

*Electronic Supplementary Information for:*

## **Discrimination of Cryptochirality in Chiral Isotactic Polystyrene by Asymmetric Autocatalysis**

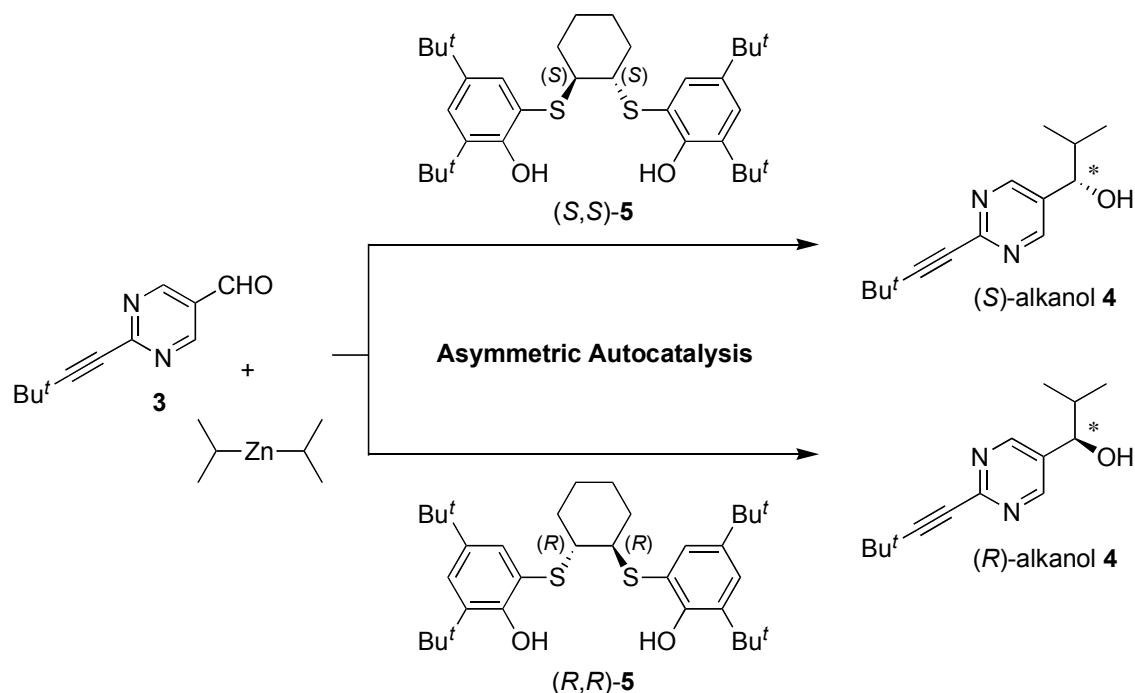
Tsuneomi Kawasaki,<sup>a,b</sup> Christiane Hohberger,<sup>c</sup> Yuko Araki,<sup>a</sup> Kunihiko Hatase,<sup>a</sup>  
Klaus Beckerle,<sup>c</sup> Jun Okuda<sup>c\*</sup> and Kenso Soai<sup>a,b\*</sup>

<sup>a</sup> *Department of Applied Chemistry, Tokyo University of Science, Kagurazaka, Shinjuku-ku, Tokyo  
162-8601 (Japan), E-mail: soai@rs.kagu.tus.ac.jp*

<sup>b</sup> *Research Institute of Science and Technology, Tokyo University of Science, Kagurazaka, Shinjuku-ku,  
Tokyo 162-8601 (Japan)*

<sup>c</sup> *Institute of Inorganic Chemistry, RWTH Aachen University, Landoltweg 1, D-52074 Aachen  
(Germany), E-mail: jun.okuda@ac.rwth-aachen.de*

**Table S1:** Stereochemical relationship between bis(phenol) **5** and 5-pyrimidyl alkanol **4** obtained from the asymmetric autocatalysis.



entry <sup>[a]</sup>	config. of bis(phenol) <b>5</b>	5-pyrimidyl alkanol <b>4</b>		
		isolated yield	ee (%) <sup>[b]</sup>	config.
1	( <i>S,S</i> )	94	92	<i>S</i>
2	( <i>S,S</i> )	94	95	<i>S</i>
3	( <i>S,S</i> )	88	94	<i>S</i>
4	( <i>R,R</i> )	90	91	<i>R</i>
5	( <i>R,R</i> )	87	91	<i>R</i>
6	( <i>R,R</i> )	90	86	<i>R</i>
7	( <i>R,R</i> )	88	86	<i>R</i>

[a] The molar ratio of bis(phenol) **5** / pyrimidine-5-carbaldehyde **3** / *i*Pr<sub>2</sub>Zn = 0.015 / 0.525 / 1.18 (mmol). General procedure for asymmetric autocatalysis (Entry 1): To a toluene (0.45 mL) solution of (*S,S*)-**5** (5.0 mg, 0.015 mmol) was added *i*Pr<sub>2</sub>Zn (0.08 mmol, 0.8 mL, 1.0 M toluene solution) at 0 °C. To this solution was added a toluene (0.25 mL) solution of aldehyde **3** (4.7 mg, 0.025 mmol) over a period of 2 h at 0 °C. After the mixture was stirred for 12 h, toluene (1.0 mL) and *i*Pr<sub>2</sub>Zn (0.3 mmol, 0.3 mL, 1.0 M toluene solution) was then slowly added at 0 °C and the mixture was stirred for 15 min. A toluene (0.75 mL) solution of **3** (18.8 mg, 0.1 mmol) was slowly added, and the reaction

mixture stirred at 0 °C for 2 h. Then, toluene (5.0 mL), *i*-Pr<sub>2</sub>Zn (0.8 mmol, 0.8 mL, 1.0 M toluene solution) and a toluene (2.0 mL) solution of **3** (75.3 mg, 0.4 mmol) were added successively at 0 °C. After the mixture was stirred for 2 h, the reaction was quenched with HCl (1 M, 3 mL) and neutralized with a saturated NaHCO<sub>3</sub> solution (10 mL). The mixture was then filtered through celite and the filtrate extracted with AcOEt (3 times). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated *in vacuo*. Purification of the residue by silica gel column chromatography on silica gel (hexane/AcOEt, 3:1, *v/v*) gave the (*S*)-pyrimidyl alkanol **4** (115 mg, 0.495 mmol, 92% ee) in 94% yield.

[b] The ee value was determined by HPLC using a chiral stationary phase (Daicel Chiralpak IB 4.6Φ × 250 mm, 254 nm UV detector, roomt., eluent: 5% 2-propanol in hexane (*v/v*), 1.0 mL / min., retention time: 11 min for *S*-**4** and 15 min for *R*-**4**).