Supporting Information

Catalytic Asymmetric [2,3]-Sigmatropic Rearrangement of Sulfur Ylides generated from Copper(I) Carbenoids and Allyl Sulfides

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HPLC analysis was performed at HP 1100 apparatus.

Ar' = Ph, Ar = Ph, Table 1, Entry 3 (Hexane/iso-propanol 85:15)

Ar' = Ph, Ar = Ph, Table 1, Entry 7 (Hexane/iso-propanol 85:15)

Ar' = Ph, Ar = Ph, Table 1, Entry 11 (Hexane/iso-propanol 85:15)

Ar' = Ph, Ar = Ph, Racemic (Hexane/iso-propanol 90:10)

Ar' = Ph, Ar = Ph, Table 1, Entry 16 (Hexane/iso-propanol 90:10)

Ar' = 2-MePh, Ar = Ph, Racemic (Hexane/iso-propanol 90:10)

Ar' = 2-MePh, Ar = Ph, Table 1, Entry 4 (Hexane/iso-propanol 90:10)

Ar' = 2-MePh, Ar = Ph, Table 1, Entry 5 (Hexane/iso-propanol 90:10)

Ar' = 2-MePh, Ar = Ph, Table 1, Entry 6 (Hexane/iso-propanol 90:10)

Ar' = 2-MePh, Ar = Ph, Table 1, Entry 10 (Hexane/iso-propanol 90:10)

Ar' = 2-MePh, Ar = Ph, Table 1, Entry 14 (Hexane/iso-propanol 90:10)

Ar' = 2-MePh, Ar = Ph, Table 1, Entry 17 (Hexane/iso-propanol 90:10)

Ar' = 2-MePh, Ar = Ph, Table 1, Entry 18 (Hexane/iso-propanol 90:10)

Ar' = 2-MePh, Ar = Ph, Table 1, Entry 19 (Hexane/iso-propanol 90:10)

Ar' = 2-ClPh, Ar = Ph, Racemic (Hexane/iso-propanol 90:10)

Ar' = 2-ClPh, Ar = Ph, Table 1, Entry 8 (Hexane/iso-propanol 90:10)

Ar' = 2-ClPh, Ar = Ph, Table 1, Entry 12 (Hexane/iso-propanol 90:10)

Ar' = 2,6-(Me)₂Ph, Ar = Ph, Racemic (Hexane/iso-propanol 90:10)

Ar' = 2,6-(Me)₂Ph, Ar = Ph, Table 1, Entry 9 (Hexane/iso-propanol 90:10)

Ar' = 2-MePh, Ar = p-MeOPh, Racemic (Hexane/iso-propanol 90:10)

Ar' = 2-MePh, Ar = p-MeOPh, Table 1, Entry 15 (Hexane/iso-propanol 90:10)

Ar' = 2-MePh, Ar = p-MeOPh, Table 2, Entry 3 (Hexane/iso-propanol 90:10)

Ar' = 2-MePh, Ar = m-MeOPh, Racemic (Hexane/iso-propanol 99:1)

Ar' = 2-MePh, Ar = m-MeOPh, Table 2, Entry 4 (Hexane/iso-propanol 99:1)

Ar' = 2-MePh, Ar = m-MeOPh, Table 2, Entry 5 (Hexane/iso-propanol 99:1)

Ar' = 2-MePh, Ar = p-BrPh, Racemic (Hexane/iso-propanol 99 : 1)

Ar' = 2-MePh, Ar = p-BrPh, Table 2, Entry 6 (Hexane/iso-propanol 99 : 1)

Ar' = 2-MePh, *Ar* = *p*-BrPh, Table 2, Entry 7 (Hexane/iso-propanol 99 : 1)

Ar' = 2-MePh, *Ar* = *p*-PhPh, Racemic (Hexane/iso-propanol 90 : 10)

Ar' = 2-MePh, *Ar* = *p*-PhPh, Table 2, Entry 8 (Hexane/iso-propanol 90 : 10)

Ar' = 2-MePh, Ar = m-MePh, Racemic (Hexane/iso-propanol 99 : 1)

Ar' = 2-MePh, Ar = m-MePh, Table 2, Entry 9 (Hexane/iso-propanol 99 : 1)

Ar' = 2-MePh, Ar = m-MePh, Table 2, Entry 10 (Hexane/iso-propanol 99 : 1)

Ar' = 2-MePh, Ar = m-ClPh, Racemic (Hexane/iso-propanol 90 : 10)

Ar' = 2-MePh, Ar = m-ClPh, Table 2, Entry 11 (Hexane/iso-propanol 90 : 10)

Ar' = 2-MePh, Ar = m-ClPh, Table 2, Entry 12 (Hexane/iso-propanol 90 : 10)

Ar' = 2-MePh, Ar = 1-naphthyl, Racemic (Hexane/iso-propanol 95 : 5)

Ar' = 2-MePh, Ar = 1-naphthyl, Table 2, Entry 13 (Hexane/iso-propanol 95 : 5)

Ar' = 2-MePh, Ar = 1-naphthyl, Table 2, Entry 14 (Hexane/iso-propanol 95 : 5)

Ar' = vinyl, R = Ph, Racemic (Hexane/iso-propanol 90 : 10)

Scheme 4, compound 12 (Hexane/iso-propanol 90 : 10)

Figure 1. X-ray structure of **11**