## **Supplementary Information**

## (+)-BINOL and Pure Shift Experiment: A Bidirectional Approach for NMR Chiral Discrimination of Overcrowded Spectra of Primary Amines

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## Experimental considerations

Deuterated solvents (99.9% purity with 0.03% v/v of TMS) were purchased from Sigma-Aldrich<sup>®</sup>.

The chiral gas-chromatography (GC) analyses were performed in a Shimadzu GC-17A instrument with an FID detector using hydrogen as a carrier gas (100 kPa). Chiral column Chirasil-Dex CB  $\beta$ -cyclodextrin (25 m × 0.25 mm) was used for the determination of enantiomers molar ratio.

500 MHz acquired the NMR spectra. The model of NMR equipment 500 MHz is an Agilent equipped with a BBO (direct broad-band observe) probe. The <sup>1</sup>H NMR chemical shifts are reported in parts *per* million (ppm) relative to tetramethylsilane (TMS) peak ( $\delta$  0.0 ppm). The data are reported as follows: chemical shift ( $\delta$ ), multiplicity (s = singlet, s = broad singlet, d = doublet, t = triplet, q = quadruplet, qt = quintet, st = sextuplet, m = multiplet), features of signal (br = broad, ap = apparent) and coupling constant (*J*) in hertz and integrated intensity.

Typical procedure for <sup>1</sup>H NMR chiral discrimination of primary amines

The <sup>1</sup>H NMR spectra were recorded at 500 MHz using 8 scans and 4.67 s of acquisition time at 27 °C probe temperature. For processing the NMR spectra was used 0.1 of line broadening and 64 K of sized of fid. Samples for NMR spectroscopy were prepared by weighing and dissolving the appropriate amount of substrate in the respective deuterated solvent to prepare a 0.1 mM solution. The solutions were shaken for 2 min for equilibration time.

The <sup>1</sup>H NMR pure-shift experiments were acquired using the pure shift 1D pulse sequence from Agilent Technologies Inc. 2014 (VNMRJ 4.2) with 64 scans, 1.68 s of acquisition time, 2 s of relaxation delay, 60 m of slice selection bandwidth and 10 Hz for coupling constant (J) delay.

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**Figure S1.** <sup>1</sup>H NMR spectrum (500 MHz, CDCl<sub>3</sub>) for chiral discrimination of amine **2a** by 0.5 equiv. of (+)-BINOL at 27 °C.



**Figure S2.** <sup>1</sup>H NMR spectrum (500 MHz, CDCl<sub>3</sub>) for chiral discrimination of amine **2a** by 1.0 equiv. of (+)-BINOL at 27 °C.



**Figure S3.** <sup>1</sup>H NMR spectrum (500 MHz, CDCl<sub>3</sub>) for chiral discrimination of amine **2a** by 2.0 equiv. of (+)-BINOL at 27 °C.



**Figure S4.** <sup>1</sup>H NMR spectra (500 MHz, CDCl<sub>3</sub>) of methylene CH<sub>3</sub> and methine CH groups for chiral discrimination of amine **2a** using 0.5, 1.0 and 2.0 equiv. of (+)-BINOL at 27 °C.



**Figure S5.** Determination of enantiomers molar ratio by chiral gas-chromatography analysis of acetyl amide prepared from amine **2a**. The chiral GC analysis of primary amine **2a** has shown a lower baseline-resolution.



**Figure S6.** <sup>1</sup>H NMR spectrum (500 MHz, CDCl<sub>3</sub>) for chiral discrimination of amine **2b** by 2.0 equiv. of (+)-BINOL at 27 °C.



**Figure S7.** <sup>1</sup>H NMR spectrum (500 MHz, CDCl<sub>3</sub>) for chiral discrimination of amine **2c** by 2.0 equiv. of (+)-BINOL at 27 °C.



**Figure S8.** <sup>1</sup>H NMR spectrum (500 MHz, CDCl<sub>3</sub>) for chiral discrimination of amine **2d** by 2.0 equiv. of (+)-BINOL at 27 °C.



**Figure S9.** <sup>1</sup>H NMR spectrum (500 MHz, CDCl<sub>3</sub>) for chiral discrimination of amine **2e** by 2.0 equiv. of (+)-BINOL at 27 °C.



**Figure S10.** <sup>1</sup>H NMR spectrum (500 MHz, CDCl<sub>3</sub>) for chiral discrimination of amine **2f** by 2.0 equiv. of (+)-BINOL at 27 °C.



**Figure S11.** <sup>1</sup>H NMR spectrum (500 MHz, CDCl<sub>3</sub>) for chiral discrimination of amine **2g** by 2.0 equiv. of (+)-BINOL at 27  $^{\circ}$ C.



**Figure S12.** <sup>1</sup>H NMR spectrum (500 MHz, CDCl<sub>3</sub>) for chiral discrimination of amine **2h** by 2.0 equiv. of (+)-BINOL at 27  $^{\circ}$ C.



**Figure S13.** <sup>1</sup>H NMR spectrum (500 MHz, CDCl<sub>3</sub>) for chiral discrimination of amine **2i** by 2.0 equiv. of (+)-BINOL at 27 °C.



**Figure S14.** <sup>1</sup>H NMR spectrum (500 MHz, CDCl<sub>3</sub>) for chiral discrimination of amine **2j** by 2.0 equiv. of (+)-BINOL at 27 °C.



**Figure S15.** <sup>1</sup>H pure-shift NMR spectrum (500 MHz,  $CDCl_3$ ) for chiral discrimination of amine **2i** by 2.0 equiv. of (+)-BINOL at 27 °C.



**Figure S16.** <sup>1</sup>H pure-shift NMR spectrum (500 MHz, CDCl<sub>3</sub>) for chiral discrimination of amine **2e** by 2.0 equiv. of (+)-BINOL at 27  $^{\circ}$ C.



**Figure S17.** <sup>1</sup>H pure-shift NMR spectrum (500 MHz, CDCl<sub>3</sub>) for chiral discrimination of amine **2j** by 2.0 equiv. of (+)-BINOL at 27  $^{\circ}$ C.



**Figure S18.** *J*-Resolved NMR 2D spectrum (500 MHz, CDCl<sub>3</sub>) for chiral discrimination of primary amine **2g** by 2.0 equiv. of (+)-BINOL at 27 °C.



**Figure S19.** Deconvolution fit of chiral discrimination of primary amine 2g by 2.0 equiv. of (+)-BINOL in CDCl<sub>3</sub> at 27 °C.



**Figure S20.** HSQC-edited NMR 2D spectrum (500 MHz, CDCl<sub>3</sub>) for chiral discrimination of primary amine **2d** by 2.0 equiv. of (+)-BINOL at 27 °C.



**Figure S21.** <sup>1</sup>H NMR spectrum (500 MHz, benzene- $d_6$ ) for chiral discrimination of amine **2e** by 2.0 equiv. of (+)-BINOL at 27 °C.

![](_page_22_Figure_0.jpeg)

**Figure S22.** <sup>1</sup>H NMR spectrum (500 MHz, benzene- $d_6$ ) for chiral discrimination of amine **2j** by 2.0 equiv. of (+)-BINOL at 27 °C.

![](_page_23_Figure_0.jpeg)

**Figure S23.** <sup>1</sup>H NMR spectrum (500 MHz, benzene- $d_6$ ) for chiral discrimination of amine **2d** by 2.0 equiv. of (+)-BINOL at 27 °C.

![](_page_24_Figure_0.jpeg)

Figure S24. <sup>1</sup>H pure-shift NMR spectrum (500 MHz, benzene- $d_6$ ) for chiral discrimination of amine 2d by 2.0 equiv. of (+)-BINOL at 27 °C.

![](_page_24_Figure_2.jpeg)

**Figure S25.** Effect of (+)-BINOL 1b on chemical shift differences ( $\Delta \delta$ ) and chemical shifts ( $\delta$ ) of enantiomers in the NMR chiral discrimination of the primary amine 2g. Lower spectrum is amine 2g without (+)-BINOL 1b and upper spectrum is amine 2g with 2.0 equiv. of (+)-BINOL 1b.