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**Title:** Fe-Catalyzed Coupling of Propargyl Bromides and Alkyl Grignard Reagents

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# Fe-Catalyzed Coupling of Propargyl Bromides and Alkyl Grignard Reagents

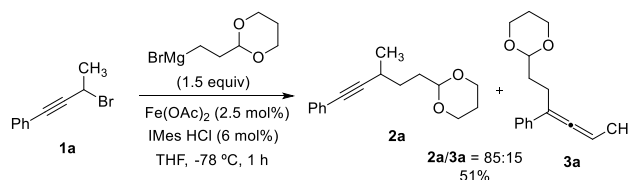
Pablo Domingo-Legarda, Rita Soler-Yanes, M. Teresa Quirós, Elena Buñuel, and Diego J. Cárdenas\*<sup>[a]</sup>

**Abstract:** We describe the Fe-catalyzed Kumada-type cross-coupling reaction of propargyl halides with alkylmagnesium reagents. The reaction is fast, takes place in smooth conditions, tolerates several functional groups that would be able to react with the Grignard reagent, and may afford either allene or propargyl coupling derivatives. Factors involved in the observed regioselectivity have been studied.

The undoubted importance of cross-coupling reactions has prompted new developments during the last years. Advances are related to the replacement of the classical Pd catalysts by inexpensive and more convenient first row transition metal derivatives, and to the use of previously avoided basic nucleophiles such as Grignard reagents. Traditionally, the success of cross-couplings as synthetic tools has relied on the use of reagents with low basicity and nucleophilicity, such as organozinc, boron, tin or silicon compounds. Nevertheless, highly active catalytic systems recently developed allow the chemo-selective formation of carbon-carbon bonds by cross-coupling even when formerly incompatible functional groups are present. Since the preparation of less reactive nucleophiles such as organozinc, organotin and organoboron compounds usually involves Grignard reagents, the use of the latter derivatives as nucleophiles simplifies the synthetic route. A major challenge is to find conditions for the catalyzed cross-coupling of functionalized electrophiles containing reactive groups. Ni-catalysis has demonstrated its utility in the field of alkyl-alkyl cross-coupling reactions through the involvement of highly active catalytic systems for which coupling is much faster than other feasible and usual reactions.<sup>[1]</sup> On the other hand, allenes can be prepared by metal-catalyzed reactions involving propargyl electrophiles.<sup>[2]</sup> This approach constitutes a convenient method since formation of the allene occurs along with C-C bond formation. Pd,<sup>[3]</sup> Cu,<sup>[4]</sup> Rh,<sup>[5]</sup> Fe,<sup>[6]</sup> and Ni<sup>[7]</sup> derivatives have been used as catalysts in these reactions for the activation of propargyl halides, esters, carbonates and phosphonates. We recently reported the formation of allenes by Ni-catalyzed coupling of propargyl bromides and alkylzinc reagents.<sup>[8]</sup> This interesting reaction shows complementary regioselectivity with the previously reported reaction of propargyl halides with R<sub>2</sub>Zn or RZnX reagents to afford the corresponding propargyl coupled

compounds.<sup>[9]</sup> Preparation of chiral allenes has been achieved by both transfer of stereochemical information from optically pure propargyl derivatives, or by using chiral ligands.<sup>[10]</sup> During the last years, we have been working on the development of novel cross-coupling reactions involving first-row transition metals, which are more convenient for economic and environmental issues. In this respect, in addition to the already mentioned preparation of allenes from propargyl bromides,<sup>[8]</sup> we have reported alkyl-alkyl,<sup>[11]</sup> and alkyl-aryl<sup>[12]</sup> Ni-catalyzed cross-coupling reactions of alkyl electrophiles; as well as the first general Fe-catalyzed Kumada-type alkyl-alkyl coupling.<sup>[13]</sup> Fe-catalyzed cross-coupling reactions are well-established, especially those involving aryl electrophiles.<sup>[14]</sup> Nevertheless, very few examples of Fe-catalyzed alkyl-alkyl cross-couplings have been reported to date.<sup>[13,15]</sup> In addition, the reaction pathways are not fully understood in spite of a number of mechanistic studies.<sup>[16]</sup> In fact, there is a whole family of different Fe-catalyzed cross-coupling reactions. Electrophiles with different kinds of carbon atoms and leaving groups, nucleophiles with different metals, as well as different ligands and catalytic systems can give the desired reactions. Thus, Fe(II), Fe(I), Fe(0) complexes and even lower oxidation states have been proposed as the active species. Regarding the activation of the electrophile, it has been demonstrated that reaction of alkyl halides may take place through homolytic carbon-halogen cleavage.

Fe catalysis involving propargyl electrophiles has been far less explored. In fact they have been restricted to epoxides and carbonates, and previously described reactions afford the formation of allenes.<sup>[6]</sup> In this work we report the formation of either allenes or propargyl derivatives by Fe-catalyzed cross-coupling of propargyl halides and alkyl-Grignard reagents.



**Scheme 1.** Model Fe-catalyzed reaction of propargyl bromide with alkyl Grignard.

We started searching for reaction conditions with model propargyl bromide **1a** and (1,3-dioxan-2-ylethyl)magnesium bromide. The best yield was obtained using 1.5 equiv of Grignard reagent, 2.5 mol% Fe(OAc)<sub>2</sub> as catalyst, 6 mol% of IMes as ligand, in THF at -78 °C for 1 hour (for the optimization process see Supporting Information). Under these conditions, a mixture of propargyl (**2a**) and allene (**3a**) regioisomers were

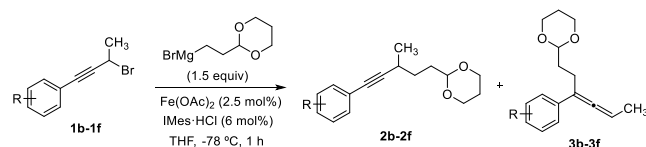
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obtained in 85:15 ratio (51% yield, Scheme 1).

In order to investigate the reaction scope, different aryl substituted propargylic bromides were subjected to the reaction conditions (Table 1).

**Table 1.** Scope and regioselectivity for secondary propargyl derivatives

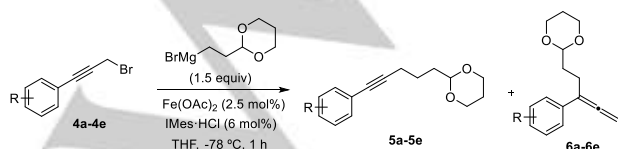


Entry	R	2:3 ratio	Yield (%)
1	<b>1b</b> , 3-OMe	71:29	31
2	<b>1c</b> , 4-CN	45:55	39
3	<b>1d</b> , 4-CO <sub>2</sub> Me	31:69	37
4	<b>1e</b> , 4-Me	>98:<2	41
5	<b>1f</b> , 2-Naphthyl	-	-

We have observed that the reactivity depends on the electron richness of the aromatic ring. When electron deficient *m*-MeO substituted substrate **1b** was used, a decrease of the regioselectivity to 71:29 (entry 1) was observed. This decrease is even more pronounced in the case of substrates **1c** and **1d**, with electron-withdrawing substituents (CN and CO<sub>2</sub>Me, respectively) in *para* position. In these cases, regioselectivity was completely lost (entries 2 and 3). Nevertheless, in the case of the reaction with the *para* methyl substituted substrate **1e**, the exclusive formation of the propargyl derivative took place, although in moderate yield (entry 4). The reaction of 2-naphthyl derivative **1f** gave a complex mixture of products that were not identified (entry 5).

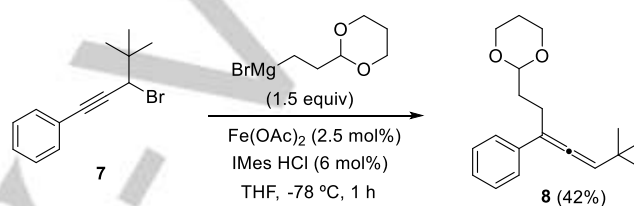
In contrast with the above-mentioned results, the use of primary propargylic substrates **4** led to better yields and the regioselective formation of the propargyl coupling products, regardless of the electronic nature of the benzene ring (Table 2). Thus, substrate **4a** with *m*-MeO substitution in the aromatic ring, afforded a 93:7 mixture in 51% yield (entry 1). The *p*-CN derivative **4b** provided a mixture of regioisomers 92:8 in 66% yield (entry 2). The regioselectivity was complete for the reaction of the *p*-Me substituted compound **4c** (entry 3). *p*-MeO derivative **4d** provided a 96:4 mixture in 46% yield (entry 4). 2-Naphthyl derivative **4e** afforded good regioselectivity although in modest yield (93:7 ratio, 38% yield, entry 5).

**Table 2.** Scope and regioselectivity for primary propargyl derivatives



Entry	R	5:6 ratio	Yield (%)
1	<b>4a</b> , 3-OMe	93:7	51
2	<b>4b</b> , 4-CO <sub>2</sub> Me	92:8	66
3	<b>4c</b> , 4-Me	>98:2	48
4	<b>4d</b> , 4-OMe	96:4	46
5	<b>4e</b> , 2-Naphthyl	93:7	38

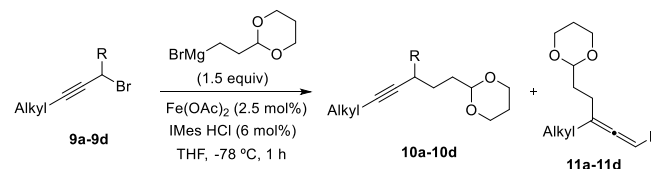
Large substituents on the propargylic position tend to favour formation of the allene coupling product by formation of the new C-C bond at the distal carbon. Thus, compound **7**, with a *t*-Bu group afforded allene **8** exclusively (Scheme 2).



**Scheme 2.** Reaction of *t*-butyl substituted propargyl bromide is regioselective.

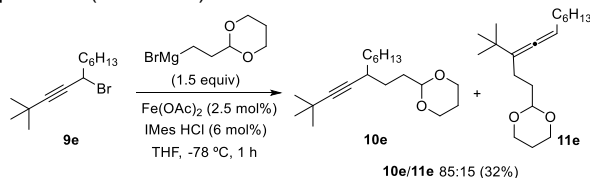
On the other hand, the electronic nature of the substituent on the alkyne has also a strong influence on the regioselectivity. Thus, we observed that the regioselectivity changed completely when using alkyl-substituted alkynes as the reaction substrates, obtaining only the allenic products from compounds **9a** and **9b** (Table 3, entries 1 and 2). When substrates with a cyclohexyl substituent were used as starting materials (**9c** and **9d**), mixtures of the two regioisomers were observed, being the propargyl coupling products the major ones (entries 3 and 4). These results indicate that the steric hindrance on the other side of the triple bond also influences the regioselectivity. We can conclude that both electronic and steric factors control the reaction outcome.

**Table 3.** Scope and regioselectivity for alkyl-substituted alkynes.



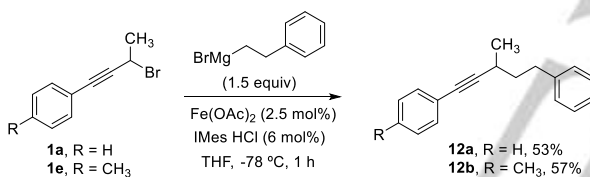
Entry	Compound	Alkyl	R	10:11 ratio	Yield (%)
1	<b>9a</b>	<i>n</i> -octyl	H	<2:>98	51
2	<b>9b</b>	<i>n</i> -octyl	CH <sub>3</sub>	<2:>98	66
3	<b>9c</b>	cyclohexyl	H	75:25	45
4	<b>9d</b>	cyclohexyl	CH <sub>3</sub>	67:33	38

With the idea of further investigating the dependence of the regioselectivity on steric hindrance; we decided to perform the reaction with substrate **9e**, which has a *tert*-butyl substituent directly bonded to the triple bond. Formation of the propargylic coupling product was mostly observed even for a hexyl substituent on the propargyl carbon, which is consistent with our hypothesis (Scheme 3).



**Scheme 3.** Steric hindrance on the alkyne favours the formation of the propargyl coupling derivative.

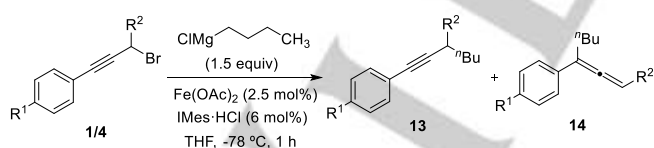
Interestingly, the use of a different Grignard reagent, lacking O atoms able to coordinate the metal, gave good results.<sup>[15a]</sup> Thus, the reaction of substrates **1a** and **1e**, led to the exclusive formation of propargyl coupling products. In contrast, our previously reported Fe-catalyzed Kumada alkyl-alkyl coupling gave no positive results for this kind of alkyl nucleophiles<sup>[13]</sup> (Scheme 4).



**Scheme 4.** Reaction with alkyl-Mg reagent without coordinating atoms affords the expected propargyl coupling compounds.

In contrast, the regioselectivity is lower when using *n*-BuMgCl, especially for the secondary bromides (Table 4).

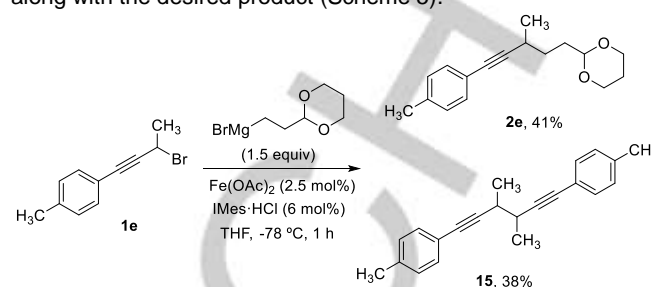
**Table 4.** Reactions with *n*-butylmagnesium chloride.



Entry	R <sup>1</sup>	R <sup>2</sup>	13:14 ratio	Yield (%)
1	<b>1d</b> , CO <sub>2</sub> Me	CH <sub>3</sub>	31:68	83
2	<b>1e</b> , CH <sub>3</sub>	CH <sub>3</sub>	37:63	68
3	<b>4f</b> , H	H	95:5	43

The reason for the moderate yields observed in some of the cases is the formation of homocoupling compounds from the

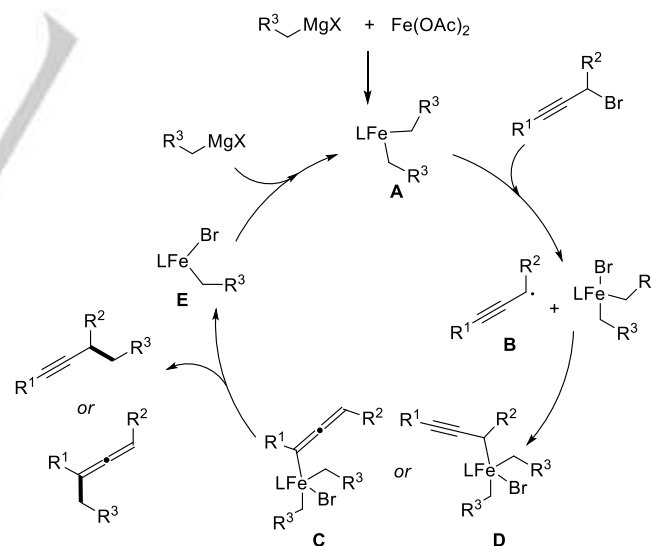
electrophile. The reaction of substrate **1e** under the optimized reaction conditions allowed us to isolate the homocoupling compound derived from the propargyl bromide (**15**) in 38% yield, along with the desired product (Scheme 5).



**Scheme 5.** Isolation of homocoupling compound.

Formation of the compound resulting from the homocoupling of the propargyl bromide suggests the intermediacy of propargyl radicals. To get some more insight in the formation of these byproducts, we performed the reaction with a substoichiometric amount of Grignard reagent (30 mol%, just to activate the catalyst, as previously determined).<sup>[13]</sup> The starting material was recovered unaltered, what suggests that the nucleophile is necessary for the side reaction to occur.

Although more studies would be necessary in order to propose a detailed mechanism, a recent work by Neidig,<sup>[15a]</sup> on our Kumada-type Fe-catalyzed alkyl-alkyl coupling reaction,<sup>[13]</sup> may help us to outline a simplified preliminary proposal (Scheme 6).<sup>[15a]</sup>



**Scheme 6.** Simplified mechanistic proposal for the cross-coupling reaction.

The alkyl-Mg reagent has been shown to react with IMes-Fe complex in a double transmetalation process to give a IMes-Fe(II)-dialkyl derivative **A**. This complex then activates the propargyl bromide, probably through homolytic C-Br bond cleavage.<sup>[13,15h]</sup> The resulting propargyl radical **B** would explain

the formation of the homocoupling compound. Depending on the substituents, the propargyl radical could coordinate to the metal complex to give the allene- (C) or the propargyl-Fe (D) complexes, which would afford the final product through C-C reductive elimination. Subsequent transmetalation involving complex E would regenerate the active species. Participation of monoalkyl-Fe complexes as productive intermediates cannot be discarded according to the previous study.<sup>[15a]</sup> We cannot completely rule out a mechanism involving activation of the bromide by a non-radical mechanism. Kambe has recently reported an Fe-catalyzed alkyl cross-coupling that seems to follow this alternative pathway.<sup>[15a]</sup> Moreover, reduction of Fe(II) salts by the Grignard reagent cannot be excluded, and the actual catalytically active species, and consequently the rest of the intermediate complexes, could have different oxidation states.<sup>[16,17]</sup>

In conclusion, we have developed a Fe-catalyzed cross-coupling reaction of propargyl bromides that affords either propargyl or allene coupling compounds. The reaction is fast enough to tolerate the presence of nitrile and ester groups, and shows a high regioselectivity in many cases. The formation of the possible regioisomers depends on both the kind of substituents on the triple bond, and the steric hindrance on both the alkyne and the propargylic carbon. The reaction seems to involve radical species. Further studies are necessary to ascertain the intimate details of the mechanism.

## Experimental Section

General procedure for the cross-coupling reaction:

The active catalytic species is generated first: Fe(OAc)<sub>2</sub> (0.9 mg, 0.005 mmol, 2.5 mol%) and 1,3-dimesityl-1H-imidazol-3-ium chloride (4.1 mg, 0.012 mmol, 6 mol%) were placed in Schlenk flask and dried under vacuum. Then dry THF (1 mL, 0.2 M) was added and the mixture was heated at 50-60 °C under Ar. A 0.5 M solution of alkylmagnesium bromide (0.12 mL, 0.06 mmol, 30 mol%) was slowly added and the reaction mixture was stirred at 50-60 °C for 20 min. After cooling at -78 °C, the corresponding propargyl bromide (0.2 mmol) was incorporated, followed by the dropwise addition of 0.5 M solution of alkylmagnesium bromide (0.3 mmol, 1.5 equiv). The reaction was stirred and monitored by TLC until completion. After reaction was completed, saturated aqueous NH<sub>4</sub>Cl solution was added (2 mL). The aqueous phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 5 mL) and the combined organic phases were dried over MgSO<sub>4</sub>. The solvent was evaporated under vacuum and the product was purified by column chromatography in silica gel using mixtures of cyclohexane and EtOAc as eluent.

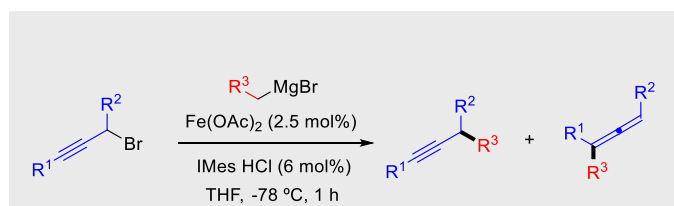
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**Keywords:** C-C coupling • iron • Grignard reactions • radical reactions • homogeneous catalysis

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**Layout 2:****SHORT COMMUNICATION**

The Fe-catalyzed cross-coupling reaction of propargyl bromides with alkylmagnesium reagents affords either allene or propargyl coupled products in smooth conditions, and tolerates the presence of functional groups.

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