Synthesis of 1,1-Disubstituted Olefins via Catalytic Alkyne Hydrothiolation/Kumada Cross-Coupling
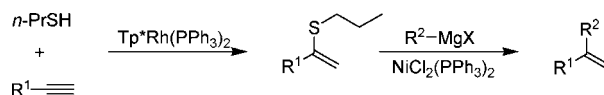
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ABSTRACT

Using recently developed methodology for the regioselective formation of branched alkyl vinyl sulfides, we report a convenient route to 1,1-disubstituted olefins. We demonstrate that *n*-propanethiol successfully undergoes catalytic alkyne hydrothiolation with both aryl and aliphatic alkynes using Tp*Rh(PPh₃)₂ as the catalyst. The resulting vinyl sulfides undergo Kumada cross-coupling to afford the desired disubstituted alkene. Both two-step and one-pot procedures are reported.

1,1-Disubstituted olefins are present in many biologically active molecules and synthetic intermediates.[1–3] Examples of natural products containing this moiety include the antitumor agent dysidiolide,[4] the CNS stimulant kainic acid,[5] the microtubule stabilizer laulimalide,[6] and the potent neurotoxin pinnatoxin A.[7] The development of reactions for the selective construction of 1,1,-disubstituted olefins is therefore an area of considerable interest. Notwithstanding the significant research efforts to date, methods for assembling 1,1-disubstituted olefins have been developed to a much lesser extent than those for 1,2-disubstituted olefins. We envisioned a one-pot procedure for the synthesis of 1,1-disubstituted olefins from readily available alkynes based on a sequential catalytic alkyne hydrothiolation/cross-coupling strategy (Scheme 1). We report herein the results of this study.

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Scheme 1. One-Pot Strategy toward the Synthesis of 1,1-Disubstituted Olefins
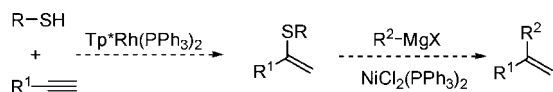
A few metal-catalyzed procedures are available for the formation of 1,1-disubstituted olefins. Among the most widely used is the cationic Heck reaction[8−11] which involves the use of an organohalide, typically an aryl halide, and a monosubstituted olefin. Although the corresponding reactions using alkyl halides have been reported, they have been limited mainly to activated alkyl halides and those lacking β-hydrogens.[12−16] Only a few examples of the Heck reaction involving unactivated alkyl halides have been published.[17] An alternate strategy involves the cross-coupling of an aryl halide with a vinyl organometallic reagent, typically derived from a vinyl halide.[18,19] A significant drawback to using vinyl halides is the requirement for use of a strong Lewis or Bronsted acid, such as BBr$_3$ or HBr, for their synthesis; these harsh conditions have evident functional group incompatibility. Likewise, although vinyl triflates can also be used in transition-metal-catalyzed cross-coupling, their synthesis also presents some functional group incompatibility.[18−21]

Other cross-coupling partners, including vinyl sulfides, have also been reported to undergo cross-coupling.[22−29] For example, Wenkert[23−25] and Takei[26] independently discovered that vinyl and aryl sulfides could generate 1,2-disubstituted olefins via Kumada-type coupling. Both researchers reported that vinyl sulfides show higher reactivity than aryl sulfides. Takei later reported that allylic sulfides were also suitable substrates for the cross-coupling reaction.[27] Tri-[28] and tetrasubstituted[29] olefins have also been generated by cross-coupling of the corresponding vinyl sulfides. In 1987, Naso and co-workers reported that 1,1-disubstituted vinyl sulfides were also suitable substrates for cross-coupling, although only two examples were given.[30,31] We envisioned that this process could serve as a convenient method for constructing 1,1-disubstituted olefins.

For the Kumada-type cross-coupling protocol to be synthetically useful, a variety of 1,1-disubstituted vinyl sulfides must be readily available. Until recently, the regioselective synthesis of branched alkyl vinyl sulfides had been elusive. Although there had been several metal-catalyzed reactions involving thiols that have been reported for the synthesis of aryl vinyl sulfides,[32] reactions involving alkyl thiols had been explored to a lesser extent.[33−35] Our recent discovery that Tp*Rh(PPh$_3$)$_2$ [Tp* = hydrotris(3,5-dimethylpyrazolylborate)] (Figure 1) catalyzes alkyne hydrothiolation of a wide range of alkynes (aliphatic, aromatic, internal) and thiols to afford 1,1-disubstituted vinyl sulfides in high yields and selectivity has alleviated this shortcoming.[36] As such, we anticipated that this methodology could be used to assemble vinyl sulfides for use in Kumada-type cross-coupling.

An ideal vinyl sulfide cross-coupling partner would undergo efficient cross-coupling and would have a leaving group of low molecular weight in order to minimize waste.

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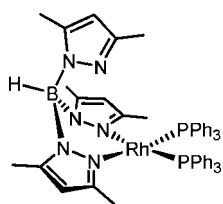(36) Cao, C; Fraser, L. R.; Love, J. A. *J. Am. Chem. Soc.* **2005**, *127*, 17614−17615.

Figure 1. Catalyst for alkyne hydrothiolation: Tp*Rh(PPh₃)₂.

We selected *n*-propylthiolate for this role as it is of comparable mass to bromide, a typical leaving group in cross-coupling chemistry.

In our original communication on catalytic hydrothiolation, we had established that *n*-propanethiol reacted in high yield and selectivity in hydrothiolation, although only one example was reported.[36] Therefore, our first goal was to establish that hydrothiolation using *n*-propanethiol could proceed with a broader range of alkynes in high selectivity and with acceptable yields.

A variety of aryl and aliphatic alkynes were selected for study using our previously established conditions for catalytic hydrothiolation (Table 1). We found that all the alkynes

Table 1. Catalytic Alkyne Hydrothiolation

entry[a]	alkyne	product	time, yield
1			2 h, 74%
2			2 h, 72%
3			16 h, 15%
4			2 h, 83%
5			16 h, 86%

[a] Reactions conducted with 0.03 equiv of Tp*Rh(PPh₃)₂, 1 equiv of alkyne, and 1.1 equiv of thiol.

investigated reacted with high selectivity. A series of para-substituted aryl alkynes were chosen to examine the effect of electronics on the reaction (entries 1–4). Both phenylacetylene and 4-ethynylanisole provided the corresponding branched vinyl sulfides in good isolated yields (entries 1 and

2, respectively). In comparison, the use of a strongly electron-withdrawing substituent led to a significant decrease in efficiency and yield (entry 3). We concluded that vinyl sulfides derived from either unsubstituted or electron-rich alkynes would serve as suitable substrates for cross-coupling. Both aliphatic alkynes examined reacted in high isolated yields and with high selectivity (entries 4 and 5). As such, both products were deemed to be suitable for further study in cross-coupling to generate 1,1-disubstituted olefins. It is noteworthy that we had previously found that alkyl vinyl sulfides as in entry 5 were prone to isomerization; we have subsequently found that avoiding the use of chloroform as a solvent for either chromatography or NMR spectroscopy precludes this isomerization.

With this series of vinyl sulfides in hand, we were now poised to test the Kumada-type cross-coupling methodology. Our initial study focused on the use of isolated alkyl vinyl sulfides in cross-coupling reactions with various Grignard reagents (alkyl, vinyl and aryl) using 10 mol % NiCl₂(PPh₃)₂ as the catalyst (Table 2). PhCH₂MgCl, ArMgBr, and

Table 2. Nickel-Catalyzed Cross-Coupling of Vinyl Sulfide with Grignard Reagent

entry[a]	vinyl sulfide	Grignard	product	yield[b]
1		PhCH₂MgCl		51%[c]
2		PhCH₂MgCl		61%
3		PhMgBr		43%
4		*p*-FC₆H₄MgBr		38%
5		TMS-CH₂MgCl		60%[d]
6		PhCH₂MgCl		55%
7		PhMgBr		41%
8		*p*-FC₆H₄MgBr		37%
9		TMS-CH₂MgCl		81%
10		PhCH₂MgCl		51%

[a] Reaction conducted with 0.1 equiv of NiCl₂(PPh₃)₂, 1 equiv of vinyl sulfide, and 4 equiv of Grignard reagent (1.0 M in THF or Et₂O). [b] Isolated yields. [c] Yield determined by ¹H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard. [d] R¹ = CH₃.

TMS−CH₂MgCl afforded the desired 1,1-disubstituted olefin in moderate isolated yields, comparable to those obtained by Wenkert and Takei.[23−26] Higher yields were precluded by competing homocoupling of the Grignard reagent and byproduct volatility. Given the superiority of selenium to sulfur in nickel-catalyzed additions to alkynes,[31] vinyl selenides could also serve as potential cross-coupling partners for future study. Use of *n*-butylmagnesium chloride and vinylmagnesium bromide did not give the desired substituted olefins. In the latter case, we observe reduction of the vinyl

sulfide.[23,37] For the reaction using the vinyl sulfide derived from 4-ethynylanisole, only the desilylated product was obtained when TMSCH₂MgCl was used in cross-coupling (entry 5). In comparison, the vinyl sulfide derived from ethynylcyclohexene provided the corresponding allyl silane in high yield (entry 9). Such allyl silanes have had widespread use for allylation reactions or as nucleophiles in other cross-coupling processes.[38a−d] Notably, the cross-coupling products derived from ethynylcyclohexene are also potential Diels−Alder substrates.[39,40]

Having established the viability of the cross-coupling methodology for the synthesis of 1,1-disubstituted olefins, we now turned our attention to feasibility of combining both the hydrothiolation and cross-coupling steps in a one-pot procedure. In our initial studies, a 1:1 mixture of 1,2-dichloroethane/toluene was used as the solvent for hydrothiolation, based on previous optimization studies.[36] In comparison, THF was used for the Kumada-type coupling (Table 2). To facilitate the one-pot procedure, we elected to use THF as the solvent for both reactions. In a typical experiment, n-propanethiol (0.99 mmol), alkyne (0.9 mmol), and Tp*Rh(PPh₃)₂ (0.027 mmol) were dissolved in 2.5 mL of THF. The mixture was stirred for 2−16 h at rt, and the reaction progress was monitored by tlc. Upon completion of hydrothiolation, 10 mL of THF was added, followed by NiCl₂(PPh₃)₂ (0.072 mmol) and Grignard reagent (3.6 mmol). The reaction mixture was stirred at 75 °C for 16 h. The desired 1,1-disubstituted olefins were obtained in isolated yields comparable or superior (Table 3) to those obtained using the two-step protocol. The greater efficiency of the one-pot procedure may result from the need for one fewer purification step.

In summary, we have shown that Tp*Rh(PPh₃)₂ catalyzes alkyne hydrothiolation using n-propanethiol with both aliphatic and aryl alkynes. The resulting alkyl vinyl sulfides can undergo nickel-catalyzed Kumada-type cross-coupling with Grignard reagents to afford 1,1-disubstituted olefins.

Table 3. One-Pot Catalytic Alkyne Hydrothiolation/Kumada Cross-Coupling

entry[a]	alkyne	Grignard	product	yield[b]
1		PhCH₂MgCl		30%[c]
2		PhCH₂MgCl		65%
3		PhMgBr		37%
4		p-FC₆H₄MgBr		37%
5	MeO	TMS-CH₂MgCl		63%[d]
6		PhCH₂MgCl		66%
7		PhMgBr		30%
8		p-FC₆H₄MgBr		40%
9		TMS-CH₂MgCl		60%
10	n-C₆H₁₃	PhCH₂MgCl	n-C₆H₁₃	78%

[a] Reactions conducted with 0.027 mmol of Tp*Rh(PPh₃)₂, 0.9 mmol of alkyne, 0.99 mmol of thiol, 0.09 mmol of NiCl₂(PPh₃)₂, and 3.6 mmol of Grignard reagent (1.0 M in THF or Et₂O). [b] Isolated yields. [c] Yield determined by ¹H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard. [d] R¹ = CH₃.

Furthermore, a one-pot procedure provides comparable or superior isolated yields to the two-pot process, with the additional benefit of requiring only a single purification step. We anticipate that this protocol will be a useful alternative to existing methodologies for the synthesis of 1,1-disubstituted olefins from readily available precursors.

Supporting Information Available: Complete experimental details for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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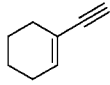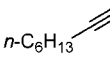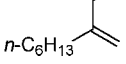(37) Trost, B. M.; Ornstein, P. L. *Tetrahedron Lett.* **1981**, *22*, 3463–3466.
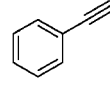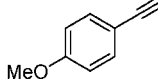
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