

## Thermal rearrangement of bis(hydroxymethyl)phosphines as a way to *P*-chiral phosphine oxides

Irina R. Dayanova, Alexey V. Kurenkov, Kamil D. Akhmadgaleev, Kamila R. Trigulova, Daut R. Islamov, Olga E. Naumova, Igor D. Strel'nik, Elvira I. Musina and Andrey A. Karasik

### Experimental section

**General procedures.** (2-Pyridyl)phosphine and [2-(2-pyridyl)ethyl]phosphine were obtained as reported [S1,S2]. All reactions and purifications were carried out under a dry argon atmosphere by using standard vacuum-line techniques. Commercially available solvents were purified, dried, deoxygenated and distilled before use.

<sup>1</sup>H NMR (600.1 MHz) and <sup>31</sup>P NMR (242.9 MHz) spectra were recorded on a Bruker Avance 600 spectrometer and <sup>1</sup>H NMR (400.13 MHz) and <sup>31</sup>P NMR (161.96 MHz) spectra were recorded on a Bruker Avance 400 spectrometer by using the residual solvent as an internal reference for <sup>1</sup>H ( $\delta = 7.26$  in CDCl<sub>3</sub>) and 85% aqueous solution of H<sub>3</sub>PO<sub>4</sub> as an external reference for <sup>31</sup>P. Chemical shifts are reported in ppm and coupling constants (J) are reported in Hz.

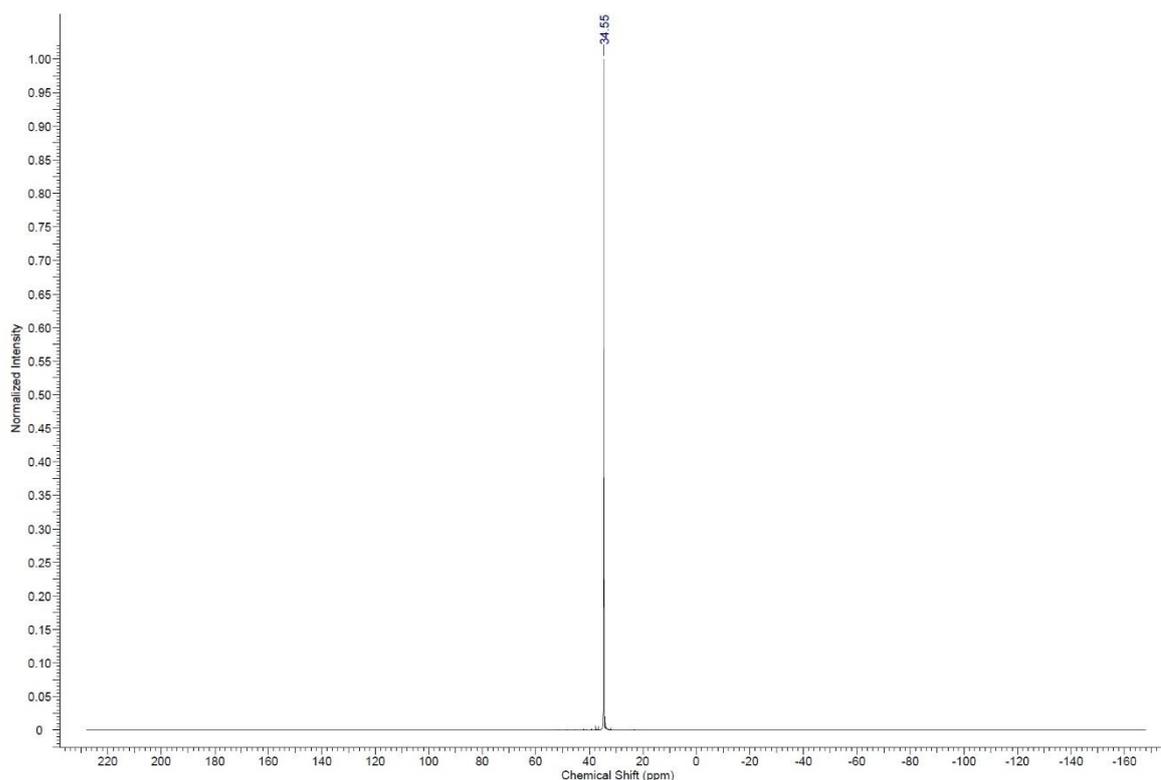
Data set for single crystal of **3b** was collected on a Rigaku XtaLab Synergy S instrument with a HyPix detector and a PhotonJet microfocuss X-ray tube using Cu K $\alpha$  (1.54184 Å) radiation at room temperature. Images were indexed and integrated using the CrysAlisPro data reduction package. Data were corrected for systematic errors and absorption using the ABSPACK module: numerical absorption correction based on Gaussian integration over a multifaceted crystal model and empirical absorption correction based on spherical harmonics according to the point group symmetry using equivalent reflections. The GRAL module was used for analysis of systematic absences and space group determination. The structure was solved by direct methods using SHELXT [S3] and refined by the full-matrix least-squares on F<sup>2</sup> using SHELXL [S4]. Non-hydrogen atoms were refined anisotropically. The hydrogen atoms were inserted at the calculated positions and refined as riding atoms. Crystals were obtained by slow evaporation from the ethanol:toluene (ratio 1:10) mixture.

### General synthetic procedures

Primary phosphine (1.8 mmol) **1a,b** and paraformaldehyde (3.6 mmol) were mixed, and the mixtures were stirred at 120 °C until the homogenization. After that the temperature was raised up to 180 °C, and the mixtures were stirred at this temperature for 4 hours. The resulted oil was dissolved in a mixture of ethanol and toluene of 1:10 ratio. The mixture was kept under the slow evaporation conditions until the oily product formed. The solvent was removed by decantation, and the oil was dried in vacuum to leave pure phosphine oxides **3a,b** as viscous oils. The crystalline sample of **3b** was obtained by crystallization of the oily product from the ethanol/toluene (1:10 ratio) solution.

*P*-Hydroxymethyl-*P*-methyl-*P*-(2-pyridyl)phosphine oxide **3a**. Yield: 75%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , ppm):  $\delta_{\text{H}}$  8.68 (m, 1H,  $^3J_{\text{HH}} = 4.78$ , H in Py), 8.07 (m,  $^3J_{\text{HH}} = 7.69$ ,  $^4J_{\text{HH}} = 6.58$  Hz, 1H, H in Py), 7.86 (dd,  $^3J_{\text{HH}} = 7.77$ ,  $^3J_{\text{HH}} = 7.69$  Hz, 1H, H in Py), 7.43 (m,  $^3J_{\text{HH}} = 7.77$  Hz,  $^3J_{\text{HH}} = 4.78$  Hz,  $^4J_{\text{HH}} = 6.58$ , 1H, H in Py), 4.26 (d,  $^2J_{\text{PH}} = 13.92$  Hz, 1H, P-CH<sub>2</sub>), 4.13 (m.,  $^2J_{\text{PH}} = 5.72$ , 1H, P-CH<sub>2</sub>), 1.81 (d,  $^2J_{\text{PH}} = 13.41$  Hz, 3H, H in PCH<sub>3</sub>).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta_{\text{P}}$  34.5 ppm.

*P*-Hydroxymethyl-*P*-methyl-*P*-[2-(2-pyridyl)ethyl]phosphine oxide **3b**. Yield: 82%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , ppm):  $\delta_{\text{H}}$  8.41 (d, 1H,  $^3J_{\text{HH}} = 4.52$ , H in Py), 7.60 (dd,  $^3J_{\text{HH}} + ^3J_{\text{HH}} = 15.43$ , 1H, H in Py), 7.19 (d,  $^3J_{\text{HH}} = 8.88$ , 1H, H in Py), 7.13 (m,  $^3J_{\text{HH}} + ^3J_{\text{HH}} = 12.45$  Hz, 1H, H in Py), 3.8 (m, 2H, P-CH<sub>2</sub>-OH), 3.20 (m., 1H, Py-CH<sub>2</sub>), 3.09 (m., 1H, Py-CH<sub>2</sub>), 2.34 (m., 1H, P-CH<sub>2</sub>), 2.11 (m., 1H, P-CH<sub>2</sub>), 1.48 (d,  $^2J_{\text{PH}} = 12.61$  Hz, 3H, H in P-CH<sub>3</sub>).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta_{\text{P}}$  48.5 ppm.



**Figure S1.**  $^{31}\text{P}$  NMR spectrum of compound **3a**

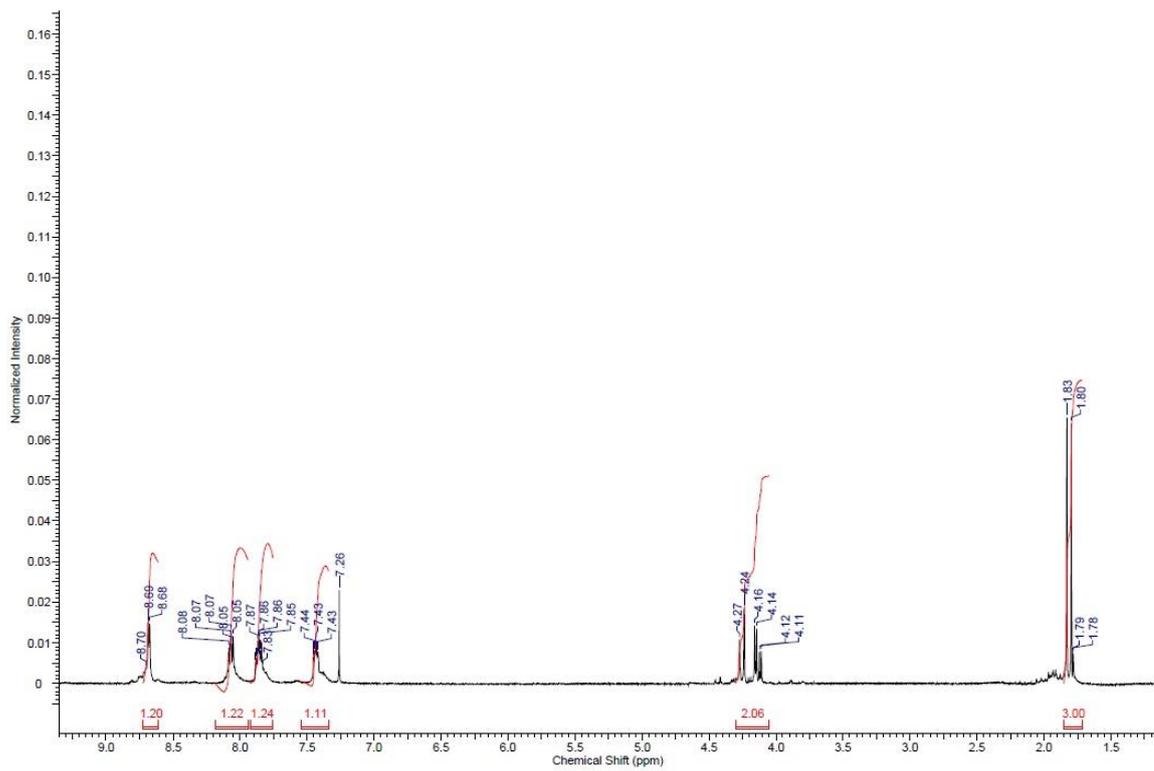


Figure S2. <sup>1</sup>H NMR spectrum of compound 3a

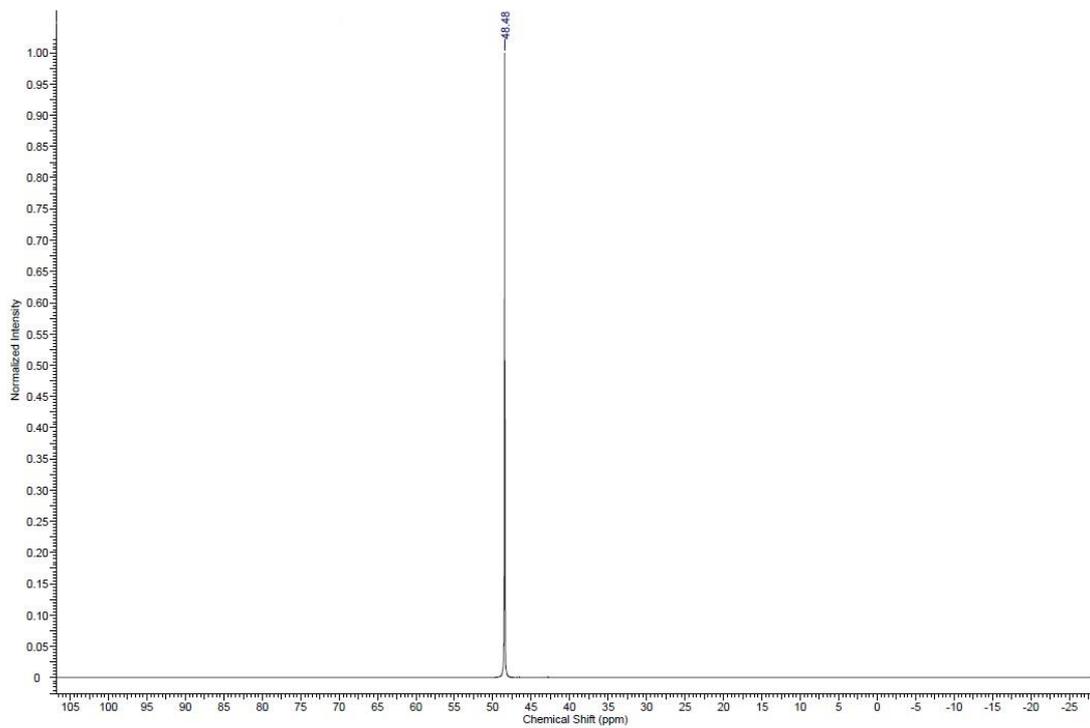
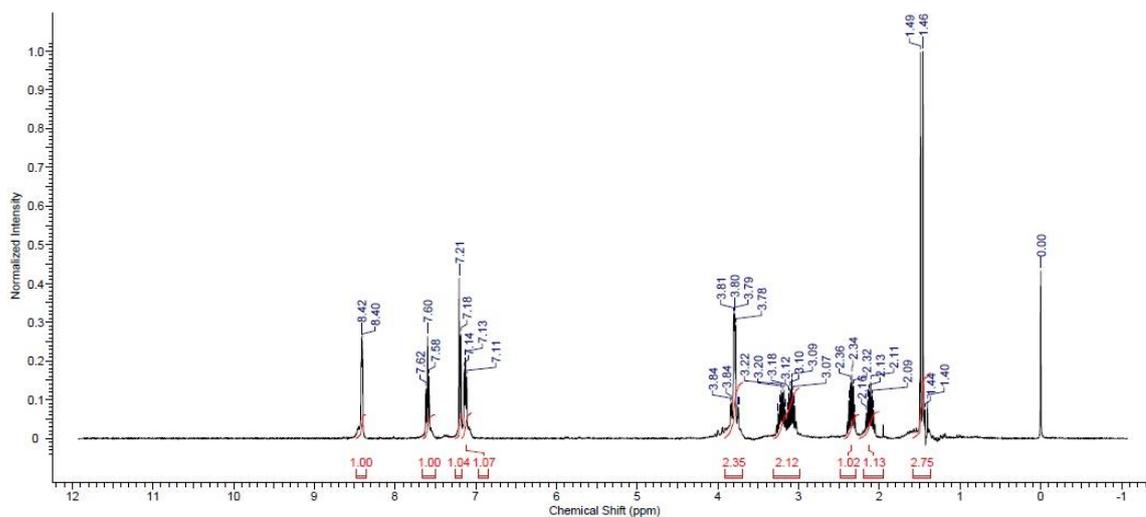
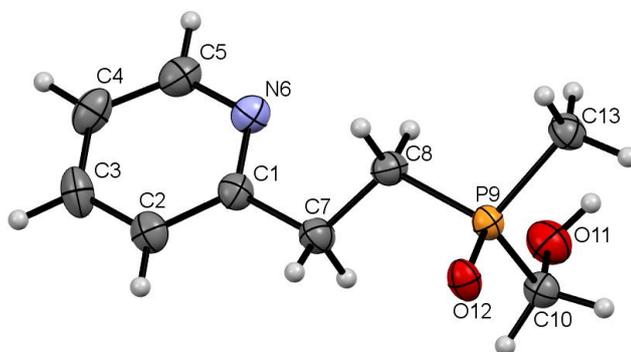


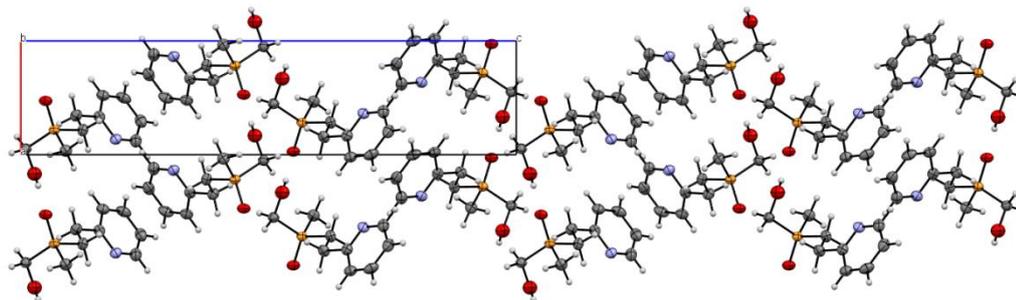
Figure S3. <sup>31</sup>P NMR spectrum of compound 2



**Figure S4.**  $^1\text{H}$  NMR spectrum of compound **3b**



**Figure S5.** ORTEP representation of **3b** showing 50% probability thermal ellipsoids. C atoms are grey, N atoms are blue, O atoms are red, P atom is orange. Selected bond lengths: P9-O12=1.505(4) Å; P9-C10=1.815(6) Å; P9-C13=1.802(6) Å; P9-C8=1.797(6) Å. Selected bond angles: O12-P9-C10=111.6(3)°; O12-P9-C13=113.6(3)°; O12-P9-C8=113.0(3)°; C13-P9-C10=105.9(3)°; C8-P9-C10=106.8(3)°; C8-P9-C13=105.3(3)°.



**Figure S6.** Crystal packing of **2** view along *b* axes.

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