

SUPPORTING INFORMATION

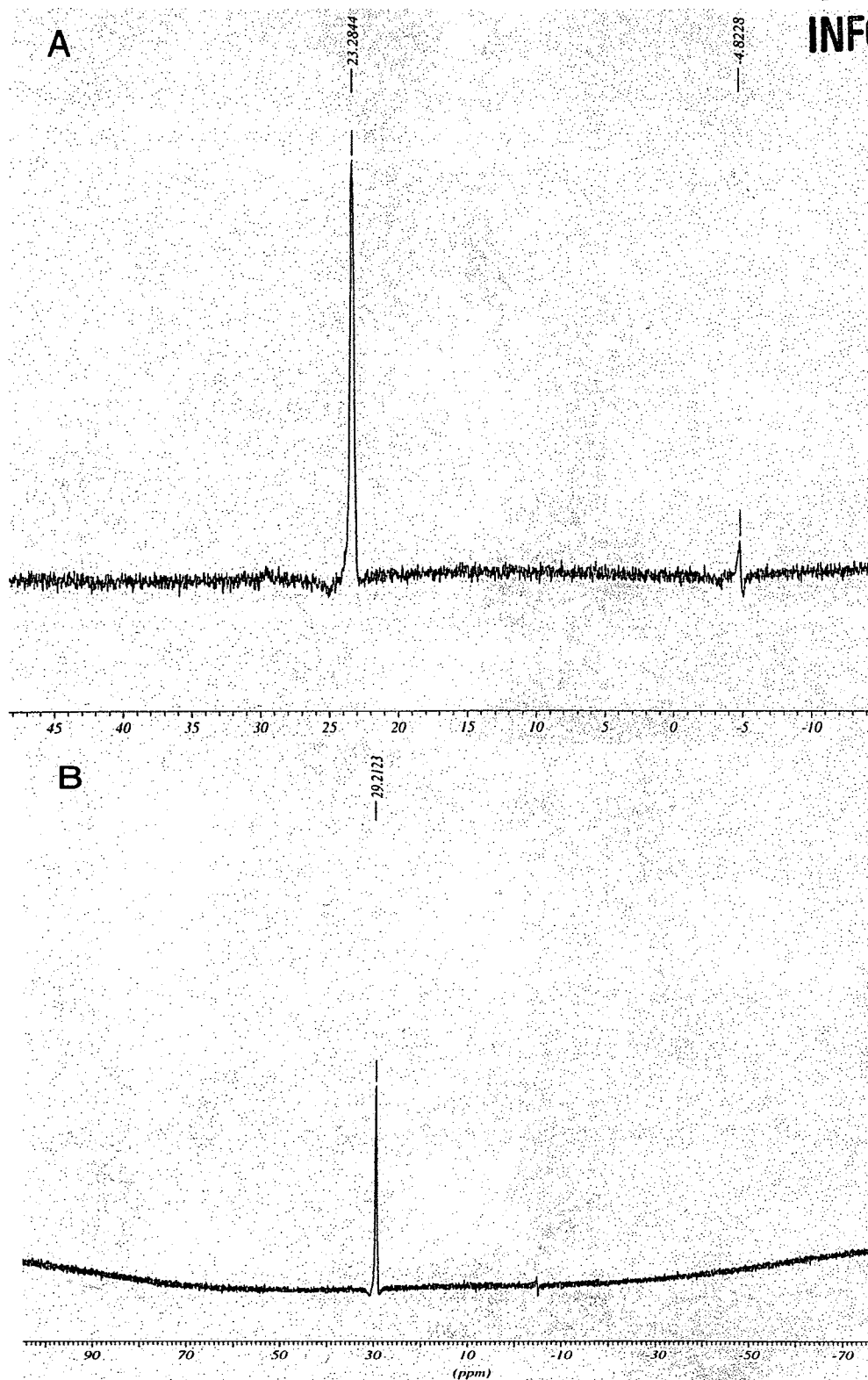


Figure A - ^{31}P NMR spectrum of a mixture of triphenylphosphine and ethyldiazoacetate 1:1 in chloroform (measured after 5 min reaction time). The signal at 23.3 ppm corresponds to the formed phosphazine and the one at -4.8 ppm to a small amount of unreacted triphenylphosphine.

Figure B - ^{31}P NMR spectrum of a mixture of triphenylphosphine, ethyldiazoacetate and 4-nitrobenzaldehyde 1:1:1. The signal at 29.2 ppm corresponds to the formed triphenylphosphine oxide (see eq 2 and article text for explanation).

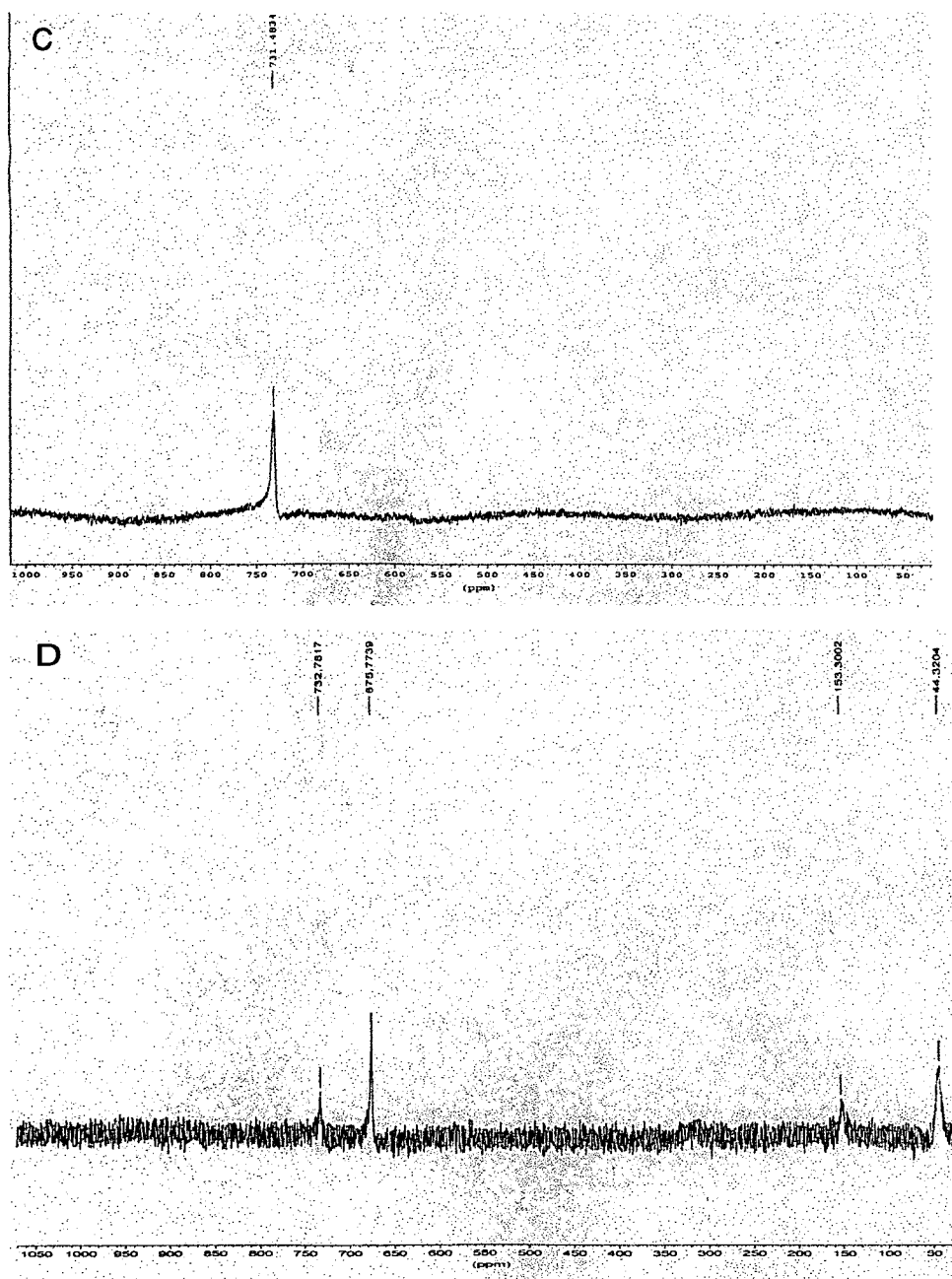


Figure C - ^{17}O -NMR spectrum of compound **1** in chloroform at room temperature. The sample has been labeled with ^{17}O in order to get spectra of sufficient quality in about 5 min measurement time.

Figure D - ^{17}O -NMR spectrum of the reaction of ^{17}O labeled compound **1** with phosphazine after a few minutes reaction time. The signal at ca. 732 ppm stems from still not reacted complex **1**, the signal at ca. 676 ppm is due to compound **B** (see Scheme 1), the signal at ca. 44 ppm originates from triphenylphosphine oxide, the signal at ca. 153 ppm and the broad peak centered at ca. 330 ppm belong to the two oxygen atoms in $\text{C}(\text{O})\text{OEt}$. The chemical shifts of these latter oxygens do not change significantly - in comparison to the measurement error - during the course of the reaction with respect to the starting materials.

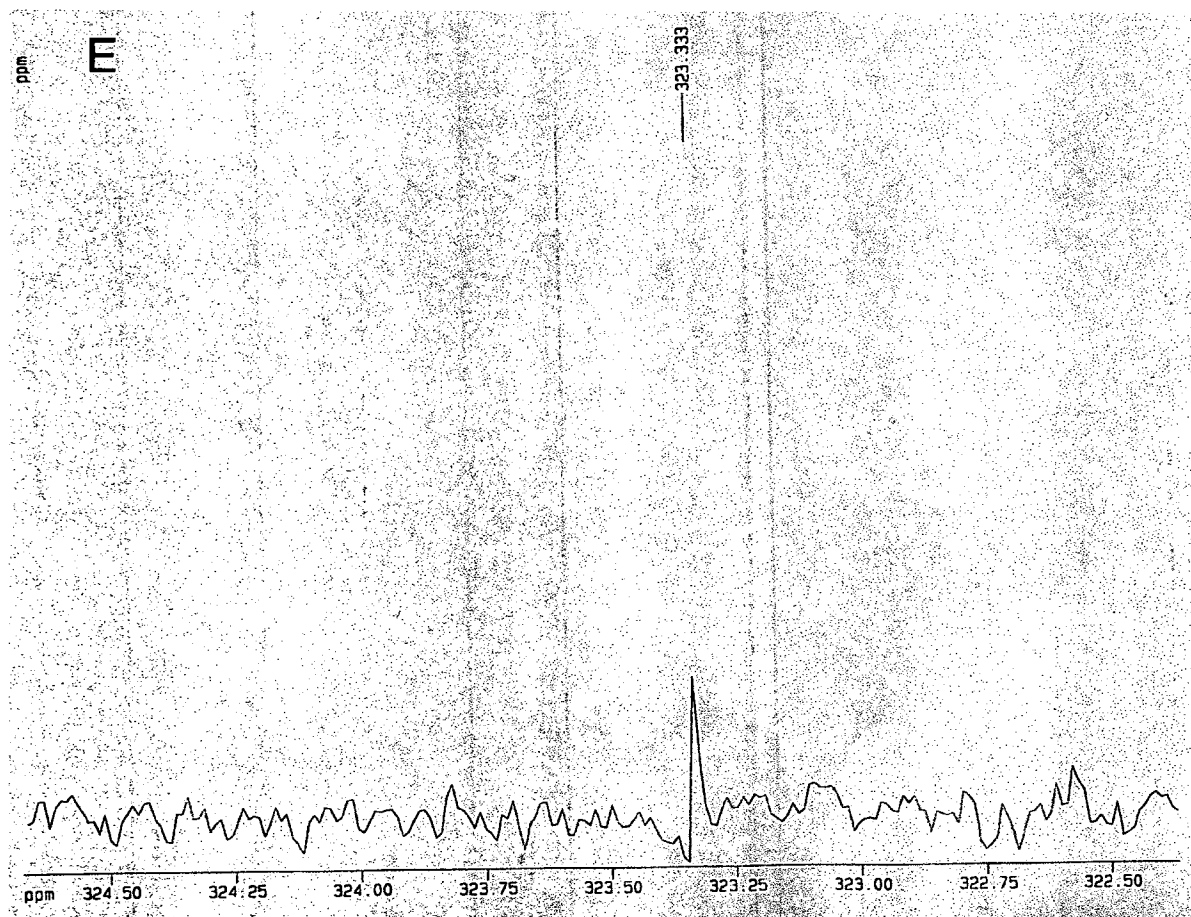


Figure E - ^{13}C -NMR signal of the carbene C-atom ($\text{Re}=\text{C}$) of compound **B** (see Scheme 1) after 10 min measurement time at a temperature of $-30\text{ }^{\circ}\text{C}$. Compound **B** has been prepared for this experiment from a mixture of triphenylphosphine, ethyl diazoacetate and compound **1** 1:1:0.5.

Sample preparation: (0.1g, 0.38 mmol) of triphenylphosphine were dissolved at room temperature in 0.4 mL of deuterated chloroform. To this solution (40 μL , 0.38 mmol) of ethyldiazoacetate were added at the same temperature, and the mixture was allowed to react for 15 min. The solution containing the resulting phosphazine was transferred to an NMR tube and frozen in a isopropanol/liquid N_2 bath. To the frozen solution, (0.078g, 0.19 mmol) of compound **1** were added. The mixture was allowed to liquefy, homogenized and inserted in the spectrometer which was set to $-30\text{ }^{\circ}\text{C}$ measurement temperature before. The measurement was performed after equilibrating the sample at $-30\text{ }^{\circ}\text{C}$ for ca. 10 min. Due to the high concentration of the reaction mixture, 10 - 15 min were enough to obtain spectra of sufficient quality. The reaction mixture was then slowly brought to 0°C and the same ^{13}C -NMR signals were obtained. However, at room temperature, the decomposition of the intermediate in the absence of the aldehyde is very quick and the carbene signal disappeared quickly.