

## Supporting Information

### Asymmetric aldol reactions catalyzed by tryptophan in water

Zhaoqin Jiang,<sup>a,b</sup> Zhian Liang,<sup>a</sup> Xiaoyu Wu<sup>a</sup> and Yixin Lu<sup>\*a,b</sup>

<sup>a</sup> Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore, 117543, Republic of Singapore. Fax: +65-6779-1691; Tel: +65-6516-1569; Email: [chmlyx@nus.edu.sg](mailto:chmlyx@nus.edu.sg)

<sup>b</sup> The Medicinal Chemistry Program, Office of Life Sciences, National University of Singapore

#### General methods

Chemicals and solvents were purchased from commercial suppliers and used as received. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker ACF300 (300MHz) or AMX500 (500MHz) spectrometer. Chemical shifts are reported in parts per million (ppm), and the residual solvent peak was used as an internal reference. Low resolution mass spectra were obtained on a VG Micromass 7035 spectrometer in EI mode, a Finnigan/MAT LCQ spectrometer in ESI mode, and a Finnigan/MAT 95XL-T mass spectrometer in FAB mode. All high resolution mass spectra were obtained on a Finnigan/MAT 95XL-T spectrometer. For thin-layer chromatography (TLC), Merck pre-coated TLC plates (Merck 60 F<sub>254</sub>) was used, and compounds were visualized with a UV light at 254 nm. Further visualization was achieved by staining with 5% ninhydrin in ethanol, ceric molybdate or KMnO<sub>4</sub> solution followed by heating on a hot plate. Flash chromatography separations were performed on Merck 60 (0.040 - 0.063mm) mesh silica gel. All the aldol reactions were performed under an atmosphere of air in a closed system at ambient temperature.

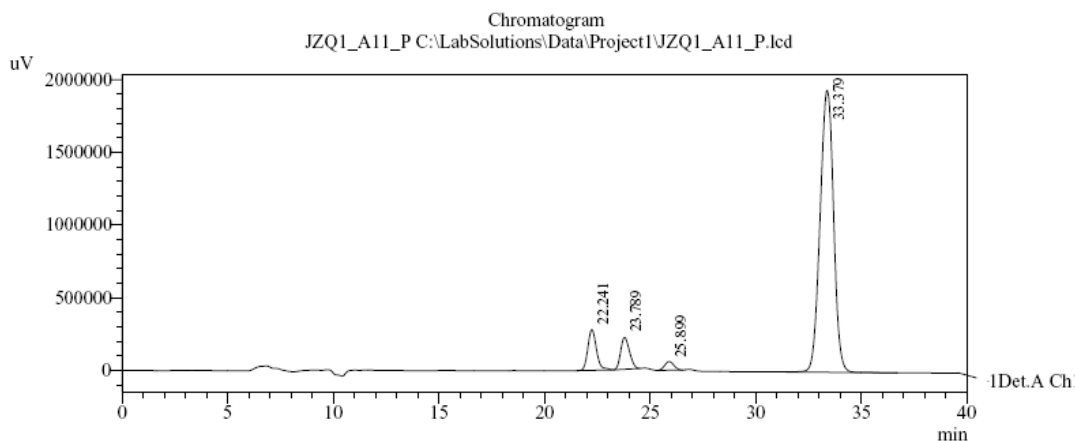
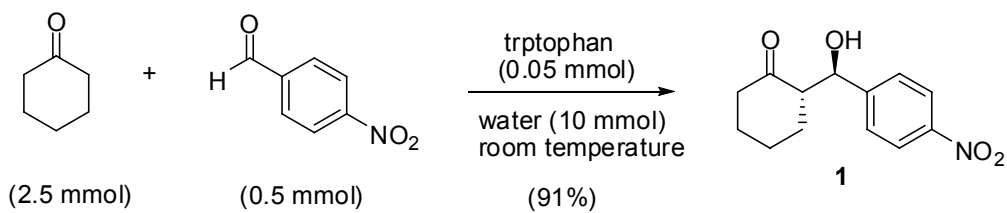
All the substrates are commercially available and used as received: cyclohexanone (108-94-1), cyclopentanone (120-92-3), cycloheptanone (502-42-1), 4-nitrobenzaldehyde (555-16-8), 2-nitrobenzaldehyde (552-89-6), 4-cyanobenzaldehyde (105-07-7), 4-bromobenzaldehyde (1122-91-4), 4-methoxybenzaldehyde (123-11-5), benzaldehyde (100-52-7), 2-thiophenecarboxaldehyde (98-03-3), 2-fluorobenzaldehyde (446-52-6), 2-naphthaldehyde (66-99-9).

#### Standard procedures and product characterizations

Reactions were performed using the typical procedure described in the article. The assignments of *syn* and *anti* isomers and the diastereomeric ratios of aldol products were determined by <sup>1</sup>H NMR analysis. The enantiomeric excesses were determined by chiral-phase HPLC analysis. The absolute stereochemistry was determined by the comparison with the literature data.<sup>1,2</sup> All the aldol products **1-7**,<sup>1,2</sup> **8**,<sup>3</sup> **9-11**,<sup>1,2</sup> **12**<sup>4</sup> and **13**<sup>5</sup> are all known compounds.

## Supporting Information

### A typical HPLC chromatogram of the aldol product (1):



ID#	Name	Ret. Time	Area	Height	Area %
1	RT22.241	22.241	7978916	279992	7.796
2	RT23.789	23.789	6395511	218759	6.249
3	RT25.899	25.899	1793014	59296	1.752
4	RT33.379	33.379	86175732	1939233	84.203

(HPLC conditions: Chiralcel AD-H column,  $\lambda = 254$  nm, *i*-PrOH/Hexane = 20/80, flow rate: 0.5 ml/minute).

<sup>1</sup> N. Mase, Y. Nakai; N. Ohara, H. Yoda, K. Takabe, F. Tanaka, C. F. Barbas, III, *J. Am. Chem. Soc.*, 2006, **128**, 734.

<sup>2</sup> Y. Hayashi, T. Sumiya, J. Takahashi, H. Gotoh, T. Urushima, M. Shoji, *Angew. Chem. Int. Ed.*, 2006, **45**, 958.

<sup>3</sup> M. Kawai, M. Onaka, Y. Izumi, *Bull. Chem. Soc. Jpn.*, 1988, **61**, 1237.

<sup>4</sup> Y.-Y. Peng, Q.-P. Ding, Z. Li, P. Wang George, J. P. Cheng, *Tetrahedron Lett.*, 2003, **44**, 3871-3875.

<sup>5</sup> Y.-S. Wu, Y. Chen, D.-S. Deng, J. Cai, *Synlett.*, 2005, 1627.