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E thesis abstract

This thesis describes a systematic investigation of the mechanistic and synthetic aspects of intramolecular reactions of a series of α-diazo-β-oxo sulfone derivatives using copper and, to a lesser extent, rhodium catalysts. The key reaction pathways explored were C–H insertion and cyclopropanation, with hydride transfer competing in certain instances. Significantly, up to 98% ee has been achieved in the C–H insertion processes using copper-NaBARF-bisoxazoline catalysts, with the presence of the additive NaBARF critical to the efficiency of the transformations. This novel synthetic methodology provides access to a diverse range of enantioenriched heterocyclic compounds including thiopyrans, sulfolanes, β- and ɣ-lactams, in addition to carbocycles such as fused cyclopropanes. The synthesis of the α-diazosulfones required for subsequent investigations is initially described. Of the twenty seven diazo sulfones described, nineteen are novel and are fully characterised in this work. The discussion is subsequently focused on a study of the copper and rhodium catalysed reactions of the α -diazosulfones with Chapter Four concentrated on highly enantioselective C–H insertion to form thiopyrans and sufolanes, Chapter Five focused on C–H insertion to form fused sulfolanes, Chapter Six focused on C–H insertion in sulfonyl α-diazoamides where both lactam formation and / or thiopyran / sulfolane formation can result from competing C–H insertion pathways, while Chapter Seven focuses on cyclopropanation to yield fused cyclopropane derviatives. One of the key outcomes of this work is an insight into the steric and / or electronic factors on both the substrate and the catalyst which control regio-, diastereo- and enantioselectivity patterns in these synthetically powerful transformations. Full experimental details for the synthesis and spectral characterisation of the compounds are included at the end of each Chapter, with details of chiral stationary phase HPLC analysis and assignment of absolute stereochemistry included in the appendix.