Palladium(0)-Catalyzed Asymmetric Synthesis of 1,2,3,4-Tetrahydro-2-vinylquinoxalines

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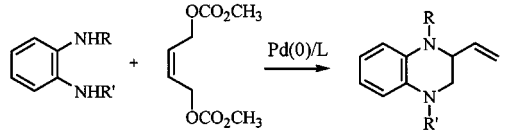
Reaction of (*Z*)-1,2-bis(methoxycarbonyloxy)but-2-ene (**2**) with various *N*,*N*-bis(arylsulfonyl)-*o*-phenylenediamines **1** was catalyzed by a palladium complex associated with chiral ligands to give optically active 1,4-bis(arylsulfonyl)-1,2,3,4-tetrahydro-2-vinylquinoxalines **3** with up to 62% ee. The use of (*S*)-MeOBIPHEP as the chiral ligand and *N*,*N*-bis(*p*-tolylsulfonyl)-*o*-phenylenediamine (**1i**) as the nucleophile led to the highest ee at 25 °C, regardless of the solvent used. The enantioselectivity of the cyclization is strongly affected by the nature of the substituents at the nitrogen atom.

Piperazine derivatives have aroused increasing interest due to the presence of this heterocyclic skeleton in a large number of therapeutically and biologically active compounds.[1] The synthesis of optically active 2-substituted piperazines has been generally carried out by resolution[2] and only one asymmetric synthesis of (*R*)-piperazine-2-carboxylic acid has been reported to date.[3] Recently, it was reported by Saegusa and co-workers[4] that 2-butene-1,4-diyl dicarboxylates reacted with 1,2-diaminoethanes in the presence of a palladium catalyst to give the piperazine skeleton. This methodology was used by Hayashi et al.[5] and Achiwa et al.[6] to prepare optically active piperazine derivatives with an ee of up to 65% using a palladium complex coordinated with various chiral phosphanes.

In previous papers, we showed the effectiveness of the catalytic synthesis of 2-vinylbenzodioxane[7] and 2-vinylbenzomorpholine[8] by palladium-catalyzed cyclization of catechol or 2-aminophenol with (*Z*)-1,4-bis(methoxycarbonyloxy)but-2-ene. We wish to report the extension of this cyclization reaction for the construction of chiral 1,2,3,4-tetrahydro-2-vinylquinoxalines, compounds that are of interest as models for e.g. tetrahydrofolic acid.[9]

We first focused on the synthesis of racemic 1,2,3,4-tetrahydro-2-vinylquinoxaline**s**. The reaction of various substituted 1,2-diaminobenzenes (**1a**−**h**) with (*Z*)-1,4-bis(methoxycarbonyloxy)but-2-ene (**2**) was carried out in the presence of a palladium complex generated in situ by mixing dppb [1,4-bis(diphenylphosphanyl)butane] with $Pd_2(dba)_3$ [tris(dibenzylidenacetone)dipalladium]. The results summarized in Table 1 show that the formation of the 1,2,3,4-tetrahydro-2-vinylquinoxaline structure **3** is not observed using *o*-phenylenediamine (**1a**), *N*,*N*-bis(methylsulfonyl)-*o*-phenylenediamine (**1c**), or *N*,*N*-diacetyl-*o*-phenylenediamine (**1d**) as the nucleophiles (entries 1 and 3−6). In the case of **1a**, the disappearance of the starting material precludes the probable formation of polymers, although for compounds **1c** and **1d**, the nucleophiles were recovered unchanged after 24 h, even when performing the reaction in DMF. The presence of a strong base such as DBU gave no more cyclized product.



1a-n **2** **3a-n**

a: R = R' = H
b: R = R' = 4-$CH_3C_6H_4SO_2$
c: R = R' = CH_3SO_2
d: R = R' = CH_3CO
e: R = R' = CH_3OCO
f: R = R' = $C_6H_4CH_2OCO$
g: R = 4-$CH_3C_6H_4SO_2$, R' = H
h: R = CH_3SO_2, R' = 4-$CH_3C_6H_4SO_2$
i: R = R' = $C_6H_5SO_2$
j: R = R' = 2,4,6-tri$CH_3C_6H_2SO_2$
k: R = R' = 1-naphtylSO_2
l: R = R' = 2-$NO_2C_6H_4SO_2$
m: R = R' = 4-$CH_3OC_6H_4SO_2$
n: R = R' = 4-$NO_2C_6H_4SO_2$

Scheme 1. Preparation of 1,2,3,4-tetrahydro-2-vinylquinoxalines

Table 1. Palladium-catalyzed synthesis of 1,2,3,4-tetrahydro-2-vinylquinoxalines **3**[a]

Entry	Substrate **1**	Solvent	*T* [°C]	Yield of **3** (%)[b]
1	**a**	THF	25	0
2	**b**	THF	25	51
3	**c**	THF	50	0
4	**c**	DMF	50	0
5	**d**	THF	50	0
6	**d**	DMF	50	0
7	**e**	THF	25	70
8	**f**	THF	25	50
9	**g**	THF	25	20
10	**h**	THF	25	58

[a] All entries carried out under N_2 for 12 h in the presence of palladium catalyst prepared in situ by mixing $Pd_2(dba)_3$ (5 mol-% Pd) and ligand dppb ([Pd]/[P] = 1:2). The ratio of **1**/**2** = 1:1.5. − [b] Isolated yield after silica gel column chromatography and not optimized.

The cyclization reaction was successfully performed using the *p*-tolylsulfonyl and carbamate derivatives **1b**, **1e**, and **1f**, to give the corresponding 1,2,3,4-tetrahydro-2-vinylquinoxalines **3b**, **3e**, and **3f**, in 51, 70, and 50% yields, respectively (entries 2, 7, and 8).

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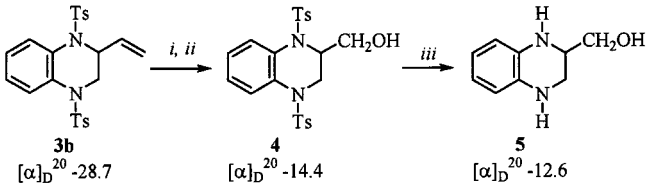
Reaction of *N*-*p*-tosyl-*o*-phenylenediamine (**1g**) with dicarbonate **2** afforded the cyclized product **3g** as a single regioisomer, although in low yield. The structure of **3g** was established by ^{1}H-NMR spectroscopy. According to previous studies,[10] the introduction of a tosyl group on a nitrogen atom produces a greater downfield chemical shift difference for the 2-H signal than for that of 3-H. We observed effectively two signals at δ = 2.74 and 3.14 for the methylenic proton of **3g**, compared to the signals at δ = 3.28 and 4.04 for **3b** (Δδ = 0.54 and 0.90 ppm, respectively), and one signal at δ = 4.90 for **3g** and δ = 5.04 for **3b** for the methine proton 2-H (Δδ = 0.14 ppm).

Reaction of *N*-methylsulfonyl-*N*-*p*-tolylsulfonyl-*o*-phenylenediamine (**1h**) with **2** gave a single product **3h** in 58% yield. The regioselectivity of the cyclization was also determined by ^{1}H-NMR spectroscopy. Compound **3h** exhibited signals at δ = 3.76 and 4.07 for the methylenic proton.

We then turned our attention to the asymmetric synthesis of 1,4-bis(arylsulfonyl)-1,2,3,4-tetrahydro-2-vinylquinoxaline. The reaction of dicarbonate **2** with 1,2-bis(*p*-tolylsulfonyl)-*o*-phenylenediamine (**3b**) was carried out in the presence of a palladium complex generated in situ by mixing a chiral ligand with $Pd_2(dba)_3$ as catalyst. The results summarized in Table 2 reveal that among the ligands investigated the most stereoselective phosphane ligand is (*S*)-MeOBIPHEP, giving **3b** with 52% ee and in 40% yield (entry 9). The use of analogs such as (*S*)-BINAP (entry 7) or (*R*)-BIPHEMP (entry 8) gave **3b** with lower enantioselectivities (28% and 33%, respectively). Palladium complexes of the 1,2-diphosphanes Chiraphos and Norphos (entries 1 and 2), as well as the "Togni ligand" (entry 12) also gave moderate enantioselectivities. Palladium complexes of diphosphanes such as (*S*,*S*)-BDPP (entry 3), (*S*,*S*)-DIOP (entry 4) and (2*S*,4*S*)-BPPM were catalytically more active, but were not stereoselective. Surprisingly the "Trost ligand" gave very low enantioselectivity, starting from $Pd_2(dba)_3$ or $[Pd(\eta\text{-}C_3H_5)Cl]_2$ as the palladium precursor (entries 10 and 11).

The absolute configuration of (−)-**3b** was determined by correlation with the known compound 1,2,3,4-tetrahydro-2-(hydroxymethyl)quinoxaline (**5**).[10] Oxidation of (−)-**3b** (52% ee) by osmium tetroxide/sodium periodate, followed by reduction with sodium tetrahydroborate, gave compound **4** {$[\alpha]_D^{20}$ = −14.4 (*c* = 0.54, $CHCl_3$)}. This bis(sulfonamide) **4** was desulfonylated in concentrated sulfuric acid to give the 1,2,3,4-tetrahydro-2-(hydroxymethyl)quinoxaline (**5**), which turned out to be the (*R*) isomer by measurement of the optical rotation {from (−)-**5**: $[\alpha]_D^{20}$ = −12.6 (*c* = 0.4, $CHCl_3$); ref.[10] for (*R*)-**5**: $[\alpha]_D^{20}$ = −25.8 (*c* = 1, $CHCl_3$)}.

In order to improve the enantioselectivity of the cyclization, we studied the influence of the temperature and the solvent on the ee using (*S*)-MeOBIPHEP as the chiral ligand. The results summarized in Table 3 show that the highest enantioselectivity using THF as the solvent is obtained at 25°C (entry 2). Lowering the reaction temperature decreases both the chemical yield and the enantioselectivity of the cyclization (entry 1), although performing the reaction at 50°C gives a higher yield of cyclized compound but with a lower enantioselectivity (entry 3).



Scheme 2. *i:* OsO_4, $NaIO_4$. − *ii:* $NaBH_4$. − *iii*: H_2SO_4.

Table 2. Palladium-catalyzed asymmetric synthesis of **3b** from **1b** and **2**[a]

Entry	Phosphane	Yield (%)[b]	ee (%) (config.)[c]
1	(*S*,*S*)-Chiraphos[d]	34	28 (*R*)
2	(*R*,*R*)-Norphos[e]	60	19 (*S*)
3	(*S*,*S*)-BDPP[f]	68	1 (*R*)
4	(*S*,*S*)-DIOP[g]	69	0
5	(2*S*,4*S*)-BPPM[h]	87	2 (*R*)
6	NMDPP[i]	8	9 (*R*)
7	(*S*)-BINAP[j]	45	28 (*R*)
8	(*R*)-BIPHEMP[k]	65	33 (*S*)
9	(*S*)-MeOBIPHEP[l]	40	52 (*R*)[m]
10	(*R*,*R*)-Trost ligand[n]	65	7 (*R*)
11[o]	(*R*,*R*)-Trost ligand	30	4 (*R*)
12	Togni ligand[p]	87	30 (*R*)
13	Ephos[q]	10	6 (*R*)

[a] All entries carried out in THF at 25°C under N_2 for 24 h in the presence of palladium catalyst prepared in situ by mixing $Pd_2(dba)_3$ (5 mol-% Pd) and ligand ([Pd]/[P] = 1:2). The ratio of **1b**/**2** = 1:1.5. − [b] Isolated yield after silica gel column chromatography and not optimized. − [c] Determined by HPLC analysis with a chiral stationary phase column (<emphasis type="scaps"Chiralpak ad, *n*-hexane/2-propanol = 80:20). Absolute configuration in parentheses. − [d] (2*S*,3*S*)-2,3-Bis(diphenylphosphanyl)butane. − [e] (2*R*,3*R*)-2,3-Bis(diphenylphosphanyl)bicyclo[2.2.1]hept-5-ene. − [f] (2*S*,4*S*)-2,4-Bis(diphenylphosphanyl)pentane. − [g] (2*R*,3*R*)-2,3-*O*-Isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphanyl)butane. − [h] (2*S*,4*S*)-1-(*tert*-Butoxycarbonyl)-4-(diphenylphosphanyl)-2-[(diphenylphosphanyl)methyl]pyrrolidine. − [i] (1*S*,2*S*,5*R*)-1-(Diphenylphosphanyl)-2-isopropyl-5-methylcyclohexane. − [j] (*S*)-2,2′-Bis-(diphenylphosphanyl)-1,1′-binaphthyl. − [k] (*R*)-2,2′-Bis(diphenylphosphanyl)-6,6′-dimethyl-1,1′-biphenyl. − [l] (*S*)-2,2′-Bis(diphenylphosphanyl)-6,6′-dimethoxy-1,1′-biphenyl. − [m] $[\alpha]_D^{20}$ = −28.7 (*c* = 0.67, $CHCl_3$). − [n] (1*R*,2*R*)-1,2-Bis{[2′-(diphenylphosphanyl)benzoyl]amino}cyclohexane. − [o] $[PdCl(\eta\text{-}C_3H_5)]_2$ was used in place of $Pd_2(dba)_3$. − [p] 1-{(*S*)-1-[(*R*)-2-(Diphenylphosphanyl)-ferrocenyl]ethyl}-3,5-dimethyl-1*H*-pyrazole. − [q] *O*,*N*-Bis(dicyclohexylphosphanyl)ephedrine.

The nature of the solvent seems to have little influence on the selectivity; however, the highest yield was obtained when the reaction was conducted in $CHCl_3$ (entry 5).

We also studied the influence of the substituents at the nitrogen atom on the enantioselectivity and the yield of cyclized product (Table 4). All reactions were performed in THF at 25°C using $Pd_2(dba)_3$ in association with (*S*)-MeOBIPHEP. It is noteworthy that all *p*-substituted arenesulfonamides gave almost the same enantioselectivities in this cyclization reaction: 52%, 55%, and 49% for **3b**, **3m**, and **3n**, respectively (entries 1, 6, and 7). However, the yield of cyclized product **3n** was only 10%, in agreement with previous observations.[8] These values show clearly that the highest yields are obtained using arenesulfonamides pos-

Table 3. Palladium-catalyzed asymmetric synthesis of **3b** using (*S*)-MeOBIPHEP as the ligand; influence of the temperature and the solvent on the enantioselectivity[a]

Entry	Solvent	*T* [°C]	Yield (%)[b]	ee (%) (config.)[c]
1	THF	0	13	31 (*R*)
2	THF	25	40	52 (*R*)
3	THF	50	70	24 (*R*)
4	CH_2Cl_2	25	24	44 (*R*)
5	$CHCl_3$	25	84	49 (*R*)
6	C_6H_6	25	16	42 (*R*)
7	DEE[d]	25	43	49 (*R*)

[a] All entries carried out under N_2 for 24 h in the presence of a palladium catalyst prepared in situ by mixing $Pd_2(dba)_3$ (5 mol-% Pd) and ligand (*S*)-MeOBIPHEP ([Pd]/[P] = 1:2). The ratio of **1b**/**2** = 1:1.5. − [b] Isolated yield after silica gel column chromatography and not optimized. − [c] Determined by HPLC analysis with a chiral stationary phase column (C*HIRALPAK AD*, *n*-hexane/2-propanol, 80:20). Absolute configuration in parentheses. − [d] DEE: 1,2-diethoxyethane.

sessing electron-donating groups, although the ee is independent of the nature of the *para* substituent.

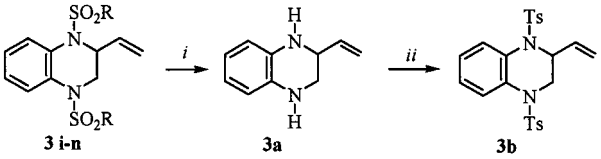
Table 4. Palladium-catalyzed cyclisation of various bis(arylsulfonyl)-*o*-phenylenediamines[a]

Entry	Substrate **1**	Yield in **3** (%)[b]	$[\alpha]_D^{20}$ ($CHCl_3$)	ee (%) (config.)[c]
1	**b**	40	−28.6 (*c* = 0.7)	52 (*R*)
2	**i**	62	−20.1 (*c* = 0.9)	21 (*R*)
3	**j**	50	−4.9 (*c* = 1.1)	10 (*R*)[d]
4	**k**	40	+1.5 (*c* = 0.5)	6 (*R*)
5	**l**	36	−25.9 (*c* = 0.6)	62 (*R*)
6	**m**	50	−57.5 (*c* = 0.4)	55 (*R*)
7	**n**	10[e]	−25.9 (*c* = 0.6)	49 (*R*)
8	**g**	17	−11.5 (*c* = 0.7)	32 (*R*)

[a] All entries carried out in THF at 25°C under N_2 for 24 h in the presence of a palladium catalyst prepared in situ by mixing $Pd_2(dba)_3$ (5 mol-% Pd) and ligand (*S*)-MeOBIPHEP ([Pd]/[P] = 1:2). The ratio of **1b**/**2** = 1:1.5. − [b] Isolated yield after silica gel column chromatography and not optimized. − [c] Determined by HPLC analysis with a chiral stationary phase column (C*HIRALPAK AD*, *n*-hexane/2-propanol = 80:20) after transformation into **3b**. Absolute configuration in parentheses by reference to **3b**. − [d] 12% ee without transformation into **3b**. − [e] Reaction performed at 50°C.

Conversely, the nature of the *ortho* substituent greatly affected the enantioselectivity of the cyclization. It appears from entries 2−4 that a bulky substituent gives a lower enantioselectivity. However, we also noticed that the *o*-nitro group gave the cyclized compound **3l** with an ee of up to 62% (entry 5). So it seems that the enantioselectivity is, in this case, under steric and electronic control.

The ee of 1,2,3,4-tetrahydro-1,4-bis(*p*-tolylsulfonyl)-2-vinylquinoxaline (**3b**) was determined by HPLC analysis using a chiral stationary column Chiralpak AD, and **3j** was also analyzed in this way. The ee of the other 1,4-bis(arylsulfonyl)-1,2,3,4-tetrahydro-2-vinylquinoxalines **3i** and **3k**−**n** were determined after transformation into **3b**. Desulfonylation of **3i** and **3k**−**n** was performed in sulfuric acid at room temperature to give quantitatively 1,2,3,4-tetrahydro-2-vinylquinoxaline (**3a**), which was tosylated to give 1,2,3,4-tetrahydro-1,4-bis(*p*-tolylsulfonyl)-2-vinylquinoxaline (**3b**) using tosyl chloride in pyridine at reflux. The whole sequence proceeded without racemization.



Scheme 3. *i:* Sulfuric acid. − *ii:* TsCl, C_4H_5N, reflux.

In conclusion, the asymmetric construction of 1,2,3,4-tetrahydro-2-vinylquinoxalines is possible through a tandem allylic substitution reaction between 1,4-bis(methoxycarbonyloxy)but-2-ene and various *N*,*N*-bis(arylsulfonyl)-*o*-phenylenediamines catalyzed by a palladium complex associated with an optically active phosphane. Work is now in progress in order to understand the factors controlling the asymmetric induction and to improve the enantioselectivity using a double asymmetric induction.

Experimental Section

General: ^{1}H-NMR (200 MHz) and ^{13}C-NMR (50 MHz) spectra were obtained using a Bruker AM 200 spectrometer. Chemical shifts are reported on the δ scale with reference to tetramethylsilane as an internal standard. − Optical rotations were determined using a Perkin-Elmer 241 polarimeter. − Silica gel column chromatography was carried out using Merck silica gel 60 Gerudan (40−63 μm). − Analytical HPLC was performed using a Shimadzu instrument with a UV detector. − Reactions involving organometallic catalysis were carried out in Schlenk tubes under an inert atmosphere. Tetrahydrofuran was distilled from sodium/benzophenone. The following compounds were prepared according to literature procedures: (*Z*)-1,4-bis(methoxycarbonyloxy)but-2-ene (**2**),[4] *N*,*N*-bis(*p*-tolylsulfonyl)-*o*-phenylenediamine (**1b**),[11] *N*,*N*-bis(methylsulfonyl)-*o*-phenylenediamine (**1c**),[12] *N*,*N*-bis(benzyloxycarbonyl)-*o*-phenylenediamine (**1f**),[13] *N*-(*p*-tolylsulfonyl)-*o*-phenylenediamine (**1g**),[14] *N*,*N*-bis(phenylsulfonyl)-*o*-phenylenediamine (**1i**),[15] *N*,*N*-bis[(2,4,6-trimethylphenyl)sulfonyl]-*o*-phenylenediamine (**1j**),[12] *N*,*N*-bis[(2-nitrophenyl)sulfonyl]-*o*-phenylenediamine (**1l**),[16] and (1*R*,2*R*)-1,2-bis{[2′-(diphenylphosphanyl)benzoyl]amino}cyclohexane.[17] (2*R*,3*R*)-2,3-Bis(diphenylphosphanyl)bicyclo[2.2.1]hept-5-ene (Norphos) was a gift from Prof. Brunner (Regensburg, Germany), (*R*)-6,6′-dimethyl-2,2′-bis(diphenylphosphanyl)-1,1′-biphenyl (BIPHEMP) and (*S*)-6,6′-dimethoxy-2,2′-bis(diphenylphosphanyl)-1,1′-biphenyl (MeOBIPHEP) were gifts from Dr. Schmid (Hofmann La Roche, Basel, Switzerland), 1-{(*S*)-1-[(*R*)-3,5-dimethyl-2-(diphenylphosphanyl)ferrocenyl]ethyl}-1*H*-pyrazole was a gift from Prof. Togni (Zürich, Switzerland) and *O*,*N*-bis(dicyclohexylphosphanyl)ephedrine was a gift from Prof. Mortreux (Lille, France).

***N*,*N*-Bis(methoxycarbonyl)-*o*-phenylenediamine (1e):** To a solution of 1,2-diaminobenzene (2 g, 18.5 mmol) and pyridine (3.2 mL, 40 mmol) in THF (15 mL) was slowly added a solution of methyl chloroformate (3.1 mL, 40 mmol) in 15 mL of THF at 0°C. After being stirred for 12 h, the solution was hydrolyzed with 50 mL of water. The mixture was extracted with CH_2Cl_2 (2 × 30 mL) and the solution dried with Na_2SO_4. Concentration under reduced pressure gave a solid, which was washed with ethanol to give 1.8 g of **1e** (43%); m.p. 153−153.5°C. − ^{1}H NMR ([D$_6$]acetone): δ = 3.70 (s, 6 H, 2 × CH_3), 7.12−7.17 (m, 2 H, aromatic H), 7.55−7.59 (m, 2

H, aromatic H), 8.20 (br. s, 2 H, NH). – ^{13}C NMR ([D$_6$]acetone): δ = 52.92 (CH_3), 126.06, 126.47, and 131.80 (aromatic C), 156.21 (CO). – $C_{10}H_{12}N_2O_4$ (224.21): calcd. C 53.57, H 5.39; found C 53.41, H 5.43.

***N*-Methylsulfonyl-*N*-(*p*-tolylsulfonyl)-*o*-phenylenediamine (1h):** To a solution of *N*-(*p*-tolylsulfonyl)-*o*-phenylenediamine (**1g**) (1 g, 3.8 mmol) in 2.5 mL of pyridine was added mesyl chloride (0.3 mL, 3.8 mmol) at 0°C. After being stirred for 12 h, the solution was hydrolyzed with water (10 mL) and extracted with CH_2Cl_2 (2 × 20 mL). Evaporation of the solvent gave a residue, which was recrystallized from ethanol to give 805 mg of **1h** (62%); m.p. 176–178°C. – ^{1}H NMR ([D$_6$]acetone): δ = 2.40 (s, 3 H, CH_3), 2.99 (s, 3 H, CH_3), 7.05–7.15 (m, 2 H, aromatic H), 7.25 (dd, *J* = 7.3, 1.8 Hz, 1 H, aromatic H), 7.35 (d, *J* = 8.1 Hz, 2 H, aromatic H), 7.51 (dd, *J* = 8.1, 1.1 Hz, 1 H, aromatic H), 7.64 (d, *J* = 8.5 Hz, 2 H, aromatic H), 8.20 (br. s, 2 H, NH). – ^{13}C NMR ([D$_6$]acetone): δ = 21.39 (CH_3), 39.23 (CH_3), 125.22, 126.88, 127.21, 128.21, 128.28, 130.43, 131.09, 133.26, and 144.92 (aromatic C). – $C_{14}H_{16}N_2O_4S_2$ (340.41): calcd. C 49.40, H 4.74; found C 49.33, H 4.72.

General Procedure for the Preparation of *N*,*N*-Bis(arylsulfonyl)-*o*-phenylenediamine: To a mixture of *o*-phenylenediamine (540 mg, 5 mmol) and pyridine (800 μL, 10 mmol) in CH_2Cl_2 (10 mL) was slowly added at 0°C arenesulfonyl chloride (10 mmol). After the disappearance of the diamine, as shown by TLC, water (10 mL) was added. The precipitate was filtered off and recrystallized from ethanol.

***N*,*N*-Bis(1-naphthylsulfonyl)-*o*-phenylenediamine (1k):** Solid; 74% yield; m.p. 238–240°C. – ^{1}H NMR ([D$_6$]acetone): δ = 6.75–6.86 (m, 4 H, aromatic H), 7.53 (dd, *J* = 8.2, 7.5 Hz, 2 H, aromatic H), 7.64–7.77 (m, 4 H, aromatic H), 8.06–8.11 (m, 4 H, aromatic H), 8.21 (d, *J* = 8.2 Hz, 2 H, aromatic H), 8.71–8.76 (m, 2 H, aromatic H), 8.81 (br. s, 2 H, NH). – ^{13}C NMR ([D$_6$]acetone): δ = 126.12, 125.51, 125.95, 127.43, 127.93, 129.03, 129.21, 130.03, 131.01, 131.75, 135.00, 135.21, 135.65 (aromatic C).

***N*,*N*-Bis[(4-methoxyphenyl)sulfonyl]-*o*-phenylenediamine (1m):** Solid; 60% yield; m.p. 135–137°C. – ^{1}H NMR ([D$_6$]acetone): δ = 3.86 (s, 6 H, CH_3), 6.99–7.06 (m, 8 H, aromatic H), 7.60–7.66 (m, 4 H, aromatic H), 8.38 (br. s, 2 H, NH). – ^{13}C NMR ([D$_6$]acetone): δ = 56.14 (CH_3), 115.00, 126.22, 122.52, 130.44, 130.77, 131.31, 164.24 (aromatic C). – $C_{20}H_{20}N_2O_6S_2$ (448.51): calcd. C 53.56, H 4.49; found C 53.00, H 4.45.

1,2-Bis[(4-nitrophenyl)sulfonylamino]benzene (1n): Solid; 65% yield; m.p. 234–236°C. – ^{1}H NMR ([D$_6$]acetone): δ = 7.06–7.20 (m, 4 H, aromatic H), 7.97 (m, 4 H, aromatic H), 8.38 (m, 4 H, aromatic H), 8.72 (br. s, 2 H, NH). – ^{13}C NMR ([D$_6$]acetone): δ = 125.27, 127.27, 128.74, 129.78, 131.28, 145.27 (aromatic C). – $C_{18}H_{14}N_4O_8S_2$ (478.45): calcd. C 45.19, H 2.95; found C 44.87, H 3.08.

General Procedure for the Cyclization Reaction: A solution of tris(dibenzylideneacetone)dipalladium (6.5 mg, 0.0063 mmol) and the ligand (0.025 mmol for dppb and 0.0125 mmol for a chiral ligand) in 3 mL of THF was stirred at room temperature for 30 min. To the solution were added the amino compound **1** (0.25 mmol) and the dicarbonate **2** (71.4 mg, 0.35 mmol), dissolved in 3 mL of THF. The mixture was stirred at the desired temperature for 24 h. The solution was concentrated under reduced pressure and the residue was chromatographed on silica gel to give the cyclized product.

1,2,3,4-Tetrahydro-1,4-bis(*p*-tolylsulfonyl)-2-vinylquinoxaline (3b): Yellow solid; 51% yield; R_f = 0.7 (eluent: petroleum ether/diethyl ether, 1:2.5); m.p. 86–88°C. – ^{1}H NMR ($CDCl_3$): δ = 2.40 (s, 6 H, CH_3), 3.28 (dd, *J* = 12.8, 4.4 Hz, 1 H, 3-H_{ax}), 4.04 (dd, *J* = 12.8, 4.0 Hz, 1 H, 3-H_{eq}), 5.04–5.05 (m, 1 H, 2-H), 5.13 (d, *J* = 10.5 Hz, 1 H, CH_2), 5.28 (d, *J* = 17.2 Hz, 1 H, CH_2), 5.62 (ddd, *J* = 17.2, 10.5, 4.8 Hz, 1 H, CH=), 7.21–7.78 (m, 12 H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 21.57 (CH_3), 21.61 (CH_3), 47.92 (CH_2N), 55.76 (CHN), 118.78 (=CH_2), 133.40 (CH=), 119.51, 123.74, 125.66, 126.09, 126.01, 127.05, 127.28, 129.76, 129.86, 130.66, 135.68, 136.42, 144.17, 144.21 (aromatic C). – $C_{24}H_{24}N_2O_4S_2$ (468.59): calcd. C 61.54, H 5.12; found C 61.32, H 5.23.

1,2,3,4-Tetrahydro-1,4-bis(methoxycarbonyl)-2-vinylquinoxaline (3e): Yellow oil; 70% yield; R_f = 0.46 (eluent: petroleum ether/ethyl acetate, 2:1). – ^{1}H NMR ($CDCl_3$): δ = 3.79 (s, 6 H, OCH_3), 3.89 (d, *J* = 5.2 Hz, 2 H, 3-H), 5.12 (m, 1 H, 2-H), 5.18 (d, *J* = 17.2 Hz, 1 H, =CH_2), 5.20 (d, *J* = 10.1 Hz, 1 H, =CH_2), 5.72 (ddd, *J* = 17.2, 10.1, 5.6 Hz, 1 H, CH=), 7.03–7.14 (m, 2 H, aromatic H), 7.60 (m, 1 H, aromatic H), 7.79–7.85 (m, 1 H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 48.15 (CH_2N), 53.35 (CH_3), 53.39 (CH_3), 56.86 (CHN), 117.39 (=CH_2), 123.73, 124.04, 124.17, 124.63, 130.19, 131.17 (aromatic C), 134.75 (CH=), 154.76 (CO), 154.78 (CO). – $C_{14}H_{16}N_2O_4$ (276.29): calcd. C 60.86, H 5.84; found C 60.92, H 6.02.

1,4-Bis(benzyloxycarbonyl)-1,2,3,4-tetrahydro-2-vinylquinoxaline (3f): White solid; 55% yield; R_f = 0.57 (eluent: dichloromethane/petroleum ether/diethyl ether, 9:9:1); m.p. 86–86.5°C. – ^{1}H NMR ($CDCl_3$): δ = 3.82 (dd, *J* = 13.2, 5.0 Hz, 1 H, 3-H_{ax}), 3.98 (dd, *J* = 13.2, 4.6 Hz, 1 H, 3-H_{eq}), 5.06–5.29 (m, 7 H, 2-H, CH_2C$_6$H$_5$, =CH_2), 5.68 (ddd, *J* = 17.3, 10.4, 4.9 Hz, 1 H, CH=), 7.01–7.09 (m, 2 H, aromatic H), 7.36 (br. s, 10 H, aromatic H), 7.66 (br. s, 1 H, aromatic H), 7.88–7.94 (br. s, 1 H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 47.83 (CH_2N), 56.67 (CHN), 67.93 (CH_2Bn), 68.00 (CH_2Bn), 117.37 (=CH_2), 134.51 (CH=), 123.82, 124.54, 128.33, 128.14, 128.22, 128.30, 128.33, 128.60, 128.62, 130.58, 130.70, 135.92, 136.02 (aromatic H), 153.86 (CO), 153.97 (CO). – $C_{26}H_{24}N_2O_4$ (428.49): calcd. C 72.88, H 5.65; found C 72.89, H 5.86.

1,2,3,4-Tetrahydro-1-(*p*-tolylsulfonyl)-2-vinylquinoxaline (3g): Yellow oil; 20% yield; R_f = 0.45 (eluent: petroleum ether/diethyl ether, 1:2.5). – ^{1}H NMR ($CDCl_3$): δ = 2.38 (s, 3 H, CH_3), 2.74 (dd, *J* = 11.8, 3.93 Hz, 1 H, 3-H_{ax}), 3.14 (dd, *J* = 11.8, 1.64 Hz, 1 H, 3-H_{eq}), 3.80 (s, 1 H, NH), 4.88–4.93 (m, 1 H, 2-H), 5.14 (ddd, *J* = 10.4, 1.6, 1.2 Hz, 1 H, =CH_2), 5.30 (ddd, *J* = 17.2, 1.6, 1.3 Hz, 1 H, =CH_2), 5.68 (ddd, *J* = 17.2, 10.4, 4.5 Hz, 1 H, CH=), 6.46 (dd, *J* = 8.0, 1.4 Hz, 1 H, aromatic H), 6.72 (ddd, *J* = 8.5, 8.0, 1.3 Hz, 1 H, aromatic H), 6.98 (ddd, *J* = 8.5, 8.2, 1.4 Hz, 1 H, aromatic H), 7.20 (d, *J* = 8.3 Hz, 2 H, aromatic H), 7.47 (d, *J* = 8.3 Hz, 2 H, aromatic H), 7.74 (dd, *J* = 8.2, 1.3 Hz, 1 H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 21.66 (CH_3), 42.2 (CH_2N), 53.31 (CHN), 117.77 (=CH_2), 134.76 (CH=), 114.76, 117.60, 120.36, 126.34, 126.80, 127.44, 129.75, 136.40, 137.10, 143.75 (aromatic C). – $C_{17}H_{18}N_2O_2S$ (314.40): calcd. C 64.94, H 5.77; found C 64.78, H 5.79.

1,2,3,4-Tetrahydro-1-(methylsulfonyl)-4-(*p*-tolylsulfonyl)-2-vinylquinoxaline (3h): Yellow oil; 58% yield; R_f = 0.54 (eluent: petroleum ether/diethyl ether, 1:2.5). – ^{1}H NMR ($CDCl_3$): δ = 2.42 (s, 3 H, CH_3), 2.68 (s, 3 H, CH_3), 3.76 (dd, *J* = 13.4, 6.9 Hz, 1 H, 3-H_{ax}), 4.07 (dd, *J* = 13.4, 5.9 Hz, 1 H, 3-H_{eq}), 4.98–5.02 (m, 1 H, 2-H), 5.22 (d, *J* = 10.3 Hz, 1 H, aromatic H), 5.30 (d, *J* = 17.0 Hz, 1 H, aromatic H), 5.72 (ddd, *J* = 17.0, 10.3, 5.8 Hz, 1 H, aromatic H), 7.22–7.79 (m, 8 H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 21.53 (CH_3), 38.92 (CH_3), 50.64 (CH_2N), 58.6 (CHN), 118.78 (=CH_2), 134.08 (CH=), 122.93, 124.57, 125.55, 125.76, 127.19, 129.62, 130.07, 130.54, 131.41, 144.53 (aromatic C).

− $C_{18}H_{20}N_2O_4S_2$ (392.49): calcd. C 55.08, H 5.14; found C 55.14, H 5.28.

1,2,3,4-Tetrahydro-1,4-bis(phenylsulfonyl)-2-vinylquinoxaline (3i): Yellow oil; 62% yield; R_f = 0.54 (eluent: petroleum ether/ethyl acetate, 1:5/1). − ^{1}H NMR ($CDCl_3$): δ = 3.35 (dd, *J* = 12.9, 4.7 Hz, 1 H, 3-H_{ax}), 3.99 (dd, *J* = 12.9, 4.4 Hz, 1 H, 3-H_{eq}), 5.03−5.1 (m, 1 H, 2-H), 5.15 (d, *J* = 10.4 Hz, 1 H, aromatic H), 5.30 (d, *J* = 17.2 Hz, 1 H, aromatic H), 5.64 (ddd, *J* = 17.2, 10.4, 4.9 Hz, 1 H, aromatic H), 7.02−7.11 (m, 2 H, aromatic H), 7.38−7.78 (m, 12 H, aromatic H). − ^{13}C NMR ($CDCl_3$): δ = 48.17 (CH_2N), 56.14 (CHN), 118.88 (=CH_2), 133.26 (CH=), 119.73, 124.03, 125.89, 126.21, 126.24, 126.88, 127.18, 129.28, 130.85, 133.30, 138.48, 139.26 (aromatic C). − $C_{22}H_{20}N_2O_4S_2$ (440.53): calcd. C 59.98, H 4.57; found C 59.94, H 4.65.

1,2,3,4-Tetrahydro-1,4-bis[(2,4,6-trimethylphenyl)sulfonyl]-2-vinylquinoxaline (3j): Yellow oil; 49% yield; R_f = 0.71 (eluent: petroleum ether/ethyl acetate, 3:1). − ^{1}H NMR ($CDCl_3$): δ = 2.17 (s, 3 H, CH_3), 2.33 (s, 3 H, CH_3), 2.34 (s, 3 H, CH_3), 2.56 (s, 6 H, CH_3), 2.58 (s, 3 H, CH_3), 3.57 (dd, *J* = 13.0, 3.2 Hz, 1 H, 3-H_{ax}), 4.61 (dd, *J* = 13.0, 2.3 Hz, 1 H, 3-H_{eq}), 4.93 (br. s, 1 H, 2-H), 5.17−5.24 (m, 2 H, =CH_2), 5.69 (ddd, *J* = 17.3, 10.3, 4.9 Hz, 1 H, CH=), 6.87−7.04 (m, 6 H, aromatic H), 7.3−7.44 (m, 2 H, aromatic H). − ^{13}C NMR ($CDCl_3$): δ = 22.81 (3 × CH_3), 22.84 (3 × CH_3), 47.13 (CH_2N), 52.44 (CHN), 119.16 (=CH_2), 132.66 (CH=), 118.87, 122.82, 125.22, 125.34, 125.49, 131.07, 132.33, 132.46, 133.00, 136.01, 139.17, 140.45, 143.02, 143.52 (aromatic C). − $C_{28}H_{28}N_2O_4S_2$ (520.66): calcd. C 64.59, H 5.42; found C 64.47, H 5.25.

1,2,3,4-Tetrahydro-1,4-bis(1-naphthylsulfonyl)-2-vinylquinoxaline (3k): Yellow oil; 40% yield; R_f = 0.53 (eluent: petroleum ether/diethyl ether, 1:2.5). − ^{1}H NMR ($CDCl_3$): δ = 2.9 (dd, *J* = 12.9, 3.6 Hz, 1 H, 3-H_{ax}), 4.29 (dd, *J* = 12.9, 3.0 Hz, 1 H, 3-H_{eq}), 5.07 (br. s, 1 H, 2-H), 5.19 (d, *J* = 10.4 Hz, 1 H, =CH_2), 5.35 (d, *J* = 17.2 Hz, 1 H, =CH_2), 5.70 (ddd, *J* = 17.2, 10.4, 4.4 Hz, 1 H, CH=), 6.99−8.44 (m, 18 H, aromatic H). − ^{13}C NMR ($CDCl_3$): δ = 46.88 (CH_2N), 54.13 (CHN), 119.49 (=CH_2), 135.00 (CH=), 120.18, 123.46, 124.03, 124.20, 124.54, 124.73, 125.10, 125.54, 125.76, 126.24, 126.72, 127.03, 127.19, 128.06, 128.14, 128.39, 128.86, 128.88, 130.25, 130.82, 132.55, 133.96, 134.2, 134.31, 134.41, and 136.13 (aromatic C). − $C_{30}H_{24}N_2O_4S_2$ (540.65): calcd. C 66.65, H 4.47; found C 66.02, H 4.82.

1,2,3,4-Tetrahydro-1,4-bis[(2-nitrophenyl)sulfonyl]-2-vinylquinoxaline (3l): Brown solid; 36% yield; R_f = 0.55 (eluent: dichloromethane/petroleum ether, 7:1). − ^{1}H NMR ($CDCl_3$): δ = 3.88 (dd, *J* = 13.5, 5.2 Hz, 1 H, 3-H_{ax}), 4.06 (dd, *J* = 13.5, 4.9 Hz, 1 H, 3-H_{eq}), 5.23−5.28 (m, 1 H, 2-H), 5.25 (d, *J* = 10.3 Hz, 1 H, =CH_2), 5.38 (d, *J* = 17.2 Hz, 1 H, =CH_2), 5.77 (ddd, *J* = 17.2, 10.3, 5.2 Hz, 1 H, CH=), 7.05−7.25 (m, 4 H, aromatic H), 7.56−7.83 (m, 8 H, aromatic H). − ^{13}C NMR ($CDCl_3$): δ = 50.02 (CH_2N), 57.64 (CHN), 119.58 (=CH_2), 133.15 (CH=), 121.67, 124.63, 124.97, 125.57, 125.65, 126.25, 127.86, 130.50, 131.14, 131.33, 131.88, 132.12, 132.62, 133.15, 134.11, 134.33, 134.49, 147.91 (aromatic C). − $C_{22}H_{18}N_4O_8S_2$ (530.53): calcd. C 49.81, H 3.42; found C 50.63, H 3.97.

1,2,3,4-Tetrahydro-1,4-bis[(4-methoxyphenyl)sulfonyl]-2-vinylquinoxaline (3m): Yellow oil; 50% yield; R_f = 0.34 (eluent: petroleum ether/diethyl ether, 1:2.5). − ^{1}H NMR ($CDCl_3$): δ = 3.29 (dd, *J* = 12.8, 4.5 Hz, 1 H, 3-H_{ax}), 3.86 (s, 3 H, OCH_3), 3.87 (s, 3 H, OCH_3), 4.06 (dd, *J* = 12.8, 4.0 Hz, 1 H, 3-H_{eq}), 5.04−5.06 (m, 1 H, 2-H), 5.15 (ddd, *J* = 10.3, 1.6, 0.9 Hz, 1 H, =CH_2), 5.3 (ddd, *J* = 17.1, 1.4, 0.9 Hz, 1 H, =CH_2), 5.64 (ddd, *J* = 17.1, 10.3, 4.8 Hz, 1 H, CH=), 6.84−6.93 (m, 4 H, aromatic H), 7.02−7.1 (m, 2 H, aromatic H), 7.45−7.63 (m, 5 H, aromatic H), 7.75−7.80 (m, 1 H, aromatic H). − ^{13}C NMR ($CDCl_3$): δ = 47.85 (CH_2N), 55.63 (CHN), 55.73 (2 × OCH_3), 118.81 (=CH_2), 133.6 (CH=), 114.40, 114.53, 119.44, 123.70, 125.84, 125.97, 126.41, 129.35, 129.46, 130.24, 130.66, 130.87, 163.4 (aromatic C). − $C_{24}H_{24}N_2O_6S_2$ (500.59): calcd. C 57.58, H 4.83; found C 57.54, H, 4.74.

1,2,3,4-Tetrahydro-1,4-bis[(4-nitrophenyl)sulfonyl]-2-vinylquinoxaline (3n): Brown oil; 10% yield; R_f = 0.6 (eluent: petroleum ether/dichloromethane, 1:7). − ^{1}H NMR ($CDCl_3$): δ = 3.59 (dd, *J* = 13.3, 7.3 Hz, 1 H, 3-H_{ax}), 3.93 (ddd, *J* = 13.3, 6.3, 1.5 Hz, 1 H, 3-H_{eq}), 5.07−5.13 (m, 1 H, 2-H), 5.25 (d, *J* = 10.4 Hz, 1 H, =CH_2), 5.37 (d, *J* = 17.0 Hz, 1 H, =CH_2), 5.69 (ddd, *J* = 17.0, 10.4, 5.6 Hz, 1 H, CH=), 7.14−7.37 (m, 4 H, aromatic H), 7.77 (dd, *J* = 8.8, 1.5 Hz, 2 H, aromatic H), 7.91 (dd, *J* = 8.8, 1.5 Hz, 2 H, aromatic H), 8.31 (d, *J* = 8.8, 1.5 Hz, 4 H, aromatic H). − ^{13}C NMR ($CDCl_3$): δ = 50.85 (CH_2N), 59.94 (CHN), 119.50 (=CH_2), 133.47 (CH=), 122.04, 124.58, 124.76, 126.23, 126.55, 126.92, 128.19, 128.59, 129.13, 132.59, 143.86, 145.05, 150.52 (aromatic C).

Determination of the Configuration of Compound 3: A solution of **3b** (65 mg, 0.14 mmol), exhibiting $[\alpha]_D^{20}$ = −28.7 (*c* = 0.54, $CHCl_3$), in 1.4 mL of acetone/water (3:1) was treated with a solution of osmium tetroxide (2.5% in ethanol) at 0°C, and then with sodium periodate (91 mg, 0.42 mmol). The mixture was stirred for 4 h at room temperature, then diluted with 9 mL of water, and extracted with 25 mL of ethyl acetate. Evaporation of the solvent under reduced pressure gave 71.5 mg of 2-formyl-1,2,3,4-tetrahydro-1,4-bis(*p*-tolylsulfonyl)quinoxaline. A solution of this compound in 2 mL of ethanol was stirred with $NaBH_4$ (22 mg, 2.2 equiv./aldehyde group) at 0°C for 30 min. Evaporation of the solvent gave a residue that was chromatographed on silica gel to give 40.6 mg of 1,2,3,4-tetrahydro-2-(hydroxymethyl)-1,4-bis(*p*-tolylsulfonyl)quinoxaline (**4**) as an oil (62%) having $[\alpha]_D^{20}$ = −14.4 (*c* = 0.53, $CHCl_3$); R_f = 0.44 (eluent: petroleum ether/diethyl ether, 1:4.5). − ^{1}H NMR ($CDCl_3$): δ = 2.34 (s, 6 H, CH_3), 3.19 (dd, *J* = 13.2, 4.8 Hz, 1 H, 3-H_{eq}), 3.48−3.55 (m, 2 H, CH_2OH), 3.86 (dd, *J* = 13.2, 5.2 Hz, 1 H, 3-H_{ax}), 4.45−4.49 (m, 1 H, 2-H), 6.96−7.04 (m, 2 H, aromatic H), 7.12−7.22 (m, 4 H, aromatic H), 7.30−7.37 (m, 3 H, aromatic H), 7.56 (d, *J* = 8.3 Hz, 2 H, aromatic H), 7.72−7.77 (m, 1 H, aromatic H). − ^{13}C NMR ($CDCl_3$): δ = 20.57 (CH_3), 20.62 (CH_3), 44.06 (CH_2N), 55.66 (CHN), 60.82 (CH_2OH), 118.75, 123.15, 124.90, 125.54, 125.62, 125.84, 126.32, 128.93, 130.16, 133.71, 135.79, 143.28, 143.51 (aromatic C). − These data are in agreement with those reported in the literature.[10] A solution of compound **4** (60 mg, 0.13 mmol) in 636 μL of sulfuric acid was stirred for 2 h at room temperature. Water (1 mL) and a solution of sodium hydroxide was added until pH = 10. The aqueous mixture was extracted with CH_2Cl_2 (3 × 10 mL). Evaporation of the solvent gave 9.5 mg of 1,2,3,4-tetrahydro-2-(hydroxymethyl)quinoxaline (**5**) as an oil (45%) having $[\alpha]_D^{20}$ = −12.6 (*c* = 0.4, $CHCl_3$); R_f = 0.39 (eluent: petroleum ether/ethyl acetate, 1:3). − ^{1}H NMR ($CDCl_3$): δ = 2.53−3.11 (br. s, 3 H, OH, NH), 3.24−3.37 (m, 2 H, CH_2OH), 3.60−3.85 (m, 3 H, CH, CH_2), 6.49−6.64 (m, 4 H, aromatic H). − ^{13}C NMR ($CDCl_3$): δ = 41.71 (CH_2N), 50.62 (CHN), 63.82 (CH_2OH), 113.74, 113.97, 117.83, 128.94, 131.86, 132.19 (aromatic C). − These data are in agreement with those reported in the literature.[10]

Determination of the Enantiomeric Excess of 1,4-Bis(arylsulfonyl)-1,2,3,4-tetrahydro-2-vinylquinoxalines: The enantiomeric excess of 1,2,3,4-tetrahydro-1,4-bis(*p*-tosylsulfonyl)-2-vinylquinoxaline (**3b**) was determined by HPLC analysis with a chiral stationary phase column (Chiralpak AD, eluent: *n*-hexane/2-propanol, 80:20), with the enantiomer (*R*) being eluted first. All the other arylsulfonyl

derivatives were transformed into compound **3b**. A solution of compound **3** (0.15 mmol) in 0.74 mL of sulfuric acid was stirred at room temperature for 24 h. Then 1 mL of water was added, followed by a solution of 2 N sodium hydroxide until pH = 10. The mixture was extracted with CH_2Cl_2 (2 × 5 mL). Evaporation of the solvent gave compound **3a** as an oil. A mixture containing compound **4** (40 mg, 0.25 mmol), tosyl chloride (239 mg, 1.25 mmol), and pyridine (121 μL, 1.5 mmol) was refluxed for 3 h. After being cooled to room temperature, the reaction mixture was hydrolyzed with water (1 mL), and extracted with CH_2Cl_2. Evaporation of the solvent gave compound **3b**.

1,2,3,4-Tetrahydro-2-vinylquinoxaline (3a): Brown oil; 100% yield; R_f = 0.62 (eluent: petroleum ether/diethyl ether, 1:2.5). – ^{1}H NMR ($CDCl_3$): δ = 3.19 (dd, *J* = 10.9, 7.4 Hz, 1 H, 3-H_{ax}), 3.41 (dd, *J* = 10.9, 3.2 Hz, 1 H, 3-H_{eq}), 3.37–3.92 (m, 2 H, NH), 5.92–4.0 (m, 1 H, 2-H), 5.21 (ddd, *J* = 10.2, 1.2, 1.1 Hz, 1 H, =CH_2), 5.34 (ddd, *J* = 17.1, 1.3, 1.2 Hz, 1 H, =CH_2), 5.91 (ddd, *J* = 17.1, 10.2, 6.7 Hz, 1 H, CH=), 6.51–6.75 (m, 4 H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 45.47 (CH_2N), 51.99 (CHN), 115.39 (=CH_2), 113.49, 113.62, 117.71, 117.93, 131.92, 132.14 (aromatic C), 137.03 (CH=).

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