Structural isomerisation via radical pathway to a-arylated ketones

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Isomerisation reactions provide streamlined routes to organic compounds which are otherwise hard to directly synthesise. The most common forms are positional, geometrical or stereochemical isomerisations which involve the relocation of a double bond or a change in relative location of groups in space.[1] In contrast, far fewer examples of structural (or constitutional) isomerisations exists where the connectivity between atoms is altered. The development of platforms capable of such rearrangement poses a unique set of challenges because chemical bonds must be selectively cleaved, and new ones formed without overall additional or removal of atoms.

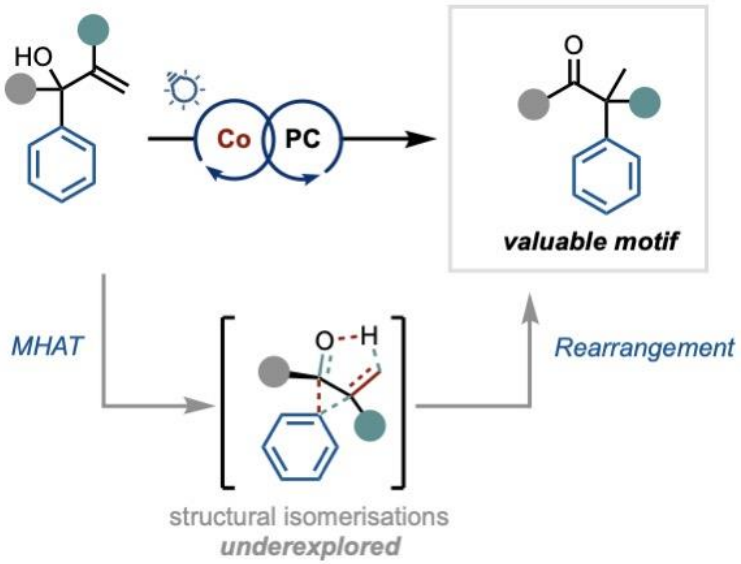

Figure 1. Dual-catalytic system to access structural isomers from allylic alcohols.

Here we disclose a dual catalytic system that can enable the structural isomerisation of readily available allylic alcohols into more challenging to synthesise a-arylated ketones providing an unusual disconnection to structural motifs which are difficult to access by conventional direct arylation methods.[2,3]

1 Molloy, J. J., Morack, T. & Gilmour, R. Angew. Chem. Int. Ed. **2019** 58, 13654–13664.
2 Alsabeh, P. G. & Stradiotto, M. Angew. Chem. Int. Ed.**2013** 52, 7242–7246.
3 Lunic, D., Vystavkin, N., Qin, J. & C.J. Teskey. Angew. Chem. Int. Ed. **2024**, 63, e202409388