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Accessing 2-(Hetero)arylmethyl-, -allyl-, and -propargyl-2,1-borazaronaphthalenes: Palladium-Catalyzed Cross-Couplings of 2-(Chloromethyl)-2,1-borazaronaphthalenes

Accessing 2-(Hetero)arylmethyl-, -allyl-, and -propargyl-2,1-borazaronaphthalenes

Significance: The authors expanded the electrophilic nature of 2-(chloromethyl)-2,1-borazaronaphthalene. In addition to substitution reactions, now also several metal-catalyzed reactions were performed. Potassium (hetero)aryl and alkenyl trifluoroborates as well as terminal alkynes were successfully used as nucleophiles.

Comment: Impressively, a wide variety of substituted azaborines were prepared starting from one common azaborinyl building block. This new methodology gives access to a whole library of pseudobenzylic-substituted azaborines.

Selected examples:

B\(\text{H}^+\)NCl(Het)ArBF\(_3\)K+ 
\(\text{Pd}_2\text{dba}_3\) (1.25 mol%) 
RuPhos (2.5 mol%) 
Cs\(_2\)CO\(_3\) (2.0 equiv) 
PhMe–H\(_2\)O 
80 °C, 18 h

80% yield

B\(\text{H}^+\)NAr 
80% yield

B\(\text{H}^+\)NCO\(_2\)Me 
58% yield

B\(\text{H}^+\)N 
67% yield

O

B\(\text{H}^+\)N 
70% yield

S

B\(\text{H}^+\)NCl(alkenyl)BF\(_3\)K+ 
\(\text{Pd}_2\text{dba}_3\) (1.25 mol%) 
RuPhos (2.5 mol%) 
Cs\(_2\)CO\(_3\) (2.0 equiv) 
PhMe–H\(_2\)O 
80 °C, 18 h

90% yield

B\(\text{H}^+\)N 
80% yield

83% yield

B\(\text{H}^+\)N 
79% yield

N \(\text{t}-\text{Bu}\)O

83% yield