

Introduction

Functionalized aryl and heteroaryl alkynes are powerful building blocks in chemical synthesis because of their versatility to be transformed into various useful molecules and also their ubiquity in natural product synthesis, pharmaceuticals, and advanced materials. Consequently, much effort has been expended to develop efficient methods to install various alkynyl groups. Some of the strategies which have been established include: 1) Sonogashira palladium/copper-catalyzed $sp^2$-$sp$ cross-coupling of aryl halides with terminal alkynes; 2) direct alkynylation of unreactive alkyl and aryl $C$–$H$ bonds with pre-functionalized alkylnating reagents such as alkynyl halides. The latter problem seems to arise from the slow reduction of the fluoroaryl alkyne from Pd to Cu, which leads to competing reverse transmetalation processes, that is, transmetalation accompanied by homocoupling of the terminal alkyne.

Copper-Catalyzed Oxidative Cross-Coupling of Electron-Deficient Polyfluorophenylboronate Esters with Terminal Alkynes

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Abstract: We report herein a mild procedure for the copper-catalyzed oxidative cross-coupling of electron-deficient polyfluorophenylboronate esters with terminal alkynes. This method displays good functional group tolerance and broad substrate scope, generating cross-coupled alkynyl(flouro)arene products in moderate to excellent yields. Thus, it represents a simple alternative to the conventional Sonogashira reaction.

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https://doi.org/10.1002/chem.202002888.

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cross-coupling of terminal alkynes with arylboronic acids was first disclosed by Zou and co-workers (Scheme 1b). In the past few years, various modifications of this Pd-catalyzed reaction have been developed. However, palladium is costly and only a few electron-withdrawing substituents on the aromatic ring of arylboronic acids were employed. Recently, Cheng et al. disclosed a copper-catalyzed oxidative coupling of arylboronic acids with terminal alkynes. However, the reported method suffers from some disadvantages including high reaction temperature, long reaction time (36 h), and only moderate yields. From a synthetic point of view, the development of an improved procedure employing an inexpensive catalyst for widespread application has remained a highly desirable goal.

We reported the C-F borylation of fluoroarenes using a NHC (N-heterocyclic carbene)-ligated Ni complex as a catalyst to generate fluorinated arylboron pinacol esters (ArF-Bpin) in good to excellent yields. Very recently, we reported optimized conditions for the Suzuki-Miyaura cross-coupling of ArF-Bpin with aryl iodides and bromides using a combination of CuI and phenanthroline as a catalyst precursor to generate cross-coupled products in moderate to excellent yields. We have recently reported the palladium-catalyzed homocoupling of fluorinated arylboronates and the borylation of arylboronic acids with terminal alkynes, and the borylation of arylboronic acids was readily prepared NHC-stabilized Cu catalyst. Inspired by these results, we attempted to develop a Cu-catalyst system for the oxidative cross-coupling of ArF-Bpin compounds with terminal alkynes.

**Scheme 1.** Selected oxidative cross-coupling reactions of alkynes.

**Table 1.** Optimization of reaction conditions.

| Entry | [Cu] Base Additive Solvent Yield [%] |
|-------|-------------------------------------|-----------------|
| 1     | CuBr₂ tBuOLi – DMF 24 h 0 65 36 |
| 2     | CuCl tBuOLi – DMF 24 h 10 55 35 |
| 3     | Cu(OAc)₂ tBuOLi – DMF 24 h 18 60 35 |
| 4     | Cu(OAc)₂ K₂PO₃ – DMF 24 h 35 52 8 |
| 5     | Cu(OAc)₂ K₂PO₃ DDQ DMF 24 h 58 5 8 |
| 6     | Cu(OAc)₂ Cs₂CO₃ DDQ DMF 24 h 11 25 25 |
| 7     | Cu(OAc)₂ K₂CO₃ DDQ DMF 24 h 82 3 4 |
| 8     | Cu(OAc)₂ K₂CO₃ DMF 24 h 15 10 45 |
| 9     | Cu(OAc)₂ K₂CO₃ DDQ MBT 24 h 0 5 35 |
| 10    | Cu(OAc)₂ K₂CO₃ DDQ DCE 24 h 0 5 0 |
| 11    | Cu(OAc)₂ K₂CO₃ DDQ toluene 24 h 0 10 10 |
| 12    | Cu(OAc)₂ K₂CO₃ DDQ DMSO 24 h 25 15 20 |
| 13    | Cu(OAc)₂ K₂CO₃ DDQ CH₃CN 24 h 10 15 10 |
| 14    | Cu(OAc)₂ K₂CO₃ DDQ THF 24 h 5 10 15 |
| 15    | Cu(OAc)₂ K₂CO₃ DDQ DMF 24 h 5 10 40 |
| 16    | Cu(OAc)₂ K₂CO₃ DDQ DMF 24 h 5 10 35 |
| 17    | Cu(OAc)₂ K₂CO₃ DDQ DMF 24 h 6 10 0 |
| 18    | Cu(OAc)₂ K₂CO₃ DDQ DMF 24 h 35 5 30 |
| 19    | Cu(OAc)₂ K₂CO₃ DDQ DMF 24 h 25 28 30 |

[a] Reaction conditions: 1 a (0.4 mmol), 2 a (0.45 mmol), Cu(OAc)₂ (15 mol %), phenanthroline (Phen, 15 mol %), Ag₂O (1.8 equiv), DDQ (40 mol %), base (2.0 equiv), anhydrous and degassed solvent (5 mL). The mixture was stirred at 40 °C under argon, in a sealed tube for 12 h. [b] 3 a: isolated yield. 4: isolated yield, 5: the yields were determined by GC-MS analysis vs. a calibrated internal standard (n-dodecane) and are averages of two runs. [c] The reaction was performed in air. [d] Room temperature. [e] In the absence of Ag₂O. [f] Under O₂. [g] Ag₂O (1.2 equiv). [h] Base (1.0 equiv).
In addition, reaction optimization also revealed that the solvent had a significant impact on this reaction. Lower yields were observed when reactions were performed in other solvents such as 1,2-dichloroethane (DCE), CH₃CN, THF, DMSO, methyl tert-butyl ether (MTBE), and toluene (entries 9–14). Notably, the replacement of Ag₂O with O₂ failed to give any desired product (entry 17), indicating the unique roles of Ag₂O in promoting this reaction. Attempts to run the reaction in air resulted in a very low yield of the desired product (entry 15). Reducing the amount of K₂CO₃ and Ag₂O also diminished the yield (Table 1, entries 18 and 19).

With the optimized conditions in hand, we focused our attention on investigating the scope and limitations of the oxidative cross-coupling reaction. As shown in Scheme 2, various polyfluorophenyl boronate substrates 1 containing 1–4 fluorine atoms were tested. Under the standard conditions (Table 1, entry 7), different tetrafluorophenylboronate esters and trifluorophenylboronate esters smoothly underwent alkylation giving good to excellent yields (Scheme 2, 3b–3f). However, these reaction conditions were not suitable for Ar₂Bpin substrates containing di- or mono-fluorinated aryloboranes such as 2,5- or 2,3-difluorophenyl-Bpin (1g and 1i) and 3-fluorophenyl-Bpin (1h), perhaps due to the lower Lewis acidity of the boronates which is impacted by the number of fluorines and, especially, ortho-fluorine substituents. We speculated that increasing the temperature might be crucial for overcoming the barrier to C–B bond activation and thus to obtaining efficient catalysis. When reactions were performed at 80 °C, the corresponding products 3g and 3i were formed in good yields. It is also noteworthy that replacement of the weak base with a stronger base afforded the corresponding product in good yield (3h).

The substituents of alkynes 2 were then varied in order to explore further the scope of the reaction. As shown in Scheme 3, a series of alkynes 2 with different electron-withdrawing and electron-donating substituents on the aromatic ring were subjected to the optimal conditions. The experimental results showed that a broad range of substituents on the arylalkynes 2, including methyl, methoxy, chloro, bromo, and fluoro groups at the ortho-, meta-, and para-positions of the aromatic ring were well tolerated, providing the desired compounds in moderate to excellent yields (Scheme 3, 6a–6h).

Furthermore, the structures of compounds 6a and 6g were unambiguously confirmed via single crystal X-ray diffraction (see below). An ester group, which may not be tolerated in reactions employing organozinc reagents, is also compatible with this reaction (6i). Importantly, aliphatic alkynes proceeded to give the desired products in moderate to good yields (6j and 6k). With a highly electron-withdrawing CF₃ substituent, only moderate yields were observed (6l and 6m). Unfortunately, less reactive 4-nitro-phenyl and 4-cyano-phenyl alkynes were not suitable for the reaction under the standard conditions.

To examine the feasibility of scaling up the reaction, a gram-scale coupling of C₆F₅-Bpin with phenylacetylene was em-
ployed (Scheme 4). The desired coupling product was obtained with minimal loss of yield (72\%).

Based on previous reports\(^\text{[22]}\) and the aforementioned observations, a plausible catalytic cycle for our oxidative cross-coupling reaction is shown in Scheme 5. The first step would involve the addition of alkynyl anion leading to the formation of alkynylcopper(II) species B. Subsequent transmetalation between Ar\(_1\)Bpin and intermediate B occurs to form intermediate

Scheme 3. Scope of the reaction with respect to the different terminal alkyne substrates 2.\(^{[a,b]}\) [a] Reaction conditions: 1a (0.4 mmol), 2 (0.45 mmol), Cu(OAc)\(_2\) (15 mol\%), Phen (15 mol\%), Ag\(_2\)O (1.8 equiv), DDQ (40 mol\%), K\(_2\)CO\(_3\) (2.0 equiv), DMF (4 mL), 40 °C, 12 h, Ar. [b] 6: isolated yield. [c] 24 h.

Scheme 4. Gram-scale synthesis of 3a.

Scheme 5. Proposed mechanism.
The desired product 3a would be generated by C–C reductive elimination. The Cu²⁺ species formed is reoxidized by DDQ (see above)⁵⁰,⁵¹ to regenerate A, completing the catalytic cycle.

Molecular and crystal structures: intermolecular π–π stacking interactions

The crystal structures of the cross-coupling products 6a and 6g were analyzed using single-crystal X-ray diffraction. The molecular geometries of these compounds in their crystal structures are shown in Figure 1. The central C=C bond lengths are 1.195(2) and 1.1996(6) Å (Table 2) and, hence, typical of C=C triple bonds (1.192 Å).⁵² The sp-sp² C–C single bonds between the alkyne and the fully fluorinated phenyl rings are slightly shorter (1.4265(7) and 1.427(2) Å) than the corresponding bonds to the mesityl ring of 6a (1.4350(7) Å) or the para-mono-fluorinated phenyl ring of 6g (1.4372(2) Å). The sp-sp² C–C bonds to tetra- or pentafuorinated phenyl rings are also shorter than those to the fully or mostly hydrogen-containing phenyl rings of mixed compounds in other partially fluorinated tolans,⁵³ rod-like 1,4-bis(phenylethynyl)benzenes,⁵⁴ and phenyl and perfluorophenyl end-capped polyynes.⁵⁵ The shortening is due to the strong electron-withdrawing nature of the fluorine atoms, and the length difference is also observed in the co-crystals of fully hydrogen-containing and fully fluorinated tolans⁵² rod-like 1,4-bis(phenylethynyl)benzenes,⁵⁴ and phenyl end-capped polyynes.⁵⁵ The molecules of 6a and 6g are nearly planar with a very small twist between the aryl moieties (2.959(3) and 3.04(5)°, Table 2). A small twist angle of between 0° and 6° is also typical of the hydrogenated and fluorinated tolans, rod-like 1,4-bis(phenylethynyl)benzenes, and phenyl endcapped polyynes.⁵⁴-⁵⁷ Larger twist angles were reported for compounds related to 6g in which the fluorine atom at the para-position of the phenyl ring is substituted by iodine (9.4(2)°), bromine (15.69(8)°), and NO₂ (9.90(7)°).⁵⁸ This may be related to the prevalence of different intermolecular interactions in these compounds (see below).

In compounds 6a and 6g, the nearly planar molecules are related by inversion symmetry and are oriented offset face-to-face in a head-to-tail fashion forming infinite π-stacks (Figure 2). The interplanar separations between the aromatic rings (3.325(3) – 3.438(2) Å, Table 2) are in the normal range of π–π stacking interactions, which are typical of molecules for which the packing is dominated by arene-perfluoroarene interactions. The differences in electronegativity of hydrogen and fluorine atoms with respect to the carbon atoms lead to the formation of opposite multipole for fully fluorinated and non-fluorinated aryl groups and, hence, to attractive multipole forces between these groups.⁵⁹ Head-to-tail stacking via arene-perfluoroarene interactions, analogous to that observed in 6a and 6g, is commonly found in self-complementary compounds that contain both fluorinated and nonfluorinated aryl groups. Examples are partially fluorinated tolans⁵⁵ and phenyl-endcapped polyynes,⁵⁵ but also co-crystals of bis(phenylethynyl)benzenes with partially alternating fluorinated and non-fluorinated phenyl rings.⁵⁴ We conclude that methylation at the 2-, 4-, and 6-positions of partially fluorinated tolans on the same para position did not alter this common stacking motif and, hence, the influence of arene-perfluoroarene interaction on the molecular packing. Arene-perfluoroarene π-stacking was also observed in the 1:1 co-crystal of mesitylene and hexafluorobenzene.⁶⁰ Weak intermolecular C–H···F, C–F, and F–F interactions exist between adjacent stacks in 6a and 6g (Figure 2, Table S2 in the Supporting Information). Mono-fluorination at the para-position of the phenyl ring in 6g does not have a significant influence on the arene-perfluoroarene packing, which is very similar to that of 1-pentafluorophenyl-2-phenylacetylene.⁵⁴ This was expected as the mono-chlorination of partially fluorinated tolan at the same para position did not alter the packing motif.⁶² The effect of halogenation with chlorine, bromine, and iodine atoms at the para-positions of partially fluorinated tolans on the presence of arene-perfluoroarene interaction, studied earlier by Marder and co-workers,⁶²[a] revealed the absence of arene-perfluoroarene stacking only for the compounds substituted with the heavier halogens (Br, I). This was explained by the prevalence of BrBr and I–I interactions determining the packing of the molecules.⁶²[a] Also note the larger twist angle between the phenyl rings in these compounds (15.69(8)° and 9.4(2)°) when compared to those in arene-perfluoroarene π-stacked tolan (see discussion above). Similarly, the substitution of other strong electron-withdrawing groups such as NO₂ and CN at the para-position of the phenyl ring in partially fluorinated tolans showed the prevalence of O–O and C–H···N in-

Table 2. Selected bond lengths (Å) and angles (°) of 6a and 6g, and π–π stacking distances (Å).

|                  | 6a                  | 6g                  |
|------------------|---------------------|---------------------|
| C=C triple bond  | 1.196(6)            | 1.195(2)            |
| C_Crystal-Crystal| 1.4350(7)           | 1.437(2)            |
| C_Crystal-Crystal| 1.4265(7)           | 1.427(2)            |
| F Aryl(FF)- Aryl(FF) | 2.959(3)            | 3.04(5)             |
| Centroid-centroid distance | 3.586(3) | 3.705(3) |
| Interplanar separation | 3.361(3)/3.424(3) | 3.349(2)/3.415(2) |
| Offset shift[a]  | 1.248(3)/1.064(2)   | 1.586(3)/1.439(3)   |
|                  | 1.455(2)/1.132(2)   | 1.975(3)/1.868(3)   |

[a] The offset shift, also called inter-centroid shift, is the distance within a plane of an aryl ring between the centroid of the respective aryl ring and the intersection point with the normal to the plane through the centroid of the other aryl ring.
teractions and the absence of arene-perfluoroarene interactions in their crystal structures.[28b]

Conclusion

In conclusion, we have developed a copper-catalyzed method for the direct alkynylation of electron-deficient polyfluorophenylboronate esters with terminal alkynes. This reaction features broad functional group tolerance, mild reaction conditions, and simple operation. From a synthetic point of view, the present reaction has the potential to be applied widely in organic synthesis because many shelf-stable aryl and alkyl boronate esters are commercially available. The partially fluorinated tolans also display interesting fluoroarene-arene π-stacking interactions in the solid-state as demonstrated by single-crystal X-ray diffraction in two cases.

Crystallographic details

Crystal data collection and processing parameters are given in the Supporting Information. Deposition Numbers 2000968 (6a), and 2000970 (6g) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

Acknowledgements

Z.L. is grateful to the China Scholarship Council for providing a PhD scholarship. Y.P.B. thanks the Indonesia Endowment Fund for Education (LPDP) for a PhD scholarship. T.B.M. and U.R. thank the Julius-Maximilians-Universität Würzburg and the Deutsche Forschungsgemeinschaft (DFG) for support. S.A.W. acknowledges support from the Natural Science and Engineering Research Council of Canada. We thank AllyChem Co. Ltd. for a generous gift of B\textsubscript{2}pin\textsubscript{2}. Open access funding enabled and organized by Projekt DEAL.

Conflict of interest

The authors declare no conflict of interest.

Keywords: boronate esters · coupling reactions · fluorine · fluoroarenes · Sonogashira reaction

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Manuscript received: June 15, 2020
Accepted manuscript online: July 22, 2020
Version of record online: November 9, 2020