Thioarylation of Alkynes to Generate Dihydrothiopheniums through Gold(I)/(III)-Catalyzed Cyclization–Cross-Coupling

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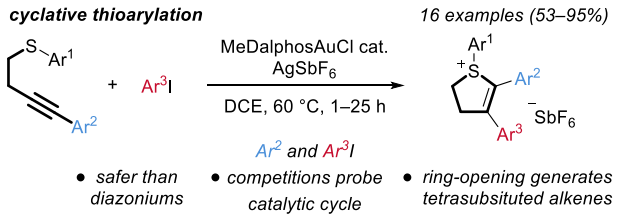
Supporting Information Placeholder



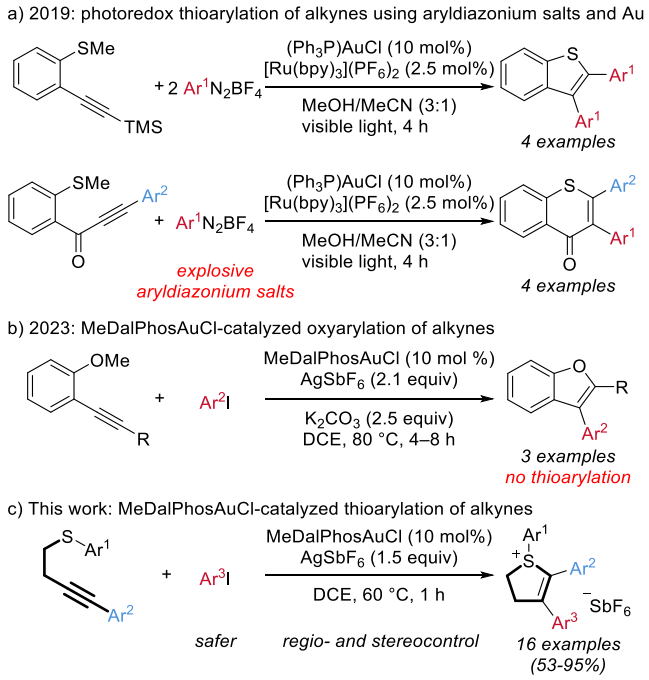
ABSTRACT: A thioarylation method is developed for the synthesis of 2,3-dihydrothiopheniums through an electrophilic-cyclization–cross-coupling mechanism, harnessing the gold(I)/(III) cycle of the recently developed MeDalPhosAuCl catalyst. Single-crystal X-ray crystal structural analysis of the dihydrothiophenium products characterized the anti-addition of the sulfur and Csp^2 group to the alkyne and a preference for 5-endo dig cyclization. The dihydrothiophenium products are demonstrated as synthetic building blocks for stereodefined acyclic tetrasubstituted alkenes upon ring-opening reaction with amines. Intramolecular competition experiments show the favorability of Csp^3 tether cyclizations over Csp^2 tethers, preferentially generating dihydrothiopheniums over thiopheniums. Intermolecular competition experiments of alkyne aryl groups and an intermolecular aryl iodide competition suggest a rate-determining reductive elimination step in the gold(I)/gold(III) catalytic cycle. This rate-determining step is further supported by HRMS analysis of reaction intermediates that identify the catalyst resting state under turnover conditions. Catalyst poisoning experiments provide evidence of substrate inhibition, further consistent with these conclusions.

Introduction

S-Heterocycles and thioalkenes are represented in pharmaceuticals and bioactive molecules.[1–7] Transition metal mediated and catalyzed alkyne addition reactions[2,8–14] provide complementary bond disconnections to access these structures. For example, in 1994, Pfeffer thioarylated alkynes by the action of stoichiometric palladium.[15] Since then, platinum-,[16–18] rhodium-,[19] iron-,[20] palladium-,[21–24] nickel-,[25,26] and gold-catalyzed reactions (Scheme 1a)[27] have produced a range of acyclic thioalkenes and *S*-heterocycles. Each reported method has demonstrated limitations, however—for example, restriction to terminal alkynes,[17–19,22–26] low stereocontrol for iron,[20] low yields for electron-neutral and electron-rich cross-coupling partners,[21] or the requirement for explosive[28,29] aryldiazonium salts.[27]

The recently reported MeDalPhosAuCl catalyst provides an intriguing opportunity to avoid these limitations. The reactivity imparted through the MeDalPhos ligand is reported to enable access to gold(I)/(III) cross-coupling catalysis with aryl iodide partners[30–32] without requiring light activation or highly activated aryldiazonium salts to circumvent the high energy barrier to oxidative addition. MeDalPhosAuCl has been demonstrated to be effective in *O*-, *N*-, and *C*-cyclization– arylations of alkenes.[31] To date, however, there are only two

Scheme 1. Gold-catalyzed heteroarylations of alkynes



reports of *C*- and *O*-cyclization–arylation of alkynes, which are plausibly the most closely related reactions to those developed here (Scheme 1b).[31,33] Additionally, MeDalPhosAuCl has been used as a π Lewis acid to activate alkyne amidation with nitrogen nucleophiles while remaining at gold(I) or gold(III), and without undergoing gold(I/III) cross-coupling catalysis.[34] The comparatively sparse development of MeDalPhosAuCl to promote heteroarylations of alkynes, despite the established activation of alkynes by gold(III) generally,[35–38] suggests untapped potential toward alkyne thioarylation with MeDalPhosAuCl.

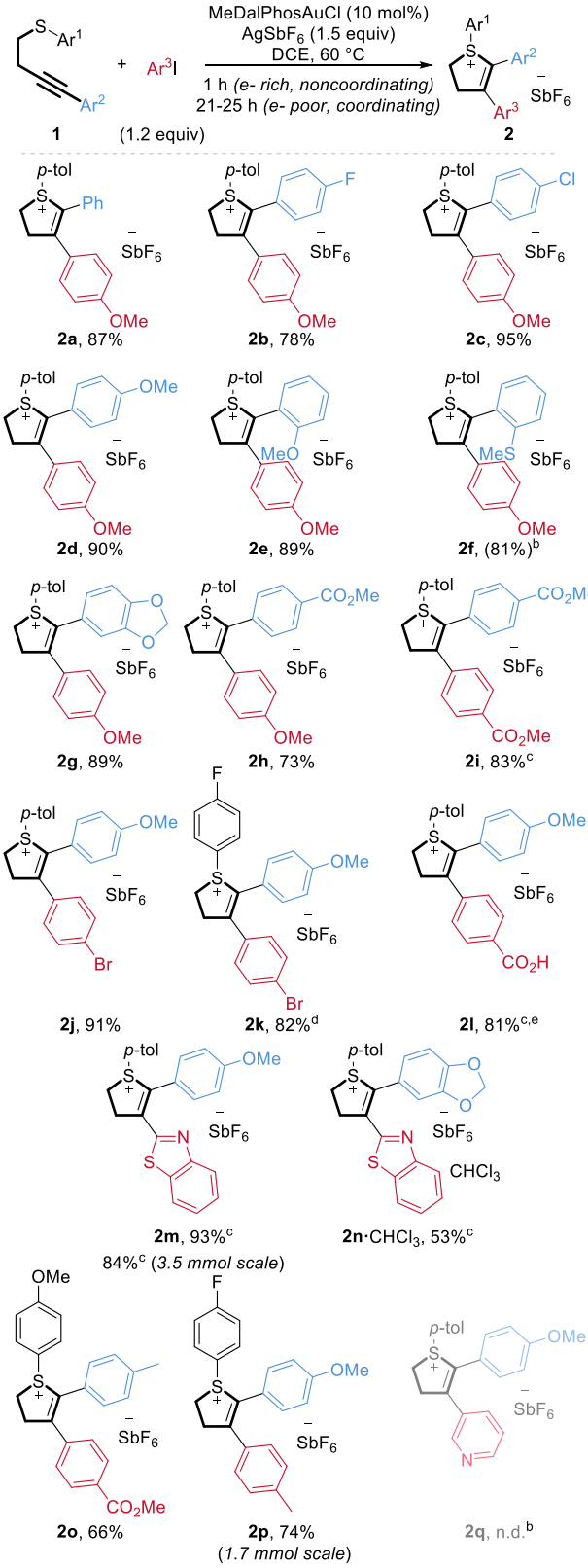
Herein, a method is developed for adding a sulfur and Csp^2 coupling partners across alkynes through a tandem electrophilic-cyclization–cross-coupling reaction (Scheme 1c). The developed reaction provides access to dihydrothiopheniums, which are found in glucosidase inhibitors;[6] their use as synthetic precursors to stereo- and regiodefined tetrasubstituted alkenes is also developed and demonstrated. Further, these reactions provided a platform for mechanistic investigations that offered principles suitable for guiding further catalytic reaction development.

Results and Discussion

Substrates **1** were produced by first substituting 4-bromobut-1-yne with aryl thiols. Functionalization of the resulting terminal alkynes with aryl iodides via Sonogashira cross-coupling reactions produced **1**. Combination of **1** with an array of aryl iodides, MeDalPhosAuCl, and $AgSbF_6$ in DCE at 60 °C afforded dihydrothiopheniums **2** (Scheme 2). These thioarylation reactions were performed in air, providing enhanced operational simplicity. The reaction was complete in an hour in most cases as determined by ^{1}H NMR spectroscopy, with the exception of those reactions generating soft Lewis-base-containing (**2f**, **2m**, **2n**) or electron-poor (**2i**, **2l**,) products, which required 21–25 h. The longer reaction times required to generate electron-poor products was initially hypothesized to be due to the increased unfavorability of the reductive elimination from gold(III), whereas this increased-time effect with soft Lewis-base-containing products was hypothesized to arise from inhibitory coordination with $AgSbF_6$ or the gold catalyst. These early observations thus provided springboards for mechanistic investigations, as will be discussed later.

Products **2** are ion pairs, suggesting that the organic fragment of **2** was reductively eliminated as a sulfonium cation. Consistent with this assessment, reductive elimination from gold(III) to form phosphonium[39] and ammonium products[39,40] has been reported. By contrast, other investigations of MeDalPhosAuCl-catalyzed electrophilic-cyclization–arylation reactions indicate the accessibility of an alternative neutral-product reductive elimination pathway. The major difference between these reported neutral reductive eliminations and the current reaction, however, is the availability in those cases of an acidic proton on the cationic fragment formed during the cyclization step, thus providing a pathway for deprotonation and neutralization. There is one example of a cyclization–demethylation that plausibly proceeds through reductive elimination of an oxonium followed by neutralizing demethylation;[41] however this step of the mechanism was not investigated, and thus the order of neutralization is unclear (i.e., demethylation/neutralization before or after reductive elimination). In the current thioarylation reaction dealkylation does not occur, indicating likely direct reductive elimination of cationic **2**.

Scheme 2. MeDalPhosAuCl-catalyzed thioarylation–cyclization reaction yielding 2,3-dihydrothiopheniums 2, substrate scope[a]



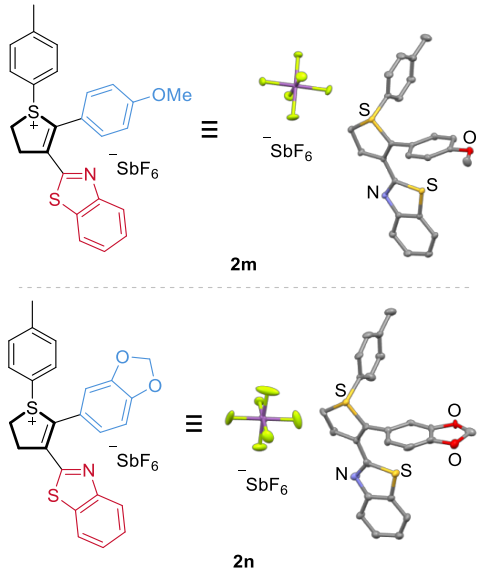
[a]0.100 mmol scale unless otherwise stated. [b]$AgSbF_6$ (3 equiv) for 23 h. [c]21–25 h. [d]0.500 mmol scale with $AgSbF_6$ (1.6 equiv) and Ar^3I (1.5 equiv). [e]0.200 mmol scale.

Yields of **2** ranged from 53%–95%. Notably, the reaction was chemoselective for the coupling of aryl iodides over the aryl fluorides, chlorides, and bromides present in substrates, to produce **2b** (78%), **2c** (95%), **2j** (91%), **2k** (82%), and **2p** (74%). The reaction tolerated carboxylic acids to generate **2l** (81%). High yields of products **2g** (89%) and **2m** (93%) showed that certain spectator *O*, *N*, and *S*-heterocycles were well-tolerated. Additionally, the reaction proceeded smoothly on the mmol scale (**2m**, 84% and **2p** 74%). Products **2e** (89%), **2f** (81% NMR spectroscopy yield), and **2g** also show that ortho- and meta-substituted benzene substrates can be tolerated. Product **2f** was sensitive toward decomposition during attempted isolation.

The attempted coupling with 3-iodopyridine to produce **2q** identified a limitation of this method (yield not determined). Sluggish conversion and a reaction that appeared to "stall" were not overcome by increasing the reaction time from 1 h to 23 h, nor by further increasing the amount of $AgSbF_6$ to 3 equiv or 6 equiv (see SI S107 for comparison of crude ^{1}H NMR spectra). Moreover, attempted purification of the crude product by normal phase column chromatography appeared to cause further degradation. The failure of this coupling partner was plausibly caused by inhibitory coordination of pyridine to the gold catalyst and/or its participation as a nucleophile in dihydrothiophenium ring-opening reactions (vide infra, Scheme 9). Aliphatic thiol ethers dealkylate rapidly in the presence of halides under similar cyclization conditions,[8,42–44] thus this synthetic method development harnessed aromatic thiol ether substrates.

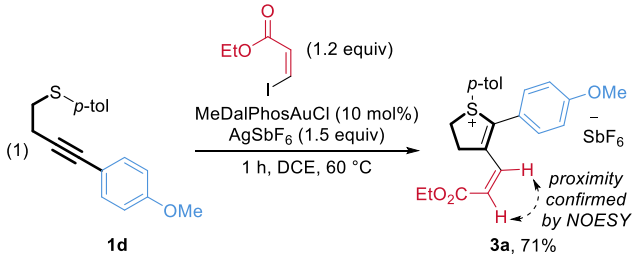
Single-crystal X-ray analysis of products **2m** and **2n** characterized the 5-endo-dig cyclization selectivity of this reaction (Scheme 3). The resulting regiochemistry was consistent with analogous reported electrophilic thiocyclizations with boron and iodine electrophiles, which suggested that the cyclization mechanism is likely a similar activation of the alkyne by an electrophile followed by thiocyclization.[45–48]

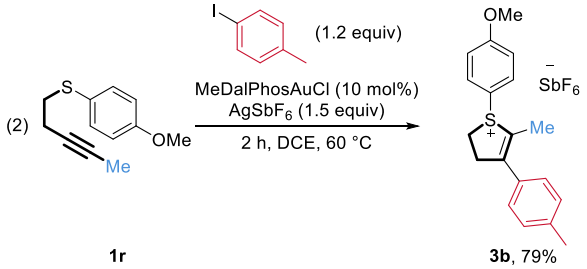
Scheme 3. X-ray crystal structures of products 2m and 2n with thermal ellipsoids shown at 50% probability



Next, thio*alkenyl*ation was tested using ethyl (*Z*)-3-iodoacrylate (eq 1). The reaction generated dihydrothiophenium **3a** (71%). Proximity analysis by ^{1}H NOESY NMR spectroscopy confirmed retention of the cis alkene stereochemistry, consistent with other reported iodoalkene couplings with

MeDalPhosAuCl.[41,49,50] To test if groups other than aryl Ar^2 at the alkyne position were amenable to the thioarylation reaction, methyl-substituted-alkyne substrate **1r** was subjected to reaction conditions with 4-iodotolene (eq 2). The reaction yielded sulfonium **3b** (79%), indicating that the thioarylation reaction is amenable to alkyl substitution in addition to the aryl substituted alkynes mainly demonstrated.

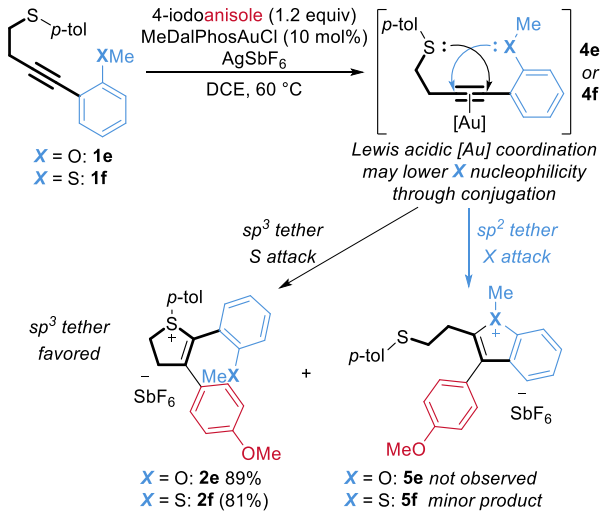




The reactions to form products **2e** and **2f** provided and intramolecular competition platform, competing between an *O*-phenyl tether (in catalytic intermediate **4e**) or *S*-phenyl tether (in catalytic intermediate **4f**) cyclization (Scheme 4). Specifically, **1e** contained an ortho methoxy group on Ar^2, with established potential to oxyarylate the alkyne under similar conditions with MeDalPhosAuCl;[41] however, in this competition, only product **2e** was observed in the crude ^{1}H NMR spectrum (see SI). The selectivity for **2e** over **5e** suggested the favorability of sulfur with an alkyl tether over oxygen with a phenyl tether, presumably due to its higher nucleophilicity.[51]

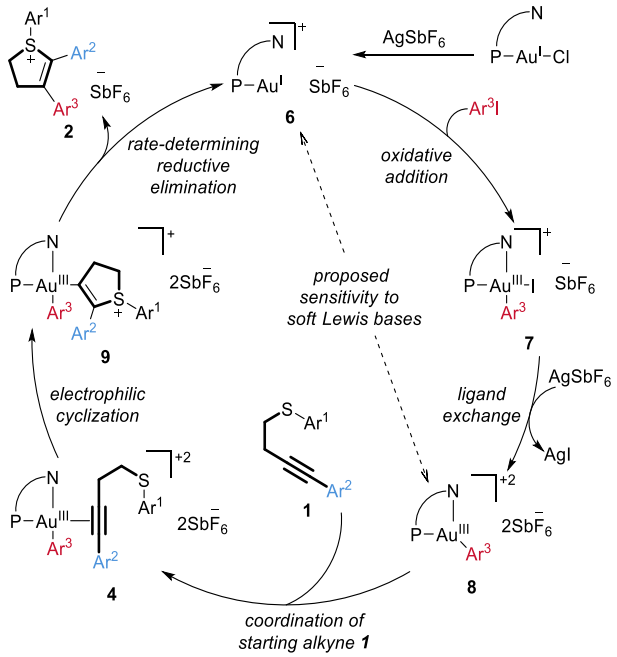
Swapping the ortho substituted O for S resulted in a competition experiment between two types of sulfur nucleophiles in substrate **1f**: *S*-alkyl and *S*-phenyl. This reaction formed dihydrothiophenium **2f** as the major product, again favoring the *S*-alkyl tether cyclization. In this case, however, ^{1}H NMR spectroscopic analysis of the crude reaction mixture indicated that a second product was formed, plausibly the benzothiophenium product **5f**, from competing minor *o*-ArSMe cyclization (see SI S111 for annotated crude ^{1}H NMR spectra). The favorability of cyclization with an sp^3 over an sp^2 tether is consistent with analogous electrophilic heterocyclizations with sulfur.[42]

Scheme 4. Internal competition experiments



The catalytic cycle in Scheme 5 is proposed on the basis of known oxidative addition/reductive elimination steps for gold(I)/gold(III)[31,52,53] complexes, and on steps in related electrophilic cyclization chemistry[45–47]. In order to test this preliminary mechanism and to gain an understanding of the plausible rate-determining and selectivity determining step(s) and catalyst resting state, additional mechanistic experiments were next performed.

Scheme 5. Proposed catalytic cycle

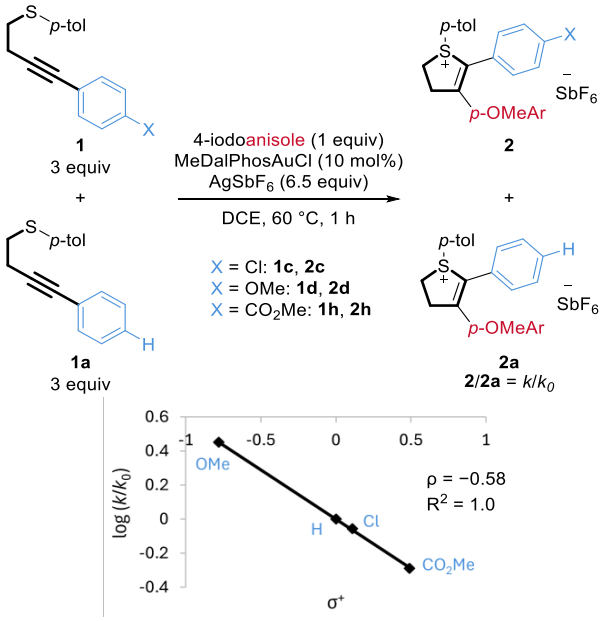


A set of intermolecular competition experiments examined the electronic effect at the alkyne through varying the substitution at the para position of Ar^2 (Scheme 6). The resulting product ratios produced the Hammett plot shown in Scheme 6, with a ρ of -0.58 when comparing $\log(k/k_0)$ to σ^+. A better fit was obtained with σ^+ (shown, $R^2 = 1.0$) than with σ_p (see SI). This negative ρ is consistent with stabilization of the rate-determining transition state by electron-rich groups on Ar^2, suggesting partial positive charge build-up on the alkyne during

this step. The better fit with σ^+ is consistent with this buildup of a positive charge at a position that is in direct conjugation with the para substituent.[51]

Together, these outcomes narrow the candidates for rate-determining step to two of the steps shown in the plausible catalytic cycle in Scheme 5: coordination of **1** to **8**, or reductive elimination from **9**. Coordination of **1** to **8** should generate a partial positive charge on the alkyne, and this partial positive would be in direct conjugation with Ar^2, consistent with the observed trend. Alternatively, the rate of sp^2–sp^2 reductive elimination from gold(III) was reported to be slower with increasingly electron-deficient groups;[39,54] assuming similarity to these prior reports, reductive elimination from **9** would also be slower for electron-deficient Ar^2, consistent with the observed trend. By contrast, electrophilic cyclization of **4** to generate **9** would be expected to be accelerated by more electron-deficient Ar^2, which would increase the electrophilicity of the alkyne, making it more susceptible to nucleophilic attack by sulfur during cyclization.

Scheme 6. Hammett plot from intermolecular alkyne competition.

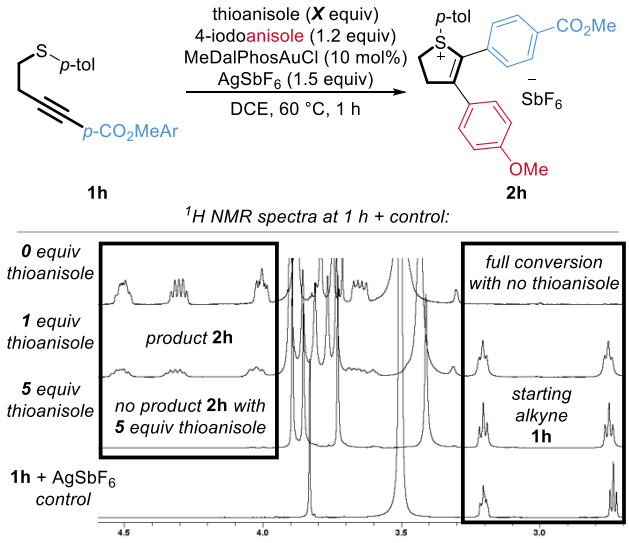


Unexpectedly, this reaction appeared to display substrate inhibition. Specifically, substrate inhibition was observed during a preliminary attempt at the above-mentioned intermolecular competition experiment, wherein excess alkynes **1a** and **1d** (3 equiv each) reacted with 4-iodoanisole (1 equiv), $AgSbF_6$ (1.1 equiv), and MeDalPhosAuCl (10 mol%) in DCE (0.1 M) for 1 h at 60 °C. Despite the prior observations that reactions of **1a** or **1d** were complete under similar conditions when **1** was the limiting reagent (Scheme 2), no conversion was observed when **1** was added in 6× excess relative to 4-iodoanisole. Due to lack of conversion, the initial competition experiment did not provide results under these conditions. This issue of no conversion, however, was resolved by modifying the reaction conditions to add 6.5 equiv of $AgSbF_6$ (rather than 1.1), which resulted in full conversion of aryl iodide under otherwise identical conditions and these conditions were employed to obtain the Hammett correlation in Scheme 6. A plausible interpretation of these sensitivities to reagent equivalents is that competitive coordination by the large excess of the thioether in starting materials **1** to the $AgSbF_6$ (or perhaps to the catalytic gold species) inhibited the reaction. The coordinated silver would then be coordinatively saturated and unable to extract halide, preventing reaction. Alternatively, alkynyl sulfides could bind to coordinatively unsaturated gold complexes **6** or **8**, causing inhibition. The addition of excess silver overcame these competitive coordinations by either providing sufficient silver for halide sequestration despite this binding, or by the excess silver outcompeting gold catalyst for thioether binding, enabling progression of the catalytic cycle. While not neutral thioethers, previous reports have demonstrated the deleterious effects of sulfur anions on gold(I)/(III) catalysis and even show the importance of silver salts in freeing gold complexes analogous to **6** from unproductive complexation with sulfur anions.[55–57] Complexation of sulfur anions to catalytic species analogous to **8** were also proposed as a productive part of C–S cross-coupling catalysis.[55–57] These prior reports lend credibility to the proposed coordination in the current system.

The plausibility of inhibitory thioether binding was next investigated separately in more detail. First, coordination of **1** to silver was explored by ^{1}H NMR spectroscopy, which revealed shifted resonances of **1h** in the presence of 1.5 equiv $AgSbF_6$ (Scheme 7) compared to in its absence (see SI, S126), supporting the premise of the hypothesis.

Second, exogenous thioanisole was added to the otherwise standard reaction, as a noncyclizable analog for excess starting material **1** (Scheme 7). ^{1}H NMR spectroscopic comparison of reaction progress showed that under otherwise identical reaction conditions and timing, the addition of 1 equiv of thioanisole slowed the reaction. This result was consistent with the substrate inhibition previously observed under intermolecular competition reaction conditions. Despite the sum of 1 equiv of thioanisole and 1 equiv thioalkyne **1h** resulting in 2 equiv "total thioether," compared to 1.5 equiv of $AgSbF_6$ (i.e., a slight excess), there was still some conversion to product at 1 h, suggesting reversible coordination to silver. Addition of 5 equiv of thioanisole completely inhibited conversion to **2h**, as established by the absence of any conversion at 1 h. Together, these results displayed an inhibiting effect of thioethers and thus support the hypothesis that excess alkynyl sulfide starting material **1** could inhibit the cyclization–thioarylation reaction. The inhibiting effect of sulfur may, in part, explain why reactions forming **2f**, **2m**, and **2n**, which contained additional sulfur-containing functionality, were incomplete in 1 h and required longer reaction times to achieve synthetically viable yields (Scheme 2).

Scheme 7. Thioanisole inhibited product formation as determined by ^{1}H NMR spectroscopy.



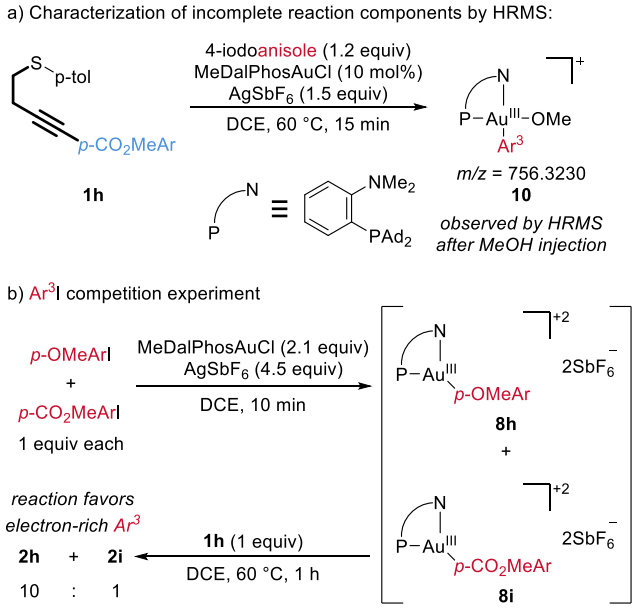
Examination of the reaction at partial conversion (15 min) enabled characterization of the catalyst resting state under turnover conditions (Scheme 8a). Analysis of an aliquot of the ongoing reaction mixture by HRMS detected gold(III) species **10** (*m/z* = 756.3230), plausibly produced from proposed catalytic intermediate **8** (Scheme 5) after reaction with methanol during MS analysis. Intentional reactions of methanol with MeDalPhosAuCl have yielded an analogous complex.[58] Catalytic intermediate **8** is the most straightforward assignment of resting state; however, alternatively **8** could be formed during MS analysis from resting states **4** or **9** upon reversion in the presence of methanol. Regardless, this detection of gold(III) in solution strongly suggests that the rate-determining step of the reaction occurs after oxidative addition, because oxidative addition must occur for gold(III) to be produced and for it to pool. This observation is consistent with conclusions from preceding experiments as well.

To complement the mass spectrometry analysis of the reaction of **1h** prior to reaction completion, ^{1}H and ^{31}P NMR spectroscopic analyses of the incomplete reaction were also performed (see SI, S10 for procedure and S121 for spectra). Analysis by ^{1}H NMR spectroscopy established incomplete conversion of **1h** after 15 min and provided evidence for two cyclized sulfonium compounds: The characteristic diastereotopic ^{1}H peaks of the dihydrothiophenium product **2h** were present as were another set of diastereotopic ^{1}H peaks, suggesting a second cyclic sulfonium was present in the reaction mixture, plausibly catalytic intermediate **9**. An accompanying ^{31}P NMR spectrum of the solution showed only one peak at 47 ppm, indicative of one gold catalyst species. Reaction solutions designed to generate Au species **6**, **7**,[30,41,59] **8**, and **6** coordinated to alkyne[41] through stepwise stochiometric reactions generated ^{31}P NMR spectroscopy shifts different from that observed in the 15 min reaction mixture, excluding such gold species from assignment possibility.

^{1}H NMR analysis of the reaction mixture at 1 h showed complete consumption of the alkyne **1h** and loss of the major ^{31}P NMR spectroscopy peak at 47 ppm, instead showing a major peak that was be attributed to catalyst species **8** through comparison with the stepwise stochiometric reactions described above. In summary, the evidence of pooling at **9** is therefore provided by ^{1}H NMR and ^{31}P NMR spectroscopy; the HRMS evidence of **10** suggests reversibility of **9** back to **4** and **8**.

To further investigate the nature of the rate-determining step, a competition experiment was performed to characterize the selectivity between stoichiometric gold(III) complexes derived from 4-iodoanisole and methyl 4-iodobenzoate (Scheme 8b). First, the two aryl iodides (1 equiv each) were combined with MeDalPhosAuCl (2.1 equiv) and $AgSbF_6$ (4.5 equiv) and the mixture was stirred at ambient temperature for 10 min to form oxidative addition products **8h** and **8i** (or possibly the corresponding pre-salt-metathesis **7h** and **7i**). Oxidative addition of **6** to aryl iodides to form **7** is reported to be complete in under 1 min at ambient temperature,[60] leading to our selection of 10 min for targeting full conversion for both reactions. This pre-formation process ensured that only the steps after oxidative addition were involved in the final selectivity competition reaction steps with **1h** as next described.

Scheme 8. Rate-determining step mechanistic investigations

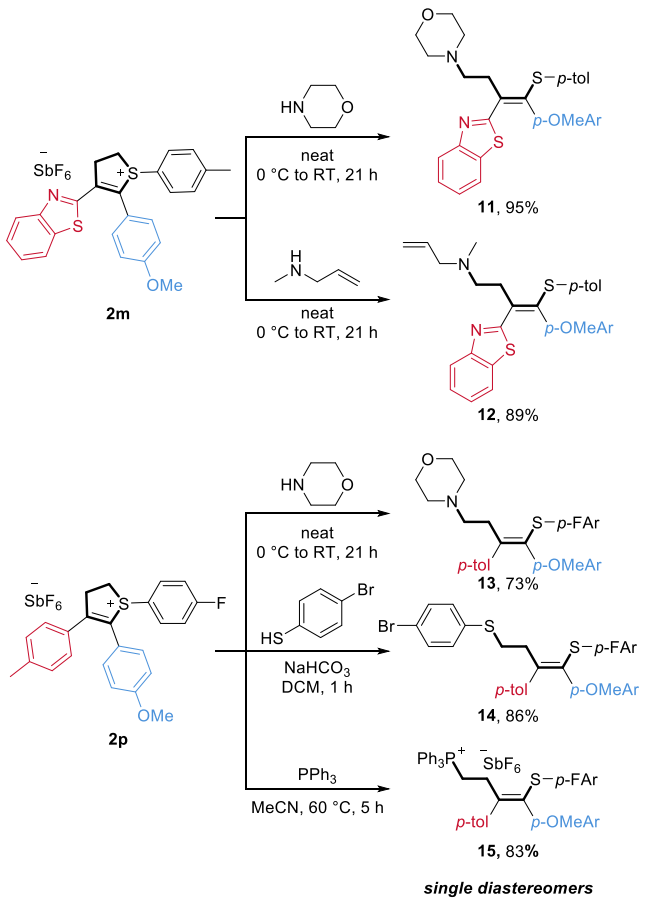


Next, alkyne **1h** (1.0 equiv) was added. This step of the reaction resulted in a 10:1 ratio of dihydrothiopheniums **2h** (Ar^3 = *p*-OMeAr)–to–**2i** (Ar^3 = *p*-CO_2MeAr) which established that the more electron-rich gold complex **8h** reacted faster. The resulting ratio suggests that reductive elimination from **9** to product **2** with regeneration of gold(I) **6** is the rate-determining and selectivity-determining step in this stoichiometric reaction because reductive elimination of Csp^2–Csp^2 bonds from gold(III) is reported to be faster with electron donating groups and slower with electron withdrawing groups.[39,54] (Interpretation of this experiment depends on oxidative addition being irreversible.) In contrast, alternative rate-determining steps that agree with pooling of the catalyst after oxidative addition (i.e., coordination of alkyne **1** to **8** or cyclization to generate **9**) would be accelerated by an electron poor gold(III) caused by

electron withdrawing groups on Ar[3], which was not observed. Extension of the lessons learned from this stoichiometric reaction to the catalytic reaction suggested that reductive elimination from **9** is the rate-determining step.

The dihydrothiophenium products proved to be viable precursors to stereo- and regiodefined acyclic tetrasubstituted alkenes (Scheme 9). Amination product **11** (95%) was afforded from **2m** upon ring-opening treatment with neat morpholine; amine **12** (89%) was obtained from **2m** upon treatment with neat *N*-allylmethylamine. Access to diastereomerically and regiochemically pure alkenes (as established in the crude ^{1}H NMR spectra) harnesses the regio- and stereochemistry embedded in the dihydrothiopheniums as set through the cyclization–cross-coupling reaction. Sulfonium **2p** was similarly afforded from morpholine to yield **13** (73%).

Scheme 9. Downstream functionalization of 2m through ring opening



The sulfonium products were also amenable to sulfur and phosphorous substitution. Substitution of **2p** by 4-bromobenzenthiol generated **14** (86%), and by triphenylphosphine generated **15** (83%), which is a potential Wittig reagent.[61] In the five examples in Scheme 9, access to diastereomerically and regiochemically pure alkenes (purity as established in the crude ^{1}H NMR spectra) harnessed the regio- and stereochemistry embedded in the dihydrothiopheniums as set through the cyclization–cross-coupling reaction.

Conclusions

An alkyne thioarylation method was developed to create substituted 2,3-dihydrothiophenium salts (**2**). The method progresses through an electrophilic-cyclization–cross-coupling reaction of alkynyl sulfides and aryl iodides. This development expanded the cross-coupling reactivity of MeDalPhosAuCl to include carbothiolation. Catalyst poisoning studies established the inhibitory effect of substrates and thioethers generally and provided a strategy with excess $AgSbF_6$ to overcome this inhibition. Mechanistic studies identified a plausible rate-determining reductive elimination step. The reaction products were amenable to ring-opening substitutions, which demonstrated this reaction's potential to create tetrasubstituted alkenes with regio- and stereocontrol. This electrophilic-cyclization–cross-coupling reaction provides a complementary method in the sparse field of alkyne thioarylations, which may assist in the synthesis of novel and useful *S*-heterocycles and regio- and stereodefined thioalkenes.

Experimental Section

Procedure A: Preparation of alkynyl sulfide substrates 1. A 3-neck round bottom flask equipped with stir bar was charged with aryl iodide (2.40 mmol, 1.2 equiv), copper(I) iodide (19.0 mg, 100. µmol, 5.0 mol%), and $(PPh_3)_2PdCl_2$ (35.1 mg, 50.0 µmol, 2.5 mol%). To the vertical neck was attached a dropping funnel capped with a rubber septum. One side-neck was connected to a Schlenk line, and the other side-neck was sealed with a stopper. Each ground-glass connection in the setup was fitted with a PTFE O-ring. The apparatus was evacuated and backfilled with N_2 3×. In a 25 mL conical flask sealed with a rubber septum, NEt_3 (20 mL) was sparged with N_2 for 30 min. The sparged NEt_3 was then transferred to the round bottom flask by syringe through the septum atop the open dropping funnel. This mixture was allowed to stir at ambient temperature. A 25 mL conical flask was then charged with terminal alkyne (2.00 mmol, 1.0 equiv) and THF (5 mL). The conical flask was sealed with a rubber septum and the solution inside was sparged with N_2 for 10–15 min. The solution was then transferred by syringe through the septum atop the closed dropping funnel. The funnel was then adjusted to allow addition of the solution slowly dropwise while the round bottom flask mixture was stirred overnight. The reaction mixture was then transferred to a separatory funnel along with 30 mL EtOAc. The mixture was washed with saturated NH_4Cl solution (2 × 10 mL), DI H_2O (1 × 10 mL) and brine (1 × 10 mL). The aqueous layers were combined and extracted with EtOAc (2 × 10 mL). The organic layers were combined dried with Na_2SO_4. The dried solution was then decanted and concentrated in vacuo to give a crude material.

*(4-phenylbut-3-yn-1-yl)(p-tolyl)sulfane (**1a**)*. Prepared according to Procedure A with no modifications. The reaction mixture was stirred for 22 h. The resulting crude material was purified via normal phase column chromatography (0–20% DCM in

hexanes) to afford alkyne **1a** as a clear, colorless oil (466 mg, 92%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 (m, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.28 (m, 3H), 7.12 (d, *J* = 7.9 Hz, 2H), 3.11 (t, *J* = 7.6 Hz, 2H), 2.69 (t, *J* = 7.6 Hz, 2H), 2.33 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 136.9, 131.7, 131.7, 131.1, 129.9, 128.3, 127.9, 123.6, 88.1, 81.8, 33.9, 21.2, 20.7. HRMS (EI-TOF) *m/z* $[M]^+$ calcd for $C_{17}H_{16}S$ 252.0973, found 252.0971.

*(4-(4-fluorophenyl)but-3-yn-1-yl)(p-tolyl)sulfane (**1b**)*. A 3-neck round bottom flask equipped with stir bar was charged with 1-fluoro-4-iodobenzene (333 mg, 1.50 mmol, 1.5 equiv) copper(I) iodide (9.5 mg, 50. µmol, 5.0 mol%), and $(PPh_3)_2PdCl_2$ (17.5 mg, 25.0 µmol, 2.5 mol). One neck was connected to a Schlenk line, and the other two necks were sealed with a rubber septum. Each ground-glass connection in the setup was fitted with a PTFE O-ring. The apparatus was evacuated and backfilled with N_2 3×. In a 25 mL conical flask sealed with a rubber septum, NEt_3 (3 mL) was sparged with N_2 for 30 min. The sparged NEt_3 was then transferred to the round bottom flask by syringe through a rubber septum. This mixture was allowed to stir at ambient temperature. A 25 mL conical flask was then charged with but-3-yn-1-yl(p-tolyl)sulfane (176 mg, 1.00 mmol, 1.0 equiv) and NEt_3 (2 mL). The conical flask was sealed with a rubber septum and the solution inside was sparged with N_2 for 10 min. The solution was then added by syringe dropwise through a rubber septum into the 3-neck flask while stirring. The reaction mixture was then transferred to a separatory funnel along with DCM (1 mL). The mixture was washed 1 M HCl solution (1 × 30 mL). The aqueous layer was extracted with EtOAc (3 × 20 mL). The organic layers were combined and dried with Na_2SO_4. The dried solution was decanted and concentrated in vacuo to give a crude material. The crude material was purified by normal phase column chromatography (0–20% DCM in hexanes) to yield internal alkyne **1b** as a clear, colorless oil (150 mg, 55%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 (m, 2H), 7.33(m, 2H), 7.12 (d, *J* = 7.8 Hz, 2H), 6.97 (m, 2H), 3.09 (m, 2H), 2.67 (t, *J* = 7.5 Hz, 2H), 2.33 (s, 3H). The ^{1}H NMR spectrum agrees with the previously reported spectrum.[47]

*(4-(4-chlorophenyl)but-3-yn-1-yl)(p-tolyl)sulfane (**1c**)*. Prepared according to Procedure A with no modifications. The reaction mixture was stirred for 20 h. The resulting crude material was purified via normal phase column chromatography (0–30% DCM in hexanes) to afford alkyne **1b** as a clear, colorless oil (549 mg, 96%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.5 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 7.13 (d, *J* = 7.9 Hz, 2H), 3.10 (t, *J* = 7.5 Hz, 2H), 2.68 (t, *J* = 7.5 Hz, 2H), 2.34 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 137.0, 133.9, 133.0, 131.6, 131.1, 130.0, 128.6, 122.1, 89.2, 80.8, 33.8, 21.2, 20.7. HRMS (EI-TOF) *m/z* $[M]^+$ calcd for $C_{17}H_{15}ClS$ 286.0583, found 286.0591.

*(4-(4-methoxyphenyl)but-3-yn-1-yl)(p-tolyl)sulfane (**1d**)*. A 3-neck round bottom flask equipped with stir bar was charged with 4-iodoanisole (328 mg, 1.40 mmol, 1.5 equiv) copper(I) iodide (9.5 mg, 50. µmol, 5.0 mol%), and $(PPh_3)_2PdCl_2$ (17.5 mg, 25.0 µmol, 2.5 mol). One neck was connected to a Schlenk line, and the other two necks were sealed with rubber septa. Each ground-glass connection in the setup was fitted with a PTFE O-ring. The apparatus was evacuated and backfilled with N_2 3×. In a 25 mL conical flask sealed with a rubber septum, NEt_3 (3 mL) was sparged with N_2 for 30 min. The sparged NEt_3 was then transferred to the round bottom flask by syringe through a rubber septum. This mixture was allowed to stir at ambient temperature. A 25 mL conical flask was then charged with but-3-yn-1-yl(p-tolyl)sulfane (176 mg, 1.00 mmol, 1.0 equiv) and NEt_3 (2 mL). The conical flask was sealed with a rubber septum and the solution inside was sparged with N_2 for 10 min. The solution was then added by syringe dropwise through a rubber septum into the 3-neck flask while stirring. The reaction mixture was then transferred to a separatory funnel along with DI H_2O (10 mL). The mixture was extracted with EtOAc (3 × 10 mL). The organic layers were combined and washed with saturated NH_4Cl solution (2 × 10 mL), and brine (1 x 10 mL). The organic layer was then dried with Na_2SO_4. The dried solution was decanted and concentrated in vacuo to give a crude material. The crude material was purified by normal phase column chromatography (0–30% DCM in hexanes) to yield internal alkyne **1b** as a colorless solid (147 mg, 52%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 (m, 4H), 7.12 (d, *J* = 8.0 Hz, 2H), 6.81 (m, 2H), 3.80 (s, 3H), 3.09 (t, *J* = 7.6 Hz, 2H), 2.66 (t, *J* = 7.6 Hz, 2H), 2.33 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 159.4, 136.9, 133.1, 131.8, 131.0, 129.9, 115.8, 114.0, 86.5, 81.6, 55.4, 34.0, 21.2, 20.7. HRMS (CI-TOF) *m/z* $[M]^+$ calcd for $C_{18}H_{18}OS$ 282.1078, found 282.1090.

*(4-(2-methoxyphenyl)but-3-yn-1-yl)(p-tolyl)sulfane (**1e**)*. Prepared according to Procedure A with the following modification: the reaction scale was lowered such that 1.36 mmol of alkyne was used. The reaction mixture was stirred for 21 h. The resulting crude material was purified via normal phase column chromatography (0–30% EtOAc in hexanes) to afford internal alkyne **1e** as a yellow oil (147 mg, 38%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (dd, *J* = 7.6 Hz, *J* = 1.7 Hz, 1H), 7.33 (m, 2H), 7.25 (m, 1H), 7.12 (d, *J* = 7.9 Hz, 2H), 6.87 (m, 2H), 3.87 (s, 3H), 3.13 (m, 2H), 2.74 (m, 2H), 2.33 (s, 3 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 160.0, 136.9, 133.9, 131.7, 131.1, 129.9, 129.4, 120.5, 112.7, 110.7, 92.3, 77.9, 55.9, 33.9, 21.2, 21.0. HRMS (CI-TOF) *m/z* $[M]^+$ calcd for $C_{18}H_{18}OS$ 282.1078, found 282.1073.

*methyl(2-(4-(p-tolylthio)but-1-yn-1-yl)phenyl)sulfane (**1f**)*. Prepared according to Procedure A with the following modification: the reaction scale was halved such that 1.00 mmol of alkyne was used. The reaction mixture was stirred for 18 h. The resulting crude material was purified via normal phase column chromatography (0–40% DCM in hexanes) to afford alkyne **1f** as a clear, yellow oil (230 mg, 77%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 (m, 3H), 7.26 (m, 1H), 7.12, (m, 3H), 7.05 (t, *J* = 7.5 Hz, 1H), 3.14 (t, *J* = 7.6 Hz, 2H), 2.75 (t, *J* = 7.6 Hz, 2H), 2.47 (s, 3H), 2.33 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 141.4, 137.0, 132.5, 131.6, 131.2, 129.9, 128.5, 124.3, 124.0, 121.6, 94.9, 79.3, 33.9, 21.2, 20.9, 15.2. HRMS (EI-TOF) *m/z* $[M]^+$ calcd for $C_{18}H_{18}S_2$ 298.0850, found 298.0855.

*5-(4-(p-tolylthio)but-1-yn-1-yl)benzo[d][1,3]dioxole (**1g**)*. Prepared according to Procedure A with the following modification: the reaction scale was halved such that 1.00 mmol of alkyne was used. The reaction mixture was stirred for 20 h. The resulting crude material was purified via normal phase column chromatography (0–50% DCM in hexanes) to afford alkyne **1g** as a light orange solid (264 mg, 89%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 6.89 (dd, *J* =

8.0 Hz, *J* = 1.2 Hz, 1H), 6.82 (d, *J* = 1.2 Hz, 1H), 6.72 (d, *J* = 8.0 Hz, 1H), 5.95 (s, 2H), 3.08 (t, *J* = 7.6 Hz, 2H), 2.65 (t, *J* = 7.6 Hz, 2H), 2.33 (s, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 147.6, 147.4, 137.0, 131.6, 131.2, 129.9, 126.2, 116.9, 111.8, 108.5, 101.3, 86.4, 81.6, 33.9, 21.2, 20.6. HRMS (EI-TOF) *m/z* $[M]^+$ calcd for $C_{18}H_{16}O_2S$ 296.0871, found 296.0861.

*methyl 4-(4-(p-tolylthio)but-1-yn-1-yl)benzoate (**1h**)*. Prepared according to Procedure A with no modifications. The resulting crude material was purified by recrystallization in hot EtOH. Added hot EtOH until solid was almost completely dissolved then added more EtOH (ca. 1 mL). The solution was decanted into a 20 mL scintillation vial, leaving behind an insoluble solid. The scintillation vial contained the solution was capped with a plastic screw cap and allowed to cool at ambient temperature for 1 d and then at 6 ºC for 1 h. The resulting crystalline solid was filtered through a glass frit and rinsed with cold ethanol. Crystals were collected and residual solvent was removed in vacuo to afford alkyne **1h** as light amber flaky crystals (435 mg, 70%). ^1H NMR (600 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.3 Hz, 2H), 7.42 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 7.9 Hz, 2H), 3.91 (s, 3H), 3.10 (t, *J* = 7.5 Hz, 2H), 2.70 (t, *J* = 7.5 Hz, 2H), 2.33 (s, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 166.7, 137.1, 131.7, 131.5, 131.2, 130.0, 129.5, 129.3, 128.4, 91.5, 81.3, 52.3, 33.7, 21.2, 20.7. HRMS (CI-TOF) *m/z* $[M]^+$ calcd for $C_{19}H_{18}O_2S$ 310.1028, found 310.1013.

*(4-fluorophenyl)(4-(4-methoxyphenyl)but-3-yn-1-yl)sulfane (**1k**)*. Prepared according to Procedure A with the following modifications: the reaction scale was increased by 2.5× such that 5.00 mmol of alkyne was used, and reaction mixture was stirred for 3 h. The resulting crude material was purified by normal phase column chromatography (0–100% DCM in hexanes). The product-containing fractions were combined and concentrated in vacuo. The resulting crude oil was dissolved in hot hexanes and decanted. The resulting hexanes solution was concentrated in vacuo to yield alkyne **1k** as an amber oil (1.22 g, 85%). ^1H NMR (600 MHz, $CDCl_3$) δ 7.42 (m, 2H), 7.31 (m, 2H), 7.01 (m, 2H), 6.81 (m, 2H), 3.80 (s, 3H), 3.09 (t, *J* = 7.6 Hz, 2H), 2.66 (t, *J* = 7.5 Hz, 2H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 162.2 (d, *J* = 246.8 Hz), 159.4, 133.3 (d, *J* = 8.0 Hz), 133.1, 130.4 (d, *J* = 3.3 Hz), 116.3 (d, *J* = 21.8 Hz), 115.6, 113.9, 86.2, 81.8, 55.4, 34.5, 20.6. HRMS (CI-TOF) *m/z* $[M]^+$ calcd for $C_{17}H_{15}FOS$ 286.0828, found 286.0831.

*(4-methoxyphenyl)(4-(p-tolyl)but-3-yn-1-yl)sulfane (**1o**)*. Prepared according to Procedure A with the following modification: the reaction scale was decreased such that 1.56 mmol of alkyne was used. The reaction mixture was stirred for 16 h. The resulting crude material was purified by normal phase column chromatography (0–10% EtOAc in hexanes) to yield internal alkyne **1o** a clear, colorless oil (250 mg, 57%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.42 (m, 2H), 7.28 (m, 2H), 7.09 (d, *J* = 7.9 Hz, 2H), 6.86 (m, 2 H), 3.80 (s, 3H), 3.03 (t, *J* = 7.6 Hz, 2H), 2.64 (t, *J* = 7.6 Hz, 2H), 2.33 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 159.4, 137.9, 134.2, 129.1, 125.5, 120.5, 114.8, 87.4, 81.8, 55.5, 35.2, 21.5, 20.7. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{18}H_{18}OSH$ 283.1157, found 283.1151.

*Pent-3-yn-1-yl methanesulfonate (**SI-1r**).* Compound synthesized according to modified procedure[62] as described below. To an oven-dried 500 mL RBF flushed with argon was added DCM (260 mL). The flask was sealed with a rubber septum and cooled to ca. −10 °C in an ice-salt bath. To this flask was added via syringe triethylamine (11 mL, 80 mmol, 1.6 equiv), pent-3-yn-1-ol (4.3 g, 51 mmol, 1.0 equiv), and methanesulfonyl chloride (4.3 mL, 56 mmol, 1.1 equiv). The resulting solution was stirred for 30 min then quenched with ice-water (30 mL). The organic layer was separated in a separatory funnel and washed with 1 M HCL (1 × 30 mL), saturated NaHCO3 solution (1 × 30 mL) and brine (1 × 30 mL). The organic layer was dried over $MgSO_4$, vacuum filtered, and concentrated in vacuo to give crude **SI-1r**. This material was carried over to the next step without further purification.

*(4-methoxyphenyl)(pent-3-yn-1-yl)sulfane (**1r**).* To a 50 mL round bottom flask equipped with stir bar was added 4-methoxybenzenethiol (140. mg, 1.00 mmol, 0.95 equiv), K_2CO_3 (207 mg, 1.50 mmol, 1.4 equiv), and acetone (2 mL). While stirring, methyl pent-3-yn-1-yl sulfate (**SI-1r**, 170. mg, 1.05 mmol, 1.0 equiv) was added dropwise. The round bottom flask was equipped with an aluminum finned condenser and the condenser was capped with a rubber septum. The rubber septum was pierced with a needle connected to a Schlenk line and N_2 was blown through the condenser to flush air from the reaction vessel. The reaction vessel and Schlenk line were then left under static nitrogen pressure for the duration of the reaction. The mixture was then placed on an aluminum block set to 65 °C and allowed to reflux for 20 h. Then more 4-methoxybenzenethiol was added (70.0 mg, 0.500 mmol, 0.48 equiv) and N_2 was blown through the condenser to flush air from the reaction vessel again. The reaction vessel and Schlenk line were again left under static nitrogen pressure for the rest of the reaction. The mixture was then replaced on the aluminum block set to 65 °C and allowed to reflux for another 20 h. The mixture was then cooled, and the suspension was vacuum filtered to remove solids. The solids were rinsed well with acetone during the filtration, by crushing up the solids with a spatula while rinsing. The filtrate was collected and concentrated in vacuo. The resulting crude material was dissolved in EtOAc (10 mL), transferred to a separatory funnel, and washed with DI H_2O (50 mL). The aqueous layer was washed with EtOAc (2 × 10 mL). The organic layers were combined and washed with 1 M NaOH (1 × 20 mL), DI H_2O (1 × 20 mL), and brine (1 × 20 mL). The organic layer was and dried with Na_2SO_4. The dried solution was decanted using a beaker, transferred to a round bottom flask and concentrated in vacuo, leaving a crude material. The crude material was purified by normal phase column chromatography (0–20% EtOAc in hexanes) to yield **1r** as a yellow oil (148 mg, 72%). ^1H NMR (600 MHz, $CDCl_3$) δ 7.36 (m, 2H), 6.84 (m, 2H), 3.78 (s, 3H), 2.90 (t, *J* = 7.5 Hz, 2H), 2.36 (tq, *J* = 7.6 Hz, *J* = 2.5 Hz, 2H), 1.76 (t, *J* = 2.5 Hz, 2H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 159.3, 133.9, 125.7, 114.7, 77.4, 76.9, 55.4, 35.4, 19.9, 3.6. HRMS (EI-TOF) m/z $[M]^+$ calcd for $C_{12}H_{14}OS$ 206.0765, found 206.0764.

Procedure B: Preparation of dihydrothiopheniums 2 and 3. To a 1 dram vial equipped with stir bar was added $AgSbF_6$ (51.5 mg, 150. µmol, 1.5 equiv). A separate 1 dram vial was charged with a starting alkyne (100. µmol, 1.0 equiv), an aryl iodide (120. µmol, 1.2 equiv), and MeDalPhosAuCl (6.5 mg, 10. µmol, 10 mol%) in DCE (0.4 mL). The DCE solution was transferred to the $AgSbF_6$ vial, and DCE (2 × 0.3 mL) was used to rinse any

remaining starting materials into the $AgSbF_6$ vial. The mixture-containing vial was then capped with a plastic screw cap and placed in an aluminum block on a hot plate set to 60 °C. The mixture was stirred for 1 h then removed from the hot plate.

*4-(4-methoxyphenyl)-5-phenyl-1-(p-tolyl)-2,3-dihydro-1H-thiophen-1-ium hexafluorostibate(V) (**2a**)*. Prepared according to Procedure B with no modifications. Reaction mixture was filtered through cotton and rinsed with DCM (3 × 1 mL). The filtrate was transferred to a separatory funnel and washed with DI H_2O (1 × 5 mL). The aqueous layer was back extracted with DCM (1 × 5 mL). The organic layers were then combined and dried with Na_2SO_4. The solution was then decanted and concentrated in vacuo. The resulting crude was purified by normal phase column chromatography (100% DCM). Product-containing fractions were concentrated in vacuo in a 20 mL scintillation vial and redissolved in DCM (2 mL). The scintillation vial was capped with a plastic screw cap and left at ambient temperature for 2 h which allowed a solid impurity to precipitate. The DCM solution was decanted and concentrated in vacuo to yield dihydrothiophenium **2a** as a yellow solid (51.8 mg, 87%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.3 Hz, 2H), 7.41 (d, *J* = 8.2 Hz, 2H), 7.30–7.22 (m, 7H) 6.78 (d, *J* = 8.8 Hz, 2H), 4.45–4.39 (m, 1H) 4.20–4.13 (m, 1H), 3.79–3.73 (m, 4H), 3.70–3.64 (m, 1H), 2.38 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 161.4, 153.1, 146.9, 132.5, 130.6, 130.3, 130.2, 129.9, 129.7, 128.9, 124.5, 121.8, 121.2, 114.4, 55.5, 43.0, 39.4, 21.8. HRMS (ESI-TOF) *m/z* $[M-^{-}SbF_6]^+$ calcd for $C_{24}H_{23}OS$ 359.1470, found 359.1487.

*5-(4-fluorophenyl)-4-(4-methoxyphenyl)-1-(p-tolyl)-2,3-dihydro-1H-thiophen-1-ium hexafluorostibate(V) (**2b**)*. Prepared according to Procedure B with no modifications. Reaction mixture was filtered through cotton and rinsed with DCM (3 × 1 mL). The filtrate was transferred to a separatory funnel and washed with DI H_2O (1 × 5 mL). The aqueous layer was back extracted with DCM (1 × 5 mL). The organic layers were then combined and dried with Na_2SO_4. The solution was then decanted and concentrated in vacuo. The resulting crude was purified by normal phase column chromatography (100% DCM). Product-containing fractions were concentrated in vacuo in a 20 mL scintillation vial and redissolved in DCM (2 mL). The scintillation vial was capped with a plastic screw cap and left at ambient temperature for 2 h which allowed a solid impurity to precipitate. The DCM solution was decanted and concentrated in vacuo to yield dihydrothiophenium **2b** as a yellow solid (41.8 mg, 78%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.6 Hz, 2H), 7.22 (dd, *J* = 8.4 Hz, *J* = 5.2 Hz, 2H), 6.93 (d, *J* = 8.4 Hz, 2H), 6.79 (d, *J* = 8.4 Hz, 2H), 4.46–4.40 (m, 1H), 4.19–4.13 (m, 1H), 3.79–3.74 (m, 4H), 3.70–3.64 (m, 1H), 2.39 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 163.4 (d, *J* = 252.5 Hz), 161.4, 153.5, 147.0, 132.5, 132.2 (d, *J* = 8.6 Hz), 130.6, 130.4, 124.9 (d, *J* = 3.4 Hz), 124.3, 121.0, 120.9, 117.0 (d, *J* = 22.1 Hz), 114.5, 55.5, 43.1, 39.4, 21.8. HRMS (ESI-TOF) *m/z* $[M-^{-}SbF_6]^+$ calcd for $C_{24}H_{22}FOS$ 377.1375, found 377.1367.

*5-(4-chlorophenyl)-4-(4-methoxyphenyl)-1-(p-tolyl)-2,3-dihydro-1H-thiophen-1-ium hexafluorostibate(V) (**2c**)*. Prepared according to Procedure B with no modifications. Reaction mixture was filtered through cotton and rinsed with DCM (3 × 1 mL). The filtrate was transferred to a separatory funnel and washed with DI H_2O (1 × 5 mL). The aqueous layer was back extracted with DCM (1 × 5 mL). The organic layers were then combined and dried with Na_2SO_4. The solution was then decanted and concentrated in vacuo. The resulting crude was purified by normal phase column chromatography (100% DCM). Product-containing fractions were concentrated in vacuo to yield dihydrothiophenium **2c** as a yellow solid (60.1 mg, 95%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.9 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.3 Hz, 2H), 7.21 (d, *J* = 8.3 Hz, 2H), 7.17 (d, *J* = 8.3 Hz, 2H), 6.80 (d, *J* = 8.3 Hz, 2H), 4.47–4.41 (m, 1H), 4.20–4.13 (m, 1H), 3.81–3.74 (m, 4H), 3.70–3.64 (m, 1H), 2.39 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 161.5, 153.9, 147.1, 136.4, 132.6, 131.3, 130.6, 130.3, 130.0, 127.4, 124.2, 120.9, 120.7, 114.6, 55.5, 43.2, 39.5, 21.8. HRMS (ESI-TOF) *m/z* $[M-^{-}SbF_6]^+$ calcd for $C_{24}H_{22}ClOS$ 393.1080, found 393.1087.

*4,5-bis(4-methoxyphenyl)-1-(p-tolyl)-2,3-dihydro-1H-thiophen-1-ium hexafluorostibate(V) (**2d**)*. Prepared according to Procedure B with no modifications. The reaction mixture was filtered through cotton and rinsed with DCM (3 × 1 mL). The filtrate was transferred to a separatory funnel and washed with DI H_2O (1 × 5 mL). The aqueous layer was back extracted with DCM (1 × 5 mL). The organic layers were then combined and dried with Na_2SO_4. The solution was then decanted and concentrated in vacuo. The resulting crude was purified by normal phase column chromatography (100% DCM). Product-containing fractions were concentrated in vacuo in a 20 mL scintillation vial and redissolved in $CHCl_3$ (1 mL). The scintillation vial was capped with a plastic screw cap and left at 6 °C for overnight which allowed a solid impurity to precipitate. The $CHCl_3$ mixture was filtered through celite and cotton and rinsed with cold $CHCl_3$ (3 mL). The filtrate was concentrated in vacuo to yield dihydrothiophenium **2d** as a yellow solid (56.5 mg, 90%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.1 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.7 Hz, 2H), 7.15 (d, *J* = 8.7 Hz, 2H), 6.81 (d, *J* = 8.7 Hz, 2H), 6.76 (d, *J* = 8.6 Hz, 2H), 4.41–4.36 (m, 1H), 4.15–4.09 (m, 1H), 3.79 (s, 3H), 3.75–3.72 (m, 4H), 3.67–3.62 (m, 1H), 2.40 (s, 3 H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 161.3, 160.9, 151.5, 146.8, 132.5, 131.4, 130.5, 130.2, 124.7, 122.0, 121.2, 120.6, 115.2, 114.5, 55.5, 55.4, 42.7, 39.3, 21.8. HRMS (ESI-TOF) *m/z* $[M-^{-}SbF_6]^+$ calcd for $C_{25}H_{25}O_2S$ 389.1575, found 389.1582.

*5-(2-methoxyphenyl)-4-(4-methoxyphenyl)-1-(p-tolyl)-2,3-dihydro-1H-thiophen-1-ium hexafluorostibate(V) (**2e**)*. Prepared according to Procedure B with no modifications. The reaction mixture was filtered through celite and cotton and rinsed with $CHCl_3$ (3 × 1 mL). The filtrate was transferred to a separatory funnel and washed with DI H_2O (1 × 5 mL). The aqueous layer was back extracted with $CHCl_3$ (1 × 5 mL). The organic layers were then combined and dried with Na_2SO_4. The solution was then decanted and concentrated in vacuo. The resulting crude was purified by normal phase column chromatography (100% DCM). Product-containing fractions were concentrated in vacuo in a 20 mL scintillation vial and redissolved in $CHCl_3$ (1 mL). The scintillation vial was capped with a plastic screw cap and left at 6 °C for overnight which allowed a solid impurity to precipitate. The $CHCl_3$ mixture was filtered through celite and cotton and rinsed with cold $CHCl_3$ (3 mL). The filtrate was concentrated in vacuo to yield dihydrothiophenium **2e** as a yellow

solid (58.7 mg, 89%). ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.80 (d, *J* = 8.3 Hz, 2H), 7.45(d, *J* = 8.2 Hz, 2H), 7.37–7.33 (m, 1H), 7.29 (d, *J* = 8.9 Hz, 2H), 7.06 (d, *J* = 8.3 Hz, 1H), 7.02 (dd, *J* = 7.6 Hz, *J* = 1.5 Hz, 1H), 6.90 (d, *J* = 8.9 Hz, 2H), 6.83 (t, *J* = 7.5 Hz, 1H), 4.53–4.47 (m, 1H), 4.21–4.15 (m, 1H), 4.01–3.95 (m, 1H), 3.75 (s, 3H), 3.68 (s, 3H), 3.63–3.57 (m, 1H), 2.37 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, DMSO-d_6) δ 160.5, 157.0, 152.9, 145.1, 132.0, 131.9, 131.2, 130.8, 130.0, 125.4, 122.7, 121.1, 120.0, 117.5, 114.0, 112.2, 55.8, 55.3, 43.2 ,38.0, 21.0. HRMS (ESI-TOF) *m/z* [M–$^-$SbF$_6$]$^+$ calcd for $C_{25}H_{25}O_2S$ 389.1575, found 389.1580.

*4-(4-methoxyphenyl)-5-(2-(methylthio)phenyl)-1-(p-tolyl)-2,3-dihydro-1H-thiophen-1-ium hexafluorostibate(V) (**2f**) NMR yield*. A 1 dram vial was charged with alkyne **1f** (14.9 mg, 50.0 µmol, 1.0 equiv), internal standard phenanthrene (2.9 mg, 16 µmol, 0.33 equiv), and $CDCl_3$ (ca. 0.5 mL). This solution was transferred to an NMR tube and analyzed by ^{1}H NMR spectroscopy. Then the NMR solution was transferred back to the 1 dram vial and rinsed with DCM (1 mL). The solution was then concentrated in vacuo. The vial was then charged with MeDalPhosAuCl (3.3 mg, 5.0 µmol, 10 mol%) in DCE (0.2 mL). To a separate 1 dram vial equipped with stir bar was added $AgSbF_6$ (51.5 mg, 150. µmol, 3.0 equiv). The DCE solution was transferred to the $AgSbF_6$ vial, and DCE (2 × 0.15 mL) was used to rinse any remaining starting materials into the $AgSbF_6$ vial. The mixture-containing vial was then capped with a plastic screw cap and placed in an aluminum block on a hot plate set to 60 °C. The mixture was stirred for 23 h then removed from the hot plate. The mixture was concentrated in vacuo to then dissolved in DMSO-d_6. The solution was transferred to an NMR tube and analyzed by ^{1}H NMR spectroscopy. An NMR yield of 81% for dihydrosulfonium **2f** was determined by the ratio of internal standard to product peaks in the crude reaction mixture at 23 h compared to the spectrum of starting alkyne and internal standard in $CDCl_3$. The peaks integrated for this experiment were at 8.70 ppm (internal standard), 3.15 ppm (starting material) for the initial spectrum, and 8.82 ppm (internal standard) and 4.13 ppm (product) for the crude reaction mixture at 23 h.

*5-(benzo[d][1,3]dioxol-5-yl)-4-(4-methoxyphenyl)-1-(p-tolyl)-2,3-dihydro-1H-thiophen-1-ium hexafluorostibate(V) (**2g**)*. Prepared according to Procedure B with no modifications. Reaction mixture was filtered through cotton and rinsed with DCM (3 × 1 mL). The filtrate was transferred to a separatory funnel and washed with DI H_2O (1 × 5 mL). The aqueous layer was back extracted with DCM (1 × 5 mL). The organic layers were then combined and dried with Na_2SO_4. The solution was then decanted and concentrated in vacuo. The resulting crude was purified by normal phase column chromatography (100% DCM). Product-containing fractions were concentrated in vacuo in a 20 mL scintillation vial and redissolved in DCM (2 mL). The scintillation vial was capped with a plastic screw cap and left at ambient temperature for 2 h which allowed a solid impurity to precipitate. The DCM solution was decanted and concentrated in vacuo to yield dihydrothiophenium **2g** as a yellow solid (56.7 mg, 89%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.9 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.3 Hz, 2H), 6.81 (d, *J* = 8.1 Hz, 2H), 6.74 (d, *J* = 8.1 Hz, 1H), 6.65 (d, *J* = 8.0 Hz, 1H), 6.63 (br s, 1H), 5.91 (d, *J* = 4.9 Hz, 2H), 4.40–4.34 (m, 1H), 4.17–4.10 (m, 1H), 3.78 (s, 3H), 3.74–3.70 (m, 1H), 3.66–3.61 (m, 1H), 2.40 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 161.3, 152.1, 149.3, 148.6, 146.9, 132.5, 130.5, 130.3, 124.7, 124.6, 122.0, 121.7, 121.1, 114.5, 109.8, 109.5, 101.9, 55.5, 42.7, 39.3, 21.8. HRMS (ESI-TOF) *m/z* [M–$^-$SbF$_6$]$^+$ calcd for $C_{25}H_{23}O_3S$ 403.1368, found 403.1366.

*5-(4-(methoxycarbonyl)phenyl)-4-(4-methoxyphenyl)-1-(p-tolyl)-2,3-dihydro-1H-thiophen-1-ium hexafluorostibate(V) (**2h**)*. Prepared according to Procedure B with no modifications. The reaction mixture was filtered through cotton and rinsed with DCM (3 × 1 mL). The filtrate was transferred to a separatory funnel and washed with DI H_2O (1 × 5 mL). The aqueous layer was back extracted with DCM (1 × 5 mL). The organic layers were then combined and dried with Na_2SO_4. The solution was then decanted and concentrated in vacuo. The resulting crude was purified by normal phase column chromatography (0–10% MeOH in DCM). Product-containing fractions were concentrated in vacuo in a 20 mL scintillation vial and redissolved in $CHCl_3$ (1 mL). The scintillation vial was capped with a plastic screw cap and left at 6 °C for overnight which allowed a solid impurity to precipitate. The $CHCl_3$ mixture was filtered through celite and cotton and rinsed with cold $CHCl_3$ (3 mL). The filtrate was concentrated in vacuo to yield dihydrothiophenium **2h** as a yellow solid (47.7 mg, 73%). ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.90–7.85 (m, 4H), 7.47 (d, *J* = 8.2 Hz, 2H), 7.39 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.8 Hz, 2H), 6.94 (d, *J* = 8.8 Hz, 2H), 4.52–4.47 (m, 1H), 4.34–4.28 (m, 1H), 4.04–3.99 (m, 1H), 3.81 (s, 3H), 3.76 (s, 3H), 3.68–3.62 (m, 1H), 2.37 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, DMSO-d_6) δ 165.4, 160.7, 153.2, 145.4, 134.3, 131.5, 130.9, 130.4, 130.3, 130.1, 130.0, 124.8, 122.7, 122.1, 114.3, 55.3, 52.4, 43.2, 39.4, 21.0 HRMS (ESI-TOF) *m/z* [M–$^-$SbF$_6$]$^+$ calcd for $C_{26}H_{25}O_3S$ 417.1524, found 417.1534.

*4,5-bis(4-(methoxycarbonyl)phenyl)-1-(p-tolyl)-2,3-dihydro-1H-thiophen-1-ium hexafluorostibate(V) (**2i**)*. Prepared according to Procedure B with no modifications. The reaction mixture was filtered through celite and cotton and rinsed with $CHCl_3$ (3 × 1 mL). The filtrate was transferred to a separatory funnel and washed with DI H_2O (1 × 5 mL). The aqueous layer was back extracted with $CHCl_3$ (1 × 5 mL). The organic layers were then combined and dried with Na_2SO_4. The solution was then decanted and concentrated in vacuo. The resulting crude was purified by normal phase column chromatography (0–10% MeOH in DCM) yield dihydrothiophenium **2i** as a colorless solid (56.4 mg, 83%). ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.95 (d, *J* = 8.5 Hz, 2H), 7.91 (d, *J* = 8.4 Hz, 2H), 7.85 (d, *J* = 8.5 Hz, 2H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 8.5 Hz, 2H), 4.57–4.51 (m, 1H), 4.39–4.33 (m, 1H), 4.12–4.07 (m, 1H), 3.84 (s, 3H), 3.78 (s, 3H), 3.72–3.66 (m, 1H), 2.37 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, DMSO-d_6) δ 165.5, 165.3, 152.4, 145.6, 137.7, 133.2, 131.5, 131.1, 130.7, 130.6, 130.1, 130.0, 129.6, 128.9, 126.7, 122.4, 52.4, 43.7, 40.0, 21.0. HMQC NMR spectroscopic analysis confirms that two ^{13}C peaks are overlapping at 52.4 ppm. HRMS (ESI-TOF) *m/z* [M–$^-$SbF$_6$]$^+$ calcd for $C_{27}H_{25}O_4S$ 445.1474, found 445.1470.

*4-(4-bromophenyl)-5-(4-methoxyphenyl)-1-(p-tolyl)-2,3-dihydro-1H-thiophen-1-ium hexafluorostibate(V) (**2j**)*. Prepared according to Procedure B with no modifications. The reaction mixture was filtered through celite and cotton and rinsed with DCM (3 × 1 mL). The filtrate was transferred to a separatory

funnel and washed with DI H_2O (1 × 5 mL). The aqueous layer was back extracted with DCM (1 × 5 mL). The organic layers were then combined and dried with Na_2SO_4. The solution was then decanted and concentrated in vacuo. The resulting crude was purified by normal phase column chromatography (0–10% MeOH in DCM). Product-containing fractions were concentrated in vacuo in a 20 mL scintillation vial and redissolved in $CHCl_3$ (1 mL). The scintillation vial was capped with a plastic screw cap and stored at 6 °C for overnight which allowed a solid impurity to precipitate. The $CHCl_3$ mixture was filtered through celite and cotton and rinsed with DCM (3 mL). The filtrate was concentrated in vacuo to yield dihydrothiophenium **2j** as a colorless solid (61.6 mg, 91%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66 (m, 2H), 7.42 (m, 4H), 7.24 (m, 2H), 7.13 (m, 2H), 6.72 (m, 2H), 4.52–4.35 (m, 1H), 4.23–4.10 (m, 1H), 3.82–3.74 (m, 1H), 3.72 (s, 3H), 3.68–3.60 (m, 1H), 2.38 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 161.1, 150.4, 147.0, 132.6, 132.3, 131.7, 131.5, 130.6, 130.4, 125.5, 124.7, 120.8, 119.7, 115.2, 55.5, 43.2, 39.8, 21.9. HRMS (ESI-TOF) *m/z* $[M-^{-}SbF_6]^+$ calcd for $C_{24}H_{22}BrOS$ 437.0575, found 437.0594.

*4-(4-bromophenyl)-1-(4-fluorophenyl)-5-(4-methoxyphenyl)-2,3-dihydro-1H-thiophen-1-ium hexafluorostibate(V) (**2k**)*. To a 1 dram vial equipped with stir bar was added $AgSbF_6$ (275 mg, 800. µmol, 1.6 equiv). A separate 1 dram vial was charged with a starting alkyne **1k** (143 mg, 500. µmol, 1.0 equiv), 1-bromo-4-iodobenzene (212 mg, 750. µmol, 1.5 equiv), and MeDalPhosAuCl (32.7 mg, 50.0 µmol, 10 mol%) in DCE (2 mL). The DCE solution was transferred to the $AgSbF_6$ vial, and DCE (2 × 1.5 mL) was used to rinse any remaining starting materials into the $AgSbF_6$ vial. The mixture-containing vial was then capped with a plastic screw cap and placed in an aluminum block on a hot plate set to 60 °C. The mixture was stirred for 1 h then removed from the hot plate. Filtered reaction mixture through celite and rinsed with DCM (10 mL). The filtrate was concentrated in vacuo. The resulting crude material was purified by normal phase column chromatography (0–10% MeOH in DCM) to afford dihydrothiophenium **2k** as a yellow-green solid (277 mg, 82%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83, 7.45(m, 2H), 7.32(m, 2H), 7.23(m, 2H), 7.13 (m, 2H), 6.76 (m, 2H), 4.45 (m, 1H), 4.18 (m, 1H), 3.85 (m, 1H), 3.75 (s, 3H), 3.64 (m, 1H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 166.8 (d, *J* = 260.2 Hz), 161.3, 150.9, 133.5 (d, *J* = 9.9 Hz), 132.5, 131.4, 130.2, 125.3, 125.1, 119.5 (d, *J* = 23.3 Hz), 199.5 (*J* = 2.9Hz), 119.4, 115.4, 55.5, 43.0, 39.6. NMR spectroscopic analysis of a more concentrated solution of a more concentrated solution of **2k** suggests a concentration dependence on both ^{1}H and ^{13}C peaks. This difference in shifts also unveils two ^{13}C peaks at 131.4 ppm which are both confirmed to be part of the product by HMQC and HMBC NMR spectroscopic analysis. This suggests that the peak at 131.4 ppm in the ^{13}C peak list above is from two overlapping ^{13}C peaks. HRMS (ESI-TOF) *m/z* $[M-^{-}SbF_6]^+$ calcd for $C_{23}H_{19}BrFOS$ 441.0324, found 441.0323.

*4-(4-carboxyphenyl)-5-(4-methoxyphenyl)-1-(p-tolyl)-2,3-dihydro-1H-thiophen-1-ium hexafluorostibate(V) (**2l**)*. Prepared according to Procedure B with the following modifications: the reaction scale was doubled such that 200. µmol of alkyne **1d** was used and the reaction mixture was heated and stirred for 25 h. The reaction mixture was concentrated in vacuo to remove solvent. The crude material was purified by normal phase column chromatography (0–10% MeOH in DCM) to afford dihydrothiophenium **2l** as a brown solid (103 mg, 81%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 13.17 (br s, 1H), 7.93 (d, *J* = 8.3 Hz, 2H), 7.89 (d, *J* = 8.2 Hz, 2H), 7.49 (m, 4H), 7.16 (d, *J* = 8.8 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 4.49–4.43 (m, 1H), 4.32–4.25 (m, 1H), 4.03–3.98 (m, 1H), 3.69 (s, 3H), 3.65–3.59 (m, 1H), 2.38 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 166.7, 160.3, 149.4, 145.4, 137.8, 131.5, 131.2, 131.0, 129.6, 128.7, 127.3, 122.4, 120.3, 114.8, 55.2, 42.9, 39.7, 21.0. HMQC and HMBC NMR spectroscopic analysis suggests that the ^{13}C peak at 131.5 ppm is two overlapping ^{13}C peaks. HRMS (ESI-TOF) *m/z* $[M-^{-}SbF_6]^+$ calcd for $C_{25}H_{23}O_3S$ 403,1368, found 403.1384.

*4-(benzo[d]thiazol-2-yl)-5-(4-methoxyphenyl)-1-(p-tolyl)-2,3-dihydro-1H-thiophen-1-ium hexafluorostibate(V) (**2m**)*. Prepared according to Procedure B with the following modification: the reaction mixture was heated and stirred for 23 h. The reaction mixture was then filtered through cotton and rinsed with DCM (3 mL). The filtrate was transferred to a separatory funnel and washed with DI H_2O (1 × 5 mL). The aqueous layer was back extracted with DCM (1 × 5 mL). The organic layers were then combined and dried with Na_2SO_4. The solution was then decanted and concentrated in vacuo. The crude material was dissolved in DCM (2 mL) stored at 6 °C for 2 d which allowed a solid impurity to precipitate. Filtered solution through celite and cotton, rinsing with cold DCM (3 mL). Concentrated the filtrate and purified the resulting crude material by normal phase column chromatography (0-10% DCM in MeOH) to yield dihydrothiophenium **2m** as a yellow solid (60.4 mg, 93%).

*4-(benzo[d]thiazol-2-yl)-5-(4-methoxyphenyl)-1-(p-tolyl)-2,3-dihydro-1H-thiophen-1-ium hexafluorostibate(V) (**2m**) 3.5 mmol scale*. To a 100 mL round bottom flask equipped with stir bar was added $AgSbF_6$ (1.83 g, 5.31 mmol, 1.5 equiv), starting alkyne **1d** (1.00 g, 3.54 mmol, 1.0 equiv), 2-iodobenzo[*d*]thiazole (1.11 g, 4.25 mmol, 1.2 equiv), and MeDalPhosAuCl (232 mg, 354 mmol, 10 mol%), and DCE (30 mL). The round bottom flask was capped with a rubber septum and the septum was pierced with a needle to allow pressure equilibration. An aluminum block on a hot plate set to 60 °C was then raised onto the round bottom flask and the mixture was allowed to stir. The flask was covered with aluminum foil to block out light. After stirring at 60 °C for 24 h, the mixture was concentrated in vacuo and purified by normal phase column chromatography (0–10% MeOH in DCM) to afford dihydrothiophenium **2m** as a yellow solid (1.95 g, 84%). NOTE: After column purification, the product foamed from solvent removal in vacuo. A 500 mL round bottom flask was almost completely filled with this foam. ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.13 (d, *J* = 8.2 Hz, 1H), 8.06 (d, *J* = 8.0 Hz, 1H), 7.94 (d, *J* = 8.3 Hz, 2H), 7.58 (m, 1H), 7.50 (m, 3H), 7.37 (d, *J* = 8.8 Hz, 2H), 7.07 (d, *J* = 8.8 Hz, 2H), 4.61–4.55 (m, 1H), 4.41–4.34 (m, 1H), 4.13–4.05 (m, 2H), 3.79 (s, 3H), 2.41 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, DMSO-d_6) δ 161.7, 159.4, 151.5, 145.7, 144.1, 135.0, 133.2, 131.9, 131.6, 131.5, 127.1, 123.5, 122.5, 122.4, 118.8, 115.5, 55.4, 43.8, 38.0, 21.1. HSQC NMR spectroscopic analysis of 2m shows that the ^{13}C peak at 127.1 ppm is two overlapping ^{13}C peaks. HRMS (ESI-TOF) *m/z* $[M-^{-}SbF_6]^+$ calcd for $C_{25}H_{22}NOS_2$ 416.1143, found 416.1135. For sample preparation for crystals for single-crystal X-ray analysis, see the separate paragraph below.

*5-(benzo[d][1,3]dioxol-5-yl)-4-(benzo[d]thiazol-2-yl)-1-(p-tolyl)-2,3-dihydro-1H-thiophen-1-ium hexafluorostibate(V) trichloromethane (**2n**·$CHCl_3$)*. Prepared according to Procedure B with the following modification: the reaction mixture was heated and stirred for 24 h. The reaction mixture was filtered through cotton and rinsed with DCM (5 mL). The filtrate was transferred to a separatory funnel and washed with DI H_2O (1 × 5 mL). The aqueous layer was back extracted with DCM (2 × 5 mL). The organic layers were then combined and dried with Na_2SO_4. The solution was then decanted and concentrated in vacuo. The resulting crude was purified by normal phase column chromatography (0–10% MeOH in DCM). Product-containing fractions were concentrated in vacuo then recrystallized with hot $CHCl_3$ to afford dihydrothiophenium **2n**·$CHCl_3$ as a yellow solid (42 mg, 53%). ^{1}H NMR (600 MHz, CD_2Cl_2) δ 8.10 (m, 1H), 7.82 (d, *J* = 8.1 Hz, 1H), 7.70 (d, *J* = 8.5 Hz, 2H), 7.56 (m, 1H), 7.51 (d, *J* = 8.2 Hz, 2H), 7.48 (m, 1H), 7.32 (s, 1H), 6.87 (m, 2H), 6.77 (m, 1H), 6.06 (d, *J* = 5.9 Hz, 2H), 4.63–4.58 (m, 1H), 4.45–4.40 (m, 1H), 4.30–4.24 (m, 1H), 3.96–3.92 (m, 1H), 2.48 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, CD_2Cl_2) δ 158.3, 152.5, 151.6, 149.7, 148.4, 146.9, 136.4, 133.0, 131.4, 131.1, 127.9, 127.5, 125.8, 124.6, 122.1, 120.7, 119.2, 110.3, 110.0, 102.9, 77.9, 44.0, 38.5, 22.0. HRMS (ESI-TOF) *m/z* [M−$^-$$SbF_6$]$^+$ calcd for $C_{25}H_{20}NO_2S_2$ 430.0935, found 430.0915. For sample preparation for crystals for single-crystal X-ray analysis, see the separate paragraph below.

*4-(4-(methoxycarbonyl)phenyl)-1-(4-methoxyphenyl)-5-(p-tolyl)-2,3-dihydro-1H-thiophen-1-ium hexafluorostibate(V) (**2o**)*. Prepared according to Procedure B with no modifications. the reaction mixture was heated and stirred for 24 h. The reaction mixture was filtered through cotton and rinsed with DCM (5 mL). The filtrate was transferred to a separatory funnel and washed with DI H_2O (1 × 5 mL). The aqueous layer was back extracted with DCM (2 × 5 mL). The organic layers were then combined and dried with Na_2SO_4. The solution was then decanted and concentrated in vacuo. The resulting crude was purified by normal phase column chromatography (0–10% MeOH in DCM). Product-containing fractions were concentrated in vacuo then recrystallized with hot $CHCl_3$ to afford dihydrothiophenium **2o** as a yellow solid (43 mg, 66%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.5 Hz, 2H), 7.72 (m, 2H), 7.42 (d, *J* = 8.5 Hz, 2H), 7.09 (m, 2H), 7.05 (d, *J* = 8.3 Hz, 2H), 7.00 (d, *J* = 8.2 Hz, 2H), 4.48–4.41 (m, 1H), 4.26–4.18 (m, 1H), 3.88 (s, 3H), 3.83–3.77 (m, 4H), 3.70–3.62 (m, 1H), 2.23 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.3, 165.3, 150.8, 141.2, 137.2, 132.8, 131.5, 130.4, 130.2, 129.8, 128.8, 127.2, 124.7, 117.4, 113.3, 56.1, 52.5, 43.4, 39.7, 21.5. HRMS (ESI-TOF) *m/z* [M−$^-$$SbF_6$]$^+$ calcd for $C_{26}H_{25}O_3S$ 417.1524, found 417.1523.

*1-(4-fluorophenyl)-5-(4-methoxyphenyl)-4-(p-tolyl)-2,3-dihydro-1H-thiophen-1-ium (**2p**).* To a 500 mL round bottom flask equipped with stir bar was added $AgSbF_6$ (876 mg, 2.55 mmol, 1.5 equiv), starting alkyne **1k** (486 mg, 1.70 mmol, 1.0 equiv), 4-iodotoluene (445 g, 2.04 mmol, 1.2 equiv), and MeDalPhosAuCl (111 mg, 170. mmol, 10 mol%), and DCE (10 mL). The round bottom flask was capped with a rubber septum and the septum was pierced with a needle to allow pressure equilibration. An aluminum block on a hot plate set to 60 °C was then raised onto the round bottom flask and stirring of the mixture was initiated. The flask was covered with aluminum foil to block out light. After stirring at 60 °C for 1 h, the mixture was concentrated in vacuo and purified by normal phase column chromatography (0–10% MeOH in DCM) to afford dihydrothiophenium **2p** as a brown solid (768 mg, 74%). NOTE: After column purification, the product foamed from solvent removal in vacuo. A large enough RBF was necessary to prevent bumping of the foam and loss of material. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 (m, 2H), 7.20 (t, *J* = 8.4 Hz, 2H), 7.14 (d, *J* = 8.1 Hz, 2H), 7.05 (d, *J* = 8.8 Hz, 2H), 7.00 (d, *J* = 8.1 Hz, 2H), 6.64 (d, *J* = 8.8 Hz, 2H), 4.33–4.27 (m, 1H), 4.13–4.06 (m, 1H), 3.74–3.69 (m, 1H), 3.62 (s, 3H), 3.55–3.49 (m, 1H), 2.21 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 166.6 (d, *J* = 259.6 Hz), 161.0, 152.2, 141.1, 133.4 (d, *J* = 9.9 Hz), 131.4, 129.8, 129.6, 128.6, 123.4, 120.1, 119.8 (d, *J* = 3.1 Hz), 119.3 (d, *J* = 23.2 Hz), 115.2, 55.4, 42.8, 39.6, 21.5. HRMS (ESI-TOF) *m/z* [M−$^-$$SbF_6$]$^+$ calcd for $C_{24}H_{22}FOS$ 377.1375, found 377.1373.

Formation of crystals of 2m for Single-Crystal X-ray Analysis. A 1 dram vial was charged with product **2m** (ca. 50 mg) followed by DCM (1 mL). A 20 mL scintillation vial was charged with $CHCl_3$ (3 mL). The 1 dram vial was then lowered into the 20 mL vial. The 20 mL vial was capped with a plastic screwcap and placed in a refrigerator with temperature set to 6 °C. After leaving for 3 d, the vial was removed from the refrigerator and the formed crystals were submitted to the X-ray crystallography facility for characterization.

Formation of crystals of 2n for Single-Crystal X-ray Analysis. To a 1 dram vial charged with $AgSbF_6$ (51.5 mg, 0.150 mmol, 1.5 equiv) and equipped with a magnetic stir bar was added MeDalPhosAuCl (6.5 mg, 0.10 mmol,10 mol%), internal alkyne **1g** (29.6 mg, 0.100 mmol, 1.0 equiv), 2-iodobenzo[*d*]thiazole (31.3 mg, 0.120 mmol, 1.2 equiv), and DCE (1.0 mL). The reaction mixture placed in an aluminum block set to 60 °C and was left to stir for 1 h. The resulting mixture was filtered through cotton and rinsed with DCM (3 mL). The filtrate was washed with H_2O (5 mL) and the resulting aqueous layer was extracted with DCM (2 × 5 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by normal phase column chromatography. Fractions were combined and concentrated in vacuo to yield a yellow, sticky oil. To a 1 dram vial charged with resultant oil (ca. 20 mg) was added $CDCl_3$ (ca. 0.5 mL). The vial was capped with a plastic screw cap and left at ambient temperature. After 7 d, the solvent had evaporated from the vial and yielded thin, yellow crystals. The crystals were collected for X-ray crystallography.

*(Z)-4-(3-ethoxy-3-oxoprop-1-en-1-yl)-5-(4-methoxyphenyl)-1-(p-tolyl)-2,3-dihydro-1H-thiophen-1-ium hexafluorostibate(V) (**3a**)*. Prepared according to Procedure B with no modifications. the reaction mixture was heated and stirred for 24 h. The reaction mixture was filtered through cotton and rinsed with DCM (5 mL). The filtrate was transferred to a separatory funnel and washed with DI H_2O (1 × 5 mL). The aqueous layer was back extracted with DCM (2 × 5 mL). The organic layers were then combined and dried with Na_2SO_4. The solution was then decanted and concentrated in vacuo. The resulting crude was purified by normal phase column chromatography (0–10% MeOH in DCM). Product-containing fractions were concentrated in vacuo then recrystallized with hot $CHCl_3$ to afford dihydrothiophenium **3a** as a yellow solid (43 mg, 71%). ^{1}H NMR (400 MHz,

$CDCl_3$) δ 7.82 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.8 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 6.69 (d, *J* = 12.0 Hz, 1H), 6.19 (d, *J* = 12.0 Hz, 1H), 4.46–4.39 (m, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 4.17–4.09 (m, 1H), 3.76 (s, 3H), 3.70–3.64 (m, 1H), 3.46–3.38 (m, 1H), 2.40 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 165.4, 161.6, 148.7, 146.8, 136.6, 132.4, 131.3, 130.6, 128.2, 126.7, 120.7, 119.7, 115.0, 61.5, 55.6, 44.5, 37.8, 21.8, 14.3. HRMS (ESI-TOF) *m/z* $[M-^{-}SbF_6]^+$ calcd for $C_{23}H_{25}O_3S$ 381.1524, found 381.1524.

*1-(4-methoxyphenyl)-5-methyl-2,3-dihydro-1H-thiophen-1-ium (**3b**)*. Prepared according to Procedure B with no modifications using starting alkyne **1r** (20.6 mg, 0.100 mmol, 1.0 equiv). The reaction mixture was heated and stirred for 2 h. The reaction mixture was filtered through cotton and rinsed with DCM (5 mL). The filtrate was transferred to a separatory funnel and washed with DI H_2O (1 × 5 mL). The aqueous layer was back extracted with DCM (2 × 5 mL). The organic layers were then combined and dried with Na_2SO_4. The solution was then decanted and concentrated in vacuo. The resulting crude was purified by normal phase column chromatography (0–10% MeOH in DCM). Product-containing fractions were concentrated in vacuo then recrystallized with hot $CHCl_3$ to afford dihydrothiophenium **3b** as a brown solid (42 mg, 79%). ^1H NMR (600 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.7 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 7.9 Hz, 2H), 7.17 (d, *J* = 8.7 Hz, 2H), 4.33–4.27 (m, 1H), 3.88 (s, 3H), 3.85–3.77 (m, 1H), 3.65–3.60 (m, 1H), 3.56–3.48 (m, 1H), 2.38 (s, 3H), 2.03 (s, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 165.3, 153.3, 140.7, 132.6, 130.0, 129.7, 128.1, 120.6, 117.5, 113.6, 56.2, 43.8, 38.8, 21.5, 13.2. HRMS (ESI-TOF) *m/z* $[M-^{-}SbF_6]^+$ calcd for $C_{19}H_{21}OS$ 297.1313, found 297.1313.

Internal competition experiment using substrate 1e. Prepared according to Procedure B with the following modification: The reaction was run at half scale such that 50.0 µmol of substrate **1e** was used. The reaction mixture was then concentrated in vacuo. The resulting crude material was dissolved as well as possible in $CDCl_3$ (ca. 0.5 mL) then analyzed by ^1H NMR spectroscopy. There was a remaining oil in the 1 dram vial that was insoluble in the initial $CDCl_3$ solubilization, so the remaining material was dissolved in DMSO-d_6 and analyzed by ^1H NMR spectroscopy. Each spectrum showed evidence of product **2e** but no evidence of an alternative product.

Internal competition experiment using substrate 1f. Prepared according to Procedure B with the following modifications: The reaction was run with 3 equiv $AgSbF_6$, run for 23 h and run at half scale such that 50.0 µmol of substrate **1f** was used. The reaction mixture was then concentrated in vacuo. The resulting crude material was dissolved DMSO-d_6 (ca. 0.5 mL) then analyzed by ^1H NMR spectroscopy. Triplet peaks present at 3.0–3.5 ppm suggest either unreacted starting material or a product different from **2f**. The NMR tube containing the analyzed mixture was charged with **1f** (1.5 mg, 5.0 µmol, 10. mol%) in DMSO-d_6 (0.1 mL) and analyzed by ^1H NMR spectroscopy. The **1f**-doped spectrum confirms that the unknown peaks are unreacted **1f** by showing that peaks from **1f** and the peaks present at 3.0–3.5 ppm are not overlapping.

Alkynyl Ar^2 competition experiments. To a 1 dram vial was added 4-iodoanisole (7.0 mg, 30. µmol, 1 equiv) alkynes **1a** (22.7 mg, 90.0 µmol, 3 equiv), and either **1c** (25.8 mg, 90.0 µmol, 3 equiv), **1d** (25.4 mg, 90.0 µmol, 3 equiv), or **1h** (27.9 mg, 90.0 µmol, 3 equiv). The reagents were dissolved in $CDCl_3$ (ca. 0.5 mL) and the solution was mixed well by pipette. The solution was then analyzed by ^1H NMR spectroscopy to ensure the correct ratio of reagents. The solution was then transferred back to the 1 dram vial and concentrated in vacuo. The resultant oil was then dissolved 1 mL DCE and transferred to a vial charged with MeDalPhosAuCl (2.0 mg, 3.0 µmol, 10 mol%). This solution was then transferred to a 1 dram vial charged with AgSbF6 (67.0 mg, 195 µmol, 6.5 equiv) and equipped with a stir bar. The vial was then capped with a plastic screw cap and placed on an aluminum heating block set to 60 °C. The reaction mixture was allowed to stir for 1 h before the vial was removed from the hot plate. After allowing the vial to cool to ambient temperature, DCM (2 mL) was added and the mixture was filtered through celite over cotton. The mixture was rinsed with DCM (3 × 1 mL). The resulting filtrate was then transferred to a separatory funnel and washed with DI H_2O (1 × 10 mL). The organic layer was then collected and dried with Na_2SO_4 then filtered through cotton. The filtrate was concentrated and purified by normal phase column chromatography. First a gradient from 0–50% EtOAc was used to remove excess alkyne. Then the solvent system was switched to DCM and a gradient was run from 0–10% MeOH in DCM. Care was taken to collect a wide range of fractions after the solvent system swap to ensure no small amounts of product were left behind and an accurate ratio of products could be determined. The product-containing fractions were combined and concentrated in vacuo then dissolved in $CDCl_3$ (for **1a** vs **1c**) or DMSO-d_6 (for **1a** vs **1h** or **1d**) for ^1H NMR spectroscopic analysis.

Thioanisole poisoning experiments. To a 1 dram vial equipped with stir bar was added $AgSbF_6$ (25.8 mg, 75.0 µmol, 1.5 equiv). A separate 1 dram vial was charged with alkyne **1h** (15.5 mg, 50.0 µmol, 1 equiv), thioanisole (6.2 mg, 50. µmol, 1 equiv), 4-iodoanisole (14.0 mg, 60.0 µmol, 1.2 equiv), and MeDalPhosAuCl (3.3 mg, 5.0 µmol, 10 mol%) in DCE (0.2 mL). The DCE solution was transferred to the $AgSbF_6$ vial, and DCE (2 × 1.5 mL) was used to rinse any remaining starting materials into the $AgSbF_6$ vial. The mixture-containing vial was then capped with a plastic screw cap and placed in an aluminum block on a hot plate set to 60 °C. The mixture was stirred for 1 h then removed from the hot plate. The mixture was concentrated in vacuo. To the remaining material was added DMSO-d_6 (ca. 0.5 mL). The resulting mixture was mixed by pipette then transferred to an NMR tube and analyzed by ^1H NMR spectroscopy. This experiment was repeated for 5 equiv thioanisole (31.1 mg, 250. µmol) and 0 equiv thioanisole.

^1H NMR spectrum of alkyne 1h with $AgSbF_6$. A 1 dram vial was charged with with $AgSbF_6$ (25.8 mg, 75.0 µmol, 1.5 equiv) and alkyne **1h** (15.5 mg, 50.0 µmol, 1.0 equiv) then dissolved the mixture in DMSO-d_6 (ca. 0.5 mL). The solution was then transferred to an NMR tube and analyzed by ^1H NMR spectroscopy. This data is included in Scheme 5 for better comparison of alkyne **1h** in reaction conditions as coordination to $AgSbF_6$ shifts the peaks of alkynes **1h**. ^1H NMR (600 MHz, DMSO-d_6) δ 7.90 (d, *J* = 8.2 Hz, 2H), 7.47 (d, *J* = 8.1 Hz, 2H), 7.40 (m, 2H), 7.19 (d, *J* = 7.8 Hz, 2H), 3.83 (s, 3H), 3.21 (m, 2H), 2.74 (t, *J* = 6.9 Hz, 2H), 2.26 (s, 3H).

Characterization of incomplete reaction component 10 by HRMS. To a 1 dram vial equipped with stir bar was added $AgSbF_6$ (25.8 mg, 75.0 µmol, 1.5 equiv). A separate 1 dram vial was charged with internal alkyne **1h** (15.5 mg, 50.0 µmol, 1 equiv), 4-iodoanisole (14.0 mg, 60.0 µmol, 1.2 equiv), and MeDalPhosAuCl (3.3 mg, 5.0 µmol, 10 mol%) in DCE (0.2 mL). The DCE solution was transferred to the $AgSbF_6$ vial, and DCE (2 × 1.5 mL) was used to rinse any remaining starting materials into the $AgSbF_6$ vial. The mixture-containing vial was then capped with a plastic screw cap and placed in an aluminum block on a hot plate set to 60 °C. The mixture was stirred for 15 min then removed from the hot plate. A 0.05 mL sample of the reaction mixture was removed and filtered through celite and cotton, using DCM (1 mL) to rinse through any material. The resulting filtrate was diluted in MeOH and analyzed by high resolution LCMS. HRMS (ESI-TOF) *m/z* $[M]^+$ calcd for $C_{36}H_{50}AuNO_2P$ 756.3245, found 756.3230.

Aryl iodide competition experiment. Methyl 4-iodobenzoate (6.6 mg, 25 µmol, 1.0 equiv) and 4-iodoanisole (5.9 mg, 25 µmol, 1.0 equiv) were combined in $CDCl_3$ (ca 0.5 mL) and analyzed by ^1H NMR spectroscopy to confirm an equal molar ratio of the aryl iodides. The $CDCl_3$ solution was then transferred to a 1 dram vial, rinsing with DCM (1 mL). The solution was concentrated in vacuo. The vial was then charged with MeDalPhosAuCl (34 mg, 53 µmol, 2.1 equiv) dissolved in DCE (0.2 mL). The DCE solution was transferred to a separate vial containing $AgSbF_6$ (39 mg, 4.5 equiv, 0.11 mmol), and more DCE (2 × 0.2 mL) was used to rinse any remaining starting materials into the $AgSbF_6$ vial. The resulting mixture was equipped with a stir bar and stirred for 10 min at ambient temperature. Then alkyne **1h** (7.8 mg, 25 µmol, 1.0 equiv) in DCE (0.4 mL) was added to the reaction mixture. The mixture-containing vial was then capped with a plastic screw cap and placed in an aluminum block on a hot plate set to 60 °C. The mixture was stirred for 1 h then removed from the hot plate. The reaction mixture was then filtered through celite and cotton, rinsing through with DCM (5 mL). The filtrate was transferred to a separatory funnel and washed with DI H_2O (1 × 10 mL). The aqueous layer was then back extracted with DCM (2 × 5 mL). The organic layers were combined and dried with Na_2SO_4. The solution was then decanted and concentrated in vacuo. The resulting crude material was purified by normal phase column chromatography (0–10% MeOH in DCM). Product-containing fractions were identified by UV chromatogram. Care was taken to combine a wide range of fractions around the identified product-containing fractions to avoid missing product. The combined fractions were then concentrated in vacuo and analyzed by ^1H NMR spectroscopy in DMSO-d_6.

*(E)-4-(3-(benzo[d]thiazol-2-yl)-4-(4-methoxyphenyl)-4-(p-tolylthio)but-3-en-1-yl)morpholine (**11**).* To a 1 dram vial equipped with a stir bar was added dihydrothiophenium 2m (65.2 mg, 0.100 mmol, 1.0 equiv). A separate 1 dram vial was charged with morpholine (0.50 g, 0.50 mL, 5.8 mmol, 58 equiv). Each vial was then capped with a plastic screwcap and inserted into an ice bath prepared in a Dewar flask to precool. After 30 min, the screwcaps were removed and the morpholine was transferred into the vial containing **2m**. The vial was capped again and allowed to stir for 21 h. The ice bath was allowed to warm to ambient temperature during the reaction time. The resulting reaction solution was transferred to a separatory funnel and diluted with DCM (10 mL). The solution was washed with 0.1 M NaOH (1 × 10 mL) and DI H_2O (1 × 10 mL). The aqueous layers were combined and back extracted with DCM (2 × 5 mL). The organic layers were combined and dried with Na_2SO_4. The solution was then decanted and concentrated in vacuo. The resulting crude material was purified by normal phase HPLC (0–50% EtOAc in hexanes with 1% NEt_3) to afford amine **11** as a yellow oil. (48.0 mg, 95%). ^1H NMR (600 MHz, $CDCl_3$) δ 7.94 (m, 1H), 7.59 (m, 1H), 7.37 (m, 1H), 7.24 (m, 1H), 7.08–7.04 (m, 4H), 6.90 (m, 2H), 6.62 (m, 2H), 3.72 (s, 3H), 3.70 (m, 4H), 3.56 (m, 2H), 2.65 (m, 2H), 2.59 (br s, 4H), 2.21 (s, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 168.1, 159.9, 152.3, 144.7, 137.7, 136.2, 133.6, 133.4, 132.4, 129.7, 129.5, 128.9, 125.8, 124.9, 123.0, 121.2, 113.7, 67.2, 57.6, 55.3, 53.8, 33.1, 21.2. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{29}H_{30}N_2O_2S_2H$ 503.1827, found 503.1829.

*(E)-N-allyl-3-(benzo[d]thiazol-2-yl)-4-(4-methoxyphenyl)-N-methyl-4-(p-tolylthio)but-3-en-1-amine (**12**).* To a 1 dram vial equipped with a stir bar was added dihydrothiophenium **2m** (65.2 mg, 0.100 mmol, 1.0 equiv). A separate 1 dram vial was charged with *N*-methylallylamine (0.37 g, 0.50 mL, 5.2 mmol, 52 equiv). Each vial was then capped with a plastic screwcap and inserted into an ice bath prepared in a Dewar flask to precool. After 30 min, the screwcaps were removed and the morpholine was transferred into the vial containing **2m**. The vial was capped again and allowed to stir for 21 h. The ice bath was allowed to warm to ambient temperature during the reaction time. The resulting reaction solution was transferred to a separatory funnel and diluted with DCM (10 mL). The solution was washed with 0.1 M NaOH (1 × 10 mL) and DI H_2O (1 × 10 mL). The aqueous layers were combined and back extracted with DCM (2 × 5 mL). The organic layers were combined and dried with Na_2SO_4. The solution was then decanted and concentrated in vacuo. The resulting crude material was purified by normal phase HPLC (0–50% EtOAc in hexanes with 1% NEt_3) to afford amine **12** as a yellow oil. (43.1 mg, 89%). ^1H NMR (600 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.2 Hz, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.38 (m, 1H), 7.24 (m, 1H), 7.09–7.03 (m, 4H), 6.90 (d, *J* = 8.0 Hz, 2H), 6.62 (d, *J* = 8.7 Hz, 2H), 5.94–5.86 (m, 1H), 5.19 (dd, *J* = 17.2 Hz, *J* = 1.4 Hz, 1H), 5.10 (m, 1H), 3.72 (s, 3H), 3.55 (m, 2H), 3.14 (d, *J* = 6.5 Hz, 2H), 2.70 (m, 2H), 2.36 (s, 3H), 2.21 (s, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 168.0, 159.9, 152.4, 144.6, 137.7, 136.2, 136.0, 133.7, 133.5, 132.4, 129.7, 129.4, 129.0, 125.7, 124.9, 123.0, 121.1, 117.5, 113.7, 60.6, 55.7, 55.3, 42.1, 33.4, 21.2. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{29}H_{30}N_2OS_2H$ 487.1878, found 487.1860.

*(E)-4-(4-((4-fluorophenyl)thio)-4-(4-methoxyphenyl)-3-(p-tolyl)but-3-en-1-yl)morpholine (**13**).* To a 1 dram vial equipped with a stir bar was added dihydrothiophenium **2p** (61.3 mg, 0.100 mmol, 1.0 equiv). A separate 1 dram vial was charged with *N*-methylallylamine (0.37 g, 0.50 mL, 5.2 mmol, 52 equiv). Each vial was then capped with a plastic screwcap and inserted into an ice bath prepared in a Dewar flask to precool. After 30 min, the screwcaps were removed and the morpholine was transferred into the vial containing **2p**. The vial was capped again and allowed to stir for 21 h. The ice bath was allowed to warm to ambient temperature during the reaction time. The resulting reaction solution was transferred to a separatory

funnel and diluted with DCM (10 mL). The solution was washed with 0.1 M NaOH (1 × 5 mL), DI H_2O (1 × 5 mL), and brine (1 × 5 mL). The aqueous layers were combined and back extracted with DCM (2 × 5 mL). The organic layers were combined and dried with Na_2SO_4. The solution was then decanted and concentrated in vacuo. The resulting crude material was purified by normal phase HPLC (0–50% EtOAc in hexanes with 1% NEt_3) to afford alkene **13** as a yellow oil. (43.0 mg, 73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (dd, J = 8.7 Hz, *J* = 5.3 Hz, 2H), 6.97 (d, *J* = 8.7 Hz, 2H), 6.93 (s, 4H), 6.79 (t, *J* = 8.7 Hz, 2H), 6.46 (d, *J* = 8.7 Hz, 2H), 3.71 (t, *J* = 4.5 Hz, 4H), 3.64 (s, 3H), 3.21 (m, 2H), 2.49 (br s, 4H), 2.41 (m, 2H), 2.24 (s, 3H).^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 161.6 (d, *J* = 245.9 Hz), 158.0, 143.8, 139.0, 136.2, 132.8, 132.3 (d, *J* = 8.1 Hz), 132.2, 131.6, 130.3 (d, *J* = 3.2 Hz), 129.4, 128.8, 115.7 (d, *J* = 21.9 Hz), 112.8, 67.1, 57.4, 55.1, 53.8, 35.6, 21.3. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{28}H_{30}FN_2OSH$ 464.2060, found 464.2065.

*(E)-(4-bromophenyl)(4-((4-fluorophenyl)thio)-4-(4-methoxyphenyl)-3-(p-tolyl)but-3-en-1-yl)sulfane (**14**).* To a 1 dram vial equipped with stir bar was added **2p** (61.3 mg, 0.100 mmol, 1.00 equiv) 4-bromobenzenethiol (19.9 mg, 0.105 mmol, 1.05 equiv), and $NaHCO_3$ (25.2 mg, 0.300 mmol, 3.00 equiv). The vial was capped with a plastic screwcap and the mixture was stirred at ambient temperature for 1 h. The mixture was then transferred to a separatory funnel containing 1 M NaOH (5 mL). The mixture was then extracted with DCM (3 × 5 mL). The combined organic layers were washed with 1 M NaOH (1 × 5 mL), DI H_2O (1 × 5 mL), and brine (1 × 5 mL). The organic layer was then dried with Na2SO4, decanted using a beaker, and concentrated in vacuo. The remaining crude material was purified by column was purified by normal phase HPLC (0–30% EtOAc in hexanes) to afford alkene **14** as a colorless solid (38.5 mg, 86%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 (m, 2H), 7.13 (m, 2H), 7.12–7.08 (m, 2H), 6.97 (m, 2H), 6.94 (d, *J* = 7.9 Hz, 2H), 6.90 (d, *J* = 8.2 Hz, 2H), 6.82–6.77 (m, 2H), 6.47 (m, 2H), 3.64 (s, 3H), 3.31 (m, 2H), 2.93 (m, 2H), 2.26 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 161.7 (d, *J* = 246.1 Hz), 158.2, 143.4, 138.2, 136.5, 135.9, 133.9, 132.4 (d, *J* = 8.0 Hz), 132.2, 131.9, 131.4, 130.4 130.0 (d, *J* = 3.3 Hz), 129.5, 128.9, 119.5, 115.8 (d, *J* = 21.9 Hz), 112.9, 55.1, 38.0, 31.9, 21.3. HRMS (ESI and GC-MS-EI) was attempted, but satisfactory mass analysis was not obtained, potentially due to decomposition of the compound at the elevated temperatures needed for GC and the lack of ionization of this nonpolar compound under ESI conditions.

*(E)-(4-((4-fluorophenyl)thio)-4-(4-methoxyphenyl)-3-(p-tolyl)but-3-en-1-yl)triphenylphosphonium hexafluorostibate(V) (**15**).* Reaction was carried out in a glovebox under N_2 atmosphere. To a 1 dram vial equipped with stir bar was added **2p** (61.3 mg, 0.100 mmol, 1.00 equiv), PPh_3 (52.5 mg, 0.500 mmol, 5.00 equiv), and MeCN (0.33 mL). The vial was capped with a plastic screwcap and placed on a hot plate set to 60 °C. The mixture was allowed to stir on the hot plate for 5 h. The vial was then removed from the glovebox and concentrated in vacuo to remove the MeCN. The crude material was then purified by normal phase column chromatography (0–70% EtOAc in hexanes) to afford alkene **15** as a yellow solid (72.3 mg, 83%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (m, 3H), 7.68 (m, 6H), 7.61–7.56 (m, 6H), 7.12–7.08 (m, 2H), 6.98–6.94 (m, 4H), 6.89 (d, *J* = 8.1 Hz, 2H), 6.81–6.76 (m, 2H), 6.45 (m, 2H), 3.60 (s, 3H), 3.36–3.31 (m, 2H), 3.15–3.09 (m, 2H), 2.23 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 161.9 (d, *J* = 246.9 Hz), 158.5, 140.4 (d, *J* = 15.3 Hz), 137.3, 136.8, 135.8, 135.7 (d, *J* = 2.9 Hz), 133.4 (d, *J* = 10.0 Hz), 132.9 (d, *J* = 8.2 Hz), 132.2, 130.9 (d, *J* = 12.6 Hz), 130.4, 129.5 (d, *J* = 2.8 Hz), 128.8 (d, *J* = 3.1 Hz), 117.7, 117.2, 116.0 (d, *J* = 22.0 Hz), 113.0, 55.1, 31.0 (d, *J* = 2.2 Hz), 21.7 (d, *J* = 48.9 Hz), 21.3. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{42}H_{37}FOPS$ 639.2287, found 639.2287.

ASSOCIATED CONTENT

Data Availability Statement

The data underlying this study are available in the published article and its Supporting Information.

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

General considerations, terminal alkyne precursor synthesis, attempted syntheses of **2q**, Hammett plot data, stepwise reaction data, synthesis and attempted isolation of **SI-2s**, single crystal X-ray structure information, ^{1}H, ^{13}C, and ^{31}P NMR spectra

Accession Codes

CCDC 2369078 and 2369079 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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