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Asymmetric aminoarylation for the synthesis of *trans*-3-amino-4-aryltetrahydroquinolines: An access to aza-analogue of dihydrexidine

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ABSTRACT

A proficient stereoselective aminoarylation reaction of *N*-cinnamylanilines, based on a two-step protocol of catalytic enantioselective aziridination and subsequent *6-endo-tet* Friedel-Crafts cyclization, has been developed and demonstrated. A pair of chiral bis-oxazoline ligand and $Cu(OTf)_2$ offered an effective combination in the synthesis of *trans*-3-amino-4-aryltetrahydroquinolines with excellent diastereo- and enantioselectivity (dr: >99: 1 and ee up to 97%). In continuation, a *trans*-3-amino-4-aryltetrahydroquinoline, availed in one-pot stereoselective aminoarylation reaction, was extended toward a concise synthesis of aza-analogue of dihydrexdine, a potent and selective full dopamine-D1 agonist.

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1. Introduction

Constructing the core of a wide range of biologically significant small organic molecules, nitrogen-containing heterocycles received major attention. This is largely because of their detailed history of being in the center of several medicinal pharmacophores. Among them, tetrahydroquinolines represent a class of privileged heterocycles owing to their abundance of natural products and rich biological background [1–5]. Chiral 1, 2, 3, 4-tetrahydroquinolines, particularly, 3-aminotetrahydroquinolines [3,4] and 4-aryltetrahydroquinolines [5] feature in numerous pharmacological agents and natural products such as compounds **A-D** (Fig. 1). PNU 95666 E (**A**) is a selective dopamine D2 agonist and a potential molecule to treat Parkinson's disease; anachellin H chromophore **B** is a microbial agent isolated from the cyanobacterium *Anabaena cylindrica* and with moderate antibiotic activity. In addition, 4-aryltetrahydroquinolines based compounds **C** and **D** are potent liver-receptors agonists and with antichagasic activities, respectively [5]. Further, 3-amino-4-aryltetrahydroquinoline **E** may emerge with dopaminergic property in the form of aza-analogue of dihydrexidine and doxanthrine, the two selective dopamine D1 agonists and potential drug candidates for the treatment of Parkinson's disease [6,7]. Thus, extensive research efforts were made in the synthesis of substituted tetrahydro quinolines [1,8,9], but the asymmetric synthesis of 3-aminotetrahydroquinolines are still sparse in the literature [9].

We envisioned that stereoselective intramolecular Friedel-Crafts cyclization of the *in situ* generated tethered chiral aziridine **2** derived from *N*-cinnamylanilines **1** would be routed to 3-amino-4-aryltetrahydroquinolines **3** (Scheme 1). Herein, we report asymmetric aminoarylation reactions of olefins **1**, having a pendant aryl unit, toward a catalytic and asymmetric synthesis of *trans*-3-amino-4-aryltetrahydroquinolines with high diastereo- (>99:1) and enantioselectivity (up to 97% ee) and the application in the asymmetric synthesis of aza-analogue of dihydrexidine derivative.

2. Results and discussion

Stereoselective aziridination [10] of alkenes has extensively been studied and well-explored in our laboratory in the recent past [11]. PhINNs in combination with $Cu(OTf)_2$ offered the best choice

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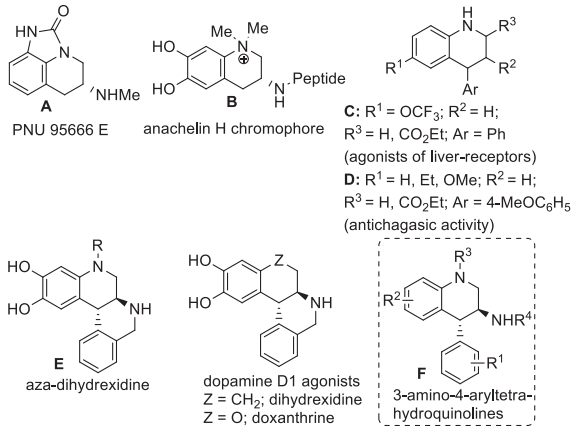
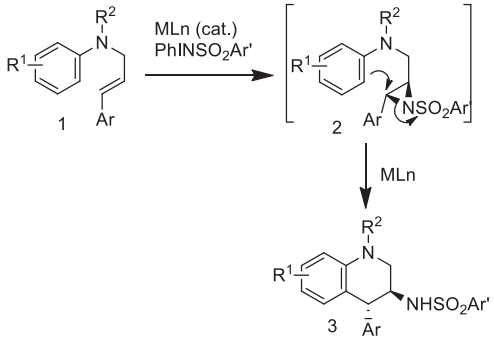
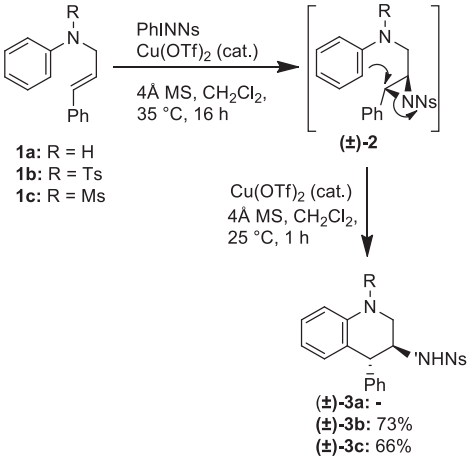


Fig. 1. Representative 3-amino- and 4-aryl-tetrahydroquinoline containing bioactive molecules.



Scheme 1. Proposed reaction for the synthesis of aminotetrahydroquinolines.

as a precursor of nitrene to transfer it to the double bond and dually functioning $Cu(OTf)_2$ served as an effective catalyst for the Friedel-Crafts reaction too. Hence, the pair was used in the reaction of *N*-cinnamylaniline **1** under the well-established condition *i.e.* the reaction with PhINNs in the presence of $Cu(OTf)_2$ catalyst and molecular sieves (MS 4 Å) in CH_2Cl_2. Since substrates with exchangeable proton are not suitable for such reaction, the *N*-protection was expected to be obligatory for this purpose. We also found that the reaction of **1a,** having a bare −NH, led to an

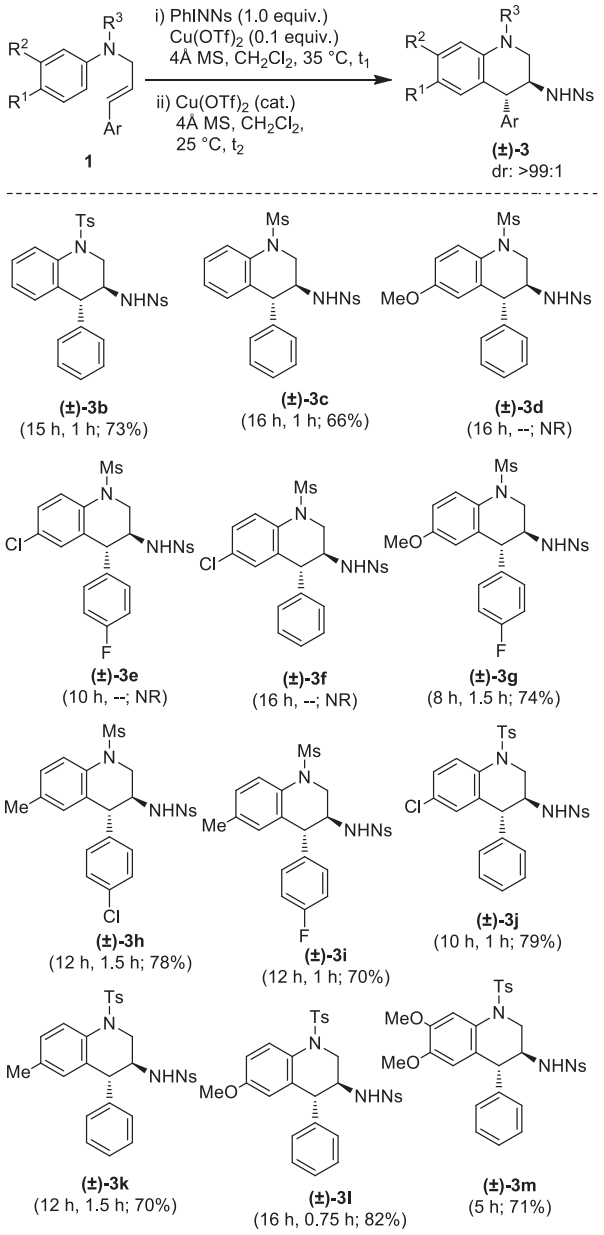


Scheme 2. Screening of *N*-protecting group for the aminoarylation.

intractable reaction mixture. Accordingly, *N*-protected-*N*-cinnamylanilines **1b** and **1c** were employed under the same reaction conditions that brought in some encouraging results (Scheme 2). The reaction of **1b** with PhINNs in the presence of $Cu(OTf)_2$ at rt (25 °C) was slow (no noticeable reaction till 24 h). So, we performed the reaction at elevated temperature (35 °C) and observed the full consumption of nitrenoid reagent after 24 h forming the aziridine (±)-**2b** (confirmed by ^1H NMR of the crude reaction mixture). The reaction mixture was then subjected to supplementary $Cu(OTf)_2$ aiming toward a one-pot Friedel-Crafts cyclization, but even after 24 h, it was unsuccessful. The aziridine (±)-**2b** was isolated by column chromatography and detailed spectral analysis confirmed it as pure *trans*-aziridine (±)-**2b**. When the aziridine (±)-**2b** was treated with 0.1 equiv. of $Cu(OTf)_2$ in CH_2Cl_2 at rt in the presence of molecular sieves (MS 4 Å), it exclusively transformed into the *trans*-cyclized product (±)-**3b** (dr > 99:1) within 1 h (Scheme 2). Next, we implemented a useful protocol within the course of the reaction where we skipped the aziridine isolation step. We filtered the reaction mixture through a short plug of silica gel and then proceed with the semi-crude reaction mixture for Friedel-Crafts cyclization with additional $Cu(OTf)_2$. Such an alteration was found to fit well in this reaction and hence adopted. Mesyl protected substrate **1c** did not appreciably improve the result but experienced a very similar outcome, providing the cyclized product (±)-**3c** *via* the protocol of aziridination and Friedel-Crafts cyclization (Scheme 2).

All acyl (RCO-) protecting groups [acetyl (Ac), benzoyl (Bz), pivaloyl (Piv), 4-nitrobenzoyl (NBz)] containing *N*-cinnamylanilines were found unsuitable for aziridination reaction under the developed conditions. We continued to investigate the scope of this catalytic method for the synthesis of *N*-protected tetrahydroaminoquinoline derivatives (±)-**3** under the optimized reaction condition with a panel of *N*-tosyl and *N*-mesyl-protected *N*-cinnamylanilines **1d-1m**, containing both electron-donating and -withdrawing groups attached to either of the arene rings (Scheme 3). In our earlier studies, the aryl group on the aziridine was found to be mandatory for the cyclization, where an alkyl substituent on aziridine could not accomplish to a similar intramolecular cyclization under such reaction conditions [11c,11g]. Thus herein we focused only on aryl-substituted alkene substrates **1**. Mesyl protected substrate **1d,** having a *para*-methoxy substituent provided an inseparable mixture of products after 16 h at 35 °C. Another mesyl-protected substrate **1e**, having *para*-chloro and *para*-fluoro groups at either end, did not respond in aziridination reaction and the nitenoid reagent decomposed to $NsNH_2$. A similar reaction outcome was noticed for the substrate **1f**. However, *para*-methoxy and *para*-fluoro-containing substrate **1g** stood well in aziridination-cyclization, and the corresponding cyclized product (±)-**3g** was isolated in 74% of yield. Similarly, substrates **1h** and **1i**, in reaction with PhINNs and $Cu(OTf)_2$ followed by Friedel-Crafts cyclization, provided the products (±)-**3h** and (±)-**3i** in 78% and 70% of yields, respectively. All tosyl (Ts) protected substrates **1j**, **1k**, **1l,** and **1m** rendered better results under the standard protocol of aminoarylation reaction, and among them, 4-methoxy containing substrate **1l** earned (±)-**3l** with a maximum yield of 82%. More electron-donating *N*-cinnamyl-3,4-dimethoxyaniline **1m** underwent a direct cyclization of the *in situ* generated aziridine in one-pot without any additional $Cu(OTf)_2$ to provide the *trans*-cyclized product (±)-**3m** in 71% yield.

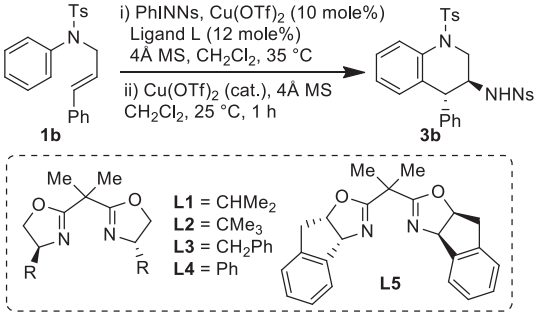
The fruitful synthesis of (±)-*trans*-3-amino-4-aryltetrahydroquinolines **(±)-3** *via* two-step aminoarylation reaction prompted us to investigate the scope of its catalytic enantioselective version. Purposefully, the reaction was introduced to chiral Box ligand chelated copper catalyst for chiral induction. The in-depth study was set with the reaction of *N*-tosyl-*N*-cinnamylaniline **1b** with PhINNs in the presence of $Cu(OTf)_2$ and bis-oxazoline



Scheme 3. Cu(OTf)$_2$-catalyzed synthesis of *N*-protected *trans*-3-amino-4-aryltetrahydroquinolins **(±)-3**.

(Box) ligands **L1-L5,** mainly derived from L-amino alcohols (Table 1). Aziridination with bis-oxazoline ligand **L1,** under the optimum method, ended in 16 h that on further treatment with Cu(OTf)$_2$ afforded the *trans*-cyclized product **3b** within 1 h in 34% yield. HPLC analysis of **3b** exhibited 26% ee. Maintaining the identical reaction conditions, we examined other Box ligands as well. Box ligand **L2** furnished almost a similar result to that of the ligand **L1** with a lower yield of 29% (Table 1; entries 1, 2). Enantioselectivity of the cyclized product **3b** was also found similar to that for the ligand **L1** (entry 2). The structural difference between **L3** and **L4** is the presence of benzylic methylenes (CH_2) in **L3**, which distanced the phenyl rings from the chiral centers. As a result, the enantioselectivity of product **3b** reduced (entry 3). When *L*-phenylglycinol derived Box ligand **L4** was deployed, it earned an improved yield of tetrahydroquinoline **3b** (44%), and the enantioselectivity also appreciably enhanced to 57% (Table 1; entry 4). Further

Table 1
Optimization of catalytic asymmetric aminoarylation using Cu(OTf)$_2$-BOX catalyst.



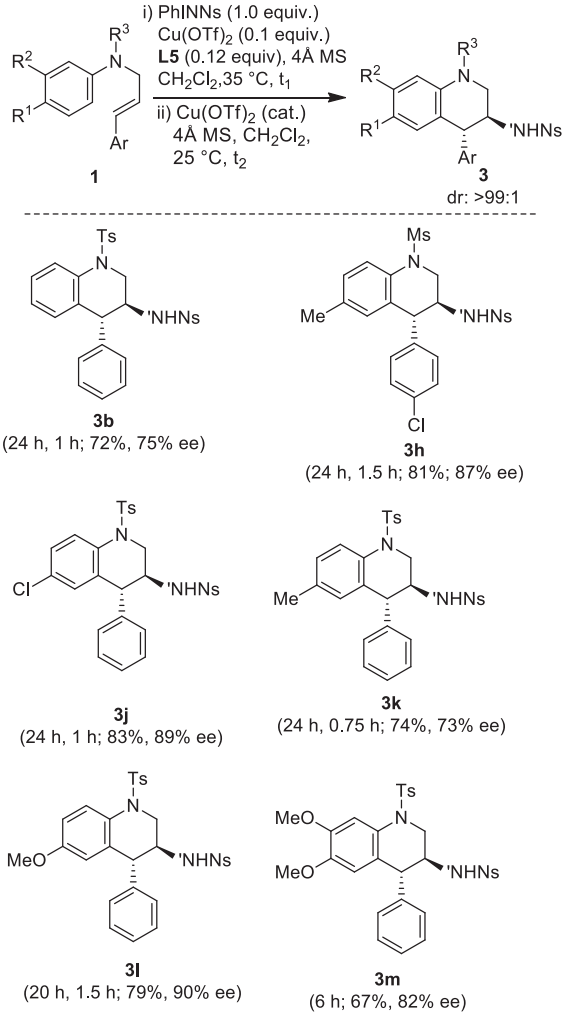
Entry	Ligand	Time (h)	Yield 3b[a] (%)	ee 3b[b] (%)
1	**L1**	16	34	26[c]
2	**L2**	16	29	29[c]
3	**L3**	16	28	17[c]
4	**L4**	16	44	57[c]
5	**L5**	**24**	**72**	**75**
6[d]	**L5**	24	31	54

[a] Isolated yield of **3b** after column chromatography.
[b] Enantiomeric excess (ee) was determined by chiral HPLC using AD-H column.
[c] The other enantiomer *ent*-**3b** was formed.
[d] Dichloroethane (DCE) was used instead of CH_2Cl_2.

improvement of enantioselectivity was accomplished when the Box ligand **L5** derived from (1*R*, 2*S*)-indanol amine was used. In an extended reaction time of 24 h, an enhanced yield (72%) and enantioselectivity of *trans*-cyclized product **3b** (75%) was achieved (Table 1; entry 5).

Between the indenyl amine derived Box L5 and phenyl Box L4, the former being more rigid (the oxazoline units held the phenyl rings with an extra methylene bridge, which brings more rigidity into the structure) offers more chiral-induction, which ultimately manifested in higher ee. The reaction was initiated in a catalytic enantioselective aziridination and the same selectivity was retained through the next step, the stereospecific S_N2 ring-opening of aziridine. Our group has already reported such a relay of enantioselectivity [11]. The absolute stereochemistry of *trans*-cyclized product **3b** was assigned by analogy with the literature and our earlier works [10,11]. The two-step asymmetric aminoarylation protocol was also studied in different solvents using indenyl Box ligand **L5**. The reaction of **1b** with PhINNs in $CHCl_3$ provided traces of the aziridine **2b**, whereas there was a poor reaction or no reaction in solvents like CH_3CN, DME, and C_6H_6, rather complete decomposition of PhINNs to $NsNH_2$ was observed (not shown in Table 1). Reaction in DCE provided the desired cyclized product **3b** in 31% of yield without any notable increase in ee (Table 1; entry 6).

We implemented this two-step catalytic asymmetric protocol with some tosyl and mesyl protected *N*-cinnamylaniline derivatives under the optimal reaction conditions (Scheme 4). Among all the mesyl-protected *N*-cinnamylanilines, only **1h** finished the reaction and the cyclized product **3h** was isolated in high yield (81%) with an ee of 87%. The tosyl protected *N*-cinnamyl-4-chloroaniline **1j** reacted efficiently to afford the tetrahydroquinoline compound **3j**, which exhibited quite a high ee (89%), isolated in 83% yield. *N*-Tosyl-*N*-cinnamyl-4-methylaniline **1k** offered a satisfactory yield in aziridination-cyclization (74%), yet ee of the corresponding aminotetrahydroquinoline **3k** dropped to 73%. Substrate **1l**, having an electron-donating methoxy group went through a smooth aziridination and the end cyclized product **3l** was obtained in a decent yield (79%) with 90% of ee. More electron-rich substrate **1m** containing two methoxy groups underwent relatively faster reaction

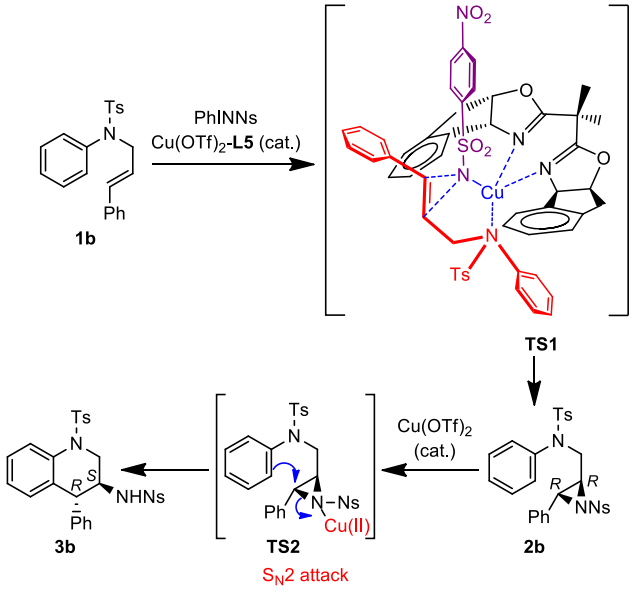


Scheme 4. Asymmetric synthesis of *trans*-3-amino-4-aryltethrahydro-quinolines **3** *via* two-step reactions.

and within 6 h at 35 °C it provided the one-pot cyclized product **3m** without any additional Lewis acid in 67% of yield and satisfactory ee of 82%.

Since aziridination is the first stereo-induction step, thus the stereochemistry of the intermediate aziridine **2** is expected to dictate the absolute configuration of the aminotetrahydroquinolines **3**. The former is assigned based on the literature reports [10,11] and accordingly, a plausible mechanism is proposed (Scheme 5). The chirality of $Cu(OTf)_2$-**L5** complex and the coordination of the nitrogen of the N-cinnamyl aniline **1b** to the copper of the catalyst orient the double bond towards the metal-nitrene for preferential attack from the top as shown in the transition state model TS1. This leads to the formation of **2b** with a configuration of (2*R*, 3*R*). In the second step, the nitrogen of the aziridine coordinates to the $Cu(OTf)_2$ catalyst activating the benzylic position of the aziridine towards *6-endo-tet* Friedel-Crafts cyclization via S_N2 mechanism [11] and affords the 3-amino-4-phenyl tetrahydroquinoline **3b** with *trans*-stereochemistry having (3*S*,4*R*)-configuration.

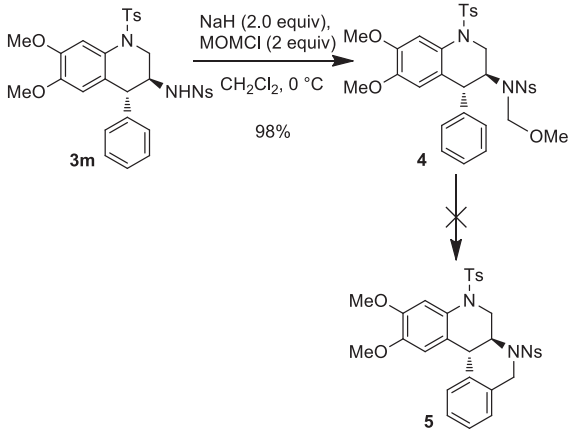
After the successful development of the catalytic asymmetric protocol for the synthesis of *trans*-3-amino-4-aryltetrahydroquinolines **3**, we set our strategy to the synthesis of *N*-bioisostere of dihydrexidine. 3-Amino-4-phenyl-tetrahydroquinoline **3m** was synthesized considering it could be an



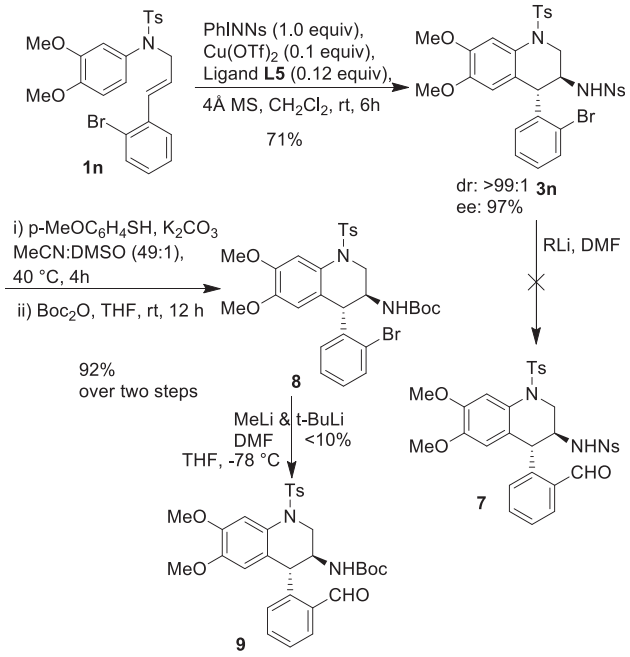
Scheme 5. A proposed mechanism of asymmetric aminoarylation.

immediate precursor for the asymmetric synthesis of *N*-bioisostere of dihydrexidine *via* Pictet-Spengler cyclization. Toward that, sodium salt of 3- amino-4-phenyltetrahydroquinoline **3m** was treated with MOMCl in CH_2Cl_2 at 0 °C. The reaction was completed within 4 h and provided the *N*-MOM compound **4** in an excellent yield of 98% (Scheme 6). Having compound **4**, we attempted the Pictet-Spengler cyclization using TMSOTf and also with BF_3—OEt_2 in CH_2Cl_2 at different temperatures and conditions [11d]. Unfortunately, none of the conditions was successful to provide the desired product but ended up with MOM-deprotected compound **3m** as the only product.

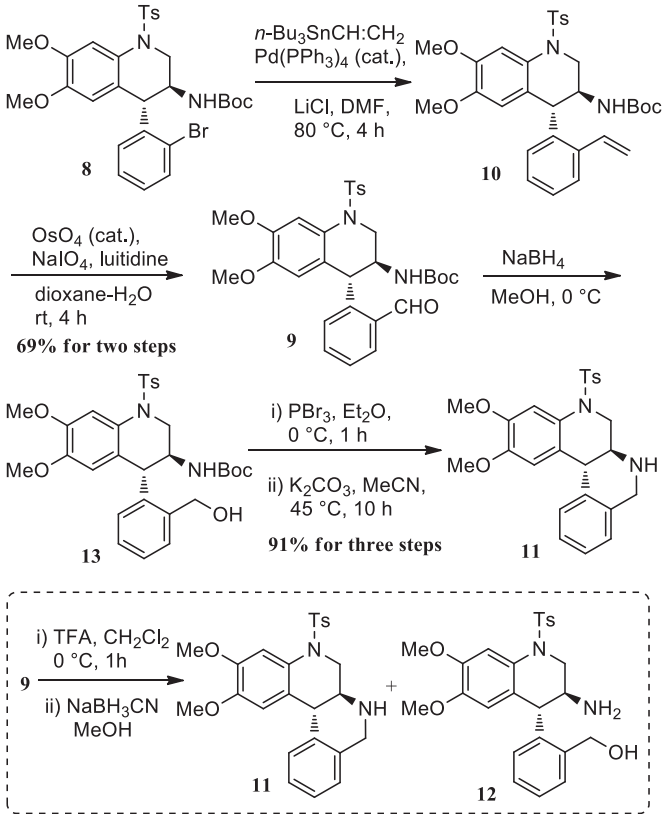
The above unsuccessful result led us to envision the synthesis of 3-amino-4-aryl-tetrahydroquinoline intermediate **3n,** where late-stage incorporation of an aldehyde group at the *ortho*-position would be an alternate strategy. Accordingly, alkene **1n** was subjected to the optimized aminoarylation reaction conditions. To our delight, the substrate **1n** experienced a smooth reaction to produce the *trans*-3-amino-4-aryl-tetrahydroquinoline **3n** directly in 71% yield with an excellent ee of 97% (Scheme 7). Such high enantioselectivity might be attributed due to the extra added bulk of *ortho*-bromo-substituent to the substrate **1n**. Our initial attempts of



Scheme 6. Attempt toward Pictet-Spengler cyclization of **3m**.



Scheme 7. Catalytic asymmetric aminoarylation of **1n** and formylation attempt.



Scheme 8. Asymmetric synthesis of *N,O*-protected aza-dihydrexidine.

bromine-lithium exchange followed by formylation with DMF using *n*-BuLi or *t*-BuLi or a combination of MeLi/*t*-BuLi on N-nosyl compound **3n** were not successful [12]. However, N-Boc substrate **8**, which was obtained by two-step protocol from **3n**, gave the desired formylated product **9**, but with poor yield (<10%), when the combination of MeLi/*t*-BuLi and DMF was used (Scheme 7). Screening of the several reaction conditions was failed to improve the yield of the desired aldehyde **9**.

The above formylation results led us to opt for the Stille vinylation reaction followed by oxidative cleavage. For this. purpose, compound **8** was treated with 1.5 equiv. of tributylvinyl tin in the presence of 10 mol% of $Pd(PPh_3)_4$ catalyst and LiCl additive in DMF, 4 h heating at 80 °C furnished the expected *ortho*-vinyl compound **10** (Scheme 8). The next was the oxidative cleavage of the vinyl unit into the desired aldehyde compound **9**. We followed the classical OsO_4–$NaIO_4$ mediated oxidative cleavage reaction [13]. The reaction in the presence of 2, 6-lutidine as an additive in 1:1 dioxane-water at rt successfully converted the vinyl group in compound **10** into the requisite aldehyde functionality in 69% yield in two steps. After the installation of the aldehyde group, the Boc-group was deprotected on treatment with TFA at 0 °C producing the intermediate imine and amino aldehyde mixture, as expected. Further reduction of the crude mixture with $NaBH_3CN$ or $NaBH(OAc)_3$ at 0 °C was presumed to favor the selective imine reduction and hence to facilitate the imine-amino aldehyde equilibrium towards imine reduced cyclized product **11**. However, we ended up with a mixture of **11** and amino alcohol **12**. Changing the borohydride proportion or temperature did not improve the result. In an alternative route, the Boc-deprotection was postponed until the requisite final cyclization and the compound **9** was subjected to $NaBH_4$ reduction at 0 °C that readily transformed it into compound **13**, which without further purification upon treatment with PBr_3 in the ethereal solution provided an intermediate compound having a benzylic bromo-functionality. Detailed mass spectroscopy analysis of the intermediate compound revealed that it did not have the Boc component on it. We assumed that acidic medium created in presence of PBr_3 led to Boc-deprotection in this step. The crude compound, after isolation used for the K_2CO_3-promoted cyclization in CH_3CN at 45 °C. The overnight reaction led to achieve the final cyclization to furnish compound **11** in 91% yield over the last three steps. Compound **11** is an advanced intermediate for the synthesis of nitrogen bioisostere of dihydrexidine. Tosyl deprotection and demethylation would complete the synthesis. However, our attempts for the deprotection of the *N*-tosyl group were unsuccessful.

3. Conclusion

We have developed a two-step protocol for the efficient synthesis of *trans*-3-amino-4-aryl tetrahydroquinolines with excellent diastereo- and enantioselectivity (dr: >99: 1 and ee up to 97%). The method is based on catalytic enantioselective aziridination and subsequent 6-*endo-tet* Friedel-Crafts cyclization called aminoarylation. It originates the enantioselectivity at the aziridination step and carries forwarded to the cyclization. In application, a synthesis of aza-analogue of dihydrexdine derivative is efficiently accomplished from easily accessible 3-amino-4-aryl tetrahydroquiniline. Combination of several anilines and cinnamyl units can enlist a wide variety of substrates and a subsequent asymmetric aminoarylation can attain a pool of tetrahydroquinolines enriched in diversity, which will be beneficial in medicinal and drug discovery chemistry.

4. Experimental section

4.1. General methods

We conducted all reactions using oven-dried glassware under Argon atmosphere. We used commercial grade reagents without further purification. Solvents were dried and distilled following standard protocols. Flash chromatography was carried out using

silica gel (230–400 mesh). TLC was performed on aluminium-backed plates coated with silica gel 60 with F_{254} indicator. The ^1H NMR and ^{13}C NMR spectra were recorded with 400 MHz and 100 MHz using $CDCl_3$. ^1H NMR chemical shifts are expressed in parts per million (δ) relative to $CHCl_3$ (d = 7.26); ^{13}C NMR chemical shifts are expressed in parts per million (δ) relative to the $CDCl_3$ resonance (δ = 77.0). High resolution mass spectra (HRMS) and electron spray ionization (ESI) mass spectrometry (MS) experiment were performed on Agilent Technologies 6530 Accurate-Mass Q-TOF LC/MS. Elemental analyses were carried out on a PerkinElmer 2400-II (IIT Kharagpur). HPLC analyses were done with a chiral stationary phase using Chiralpak AD-H column (4.6 mm × 150 mm) and AD-3 column (4.6 mm × 250 mm and particle size 5 μm and 3 μm). Specific optical rotation values were measured on a Jasco-P1200 polarimeter.

Nitrenoid reagent [14] (PhINNs) and bis(oxazoline) ligands [15] **L** were prepared according to standard procedures.

General procedure for the synthesis of *N*-protected-*N*-cinnamylanilines.

Synthesis of N-protected-N-cinnamylanilines **1b, 1c**.

Coupling of *N*-cinnamylaniline [16a] **1a** (2.40 mmol) and different acyl or sulfonyl chloride (2.88 mmol) using Et_3N (3.60 mmol) in CH_2Cl_2 afforded the *N*-protected-*N*-cinnamylanilines **1b** and **1c**.

Synthesis of N-protected-N-cinnamylanilines **1d-1n**.

Rest of the *N*-protected-*N*-cinnamylanilines [16b] **1d-1n** were prepared by conventional alkylation method *via* the reaction of protected aniline derivatives (5.08 mmol) with corresponding cinnamyl bromide derivatives (7.61 mmol) in the presence of NaH (10.15 mmol) in THF.

Analytical Data of N-protected-N-cinnamylanilines **1a-1n**:

N-cinnamylaniline, ***1a***. Yield = 95%; ^1H NMR ($CDCl_3$, 200 MHz): δ 7.43–7.10 (m, 7H), 6.82–6.59 (m, 4H), 6.36 (dt, *J* = 12.0, 6.0 Hz, 1H), 3.95 (d, *J* = 6.0 Hz, 2H), 3.74 (bs, 1H).

N-cinnamyl-4-methyl-N-phenylbenzenesulfonamide, ***1b***. Yield = 84%; ^1H NMR ($CDCl_3$, 200 MHz): δ 7.52 (d, *J* = 8.0 Hz, 2H), 7.26–7.23 (m, 10H), 7.08 (d, *J* = 8.0 Hz, 2H), 6.37 (d, *J* = 15.8 Hz, 1H), 6.16–6.02 (m, 1H), 4.33 (d, *J* = 6.6 Hz, 2H), 2.43 (3H, s).

N-cinnamyl-N-phenylmethanesulfonamide, ***1c***. Yield = 80%; ^1H NMR ($CDCl_3$, 200 MHz): δ 7.44–7.25 (m, 10H), 6.48 (d, *J* = 15.8 Hz, 1H), 6.27–6.16 (m, 1H), 4.44 (d, *J* = 6.6 Hz, 2H), 2.94 (s, 3H).

N-cinnamyl-N-(4-methoxyphenyl)methanesulfonamide, ***1d***. Yield = 86%; ^1H NMR ($CDCl_3$, 200 MHz): δ 7.29–7.23 (m, 7H), 6.88 (d, *J* = 8.8 Hz, 2H), 6.45 (d, *J* = 15.8 Hz, 1H), 6.27–6.12 (m, 1H), 4.38 (d, *J* = 6.4 Hz, 2H), 3.79 (s, 3H), 2.93 (s, 3H).

(E)-N-(4-chlorophenyl)-N-(3-(4-fluorophenyl)allyl)-methanesulfonamide, ***1e***. Yield = 70%; ^1H NMR ($CDCl_3$, 200 MHz): δ 7.38–7.23 (m, 6H), 6.97 (t, *J* = 8.4 Hz, 2H), 6.42 (d, *J* = 15.8 Hz, 1H), 6.15–6.04 (m, 1H), 4.40 (d, *J* = 6.4 Hz, 2H), 2.93 (s, 3H).

N-(4-chlorophenyl)-N-cinnamylmethanesulfonamide, ***1f.*** Yield = 80%; ^1H NMR ($CDCl_3$, 200 MHz): δ 7.29–7.22 (m, 7H), 7.02 (d, *J* = 8.6 Hz, 2H), 6.41 (d, *J* = 15.8 Hz, 1H), 6.17–6.04 (m, 1H), 4.41 (d, *J* = 6.4 Hz, 2H), 2.93 (s, 3H).

(E)-N-(3-(4-fluorophenyl)allyl)-N-(4-methoxyphenyl)-methanesulfonamide, ***1g***. Yield = 81%; ^1H NMR ($CDCl_3$, 200 MHz): δ 7.30–7.23 (m, 4H), 7.01–6.86 (m, 4H), 6.41 (d, *J* = 15.8 Hz, 1H), 6.17–6.03 (m, 1H), 4.36 (d, *J* = 6.4 Hz, 2H), 3.78 (s, 3H), 2.92 (s, 3H).

(E)-N-(3-(4-chlorophenyl)allyl)-N-(p-tolyl)methane-sulfonamide, ***1h***. Yield = 78%; ^1H NMR ($CDCl_3$, 200 MHz): δ 7.30–7.13 (m, 6H), 6.97 (t, *J* = 8.4 Hz, 2H), 6.43 (d, *J* = 15.8 Hz, 1H), 6.18–6.03 (m, 1H), 4.40 (d, *J* = 6.4 Hz, 2H), 2.93 (s, 3H), 2.34 (s, 3H).

(E)-N-(3-(4-fluorophenyl)allyl)-N-(p-tolyl)methane-sulfonamide, ***1i***. Yield = 68%; ^1H NMR ($CDCl_3$, 200 MHz): δ 7.29–7.15 (m, 8H), 6.42 (d, *J* = 15.8 Hz, 1H), 6.23–6.12 (m, 1H), 4.39 (d, *J* = 6.4 Hz, 2H), 2.92 (s, 3H), 2.34 (s, 3H).

N-(4-chlorophenyl)-N-cinnamyl-4-methylbenzene-sulfonamide, ***1j***. Yield = 88%; ^1H NMR ($CDCl_3$, 200 MHz): δ 7.52 (d, *J* = 8.2 Hz, 2H), 7.29–7.22 (m, 9H), 7.02 (d, *J* = 8.6 Hz, 2H), 6.40 (d, *J* = 16.0 Hz, 1H), 6.13–6.02 (m, 1H), 4.30 (d, *J* = 6.6 Hz, 2H), 2.43 (s, 3H).

N-cinnamyl-4-methyl-N-(p-tolyl)benzenesulfonamide, ***1k***. Yield = 90%; ^1H NMR ($CDCl_3$, 200 MHz): δ 7.53 (d, *J* = 8.0 Hz, 2H), 7.27–7.24 (m, 7H), 7.07 (d, *J* = 8.2 Hz, 2H), 6.94 (d, *J* = 8.2 Hz, 2H), 6.36 (d, *J* = 15.8 Hz, 1H), 6.15–6.05 (m, 1H), 4.30 (d, *J* = 6.4 Hz, 2H), 2.43 (s, 3H), 2.30 (s, 3H).

N-cinnamyl-N-(4-methoxyphenyl)-4-methylbenzene-sulfonamide, ***1l***. Yield = 91%; ^1H NMR ($CDCl_3$, 200 MHz): δ 7.53 (d, *J* = 8.0 Hz, 2H), 7.27–7.24 (m, 7H), 6.96 (d, *J* = 9.0 Hz, 2H), 6.77 (d, *J* = 9.0 Hz, 2H), 6.35 (d, *J* = 16.0 Hz, 1H), 6.15–6.01 (m, 1H), 4.29 (d, *J* = 6.4 Hz, 2H), 3.77 (s, 3H), 2.43 (s, 3H).

N-cinnamyl-N-(3,4-dimethoxyphenyl)-4-methyl-benzenesulfonamide, ***1m***. Yield = 88%; ^1H NMR ($CDCl_3$, 200 MHz): δ 7.55 (d, *J* = 8.2 Hz, 2H), 7.35–7.15 (m, 7H), 6.72 (d, *J* = 8.2 Hz, 1H), 6.58–6.52 (m, 2H), 6.37 (d, *J* = 15.8 Hz, 1H), 6.18–6.07 (m, 1H), 4.29 (d, *J* = 6.4 Hz, 2H), 3.83 (s, 3H), 3.72 (s, 3H), 2.43 (s, 3H).

(E)-N-(3-(2-bromophenyl)allyl)-N-(3,4-dimethoxyphenyl)-4-methylbenzenesulfonamide, ***1n***. Yield = 89%; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.58–7.53 (m, 2H), 7.48 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.34 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.30–7.25 (m, 2H), 7.23–7.19 (m, 1H), 7.09–7.04 (m, 1H), 6.74–6.69 (m, 2H), 6.61–6.57 (m, 2H), 6.09–6.02 (m, 1H), 4.33 (dd, *J* = 6.6, 1.5 Hz, 2H), 3.85 (s, 3H), 3.74 (s, 3H), 2.43 (s, 3H).

4.2. General procedure for synthesis of racemic 3-amino-4-aryltetrahydroquinolines (±)-3

To a well-stirred suspended solution of PhINNs (1.0 equiv) and *N*-cinnamylaniline **1** (5.0 equiv) and 4 Å MS in 2.4 mL CH_2Cl_2, $Cu(OTf)_2$ (0.1 equiv) was added and the reaction was allowed to stir at 35 °C under an argon atmosphere. The reaction was judged to be complete as soon as the entire nitrenoid reagent was dissolved in the reaction medium. On completion, the reaction mixture was diluted with CH_2Cl_2 (10 mL) and filtered through a short plug of silica gel. The silica gel was washed with an additional 10 mL of CH_2Cl_2. The filtrate was concentrated by rotary evaporation under reduced pressure. The semi-crude reaction mass was taken in a 10 mL two-neck round-bottom flask and dry CH_2Cl_2 (4 mL) was added. $Cu(OTf)_2$ (0.1 equiv) and 0.2 g of powdered molecular sieves (4 Å) were added and the reaction mixture was allowed to stir at rt under an argon atmosphere. Within 0.75–2 h, the reaction was completed and the crude mass was purified by column chromatography using EtOAc/hexane as an eluent, which provided the 3-amino-4-aryltetrahydroquinoline ***(±)-3***.

4.3. General procedure for asymmetric synthesis of 3-amino-4-aryltetrahydroquinolines 3

A 10 mL two-neck round-bottom flask was charged with Box ligand (1*R*, 2*S*)-**L5** (0.011 g, 0.03 mmol, 0.12 equiv) and $Cu(OTf)_2$ (0.009 g, 0.025 mmol, 0.1 equiv). Anhydrous CH_2Cl_2 (1.2 mL) was added by syringe and the resulting mixture was stirred for 30 min. To this solution, substrate **1b** (0.449 g, 1.23 mmol, 5.0 equiv) taken in 1.2 mL CH_2Cl_2, PhINNs (0.1 g, 0.24 mmol, 1.0 equiv), and 0.2 g of powdered molecular sieves (4 Å) were added and the reaction mixture was allowed to stir at 35 °C under argon atmosphere. As soon as the entire nitrenoid reagent was dissolved in the reaction medium, the reaction mixture was diluted with CH_2Cl_2 (10 mL) and filtered through a short plug of silica gel. The silica gel was washed with an additional 10 mL of CH_2Cl_2. The filtrate was concentrated by rotary evaporation under reduced pressure. The semi-crude reaction mass was taken in a 10 mL two-neck round-bottom flask and

4 mL dry CH_2Cl_2 was added. $Cu(OTf)_2$ (0.009 g, 0.025 mmol, 0.1 equiv) and 0.2 g of powdered molecular sieves (4 Å) were added and the reaction mixture was allowed to stir at rt under an argon atmosphere. Within 1 h, the reaction was completed and the crude mass was purified by column chromatography using EtOAc/hexane as an eluent, which provided the 3-amino-4-aryltetrahydroquinoline **3b** (0.1 g, 72% yield).

4.3.1. Analytical data of aziridine (±)-2b and 3-amino-4-aryltetrahydroquinolines 3

4.3.1.1. 4-Methyl-N-(((2R,3R)-1-((4-nitrophenyl)sulfonyl)-3-phenylaziridin-2-yl)methyl)-N-phenylbenzenesulfonamide (±)-2b. ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.29 (d, J = 8.4 Hz, 2H), 8.05 (d, J = 8.6 Hz, 2H), 7.51 (d, J = 7.6 Hz, 2H), 7.34–7.20 (m, 8H), 7.03 (d, J = 5.4 Hz, 2H), 6.86 (d, J = 5.8 Hz, 2H) 4.62 (dd, J = 14.4, 3.2 Hz, 1H), 3.95 (dd, J = 14.4, 9.8 Hz, 1H), 3.68 (d, J = 4.0 Hz, 1H),3.26–3.20 (m, 1H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 129.7, 129.5, 129.1, 128.7, 128.6, 128.6, 128.4, 127.7, 126.3, 124.3, 50.8, 50.3, 50.0, 21.6; Anal. (CHN %) Calcd for $C_{28}H_{25}N_3O_6S_2$: C, 59.67; H, 4.47; N, 7.46. Found: C, 59.74; H, 4.54; N, 7.35.

4.3.1.2. 4-Nitro-N-[4-phenyl-1-(toluene-4-sulfonyl)-1,2,3,4-tetrahydro-quinolin-3-yl]-benzenesulfonamide ***3b.*** 0.100 g, 72% yield; white solid, mp 200–201 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, J = 8.8 Hz, 2H), 7.87 (d, J = 8.4 Hz, 2H), 7.70 (d, J = 8.4 Hz, 2H), 7.54 (d, J = 8.8 Hz, 2H), 7.29 (2H, d, J = 8.0 Hz), 7.22 (1H, t, J = 8.4 Hz), 7.08 (1H, t, J = 7.2 Hz), 6.98 (t, J = 7.6 Hz, 1H), 6.92 (t, J = 7.2 Hz, 2H), 6.58 (d, J = 7.6 Hz, 1H), 6.36 (d, J = 7.6 Hz, 2H), 4.77 (d, J = 5.2 Hz, 1H), 4.58–4.50 (m, 1H), 3.63 (d, J = 8.0 Hz, 1H), 3.46–3.40 (m, 2H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.6, 145.0, 144.1, 140.9, 136.4, 135.7, 130.6, 130.1, 129.9 (2C), 128.65 (2C), 128.63 (2C), 127.82 (2C), 127.81 (3C), 127.6, 127.3, 124.4, 123.9 (2C), 52.9, 50.6, 50.3, 21.6; Anal. (CHN %) Calcd for $C_{28}H_{25}N_3O_6S_2$: C, 59.67; H, 4.47; N, 7.46. Found: C, 59.75; H, 4.56; N, 7.36; HPLC: Daicel Chiralpak AD-H, hexane/*i*-propanol = 80/20, 1.0 ml/min, 220 nm, major 11.7 min and minor 22.9 min; $[\alpha]_D^{28} = -97$ (c 0.30, CH_2Cl_2) for 75% ee.

4.3.1.3. N-(1-Methanesulfonyl-4-phenyl-1,2,3,4-tetrahydro-quinolin-3-yl)-4-nitro-benzenesulfonamide (±)-3c. 0.080 g, 66% yield; white solid, mp 165–166 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (d, J = 8.4 Hz, 2H), 7.76 (d, J = 8.4 Hz, 2H), 7.59 (d, J = 8.4 Hz, 1H), 7.26–7.11 (m, 4H), 6.98 (t, J = 7.6 Hz, 1H), 6.87 (t, J = 7.2 Hz, 2H), 6.76 (d, J = 8.0 Hz, 1H), 5.28 (d, J = 6.4 Hz, 1H), 4.11 (dd, J = 2.4, 7.6 Hz, 1H), 3.96 (d, J = 7.2 Hz, 1H), 3.76 (d, J = 5.2 Hz, 1H), 3.55 (dd, J = 8.0, 13.2 Hz, 1H), 3.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.8, 144.8, 141.1, 136.1, 131.3, 128.9 (2C), 128.5 (2C), 128.0 (2C), 127.9, 127.7, 127.5, 124.8, 124.2 (2C), 121.3, 54.1, 50.1, 48.3, 40.1; Anal. (CHN %) Calcd for $C_{22}H_{21}N_3O_6S_2$: C, 54.20; H, 4.34; N, 8.62. Found: C, 54.32; H, 4.29; N, 8.72.

4.3.1.4. N-[4-(4-Fluoro-phenyl)-1-methanesulfonyl-6-methoxy-1,2,3,4-tetrahydro-quinolin-3-yl]-4-nitro-benzenesulfonamide (±)-3g. 0.098 g, 74% yield; white solid, mp 155–156 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (d, J = 8.8 Hz, 2H), 7.83 (d, J = 8.8 Hz, 2H), 7.48 (d, J = 8.8 Hz, 1H), 6.92–6.79 (m, 5H), 6.24 (d, J = 2.8 Hz, 1H), 5.15 (bs, 1H), 3.97–3.92 (m, 2H), 3.78–3.74 (m, 1H), 3.63 (m, 3H), 3.56–3.51 (m, 1H), 3.14 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.8 (d, J = 245.1 Hz, 1C), 156.7, 149.3, 146.0, 137.1, 131.4, 130.48, 130.40, 129.0, 127.7 (2C), 124.1, 123.8 (2C), 115.5, 115.4, 115.2, 113.2, 55.2, 54.6, 50.0, 48.9, 39.7; Anal. (CHN %) Calcd for $C_{23}H_{22}FN_3O_7S_2$: C, 51.58; H, 4.14; N, 7.85. Found: C, 51.70; H, 4.19; N, 7.77.

4.3.1.5. N-[4-(4-Chloro-phenyl)-1-methanesulfonyl-6-methyl-1,2,3,4-tetrahydro-quinolin-3-yl]-4-nitro-benzenesulfonamide ***3h.*** 0.107 g, 81% yield; white solid, mp 64–65 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.22 (d, J = 8.8 Hz, 2H), 7.83 (d, J = 8.8 Hz, 2H), 7.46 (d, J = 9.0 Hz, 1H), 7.15–7.04 (m, 3H), 6.85 (2H, d, J = 8.2 Hz), 6.55 (1H, s), 5.06 (1H, d, J = 7.0 Hz), 3.96–3.90 (m, 2H), 3.80–3.65 (m, 1H), 3.59–3.48 (m, 1H), 3.15 (s, 3H), 2.16 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.8, 145.0, 139.8, 134.9, 133.6, 133.5, 131.4, 129.9 (2C), 128.9 (2C), 128.6, 128.0 (2C), 124.2 (3C), 121.5, 54.4, 49.4, 48.4, 40.1, 20.5; Anal. (CHN %) Calcd for $C_{23}H_{22}ClN_3O_6S_2$: C, 51.54; H, 4.14; N, 7.84. Found: C, 51.62; H, 4.29; N, 7.80; HPLC: Daicel Chiralpak AD-H, hexane/*i*-propanol = 80/20, 1.0 ml/min, 220 nm, major 12.9 min and minor 18.8 min; $[\alpha]_D^{28} = -32$ (c 0.30, CH_2Cl_2) for 87% ee.

4.3.1.6. N-[4-(4-Fluoro-phenyl)-1-methanesulfonyl-6-methyl-1,2,3,4-tetrahydro-quinolin-3-yl]-4-nitro-benzenesulfonamide (±)-3i. 0.090 g, 70% yield; white solid, mp 95–96 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.23 (d, J = 8.6 Hz, 2H), 7.87 (d, J = 9.0 Hz, 2H), 7.48 (d, J = 8.4 Hz, 1H), 7.06 (d, J = 8.6 Hz, 1H), 6.88 (d, J = 7.0 Hz, 4H), 6.58 (s, 1H), 5.06 (d, J = 4.2 Hz, 1H), 4.00–3.76 (m, 3H), 3.89–3.65 (m, 2H), 3.61–3.51 (m, 1H), 3.14 (s, 3H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.9 (1C, d, J = 246.0 Hz), 149.8, 145.1, 137.2, 134.7, 133.5, 131.5, 130.2, 130.1, 128.8, 128.1 (2C), 127.3, 124.4 (2C), 121.2, 115.8, 115.7, 54.3, 49.2, 48.1, 40.0, 20.5; Anal. (CHN %) Calcd for $C_{23}H_{22}FN_3O_6S_2$: C, 53.17; H, 4.27; N, 8.09. Found: C, 53.28; H, 4.30; N, 7.98.

4.3.1.7. N-[6-Chloro-4-phenyl-1-(toluene-4-sulfonyl)-1,2,3,4-tetrahydro-quinolin-3-yl]-4-nitro-benzenesulfonamide ***3j.*** 0.123 g, 83% yield; white solid, mp 195–196 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.07 (d, J = 8.8 Hz, 2H), 7.90 (d, J = 9.0 Hz, 1H), 7.76 (d, J = 8.2 Hz, 2H), 7.58 (d, J = 9.0 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 7.22–7.13 (m, 2H), 6.99 (t, J = 7.4 Hz, 2H), 6.60 (s, 1H), 6.40 (t, J = 7.2 Hz, 2H), 4.67 (d, J = 5.2 Hz, 1H), 4.60–4.54 (m, 1H), 3.63 (d, J = 7.8 Hz, 1H), 3.48–3.42 (m, 2H), 2.53 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.5, 145.7, 143.8, 140.5, 135.8, 133.8, 133.7, 130.7, 129.8, 129.6 (2C), 128.3 (2C), 127.8 (2C), 127.4 (2C), 126.8 (3C), 126.5, 126.0, 123.1 (2C), 51.4, 51.1, 48.6, 21.1; Anal. (CHN %) Calcd for $C_{28}H_{24}ClN_3O_6S_2$: C, 56.23; H, 4.04; N, 7.03. Found: C, 56.33; H, 4.13; N, 6.96. HPLC: Daicel Chiralpak AD-H, hexane/*i*-propanol = 80/20, 1.0 ml/min, 220 nm, major 9.7 min and minor 46.3 min; $[\alpha]_D^{28} = -101$ (c 0.30, CH_2Cl_2) for 89% ee.

4.3.1.8. N-[6-Methyl-4-phenyl-1-(toluene-4-sulfonyl)-1,2,3,4-tetrahydro-quinolin-3-yl]-4-nitro-benzenesulfonamide ***3k.*** 0.106 g, 74% yield; white solid, mp 270–271 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, J = 7.6 Hz, 2H), 7.81–7.72 (m, 3H), 7.57 (d, J = 8.8 Hz, 2H), 7.35–7.29 (m, 1H), 7.11–6.91 (4H, m), 6.42 (3H, d, J = 6.2 Hz), 4.88 (1H, d, J = 5.4 Hz), 4.57–4.52 (m, 1H), 3.62 (d, J = 8.0 Hz, 1H), 3.45–3.40 (m, 2H), 2.50 (s, 3H), 2.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.9, 146.1, 143.7, 141.7, 136.6, 135.4, 133.0, 131.5, 130.8, 129.7 (2C), 128.8 (2C), 128.0, 127.9 (2C), 127.8 (2C), 127.2 (2C), 126.6, 124.8, 123.5 (2C), 52.5, 51.4, 49.4, 21.4, 20.6; Anal. (CHN %) Calcd for $C_{29}H_{27}N_3O_6S_2$: C, 60.30; H, 4.71; N, 7.27. Found: C, 60.43; H, 4.78; N, 7.19; HPLC: Daicel Chiralpak AD-H, hexane/*i*-propanol = 80/20, 1.0 ml/min, 220 nm, major 9.1 min and minor 33.0 min; $[\alpha]_D^{28} = -87$ (c 0.30, CH_2Cl_2) for 73% ee.

4.3.1.9. N-[6-Methoxy-4-phenyl-1-(toluene-4-sulfonyl)-1,2,3,4-tetrahydro-quinolin-3-yl]-4-nitro-benzenesulfonamide ***3l.*** 0.116 g, 79% yield; white solid, mp 172–173 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, J = 8.4 Hz, 2H), 7.80 (d, J = 8.8 Hz, 1H), 7.67 (d, J = 8.0 Hz, 2H), 7.49 (d, J = 8.8 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 7.05 (t, J = 7.6 Hz, 1H), 6.87 (t, J = 7.6 Hz, 2H), 6.78 (dd, J = 2.8, 9.2 Hz, 1H), 6.28 (d, J = 7.2 Hz, 2H), 6.02 (d, J = 2.8 Hz, 1H), 4.91 (d, J = 6.4 Hz, 1H), 4.60–4.53 (m, 1H), 3.59 (s, 3H), 3.54 (d, J = 9.2 Hz, 1H), 3.40–3.30 (m, 2H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.2,

149.4, 144.9, 144.0, 140.5, 136.2, 132.0, 129.8 (3C), 128.5 (4C), 127.9 (2C), 127.6 (2C), 127.3, 126.2, 123.8 (2C), 115.2, 113.1, 55.2, 52.6, 50.7 (2C), 21.5; Anal. (CHN %) Calcd for $C_{29}H_{27}N_3O_7S_2$: C, 58.67; H, 4.58; N, 7.08. Found: C, 58.72; H, 4.61; N, 6.91; HPLC: Daicel Chiralpak AD-H, hexane/*i*-propanol = 80/20, 1.0 ml/min, 220 nm, major 13.6 min and minor 48.4 min; $[\alpha]_D^{28} = -137$ (c 0.30, CH_2Cl_2) for 90% ee.

4.3.1.10. N-[6,7-Dimethoxy-4-phenyl-1-(toluene-4-sulfonyl)-1,2,3,4-tetrahydro-quinolin-3-yl]-4-nitro-benzenesulfonamide ***3m***. 0.103 g, 67% yield; white solid, mp 235–236 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, J = 8.8 Hz, 2H), 7.71 (d, J = 8.0 Hz, 2H), 7.50 (d, J = 9.2 Hz, 3H), 7.31 (d, J = 8.0 Hz, 2H), 7.06 (t, J = 7.6 Hz, 1H), 6.89 (t, J = 7.6 Hz, 2H), 6.28 (d, J = 7.6 Hz, 2H), 5.94 (s, 1H), 4.87 (d, J = 7.6 Hz, 1H), 4.64–4.60 (dd, J = 3.2, 13.6 Hz, 1H), 3.90 (s, 3H), 3.54 (d, J = 7.2 Hz, 1H), 3.53 (s, 3H), 3.41–3.27 (m, 2H), 3.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.1, 147.8, 147.1, 145.6, 143.9, 141.3, 136.2, 129.7 (2C), 128.5 (2C), 128.1 (2C), 127.9 (2C), 127.4 (2C), 126.9, 123.6 (3C), 123.3, 111.8, 108.1, 56.0, 55.6, 52.6, 51.4, 49.7, 21.5; DEPT-135 NMR (100 MHz, $CDCl_3$): δ 130.7, 129.9, 128.7, 128.6, 127.8, 127.8, 127.6, 127.4, 125.8, 124.4, 123.9, 52.9, 50.7, 50.4, 21.6; Anal. (CHN %) Calcd for $C_{30}H_{29}N_3O_8S_2$: C, 57.77; H, 4.69; N, 6.74. Found: C, 57.83; H, 4.56; N, 6.76; HPLC: Daicel Chiralpak AD-H, hexane/*i*-propanol = 80/20, 1.0 ml/min, 220 nm, major 16.0 min and minor 37.7 min; $[\alpha]_D^{28} = -133$ (c 0.30, CH_2Cl_2) for 82% ee.

4.3.1.11. N-((3S,4S)-4-(2-bromophenyl)-6,7-dimethoxy-1-tosyl-1,2,3,4-tetrahydroquinolin-3-yl)-4-nitrobenzene-sulfonamide ***3n***. 0.123 g, 71% yield; white solid, mp 211–213 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, J = 8.8 Hz, 2H), 7.74 (d, J = 8.2 Hz, 2H), 7.56 (d, J = 8.8 Hz, 2H), 7.46 (s, 1H), 7.34 (d, J = 8.0 Hz, 2H), 7.13 (dd, J = 8.2, 1.3 Hz, 1H), 6.82–6.78 (m, 1H), 6.62 (t, J = 7.6 Hz, 1H), 5.78 (s, 1H), 5.15 (d, J = 6.9 Hz, 1H), 4.62 (d, J = 10.1 Hz, 1H), 4.26 (d, J = 9.1 Hz, 1H), 3.90 (s, 3H), 3.50 (s, 3H), 2.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.5, 148.2, 147.4, 145.2, 144.2, 136.4, 132.5, 129.9, 128.9, 128.7, 128.2, 127.8, 127.6, 127.5, 125.1, 124.4, 123.8, 122.4, 111.4, 108.3, 77.4, 77.1, 76.8, 56.1, 55.8, 53.6, 51.4, 48.1, 21.7; ESI-MS *m/z*: $[M+H]^+$ Calcd for $C_{30}H_{28}BrN_3O_8S_2$ 702.0579; found 702.0582; HPLC: Daicel Chiralpak AD-3, hexane/*i*-propanol = 70/30, 1.0 ml/min, 254 nm, major 13.4 min and minor 31.4 min; $[\alpha]_D^{28} = -152$ (c 0.50, CH_2Cl_2) for 98% ee.

4.3.2. Experimental procedure and analytical data of compounds 4, 8, 10, 9, 13, 11

4.3.2.1. N-[6,7-Dimethoxy-4-phenyl-1-(toluene-4-sulfonyl)-1,2,3,4-tetrahydro-quinolin-3-yl]-N-methoxymethyl-4-nitro-benzenesulfonamide ***4***. NaH (0.13 g, 0.321 mmol) was added to a solution of **3m** (0.1 g, 0.160 mmol) in CH_2Cl_2 (3 mL) at 0 °C and allowed to stir for 30 min under argon atmosphere. MOMCl (2 equiv, 0.025 mL, 0.321 mmol) was added to the reaction mixture slowly and stirred. After 4 h, the reaction was quenched with a saturated NH_4Cl solution and extracted with CH_2Cl_2 and dried with $NaSO_4$. The reaction mixture was subjected to column purification using 20% ethyl acetate in hexane as an eluent to obtain compound 4 (0.102 g, 95%). White solid, mp 190 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, J = 8.4 Hz, 2H), 7.77 (d, J = 8.0 Hz, 2H), 7.45 (t, J = 9.2 Hz, 3H), 7.35 (d, J = 8.0 Hz, 2H), 6.96 (t, J = 7.2 Hz, 1H), 6.74 (t, J = 7.6 Hz, 2H), 6.09 (d, J = 7.2 Hz, 2H), 5.90 (s, 1H), 5.02 (d, J = 11.2 Hz, 1H), 4.69–4.64 (m, 2H), 4.04 (d, J = 10.8 Hz, 1H), 3.90 (s, 3H), 3.91–3.87 (m, 1H), 3.58 (t, J = 13.2 Hz, 1H), 3.50 (s, 3H), 3.40 (s, 3H), 2.53 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.2, 147.7, 147.2, 145.2, 143.9, 141.8, 136.5, 129.8 (2C), 128.5 (2C), 128.2, 128.1 (4C), 127.8 (2C), 126.8, 124.4, 123.5 (2C), 111.8, 108.1, 75.9, 56.9, 56.0, 55.63, 55.60, 50.4, 46.0, 21.6; Anal. (CHN %) Calcd for $C_{32}H_{33}N_3O_9S_2$: C, 57.56; H, 4.98; N, 6.29. Found: C, 57.65; H, 5.09; N, 6.21; $[\alpha]_D^{28} = -113$ (c 0.30, CH_2Cl_2).

4.3.2.2. tert-butyl ((3S,4S)-4-(2-bromophenyl)-6,7-dimethoxy-1-tosyl-1,2,3,4-tetrahydroquinolin-3-yl)carbamate ***8***. To a well stirred solution of 3n (0.137 g, 0.195 mmol) taken in 4 mL CH_3CN:DMSO (49:1) at 40 °C, 1.2 equiv 4-methoxythiophenol (0.03 mL, 0.234 mmol) and 1.2 equiv of activated K_2CO_3 (0.032 g, 0.234 mmol) were added and the heterogeneous reaction mixture was allowed to stir vigorously at 40 °C for 4 h. Upon completion of the reaction the solvent was evaporated under reduced pressure and the residue was taken in ethyl acetate (10 mL). The organic portion was washed with water, brine, dried over Na_2SO_4, and concentrated. The denosylated compound formed exclusively as confirmed from LCMS data taken from the crude reaction mass and hence not subjected to further purification instead used in the next step. ESI-MS *m/z*: $[M+H]^+$ Calcd for $C_{24}H_{25}BrN_2O_4S$ 517.0797; found 517.0809.

The crude reaction mass containing nosyl deprotected compound was taken in 2 mL dry THF. 3 equiv of Boc_2O (0.135 mL, 0.586 mmol) was added and the reaction mixture was allowed to stir for overnight. The solvent was evaporated under reduced pressure and 10 mL of ethyl acetate was added. The organic layer was washed with water, brine and dried over Na_2SO_4. After solvent evaporation, the crude reaction mixture was subjected to column purification using 15% ethyl acetate and pet-ether as an eluent to afford titled compound **8** as white solid (0.110 g, yield 92% in overall two steps). White solid, mp 151–153 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, J = 7.8 Hz, 2H), 7.56 (s, 1H), 7.50 (dd, J = 8.1, 1.2 Hz, 1H), 7.28 (d, J = 8.0 Hz, 2H), 7.03–6.99 (m, 1H), 6.86–6.82 (m, 1H), 6.01 (s, 1H), 5.70 (d, J = 7.8 Hz, 1H), 4.51 (s, 1H), 4.32 (dd, J = 23.7, 11.2 Hz, 2H), 3.93 (s, 3H), 3.86–3.71 (m, 1H), 3.59 (s, 3H), 3.56–3.42 (m, 1H), 2.44 (s, 3H), 1.38 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.5, 148.0, 146.9, 143.9, 141.8, 136.3, 132.5, 130.1, 129.9, 129.4, 128.5, 128.0, 127.6, 125.3, 122.1, 112.0, 107.3, 79.7, 56.1, 55.9, 49.6, 48.2, 28.3, 21.6; ESI-MS *m/z*: $[M+Na]^+$ Calcd for $C_{29}H_{33}BrN_2O_6S$ 639.1140; found 639.1131.

4.3.2.3. tert-butyl ((3S,4R)-6,7-dimethoxy-1-tosyl-4-(2-vinylphenyl)-1,2,3,4-tetrahydroquinolin-3-yl)carbamate ***10***. To a solution of compound 8 (0.1 g, 0.162 mmol) in dry DMF (1.6 mL), 2 equiv LiCl (0.014 g, 0.324 mmol) and 10 mol% $Pd(PPh_3)_4$ catalyst (0.019 g, 0.016 mmol) were added under argon atmosphere. Five times evacuation of the reaction vessel and consequent argon purge-in process was conducted before the addition of 1.5 equivalent of tributyl vinyl tin reagent (0.07 mL, 0.243 mmol). The reaction mixture was heated to 80 °C and stirred for 4 h. After completion of the reaction, the reaction mixture was quenched with water and extracted with ethyl acetate (3X10 mL). The combined extracts were dried over sodium sulfate and evaporated. LCMS data from the crude mixture detects the formation of compound 10 along with excess tributyl vinyl tin reagent. Finally, the crude mass was triturated using distilled n-pentane (5 times) to remove excess tributyl vinyl tin reagent which provided a sufficiently pure compound 10 for the next step. ESI-MS *m/z*: $[M+Na]^+$ Calcd for $C_{31}H_{36}N_2O_6S$ 587.2192; found 587.2192.

4.3.2.4. tert-butyl ((3S,4R)-4-(2-formylphenyl)-6,7-dimethoxy-1-tosyl-1,2,3,4-tetrahydroquinolin-3-yl)carbamate ***9***. The crude vinylated compound 10 (0.089 g, 0.158 mmol) was dissolved in 1:1 dioxane-water (3 mL). 4 equiv of both 2, 6-lutidine (0.075 mL, 0.63 mmol) and $NaIO_4$ (0.135 g, 0.63 mmol) were added and the reaction flask was covered with aluminium foil. 0.05(M) solution of OsO_4 in H_2O (0.16 mL, 0.008 mmol, 5 mol%) was cautiously added to the reaction mixture and allowed it to stir at room temperature with constant monitoring by TLC. After 4 h, the reaction mixture was quenched by saturated aq. $NaHSO_3$ and extracted with ethyl acetate (3x10 mL). Combined organic layers were washed with

brine and dried over Na_2SO_4. The solvent was evaporated in vacuo and the crude product was purified by flash chromatography using 10% ethyl acetate and hexane to get the titled aldehyde compound 9 (0.063 g, yield 69% in overall two steps). Gummy liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.12 (s, 1H), 7.82–7.66 (m, 3H), 7.58 (s, 1H), 7.37 (t, J = 7.5 Hz, 1H), 7.27 (d, J = 7.3 Hz, 2H), 7.11–7.07 (m, 1H), 5.88–5.83 (m, 2H), 5.07 (d, J = 9.4 Hz, 1H), 5.01 (d, J = 6.8 Hz, 1H), 4.52 (d, J = 12.6 Hz, 1H), 3.94 (s, 3H), 3.67–3.53 (m, 1H), 3.42 (s, 3H), 3.38 (t, J = 12.7 Hz, 1H), 2.44 (s, 3H), 1.35 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.5(CHO), 154.7, 147.9, 146.9, 145.3, 143.8, 139.3, 136.4, 134.6, 134.0, 133.7, 130.4, 129.8, 128.1, 127.4, 123.3, 112.4, 107.7, 79.4, 56.1, 55.8, 51.1, 49.9, 42.5, 28.3, 21.6; ESI-MS *m/z*: $[M+Na]^+$and $[M + MeOH + Na]^+$ Calcd for $C_{30}H_{34}N_2O_7S$ 589.1984 and 621.2247; found 589.1982 and 621.2245.

4.3.2.5. tert-butyl ((3S,4R)-4-(2-(hydroxymethyl)phenyl)-6,7-dimethoxy-1-tosyl-1,2,3,4-tetrahydroquinolin-3-yl)carbamate ***13***. To a well stirred solution of aldehyde 9 (0.1 g, 0.177 mmol) in dry methanol (4 mL), were added $NaBH_4$ (1.5 equiv, 0.010 g, 0.265 mmol) in one portion under argon atmosphere at 0 °C. The reaction mixture was allowed to stir and monitored by TLC. Within 15 min, the reaction was completed (compound 13 was detected in LCMS as a sole product from the reaction mixture) and quenched with saturated aqueous NH_4Cl. The reaction mixture was concentrated and extracted with ethyl acetate (3x10 mL). After washed with brine, the combined extracts were dried over sodium sulfate, evaporated and used in the next step. ESI-MS *m/z*: $[M+Na]^+$ Calcd for $C_{30}H_{36}N_2O_7S$ 591.2141; found 591.2138.

4.3.2.6. (6aS,12bR)-2,3-dimethoxy-5-tosyl-5,6,6a,7,8,12b hexahydrodibenzo[c,f] [1,7]naphthyridine ***11***. The crude compound 13, yielded in the last step, dissolved in dry diethyl ether (2.5 mL) and thereafter 1 equiv of PBr_3 (0.017 mL, 0.177 mmol) was added slowly under argon atmosphere at 0 °C. The reaction mixture was allowed to stir for 1h. The brominated compound was detected exclusively in LCMS after the complete reaction. The reaction mixture was quenched with crushed ice and stirred with excess solid $NaHCO_3$. The mixture was extracted with diethyl ether (2x10 mL), washed with brine, and the combined extracts were dried over sodium sulfate. Finally, it was concentrated and directly processed without further purification. ESI-MS *m/z*: $[M+H]^+$Calcd for $C_{25}H_{27}BrN_2O_4S$ 531.0953; found 533.0906. Activated K_2CO_3 (5 equiv, 0.122g, 0.883 mmol) was added to the solution of crude bromide compound from the previous step in dry CH_3CN (2.5 mL). The heterogeneous mixture was warmed to 45 °C with vigorous stirring. In 10h reaction time, the cyclized product 11 was detected in TLC and LCMS from the reaction mixture. The yellow colored suspension was concentrated in vacuo and extracted with ethyl acetate (3x10 mL). The combined extracts were washed with brine, dried over sodium sulphate, and then concentrated. The resultant crude mass was subjected to column purification using basic alumina to afford the entitled compound 11 (0.071 g, yield 91% in overall three steps), as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (d, J = 8.3 Hz, 2H), 7.37 (s, 1H), 7.24–7.16 (m, 4H), 7.11–7.01 (m, 2H), 6.64 (s, 1H), 3.96 (m, 6H), 3.73 (s, 3H), 3.50 (dd, J = 11.8, 10.7 Hz, 1H), 2.79–2.72 (m, 1H), 2.55 (d, J = 10.6 Hz, 1H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.6, 147.1, 143.7, 137.0, 135.4, 132.1, 129.7, 129.5, 127.7, 127.0, 126.9, 126.6, 126.2, 112.0, 107.5, 59.9, 56.2, 56.0, 51.1, 48.9, 41.7, 21.5; DEPT-135 NMR (100 MHz, $CDCl_3$): δ 129.5, 127.0, 126.9, 126.6, 126.2, 112.0, 107.5, 59.9, 56.2, 56.0, 51.1, 48.9, 41.7, 21.5; ESI-MS *m/z*: $[M+H]^+$Calcd for $C_{25}H_{26}N_2O_4S$ 451.1692; found 451.1661.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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