JOC The Journal of Organic Chemistry

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Gold-Catalyzed Domino Aminocyclization/1,3-Sulfonyl Migration of N-Substituted *N*-Sulfonyl-aminobut-3-yn-2-ols to 1-Substituted 3-Sulfonyl-1*H*-pyrroles

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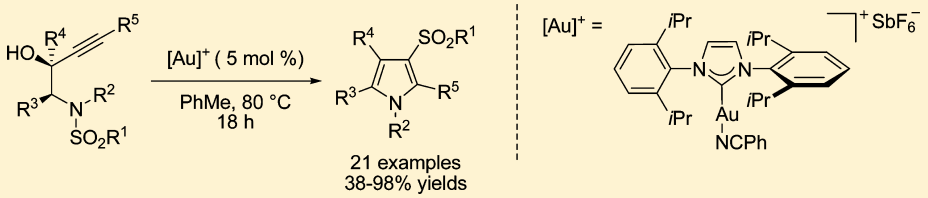
Supporting Information



ABSTRACT: A method to prepare 1-substituted 3-sulfonyl-1*H*-pyrroles efficiently that relies on the gold(I)-catalyzed cycloisomerization of N-substituted *N*-sulfonyl-aminobut-3-yn-2-ols is described. The method was shown to be applicable to a broad range of 1,7-enyne alcohols containing electron-withdrawing, electron-donating, and sterically demanding substrate combinations. The mechanism is suggested to involve activation of the propargylic alcohol by the Au(I) catalyst, which causes the intramolecular nucleophilic addition of the sulfonamide unit to the alkyne moiety. The resulting nitrogen-containing heterocyclic intermediate undergoes dehydration and deaurative 1,3-sulfonyl migration, a process that remains rare in gold catalysis, to give the aromatic nitrogen-containing product.

INTRODUCTION

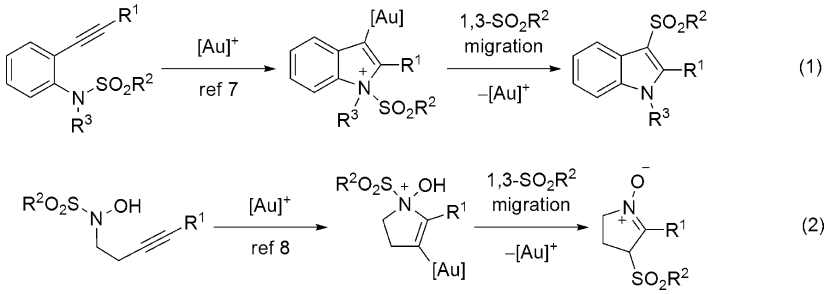
Gold-catalyzed organic transformations have received an immense amount of attention over the years because of their remarkable ability to deliver efficiently a diverse range of synthetically useful complex molecules from simple and readily accessible substrates.[1−12] From a mechanistic viewpoint, the reactions have generally relied on the gold-mediated activation of the π bonds of alkenes, allenes, and alkynes to attack by a nucleophile. This is then followed by protodeauration of the resulting organogold species generated in situ in the final step of the catalytic cycle to regenerate the metal catalyst and give the product.[1,2,9−12] Another approach to regenerate the metal catalyst that has come under increasing scrutiny has been carbodeauration, involving the substitution of the carbon−gold bond by an allyl/α-alkoxy alkyl, iminium, or benzyl functional group.[3−6] The incorporation of a heteroatom into the product at the electrophilic deauration step, by contrast, has been less well investigated.[7−10] This approach to regenerate the Lewis acid catalyst has been reported only twice before in gold catalysis, presumably because of the more favorable aforementioned carbodeauration and protodeauration pathways. In this context, a recent notable advance is that by Nakamura and co-workers who showed that the deauration step involves 1,3-sulfonyl migration in the gold-catalyzed cycloisomerization of *o*-alkynyl-*N*-sulfonamides to the corresponding 3-sulfonylindole derivatives (Scheme 1, eq 1).[7,13] Following this seminal work, Shin and co-workers reported a similar deaurative 1,3-sulfonyl migration step to occur in the gold-catalyzed [3 + 2] cycloadditions of *N*-sulfonyl hydroxylamines with a pendent alkyne moiety to 4-sulfonyl-dihydropyrrole-oxides (Scheme 1, eq 2).[8] More recently, during the course of an ongoing program examining the utility of gold catalysis in *N*-heterocyclic synthesis,[11] we found one further example of this type of deaurative process (Scheme 2, pathway 1).[9] With NHC−gold(I) complex **A** shown in Figure 1 as the catalyst,[12] 3-tosyl *N*-allyl pyrrole **2a** and the 1,6-allene **3a** were obtained in 20 and 29% yield, respectively, instead of the anticipated cyclobutane-fused piperidine **4a** from 1,7-enyne benzoate **1a**. In a continuation of these investigations, we reasoned that the chemical yield of the potentially useful aromatic N-heterocyclic adduct could be enhanced by the use of the corresponding 1,7-enyne alcohol as the substrate and by identifying the appropriate reaction conditions. Herein, we describe the details of this study involving the Au(I)-catalyzed tandem aminocyclization/1,3-sulfonyl shift of N-substituted *N*-sulfonyl-aminobut-3-yn-2-ols (Scheme 2, pathway 2). This process provides a convenient and operationally straightforward route to 1-substituted 3-sulfonyl-1*H*-pyrroles in good to excellent yields for a wide variety of substrates.

RESULTS AND DISCUSSION

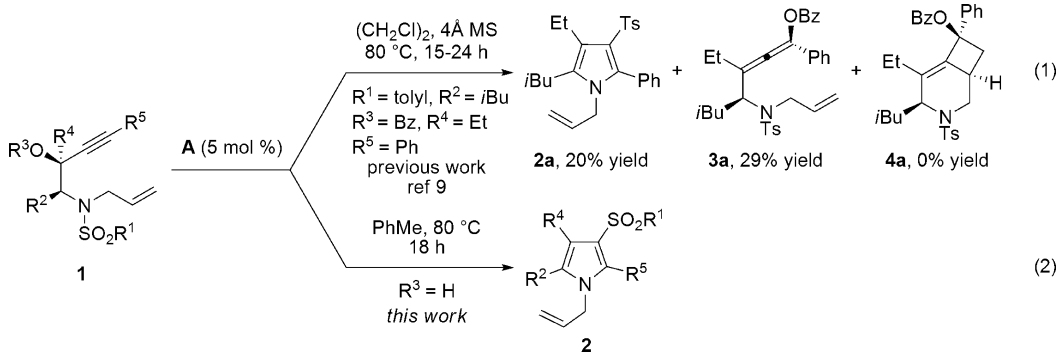
To test the feasibility of our hypothesis, we choose **1b** as the model substrate to establish the reaction conditions (Table 1).[15] This study revealed that treating **1b** with 5 mol % of

Received: May 16, 2013
Published: July 2, 2013

Scheme 1. Gold-Catalyzed Cycloisomerizations of Propargylic Substrates Involving a 1,3-Sulfonyl Migration Step



Scheme 2. Gold-Catalyzed Cycloisomerization of 1,7-Enyne Benzoates and Alcohols



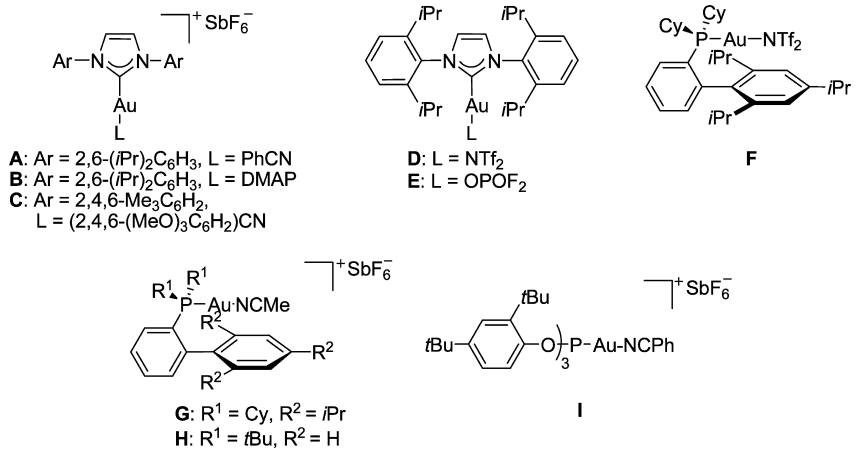


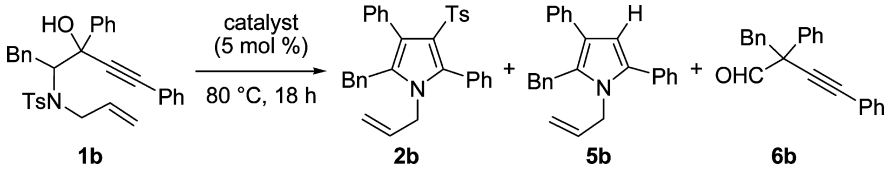
Figure 1. Gold(I) complexes examined in this study.[12,14]

NHC–gold(I) complex **A** at 80 °C for 18 h gave the best result, affording 1-allyl-2-benzyl-3,5-diphenyl-4-tosyl-1*H*-pyrrole **2b** in 70% yield (entry 1). The structure of the aromatic nitrogen-containing heterocycle was confirmed by X-ray crystal structure analysis.[16] Lower product yields were obtained when the reaction was carried out at room temperature or employed THF or 1,2-dichloroethane in place of toluene as the solvent (entries 2, 4, and 5). In the latter two control experiments, trisubstituted pyrrole **5b** was also furnished in low yields of 10 and 6% (entries 4 and 5), respectively. With 1,2-dichloroethane as the solvent, a similar outcome was found when the reaction was conducted with NHC–gold(I) complexes **C**–**E**,[14] gold(I) phosphine complexes **F**–**H**, and gold(I) phosphite complex **I** shown in Figure 1 and with $Ph_3PAuNTf_2$ in place of **A** as the catalyst (entries 7–13 and 15). In contrast, for the analogous control experiments with NHC–gold(I) complex **B** shown in Figure 1, $(4\text{-}CF_3Ph)_3PAuCl/AgSbF_6$ or AuCl as the catalyst or MeCN as the reaction solvent were found to be less effective (entries 3, 6, 14, and 16). Subjecting **1b** to these catalysts in 1,2-dichloroethane or NHC–gold(I) complex **A** with MeCN as the solvent led to a variety of unidentifiable decomposition products being detected by ^1H NMR measurements of the crude reaction mixtures. Likewise, $AuBr_3$ and $InBr_3$, reported to promote the cycloisomerization of *o*-alkynyl-*N*-sulfonylanilines to 3- and 5-sulfonyl substituted indoles,[7] were found to result in the recovery of **1b** in 89% yield or a mixture of decomposition products, respectively (entries 17 and 18). Control experiments with $AgSbF_6$, $AgNTf_2$, and the Brønsted acids TfOH and Tf_2NH as the catalyst also led to the formation of a mixture of decomposition products as well as provided evidence that the cationic Au(I) complex is the active species (entries 19–22).

To define the scope of the present procedure, we next sought to assess its generality for a series of N-substituted *N*-sulfonylaminobut-3-yn-2-ols, and the results are summarized in Table 2. Overall, the reaction conditions were found to be general, and a variety of 3-sulfonyl-substituted pyrrole derivatives were

dx.doi.org/10.1021/jo401083m | J. Org. Chem. 2013, 78, 7508–7517

Table 1. Optimization of the Reaction Conditions[a]



1b 2b 5b 6b

			yield (%)		
entry	catalyst	solvent	2b	5b	6b
1	**A**	PhMe	70		
2[b]	**A**	PhMe	57		
3	**A**	MeCN	[c]		
4	**A**	THF	62	10	
5	**A**	$(CH_2Cl)_2$	68	6	
6	**B**	$(CH_2Cl)_2$	[d]		
7	**C**	$(CH_2Cl)_2$	36		
8	**D**	$(CH_2Cl)_2$	67	6	
9	**E**	$(CH_2Cl)_2$	52	7	
10	**F**	$(CH_2Cl)_2$	50	25	
11	**G**	$(CH_2Cl)_2$	30	28	
12	**H**	$(CH_2Cl)_2$	33	15	
13	**I**	$(CH_2Cl)_2$	49		
14	$(4\text{-}CF_3Ph)_3PAuCl/AgSbF_6$	$(CH_2Cl)_2$	[e]		
15	PPh_3AuNTf_2	$(CH_2Cl)_2$	38		
16	AuCl	$(CH_2Cl)_2$	[c]		
17	$AuBr_3$	$(CH_2Cl)_2$	[d]		
18	$InBr_3$	$(CH_2Cl)_2$	[c]		
19	$AgSbF_6$	$(CH_2Cl)_2$			37
20	$AgNTf_2$	$(CH_2Cl)_2$			10
21	TfOH	$(CH_2Cl)_2$	[c]		
22	Tf_2NH	$(CH_2Cl)_2$	[c]		

[a]All reactions conducted on the 0.2 mmol scale with 5 mol % of catalyst at 80 °C for 18 h. [b]Reaction carried out at room temperature. [c]Mixture of unknown side products were furnished on the basis of ^{1}H NMR analysis of the crude mixture. [d]No reaction on the basis of TLC or ^{1}H NMR analysis of the crude mixture. [e]Recovery of **1b** in 66% yield.

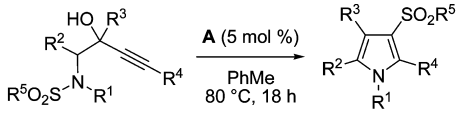
afforded in 38−98% yield from corresponding starting alcohols **1c−v**. Propargyl alcohols in which the carbinol carbon center is occupied by a pendant phenyl group with an electron-donating (**1c**) or electron-withdrawing (**1d**) substituent at the para position gave corresponding products **2c** and **2d** in 56 and 41% yield, respectively. Replacing the phenyl substituent at this position with a 2-thiophenyl (**1e**) or Et (**1f**) moiety was found to have no influence on the course of the reaction, affording **2e** and **2f** in respective yields of 52 and 43%. Likewise, the reactions of substrates with the C≡C bond substituted with an aryl, thiophene, alkyl, or cycloalkyl group, as in **1g−l**, were found to be well tolerated and afforded corresponding products **2g−l** in 59−93% yield. However, the presence of a terminal alkyne moiety on the substrate (**1m**) was found to give corresponding pyrrole adduct **2m** in a lower yield of 45%. Increasing the steric demand of the substituent at the amino carbon (**1n** and **1o**) was also found to play a role. In these reactions, cycloisomerization of **1n**, with a pendant Ph group at the amino carbon center, gave **2n** in 74% yield, whereas the analogous reaction of **1o** containing the more sterically bulky *i*Pr moiety at the same position afforded **2o** in 38% yield. Likewise, increasing the steric demand of the alkyl group (**1p−s**) or decreasing the electron-donating ability of the sulfonyl moiety (**1t−v**) on the amino center of the substrate was found to give a similar outcome. Under standard conditions, the corresponding *N*-methyl (**2p**), *N*-butyl (**2q**), *N*-benzyl (**2r**), and *N*-cinnamyl (**2s**) protected products were obtained in 40−98% yield. For reactions with *N*-(4-methoxyphenylsulfonyl) (**1t**), *N*-(4-chlorophenylsulfonyl) (**1u**), and *N*-mesyl (**1v**) protected substrates, corresponding 3-sulfonyl pyrrole adducts **2t−v** were furnished in 67, 54, and 43% yields, respectively.

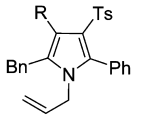
To demonstrate that the deaurative 1,3-sulfonyl migration step proceeds in an intramolecular manner that leads to the formation of the 3-sulfonyl-substituted pyrrole adduct, we next examined the crossover experiment of 1 equiv of **1p** with 1 equiv of **1v** in the presence of 5 mol % **A** in toluene at 80 °C for 18 h (Scheme 3, eq 1). Under these conditions, both **2p** and **2v** were afforded as the only products in respective yields of 42 and 58%, with the analysis of the crude reaction mixture by ^{1}H NMR spectroscopy and mass spectrometry showing no other cyclic products being detected. Our findings that show the near-quantitative recovery of starting materials for the reaction of **5b** with *p*TsCl exposed to 5 mol % of **A** under the standard conditions described in Scheme 3, eq 2 led us to also posit that an intermolecular deaurative sulfonylation step was unlikely.

Although speculative, the mechanism for the present Au(I)-catalyzed 3-sulfonyl-pyrrole-forming reaction is outlined in Scheme 4. This could involve the activation of the propargylic alcohol through coordination of the metal catalyst with the alkyne moiety of the adduct to give Au(I)-coordinated intermediate **A**. As a result, this triggers the intramolecular aminocyclization process involving anti addition of the N,N-disubstituted amino moiety to the C≡C bond to provide vinyl gold complex **B**. At this juncture, dehydration of this newly

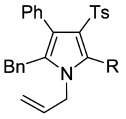
dx.doi.org/10.1021/jo401083m | J. Org. Chem. 2013, 78, 7508−7517

Table 2. Cycloisomerization of 1c−v Catalyzed by A[a]

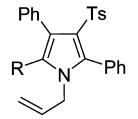




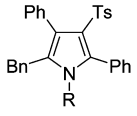
2c: R = *p*MeC$_6$H$_4$ (56%)
2d: R = *p*ClC$_6$H$_4$ (41%)
2e: R = 2-thiophenyl (52%)
2f: R = Et (43%)



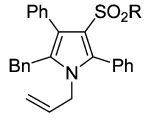
2g: R = *p*MeC$_6$H$_4$ (61%)
2h: R = *p*BrC$_6$H$_4$ (59%)
2i: R = 3-thiophenyl (64%)
2j: R = *n*Bu (80%)
2k: R = *c*C$_3$H$_5$ (77%)
2l: R = 1-cyclohexenyl (93%)
2m: R = H (45%)



2n: R = Ph (74%)
2o: R = *i*Pr (38%)



2p: R = Me (98%)
2q: R = *n*Bu (80%)
2r: R = Bn (60%)
2s: R = CH$_2$CH=CHC$_6$H$_5$ (40%)



2t: R = *p*MeOC$_6$H$_4$ (67%)
2u: R = *p*ClC$_6$H$_4$ (54%)
2v: R = Me (43%)

[a]All reactions were conducted on the 0.2 mmol scale with 5 mol % of **A** in toluene at 80 °C for 18 h. The values in parentheses denote product yields.

formed organogold intermediate might lead to the formation of cationic pyrrole-gold adduct **C** and the generation of one molecule of H_2O (Scheme 4, path a). Subsequent 1,3-sulfonyl migration of this putative species might then result in the deauration and regeneration of the Lewis acid catalyst and delivery of the product. Alternatively, vinyl gold complex **B** could undergo the deaurative 1,3-sulfonyl migration process first to give 2,3-dihydro-1*H*-pyrrol-3-ol adduct **D** that upon dehydrative aromatization would provide **2** (Scheme 4, path b). The formation of **5b** under certain conditions described in Table 1 could be due to a competing pathway in which intermediates **B** or **C** undergoes protodeauration. The premise that the deauration step involves 1,3-sulfonyl migration would also be consistent with the gradual decrease in product yield as the steric and electronic nature of the pendant group at the amino carbon or amine center increases upon going from **1b** → **1n** → **1o** and **1p** → **1q** → **1b** → **1r** → **1s** or a less electron-donating *N*-sulfonyl protecting group upon going from **1b** or **1t** → **1u**. It might be anticipated that such a pathway would not be expected to be as efficient because steric interactions between the substituents on the pyrrole ring and the migrating sulfonyl moiety increase as a result of either of these functional groups increasing. In the case of the observed trend when varying the substitutent R^1, this could be due to competition between the alkyl and sulfonyl groups on the amine center to migrate as a result of the ability of the former to stabilize a partial positive charge as it increases in steric bulk and π conjugation. Similarly, the lower product yields furnished upon going from substrates containing a *N*-(4-tolylsulfonyl) or *N*-(4-methoxyphenylsulfonyl) to a *N*-(4-chlorophenylsulfonyl) protecting group would be in good agreement with the typically lower migratory aptitudes of less electron-rich moieties. However, the low product yield obtained for the cycloisomerization of *N*-mesyl-protected starting alcohol **1v** could be due the competitive deprotonation of the mesylate cation to form sulphene during the 1,3-migration process.

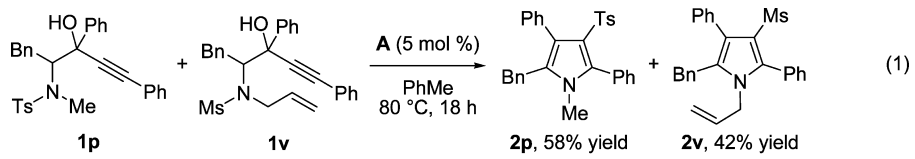
CONCLUSIONS

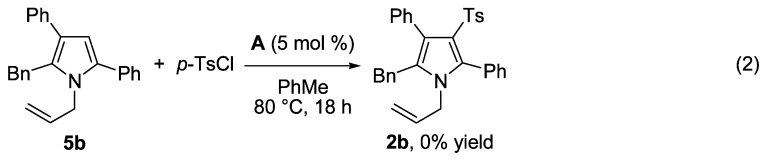
We have demonstrated a gold(I)-catalyzed synthesis strategy for the construction of 1-substituted 3-sulfonyl-1*H*-pyrroles from N-substituted *N*-sulfonyl-amonibut-3-yn-2-ols. The reaction was shown to be applicable to a diverse set of propargylic alcohols and provided a number of new pyrrole-family compounds for potential applications in medicinal chemistry. Our studies suggest that the nitrogen-containing ring-forming process likely involves dehydrative aminocyclization followed by deaurative 1,3-sulfonyl migration. Efforts to explore the synthesis applications of the present reaction are currently underway and will be reported in due course.

EXPERIMENTAL SECTION

General Considerations. Unless otherwise stated, all reactions were performed in oven-dried glassware under an argon atmosphere. All reagents and starting materials were purchased from commercial sources and used as received unless otherwise specified. Gold(I) complexes **A**−**D** and **F**−**I** were purchased from commercial sources or prepared following literature procedures.[9,12] *α*-Tosylamino ketones **S1** were prepared from the corresponding L-*α*-amino acids following literature procedures.[9] Analytical TLC was performed using a precoated silica gel plate and was visualized with ultraviolet radiation at 254 nm through staining with a potassium permanganate solution. Flash chromatography was performed using silica gel and a gradient solvent system (EtOAc/*n*-hexane as eluent). ^{1}H and ^{13}C NMR spectra were recorded on a 300 or 400 MHz NMR spectrometer with tetramethylsilane (TMS) as the internal standard. Chemical shifts were reported in parts per million (ppm) with coupling constants reported in Hertz (Hz). Multiplicities are given as s (singlet), br s (broad singlet), d (doublet), t (triplet), dd (doublet of doublets), or m (multiplet). The number of protons (*n*) for a given resonance is indicated by *n*H. Infrared spectra were recorded on an FTIR

Scheme 3. Control Experiments with 1p, 1v, and 5b Catalyzed by A





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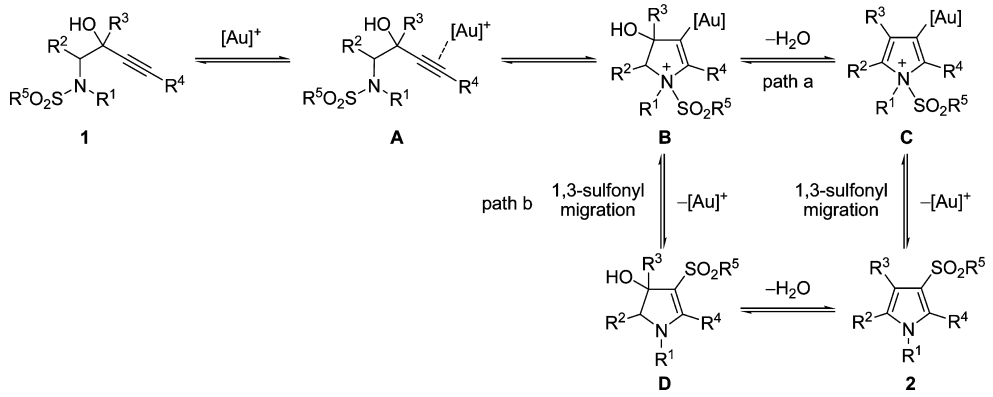
Scheme 4. Proposed Mechanism for the Au(I)-Catalyzed Cycloisomerization of 1



spectrometer. Solid samples were examined as a thin film between NaCl salt plates. Low-resolution mass spectra were determined on a mass spectrometer and reported in units of mass to charge (m/z). High-resolution mass spectra (HRMS) were obtained on a LC/HRMS TOF spectrometer using simultaneous electrospray ionization (ESI).

Procedure for the Synthesis of Gold(I) Complex E.[14] To a solution of IPrAuCl (150 mg, 0.24 mmol) in CH_2Cl_2 (2 mL) was added a solution of $AgPF_6$ (60.7 mg, 0.24 mmol) in CH_2Cl_2 (1 mL) at room temperature. The mixture was stirred for 1 h, and the resulting reaction mixture was filtered, washed with CH_2Cl_2 (2 × 4 mL), and concentrated under reduced pressure. Diethyl ether (5 mL) was then slowly added, which resulted in the immediate precipitation of a solid. The precipitate was filtered, washed with diethyl ether (2 × 5 mL), and dried under reduced pressure. This gave the title compound as a light-pink, air-stable solid (129.5 mg, 78% yield): mp = 199–201 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.22 (d, 14H, J = 6.4 Hz), 1.31 (d, 11H, J = 4.8 Hz), 2.47–2.51 (m, 4H), 7.26–7.31 (m, 6H), 7.50–7.52 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 24.1, 24.3, 28.8, 123.8, 124.4, 131.0, 133.6, 145.5; ^{31}P NMR (161.98 MHz, $CDCl_3$) δ −14.04 (t, $^1J(^{19}F-^{31}P)$ = 980.0 Hz); HRMS (DART) calcd for $C_{27}H_{38}N_2OAu$ (M^+-POF_2), 603.2650; found, 603.2632.

General Procedure for the Preparation of 1b–v. To a round-bottomed flask containing 4-methyl-*N*-(1,2-disubstituted)-benzenesulfonamide[9] (3.0 mmol) was added K_2CO_3 (9.0 mmol) followed by dimethylformamide (10 mL). The corresponding allyl/alkyl bromide or MeI (9.0 mmol) was then added, and the reaction mixture was allowed to stir for 12–48 h at room temperature. On completion, H_2O (10 mL) and diethyl ether (10 mL) were sequentially added to the reaction mixture. The aqueous layer was extracted with ether (3 × 20 mL), and the organic layers were combined, dried over $MgSO_4$, and concentrated under reduced pressure. The crude mixture was then purified by flash column chromatography on silica gel (eluent: *n*-hexane/EtOAc = 6:1) to afford the α-allylsulfonylamino ketone product, which was used directly for the next step. To a solution of ethynylbenzene (3.0 mmol) in THF (15 mL) was added LDA (2.0 M in THF, 1.5 mL, 3.0 mmol) at −78 °C. The resulting solution was stirred for 1 h at −78 °C. The α-allylsulfonylamino ketone (1 mmol) in THF (2 mL) was subsequently added dropwise to the reaction mixture at −78 °C. The resulting reaction mixture was slowly warmed to room temperature and stirred for 16 h. On completion, the reaction mixture was quenched by the addition of saturated NH_4Cl (10 mL) and extracted with EtOAc (2 × 30 mL). The combined organic layers were washed with brine (20 mL), dried over $MgSO_4$, concentrated under reduced pressure, and purified by flash column chromatography on silica gel (eluent: *n*-hexane/EtOAc = 7:1) to afford the title compound.

General Experimental Procedure for NHC–Gold(I) Complex A-Catalyzed Cycloisomerization of 1b–v. A two-neck round-bottomed flask containing 1,7-enyne alcohol **1** (0.19 mmol) and NHC–gold(I) complex **A** (0.01 mmol) was purged twice with argon gas before toluene (2 mL) was added. The resulting reaction mixture was then stirred at 80 °C for 18 h. On completion, the reaction mixture was concentrated under reduced pressure and purified by flash column chromatography on silica gel (eluent: *n*-hexane/EtOAc = 6:1) to afford product **2**.

***N*-Allyl-*N*-(3-hydroxy-1,3,5-triphenylpent-4-yn-2-yl)-4-methylbenzenesulfonamide (1b).**[15] Colorless solid: yield 86%; 0.449 g; mp = 155–157 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.32 (s, 3H), 2.85 (d, 1H, J = 14.1 Hz), 2.98 (d, 1H, J = 11.1 Hz), 3.61 (s, 1H), 4.31 (d, 1H, J = 6.0 Hz), 4.37 (d, 1H, J = 13.2 Hz), 4.89 (d, 1H, J = 9.2 Hz), 5.05 (d, 1H, J = 10.1 Hz), 5.16 (d, 1H, J = 17 Hz), 5.79–5.83 (m, 1H), 6.83 (d, 2H, J = 6.6 Hz), 6.94 (d, 2H, J = 7.7 Hz), 7.10–7.15 (m, 5H), 7.36–7.39 (m, 4H), 7.45 (t, 2H, J = 7.5 Hz), 7.53–7.55 (m, 2H), 7.89 (d, 2H, J = 7.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.5, 34.3, 46.8, 69.6, 75.3, 89.0, 89.3, 117.3, 122.1, 126.3, 126.8, 127.9, 128.5, 128.55, 128.58, 129.0, 129.2, 131.7, 135.9, 136.9, 138.0, 142.9, 143.1; IR (NaCl, neat) ν 3412, 3021, 1599, 1325 cm^{-1}; HRMS (ESI) $[M + Na]^+$ calcd for $C_{33}H_{31}NO_3SNa$, 544.1922; found, 544.1926.

***N*-Allyl-*N*-(3-hydroxy-1,5-diphenyl-3-(*p*-tolyl)pent-4-yn-2-yl)-4-methylbenzenesulfonamide (1c).** Yellow solid: yield 75%; 0.402 g; mp = 56–58 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.32 (s, 3H), 2.40 (s, 3H), 2.83 (d, 1H, J = 14.5 Hz), 2.96 (d, 1H, J = 11.6 Hz), 3.52 (s, 1H), 4.30 (d, 1H, J = 6.0 Hz), 4.37 (d, 1H, J = 13.6 Hz), 4.89 (d, 1H, J = 9.4 Hz), 5.04 (d, 1H, J = 10.1 Hz), 5.15 (d, 1H, J = 17.1 Hz), 5.79–5.82 (m, 1H), 6.85 (d, 2H, J = 6.9 Hz), 6.94 (d, 2H, J = 7.9 Hz), 7.09–7.16 (m, 4H), 7.25 (d, 3H, J = 7.8 Hz), 7.35–7.38 (m, 3H), 7.51–7.54 (m, 2H), 7.77 (d, 2H, J = 8.1 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.2, 21.5, 34.4, 46.8, 69.6, 75.2, 89.2, 117.3, 122.2, 126.3, 126.7, 127.9, 128.5, 128.6, 129.0, 129.16, 129.24, 131.7, 136.0, 137.0, 138.1, 138.2, 140.3, 142.9; IR (NaCl, neat) ν 3460, 3019, 1599, 1454 cm^{-1}; HRMS (ESI) $[M + Na]^+$ calcd for $C_{34}H_{33}NO_3SNa$, 558.2079; found, 558.2076.

***N*-Allyl-*N*-(3-(4-chlorophenyl)-3-hydroxy-1,5-diphenylpent-4-yn-2-yl)-4-methylbenzenesulfonamide (1d).** Yellow solid: yield 65%; 0.361 g; mp = 127–129 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.33 (s, 3H), 2.84 (d, 1H, J = 14.0), 2.97 (d, 1H, J = 11.1 Hz), 3.64 (s, 1H), 4.26 (d, 1H, J = 4.6 Hz), 4.34 (d, 1H, J = 12.9 Hz), 4.84 (d, 1H, J = 8.6 Hz), 5.06 (d, 1H, J = 10.0 Hz), 5.16 (d, 1H, J = 17.1 Hz), 5.70–5.90 (m, 1H), 6.85 (d, 2H, J = 6.4 Hz), 6.96 (d, 2H, J = 7.3 Hz), 7.08–7.17 (m, 5H), 7.38–7.40 (m, 5H), 7.51–7.53 (m, 2H), 7.80 (d, 2H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.5, 34.4, 46.8, 69.4, 75.0, 88.6, 89.5, 117.5, 121.9, 126.4, 127.9, 128.4, 128.5, 128.6, 129.16, 129.2, 131.7, 134.3, 135.7, 136.7, 137.7, 141.7, 143.1; IR (NaCl, neat) ν 3480, 3019, 1597, 1489 cm^{-1}; HRMS (ESI) $[M + Na]^+$ calcd for $C_{33}H_{30}ClNO_3S$, 578.1533; found, 578.1538.

***N*-Allyl-*N*-(3-hydroxy-1,5-diphenyl-3-(thiophen-2-yl)pent-4-yn-2-yl)-4-methylbenzenesulfonamide (1e).** Yellow solid: yield 72%; 0.380 g; mp = 129–131 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.33 (s, 3H), 2.96–3.04 (m, 2H), 3.78 (s, 1H), 4.30–4.36 (m, 2H), 4.91 (d, 1H, J = 7.6 Hz), 5.08 (d, 1H, J = 10.1 Hz), 5.18 d, 1H, J = 17.2 Hz), 5.70–5.86 (m, 1H), 6.91–6.97 (m, 4H), 7.03 (dd, 1H, J = 5.1, 3.6 Hz), 7.09–7.17 (m, 5H), 7.34–7.39 (m, 4H), 7.43 (dd, 1H, J = 3.5, 1.0 Hz), 7.52–7.54 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.5, 34.9, 46.8, 69.7, 72.7, 88.1, 88.6, 117.4, 121.9, 126.2, 126.3, 126.4,

dx.doi.org/10.1021/jo401083m | J. Org. Chem. 2013, 78, 7508–7517

127.0, 127.9, 128.5, 128.6, 129.16, 129.21, 131.7, 136.0, 136.8, 137.9, 143.0, 148.3; IR (NaCl, neat) ν 3429, 3019, 1599, 1493, 1090 cm^{-1}; HRMS (ESI) $[M + Na]^+$ calcd for $C_{31}H_{29}NO_3S_2Na$, 550.1487; found, 550.1469.

***N*-Allyl-*N*-(3-ethyl-3-hydroxy-1,5-diphenylpent-4-yn-2-yl)-4-methylbenzenesulfonamide (1f).** Pale-yellow solid: yield 85%; 0.369 g; mp = 83−85 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.21 (t, 3H, J = 7.3 Hz), 1.84−2.01 (m, 2H), 2.33 (s, 3H), 2.63 (s, 1H), 3.02 (dd, 1H, J = 14.4, 10.3 Hz), 3.32 (d, 1H, J = 12.6 Hz), 4.12 (dd, 1H, J = 16.1, 6.1 Hz), 4.22 (dd, 1H, J = 16.2, 5.0 Hz), 4.59 (d, 1H, J = 6.8 Hz), 3.57 (d, 1H, J = 10.1 Hz), 5.17 (d, 1H, J = 17.2 Hz), 5.79−5.85 (m, 1H), 6.46 (d, 2H, J = 7.6 Hz), 7.09−7.15 (m, 4H), 7.18−7.21 (m, 3H), 7.30−7.33 (m, 3H), 7.42−7.44 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 8.5, 21.5, 34.0, 35.4, 47.0, 67.2, 74.8, 86.8, 90.3, 117.5, 122.4, 126.4, 127.8, 128.4, 128.6, 129.2, 129.4, 131.7, 136.1, 137.0, 138.75, 142.8; IR (NaCl, neat) ν 3524, 3019, 1599 cm^{-1}; HRMS (ESI) $[M + H]^+$ calcd for $C_{29}H_{32}NO_3S$, 474.2103; found, 474.2123.

***N*-Allyl-*N*-(3-hydroxy-1,3-diphenyl-5-(p-tolyl)pent-4-yn-2-yl)-4-methylbenzenesulfonamide (1g).** Yellow solid: yield 76%; 0.407 g; mp = 116−118 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.32 (s, 3H), 2.38 (s, 3H), 2.84 (d, 1H, J = 13.7 Hz), 2.97 (d, 1H, J = 11.4 Hz), 3.58 (s, 1H), 4.31−4.36 (m, 2H), 4.89 (d, 1H, J = 8.5 Hz), 5.05 (d, 1H, J = 9.8 Hz), 5.16 (d, 1H, J = 16.9 Hz),5.65−5.81 (m, 1H), 6.83 (d, 2H, J = 5.4 Hz), 6.94 (d, 2H, J = 7.4 Hz), 7.10−7.19 (m, 7H), 7.37−7.46 (m, 5H), 7.89 (d, 2H, J = 7.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.5, 21.6, 34.4, 46.7, 69.6, 75.4, 88.3, 89.5, 117.3, 119.1, 126.3, 126.9, 127.9, 128.4, 128.5, 129.16, 129.19, 129.3, 131.6, 136.0, 137.0, 138.0, 139.2, 142.9, 143.2; IR (NaCl, neat) ν 3443, 3019, 1599, 1454 cm^{-1}; HRMS (ESI) $[M + H]^+$ calcd for $C_{34}H_{34}NO_3S$, 536.2259; found, 536.2249.

***N*-Allyl-*N*-(5-(4-bromophenyl)-3-hydroxy-1,3-diphenylpent-4-yn-2-yl)-4-methylbenzenesulfonamide (1h).** Yellow solid: yield 72%; 0.432 g; mp = 64−66 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.31 (s, 3H), 2.84 (d, 1H, J = 14.0 Hz), 2.94 (d, 1H, J = 10.8 Hz), 3.65 (s, 1H), 4.25−4.36 (m, 2H), 4.88 (d, 1H, J = 8.6 Hz), 5.04 (d, 1H, J = 10.0 Hz), 5.14 (d, 1H, J = 16.8 Hz), 5.76−5.80 (m, 1H), 6.82 (d, 2H, J = 6.5 Hz), 6.93 (d, 2H, J = 7.5 Hz), 7.08−7.17 (m, 5H), 7.37−7.40 (m, 3H), 7.42−7.52 (m, 4H), 7.86 (d, 2H, J = 7.5 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.5, 34.3, 46.7, 69.5, 75.5, 88.0, 90.2, 117.3, 121.0, 123.3, 126.3, 126.7, 127.9, 128.4, 128.6, 129.1, 129.2, 131.5, 131.8, 133.1, 135.9, 136.9, 142.9, 143.0; IR (NaCl, neat) ν 3447, 3019, 1599, 1487, 754 cm^{-1}; HRMS (ESI) $[M + Na]^+$ calcd for $C_{33}H_{30}BrNO_3SNa$, 622.1027; found, 622.1012.

***N*-Allyl-*N*-(3-hydroxy-1,3-diphenyl-5-(thiophen-3-yl)pent-4-yn-2-yl)-4-methylbenzenesulfonamide (1i).** Yellow solid: yield 90%; 0.475 g; mp = 154−156 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.32 (s, 3H), 2.82 (d, 1H, J = 14.1 Hz), 2.95 (d, 1H, J = 11.2 Hz), 3.59 (s, 1H), 4.27 (d, 1H, J = 6.2 Hz), 4.36 (d, 1H, J = 14.1 Hz), 4.89 (d, 1H, J = 8.9 Hz), 5.06 (d, 1H, J = 9.9 Hz), 5.16 (d, 1H, J = 17.0 Hz), 5.82−5.83 (m, 1H), 6.83 (d, 2H, J = 6.5 Hz), 6.94 (d, 2H, J = 7.7 Hz), 7.08−7.15 (m, 5H), 7.19 (dd, 1H, J = 5.0, 0.7 Hz), 7.32 (dd, 1H, J = 4.9, 3.0 Hz), 7.36−7.39 (m, 1H), 7.45 (t, 2H, J = 7.5 Hz), 7.55 (d, 1H, J = 2.0 Hz), 7.87 (d, 2H, J = 7.5 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.5, 34.3, 46.7, 69.5, 75.4, 84.6, 88.4, 117.2, 121.1, 125.8, 126.3, 126.8, 127.9, 128.4, 128.5, 129.2, 129.5, 129.7, 136.0, 136.9, 137.9, 142.9, 143.0; IR (NaCl, neat) ν 3414, 3022, 1599, 1449 cm^{-1}; HRMS (ESI) $[M + H]^+$ calcd for $C_{31}H_{30}NO_3S_2$, 528.1667; found, 528.1668.

***N*-Allyl-*N*-(3-hydroxy-1,3-diphenylnon-4-yn-2-yl)-4-methylbenzenesulfonamide (1j).** Yellow solid: yield 94%; 0.472 g; mp = 55−57 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.95 (t, 3H, J = 7.3 Hz), 1.44−1.53 (m, 2H), 1.57−1.64 (m, 2H), 2.31 (s, 3H), 2.38 (t, 2H, J = 7.0 Hz), 2.75 (d, 1H, J = 14.3 Hz), 2.87 (d, 1H, J = 11.2 Hz), 3.41 (s, 1H), 4.20−4.29 (m, 2H), 4.77 (d, 1H, J = 9.2 Hz), 5.04 (d, 1H, J = 10.0 Hz), 5.15 (d, 1H, J = 17.1 Hz), 5.75−5.77 (m, 1H), 6.80 (d, 2H, J = 6.7 Hz), 6.92 (d, 2H, J = 7.8 Hz), 7.06−7.14 (m, 5H), 7.34−7.36 (m, 1H), 7.41 (t, 2H, J = 7.4 Hz), 7.81 (d, 2H, J = 7.5 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 13.6, 18.6, 21.4, 22.2, 30.6, 34.4, 46.6, 69.3, 75.0, 80.2, 90.2, 116.8, 126.2, 126.8, 127.9, 128.2, 128.3, 128.4, 129.07, 129.14, 136.1, 137.2, 138.2, 142.8, 143.6; IR (NaCl, neat) ν 3410, 3019, 1599, 1449 cm^{-1}; HRMS (ESI) $[M + H]^+$ calcd for $C_{31}H_{36}NO_3S$, 502.2416; found, 502.2421.

***N*-Allyl-*N*-(5-cyclopropyl-3-hydroxy-1,3-diphenylpent-4-yn-2-yl)-4-methylbenzenesulfonamide (1k).** Colorless solid: yield 86%; 0.418 g; mp = 105−107 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.77−0.81 (m, 2H), 0.83−0.88 (m, 2H), 1.39−1.43 (m, 1H), 2.31 (s, 3H), 2.71 (d, 1H, J = 14.0 Hz), 2.85 (d, 1H, J = 11.2 Hz), 3.36 (s, 1H), 4.22−4.31 (m, 2H), 4.76 (d, 1H, J = 9.2 Hz), 5.05 (d, 1H, J = 9.6 Hz), 5.18 (d, 1H, J = 17.2 Hz), 5.65−5.75 (m, 1H), 6.81 (d, 2H, J = 6.8 Hz), 6.93 (d, 2H, J = 7.8 Hz), 7.05−7.16 (m, 5H), 7.32−7.36 (m, 1H), 7.39−7.43 (m, 2H), 7.79 (d, 2H, J = 7.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ −0.4, 8.26, 8.28, 21.5, 34.3, 46.6, 69.4, 74.9, 75.2, 93.1, 116.9, 126.2, 126.8, 127.9, 128.2, 128.3, 128.4, 129.1, 129.2, 136.2, 137.0, 138.1, 142.8, 143.5; IR (NaCl, neat) ν 3480, 3026, 1599, 1454 cm^{-1}; HRMS (ESI) $[M + H]^+$ calcd for $C_{30}H_{32}NO_3S$, 486.2103; found, 486.2102.

***N*-Allyl-*N*-((2*S*,3*S*)-5-(cyclohex-1-en-1-yl)-3-hydroxy-1,3-diphenylpent-4-yn-2-yl)-4-methylbenzenesulfonamide (1l).** Yellow solid: yield 80%; 0.421 g; mp = 117−119 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.61−1.70 (m, 4H), 2.13−2.15 (m, 2H), 2.20−2.22 (m, 2H), 2.32 (s, 3H), 2.75 (d, 1H, J = 14.4 Hz), 2.88 (d, 1H, J = 10.9 Hz), 3.41 (s, 1H), 4.26−4.28 (m, 2H), 4.82 (d, 1H, J = 9.0 Hz), 5.05 (d, 1H, J = 10.0 Hz), 5.17 (d, 1H, J = 17.2 Hz), 5.75−5.77 (m, 1H), 6.22−6.24 (m, 1H), 6.82 (d, 2H, J = 7.0 Hz), 6.94 (d, 2H, J = 7.9 Hz), 7.08−7.14 (m, 5H), 7.36 (t, 1H, J = 7.2 Hz), 7.42 (t, 2H, J = 7.8 Hz), 7.82 (d, 2H, J = 7.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.5, 22.2, 25.7, 29.0, 34.4, 46.7, 69.5, 75.2, 86.2, 91.2, 117.1, 120.0, 126.2, 126.9, 127.9, 128.3, 128.4, 129.1, 129.2, 136.1, 137.2, 138.1, 142.8, 143.4; IR (NaCl, neat) ν 3400, 3019, 1599, 1449 cm^{-1}; HRMS (ESI) $[M + H]^+$ calcd for $C_{33}H_{36}NO_3S$, 526.2416; found, 526.2421.

***N*-Allyl-*N*-(3-hydroxy-1,3-diphenylpent-4-yn-2-yl)-4-methylbenzenesulfonamide (1m).** Colorless oil: yield 73%; 0.325 g; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.32 (s, 3H), 2.78 (d, 1H, J = 14.4 Hz), 2.91−2.98 (m, 2H), 3.61 (s, 1H), 4.27−4.29 (m, 2H), 4.80 (d, 1H, J = 9.6 Hz), 5.06 (d, 1H, J = 10 Hz), 5.19 (d, 1H, J = 17.2 Hz), 5.71−5.74 (m, 1H), 6.80 (d, 2H, J = 6.4 Hz), 6.93 (d, 2H, J = 8.0 Hz), 7.05−7.15 (m, 5H), 7.35−7.46 (m, 3H), 7.83 (d, 2H, J = 7.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.5, 34.2, 46.6, 74.9, 77.8, 83.7, 117.4, 126.3, 126.7, 127.9, 128.4, 128.5, 129.1, 135.7, 136.9, 137.9, 142.6, 142.9; IR (NaCl, neat) ν 3300, 3026, 1599, 1454 cm^{-1}; HRMS (ESI) $[M + H]^+$ calcd for $C_{27}H_{28}NO_3S$, 446.1790; found, 446.1784.

***N*-Allyl-*N*-(2-hydroxy-1,2,4-triphenylbut-3-yn-1-yl)-4-methylbenzenesulfonamide (1n).** Colorless solid: yield 76%; 0.386 g; mp = 117−119 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.29 (s, 3H), 3.99 (dd, 1H, J = 16.7, 5.9 Hz), 4.29 (dd, 1H, J = 16.7, 6.4 Hz), 5.07 (dd, 1H, J = 10.2, 1.2 Hz), 5.19 (dd, 1H, J = 1.4 Hz), (s, 1H), 5.79−5.90 (m, 1H), 7.00 (d, 2H, J = 8.1 Hz), 7.15−7.24 (m, 5H), 7.33−7.35 (m, 3H), 7.40−7.44 (m, 4H), 7.52−7.60(m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.4, 49.4, 70.4, 88.1, 91.2, 117.4, 122.4, 126.5, 127.8, 127.9, 127.96, 128.02, 128.4, 128.7, 129.1, 130.8, 131.9, 135.2, 136.4, 137.4, 142.4, 143.0; IR (NaCl, neat) ν 3019, 1599, 1327 cm^{-1}; HRMS (ESI) $[M + Na]^+$ calcd for $C_{32}H_{29}NO_3SNa$, 530.1766; found, 530.1776.

***N*-Allyl-*N*-((3*S*,4*S*)-4-hydroxy-2-methyl-4,6-diphenylhex-5-yn-3-yl)-4-methylbenzenesulfonamide (1o).** Yellow solid: yield 74%; 0.350 g; mp = 101−103 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.50 (d, 3H, J = 6.6 Hz), 0.82 (d, 3H, J = 6.6 Hz), 2.26−2.28 (m, 1H), 2.41 (s, 3H), 3.03 (s, 1H), 4.25 (dd, 1H, J = 16.4, 5.6 Hz), 4.38 (d, 1H, J = 7.6 Hz), 4.44 (d, 1H, J = 9.8 Hz), 5.09 (dd, 1H, J = 10.1, 1.1 Hz), 5.24 (dd, 1H, J = 17.1, 1.1 Hz), 6.00−6.08 (m, 1H), 7.28 (d, 1H, J = 8 Hz), 7.32−7.43 (m, 6H), 7.48−7.51 (m, 2H), 7.82−7.88 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.5, 21.6, 22.0, 29.7, 47.5, 72.5, 74.3, 88.8, 89.9, 117.8, 122.2, 127.0, 128.3, 128.4, 128.5, 128.6, 129.0, 129.3, 131.6, 135.8, 137.8, 143.3, 144.6; IR (NaCl, neat) ν 3501, 3019, 1599, 1449 cm^{-1}; HRMS (ESI) $[M + Na]^+$ calcd for $C_{29}H_{31}NO_3SNa$, 496.1922; found, 496.1925.

***N*-(3-Hydroxy-1,3,5-triphenylpent-4-yn-2-yl)-*N*,4-dimethylbenzenesulfonamide (1p).** Yellow solid: yield 99%; 0.491 g; mp = 129−131 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.31 (s, 3H), 2.82−2.97 (m, 2H), 3.04 (s, 3H), 3.52 (s, 1H), 4.83 (dd, 1H, J = 11.0, 3.3 Hz), 6.85 (d, 2H, J = 7.2 Hz), 6.93 (d, 2H, J = 8.2 Hz), 7.00 (d, 2H, J = 8.3

dx.doi.org/10.1021/jo401083m | J. Org. Chem. 2013, 78, 7508−7517

Hz), 7.07−7.15 (m, 3H), 7.35−7.40 (m, 4H), 7.43−7.47 (m, 2H), 7.52−7.55 (m, 2H), 7.90 (d, 2H, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.5, 29.7, 33.6, 68.8, 75.3, 89.2, 122.2, 126.4, 126.9, 127.6, 128.5, 128.58, 128.61, 129.0, 129.3, 131.7, 135.7, 138.0, 142.70, 132.74; IR (NaCl, neat) ν 3410, 3019, 1599, 1327 cm^{-1}; HRMS (ESI) $[M + H]^+$ calcd for $C_{31}H_{30}NO_3S$, 496.1946; found, 496.1952.

_N_-Butyl-_N_-(3-hydroxy-1,3,5-triphenylpent-4-yn-2-yl)-4-methylbenzenesulfonamide (1q). White solid: yield 89%; 0.382 g; mp = 184−186 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.84 (t, 3H, J = 7.2 Hz), 1.18−1.22 (m, 2H), 1.85−1.94 (m, 2H), 2.32 (s, 3H), 2.81 (d, 1H, J = 14.3 Hz), 2.90 (d, 1H, J = 10.2 Hz), 3.42−3.57 (m, 2H), 3.94 (s, 1H), 4.73 (d, 1H, J = 8.2 Hz), 6.69 (d, 2H, J = 7.1 Hz), 7.01 (t, 2H, J = 7.4 Hz), 7.07−7.16 (m, 3H), 7.34−7.44 (m, 6H), 7.53−7.56 (m, 2H), 7.87 (d, 2H, J = 7.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 13.7, 20.7, 21.5, 32.8, 34.3, 44.5, 75.2, 88.7, 89.0, 122.2, 126.2, 126.9, 127.5, 128.4, 128.46, 128.52, 128.91, 128.94, 129.3, 131.6, 136.6, 137.8, 142.9, 143.3; IR (NaCl, neat) ν 3444, 3053, 1599, 1448 cm^{-1}; HRMS (ESI) $[M + H]^+$ calcd for $C_{34}H_{35}NO_3S$, 538.2418; found, 538.2418.

_N_-Benzyl-_N_-(3-hydroxy-1,3,5-triphenylpent-4-yn-2-yl)-4-methylbenzenesulfonamide (1r). Yellow solid; yield: 80%; 0.457 g; mp = 165−167 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.28 (s, 3H), 2.84 (d, 1H, J = 13.8 Hz), 2.94 (d, 1H, J = 9.32 Hz), 3.59−3.73 (m, 1H), 4.92−5.00 (m, 2H), 6.64−6.66 (m, 2H), 6.83−6.86 (m, 2H), 7.04−7.19 (m, 8H), 7.30−7.45 (m, 10H), 7.89−7.91 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.4, 34.9, 48.2, 69.5, 75.3, 88.8, 89.9, 122.1, 126.2, 126.8, 127.3, 127.6, 128.1, 128.2, 128.5, 128.6, 128.9, 129.1, 129.4, 131.7, 137.3, 137.7, 142.6, 143.5; IR (NaCl, neat) ν 3419, 3019, 1599, 1447 cm^{-1}; HRMS (ESI) $[M + Na]^+$ calcd for $C_{37}H_{33}NO_3SNa$, 594.2079; found, 594.2099.

_N_-Cinnamyl-_N_-(3-hydroxy-1,3,5-triphenylpent-4-yn-2-yl)-4-methylbenzenesulfonamide (1s). Yellow solid: yield 49%; 0.293 g; mp = 79−81 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.23 (s, 3H), 2.92 (d, 1H, J = 14.1 Hz), 3.04 (d, 1H, J = 11.2 Hz), 3.56 (s, 1H), 4.46 (dd, 1H, J = 16.1, 5.4 Hz), 4.56 (dd, 1H, J = 16.3, 6.9 Hz), 5.03 (d, 1H, J = 9.3 Hz), 5.82−5.89 (m, 1H), 6.37 (d, 1H, J = 15,9 Hz), 6.85−6.92 (m, 3H), 7.03−7.09 (m, 4H), 7.13−7.25 (m, 7H), 7.34−7.40 (m, 4H), 7.46 (t, 2H, J = 7.4 Hz), 7.53 (d, 2H, J = 6.2 Hz), 7.92 (d, 2H, J = 7.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.4, 34.6, 46.2, 69.3, 75.5, 89.2, 89.5, 122.1, 126.3, 126.4, 126.7, 126.8, 127.7, 128.0, 128.5, 128.57, 128.61, 129.05, 129.12, 129.4, 131.7, 132.2, 136.4, 137.5, 138.0, 142.9, 143.1; IR (NaCl, neat) ν 3400, 3019, 1599, 1449 cm^{-1}; HRMS (ESI) $[M + H]^+$ calcd for $C_{39}H_{36}NO_3S$, 598.2416; found, 598.2406.

_N_-Allyl-_N_-(3-hydroxy-1,3,5-triphenylpent-4-yn-2-yl)-methanesulfonamide (1t). Brown solid: yield 75%; 0.334 g; mp = 100−102 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.23 (s, 3H), 2.94 (d, 1H, J = 14.2 Hz), 3.04 (d, 1H, J = 11.4 Hz), 3.27 (s, 1H), 4.21−4.30 (m, 2H), 4.73 (d, 1H, J = 9.9 Hz), 5.21 (d, 1H, J = 9.6 Hz), 5.33 (d, 1H, J = 17.2), 6.12−6.15 (m, 1H), 7.06 (d, 2H, J = 7.2 Hz), 7.15−7.18 (m, 1H), 7.22−7.25 (m, 2H), 7.35−7.39 (m, 4H), 7.45 (t, 2H, J = 7.5 Hz), 7.53−7.56 (m, 2H), 7.85 (d, 2H, J = 7.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 34.4, 41.0, 46.9, 69.3, 75.6, 89.1, 118.7, 122.0, 126.7, 126.9, 128.55, 128.59, 128.6, 129.1, 129.3, 131.7, 135.5, 138.0, 143.3; IR (NaCl, neat) ν 3458, 3019, 1599, 1449 cm^{-1}; HRMS (ESI) $[M + Na]^+$ calcd for $C_{27}H_{27}NO_3S$, 468.1609; found, 468.1618.

_N_-Allyl-4-chloro-_N_-(3-hydroxy-1,3,5-triphenylpent-4-yn-2-yl)benzenesulfonamide (1u). Pale-yellow solid: yield 76%; 0.412 g; mp = 137−139 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.89 (d, 1H, J = 14.2 Hz), 2.97 (d, 1H, J = 11.0 Hz), 3.55 (s, 1H), 4.27−4.38 (m, 2H), 4.90 (d, 1H, J = 9.5 Hz), 5.03 (d, 1H, J = 10.1 Hz), 5.16 (d, 1H, J = 17.1 Hz), 5.73−5.77 (m, 1H), 6.85 (d, 2H, J = 7.1 Hz), 7.04 (s, 4H), 7.10−7.20 (m, 3H), 7.33−7.39 (m, 4H), 7.45 (t, 2H, J = 7.5 Hz), 7.50−7.53 (m, 2H), 7.90 (d, 2H, J = 7.5 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 34.4, 46.9, 69.9, 75.4, 89.0, 89.4, 117.7, 122.0, 125.4, 126.6, 126.8, 128.7, 129.1, 129.25, 129.32, 131.7, 135.6, 138.1, 138.4, 138.9, 143.2, 150.9; IR (NaCl, neat) ν 3019, 1585, 1329 cm^{-1}; HRMS (ESI) $[M + Na]^+$ calcd for $C_{32}H_{28}ClNO_3SNa$, 564.1376; found, 564.1369.

_N_-Allyl-_N_-(3-hydroxy-1,3,5-triphenylpent-4-yn-2-yl)-4-methoxybenzenesulfonamide (1v). Pale-yellow solid: yield 92%; 0.369 g; mp = 122−124 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.85 (d, 1H, J = 14.4 Hz), 2.96−3.02 (m, 1H), 3.68 (s, 1H), 3.77 (s, 3H), 4.23−4.39 (m, 2H), 4.90 (d, 1H, J = 9.6 Hz), 5.04 (d, 1H, J = 10.0 Hz), 5.15 (d, 1H, J = 17.2 Hz), 5.81−5.83 (m, 1H), 6.60 (d, 2H, J = 8.6 Hz), 6.84 (d, 2H, J = 6 Hz), 7.11−7.14 (m, 5H), 7.35−7.39 (m, 4H), 7.45 (t, 2H, J = 7.5 Hz), 7.52−7.54 (m, 2H), 7.90 (d, 2H, J = 7.5 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 34.3, 46.7, 55.5, 69.6, 75.4, 89.0, 89.3, 113.7, 117.2, 122.1, 126.4, 126.8, 128.47, 128.54, 128.6, 129.2, 130.0, 131.5, 131.7, 136.0, 138.0, 143.1, 162.5; IR (NaCl, neat) ν 3057, 1597, 1490 cm^{-1}; HRMS (ESI) $[M + Na]^+$ calcd for $C_{33}H_{31}NO_4SNa$, 560.1872; found, 560.1871.

1-Allyl-2-benzyl-3,5-diphenyl-4-tosyl-1_H_-pyrrole (2b).[16] Colorless solid: 0.068 g; mp = 118−119 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.32 (s, 3H), 3.78 (s, 2H), 4.00−4.01 (m, 2H), 4.66 (dd, 1H, J = 17.1, 0.9 Hz), 5.04 (dd, 1H, J = 10.4, 0.92 Hz), 5.51−5.59 (m, 1H), 6.98−7.00 (m, 4H), 7.14−7.18 (m, 3H), 7.22−7.30 (m, 7H), 7.33−7.43 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.5, 30.3, 47.0, 116.6, 120.4, 123.7, 126.4, 127.1, 127.6, 127.75, 127.80, 128.68, 128.72, 129.0, 129.6, 130.6, 131.3, 131.5, 133.4, 133.6, 136.7, 138.8, 141.0, 142.3; IR (NaCl, neat) ν 3019, 1599, 1493, 1454 cm^{-1}; HRMS (ESI) $[M + Na]^+$ calcd for $C_{33}H_{29}NO_2S$, 526.1817; found, 526.1835.

1-Allyl-2-benzyl-5-phenyl-3-(_p_-tolyl)-4-tosyl-1_H_-pyrrole (2c). Brown solid: 0.055 g; mp = 128−130 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.32 (s, 3H), 2.36 (s, 3H), 3.78 (s, 2H), 3.98−3.99 (m, 2H), 4.65 (dd, 1H, J = 17.1, 0.8 Hz), 5.02 (dd, 1H, J = 10.4, 0.9 Hz), 5.51−5.57 (m, 1H), 6.97−7.01 (m, 4H), 7.10 (d, 2H, J = 7.9 Hz), 7.15−7.18 (m, 4H), 7.21−7.25 (m, 3H), 7.31−7.42 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.4, 21.5, 30.3, 47.0, 116.5, 120.4, 123.7, 126.4, 127.2, 127.8, 127.8, 128.3, 128.7, 128.7, 129.0, 129.6, 130.6, 131.3, 133.4, 136.7, 136.8, 138.9, 141.2, 142.3; IR (NaCl, neat) ν 3019, 2399, 1599, 1495 cm^{-1}; HRMS (ESI) $[M + H]^+$ calcd for $C_{34}H_{32}NO_2S$, 518.2154; found, 518.2171.

1-Allyl-2-benzyl-3-(4-chlorophenyl)-5-phenyl-4-tosyl-1_H_-pyrrole (2d). Gray solid: 0.042 g; mp = 155−157 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.33 (s, 3H), 3.77 (s, 2H), 4.00−4.01 (m, 2H), 4.65 (dd, 1H, J = 17.1, 0.8 Hz), 5.04 (dd, 1H, J = 10.4, 0.8 Hz), 5.51−5.60 (m, 1H), 6.95 (d, 2H, J = 7.1 Hz), 7.02 (d, 2H, J = 8.1 Hz), 7.15−7.28 (m, 9H), 7.31−7.33 (m, 2H), 7.37−7.43 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.5, 30.2, 47.0, 116.7, 120.4, 122.3, 126.6, 127.1, 127.7, 127.79, 127.81, 128.7, 128.8, 129.1, 129.7, 130.3, 131.3, 132.2, 132.8, 133.3, 137.1, 138.5, 140.9, 142.6; IR (NaCl, neat) ν 3019, 2399, 1597, 1489 cm^{-1}; HRMS (ESI) $[M + H]^+$ calcd for $C_{33}H_{29}ClNO_2S$, 538.1639; found, 538.1619.

1-Allyl-2-benzyl-5-phenyl-3-(thiophen-2-yl)-4-tosyl-1_H_-pyrrole (2e). Brown solid: 0.049 g; mp = 133−135 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.34 (s, 3H), 3.88 (s, 2H), 3.99−4.00 (m, 2H), 4.67 (dd, 1H, J = 17.0, 0.5 Hz), 5.03 (dd, 1H, J = 15.0, 0.6 Hz), 5.48−5.58 (m, 1H), 7.00−7.06 (m, 6H), 7.15−7.19 (m, 1H), 7.15−7.29 (m, 5H), 7.32−7.34 (m, 2H), 7.34−7.44 (m, 3H); ^{13}C NMR ($CDCl_3$,100 MHz) δ 21.5, 30.5, 47.1, 11.5.1, 116.8, 126.2, 126.5, 126.7, 127.2, 127.8, 127.9, 128.7, 128.9, 129.1, 130.1, 130.3, 131.2, 131.9, 133.1, 133.3, 137.3, 138.4, 140.7, 142.5, 143.1; IR (NaCl, neat) ν 3019, 2399, 1597, 1472 cm^{-1}; HRMS (ESI) $[M + H]^+$ calcd for $C_{31}H_{28}NO_2S_2$, 510.1561; found, 510.1571.

1-Allyl-2-benzyl-3-ethyl-5-phenyl-4-tosyl-1_H_-pyrrole (2f). Brown solid: 0.037 g; mp = 135−137 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.15 (t, 3H, J = 7.4 Hz), 2.35 (s, 3H), 2.83 (q, 2H, J = 7.6 Hz), 3.92−3.95 (m, 4H), 4.59 (dd, 1H, J = 17.1, 0.8 Hz), 5.00 (dd, 1H, J = 10.4, 0.8 Hz), 5.48−5.55 (m, 1H), 7.05 (d, 2H, J = 7.2 Hz), 7.11 (d, 2H, J = 8.1 Hz), 7.14−7.18 (m, 2H), 7.20 (d, 1H, J = 7.3 Hz), 7.28−7.32 (m, 4H), 7.36 (d, 1H, J = 7.4 Hz), 7.44 (d, 2H, J = 8.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 16.8, 18.1, 21.5, 29.8, 46.8, 116.3, 123.8, 126.5, 126.7, 127.6, 127.8, 128.4, 128.7, 128.8, 129.0, 129.4, 130.5, 131.4, 133.6, 136.7, 138.8, 142.3; IR (NaCl, neat) ν 3019, 2438, 1599, 1495 cm^{-1}; HRMS (ESI) $[M + H]^+$ calcd for $C_{29}H_{30}NO_2S$, 456.1997; found, 456.2005.

1-Allyl-2-benzyl-3-phenyl-5-(p-tolyl)-4-tosyl-1_H_-pyrrole (2g). Dark-brown solid: 0.060 g; mp = 67−70 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.32 (s, 3H), 2.40 (s, 3H), 3.77 (s, 2H), 4.00−4.01 (m, 2H), 4.67 (dd, 1H, J = 17.1, 0.8 Hz), 5.04 (dd, 1H, J = 10.4, 0.8 Hz), 5.53−5.60 (m, 1H), 6.97−7.00 (m, 4H), 7.15−7.19 (m, 3H), 7.21−7.29 (m, 11H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.49, 21.51, 30.3,

dx.doi.org/10.1021/jo401083m | J. Org. Chem. 2013, 78, 7508−7517

46.9, 116.5, 120.3, 123.6, 126.4, 127.12, 127.14, 127.5, 127.6, 127.8, 128.5, 128.67, 128.70, 129.5, 131.1, 131.6, 133.5, 133.6, 137.0, 138.83, 138.84, 141.1, 142.3; IR (NaCl, neat) ν 3019, 2399, 1599, 1493, 1389 cm^{-1}; HRMS (ESI) $[M + H]^+$ calcd for $C_{34}H_{32}NO_2S$, 518.2154; found, 518.2153.

1-Allyl-2-benzyl-5-(4-bromophenyl)-3-phenyl-4-tosyl-1*H*-pyrrole (2h). Brown solid: 0.065 g; mp = 129−131 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.32 (s, 3H), 3.77 (s, 2H), 4.00−4.01 (m, 2H), 4.65 (dd, 1H, J = 17.1, 0.6 Hz), 5.05 (dd, 1H, J = 10.4, 0.7 Hz), 5.50−5.60 (m, 1H), 6.96−7.01 (m, 4H), 7.13−7.18 (m, 3H), 7.22−7.25 (m, 6H), 7.27−7.29 (m, 3H), 7.52 (d, 2H, J = 1.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.5, 30.3, 47.0, 116.7, 120.8, 123.6, 123.8, 126.5, 127.1, 127.3, 127.6, 127.8, 128.7, 128.8, 129.6, 130.1, 131.1, 131.5, 132.9, 133.2, 133.3, 135.3, 138.6, 140.7, 142.6; IR (NaCl, neat) ν 3019, 2399, 1597, 1493 cm^{-1}; HRMS (ESI) $[M + H]^+$ calcd for $C_{33}H_{29}BrNO_2S$, 582.1102; found, 582.1113.

1-Allyl-2-benzyl-3-phenyl-5-(thiophen-3-yl)-4-tosyl-1*H*-pyrrole (2i). Brown solid: 0.062 g; mp = 83−85 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.32 (s, 3H), 3.77 (s, 2H), 4.04−4.05 (m, 2H), 4.68 (dd, 1H, J = 17.1, 0.9 Hz), 5.05 (dd, 1H, J = 10.4, 0.9 Hz), 5.55−5.63 (m, 1H), 6.97−7.02 (m, 4H), 7.07 (dd, 1H, J = 4.6, 1.5 Hz), 7.16−7.23 (m, 5H), 7.26−7.34 (m, 7H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.5, 30.3, 47.1, 116.5, 121.1, 124.0, 124.6, 126.5, 127.0, 127.2, 127.6, 127.9, 128.7, 128.8, 129.7, 130.0, 130.2, 131.5, 133.5, 133.6, 138.6, 140.9, 132.4; IR (NaCl, neat) ν 3019, 2399, 1599, 1495 cm^{-1}; HRMS (ESI) $[M + H]^+$ calcd for $C_{31}H_{28}NO_2S_2$, 510.1561; found, 510.1566.

1-Allyl-2-benzyl-5-butyl-3-phenyl-4-tosyl-1*H*-pyrrole (2j). Dark-yellow oil: 0.074 g; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.95 (t, 3H, J = 7.3 Hz), 1.41−1.50 (m, 2H), 1.59−1.66 (m, 2H), 2.33 (s, 3H), 2.99−3.03 (m, 2H), 3.67 (s, 2H), 4.23−4.24 (m, 2H), 4.74 (d, 1H, J = 17.1 Hz), 5.10 (d, 1H, J = 11.0 Hz), 5.65−5.70 (m, 1H), 6.93 (d, 2H, J = 7.1 Hz), 7.02−7.07 (m, 4H), 7.15−7.25 (m, 6H), 7.29 (d, 2H, J = 8.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 13.9, 21.5, 23.0, 24.8, 30.2, 33.1, 46.2, 116.4, 117.5, 123.3, 126.4, 126.9, 127.4, 127.7, 128.6, 128.8, 128.9, 131.6, 133.2, 133.6, 138.3, 138.9, 141.3, 142.2; IR (NaCl, neat) ν 3019, 2399, 1601, 1408 cm^{-1}; HRMS (ESI) $[M + H]^+$ calcd for $C_{31}H_{34}NO_2S$, 484.2310; found, 484.2318.

1-Allyl-2-benzyl-5-cyclopropyl-3-phenyl-4-tosyl-1*H*-pyrrole (2k). Dark-green solid: 0.067 g; mp = 107−109 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.89−0.91 (m, 2H), 1.05−1.10 (m, 2H), 1.69−1.76 (m, 1H), 2.32 (s, 3H), 3.68 (s, 2H), 4.46−4.48 (m, 2H), 4.72 (dd, 1H, J = 17.1, 0.8 Hz), 5.11 (dd, 1H, J = 10.4, 0.8 Hz), 5.71−5.79 (m, 1H), 6.93 (d, 2H, J = 7.1 Hz), 7.02 (d, 2H, 8.0 Hz), 7.07−7.10 (m, 2H), 7.14−7.25 (m, 6H), 7.36 (d, 2H, J = 8.3 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 6.7, 8.2, 21.5, 30.1, 46.7, 116.1, 120.3, 123.5, 126.4, 126.9, 127.0, 127.4, 127.7, 128.6, 128.7, 128.8, 131.4, 133.5, 133.8, 137.4, 138.9, 141.2, 142.3; IR (NaCl, neat) ν 3019, 2399, 1601, 1454 cm^{-1}; HRMS (ESI) $[M + H]^+$ calcd for $C_{30}H_{30}NO_2S$, 468.1997; found, 468.2007.

1-Allyl-2-benzyl-5-(cyclohex-1-en-1-yl)-3-phenyl-4-tosyl-1*H*-pyrrole (2l). Yellow oil: 0.093 g; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.60−1.81 (m,4H), 2.02−2.27 (m, 3H), 2.33 (s, 3H), 2.57−2.61 (m, 1H), 3.71 (d, 2H, J = 8.6 Hz), 4.09 (d, 1H, J = 16.2 Hz), 4.25 (d, 1H, J = 12.7 Hz), 4.79 (dd, 1H, J = 17.1, 0.8 Hz), 5.08 (dd, 1H, J = 10.3, 0.8 Hz), 5.64−5.71 (m, 2H), 6.93 (d, 2H, J = 7.2 Hz), 7.05 (d, 2H, J = 8.0 Hz), 7.15−7.16 (m, 3H), 7.20−7.25 (m, 5H), 7.33 (d, 2H, 8.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.5, 21.7, 22.7, 25.6, 30.3, 30.9, 46.8, 116.5, 118.2, 123.2, 126.4, 127.0, 127.1, 127.5, 127.8, 128.6, 128.7, 129.7, 131.5, 132.2, 133.6, 134.1, 139.0, 139.5, 141.4, 142.2; IR (NaCl, neat) ν 3019, 2399, 1599, 1495 cm^{-1}; HRMS (ESI) $[M + H]^+$ calcd for $C_{33}H_{34}NO_2S$, 508.2310; found, 508.2312.

1-Allyl-2-benzyl-3-phenyl-4-tosyl-1*H*-pyrrole (2m). Brown oil: 0.037 g; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.34 (s, 3H), 3.79 (s, 2H), 4.22 (d, 2H, J = 5.2 Hz), 5.02 (d, 1H, J = 17.0 Hz), 5.20 (d, 1H, J = 0.2 Hz), 5.71−5.81 (m, 1H), 6.95 (d, 2H, J = 7.3 Hz), 7.05 (d, 2H, J = 7.9 Hz), 7.13−7.26 (m, 8H), 7.35 (d, 2H, J = 8.0 Hz), 7.43 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.5, 30.1, 50.2, 118.7, 122.9, 123.0, 125.4, 126.5, 127.2, 127.3, 127.3, 127.7, 127.8, 128.7, 129.0, 130.8, 131.1, 132.5, 132.8, 138.5, 140.0, 142.7; IR (NaCl, neat) ν 3019, 2399, 1746, 1599 cm^{-1}; HRMS (ESI) $[M + H]^+$ calcd for $C_{27}H_{26}NO_2S$, 428.1684; found, 428.1689.

1-Allyl-2,3,5-triphenyl-4-tosyl-1*H*-pyrrole (2n). Yellow solid: 0.069 g; mp = 136−138 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.29 (s, 3H), 4.21−4.22 (m, 2H), 4.54 (dd, 1H, J = 17.1, 0.9 Hz), 4.93 (dd, 1H, J = 10.3, 0.9 Hz), 5.41−5.49 (m, 1H), 6.96 (d, 2H, J = 8.1 Hz), 7.12−7.17 (m, 9H), 7.18−7.20 (m, 3H), 7.43−7.46 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.5, 27.5, 117.0, 121.2, 123.2, 126.7, 127.1, 127.2, 127.8, 127.97, 128.04, 128.7, 129.0, 130.8, 130.9, 131.2, 131.5, 131.9, 133.1, 133.3, 133.4, 136.9, 140.8, 142.4; IR (NaCl, neat) ν 3019, 2399, 1599, 1464 cm^{-1}; HRMS (ESI) $[M + H]^+$ calcd for $C_{32}H_{28}NO_2S$, 490.1841; found, 490.1847.

1-Allyl-2-isopropyl-3,5-diphenyl-4-tosyl-1*H*-pyrrole (2o). Yellow solid: 0.033 g; mp = 114−116 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.98 (s, 3H), 0.99 (s, 3H), 2.32 (s, 3H), 2.88 (sep, 1H, J = 7.1 Hz), 4.25−4.27 (m, 2H), 4.75 (dd, 1H, J = 17.1, 0.8 Hz), 5.13 (dd, 1H, J = 10.5, 0.9 Hz), 6.99 (d, 2H, J = 8.0 Hz), 7.07 (d, 2H, J = 8.3 Hz), 7.13−7.16 (m, 2H), 7.24−7.31 (m, 3H), 7.36−7.45 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.5, 22.6, 26.4, 46.6, 116.5, 120.8, 124.3, 127.0, 127.3, 127.7, 128.7, 128.9, 131.2, 131.3, 132.3, 134.0, 134.3, 135.4, 136.1, 141.0, 142.2; IR (NaCl, neat) ν 3017, 2399, 1605, 1472 cm^{-1}; HRMS (ESI) $[M + H]^+$ calcd for $C_{29}H_{30}NO_2S$, 456.1997; found, 456.1996.

2-Benzyl-1-methyl-3,5-diphenyl-4-tosyl-1*H*-pyrrole (2p). Dark-green solid: 0.074 g; mp = 183−185 °C ^1H NMR ($CDCl_3$, 400 MHz) δ 2.30 (s, 3H), 3.05 (s, 3H), 3.81 (s, 2H), 6.97−7.00 (m, 4H), 7.13−7.18 (m, 3H), 7.22−7.30 (m, 7H), 7.34−7.36 (m, 2H), 7.41−7.44 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.5, 30.6, 32.1, 120.0, 123.1, 126.4, 127.1, 127.2, 127.6, 127.9, 128.0, 128.72, 128.74, 129.0, 129.8, 130.8, 131.3, 131.5, 133.7, 136.7, 138.5, 141.1, 142.3; IR (NaCl, neat) ν 3019, 1597, 1493, 1454 cm^{-1}; HRMS (ESI) $[M + H]^+$ calcd for $C_{31}H_{28}NO_2S$, 478.1841; found, 478.1855.

2-Benzyl-1-butyl-3,5-diphenyl-4-tosyl-1*H*-pyrrole (2q). Brown solid: 0.083 g; mp = 167−169 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.55 (t, 3H, J = 7.2 Hz), 0.87 (sextet, 2H, J = 7.2 Hz), 1.09−1.17 (m, 2H), 2.31 (s, 3H), 3.39−3.43 (m, 2H), 3.81 (s, 2H), 6.97−7.02 (m, 4H), 7.12−7.18 (m, 3H), 7.21−7.30 (m, 7H), 7.34−7.37 (m, 2H), 7.40−7.43 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 13.3, 19.8, 21.5, 30.6, 32.6, 44.7, 120.2, 123.3, 126.4, 127.08, 127.14, 127.5, 127.8, 127.9, 128.6, 128.7, 128.8, 129.3, 131.0, 131.4, 131.6, 133.8, 136.4, 138.9, 141.1, 142.2; IR (NaCl, neat) ν 3055, 2303, 1599 cm^{-1}; HRMS (ESI) $[M + H]^+$ calcd for $C_{34}H_{34}NO_2S$, 520.2310; found, 520.2301.

1,2-Dibenzyl-3,5-diphenyl-4-tosyl-1*H*-pyrrole (2r). Colorless solid: 0.063 g; mp = 194−196 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.33 (s, 3H), 3.59 (s, 2H), 4.62 (s, 2H), 6.71 (d, 2H, J = 6.6 Hz), 6.92 (d, 2H, J = 7.2 Hz), 7.01 (d, 2H, J = 8.0 Hz), 7.15−7.36 (m, 18H), ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.5, 30.5, 48.1, 120.6, 124.1, 125.6, 126.5, 127.18, 127.21, 127.4, 127.6, 127.79, 127.81, 128.7, 128.8, 129.0, 129.9, 130.4, 131.3, 131.5, 133.5, 137.1, 137.4, 138.7, 141.0, 142.4; IR (NaCl, neat) ν 3019, 2399, 1524, 1393 cm^{-1}; HRMS (ESI) $[M + H]^+$ calcd for $C_{37}H_{32}NO_2S$, 554.2154; found, 554.2145.

2-Benzyl-1-cinnamyl-3,5-diphenyl-4-tosyl-1*H*-pyrrole (2s). Reddish-brown solid: 0.044 g; mp = 153−155 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.32 (s, 3H), 3.84 (s, 2H), 4.18 (d, 2H), 5.69−5.74 (m, 1H), 5.82 (d, 1H, J = 15.9 Hz), 7.01 (t, 4H, J = 8.8 Hz), 7.12−7.19 (m, 5H), 7.23−7.35 (m, 10H), 7.35−7.44 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.5, 30.5, 46.8, 124.4, 126.4, 126.5, 127.2, 127.6, 127.8, 128.0, 128.6, 128.8, 129.0, 129.6, 130.7, 131.5, 131.6, 132.1, 133.6, 136.0, 136.9, 138.7, 141.0, 142.3; IR (NaCl, neat) ν 3019, 2399, 1599, 1391 cm^{-1}; HRMS (ESI) $[M + H]^+$ calcd for $C_{39}H_{34}NO_2S$, 580.2310; found, 580.2328.

1-Allyl-2-benzyl-4-((4-methoxyphenyl)sulfonyl)-3,5-diphenyl-1*H*-pyrrole (2t). Yellow solid: 0.066 g; mp = 57−59 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 3.78 (s, 3H), 3.99−4.01 (m, 2H), 4.66 (dd, 1H, J = 17.1, 0.7 Hz), 5.03 (dd, 1H, J = 10.4, 0.8 Hz), 5.51−5.60 (m, 1H), 6.65−6.67 (m, 2H), 6.98 (d, 2H), 7.16−7.22 (m, 3H), 7.24−7.27 (m, 7H), 7.27−7.34 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 30.3, 46.9, 55.5, 113.2, 116.5, 120.8, 123.5, 126.4, 127.1, 127.6, 127.75, 127.78, 128.7, 128.9, 129.2, 129.5, 130.6, 131.3, 131.5, 133.4, 133.6, 135.8, 136.6, 138.8, 162.2; IR (NaCl, neat) ν 3053, 2304, 1495 cm^{-1}; HRMS (ESI) $[M + H]^+$ calcd for $C_{33}H_{30}NO_3S$, 520.1946; found, 520.1948.

dx.doi.org/10.1021/jo401083m | J. Org. Chem. 2013, 78, 7508−7517

1-Allyl-2-benzyl-4-((4-chlorophenyl)sulfonyl)-3,5-diphenyl-1*H*-pyrrole (2u). Yellow solid: 0.054 g; mp = 132−134 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.79 (s, 2H), 4.01−4.03 (m, 2H), 4.66 (dd, 1H, J = 17.1, 0.8 Hz), 5.05 (dd, 1H, J = 10.4, 0.8 Hz), 5.52−5.60 (m, 1H), 6.98 (d, 2H, J = 7.2 Hz), 7.16−7.19 (m, 4H), 7.22−7.25 (m, 5H), 7.29−7.35 (m, 5H), 7.39−7.45 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 30.3, 47.0, 116.7, 126.5, 127.4, 127.7, 127.8, 127.9, 128.3, 128.6, 128.7, 129.2, 129.9, 130.3, 131.2, 131.5, 133.2, 137.2, 138.2, 138.6, 142.2; IR (NaCl, neat) ν 3019, 2399, 1584, 1476 cm^{-1}; HRMS (ESI) $[M + Na]^+$ calcd for $C_{32}H_{26}ClNO_2SNa$, 546.1270; found, 546.1280.

1-Allyl-2-benzyl-4-(methylsulfonyl)-3,5-diphenyl-1*H*-pyrrole (2v). Reddish-brown solid: 0.035 g; mp = 80−82 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.64 (s, 3H), 3.89 (s, 2H), 4.07−4.08 (m, 2H), 4.73 (d, 1H, J = 17.1 Hz), 5.10 (d, 1H, J = 10.4 Hz), 5.57−5.67 (m, 1H), 7.05 (d, 2H, J = 7.2 Hz); 7.20−7.38 (m, 6H); 7.40−7.41 (m, 5H), 7.49 (d, 2H, J = 7.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 30.4, 45.2, 47.0, 116.6, 119.9, 123.0, 126.6, 127.6, 127.8, 128.0, 128.1, 128.8, 129.2, 129.7, 130.4, 131.1, 131.3, 133.4, 133.5, 136.6, 138.7; IR (NaCl, neat) ν 3019, 2399, 1605, 1493 cm^{-1}; HRMS (ESI) $[M + H]^+$ calcd for $C_{27}H_{26}NO_2S$, 428.1684; found, 428.1699.

1-Allyl-2-benzyl-3,5-diphenyl-1*H*-pyrrole (5b). Dark-yellow oil: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.17 (s, 2H), 4.31−4.33 (m, 2H), 4.83 (dd, 1H, J = 17.1, 1.2 Hz), 5.13 (dd, 1H, J = 10.4, 1.2 Hz), 5.80−5.87 (m, 1H), 6.47 (s, 1H), 7.15−7.21 (m, 5H), 7.29−7.34 (m, 5H), 7.36−7.47 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 30.8, 46.7, 108.8, 115.9, 124.0, 125.5, 126.2, 127.0, 127.75, 127.82, 129.9, 128.4, 128.5, 128.7, 128.8, 133.5, 134.5, 135.0, 137.0, 140.1; IR (NaCl, neat) ν 3017, 1603,1493 cm^{-1}; HRMS (ESI) $[M + H]^+$ calcd for $C_{26}H_{24}N$, 530.1909; found, 350.1920.

2-Benzyl-2,4-diphenylbut-3-ynal (6b). Yellow oil: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.26 (d, 1H, J = 13.2 Hz), 3.54 (d, 1H, J = 13.2 Hz), 6.99−7.01 (m, 2H), 7.13−7.15 (m, 3H), 7.29−7.44 (m, 10H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 42.3, 59.5, 85.4, 91.5, 122.5, 126.6, 127.6, 128.2, 128.4, 128.65, 128.67, 128.71, 128.8, 130.7, 131.7, 135.4, 136.2; IR (NaCl, neat) ν 3028, 1728 cm^{-1}; HRMS (DART) $[M + H]^+$ calcd for $C_{23}H_{19}O$, 311.1436; found, 311.1431.

■ ASSOCIATED CONTENT

Supporting Information

^{1}H and ^{13}C NMR spectra for all starting materials and products and CIF files and ORTEP drawings of **1b**, **2b**, and NHC−gold(I) complex **E**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work is supported by a College of Science Start-Up Grant from Nanyang Technological University and an A*STAR-MSHE Joint Grant (122 070 3062) from A*STAR, Singapore. A Yousef Jameel Scholarship (to W.T.T.) is gratefully acknowledged, and we thank Drs. Yongxin Li and Rakesh Ganguly of this Division for providing the X-ray crystallographic data reported in this work.

■ REFERENCES

(1) For selected general reviews on gold catalysis, see: (a) Rudolph, M.; Hashmi, A. S. K. *Chem. Soc. Rev.* **2012**, *41*, 2448. (b) Garayalde, D.; Nevado, C. *ACS Catal.* **2012**, *2*, 1462. (c) Krause, N.; Winter, C. *Chem. Rev.* **2011**, *111*, 1994. (d) Corma, A.; Leyva-Pérez, A.; Sabater, M. J. *Chem. Rev.* **2011**, *111*, 1657. (e) Fürstner, A. *Chem. Soc. Rev.* **2009**, *38*, 3208. (f) Abu Sohel, S. M.; Liu, R.-S. *Chem. Soc. Rev.* **2009**, *38*, 2269. (g) Hashmi, A. S. K.; Rudolph, M. *Chem. Soc. Rev.* **2008**, *37*, 1766. (h) Jiménez-Núñez, E.; Echavarren, M. *Chem. Rev.* **2008**, *108*, 3326. (i) Gorin, D. J.; Sherry, B. D.; Toste, F. D. *Chem. Rev.* **2008**, *108*, 3351. (j) Patil, N. T.; Yamamoto, Y. *Chem. Rev.* **2008**, *108*, 3395. (k) Gorin, D. J.; Toste, F. D. *Nature* **2007**, *446*, 395. (l) Hashmi, A. S. K. *Chem. Rev.* **2007**, *107*, 3180. (m) Hashmi, A. S. K. *Angew. Chem., Int. Ed.* **2006**, *45*, 7896. (n) Zhang, L.; Sun, J.; Kozmin, S. A. *Adv. Synth. Catal.* **2006**, *348*, 2271.

(2) For selected examples of studies probing the mechanisms in gold-catalyzed organic reactions, see: (a) Hansmann, M. M.; Rominger, F.; Hashmi, A. S. K. *Chem. Sci.* **2013**, *4*, 1552. (b) Klatt, G.; Xu, R.; Pernpointner, M.; Molinari, L.; Hung, T. Q.; Rominger, F.; Hashmi, A. S. K.; Köppel, H. *Chem.−Eur. J.* **2013**, *19*, 3954. (c) Hansmann, M. M.; Rudolph, M.; Rominger, F.; Hashmi, A. S. K. *Angew. Chem., Int. Ed.* **2013**, *52*, 2593. (d) Gómez-Suárez, A.; Dupuy, S.; Slawin, A. M. Z.; Nolan, S. P. *Angew. Chem., Int. Ed.* **2013**, *52*, 938. (e) Wang, W.; Hammond, G. B.; Xu, B. J. *J. Am. Chem. Soc.* **2012**, *134*, 5697. (f) Dupuy, S.; Crawford, L.; Bühl, M.; Slawin, A. M. Z.; Nolan, S. P. *Adv. Synth. Catal.* **2012**, *354*, 2380. (g) López-Carrillo, V.; Huguet, N.; Mosquera, Á.; Echavarren, A. M. *Chem.−Eur. J.* **2011**, *17*, 10972. (h) Pérez-Galán, P.; Herrero-Gómez, E.; Hog, D. T.; Martin, N. J. A.; Maseras, F.; Echavarren, A. M. *Chem. Sci.* **2011**, *2*, 141. (i) Egorova, O. A.; Seo, H.; Kim, Y.; Moon, D.; Rhee, Y. M.; Ahn, K. H. *Angew. Chem., Int. Ed.* **2011**, *50*, 11446. (j) Hashmi, A. S. K. *Angew. Chem., Int. Ed.* **2010**, *49*, 5232. (k) Wang, Z. J.; Benitez, D.; Tkatchouk, E.; Goddard, W. A., III; Toste, F. D. J. *J. Am. Chem. Soc.* **2010**, *132*, 13064. (l) Echavarren, A. M. *Nature Chem.* **2009**, *1*, 431. (m) Mauleón, P.; Krinsky, J. L.; Toste, F. D. J. *J. Am. Chem. Soc.* **2009**, *131*, 4513. (n) Liu, L.-P.; Xu, B.; Mashuta, M. S.; Hammond, G. B. J. *J. Am. Chem. Soc.* **2008**, *130*, 17642.

(3) For a review on carbodeauration processes, see: Adcock, H. V.; Davies, P. W. *Synthesis* **2012**, 3401.

(4) (a) Park, S. R.; Kim, C.; Kim, D.-G.; Thrimurtulu, N.; Yeom, H.-S.; Jun, J.; Shin, S.; Rhee, Y. H. *Org. Lett.* **2013**, *15*, 1166. (b) Hashmi, A. S. K.; Lothschütz, C.; Döpp, R.; Ackermann, M.; Becker, J. D. B.; Rudolph, M.; Scholz, C.; Rominger, F. *Adv. Synth. Catal.* **2012**, *354*, 133. (c) Nakamura, I.; Sato, T.; Yamamoto, Y. *Angew. Chem., Int. Ed.* **2006**, *45*, 4473.

(5) Zhang, L. *J. Am. Chem. Soc.* **2005**, *127*, 16804.

(6) Dubé, P.; Toste, F. D. *J. Am. Chem. Soc.* **2006**, *128*, 12062.

(7) (a) Nakamura, I.; Yamagishi, U.; Song, D.; Konta, S.; Yamamoto, Y. *Chem.—Asian J.* **2008**, *3*, 285. (b) Nakamura, I.; Yamagishi, U.; Song, D.; Konta, S.; Yamamoto, Y. *Angew. Chem., Int. Ed.* **2007**, *46*, 2284.

(8) Yeon, H.-S.; So, E.; Shin, S. *Chem.−Eur. J.* **2011**, *17*, 1764.

(9) Rao, W.; Susanti, D.; Chan, P. W. H. *J. Am. Chem. Soc.* **2011**, *133*, 15248.

(10) For the only other examples of a heteroatom or transmetalation-triggered deaurative process in gold catalysis, see: (a) Chen, Y.; Chen, M.; Liu, Y. *Angew. Chem., Int. Ed.* **2012**, *51*, 6181. (b) Hopkinson, M. N.; Giuffredi, G. T.; Gee, A. D.; Gouverneur, V. *Synlett* **2010**, 2737. (c) Schuler, M.; Silva, F.; Bobbio, C.; Tessier, A.; Gouverneur, V. *Angew. Chem., Int. Ed.* **2008**, *47*, 7927. (d) Nakamura, I.; Sato, T.; Terada, M.; Yamamoto, Y. *Org. Lett.* **2007**, *9*, 4081.

(11) For selected examples, see ref 9 and: (a) Rao, W.; Sally; Koh, M. J.; Chan, P. W. H. *J. Org. Chem.* **2013**, *78*, 3183. (b) Rao, W.; Koh, M. J.; Kothandaraman, P.; Chan, P. W. H. *J. Am. Chem. Soc.* **2012**, *134*, 10811. (c) Kothandaraman, P.; Huang, C.; Susanti, D.; Rao, W.; Chan, P. W. H. *Chem.−Eur. J.* **2011**, *17*, 10081. (d) Kothandaraman, P.; Mothe, S. R.; Toh, S. S. M.; Chan, P. W. H. *J. Org. Chem.* **2011**, *76*, 7633. (e) Kothandaraman, P.; Rao, W.; Foo, S. J.; Chan, P. W. H. *Angew. Chem., Int. Ed.* **2010**, *49*, 4619.

(12) (a) Barabé, F.; Levesque, P.; Korobkov, L.; Barriault, L. *Org. Lett.* **2011**, *13*, 5580. (b) López-Carrillo, V.; Echavarren, A. M. *J. Am. Chem. Soc.* **2010**, *132*, 9292. (c) Amijs, C. H. M.; López-Carrillo, V.; Raducan, M.; Pérez-Galán, P.; Ferrer, C.; Echavarren, A. M. *J. Org. Chem.* **2008**, *73*, 7721. (d) Richard, L.; Gagosz, F. *Organometallics* **2007**, *26*, 4704.

(13) For selected examples of sulfonyl group migrations mediated by other Lewis and Brønsted acids or a base, see: (a) Yu, X.; Xin, X.; Wan, B.; Li, X. *J. Org. Chem.* **2013**, *78*, 4895. (b) Prasad, B.; Adepu, R.; Sandra, S.; Rambabu, D.; Krishna, G. R.; Reddy, C. M.; Deora, G. S.; Misra, P.; Pal, M. *Chem. Commun.* **2012**, *48*, 10434. (c) Xin, X.; Wang, D.; Li, X.; Wan, B. *Angew. Chem., Int. Ed.* **2012**, *51*, 1693. (d) Lee, Y. T.; Chung, Y. K. *J. Org. Chem.* **2008**, *73*, 4698. (e) Weatherhead-Kloster, R. A.; Corey, E. J. *Org. Lett.* **2006**, *8*, 171. (f) Matsumoto, S.; Kishimoto, T.; Ogura, K. *Chem. Lett.* **2002**, 134.

(14) CCDC 918205 (**E**) contains the supplementary crystallographic data for this Article. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

(15) CCDC 918206 (**1b**) contains the supplementary crystallographic data for this Article. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

(16) CCDC 918207 (**2b**) contains the supplementary crystallographic data for this Article. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.