Supporting Information for:

Homogeneous Asymmetric Transfer Hydrogenation of Ketones using a Ruthenium Catalyst Anchored on Chitosan: Natural Chirality at Work

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1. High-throughput procedures

A Freeslate core module (generation I) was used for dispensing solutions in the plate, controlling temperature and stirring. Solutions of MeONa in MeOH, tBuONa in THF and NaOEt (suspension) in MeOH were dispensed into a 96-well plate and the solvents were evaporated. iProNa and iProLi were dispensed as solutions in isopropanol, followed by the addition of solvents (isopropanol and MeOH) and acetophenone in isopropanol. The solutions were stirred for 5 minutes, at which point the catalyst in MeOH was added. The plate was sealed and stirred at 25 °C for 24 hours.

An internal standard solution (anisole) was added to the samples and aliquots of 50 uL were transferred to silica pads in a 96-well filter plate (Pall Corporation multi-well filter plates – 0.45 µm GHP 1mL wells, p/n 5054). After adsorption, 450µL of ethyl acetate was added and the plate was centrifuged.

Yields and enantiomeric excesses were determined by gas chromatography (Agilent Technologies 6850 GC), equipped with an Astec Chiraldex B-PM column (30 m x 0.25 mm x 0.2 µm, with a guard column). The inlet/detector temperatures were set to 250 °C, initial oven temperature of 90 °C held for 3 minutes, followed by a ramp of 0.5 deg/°C to 94 °C held for 1 minute (total runtime of 12 minutes). Injections of 1 uL at a split ratio of 50:1 were performed; retention times were of 2.57, 6.03, 10.01, 10.73 minutes for anisole, acetophenone, and R/S-phenylethanol respectively. Quantitation was effected by measuring the response factor through an 11-points calibration curve.

2. Spectroscopic characterization

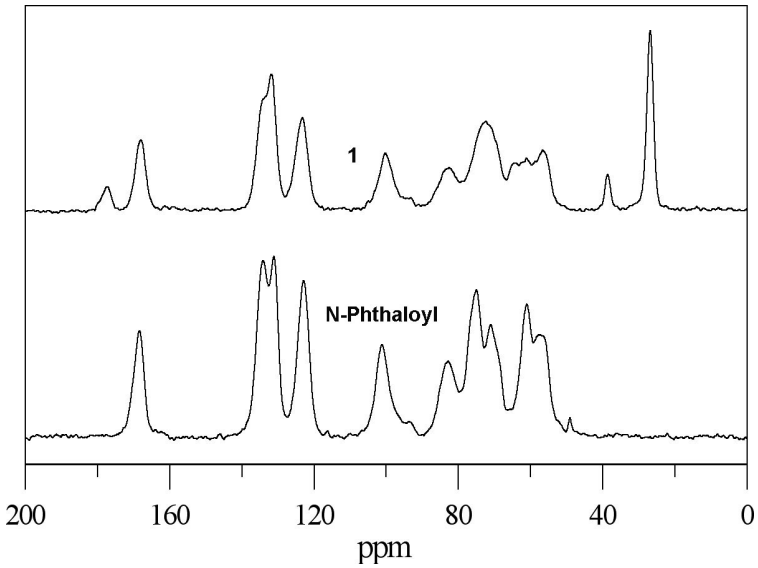

Figure S1. CP/MAS ^{13}C NMR spectra of insoluble chitosan derivative

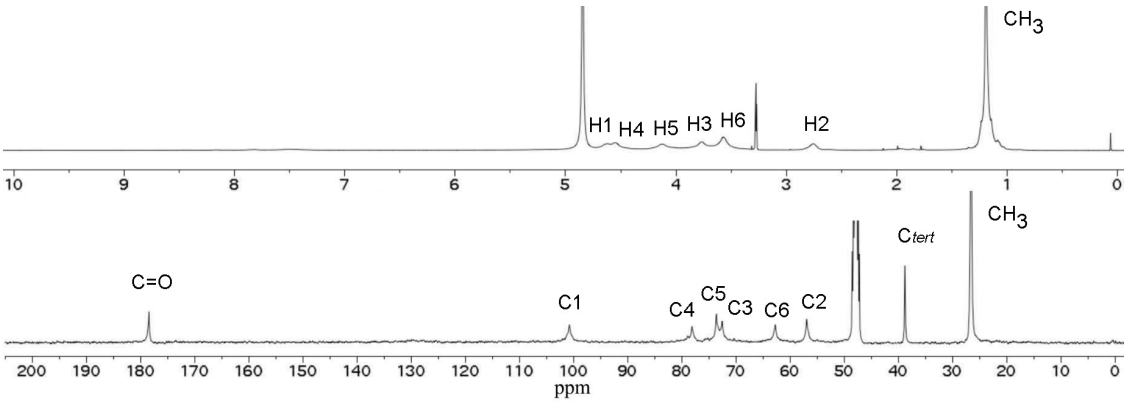

Figure S2. ^{1}H and ^{13}C NMR spectra of **2** in CD_3OD

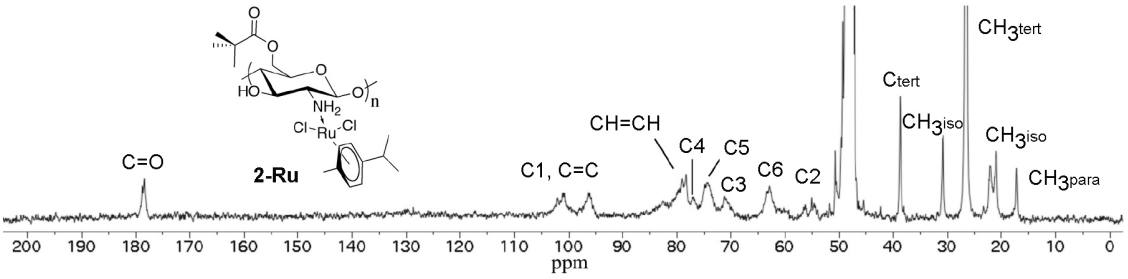

Figure S3. $^{13}C\{^{1}H\}$ NMR spectra of ruthenium complex **2-Ru** in CD_3OD

3. Results of the high-throughput experiments.