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Palladium-catalyzed bisfunctionalization of active alkenes by β -acetonitrile- α -allyl addition: application to the synthesis of unsymmetric 1,4-di(organo)fullerene derivatives

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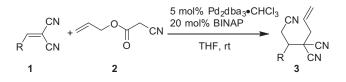
ABSTRACT

A new, efficient palladium-catalyzed bisfunctionalization of ethylidene malononitriles by addition of acetonitrile and allyl groups is developed for the construction of all-carbon quarternary and tertiary centers simultaneously. This methodology is successfully applied to the synthesis of unsymmetric 1,4-disubstituted C_{60} .

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Palladium-catalyzed β -nucleophilic- α -allyl addition of active olefins through π -allyl-palladium intermediates has emerged as a mild and efficient multiple bond-forming method for the simultaneous construction of all-carbon quaternary and tertiary centers,^{1,2} which are important structural units in a wide range of bioactive substances and natural products.³ Over the past decade, we and other groups have been interested in developing new palladiumcatalyzed β -nucleophilic- α -allyl addition reactions toward active alkenes through various π -allyl palladium intermediates, including heteroatom- and carbon-nucleophile addition/allylation,^{2e-k} bisallylation,^{2a-d} acetonation/allylation,^{2l,m} amidoallylation,²ⁿ and iminoallylation (Fig. 1).²⁰ The palladium-catalyzed decarboxylative reaction for the formation of π -allyl palladium species is an environmentally friendly and economical process^{1c,4,5}; the reaction proceeds under essentially neutral conditions with high atom economy. Based on this concept, we envisioned that the bis- π allylpalladium^{2a} analogue acetonitrile-(π -allyl)palladium complex should be formed by the reaction of cyanoacetic acid allyl ester with a palladium catalyst, which will undergo acetonitrile/allyl addition to the active alkenes (Fig. 1). Furthermore, in continuation of our interest in transition metal catalyzed functionalization of [60]fullerene (C_{60}),⁶ we reasoned that if successful, this methodology would be applicable to the selective bisfunctionalization of C_{60} because of its electrophilic nature and specialized alkene component. Transition metal catalyzed functionalization of C_{60} has emerged as a promising method for preparing functionalized C_{60} derivatives with high selectivity and high functional group compatibility under mild reaction conditions.⁷ However, investigations on the synthesis of unsymmetric 1,4-di(organo)fullerenes have been seldom studied,⁸ in particular, a one-step catalytic method has not been reported.

Herein, we report a new Pd-catalyzed bisfunctionalization of various malononitriles **1** with cyanoacetic acid allyl ester (**2**), that affords the β -acetonitrile- α -allyl addition products **3** in good to high yields (Eq. 1). Moreover, we have successfully applied this method to the synthesis of unsymmetric 1-acetonitrile-4-allyl-[60]fullerene **4a** in good yield in one step.



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