Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

for

The chameleonic reactivity of dilithio bis(alkylamido)cyclodiphosph(III)azanes with chlorophosphines

Mathew E. Otang, David Josephson, Todd Duppong, and Lothar Stahl*

Department of Chemistry, University of North Dakota, Grand Forks, ND 58202-9024 USA

E-mail: lothar.stahl@und.edu

Phone: 1-701-777-2242

NMR Spectra of compounds 1a/b through 4 (all spectra were run in C_6D_6**).**

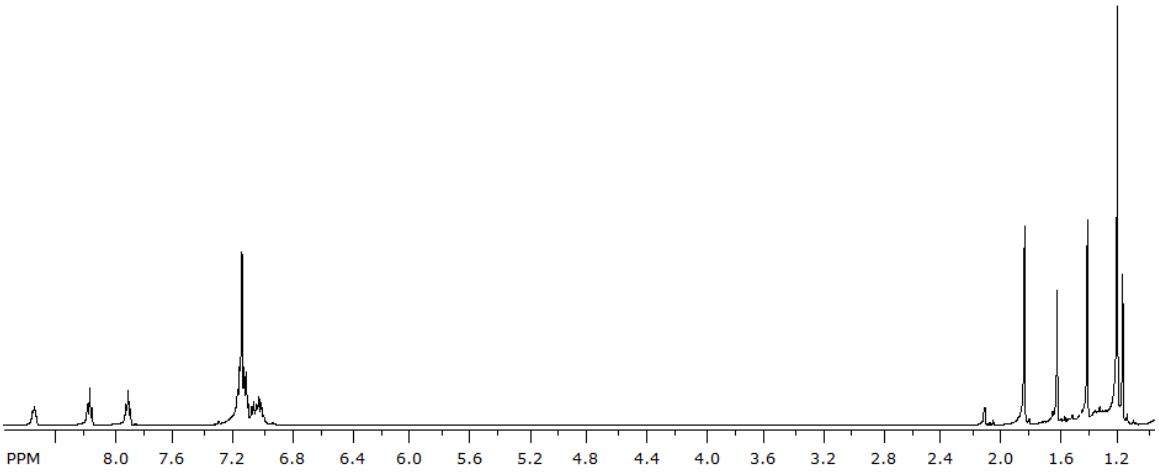


Fig. 1 ^{1}H NMR spectrum of the mixture **1a/1b**.

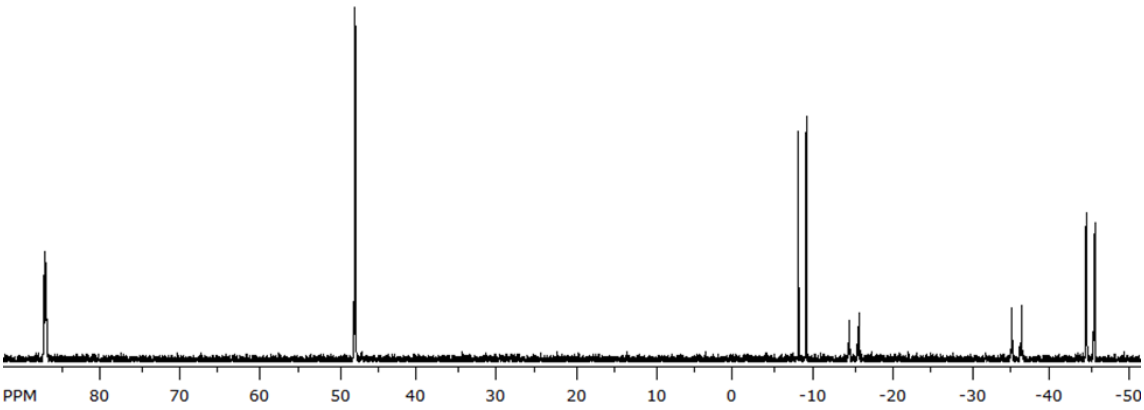


Fig. 2 $^{31}P\{^{1}H\}$ NMR spectrum of the mixture **1a/1b**.

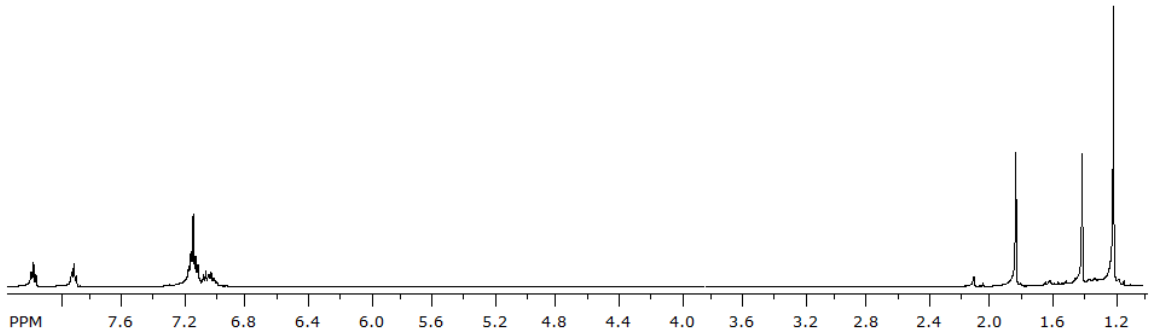


Fig. 3 ^{1}H NMR spectrum of **1a**.

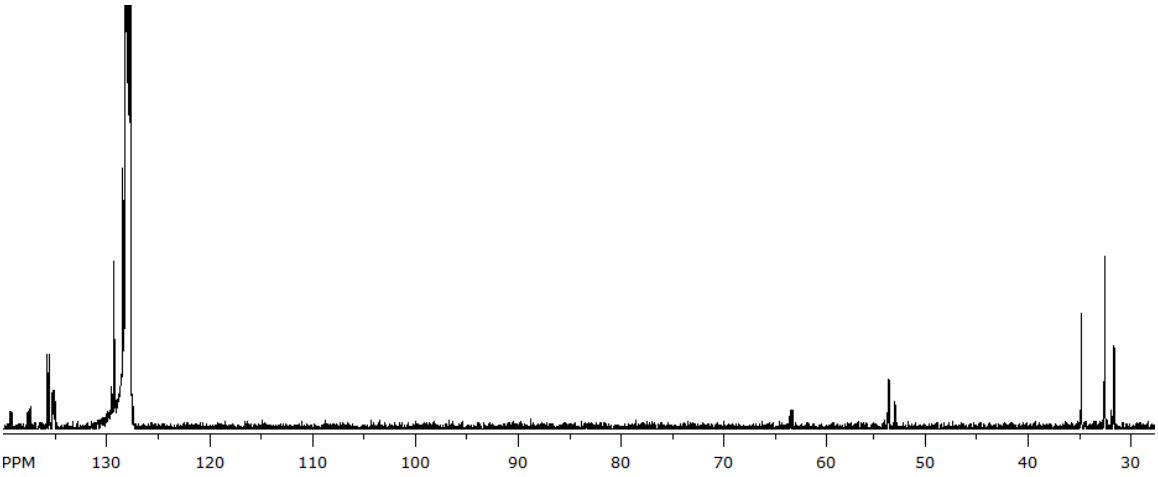


Fig. 4 ^{13}C{^{1}H} NMR spectrum of **1a**.

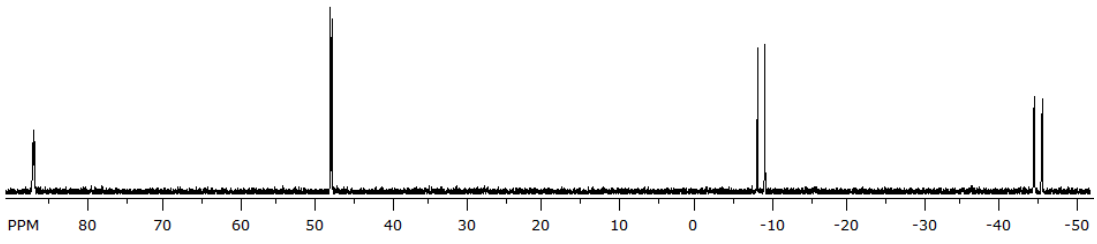


Fig. 5 ^{31}P{^{1}H} NMR spectrum of **1a**.

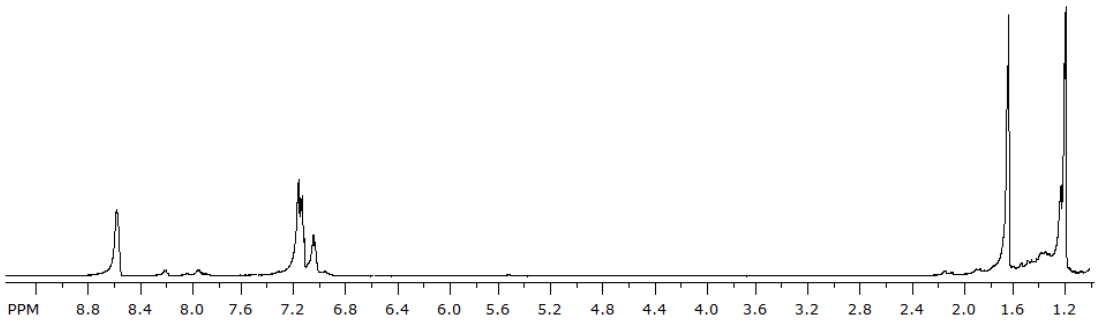


Fig. 6 ^{1}H NMR spectrum of **1b**.

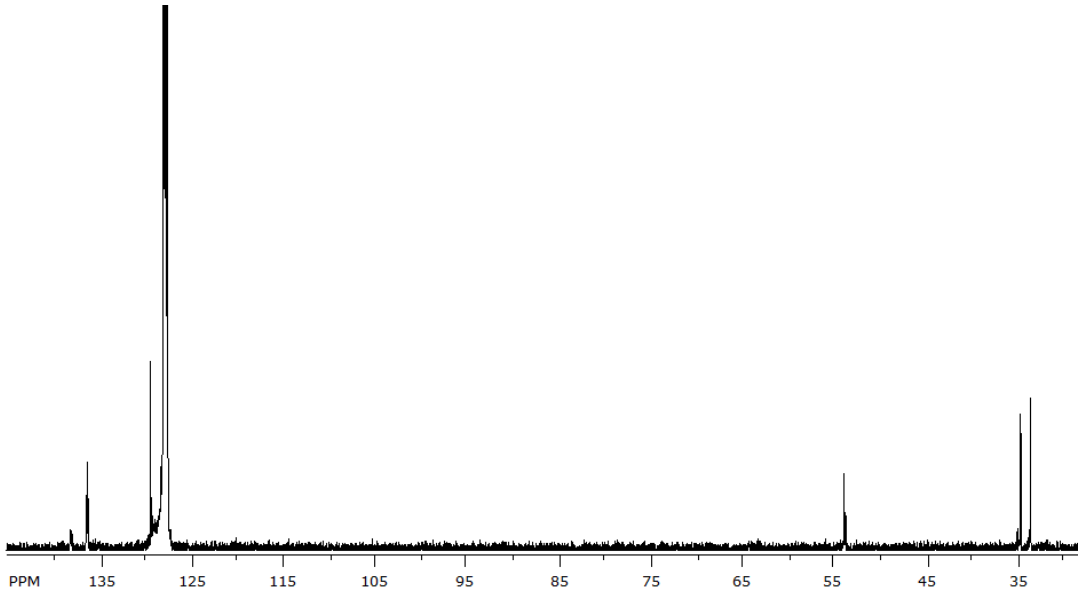


Fig. 7 ^{13}C{^{1}H} NMR spectrum of **1b**.

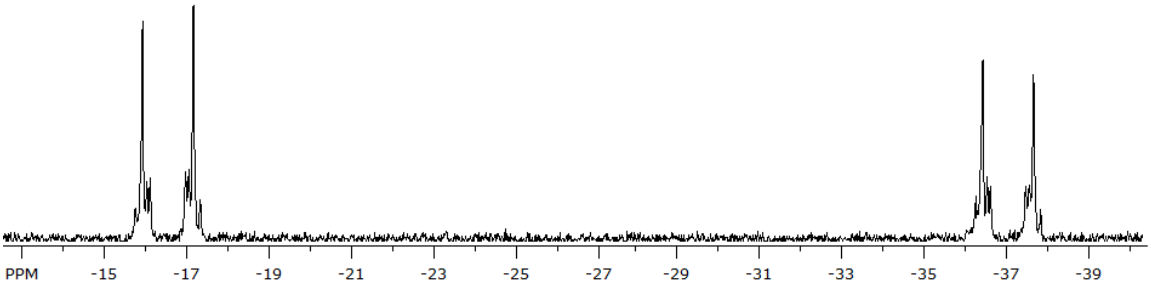


Fig. 8 ^{31}P{^{1}H} NMR spectrum of **1b**.

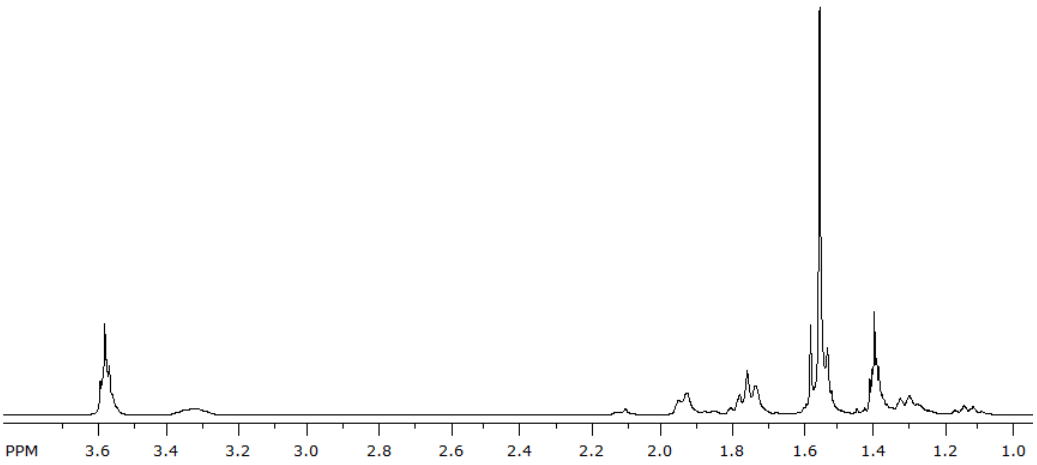


Fig. 9 ^{1}H NMR spectrum of **2**.

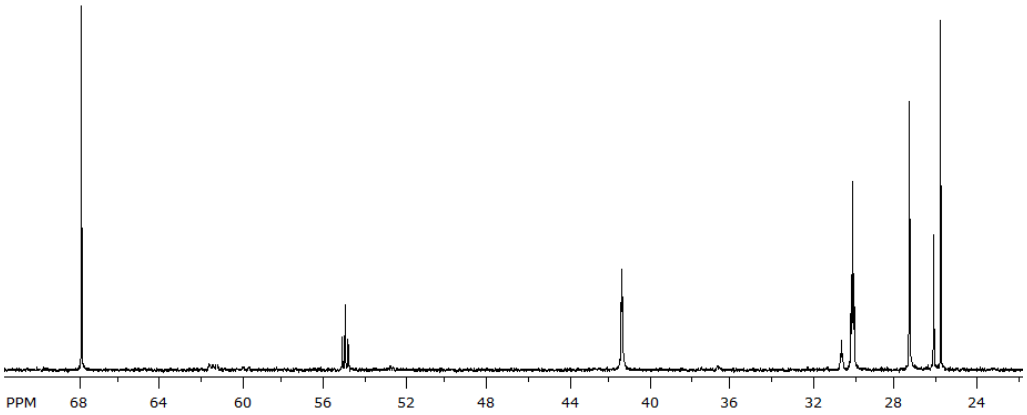


Fig. 10 ^{13}C {^{1}H} NMR spectrum of **2**

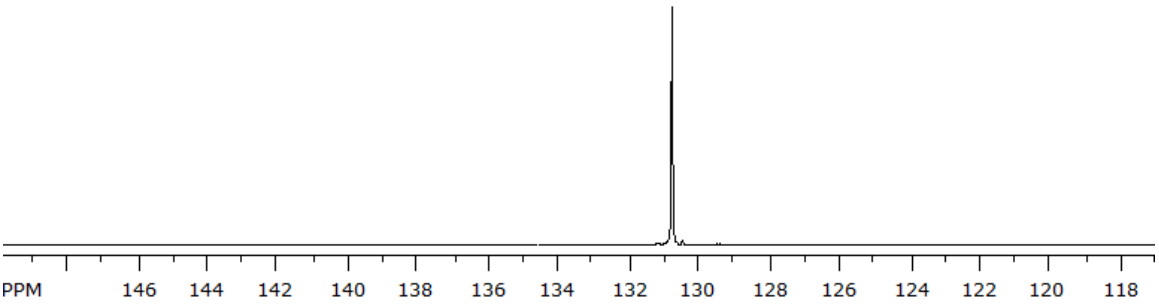


Fig. 11 ^{31}P{^{1}H} NMR spectrum of **2**.

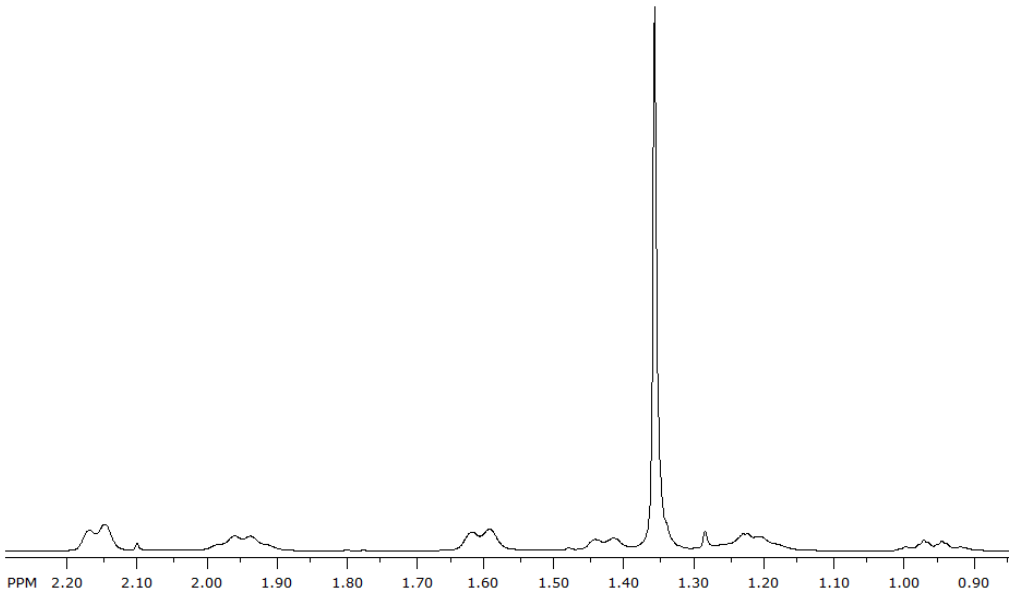


Fig. 12 ^{1}H NMR spectrum of **3**.

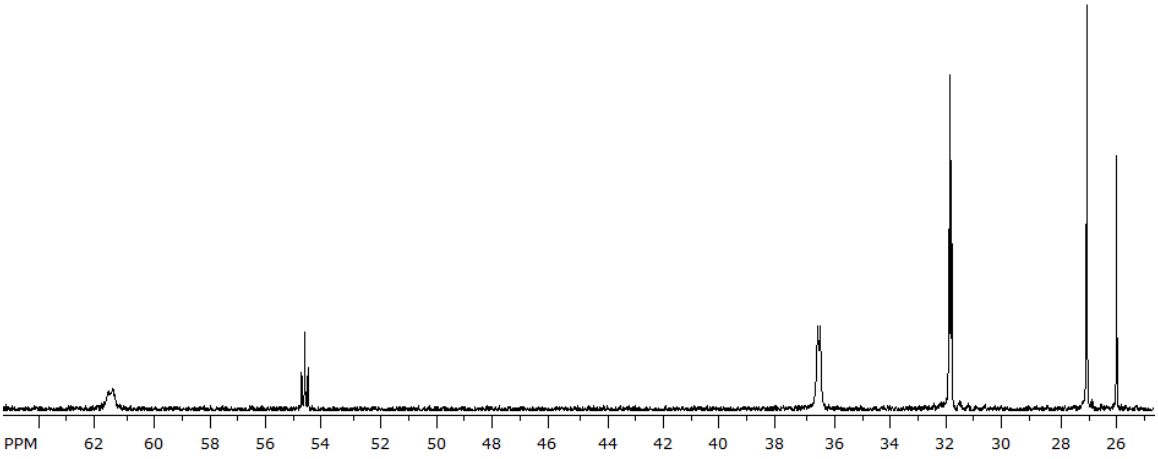


Fig. 13 ^{13}C {^{1}H*}* NMR spectrum of **3**

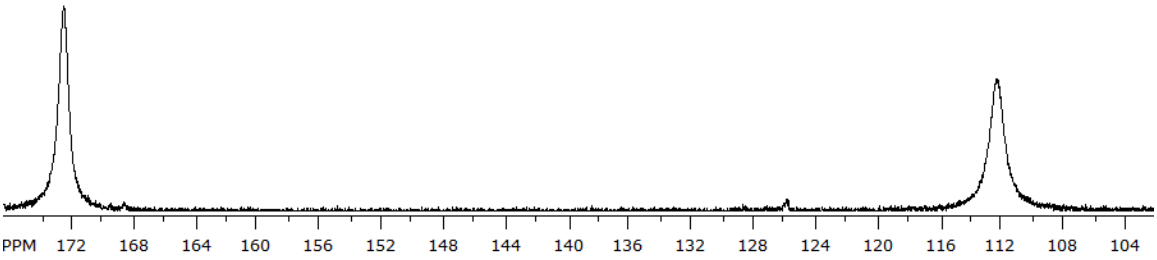


Fig. 14 ^{31}P{^{1}H} NMR spectrum of **3**.

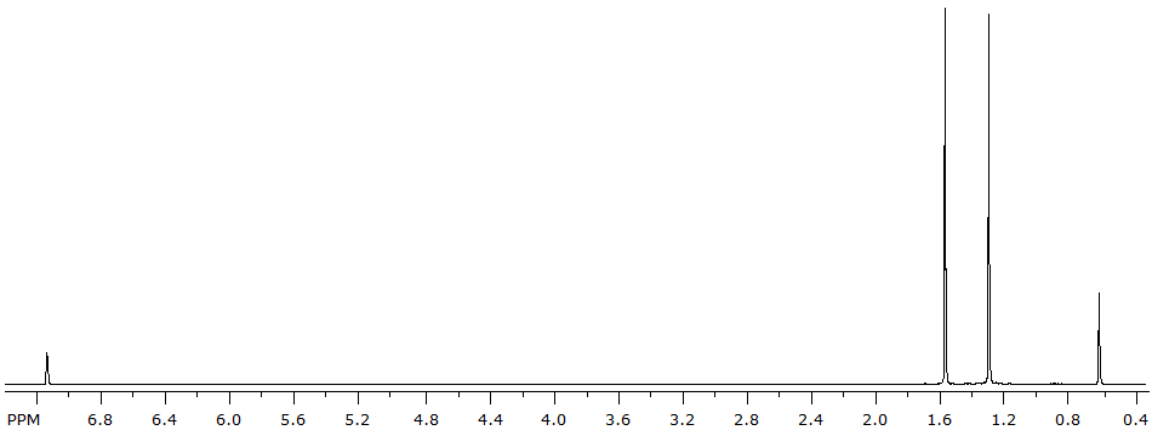


Fig. 15 ^{1}H NMR spectrum of **4**.

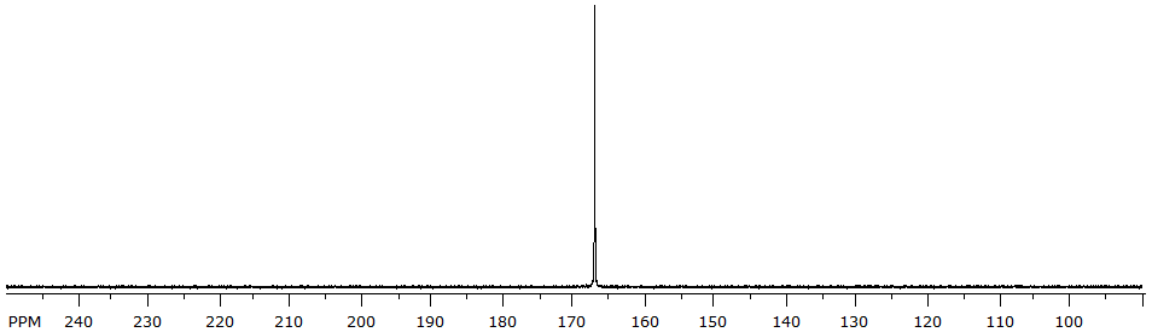


Fig. 16 ^{31}P{^{1}H} NMR spectrum of **4**.

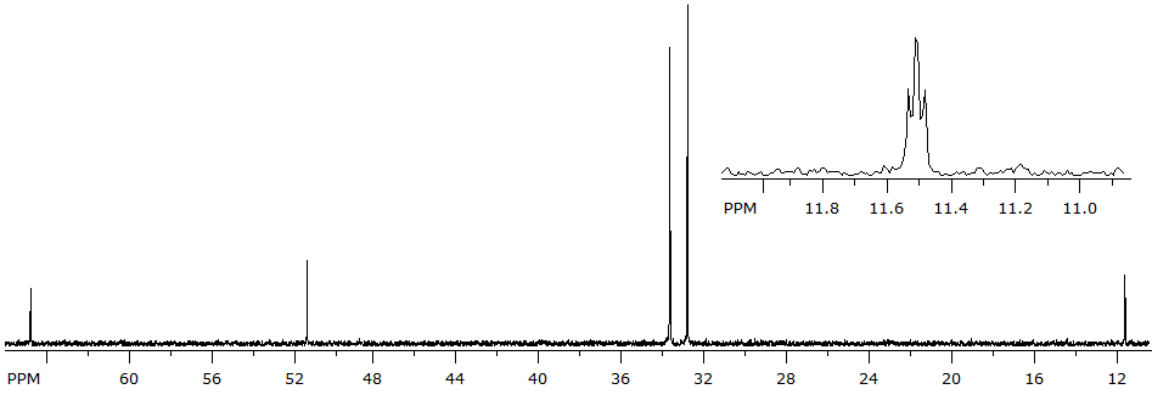


Fig. 17 ^{13}C{^{1}H} NMR spectrum of **4**.

Kinetic Studies on the Conversion of Isomer 1b to Isomer 1a

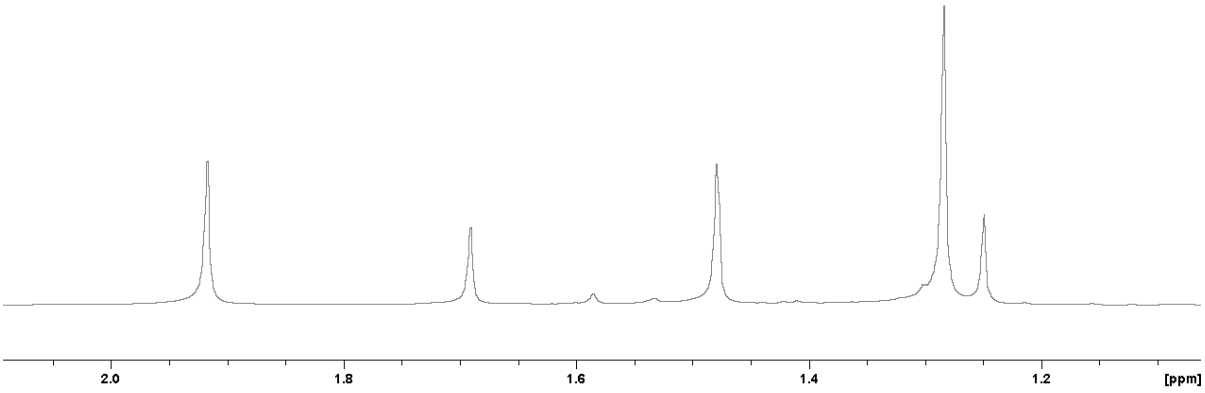


Fig. 18 Expanded region of a ^{1}H NMR spectrum, showing the well-resolved singlets that were integrated and used in the kinetic studies for the conversion of **1b** to **1a**.

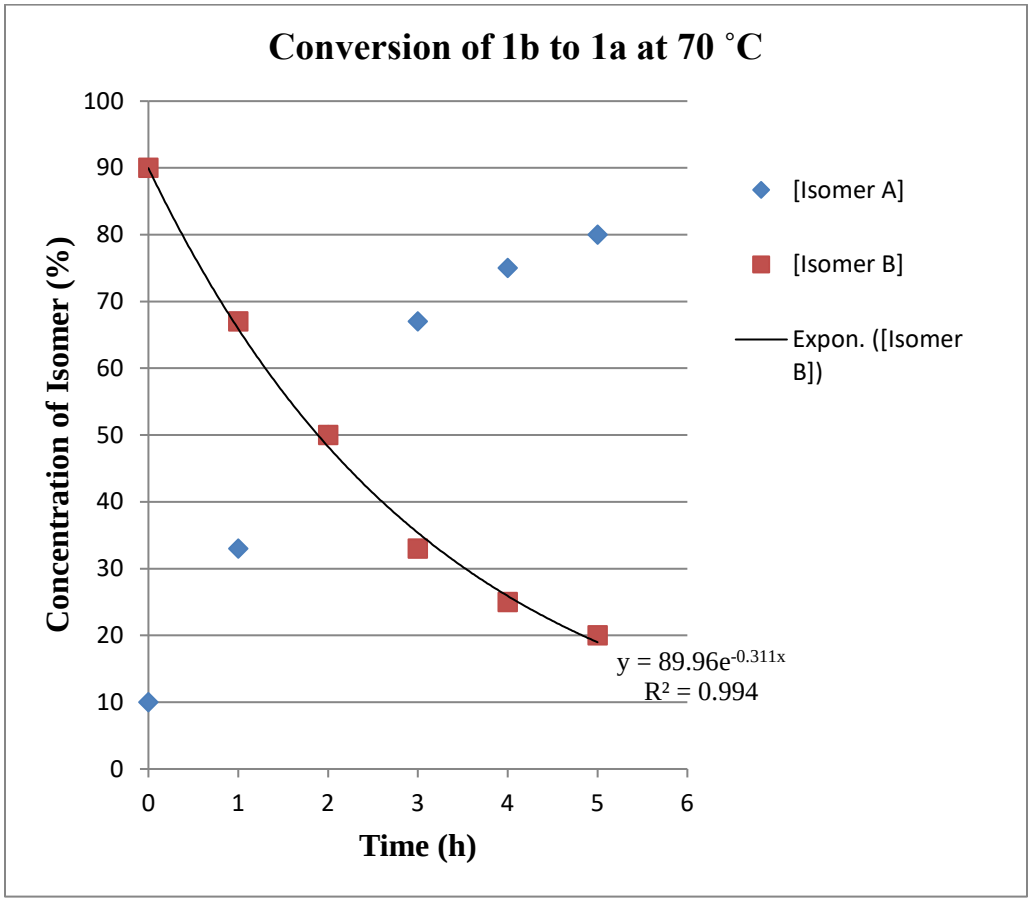
During the synthesis of isomers **1a** and **1b**, we observed that the formation of the former is favored by higher temperature while the latter is favored by lower temperature. We proceeded to study the kinetics of this isomerization by heating a sample of isomer **1b** in a sealed NMR tube at 70 °C while recording NMR spectra every 60 minutes. A graph of the rate of change of the concentration of isomer **1b** with time is shown in Figure 19.

To confirm the first order kinetics, we plotted a graph of the natural logarithm of the concentration of isomer **1b** against time (Fig. 20). The graph suggests that the isomerization of isomer **1b** to isomer **1a** is a first order process, with a rate constant, $k = 9.63 \times 10^{-5}\ s^{-1}$. Identical procedures were carried out at 60 °C, with the corresponding kinetic plots shown in Fig. 21 and Fig. 22.

The appropriate rate equations for the rearrangement process are shown as equation 1.1 (linear) and equation 1.2 (exponential):

$$\ln[\text{isomer } \mathbf{1b}] = \ln[\text{Isomer } \mathbf{1b}]_o - kt \qquad (1.1)$$

$$[\text{Isomer } \mathbf{1b}] = [\text{Isomer } \mathbf{1b}]_o e^{-kt} \qquad (1.2)$$



Fig, 19. Conversion of isomer **1b** to isomer **1a** at 70 °C.

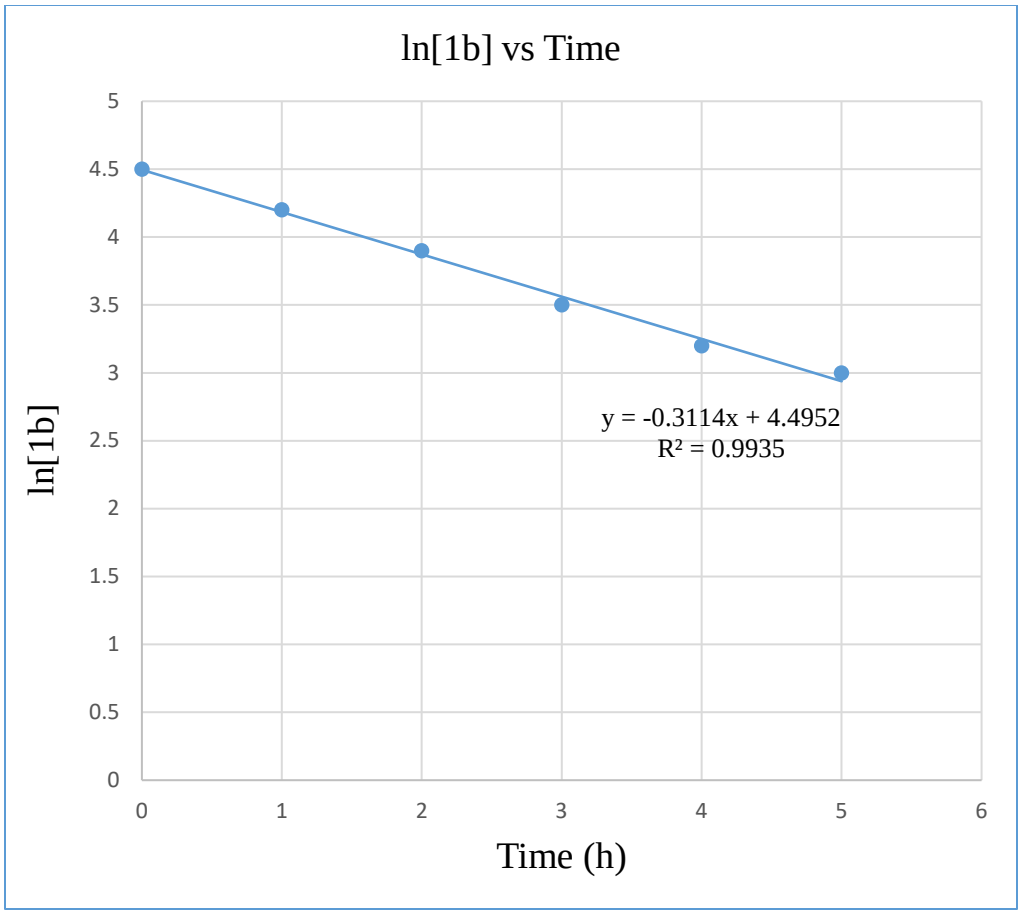
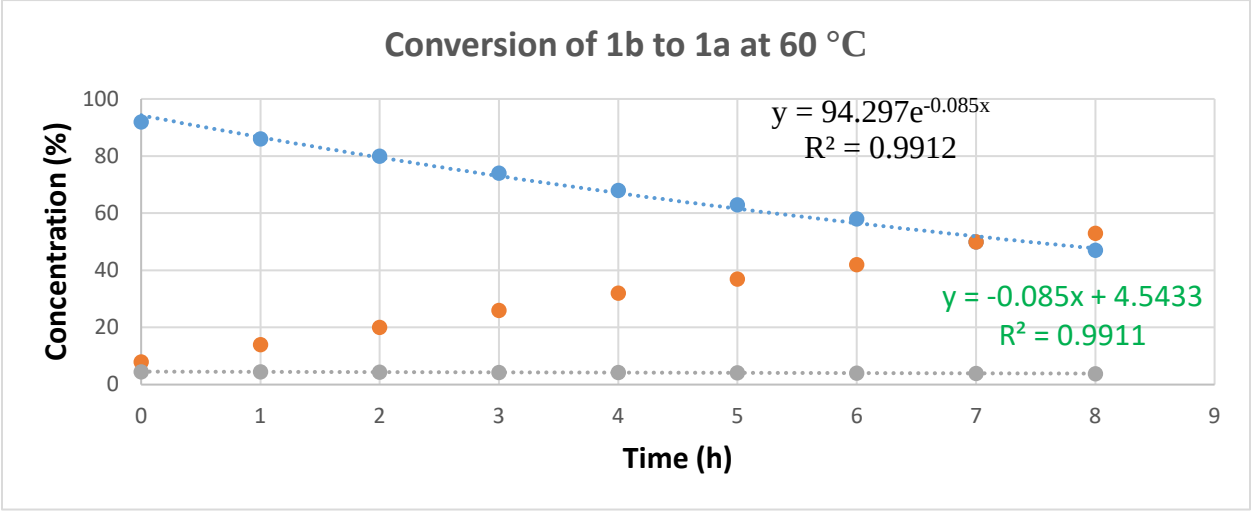


Fig. 20. Graph of ln[**1b**] versus time.



Fig, 21. Conversion of isomer **1b** to isomer **1a** at 60 °C.

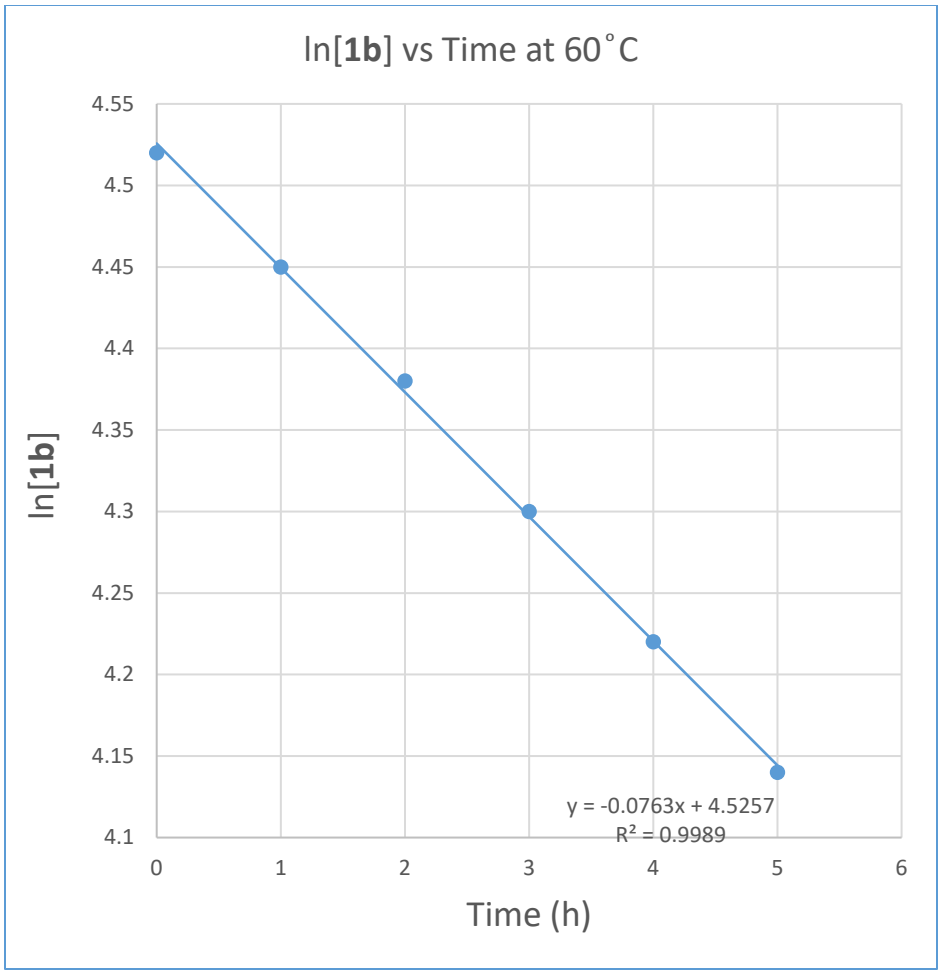


Fig. 22. Graph of ln[**1b**] versus time.

To calculate the activation energy (E_a) for this isomerization, we carried out the same process at T2 = 60 °C and obtained the rate constant $k_2 = 2.75 \times 10^{-5}$ s^{-1} at this temperature. Then, using equations 1.3–1.5, we found the activation energy for this process to be 119 kJ/mol or 28.4 kcal/mol.

$$k = Ae^{-\frac{E_a}{RT}} \qquad 1.3$$

k = rate constant

A = frequency factor

E_a = Activation energy

R = Gas constant

T = Temperature

After rearranging equation 1.3, equations 1.4 and 1.5 were obtained from which E_a was calculated, as follows.

$$\ln\left(\frac{k1}{k2}\right) = \frac{Ea}{R}\left(\frac{1}{T2} - \frac{1}{T1}\right) \qquad 1.4$$

$$E_a = \frac{R\ln\left(\frac{k2}{k1}\right)}{\left(\frac{1}{T2} - \frac{1}{T1}\right)} \qquad 1.5$$