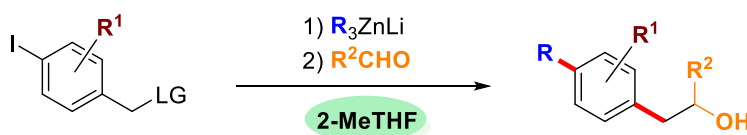


Zincate-Mediated Remote Functionalisation of *p*-Iodobenzyl Derivatives Through Metallotropy

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Metal-promoted remote functionalisation through internal induction is an efficient synthetic concept to swiftly access added-value molecular architectures with a high degree of structural diversity from simple and readily available substrates.^[1] If perfectly implemented, such an approach leads to the selective functionalisation at a site away from a functional group initially interacting with the used reagent or catalyst. In this context, through-space metal migration^[2] or intrinsic migration of the metal along a flexible carbon via unidirectional positional isomerisation sequence of a double C-C bond^[3] are the most popular used internal communication processes between initiation and functionalisation sites. By contrast, metallotropic rearrangement^[4] received very little attention from the synthetic community. In this poster, we disclose the remote functionalisation of diversely decorated 4-iodobenzyl derivatives through metallotropy by using lithium alkylzincate as reagent and 2-MeTHF as solvent.^[5] The process leads to the selective formation of both a C(sp³)-C(sp²) and a C(sp³)-C(sp³) bond at sites localised at five atoms away from one another in a single operation and with a unique organometallic reagent. Compared with the literature precedent,^[6] our reaction conditions allow reaching an unprecedented synthetic scope, both in terms of compatible substrates and electrophiles. The positive influence of the used eco-friendly solvent on key elementary steps of the overall transformation is discussed, namely (i) metalation step through I/Zn exchange,^[7] (ii) alkyl 1,2-migration and (iii) generation of a benzyl zinc intermediate after dearomatisation / rearomatisation / metallotropy chain.



- 32 examples
- High R¹ tolerance
- Compatibility with aromatic & enolisable aldehydes
- 2-MeTHF as a green reactivity booster

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