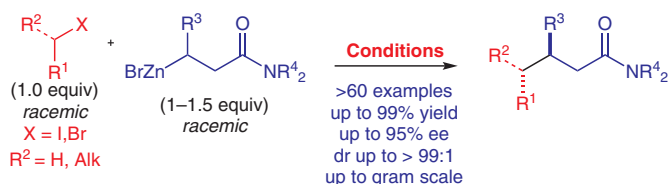


N. HUO, B. J. GORSLINE, G. C. FU* (CALIFORNIA INSTITUTE OF TECHNOLOGY, PASADENA, USA)

Catalyst-Controlled Doubly Enantioconvergent Coupling of Racemic Alkyl Nucleophiles and Electrophiles

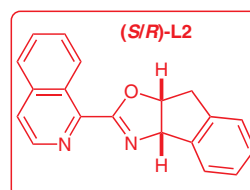
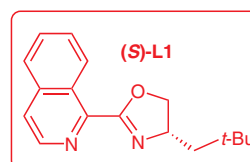
Science 2020, 367, 559–564.

Nickel-Catalyzed Enantioconvergent Coupling of Racemic Partners

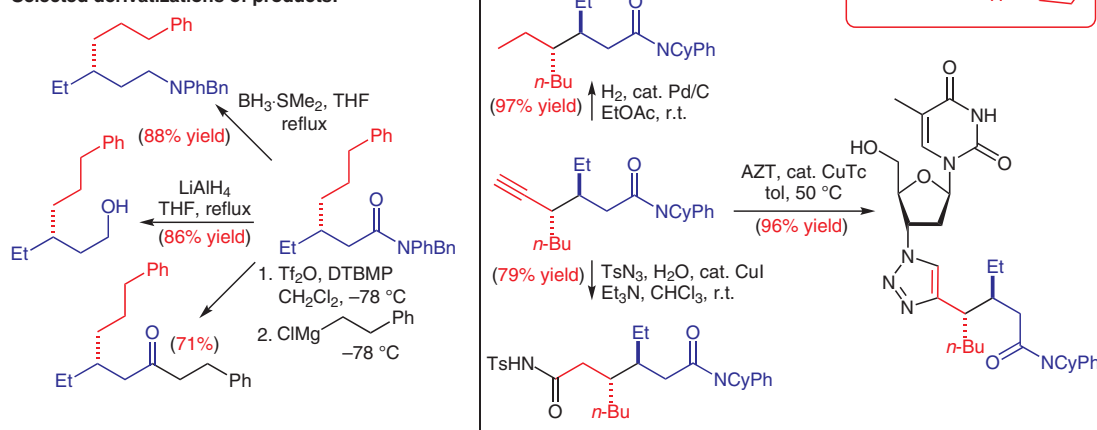


Conditions:

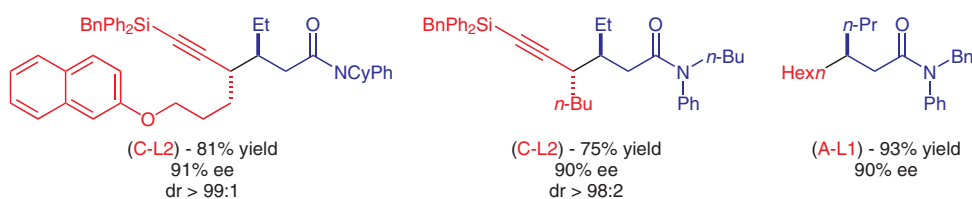
- A) $NiCl_2$ -glyme (10 mol%), (S)-L1 (12 mol%), $Ph_2P(CH_2)_5PPh_2$ (10 mol%), THF, $-5^\circ C$
B) $NiCl_2$ -glyme (12 mol%), (S)-L1 (15 mol%), $Ph_2P(CH_2)_5PPh_2$ (9 mol%), THF, $5^\circ C$
C) $NiBr_2$ -glyme (10 mol%), (S/R)-L2 (13 mol%), LiCl (1.2 equiv), THF, r.t.



Selected derivatizations of products:



Selected examples:



Significance: Fu and co-workers report a nickel-catalyzed doubly enantioconvergent alkyl–alkyl coupling of racemic partners that proceeds with unprecedented selectivity. The authors employed a chiral nickel catalytic system that generates the product as a single stereoisomer from racemic propargylic halides and racemic β -zincated amides.

Comment: The authors propose that the enantioconvergence of the starting materials is facilitated by a radical intermediate arising from both starting materials. The presence of radical intermediates was inferred by the TEMPO adducts formed from both the electrophile and nucleophile partners in the mechanistic study.

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Key words

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enantioconvergent coupling

alkyl nucleophiles

sp^3 – sp^3 bond

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