

Mechanistic aspects of the stereospecific reduction of chiral hydroxyalkyl phosphinates and phosphine oxides

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1. General information

1.1. Solvents

All solvents were purified by standard procedures or obtained from a Solvent Purification System (Braun SPS 800). Unless otherwise mentioned, all reactions were carried out under an atmosphere of dry argon.

1.2. Thin layer chromatography

Thin Layer Chromatography (TLC) was carried out on Merck silica gel 60 F₂₅₄ and visualized under ultraviolet light (254 and 366 nm), or through spraying with 5% phosphomolybdic acid in EtOH, H₂SO₄-acidified p-Anisaldehyde solution in EtOH or by placing in iodine vapor. Flash chromatography was performed with Merck silica gel 60 (230-400 mesh).

1.3. Chiral High Performance Liquid Chromatography

Solvents for chiral chromatography (*n*-hexane, EtOH) are HPLC grade, degassed and filtered on Millipore membrane 0.45 μm before use. Chiralpak IA columns (250*4.6mm) was used for the analytical separation. Chiral HPLC analyses were performed on a screening unit composed of Merck D-7000 system manager, Merck-Lachrom L-7100 pump, Merck-Lachrom L-7360 oven, Merck-Lachrom L-7400 UV detector and Jasco OR-1590 polarimetric or Jasco CD-1595 circular dichroism detector. Retention times *R_t* are given in minutes, retention factor $k_i = (R_{t_i} - R_{t_0})/R_{t_0}$ and enantioselectivity factor $\alpha = k_2/k_1$. The sign given by the chiroptical detector is the sign of the enantiomer in the mobile phase used, at the specified wavelength.

1.4. Nuclear Magnetic Resonance

¹H, ¹³C, ¹¹B and ³¹P NMR spectra were recorded on Bruker Avance III nanobay spectrometers operating at 400 and 300 MHz for ¹H. ¹³C and ³¹P nuclei were observed with ¹H decoupling. Unless

otherwise specified NMR spectra have been made in CDCl_3 . As external reference for ^{31}P NMR spectra, 85% phosphoric acid was used. Chemical shifts (δ) of ^1H and ^{13}C are reported in ppm relative to CHCl_3 ($\delta = 7.26$ for ^1H and $\delta = 77.0$ for ^{13}C) and C_6D_6 ($\delta = 7.15$ for ^1H and $\delta = 128.02$ for ^{13}C). J values are given in Hz. Proton (^1H) NMR information is given in the following format: multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; sept; septet; m, multiplet), coupling constant J , number of protons). The prefix broad or b indicates the signal in question is broadened.

1.5. Physical and Analytical Measurements

$[\alpha]_{\text{D}}^{25}$ values were determined with a Perkin-Elmer Polarimetric 341. High-resolution MS experiments were performed with a QStar Elite mass spectrometer (Applied Biosystems SCIEX, Concord, ON, Canada) equipped with an electrospray ionisation (ESI) source. In the positive ion mode, the capillary voltage was set at +5500 V and the cone voltage was set between 10-55 V. In this hybrid instrument, ions were measured using an orthogonal acceleration time-of-flight (oa-TOF) mass analyzer. In MS, accurate mass measurements were performed using two reference ions from a poly(ethylene glycol) or poly(propylene glycol) internal standards.

2. NMR spectra

Figure S1 : ^1H NMR spectrum of **4b**

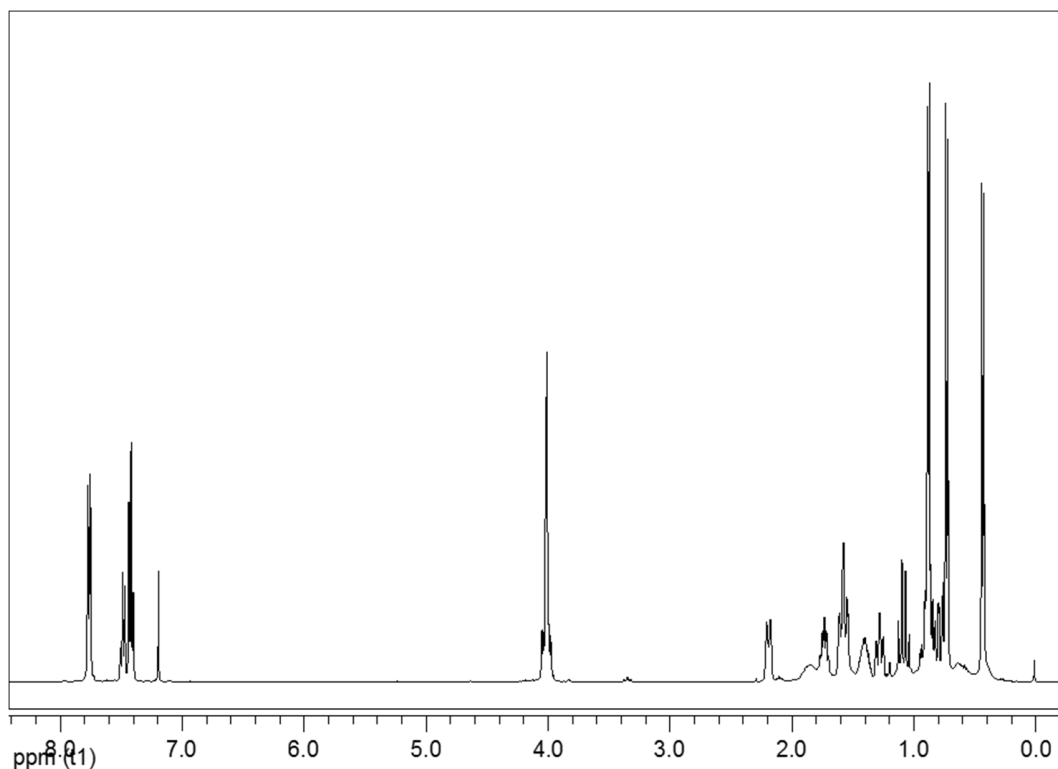


Figure S2: $^3\text{P}\{^1\text{H}\}$ NMR spectrum of **4b**

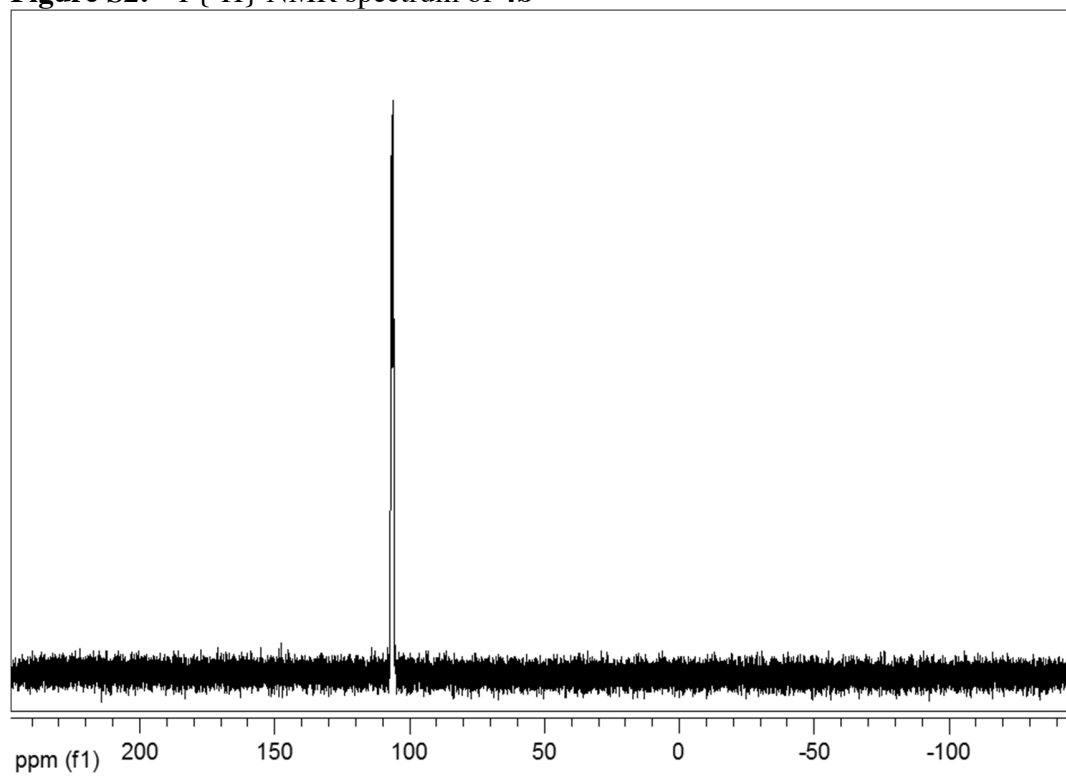


Figure S3: $^{13}\text{C}\{^1\text{H}\}$ APT NMR spectrum of **4b**

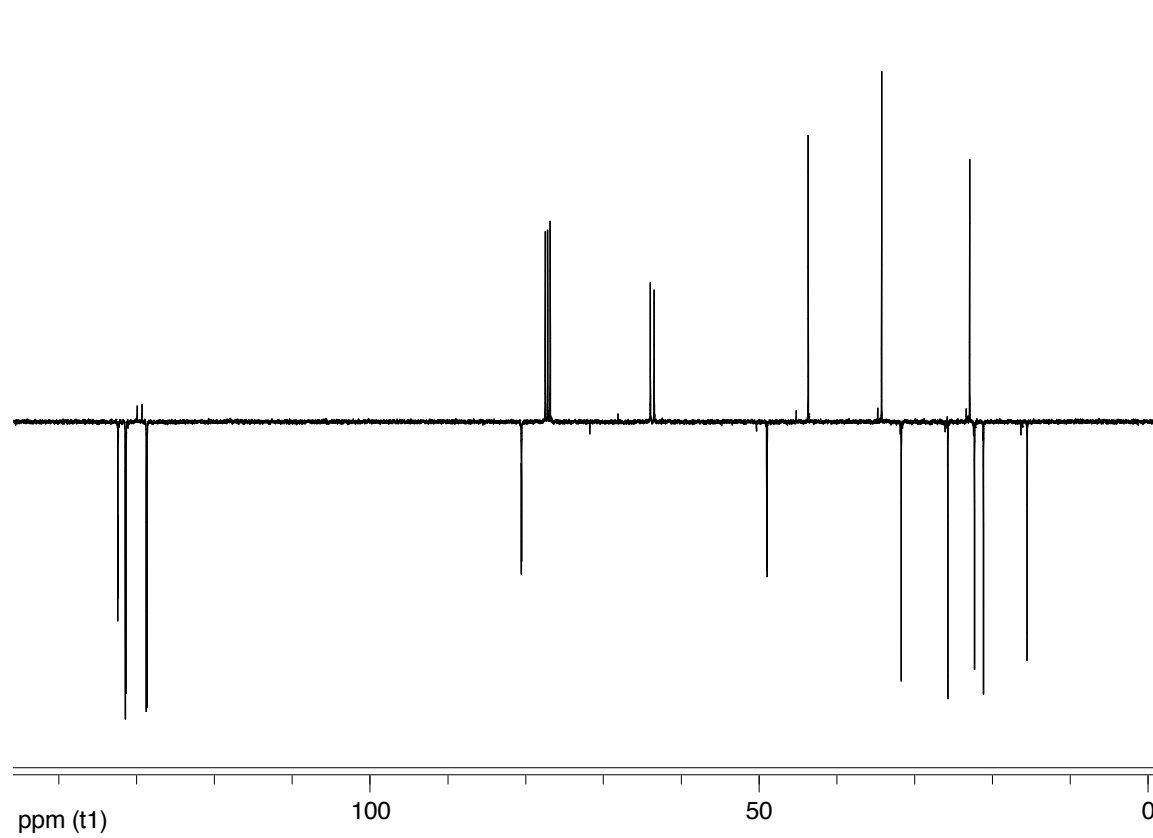
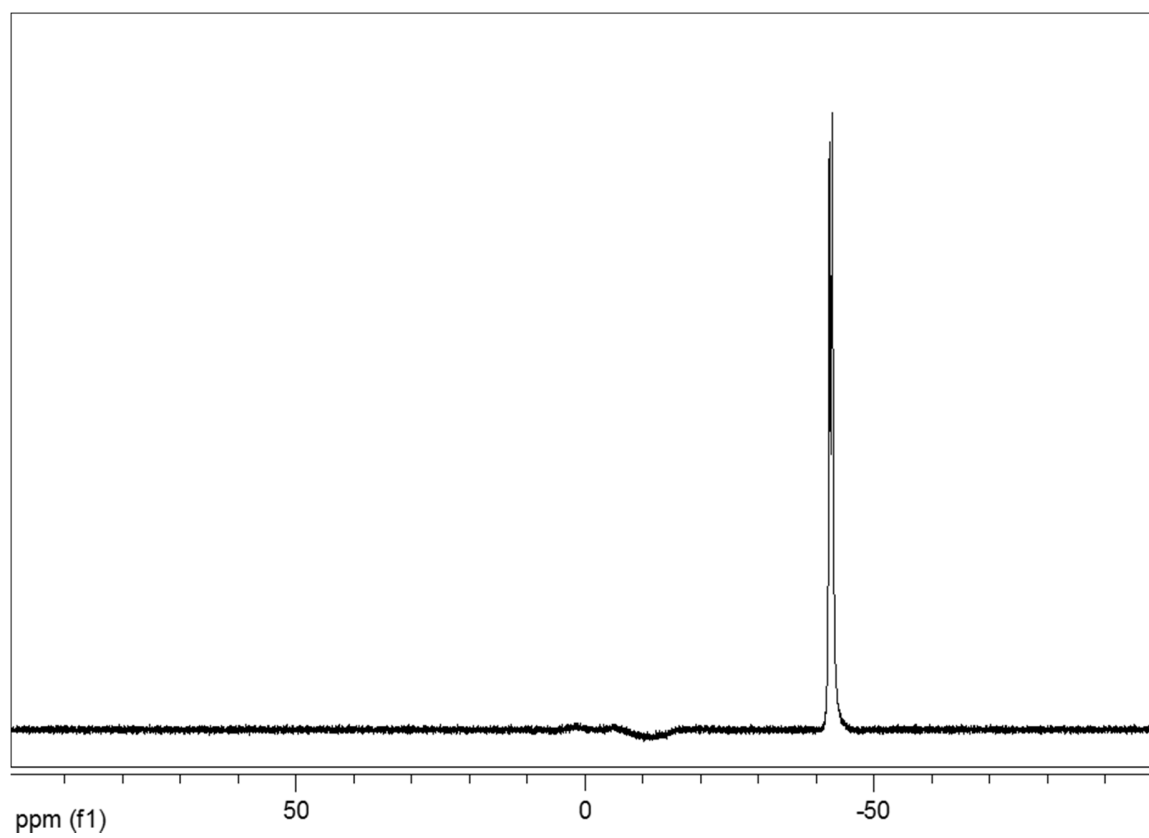


Figure S4: $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **4b**



3. HPLC chromatograms

Figure S5: HPLC chromatogram of **4b**

