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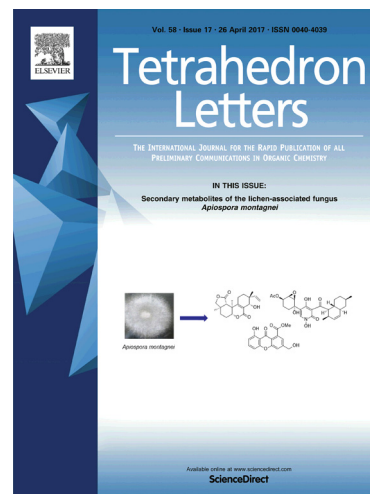
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Visible-light-promoted alkylation of unsaturated MIDA boronates using Ru(bpy)₃Cl₂ as the photoredox catalyst

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Abstract: The development of a visible light-mediated atom transfer radical addition (ATRA) of perfluoroalkyl iodides to ethynyl-, vinyl- and allyl-MIDA boronates using the reductive and oxidative quenching of [Ru(bpy)₃]Cl₂ is described. Using an operationally simple and mild protocol, the corresponding MIDA boronates containing perfluoroalkyl groups were obtained in moderate to high yields. The structures of three products were confirmed by single crystal X-ray diffraction studies.

Keywords: MIDA boronates, photoredox catalysis, perfluorohaloalkanes, ATRA.

Organoboron compounds are widely used starting materials in various chemical transformations.¹⁻⁴ However, access to these intermediates using organolithium chemistry is often challenging and requires conditions under which the majority of electrophilic groups are unproductively consumed by organolithium reagents.⁵ The recent progress in photoredox catalysis encouraged us to consider this method as a useful tool to obtain new organoboron compounds.^{6,7} Much of the promise of visible light photoredox catalysis hinges on its ability to achieve unique, if not exotic bond constructions that are not possible using established protocols.⁸ An important problem to solve is the stability of the B-C bond during photoredox catalytic processes. The number of publications involving the use of boron containing compounds in photoredox catalysis is low and typically results in cleavage of the B-C bond. For example, the aerobic oxidative hydroxylation of arylboronic acids using Ru(bpy)₃Cl₂ as the photocatalyst resulted in the formation of phenols.⁹ Other examples involve the use of organotrifluoroborate potassium salts in the photocatalytic C-C coupling of alkyl radicals with electron deficient alkenes.¹⁰ In this process which is catalyzed by 9-mesityl-10-methylacridinium perchlorate, the B-C bond is cleaved upon oxidation to form

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