D. YOSHII, T. YATABE, T. YABE, K. YAMAGUCHI* (THE UNIVERSITY OF TOKYO, JAPAN)
C(sp^3)–H Selective Benzylic Borylation by In Situ Reduced Ultrasmall Ni Species on CeO_2
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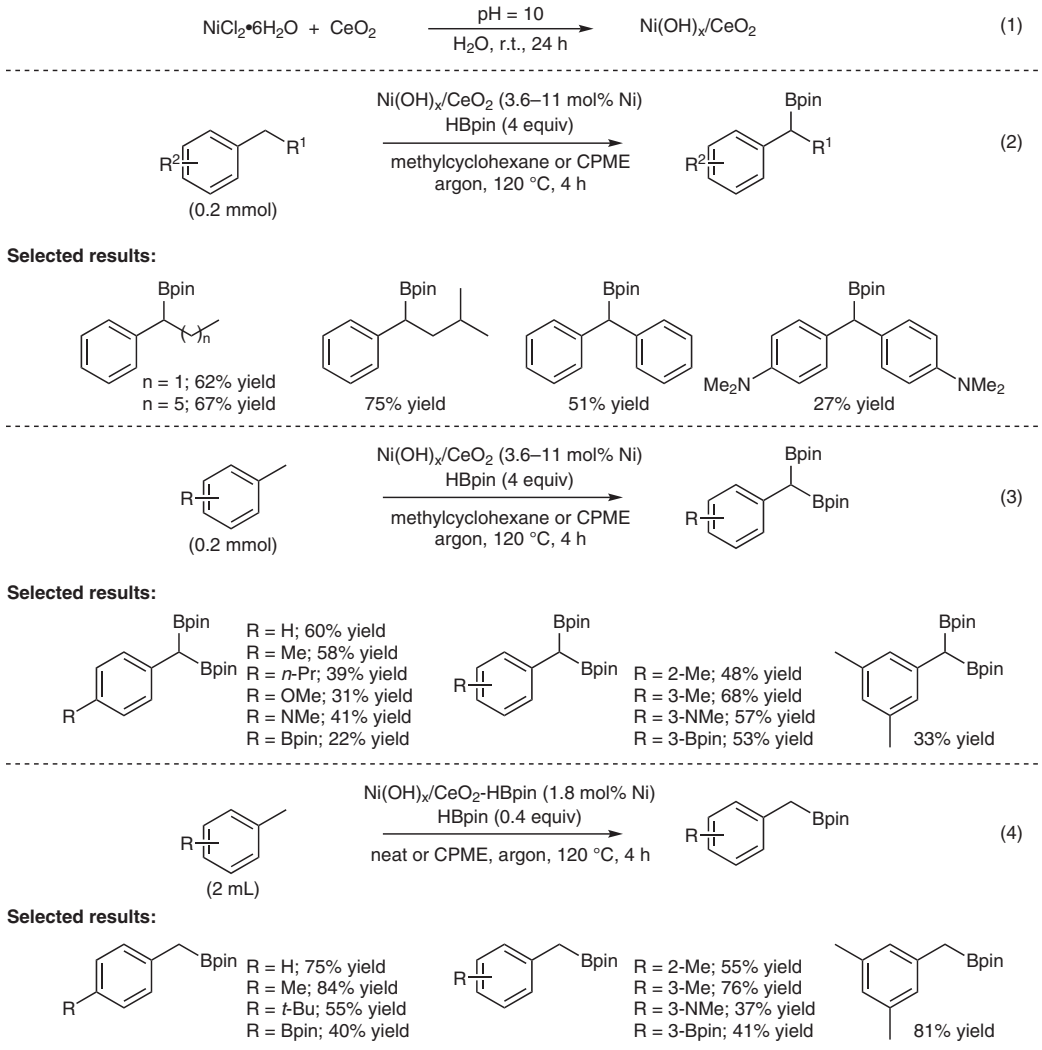
Benzylic C–H Borylation on Ceria-Supported Nickel Hydroxides



Significance: Nickel hydroxides supported on CeO_2 ($Ni(OH)_x/CeO_2$), prepared by mixing $NiCl{\cdot}6H_2O$ and CeO_2 in H_2O (pH = 10) (eq. 1), catalyzed the benzylic C–H borylation of alkylarenes or diphenylmethanes with pinacolborane to give the corresponding benzylic boronates (eq. 2). In the reaction of methylarenes, *gem*-diborylated products were obtained as the main products (eq. 3). The monoborylation of methylarenes was also achieved by using the catalyst pretreated with HBpin and with the methylarene as the solvent (eq. 4).

Comment: $Ni(OH)_x/CeO_2$ was characterized by means of XANES XPS, EXAFS, HAADF-STEM, STEM-EDS, XRD, and ICP-AES analyses. A hot-filtration experiment suggested that the reaction occurred heterogeneously.

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Polymer-Supported Synthesis

Key words
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