The continuing demand for small heterocyclic molecules with useful applications in many areas of chemistry has necessitated more expedient access to diverse range of scaffolds. Synthesis of the so-called privileged structures that possess the requisite physico-chemical characteristics gains additional significance when these are used as building blocks of complex molecular scaffolds. For applications spanning from pharmaceuticals, materials science, nanotechnology and others, as the requirement of new chemical entities with varied substitution pattern increases, the traditional methods available for their construction sometimes lack practicability. Additionally, synthesis requiring multistep sequences invariably suffer from diminishing overall yields. Such reactions frequently employ reagents that are not fully incorporated into the products and necessitate repeated use of solvents in each step. Further, even in single-step convergent reactions, such as Ugi, Passerini, Hantzsh, Strecker, Gewald and Biginelli, multiple components are linked in a particular fashion in the products. For harnessing diversity around their product cores, for example, 3,4-dihydropyrimidin-2(1H)-ones in case of Biginelli reaction, one needs to repeat the reaction,

Scheme 1. Synthetic routes (a-h) for structure diversification of 3,4-dihydropyrimidin-2(1H)-one core.
by choosing different combinations of the aldehyde, urea and alkyl acetoacetate, as many times, as the number of compounds required.

Straightforward approaches enabling rapid synthesis of the functionalized compounds, avoiding multi-step syntheses as well as repeated construction of the core-structure offers synthetic advantage. Using single-step transformations in case of 3,4-dihydropyrimidin-2(1H)-ones (Scheme 1), we have previously demonstrated structure elaboration of all key diversification centres to obtain a library of Ca\(^{2+}\) channel blockers.

Another viable alternative to the multistep syntheses for the synthesis of complex macromolecules would be to stitch the readily available building blocks, which areprefunctionalized with the required substituents. Some representative examples of such reactions include synthesis of porphyrins 2 and its analogues 3,4 using building blocks such as di(pyrrol/thien/furan-2-yl)methanes 5-7, respectively.

In this thesis, in Chapter 3, we have reported straightforward approaches to synthesise meso-elaborated di(pyrrol-2-yl)methanes building blocks for porphyrinoids, as well as a number of di(heterocyclyl)methanes using different heterocycles. In Chapter 4, we have reported single-step, highly regioselective functionalization of sulfur bridged 5,16-dihydro[22]annulene(2.1.2.1)s 3 (R = H) and hexamethoxyxalix[6]arenes 8 in a synthetically useful manner. Before discussing the results of these investigations, a review of literature on the synthetic aspects of di(heterocyclyl)methanes is presented in Chapter 2. Brief review of work related to 3 and 8 is presented in Chapter 4.