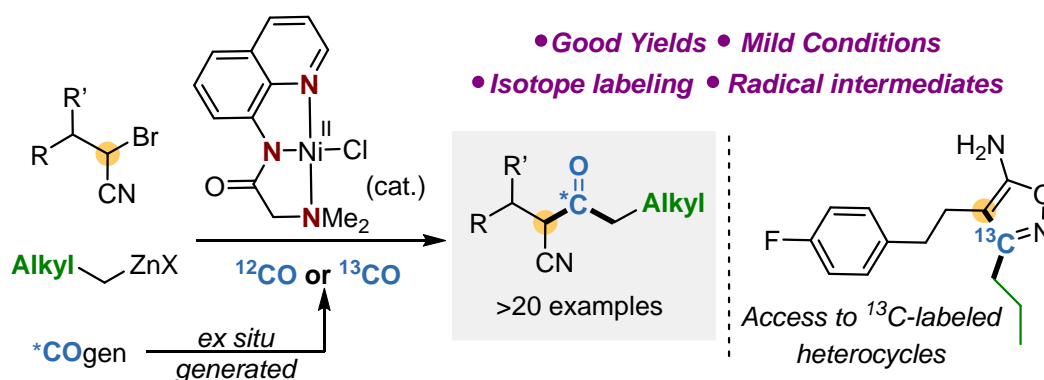


DIRECT ACCESS TO β -KETONITRILES VIA NICKEL-CATALYZED CARBONYLATIVE COUPLING OF α -BROMONITRILES WITH ALKYLZINC REAGENTS

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Herein, we describe the development of a nickel(II)-catalyzed carbonylative coupling of alkylzinc reagents and α -bromonitriles to afford β -ketonitriles in good yields under mild conditions. Key to the success of this carbonylative chemistry is the readily available nickel(II) chloride pincer complex, which forms stable nickel(II) alkyl and nickel(II) acyl complexes as observed by ^1H - and ^{13}C -NMR spectroscopy.



The combined use of the two-chamber system, COware® and the carbon monoxide releasing molecule, COgen, for *ex situ* generation of carbon monoxide, enabled a successful carbonylation.^[1] β -Ketonitriles are versatile precursors for the synthesis of heterocycles, and as such, by using ^{13}C COgen in the three-component coupling, access to ^{13}C -isotopically labeled β -ketonitriles was obtained, and their corresponding isotopically labeled heterocycles. Initial mechanistic investigations suggest the presence of radical intermediates.^[2]

[1] S. D. Friis, A. T. Lindhardt, T. Skrydstrup, *Acc. Chem. Res.* **2016**, *49*, 594.

[2] A. S. Donslund, K. T. Neumann, N. P. Cornelisussen, E. K. Grove, D. Herbstritt, K. Daasbjerg, T. Skrydstrup, Manuscript in preparation.