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A Catalytic and Enantioselective Synthesis of *trans*-2-Amino-1-aryltetralins

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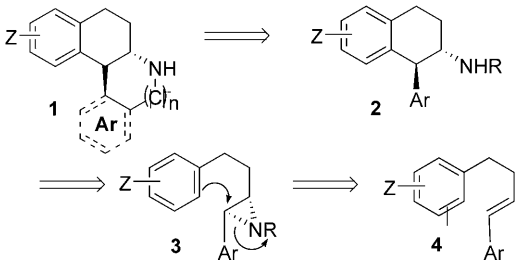
Abstract: The bis-oxazoline-copper complex-catalyzed aziridination of alkenes followed by an intramolecular Friedel–Crafts alkylation of the tethered and *in situ* generated aziridine provides a one-pot, general and efficient method for the synthesis of *trans*-2-amino-1-aryltetralins from a mixture of 2-arylethylstyrenes ($E/Z \leq 85{:}15$) with excellent diastereo- ($dr > 99{:}1$) and enantioselectivities (up to 92% *ee*).

Keywords: 2-amino-1-aryltetralins; aziridination; catalytic synthesis; enantioselectivity; Friedel–Crafts alkylation

Hexahydrobenzophenanthrenes **1** (n = 1) and their homologues **1** (n = 2) constitute important structural subunits of various natural products and pharmaceuticals.[1,2] There has been considerable interest in the synthesis of such compounds, especially in an enantioselective manner.[3] Enantioselective 1,4-conjugate addition of aryllithium reagents to nitroalkenes followed by reduction of the nitro group and cylization is an established protocol for the synthesis of such compounds.[4] We, however, envisaged the asymmetric synthesis of phenanthrenes **1** from *trans*-2-amino-1-aryltetralins **2** *via* stereoselective intramolecular arylation of tethered chiral aziridines **3** (Scheme 1). While the study on regio- and stereoselective ring-opening of aziridines is well documented,[5,6] the intramolecular Friedel–Crafts alkylation with chiral non-racemic tethered aziridines has not been reported to date.

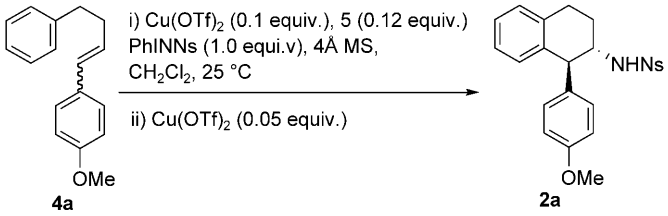
Herein, we report our results on the intramolecular arylation of *in situ* generated aziridines towards a catalytic, enantioselective and one-pot synthesis of *trans*-2-amino-1-aryltetralins **2** with high diastereo- (>99:1) and enantioselectivity (up to 92% *ee*).

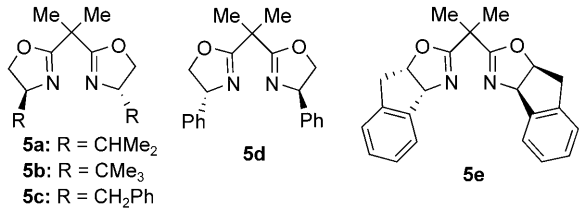


Scheme 1. Retrosynthesis for the construction of hexahydrophenanthrene **1**.

$Cu(OTf)_2$ is known to effect the aziridination[5] of alkenes and is useful for the subsequent intramolecular Friedel–Crafts alkylation of the tethered and *in situ* generated aziridines.[7] It was anticipated that the use of a chiral catalyst of copper(II) salts might provide the non-racemic *trans*-2-amino-1-aryltetralins. Consequently, we chose to investigate the well established bis-oxazoline-copper complexes, which were reported for the asymmetric aziridination of *E*-alkenes with $PhINSO_2Ar$.[8,9] Thus, our studies began with the reaction of **4a** with $PhINSO_2(4\text{-}NO_2\text{-}C_6H_4)$ [PhINNs] in the presence of $Cu(OTf)_2$ and bis-oxazoline ligands **5a–e** (Table 1). The reaction of **4a** (5.0 equiv.) with PhINNs (1.0 equiv.) was carried out in the presence of $Cu(OTf)_2$ (0.1 equiv.) and bis-oxazoline ligand **5a** (0.12 equiv.) in CH_2Cl_2 at room temperature. After 2 h, it produced aziridine **3a** as the sole product and the expected cyclized product **2a** was not formed. When the same reaction was performed with an additional amount of $Cu(OTf)_2$ (0.05 equiv.) it produced, after 20 min, the desired product **2a** with 42% *ee* in 56% of yield (entry 1). Under similar reaction conditions, the other bis-oxazoline-$Cu(OTf)_2$ catalysts **5b–e** were investigated. With the sterically demanding *tert*-butyl bis-oxazoline **5b**, there was no appreciable improvement in the yield and *ee* (entry 2). Improved enantioselectivity was observed with the benzyl-substituted bis-oxazoline **5c** (entry 3). Similar selectivity was also obtained with bis-oxazoline **5e**, derived from

Table 1. Screening of bis-oxazoline ligands for the $Cu(OTf)_2$-catalyzed aziridination-Friedel–Crafts reaction.





Entry	Ligand **5**	Yield of **2a** [%][a]	*ee*[b] [%]
1	(*S*)-**5a**	56	42
2	(*S*)-**5b**	61	45
3	(*S*)-**5c**	72	62
4	(*R*)-**5d**	85	92[c]
5	(1*R*,2*S*)-**5e**	66	69[c]

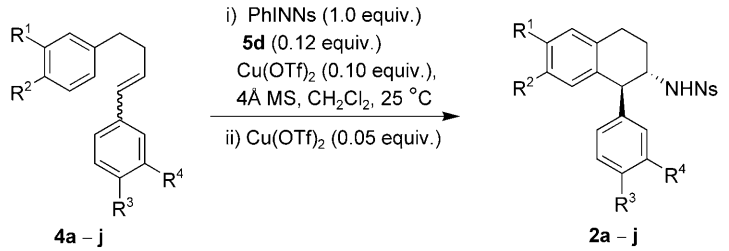
[a] Isolated yield after column chromatography.
[b] Enantiomeric excess was determined by chiral HPLC.
[c] The other enantiomer was predominantly formed.

indanolamine (entry 5). Among all the bis-oxazoline-Cu salts, **5d** was found to be the best (*ee* 92% and yield 85%; entry 4). The effect of a solvent on this reaction was substantial. Both yield and *ee* were better in CH_2Cl_2 (yield 85% and *ee* 92%) than in benzene (yield 62% and *ee* 68%), toluene (yield 61% and *ee* 65%) and acetonitrile (yield 81% and *ee* 43%) for the transformation **4a**→**2a** in the presence of **5d**.

It is worth mentioning that the copper salt must be added in two portions, at first 0.10 equivalent together with the ligand (0.12 equivalent) to obtain the aziridine and then 0.05 equivalent to achieve the Friedel–Crafts cyclization. Prolonging the reaction by 24 h without additional copper salt led to decomposition of the aziridine with the formation of a mixture of products. It seems that the ligand-complexed copper salt is not effective for the Friedel–Crafts reaction. Excess Cu salt, added as the second portion, remains free from complexation and hence causes the Friedel–Crafts reaction. When **4a** was reacted with 0.15 equivalent of $Cu(OTf)_2$ in one portion along with 0.12 equivalent of ligand **5d**, the yield of **2a** was 82%, but the *ee* dropped to 68% from 92%. This might be due to competitive racemic aziridination in the presence of the uncomplexed copper salt.

Having found **5d** to be the most effective, we next investigated the scope of the catalytic asymmetric synthesis of *N*-protected-2-amino-1-aryltetralins **2** (Table 2). Substrates **4b** and **4c** smoothly underwent

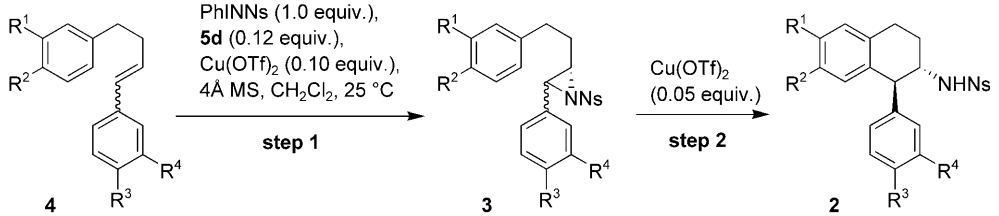
Table 2. Bis-oxazoline **5d**-$Cu(OTf)_2$ complex-catalyzed one-pot enantioselective synthesis of *trans*-2-amino-1-aryltetralins **2**.[a]



Entry	Substrate (*E*:*Z*)	R^1	R^2	R^3	R^4	Time [h][b]	Yield of **2** [%][c]	*dr* of **2** (*trans*:*cis*)	*ee* of **2** [%][d]
1	**4a** (75:25)	H	H	OMe	H	1.0	85 (**2a**)	>99:1	92
2	**4b** (74:26)	H	H	H	H	3	62 (**2b**)	>99:1	59
3	**4c** (63:37)	H	H	Me	H	1.5	77 (**2c**)	>99:1	86
4	**4d** (75:25)	H	OMe	Me	H	1.0	81 (**2d**)	>99:1	76
5	**4e** (67:33)	H	OMe	Cl	H	1.5	66 (**2e**)	>99:1	82
6	**4f** (85:15)	H	OMe	OMe	H	1.0	78 (**2f**)	>99:1	74
7	**4g** (77:23)	H	OMe	H	OMe	1.0	76 (**2g**)	>99:1	83
8	**4h** (76:24)	OMe	OMe	Me	H	1.5	71 (**2h**)	>99:1	60
9	**4i** (73:27)	H	H	H	OMe	2.5	79 (**2i**)	>99:1	73
10	**4j** (68:32)	H	H	H	Br	2.5	58 (**2j**)	>99:1	66

[a] A suspension of substrate **4** (5 equiv.), PhINNs (1.0 equiv.) and bis-oxazoline-Cu(II) complex derived from 10 mole% $Cu(OTf)_2$ and 12 mole% bis-oxazoline ligand **5d** in CH_2Cl_2 was stirred at 25 °C. After dissolution of all the nitrenoid reagents, additional 5 mole% $Cu(OTf)_2$ was added.
[b] Total time including aziridine formation and subsequent cyclization.
[c] Isolated yield after flash column chromatography.
[d] Enantiomeric excess was determined by HPLC using Chiralcel AD-H and OD-H columns.

Table 3. Two-step enantioselective synthesis of *N*-protected 2-amino-1-aryltetralins **2**.[a]



Entry	Substrate (*E*:*Z*)	**Step 1** [h]	Yield of **3**[b] [%]	*dr* of **3**[c] (*trans*:*cis*)	*ee* of **3**[d] [%]	**Step 2** [h]	Yield of **2**[b] [%]	*dr* of **2**[c] (*trans*:*cis*)	*ee* of **2**[d] [%]
1	**4a** (75:25)	0.5	83	1:2.5	ND[e]	0.5	98	>99:1	90
2	**4b** (74:26)	2.5	63	>99:1	62	1.5	98	>99:1	61
3	**4c** (63:37)	1	80	>99:1	86	1.0	97	>99:1	87
4	**4i** (73:27)	2	80	50:1	69	1.5	97	>99:1	69
5	*trans*-**4a** (>99:1)	0.5	86	1:2.5	ND[e]	0.5	97	>99:1	90
6	*cis*-**4a** (<1:99)	8	29	<1:99	80	0.5	95	>99:1	77
7	*trans*-**4b** (>99:1)	2.5	65	>99:1	62	1.5	98	>99:1	61
8	*cis*-**4b** (<1:99)	18	40	1:1	ND[e]	2	98 (97)[f]	>99:1	68
9	–	–	–	<1:99	35	12	NR	–	–

[a] **Step 1:** A suspenstion of substrate **4** (5 equiv.), PhINNs (1.0 equiv.) and bis-oxazoline-Cu(II) complex derived from 10 mole% $Cu(OTf)_2$ and 12 mole% bis-oxazoline ligand **5d** in CH_2Cl_2 was stirred at 25 °C. **Step 2:** Isolated aziridine **3** in CH_2Cl_2 was treated with 0.05 equiv of $Cu(OTf)_2$ at room temperature.

[b] Isolated yield after flash column chromatography.

[c] Diastereomeric ratio was measured from the ^1H NMR analysis of the crude reaction mixture.

[d] Enantiomeric excess was determined by HPLC using chiralcel AD-H and OD-H column.

[e] The *ee* could not be determined as the peaks of one *trans*-enantiomer and one of the *cis*-enantiomers could not be resolved under a variety of HPLC conditions.

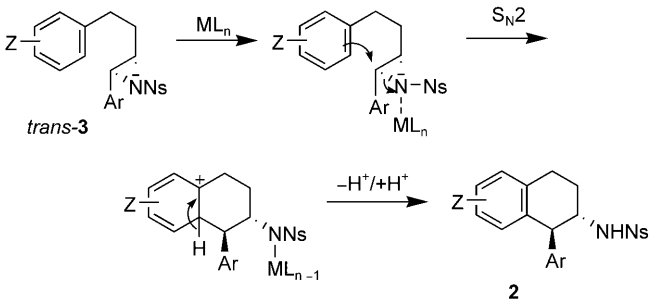
[f] Yield of the respective **2b** based on 100% conversion of aziridine **3b**. Yield in parenthesis refers to the recovered *cis*-aziridine *cis*-**3b**. ND = not determined; NR = no reaction.

the reaction and afforded products **2b** and **2c** with 59% and 86% *ee*, respectively (entries 2 and 3). Styrenes **4d–h** having electron-donor substituents on both the aromatic rings at either end of the alkene chain underwent fast reactions and gave **2d–h** with good yields and selectivities (entries 4–8). Substrates **4i** and **4j** containing *meta*-methoxy- and bromo-substituents provided good yields with 73% and 66% *ee*, respectively (entries 9 and 10).

It is likely that the enantioselectivity is controlled in the first step, i.e., aziridination step, and carried over to the subsequent Friedel–Crafts cyclization to yield non-racemic 2-amino-1-aryltetralins **2**. To support this view, the syntheses of tetralins **2a–c** and **2i** were conducted in two steps from electronically different styrenes **4a–c** and **4i** (Table 3). It was found that the *ee*s of the 2-amino-1-aryltetralins **2** were comparable with the *ee*s of isolated aziridines **3**, and also the overall yields of the two steps were very close to the yields of the one-pot version.

Aziridination of **4b** and **4c** (*E*/*Z* = 74/26 and 63/37, respectively) provided >99:1 selectivity towards *trans*-aziridines **3b** and **3c** (entries 2 and 3) and **4i** (*E*/*Z*=73/27) showed *trans*-selectivity of 50:1 (entry 4), whereas **4a** (*E*/*Z* = 75/25) provided a 1:2.5 mixture of *trans*- and *cis*-aziridine **3a** (entry 1) within 30 min in 83% of yield. Aziridination of pure *trans*-**4a** also afforded a 1:2.5 mixture of *trans*- and *cis*-**3a** in 86% yield within 30 min (entry 5), whereas pure *cis*-**4a** gave >99:1 of *cis*-**3a** after 8 h in 29% yield with 80% *ee* (entry 6). Similarly, aziridination of pure *trans*-**4b** provided >99:1 *trans*-**3b** after 2.5 h in 65% yield with 62% *ee* (entry 7), whereas pure *cis*-**4b** gave a 1:1 mixture of *trans*- and *cis*-**3b** after 18 h in 40% yield.[10] It was found that *trans*-alkenes underwent fast aziridination (0.5–2.5 h) with good yield whereas the aziridinations of *cis*-alkenes were slow (8–18 h) and low yielding (entries 6 and 8).

All *trans*-aziridines **3b**, **3c**, **3i** and mixture of *cis*/*trans*-**3a** underwent smooth intramolecular Friedel–Crafts cyclization in the presence of a catalytic amount of $Cu(OTf)_2$ and afforded exclusively *trans*-2-amino-1-aryltetralins **2** in excellent yields with *ee*s comparable with those of aziridines **3**. The isomeric cyclized product *cis*-**2a** was not detected in the ^1H NMR or HPLC analysis (entry 1). The *cis*-aziridine *cis*-**3a** (*ee* 80%) with a *para*-methoxyphenyl substituent also underwent smooth cyclization within half an hour under similar conditions and provided exclusively *trans*-**4a** in 95% of yield and 77% of *ee* (entry 6). The $Cu(OTf)_2$-catalyzed Friedel–Crafts reaction of *cis*/*trans*-**3b** provided *trans*-2-amino-1-aryl-

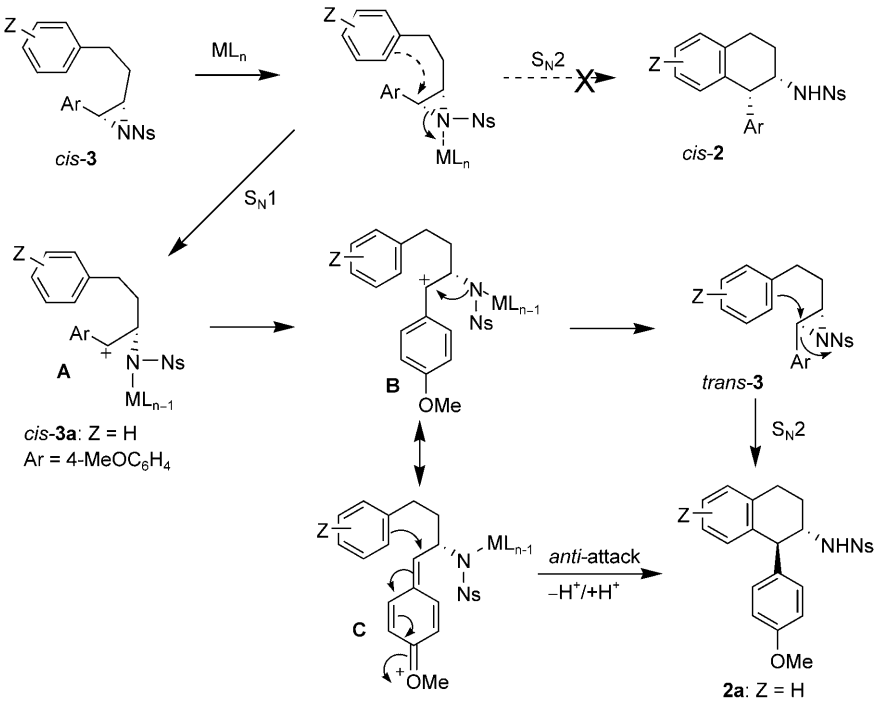


Scheme 2. Plausible mechanism for the Friedel–Crafts cyclization of *trans*-aziridines.

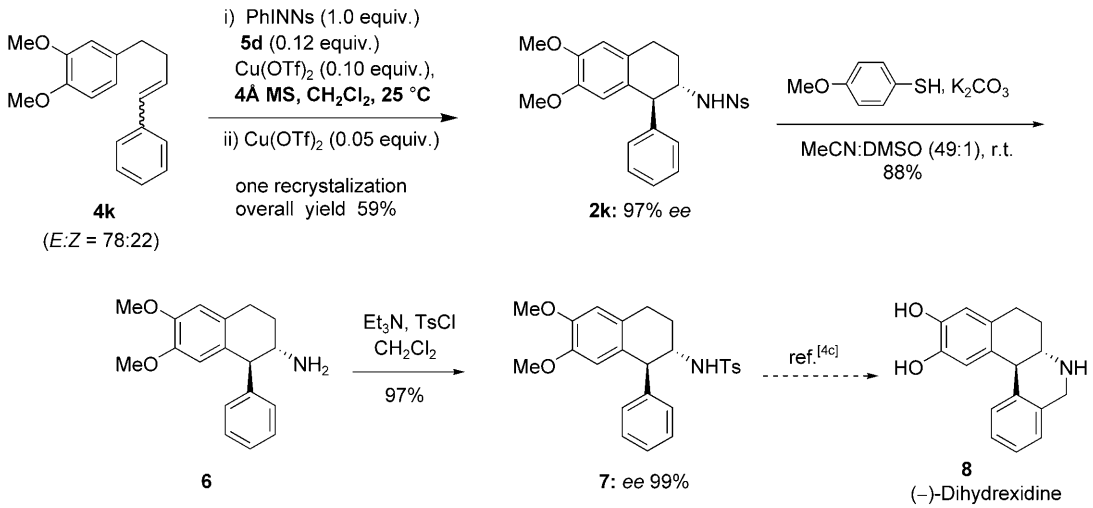
tetralin **2b** in 98% of yield (based on 100% conversion) after 1 h along with complete recovery of *cis*-**3b** (entry 8). Under similar conditions, pure *cis*-**3b** was separately reacted in the presence of the Cu catalyst and also in the presence of a stoichiometric amount of $Cu(OTf)_2$. Up to 24 h, there was no sign of reaction at room temperature (entry 9). It produced an intractable mixture when heated at 40 °C for 30 min. These results can be interpreted in terms of differential reactivities of the isomeric aziridines. The *trans*-aziridines undergo an S_N2 type Friedel–Crafts cyclization to yield *trans*-tetralins **2** (Scheme 2),[11] whereas *cis*-aziridines are not reactive to S_N2 ring-opening and undergo an S_N1 ring-opening mechanism followed by intramolecular Friedel–Crafts reaction to give the more stable *trans*-product only for aziridines having electron-rich aryl substituents such as **3a** (Scheme 3).[12] Alternatively, the carbocation **B** might undergo further ring closure to generate the aziridine *trans*-**3**, which subsequently undergoes an S_N2 type intramolecular Friedel–Crafts reaction to afford the *trans*-2-amino-1-aryltetralin **2** (Scheme 3).

Chiral *trans*-2-amino-1-aryltetralins **2** are the advanced precursors for the synthesis of dopamine D1 agonists such as dihydrexiridine, A-86929 and sch 39166.[4] Consequently, the developed methodology was tested on the synthesis of dihydrexiridine[2a] (Scheme 4). To this end, styrene **4k** ($E/Z = 78/22$) was reacted with PhINNs in the presence of $Cu(OTf)_2$-**5d** as catalyst. It provided exclusively *trans*-*N*-protected-2-amino-1-phenyltetralin **2k** in 85% yield with 70% *ee*. One recrystalization of the column-purified product from methanol at 5 °C afforded optically pure **2k** (97% *ee*) with 70% recovery yield. Deprotection of the *N*-nosyl group of **2k** on treatment with 4-methoxythiophenol and K_2CO_3 in CH_3CN/DMSO (49:1) at room temperature produced *trans*-2-amino-1-phenyltetralin **6** in 88% yield within 2.5 h.[13] The optical rotation of **6** {$[\alpha]_D^{25}$: −19.9 (*c* 1.3, $CHCl_3$)} was comparable with literature[4b] data {$[\alpha]_D^{25}$: −20.6 (*c* 1.3, $CHCl_3$)} thus confirming the absolute stereochemistry as 1*S*,2*S*. By analogy, the absolute stereochemistry of all compounds **2** was assumed. The Pictet–Spengler cyclization of **7** followed by demethylation to afford (−)-dihydrexiridine **8** has already been reported.[4c]

In summary, we have developed an efficient bis-oxazoline-Cu-catalyzed one-pot protocol for the asymmetric synthesis of *trans*-2-amino-1-aryltetralins with



Scheme 3. Plausible mechanism for the Friedel–Crafts cyclization of *cis*-aziridines.



Scheme 4. Asymmetric synthesis of (−)-dihydrexiridine.

high diastereo- (>99:1) and enantioselectivity (up to 92%) from a mixture *E/Z*-2-arylethylstyrenes *via* intramolecular Friedel–Crafts alkylation of *in situ* generated aziridines. An application of the present methodology in a formal synthesis of (−)-dihydrexiridine **8** has been described.

Experimental Section

General Procedure for One-Pot Enantioselective Synthesis of *N*-Protected-2-amino-1-aryltetralins (2a)

A 10-mL two-necked, round-bottom flask was charged with bis-oxazoline ligand **5d** (0.01 g, 0.03 mmol, 0.12 equiv.) and $Cu(OTf)_2$ (0.009 g, 0.025 mmol, 0.1 equiv.). Anhydrous dichloromethane (1 mL) was injected and the resulting mixture was stirred for 30 min. To this solution, PhINNs (0.1 g, 0.24 mmol, 1.0 equiv.), substrate **4a** (0.29 g, 1.23 mmol, 5.0 equiv.) and 0.2 g of powdered molecular sieves (4 Å) were added and the reaction mixture was allowed to stir at 25 °C under an argon atmosphere. As soon as all the nitrenoid reagent had dissolved in the reaction medium, an additional amount of $Cu(OTf)_2$ (0.005 g, 0.013 mmol) was added. On completion, the reaction was quenched by diluting the mixture with ethyl acetate (10 mL) and filtering through a short plug of silica gel. The silica gel was washed with additional 10 mL of ethyl acetate. The filtrate was concentrated by rotary evaporation under reduced pressure. The crude mass was subjected to purification by flash column chromatography using EtOAc/petroleum ether (60–80 °C) as an eluent, which provided aminotetralin **2a**; yield: 0.09 g (85%).

***N*-[1-(4-Methoxyphenyl)-1,2,3,4-tetrahydronaphthalen-2-yl]-4-nitrobenzenesulfonamide (2a):** White solid; mp 120–122 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.13 (d, J = 8.8 Hz, 2H), 7.67 (d, J = 8.8 Hz, 2H), 7.13 (m, 2H), 7.00 (m, 1H), 6.73 (d, J = 8.4 Hz, 2H), 6.62 (d, J = 7.6 Hz, 1H), 6.58 (d, J = 8.4 Hz, 2H), 4.75 (d, J = 7.2 Hz, 1H), 3.77 (d, J = 8.4 Hz, 1H), 3.73 (s, 3H), 3.65–3.48 (m, 1H), 3.12–2.95 (m, 1H), 2.92 (m, 1H), 2.46–2.35 (m, 1H), 1.90–1.78 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 158.6, 149.5, 145.8, 136.7, 135.3, 134.5, 130.3, 129.8 (2C), 128.5, 127.9 (2C), 126.2, 125.9, 123.9 (2C), 113.8 (2C), 57.7, 55.0, 51.3, 29.4, 22.6; HPLC analysis [Chiralcel AD-H, 10% *i*-PrOH/*n*-hexane, 1.0 mL min^{-1}, 220 nm, t_r (major) 12.93 min, t_r (minor) 15.84 min]; 92% *ee*; $[\alpha]_D^{29}$: −46.47 (c 1.00, $CHCl_3$); HR-MS (EI): m/z = 461.1147, calcd. for $C_{23}H_{22}N_2O_5S$: 461.1147 [M+Na]$^+$.

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