



Synthesis of polyfluorinated terphenyl and styrene derivatives by palladium catalysed C–F bond activation of polyfluoronitroaromatic substrates

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ABSTRACT

Short series of polyfluorinated terphenyl and styrene derivatives were synthesised by palladium catalysed carbon–fluorine bond activation processes involving cross coupling reactions of polyfluorinated nitrobenzene and aryl- and vinyl-boron substrates, respectively.

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1. Introduction

[1] Suzuki–Miyaura [2] and borylation [3] processes for highly fluorinated aromatic substrates and the field has now been very comprehensively reviewed recently by Braun and co-workers [4].

Previously, we demonstrated that highly fluorinated nitrobenzene derivatives could be used as substrates for C–F activation processes activated by inexpensive, commercially available Pd(PPh₃)₄ catalyst for the synthesis of various biphenyl [5] and aryl–alkynyl [6] derivatives by sp²–sp² and sp²–sp Suzuki–Miyaura type cross coupling processes, respectively. In this paper, we present the synthesis of some terphenyl and styrene systems by Pd catalysed C–F activation processes involving polyfluorinated nitrobenzene precursors, further extending the use of transition metal catalysed carbon–fluorine bond activation processes. The use of various nickel and palladium catalysts for the cross coupling of highly fluorinated heteroaromatic systems, such as pentafluoro- and 2,3,5,6-tetrafluoro-pyridine, with vinyl-tin based reagents by Stille processes were discussed by Braun [1b,4] but no analogous processes using vinyl boron derivatives have been reported for the synthesis of polyfluorinated styrene systems.

2. Results and discussion

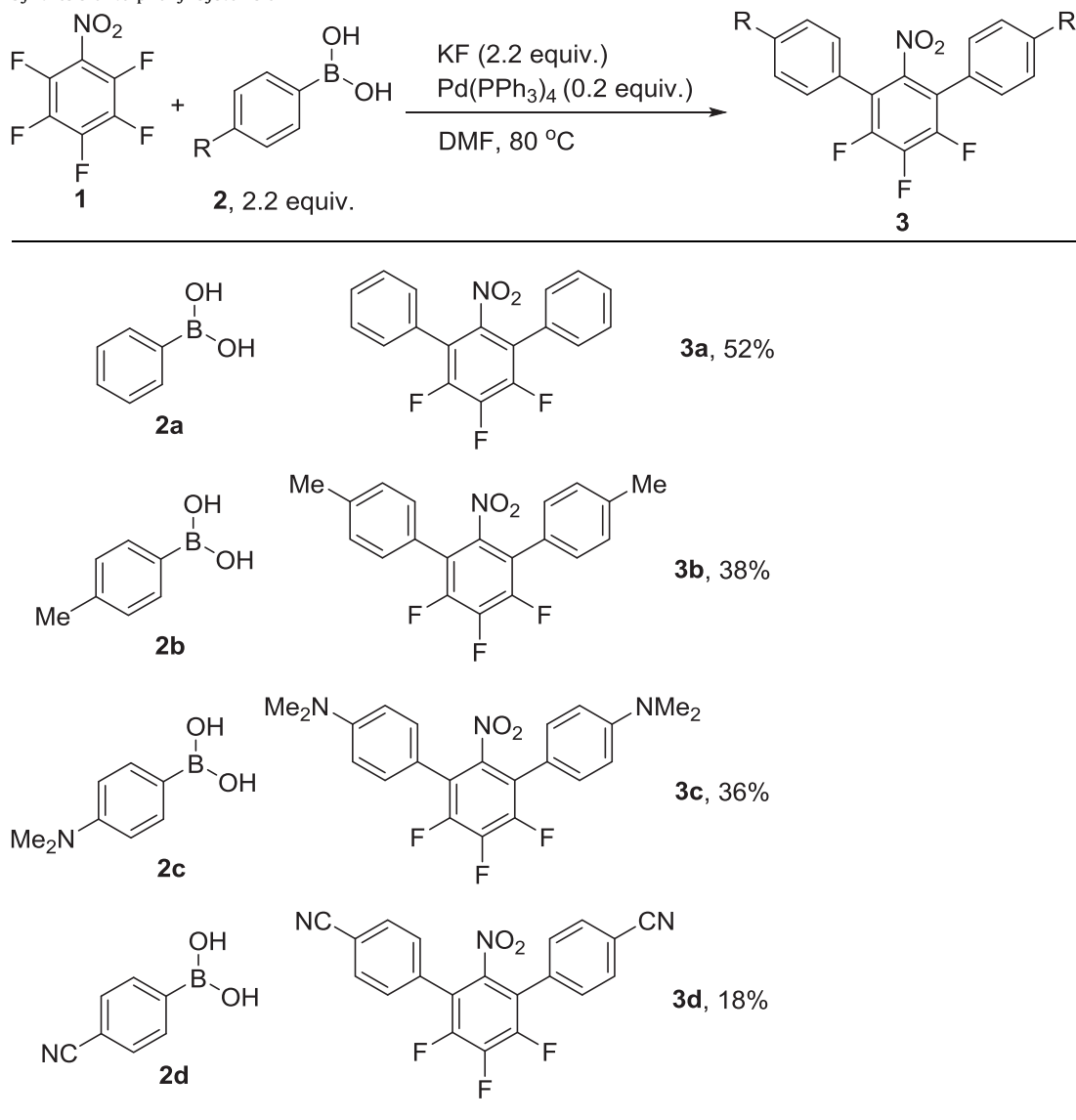
Coupling of pentafluoronitrobenzene **1a** with one equivalent of an aryl boronic acid derivative **2** catalysed by Pd(PPh₃)₄ and KF in DMF at 80 °C gives the corresponding biphenyl product arising from substitution of the fluorine atom *ortho* to the activating nitro group as we described previously [5]. Analogous reaction of **1** with 2.2 equivalents gave the terphenyl systems **3** as the only fluoroaromatic products (Table 1). In all cases, activation of positions *ortho* to the nitro group occurs selectively, demonstrating the key role played by the nitro substituent in directing the approach of the palladium catalyst to activated *ortho* positions and subsequent insertion into the carbon–fluorine bond. The structures of **3a** and **3b** were confirmed by X-ray crystallography (Fig. 1). The structure **3b** contains two independent molecules with different orientation of the substituents (Fig. 1c). Interestingly, no π...π interactions were found in both structures and the molecules in crystals **3a** and **3b** are linked together by a number of weak interactions of C–H...O and C–H...F type.

The synthesis of a short series of styrene derivatives **5** was achieved by analogous palladium catalysed cross coupling of fluorinated nitrobenzene derivatives **1** and vinyl borolane substrates **4** (Table 2). Again, in all cases fluorine attached to sites *ortho* to the nitro group were displaced by the vinyl group

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Table 1
Synthesis of terphenyl systems **3**



by Pd catalysed C–F activation following the mechanism we have previously described for related Suzuki–Miyaura processes [5].

Palladium catalysed C–F bond activation methods, therefore, allow further opportunities for the targeted synthesis of terphenyl **3** and styrene **5** derivatives where the central aryl ring bears several fluorine atom substituents.

3. Experimental

3.1. General

3.1.1. Analysis

Proton, carbon and fluorine nuclear magnetic resonance spectra (^1H NMR, ^{13}C NMR and ^{19}F NMR) were recorded (^1H NMR,

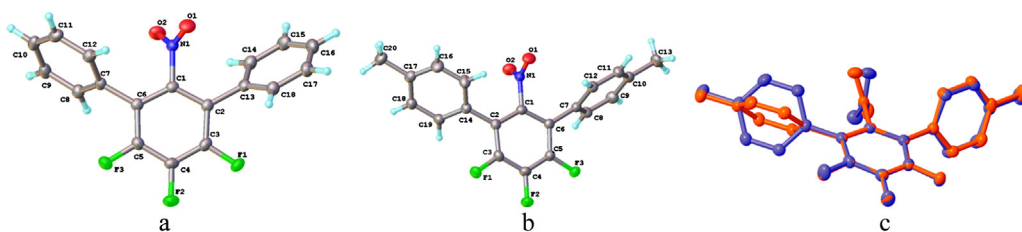


Fig. 1. Molecular structures of terphenyl systems **3a** (a) and **3b** (b, one independent molecule is shown) and an overlay of two independent molecules in the structure **3b** (c, H-atoms are omitted for clarity) showing the different conformations of the substituent. All ellipsoids are shown at 50% probability level.

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