COMPUTATIONAL INVESTIGATIONS INTO ENANTIOSELECTIVE SAMARIUM DIODIDE-MEDIATED RADICAL CYCLISATION REACTIONS

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Four decades since SmI$_2$ was first used in synthetic science, the Procter group published the first enantioselective SmI$_2$-mediated radical cyclisation where the enantioselectivity was controlled through the use of an inexpensive, recyclable chiral aminodiol (Scheme 1)[1]. This research has progressed to the point where SmI$_2$ catalysed cyclisation cascades through radical relay are now possible [2]. Throughout, computational mechanistic studies have been crucial in increasing our understanding of the cyclisation reactions.

A recent computational study using density functional theory (DFT) has improved on the mechanism proposed [1]. The generation II mechanism takes into consideration the role of the MeOH additive – crucial in providing enantioselective control in the reaction – and provides a deeper understanding of the radical forming electron transfer process. Enantio- and diastereocntrol is rationalized in the proposed mechanism and appears to be dependent on subtle structural features of the cyclisation precursor (Figure 1).
