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Supporting Information

## **Cyclopropanation Enantioselectivity is Pressure Dependent in Supercritical Fluoroform\*\***

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The following tests were performed to ensure the solubility of the reagents and the repeatability of the results. a) A series of experiments showed that the ee depends on the final  $\text{scCHF}_3$  pressure and is independent of the pressure at which the diazoacetate is introduced. b) Repeated GC injections were made of the sample from each run and the average standard deviation was found to be 1.5% ee. The average ee value from these multiple injections was taken to be the final ee value. Repeated experiments at identical  $\text{scCHF}_3$  pressures had a standard deviation of 3% ee. Product **3** was not observed. c) The solubility of the styrene in  $\text{scCHF}_3$  was confirmed by observing the phase behaviour of 100  $\mu\text{L}$  of styrene (twice the usual amount) in a high pressure cell fitted with sapphire windows. This amount of styrene

dissolved at pressures of 51 bar or above. The same exercise confirmed the solubility of the diazoacetate/styrene reagent mixture. d) The solubility of the catalyst precursor was confirmed, at least qualitatively, by a more elaborate procedure. A sample of the complex was placed in a small beaker inside the vessel, which was then pressurized to 60 bar with  $\text{scCHF}_3$  for an hour to allow for dissolution of some or all of the complex into the SCF. The vessel was then slowly vented, precipitating any dissolved complex on the walls and floor of the vessel. The beaker was removed and a cyclopropanation reaction was performed in the vessel without the vessel being washed and with no further catalyst precursor being added. Because the reaction proceeded, we conclude that enough catalyst had been extracted from the beaker to catalyze the reaction. This is qualitative evidence that the catalyst is sufficiently soluble in  $\text{scCHF}_3$  at this pressure, e) The solubility of the catalyst was further confirmed by measuring the UV spectrum of the catalyst in  $\text{scCHF}_3$  at two different pressures, 51 and 122 bar. The spectrum of the catalyst, with a maximum at 270 nm, was similar to that observed in liquid  $\text{CH}_2\text{Cl}_2$ . The absorbance was the same at the two pressures of  $\text{scCHF}_3$ , indicating that the concentration of the catalyst in the SCF phase was the same at the two pressures. This assumes, however, that the

extinction coefficient is pressure independent, which might not be the case.

In the absence of added catalyst, there is a very slow background reaction, which gives poor yields of the cyclopropane in low ee.