Organic LETTERS

Letter

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Ru-Catalyzed Regioselective CH-Hydroarylation of Alkynes with Benzylthioethers Using Sulfur as Directing Group

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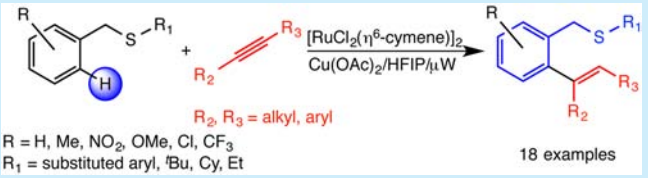
Supporting Information

ABSTRACT: Benzylthioethers react with internal alkynes in the presence of catalytic amounts of $[Ru(cymene)Cl_2]_2$ to give the corresponding *ortho*-alkenylated species, using sulfur as the sole directing group. The reaction is regiospecific, tolerates different substituents at both the sulfur and the aryl ring, and proceeds very efficiently with a large variety of electron-rich alkynes.

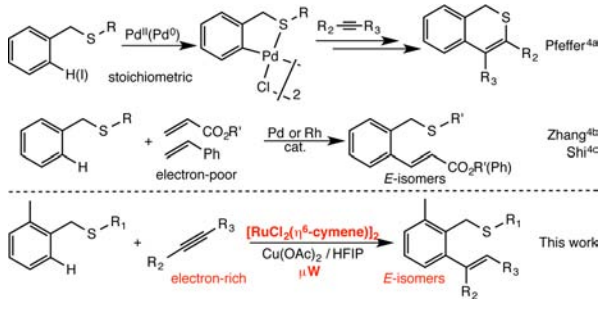


Tailored synthesis of organic compounds using metal-catalyzed C−H bond activation processes has been of much interest in recent years, due to its versatility, high activity, and selectivity.[1] Concerning the latter, the use of directing groups is one of the most studied strategies, with N-,[2] O-,[3] or P-*ortho*-directing groups being extensively used. In clear contrast, the use of S-directing groups[4] has been much less studied, despite the fact that sulfur-containing entities are building blocks of a large number of drug compounds, in either pharmaceutical activity or agrochemical applications.[5] In this respect, the thiophilicity of most transition metals and the corresponding deactivation of the catalysts could be an explanation for this rare representation, and therefore, it is an additional challenge for the study of this type of system.

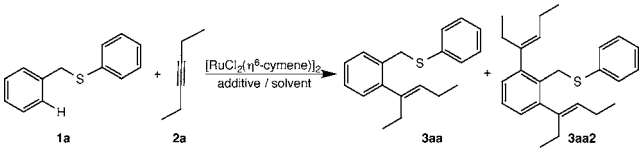
After the seminal work of Pfeffer et al. on the synthesis of sulfur heterocycles using stoichiometric amounts of Pd,[4a] recent catalytic results found in the literature deal with the olefination of thioethers,[4b,c] sulfoxides,[4d] and phosphinesulfides[4e] and with arylations[4f−h] and acylations[4i] of the same type of substrates. All of these reported cases feature the use of expensive Rh and Pd catalysts (Scheme 1). To the best of our knowledge, the use of cheaper Ru complexes (see Supporting Information (SI)) as catalysts for the S-directed functionalization has not yet been reported. Some recent contributions involve the Ru-catalyzed modification of S-containing species, but in those cases, the true directing group is an oxygen atom not the S-moiety.[6] Thioethers as traceless S-directing groups display many advantages since they can be removed or transformed into other functional entities easily. Following our previous research in Ru-catalyzed couplings,[7] we report here the use of Ru complexes as catalysts for the S-directed *ortho*-CH-hydroarylation of alkynes with benzylthioethers (Scheme 1). This reaction gives the alkenylated benzylthioethers efficiently under microwave irradiation, in short reaction times (30 min), for a variety of thioethers and electron-rich internal alkynes.

In a first step, we have optimized the reaction conditions for coupling of thioether **1a** with alkyne **2a** (Scheme 2, Table 1). Our starting point was that reported for the oxidative coupling of primary amines and internal alkynes.[7] After being heated for 24 h at 100 °C in MeOH with 10% as charge of Ru catalyst and $Cu(OAc)_2$ as additive, a low conversion (18%) of alkenylated **3aa** was obtained (entry 1). A control experiment showed that the hydroarylation did not take place at all (0% conversion) in the absence of Ru catalyst, so the process is not catalyzed by the Cu additive. Subsequent screening of solvents showed low or no conversions for ^{t}AmOH (entry 2), toluene (with or without acid additives, entry 3), and DCE (entry 4), suggesting that a certain

Scheme 1. Summary of This Work and Relationship with Published Previous Work



Scheme 2. Hydroarylation of 2a with Benzylthioether 1a



Received: May 27, 2015
Published: June 11, 2015

DOI: 10.1021/acs.orglett.5b01552
Org. Lett. 2015, 17, 3178−3181

Table 1. Optimization Conditions[a]

entry	additive	solvent	t (h)	3aa/3aa2 (%)
1	$Cu(OAc)_2$	MeOH	24	18:0
2	$Cu(OAc)_2$	^{t}AmOH	24	5:19
3	$Cu(OAc)_2$	toluene[b]	24	0:0[b]
4	$Cu(OAc)_2$	DCE	24	20:5
5	$Cu(OAc)_2$	HFIP	24	16:84
6	$Cu(OAc)_2$	HFIP	0.5[c]	**18:82**
7	AgOAc	HFIP	0.5[c]	32:0
8	NaOAc	HFIP	0.5[c]	0:0
9	$Cu(OAc)_2$ (20%) + NaOAc (80%)	HFIP	0.5[c]	<5:<5
10[d]	$Cu(OAc)_2$	HFIP	0.5[c]	11:18

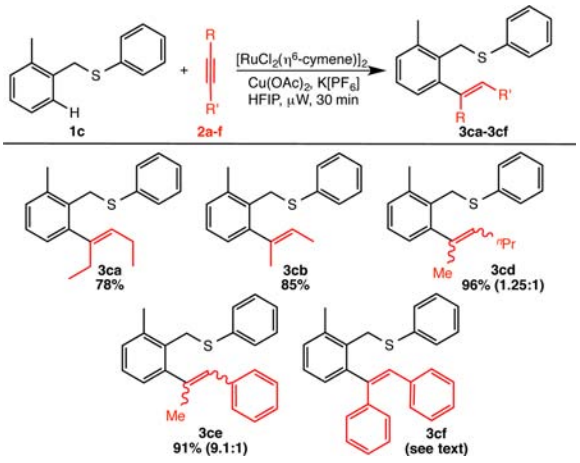
[a]Experimental conditions: **1a** (0.5 mmol), **2a** (1 mmol), [Ru] (0.05 mmol), additive (0.5 mol), KPF_6 (0.05 mmol), 100 °C; conversion of **1a** to **3aa**/**3aa2** determined by ^{1}H NMR. [b]Same result (0%) for a toluene/AcOH mixture (1 mmol). [c]Microwave irradiation (150 W, 100 °C). [d][Ru] 0.025 mmol (5%).

protic character (alcohol) seems to be advantageous for the reaction but not very acidic (AcOH). The best compromise was achieved in hexafluoroisopropanol (HFIP) (entry 5), where a full conversion was observed giving a mixture of mono- (**3aa**) and bisalkenylated (**3aa2**) compounds in 1:5.25 molar ratio. Reaction time can be reduced from 24 to 0.5 h by changing the conventional heating by microwave irradiation (entry 6) without erosion of the conversion and keeping the product distribution of **3aa**/**3aa2** almost unchanged. Further optimization was thus performed under microwave conditions. Other OAc sources, such as AgOAc (entry 7), NaOAc (entry 8), or a combination of catalytic $Cu(OAc)_2$ and stoichiometric NaOAc (entry 9), were not as efficient as $Cu(OAc)_2$ by itself. So, acetate is necessary for the C−H bond activation step, but not all sources perform equally; it seems that the presence of Cu is also mandatory. Attempts to decrease the amount of Ru catalyst (entry 10) also resulted in a clear drop of the reaction conversion.

To avoid bis-hydroarylation processes, and the subsequent mixture of compounds, we have tuned the starting material to block one of the *ortho*-positions of the benzyl fragment with either electron-releasing or electron-attracting groups (CF_3, **1b**; CH_3, **1c**; Cl, **1d**; NO_2, **1e**). Though similar results were obtained in these cases, better yields were obtained with **1c**; therefore, all work described hereafter has been performed with **1c**. Other substituted benzylthiothers were also attempted at this stage, that is, those having a 2-OMe group (**1f**) or two Me groups at 2,4-positions (**1g**) of the benzyl fragment, as well as one thiophene derivative (**1h**, SI). For **1f** and **1g**, mixtures of small amounts of the hydroarylation products and other unidentified compounds were obtained, which proved difficult to separate and purify. For **1h**, it seems that it bonds the (*S*,*S*)-chelate to Ru, stopping any further reactivity. Due to these facts, **1f**−**1h** were not further considered.

More successfully, excellent results were obtained for the coupling of **1c** with electron-rich alkynes such as 3-hexyne (**2a**), 2-butyne (**2b**), 2-hexyne (**2d**), or 1-phenylpropyne (**2e**), giving the corresponding olefinated derivatives (**3ca**, **3cb**, **3cd**, **3ce**) in yields in the range of 78−96%, as shown in Scheme 3. Hydroarylation takes place in all studied cases as a *syn* addition, as it can be inferred from the shape of the vinylic proton in the ^{1}H NMR spectra. Therefore, the geometry of the resulting trisubstituted vinylic fragment is *E*, and the coupling is *E*-stereoselective, as observed for related systems.[8] In addition,

Scheme 3. Scope of the Changing Process of Alkyne



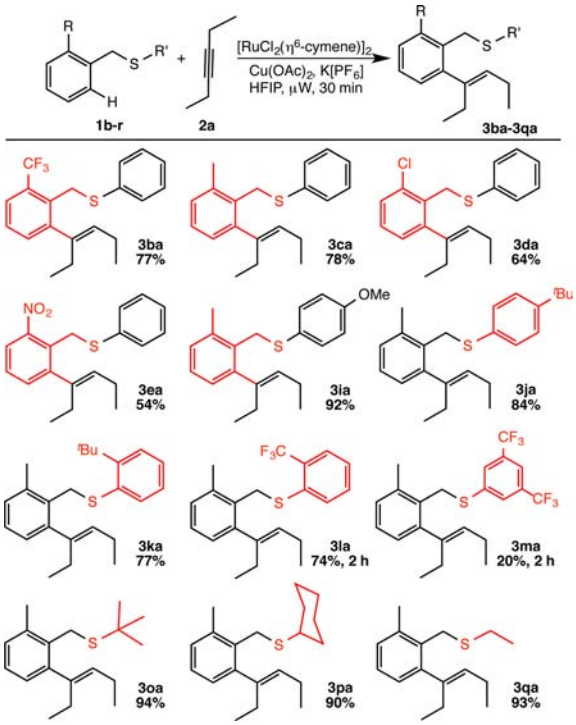
good regioselectivity was observed for the coupling of 1-phenylpropyne (**2e**) with **1c**, as deduced from the 9.1:1 molar ratio of the two regioisomers of **3ce**, being the most abundant with the two phenyl rings in *trans*-positions. This regioselectivity is not observed in the case of 2-hexyne (**1d**), for which an almost equimolar mixture is obtained. The presence of two aryl rings in the starting alkyne drops the yield of the reaction and produces higher amounts of byproducts, as we observed in coupling of **1c** with diphenylacetylene (**2f**) to give **3cf** in about 45% isolated yield, contaminated with minor amounts of impurities. **3cf** was reluctant to be purified using chromatography or Kugelrohr distillation techniques, although its characterization was unambiguous. Coupling of **1c** with sterically hindered 4,4-dimethyl-2-pentyne **2c** gave mixtures of unidentified compounds, showing the critical role of steric factors in the process.

After different alkynes were tested, we focused on the effect of substituents in the benzyl and phenyl moieties at the S atom. As stated previously, similar yields were obtained when the methyl at the 2-position of the benzyl group (**3ca**) was changed by an electron-attracting group, such as CF_3 (**3ba**), but a decrease is observed when 2-Cl (**3da**) or 2-NO_2 (**3ea**) was present (Scheme 4). Notably, the presence of strongly deactivating groups at the ring where the C−H activation is produced does not have a critical role in the reaction yield.

Interestingly, the fine-tuning of the electron density at the sulfur atom promotes notable changes in the conversion of the reaction and in the reaction yield. In the cases where the *S*-phenyl group was present, this modulation has been achieved by the tailored change of the nature and position of the substituents at that phenyl ring (Scheme 4). In this way, strong electron-donating groups such as 4-OMe or 4-^{t}Bu give very good yields of the alkenylated derivatives (92% **3ia**; 84% **3ja**) in only 30 min reaction time, but a lower yield is observed when the electron-rich substituent is at the 2-position (77%, **3ka**), probably due to steric effects. The reaction tolerates the presence of a single electron-attracting substituent very well at the SPh moiety but needs prolonged heating under microwave irradiation to achieve comparable yields (2 h instead of 30 min). Using long reaction times, good yields were obtained in the case of 2-CF_3 (**3la**, 74%). The decrease of the reaction yield associated with the electron-withdrawing nature of the S-substituents is amplified if additional groups are introduced at the *S*-phenyl ring. Therefore, **3ma** (2 CF_3 groups at 3- and 5-positions) is obtained in only 20% yield after 2 h of microwave irradiation, and a complete lack of

DOI: 10.1021/acs.orglett.5b01552
Org. Lett. 2015, 17, 3178−3181

Scheme 4. Scope of the Changing Process of Thioether



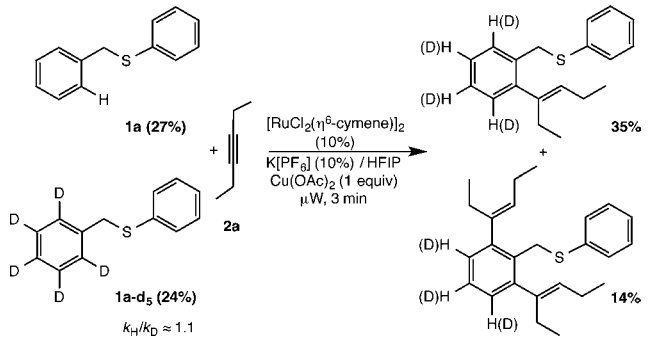
reactivity is observed in the case of the SC_6F_5 group because **3na** was not observed even trace levels.

Use of alkyl groups as S-substituents allows the reactions to proceed with very good yields, in good agreement with the electron-donating character of the alkyl unit. When *tert*-butyl, cyclohexyl, or ethyl groups were used as S-substituents, the corresponding compounds (**3oa**−**3qa**) were obtained in yields greater than 90%. Remarkably, when a SMe unit is present, the reaction does not take place at all, and compound **3ra** was not detected. This fact could probably be related to the known demethylation of SMe thioethers.[9]

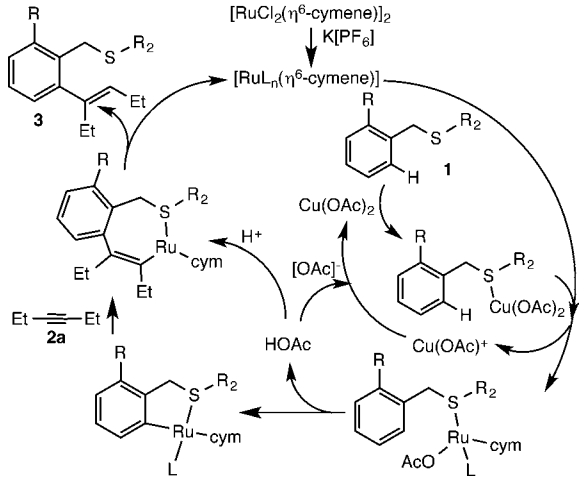
The observed experimental trends suggest that the reaction yield is not critically affected by the presence of substituents of different electronic nature at the aryl ring of the *S*-benzyl unit, while the modulation of charge at the *S*-aryl moiety has a great effect on the reaction yield, even stopping the reaction when more than one electron-withdrawing group is present. Aiming to gain further insight about the mechanism of this process, we have performed a study of the intermolecular kinetic isotopic effect (KIE) in the oxidative coupling between an equimolar mixture of **1a**/**1a**-d_5 and alkyne **2a**. After 3 min heating, the reaction was quenched and the distribution of different compounds is presented in Scheme 5. Details of this measurement are given in Supporting Information. As can be seen, the ratio k_H/k_D is 1.1, implying that the C−H bond activation is not the rate-determining step.[10] It is important to note that no deuterium incorporation on the olefinic fragment was detected, suggesting that the arene activation is not produced by oxidative addition. With these data, we propose for this process the mechanism shown in Scheme 6.

A plausible initial step should be the S-bonding of thioether **1** to the $Cu(OAc)_2$, with this fact explaining the mandatory presence of stoichiometric $Cu(OAc)_2$ as a source of OAc ligands. Probably, the S-bonding of **1** to Cu also prevents the poisoning of the Ru catalyst. This proposed $Cu(OAc)_2$(*S*-**1**) intermediate could then transfer one acetate and the thioether **1** to the Ru

Scheme 5. KIE Determination of Compound 1a



Scheme 6. Proposed Mechanism



center. The presence of acetate on the Ru center to promote the acetate-assisted C−H bond activation is necessary,[11] as we have seen during the optimization process (Scheme 2, Table 1). We also confirmed recently the best reactivity of $Cu(OAc)_2$ (among acetate sources) toward Ru complexes in the study of the cycloruthenation of heterocycle imines through CH bond activation.[12] The so-formed *ortho*-ruthenated derivative reacts with the internal alkyne through π-bonding and migratory *syn*-insertion. The selectivity observed for the *syn*-insertion is complete, as it can be inferred from the *E*-geometry of the olefinic fragment formed. This fact precludes a cationic catalysis via alkyne activation and suggests a cationic catalysis via arene activation.[8c] The last step of the catalytic cycle is the protodemetalation and the release of the *ortho*-vinyl thioether.

To summarize, a general method for the synthesis of *ortho*-alkenylated benzylthioethers has been achieved. The reaction is catalyzed by a simple Ru complex and involves the hydroarylation of an internal alkyne by a benzylthioether. The sulfur atom behaves as an efficient directing group, allowing regioselective *ortho*-substitution. The reaction is stereospecific because only the *E*-olefin is obtained. In addition, the reaction takes place using a large variety of thioethers and alkynes; therefore, it is of wide applicability. In addition to the intrinsic interest of the obtained products, it shows the potential of the sulfur-containing directing groups in CH-mediated functionalizations. Further work in this area is in progress.

DOI: 10.1021/acs.orglett.5b01552
Org. Lett. 2015, 17, 3178−3181

■ ASSOCIATED CONTENT

Supporting Information

Full experimental section with detailed procedures and characterization data (^{1}H and ^{13}C NMR spectra). The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b01552.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Funding by Gobierno de Aragón (Spain, group E97) is gratefully acknowledged. P.V. thanks CSIC for a Juan de la Cierva contract.

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