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Gold-Catalyzed Cycloisomerizations of 1-(2-(Tosylamino)phenyl)prop-2-yn-1-ols to 1*H*-Indole-2-carbaldehydes and (*E*)-2-(Iodomethylene)indolin-3-ols

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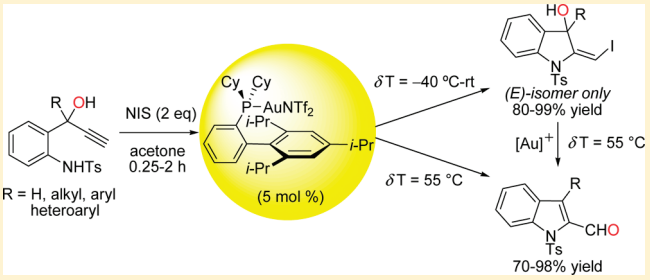
Supporting Information

ABSTRACT: A method to prepare 1*H*-indole-2-carbaldehydes and (*E*)-2-(iodomethylene)indolin-3-ols by gold(I)-catalyzed cycloisomerization of 1-(2-(tosylamino)phenyl)prop-2-yn-1-ols with *N*-iodosuccinimide (NIS) is reported. The reactions were shown to be operationally simplistic and proceed efficiently for a wide variety of substrates, affording the corresponding products in good to excellent yields (70−99%). The mechanism is suggested to involve activation of the alkyne moiety of the substrate by the gold(I) catalyst. This triggers intramolecular addition of the tethered aniline moiety to give a vinyl gold intermediate, which undergoes iododeauration with NIS to give the (*E*)-2-(iodomethylene)indolin-3-ol adduct. Subsequent 1,3-allylic alcohol isomerization (1,3-AAI) followed by formylation of this vinyl iodide intermediate then gives the 1*H*-indole-2-carbaldehyde.



INTRODUCTION

1*H*-Indole-2-carbaldehydes are immensely important targets in organic synthesis because of their frequent use as building blocks in numerous strategies to natural products and bioactive compounds of current therapeutic interest.[1] The presence of the vinyl iodide moiety in (*E*)-2-(iodomethylene)indolin-3-ols also makes this class of compounds a potentially valuable coupling partner in the field of transition metal-catalyzed cross-coupling reactions.[2] Generally, synthetic methods to the former have relied on oxidation or formylation of a prefunctionalized indole substrate, while there are no known examples to the latter. In the case of 1*H*-indole-2-carbaldehyde synthesis, this is far from ideal as each step in such stepwise transformations often require their own set of stoichiometric or excess amounts of various reagents that can lead to equimolar or more amounts of waste products. In this regard, it is therefore surprising to find that single step or one-pot intramolecular strategies to these synthetically useful compounds have not been widely investigated. This is all the more so given the myriad of works to other members of the indole family using this more atom economical synthetic approach.[3,4] Hence, synthetic methods to 1*H*-indole-2-carbaldehydes and (*E*)-2-(iodomethylene)indolin-3-ols that can construct both the indole ring and aldehyde or vinyl iodide moiety in one step or in a one-pot manner from readily available, low cost, and simple acyclic substrates are desirable.

Within the emerging field of gold catalysis, the in situ formation of a putative vinyl gold species is often put forward as a key intermediate in reactions involving alkyne substrates.[5−8] Evidence for the involvement of this transient organometallic species was first reported by the groups of Hammond and Hashmi by isolating and characterizing the vinyl gold complex by X-ray crystallography in the respective Au(I)-catalyzed cycloisomerizations of allenoates[6c] to γ-lactones and *N*-propargylcarboxamides to aromatic oxazoles.[6a] At about the same time, Fürstner and co-workers showed that rearrangement of 3,3-disubstituted cyclopropenes with Au(I) salts gave the corresponding vinyl gold complexes based on ^{1}H and ^{31}P NMR measurements.[6b] Following these seminal works, an increasing number of reports have provided further experimental evidence for the involvement of such a reactive species in a variety of gold-mediated reactions.[7,8] This has hitherto included trapping the vinyl gold species with an iodide source such as NIS to give the vinyl iodide derivative[8] and its further functionalization by using Pd-catalyzed cross-coupling chemistry.[7] Examples of iododeaurations followed by in situ formylation, by contrast, have not been widely investigated. As part of an ongoing program exploring the scope of gold catalysis in heterocyclic synthesis,[9] we report herein that the Au(I) complex **A** can mediate cascade cycloisomerization/1,3-AAI/formylation of propargylic alcohols of the type **1** with NIS (Scheme 1, route 1). This process provides a convenient synthetic route to 1*H*-indole-2-carbaldehydes in 70−98% yield for a wide variety of substrates under mild conditions. By lowering the reaction temperature, the transformation could also be halted at the

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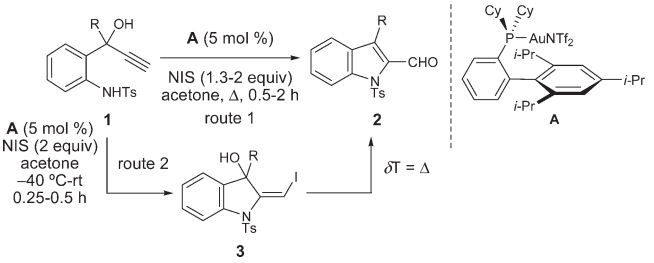
Scheme 1. Gold(I)-Catalyzed Cycloisomerization Reactions of 2-Tosylaminophenylprop-1-yn-3-ols with NIS (Cy = Cyclohexane)

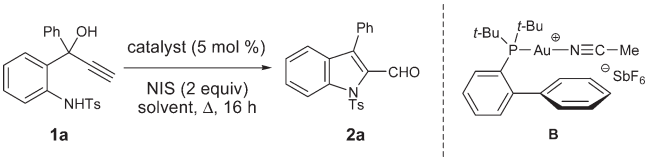


iododeauration step to afford the (*E*)-2-(iodomethylene)indolin-3-ol adduct (Scheme 1, route 2).

RESULTS AND DISCUSSION

To test the feasibility of our hypothesis, the propargylic alcohol **1a** was prepared and treated with a variety of gold catalysts and NIS to establish the reaction conditions (Table 1). This initially revealed treatment of **1a** with 5 mol % of the Au(I) complex **A** and 2 equiv of NIS in toluene at reflux for 3 h afforded **2a** in 90% yield (entry 1). Our studies subsequently showed that a further increase of 8% in product yield could be achieved when the reaction was repeated in acetone in place of toluene (entry 2). On the other hand, lower product yields (62−85%) were obtained on employing chlorinated solvents such as CH_2Cl_2 and 1,2-dichloroethane or decreasing the amount of NIS employed from 2 to 1.3 equiv (entries 3−5). Similarly, a survey of other Lewis acidic gold catalysts was found to give **2a** in lower yields of 72−85% (entries 6−8). More notably, the near-quantitative recovery of the starting alcohol when the reaction was carried out in the absence of the gold catalyst demonstrated that NIS alone could not effect the indole forming process (entry 9). Likewise, molecular iodine, reported to promote the intramolecular cyclization of substituted 2-alkynylanilines to 2-acyl-1*H*-indoles and quinolines, was found to be ineffective (entry 10).[10] On the basis of the above results, reaction of **1a** in the presence of 2 equiv of NIS in acetone at reflux for 2 h was deemed to provide the optimal conditions.

Table 1. Optimization of the Reaction Conditions[a]



entry	catalyst	solvent	yield (%)
1[b]	**A**	toluene	90
2[c]	**A**	acetone	98
3[d]	**A**	acetone	85
4	**A**	CH_2Cl_2	62
5	**A**	$(CH_2Cl)_2$	72
6	**B**	acetone	85
7[e]	$Ph_3PAuNTf_2$	acetone	82
8	AuCl/AgOTf	acetone	72
9	*f*	acetone	*g*
10	I_2	acetone	*g*

[a] Unless otherwise stated, all reactions were performed at reflux for 16 h with catalyst/**1a**/NIS ratio = 1:20:40. [b] Reaction time = 3 h. [c] Reaction time = 2 h. [d] Reaction performed with 1.3 equiv of NIS for 18 h. [e] Reaction time = 6 h. [f] Reaction conducted in the absence of a gold catalyst at room temperature. [g] Recovery of **1a** in near quantitative yield.

Having established the reaction conditions, we next sought to define the scope of the present procedure to a variety of terminal propargylic alcohols, and the results are summarized in Table 2. In general, these experiments showed the reaction conditions to be broad, providing a variety of substituted indole-2-carbaldehydes in good to excellent yields. Substrates containing an electron-donating group on the aniline ring were found to be well tolerated and afforded the corresponding products **2b** and **2c** in good yields of 75 and 70%, respectively. Similarly, reaction of starting alcohols with an embedded naphthalene ring moiety as in **1g** and **1l** were found to proceed well, furnishing **2g** and **2l** in 78 and 90% yield, respectively. Indole-2-carbaldehydes **2h**−**k** with a pendant electron-donating or electron-withdrawing group at the C-3 position were also obtained in excellent yields of 82−88% from the corresponding propargylic alcohols **1h**−**k**. In contrast, no product formation was observed for reactions of substrates **1d** and **1e** containing an electron-withdrawing group on the aniline ring, even when the reaction time was extended to 18 h. In these reactions, only the *trans*-iodomethylene adducts **3d** and **3e** were obtained in 98 and 96% yields, respectively. The *o*,*p*-dimethylaniline alcohol **1f** was also found to proceed less well under the standard reaction conditions, giving a mixture of decomposition products based on TLC and ^{1}H NMR analysis of the crude mixture. On the other hand, reactions of alcohols **1m**−**p** with a pendent alkyl or thiophene group on the carbinol carbon were found to rapidly give the corresponding products **2m**−**p** in yields of 78−84% at room temperature. Reaction of the secondary alcohol **1q** was also shown to work well to produce **2q** in 72% yield at room temperature and with 1.3 equiv of NIS. The more reactive nature of these latter substrates was further underlined by repeating the reactions under the optimal conditions and finding only a variety of byproducts that could not be identified based on TLC and ^{1}H NMR analysis of the crude mixtures.

With the reaction conditions to indole-2-carbaldehydes established, we then proceeded to examine the scope of this new methodology for (*E*)-2-(iodomethylene)indolin-3-ol synthesis (Table 3). Based on the rationale illustrated in Scheme 1, we anticipated such control in product chemoselectivity could be achieved by simply conducting the cycloisomerization process at a lower temperature. With this in mind, we first tested the reaction of **1a** with 5 mol % of **A** under the standard conditions at room temperature and found that (*E*)-**3a** could be obtained as the sole product in near quantitative yield. Under similar conditions, repeating the reaction with **1d**,**e**,**j**,**g**,**h**,**o**,**q** as representative examples gave the corresponding (*E*)-indolin-3-ol products **3d**,**e**,**j**,**g**,**h**,**o**,**q** in excellent yields of 80−99% yield. In these latter reactions, the *trans* stereochemistry and structure of the indolin-3-ol products were determined on the basis of X-ray crystal structure analysis of **3e** (see Figure S40 in the Supporting Information).[11] Additionally, no other side products were detected by TLC and ^{1}H NMR analysis of the crude mixtures.

A tentative mechanism for the present Au(I)-catalyzed indole forming reaction is outlined in Scheme 2. This could involve activation of the alkyne moiety of **1** by the gold catalyst that results in cyclization of the pendant aniline group to the alkyne

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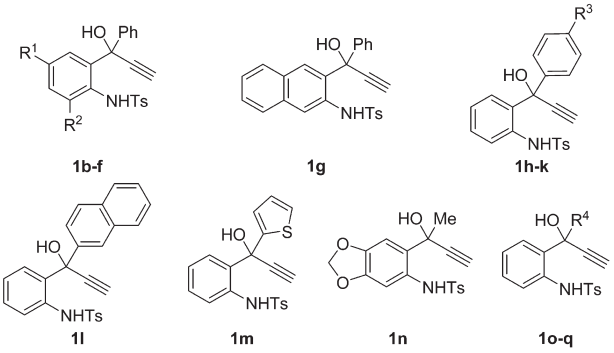
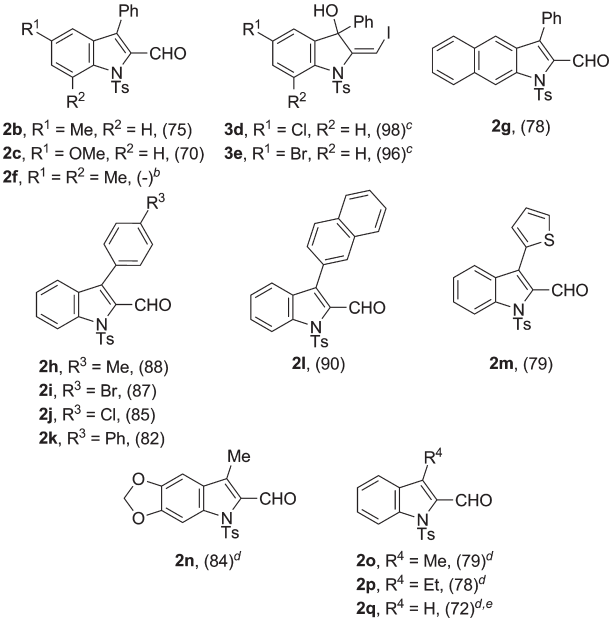
Table 2. Tandem Cycloisomerization/Formylation of 2-Tosylaminophenylprop-1-yn-3-ols 1b−q Catalyzed by A[a]

substrate



product

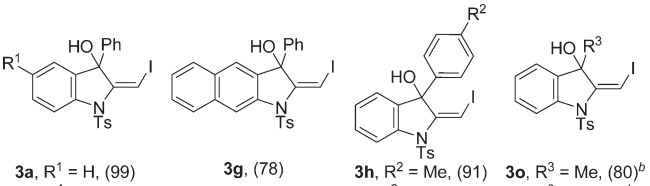


[a] Unless otherwise stated, all reactions were performed at reflux for 2 h with **A**/**1**/NIS ratio = 1:20:40. Values in parentheses denote product yields. [b] Mixture of unknown side products based on ^{1}H NMR analysis of the crude reaction mixture. [c] Reaction time = 18 h. [d] Reaction performed at room temperature for 0.5 h. [e] Reaction performed with 1.3 equiv of NIS.

moiety and formation of the putative vinyl gold species **I**. Iododeauration of this newly formed organogold intermediate with NIS then delivers **3**, which can rapidly undergo Au(I)-mediated 1,3-AAI when the reaction is carried out at reflux. This gives the iodomethanol intermediate **II** that subsequently eliminates HI to provide **2**.

To demonstrate that **3** is the actual intermediate that leads to the formation of **2**, we first examined the reaction of **3a** to 5 mol % of **A** in acetone at reflux for 2 h. This afforded **2a** in 98% yield, which is the same as that directly furnished from **1a** as described in entry 2 in Table 1. The role of the gold catalyst in facilitating the 1,3-AAI step could also be shown by repeating the reaction in the absence of the catalyst, which gave only recovery of the starting iodide in near quantitative yield. The premise that the isomerization occurs in an intramolecular manner was supported by our findings for the reactions of **1a** in the presence of 5 mol %

Table 3. Synthesis of (*E*)-2-(Iodomethylene)indolin-3-ols 3a,d−e,j,g−h,o,q[a]



[a] Unless otherwise stated, all reactions were performed at room temperature for 0.25 h with **A**/**1**/NIS ratio = 1:20:40. Values in parentheses denote product yields. [b] Reaction performed at −40 °C. [c] Reaction performed with 1.3 equiv of NIS.

Scheme 2. Proposed Mechanism

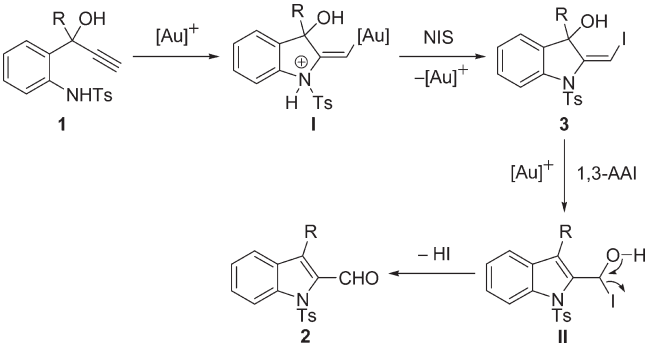
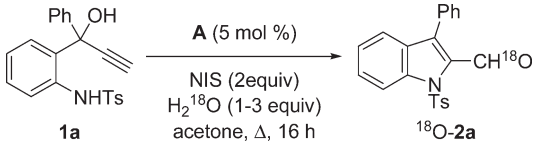


Table 4. Gold(I)-Catalyzed Reactions of 1a with NIS in the Presence of $H_2{}^{18}O$[a]



$H_2{}^{18}O$ (equiv)	yield (%)	^{18}O incorporation (%)
1	96	0
3	93	11

[a] All reactions were performed at reflux for 16 h with **A**/**1**/NIS ratio = 1:20:40 and 1−3 equiv of $H_2{}^{18}O$ in acetone.

of **A** and 1 or 3 equiv of $H_2{}^{18}O$ (Table 4). These latter experiments showed that there was either no or only 11% ^{18}O incorporation in the respective aldehydes obtained on the basis of LCMS analysis of the crude reaction mixtures. Our previous finding showing **3d** and **3e** could only be obtained additionally hints to the possibility that the rearrangement could be cationic in nature since such a process may not be expected to be favorable in substrates with an electron-withdrawing group.

CONCLUSION

In summary, we have described a mild method for the prepartion of 1*H*-indole-2-carbaldehydes and (*E*)-2-(iodomethylene)indolin-3-ols. The attractiveness of the synthetic approach lies in the fact

that both the indole ring and aldehyde or vinyl iodide moiety are sequentially formed from cycloisomerization of a common alcoholic substrate. The reactions are also operationally simplistic and rapid and can make use of a wide variety of starting alcohols and a catalytic system that are readily available and ecologically benign.

EXPERIMENTAL SECTION

General Remarks. All reactions were performed under an argon atmosphere. 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 plate. Visualization was achieved by UV light (254 nm). Flash chromatography was performed using silica gel and gradient solvent system (*n*-hexane/EtOAc as eluent). ^{1}H and ^{13}C NMR spectra were measured on 300, 400, and 500 MHz spectrometers. Chemical shifts (ppm) were recorded with tetramethylsilane (TMS) as the internal reference standard. Multiplicities are given as follows: s (singlet), brs (broad singlet), d (doublet), t (triplet), dd (doublet of doublets), q (quartet), 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 (Hz). Infrared spectra were recorded on an FTIR spectrometer. Solid samples were examined as a thin film between NaCl salt plates. 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 on a LC/HRMS mass spectrometer.

General Procedure for the Synthesis of Propargylic Alcohols 1a−l,n,o,q. To a solution of the appropriate 1-(2-aminophenyl)ketone or aldehyde (1.1 mmol) in pyridine (0.4 mL) was added *p*-TsCl (1.6 mmol) at room temperature. The resulting solution was stirred for 4 h at room temperature. On completion, the reaction mixture was quenched by addition of H_2O (5 mL) and filtered. The resulting solid was dried and then used directly for the next step. The solid (0.51 mmol) was dissolved in anhydrous THF (8 mL), and a solution of ethynylmagnesium bromide (0.5 M THF solution; 1.5 mmol) was added at room temperature. The resulting mixture was allowed to reflux for 3 h. On completion, the reaction mixture was cooled to room temperature and treated with saturated NH_4Cl (7 mL). After additional stirring at room temperature for 10 min, EtOAc (15 mL) was added, and the phases were separated. The aqueous phase was extracted with EtOAc (3 × 5 mL), and the combined organic layers were washed with brine solution, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. Purification by flash column chromatography on silica gel (eluent: *n*-hexane/EtOAc = 9:1) gave the title compound.

Procedure for the Synthesis of Propargylic Alcohols 1m and 1p. To a solution of **1q** (0.66 mmol) in CH_2Cl_2 (5 mL) was added MnO_2 (9.9 mmol) at room temperature. The resulting mixture was stirred for 3 h at reflux temperature. On completion, the reaction mixture was cooled to room temperature and filtered through a Celite pad. The resulting solvent (filterate) was removed under reduced pressure gave the ketone derivative of **1q**, which was used directly for the next step without purification. For the synthesis of **1m**, 2-thienyllithium (1 M solution in THF, 0.5 mmol) was slowly added to a solution of the ketone (0.16 mmol) in anhydrous THF (3 mL) at −78 °C; the reaction mixture was then stirred at −78 °C for 2 h and a further 1 h at room temperature. For the synthesis of **1p**, ethylmagnesium bromide (1 M THF solution, 0.5 mmol) in place of 2-thienyllithium was added at room temperature, and the reaction mixture was refluxed for 3 h. On completion, the reaction mixture was quenched by addition of saturated NH_4Cl (10 mL) at room temperature. After additional stirring at room temperature for 10 min, EtOAc (15 mL) was added, and the phases were separated. The aqueous phase was extracted with EtOAc (3 × 5 mL), and the combined organic layers were washed with brine solution, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. Purification by flash column chromatography on silica gel (eluent: *n*-hexane/EtOAc = 10:1) gave the title compound.

General Procedure for Optimizing the Lewis Acid Catalyzed Cycloisomerization of 1-Phenyl-1-(2-(tosylamino)phenyl)prop-2-yn-1-ol (1a). For reactions with a gold/silver catalyst combination, the gold (13.2 μmol) and silver (13.2 μmol) catalysts were first stirred in the respective solvent (1 mL) at room temperature for 10 min. In all other cases, the catalyst was added to a respective solvent prior to adding the starting materials. A solution of NIS (0.52 mmol) in acetone (0.5 mL) was then added and stirred for another 10 min at room temperature followed by slow dropwise addition of a solution of **1a** (0.26 mmol) in acetone (1 mL). The resultant reaction mixture was stirred at reflux and monitored to completion by TLC analysis. On cooling to room temperature, the solvent was removed under reduced pressure, and the residue obtained was purified by flash column chromatography on silica gel (eluent: *n*-hexane/EtOAc = 24:1) to give **2a**.

General Procedure for Gold(I)-Catalyzed Cycloisomerization of 1-(2-(Tosylamino)phenyl)prop-2-yn-1-ol (1). To a solution of the gold(I) complex **A** (13.2 μmol) in acetone (1 mL) was added a solution of NIS (0.52 mmol) in acetone (0.5 mL) and stirred for 10 min at room temperature. A solution of **1** (0.26 mmol) in acetone (1 mL) was then added slowly dropwise, and the reaction mixture was stirred at reflux and monitored by TLC analysis (note: for compounds **2n**−**q** the reaction was performed at room temperature for 0.5 h). On completion, the reaction mixture was quenched by addition of 10% $Na_2S_2O_3 \cdot 5H_2O$ (5 mL) at room temperature and extracted with EtOAc (2 × 10 mL). The combined organic layers were washed with brine, dried over Mg_2SO_4, and concentrated under reduced pressure. Purification by flash column chromatography on silica gel (*n*-hexane/EtOAc 24:1 as eluent) gave the indole-2-carbaldehyde product **2**.

General Procedure for Gold(I)-Catalyzed Cycloisomerization of Propargylic Alcohols 1a,d,e,j,g−h,o,q. To a solution of the gold(I) complex **A** (13.2 μmol) in acetone (1 mL) was added a solution of NIS (0.52 mmol) in acetone (0.5 mL) and stirred for 10 min at room temperature (note: for reactions with **1o** and **1q**, the resulting mixture was cooled to −40 °C and 0.34 mmol of NIS was added for **1q**). A solution of **1** (0.26 mmol) in acetone (1 mL) was then added slowly dropwise, and the reaction mixture was stirred at room temperature (or −40 °C for **1o** and **1q**) and monitored by TLC analysis. On completion, the reaction mixture was quenched by adding 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 Mg_2SO_4, and concentrated under reduced pressure. Purification by flash column chromatography on silica gel (*n*-hexane/EtOAc 24:1 as eluent) gave the product **3**.

Procedure for Gold(I)-Catalyzed Cycloisomerization of 1-Phenyl-1-(2-(tosylamino)phenyl)prop-2-yn-1-ol (1a) in the Presence of $H_2{}^{18}O$. To a solution of the gold(I) catalyst **A** (13.2 μmol) in acetone (1 mL) was added a solution of NIS (0.52 mmol) in acetone (0.5 mL) and the mixture stirred for 10 min at room temperature. $H_2{}^{18}O$ (1 or 3 equiv). A solution of **1a** (0.26 mmol) in acetone (1 mL) was then added slowly dropwise and the reaction mixture stirred at reflux and monitored by TLC analysis. On completion, the reaction mixture was quenched by adding 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 Mg_2SO_4, and concentrated under reduced pressure. Purification by flash column chromatography on silica gel (*n*-hexane/EtOAc 24:1 as eluent) gave the indole-2-carbaldehyde product ^{18}O-**2a**.

*1-Phenyl-1-(2-(tosylamino)phenyl)prop-2-yn-1-ol (**1a**)*:[4a] yield 89%; yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.47 (1H, brs), 7.54 (1H, dd, *J* = 8.32, 12.4 Hz), 7.38 (2H, d, *J* = 6.6 Hz), 7.29−7.36 (5H, m), 7.21 (1H, d, *J* = 7.5 Hz), 7.05 (2H, d, *J* = 8.0 Hz), 6.98 (1H, t, *J* = 7.6 Hz) 3.22 (1H, brs), 2.90 (1H, s), 2.33 (3H, s); ^{13}C NMR

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($CDCl_3$, 100 MHz) δ 143.4, 142.2, 136.3, 135.8, 130.1, 129.6, 129.4, 128.8, 128.7, 128.3, 127.3, 125.8, 122.8, 119.0, 84.4, 77.8, 74.9, 21.5.

1-(5-Methyl-2-(tosylamino)phenyl)-1-phenylprop-2-yn-1-ol (**1b**): yield 82%; yellow solid; mp 136−139 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.46 (1H, brs), 7.43 (1H, d, J = 8.3 Hz), 7.24−7.36 (8H, m), 7.00 (3H, dd, J = 6.9 Hz, J = 7.7 Hz), 3.77 (1H, s), 2.87 (1H, s), 2.31 (3H, s), 2.24 (3H, s); ^{13}C NMR ($CDCl_3$,100 MHz) δ 143.3, 142.5, 136.4, 133.2, 132.6, 130.3, 130.1, 129.5, 129.4, 128.7, 128.2, 127.4, 125.9, 119.3, 84.7, 77.6, 74.9, 21.5, 20.9; IR (NaCl, neat) ν 3419, 3305, 3022, 2113, 1647, 1635, 1498, 1392, 1330, 1157, 1091, 844, 813 cm^{-1}; MS (ESI) m/z 414 [M + Na]$^+$; HRMS (ESI) calcd for $C_{23}H_{21}NO_3SNa$ (M^+ + Na) 414.1140, found 414.1143.

1-(5-Methoxy-2-(tosylamino)phenyl)-1-phenylprop-2-yn-1-ol (**1c**): yield 75%; brown solid; mp 144−146 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.05 (1H, brs), 7.49 (1H, d, J = 8.8 Hz), 7.26−7.40 (8H, m), 7.14 (1H, d, J = 2.8 Hz), 7.06 (2H, d, J = 8.8 Hz), 6.76 (1H, dd, J = 2.8 Hz, J = 8.9 Hz), 3.73 (3H, s), 3.30 (1H, s), 2.87 (1H, s), 2.35 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 155.4, 143.3, 142.2, 136.5, 132.7, 129.4, 128.7, 128.6, 128.3, 127.3, 125.8, 121.6, 115.4, 113.7, 84.6, 77.5, 74.7, 55.4, 21.5; IR (NaCl, neat) ν 3392, 3292, 3020, 2113, 1153, 1089, 1035, 844, 812 cm^{-1}; MS (ESI) m/z 430 [M + Na]$^+$; HRMS (ESI) calcd for $C_{23}H_{21}NO_4SNa$ (M^+ + Na) 430.1089, found 430.1082.

1-(5-Chloro-2-(tosylamino)phenyl)-1-phenylprop-2-yn-1-ol (**1d**): yield 84%; yellow solid; mp 152−154 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.52 (1H, brs), 7.57 (1H, s), 7.49 (1H, d, J = 8.5 Hz), 7.16−7.36 (8H, m), 7.03 (2H, d, J = 7.3 Hz), 3.80 (1H, s), 2.91 (1H, s), 2.33 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.7, 141.6, 135.8, 134.4, 131.9, 129.5, 129.4, 128.8, 128.7, 128.6, 128.3, 127.3, 125.8, 120.2, 83.8, 78.3, 74.4, 21.5; IR (NaCl, neat) ν 3406, 3302, 3018, 2113, 1637, 1485, 1332, 1157, 1089, 813 cm^{-1}; MS (ESI) m/z 434 [M + Na]$^+$; HRMS (ESI) calcd for $C_{22}H_{18}ClNO_3SNa$ (M^+ + Na) 434.0594, found 434.0598.

1-(5-Bromo-2-(tosylamino)phenyl)-1-phenylprop-2-yn-1-ol (**1e**): yield 79%; white solid; mp 164−166 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.46 (1H, brs), 7.72 (1H, d, J = 2.1 Hz), 7.44 (1H, d, J = 8.8 Hz), 7.26−7.38 (8H, m), 7.04 (2H, d, J = 8.1 Hz), 3.58 (1H, s), 2.93 (1H, s), 2.34 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 143.8, 141.5, 135.8, 135.0, 132.5, 132.1, 131.5, 129.5, 128.9, 128.6, 127.4, 125.8, 120.5, 115.8, 83.8, 78.4, 74.4, 21.5; IR (NaCl, neat) ν 3406, 3292, 3018, 2113, 1595, 1481, 1382, 1321, 1153, 1087, 883, 819 cm^{-1}; MS (ESI) m/z 478 [M + Na]$^+$; HRMS (ESI) calcd for $C_{22}H_{18}BrNO_3SNa$ (M^+ + Na) 478.0088, found 478.0082.

1-(3,5-Dimethyl-2-(tosylamino)phenyl)-1-phenylprop-2-yn-1-ol (**1f**): yield 77%; white solid; mp 74−78 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.65 (2H, d, J = 8.3 Hz), 7.49 (2H, dd, J = 1.8 Hz, J = 8.2 Hz), 7.30−7.37 (3H, m), 7.21 (3H, d, J = 8.1 Hz), 7.02 (1H, brs), 6.96 (1H, s), 4.48 (1H, s), 2.90 (1H, s), 2.40 (3H, s), 2.23 (3H, s), 1.86 (3H, s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 143.8, 143.6, 139.7, 138.1, 138.0, 136.6, 132.7, 130.2, 129.5, 128.6, 128.4, 128.1, 127.3, 126.3, 86.3, 77.5, 74.4, 21.6, 21.1, 19.5; IR (NaCl, neat) ν 3419, 3302, 3020, 2112, 1637, 1473, 1381, 1321, 1155, 1091, 813 cm^{-1}; MS (ESI) m/z 428 [M + Na]$^+$; HRMS (ESI) calcd for $C_{24}H_{23}NO_3SNa$ (M^+ + Na) 428.1296, found 428.1290.

1-Phenyl-1-(2-(tosylamino)naphthalen-3-yl)prop-2-yn-1-ol (**1g**): yield 83%; yellow solid; mp 200−203 °C; ^{1}H NMR ($(CD_3)_2CO$, 400 MHz) δ 9.18 (1H, brs), 8.30 (1H s), 7.97 (1H, s), 7.76 (2H, dd, J = 8.2 Hz, J = 12.7 Hz), 7.43−7.46 (3H, m), 7.31−7.39 (6H, m), 7.07 (2H, dd, J = 8.1 Hz), 3.59 (1H, s), 3.06 (1H, s), 2.22 (3H, s); ^{13}C NMR ($(CD_3)_2CO$, 100 MHz) δ 143.7, 143.3, 136.2, 134.0, 133.6, 131.0, 129.5, 128.9, 128.7, 128.5, 128.1, 128.0, 127.5, 127.3, 126.7, 125.7, 125.3, 114.2, 85.0, 78.5, 74.6, 20.5; IR (NaCl, neat) ν 3381, 3294, 3018, 2117, 1633, 1469, 1336, 1155, 1089, 891, 869 cm^{-1}; MS (ESI) m/z 450 [M + Na]$^+$; HRMS (ESI) calcd for $C_{26}H_{21}NO_3SNa$ (M^+ + Na) 450.1140, found 450.1144.

1-p-Tolyl-1-(2-(tosylamino)phenyl)prop-2-yn-1-ol (**1h**):[4a] yield 80%; yellow gum; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.49 (1H, brs), 7.50 (1H, d, J = 7.5 Hz), 7.47 (1H, dd, J = 1.4 Hz, 7.9 Hz), 7.27 (2H, d, J = 8.3 Hz), 7.18−7.12 (3H, m), 7.01 (2H, d, J = 8.1 Hz), 6.97 (2H, d, J = 8.2 Hz), 6.92−6.89 (1H, m), 2.78 (1H, s), 2.29 (3H, s), 2.25 (3H, s); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 143.3, 139.4, 138.1, 136.4, 135.8, 130.2, 129.5, 129.3, 128.8, 127.3, 125.7, 122.8, 119.0, 84.6, 77.5, 74.8, 21.5, 21.2.

1-(4-Bromophenyl)-1-(2-(tosylamino)phenyl)prop-2-yn-1-ol (**1i**): yield 87%; brown solid; mp 162−164 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.43 (1H, brs), 7.71 (1H, d, J = 8.2 Hz), 7.65 (1H, d, J = 7.8 Hz), 7.27 (4H, m), 7.14 (2H, d, J = 8.5 Hz), 7.07 (3H, d, J = 8.4 Hz), 3.48 (1H, s), 2.93 (1H, s), 2.36 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 143.6, 141.4, 136.3, 135.9, 131.7, 130.0, 129.6, 129.4, 128.9, 127.3, 127.0, 123.1, 122.6, 119.4, 84.0, 78.3, 74.6, 21.6; IR (NaCl, neat) ν 3437, 3304, 3018, 2113, 1637, 1492, 1396, 1328, 1159, 1091, 891, 819 cm^{-1}; MS (ESI) m/z 478 [M + Na]$^+$; HRMS (ESI) calcd for $C_{22}H_{18}BrNO_3SNa$ (M^+ + Na) 478.0088, found 478.0082.

1-(4-Chlorophenyl)-1-(2-(tosylamino)phenyl)prop-2-yn-1-ol (**1j**): yield 82%; yellow solid; mp 169−171 °C; ^{1}H NMR ($(CD_3)_2CO$, 300 MHz) δ 9.02 (1H, brs), 7.71 (1H, dd, J = 1.5 Hz, J = 3.8 Hz), 7.68 (1H, dd, J = 1.6 Hz, J = 4.3 Hz), 7.34 (2H, d, J = 8.3 Hz), 7.32 (1H, d, J = 1.8 Hz), 7.27 (4H, d, J = 5.9 Hz), 7.14 (2H, d, J = 8.0 Hz), 7.03 (1H, td, J = 1.2 Hz, J = 7.7 Hz), 3.52 (1H, s), 2.33 (3H, s); ^{13}C NMR ($(CD_3)_2CO$, 75 MHz) δ 143.7, 142.6, 136.7, 136.3, 133.4, 130.3, 129.5, 129.4, 128.9, 128.4, 127.3, 126.9, 122.7, 118.4, 84.6, 78.5, 74.1, 20.7; IR (NaCl, neat) ν 3435, 3292, 3018, 2113, 1490, 1396, 1328, 1159, 1091, 893, 821 cm^{-1}; MS (ESI) m/z 434 [M + Na]$^+$; HRMS (ESI) calcd for $C_{22}H_{18}ClNO_3S$-Na (M^+ + Na) 434.0594, found 434.0601.

1-(Biphenyl-4-yl)-1-(2-(tosylamino)phenyl)prop-2-yn-1-ol (**1k**): yield 79%; white solid; mp 145−147 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.55 (1H, brs), 7.65 (2H, d, J = 8.3 Hz), 7.61 (2H, d, J = 3.5 Hz), 7.34−7.59 (9H, m), 7.24 (1H, dd, J = 1.5 Hz, J = 8.7 Hz), 7.01−7.06 (1H, m), 6.95 (2H, d, J = 8.1 Hz), 3.41 (1H, s), 2.93 (1H, s), 2.19 (3H, s); ^{13}C NMR ($(CD_3)_2CO$, 75 MHz) δ 143.5, 142.7, 140.4, 140.1, 136.7, 136.4, 130.6, 129.4, 129.3, 129.0, 127.6, 127.1, 126.9, 126.8, 126.2, 122.5, 118.0, 85.0, 78.1, 74.5, 20.4; IR (NaCl, neat) ν 3419, 3032, 2113, 1490, 1330, 1157, 1089, 837, 812 cm^{-1}; MS (ESI) m/z 476 [M + Na]$^+$; HRMS (ESI) calcd for $C_{28}H_{23}NO_3SNa$ (M^+ + Na) 476.1296, found 476.1292.

1-(Naphthalen-2-yl)-1-(2-(tosylamino)phenyl)prop-2-yn-1-ol (**1l**): yield 73%; white solid; mp 145−151 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.64 (1H, brs), 7.80 (2H, d, J = 6.3 Hz), 7.69 (4H, dd, J = 7.5 Hz, J = 8.7 Hz), 7.47−7.68 (2H, m), 7.34 (1H, dd, J = 1.9 Hz, J = 8.7 Hz), 7.28 (1H, dd, J = 1.5 Hz, J = 7.5 Hz), 7.06 (2H, d, J = 8.3 Hz), 7.02 (1H, dd, J = 0.9 Hz, J = 7.6 Hz), 6.57 (2H, d, J = 8.1 Hz), 3.67 (1H, s), 2.93 (1H, s), 2.15 (3H, s); ^{13}C NMR ($(CD_3)_2CO$, 75 MHz) δ 143.3, 140.9, 136.4, 136.3, 133.1, 133.0, 130.6, 129.3, 129.1, 129.0, 128.4, 128.3, 127.6, 126.8, 126.5, 124.0, 123.9, 122.6, 118.1, 84.9, 78.4, 74.6, 20.5; IR (NaCl, neat) ν 3414, 3304, 3026, 2115, 1647, 1490, 1398, 1332, 1157, 1089, 896, 812 cm^{-1}; MS (ESI) m/z 450 [M + Na]$^+$; HRMS (ESI) calcd for $C_{26}H_{21}NO_3SNa$ (M^+ + Na) 450.1140, found 450.1142.

1-(Thiophene-2-yl)-1-(2-(tosylamino)phenyl)prop-2-yn-1-ol (**1m**): yield 78%; yellow solid; mp 147−150 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.79 (1H, brs), 7.60 (1H, d, J = 8.2 Hz), 7.51−7.46 (3H, m), 7.26−7.20 (2H, m), 7.10 (2H, d, J = 8.0 Hz), 6.99 (1H, t, J = 7.6 Hz), 6.84−6.78 (2H, m), 4.15 (1H, s), 2.87 (1H, s), 2.31 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 147.1, 143.5, 136.4, 135.9, 129.8, 129.7, 129.5, 128.4, 127.3, 126.8, 126.7, 126.1, 123.0, 119.1, 83.9, 77.1, 72.8, 21.5; IR (NaCl, neat) ν 3392, 3288, 1635, 1583, 1494, 1371, 1278, 1157, 1087, 1051, 964 cm^{-1}; MS (ESI) m/z 406 [M + Na]$^+$; HRMS (ESI) calcd for $C_{20}H_{17}NO_3S_2Na$ (M^+ + Na) 406.0548, found 406.0545.

2-(5-(Tosylamino)benzo[d][1,3]dioxol-6-yl)but-3-yn-2-ol (**1n**): yield 90%; yellow solid; mp 130−133 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.97 (1H, brs), 7.72 (2H, d, J = 8.4 Hz), 7.24 (2H, d, J = 8.1 Hz), 7.12 (1H, s), 7.03 (1H, s), 5.90 (2H, s), 3.54 (1H, brs), 2.68 (1H, s), 2.36

(3H, s), 1.54 (3H, s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 147.7, 143.8, 143.8, 136.9, 129.8, 129.6, 127.2, 125.0, 107.3, 102.6, 101.6, 85.8, 74.5, 71.2, 31.3, 21.5; IR (NaCl, neat) ν 3441, 3020, 1627, 1598, 1506, 1487, 1350, 1290, 1253, 1157, 1091, 1041 cm^{-1}; MS (ESI) m/z 360 $[M + H]^+$; HRMS (ESI) calcd for $C_{18}H_{18}NO_5S$ (M^+ + H) 360.0906, found 360.0917.

2-(2-(Tosylamino)phenyl)but-3-yn-2-ol (***1o***). yield 93%; white solid; mp 107−109 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.19 (1H, brs), 7.73 (2H, d, J = 8.3 Hz), 7.53 (2H, d, J = 8.0 Hz), 7.20 (3H, d, J = 8.3 Hz), 6.97 (1H, td, J = 1.0 Hz, J = 7.7 Hz), 3.62 (1H, s), 2.69 (1H, s), 2.34 (3H, s), 1.67 (3H, s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 143.8, 137.0, 135.6, 130.9, 129.7, 129.1, 127.3, 127.2, 123.5, 119.9, 85.7, 74.7, 71.6, 31.2, 21.5; IR (NaCl, neat) ν 3498, 3307, 3028, 2115, 1635, 1600, 1496, 1375, 1332, 1159, 1091, 871, 813 cm^{-1}; MS (ESI) m/z 338 $[M + Na]^+$; HRMS (ESI) calcd for $C_{17}H_{17}NO_3SNa$ (M^+ + Na) 338.0827, found 338.0830.

3-(2-(Tosylamino)phenyl)pent-1-yn-3-ol (***1p***): yield 55%; yellow solid; mp 125−128 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 9.09 (1H, brs), 7.73 (2H, d, J = 6.8 Hz), 7.60 (1H, dd, J = 1.0 Hz, 8.25 Hz), 7.55 (1H, dd, J = 1.5 Hz, 7.9 Hz), 7.23−7.19 (3H, m), 7.01−6.98 (1H, td, J = 1.1 Hz, 7.75 Hz), 3.26 (1H, brs), 2.76 (1H, s), 2.35 (3H, s), 1.28−1.75 (1H, m), 1.69−1.61 (1H, m), 0.75 (3H, t, J = 7.4 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 143.7, 137.5, 135.6, 129.7, 129.6, 129.0, 128.6, 127.1, 123.3, 120.3, 84.3, 76.4, 76.1, 35.6, 21.4, 8.9; IR (NaCl, neat) ν 3423, 3302, 1635, 1598, 1492, 1338, 1288, 1271, 1161, 1091, 1058, 933 cm^{-1}; MS (ESI) m/z 352 $[M + Na]^+$; HRMS (ESI) calcd for $C_{18}H_{19}NO_3SNa$ (M^+ + Na) 352.0983, found 352.0990.

1-(2-(Tosylamino)phenyl)prop-2-yn-1-ol (***1q***): yield 90%; yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.92 (1H, brs), 7.66 (2H, d, J = 8.0 Hz), 7.52 (1H, d, J = 7.6 Hz), 7.32 (2H, d, J = 8.0 Hz), 7.24 (2H, dd, J = 8.0 Hz, J = 13.2 Hz), 7.13 (1H, t, J = 7.6 Hz), 5.33 (1H, d, J = 2.4 Hz), 3.61 (1H, brs), 2.64 (1H, d, J = 2.0 Hz), 2.35 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 144.1, 136.5, 135.2, 131.4, 129.7, 129.6, 128.4, 127.3, 125.6, 123.4, 81.6, 76.4, 62.3, 21.6; IR (NaCl, neat) ν 3423, 3302, 3020, 2121, 1635, 1492, 1400, 1328, 1159, 1091, 833, 813 cm^{-1}; MS (ESI) m/z 324 $[M + Na]^+$; HRMS (ESI) calcd for $C_{16}H_{15}NO_3SNa$ (M^+ + Na) 324.0670, found 324.0671.

3-Phenyl-1-tosyl-1H-indole-2-carbaldehyde (***2a***): yellow solid; mp 147−150 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 10.22 (1H, s), 8.30 (1H, d, J = 8.5 Hz), 7.83 (2H, d, J = 8.3 Hz), 7.52−7.58 (2H, m), 7.45 (5H, m), 7.26 (1H, m), 7.24 (2H, d, J = 6.5 Hz), 2.36 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 182.4, 145.3, 138.2, 135.8, 135.2, 132.5, 130.5, 130.4, 129.7, 129.3, 129.2, 129.0, 128.4, 127.2, 124.6, 122.6, 115.7, 21.7; IR (NaCl, neat) ν 3064, 3030, 2920, 1683, 1598, 1543, 1444, 1369, 1172, 1089, 906, 812 cm^{-1}; MS (ESI) m/z 376 $[M + H]^+$; HRMS (ESI) calcd for $C_{22}H_{18}NO_3S$ (M^+ + H) 376.1007, found 376.1006.

5-Methyl-3-phenyl-1-tosyl-1H-indole-2-carbaldehyde (***2b***): yellow gum; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 10.21 (1H, s), 8.17 (1H, d, J = 8.6 Hz), 7.79 (2H, d, J = 8.2 Hz), 7.45 (5H, m), 7.36 (1H, d, J = 7.0 Hz), 7.22−7.29 (3H, m), 2.38 (3H, s), 2.36 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 182.5, 145.2, 136.5, 135.6, 135.1, 134.6, 132.6, 130.6, 130.5, 129.7, 129.6, 129.5, 129.0, 128.4, 127.2, 122.1, 115.5, 21.7, 21.3; IR (NaCl, neat) ν 3061, 3026, 2922, 1681, 1597, 1543, 1492, 1369, 1172, 1087, 837, 812 cm^{-1}; MS (ESI) m/z 390 $[M + H]^+$; HRMS (ESI) calcd for $C_{23}H_{20}NO_3S$ (M^+ + H) 390.1164, found 390.1166.

5-Methoxy-3-phenyl-1-tosyl-1H-indole-2-carbaldehyde (***2c***): yellow solid; mp 129−132 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 10.23 (1H, s), 8.19 (1H, d, J = 9.2 Hz), 7.76 (2H, d, J = 8.3 Hz), 7.43 (5H, m), 7.22 (2H, d, J = 8.0 Hz), 7.16 (1H, dd, J = 2.6 Hz, J = 9.2 Hz), 6.86 (1H, d, J = 2.4 Hz), 3.76 (3H, s), 2.36 (3H s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 182.6, 157.3, 145.2, 135.4, 134.9, 133.1, 132.8, 130.6, 130.4, 129.7, 128.9, 128.4, 127.1, 119.2, 116.9, 103.4, 55.7, 21.6; IR (NaCl, neat) ν 3020, 2926, 1681, 1597, 1541, 1492, 1371, 1174, 1087, 812 cm^{-1}; MS (ESI) m/z 406 $[M + H]^+$; HRMS (ESI) calcd for $C_{23}H_{20}NO_4S$ (M^+ + H) 406.1113, found 406.1115.

3-Phenyl-1-tosyl-1H-benzo[f]indole-2-carbaldehyde (***2g***): yellow solid; mp 172−175 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 10.33 (1H, s), 8.71 (1H, s), 8.04 (1H, d, J = 8.4 Hz), 7.97 (1H, s), 7.83 (1H, d, J = 8.3 Hz), 7.74 (2H, d, J = 8.3 Hz), 7.44 (7H, m), 7.16 (2H, d, J = 8.2 Hz), 2.30 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 183.0, 145.2, 136.4, 135.7, 134.7, 134.3, 133.8, 131.0, 130.6, 130.2, 130.0, 129.7, 129.2, 128.5, 128.4, 127.2, 126.8, 125.5, 122.1, 113.3, 21.6; IR (NaCl, neat) ν 3030, 2926, 1681, 1593, 1548, 1489, 1363, 1118, 1085, 948, 918, 875, 844, 812 cm^{-1}; MS (ESI) m/z 426 $[M + H]^+$; HRMS (ESI) calcd for $C_{26}H_{20}NO_3S$ (M^+ + H) 426.1164, found 426.1161.

3-p-Tolyl-1-tosyl-1H-indole-2-carbaldehyde (***2h***): yellow solid; mp 147−150 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 10.2 (1H, s), 8.29 (1H, d, J = 8.4 Hz), 7.82 (2H, d, J = 8.4 Hz), 7.52 (2H, d, J = 7.8 Hz), 7.32 (2H, d, J = 8.1 Hz), 7.23 (5H, m), 2.42 (3H, s), 2.36 (3H, s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 182.4, 145.2, 139.0, 138.3, 136.1, 135.2, 132.5, 130.4, 129.7, 129.3, 129.1, 127.2, 124.6, 122.7, 115.7, 79.5, 21.6, 21.4; IR (NaCl, neat) ν 3026, 2922, 1681, 1597, 1544, 1369, 1174, 1089, 920, 812 cm^{-1}; MS (ESI) m/z 390 $[M + H]^+$; HRMS (ESI) calcd for $C_{23}H_{20}NO_3S$ (M^+ + H) 390.1164, found 390.1166.

3-(4-Bromophenyl)-1-tosyl-1H-indole-2-carbaldehyde (***2i***): yellow solid; mp 139−141 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 10.31 (1H, s), 8.29 (1H, d, J = 8.5 Hz), 7.77 (2H, d, J = 8.2 Hz), 7.54 (3H, m), 7.46 (1H, d, J = 7.4 Hz), 7.30 (3H, m), 7.23 (2H, d, J = 8.0 Hz), 2.36 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 182.6, 145.5, 137.8, 134.8, 133.6, 132.4, 132.1, 131.6, 129.8, 129.4, 129.3, 129.1, 127.1, 124.9, 123.3, 122.3, 115.7, 21.7; IR (NaCl, neat) ν 3066, 3020, 2922, 1681, 1595, 1539, 1485, 1371, 1172, 1087, 920, 812 cm^{-1}; MS (ESI) m/z 454 $[M + H]^+$; HRMS (ESI) calcd for $C_{22}H_{17}BrNO_3S$ (M^+ + H): 454.0113, found 454.0115.

3-(4-Chlorophenyl)-1-tosyl-1H-indole-2-carbaldehyde (***2j***): white solid; mp 140−143 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 10.31 (1H, s), 8.29 (1H, d, J = 8.6 Hz), 7.77 (2H, d, J = 8.4 Hz), 7.54 (1H, td, J = 1.2 Hz, J = 8.5 Hz), 7.38−7.49 (5H, m), 7.29 (1H, d, J = 7.9 Hz), 7.23 (1H, d, J = 9.3 Hz), 2.36 (3H, s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 182.6, 162.3, 145.5, 137.8, 135.0, 134.8, 133.6, 132.5, 131.8, 129.8, 129.3, 129.1, 128.9, 128.6, 127.1, 124.9, 122.3, 115.7, 21.7; IR (NaCl, neat) ν 3026, 2922, 1681, 1597, 1541, 1487, 1371, 1174, 1089, 920, 812 cm^{-1}; MS (ESI) m/z 410 $[M + H]^+$; HRMS (ESI) calcd for $C_{22}H_{17}ClNO_3S$ (M^+ + H) 410.0618, found 410.0619.

3-(Biphenyl-4-yl)-1-tosyl-1H-indole-2-carbaldehyde (***2k***): yellow solid; mp 137−140 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 10.28 (1H, s), 8.31 (1H, d, J = 8.4 Hz), 7.82 (2H, d, J = 8.4 Hz), 7.71−7.53 (8H, m), 7.44−7.48 (2H, m), 7.29−7.39 (2H, m), 7.24 (2H, d, J = 8.1 Hz), 2.37 (3H, s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 182.6, 145.3, 141.8, 140.4, 138.2, 135.3, 135.1, 132.5, 131.0, 129.8, 129.2, 128.9, 127.7, 127.2, 127.1, 127.0, 124.7, 122.7, 115.8, 36.6, 24.7, 21.7; IR (NaCl, neat) ν 3066, 3030, 2958, 2924, 1683, 1597, 1544, 1508, 1487, 1444, 1371, 1172, 1089, 921, 846, 812 cm^{-1}; MS (ESI) m/z 452 $[M + H]^+$; HRMS (ESI) calcd for $C_{28}H_{22}NO_3S$ (M^+ + H) 452.1320, found 452.1321.

3-(Naphthalen-2-yl)-1-tosyl-1H-indole-2-carbaldehyde (***2l***): yellow oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 10.27 (1H, s), 8.33 (1H, d, J = 8.5 Hz), 7.85 (6H, m,), 7.50 (5H, m), 7.25 (3H, m), 2.37 (3H, s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 182.5, 145.3, 138.2, 135.7, 135.3, 133.3, 133.0, 132.7, 130.1, 129.8, 129.4, 129.2, 128.2, 128.0, 127.9, 127.8, 127.3, 126.9, 126.6, 124.7, 122.7, 115.8, 76.6, 21.7; IR (NaCl, neat) ν 3055, 3020, 2924, 1676, 1598, 1541, 1442, 1369, 1174, 1089, 962, 925, 862, 812 cm^{-1}; MS (ESI) m/z 426 $[M + H]^+$; HRMS (ESI) calcd for $C_{26}H_{20}NO_3S$ (M^+ + H) 426.1164, found 426.1164.

3-(Thiophen-2-yl)-1-tosyl-1H-indole-2-carbaldehyde (***2m***): colorless gum; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 10.30 (1H, s), 8.29 (1H, d, J = 8.5 Hz), 7.84 (1H, d, J = 8.1 Hz), 7.79 (2H, d, J = 8.2 Hz), 7.58−7.48 (3H, m), 7.36 (1H, t, J = 7.8 Hz), 7.23 (2H, d, J = 8.1 Hz), 7.19 (1H, t, J = 3.9 Hz), 2.35 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 182.1, 145.3, 137.9, 134.8, 131.0, 130.4, 129.7, 129.2, 129.1, 128.3, 127.6, 127.4, 127.2, 124.8, 122.8, 115.6, 21.6; IR (NaCl, neat) ν 3421, 1681, 1598, 1506, 1492, 1444, 1429, 1369, 1172, 1087, 929, 812 cm^{-1}; MS (ESI) m/z 382

$[M + H]^+$; HRMS (ESI) calcd for $C_{20}H_{16}NO_3S_2$ ($M^+ + H$) 382.0572, found 382.0590.

7-Methyl-5-tosyl-5H-[1,3]dioxolo[4,5-f]indole-6-carbaldehyde (**2n**): colorless gum; ^1H NMR ($CDCl_3$, 400 MHz) δ 10.50 (1H, s), 7.71 (1H, s), 7.58 (2H, d, J = 8.2 Hz), 7.19 (2H, d, J = 8.2 Hz), 6.87 (1H, s) 6.07 (2H, s), 2.45 (3H, s), 2.35 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 184.3, 150.3, 146.3, 145.2, 134.2, 133.5, 132.7, 129.8, 126.7, 125.2, 102.0, 99.1, 96.7, 21.6, 10.8; IR (NaCl, neat) ν 3421, 3018, 1656, 1597, 1529, 1460, 1425, 1365, 1332, 1278, 1178, 1087, 1035, 902, 848 cm^{-1}; MS (ESI) m/z 358 $[M + H]^+$; HRMS (ESI) calcd for $C_{18}H_{16}NO_5S$ ($M^+ + H$) 358.0749, found 358.0744.

3-Methyl-1-tosyl-1H-indole-2-carbaldehyde (**2o**): white solid; mp 193−195 °C; ^1H NMR ($CDCl_3$, 300 MHz) δ 10.61 (1H, s), 8.20 (1H, d, J = 8.5 Hz), 7.55 (3H, d, J = 8.2 Hz), 7.50 (1H, dd, J = 1.1 Hz, J = 8.4 Hz), 7.29 (1H, dd, J = 0.7 Hz, J = 7.9 Hz), 7.12 (2H, d, J = 8.1 Hz), 2.51 (3H, s), 2.30 (3H, s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 185.3, 145.3, 137.5, 134.2, 133.0, 132.1, 130.6, 129.8, 129.1, 126.7, 124.6, 121.6, 115.8, 21.6, 10.5; IR (NaCl, neat) ν 3057, 2910, 1672, 1595, 1556, 1490, 1444, 1415, 1363, 1172, 1089, 954, 879, 813 cm^{-1}; MS (ESI) m/z 314 $[M + H]^+$; HRMS (ESI) calcd for $C_{17}H_{16}NO_3S$ ($M^+ + H$) 314.0851, found 314.0853.

3-Ethyl-1-tosyl-1H-indole-2-carbaldehyde (**2p**): colorless gum; ^1H NMR ($CDCl_3$, 400 MHz) δ 10.58 (1H, s), 8.22 (1H, d, J = 8.5 Hz), 7.59−7.49 (4H, m), 7.33 (1H, t, J = 7.5 Hz), 7.14 (2H, d, J = 8.2 Hz), 2.99 (2H, q, J = 7.5 Hz), 2.30 (3H, s), 1.18 (3H, t, J = 7.5 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 184.9, 145.2, 138.4, 137.8, 134.1, 132.3, 129.7, 129.6, 128.9, 126.7, 124.6, 121.4, 116.0, 21.5, 18.1, 14.4; IR (NaCl, neat) ν 3439, 1676, 1597, 1550, 1490, 1444, 1411, 1357, 1172, 1087, 981, 906, 810 cm^{-1}; MS (ESI) m/z 328 $[M + H]^+$; HRMS (ESI) calcd for $C_{18}H_{18}NO_3S$ ($M^+ + H$) 328.1007, found 328.1013.

1-Tosyl-1H-indole-2-carbaldehyde (**2q**):[12] colorless oil; ^1H NMR ($CDCl_3$, 400 MHz) δ 10.53 (1H, s), 8.24 (1H, d, J = 8.6 Hz), 7.66 (2H, d, J = 8.3 Hz), 7.63 (1H, d, J = 8.0 Hz), 7.54 (1H, t, J = 7.8 Hz), 7.46 (1H, s), 7.33 (1H, t, J = 7.6 Hz), 7.20 (2H, d, J = 8.2 Hz), 2.32 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 183.3, 145.6, 138.5, 137.8, 134.6, 129.9, 128.8, 128.2, 126.6, 124.8, 123.6, 118.3, 115.4, 21.5.

(E)-2-(Iodomethylene)-3-phenyl-1-tosylindolin-3-ol (**3a**): yellow solid; mp 84−86 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.91 (1H, d, J = 8.3 Hz), 7.58 (2H, d, J = 8.2 Hz), 7.31 (2H, d, J = 8.2 Hz), 7.24 (2H, d, J = 8.1 Hz), 7.12 (3H m), 7.01 (3H, m), 6.95 (1H, d, J = 7.5 Hz), 2.65 (1H, s), 2.41 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 148.0, 145.3, 142.3, 139.7, 135.1, 133.6, 130.2, 129.8, 128.2, 127.6, 127.3, 126.0, 125.6, 125.3, 116.6, 82.9, 65.9, 21.7; IR (NaCl, neat) ν 3446, 3105, 1807, 1624, 1598, 1462, 1365, 1292, 1257, 1172, 1087, 1074, 810 cm^{-1}; MS (ESI) m/z 504 $[M + H]^+$; HRMS (ESI) calcd for $C_{22}H_{19}INO_3S$ ($M^+ + H$) 504.0130, found 504.0135.

(E)-5-Chloro-2-(iodomethylene)-3-phenyl-1-tosylindolin-3-ol (**3d**): yellow solid; mp 138−141 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.86 (1H, d, J = 8.8 Hz), 7.58 (2H, d, J = 8.0 Hz), 7.14−7.33 (7H, m), 6.98 (2H, d, J = 7.2 Hz), 6.92 (1H, d, J = 1.2 Hz), 2.73 (1H, s), 2.44 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 147.7, 145.6, 141.6, 138.3, 136.6, 133.3, 131.3, 130.4, 130.0, 128.4, 127.7, 127.6, 125.5, 125.4, 117.7, 82.7, 66.2, 21.7; IR (NaCl, neat) ν 3446, 3109, 1637, 1595, 1458, 1363, 1172, 1039, 883, 823 cm^{-1}; MS (ESI) m/z 537 $[M + H]^+$; HRMS (ESI) calcd for $C_{22}H_{18}ClINO_3S$ ($M^+ + H$) 537.9741, found 537.9744.

(E)-5-Bromo-2-(iodomethylene)-3-phenyl-1-tosylindolin-3-ol (**3e**): yellow solid; mp 103−106 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.80 (1H, d, J = 8.8 Hz), 7.58 (2H, d, J = 8.2 Hz), 7.42 (1H, dd, J = 1.8 Hz, J = 8.8 Hz), 7.32 (1H, s), 7.14−7.30 (5H, m), 7.06 (1H, d, J = 1.7 Hz), 6.98 (2H, d, J = 7.5 Hz), 2.75 (1H, s), 2.44 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 147.6, 145.6, 141.6, 138.8, 136.9, 133.3, 133.2, 130.0, 128.4, 128.3, 127.7, 127.6, 125.4, 118.8, 118.1, 82.6, 66.1, 21.7; IR (NaCl, neat) ν 3442, 3109, 1633, 1595, 1417, 1361, 1172, 1128, 1076, 1035, 883, 812 cm^{-1}; MS (ESI) m/z 581 $[M + H]^+$; HRMS (ESI) calcd for $C_{22}H_{18}BrINO_3S$ ($M^+ + H$) 581.9236, found 581.9249.

(E)-2-(Iodomethylene)-3-phenyl-1-tosyl-2,3-dihydro-1H-benzo[f]indol-3-ol (**3g**): yellow solid; mp 135−137 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.33 (1H, s), 7.88 (1H, d, J = 8.3 Hz), 7.62 (3H, t, J = 8.4 Hz), 7.32−7.48 (4H, m), 7.12−7.25 (5H, m), 7.05 (2H, d, J = 7.4 Hz), 2.90 (1H, s), 2.39 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 147.8, 145.4, 142.8, 137.6, 135.3, 134.6, 134.0, 131.6, 129.9, 128.3, 128.2, 128.1, 127.6, 127.4, 127.0, 125.5, 125.2, 113.0, 82.5, 64.5, 21.7; IR (NaCl, neat) ν 3442, 3105, 1633, 1504, 1489, 1446, 1361, 1170, 1153, 1089, 1047, 947 cm^{-1}; MS (ESI) m/z 576 $[M + Na]^+$; HRMS (ESI) calcd for $C_{26}H_{20}INO_3SNa$ ($M^+ + Na$) 576.0106, found 576.0103.

(E)-2-(Iodomethylene)-3-(p-tolyl)-1-tosylindolin-3-ol (**3h**): colorless gum; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.92 (1H, d, J = 8.3 Hz), 7.58 (2H, d, J = 8.1 Hz), 7.31 (1H, d, J = 8.0 Hz), 7.30 (1H, s), 7.24 (2H, d, J = 7.7 Hz), 7.07 (1H, t, J = 7.5 Hz), 6.97−6.90 (5H, m), 2.64 (1H, s), 2.41 (3H, s), 2.27 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 148.0, 145.3, 139.6, 139.3, 137.0, 135.1, 133.6, 130.0, 129.8, 128.8, 127.6, 125.9, 125.3, 125.1, 116.5, 82.8, 65.6, 21.7, 21.1; IR (NaCl, neat) ν 3444, 3113, 1710, 1627, 1598, 1462, 1365, 1292, 1172, 1076 cm^{-1}; MS (ESI) m/z 540 $[M + Na]^+$; HRMS (ESI) calcd for $C_{23}H_{20}INO_3SNa$ ($M^+ + Na$) 540.0106, found 540.0102.

(E)-3-(4-Chlorophenyl)-2-(iodomethylene)-1-tosylindolin-3-ol (**3j**): colorless gum; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.93 (1H, d, J = 8.3 Hz), 7.58 (2H, d, J = 8.1 Hz), 7.37 (1H, d, J = 7.9 Hz), 7.33 (1H, s), 7.26 (2H, d, J = 7.9 Hz), 7.12 (2H, d, J = 8.5 Hz), 7.07 (1H, d, J = 7.4 Hz), 6.96−6.91 (3H, m). 2.50 (1H, s), 2.42 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 147.5, 145.4, 140.7, 139.7, 134.7, 133.5, 133.2, 130.4, 129.8, 128.3, 127.6, 127.1, 126.1, 125.1, 116.7, 82.4, 66.3, 21.6; IR (NaCl, neat) ν 3444, 1625, 1597, 1462, 1365, 1292, 1259, 1172, 1089, 1076, 804 cm^{-1}; MS (ESI) m/z 559.9 $[M + Na]^+$; HRMS (ESI) calcd for $C_{22}H_{17}INO_3SClNa$ ($M^+ + Na$) 559.9560, found 559.9556.

(E)-2-(Iodomethylene)-3-methyl-1-tosylindolin-3-ol (**3o**): colorless gum; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.82 (1H, d, J = 8.2 Hz), 7.48 (2H, d, J = 8.2 Hz), 7.37 (1H, t, J = 8.2 Hz), 7.25 (1H, d, J = 7.5 Hz), 7.19 (3H, d, J = 8.2 Hz), 7.08 (1H, s), 2.37 (1H, s), 2.35 (3H, s), 1.10 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 147.3, 145.0, 139.1, 135.9, 133.8, 130.0, 129.6, 127.4, 126.0, 123.2, 117.2, 79.5, 63.2, 26.5, 21.5; IR (NaCl, neat) ν 3442, 2918, 1670, 1597, 1550, 1492, 1446, 1415, 1367, 1172, 1089, 954, 881, 812 cm^{-1}; MS (ESI) m/z 463.9 $[M + Na]^+$; HRMS (ESI) calcd for $C_{17}H_{16}NO_3SNaI$ ($M^+ + Na$) 463.9793, found 463.9795.

(E)-2-(Iodomethylene)-1-tosylindolin-3-ol (**3q**): colorless gum; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.81 (1H, d, J = 8.2 Hz), 7.52 (2H, d, J = 8.0 Hz), 7.41 (1H, d, J = 7.6 Hz), 7.37 (1H, d, J = 7.5 Hz), 7.26 (1H, s), 7.19−7.16 (3H, m), 5.29, (1H, d, J = 5.6 Hz), 2.34 (3H, s), 1.82 (1H, d, J = 6.5 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 145.9, 145.0, 142.0, 133.4, 130.6, 129.7, 129.6, 127.3, 125.8, 125.7, 117.1, 73.7, 70.0, 21.6. IR (NaCl, neat) ν 3446, 3018, 1670, 1595, 1490, 1365, 956, 880 cm^{-1}; MS (ESI) m/z 450 $[M + Na]^+$; HRMS (ESI) calcd for $C_{16}H_{14}NO_3SNaI$ ($M^+ + Na$) 449.9637, found 449.9622.

■ ASSOCIATED CONTENT

Supporting Information. ^1H and ^{13}C NMR spectra for all starting materials and products, LCMS spectrum of ^{18}O-**2a**, and X-ray data for **3e** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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