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[Cu(NHC)]-Catalyzed C–H Allylation and Alkenylation of both Electron-Deficient and Electron-Rich (Hetero)arenes with Allyl Halides

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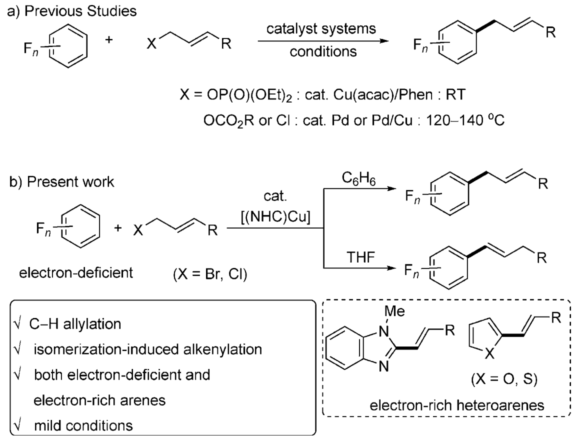
Abstract: *New reactivity of a [Cu(NHC)] (NHC = N-heterocyclic carbene) catalyst is disclosed for the efficient C–H allylation of polyfluoroarenes using allyl halides in benzene at room temperature. The same catalyst system also promotes an isomerization-induced alkenylation of initially the generated allyl arenes when the reaction is run in tetrahydrofuran. Significantly, not only electron-deficient but also electron-rich (hetero)arenes undergo this double-bond migration process, thus leading to alkenylated products. The present system features mild reaction conditions, broad scope with respect to the arene substrates and allyl halide reactants, good functional-group tolerance, and high stereoselectivity.*

The introduction of an allyl or vinyl group into organic molecules is an important step for further transformations in organic synthesis,[1] polymer, and materials chemistry.[2] As a result, the development of selective catalytic systems is highly desirable for the facile construction of the unsaturated synthons. Transition metal catalyzed allylation of aryl electrophiles represents a powerful tool for accessing allyl arenes.[3] In this context, direct C–H allylation of electron-deficient arenes is noteworthy since conventional approaches, such as Friedel–Crafts allylation or arylmetal coupling reactions, are not effectively applicable for these substrates.[3,4] Thus far, only limited examples have been revealed for the direct allylation of electron-deficient arenes (Scheme 1 a).[5] For instance, Miura et al. employed allyl phosphates as the allyl source under the [Cu(acac)$_2$]/Phen catalyst system.[5a] Zhang et al. reported a palladium-catalyzed allylation of polyfluorobenzenes with either allylcarbonates or allylchlorides under rather harsh reaction conditions.[5b,c] Meanwhile, an isomerization-induced alkenylation can be envisaged to be an attractive approach for the transformation of a pre-existing allyl moiety into vinyl groups while leaving the other parts intact.[6]

Considering the fact that polyfluoroarenes represent an important structural motif in materials and medicinal chemistry owing to the unique property of fluorine atom,[7] the development of efficient and selective functionalization of fluoroarenes is highly valuable. In this regard, presented herein is a new protocol for the C–H allylation of fluoroarenes by using a [Cu(NHC)] (NHC = N-heterocyclic carbene) catalyst under mild reaction conditions (Scheme 1 b). Interestingly, an isomerization pathway of the initially formed allyl arenes was subsequently discovered to work efficiently to deliver vinylarene compounds. Moreover, this catalytic system was also successfully applied to the isomerization-induced alkenylation of electron-rich heterocycles such as (benzo)thiophenes and (benzo)furans. To the best of our knowledge, this study represents the first example of direct C–H allylation and alkenylation operating with both electron-deficient and electron-rich (hetero)arenes.



Scheme 1. Direct C–H allylation of polyfluoroarenes and isomerization-induced alkenylation of heteroarenes.

Recently, copper complexes bearing NHCs have been fruitfully utilized in various catalytic reactions.[8] In 2010, Nolan et al. reported the use of [(IPr)Cu(OH)] [IPr = *N,N'*-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene] in the activation of C–H bonds of 1,2,4,5-tetrafluorobenzene in a stoichiometric manner.[9] In line with this work, and given our continuing efforts on NHC chemistry,[10] it was envisaged that [Cu(NHC)] complexes might be potent for the catalytic allylation of polyfluorobenzenes.[11]

We commenced our study by optimizing the allylation of pentafluorobenzene with *trans*-cinnamyl bromide by examining various copper catalyst systems (Scheme 2; see Table S1 in the Supporting Information for details). It was observed that the use of [(I*i*Pr)CuCl] (**3**;[12] I*i*Pr = 1,3-diisopropylimidazol-2-ylidene; 2.0 mol %) in the presence of NaO*t*Bu (1.5 equiv) afforded an allylated product with excellent yield (5 min at 25 °C) when using benzene as the solvent. However, the copper species **1**, bearing IPr, was totally ineffective and the

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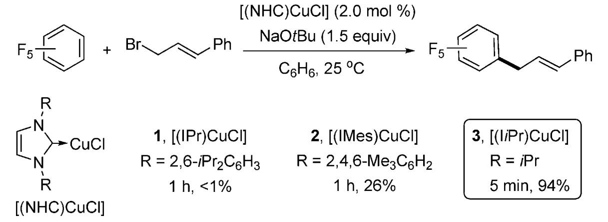


Scheme 2. Catalyst screening for the C–H allylation of pentafluorobenzene.

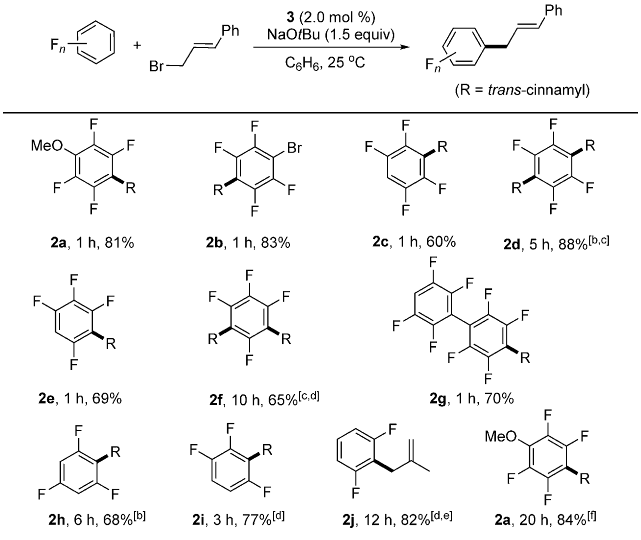
activity of [(IMes)CuCl] (**2**; IMes = *N*,*N*′-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene) was only moderate.

With the optimized reaction conditions in hand, a range of allyl halides were examined in reactions with pentafluorobenzene (see Table S2). It was found that allyl bromide and its alkyl-substituted derivatives reacted smoothly to afford the corresponding allyl(pentafluoro)benzenes in high yields. Significantly, secondary allyl bromides were also facile reactants under the present system and a similar range of allylation efficiency was observed even with allyl chlorides, albeit under slightly more demanding reaction conditions (5.0 mol% of **3**; 20 h; 25 °C).

We next examined the scope with respect to the polyfluoroarenes,[13] in reaction with cinnamyl bromide as a representative reactant (Table 1). Various types of polyfluoroarenes were allylated in good yields without difficulty (**2a**–**j**), and more challenging substrates such as trifluoro- or difluorobenzenes also reacted under the present allylation protocol. Interestingly, when two equivalent C–H bonds are present, mono- and di-allylation could be controlled by changing the stoichiometry of the allylating reagent and base (**2c**–**f**).

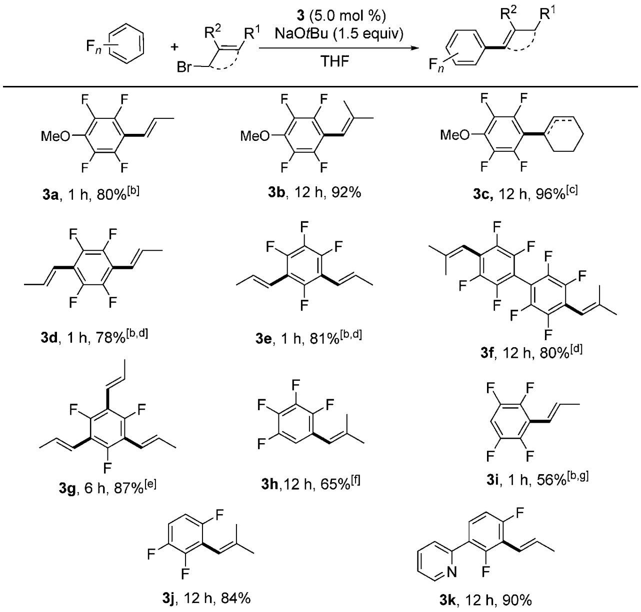
During the course of the allylation study, we observed an intriguing phenomenon of double-bond isomerization of the initially formed allyl arenes when the benzene solvent was replaced by tetrahydrofuran (THF). A model reaction of 2,3,5,6-tetrafluoroanisole with methallyl bromide was monitored by ^{1}H NMR spectroscopy (see Figure S2). It was shown that an alkenylated product was formed gradually over 10 hours in $[D_8]$THF at 60 °C, a product arising from the isomerization of the allylarene. Other solvents such as 1,4-dioxane, *tert*-butanol, and 2,5-(Me)$_2$-THF displayed only moderate efficiency. A *tert*-butoxide base with either a potassium or lithium counter cation did not result in olefin isomerization although the exact reason is not clear at present.

Table 1: Scope of polyfluoroarenes in allylation with cinnamyl bromide.[a]



[a] Reaction conditions: Cinnamyl bromide (1.0 mmol), fluoroarene (1.05 equiv), NaO*t*Bu (1.5 equiv), and **3** (2.0 mol %) in C$_6$H$_6$ (3.0 mL) at 25 °C. Yields are those of the isolated products. [b] **3** (5.0 mol%). [c] Base (2.2 equiv), cinnamyl bromide (2.2 equiv). [d] **3** (10.0 mol %). [e] Methallyl bromide was used. [f] Cinnamyl chloride was used.

Table 2: Scope with respect to the fluoroarenes in the isomerization-induced alkenylation.[a]



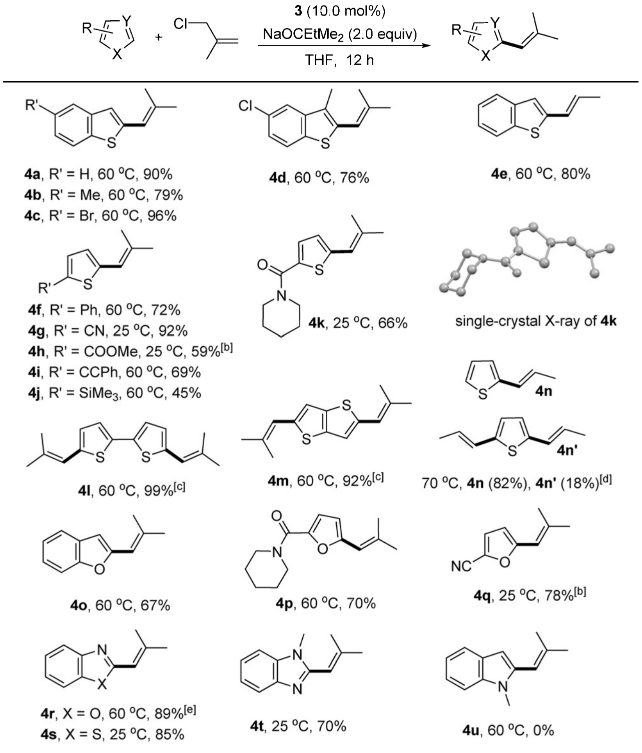
[a] Reaction conditions: allyl bromides (1.0 mmol), arenes (1.05 equiv), NaO*t*Bu (1.5 equiv), and **3** (5.0 mol%) in THF (3.0 mL) at 60 °C. Yields are those of isolated products. [b] **3** (2.0 mol %) at 25 °C. [c] A mixture of allyl and alkenyl isomers (1:1). [d] Allyl bromide (3.0 equiv) and base (3.0 equiv). [e] Allyl bromide (5.0 equiv) and base (6.0 equiv). [f] 1,2,3,4-Tetrafluorobenzene (3.0 equiv). [g] 1,2,4,5-Tetrafluorobenzene (8.0 equiv).

The above isomerization-induced vinylation approach was successfully applied to a wide range of polyfluoroarene substrates in reactions with allyl bromides in good yields (Table 2). It is worth mentioning that the newly isomerized double bonds were exclusively in the *E* conformation. The isomerization efficiency was found to be affected to some extent by the initially introduced allyl groups. For instance, while the double-bond migration was smooth in acyclic allyl arenes, a cyclic olefin was isomerized less efficiently (**3c**). Fluoroarenes bearing multiple reactive C–H bonds were alkenylated in a selective manner by controlling the stoichiometry of the allyl halide. For instance, doubly vinylated polyfluoroarenes were obtained in high yields (**3d**–**f**), and the introduction of three 1-propenyl groups to 1,3,5-trifluorobenzene was also efficient (**3g**). In contrast, selective monovinylation among multiple reactive C–H bonds was readily performed in moderate to good yields by using allyl bromides as the limiting reactant (**3h**–**k**).

Next, we were curious about the applicability of the present system for more challenging electron-rich heteroarenes. Introduction of alkenyl groups onto heteroarenes is synthetically valuable because olefinated heteroarenes are widely utilized in polymer and materials chemistry.[15] For this purpose, palladium catalyst systems were previously developed, including the Fujiwara–Moritani reaction.[16] More recently, rhodium, iridium, and ruthenium catalysts have been examined for the introduction of vinyl groups onto heteroarenes.[17] In this context, the development of efficient and selective catalytic systems based on the first-row transition metals is highly desirable.

Upon the screening of reaction parameters (see Table S8), it was found that benzothiophene reacted smoothly with methallyl chloride in the presence of $NaOCEtMe_2$ to give excellent product yield (92 %) at 60 °C in THF. As presented in Table 3, benzothiophenes substituted with methyl or a more labile bromo group at the 5-position underwent the alkenylation in excellent yields (**4a**–**c**). 5-Chlorobenzo[*b*]thiophene, having a substituent at the 3-position, also underwent the alkenylation efficiently (**4d**). Unsubstituted allyl chloride could be employed without difficulty (**4e**). We were delighted to see that thiophenes reacted to give alkenylated products. For instance, 2-phenylthiophene was alkenylated in high yield (**4f**). Moreover, various functional groups such as cyano, ester, alkynyl, silyl, and amide substituents were all compatible with the present catalytic system (**4g**–**k**).[18] An X-ray crystallographic structure of **4k** was obtained.

Table 3: Scope with respect to the heteroarenes in the C–H alkenylation.[a]



4a, R' = H, 60 °C, 90%
4b, R' = Me, 60 °C, 79%
4c, R' = Br, 60 °C, 96%

4d, 60 °C, 76%

4e, 60 °C, 80%

4f, R' = Ph, 60 °C, 72%
4g, R' = CN, 25 °C, 92%
4h, R' = COOMe, 25 °C, 59%[b]
4i, R' = CCPh, 60 °C, 69%
4j, R' = $SiMe_3$, 60 °C, 45%

4k, 25 °C, 66%

4l, 60 °C, 99%[c]

4m, 60 °C, 92%[c]

70 °C, **4n** (82%), **4n'** (18%)[d]

4o, 60 °C, 67%

4p, 60 °C, 70%

4q, 25 °C, 78%[b]

4r, X = O, 60 °C, 89%[e]
4s, X = S, 25 °C, 85%

4t, 25 °C, 70%

4u, 60 °C, 0%

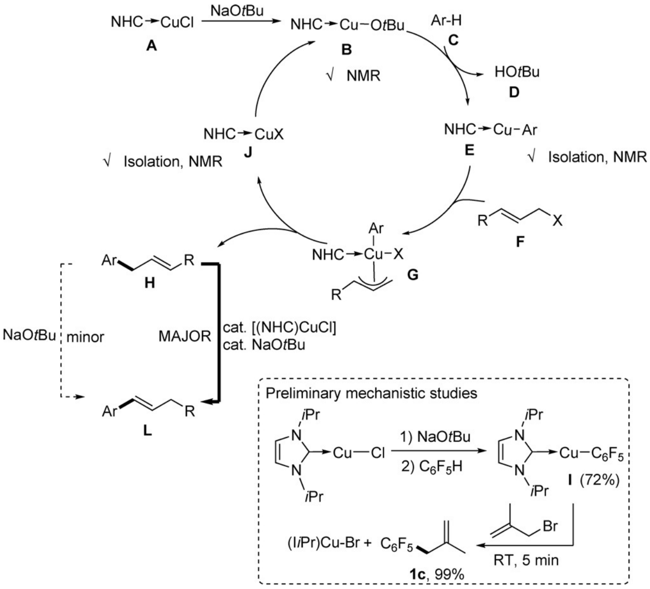
[a] Reaction conditions: heteroarene (0.20 mmol), methallyl chloride (1.5 equiv), base (2.0 equiv) and catalyst **3** (10.0 mol %) in THF (0.5 mL). Yields are those of isolated products. [b] Methallyl chloride (0.20 mmol), heteroarene (2.0 equiv), base (1.2 equiv). [c] Methallyl chloride (5.0 equiv), base (5.0 equiv). [d] GC-MS yield. [e] NaO*t*Bu (1.5 equiv) used as the base.

It is worthwhile noting that whereas thiophene carboxylate ester was previously employed for the ruthenium-catalyzed alkenylation using ester as a directing group,[17c] the current copper catalyst system enabled C5-olefination (**4h**; Table 3). Interestingly, 2,2′-bithiophene underwent the olefination twice at the 5,5′-position in quantitative yield when using excess amounts of both methallyl chloride and $NaOCEtMe_2$ (**4l**). Similarly, alkenylation of thieno[3,2-*b*]thiophene proceeded with excellent efficiency and selectivity (**4m**). Unsubstituted thiophene was also alkenylated without difficulty (**4n** and **4n′**). Furan and benzofuran derivatives were also reacted to afford C2 alkenylated products (**4o**–**q**). Azole heterocycles were observed to undergo olefination in high yields (**4r**–**t**). However, the system was not applicable for an indole derivative, presumably because of its high pK_a value (pK_a = 37.7).[13a]

To shed light on the reaction pathway, a series of mechanistic studies were designed (see the Supporting Information for details). When [(I*i*Pr)CuCl] (**3**) was treated with a stoichiometric amount of NaO*t*Bu and then pentafluorobenzene, a C–H activated aryl copper species, [(I*i*Pr)Cu-C_6F_5] (**I**), was observed.[19] Although an X-ray crystallographic analysis of **I** failed, its structure was confirmed by NMR spectroscopy. The isolated copper complex **I** was readily reacted with methallyl bromide to give [(NHC)Cu-Br] and an allylated product (**1c**) quantitatively, thus strongly suggesting that **I** is involved in the catalytic cycle. In addition, the observation that the stereochemistry of the double bond of allyl bromide was transferred to the allylated products led us to postulate that the double-bond insertion into **I** most likely proceeds via a tightly bound transition state.[5a,20]

In addition, kinetic isotope effects (KIE) were not measured ($k_H/k_D = 1.0$) and imply that the C–H cleavage of polyfluoroarenes may not be connected to the turnover-limiting stage. When the allylated arene compound **2k** was isomerized, catalytic amounts of both copper and NaO*t*Bu were essential to bring about the olefin isomerization, thus leading to the vinyl arene compound **3b**. For the alkenylation of electron-rich heteroarenes, a base-promoted electron transfer pathway can also be considered,[21] but it turned out to be unlikely since the addition of TEMPO or 1,1-diphenylethene did not affect the reaction progress.

Based on the above results and literature precedents,[5a,9,20] a proposed pathway of the present [Cu(NHC)]-catalyzed allylation is shown in Scheme 3. A ligand exchange of [(NHC)Cu-Cl] (**A**) with the base (NaO*t*Bu) leads to [(NHC)Cu-O*t*Bu] (**B**), which is believed to react with (hetero)arenes to form a copper-aryl intermediate (**E**). An oxidative insertion of allyl halides into **E** is then assumed to occur, thus giving rise to an π-allyl Cu^{III} complex (**G**), presumably through a tightly bound transition state, thus

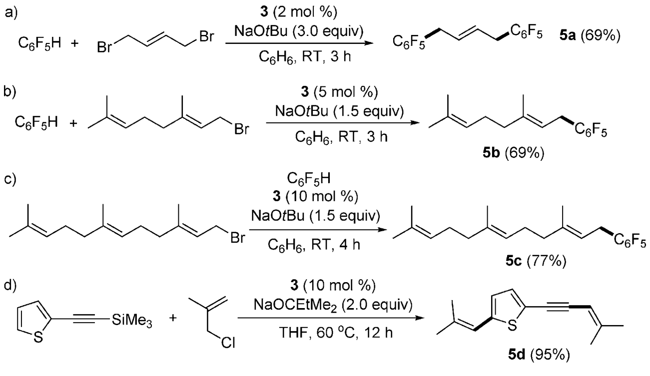


Scheme 3. Possible mechanism for the reactions.

enabling the stereochemistry of allyl halides being transferred to allyl arene products.[20] As the final stage, a reductive elimination of the **G** affords the allylated product **H** with the regeneration of catalyst [(NHC)Cu-X].

Although more comprehensive studies are required to delineate the isomerization of the initially generated allyl arenes to a vinyl group in THF, we assume that it is initiated mainly by the copper-mediated allyl C–H bond activation of allyl arenes to form a π-allyl/Cu^{III} species, which undergoes protonolysis by *t*BuOH (major pathway). This proposal is based on the fact that allyl arenes bear an allyl C–H bond with pK_a values lower than 34[13c] and is therefore readily deprotonated by [(NHC)Cu-O*t*Bu]. However, this isomerization was observed to take place also by NaO*t*Bu alone, albeit with much lower efficiency (minor pathway).

Synthetic utility of the present protocol was demonstrated by examining several interesting reactants. Double arylation of *trans*-1,4-dibromo-2-butene occurred smoothly and selectively (Scheme 4a). Given that geranyl and farnesyl groups are valuable synthons in organic synthesis, their facile transformations are highly desirable.[22] In our case, geranyl and farnesyl bromide were readily reacted to afford the corresponding products stereoselectively in high yields (Scheme 4b and c). Despite the fact that highly conjugated thiophene derivatives have been widely employed in synthetic and materials chemistry,[23] preparative routes to these motifs are mainly limited to tedious stepwise approaches. In this context, the direct vinylation of an alkyne-substituted thiophene is especially noteworthy (**5d**), in which the trimethylsilyl moiety also reacts with the copper species presumably to form a copper acetylene species,[24] which then undergoes allylation followed by double-bond isomerization.



Scheme 4. Synthetic applications.

In summary, we have developed the [Cu(NHC)]-catalyzed C–H allylation of polyfluoroarenes by using allyl halides as the reactants. The same catalyst system was found to also be effective for the double-bond migration of the initially generated allyl arenes by changing the solvent, thus leading to vinyl arene products. This system was successfully utilized for the alkenylation of various types of electron-rich heterocycles such as (benzo)thiophenes and (benzo)furans. This procedure features high efficiency, mild reaction conditions, controllable selectivity, broad scope, and high functional-group tolerance, and is thus anticipated to find utility in synthetic, polymer, and materials chemistry.

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Keywords: alkenes · allylic compounds · copper · isomerization · N-heterocyclic carbenes

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Angew. Chem. **2016**, *128*, 1908–1912

[1] a) K. Mackenzie in *The Chemistry of Alkenes*; (Ed.: S. Patai), Wiley, New York, **1964**; b) R. C. Larock in *Comprehensive Organic Transformations: A Guide to Functional Group Preparations*, 2nd ed., VCH, New York, **1999**.

[2] a) H. R. Kricheldorf, O. Nuyken, G. Swift, in *Handbook of Polymer Synthesis*, 2nd ed., Marcel Dekker, New York, **2005**; b) G. Natta, A. Zambelli, I. Pasquon, F. Ciampelli, *Makromol. Chem.* **1964**, *79*, 161; c) P. Longo, S. Pragliola, G. Milano, G. Guerra, *J. Am. Chem. Soc.* **2003**, *125*, 4799.

[3] a) F. C. Pigge, *Synthesis* **2010**, 1745; b) D. Bouyssi, V. Gerusz, G. Balme, *Eur. J. Org. Chem.* **2002**, 2445; c) R. Singh, M. S. Viciu, N. Kramareva, O. Navarro, S. P. Nolan, *Org. Lett.* **2005**, *7*, 1829; d) H. Ohmiya, Y. Makida, T. Tanaka, M. Sawamura, *J. Am. Chem. Soc.* **2008**, *130*, 17276; e) H. Ohmiya, Y. Makida, D. Li, M. Tanabe, M. Sawamura, *J. Am. Chem. Soc.* **2010**, *132*, 879.

[4] a) M. Kodomari, S. Nawa, T. Miyoshi, *J. Chem. Soc. Chem. Commun.* **1995**, 1895; b) A. Hasegawa, K. Ishihara, H. Yamamoto, *Angew. Chem. Int. Ed.* **2003**, *42*, 5731; *Angew. Chem.* **2003**, *115*, 5909; c) R. Hayashi, G. R. Cook, *Org. Lett.* **2007**, *9*, 1311.

[5] a) T. Yao, K. Hirano, T. Satoh, M. Miura, *Angew. Chem. Int. Ed.* **2011**, *50*, 2990; *Angew. Chem.* **2011**, *123*, 3046; b) S. Fan, F. Chen, X. Zhang, *Angew. Chem. Int. Ed.* **2011**, *50*, 5918; *Angew. Chem.* **2011**, *123*, 6040; c) Y.-B. Yu, S. Fan, X. Zhang, *Chem. Eur. J.* **2012**, *18*, 14643; d) H. Jiang, W. Yang, H. Chen, J. Li, W. Wu, *Chem. Commun.* **2014**, *50*, 7202; for the Cu-catalyzed allylation

of electron-deficient azoles, see: e) Y. Makida, H. Ohmiya, M. Sawamura, *Angew. Chem. Int. Ed.* **2012**, *51*, 4122; *Angew. Chem.* **2012**, *124*, 4198.

[6] a) G. Erdogan, D. B. Grotjahn, *J. Am. Chem. Soc.* **2009**, *131*, 10354; b) T. J. Donohoe, T. J. C. O'Riordan, C. P. Rosa, *Angew. Chem. Int. Ed.* **2009**, *48*, 1014; *Angew. Chem.* **2009**, *121*, 1032; c) D. Gauthier, A. T. Lindhardt, E. P. K. Olsen, J. Overgaard, T. Skrydstrup, *J. Am. Chem. Soc.* **2010**, *132*, 7998; d) M. Mayer, A. Welther, A. Jacobi von Wangelin, *ChemCatChem* **2011**, *3*, 1567; e) A. Schmidt, A. R. Nödling, G. Hilt, *Angew. Chem. Int. Ed.* **2015**, *54*, 801; *Angew. Chem.* **2015**, *127*, 814.

[7] a) E. A. Meyer, R. K. Castellano, F. Diederich, *Angew. Chem. Int. Ed.* **2003**, *42*, 1210; *Angew. Chem.* **2003**, *115*, 1244; b) K. Müller, C. Faeh, F. Diederich, *Science* **2007**, *317*, 1881; c) A. R. Murphy, J. M. J. Fréchet, *Chem. Rev.* **2007**, *107*, 1066; d) S. Xu, G. Wu, F. Ye, X. Wang, H. Li, X. Zhao, Y. Zhang, J. Wang, *Angew. Chem. Int. Ed.* **2015**, *54*, 4669; *Angew. Chem.* **2015**, *127*, 4752.

[8] a) M. N. Hopkinson, C. Richter, M. Schedler, F. Glorius, *Nature* **2014**, *510*, 485; b) S. Gaillard, C. S. J. Cazin, S. P. Nolan, *Acc. Chem. Res.* **2012**, *45*, 778; c) J. D. Egbert, C. S. J. Cazin, S. P. Nolan, *Catal. Sci. Technol.* **2013**, *3*, 912; d) F. Lazreg, C. S. J. Cazin, in *N-Heterocyclic Carbenes—Effective Tools for Organometallic Synthesis* (Ed.: S. P. Nolan), Wiley-VCH, Weinheim, **2014**, 199–242; e) F. Lazreg, F. Nahra, C. S. J. Cazin, *Coord. Chem. Rev.* **2015**, *293*, 48.

[9] G. C. Fortman, A. M. Z. Slawin, S. P. Nolan, *Organometallics* **2010**, *29*, 3966.

[10] a) E. J. Park, S. H. Kim, S. Chang, *J. Am. Chem. Soc.* **2008**, *130*, 17268; b) M. Kim, J. Kwak, S. Chang, *Angew. Chem. Int. Ed.* **2009**, *48*, 8935; *Angew. Chem.* **2009**, *121*, 9097; c) M. Kim, J. Lee, H.-Y. Lee, S. Chang, *Adv. Synth. Catal.* **2009**, *351*, 1807; d) M. Kim, S. Chang, *Org. Lett.* **2010**, *12*, 1640; e) J. Kwak, M. Kim, S. Chang, *J. Am. Chem. Soc.* **2011**, *133*, 3780; f) H. J. Kim, M. Kim, S. Chang, *Org. Lett.* **2011**, *13*, 2368; g) J. Kwak, Y. Ohk, Y. Jung, S. Chang, *J. Am. Chem. Soc.* **2012**, *134*, 17778; h) B. Li, S. Lee, K. Shin, S. Chang, *Org. Lett.* **2014**, *16*, 2010.

[11] For selected examples of (NHC)Cu complexes employed in the functionalization of polyfluorobenzenes, see: a) I. I. F. Boogaerts, G. C. Fortman, M. R. L. Furst, C. S. J. Cazin, S. P. Nolan, *Angew. Chem. Int. Ed.* **2010**, *49*, 8674; *Angew. Chem.* **2010**, *122*, 8856; b) M. Lesieur, F. Lazreg, C. S. J. Cazin, *Chem. Commun.* **2014**, *50*, 8927.

[12] The structure of complex **3** was unambiguously confirmed by X-ray crystallographic analysis which shows that the $\mathrm{Cu{-}C_{NHC}}$ bond length is 1.8819(13) Å (see the Supporting Information for details).

[13] For pK_a values of polyfluoroarenes and heteroarenes, see: a) K. Shen, Y. Fu, J.-N. Li, L. Liu, Q.-X. Guo, *Tetrahedron* **2007**, *63*, 1568; b) A. E. Wendlandt, A. M. Suess, S. S. Stahl, *Angew. Chem. Int. Ed.* **2011**, *50*, 11062; *Angew. Chem.* **2011**, *123*, 11256; c) K. Bowden, R. S. Cook, *J. Chem. Soc. Perkin Trans. 2* **1972**, 1407; and also, in a preliminary study, the allylation reactivity was observed to vary dramatically by the acidity of substrates' C–H bonds (see Figure S1 for details).

[14] One example of the Cu-catalyzed vinylation of polyfluoroarenes with vinyl bromide was shown in the following report: H.-Q. Do, O. Daugulis, *J. Am. Chem. Soc.* **2008**, *130*, 1128.

[15] a) D. J. Schipper, K. Fagnou, *Chem. Mater.* **2011**, *23*, 1594; b) Y. Liu, X. Wan, F. Wang, J. Zhou, G. Long, J. Tian, Y. Chen, *Adv. Mater.* **2011**, *23*, 5387; c) G. He, L. Kang, W. T. Delgado, O. Shynkaruk, M. J. Ferguson, R. McDonald, E. Rivard, *J. Am. Chem. Soc.* **2013**, *135*, 5360.

[16] a) R. Asano, I. Moritani, Y. Fujiwara, S. Teranishi, *Bull. Chem. Soc. Jpn.* **1973**, *46*, 663; b) Y. Fujiwara, O. Maruyama, M. Yoshidomi, H. Taniguchi, *J. Org. Chem.* **1981**, *46*, 851; c) N. P. Grimster, C. Gauntlett, C. R. A. Godfrey, M. J. Gaunt, *Angew. Chem. Int. Ed.* **2005**, *44*, 3125; *Angew. Chem.* **2005**, *117*, 3185; d) E. M. Beck, N. P. Grimster, R. Hatley, M. J. Gaunt, *J. Am. Chem. Soc.* **2006**, *128*, 2528; e) N. Gigant, J.-E. Bäckvall, *Org. Lett.* **2014**, *16*, 4432.

[17] a) S. Mochida, K. Hirano, T. Satoh, M. Miura, *J. Org. Chem.* **2011**, *76*, 3024; b) S. Park, J. Y. Kim, S. Chang, *Org. Lett.* **2011**, *13*, 2372; c) K. Padala, S. Pimparkar, P. Madasamy, M. Jeganmohan, *Chem. Commun.* **2012**, *48*, 7140; d) H. Wang, N. Schröder, F. Glorius, *Angew. Chem. Int. Ed.* **2013**, *52*, 5386; *Angew. Chem.* **2013**, *125*, 5495; e) C. S. Sevov, J. F. Hartwig, *J. Am. Chem. Soc.* **2014**, *136*, 10625.

[18] Functional-group tolerance was conveniently tested in the allylation of pentafluorobenzene using the Glorius' method to reveal that the allylation yield was not affected by some additives containing cyano, ester, or chloride groups and that the additives were not decomposed during the course of the allylation reaction (see the Supporting Information for details): K. D. Collins, F. Glorius, *Nat. Chem.* **2013**, *5*, 597.

[19] Nolan and co-workers reported that $C_6F_4H_2$ is activated by a copper complex [(IPr)Cu(OH)] to form [(IPr)Cu-C_6F_4H], see: Ref. [9]. In our case, it is assumed that C_6F_5H reacts with in situ generated [(I*i*Pr)Cu-O*t*Bu], thus leading to **I**.

[20] In analogy to Miura's system, a process of the σ–π conversion of the σ-allyl copper species is probably much faster than the related *E*/*Z* isomerization which will lead to erosion of the stereochemistry. π-Allyl copper(III) intermediates are known to give mainly S_N2 products while the corresponding σ-allyl copper(III) intermediates were shown to afford S_N2' products: a) E. R. Bartholomew, S. H. Bertz, S. Cope, M. Murphy, C. A. Ogle, *J. Am. Chem. Soc.* **2008**, *130*, 11244; b) Rotation of σ-allyl isomers is known to be much slower than the formation of σ–π allyl copper(III) intermediates: Ref. [5a].

[21] For the base-promoted C–H activation of arenes by an electron-transfer pathway, see: a) C.-L. Sun, H. Li, D.-G. Yu, M. Yu, X. Zhou, X.-Y. Lu, K. Huang, S.-F. Zheng, B.-J. Li, Z.-J. Shi, *Nat. Chem.* **2010**, *2*, 1044; b) A. Studer, D. P. Curran, *Angew. Chem. Int. Ed.* **2011**, *50*, 5018; *Angew. Chem.* **2011**, *123*, 5122.

[22] a) J. Llaveria, Á. Beltrán, W. M. C. Sameera, A. Locati, M. M. Díaz-Requejo, M. I. Matheu, S. Castillón, F. Maseras, P. J. Pérez, *J. Am. Chem. Soc.* **2014**, *136*, 5342; b) Y. Zou, Z. Zhan, D. Li, M. Tang, R. A. Cacho, K. Watanabe, Y. Tang, *J. Am. Chem. Soc.* **2015**, *137*, 4980.

[23] a) V. Gevorgyan, K. Tando, N. Uchiyama, Y. Yamamoto, *J. Org. Chem.* **1998**, *63*, 7022; b) H.-Y. Jang, R. R. Huddleston, M. J. Krische, *J. Am. Chem. Soc.* **2004**, *126*, 4664.

[24] A similar pathway was previously proposed: H. Ito, K. Arimoto, H. Sensul, A. Hosomi, *Tetrahedron Lett.* **1997**, *38*, 3977.

[25] CCDC 1434042 (**3**) and 1434043 (**4k**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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