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Copper(II) Triflate-Catalyzed Intramolecular Hydroamination of Homoallylic Amino Alcohols as an Expedient Route to *trans*-2,5-Dihydro-1*H*-pyrroles and 1,2-Dihydroquinolines

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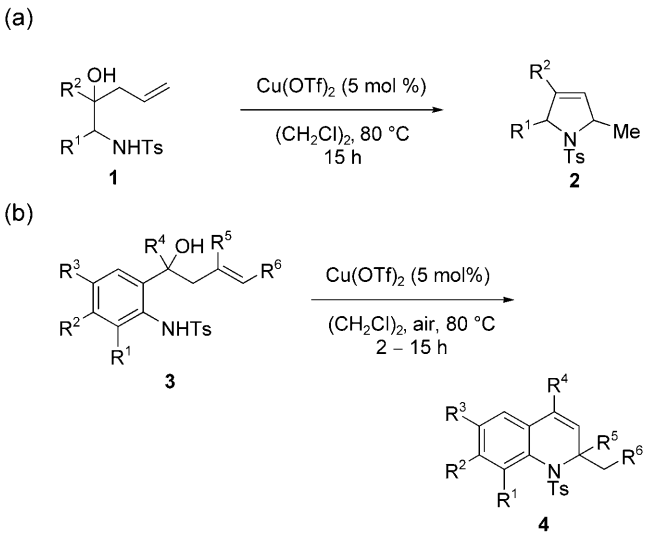
Abstract: A new efficient synthetic route to *trans*-2,5-dihydro-1*H*-pyrroles and 1,2-dihydroquinolines that relies on copper(II) triflate-catalyzed intramolecular hydroamination of homoallylic amino alcohols under mild and operationally straightforward conditions is described. For reactions leading to the *trans*-2,5-dihydro-1*H*-pyrrole product, yields of 52–83% along with *trans* selectivities up to >99:1 *dr* and *ee* values up to 97% were accomplished from enantioenriched 1-(tosylamino)pent-4-en-2-ols ranging from 91–99% *ee*. Without the need for inert and moisture-free conditions, reactions involving 1-[2-(tosylamino)phenyl]but-3-en-1-ols afforded the corresponding 1,2-dihydroquinoline products in excellent yields up to 99% and with complete chemoselectivity. The mechanism is suggested to involve copper(II)-mediated dehydration of the homoallylic amino alcohol. Protonation of the resultant copper(II)-activated aminodiene is then thought to trigger subsequent intramolecular hydroamination to give the partially hydrogenated nitrogen heterocycle.

Keywords: aminodienes; copper catalysis; 2,5-dihydro-1*H*-pyrroles; 1,2-dihydroquinolines; intramolecular hydroamination

Introduction

Intramolecular hydroaminations, the formal addition of a nitrogen and hydrogen atom to an unsaturated C–C bond, mediated typically in the presence of transition metal catalysts provide a convenient synthetic route to nitrogen-containing heterocycles.[1–7] Although this has led to a myriad of studies devoted to this reaction, the majority have been focused on intramolecular hydroamination of amino-tethered alkenes, alkynes and allenes.[1–4] In contrast and despite recent notable advances made in metal-mediated intermolecular hydroaminations of dienes,[6] synthetic methods reporting the analogous intramolecular version of this reaction with aminodienes have remained sparse.[5]

Over the last decade, the use of alcohol pro-electrophiles in Lewis acid-catalyzed C–N bond formation strategies has received an increasing amount of attention.[8–10] For example, we recently reported an efficient method for pyrrolidine synthesis based on AuCl/AgOTf-catalyzed tandem amination/ring expansion of cyclopropylmethanols with aryl sulfonamides that was thought to putatively proceed *via* intramolecular hydroamination of an aminoalkene intermediate.[9d] As part of an ongoing program to develop such reactions,[9] our discovery that $Cu(OTf)_2$ can effect intramolecular hydroamination of aminodienes generated *in situ* from the respective homoallylic amino alcohols **1** and **3** is reported herein (Scheme 1). This process delivers an expedient route to *trans*-2,5-dihydro-1*H*-pyrroles **2** and 1,2-dihydroquinolines **4**, which are common building blocks in organic synthesis and key components in a myriad of bioactive compounds.[11] The *trans*-pyrrolidine adducts were also obtained with high *ee* values that demonstrated efficient chirality transfer from the enantioenriched starting materials to the products. In addition, the reactions were accomplished with a readily available and inexpensive copper catalyst that did not need additives and/or a ligand support or exclusion of air and moisture for re-



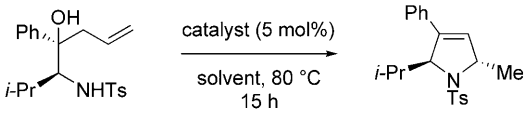
Scheme 1. Intramolecular hydroamination of homoallylic amino alcohols catalyzed by $Cu(OTf)_2$.

actions leading to the construction of **4**. While copper complexes have recently gained momentum as a potentially more ecologically benign hydroamination catalyst, their synthetic utility has often been offset by the need for additives and/or ligands under inert and moisture-free conditions.[3]

Results and Discussion

We began by examining the intramolecular hydroamination of *cis*-(−)-**1a**, prepared from L-valine in >20:1 *dr* and 97% *ee* following literature methods, by a variety of Lewis and Brønsted acid catalysts to establish the reaction conditions (Table 1). The structure and *cis* stereochemistry of the starting alcohol were determined by NMR measurements and X-ray crystal structure analysis of a closely related adduct (*vide infra*). This revealed that treating *cis*-(−)-**1a** in 1,2-dichloroethane with 5 mol% of $Cu(OTf)_2$ at 80 °C for 15 h gave the best result, furnishing *trans*-(+)-**2a** as the sole product in 70% yield, >20:1 *dr trans* selectivity and 93% *ee* (entry 1). The structure and *trans* stereochemistry of the pyrrolidine product were determined by NMR measurements and X-ray crystal structure analysis of two closely related products (*vide infra*). Lower product yields were obtained when the reaction was repeated under atmospheric conditions or in PhMe or $MeNO_2$ as solvent (entries 2, 4 and 5). In contrast, the introduction of a catalytic amount of inorganic base or the use of MeCN or THF as solvent was shown to lead to no reaction and recovery of the starting alcohol (entries 3, 6 and 7). Similarly, a survey of other Lewis and Brønsted acid catalysts did not give improved results with either lower product yields or no reaction found (entries 8–20). Notably, the lower catalytic activity observed in reactions in the presence of TfOH and other metal triflates also provided evidence to discount a process mediated solely by the Brønsted acid (entries 7, 9–17 and 18).[7,12]

Table 1. Optimization of the reaction conditions.[a]

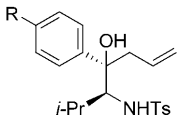
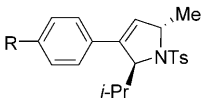
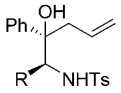
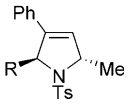
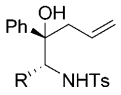
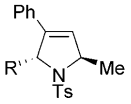


Entry	Catalyst	Solvent	Yield [%][b]	*dr*[c]
1	$Cu(OTf)_2$	$(CH_2Cl)_2$	70	>20:1[d]
2[e]	$Cu(OTf)_2$	$(CH_2Cl)_2$	58	>20:1
3[f]	$Cu(OTf)_2$	$(CH_2Cl)_2$	–[g]	–
4	$Cu(OTf)_2$	PhMe	59	>20:1
5	$Cu(OTf)_2$	$MeNO_2$	21	>20:1
6	$Cu(OTf)_2$	MeCN	–[g]	–
7	$Cu(OTf)_2$	THF	–[g]	–
8	$Cu(OAc)_2$	$(CH_2Cl)_2$	–[g]	–
9	CuOTf	$(CH_2Cl)_2$	–[g]	–
10	CuI	$(CH_2Cl)_2$	–[g]	–
11	$Bi(OTf)_3$	$(CH_2Cl)_2$	49	>20:1
12	$In(OTf)_3$	$(CH_2Cl)_2$	28	>20:1
13	$Sc(OTf)_3$	$(CH_2Cl)_2$	9	–[h]
14	$Yb(OTf)_3$	$(CH_2Cl)_2$	15	–[h]
15	AgOTf	$(CH_2Cl)_2$	48	>20:1
16	AuCl/AgOTf	$(CH_2Cl)_2$	62	>20:1
17	$AuCl_3$/AgOTf	$(CH_2Cl)_2$	42	>20:1
18	$FeCl_3$	$(CH_2Cl)_2$	–[g]	–
19	TfOH	$(CH_2Cl)_2$	27	–[h]
20	Tf_2NH	$(CH_2Cl)_2$	22	–[h]

[a] All reactions were performed at 80 °C for 15 h with **1a**:catalyst ratio = 20:1.
[b] Isolated yield.
[c] Determination of *trans* product *dr* was based on ^{1}H NMR analysis of the crude mixture.
[d] Product obtained in 93% *ee* based on chiral HPLC analysis.
[e] Reaction conducted without the exclusion of air or moisture.
[f] Reaction conducted in the presence of 10 mol% K_2CO_3.
[g] No reaction based on TLC and ^{1}H NMR analysis and near quantitative recovery of the starting alcohol.
[h] Product *dr* could not be determined due to overlapping impurity signals in the ^{1}H NMR spectrum of the crude mixture.

To define the scope of the present procedure, we turned our attention to the reactions of a variety of enantioenriched *cis*-1-(tosylamino)pent-4-en-2-ols ranging from 91–99% *ee* (Table 2). The structure, *cis* stereochemistry and (2*S*,3*R*) absolute configuration of *cis*-(−)-**1h** was determined by X-ray crystallography.[13] Experiments showed that in the presence of 5 mol% of $Cu(OTf)_2$ as catalyst, starting alcohols *cis*-(−)-**1b–h** and *cis*-(+)-**1i**, **j** efficiently underwent the

Table 2. Intramolecular hydroamination of **1b–j** catalyzed by $Cu(OTf)_2$.[a]

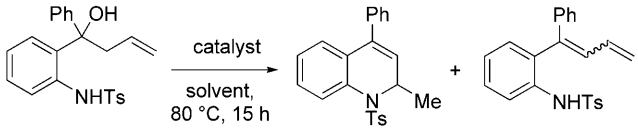
Substrate		Product	
	**1b**, R = Me, 99% *ee* **1c**, R = Ph, 7:1 *dr*, 98% *ee*		**2b**, R = Me, (79, >99:1, 97) **2c**, R = Ph, (83, >99:1, 96)
	**1d**, R = Me, 98% *ee* **1e**, R = Et, 98% *ee* **1f**, R = *n*-Pr, 98% *ee* **1g**, R = Bn, 97% *ee* **1h**, R = Ph, 94% *ee*		**2d**, R = Me, (60, >13:1, 96) **2e**, R = Et, (56, >15:1, 97) **2f**, R = *n*-Pr, (52, >20:1, 93) **2g**, R = Bn, (71, >99:1, 91) **2h**, R = Ph, (65, >99:1, 93)
	**1i**, R = *i*-Pr, 91% *ee* **1j**, R = Bn, 96% *ee*		**2i**, R = *i*-Pr, (72, >20:1, 91) **2j**, R = Bn, (72, >99:1, 96)

[a] All reactions were performed at 80 °C in $(CH_2Cl)_2$ for 15 h with **1**:$Cu(OTf)_2$ ratio = 20:1 and values in parenthesis represent isolated yield (%), *dr* and *ee* (%) of product. Measurement of *trans* product *dr* and *ee* values based on ^{1}H NMR and chiral HPLC analysis.

intramolecular hydroamination process and gave the corresponding products *trans*-(+)-**2b–h** and *trans*-(−)-**2i**, **j** in good to excellent yields. In these reactions, the 2,5-dihydro-1*H*-pyrrole adducts were also obtained with *trans* selectivities up to >99:1 *dr* and *ee* values of 91–97% that were comparable to those of the respective substrates and consistent with our earlier findings for *cis*-(−)-**1a**. The structure and *trans* stereochemistry of *trans*-(+)-**2c** and *trans*-(+)-**2g** were determined by X-ray crystallographic analysis, with the absolute configuration being (2*S*,5*S*).[13] Similarly, the structure and *trans* stereochemistry of *trans*-(−)-**2j** were confirmed by X-ray crystallography, with the absolute configuration being (2*R*,5*R*).[13]

We next sought to assess the scope of this new methodology and with this mind, first tested the reaction of **3a** (Table 3). This led us to find the cyclization process to proceed well on applying the standard conditions with 5 mol% of $Cu(OTf)_2$ as catalyst, giving **4a** in 97% yield (entry 1). Moreover, the same product yield could be reproduced when the reaction was repeated without the exclusion of air and moisture (entry 2). On the other hand and consistent with our earlier findings for *cis*-(−)-**1a**, reactions of **3a** with other solvents and Lewis and Brønsted acids were found to lead to lower yields and/or formation of the diene side product **5** (entries 3–13). Interestingly, while $FeCl_3$ and TfOH were among the catalysts examined that resulted in lower products yields (entries 11–13), their ability to effect cyclization is nonetheless noteworthy given that intramolecular hydroaminations mediated by such Lewis and Brønsted acids have remained sparse.[4,7] In addition, our earlier results revealed the same catalysts to be markedly less effective for the reaction of **1a** (entries 18 and 19 in Table 1).

Table 3. Intramolecular hydroamination of **3a** catalyzed by a variety of Lewis and Brønsted acids.[a]

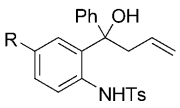
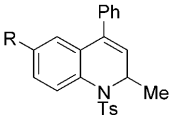
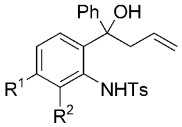
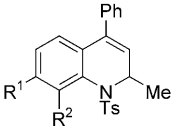
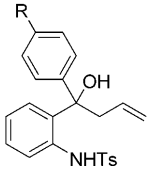
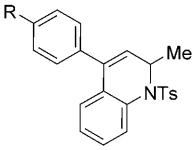
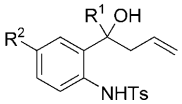
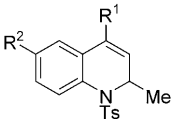
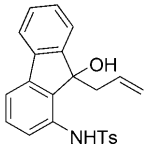
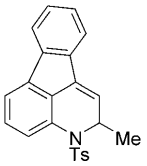
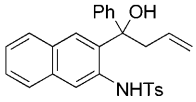
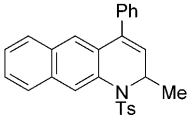
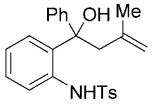
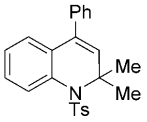
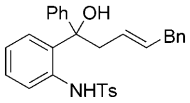
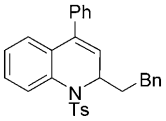


3a **4a** **5**

Entry	Catalyst	Solvent	Yield [%][b]	
			4a	**5**
1	$Cu(OTf)_2$	$(CH_2Cl)_2$	97	–
2[c]	$Cu(OTf)_2$	$(CH_2Cl)_2$	97	–
3	$Cu(OTf)_2$	PhMe	93	–
4	$Cu(OTf)_2$	$MeNO_2$	78	–
5	$Cu(OTf)_2$	MeCN	64	30
6	CuOTf	PhMe	–[d]	–
7	CuI	PhMe	–[d]	–
8	AgOTf	PhMe	–[d]	54
9	AuCl/AgOTf	PhMe	89	–
10	$Yb(OTf)_3$	PhMe	16[e]	–
11	$FeCl_3$	PhMe	80	–
12	$FeCl_3 \cdot 6H_2O$	PhMe	80	–
13	TfOH	PhMe	83	–

[a] All reactions were performed at 80 °C for 15 h with **1**:catalyst ratio = 20:1.
[b] Isolated yield.
[c] Reaction conducted under atmospheric conditions.
[d] No reaction based on TLC and ^{1}H NMR analysis and near quantitative recovery of the starting alcohol or 43% yield in the case of AgOTf.
[e] Starting material was also recovered in 56% yield.

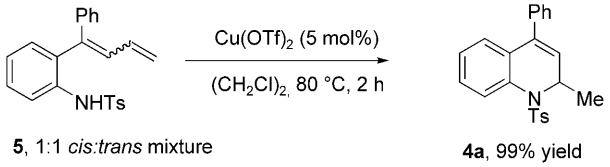
Table 4. Intramolecular hydroamination of **3b–p** catalyzed by $Cu(OTf)_2$.[a]

Substrate		Product	
	**3b**, R = Me **3c**, R = OMe **3d**, R = Br		**4b**, R = Me, (93) **4c**, R = OMe, (87) **4d**, R = Br, (75)
	**3e**, R^1 = Me, R^2 = H **3f**, R^1 = H, R^2 = OMe		**4e**, R^1 = Me, R^2 = H, (98) **3f**, R^1 = H, R^2 = OMe (75)
	**3g**, R = Me **3h**, R = Cl **3i**, R = Br		**4g**, R = Me, (97) **4h**, R = Cl, (91) **4i**, R = Br, (95)
	**3j**, R^1 = Me, R^2 = H **3k**, R^1 = *c*-Pr, R^2 = Me **3l**, R^1 = C≡CPh, R^2 = Me		**4j**, R^1 = Me, R^2 = H, (93) **4k**, R^1 = *c*-Pr, R^2 = Me, (79) **4l**, R^1 = C≡CPh, R^2 = Me, (84)
	**3m**		**4m**, (71)
	**3n**		**4n**, (99)
	**3o**		**4o**, (94)
	**3p**		**4p**, (89)

[a] All reactions were performed at 80 °C in $(CH_2Cl)_2$ for 2-15 h under atmospheric conditions with **3**:$Cu(OTf)_2$ ratio = 20:1. Values in parenthesis represent isolated product yield.[14]

Intramolecular hydroamination of a variety of 1-(2-(tosylamino)phenyl)but-3-en-1-ols **3b–p** was also found to proceed smoothly under these slightly modified conditions (Table 4). With 5 mol% of $Cu(OTf)_2$ as catalyst, these reactions gave the corresponding 1,2-dihydroquinolines **4b–p** in excellent yields. This included one example of a fused tetracycle (**4m**). In these reactions, the structure of **4c** was also confirmed by X-ray crystallographic analysis[13] and no other by-products were detected by ^{1}H NMR analysis of the crude mixtures.

The competitive formation of the diene side product **5** for the cyclizations of **3a** under certain conditions mentioned earlier in Table 3 led us to speculate on its possible involvement as intermediate in the present $Cu(OTf)_2$-catalyzed reactions. Indeed, this is further supported by the fact that **4a** could be obtained in 99% yield when a 1,2-dichloroethane solution containing **5** was treated with 5 mol% of $Cu(OTf)_2$ under the standard conditions shown in Scheme 2.



5, 1:1 *cis:trans* mixture

4a, 99% yield

Scheme 2. Intramolecular hydroamination of aminodiene **5** catalyzed by $Cu(OTf)_2$.

It is worth noting that the fact that the *trans* isomer of **5** can also undergo intramolecular hydroamination additionally suggests a reaction involving an intermediate that contains an allylbenzylic carbocation moiety. This is evident in a number of control experiments examined in this work that supports the cooperative involvement of the Brønsted acid with $Cu(OTf)_2$ in the catalytic cycle. First is the ability of TfOH to cyclize both **1a** and **3a** albeit less efficiently. Added to this is the near quantitative recovery of **1a** in reactions with less acidic Cu(I) and Cu(II) salts or polar aprotic solvents such as THF and MeCN or in the presence of 10 mol% K_2CO_3 and lower product yields obtained with other metal triflates shown in Table 1.

On the basis of the above results, we tentatively propose the mechanism outlined in Scheme 3 for the reaction of *cis*-(−)-**1a**, although it is highly speculative. This could involve activation of the alcohol substrate through coordination of the catalyst with the OH group that results in its elimination and formation of the aminodiene **A**. Further coordination of this newly formed adduct to $Cu(OTf)_2$, re-generated from [Cu]−OH by protonolysis, gives Cu(II)-activated aminodiene species **B**. The released TfOH leads to protonation of the diene moiety of **B** and formation of resonance stabilized allylic cation **C** that is further stabilized through ion pairing with the resultant $^{-}$OTf anion formed. This is the active species that undergoes the intramolecular hydroamination process to afford the *trans*-(+)-**2a**.[15] The origin of the *trans* selectivity could be due carbocationic species adopting the conformer shown in Scheme 3 so that the potential for $A^{1,3}$ strain between the substitutents in allylic cation **C** can be kept to a minimum. In this manner, this would also allow the possibility of unfavourable transannular strain between the *i*-Pr and Me groups to be avoided upon cyclization. The comparable substrate and product *ee* values also suggest that neither the starting alcohol nor any of the putative intermediates are prone to racemization. This consequently allows efficient transfer of the retained chirality at the α-carbon centre to the amino group and the high enantioselectivities observed at the newly formed C–N bond.

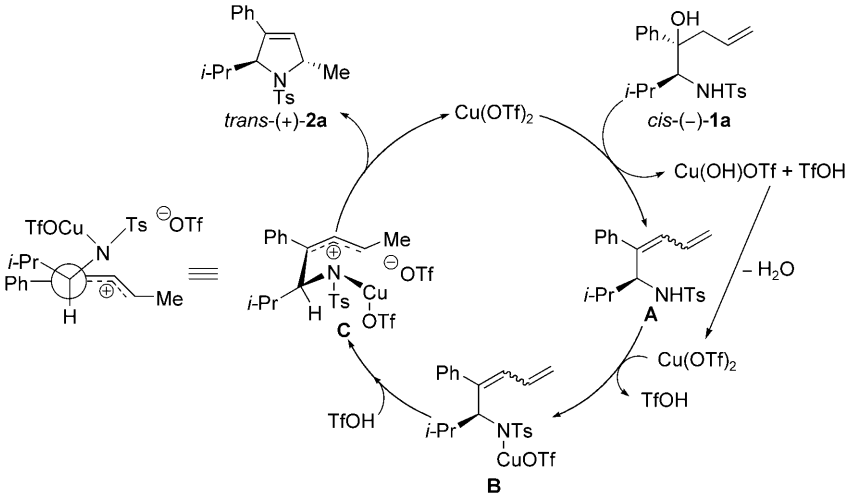
Conclusions

In summary, an efficient synthetic strategy for the intramolecular hydroamination of aminodienes generated *in situ* from easily accessible homoallylic alcohols in the presence of an ecologically benign and low cost copper catalyst has been reported. This provided a practical and operationally simplistic route to enantiopure *trans*-2,5-dihydro-1*H*-pyrroles with high *ee* values that relied on chirality transfer from enantioenriched substrates as well as 1,2-dihydroquinolines under mild conditions. In the latter case, this included conditions that did not need the exclusion of air or moisture. Our studies revealed that TfOH can also catalyze the intramolecular hydroamination process. However, the lower product yields and selectivities exhibited by the Brønsted acid along with the milder conditions of copper catalysis provide an attractive alternative synthetic approach for the formation of these nitrogen heterocycles.

Experimental Section

Representative Experimental Procedure for $Cu(OTf)_2$-Catalyzed Intramolecular Hydroamination of Enantioenriched 1-(Tosylamino)pent-4-en-2-ols (1a–1j)

To a solution of the enantioenriched 1-(tosylamino)pent-4-en-2-ol **1** (0.3 mmol) in 1,2-dichloroethane (3 mL) was



Scheme 3. Tentative mechanism for intramolecular hydroamination of **1a** catalyzed by $Cu(OTf)_2$.

added $Cu(OTf)_2$ (15 μmol) under an argon atmosphere. The reaction mixture was stirred at 80 °C and monitored to completion by TLC analysis. The reaction mixture was then cooled to room temperature and the solvent was removed under reduced pressure. Purification by flash column chromatography on silica gel (*n*-hexane/EtOAc = 9:1 as eluent) gave the product **2**.

Representative Experimental Procedure for $Cu(OTf)_2$-Catalyzed Intramolecular Hydroamination of 1-[2-(Tosylamino)phenyl]but-3-en-1-ols (3a–3p)

To a solution of 1-[2-(tosylamino)phenyl]but-3-en-1-ol **3** (0.3 mmol) in 1,2-dichloroethane (3 mL) was added $Cu(OTf)_2$ (15 μmol) under atmospheric conditions. The reaction mixture was stirred at 80 °C and monitored to completion by TLC analysis. The reaction mixture then cooled and the solvent was removed under reduced pressure. Purification by flash column chromatography on silica gel (*n*-hexane/EtOAc = 7:1 as eluent) gave the product **4**.

(2*S*,5*S*)-2-Isopropyl-5-methyl-3-phenyl-1-tosyl-2,5-dihydro-1*H*-pyrrole (2a): Brown oil; ^{1}H NMR ($CDCl_3$, 300 MHz): δ (*major isomer*) = 0.63 (d, 3H, J = 7.2 Hz), 0.70 (d, 3H, J = 6.8 Hz), 1.42 (d, 3H, J = 6.5 Hz), 2.41 (s, 3H), 2.64–2.72 (m, 1H), 4.60–4.68 (m, 1H), 5.24 (s, 1H), 5.71 (s, 1H), 7.27–7.30 (m, 7H), 7.77 (d, 2H, J = 8.3 Hz); δ (*minor isomer*) = 0.79 (d, 3H, J = 7.0 Hz), 1.05 (d, 3H, J = 7.0 Hz), 4.91(s, 1H), 5.59 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 16.3, 20.2, 20.9, 21.5, 33.3, 63.1, 73.9, 126.7, 126.9, 128.0, 128.5, 129.5, 129.5, 135.7, 139.6, 140.2, 142.7; IR (NaCl, neat): ν = 2967, 1599, 1495, 1339, 1159, 814, 758 cm^{-1}; MS (ESI): m/z = 356 $[M+H]^+$; HRMS (ESI): m/z = 356.1687, calcd. for $C_{21}H_{26}NO_2S$ (M^++H): 356.1684; HPLC (Chiralcel OD-H, 3% *i*-PrOH/*n*-hexanes, 0.3 mL min^{-1}): t_R (minor) = 32.1 min, t_R (major) = 39.7 min; 93% *ee*; $[\alpha]_D^{25}$: +226.0° (*c* 1.0, $CHCl_3$).

(2*S*,5*S*)-2-Isopropyl-5-methyl-3-*p*-tolyl-1-tosyl-2,5-dihydro-1*H*-pyrrole (2b): Pale-yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.56 (d, 3H, J = 7.2 Hz), 0.62 (d, 3H, J = 6.8 Hz), 1.32 (d, 3H, J = 6.5 Hz), 2.25 (s, 3H), 2.32 (s, 3H), 2.54–2.61 (m, 1H), 4.51–4.57 (m, 1H), 5.14 (s, 1H), 5.59 (s, 1H), 7.03–7.20 (m, 6H), 7.69 (d, 2H, J = 8.3 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 16.3, 20.2, 20.9, 21.2, 21.5, 33.3, 63.0, 73.8, 126.6, 126.8, 128.7, 129.2, 129.5, 132.7, 137.9, 139.5, 140.2, 142.6; IR (NaCl, neat): ν = 2967, 1599, 1337, 1159, 818 cm^{-1}; MS (ESI): m/z = 370 $[M+H]^+$; HR-MS (ESI): m/z = 370.1848, calcd. for $C_{22}H_{28}NO_2S$ (M^++H): 370.1841; HPLC (Chiralcel OD-H, 3% *i*-PrOH/*n*-hexanes, 0.3 mL min^{-1}): t_R (minor) = 26.3 min, t_R (major) = 28.2 min; 97% *ee*; $[\alpha]_D^{25}$: +224.6° (*c* 1.0, $CHCl_3$).

(2*S*,5*S*)-3-(Biphenyl-4-yl)-2-isopropyl-5-methyl-1-tosyl-2,5-dihydro-1*H*-pyrrole(2c): Gray solid; mp 160–161 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.71 (d, 3H, J = 7.2 Hz), 0.75 (d, 3H, J = 6.8 Hz), 1.44 (d, 3H, J = 6.5 Hz), 2.42 (s, 3H), 2.67–2.74 (m, 1H), 4.64–4.70 (m, 1H), 5.29 (dd, 1H, J = 2.9, 4.3 Hz), 5.78 (s, 1H), 7.29–7.47 (m, 7H), 7.56–7.61 (m, 4H), 7.80 (d, 2H, J = 8.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 16.4, 20.3, 20.9, 21.5, 33.4, 63.1, 73.8, 126.7, 127.0, 127.1, 127.3, 127.5, 128.9, 129.5, 134.5, 139.2, 140.1, 140.4, 140.8, 142.7; IR (NaCl, neat): ν = 2970, 1599, 1487, 1337, 1159, 1061, 670 cm^{-1}; MS (ESI): m/z = 432 $[M+H]^+$; HR-MS (ESI): m/z = 432.1979, calcd. for $C_{22}H_{28}NO_2S$ (M^++H): 370.1841; HPLC:(Chiralcel OD, 3% *i*-PrOH/*n*-hexanes, 0.5 mL min^{-1}): t_R (minor) = 19.0 min, t_R (major) = 20.7 min; 96% *ee*; $[\alpha]_D^{25}$: +304.0° (*c* 1.0, $CHCl_3$).

(2*S*,5*S*)-2,5-Dimethyl-3-phenyl-1-tosyl-2,5-dihydro-1*H*-pyrrole (2d): Brown oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ (*major isomer*) = 1.43 (d, 3H, J = 6.3 Hz), 1.45 (d, 3H, J = 6.4 Hz), 2.41 (s, 3H), 4.70–4.76 (m, 1H), 5.15–5.21 (m, 1H), 5.80 (s, 1H), 7.26–7.36 (m, 7H), 7.80 (d, 2H, J = 8.3 Hz); δ (*minor isomer*) = 1.48–1.51(m, 6H), 2.38 (s, 3H), 4.54–4.57 (m, 1H), 4.89–4.94 (m, 1H), 5.77 (s, 1H), 7.75 (d, 2H, J = 8.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 20.7, 21.5, 21.5, 62.2, 63.6, 125.4, 126.3, 127.0, 128.2, 128.7, 129.5, 132.9, 139.5, 141.7, 142.8; IR (NaCl, neat): ν = 2971, 1598, 1493, 1335, 1154, 815 cm^{-1}; MS (ESI): m/z = 328 $[M+H]^+$; HR-MS (ESI): m/z = 328.1377, calcd. for $C_{19}H_{22}NO_2S$ (M^++H): 328.1371; HPLC (Chiralcel OJ-H, 5% *i*-PrOH/*n*-hexanes, 1 mL min^{-1}): t_R (minor) = 58.4 min, t_R (major) = 81.9 min; 96% *ee*; $[\alpha]_D^{25}$: +65.6° (*c* 1.0, $CHCl_3$).

(2*S*,5*S*)-2-Ethyl-5-methyl-3-phenyl-1-tosyl-2,5-dihydro-1*H*-pyrrole (2e): Brown oil; ^{1}H NMR ($CDCl_3$, 300 MHz): δ (*major isomer*) = 0.55 (t, 3H, J = 7.3 Hz), 1.43 (d, 3H, J = 6.4 Hz), 1.55–1.65 (m, 1H), 2.30–2.38 (m, 1H), 2.41 (s, 3H), 4.69–4.76 (m, 1H), 5.27 (s, 1H), 5.86 (s, 1H), 7.26–7.75 (m, 7H), 7.79 (d, 2H, J = 8.2 Hz); δ (*minor isomer*) = 0.83 (t, 3H, J = 7.3 Hz), 4.51–4.54 (m, 1H), 5.00 (s, 1H), 5.72 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 6.5, 21.4, 21.5, 24.5, 63.7, 67.9, 126.4, 126.8, 127.0, 128.2, 128.7, 129.5, 133.2, 138.8, 139.6, 142.7; IR (NaCl, neat): ν = 2970, 1599, 1495, 1338, 1162, 1121, 814, 673 cm^{-1}; MS (ESI): m/z = 342 $[M+H]^+$; HR-MS (ESI): m/z = 342.1531, calcd. for $C_{20}H_{24}NO_2S$ (M^++H): 342.1528; HPLC (Chiralcel AD-H, 3% *i*-PrOH/*n*-hexanes, 0.3 mL min^{-1}): t_R (minor) = 50.6 min, t_R (major) = 55.0 min; 97% *ee*; $[\alpha]_D^{25}$: +226.0° (*c* 1.0, $CHCl_3$).

(2*S*,5*S*)-5-Methyl-3-phenyl-2-propyl-1-tosyl-2,5-dihydro-1*H*-pyrrole (2f): Brown oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ (*major isomer*) = 0.61 (t, 3H, J = 7.4 Hz), 0.92–1.05 (m, 2H), 1.44 (d, 3H, J = 6.4 Hz), 1.52–1.62 (m, 1H), 2.15–2.25 (m, 1H), 2.41 (s, 3H), 4.69–4.75 (m, 1H), 5.25 (s, 1H), 5.82 (s, 1H), 7.26–7.36 (m, 7H), 7.79 (d, 2H, J = 8.2 Hz); δ (*minor isomer*) = 0.82 (t, 3H, J = 7.4 Hz), 2.37 (s, 3H), 4.52–4.55 (m, 1H), 4.98 (s, 1H), 5.70 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 13.7, 15.6, 21.4, 21.5, 33.9, 63.6, 67.5, 126.3, 126.7, 126.8, 128.2, 128.7, 129.5, 133.2, 139.3, 139.6, 142.7; IR (NaCl, neat): ν = 2960, 1599, 1337, 1161 cm^{-1}; MS (ESI): m/z = 356 $[M+H]^+$; HR-MS (ESI): m/z = 356.1688, calcd. for $C_{21}H_{26}NO_2S$ (M^++H): 356.1684; HPLC (Chiralcel AD-H, 3% *i*-PrOH/*n*-hexanes, 0.3 mL min^{-1}): t_R (minor) = 46.5 min, t_R (major) = 64.5 min; 93% *ee*; $[\alpha]_D^{25}$: +240.8° (*c* 1.0, $CHCl_3$).

(2*S*,5*S*)-2-Benzyl-5-methyl-3-phenyl-1-tosyl-2,5-dihydro-1*H*-pyrrole (2g): White solid; mp 155–156 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.16 (d, 3H, J = 6.6 Hz), 2.41 (s, 3H), 2.96 (dd, 1H, J = 13.7, 2.0 Hz), 3.72 (dd, 1H, J = 13.7, 4.8 Hz), 4.00–4.07 (m, 1H), 5.48 (s, 1H), 5.60 (s, 1H), 7.07–7.18 (m, 5H), 7.25–7.38 (m, 7H), 7.82 (d, 2H, J = 8.3 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 19.7, 21.5, 39.0, 63.5, 68.4, 126.3, 126.4, 126.6, 127.5, 127.7, 128.3, 128.9, 129.6, 130.9, 133.1, 136.3, 138.5, 140.7, 142.8; IR (NaCl, neat): ν = 3026, 1601, 1495, 1452, 1339, 1157, 1111, 1076, 818 cm^{-1}; MS (ESI): m/z = 404 $[M+H]^+$; HR-MS (ESI): m/z = 404.1678, calcd. for $C_{25}H_{26}NO_2S$ (M^++H): 404.1684; HPLC: (Chiralcel OD-H, 3% *i*-PrOH/*n*-hexanes, 0.3 mL min^{-1}): t_R

(minor) = 36.9 min, t_R (major) = 44.9 min; 91% *ee*; $[\alpha]_D^{25}$: +317.5° (*c* 1.0, $CHCl_3$).

(2*S*,5*S*)-5-Methyl-2,3-diphenyl-1-tosyl-2,5-dihydro-1*H*-pyrrole (2h): Gray solid; mp 123–124 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.71 (d, 3H, *J* = 6.3 Hz), 2.30 (s, 3H), 4.72–4.79 (m, 1H), 6.07 (d, 1H, *J* = 4.3 Hz), 6.14(s, 1H), 6.91–7.23 (m, 14H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 21.4, 22.7, 62.4, 71.7, 126.3, 126.6, 126.9, 127.9, 128.0, 128.2, 128.4, 128.8, 129.2, 132.3, 137.5, 137.7, 139.7, 141.9; IR (NaCl, neat): ν = 3023, 2958, 1600, 1340, 1150 cm^{-1}; MS (ESI): *m/z* = 390 $[M+H]^+$; HRMS (ESI): *m/z* = 390.1515, calcd. for $C_{24}H_{24}NO_2S$ (M^++H): 390.1528; HPLC (Chiralcel OJ-H, 5% *i*-PrOH/*n*-hexanes, 1 mL min^{-1}): t_R (minor) = 38.2 min, t_R (major) = 48.5 min; 93% *ee*; $[\alpha]_D^{25}$: +58.8° (*c* 1.0, $CHCl_3$).

(2*R*,5*R*)-2-Isopropyl-5-methyl-3-phenyl-1-tosyl-2,5-dihydro-1*H*-pyrrole (2i): Brown oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ(*major isomer*) = 0.63 (d, 3H, *J* = 7.2 Hz), 0.70 (d, 3H, *J* = 6.8 Hz), 1.42 (d, 3H, *J* = 6.5 Hz), 2.41 (s, 3H), 2.66–2.71 (m, 1H), 4.61–4.67 (m, 1H), 5.24 (s, 1H), 5.71 (s, 1H), 7.27–7.32 (m, 7H), 7.77 (d, 2H, *J* = 8.3 Hz); δ(*minor isomer*) = 0.79 (d, 3H, *J* = 7.0 Hz), 1.05 (d, 3H, *J* = 7.0 Hz), 4.50–4.52 (m, 1H), 4.92 (s, 1H), 5.59 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 16.3, 20.2, 20.9, 21.5, 33.3, 63.0, 73.8, 126.6, 126.9, 128.0, 128.5, 129.5, 129.5, 135.6, 139.6, 140.1, 142.6; IR (NaCl, neat): ν = 2970, 1599, 1495, 1337, 1159, 814, 756 cm^{-1}; MS (ESI): *m/z* = 356 $[M+H]^+$; HR-MS (ESI): *m/z* = 356.1672, calcd. for $C_{21}H_{26}NO_2S$ (M^++H): 356.1684; HPLC (Chiralcel OD-H, 3% *i*-PrOH/*n*-hexanes, 0.3 mL min^{-1}): t_R (minor) = 31.9 min, t_R (major) = 40.1 min; 91% *ee*; $[\alpha]_D^{25}$: −217.9° (*c* 1.0, $CHCl_3$).

(2*R*,5*R*)-2-Benzyl-5-methyl-3-phenyl-1-tosyl-2,5-dihydro-1*H*-pyrrole (2j): White solid; mp 155–156 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.16 (d, 3H, *J* = 6.6 Hz), 2.41 (s, 3H), 2.96 (dd, 1H, *J* = 13.7, 2.0 Hz), 3.72 (dd, 1H, *J* = 13.7, 4.8 Hz), 4.00–4.06 (m, 1H), 5.48 (s, 1H), 5.60 (s, 1H), 7.08–7.17 (m, 5H), 7.25–7.40 (m, 7H), 7.82 (d, 2H, *J* = 8.3 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 19.7, 21.5, 39.0, 63.5, 68.4, 126.3, 126.4, 126.6, 127.5, 127.7, 128.3, 128.9, 129.6, 130.9, 133.1, 136.3, 138.5, 140.7, 142.8; MS (ESI): *m/z* = 403 $[M+H]^+$; HR-MS (ESI): *m/z* = 404.1679, calcd. for $C_{25}H_{26}NO_2S$ (M^++H): 404.1684; HPLC (Chiralcel OD-H, 3% *i*-PrOH/*n*-hexanes, 0.3 mL min^{-1}): t_R (minor) = 37.1 min, t_R (major) = 46.9 min; 96% *ee*; $[\alpha]_D^{25}$: −345.3° (*c* 1.0, $CHCl_3$).

2-Methyl-4-phenyl-1-tosyl-1,2-dihydroquinoline (4a): Reaction time = 15 h; white solid; mp 162–163 °C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.20 (d, 3H, *J* = 6.9 Hz), 2.27 (s, 3H), 5.08–5.14 (m, 1H), 5.62 (d, 1H, *J* = 6.0 Hz), 6.72 (d, 2H, *J* = 5.9 Hz), 6.86 (d, 1H, *J* = 7.7 Hz), 7.02 (d, 2H, *J* = 8.0 Hz), 7.12 (t, 1H, *J* = 7.5 Hz), 7.23–7.34 (m, 6H), 7.81 (d, 1H, *J* = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 19.3, 21.4, 50.8, 125.8, 126.5, 127.5, 127.5, 128.0, 128.2, 128.8, 129.0, 129.9, 133.0, 135.9, 136.4, 138.2, 143.3; IR (NaCl, neat): ν = 3018, 1477, 1341, 1084, 813 cm^{-1}; MS (ESI): *m/z* = 398 $[M+Na]^+$; HR-MS (ESI): *m/z* = 398.1192, calcd. for $C_{23}H_{21}NO_2SNa$ (M^++Na): 398.1191.

2,6-Dimethyl-4-phenyl-1-tosyl-1,2-dihydroquinoline (4b): Reaction time = 6 h; white solid; mp 158–160 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.19 (d, 3H, *J* = 6.9 Hz), 2.23 (s, 3H), 2.27 (s, 3H), 5.03–5.11 (m, 1H), 5.68 (d, 1H, *J* = 6.0 Hz), 6.64 (s, 1H), 6.71–6.74 (m, 2H), 7.02 (d, 2H, *J* = 8.1 Hz), 7.14 (d, 1H, *J* = 6.8 Hz), 7.15–7.32 (m, 5H), 7.68 (d, 1H, *J* = 8.1 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 19.2, 21.2, 21.4, 50.7, 126.2, 127.5, 127.5, 128.0, 128.6, 128.7, 129.0, 129.6, 130.4, 135.9, 136.3, 136.5, 138.4, 143.2; IR (NaCl, neat): ν = 3021, 1485, 1342, 1167, 1038, 885 cm^{-1}; MS (ESI): *m/z* = 390 $[M+1]^+$; HR-MS (ESI): *m/z* = 390.1521, calcd. for $C_{24}H_{24}NO_2S$ (M^++H): 390.1528.

6-Methoxy-2-methyl-4-phenyl-1-tosyl-1,2-dihydroquinoline (4c): Reaction time = 3 h; white solid; mp 146–147 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.12 (d, 3H, *J* = 6.9 Hz), 2.27 (s, 3H), 3.69 (s, 3H), 5.03–5.12 (m, 1H), 5.61 (d, 1H, *J* = 5.9 Hz), 6.38 (d, 1H, *J* = 2.9 Hz), 6.69–6.72 (m, 2H), 6.88 (dd, 1H, *J* = 8.8, 2.9 Hz),7.02 (d, 2H, *J* = 8.0 Hz), 7.73 (d, 1H, *J* = 8.8 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 19.2, 21.4, 50.8, 55.4, 111.5, 113.0, 125.8, 127.6, 128.0, 128.1, 128.6, 129.1, 130.1, 131.0, 135.8, 136.4, 138.1, 143.2, 157.9; IR (NaCl, neat): ν = 3019, 1485, 1341, 1092 cm^{-1}; MS (ESI): *m/z* = 428 $[M+Na]^+$; HR-MS (ESI): *m/z* = 428.1288, calcd. for $C_{24}H_{23}NO_3SNa$ (M^++Na): 428.1296.

6-Bromo-2-methyl-4-phenyl-1-tosyl-1,2-dihydroquinoline (4d): Reaction time = 4 h; white solid; mp 143–145 °C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.19 (d, 3H, *J* = 6.9 Hz), 2.29 (s, 3H), 5.06–5.15 (m, 1H), 5.65 (d, 1H, *J* = 6.0 Hz), 6.69–6.72 (m, 2H), 6.98 (d, 1H, *J* = 2.3 Hz), 7.06 (d, 2H, *J* = 8.1 Hz), 7.23–7.33 (m, 5H), 7.45 (dd, 1H, *J* = 2.3, 8.6 Hz), 7.69 (d, 1H, *J* = 8.6 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 19.3, 21.4, 50.8, 120.2, 127.4, 127.9, 128.2, 128.5, 128.8, 129.2, 130.4, 131.1, 131.6, 132.1, 135.6, 135.7, 137.4, 143.6; IR (NaCl, neat): ν = 3019, 1474, 1339, 1167, 808 cm^{-1}; MS (ESI): *m/z* = 454 $[M+1]^+$; HR-MS (ESI): *m/z* = 454.0492, calcd. for $C_{23}H_{21}NO_2SBr$ (M^++H): 454.0476.

2,7-Dimethyl-4-phenyl-1-tosyl-1,2-dihydroquinoline (4e): Reaction time = 3 h; white solid; mp 139–140 °C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.19 (d, 3H, *J* = 6.9 Hz), 2.26 (s, 3H), 2.41 (s, 3H), 5.04–5.11 (m, 1H), 5.54 (d, 1H, *J* = 6.0 Hz), 6.71–6.75 (m, 3H), 6.93 (d, 1H, *J* = 7.8 Hz), 7.01 (d, 1H, *J* = 8.0 Hz), 7.20–7.31 (m, 5H), 7.63 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 19.3, 21.4, 21.5, 50.8, 125.6, 126.3, 127.2, 127.3, 127.5, 127.5, 127.9, 128.6, 129.0, 129.3, 132.9, 135.9, 136.3, 138.4, 143.2; IR (NaCl, neat): ν = 3024, 1493, 1445, 1344, 1167, 1090 cm^{-1}; MS (ESI): *m/z* = 390 $[M+1]^+$; HR-MS (ESI): *m/z* = 390.1523, calcd. for $C_{24}H_{24}NO_2S$ (M^++H): 390.1528.

8-Methoxy-2-methyl-4-phenyl-1-tosyl-1,2-dihydroquinoline (4f): Reaction time = 4 h; white solid; mp 165–167 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.17 (d, 3H, *J* = 6.9 Hz), 2.26 (s, 3H), 3.95 (s, 3H), 4.90–4.97 (m, 1H), 5.60 (d, 1H, *J* = 5.8 Hz), 6.55 (d, 1H, *J* = 7.7 Hz), 6.85–6.88 (m, 2H), 6.99 (d, 1H, *J* = 8.3 Hz), 7.07–7.14 (m, 3H), 7.23–7.26 (m, 3H), 7.48 (d, 1H, *J* = 8.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 18.1, 21.4, 51.0, 56.5, 113.1, 118.2, 121.9, 127.5, 127.5, 127.9, 127.9, 128.7, 129.0, 129.1, 132.0, 136.7, 136.8, 138.1, 143.1, 157.5; IR (NaCl, neat): ν = 3019, 1574, 1476, 1271, 1165, 1076, 795 cm^{-1}; MS (ESI): *m/z* = 428 $[M+Na]^+$; HR-MS (ESI): *m/z* = 428.1280, calcd. for $C_{24}H_{23}NO_3SNa$ (M^++Na): 428.1296.

2-Methyl-4-*p*-tolyl-1-tosyl-1,2-dihydroquinoline (4g): Reaction time = 3 h; white solid; mp 149–150 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.19 (d, 3H, *J* = 6.9 Hz), 2.27 (s, 3H), 2.34 (s, 3H), 5.06–5.13 (m, 1H), 5.59 (d, 1H, *J* = 6.0 Hz), 6.61 (d, 2H, *J* = 7.9 Hz), 6.86 (d, 1H, *J* = 7.7 Hz), 7.01 (d, 2H, *J* = 8.2 Hz), 7.10–7.13 (m, 5H), 7.25–7.33 (m, 3H), 7.79 (d, 1H, *J* = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 19.3, 21.2, 21.4, 50.8, 125.8, 126.4, 127.1, 127.5, 128.1, 128.5, 128.7,

128.8, 129.0, 130.0, 133.0, 135.3, 135.9, 136.3, 137.3, 143.3; IR (NaCl, neat): ν= 3021, 1344, 1167, 1091 cm^{-1}; MS (ESI): m/z = 390 $[M+1]^+$; HR-MS (ESI): m/z = 390.1527, calcd. for $C_{24}H_{24}NO_2S$ (M^+ + H): 390.1528.

4-(4-Chlorophenyl)-2-methyl-1-tosyl-1,2-dihydroquinoline (4h): Reaction time = 5 h; white solid; mp 172–173 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.19 (d, 3H, J = 6.9 Hz), 2.28 (s, 3H), 5.57–5.14 (m, 1H), 5.61 (d, 1H, J = 6.0 Hz), 6.66 (d, 2H, J = 8.3 Hz), 6.81 (d, 1H, J = 7.8 Hz), 7.02 (d, 2H, J = 8.2 Hz), 7.12–7.37 (m, 6H), 7.81 (d, 1H, J = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 19.2, 21.4, 50.7, 125.5, 126.6, 127.5, 127.9, 128.2, 128.5, 129.0, 129.0, 129.5, 129.9, 133.0, 133.5, 135.4, 135.8, 136.7, 143.3; IR (NaCl, neat): ν = 3022, 1344, 1165, 1088 cm^{-1}; MS (ESI): m/z = 410 $[M+1]^+$; HR-MS (ESI): m/z = 410.0995, calcd. for $C_{23}H_{21}NO_2SCl$ (M^+ + H): 410.0982.

4-(4-Bromophenyl)-2-methyl-1-tosyl-1,2-dihydroquinoline (4i): Reaction time = 3 h; white solid; mp 164–165 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.19 (d, 3H, J = 6.9 Hz), 2.28 (s, 3H), 5.07–5.14 (m, 1H), 5.62 (d, 2H, J = 6.0 Hz), 6.60 (d, 2H, J = 8.3 Hz), 6.82 (d, 1H, J = 7.7 Hz), 7.02 (d, 2H, J = 8.2 Hz), 7.13 (t, 1H, J = 7.5 Hz), 7.26–7.38 (m, 5H), 7.81 (d, 1H, J = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 19.2, 21.4, 50.7, 121.6, 125.5, 126.6, 127.5, 127.9, 128.5, 129.0, 129.0, 129.4, 130.3, 131.2, 133.0, 135.4, 135.8, 137.2, 143.3; IR (NaCl, neat): ν = 3019, 1485, 1341, 814 cm^{-1}; MS (ESI): m/z = 454 $[M+1]^+$; HR-MS (ESI): m/z = 454.0494, calcd. for $C_{23}H_{21}NO_2SBr$ (M^+ + H): 454.0476.

2,4-Dimethyl-1-tosyl-1,2-dihydroquinoline (4j): Reaction time = 20 h; white solid; mp 68–69 °C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.09 (d, 3H, J = 6.9 Hz), 1.58 (s, 3H), 2.32 (s, 3H), 4.81–4.87 (m, 1H), 5.37 (d, 1H, J = 5.8 Hz), 7.02–7.32 (m, 7H), 7.72 (d, 1H, J = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 17.7, 19.6, 21.4, 50.7, 123.1, 126.2, 126.6, 127.3, 127.8, 128.3, 128.8, 128.9, 130.5, 132.7, 135.9, 143.1; IR (NaCl, neat): ν = 3012, 1485, 1450, 1344, 1165, 1051 cm^{-1}; MS (ESI): m/z = 336 $[M+Na]^+$; HR-MS (ESI): m/z = 336.1035, calcd. for $C_{18}H_{19}NO_2SNa$ (M^+ + Na): 336.1034.

4-Cyclopropyl-2,6-dimethyl-1-tosyl-1,2-dihydroquinoline (4k): Reaction time = 6 h; white solid; mp 105–106 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = −0.44–−0.38 (m, 1H), 0.00–0.07 (m, 1H), 0.40–0.47 (m, 1H), 0.59–0.65 (m, 1H), 1.07 (d, 3H, J = 6.8 Hz), 1.21–1.28 (m, 1H), 2.32 (s, 3H), 2.37 (s, 3H), 4.82–4.88 (m, 1H), 5.33 (dd, 1H, J = 5.9, 1.5 Hz), 7.03 (d, 2H, J = 8.1 Hz), 7.11(dd, 1H, J = 8.1, 1.5 Hz), 7.19–7.24 (m, 3H), 7.59 (d, 1H, J = 8.1 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 4.1, 5.6, 11.6, 19.6, 21.4, 50.7, 124.1, 124.9, 127.3, 128.1, 128.4, 128.8, 129.8, 130.3, 134.4, 136.1, 136.2, 143.1; IR (NaCl, neat): ν = 3017, 1487, 1344, 1163, 1094, 1040, 814 cm^{-1}; MS (ESI): m/z = 376 $[M+Na]^+$; HR-MS (ESI): m/z = 376.1341, calcd. for $C_{21}H_{23}NO_2SNa$ (M^+ + Na): 376.1347.

2,6-Dimethyl-4-(phenylethynyl)-1-tosyl-1,2-dihydroquinoline (4l): Reaction time = 2 h; yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.16 (d, 3H, J = 6.9 Hz), 2.29 (s, 3H), 2.38 (s, 3H), 4.93–5.00 (m, 1H), 5.96 (d, 1H, J = 6.0 Hz), 7.10 (d, 2H, J = 8.3 Hz), 7.17 (dd, 1H, J = 8.2, 1.7 Hz), 7.26–7.45 (m, 8H), 7.61 (d, 1H, J = 8.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 19.2, 21.3, 21.5, 50.9, 84.9, 91.2, 118.3, 122.9, 125.8, 127.2, 127.2, 128.0, 128.4, 128.5, 129.2, 129.6, 129.8, 131.5, 134.5, 135.6, 136.6, 143.6; IR (NaCl, neat): ν = 3021, 1489, 1344, 1159, 1092, 812 cm^{-1}; MS (ESI): m/z = 436 $[M+Na]^+$; HR-MS (ESI): m/z = 436.1345, calcd. for $C_{26}H_{23}NO_2SNa$ (M^+ + Na): 436.1347.

2-Methyl-3-tosyl-2,3-dihydroindeno[1,2,3-*de*]quinoline (4m): Reaction time = 3 h; pale-yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.44 (d, 3H, J = 6.8 Hz), 2.23 (s, 3H), 5.33–5.39 (m, 1H), 6.29 (d, 1H, J = 5.0 Hz), 7.02 (d, 2H, J = 8.0 Hz), 7.26–7.45 (m, 6H), 7.55 (d, 1H, J = 7.5 Hz), 7.68–7.71 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 21.4, 23.1, 54.9, 116.7, 120.9, 122.0, 122.5, 126.7, 127.1, 128.2, 128.7, 129.4, 129.7, 131.4, 132.2, 135.4, 136.1, 137.0, 141.2, 143.6; IR (NaCl, neat): ν = 3022, 1612, 1595, 1445, 1437, 1163, 812 cm^{-1}; MS (ESI): m/z = 374 $[M+1]^+$; HR-MS (ESI): m/z = 374.1183, calcd. for $C_{23}H_{20}NO_2S$ (M^+ + H): 374.1215.

2-Methyl-4-phenyl-1-tosyl-1,2-dihydrobenzo[*g*]quinoline (4n): Reaction time = 4 h; pale-yellow solid, mp 163–164 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.25 (d, 3H, J = 6.9 Hz), 2.25 (s, 3H), 5.14–5.21 (m, 1H), 5.76 (1H, J = 6.0 Hz), 6.81 (d, 1H, J = 5.8 Hz), 6.98 (d, 1H, J = 8.2 Hz), 7.27–7.49 (m, 8H), 7.60 (d, 1H, J = 8.1 Hz), 7.90 (d, 1H, J = 8.2 Hz), 8.29 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 19.9, 21.4, 51.0, 126.1, 126.3, 126.6, 127.4, 127.5, 127.7, 128.0, 128.0, 128.1, 128.8, 129.1, 129.2, 130.9, 131.8, 133.0, 136.1, 136.8, 138.5, 143.3; IR (NaCl, neat): ν= 3019, 1493, 1346, 1167, 1094, 1028, 903 cm^{-1}; MS (ESI): m/z = 426 $[M+1]^+$; HR-MS (ESI): m/z = 426.1531, calcd. for $C_{27}H_{24}NO_2S$ (M^+ + H): 426.1528.

2,2-Dimethyl-4-phenyl-1-tosyl-1,2-dihydroquinoline (4o): Reaction time = 4 h; white solid, mp 159–160 °C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.56 (s, 6H), 2.24 (s, 3H), 5.46 (s, 1H), 6.86–6.87 (m, 2H), 6.95 (d, 1H, J = 7.6 Hz), 7.02 (d, 2H, J = 8.0 Hz), 7.16–7.37 (m, 7H), 7.78 (d, 1H, J = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 21.4, 28.2, 58.2, 125.4, 126.6, 127.6, 127.7, 127.9, 128.0, 128.7, 129.1, 130.6, 130.9, 133.5, 136.7, 136.9, 137.7, 137.8, 142.9; IR (NaCl, neat): ν = 3021, 1599, 1348, 1159, 1090, 984 cm^{-1}; MS (ESI): m/z = 390 $[M+1]^+$; HR-MS (ESI): m/z = 390.1529, calcd. for $C_{24}H_{24}NO_2S$ (M^+ + H): 390.1528.

2-Phenethyl-4-phenyl-1-tosyl-1,2-dihydroquinoline (4p): Reaction time = 2 h; white solid, mp 155–156 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.67–1.82 (m, 2H), 2.26 (s, 3H), 2.74–2.82 (m, 1H), 2.86–2.93 (m, 1H), 4.96–5.01 (m, 1H), 5.69 (d, 1H, J = 6.0 Hz), 6.68 (d, 2H, J = 7.0 Hz), 6.85 (d, 1H, J = 7.7 Hz), 7.00 (d, 2H, J = 8.0 Hz), 7.10–7.35 (m, 12H), 7.82 (d, 1H, J = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 21.4, 31.7, 34.3, 54.7, 125.9, 125.9, 126.5, 126.6, 127.5, 127.6, 128.0, 128.4, 128.6, 128.6, 128.8, 129.1, 130.2, 133.1, 135.9, 137.0, 138.2, 141.6, 143.4; IR (NaCl, neat): ν = 3022, 1599, 1450, 1072, 812 cm^{-1}; MS (ESI): m/z = 466 $[M+1]^+$; HR-MS (ESI): m/z = 466.1838, calcd. for $C_{30}H_{28}NO_2S$ (M^+ + H): 466.1841.

4-Methyl-*N*-(2-(1-phenylbuta-1,3-dienyl)phenyl)benzenesulfonamide (5): Yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.34 (s, 3H), 2.37 (s, 3H), 5.10 (d, 1H, J = 10.1 Hz), 5.24 (t, 2H, J = 8.7 Hz), 5.40 (d, 1H, J = 16.8 Hz), 5.80–5.89 (m, 2H), 6.26 (s, 1H), 6.47–5.60 (m, 2H), 6.82 (d, 1H, J = 11.0 Hz), 7.00–7.47 (m, 22H), 7.60 (d, 1H, J = 8.2 Hz), 7.76 (d, 2H, J = 8.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 21.5, 119.8, 120.7, 120.9, 123.0, 124.4, 125.3, 126.3, 127.2, 127.3, 128.2, 128.4, 128.7, 128.9, 129.0, 129.3, 129.4, 129.5, 129.6, 130.8, 130.8, 131.3, 132.6, 133.5, 133.6, 134.3, 134.7, 136.0, 136,0, 136.1, 137.2, 138.1, 138.5, 139.0, 143.6, 143.7; IR (NaCl, neat): ν = 3275, 1491, 1452, 911 cm^{-1}; MS (ESI):

$m/z = 376$ $[M+1]^+$; HR-MS (ESI): $m/z = 376.1359$, calcd. for $C_{23}H_{22}NO_2S$ ($M^+ + H$): 376.1371.

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[13] Please refer to Figures S91–S95 in the Supporting Information for ORTEP drawings of **1h**, **2c**, **2g**, **2j** and **4c**.

[14] Please refer to the Supporting Information for the reaction times.

[15] Intermediates similar to those depicted in Scheme 3 have also been proposed in other copper catalyzed hydroamination reactions, please refer to ref.[3]

