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Silver Acetate Catalyzed Hydroamination of 1-(2-(Sulfonylamino)phenyl)prop-2-yn-1-ols to (*Z*)-2-Methylene-1-sulfonylindolin-3-ols

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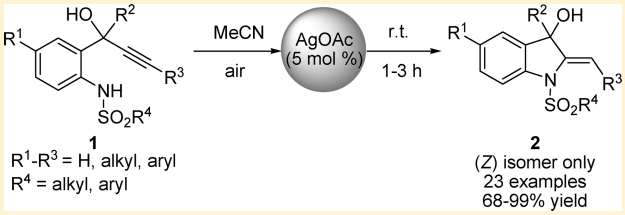
Supporting Information

ABSTRACT: A method to prepare (*Z*)-2-methylene-1-sulfonylindolin-3-ols efficiently that relies on silver acetate catalyzed hydroamination of 1-(2-(sulfonylamino)phenyl)prop-2-yn-1-ols is reported. The reactions proceed rapidly at room temperature with catalyst loadings as low as 1 mol % under conditions that did not require the exclusion of air or moisture. The utility of this *N*-heterocyclic ring-forming strategy as a synthetic tool that makes use of unsaturated alcohols was exemplified by the conversion of the (*Z*)-2-methylene-1-sulfonylindolin-3-ol to examples of other members of the indole family of compounds.



INTRODUCTION

The indole ring system is a common structural motif found in a myriad of bioactive natural compounds and pharmaceutical products as well as optoelectronic functional materials.[1−4] Added to this is their utility as substrates in strategies to various synthetically valuable products. While this has led to a number of impressive works to this class of compounds being developed over the years, those that focus on the synthesis of (*Z*)-2-methylene-1-sulfonylindolin-3-ols have been less well explored.[3] This is surprising given the potential of this member of the indole family of compounds to serve as a versatile building block in organic synthesis and their presence in a number of bioactive natural products.[4] For this reason, it is desirable to establish new synthetic methods to prepare (*Z*)-2-methylene-1-sulfonylindolin-3-ols in an efficient manner and with selective control of substitution patterns under mild conditions from acyclic substrates and a catalyst system that are readily accessible, atom-economical, and low cost.

Lewis acid catalyzed reactions of unsaturated alcohols with amine nucleophiles have come under increasing scrutiny in recent years as efficient and convenient strategies for *N*-heterocyclic synthesis.[5−7] For example, we described one method to prepare a variety of benzo-fused and 2,3-disubstituted indoles that relied on gold(I) catalyzed cycloisomerization of 1-(2-(tosylamino)phenyl)prop-2-yn-1-ols.[2d] In the course of this work, we noticed in one control experiment that when 1,3-diphenyl-1-(2-(tosylamino)phenyl)prop-2-yn-1-ol (**1a**, $R^1 = R^2 = Ph$) was treated with AgOTf as the catalyst, (*Z*)-benzylidene-3-phenyl-1-tosylindolin-3-ol **2a** was obtained as the product instead of the anticipated indenyl-fused indole **3a**.[2d] In a continuation of this study, a significant expansion of this chemistry with the discovery that under the appropriate conditions, simple silver(I) salts can efficiently effect the hydroamination of propargylic alcohols **1** is reported herein (Scheme 1, eq 2).[8,9] This process provides a convenient and operationally straightforward synthetic method that provides (*Z*)-2-methylene-1-sulfonylindolin-3-ols in excellent yields for a variety of substrates under mild conditions that did not require the exclusion of air or moisture at room temperature. The application of this catalytic nitrogen ring formation process to the synthesis of other members of the indole family of compounds is also presented.

RESULTS AND DISCUSSION

Our studies began by examining the silver(I) catalyzed hydroamination of **1a** to establish the reaction conditions (Table 1). This initially revealed that treating a MeCN solution of **1a** contained in an open round-bottom flask with 10 mol % of AgOAc at room temperature for 15 min furnished **2a** in near quantitative yield (entry 1). Our studies subsequently showed that a gradual decrease in the catalyst loading of AgOAc from 10 to 5 to 1 mol % also provided the *N*-heterocycle in near quantitative yield albeit with the need for longer reaction times of 1 and 18 h, respectively (entries 2 and 3). A similar outcome was found on changing the solvent from MeCN to PhMe and CH_2Cl_2 or performing the reaction with other inexpensive and readily available silver(I) salts in place of AgOAc as the catalyst (entries 5−6 and 8−13). On the other hand, the analogous reactions with THF as the solvent or $AgSbF_6$ as the catalyst were found to give a markedly lower product yield of 17 and 27%, respectively (entries 4 and 7). Low product yields were also obtained in control experiments with the Brønsted acid catalysts TfOH and Tf_2NH, whereas AcOH was found to result in the recovery of the substrate in near quantitative yield

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Scheme 1. Silver-Catalyzed Cycloisomerization of 1-(2-(Tosylamino)phenyl)prop-2-yn-1-ols (1)

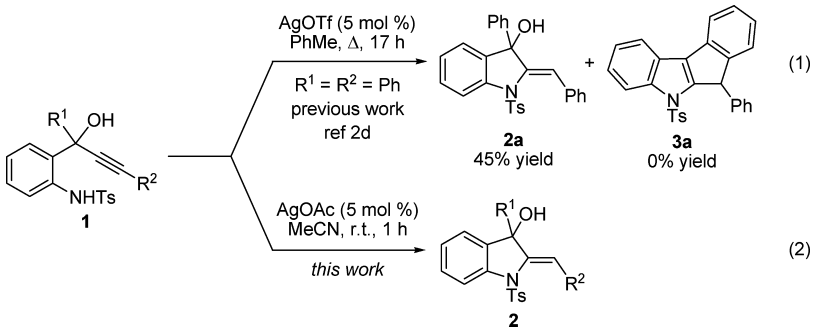
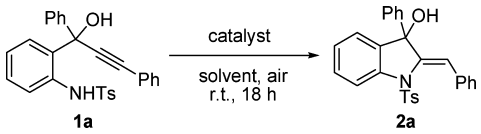


Table 1. Optimization of the Reaction Conditions[a]



entry	solvent	catalyst	yield[b] (%)
1[c]	MeCN	AgOAc	99
2[d]	MeCN	AgOAc	99 (99)[e]
3[f]	MeCN	AgOAc	99
4	THF	AgOAc	17
5	PhMe	AgOAc	99
6	CH_2Cl_2	AgOAc	99
7	MeCN	$AgSbF_6$	27
8	MeCN	$AgBF_4$	94
9[g]	MeCN	Ag_2CO_3	99
10	MeCN	$AgNO_3$	99
11	MeCN	AgOTf	99
12[h]	MeCN	Ag_2O	99
13	MeCN	$AgNTf_2$	99
14	MeCN	CH_3CO_2H	*i*
15	MeCN	TfOH	11
16	MeCN	Tf_2NH	11

[a]All reactions were performed with 0.2 mmol of **1a** and 5 mol % of catalyst at room temperature for 18 h. [b]^{1}H NMR yield with CH_2Br_2 as the internal standard. [c]Reaction performed with 10 mol % catalyst loading for 15 min. [d]Reaction performed with 5 mol % catalyst loading for 1 h. [e]Value in parentheses denotes isolated product yield. [f]Reaction performed with 1 mol % catalyst loading. [g]Reaction performed with 2.5 mol % catalyst loading. [h]Reaction performed with 2.5 mol % catalyst loading for 4.5 h. [i]Recovery of starting material in near-quantitative yield.

(entries 14–16). On the basis of the above results, reaction of **1a** in the presence of 5 mol % of AgOAc in MeCN at room temperature for 1 h contained in an open round-bottom flask was deemed to provide the optimum conditions.

To define the generality of the present procedure, we next turn our attentions to the reactions of a variety of 1-(2-(sulfonylamino)phenyl)prop-2-yn-1-ols and the results are summarized in Table 2. In general, these experiments demonstrated that by using AgOAc as the catalyst, the reaction conditions proved to be broad and a wide variety of substituted (*Z*)-2-methylene-1-sulfonylindolin-3-ols could be furnished in good to excellent yields. In our hands, no other side products arising from 6-endo-trig cyclization of the substrate was detected by TLC and ^{1}H NMR analysis of the crude reaction mixtures. Reactions of **1b-1d** with an electron-donating or electron-withdrawing substituent on the aniline ring were shown to be well tolerated and afford the corresponding products **2b–2d** in excellent yields of 87–97%. Similarly, starting alcohols with an embedded naphthalene ring moiety (**1e**) or a pendant of electron-withdrawing and electron-donating containing phenyl ring on the carbinol carbon center (**1f-1h**) were found to proceed well, furnishing **2e-2h** in excellent yields of 92–99%. Likewise, the present procedure was found to work well for substrates **1i-1n** where the propargylic carbon center contained a thiophene, alkyl or cycloalkane moiety or a phenyl group with an electron-withdrawing or electron-donating substituent at the para position. In these reactions, the corresponding (*Z*)-2-methylene-1-sulfonylindolin-3-ol adducts **2i-2n** were obtained in 88–99% yield. The presence of a methyl and *n*-butyl group on the respective carbinol and propargylic carbon centers was found to have no influence on the outcome of the reaction with **2o** afforded in 98% yield. Additionally, substrates with either a pendant terminal alkyne moiety or where the carbinol carbon center is a secondary alcohol, as in **1p–1u**, were found to proceed well and provide **2p-2u** in 68–96% yield. Substrates containing an Ns (**1v**), Ms (**1w**), Ac (**1x**) or Boc (**1y**) instead of a Ts protecting group on the nitrogen center were also examined under the standard conditions. In these experiments, the corresponding *N*-sulfonyl protected products **2v** and **2w** were both obtained in near quantitative yield. In contrast, those with the Ac or Boc protecting group on the nitrogen center were found to be unreactive and resulted in recovery of starting materials in near quantitative yields.

A tentative mechanism for the present Ag(I) catalyzed (*Z*)-2-methylene-1-sulfonylindolin-3-ol forming reaction is illustrated in Scheme 2. This could initially involve activation of **1** through coordination of the metal catalyst with the alkyne moiety of the substrate to provide the silver(I) coordinated intermediate **A**. This is the active species that undergoes the intramolecular amination process involving anti addition of the sulfonamide moiety to the alkyne bond to afford the vinyl silver complex **B**.[10] Protodemetalation of this putative organosilver complex would then provide **2**. The role of the silver(I) catalyst in triggering the hydroamination process by coordinating to the alkyne moiety of the substrate was supported by repeating the Ag(I) catalyzed reaction of **1a** in the presence of D_2O under the conditions described in Scheme 3. This test led to the formation of d_1-**2a** in 99% yield with 55% deuterium incorporation.

Next, the synthetic utility of the (*Z*)-2-methylene-1-sulfonylindolin-3-ols obtained via the Ag(I) catalyzed hydroamination reaction was examined (Scheme 4). First, we demonstrated that Brønsted acid catalyzed 1,3-allylic alcohol isomerization (1,3-AAI) of **2a** to the (1*H*-indol-2-yl)methanol

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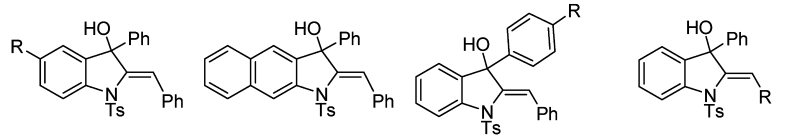
Table 2. Cycloisomerization of 1b−y Catalyzed by AgOAc[a]

1 **2**

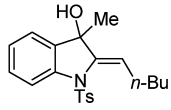


2b, R = Me (97)
2c, R = Br (87)
2d, R = Cl (96)

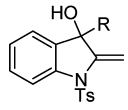
2e, (99)

2f, R = Me (92)
2g, R = Cl (97)
2h, R = Br (99)

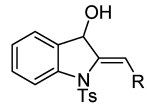
2i, R = *p*-FC_6H_5 (88)
2j, R = *p*-$CF_3C_6H_5$ (96)
2k, R = *p*-MeC_6H_5 (99)
2l, R = 3-thiophene (99)
2m, R = *c*-C_3H_5 (98)
2n, R = *n*-C_4H_9 (98)



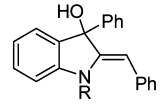
2o, (98)



2p, R = Ph (87)[b]
2q, R = Me (96)[c]



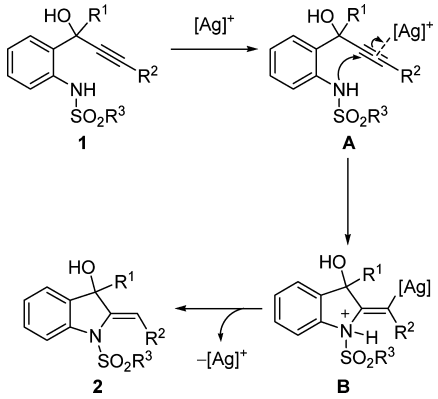
2r, R = Ph (86)[d]
2s, R = Me (68)[e]
2t, R = *n*-C_4H_9 (71)
2u, R = *c*-C_3H_5 (77)



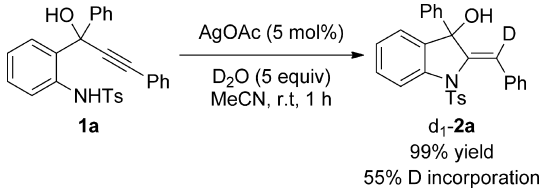
2v, R = Ns (99)
2w, R = Ms (99)
2x, R = Ac (-)[f]
2y, R = Boc (-)[f]

[a]Unless otherwise stated, all reactions were performed in MeCN at room temperature for 1 h with 0.2 mmol of **1a** in the presence of 5 mol % of AgOAc. Values in parentheses denote isolated product yields. [b]Reaction time = 1.5 h. [c]Reaction time = 2.5 h. [d]Reaction time = 3 h. [e]Reaction time = 2 h. [f]Recovery of starting material in near-quantitative yield.

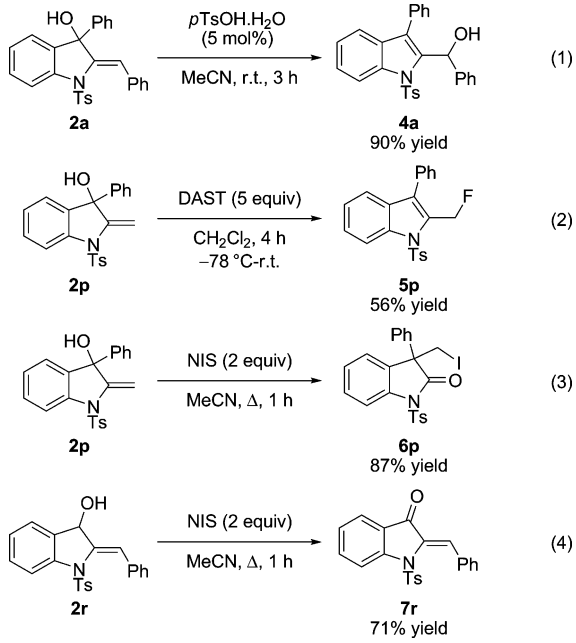
Scheme 2. Proposed Mechanism



Scheme 3. Hydroamination of 1a in the Presence of D_2O Catalyzed by AgOAc



Scheme 4. Selective Transformations of (*Z*)-2-Methylene-1-sulfonylindolin-3-ols 2a, 2p, and 2r



4a could be achieved in 90% yield in the presence of 5 mol % of *p*-TsOH·H_2O under the conditions depicted in Scheme 4, eq 1.[11] On the other hand, subjecting **2p** to 5 equiv of DAST in dichloromethane from −78 °C to room temperature over 4 h provided the 2-fluoromethylindole **5p** in 56% yield (Scheme 4, eq 2).[12] Treating the same starting material to 2 equiv of NIS (*N*-iodosuccinimide) in MeCN at reflux for 1 h gave the 3-iodomethyloxindole **6p** in 87% yield (Scheme 4, eq 3).[13,14] Finally, the indolin-3-one **7r** could be furnished in 71% yield on exposing the secondary alcohol **2r** to the same conditions of 2 equiv of NIS in MeCN at reflux for 1 h (Scheme 4, eq 4).

CONCLUSION

In summary, an efficient silver(I) catalyzed synthetic route to (*Z*)-2-methylene-1-sulfonylindolin-3-ols based on intramolecular hydroamination of 1-(2-(sulfonylamino)phenyl)prop-2-yn-1-ols has been reported. Achieved under mild conditions at room temperature and without the need to exclude air or moisture, the reaction was shown to be applicable to a wide

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range of alcohol substrates containing electron-withdrawing, electron-donating and sterically demanding functional groups. The synthetic utility of the present method to this partially hydrogenated member of this indole family was also demonstrated in 1,3-AAI, nucleophilic substitution, oxidation, and rearrangement reactions.

EXPERIMENTAL SECTION

General Considerations. All reactions were performed under atmospheric conditions unless otherwise stated. Unless specified, all reagents and starting materials were purchased from commercial sources and used as received. Solvents were purified following standard literature procedures. Analytical thin-layer chromatography (TLC) was performed using precoated silica gel plates. Visualization was achieved by UV light (254 nm). Flash chromatography was performed using silica gel and gradient solvent system (EtOAc/*n*-hexane as eluent). ^{1}H and ^{13}C NMR spectra were measured on 300 and 400 MHz NMR spectrometers. Chemical shifts (ppm) were recorded with tetramethylsilane (TMS) as the internal reference standard. Multiplicities are given as: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), dt (doublet of triplets), tq (triplet of quartets) or m (multiplet). The number of protons (*n*) for a given resonance is indicated by *n*H, and coupling constants are reported as a *J* value in Hz. Infrared spectra were recorded on an FTIR spectrometer. All samples were examined as a thin film between NaCl salt plates. Solid samples were examined as a thin film between NaCl salt plates using chloroform as the solvent. Low-resolution mass spectra were determined on a mass spectrometer and are reported in units of mass to charge (*m*/*z*). High resolution mass spectra (HRMS) were obtained using a TOF spectrometer using simultaneous electrospray (ESI).

General Experimental Procedure for the Preparation of 1a–o,r–u. To a solution of the appropriate 1-(2-aminophenyl)ketone or aldehyde (1 mmol) in pyridine (0.5 mL) was added *p*-TsCl (0.23 g, 1.2 mmol) at room temperature under an nitrogen atmosphere. The resulting solution was stirred for 4 h at room temperature. On completion, the reaction mixture was quenched by adding H_2O (5 mL), filtered, dried, and used directly for the next step. To a stirred solution of diisopropylamine (0.21 mL 1.5 mmol) in anhydrous THF at −20 °C was added *n*-butyllithium (2.0 M in cyclohexane solution, 0.75 mL, 1.5 mmol) dropwise, and the resulting solution was allowed to stirred at the same temperature for 10 min. On lowering the reaction temperature to −78 °C, the appropriate alkyne (1 mmol) was added in a dropwise manner. The resulting mixture was stirred at the same temperature for 1 h. The ketone (0.5 mmol) obtained from the previous step was dissolved in THF (2 mL) and added to the reaction mixture dropwise and allowed to stir for 1 h at the same temperature. The reaction mixture was slowly warmed up to room temperature and stirred for a further 1 h. Upon completion, the reaction mixture was quenched by adding saturated NH_4Cl (10 mL) and extracted with EtOAc (2 × 10 mL). The combined organic layers were washed with brine (20 mL), dried over $MgSO_4$, and concentrated under reduced pressure. Purification by flash column chromatography on silica gel (10% EtOAc/*n*-hexane) gave the title compound.

General Experimental Procedure for the Preparation of 1p,q. To a solution of the appropriate 1-(2-aminophenyl)ketone (1 mmol) in pyridine (0.5 mL) was added *p*-TsCl (0.23 g, 1.2 mmol) at room temperature under nitrogen atmosphere. The resulting solution was stirred for 4 h at room temperature. On completion, the reaction mixture was quenched by adding H_2O (5 mL), filtered, dried, and used directly for the next step. The solid (0.5 mmol) was dissolved in THF (5 mL), and a solution of ethynylmagnesium bromide (0.5 M in THF solution, 3 mL, 1.5 mmol) was added at room temperature, brought up to reflux, and allowed to stir at this temperature for 3 h. Upon completion, the reaction mixture was cooled to room temperature and quenched by addition of saturated NH_4Cl (10 mL). The reaction mixture was extracted with EtOAc (2 × 10 mL), washed with brine (20 mL), dried over $MgSO_4$, and concentrated under reduced pressure. Purification by flash column chromatography on silica gel (10% EtOAc/*n*-hexane) gave the title compound.

General Experimental Procedure for the Preparation of 1v–x. To a mixture of 2-aminobenzophenone (0.493 g, 2.5 mmol) and pyridine (1.21 mL, 15 mmol) in dichloromethane (10 mL) was added the corresponding sulfonyl chloride (3 mmol, for **1v** and **1w**) or acyl chloride (3 mmol, for **1x**) at 0 °C for 15 min. The reaction mixture was then brought up to room temperature and stirred for 4 h. Upon completion, the reaction mixture was quenched with 10% aqueous HCl (10 mL) and extracted with dichloromethane (2 × 10 mL). The combined organic layers were washed with brine (15 mL), dried over $MgSO_4$, concentrated under reduced pressure, and dried under vacuum to afford the ketone as solid which was used directly for the next step. To a stirred solution of diisopropylamine (0.21 mL, 1.5 mmol) in anhydrous THF at −20 °C was added *n*-butyllithium (2.0 M in cyclohexane solution, 0.75 mL, 1.5 mmol) dropwise, and the resulting solution was allowed to stirred at the same temperature for 10 min. On lowering the reaction temperature to −78 °C, the appropriate alkyne (1 mmol) was added in a dropwise manner. The resulting mixture was stirred at the same temperature for 1 h. The ketone (0.5 mmol) obtained from the previous step was dissolved in THF (2 mL), added to the reaction mixture dropwise, and allowed to stir for 1 h at the same temperature. The reaction mixture was slowly warmed up to room temperature and stirred for a further 1 h. Upon completion, the reaction mixture was quenched by adding saturated NH_4Cl (10 mL) and extracted with EtOAc (2 × 10 mL). The combined organic layers were washed with brine (20 mL), dried over $MgSO_4$, and concentrated under reduced pressure. Purification by flash column chromatography on silica gel (15% EtOAc/*n*-hexane) gave the title compound.

Experimental Procedure for the Preparation of 1y. To a mixture of 2-aminobenzophenone (0.986 g, 5 mmol) and DMAP (0.061 g, 0.5 mmol) in CH_2Cl_2 (10 mL) at 0 °C was added Boc_2O (1.378 mL, 6 mmol) and Et_3N (0.766 mL, 5.5 mmol). The reaction mixture was allowed to warm to room temperature and stirred for 15 h. Upon completion, H_2O (10 mL) was added to the reaction mixture and extracted with CH_2Cl_2 (2 × 10 mL). The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure to give the ketone as yellow liquid which was used directly to the next step. To a stirred solution of diisopropylamine (0.21 mL, 1.5 mmol) in anhydrous THF at −20 °C was added *n*-butyllithium (2.0 M in cyclohexane solution, 0.75 mL, 1.5 mmol) dropwise and the resulting solution was allowed to stirred at the same temperature for 10 min. On lowering the reaction temperature to −78 °C, the appropriate alkyne (1 mmol) was added in a dropwise manner. The resulting mixture was stirred at the same temperature for 1 h. The ketone (0.5 mmol) obtained from the previous step was dissolved in THF (2 mL) and added to the reaction mixture dropwise and allowed to stir for 1 h at the same temperature. The reaction mixture was slowly warmed up to room temperature and stirred for a further 1 h. Upon completion, the reaction mixture was quenched by adding saturated NH_4Cl (10 mL) and extracted with EtOAc (2 × 10 mL). The combined organic layers were washed with brine (20 mL), dried over $MgSO_4$, and concentrated under reduced pressure. Purification by flash column chromatography on silica gel (12% EtOAc/*n*-hexane) gave the title compound.

General Experimental Procedure for Optimizing the Hydroamination of 1a. To a solution of **1a** (0.2 mmol) in the appropriate solvent (2 mL) was added the appropriate catalyst (0.01 mmol). The reaction was stirred at room temperature and monitored by TLC analysis. Upon completion, the reaction mixture was filtered through Celite, washed with CH_2Cl_2 (10 mL) and concentrated under reduced pressure. Purification by flash column chromatography on silica gel (10% EtOAc/*n*-hexane) gave **2a**.

General Experimental Procedure for AgOAc Catalyzed Hydroamination of 1. To a solution of **1** (0.2 mmol) in acetonitrile (2 mL) was added AgOAc (0.01 mmol). The reaction was stirred at room temperature and monitored by TLC analysis. Upon completion, the reaction mixture was filtered through Celite, washed with CH_2Cl_2 (10 mL), and concentrated under reduced pressure. Purification by

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flash column chromatography on silica gel (10% EtOAc/*n*-hexane) gave **2**.

Experimental Procedure for AgOAc Catalyzed Hydroamination of 1a in the Presence of D_2O. To a solution of **1a** (90.7 mg, 0.2 mmol) and D_2O (18 μL, 1 mmol) in anhydrous acetonitrile (2 mL) was added AgOAc (0.01 mmol). The reaction was stirred at room temperature under nitrogen atmosphere and monitored by by TLC analysis. Upon completion, the reaction mixture was filtered through Celite, washed with CH_2Cl_2 (10 mL) and concentrated under reduced pressure. Purification by flash column chromatography on silica gel (10% EtOAc/*n*-hexane) gave (d_1-**2a**).

***N*-(2-(1-Hydroxy-1,3-diphenylprop-2-yn-1-yl)phenyl)-4-methylbenzenesulfonamide (1a):**[2d] yield 90%; 0.204 g; white solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.89 (1H, brs), 7.58 (1H, d, J = 7.8 Hz), 7.52 (1H, d, J = 8.16 Hz), 7.40−7.46 (4H, m), 7.31 (2H, d, J = 8.16 Hz), 7.23−7.28 (6H, m), 7.14−7.20 (1H, m), 6.93−6.97 (3H, m), 4.24 (1H, brs), 2.23 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 143.4, 143.1, 136.3, 136.0, 131.8, 130.9, 129.5, 129.4, 129.0, 128.7, 128.4, 128.1, 127.4, 126.1, 122.8, 122.0, 118.7, 90.0, 89.1, 75.5, 21.5.

***N*-(2-(1-Hydroxy-1,3-diphenylprop-2-yn-1-yl)-4-methylphenyl)-4-methylbenzenesulfonamide (1b):** yield 80%; 0.187 g; white solid; mp 140−142 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.67 (1H, brs), 7.59 (2H, t, J = 8.8 Hz), 7.44−7.46 (2H, m), 7.38 (2H, d, J = 8.24 Hz), 7.28−7.34 (5H, m), 7.19−7.24 (1H, m), 7.10 (2H, d, J = 8.04 Hz), 6.97−7.01 (3H, m), 3.32 (1H, brs), 2.38 (3H, s), 2.30 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 143.3, 139.9, 138.0, 136.5, 136.0, 131.8, 130.8, 129.4, 129.3, 129.0, 128.8, 128.4, 127.4, 126.0, 122.8, 121.9, 118.8, 89.9, 89.1, 75.4, 21.5, 21.2; IR (NaCl, neat) ν 3445, 3019, 2399, 1491, 1159 cm^{-1}; HRMS (ESI) calcd for $C_{29}H_{26}NO_3S$ (M^+ + H) 468.1655, found 468.1633.

***N*-(4-Bromo-2-(1-hydroxy-1,3-diphenylprop-2-yn-1-yl)-phenyl)-4-methylbenzenesulfonamide (1c):**[2d] yield 96%; 0.256 g; white solid; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.54 (1H, brs), 7.68 (2H, td, J = 7.71, 1.47 Hz), 7.42−7.45 (2H, m), 7.30−7.36 (8H, m), 7.21 −7.26 (2H, m), 7.03−7.08 (3H, m), 3.35 (1H, brs), 2.35 (3H, s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 143.6, 142.3, 136.2, 135.9, 131.8, 131.5, 130.4, 129.8, 129.5, 129.1, 129.1, 128.4, 127.6, 127.0, 123.1, 122.3, 121.7, 119.2, 89.7, 89.4, 75.1, 21.6.

***N*-(4-Chloro-2-(1-hydroxy-1,3-diphenylprop-2-yn-1-yl)-phenyl)-4-methylbenzenesulfonamide (1d):**[2d] yield 94%; 0.229 g; yellow solid; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.70 (1H, brs), 7.57 (1H, s), 7.42−7.50 (5H, m), 7.23−7.31 (8H, m), 7.14 (1H, dd, J = 2.22, 8.73 Hz), 6.97 (2H, d, J = 8.01 Hz), 3.88 (1H, brs), 2.28 (3H, s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 143.7, 142.3, 135.9, 134.5, 132.6, 131.8, 129.5, 129.3, 129.2, 128.8, 128.4, 128.2, 127.4, 126.0, 121.6, 120.0, 89.7, 89.1, 75.0, 21.5.

***N*-(3-(1-Hydroxy-1,3-diphenylprop-2-yn-1-yl)naphthalen-2-yl)-4-methylbenzenesulfonamide (1e):**[2d] yield 75%; 0.189 g; pale yellow solid; ^{1}H NMR ($(CD_3)_2CO$, 400 MHz) δ 9.31 (1H, brs), 8.35 (1H, s), 7.96 (1H, s), 7.87 (1H, d, J = 8.08, Hz), 7.79 (1H, d, J = 8.16 Hz), 7.46−7.53 (5H, m), 7.36−7.42 (9H, m), 7.23 (1H, s), 7.09 (2H, d, J = 8 Hz), 2.88 (1H, brs), 2.26 (3H, s); ^{13}C NMR ($(CD_3)_2CO$, 100 MHz) δ 143.6, 136.3, 134.1, 133.6, 131.5, 131.4, 129.4, 129.0, 128.9, 128.6, 128.5, 128.2, 128.0, 127.4, 127.2, 126.7, 125.8, 125.1, 122.2, 114.1, 90.6, 88.5, 75.1, 20.4.

***N*-(2-(1-Hydroxy-3-phenyl-1-(*p*-tolyl)prop-2-yn-1-yl)phenyl)-4-methylbenzenesulfonamide (1f):**[2d] yield 82%; 0.192 g; pale yellow solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.55−7.60 (2H, m), 7.46−7.47 (2H, m), 7.40 (2H, d, J = 8.28 Hz), 7.29−7.35 (5H, m), 7.22 (2H, td, J = 8.32, 1.4 Hz), 7.11 (2H, d, J = 8.08 Hz), 6.97−7.03 (3H, m), 2.38 (3H, s), 2.31 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 143.3, 140.0, 138.0, 136.4, 136.0, 131.8, 130.9, 129.4, 129.3, 129.3, 128.9, 128.9, 128.4, 127.4, 126.0, 122.8, 121.9, 118.8, 90.0, 89.0, 75.4, 21.5, 21.2.

***N*-(2-(1-(4-Chlorophenyl)-1-hydroxy-3-phenylprop-2-yn-1-yl)phenyl)-4-methylbenzenesulfonamide (1g):**[2d] yield 93%; 0.227 g; white solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.56 (1H, brs), 7.70 (2H, td, J = 7.92, 1.28 Hz), 7.44 (2H, dd, J = 7.84, 1.6 Hz), 7.26−7.36 (8H, m), 7.18 (2H, d, J = 8.48 Hz), 7.04−7.07 (3H, m), 3.42 (1H, brs), 2.34 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 143.5, 141.5, 136.3, 136.0, 134.1, 131.8, 130.3, 129.8, 129.4, 129.2, 128.9, 128.6, 128.4, 127.2, 127.0, 123.0, 121.6, 119.3, 89.7, 89.3, 75.1, 21.5.

***N*-(2-(1-(4-Bromophenyl)-1-hydroxy-3-phenylprop-2-yn-1-yl)phenyl)-4-methylbenzenesulfonamide (1h):**[2d] yield 64%; 0.171 g; white solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.57 (1H, brs), 7.71 (2H, t, J = 7.8 Hz), 7.43 (2H, d, J = 6.72 Hz), 7.21−7.34 (10H, m), 7.03−7.07 (3H, m), 3.45 (1H, brs), 2.35 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 143.5, 142.0, 136.3, 136.0, 131.8, 131.6, 130.2, 129.9, 129.4, 129.2, 128.9, 128.4, 127.5, 127.0, 123.0, 122.4, 121.5, 119.2, 89.8, 89.2, 75.2, 21.6.

***N*-(2-(3-(4-Fluorophenyl)-1-hydroxy-1-phenylprop-2-yn-1-yl)phenyl)-4-methylbenzenesulfonamide (1i):**[2d] yield 94%; 0.222 g; white solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.61 (1H, brs), 7.53 (2H, t, J = 7.32 Hz), 7.44−7.47 (4H, m), 7.39 (2H, d, J = 8.16 Hz), 7.32−7.35 (3H, m), 7.22 (2H, t, J = 7.8 Hz), 6.98−7.05 (5H, m), 3.23 (1H, brs), 2.32 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 161.7 (1C, d, J_{C-F} = 249 Hz), 142.7 (1C, d, J_{C-F} = 74.5 Hz), 136.5, 136.0, 133.9, 133.8, 130.6, 129.6, 129.4, 128.7 (1C, d, J_{C-F} = 11 Hz), 128.3, 127.4, 126.0, 122.8, 118.9, 115.6 (1C, d, J_{C-F} = 22 Hz), 89.4, 88.3, 75.5, 21.5.

***N*-(2-(1-Hydroxy-1-phenyl-3-(4-(trifluoromethyl)phenyl)-prop-2-yn-1-yl)phenyl)-4-methylbenzenesulfonamide (1j):** yield 70%; 0.183 g; yellow solid; mp 70−73 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.67 (1H, brs), 7.56 (4H, s), 7.46−7.54 (4H, m), 7.33−7.39 (5H, m), 7.22 (1H, t, J = 7.84 Hz), 6.98−7.04 (3H, m), 3.67 (1H, brs), 2.31 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 143.5, 142.4, 136.5, 136.1, 132.1, 130.5, 129.7, 129.5, 128.8, 128.8, 128.4, 127.3, 126.1, 125.6, 125.3 (1C, q, J_{C-F} = 3.6 Hz), 122.9, 119.0, 92.0, 87.7, 75.5, 21.5; IR (NaCl, neat) ν 3423, 3019, 2399, 1603, 1493, 1323, 1159, 1092 cm^{-1}; HRMS (ESI) calcd for $C_{29}H_{23}F_3$ NO_3S (M^+ + H) 522.1351, found 522.1360.

***N*-(2-(1-Hydroxy-1-phenyl-3-*p*-tolylprop-2-yn-1-yl)phenyl)-4-methylbenzenesulfonamide (1k):**[2d] yield 88%; 0.206 g; white solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.73 (1H, brs), 7.56 (2H, dd, J = 7.84, 16.4 Hz), 7.44−7.46 (2H, m), 7.29−7.36 (7H, m), 7.19 (1H, t, J = 7.52 Hz), 7.10 (2H, d, J = 7.88 Hz), 6.96−7.00 (3H, m), 3.53 (1H, brs), 2.33 (3H, s), 2.28 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 143.4, 143.0, 139.3, 136.4, 136.0, 131.7, 130.8, 129.4, 129.1, 128.9, 128.6, 128.2, 127.4, 126.1, 122.8, 118.8, 89.5, 89.2, 75.5, 21.6, 21.5.

***N*-(2-(1-Hydroxy-1-phenyl-3-(thiophene-3-yl)prop-2-yn-1-yl)phenyl)-4-methylbenzenesulfonamide (1l):** yield 88%; 0.202 g; white solid; mp 126−127 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.64 (1H, brs), 7.51−7.55 (3H, m), 7.45−7.47 (2H, m), 7.38 (2H, d, J = 8.24 Hz), 7.31−7.34 (3H, m). 7.27−7.30 (2H, m), 7.22 (1H, td, J = 1.28, 7.12 Hz), 7.13 (1H, d, J = 4.96 Hz), 6.97−7.04 (3H, m), 3.31 (1H, brs), 2.32 (3H, s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 162.3, 143.4, 142.8, 136.4, 136.0, 130.7, 129.9, 129.8, 129.4, 128.9, 128.7, 128.2, 127.4, 126.1, 125.6, 122.8, 120.8, 118.8, 89.4, 84.6, 75.6, 21.5; IR (NaCl, neat) ν 3447, 3019, 2243, 1601, 1493, 1335, 1159, 1092 cm^{-1}; HRMS (ESI) calcd for $C_{26}H_{22}NO_3S_2$ (M^+ + H) 460.1041, found 460.1049.

***N*-(2-(3-Cyclopropyl-1-hydroxy-1-phenylprop-2-yn-1-yl)-phenyl)-4-methylbenzenesulfonamide (1m):**[2d] Yield 80%; 0.167 g; white solid; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.58 (1H, brs), 7.50 (2H, d, J = 8.1 Hz), 7.25−7.38 (7H, m), 7.18 (1H, td, J = 1.44, 7.02 Hz), 7.05 (2H, d, J = 8.1 Hz), 6.97 (1H, td, J = 1.11, 7.68 Hz), 3.09 (1H, brs), 2.32 (3H, s), 1.28−1.36 (1H, m), 0.75−0.83 (4H, m); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 143.3, 143.2, 136.5, 135.8, 131.1, 129.4, 129.3, 128.7, 128.5, 128.0, 127.4, 125.9, 122.7, 118.6, 93.7, 76.4, 75.0, 21.5, 8.5, −0.4.

***N*-(2-(1-Hydroxy-1-phenylhept-2-yn-1-yl)phenyl)-4-methylbenzenesulfonamide (1n):**[2d] yield 80%; 0.173 g; white solid; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.67 (1H, brs), 7.58 (1H, dd, J = 1.41, 7.83 Hz), 7.51 (1H, d, J = 7.41 Hz), 7.24−7.38 (6H, m), 7.17 (1H, td, J = 1.47, 8.25 Hz), 6.94−7.03 (3H, m), 3.38 (1H, brs), 2.30 (3H, s), 2.27 (2H, t, J = 7.17 Hz), 1.47−1.54 (2H, m), 1.34−1.42 (2H, m), 0.88 (3H, t, J = 7.26 Hz), ^{13}C NMR ($CDCl_3$, 75 MHz) δ 143.5, 143.3, 136.4, 135.8, 131.2, 129.4, 129.3, 128.8, 128.5, 127.9, 127.4, 125.9, 122.7, 118.6, 90.9, 81.4, 75.1, 30.4, 22.1, 21.5, 18.6, 13.6.

***N*-(2-(2-Hydroxyoct-3-yn-2-yl)phenyl)-4-methylbenzenesulfonamide (1o):** yield 70%; 0.130 g; colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.19 (1H, brs), 7.76 (2H, d, J = 8.24 Hz), 7.57 (1H, dd, J

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= 1.2, 7.88 Hz), 7.53 (1H, d, J = 8.2 Hz), 7.16−7.26 (3H, m), 6.99 (1H, t, J = 7.44 Hz), 3.00 (1H, brs), 2.36 (3H, s), 2.26 (2H, t, J = 7 Hz), 1.60 (3H, s), 1.49−1.56 (2H, m), 1.38−1.46 (2H, m), 0.91 (3H, t, J = 7.32 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 143.7, 137.2, 135.6, 131.9, 129.6, 128.8, 127.4, 127.2, 123.3, 119.7, 87.8, 82.4, 71.9, 31.6, 30.5, 22.0, 21.5, 18.4, 13.6; IR (NaCl, neat) ν 3453, 3225, 2957, 2932, 2243, 1584, 1495, 1333, 1159, 1092 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{26}NO_3S$ (M^+ + H) 372.1633, found 372.1652.

***N*-(2-(1-Hydroxy-1-phenylprop-2-yn-1-yl)phenyl)-4-methylbenzenesulfonamide (1p):**[2b,d] yield 88%; 0.166 g; white solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.63 (1H, brs), 7.55 (2H, d, J = 6.4 Hz), 7.25−7.40 (7H, m), 7.21 (1H, t, J = 8.24 Hz), 7.04 (2H, d, J = 7.76 Hz), 6.99 (1H, t, J = 7.8 Hz), 3.81 (1H, brs), 2.88 (1H, s), 2.31 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 143.6, 142.4, 136.3, 135.9, 130.3, 129.7, 129.5, 129.0, 128.8, 128.4, 127.4, 126.0, 123.0, 119.0, 84.6, 77.9, 75.0, 21.6.

***N*-(2-(2-Hydroxybut-3-yn-2-yl)phenyl)-4-methylbenzenesulfonamide (1q):** yield 71%; 0.112 g; white solid; mp 109−110 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.13 (1H, brs), 7.75 (2H, d, J = 8.25 Hz), 7.55 (2H, d, J = 8.07 Hz), 7.17−7.25 (3H, m), 7.00 (1H, t, J = 7.77 Hz), 3.40 (1H, brs), 2.70 (1H, s), 2.35 (3H, s), 1.67 (3H, s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 143.8, 137.1, 135.6, 130.8, 129.7, 129.1, 127.3, 127.3, 123.5, 119.9, 85.7, 74.8, 71.6, 31.2, 21.5; IR (NaCl, neat) ν 3444, 3302, 3021, 2132, 1599, 1584, 1334, 1161, 1092 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{17}NO_3SNa$ (M^+ + Na) 338.0827, found 338.0810.

***N*-(2-(1-Hydroxy-3-phenylprop-2-yn-1-yl)phenyl)-4-methylbenzenesulfonamide (1r):** yield 85%; 0.160 g; pale yellow solid; mp 139−141 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.69 (2H, d, J = 7.72 Hz), 7.56 (1H, d, J = 7.36 Hz), 7.42−7.46 (3H, m), 7.26−7.34 (4H, m), 7.11−7.17 (3H, m), 5.52 (1H, s), 2.87 (1H, brs), 2.34 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 143.9, 136.7, 135.5, 131.8, 130.9, 129.7, 129.0, 128.4, 127.2, 125.2, 122.8, 121.9, 88.5, 86.4, 63.4, 21.6; IR (NaCl, neat) ν 3448, 3019, 2230, 1587, 1491, 1331, 1159, 1092 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{19}NO_3SNa$ (M^+ + Na) 400.0983, found 400.0992.

***N*-(2-(1-Hydroxybut-2-yn-1-yl)phenyl)-4-methylbenzenesulfonamide (1s):** yield 97%; 0.153 g; white solid; mp 128−130 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.68 (2H, d, J = 8.2 Hz), 7.42−7.47 (2H, m), 7.21−7.26 (3H, m), 7.10 (1H, t, J = 7.56 Hz), 5.21 (1H, d, J = 1.92 Hz), 2.38 (3H, s), 1.90 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 143.9, 136.9, 135.5, 131.2, 129.7, 129.5, 128.2, 127.2, 125.0, 122.7, 85.3, 76.9, 63.2, 21.6, 3.8; IR (NaCl, neat) ν 3442, 3026, 2399, 1491, 1215, 1159, 1092 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{18}NO_3S$ (M^+ + H) 316.1007, found 316.1005.

***N*-(2-(1-Hydroxyhept-2-yn-1-yl)phenyl)-4-methylbenzenesulfonamide (1t):** yield 71%; 0.127 g; yellow solid; mp 92−94 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.00 (1H, brs), 7.67 (2H, d, J = 8.22 Hz), 7.48 (1H, d, J = 7.44 Hz), 7.39 (1H, d, J = 7.92 Hz), 7.19−7.26 (3H, m), 7.09 (1H, t, J = 7.29 Hz), 5.24 (1H, s), 2.89 (1H, brs), 2.36 (3H, s), 2.24 (2H, t, J = 7.08 Hz), 1.46−1.54 (2H, m), 1.34−1.44 (2H, m), 0.90 (3H, t, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 143.8, 136.8, 135.4, 131.5, 129.7, 129.4, 128.2, 127.2, 125.1, 122.7, 89.7, 77.8, 62.9, 30.5, 22.0, 21.5, 18.5, 13.6; IR (NaCl, neat) ν 3566, 3472, 3462, 3312, 3019, 2959, 2934, 1587, 1493, 1458, 1333, 1161, 1092 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{24}NO_3S$ (M^+ + H) 358.1477, found 358.1467.

***N*-(2-(3-Cyclopropyl-1-hydroxyprop-2-yn-1-yl)phenyl)-4-methylbenzenesulfonamide (1u):** yield 74%; 0.126 g; white solid; mp 116−118 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.96 (1H, brs), 7.68 (2H, d, J = 8.25 Hz), 7.38−7.44 (2H, m), 7.20−7.26 (3H, m), 7.08 (1H, td, J = 0.87, 7.56 Hz), 5.20 (1H, s), 2.71 (1H, brs), 2.37 (3H, s), 1.25−1.32 (1H, m), 0.78−0.83 (2H, m), 0.73−0.76 (2H, m); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 143.9, 136.8, 135.5, 131.2, 129.7, 129.4, 128.2, 127.2, 125.0, 122.6, 92.8, 72.9, 63.1, 21.5, 8.4, −0.5; IR (NaCl, neat) ν 3429, 3019, 2236, 1587, 1491, 1458, 1331, 1277, 1159, 1092 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{20}NO_3S$ (M^+ + H) 342.1164, found 342.1177.

***N*-(2-(1-Hydroxy-1,3-diphenylprop-2-yn-1-yl)phenyl)-4-nitrobenzenesulfonamide (1v):** yield 90%; 0.218 g; yellow solid; mp 83−85 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.08 (1H, brs); 7.90 (2H, d, J = 8.48 Hz), 7.68 (1H, d, J = 8.12 Hz), 7.60 (1H, d, J = 7.6 Hz), 7.52 (2H, d, J = 8.56 Hz), 7.37 (4H, d, J = 7.24 Hz), 7.22−7.33 (7H, m), 7.07 (1H, t, J = 7.52 Hz), 3.91 (1H, brs); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 149.7, 144.8, 142.8, 135.1, 131.7, 131.4, 129.8, 129.4, 129.2, 128.7, 128.5, 128.3, 128.2, 125.9, 124.0, 123.9, 121.5, 119.3, 89.5, 75.6; IR (NaCl, neat) ν 3453, 3264, 3019, 1605, 1531, 1491, 1348, 1261, 1043 cm^{-1}; HRMS (ESI) calcd for $C_{27}H_{20}N_2O_5SNa$ (M^+ + Na) 507.0991, found 507.0997.

***N*-(2-(1-Hydroxy-1,3-diphenylprop-2-yn-1-yl)phenyl)-methanesulfonamide (1w):** yield 83%; 0.157 g; pale yellow solid; mp 141−143 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.31 (1H, brs), 7.83 (1H, d, J = 7.8 Hz), 7.71 (1H, d, J = 8.08 Hz), 7.57 (2H, d, J = 7.28 Hz), 7.47 (2H, dd, J = 1.48, 7.52 Hz), 7.31−7.40 (7H, m), 7.17 (1H, td, J = 0.8, 7.72 Hz), 3.74 (1H, brs), 2.09 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 143.4, 135.9, 132.7, 131.8, 130.0, 129.2, 128.8, 128.5, 128.3, 126.0, 124.0, 121.6, 120.9, 89.6, 89.5, 75.1, 38.0; IR (NaCl, neat) ν 3447, 3019, 2376, 1395, 1335, 1215, 1043 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{20}NO_3S$ (M^+ + H) 378.1164, found 378.1156.

***N*-(2-(1-Hydroxy-1,3-diphenylprop-2-yn-1-yl)phenyl)-acetamide (1x):** yield 76%; 0.130 g; pale yellow solid; mp 72−75 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.68 (1H, brs), 7.96 (1H, d, J = 8 Hz), 7.72 (1H, d, J = 7.48 Hz), 7.51 (2H, d, J = 7.12 Hz), 7.42 (2H, d, J = 6.68 Hz), 7.26−7.34 (7H, m), 7.11 (1H, t, J = 7.48 Hz), 4.44 (1H, brs), 1.77 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.3, 143.3, 136.2, 132.8, 131.7, 129.2, 128.9, 128.5, 128.4, 128.1, 128.0, 125.9, 124.2, 123.8, 122.1, 90.1, 88.8, 75.0, 24.3; IR (NaCl, neat) ν: 3564, 3364, 3017, 2359, 1678, 1491, 1215, 1042 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{19}NO_2Na$ (M^+ + Na): 364.1313, found 364.1313.

***tert*-Butyl (2-(1-hydroxy-1,3-diphenylprop-2-yn-1-yl)-phenyl)carbamate (1y):** yield 25%; 0.1 g; pale yellow solid; mp 67−69 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.73−7.77 (2H, m), 7.59 (1H, d, J = 7.68 Hz), 7.46 (2H, d, J = 7.56 Hz), 7.38 (2H, d, J = 5.76 Hz), 7.20−7.27 (7H, m), 6.97 (1H, t, J = 7.56 Hz), 3.39 (1H, brs), 1.24 (9H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.0, 143.2, 136.8, 131.8, 129.3, 128.9, 128.4, 128.3, 128.0, 127.7, 126.0, 122.8, 122.1, 90.2, 88.8, 79.8, 75.0, 28.2; IR (NaCl, neat) ν 3402, 2978, 1719, 1587, 1491, 1159, 1026 cm^{-1}; HRMS (ESI) calcd for $C_{26}H_{25}NO_3Na$ (M^+ + Na) 422.1732, found 422.1732.

***(Z)*-2-Benzylidene-3-phenyl-1-tosylindolin-3-ol (2a):**[2d] 0.089 g; pale yellow solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.90 (1H, d, J = 8.08 Hz), 7.66 (2H, d, J = 7.2 Hz), 7.42 (1H, t, J = 7.8 Hz), 7.30−7.37 (4H, m), 7.14−7.23 (7H, m), 6.96−7.02 (3H, m), 6.26 (1H, s), 2.28 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 145.4, 144.8, 142.5, 141.9, 138.2, 135.6, 133.0, 130.0, 129.6, 129.4, 128.3, 127.9, 127.9, 127.8, 127.3, 126.9, 126.7, 125.4, 124.8, 119.5, 81.8, 21.6.

***(Z)*-2-Benzylidene-5-methyl-3-phenyl-1-tosylindolin-3-ol (2b):** 0.091 g; white solid; mp 147−148 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.90 (1H, d, J = 8.08 Hz), 7.66 (2H, d, J = 7.72 Hz), 7.42 (1H, td, J = 1.12, 8.2 Hz), 7.31−7.36 (4H, m), 7.20−7.24 (1H, m), 7.16 (1H, t, J = 7.44 Hz), 7.08 (2H, d, J = 8.04 Hz), 6.97−7.02 (5H, m), 6.27 (1H, s), 2.29 (3H, s), 2.29 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 145.4, 144.8, 141.9, 139.5, 138.3, 137.0, 135.7, 133.1, 129.9, 129.6, 129.3, 128.6, 128.3, 127.9, 127.7, 126.8, 126.6, 125.3, 124.6, 119.5, 81.8, 21.6, 21.1; IR (NaCl, neat) ν 3566, 3026, 2872, 1616, 1599, 1449, 1366, 1169, 1086 cm^{-1}; HRMS (ESI) calcd for $C_{29}H_{25}NO_3SNa$ (M^+ + Na) 490.1453, found 490.1465.

***(Z)*-2-Benzylidene-5-bromo-3-phenyl-1-tosylindolin-3-ol (2c):** 0.093 g; white solid; mp 149−151 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.92 (1H, d, J = 8.12 Hz), 7.66 (2H, d, J = 7.52 Hz), 7.46 (1H, t, J = 7.4 Hz), 7.19−7.36 (8H, m), 7.06 (4H, t, J = 8.52 Hz), 6.99 (1H, d, J = 7.56 Hz), 6.27 (1H, s), 2.34 (3H, s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 145.0, 145.0, 141.9, 141.7, 135.3, 133.1, 131.0, 130.2, 129.6, 129.4, 128.5, 128.3, 127.9, 126.9, 125.2, 124.8, 121.6, 119.6, 81.6, 21.6; IR (NaCl, neat) ν 3566, 3026, 2872, 1616, 1599, 1445, 1371, 1171, 1038 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{22}BrNO_3SNa$ (M^+ + Na) 554.0401, found 554.0394.

***(Z)*-2-Benzylidene-5-chloro-3-phenyl-1-tosylindolin-3-ol (2d):** 0.094 g; yellow solid; mp 102−107 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.85 (1H, d, J = 8.64 Hz), 7.63 (2H, d, J = 7.48 Hz), 7.32−7.42 (4H, m), 7.22−7.26 (7H, m), 7.09 (2H, d, J = 8.2 Hz), 6.95 (1H,

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d, J = 2.12 Hz), 6.24 (1H, s), 2.35 (3H, s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 145.1, 144.9, 141.9, 140.4, 140.1, 135.3, 132.8, 132.2, 130.1, 129.6, 128.4, 128.1, 127.9, 127.6, 126.6, 125.5, 125.3, 120.7, 81.7, 21.6; IR (NaCl, neat) ν 3570, 3026, 2872, 1616, 1599, 1462, 1445, 1371, 1171, 1038 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{22}ClNO_3SNa$ (M^+ + Na) 510.0907, found 510.0893.

(*Z*)-2-Benzylidene-3-phenyl-1-tosyl-2,3-dihydro-1*H*-benzo[*f*]indol-3-ol (2e): 0.1 g; yellow solid; mp 123−125 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.31 (1H, s), 7.96 (1H, d, J = 8.24 Hz), 7.70 (3H, d, J = 7.76 Hz), 7.54 (1H, t, J = 7.2 Hz), 7.34−7.47 (6H, m), 7.18−7.27 (6H, m), 6.94 (2H, d, 8.04 Hz), 6.33 (1H, s), 2.25 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 145.3, 144.6, 142.2, 139.4, 137.8, 135.7, 134.4, 133.6, 132.1, 129.5, 129.3, 128.4, 128.3, 128.0, 127.8, 127.5, 127.2, 126.9, 125.9, 125.0, 124.0, 116.3, 81.7, 21.5; IR (NaCl, neat) ν 3570, 3026, 2872, 1616, 1599, 1506, 1445, 1371, 1038 cm^{-1}; HRMS (ESI) calcd for $C_{32}H_{25}NO_3SNa$ (M^+ + Na) 526.1453, found 526.1454.

(*Z*)-2-Benzylidene-3-*p*-tolyl-1-tosylindolin-3-ol (2f): 0.086 g; white solid; mp 145−147 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.91 (1H, d, J = 8.12 Hz), 7.66 (2H, d, J = 7.64 Hz), 7.43 (1H, t, J = 7.96 Hz), 7.32−7.38 (4H, m), 7.16−7.24 (2H, m), 7.10 (2H, d, J = 7.96 Hz), 7.04 (2H, d, J = 8 Hz), 7.00 (3H, d, J = 8.44 Hz), 6.27 (1H, s), 2.32 (3H, s), 2.30 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 145.4, 144.8, 141.9, 139.5, 138.4, 137.0, 135.7, 133.1, 129.9, 129.6, 129.3, 128.6, 128.3, 127.9, 127.7, 126.8, 126.6, 125.3, 124.6, 119.5, 81.8, 21.6, 21.1; IR (NaCl, neat) ν 3566, 3016, 2924, 1628, 1597, 1462, 1445, 1368, 1088 cm^{-1}; HRMS (ESI) calcd for $C_{29}H_{25}NO_3SNa$ (M^+ + Na) 490.1453, found 490.1457.

(*Z*)-2-Benzylidene-3-(4-chlorophenyl)-1-tosylindolin-3-ol (2g): 0.095 g; white solid; mp 94−95 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.92 (1H, d, J = 8.12 Hz), 7.66 (2H, d, J = 7.64 Hz), 7.46 (1H, t, J = 7.84 Hz), 7.34 (4H, t, J = 7.2 Hz), 7.19−7.27 (3H, m), 7.12−7.17 (4H, m), 7.05 (2H, d, J = 8.04 Hz), 6.99 (1H, d, J = 7.52 Hz), 6.26 (1H, s), 2.33 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 145.0, 141.9, 141.1, 137.7, 135.3, 133.3, 133.1, 130.2, 129.6, 129.4, 128.3, 128.1, 128.1, 127.9, 126.9, 125.2, 124.8, 119.6, 81.6, 21.6; IR (NaCl, neat) ν 3445, 3024, 2924, 1628, 1597, 1489, 1462, 1368, 1071 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{22}ClNO_3SNa$ (M^+ + Na) 510.0907, found 510.0889.

(*Z*)-2-Benzylidene-3-(4-bromophenyl)-1-tosylindolin-3-ol (2h): 0.105 g; yellow solid; mp 105−107 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.91 (1H, d, J = 8.12 Hz), 7.66 (2H, d, J = 7.64 Hz), 7.45 (1H, t, J = 7.96 Hz), 7.18−7.35 (8H, m), 6.98−7.06 (5H, m), 6.28 (1H, s), 2.32 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 145.0, 145.0, 141.9, 141.7, 137.6, 135.3, 133.1, 131.0, 130.2, 129.6, 129.4, 128.5, 128.3, 127.9, 127.0, 125.2, 124.8, 121.6, 119.6, 81.6, 21.6; IR (NaCl, neat) ν 3445, 3019, 2924, 1628, 1597, 1489, 1462, 1370, 1171, 1088, 1011 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{22}BrNO_3SNa$ (M^+ + Na) 554.0401, found 554.0407.

(*Z*)-2-(4-Fluorobenzylidene)-3-phenyl-1-tosylindolin-3-ol (2i): 0.083 g; white solid; mp 162−163 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.90 (1H, d, J = 8.08 Hz), 7.65 (2H, t, J = 7.56 Hz), 7.43 (1H, t, J = 7.8 Hz), 7.36 (2H, d, J = 7.92 Hz), 7.16−7.24 (6H, m), 6.97−7.05 (5H, m), 6.22 (1H, s), 2.31 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.8 (1C, d, J_{C-F} = 247 Hz), 145.2, 144.9, 141.8 (1C, d, J_{C-F} = 62 Hz), 138.2, 133.0, 131.6, 131.4, 131.3, 130.0, 129.4, 128.3, 128.0, 127.4, 126.9, 126.7, 125.4, 123.7, 119.5, 114.8 (1C, d, J_{C-F} = 21 Hz), 81.8, 21.6; IR (NaCl, neat) ν 3445, 3019, 2924, 1636, 1603, 1509, 1462, 1171, 1088 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{22}FNO_3SNa$ (M^+ + Na) 494.1202, found 494.1208.

(*Z*)-3-Phenyl-1-tosyl-2-(4-(trifluoromethyl)benzylidene)-indolin-3-ol (2j): 0.1 g; white solid; mp 178−179 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.91 (1H, d, J = 8.12 Hz), 7.74 (2H, d, J = 8.08 Hz), 7.56 (2H, d, J = 8.12 Hz), 7.45 (1H, t, J = 7.8 Hz), 7.35 (2H, d, J = 8.04 Hz), 7.18−7.24 (6H, m), 6.99−7.04 (3H, m), 6.27 (1H, s), 2.31 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 147.6, 145.1, 142.2, 141.7, 139.4, 137.8, 132.9, 130.2, 129.7, 129.4, 129.4, 128.3, 128.0, 127.5, 127.0, 126.6, 125.4, 124.8(1C, q, J = 3.71 Hz), 122.8, 119.4, 81.9, 21.6; IR (NaCl, neat) ν 3564, 3019, 2924, 1659, 1628, 1616, 1597, 1462, 1369, 1323, 1171, 1088, 1019 cm^{-1}; HRMS (ESI) calcd for $C_{29}H_{22}F_3NO_3SNa$ (M^+ + Na) 544.1170, found 544.1183.

(*Z*)-2-(4-Methylbenzylidene)-3-phenyl-1-tosylindolin-3-ol (2k): 0.093 g; yellow solid; mp 137−139 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.92 (1H, d, J = 8.08 Hz), 7.57 (2H, d, J = 7.64 Hz), 7.43 (1H, t, J = 7.76 Hz), 7.37 (2H, d, J = 7.76 Hz), 7.13−7.24 (8H, m), 7.04 (2H, d, J = 7.96 Hz), 6.97 (1H, d, J = 7.52 Hz), 6.22 (1H, s), 2.34 (3H, s), 2.31 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 144.8, 144.5, 142.6, 142.0, 138.4, 137.8, 133.1, 132.6, 129.9, 129.6, 129.4, 128.6, 128.4, 127.9, 127.3, 126.8, 126.7, 125.3, 125.1, 119.6, 81.8, 21.6, 21.5; IR (NaCl, neat) ν 3441, 3019, 2924, 1659, 1628, 1512, 1462, 1369, 1171, 1088, 1015 cm^{-1}; HRMS (ESI) calcd for $C_{29}H_{25}NO_3SNa$ (M^+ + Na) 490.1453, found 490.1458.

(*Z*)-3-Phenyl-2-(thiophene-3-ylmethylene)-1-tosylindolin-3-ol (2l): 0.091 g; yellow oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.91 (1H, d, J = 8.07 Hz), 7.71 (1H, d, J = 4.83 Hz), 7.36−7.45 (4H, m), 7.27−7.28 (1H, m), 7.19 (6H, s), 6.96−7.04 (3H, m), 6.32 (1H, s), 2.31 (3H, s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 162.3, 144.8, 144.0, 142.0, 138.4, 136.4, 133.0, 129.9, 129.3, 128.7, 128.4, 127.9, 127.3, 126.9, 126.7, 126.5, 125.4, 124.4, 119.8, 119.5, 81.8, 21.6; IR (NaCl, neat) ν 3564, 3019, 2870, 1670, 1521, 1464, 1362, 1169, 1087, 1056, 1030 cm^{-1}; HRMS (ESI) calcd for $C_{26}H_{21}NO_3S_2Na$ (M^+ + Na) 482.0861, found 482.0869.

(*Z*)-2-(Cyclopropylmethylene)-3-phenyl-1-tosylindolin-3-ol (2m): 0.082 g; yellow solid; mp 174−176 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.87 (1H, d, J = 8.12 Hz), 7.42 (2H, d, J = 8.16 Hz), 7.38 (1H, t, J = 7.64 Hz), 7.06−7.17 (8H, m), 6.90 (1H, d, J = 7.48 Hz), 4.75 (1H, d, J = 10.44 Hz), 2.40−2.48 (1H, m), 2.32 (3H, s), 0.94−1.00 (1H, m), 0.81−0.88 (1H, m), 0.42−0.48 (1H, m), 0.24−0.30 (1H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 144.6, 143.9, 142.8, 142.1, 138.5, 133.3, 133.2, 129.7, 129.4, 128.2, 127.7, 127.0, 126.7, 126.5, 125.2, 119.6, 80.9, 21.6, 12.0, 8.3, 7.7; IR (NaCl, neat) ν 3568, 3019, 1670, 1636, 1597, 1449, 1364, 1169, 1090, 1018 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{23}NO_3SNa$ (M^+ + Na) 440.1296, found 440.1303.

(*Z*)-2-Pentylidene-3-phenyl-1-tosylindolin-3-ol (2n): 0.085 g; yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.85 (1H, d, J = 8.12 Hz), 7.36−7.40 (3H, m), 7.10−7.18 (6H, m), 7.05 (2H, d, J = 8.4 Hz), 6.92 (1H, d, J = 7.6 Hz), 5.41 (1H, t, J = 8 Hz), 2.58−2.65 (1H, m), 2.50−2.55 (1H, m), 2.32 (3H, s), 1.23−1.35 (4H, m), 0.87 (3H, t, J = 6.8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 145.3, 144.6, 142.8, 142.1, 138.4, 133.5, 129.7, 129.4, 129.1, 128.1, 127.7, 127.1, 126.7, 126.5, 125.2, 119.4, 81.0, 31.4, 29.0, 22.4, 21.6, 13.9; IR (NaCl, neat) ν 3547, 3028, 2957, 1670, 1636, 1597, 1449, 1366, 1173, 1090, 1016 cm^{-1}; HRMS (ESI) calcd for $C_{26}H_{27}NO_3SNa$ (M^+ + Na) 456.1609, found 456.1619.

(*Z*)-3-Methyl-2-pentylidene-1-tosylindolin-3-ol (2o): 0.073 g; yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.80 (1H, d, J = 8.08 Hz), 7.34−7.39 (3H, m), 7.17−7.24 (2H, m), 7.12 (2H, d, J = 8.12 Hz), 5.75 (1H, t, J = 7.2 Hz), 2.59−2.61 (2H, m), 2.32 (3H, s), 1.36−1.47 (4H, m), 1.07 (3H, s), 0.93 (3H, t, J = 7.08 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 144.7, 144.1, 141.2, 138.2, 133.6, 129.5, 129.4, 128.0, 126.4, 124.7, 123.1, 119.6, 76.4, 31.7, 28.9, 26.6, 22.5, 21.5, 14.0; IR (NaCl, neat) ν 3523, 3019, 2871, 1670, 1521, 1464, 1362, 1171, 1088, 1056, 1030 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{25}NO_3SNa$ (M^+ + Na) 394.1453, found 394.1458.

2-Methylene-3-phenyl-1-tosylindolin-3-ol (2p): 0.066 g; white solid; mp 160−161 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.97 (1H, d, J = 8.28 Hz), 7.59 (2H, d, J = 8.04 Hz), 7.37 (1H, t, J = 7.84 Hz), 7.01−7.16 (7H, m), 6.92 (2H, d, J = 7.68 Hz), 5.88 (1H, s), 4.91 (1H, s), 2.37 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.4, 144.8, 143.6, 140.9, 135.4, 134.0, 130.3, 129.6, 127.9, 127.4, 127.2, 125.6, 125.5, 125.2, 116.4, 101.6, 80.7, 21.6; IR (NaCl, neat) ν 3441, 3019, 2924, 1638, 1628, 1601, 1462, 1362, 1171, 1088, 1011 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{19}NO_3SNa$ (M^+ + Na) 400.0983, found 400.0997.

3-Methyl-2-methylene-1-tosylindolin-3-ol (2q): 0.061 g; colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.87 (1H, d, J = 8.24 Hz), 7.57 (2H, d, J = 8.12 Hz), 7.26−7.37 (2H, m), 7.13−7.18 (3H, m), 5.78 (1H, s), 5.14 (1H, s), 2.34 (3H, s), 1.17 (3H, s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 152.8, 144.7, 140.0, 135.4, 134.0, 129.9, 129.4, 127.3, 125.3, 123.3, 116.6, 98.6, 28.9, 21.5; IR (NaCl, neat) ν 3581, 3019,

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2976, 2924, 1659, 1603, 1462, 1360, 1173, 1090 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{17}NO_3SNa$ (M^+ + Na) 338.0827, found 338.0839.

(*Z*)-2-Benzylidene-1-tosylindolin-3-ol (2r): 0.065 g; yellow solid; mp 122−123 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.77−7.81 (3H, m), 7.33−7.42 (4H, m), 7.19−7.29 (4H, m), 7.08 (2H, d, J = 8.12 Hz), 6.59 (1H, s), 4.84 (1H, s), 2.32 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 144.8, 142.5, 141.3, 134.9, 134.8, 133.0, 129.8, 129.7, 129.3, 128.1, 128.0, 126.8, 124.6, 123.6, 120.3, 73.7, 21.6; IR (NaCl, neat) ν 3447, 3019, 1670, 1636, 1521, 1464, 1368, 1171, 1088, 1056, 1030 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{19}NO_3SNa$ (M^+ + Na) 400.0983, found 400.0981.

(*Z*)-2-Ethylidene-1-tosylindolin-3-ol (2s): 0.043 g; yellow oil; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.73 (1H, d, J = 8.08 Hz), 7.34−7.38 (3H, m), 7.15−7.22 (2H, m), 7.11 (2H, d, J = 8.08 Hz), 5.89 (1H, qd, J = 1.48, 7.16 Hz), 4.66 (1H, s), 2.33 (3H, s), 2.08 (3H, dd, J = 1.4, 7.16 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 144.6, 142.6, 142.3, 135.0, 133.2, 129.6, 129.3, 127.9, 126.5, 124.6, 122.4, 120.2, 72.7, 21.6, 15.0; IR (NaCl, neat) ν 3422, 3028, 1670, 1636, 1522, 1462, 1358, 1169, 1088, 1055, 1030 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{17}NO_3SNa$ (M^+ + Na) 338.0827, found 338.0820.

(*Z*)-2-Pentylidene-1-tosylindolin-3-ol (2t). 0.051 g; white solid; mp 117−120 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.74 (1H, d, J = 8.08 Hz), 7.33−7.39 (3H, m), 7.16−7.23 (2H, m), 7.10 (2H, d, J = 8.12 Hz), 5.77 (1H, td, J = 1.16, 7.24 Hz), 4.66 (1H, d, J = 9.84 Hz), 2.58−2.63 (2H, m), 2.33 (3H, s), 1.39−1.47 (4H, m), 0.93 (3H, t, J = 7.08 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 144.6, 142.6, 141.0, 135.0, 133.2, 129.6, 129.3, 128.0, 127.9, 126.5, 124.6, 120.2, 72.7, 31.5, 28.6, 22.5, 21.6, 14.0; IR (NaCl, neat) ν 3419, 3019, 2871, 1670, 1636, 1522, 1464, 1358, 1169, 1088, 1055, 1030 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{23}NO_3SNa$ (M^+ + Na) 380.1296, found 380.1300.

(*Z*)-2-(Cyclopropylmethylene)-1-tosylindolin-3-ol (2u): 0.053 g; white solid; mp 97−99 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.75 (1H, d, J = 8.08 Hz), 7.34−7.39 (3H, m), 7.15−7.22 (2H, m), 7.11 (2H, d, J = 8.08 Hz), 5.12 (1H, d, J = 10.4 Hz), 4.64 (1H, s), 2.35−2.42 (1H, m), 2.33 (3H, s), 0.95−0.99 (2H, m), 0.51−0.53 (2H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 144.6, 142.7, 139.5, 135.0, 133.1, 132.2, 129.6, 129.3, 128.0, 126.5, 124.6, 120.3, 72.7, 21.6, 11.6, 8.0, 8.0; IR (NaCl, neat) ν 3565, 3019, 2870, 1670, 1521, 1464, 1362, 1169, 1088, 1056, 1030 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{19}NO_3SNa$ (M^+ + Na) 364.0983, found 364.0986.

(*Z*)-2-Benzylidene-1-((4-nitrophenyl)sulfonyl)-3-phenylindolin-3-ol (2v): 0.096 g; yellow solid; mp 108−110 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.94 (1H, d, J = 8.12 Hz), 7.87 (2H, d, J = 8.6 Hz), 7.68 (2H, d, J =7.48 Hz), 7.54 (2H, d, J = 8.64 Hz), 7.49 (1H, t, J = 8.08 Hz), 7.36 (2H, t, J = 7.76 Hz), 7.19−7.29 (4H, m), 7.08−7.15 (5H, m), 6.55 (1H, s), 2.12 (1H, brs); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 144.9, 141.8, 141.1, 137.4, 135.2, 130.4, 129.6, 129.4, 128.3, 128.2, 128.0, 127.2, 126.6, 125.6, 124.0, 123.5, 119.1, 82.2; IR (NaCl, neat) ν 3443, 3022, 1667, 1604, 1530, 1348, 1172, 1063 cm^{-1}; HRMS (ESI) calcd for $C_{27}H_{20}N_2O_5SNa$ (M^+ + Na) 507.0991, found 507.0976.

(*Z*)-2-Benzylidene-1-(methylsulfonyl)-3-phenylindolin-3-ol (2w): 0.075 g; pale yellow solid; mp 79−81 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.71 (1H, d, J = 8 Hz), 7.61 (2H, d, J = 7.36 Hz), 7.51 (2H, d, J = 6.68 Hz), 7.43 (1H, t, J = 7.52 Hz), 7.30−7.38 (5H, m), 7.17−7.26 (3H, m), 6.24 (1H, s), 2.88 (1H, brs), 2.72 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 145.4, 142.2, 141.7, 138.1, 135.3, 130.4, 129.4, 128.3, 128.1, 128.0, 127.0, 126.8, 125.1, 123.9, 118.4, 82.8, 37.8; IR (NaCl, neat) ν 3462, 3021, 1602, 1462, 1321, 1215, 1161, 1082 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{19}NO_3SNa$ (M^+ + Na) 400.0983, found 400.0984.

(*Z*)-2-Benzylidene-3-phenyl-1-tosylindolin-3-ol (d_1-2a): 0.09 g; white solid; mp 163−165 °C; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.91 (1H, d, J = 8.07 Hz), 7.66 (2H, d, J = 7.53 Hz), 7.30−7.45 (5H, m), 7.14−7.24 (8H, m), 6.96−7.03 (3H, m), 6.26 (0.45H, s), 2.29 (3H, s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 145.4, 144.8, 142.5, 141.9, 138.3, 135.6, 133.1, 130.0, 129.6, 129.4, 128.4, 127.9, 127.9, 127.8, 127.3, 126.9, 126.7, 125.4, 124.8, 119.5, 81.8, 21.6; IR (NaCl, neat) ν 3526, 3078, 2956, 2860, 1718, 1660, 1598, 1450, 1367, 1186, 1172 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{22}DNO_3SNa$ (M^+ + Na) 477.1359, found 477.1361.

Phenyl(3-phenyl-1-tosyl-1*H*-indol-2-yl)methanol (4a).[2d] To a stirred solution of **2a** (90.7 mg, 0.2 mmol) in acetonitrile (2 mL) was added *p*-TsOH.H_2O (1.9 mg, 0.01 mmol) at atmospheric condition. The reaction mixture was allowed to stir for 3 h at room temperature. Upon completion, the reaction mixture was added H_2O (5 mL), extracted with EtOAc (2 × 10 mL), washed with brine (20 mL), dried over $MgSO_4$, and concentrated under reduced pressure. Purification by flash column chromatography on silica gel (15% EtOAc/*n*-hexane) gave title compound as a yellow oil (81.6 mg, 90%): ^1H NMR ($CDCl_3$, 400 MHz) δ 8.05 (1H, d, J = 8.4 Hz), 7.49 (2H, d, J = 7.12 Hz), 7.44 (3H, t, J = 7.76 Hz), 7.32−7.38 (4H, m), 7.20−7.26 (7H, m), 7.06 (2H, d, J = 8.2 Hz), 6.30 (1H, d, J = 11.84 Hz), 4.72 (1H, d, J = 11.8 Hz), 2.29 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 144.9, 142.5, 137.2, 136.4, 135.3, 132.3, 130.2, 129.7, 128.9, 128.2, 128.2, 127.2, 126.9, 125.7, 125.6, 123.9, 120.7, 114.7, 68.6, 21.6.

2-(Fluoromethyl)-3-phenyl-1-tosyl-1*H*-indole (5p). To a solution of **2p** (37.7 mg, 0.1 mmol) in dry CH_2Cl_2 (1 mL) at −78 °C was added *N*,*N*-diethylaminosulfur trifluoride (66 μL, 0.5 mmol). After stirring for 1 h at this temperature, the reaction mixture was warmed up to room temperature. After stirring for 3 h at this temperature, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ (5 mL) dropwise at 0 °C. The reaction mixture was allowed to stir for 5 min at room temperature, extracted with CH_2Cl_2 (3 × 10 mL), and washed with brine (20 mL). The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. Purification by flash column chromatography on silica gel (5% EtOAc/*n*-hexane) gave the title compound as a white solid (21.2 mg, 56%): mp 111−113 °C ; ^1H NMR ($CDCl_3$, 400 MHz) δ 9.25 (1H, d, J = 8.44 Hz), 8.92 (2H, d, J = 8.16 Hz), 8.55 (1H, d, J = 7.8 Hz), 8.41−8.48 (6H, m), 8.21−8.28 (3H, m), 6.72 (2H, d, J_{H-F} = 48.4 Hz), 3.34 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 145.0, 136.4, 135.5, 130.2, 130.1, 129.7, 128.8, 128.4, 127.3, 127.2, 126.5, 123.9, 120.9, 114.9, 73.9 (1C, d, J_{C-F} = 163.2 Hz), 21.6; IR (NaCl, neat) ν 3019, 1599, 1497, 1454, 1375, 1279, 1175, 1090, 1053, 1026 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{19}FNO_2S$ (M^+ + H) 380.1121, found 380.1128.

3-(Iodomethyl)-3-phenyl-1-tosylindolin-2-one (6p). To a solution of **2p** (37.7 mg, 0.1 mmol) in anhydrous MeCN (1 mL) was added NIS (45 mg, 0.2 mmol). The reaction mixture was stirred for 1 h at reflux and monitored by TLC analysis. Upon completion, the reaction mixture was cooled to room temperature, quenched by addition of 10% $Na_2S_2O_3{\cdot}5H_2O$ (5 mL) and extracted with EtOAc (2 × 10 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. Purification by flash column chromatography on silica gel (5% EtOAc/*n*-hexane) gave the title compound as white solid (43.7 mg, 87%): mp 148−151 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.05 (1H, d, J = 8.24 Hz), 7.98 (2H, d, J = 8.24 Hz), 7.48 (1H, t, J = 8.2 Hz), 7.24−7.32 (9H, m), 3.99 (1H, d, J = 9.92 Hz), 3.53 (1H, d, J = 9.88 Hz), 2.39 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 174.8, 145.8, 139.7, 136.6, 134.9, 129.9, 129.8, 129.7, 129.1, 128.6, 128.3, 127.0, 125.1, 114.1, 57.2, 21.7, 9.2; IR (NaCl, neat) ν 3059, 2962, 1597, 1381, 1176, 575, 544 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{19}INO_3S$ (M^+ + H) 504.0130, found 504.0130.

(*Z*)-2-Benzylidene-1-tosylindolin-3-one (7r). To a solution of **2r** (37.7 mg, 0.1 mmol) in MeCN (1 mL) was added NIS (45 mg, 0.2 mmol). The reaction mixture was stirred at reflux for 1 h and monitored by TLC analysis. Upon completion, the reaction mixture was cooled to room temperature, quenched by addition of 10% $Na_2S_2O_3{\cdot}5H_2O$ (5 mL), and extracted with EtOAc (2 × 10 mL). The combined organic layers were washed with brine (20 mL), dried over $MgSO_4$, and concentrated under reduced pressure. Purification by flash column chromatography on silica gel (5% EtOAc/*n*-hexane) gave the title compound as a yellow solid (26.7 mg, 71%): mp 110−112 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.14 (1H, d, J = 8.28 Hz), 8.0 (1H, s), 7.87−7.89 (2H, m), 7.61−7.69 (2H, m), 7.42−7.45 (5H, m), 7.25 (1H, t, J = 7.52 Hz), 7.12 (2H, d, J = 8 Hz), 2.32 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 183.1, 148.5, 145.2, 136.0, 133.6, 133.1, 133.0, 132.3, 131.3, 130.6, 129.7, 128.1, 127.4, 126.7, 125.6, 124.3, 118.9, 21.6; IR (NaCl, neat) ν 3019, 1701, 1616, 1474, 1460, 1364, 1119, 1090 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{18}NO_3S$ (M^+ + H) 376.1007, found 376.1012.

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■ ASSOCIATED CONTENT

Supporting Information

^{1}H and ^{13}C NMR spectra for all starting materials and products, LC−MS spectrum of d_1-**2a**, and X-ray data for **5p** and **6p** (CIF). 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.

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