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Synthesis of a Chiral Binaphthyldisulfide: A Potentially Useful Reagent for Catalytic Asymmetric Synthesis

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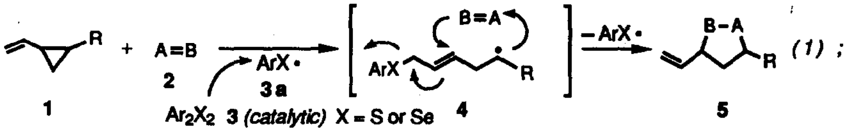
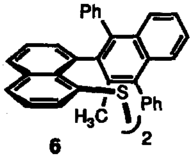
Abstract: *Diels Alder cycloaddition/oxygen-atom-extrusion provides the means to unite two naphthylene fragments and affords a highly functionalized, racemic binaphthyl iodide. Resolution of a derived thiol then furnishes, after appropriate manipulation, enantiomerically pure binaphthyldisulfide precatalysts.*

The preparation of various vinyl-substituted five membered heterocyclic and carbocyclic rings by combination of unsaturated two atom addends (A=B) with functionalized vinylcyclopropanes is catalyzed by small amounts (1-10 mol %) of arylthio or arylseleno radicals (eq (1)).[1] In this multistep process, the arylthio (arylseleno) moiety is covalently attached to key intermediate species while bond formation (C-A and C-B) occurs. Hence, access to a chiral version of radical **3a** may allow development of a catalytic asymmetric variant of this [3+2] addition reaction.[2] Towards this end, the binaphthyldisulfide radical precursor **6** was selected as an initial entry into this chemistry, as it appeared via molecular modeling studies that the chiral cleft defined by the basal naphthylene ring and the two phenyl "walls" might bias the conformation of an attached substrate (cf. **4**) to the extent that enantiofacial selectivity upon bond formation might be observed. The concise, convergent synthesis of racemic **6**, along with its resolution to afford both enantiomerically pure pre-catalyst disulfides, is described in this Letter.



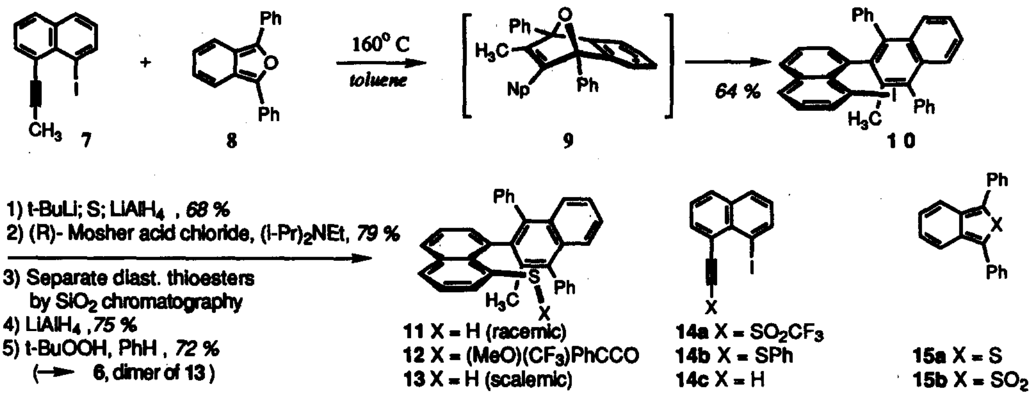


6

The key step in the preparation of binaphthyl disulfide **6** is the Diels Alder cycloaddition/oxygen extrusion sequence between naphthylpropyne **7**[3] and diphenylisobenzofuran (**8**) to afford the substituted binaphthyl framework directly (Scheme). Conversion of binaphthyl iodide **10** to the racemic thiol **11** proceeded most reproducibly with doubly sublimed sulfur as an electrophilic S source. The thiol **11** was conveniently resolved via the Mosher esters **12**, and then the separated thioesters were independently converted to the enantiomerically pure binaphthyldisulfide precatalysts **6** and **ent-6** as shown. The absolute configurations of these precatalysts have not yet been determined.

Several features of the Diels Alder transformation are worthy of further comment. The extrusion of "oxygen" from intermediate **9**, while not unprecedented,[4] is rather unusual. The ultimate fate of this bridging atom is not clear--inclusion of Ph_3P in the reaction medium neither accelerated the conversion to **10** nor led to formation of Ph_3PO. In addition, the bridged adduct **9** could be isolated in 51% yield upon combination of **7** with **8** at temperatures less than 150°C, and then processed on to binaphthyl **10** by subsequent heating as described above. Finally, several other plausible diene/dienophile combinations related to **7**/**8** were explored in preliminary experiments directed toward the synthesis of appropriately substituted binaphthyls similar to **10**.

Scheme[8]



7 **8** **9** **10**

11 X = H (racemic)
12 X = (MeO)(CF$_3$)PhCCO
13 X = H (scalemic)

14a X = SO$_2$CF$_3$
14b X = SPh
14c X = H

15a X = S
15b X = SO$_2$

Unfortunately, the thio and sulfonyl analogs of **8**, **15a**[5] and **15b**,[6] respectively, did not engage in useful reaction with any of the alkynyl-substituted naphthyl iodides **14a**-**14c** examined. However, the triflyl, thiophenyl, and hydrogen-substituted alkynes **14a**-**14c**,[7] respectively, all afforded oxygen-bridged Diels Alder adducts analogous to **9** upon heating (80-110°C) with diphenylisobenzofuran (**8**) (**14a**, 76%; **14b**, 69%; **14c**, 49%). The simple methyl-substituted binaphthyl thiol **13** proved thermally stable to racemization (80°C, 8 h) and so we did not pursue these other more sterically encumbered analogs.

In conclusion, the strategy for the efficient synthesis of structurally complex chiral binaphthyl disulfides has been brought to fruition with the construction of **6**. Experiments which probe asymmetric induction as per eq(1) with this compound are underway.

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7) Prepared as follows: Pd(0)/CuI mediated coupling of 1,8 diiodonaphthylene with TMSCCH (55%), followed by desilylation (K$_2$CO$_3$, CH$_3$OH, 92%) furnished **14c**. Trapping the alkynyl anion derived from **14c** (n-BuLi or LDA) with either Tf$_2$O or Ph$_2$S$_2$ led to the alkynyl triflate **14a** (27%) or the phenylsulfide **14b** (74%), respectively.
8) All new compounds exhibited satisfactory spectral data (^{1}H NMR, ^{13}C NMR, IR, MS, HRMS).

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