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Synthesis of Carbazoles and Carbazole-Containing Heterocycles via Rhodium-Catalyzed Tandem Carbonylative Benzannulations

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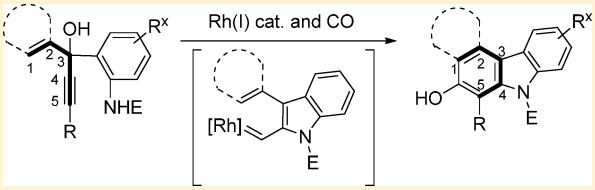
Supporting Information

ABSTRACT: Polycyclic aromatic compounds are important constituents of pharmaceuticals and other materials. We have developed a series of Rh-catalyzed tandem carbonylative benzannulations for the synthesis of tri-, tetra-, and pentacyclic heterocycles from different types of aryl propargylic alcohols. These tandem reactions provide efficient access to highly substituted carbazoles, furocarbazoles, pyrrolocarbazoles, thiophenocarbazoles, and indolocarbazoles. While tricyclic heterocycles could be derived from vinyl aryl propargylic alcohols, tetra- and pentacyclic heterocycles were synthesized from diaryl propargylic alcohols. The tandem carbonylative benzannulation is initiated by a π-acidic rhodium(I) catalyst-mediated nucleophilic addition to alkyne to generate a key metal-carbene intermediate, which is then trapped by carbon monoxide to form a ketene species for 6π electrocyclization. Overall, three bonds and two rings are formed in all of these tandem carbonylative benzannulation reactions.



1. INTRODUCTION

The majority of top-selling drugs and many bioactive compounds contain a benzene ring, which is often fused with one or more additional rings, comprising a polycyclic system. Electrophilic aromatic substitutions are the most widely used methods for the synthesis of substituted benzene derivatives. However, these methods often rely on the strong directing groups for regioselective substitution. De novo synthesis of benzene ring by benzannulation will complement existing methods for the synthesis of both mono- and polycyclic aromatic systems. Very few strategies for de novo synthesis of benzene rings are available, and even fewer of them are general enough for the preparation of various highly substituted polycyclic heterocycles.[1] One of the exceptions is Dötz−Wulff carbonylative benzannulation,[2] which has been widely applied to the synthesis of various aromatic compounds including complex natural products.[3] However, stoichiometric amounts of toxic Fischer carbenes are generally employed in this powerful benzannulation reaction.

Tricyclic carbazoles and their related analogues have diverse biological activities.[4] For example, natural products glycosinine **1** showed significant anti-HIV activity (Figure 1).[5] Heptapylline **2** and its derivatives have remarkably selective and potent anticancer activity.[6] Synthetic carbazole DCAP **3** targets bacteria membrane and has broad-spectrum antibiotic activity.[7] KL001 **4** can prevent ubiquitin-dependent degradation of cryptochrome (CRY) by binding to CRY and is a useful small molecule tool for the study of CRY-dependent physiology such as diabetes.[8]

Carbazoles often fuse with one or more additional rings to form complex polycyclic systems. For example, mahanimbine **5** has an additional 2H-pyran ring, and this compound showed antihyperglycemic/antilipidemic effects in diabetic and obese rats.[9] In addition to a pyran ring, carbazole can be fused with other heterocycles such as furan in furostifoline **6**[10] and eustifoline-D **7**,[10a] indole in ancorinazole **8**,[11] and pyrrole in dictyodendrin A **9**.[12]

We recently reported a Rh-catalyzed tandem annulation and [5 + 1] cycloaddition for the synthesis of highly substituted carbazoles **11** (Scheme 1).[13] The 3-hydroxy-1,4-enyne moiety highlighted in **10** served as the novel five-carbon component for the [5 + 1] cycloaddition. We proposed that intermediates **12**, **13**, and **14** might be involved in this tandem process. Overall, three bonds and two rings are formed in the tandem carbonylative benzannulation of vinyl aryl propargylic alcohols.

In the oxidative cyclization step, the OH group in **12** is the leaving group, while Boc-activated aniline serves as nucleophile. In our previous communication,[13] the activating group for the aniline nucleophile was limited to Boc in all examples. In this article, we try to further expand the scope of the activating group to different sulfonamides and found that the tandem reaction worked well for terminal alkynes. Interestingly, we observed unexpected product **16** for substrates with an internal alkyne such as **15** in Scheme 2.

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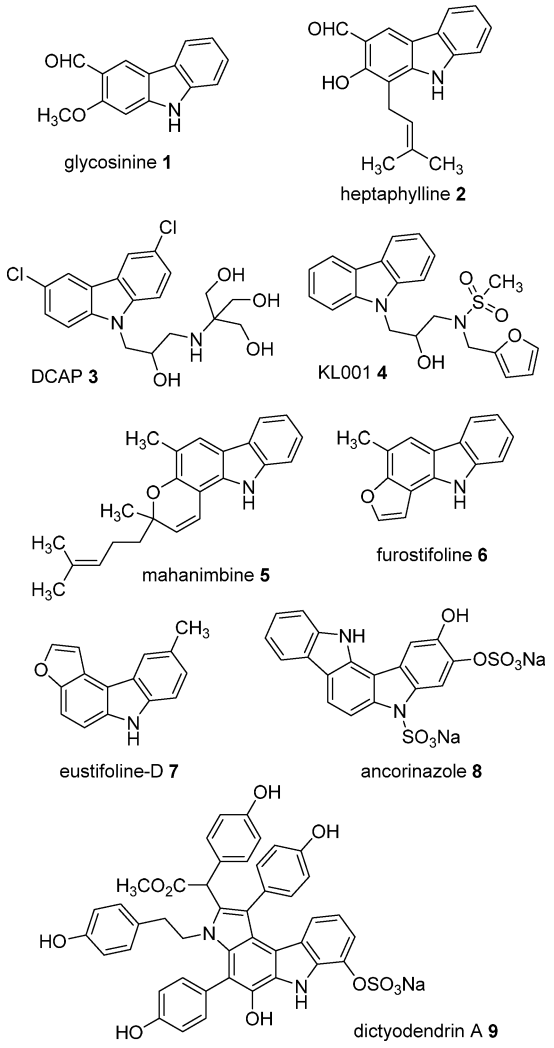
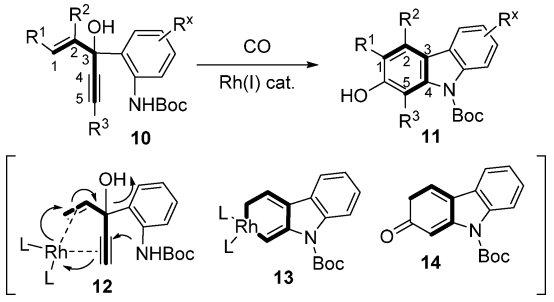


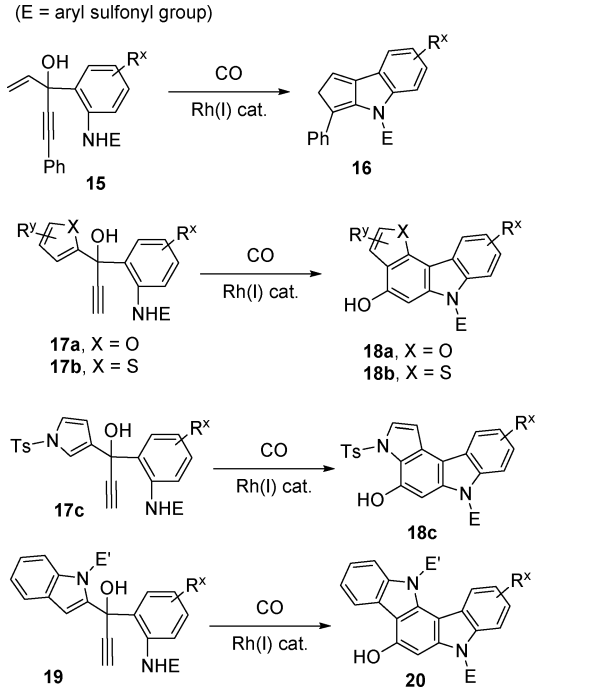
Figure 1. Selected carbazoles and carbazole-containing heterocycles.

Scheme 1. 3-Hydroxy-1,4-enyne as a New 5-Carbon Building Block for [5 + 1] Cycloaddition



More importantly, we discovered that the alkene moiety in **10** could be replaced by an aromatic ring in substrates **17** and **19** when sulfonamide was employed as the nucleophile (Scheme 2). The scope of the tandem carbonylative benzannulation is now expanded from the formation of tricyclic carbazoles to the construction of tetracyclic furocarbazoles **18a**, thiophenocarbazole **18b**, pyrrolocarbazole **18c**, and even pentacyclic indolocarbazole **20**. Being able to replace the vinyl group in propargylic alcohol **10** with the aromatic ring in substrates **17** and **19** also suggests that there are other potential mechanistic pathways besides the oxidative cyclization mechanism shown in Scheme 1.

Scheme 2. Polycyclic Heterocycles Derived from Vinyl Aryl Propargylic Alcohols and Diaryl Propargylic Alcohols



In this article, we report the full scope of the Rh-catalyzed tandem carbonylative benzannulation for the synthesis of tricyclic carbazoles from vinyl aryl propargylic alcohols, the synthesis of tetra- and pentacyclic heterocycles from diaryl propargylic alcohols, for the first time, and potential mechanisms involving metal carbene intermediates that can account for all of our experimental results.[14]

2. RESULTS AND DISCUSSION

As reported in our previous communication,[13] substrate **21a** was prepared by sequential addition of vinyl and alkynyl Grignard reagents to the corresponding carboxylic acid derivative (Table 1). Among all conditions we screened, we found that product **22a** was prepared in good yields in the presence of $[Rh(CO)_2Cl]_2$ catalyst and CO (1 atm). The scope of the tandem annulation and [5 + 1] cycloaddition was investigated for the synthesis of various substituted carbazoles and related heterocycles. Various substituents including alkyl, cyclopropyl, and aryl groups could be tolerated on the alkene termini. Substrate **21b** is one of many examples. It is worth pointing out that it would be difficult to introduce some of these substituents to carbazoles by existing methods.[4a,b] Various substituents on the aniline ring such as bromine, methoxy, and trifluoromethyl groups could all be tolerated.[13] We also found that electron-poor ligand $(CF_3CH_2O)_3P$ was beneficial for the formation of products **22c** and **22d**.[15] No desired product was obtained when both alkene and alkyne have a substituent as shown in substrate **21e**. Phenol **23** could also participate in this tandem carbonylative benzannulation to afford dibenzofuran product **24**.

Under condition A in Table 1, product **22f** (Scheme 3) was isolated in 52% yield. When we examined this substrate in the presence of $(CF_3CH_2O)_3P$ ligand, byproduct **22f′** was isolated in 32% yield in addition to 56% of the desired product **22f**. Substrates **25** with two methyl groups on the terminal position of the alkene afforded cyclohexadienones **26** efficiently in 75% yield.

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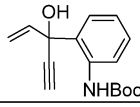
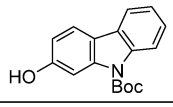
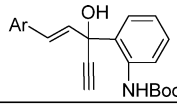
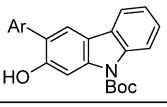
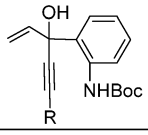
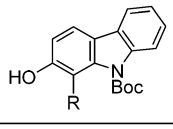
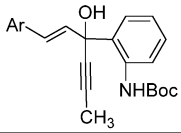
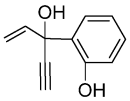
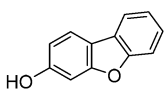
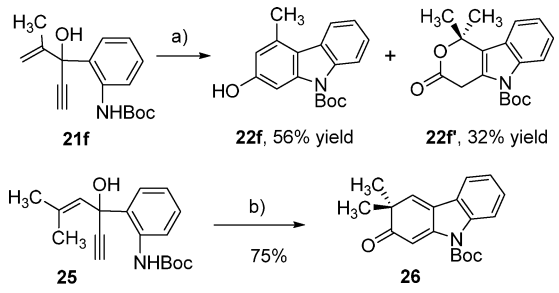
Table 1. Representative Examples for the Rh-Catalyzed Tandem Annulation and [5 + 1] Cycloaddition Using Boc-Anilines as Nucleophiles for the Synthesis of Carbazoles and Dibenzofurans[13]

Substrate	Product	Yield (%)[a]
		
21a	**22a**	81
		
21b, Ar = pFC_6H_4	**22b**	70
		
21c, R = CH_3	**22c**	36,[a] 81[b]
21d, R = Ph	**22d**	56[b]
	-	
21e, Ar = pFC_6H_4	-	Complex[a,b]
		
23	**24**	67[c]

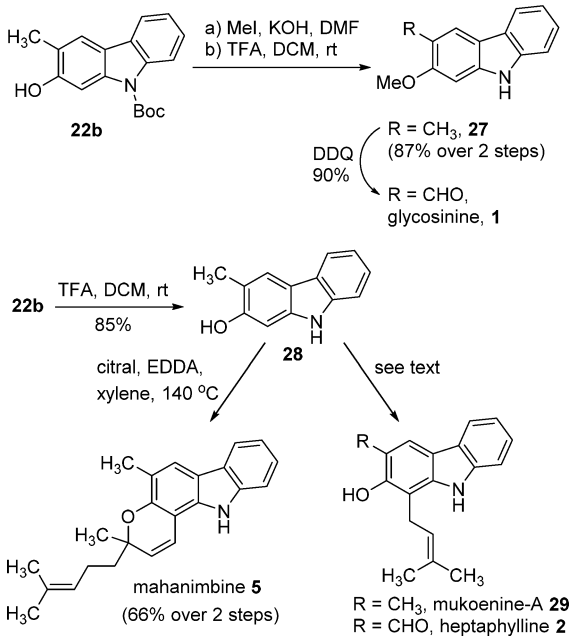
[a]Unless noted otherwise, Condition A: $[Rh(CO)_2Cl]_2$ (5 mol %), DCE, CO (1 atm), 60 °C. Yields were isolated yields. [b]Condition B: $[Rh(CO)_2Cl]_2$ (5 mol %), $(CF_3CH_2O)_3P$ (20 mol %), THF, CO (1 atm), 60 °C. [c]Condition C: $[Rh(CO)_2Cl]_2$ (5 mol %), dioxane, CO (1 atm), 60 °C.

Scheme 3. Generation of Non-Carbazole Products from 3-Hydroxy-1,4-enynes[13]



A number of carbazole alkaloids have a hydroxy or alkoxy substituent on the 2-position.[4a,b] Our tandem annulation [5 + 1] cycloaddition method is well suited for these natural products. To demonstrate this, we prepared natural products **27**, **1**, and **5** as shown in Scheme 4.[16] The synthesis of natural product 2-methoxy-3-methylcarbazole **27**[17] represents a formal synthesis of glycosinine **1** (or *O*-methylmukonal),[17a,b,18] which

Scheme 4. Synthesis of Carbazole Cores in Natural Products



has significant anti-HIV activity.[5] Intermediate **28** could be converted to bioactive natural product mahanimbine **5**[9,19] by annulation with citral using ethylenediammonium diacetate reagent.[20] The last annulation step was reported for the synthesis of **5**,[19] but the yield was only 35%. Ma and co-workers recently reported the preparation of natural products mukoenine-A **29** and heptaphylline **2** from intermediate **28**.[21] The transformations included either a sequence of O-allylation and Claisen rearrangement or sequential O-allylation, DDQ oxidation, and Claisen rearrangement. We thus realized the formal syntheses of these two important bioactive natural products as well.[6]

We have seen dramatically different behaviors between Boc- and Ts-activated anilines in Rh-catalyzed reactions recently.[22] We next prepared three sulfonamides substrates **30a–c** for the tandem annulation [5 + 1] cycloaddition (Table 2). Surprisingly, the reaction occurred smoothly at room temperature. Previously, heating was required when Boc was employed as the activating group in substrate **21a**. The isolated yields of products **31a** and **31c** were slightly higher than that of **31b**. We then further tested substrates **30d** and **30e** and found that they behaved similarly.

When we had a phenyl-substituted internal alkyne in substrate **21d**, product **22d** was isolated in moderate yield. We then prepared sulfonamides **30f** and **30g** to test if the yield of the tandem annulation [5 + 1] cycloaddition can be improved for substrates with a phenyl-substituted internal alkyne. Surprisingly, products with a cyclopentadiene moiety were formed. We did not observe any [5 + 1] benzannulation product. When we have substituents on both the alkene and alkyne, a similar cyclopentadiene product **33** was isolated in 78% yield.

As discussed at the beginning, many polycyclic heterocycles have carbazoles fused with additional carbo- or heterocycles. We envisioned that we might be able to access tetracyclic heterocycles by replacing the alkene moiety of 3-hydroxy-1,4-enyne with an aromatic ring (Scheme 5). When substrate **34**[23] was treated with Rh-catalyst in the presence of a CO balloon, only a trace amount of tetracyclic product **35** was observed, which was very encouraging because a challenging dearomatization

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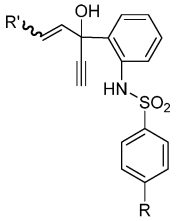
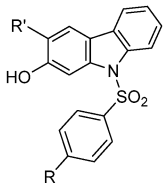
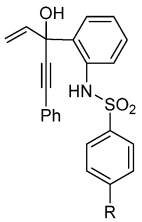
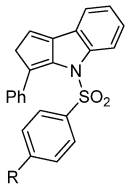
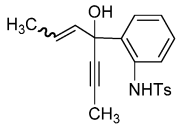
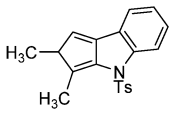
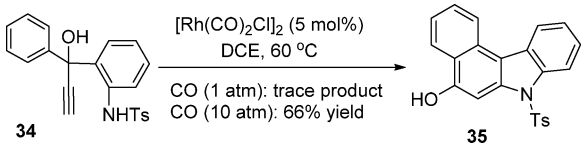
Table 2. Using Sulfonamides as Nucleophiles[a]

substrate	Product	Yield (%)
		
30a, R = CH_3, R' =H	**31a**	81
30b, R = NO_2, R' = H	**31b**	70
30c, R = CH_3O, R' = H	**31c**	78
30d, R = R' = CH_3	**31d**	86
30e, R = CH_3O, R' = CH_3	**31e**	82
		
30f, R = CH_3	**32a**	57[b]
30g, R = CH_3O	**32b**	58[b]
		
30h	**33**	78

[a]Unless noted otherwise, Condition A: $[Rh(CO)_2Cl]_2$ (5 mol %), DCE, CO (1 atm), rt, 8−12 h. Yields are isolated yields. [b]Condition B: $[Rh(CO)_2Cl]_2$ (5 mol %), $(CF_3CH_2O)_3P$ (20 mol %), DCE, CO (1 atm), 60 °C, 8−12 h.

Scheme 5. Rh-Catalyzed Carbonylative Benzannulation of Diaryl Propargylic Alcohols



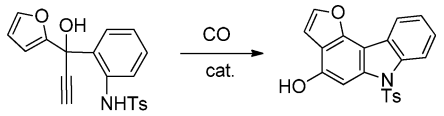
34 35

step was involved in this process. Under 10 atm of CO, phenyl-fused carbazole product **35** could be isolated in 66% yield.

We reasoned that breaking the aromaticity of a nonbenzene heterocycle would be easier than the benzene ring itself.[24] Substrate **36a**[25] with a furan ring was then prepared (Table 3). In the presence of just a CO balloon, product **37a** was obtained in 60% yield (entry 1, Table 3). Simply lowering the temperature to room temperature, the yield based on ^1H NMR was improved to 79% (entry 2).

No or a trace amount of desired product was observed for cationic $[Rh(COD)_2]BF_4$ or Wilkinson's catalyst $Rh(Ph_3P)_3Cl$ (entries 3 and 4). Lower yields were obtained in the presence of phosphine ligand $(4\text{-}CF_3C_6H_4)_3P$ (entries 5 and 6). The highest yield was obtained in 1,2-dichloroethane (DCE) among all solvents we screened including DCM, $CHCl_3$, THF, dioxane, and toluene. We also investigated a few other catalysts.

Table 3. Screening of Conditions for Substrate 36a[a]



36a 37a

entry	conditions	yield of **37a** (%)[b]
1	$[Rh(CO)_2Cl]_2$ (5 mol %), 60 °C	60
2	$[Rh(CO)_2Cl]_2$ (5 mol %), rt	79
3	$[Rh(COD)_2]BF_4$ (5 mol %), rt	0
4	$[Rh(PPh_3)_3Cl]$ (5 mol %), rt	trace
5	$[Rh(COD)Cl]_2$ (5 mol %), $(4\text{-}CF_3C_6H_4)_3P$ (30 mol %), rt	trace
6	$[Rh(COD)Cl]_2$ (5 mol %), $(4\text{-}CF_3C_6H_4)_3P$ (30 mol %), 60 °C	32
7	$[Ir(COD)Cl]_2$ (5 mol %)	0
8	$[Ir(CO)(PPh_3)_2Cl]$ (5 mol %)	0
9	$Pd(OAc)_2$ (5 mol %)	0
10	$PtCl_2$ (5 mol %)	0
11	$Au(PPh_3)Cl$ (5 mol %)	0

[a]Conditions: DCE, CO (1 atm), 6 h, unless noted otherwise. [b]The yield was determined by ^1H NMR of crude product using CH_2Br_2 as the internal standard.

However, no desired product was observed in the presence of $[Ir(COD)Cl]_2$, $[Ir(CO)(PPh_3)_2Cl]$, $Pd(OAc)_2$, $PtCl_2$, or $Au(PPh_3)Cl$ (entries 7−11).

A variety of diaryl propargylic alcohols were prepared to explore the scope of the Rh-catalyzed carbonylative benzannulation for the synthesis of tetra- and even pentacyclic heterocycles (Table 4). Furocarbazole **37a** was isolated in 73% yield under condition A. The effect of the activating group was examined by replacing the Ts group in **36a** with *para*-nitrobenzenesulfonamide or *para*-methoxybenzenesulfonamide in **36b** or **36c**, respectively. It was found that the electron-donating sulfonamide worked better and afforded 76% yield of product **37c**, comparable to the yield of **37a**.

Substrates **36d−36g** were prepared to examine the effect of substituents on the furan ring. The yields were generally higher for products **37d−37f** under heating conditions. An unexpected fragmentation reaction occurred for more electron-deficient furan in substrate **36g** and afforded ketone **37g** at room temperature.

Substrates **36h−36k** were prepared to examine the effect of substituents on the benzene motif of aniline. Having an alkyl substituent on the ortho-position did not impact the reaction much. Both electron-withdrawing and electron-donating groups could be tolerated. The bromine substituent in product **37k** remained unchanged and could be further functionalized by Pd-catalyzed cross-coupling reactions.

We then explored heterocycles beyond furan. Carbazoles fused with a thiophene such as **37l** and **37m** could be prepared successfully. No desired product was observed for substrate **36n** bearing a 2-substituted *N*-methyl pyrrole. On the other hand, product **37o** could be prepared from substrate **36o** with a 3-substituted *N*-tosyl pyrrole. Indolyl fused carbazole **37p** was prepared from substrate **36p** in 71% yield, demonstrating the feasibility of synthesizing pentacyclic heterocycles from relative simple diaryl propargylic alcohols by this tandem reaction. We did not observe any desired product for substrates **36q** and **36r** with an internal alkyne, regardless of the activating group on the aniline nitrogen.

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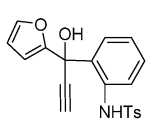
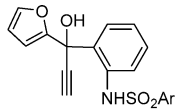
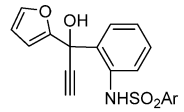
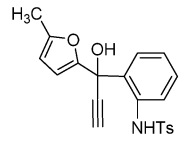
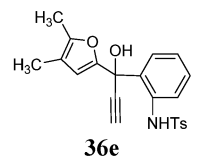
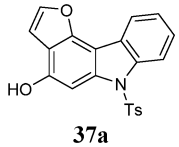
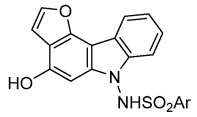
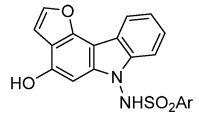
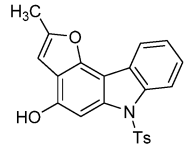
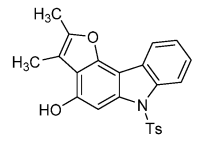
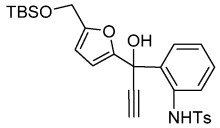
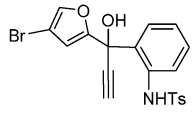
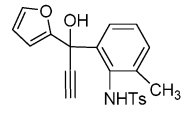
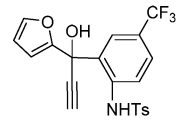
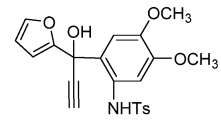
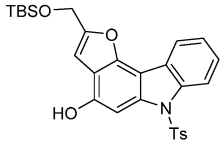
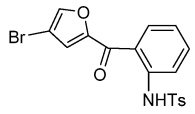
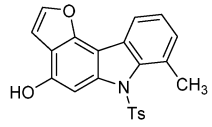
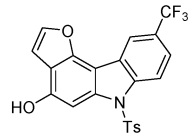
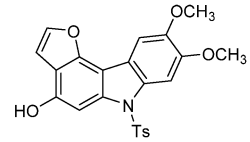
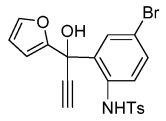
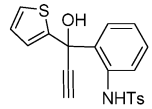
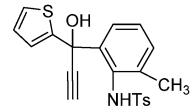
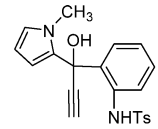
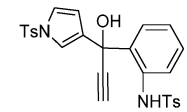
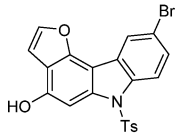
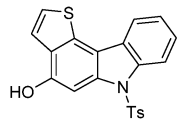
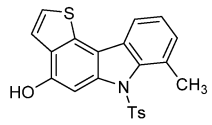
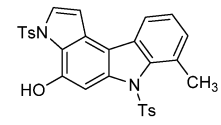
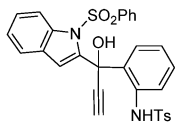
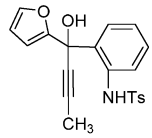
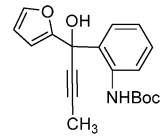
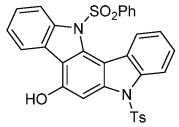
Table 4. Scope of Tandem Annulation and [5 + 1] Cycloaddition for the Synthesis of Polycyclic Heterocycles[a]

substrate	 **36a**	 **36b** (Ar = pNO$_2$C$_6$H$_4$)	 **36c** (Ar = pCH$_3$OC$_6$H$_4$)	 **36d**	 **36e**
product	 **37a**	 **37b** (Ar = pNO$_2$C$_6$H$_4$)	 **37c** (Ar = pCH$_3$OC$_6$H$_4$)	 **37d**	 **37e**
yield (%)	73	42	76	64[b]	55[b]
substrate	 **36f**	 **36g**	 **36h**	 **36i**	 **36j**
product	 **37f**	 **37g**	 **37h**	 **37i**	 **37j**
yield (%)	61[b]	51	54	58	44
substrate	 **36k**	 **36l**	 **36m**	 **36n**	 **36o**
product	 **37k**	 **37l**	 **37m**	–	 **37o**
yield (%)	60	63	53	–	55[b]
substrate	 **36p**	 **36q**	 **36r**		
product	 **37p**	-	-		
yield (%)	71	Complex mixture	Complex mixture		

[a]Unless otherwise noted, Condition A was employed: [Rh(CO)$_2$Cl]$_2$ (5 mol %), DCE, CO (1 atm), rt, 6−12 h. Yields were isolated yields. [b]Condition B: 60 °C.

Previously, we[26] and others[27] have demonstrated that 3-acyloxy-1,4-enyne **38** can serve as the five-carbon component in Rh-catalyzed [5 + 1] cycloaddition, and we also extended it to [5 + 2] cycloaddition[15,28] as shown in Scheme 6A. DFT calculations suggested a rhodium-mediated concerted oxidative cyclization accompanied by 1,2-acyloxy migration as shown in **39** for the formation of metallacycle **40** from ester **38**.[29] Based on this, we proposed the mechanism for the tandem annulation and [5 + 1] cycloaddition in Scheme 6B. A new metallacycle **42** might be generated for cycloadditions by replacing the ester group in enyne **39** by a OH leaving group and a Boc-NH nucleophile in 1,4-enyne **41**. Insertion of CO will produce cyclohexadiene intermediate **43**, which can immediately undergo aromatization to yield products **22a** or **31a**. Alternatively, a 6π electrocyclic ring opening can afford carbene **44**, which can undergo CO insertion to afford ketene **45**.

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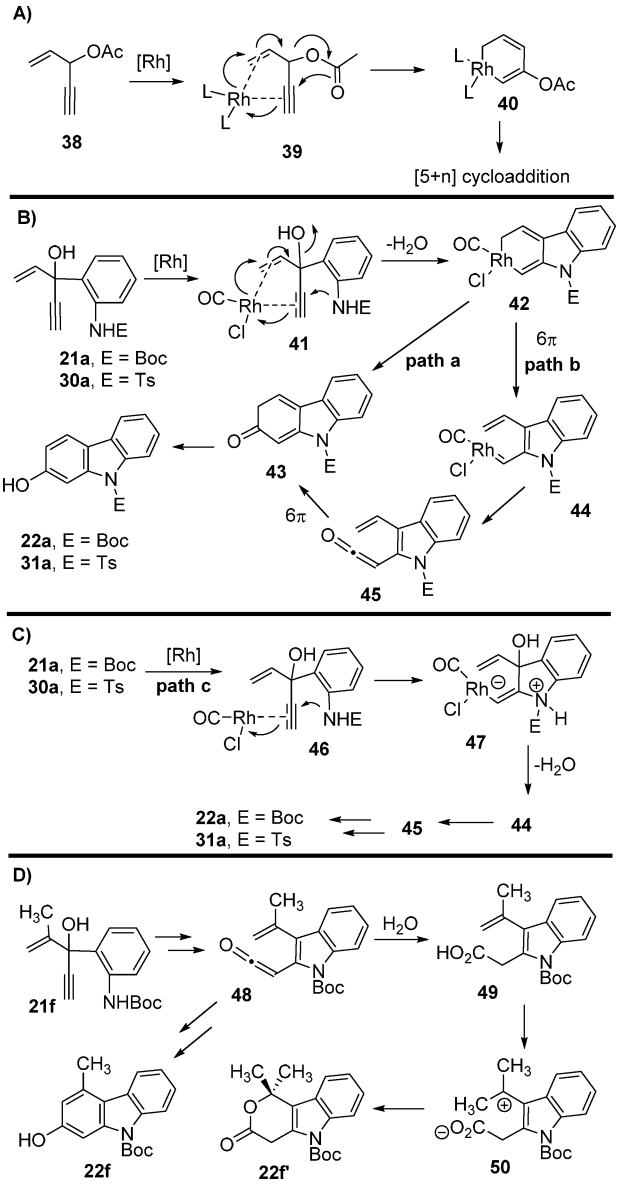
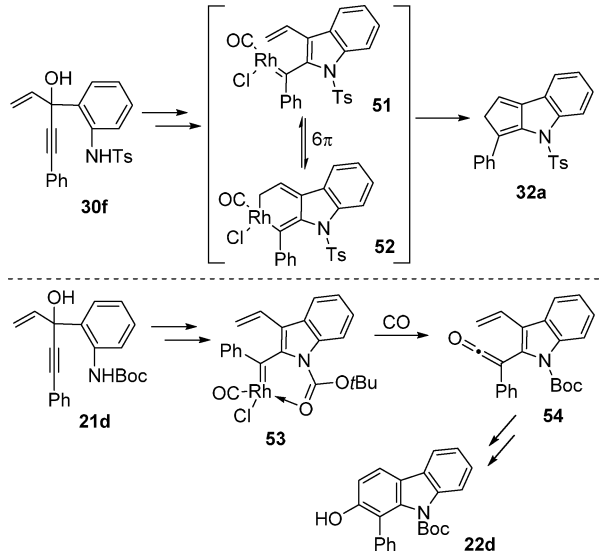
Scheme 6. Proposed Mechanisms for the Tandem Annulation [5 + 1] Cycloaddition of 3-Hydroxy-1,4-Enynes with CO



An alternative mechanism involving the formation of Rh(I) carbene **44** by eliminating water from intermediate **47** can also be proposed (Scheme 6C). Previously, we[30] and others[31] have generated metal carbenes from propargylic ethers by eliminating methanol from a similar intermediate. The dienyl metal carbene **44** can then undergo CO insertion, 6π electrocyclization, and aromatization to yield products **22a** or **31a**. The formation of lactone byproduct **22e′** from substrate **21e** may be explained by the generation of ketene **48**, carboxylic acid **49**, and a relatively stable tertiary carbocation **50** (Scheme 6D). The isolation of byproduct **22e′** supports the involvement of metal carbene and ketene intermediates.

We observed the formation of product **32a** from substrate **30f** with a tosyl amide and a phenylacetylene moiety (Scheme 7). Apparently, the CO insertion to metallacycle **52** or the corresponding metal carbene intermediate **51** is much slower than the reductive elimination of metallacycle **52**. Interestingly, when the nitrogen nucleophile was switched to Boc-aniline in

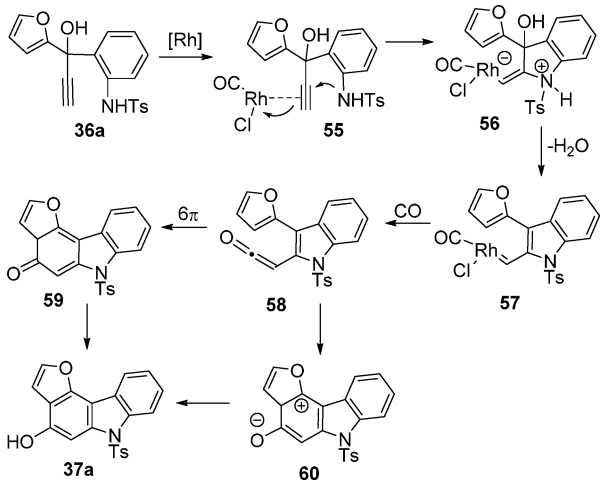
Scheme 7. Proposed Mechanism for the Divergent Reactivity of Metal Carbenes Derived from 3-Hydroxy-1,4-enynes



substrate **21d**, the desired tandem annulation [5 + 1] cycloaddition product **22d** was obtained. We hypothesize that the coordination of carbonyl oxygen in **53** prevents the formation of the corresponding metallacyclohexadiene.[22] Carbazole fused with a five-membered ring product was therefore not observed.

In the case of diaryl propargylic alcohol substrate **36a**, the furan moiety is less likely to coordinate to rhodium metal than the isolated alkene in enynes **21a** or **30a**. The mechanism for the tandem carbonylative benzannulation of substrate **36a** is then proposed in Scheme 8 based on Scheme 6C. The tandem

Scheme 8. Proposed Mechanism for Rh-Catalyzed Carbonylative Benzannulation of Diaryl Propargylic Alcohols



reaction is initiated by acidic Rh-mediated nucleophilic addition of sulfonamide nitrogen to alkyne as shown in complex **55**. Elimination of a water molecule from intermediate **56** will afford Rh(I) carbene **57**. Insertion of CO, 6π electrophilic ring closure accompanied by dearomatization of the furan ring, and rearomatization will furnish the final product **37a**. Friedel–Crafts acylation through intermediate **60** is also a possible pathway.

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3. CONCLUSION

In summary, we have developed a series of carbonylative benzannulation for the synthesis of substituted carbazoles and carbazoles fused with various heterocycles from relatively simple propargylic alcohols. In most of these transformations, one C−N bond and two C−C bonds are formed, while classical cycloadditions generally involve the construction of just two bonds. The strategy of using propargylic alcohol as the Rh(I) carbene precursor should have broad implications in transition-metal catalysis and metal carbene chemistry.

4. EXPERIMENTAL SECTION

General Information. Unless otherwise noted, all reactions in nonaqueous media were conducted under dry argon in glassware that had been oven-dried prior to use. Anhydrous solutions of reaction mixtures were transferred via an oven-dried syringe or cannula. All solvents were dried prior to use. Thin-layer chromatography was performed using precoated silica gel plates. Flash column chromatography was performed with silica gel (40−63 μm). Infrared spectra (IR) were obtained as neat oils. ^{1}H and ^{13}C nuclear magnetic resonance spectra (NMR) were obtained on 400 or 500 MHz recorded in ppm (δ) downfield of TMS (δ = 0) in $CDCl_3$. Signal splitting patterns were described as singlet (s), doublet (d), triplet (t), quartet (q), quintet (quint), or multiplet (m), with coupling constants (J) in hertz. High-resolution mass spectra (HRMS) were performed on an electron spray injection (ESI) TOF mass spectrometer. The preparation procedures and characterization data for all substrates and products in Table 1 and Schemes 3 and 4, except **21e**, have been reported in our communication.[13] Substrate **21e** was prepared according to previously reported procedure.[13]

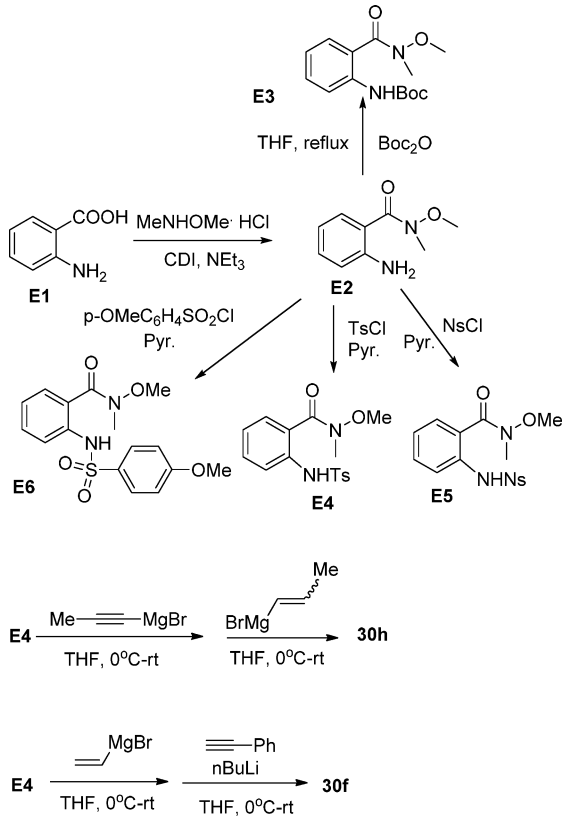
*(E)-tert-Butyl (2-(1-(4-fluorophenyl)-3-hydroxyhex-1-en-4-yn-3-yl)phenyl)carbamateb (**21e**).* 106 mg, 56% over 2 steps. Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 8.10 (s, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.71 (d, J = 8.0 Hz, 1H), 7.36−7.29 (m, 3H), 7.05 (t, J = 7.6 Hz, 1H), 6.98 (t, J = 8.8 Hz, 2H), 6.787 (d, J = 15.6 Hz, 1H), 6.29 (d, J = 15.6 Hz, 1H), 3.15 (s, 1H), 1.98 (s, 3H), 1.37 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.7 (d, J = 246.0 Hz), 153.4, 137.1, 132.4 (d, J = 3.3 Hz), 130.8, 130.7 (d, J = 2.0 Hz), 129.3, 128.7, 128.6, 128.5, 127.4, 123.1, 115.6 (d, J = 21.5 Hz), 85.8, 80.2, 79.3, 73.6, 28.4, 4.1. IR (neat) ν 3377, 2981, 1587, 1509, 1445, 1265, 1231, 1158. HRMS (ESI) m/z calcd for $C_{23}H_{24}FNO_3$ $(M + Na)^+$ 404.1632, found 404.1638.

General Strategy for the Preparation of Substrates 30a−30h in Table 2. Scheme 9 shows the preparation of **30a−30h**.

*Procedures for the Preparation of **30h** and **30f**.* To a stirred solution of commercially available 2-animobenzoic acid **E1** (2.1 g, 10 mmol) in anhydrous THF (80 mL) was added 1,1′-carbonyldiimidazole (1.6 g, 10 mmol) at 0 °C under argon atmosphere. The reaction mixture was allowed to warm to room temperature and stirred for 2 h, then a suspension of *N*,*O*-dimethylhydroxylamine hydrochloride (0.97g, 10 mmol) and Et_3N (1.0 g, 10 mmol) in THF (20 mL) was added, and the reaction mixture was stirred overnight. When the reaction was complete as determined by TLC, the volatile solvent was removed under reduced pressure. The residue was poured into H_2O (100 mL). The pH was adjusted to neutral with 5% NaOH solution. The mixture was extracted with ethyl acetate (3 × 50 mL). The combined organic layers were washed with brine (1 × 100 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography (hexane/ethyl acetate = 50:50) to yield Weinreb amide **E2** (2.2 g, 86%) as a white solid.

To a stirred solution of the above Weinreb amide **E2** (2.2 g, 8.6 mmol) in anhydrous THF (80 mL) was added Boc-anhydride (1.8 g, 9.0 mmol) at room temperature. The reaction mixture was stirred overnight under reflux. When the reaction was complete as determined by TLC, the volatile solvent was removed under reduced pressure. The residue was purified by flash column chromatography (hexane/ethyl acetate = 85:15) to give the corresponding Boc-aniline product **E3** (2.5 g, 90%) as a white solid.

Scheme 9. Synthesis of Substrates 30h and 30f and Intermediates for Other Substrates in Table 2



To a stirred solution of Weinreb amide **E2** (360 mg, 2 mmol) in pyridine (2.5 mL) was added tosyl chloride (477 mg), and the resulting solution was stirred at 105 °C overnight under argon. The reaction mixture was cooled to room temperature and diluted with EtOAc. The mixture was washed with 3 M HCl and brine, dried over Na_2SO_4, and concentrated under vacuum. The resulting residue was purified with flash column chromatography (10−30% EtOAc in hexanes) to give the pure product **E4** (541 mg, 81%) as a white solid.

To a stirred solution of Weinreb amide **E2** (360 mg, 2 mmol) in pyridine (2.5 mL) was added *p*-nitrobenzenesulfonyl chloride (553 mg), and the resulting solution was stirred at 105 °C overnight under argon. The reaction mixture was cooled to room temperature and diluted with EtOAc. The mixture was washed with 3 M HCl and brine, dried over Na_2SO_4, and concentrated under vacuum. The resulting residue was purified with flash column chromatography (10−30% EtOAc in hexanes) to give the pure product **E5** (613 mg, 84%) as a white solid.

To a stirred solution of Weinreb amide **E2** (360 mg, 2 mmol) in pyridine (2.5 mL) was added *p*-methoxybenzenesulfonyl chloride (517 mg), and the resulting solution was stirred at 105 °C overnight under argon. The reaction mixture was cooled to room temperature and diluted with EtOAc. The mixture was washed with 3 M HCl and brine, dried over Na_2SO_4, and concentrated under vacuum. The resulting residue was purified with flash column chromatography (10−30% EtOAc in hexanes) to give the pure product **E6** (560 mg, 80%) as a white solid.

To a stirred solution of amide **E4** (0.43 g, 1.5 mmol) in anhydrous THF (20 mL) was added 1-propynylmagnesium bromide solution in THF (0.5 M, 10.0 mL, 5.0 mmol) at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred overnight. When the reaction was completed as determined by TLC, the reaction mixture was poured into ice-HCl (4 M) and extracted with ethyl acetate (3 × 20 mL). The combined organic layers were washed with brine (1 × 60 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash column

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chromatography (25% EtOAc in hexanes) to yield the ynone intermediate (224 mg, 50%) as a yellow solid. To a stirred solution of this ynone (115 mg, 0.38 mmol) in THF (5 mL) was added 1-propenylmagnesium bromide solution in THF (0.5 M, 6.0 mL, 3.0 mmol) at −78 °C. After the addition was completed, the reaction was stirred for 7 h at room temperature. When the reaction was completed as determined by TLC, the reaction mixture was quenched by addition of saturated aqueous ammonium chloride (5 mL) and extracted with Et_2O (3 × 10 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was purified by flash column chromatography (25% EtOAc in hexanes) to yield pure product **30h** (105 mg, 78%) as a colorless oil.

To a stirred solution of amide **E4** (0.56 g, 2.0 mmol) in anhydrous THF (40 mL) was added vinylmagnesium bromide solution in THF (1.0 M, 6.0 mL, 6.0 mmol) at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for 4 h. When the reaction was completed as determined by TLC, the reaction mixture was poured into saturated aqueous ammonium chloride (100 mL) and extracted with ethyl acetate (3 × 50 mL). The combined organic layers were washed with brine (1 × 100 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography (10% EtOAc in hexanes) to yield the enone intermediate (420 mg, 86%) as a colorless oil. To a stirred solution of phenylacetylene (345 mg, 4.2 mmol) in anhydrous THF (30 mL) was added *n*-BuLi in hexane (2.5 M, 1.7 mL, 4.2 mmol) at −78 °C. After stirring for 30 min at −78 °C, the enone intermediate (511 mg, 1.7 mmol) in THF (5 mL) was added to the reaction mixture dropwise. After the addition was completed, the reaction was stirred for 2 h at −78 °C. When the reaction was completed as determined by TLC, the reaction mixture was quenched by addition of saturated aqueous ammonium chloride (100 mL) and extracted with Et_2O (3 × 50 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was purified by flash column chromatography (15% EtOAc in hexanes) to yield pure product **30f** (582 mg, 85%) as a colorless oil.

Other substrates in Table 2 were prepared according to the above procedures.

*N-(2-(3-Hydroxypent-1-en-4-yn-3-yl)phenyl)-4-methylbenzenesulfonamide (**30a**).* 176 mg, 54% over 4 steps. Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 8.69 (s, 1H), 7.74 (d, J = 10.0 Hz, 2H), 7.60 (d, J = 10.5 Hz, 1H), 7.51 (d, J = 9.5 Hz, 1H), 7.26−7.21 (m, 3H), 7.01 (t, J = 10.0 Hz, 1H), 5.90 (dd, J = 21.0, 12.5 Hz, 1H), 5.49 (d, J = 21.5 Hz, 1H), 5.17 (d, J = 12.5 Hz, 1H), 2.96 (s, 1H), 2.82 (s, 1H), 2.37 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.9, 138.7, 137.3, 136.2, 129.8, 129.7, 128.8, 128.3, 127.7, 123.7, 120.2, 116.4, 83.0, 77.6, 74.4, 21.8. IR (neat) ν 3055, 2359, 1622, 1475, 1367, 1266, 1119, 1091, 953, 813. HRMS (ESI) m/z calcd for $C_{18}H_{17}NO_3S$ (M + Na)$^+$ 350.0821, found 350.0818.

*N-(2-(3-Hydroxypent-1-en-4-yn-3-yl)phenyl)-4-nitrobenzenesulfonamide (**30b**).* 200 mg, 56% over 4 steps. Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 8.93 (s, 1H), 8.27 (d, J = 9.0 Hz, 2H), 8.02 (d, J = 8.5 Hz, 2H), 7.63 (d, J = 8.0 Hz, 1H), 7.51 (d, J = 8.0 Hz, 1H), 7.29 (t, J = 7.5 Hz, 1H), 7.08 (t, J = 7.5 Hz, 1H), 5.92 (dd, J = 17.0, 10.0 Hz, 1H), 5.49 (d, J = 17.0 Hz, 1H), 5.18 (d, J = 10.0 Hz, 1H), 3.00 (s, 1H), 2.80 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.4, 145.9, 138.7, 135.3, 130.0, 129.3, 128.9, 128.7, 124.7, 124.3, 120.5, 116.7, 82.7, 77.8, 74.4. IR (neat) ν 3055, 2360, 1600, 1470, 1267, 1108, 1094, 940, 831. HRMS (ESI) m/z calcd for $C_{17}H_{14}N_2O_5S$ (M + Na)$^+$ 381.0521, found 381.0529.

*N-(2-(3-Hydroxypent-1-en-4-yn-3-yl)phenyl)-4-methoxybenzenesulfonamide (**30c**).* 182 mg, 53% over 4 steps. Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 8.63 (s, 1H), 7.79 (d, J = 9.0 Hz, 2H), 7.60 (d, J = 8.5 Hz, 1H), 7.54 (d, J = 8.0 Hz, 1H), 7.26−7.24 (m, 1H), 7.01 (t, J = 7.5 Hz, 1H), 6.89 (d, J = 9.0 Hz, 2H), 5.93 (dd, J = 17.0, 10.0 Hz, 1H), 5.51 (d, J = 17.0 Hz, 1H), 5.20 (d, J = 10.0 Hz, 1H), 3.82 (s, 3H), 2.87 (s, 1H), 2.84 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.1, 138.5, 136.1, 131.7, 129.6, 128.6, 128.1, 123.4, 120.0, 116.2, 114.1, 82.8, 77.3, 74.2, 55.6. IR (neat) ν 3299, 3055, 1581, 1497, 1264, 1157, 1096, 939, 835. HRMS (ESI) m/z calcd for $C_{18}H_{17}NO_4S$ (M + Na)$^+$ 366.0770, found 366.0757.

*N-(2-(3-Hydroxyhex-4-en-1-yn-3-yl)phenyl)-4-methylbenzenesulfonamide (**30d**).* 170 mg, 50% over 4 steps. Colorless oil. E/Z = 2:1 ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ major isomer: 8.80 (s, 1H), 7.75 (d, J = 10.8 Hz, 2H), 7.58 (d, J = 8.0 Hz, 1H), 7.51 (d, J = 8.0 Hz, 1H), 7.26−7.19 (m, 3H), 7.02−6.97 (m, 1H), 5.99 (dq, J = 15.4, 6.4 Hz, 1H), 5.60 (d, J = 15.6 Hz, 1H), 2.88 (s, 1H), 2.79 (s, 1H), 2.37 (s, 3H), 1.69 (d, J = 6.8 Hz, 3H) . ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.9, 137.4, 136.1, 130.4, 132.2, 129.8, 129.6, 128.5, 128.3, 127.6, 123.6, 120.0, 83.6, 77.2, 74.2, 21.8, 17.6. IR (neat) ν 2349, 1642, 1469, 1334, 1265, 1161, 1093, 897. HRMS (ESI) m/z calcd for $C_{19}H_{19}NO_3S$ (M + Na)$^+$ 364.0977, found 364.0964.

*N-(2-(3-Hydroxyhex-4-en-1-yn-3-yl)phenyl)-4-methoxybenzenesulfonamide (**30e**).* 164 mg, 46% over 4 steps. Colorless oil. E/Z = 4:1 (the two isomers were partially separated after column chromatography). ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ major isomer: 8.73 (s, 1H), 7.81 (d, J = 11.5 Hz, 2H), 7.58 (d, J = 8.0 Hz, 1H), 7.51 (d, J = 8.0 Hz, 1H), 7.22 (t, J = 8.0 Hz, 1H), 7.00 (t, J = 7.5 Hz, 1H), 6.89 (d, J = 12.0 Hz, 2H), 6.03−5.98 (m, 1H), 5.60 (d, J = 15.5 Hz, 1H), 3.82 (s, 3H), 2.81 (s, 1H), 2.75 (s, 1H), 1.71 (d, J = 7.0 Hz, 3H) . ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.3, 136.2, 132.2, 132.0, 129.8, 129.6, 129.4, 128.6, 128.3, 123.5, 120.0, 114.3, 83.6, 77.2, 74.2, 55.8, 17.6. IR (neat) ν 3055, 1586, 1468, 1254, 1158, 1046, 835. HRMS (ESI) m/z calcd for $C_{19}H_{19}NO_4S$ (M + Na)$^+$ 380.0932, found 380.0927.

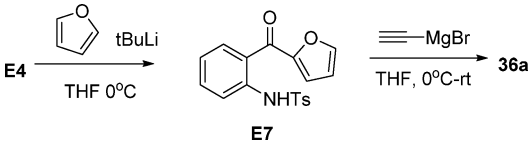
*N-(2-(3-Hydroxy-5-phenylpent-1-en-4-yn-3-yl)phenyl)-4-methylbenzenesulfonamide (**30f**).* 582 mg, 50% over 4 steps. Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 8.83 (s, 1H), 7.74 (d, J = 8.5 Hz, 2H), 7.61−7.58 (m, 2H), 7.48−7.46 (m, 2H), 7.35−7.31 (m, 3H), 7.23 (t, J = 8.0 Hz, 1H), 7.15 (d, J = 8.0 Hz, 2H), 7.02 (t, J = 7.5 Hz, 1H), 5.99 (dd, J = 17.0, 10.0 Hz, 1H), 5.53 (d, J = 17.0 Hz, 1H), 5.18 (d, J = 10.5 Hz, 1H), 3.05 (s, 1H), 2.33 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.9, 139.1, 137.3, 136.3, 132.0, 129.9, 129.7, 129.7, 129.3, 128.4, 127.7, 127.5, 123.6, 121.9, 119.9, 116.0, 89.3, 88.1, 74.9, 21.7. IR (neat) ν 3239, 2924, 1584, 1492, 1333, 1166, 1090, 813, 755. HRMS (ESI) m/z calcd for $C_{24}H_{21}NO_3S$ (M + Na)$^+$ 426.1134, found 426.1117.

*N-(2-(3-Hydroxy-5-phenylpent-1-en-4-yn-3-yl)phenyl)-4-methoxybenzenesulfonamide (**30g**).* 210 mg, 50% over 4 steps. Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 8.81 (s, 1H), 7.79 (d, J = 8.8 Hz, 2H), 7.60 (d, J = 8.4 Hz, 2H), 7.48 (d, J = 7.2 Hz, 2H), 7.37−7.33 (m, 3H), 7.24 (t, J = 8.8 Hz, 1H), 7.02 (t, J = 8.4 Hz, 1H), 6.81 (d, J = 8.8 Hz, 2H), 6.01 (dd, J = 16.8, 10.0 Hz, 1H), 5.54 (d, J = 16.8 Hz, 1H), 5.21 (d, J = 10.0 Hz, 1H), 3.78 (s, 3H), 3.09 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.2, 139.2, 136.3, 132.0, 131.8, 129.8, 129.7, 129.3, 129.3, 128.7, 128.4, 123.5, 121.9, 119.8, 116.0, 114.2, 89.3, 88.1, 74.8, 55.8. IR (neat) ν 3053, 2987, 1581, 1497, 1158, 1095, 834. HRMS (ESI) m/z calcd for $C_{24}H_{21}NO_4S$ (M + Na)$^+$ 442.1083, found 442.1069.

*N-(2-(4-Hydroxyhept-2-en-5-yn-4-yl)phenyl)-4-methylbenzenesulfonamide (**30h**).* 105 mg, 27% over 4 steps. White solid, mp = 121−123 °C. E/Z = 2.5:1, ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ major isomer: 8.46 (s, 1H), 7.77−7.69 (m, 3H), 7.63 (d, J = 8.0 Hz, 1H), 7.53 (dd, J = 12.0, 7.8 Hz, 1H), 7.26−7.19 (m, 2H), 7.03−6.99 (m, 1H), 5.52−5.49 (m, 1H), 5.41−5.35 (m, 1H), 2.61 (s, 1H), 2.37 (s, 3H), 1.94 (s, 3H), 1.51 (d, J = 7.2 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.8, 137.4, 136.0, 133.2, 132.2, 129.6, 129.4, 129.3, 128.2, 127.5, 123.5, 120.3, 85.1, 80.0, 72.6, 21.7, 13.9, 4.0. IR (neat) ν 3054, 2987, 1584, 1369, 1161, 1092, 894. HRMS (ESI) m/z calcd for $C_{20}H_{21}NO_3S$ (M + Na)$^+$ 378.1134, found 378.1120.

General Strategy for the Preparation of Substrates in Table 4 (Scheme 10). *Procedures for the Preparation of Substrate **36a**.*[25] To a solution of furan (0.72 mL, 10.0 mmol) in THF (20 mL) was added *t*-BuLi (1.25 mL, 1.6 M in hexanes, 2.00 mmol) dropwise at −78 °C.

Scheme 10. Synthesis of Substrates 36a



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The solution was then allowed to warm to 0 °C and stirred 1 h. To this solution was added amide **E4** (0.34 g, 1.0 mmol) in THF (2 mL). After the addition was complete, the reaction was stirred at 0 °C for 4 h. Reaction was diluted with EtOAc and quenched with saturated aqueous NH_4Cl. The aqueous phase was extracted with EtOAc, and the combined organic layers were washed with brine and dried over Na_2SO_4. The solvent was removed under vacuum, and the resulting residue was purified by flash column chromatography (10−30% EtOAc in hexanes) to give product **E7** (0.25 g, 74%) as colorless oil.

To a solution of the above ketone **E7** (341 mg, 1 mmol) in THF (20 mL) was added ethynylmagnesium bromide (10 mL, 0.5 M in THF) at 0 °C. Then the mixture was allowed to warm up to room temperature and stirred overnight. The reaction was quenched by saturated aqueous NH_4Cl. The mixture was extracted with EtOAc, and the combined organic layers were washed with brine and dried over Na_2SO_4. The solvent was removed under vacuum, and the resulting residue was purified by flash column chromatography (10−30% EtOAc in hexanes) to give product **36a** (253 mg, 69%) as white solid.

Other substrates in Table 4 (**36b**−**36n** and **36p**) were prepared according to the above procedure.

*N-(2-(1-(Furan-2-yl)-1-hydroxyprop-2-yn-1-yl)phenyl)-4-nitrobenzenesulfonamide (**36b**).* 146 mg, 37% over 4 steps. Brown solid, mp = 138−140 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 9.02 (s, 1H), 8.21 (d, J = 8.8 Hz, 2H), 7.93 (d, J = 9.2 Hz, 2H), 7.68 (d, J = 8.4 Hz, 1H), 7.37−7.29 (m, 3H), 7.06 (t, J = 8.8 Hz, 1H), 6.26−6.24 (m, 1H), 6.12−6.10 (m, 1H), 3.74 (s, 1H), 2.83 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.9, 150.3, 145.6, 143.9, 135.5, 130.3, 129.4, 128.8, 128.2, 124.5, 124.3, 120.3, 110.8, 109.0, 82.3, 77.1, 71.5. IR (neat) ν 2922, 1606, 1529, 1348, 1162, 1090, 1013, 854, 737. HRMS (ESI) m/z calcd for $C_{19}H_{14}N_2O_6S$ $(M + Na)^+$ 421.0464, found 421.0463.

*N-(2-(1-(Furan-2-yl)-1-hydroxyprop-2-yn-1-yl)phenyl)-4-methoxybenzenesulfonamide (**36c**).* 134 mg, 35% over 4 steps. White solid, mp = 125−127 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 8.78 (s, broad, 1H), 7.70 (d, J = 8.8 Hz, 2H), 7.60 (d, J = 8.0 Hz, 1H), 7.37−7.33 (m, 2H), 7.24 (t, J = 8.4 Hz, 1H), 6.98 (t, J = 8.0 Hz, 1H), 6.84 (d, J = 8.8 Hz, 2H), 6.28 (dd, J = 3.2, 1.6 Hz, 1H), 6.16 (d, J = 3.6 Hz, 1H), 3.79 (s, 3H), 2.83 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.2, 153.0, 143.7, 136.5, 131.4, 130.0, 129.8, 128.9, 127.6, 123.3, 119.5, 114.2, 110.8, 109.0, 82.5, 76.8, 71.3, 55.8. IR (neat) ν 3295, 2360, 1596, 1497, 1335, 1155, 1094, 944, 833. HRMS (ESI) m/z calcd for $C_{20}H_{17}NO_5S$ $(M + Na)^+$ 406.0719, found 406.0707.

*N-(2-(1-Hydroxy-1-(5-methylfuran-2-yl)prop-2-yn-1-yl)phenyl)-4-methylbenzenesulfonamide (**36d**).* 128 mg, 34% over 4 steps. White solid, mp = 69−71 °C. ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 8.75 (s, 1H), 7.69 (d, J = 8.0 Hz, 2H), 7.60 (d, J = 8.5 Hz, 1H), 7.36 (d, J = 8.0 Hz, 1H), 7.25 (d, J = 8.0 Hz, 1H), 7.19 (d, J = 8.5 Hz, 2H), 6.98 (t, J = 7.5 Hz, 1H), 5.99 (d, J = 3.5 Hz, 1H), 5.87−5.86 (m, 1H), 3.48 (s, 1H), 2.79 (s, 1H), 2.36 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.9, 150.8, 143.8, 137.1, 136.5, 130.0, 129.7, 128.9, 127.7, 123.3, 119.5, 110.2, 106.8, 82.6, 76.0, 71.2, 21.8, 13.9. IR (neat) ν 2361, 1600, 1495, 1333, 1158, 1092, 978, 736. HRMS (ESI) m/z calcd for $C_{21}H_{19}NO_4S$ $(M + Na)^+$ 404.0927, found 404.0926.

*N-(2-(1-(4,5-Dimethylfuran-2-yl)-1-hydroxyprop-2-yn-1-yl)-phenyl)-4-methylbenzenesulfonamide (**36e**).* 127 mg, 32% over 4 steps. White solid, mp = 82−84 °C. ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 8.73 (s, 1H), 7.70 (d, J = 8.0 Hz, 2H), 7.61 (d, J = 8.0 Hz, 1H), 7.38 (d, J = 8.0 Hz, 1H), 7.26−7.22 (m, 1H), 7.19 (d, J = 8.0 Hz, 2H), 6.98 (t, J = 8.0 Hz, 1H), 5.91 (s, 1H), 3.36 (s, 1H), 2.79 (s, 1H), 2.36 (s, 3H), 2.18 (s, 3H), 1.87 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 149.5, 149.3, 143.8, 137.2, 136.5, 130.0, 129.7, 129.0, 127.7, 127.6, 123.3, 119.4, 115.3, 112.6, 82.8, 76.5, 71.2, 21.8, 11.8, 10.0. IR (neat) ν 2369, 2339, 1495, 1326, 1159, 1091, 865, 815. HRMS (ESI) m/z calcd for $C_{22}H_{21}NO_4S$ $(M + Na)^+$ 418.1083, found 418.1080.

*N-(2-(1-(5-(((tert-Butyldimethylsilyl)oxy)methyl)furan-2-yl)-1-hydroxyprop-2-yn-1-yl)phenyl)-4-methylbenzenesulfonamide (**36f**).* 171 mg, 33% over 4 steps. Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 8.74 (s, 1H), 7.69 (d, J = 8.4 Hz, 2H), 7.61 (d, J = 8.4 Hz, 1H), 7.33 (d, J = 8.0 Hz, 1H), 7.26−7.22 (m, 1H), 7.19 (d, J = 8.4 Hz, 2H), 6.98 (t, J = 7.6 Hz, 1H), 6.12 (d, J = 3.2 Hz, 1H), 6.05 (d, J = 3.2 Hz, 1H), 4.60 (s, 2H), 3.55 (s, 1H), 2.79 (s, 1H), 2.37 (s, 3H), 0.88 (s, 9H), 0.05 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.0, 152.1, 143.8, 137.2, 136.5, 130.1, 129.7, 129.0, 127.7, 127.6, 123.4, 119.7, 109.8, 108.1, 82.5, 76.8, 71.3, 58.4, 26.1, 21.8, 18.6, −4.9. IR (neat) ν 2931, 2858, 1599, 1496, 1409, 1334, 1253, 1158, 1068, 835. HRMS (ESI) m/z calcd for $C_{27}H_{33}NO_5SSi$ $(M + Na)^+$ 534.1740, found 534.1746.

*N-(2-(1-(4-Bromofuran-2-yl)-1-hydroxyprop-2-yn-1-yl)phenyl)-4-methylbenzenesulfonamide (**36g**).* 159 mg, 36% over 4 steps. Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 8.41 (s, 1H), 7.65 (d, J = 8.0 Hz, 2H), 7.56 (t, J = 7.5 Hz, 2H), 7.29−7.25 (m, 2H), 7.19 (d, J = 8.0 Hz, 2H), 7.04 (t, J = 7.5 Hz, 1H), 6.39 (d, J = 2.0 Hz, 1H), 3.66 (s, 1H), 2.95 (s, 1H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.4, 143.9, 142.5, 137.3, 136.6, 130.5, 129.8, 129.3, 127.6, 126.8, 123.4, 119.6, 116.2, 97.7, 81.2, 78.3, 71.7, 21.8. IR (neat) ν 3381, 2944, 1734, 1587, 1501, 1312, 1157, 1025, 732. HRMS (ESI) m/z calcd for $C_{20}H_{16}BrNO_4S$ $(M + Na)^+$ 467.9881, found 467.9885.

*N-(2-(1-(Furan-2-yl)-1-hydroxyprop-2-yn-1-yl)-6-methylphenyl)-4-methylbenzenesulfonamide (**36h**).* 152 mg, 40% over 4 steps. White solid, mp = 108−110 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.73 (d, J = 8.4 Hz, 2H), 7.63 (s, 1H), 7.43−7.42 (m, 1H), 7.31−7.27 (m, 3H), 7.18−7.14 (m, 2H), 6.46−6.45 (m, 1H), 6.41−6.39 (m, 1H), 4.38 (s, 1H), 2.91 (s, 1H), 2.43 (s, 3H), 1.97 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.9, 143.9, 143.2, 138.4, 138.1, 136.8, 133.4, 132.6, 129.7, 127.5, 127.4, 127.1, 110.9, 109.1, 83.7, 76.5, 71.1, 21.8, 20.0. IR (neat) ν 3258, 2877, 2253, 1761, 1137, 1088, 917, 717. HRMS (ESI) m/z calcd for $C_{21}H_{19}NO_4S$ $(M - H)^-$ 380.0962, found 380.0953.

*N-(2-(1-(Furan-2-yl)-1-hydroxyprop-2-yn-1-yl)-4-(trifluoromethyl)-phenyl)-4-methylbenzenesulfonamide (**36i**).* 152 mg, 35% over 4 steps. Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 8.91 (s, 1H), 7.91 (s, 1H), 7.68 (d, J = 8.4 Hz, 2H), 7.45 (d, J = 8.4 Hz, 1H), 7.38−7.37 (m, 1H), 7.22−7.20 (m, 3H), 6.33−6.31 (m, 1H), 6.25−6.24 (m, 1H), 3.84 (s, 1H), 2.87 (s, 1H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.2, 144.4, 144.0, 137.1, 136.3, 132.2 (q, J = 32.7 Hz), 130.8, 129.9, 129.5, 127.9, 123.7 (q, J = 271.2 Hz), 119.84 (q, J = 3.7 Hz), 116.18 (q, J = 4.0 Hz), 110.9, 109.5, 81.8, 77.4, 71.0, 21.8. IR (neat) ν 3286, 1706, 1587, 1408, 1331, 1264, 1160, 1089, 814, 714. HRMS (ESI) m/z calcd for $C_{21}H_{16}F_3NO_4S$ $(M + Na)^+$ 458.0644, found 458.0640.

*N-(2-(1-(Furan-2-yl)-1-hydroxyprop-2-yn-1-yl)-4,5-dimethoxyphenyl)-4-methylbenzenesulfonamide (**36j**).* 166 mg, 39% over 4 steps. Yellow solid, mp = 90−92 °C. ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 8.38 (s, 1H), 7.63 (d, J = 8.5 Hz, 2H), 7.36 (s, 1H), 7.25 (s, 1H), 7.18 (d, J = 8.0 Hz, 2H), 6.89 (s, 1H), 6.26−6.25 (m, 1H), 6.09−6.08 (m, 1H), 3.84 (s, 3H), 3.75 (s, 3H), 3.47 (s, 1H), 2.81 (s, 1H), 2.38 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.2, 149.7, 145.0, 143.9, 143.7, 137.0, 129.724, 129.673, 127.8, 120.3, 112.1, 110.8, 108.9, 105.1, 82.8, 76.5, 70.8, 56.2, 21.8. IR (neat) ν 2928, 1759, 1520, 1357, 1163, 1089, 1011, 839. HRMS (ESI) m/z calcd for $C_{22}H_{21}NO_6S$ $(M - H)^-$ 426.1016, found 426.1014.

*N-(4-Bromo-2-(1-(furan-2-yl)-1-hydroxyprop-2-yn-1-yl)phenyl)-4-methylbenzenesulfonamide (**36k**).* 155 mg, 35% over 4 steps. White solid, mp = 127−129 °C. ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 8.65 (s, 1H), 7.65 (d, J = 8.0 Hz, 2H), 7.53 (d, J = 9.0 Hz, 1H), 7.49 (d, J = 2.0 Hz, 1H), 7.39−7.35 (m, 2H), 7.21 (d, J = 8.5 Hz, 2H), 6.31−6.30 (m, 1H), 6.22−6.20 (m, 1H), 3.57 (s, 1H), 2.86 (s, 1H), 2.38(s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.2, 144.2, 144.1, 136.7, 135.6, 133.0, 131.7, 129.8, 129.5, 127.7, 121.2, 116.3, 111.0, 109.4, 81.8, 77.4, 70.7, 21.8. IR (neat) ν 3281, 2944, 1704, 1515, 1350, 1161, 1087, 720. HRMS (ESI) m/z calcd for $C_{20}H_{16}BrNO_4S$ $(M + Na)^+$ 467.9881, found 467.9879.

*N-(2-(1-Hydroxy-1-(thiophen-2-yl)prop-2-yn-1-yl)phenyl)-4-methylbenzenesulfonamide (**36l**).* 157 mg, 41% over 4 steps. Yellow solid, mp = 148−150 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 8.67 (s, 1H), 7.61 (d, J = 8.0 Hz, 1H), 7.52−7.49 (m, 3H), 7.29 (dd, J = 5.2, 1.2 Hz, 1H), 7.27−7.22 (m, 1H), 7.12 (d, J = 8.0 Hz, 2H), 6.99 (t, J = 7.6 Hz, 1H), 6.87−6.84 (m, 1H), 6.82−6.80 (m, 1H), 3.71 (s, 1H), 2.90 (s, 1H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.2, 143.7, 136.8, 136.2, 130.1, 129.9, 129.7, 128.6, 127.6, 127.0, 126.4,

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123.3, 119.5, 84.1, 77.3, 73.0, 21.7. IR (neat) ν 3371, 3288, 1634, 1587, 1494, 1372, 1168, 1081. HRMS (ESI) m/z calcd for $C_{20}H_{17}NO_3S_2$ $(M + Na)^+$ 406.0548, found 406.0544.

*N-(2-(1-Hydroxy-1-(thiophen-2-yl)prop-2-yn-1-yl)-6-methylphenyl)-4-methylbenzenesulfonamide (**36m**).* 151 mg, 38% over 4 steps. White solid, mp = 153−155 °C. ^{1}H NMR (400 MHz, CD_3OD): δ 7.61 (d, J = 8.4 Hz, 2H), 7.34−7.32 (m, 2H), 7.28 (d, J = 8.0 Hz, 2H), 7.16 (d, J = 6.8 Hz, 1H), 7.05 (t, J = 7.6 Hz, 1H), 6.88−6.87 (m, 2H), 3.24 (s, 1H), 2.41 (s, 3H), 2.15 (s, 1H), 2.08 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.4, 143.8, 138.8, 138.5, 138.2, 133.4, 132.6, 129.7, 127.4, 127.3, 126.9, 126.8, 126.8, 126.6, 85.5, 76.9, 72.7, 21.8, 20.2. IR (neat) ν 2967, 2891, 1701, 1507, 1336, 1157, 1037, 848. HRMS (ESI) m/z calcd for $C_{21}H_{19}NO_3S_2$ $(M + H)^+$ 398.0879, found 398.0877.

*N-(2-(1-Hydroxy-1-(1-methyl-1H-pyrrol-2-yl)prop-2-yn-1-yl)-phenyl)-4-methylbenzenesulfonamide (**36n**).* 152 mg, 40% over 4 steps. Colorless oil. ^{1}H NMR (500 MHz, $(CD_3)_2CO$): δ 9.42 (s, 1H), 7.71−7.69 (m, 3H), 7.32 (d, J = 8.0 Hz, 2H), 7.28 (t, J = 8.5 Hz, 1H), 7.11 (d, J = 8.0 Hz, 1H), 6.96 (t, J = 8.0 Hz, 1H), 6.75 (t, J = 2.5 Hz, 1H), 6.19 (dd, J = 4.0, 2.0 Hz, 1H), 5.99 (dd, J = 3.5, 2.5 Hz, 1H), 3.39 (s, 1H), 3.35 (s, 3H), 2.94 (s, 1H), 2.38 (s, 3H). ^{13}C NMR (125 MHz, $(CD_3)_2CO$): δ 144.6, 137.5, 137.4, 132.1, 130.3, 130.2, 129.9, 129.0, 128.5, 126.5, 123.5, 118.9, 111.1, 106.8, 84.7, 77.0, 71.4, 35.6, 21.4. IR (neat) ν 2905, 1608, 1406, 1375, 1250, 1159, 1091, 933. HRMS (ESI) m/z calcd for $C_{21}H_{20}N_2O_3S$ $(M + Na)^+$ 403.1087, found 403.1080.

*N-(2-(1-Hydroxy-1-(1-(phenylsulfonyl)-1H-indol-2-yl)prop-2-yn-1-yl)phenyl)-4-methylbenzenesulfonamide (**36p**).* 233 mg, 42% over 4 steps. White solid, mp = 126−128 °C. ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 9.33 (s, 1H), 7.95 (d, J = 8.5 Hz, 1H), 7.84 (d, J = 7.5 Hz, 2H), 7.70 (d, J = 8.0 Hz, 1H), 7.65−7.62 (m, 1H), 7.58−7.56 (m, 1H), 7.55−7.40 (m, 4H), 7.33 (t, J = 8.5 Hz, 1H), 7.28 (t, J = 8.5 Hz, 1H), 7.17 (t, J = 7.5 Hz, 1H), 7.15−7.12 (m, 1H), 7.03 (t, J = 7.5 Hz, 1H), 6.96 (d, J = 8.0 Hz, 2H), 6.69 (s, 1H), 5.78 (s, 1H), 2.98 (s, 1H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.7, 141.5, 138.5, 138.2, 137.2, 137.0, 134.5, 130.3, 129.8, 129.7, 129.6, 129.3, 128.0, 127.4, 126.7, 126.4, 124.4, 123.4, 122.3, 119.6, 116.2, 115.3, 82.9, 78.7, 72.9, 21.8. IR (neat) ν 3354, 2962, 1612, 1538, 1206, 1122, 1010, 896. HRMS (ESI) m/z calcd for $C_{30}H_{24}N_2O_5S_2$ $(M + Na)^+$ 579.1024, found 579.1019.

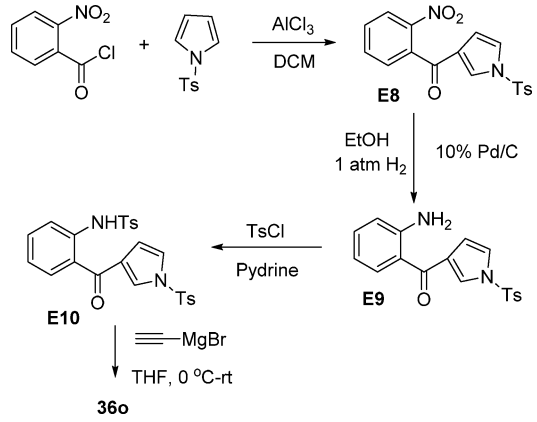
*N-(2-(1-(Furan-2-yl)-1-hydroxybut-2-yn-1-yl)phenyl)-4-methylbenzenesulfonamide (**36q**).* 156 mg, 41% over 4 steps. Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 8.80 (s, 1H), 7.67 (d, J = 8.0 Hz, 2H), 7.56 (d, J = 8.5 Hz, 1H), 7.35−7.34 (m, 2H), 7.2−7.16 (m, 3H), 6.97 (t, J = 7.5 Hz, 1H), 6.26 (dd, J = 3.0, 1.5 Hz, 1H), 6.12 (d, J = 3.0 Hz, 1H), 3.40 (s, 1H), 2.36 (s, 3H), 1.93 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.9, 143.8, 143.4, 137.1, 136.4, 129.8, 129.7, 128.9, 128.5, 127.7, 123.2, 119.2, 110.7, 108.6, 85.6, 78.4, 71.4, 21.7, 4.1. IR (neat) ν 2255, 1585, 1494, 1333, 1158, 1092, 907, 813. HRMS (ESI) m/z calcd for $C_{21}H_{19}NO_4S$ $(M + Na)^+$ 404.0927, found 404.0938.

*tert-Butyl (2-(1-(Furan-2-yl)-1-hydroxybut-2-yn-1-yl)phenyl)-carbamate (**36r**).* 147 mg, 45% over 4 steps. White solid, mp = 45−46 °C. ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 8.00 (s, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.46 (d, J = 7.5 Hz, 1H), 7.39 (s, 1H), 7.32 (t, J = 8.0 Hz, 1H), 7.03 (t, J = 7.5 Hz, 1H), 6.31 (dd, J = 3.0, 2.0 Hz, 1H), 6.24 (d, J = 3.5 Hz, 1H), 3.29 (s, 1H), 1.96 (s, 3H), 1.44 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.3, 153.4, 143.2, 137.3, 130.0, 129.6, 127.8, 123.2, 123.0, 110.6, 108.0, 85.1, 80.1, 78.6, 70.9, 28.6, 4.1. IR (neat) ν 2364, 1709, 1589, 1521, 1301, 1158, 1004, 750. HRMS (ESI) m/z calcd for $C_{19}H_{21}NO_4$ $(M + Na)^+$ 350.1363, found 350.1370.

Strategy for the Preparation of Substrate 36o in Table 4. Scheme 11 outlines the preparation of **36o**.

Compound **E8** was prepared following literature procedure.[32] To a stirred suspension of anhydrous aluminum trichloride (100 mg, 7.5 mmol) in anhydrous dichloromethane (6 mL) at 0 °C and under argon was added *o*-nitrobenzoyl chloride (0.13 mL, 0.7 mmol), and the mixture was stirred for 10 min. A solution of 1-(4-methylphenyl)-sulfonyl-1H-pyrrole (112 mg, 0.5 mmol) in anhydrous dichloromethane (3 mL) was added dropwise, and then the temperature was allowed to

Scheme 11. Synthesis of Substrates 36o



reach room temperature for 1 h. The reaction mixture was poured into ice water (13 mL), and the aqueous layer extracted with dichloromethane (3 × 10 mL). The combined organic layers were treated with saturated $NaHCO_3$, washed with brine, dried over Na_2SO_4, and evaporated under reduced pressure to give a dark oil. The residue was subjected to column chromatography (10% EtOAc in hexanes) to give [1-[(4-methylphenyl)sulfonyl]-1H-pyrrol-3-yl](2-nitrophenyl)methanone **E8** (73 mg, 40%) as a white solid.

To a solution of the above ketone **E8** (73 mg, 0.2 mmol) in ethanol (3 mL) was added Pd/C (10%) (20.4 mg), and the mixture was allowed to stir under H_2 (1 atm) for 5 h. The reaction mixture was filtered over a pad of Celite and concentrated to give crude amine **E9** (68 mg, 99%), which was used in next step without purification.

To a stirred solution of the above crude amine **E9** (68 mg, 0.2 mmol) in pyridine (1 mL) was added tosyl chloride (47.5 mg), and the resulting solution was stirred at 105 °C overnight. The reaction mixture was cooled to room temperature and diluted with EtOAc. The mixture was washed with 3 M HCl and brine, dried over Na_2SO_4, and concentrated under vacuum. The resulting residue was purified by flash column chromatography (10−30% EtOAc in hexanes) to give the pure product **E10** (72 mg, 75%) as a colorless oil.

To a solution of **E10** (72 mg, 0.15 mmol) in THF (3 mL) was added ethynylmagnesium bromide (1.5 mL, 0.5 M in THF) at 0 °C. Then the mixture was allowed to warm up to room temperature and stirred overnight. The reaction was quenched by saturated aqueous NH_4Cl. The mixture was extracted with EtOAc, and the combined organic layers were washed with brine and dried over Na_2SO_4. The solvent was removed under vacuum, and the resulting residue was purified by flash column chromatography (10−30% EtOAc in hexanes) to give product **36o** (55 mg, 70%) as a colorless oil.

*N-(2-(1-Hydroxy-1-(1-tosyl-1H-pyrrol-3-yl)prop-2-yn-1-yl)-phenyl)-4-methylbenzenesulfonamide (**36o**).* 55 mg, 21% over 4 steps. Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 8.60 (s, 1H), 7.76 (d, J = 8.0 Hz, 2H), 7.56−7.52 (m, 3H), 7.37 (d, J = 8.0 Hz, 1H), 7.30 (d, J = 8.0 Hz, 2H), 7.23 (s, 1H), 7.20 (t, J = 7.8 Hz, 1H), 7.15 (d, J = 8.0 Hz, 2H), 7.05 (t, J = 3.0 Hz, 1H), 6.94 (t, J = 7.5 Hz, 1H), 6.10 (s, 1H), 3.11 (s, 1H), 2.78 (s, 1H), 2.38 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.6, 143.8, 136.9, 136.2, 135.9, 131.6, 130.5, 129.9, 129.8, 129.3, 128.4, 127.5, 127.3, 123.3, 122.0, 119.4, 118.9, 112.4, 84.2, 76.5, 71.3, 21.9, 21.8. IR (neat) ν 3280, 2926, 1598, 1338, 1063, 924, 815, 760. HRMS (ESI) m/z calcd for $C_{27}H_{24}N_2O_5S_2$ $(M + Na)^+$ 543.1018, found 543.1027.

General Procedure for the Rh-Catalyzed Tandem Annulation [5 + 1] Cycloaddition in Table 2. Condition A: To an oven-dried flask were added enyne substrate (0.1 mmol), anhydrous DCE (2 mL) and $[Rh(CO)_2Cl]_2$ (2.0 mg, 0.005 mmol). The flask was degassed, filled with CO, and attached with a CO balloon. The oil bath was heated to 60 °C. The reaction was monitored by TLC. After the reaction was completed, the solvent was evaporated, and the residue was purified by flash column chromatography.

Condition B: The condition was modified by adding ligand $(CF_3CH_2O)_3P$ (6.6 mg, 0.02 mmol) based on Condition A.

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Condition C: The condition was modified by replacing THF with dioxane (2 mL) based on Condition B.

General Procedure for the Rh-Catalyzed Tandem Annulation [5 + 1] Cycloaddition in Table 2. Condition A: To an oven-dried flask were added propargylic alcohol substrate (0.1 mmol), anhydrous DCE (2 mL), and $[Rh(CO)_2Cl]_2$ (2.0 mg, 0.005 mmol). The flask was degassed, filled with CO, and attached with a CO balloon. The reaction was stirred at room temperature. The reaction was monitored by TLC. After the reaction was completed, the solvent was evaporated, and the residue was purified by flash column chromatography.

Condition B: The condition was modified by adding ligand $(CF_3CH_2O)_3P$ (6.6 mg, 0.02 mmol) based on Condition A.

*9-Tosyl-9H-carbazol-2-ol (**31a**).* Condition A. 27.3 mg, 81%. Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 8.25 (d, J = 8.0 Hz, 1H), 7.84 (d, J = 2.0 Hz, 1H), 7.78 (d, J = 8.0 Hz, 1H), 7.73 (d, J = 8.4 Hz, 1H), 7.69 (d, J = 8.0 Hz, 2H), 7.39 (t, J = 8.4 Hz, 1H), 7.31 (t, J = 7.6 Hz, 1H), 7.09 (d, J = 8.0 Hz, 2H), 6.89 (dd, J = 8.4, 2.4 Hz, 1H), 5.25 (s, 1H), 2.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.8, 145.2, 139.9, 138.5, 135.2, 129.9, 126.7, 126.7, 126.4, 124.2, 121.1, 120.3, 119.4, 115.2, 112.8, 102.3, 21.8. IR (neat) ν 2963, 1454, 1362, 1099, 1023, 872, 802. HRMS (ESI) m/z calcd for $C_{19}H_{15}NO_3S$ $(M + Na)^+$ 360.0664, found 360.0648.

*9-((4-Nitrophenyl)sulfonyl)-9H-carbazol-2-ol (**31b**).* Condition A. 25.8 mg, 70%. Yellow oil. ^{1}H NMR (500 MHz, CD_3OD): δ 8.22 (d, J = 8.5 Hz, 1H), 8.20 (d, J = 9.0 Hz, 2H), 8.01 (d, J = 9.5 Hz, 2H), 7.81 (d, J = 7.5 Hz, 1H), 7.75 (d, J = 6.0 Hz, 1H), 7.74 (d, J = 4.5 Hz, 1H), 7.41 (t, J = 7.5 Hz, 1H), 7.33 (t, J = 7.5 Hz, 1H), 6.87 (dd, J = 8.5, 2.0 Hz, 1H). ^{13}C NMR (100 MHz, CD_3OD): δ 159.4, 152.4, 143.5, 140.8, 139.2, 129.0, 128.6, 127.1, 125.9, 125.4, 122.1, 120.3, 120.3, 116.2, 114.6, 103.0. IR (neat) ν 2925, 1620, 1531, 1459, 1377, 1179, 991, 854. HRMS (ESI) m/z calcd for $C_{18}H_{12}N_2O_5S$ $(M + Na)^+$ 391.0359, found 391.0344.

*9-((4-Methoxyphenyl)sulfonyl)-9H-carbazol-2-ol (**31c**).* Condition A. 27.5 mg, 78%. White solid, mp = 179−181 °C. ^{1}H NMR (500 MHz, CD_3OD): δ 8.21 (d, J = 8.0 Hz, 1H), 7.80 (d, J = 7.5 Hz, 1H), 7.75−7.73 (m, 2H), 7.70 (d, J = 9.0 Hz, 2H), 7.37 (t, J = 8.5 Hz, 1H), 7.29 (t, J = 8.5 Hz, 1H), 6.85 (dd, J = 8.5, 2.5 Hz, 1H), 6.82 (d, J = 9.0 Hz, 2H), 3.69 (s, 3H). ^{13}C NMR (100 MHz, CD_3OD): δ 165.6, 159.0, 141.2, 139.6, 130.3, 129.8, 128.3, 126.7, 125.2, 121.8, 120.2, 120.0, 116.1, 115.3, 113.9, 102.9, 56.1. IR (neat) ν 2925, 1714, 1593, 1459, 1366, 1264, 1090, 989, 830. HRMS (ESI) m/z calcd for $C_{19}H_{15}NO_4S$ $(M + Na)^+$ 376.0614, found 376.0600.

*3-Methyl-9-tosyl-9H-carbazol-2-ol (**31d**).* Condition A. 30.1 mg, 86%. White solid, mp = 184−186 °C. ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 8.23 (d, J = 8.5 Hz, 1H), 7.78 (s, 1H), 7.75 (d, J = 8.0 Hz, 1H), 7.67 (d, J = 8.5 Hz, 2H), 7.61 (s, 1H), 7.37 (t, J = 8.5 Hz, 1H), 7.30 (t, J = 7.5 Hz, 1H), 7.09 (d, J = 8.0 Hz, 2H), 5.15 (s, 1H), 2.36 (s, 3H), 2.26 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 154.1, 145.0, 138.5, 138.1, 135.2, 129.9, 126.9, 126.7, 126.1, 124.1, 121.8, 121.4, 120.0, 119.3, 115.3, 101.8, 21.7, 16.3. IR (neat) ν 2923, 1627, 1597, 1451, 1367, 1265, 1029, 954, 812. HRMS (ESI) m/z calcd for $C_{20}H_{17}NO_3S$ $(M + Na)^+$ 374.0821, found 374.0811.

*9-((4-Methoxyphenyl)sulfonyl)-3-methyl-9H-carbazol-2-ol (**31e**).* Condition A. 30.0 mg, 82%. White solid, mp = 197−199 °C. ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 8.23 (d, J = 8.5 Hz, 1H), 7.79 (s, 1H), 7.75 (d, J = 8.0 Hz, 1H), 7.71 (d, J = 9.0 Hz, 2H), 7.61 (s, 1H), 7.36 (t, J = 7.5 Hz, 1H), 7.29 (t, J = 7.5 Hz, 1H), 6.72 (d, J = 9.0 Hz, 2H), 5.24 (s, 1H), 3.69 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.9, 154.1, 138.5, 138.1, 129.7, 128.9, 126.9, 126.1, 124.1, 121.8, 121.4, 120.1, 119.3, 115.3, 114.4, 101.8, 55.7, 16.3. IR (neat) ν 2925, 2341, 1593, 1494, 1340, 1263, 1018, 954, 829. HRMS (ESI) m/z calcd for $C_{20}H_{17}NO_4S$ $(M + Na)^+$ 390.0770, found 390.0761.

*3-Phenyl-4-tosyl-2,4-dihydrocyclopenta[b]indole (**32a**, Figure 2).* Condition B. 22.0 mg, 57%. Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 7.71 (d, J = 8.0 Hz, 1H), 7.52 (d, J = 7.5 Hz, 1H), 7.43−7.41 (m, 2H), 7.36−7.33 (m, 4H), 7.30−7.25 (m, 3H), 7.10 (d, J = 8.0 Hz, 2H), 5.93 (t, J = 4.5 Hz, 1H), 4.49 (d, J = 5.0 Hz, 2H), 2.28 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.1, 135.9, 135.1, 131.7, 129.5, 129.1, 129.0, 129.0, 128.8, 128.6, 127.5, 127.3, 127.2, 125.8, 122.9, 120.7, 91.7, 84.8, 45.8, 21.7. IR (neat) ν 2212, 1598, 1490, 1353, 1265, 1089, 894, 814. HRMS (ESI) m/z calcd for $C_{24}H_{19}NO_2S$ $(M + Na)^+$ 408.1028, found 408.1031.

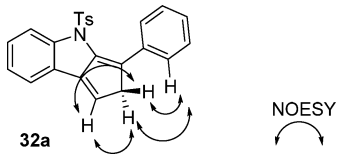

Figure 2. NOESY Study for **32a**.

*4-((4-Methoxyphenyl)sulfonyl)-3-phenyl-2,4-dihydrocyclopenta-[b]indole (**32b**).* Condition B. 23.3 mg, 58%. Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.70 (d, J = 8.0 Hz, 1H), 7.52 (d, J = 7.6 Hz, 1H), 7.43−7.41 (m, 2H), 7.36−7.30 (m, 5H), 7.30−7.25 (m, 2H), 6.77 (d, J = 9.2 Hz, 2H), 5.94 (t, J = 4.8 Hz, 1H), 4.48 (d, J = 4.8 Hz, 2H), 3.69 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.5, 135.2, 131.8, 130.4, 129.7, 129.1, 129.0, 128.8, 128.6, 127.5, 127.2, 125.8, 122.9, 120.7, 114.1, 91.8, 84.9, 55.7, 45.8. IR (neat) ν 2212, 1596, 1497, 1352, 1264, 1160, 1091, 817. HRMS (ESI) m/z calcd for $C_{24}H_{19}NO_3S$ $(M + Na)^+$ 424.0977, found 424.0968.

*2,3-Dimethyl-4-tosyl-2,4-dihydrocyclopenta[b]indole (**33**).* Condition B. 26.2 mg, 78%. Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.70 (d, J = 8.0 Hz, 1H), 7.44 (d, J = 7.6 Hz, 1H), 7.32 (t, J = 8.0 Hz, 1H), 7.26−7.21 (m, 3H), 7.08 (d, J = 8.4 Hz, 2H), 5.83 (d, J = 6.0 Hz, 1H), 4.93 (dq, J = 6.6, 6.4 Hz, 1H), 2.34 (s, 3H), 1.96 (s, 3H), 1.13 (d, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.7, 135.9, 133.4, 132.5, 129.4, 128.8, 128.0, 127.3, 126.7, 125.6, 118.9, 110.0, 88.2, 75.4, 51.1, 21.7, 19.6, 4.4. IR (neat) ν 2361, 1600, 1484, 1344, 1166, 1088, 813. HRMS (ESI) m/z calcd for $C_{20}H_{19}NO_2S$ $(M + Na)^+$ 360.1028, found 360.1024.

General Procedure for the Rh-Catalyzed Tandem Annulation [5 + 1] Cycloaddition in Table 4. Condition A: To an oven-dried flask were added propargylic alcohol substrate (0.1 mmol), anhydrous DCE (2 mL), and $[Rh(CO)_2Cl]_2$ (2.0 mg, 0.005 mmol). The flask was degassed, filled with CO, and attached with a CO balloon. The mixture was stirred at room temperature. The reaction was monitored by TLC. After the reaction was completed, the solvent was evaporated, and the residue was purified by flash column chromatography.

Condition B: The reaction was carried out at 60 °C instead of room temperature.

Condition C: The reaction was carried out at 60 °C under 10 atm of CO instead of room temperature and a CO balloon.

*6-Tosyl-6H-furo[3,2-c]carbazol-4-ol (**37a**).* Condition A. 27.5 mg, 73%. Brown solid, mp = 149−151 °C. ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 8.31 (d, J = 10.0 Hz, 1H), 8.10 (d, J = 9.5 Hz, 1H), 7.81 (s, 1H), 7.68−7.66 (m, 3H), 7.42−7.37 (m, 2H), 7.05 (d, J = 10.0 Hz, 2H), 6.98−6.97 (m, 1H), 5.89 (s, broad, 1H), 2.22 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.0, 149.3, 145.2, 144.0, 138.1, 137.6, 135.0, 129.9, 126.7, 125.9, 124.6, 124.6, 121.5, 115.3, 114.2, 106.5, 104.2, 96.5, 21.7. IR (neat) ν 2924, 1650, 1597, 1458, 1362, 1171, 1090, 1053, 752. HRMS (ESI) m/z calcd for $C_{21}H_{15}NO_4S$ $(M + Na)^+$ 400.0614, found 400.0606.

*6-((4-Nitrophenyl)sulfonyl)-6H-furo[3,2-c]carbazol-4-ol (**37b**).* Condition A. Seventeen mg, 42%. Brown solid, mp = 83−85 °C. ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 8.29−8.27 (m, 1H), 8.13−8.10 (m, 3H), 7.93 (d, J = 9.0 Hz, 2H), 7.73 (s, 1H), 7.70 (d, J = 2.5 Hz, 1H), 7.47−7.42 (m, 2H), 6.98 (d, J = 2.0 Hz, 1H), 5.51 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.5, 147.3, 144.5, 142.8, 137.7, 137.1, 127.9, 126.3, 125.5, 125.1, 124.5, 121.9, 115.4, 115.0, 110.0, 104.2, 96.6. IR (neat) ν 2925, 2854, 1531, 1348, 1175, 1138, 1054, 738. HRMS (ESI) m/z calcd for $C_{20}H_{12}N_2O_6S$ $(M + Na)^+$ 431.0308, found 431.0304.

*6-((4-Methoxyphenyl)sulfonyl)-6H-furo[3,2-c]carbazol-4-ol (**37c**).* Condition A. 29.8 mg, 76%. Colorless oil. ^{1}H NMR (500 MHz, $(CD_3)_2CO$): δ 8.32 (d, J = 9.0 Hz, 1H), 8.07 (d, J = 8.5 Hz, 1H), 7.90 (d, J = 3.0 Hz, 1H), 7.83 (s, 1H), 7.80 (d, J = 11.5 Hz, 2H), 7.48−7.43 (m, 2H), 7.11 (d, J = 3.0 Hz, 1H), 6.91 (d, J = 11.0 Hz, 2H), 3.74 (s, 3H). ^{13}C NMR (100 MHz, $(CD_3)_2CO$): δ 165.1, 152.1, 150.5, 145.0, 138.7, 138.6, 129.9, 129.6, 126.3, 125.3, 125.3, 121.6, 115.9,

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115.3, 115.2, 105.3, 96.7, 56.1. IR (neat) ν 3055, 1652, 1594, 1496, 1365, 1264, 1144, 1055, 835. HRMS (ESI) m/z calcd for $C_{21}H_{15}NO_5S$ $(M + H)^+$ 394.0743, found 394.0746.

2-Methyl-6-tosyl-6H-furo[3,2-c]carbazol-4-ol (**37d**). Condition B. 25.0 mg, 64%. Yellow solid, mp = 196−198 °C. ^{1}H NMR (500 MHz, $(CD_3)_2CO$): δ 9.22 (s, 1H), 8.33 (d, J = 7.0 Hz, 1H), 8.07 (d, J = 7.0 Hz, 1H), 7.79 (s, 1H), 7.74 (d, J = 9.0 Hz, 2H), 7.50−7.43 (m, 2H), 7.25 (d, J = 8.0 Hz, 2H), 6.73 (s, 1H), 2.55 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, $(CD_3)_2CO$): δ 155.1, 151.3, 150.0, 146.3, 138.7, 137.9, 135.5, 130.7, 127.3, 126.2, 125.5, 125.3, 121.7, 116.6, 115.9, 105.5, 101.1, 96.7, 21.3, 14.0. IR (neat) ν 2923, 1597, 1459, 1368, 1176, 1091, 812, 740. HRMS (ESI) m/z calcd for $C_{22}H_{17}NO_4S$ $(M + Na)^+$ 414.0770, found 414.0772.

2,3-Dimethyl-6-tosyl-6H-furo[3,2-c]carbazol-4-ol (**37e**). Condition B. 22.3 mg, 55%. Yellow solid, mp = 210−212 °C. ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 8.27 (d, J = 7.0 Hz, 1H), 8.08 (d, J = 7.0 Hz, 1H), 7.65−7.62 (m, 3H), 7.39−7.36 (m, 2H), 7.05 (d, J = 8.0 Hz, 2H), 5.45 (s, 1H), 2.42 (s, 3H), 2.38 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.0, 149.5, 148.9, 145.0, 138.1, 136.6, 135.0, 129.8, 126.7, 125.6, 125.0, 124.4, 121.5, 116.0, 115.3, 109.8, 106.1, 96.2, 21.7, 11.9, 10.0. IR (neat) ν 2926, 2342, 1648, 1435, 1368, 1190, 1098, 746. HRMS (ESI) m/z calcd for $C_{23}H_{19}NO_4S$ $(M + Na)^+$ 428.0927, found 428.0928.

2-(((tert-Butyldimethylsilyl)oxy)methyl)-6-tosyl-6H-furo[3,2-c]-carbazol-4-ol (**37f**). Condition B. 31.7 mg, 61%. Yellow solid, mp = 161−163 °C. ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 8.29 (d, J = 7.5 Hz, 1H), 8.09 (d, J = 7.5 Hz, 1H), 7.74 (s, 1H), 7.66 (d, J = 8.5 Hz, 2H), 7.42−7.38 (m, 2H), 7.07 (d, J = 8.5 Hz, 2H), 6.80 (s, 1H), 5.61 (s, 1H), 4.86 (s, 2H), 2.25 (s, 3H), 0.96 (s, 9H), 0.17 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.3, 149.8, 149.1, 145.1, 138.1, 137.4, 135.0, 129.9, 126.7, 125.8, 124.6, 124.5, 121.5, 115.3, 115.0, 106.4, 101.4, 96.5, 58.9, 26.2, 21.7, 18.8, −4.8. IR (neat) ν 2929, 2857, 1651, 1612, 1460, 1370, 1189, 1090, 837, 799. HRMS (ESI) m/z calcd for $C_{28}H_{31}NO_5SSi$ $(M + Na)^+$ 544.1584, found 544.1584.

N-(2-(4-Bromofuran-2-carbonyl)phenyl)-4-methylbenzenesulfonamide (**37g**). Condition A. 21.3 mg, 51%. Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 9.66 (s, 1H), 7.74−7.72 (m, 2H), 7.57 (d, J = 8.0 Hz, 2H), 7.53−7.48 (m, 2H), 7.16 (t, J = 7.5 Hz, 1H), 7.07 (d, J = 8.0 Hz, 2H), 6.67 (d, J = 1.5 Hz, 1H), 2.25 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 183.4, 147.6, 146.0, 143.7, 138.7, 136.2, 134.1, 132.0, 129.7, 127.5, 126.0, 124.0, 123.7, 118.0, 110.7, 21.7. IR (neat) ν 2924, 1626, 1543, 1378, 1261, 1161, 1090, 924, 864. HRMS (ESI) m/z calcd for $C_{18}H_{14}BrNO_4S$ $(M + Na)^+$ 441.9719, found 441.9724.

7-Methyl-6-tosyl-6H-furo[3,2-c]carbazol-4-ol (**37h**). Condition A. 21.1 mg, 54%. Yellow solid, mp = 162−165 °C. ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 7.77 (d, J = 9.0 Hz, 1H), 7.63−7.61 (m, 2H), 7.30 (t, J = 9.5 Hz, 1H), 7.23 (d, J = 9.5 Hz, 1H), 7.06 (d, J = 10.5 Hz, 2H), 6.92 (d, J = 3.0 Hz, 1H), 6.84 (d, J = 10.5 Hz, 2H), 5.55 (s, 1H), 2.84 (s, 3H), 2.17 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 149.5, 148.7, 144.5, 144.2, 140.4, 140.0, 132.6, 130.9, 129.6, 129.0, 127.1, 126.3, 118.8, 115.4, 109.5, 104.3, 100.7, 22.2, 21.7. IR (neat) ν 2952, 1701, 1613, 1495, 1364, 1175, 1038, 736. HRMS (ESI) m/z calcd for $C_{22}H_{17}NO_4S$ $(M + H)^+$ 392.0951, found 392.0963.

6-tosyl-9-(Trifluoromethyl)-6H-furo[3,2-c]carbazol-4-ol (**37i**). Condition A. 25.8 mg, 58%. White solid, mp = 193−195 °C. ^{1}H NMR (500 MHz, $(CD_3)_2CO$): δ 8.48 (s, 1H), 8.12 (d, J = 8.0 Hz, 1H), 7.82 (d, J = 2.0 Hz, 1H), 7.69 (s, 1H), 7.66−7.63 (m, 3H), 7.15 (d, J = 8.0 Hz, 2H), 7.01 (d, J = 2.0 Hz, 1H), 2.14 (s, 3H). ^{13}C NMR (100 MHz, $(CD_3)_2CO$): δ 153.6, 150.6, 147.0, 145.4, 139.8, 138.0, 135.2, 131.0, 128.3, 127.4, 127.2 (q, J = 32.1 Hz), 125.7 (q, J = 270 Hz), 122.25 (q, J = 3.6 Hz), 122.16, 115.7, 112.6 (q, J = 4.3 Hz), 105.4, 104.6, 96.5, 21.4. IR (neat) ν 2926, 1651, 1597, 1323, 1169, 1130, 1052, 738. HRMS (ESI) m/z calcd for $C_{22}H_{14}F_3NO_4S$ $(M + Na)^+$ 468.0487, found 468.0480.

8,9-Dimethoxy-6-tosyl-6H-furo[3,2-c]carbazol-4-ol (**37j**). Condition A. 19.2 mg, 44%. Yellow solid, mp = 189−191 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.92 (s, 1H), 7.72 (s, 1H), 7.66 (s, 1H), 7.60 (d, J = 8.4 Hz, 2H), 7.54 (s, 1H), 7.06 (d, J = 8.0 Hz, 2H), 6.96 (d, J = 2.4 Hz, 1H), 5.44 (s, 1H), 4.05 (s, 3H), 4.02 (s, 3H), 2.25 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 148.5, 148.0, 147.7, 145.1, 143.8, 137.3, 134.8, 132.3, 129.9, 126.6, 117.5, 114.2, 107.1, 104.3, 103.2, 99.8, 97.0, 56.7, 56.5, 21.7. IR (neat) ν 2925, 1650, 1484, 1363, 1165, 1054, 849, 811. HRMS (ESI) m/z calcd for $C_{23}H_{19}NO_6S$ $(M + Na)^+$ 460.0825, found 460.0832.

9-Bromo-6-tosyl-6H-furo[3,2-c]carbazol-4-ol (**37k**). Condition A. 27.2 mg, 60%. Yellow solid, mp = 156−158 °C. ^{1}H NMR (500 MHz, $(CD_3)_2CO$): δ 8.14 (d, J = 9.0 Hz, 1H), 8.02 (d, J = 2.0 Hz, 1H), 7.80 (d, J = 2.0 Hz, 1H), 7.66 (s, 1H), 7.62 (d, J = 9.0 Hz, 2H), 7.49 (dd, J = 9.0, 2.5 Hz, 1H), 7.14 (d, J = 8.0 Hz, 2H), 6.99 (d, J = 2.0 Hz, 1H), 2.14 (s, 3H). ^{13}C NMR (125 MHz, $(CD_3)_2CO$): δ 152.9, 150.4, 146.8, 145.3, 139.1, 137.5, 135.2, 130.9, 128.9, 127.4, 127.2, 124.0, 118.0, 117.6, 115.5, 105.4, 104.5, 96.6, 21.4. IR (neat) ν 2922, 2357, 1585, 1251, 1185, 1154, 810, 761. HRMS (ESI) m/z calcd for $C_{21}H_{14}BrNO_4S$ $(M + Na)^+$ 477.9719, found 477.9711.

6-Tosyl-6H-thieno[3,2-c]carbazol-4-ol (**37l**). Condition A. 24.7 mg, 63%. Yellow solid, mp = 194−196 °C. ^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ 8.35−8.32 (m, 1H), 7.95 (s, 1H), 7.90−7.87 (m, 1H), 7.73 (d, J = 8.4 Hz, 2H), 7.68−7.63 (m, 2H), 7.49−7.46 (m, 2H), 7.21 (d, J = 8.0 Hz, 2H), 2.22 (s, 3H). ^{13}C NMR (125 MHz, CD_3OD): δ 154.2, 146.8, 139.3, 138.8, 135.9, 134.5, 130.7, 129.4, 127.5, 127.4, 125.5, 124.5, 122.0, 121.0, 116.3, 113.9, 98.1, 21.4. IR (neat) ν 2925, 1582, 1407, 1170, 1147, 1090, 1026, 977, 748. HRMS (ESI) m/z calcd for $C_{21}H_{15}NO_3S_2$ $(M + Na)^+$ 416.0385, found 416.0386.

7-Methyl-6-tosyl-6H-thieno[3,2-c]carbazol-4-ol (**37m**). Condition A. 21.6 mg, 53%. Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.77 (s, 1H), 7.60−7.57 (m, 2H), 7.41 (d, J = 5.6 Hz, 1H), 7.35 (t, J = 7.6 Hz, 1H), 7.26−7.24 (m, 1H), 7.08 (d, J = 8.4 Hz, 2H), 6.83 (d, J = 8.0 Hz, 2H), 5.89 (s, 1H), 2.86 (s, 3H), 2.15 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.5, 144.6, 140.1, 133.2, 132.6, 130.9, 130.6, 129.7, 129.1, 128.6, 127.0, 126.2, 124.6, 120.7, 117.9, 117.6, 101.9, 22.2, 21.7. IR (neat) ν 3055, 2952, 1597, 1452, 1366, 1166, 1089, 936, 812. HRMS (ESI) m/z calcd for $C_{22}H_{17}NO_3S_2$ $(M + Na)^+$ 430.0542, found 430.0530.

3,6-Ditosyl-3,6-dihydropyrrolo[2,3-c]carbazol-4-ol (**37o**). Condition B. 28.6 mg, 55%. White solid, mp = 214−216 °C. ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 9.00 (s, 1H), 8.32 (d, J = 8.5 Hz, 1H), 7.96 (s, 1H), 7.84 (d, J = 7.5 Hz, 1H), 7.71−7.68 (m, 4H), 7.64 (d, J = 4.0 Hz, 1H), 7.39 (t, J = 7.5 Hz, 1H), 7.34 (t, J = 7.5 Hz, 1H), 7.21 (d, J = 8.5 Hz, 2H), 7.14 (d, J = 3.5 Hz, 1H), 7.09 (d, J = 8.0 Hz, 2H), 2.32 (s, 3H), 2.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.0, 145.1, 144.9, 138.5, 137.2, 135.2, 134.0, 130.4, 129.9, 129.8, 127.3, 127.2, 126.8, 126.4, 125.9, 124.2, 121.2, 120.1, 115.4, 111.7, 110.0, 100.9, 21.9, 21.8. IR (neat) ν 2923, 2360, 1588, 1454, 1367, 1170, 947, 812, 735. HRMS (ESI) m/z calcd for $C_{28}H_{22}N_2O_5S_2$ $(M + Na)^+$ 553.0862, found 553.0867.

12-(Phenylsulfonyl)-5-tosyl-5,12-dihydroindolo[3,2-a]carbazol-7-ol (**37p**). Condition A. 40.1 mg, 71%. Yellow solid, mp = 141−143 °C. ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 8.63 (d, J = 7.0 Hz, 1H), 8.31 (d, J = 7.5 Hz, 1H), 8.18 (d, J = 8.0 Hz, 1H), 7.98 (s, 1H), 7.87 (d, J = 7.5 Hz, 1H), 7.69 (d, J = 8.0 Hz, 2H), 7.46−7.41 (m, 2H), 7.39−7.36 (m, 1H), 7.30−7.23 (m, 2H), 7.12 (d, J = 8.5 Hz, 2H), 6.91 (dd, J = 7.5, 8.5 Hz, 2H), 6.75 (d, J = 8.0 Hz, 2H), 6.15 (s, 1H), 2.26 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.8, 145.4, 141.1, 140.0, 138.8, 136.3, 134.8, 133.7, 133.4, 129.9, 129.6, 129.5, 127.9, 127.3, 126.8, 126.7, 126.5, 126.3, 126.1, 125.3, 123.9, 122.7, 119.6, 117.3, 114.9, 100.9, 21.8. IR (neat) ν 2920, 2851, 1693, 1448, 1412, 1369, 1265, 1174, 1072, 836. HRMS (ESI) m/z calcd for $C_{31}H_{22}N_2O_5S_2$ $(M + Na)^+$ 589.0862, found 589.0860.

7-Tosyl-7H-benzo[c]carbazol-5-ol (**35**). Condition C. 25.5 mg, 66%. White solid, mp = 205−207 °C. ^{1}H NMR (500 MHz, $(CD_3)_2CO$): δ 8.61 (d, J = 8.5 Hz, 1H), 8.34−8.28 (m, 3H), 8.02 (s, 1H), 7.63−7.59 (m, 3H), 7.43 (t, J = 8.5 Hz, 1H), 7.35−7.33 (m, 2H), 7.09 (d, J = 8.5 Hz, 2H), 2.10 (s, 3H). ^{13}C NMR (125 MHz, $(CD_3)_2CO$): δ 154.9, 146.5, 138.524, 138.456, 135.7, 130.8, 130.2, 129.0, 128.3, 127.3, 125.6, 125.4, 125.0, 124.343, 124.317, 124.1, 121.9, 115.9, 113.2, 98.2, 21.3. IR (neat) ν 2964, 2927, 1587, 1450, 1170, 1089, 936, 812, 759. HRMS (ESI) m/z calcd for $C_{23}H_{17}NO_3S$ $(M + Na)^+$ 410.0821, found 410.0815.

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■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b00212.

Copies of ^{1}H NMR and ^{13}C NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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