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Diisopropyl L-Malate as a New Chiral Auxiliary for Dynamic Kinetic Resolution of α-Bromo Esters and Asymmetric Syntheses of Aminoflavones and Dihydroquinoxalinones

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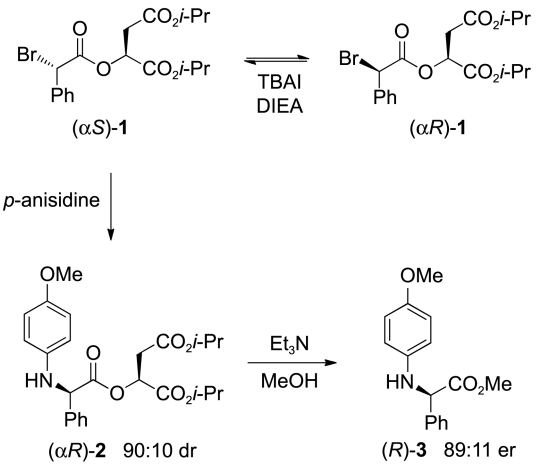
Malic acid is the active ingredient in many sour foods and found mostly in unripe fruits. The dicarboxylic acid is relatively inexpensive and commercially available in both enantiomeric forms. The application of malic acid derivatives as a chiral auxiliary is, however, not well known in the area of asymmetric synthesis.[1] We herein report the first example of L-malate-mediated dynamic kinetic resolution of α-bromo esters in nucleophilic substitution with various arylamines.[2]

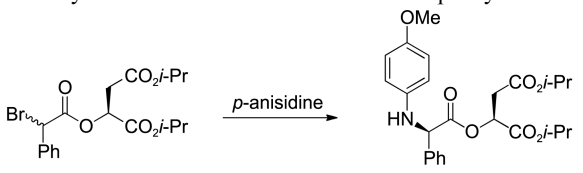
Treatment of diisopropyl L-malate with racemic α-bromo phenylacetic acid in the presence of DCC and DMAP provided α-bromo phenylacetate (α*RS*)-**1** in 77% yield with about 50:50 diastereomeric ratio (dr). When the two diastereomeric mixture of (α*RS*)-**1** was treated with *p*-anisidine (1.5 equiv), tetrabutylammonium iodide (TBAI, 1.0 equiv) and diisopropylethylamine (DIEA, 1.0 equiv) in CH_2Cl_2 at room temperature for 12 h, *N*-aryl amino ester **2** was produced in 81% yield with 90:10 dr as shown in Scheme 1. Subsequent removal of diisopropyl L-malate with MeOH and Et_3N gave *N*-aryl phenylglycinate (*R*)-**3** in 71% yield with 89:11 enantiomeric ratio (er).[3a,c] The yield and stereoselectivity of the substitution imply that α-bromo stereogenic center is configurationally labile with respect to the rate of substitution and (α*RS*)-**1** is dynamically resolved under the reaction condition.



Scheme 1. Nucleophilic substitution with *p*-anisidine.

In order to understand the effect of additives and reaction pathway, we carried out a series of reactions as shown in Table 1. In the absence of both TBAI and DIEA, the substitution of **1** was very slow to provide **2** with 71:29 dr in 27% yield after 12 h (entry 1). Also, the rate of the substitution was substantially decreased in the absence of DIEA to provide **2** in 47% yield with 90:10 dr, whereas the reaction in the absence of TBAI gave **2** with both lower yield and stereoselectivity (entries 2-3). The results in entries 1-3 show the importance of the presence of halide ion and base for sufficient rate acceleration and selectivity. When the mixture of two diastereomers of **1** (70:30 dr) was allowed to reach thermodynamic equilibrium in the presence of TBAI and DIEA, the diastereomeric ratio of recovered **1** was analyzed by ^{1}H NMR, and determined to be 51:49 (entry 4). The result implies that α-bromo phenylacetate **1** is configurationally labile under the reaction condition and the thermodynamic stabilities of two diastereomers are almost same, ruling out dynamic thermodynamic resolution as a primary pathway.[2] In the reaction of **1** (75:25 dr) with *p*-anisidine, DIEA and

Table 1. Dynamic kinetic resolution of α-bromo phenylacetate **1**



Entry	Substrate (dr)[a]	Additive	Yield (%)[b]	Product (dr)[a]
1	**1** (50:50)	None	27	**2** (71:29)
2	**1** (50:50)	TBAI	47	**2** (90:10)
3	**1** (50:50)	DIEA	41	**2** (83:17)
4	**1** (70:30)[c]	DIEA, TBAI	88	**1** (51:49)
5	**1** (75:25)[c]	DIEA, TBAI	79	**2** (89:11)
6	**2** (80:20)[c]	DIEA, TBAI	87	**2** (80:20)

[a]The drs are determined by ^{1}H NMR. [b]Isolated yields after 12 h. [c]The diastereomeric mixtures are prepared by column chromatography with fractional collection.

TBAI as shown in entry 5, almost same dr of **2** (89:11 dr) was observed as in the reaction of **1** of 50:50 dr shown in Scheme 1. Thus, the dr of product **2** is not dependent on the starting ratio of two diastereomers of **1**. When the configurational stability of **2** (80:20 dr) under the reaction condition was examined by the treatment with *p*-anisidine (1.5 equiv), TBAI (1.0 equiv) and DIEA (1.0 equiv) in CH_2Cl_2 for 12 h, no epimerization was detected by ^{1}H-NMR, which can rule out the possibility of epimerization after the nucleophilic substitution reaction (entry 6). To summarize the results in Table 1, we have found that the epimerization promoted by TBAI and DIEA is sufficiently fast with respect to the rate of substitution and the primary pathway of the asymmetric induction is a dynamic kinetic resolution.

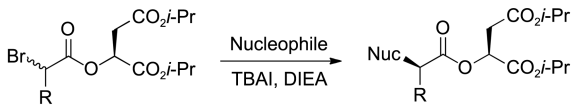
The scope of the dynamic kinetic resolution has been investigated with various substrates and arylamines as shown in Table 2. The treatment of α-bromo propanoate **4** with *p*-anisidine (1.5 equiv) in CH_2Cl_2 for 12 h at room temperature gave *N*-aryl amino ester **6** in 60% yield with 83:17 dr (entry 1). Under the same reaction condition, the reactions of α-bromo butanoate **5** gave amino ester **7** with 85:15 dr (entry 2). The reactions of **1** and **4** with *o*-anisidine as a nucleophile provided *N*-aryl amino esters **8** and **9** with slightly lower stereoselectivities compared to the reactions with *p*-anisidine (entries 3-4). In the reactions with two different aminoanthracenes, *N*-anthracenyl amino ester **10** of 86:14 dr was obtained with 1-aminoanthracene (entry 5), whereas 2-aminoanthracene gave slightly higher stereoselectivities (entry 6).

In the context of our continuing investigation on the stereoselective preparation of flavonoid derivatives and their activity studies,[4] we have attempted to synthesize enantioenriched *N*-alkylated aminoflavones **12-14** as shown in entries 7-9. When α-bromo phenylacetate **1** was treated with 6-aminoflavone, DIEA and TBAI for 12 h, the substitution provided aminoflavone derivative **12** in 74% yield with 87:13 dr. Analogous to the reactions of **4** with *p*-anisidine and *o*-anisidine, the reaction of **4** with 6-aminoflavone gave lower selectivity of 82:18 dr (entries 7-8). Also, the substitution of **1** with 7-aminoflavone provided aminoflavone derivative **14** in 64% yield with 83:17 dr under the same condition (entry 9) and the reactions of **4** with 7-aminoflavone did not provide the substituted product. Thus, limited results in Table 2 indicate that α-substituent of substrate and substituents of arylamine have significant effects on the stereoselectivity of nucleophilic substitution.

With the identification of diisopropyl L-malate as an effective and convenient stereocontrolling element for the reactions of α-bromo acetates with various arylamines, we examined the dynamic kinetic resolution in substitutions with various 1,2-diaminobenzene nucleophiles for asymmetric syntheses of dihydroquinoxalinones as shown in Table 3. Dihydroquinoxalinone structural cores are of interest as important pharmacophores in many biologically active compounds and there is growing interest in the preparation of them.[5] When α-bromo phenylacetate **1** was treated with 1,2-phenylenediamine, TBAI and DIEA in CH_2Cl_2 for 24 h at room temperature, the substitution and following spontaneous cyclization gave 3-phenyl dihydroquinoxalinone **15** in 85% yield with 88:12 er (entry 1). Notably, treatment of α-bromo ester **1** with 2,3-diaminotoluene that is non-symmetric diaminobenzene nucleophile gave 3-phenyl-8-methyl dihydroquinoxalinone (**16**) as a major product with 84:16 er and no trace of the regioisomer was detected (entry 2). The regioselectivity suggests significantly different reactivities of two amino groups in the reaction of α-bromo phenylacetate **1**. The sterically less hindered amino group of the nucleophile is more reactive than the amino group with two *ortho*-substituents. The regiochemistry of **16** was assigned by comparison to the ^{1}H-NMR of authentic material individually prepared.[3b] Treatment of **1** with 4,5-dimethyl-*o*-phenylenediamine, TBAI and DIEA for 24 h at room temperature gave 3-phenyl dihydroquinoxalinone (**18**) in 79% yield with 88:12 er (entry 4), whereas the reactions of α-bromo butanoate **5** with 4,5-dimethyl-*o*-phenylenediamine took place to afford 3-ethyl substituted dihydroquinoxalinones **17** with lower stereoselectivity of 78:22 er (entry 3). When the reaction of **1** with 1,2-phenylenediamine were carried out in CH_3CN, **15** was obtained with lower yield (40%) and lower enantioselectivity (81:19 er) compared to the reaction in CH_2Cl_2.

In this paper, we report that diisopropyl L-malate is a new effective chiral auxiliary for dynamic kinetic resolution of α-bromo esters in nucleophilic substitution with arylamines. The methodology can provide a general procedure for asymmetric syntheses of various *N*-aryl (*R*)-amino acid derivatives. In addition, the substitution with 1,2-diaminobenzene and subsequent spontaneous cyclization can provide an efficient method for asymmetric syntheses of dihydroquinoxalinones. We have found that the stereoselectivity of the substitution depends critically on the structure of arylamine and α-substituent of substrate. Simple and easy procedure in obtaining optically active *N*-aryl amino esters suggests that diisopropyl L-malate-mediated nucleophilic substitution

Table 2. Substitutions with various arylamine nucleophiles



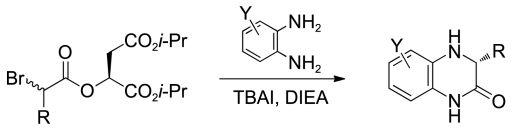
1 (R = Ph)
4 (R = Me)
5 (R = Et)

6-14

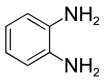
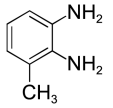
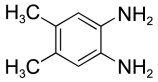
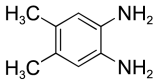
Entry[a]	R	Nucleophile	Yield[b] (%)	dr[c]
1	Me	*p*-anisidine	60 (**6**)	83:17
2	Et	*p*-anisidine	80 (**7**)	85:15
3	Ph	*o*-anisidine	80 (**8**)	84:16
4	Me	*o*-anisidine	66 (**9**)	82:18
5	Ph	1-aminoanthracene	49 (**10**)	86:14
6	Ph	2-aminoanthracene	51 (**11**)	88:12
7	Ph	6-aminoflavone	74 (**12**)	87:13
8	Me	6-aminoflavone	60 (**13**)	82:18
9	Ph	7-aminoflavone	64 (**14**)	83:17

[a]All reactions were carried out in CH_2Cl_2. [b]Isolated yields. [c]The drs are determined by ^{1}H NMR of reaction mixture.

Table 3. Asymmetric syntheses of dihydroquinoxalinones



1 and **5** **15-18**

Entry[a]	R	Nucleophile	Yield (%)[b]	er (*R*:*S*)[c]
1	Ph		85 (**15**)	88:12
2	Ph		71 (**16**)	84:16
3	Et		69 (**17**)	78:22
4	Ph		79 (**18**)	88:12

[a]All reactions were carried out in CH_2Cl_2. [b]Isolated yields after 24 h. [c]The ers are determined by CSP-HPLC (Chiralcel OJ-H column).

should be further developed.

Experimental

General Procedure for the Asymmetric Nucleophilic Substitution *via* Dynamic Kinetic Resolution. To a solution of α-bromo ester (**1**, **4** and **5**) in CH_2Cl_2 (*ca*. 0.1 M) at room temperature were added DIEA (1.0 equiv), TBAI (1.0 equiv) and an arylamine nucleophile (1.5 equiv). After the resulting reaction mixture was stirred at room temperature for 12-24 h, the solvent was evaporated and the crude material was purified by column chromatography to give a α-amino ester. The drs of **2** and **6-14** were determined by ^{1}H NMR integration of hydrogens of two diastereomers and the ers of **3** and **15-18** were determined by chiral stationary phase HPLC.

2-(*p*-Methoxyanilino)-(*R*)-phenylacetic Acid L-Diisopropyl Malate Ester (2). A yellow oil was obtained in 81% yield. ^{1}H NMR ($CDCl_3$, 400 MHz, major diastereomer) 7.48 (m, 2H), 7.32 (m, 3H), 6.73 (d, J = 7.2 Hz, 2H), 6.56 (d, J = 7.2 Hz, 2H), 5.43 (t, J = 6.0 Hz, 1H), 5.11 (s, 1H), 5.07 (m, 1H), 4.78 (m, 1H), 3.71 (s, 3H), 2.74 (d, J = 6.4 Hz, 2H), 1.28-1.01 (m, 12H); ^{13}C NMR ($CDCl_3$, 100 MHz, major diastereomer) 171.1, 168.1, 167.9, 152.5, 140.1, 137.3, 128.9, 128.4, 127.5, 114.8, 114.7, 69.9, 69.5, 68.7, 61.5, 55.7, 36.4, 21.8, 21.6. For removal of chiral auxiliary, the mixture of **2** and Et_3N (10 equiv) in methanol (0.05 M) was stirred at room temperature for a day. The solvent was evaporated and the crude material was purified by column chromatography to give (*R*)-**3** in 71% yield. ^{1}H NMR ($CDCl_3$, 400 MHz) 7.48-7.25 (m, 5H), 6.69 (d, J = 8.9 Hz, 2H), 6.52 (d, J = 8.9 Hz, 2H), 5.00 (s, 1H), 4.67 (br, 1H), 3.72 (s, 3H), 3.67 (s, 3H). The spectral data of **3** were identical to those of the authentic material reported in ref. 3. Chiral HPLC: 87:13 er, t_R (*R*)-major enantiomer, 67.2 min; t_R (*S*)-minor enantiomer, 76.3 min (Chiralcel OJ-H column; 20% 2-propanol in hexane; 0.5 mL/min).

2-(*p*-Methoxyanilino)-(*R*)-Propanoic Acid L-Diisopropyl Malate Ester (6). A yellow oil was obtained in 60% yield. ^{1}H NMR ($CDCl_3$, 400 MHz, major diastereomer) 6.74 (d, J = 7.2 Hz, 2H), 6.60 (d, J = 7.2 Hz, 2H), 5.44 (m, 1H), 5.05 (m, 1H), 4.97 (m, 1H), 4.14 (q, J = 6.8 Hz, 1H), 3.73 (s, 3H), 2.80 (m, 2H), 1.49 (d, J = 6.8 Hz, 3H), 1.21 (m, 12H); ^{13}C NMR ($CDCl_3$, 100 MHz, major diastereomer) 173.8, 168.4, 168.0, 152.8, 140.6, 115.1, 114.9, 69.7, 68.9, 68.8, 55.7, 52.9, 36.5, 21.7, 21.6, 19.0.

2-(*p*-Methoxyanilino)-(*R*)-Butanoic Acid L-Diisopropyl Malate Ester (7). A pale yellow oil was obtained in 80% yield. ^{1}H NMR ($CDCl_3$, 400 MHz, major diastereomer) 6.75 (d, J = 7.2 Hz, 2H), 6.61 (d, J = 7.2 Hz, 2H), 5.44 (t, J = 6.4 Hz, 1H), 5.04 (m, 1H), 4.97 (m, 1H), 4.01 (t, J = 6.4 Hz, 1H), 3.73 (s, 3H), 2.80 (d, J = 6.4 Hz, 2H), 1.91-1.78 (m, 2H), 1.22 (m, 12H), 1.04 (t, J = 7.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, major diastereomer) 173.4, 168.5, 168.1, 152.7, 140.8, 115.3, 114.9, 69.9, 68.9, 68.6, 58.8, 55.7, 36.6, 26.2, 21.7, 21.5, 10.1.

2-(*o*-Methoxyanilino)-(*R*)-Phenylacetic Acid L-Diisopropyl Malate Ester (8). A yellow oil was obtained in 80% yield. ^{1}H NMR ($CDCl_3$, 400 MHz, major diastereomer) 7.51 (m, 2H), 7.33 (m, 3H), 6.73 (m, 3H), 6.41 (m, 1H), 5.43 (t, J = 6.0 Hz, 1H), 5.36 (d, J = 6.0 Hz, 1H), 5.16 (d, J = 6.0 Hz, 1H), 5.07 (m, 1H), 4.79 (m, 1H), 3.86 (s, 3H), 2.74 (d, J = 6.4 Hz, 2H), 1.25-1.00 (m, 12H); ^{13}C NMR ($CDCl_3$, 100 MHz, major diastereomer) 170.8, 168.1, 167.9, 147.0, 137.2, 135.9, 128.8, 128.3, 127.5, 121.1, 117.5, 110.7, 109.5, 69.8, 69.5, 68.7, 60.6, 55.4, 36.4, 21.6, 21.5.

2-(*o*-Methoxyanilino)-(*R*)-Propanoic Acid L-Diisopropyl Malate Ester (9). A pale yellow oil was obtained in 66% yield. ^{1}H NMR ($CDCl_3$, 400 MHz, major diastereomer) 6.84-6.55 (m, 4H), 5.45 (m, 1H), 5.06 (m, 1H), 4.96 (m, 1H), 4.65 (br, 1H), 4.21 (m, 1H), 3.85 (s, 3H), 2.81 (m, 2H), 1.54 (d, J = 6.8 Hz, 3H), 1.22 (m, 12H); ^{13}C NMR ($CDCl_3$, 100 MHz, major diastereomer) 173.4, 168.5, 168.1, 152.7, 140.8, 115.3, 114.9, 69.7, 69.0, 68.8, 55.4, 51.6, 36.5, 21.7, 21.6, 18.9.

2-(1-Anthracenylamino)-(*R*)-Phenylacetic Acid L-Diisopropyl Malate Ester (10). A yellow oil was obtained in 49% yield. ^{1}H NMR ($CDCl_3$, 400 MHz, major diastereomer) 8.55 (s, 1H), 8.35 (s, 1H), 8.06 (m, 1H), 7.98 (m, 1H), 7.62-7.21 (m, 9H), 6.32 (d, J = 7.2 Hz, 1H), 5.51 (t, J = 6.0 Hz, 1H), 5.43 (s, 1H), 5.10 (m, 1H), 4.78 (m, 1H), 2.80 (d, J = 6.0 Hz, 2H), 1.25 (m, 6H), 1.10 (d, J = 6.0 Hz, 3H), 1.02 (d, J = 6.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, major diastereomer) 171.0, 168.0, 167.9, 140.5, 136.8, 131.6, 131.0, 129.0, 128.5, 127.8, 127.4, 126.7, 125.9, 125.6, 125.2, 118.9, 118.4, 103.6, 70.0, 69.8, 68.9, 60.8, 36.4, 31.0, 21.7.

2-(2-Anthracenylamino)-(*R*)-Phenylacetic Acid L-Diisopropyl Malate Ester (11). A yellow oil was obtained in 51% yield. ^{1}H NMR ($CDCl_3$, 400 MHz, major diastereomer) 8.22 (s, 1H), 8.05 (s, 1H), 7.83 (m, 3H), 7.58 (m, 2H), 7.36 (m, 5H), 7.03 (m, 1H), 6.73 (s, 1H), 5.47 (t, J = 6.0 Hz, 1H),

5.34 (s, 1H), 5.08 (m, 2H), 4.77 (m, 1H), 2.77 (d, J = 6.4 Hz, 2H), 1.29-1.00 (m, 12H); ^{13}C NMR ($CDCl_3$, 100 MHz, major diastereomer) 171.0, 168.0, 167.9, 142.6, 136.8, 133.2, 132.4, 129.7, 129.5, 129.0, 128.6, 128.2, 127.6, 127.4, 126.1, 125.3, 123.8, 123.1, 120.1, 103.3, 70.0, 69.7, 68.8, 60.9, 36.4, 31.6, 21.6, 21.5.

2-[(4-Oxo-2-phenyl-4*H*-chromem-6-yl)amino]phenyl-acetic Acid L-Diisopropyl Malate Ester (12). A colorless oil was obtained in 74% yield. ^{1}H NMR ($CDCl_3$, 400 MHz, major diastereomer) 7.87 (m, 2H), 7.53-7.23 (m, 10H), 7.02 (m, 1H), 6.74 (s, 1H), 5.44 (m, 1H), 5.32 (d, J = 6.0 Hz, 1H), 5.19 (d, J = 6.0 Hz, 1H), 5.09 (m, 1H), 4.81 (m, 1H), 2.76 (d, J = 6.4 Hz, 2H), 1.24 (d, J = 6.4 Hz, 3H), 1.20 (d, J = 6.4 Hz, 3H), 1.12 (d, J = 6.4 Hz, 3H), 1.05 (d, J = 6.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, major diastereomer) 178.3, 170.6, 168.0, 167.7, 162.7, 149.8, 143.3, 136.4, 132.1, 131.3, 129.0, 128.9, 128.6, 127.3, 126.2, 124.7, 121.1, 119.1, 106.7, 105.7, 70.0, 69.9, 68.8, 60.4, 36.2, 29.7, 21.6.

2-[(4-Oxo-2-phenyl-4*H*-chromem-6-yl)amino]propanoic Acid L-Diisopropyl Malate Ester (13). A colorless oil was obtained in 60% yield. ^{1}H NMR ($CDCl_3$, 400 MHz, major diastereomer) 7.91 (m, 2H), 7.52 (m, 3H), 7.44 (d, J = 8.8 Hz, 1H), 7.31 (m, 1H), 7.04 (dd, J = 2.8 and 8.8 Hz, 1H), 6.78 (s, 1H), 5.46 (m, 1H), 5.05 (m, 1H), 4.98 (m, 1H), 4.41 (m, 1H), 2.86 (m, 2H), 1.55 (d, J = 6.4 Hz, 3H), 1.23 (m, 12H); ^{13}C NMR ($CDCl_3$, 100 MHz, major diastereomer) 178.4, 173.0, 168.4, 167.9, 162.8, 150.0, 144.0, 132.1, 131.3, 129.0, 126.2, 124.8, 121.3, 119.2, 106.7, 105.3, 69.9, 69.3, 68.8, 51.9, 36.4, 21.8, 21.6, 18.7.

2-[(4-Oxo-2-phenyl-4*H*-chromem-7-yl)amino]phenyl-acetic Acid L-Diisopropyl Malate Ester (14). A colorless oil was obtained in 64% yield. ^{1}H NMR ($CDCl_3$, 400 MHz, major diastereomer) 7.99 (d, J = 8.8 Hz, 1H), 7.81 (m, 2H), 7.53-7.41 (m, 8H), 6.71 (m, 1H), 6.69 (s, 1H), 6.51 (d, J = 2.1 Hz, 1H), 5.48 (m, 2H), 5.28 (d, J = 5.6 Hz, 1H), 5.09 (m, 1H), 4.79 (m, 1H), 2.79 (d, J = 6.0 Hz, 2H), 1.22 (m, 6H), 1.12 (d, J = 6.0 Hz, 3H), 1.04 (d, J = 6.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, major diastereomer) 177.7, 170.0, 167.9, 167.7, 162.4, 158.4, 150.0, 135.7, 132.1, 131.1, 129.2, 128.9, 128.8, 127.3, 126.9, 126.1, 115.7, 113.4, 107.4, 98.3, 70.2, 69.9, 68.9, 60.1, 36.3, 31.0, 21.6.

3-Phenyl-3,4-dihydro-1,4-quinoxalin-2-one (15). A white solid was obtained in 85% yield. ^{1}H NMR ($CDCl_3$, 400 MHz) 7.95 (br, 1H), 7.43-6.70 (m, 9H), 5.08 (s, 1H), 4.28 (br, 1H). The spectral data were identical to those of the authentic material reported in ref. 3. Chiral HPLC: 88:12 er, t_R (*R*)-major enantiomer, 39.3 min; t_R (*S*)-minor enantiomer, 44.0 min (Chiralcel OJ-H column; 20% 2-propanol in hexane; 0.5 mL/min).

8-Methyl-3-phenyl-3,4-dihydro-1,4-quinoxalin-2-one (16). A pale yellow oil was obtained in 71% yield. ^{1}H NMR ($CDCl_3$, 400 MHz) 8.45 (br, 1H), 7.40-7.23 (m, 5H), 6.82-6.55 (m, 3H), 5.00 (s, 1H), 4.30 (br, 1H), 2.16 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) 167.6, 139.3, 133.5, 131.4, 129.2, 127.6, 125.9, 124.0, 121.7, 119.2, 114.2, 61.0, 17.0. Chiral HPLC: 84:16 er, t_R (*R*)-major enantiomer, 35.8 min; t_R (*S*)-minor enantiomer, 42.0 min (Chiralcel OJ-H column; 20% 2-propanol in hexane; 0.5 mL/min).

6,7-Dimethyl-3-ethyl-3,4-dihydro-1,4-quinoxalin-2-one (17). A pale yellow oil was obtained in 69% yield. ^{1}H NMR ($CDCl_3$, 400 MHz) 8.44 (br, 1H), 6.51 (s, 1H), 6.49 (s, 1H), 3.80 (m, 2H), 2.15 (s, 6H), 1.79 (m, 2H), 1.02 (t, J = 7.4 Hz, 3H). The spectral data were identical to those of the authentic material reported in ref. 3. Chiral HPLC: 78:22 er, t_R (*R*)-major enantiomer, 19.3 min; t_R (*S*)-minor enantiomer, 26.6 min (Chiralcel OJ-H column; 15% 2-propanol in hexane; 0.5 mL/min).

6,7-Dimethyl-3-phenyl-3,4-dihydro-1,4-quinoxalin-2-one (18). A white solid was obtained in 79% yield. ^{1}H NMR ($CDCl_3$, 400 MHz) 8.44 (br, 1H), 7.41-7.28 (m, 5H), 6.50 (s, 2H), 5.01 (s, 1H), 4.11 (br, 1H), 2.15 (s, 3H), 2.14 (s, 3H). The spectral data were identical to those of the authentic material reported in ref. 3. Chiral HPLC: 88:12 er, t_R (*R*)-major enantiomer, 34.1 min; t_R (*S*)-minor enantiomer, 45.8 min (Chiralcel OJ-H column; 20% 2-propanol in hexane; 0.5 mL/min).

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References and Notes

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