ORGANIC CHEMISTRY - EXAM **07/18/2011**

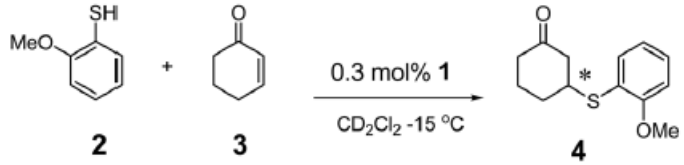
The questions are based on the following article:

Jiaobing Wang and Ben L. Feringa, **Dynamic Control of Chiral Space in a Catalytic Asymmetric Reaction Using a Molecular Motor**

Science, **2011**, *331*, 1429–1432.

(1) The test reaction used by the authors is shown below:

A

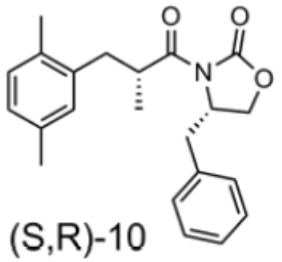


2 3 4

Provide a detailed description of the mechanism of this reaction including the explanation of enantioselection. **(4 points)**

(2) The authors used chiral HPLC to determine the optical purity of their products. Assuming that chiral HPLC is not available to you, propose one alternative method to determine optical purity. Explain the mechanism of enantioselection in your proposed method. (**3points**)

(3) The structure and the NMR data of compound (S,R)-**10** are provided below:
Assign the signals to the appropriate nuclei. (**3 points**)



(S,R)-10

pentane/DCM (2/3) as the eluant affording 1.0 g (57%) of (*S,R*)-**10** as a colorless oil. ^{1}H NMR (CD_2Cl_2): δ = 7.31-7.20 (m, 3H), 7.08-6.98 (m, 4H), 6.92 (d, *J* = 8.0 Hz, 1H), 4.75-4.62 (m, 1H), 4.28-4.02 (m, 3H), 3.11-3.02 (m, 2H), 2.73 (dd, *J* = 13.6, 8.8 Hz, 1H), 2.54 (dd, *J* = 13.6, 9.2 Hz, 1H), 2.34 (s, 3H), 2.25 (s, 3H), 1.21 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (CD_2Cl_2): 177.0, 153.0, 137.1, 135.2, 135.1, 133.5, 130.7, 130.2, 129.3, 128.9, 127.3, 127.2, 65.8, 55.0, 38.0, 37.7, 37.0, 20.9, 19.1, 17.3. HRMS: m/z calcd for $C_{22}H_{26}NO$

Green Chemistry: **(2 points)**

The synthesis of a precursor compound is shown below. Evaluate the reaction steps from a green chemistry point of view and propose a greener alternative for reaction(s) that you find undesirable.

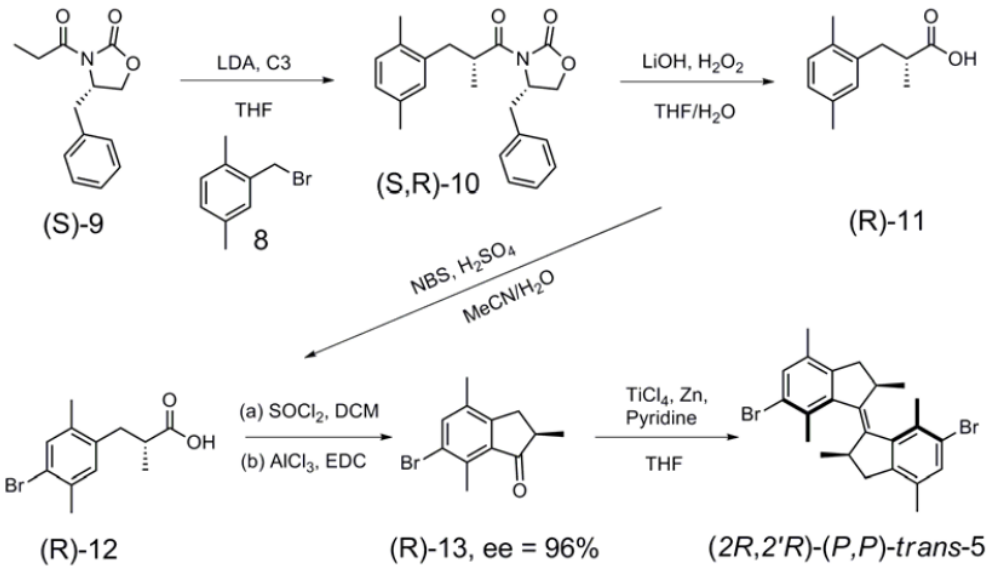


Fig. S3. Asymmetric synthesis (see also *S2,3*) of the precursor compound (*2R,2'R*)-(*P,P*)-*trans*-**5**, which was used for the asymmetric synthesis of (*2R,2'R*)-(*P,P*)-*trans*-**1** following the procedure shown in Fig S1.