1. In 2009, the Chida group reported the synthesis of (−)-agelastatin A, using two sequential rearrangements as their key steps. Please provide the missing compound and intermediate, as well as, the names and mechanisms for the 2 rearrangements. (Hama, N.; Matsuda, T.; Sato, T.; Chida, N. Org. Lett. 2009, 11, 2687.)

PhS-CH2-CH=CH-CH=CH-Ph

(Derived from D-tartaric acid)

Cl3CCN, DBU

DCM, −20 °C to rt

Na2CO3

o-xylene, 140 °C

58% over 2 steps

Name & Mechanism

PhS-CH2-CH=CH-NH-C(Cl)3

mCPBA

DCM, −20 °C

97%

2. In 1991, the Pirrung group reported the synthesis of (+)-griseofulvin. Their synthesis contains three rearrangements, with one serving as their key step. Please provide the missing compounds, as well as, the names and mechanisms for the 3 rearrangements. (Pirrung, M. C.; Brown, W. L.; Rege, S.; Laughton, P. J. Am. Chem. Soc. 1991, 113, 8561.)

O

1. SO2Cl2

2. Ac2O, pyridine

AlCl3

chlorobenzene, reflux

30 min

Name & Mechanism

O

Rh2(OPiv)4 (5 mol%)

benzene, reflux, 1h

Name & Mechanism

1. P(O)(OPh)2N3, NEt3

2. HCl, H2O

Name & Mechanism