Supporting Information for

Carbonyl Orientation Determines Regio- and Enantio-Selectivity in 1,2-/1,4-Reduction of an NAD Model Compound

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Experimental

Preparation of Optically active 1. To the solution of enantiomerically-pure **2**[1] (82.3 mg, 0.29 mmol) in anhydrous acetonitrile (145 mL), the solution (100 mL) of methyl benzoylformate (476 mg, 2.9 mmol) and magnesium perchlorate (64.7 mg, 0.29 mmol) in the same solvent was injected. The reaction was run for 1 h at room temperature in the dark under argon atmosphere. After removal of the solvent, water was added and inside the flask was washed with ether three times. Then, the water layer was extracted with dichloromethane three times. The combined dichloromethane layer was dried and evaporated to give optically-active **1** as a perchlorate salt in ~50% yield. The enantiomer excess of **1** was checked by HPLC (column: Daicel CHIRALCEL OD®).[1]

Reaction. To the anhydrous acetonitrile solution (0.5 mL) of chiral **1**·ClO_4 (1.76 mg, 4.6 μmol), 0.5 mL solution of **4** (1eq.) in the same solvent was injected under argon atmosphere at room temperature in the dark. After being stirred for 36h at room temperature, the solvent was evaporated and the residue was subjected to ^{1}H NMR and

HPLC (column: Daicel CHIRALCEL OD®) analysis. Examples of ^{1}H NMR and HPLC charts for typical experiments were shown in Figures S1 and S2.

(1) Mikata, Y.; Mizukami, K.; Hayashi, K.; Matsumoto, S.; Yano, S.; Yamazaki, N.; Ohno, A. *J. Org. Chem*. **2001**, *66*, 1590.

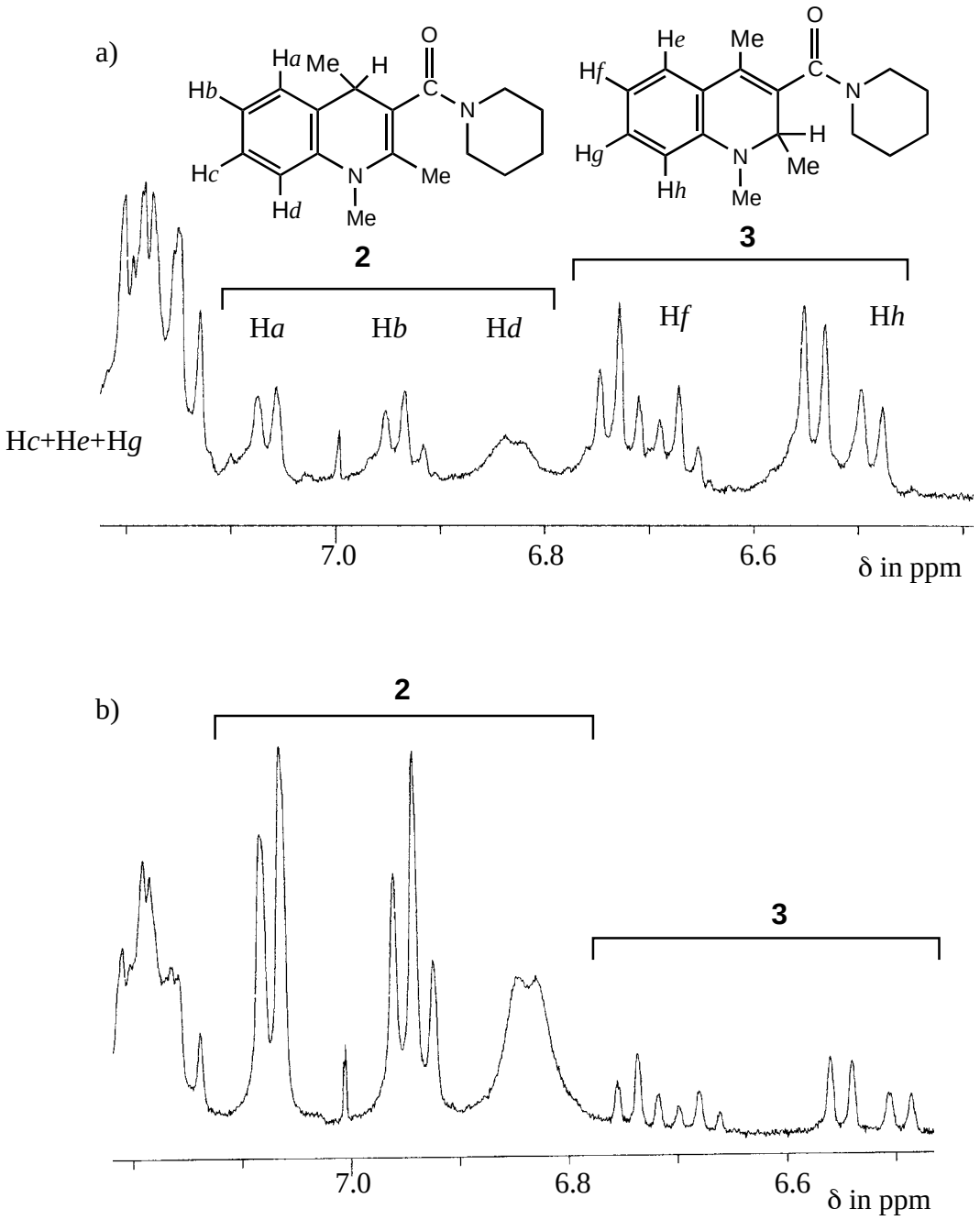

Figure S1. (a) Partial ^{1}H NMR spectrum of the product of the reaction of (*R*)-**1** with (*R*)-**4**. (b) Partial ^{1}H NMR spectrum of the product of the reaction of (*R*)-**1** with (*S*)-**4**. Solvent: $CDCl_3$.

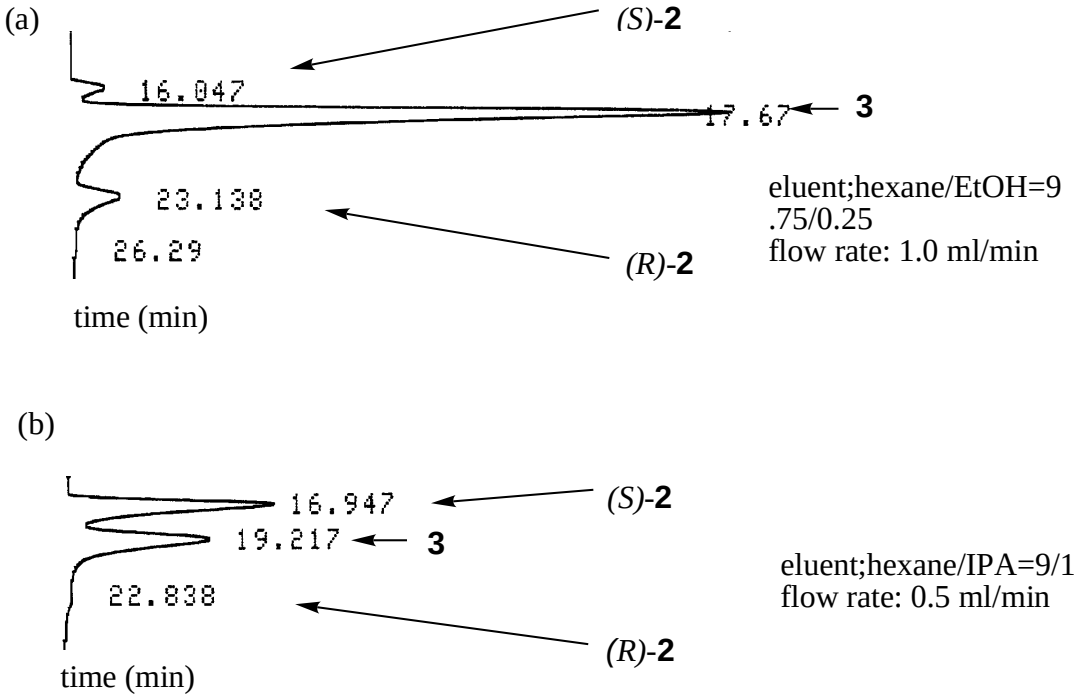

Figure S2. (a) HPLC trace of the product of the reaction of (*R*)-**1** with (*R*)-**4**. (b) HPLC trace of the product of the reaction of (*R*)-**1** with (*S*)-**4**.