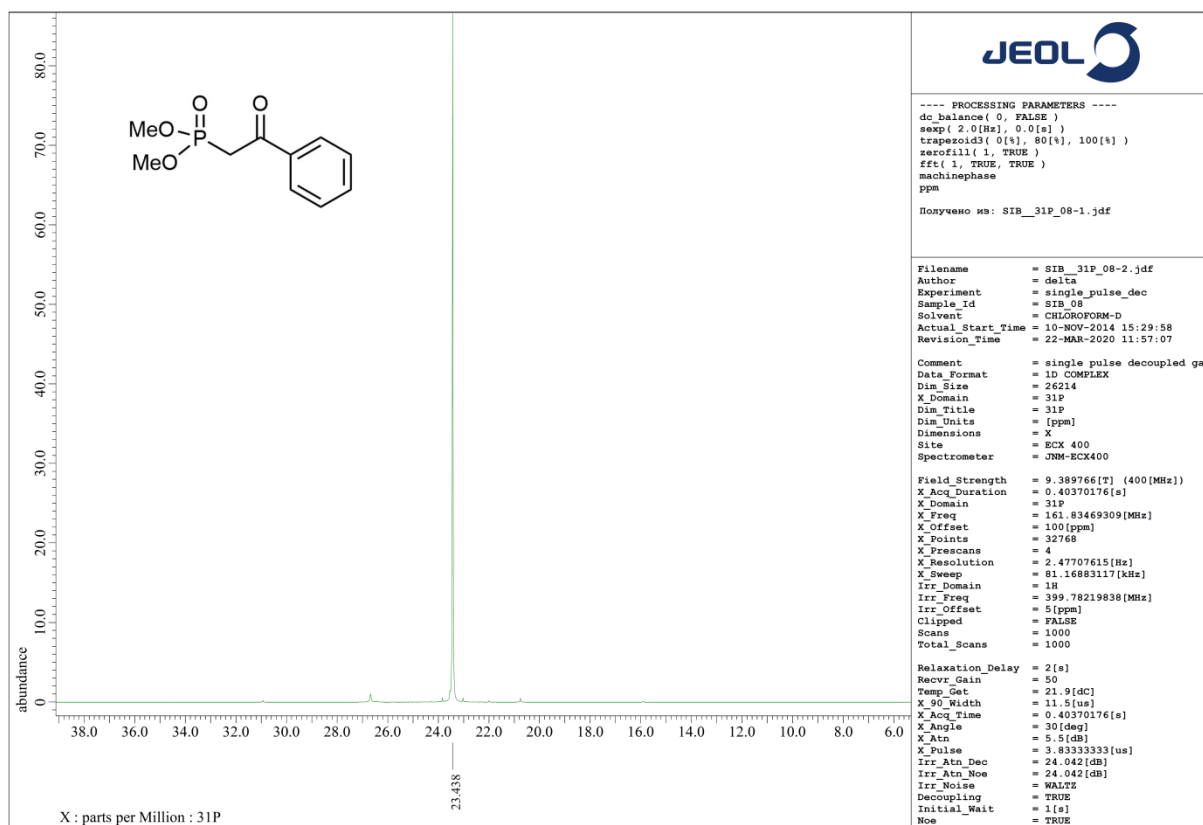
¹H NMR spectra of dimethyl (2-oxo-2-phenylethyl)phosphonate **Vla** in CDCl₃



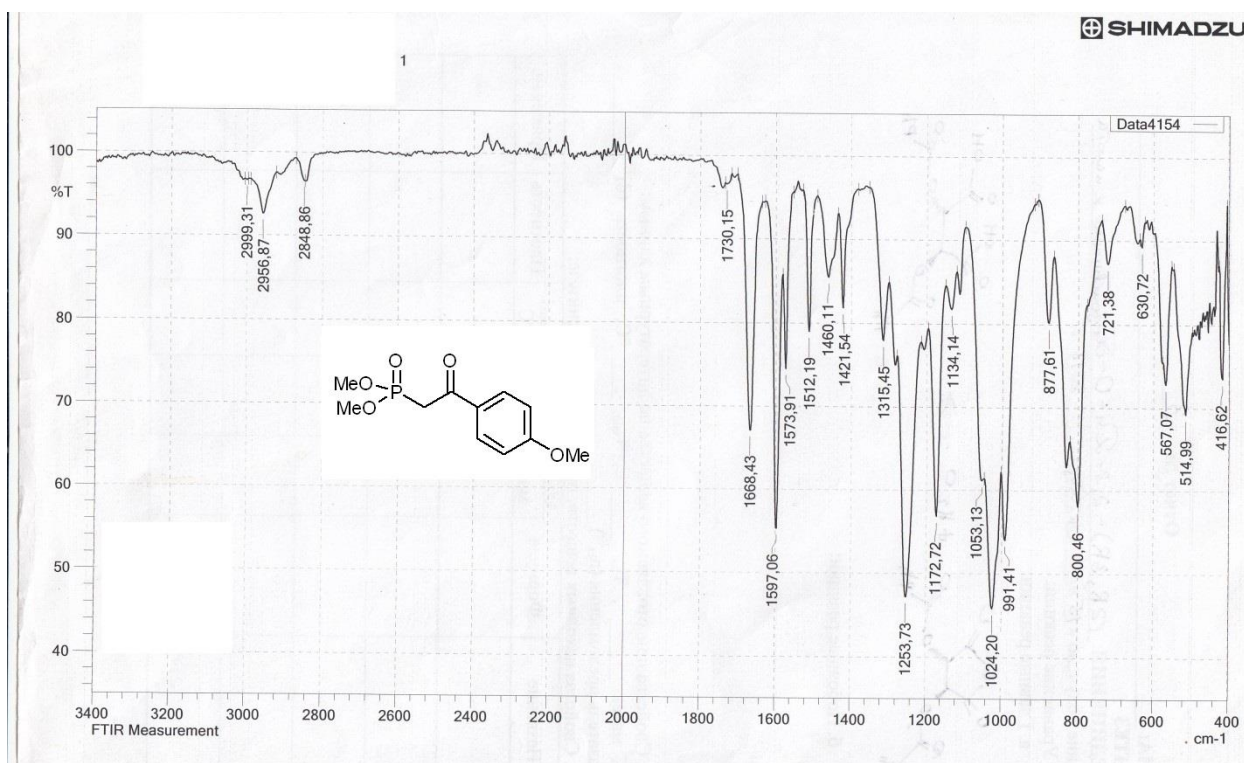
¹³C NMR spectra of dimethyl (2-oxo-2-phenylethyl)phosphonate **Vla** in CDCl₃



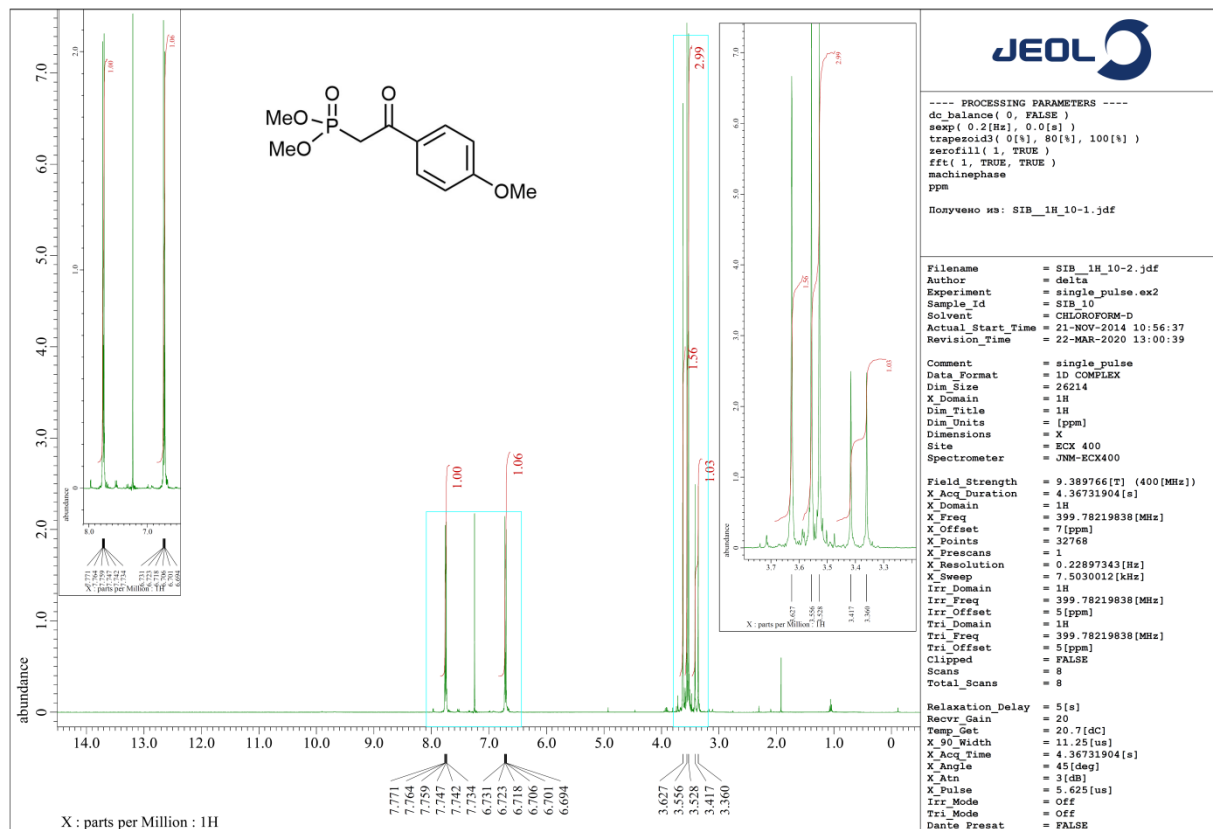
³¹P NMR spectra of dimethyl (2-oxo-2-phenylethyl)phosphonate **Vla** in CDCl₃



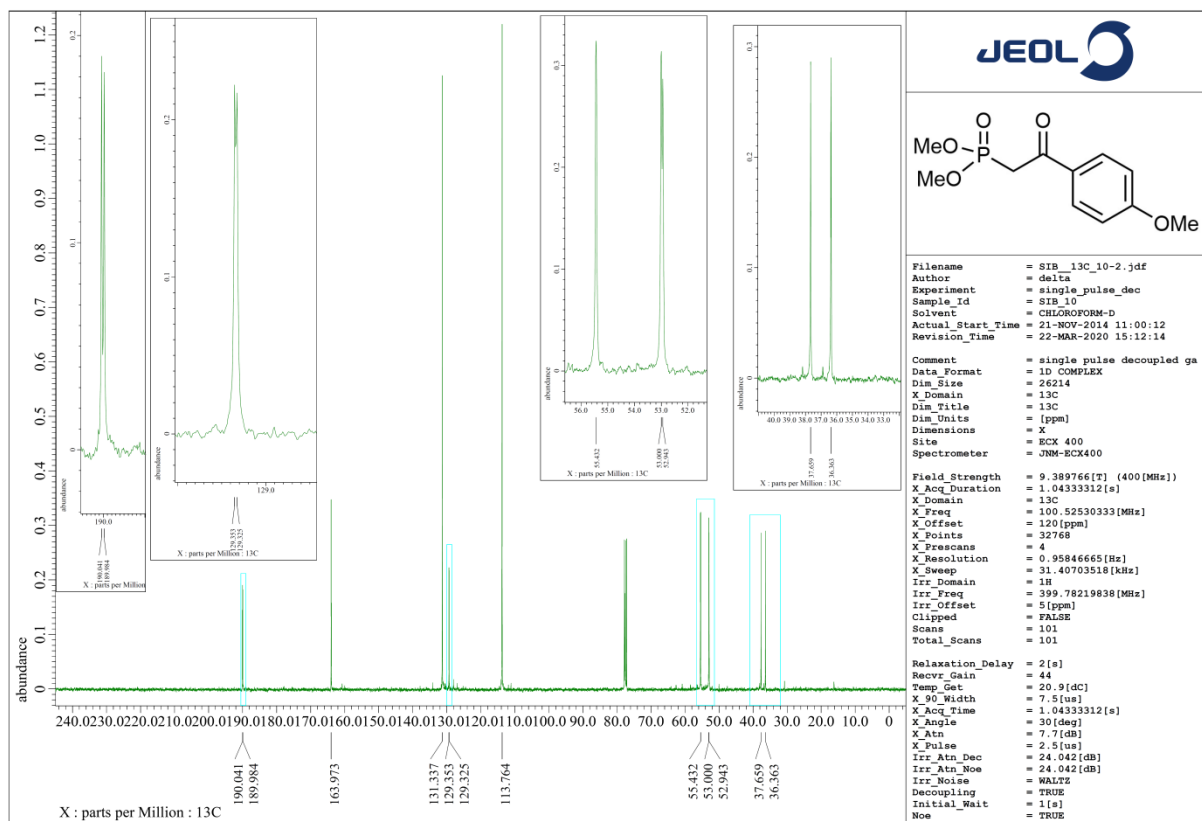
FTIR spectra of dimethyl [2-(4-methoxyphenyl)-2-oxoethyl]phosphonate **Vlb**



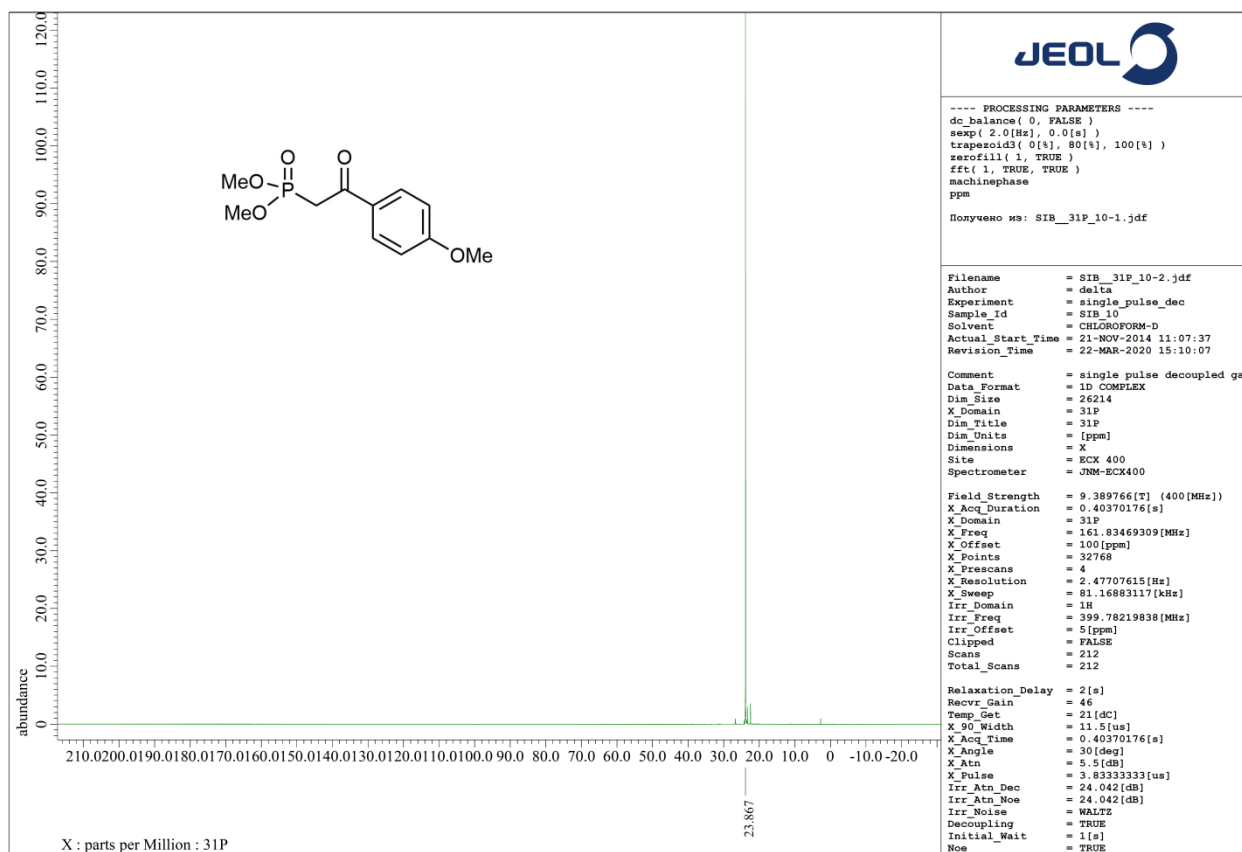
¹H NMR spectra of dimethyl [2-(4-methoxyphenyl)-2-oxoethyl]phosphonate **Vib** in CDCl₃



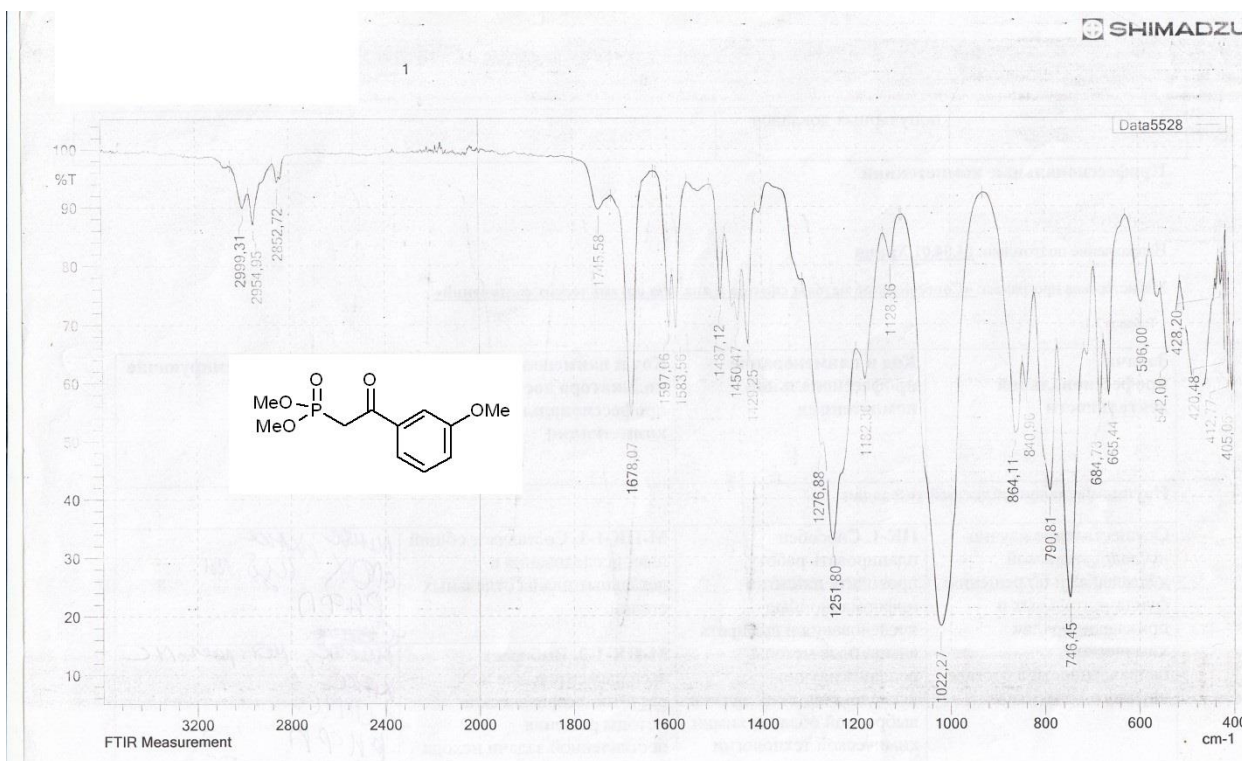
¹³C NMR spectra of dimethyl [2-(4-methoxyphenyl)-2-oxoethyl]phosphonate **Vib** in CDCl₃

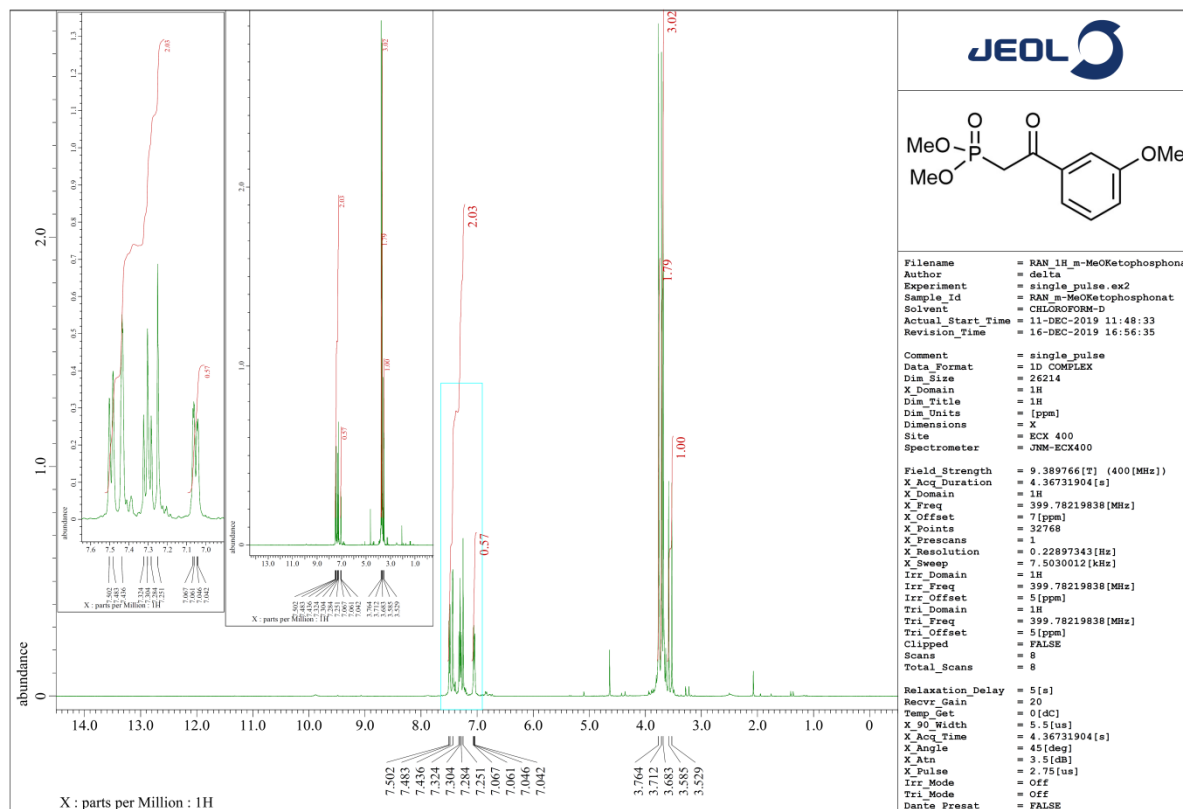
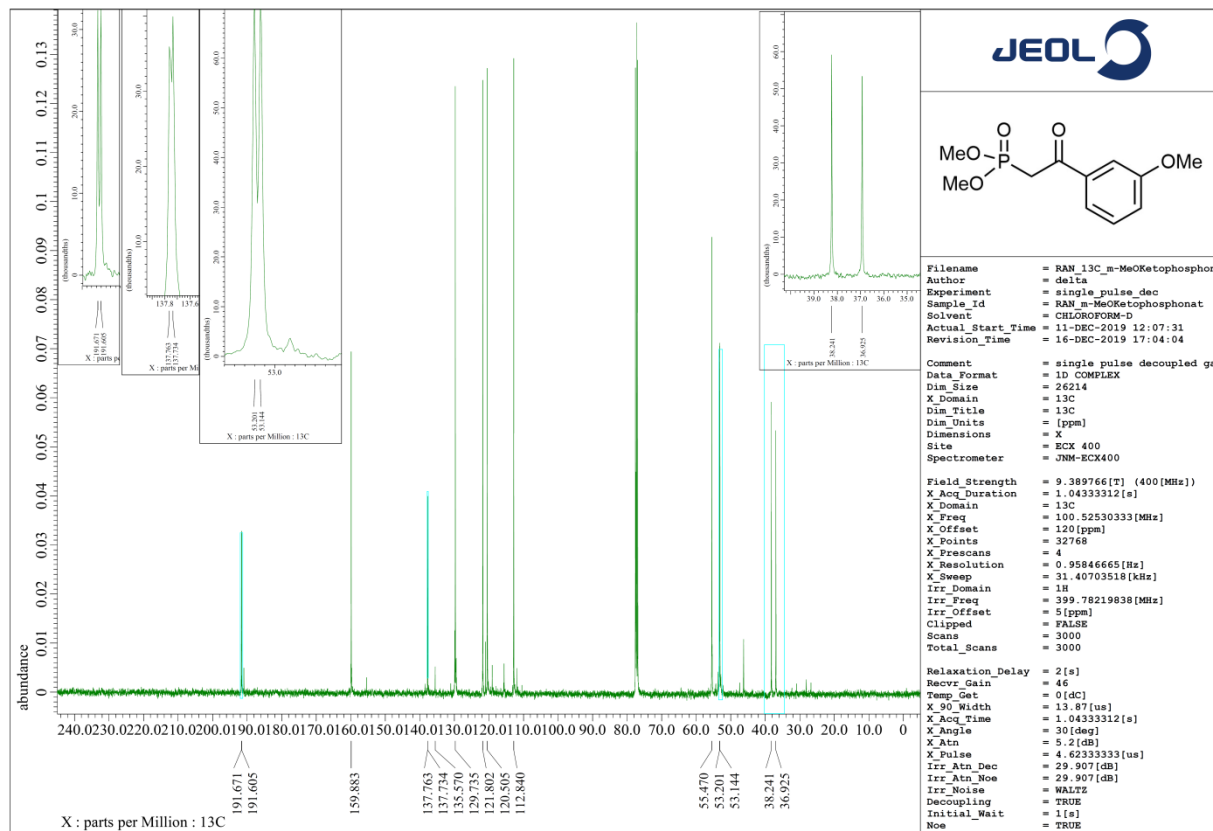


³¹P NMR spectra of dimethyl [2-(4-methoxyphenyl)-2-oxoethyl]phosphonate **Vib** in CDCl₃

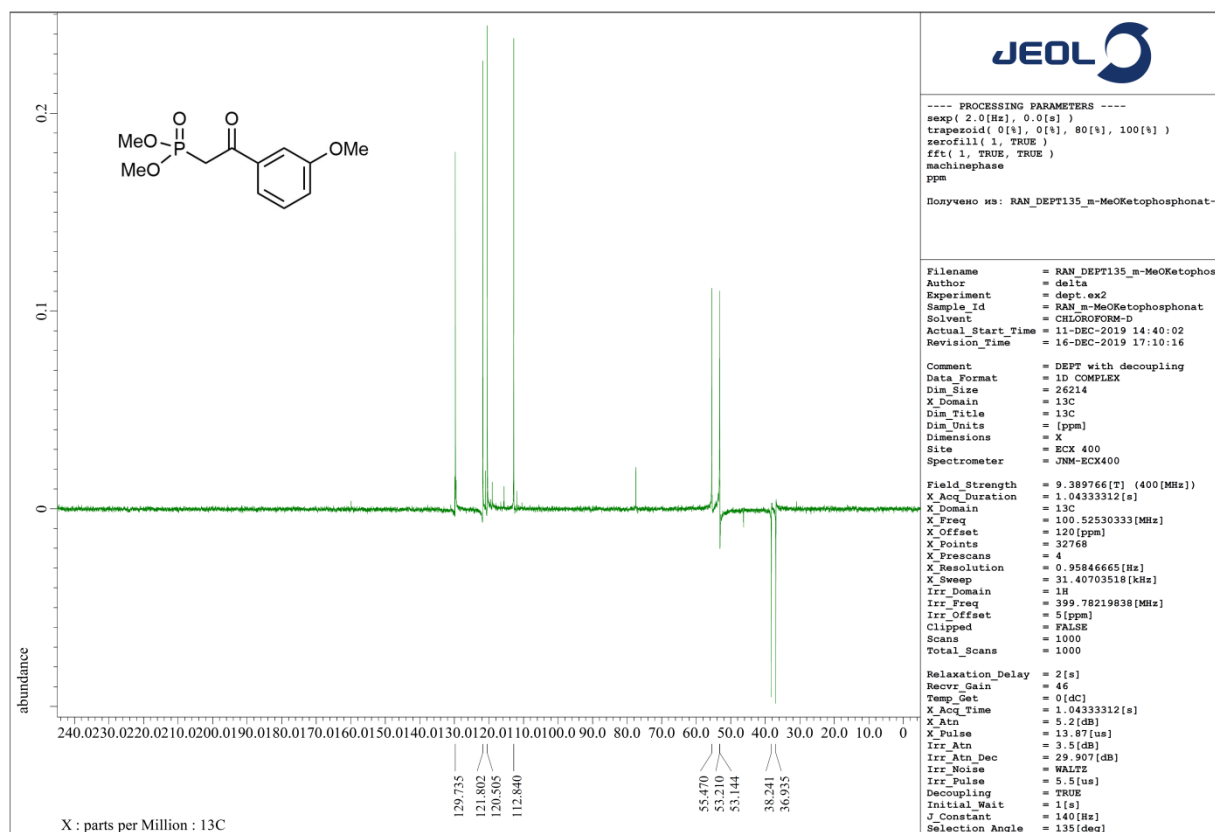


FTIR spectra of dimethyl [2-(3-methoxyphenyl)-2-oxoethyl]phosphonate **Vic**

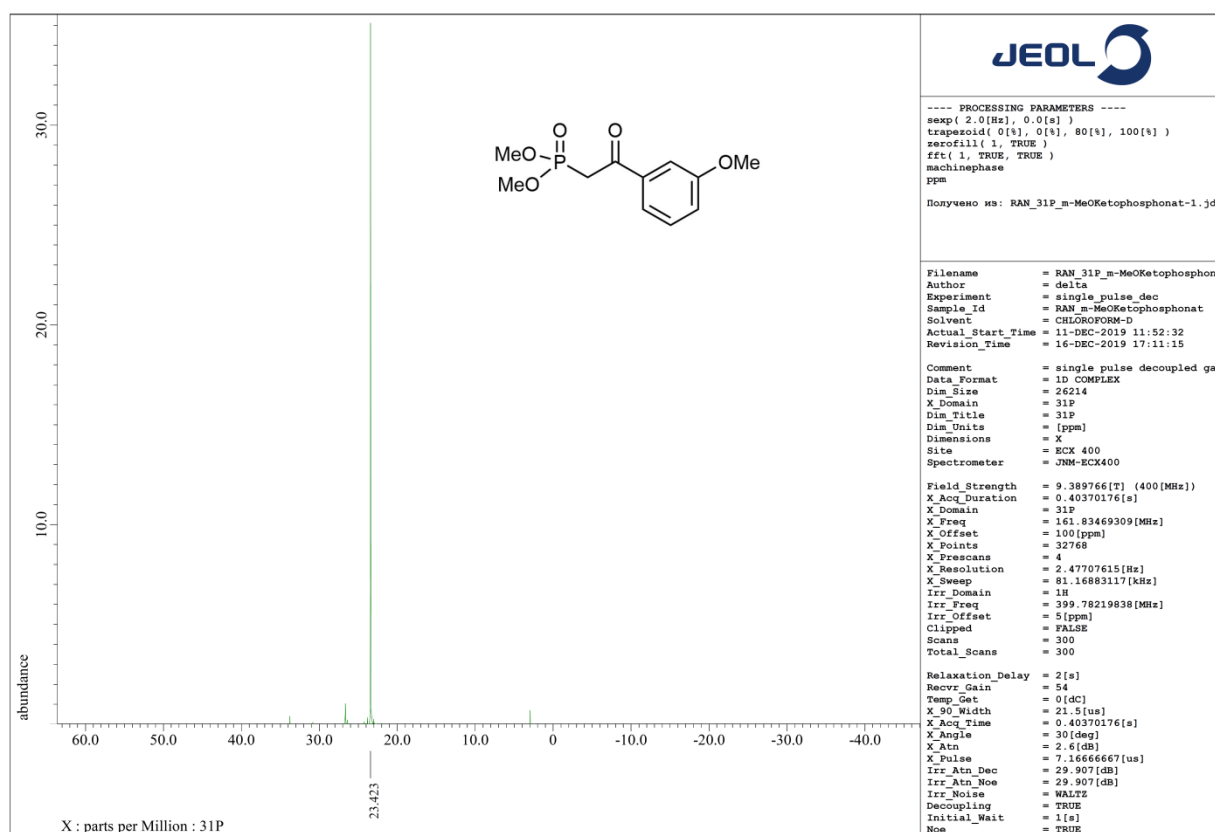


¹H NMR spectra of dimethyl [2-(3-methoxyphenyl)-2-oxoethyl]phosphonate **Vlc** in CDCl₃¹³C NMR spectra of dimethyl [2-(3-methoxyphenyl)-2-oxoethyl]phosphonate **Vlc** in CDCl₃

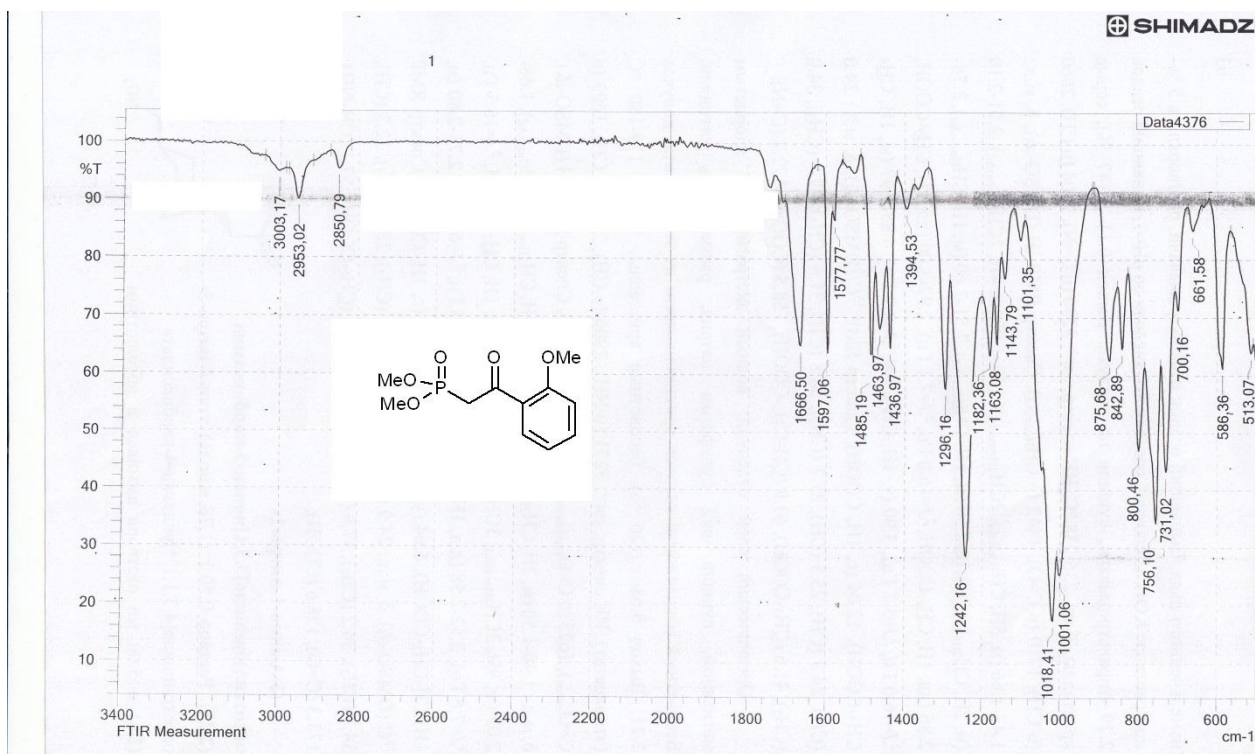
DEPT NMR spectra of dimethyl [2-(3-methoxyphenyl)-2-oxoethyl]phosphonate **Vlc** in CDCl₃



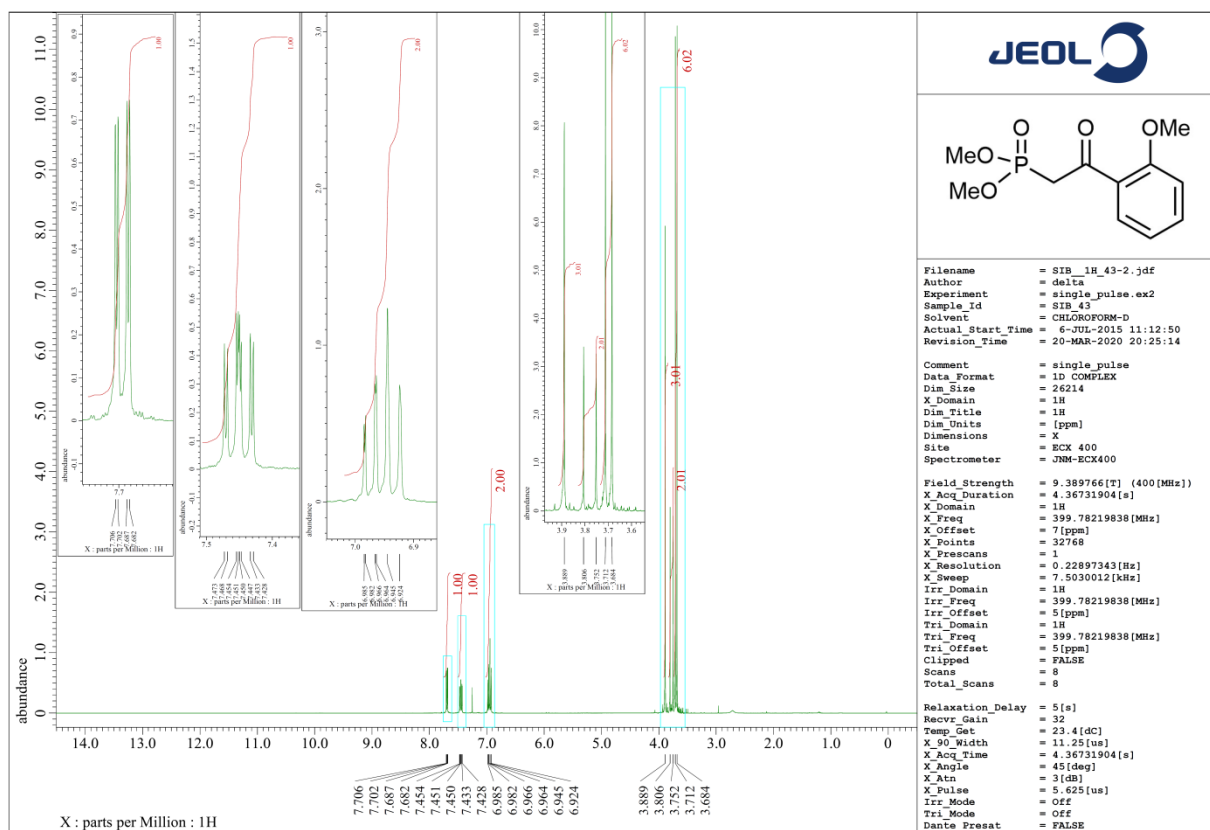
³¹P NMR spectra of dimethyl [2-(3-methoxyphenyl)-2-oxoethyl]phosphonate **Vlc** in CDCl₃



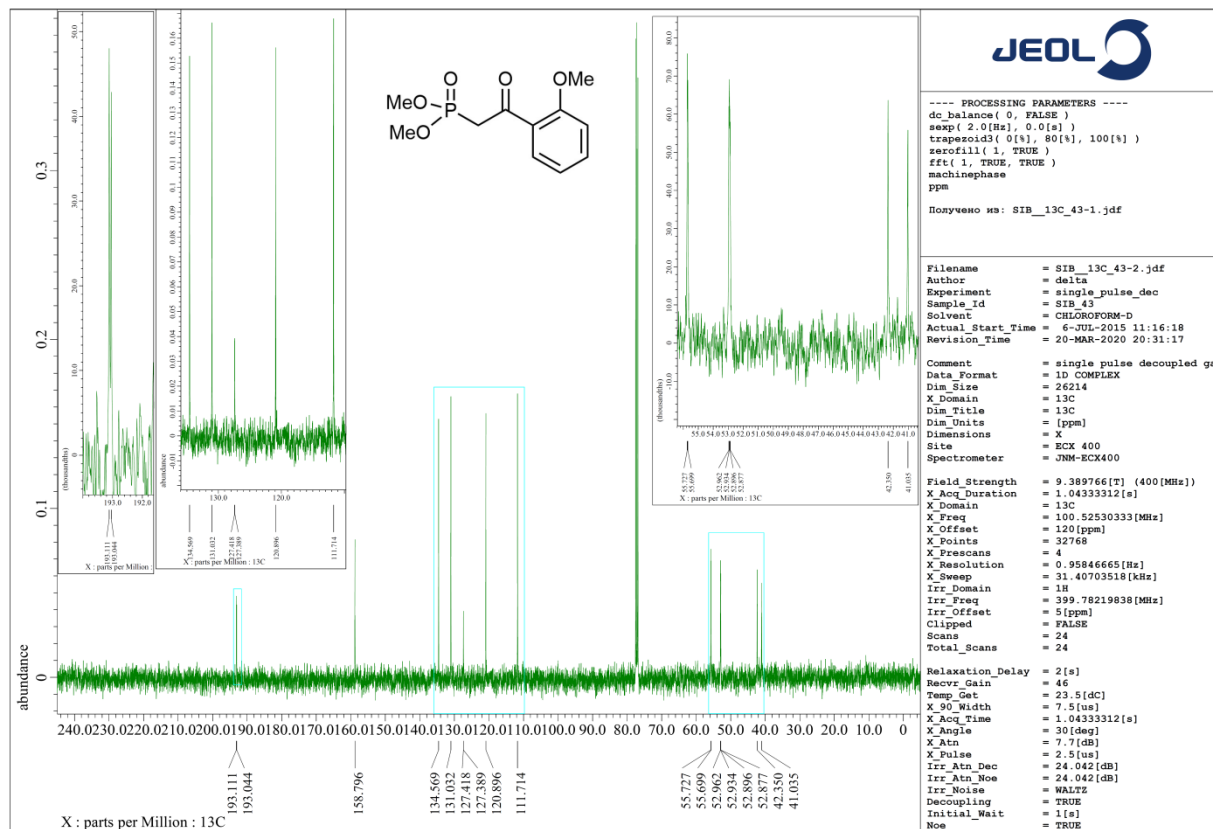
FTIR spectra of dimethyl [2-(2-methoxyphenyl)-2-oxoethyl]phosphonate **VId**



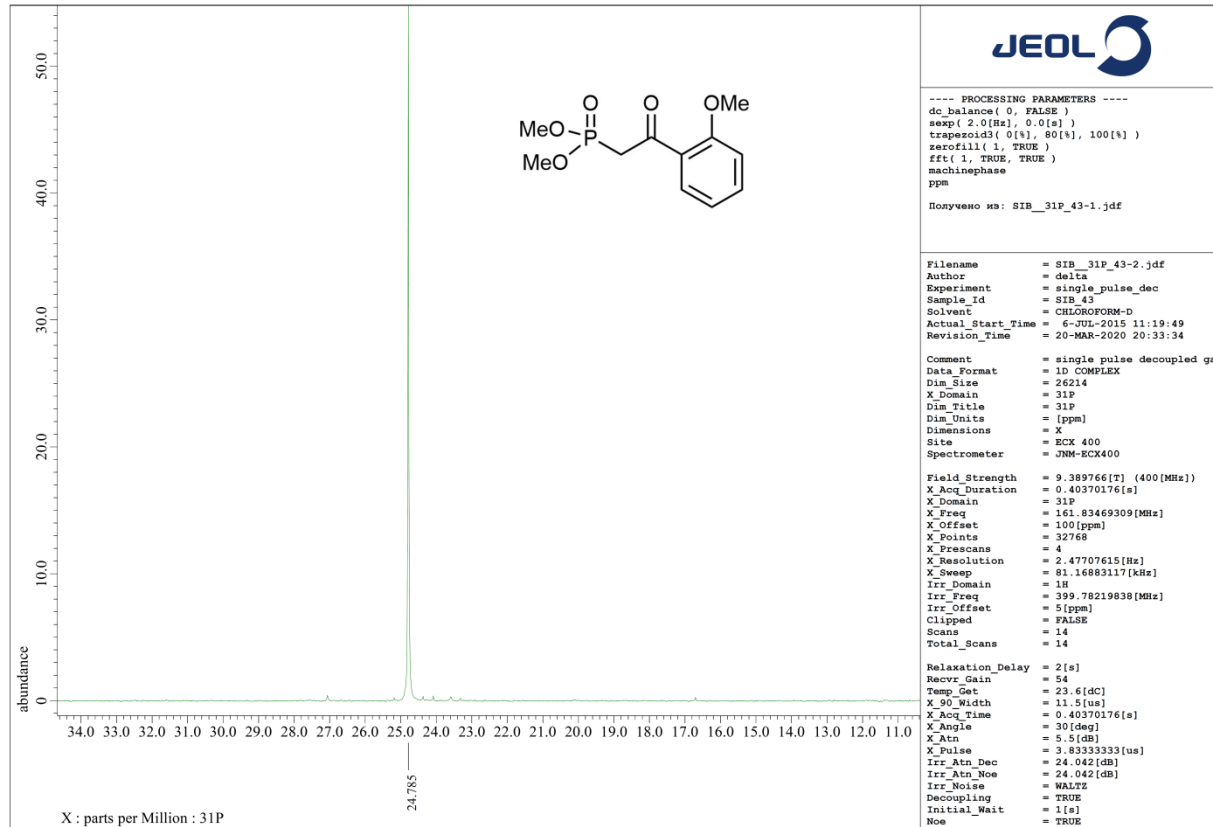
¹H NMR spectra of dimethyl [2-(2-methoxyphenyl)-2-oxoethyl]phosphonate **VId** in CDCl₃



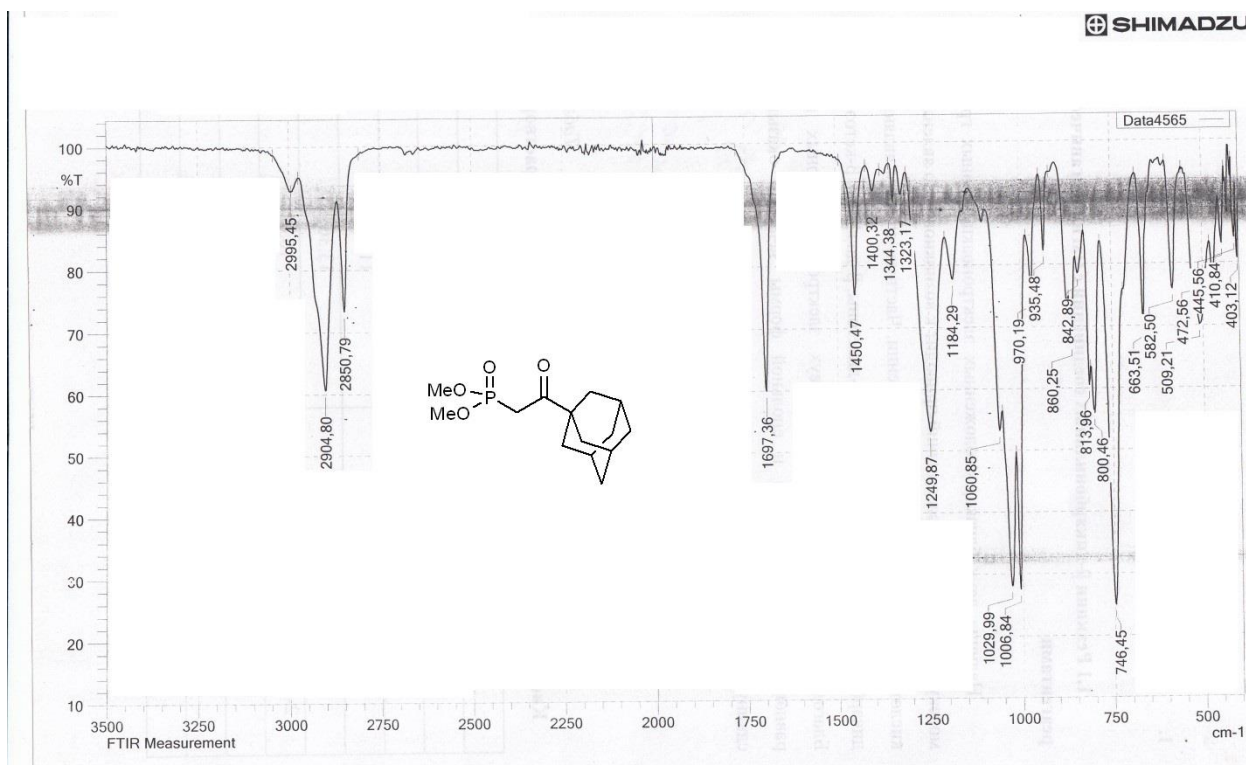
¹³C NMR spectra of dimethyl [2-(2-methoxyphenyl)-2-oxoethyl]phosphonate **VId** in CDCl₃



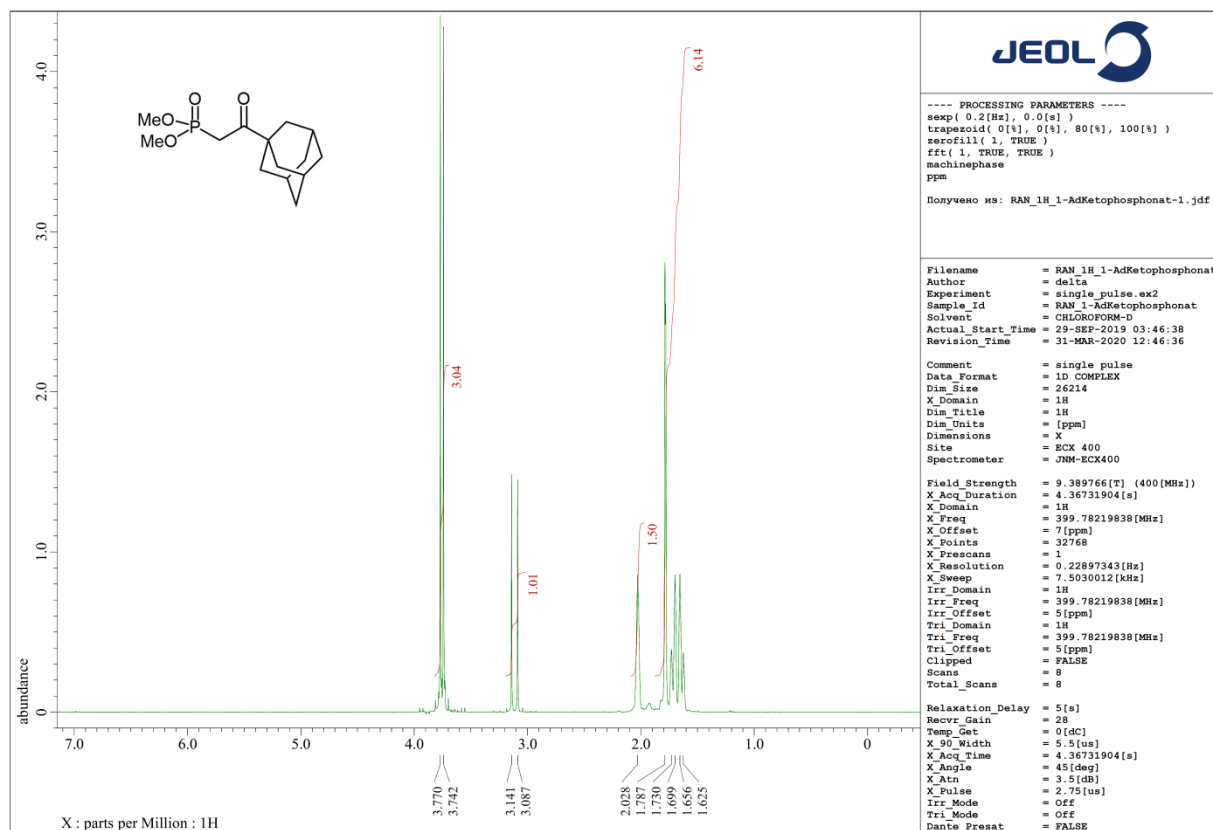
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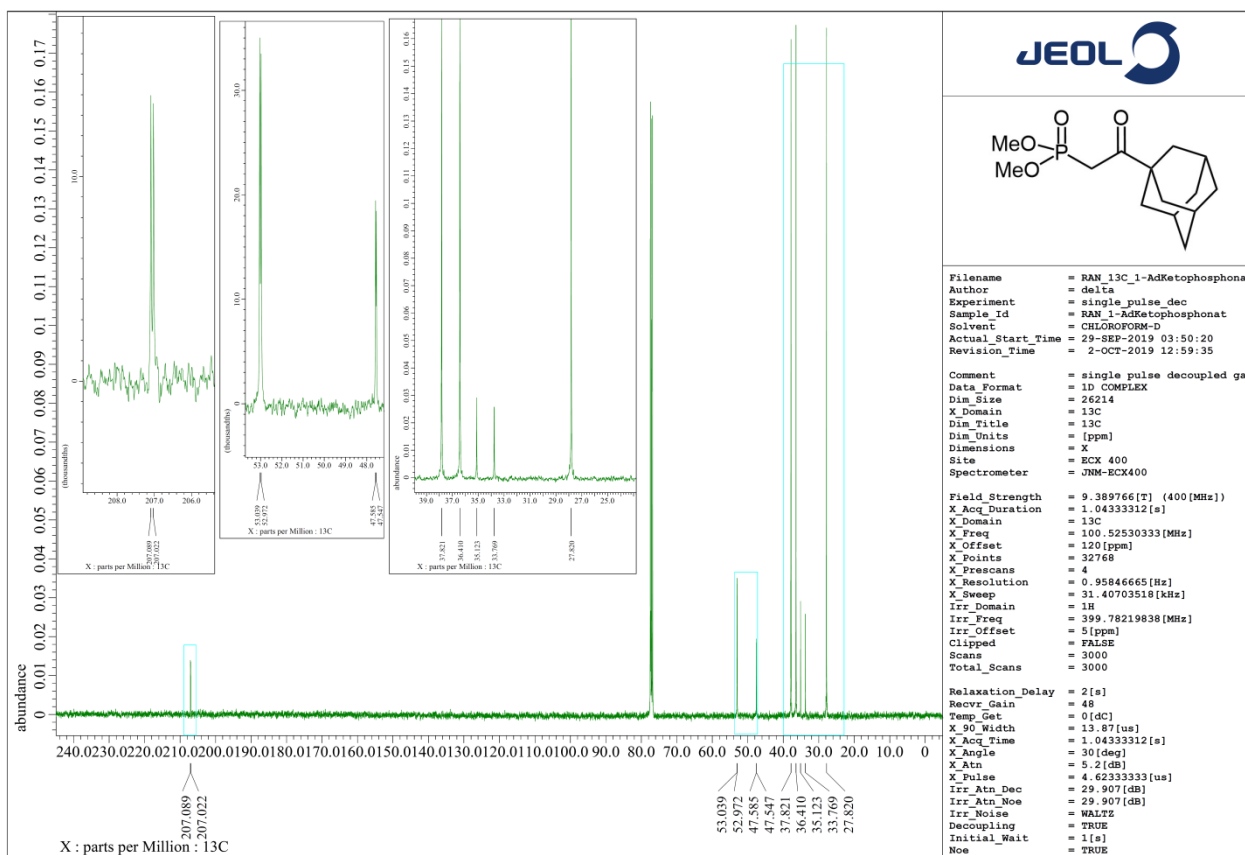
FTIR spectra of dimethyl (2-(adamantan-1-yl)-2-oxoethyl)phosphonate **Vle**



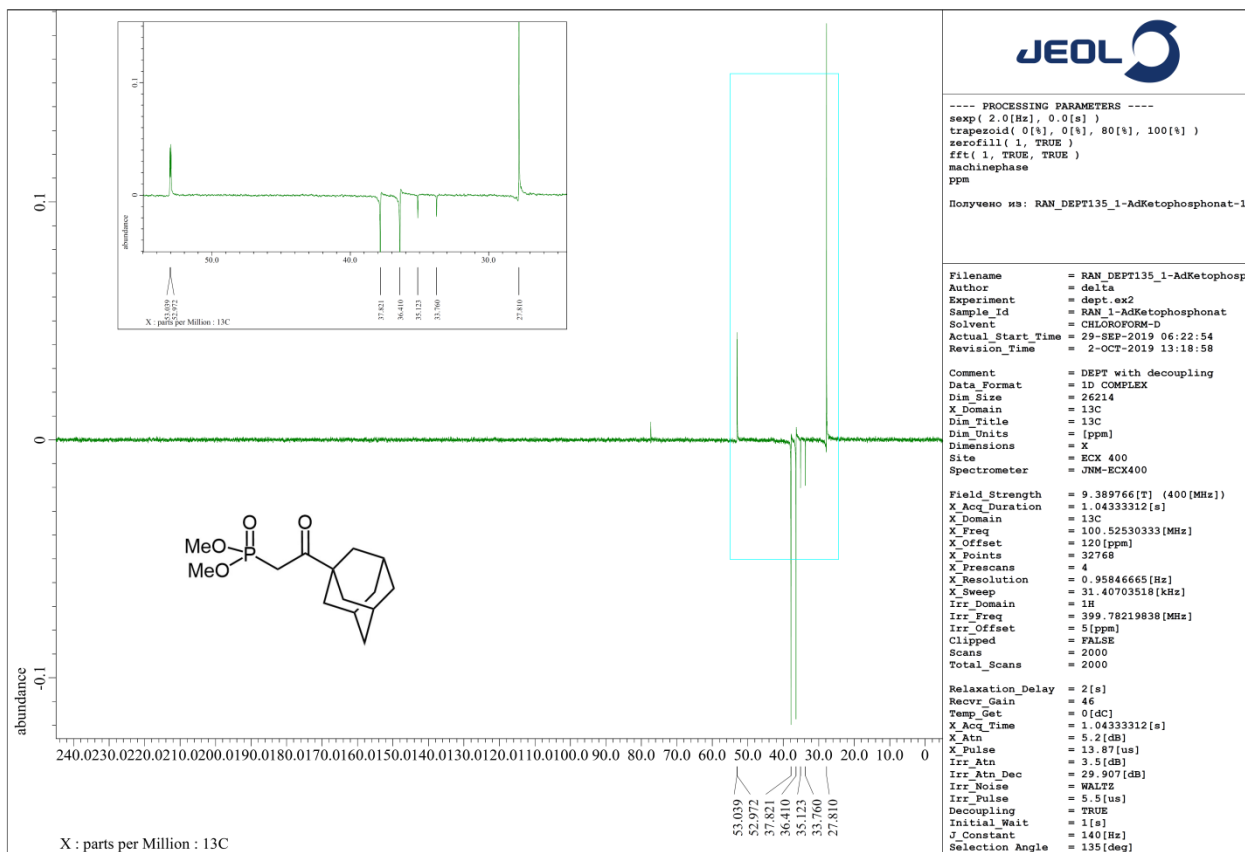
¹H NMR spectra of dimethyl (2-(adamantan-1-yl)-2-oxoethyl)phosphonate **Vle** in CDCl₃



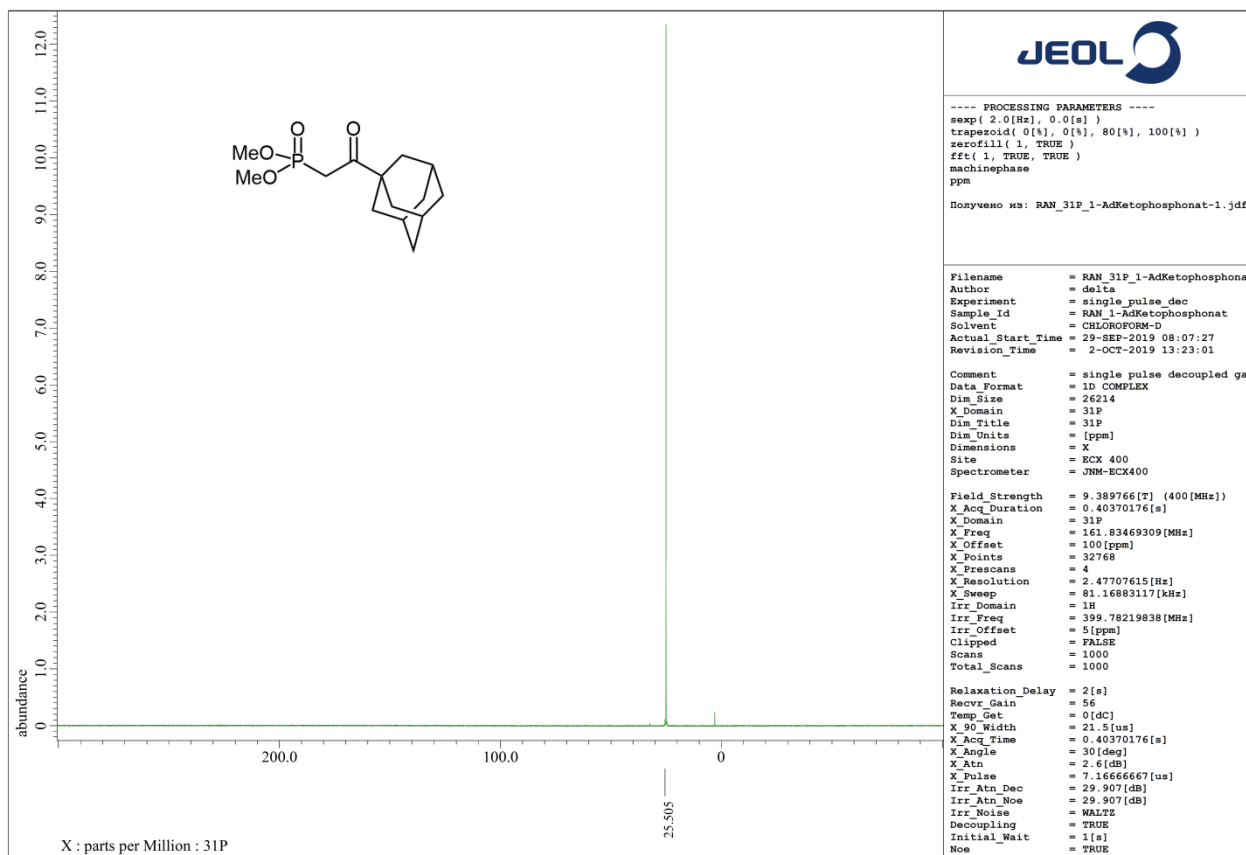
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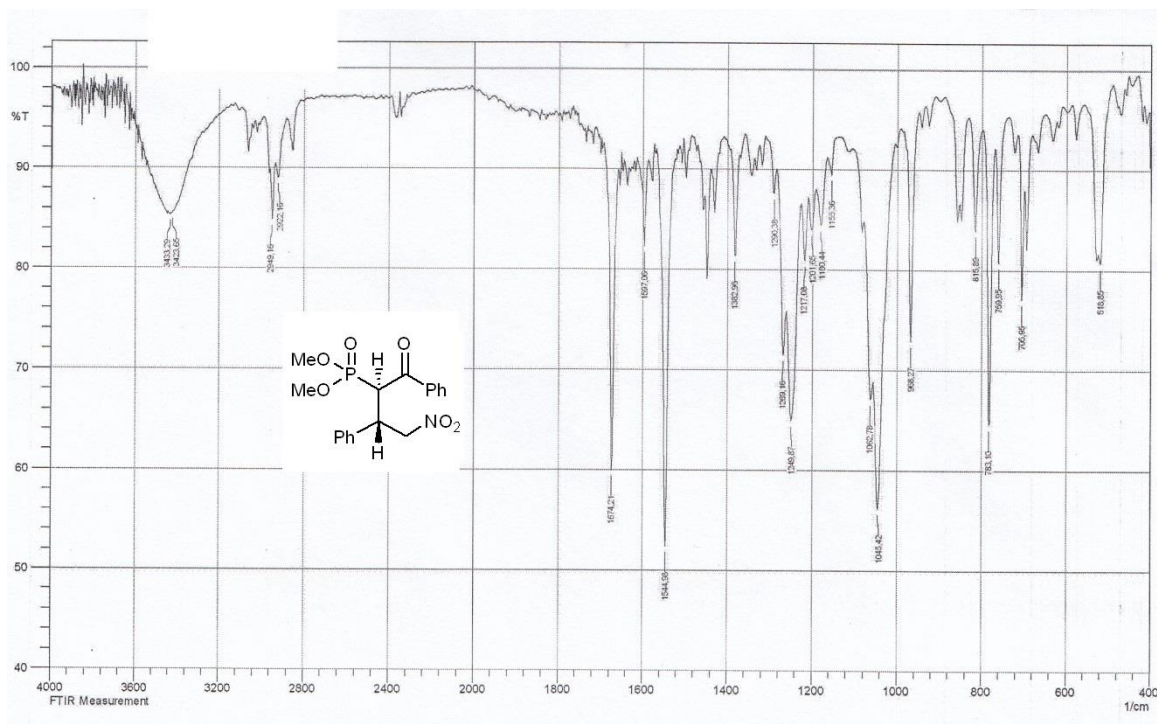
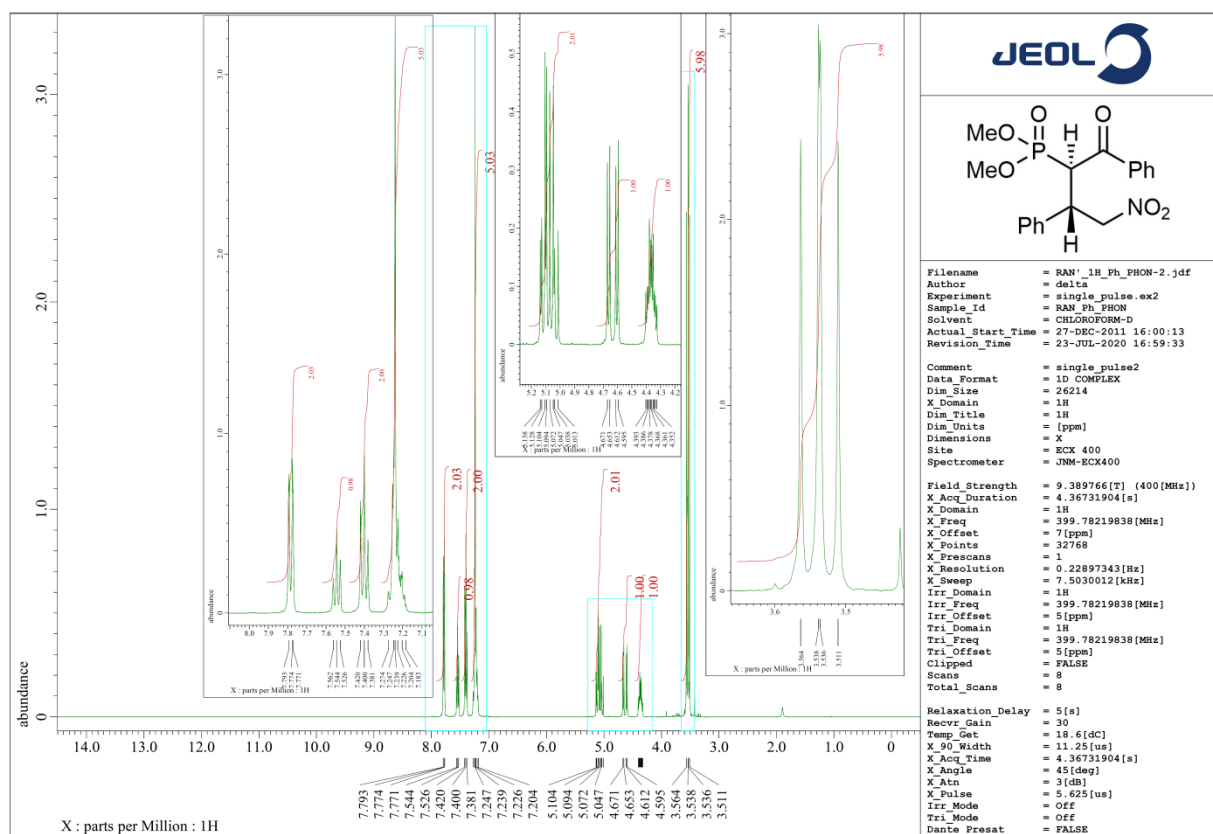
DEPT NMR spectra of dimethyl (2-(adamantan-1-yl)-2-oxoethyl)phosphonate **Vle** in CDCl₃



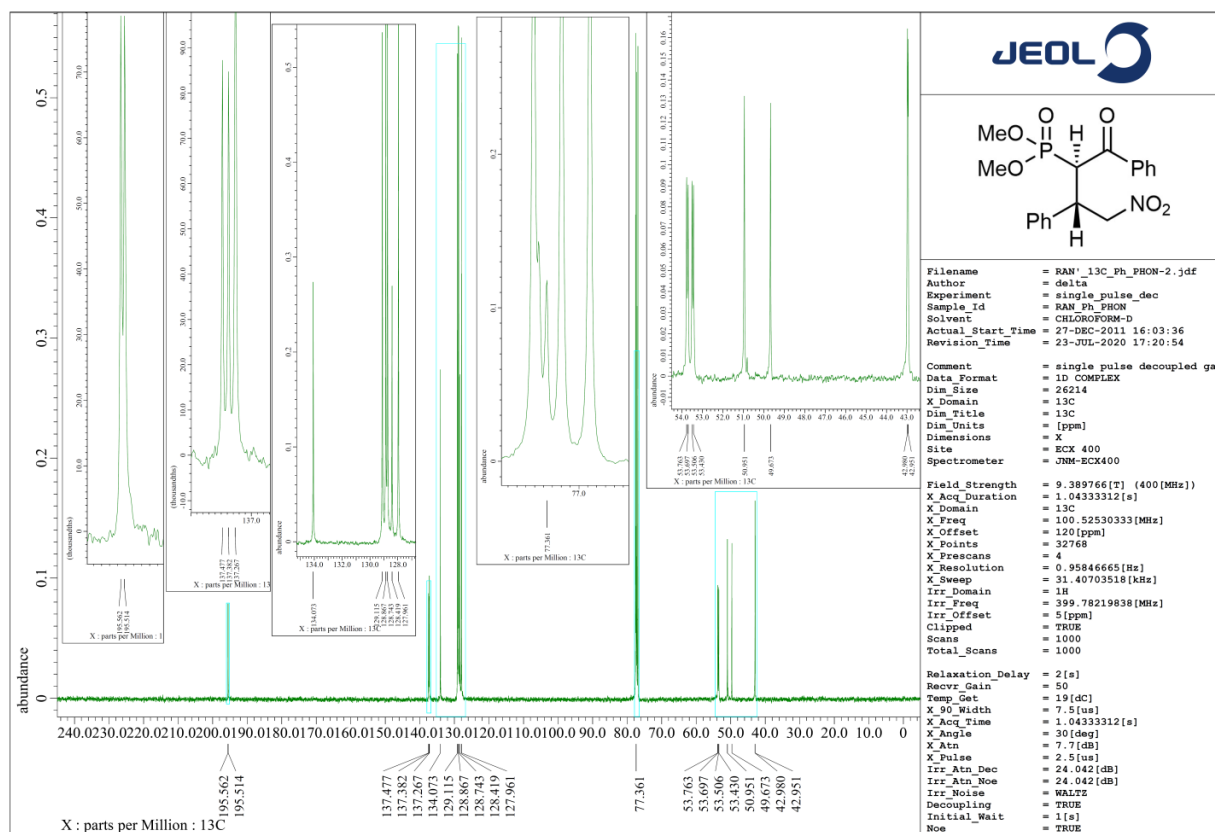
³¹P NMR spectra of dimethyl (2-(adamantan-1-yl)-2-oxoethyl)phosphonate **Vle** in CDCl₃



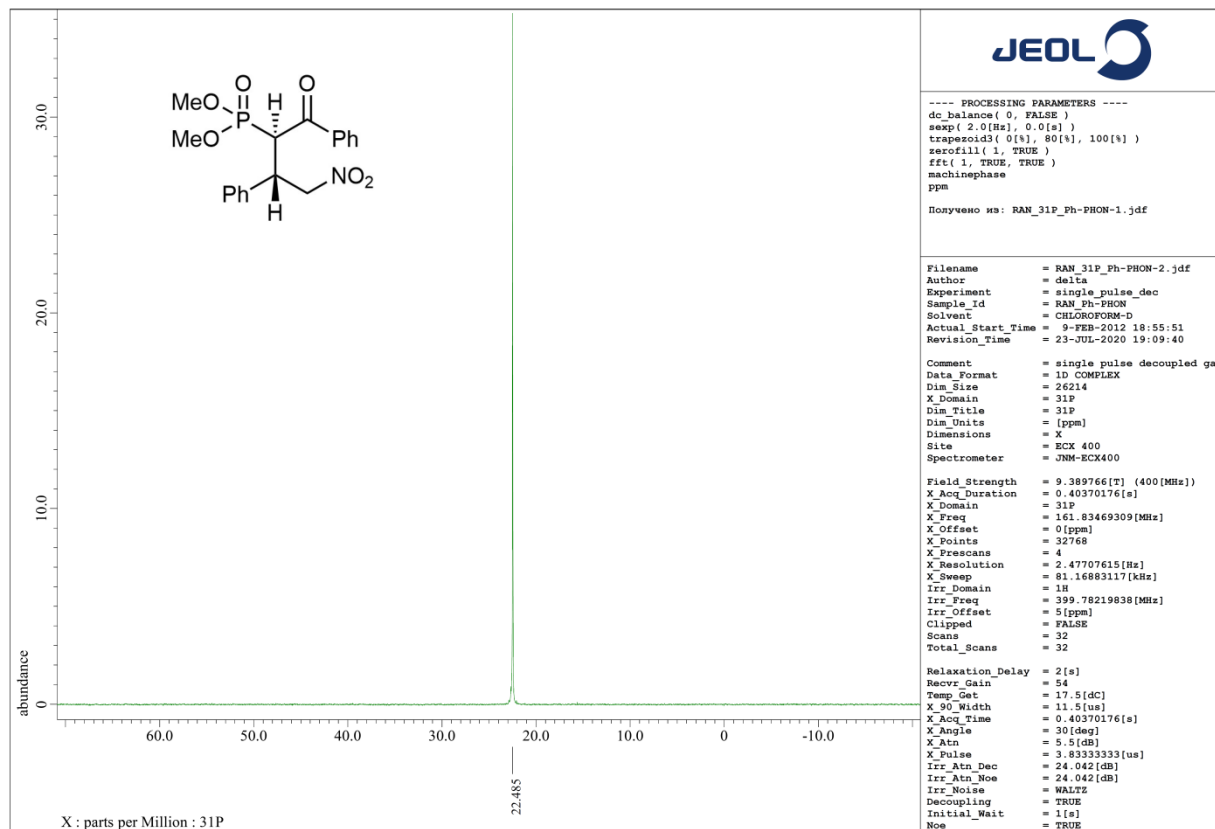
7. Copies of NMR, FTIR and mass spectra for phosphonates 6a-f

FTIR spectra of dimethyl [(2*R*,3*S*)-4-nitro-1-oxo-1,3-diphenylbutan-2-yl]phosphonate (**6a**)¹H NMR spectra of dimethyl [(2*R*,3*S*)-4-nitro-1-oxo-1,3-diphenylbutan-2-yl]phosphonate (**6a**) in CDCl₃

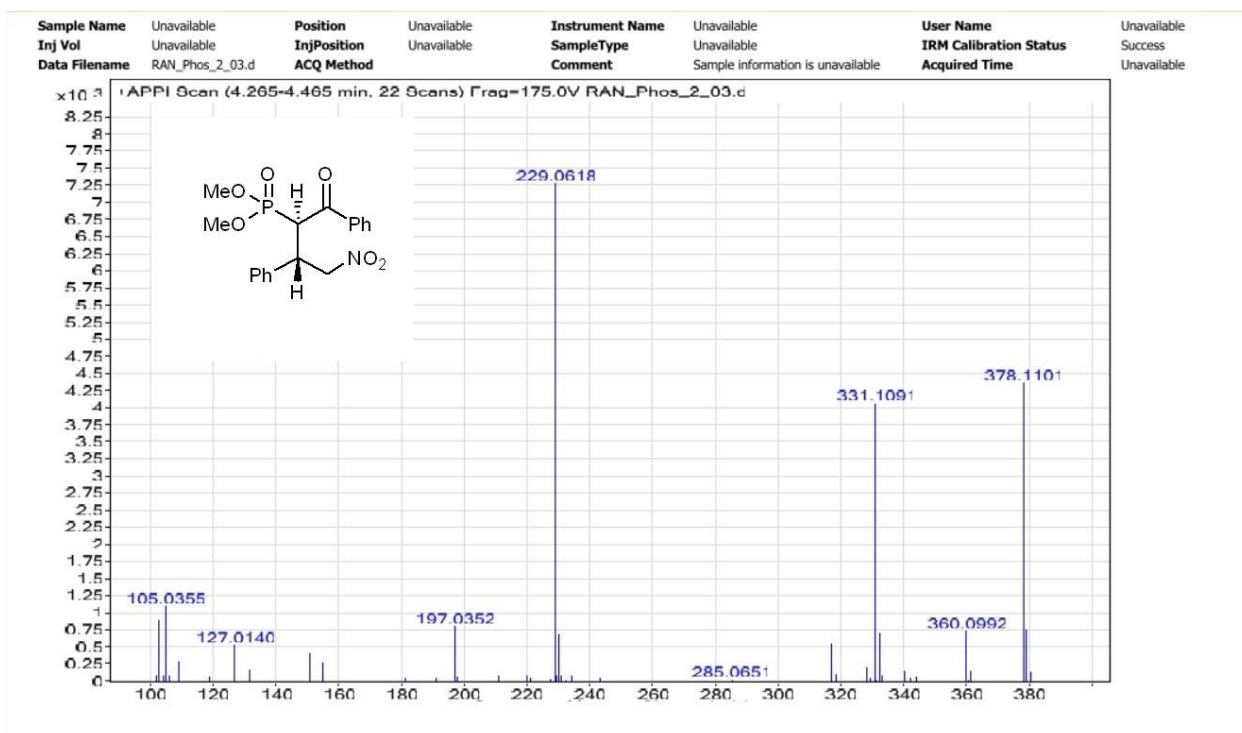
¹³C NMR spectra of dimethyl [(2*R*,3*S*)-4-nitro-1-oxo-1,3-diphenylbutan-2-yl]phosphonate (**6a**) in CDCl₃



³¹P NMR spectra of dimethyl [(2*R*,3*S*)-4-nitro-1-oxo-1,3-diphenylbutan-2-yl]phosphonate (**6a**) in CDCl₃

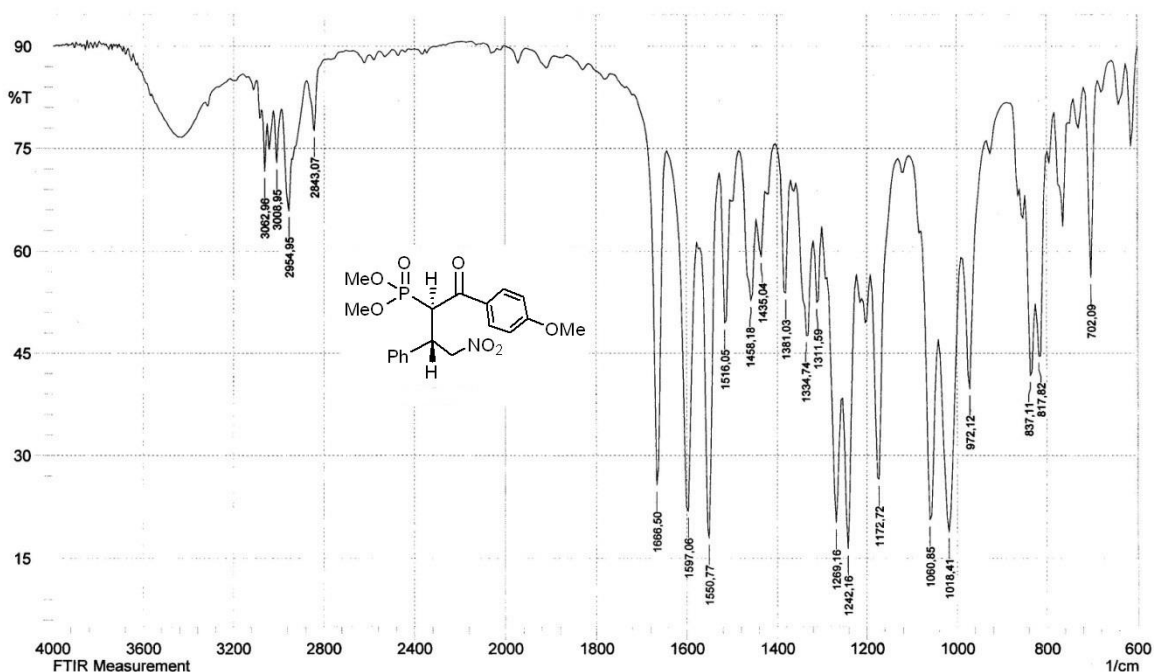


HRMS of dimethyl [(2*R*,3*S*)-4-nitro-1-oxo-1,3-diphenylbutan-2-yl]phosphonate (**6a**)

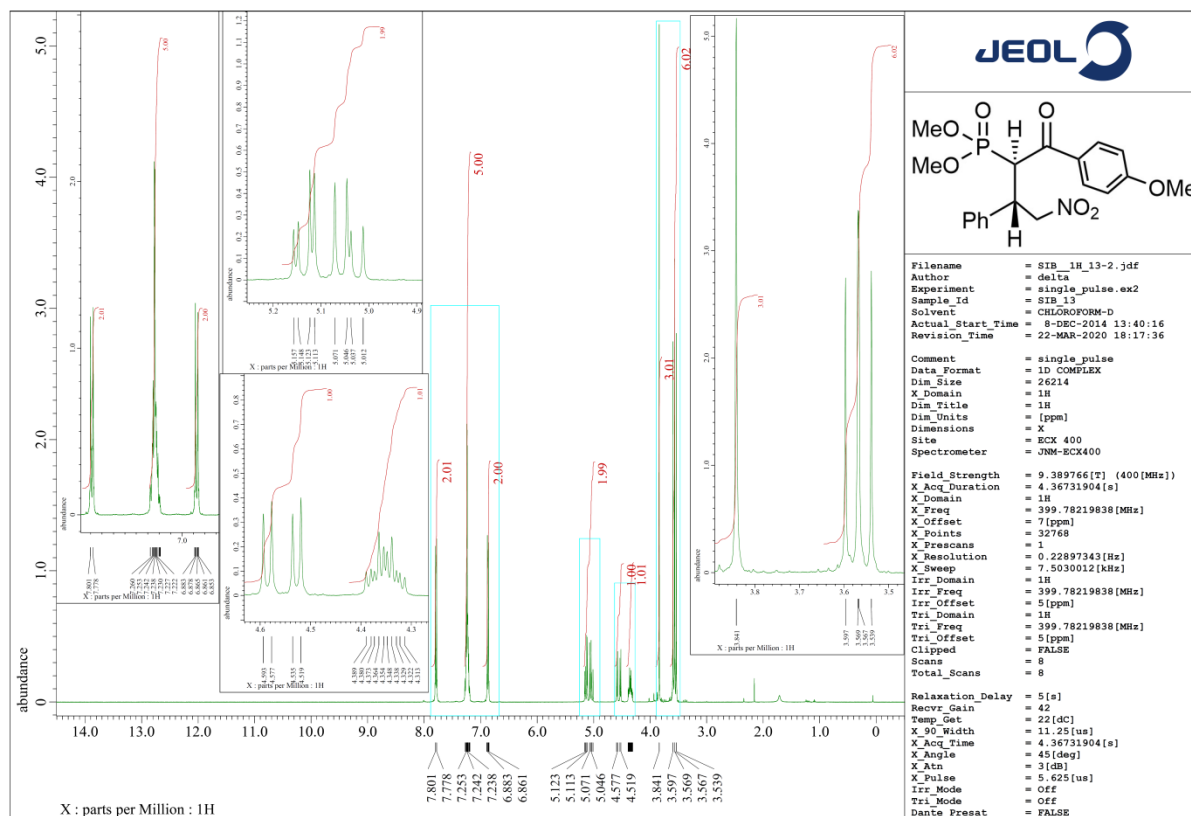


FTIR spectra of dimethyl [(2*R*,3*S*)-1-(4-methoxyphenyl)-4-nitro-1-oxo-3-phenylbutan-2-yl]-phosphonate

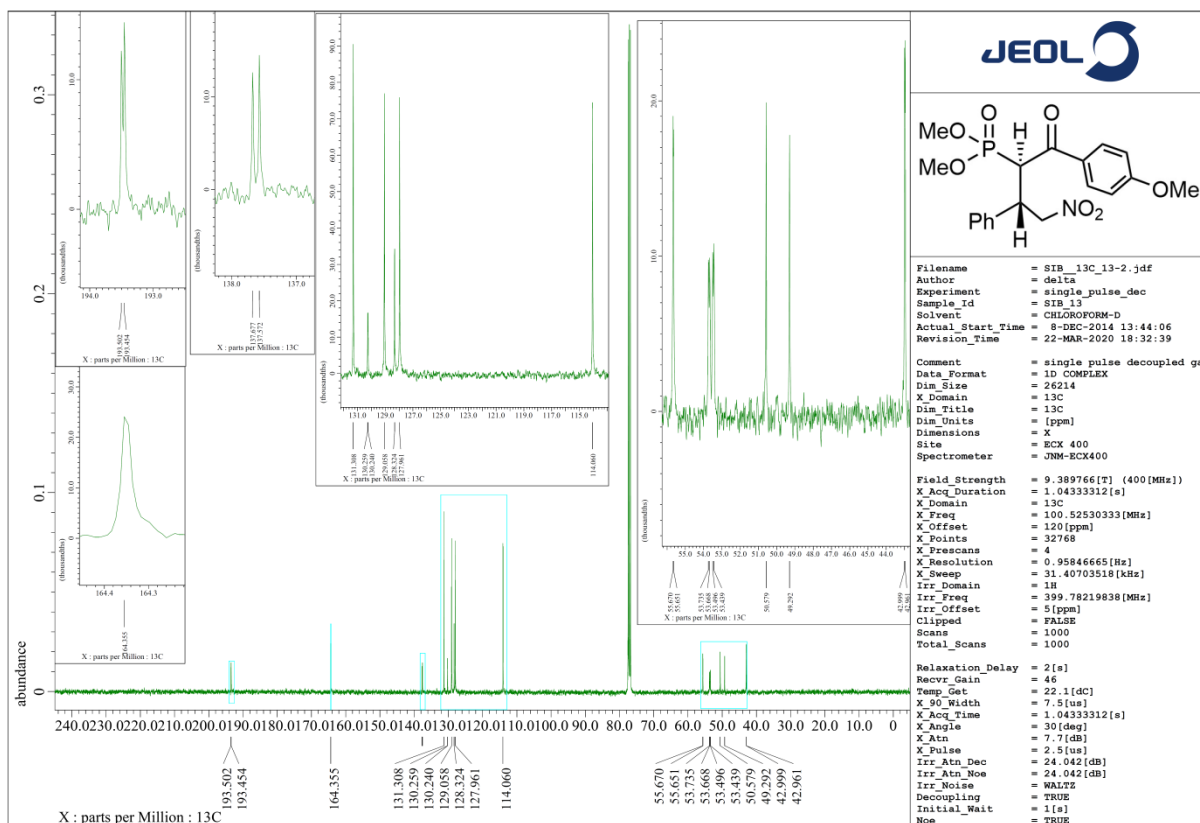
(**6b**)



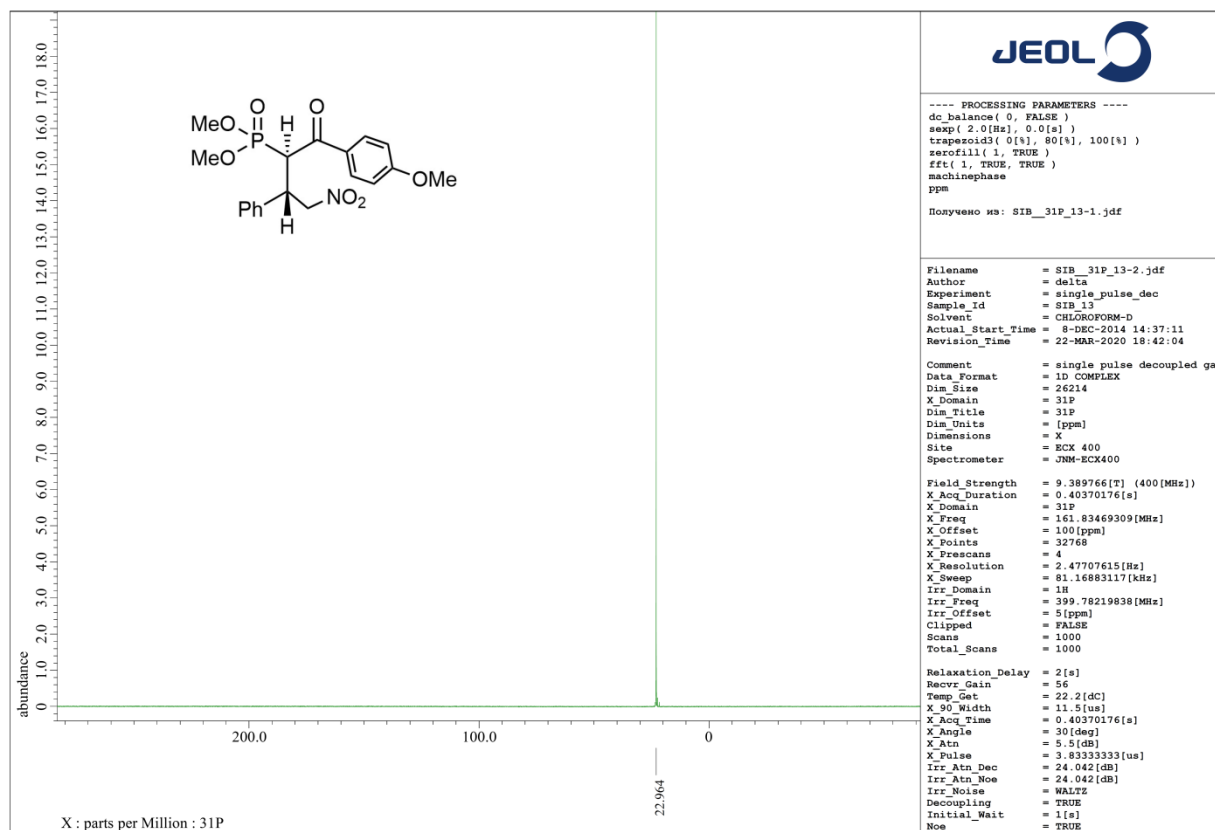
¹H NMR spectra of dimethyl [(2*R*,3*S*)-1-(4-methoxyphenyl)-4-nitro-1-oxo-3-phenylbutan-2-yl]-phosphonate (**6b**) in CDCl₃



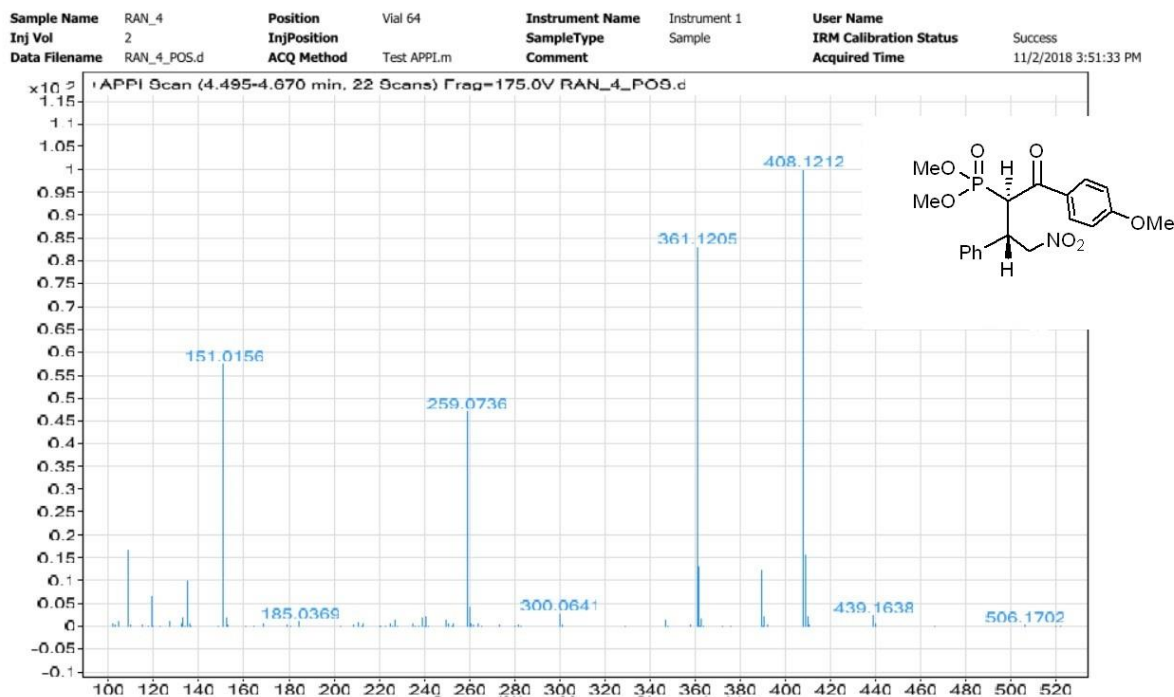
¹³C NMR spectra of dimethyl [(2*R*,3*S*)-1-(4-methoxyphenyl)-4-nitro-1-oxo-3-phenylbutan-2-yl]-phosphonate (**6b**) in CDCl₃



³¹P NMR spectra of dimethyl [(2*R*,3*S*)-1-(4-methoxyphenyl)-4-nitro-1-oxo-3-phenylbutan-2-yl]-phosphonate (**6b**) in CDCl₃

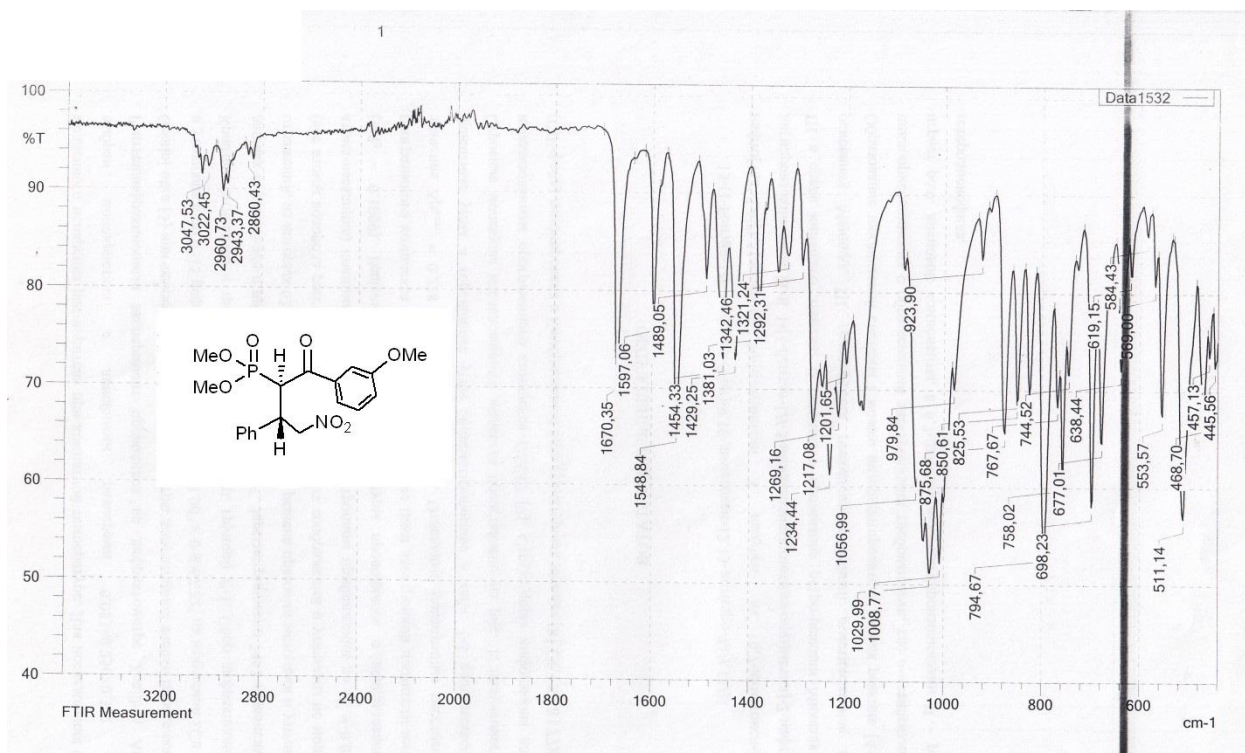


HRMS of dimethyl [(2*R*,3*S*)-1-(4-methoxyphenyl)-4-nitro-1-oxo-3-phenylbutan-2-yl]-phosphonate (**6b**)



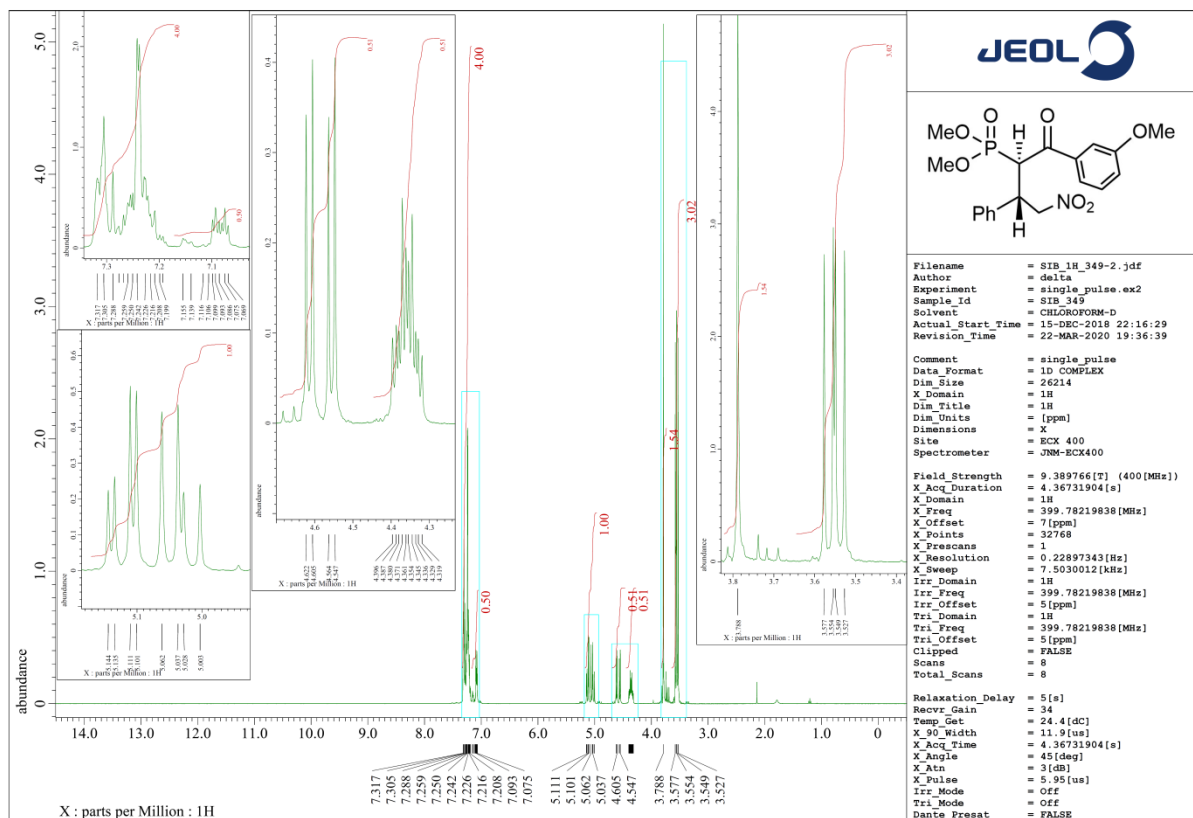
FTIR spectra of dimethyl [(2*R*,3*S*)-1-(3-methoxyphenyl)-4-nitro-1-oxo-3-phenylbutan-2-yl]phosphonate

(6c)

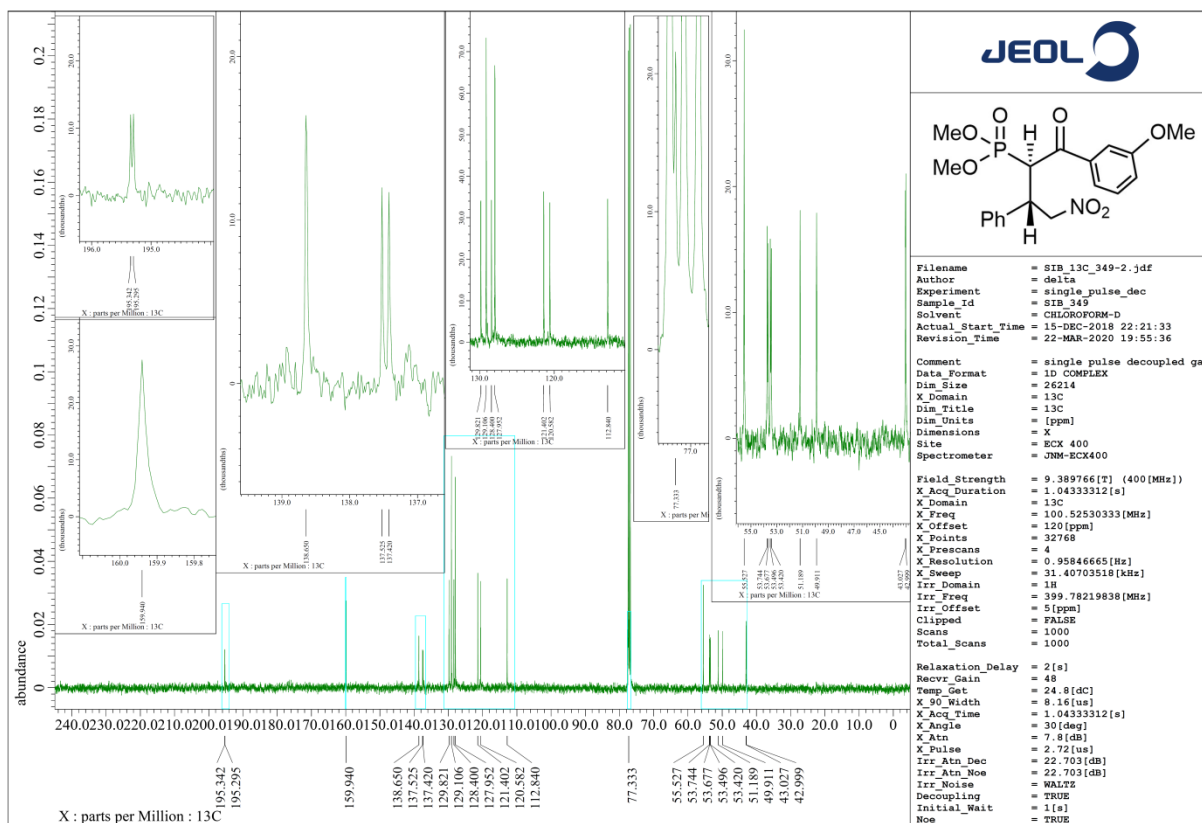


¹H NMR spectra of dimethyl [(2*R*,3*S*)-1-(3-methoxyphenyl)-4-nitro-1-oxo-3-phenylbutan-2-yl]phosphonate

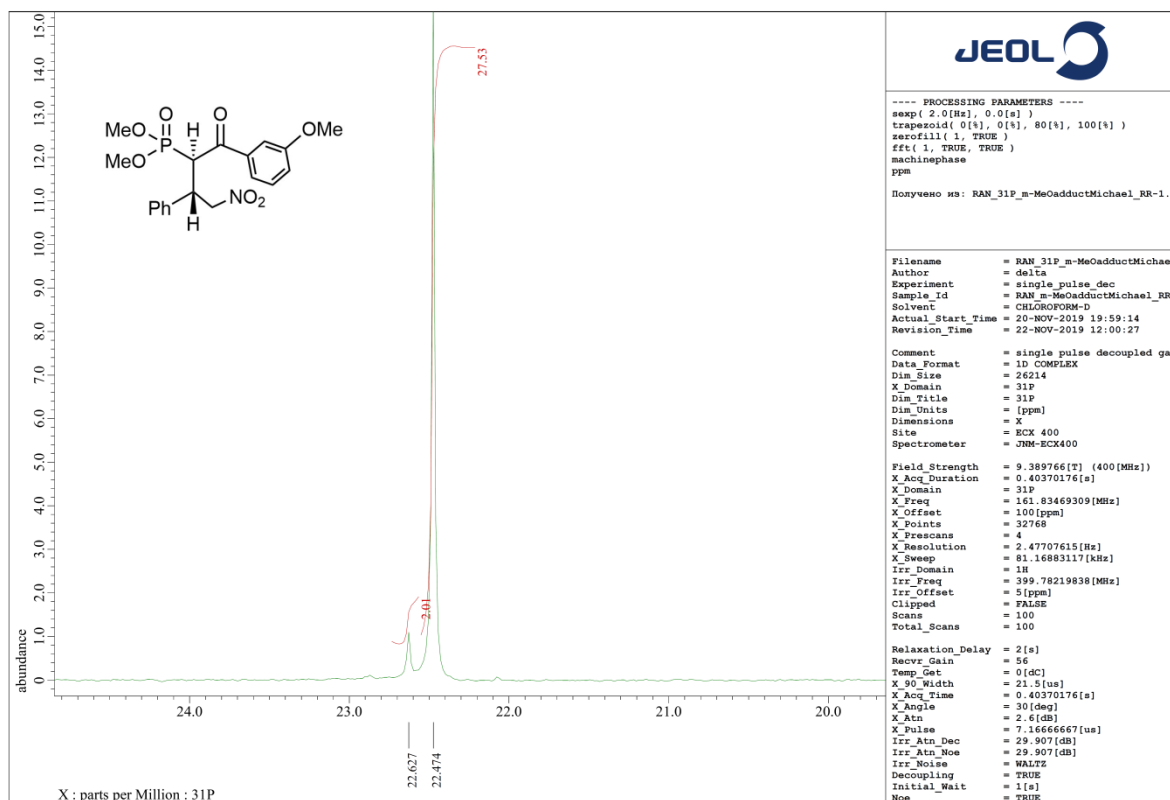
(6c) in CDCl₃



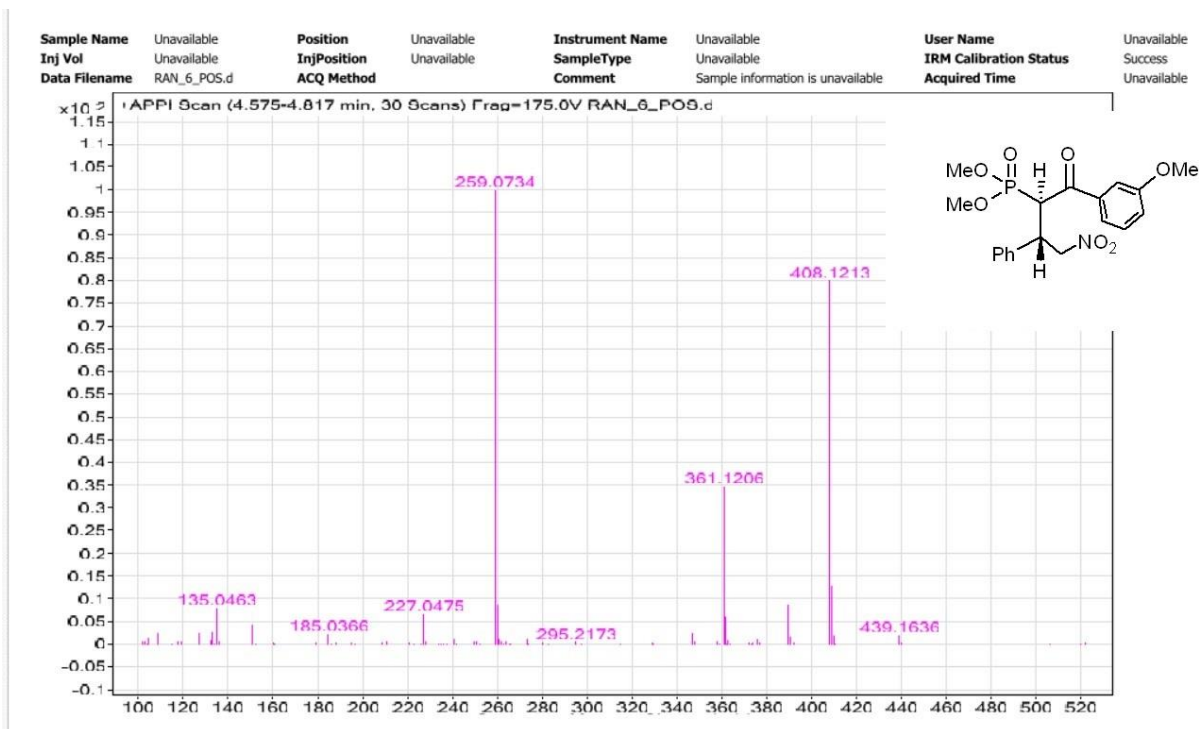
¹³C NMR spectra of dimethyl [(2*R*,3*S*)-1-(3-methoxyphenyl)-4-nitro-1-oxo-3-phenylbutan-2-yl]phosphonate (**6c**) in CDCl₃



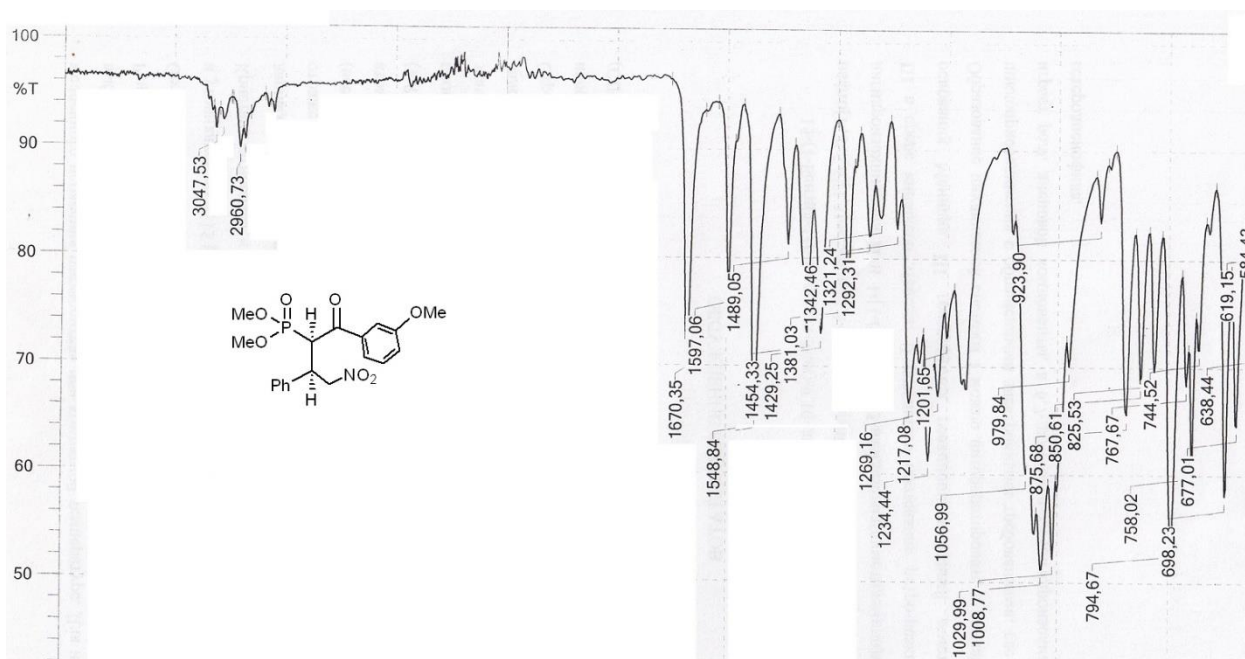
³¹P NMR spectra of dimethyl [(2*R*,3*S*)-1-(3-methoxyphenyl)-4-nitro-1-oxo-3-phenylbutan-2-yl]phosphonate (**6c**) in CDCl₃



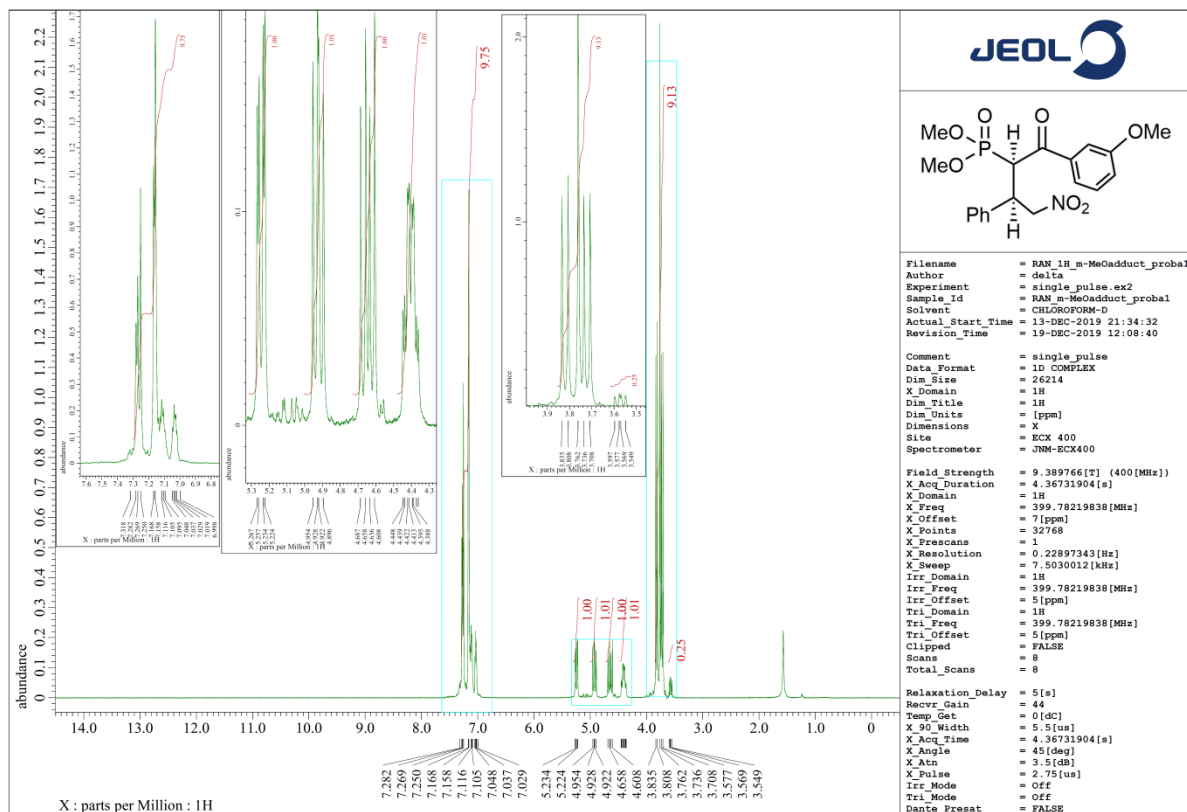
HRMS of dimethyl [(2*R*,3*S*)-1-(3-methoxyphenyl)-4-nitro-1-oxo-3-phenylbutan-2-yl]phosphonate (**6c**)



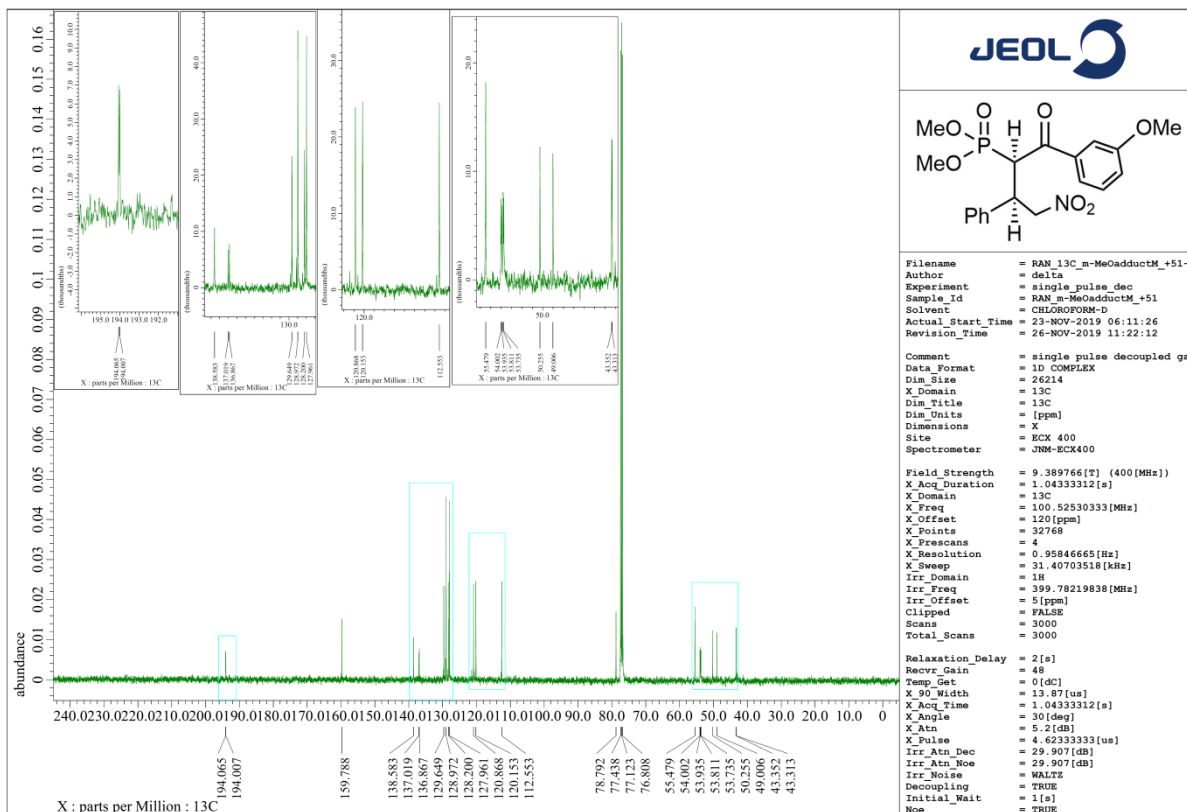
FTIR spectra of dimethyl [(2*R*,3*R*)-1-(3-methoxyphenyl)-4-nitro-1-oxo-3-phenylbutan-2-yl]phosphonate (**6c**)



¹H NMR spectra of dimethyl [(2*R*,3*R*)-1-(3-methoxyphenyl)-4-nitro-1-oxo-3-phenylbutan-2-yl]phosphonate
(**6c**) in CDCl₃



¹³C NMR spectra of dimethyl [(2*R*,3*R*)-1-(3-methoxyphenyl)-4-nitro-1-oxo-3-phenylbutan-2-yl]phosphonate (**6c**) in CDCl₃



Chemical Structure: (S)-1-methoxy-2-phenyl-3-nitropropan-1-ol

13C NMR Spectrum Data:

Chemical Shift (ppm)	Assignment
129.830	Aromatic C-O
129.649	Aromatic C-O
129.125	Aromatic C-O
128.972	Aromatic C-O
128.419	Aromatic C-O
128.200	Aromatic C-O
127.961	Aromatic C-O
121.411	Aromatic C-O
120.868	Aromatic C-O
120.620	Aromatic C-O
120.153	Aromatic C-O
112.811	Aromatic C-O
112.553	Aromatic C-O
78.801	CH-OH
55.489	CH-OCH ₃
54.011	CH-OCH ₃
53.944	CH-OCH ₃
53.811	CH-OCH ₃
53.754	CH-OCH ₃
50.255	CH-OCH ₃
49.006	CH-OCH ₃
43.456	CH-OCH ₃
43.313	CH-OCH ₃

Acquisition Parameters:

Filename	= RAM_DEPT135_m-MeOadductM
Author	= de1ta
Experiment	= dept.ex2
Sample_Id	= RAM_m-MeOadductM +51
Solvent	= CHLOROFORM-D
Actual_Start_Time	= 23-NOV-2019 08:44:02
Revision_Time	= 26-NOV-2019 11:33:14
Comment	= DEPT with decoupling
Data Format	= 1D COMPLEX
Dim_Size	= 26214
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Dim_Title	= 13C
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Spectrometer	= JNM-ECX400
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X_Acq_Duration	= 1.04333312[s]
X_Domain	= 13C
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X_Offset	= 120 [ppm]
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Irr_Offset	= 5 [ppm]
Clipped	= FALSE
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X_Acq_Time	= 1.04333312[s]
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Irr_Atn_Dec	= 29.907 [dB]
Irr_Noise	= WALTZ
Irr_Pulse	= 5.5 [us]
Decoupling	= TRUE
Initial_Wait	= 1[s]
O_Constant	= 140 [Hz]
Selection_Angle	= 140 [deg]

JEOL

Chemical structure of compound 15-35:

COC(=O)C(COP(=O)(OC)OC)Cc1ccc(OC)cc1[N+](=O)[O-]

NMR Spectrum Data:

Trace Color	Peak Label	Chemical Shift (ppm)
Green	-	22.627
Green	-	22.489
Red	15-35	~22.6
Red	1.94	1.94

X : parts per Million : 31P

```

---- PROCESSING PARAMETERS ----
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trapzoid: 0[%], 0[%], 80[%], 100[%] )
zerofill: ( 1, TRUE )
fft: ( 1, TRUE, TRUE )
machinphase
ppm

Получено из: RAN_31P_m-MeOadductM_+51-1.jdf

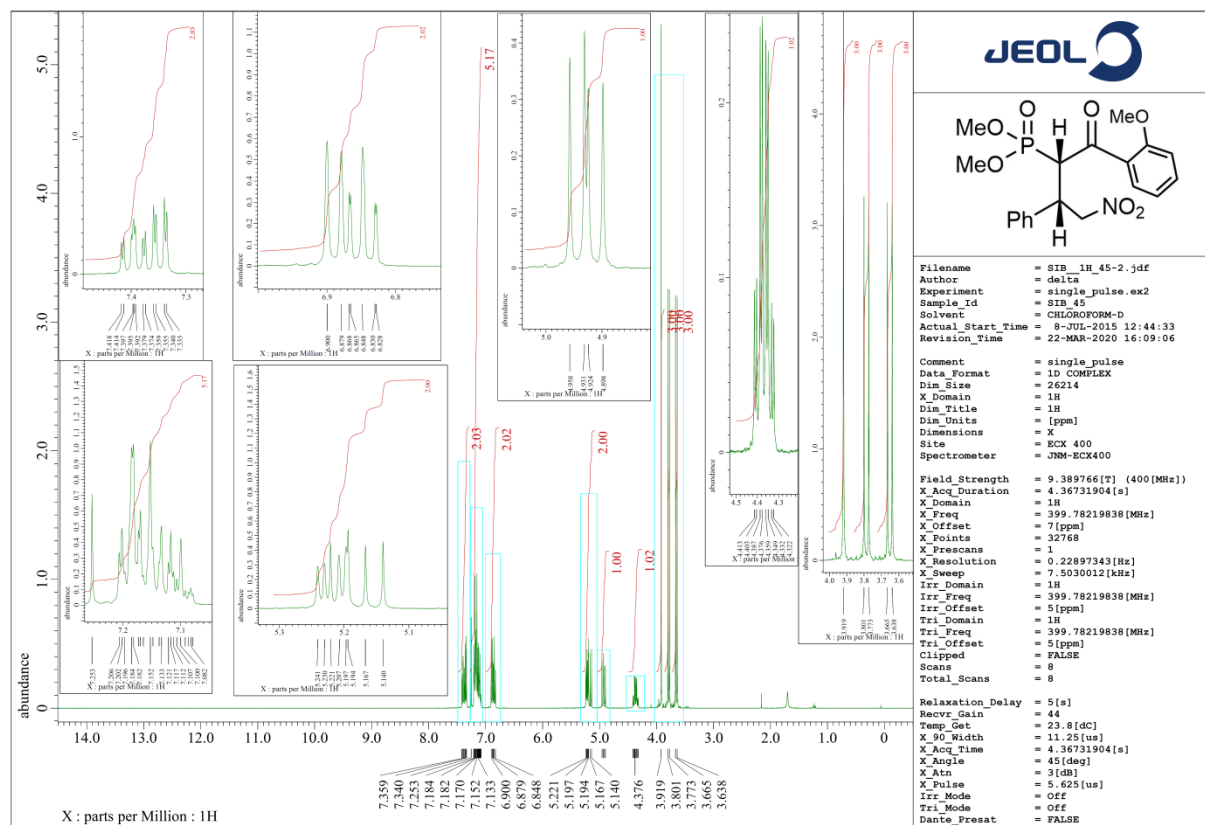
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Solvent      = CHLOROFORM-D
Actual_Start_Time = 20-NOV-2019 23:52:53
Revision_Time  = 21-NOV-2019 16:45:54

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Data Format   = 1D COMPLEX
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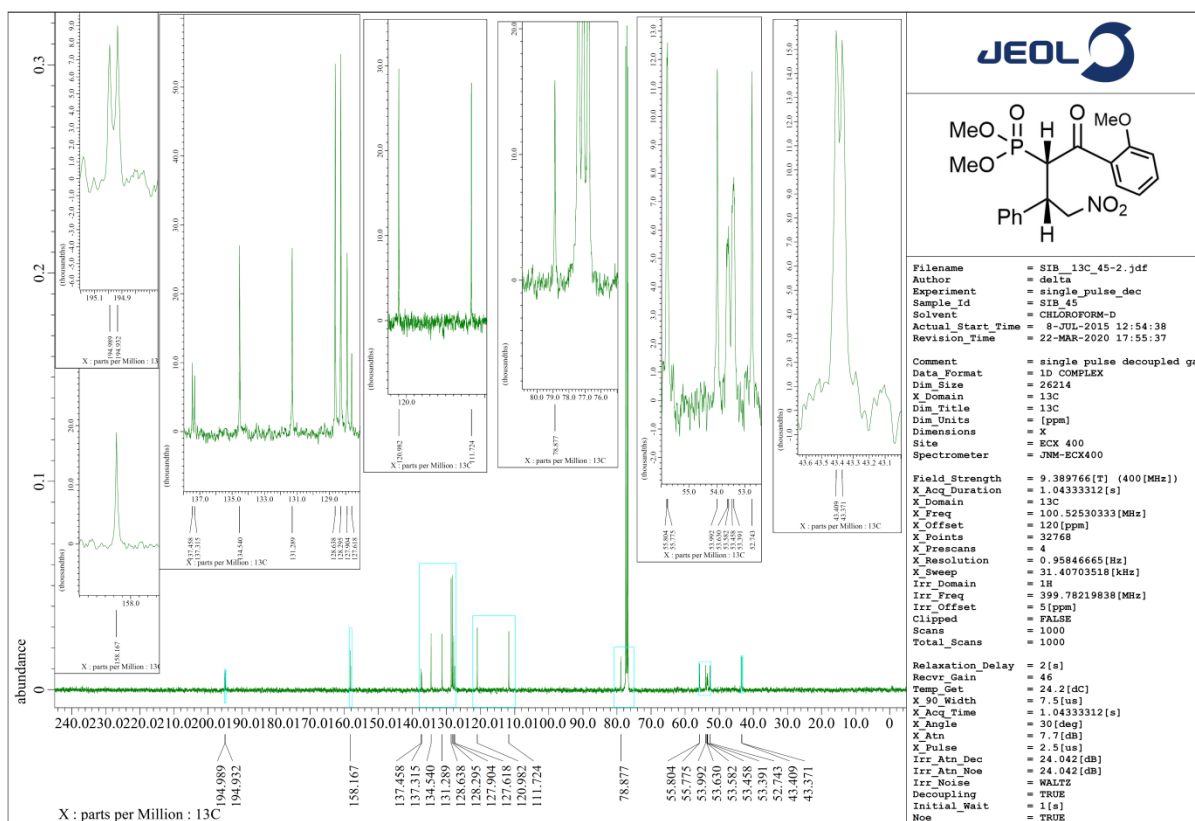
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X_Pulse         = 7.16666667[us]
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Irr_Noise      = WALTZ
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Noise           = TRUE
  
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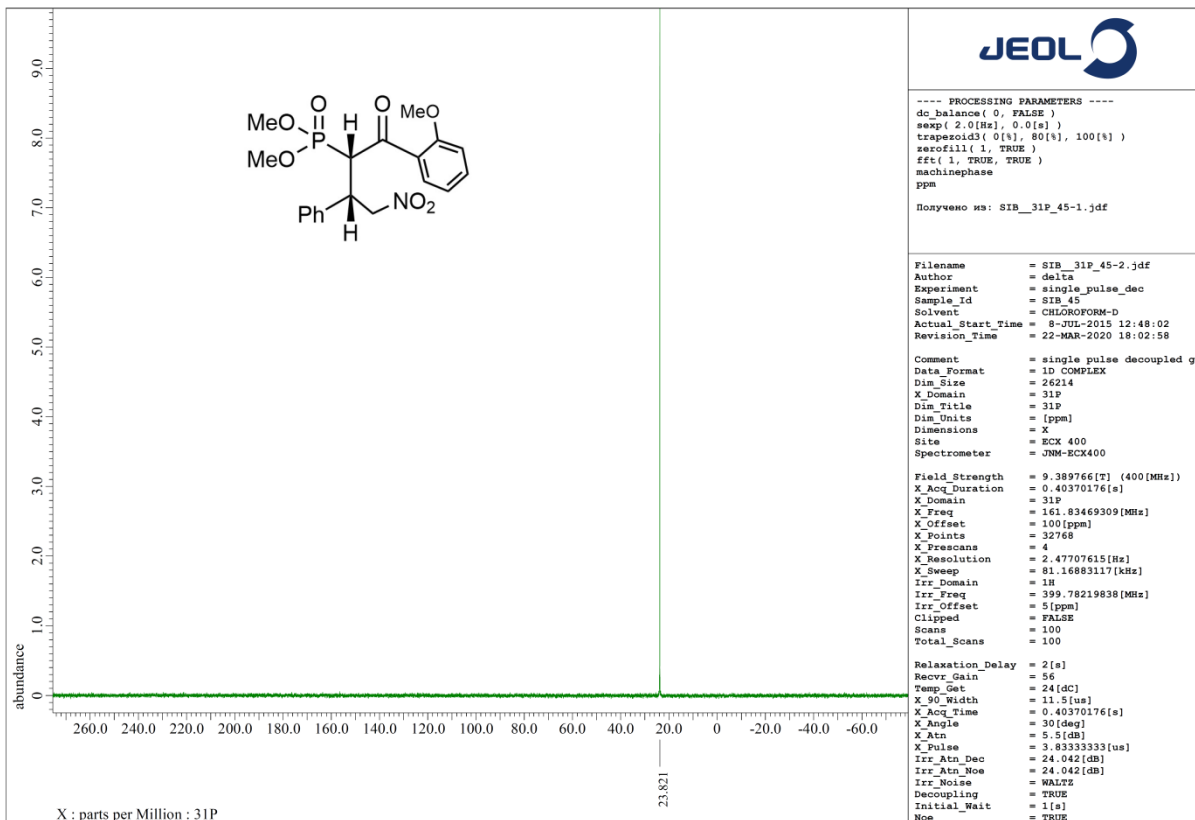

(6d)



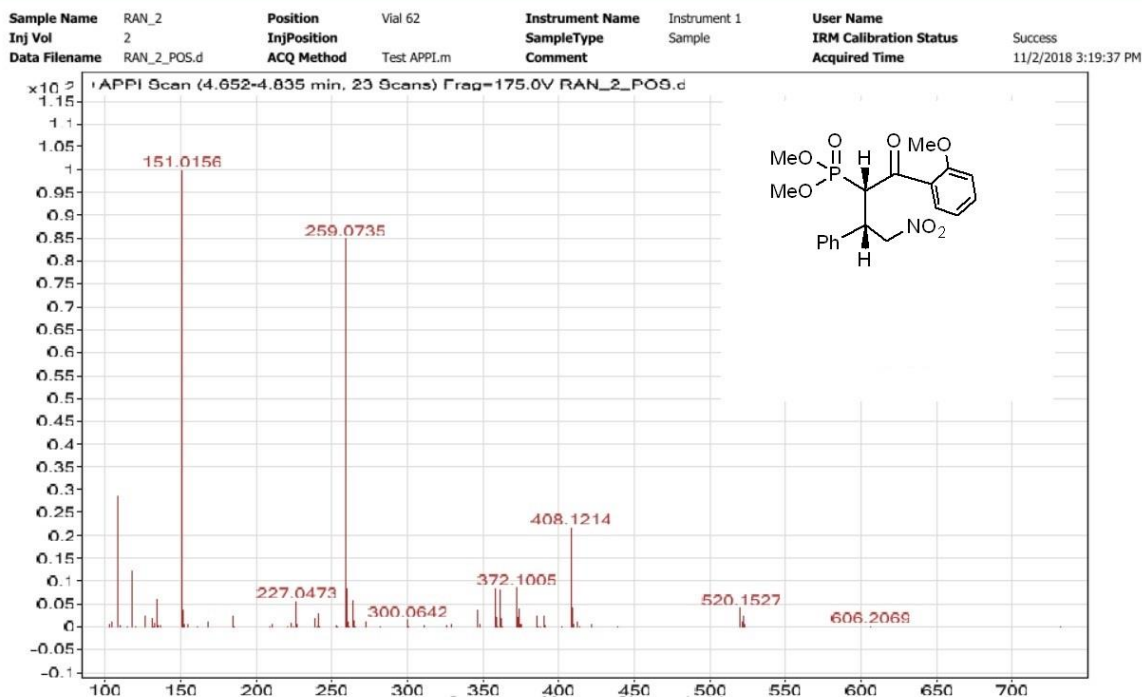
¹³C NMR spectra of dimethyl [(2S,3S)-1-(2-methoxyphenyl)-4-nitro-1-oxo-3-phenylbutan-2-yl]phosphonate (**6d**) in CDCl₃



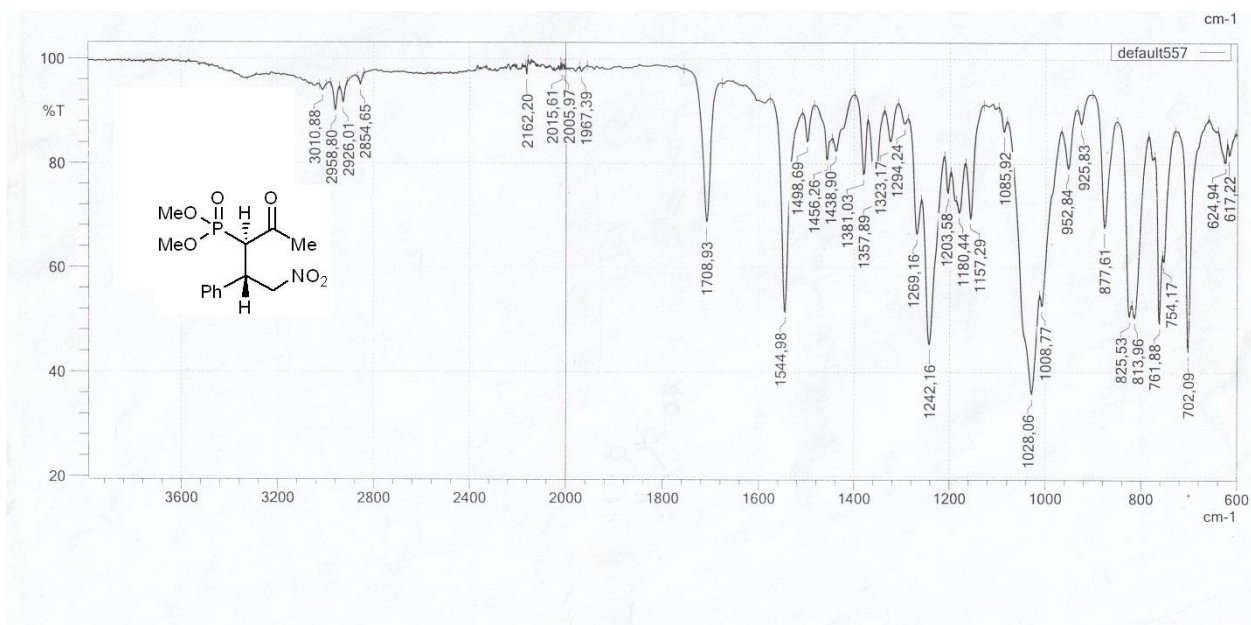
³¹P NMR spectra of dimethyl [(2S,3S)-1-(2-methoxyphenyl)-4-nitro-1-oxo-3-phenylbutan-2-yl]phosphonate (**6d**) in CDCl₃



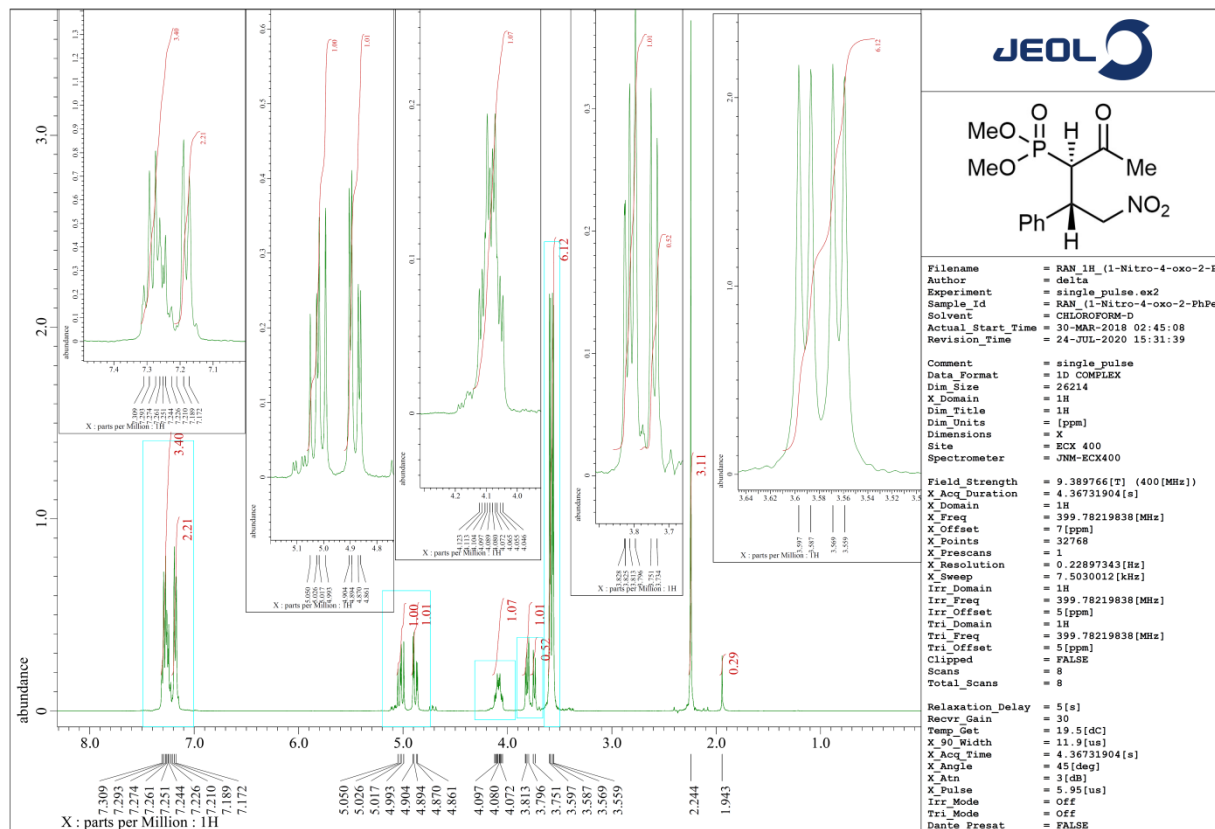
HRMS of dimethyl [(2S,3S)-1-(2-methoxyphenyl)-4-nitro-1-oxo-3-phenylbutan-2-yl]phosphonate (**6d**)



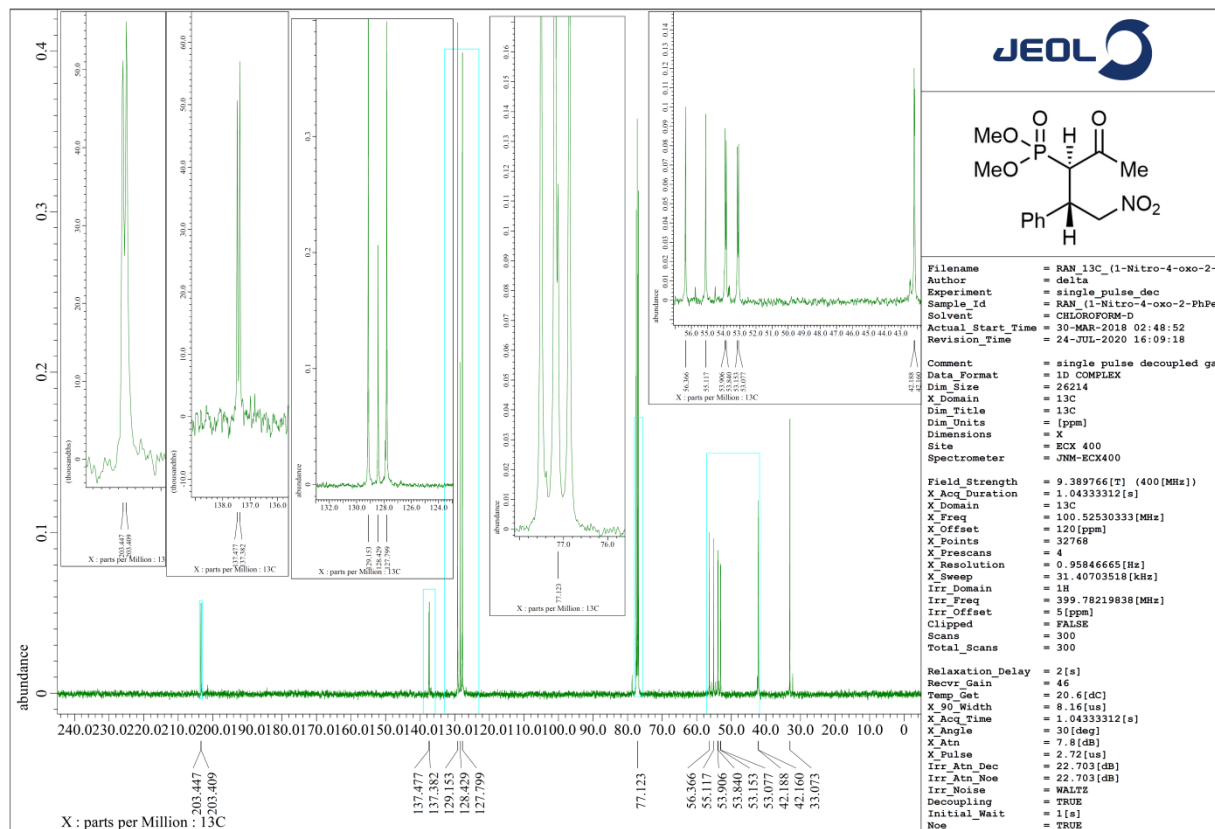
FTIR spectra of dimethyl [(2S,3R)-1-nitro-4-oxo-2-phenylpentan-3-yl]phosphonate (**6e**)



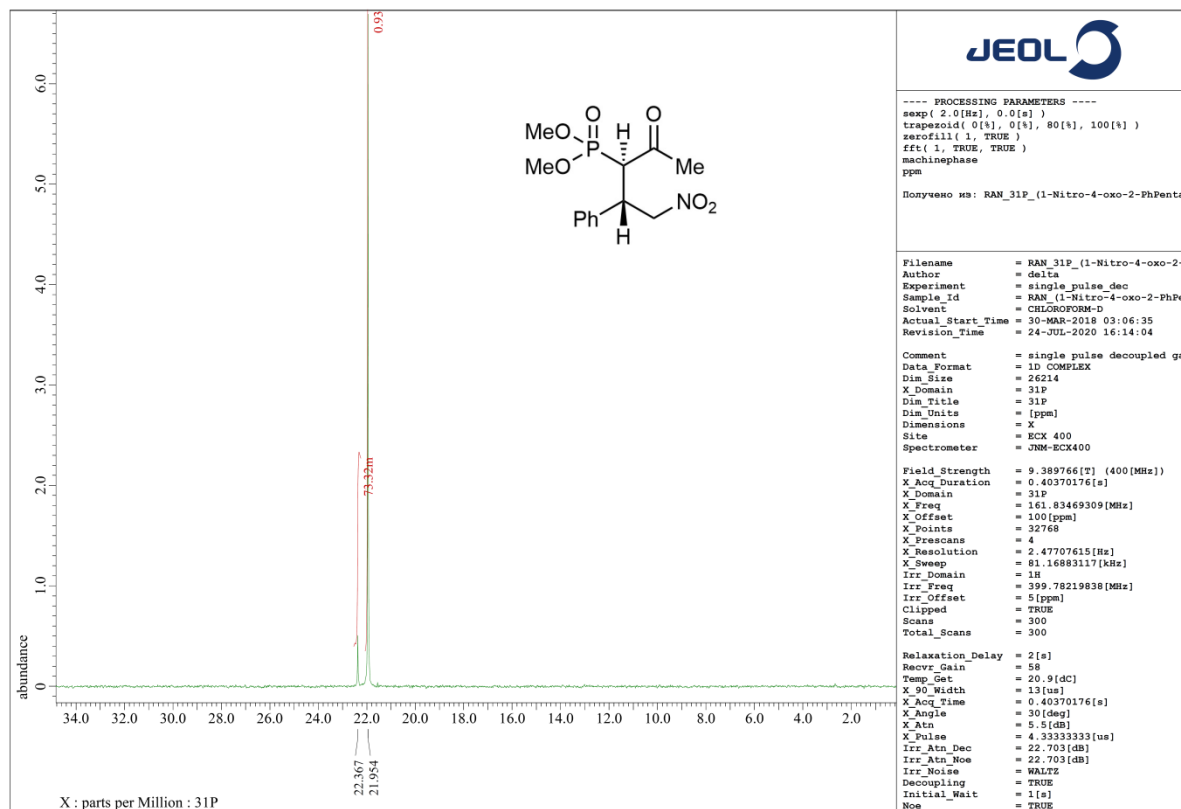
¹H NMR spectra of dimethyl [(2*S*,3*R*)-1-nitro-4-oxo-2-phenylpentan-3-yl]phosphonate (**6e**) in CDCl₃



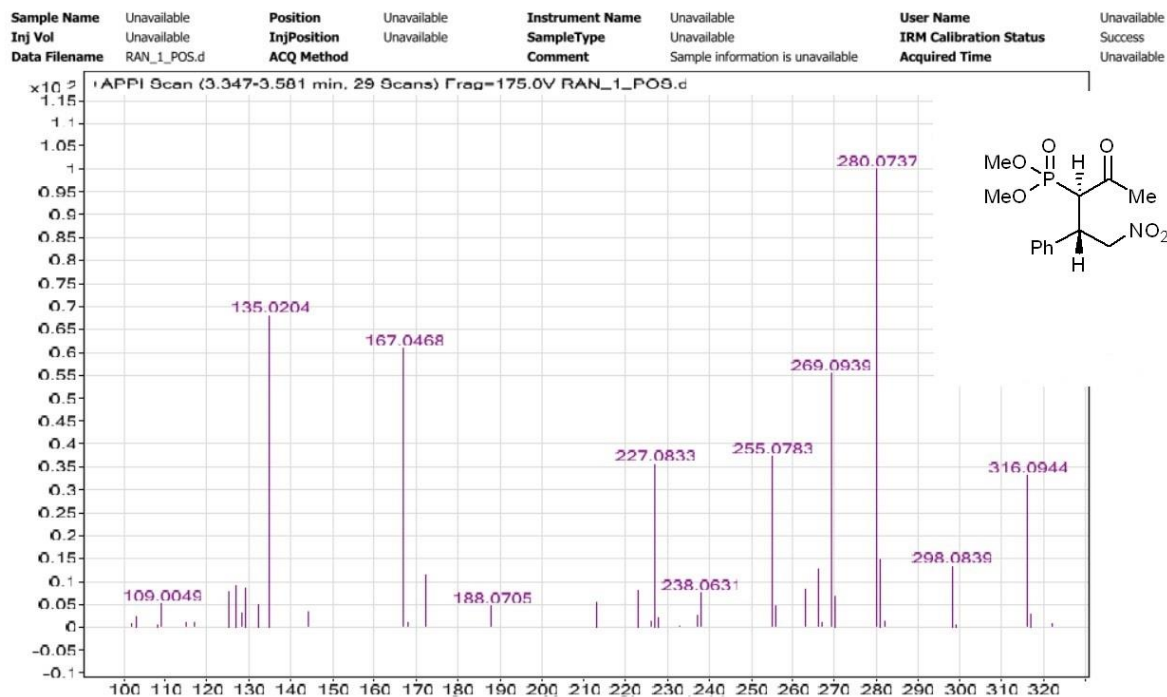
¹³C NMR spectra of dimethyl [(2*S*,3*R*)-1-nitro-4-oxo-2-phenylpentan-3-yl]phosphonate (**6e**) in CDCl₃



³¹P NMR spectra of dimethyl [(2*S*,3*R*)-1-nitro-4-oxo-2-phenylpentan-3-yl]phosphonate (**6e**) in CDCl₃



HRMS of dimethyl [(2*S*,3*R*)-1-nitro-4-oxo-2-phenylpentan-3-yl]phosphonate (**6e**)



FTIR spectrum of compound **1**. The x-axis represents the wavenumber in cm⁻¹ (ranging from 3750 to 500), and the y-axis represents the percentage of transmittance (%T, ranging from 30 to 100). The chemical structure of **1** is shown as an inset.

Chemical structure of **1**: COC(=O)[C@H](c1ccccc1)[C@@H](O)C(=O)O

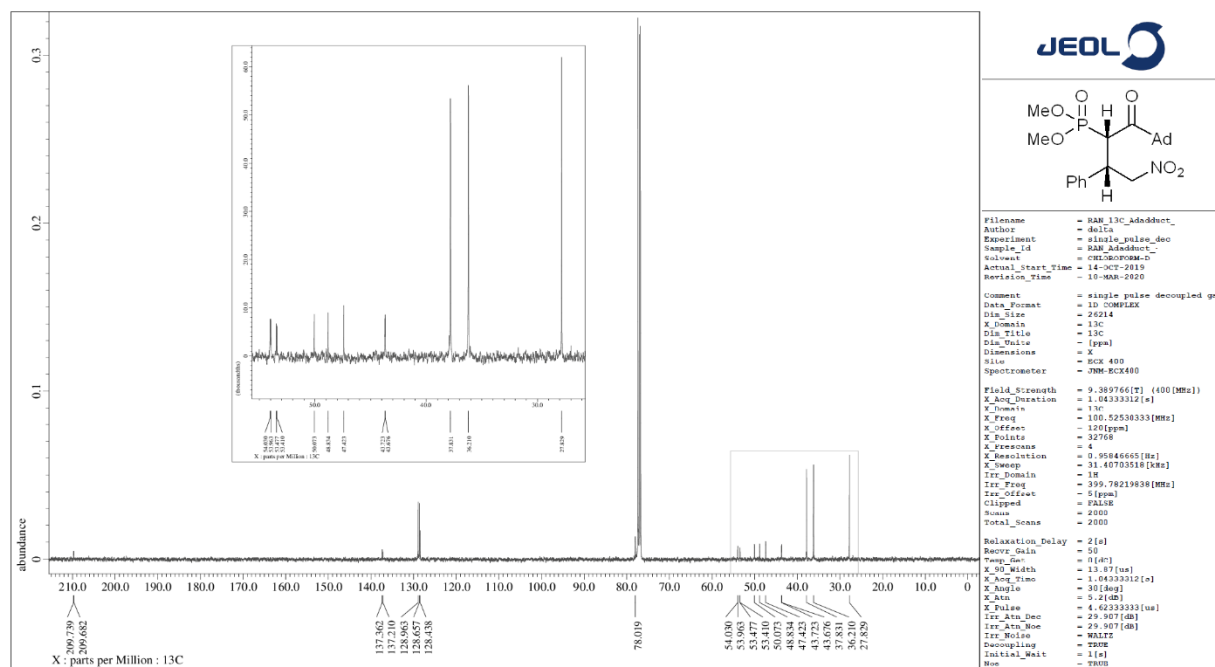
Key FTIR peaks (cm⁻¹):

- 3032.10
- 2916.37
- 2854.65
- 1689.64
- 1602.85
- 1546.91
- 1519.91
- 1379.10
- 1344.38
- 1307.74
- 1232.51
- 1176.58
- 1141.86
- 1058.92
- 1016.49
- 999.13
- 979.84
- 867.97
- 821.68
- 812.03
- 775.38
- 759.95
- 744.52
- 702.09
- 590.22
- 555.50
- 528.50
- 495.71
- 412.77
- 408.91

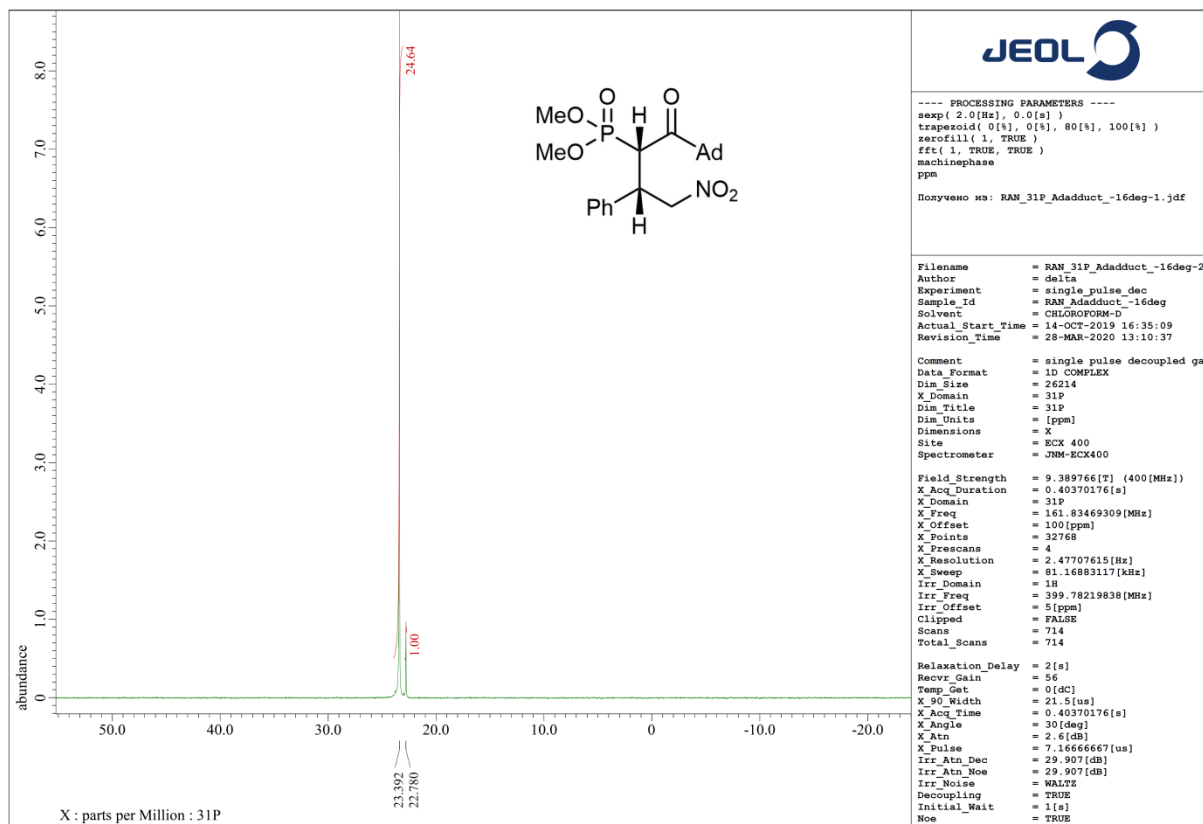
Chemical structure of compound 10: CC(=O)C(Cc1ccccc1)COP(=O)(OC)OC

¹H NMR spectrum (CDCl₃) of compound 10. The x-axis represents chemical shift in ppm (delta), ranging from 0 to 10. The y-axis represents abundance. The spectrum shows several peaks: a multiplet at 7.2-7.4 ppm (aromatic protons), a doublet at 6.46 ppm (CH=CH₂), a multiplet at 5.8-6.0 ppm (CH=CH₂), a multiplet at 4.0-4.5 ppm (CH₂), a doublet at 3.82 ppm (CH₂), a doublet at 3.02 ppm (CH₂), a doublet at 2.75 ppm (CH₂), and a doublet at 1.335 ppm (CH₃). Two insets are provided: one for the aromatic region (7.1-7.3 ppm) and another for the aliphatic region (2.7-3.1 ppm). The chemical structure of compound 10 is shown in the top right corner.

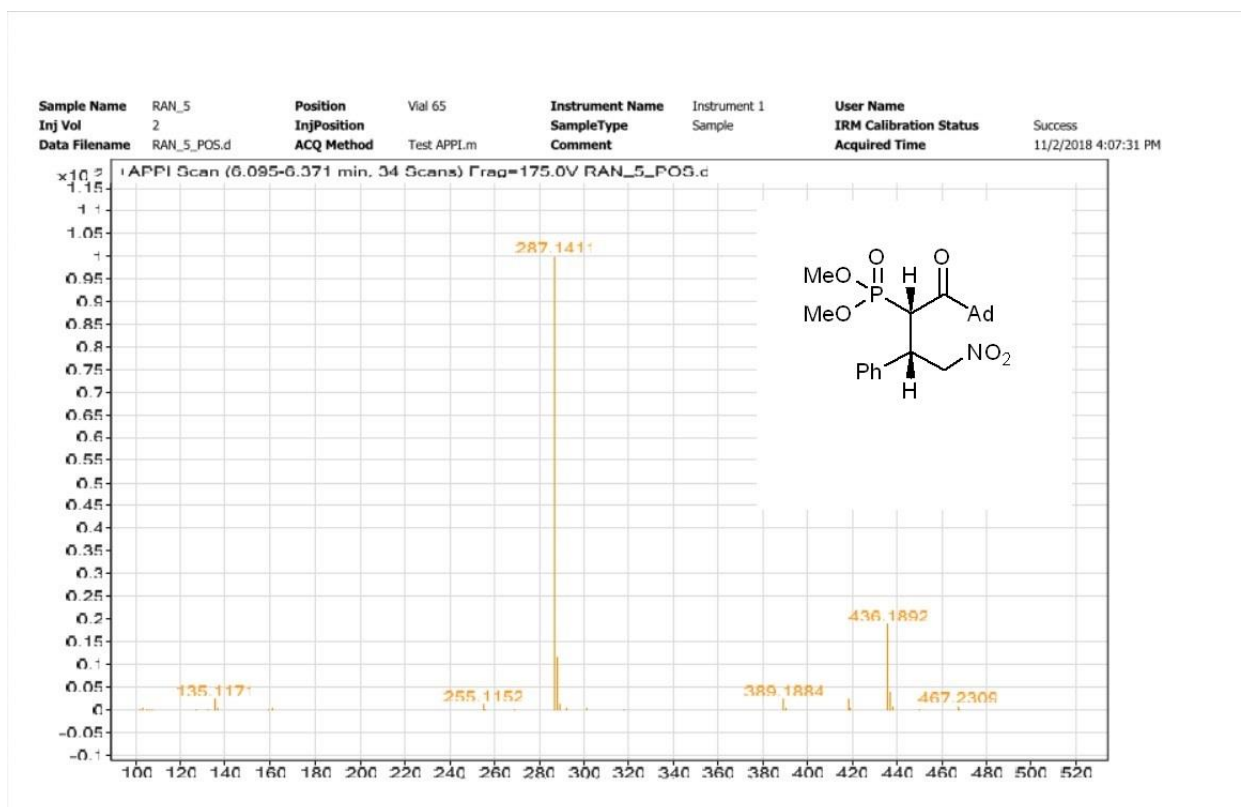
¹³C NMR spectra of dimethyl [(2S,3S)-1-(adamantan-1-yl)-4-nitro-1-oxo-3-phenylbutan-2-yl]phosphonate
(6f) in CDCl₃



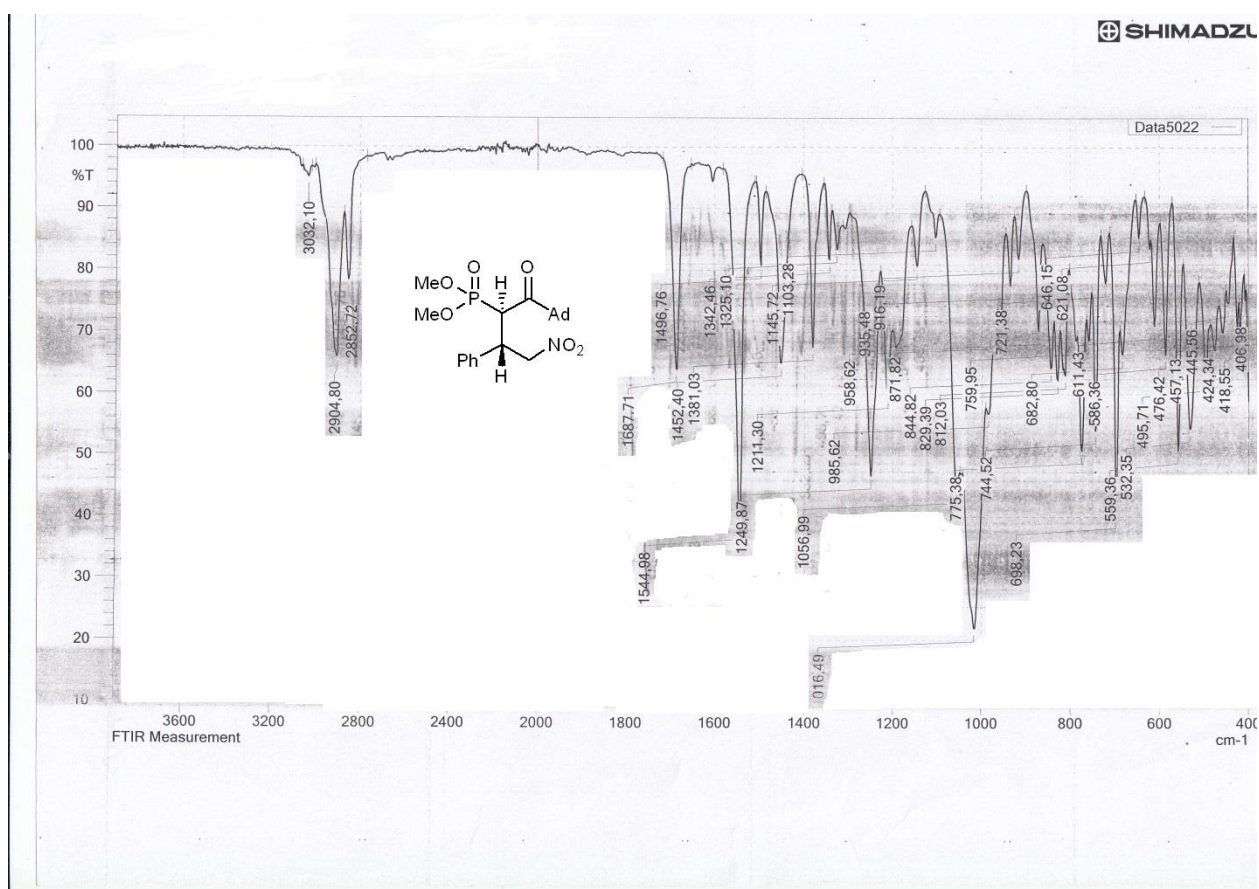
³¹P NMR spectra of dimethyl [(2S,3S)-1-(adamantan-1-yl)-4-nitro-1-oxo-3-phenylbutan-2-yl]phosphonate
(6f) in CDCl₃



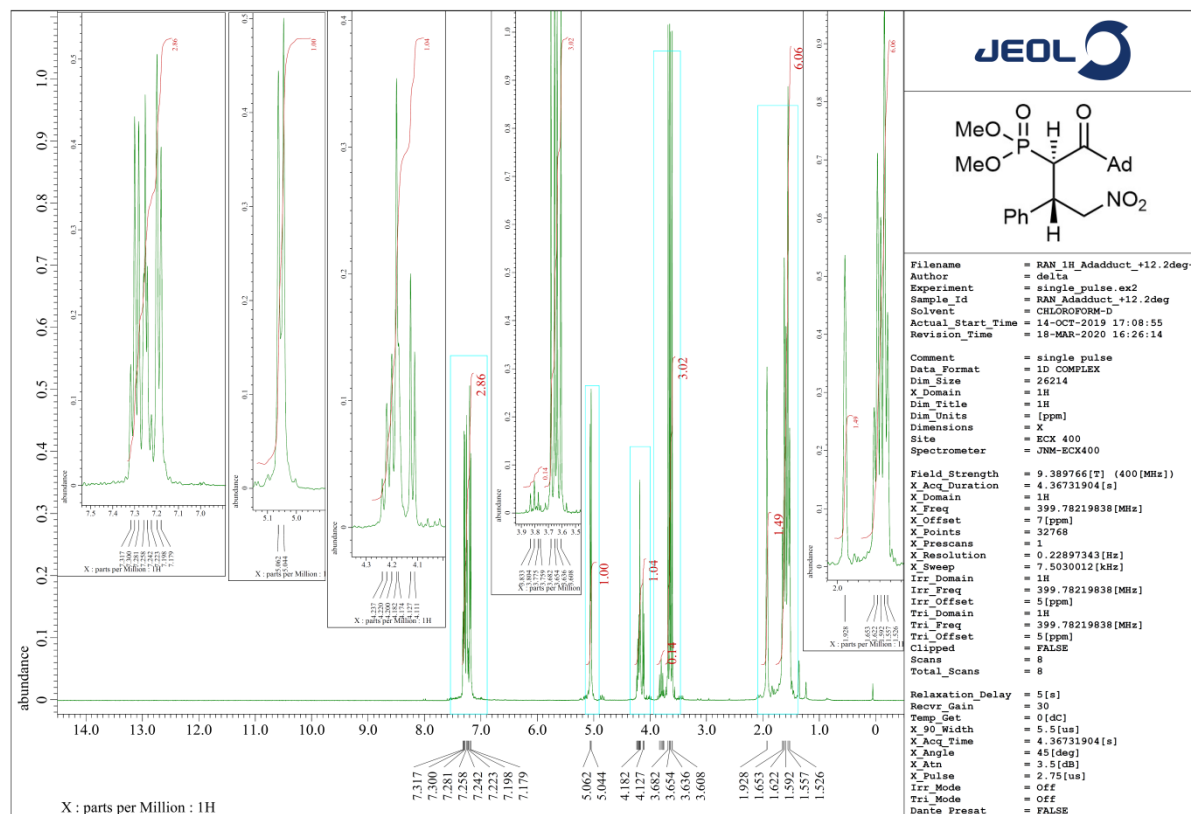
HRMS of dimethyl [(2*S*,3*S*)-1-(adamantan-1-yl)-4-nitro-1-oxo-3-phenylbutan-2-yl]phosphonate (**6f**)



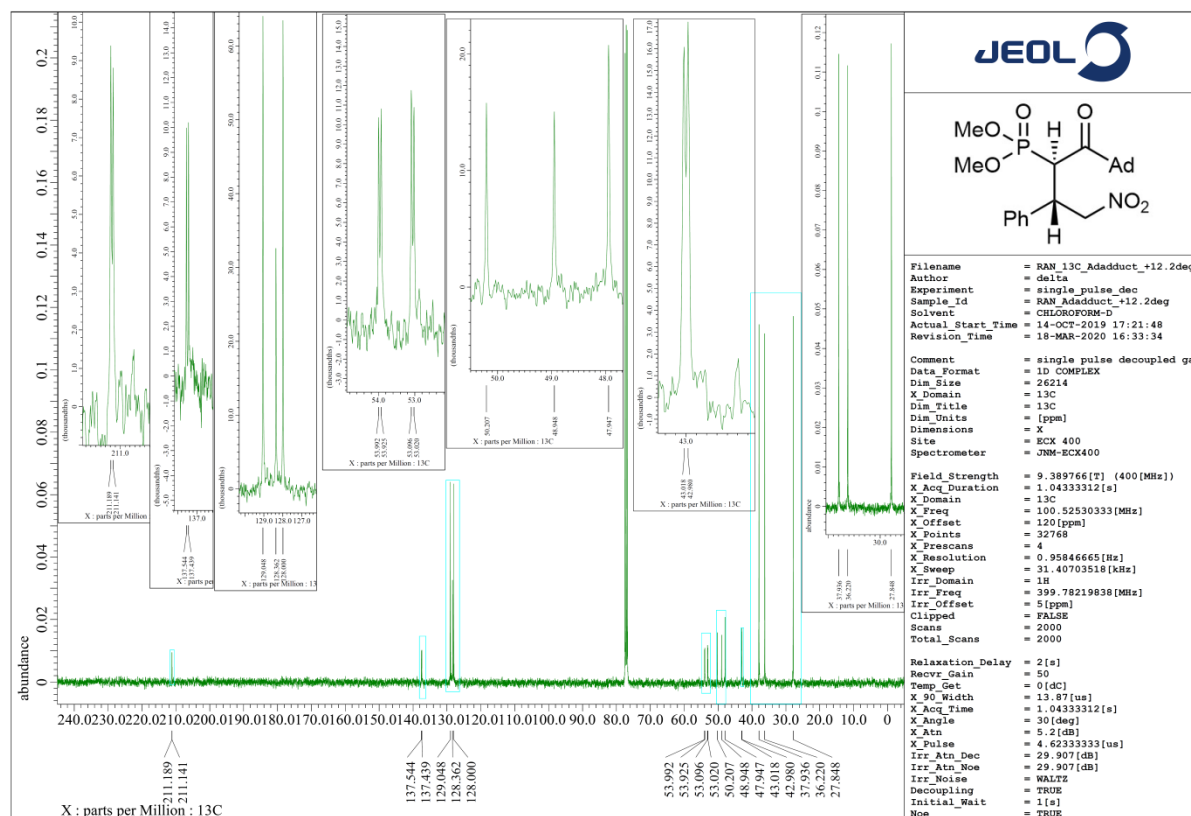
FTIR spectra of dimethyl [(2*R*,3*S*)-1-(adamantan-1-yl)-4-nitro-1-oxo-3-phenylbutan-2-yl]phosphonate (**6f**)



¹H NMR spectra of dimethyl [(2*R*,3*S*)-1-(adamantan-1-yl)-4-nitro-1-oxo-3-phenylbutan-2-yl]phosphonate
(**6f**) in CDCl₃

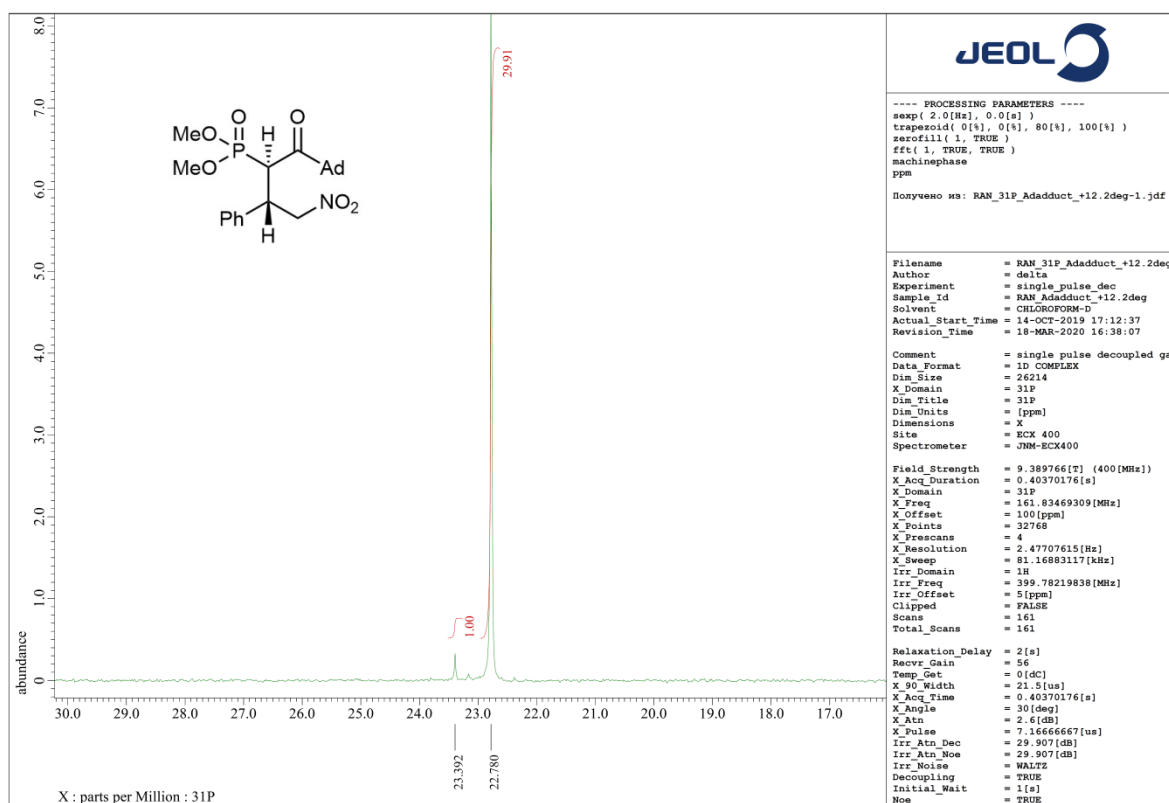


¹³C NMR spectra of dimethyl [(2*R*,3*S*)-1-(adamantan-1-yl)-4-nitro-1-oxo-3-phenylbutan-2-yl]phosphonate
(**6f**) in CDCl₃



³¹P NMR spectra of dimethyl [(2*R*,3*S*)-1-(adamantan-1-yl)-4-nitro-1-oxo-3-phenylbutan-2-yl]phosphonate

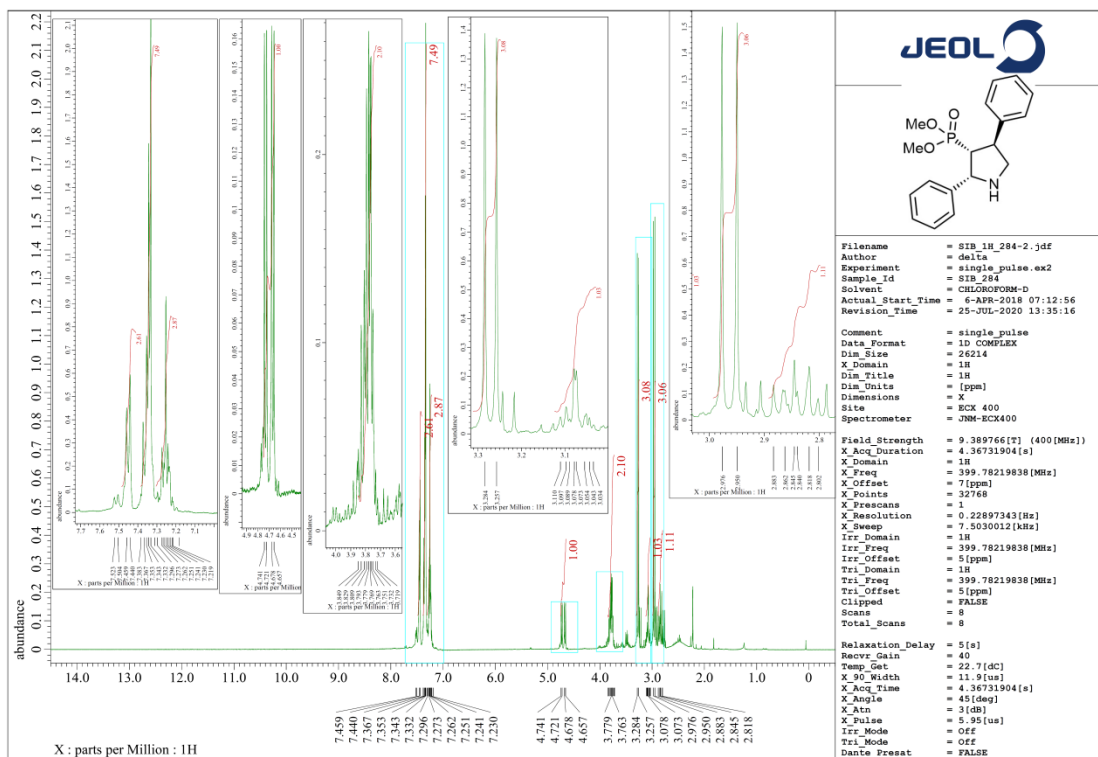
(6f) in CDCl₃



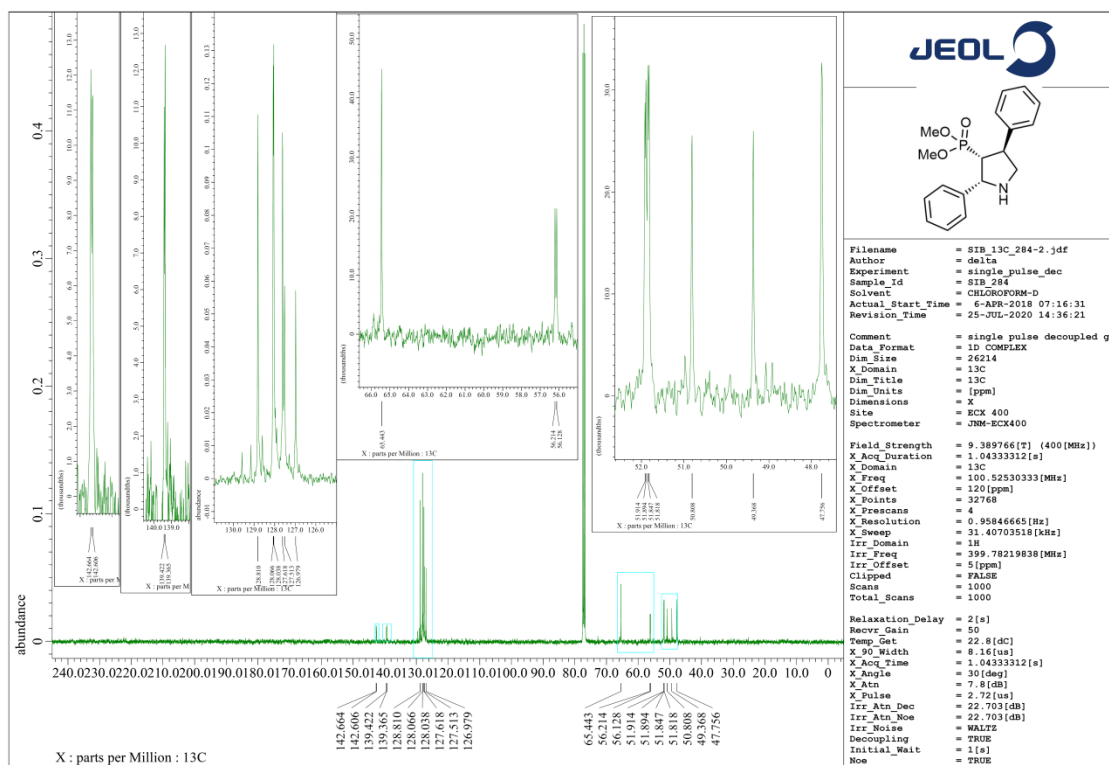
8. Copies of NMR, FTIR and mass spectra for compounds 7-14

¹H NMR spectra of dimethyl [(2*R*,3*R*,4*S*)-2,4-diphenylpyrrolidin-3-yl]phosphonate (**7**)

(crude reaction mixture) in CDCl_3

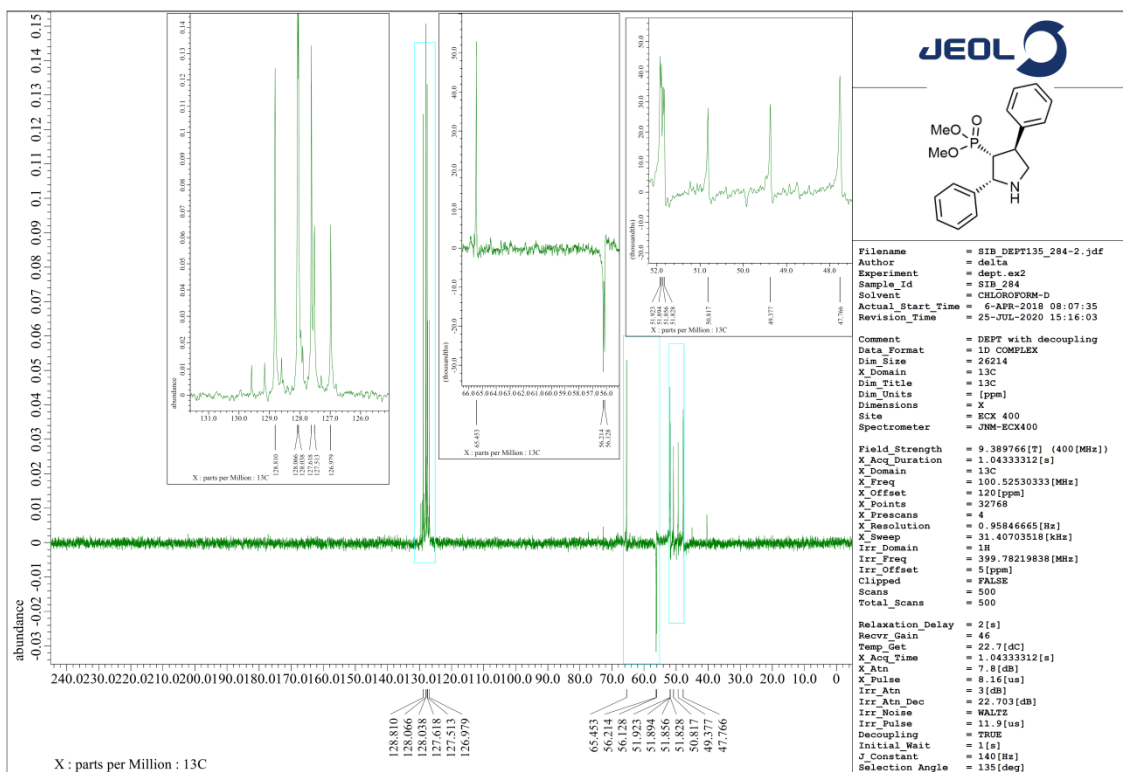
¹³C NMR spectra of dimethyl [(2*R*,3*R*,4*S*)-2,4-diphenylpyrrolidin-3-yl]phosphonate (**7**)

in CDCl_3



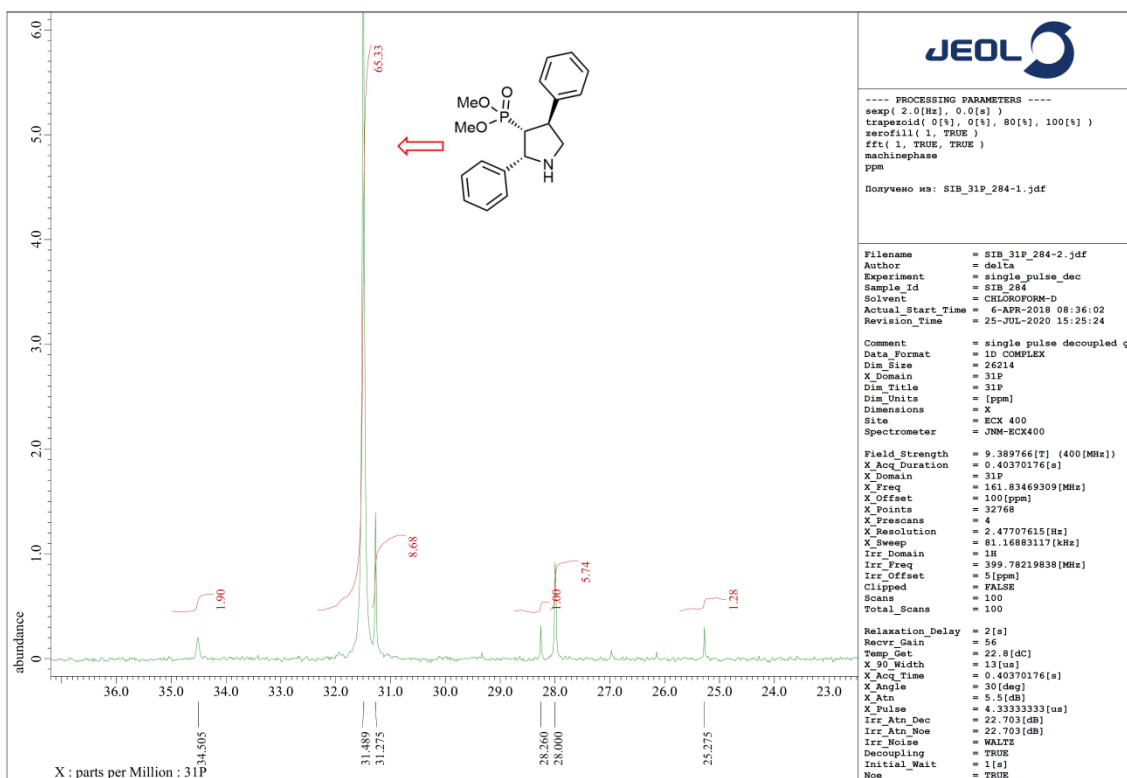
DEPT NMR spectra of dimethyl [(2*R*,3*R*,4*S*)-2,4-diphenylpyrrolidin-3-yl]phosphonate (**7**)

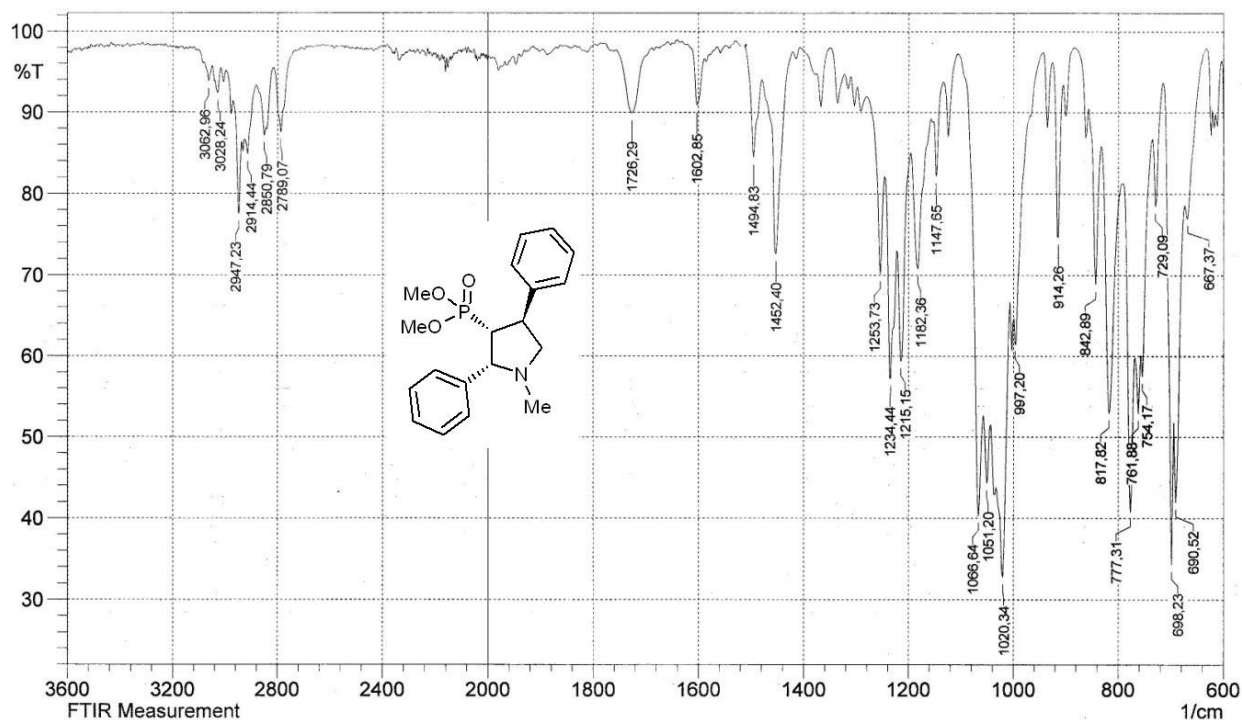
in CDCl₃



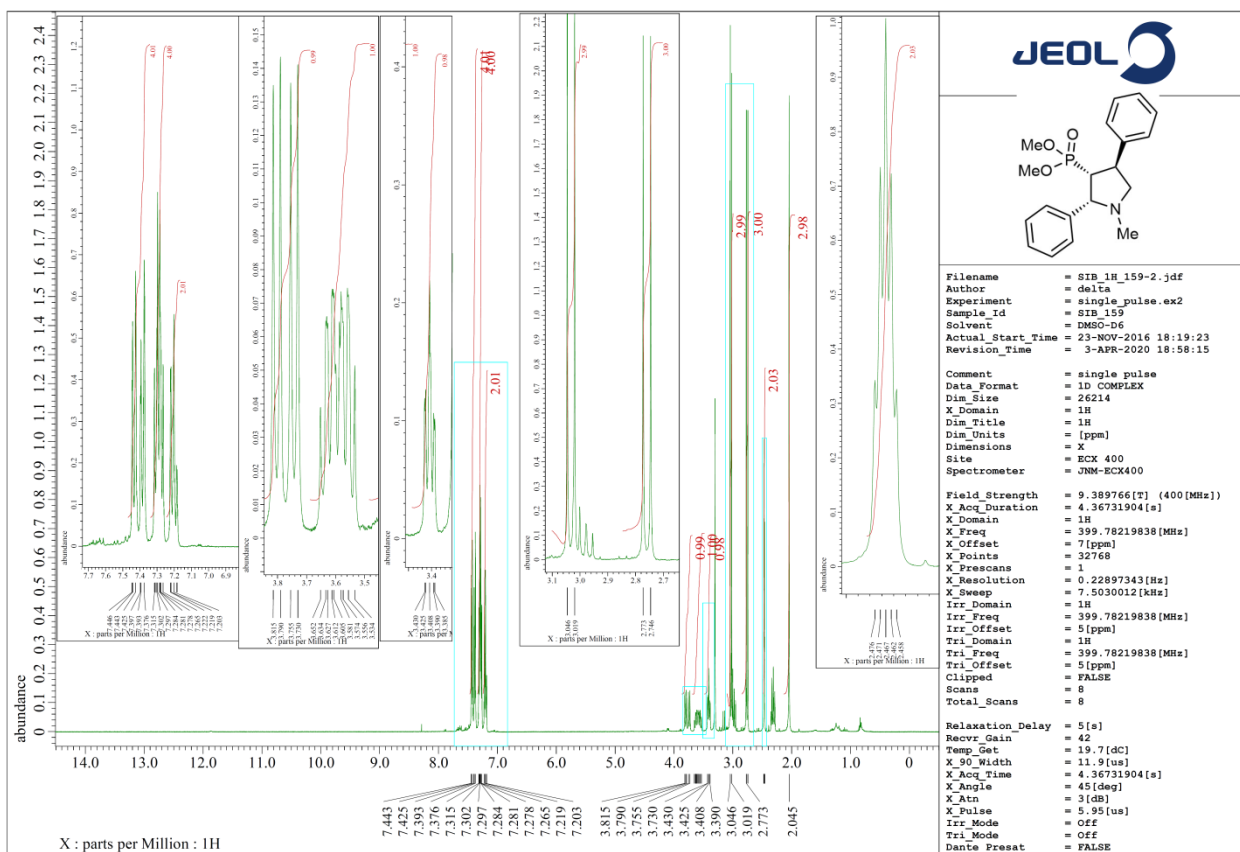
³¹P NMR spectra of dimethyl [(2*R*,3*R*,4*S*)-2,4-diphenylpyrrolidin-3-yl]phosphonate (**7**)

in CDCl₃

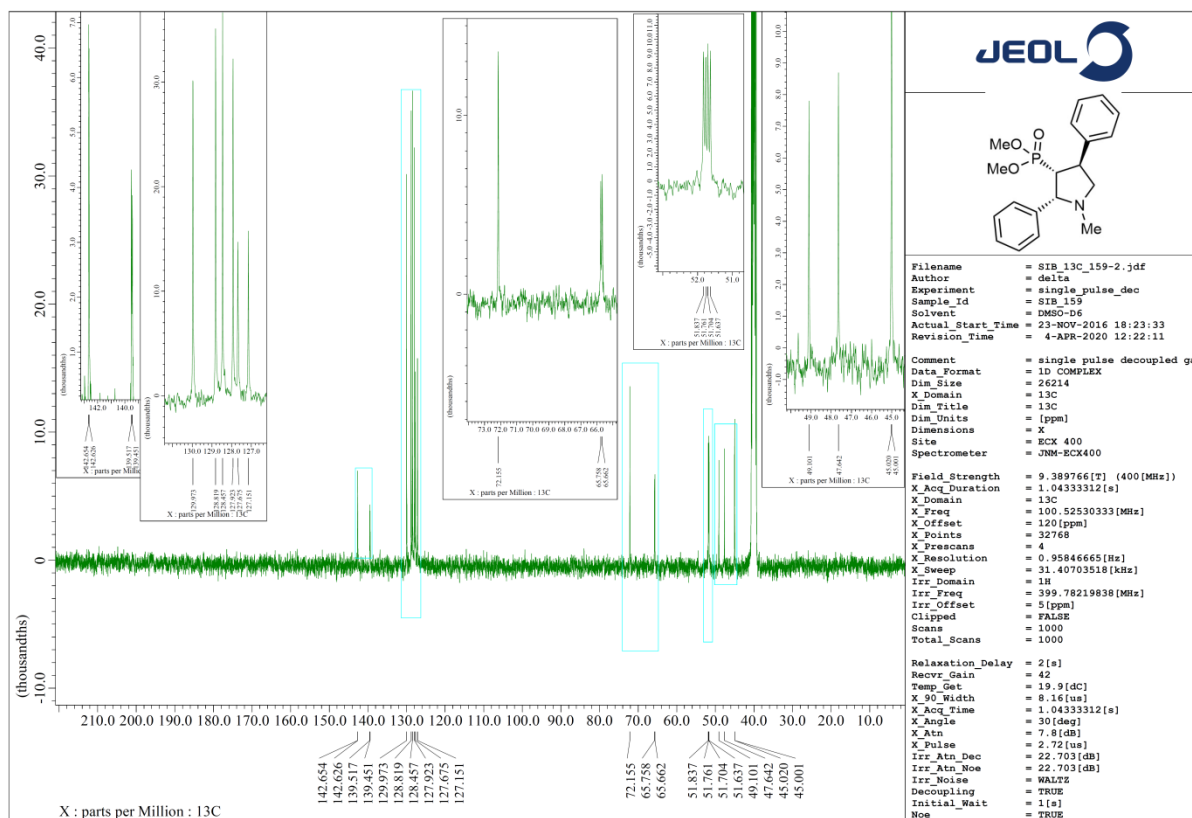


FTIR spectra of dimethyl [(2*R*,3*R*,4*S*)-1-methyl-2,4-diphenylpyrrolidin-3-yl]phosphonate (**8**)

¹H NMR spectra of dimethyl [(2*R*,3*R*,4*S*)-1-methyl-2,4-diphenylpyrrolidin-3-yl]phosphonate (**8**)

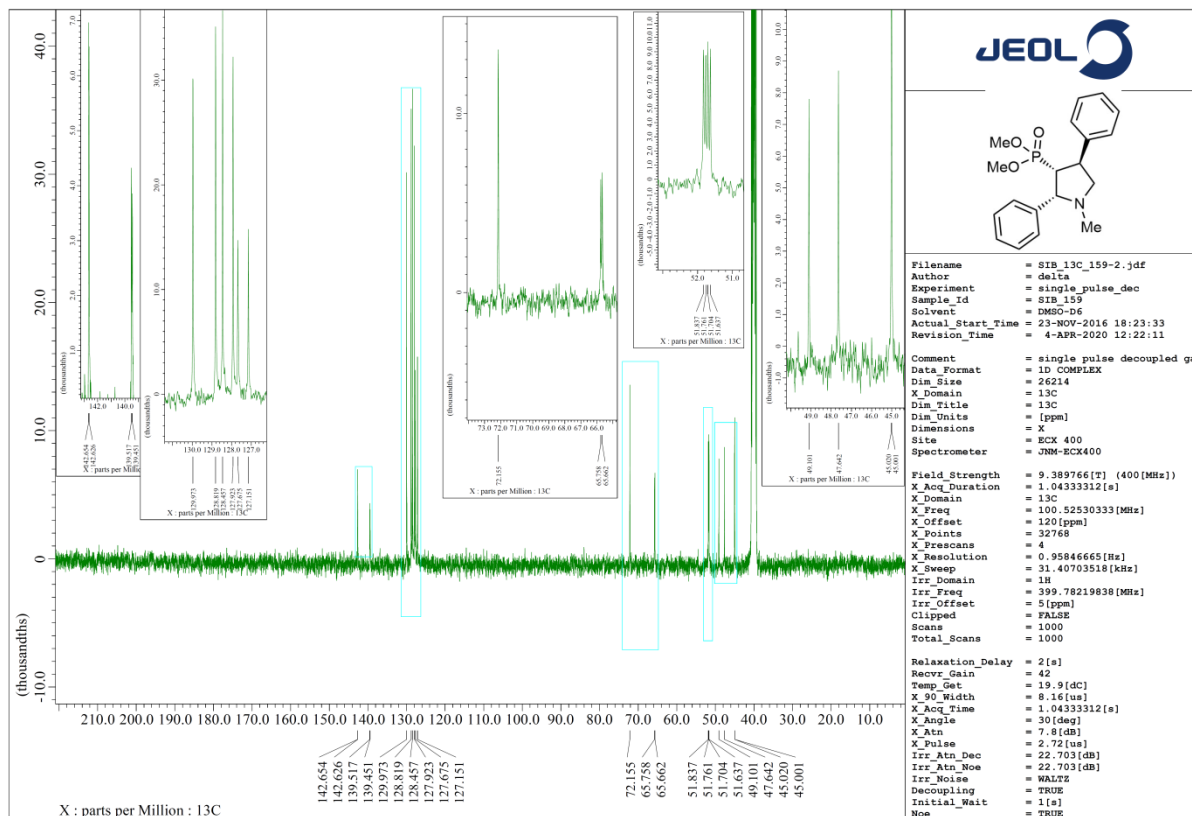
in DMSO-d⁶

¹³C NMR spectra of dimethyl [(2*R*,3*R*,4*S*)-1-methyl-2,4-diphenylpyrrolidin-3-yl]phosphonate (**8**)
in DMSO-d₆

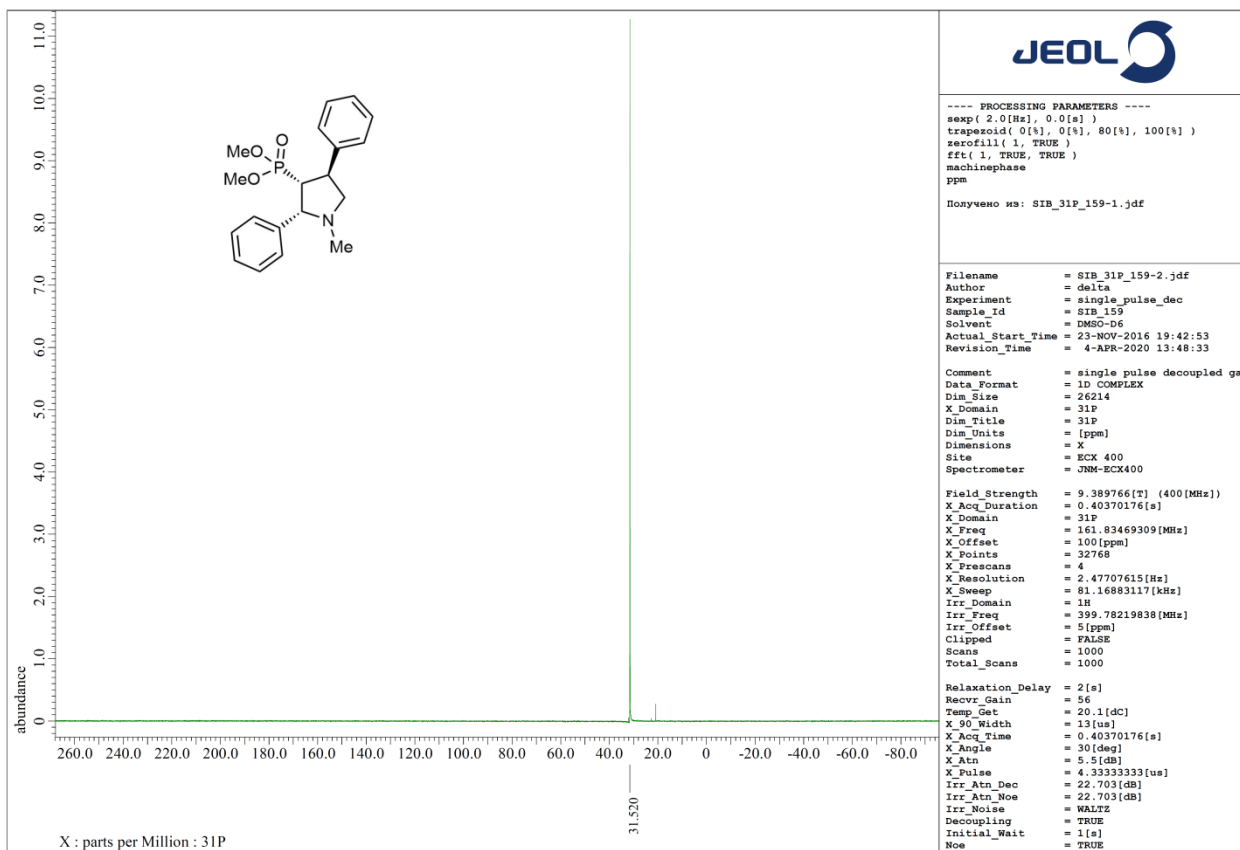


DEPT NMR spectra of dimethyl [(2*R*,3*R*,4*S*)-1-methyl-2,4-diphenylpyrrolidin-3-yl]phosphonate (**8**)

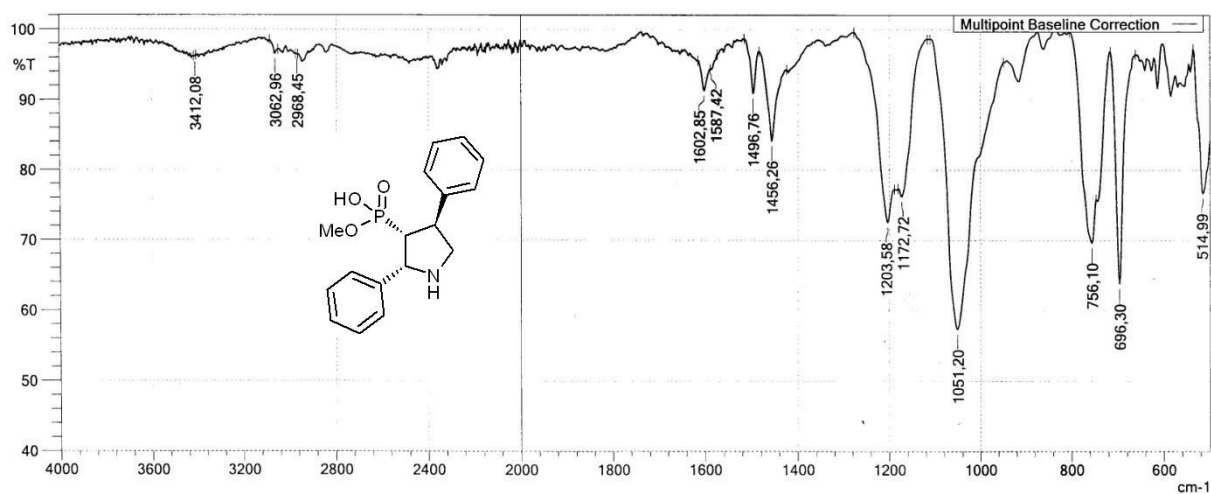
In DMSO-d₆



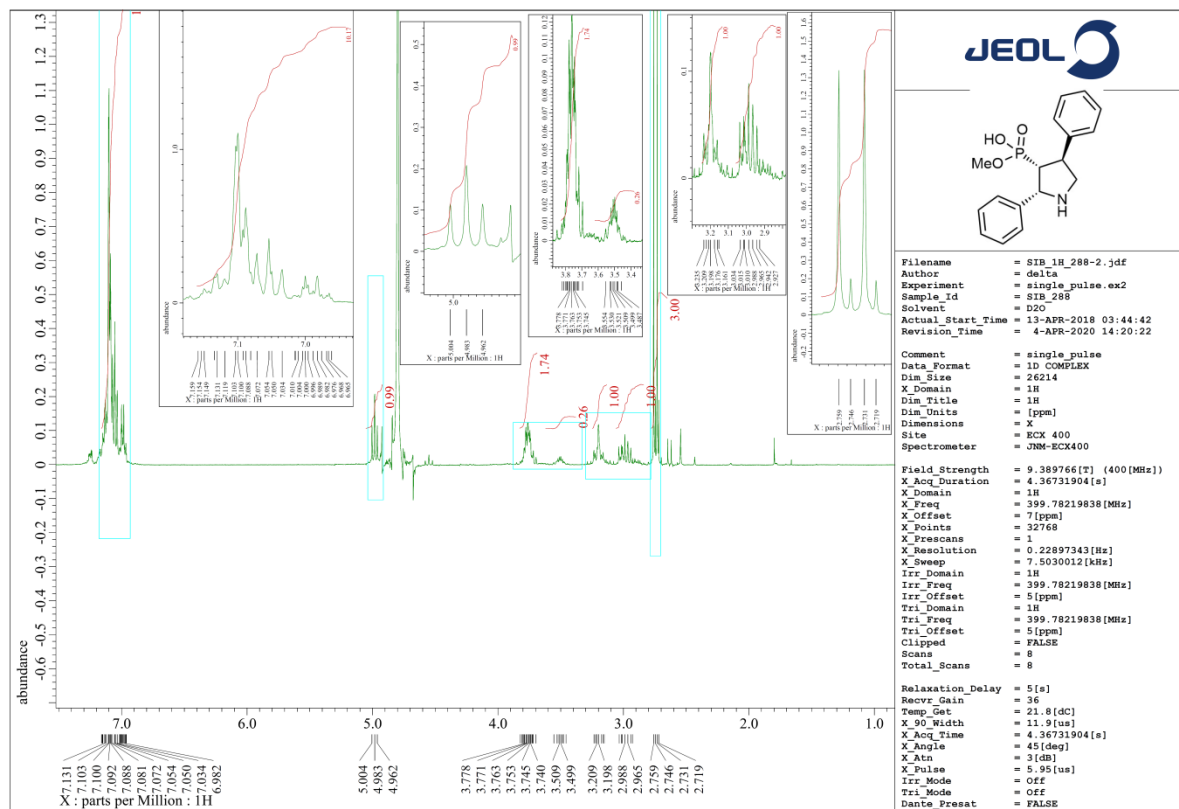
³¹P NMR spectra of dimethyl [(2*R*,3*R*,4*S*)-1-methyl-2,4-diphenylpyrrolidin-3-yl]phosphonate (**8**)
in DMSO-*d*⁶



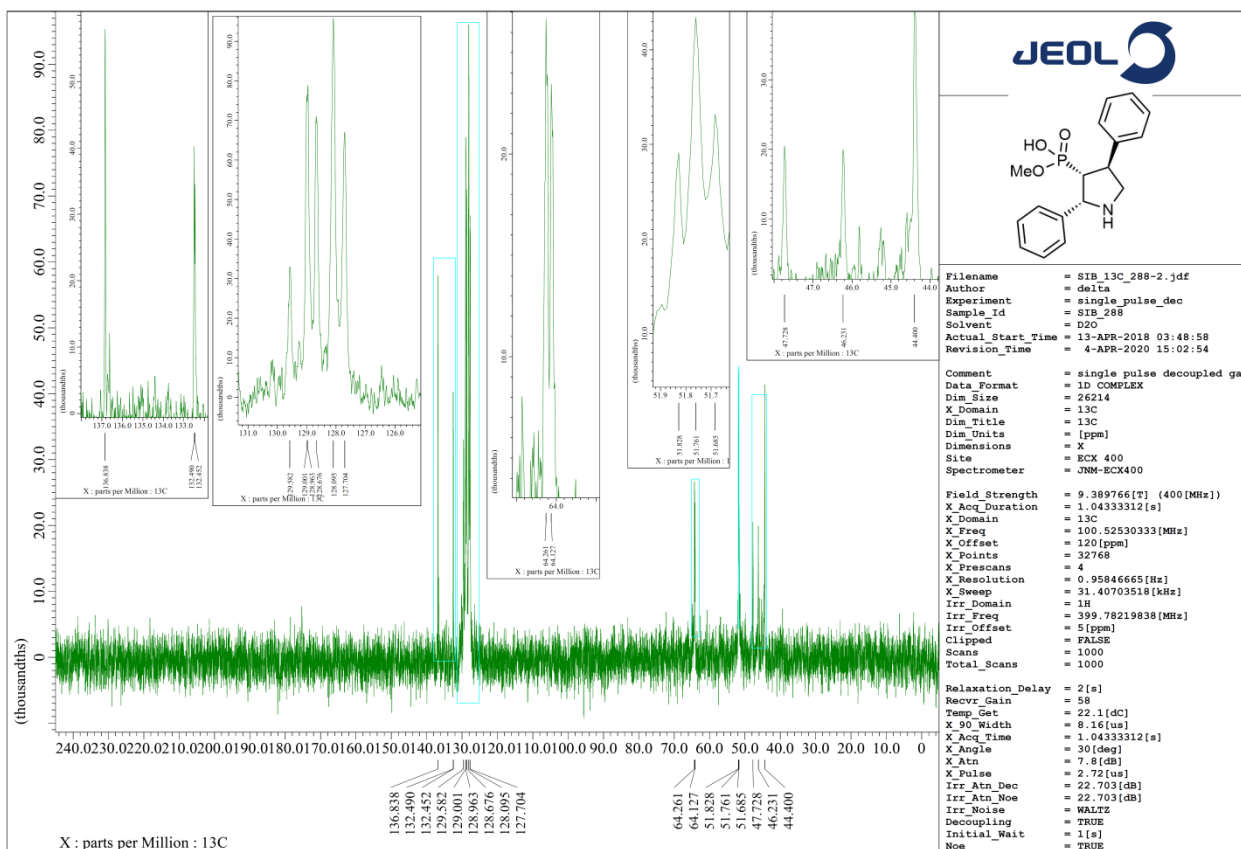
FTIR spectra of methyl hydrogen ((2*R*,3*R*,4*S*)-2,4-diphenylpyrrolidin-3-yl)phosphonate (**9**)



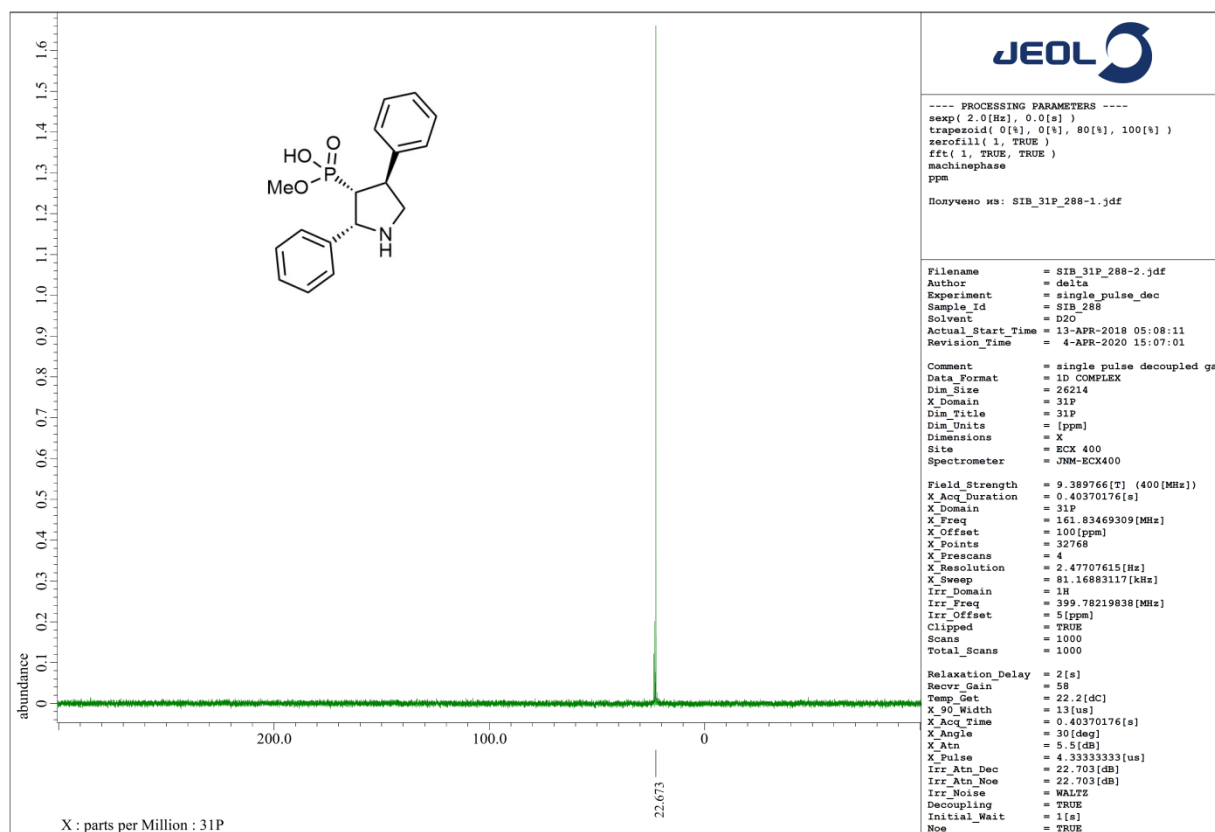
¹H NMR spectra of methyl hydrogen ((2*R*,3*R*,4*S*)-2,4-diphenylpyrrolidin-3-yl)phosphonate (**9**) in D₂O



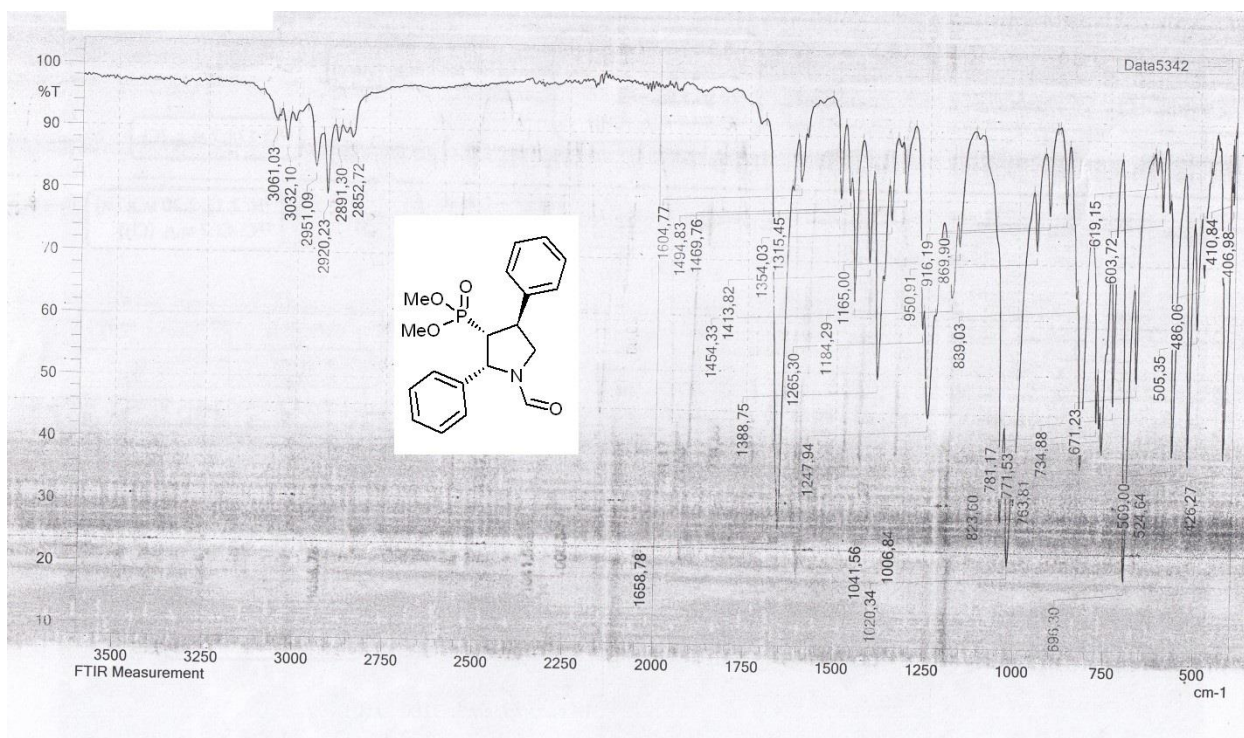
¹³C NMR spectra of methyl hydrogen ((2*R*,3*R*,4*S*)-2,4-diphenylpyrrolidin-3-yl)phosphonate (**9**) in D₂O



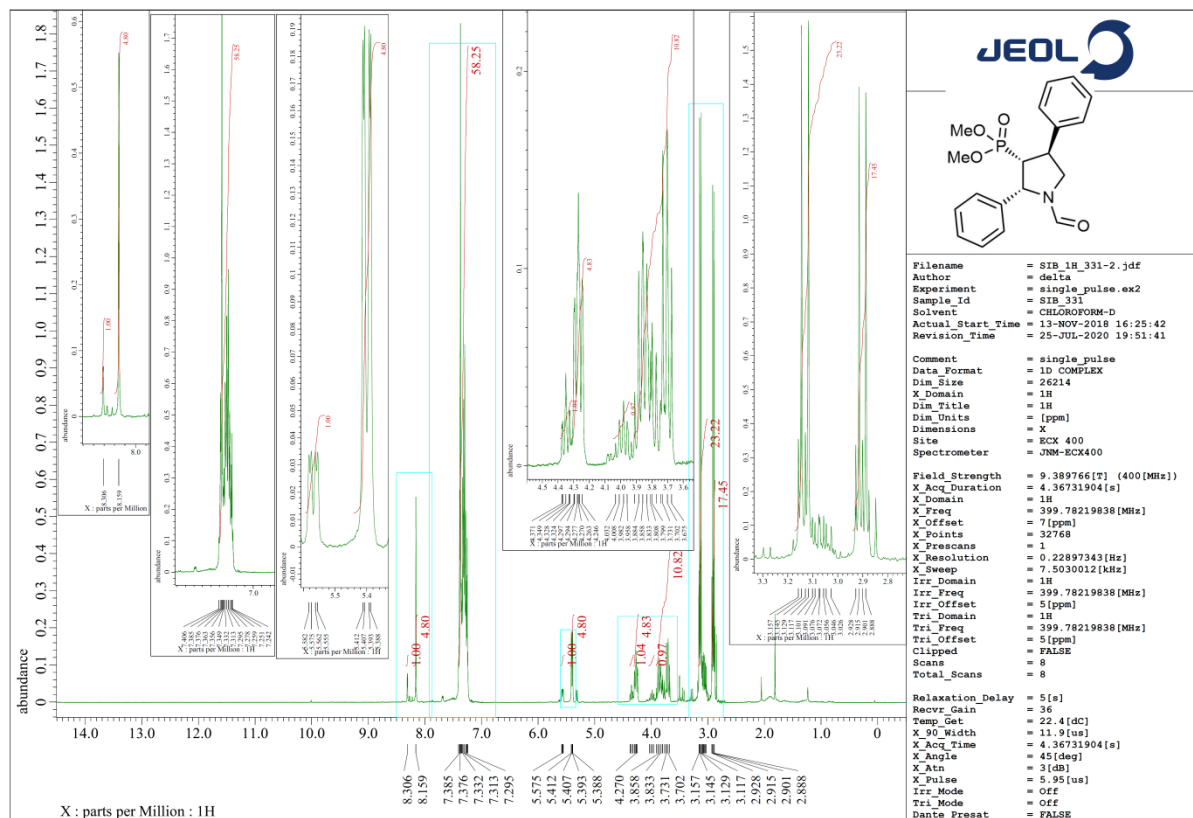
³¹P NMR spectra of methyl hydrogen ((2*R*,3*R*,4*S*)-2,4-diphenylpyrrolidin-3-yl)phosphonate (**9**) in D₂O



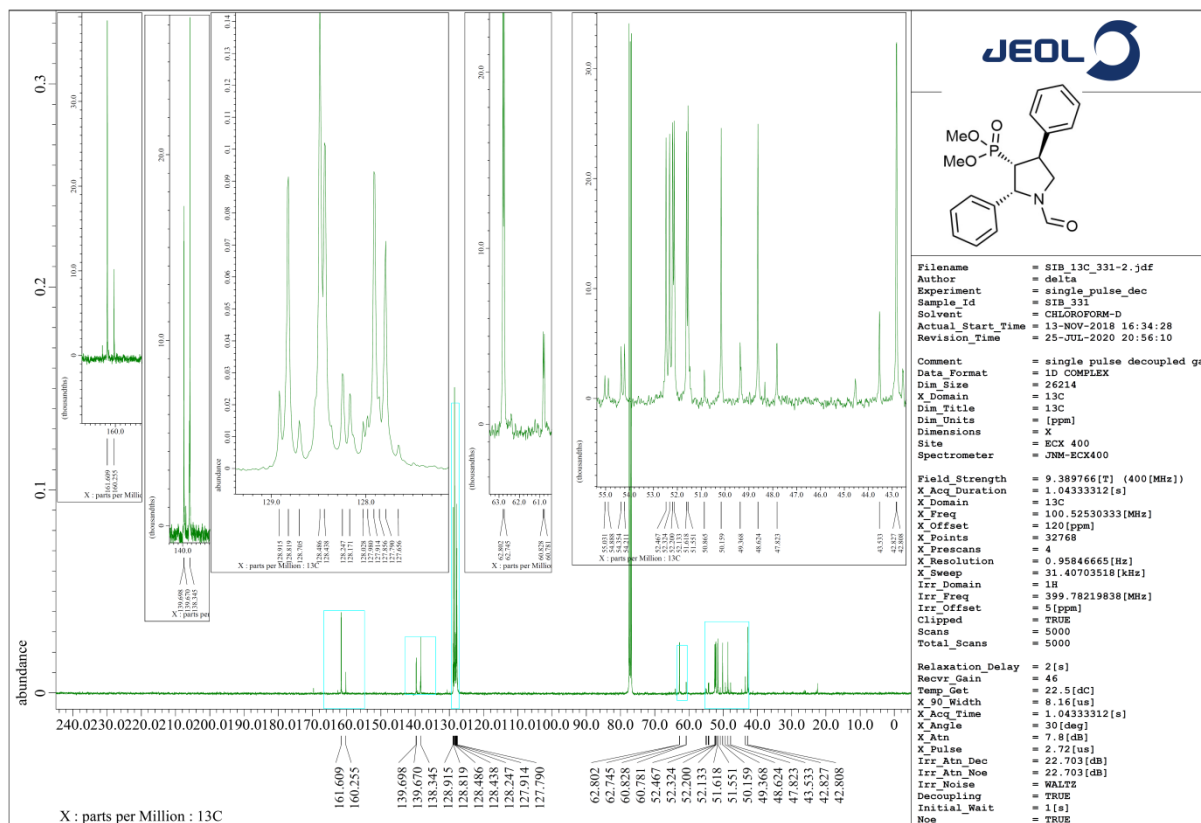
FTIR spectra of dimethyl [(2*R*,3*R*,4*S*)-1-formyl-2,4-diphenylpyrrolidin-3-yl]phosphonate (**10a**)



¹H NMR spectra of dimethyl [(2*R*,3*R*,4*S*)-1-formyl-2,4-diphenylpyrrolidin-3-yl]phosphonate (**10a**) in CDCl₃

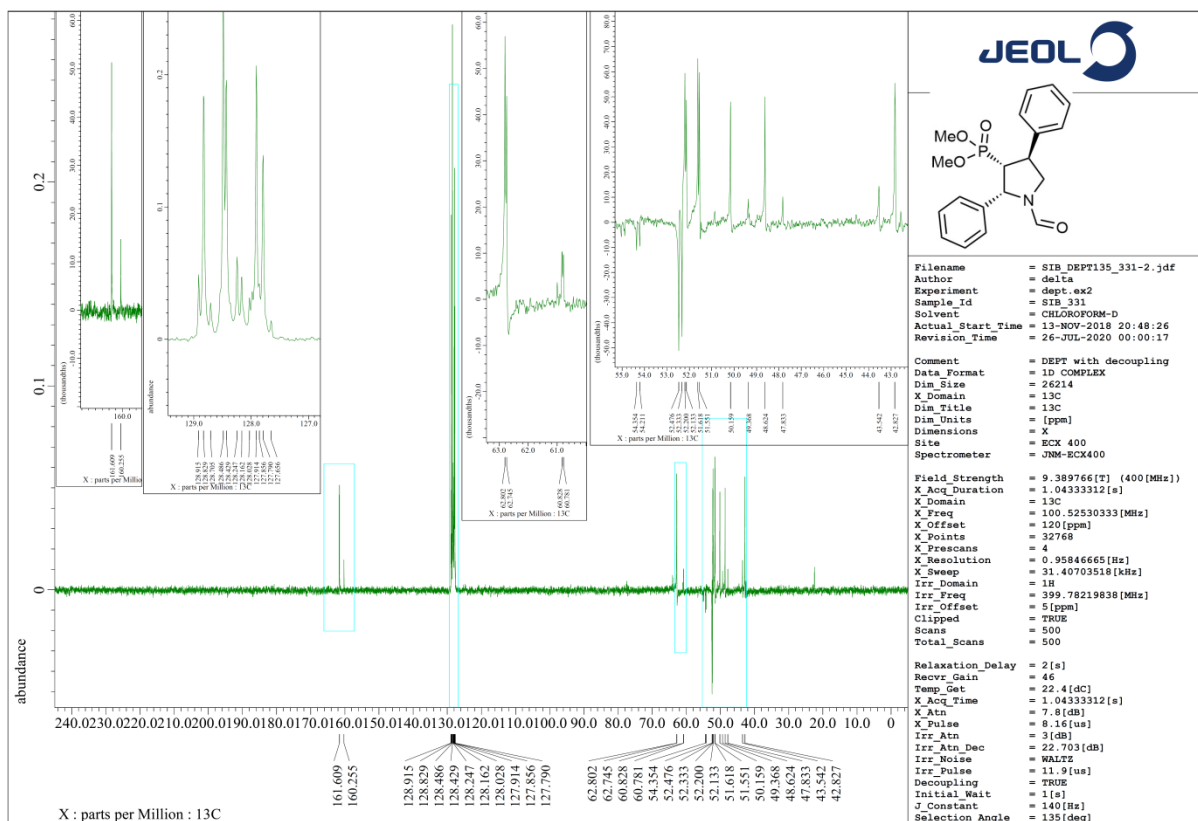


¹³C NMR spectra of dimethyl [(2*R*,3*R*,4*S*)-1-formyl-2,4-diphenylpyrrolidin-3-yl]phosphonate (**10a**) in CDCl₃

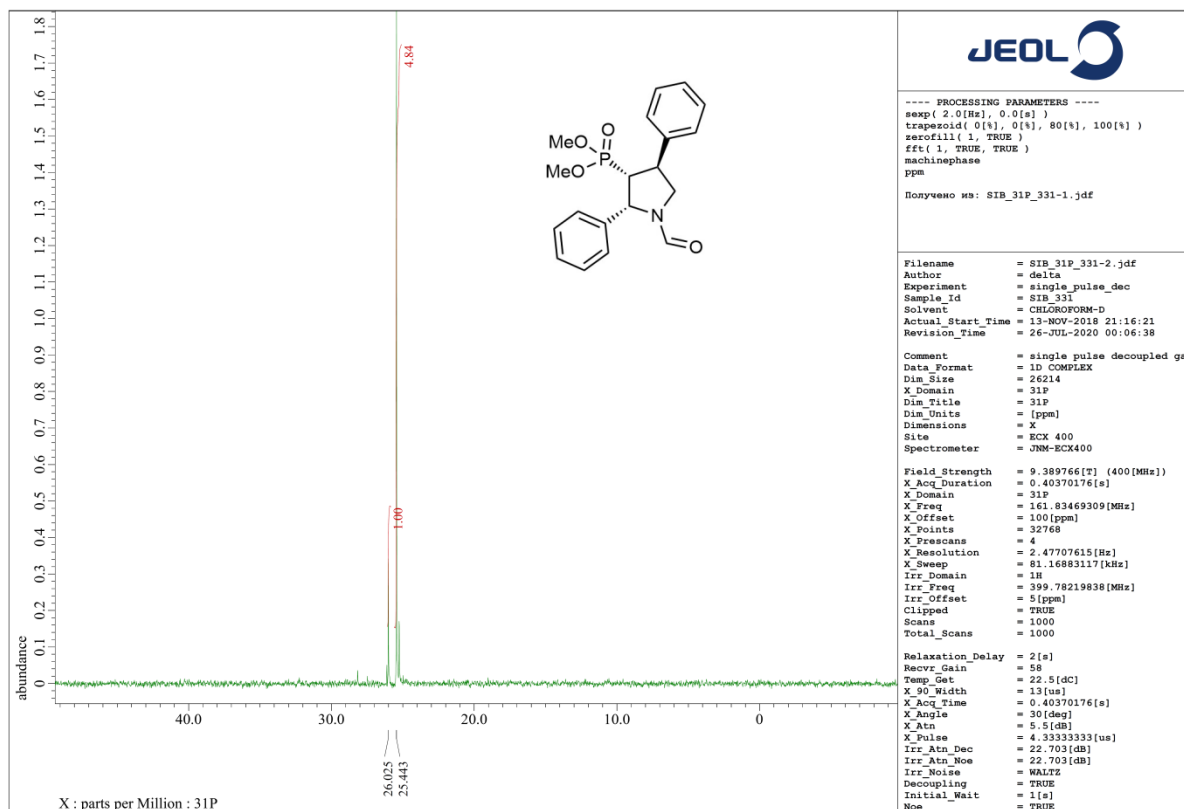


DEPT NMR spectra of dimethyl [(2*R*,3*R*,4*S*)-1-formyl-2,4-diphenylpyrrolidin-3-yl]phosphonate (**10a**) in

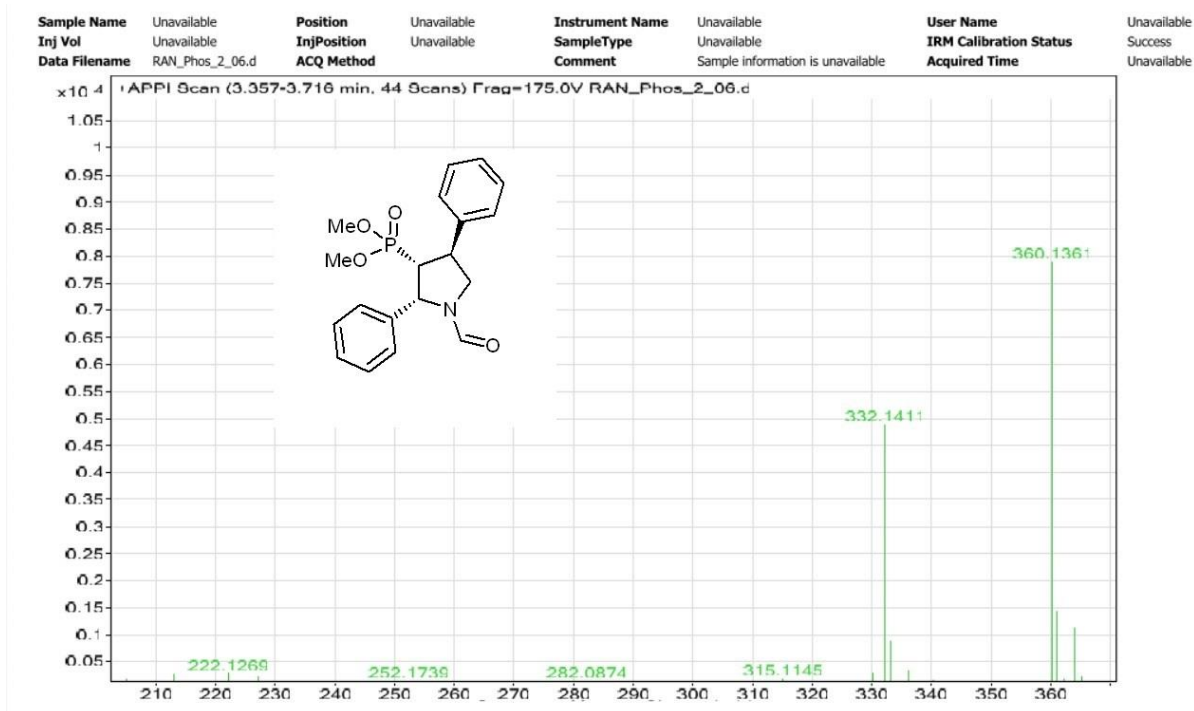
CDCl₃



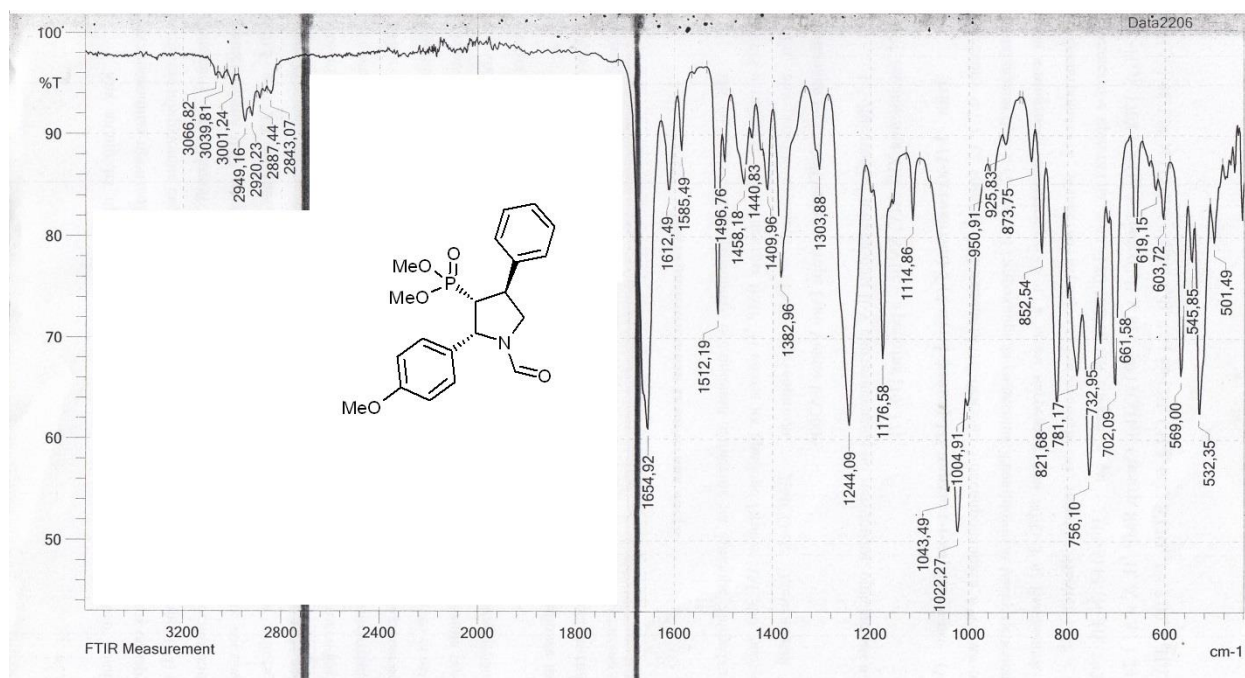
³¹P NMR spectra of dimethyl [(2*R*,3*R*,4*S*)-1-formyl-2,4-diphenylpyrrolidin-3-yl]phosphonate (**10a**) in CDCl₃



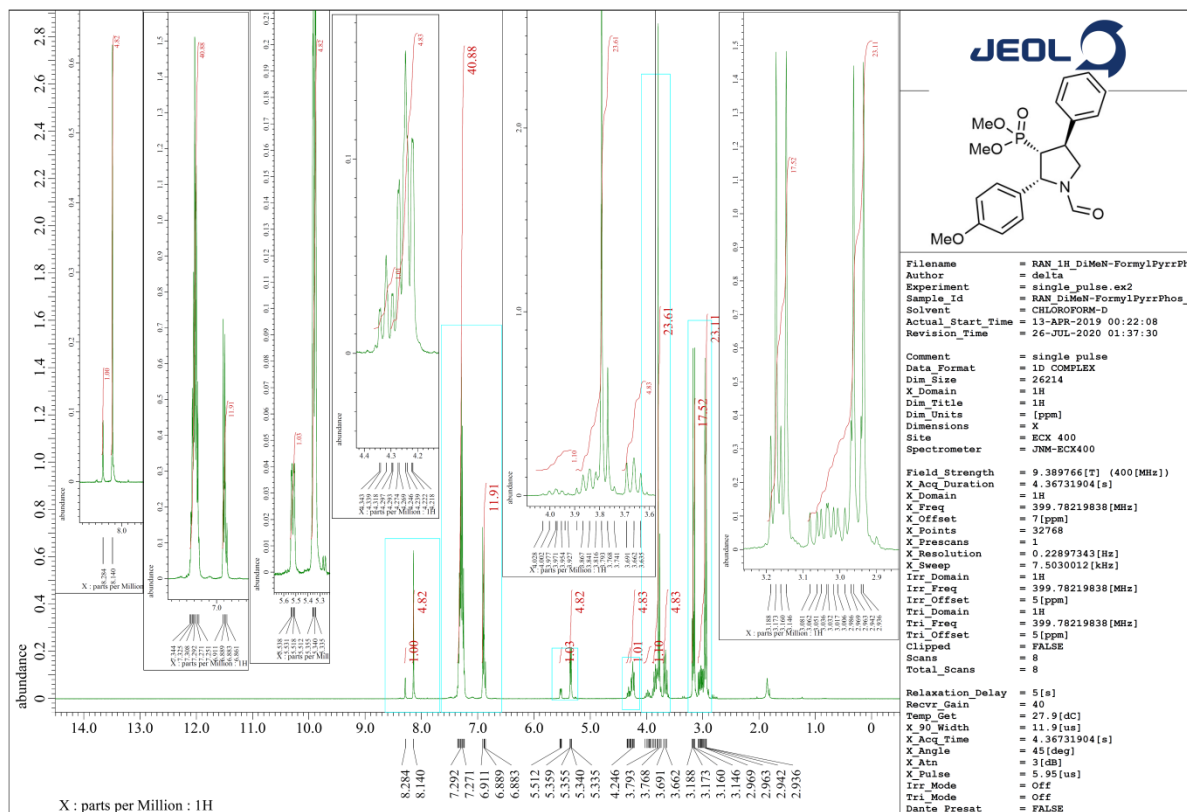
HRMS of dimethyl [(2*R*,3*R*,4*S*)-1-formyl-2,4-diphenylpyrrolidin-3-yl]phosphonate (**10a**)



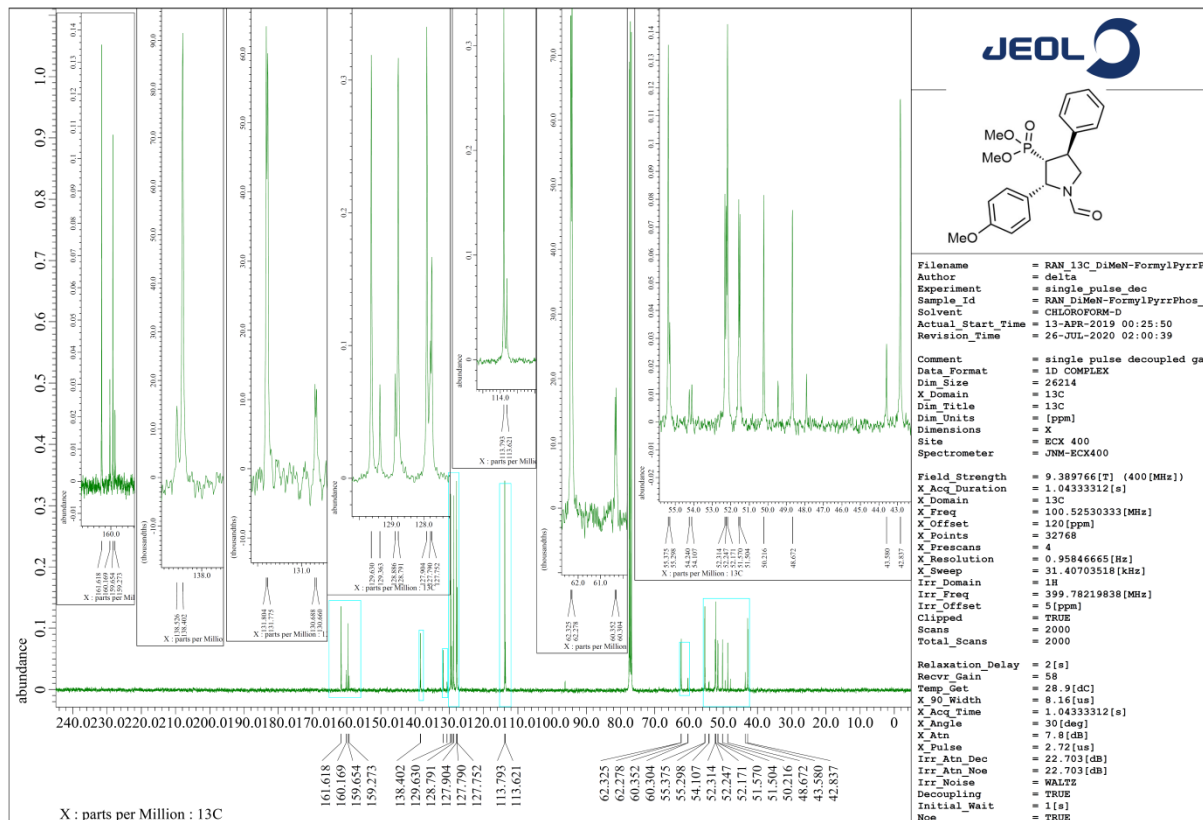
FTIR spectra of dimethyl [(2*R*,3*R*,4*S*)-1-formyl-2-(4-methoxyphenyl)-4-phenylpyrrolidin-3-yl]-phosphonate (**10b**)



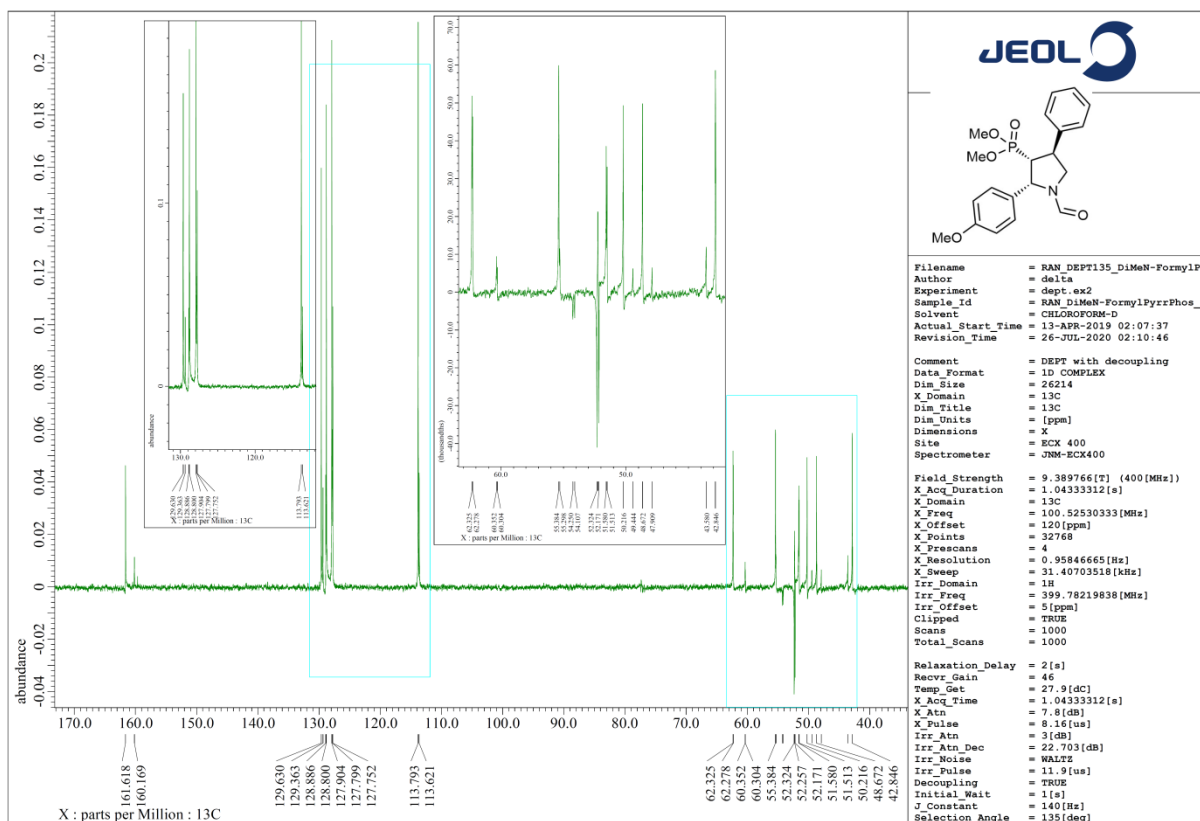
¹H NMR spectra of dimethyl [(2*R*,3*R*,4*S*)-1-formyl-2-(4-methoxyphenyl)-4-phenylpyrrolidin-3-yl]-phosphonate (**10b**) in CDCl₃



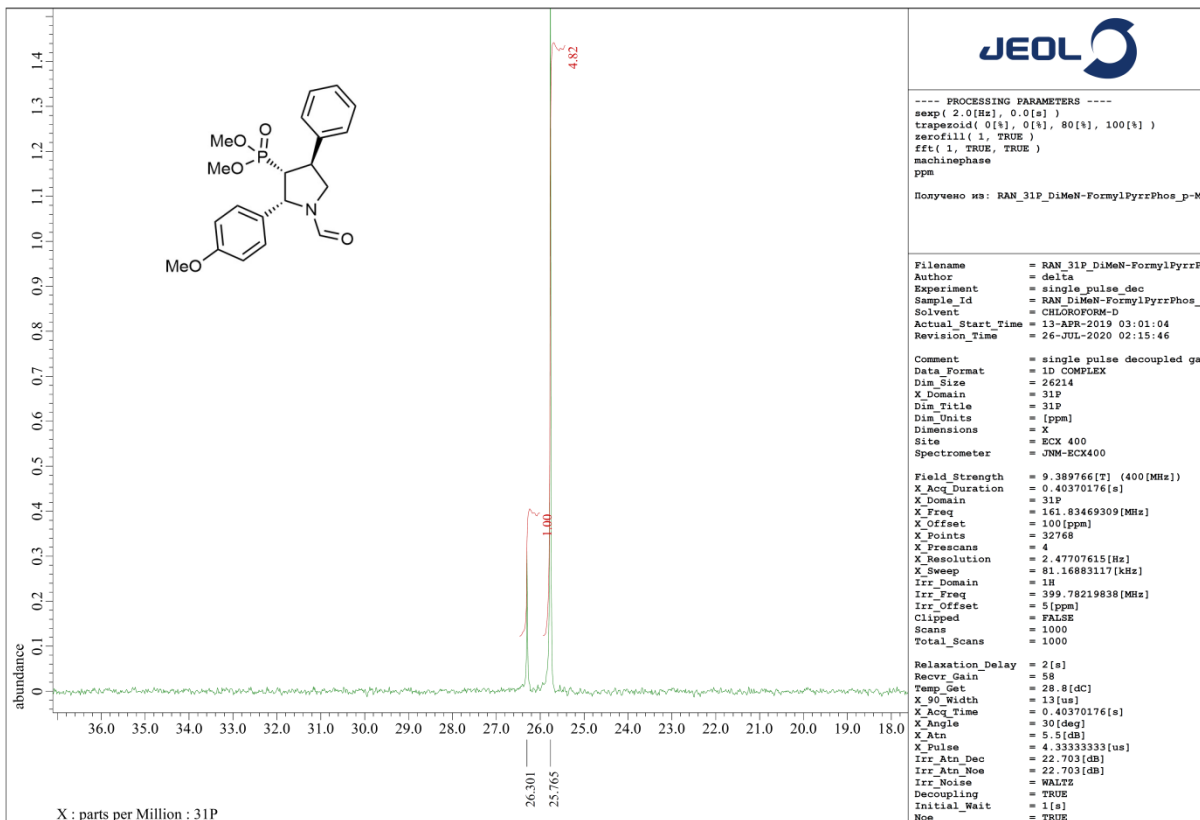
¹³C NMR spectra of dimethyl [(2*R*,3*R*,4*S*)-1-formyl-2-(4-methoxyphenyl)-4-phenylpyrrolidin-3-yl]-phosphonate (**10b**) in CDCl₃



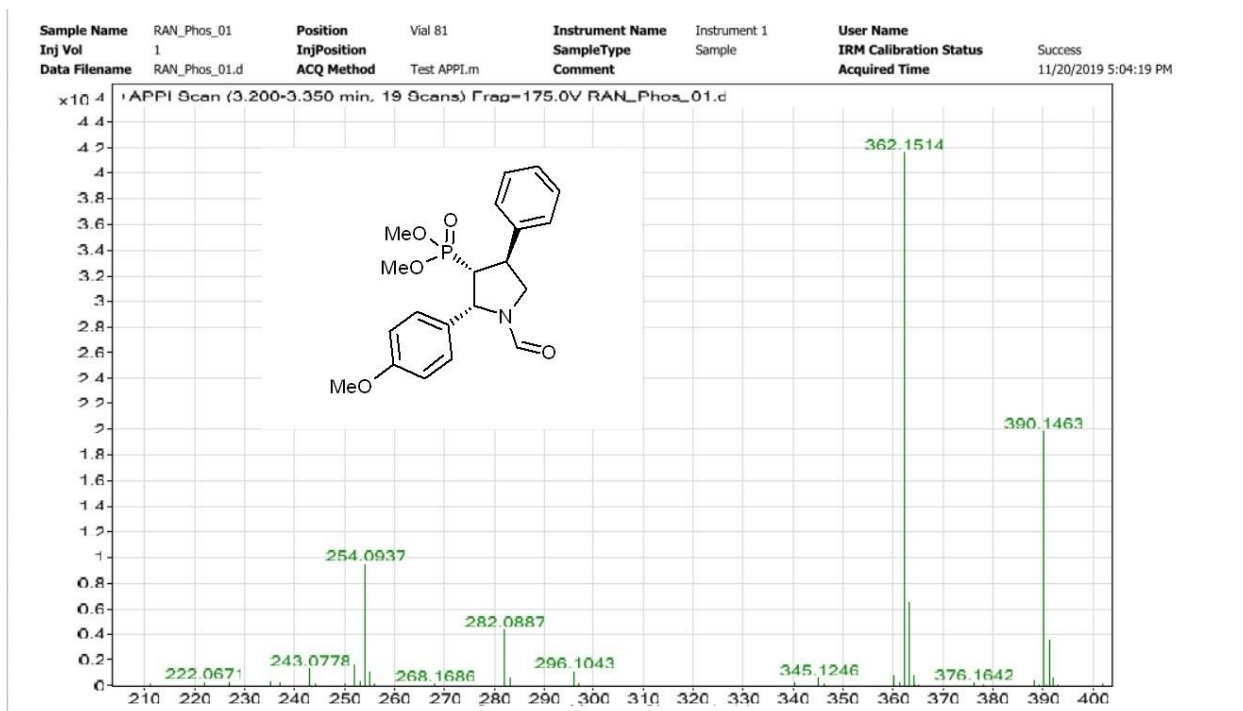
DEPT NMR spectra of dimethyl [(2*R*,3*R*,4*S*)-1-formyl-2-(4-methoxyphenyl)-4-phenylpyrrolidin-3-yl]-
phosphonate (**10b**) in CDCl₃



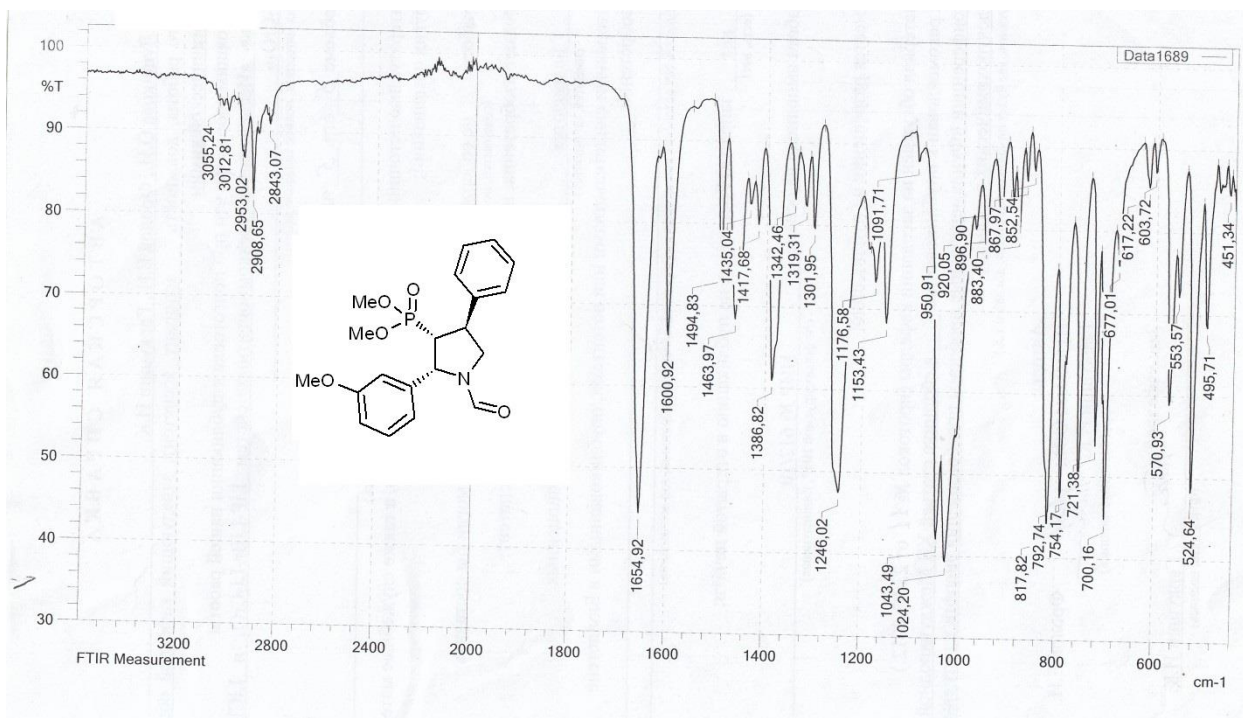
³¹P NMR spectra of dimethyl [(2*R*,3*R*,4*S*)-1-formyl-2-(4-methoxyphenyl)-4-phenylpyrrolidin-3-yl]-
phosphonate (**10b**) in CDCl₃



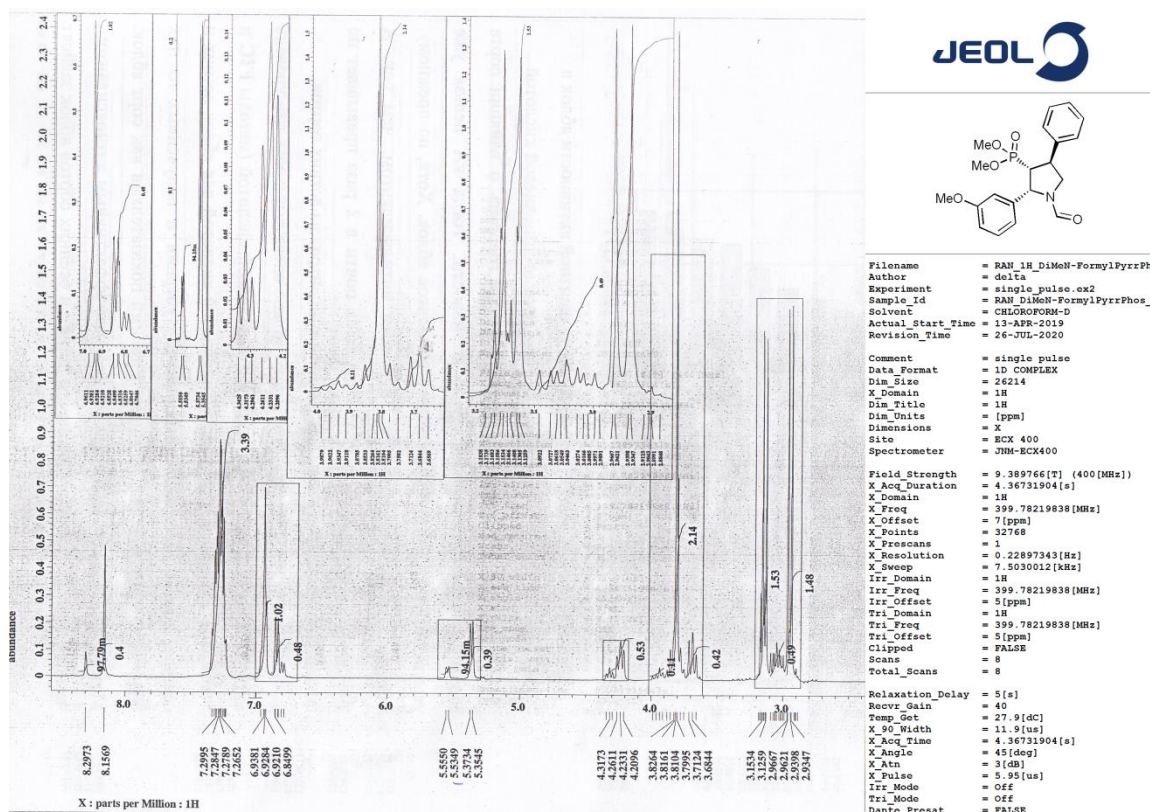
HRMS of dimethyl [(2*R*,3*R*,4*S*)-1-formyl-2-(4-methoxyphenyl)-4-phenylpyrrolidin-3-yl]-phosphonate (**10b**)



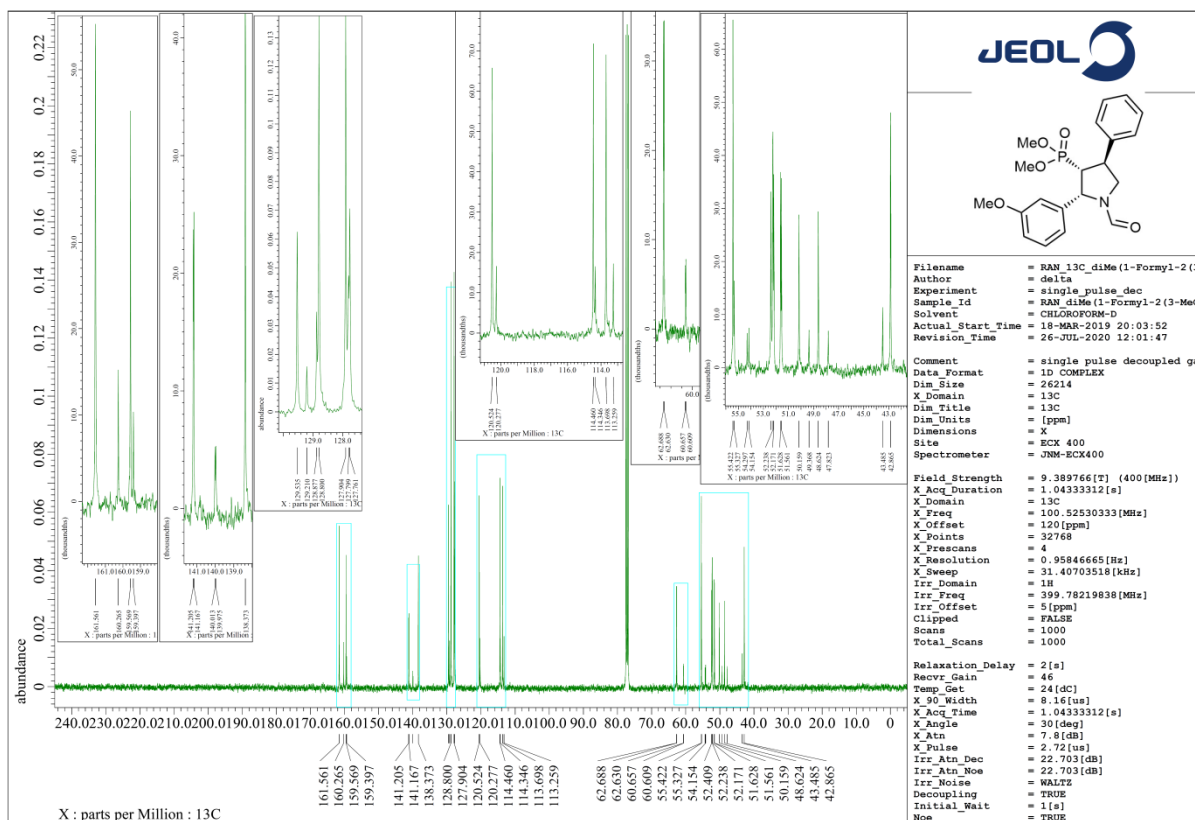
FTIR spectra of dimethyl [(2*R*,3*R*,4*S*)-1-formyl-2-(3-methoxyphenyl)-4-phenylpyrrolidin-3-yl]-phosphonate (**10c**)



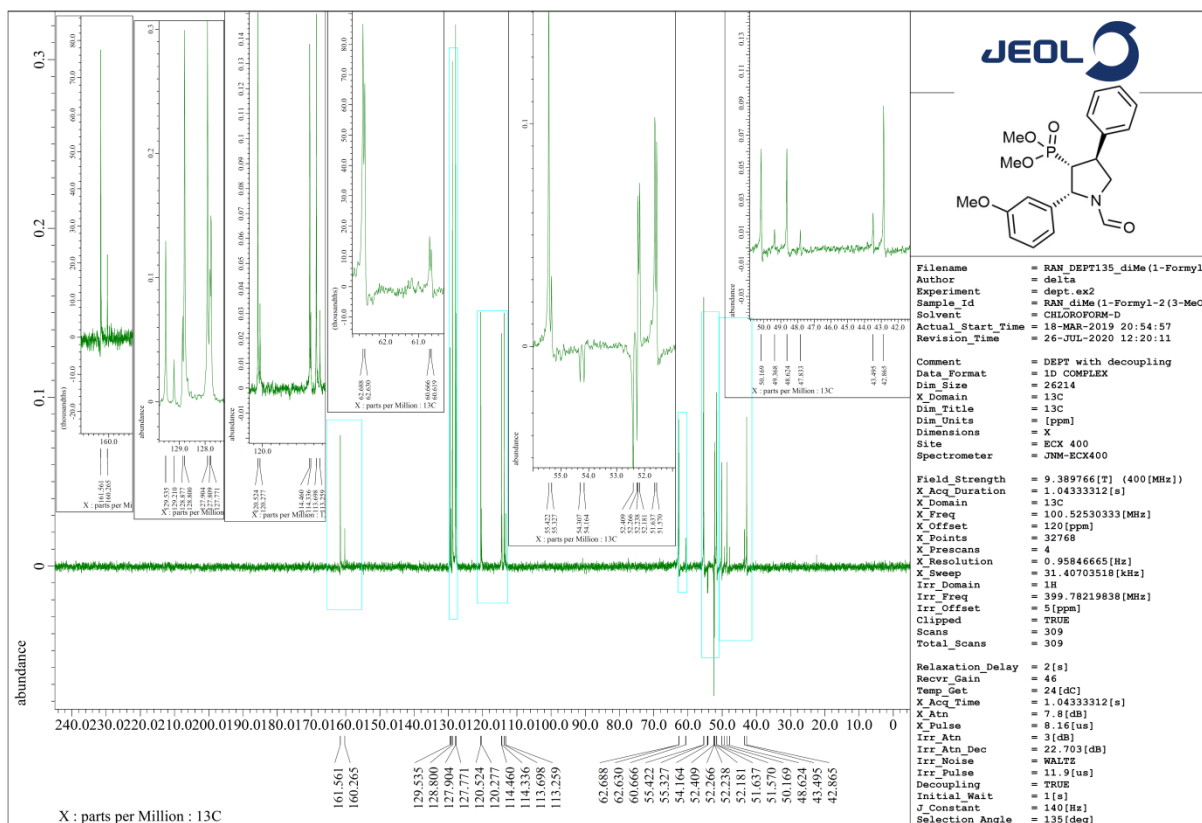
¹H NMR spectra of dimethyl [(2*R*,3*R*,4*S*)-1-formyl-2-(3-methoxyphenyl)-4-phenylpyrrolidin-3-yl]-phosphonate (**10c**) in CDCl₃



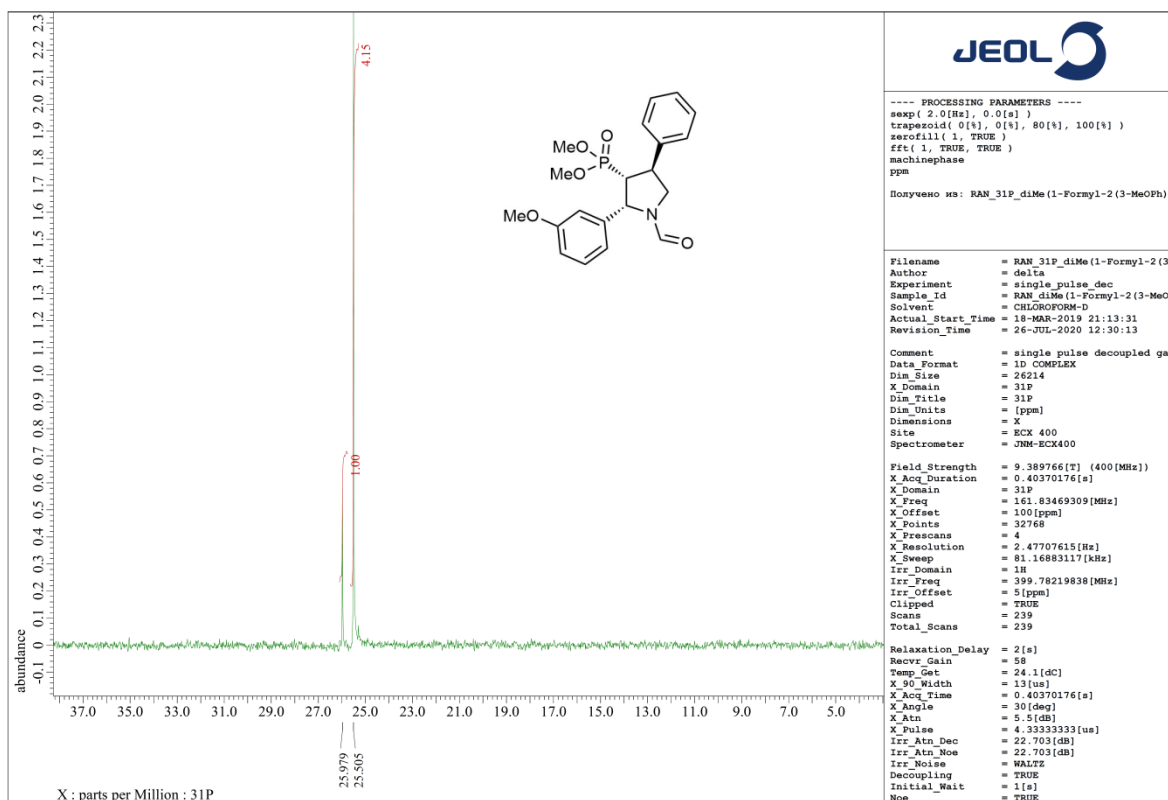
¹³C NMR spectra of dimethyl [(2*R*,3*R*,4*S*)-1-formyl-2-(3-methoxyphenyl)-4-phenylpyrrolidin-3-yl]-phosphonate (**10c**) in CDCl₃



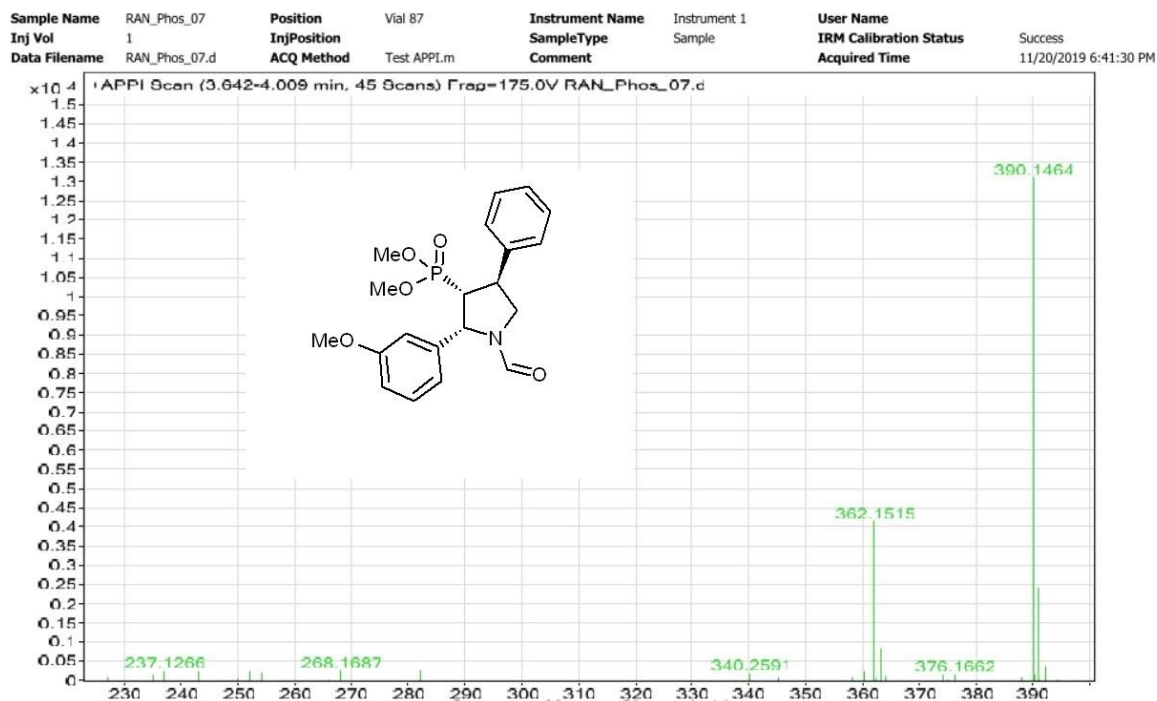
DEPT NMR spectra of dimethyl [(2*R*,3*R*,4*S*)-1-formyl-2-(3-methoxyphenyl)-4-phenylpyrrolidin-3-yl]-phosphonate (**10c**) in CDCl₃



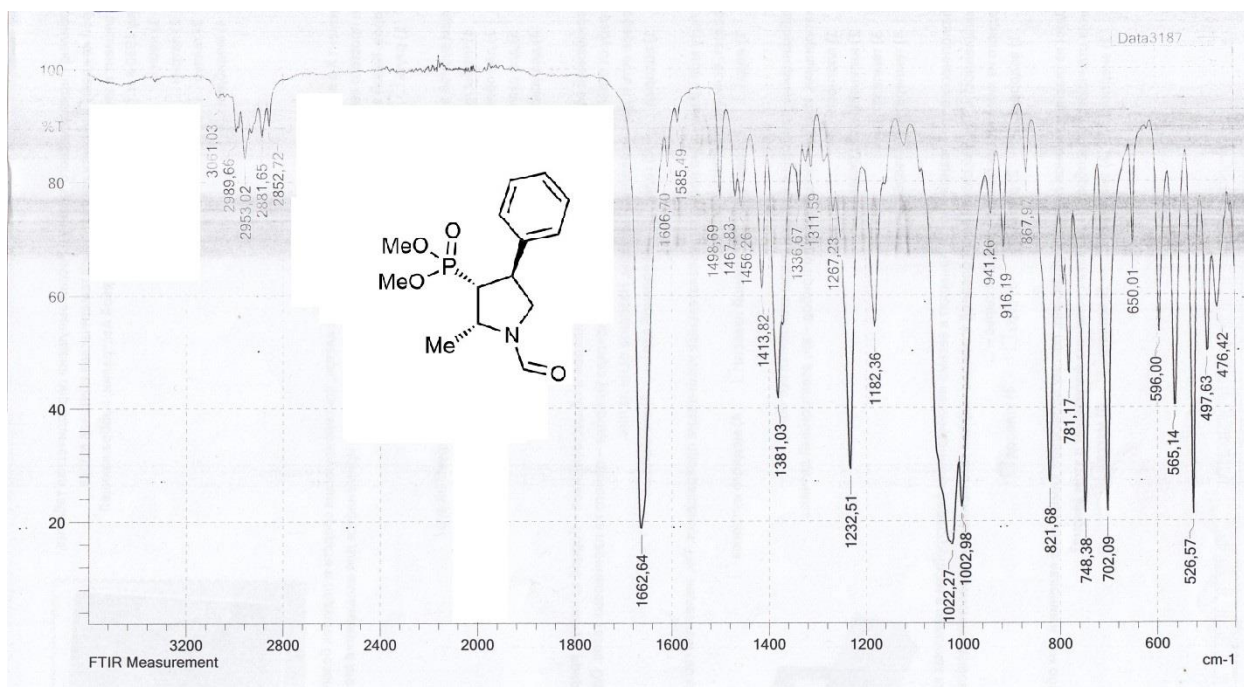
³¹P NMR spectra of dimethyl [(2*R*,3*R*,4*S*)-1-formyl-2-(3-methoxyphenyl)-4-phenylpyrrolidin-3-yl]-phosphonate (**10c**) in CDCl₃



HRMS of dimethyl [(2*R*,3*R*,4*S*)-1-formyl-2-(3-methoxyphenyl)-4-phenylpyrrolidin-3-yl]-phosphonate (**10c**)

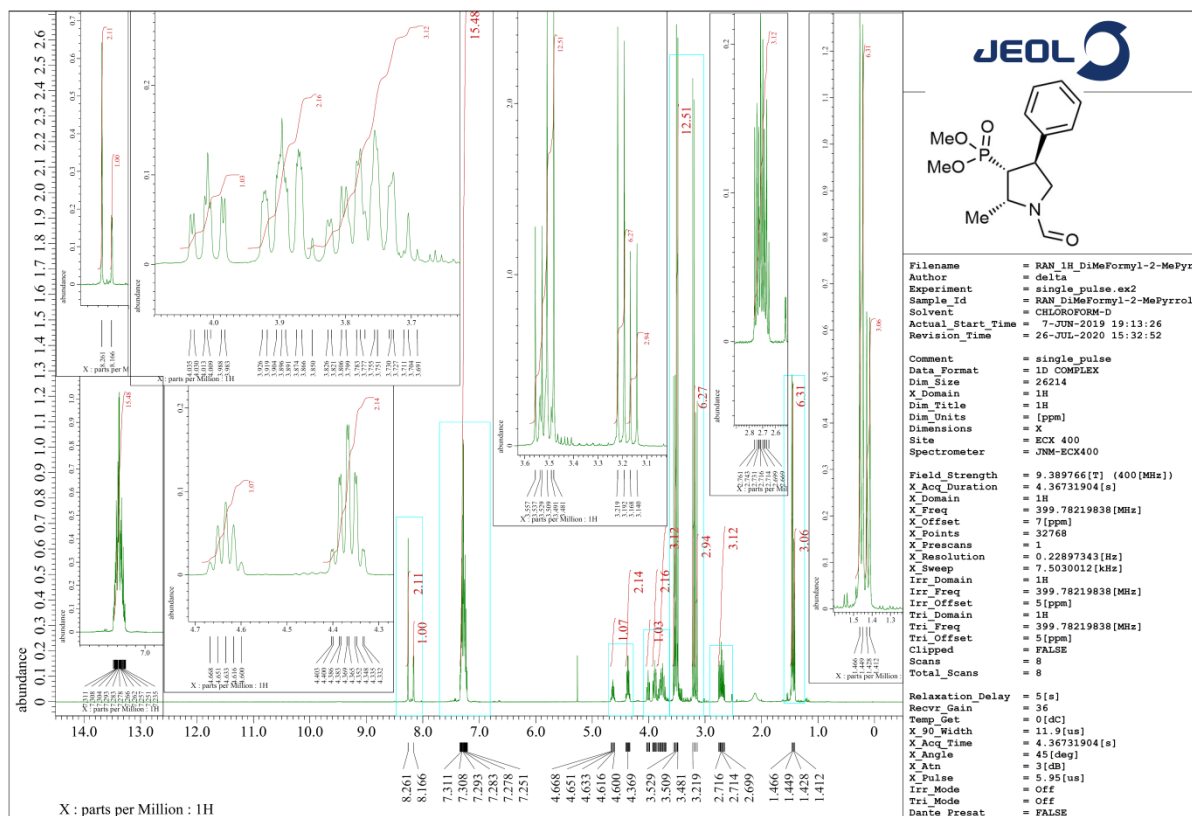


FTIR spectra of dimethyl [(2*R*,3*R*,4*S*)-1-formyl-2-methyl-4-phenylpyrrolidin-3-yl]phosphonate (**10d**)



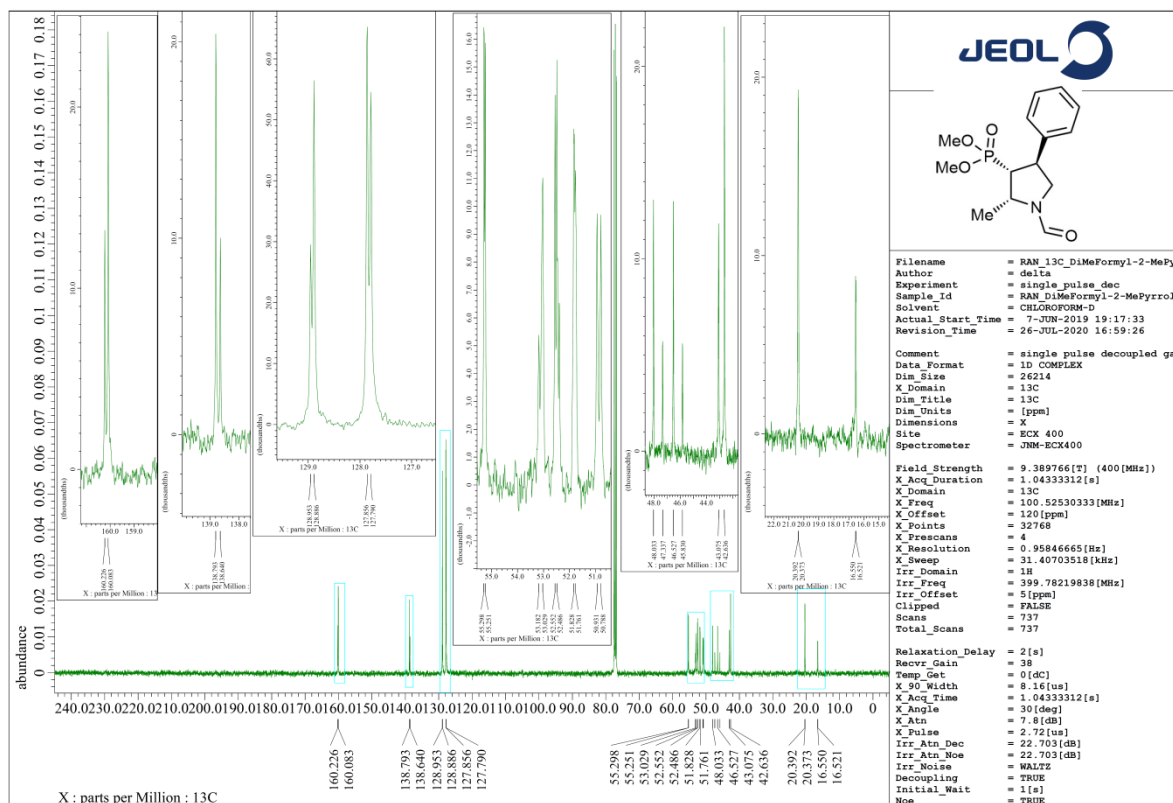
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CDCl₃



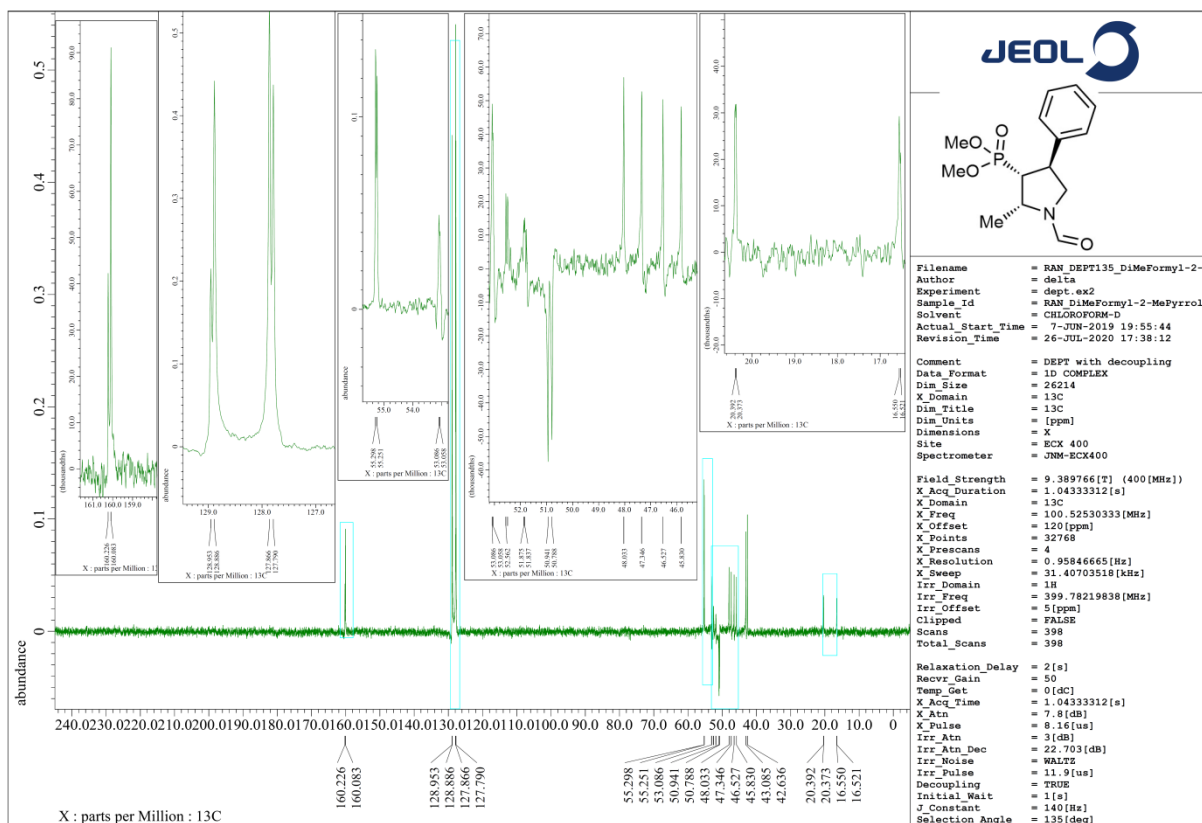
¹³C NMR spectra of dimethyl [(2*R*,3*R*,4*S*)-1-formyl-2-methyl-4-phenylpyrrolidin-3-yl]phosphonate (**10d**) in

CDCl₃



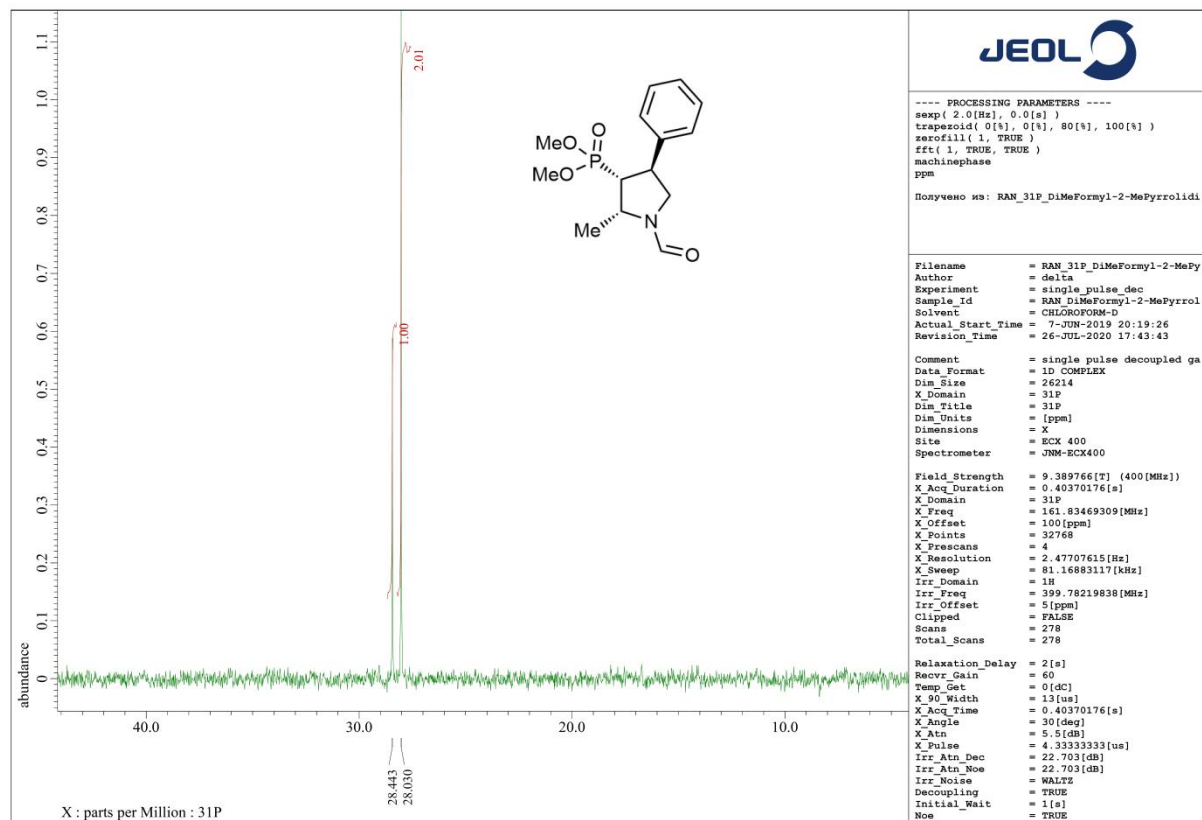
DEPT NMR spectra of dimethyl [(2*R*,3*R*,4*S*)-1-formyl-2-methyl-4-phenylpyrrolidin-3-yl]phosphonate (**10d**)

in CDCl₃

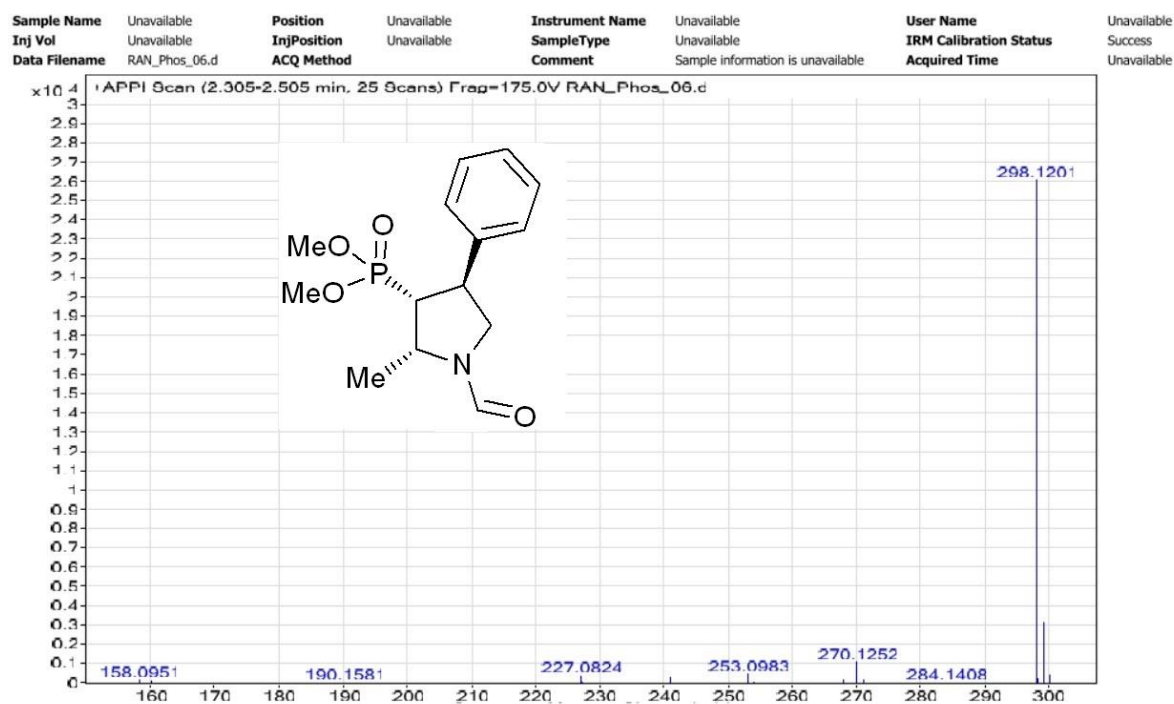


³¹P NMR spectra of dimethyl [(2*R*,3*R*,4*S*)-1-formyl-2-methyl-4-phenylpyrrolidin-3-yl]phosphonate (**10d**) in

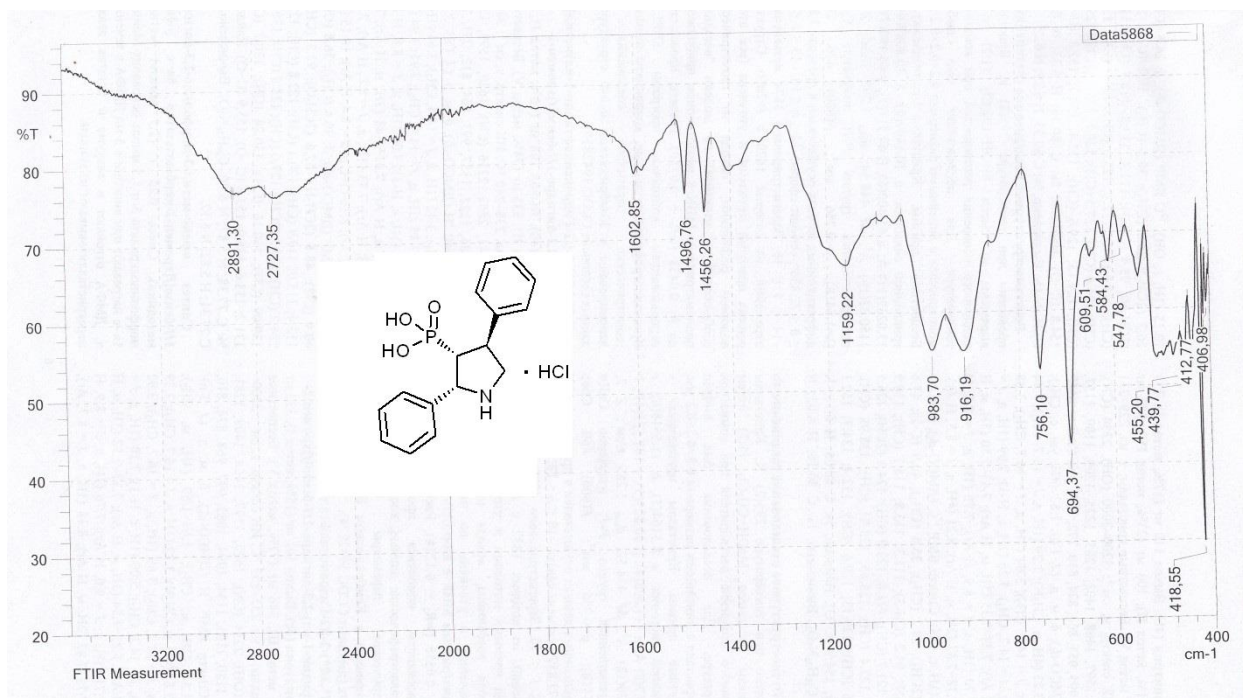
CDCl₃



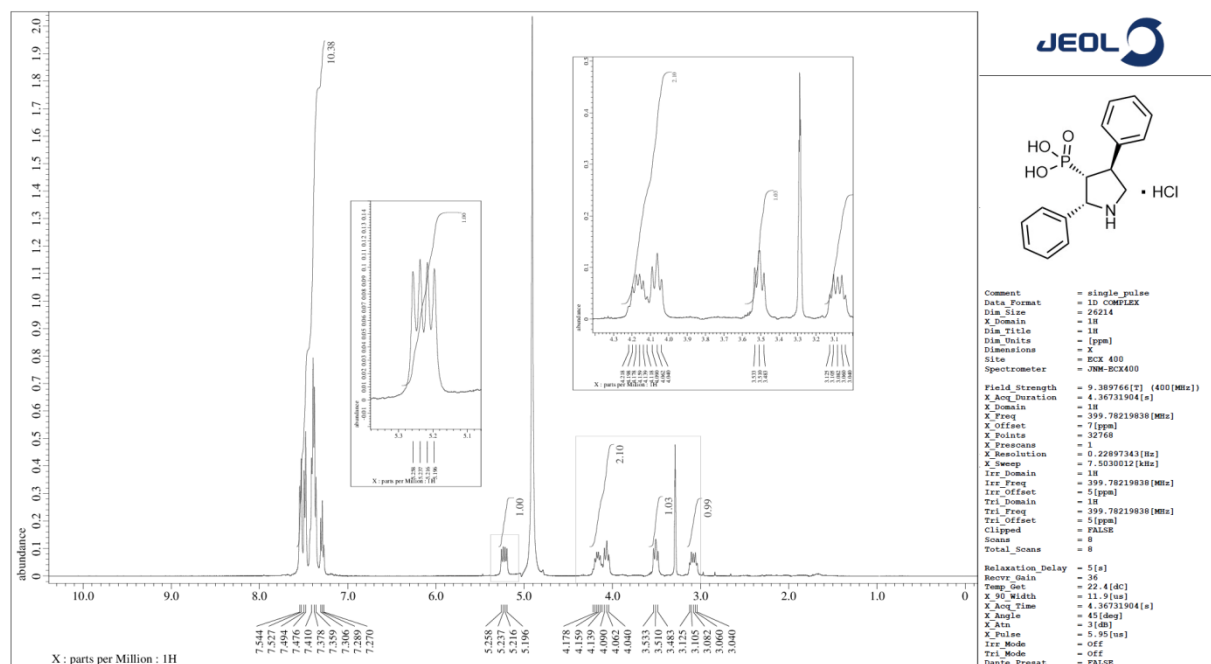
HRMS of dimethyl [(2*R*,3*R*,4*S*)-1-formyl-2-methyl-4-phenylpyrrolidin-3-yl]phosphonate (**10d**)



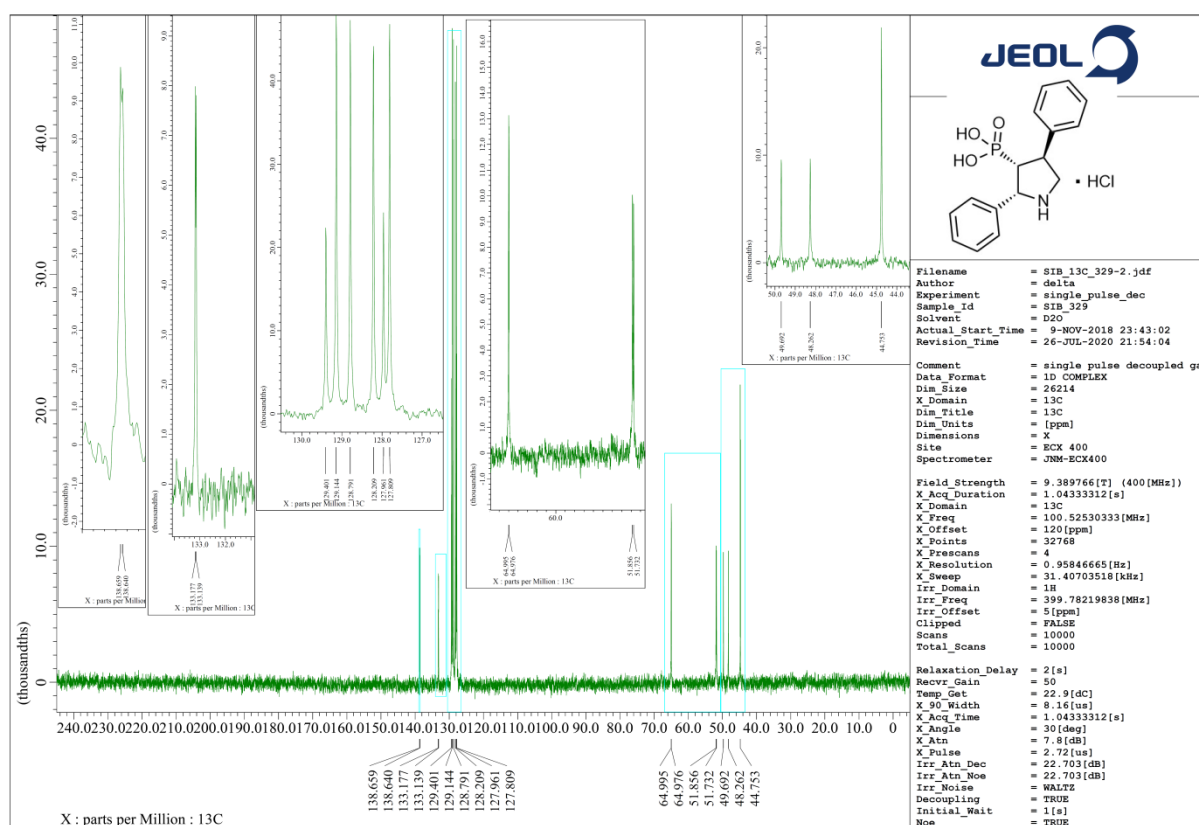
FTIR spectra of (2*R*,3*R*,4*S*)-2,4-Diphenylpyrrolidin-3-ylphosphonic acid hydrochloride (**11a**)



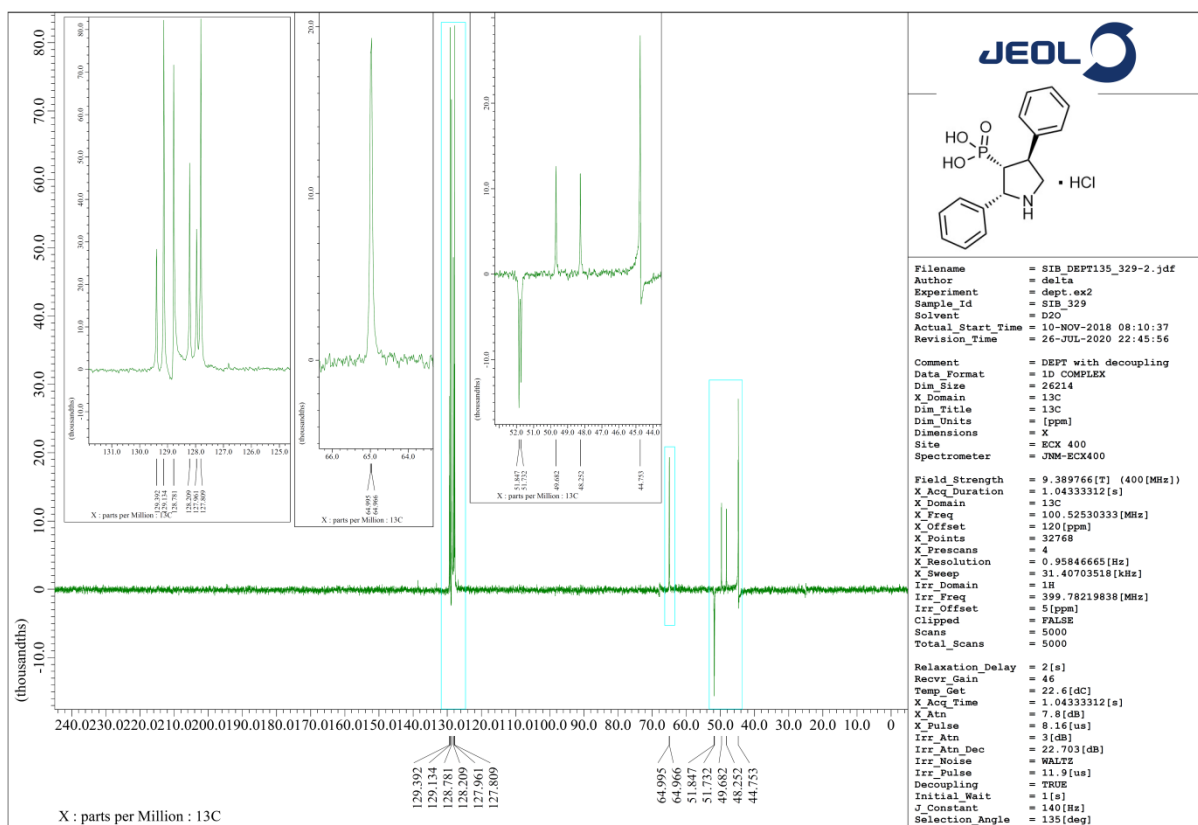
¹H NMR spectra of (2*R*,3*R*,4*S*)-2,4-Diphenylpyrrolidin-3-ylphosphonic acid hydrochloride (**11a**) in D₂O



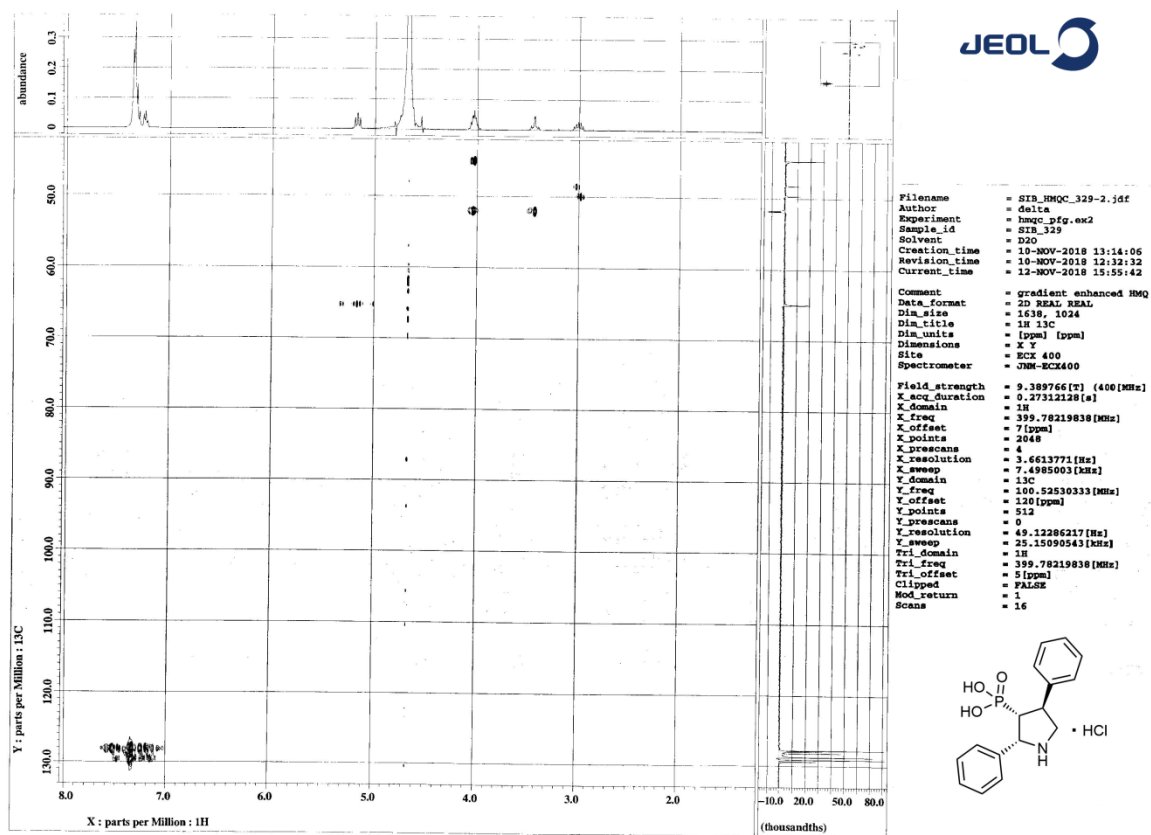
¹³C NMR spectra of (2*R*,3*R*,4*S*)-2,4-Diphenylpyrrolidin-3-ylphosphonic acid hydrochloride (**11a**) in D₂O



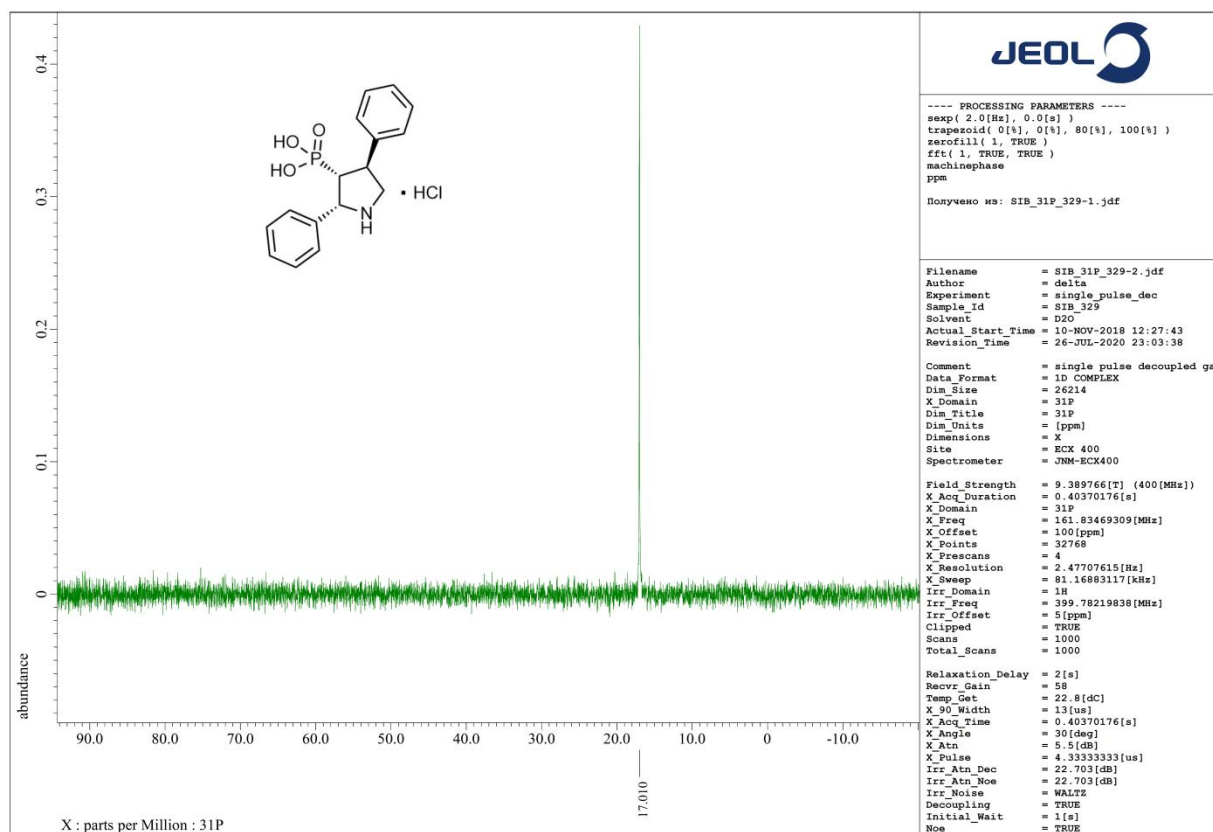
DEPT NMR spectra of (2R,3R,4S)-2,4-Diphenylpyrrolidin-3-ylphosphonic acid hydrochloride (**11a**) in D₂O



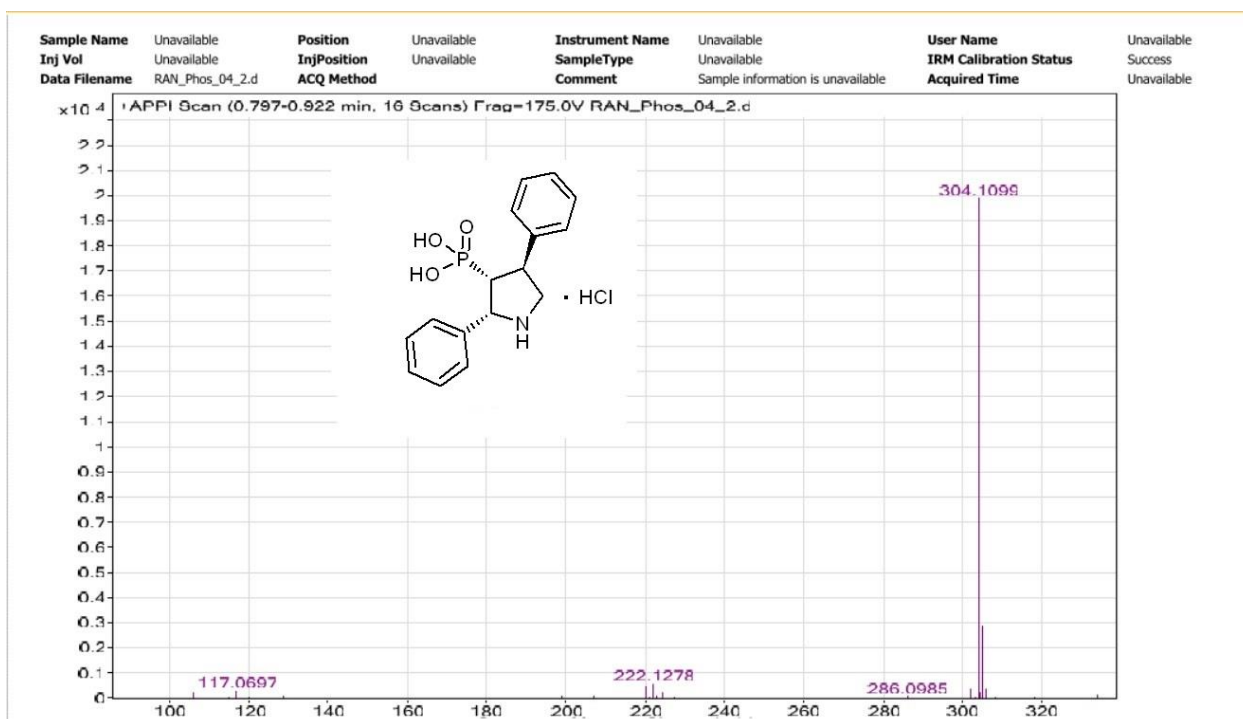
HMQC NMR spectra of (2R,3R,4S)-2,4-Diphenylpyrrolidin-3-ylphosphonic acid hydrochloride (**11a**) in D₂O



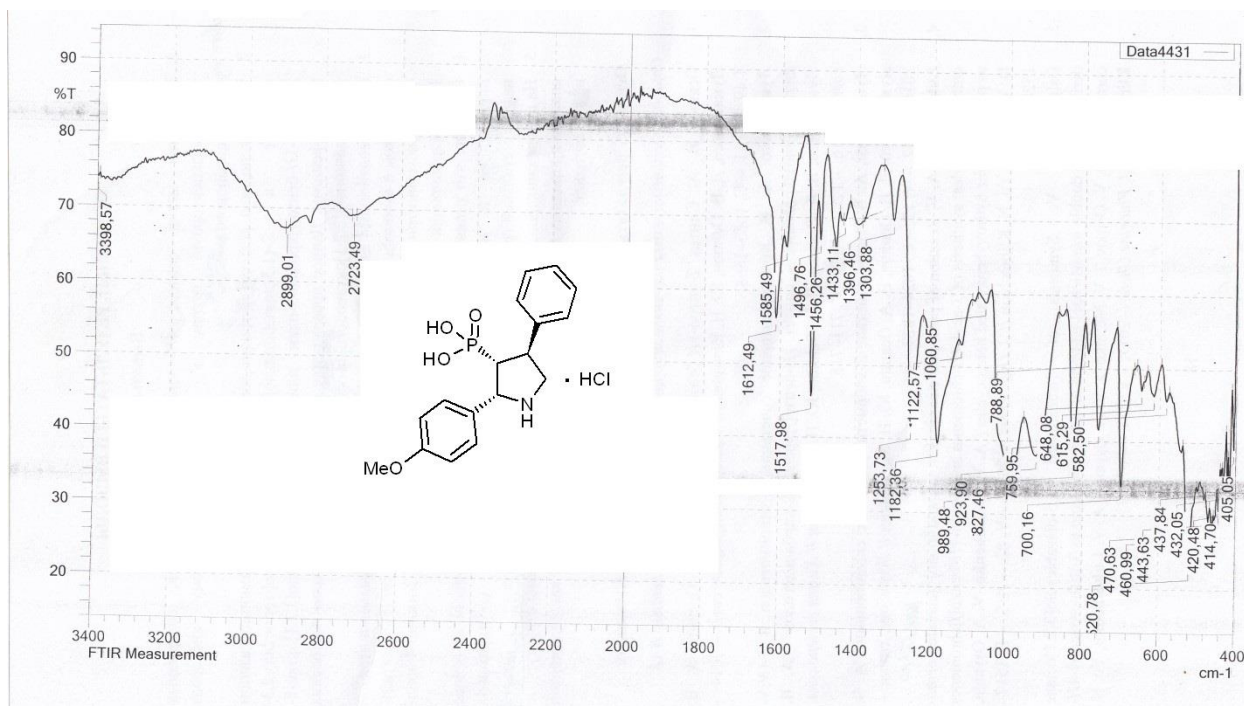
³¹P NMR spectra of (2*R*,3*R*,4*S*)-2,4-Diphenylpyrrolidin-3-ylphosphonic acid hydrochloride (**11a**) in D₂O



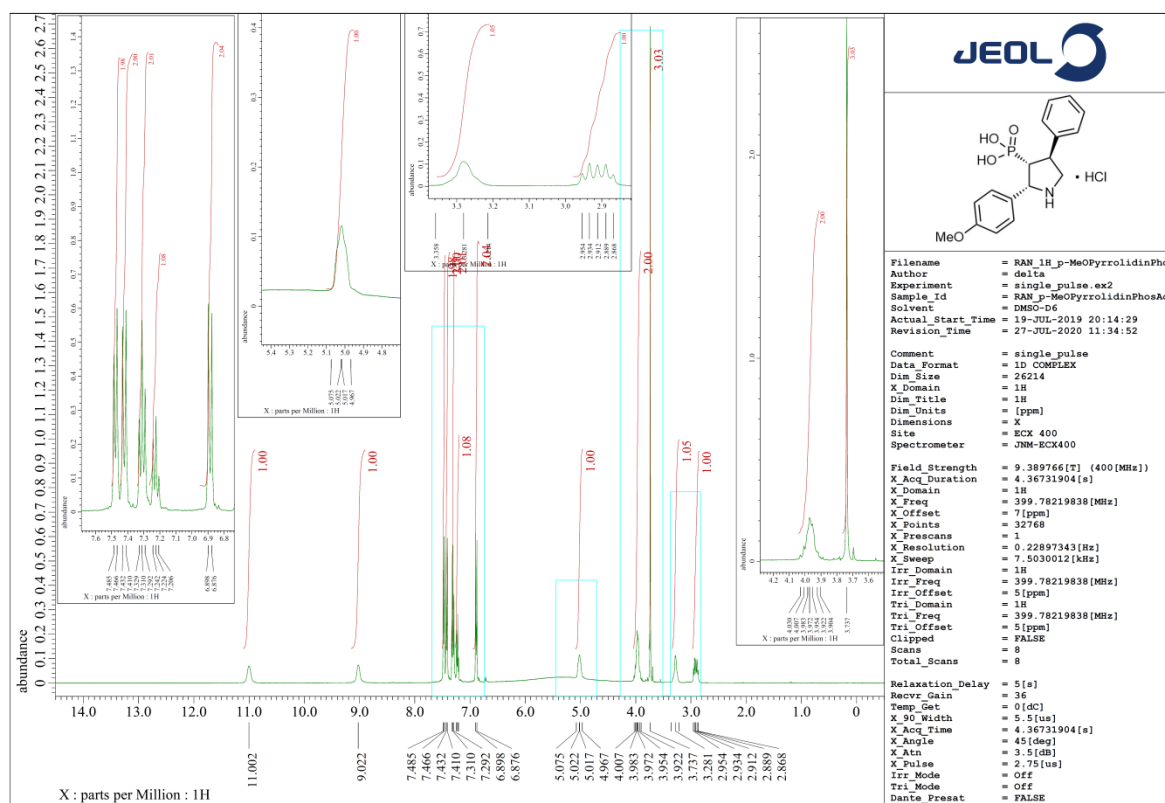
HRMS of (2*R*,3*R*,4*S*)-2,4-Diphenylpyrrolidin-3-ylphosphonic acid hydrochloride (**11a**)



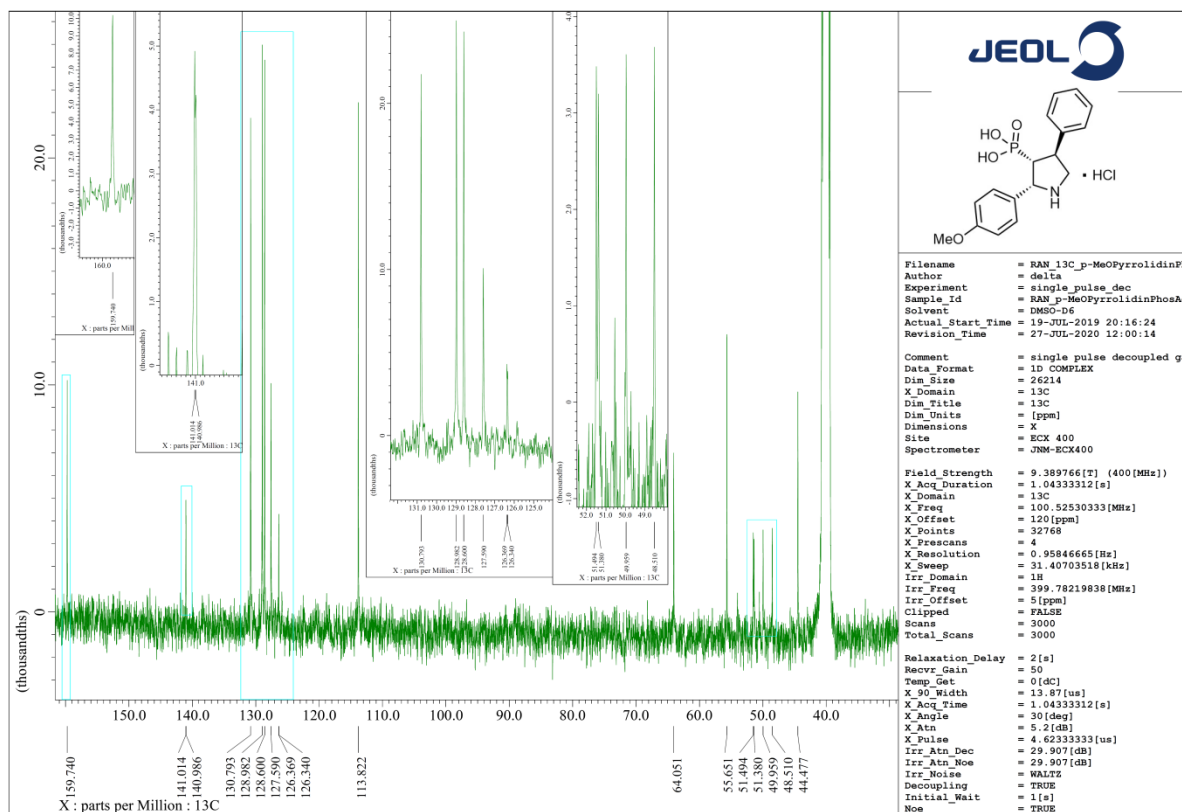
(11b)



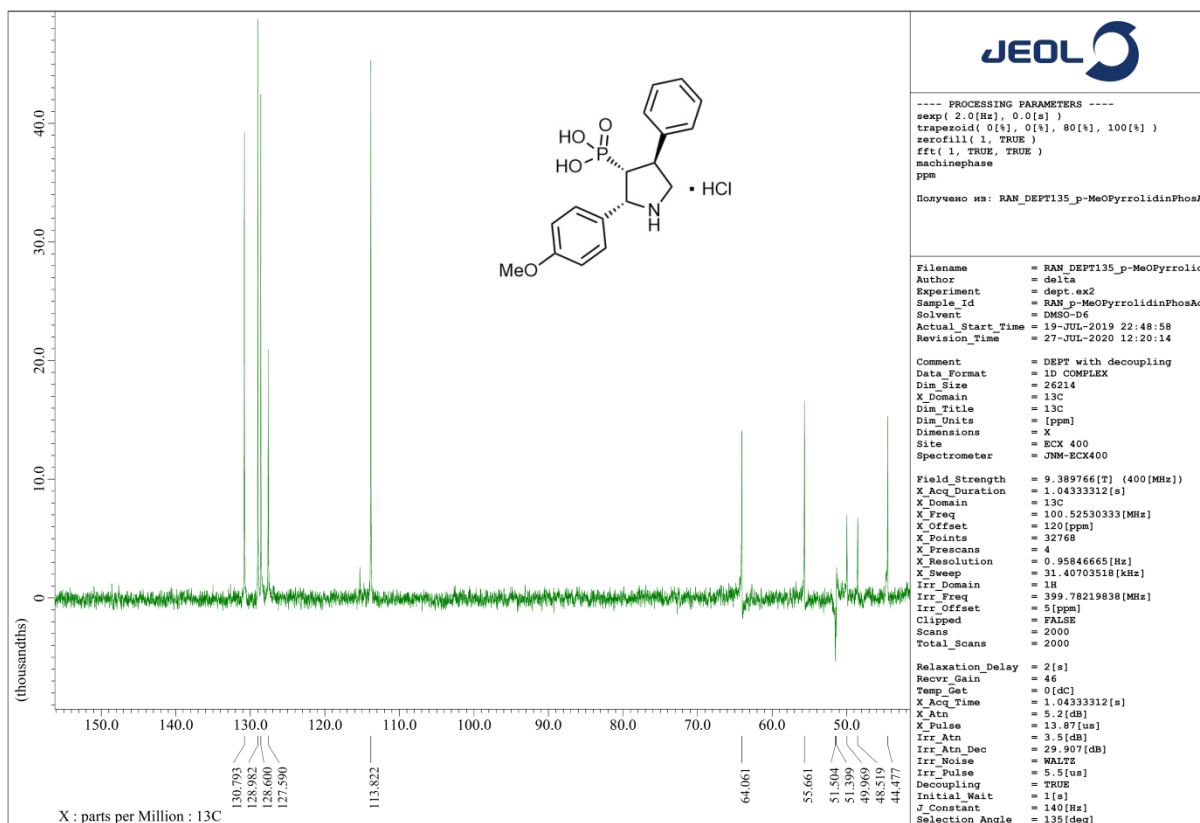
(11b) in DMSO- d^6



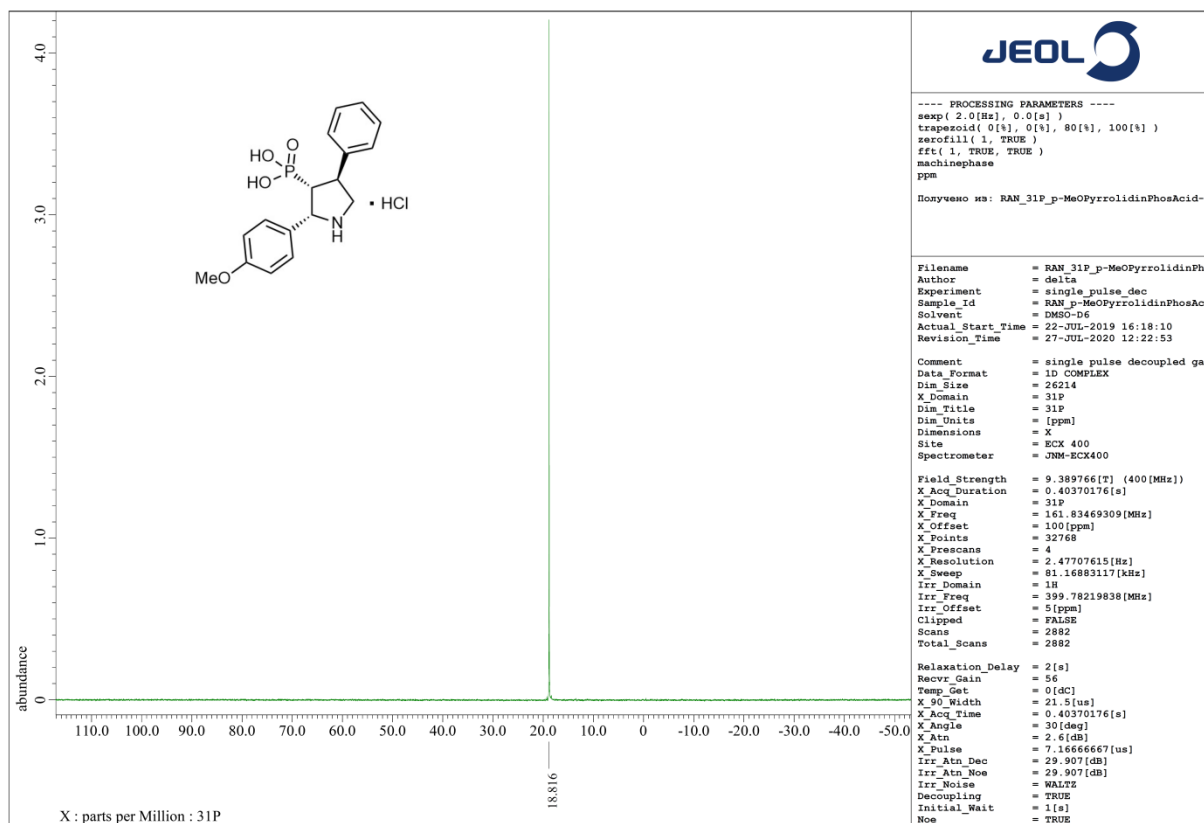
¹³C NMR spectra of (2*R*,3*R*,4*S*)-2-(4-methoxyphenyl)-4-phenylpyrrolidin-3-ylphosphonic acid hydrochloride (**11b**) in DMSO-*d*⁶



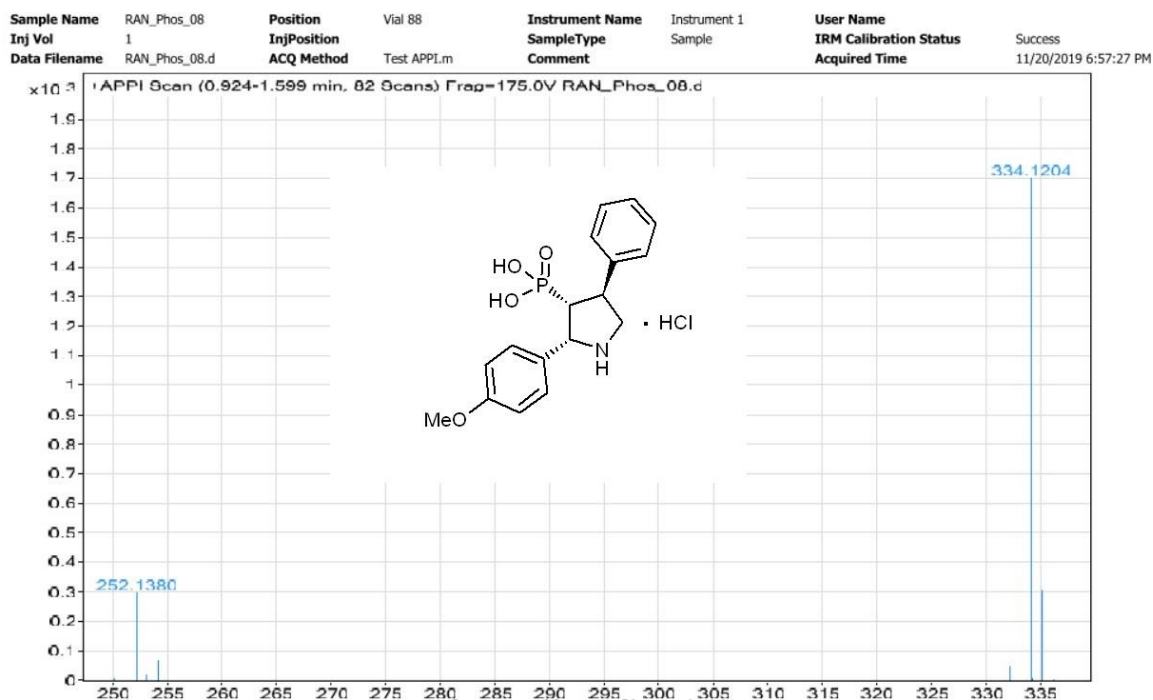
DEPT NMR spectra of (2*R*,3*R*,4*S*)-2-(4-methoxyphenyl)-4-phenylpyrrolidin-3-ylphosphonic acid hydrochloride (**11b**) in DMSO-*d*⁶



³¹P NMR spectra of (2*R*,3*R*,4*S*)-2-(4-methoxyphenyl)-4-phenylpyrrolidin-3-ylphosphonic acid hydrochloride (**11b**) in DMSO-*d*⁶

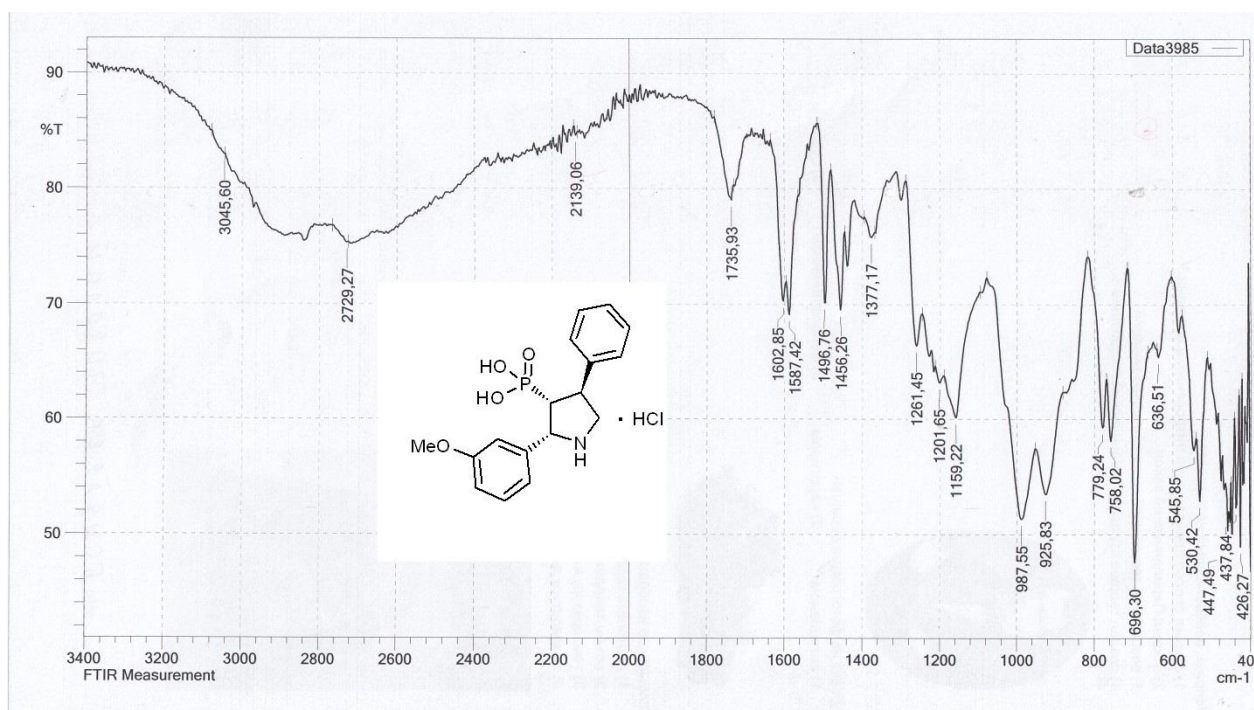


HRMS of (2*R*,3*R*,4*S*)-2-(4-methoxyphenyl)-4-phenylpyrrolidin-3-ylphosphonic acid hydrochloride (**11b**)



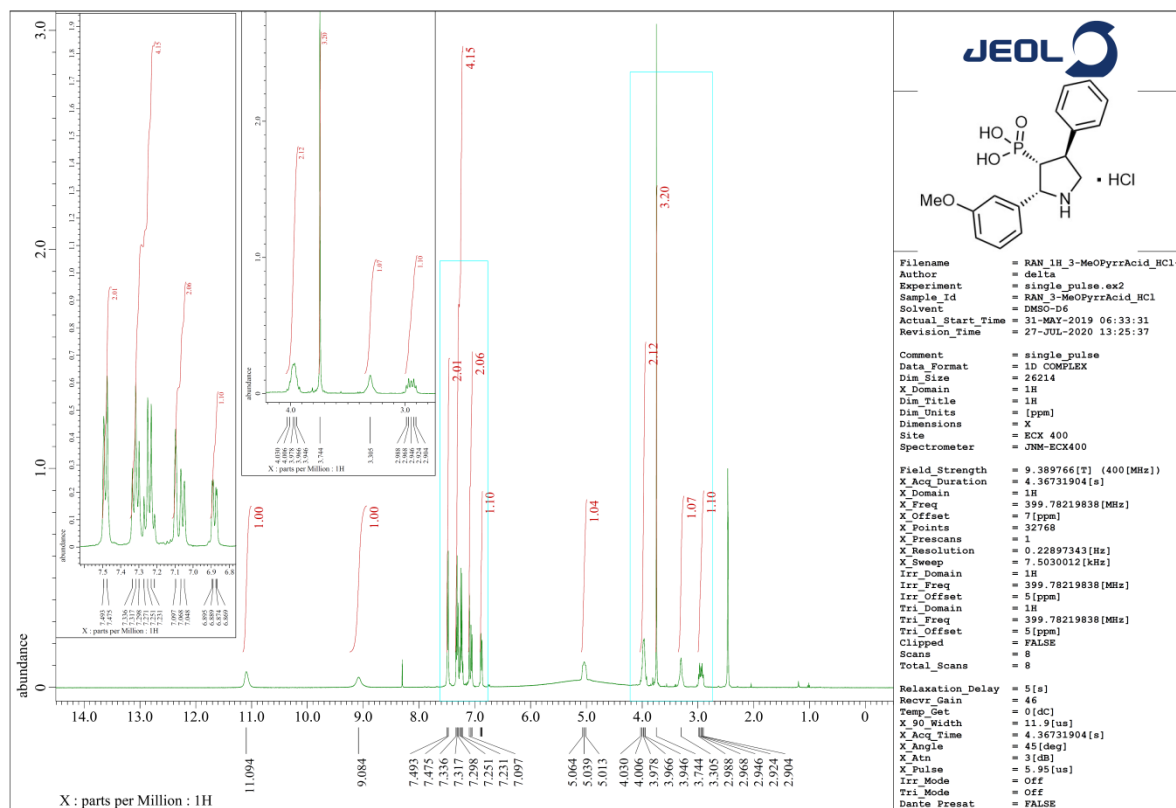
FTIR spectra of (2*R*,3*R*,4*S*)-2-(3-methoxyphenyl)-4-phenylpyrrolidin-3-ylphosphonic acid hydrochloride

(11c)

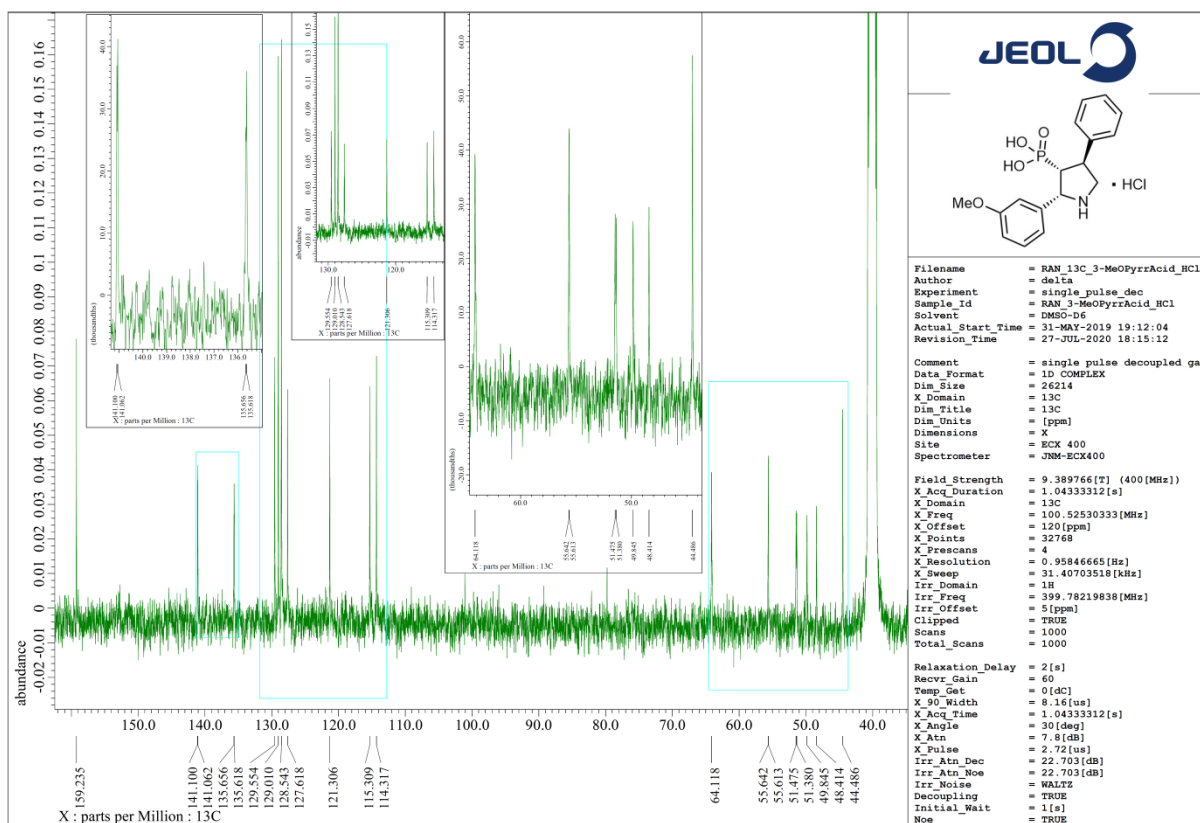


¹H NMR spectra of (2*R*,3*R*,4*S*)-2-(3-methoxyphenyl)-4-phenylpyrrolidin-3-ylphosphonic acid hydrochloride

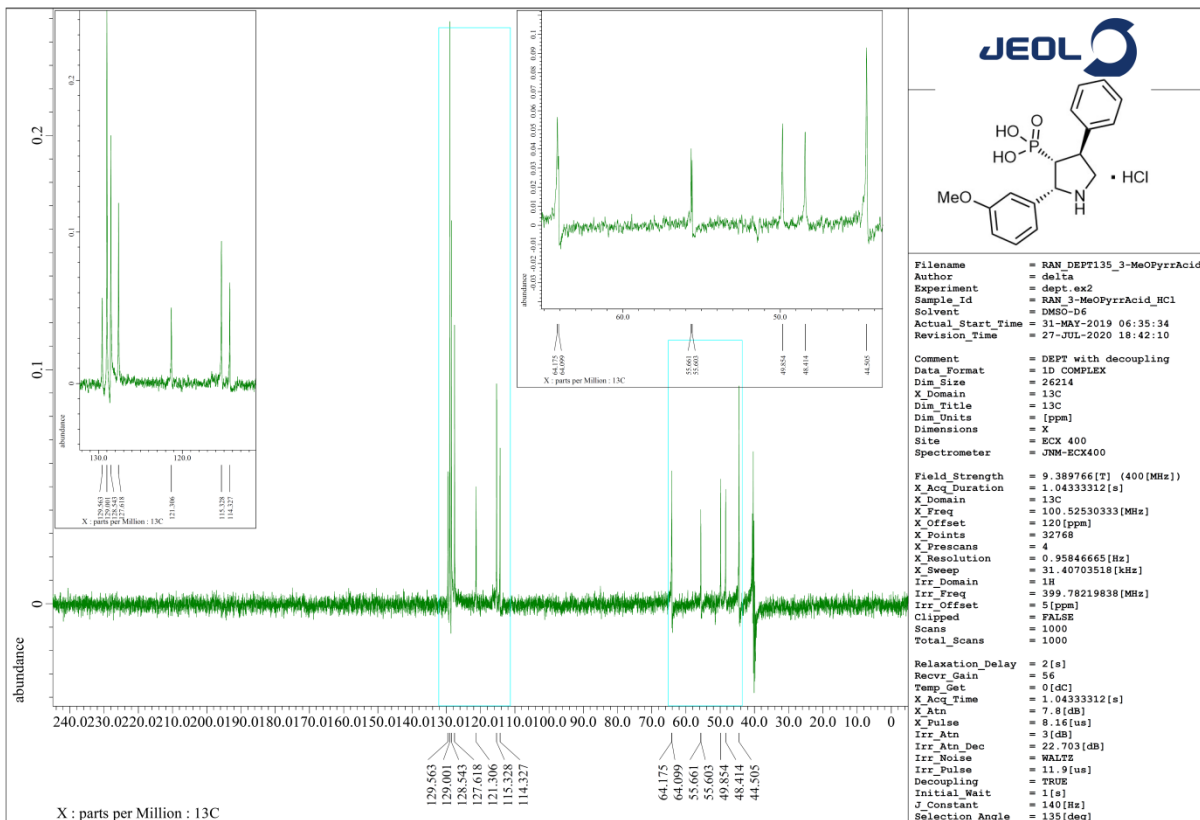
(11c) in DMSO-*d*⁶



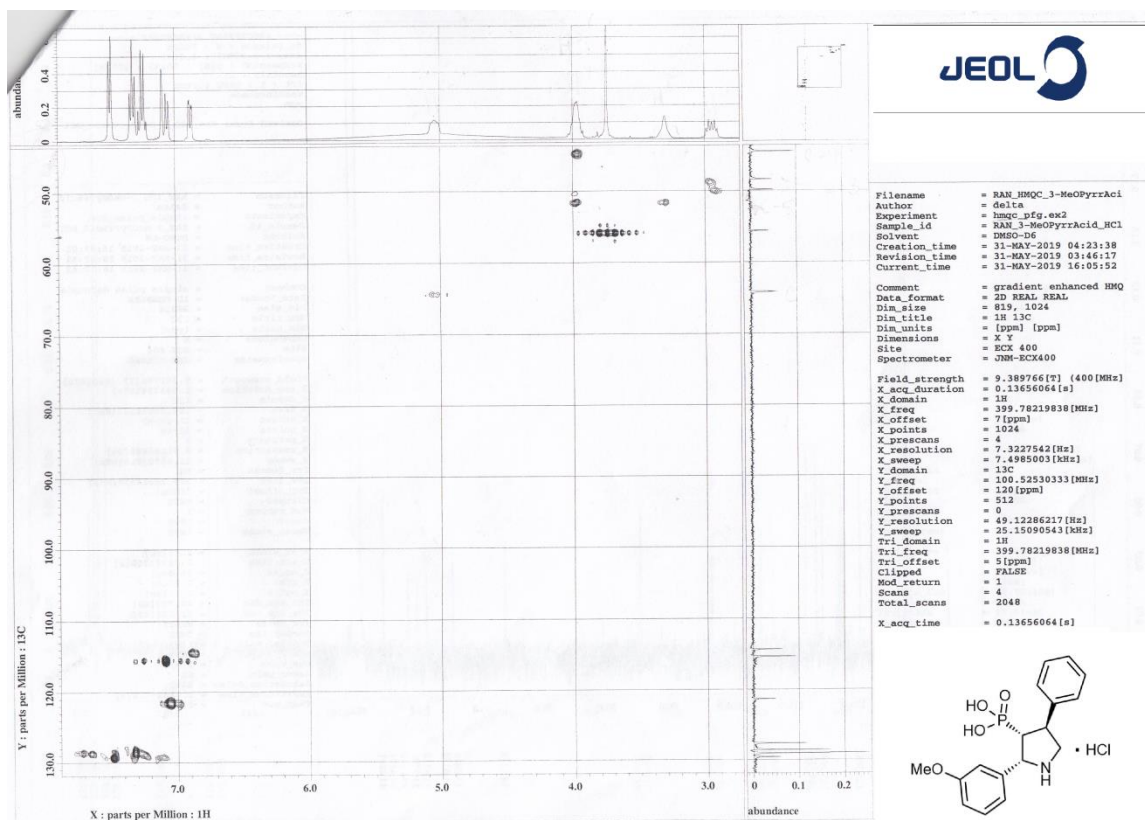
¹³C NMR spectra of (2*R*,3*R*,4*S*)-2-(3-methoxyphenyl)-4-phenylpyrrolidin-3-ylphosphonic acid hydrochloride (**11c**) in DMSO-*d*₆



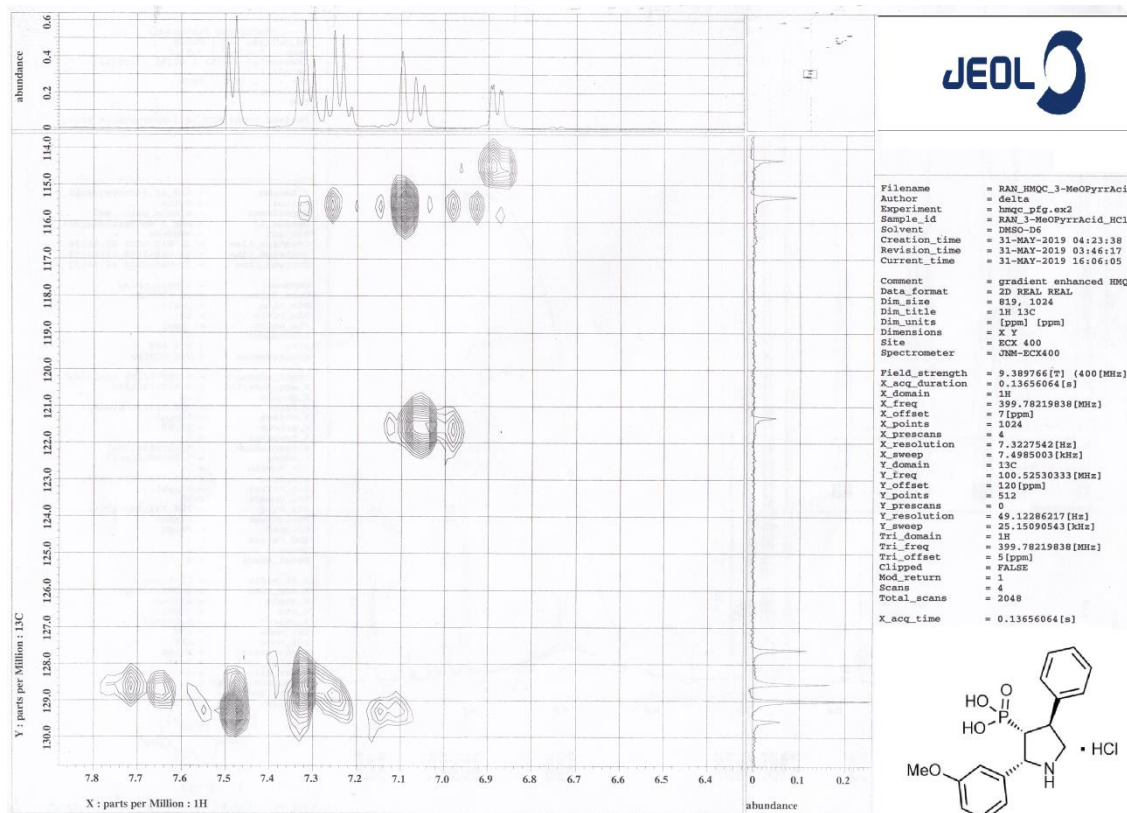
DEPT NMR spectra of (2*R*,3*R*,4*S*)-2-(3-methoxyphenyl)-4-phenylpyrrolidin-3-ylphosphonic acid hydrochloride (**11c**) in DMSO-*d*₆



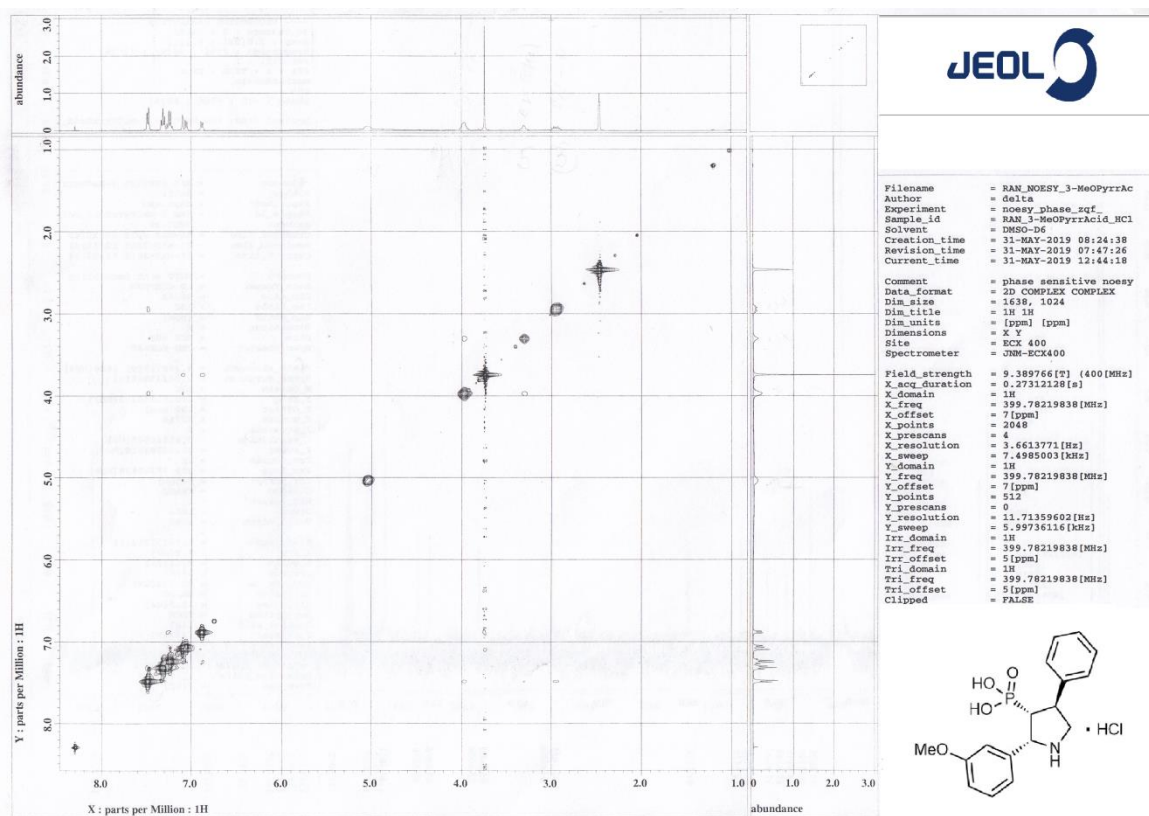
HMQC NMR spectra of (2R,3R,4S)-2-(3-methoxyphenyl)-4-phenylpyrrolidin-3-ylphosphonic acid
hydrochloride (**11c**) in DMSO-*d*⁶



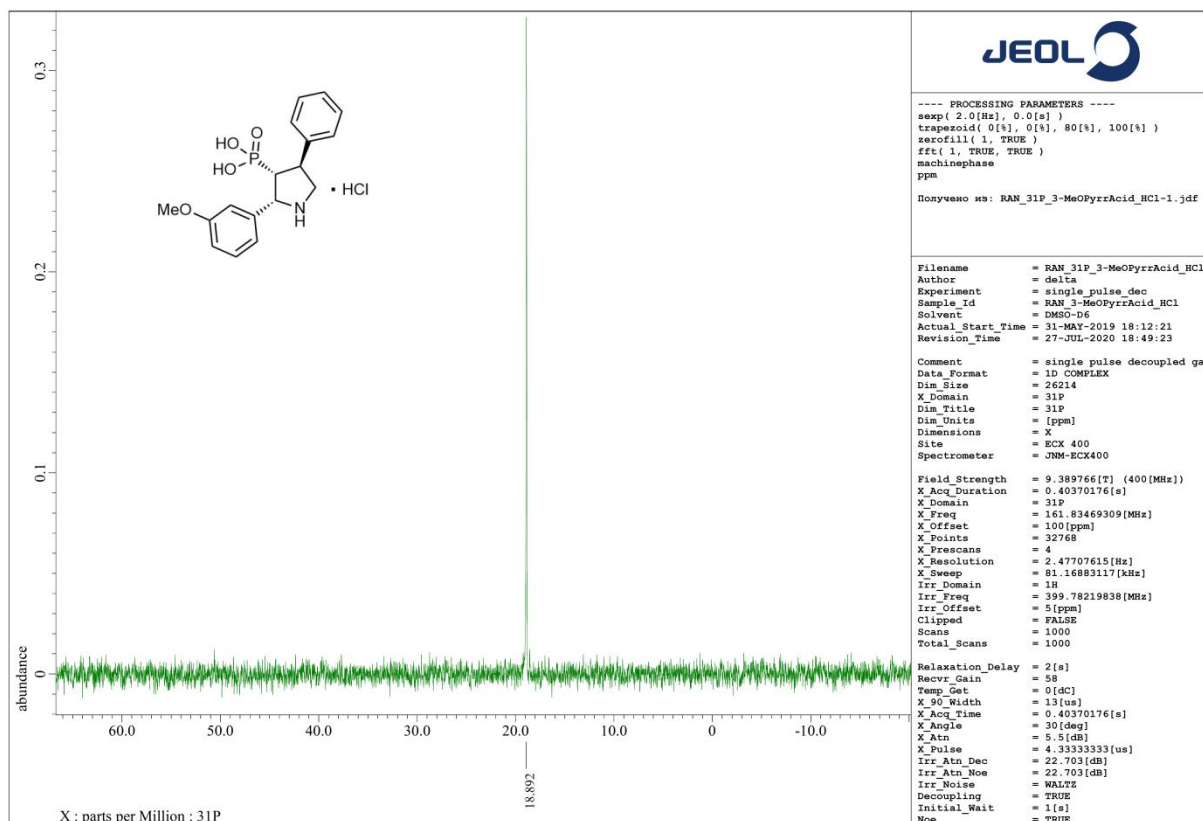
HMQC NMR spectra of (2R,3R,4S)-2-(3-methoxyphenyl)-4-phenylpyrrolidin-3-ylphosphonic acid
hydrochloride (**11c**) in DMSO-*d*⁶



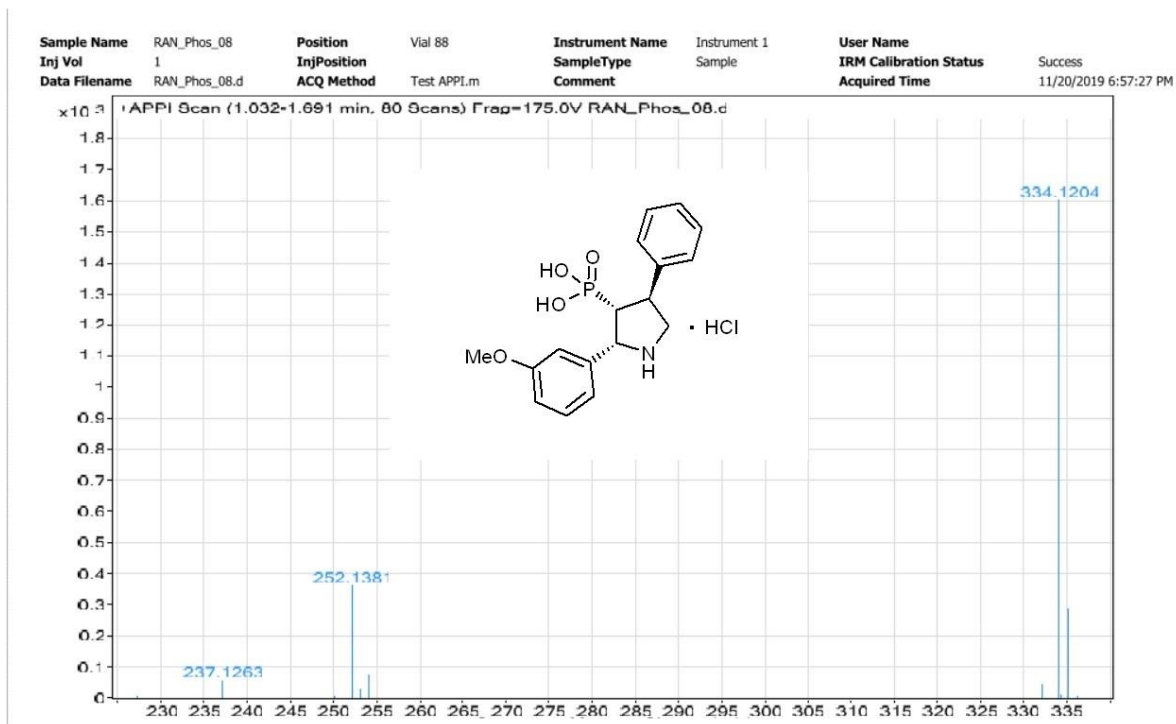
NOESY NMR spectra of (2*R*,3*R*,4*S*)-2-(3-methoxyphenyl)-4-phenylpyrrolidin-3-ylphosphonic acid hydrochloride (**11c**) in DMSO-*d*⁶



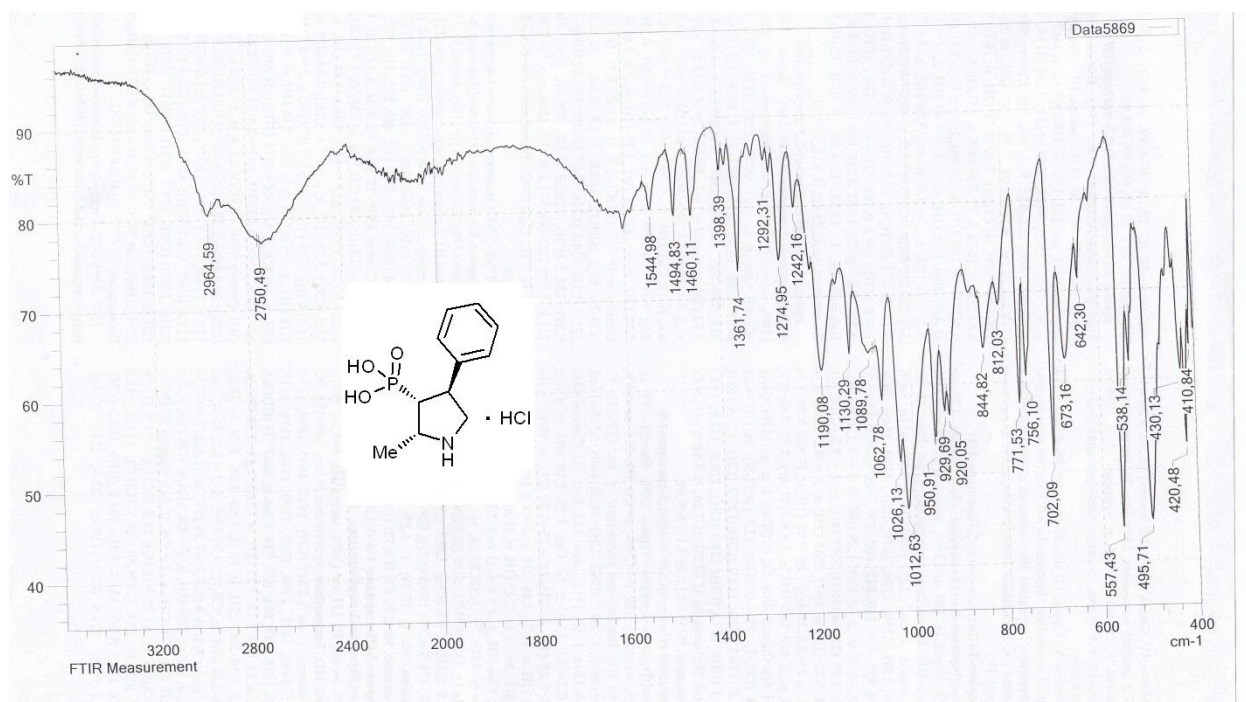
³¹P NMR spectra of (2*R*,3*R*,4*S*)-2-(3-methoxyphenyl)-4-phenylpyrrolidin-3-ylphosphonic acid hydrochloride (**11c**) in DMSO-*d*⁶



HRMS of (2*R*,3*R*,4*S*)-2-(3-methoxyphenyl)-4-phenylpyrrolidin-3-ylphosphonic acid hydrochloride (**11c**)

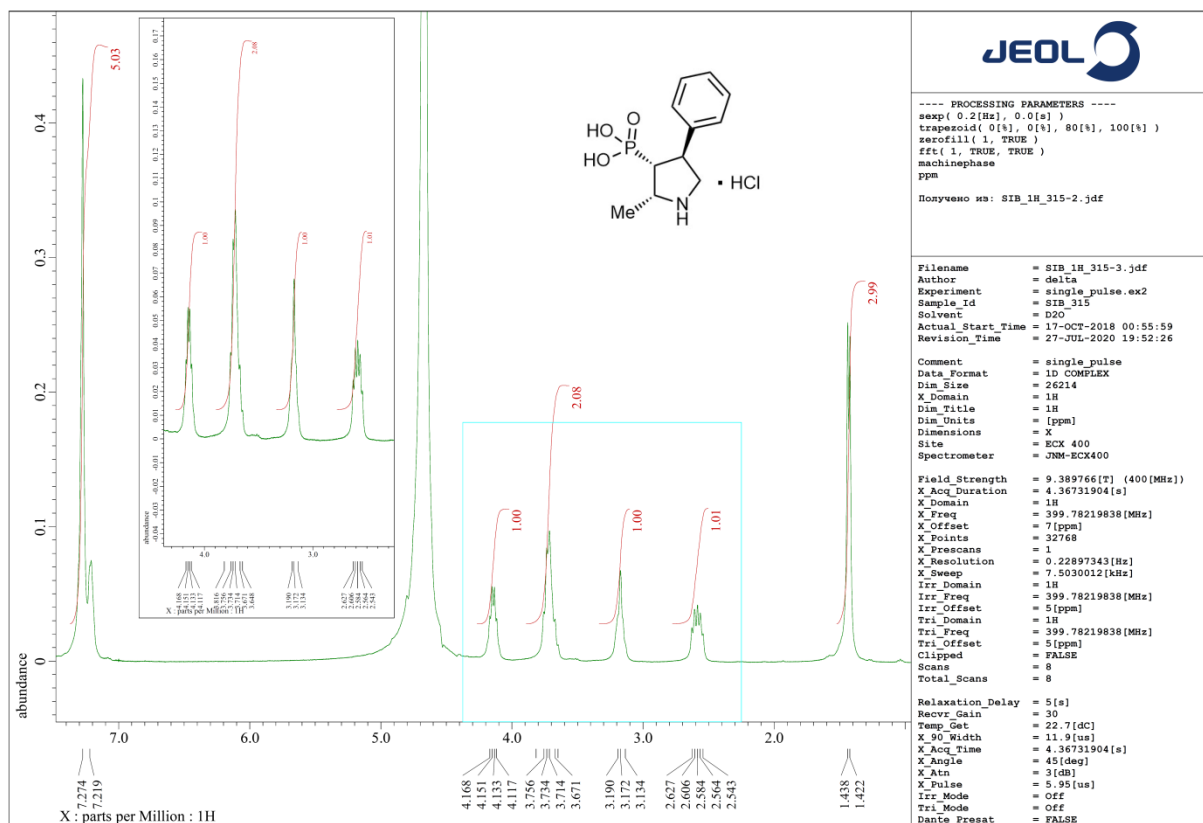


FTIR spectra of (2*R*,3*R*,4*S*)-2-methyl-4-phenylpyrrolidin-3-ylphosphonic acid hydrochloride (**11d**)



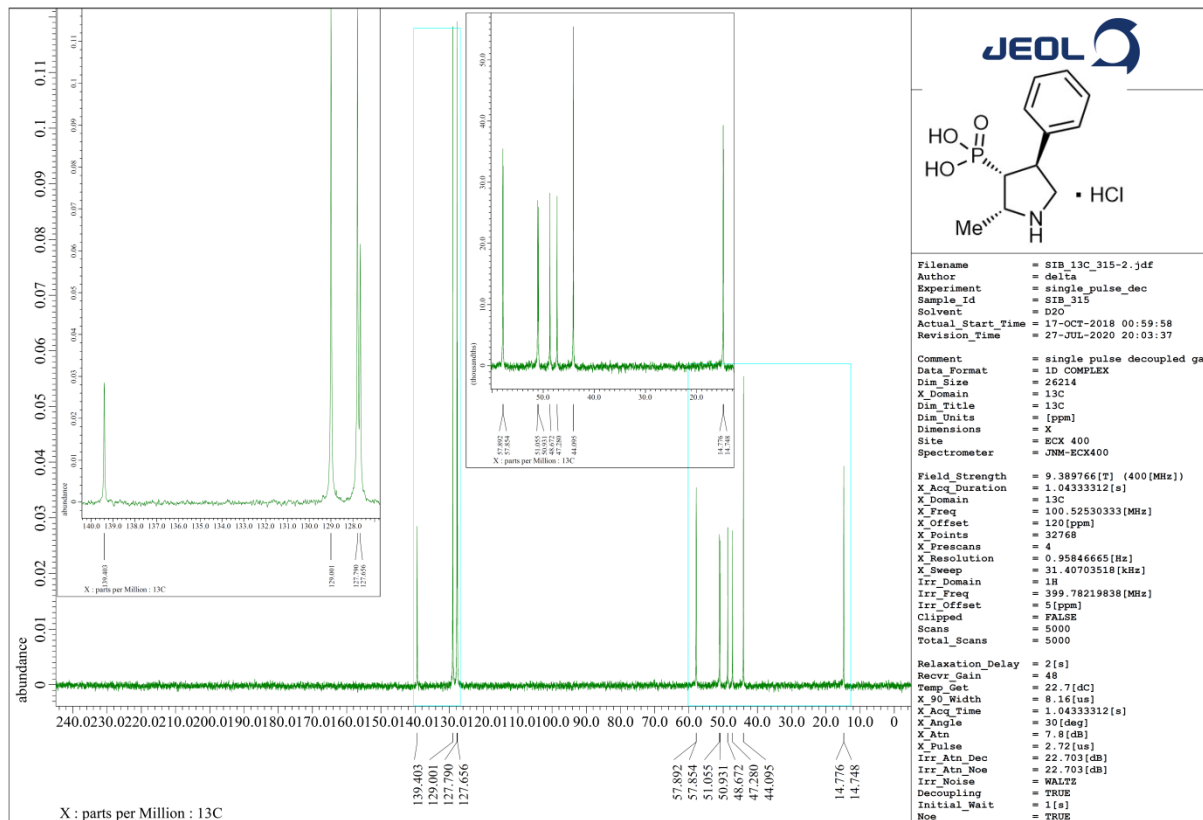
¹H NMR spectra of (2*R*,3*R*,4*S*)-2-methyl-4-phenylpyrrolidin-3-ylphosphonic acid hydrochloride (**11d**) in

D₂O



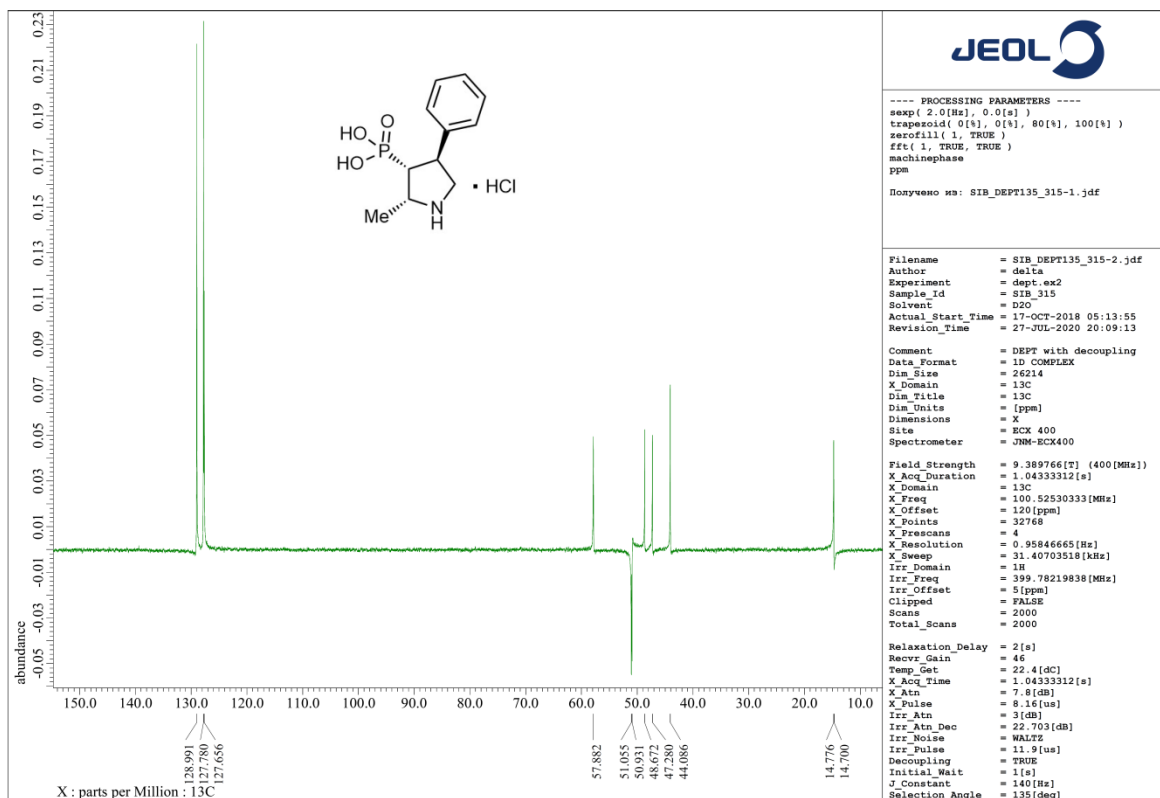
¹³C NMR spectra of (2*R*,3*R*,4*S*)-2-methyl-4-phenylpyrrolidin-3-ylphosphonic acid hydrochloride (**11d**) in

D₂O



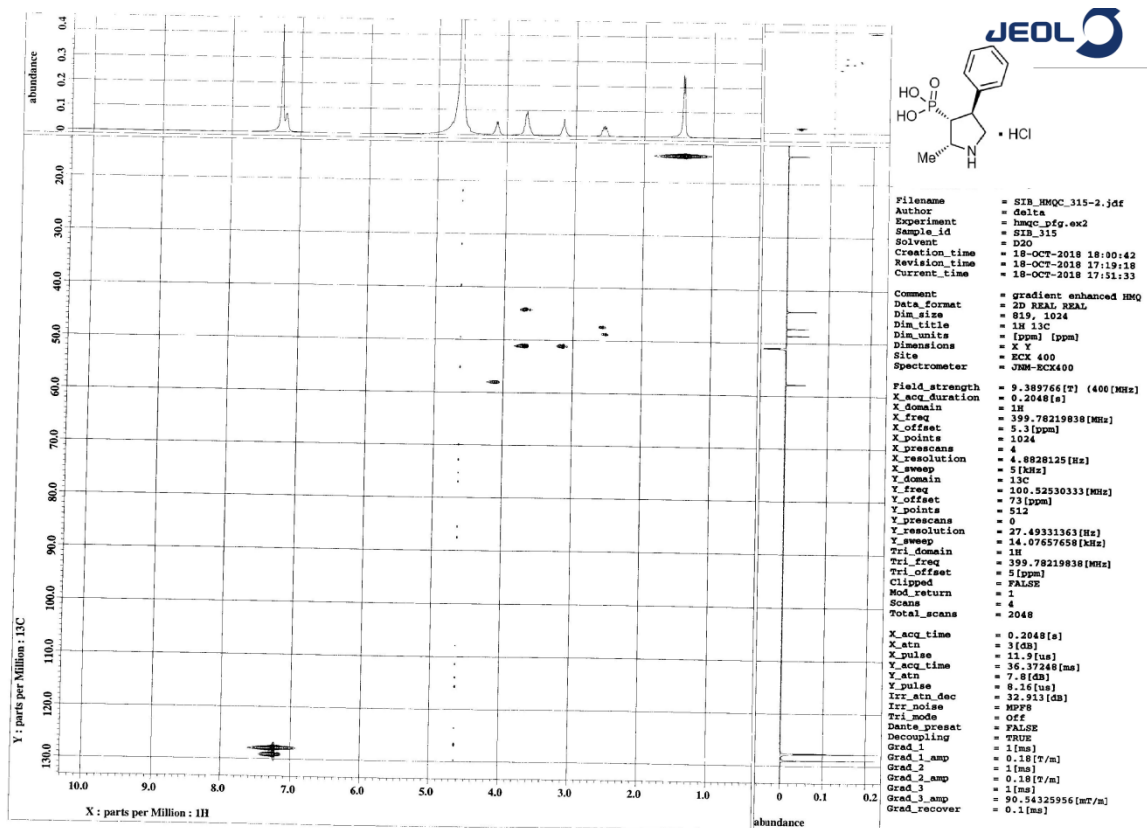
DEPT NMR spectra of (2*R*,3*R*,4*S*)-2-methyl-4-phenylpyrrolidin-3-ylphosphonic acid hydrochloride (**11d**) in

D₂O

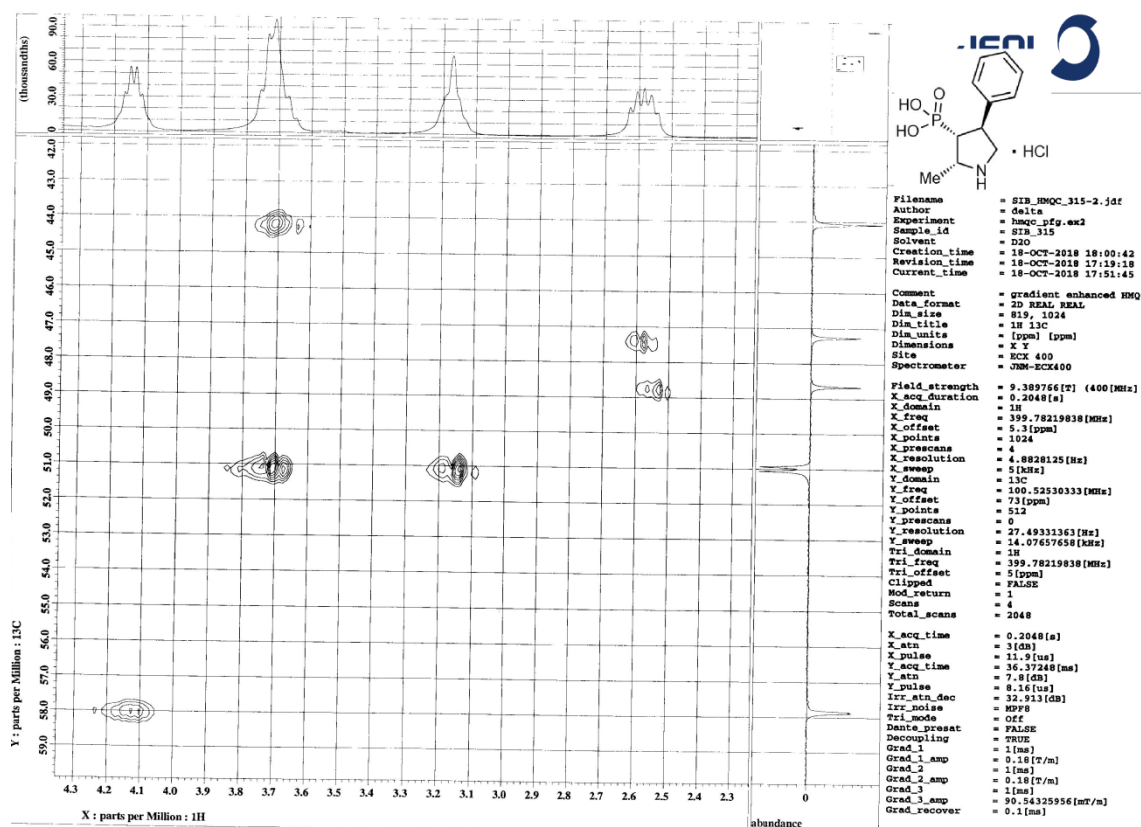


HMQC NMR spectra of (2*R*,3*R*,4*S*)-2-methyl-4-phenylpyrrolidin-3-ylphosphonic acid hydrochloride (**11d**)

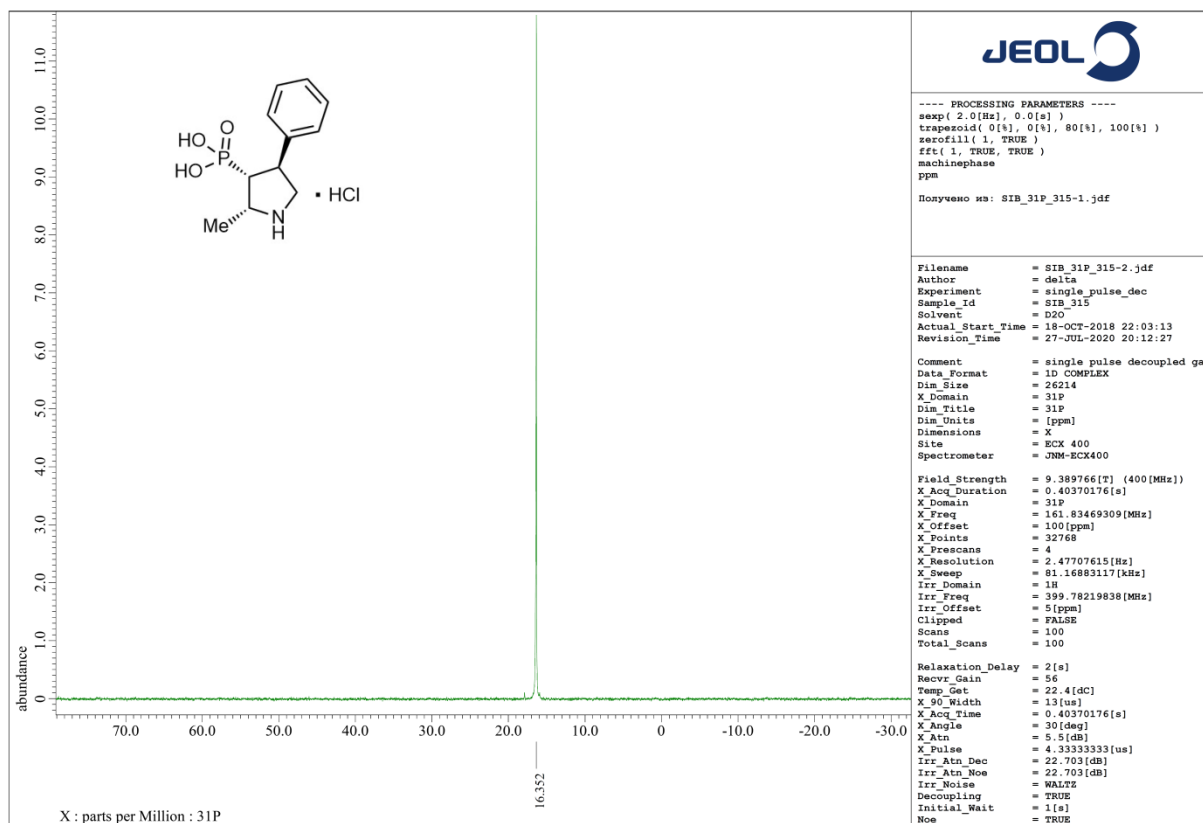
in D₂O



HMQC NMR spectra of (2*R*,3*R*,4*S*)-2-methyl-4-phenylpyrrolidin-3-ylphosphonic acid hydrochloride (**11d**)
in D₂O

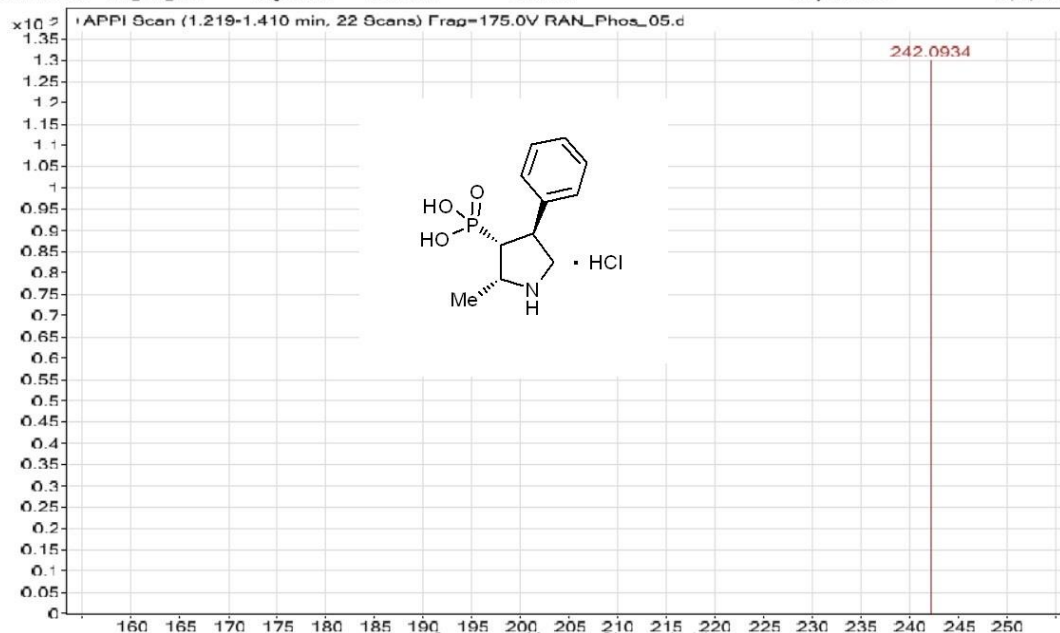


³¹P NMR spectra of (2*R*,3*R*,4*S*)-2-methyl-4-phenylpyrrolidin-3-ylphosphonic acid hydrochloride (**11d**) in
D₂O

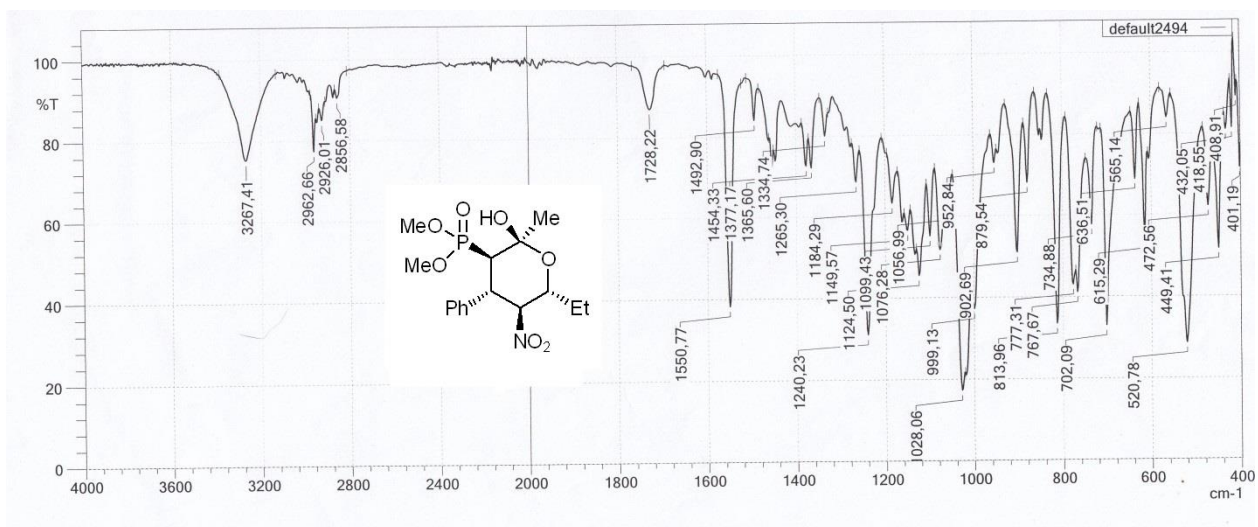


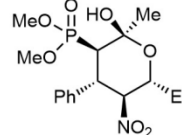
HRMS of (2*R*,3*R*,4*S*)-2-methyl-4-phenylpyrrolidin-3-ylphosphonic acid hydrochloride (**11d**)

Sample Name	RAN_Phos_05	Position	Vial 85	Instrument Name	Instrument 1	User Name	
Inj Vol	1	InjPosition		SampleType	Sample	IRM Calibration Status	Success
Data Filename	RAN_Phos_05.d	ACQ Method	Test APPL.m	Comment		Acquired Time	11/20/2019 6:25:23 PM



FTIR spectra of dimethyl [(2*S*,3*R*,4*S*,5*S*,6*R*)-6-ethyl-2-hydroxy-2-methyl-5-nitro-4-phenyltetrahydro-2*H*-pyran-3-yl)phosphonate (**13a**)



2H-pyran-3-yl)phosphonate (**13a**) in CDCl₃

```

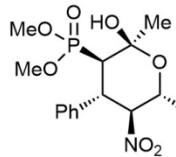
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PilotName         = delta
Experiment        = single_pulse.ex2
Sample_ID         = RAN_tetrahydroypr
Solvent           = CDCl3CDCl3-D
Actual_Start_Time = 27-APR-2018 17:42:20
Revision_Time     = 27-JUL-2020 23:34:10

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Dim_Size          = 26214
X_Domain          = 1H
X_Title           = 1H
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECK 400
Spectrometer      = JNM-ECK400

Field_Strength    = 9.389766[T] (400[MHz])
Acq_Duration      = 3.36731904[s]
X_Domain          = 1H
X_Freq            = 399.78219838 [MHz]
X_Offset          = 7[ppm]
Points            = 2768
Prescans          = 1
X_Resolution      = 0.2289343[Hz]
X_Sweep           = 7.5030012[kHz]
X_Domain          = 1H
Irr_Freq          = 399.78219838 [MHz]
Irr_Offset        = 5[ppm]
Irr_Domain        = 1H
X_Domain          = 1H
Irr_Freq          = 399.78219838 [MHz]
Tri_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 8
Total_Scans       = 8

Relaxation_Delay  = 5[s]
Recvr_Gain        = 36
Temp_Gat          = 30[OC]
X_90_Width        = 13.9[us]
Acq_Time          = 4.36731904[s]
X_Angle           = 45[deg]
X_Ato             = 3[deg]
X_Pulse           = 9.95[us]
Irr_Mode          = Off
Irr_Mode          = Off
DANTE_Pressat     = FALSE

```

2*H*-pyran-3-yl)phosphonate (**13a**) in CDCl₃

```

---- PROCESSING PARAMETERS ----
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1, TRUE )
fft( 1, TRUE, TRUE )
machinephase
ppm

```

Получено из: RAN_13C_tetrahydropyr-2.jdf

```

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Author            = delta
Experiment         = single_pulse_dec
Sample_Id         = RAN_tetrahydopyr
Solve             = LSCROPOW-D
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Revision_Time     = 28-JUL-2020 00:32:01

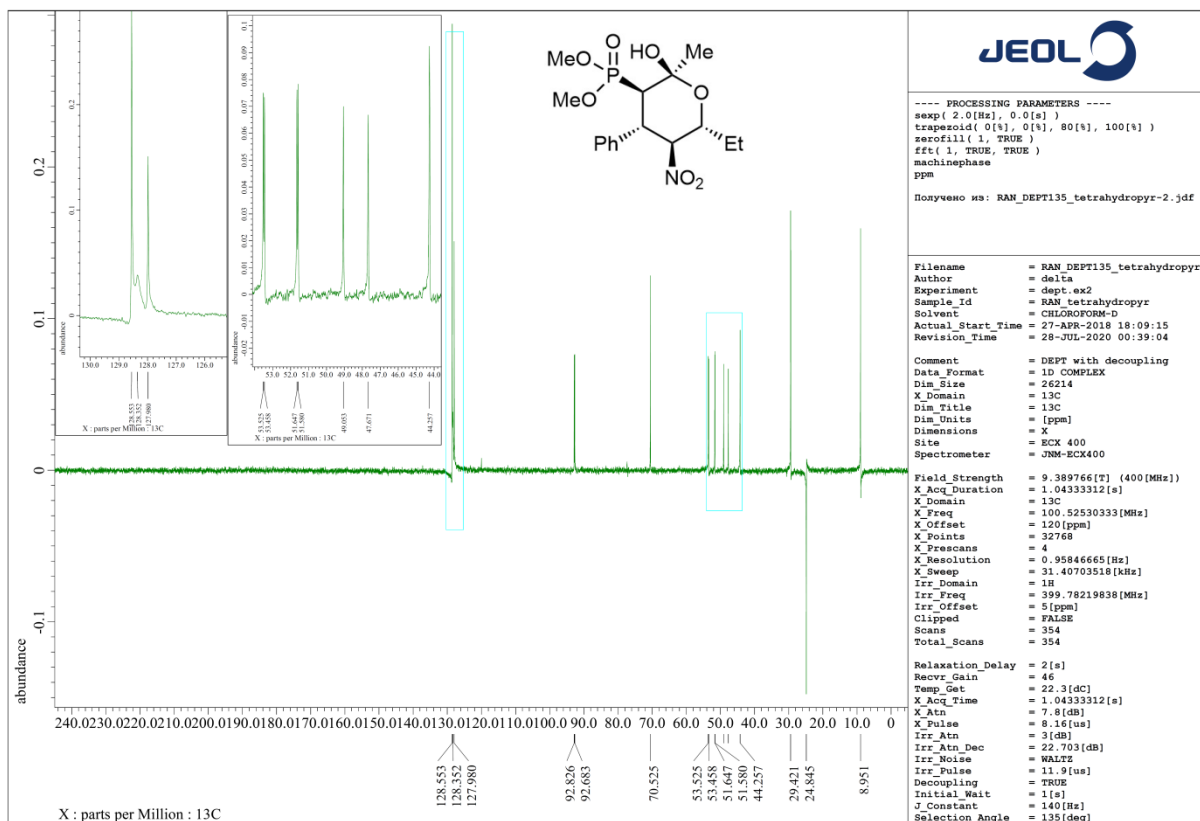
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X_Title           = 13C
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Dimensions        = X
Site              = ECK 400
Spectrometer      = JNM-ECK400

Field_Strength    = 9.398766[T] (400[MHz])
Acq_Duration      = 1.04333312[s]
X_Domain          = 13C
X_Freq            = 100.52530333[MHz]
X_Offset          = 120[ppm]
X_Points          = 2768
X_Frecans         = 4
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X_Sweep           = 31.40703518[kHz]
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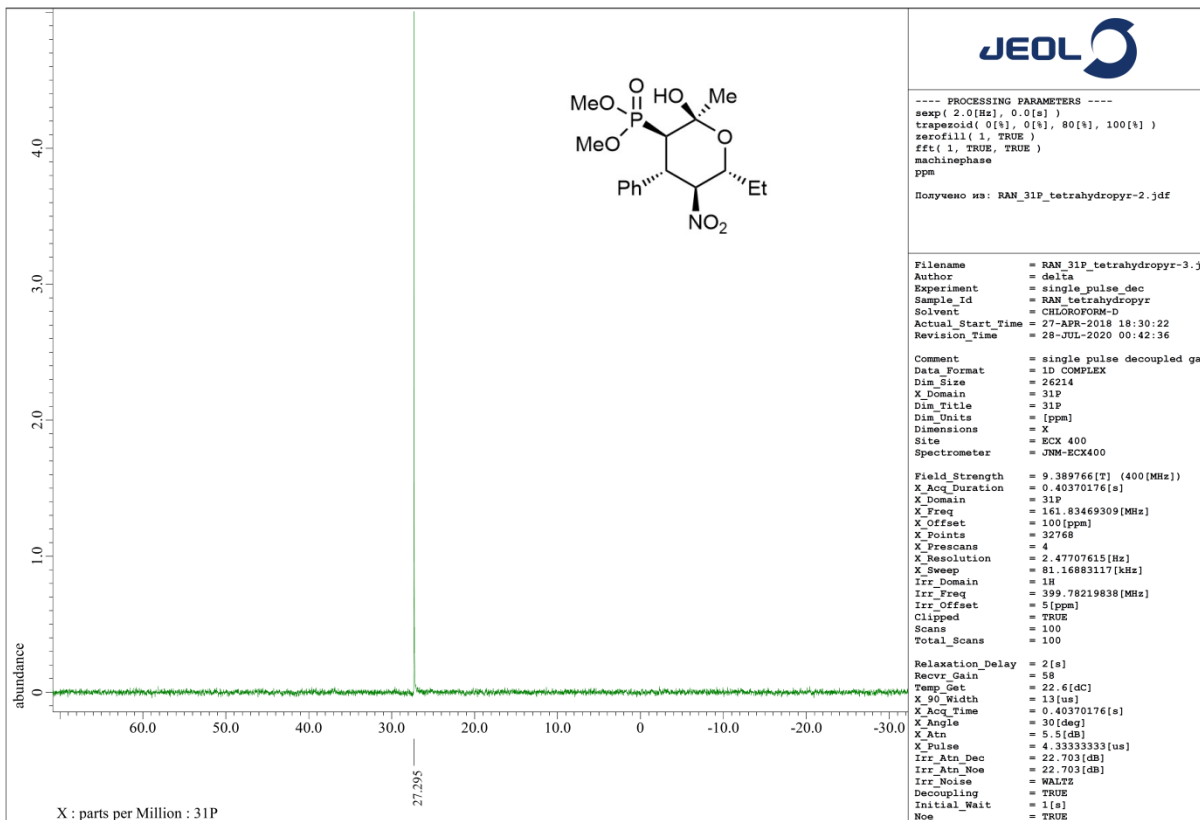
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X_Angle           = 30[deg]
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X_Pulse           = 2.72[us]
Irr_Atn_Dec       = 22.703[db]
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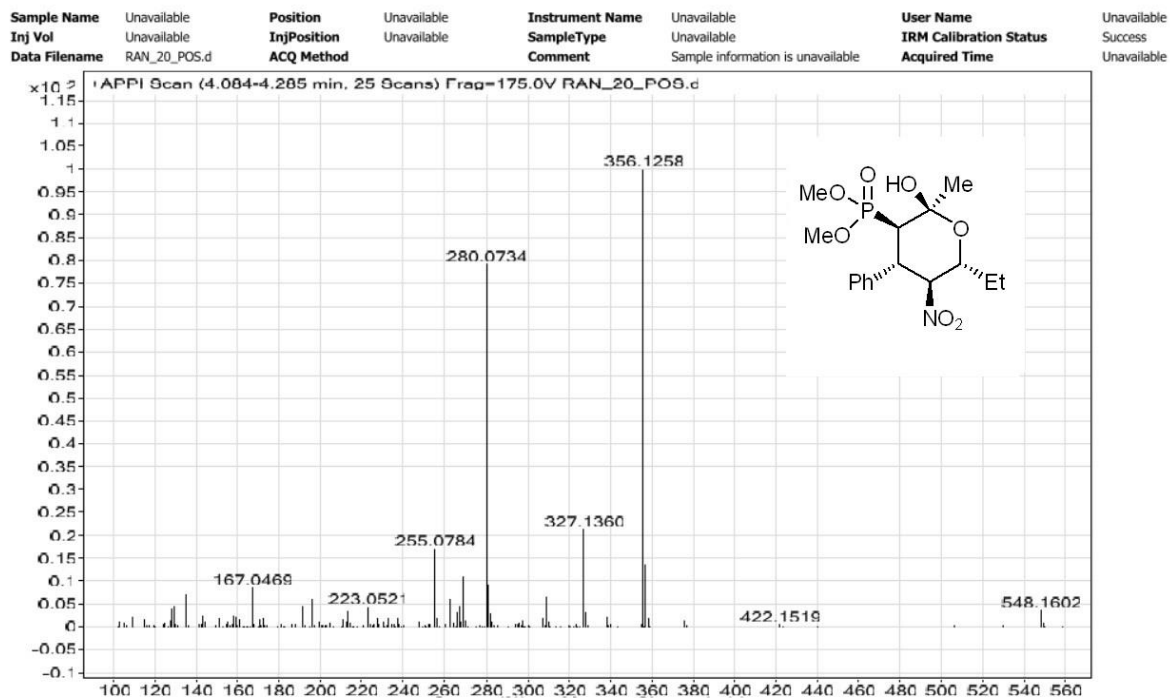

DEPT NMR spectra of dimethyl [(2*S*,3*R*,4*S*,5*S*,6*R*)-6-ethyl-2-hydroxy-2-methyl-5-nitro-4-phenyltetrahydro-2*H*-pyran-3-yl)phosphonate (**13a**) in CDCl₃



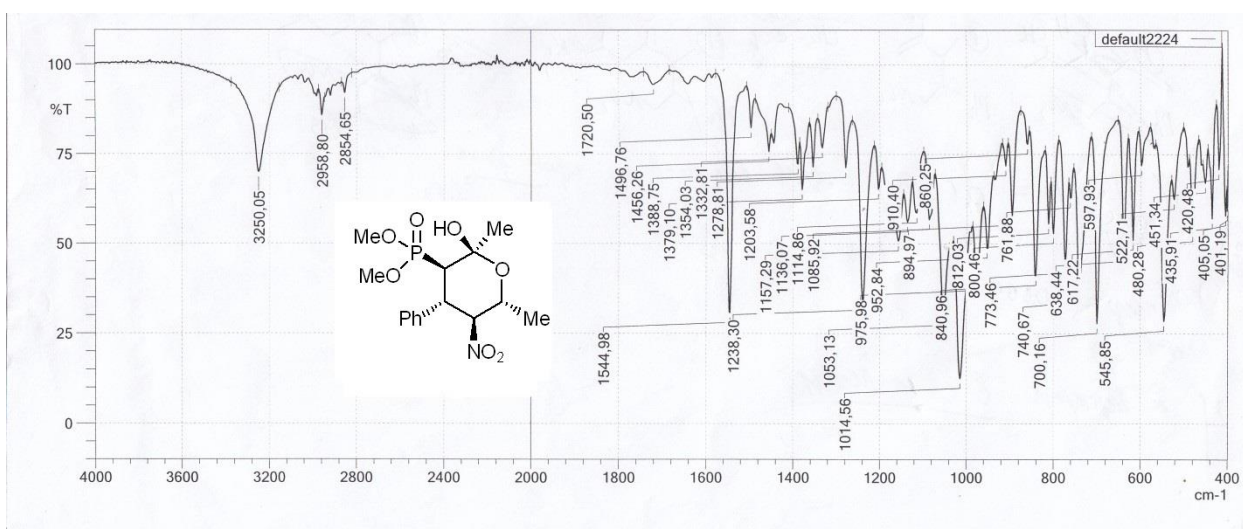
³¹P NMR spectra of dimethyl [(2*S*,3*R*,4*S*,5*S*,6*R*)-6-ethyl-2-hydroxy-2-methyl-5-nitro-4-phenyltetrahydro-2*H*-pyran-3-yl)phosphonate (**13a**) in CDCl₃

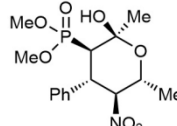


HRMS of dimethyl [(2*S*,3*R*,4*S*,5*S*,6*R*)-6-ethyl-2-hydroxy-2-methyl-5-nitro-4-phenyltetrahydro-2*H*-pyran-3-yl]phosphonate (**13a**)



FTIR spectra of dimethyl [(2*S*,3*R*,4*S*,5*S*,6*R*)-2-hydroxy-2,6-dimethyl-5-nitro-4-phenyltetrahydro-2*H*-pyran-3-yl]phosphonate (**13b**)



pyran-3-yl]phosphonate (**13b**) in CDCl₃

```

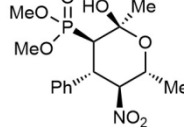
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Author            = delta
Experiment         = single_pulse.ex2
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Solvent           = CHLOROFORM-D
Actual_StartTime  = 4-MAY-2018 01:09:17
RevisionTime      = 28-JULY-2020 01:04:40

Comment           = single_pulse
Data_Format       = 1D_COMPLEX
Dim_Size          = 26214
X_Domain          = 1H
Dim_Title         = 1H
Dim_Units         = [ppm]
Dimensions        = CX
Site              = CXC 400
Spectrometer      = JNM-ECX400

Field_Strength     = 9.389766[T] (400[MHz])
XAcqDuration      = 4.36731904[s]
X_Domain          = 1H
X_Freq            = 399.78219838 [MHz]
X_Offset          = 7[ppm]
Pulse              = 2768
P_Prescans        = 1
X_Resolution      = 0.22897343[Hz]
X_Sweep           = 7.5030012[kHz]
X_Domain          = 1H
Irr_Freq          = 399.78219838 [MHz]
Irr_Offset        = 5[ppm]
Irr_Domain        = 1H
X_Freq           = 399.78219838 [MHz]
Tri_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 8
Total_Scans       = 8

Relaxation_Delay   = 5[s]
Recvr_Gain        = 36
Pump_Gat          = 45[deg]
X_90_Width        = 13.9.us(10)
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X_Angle           = 45[deg]
X_Ato             = 3[deg]
X_Pulse           = 95[ppm]
Irr_Mode          = OFF
Tri_Mode          = OFF
DANTE_Pressat     = FALSE

```

pyran-3-yl]phosphonate (**13b**) in CDCl_3 

```

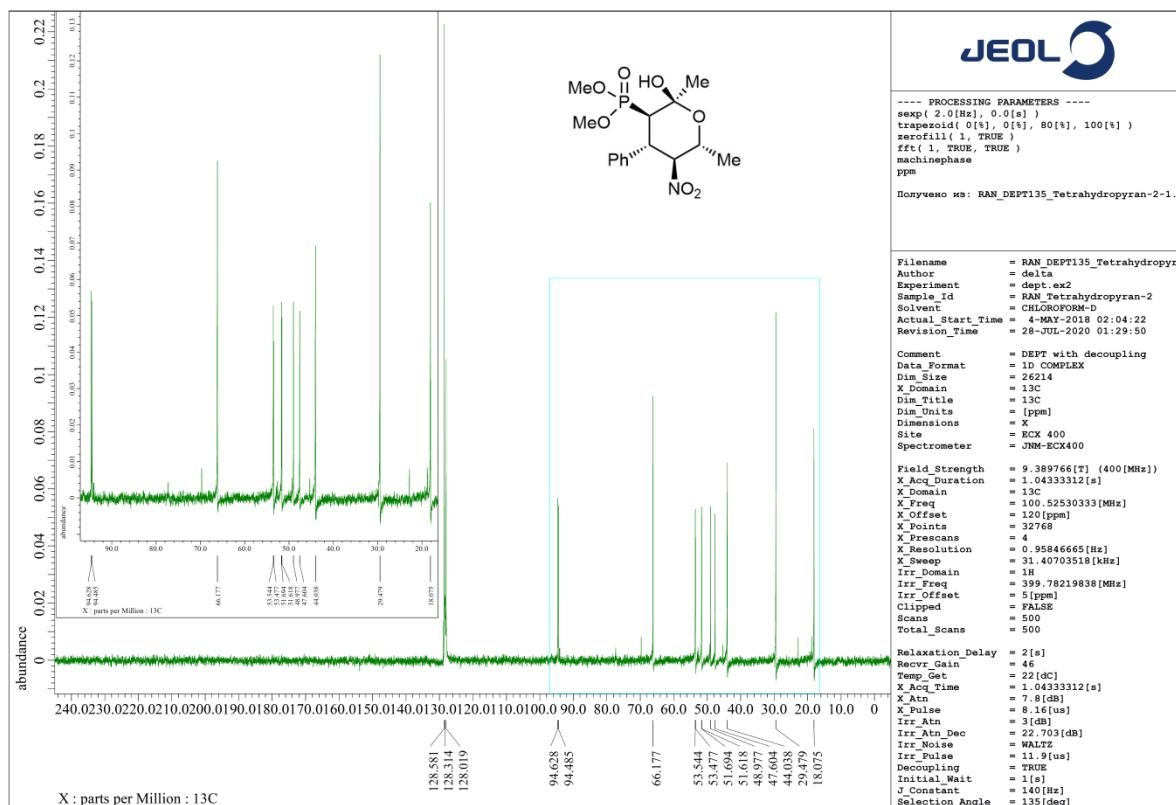
---- PROCESSING PARAMETERS ----
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trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1, TRUE )
fft( 1, TRUE, TRUE )
machinephase
ppm

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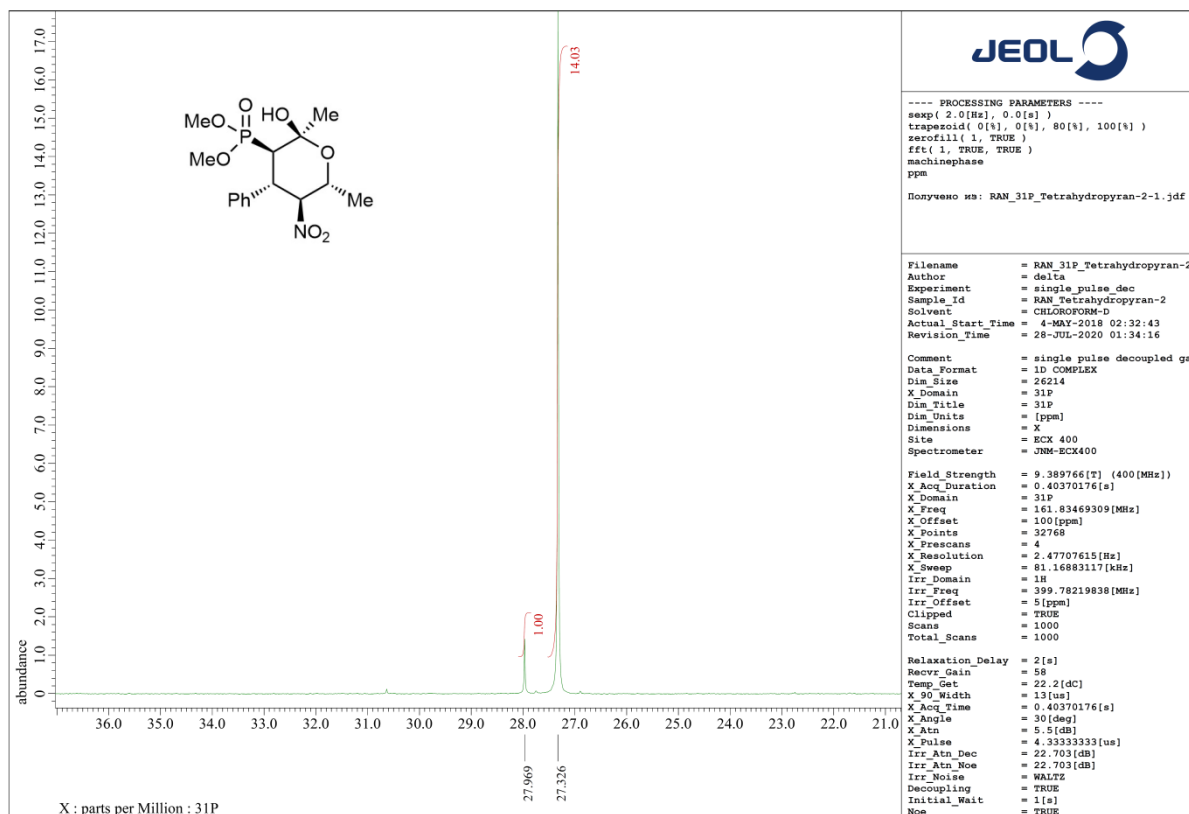
Получено из: RAN 13C Tetrahydropyran-2-1.idf

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Author	=	delc
Experiment	=	single_pulse_dec
Sample_Id	=	RAN_Tetrahedropyran-2
Sample_Prm	=	CPDPRISM-0
Actual_Start_Time	=	4-MAY-2018 01:13:18
Revision_Time	=	28-JUL-2020 01:24:50
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Data_Format	=	1D COMPLEX
Dim_Size	=	26214
X_Domain	=	1.6333312[s]
Dim_Title	=	13C
Dim_Units	=	[ppm]
Dimensions	=	X
Site	=	CECK 400
Spectrometer	=	JNM-ECX400
Field_Strength	=	9.389766[T] (400[MHz])
X_Freq	=	100.3333312[s]
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X_Freq	=	100.52530333[MHz]
X_Offset	=	120[ppm]
X_Pos	=	2768
X_Prescans	=	4
X_Resolution	=	0.95846665[Hz]
X_Sweep	=	31.40703518[kHz]
Y_Domain	=	13C
Y_Freq	=	399.78219838[MHz]
Y_Offset	=	5[ppm]
Clipped	=	FALSE
Scans	=	1000
Total_Scans	=	1000
Relaxation_Delay	=	2[s]
Recvr_Gain	=	46
Temp_Cel	=	22.3[dC]
X_90_Width	=	1.1643[s]
X_Acq_Time	=	0.804333312[s]
X_Angle	=	0[deg]
X_Atn	=	7.8[db]
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Yrr_Atn_Doe	=	22.703[db]
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Yrr_Noise	=	WALTZ
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Initial_Wait	=	1[s]
Yrr_Prm	=	WALTZ

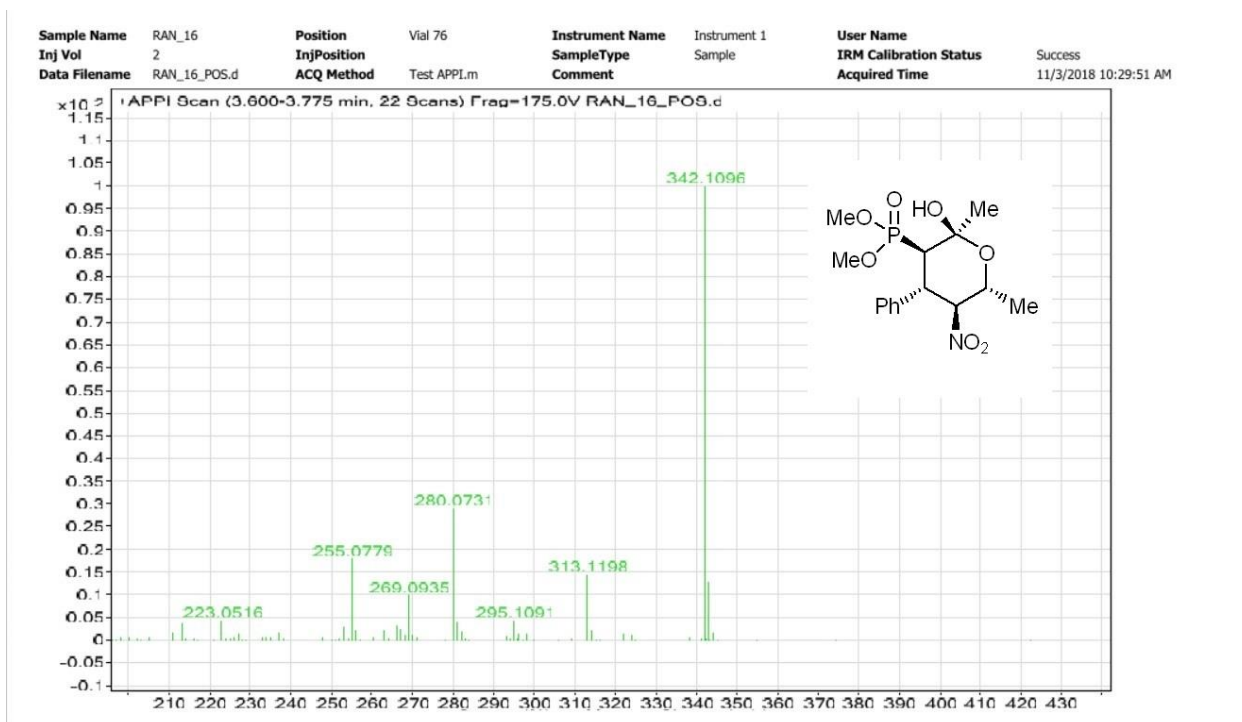
DEPT NMR spectra of dimethyl [(2*S*,3*R*,4*S*,5*S*,6*R*)-2-hydroxy-2,6-dimethyl-5-nitro-4-phenyltetrahydro-2*H*-pyran-3-yl]phosphonate (**13b**) in CDCl₃



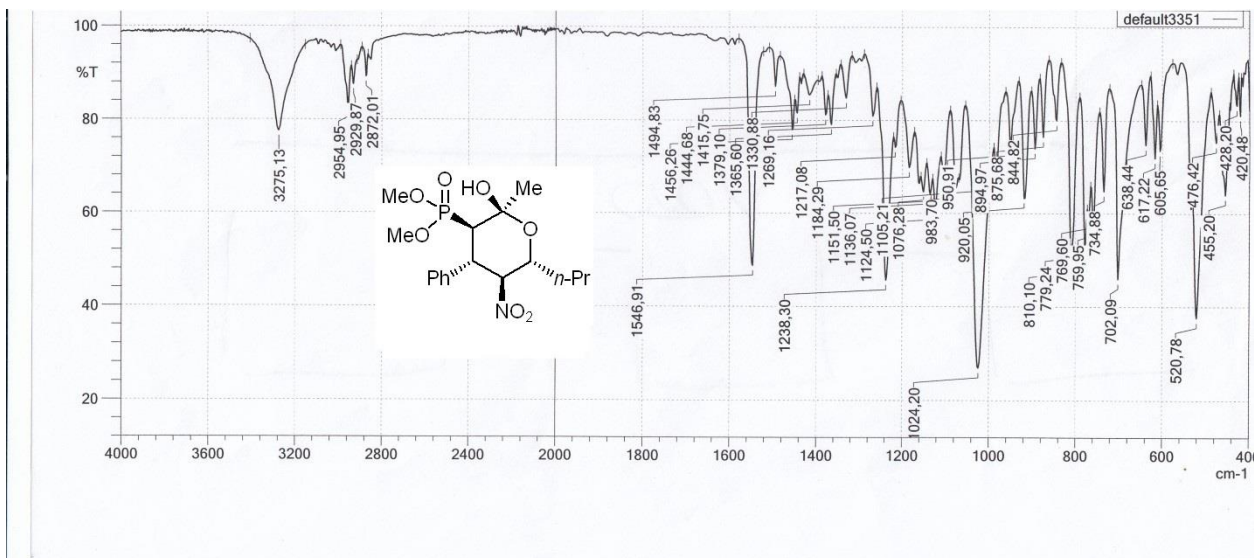
³¹P NMR spectra of dimethyl [(2*S*,3*R*,4*S*,5*S*,6*R*)-2-hydroxy-2,6-dimethyl-5-nitro-4-phenyltetrahydro-2*H*-pyran-3-yl]phosphonate (**13b**) in CDCl₃



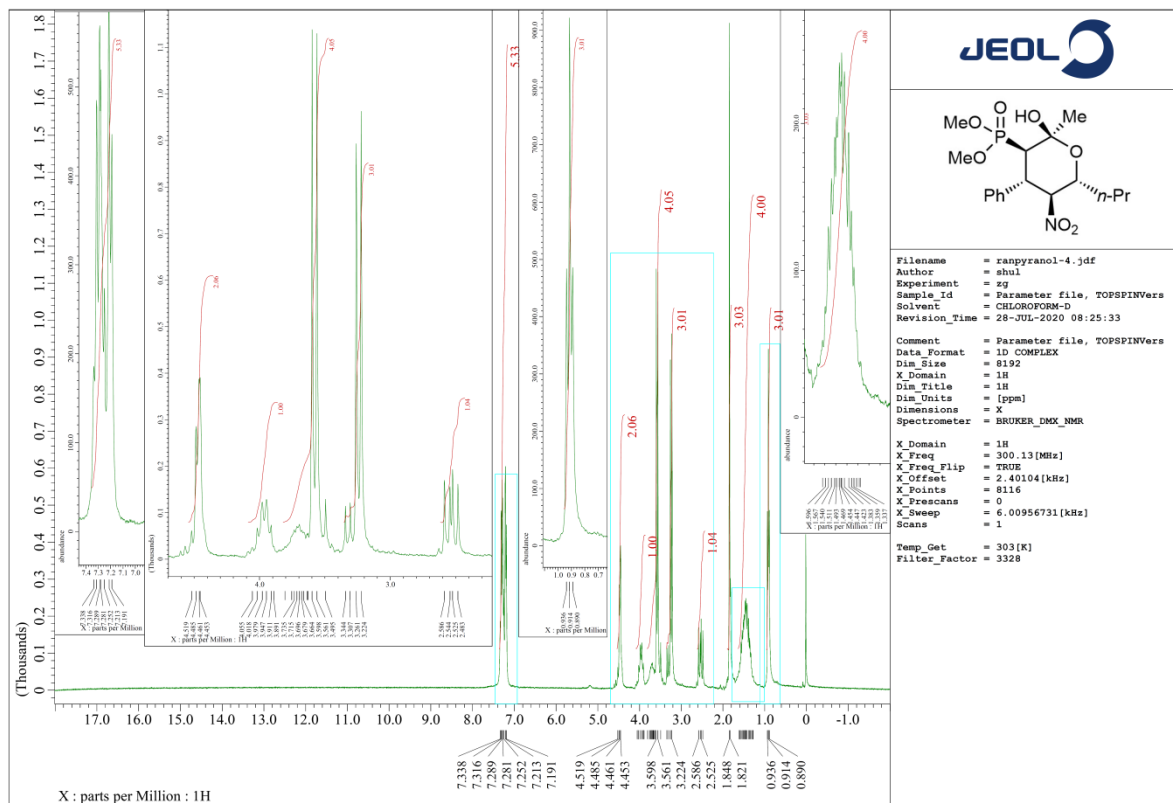
HRMS of dimethyl [(2*S*,3*R*,4*S*,5*S*,6*R*)-2-hydroxy-2,6-dimethyl-5-nitro-4-phenyltetrahydro-2*H*-pyran-3-yl]phosphonate (**13b**)



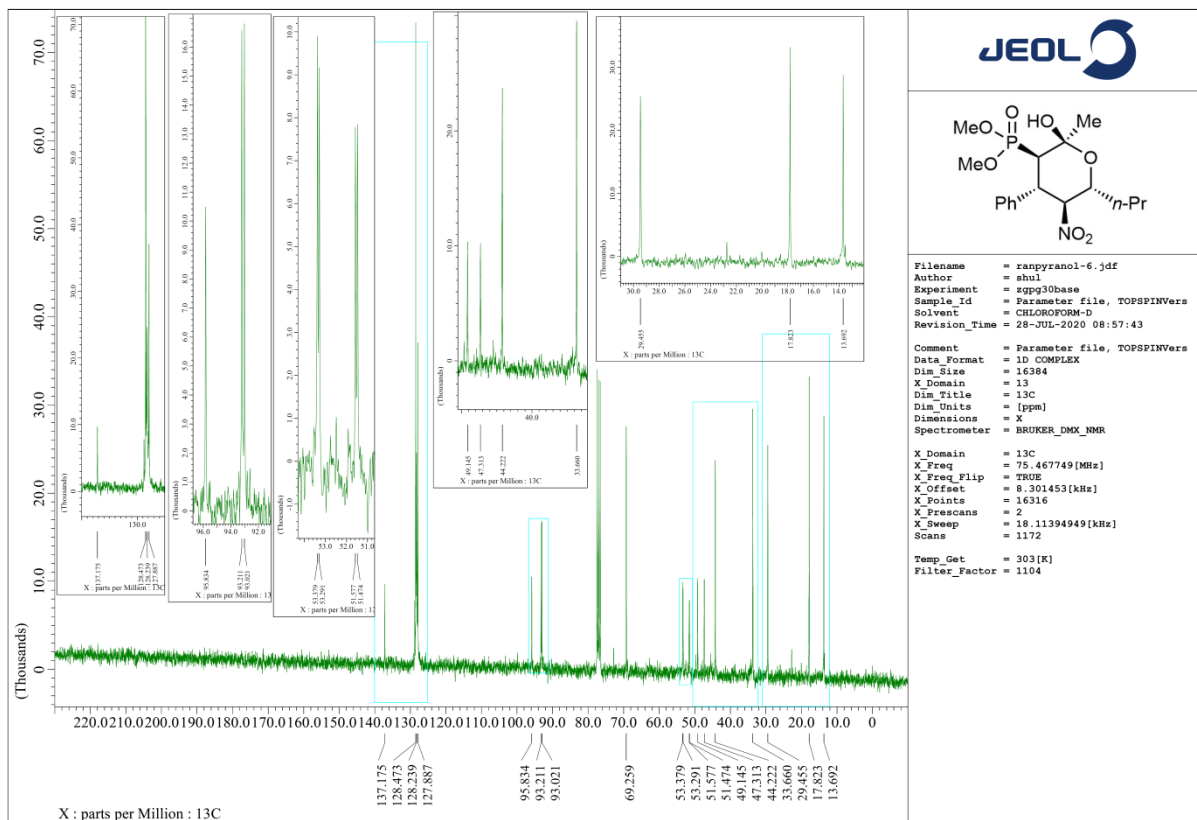
FTIR spectra of dimethyl [(2*S*,3*R*,4*S*,5*S*,6*R*)-2-hydroxy-2-methyl-5-nitro-4-phenyl-6-propyl-tetrahydro-2*H*-pyran-3-yl]phosphonate (**13c**)



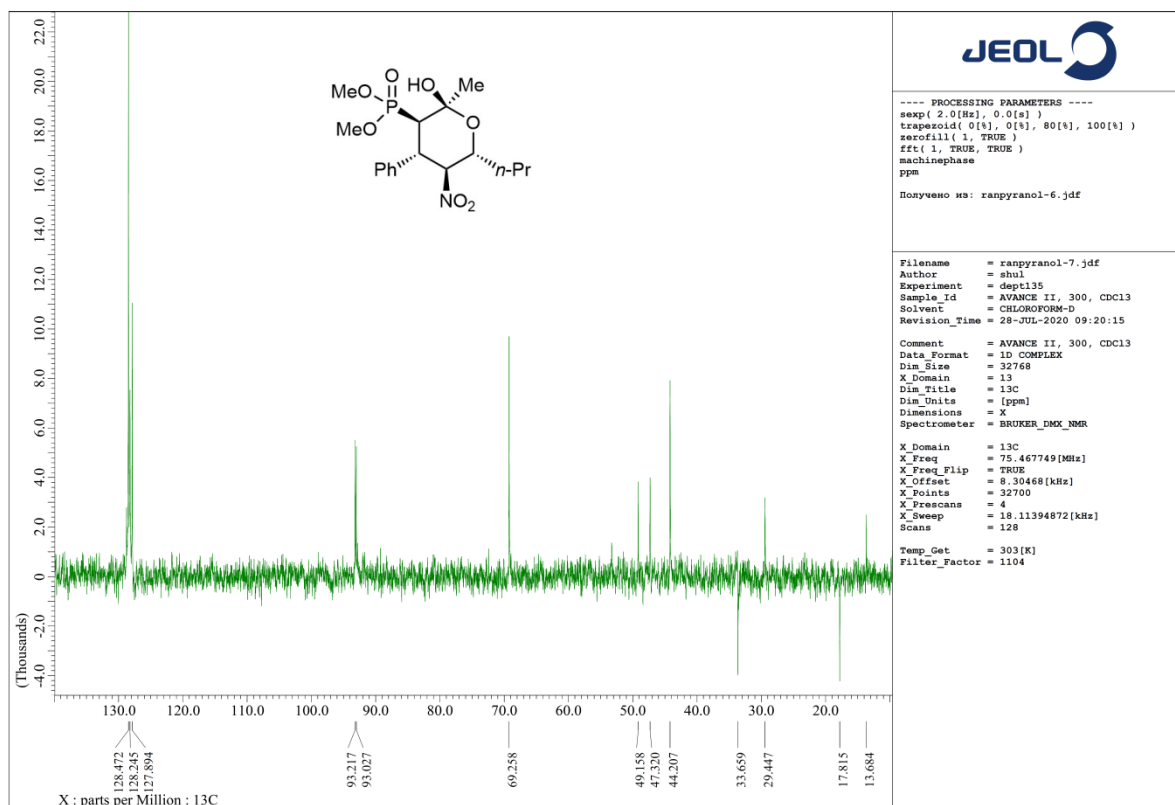
¹H NMR spectra of dimethyl [(2*S*,3*R*,4*S*,5*S*,6*R*)-2-hydroxy-2-methyl-5-nitro-4-phenyl-6-propyl-tetrahydro-2*H*-pyran-3-yl)phosphonate (**13c**) in CDCl₃



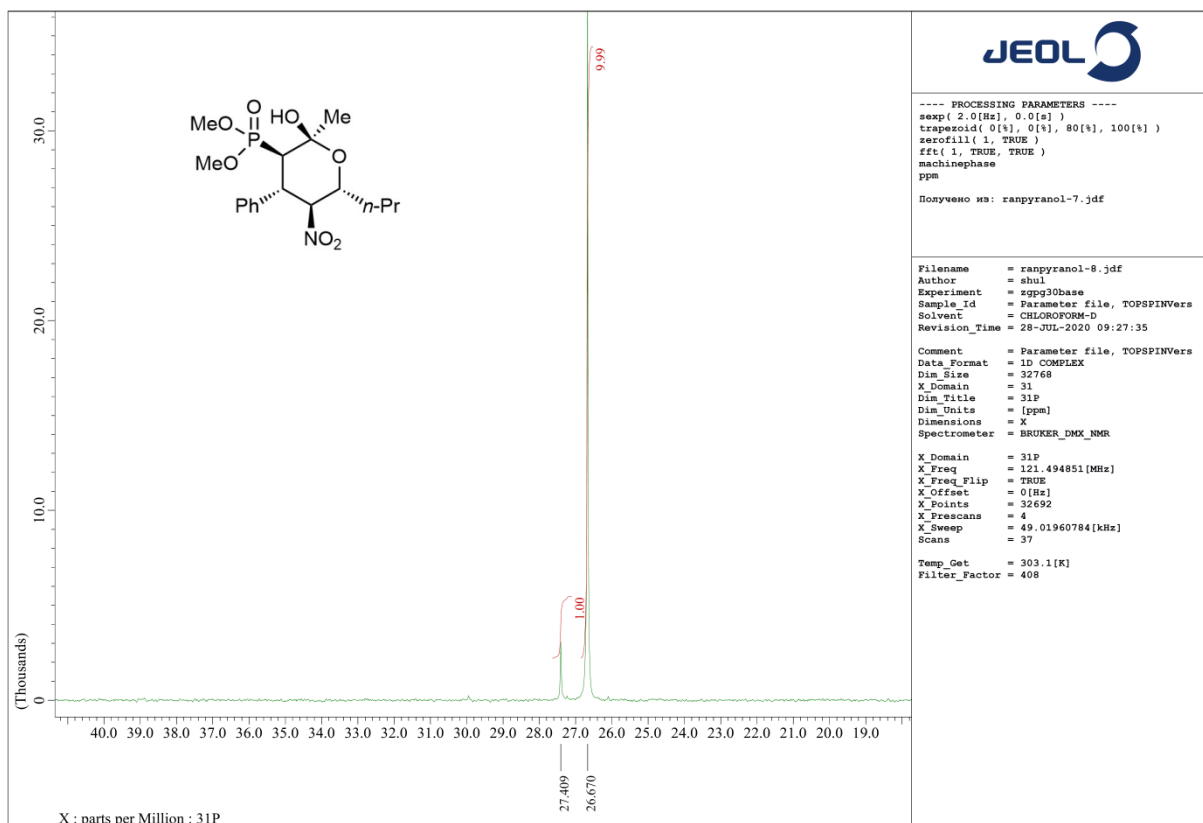
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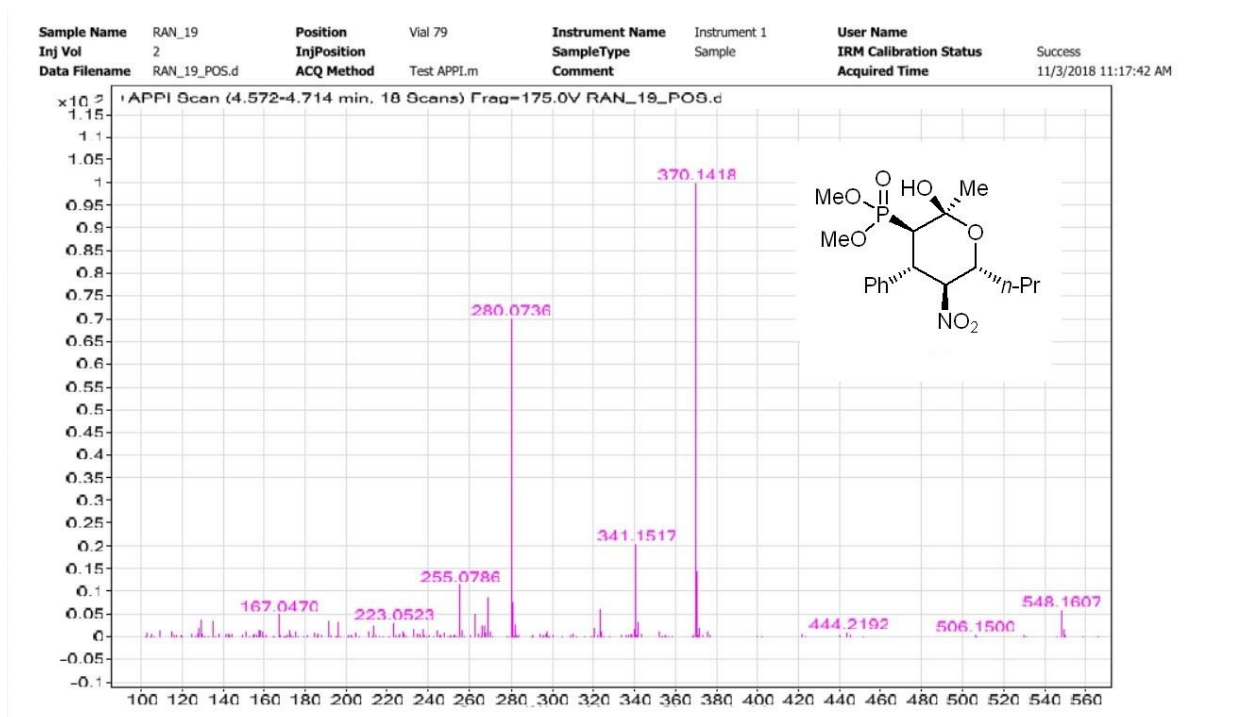
DEPT NMR spectra of dimethyl [(2*S*,3*R*,4*S*,5*S*,6*R*)-2-hydroxy-2-methyl-5-nitro-4-phenyl-6-propyl-tetrahydro-2*H*-pyran-3-yl)phosphonate (**13c**) in CDCl₃



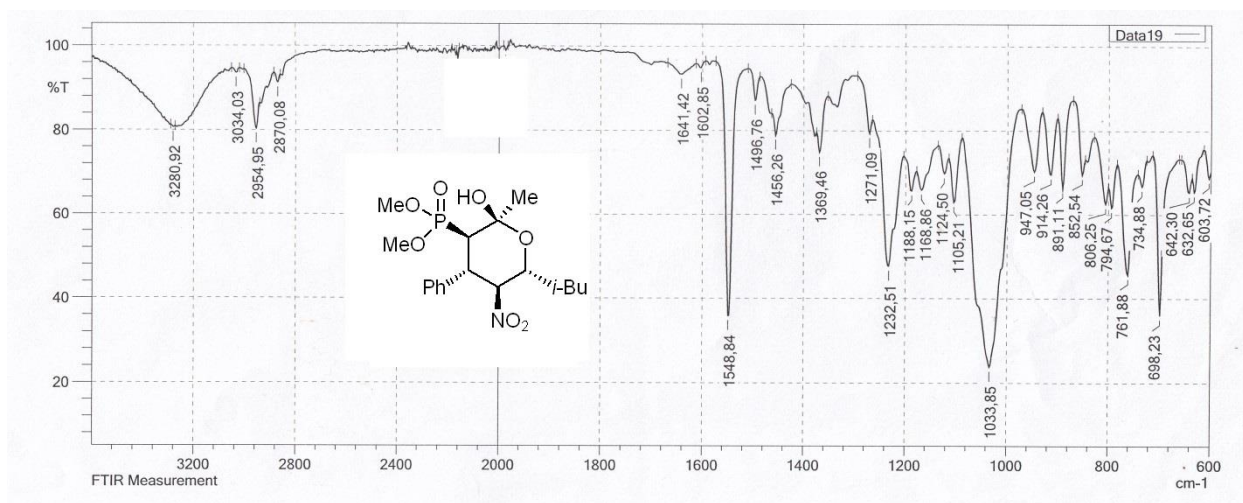
³¹P NMR spectra of dimethyl [(2*S*,3*R*,4*S*,5*S*,6*R*)-2-hydroxy-2-methyl-5-nitro-4-phenyl-6-propyl-tetrahydro-2*H*-pyran-3-yl)phosphonate (**13c**) in CDCl₃



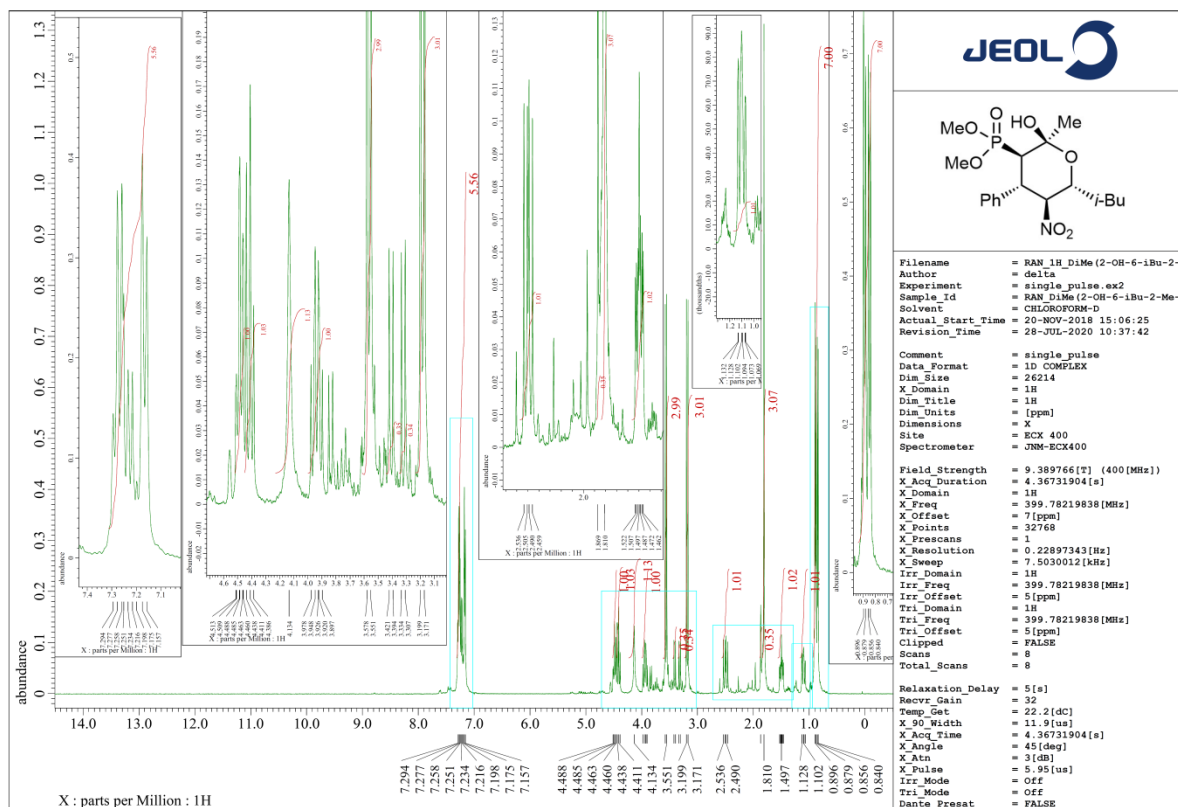
HRMS of dimethyl [(2*S*,3*R*,4*S*,5*S*,6*R*)-2-hydroxy-2-methyl-5-nitro-4-phenyl-6-propyl-tetrahydro-2*H*-pyran-3-yl)phosphonate (**13c**)



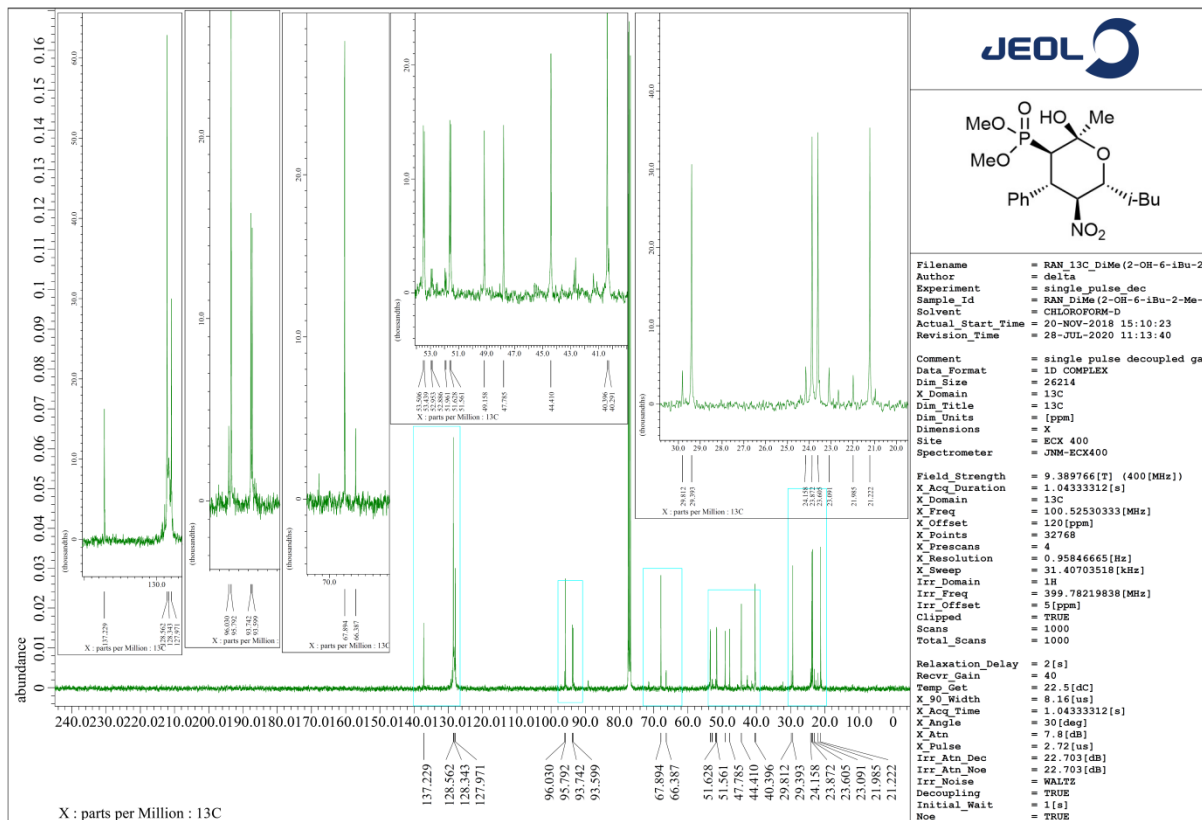
FTIR spectra of dimethyl [(2*S*,3*R*,4*S*,5*S*,6*R*)-2-hydroxy-6-isobutyl-2-methyl-5-nitro-4-phenyl-tetrahydro-2*H*-pyran-3-yl)phosphonate (**13d**)



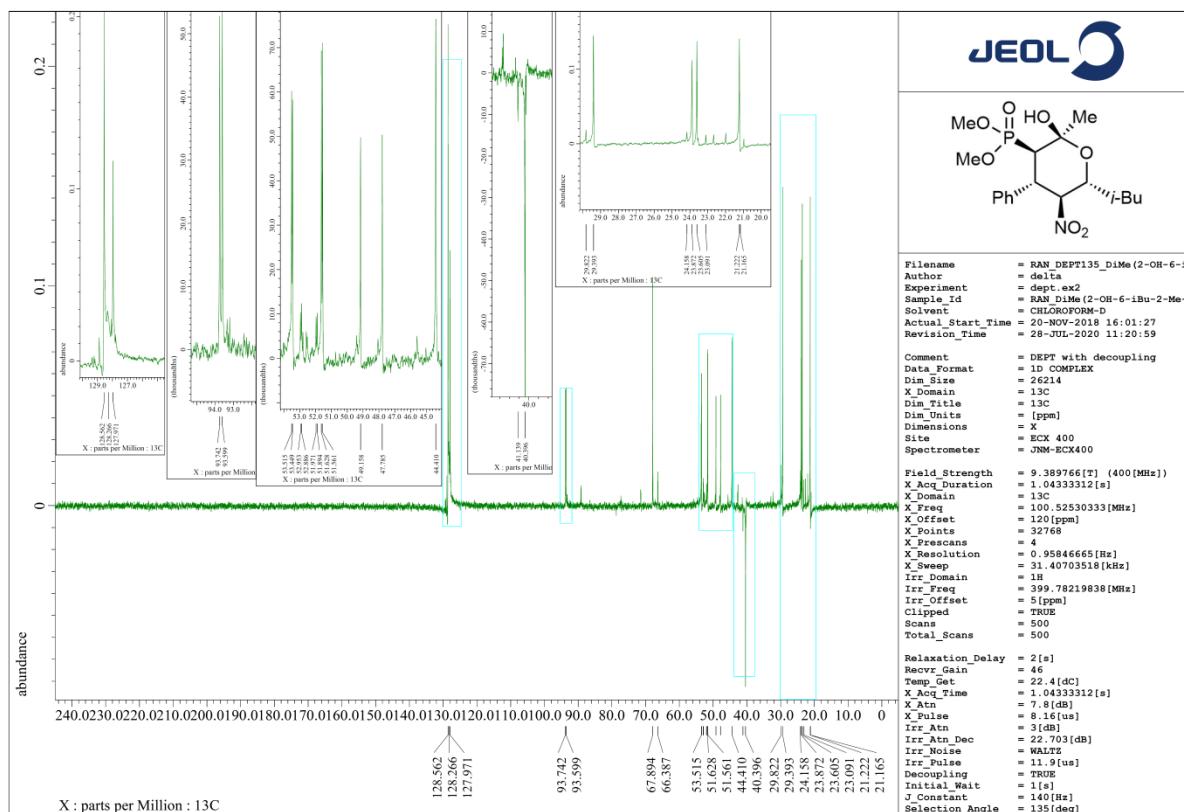
¹H NMR spectra of dimethyl [(2*S*,3*R*,4*S*,5*S*,6*R*)-2-hydroxy-6-isobutyl-2-methyl-5-nitro-4-phenyl-tetrahydro 2*H*-pyran-3-yl]phosphonate (**13d**) in CDCl₃



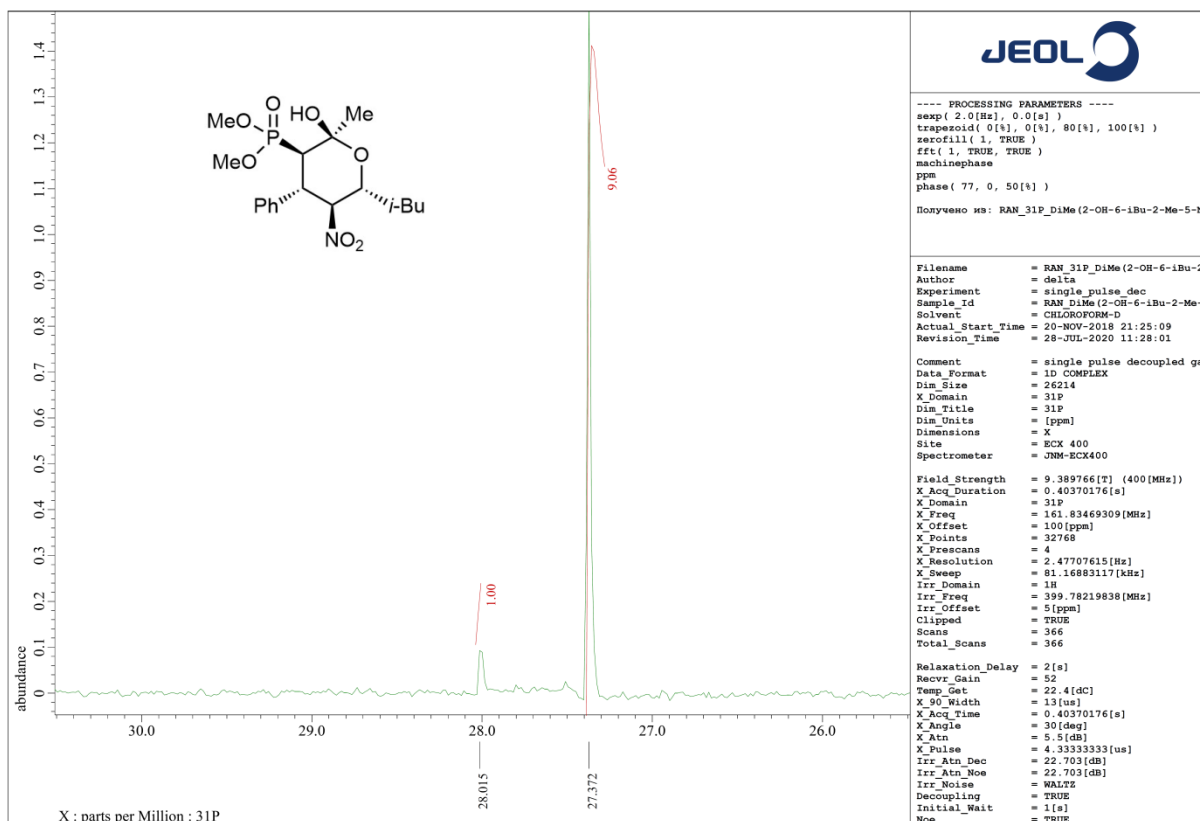
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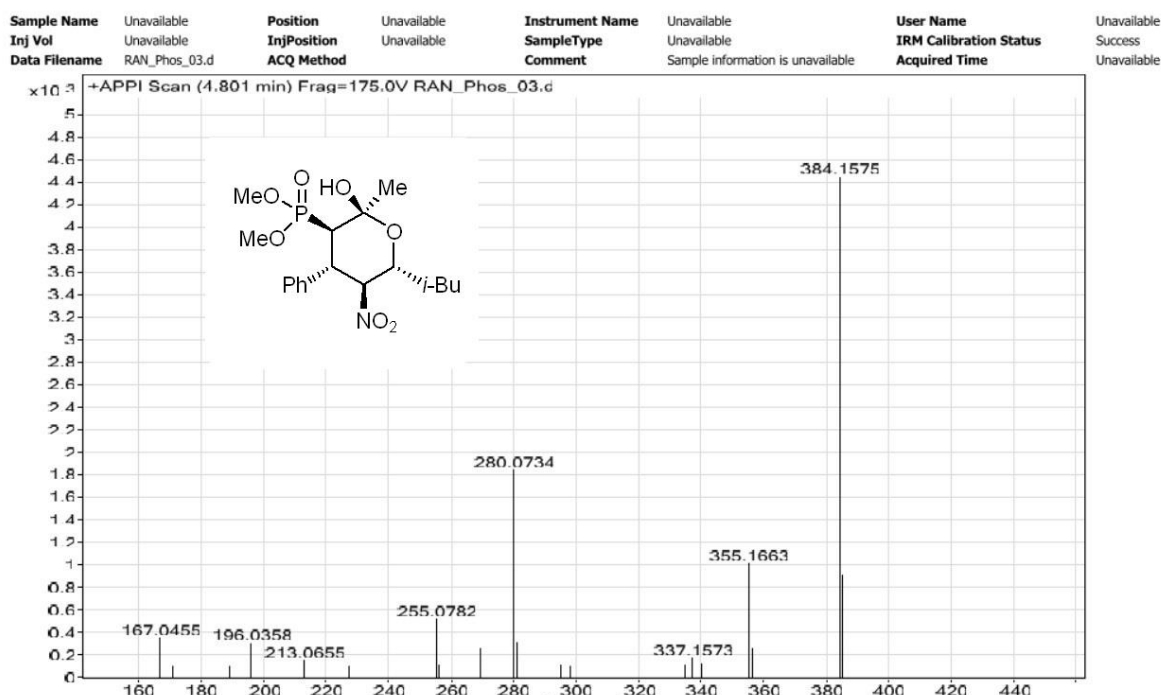
DEPT NMR spectra of dimethyl [(2*S*,3*R*,4*S*,5*S*,6*R*)-2-hydroxy-6-isobutyl-2-methyl-5-nitro-4-phenyl-tetrahydro 2*H*-pyran-3-yl)phosphonate (**13d**) in CDCl₃



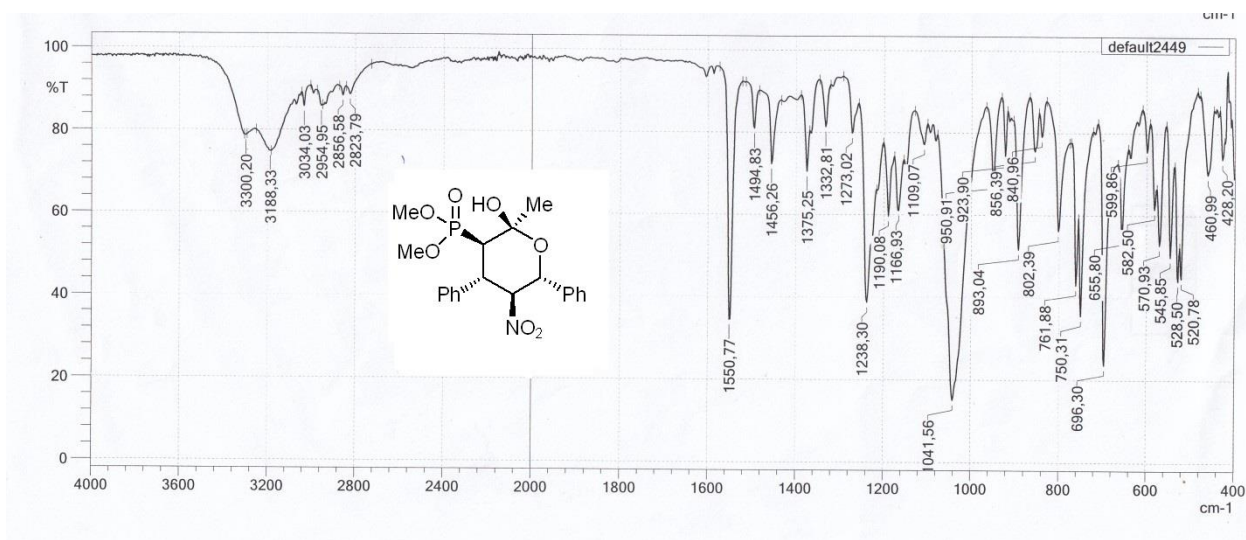
³¹P NMR spectra of dimethyl [(2*S*,3*R*,4*S*,5*S*,6*R*)-2-hydroxy-6-isobutyl-2-methyl-5-nitro-4-phenyl-tetrahydro 2*H*-pyran-3-yl)phosphonate (**13d**) in CDCl₃



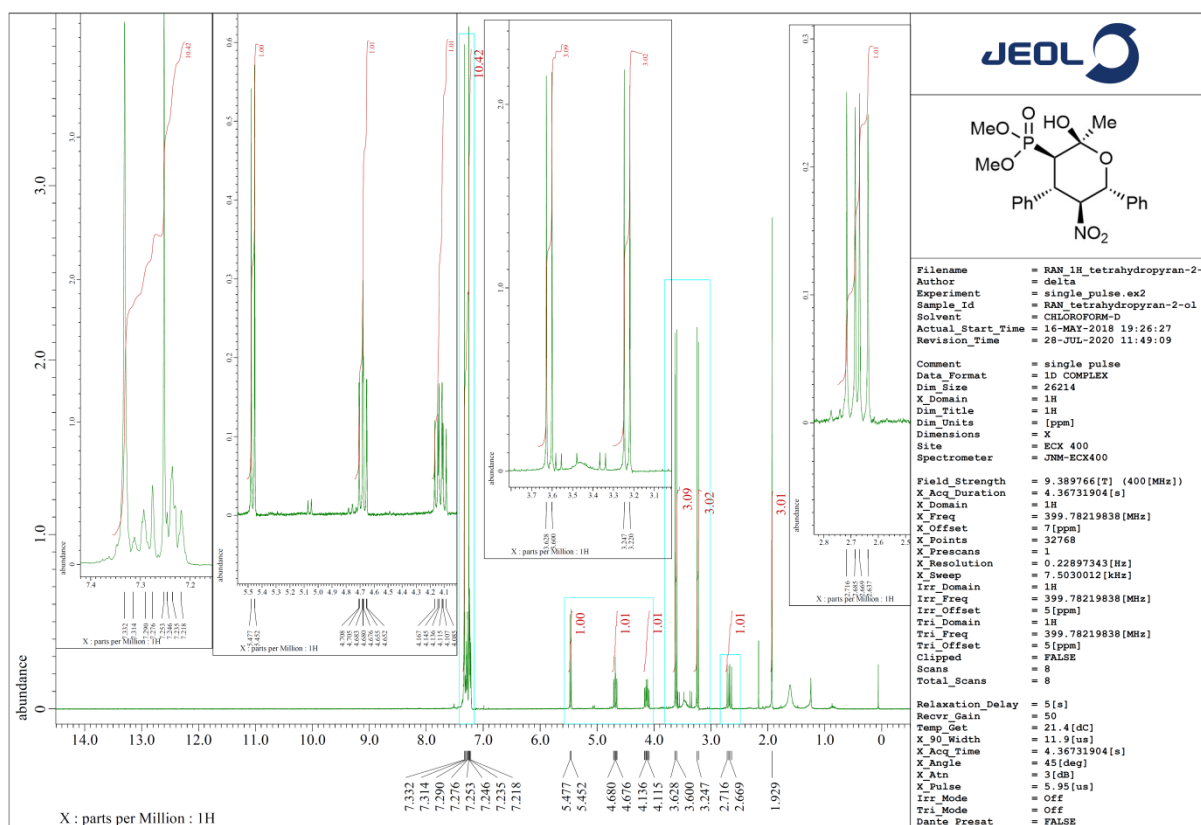
HRMS of dimethyl [(2*S*,3*R*,4*S*,5*S*,6*R*)-2-hydroxy-6-isobutyl-2-methyl-5-nitro-4-phenyl-tetrahydro 2*H*-pyran-3-yl]phosphonate (**13d**)



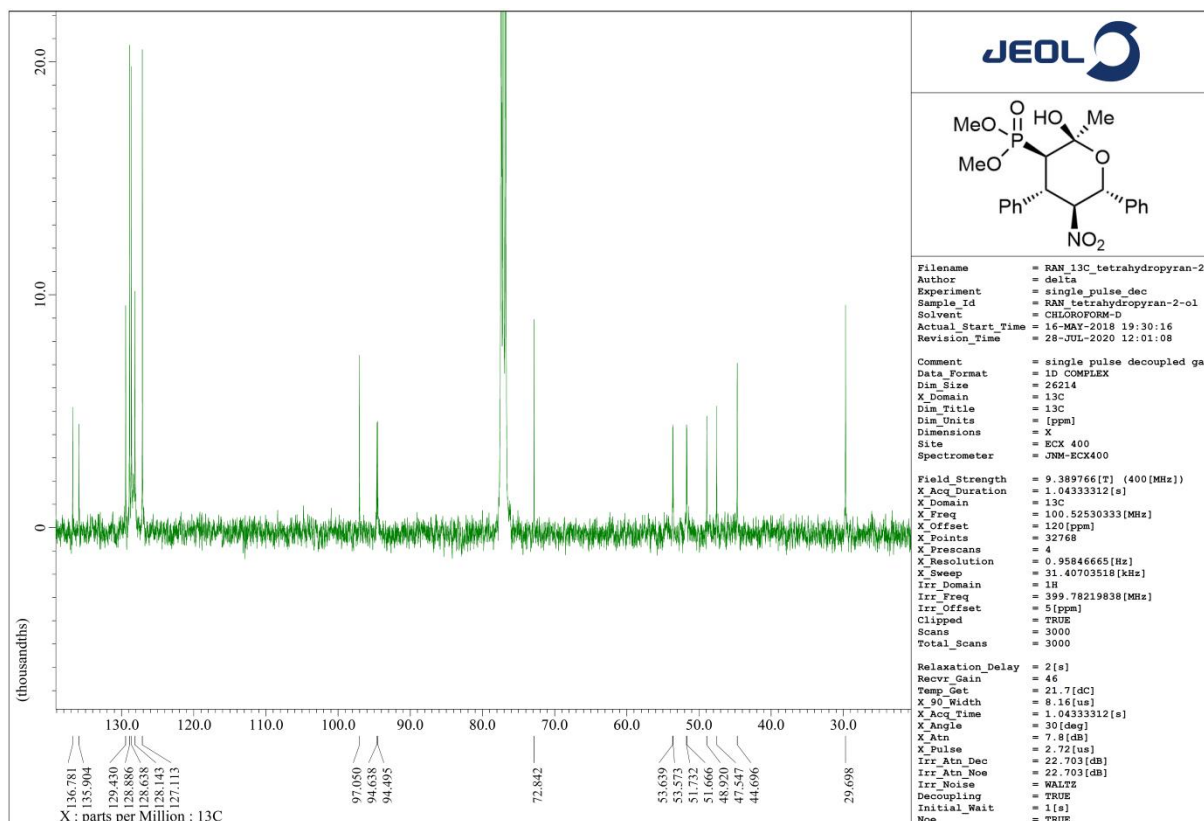
FTIR spectra of dimethyl [(2*S*,3*R*,4*S*,5*S*,6*R*)-2-hydroxy-2-methyl-5-nitro-4,6-diphenyltetrahydro-2*H*-pyran-3-yl]phosphonate (**13e**)



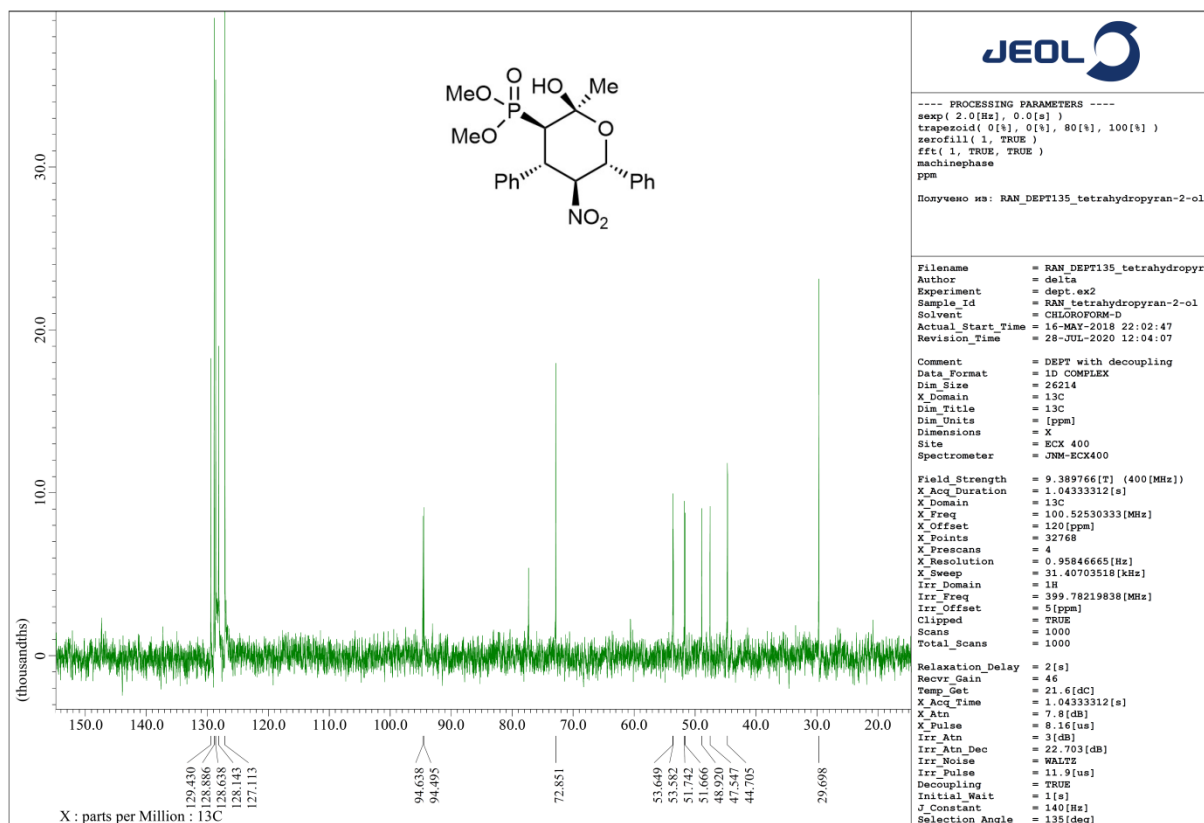
¹H NMR spectra of dimethyl [(2*S*,3*R*,4*S*,5*S*,6*R*)-2-hydroxy-2-methyl-5-nitro-4,6-diphenyltetrahydro-2*H*-pyran-3-yl]phosphonate (**13e**) in CDCl₃



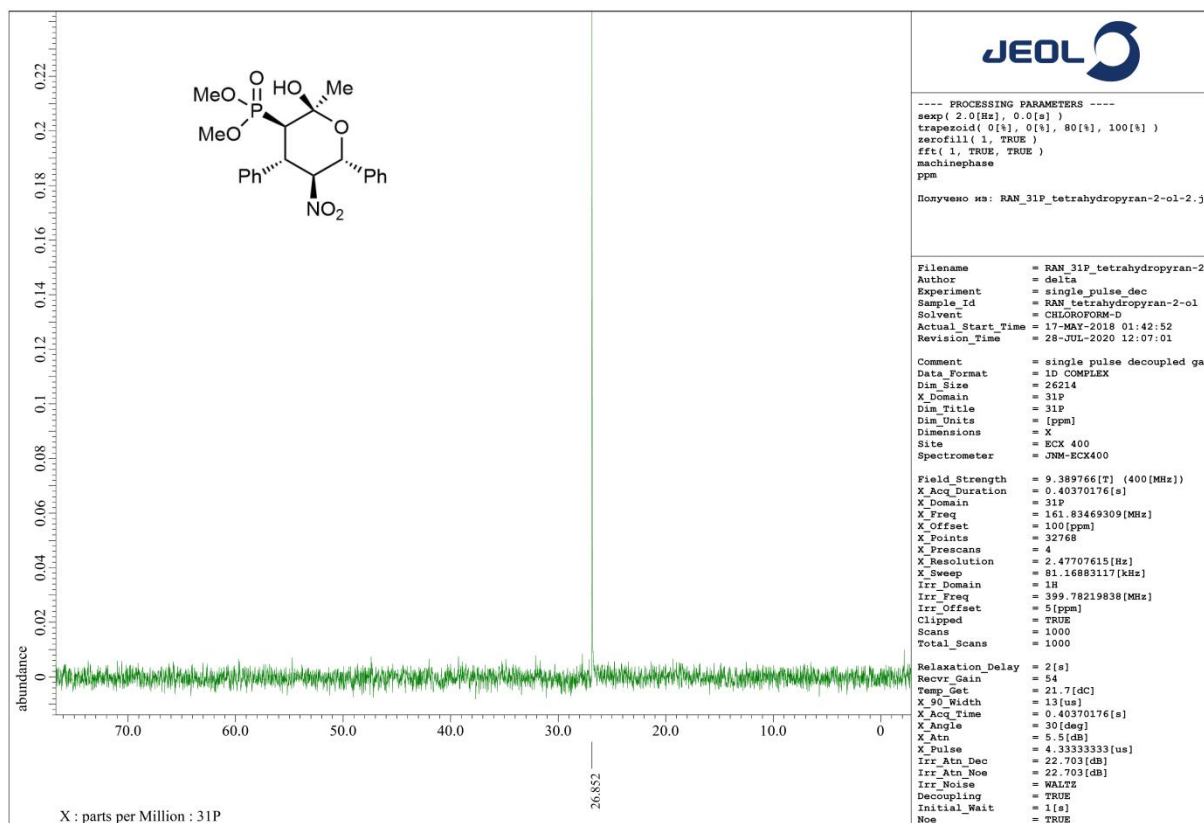
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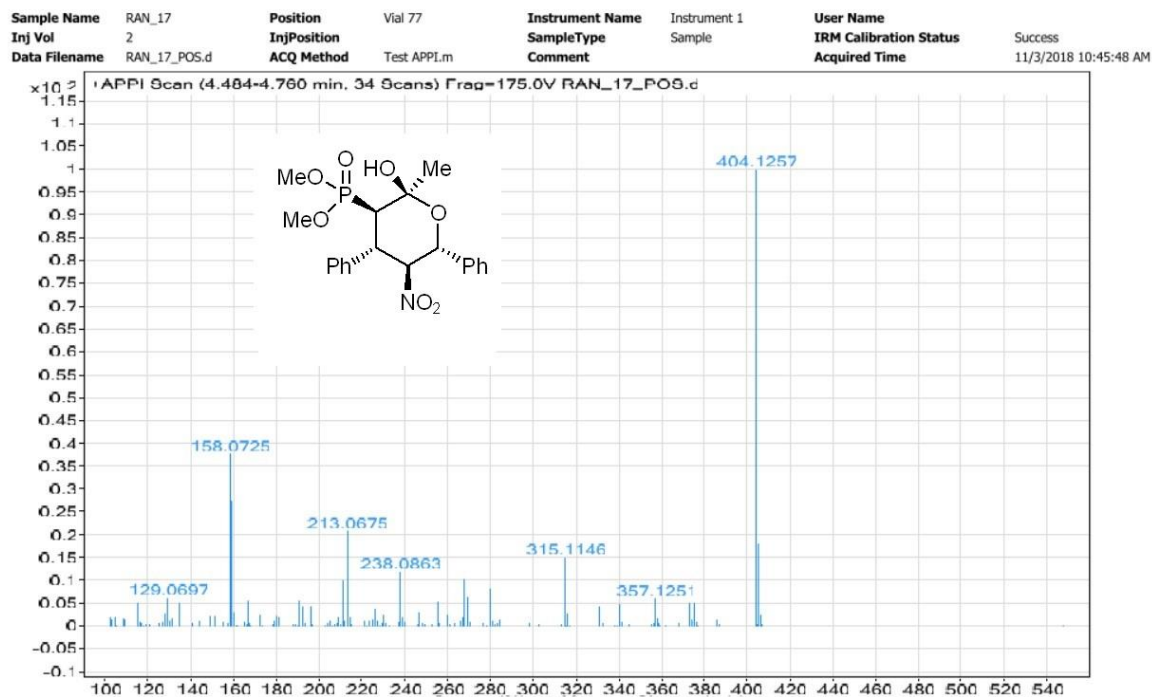
DEPT NMR spectra of dimethyl [(2*S*,3*R*,4*S*,5*S*,6*R*)-2-hydroxy-2-methyl-5-nitro-4,6-diphenyltetrahydro-2*H*-pyran-3-yl]phosphonate (**13e**) in CDCl₃



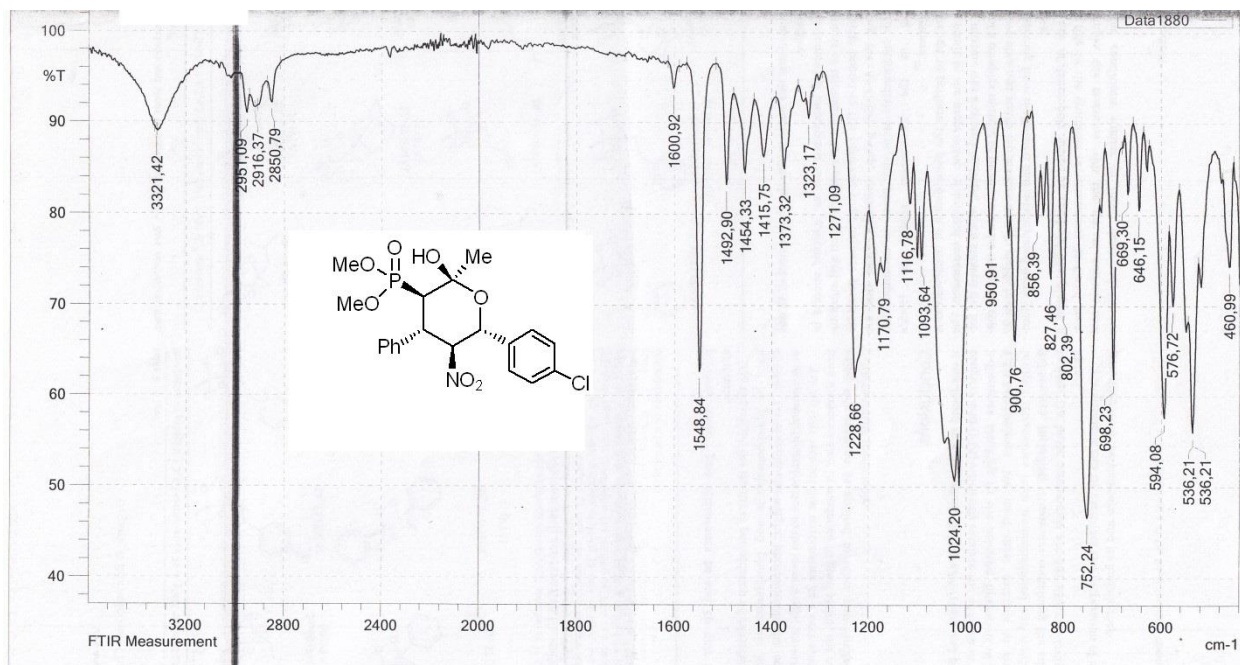
³¹P NMR spectra of dimethyl [(2*S*,3*R*,4*S*,5*S*,6*R*)-2-hydroxy-2-methyl-5-nitro-4,6-diphenyltetrahydro-2*H*-pyran-3-yl]phosphonate (**13e**) in CDCl₃



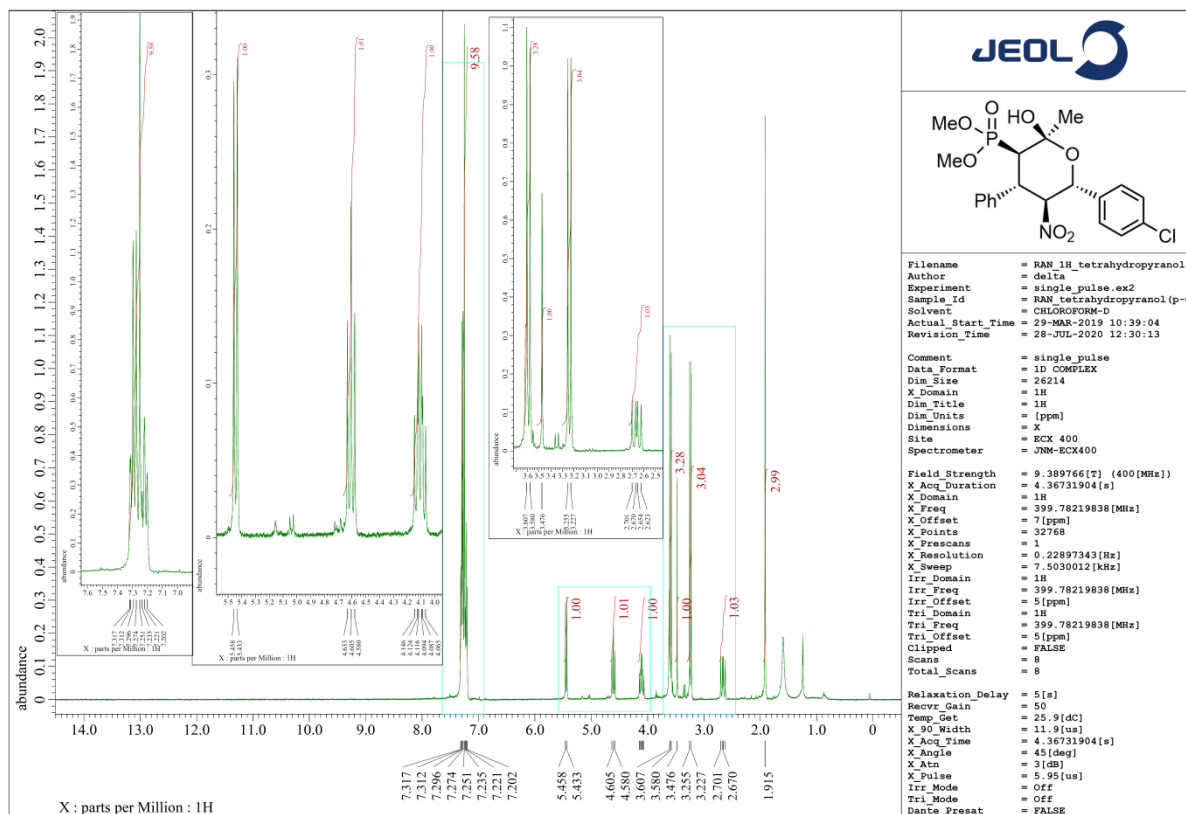
HRMS of dimethyl [(2*S*,3*R*,4*S*,5*S*,6*R*)-2-hydroxy-2-methyl-5-nitro-4,6-diphenyltetrahydro-2*H*-pyran-3-yl]phosphonate (**13e**)



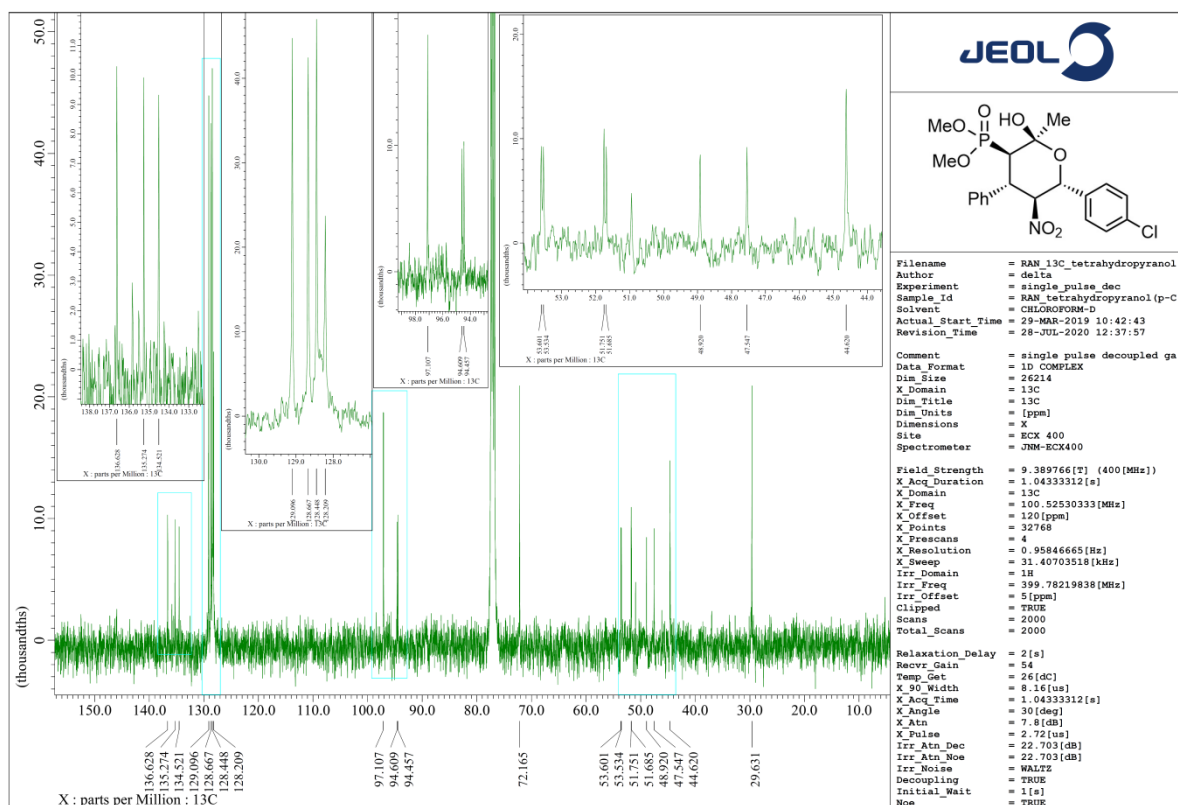
FTIR spectra of dimethyl [(2*S*,3*R*,4*S*,5*S*,6*R*)-6-(4-chlorophenyl)-2-hydroxy-2-methyl-5-nitro-4-phenyltetrahydro-2*H*-pyran-3-yl]phosphonate (**13f**)



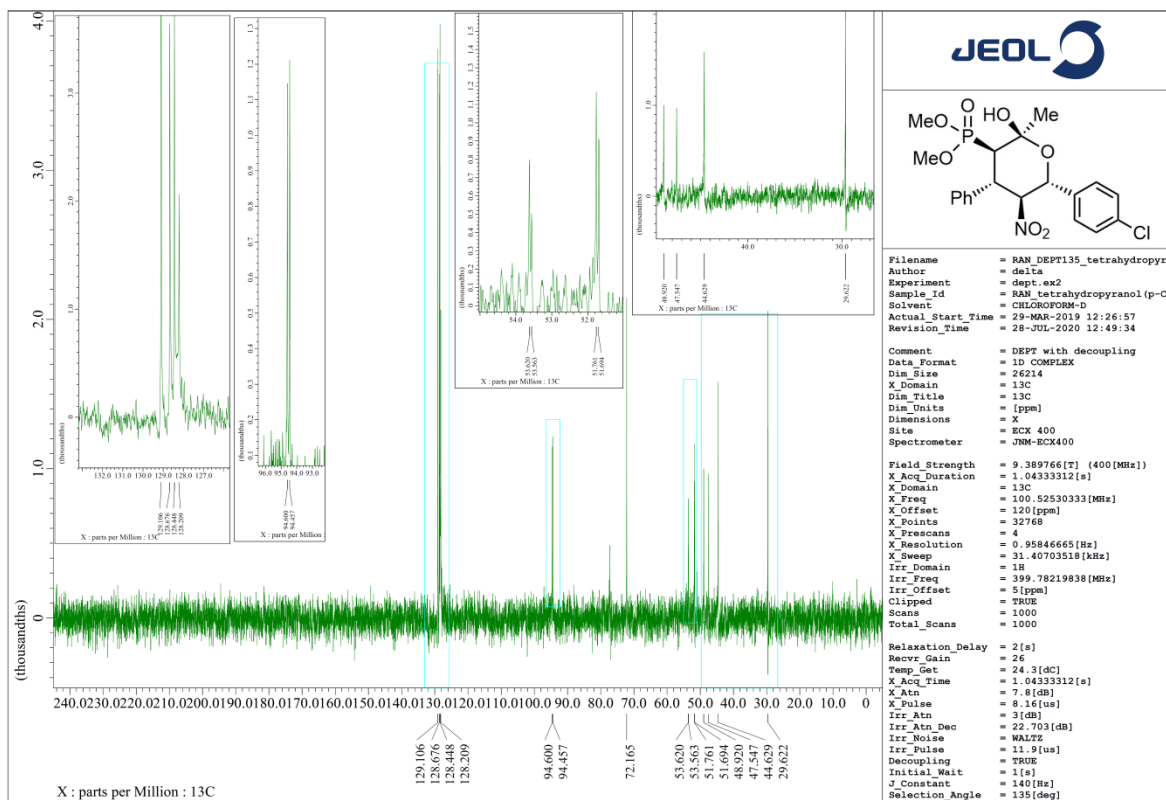
¹H NMR spectra of dimethyl [(2*S*,3*R*,4*S*,5*S*,6*R*)-6-(4-chlorophenyl)-2-hydroxy-2-methyl-5-nitro-4-phenyltetrahydro-2*H*-pyran-3-yl]phosphonate (**13f**) in CDCl₃



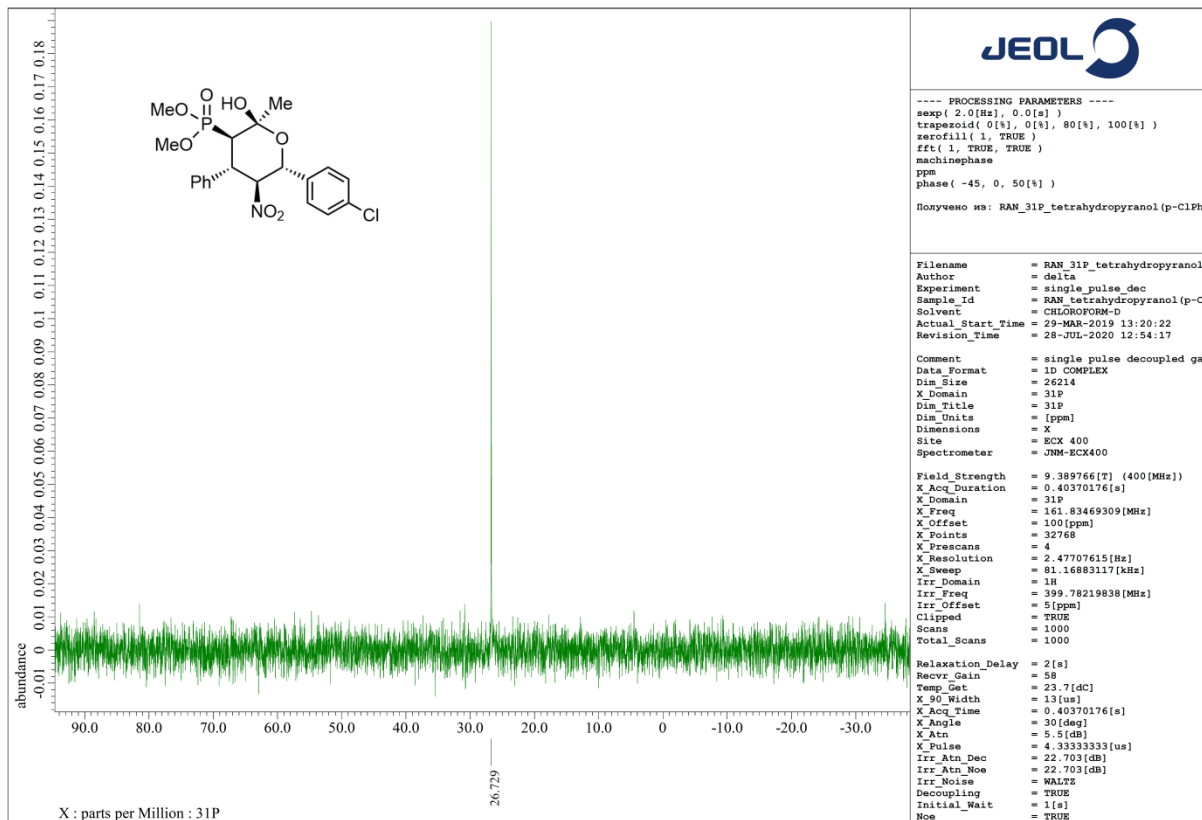
¹³C NMR spectra of dimethyl [(2*S*,3*R*,4*S*,5*S*,6*R*)-6-(4-chlorophenyl)-2-hydroxy-2-methyl-5-nitro-4-phenyltetrahydro-2*H*-pyran-3-yl]phosphonate (**13f**) in CDCl₃



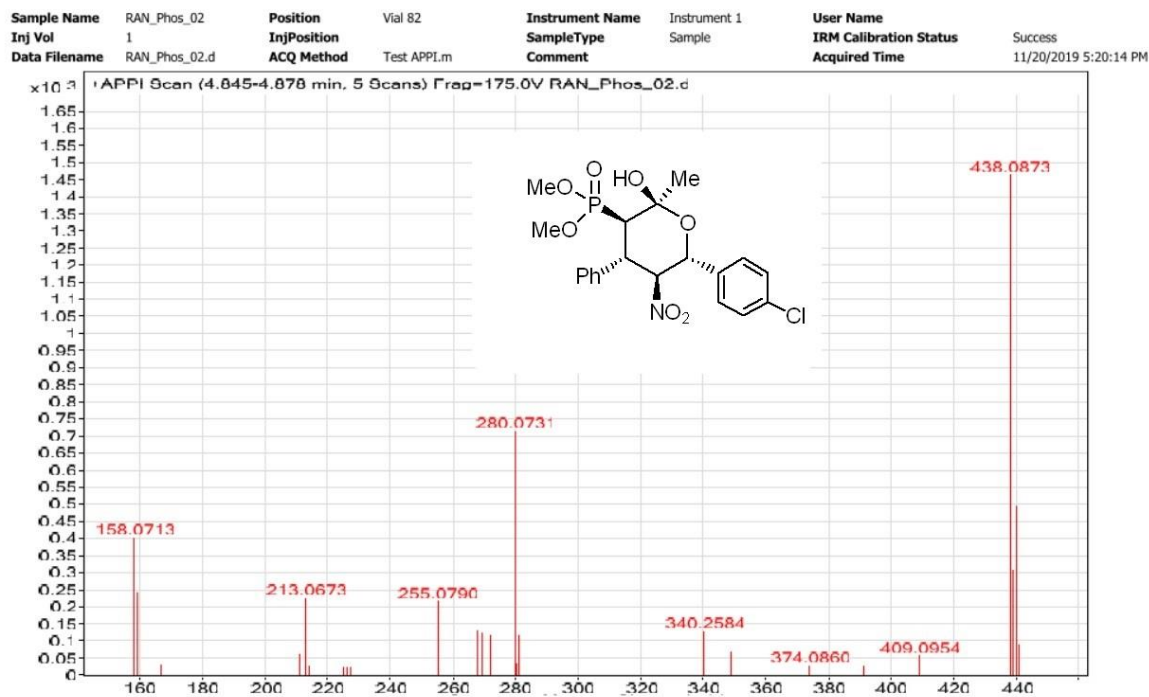
DEPT NMR spectra of dimethyl [(2*S*,3*R*,4*S*,5*S*,6*R*)-6-(4-chlorophenyl)-2-hydroxy-2-methyl-5-nitro-4-phenyltetrahydro-2*H*-pyran-3-yl]phosphonate (**13f**) in CDCl₃



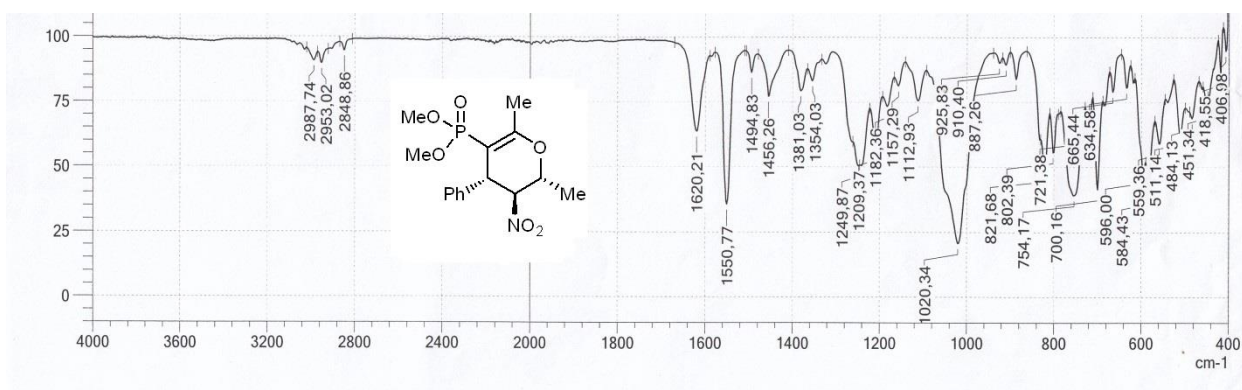
³¹P NMR spectra of dimethyl [(2*S*,3*R*,4*S*,5*S*,6*R*)-6-(4-chlorophenyl)-2-hydroxy-2-methyl-5-nitro-4-phenyltetrahydro-2*H*-pyran-3-yl]phosphonate (**13f**) in CDCl₃



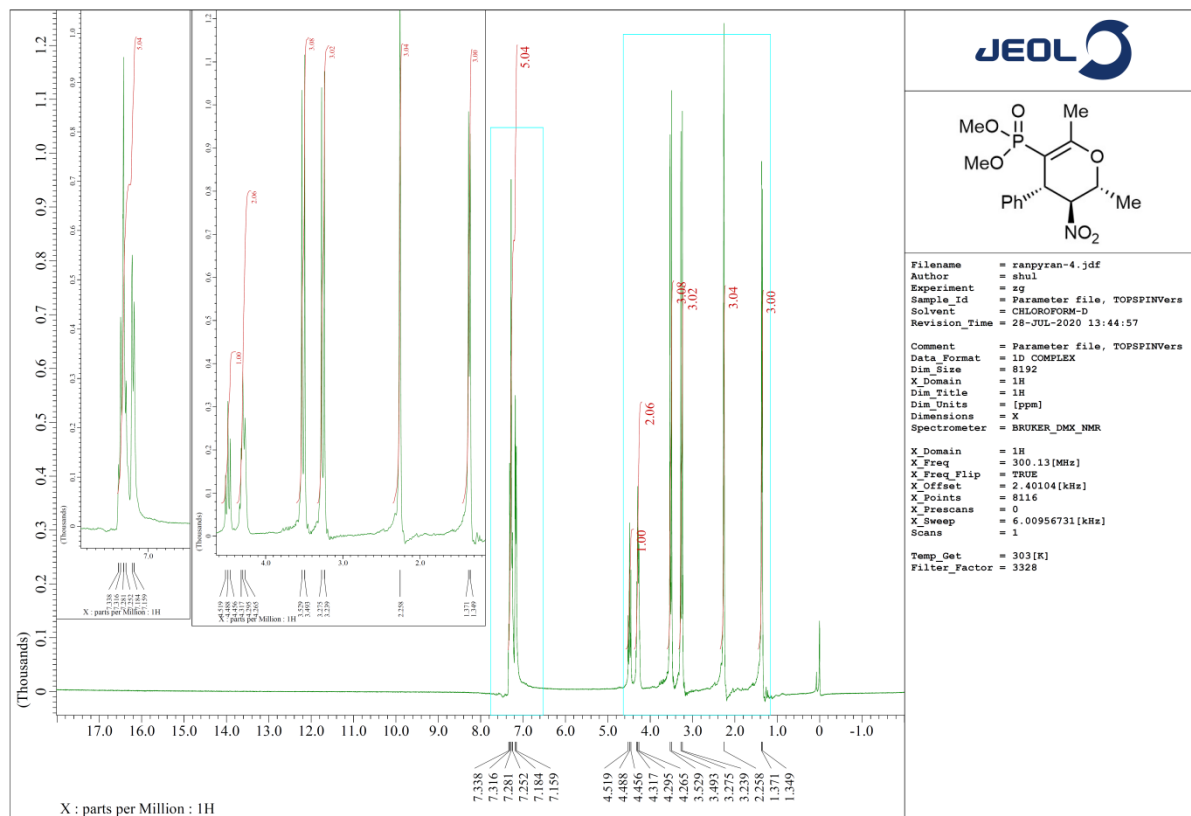
HRMS of dimethyl [(2*S*,3*R*,4*S*,5*S*,6*R*)-6-(4-chlorophenyl)-2-hydroxy-2-methyl-5-nitro-4-phenyltetrahydro-2*H*-pyran-3-yl]phosphonate (**13f**)



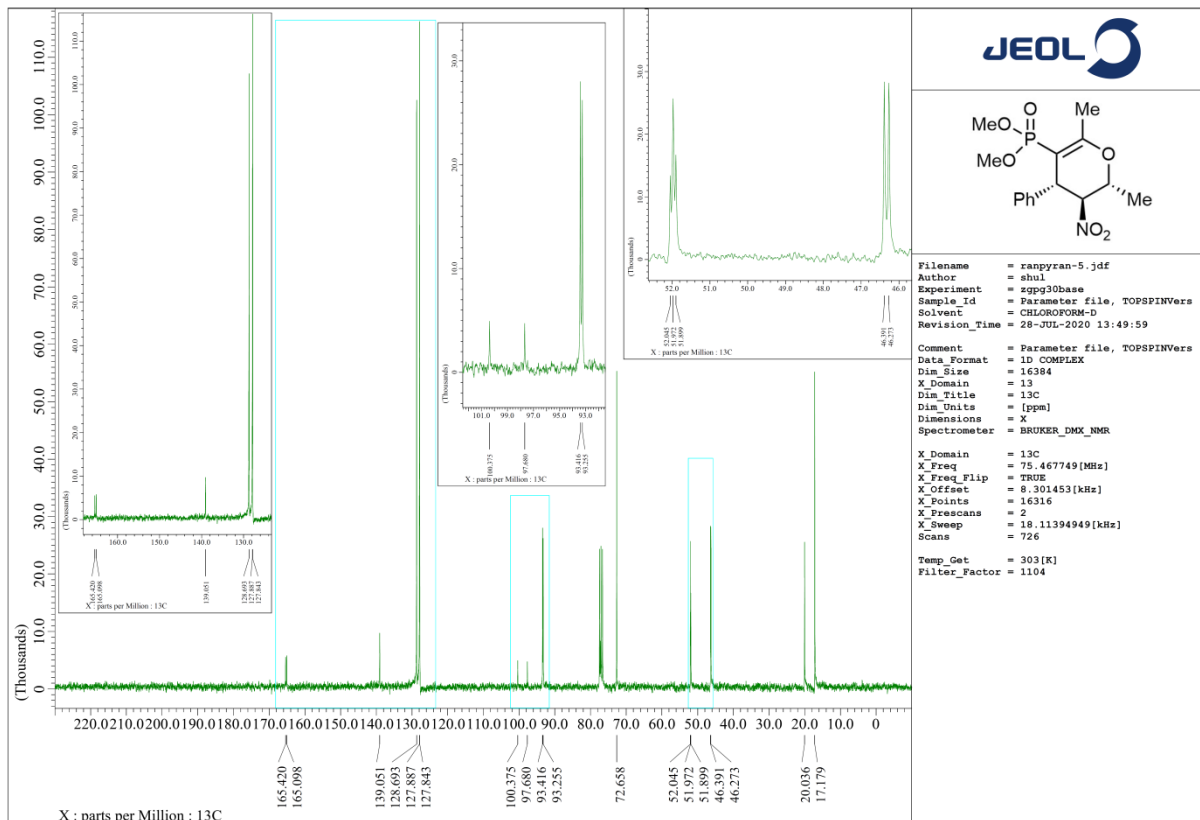
FTIR spectra of dimethyl [(2*R*,3*S*,4*S*)-2,6-dimethyl-3-nitro-4-phenyl-3,4-dihydro-2*H*-pyran-5-yl]phosphonate (**14**)



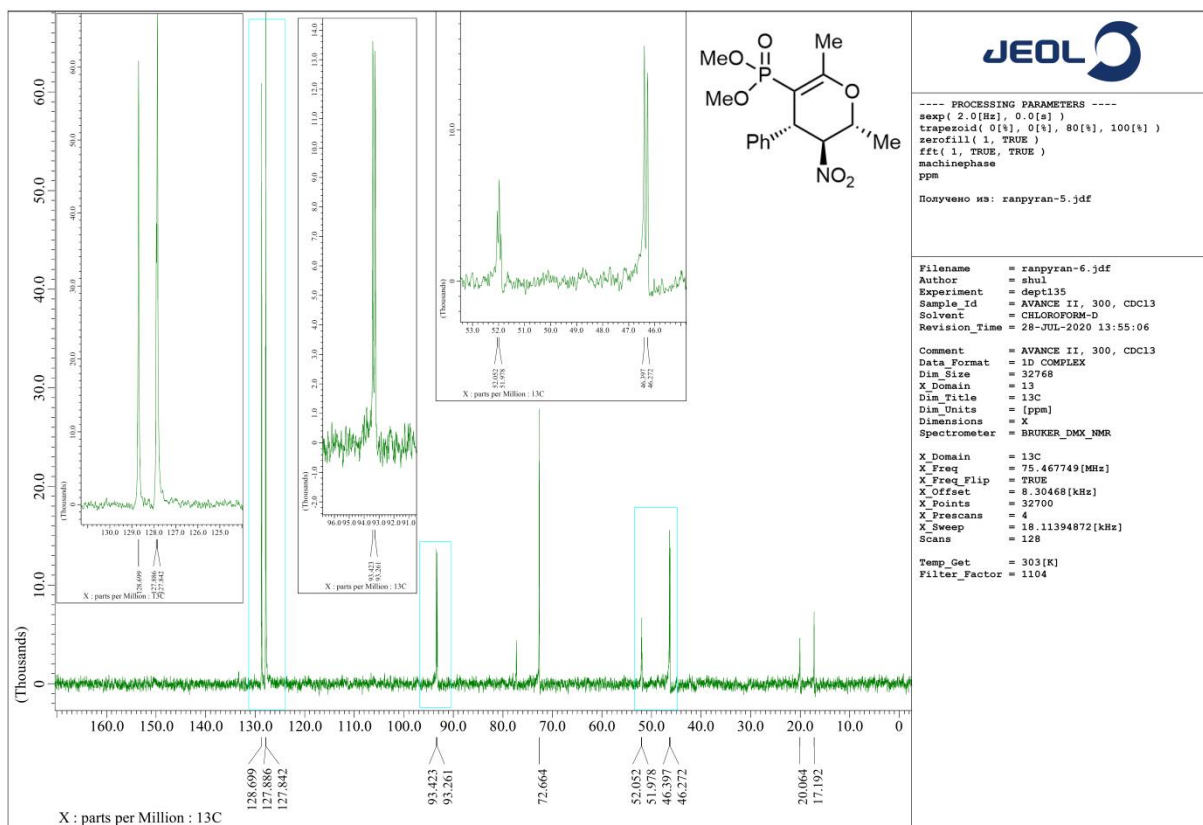
¹H NMR spectra of dimethyl [(2*R*,3*S*,4*S*)-2,6-dimethyl-3-nitro-4-phenyl-3,4-dihydro-2*H*-pyran-5-yl]phosphonate (**14**) in CDCl₃



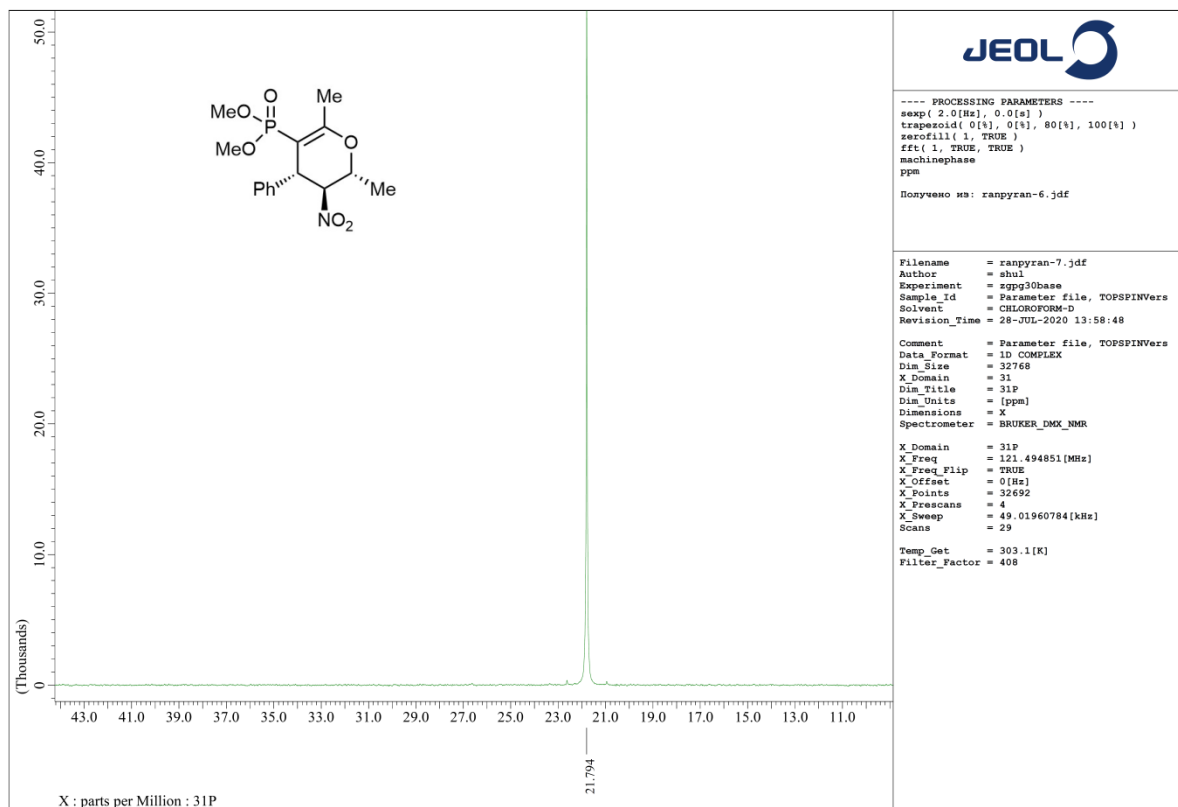
¹³C NMR spectra of dimethyl [(2*R*,3*S*,4*S*)-2,6-dimethyl-3-nitro-4-phenyl-3,4-dihydro-2*H*-pyran-5-yl]phosphonate (**14**) in CDCl₃



DEPT NMR spectra of dimethyl [(2*R*,3*S*,4*S*)-2,6-dimethyl-3-nitro-4-phenyl-3,4-dihydro-2*H*-pyran-5-yl]phosphonate (**14**) in CDCl₃

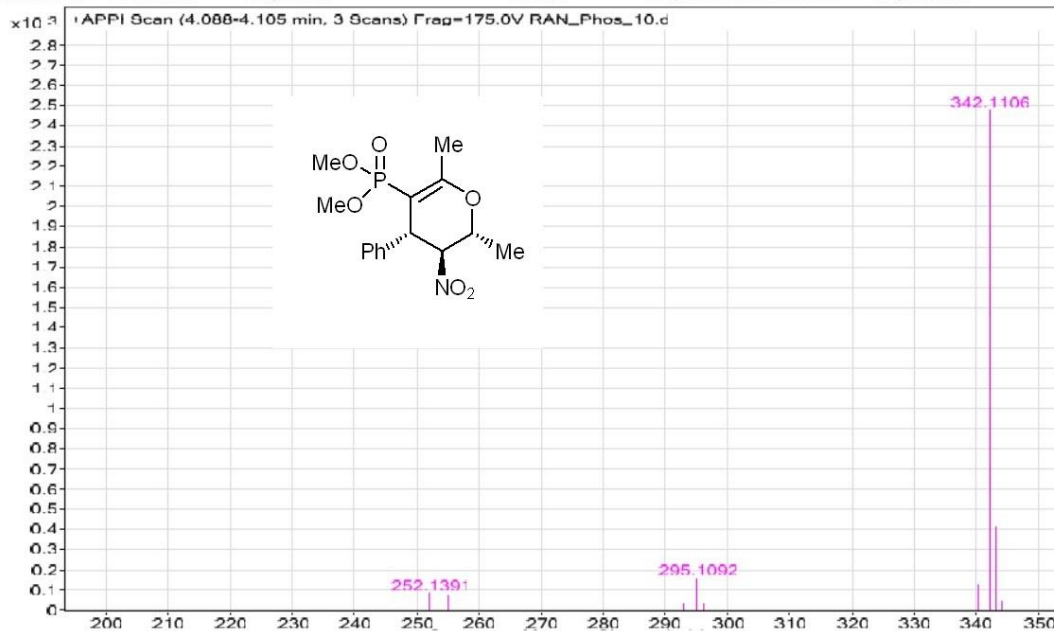


³¹P NMR spectra of dimethyl [(2*R*,3*S*,4*S*)-2,6-dimethyl-3-nitro-4-phenyl-3,4-dihydro-2*H*-pyran-5-yl]phosphonate (**14**) in CDCl₃



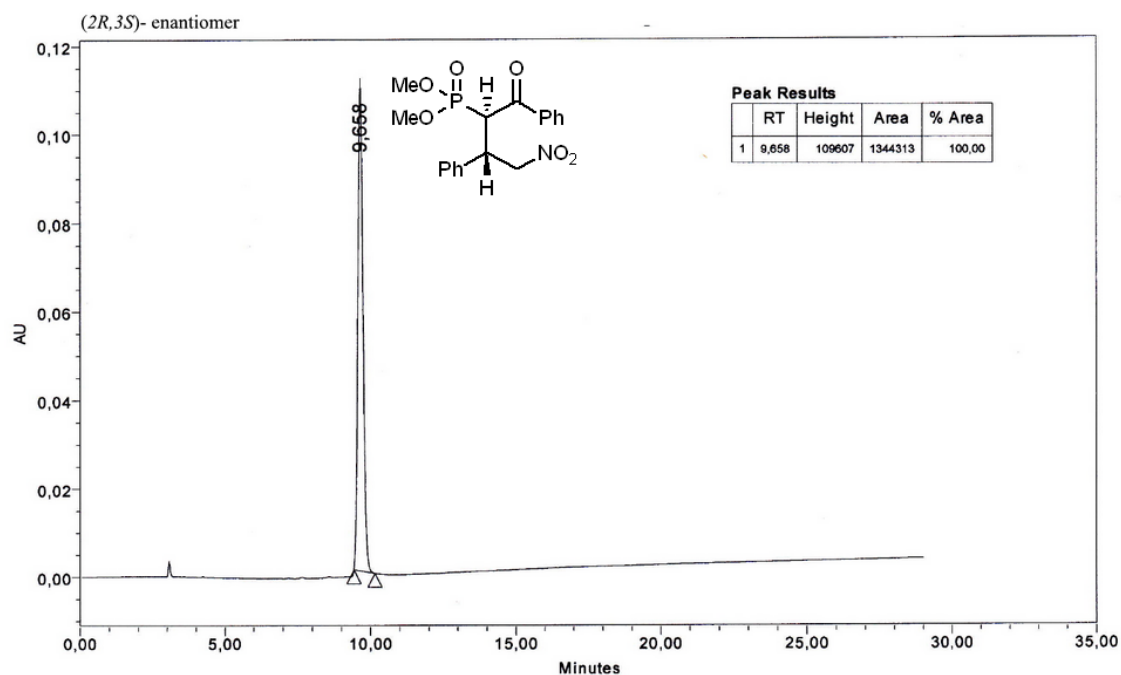
HRMS of dimethyl [(2*R*,3*S*,4*S*)-2,6-dimethyl-3-nitro-4-phenyl-3,4-dihydro-2*H*-pyran-5-yl]phosphonate (**14**)

Sample Name	Unavailable	Position	Unavailable	Instrument Name	Unavailable	User Name	Unavailable
Inj Vol	Unavailable	InjPosition	Unavailable	SampleType	Unavailable	IRM Calibration Status	Success
Data Filename	RAN_Phos_10.d	ACQ Method		Comment	Sample information is unavailable	Acquired Time	Unavailable

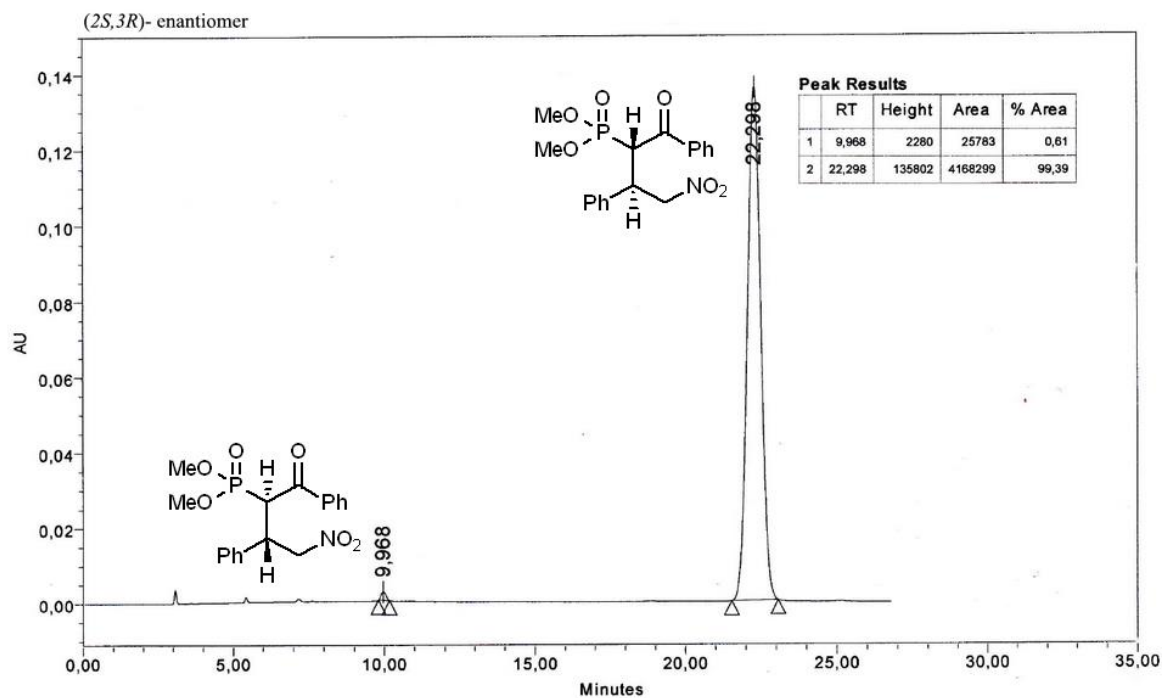


9. Copies of HPLC chromatograms for compounds 6a–d,f and 13b

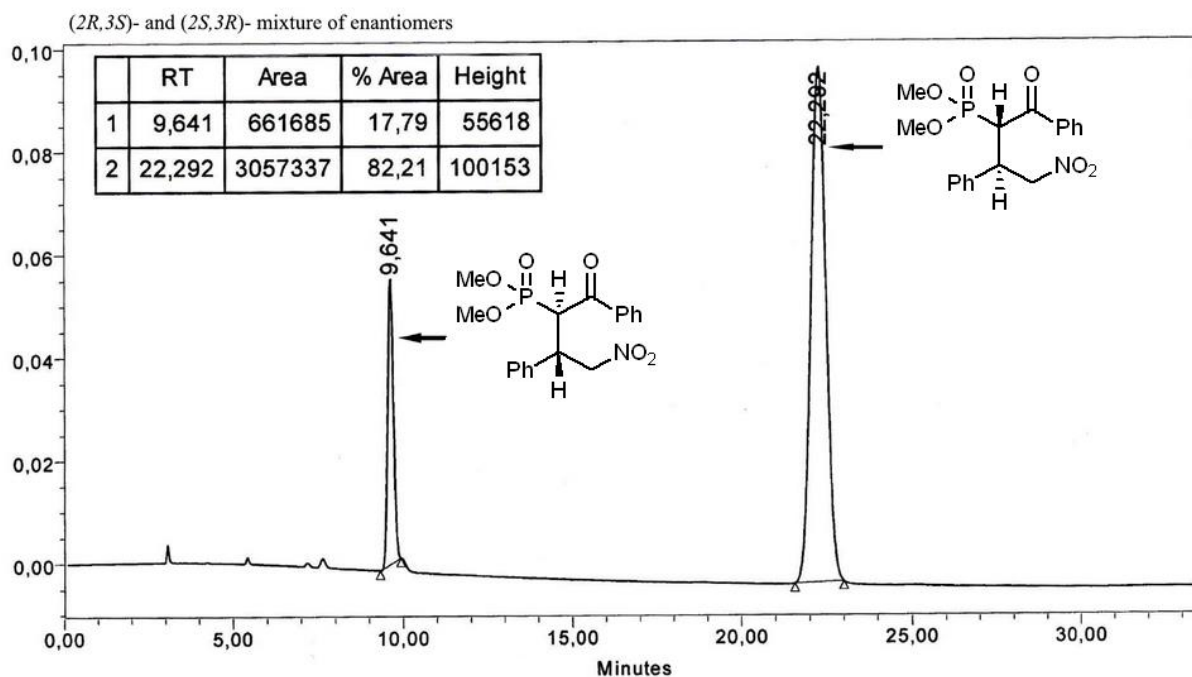
HPLC for dimethyl [(2*R*,3*S*)-4-nitro-1-oxo-1,3-diphenylbutan-2-yl]phosphonate (**6a**)



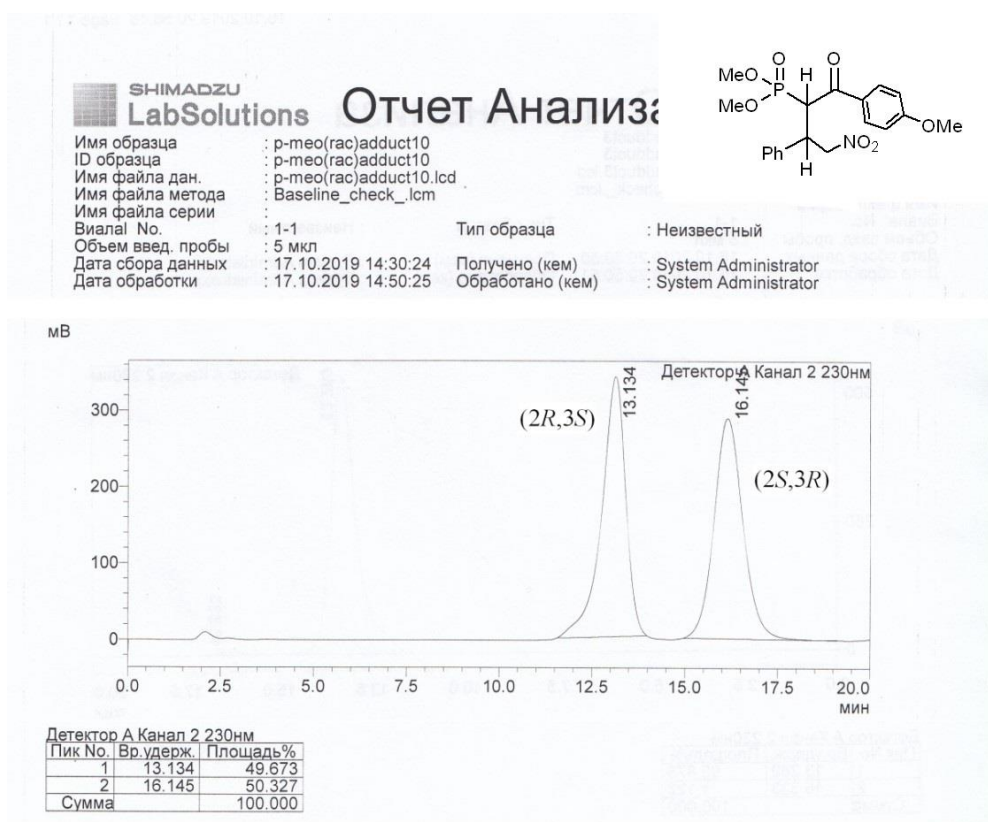
HPLC for dimethyl [(2*S*,3*R*)-4-nitro-1-oxo-1,3-diphenylbutan-2-yl]phosphonate (**6a**)

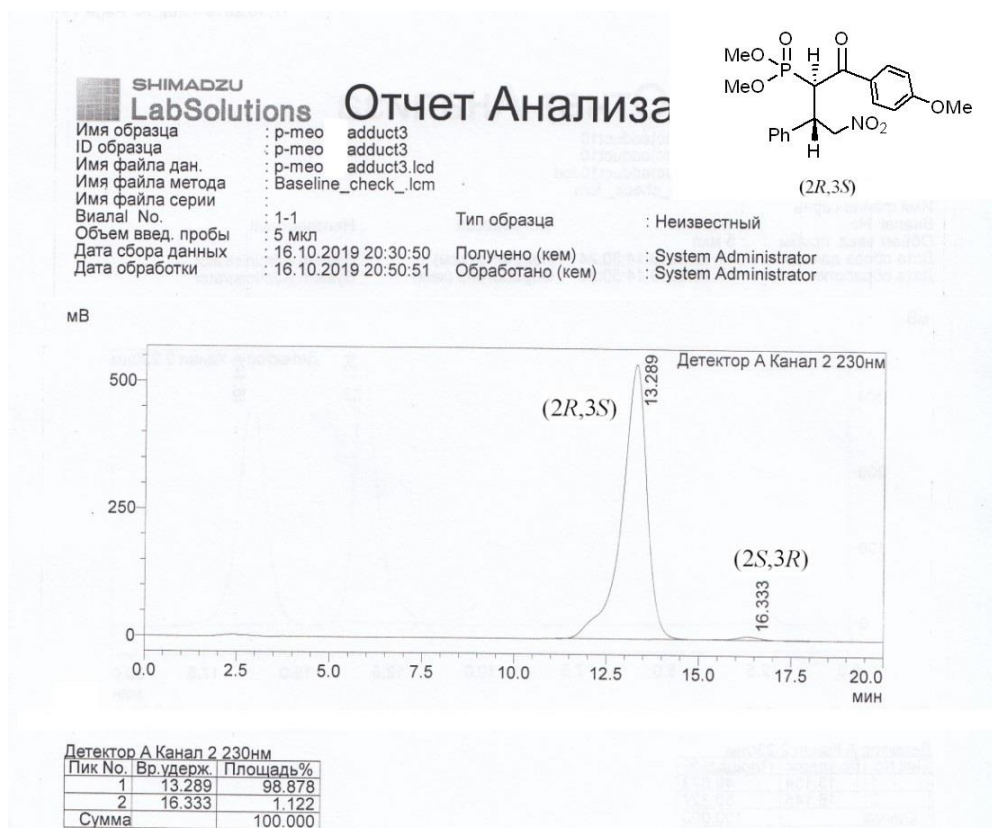
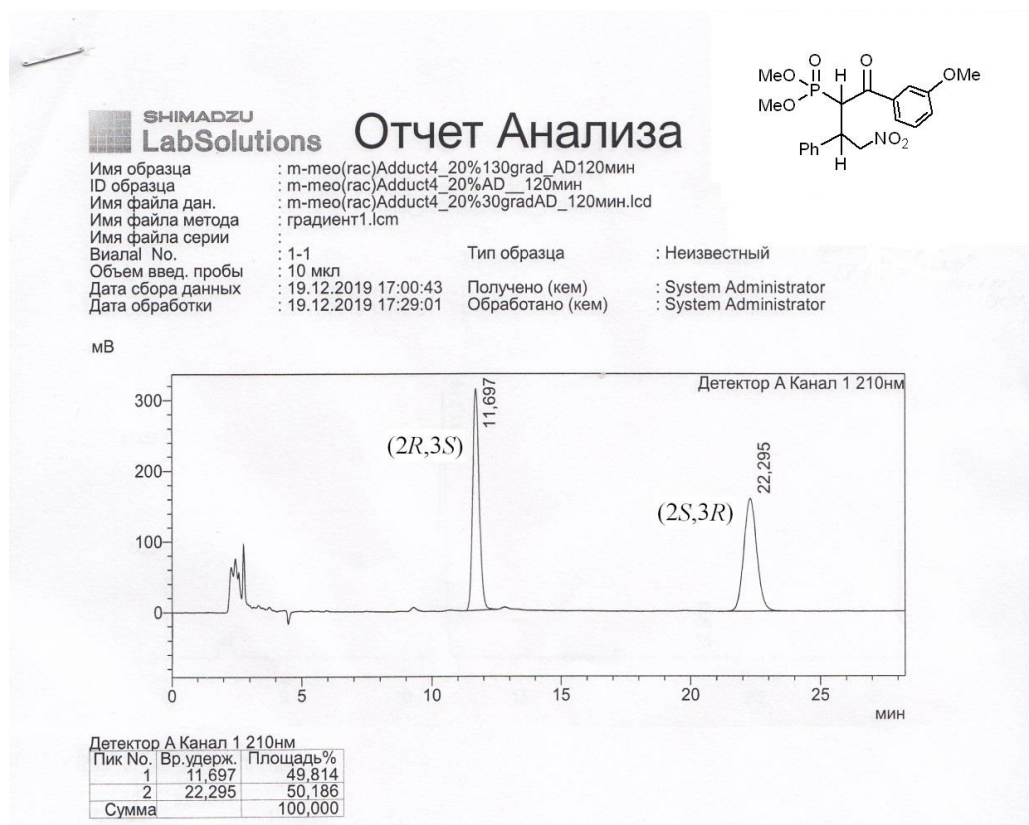


HPLC for mixture of (2*R*,3*S*)-**6a** and (2*S*,3*R*)-**6a** enantiomers

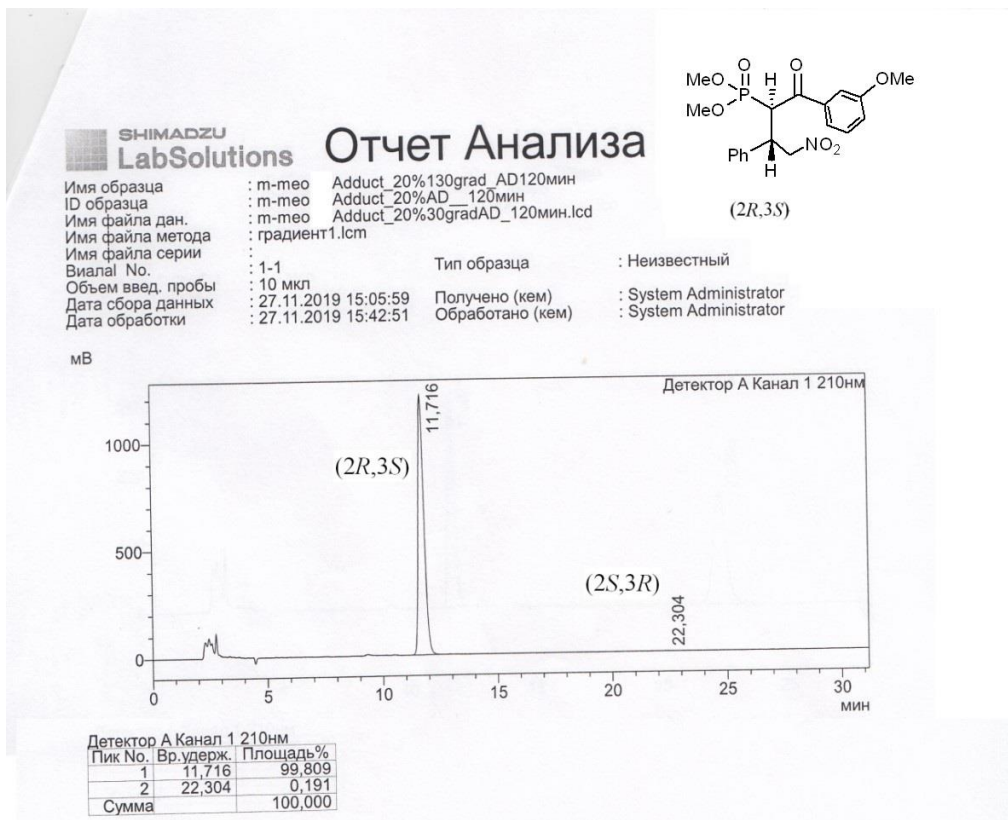


HPLC for racemic dimethyl [1-(4-methoxyphenyl)-4-nitro-1-oxo-3-phenylbutan-2-yl]-phosphonate (**6b**)

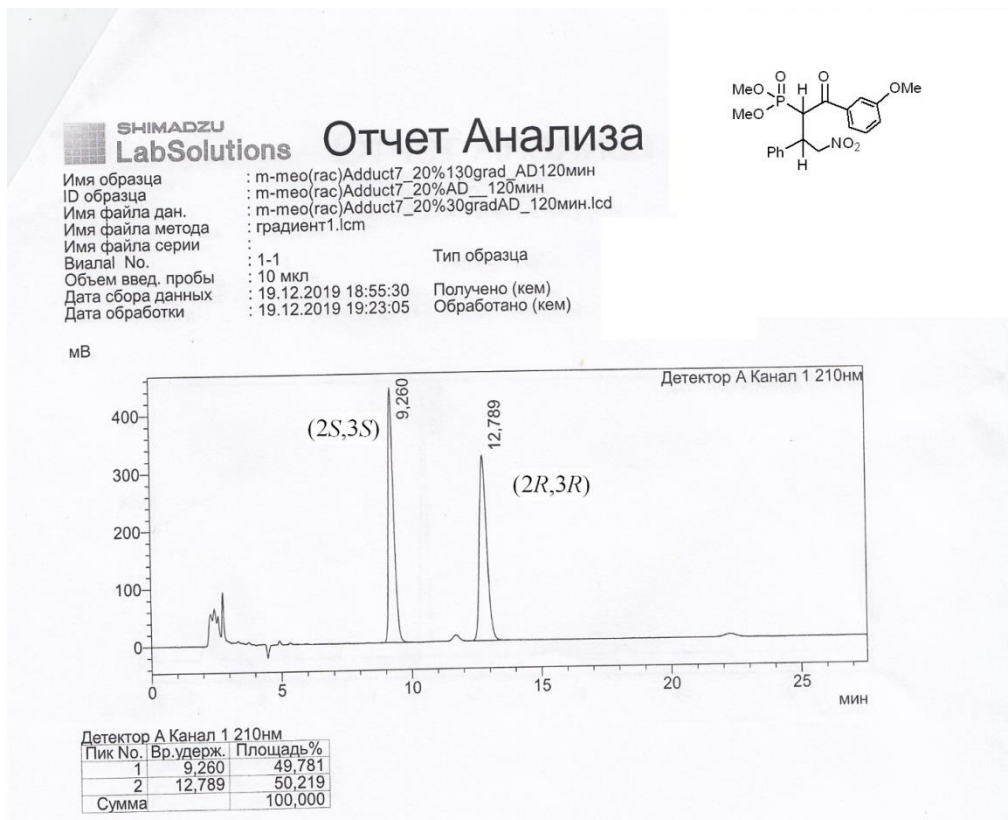


HPLC for dimethyl [(2*R*,3*S*)-1-(4-methoxyphenyl)-4-nitro-1-oxo-3-phenylbutan-2-yl]-phosphonate (**6b**)HPLC for racemic dimethyl [1-(3-methoxyphenyl)-4-nitro-1-oxo-3-phenylbutan-2-yl]phosphonate (**6c**)

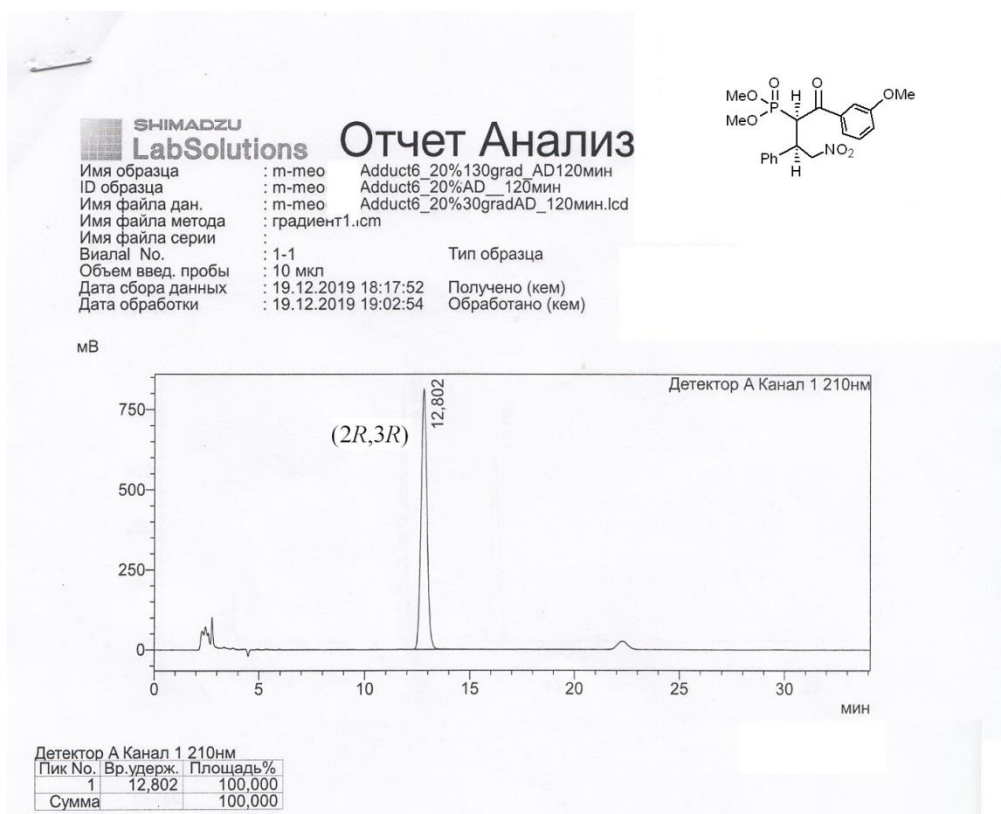
HPLC for dimethyl [(2*R*,3*S*)-1-(3-methoxyphenyl)-4-nitro-1-oxo-3-phenylbutan-2-yl]phosphonate (**6c**)



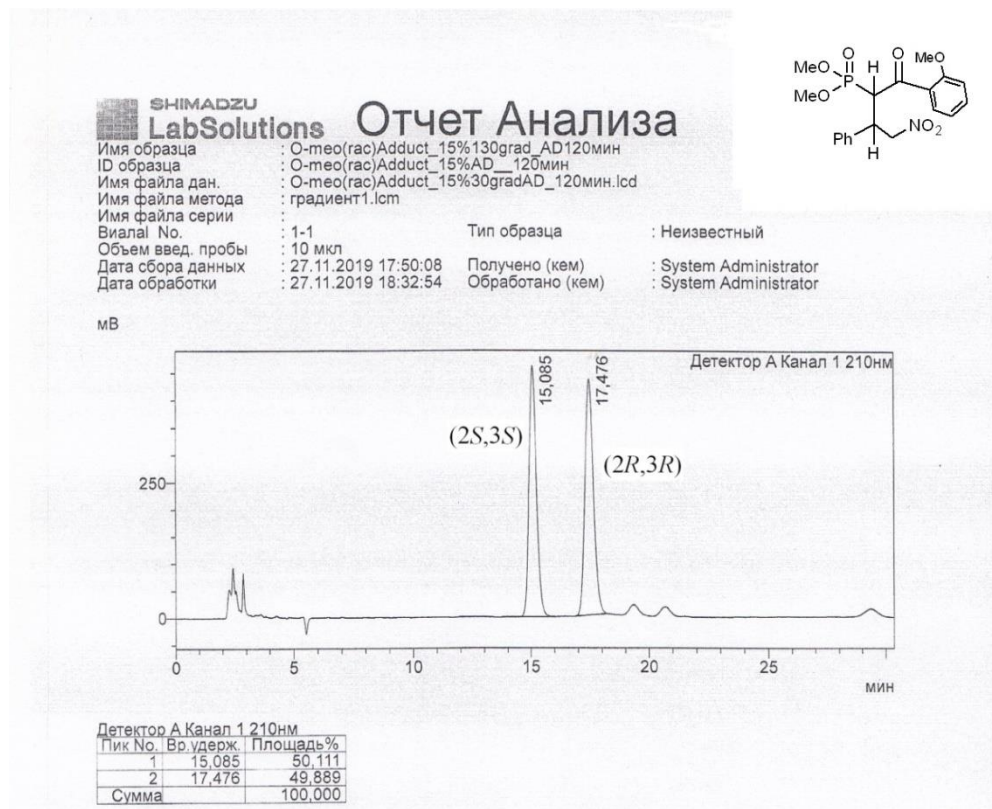
HPLC for racemic dimethyl [1-(3-methoxyphenyl)-4-nitro-1-oxo-3-phenylbutan-2-yl]phosphonate



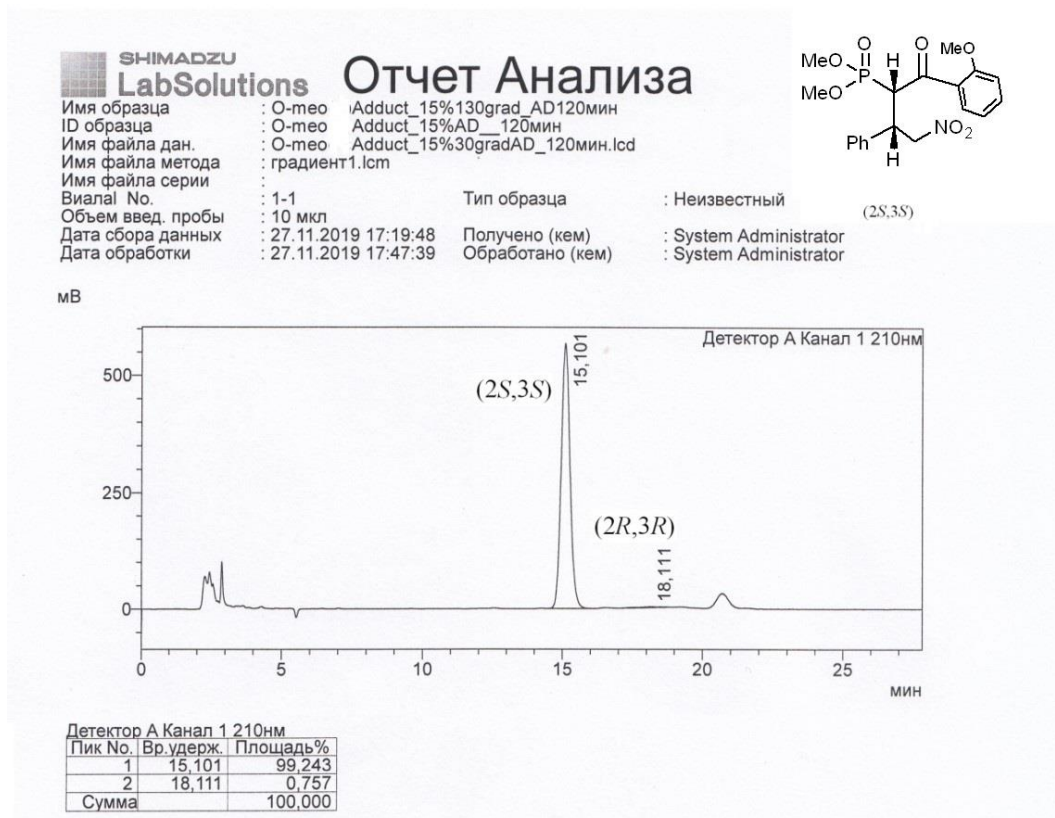
HPLC for dimethyl [(2*R*,3*R*)-1-(3-methoxyphenyl)-4-nitro-1-oxo-3-phenylbutan-2-yl]phosphonate



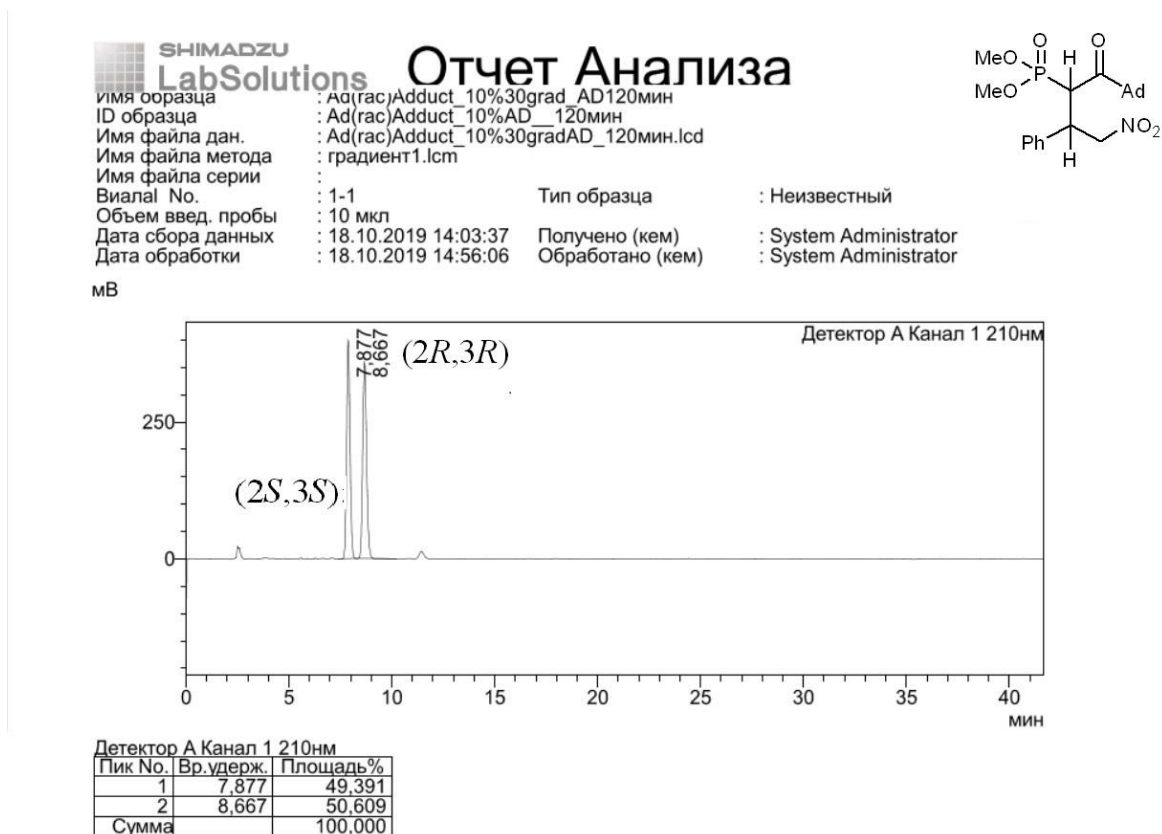
HPLC for racemic dimethyl [1-(2-methoxyphenyl)-4-nitro-1-oxo-3-phenylbutan-2-yl]phosphonate



HPLC for dimethyl [(2S,3S)-1-(2-methoxyphenyl)-4-nitro-1-oxo-3-phenylbutan-2-yl]phosphonate (**6d**)



HPLC for racemic dimethyl [1-(adamantan-1-yl)-4-nitro-1-oxo-3-phenylbutan-2-yl]phosphonate



HPLC for dimethyl [(2S,3S)-1-(adamantan-1-yl)-4-nitro-1-oxo-3-phenylbutan-2-yl]phosphonate (**6f**)

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Отчет Анализа

Имя образца
ID образца
Имя файла дан.
Имя файла метода
Имя файла серии
ВИАЛА! No.
Объем введ. пробы
Дата сбора данных
Дата обработки

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: 18.10.2019 15:04:57
: 18.10.2019 15:33:02

Тип образца

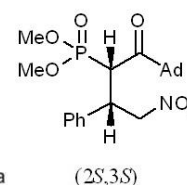
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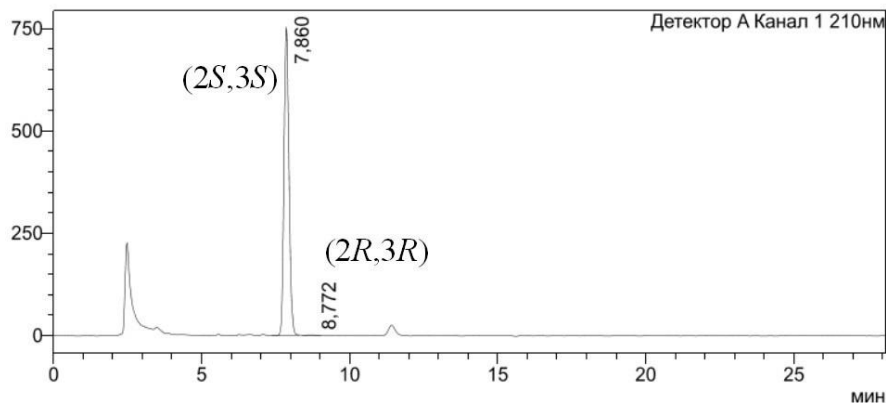
: System Administra

Обработано (кем)

: System Administra



мВ



Детектор А Канал 1 210нм

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1	7.860	99.787
2	8.772	0.213
Сумма		100.000

HPLC for racemic dimethyl [2-hydroxy-2,6-dimethyl-5-nitro-4-phenyltetrahydro-2H-pyran-3-yl]phosphonate

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Отчет Анализа

Имя образца
ID образца
Имя файла дан.
Имя файла метода
Имя файла серии
ВИАЛА! No.
Объем введ. пробы
Дата сбора данных
Дата обработки

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: 10 мкл
: 20.03.2020 19:51:10
: 20.03.2020 20:50:29

Тип образца

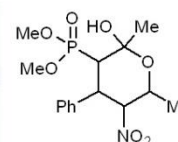
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Получено (кем)

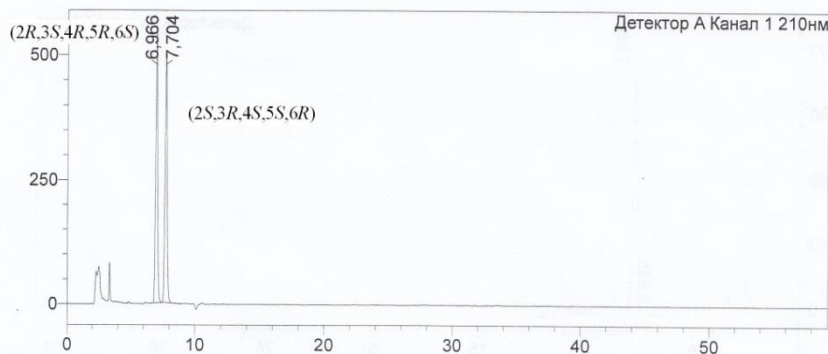
: System Administrator

Обработано (кем)

: System Administrator



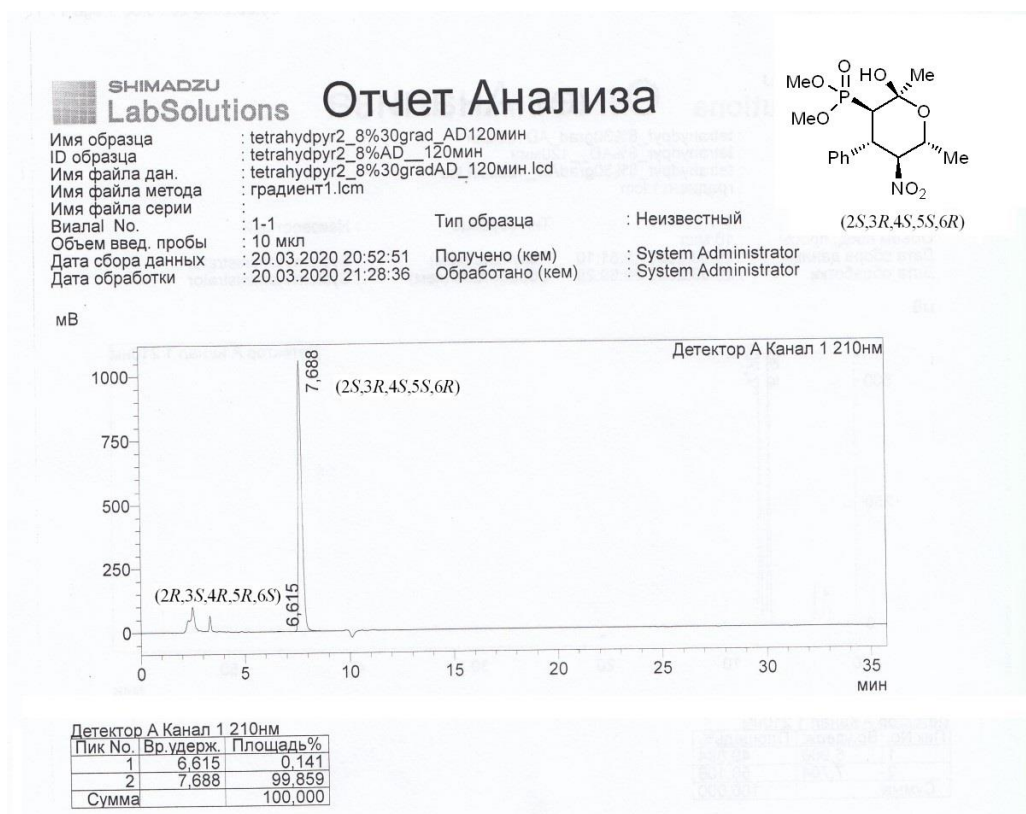
мВ



Детектор А Канал 1 210нм

Пик No.	Вр. удерж.	Площадь%
1	6.966	49.894
2	7.704	50.106
Сумма		100.000

HPLC for dimethyl [(2*S*,3*R*,4*S*,5*S*,6*R*)-2-hydroxy-2,6-dimethyl-5-nitro-4-phenyltetrahydro-2*H*-pyran-3-yl]phosphonate (**13b**)



10. X-Ray diffraction data of compounds 10a and 13b

X-ray data for compounds **10a** and **13b** were obtained with a Enraf-Nonius CAD-4 diffractometer. CCDC 1919294 and 1846644 deposits contain the supplementary crystallographic data for this article [7,8]. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via <http://www.ccdc.cam.ac.uk>.

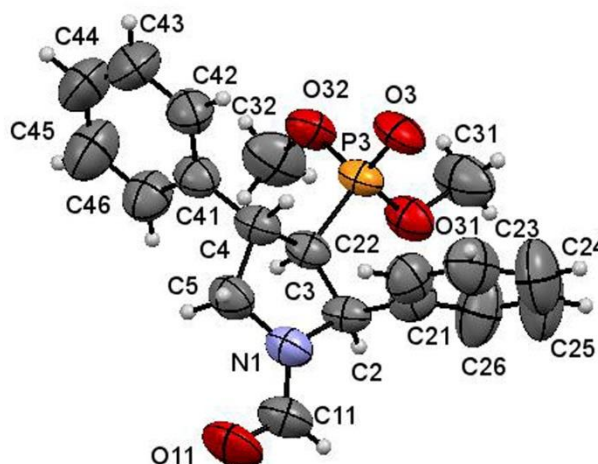


Table S2. X-ray diffraction data for dimethyl [(2*R*,3*R*,4*S*)-1-formyl-2,4-diphenylpyrrolidin-3-yl]phosphonate (**10a**) [7]

CCDC 1919294	
Empirical formula	C ₁₉ H ₂₂ NO ₄ P
Formula weight	359.34
Temperature	295(2) K
Wavelength	1.54186 Å (CuKα)
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁
Unit cell dimensions	<i>a</i> = 9.1358(13) Å α = 90° <i>b</i> = 10.4978(19) Å β = 96.830(10)° <i>c</i> = 13.5078(17) Å γ = 90°
Volume	1286.3(3) Å ³
<i>Z</i>	2
Density (calculated)	0.928 g/cm ³
Absorption coefficient	1.087 mm ⁻¹
<i>F</i> (000)	380
Crystal size	0.020×0.020×0.020 mm

Theta range for data collection	4.875 to 74.995°
Index ranges	-11 ≤ <i>h</i> ≤ 11, -13 ≤ <i>k</i> ≤ 13, 0 ≤ <i>l</i> ≤ 16
Reflections collected	5235
Independent reflections	3276
Absorption correction	refdelf
Data / restraints / parameters	5235 / 1 / 202
Goodness-of-fit on <i>F</i> ²	1.058
Final R indices [<i>I</i> > 2σ(<i>I</i>)]	R1 = 0.1174 wR2 = 0.2912
R indices (all data)	R1 = 0.1461 wR2 = 0.3231
Absolute structure (Flack) parameter	0.10(8)

Table S3. Selected bond lengths for compound 10a

Nº	Bond	Bondlength (Å)	Nº	Bond	Bondlength (Å)
1	N(1)-C(11)	1.344(13)	25	C(25)-C(26)	1.3900
2	N(1)-C(5)	1.444(14)	26	C(25)-H(25)	0.9300
3	N(1)-C(2)	1.464(12)	27	C(26)-H(26)	0.9300
4	C(2)-C(21)	1.507(11)	28	P(3)-O(3)	1.472(7)
5	C(2)-C(3)	1.521(13)	29	P(3)-O(32)	1.562(7)
6	C(2)-H(2)	0.9800	30	P(3)-O(31)	1.566(8)
7	C(3)-C(4)	1.533(13)	31	O(31)-C(31)	1.430(14)
8	C(3)-P(3)	1.803(9)	32	C(31)-H(31a)	0.9600
9	C(3)-H(3)	0.9800	33	C(31)-H(31b)	0.9600
10	C(4)-C(41)	1.503(12)	34	C(31)-H(31c)	0.9600
11	C(4)-C(5)	1.537(13)	35	O(32)-C(32)	1.447(17)
12	C(4)-H(4)	0.9800	36	C(32)-H(32a)	0.9600
13	C(5)-H(5a)	0.9700	37	C(32)-H(32b)	0.9600
14	C(5)-H(5b)	0.9700	38	C(32)-H(32c)	0.9600
15	C(11)-O(11)	1.234(15)	39	C(41)-C(46)	1.3900
16	C(11)-H(11)	0.9300	40	C(41)-C(42)	1.3900
17	C(21)-C(22)	1.3900	41	C(46)-C(45)	1.3900
18	C(21)-C(26)	1.3900	42	C(46)-H(46)	0.9300
19	C(22)-C(23)	1.3900	43	C(45)-C(44)	1.3900
20	C(22)-H(22)	0.9300	44	C(45)-H(45)	0.9300
21	C(23)-C(24)	1.3900	45	C(44)-C(43)	1.3900
22	C(23)-H(23)	0.9300	46	C(44)-H(44)	0.9300
23	C(24)-C(25)	1.3900	47	C(43)-C(42)	0.9300
24	C(24)-H(24)	0.9300	48	C(43)-H(43)	0.9300

Table S4. Selected bond angles for compound 10a

No	Angle	(°)		No	Angle	(°)
1	C(11)-N(1)-C(5)	123.3(10)		44	C(26)-C(25)-H(25)	120.0
2	C(11)-N(1)-C(2)	122.7(10)		45	C(24)-C(25)-H(25)	120.0
3	C(5)-N(1)-C(2)	113.4(8)		46	C(25)-C(26)-C(21)	120.0
4	N(1)-C(2)-C(21)	112.4(7)		47	C(25)-C(26)-H(26)	120.0
5	N(1)-C(2)-C(3)	100.2(8)		48	C(21)-C(26)-H(26)	120.0
6	C(21)-C(2)-C(3)	117.4(7)		49	O(3)-P(3)-O(32)	109.1(5)
7	N(1)-C(2)-H(2)	108.8		50	O(3)-P(3)-O(31)	114.9(5)
8	C(21)-C(2)-H(2)	108.8		51	O(32)-P(3)-O(31)	106.0(4)
9	C(3)-C(2)-H(2)	108.8		52	O(3)-P(3)-C(3)	116.6(4)
10	C(2)-C(3)-C(4)	104.9(7)		53	O(32)-P(3)-C(3)	107.5(4)
11	C(2)-C(3)-P(3)	117.8(7)		54	O(31)-P(3)-C(3)	101.9(4)
12	C(4)-C(3)-P(3)	112.9(6)		55	C(31)-O(31)-P(3)	119.7(8)
13	C(2)-C(3)-H(3)	106.9		56	O(31)-C(31)-H(31a)	109.5
14	C(4)-C(3)-H(3)	106.9		57	O(31)-C(31)-H(31b)	109.5
15	P(3)-C(3)-H(3)	106.9		58	H(31a)-C(31)-H(31b)	109.5
16	C(41)-C(4)-C(3)	117.2(8)		59	O(31)-C(31)-H(31c)	109.5
17	C(41)-C(4)-C(5)	112.2(8)		60	H(31a)-C(31)-H(31c)	109.5
18	C(3)-C(4)-C(5)	100.5(8)		61	H(31b)-C(31)-H(31c)	109.5
19	C(41)-C(4)-H(4)	108.8		62	C(32)-O(32)-P(3)	120.0(8)
20	C(3)-C(4)-H(4)	108.8		63	O(32)-C(32)-H(32a)	109.5
21	C(5)-C(4)-H(4)	108.8		64	O(32)-C(32)-H(32b)	109.5
22	N(1)-C(5)-C(4)	104.7(8)		65	H(32a)-C(32)-H(32b)	109.5
23	N(1)-C(5)-H(5a)	110.8		66	O(32)-C(32)-H(32c)	109.5
24	C(4)-C(5)-H(5a)	110.8		67	H(32a)-C(32)-H(32c)	109.5
25	N(1)-C(5)-H(5b)	110.8		68	H(32b)-C(32)-H(32c)	109.5
26	C(4)-C(5)-H(5b)	110.8		69	C(46)-C(41)-C(42)	120.0
27	H(5A)-C(5)-H(5b)	108.9		70	C(46)-C(41)-C(4)	121.5(6)
28	O(11)-C(11)-N(1)	121.8(13)		71	C(42)-C(41)-C(4)	118.5(6)
29	O(11)-C(11)-H(11)	119.1		72	C(41)-C(46)-C(45)	120.0
30	N(1)-C(11)-H(11)	119.1		73	C(41)-C(46)-H(46)	120.0
31	C(22)-C(21)-C(26)	120.0		74	C(45)-C(46)-H(46)	120.0
32	C(22)-C(21)-C(2)	122.0(6)		75	C(44)-C(45)-C(46)	120.0
33	C(26)-C(21)-C(2)	118.0(6)		76	C(44)-C(45)-H(45)	120.0
34	C(23)-C(22)-C(21)	120.0		77	C(46)-C(45)-H(45)	120.0
35	C(23)-C(22)-H(22)	120.0		78	C(43)-C(44)-C(45)	120.0
36	C(21)-C(22)-H(22)	120.0		79	C(43)-C(44)-H(44)	120.0
37	C(22)-C(23)-C(24)	120.0		80	C(45)-C(44)-H(44)	120.0
38	C(22)-C(23)-H(23)	120.0		81	C(44)-C(43)-C(42)	120.0
39	C(24)-C(23)-H(23)	120.0		82	C(44)-C(43)-H(43)	120.0
40	C(23)-C(24)-C(25)	120.0		83	C(42)-C(43)-H(43)	120.0
41	C(23)-C(24)-H(24)	120.0		84	C(43)-C(42)-C(41)	120.0

42	C(25)-C(24)-H(24)	120.0	85	C(43)-C(42)-H(42)	120.0
43	C(26)-C(25)-C(24)	120.0	86	C(41)-C(42)-H(42)	120.0

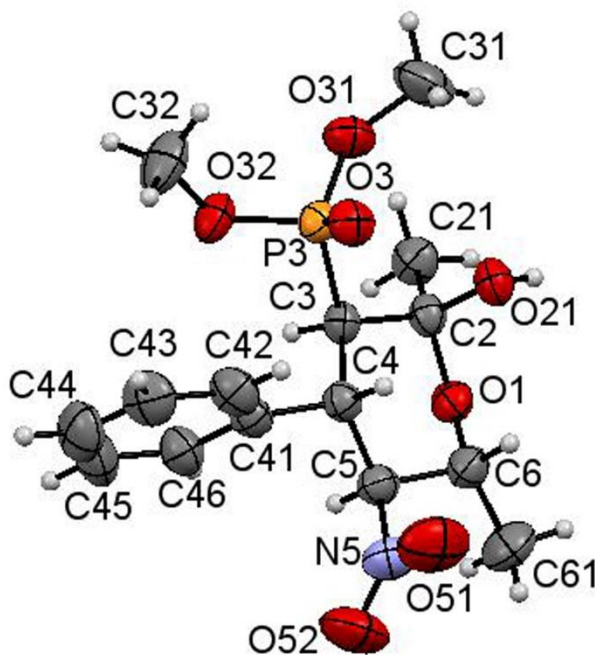


Table S5. X-ray diffraction data for dimethyl [(2*S*,3*R*,4*S*,5*S*,6*R*)-6-ethyl-2-hydroxy-2-methyl-5-nitro-4-phenyltetrahydro-2*H*-pyran-3-yl]phosphonate (**13b**) [8]

CCDC 1846644	
Empirical formula	C ₁₅ H ₂₂ NO ₇ P
Formula weight	359.31
Temperature	295(2) K
Wavelength	1.54184 Å
Crystal system	orthorhombic
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁
Unit cell dimensions	<i>a</i> = 9.6607(9) Å α = 90°
	<i>b</i> = 11.0178(10) Å β = 90°
	<i>c</i> = 17.0785(17) Å γ = 90°
Volume	1817.8(3) Å ³
<i>Z</i>	4
Density (calculated)	1.313 g/cm ³
Absorption coefficient	1.660 mm ⁻¹
<i>F</i> (000)	760
Crystal size	0.020×0.020×0.020 mm
Theta range for data collection	4.776 to 74.882°
Index ranges	-11 ≤ <i>h</i> ≤ 12, -13 ≤ <i>k</i> ≤ 13, -20 ≤ <i>l</i> ≤ 21
Reflections collected	3613
Independent reflections	3175

Absorption correction	refdelf
Data / restraints / parameters	3613 / 0 / 221
Goodness-of-fit on F^2	1.026
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0335$ $wR2 = 0.0800$
R indices (all data)	$R1 = 0.0402$ $wR2 = 0.0835$
Absolute structure (Flack) parameter	0.001(15)

Table S6. Selected bond lengths for compound 13b

Nº	Bond	Bondlength (Å)	Nº	Bond	Bondlength (Å)
1	P(3)-O(3)	1.4634(18)	25	C(31)-H(31a)	0.9600
2	P(3)-O(31)	1.568(2)	26	C(31)-H(31b)	0.9600
3	P(3)-O(32)	1.5685(19)	27	C(31)-H(31c)	0.9600
4	P(3)-C(3)	1.825(3)	28	O(32)-C(32)	1.452(4)
5	O(1)-C(6)	1.423(3)	29	C(32)-H(32a)	0.9600
6	O(1)-C(2)	1.431(3)	30	C(32)-H(32b)	0.9600
7	C(2)-O(21)	1.401(3)	31	C(32)-H(32c)	0.9600
8	C(2)-C(21)	1.508(4)	32	C(41)-C(46)	1.386(4)
9	C(2)-C(3)	1.547(3)	33	C(41)-C(42)	1.388(4)
10	C(3)-C(4)	1.557(3)	34	C(42)-C(43)	1.388(4)
11	C(3)-H(3)	0.9800	35	C(42)-H(42)	0.9300
12	C(4)-C(41)	1.524(3)	36	C(43)-C(44)	1.379(5)
13	C(4)-C(5)	1.526(4)	37	C(43)-H(43)	0.9300
14	C(4)-H(4)	0.9800	38	C(44)-C(45)	1.371(5)
15	C(5)-N(5)	1.504(4)	39	C(44)-H(44)	0.9300
16	C(5)-C(6)	1.524(4)	40	C(45)-C(46)	1.391(4)
17	C(5)-H(5)	0.9800	41	C(45)-H(45)	0.9300
18	C(6)-C(61)	1.499(4)	42	C(46)-H(46)	0.9300
19	C(6)-H(6)	0.9800	43	N(5)-O(51)	1.214(4)
20	C(21)-H(21a)	0.9600	44	N(5)-O(52)	1.220(3)
21	C(21)-H(21b)	0.9600	45	C(61)-H(61a)	0.9600
22	C(21)-H(21c)	0.9600	46	C(61)-H(61b)	0.9600
23	O(21)-H(21)	0.79(3)	47	C(61)-H(61c)	0.9600
24	O(31)-C(31)	1.443(4)	48		

Table S7. Selected bond angles for compound 13b

Nº	Angle	(°)	Nº	Angle	(°)
1	O(3)-P(3)-O(31)	112.32(12)	45	C(31)-O(31)-P(3)	122.7(2)
2	O(3)-P(3)-O(32)	115.09(12)	46	O(31)-C(31)-H(31a)	109.5
3	O(31)-P(3)-O(32)	102.67(12)	47	O(31)-C(31)-H(31b)	109.5
4	O(3)-P(3)-C(3)	114.77(12)	48	H(31a)-C(31)-H(31b)	109.5
5	O(31)-P(3)-C(3)	110.55(12)	49	O(31)-C(31)-H(31c)	109.5
6	O(32)-P(3)-C(3)	100.22(11)	50	H(31a)-C(31)-H(31c)	109.5
7	C(6)-O(1)-C(2)	115.6(2)	51	H(31b)-C(31)-H(31c)	109.5
8	O(21)-C(2)-O(1)	110.1(2)	52	C(32)-O(32)-P(3)	118.4(2)
9	O(21)-C(2)-C(21)	113.6(2)	53	O(32)-C(32)-H(32a)	109.5
10	O(1)-C(2)-C(21)	103.8(2)	54	O(32)-C(32)-H(32b)	109.5
11	O(21)-C(2)-C(3)	106.4(2)	55	H(32a)-C(32)-H(32b)	109.5
12	O(1)-C(2)-C(3)	109.5(2)	56	O(32)-C(32)-H(32c)	109.5
13	C(21)-C(2)-C(3)	113.5(2)	57	H(32a)-C(32)-H(32c)	109.5

14	C(2)-C(3)-C(4)	114.1(2)	58	H(32b)-C(32)-H(32c)	109.5
15	C(2)-C(3)-P(3)	112.96(18)	59	C(46)-C(41)-C(42)	119.3(3)
16	C(4)-C(3)-P(3)	107.05(17)	60	C(46)-C(41)-C(4)	120.6(2)
17	C(2)-C(3)-H(3)	107.5	61	C(42)-C(41)-C(4)	120.1(3)
18	C(4)-C(3)-H(3)	107.5	62	C(43)-C(42)-C(41)	120.3(3)
19	P(3)-C(3)-H(3)	107.5	63	C(43)-C(42)-H(42)	119.9
20	C(41)-C(4)-C(5)	112.4(2)	64	C(41)-C(42)-H(42)	119.9
21	C(41)-C(4)-C(3)	111.5(2)	65	C(44)-C(43)-C(42)	120.1(3)
22	C(5)-C(4)-C(3)	109.2(2)	66	C(44)-C(43)-H(43)	120.0
23	C(41)-C(4)-H(4)	107.9	67	C(42)-C(43)-H(43)	120.0
24	C(5)-C(4)-H(4)	107.9	68	C(45)-C(44)-C(43)	119.9(3)
25	C(3)-C(4)-H(4)	107.9	69	C(45)-C(44)-H(44)	120.1
26	N(5)-C(5)-C(6)	108.5(2)	70	C(43)-C(44)-H(44)	120.1
27	N(5)-C(5)-C(4)	109.7(2)	71	C(44)-C(45)-C(46)	120.6(3)
28	C(6)-C(5)-C(4)	111.2(2)	72	C(44)-C(45)-H(45)	119.7
29	N(5)-C(5)-H(5)	109.1	73	C(46)-C(45)-H(45)	119.7
30	C(6)-C(5)-H(5)	109.1	74	C(41)-C(46)-C(45)	119.9(3)
31	C(4)-C(5)-H(5)	109.1	75	C(41)-C(46)-H(46)	120.1
32	O(1)-C(6)-C(61)	107.3(3)	76	C(45)-C(46)-H(46)	120.1
33	O(1)-C(6)-C(5)	105.6(2)	77	O(51)-N(5)-O(52)	124.2(3)
34	C(61)-C(6)-C(5)	114.4(3)	78	O(51)-N(5)-C(5)	118.3(3)
35	O(1)-C(6)-H(6)	109.8	79	O(52)-N(5)-C(5)	117.5(3)
36	C(61)-C(6)-H(6)	109.8	80	C(6)-C(61)-H(61a)	109.5
37	C(5)-C(6)-H(6)	109.8	81	C(6)-C(61)-H(61b)	109.5
38	C(2)-C(21)-H(21a)	109.5	82	H(61a)-C(61)-H(61b)	109.5
39	C(2)-C(21)-H(21b)	109.5	83	C(6)-C(61)-H(61c)	109.5
40	C(2)-C(21)-H(21c)	109.5	84	H(61a)-C(61)-H(61c)	109.5
41	H(21a)-C(21)-H(21b)	109.5	85	H(61b)-C(61)-H(61c)	109.5
42	H(21a)-C(21)-H(21c)	109.5			
43	H(21b)-C(21)-H(21c)	109.5			
44	C(2)-O(21)-H(21)	100(2)			

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