Dehydrogenative Coupling

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Iron-Facilitated Oxidative Dehydrogenative C–O Bond Formation by Propargylic C_{sp^3}–H Functionalization**

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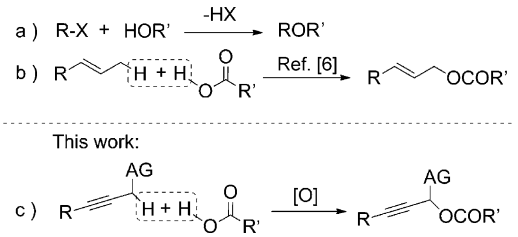
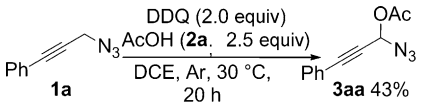
The formation of carbon–heteroatom bonds is one of the most attractive and fundamental transformations in organic synthesis.[1] For example, the construction of C–O bonds plays an important role in producing alcohols, ethers, and esters in the synthesis of drugs, materials, and natural products.[2] In general, great progress has been made in C–O bond formation from carbon–halide bonds,[1,3] although prefunctionalization of the substrates was often required and halide-containing by-products were formed during the process (Scheme 1 a). Thus, the alternative strategy involving direct propargylic C_{sp^3}–H bond activation has not been reported (Scheme 1 c).



Scheme 1. The strategy for propargylic C_{sp^3}–H functionalization with carboxylic acids. AG = assisting group.

C–H/O–H oxidative coupling has assumed increasing importance from the perspective of atom economy.[4] In this context, some couplings have been achieved by employing carboxylic acids as the O–H donators.[5,6] Despite a significant number of successful examples, most direct C_{sp^3}–H/O–H oxidative couplings are still restricted to allylic C_{sp^3}–H functionalization by palladium catalysis, as developed by the groups of Åkermark, Larsson, and White (Scheme 1 b).[6] To the best of our knowledge, until now the direct C–O bond formation through

We began our study by examining the oxidative rearrangement reaction of (3-azidoprop-1-ynyl)benzene (**1a**).[7] Interestingly, the dehydrogenation product, 1-azido-3-phenylprop-2-ynyl acetate (**3aa**), was obtained in 43% yield in the presence of acetic acid **2a** [Eq. (1); DCE = dichloroethane, DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone]. In contrast, the reaction of **4**, which has a similar structure to **1a** but does not contain an azido group, did not afford the corresponding C–O coupling product **5** [Eq. (2)]; this result indicates that the azido group acted as an assisting group to facilitate this C_{sp^3}–H functionalization. Subsequently, the yield of **3aa** was improved to 49% in a one-pot procedure when 3-chloro-1-phenyl-1-propyne (**4a**) was employed as a precursor of **1a** (Table 1, entry 1).



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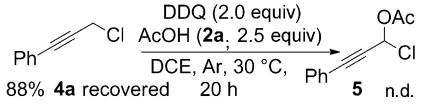

(2)

Recently, iron catalysts have attracted a lot of attention in catalysis owing to their cheap, environmentally benign, and insensitive characteristics.[8] Iron-catalyzed oxidative C_{sp^3}–H functionalizations for carbon–heteroatom bond formations have been recently disclosed in a limited number of cases.[9] To our delight, iron salts such as $FeCl_2$ were very effective in the oxidative coupling (Table 1, entries 2, and 4–6). Attempts to use other oxidants and solvents were not successful (see the Supporting Information for more details). Pivalic acid **2b**, instead of **2a**, was used in the reaction and produced the corresponding product **3ab** in a similar moderate yield (Table 1, entry 7). By increasing the amount of **2b** used, **3ab** was obtained in 70% yield (Table 1, entry 8). The model reaction in the presence of 2,2,6,6,-tetramethylpiperidine-*N*-oxyl (TEMPO; 2 equiv) or O_2 produced the desired **3ab** with low yields (see Table 1, entry 10, and the Supporting Information). Attempts to use other catalysts such as manganese salts (Table 1, entries 12 and 13) resulted in lower yields.

With the optimized conditions established, the substrate scope was investigated. A diverse range of carboxylic acids

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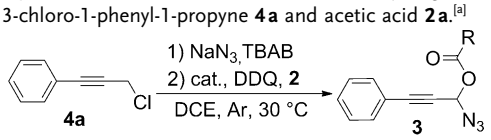
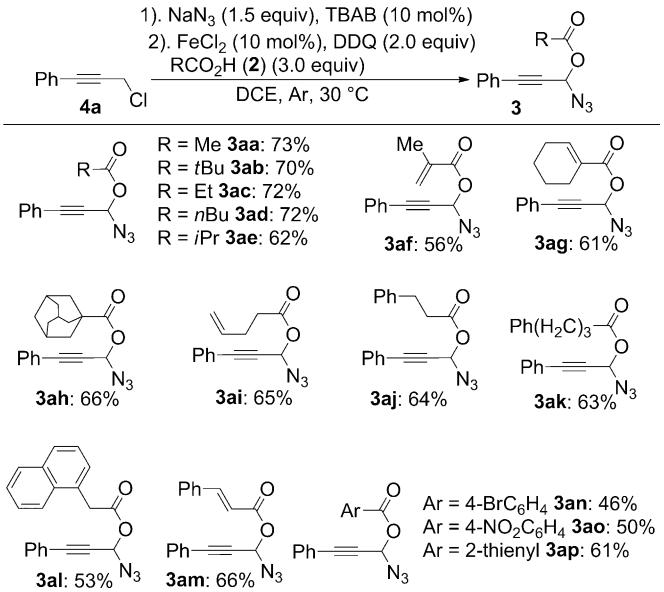
Table 1: Optimization of reaction conditions for dehydrogenative coupling of 3-chloro-1-phenyl-1-propyne **4a** and acetic acid **2a**.[a]



2a: AcOH; **2b**: PivOH

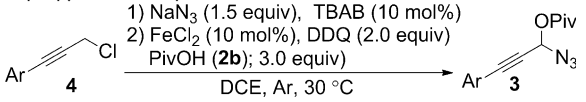
Entry	Cat.	RCO_2H	Yield of **3** [%]
1	–	**2a**	49 (**3aa**)
2	$FeCl_2$	**2a**	64 (**3aa**)
3	$CuBr_2$	**2a**	43 (**3aa**)
4	$FeCl_3$	**2a**	55 (**3aa**)
5	$FeBr_2$	**2a**	60 (**3aa**)
6	FeF_2	**2a**	61 (**3aa**)
7[c]	$FeCl_2$	**2b**	63 (**3ab**)
8[d]	$FeCl_2$	**2b**	70 (**3ab**)
9[d,e]	$FeCl_2$	**2b**	59 (**3ab**)
10[d,f]	$FeCl_2$	**2b**	57 (**3ab**)
11[d,g]	$FeCl_2$	**2b**	50 (**3ab**)
12[d]	$MnBr_2$	**2b**	30 (**3ab**)
13[d]	$MnCl_2$	**2b**	trace (**3ab**)

[a] Reaction conditions: **4a** (0.2 mmol), sodium azide (0.3 mmol), TBAB (0.02 mmol) in anhydrous DCE (2.0 mL) at 30 °C under Ar for 24 h, then acetic acid **2a** (0.5 mmol), DDQ (0.4 mmol), and catalyst (10 mol%) were added to the mixture, which was stirred at 30 °C for 16 h. [b] Yields of the isolated products. [c] Pivalic acid (**2b**) was added instead of **2a**. [d] **2b** (0.6 mmol) was used. [e] 20 mol% of $FeCl_2$ was used. [f] This reaction was carried out under O_2. [g] In the second step the reaction mixture was stirred at 50 °C for 6 h. Piv = trimethylacetyl, TBAB = tetrabutylammonium bromide.



Scheme 2. Iron-catalyzed oxidative C–O coupling of 3-chloro-1-phenyl-1-propyne (**4a**) with various carboxylic acids **2**. Reaction conditions: 3-Chloro-1-phenyl-propyne (**4a;** 0.2 mmol), sodium azide (0.3 mmol), and TBAB (0.02 mmol) in anhydrous DCE (2.0 mL) at 30 °C under Ar for 24 h, then carboxylic acid **2** (0.6 mmol), DDQ (0.4 mmol) and $FeCl_2$ (10 mol%) were added to the mixture, which was stirred at 30 °C for 16 h. Yields are of the isolated products.

Table 2: Iron-catalyzed oxidative C–O coupling of various 3-chloro-1-aryl-1-propynes **1** with pivalic acid **2b**.[a,b]



Entry	Ar	**4**	Yield of **3** [%]
1	$2\text{-}MeC_6H_4$	**4b**	67 (**3bb**)
2	$3\text{-}MeC_6H_4$	**4c**	80 (**3cb**)
3	$4\text{-}MeC_6H_4$	**4d**	74 (**3db**)
4	$2\text{-}OMeC_6H_4$	**4e**	83 (**3eb**)
5	$3\text{-}OMeC_6H_4$	**4f**	68 (**3fb**)
6	$2,4\text{-}Me_2C_6H_3$	**4g**	56 (**3gb**)
7	$4\text{-}FC_6H_4$	**4h**	58 (**3hb**)
8	$4\text{-}ClC_6H_4$	**4i**	80 (**3ib**)
9	$4\text{-}BrC_6H_4$	**4j**	56 (60)[c] (**3jb**)
10	$3\text{-}ClC_6H_4$	**4k**	74 (**3kb**)
11	1-naphthyl	**4l**	45 (**3lb**)
12	2-thienyl	**4m**	57 (**3mb**)

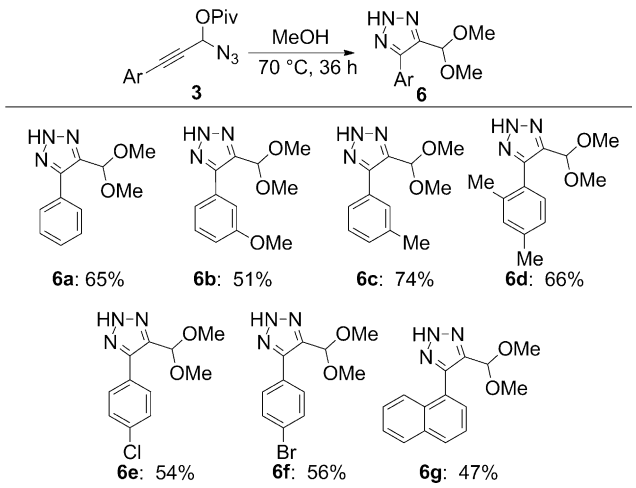
[a] Reaction conditions: 3-chloro-1-aryl-propyne **4** (0.2 mmol), sodium azide (0.3 mmol), and TBAB (0.02 mmol) in dry DCE (2.0 mL) at 30 °C under Ar for 24 h, then pivalic acid **2b** (0.6 mmol), DDQ (0.4 mmol) and $FeCl_2$ (10 mol%) were added to the mixture, which was stirred at 30 °C for 16 h. [b] Yields are of the isolated product. [c] Yield for a larger scale (5 mmol) reaction, see the Supporting Information for details.

were employed in the oxidative coupling with **4a** (Scheme 2). Most aliphatic acids gave the desired propagyl carboxylic acid esters in good yields (**3aa**–**3al**); substrates containing aryl groups and double bonds were tolerated (see products **3af**, **3ag**, and **3ai**–**3al**). Sterically hindered carboxylic acids also performed well in the coupling. For instance, the reaction of adamantane-1-carboxylic acid (**2h**) gave **3ah** in 66% yield. A few aromatic acids including heterocyclic acid **2p** were employed in this transformation to give the corresponding products in moderate yield. Moreover, **3am** was obtained from cinnamic acid in 66% yield. Crystals of compound **3an** that were suitable for X-ray crystallographic analysis were obtained, thus enabling the structure to be confirmed (see the Supporting Information, Figure S1).

Subsequently, a range of different aryl propyne substrates were used in the transformation with pivalic acid (Table 2). It is noteworthy that the substrates containing electron-rich arenes were well tolerated in this transformation (Table 2, entries 2 and 4). Additionally, aromatic halides gave the desired products in moderate yields under the standard reaction conditions (Table 2, entries 7–10), thus providing the possibility to perform other transformations in sequence. Aromatic heterocyclic compounds were also tolerated in this transformation (Table 2, entry 12).

Many studies have revealed that derivatives of 4,5-disubstituted-1,2,3-triazoles are chemically and biologically active.[10] However, few methods have been developed that provide an efficient entry to these aforementioned triazoles.[11] The copper-catalyzed azide-alkyne cycloaddition reaction (CuAAC)[12] often gives *N*-substituted products.[11c] It has been reported that propargyl azides can isomerize to the allenyl azides by the shift of azide group, followed by rapid cyclization to give 4,5-disubstituted-1,2,3-triazoles.[13] Therefore, an advantage of the present protocol is that the products could potentially undergo click reactions in an efficient one-pot procedure. A brief investigation of the

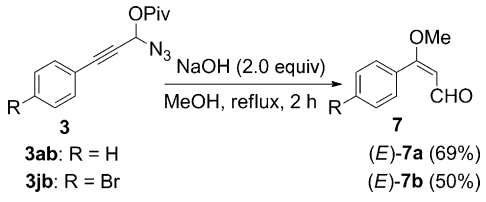
conditions for the rearrangement of propargyl azide **3ab**, showed methanol to be the optimal solvent. After a solution of **3ab** in methanol was heated to reflux for 36 hours in the absence of any other additives, 4-(dimethoxymethyl)-5-phenyl-1,2,3-triazole **6a** was obtained in 65% yield (Scheme 3).



Scheme 3. Formation of 4-(dimethoxymethyl)-5-aryl-1,2,3-triazoles **6** in methanol. Reaction conditions: 1-azido-3-arylprop-2-ynyl carboxylic ester **3** (0.2 mmol) in methanol (2.0 mL) at reflux under Ar for 36 h. Yields are of the isolated products.

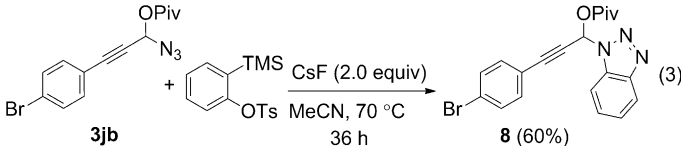
The scope of the formation of triazoles **6** was examined with a series of aryl propargyl azides **3** (Scheme 3). The substrates with electron-rich substituents at a variety of positions on the aryl ring gave the corresponding products (**6b–6d**) in good yields (51–74%). Aryl propargyl azides with chloro- and bromo- substituents at the *para*-position gave the corresponding triazoles (**6e**, and **6f**) in moderate yields (54 and 56%, respectively). Triazole **6g**, containing an napthalene group, was obtained in 47% yield. The structure of the triazoles was confirmed by X-ray crystallographic analysis of **6f** (see the Supporting Information, Figure S2).

Interestingly, in the presence of inorganic bases such as NaOH 3-alkoxyenal analogues (*E*)-**7**, instead of **6**, were stereoselectively obtained[14] as the sole products (Scheme 4). Walizei and Breitmaier have shown that these 3-alkoxyenal analogues are useful synthons for a wide range of synthetic targets.[15] As an example, 2-substituted pyrroles have been produced by the reaction of 3-alkoxypropenals with glycine esters.[15]



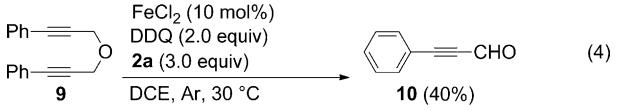
Scheme 4. Base-facilitated formation of (*E*)-3-methoxy-3-arylacrylaldehyde **7**.

Furthermore, the present novel method for propargylic C_{sp^3}–H functionalization can be combined with many transformations. For example, compounds containing Bt–C–O functional groups have been proven to be efficient building blocks in organic sythesis.[16] These compounds can be smoothly prepared from our multifunctionalized products by a simple click reaction with benzyne precursors [Eq. (3);TMS = trimethylsilyl, Ts = *p*-toluenesulfonyl]. For

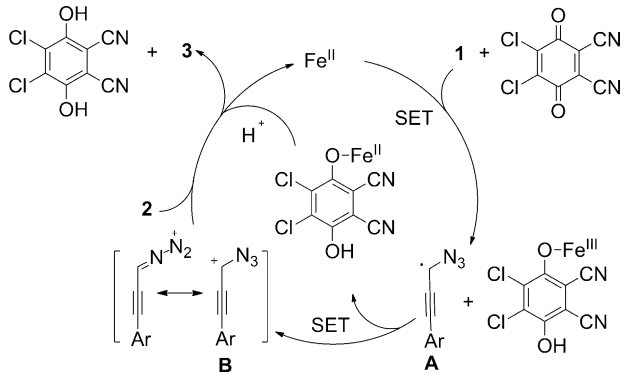


example, when **3jb** was treated with 2-(trimethylsilyl)-phenyl-4-methylbenzenesulfonate benzotriazole **8** was obtained in 60% yield.

To obtain further understanding of the oxidative coupling of carboxylic acids with propargyl azides, a propargyl ether **9** was treated to the standard reaction conditions. However, the desired coupling product, which would be formed via an oxonium intermediate,[17] was not observed and instead phenylpropiolaldehyde **10** was obtained in 40% yield [Eq. (4)]; this result indicates that azide groups are the appropriate assisting groups in this coupling.



On the basis of the above results, a plausible mechanism is proposed in Scheme 5. Initially, substrates **1** undergo hydrogen abstraction through an iron-facilitated single-electron oxidation with DDQ[18] to form the radical species **A**, which may be stabilized by the azido group.[19] Subsequently, radical species **A** was further oxidized to give the aryl propargyl cation **B**. Then, nucleophilic attack of cation **B** by carboxylic acid **2** gave the desired product **3** with the regeneration of the catalyst.



Scheme 5. Proposed mechanism for this oxidative dehydrogenative C–O bond formation.

In conclusion, we have demonstrated a novel and practical protocol for iron-promoted C_{sp^3}–H functionalization of aryl propargyl azides. This method offers an opportunity to achieve propargylic C_{sp^3}–H functionalization under mild reaction conditions and also may involve the application of azido group as an assisting group in C–H activation. The products of this oxidative dehydrogenative coupling are useful synthons for a wide range of synthetic targets such as 4,5-disubstituted-1,2,3-triazoles, 3-alkoxyenals, and benzotriazoles. Further studies on the mechanism and applications of this transformation are in progress in our laboratory.

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