

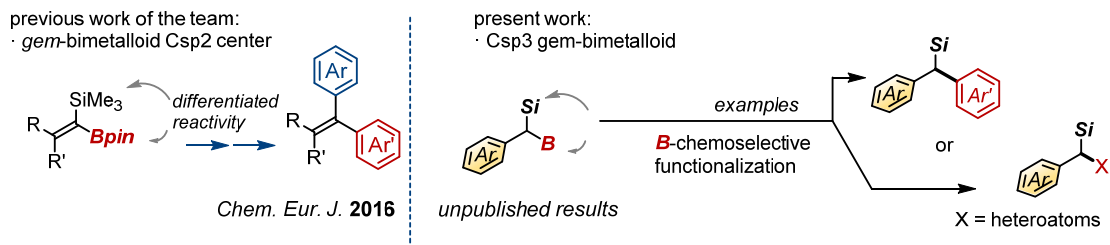
GEMINAL SILICON/BORON BIMETALLOIDS: VERSATILE BUILDING BLOCKS FOR MOLECULAR DIVERSITY

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Within the ever-expanding search for methods to access multi-substituted carbon centers, a particularly interesting class of substrates are those containing more than one geminally disposed metalloid fragments. Such species have the potential to engage in complexity-generating coupling sequences [1], especially when bearing chemically differentiated metalloid groups, a scenario which may enable chemoselective iterative C–C and C–heteroatom bond-forming processes [2]. In this context, we recently described the synthesis and reactivity of a new class of such building block, in which an olefinic C(sp²) atom bears a *gem* –SiR₃ / B(OR)₂ pair. We showed that species of this type enabled interesting reactivity sequences, including a modular stereoselective an all-carbon substituted olefins, such as the Tamoxifen core [3].

As an expansion, we have now explored the synthesis and reactivity of the saturated benzylic Csp³-centered *gem*-silyl / boryl compounds, including their chemoselective functionalization by either metal-assisted or metal-free cross-coupling reactions. We hope this work would help reinforce the notion that differentiated main-group *gem* dimetalloids indeed constituted a powerful reagent class suitable for the development of game-changing reactivity patterns.



[1] J. Royes, A. B. Cuenca, E. Fernández, *Eur. J. Org. Chem.* **2018**, 22, 2728-2739.

[2] a) A. A. Szymaniak, C. Zhang, J. R. Coombs, J. P. Morken. *ACS Catal.* **2018**, 8, 2897-2901; b) J. Kim, S. H. Cho, *ACS Catal.* **2019**, 9, 9, 230-235.

[3] E. Lacascia, A. B. Cuenca, E. Fernández, *Chem. Eur. J.* **2016**, 22, 18737-18741.