Synthesis of new chiral diaza 18-crown-6 ethers from chiral amines

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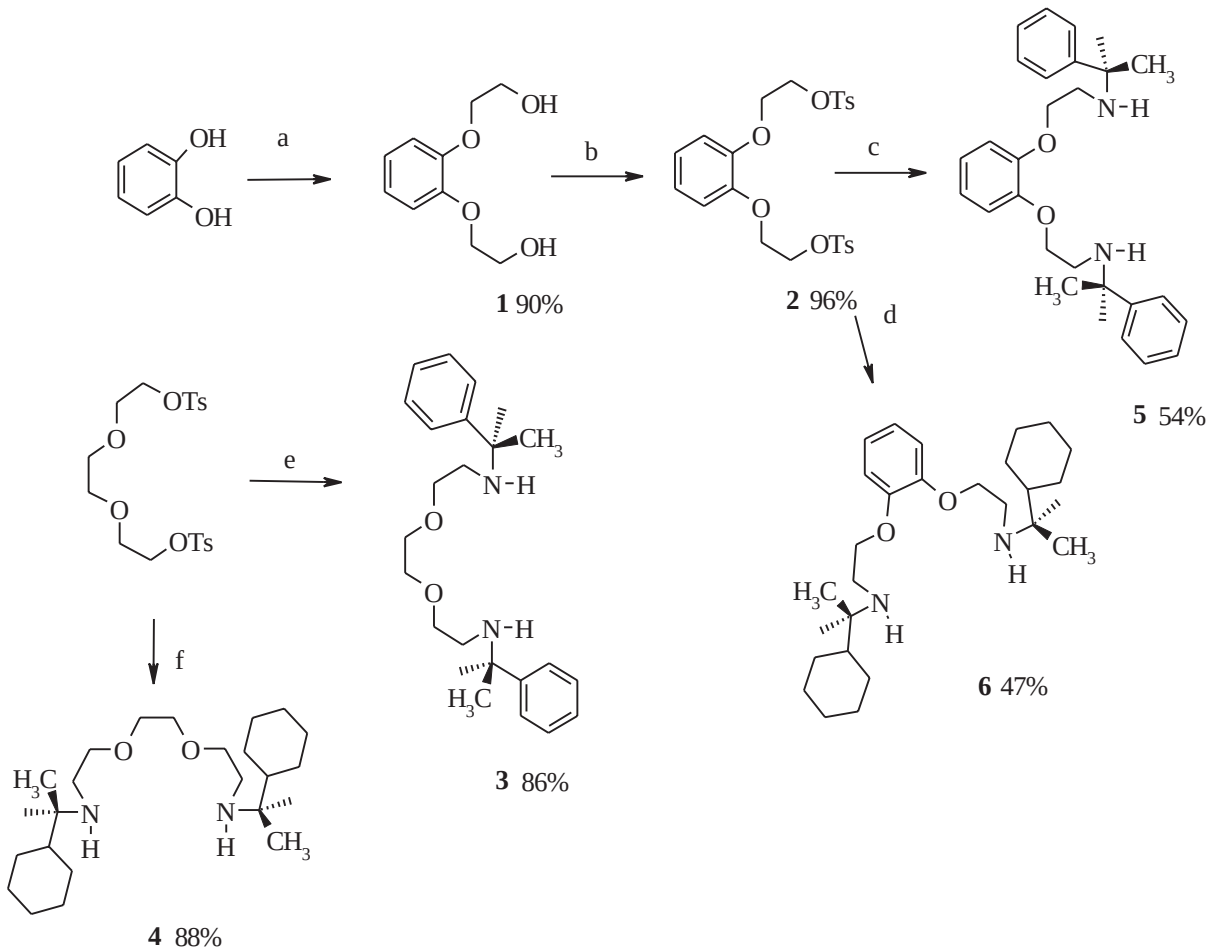
Practical syntheses of versatile building blocks of crown ethers **1** and **2**, chiral amine precursors **3–6** and chiral diaza 18-crown-6 ethers **7–12** are reported starting from chiral amines.

Keywords: molecular recognition, transport, chiral crown ether,

Crown ethers, first introduced in 1967 by Pedersen[1,2] are macrocyclic polyethers which are able to form stable and selective complexes with alkali metal, alkaline-earth metal, and primary ammonium cations. Following this fascinating discovery, chemists realized that asymmetric derivatives of these molecules could serve as models for the study of chiral recognition in enzymatic and other reactions. Ever since chiral crown ethers were first introduced by Stoddart[3] and Cram[4-6] by incorparating chiral units into the crown ether moeity and utilising them for the discrimination of enantiomers, chiral crown ethers have gained much importance. In particular, these chiral receptors were found to be behave as chiral reagents or chiral catalysts for enantioselective reactions.[7-9] Among the artificial carriers previously developed, macrocyclic polyethers and crown ethers have been well-recognized as potential carrier models for selective transport of cations. The transport capability of crown ethers has been shown to be strongly dependent on the nature, size and geometry of the macrocyclic cavity. Furthermore, for some lariat ethers, the presence of a flexible sidearm with an electron donor site is well known to enhance the binding ability of the ligand by participation of this additional donor group in the complexation, providing a three dimensional cavity. Gokel and co-workers[10] described the first



Scheme1 *Reagents:* (a) Ethylene oxide, piperidine hydrochloride, MeOH, 40 °C; (b) TsCl, pyridine, -10 °C; (c) *R*(+)-1-phenylethylamine (10 eq.), xylene, 120 °C; (d) *R*(-)-1-cyclohexylethylamine (10 eq.), xylene, 120 °C; (e) *R*(+)-1-phenylethylamine (10 eq.), xylene, 120 °C; (f) *R*(-)-1-cyclohexylethylamine (10 eq.), xylene, 120 °C

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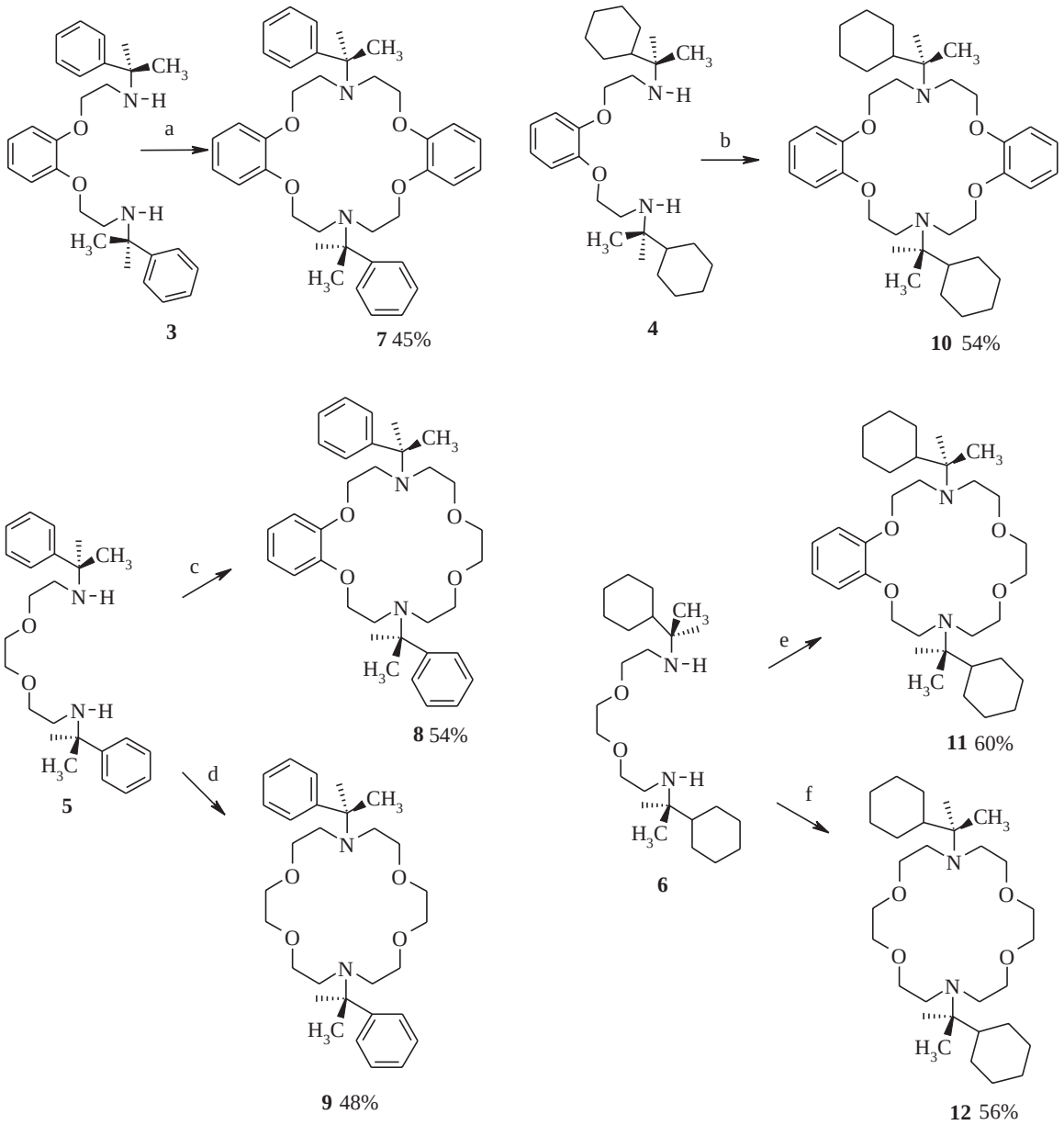

Scheme 2 *Reagents:* (a) tripropylamine (10 eq.), 2, xylene, 120 °C, 48 h; (b) Cs_2CO_3 (10 eq.), 2, CH_3CN, 80 °C, 48 h; (c) tripropylamine (10 eq.), 2, xylene, 120 °C, 48 h; (d) tripropylamine (10 eq.), triethylene glycol ditosylate, xylene, 120 °C, 48 h; (e) Cs_2CO_3 (10 eq.), 2, CH_3CN, 80 °C, 48 h; (f) Cs_2CO_3 (10 eq.), triethylene glycol ditosylate, CH_3CN, 80 °C, 48 h.

enantioselective transport of Z-amino acid and dipeptide K^+ carboxylates through a bulky membrane by two lariat ethers bearing N-pivot dipeptide arms. Herein we report practical syntheses of versatile building blocks of crown ethers, chiral amine precursors and new lariat type ethers(Schemes 1 and 2).

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Caution: $NaClO_4.H_2O$ is explosive when mixed with organic compounds and appropriate precautions should be taken.

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