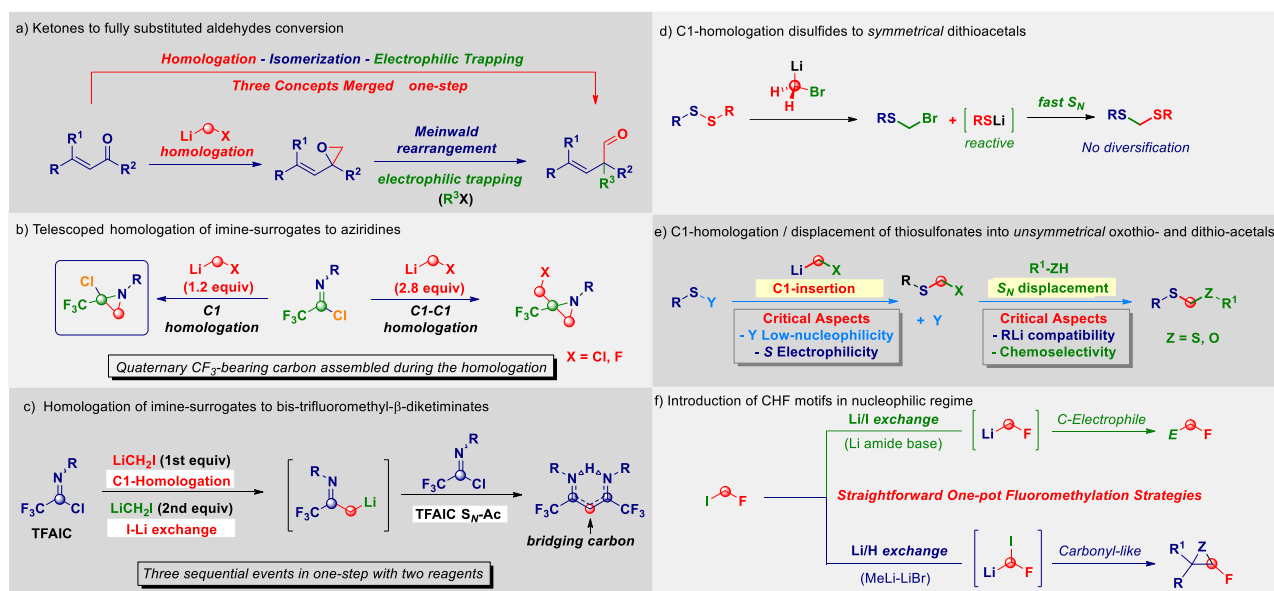


# Designing New Synthetic Concepts in Homologation Chemistry

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The direct transfer of a reactive nucleophilic  $\text{CH}_2\text{X}$  unit into an existing linkage enables the formal introduction of the moiety with the precisely defined degree of functionalization.<sup>1</sup> Upon the fine tuning of the reaction conditions governing the transformation, the initial homologation event can serve as the manifold for triggering unusual rearrangement sequences leading to complex architectures through a unique synthetic operation. The direct – full chemoselective – conversion of a ketone into the homologated all-carbon quaternary aldehyde (*via a*)<sup>2</sup>, the telescoped homologation of imine-surrogates to quaternary aziridines (*via b*)<sup>3</sup> and bis-trifluoromethyl- $\beta$ -diketiminates (*via c*) will illustrate these unprecedented concepts. Additionally, the homologation of disulfides and thiosulfonates will furnish symmetrical (*via d*) and unsymmetrical oxothio- and dithio-acetals (*via e*). The one-step mono-fluoromethylation of carbon electrophiles with extremely labile fluoromethyl lithium reagents will provide a novel entry to valuable fluorinated building-blocks without the needing of using protecting elements for fluoro-containing carbanions (*via f*).<sup>4</sup> Finally, the development of homologation strategies not relying on the use of external C1-sources will be discussed.<sup>5</sup>



## References

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