

Title: **Towards the synthesis of dbCOT: Condensation reaction approach**

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General procedure

Dibenzo[*a,e*]cyclooctatetraene or dbCOT is a commonly used ligand in transition metal catalysis. Moreover, the Strand group has been using its properties to change shape (from tub-shaped to planar and vice versa upon reduction/oxidation) to develop novel molecular machines. However, the use of dbCOT in both transition metal catalysis and as a building block for molecular machines has been limited by its difficult synthesis.

This thesis is focused on developing an improved synthetic route towards dbCOT based on the condensation approach previously reported by Fieser and Pechet in 1946. Besides this, the aim is to develop more convenient and efficient synthesis compared to the currently used. Finally, the synthesis should be performed on a reasonably large scale.

Herein, we present two paths towards dbCOT. Both routes start with condensation reaction of *o*-phthalaldehyde and *o*-phenylenediacetonitrile to produce 5,12-dinitrile dbCOT. The first route proceeds through an acid hydrolysis of the 5,12-dinitrile dbCOT producing the inseparable mixture of 5,12-dicarboxylic acid of dbCOT and 12-carbamide-5-carboxylic acid of dbCOT. The mixture is esterified and 5,12-dimethyl ester of dbCOT was isolated after column chromatography. After hydrolysis of dimethyl ester, the 5,12-dicarboxylic acid of dbCOT was obtained. The second route proceeds through a basic hydrolysis of 5,12-dinitrile dbCOT to produce directly 5,12-dicarboxylic acid of dbCOT. The final step for both routes is a copper mediated Protodecarboxylation of 5,12-dicarboxylic acid of dbCOT to produce dbCOT.

The condensation reaction and acid hydrolysis reaction have been scaled up. The basic hydrolysis and copper mediated protodecarboxylation have been optimised in several factors: reagents, stoichiometries, ligands and reaction temperatures. However, the most optimal conditions have not yet been achieved.

5,12-dicarboxylic acid-dbCOT was isolated in 37% yield through the acid hydrolysis route. Yields for the basic hydrolysis and decarboxylation reactions have not been obtained, but the results reported show promising prospects.

Popular science abstract

Organic synthesis was defined by Nicolau, K. C. (1996) as “the science of constructing molecules from atoms and/or simpler molecules”. Its objective is to obtain natural products and non-natural products which could possess interesting or special qualities. One of these qualities, which the molecule in this thesis possesses, is catalytical action.

Catalysis offers the possibility to speed up chemical reactions, it makes possible to reduce costs of time, energy and matter. However, the synthesis of organic compounds is often complicated and dbCOT is one example.

Its synthesis was first completed in 1946, but its applications were not fully explored after decades later because of its complicated synthesis. Although new synthetic methods have been presented recently, all of them present clear drawbacks such as hazardous conditions, excess of dangerous reagents or difficult procedures.

This thesis presents two new synthetic paths towards dbCOT, in a more convenient, more efficient, cheaper, safer and more environmentally friendly procedure. It will allow for the exploration of all the interesting properties of dbCOT.