SYNFORM

People, Trends and Views in Synthetic Organic Chemistry

2013/1

Dear readers,

This issue completes the seventh year of SYNFORM, which was first published in June 2007. Since then we have published an awful lot of exciting organic chemistry, often from a rather peculiar perspective, quite different relative to what is published in other journalistic-type publications, and definitely very different from what can be found in the primary literature. We hope you are still finding SYNFORM a useful tool for staying up-to-date with the most recent and exciting research developments in organic chemistry, and hopefully a pleasant and rewarding reading too. From our side, we guarantee that we will definitely continue to strive to publish high quality reports featuring great science from the best chemists worldwide. Dulcis in fundo, this last 2013 issue presents a collection of outstanding pieces of research, starting from the fluorostannylation of arynes developed by Professor Yoshida (Japan). Next, we can learn more about the groundbreaking use of textiles as supports for organocatalysts developed by Professor List and colleagues (Germany). The third SYNSTORY covers a Ni-catalyzed cross-coupling reaction between alkyl halides recently published by Professor Gong (P. R. of China). The very last article of the year is an Editorial Board Focus on Professor Rovis (USA).

Enjoy your reading and have a fantastic Christmas time!!

Editor of SYNFORM

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tinued Professor Yoshida. “In addition, we have never encountered an example of aryne insertion into an F–Si bond of Me_3SiF, generated from 2-(trimethylsilyl)aryl triflate, an aryne precursor, and a fluoride ion.”

In 2004, Professor Yoshida’s group reported on the aryne insertion into anaFi nt te

Organic catalysts represent a relativelyan

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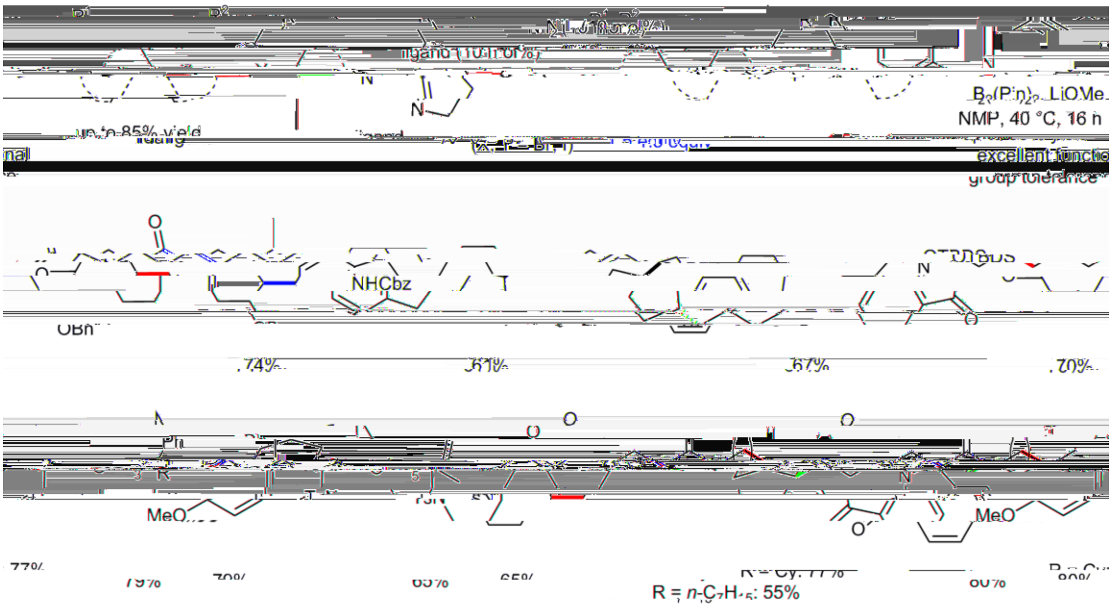
A fundamental issue in organic synthesis is selectivity. Conventional catalytic cross-coupling methods take advantage of reactions between a nucleophile, such as an organometallic species, and an electrophile, for example an alkyl halide or a Michael acceptor, in the presence of a transition-metal catalyst. However, coupling of two structurally and electronically similar electrophiles, such as two alkyl halides, suffers a severe selectivity issue. For instance, the Ullman reaction, discovered in 1901, is generally limited to homo-couplings. The coupling of alkyl halides to form a new $C(sp^3)–C(sp^3)$ bond is particularly challenging due to slow oxidative addition and possible β-elimination problems.

Professor Hegui Gong from the Department of Chemistry, Shanghai University (P. R. of China) remarked: "When I started my independent career in late 2008, I was fascinated with developing a convenient approach to the construction of $C(sp^3)–C(sp^3)$ bonds that did not need preparation of organometallic reagents such as Grignards and organozincs. We believed this could significantly reduce the laborious operations involved in this process, and might lead to new reaction mechanisms that differ from the conventional coupling reactions." Inspired by the Ni-catalyzed Negishi coupling of alkylzincs with alkyl halides, pioneered by Knochel and Fu, Professor Gong's group initiated their first attempt by mixing two different alkyl halides in the presence of zinc powder and catalytic amounts of a Ni/pybox ligand. This strategy efficiently provided alkyl–alkyl compounds in moderate to good yields with excellent functional group tolerance; however, one of the coupling halides was required in excess (3 equiv). The highly competitive homo-coupling side reaction was problematic, suggesting that the Ni/Zn reductive conditions could not effectively bias the two alkyl coupling partners (*Org. Lett.* **2011**, *13*, 2138).

"In order to promote the chemoselectivity of the Ni-catalytic conditions, we turned our attention to boron reductants," said Professor Gong. "We anticipated that a possible Ni–B complex might differentiate the two alkyl halides' oxidative coupling stage by taking advantage of subtle electronic and steric differences in the two alkyl partners. After tremendous effort, my co-worker Hailiang Xu eventually dis-



covered that (Bpin)2 serves this purpose.” The reaction requires only 1.5 equivalents of the second alkylthantr

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In the next issues:

SYNSTORIES

(Focus on an article from the current literature)

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