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DIASTEREOSELECTIVE SYNTHESIS OF 2,4-SUBSTITUTED TETRAHYDROQUINOLINES VIA $Hf(OTf)_4$-CATALYZED SUBSTITUTION/CYCLIZATION OF 2-AMINOBENZYL ALCOHOLS WITH STYRENES

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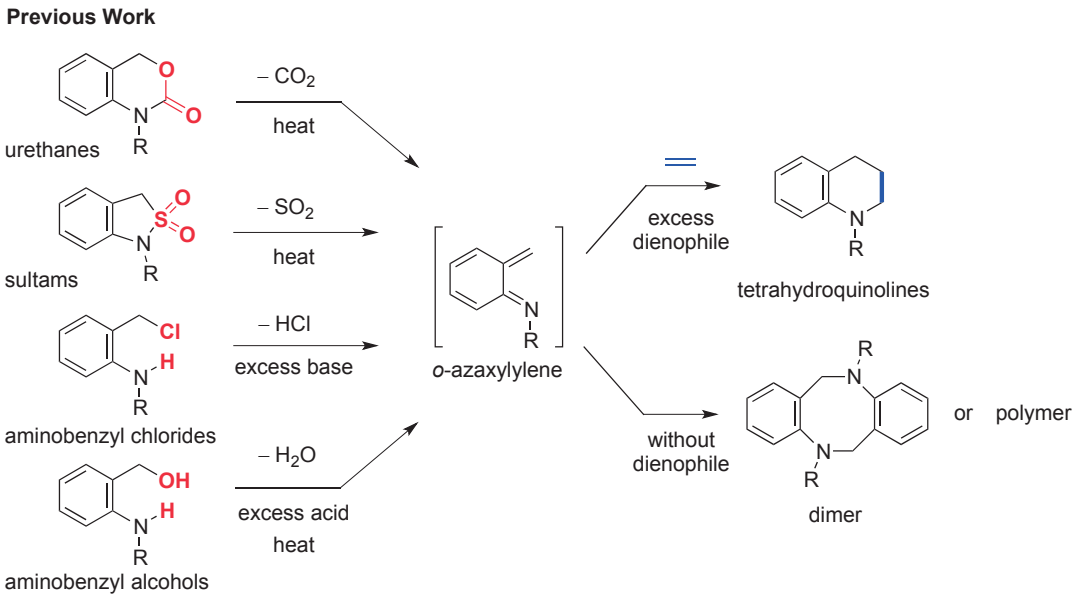
Abstract – An efficient and convenient stereoselective synthetic approach to 2,4-substituted 1,2,3,4-tetrahydroquinoline has been developed. This catalytic procedure involves a sequential reaction of 2-aminobenzyl alcohol with styrenes in the presence of $Hf(OTf)_4$ catalyst followed by intramolecular cyclization of the resulting cation species to give a variety of *cis*-2,4-substituted tetrahydroquinolines in good yield and diastereoselectivity.

INTRODUCTION

Tetrahydroquinolines are important heterocyclic motifs in synthetic organic chemistry because they are found in many synthetic and natural bioactive compounds.[1] Therefore, continuous efforts have been made for the syntheses of a variety of tetrahydroquinoline derivatives.[2] Although a number of methods of stereoselective synthesis of tetrahydroquinolines are available, construction of tetrahydroquinolines bearing multiple stereogenic centers is still challenging. Among many methods, the hetero Diels–Alder reaction of *o*-azaxylylenes with suitable dienophiles is the most straightforward and step-economical method.[3,4] The *o*-azaxylylenes can be generated *in situ* by the elimination of CO_2, SO_2, HCl, and H_2O from urethanes,[5] sultams,[6] 2-aminobenzyl chlorides,[7] and 2-aminobenzyl alcohols, respectively,[8] and then subsequent [4+2] cycloadditions with electron-rich or electron-deficient dienophiles are undergone to afford tetrahydroquinolines (Scheme 1). However, large excesses of dienophiles are often necessary for capturing *o*-azaxylylenes in the intermolecular cycloadditions[9] because they easily undergo dimerization

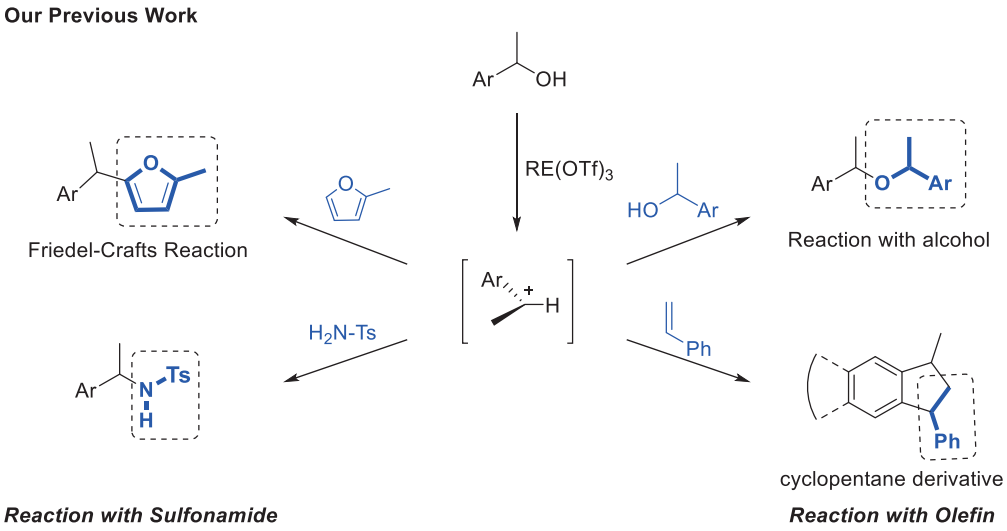
and/or polymerization,[4] diminishing the yield of the desired tetrahydroquinolines. In addition, dienophiles of these reactions are generally limited to activated olefins, i.e., electron-deficient or electron-rich alkenes, such as maleimides, maleates, enol ethers, and allylsilanes, and examples with non-activated olefins are quite rare. Moreover, harsh reaction conditions, such as elevated temperature or the use of more than stoichiometric acid or base, are required for the generation of *o*-azaxylylene intermediates. Therefore, there still exists a need for a more efficient and general approach to synthesize tetrahydroquinolines with high stereoselectivity.[10]



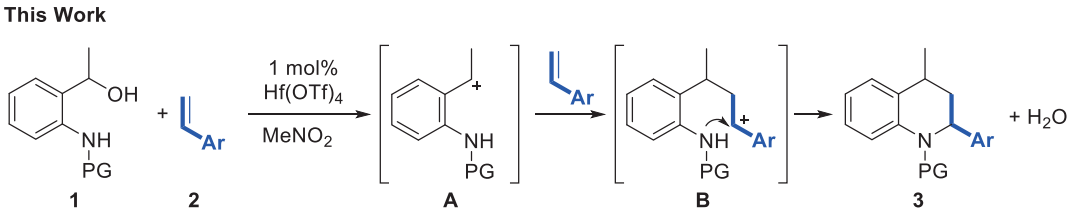
Scheme 1. Synthesis of tetrahydroquinoline derivatives via an *o*-azaxylylene intermediate

Recently, we developed rare-earth metal-based Lewis acid-catalyzed highly efficient and convenient benzylation of various nucleophiles such as alcohols, 1,3-dicarbonyl compounds, enol acetates, aromatic compounds, amides, sulfonamides, allylsilane, and olefins[11] (Scheme 2). We have proposed that these reactions proceeded through the formation of a benzylic cation, which can be generated by dehydroxylation of benzylic alcohols. In this study, we found that the reaction of the benzylic cation with styrene afforded a fused-cyclopentane derivative.[12] Based on these observations, we envisioned that the reaction of 2-aminobenzyl alcohol derivatives with styrene would afford tetrahydroquinoline derivatives (Scheme 3). Thus, a stepwise process would be initiated by the reaction of benzylic cation **A** generated from 2-aminobenzyl alcohol **1** with a metal triflate. Subsequent electrophilic reaction of cation **A** with styrene **2** would furnish a new cationic center at the benzylic position in cation **B**.[13] Cation **B** would then be captured by an amino group to afford the desired tetrahydroquinoline derivative. Herein, we report the synthesis of tetrahydroquinolines by metal triflate-catalyzed cyclization of 2-aminobenzyl alcohol with styrene. In these reactions, a variety of 2,4-substituted tetrahydroquinolines were obtained with good to

high *cis*-selectivities. This catalytic protocol can be conducted under nearly neutral conditions without stoichiometric amounts of acids or bases and elevated temperatures, which are milder conditions compared to those in the [4+2] cycloaddition protocol described above. In addition, the application of this catalytic process is an environmentally benign approach to tetrahydroquinoline synthesis because the byproduct of this process is only water.[14]



Scheme 2. Rare-earth metal triflate-catalyzed benzylation of various nucleophiles

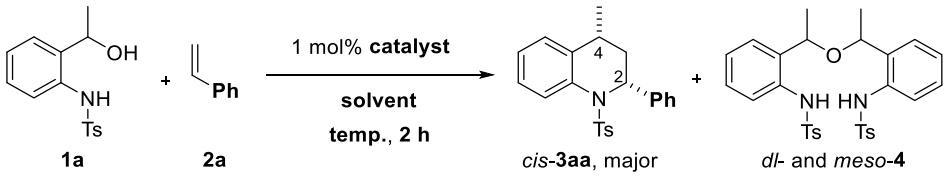


Scheme 3. Synthesis of tetrahydroquinoline derivatives via stepwise cyclization

RESULTS AND DISCUSSION

Initially, we commenced our studies with the reaction between aminobenzyl alcohol **1a** and styrene (**2a**) using different metal triflate catalysts at 40–80 °C in several solvents. Although $La(OTf)_3$, $Yb(OTf)_3$, and $Sc(OTf)_3$ showed poor catalytic activities, $Hf(OTf)_4$[11,15] could effectively promote the reaction to afford the desired tetrahydroquinoline **3aa** in 94% yield with a 3.7:1 diastereomeric ratio (entries 1–4). Among solvents examined, $MeNO_2$ was found to be the most effective for obtaining high yield and diastereoselectivity (entries 4–7). The major diastereomer *cis*-**3aa** could be easily separated by silica gel column chromatography and its stereochemistry was confirmed as the 2,4-*cis*-configuration by X-ray crystallographic analysis (Figure 1).

Table 1. Optimization of reaction conditions: catalyst, solvent, and reaction temperature



entry	catalyst	solvent	temp. (°C)	yield of **3aa** (%)	ratio (*cis* : *trans*)	yield of **4** (%)[a]	recov. **1a** (%)
1	$La(OTf)_3$	$MeNO_2$	80	0	-	0	97
2	$Yb(OTf)_3$	$MeNO_2$	80	22	3.7 : 1	26	46
3	$Sc(OTf)_3$	$MeNO_2$	80	23	3.7 : 1	25	23
4	**$Hf(OTf)_4$**	**$MeNO_2$**	**80**	**94**	**3.7 : 1**	0	0
5	$Hf(OTf)_4$	toluene	80	65	1.9 : 1	0	0
6	$Hf(OTf)_4$	$ClCH_2CH_2Cl$	80	86	2.9 : 1	0	0
7	$Hf(OTf)_4$	CH_2Cl_2	40	32	2.4 : 1	48	7

[a]Yield of ether **4** was calculated based on **1a** equivalence.

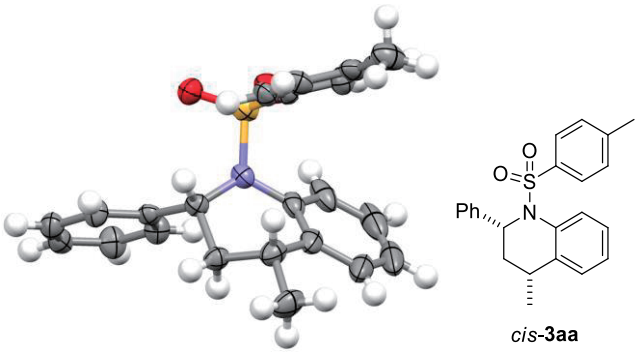
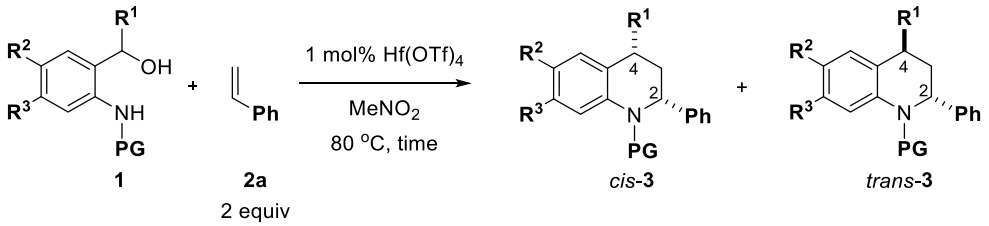


Figure 1. X-Ray crystal structure of ***cis*-3aa**

Having established optimal conditions for the catalytic preparations of tetrahydroquinolines, we next examined the substrate scope with regard to aminobenzyl alcohols **1** (Table 2). Both *N*-alkyl and arylsulfonyl groups were compatible with the reaction to afford the corresponding *N*-sulfonyltetrahydroquinolines in good yields with *cis*-selectivity, although the reactions with an electron deficient *N*-2-nitrobenzenesulfonyl derivative and the bulky *N*-trisyl derivative required longer reaction times (entries 1–5); however, *N*-benzyl group was incompatible with the reaction (entry 9). Steric bulkiness of R-sulfonyl group on nitrogen atom proved to be less sensitive to the diastereoselectivity (entries 1–5). Tetrahydroquinolines bearing a 4-phenyl or 6,7-methylenedioxy group **3fa** and **3ha** were obtained in good yields (entries 6 and 8). The reaction of α-isopropyl-2-aminobenzyl alcohol **1g** gave the

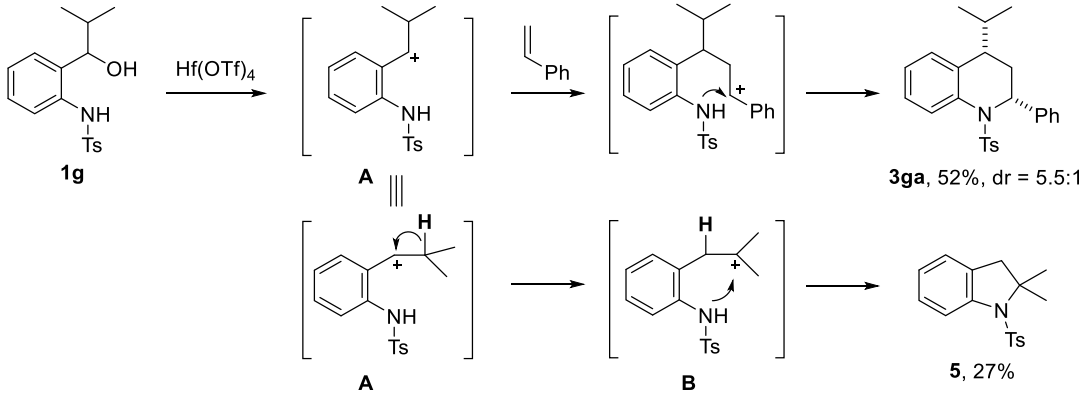
desired 4-isopropylquinoline **3ga** in 52% yield with a good diastereoselectivity of 5.5:1, along with formation of 2,2-dimethylindoline **5** (entry 7, Scheme 4). The formation of **5** can be explained by 1,2-hydride migration of a secondary benzylic cation (**A**) to generate a tertiary alkyl cation (**B**) followed by cyclization to give indoline **5**.

Table 2. Reactions of various 2-aminobenzyl alcohols **1** with styrene



entry	**1**	PG	R^1	R^2	R^3	**3**	temp. (°C)	time (h)	yield (%)	ratio (*cis* : *trans*)
1	**1a**	Ts	Me	H	H	**3aa**	80	2	94	3.7[a] : 1
2	**1b**	Ms	Me	H	H	**3ba**	80	4	90	4.4[a] : 1
3	**1c**	Ns[b]	Me	H	H	**3ca**	80	8	72	4.0 : 1
4	**1d**	Nas[c]	Me	H	H	**3da**	80	2	90	3.3[a] : 1
5	**1e**	Trisyl[d]	Me	H	H	**3ea**	80	12	75	3.4 : 1
6	**1f**	Ts	Ph	H	H	**3fa**	80	2	88	2.9[a] : 1[a]
7	**1g**	Ts	*i*-Pr	H	H	**3ga**	80	2	52	5.5[a] : 1
8	**1h**	Ts	Me	OCH_2O		**3ha**	80	1	83	3.5[a] : 1[a]
9	**1i**	Bn	Me	H	H	-	80	2	0	-

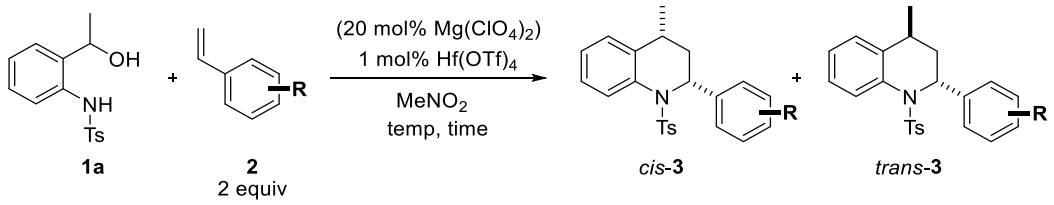
[a]Structure was determined by X-ray crystallographic analysis. [b]2-Nitrobenzenesulfonyl. [c]1-Naphthalenesulfonyl. [d]2,4,6-Triisopropylbenzenesulfonyl.



Scheme 4. Reaction pathways for tetrahydroquinoline **3ga** and indoline **5**

Next, reactions with different styrenes were examined (Table 3). As expected, the reaction with methylstyrenes (**2b**, **c**) afforded the corresponding tetrahydroquinoline **3ab** and **3ac** with good to high yields and diastereoselectivities compared to styrene **2a** (entries 2 and 3). 4-Acetoxystyrene (**2e**) was also compatible with the reaction conditions to give **3ae** in 81% yield with a 3.9:1 diastereomeric ratio (entry 5). When 4-methoxystyrene (**2f**) was used, the methoxyphenyl derivative (**3af**) was obtained in a low yield,[16] albeit the diastereomeric ratio of **3af** was excellent (entry 6). Although the reaction could be applied to chlorostyrenes (**2g**–**i**) and nitrostyrene (**2j**), the consumption of these styrenes required prolonged reaction times and provided only low to moderate yields, even at 100 °C (entries 7–10); however, addition of $Mg(ClO_4)_2$, which is known to be an effective reagent for enhancing S_N1-type solvolysis,[17] could significantly improve the yields of desired tetrahydroquinolines **3ag**–**j** without erosion of the diastereomeric ratios. In general, cation intermediates gradually decompose to form olefinic byproducts at higher temperatures. The salt additive may stabilize the benzylic cation intermediate by increasing the polarity of the reaction medium to prevent decomposition of the cation intermediate during the reaction.

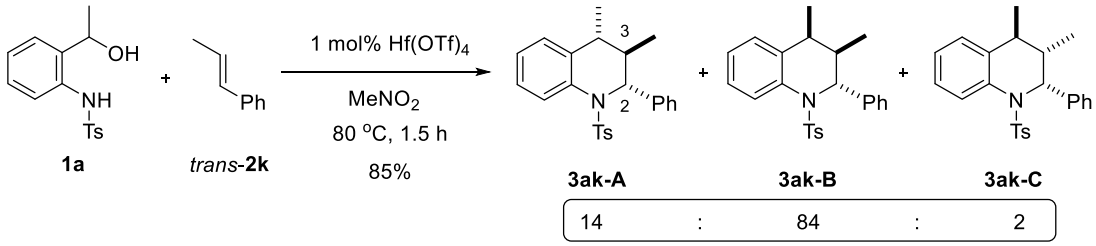
Table 3. Reactions with various styrenes



entry	R	olefin	temp. (°C)	time (h)	product	ratio (*cis* : *trans*)	yield (%)
1	H	**2a**	80	2	**3aa**	3.7[a] : 1	91
2	2-Me	**2b**	100	24	**3ab**	6.1[a] : 1	96
3	3-Me	**2c**	100	24	**3ac**	3.8[a] : 1[a]	91
4	4-Me	**2d**	80	24	**3ad**	5.3[a] : 1	42
5	4-OAc	**2e**	80	1.5	**3ae**	3.9[a] : 1	81
6	4-OMe	**2f**	80	2	**3af**	9.2 : 1	6
7	2-Cl	**2g**	100	24	**3ag**	3.5-3.4[a] : 1	24 (74)[b]
8	3-Cl	**2h**	100	24	**3ah**	2.9-3.0[a] : 1	35 (79)[b]
9	4-Cl	**2i**	100	24	**3ai**	3.5-3.6[a] : 1	54 (84)[b]
10	3-NO_2	**2j**	100	24	**3aj**	3.4-3.1[a] : 1[a]	18 (39)[b]

[a]The structure was determined by X-ray crystallographic analysis. [b]$Mg(ClO_4)_2$ (20 mol%) was added.

To further demonstrate the synthetic potential of this method, we briefly synthesized trisubstituted tetrahydroquinolines possessing three consecutive chiral carbons at C2, C3, and C4 positions. As shown in Scheme 5, the reaction of aminobenzyl alcohol **1a** with *trans*-**2k** proceeded smoothly to give 2,3,4-trisubstituted quinolines **3ak-A**–**C** in a 85% combined yield, and 2,3-*trans*-2,4-*trans*-diastereomer **3ak-B** was obtained as the major isomer with high diastereoselectivity. These isolated diastereomers can be separated by silica gel column chromatography and their stereochemistries were confirmed by X-ray crystallographic analyses (Figure 2).



Scheme 5. Reaction of *trans*-β-methylstyrenes (*trans*-**2k**)

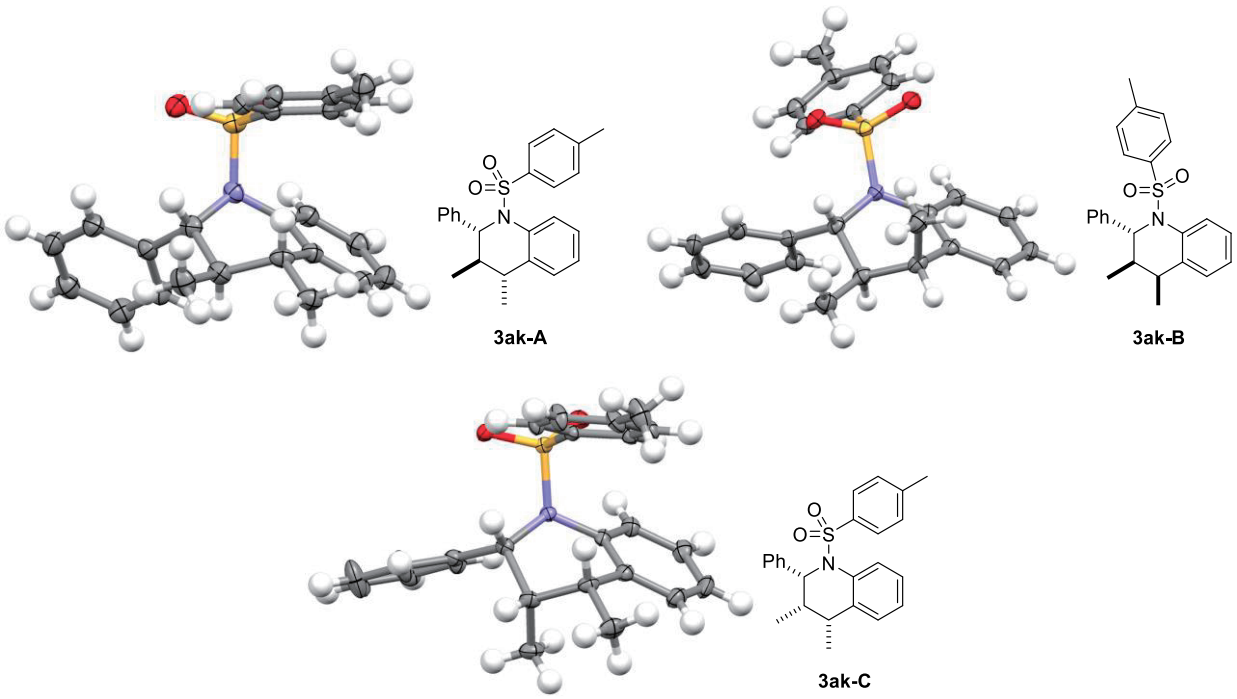


Figure 2. X-Ray crystal structure of **3ak-A**, **3ak-B**, and **3ak-C**

CONCLUSION

We have developed a convenient method for the diastereoselective synthesis of 2,4-*cis*-substituted 1,2,3,4-tetrahydroquinolines from readily available 2-aminobenzyl alcohols **1** with styrenes **2** via $Hf(OTf)_4$-catalyzed step-wise substitution/cyclization. The reaction could be performed with only 1 mol%

of $Hf(OTf)_4$ under milder temperature conditions. This process is also applicable to synthesizing 2,3,4-trisubstituted tetrahydroquinolines. Most diastereomers were easily separated by silica gel column chromatography and the stereochemistry of the diastereomers isolated were confirmed by X-ray crystallographic analysis. This approach provides convenient and rapid access for the construction of tetrahydroquinoline derivatives with an environmentally benign process. Further studies on the mechanism of this reaction and expanding the substrate scope for synthesizing fused-quinoline derivatives are now underway.

EXPERIMENTAL

General Methods. Synthesis of tetrahydroquinolines **3** and reduction of keto-sulfonamides were carried out under air without anhydrous conditions. Other reactions for the syntheses of alcohol **1** were conducted in anhydrous conditions under an argon atmosphere. All solvents and reagents were used as received. ^1H and $^{13}C\{^1H\}$ NMR spectra were collected with spectrometers operating at 300, 400, or 500 MHz for proton nuclei in the solvents indicated. ^1H chemical shifts are reported in δ ppm with tetramethylsilane (TMS) as an internal standard. $^{13}C\{^1H\}$ chemical shifts are reported relative to the central peak of $CDCl_3$ (77.0 ppm). Infrared spectra were collected using an FT-IR spectrometer. Melting points were measured on a hot-plate melting-point apparatus and are uncorrected. High-resolution mass spectra were obtained on a double-focusing high-resolution magnetic-sector mass analyzer operating in electron impact (EI) mode. Chromatographic purifications were performed on silica gel (40–50 μm, spherical) or alumina (activity III). 1-(2-(Benzylamino)phenyl)ethanol (**1i**)[18] was prepared as described in the literature.

General Procedure A: Sulfonylation of amino-ketones. To a solution of 2′-aminoacetophenone (1 equiv), pyridine (1.3 equiv) in CH_2Cl_2 (0.5 mol/L) was added TsCl (1.05 equiv) at 0 °C. The mixture was gradually warmed to room temperature and stirred for 12 h. The resulting reaction mixture was concentrated to one-third volume. Water was added and the mixture was extracted with EtOAc. The combined organic layer was washed successively with 1 mol/L HCl, H_2O, and sat. aqueous NaCl, dried over $MgSO_4$, and filtered. The filtrate was concentrated under reduced pressure. The crude product was purified by recrystallization or chromatographic purification of the crude product to give keto-sulfonamides **1a–f-1** and **1h-1**.

General Procedure B: Reduction of keto-sulfonamides. To a solution of keto-sulfonamide (1 equiv) in EtOH (0.5 mol/L), $NaBH_4$ (1 equiv) was added and the mixture was stirred at reflux temperature for 2 h. The resulting reaction mixture was concentrated to one-third volume. Water was added, and the mixture was extracted with EtOAc. The combined organic layer was washed with sat. aqueous NaCl, dried over

$MgSO_4$, and filtered. The filtrate was concentrated under reduced pressure. Recrystallization or chromatographic purification of the crude product gave keto-sulfonamides **1a–f** and **1h**.

***N*-(2-Acetylphenyl)methanesulfonamide[19] (1a-1).** Sulfonylation was carried out according to general procedure A. The crude product was recrystallized from 2-propanol to give sulfonamide **1a-1** (6.09 g, 95%) as colorless prisms: mp 150–151 °C; TLC R_f = 0.30 (silica gel, EtOAc/*n*-hexane/CH_2Cl_2 = 1:2:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 11.46 (1H, s), 7.79 (1H, dd, *J* = 7.8, 1.4 Hz), 7.74 (2H, d, *J* = 8.3 Hz), 7.69 (1H, dd, *J* = 8.4, 0.7 Hz), 7.48–7.42 (1H, m), 7.22 (2H, d, *J* = 8.1 Hz), 7.09–7.03 (1H, m), 2.56 (3H, s), 2.36 (3H, s); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 202.3, 143.8, 140.0, 136.6, 134.9, 131.9, 129.6, 127.2, 122.5, 122.2, 119.0, 28.1, 21.5; IR (KBr) cm^{-1}: 3036 (m), 1651 (s), 1493 (m), 1451 (m), 1250 (s), 1167 (m), 1090 (m), 913 (s), 767 (s), 566 (s); EI-MS (70 eV) *m*/*z* (relative intensity): 289 (M^+, 100), 155 (14), 134 (78), 120 (11), 106 (17), 91 (61); HRMS (EI) *m*/*z*: M^+ Calcd for $C_{15}H_{15}NO_3S$ 289.0773; Found 289.0771; Anal. Calcd for $C_{15}H_{15}NO_3S$: C, 62.26; H, 5.23; N, 4.84. Found: C, 62.26; H, 5.32; N, 4.55.

***N*-(2-(1-Hydroxyethyl)phenyl)-4-methylbenzenesulfonamide[20] (1a).** Reduction was carried out according to general procedure B. The crude product was recrystallized with hexane-EtOAc from 70 °C to 4 °C to give alcohol **1a** (8.29 g, 71%) as colorless prisms: mp 76–78 °C; TLC R_f = 0.21 (silica gel, 30% EtOAc/*n*-hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.33 (1H, brs), 7.68 (2H, d, *J* = 8.3 Hz), 7.41 (1H, dd, *J* = 8.9, 0.98 Hz), 7.21 (2H, d, *J* = 8.3 Hz), 7.16 (1H, td, *J* = 7.7, 1.6 Hz), 7.08 (1H, dd, *J* = 7.8, 2.0 Hz), 7.02 (1H, td, *J* = 7.4, 1.1 Hz), 4.85 (1H, dq, *J* = 13.2, 3.6 Hz), 2.36 (3H, s), 2.35 (1H, d, *J* = 3.9 Hz), 1.37 (3H, d, *J* = 6.3 Hz); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 143.7, 137.4, 135.8, 134.4, 129.6, 128.5, 127.2, 127.0, 124.7, 122.1, 69.7, 22.9, 21.4; IR (KBr) cm^{-1}: 3482 (s), 3131 (s), 1598 (m), 1459 (s), 1328 (s), 1158 (s), 897 (m), 699 (m); EI-MS (70 eV) *m*/*z* (relative intensity): 291 (M^+, 30), 136 (33), 118 (100), 91(44), 65 (16); HRMS (EI) *m*/*z*: M^+ Calcd for $C_{15}H_{17}NO_3S$ 291.0929; Found 291.0930; Anal. Calcd for $C_{15}H_{17}NO_3S$: C, 61.83; H, 5.88; N, 4.81. Found: C, 61.58; H, 5.85; N, 4.64.

***N*-(2-Acetylphenyl)methanesulfonamide[21] (1b-1).** Sulfonylation was carried out according to general procedure A. The crude product was recrystallized from *n*-hexane/EtOAc = 1:1 to give sulfonamide **1b-1** (4.09 g, 87%) as colorless prisms: mp 100–105 °C; TLC R_f = 0.20 (silica gel, EtOAc/*n*-hexane/CH_2Cl_2 = 1:2:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 11.34 (1H, s), 7.95 (1H, dd, *J* = 7.9, 1.5 Hz), 7.74 (1H, d, *J* = 8.2 Hz), 7.57 (1H, td, *J* = 7.9, 1.4 Hz), 7.17 (1H, td, *J* = 7.7, 1.1 Hz), 3.07 (3H, s), 2.68 (3H, s); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 202.4, 140.3, 135.3, 132.3, 122.5, 121.6, 117.8, 40.1, 28.1; IR (KBr) cm^{-1}: 3055 (m), 1654 (s), 1579 (m), 1496 (s), 1456 (s), 1320 (m), 1248 (m), 1164 (m), 961 (w), 765 (s); EI-MS (70 eV) *m*/*z* (relative intensity): 213 (M^+, 100), 198 (61), 134 (93), 119 (36), 106 (51), 92 (21); HRMS

(EI) *m*/*z*: M^+ Calcd for $C_9H_{11}NO_3S$ 213.0460; Found 213.0461; Anal. Calcd for $C_9H_{11}NO_3S$: C, 50.69; H, 5.20; N, 6.57. Found: C, 50.71; H, 5.35; N, 6.56.

***N*-(2-(1-Hydroxyethyl)phenyl)methanesulfonamide (1b).** Reduction was carried out according to general procedure B. The crude product was purified by column chromatography (silica gel, 10–80% EtOAc/*n*-hexane) to give alcohol **1b** (2.22 g, 73%) as colorless solid: mp 49–50 °C; TLC R_f = 0.20 (silica gel, EtOAc/*n*-hexane/CH_2Cl_2 = 1:2:1), 0.11 (silica gel, 28% EtOAc/*n*-hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.35 (1H, brs), 7.55 (1H, d, *J* = 8.2 Hz), 7.31–7.28 (1H, m), 7.19 (1H, dd, *J* = 7.6, 1.5 Hz), 7.11 (1H, td, *J* = 7.6, 1.1 Hz), 5.08 (1H, q, *J* = 6.6 Hz), 3.06 (3H, s), 2.53 (1H, brs), 1.61 (3H, d, *J* = 6.7 Hz); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 136.1, 133.1, 128.9, 127.4, 124.5, 120.4, 70.2, 40.0, 23.2; IR (neat) cm^{-1}: 3437 (w), 1571 (w), 1474 (m), 1315 (w), 1099 (w), 1024 (s), 980 (s), 909 (m), 808 (s), 622 (w); EI-MS (70 eV) *m*/*z* (relative intensity): 215 (M^+, 22), 197 (12), 136 (16), 118 (100), 91 (22); HRMS (EI) *m*/*z*: M^+ Calcd for $C_9H_{13}NO_3S$ 215.0616; Found 215.0611; Anal. Calcd for $C_9H_{13}NO_3S$ C, 50.21; H, 6.09; N, 6.51. Found: C, 50.18; H, 6.28; N, 46.38.

***N*-(2-Acetylphenyl)-2-nitrobenzenesulfonamide (1c-1).** Sulfonylation was carried out using 2-nitrobenzenesulfonyl chloride (2.6 equiv) and pyridine (4.5 equiv) according to general procedure A. The crude product was recrystallized from *n*-hexane/CH_2Cl_2 = 1:1 to give **1c-1** (4.51 g, 63%) as colorless prisms: mp 220–225 °C; TLC R_f = 0.20 (silica gel, EtOAc/*n*-hexane/CH_2Cl_2 = 1:2:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 12.09 (1H, s), 8.16 (1H, d, *J* = 7.6 Hz), 7.87 (1H, d, *J* = 7.9 Hz), 7.80–7.78 (2H, m), 7.72–7.68 (2H, m), 7.50 (1H, t, *J* = 7.9 Hz), 7.12 (1H, t, *J* = 7.5 Hz), 2.63 (3H, s); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 201.9, 148.2, 139.1, 134.9, 134.0, 133.0, 132.3, 132.1, 131.1, 125.3, 122.9, 122.4, 118.1, 28.1; IR (KBr) cm^{-1}: 3098 (m), 1648 (s), 1493 (s), 1360 (m), 1249 (s), 1159 (m), 1077 (m), 931 (s), 729 (m), 694 (m); EI-MS (70 eV) *m*/*z* (relative intensity): 320 (M^+, 100), 305 (15), 186 (21), 134 (78), 119 (12), 106 (28), 92 (11); HRMS (EI) *m*/*z*: M^+ Calcd for $C_{14}H_{12}N_2O_5S$ 320.0467; Found 320.0468; Anal. Calcd for $C_{14}H_{12}N_2O_5S$: C, 52.49; H, 3.78; N, 8.75. Found: C, 52.36; H, 3.92; N, 8.74.

***N*-(2-(1-Hydroxyethyl)phenyl)-2-nitrobenzenesulfonamide (1c).** Reduction was carried out according to general procedure B. The crude product was purified by column chromatography (silica gel, 5–40% EtOAc/*n*-hexane + 17% CH_2Cl_2) to give alcohol **1c** (699 mg, 21%) as pale yellow oil: TLC R_f = 0.20 (silica gel, EtOAc/*n*-hexane/CH_2Cl_2 = 1:2:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.66 (1H, brs), 7.95 (1H, dd, *J* = 7.9, 1.5 Hz), 7.86 (1H, dd, *J* = 7.9, 1.2 Hz), 7.72 (1H, td, *J* = 7.7, 1.4 Hz), 7.64 (1H, td, *J* = 7.8, 1.2 Hz), 7.32 (1H, dd, *J* = 7.8, 1.4 Hz), 7.29 (1H, dd, *J* = 7.5, 1.7 Hz), 7.20 (1H, td, *J* = 7.6, 1.9 Hz), 7.17 (1H, td, *J* = 7.40, 1.6 Hz), 5.10 (1H, q, *J* = 6.6 Hz), 2.45 (1H, brs), 1.47 (3H, d, *J* = 6.71 Hz); ^{13}C{^{1}H} NMR

(125 MHz, $CDCl_3$) δ: 148.1, 136.9, 134.3, 133.8, 133.5, 132.6, 131.2, 128.5, 127.1, 126.2, 125.2, 123.3, 67.9, 22.8; IR (neat) cm^{-1}: 3524 (s), 3236 (s), 1542 (s), 1495 (m), 1362 (s), 1169 (s), 942 (m), 758 (s), 586 (s); EI-MS (70 eV) *m*/*z* (relative intensity): 322 (M^+, 15), 304 (20), 118 (100), 91 (12); HRMS (EI) *m*/*z*: M^+ Calcd for $C_{14}H_{14}N_2O_5S$ 322.0623; Found 322.0622.

***N*-(2-Acetylphenyl)naphthalene-1-sulfonamide[22] (1d-1).** Sulfonylation was carried out using 1-naphthalenesulfonyl chloride (1.2 equiv) and pyridine (30 equiv) at 0 °C to room temperature for 20 h. The reaction mixture was diluted with H_2O, and solid was collected by filtration. The crude product was recrystallized from EtOAc to give sulfonamide **1d-1** (6.77 g, 94%) as pale yellow prisms: mp 203–205 °C; TLC R_f = 0.49 (silica gel, EtOAc/*n*-hexane/CH_2Cl_2 = 1:2:1); ^1H NMR (400 MHz, $CDCl_3$) δ: 11.94 (1H, s), 8.69 (1H, d, *J* = 8.8 Hz), 8.36 (1H, dd, *J* = 7.3, 1.0 Hz), 8.02 (1H, d, *J* = 8.3 Hz), 7.88 (1H, d, *J* = 8.3 Hz), 7.71–7.66 (2H, m), 7.62 (1H, d, *J* = 8.8 Hz), 7.56 (1H, t, *J* = 7.6 Hz), 7.50 (1H, t, *J* = 7.8 Hz), 7.39–7.34 (1H, m), 6.96 (1H, t, *J* = 7.8 Hz), 2.48 (3H, s); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ: 202.3, 140.0, 134.8, 134.7, 134.3, 134.2, 131.8, 130.3, 128.9, 128.5, 128.0, 127.0, 124.4, 123.9, 122.1, 121.8, 118.1, 27.9; IR (KBr) cm^{-1}: 3056 (m), 1646 (s), 1492 (s), 1358 (m), 1251 (s), 1155 (m), 914 (s), 772 (s), 582 (s); EI-MS (70 eV) *m*/*z* (relative intensity): 325 (M^+, 82), 260 (45), 246 (8), 218 (13), 134 (20), 127 (100); HRMS (EI) *m*/*z*: M^+ Calcd for $C_{18}H_{15}NO_3S$ 325.0773; Found 325.0774; Anal. Calcd for $C_{18}H_{15}NO_3S$ C, 66.44; H, 4.65; N, 4.30. Found: C, 66.37; H, 4.75; N, 4.23.

***N*-(2-(1-Hydroxyethyl)phenyl)naphthalene-1-sulfonamide (1d).** Reduction was carried out in EtOH/THF = 1:1 (0.2 mol/L) at room temperature for 20 h according to general procedure B. The crude product was purified by column chromatography (silica gel, 5–40% EtOAc/*n*-hexane + 16% CH_2Cl_2) to give alcohol **1d** (6.23 g, 92%) as colorless prisms: mp 139–142 °C; TLC R_f = 0.29 (silica gel, EtOAc/*n*-hexane/CH_2Cl_2 = 1:2:1); ^1H NMR (500 MHz, $CDCl_3$) δ: 8.78 (1H, s), 8.72 (1H, d, *J* = 8.9 Hz), 8.30 (1H, dd, *J* = 7.9, 1.1 Hz), 8.04 (1H, d, *J* = 8.2 Hz), 7.91 (1H, d, *J* = 7.9 Hz), 7.67–7.63 (1H, m), 7.59–7.56 (1H, m), 7.50 (1H, t, *J* = 7.8 Hz), 7.27 (1H, dd, *J* = 8.4, 1.1 Hz), 7.09 (1H, td, *J* = 7.8, 1.7 Hz), 7.02 (1H, dd, *J* = 7.6, 1.5 Hz), 6.96 (1H, td, *J* = 7.5, 1.1 Hz), 4.83 (1H, dq, *J* = 6.5, 3.0 Hz), 2.25 (1H, d, *J* = 3.4 Hz), 1.37 (3H, d, *J* = 6.7 Hz); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ: 135.8, 135.1, 134.5, 134.3, 133.5, 130.0, 129.1, 128.4, 128.3, 128.2, 126.92, 126.86, 124.6, 124.3, 124.1, 120.9, 70.0, 22.6; IR (KBr) cm^{-1}: 3503 (m), 3184 (m), 2980 (m), 1585 (m), 1541 (m), 1506 (s), 1325 (s), 1161 (s), 1132 (s), 397 (m), 768 (m); EI-MS (70 eV) *m*/*z* (relative intensity): 327 (M^+, 83), 244 (21), 230 (13), 136 (55), 135 (22), 127 (72), 118 (100), 94 (10), 91 (11); HRMS (EI) *m*/*z*: M^+ Calcd for $C_{18}H_{17}NO_3S$ 327.0929; Found 327.0925; Anal. Calcd for $C_{18}H_{17}NO_3S$ C, 66.03; H, 5.23; N, 4.28. Found: C, 66.11; H, 5.23; N, 4.18.

***N*-(2-Acetylphenyl)-2,4,6-triisopropylbenzenesulfonamide (1e-1).** Sulfonylation was carried out with 30 equiv NEt_3 and 0.5 equiv DMAP instead of pyridine according to general procedure A. The crude product was purified by column chromatography (silica gel, 1–10% EtOAc/*n*-hexane + 9% CH_2Cl_2) and recrystallization from toluene-CH_2Cl_2 to give sulfonamide **1e-1** (1.02 g, 12%) as colorless prisms: mp 155–156 °C; TLC R_f = 0.08 (silica gel, EtOAc/*n*-hexane/CH_2Cl_2 = 1:10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 11.64 (1H, s), 7.82 (1H, dd, *J* = 7.9, 1.53 Hz), 7.44 (1H, dd, *J* = 8.4, 1.1 Hz), 7.40–7.37 (1H, m), 7.14 (2H, s), 7.03–6.99 (1H, m), 4.29 (2H, sept, *J* = 6.7 Hz), 2.87 (1H, sept, *J* = 7.0 Hz), 2.59 (3H, s), 1.23 (18H, d, *J* = 6.7 Hz); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 202.2, 153.3, 150.6, 140.7, 134.7, 132.6, 131.9, 124.0, 121.6, 121.4, 117.8, 34.1, 29.6, 28.0, 24.7, 23.5; IR (KBr) cm^{-1}: 2928 (m), 1646 (s), 1575 (m), 1500 (s), 1365 (m), 1258 (s), 1147 (s), 914 (s), 756 (s); EI-MS (70 eV) *m*/*z* (relative intensity): 401 (M^+, 0.1), 187 (11), 175 (3), 159 (4), 145 (3), 135 (100), 91 (6); HRMS (EI) *m*/*z*: M^+ Calcd for $C_{23}H_{31}NO_3S$ 401.2025; Found 401.2020; Anal. Calcd for $C_{23}H_{31}NO_3S$ C, 68.79; H, 7.78; N, 3.49. Found: C, 68.82; H, 7.81; N, 3.29.

***N*-(2-(1-Hydroxyethyl)phenyl)-2,4,6-triisopropylbenzenesulfonamide (1e).** Reduction was carried out in EtOH/THF = 1:1 (0.2 mol/L) at room temperature for 1 h according to general procedure B. The crude product was purified by column chromatography (silica gel, 4–32% EtOAc/*n*-hexane + 14% CH_2Cl_2) to give alcohol **1e** (913 mg, 89%) as colorless prisms: mp 116–118 °C; TLC R_f = 0.21 (silica gel, EtOAc/*n*-hexane/CH_2Cl_2 = 1:5:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.03 (1H, s), 7.21 (1H, dd, *J* = 7.5, 1.7 Hz), 7.16 (2H, s), 7.13 (1H, td, *J* = 7.6, 1.9 Hz), 7.08 (1H, td, *J* = 7.4, 1.4 Hz), 6.98 (1H, dd, *J* = 7.9, 1.2 Hz), 5.04 (1H, q, *J* = 6.1 Hz), 4.06 (2H, sept, *J* = 6.7 Hz), 2.91 (1 H, sept, *J* = 6.7 Hz), 2.25 (1H, s), 1.52 (3H, d, *J* = 6.4 Hz), 1.26 (6H, d, *J* = 6.7 Hz), 1.20 (6H, d, *J* = 6.7 Hz), 1.18 (6H, d, *J* = 6.7 Hz); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 153.1, 150.3, 136.1, 135.8, 133.8, 128.3, 126.9, 125.2, 123.9, 123.5, 68.9, 34.1, 30.0, 24.74, 24.67, 23.5, 22.7; IR (KBr) cm^{-1}: 3435 (s), 2963 (s), 1599 (m), 1460 (m), 1385 (m), 1160 (s), 1081 (m), 768 (m), 705 (s), 566 (s); EI-MS (70 eV) *m*/*z* (relative intensity): 403 (M^+, 2), 306 (3), 267 (5), 251 (3), 187 (10), 159 (4), 137 (100), 131 (3), 119 (54), 91 (9); HRMS (EI) *m*/*z*: M^+ Calcd for $C_{23}H_{33}NO_3S$ 403.2181; Found 403.2184; Anal. Calcd for $C_{23}H_{33}NO_3S$ C, 68.45; H, 8.24; N, 3.47. Found: C, 68.44; H, 8.19; N, 3.40.

***N*-(2-Benzoylphenyl)-4-methylbenzenesulfonamide[23] (1f-1).** Sulfonylation was carried out using TsCl (1 equiv), pyridine (1 equiv) in CH_2Cl_2 (1.0 mol/L) at room temperature for 24 h. The crude product was purified by column chromatography (silica gel, 2–18% EtOAc/*n*-hexane + 8% CH_2Cl_2) to give sulfonamide **1f-1** (869 mg, 97%) as colorless prisms: mp 170–171 °C; TLC R_f = 0.13 (silica gel, EtOAc/*n*-hexane/CH_2Cl_2 = 1:2:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 9.99 (1H, s), 7.80 (1H, d, *J* = 8.2 Hz),

7.57–7.56 (3H, m), 7.52 (1H, td, *J* = 7.9, 1.3 Hz), 7.41–7.38 (5H, m), 7.10 (1H, tt, *J* = 7.6, 0.9 Hz), 7.04 (2H, d, *J* = 8.5 Hz), 2.23 (3H, s); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ: 143.6, 139.1, 137.6, 136.0, 133.7, 133.0, 132.6, 129.8, 129.5, 128.1, 127.2, 126.2, 123.4, 123.1, 21.4; IR (KBr) cm^{-1}: 3247 (s), 1648 (m), 1597 (m), 1482 (m), 1448 (m), 1394 (m), 1169 (m), 943 (m), 899 (m), 709 (s), 558 (m); EI-MS (70 eV) *m*/*z* (relative intensity): 351 (M^+, 87), 196 (100), 167 (26), 91 (18); HRMS (EI) *m*/*z*: M^+ Calcd for $C_{20}H_{17}NO_3S$ 351.0929; Found 351.0930; Anal. Calcd for $C_{20}H_{17}NO_3S$ C, 68.36; H, 4.88; N, 3.99. Found: C, 68.58; H, 4.97; N, 3.82.

***N*-(2-(Hydroxy(phenyl)methyl)phenyl)-4-methylbenzenesulfonamide[21,24] (1f).** Reduction was carried out at room temperature for 2 h according to general procedure B. The crude product was recrystallized from toluene to give alcohol **1f** (3.93 g, 78%) as a colorless solid: mp 134–135 °C; TLC R_f = 0.53 (silica gel, EtOAc/*n*-hexane/CH_2Cl_2 = 1:2:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.01 (1H, s), 7.48–7.44 (3H, m), 7.48–7.43 (3H, m), 7.20 (1H, td, *J* = 7.8, 1.5 Hz), 7.18–7.12 (4H, m), 7.01 (1H, td, *J* = 7.5, 1.2 Hz), 6.91 (1H, dd, *J* = 7.8, 1.7 Hz), 5.67 (1H, d, *J* = 3.4 Hz), 2.77 (1H, d, *J* = 3.7 Hz), 2.37 (3H, s); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ: 143.6, 141.0, 136.6, 135.8, 133.1, 129.5, 129.04, 129.02, 129.0, 128.6, 127.8, 127.2, 126.3, 124.6, 122.1, 74.7, 21.5; IR (KBr) cm^{-1}: 3440 (s), 3284 (m), 1496 (s), 1314 (s), 1156 (s), 1092 (m), 940 (m), 735 (m), 661 (m), 568 (m); EI-MS (70 eV) *m*/*z* (relative intensity): 353 (M^+, 14), 198 (100), 196 (31), 180 (94), 120 (21), 105 (14), 91 (16), 77 (11); HRMS (EI) *m*/*z*: M^+ Calcd for $C_{20}H_{19}NO_3S$ 353.1086; Found 353.1085; Anal. Calcd for $C_{20}H_{19}NO_3S$ C, 67.97; H, 5.42; N, 3.96. Found: C, 68.27; H, 5.54; N, 3.76.

***N*-(2-(Hydroxymethyl)phenyl)-4-methylbenzenesulfonamide (1g-1).** Sulfonylation of 2′-aminobenzyl alcohol was carried out according to the literature.[20,24] The crude product was recrystallized from EtOH to give sulfonamide **1g-1** (8.02 g, 89%) as colorless prisms: mp 149–150 °C; TLC R_f = 0.24 (silica gel, EtOAc/*n*-hexane/CH_2Cl_2 = 2:4:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.89 (1H, s), 7.64 (2H, d, *J* = 8.2 Hz), 7.41 (1H, d, *J* = 7.9 Hz), 7.26–7.20 (3H, m), 7.10–7.06 (2H, m), 4.39 (2H, d, *J* = 5.8 Hz), 2.38 (3H, s), 2.24 (1H, t, *J* = 5.7 Hz); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ: 143.8, 136.9, 136.4, 131.7, 129.6, 129.2, 129.0, 127.1, 125.4, 123.4, 63.8, 21.5; IR (KBr) cm^{-1}: 3440 (m), 1597 (m), 1456 (m), 1413 (m), 1318 (s), 1154 (s), 1032 (m), 930 (m), 719 (m), 563 (m); EI-MS (70 eV) *m*/*z* (relative intensity): 277 (M^+, 100), 259 (11), 194 (46), 180 (28), 139 (15), 122 (92), 104 (13), 93 (68), 91 (54), 77 (26), 65 (21); HRMS (EI) *m*/*z*: M^+ Calcd for $C_{14}H_{15}NO_3S$ 277.0773; Found 277.0771; Anal. Calcd for $C_{14}H_{15}NO_3S$ C, 60.63; H, 5.45; N, 5.05. Found: C, 60.73; H, 5.45; N, 4.81.

***N*-(2-Formylphenyl)-4-methylbenzenesulfonamide (1g-2).** Oxidation was carried out using MnO_2 (5

equiv) in toluene at 80 °C for 48 h according to the literature.[25] The crude product was recrystallized from acetone to give aldehyde **1g-2** (3.83 g, 96%) as colorless prisms: mp 135–136 °C; TLC R_f = 0.14 (silica gel, EtOAc/*n*-hexane/CH_2Cl_2 = 1:4:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 10.78 (1H, s), 9.83 (1H, s), 7.77 (2H, dt, *J* = 8.5, 1.9 Hz), 7.69 (1H, d, *J* = 8.2 Hz), 7.59 (1H, dd, *J* = 7.6, 1.5 Hz), 7.51 (1H, dt, *J* = 11.1, 4.0 Hz), 7.24 (2H, d, *J* = 7.9 Hz), 7.16 (1H, td, *J* = 7.6, 0.9 Hz), 2.36 (3H, s); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 194.9, 144.1, 140.0, 136.5, 136.1, 135.8, 129.7, 127.3, 122.9, 121.9, 117.8, 21.5; IR (KBr) cm^{-1}: 3141 (m), 1675 (s), 1496 (s), 1411 (m), 1156 (s), 1090 (s), 930 (m), 662 (m), 564 (s); EI-MS (70 eV) *m*/*z* (relative intensity): 275 (M^+, 46), 120 (100), 91 (46), 65 (17); HRMS (EI) *m*/*z*: M^+ Calcd for $C_{14}H_{13}NO_3S$ 275.0616; Found 275.0615; Anal. Calcd for $C_{14}H_{13}NO_3S$ C, 61.07; H, 4.76; N, 5.09. Found: C, 61.30; H, 4.86; N, 4.83.

***N*-(2-(1-Hydroxy-2-methylpropyl)phenyl)-4-methylbenzenesulfonamide (1g).** Grignard reaction of *i*-PrMgCl and **1g-2** was carried out according to the literature.[20] The crude product was purified by column chromatography (silica gel, 5–40% EtOAc/*n*-hexane) to give alcohol **1g** (1.61 g, 92%) as colorless prisms: mp 129–130 °C; TLC R_f = 0.18 (silica gel, EtOAc/*n*-hexane = 1:4); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.39 (1H, brs), 7.69 (2H, dt, *J* = 8.5, 1.8 Hz), 7.51 (1H, dd, *J* = 8.2, 0.9 Hz), 7.22 (2H, d, *J* = 7.9 Hz), 7.19–7.18 (1H, m), 7.00 (1H, td, *J* = 7.4, 1.1 Hz), 6.96 (1H, dd, *J* = 7.6, 1.8 Hz), 4.22 (1H, dd, *J* = 9.0, 3.2 Hz), 2.43–2.42 (1H, m), 2.37 (3H, s), 1.75–1.66 (1H, m), 1.01 (3H, d, *J* = 6.4 Hz), 0.44 (3H, d, *J* = 6.7 Hz); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 143.7, 137.0, 135.9, 131.9, 129.5, 129.2, 128.4, 127.1, 123.9, 121.3, 81.5, 33.4, 21.5, 19.4, 19.2; IR (KBr) cm^{-1}: 3463 (br), 3096 (m), 1595 (m), 1468 (m), 1324 (s), 1157 (s), 1021 (m), 818 (m), 763 (s), 731 (s); EI-MS (70 eV) *m*/*z* (relative intensity): 319 (M^+, 39), 276 (78), 248 (29), 164 (12), 155 (100), 146 (29), 137 (100), 121 (23), 93 (30), 91 (67); HRMS (EI) *m*/*z*: M^+ Calcd for $C_{17}H_{21}NO_3S$ 319.1242; Found 319.1241; Anal. Calcd for $C_{17}H_{21}NO_3S$ C, 63.92; H, 6.63; N, 4.39. Found: C, 63.89; H, 6.88; N, 4.22.

***N*-(6-Acetylbenzo[*d*][1,3]dioxol-5-yl)-4-methylbenzenesulfonamide[19] (1h-1).** Sulfonylation was carried out using TsCl (3 equiv) and pyridine (10 equiv) according to general procedure A. The crude product was purified by recrystallization from EtOAc to sulfonamide **1h-1** (1.55 g, 84%) as colorless prisms: mp 189–190 °C; TLC R_f = 0.46 (silica gel, EtOAc/*n*-hexane/CH_2Cl_2 = 1:2:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 11.77 (1H, s), 7.69 (2H, d, *J* = 8.2 Hz), 7.27 (1H, s), 7.22 (2H, d, *J* = 7.9 Hz), 7.13 (1H, s), 6.00 (2H, s), 2.44 (3H, s), 2.37 (3H, s); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 200.1, 152.8, 143.8, 143.1, 138.0, 136.5, 129.6, 127.2, 116.1, 109.7, 102.3, 100.6, 28.1, 21.5; IR (KBr) cm^{-1}: 2925 (m), 1637 (s), 1505 (s), 1433 (m), 1348 (m), 1244 (m), 1044 (s), 902 (s), 666 (s), 554 (s); EI-MS (70 eV) *m*/*z* (relative intensity): 333 (M^+, 100), 178 (79), 150 (65), 91 (12); HRMS (EI) *m*/*z*: M^+ Calcd for $C_{16}H_{15}NO_5S$ 333.0671; Found

333.0670; Anal. Calcd for $C_{16}H_{15}NO_5S$ C, 57.65; H, 4.54; N, 4.20. Found: C, 57.58; H, 4.63; N, 3.96.

***N*-(6-(1-Hydroxyethyl)benzo[*d*][1,3]dioxol-5-yl)-4-methylbenzenesulfonamide (1h).** Reduction was carried out in EtOH/THF = 1:1 (0.25 mol/L) at room temperature according to general procedure B. The crude product was purified by recrystallization from $CHCl_3$ to give alcohol **1h** (1.77g, 99%) as colorless prisms: mp 147–148 °C; TLC R_f = 0.29 (silica gel, EtOAc/*n*-hexane/CH_2Cl_2 = 1:2:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.65 (2H, d, *J* = 8.0 Hz), 7.64 (1H, s), 7.25 (2H, d, *J* = 8.9 Hz), 6.79 (1H, s), 6.67 (1H, s), 5.93 (2H, s), 4.75–4.73 (1H, m), 2.40 (3H, s), 2.21 (1H, d, *J* = 4.6 Hz), 1.30 (3H, d, *J* = 6.4 Hz); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 147.2, 145.7, 143.8, 136.7, 130.9, 129.6, 128.6, 127.2, 106.4, 105.7, 101.6, 67.6, 22.7, 21.5; IR (KBr) cm^{-1}: 3536 (s), 3238 (s), 1507 (m), 1489 (s), 1340 (m), 1155 (s), 1032 (s), 897 (m), 674 (s), 556 (s); EI-MS (70 eV) *m*/*z* (relative intensity): 335 (M^+, 7), 317 (46), 162 (63), 132 (100), 104 (29), 91 (13); HRMS (EI) *m*/*z*: M^+ Calcd for $C_{16}H_{17}NO_5S$ 335.0827; Found 335.0831; Anal. Calcd for $C_{16}H_{17}NO_5S$ C, 57.30; H, 5.11; N, 4.18. Found: C, 57.48; H, 5.07; N, 4.11.

General Procedure C: Synthesis of tetrahydroquinolines 3. To a mixture of $Hf(OTf)_4$ (3.00 μmol) in $MeNO_2$ (600 μL) was added **1** (300 μmol) and styrenes (600 μmol) at room temperature. The resulting mixture was stirred at 20–100 °C for 2–24 h under air with a balloon. The reaction was monitored by TLC. After the reaction was complete, water (5 mL) was added and the mixture was extracted with EtOAc (4×5 mL). The extracts were dried over $MgSO_4$ and filtered. The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography to give tetrahydroquinoline **3**.

4-Methyl-2-phenyl-1-tosyl-1,2,3,4-tetrahydroquinoline (3aa, diastereomixture) (*cis*/*trans* = 3.7:1) Purified by silica gel column chromatography (2–20% Et_2O/*n*-hexane) to give 134 mg (94%) of colorless amorphous solid: mp 140–141 °C. R_f = 0.23 (silica gel, EtOAc/*n*-hexane/CH_2Cl_2 = 1:4:1). IR (KBr) cm^{-1}: 2927 (m), 1602 (m), 1484 (s), 1456 (s), 1350 (s), 1165 (m), 1092 (m), 965 (m), 705 (m), 661 (m). EI-MS (70 eV) *m*/*z* (relative intensity): 377 (M^+, 60), 222 (100), 206 (27), 91 (19). HRMS (EI) *m*/*z*: M^+ Calcd for $C_{23}H_{23}NO_2S$ 377.1449; Found 377.1446. Anal. Calcd for $C_{23}H_{23}NO_2S$: C, 73.18; H, 6.14; N, 3.71. Found: C, 73.36; H, 6.12; N, 3.49.

(2*RS*,4*RS*)-4-Methyl-2-phenyl-1-tosyl-1,2,3,4-tetrahydroquinoline (*cis*-3aa, major): TLC R_f = 0.17 (silica gel, 10% Et_2O/*n*-hexane); mp 143–144 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.80 (1H, dd, *J* = 7.93, 0.92 Hz), 7.36–7.27 (7H, m), 7.23–7.19 (2H, m), 7.14 (2H, d, *J* = 8.2 Hz), 7.08 (1H, d, *J* = 7.6 Hz), 5.23 (1H, dd, *J* = 10.8, 7. 8 Hz), 2.38 (3H, s), 2.34 (1H, ddd, *J* = 13.1, 7.9, 3.1 Hz), 1.76–1.68 (1H, m), 1.43–1.33 (1H, m), 1.10 (3H, d, *J* = 6.7 Hz); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 144.3, 143.3, 140.9, 136.23,

136.22, 129.3, 128.5, 127.6, 127.1, 127.0, 126.9, 126.1, 126.0, 123.4, 60.8, 44.7, 29.7, 21.5, 17.0; IR (KBr) cm^{-1}: 2926 (m), 1602 (m), 1483 (m), 1450 (m), 1350 (s), 1165 (s), 1116 (m), 1092 (m), 1050 (m), 704 (m), 661 (m), 603 (m); EI-MS (70 eV) *m*/*z* (relative intensity): 377 (M^+, 69), 222 (100), 206 (30), 91 (19); HRMS (EI) *m*/*z*: M^+ Calcd for $C_{23}H_{23}NO_2S$ 377.1449; Found 377.1447; Anal. Calcd for $C_{23}H_{23}NO_2S$: C, 73.18; H, 6.14; N, 3.71. Found: C, 73.14; H, 6.23; N, 3.55.

(2*RS*,4*SR*)-4-Methyl-2-phenyl-1-tosyl-1,2,3,4-tetrahydroquinoline (*trans*-3aa, minor): TLC R_f = 0.13 (silica gel, 10% Et_2O/*n*-hexane); mp 145–146 °C; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.92 (1H, d, *J* = 8.5 Hz), 7.49 (2H, d, *J* = 8.2 Hz), 7.29–7.14 (8H, m), 7.07–7.05 (2H, m), 5.56 (1H, t, *J* = 4.9 Hz), 2.67–2.60 (1H, m), 2.38 (3H, s), 2.17 (1H, ddd, *J* = 14.0, 6.3, 4.8 Hz), 1.58 (1H, ddd, *J* = 14.4, 4.6, 2.3 Hz), 0.92 (3H, d, *J* = 7.0 Hz); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ: 143.5, 140.7, 136.8, 135.4, 134.9, 129.4, 128.4, 127.8, 127.4, 126.9, 126.6, 126.2, 125.6, 125.1, 57.1, 35.0, 27.8, 21.5, 20.4; IR (KBr) cm^{-1}: 2925 (m), 1598 (m), 1489 (m), 1455 (m), 1348 (s), 1168 (s), 1050 (m), 1092 (m), 1049 (m), 756 (m), 667 (m), 550 (m); EI-MS (70 eV) *m*/*z* (relative intensity): 377 (M^+, 77), 222 (100), 206 (29), 91 (19); HRMS (EI) *m*/*z*: M^+ Calcd for $C_{23}H_{23}NO_2S$ 377.1449; Found 377.1450; Anal. Calcd for $C_{23}H_{23}NO_2S$: C, 73.18; H, 6.14; N, 3.71. Found: C, 73.29; H, 6.34; N, 3.46.

4-Methyl-1-(methylsulfonyl)-2-phenyl-1,2,3,4-tetrahydroquinoline (3ba, diastereomixture) (*cis*/*trans* = 4.4:1) Purified by silica gel column chromatography (7–35% Et_2O/*n*-hexane) to give 82.8 mg (90%) of colorless amorphous solid: TLC R_f = 0.20, 0.11 (silica gel, 29% Et_2O/*n*-hexane); mp 123–128 °C; IR (KBr) cm^{-1}: 2930 (m), 1485 (m), 1451 (m), 1344 (s), 1156 (s), 970 (m), 781 (m), 701 (m), 511 (m); EI-MS (70 eV) *m*/*z* (relative intensity): 301 (M+, 62), 222 (100), 206 (33), 144 (12), 130 (13), 91 (18); HRMS (EI) *m*/*z*: M^+ Calcd for $C_{17}H_{19}NO_2S$ 301.1136; Found 301.1136.

(2*RS*,4*RS*)-4-Methyl-1-(methylsulfonyl)-2-phenyl-1,2,3,4-tetrahydroquinoline (*cis*-3ba, major): Colorless prisms; TLC R_f = 0.11 (silica gel, 29% Et_2O/*n*-hexane); mp 123–128 °C; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.60 (1H, d, *J* = 7.8 Hz), 7.33–7.20 (8H, m), 5.37 (1H, dd, *J* = 10.7, 7.8 Hz), 2.84–2.75 (1H, m), 2.72 (3H, s), 2.56 (1H, ddd, *J* = 13.1, 8.3, 2.3 Hz), 1.52 (1H, ddd, *J* = 12.7, 11.2, 5.6 Hz), 1.37 (3H, d, *J* = 6.8 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 143.6, 139.5, 136.4, 128.6, 127.3, 127.2, 126.1, 125.6, 125.3, 123.8, 60.7, 44.9, 39.4, 30.6, 17.0; IR (KBr) cm^{-1}: 1685 (m), 1654 (m), 1559 (w), 1548 (s), 1512 (s), 1456 (m), 1341 (w), 1151 (s), 970 (s), 776 (s); EI-MS (70 eV) *m*/*z* (relative intensity): 301 (M^+, 62), 222 (100), 206 (29), 144 (11), 130 (12), 91 (19); HRMS (EI) *m*/*z*: M^+ Calcd for $C_{17}H_{19}NO_2S$ 301.1136; Found 301.1138; Anal. Calcd for $C_{17}H_{19}NO_2S$: C, 67.74; H, 6.35; N, 4.65. Found: C, 66.77; H, 6.52; N, 4.56.

(2*RS*,4*SR*)-4-Methyl-1-(methylsulfonyl)-2-phenyl-1,2,3,4-tetrahydroquinoline (*trans*-3ba, minor): Colorless oil; TLC R_f = 0.20 (silica gel, 29% Et_2O/*n*-hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.69 (1H, d, *J* = 8.3 Hz), 7.30–7.19 (7H, m), 7.10–7.06 (1H, m), 5.63 (1H, t, *J* = 6.1 Hz), 2.87 (3H, s), 2.85–2.78 (1H, m), 2.30 (1H, ddd, *J* = 13.7, 6.3, 5.4 Hz), 2.21–2.14 (1H, m), 1.38 (3H, d, *J* = 6.8 Hz); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 141.2, 135.8, 134.5, 128.6, 128.0, 127.2, 127.1, 126.3, 124.3, 122.4, 57.2, 40.7, 38.1, 28.9, 19.8; IR (neat) cm^{-1}: 3061 (m), 2962 (s), 1582 (w), 1489 (s), 1339 (s), 1282 (m), 1155 (s); EI-MS (70 eV) *m*/*z* (relative intensity): 301 (M^+, 65), 222 (100), 206 (27), 144 (11), 130 (11), 91 (17); HRMS (EI) *m*/*z*: M^+ Calcd for $C_{17}H_{19}NO_2S$ 301.1136; Found 301.1136.

(2*RS*,4*RS*)-4-Methyl-1-((2-nitrophenyl)sulfonyl)-2-phenyl-1,2,3,4-tetrahydroquinoline (3ca, diastereomixture) (*cis*/*trans* = 4.0:1) Purified by Al_2O_3 column chromatography (2–18% EtOAc/*n*-hexane + 8% CH_2Cl_2) to give 34.8 mg (72%) of yellow amorphous solid: TLC R_f = 0.14 (Al_2O_3, EtOAc/*n*-hexane/CH_2Cl_2 = 1/9/1); mp 37–44 °C; IR (neat) cm^{-1}: 3335 (m), 3062 (m), 1539 (s), 1488 (s), 1456 (m), 1369 (s), 1172 (s), 748 (s), 697 (s), 609 (s); EI-MS (70 eV) *m*/*z* (relative intensity): 408 (M^+, 41), 222 (100), 206 (20), 144 (11), 130 (7), 91 (13); HRMS (EI) *m*/*z*: M^+ Calcd for $C_{22}H_{20}N_2O_4S$ 408.1144; Found 408.1141; Major diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.87 (1H, d, *J* = 7.9 Hz), 7.60–7.56 (1H, m), 7.52–7.51 (1H, m), 7.37–7.12 (10H, m), 5.59 (1H, dd, *J* = 10.1, 8.5 Hz), 2.60 (1H, ddd, *J* = 13.1, 8.6, 3.4 Hz), 2.21–2.18 (1H, m), 1.46 (1H, td, *J* = 12.7, 10.4 Hz), 1.18 (3H, d, *J* = 6.7 Hz); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 147.8, 143.8, 141.3, 135.2, 133.5, 131.6, 131.1, 130.8, 128.5, 127.2, 127.1, 127.0, 126.7, 126.1, 123.7, 123.6, 60.4, 44.5, 29.8, 16.8; Minor diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.82 (1H, d, *J* = 8.2 Hz), 7.66–7.64 (1H, m), 7.60–7.56 (2H, m), 7.53–7.49 (1H, m), 7.37–7.12 (8H, m), 5.64 (1H, t, *J* = 4.7 Hz), 2.76–2.68 (1H, m), 2.32 (1H, ddd, *J* = 14.3, 6.2, 4.7 Hz), 1.84–1.78 (1H, m), 1.02 (3H, d, *J* = 7.0 Hz); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 148.2, 140.0, 135.2, 134.7, 133.8, 132.3, 131.2, 130.8, 128.4, 128.0, 127.0, 126.7, 126.2, 125.7, 125.3, 123.9, 57.4, 35.4, 27.9, 20.5. (The configuration was deduced from the comparison of the ^{1}H-NMR spectra to those of other quinoline derivatives.)

4-Methyl-1-(1-naphthalenesulfonyl)-2-phenyl-1,2,3,4-tetrahydroquinoline (3da, diastereomixture) (*cis*/*trans* = 3.3:1) Purified by silica gel column chromatography (1–10% EtOAc/*n*-hexane + 5% CH_2Cl_2) to give 136.1 mg (90%) of colorless amorphous solid: TLC R_f = 0.18 (silica gel, EtOAc/*n*-hexane/CH_2Cl_2 = 1/20/1); mp 43–49 °C; IR (KBr) cm^{-1}: 2963 (m), 1485 (s), 1352 (s), 1163 (s), 1138 (m), 979 (m), 805 (m), 771 (s), 757 (s), 601 (m), 518 (s). EI-MS (70 eV) *m*/*z* (relative intensity): 413 (M^+, 56), 349 (58), 222 (100), 206 (29), 127 (14), 91 (11). HRMS (EI) *m*/*z*: M^+ Calcd for $C_{26}H_{23}NO_2S$ 413.1449; Found 413.1449.

(2*RS*,4*RS*)-4-Methyl-1-(1-naphthalenesulfonyl)-2-phenyl-1,2,3,4-tetrahydroquinoline (*cis*-3da, major): TLC R_f = 0.15 (silica gel, EtOAc/*n*-hexane/CH_2Cl_2 = 1/20/1); mp 50–52 °C; IR (KBr) cm^{-1}: 2958 (m), 1489 (m), 1348 (s), 1162 (s), 1138 (m), 805 (s), 771 (s), 743 (m), 685 (s), 590 (s), 521 (m); ^1H NMR (500 MHz, $CDCl_3$) δ: 8.20 (1H, dd, *J* = 7.5, 1.1 Hz), 8.02 (1H, d, *J* = 8.9 Hz), 7.99 (1H, d, *J* = 7.9 Hz), 7.80 (1H, d, *J* = 8.2 Hz), 7.71 (1H, dd, *J* = 7.9, 1.2 Hz), 7.46 (1H, t, *J* = 7.8 Hz), 7.43–7.40 (1H, m), 7.32–7.25 (5H, m), 7.19 (3H, m), 6.90 (1H, d, *J* = 7.6 Hz), 5.27 (1H, dd, *J* = 10.4, 8.2 Hz), 2.27 (1H, ddd, *J* = 13.2, 8.2, 3.1 Hz), 1.58–1.51 (1H, m), 1.33 (1H, ddd, *J* = 12.8, 10.6, 5.3 Hz), 0.90 (3H, d, *J* = 6.7 Hz); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ: 144.0, 141.6, 136.1, 134.6, 134.2, 134.1, 130.5, 128.7, 128.4, 128.3, 127.7, 127.3, 127.0, 126.8, 126.6, 126.2, 126.1, 125.1, 123.9, 123.3, 60.1, 44.6, 29.5, 16.7; IR (KBr) cm^{-1}: 2963 (m), 1485 (m), 1353 (s), 1162 (s), 1137 (m), 978 (m), 772 (s), 698 (s), 602 (m); EI-MS (70 eV) *m*/*z* (relative intensity): 413 (M^+, 51), 349 (43), 222 (100), 206 (27), 127 (14), 91 (10); HRMS (EI) *m*/*z*: M^+ Calcd for $C_{26}H_{23}NO_2S$ 413.1449; Found 413.1450.

(2*RS*,4*SR*)-4-Methyl-1-(1-naphthalenesulfonyl)-2-phenyl-1,2,3,4-tetrahydroquinoline (*trans*-3da, minor): TLC R_f = 0.18 (silica gel, EtOAc/*n*-hexane/CH_2Cl_2 = 1/20/1); mp 42–49 °C; IR (KBr) cm^{-1}: 2958 (m), 1489 (m), 1348 (s), 1162 (s), 1138 (m), 805 (s), 771 (s), 743 (m), 685 (s), 590 (s), 521 (m); ^1H NMR (500 MHz, $CDCl_3$) δ: 8.32 (1H, dd, *J* = 7.3, 1.2 Hz), 8.06 (1H, d, *J* = 8.5 Hz), 8.05 (1H, d, *J* = 8.2 Hz), 7.88 (1H, dd, *J* = 8.2, 1.2 Hz), 7.86 (1H, dd, *J* = 8.2, 0.6 Hz), 7.53 (1H, t, *J* = 7.8 Hz), 7.46–7.43 (1H, m), 7.31–7.29 (2H, m), 7.25–7.19 (4H, m), 7.13 (1H, t, *J* = 7.2 Hz), 7.08 (1H, td, *J* = 7.5, 1.2 Hz), 6.94 (1H, d, *J* = 7.6 Hz), 5.45 (1H, t, *J* = 4.3 Hz), 2.53–2.49 (1H, m), 2.04 (1H, ddd, *J* = 14.0, 3.5, 1.7 Hz), 0.99 (1H, ddd, *J* = 14.9, 4.7, 2.3 Hz), 0.52 (3H, d, *J* = 7.0 Hz); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ: 139.8, 135.4, 135.3, 134.7, 134.3, 130.5, 128.9, 128.5, 128.4, 127.7, 127.5, 126.9, 126.8, 126.47, 126.45, 126.3, 125.5, 125.3, 124.1, 56.6, 33.8, 27.0, 20.2; EI-MS (70 eV) *m*/*z* (relative intensity): 413 (M^+, 63), 349 (47), 222 (100), 206 (26), 127 (14), 91 (9); HRMS (EI) *m*/*z*: M^+ Calcd for $C_{26}H_{23}NO_2S$ 413.1449; Found 413.1452.

(2*RS*,4*SR*)-4-Methyl-2-phenyl-1-((2,4,6-triisopropylphenyl)sulfonyl)-1,2,3,4-tetrahydroquinoline (3ea, diastereomixture) (major/minor = 3.4:1) Purified by silica gel column chromatography (0–6% EtOAc/*n*-hexane) to give 83.9 mg (75%) of colorless amorphous solid: TLC R_f = 0.15 (silica gel, 3% EtOAc/*n*-hexane); mp 115–118 °C; IR (KBr) cm^{-1}: 2958 (s), 1598 (m), 1462 (m), 1316 (m), 1152 (s), 1038 (m), 884 (m), 701 (m), 667 (m); EI-MS (70 eV) *m*/*z* (relative intensity): 489 (M^+, 5), 223 (100), 206 (7), 91 (5); HRMS (EI) *m*/*z*: M^+ Calcd for $C_{31}H_{39}NO_2S$ 489.2702; Found 489.2700. Minor diastereomer: TLC R_f = 0.15 (silica gel, EtOAc/*n*-hexane/CH_2Cl_2 = 1/40/1); ^1H NMR (500 MHz, $CDCl_3$) δ: 7.38 (1H, dd, *J* = 7.9, 1.5 Hz), 7.28–7.03 (10H, m), 5.68–5.62 (1H, m), 3.96–3.88 (2H, m), 2.92–2.90 (1H, m), 2.66 (1H, ddd, *J* = 18.8, 6.2, 3.1 Hz), 2.35 (1H, ddt, *J* = 13.8, 3.3, 1.7 Hz), 2.08–2.02 (1H, m), 1.29 (3H, d, *J* =

7.0 Hz), 1.26 (6H, d, *J* = 6.7 Hz), 1.16 (6H, d, *J* = 6.7 Hz), 1.10 (6H, d, *J* = 6.7 Hz); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ: 153.2, 151.3, 140.1, 136.0, 135.0, 133.4, 128.3, 127.9, 126.7, 126.4, 126.3, 125.3, 124.9, 124.2, 55.5, 35.3, 34.1, 29.7, 27.2, 24.9, 24.7, 23.6, 23.5, 20.7.

(2*RS*,4*RS*)-4-Methyl-2-phenyl-1-((2,4,6-triisopropylphenyl)sulfonyl)-1,2,3,4-tetrahydroquinoline (*cis*-3ea, major): The configuration was deduced from comparison of the ^{1}H-NMR spectra to those of other quinoline derivatives. TLC R_f = 0.14 (silica gel, EtOAc/*n*-hexane/CH_2Cl_2 = 1/40/1); mp 133–135 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.28–7.16 (7H, m), 7.07–7.05 (3H, m), 6.79 (1H, dd, *J* = 7.9, 1.2 Hz), 5.65 (1H, dd, *J* = 10.2, 8.4 Hz), 3.59–3.51 (2H, m), 2.99–2.92 (1H, m), 2.88–2.85 (1H, m), 2.54 (1H, ddd, *J* = 13.0, 8.4, 3.4 Hz), 1.50 (1H, ddd, *J* = 12.7, 10.3, 5.1 Hz), 1.31 (3H, d, *J* = 6.7 Hz), 1.23 (6H, d, *J* = 7.0 Hz), 0.94 (6H, d, *J* = 6.4 Hz), 0.93 (6H, d, *J* = 6.4 Hz); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ: 153.3, 151.8, 144.1, 143.7, 136.5, 132.3, 128.4, 128.0, 127.0, 126.7, 126.54, 126.46, 124.0, 123.8, 57.7, 44.4, 34.1, 30.3, 29.5, 24.8, 24.3, 23.6, 23.5, 17.0; IR (KBr) cm^{-1}: 2957 (m), 1598 (m), 1459 (m), 1314 (m), 1151 (s), 1038 (m), 883 (m), 666 (m), 602 (m); EI-MS (70 eV) *m*/*z* (relative intensity): 489 (M^+, 5), 223 (100); HRMS (EI) *m*/*z*: M^+ Calcd for $C_{31}H_{39}NO_2S$ 489.2702; Found 489.2706.

2,4-Diphenyl-1-tosyl-1,2,3,4-tetrahydroquinoline (3fa, diastereomixture) (*cis*/*trans* = 2.9:1) Purified by Al_2O_3 column chromatography (1–10% EtOAc/*n*-hexane + 5% CH_2Cl_2) to give 126 mg (88%) of colorless prisms: TLC R_f = 0.12 (silica gel, EtOAc/*n*-hexane/CH_2Cl_2 = 1/20/1), 0.20 (Al_2O_3, EtOAc/*n*-hexane/CH_2Cl_2 = 1/20/1); mp 200–206 °C; IR (KBr) cm^{-1}: 3026 (m), 1599 (m), 1493 (m), 1452 (s), 1355 (s), 1170 (s), 1090 (m), 968 (m), 765 (m), 701 (s), 661 (m), 575 (s); EI-MS (70 eV) *m*/*z* (relative intensity): 439 (M^+, 96), 284 (100), 206 (44), 193 (13), 180 (10), 165 (10), 91 (22); HRMS (EI) *m*/*z*: M^+ Calcd for $C_{28}H_{25}NO_2S$ 439.1606; Found 439.1607; Anal. Calcd for $C_{28}H_{25}NO_2S$: C, 76.51; H, 5.73; N, 3.19.

(2*RS*,4*SR*)-2,4-Diphenyl-1-tosyl-1,2,3,4-tetrahydroquinoline (*cis*-3fa, major): Purified by silica gel column chromatography (silica gel, 2–20% Et_2O/*n*-hexane): TLC R_f = 0.11 (silica gel, 10% Et_2O/*n*-hexane); mp 210–211 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.84 (1H, dd, *J* = 7.9, 1.2 Hz), 7.40–7.38 (4H, m), 7.34–7.31 (3H, m), 7.30–7.23 (6H, m), 7.05 (1H, td, *J* = 7.6, 1.2 Hz), 6.79 (2H, d, *J* = 6.7 Hz), 6.36 (1H, d, *J* = 7.6 Hz), 5.32 (1H, dd, *J* = 11.1, 8.1 Hz), 2.58–2.55 (2H, m), 2.47 (3H, s), 1.99 (1H, td, *J* = 13.1, 11.1 Hz); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ: 143.9, 143.6, 141.3, 140.0, 135.9, 135.8, 129.4, 128.7, 128.6, 128.6, 128.4, 128.1, 127.3, 127.2, 127.1, 126.11, 126.07, 125.4, 60.8, 43.0, 42.3, 21.5; IR (KBr) cm^{-1}: 3002 (m), 1599 (m), 1493 (s), 1453 (s), 1357 (s), 1170 (s), 1090 (m), 970 (m), 766 (m), 701 (s), 576 (s); EI-MS (70 eV) *m*/*z* (relative intensity): 439 (M^+, 89), 284 (100), 206 (50), 193 (14),

180 (12), 165 (11), 91 (23); HRMS (EI) *m*/*z*: M^+ Calcd for $C_{28}H_{25}NO_2S$ 439.1606; Found 439.1605; Anal. Calcd for $C_{28}H_{25}NO_2S$: C, 76.51; H, 5.73; N, 3.19. Found: C, 76.48; H, 5.68; N, 2.98.

(2*RS*,4*RS*)-2,4-Diphenyl-1-tosyl-1,2,3,4-tetrahydroquinoline (*trans*-3fa, minor): Purified by silica gel column chromatography (silica gel, 2–20% Et_2O/*n*-hexane): TLC R_f = 0.15 (silica gel, 10% Et_2O/*n*-hexane); mp 178–179 °C; ^1H NMR (500 MHz, $CDCl_3$) δ: 8.10 (1H, dd, *J* = 8.4, 1.1 Hz), 7.58 (2H, dt, *J* = 8.5, 1.9 Hz), 7.35 (2H, d, *J* = 8.2 Hz), 7.26–7.21 (6H, m), 7.15–7.11 (3H, m), 6.93 (1H, td, *J* = 7.6, 1.2 Hz), 6.61 (1H, dt, *J* = 7.6, 1.2 Hz), 6.57 (2H, dt, *J* = 6.1, 1.6 Hz), 5.80 (1H, t, *J* = 3.8 Hz), 3.67 (1H, dd, *J* = 12.1, 6.6 Hz), 2.42 (3H, s), 2.38 (1H, dq, *J* = 14.3, 3.3 Hz), 1.91 (1H, ddd, *J* = 15.4, 10.8, 3.2 Hz); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ: 144.7, 143.8, 139.5, 136.8, 135.9, 132.5, 130.3, 129.7, 128.6, 128.4, 128.4, 127.6, 127.0, 126.9, 126.5, 126.1, 125.6, 125.2, 57.3, 40.0, 34.5, 21.5; IR (KBr) cm^{-1}: 2931 (m), 1599 (m), 1493 (m), 1449 (m), 1348 (s), 1170 (s), 1033 (m), 766 (m), 673 (m), 570 (s); EI-MS (70 eV) *m*/*z* (relative intensity): 439 (M^+, 84), 284 (100), 206 (52), 193 (14), 180 (11), 165 (12), 91 (24); HRMS (EI) *m*/*z*: M^+ Calcd for $C_{28}H_{25}NO_2S$ 439.1606; Found 439.1605; Anal. Calcd for $C_{28}H_{25}NO_2S$: C, 76.51; H, 5.73; N, 3.19. Found: C, 76.19; H, 5.80; N, 2.94.

4-Isopropyl-2-phenyl-1-tosyl-1,2,3,4-tetrahydroquinoline (3ga, diastereomixture) (*cis*:*trans* = 5.5:1) Purified by silica gel column chromatography (2–20% Et_2O/*n*-hexane) to give 54.3 mg (52%) of colorless amorphous solid: TLC R_f = 0.13 (minor), 0.09 (major) (silica gel, 10% Et_2O/*n*-hexane); mp 82–83 °C; IR (KBr) cm^{-1}: 2871 (m), 1600 (s), 1484 (s), 1454 (s), 1355 (s), 1454 (s), 1355 (s), 1165 (s), 904 (m), 761 (m), 660 (m), 548 (m); EI-MS (70 eV) *m*/*z* (relative intensity): 405 (M^+, 70), 250 (53), 206 (100), 130 (15), 91 (12); HRMS (EI) *m*/*z*: M^+ Calcd for $C_{25}H_{27}NO_2S$ 405.1762; Found 405.1764.

(2*RS*,4*SR*)-4-Isopropyl-2-phenyl-1-tosyl-1,2,3,4-tetrahydroquinoline (*cis*-3ga, major): TLC R_f = 0.09 (silica gel, 10% Et_2O/*n*-hexane); mp 150–151 °C; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.78 (1H, d, *J* = 7.9 Hz), 7.33–7.30 (7H, m), 7.22–7.21 (2H, m), 7.14 (2H, d, *J* = 8.2 Hz), 7.09 (1H, d, *J* = 7.6 Hz), 5.15 (1H, dd, *J* = 10.4, 7.6 Hz), 2.37 (3H, s), 2.34–2.32 (1H, m), 2.19–2.13 (1H, m), 1.30–1.19 (2H, m), 0.82 (3H, d, *J* = 6.7 Hz), 0.73 (3H, d, *J* = 6.7 Hz); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ: 144.4, 143.4, 139.9, 136.8, 136.1, 129.2, 128.5, 128.2, 127.1, 127.0, 126.7, 126.1, 126.0, 123.6, 61.4, 40.9, 37.1, 25.5, 21.6, 21.4, 16.8; IR (KBr) cm^{-1}: 2965 (m), 1483 (m), 1453 (m), 1362 (s), 1167 (s), 1068 (m), 905 (m), 767 (s), 661 (s), 532 (m); EI-MS (70 eV) *m*/*z* (relative intensity): 405 (M^+, 53), 362 (15), 250 (49), 206 (100), 130 (16), 91 (15); HRMS (EI) *m*/*z*: M^+ Calcd for $C_{25}H_{27}NO_2S$ 405.1762; Found 405.1763; Anal. Calcd for $C_{25}H_{27}NO_2S$: C, 74.04; H, 6.71; N, 3.45. Found: C, 73.78; H, 6.71; N, 3.20.

(2*RS*,4*RS*)-4-Isopropyl-2-phenyl-1-tosyl-1,2,3,4-tetrahydroquinoline (*trans*-3ga, minor): TLC R_f = 0.13 (silica gel, 10% Et_2O/*n*-hexane); ^1H NMR (500 MHz, $CDCl_3$) δ: 7.95 (1H, dd, *J* = 8.2, 0.9 Hz), 7.78 (1H, d, *J* = 8.2 Hz), 7.44 (2H, t, *J* = 4.1 Hz), 7.34–7.14 (7H, m), 7.07 (1H, td, *J* = 7.4, 1.1 Hz), 7.00–6.97 (1H, m), 5.30 (1H, dd, *J* = 9.2, 6.1 Hz), 2.35 (1H, s), 2.25–2.21 (1H, m), 2.17 (2H, dt, *J* = 13.8, 6.0 Hz), 1.89–1.83 (1H, m), 1.30–1.26 (2H, m), 0.64 (3H, d, *J* = 6.7 Hz), 0.58 (3H, d, *J* = 6.4 Hz); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ: 143.5, 143.2, 136.5, 136.2, 135.8, 129.3, 129.0, 128.4, 127.3, 126.9, 126.8, 126.0, 125.6, 124.7, 57.8, 42.8, 33.7, 28.2, 21.4, 21.3, 18.7; IR (KBr) cm^{-1}: 2961 (m), 1560 (m), 1487 (s), 1455 (m), 1349 (s), 1165 (s), 1090 (m), 1021 (m), 675 (m); EI-MS (70 eV) *m*/*z* (relative intensity): 405 (M^+, 91), 362 (30), 250 (47), 206 (100), 130 (13), 91 (11); HRMS (EI) *m*/*z*: M^+ Calcd for $C_{25}H_{27}NO_2S$ 405.1762; Found 405.1760.

8-Methyl-6-phenyl-5-tosyl-5,6,7,8-tetrahydro-[1,3]dioxolo[4,5-*g*]quinoline (3ha, diastereomixture) (*cis*/*trans* = 3.5:1) Purified by silica gel column chromatography (1–10% EtOAc/*n*-hexane + 5% CH_2Cl_2) to give 129.6 mg (83%) of colorless amorphous solid: TLC R_f = 0.21 (silica gel, EtOAc/*n*-hexane/CH_2Cl_2 = 1/9/1); mp 60–64 °C; IR (KBr) cm^{-1}: 2961 (m), 1599 (m), 1482 (s), 1351 (s), 1272 (m), 1224 (m), 1159 (s), 1124 (m), 1091 (m), 1038 (s), 933 (m), 661 (s), 545 (s); EI-MS (70 eV) *m*/*z* (relative intensity): 421 (M^+, 32), 266 (100); HRMS (EI) *m*/*z*: M^+ Calcd for $C_{24}H_{23}NO_4S$ 421.1348; Found 421.1344; Anal. Calcd for $C_{24}H_{23}NO_4S$: C, 68.39; H, 5.50; N, 3.32. Found: C, 68.79; H, 5.64; N, 3.20.

(6*RS*,8*RS*)-8-Methyl-6-phenyl-5-tosyl-5,6,7,8-tetrahydro-[1,3]dioxolo[4,5-*g*]quinoline (*cis*-3ha, major): Purified by silica gel column chromatography (1–10% EtOAc/*n*-hexane + 5% CH_2Cl_2); TLC R_f = 0.04 (silica gel, EtOAc/*n*-hexane/CH_2Cl_2 = 1/20/1); mp 153–155 °C; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.41 (2H, d, *J* = 8.2 Hz), 7.31 (1H, s), 7.29–7.28 (4H, m), 7.23–7.20 (1H, m), 7.18 (2H, d, *J* = 8.2 Hz), 6.58 (1H, s), 6.01 (1H, d, *J* = 1.2 Hz), 5.97 (1H, d, *J* = 1.5 Hz), 5.20 (1H, dd, *J* = 10.7, 8.2 Hz), 2.39 (3H, s), 2.32 (1H, ddd, *J* = 13.1, 8.2, 3.0 Hz), 1.53 (1H, dq, *J* = 12.4, 3.2 Hz), 1.31 (1H, td, *J* = 12.7, 10.7 Hz), 1.02 (3H, d, *J* = 6.7 Hz); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ: 146.0, 144.1, 143.4, 136.1, 135.4, 129.4, 129.3, 128.5, 127.1, 127.0, 126.0, 109.6, 103.8, 101.3, 60.4, 44.8, 29.6, 21.5, 17.3; IR (KBr) cm^{-1}: 2955 (m), 1482 (s), 1354 (m), 1266 (m), 1171 (s), 1033 (m), 927 (m), 890 (m), 708 (m), 663 (s), 546 (s); EI-MS (70 eV) *m*/*z* (relative intensity): 421 (M^+, 35), 266 (100); HRMS (EI) *m*/*z*: M^+ Calcd for $C_{24}H_{23}NO_4S$ 421.1348; Found 421.1346; Anal. Calcd for $C_{24}H_{23}NO_4S$: C, 68.39; H, 5.50; N, 3.32. Found: C, 68.44; H, 5.53; N, 3.15.

(6*RS*,8*SR*)-8-Methyl-6-phenyl-5-tosyl-5,6,7,8-tetrahydro-[1,3]dioxolo[4,5-*g*]quinoline (*trans*-3ha, minor): Purified by silica gel column chromatography (1–10% EtOAc/*n*-hexane + 5% CH_2Cl_2); TLC R_f

= 0.09 (silica gel, EtOAc/*n*-hexane/CH_2Cl_2 = 1/20/1); mp 163–164 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.52–7.50 (2H, m), 7.44 (1H, s), 7.29–7.28 (2H, m), 7.24–7.22 (4H, m), 7.16–7.15 (1H, m), 6.47 (1H, d, *J* = 0.6 Hz), 5.94 (1H, d, *J* = 1.5 Hz), 5.90 (1H, d, *J* = 1.5 Hz), 5.51 (1H, t, *J* = 4.4 Hz), 2.57–2.49 (1H, m), 2.39 (3H, s), 2.15 (1H, ddd, *J* = 14.2, 3.6, 1.8 Hz), 1.42 (1H, ddd, *J* = 14.8, 4.7, 2.4 Hz), 0.81 (3H, d, *J* = 6.7 Hz); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 146.0, 145.5, 143.6, 140.1, 136.6, 129.5, 128.9, 128.6, 128.3, 127.6, 126.8, 126.2, 107.5, 106.9, 101.2, 56.9, 33.8, 27.7, 21.5, 21.0. EI-MS (70 eV) *m*/*z* (relative intensity): 421 (M^+, 35), 266 (100), 250 (8); HRMS (EI) *m*/*z*: M^+ Calcd for $C_{24}H_{23}NO_4S$ 421.1348; Found 421.1346; Anal. Calcd for $C_{24}H_{23}NO_4S$: C, 68.39; H, 5.50; N, 3.32. Found: C, 68.15; H, 5.59; N, 3.10.

2-(2-Methylphenyl)-4-methyl-1-tosyl-1,2,3,4-tetrahydroquinoline (3ab, diastereomixture) (*cis*/*trans* = 6.1:1) Purified by silica gel column chromatography (2–15% EtOAc/*n*-hexane) to give 119.3 mg (95%) of colorless amorphous solid: TLC R_f = 0.20 (silica gel, 9% EtOAc/*n*-hexane); mp 131–139 °C; IR (KBr) cm^{-1}: 2966 (m), 1600 (m), 1485 (s), 1355 (s), 1166 (s), 1091 (m), 957 (m), 760 (m), 661 (s); EI-MS (70 eV) *m*/*z* (relative intensity): 391 (M^+, 65), 236 (100), 220 (28), 105 (14), 91 (12); HRMS (EI) *m*/*z*: M^+ Calcd for $C_{24}H_{25}NO_2S$ 391.1606; Found 391.1604; Anal. Calcd for $C_{24}H_{25}NO_2S$: C, 73.62; H, 6.44; N, 3.58. Found: C, 73.85; H, 6.43; N, 3.35. Minor diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.86 (1H, d, *J* = 8.2 Hz), 7.41 (2H, d, *J* = 8.2 Hz), 7.23–7.21 (2H, m), 7.14–7.07 (6H, m), 7.05–7.01 (1H, m), 5.61 (1H, dd, *J* = 8.4, 6.3 Hz), 2.72 (1H, dt, *J* = 18.9, 6.8 Hz), 2.45 (3H, s), 2.33 (3H, s), 1.93 (1H, dt, *J* = 13.8, 6.2 Hz), 1.85 (1H, ddd, *J* = 13.7, 8.5, 4.9 Hz), 0.85 (3H, d, *J* = 7.0 Hz). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 143.4, 141.6, 136.5, 136.4, 136.2, 133.7, 130.4, 129.3, 127.6, 127.4, 126.9, 126.8, 126.4, 126.3, 124.6, 124.3, 54.7, 37.5, 30.2, 21.4, 19.1, 18.7.

(2*RS*,4*RS*)-2-(2-Methylphenyl)-4-methyl-1-tosyl-1,2,3,4-tetrahydroquinoline (*cis*-3ab, major): TLC R_f = 0.21 (silica gel, 9% EtOAc/*n*-hexane); mp 144–147 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.83 (1H, d, *J* = 7.9 Hz), 7.35–7.34 (3H, m), 7.24–7.21 (2H, m), 7.15 (2H, d, *J* = 7.9 Hz), 7.11–7.09 (4H, m), 5.36 (1H, dd, *J* = 11.4, 7.5 Hz), 2.47 (3H, s), 2.38 (3H, s), 2.26 (1H, ddd, *J* = 13.3, 7.5, 2.8 Hz), 1.76–1.71 (1H, m), 1.28–1.20 (1H, m), 1.12 (3H, d, *J* = 6.7 Hz); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 143.3, 143.3, 140.7, 136.8, 136.2, 133.4, 130.2, 129.3, 127.3, 127.10, 127.07, 126.7, 126.6, 126.3, 125.9, 123.3, 57.9, 43.5, 30.0, 21.5, 19.1, 17.0; IR (KBr) cm^{-1}: 2968 (m), 1601 (m), 1486 (s), 1451 (m), 1353 (s), 1172 (s), 956 (m), 895 (m), 777 (m), 763 (m), 660 (s); EI-MS (70 eV) *m*/*z* (relative intensity): 391 (M^+, 64), 236 (100), 220 (30), 144 (10), 105 (12), 91 (12); HRMS (EI) *m*/*z*: M^+ Calcd for $C_{24}H_{25}NO_2S$ 391.1606; Found 391.1604.

4-Methyl-2-(*m*-tolyl)-1-tosyl-1,2,3,4-tetrahydroquinoline (3ac, diastereomixture) (*cis*/*trans* = 3.8:1) Purified by silica gel column chromatography (2–14% EtOAc/*n*-hexane) to give 104 mg (91%) of

colorless amorphous solid; TLC R_f = 0.20 (silica gel, 9% EtOAc/*n*-hexane); mp 129–130 °C; IR (KBr) cm^{-1}: 2925 (m), 1605 (m), 1487 (s), 1352 (s), 1165 (m), 1091 (m), 891 (m), 756 (m), 661 (m); EI-MS (70 eV) *m*/*z* (relative intensity): 391 (M^+, 67), 236 (100), 220 (30), 144 (10), 105 (11), 91 (12); HRMS (EI) *m*/*z*: M^+ Calcd for $C_{24}H_{25}NO_2S$ 391.1606; Found 391.1605.

(2*RS*,4*RS*)-4-Methyl-2-(*m*-tolyl)-1-tosyl-1,2,3,4-tetrahydroquinoline (*cis*-3ac, major): TLC R_f = 0.13 (silica gel, 9% Et_2O/*n*-hexane); mp 129–130 °C. ^1H NMR (500 MHz, $CDCl_3$) δ: 7.81 (1H, d, *J* = 7.9 Hz), 7.36–7.30 (3H, m), 7.23–7.07 (7H, m), 7.02 (1H, d, *J* = 7.3 Hz), 5.18 (1H, dd, *J* = 11.0, 7.9 Hz), 2.37 (3H, s), 2.33–2.30 (1H, m), 2.31 (3H, s), 1.72–1.68 (1H, m), 1.37–1.33 (1H, m), 1.09 (3H, d, *J* = 7.0 Hz); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ: 144.2, 143.3, 140.9, 138.0, 136.3, 136.2, 129.3, 128.4, 127.7, 127.6, 127.1, 127.0, 126.7, 126.0, 123.3, 123.1, 60.8, 44.8, 29.7, 21.5, 17.0; IR (KBr) cm^{-1}: 2916 (m), 1599 (m), 1482 (m), 1355 (s), 1353 (s), 1173 (s), 953 (m), 760 (m), 660 (s), 552 (m); EI-MS (70 eV) *m*/*z* (relative intensity): 391 (M^+, 70), 236 (100), 220 (31), 144 (10), 91 (13); HRMS (EI) *m*/*z*: M^+ Calcd for $C_{24}H_{25}NO_2S$ 391.1606; Found 391.1605; Anal. Calcd for $C_{24}H_{25}NO_2S$: C, 73.62; H, 6.44; N, 3.58. Found: C, 73.68; H, 6.55; N, 3.36.

(2*RS*,4*SR*)-4-Methyl-2-(*m*-tolyl)-1-tosyl-1,2,3,4-tetrahydroquinoline (*trans*-3ac, minor): TLC R_f = 0.17 (silica gel, 9% Et_2O/*n*-hexane); mp 130–131 °C. ^1H NMR (500 MHz, $CDCl_3$) δ: 7.92 (1H, d, *J* = 8.2 Hz), 7.48 (2H, d, *J* = 8.2 Hz), 7.22–7.15 (3H, m), 7.12–7.04 (5H, m), 6.96 (1H, d, *J* = 7.3 Hz), 5.51 (1H, t, *J* = 4.9 Hz), 2.68–2.61 (1H, m), 2.37 (3H, s), 2.25 (3H, s), 2.15 (1H, ddd, *J* = 13.9, 6.1, 5.0 Hz), 1.59–1.54 (1H, m), 0.91 (3H, d, *J* = 7.0 Hz); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ: 143.5, 140.7, 137.9, 136.8, 135.4, 135.1, 129.4, 128.2, 127.7, 127.6, 127.4, 127.0, 126.6, 125.6, 125.0, 123.2, 57.1, 35.1, 27.9, 21.49, 21.46, 20.3; IR (KBr) cm^{-1}: 2963 (m), 1606 (m), 1487 (m), 1345 (s), 1166 (s), 1090 (m), 962 (m), 765 (m), 682 (m), 571 (s); EI-MS (70 eV) *m*/*z* (relative intensity): 391 (M^+, 78), 236 (100), 220 (30), 144 (10), 91 (13); HRMS (EI) *m*/*z*: M^+ Calcd for $C_{24}H_{25}NO_2S$ 391.1606; Found 391.1609; Anal. Calcd for $C_{24}H_{25}NO_2S$: C, 73.62; H, 6.44; N, 3.58. Found: C, 73.91; H, 6.57; N, 3.33.

4-Methyl-2-(*p*-tolyl)-1-tosyl-1,2,3,4-tetrahydroquinoline (3ad, diastereomixture) (*cis*/*trans* = 5.3:1) Purified by preparative TLC (30% EtOAc/*n*-hexane) to give 56.9 mg (42%) of colorless amorphous solid: TLC R_f = 0.44 (silica gel, 30% EtOAc/*n*-hexane); mp 45–48 °C; IR (KBr) cm^{-1}: 2958 (s), 1716 (s), 1514 (m), 1482 (m), 1358 (s), 1241 (s), 1092 (s), 965 (m), 814 (s), 710 (m), 661 (m); EI-MS (70 eV) *m*/*z* (relative intensity): 391 (M^+, 69), 236 (100), 220 (28), 105 (24), 91 (10); HRMS (EI) *m*/*z*: M^+ Calcd for $C_{24}H_{25}NO_2S$ 391.1606; Found 391.1603; Anal. Calcd for $C_{24}H_{25}NO_2S$: C, 73.62; H, 6.44; N, 3.58. Found: C, 73.78; H, 6.37; N, 3.45. Minor diastereomer: ^1H NMR (500 MHz, $CDCl_3$) δ: 7.91 (1H, d, *J* = 8.8 Hz),

7.48 (2H, d, *J* = 8.3 Hz), 7.24–7.01 (9H, m), 5.52 (1H, t, *J* = 4.9 Hz), 2.65–2.61 (1H, m), 2.30 (3H, s), 2.25 (3H, s), 2.17–2.15 (1H, m), 1.55–1.51 (1H, m), 0.90 (3H, d, *J* = 6.8 Hz); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ: 143.5, 137.5, 136.8, 136.3, 135.3, 134.9, 129.4, 129.0, 127.7, 127.4, 126.5, 126.1, 125.6, 125.0, 56.9, 34.8, 27.6, 21.5, 20.9, 20.5.

(2*RS*,4*RS*)-4-Methyl-2-(*p*-tolyl)-1-tosyl-1,2,3,4-tetrahydroquinoline (*cis*-3ad, major): TLC R_f = 0.44 (silica gel, 30% EtOAc/*n*-hexane); mp 148–151 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.79 (1H, d, *J* = 7.9 Hz), 7.35 (2H, d, *J* = 8.2 Hz), 7.32–7.29 (1H, m), 7.20–7.18 (3H, m), 7.12 (2H, d, *J* = 8.2 Hz), 7.09–7.07 (3H, m), 5.18 (1H, dd, *J* = 10.5, 8.0 Hz), 2.35 (3H, s), 2.33–2.30 (1H, m), 2.29 (3H, s), 1.71–1.67 (1H, m), 1.38–1.31 (1H, m), 1.08 (3H, d, *J* = 6.71 Hz); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ: 143.3, 141.3, 140.9, 136.5, 136.19, 136.18, 129.2, 129.1, 127.5, 127.0, 126.9, 126.0, 125.9, 123.3, 60.6, 44.7, 29.7, 21.4, 21.0, 17.0; IR (KBr) cm^{-1}: 2926 (m), 1599 (m), 1485 (m), 1355 (s), 1163 (s), 1092 (m), 964 (m), 596 (m), 815 (m), 661 (m); EI-MS (70 eV) *m*/*z* (relative intensity): 391 (M^+, 69), 236 (100), 220 (28), 105 (24), 91 (10); HRMS (EI) *m*/*z*: M^+ Calcd for $C_{24}H_{25}NO_2S$ 391.1606; Found 391.1605; Anal. Calcd for $C_{24}H_{25}NO_2S$: C, 73.62; H, 6.44; N, 3.58. Found: C, 73.99; H, 6.59; N, 3.36.

4-(4-Methyl-1-tosyl-1,2,3,4-tetrahydroquinolin-2-yl)phenyl acetate (3ae, diastereomixture) (*cis*/*trans* = 3.4:1) Purified by silica gel column chromatography (2–18% EtOAc/*n*-hexane + 8% CH_2Cl_2) to give 122 mg (81%) of colorless amorphous solid: TLC R_f = 0.15 (silica gel, EtOAc/*n*-hexane/CH_2Cl_2 = 1:10:1); mp 139–140 °C; IR (KBr) cm^{-1}: 2963 (m), 1758 (s), 1599 (m), 1506 (s), 1351 (s), 1199 (s), 1165 (s), 914 (m), 770 (m), 661 (s); EI-MS (70 eV) *m*/*z* (relative intensity): 435 (M^+, 100), 280 (73), 238 (76), 144 (12), 107 (36); HRMS (EI) *m*/*z*: M^+ Calcd for $C_{25}H_{25}NO_4S$ 435.1504; Found 435.1501; Anal. Calcd for $C_{25}H_{25}NO_4S$: C, 68.94; H, 5.79; N, 3.22. Found: C, 68.58; H, 5.98; N, 2.95. Minor diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.90 (1H, d, *J* = 7.9 Hz), 7.47 (2H, d, *J* = 8.2 Hz), 7.30–7.28 (3H, m), 7.21–7.18 (2H, m), 7.06–7.05 (2H, m), 6.95 (2H, dt, *J* = 9.2, 2.4 Hz), 5.54 (1H, t, *J* = 4.9 Hz), 2.64 (1H, dq, *J* = 18.5, 5.5 Hz), 2.36 (3H, s), 2.24 (3H, s), 2.14 (1H, ddd, *J* = 14.1, 6.3, 4.7 Hz), 1.59–1.53 (1H, m), 0.91 (3H, d, *J* = 6.7 Hz); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ: 149.4, 143.6, 138.1, 136.4, 135.1, 134.8, 129.4, 127.8, 127.5, 127.4, 127.3, 126.7, 125.6, 125.2, 121.4, 56.6, 34.9, 27.6, 21.4, 21.0, 20.3.

4-((2*RS*,4*RS*)-4-Methyl-1-tosyl-1,2,3,4-tetrahydroquinolin-2-yl)phenyl acetate (*cis*-3ae, major): Purified by recrystallization from *n*-hexane/toluene = 5:2. Colorless prisms: mp 155–156 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.77 (1H, dd, *J* = 7.9, 1.2 Hz), 7.36–7.30 (5H, m), 7.22 (1H, td, *J* = 7.5, 1.2 Hz), 7.14 (2H, d, *J* = 7.9 Hz), 7.08 (1H, d, *J* = 7.6 Hz), 7.01 (2H, dt, *J* = 9.2, 2.4 Hz), 5.24 (1H, dd, *J* = 10.7, 7.9 Hz), 2.37 (3H, s), 2.33 (1H, ddd, *J* = 13.1, 7.9, 3.1 Hz), 2.27 (3H, s), 1.72–1.68 (1H, m), 1.37–1.35

(1H, m), 1.09 (3H, d, *J* = 6.7 Hz); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ: 169.4, 149.6, 143.4, 141.7, 140.9, 136.1, 136.0, 129.3, 127.6, 127.2, 127.1, 127.0, 126.2, 123.4, 121.5, 60.2, 44.6, 29.7, 21.5, 21.1, 16.9; IR (KBr) cm^{-1}: 2969 (m), 1763 (s), 1596 (m), 1496 (m), 1357 (s), 1211 (s), 1169 (s), 906 (m), 659 (m), 547 (m); EI-MS (70 eV) *m*/*z* (relative intensity): 435 (M^+, 100), 280 (73), 238 (81), 222 (25), 144 (13), 107 (32); HRMS (EI) *m*/*z*: M^+ Calcd for $C_{25}H_{25}NO_4S$ 435.1504; Found 435.1501; Anal. Calcd for $C_{25}H_{25}NO_4S$: C, 68.94; H, 5.79; N, 3.22. Found: C, 68.94; H, 5.79; N, 3.22.

2-(4-Methoxyphenyl)-4-methyl-1-tosyl-1,2,3,4-tetrahydroquinoline (3af, diastereomixture) (*cis*/*trans* = 9.2:1) Purified by preparative TLC (EtOAc/*n*-hexane/CH_2Cl_2 = 1:8:1) to give 15.7 mg (6%) of colorless amorphous solid: TLC R_f = 0.25 (silica gel, EtOAc/*n*-hexane/CH_2Cl_2 = 1:8:1); mp 60–65 °C; IR ($CHCl_3$) cm^{-1}: 3030 (m), 2963 (m), 2932 (m), 1719 (m), 1610 (m), 1513 (s), 1350 (m), 1165 (s), 1091 (m), 1037 (m); EI-MS (70 eV) *m*/*z* (relative intensity): 407 (M^+, 51), 252 (100), 236 (27), 144 (15), 121 (98), 91 (16); HRMS (EI) *m*/*z*: M^+ Calcd for $C_{24}H_{25}NO_3S$ 407.1555; Found 407.1553. Major diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.76 (2H, dd, *J* = 7.9, 1.2 Hz), 7.35 (2H, d, *J* = 8.2 Hz), 7.32–7.29 (1H, m), 7.24–7.17 (2H, m), 7.14 (2H, d, *J* = 8.5 Hz), 7.08 (1H, d, *J* = 7.6 Hz), 6.83 (2H, d, *J* = 9.5 Hz), 5.19 (1H, dd, *J* = 11.0, 7.9 Hz), 3.77 (3H, s), 2.37 (3H, s), 2.31 (1H, ddd, *J* = 13.1, 7.9, 3.1 Hz), 1.71–1.69 (1H, m), 1.36 (1H, td, *J* = 12.7, 11.1 Hz), 1.09 (3H, d, *J* = 6.71 Hz); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ: 158.4, 143.5, 140.8, 136.9, 135.3, 135.0, 129.4, 127.8, 127.45, 127.41, 126.6, 125.7, 125.1, 113.8, 56.6, 55.2, 34.8, 27.6, 21.5, 20.5. Minor diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.88 (1H, d, *J* = 8.2 Hz), 7.48 (2H, d, *J* = 8.2 Hz), 7.38 (1H, d, *J* = 8.5 Hz), 7.32–7.29 (1H, m), 7.24–7.17 (3H, m), 7.06–7.04 (2H, m), 6.75 (2H, d, *J* = 8.5 Hz), 5.52 (1H, t, *J* = 4.7 Hz), 3.73 (3H, s), 2.68–2.61 (1H, m), 2.37 (3H, s), 2.14 (1H, ddd, *J* = 14.1, 6.5, 4.7 Hz), 1.54–1.52 (1H, m), 0.92 (3H, d, *J* = 7.0 Hz); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ: 158.6, 143.3, 141.0, 136.5, 136.3, 136.2, 129.3, 127.6, 127.3, 127.1, 127.0, 126.0, 123.3, 113.9, 60.3, 55.3, 44.7, 29.7, 21.5, 17.0.

2-(2-Chlorophenyl)-4-methyl-1-tosyl-1,2,3,4-tetrahydroquinoline (3ag, diastereomixture) (*cis*/*trans* = 3.4:1) Purified by silica gel column chromatography (2–14% EtOAc/*n*-hexane) to give 91.2 mg (74%) of colorless needles: TLC R_f = 0.20 (silica gel, 9% EtOAc/*n*-hexane); mp 137–159 °C; IR (KBr) cm^{-1}: 2970 (m), 1597 (m), 1484 (m), 1444 (m), 1354 (s), 1167 (s), 1032 (m), 754 (m), 659 (s), 550 (s); EI-MS (70 eV) *m*/*z* (relative intensity): 413 (M+2, 24), 411 (M^+, 62), 258 (32), 256 (100), 240 (16), 91 (12). HRMS (EI) *m*/*z*: M^+ Calcd for $C_{23}H_{22}NO_2SCl$ 411.1060; Found 411.1056.; Anal. Calcd for $C_{23}H_{22}NO_2SCl$: C, 67.06; H, 5.38; N, 3.40. Found: C, 67.00; H, 5.47; N, 3.14. Minor diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.03 (1H, dd, *J* = 8.2, 0.9 Hz), 7.48 (2H, d, *J* = 8.2 Hz), 7.41–7.06 (9H, m), 5.68 (1H, dd, *J* = 9.0, 6.0 Hz), 2.67–2.60 (1H, m), 2.34 (3H, s), 1.97 (1H, dt, *J* = 13.7, 6.0 Hz), 1.85 (1H,

ddd, *J* = 13.7, 9.0, 5.0 Hz), 0.73 (3H, d, *J* = 7.3 Hz); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ: 143.7, 141.2, 136.2, 136.1, 135.5, 131.0, 129.4, 128.0, 127.8, 127.7, 127.6, 127.21, 127.17, 127.1, 124.8, 124.7, 55.0, 36.7, 30.2, 21.4, 18.5.

(2*RS*,4*RS*)-2-(2-Chlorophenyl)-4-methyl-1-tosyl-1,2,3,4-tetrahydroquinoline (*cis*-3ag, major): mp 169–170 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.91 (1H, d, *J* = 7.9 Hz), 7.43 (1H, dd, *J* = 7.8, 1.7 Hz), 7.40–7.35 (3H, m), 7.31 (1H, dd, *J* = 7.9, 0.6 Hz), 7.25–7.12 (5H, m), 7.10 (1H, d, *J* = 7.6 Hz), 5.52 (1H, dd, *J* = 11.3, 7.3 Hz), 2.45 (1H, ddd, *J* = 13.1, 7.3, 2.8 Hz), 2.38 (3H, s), 1.71–1.62 (1H, m), 1.15–1.10 (1H, m), 1.10 (3H, d, *J* = 6.7 Hz); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ: 143.5, 142.2, 140.7, 136.4, 135.5, 131.1, 129.4, 129.2, 128.0, 127.6, 127.5, 127.4, 127.2, 127.1, 126.1, 123.4, 58.0, 42.2, 29.8, 21.5, 17.0; IR (KBr) cm^{-1}: 2971 (m), 1596 (m), 1483 (m), 1443 (m), 1353 (s), 1166 (s), 1032 (m), 755 (m), 659 (s), 550 (s); EI-MS (70 eV) *m*/*z* (relative intensity): 413 (M+2, 24), 411 (M^+, 59), 258 (32), 256 (100), 240 (17), 91 (12); HRMS (EI) *m*/*z*: M^+ Calcd for $C_{23}H_{22}NO_2SCl$ 411.1060; Found 411.1061; Anal. Calcd for $C_{23}H_{22}NO_2SCl$: C, 67.06; H, 5.38; N, 3.40. Found: C, 67.26; H, 5.38; N, 3.40.

2-(3-Chlorophenyl)-4-methyl-1-tosyl-1,2,3,4-tetrahydroquinoline (3ah, diastereomixture) (*cis*/*trans* = 3.0:1) Purified by silica gel column chromatography (2–18% EtOAc/*n*-hexane) to give 120.8 mg (79%) of colorless needles: TLC R_f = 0.20 (silica gel, 9% EtOAc/*n*-hexane); mp 130–155 °C; IR (KBr) cm^{-1}: 2929 (m), 1595 (s), 1483 (s), 1350 (s), 1165 (m), 1092 (m), 967 (m), 821 (m), 662 (m); EI-MS (70 eV) *m*/*z* (relative intensity): 413 (M+2, 24), 411 (M^+, 60), 258 (32), 256 (100), 240 (23); HRMS (EI) *m*/*z*: M^+ Calcd for $C_{23}H_{22}NO_2SCl$ 411.1060; Found 411.1055; Anal. Calcd for $C_{23}H_{22}NO_2SCl$: C, 67.06; H, 5.38; N, 3.40. Found: C, 66.71; H, 5.72; N, 3.12. Minor diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.94 (1H, d, *J* = 8.2 Hz), 7.47 (2H, d, *J* = 8.5 Hz), 7.36–7.03 (9H, m), 5.49 (1H, t, *J* = 5.0 Hz), 2.67–2.57 (1H, m), 2.37 (3H, s), 2.11 (1H, dt, *J* = 14.3, 5.6 Hz), 1.60–1.54 (1H, m), 0.88 (3H, d, *J* = 7.0 Hz); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ: 143.8, 143.0, 136.4, 135.0, 134.9, 134.3, 129.7, 129.5, 127.8, 127.4, 127.0, 126.8, 126.4, 125.7, 125.3, 124.5, 56.7, 35.0, 27.9, 21.5, 20.3.

(2*RS*,4*RS*)-2-(3-Chlorophenyl)-4-methyl-1-tosyl-1,2,3,4-tetrahydroquinoline (*cis*-3ah, diastereomixture): TLC R_f = 0.21 (silica gel, 9% EtOAc/*n*-hexane): mp 165–167 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.83 (1H, dd, *J* = 7.9, 1.2 Hz), 7.36–7.33 (3H, m), 7.28–7.27 (1H, m), 7.24–7.17 (4H, m), 7.15 (2H, d, *J* = 8.2 Hz), 7.08 (1H, d, *J* = 7.6 Hz), 5.17 (1H, dd, *J* = 11.0, 7.9 Hz), 2.38 (3H, s), 2.31 (1H, ddd, *J* = 13.2, 7.9, 3.0 Hz), 1.68 (1H, tdd, *J* = 12.9, 6.5, 2.7 Hz), 1.32 (1H, ddd, *J* = 12.7, 11.1, 5.5 Hz), 1.10 (3H, d, *J* = 7.0 Hz); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ: 146.3, 143.6, 140.7, 135.9, 135.8, 134.3, 129.8, 129.4, 127.6, 127.2, 127.2, 127.1, 126.3, 126.2, 124.2, 123.4, 60.3, 44.5, 29.7, 21.5, 16.9; IR (KBr)

cm^{-1}: 2930 (m), 1595 (s), 1483 (s), 1350 (m), 1164 (m), 1091 (m), 967 (m), 820 (m), 661 (m); EI-MS (70 eV) *m*/*z* (relative intensity): 413 (M+2, 24), 411 (M^+, 61), 258 (32), 256 (100), 240 (21); HRMS (EI) *m*/*z*: M^+ Calcd for $C_{23}H_{22}NO_2SCl$ 411.1060; Found 411.1059; Anal. Calcd for $C_{23}H_{22}NO_2SCl$: C, 67.06; H, 5.38; N, 3.40. Found: C, 67.05; H, 5.45; N, 3.34.

2-(4-Chlorophenyl)-4-methyl-1-tosyl-1,2,3,4-tetrahydroquinoline (3ai, diastereomixture) (*cis*/*trans* = 3.6:1) Purified by silica gel column chromatography (2–18% EtOAc/*n*-hexane) to give 44.8 mg (84%) of colorless needles: TLC R_f = 0.20 (silica gel, 9% EtOAc/*n*-hexane); mp 130–131 °C; IR (KBr) cm^{-1}: 1653 (s), 1491 (s), 1350 (s), 1165 (s), 1092 (m), 819 (m), 661 (m); EI-MS (70 eV) *m*/*z* (relative intensity): 413 (M+2, 20), 411 (M^+, 49), 258 (32), 256 (100), 240 (23); HRMS (EI) *m*/*z*: M^+ Calcd for $C_{23}H_{22}NO_2SCl$ 411.1060; Found 411.1058; Anal. Calcd for $C_{23}H_{22}NO_2SCl$: C, 67.06; H, 5.38; N, 3.40. Found: C, 66.97; H, 5.45; N, 3.19. Minor diastereomer: ^1H NMR (500 MHz, $CDCl_3$) δ: 7.92 (1H, dd, *J* = 8.2, 0.9 Hz), 7.48 (2H, d, *J* = 8.2 Hz), 7.35–7.04 (9H, m), 5.50 (1H, t, *J* = 5.0 Hz), 2.65–2.57 (1H, m), 2.37 (3H, s), 2.12 (1H, ddd, *J* = 14.0, 6.4, 4.9 Hz), 1.57–1.54 (1H, m), 0.89 (3H, d, *J* = 6.7 Hz); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ: 143.7, 139.3, 136.5, 135.0, 134.8, 132.6, 129.5, 128.5, 127.8, 127.7, 127.4, 126.8, 125.7, 125.3, 56.6, 34.8, 27.7, 20.4, 0.99.

(2*RS*,4*RS*)-2-(4-Chlorophenyl)-4-methyl-1-tosyl-1,2,3,4-tetrahydroquinoline (*cis*-3ai, major): TLC R_f = 0.21 (silica gel, 9% EtOAc/*n*-hexane); mp 157–159 °C; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.80 (1H, dd, *J* = 8.2, 1.2 Hz), 7.36–7.30 (3H, m), 7.27–7.21 (5H, m), 7.15 (2H, d, *J* = 7.9 Hz), 7.08 (1H, dt, *J* = 7.6, 1.2 Hz), 5.18 (1H, dd, *J* = 11.0, 7.9 Hz), 2.37 (3H, s), 2.31 (1H, ddd, *J* = 13.2, 7.9, 3.0 Hz), 1.71–1.67 (1H, m), 1.32 (1H, td, *J* = 12.7, 11.2 Hz), 1.09 (3H, d, *J* = 6.7 Hz); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ: 143.5, 142.8, 140.7, 135.9, 135.9, 132.7, 129.4, 128.6, 127.51, 127.47, 127.10, 127.08, 126.2, 123.4, 60.2, 44.5, 29.7, 21.5, 17.0; IR (KBr) cm^{-1}: 2918 (m), 1600 (m), 1485 (s), 1349 (s), 1167 (s), 1091 (m), 963 (m), 819 (m), 774 (m), 711 (m), 661 (s), 597 (s), 546 (s); EI-MS (70 eV) *m*/*z* (relative intensity): 413 (M+2, 22), 411 (M^+, 56), 258 (32), 256 (100), 240 (30); HRMS (EI) *m*/*z*: M^+ Calcd for $C_{23}H_{22}NO_2SCl$ 411.1060; Found 411.1059; Anal. Calcd for $C_{23}H_{22}NO_2SCl$: C, 67.06; H, 5.38; N, 3.40. Found: C, 66.83; H, 5.29; N, 3.32.

4-Methyl-2-(3-nitrophenyl)-1-tosyl-1,2,3,4-tetrahydroquinoline (3aj, diastereomixture) (*cis*/*trans* = 3.1:1) Purified by silica gel column chromatography (2–14% EtOAc/*n*-hexane + 8% CH_2Cl_2) and Al_2O_3 column chromatography (2–18% EtOAc/*n*-hexane) to give 60.7 mg (39%) of pale yellow solid: TLC R_f = 0.18 (silica gel, EtOAc/*n*-hexane/CH_2Cl_2 = 1:10:1), R_f = 0.20 (silica gel, EtOAc/*n*-hexane = 1:10); mp 176–177 °C; IR (KBr) cm^{-1}: 2963 (m), 1525 (s), 1485 (s), 1358 (s), 1169 (m), 1190 (m), 1055 (m), 957

(m), 816 (m), 659 (s); EI-MS (70 eV) *m*/*z* (relative intensity): 422 (M^+, 67), 267 (100), 251 (11), 221 (32), 205 (11), 91 (13); HRMS (EI) *m*/*z*: M^+ Calcd for $C_{23}H_{22}N_2O_4S$ 422.1300; Found 422.1297; Anal. Calcd for $C_{23}H_{22}N_2O_4S$: C, 65.38; H, 5.25; N, 6.63. Found: C, 65.13; H, 5.38; N, 3.65.

(2*RS*,4*RS*)-4-Methyl-2-(3-nitrophenyl)-1-tosyl-1,2,3,4-tetrahydroquinoline (*cis*-3aj, major): Purified by silica gel column chromatography (10–70% CH_2Cl_2/cyclohexane). Colorless needles: TLC R_f = 0.18 (silica gel, 50% CH_2Cl_2/cyclohexane); mp 193–194 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.17 (1H, t, *J* = 2.0 Hz), 8.09 (1H, ddd, *J* = 8.0, 2.1, 1.0 Hz), 7.88 (1H, dd, *J* = 7.9, 1.2 Hz), 7.72 (1H, dt, *J* = 7.7, 0.8 Hz), 7.49 (1H, t, *J* = 7.9 Hz), 7.39–7.34 (3H, m), 7.25 (1H, td, *J* = 7.6, 1.2 Hz), 7.17 (2H, dd, *J* = 8.5, 0.6 Hz), 7.10 (1H, dt, *J* = 7.6, 1.2 Hz), 5.28 (1H, dd, *J* = 11.1, 7.8 Hz), 2.39 (3H, s), 2.36 (1H, ddd, *J* = 9.7, 3.4, 1.7 Hz), 1.69 (1H, tdd, *J* = 12.9, 6.4, 2.8 Hz), 1.38–1.32 (1H, m), 1.12 (3H, d, *J* = 6.7 Hz); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 148.4, 146.5, 143.9, 140.5, 135.6, 135.4, 132.2, 129.6, 129.5, 127.6, 127.4, 127.1, 126.5, 123.6, 122.1, 121.2, 60.2, 44.3, 29.7, 21.5, 17.0; IR (KBr) cm^{-1}: 2964 (m), 1525 (s), 1485 (s), 1356 (s), 1170 (m), 1189 (m), 1055 (m), 958 (m), 816 (m), 658 (s); EI-MS (70 eV) *m*/*z* (relative intensity): 422 (M^+, 70), 267 (100), 251 (11), 221 (32), 205 (11), 91 (14); HRMS (EI) *m*/*z*: M^+ Calcd for $C_{23}H_{22}N_2O_4S$ 422.1300; Found 422.1299; Anal. Calcd for $C_{23}H_{22}N_2O_4S$: C, 65.38; H, 5.25; N, 6.63. Found: C, 65.58; H, 5.27; N, 6.92.

(2*RS*,4*SR*)-4-Methyl-2-(3-nitrophenyl)-1-tosyl-1,2,3,4-tetrahydroquinoline (*trans*-3aj, minor): Purified by silica gel column chromatography (10–70% CH_2Cl_2/cyclohexane). Colorless needles: TLC R_f = 0.17 (silica gel, 50% CH_2Cl_2/cyclohexane); mp 173–174 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.14 (1H, t, *J* = 2.0 Hz), 8.05–8.02 (1H, m), 8.00 (1H, dd, *J* = 8.4, 1.1 Hz), 7.72–7.69 (1H, m), 7.48 (2H, d, *J* = 8.5 Hz), 7.43 (1H, t, *J* = 7.9 Hz), 7.27–7.23 (1H, m), 7.23–7.21 (2H, m), 7.10 (1H, td, *J* = 7.5, 1.2 Hz), 7.05 (1H, dd, *J* = 7.8, 1.4 Hz), 5.55 (1H, t, *J* = 5.3 Hz), 2.65–2.61 (1H, m), 2.39 (3H, s), 2.17 (1H, ddd, *J* = 14.3, 6.1, 5.5 Hz), 1.66 (1H, ddd, *J* = 14.4, 9.1, 5.1 Hz), 0.85 (3H, d, *J* = 6.7 Hz); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 148.4, 144.0, 143.5, 136.0, 134.9, 134.7, 132.6, 129.6, 129.5, 128.0, 127.5, 127.1, 125.9, 125.6, 122.1, 121.2, 56.7, 35.1, 28.1, 21.5, 20.3; IR (KBr) cm^{-1}: 2963 (m), 1523 (s), 1487 (s), 1341 (s), 1167 (s), 1189 (m), 1054 (m), 772 (m), 670 (s); EI-MS (70 eV) *m*/*z* (relative intensity): 422 (M^+, 84), 267 (100), 251 (7), 221 (30), 205 (10), 91 (13); HRMS (EI) *m*/*z*: M^+ Calcd for $C_{23}H_{22}N_2O_4S$ 422.1300; Found 422.1302; Anal. Calcd for $C_{23}H_{22}N_2O_4S$: C, 65.38; H, 5.25; N, 6.63. Found: C, 65.58; H, 5.27; N, 6.92.

3,4-Dimethyl-2-phenyl-1-tosyl-1,2,3,4-tetrahydroquinoline (3ak, diastereomixture) (A:B:C = 14:84:2). Purified by silica gel column chromatography (1–10% EtOAc/*n*-hexane + 5% CH_2Cl_2) to give 230 mg (85%) of colorless needles: mp 125–126 °C; TLC R_f = 0.25 (silica gel, 9%

EtOAc/*n*-hexane/CH_2Cl_2 = 1:18:1); IR (KBr) cm^{-1}: 1657 (m), 1638 (m), 1491 (m), 1335 (m), 1153 (m), 1091 (m), 661 (m); GC EI-MS (70 eV) *m/z* (relative intensity): **3ak-A**: 19.73 min, 391 (M^+, 51), 236 (100), 206 (15), 91 (16). **3ak-B**: 19.89 min, 391 (M^+, 68), 236 (100), 206 (15), 91 (14). **3ak-C**: 19.95 min, 391 (M^+, 44), 236 (100), 206 (14), 91 (18); GC HRMS (EI) *m/z*: M^+ Calcd for $C_{24}H_{25}NO_2S$, 391.1606; found, 391.1607 (**3ak-A**), 391.1602 (**3ak-B**), 391.1598 (**3ak-C**); Anal. Calcd for $C_{24}H_{25}NO_2S$: C, 73.63; H, 6.44; N, 3.58. Found: C, 73.77; H, 6.57; N, 3.57.

(2*RS*,3*RS*,4*RS*)-3,4-Dimethyl-2-phenyl-1-tosyl-1,2,3,4-tetrahydroquinoline (3ak-A). Purified by silica gel column chromatography (2–18% Et_2O/*n*-hexane). Colorless needles: TLC R_f = 0.12 (silica gel, 9% Et_2O/*n*-hexane); mp 114–115 °C; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.64 (1H, dd, *J* = 7.9, 1.2 Hz), 7.36 (2H, dt, *J* = 8.4, 1.8 Hz), 7.32–7.29 (1H, m), 7.28–7.20 (4H, m), 7.19–7.17 (2H, m), 7.13 (3H, m), 4.61 (1H, d, *J* = 9.2 Hz), 2.37 (3H, s), 1.50–1.39 (2H, m), 1.11 (3H, d, *J* = 6.4 Hz), 0.94 (3H, d, *J* = 6.1 Hz); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ: 143.8, 143.2, 140.5, 136.9, 136.5, 129.3, 128.3, 127.5, 127.2, 127.1, 127.0, 126.9, 126.2, 123.4, 68.0, 48.0, 35.3, 21.5, 17.2, 13.5; IR (KBr) cm^{-1}: 2993 (m), 1599 (s), 1486 (s), 1455 (s), 1355 (s), 1165 (s), 1029 (m), 925 (m), 814 (m), 661 (m), 605 (m); EI-MS (70 eV) *m/z* (relative intensity): 391 (M^+, 67), 236 (100), 220 (12), 206 (15), 91 (14); HRMS (EI) *m/z*: M^+ Calcd for $C_{24}H_{25}NO_2S$ 391.1606; Found 391.1605; Anal. Calcd for $C_{24}H_{25}NO_2S$: C, 73.62; H, 6.44; N, 3.58. Found: C, 73.66; H, 6.46; N, 3.32.

(2*RS*,3*RS*,4*SR*)-3,4-Dimethyl-2-phenyl-1-tosyl-1,2,3,4-tetrahydroquinoline (3ak-B). Purified by silica gel column chromatography (2–18% Et_2O/*n*-hexane). Colorless prisms: TLC R_f = 0.14 (silica gel, 9% Et_2O/*n*-hexane); mp 137–138 °C; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.61 (1H, d, *J* = 8.2 Hz), 7.36 (2H, d, *J* = 8.2 Hz), 7.28–7.17 (6H, m), 7.09–7.07 (4H, m), 4.93 (1H, d, *J* = 9.5 Hz), 2.64 (1H, dq, *J* = 14.4, 3.7 Hz), 2.32 (3H, s), 2.04–1.97 (1H, m), 0.95 (3H, d, *J* = 6.7 Hz), 0.89 (3H, d, *J* = 7.3 Hz); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ: 143.5, 143.2, 137.9, 137.6, 136.1, 129.2, 128.3, 127.41, 127.37, 127.2, 127.1, 126.9, 124.5, 123.1, 64.4, 42.5, 37.0, 21.4, 16.1, 13.1; IR (KBr) cm^{-1}: 2960 (m), 1598 (m), 1488 (m), 1453 (m), 1336 (s), 1155 (m), 1023 (m), 920 (m), 703 (m), 664 (s), 581 (m), 536 (m); EI-MS (70 eV) *m/z* (relative intensity): 391 (M^+, 60), 236 (100), 220 (10), 206 (14), 91 (15); HRMS (EI) *m/z*: M^+ Calcd for $C_{24}H_{25}NO_2S$ 391.1606; Found 391.1608; Anal. Calcd for $C_{24}H_{25}NO_2S$: C, 73.63; H, 6.44; N, 3.58. Found: C, 73.74; H, 6.54; N, 3.41.

(2*RS*,3*SR*,4*SR*)-3,4-Dimethyl-2-phenyl-1-tosyl-1,2,3,4-tetrahydroquinoline (3ak-C). Purified by silica gel column chromatography (2–18% Et_2O/*n*-hexane). Colorless needles: TLC R_f = 0.09 (silica gel, 9% Et_2O/*n*-hexane); mp 156–157 °C; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.90 (1H, dd, *J* = 8.1, 1.1 Hz), 7.35–

7.30 (7H, m), 7.23–7.18 (2H, m), 7.13 (2H, d, *J* = 7.9 Hz), 6.99 (1H, d, *J* = 7.6 Hz), 5.29 (1H, d, *J* = 7.3 Hz), 2.40–2.33 (1H, m), 2.37 (3H, s), 1.98 (1H, ddd, *J* = 13.8, 6.8, 2.7 Hz), 1.09 (3H, d, *J* = 7.0 Hz), -0.03 (3H, d, *J* = 7.0 Hz); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ: 143.4, 142.0, 137.4, 136.5, 135.4, 129.2, 128.2, 127.3, 126.9, 126.7, 126.6, 126.5, 126.0, 124.9, 65.9, 42.4, 34.4, 21.5, 14.8, 9.1; IR (KBr) cm^{-1}: 3429 (br), 2890 (m), 1601 (m), 1483 (m), 1452 (m), 1352 (s), 1169 (s), 1092 (m), 1003 (m), 768 (m), 670 (s), 548 (m); EI-MS (70 eV) *m*/*z* (relative intensity): 391 (M^+, 58), 236 (100), 220 (11), 206 (14), 91 (15); HRMS (EI) *m*/*z*: M^+ Calcd for $C_{24}H_{25}NO_2S$ 391.1606; Found 391.1605; Anal. Calcd for $C_{24}H_{25}NO_2S$: C, 73.62; H, 6.44; N, 3.58. Found: C, 73.46; H, 6.47; N, 3.21.

***N*,*N*'-((Oxybis(ethane-1,1-diyl))bis(2,1-phenylene))bis(4-methylbenzenesulfonamide) 4** (major/minor = 1.7:1) The reaction was conducted according to general procedure C without styrene at 20 °C for 48 h. The crude material was purified by silica gel column chromatography (0–6% EtOH/ CH_2Cl_2) to give 93.4 mg (63%) of colorless amorphous solid: TLC R_f = 0.33, 0.27 (silica gel, EtOAc/*n*-hexane/CH_2Cl_2 = 1:4:1): mp 59–60 °C; IR (KBr) cm^{-1}: 3260 (brs), 1925 (m), 1722 (s), 1597 (s), 1501 (s), 1333 (s), 1158 (s), 1092 (s), 918 (s), 764 (s), 664 (s); EI-MS (70 eV) *m*/*z* (relative intensity): 564 (M+, 7), 274 (100), 210 (17), 119 (71), 91 (20); HRMS (EI) *m*/*z*: M^+ Calcd for $C_{30}H_{32}N_2O_5S_2$ 564.1753; Found 564.1754. Major diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.19 (2H, brs), 7.78 (4H, dt, *J* = 8.5, 1.8 Hz), 7.60 (2H, dd, *J* = 8.1, 1.1 Hz), 7.28–7.22 (6H, m), 6.98 (2H, td, *J* = 7.5, 1.0 Hz), 6.78 (2H, dd, *J* = 7.5, 1.7 Hz), 4.32 (2H, q, *J* = 6.8 Hz), 2.39 (6H, s), 1.23 (6H, d, *J* = 6.7 Hz). Minor diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.69 (2H, b s), 7.60 (4H, dt, *J* = 8.5, 1.8 Hz), 7.27–7.25 (2H, m), 7.22 (4H, d, *J* = 7.9 Hz), 7.19–7.16 (2H, m), 7.05–7.00 (4H, m), 4.63 (2H, q, *J* = 6.6 Hz), 2.38 (6H, s), 1.33 (6H, d, *J* = 6.4 Hz). Diastereomixture: $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ: 144.0, 143.7, 136.9, 136.9, 135.6, 134.9, 132.6, 129.7, 129.7, 129.4, 129.0, 128.9, 128.7, 128.0, 127.2, 124.9, 124.2, 121.7, 120.2, 77.2, 76.3, 75.0, 21.8, 21.5, 21.5, 20.9.

2,2-Dimethyl-1-tosylindoline (5): ^{1}H-NMR ($CDCl_3$) δ: 7.79 (2H, dd, *J* = 8.2, 1.2 Hz), 7.46 (1H, d, *J* = 8.2 Hz), 7.23 (2H, d, *J* = 7.9 Hz), 7.13 (1H, t, *J* = 7.8 Hz), 7.08 (1H, d, *J* = 7.3 Hz), 6.93 (1H, t, *J* = 7.5 Hz), 2.97 (2H, s), 2.37 (3H, s), 1.66 (6H, s); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ: 143.3, 142.0, 139.3, 129.5, 128.2, 127.6, 126.7, 125.0, 122.6, 114.1, 69.9, 46.1, 28.5, 21.5; IR (KBr) cm^{-1}: 2967 (m), 1600 (m), 1479 (m), 1460 (m), 1348 (s), 1158 (s), 997 (m), 684 (m), 581 (s); EI-MS (70 eV) *m*/*z* (relative intensity): 301 (M^+, 79), 286 (64), 155 (28), 146 (100), 131 (37), 91 (20); HRMS (EI) *m*/*z*: M^+ Calcd for $C_{17}H_{19}NO_2S$ 301.1136; Found 301.1135.

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