ASYMMETRIC SYNTHESIS OF CYCLOPROPANES FROM LITHIATED ARYLOXIRANES AND α,β - UNSATURATED FISCHER CARBENE COMPLEXES

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Supporting Information

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General Experimental Methods. Tetrahydrofuran (THF) was freshly distilled under a nitrogen atmosphere over sodium/benzophenone ketyl. *N,N,N',N'*-Tetramethylethylenediamine (TMEDA) was distilled over finely powdered calcium hydride. (*S*)- and (*R*)-Styrene oxides, (*R,R*)- and (*R,S*)-phenylpropylene oxides are commercially available with er > 98:2 and, together with all other chemicals of commercial grade, were used without further purification. Petroleum ether refers to the 40-60 °C boiling fraction. Commercial solution of *s*-BuLi (1.3 M solution in cyclohexane) was titrated by using *N*-pivaloyl-*o*-toluidine prior to use.¹ For the ¹H and ¹³C NMR spectra (¹H NMR 300, 500 MHz; ¹³C NMR 75.4, 125 MHz), CDCl₃ was used as the solvent. GC-MS spectrometry analyses were performed on a gas chromatograph HP 6890 (dimethylsilicon capillary column, 30 m, 0.25 mm i.d.) equipped with a mass selective detector operating at 70 eV (EI). Optical rotations were performed on purified compounds and measured with a Perkin-Elmer 341 polarimeter, using a cell of 1 dm path length at 20 °C; the concentration (c) is expressed in g/100 mL. Analytical thin-layer chromatography (TLC) was carried out on Merck precoated 0.25 mm thick plates of Kieselgel 60 F₂₅₄; visualization was accomplished by UV light (254 nm) or by spraying with a solution of 5 % (w/v) ammonium molybdate and 0.2 % (w/v) cerium(III) sulfate in 100 ml 17.6 % (w/v) aqueous sulphuric acid and heating to 200 °C for some time until blue spots appear. All reactions involving air-sensitive reagents were performed under nitrogen in oven-dried glassware using syringe-septum cap technique. Enantiomeric purity assays were carried out with both racemic and optically active substrates. (*S*)-(+)-MTPA-Cl was used to ascertain, via NMR,² the enantiomeric purity. Compounds **4a-f**,³ **4g**,⁴ racemic *trans*- and *cis*-phenylpropylene oxides (*R*,R**)-**2** and (*R*,S**)-**2**⁵ were prepared according to the reported procedure. Spectroscopic data of **7a**⁶ have been also reported.

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Figure S1. Ortep view of compound **6i**