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Efficient Synthesis of Isothiochromene Derivatives by Pd-Catalyzed Hydrothiolation Reaction

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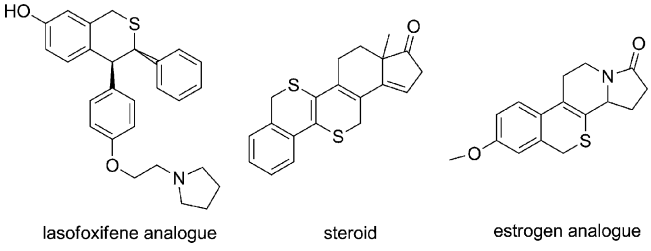
Keywords: Heterogeneous catalysis / Synthetic methods / Palladium / Sulfur heterocycles / Cyclization / Isothiochromene derivatives

An efficient method for the preparation of isothiochromene derivatives through the palladium-catalyzed intramolecular hydrothiolation reaction of halides and thiourea is reported. Two carbon–sulfur bonds are formed in this one-pot palladium-catalyzed cascade reaction. This new protocol is free from foul-smelling thiols and operates under mild conditions to give isothiochromene derivatives in excellent yields and with excellent 6-*endo*-*dig* selectivity.

Introduction

Sulfur-containing heterocyclic compounds commonly exhibit biological activity, and hence are frequently found in naturally occurring compounds.[1] Among them, isothiochromane and isothiochromene ring systems display a wide range of interesting biological properties as structural analogs of many bicyclic systems, such as chroman, isochroman, tetrahydroisoquinoline etc., which are widespread in natural products (Scheme 1).[2] Moreover, these compounds have found important applications in total synthesis for the preparation of a wide range of functionalized molecules.[3]



Scheme 1. Examples of sulfur-containing biologically active compounds.

The approaches to synthesize isothiochromene derivatives commonly include cyclization reactions,[4] free-radical reactions,[5] and reactions with cyclic sulfur ylides.[6] Despite a considerable number of reports on the synthesis of isothiochromene derivatives, a survey of the literature revealed that the synthesis of 3-substituted 1*H*-isothiochromenes has not been explored extensively. Initially, compounds of this ring system were prepared by the insertion of an alkyne into the metal–carbon bond of five-membered sulfur-containing cyclopalladated complexes.[7] Later, 4-iodo-3-substituted 1*H*-isothiochromenes were synthesized through an electrophilic cyclization reaction in moderate yields that used iodine as the electrophilic source.[8] However, these methods suffer from one or more drawbacks, such as a multi-step procedure, low yields, long reaction times, and the use of expensive and hazardous reagents. The synthesis of various tellurium- or selenium-containing heterocycles, which bear similar ring structures, by a base-catalyzed intramolecular cyclization of the tellurol or selenol moieties has been reported,[9] but there was no report on thiol intramolecular cyclization reactions to synthesize 1*H*-isothiochromenes.

As for intramolecular cyclization reactions, there exist two potential products: 6-*endo*-*dig* or 5-*exo*-*dig* products. Many reports discuss the regioselectivity in intramolecular hydroamination and hydrogenation reactions, but, in the case of intramolecular hydrothiolation reactions, few references involve regioselectivity.[9b] Thus, a general protocol for the selective synthesis of 3-substituted 1*H*-isothiochromenes remains a challenge.

Recently, transition-metal-catalyzed cyclization reactions, especially the sequential reactions that involve a hydro-element addition, which relies on the catalytic activation of the C–C triple bond, followed by attack of an internal nucleophile, has attracted significant interest because of its synthetic utility and become a rapid and powerful approach to prepare cyclic derivatives in organic synthesis.[10] In the past few years, gold complexes, palladium complexes and so on have emerged as powerful catalysts for this purpose.[11] These cyclic processes have been successfully applied for selective product formation. Among them, transition-metal-catalyzed hydrothiolation reactions are well studied.[12] With the aim to selectively synthesize 6-

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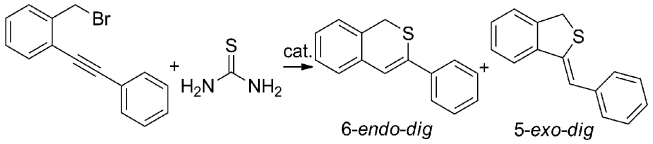
endo-dig or 5-*exo-dig* isothiochromene derivatives, we report herein the use of palladium complexes to selectively synthesize isothiochromene derivatives through intramolecular hydrothiolation reaction of 2-(phenylethynyl)benzylthiol.

We tried to use other sulfur sources to replace thiol because of its disagreeable smell. In continuation of our work on "thiolation" reactions, we focused our attention on the synthesis of 3-substituted 1*H*-isothiochromene derivatives by using thiourea as the "sulfur" source. Thus, we designed a cascade reaction through the in situ generation of *S*-alkylisothiouronium salts in place of thiols,[13] which are formed by halides and thiourea. The thiolation protocol and the intramolecular hydrothiolation reaction can proceed in sequence in one pot without the need for multi-step reactions.

Results and Discussion

We began our studies by exploring catalysts for the intramolecular hydrothiolation reaction. Some commercially available palladium catalysts and some other transition-metal catalysts were initially screened in the intramolecular hydrothiolation reaction of 2-(phenylethynyl)benzyl bromide with thiourea (Table 1). No products were obtained in the absence of base (Table 1, Entry 1). A small amount of 2-(phenylethynyl)benzyl bromide was converted only in the presence of base (Table 1, Entry 2). The addition of palladium catalyst accelerated the reaction (Table 1, Entries 3–8 and 12). Among them, $Pd(dppf)Cl_2$ [dppf = 1,1′-bis(diphenylphosphino)ferrocene] showed the best results (Table 1, Entry 5). Like intramolecular hydroamination and hydrogenation reactions, both the 6-*endo-dig* and 5-*exo-dig* products were observed in the hydrothiolation reaction. The 6-*endo-dig* mode cyclization was preferred in the palladium-catalyzed case. Ligand and temperature were found to influence the selectivity between 6-*endo* and 5-*exo* products. With an appropriate ligand [$Pd(dppf)Cl_2$ showed the best result here], 6-*endo-dig* products could be obtained selectively at room temperature. An increase in the reaction temperature sped up the reaction but decreased the selectivity (Table 1, Entry 8). It is also worth mentioning that pincer-palladium complexes survived the reaction with high yields and selectivities (Table 1, Entry 12). Other transition-metal catalysts were also tested but gave unsatisfactory results (Table 1, Entries 9–11).

Table 1. Catalyst selection for intramolecular hydrothiolation reactions.[a]

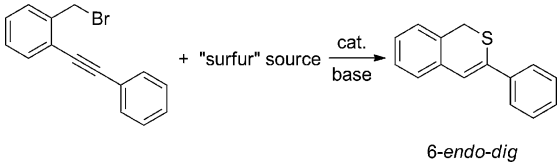


Entry	Base	Catalyst	Yield [%][b]	6-*endo*/5-*exo*[c]
1	–	$Pd(dppf)Cl_2$	0	–
2	K_2CO_3	–	11	–
3	K_2CO_3	$Pd(OAc)_2$	64	95:5
4	K_2CO_3	$PdCl_2$	56	91:9
5	K_2CO_3	$Pd(dppf)Cl_2$	98	100:0
6	K_2CO_3	$Pd(PPh_3)_2Cl_2$	83	96:4
7	K_2CO_3	Pd(amphos)Cl_2[d]	75	90:10
8[e]	K_2CO_3	$Pd(dppf)Cl_2$	96	64:36
9	K_2CO_3	$AgCF_3SO_3$	0	–
10	K_2CO_3	CuI	42	78:22
11	K_2CO_3	$AuCl_3$	0	–
12	K_2CO_3	pincer-Pd[f]	99	99:1

[a] Reaction conditions: halides (0.5 mmol), thiourea (1 mmol), K_2CO_3 (0.5 mmol), catalyst (0.005 mmol), DMSO (2 mL; contained a trace amount of water), room temp., 2 h. [b] Isolated yield. [c] Determined by ^1H NMR spectroscopy. [d] amphos = di-*tert*-butyl[4-(dimethylamino)phenyl]phosphine. [e] The reaction was conducted at 110 °C for 15 min. [f] Pd[(1*E*,1′*E*)-1,1′-(1,3-phenylene)bis(*N*-phenylmethanimine)]Br was used (see the Supporting Information, chapter 3.1).

Reaction conditions were then screened to establish the optimum conditions. Different "sulfur" sources were explored. Sulfur and sodium thiosulfate were found to be ineffective for this reaction (Table 2, Entries 3 and 4). The use of Na_2S led to a series of byproducts (Table 2, Entry 2), whereas excellent yields were observed in the presence of thiourea (almost quantitative). Screening bases revealed that stronger bases performed better under the reaction conditions. The reaction was initially conducted in water; however, the disulfide product was obtained. (Table 2, Entry 8). Other solvents, such as toluene and acetonitrile, were tested but none were suitable for this reaction (Table 2, Entries 9 and 10).

Table 2. Optimum conditions of intramolecular hydrothiolation.[a]



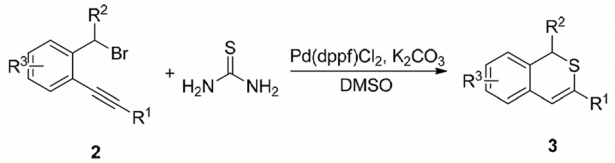
Entry	Sulfur source	Base	Solvent	Yield [%][b]
1	thiourea	K_2CO_3	DMSO	96
2	Na_2S	K_2CO_3	DMSO	52
3	S	K_2CO_3	DMSO	0
4	$Na_2S_2O_3$	K_2CO_3	DMSO	23
5	thiourea	NaOH	DMSO	97
6	thiourea	NaOAc	DMSO	32
7	thiourea	Et_3N	DMSO	0
8	thiourea	K_2CO_3	H_2O	0
9	thiourea	K_2CO_3	toluene	11
10	thiourea	K_2CO_3	CH_3CN	46

[a] Reaction conditions: halides (0.5 mmol), sulfur source (1 mmol), base (0.5 mmol), $Pd(dppf)Cl_2$ (0.005 mmol), solvent (2 mL), room temp., 2 h. [b] Isolated yield of 6-*endo-dig* product.

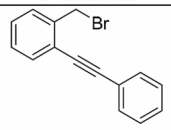
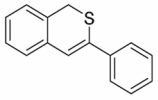
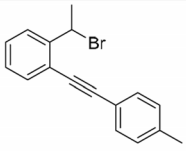
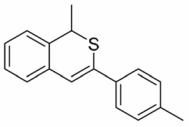
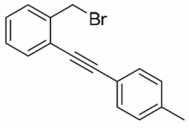
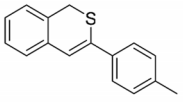
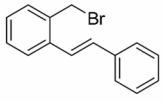
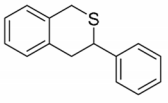
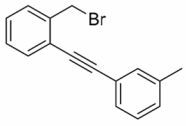
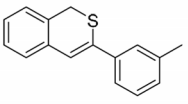
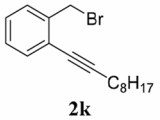
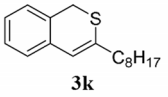
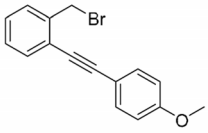
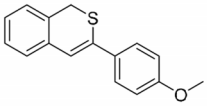
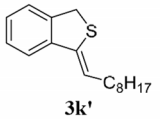
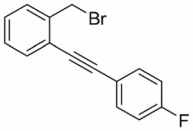
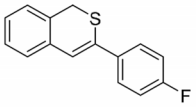
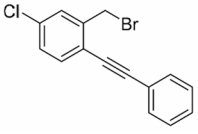
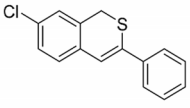
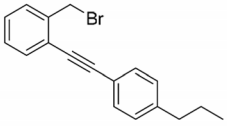
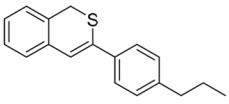
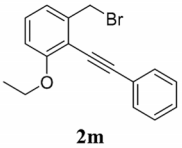
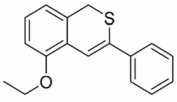
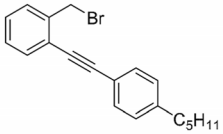
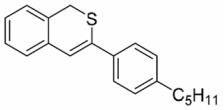
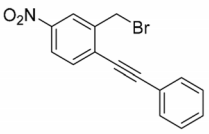
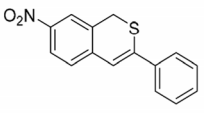
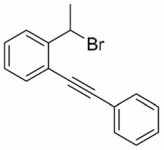
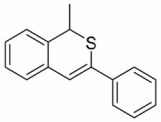
With the optimized conditions in hand, a series of alkynylbenzyl bromides were chosen to establish the scope and generality of the method (Table 3). Initially, the alkynylbenzyl bromides were synthesized from the related alcohols. *o*-Iodobenzyl alcohol and alkyne underwent Sonogashira coupling smoothly in the presence of $Pd(PPh_3)_2Cl_2$ with Et_3N as base and solvent simultaneously. The obtained alkynylbenzyl alcohols were brominated with PBr_3 to give

the desired alkynylbenzyl bromides in good to excellent yields (Scheme 2).[14] The effect of the R^1 group was also investigated. Excellent yields were obtained when R^1 was an aryl group. It is noteworthy that both electron-withdrawing and electron-donating substituents survived the reaction conditions well to give the 6-*endo-dig* products selectively in most cases. Substituents that bore electron-withdrawing groups showed higher yields (Table 3, Entry 5). As

Table 3. Substrate scope of the intramolecular hydrothiolation.[a]

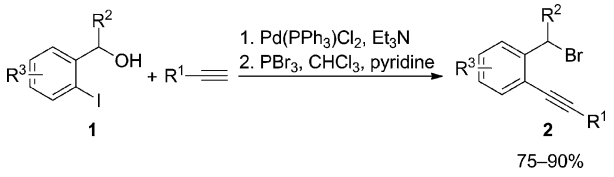


2 **3**

Entry	Substrate **2**	Major product	Yield (%)[b]	Entry	Substrate **2**	Major product	Yield (%)[b]
1	 **2a**	 **3a**	96	9	 **2i**	 **3i**	92
2	 **2b**	 **3b**	95	10	 **2j**	 **3j**	41
3	 **2c**	 **3c**	94	11	 **2k**	 **3k**	60[c]
4	 **2d**	 **3d**	89			 **3k'**	29[c]
5	 **2e**	 **3e**	99	12	 **2l**	 **3l**	93
6	 **2f**	 **3f**	92	13	 **2m**	 **3m**	82
7	 **2g**	 **3g**	85	14	 **2n**	 **3n**	0 (45
8	 **2h**	 **3h**	95				

[a] Reaction conditions: halides (0.5 mmol), thiourea (1 mmol), K_2CO_3 (0.5 mmol), $Pd(dppf)Cl_2$ (0.005 mmol), DMSO (2 mL; contained a trace amount of water), room temp., 2 h. [b] Isolated yield. [c] Determined by ^1H NMR spectroscopy. [d] Yield of debromination product.

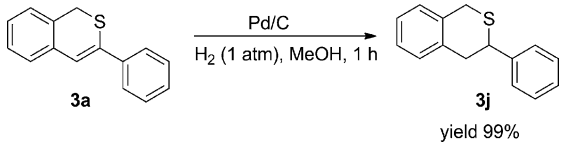
expected, there is a slight decrease of the yield when hindered R^1 groups were used (Table 3, Entries 6 and 7). Interestingly, a mixture of 5-*exo-dig* and 6-*endo-dig* products was observed when R^1 was an alkylalkyne. Yields of 29 and 60%, respectively, were obtained with 2-decynylbenzyl bromide and thiourea (Table 3, Entry 11).



Scheme 2. Synthesis of alkynylbenzyl bromides.

Alkynylbenzyl bromides with different substituents on the benzyl ring were tested. When R^3 was a halogen or an electronic-donating group, the corresponding alkynylbenzyl bromides converted into isothiochromanes smoothly in good to excellent yields (Table 3, Entries 12 and 13). However, when R^3 was a nitro group, the debromination product was formed unexpectedly in 45% yield. Likewise, we also explored substituted α-substituted alkynylbenzyl bromides. Unlike the hydroamination reaction reported by Santos,[15] α-substituted groups did not appear to influence selectivity between 6-*endo-dig* and 5-*exo-dig* products in this palladium-catalyzed protocol (Table 3, Entries 8 and 9).

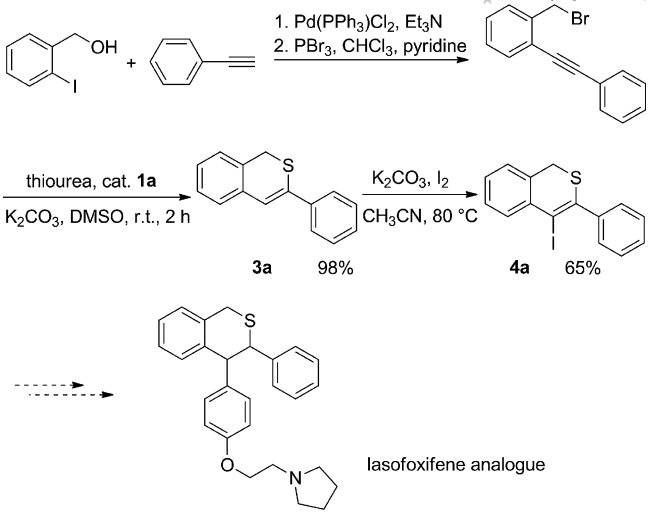
To expand our methodology, we carried out the hydrogenation reaction of the generated double bond to give rise to isothiochromane derivatives. The reduction was easily accomplished by using a Pd/C-catalyzed hydrogenation process with excellent yields (Scheme 3).



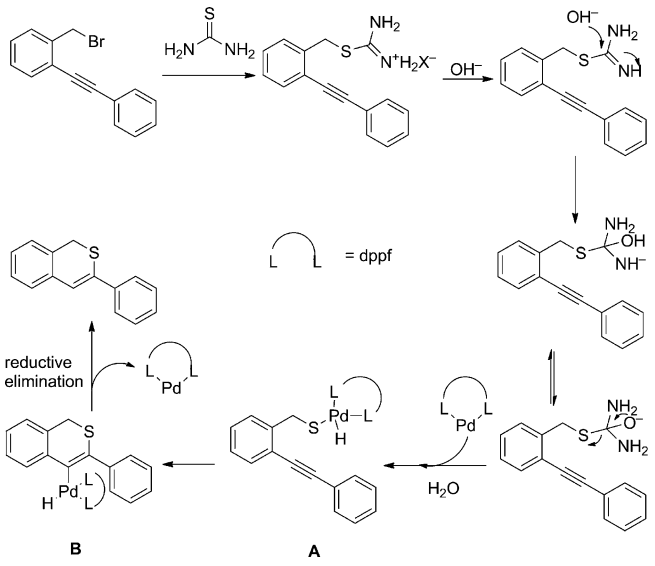
Scheme 3. Reduction of isothiochromenes.

To highlight the potential of this methodology, isothiochromene **3a** – a crucial intermediate for a lasofoxifene analogue – was synthesized in a one-pot, odorless procedure (Scheme 4), rather than by using foul-smelling thiol and organolithium reagents in a multistep protocol as previously reported.[2f]

Finally, a proposed mechanism for the protocol is illustrated in Scheme 5. The reaction proceeds by in situ generation of an *S*-alkylisothiouronium salt, which is hydrolyzed to produce a thiolate moiety and urea. The generated thiolate ion and the palladium complex react to form Pd–S intermediate **A**, which can react with the alkyne to form palladium hydride intermediate **B**. Reductive elimination yields the final products and regenerates the catalyst. The alkyne may also be activated by the palladium complex, which is not shown.



Scheme 4. Potential application of the protocol for the synthesis of a bioactive lasofoxifene analogue.



Scheme 5. Proposed mechanism for the Pd-catalyzed hydrothiolation reaction.

Conclusions

We have developed a method to synthesize 3-substituted 1*H*-isothiochromene derivatives by means of a palladium-catalyzed intramolecular hydrothiolation reaction. Excellent regioselectivity and product yields are obtained efficiently in the presence of $Pd(dppf)Cl_2$ under mild conditions. Two C–S bonds are formed in the one-pot cascade reaction, and this newly developed procedure is free of foul-smelling thiols. In addition, the isothiochromene derivatives react easily to form the respective isothiochromane derivatives and other useful synthetic intermediates.

Experimental Section

General Remarks: All the reagents were commercially available and used without any further purification. Dimethyl sulfoxide (DMSO) was used without drying. Alkynylbenzyl bromides were synthesized according to literature procedures.[14] GC–MS analyses were performed with an Agilent 7890A-5975C instrument (Column: DB-5 MS). ^{1}H NMR spectroscopic data was recorded with a Bruker DRX 500, and tetramethylsilane was used as a reference. Elemental analysis was performed with a Yanagimoto MT3CHN instrument.

General Procedure for the Synthesis of Alkynylbenzyl Bromides: To a mixture of alkyne and *o*-iodobenzyl alcohol (10 mmol) in piperidine (20 mL) were added $Pd(PPh_3)_2Cl_2$ (70.2 mg, 0.1 mmol). The mixture was stirred at 70 °C under argon for 12 h. After that, cold water (30 mL) was added to the mixture, and the resulting aqueous mixture was extracted with diethyl ether (3× 20 mL). The combined organic extracts were washed with hydrochloric acid (3× 20 mL), satd. aqueous $NaHCO_3$ (20 mL), and then dried (Na_2SO_4). The solvent was removed in vacuo. The red residual oil was purified by silica gel chromatography (hexane/ethyl acetate, 90:10) to give the pure alkynylbenzyl alcohol. To a mixture of the alkynylbenzyl alcohol (5 mmol) and pyridine (0.51 g, 6.5 mmol) in chloroform (10 mL) at 0 °C was slowly added phosphorus tribromide (1.5 g, 5.5 mmol) over 1 h. After the addition, the mixture was stirred at room temperature for 12 h. Upon completion of the reaction, the mixture was poured onto ice/water. The resulting aqueous mixture was extracted with CH_2Cl_2 (3× 20 mL), and the combined organic extracts were washed with brine (2× 20 mL) and then dried (Na_2SO_4). After removal of the organic solvent in vacuo, the residual oil was purified by silica gel chromatography (*n*-hexane) to give the pure benzyl bromide.

General Procedure for the Synthesis of the Isothiochromene Derivatives: A mixture of halide (0.5 mmol), thiourea (1.0 mmol), $Pd(dppf)Cl_2$ (0.005 mmol) and K_2CO_3 (0.5 mmol) in DMSO (2.0 mL) was stirred at room temperature for 2 h. Upon completion of the reaction, the mixture was extracted with diethyl ether (3× 5.0 mL). The volatiles were removed in vacuo to afford the crude product. Column chromatography on silica gel (hexane/ethyl acetate, 99:1) afforded the pure desired product.

General Procedure for the Reduction of the Isothiochromenes: A mixture of **3a** (0.5 mmol) and Pd/C (0.025 mmol) in MeOH (1.0 mL) was introduced in a pressure reactor. The suspension was stirred at room temperature under 5 atm of hydrogen for 6 h. After this, the pressure was released and the mixture filtered through a pad of Celite® and washed with ethyl acetate. Evaporation of the solvents rendered compound **3j** without further purification.

General Procedure for the Synthesis of 4a: A mixture of **3a** (0.5 mmol) and K_2CO_3 (0.5 mmol) in CH_3CN (1.0 mL) was stirred at 0 °C. Then iodine was added slowly. The mixture was then stirred at 80 °C for another 24 h. Upon completion of the reaction, the mixture was added to excess sodium thiosulfate to remove the iodine. The mixture was washed with water and extracted with diethyl ether (3× 5.0 mL). The volatiles were removed in vacuo to afford the crude product. Column chromatography on silica gel (hexane/ethyl acetate, 99:1) afforded the pure desired product.

Supporting Information (see footnote on the first page of this article): General procedures, characterization data, and copies of the ^{1}H NMR and ^{13}C NMR spectra.

Acknowledgments

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