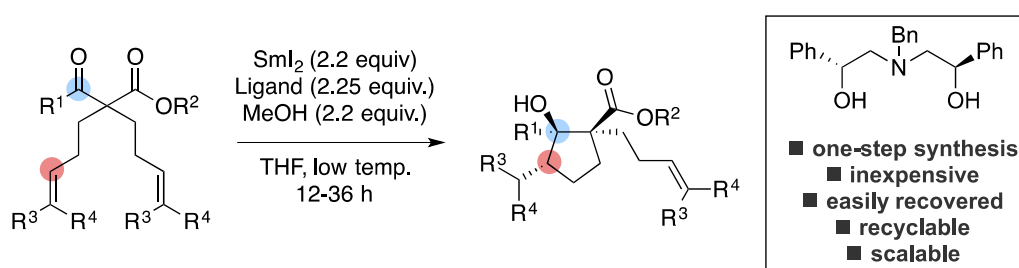


# COMPUTATIONAL INVESTIGATIONS INTO ENANTIOSELECTIVE SAMARIUM DIIODIDE-MEDIATED RADICAL CYCLISATION REACTIONS

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Four decades since  $\text{SmI}_2$  was first used in synthetic science, the Procter group published the first enantioselective  $\text{SmI}_2$ -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  $\text{SmI}_2$  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.



Scheme 1

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 diastereocontrol is rationalized in the proposed mechanism and appears to be dependent on subtle structural features of the cyclisation precursor (Figure 1).

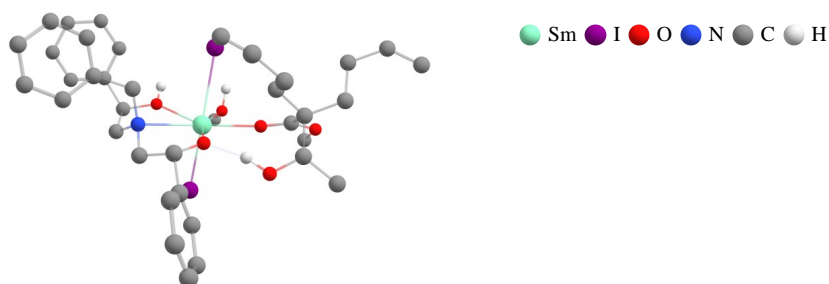


Figure 1

[1] N. Kern, M. P. Plesniak, J. J. W. McDouall, D. J. Procter, *Nature Chem.*, 2017, **9**, 1198-1204

[2] H-M. Huang, J. J. W. McDouall, D. J. Procter, *Nature Catal.*, 2019, **2**, 211-218