

Supplementary Information for:

**Rhodium-catalyzed asymmetric arylation of *N*- and *O*-containing cyclic
aldimines: facile and efficient access to highly optically active
3,4-dihydrobenzo[1,4]oxazin-2-ones and dihydroquinoxalinones**

Xu Zhang,^{a,b} Bin Xu,^{a,*} Ming-Hua Xu^{b,*}

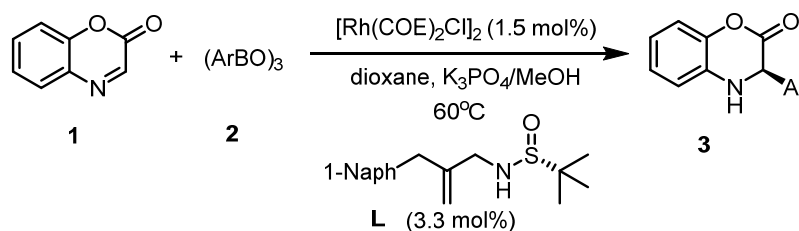
^a*Department of Chemistry, Innovative Drug Research Center, Shanghai University, Shanghai 200444,*
and ^b*State Key Laboratory of Drug Research, Shanghai Institute of Materia Medica, Chinese Academy*
of Sciences, Shanghai 2010203, China

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1. General

Solvents were dried and distilled by standard procedures. NMR spectra were recorded on Varian spectrometers (300 MHz for ^1H ; 126 MHz, 151 MHz for ^{13}C). Chemical shifts are reported in δ ppm referenced to an internal SiMe_4 standard for ^1H NMR and chloroform-d (δ 77.16) for ^{13}C NMR. Chiral HPLC was performed on a JASCO 2000 instrument by using Daicel chiral columns with 2-propanol/hexane as the eluent at 254 nm. High Resolution Mass Spectra (HRMS) were recorded on an Orbitrap mass spectrometer with ESI resource. Optical rotation were measured using a Rudolph Autopol VI Automatic Polarimeter. benzoxazinones **1**¹ and quinoxalinones **3**² were prepared according to the known literatures.

2. General procedure for Rh-catalyzed asymmetric arylation of benzoxazinones 1:



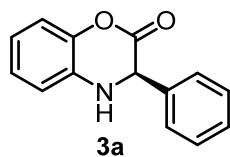
Under Ar atmosphere, benzoxazinones **1** (0.1 mmol), arylboroxine **2** (1.2 mmol), $[\text{Rh}(\text{COE})_2\text{Cl}]_2$ (1.1 mg, 0.003 of Rh), **L2** (1.0 mg, 0.0033 mmol) and anhydrous K_3PO_4 in 1.0 mL of anhydrous dioxane was stirred at room temperature for 30 min. To this mixture was added absolute methanol (16 μL , 0.4 mmol). After being stirred at 60°C for 2-12 h, a saturated aq. NH_4Cl was added and the mixture was extracted with EtOAc (10 mL \times 3). The combined organic phase was dried over Na_2SO_4 , filtered, and concentrated. The residue was purified by silica gel flash chromatography, eluting with petroleum ether/EtOAc (10–30% EtOAc), to afford the corresponding products **3**.

3. General procedure for Rh-catalyzed asymmetric arylation of quinoxalinones 3:

Under Ar atmosphere, quinoxalinones **4** (0.1 mmol), arylboroxine **2** (1.2 mmol), $[\text{Rh}(\text{COE})_2\text{Cl}]_2$ (1.1 mg, 0.003 of Rh), **L2** (1.0 mg, 0.0033 mmol) and anhydrous K_3PO_4 in 1.0 mL of anhydrous dioxane was stirred at room temperature for 30 min. To this mixture was added absolute methanol (16 μL , 0.4 mmol). After being stirred at 60°C for 2-12 h, a saturated aq. NH_4Cl was added and the mixture was extracted with EtOAc (10 mL \times 3). The combined organic phase was dried over Na_2SO_4 , filtered, and concentrated. The residue was purified by silica gel flash chromatography, eluting with petroleum ether/EtOAc (10–30% EtOAc), to afford the corresponding products **5**.

4. Characterization data and HPLC chromatogram of products 3a-q, 5a-k

(*R*)-3-phenyl-3,4-dihydro-2*H*-benzo[*b*][1,4]oxazin-2-one (**3a**):



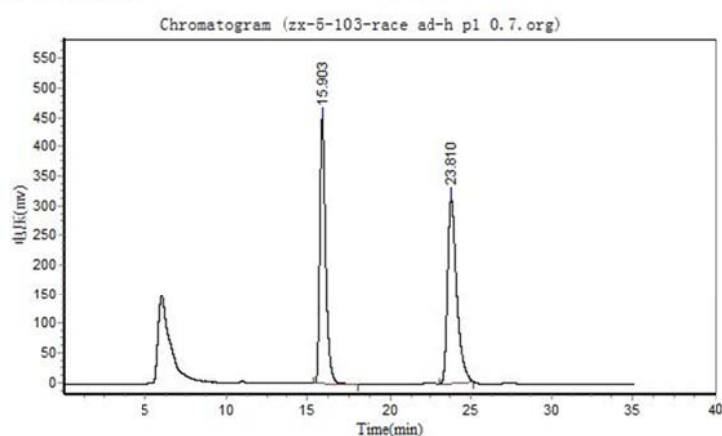
White solid, 93% yield, 99.9% ee

$[\alpha]_D^{20} = -110.4$ (*c* 0.80, CHCl₃) [Lit.³: $[\alpha]_D^{20} = +106.5$ (*c* 0.40, CHCl₃) for 97% ee]; ¹H NMR (300 MHz, CDCl₃): δ 7.36-7.41 (m, 5H), 7.00-7.07 (m, 2H),

6.81-6.90 (m, 2H), 5.06 (d, *J* = 1.8 Hz, 1H), 4.26 (s, 1H).

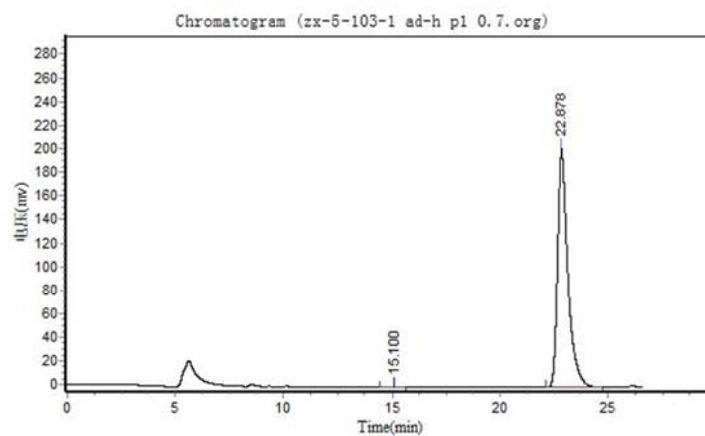
HPLC analysis: Chiralpak AD-H column (250 mm); detected at 254 nm; hexane/ⁱPrOH = 80/20;

flow = 0.7 mL/min; Retention time: 15.9 min, 29.8 min (major).



Results

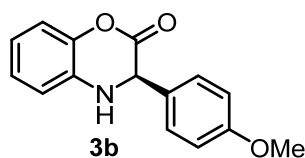
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		15.903	451509.844	11176821.000	47.8303
2		23.810	312812.781	12190820.000	52.1697
Total			764322.625	23367641.000	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		15.100	325.838	3466.810	0.0490
2		22.878	201973.984	7068321.000	99.9510
Total			202299.822	7071787.810	100.0000

(R)-3-(4-methoxyphenyl)-3,4-dihydro-2H-benzo[b][1,4]oxazin-2-one (3b)³:



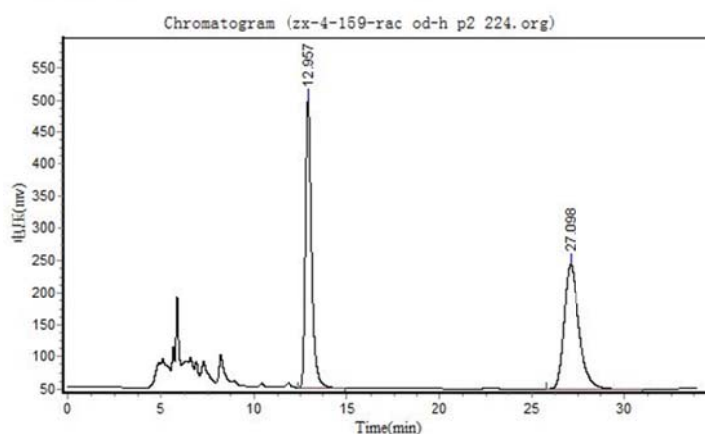
White solid, 98% yield, 99.9% ee.

$[\alpha]_D^{20} = -81.4$ (c 0.70, CHCl₃) [Lit.³: $[\alpha]_D^{20} = +69.0$ (c 0.20, CHCl₃)

for 80% ee]; ¹H NMR (300 MHz, CDCl₃): δ 7.32 (d, *J* = 8.6 Hz, 2H), 6.99-7.06 (m, 2H), 6.79-6.91 (m, 4H), 5.00 (d, *J* = 1.6 Hz, 1H), 4.20 (s, 1H), 3.80 (s, 3H);

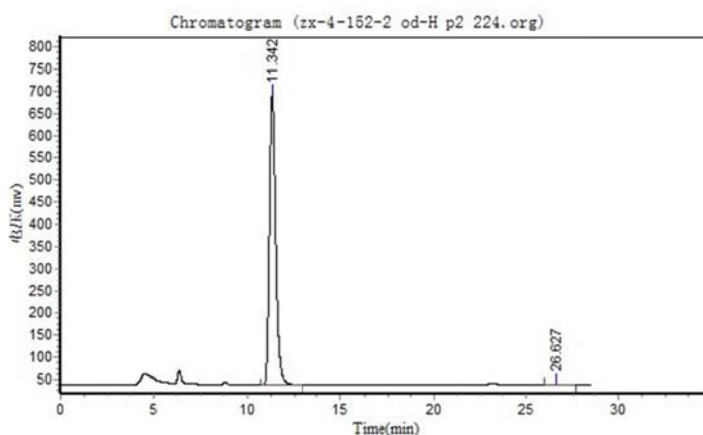
HPLC analysis: Chiralcel OD-H column (250 mm); detected at 254 nm; hexane/ⁱPrOH = 70/30;

flow = 0.7 mL/min; Retention time: 11.3 min (major), 26.6 min.



Results

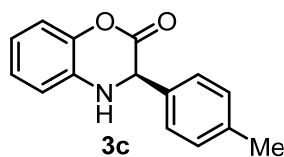
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		12.957	447704.156	10208748.000	48.2649
2		27.098	193306.578	10942735.000	51.7351
Total			641010.734	21151483.000	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.342	653779.125	15233951.000	99.9706
2		26.627	91.583	4472.408	0.0293
Total			653870.708	15238423.408	100.0000

(R)-3-p-tolyl-3,4-dihydro-2H-benzo[b][1,4]oxazin-2-one (3c)³:

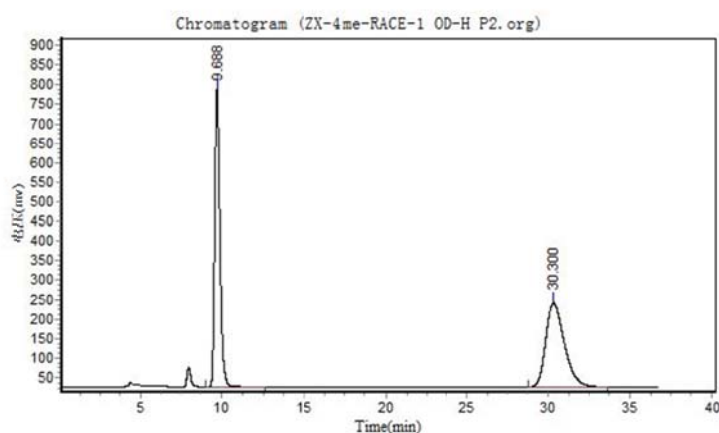


White solid, 98% yield, 99.9% ee.

$[\alpha]_D^{20} = -93.2$ (*c* 0.80, CHCl₃) [Lit.³: $[\alpha]_D^{20} = +85.0$ (*c* 0.40, CHCl₃) for

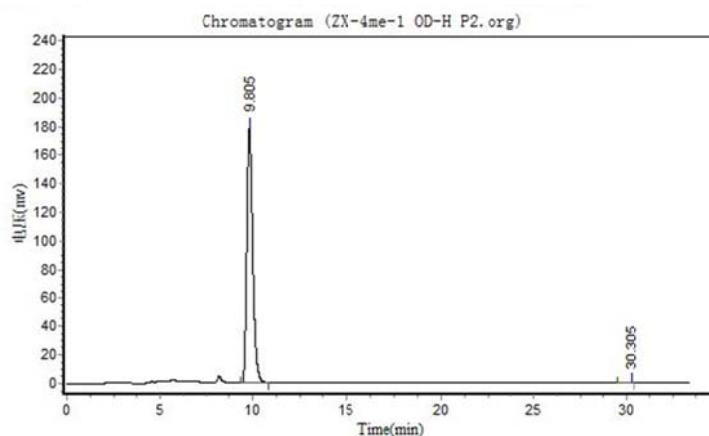
86% ee]; ¹H NMR (300 MHz, CDCl₃): δ 7.28 (d, *J* = 8.1 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.00-7.05 (m, 2H), 6.78-6.89 (m, 2H), 4.98 (d, *J* = 1.4 Hz, 1H), 4.30 (s, 1H), 2.34 (s, 3H);

HPLC analysis: Chiralcel OD-H column (250 mm); detected at 254 nm; hexane/ⁿPrOH = 70/30; flow = 0.7 mL/min; Retention time: 9.7 min (major), 30.3 min.



Results

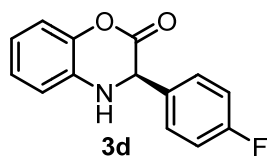
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		9.688	758634.250	16673702.000	49.9349
2		30.300	213493.000	16717189.000	50.0651
Total			972127.250	33390891.000	100.0000



Results

Peak ID	Ret Time	Height	Area	Conc.
	9.805	178065.625	3878077.000	99.9920
	30.305	11.207	312.100	0.0080
		178076.832	3878389.100	100.0000

(R)-3-(4-fluorophenyl)-3,4-dihydro-2H-benzo[b][1,4]oxazin-2-one (3d)³:

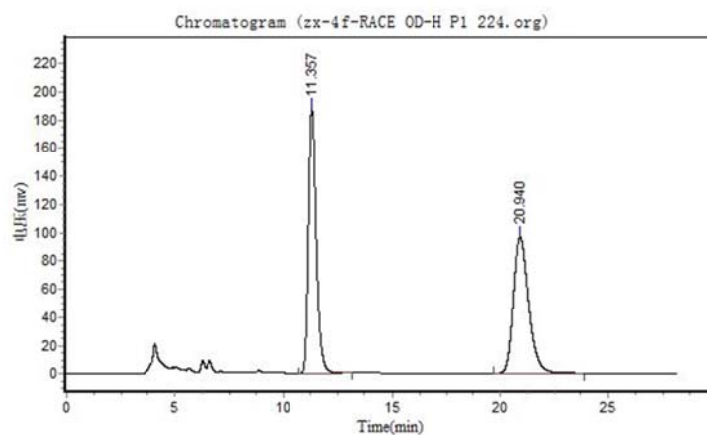


White solid, 94% yield, 99.3% ee.

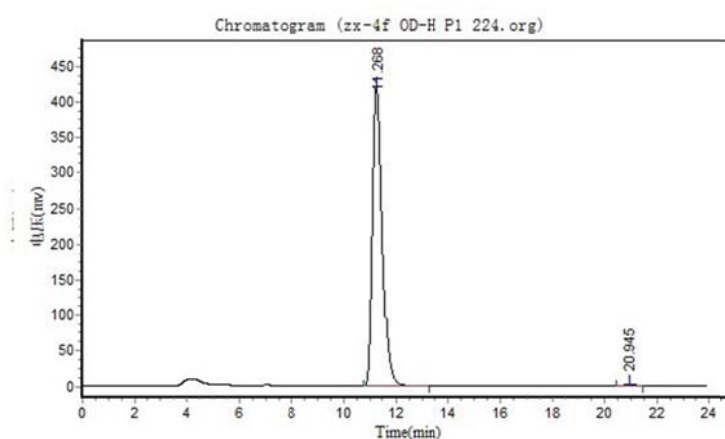
$[\alpha]_D^{20} = -105.2$ (c 0.80, CHCl_3) [Lit.³: $[\alpha]_D^{20} = +107.0$ (c 0.20, CHCl_3)

for 89% ee]; $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.39 (d, $J = 8.3$, 2H), 7.02-7.08 (m, 4H), 6.86-6.90 (m, 1H), 6.82 (m, 1H), 5.02 (d, $J = 1.7\text{Hz}$ 1H), 4.29 (s, 1H);

HPLC analysis: Chiralcel OD-H column (250 mm); detected at 254 nm; hexane/ i PrOH = 80/20; flow = 0.7 mL/min; Retention time: 11.3 min (major), 21.0 min.

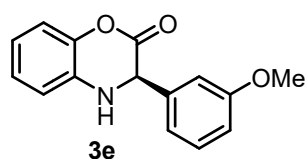


Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.357	187308.141	4708463.500	50.2722
2		20.940	96326.992	4657471.000	49.7278
Total			283635.133	9365934.500	100.0000



Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.268	418816.281	10598792.000	99.6411
2		20.945	1116.264	38170.852	0.3589
Total			419932.545	10636962.852	100.0000

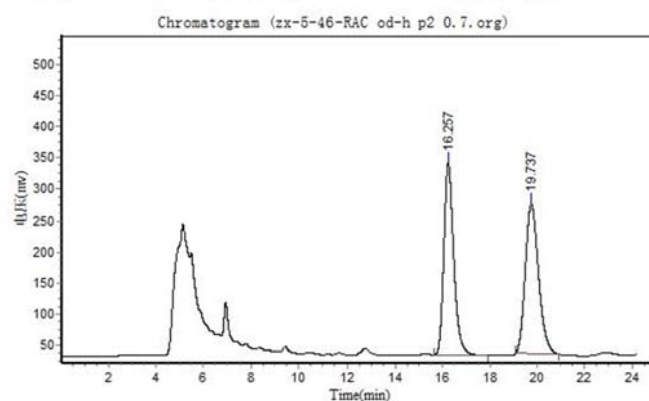
(R)-3-(3-methoxyphenyl)-3,4-dihydro-2H-benzo[b][1,4]oxazin-2-one (3e):



White solid, 98% yield, 99.9% ee.

$[\alpha]_D^{20} = -112.3$ (*c* 0.85, CHCl_3); $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.32-7.23 (m, 1H), 7.07-6.93 (m, 4H), 6.90-6.77 (m, 3H), 5.04 (s, 1H), 4.30 (s, 1H), 3.77 (s, 3H); $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 165.1, 160.0, 140.9, 137.8, 132.3, 130.0, 125.2, 120.4, 119.7, 117.0, 114.9, 114.5, 112.9, 59.2, 55.3; ESI-HRMS exact mass calculated $\text{C}_{15}\text{H}_{13}\text{NO}_3$ for $[\text{M}+\text{H}^+]$ 256.0968, found 256.0962;

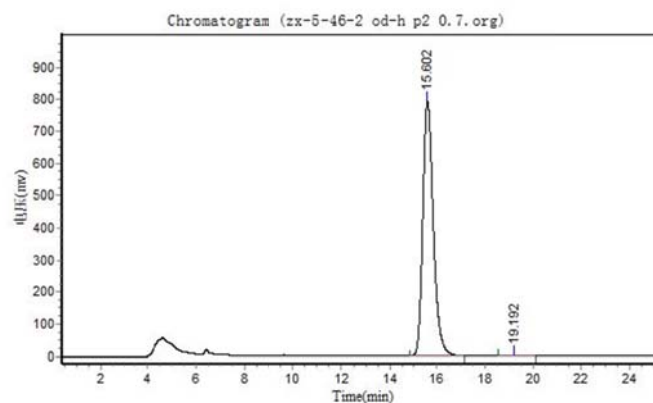
HPLC analysis: Chiralcel OD-H column (250 mm); detected at 254 nm; hexane/ $\text{PrOH} = 70/30$; flow = 0.7 mL/min; Retention time: 13.8 min (major), 21.4 min.



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		16.257	307251.469	8791903.000	48.8659
2		19.737	239444.688	9199981.000	51.1341
Total			546696.156	17991884.000	100.0000

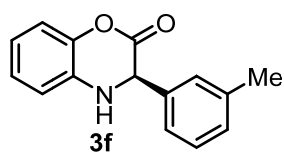
Quantification: Area/Area%



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		15.602	793814.000	24049016.000	99.8337
2		19.192	1188.766	40051.055	0.1663
Total			795002.766	24089067.055	100.0000

(R)-3-(3-methoxyphenyl)-3,4-dihydro-2H-benzo[b][1,4]oxazin-2-one (3f):



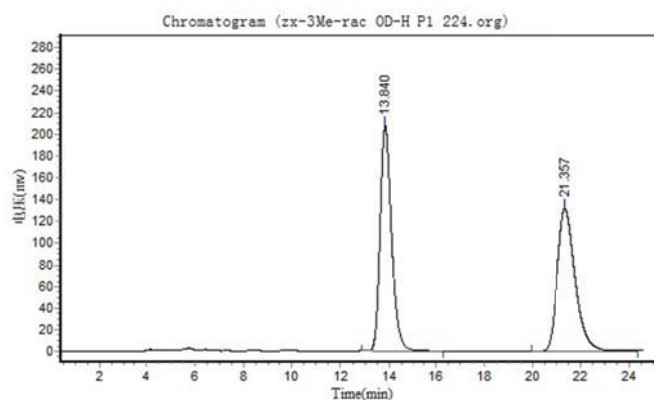
White solid, 96% yield, 99.9% ee.

$[\alpha]_D^{20} = -95.2$ (*c* 0.70, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 7.31-7.14 (m, 4H), 7.04 (m, 2H), 6.91-6.77 (m, 2H), 5.03 (d, *J* = 3.7 Hz, 1H),

4.23 (s, 1H), 2.35 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 165.3, 140.9, 138.8, 136.3, 132.4, 129.8, 128.9, 128.2, 125.1, 124.5, 120.2, 117.0, 114.8, 59.3, 21.4; ESI-HRMS exact mass calculated C₁₅H₁₃NO₂ for [M+Na⁺] 262.0838, found 262.0834;

HPLC analysis: Chiralcel OD-H column (250 mm); detected at 254 nm; hexane/PrOH = 80/20; flow = 0.7 mL/min; Retention time: 16.2 min (major), 19.7 min.

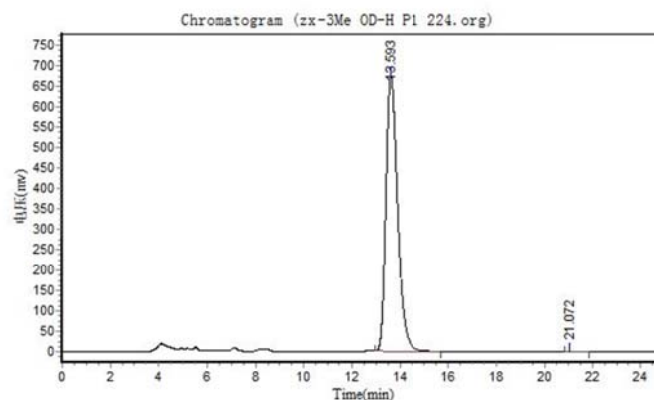
Column Temp: Prog. Temp.



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		13.840	206787.266	6813298.000	50.0907
2		21.357	131135.234	6788620.000	49.9093
Total			337922.500	13601918.000	100.0000

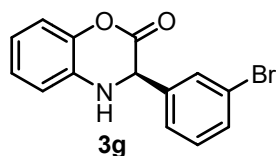
Column Temp: Prog. Temp.



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		13.593	672353.875	22707044.000	99.9844
2		21.072	116.220	3550.502	0.0156
Total			672470.095	22710594.502	100.0000

(R)-3-(3-bromophenyl)-3,4-dihydro-2H-benzo[b][1,4]oxazin-2-one (3g)



White solid, 33% yield, 99.7% ee.

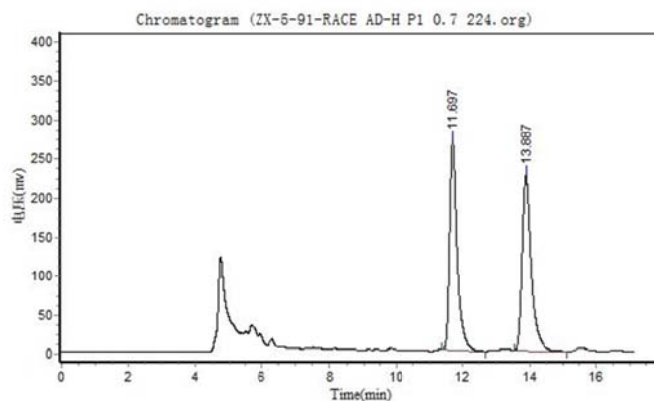
$[\alpha]_D^{20} = -94.8$ (*c* 0.80, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 7.59 (s, 1H), 7.50 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.38-7.22 (m, 2H), 7.06 (m, 2H),

6.93-6.81 (m, 2H), 5.04 (d, *J* = 2.1 Hz, 1H), 4.26 (s, 1H). ¹³C NMR (151 MHz, CDCl₃) δ 164.6, 140.8, 138.4, 132.2, 132.0, 130.7, 130.5, 126.3, 125.3, 123.0, 120.7, 117.1, 115.0, 58.7;

ESI-HRMS exact mass calculated C₁₄H₁₀BrNO₂ for [M+H⁺] 303.9803, found 303.9804;

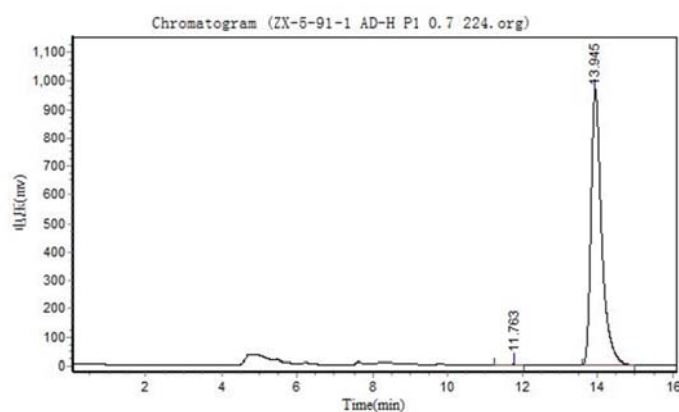
HPLC analysis: Chiralpak AD-H column (250 mm); detected at 254 nm; hexane/ⁱPrOH = 80/20;

flow = 0.7 mL/min; Retention time: 11.7 min, 13.9 min (major).



Results

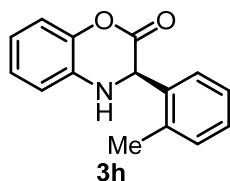
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.697	268107.469	4176594.500	49.5698
2		13.887	223315.188	4249093.500	50.4302
Total			491422.656	8425688.000	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.763	2130.996	36503.055	0.1962
2		13.945	964240.313	18569538.000	99.8038
Total			966371.308	18606041.055	100.0000

(R)-3-(2-methoxyphenyl)-3,4-dihydro-2H-benzo[b][1,4]oxazin-2-one (3h):

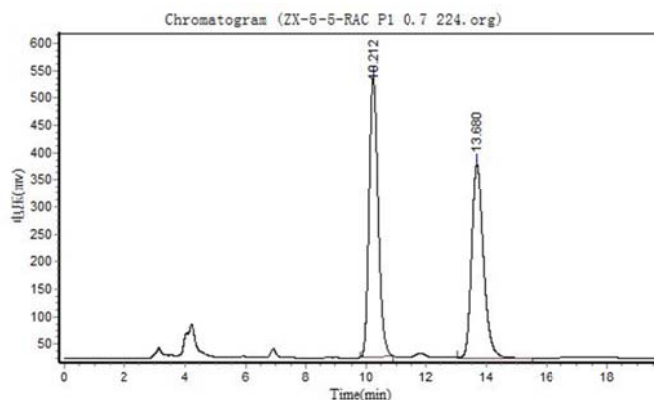


White solid, 99% yield, 99.7% ee.

$[\alpha]_D^{20} = -81.5$ (*c* 0.75, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 7.41 (d, *J* = 7.4 Hz, 1H), 7.27 (m, 3H), 7.13-7.00 (m, 2H), 6.94-6.86 (m, 1H), 6.81-6.75 (m, 1H), 5.18 (d, *J* = 1.8 Hz, 1H), 4.11 (s, 1H), 2.43 (s, 3H). ¹³C NMR (151

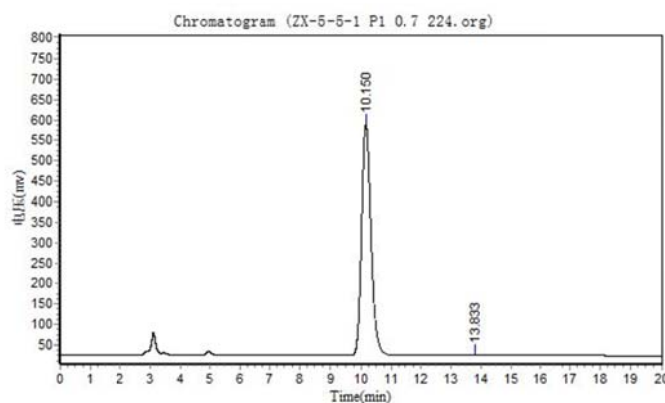
MHz, CDCl₃) δ 165.5, 141.1, 137.1, 134.6, 133.2, 131.2, 129.0, 127.9, 126.5, 125.2, 120.3, 117.0, 114.8, 57.1, 19.6; ESI-HRMS exact mass calculated C₁₅H₁₃NO₂ for [M+Na⁺] 262.0838, found 262.0834;

HPLC analysis: Chiralpak AD-H column (250 mm); detected at 254 nm; hexane/ⁱPrOH = 80/20; flow = 0.7 mL/min; Retention time: 10.2 min, 13.7 min (major).



Results

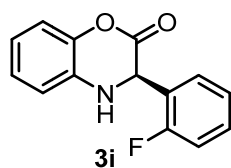
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.212	510654.906	10613470.000	52.6320
2		13.680	353922.906	9551969.000	47.3680
Total			864577.813	20165439.000	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.150	564076.438	12129605.000	99.8530
2		13.833	723.930	17852.875	0.1470
Total			564800.368	12147457.875	100.0000

(R)-3-(2-fluorophenyl)-3,4-dihydro-2H-benzo[b][1,4]oxazin-2-one (3i):



White solid, 77% yield, 99.4% ee.

$[\alpha]_D^{20} = -74.1$ (*c* 0.50, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 7.45-7.31 (m, 2H), 7.13-7.2 (m, 2H), 7.02 (dd, *J* = 8.2, 6.8 Hz, 1H), 6.93-6.85 (m, 1H), 6.71-6.81 (m, 1H), 5.36 (d, *J* = 1.7 Hz, 1H), 4.18 (s, 1H). ¹³C NMR (151

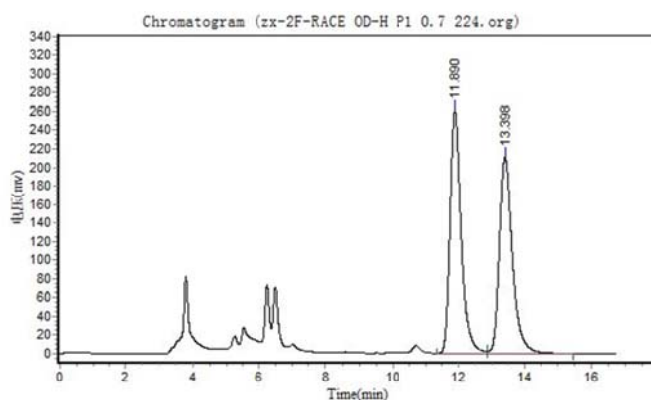
MHz, CDCl₃) δ 164.4, 160.7 (d, *J* = 249 Hz), 141.1, 132.3, 130.9, 130.8, 128.7, 128.7, 125.2,

124.7, 124.6, 123.6 (d, *J* = 13.6 Hz), 120.7, 117.0, 116.0 (d, *J* = 21 Hz), 115.1, 53.4 (d, *J* = 3 Hz);

ESI-HRMS exact mass calculated C₁₅H₁₀FNO₂ for [M+Na⁺] 266.0588, found 266.0586;

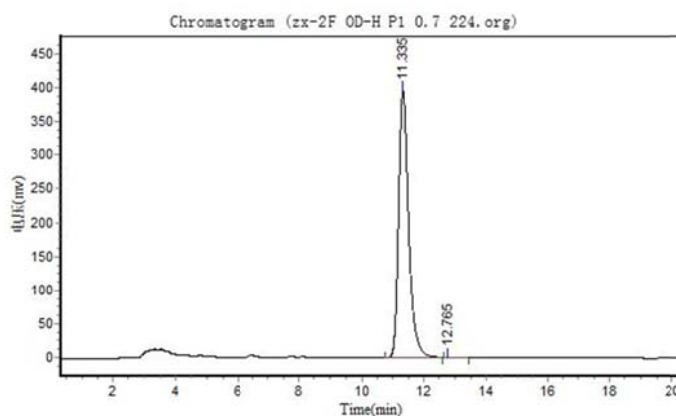
HPLC analysis: Chiralcel OD-H column (250 mm); detected at 254 nm; hexane/PrOH = 80/20;

flow = 0.7 mL/min; Retention time: 11.9 min (major), 13.4 min.



Results

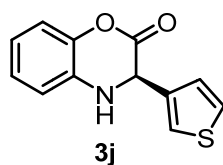
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.890	260765.922	6057864.000	51.4964
2		13.398	210748.219	5705810.500	48.5036
Total			471514.141	11763674.500	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.335	393731.156	8832826.000	99.9949
2		12.765	176.649	452.901	0.0051
Total			393907.806	8833278.901	100.0000

(R)-3-(thiophen-3-yl)-3,4-dihydro-2H-benzo[b][1,4]oxazin-2-one (3j):

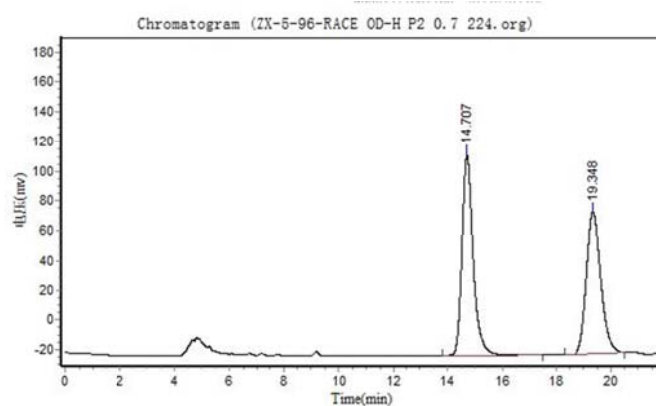


White solid, 99% yield, 99.3% ee.

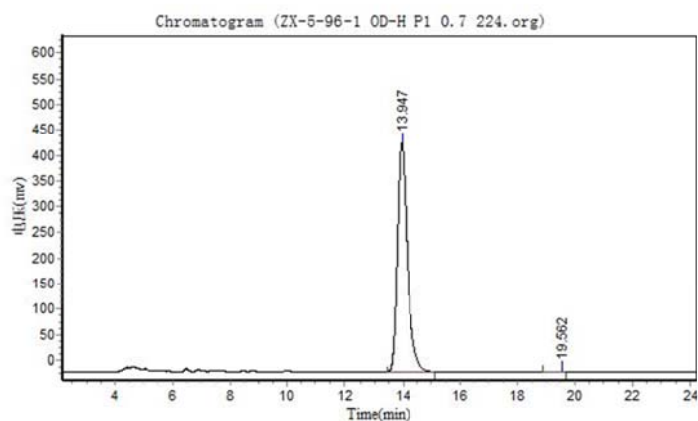
$[\alpha]_D^{20} = -54.3$ (*c* 0.50, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 7.35-7.26 (m, 2H), 7.10-7.00(m, 3H), 6.91-6.81 (m, 2H), 5.20 (s, 1H), 4.31 (s, 1H); ¹³C NMR (151 MHz, CDCl₃) δ 164.6, 140.9, 137.0, 132.0, 127.1, 126.3, 125.3,

123.7, 120.6, 117.0, 115.1, 55.3; ESI-HRMS exact mass calculated C₁₂H₉NO₂S for [M+Na⁺] 254.0246, found 254.0247;

HPLC analysis: Chiralcel OD-H column (250 mm); detected at 254 nm; hexane/PrOH = 80/20; flow = 0.7 mL/min; Retention time: 14.7 min (major), 19.3 min.

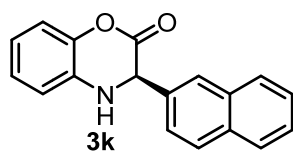


Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		14.707	134414.572	3805203.000	51.6166
2		19.348	96007.695	3568854.750	48.3834
Total			230422.367	7372057.750	100.0000



Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		13.947	446411.844	11056558.000	99.9968
2		19.562	72.622	353.400	0.0032
Total			446484.466	11056911.400	100.0000

(R)-3-(naphthalen-2-yl)-3,4-dihydro-2H-benzo[b][1,4]oxazin-2-one (3k):



White solid, 90% yield, 99.9% ee

$[\alpha]_D^{20} = -75.3$ (c 0.70, CHCl_3); $^1\text{H NMR}$ (300 MHz, CDCl_3): δ

7.90-7.77 (m, 4H), 7.51 (m, 3H), 7.11-7.01 (m, 2H), 6.94-6.78 (m,

2H), 5.22 (d, $J = 1.9$ Hz, 1H), 4.34 (s, 1H); $^{13}\text{C NMR}$ (151 MHz,

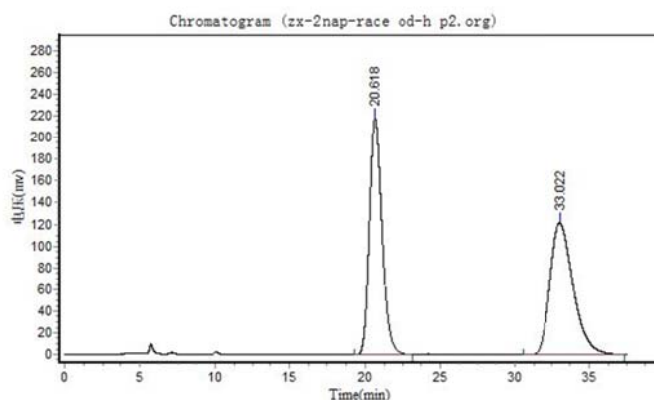
CDCl_3): δ 165.2, 141.0, 133.6, 133.4, 133.1, 132.4, 129.0, 128.1, 127.8, 127.0, 126.7, 126.6, 125.2,

124.8, 120.5, 117.0, 114.9, 59.4; ESI-HRMS exact mass calculated $\text{C}_{18}\text{H}_{13}\text{NO}_2$ for $[\text{M}+\text{Na}^+]$

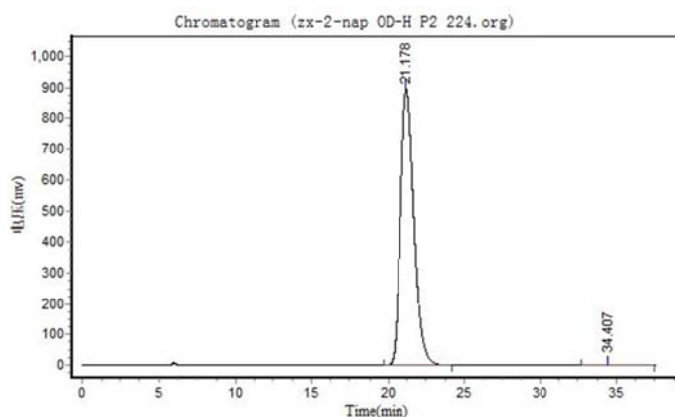
298.0838, found 298.0838;

HPLC analysis: Chiralcel OD-H column (250 mm); detected at 254 nm; hexane/ $\text{PrOH} = 70/30$;

flow = 0.7 mL/min; Retention time: 20.6 min (major), 33.1 min.

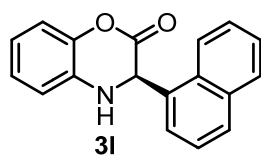


Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		20.618	217505.172	12742355.000	49.3224
2		33.022	121672.820	13092480.000	50.6776
Total			339177.992	25834835.000	100.0000



Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		21.178	893836.125	55554492.000	99.9482
2		34.407	221.477	28770.561	0.0518
Total			894077.602	55583262.561	100.0000

(R)-3-(naphthalen-2-yl)-3,4-dihydro-2H-benzo[b][1,4]oxazin-2-one (31):



White solid, 99% yield, 99.5% ee

$[\alpha]_D^{20} = -28.5$ (c 1.0, CHCl_3); $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 8.19-8.12

(m, 1H), 7.94-7.85 (m, 2H), 7.59-7.39 (m, 4H), 7.17-6.88 (m, 3H), 6.76

-6.68 (m, 1H), 5.65 (d $J = 1.8$, 1H), 4.23 (s, 1H); $^{13}\text{C NMR}$: (151 MHz, CDCl_3) δ 165.4, 141.1,

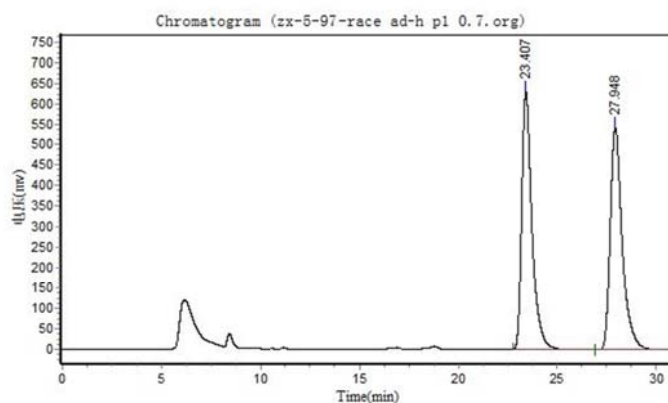
134.2, 132.8, 131.8, 130.9, 130.0, 129.1, 126.8, 126.6, 126.1, 125.2, 125.2, 123.7, 120.4, 117.1,

114.9, 57.6; ESI-HRMS exact mass calculated $\text{C}_{18}\text{H}_{13}\text{NO}_2$ for $[\text{M}+\text{Na}^+]$ 298.0838, found

298.0832;

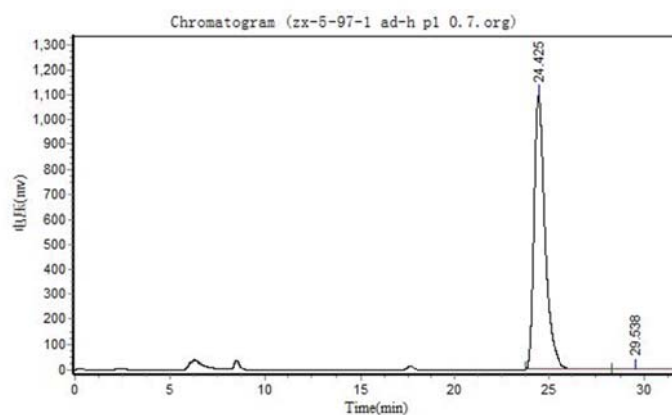
HPLC analysis: Chiralcel OD-H column (250 mm); detected at 254 nm; hexane/ i PrOH = 80/20;

flow = 0.7 mL/min; Retention time: 23.4 min (major), 27.8 min.



Results

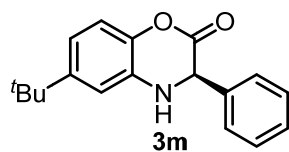
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		23.407	632583.188	22903436.000	50.1603
2		27.948	544079.563	22757048.000	49.8397
Total			1176662.750	45660484.000	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		24.425	1097013.750	43912980.000	99.6460
2		29.538	2770.197	156000.469	0.3540
Total			1099783.947	44068980.469	100.0000

(R)-6-(tert-butyl)-3-phenyl-3,4-dihydro-2H-benzo[b][1,4]oxazin-2-one (3m)⁴:



White solid, 98% yield, 99.8% ee

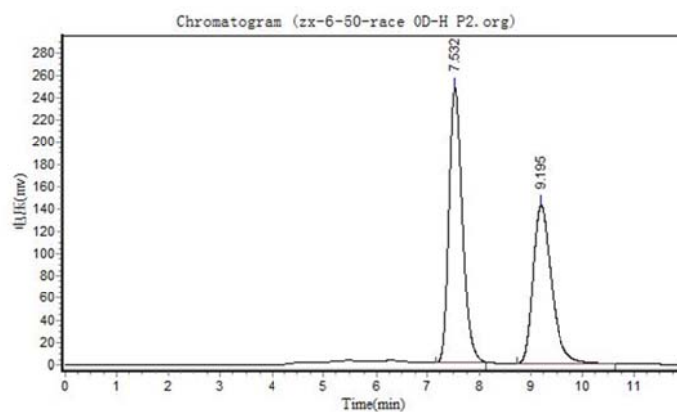
$[\alpha]_D^{20} = -110.2$ (*c* 0.90, CHCl₃) [Lit.⁴: $[\alpha]_D^{20} = +100.7$ (*c* 0.76, CHCl₃)

for 98% ee]; ¹H NMR (300 MHz, CDCl₃) δ 7.39 (m, 5H), 7.02-6.81

(m, 3H), 5.03 (s, 1H), 4.21 (s, 1H), 1.30 (s, 9H);

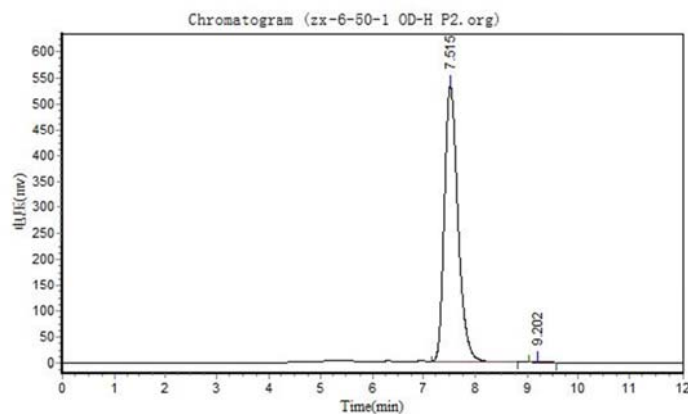
HPLC analysis: Chiralcel OD-H column (250 mm); detected at 254 nm; hexane/ⁱPrOH = 70/30;

flow = 0.7 mL/min; Retention time: 7.5 min (major), 9.2 min.



Results

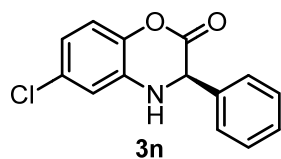
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		7.532	247042.547	4428020.000	55.2642
2		9.195	142327.297	3584438.000	44.7358
Total			389369.844	8012458.000	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		7.515	533018.438	9725139.000	99.9249
2		9.202	403.796	7310.501	0.0751
Total			533422.234	9732449.501	100.0000

(R)-6-chloro-3-phenyl)-3,4-dihydro-2H-benzo[b][1,4]oxazin-2-one (3n)⁴:



White solid, 98% yield, 99.7% ee.

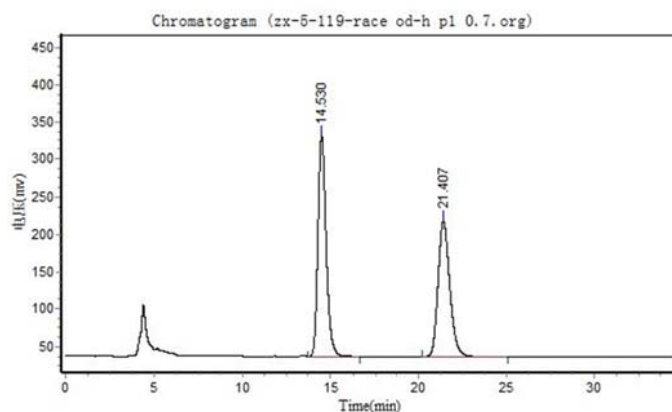
$[\alpha]_D^{20} = -129.1$ (*c* 0.84, CHCl₃) [Lit.⁴: $[\alpha]_D^{20} = +125.2$ (*c* 0.84, CHCl₃)

for 98% ee]; ¹H NMR (300 MHz, CDCl₃): δ 7.38 (s, 5H), 6.96 (d, *J* =

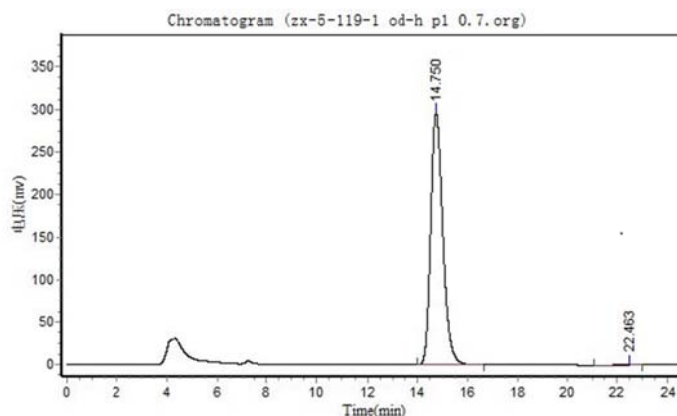
8.5 Hz, 1H), 6.83 (dd, *J* = 8.3, 1.8 Hz, 2H), 5.08 (d, *J* = 1.9 Hz, 1H), 4.38 (s, 1H);

HPLC analysis: Chiralcel OD-H column (250 mm); detected at 254 nm; hexane/ⁱPrOH = 80/20;

flow = 0.7 mL/min; Retention time: 14.5 min (major), 21.4 min.

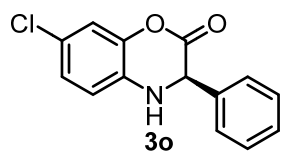


Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		14.530	294785.625	9507120.000	53.2171
2		21.407	181846.578	8357664.500	46.7829
Total			476632.203	17864784.500	100.0000



Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		14.750	296165.969	9923858.000	99.8718
2		22.463	362.932	12742.553	0.1282
Total			296528.901	9936600.553	100.0000

(R)-7-chloro-3-phenyl)-3,4-dihydro-2H-benzo[b][1,4]oxazin-2-one (3o):

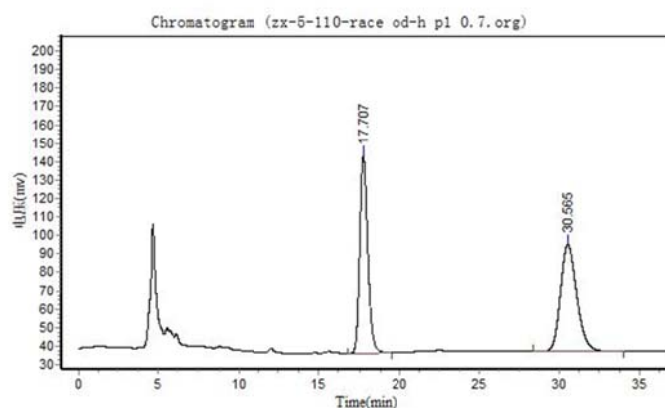


White solid, 98% yield, 99.7% ee

$[\alpha]_D^{20} = -53.6$ (c 1.0, CHCl_3); $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 7.38 (s, 5H), 7.07-6.97 (m, 2H), 6.75 (d, $J = 8.4$ Hz, 1H), 5.06 (d, $J = 1.8$ Hz,

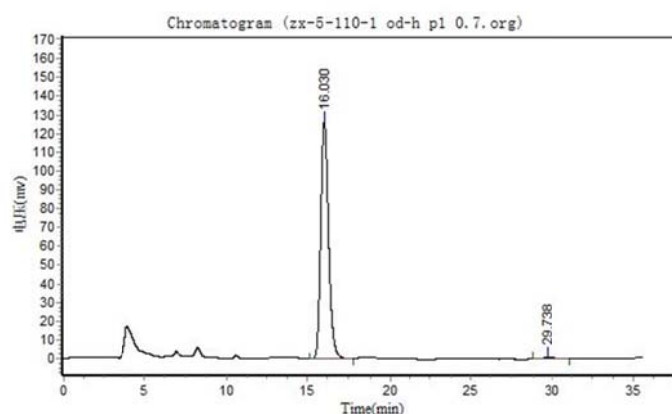
1H), 4.31 (s, 1H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3): δ 164.4, 141.1, 135.9, 131.0, 129.2, 129.1, 127.4, 125.1, 124.9, 117.3, 115.6, 59.0; ESI-HRMS exact mass calculated $\text{C}_{14}\text{H}_{10}\text{ClNO}_2$ for $[\text{M}-\text{H}]^-$ 258.0327, found 258.0325;

HPLC analysis: Chiralcel OD-H column (250 mm); detected at 254 nm; hexane/ i PrOH = 80/20; flow = 0.7 mL/min; Retention time: 17.7 min (major), 30.5 min.



Results

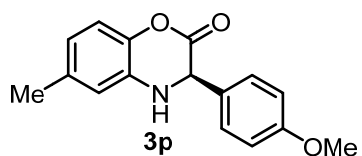
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		17.707	106635.156	3711980.750	47.7764
2		30.565	57865.395	4057505.500	52.2236
Total			164500.551	7769486.250	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		16.030	126137.570	4182616.250	99.1516
2		29.738	428.787	35790.301	0.8484
Total			126566.357	4218406.551	100.0000

(R)-6-(methyl)-3-(4-methoxyphenyl)-3,4-dihydro-2H-benzo[b][1,4]oxazin-2-one (3p):

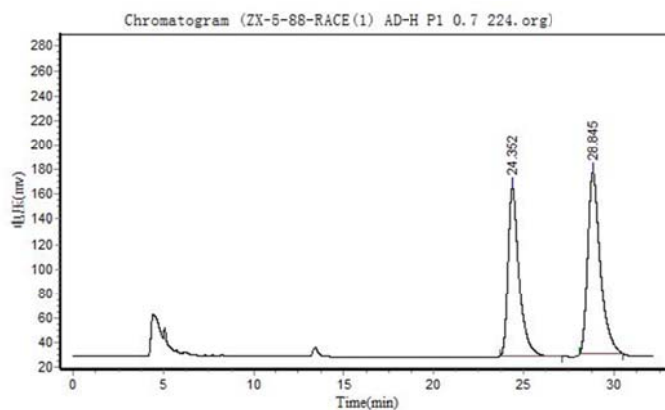


White solid, 97% yield, 99.3% ee

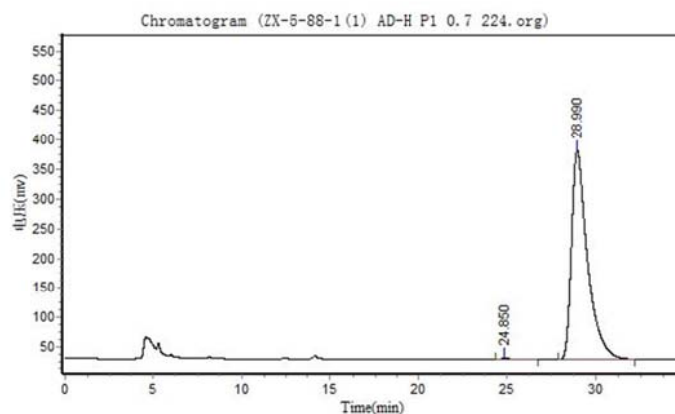
$[\alpha]_D^{20} = -117.5$ (c 0.92, CHCl_3); $^1\text{H NMR}$ (300 MHz, CDCl_3):

δ 7.32 (d, $J = 8.6$ Hz, 2H), 6.92 (m, 3H), 6.69-6.59 (m, 2H), 4.98(d, $J=1.8$, 1H), 4.12 (s, 1H), 3.80 (s, 3H), 2.29 (s, 3H); $^{13}\text{C NMR}$ (151 MHz, CDCl_3): δ 165.7, 160.0, 139.0, 135.0, 132.2, 128.8, 128.6, 120.9, 116.6, 115.3, 114.4, 58.8, 55.3, 21.0; ESI-HRMS exact mass calculated $\text{C}_{16}\text{H}_{15}\text{NO}_3$ for $[\text{M}+\text{Na}^+]$ 293.0944, found 292.0937;

HPLC analysis: Chiralpak AD-H column (250 mm); detected at 254 nm; hexane/ i PrOH = 80/20; flow = 0.7 mL/min; Retention time: 24.4 min, 28.8 min (major).

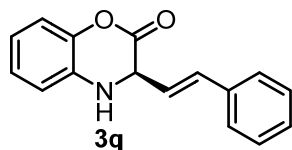


Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		24.352	136832.344	5832687.000	45.3191
2		28.845	146346.844	7037586.000	54.6809
Total			283179.188	12870273.000	100.0000



Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		24.850	1967.657	70489.516	0.3206
2		28.990	352780.500	21918850.000	99.6794
Total			354748.157	21989339.516	100.0000

(*R,E*)-3-styryl-3,4-dihydro-2*H*-benzo[*b*][1,4]oxazin-2-one (3q):



Yellow solid, 28% yield, 95% ee.

$[\alpha]_D^{20} = -40.3$ (c 0.7, CHCl_3); $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 7.40-7.28

(dd, $J = 16.4, 4.7$ Hz, 5H), 7.08-7.01 (m, 2H), 6.92-6.86 (dd, $J = 7.8,$

1.5 Hz, 1H), 6.84-6.69 (m, 2H), 6.45-6.12 (dd, $J = 15.9, 7.2$ Hz, 1H),

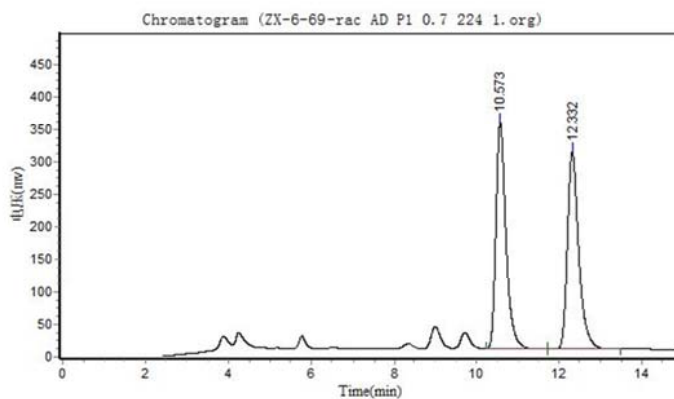
4.82-4.60 (d, $J = 7.2$ Hz, 1H), 4.12 (s, 1H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3): δ 165.61, 141.60,

136.11, 135.86, 132.49, 129.38, 129.27, 127.51, 125.87, 123.57, 121.28, 117.72, 115.88, 58.27.

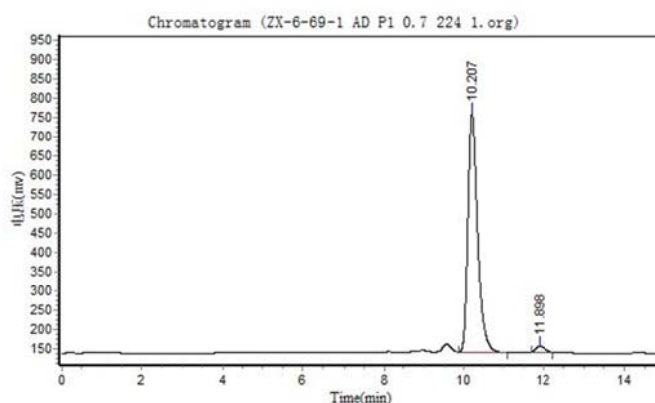
ESI-HRMS exact mass calculated $\text{C}_{16}\text{H}_{15}\text{NO}_3$ for $[\text{M}-\text{H}]^-$ 250.0874, found 250.0871;

HPLC analysis: Chiralpak AD-H column (250 mm); detected at 254 nm; hexane/ i PrOH = 80/20;

flow = 0.7 mL/min; Retention time: 10.6 min (major), 11.9 min.

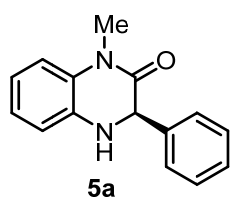


Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.573	348768.688	5849111.500	50.5249
2		12.332	303140.563	5727583.500	49.4751
Total			651909.250	11576695.000	100.0000



Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.207	620443.500	10392644.000	97.6340
2		11.898	15990.828	251852.297	2.3660
Total			636434.328	10644496.297	100.0000

(R)-1-methyl-3-phenyl-3,4-dihydroquinoxalin-2(1H)-one (5a)³:

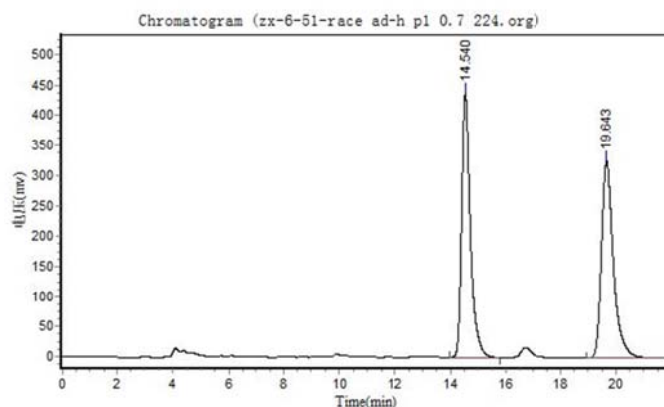


White solid, 83% yield, 99.3% ee

$[\alpha]_D^{20} = -160.1$ (*c* 0.5, CHCl₃) [Lit.³: $[\alpha]_D^{20} = +153.0$ (*c* 0.4, CHCl₃) for 92% ee]; ¹H NMR (300 MHz, CDCl₃): δ 7.41-7.26 (m, 5H), 6.98-6.86 (m, 3H), 6.78-6.73 (m, 1H), 5.07 (s, 1H), 4.34 (s, 1H), 3.40 (s, 3H); ¹³C NMR (126

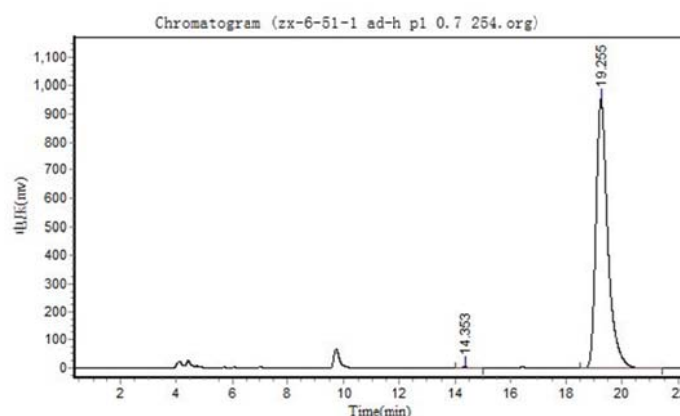
MHz, CDCl₃): δ 166.7, 139.8, 135.2, 129.4, 129.0, 129.0, 127.8, 124.5, 120.2, 115.5, 114.6, 61.5, 29.9;

HPLC analysis: Chiralpak AD-H column (250 mm); detected at 254 nm; hexane/PrOH = 80/20; flow = 0.7 mL/min; Retention time: 14.5 min, 19.6 min (major).



Results

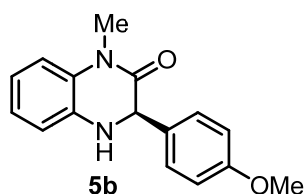
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		14.540	437921.813	9534490.000	49.7764
2		19.643	324949.719	9620146.000	50.2236
Total			762871.531	19154636.000	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		14.353	4467.999	91446.398	0.3257
2		19.255	953061.313	27986246.000	99.6743
Total			957529.311	28077692.398	100.0000

(R)-3-(4-methoxyphenyl)-1-methyl-3,4-dihydroquinoxalin-2(1H)-one (5b):



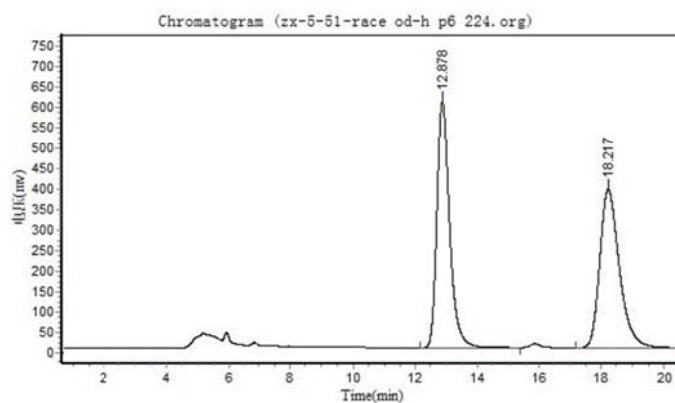
White solid, 80% yield, 99.5% ee

$[\alpha]_D^{20} = -117.2$ (*c* 0.7, CHCl₃); ¹H NMR (300 MHz, CDCl₃): δ 7.29 (d, *J* = 8.5 Hz, 2H), 6.98-6.82 (m, 5H), 6.76-6.69 (m, 1H), 4.99 (s, 1H), 4.32 (s, 1H), 3.77 (s, 3H), 3.39 (s, 3H); ¹³C NMR (151 MHz, CDCl₃):

δ 166.4, 159.5, 134.6, 131.2, 128.4, 128.3, 123.7, 119.5, 114.8, 114.1, 114.0, 60.3, 55.3, 29.2;

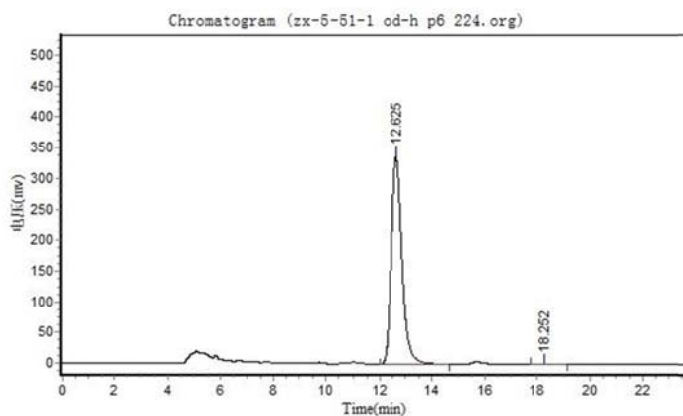
ESI-HRMS exact mass calculated C₁₆H₁₆N₂O₂ for [M+Na⁺] *m/z* 291.1109, found 291.1104;

HPLC analysis: Chiralcel OD-H column (250 mm); detected at 254 nm; hexane/ⁱPrOH = 60/40; flow = 0.7 mL/min; Retention time: 12.9 min (major), 18.2 min.



Results

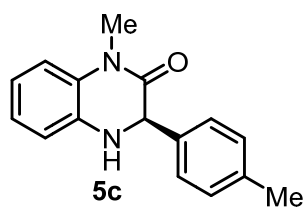
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		12.878	466111.906	13220572.000	50.2593
2		18.217	299786.250	13084137.000	49.7407
Total			765898.156	26304709.000	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		12.625	287377.313	8187170.000	99.8542
2		18.252	317.488	11954.070	0.1458
Total			287694.801	8199124.070	100.0000

(R)-3-(4-methylphenyl)-1-methyl-3,4-dihydroquinoxalin-2(1H)-one (5c)³:



White solid, 79% yield, 99.5% ee

$[\alpha]_D^{20} = -109.1$ (*c* 0.7, CHCl₃) [Lit.³: $[\alpha]_D^{20} = +106.2$ (*c* 0.4, CHCl₃)

for 89% ee]; ¹H NMR (300 MHz, CDCl₃): δ 7.28-7.24 (m, 2H), 7.12 (d, *J* = 7.8 Hz, 2H), 6.976.84 (m, 3H), 6.776.70 (m, 1H), 5.02 (s, 1H),

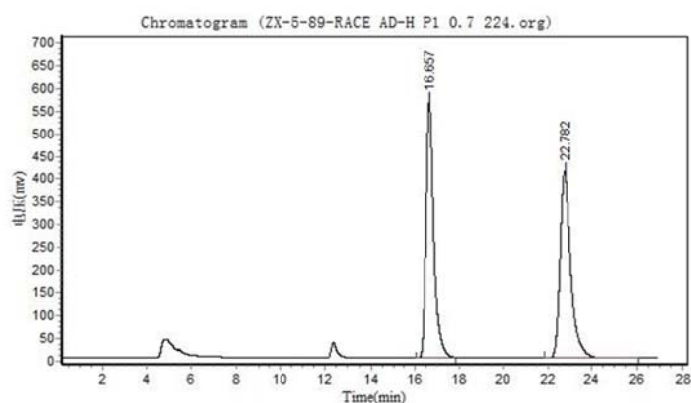
4.33 (s, 1H), 3.39 (s, 3H), 2.32 (s, 3H); ¹³C NMR (126 MHz, CDCl₃): δ 166.9, 138.8, 136.8, 135.3,

130.2, 130.1, 129.5, 127.7, 124.4, 120.2, 114.6, 61.3, 29.9, 21.8; ESI-HRMS exact mass

calculated C₁₆H₁₆N₂O₂ for [M+Na⁺] *m/z* 275.1160, found 291.1155;

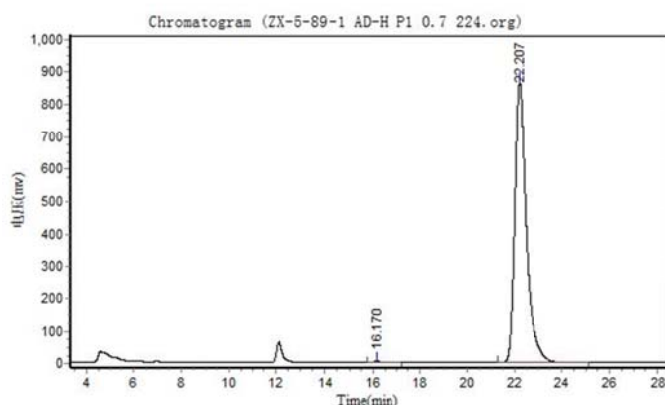
HPLC analysis: Chiralpak AD-H column (250 mm); detected at 254 nm; hexane/ⁱPrOH = 80/20;

flow = 0.7 mL/min; Retention time: 16.6 min, 22.7 min (major).



Results

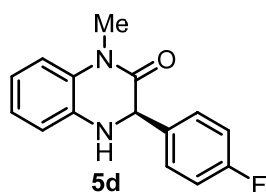
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		16.657	564434.813	13868713.000	49.8348
2		22.782	409918.188	13960644.000	50.1652
total			974353.000	27829357.000	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		16.170	2819.037	64030.500	0.2178
2		22.207	863602.563	29330020.000	99.7822
Total			866421.599	29394050.500	100.0000

(R)-3-(4-fluorophenyl)-1-methyl-3,4-dihydroquinoxalin-2(1H)-one (5d):

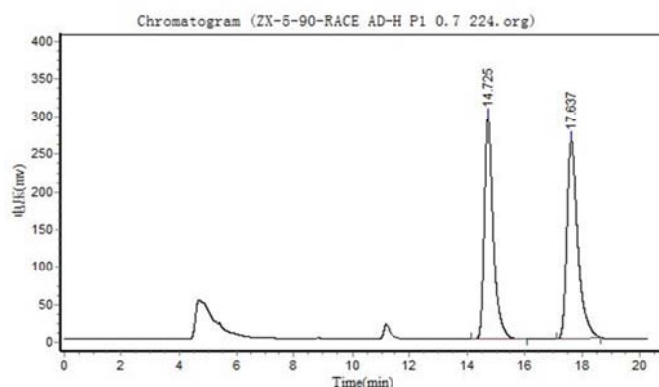


White solid, 79% yield, 99.9% ee

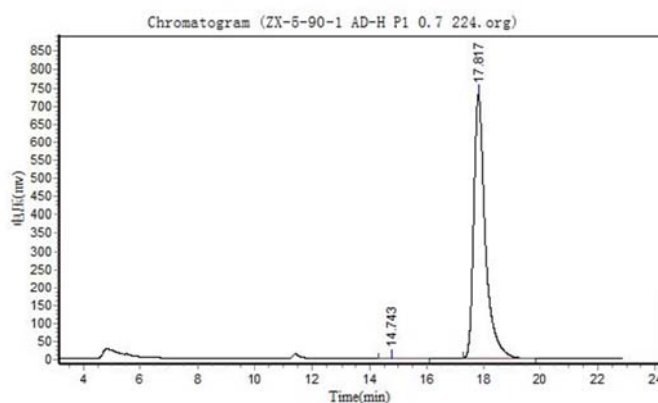
$[\alpha]_D^{20} = -150.3$ (*c* 0.5, CHCl₃) [Lit.³: $[\alpha]_D^{20} = +144.8.4$, (*c* 0.4, CHCl₃) for 92% ee]; ¹H NMR (300 MHz, CDCl₃): δ 7.40-7.33 (m, 2H), 7.04-6.88 (m, 5H), 6.75 (dd, *J* = 7.6, 1.6 Hz, 1H), 5.03 (s, 1H), 4.33 (s, 1H), 3.39

(s, 3H); ¹³C NMR (151 MHz, CDCl₃): δ 166.0, 162.6 (*d*, *J* = 247.6Hz), 134.8 (*d*, *J* = 4.5Hz), 128.9 (*d*, *J* = 9.0Hz), 128.3, 123.8, 119.7, 115.6 (*d*, *J* = 21.1Hz), 114.9, 114.0, 60.2, 29.3; ESI-HRMS exact mass calculated C₁₅H₁₃FN₂O for [M+H⁺] *m/z* 279.0910 found 279.0904;

HPLC analysis: Chiralpak AD-H column (250 mm); detected at 254 nm; hexane/ⁱPrOH = 80/20; flow = 0.7 mL/min; Retention time: 14.7 min, 17.6 min (major).

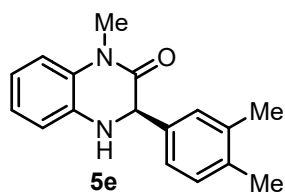


Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		14.725	293641.281	6323468.500	48.0239
2		17.637	261944.000	6843867.000	51.9761
total			555585.281	13167335.500	100.0000



Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		14.743	405.161	11496.312	0.0566
2		17.817	726920.125	20307098.000	99.9434
Total			727325.286	20318594.312	100.0000

(*R*)-3-(3,4-dimethylphenyl)-1-methyl-3,4-dihydroquinoxalin-2(1*H*)-one (**5e**):

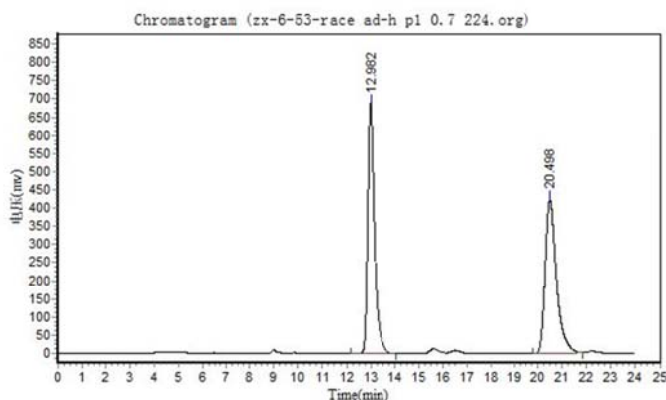


White solid, 56% yield, 99.5% ee

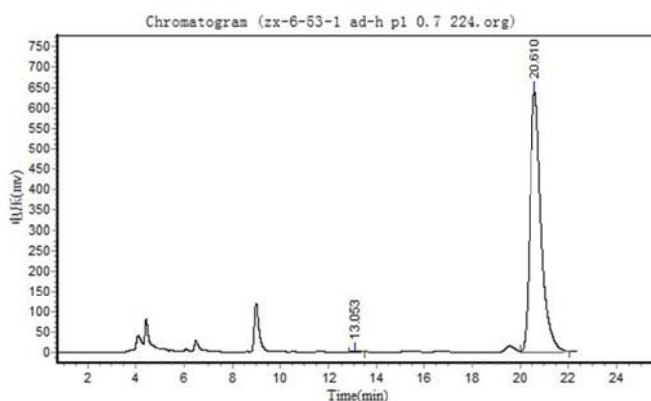
$[\alpha]_D^{20} = -57.9$ (*c* 0.5, CHCl₃); ¹H NMR (300 MHz, CDCl₃): δ 7.17 (s, 1H), 7.08 (d, *J* = 1.6 Hz, 2H), 6.97-6.86 (m, 3H), 6.76-6.70 (m, 1H), 4.99 (s, 1H), 3.40 (s, 3H), 2.23 (s, 6H); ¹³C NMR (126 MHz, CDCl₃): δ

165.9, 136.5, 136.3, 136.0, 134.2, 129.4, 128.0, 128.0, 123.9, 123.2, 119.0, 114.2, 113.4, 60.2, 28.7, 19.4, 19.0; ESI-HRMS exact mass calculated C₁₇H₁₈N₂O for [M+H⁺] *m/z* 266.1419, found 266.1411;

HPLC analysis: Chiralpak AD-H column (250 mm); detected at 254 nm; hexane/ⁱPrOH = 80/20; flow = 0.7 mL/min; Retention time: 13.0 min, 20.5 min (major).

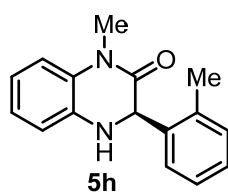


Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		12.982	686383.250	13595829.000	49.6850
2		20.498	422186.250	13768204.000	50.3150
Total			1108569.500	27364033.000	100.0000



Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		13.053	2617.071	48462.703	0.2315
2		20.610	639586.313	20885580.000	99.7685
Total			642203.384	20934042.703	100.0000

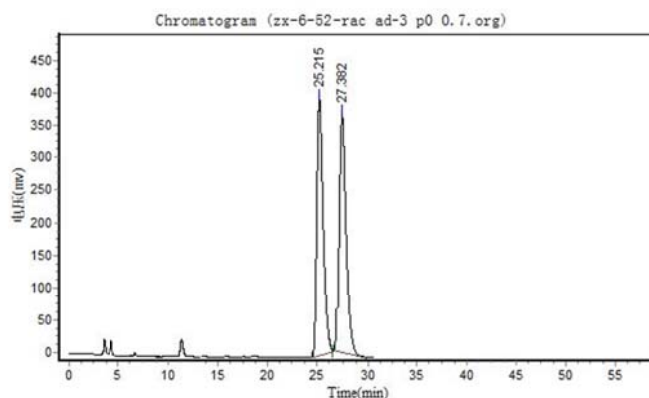
(*R*)-3-(2-methylphenyl)-1-methyl-3,4-dihydroquinoxalin-2(1H)-one (**5h**):



White solid, 79% yield, 99.7% ee

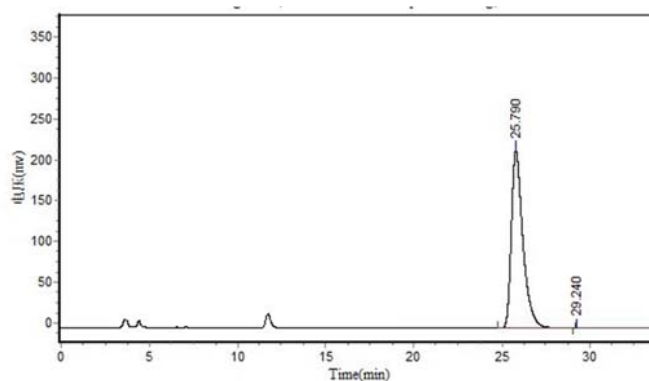
$[\alpha]_D^{20} = -127.3$ (*c* 0.6, CHCl₃); ¹H NMR (300 MHz, CDCl₃): δ 7.37 (d, *J* = 7.4 Hz, 1H), 7.24-7.17 (m, 3H), 7.00-6.90 (m, 3H), 6.71-6.65 (m, 1H), 5.24 (s, 1H), 4.17 (s, 1H), 3.42 (s, 2H), 2.46 (s, 3H); ¹³C NMR (126 MHz, CDCl₃): δ 166.0, 136.7, 136.4, 134.7, 130.5, 128.2, 127.8, 127.0, 125.9, 123.2, 119.1, 114.2, 113.4, 57.7, 28.7, 19.3; ESI-HRMS exact mass calculated C₁₆H₁₆N₂O for [M+H⁺] *m/z* 253.1335, found 253.1330;

HPLC analysis: Chiralpak AD-H column (250 mm); detected at 254 nm; hexane/ⁱPrOH = 90/10; flow = 0.7 mL/min; Retention time: 25.2 min, 27.4 min (major).



Results

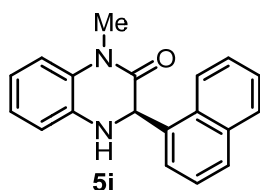
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		25.215	393965.219	17416078.000	50.7115
2		27.382	364229.688	16927390.000	49.2885
Total			758194.906	34343468.000	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		25.790	218453.563	9910515.000	99.8710
2		29.240	44.164	12320.217	0.1242

(R)-1-methyl-3-(naphthalen-1-yl)-3,4-dihydroquinoxalin-2(1H)-one (5i):

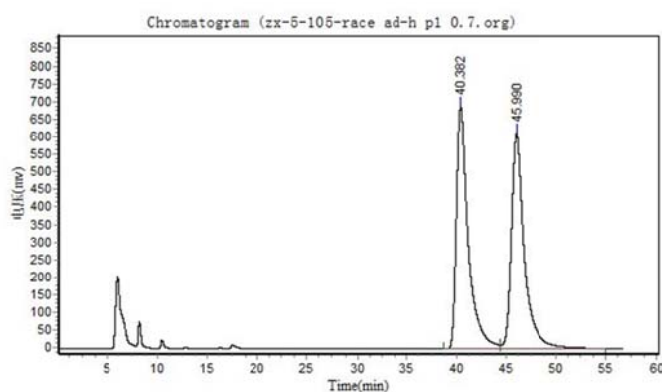


White solid, 69% yield, 99.9% ee

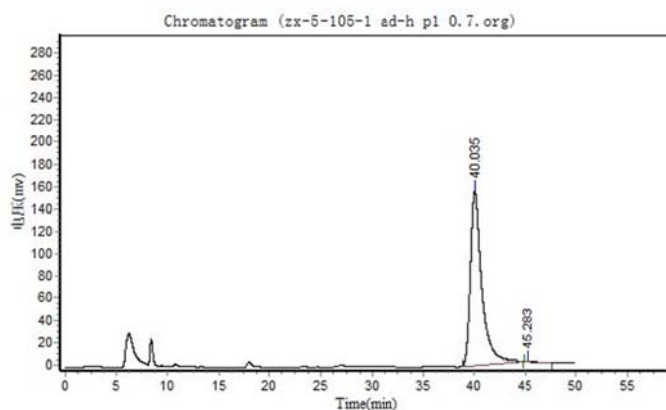
$[\alpha]_D^{20} = -53.6$ (*c* 0.6, CHCl₃); ¹H NMR (300 MHz, CDCl₃): δ 8.29 (d, *J* = 8.2 Hz, 1H), 7.95-7.72 (m, 2H), 7.60-7.33 (m, 4H), 7.10-6.82 (m, 3H), 6.66 (dd, *J* = 7.0, 2.1 Hz, 1H), 5.74 (s, 1H), 4.29 (s, 1H), 3.47 (s, 3H);

¹³C NMR (151 MHz, CDCl₃): δ 166.4, 134.9, 134.4, 134.2, 131.3, 129.3, 128.9, 128.7, 126.5, 125.8, 125.9, 125.2, 124.0, 123.7, 119.7, 114.8, 114.1, 58.7, 29.3; ESI-HRMS exact mass calculated C₁₉H₁₆N₂O for [M+H⁺] *m/z* 289.1335, found 289.1339;

HPLC analysis: Chiralcel OD-H column (250 mm); detected at 254 nm; hexane/ⁱPrOH = 80/20; flow = 0.7 mL/min; Retention time: 40.4 min (major), 46.0 min.

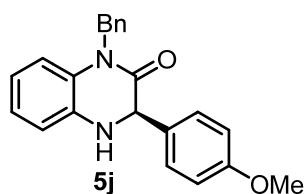


Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		40.382	689696.938	56696752.000	50.5288
2		45.990	612508.375	55510160.000	49.4712
Total			1302205.313	112206912.000	100.0000



Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		40.035	156311.125	12048941.000	99.9748
2		45.283	206.072	3033.995	0.0252
Total			156517.197	12051974.995	100.0000

(R)-1-benzyl-3-(4-methoxyphenyl)-3,4-dihydroquinoxalin-2(1H)-one (5j):

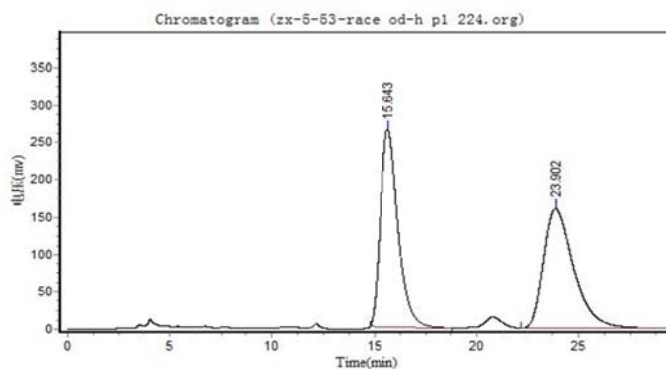


White solid, 69% yield, 98.9% ee

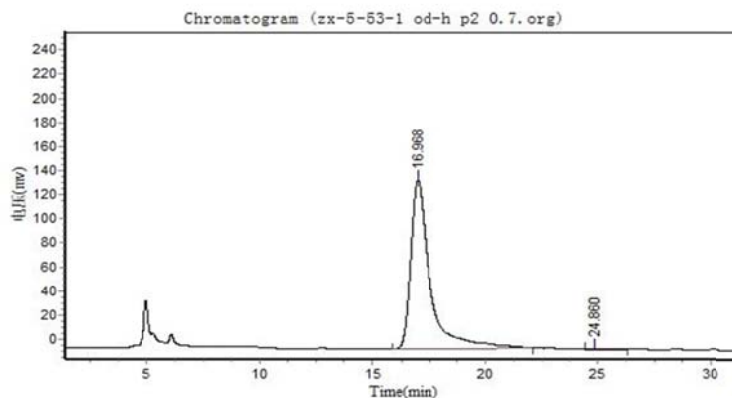
$[\alpha]_D^{20} = -80.0$ (c 0.7, CHCl_3); $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 7.36 (d, $J = 8.7$ Hz, 2H), 7.23 (m, 5H), 6.87 (m, 4H), 6.78-6.67 (m, 2H), 5.33-5.05 (m, 3H), 4.39 (s, 1H), 3.79 (s, 3H); $^{13}\text{C NMR}$ (151 MHz,

CDCl_3): δ 166.5, 159.6, 136.7, 134.7, 131.1, 128.7, 128.3, 127.6, 127.1, 126.5, 123.8, 119.5, 115.6, 114.2, 60.3, 55.3, 45.9; ESI-HRMS exact mass calculated $\text{C}_{22}\text{H}_{20}\text{N}_2\text{O}_2$ for $[\text{M}+\text{H}^+]$ m/z 345.1598, found 345.1589;

HPLC analysis: Chiralcel OD-H column (250 mm); detected at 254 nm; hexane/ i PrOH = 80/20; flow = 0.7 mL/min; Retention time: 15.6 min (major), 23.9 min.

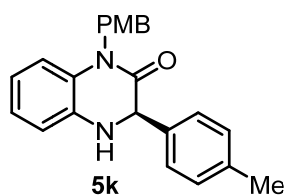


PeakNo.	Peak ID	Ret Time	Height	Area	Conc.
1		15.643	264416.531	15938082.000	49.3175
2		23.902	160449.219	16379238.000	50.6825
Total			424865.750	32317320.000	100.0000



Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		16.968	139476.031	8437684.000	99.4620
2		24.860	731.188	45638.652	0.5380
Total			140207.220	8483322.652	100.0000

(R)-1-(4-methoxybenzyl)-3-(p-tolyl)-3,4-dihydroquinoxalin-2(1H)-one (5k):

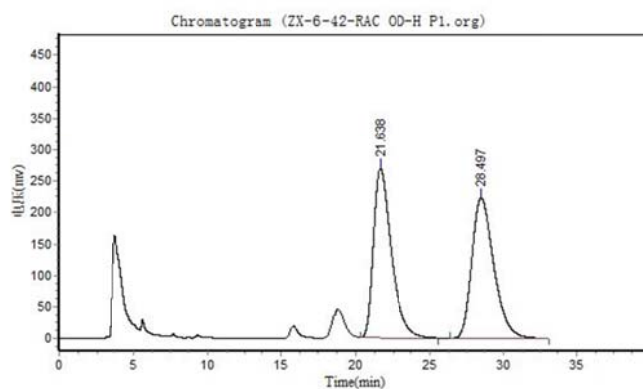


White solid, 67% yield, 99.9% ee.

$[\alpha]_D^{20} = -53.6$ (c 0.5, CHCl_3); $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 7.35-7.27 (d, $J = 7.8$ Hz, 2H), 7.17-7.06 (m, 4H), 6.94-6.69 (m, 6H), 5.27-4.98 (m, 3H), 4.49- 4.31 (s, 1H), 3.84-3.55 (d, $J = 1.2$ Hz, 3H), 2.39- 2.24 (s,

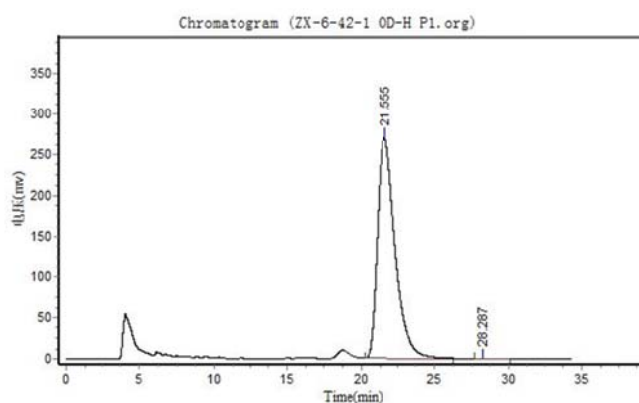
3H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3): δ 166.99, 159.39, 138.83, 136.68, 135.38, 130.15, 129.48, 128.57, 128.31, 127.68, 124.44, 120.21, 116.32, 114.89, 61.36, 55.95, 45.99, 21.85; ESI-HRMS exact mass calculated $\text{C}_{23}\text{H}_{22}\text{N}_2\text{O}$ for $[\text{M}+\text{H}^+]$ m/z 359.1754, found 359.1747;

HPLC analysis: Chiralcel OD-H column (250 mm); detected at 254 nm; hexane/ i PrOH = 80/20; flow = 0.7 mL/min; Retention time: 21.6 min (major), 28.5 min.



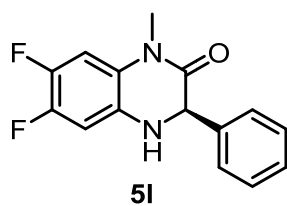
Results						
Peak No.	Peak ID	Ret Time	Height	Area	Conc.	
1		21.638	267826.313	22679680.000	49.6578	
2		28.497	222940.328	22992222.000	50.3422	
Total			490766.641	45671902.000	100.0000	

Quantification: Area/Area%



Results						
Peak No.	Peak ID	Ret Time	Height	Area	Conc.	
1		21.555	268948.625	22538076.000	99.9525	
2		28.287	130.404	10702.951	0.0475	
Total			269079.029	22548778.951	100.0000	

(*R*)-6,7-difluoro-1-methyl-3-phenyl-3,4-dihydroquinoxalin-2(1*H*)-one (**51**):



Yellow solid, 80% yield, 99.6 % ee

$[\alpha]_D^{20} = -51.0$ (c 0.8, CHCl_3); $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.42-7.25

(s, 5H), 6.85-6.68 (m, 1H), 6.60-6.47 (dd, $J = 10.8, 7.3$ Hz, 1H),

5.04-4.94 (d, $J = 1.6$ Hz, 1H), 4.53-4.36 (s, 1H), 3.34-3.24 (s, 3H); ^{13}C

NMR (125 MHz, CDCl_3) δ 165.5, 146.1(dd, $J = 242.5$ Hz, 13.7 Hz), 143.6 (dd, $J = 236.2.5$ Hz,

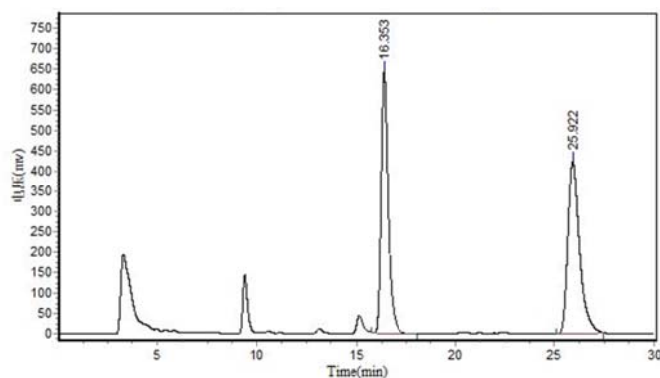
13.7 Hz), 138.3, 130.8, 128.7, 128.4, 126.9, 124.2 (d, $J = 7.5$ Hz), 104.4 (d, $J = 22.5$ Hz), 102.7

(d, $J = 22.5$ Hz), 60.4, 29.5; ESI-HRMS exact mass calculated $\text{C}_{22}\text{H}_{22}\text{N}_2\text{O}_2$ for $[\text{M}-\text{H}]^-$ m/z

273.0845, found 273.0841;

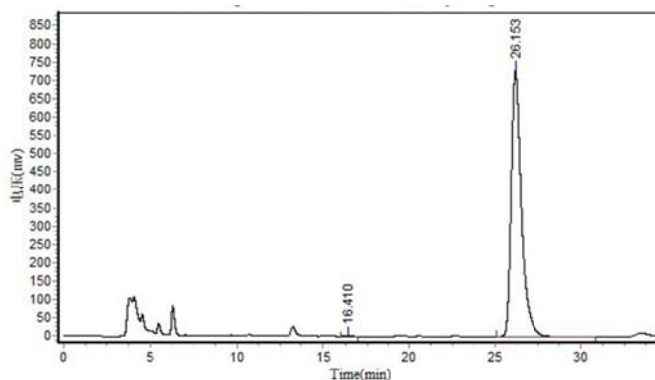
HPLC analysis: Chiralpak AD-H column (250 mm); detected at 254 nm; hexane/ i PrOH = 90/10;

flow = 0.7 mL/min; Retention time: 12.8 min (major), 17.8 min.



Results

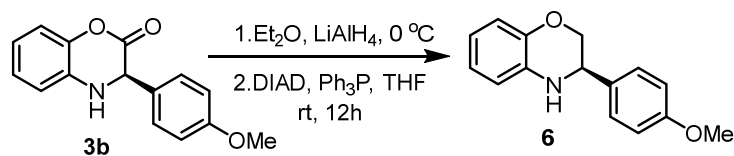
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		16.353	642079.000	15831869.000	48.0695
2		25.922	423554.750	17103514.000	51.9305
Total			1065633.750	32935383.000	100.0000



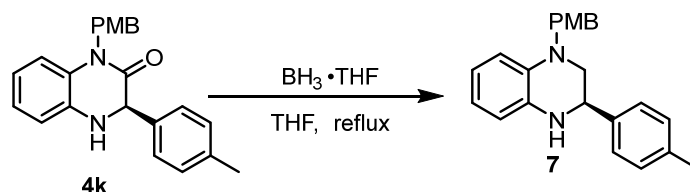
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		16.410	2282.925	56108.594	0.1878
2		26.153	726906.125	29824520.000	99.8122
Total			729189.050	29880628.594	100.0000

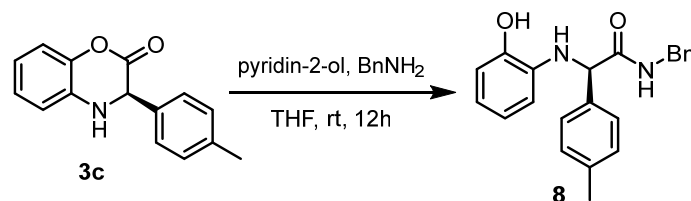
5. Synthesis of benzomorpholine **6**, tetrahydroquinoxaline **7** and glycine amide **8**:



To a solution of dihydrobenzoxazinones **3b** (0.2 mmol, 51 mg) in Et_2O , LiAlH_4 (12 mg, 0.32 mmol) was added in portions at $0\text{ }^\circ\text{C}$. The resulting mixture was stirred at $0\text{ }^\circ\text{C}$ for 1 h. After excess LiAlH_4 was decomposed by wet ether, water was added and the mixture was extracted with EtOAc . The combined extracts were washed with brine, dried (Na_2SO_4), and concentrated under reduced pressure to afford dark oil. The dark oil and triphenylphosphine (104 mg, 0.4 mmol) were dissolved in dry THF under nitrogen. DIAD (80 mg, 0.4 mmol) was added dropwise at $0\text{ }^\circ\text{C}$. The mixture was stirred at $30\text{ }^\circ\text{C}$ for 12 h. After removing the solvent in vacuo, the crude product was purified by flash chromatography (petroleum ether/ethyl acetate 10:1) to afford benzomorpholine **6** as white solid (40 mg, 83% yield, 99% ee).



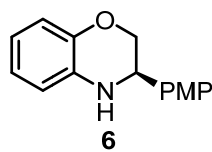
To a solution of dihydroquinoxalinones **4k** (36 mg, 0.1 mmol) in THF 1.5 mL, $\text{BH}_3 \cdot \text{THF}$ (1.0 M in THF, 0.25 mL, 0.25 mmol) was added slowly at room temperature. After the completion of the addition, the reaction was refluxed for 3 h. The reaction mixture then cooled and the solvent was evaporated in vacuo, the crude was purified by flash chromatography (petroleum ether/ethyl acetate 10:1) to afford tetrahydroquinoxaline **7** (34 mg, 99% yield, 98% ee).



Pyridin-2-ol (3 equiv) benzylamine (5 equiv) were added to a solution of dihydrobenzoxazinone **3c** in THF. The mixture was stirred at room temperature for 12 h, then diluted with water and extracted with EtOAc . The extracts were dried and evaporated. Purification of the crude product by column chromatography on silica gel (ethyl acetate/hexane) afforded the pure product **8**.

6. Characterization data and HPLC chromatogram of derivative 6, 7, 8:

(*R*)-3-(4-methoxyphenyl)-3,4-dihydro-2*H*-1,4-benzoxazine (**6**)⁵:

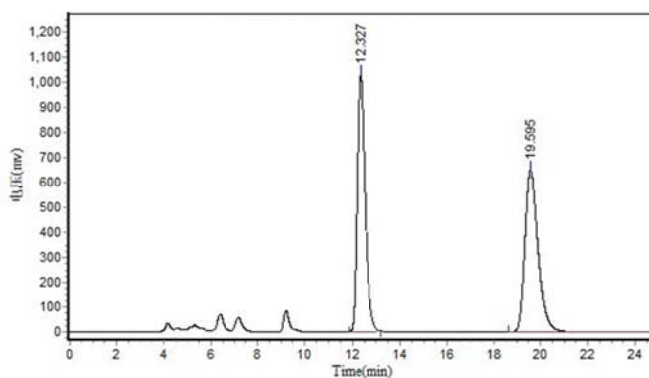


White solid, 83% yield, 99% ee

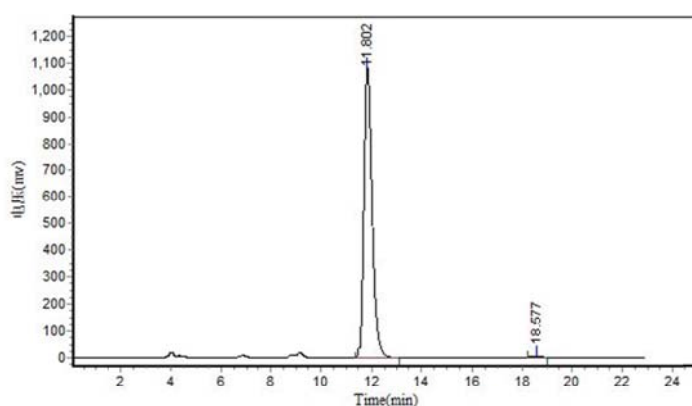
$[\alpha]_D^{20} = -60.3$ (*c* 0.6, CHCl₃) [Lit.⁵: $[\alpha]_D^{20} = +55.5$, (*c* 1.0, CHCl₃) for 98% ee];

¹H NMR (300 MHz, CDCl₃): δ 7.31 (d, *J* = 7.4 Hz, 2H), 6.94-6.87 (m, 2H), 6.87-6.61 (m, 4H), 4.45 (dd, *J* = 8.8, 2.8 Hz, 1H), 4.24 (dd, *J* = 10.6, 3.1 Hz, 1H), 3.96 (m, 1H), 3.81 (s, 3H);

HPLC analysis: Chiralcel OD-H column (250 mm); detected at 254 nm; hexane/^{*i*}PrOH = 80/20; flow = 0.7 mL/min; Retention time: 12.3 min (major), 19.6 min.

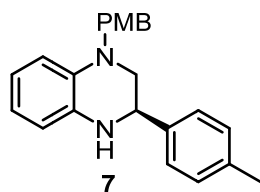


Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		12.327	1027099.000	24360364.000	49.4006
2		19.595	647153.250	24951502.000	50.5994
Total			1674252.250	49311866.000	100.0000



Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.802	1079673.875	24420142.000	99.5003
2		18.577	4557.676	122647.805	0.4997
Total			1084231.551	24542789.805	100.0000

(*R*)-1-(4-methoxybenzyl)-3-(*p*-tolyl)-1,2,3,4-tetrahydroquinoxaline (**7**):

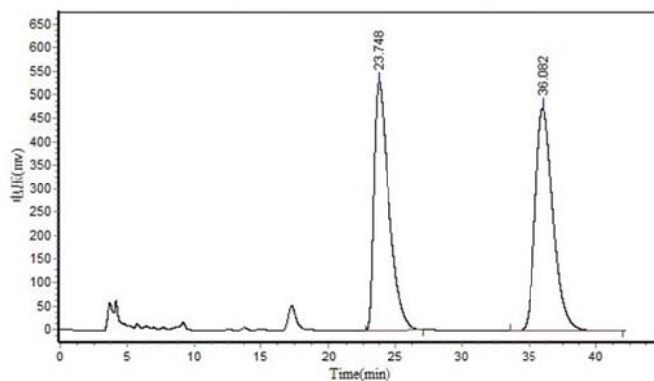


Green oil, 99% yield, 98% ee

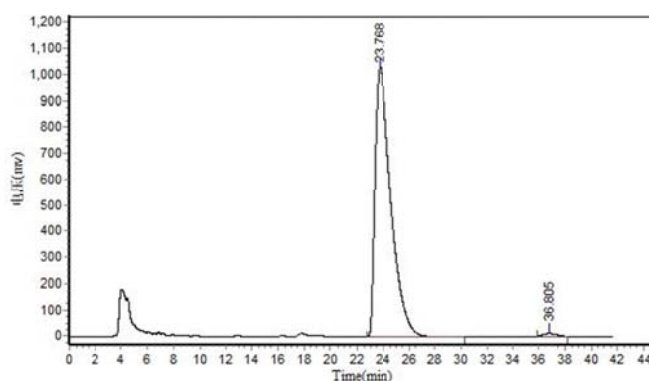
$[\alpha]_D^{20} = -41.0$ (c 0.4, CHCl_3); $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 7.43-7.19 (m, 6H), 7.00-6.76 (m, 2H), 6.71-6.58 (m, 4H), 4.58-4.44 (d, $J = 5.6$ Hz, 1H), 4.47-4.31 (s, 2H), 4.10 (s, 1H), 3.93-3.78 (d, $J = 2.0$ Hz, 3H),

3.53-3.17 (d, $J = 6.3$ Hz, 2H), 2.44-2.22 (d, $J = 2.0$ Hz, 3H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3): δ 159.33, 139.30, 138.33, 135.27, 135.16, 131.10, 129.98, 129.07, 127.66, 119.79, 118.58, 114.66, 112.80, 56.37, 55.99, 55.52, 54.70, 21.84. ESI-HRMS exact mass calculated $\text{C}_{23}\text{H}_{24}\text{N}_2\text{O}_2$ for $[\text{M}+\text{H}^+]$ m/z 345.1961, found 345.1953.

HPLC analysis: Chiralcel OD-H column (250 mm); detected at 254 nm; hexane/ i PrOH = 80/20; flow = 0.7 mL/min; Retention time: 23.7 min (major), 36.1 min.

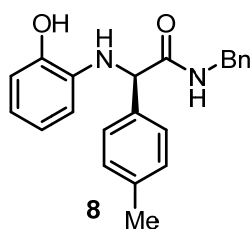


Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		23.748	527353.438	41825032.000	48.7274
2		36.082	474806.063	44009744.000	51.2726
Total			1002159.500	85834776.000	100.0000



Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		23.768	1031093.250	89244192.000	99.1239
2		36.805	10538.326	788779.500	0.8761
Total			1041631.576	90032971.500	100.0000

(R)-N-benzyl-2-((2-hydroxyphenyl)amino)-2-(p-tolyl)acetamide (8):

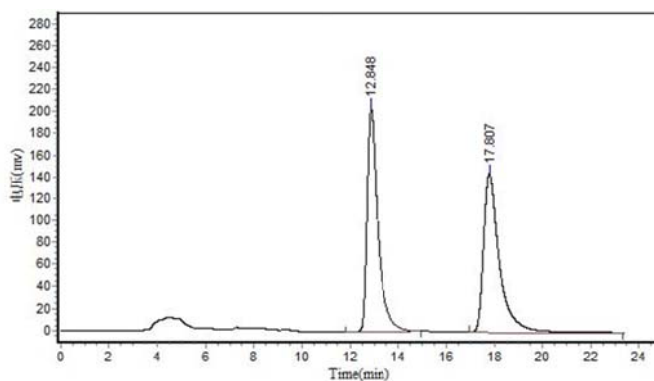


Brown solid, 90% yield, 99% ee

$[\alpha]_D^{20} = -120.0$ (c 0.5, CHCl_3); $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 7.53 (t, $J = 6.1$ Hz, 1H), 7.25 (m, 8H), 6.77 (m, 1H), 6.64 (d, $J = 6.9$ Hz, 2H), 6.54 (d, $J = 7.7$ Hz, 1H), 4.68 (s, 1H), 4.52 (dd, $J = 15.0, 6.3$ Hz, 1H), 4.36 (dd, $J = 15.0, 5.7$ Hz, 1H), 2.32 (s, 3H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3): δ 172.7,

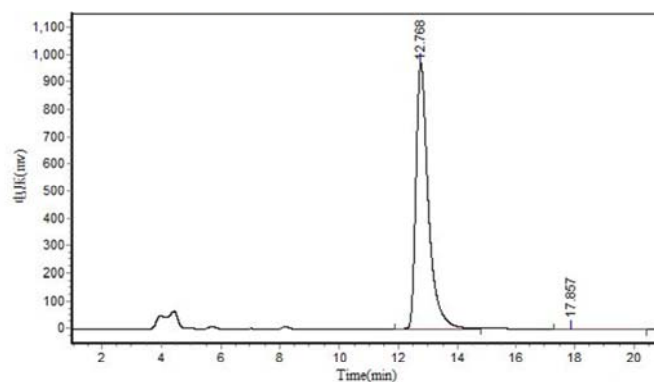
144.1, 138.4, 137.7, 135.6, 135.4, 129.8, 128.6, 127.6, 127.4, 127.3 121.0, 119.3 114.6, 112.6, 64.5, 43.4, 21.2; ESI-HRMS exact mass calculated $\text{C}_{22}\text{H}_{22}\text{N}_2\text{O}_2$ for $[\text{M}+\text{H}^+]$ m/z 347.1754, found 347.1745;

HPLC analysis: Chiralcel OD-H column (250 mm); detected at 254 nm; hexane/ $\text{PrOH} = 80/20$; flow = 0.7 mL/min; Retention time: 12.8 min (major), 17.8 min.



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		12.848	203728.484	6592162.500	49.9626
2		17.807	144449.625	6602023.500	50.0374
Total			348178.109	13194186.000	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		12.768	967877.938	28279146.000	99.8442
2		17.857	969.046	44137.438	0.1558
Total			968846.983	28323283.438	100.0000

References:

1. P.-L. Shao, J.-Y. Liao, Y. A. Ho, Y. Zhao, *Angew. Chem. Int. Ed.* **2014**, *53*, 5435.
2. A. Carrer, J.-D. Brion, S. Messaoudi, M. Alami, *Org. Lett.* **2013**, *15*, 5606.
3. Z.-Y. Xue, Y. Jiang, X.-Z. Peng, W.-C. Yuan, X.-M. Zhang, *Adv. Synth. Catal.* **2010**, *352*, 2132.
4. Q.-A. Chen, M.-W. Chen, C.-B. Yu, L. Shi, D.-S. Wang, Y. Yang, Y.-G. Zhou, *J. Am. Chem. Soc.* **2011**, *133*, 16432.
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7. Crystal analysis of 3g:

Bond precision: C-C = 0.0130 Å Wavelength=0.71073

Cell: a=4.4197(5) b=11.6677(13) c=22.915(2)
 alpha=90 beta=90 gamma=90

Temperature: 173 K

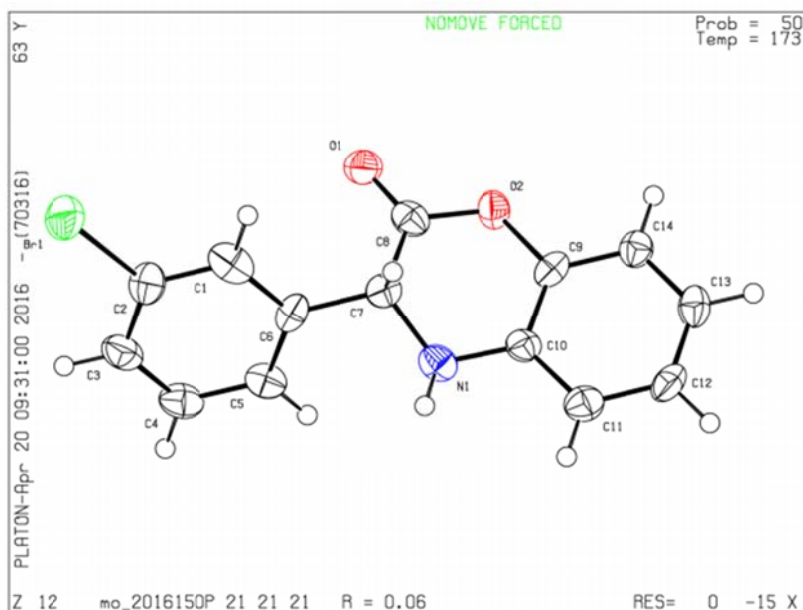
	Calculated	Reported
Volume	1181.7(2)	1181.7(2)
Space group	P 21 21 21	P 21 21 21
Hall group	P 2ac 2ab	P 2ac 2ab
Moiety formula	C14 H10 Br N O2	C14 H10 Br N O2
Sum formula	C14 H10 Br N O2	C14 H10 Br N O2
Mr	304.13	304.14
Dx, g cm-3	1.709	1.710
Z	4	4
Mu (mm-1)	3.470	3.470
F000	608.0	608.0
F000'	607.12	
h, k, lmax	5, 13, 27	5, 13, 27
Nref	2081 [1262]	2081
Tmin, Tmax	0.439, 0.500	0.453, 0.745
Tmin'	0.350	

Correction method= # Reported T Limits: Tmin=0.453 Tmax=0.745
 AbsCorr = MULTI-SCAN

Data completeness= 1.65/1.00 Theta(max)= 25.002

R(reflections)= 0.0562(1396) wR2(reflections)= 0.0994(2081)

S = 1.021 Npar= 163



8. Copies of ^1H NMR and ^{13}C NMR spectra:

