Asymmetric Organocatalytic Tandem Cyclization/Transfer Hydrogenation: A Synthetic Strategy for Enantioenriched Nitrogen Heterocycles

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Abstract: An asymmetric organocatalytic tandem reaction comprising cyclization/transfer hydrogenation has been established in a compatible and synergistic way, leading to the step-economical synthesis of enantioenriched tetrahydroquinoxalines and dihydroquinoxalinones from readily accessible materials in excellent enantioselectivity of up to >99% *ee.* This protocol of a one-operation tandem reaction combines the merits of both tandem reactions and asymmetric organocatalysis, providing an efficient strategy for concisely and enantioselectively synthesizing nitrogen heterocycles with biological relevance.

Keywords: asymmetric catalysis; enantioselectivity; organic catalysis; tandem reaction; transfer hydrogenation

Introduction

The concept of step-economy has been playing an increasingly important role in chemical and pharmaceutical synthesis.^[1] In recent years, asymmetric catalytic cascade or tandem reactions have substantially benefited from this concept and turned out to be robust step-economical tools for an easy access to complex chiral scaffolds using simple materials, featured by avoiding time-consuming isolation and purification procedures, which are inherently required in stepwise synthesis.^[2] More significantly, the catalytic asymmetric tandem reaction has been proven to enable unprecedented step-economical transformations, which can hardly be achieved by any single reaction step or paralleled by multi-step reactions due to the effect of compatibility and synergy generated in the tandem reaction. $^{[2e]}$

Chiral nitrogen heterocycles constitute the core structures of many natural alkaloids and artificial pharmaceuticals. In particular, optically pure 1,2,3,4-tetrahydroquinoxalines have exhibited great potential for medicinal applications.^[3] As indicated in Figure 1, compound **I** is utilized as a cholesterol ester transfer protein inhibitor,^[3a] and compound **II** is found to be a potent p53/Hdm2 antagonist.^[3b] Besides, compound **III** possesses the important activities of anti-atherosclerosis and anti-obesity.^[3c] Therefore, the synthesis of enantioenriched tetrahydroquinoxalines has attracted intensive attention in organic and medicinal research areas.

The known enantioselective approaches to tetrahydroquinoxaline motifs are represented by the catalytic asymmetric hydrogenation of quinoxalines.^[4] A number of metal-catalyzed [Eq. (1)]^[4a-j] and one organo-catalyzed asymmetric hydrogenation reactions [Eq. (2)]^[4k] have been established by using either hydrogen gas or a Hantzsch ester (HEH) as hydride



Figure 1. Some bioactive chiral tetrahydroquinoxalines.

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source. Although this strategy is elegant, it mostly requires pre-formed and purified quinoxalines as starting materials, and thereby suffers from low step-economy. The development of more step-economical tandem reactions for the asymmetric synthesis of optically pure tetrahydroquinoxalines from readily available starting materials continues to be desirable and challenging.

It has long been recognized that the condensation of 1,2-phenylenediamine with phenylglyoxal would give quinoxalines.^[5] But the possibility of integrating this process with the asymmetric organocatalytic hydrogenation of quinoxalines into a tandem reaction is still unknown, since a successful tandem reaction relies on the compatibility and more importantly, on the synergy of two or more reaction processes performed under the same reaction conditions. Inspired by this anticipation and our interests in enantioselective tandem reactions,^[6] we proposed a phosphoric acid-catalyzed^[7] cascade condensation/enantioselective transfer hydrogenation, enabling the direct transformation of commercially available starting materials into optically pure 1,2,3,4-tetrahydroquinoxalines (Scheme 1). Besides, this strategy may be employed to synthesize other chiral heterocycles.

In this work, we present an organocatalytic asymmetric tandem reaction comprising cyclization/transfer hydrogenation in a one-pot operation by using a bulky chiral phosphoric acid as the catalyst and a Hantzsch ester as the hydride source, which provides a step-economical synthetic strategy for enantioenriched heterocycles such as tetrahydroquinoxalines and dihydroquinoxalinones in excellent enantio-selectivity of up to >99% *ee*.

tandem cyclization\asymmetric transfer hydrogenation:



Scheme 1. Proposed strategy for organocatalytic step-economical synthesis of chiral tetrahydroquinoxalines.

Results and Discussion

The attempt to validate our proposal commenced with the reaction of 1,2-phenylenediamine **1a** with phenylglyoxal **2a** using Hantzsch ester **3a** as the hydride source, which was performed in the presence of 5 mol% of chiral phosphoric acids **5** in chloroform at 35 °C (Table 1). Unfortunately, the initial experiment only gave a tiny amount of the desired product **4aa** (entry 1). This implied that the way to fuse the two steps of cyclization and transfer hydrogenation in a compatible and synergistic mode was the key point to realize this tandem reaction. After many tries, it was found that the addition of 3 Å MS could enable the same reaction to afford the product **4aa** in a nearly quantitative yield and excellent enantioselectivity (99% and 93% *ee*, respectively, entry 2). The





Entry	5	Solvent	MS	Yield [%] ^[b]	ee [%] ^[c]
1 ^[d]	5a	CHCl ₃	_	< 10	_[e]
2	5a	CHCl ₃	3Å	99	93
3	5b	CHCl ₃	3Å	72	93
4	5c	CHCl ₃	3Å	86	94
5	5d	CHCl ₃	3Å	90	74
6	5e	CHCl ₃	3Å	91	18
7	5f	CHCl ₃	3Å	75	7
8	5a	DCE	3Å	93	91
9	5a	toluene	3Å	93	79
10	5a	EtOAc	3Å	57	83
11	5a	CHCl ₃	4Å	99	94
12	5a	CHCl ₃	5Å	76	71
13	5c	CHCl ₃	4Å	94	95
14 ^[f]	5c	CHCl ₃	4 Å	97	90

^[a] Unless indicated otherwise, the reaction was carried out on a 0.2-mmol scale under argon in a solvent (1 mL) with MS (100 mg) for 24 h, using 3a as hydride source, and the ratio of 1a:2a:3a was 1:1:3.

- ^[b] Yields refer to isolated yields.
- ^[c] The *ees* were determined by HPLC.
- ^[d] Performed in the absence of MS.
- ^[e] Not determined.
- ^[f] **3b** was employed as hydride source instead of **3a**.

crucial role of 3Å MS would be largely attributed to its action in removing the water molecules generated from the condensational cyclization of reactants 1a and 2a, thus facilitating the formation of the intermediate quinoxaline. The screening of chiral catalysts (entries 2-7) revealed that phosphoric acids 5a-5c with bulky groups at the 3,3'-positions of the BINOL backbone were much more efficient in delivering high enantioselectivity (entries 2-4) than other counterparts. We then investigated the solvent effect in the presence of catalyst 5a. Among the solvents we utilized, chloroform was proven to be the best one with regard to enantioselectivity (entries 8-10 vs. 2). Due to the importance of 3Å MS, we further studied 4Å or 5Å MS for this reaction (entries 11–12), and found 4Å MS showed a slightly higher capacity than 3Å MS in controlling the enantioselectivity (entry 11 vs. 2). Under these conditions, the replacement of catalyst 5a by 5c enhanced the enantioselectivity to the highest level of 95% ee (entry 13), but the subsequent change of Hantzsch esters from 3a to 3b did not improve the enantioselectivity (entry 14).

Under the optimal reaction conditions (Table 1, entry 13), we then examined the substrate scope of this asymmetric organocatalytic tandem cyclization/ transfer hydrogenation sequence for the synthesis of tetrahydroquinoxalines. As illustrated in Table 2, this cascade reaction is amenable to a wide scope of substituted glyoxals 2 including aryl glyoxals bearing electronically neutral, rich, or poor substituents on their aromatic rings, and a heteroaryl-substituted glyoxal as well, thus delivering structurally diverse 2substituted tetrahydroquinoxalines 4aa-4aj in excellent enantioselectivities (90-97% ee) and good to quantitative yields (57-99%). Generally, there is no significant difference in enantioselectivity among various 2-aryltetrahydroquinoxalines 4aa-4ai, and high ee values ranging from 93% to 97% were achieved regardless of the electronic nature and position of the substituents. More importantly, the heteroaryl-substituted glyoxal appeared to be a suitable substrate, offering 2-(thiophen-2-yl)tetrahydroquinoxaline 4aj in high enantioselectivity of 90% ee.

Moreover, as shown in Table 2, this approach is also applicable to various symmetrical 1,2-arylenediamines **1** with electron-rich, electron-neutral, or electron-withdrawing substituents on their benzene rings, offering tetrahydroquinoxalines **4ba–4da** in excellent levels of enantioselectivities (97–99% *ee*) and high yields (86–96%). Furthermore, these diamines **1** can smoothly participate in the tandem reactions with different aryl glyoxals **2** to provide a series of tetrahydroquinoxalines **4cc–4dc** in perfect enantioselectivities of 98–>99% *ee* and good to excellent yields of 73– 90%. Therefore, this protocol has proven to be a powerful tool in the step-economical synthesis of enantioTable 2. Substrate scope of the asymmetric organocatalytic tandem reaction for the synthesis of tetrahydroquinoxalines.^[a]



^[a] Unless indicated otherwise, the reaction was carried out on a 0.2-mmol scale under argon in CHCl₃ (1 mL) with 4Å MS (100 mg) for 24 h, and the ratio of 1:2:3a was 1:1:3. Yields refer to isolated yields and *ees* were determined by HPLC.

selective tetrahydroquinoxalines with structural diversity.

Besides, the reaction involving aliphatic glyoxals as exemplified by methylglyoxal 2k was also investigated. The reaction afforded the desired 2-methyltetrahydroquinoxaline 4ak with acceptable enantioselectivity of 70% *ee* in a two-step manner [Eq. (1)]. However, the same reaction in a one-step mode only gave product 4ak with moderate enantioselectivity of 50%



ee [Eq. (2)]. The difference between the enantioselectivity of the two reactions might be ascribed to the water molecules in the methylglyoxal solution (40 wt% in water), since water molecules could form hydrogen bonds with catalyst **5c**. This would disturb the formation of hydrogen bonds between the catalyst and the substrates, which play a crucial role in enantioselective control.

Then, we studied the regioselectivity of the reaction when unsymmetrical 1,2-arylenediamines were employed for this tandem reaction. As shown in Table 3, various unsymmetrical 1,2-arylenediamines with different types of orientating groups were utilized as substrates in the reaction, leading to two different regioselective tetrahydroquinoxalines **4** and **4'** concurrently, both in good to excellent enantioselectivities. It was found that 1,2-arylenediamine **1e** with a strong electron-withdrawing ester group showed the highest regioselectivity of 3.2:1 rr (entry 1, rr=regioselective ratio), but 1,2-arylenediamine **1h** with a strong electron-donating group exhibited poor regioselectivity of 1:1 rr (entry 4). The structure of regioselective product **4ea** was identified by X-ray single crystal analysis of *rac*-**4ea** (Figure 2).^[8] Also the structures of products **4ga** and **4ga'** were determined by comparing their NMR and HPLC spectra with those of the same known compounds.^[4k] The structures of other products were assigned by analogy. Interestingly, the *meta*directing group CO₂Et led to the formation of **4** as major regioselective product (entry 1), while the *ortho-para*-directing group Br resulted in the generation of **4'** as major regioselective product (entry 3). This difference in regioselectivity might largely be attributed to the electronic effects of these substituents, which led to differential reactivity of the two amino groups, thereby resulting in the formation of different regioselective products.

More importantly, the strategy of asymmetric organocatalytic tandem cyclization/transfer hydrogenation can be successfully employed to synthesize other enantioenriched heterocycles as exemplified by chiral 3,4-dihydroquinoxalinones, which also possess significant bioactivities^[9] but are rather limited in their enantioselective versions.^[4j,10] As indicated in Table 4,

	R NH ₂ +	HO OH O Ph 2a	5 mol% 5c , 4 A MS Hantzsch ester 3a CHCl ₃ , 35 °C R	$ \begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \end{array}\\ \end{array}\\ \end{array}\\ \end{array} \\ \begin{array}{c} \end{array}\\ \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} $ } \\ \end{array} \\ \end{array} } \\ \end{array} \\ \end{array} \\ \end{array} \\ \end{array} } \\ \end{array} \\ \end{array} } \\ \end{array} \\ \end{array} \\ \end{array} } \\ \end{array} \\ \end{array} } \\ \end{array} \\ \end{array} \\ \end{array} } \\ \end{array} \\ \end{array} \\ \end{array} } \\ \end{array} } \\ \end{array} \\ T } } \\ T } } } T } T T T T \\ T T T \\ T T T \\ T T T \\ T T \\ T T \\ T T \\ T T T \\ T T T T \\ T T \\ T T \\ T T T \\ T T T \\ T T } T T \\ T T T } T } T T } T } T } T T } T } T T } T } T T } T } T } T } T } T } T } T } T } T }	Ph
Entry	4 (4')	R (1)	rr ^[b] (4:4')	Yield [%] 4 (4') ^[c]	ee [%] 4 (4 ') ^[d]
1	4ea (4ea')	CO_2Et (1e)	3.2:1	42 (13)	79 (90)
2	4fa (4fa')	$CF_3(\mathbf{1f})$	1.3:1	39 (31)	90 (87)
3	4ga (4ga')	Br (1g)	1:1.3	37 (48)	97 (94)
4	4ha (4ha')	OMe (1h)	1:1	26 (26)	86 (89)

Table 3. The investigation on the regioselectivity of the reaction for the synthesis of tetrahydroquinoxalines.^[a]

^[a] Unless indicated otherwise, the reaction was carried out on a 0.2-mmol scale under argon in CHCl₃ (1 mL) with 4Å MS (100 mg) for 24 h, and the ratio of **1:2a:3a** was 1:1:3.

^[b] The regioselective ratio (rr) was calculated by the yields of products **4** and **4**'.

^[c] Yields refer to isolated yields.

^[d] The *ees* were determined by HPLC.

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Figure 2. X-ray single crystal structure of rac-4ea.

Table 4. Extension of the strategy to the step-economical synthesis of 3,4-dihydroquinoxalinones.^[a]



^[a] Unless indicated otherwise, the reaction was carried out on a 0.2-mmol scale under argon in THF (1 mL) for 24 h, and the ratio of **1:6:3a** was 1:1:1.5. Yields refer to isolated yields and *ees* were determined by HPLC.

the cascade cyclization/transfer hydrogenation sequence consists of the condensation-type cyclization of 1,2-phenylenediamines 1 with ethyl 2-oxo-2-phenyl-acetates 6 and the subsequent enantioselective transfer hydrogenation of the intermediate products 8 using Hantzsch ester 3a as hydride source, giving the desired chiral 3,4-dihydroquinoxalinones 7 in a step-economical fashion. Under the similar reaction conditions, the one-step, one-pot operation cascade reaction took place smoothly and was found to tolerate

a variety of 1,2-phenylenediamines **1** and ethyl 2-oxo-2-phenylacetates **6**, offering structurally diverse 3,4-dihydroquinoxalinones **7** in excellent enantioselectivities (94–99% *ee*).

The absolute configuration of product **4aa** was determined to be 2*R* by comparing its optical rotation $([\alpha]_D^{20}: -97.0)$ with that of the same known compound $([\alpha]_D^{p.t.}: -98.6)$.^[4k] The absolute configurations of other products were assigned by analogy.



Scheme 2. Proposed reaction pathway and transition state.

On the basis of our experimental results and previously reported calculations on transfer hydrogenation of imines,^[11] we proposed a possible reaction pathway and transition state to explain the stereochemistry of this reaction (Scheme 2). Initially, the condensationtype cyclization of substrates 1 and 2 or 6 in the presence of chiral phosphoric acid (B*-H) generated intermediate product 8 or 9. Subsequently, B*-H acted as a bifunctional catalyst to activate both the intermediate and HEH 3a by hydrogen-bonding interaction, thereby facilitating the asymmetric 1,4-hydride transfer pathway to generate the final product (R)-4 or 7. The two hydrogen bonds and the effect of steric hindrance created by B*-H built up a "three-point contact model",^[11a,b] which determined the excellent enantioselectivities and (R)-configurations of the products experimentally observed.

Conclusions

In summary, we have established an asymmetric organocatalytic tandem reaction of cyclization/transfer hydrogenation in a compatible and synergistic way, leading to the step-economical synthesis of enantioenriched tetrahydroquinoxalines and dihydroquinoxalinones from readily accessible materials. This protocol of a one-operation tandem reaction combines the merits of both tandem reactions and asymmetric organocatalysis, tolerating a wide range of simple substrates to concisely furnish structurally diverse tetrahydroquinoxalines and dihydroquinoxalinones in excellent enantioselectivity of up to >99% ee. This strategy not only provides an easy access to biologically significant chiral nitrogen heterocycles, but also opens a new window towards the extension of this strategy to other synthetically important compounds.

Experimental Section

General

NMR spectra were measured at 400 and 100 MHz, respectively. The solvent used for NMR spectroscopy was CDCl₃, using tetramethylsilane as the internal reference. HR-MS (ESI) were determined with a micrOTOF-QII HRMS/MS instrument (Bruker). Enantiomeric excesses (ee) were determined by chiral high-performance liquid chromatography (chiral HPLC). The chiral columns used for the determination of enantiomeric excesses by chiral HPLC were Chiralpak OD-H, AD-H and IA columns. Optical rotation values were measured with instruments operating at $\lambda = 589$ nm, corresponding to the sodium D line at the temperatures indicated. Analytic grade solvents for the column chromatography and commercially available reagents were used as received. All commercially available starting materials were used directly. Substrates 2 except for 2a and 2k were synthesized according to the literature methods.^[12]

General Procedure for the Synthesis of Chiral Tetrahydroquinoxalines 4 *via* Asymmetric Organocatalytic Tandem Cyclization/Transfer Hydrogenation

Under an argon atmosphere, chloroform (1 mL) was added to the mixture of 1,2-arylenediamine 1 (0.2 mmol), substituted glyoxal 2 (0.2 mmol), Hantzsch ester **3a** (0.6 mmol), the catalyst **5c** (0.01 mmol) and 4Å molecular sieves (100 mg). After being stirred at 35 °C for 24 h, the reaction mixture was filtered to remove molecular sieves and the solid powder was washed with ethyl acetate. The resultant solution was concentrated under the reduced pressure to give the residue, which was purified through flash column chromatography on silica gel to afford pure products **4**.

General Procedure for the Synthesis of Chiral Dihydroquinoxalinones 7 *via* Asymmetric Organocatalytic Tandem Cyclization/Transfer Hydrogenation

Under an argon atmosphere, THF (1 mL) was added to the mixture of 1,2-arylenediamine 1 (0.2 mmol), ethyl 2-oxo-2-phenylacetate 6 (0.2 mmol), Hantzsch ester 3a (0.3 mmol) and the catalyst 5a (0.01 mmol). After being stirred at 50 °C

for 24 h, the reaction mixture was purified through flash column chromatography on silica gel to afford pure products **7**.

(*R*)-2-Phenyl-1,2,3,4-tetrahydroquinoxaline (4aa): Flash column chromatography eluent, toluene/ethyl acetate = 80/1; reaction time = 24 h; yield: 39.4 mg (94%); yellow solid; mp 68–69 °C; $[\alpha]_{D}^{20}$: -97.0 (*c* 0.3, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ =7.41–7.31 (m, 5H), 6.66–6.58 (m, 4H), 4.49 (dd, *J*=8.0, 2.4 Hz, 1H), 4.16–3.15 (m, 4H); ¹³C NMR (100 MHz, CDCl₃): δ =141.8, 134.2, 132.7, 128.7, 127.9, 127.0, 119.0, 118.8, 114.8, 114.5, 54.7, 49.1; IR (KBr): ν =3383, 3357, 3357, 3252, 3061, 3031, 2914, 2850, 1949, 1869, 1595 cm⁻¹; ESI-FT-MS: *m*/*z*=211.1224, exact mass calcd. for (C₁₄H₁₄N₂+H)⁺: 211.1235; enantiomeric excess: 95%, determined by HPLC (Daicel Chirapak OD-H, hexane/2-propanol=80/20, flow rate 1.0 mLmin⁻¹, *T*=30 °C, 254 nm): t_R= 13.457 min (major), t_R=18.043 min (minor).

(R)-2-(Naphthalen-2-yl)-1,2,3,4-tetrahydroquinoxaline

(4ab): Flash column chromatography eluent, toluene/ethyl acetate = 90/1; reaction time = 24 h; yield: 38.6 mg (74%); yellow solid; mp 150–151 °C; $[\alpha]_D^{20}$: -96.5 (*c* 0.5, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ = 7.87–7.85 (m, 4H), 7.52–7.49 (m, 3H), 6.67–6.62 (m, 4H), 4.65 (d, *J*=6.4 Hz, 1H), 3.94 (s, 2H), 3.52 (d, *J*=8.8 Hz, 1H), 3.47–3.37 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ = 139.2, 134.2, 133.4, 133.2, 132.9, 128.4, 127.9, 127.7, 126.3, 126.0, 125.8, 125.1, 119.0, 118.9, 114.8, 114.5, 54.9, 49.2; IR (KBr): ν = 3351, 3054, 2922, 2834, 1591, 1504, 1454, 1299, 1271, 1119 cm⁻¹; ESI-FT-MS: *m*/*z* = 261.1382, exact mass calcd. for (C₁₈H₁₆N₂+H)⁺: 261.1392; enantiomeric excess: 94%, determined by HPLC (Daicel Chirapak AD-H, hexane/2-propanol = 70/30, flow rate 1.0 mLmin⁻¹, *T* = 30 °C, 254 nm): t_R = 14.307 min (major), t_R = 30.943 min (minor).

(R)-2-(4-Methoxyphenyl)-1,2,3,4-tetrahydroquinoxaline

(4ac): Flash column chromatography eluent, toluene/ethyl acetate = 90/1; reaction time = 24 h; yield: 47.7 mg (99%); yellow solid; mp 83–85°C; $[\alpha]_{D}^{20}$: -71.4 (c 0.9, CHCl₃); ¹H NMR (400 MHz, CDCl₃): $\delta = 7.34$ (d, J = 8.8 Hz, 2H), 6.95 (d, J=8.4 Hz, 2H), 6.89-6.67 (m, 2H), 6.62-6.60 (m, 2H), 4.46 (dd, J = 8.4, 2.8 Hz, 1H), 3.85 (s, 3H), 3.75 (s, 2H), 3.45 (dd, J=11.2, 3.2 Hz, 1H), 3.33 (dd, J=10.8, 8.0 Hz, 1 H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 159.3$, 134.3, 133.9, 132.7, 128.1, 118.9, 118.8, 114.8, 114.5, 114.0, 55.4, 54.1, 49.3; IR (KBr): v=2920, 2850, 1616, 1558, 1541, 1518, 1458, 1339, 1252, 1176, 1101 cm⁻¹; ESI-FT-MS: m/z241.1329, exact mass calcd. for $(C_{15}H_{16}N_2O + H)^+$: 241.1341; enantiomeric excess: 96%, determined by HPLC (Daicel Chirapak OD-H, hexane/2-propanol=80/20, flow rate 1.0 mLmin^{-1} , T = 30 °C, 254 nm): $t_R = 16.613 \text{ min}$ (major), $t_{R} = 23.343 \text{ min (minor)}.$

(*R*)-2-(*p*-Tolyl)-1,2,3,4-tetrahydroquinoxaline (4ad): Flash column chromatography eluent, toluene/ethyl acetate = 90/1; reaction time = 24 h; yield: 44.2 mg (99%); yellow solid; mp 93–95 °C; $[\alpha]_{D}^{20}$: -87.4 (*c* 0.7, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ = 7.64 (d, *J* = 8.0 Hz, 2 H), 7.55 (d, *J* = 7.6 Hz, 2 H), 7.01–6.91 (m, 4H), 4.80 (dd, *J* = 8.0, 2.8 Hz, 1 H), 4.11 (s, 2 H), 3.79 (dd, *J* = 10.8, 2.8 Hz, 1 H), 3.67 (dd, *J* = 11.2, 8.4 Hz, 1 H), 2.73 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ = 138.9, 137.6, 134.3, 132.8, 129.4, 126.9, 118.8, 114.8, 114.5, 54.5, 49.2, 21.2; IR (KBr): ν = 3363, 3333, 3245, 3023, 2918, 2850, 1597, 1514, 1457, 1339, 1306, 1107, 814, 739 cm⁻¹; ESI-FT-MS: *m*/z = 225.1380, exact mass calcd. for (C₁₅H₁₆N₂+

H)⁺: 225.1392; enantiomeric excess: 96%, determined by HPLC (Daicel Chirapak OD-H, hexane/2-propanol=80/20, flow rate 1.0 mLmin⁻¹, T=30 °C, 254 nm): t_R=11.510 min (major), t_R=16.790 min (minor).

(R)-2-(4-Fluorophenyl)-1,2,3,4-tetrahydroquinoxaline

(4ae): Flash column chromatography eluent, toluene/ethyl acetate = 90/1; reaction time = 24 h; yield: 45.3 mg (99%); yellow solid; mp 62–63 °C; $[\alpha]_{D}^{20}$: -98.8 (c 0.7, CHCl₃); ¹H NMR (400 MHz, CDCl₃): $\delta = 7.38 - 7.34$ (m, 2H), 7.06 (t, J = 8.8 Hz, 2 H), 6.67–6.65 (m, 2 H), 6.6–6.58 (m, 2 H), 4.47 (dd, J=8.4, 3.2 Hz, 1 H), 3.76 (s, 2 H), 3.43 (dd, J=11.2, 3.43)3.2 Hz, 1 H), 3.29 (dd, J = 10.8, 8.0 Hz, 1 H); ¹³C NMR $(100 \text{ MHz}, \text{ CDCl}_3): \delta = 163.6, 161.2, 137.6, 133.9, 132.6,$ 128.6, 119.0, 115.6, 115.4, 114.9, 114.6, 54.0, 49.2; IR (KBr): $\nu = 3357, 3338, 3277, 2917, 2849, 1601, 1509, 1457, 1305,$ 1229, 1119, 829, 751 cm⁻¹; ESI-FT-MS: m/z = 229.1130, exact mass calcd. for $(C_{14}H_{13}FN_2+H)^+$: 229.1141; enantiomeric excess: 96%, determined by HPLC (Daicel Chirapak OD-H, hexane/2-propanol=80/20, flow rate 1.0 mL min⁻¹, T =30 °C, 254 nm): $t_R = 15.657 \text{ min}$ (major), $t_R = 24.830 \text{ min}$ (minor).

(R)-2-(4-Chlorophenyl)-1,2,3,4-tetrahydroquinoxaline

(4af): Flash column chromatography eluent, toluene/ethyl acetate = 90/1; reaction time = 24 h; yield: 36.8 mg (75%); yellow solid; mp 100–101 °C; $[\alpha]_D^{20}$: -79.4 (*c* 0.3, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ =7.37–7.28 (m, 4H), 6.66–6.63 (m, 2H), 6.60–6.57 (m, 2H), 4.47 (dd, *J*=7.6, 2.8 Hz, 1H), 3.83 (s, 2H), 3.44 (dd, *J*=11.2, 2.8 Hz, 1H), 3.28 (dd, *J*=10.8, 8.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ = 140.4, 133.8, 133.6, 132.5, 128.8, 128.4, 119.2, 119.0, 114.9, 114.6, 54.1, 48.9; IR (KBr): ν =3338, 2922, 2852, 1597, 1507, 1491, 1457, 1304, 1090, 1014, 820, 741, 669 cm⁻¹; ESI-FT-MS: *m/z*=245.0835, exact mass calcd. for (C₁₄H₁₃ClN₂+H)⁺: 245.0846; enantiomeric excess: 97%, determined by HPLC (Daicel Chirapak OD-H, hexane/2-propanol=80/20, flow rate 1.0 mLmin⁻¹, *T*=30 °C, 254 nm): t_R=17.990 min (major), t_R=31.137 min (minor).

(R)-2-(4-Bromophenyl)-1,2,3,4-tetrahydroquinoxaline

(4ag): Flash column chromatography eluent, toluene/ethyl acetate = 90/1; reaction time = 24 h; yield: 34.7 mg (60 %); yellow solid; mp 117–118°C; $[\alpha]_D^{20}$: -69.8 (c 0.4, CHCl₃); ¹H NMR (400 MHz, CDCl₃): $\delta = 7.49$ (d, J = 8.0 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H), 6.66–6.64 (m, 2H), 6.59–6.56 (m, 2H), 4.45 (dd, J=8.0, 2.8 Hz, 1H), 3.86 (s, 2H), 3.43 (dd, J = 11.2, 2.8 Hz, 1 H), 3.27 (dd, J = 10.8, 8.0 Hz, 1 H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 140.9$, 133.8, 132.7, 131.8, 128.7, 121.7, 119.0, 114.8, 114.5, 54.2, 48.9; IR (KBr): $\nu =$ 3367, 3335, 3046, 2917, 2850, 1596, 1517, 1488, 1464, 1338, 1304, 1119, 1010, 816, 737 cm⁻¹; ESI-FT-MS: m/z = 289.0328, exact mass calcd. for $(C_{14}H_{13}BrN_2+H)^+$: 289.0340; enantiomeric excess: 93%, determined by HPLC (Daicel Chirapak OD-H, hexane/2-propanol=80/20, flow rate 1.0 mLmin^{-1} T = 30 °C, 254 nm): t_R = 20.063 min (major), t_R = 34.437 min (minor).

(R)-2-(3-Chlorophenyl)-1,2,3,4-tetrahydroquinoxaline

(4ah): Flash column chromatography eluent, toluene/ethyl acetate = 70/1; reaction time = 24 h; yield: 36.8 mg (75%); yellow oil; $[\alpha]_D^{20}$: -87.3 (*c* 0.6, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ = 7.37 (s, 1H), 7.29-7.24 (m, 3H), 6.65-6.55 (m, 4H), 4.44 (dd, *J* = 8.0, 2.8 Hz, 1H), 3.75 (s, 2H), 3.43 (dd, *J* = 11.2, 2.8 Hz, 1H), 3.27 (dd, *J* = 10.8, 8.4 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ = 143.9, 134.6, 133.8, 132.6,

129.9, 128.1, 127.2, 125.2, 119.2, 119.0, 114.9, 114.6, 54.3, 48.9; IR (KBr): $\nu = 2923$, 2851, 1749, 1717, 1699, 1684, 1558, 1508, 1489, 1457 cm⁻¹; ESI-FT-MS: m/z = 245.0835, exact mass calcd. for (C₁₄H₁₃ClN₂+H)⁺: 245.0846; enantiomeric excess: 94%, determined by HPLC (Daicel Chirapak AD-H, hexane/2-propanol = 70/30, flow rate 1.0 mLmin⁻¹, T = 30 °C, 254 nm): t_R = 8.400 min (major), t_R = 10.643 min (minor).

(R)-2-(3,4-Dichlorophenyl)-1,2,3,4-tetrahydroquinoxaline (4ai): Flash column chromatography eluent, toluene/ethyl acetate = 90/1; reaction time = 24 h; yield: 46.2 mg (83%); yellow solid; mp 94–95 °C; $[\alpha]_{D}^{20}$: -86.9 (c 0.5, CHCl₃); ¹H NMR (400 MHz, CDCl₃): $\delta = 7.49$ (d, J = 2.0 Hz, 1H), 7.43 (d, J=8.4 Hz, 1H), 7.22 (dd, J=8.4, 2.0 Hz, 1H), 6.67-6.64 (m, 2H), 6.61–6.57 (m, 2H), 4.45 (dd, J=7.6, 2.8 Hz, 1H), 3.86 (s, 2H), 3.44 (dd, J=10.8, 2.8 Hz, 1H), 3.26 (dd, J = 11.2, 8.0 Hz, 1 H; ¹³C NMR (100 MHz, CDCl₃): $\delta =$ 142.3, 133.4, 132.7, 131.7, 130.6, 128.9, 126.4, 119.2, 114.9, 114.6, 53.8, 48.8; IR (KBr): v = 3341, 2918, 2850, 1595, 1507, 1490, 1458, 1310, 1129, 1027, 742 cm⁻¹; ESI-FT-MS: m/z =279.0445, exact mass calcd. for $(C_{14}H_{12}Cl_2N_2 + H)^+$: 279.0456; enantiomeric excess: 97%, determined by HPLC (Daicel Chirapak OD-H, hexane/2-propanol=80/20, flow rate 1.0 mLmin⁻¹, T = 30 °C, 254 nm): t_R = 21.933 min (major), $t_R = 43.853 \text{ min (minor)}.$

(S)-2-(Thiophen-2-yl)-1,2,3,4-tetrahydroquinoxaline (4aj): Flash column chromatography eluent, toluene/ethyl acetate=90/1; reaction time=24 h; yield: 24.6 mg (57%); yellow solid; mp 73–74°C; $[\alpha]_{\rm D}^{20}$: –33.5 (*c* 0.2, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ =7.29 (d, *J*=5.2 Hz, 1 H), 7.08 (d, J = 3.2 Hz, 1 H), 7.02 (dd, J = 4.8, 3.6 Hz, 1 H), 6.68– 6.65 (m, 2H), 6.61–6.58 (m, 2H), 4.86 (dd, J=7.6, 3.2 Hz, 1H), 3.98 (s, 2H), 3.58 (dd, J=10.8, 2.8 Hz, 1H), 3.45 (dd, J=10.8, 7.6 Hz, 1 H); ¹³C NMR (100 MHz, CDCl₃): $\delta =$ 145.6, 133.2, 132.8, 126.6, 124.9, 124.2, 119.3, 119.0, 114.8, 114.8, 50.6, 49.4; IR (KBr): v = 3395, 3347, 3041, 2916, 2850, 1869, 1600, 1516, 1508, 1463, 1311, 1298, 1037, 737 cm^{-1} ; ESI-FT-MS: m/z = 217.0790, exact mass calcd. for $(C_{12}H_{12}N_2S + H)^+$: 217.0799; enantiomeric excess: 90%, determined by HPLC (Daicel Chirapak OD-H, hexane/2-propanol=80/20, flow rate 1.0 mLmin⁻¹, T=30 °C, 254 nm): t_R= 15.720 min (major), $t_R = 22.307$ min (minor).

(R)-2-Phenyl-1,2,3,4-tetrahydrobenzo[g]quinoxaline

(4ba): Flash column chromatography eluent, toluene/ethyl acetate = 90/1; reaction time = 24 h; yield: 50.4 mg (96%); gray solid; mp 168–169 °C; $[\alpha]_{D}^{20}$: 37.8 (*c* 0.6, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ =7.51–7.49 (m, 2H), 7.44–7.34 (m, 5H), 7.18–7.15 (m, 2H), 6.85 (d, *J*=4.0 Hz, 2H), 4.59 (dd, *J*=8.0, 2.8 Hz, 1H), 4.25 (s, 2H), 3.52 (dd, *J*=10.8, 3.0 Hz, 1H), 3.42–3.37(m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ =141.5, 135.5, 134.2, 129.0, 128.7, 128.1, 127.0, 125.2, 122.7, 108.1, 107.8, 54.8, 48.7; IR (KBr): *v*=3396, 3351, 3036, 2923, 2853, 1685, 1627, 1525, 1455, 1322, 1295, 1121 cm⁻¹; ESI-FT-MS: *m/z*=261.1380, exact mass calcd. for (C₁₈H₁₆N₂+H)⁺: 261.1392; enantiomeric excess: 97%, determined by HPLC (Daicel Chirapak OD-H, hexane/2-propanol=80/20, flow rate 1.0 mLmin⁻¹, *T*=30°C, 254 nm): t_R= 28.313 min (major), t_R=31.450 min (minor).

(*R*)-6,7-Dichloro-2-phenyl-1,2,3,4-tetrahydroquinoxaline (4ca): Flash column chromatography eluent, toluene/ethyl acetate = 90/1; reaction time = 24 h; yield: 48.4 mg (86%); yellow solid; mp 116–117 °C; $[\alpha]_{D}^{20}$: -75.7 (*c* 0.6, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ =7.40–7.32 (m, 5H), 6.59 (d, J=3.6 Hz, 2H), 4.43 (dd, J=8.0, 2.8 Hz, 1H), 3.96 (s, 2H), 3.44 (dd, J=10.8, 2.9 Hz, 1H), 3.27 (dd, J=11.2, 8.1 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ =140.9, 133.7, 132.5, 128.8, 128.2, 126.9, 120.6, 114.9, 54.3, 48.4; IR (KBr): ν = 3395, 3065, 3032, 2912, 2856, 1953, 1600, 1584, 1506, 1298, 1124, 1060, 849, 757, 701 cm⁻¹; ESI-FT-MS: m/z=279.0447, exact mass calcd. for (C₁₄H₁₂Cl₂N₂+H)⁺: 279.0456; enantiomeric excess: 99%, determined by HPLC (Daicel Chirapak AD-H, hexane/2-propanol=80/20, flow rate 1.0 mLmin⁻¹, T=30°C, 254 nm): t_R=13.497 min (minor), t_R=15.583 min (major).

(*R*)-6,7-Dimethyl-2-phenyl-1,2,3,4-tetrahydroquinoxaline (4da): (Flash column chromatography eluent, toluene/ethyl acetate = 90/1); reaction time = 24 h; yield: 43.9 mg (92%); yellow solid; mp 99–101 °C; $[\alpha]_D^{20}$: -33.8 (*c* 0.5, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ = 7.40–7.26 (m, 5H), 6.41 (s, 2H), 4.45 (d, *J* = 6.8 Hz, 1 H), 3.44–2.26 (m, 4H), 2.14 (s, 6H); ¹³C NMR (100 MHz, CDCl₃): δ = 142.1, 132.1, 130.4, 129.1, 128.6, 127.8, 127.4, 126.9, 126.5, 116.7, 116.2, 55.1, 49.5, 18.9; IR (KBr): ν = 3318, 3242, 1915, 2849, 1618, 1518, 1453, 1385, 1340, 1307, 1224, 868, 764, 701 cm⁻¹; ESI-FT-MS: *m*/*z* = 239.1538, exact mass calcd. for (C₁₆H₁₈N₂+H)⁺: 239.1548; enantiomeric excess: 98%, determined by HPLC (Daicel Chirapak AD-H, hexane/2-propanol = 70/30, flow rate 1.0 mLmin⁻¹, *T* = 30 °C, 254 nm): t_R = 10.207 min (minor), t_R = 11.367 min (major).

(R)-6,7-Dichloro-2-(4-methoxyphenyl)-1,2,3,4-tetrahydroquinoxaline (4cc): Flash column chromatography eluent, toluene/ethyl acetate = 90/1; reaction time = 24 h; yield: 54.7 mg (89%); yellow solid; mp 91–92 °C; $[\alpha]_{D}^{20}$: -51.7 (c 0.2, CHCl₃); ¹H NMR (400 MHz, CDCl₃): $\delta = 7.30-7.27$ (m, 2H), 6.93 (d, J=8.8 Hz, 2H), 6.61 (s, 2H), 4.40 (dd, J=8.0, 3.2 Hz, 1 H), 3.95 (s, 2 H), 3.84 (s, 3 H), 3.43 (dd, J = 11.2,3.2 Hz, 1 H), 3.27 (dd, J = 11.2, 8.0 Hz, 1 H); ¹³C NMR $(100 \text{ MHz}, \text{ CDCl}_3): \delta = 140.9, 133.8, 132.7, 131.8, 128.7,$ 121.7, 119.1, 118.9, 114.8, 114.5, 54.2, 48.9, 29.7; IR (KBr): v=3395, 2968, 2843, 1717, 1507, 1295, 1253, 1175, 857, 828 cm⁻¹; ESI-FT-MS: m/z = 309.0552, exact mass calcd. for $(C_{15}H_{14}Cl_2N_2O + H)^+$: 309.0561; enantiomeric excess: 99%, determined by HPLC (Daicel Chirapak AD-H, hexane/2propanol = 70/30, flow rate 1.0 mL min⁻¹, $T = 30 \,^{\circ}\text{C}$, 254 nm): $t_R = 12.580 \text{ min (minor)}, t_R = 17.543 \text{ min (major)}.$

(*R*)-6,7-Dichloro-2-(*p*-tolyl)-1,2,3,4-tetrahydroquinoxaline (4cd): Flash column chromatography eluent, toluene/ethyl acetate = 90/1; eeaction time = 24 h; yield: 42.6 mg (73%); yellow solid; mp 145–146 °C; $[\alpha]_D^{20}$: -71.3 (c 0.7, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ =7.16–7.09 (m, 4H), 6.50 (s, 2H), 4.31 (dd, *J*=7.6, 2.4 Hz, 1H), 3.83 (s, 2H), 3.34 (dd, *J*=11.2, 2.8 Hz, 1H), 3.17 (dd, *J*=10.8, 8.4 Hz, 1H), 2.28 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ =138.0, 137.9, 133.8, 132.2, 129.5, 126.8, 120.8, 120.5, 115.1, 114.8, 53.9, 48.5, 21.2; IR (KBr): γ 3394, 2923, 2856, 1599, 1579, 1509, 1475, 1347, 1291, 1220 cm⁻¹; ESI-FT-MS: *m/z* 293.0602, exact mass calcd for (C₁₅H₁₄Cl₂N₂+H)⁺: 293.0612; enantiomeric excess: 99%, determined by HPLC (Daicel Chirapak AD-H, hexane/2-propanol=70/30, flow rate 1.0 mLmin⁻¹, *T*=30 °C, 254 nm): t_R=9.093 min (minor), t_R=11.290 min (major).

(*R*)-6,7-Dichloro-2-(4-fluorophenyl)-1,2,3,4-tetrahydroquinoxaline (4ce): Flash column chromatography eluent, toluene/ethyl acetate =90/1; reaction time =24 h; yield: 53.6 mg (90%); yellow solid; mp 90–91 °C; $[\alpha]_D^{20}$: -16.4 (c 0.8, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ =7.33-7.29 (m, 2H), 7.06 (t, *J*=8.8 Hz, 2H), 6.58 (d, *J*=4.8 Hz, 2H), 4.41 (dd, *J*=8.0, 3.2 Hz, 1H), 3.93 (s, 2H), 3.42 (dd, *J*=11.2, 3.2 Hz, 1H), 3.23 (dd, *J*=11.2, 8.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ =163.8, 161.3, 136.6, 136.6, 133.6, 132.0, 128.6, 128.5, 120.9, 120.7, 115.8, 115.6, 115.2, 114.9, 53.5, 48.4; IR (KBr): v=3392, 2925, 2872, 1889, 1602, 1506, 1466, 1298, 1220, 1125, 1062, 849, 834, 673 cm⁻¹; ESI-FT-MS: *m/z* 297.0351, exact mass calcd. for (C₁₄H₁₁Cl₂FN₂+H)⁺: 297.0362; enantiomeric excess: >99%, determined by HPLC (Daicel Chirapak AD-H, hexane/2-propanol=70/30, flow rate 1.0 mLmin⁻¹, *T*=30°C, 254 nm): t_R=9.130 min (minor), t_R=11.257 min (major).

(R)-2-(4-Bromophenyl)-6,7-dichloro-1,2,3,4-tetrahydroquinoxaline (4cg): Flash column chromatography eluent, toluene/ethyl acetate = 100/1; reaction time = 24 h; yield: 64.4 mg (90%); yellow solid; mp 146–147 °C; $[\alpha]_{D}^{20}$: -88.1 (c 0.4, CHCl₃); ¹H NMR (400 MHz, CDCl₃): $\delta = 7.49$ (d, J =8.0 Hz, 2H), 7.22 (d, J=8.0 Hz, 2H), 6.60 (d, J=5.2 Hz, 2H), 4.41 (dd, J = 7.6, 2.8 Hz, 1H), 3.95 (s, 1H), 3.90 (s, 1 H), 3.42 (dd, J=11.2, 3.2 Hz, 1 H), 3.22 (dd, J=11.2, 7.6 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 140.1$, 133.3, 132.3, 131.9, 128.6, 122.0, 120.8, 115.1, 114.9, 53.7, 48.2; IR (KBr): v=3406, 3373, 2918, 2847, 1716, 1698, 1600, 1505, 1294, 1125, 1010 cm⁻¹; ESI-FT-MS: m/z = 356.9551, exact mass calcd. for $(C_{14}H_{11}BrCl_2N_2+H)^+$: 356.9561; enantiomeric excess: >99%, determined by HPLC (Daicel Chirapak AD-H, hexane/2-propanol = 70/30, flow rate 1.0 mL min⁻¹ T=30 °C, 254 nm): $t_{\rm R}=9.213$ min (minor), $t_{\rm R}=12.330$ min (major).

(*R*)-2-(4-Methoxyphenyl)-6,7-dimethyl-1,2,3,4-tetrahydroquinoxaline (4dc): Flash column chromatography eluent, toluene/ethyl acetate =90/1; reaction time =24 h; yield: 42 mg (78%); yellow oil; $[\alpha]_{D}^{20}$: -78.3 (*c* 0.7, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ =7.31 (d, *J*=8.4 Hz, 2H), 6.91 (d, *J*= 8.4 Hz, 2H), 6.40 (d, *J*=5.2 Hz, 2H), 4.40 (d, *J*=6.0 Hz, 1H), 3.82 (s, 3H), 3.64 (s, 2H), 3.39 (dd, *J*=10.8, 2.4 Hz, 1H), 3.29–3.24 (m, 1H), 2.14 (s, 6H); ¹³C NMR (100 MHz, CDCl₃): δ =159.2, 134.2, 132.2, 130.5, 128.1, 126.8, 126.4, 116.7, 116.1, 113.9, 55.3, 54.5, 49.7, 18.9; IR (KBr): v=3357, 2916, 2856, 1608, 1558, 1514, 1457, 1304, 1248, 1175, 1108, 1032, 863, 832 cm⁻¹; ESI-FT-MS: *m*/*z*=269.1643, exact mass calcd. for (C₁₇H₂₀N₂O+H)⁺: 269.1654; enantiomeric excess: 98%, determined by HPLC (Daicel Chirapak AD-H, hexane/2-propanol=70/30, flow rate 1.0 mLmin⁻¹, *T*=30 °C, 254 nm): t_R=12.863 min (minor), t_R=16.490 min (major).

(*R*)-2-Methyl-1,2,3,4-tetrahydroquinoxaline (4ak): Flash column chromatography eluent, petroleum ether/ethyl acetate = 10/1; Reaction time = 24 h; yield: 25.5 mg (86%); yellow solid; mp 42–43 °C; $[\alpha]_{D}^{20}$: 49.4 (*c* 2.2, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ =6.64–6.55 (m, 2H), 6.50 (dd, *J*=9.1, 4.2 Hz, 2H), 3.46–3.55 (m, 1H), 3.32 (d, *J*= 10.4 Hz, 1H), 3.09–2.99 (m, 1H), 1.19 (d, *J*=6.3 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ =133.6, 133.2, 118.7, 118.7, 114.5, 114.5, 48.2, 5.7, 19.9; IR (KBr): v=3358, 3312, 3041, 2956, 2924, 2848, 1602, 1516, 1343, 743, 677, 587, 559 cm⁻¹; ESI-FT-MS: *m/z* 149.1092, exact mass calcd. for (C₉H₁₂N₂ + H)⁺: 149.1079; enantiomeric excess: 70%, determined by HPLC (Daicel Chirapak AD-H, hexane/2-propanol=70/30, flow rate 1.0 mLmin⁻¹, *T*=30 °C, 254 nm): t_R=5.797 min (major), t_R=6.253 min (minor).

(R)-Ethyl 3-phenyl-1,2,3,4-tetrahydroquinoxaline-6-carboxylate (4ea): Flash column chromatography eluent, toluene/ethyl acetate = 120/1; reaction time = 24 h; yield: 24 mg (42%); yellow solid; mp 146–147°C; $[\alpha]_{D}^{20}$: -66.7 (c 0.8, CHCl₃); ¹H NMR (400 MHz, CDCl₃): $\delta = 7.42-7.38$ (m, 2H), 7.36 (d, J = 6.6 Hz, 3H), 7.33 (dd, J = 4.9, 3.6 Hz, 1H), 7.28 (d, J=1.8 Hz, 1 H), 6.51 (d, J=8.2 Hz, 1 H), 4.43 (dd, J=8.2, 1 H)3.2 Hz, 1 H), 4.30 (q, J=7.1 Hz, 2 H), 3.52 (dd, J=11.2,3.2 Hz, 1 H), 3.38 (dd, J = 11.2, 8.2 Hz, 1 H), 1.35 (t, J =7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 166.9$, 141.1, 137.3, 132.7, 128.7, 128.1, 126.9, 121.7, 119.8, 115.3, 112.7, 60.2, 53.9, 48.8, 14.4; IR (KBr): v=2922, 2851, 1725, 1675, 1603, 1488, 1455, 1367, 1224, 1139, 1104, 1024, 765 cm^{-1} ; ESI-FT-MS: m/z = 283.1452, exact mass calcd. for (C₁₇H₁₈N₂O₂+H)⁺: 283.1447; enantiomeric excess: 79%, determined by HPLC (Daicel Chirapak AD-H, hexane/2-propanol = 70/30, flow rate 1.0 mLmin⁻¹, T = 30 °C, 254 nm): t_R= 14.437 min (major), $t_R = 16.150$ min (minor).

(R)-Ethyl 2-phenyl-1,2,3,4-tetrahydroquinoxaline-6-carboxylate (4ea'): Flash column chromatography eluent, toluene/ethyl acetate = 120/1; reaction time = 24 h; yield: 7.3 mg (13%); yellow solid; mp 136–137°C; $[\alpha]_D^{20}$: -7.1 (c 4.2, CHCl₃); ¹H NMR (400 MHz, CDCl₃): $\delta = 7.39$ (dd, J = 8.3, 1.8 Hz, 2H), 7.36 (q, J=2.6 Hz, 3H), 7.33 (d, J=6.7 Hz, 1H), 7.27 (d, J=1.8 Hz, 1H), 6.53 (d, J=8.2 Hz, 1H), 4.57 (dd, J=7.7, 3.2 Hz,1 H), 4.31 (q, J=7.1 Hz, 2 H), 3.49 (dd, J=11.1, 3.3 Hz, 1 H), 3.29 (dd, J=11.1, 7.8 Hz, 1 H), 1.36 (t, J = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 166.6$, 140.2, 139.3, 128.8, 128.4, 126.9, 123.8, 120.1, 117.7, 113.3, 60.3, 54.3, 48.0, 14.4; IR (KBr): v=3399, 2922, 2812, 1714, 1685, 1618, 1523, 1368, 1290, 1093, 1023, 767, 682, 620 cm^{-1} ; ESI-FT-MS: m/z = 283.1455, exact mass calcd. for $(C_{17}H_{18}N_2O_2 + H)^+$: 283.1447; enantiomeric excess: 90%, determined by HPLC (Daicel Chirapak AD-H, hexane/2-propanol=70/30, flow rate 1.0 mLmin⁻¹, T=30 °C, 254 nm): t_R= 18.607 min (major), $t_R = 15.643$ min (minor).

(R)-2-Phenyl-7-(trifluoromethyl)-1,2,3,4-tetrahydroquinoxaline (4fa): Flash column chromatography eluent, toluene/ethyl acetate = 120/1; reaction time = 24 h; yield: 21 mg (39%); yellow solid; mp 112–113 °C; $[\alpha]_D^{20}$: -109.4 (c 0.6, CHCl₃); ¹H NMR (400 MHz, CDCl₃): $\delta = 7.39$ (t, J = 4.1 Hz, 1H), 7.37 (s, 3H), 7.35–7.30 (m, 1H), 6.91–6.84 (m, 1H), 6.77 (d, J=1.7 Hz, 1 H), 6.57 (d, J=8.1 Hz, 1 H), 4.52 (dd, J = 7.9, 3.2 Hz, 1 H), 4.19 (s, 1 H), 3.49 (dd, J = 11.1, 3.2 Hz, 1 H), 3.31 (dd, J = 11.0, 7.9 Hz, 1 H); ¹³C NMR (100 MHz, $CDCl_3$): $\delta = 140.9, 136.9, 131.7, 129.3, 128.7, 128.2, 127.7,$ 126.8, 120.4, 116.4, 113.3, 111.3, 54.4, 48.4; IR (KBr): v= 3424, 3405, 2921, 2852, 1614, 1598, 1494, 1462, 1356, 1087, 864, 802, 705 cm⁻¹; ESI-FT-MS: m/z = 279.1121, exact mass calcd. for $(C_{15}H_{13}F_3N_2+H)^+$: 279.1109; enantiomeric excess: 90%, determined by HPLC (Daicel Chirapak AD-H, hexane/2-propanol = 70/30, flow rate 1.0 mLmin⁻¹, T = 30 °C, 254 nm): $t_R = 6.983 \text{ min (major)}, t_R = 6.197 \text{ min (minor)}.$

(*R*)-2-Phenyl-6-(trifluoromethyl)-1,2,3,4-tetrahydroquinoxaline (4fa'): Flash column chromatography eluent, toluene/ethyl acetate = 120/1; reaction time = 24 h; yield: 17 mg (31%); yellow oil; $[\alpha]_D^{20}$: 181.8 (*c* 0.3, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ =7.42–7.32 (m, 5H), 6.88 (d, *J*= 8.1 Hz, 1H), 6.78 (d, *J*=1.5 Hz, 1H), 6.55 (d, *J*=8.1 Hz, 1H), 4.46 (dd, *J*=8.1, 3.1 Hz, 1H), 4.13 (s, 1H), 4.04 (s, 1H), 3.50 (dd, *J*=11.1, 3.0 Hz, 1H), 3.35 (dd, *J*=11.1, 8.2 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ =140.7, 134.6,

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133.6, 128.8, 128.2, 126.9, 126.1, 123.4, 121.0, 120.7, 116.1, 116.0, 116.0, 113.8, 111.0, 110.9, 54.1, 48.4; IR (KBr): v = 3445, 3297, 2922, 2851, 1651, 1631, 1262, 1024, 803, 549 cm⁻¹; ESI-FT-MS: m/z 279.1116, exact mass calcd. for (C₁₅H₁₃F₃N₂+H)⁺: 279.1109; enantiomeric excess: 87%, determined by HPLC (Daicel Chirapak AD-H, hexane/2-propanol=70/30, flow rate 1.0 mL min⁻¹, T = 30 °C, 254 nm): t_R = 7.037 min (major), t_R = 8.533 min (minor).

(R)-7-Bromo-2-phenyl-1,2,3,4-tetrahydroquinoxaline

(4ga): Flash column chromatography eluent, toluene/ethyl acetate = 90/1; reaction time = 24 h; yield: 21.4 mg (37%); yellow solid; mp 86–87 °C; $[\alpha]_D^{20}$: -95.4 (*c* 0.4, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ =7.40–7.32 (m, 5H), 6.72–6.68 (m, 2H), 6.43 (d, *J*=8.0 Hz, 1H), 4.46 (d, *J*=7.6 Hz, 1H), 3.91 (s, 2H), 3.45 (d, *J*=11.2 Hz, 1H), 3.0–3.25 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ =141.2, 135.6, 131.4, 128.8, 128.1, 126.9, 121.0, 116.6, 115.9, 110.7, 54.4, 48.7; IR (KBr): v=3346, 3032, 2918, 2852, 1594, 1506, 1456, 1300, 1234, 1074, 794, 754, 698 cm⁻¹; ESI-FT-MS: *m*/*z*=289.0330, exact mass calcd. for (C₁₄H₁₃BrN₂+H)⁺: 289.0340; enantiomeric excess: 97%, determined by HPLC (Daicel Chirapak OD-H, hexane/2-propanol=80/20, flow rate 1.0 mLmin⁻¹, *T*=30 °C, 254 nm): t_R=14.403 min (major), t_R=17.820 min (minor).

(R)-6-Bromo-2-phenyl-1,2,3,4-tetrahydroquinoxaline

(4ga'): Flash column chromatography eluent, toluene/ethyl acetate = 90/1; reaction time = 24 h; yield: 27.7 mg (48%); yellow solid; mp 103–104 °C; $[\alpha]_{D}^{20}$: -59.4 (*c* 0.3, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ =7.37–7.33 (m, 5H), 6.72–6.60 (m, 2H), 6.43 (d, *J*=8.2 Hz, 1H), 4.43 (d, *J*=8.0 Hz, 1H), 3.88 (s, 2H), 3.45 (d, *J*=10.8 Hz, 1H), 3.32–3.27 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ =141.2, 133.9, 133.0, 128.7, 128.1, 126.9, 121.2, 116.8, 115.5, 110.3, 54.4, 48.6; IR (KBr): v=3407, 3360, 3059, 3030, 2919, 2856, 1596, 508, 1455, 1301, 1249, 1074, 791, 757 cm⁻¹; ESI-FT-MS: *m*/*z*=289.0330, exact mass calcd. for (C₁₄H₁₃BrN₂+H)⁺: 289.0340; enantiomeric excess: 94%, determined by HPLC (Daicel Chirapak OD-H, hexane/2-propanol=80/20, flow rate 1.0 mLmin⁻¹, *T*=30 °C, 254 nm): t_R=13.920 min (major), t_R=17.100 min (minor).

(R)-7-Methoxy-2-phenyl-1,2,3,4-tetrahydroquinoxaline

(4ha): Flash column chromatography eluent, toluene/ethyl acetate = 120/1; reaction time = 24 h; yield: 12.6 mg (26%); yellow solid; mp 76–77 °C; $[\alpha]_D^{20}$: 54.1 (c 1.1, CHCl₃); ¹H NMR (400 MHz, CDCl₃): $\delta = 7.42 - 7.34$ (m, 4 H), 7.34– 7.27 (m, 1H), 6.54 (d, J=8.3 Hz, 1H), 6.22 (dd, J=13.1, 2.4 Hz, 2H), 4.48 (dd, J=7.7, 2.5 Hz, 1H), 3.73 (s, 3H), 3.42 (dd, J=11.1, 2.4 Hz, 1 H), 3.31–3.22 (m, 1 H); ¹³C NMR $(100 \text{ MHz}, \text{ CDCl}_3): \delta = 154.1, 141.6, 140.7, 135.8, 130.0,$ 129.1, 128.6, 127.9, 127.5, 126.9, 125.3, 116.7, 106.9, 103.5, 100.8, 55.6, 54.9, 49.3; IR (KBr): v=2923, 2852, 1619, 1509, 1494, 1455, 1413, 1375, 1216, 1173, 1118, 1025, 959, 830, 689 cm⁻¹; ESI-FT-MS: m/z = 241.1349, exact mass calcd. for $(C_{15}H_{16}N_{2}O + H)^{+}$: 241.1341; enantiomeric excess: 86%, determined by HPLC (Daicel Chirapak AD-H, hexane/2-propanol = 70/30, flow rate 1.0 mLmin⁻¹, T = 30 °C, 254 nm): t_R = 13.993 min (major), $t_R = 16.847$ min (minor).

(R)-6-Methoxy-2-phenyl-1,2,3,4-tetrahydroquinoxaline

(4ha'): Flash column chromatography eluent, toluene/ethyl acetate = 120/1; reaction time = 24 h; yield: 12.5 mg (26%); yellow solid; mp 90–91 °C; $[\alpha]_D^{20}$: -80.5 (*c* 0.9, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ = 7.43–7.28 (m, 5 H), 6.51 (d,

J=8.4 Hz, 1H), 6.21 (t, J=7.2 Hz, 2H), 4.40 (d, J=7.1 Hz, 1H), 3.73 (s, 3H), 3.44 (d, J=9.7 Hz, 1H), 3.38–3.28 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ =153.5, 143.2, 141.5, 133.7, 130.5, 129.7, 129.1, 128.6, 127.9, 127.0, 123.5, 115.4, 106.5, 103.8, 101.2, 55.6, 54.8, 49.1; IR (KBr): v=3522, 3445, 3298, 2922, 2850, 1730, 1600, 1518, 1455, 1320, 1213, 1124, 1027 cm⁻¹; ESI-FT-MS: *m/z*=241.1358, exact mass calcd. for (C₁₅H₁₆N₂O+H)⁺: 241.1341; enantiomeric excess: 89%, determined by HPLC (Daicel Chirapak IA-H, hexane/2-propanol=70/30, flow rate 1.0 mLmin⁻¹, *T*=30 °C, 254 nm): t_R= 11.760 min (major), t_R=10.713 min (minor).

(R)-3-Phenyl-3,4-dihydroquinoxalin-2(1H)-one (7aa): Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1; reaction time = 24 h; yield: 35.3 mg (79%); white solid; mp 145–146 °C; $[\alpha]_{D}^{20}$: +181.0 (*c* 0.2, MeOH); ¹H NMR (400 MHz, CDCl₃): $\delta = 8.86$ (s, 1 H), 7.42 (d, J =7.0 Hz, 2H), 7.34–7.31 (m, 3H), 6.92 (t, J=7.2 Hz, 1H), 6.78-6.67 (m, 3H), 5.07 (s, 1H), 4.30 (s, 1H); ¹³C NMR $(100 \text{ MHz}, \text{ CDCl}_3): \delta = 167.3, 139.0, 132.9, 128.8, 128.4,$ 127.2, 124.7, 124.1, 119.3, 115.6, 113.7, 60.6; IR (KBr): v= 3327, 3304, 3032, 1671, 1601, 1533, 1504, 1455, 766 cm⁻¹; ESI-FT-MS: m/z = 223.0873, exact mass calcd. for (C₁₄H₁₄N₂O-H)⁻: 223.0872; enantiomeric excess: 94%, determined by HPLC (Daicel Chirapak OD-H, hexane/2-propanol=80/20, flow rate 1.0 mLmin⁻¹, T = 30 °C, 254 nm): t_R= 23.467 min (major), t_R=14.143 min (minor).

(R)-3-Phenyl-3,4-dihydrobenzo[g]quinoxalin-2(1H)-one (7ba): Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1; reaction time = 24 h; yield: 42.7 mg (78%); white solid; mp 68–69 °C; $[\alpha]_D^{20}$: -105.8 (c 0.1, MeOH); ¹H NMR (400 MHz, acetone- d_6): $\delta = 9.61$ (s, 1 H), 7.61 (dd, J=18.2, 8.1 Hz, 2H), 7.47 (d, J=7.2 Hz, 2H), 7.34-7.23 (m, 5H), 7.22-7.16 (m, 2H), 6.17 (s, 1H), 5.14 (s, 1 H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 167.3$, 138.9, 132.9, 131.4, 129.6, 128.9, 128.6, 128.3, 127.0, 126.7, 126.2, 125.6, 125.3, 123.6, 111.6, 108.3, 60.7; IR (KBr): v = 3314, 3184, 3052, 2922, 1672, 1638, 1492, 1454, 757 cm⁻¹; ESI-FT-MS: *m*/ z 273.1031, exact mass calcd. for $(C_{18}H_{14}N_2O-H)^-$: 273.1028; enantiomeric excess: 97%, determined by HPLC (Daicel Chirapak OD-H, hexane/2-propanol=80/20, flow rate 1.0 mLmin⁻¹, T = 30 °C, 254 nm): $t_{\rm R} = 32.813$ min (major), $t_R = 27.367 \text{ min (minor)}$.

(*R*)-6,7-Dichloro-3-phenyl-3,4-dihydroquinoxalin-2(1*H*)one (7ca): Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1; reaction time = 24 h; yield: 36 mg (64%); white solid; mp 262–263 °C; $[\alpha]_D^{20}$: 190.5 (*c* 0.1, MeOH); ¹H NMR (400 MHz, acetone- d_6): δ = 9.71 (s, 1H), 7.44 (dd, *J*=8.2, 1.3 Hz, 2H), 7.40–7.35 (m, 2H), 7.34–7.29 (m, 1H), 7.07 (d, *J*=4.0 Hz, 2H), 6.37 (s, 1H), 5.13 (d, *J*= 1.9 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ =166.6, 138.3, 132.3, 129.0, 128.8, 128.3, 126.9, 121.8, 116.6, 114.7, 60.2; IR (KBr): v=3340, 3064, 2922, 2851, 1660, 1558, 1506, 1450, 1457, 755 cm⁻¹; ESI-FT-MS: *m/z* 291.0078, exact mass calcd. for (C₁₄H₁₀C₁₂N₂O–H)⁻: 291.0092; enantiomeric excess: 95%, determined by HPLC (Daicel Chirapak IA, hexane/2propanol=80/20, flow rate 1.0 mLmin⁻¹, *T*=30 °C, 254 nm): t_R=9.557 min (major), t_R=11.013 min (minor).

(*R*)-3-(4-Chlorophenyl)-3,4-dihydroquinoxalin-2(1*H*)-one (7ab): Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1; reaction time = 24 h; yield: 27.5 mg (53%); white solid; mp 203–204 °C; $[\alpha]_D^{20}$: -54.3 (*c* 0.2, MeOH); ¹H NMR (400 MHz, acetone-*d*₆): δ = 9.49 (s, 1 H),

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7.44 (d, J = 8.5 Hz, 2H), 7.38–7.29 (m, 2H), 6.92–6.79 (m, 3H), 6.76–6.64 (m, 1H), 5.96 (s, 1H), 5.04 (d, J = 1.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 166.9$, 137.3, 134.4, 132.6, 130.9, 128.9, 128.6, 124.6, 124.2, 119.6, 115.7, 113.8, 60.0; IR (KBr): v = 3416, 3055, 2923, 1614, 1518, 1504, 1470, 1421, 738 cm⁻¹; ESI-FT-MS: m/z 257.0483, exact mass calcd. for (C₁₄H₁₁ClN₂O-H)⁻: 257.0482; enantiomeric excess: 97%, determined by HPLC (Daicel Chirapak AD-H, hexane/2-propanol=70/30, flow rate 1.0 mLmin⁻¹, T = 30 °C, 254 nm): t_R = 9.170 min (major), t_R = 9.937 min (minor).

(R)-4-(3-Oxo-1,2,3,4-tetrahydrobenzo[g]quinoxalin-2-yl)benzonitrile (7ac): Flash column chromatography eluent, petroleum ether/ethyl acetate = 2/1; reaction time = 24 h; yield: 50.4 mg (84%); white solid; mp 236–237 °C; $[\alpha]_{D}^{20}$: -241.3 (c 0.5, MeOH); ¹H NMR (400 MHz, acetone- d_6): $\delta = 9.91$ (s, 1H), 7.79–7.68 (m, 4H), 7.63 (dd, J=15.5, 8.1 Hz, 2H), 7.37-7.25 (m, 3H), 7.24-7.18 (m, 1H), 6.45 (s, 1H), 5.30 (d, J=2.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 166.2$, 143.8, 132.6, 132.1, 131.4, 128.4, 127.9, 126.8, 125.7, 125.5, 123.9, 118.3, 112.5, 112.1, 108.7, 60.3; IR (KBr): v=3369, 3043, 2924, 1677, 1637, 1533, 1487, 1459, 734 cm⁻¹; ESI-FT-MS: m/z 298.0981, exact mass calcd. for $(C_{19}H_{13}N_3O-H)^-$: 298.0981; enantiomeric excess: 98%, determined by HPLC (Daicel Chirapak OD-H, hexane/2-propanol=75/25, flow rate 1.0 mL min⁻¹, T = 30 °C, 254 nm): $t_R = 34.437$ min (major), $t_R = 28.710 \text{ min}$ (minor).

(R)-3-[4-(tert-Butyl)phenyl]-3,4-dihydrobenzo[g]quinoxalin-2(1H)-one (7ad): Flash column chromatography eluent, petroleum ether/ethyl acetate = 12/1; reaction time = 24 h; yield: 53.1 mg (81%); white solid; mp 238–239°C; $[\alpha]_{\rm D}^{20}$: -45.0 (c 0.4, MeOH); ¹H NMR (400 MHz, CDCl₃): $\delta = 9.34$ (s, 1H), 7.59 (dd, J=20.5, 8.1 Hz, 2H), 7.39–7.27 (m, 5H), 7.27-7.20 (m, 1H), 7.15 (s, 1H), 7.03 (s, 1H), 5.14 (s, 1H), 1.24 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 167.9$, 151.6, 135.9, 132.6, 131.5, 128.5, 126.9, 126.7, 126.4, 125.9, 125.7, 125.2, 123.6, 111.9, 108.6, 60.4, 34.6, 31.2; IR (KBr): v =3376, 3049, 2959, 1679, 1638, 1530, 1488, 1393, 745 $\rm cm^{-1};$ ESI-FT-MS exact mass calcd. for $(C_{22}H_{22}N_2O-H)^-$: 329.1654; enantiomeric excess: 95%, determined by HPLC (Daicel Chirapak OD-H, hexane/2-propanol=70/30, flow rate 1.0 mLmin⁻¹, T = 30 °C, 254 nm): $t_{\rm R} = 16.703$ min (major), $t_R = 12.500 \text{ min (minor)}$.

(*R*)-3-(4-Methoxyphenyl)-3,4-dihydrobenzo[g]quinoxalin-2(1*H*)-one (7ae): Flash column chromatography eluent, petroleum ether/ethyl acetate =7/1; reaction time = 24 h; yield: 28.9 mg (48%); white solid; mp 202–203 °C; $[\alpha]_D^{20}$: -24.6 (*c* 0.2, MeOH); ¹H NMR (400 MHz, CDCl₃): δ =8.87 (s, 1 H), 7.60 (dd, *J*=19.4, 8.1 Hz, 2 H), 7.34–7.31 (m, 3 H), 7.25 (dd, *J*=8.8, 6.0 Hz, 1 H), 7.13 (s, 1 H), 7.02 (s, 1 H), 6.83 (d, *J*= 8.5 Hz, 2 H), 5.10 (s, 1 H), 3.74 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ =167.9, 159.8, 132.9, 131.5, 131.1, 128.4, 128.3, 126.8, 126.4, 125.7, 125.2, 123.6, 114.3, 111.7, 108.4, 60.2, 55.3; IR (KBr): v=3312, 3194, 3052, 2925, 2853, 1679, 1612, 1587, 1460, 1392, 745 cm⁻¹; enantiomeric excess: 94%, determined by HPLC (Daicel Chirapak AD-H, hexane/2-propanol=70/30, flow rate 1.0 mLmin⁻¹, *T*=30 °C, 254 nm): t_R= 21.927 min (major), t_R=17.413 min (minor).

(*R*)-3-(4-Chlorophenyl)-3,4-dihydrobenzo[*g*]quinoxalin-2(1*H*)-one (7bb): Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1; reaction time = 24 h; yield: 41.9 mg (68%); white solid; mp 93–94 °C; $[\alpha]_D^{20}$: -201.6 (*c* 0.3, MeOH); ¹H NMR (400 MHz, acetone-*d*₆): δ = 9.83 (s, 1 H), 7.62 (dd, J=18.0, 8.1 Hz, 2H), 7.51–7.46 (m, 2H), 7.39–7.31 (m, 3H), 7.28 (ddd, J=8.2, 6.9, 1.3 Hz, 1H), 7.25– 7.17 (m, 2H), 6.36 (s, 1H), 5.19–5.14 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 167.0$, 137.2, 134.6, 132.6, 131.4, 129.0, 128.4, 128.4, 126.8, 126.0, 125.7, 125.4, 123.7, 111.8, 108.5, 60.1; IR (KBr): v=3355, 3300, 3047, 2924,1683, 1597, 1530, 1489, 1393, 743 cm⁻¹; ESI-FT-MS: m/z=307.0635, exact mass calcd. for (C₁₈H₁₃ClN₂O–H)⁻: m/z=307.0638; enantiomeric excess: 99%, determined by HPLC (Daicel Chirapak AD-H, hexane/2-propanol=75/25, flow rate 1.0 mLmin⁻¹, T=30°C, 254 nm): t_R=16.067 min (major), t_R=13.707 min (minor).

(*R*)-6,7-Dichloro-3-(4-chlorophenyl)-3,4-dihydroquinoxalin-2(1*H*)-one (7cb): Flash column chromatography eluent, petroleum ether/ethyl acetate = 7/1; reaction time = 24 h; yield: 30.8 mg (47%); white solid; mp 240–241 °C; $[\alpha]_D^{20}$: +88.6 (*c* 0.2, MeOH); ¹H NMR (400 MHz, acetone-*d*₆): δ = 9.69 (s, 1 H), 7.46–7.41 (m, 2 H), 7.40–7.35 (m, 2 H), 7.04 (d, *J* = 4.6 Hz, 2 H), 6.35 (s, 1 H), 5.12 (d, *J* = 2.0 Hz, 1 H); ¹³C NMR (100 MHz, CDCl₃): δ = 166.1, 136.6, 134.8, 132.0, 129.1, 128.3, 127.0, 124.1, 122.1, 116.7, 114.8, 59.5; IR (KBr): v=3303, 3130, 2923, 1734, 1666, 1594, 1494, 1464, 1403 cm⁻¹; ESI-FT-MS: *m/z* 324.9692, exact mass calcd. for (C₁₄H₁₉C₁₃N₂O–H)⁻: 324.9702; enantiomeric excess: 97%, determined by HPLC (Daicel Chirapak OD-H, hexane/2-propanol = 80/20, flow rate 1.0 mLmin⁻¹, *T* = 30 °C, 254 nm): t_R = 12.580 min (major), t_R = 15.173 min (minor).

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