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Letter

Gold-Catalyzed Intermolecular Alkyne Oxyarylation for C3 Functionalization of Benzothiophenes

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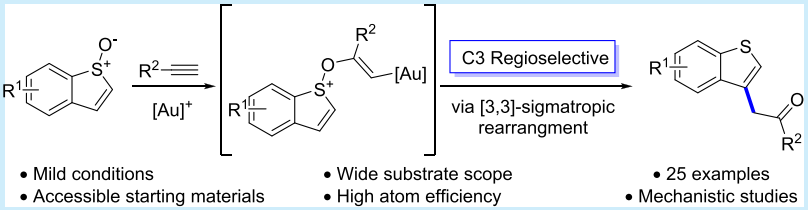


ABSTRACT: C3-selective C−C bond formation on benzothiophenes is challenging, and few direct functionalization methods are available. A gold-catalyzed reaction of alkynes with benzothiophene *S*-oxides provides regioselective entry into C3-alkylated benzothiophenes with the C7-alkylated isomer as the minor product. This oxyarylation reaction works with alkyl and aryl alkynes and substituted and unsubstituted benzothiophenes. Mechanistic studies identify that sulfoxide inhibits the catalyst [DTBPAu(PhCN)]SbF_6, which also degrades and forms the unreactive complex [$(DTBP)_2Au$]SbF_6.

Benzothiophene-containing molecules display unique photophysical and electrochemical properties[1] as well as an array of biological activities against diseases such as cancer, HIV, diabetes, and Alzheimer's disease, rendering them of interest to the materials and pharmaceutical sectors (Figure 1).[2]

The direct functionalization of a benzothiophene provides a synthetically appealing entry into more substituted species, yet diverse methods for selective and direct C−C bond formation at C3 are scarce.[3] Examples include palladium-catalyzed C−H arylations, which require relatively forcing conditions (Scheme 1a),[4] and single examples of alkynylations[5] and vinylations.[6]

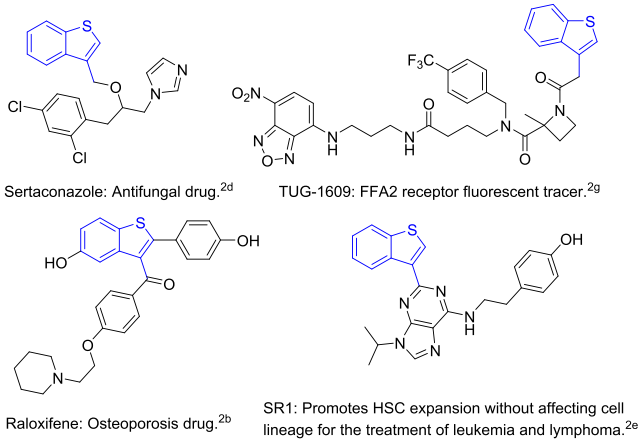
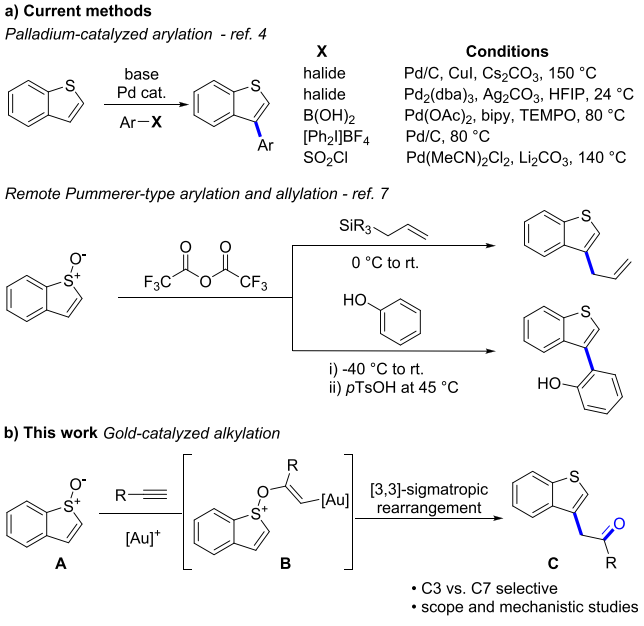


Figure 1. Biologically important molecules that contain C3-substituted benzothiophenes.

Scheme 1. Selective Benzothiophene C3 Elaboration



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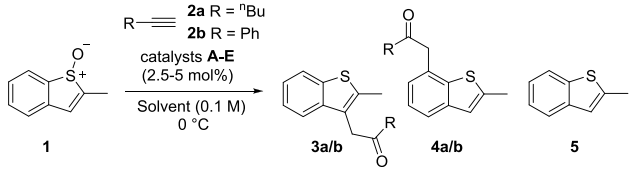
Procter's group introduced an interrupted Pummerer approach allowing C3 arylation and allylation processes on benzothiophene *S*-oxides (Scheme 1a).[7] Here we report a mechanistically distinct benzothiophene functionalization method that uses simple alkynes to access complementary functionality at C3 through a gold-catalyzed oxyarylation process (Scheme 1b).

Gold- and subsequently Brønsted acid-catalyzed C−C bond-forming rearrangements between sulfoxides and alkynes have shown great promise for atom-efficient aryl C−H functionalization and other transformations.[8] For the desired transformation, the vinylgold carbenoid intermediate **B** should evolve through a [3,3]-sigmatropic rearrangement and onto C3 rather than the C7 benzenoid position (Scheme 1b). Rearrangement must occur before the electrophilic organogold species reacts with a second equivalent of sulfoxide.[8c] Our interest in gold-catalyzed reactions with sulfoxides[9] led us to investigate the potential of oxyarylation for C3 benzothiophene elaboration.

Our study started with 2-methylbenzothiophene *S*-oxide (**1**) and 1-hexyne (**2a**), as unsubstituted benzothiophene *S*-oxide is unstable and decomposes out of solution (vide infra).[10] All reactions were performed under non-inert conditions with undried, commercial solvents. A range of Au(I) catalysts was tested (Table 1, entries 1−6). In all cases the product **3a** from reaction at C3 was preferred, but some of the C7-functionalized product **4a** was also seen. Low reactivity occurred with $SPhosAuNTf_2$ and was not improved with higher temperatures (Table 1, entries 1 and 2). Cleaner reactions and greater conversion to the desired product were seen with the phosphite-containing catalyst $[DTBPAu(PhCN)]SbF_6$ over those derived from more electron-rich ligands, with small amounts of benzothiophene **5** also observed in the latter case (Table 1, entries 1−5). Use of a more coordinating tosylate counterion saw reduced activity (Table 1, entry 6).

Table 1. Reaction Optimization Study between 2-Methylbenzothiophene *S*-Oxide and Hex-1-yne or Phenylacetylene



entry	2 (equiv)	catalyst[a]	solvent	yields (1:3:4:5) (%)[b]
1	**2a** (2)	**A**	PhMe	70:16:2:0
2	**2a** (2)	**A** (23 °C)	PhMe	74:16:2:0
3	**2a** (2)	**B**	PhMe	32:39:10:−[c]
4	**2a** (2)	**C**	PhMe	46:33:4:−[c]
5	**2a** (2)	**D**	PhMe	−[d]:55:23:0
6	**2a** (2)	**E**/AgOTs[e]	PhMe	88:6:4:0
7	**2a** (2)	**D**	CH_2Cl_2	0:64:23:−[c]
8	**2a** (2)	**D**	C_6H_5F	7:63:24:0
9	**2a** (1)	**D**	CH_2Cl_2	0:50:17:<6[f]
10	**2b** (2)	**D**	CH_2Cl_2	-[d]:51:9:−[c]
11	**2b** (2)	**D**	C_6H_5F	0:80:10:<7[f]
12	**2b** (2)[g]	**D** (2.5 mol %)	C_6H_5F	0:67:12:<10[f]
13	**2b** (1)	**D**	C_6H_5F	0:62:9:8
14	**2b** (1)[g]	**D**	C_6H_5F	−[d]:50:9:−[c]

[a]**A**, $SPhosAuNTf_2$; **B**, $IPrAuNTf_2$; **C**, $[JohnPhosAu(MeCN)]SbF_6$; **D**, $[DTBPAu(PhCN)]SbF_6$; **E**, DTBPAuCl; DTBP = (2,4-(^{t}Bu)$_2$C$_6$H$_3$O)$_3$P. [b]Yields and ratios were determined by ^{1}H NMR spectroscopy using a known concentration of 1,2,4,5-tetramethylbenzene. [c]**5** was present, but the yield could not be determined because of overlapping resonances. [d]**1** was present, but the yield could not be determined because of overlapping resonances. [e]**E** (0.05 equiv) and AgOTs (0.10 equiv). [f]Represents the maximum possible yield because of overlapping resonances. [g]2 equiv of **1**.

Improved yields were obtained in CH_2Cl_2 and fluorobenzene (Table 1, entries 7 and 8). A more substantial solvent effect was seen upon switching from hexyne to phenylacetylene (**2b**), with fluorobenzene giving a superior outcome with a 90% combined yield of oxyarylation products and much higher regioselectivity (Table 1, entry 10 vs 11). A modest reduction in yield was seen at a catalyst loading of 2.5 mol % (Table 1, entry 12). Reducing the equivalents of alkyne lowered the overall yield of **3** and **4** with both 1-hexyne and phenylacetylene (Table 1, entries 7 vs 9 and 11 vs 13). Reversing the stoichiometry of sulfoxide **1** and phenylacetylene **2b** further reduced the combined yield of **3b** and **4b** (Table 1, entry 14).

The best conditions were then applied across a range of alkynes and benzothiophene *S*-oxides (Scheme 2), with the reactions typically performed on a 0.2−0.5 mmol scale. On the 1.0 mmol scale, isomerically pure **3b** was isolated in 68% yield. Both electron-rich and electron-deficient aryl alkynes underwent oxyarylation successfully. Appreciable amounts of the free benzothiophene were observed with more electron-rich aryl alkynes (Scheme 2, compounds **6**−**9** and **24**). A low yield and poor C3:C7 regioselectivity were seen with an *o*-methoxy group on the aromatic ring. Aliphatic alkynes provided excellent yields with lower regioselectivities compared with aromatic alkynes (Scheme 2, compounds **15**−**18** and **23**). Good functional group tolerance was shown across these reactions with aryl halides, primary alkyl bromide, a tertiary amine, phthalimide, and carboxylic esters all readily incorporated.

The formation of **12**−**15** and **25** (Scheme 2) required higher temperatures for oxyarylation to occur. During the formation of **15** with 2.0 equiv of alkyne, the alkyne hydration product was also formed and was inseparable from the desired product. Using 1.0 equiv of alkyne saw no formation of the hydration side product, and **15** was isolated in good yield. No oxyarylation product was formed when diphenylacetylene and **1** were submitted to the reaction conditions. Only the benzil product from double oxidation of the alkyne was isolated (98% based on sulfoxide **1**).

Benzothiophene *S*-oxides with different substitution patterns also performed well. The reaction proceeds well in the absence of a C2 substituent, and halogen substituents are also tolerated (Scheme 2, **19**−**25**). In several cases very high regioselectivities were observed (>20:1), so simple trituration with methanol was sufficient to obtain the single C3 regioisomer (Scheme 2, **21**, **24**, and **25**). Good outcomes were also observed with an ester group at C2 (Scheme 2, **26** and **27**). The presence of a substituent at C3 did not lead to efficient formation of the C7 oxylarylation product, as a complex mixture was formed upon reaction of 3-methylbenzothiophene *S*-oxide with phenylacetylene **2b**.

As unsubstituted benzothiophene *S*-oxide is unstable when neat, a protocol was developed that telescoped together the *S*-oxidation of benzothiophene with the gold-catalyzed oxyarylation. C3-substituted benzothiophene **28** was obtained in 79% yield over two steps (see the Supporting Information for details).

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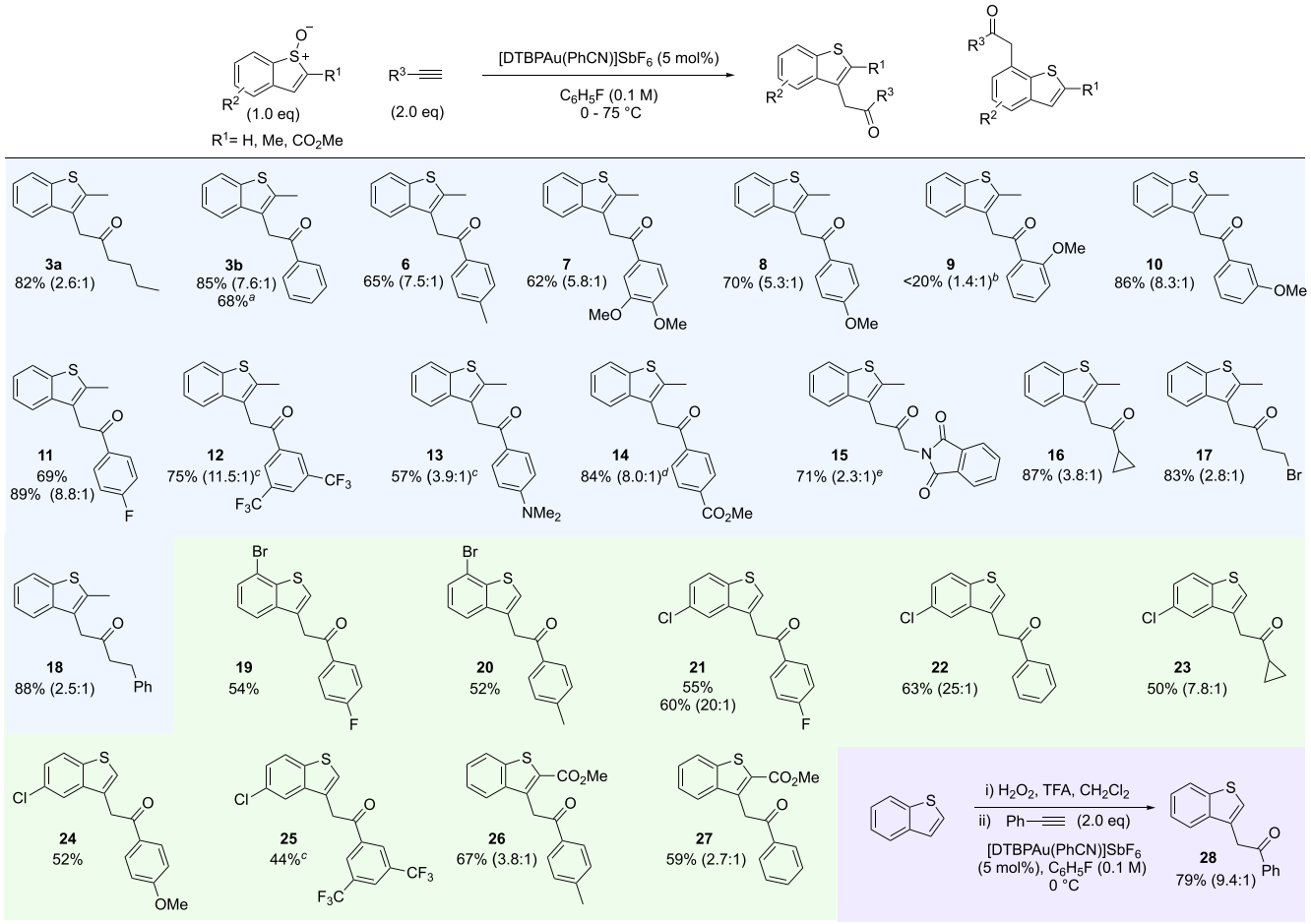
Scheme 2. Scope of Gold-Catalyzed Oxyarylation of Alkynes with Benzothiophene *S*-Oxides[f]



[a]The reaction was performed on a 1.0 mmol scale and afforded the C3:C7 mixture in 84% yield; the pure C3 isomer **3b** was isolated by column chromatography and recrystallization in 68% yield. [b]The reaction was run at 75 °C. [c]The reaction was run at 70 °C. [d]The reaction was run at 50 °C. [e]The reaction was run at 50 °C with 1.0 equiv of alkyne. [f]Ratios refer to the isolated mixtures of C3:C7 regioisomers. Where ratios are not given, the yield refers to the isolated yield of the C3 regioisomer. The standard conditions used, unless stated otherwise, are 2.0 equiv of alkyne, 5 mol % [DTBPAu(PhCN)]SbF_6, and a reaction temperature of 0 °C.

Studies were then initiated in order to gain further insight into the mechanism (Scheme 3 and further details in the Supporting Information). Crossover experiments saw the formation of the oxyarylation products from only the benzothiophene *S*-oxide component and not the benzothiophene dopant (Scheme 3a).

Higher effective equivalents of sulfoxide **1** gave reduced yields of the functionalized benzothiophenes (Table 1, entries 9, 13, and 14). Monitoring the progress of an oxyarylation reaction of **1** and **2a** by in situ ^{1}H NMR spectroscopy showed the significant effect of the sulfoxide concentration (Scheme 3b). Under otherwise identical conditions, doubling the concentration of the limiting sulfoxide reagent **1** led to a substantially lower concentration of products **3b**/**4b** over the same reaction time (Scheme 3b), with no increase in the formation of free benzothiophene **5**. No other side products were seen in either reaction. A simultaneous comparison of batch- and slow-addition of the sulfoxide showed that the latter yielded more oxyarylation products **3b**/**4b** (Scheme 3b). An increase in the yield of oxyarylation products with more equivalents of alkyne was also observed (Table 1, entries 7 vs 9 and 11 vs 13). No reduction in reaction progress was seen when a catalysis reaction was doped with an oxyarylation product (Scheme 3c).

An upfield shift in the ^{31}P NMR resonance from 88 to 81 ppm was observed upon addition of sulfoxide **1** to [DTBPAu(PhCN)]SbF_6 at 0 °C. The free DTBP ligand was not observed in the ^{31}P NMR or ^{1}H NMR spectra, while benzonitrile was observed in the ^{1}H NMR spectrum. A new minor resonance at 120 ppm was also observed, but this could also be seen in small amounts from the untreated catalyst in $CDCl_3$. Addition of phenylacetylene to [DTBPAu(PhCN)]SbF_6 resulted in the formation of several new ^{31}P resonances, with a major one at 120 ppm. This resonance was identified as [$(DTBP)_2$Au]SbF_6 by in situ synthesis and also by isolation (Scheme 3d, i). The bisphosphite complex was formed preferentially and irreversibly in the presence of free ligand, with no change observed on addition of excess benzonitrile, sulfoxide, or phenyacetylene (Scheme 3d, ii). Using [$(DTBP)_2$Au]SbF_6 in a reaction with sulfoxide **1** and phenylacetylene gave only a trace amount of product (<5%) after an extended reaction time.

On the basis of these observations, the broader mechanism is consistent with that established by Ujaque et al.,[8b] where sulfoxide addition to an alkyne−gold complex generates a

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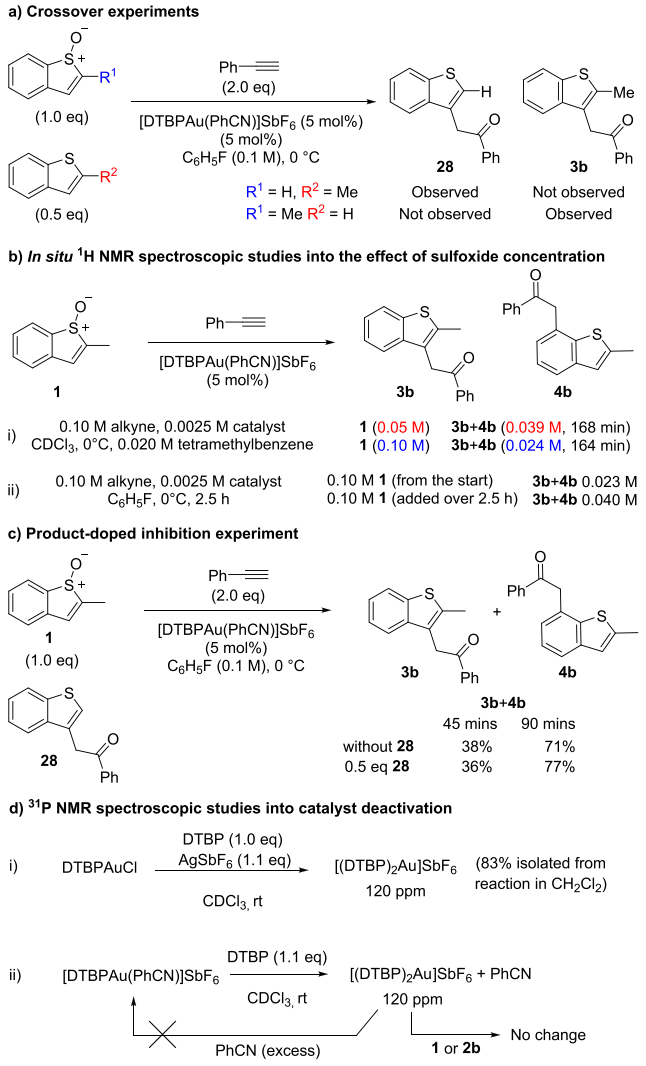
Scheme 3. Mechanistic Studies



vinylgold carbenoid intermediate that undergoes [3,3]-sigmatropic rearrangement and then rearomatization and protodeauration. The alternative carbene formation and electrophilic aromatic substitution pathway can be ruled out from the results of the crossover experiments and the ready formation of compounds **26** and **27** bearing a deactivating ester group at C2.

Sulfoxide inhibition of the reaction is seen, as are direct interactions between sulfoxide **1** and the gold complex. The release of DTBP by catalyst degradation pathways, as observed in the presence of phenylacetylene, will reduce the amount of any remaining active catalyst by formation of $[(DTBP)_2Au]SbF_6$, which is essentially a catalytic dead-end for the desired process.

In summary, gold-catalyzed reactions between readily accessed benzothiophene *S*-oxides and terminal alkynes provide efficient and selective access to C3-alkylated benzothiophenes bearing a useful carbonyl group for subsequent exploitation. The approach is compatible with a variety of electron-rich and electron-deficient aromatic and aliphatic alkynes as well as reactive functionalities including carboxylic esters, tertiary amines, phthalimide, and alkyl and aryl halides. The highest regioselectivities are seen with aryl alkynes. The reactions are straightforward to perform and do not require dry or inert conditions or high temperatures. This is the first instance of the use of gold-catalyzed oxyarylation to modify a sulfur-containing ring. The reaction is compatible with substitution around the benzothiophene, including halogens and electron-withdrawing groups. A telescoped oxidation−oxyarylation sequence has also been developed.

Sulfoxide was determined to inhibit the gold-catalyzed process, which may have wider relevance in other gold-catalyzed transformations. This study also highlights the need for further development of more robust gold complexes that retain the reactivity profile of phosphite Au(I) species.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c03596.

Details of the effect of the sulfoxide **1** concentration on oxyarylation reactions, in situ ^{31}P NMR catalyst studies, assignment of regioisomers **3b** and **4b**, experimental details, compound characterization data, and copies of NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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