

Supplementary Information:

Highly enantioselective Rh/chiral sulfur-olefin-catalyzed arylation of alkyl-substituted non-benzofused cyclic *N*-sulfonyl ketimines

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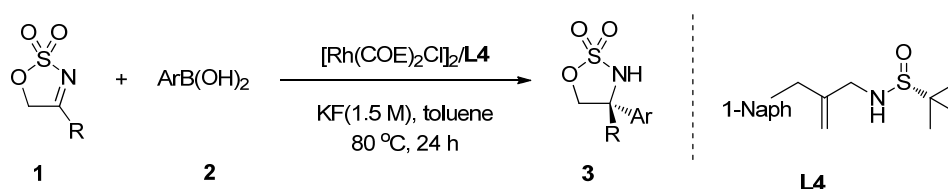
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1. General

All anaerobic and moisture-sensitive manipulations were carried out with standard Schlenk techniques under nitrogen or argon. Solvents were dried and distilled by standard procedures. NMR spectra were recorded on a Mercury 300 spectrometer (300 MHz for ^1H), and Varian spectrometer (400 MHz for ^1H , 100 MHz or 125 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 77.36) or $(\text{CD}_3)_2\text{SO}$ (δ 39.52) for ^{13}C NMR. Optical rotations were measured on a Perkin-Elmer 241 MC polarimeter. HPLC was performed on a JASCO 2000 instrument by using Daicel columns with 2-propanol/hexane as the eluent.

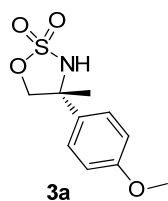
2. General procedure for Rh-catalyzed 1,2-addition of cyclic ketimines **1**



Under Ar atmosphere, a solution of substrate ketimine **1** (0.20 mmol, 1 equiv), $[\text{Rh}(\text{COE})_2\text{Cl}]_2$ (2.2 mg, 0.003 mmol, 1.5 mol%), ligand **L4** (2.0 mg, 0.0066 mmol, 3.3 mol%), and arylboronic acid **2** (0.60 mmol, 3 equiv) in 2.0 mL of toluene was stirred at room temperature for 30 min. To this mixture was added aqueous KF (0.13 mL, 1.5 M, 0.20 mmol, 1 equiv) and the resulting mixture was stirred at $80\text{ }^\circ\text{C}$ for 24 hours. Then the solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography using petroleum ether/ethyl acetate as an eluent to afford the corresponding addition product **3**. For compounds **3i**, **3j**, **3m**, **3n**, **3q-3t**, **3w** and **3x**, 6 equiv of corresponding arylboronic acid **2** (1.20 mmol) were utilized.

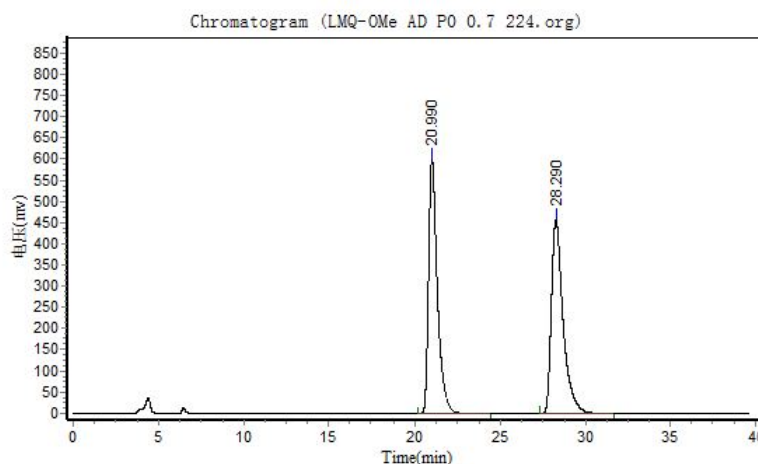
3. Characterization data and HPLC of addition products

(*R*)-4-(4-methoxyphenyl)-4-methyl-1,2,3-oxathiazolidine 2,2-dioxide (3a)^[1]



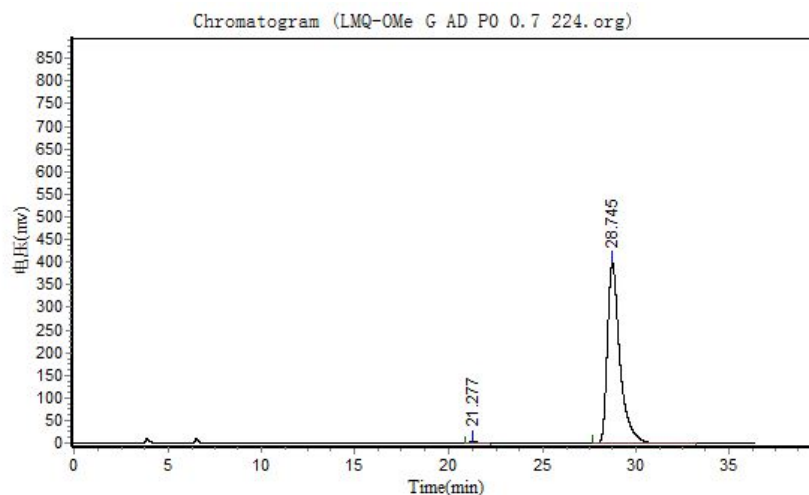
White solid, 41 mg, 85% yield, 99% ee. $[\alpha]_D^{20} = +2.6$ (c 1.14, CHCl₃). ¹H NMR (300 MHz, CDCl₃) δ 7.37 (d, *J* = 8.0 Hz, 2H), 6.94 (d, *J* = 8.0 Hz, 2H), 4.66 (s, 1H), 4.63 and 4.55 (AB q, *J* = 8.6 Hz, 1H), 3.82 (s, 3H), 1.82 (s, 3H).

HPLC: Chiralcel AD-H column (250 mm); detected at 224 nm; hexane/*i*-propanol = 90/10; flow = 0.7 mL/min; Retention time: 21.3 min, 28.7 min (major).



Results

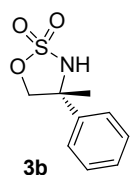
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		20.990	599496.438	21511814.000	49.6622
2		28.290	457577.688	21804456.000	50.3378
Total			1057074.125	43316270.000	100.0000



Results

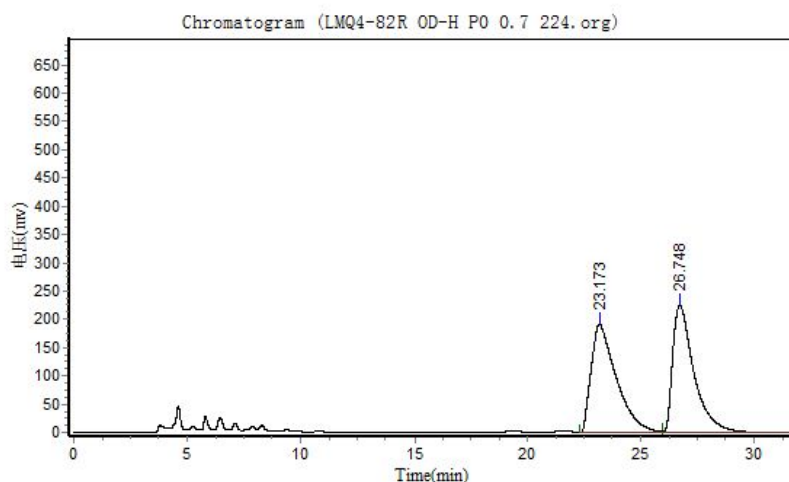
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		21.277	4558.606	137235.297	0.7332
2		28.745	398132.656	18580742.000	99.2668
Total			402691.263	18717977.297	100.0000

(R)-4-methyl-4-phenyl-1,2,3-oxathiazolidine 2,2-dioxide (3b)^[1]



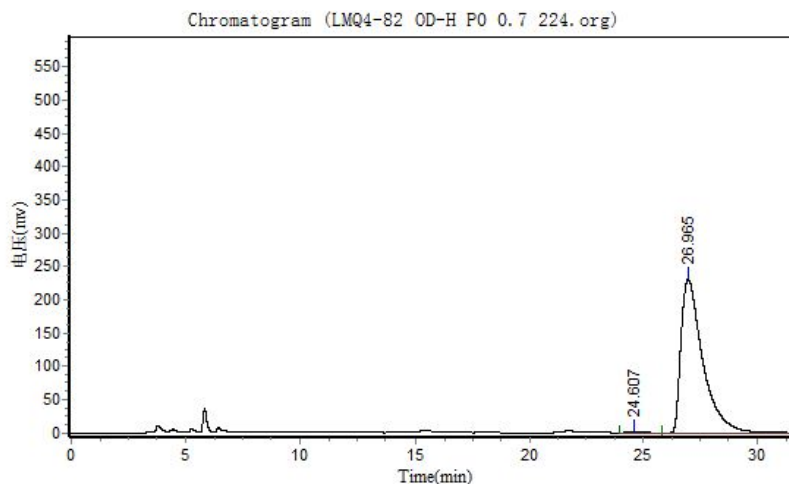
White solid, 33 mg, 76% yield, 99% ee. $[\alpha]_D^{20} = +2.4$ (c 1.08, CHCl₃). ¹H NMR (300 MHz, CDCl₃) δ 7.55-7.28 (m, 5H), 4.89 (s, 1H), 4.65 and 4.59 (AB q, $J = 8.6$ Hz, 1H), 1.82 (s, 3H).

HPLC: Chiralcel OD-H column (250 mm); detected at 224 nm; hexane/*i*-propanol = 90/10; flow = 0.7 mL/min; Retention time: 24.6 min, 27.0 min (major).



Results

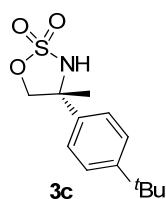
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		23.173	190906.250	14710651.000	49.8490
2		26.748	224251.000	14799754.000	50.1510
Total			415157.250	29510405.000	100.0000



Results

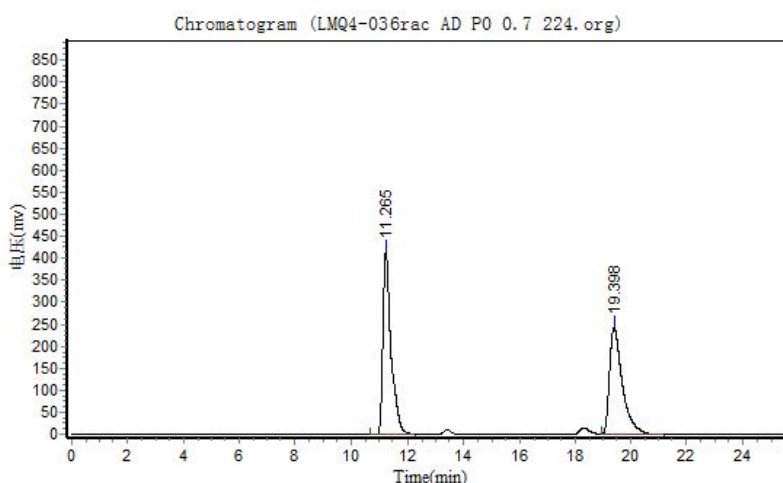
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		24.607	1430.677	63444.699	0.4121
2		26.965	230449.641	15333074.000	99.5879
Total			231880.318	15396518.699	100.0000

(R)-4-(4-(tert-butyl)phenyl)-4-methyl-1,2,3-oxathiazolidine 2,2-dioxide (3c)

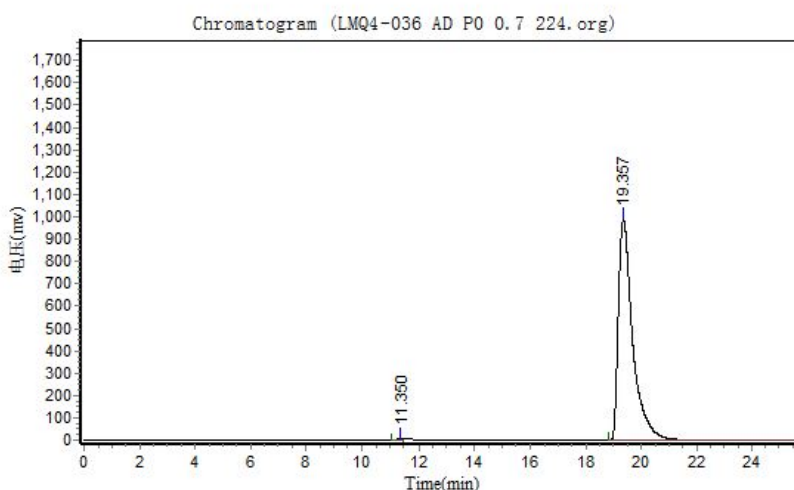


White solid, 46 mg, 85% yield, 99% ee. $[\alpha]_D^{20} = +0.8$ (c 1.16, CHCl_3). ^1H NMR (300 MHz, CDCl_3) δ 7.48-7.40 (m, 2H), 7.38-7.31 (m, 2H), 4.62 (s, 1H), 4.65 and 4.57 (AB q, $J = 8.6$ Hz, 1H), 1.83 (s, 3H), 1.32 (s, 9H). ^{13}C NMR (126 MHz, CDCl_3) δ 152.14, 138.30, 126.47, 124.98, 80.71, 65.44, 34.93, 31.55, 27.67. HRMS (EI) for $\text{C}_{13}\text{H}_{19}\text{NO}_3\text{S}$: calcd 269.1086, found 269.1089.

HPLC: Chiralcel AD-H column (250 mm); detected at 224 nm; hexane/*i*-propanol = 90/10; flow = 0.7 mL/min; Retention time: 11.4 min, 19.4 min (major).

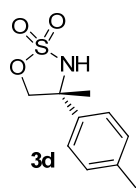


Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.265	415424.719	8464387.000	51.9116
2		19.398	241833.563	7840998.000	48.0884
Total			657258.281	16305385.000	100.0000



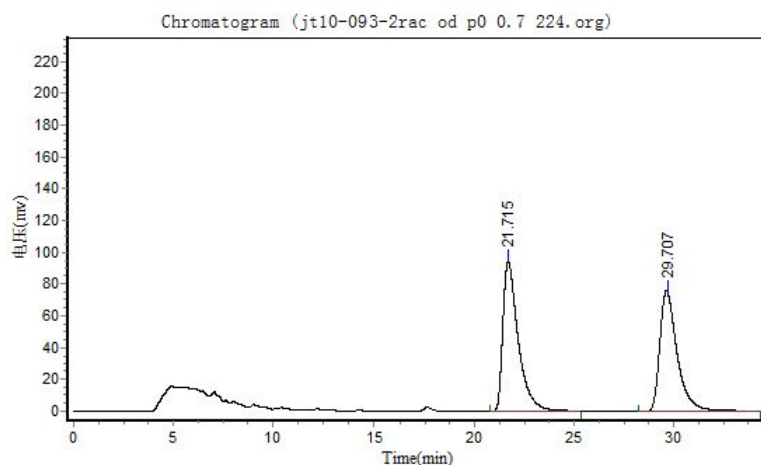
Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.350	8356.782	116010.273	0.3244
2		19.357	988498.938	35645748.000	99.6756
Total			996855.720	35761758.273	100.0000

(R)-4-methyl-4-(p-tolyl)-1,2,3-oxathiazolidine 2,2-dioxide (3d)



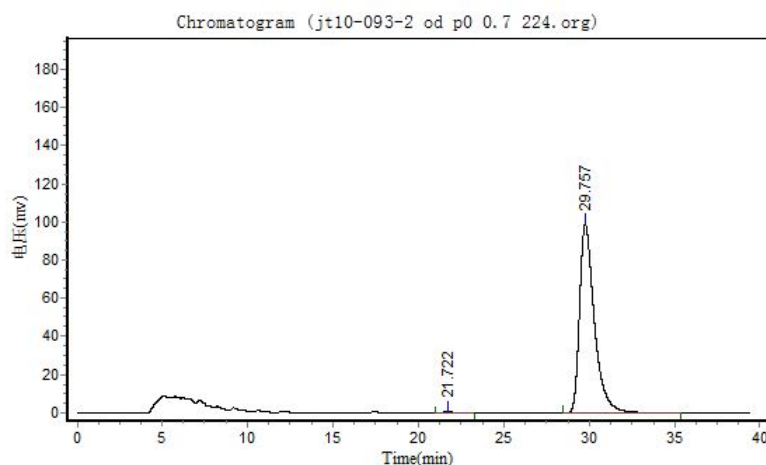
White solid, 36 mg, 79% yield, 99% ee. $[\alpha]_D^{20} = +2.6$ (c 1.30, CHCl_3). ^1H NMR (300 MHz, CDCl_3) δ 7.31 (d, $J = 7.9$ Hz, 2H), 7.22 (d, $J = 8.0$ Hz, 2H), 4.82 (s, 1H), 4.64 and 4.56 (AB q, $J = 8.7$ Hz, 1H), 2.35 (s, 3H), 1.80 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 138.79, 138.39, 130.09, 125.15, 80.77, 65.51, 27.66, 21.30. HRMS (EI) for $\text{C}_{10}\text{H}_{13}\text{NO}_3\text{S}$: calcd 227.0616, found 227.0618.

HPLC: Chiralcel OD-H column (250 mm); detected at 224 nm; hexane/*i*-propanol = 90/10; flow = 0.7 mL/min; Retention time: 21.7 min, 29.8 min (major).



Results

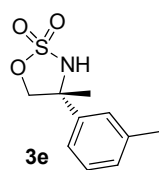
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		21.715	94552.602	5054627.500	52.6521
2		29.707	75348.438	4545414.500	47.3479
Total			169901.039	9600042.000	100.0000



Results

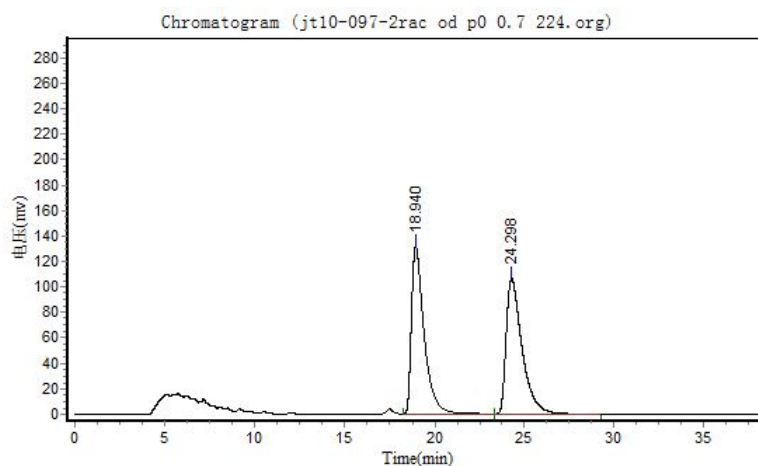
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		21.722	553.099	28871.898	0.4750
2		29.757	99084.500	6049271.500	99.5250
Total			99637.599	6078143.398	100.0000

(R)-4-methyl-4-(m-tolyl)-1,2,3-oxathiazolidine 2,2-dioxide (3e)



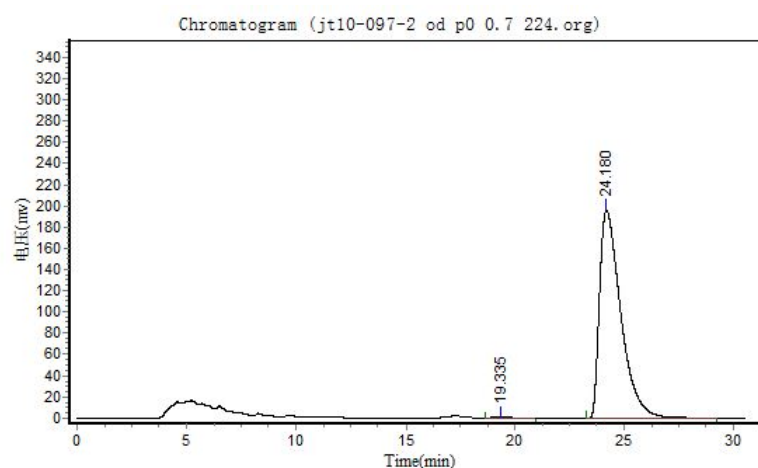
White solid, 33 mg, 73% yield, 99% ee. $[\alpha]_D^{20} = +1.5$ (c 1.03, CHCl_3). ^1H NMR (300 MHz, CDCl_3) δ 7.33-7.15 (m, 4H), 4.81 (s, 1H), 4.65 and 4.58 (AB q, $J = 8.6$ Hz, 1H), 2.38 (s, 3H), 1.81 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 141.34, 139.32, 129.62, 129.36, 125.84, 122.19, 80.64, 65.60, 27.82, 21.87. HRMS (EI) for $\text{C}_{10}\text{H}_{13}\text{NO}_3\text{S}$: calcd 227.0616, found 227.0614.

HPLC: Chiralcel OD-H column (250 mm); detected at 224 nm; hexane/*i*-propanol = 90/10; flow = 0.7 mL/min; Retention time: 19.3 min, 24.2 min (major).



Results

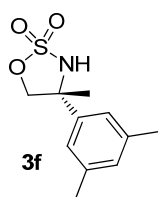
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		18.940	132039.328	6589103.000	49.8088
2		24.298	106766.273	6639703.500	50.1913
Total			238805.602	13228806.500	100.0000



Results

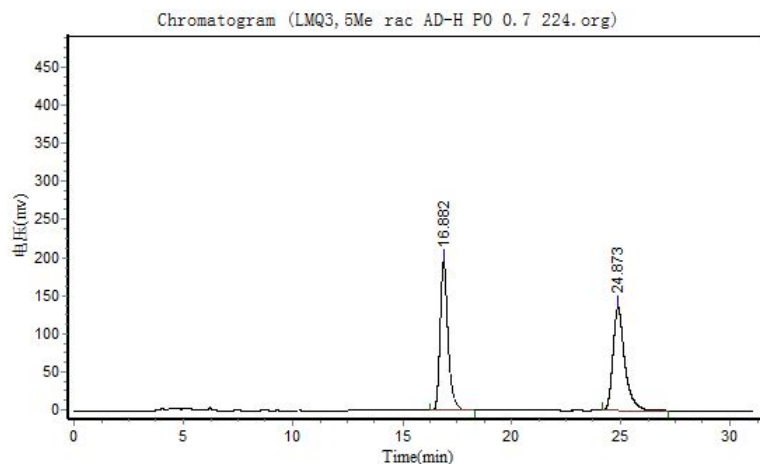
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		19.335	936.675	45982.547	0.3459
2		24.180	196174.734	13247451.000	99.6541
Total			197111.409	13293433.547	100.0000

(R)-4-(3,5-dimethylphenyl)-4-methyl-1,2,3-oxathiazolidine 2,2-dioxide (3f)



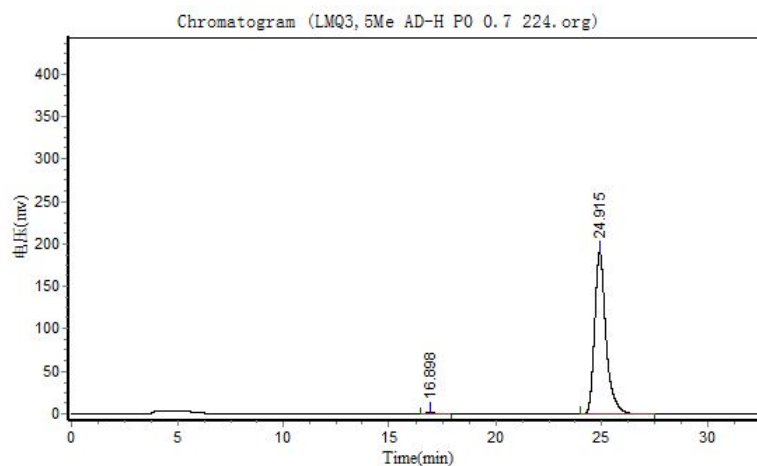
White solid, 37 mg, 76% yield, 99% ee. $[\alpha]_D^{20} = +0.6$ (c 1.04, CHCl_3). ^1H NMR (300 MHz, CDCl_3) δ 6.99 (s, 3H), 4.64 and 4.57 (AB q, $J = 8.7$ Hz, 1H), 4.53 (s, 1H), 2.34 (s, 6H), 1.82 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 141.29, 139.33, 130.60, 122.83, 80.64, 65.54, 27.91, 21.78. HRMS (EI) for $\text{C}_{11}\text{H}_{15}\text{NO}_3\text{S}$: calcd 241.0773, found 241.0767.

HPLC: Chiralcel AD-H column (250 mm); detected at 224 nm; hexane/*i*-propanol = 90/10; flow = 0.7 mL/min; Retention time: 16.9 min, 24.9 min (major).



Results

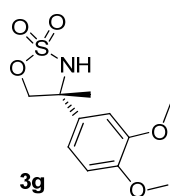
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		16.882	195057.516	4925326.000	49.3510
2		24.873	134764.500	5054861.000	50.6490
Total			329822.016	9980187.000	100.0000



Results

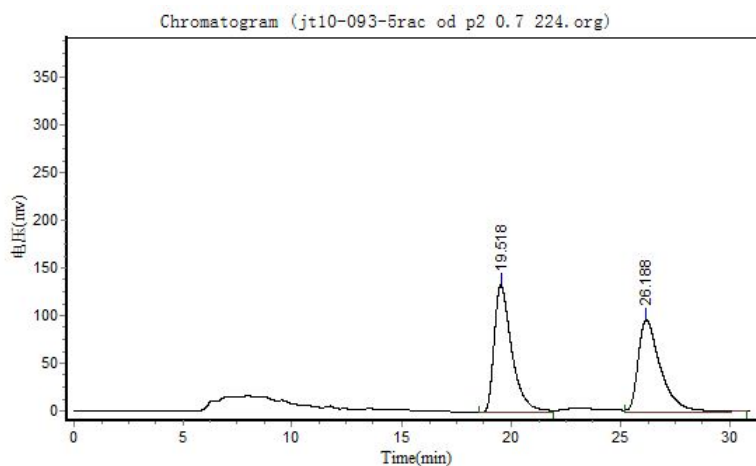
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		16.898	1684.671	41241.398	0.5771
2		24.915	190794.781	7105454.500	99.4229
Total			192479.452	7146695.898	100.0000

(R)-4-(3,4-dimethoxyphenyl)-4-methyl-1,2,3-oxathiazolidine 2,2-dioxide (3g)



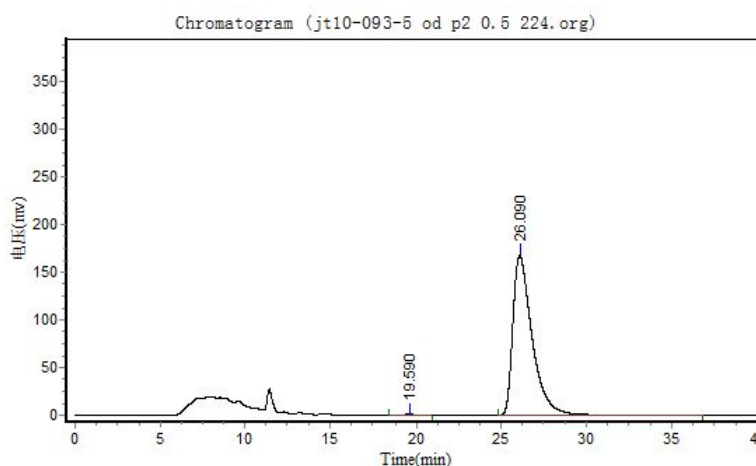
White solid, 50 mg, 92% yield, 99% ee. $[\alpha]^{20}_D = +2.3$ (c 1.34, CHCl_3). ^1H NMR (300 MHz, CDCl_3) δ 7.05-6.83 (m, 3H), 4.66 (s, 1H), 4.64 and 4.55 (AB q, $J = 8.6$ Hz, 1H), 3.91 (s, 3H), 3.89 (s, 3H), 1.83 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 149.63, 149.40, 133.84, 117.52, 111.55, 108.91, 80.80, 65.40, 56.34, 56.28, 27.50. HRMS (ESI) for $\text{C}_{11}\text{H}_{14}\text{NO}_5\text{S}[\text{M}-\text{H}]^-$: calcd 272.0598, found 272.0599.

HPLC: Chiralcel OD-H column (250 mm); detected at 224 nm; hexane/*i*-propanol = 70/30; flow = 0.7 mL/min; Retention time: 19.6 min, 26.1 min (major).



Results

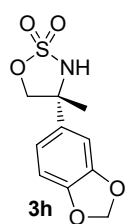
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		19.518	133520.859	7581809.000	52.5637
2		26.188	96187.008	6842237.500	47.4363
Total			229707.867	14424046.500	100.0000



Results

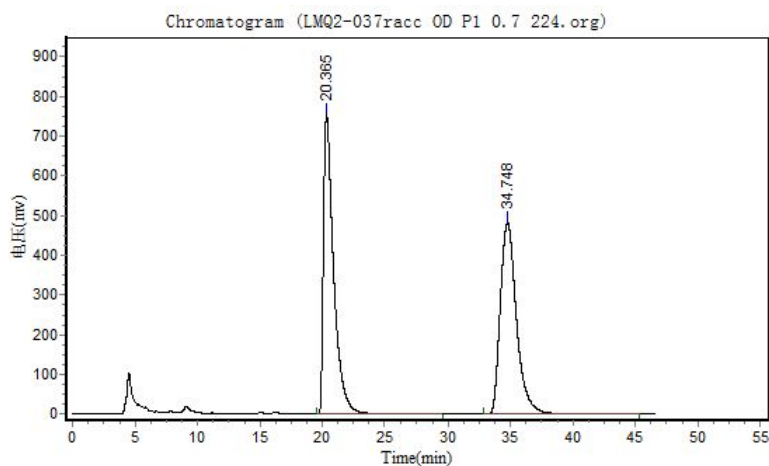
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		19.590	1335.450	76758.797	0.5751
2		26.090	167540.875	13270200.000	99.4249
Total			168876.325	13346958.797	100.0000

(R)-4-(benzo[d][1,3]dioxol-5-yl)-4-methyl-1,2,3-oxathiazolidine 2,2-dioxide (3h)



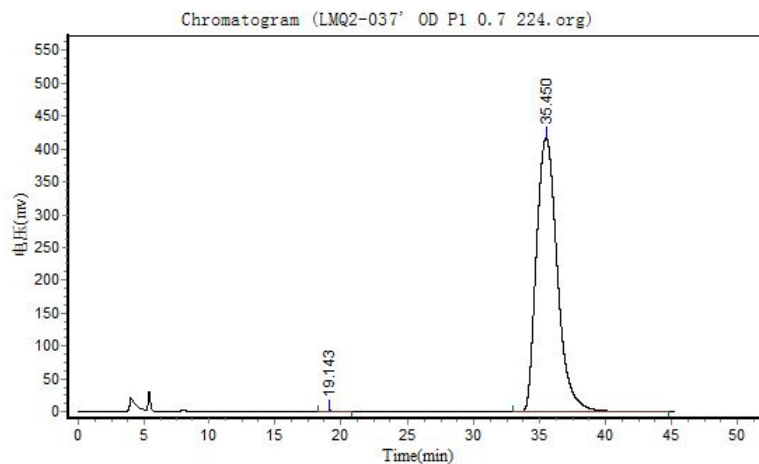
White solid, 37 mg, 72% yield, 99% ee. $[\alpha]_D^{20} = +0.2$ (c 1.20, CHCl_3). ^1H NMR (300 MHz, CDCl_3) δ 7.01-6.74 (m, 3H), 5.99 (s, 2H), 4.75 (s, 1H), 4.61 and 4.54 (AB q, $J = 8.7$ Hz, 1H), 1.79 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 148.81, 148.15, 135.22, 118.75, 108.90, 106.17, 101.91, 80.57, 65.47, 27.92. HRMS (ESI) for $\text{C}_{10}\text{H}_{10}\text{NO}_5\text{S}[\text{M}-\text{H}]^-$: calcd 256.0285, found 256.0280.

HPLC: Chiralcel OD-H column (250 mm); detected at 224 nm; hexane/*i*-propanol = 80/20; flow = 0.7 mL/min; Retention time: 19.1 min, 35.5 min (major).



Results

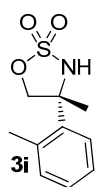
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		20.365	752650.688	42931100.000	49.6774
2		34.748	481474.531	43488712.000	50.3226
Total			1234125.219	86419812.000	100.0000



Results

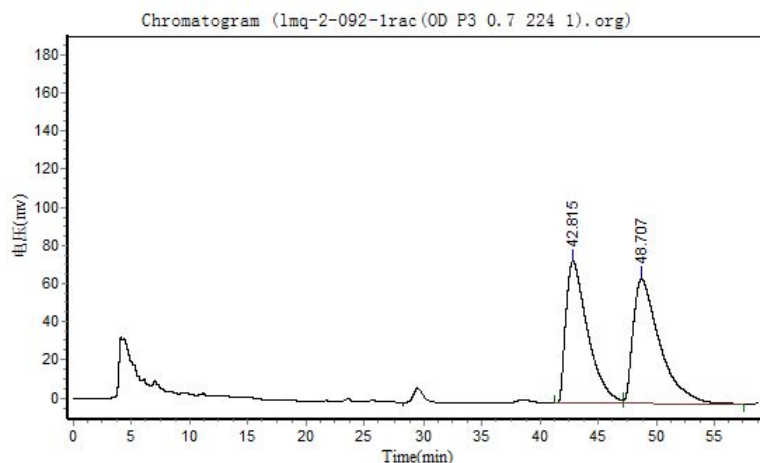
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		19.143	1610.157	86652.648	0.1878
2		35.450	417016.188	46051724.000	99.8122
Total			418626.344	46138376.648	100.0000

(R)-4-methyl-4-(o-tolyl)-1,2,3-oxathiazolidine 2,2-dioxide (3i)

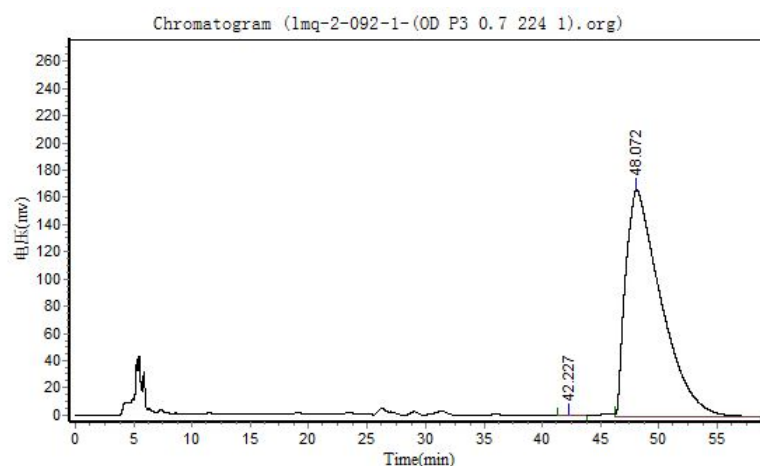


Colorless oil, 6 mg, 12% yield, 99% ee. $[\alpha]_D^{20} = +23.6$ (c 0.52, CHCl₃). ¹H NMR (300 MHz, CDCl₃) δ 7.47-7.06 (m, 4H), 4.83 and 4.77 (AB q, *J* = 8.4 Hz, 1H), 4.67 (s, 1H), 2.45 (s, 3H), 1.84 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 139.22, 134.69, 133.39, 128.95, 127.04, 125.38, 80.59, 66.57, 27.02, 21.68. HRMS (EI) for C₁₀H₁₃NO₃S: calcd 227.0616, found 227.0618.

HPLC: Chiralcel OD-H column (250 mm); detected at 224 nm; hexane/*i*-propanol = 95/5; flow = 0.7 mL/min; Retention time: 42.2 min, 48.1 min (major).

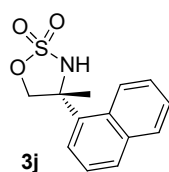


Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		42.815	74394.148	9677710.000	48.3030
2		48.707	65375.469	10357693.000	51.6970
Total			139769.617	20035403.000	100.0000



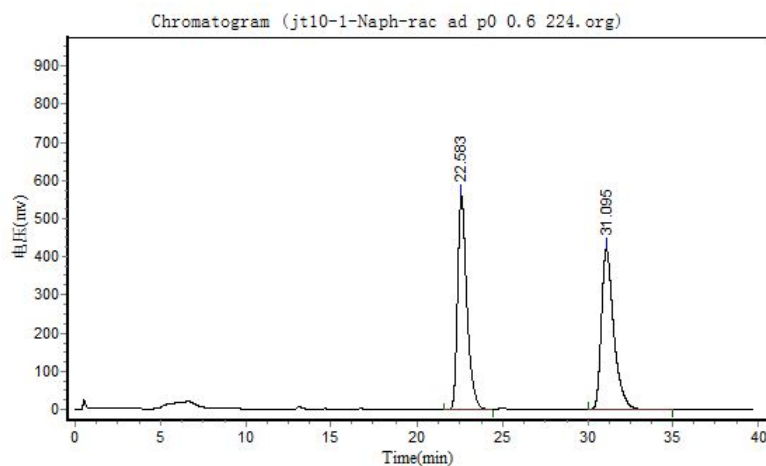
Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		42.227	204.464	17094.449	0.0487
2		48.072	166441.891	35082064.000	99.9513
Total			166646.354	35099158.449	100.0000

(R)-4-methyl-4-(naphthalen-1-yl)-1,2,3-oxathiazolidine 2,2-dioxide (3j)



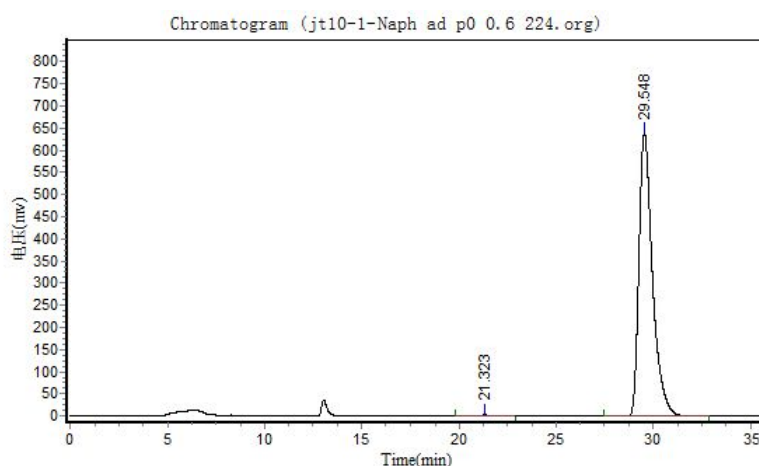
Yellow oil, 19 mg, 36% yield, 99% ee. $[\alpha]_D^{20} = +21.0$ (c 1.19, CHCl_3). ^1H NMR (300 MHz, CDCl_3) δ 8.19 (d, $J = 8.6$ Hz, 1H), 7.98-7.84 (m, 2H), 7.66-7.40 (m, 4H), 5.03 and 4.99 (AB q, $J = 8.5$ Hz, 1H), 4.75 (s, 1H), 2.08 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 136.56, 135.18, 130.45, 130.21, 129.79, 127.19, 126.43, 125.42, 124.75, 123.50, 81.15, 66.54, 27.71. HRMS (ESI) for $\text{C}_{13}\text{H}_{12}\text{NO}_3\text{S}[\text{M}-\text{H}]^-$: calcd 262.0543, found 262.0541.

HPLC: Chiralcel AD-H column (250 mm); detected at 224 nm; hexane/*i*-propanol = 90/10; flow = 0.6 mL/min; Retention time: 21.3 min, 29.5 min (major).



Results

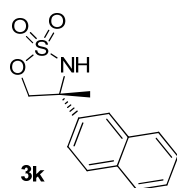
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		22.583	559195.438	21362708.000	50.0470
2		31.095	420405.438	21322548.000	49.9530
Total			979600.875	42685256.000	100.0000



Results

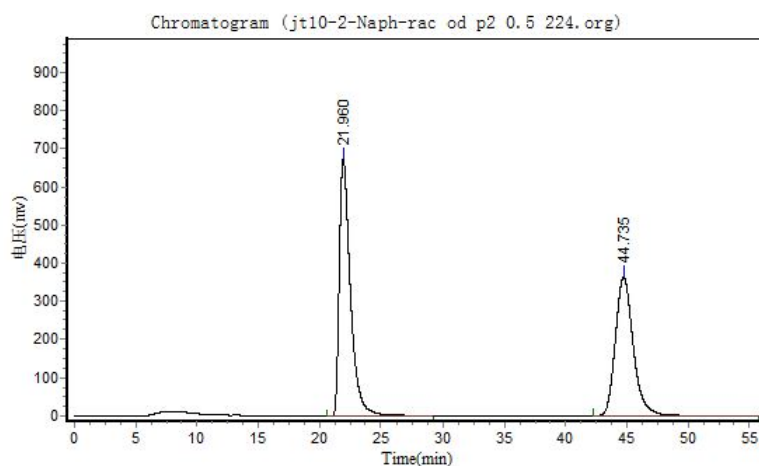
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		21.323	3035.352	131619.453	0.4226
2		29.548	638112.688	31014038.000	99.5774
Total			641148.040	31145657.453	100.0000

(R)-4-methyl-4-(naphthalen-2-yl)-1,2,3-oxathiazolidine 2,2-dioxide (3k)^[1]



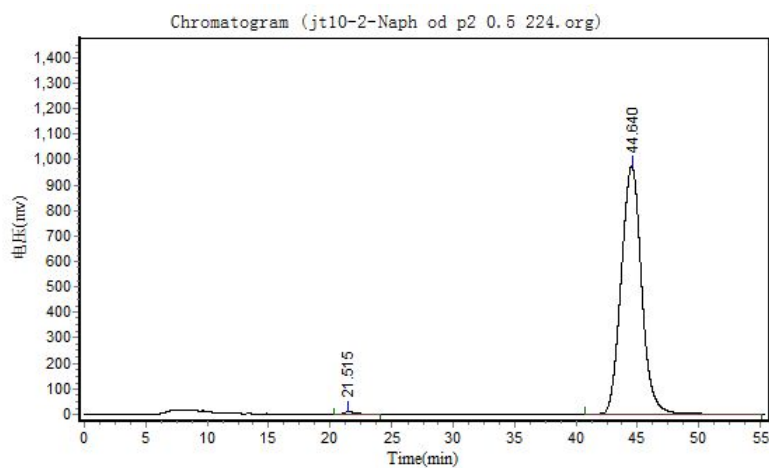
Yellow solid, 41 mg, 78% yield, 99% ee. $[\alpha]_D^{20} = +11.6$ (c 1.08, CHCl₃). ¹H NMR (300 MHz, CDCl₃) δ 8.02-7.78 (m, 4H), 7.54-7.47 (m, 3H), 4.75 and 4.65 (AB q, $J = 8.7$ Hz, 1H), 1.90 (s, 3H).

HPLC: Chiralcel OD-H column (250 mm); detected at 224 nm; hexane/*i*-propanol = 70/30; flow = 0.5 mL/min; Retention time: 21.5 min, 44.6 min (major).



Results

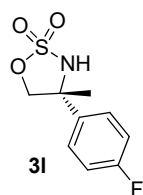
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		21.960	671555.000	42743972.000	53.5058
2		44.735	364542.406	37142692.000	46.4942
Total			1036097.406	79886664.000	100.0000



Results

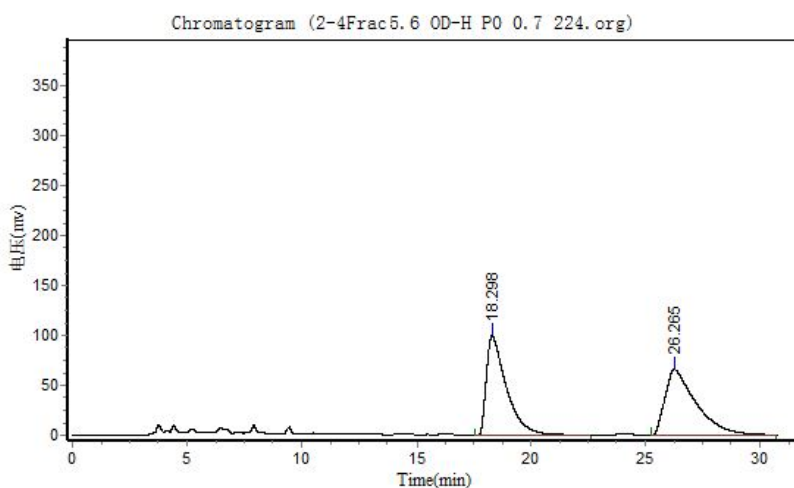
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		21.515	10389.505	629959.375	0.5553
2		44.640	973364.063	112822664.000	99.4447
Total			983753.567	113452623.375	100.0000

(R)-4-(4-fluorophenyl)-4-methyl-1,2,3-oxathiazolidine 2,2-dioxide (3I)^[2]



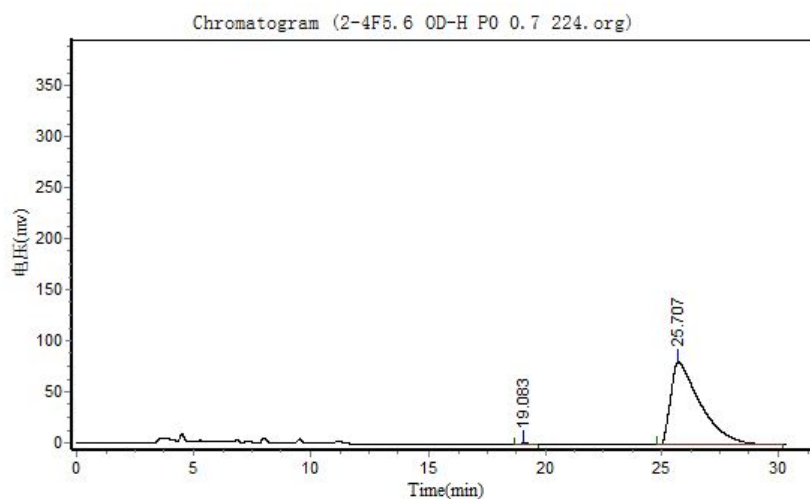
Colorless oil, 29 mg, 62% yield, 99% ee. $[\alpha]_D^{20} = +3.2$ (c 1.05, CHCl_3). ^1H NMR (300 MHz, CDCl_3) δ 7.47-7.42 (m, 2H), 7.10 (t, $J = 8.5$ Hz, 2H), 4.86 (s, 1H), 4.63 and 4.57 (AB q, $J = 8.7$ Hz, 1H), 1.81 (s, 3H).

HPLC: Chiralcel OD-H column (250 mm); detected at 224 nm; hexane/*i*-propanol = 90/10; flow = 0.7 mL/min; Retention time: 19.1 min, 25.7 min (major).



Results

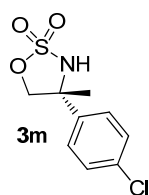
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		18.298	99346.398	5971638.500	49.2447
2		26.265	65513.113	6154815.000	50.7553
Total			164859.512	12126453.500	100.0000



Results

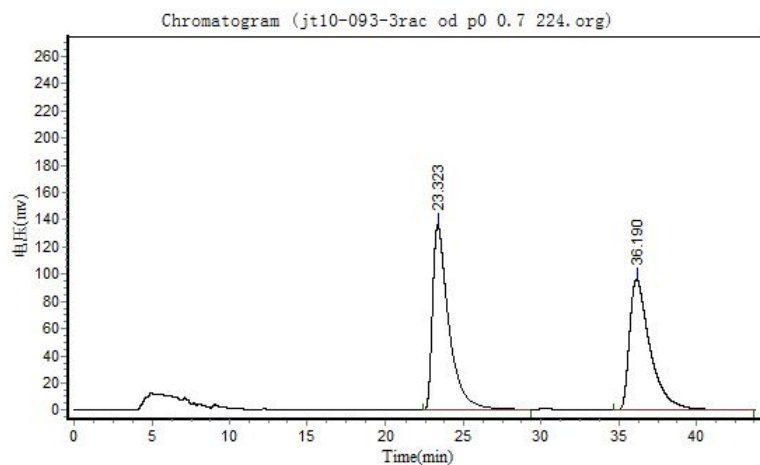
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		19.083	1194.224	51892.293	0.7105
2		25.707	81506.898	7251434.500	99.2895
Total			82701.122	7303326.793	100.0000

(R)-4-(4-chlorophenyl)-4-methyl-1,2,3-oxathiazolidine 2,2-dioxide (3m)^[1]



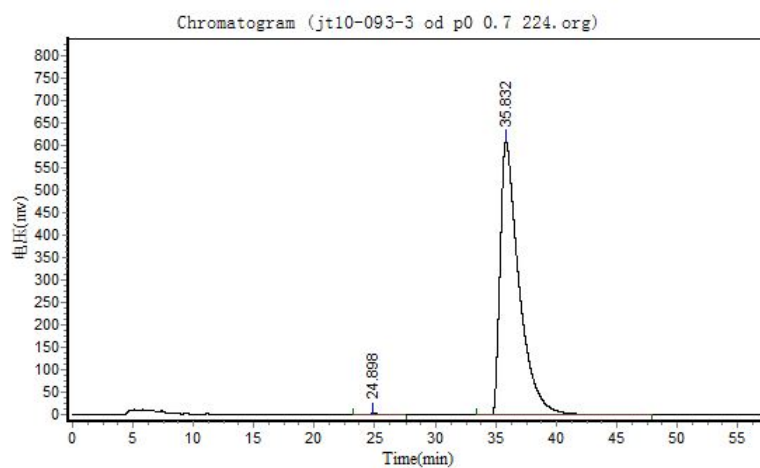
Yellow oil, 32 mg, 65% yield, 99% ee. $[\alpha]_D^{20} = +0.8$ (c 1.05, CHCl_3). ^1H NMR (300 MHz, CDCl_3) δ 7.39 (s, 4H), 4.84 (s, 1H), 4.62 and 4.57 (AB q, $J = 8.7$ Hz, 1H), 1.80 (s, 3H).

HPLC: Chiralcel OD-H column (250 mm); detected at 224 nm; hexane/*i*-propanol = 90/10; flow = 0.7 mL/min; Retention time: 24.9 min, 35.8 min (major).



Results

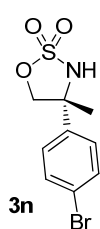
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		23.323	135941.047	9971570.000	52.7442
2		36.190	96267.984	8933969.000	47.2558
Total			232209.031	18905539.000	100.0000



Results

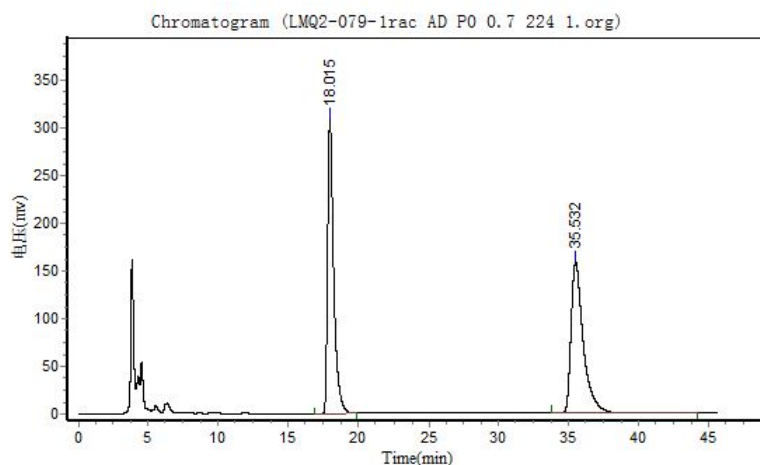
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		24.898	3380.586	250901.016	0.3747
2		35.832	611204.438	66703240.000	99.6253
Total			614585.023	66954141.016	100.0000

(R)-4-(4-bromophenyl)-4-methyl-1,2,3-oxathiazolidine 2,2-dioxide (3n)



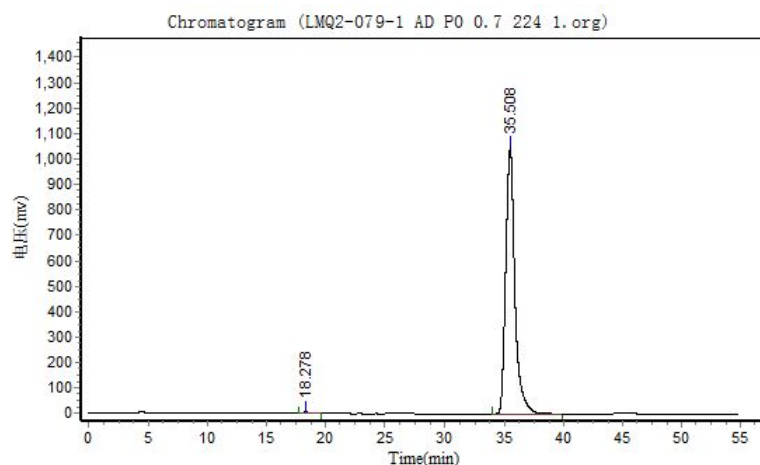
Yellow solid, 34 mg, 58% yield, 99% ee. $[\alpha]_D^{20} = +1.3$ (c 1.01, CHCl_3). ^1H NMR (300 MHz, CDCl_3) δ 7.55 (d, $J = 8.0$ Hz, 2H), 7.34 (d, $J = 8.0$ Hz, 2H), 4.75 (s, 1H), 4.62 and 4.57 (AB q, $J = 8.7$ Hz, 1H), 1.80 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 140.56, 132.59, 127.19, 123.06, 80.27, 65.33, 27.77. HRMS (EI) for $\text{C}_9\text{H}_9\text{BrNO}_3\text{S}$: calcd 290.9565, found 290.9541.

HPLC: Chiralcel AD-H column (250 mm); detected at 224 nm; hexane/*i*-propanol = 90/10; flow = 0.7 mL/min; Retention time: 18.3 min, 35.5 min (major).



Results

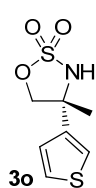
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		18.015	307294.250	9253804.000	49.0923
2		35.532	157947.953	9595999.000	50.9077
Total			465242.203	18849803.000	100.0000



Results

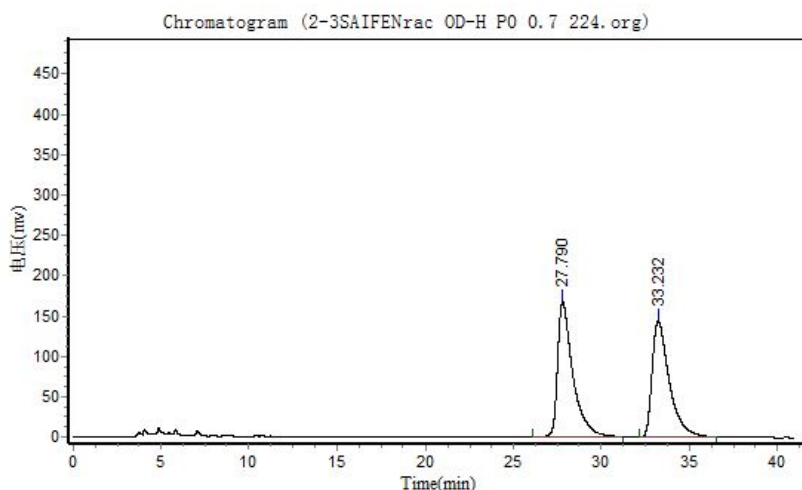
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		18.278	9426.785	289981.000	0.5135
2		35.508	1042908.875	56176892.000	99.4865
Total			1052335.660	56466873.000	100.0000

(R)-4-methyl-4-(thiophen-3-yl)-1,2,3-oxathiazolidine 2,2-dioxide (3o)



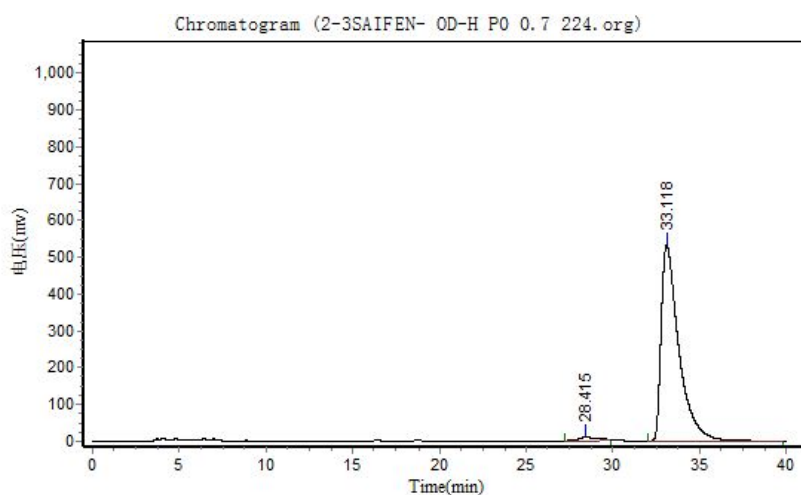
White solid, 17 mg, 38% yield, 97% ee. $[\alpha]_D^{20} = +4.5$ (c 1.20, CHCl_3). ^1H NMR (300 MHz, CDCl_3) δ 7.46-7.32 (m, 2H), 7.14-7.12 (m, 1H), 4.91 (s, 1H), 4.62 and 4.50 (AB q, $J = 8.7$ Hz, 1H), 1.84 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 142.70, 128.12, 125.18, 122.67, 80.30, 63.40, 26.80. HRMS (EI) for $\text{C}_7\text{H}_9\text{NO}_3\text{S}_2$: calcd 219.0024, found 219.0025.

HPLC: Chiralcel OD-H column (250 mm); detected at 224 nm; hexane/*i*-propanol = 90/10; flow = 0.7 mL/min; Retention time: 28.4 min, 33.1 min (major).



Results

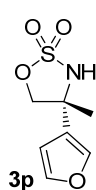
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		27.790	168048.656	10341854.000	50.9974
2		33.232	144447.219	9937322.000	49.0026
Total			312495.875	20279176.000	100.0000



Results

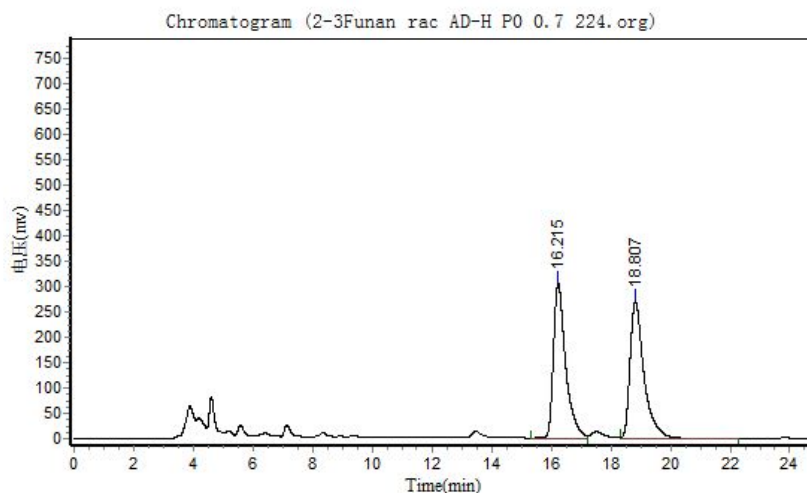
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		28.415	8477.254	636930.313	1.6528
2		33.118	533794.125	37900068.000	98.3472
Total			542271.379	38536998.313	100.0000

(R)-4-(furan-3-yl)-4-methyl-1,2,3-oxathiazolidine 2,2-dioxide (3p)



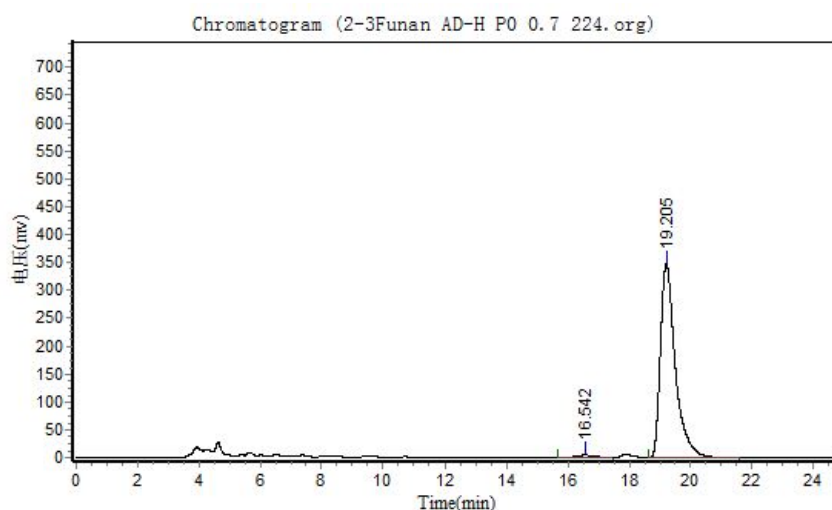
Yellow oil, 12 mg, 30% yield, 97% ee. $[\alpha]_D^{20} = +6.1$ (c 1.01, CHCl_3). ^1H NMR (300 MHz, CDCl_3) δ 7.51 (s, 1H), 7.46 (s, 1H), 6.48 (s, 1H), 4.70 (s, 1H), 4.57 and 4.46 (AB q, $J = 9.3$ Hz, 1H), 1.79 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 144.91, 140.09, 127.52, 108.24, 80.01, 60.65, 25.97. HRMS (EI) for $\text{C}_7\text{H}_9\text{NO}_4\text{S}$: calcd 203.0252, found 203.0247.

HPLC: Chiralcel AD-H column (250 mm); detected at 224 nm; hexane/*i*-propanol = 90/10; flow = 0.7 mL/min; Retention time: 16.5 min, 19.2 min (major).



Results

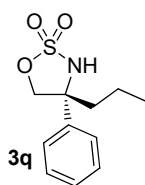
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		16.215	305568.906	8697016.000	49.8561
2		18.807	269445.938	8747223.000	50.1439
Total			575014.844	17444239.000	100.0000



Results

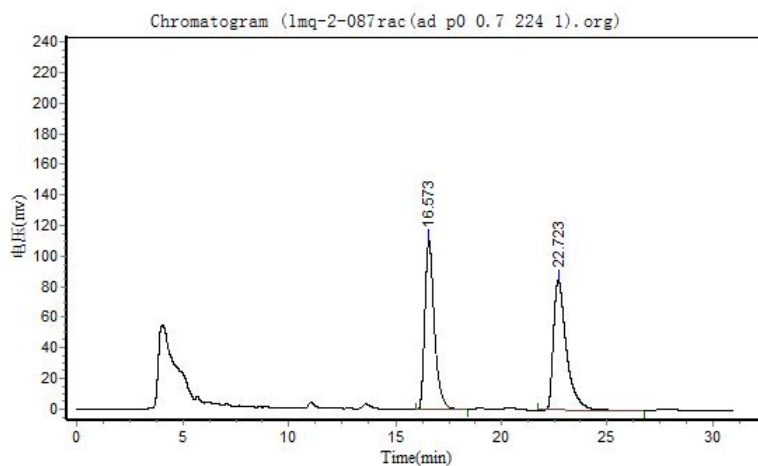
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		16.542	4312.092	170652.906	1.4434
2		19.205	348042.344	11652042.000	98.5566
Total			352354.436	11822694.906	100.0000

(R)-4-phenyl-4-propyl-1,2,3-oxathiazolidine 2,2-dioxide (3q)

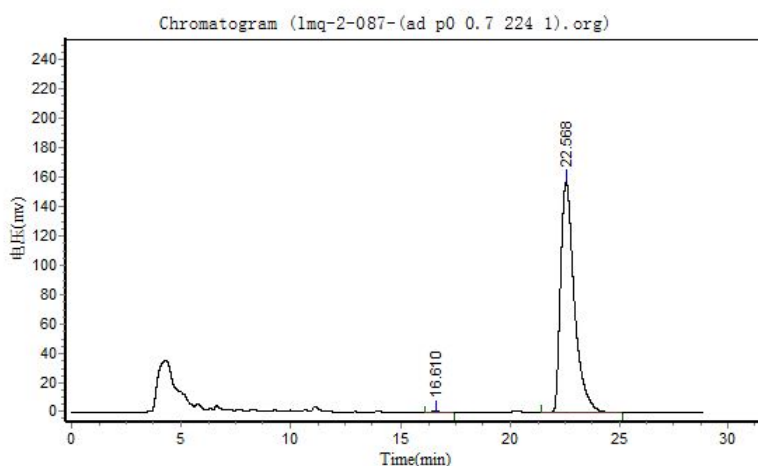


White solid, 38 mg, 78% yield, 99% ee. $[\alpha]_D^{20} = -0.1$ (c 1.15, CHCl_3). ^1H NMR (300 MHz, CDCl_3) δ 7.58-7.21 (m, 5H), 4.76 (s, 1H), 4.71-4.60 (m, 2H), 2.25-1.83 (m, 2H), 1.39-0.99 (m, 2H), 0.88 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 140.13, 129.38, 128.69, 125.51, 79.98, 68.84, 42.69, 17.57, 14.22. HRMS (EI) for $\text{C}_{11}\text{H}_{15}\text{NO}_3\text{S}$: calcd 241.0773, found 241.0771.

HPLC: Chiralcel AD-H column (250 mm); detected at 224 nm; hexane/*i*-propanol = 90/10; flow = 0.7 mL/min; Retention time: 16.6 min, 22.6 min (major).

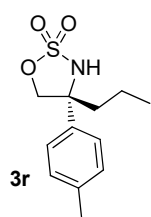


Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		16.573	110419.828	3499060.750	48.9925
2		22.723	85110.727	3642974.750	51.0075
Total			195530.555	7142035.500	100.0000



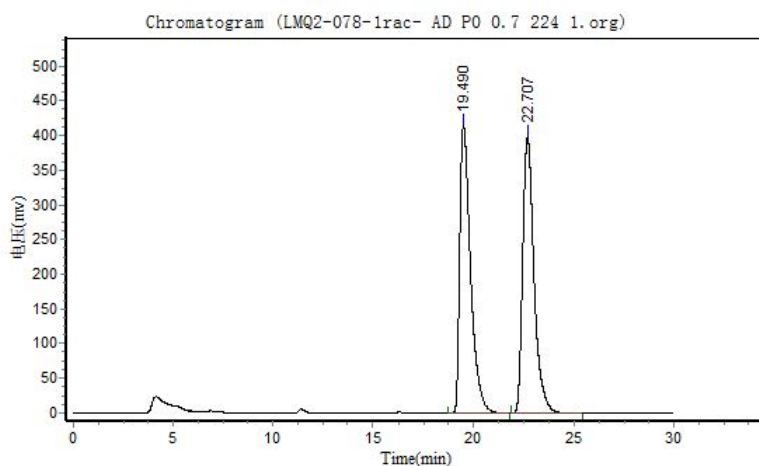
Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		16.610	1203.121	35905.977	0.5163
2		22.568	157619.484	6918864.500	99.4837
Total			158822.605	6954770.477	100.0000

(R)-4-propyl-4-(p-tolyl)-1,2,3-oxathiazolidine 2,2-dioxide (3r)



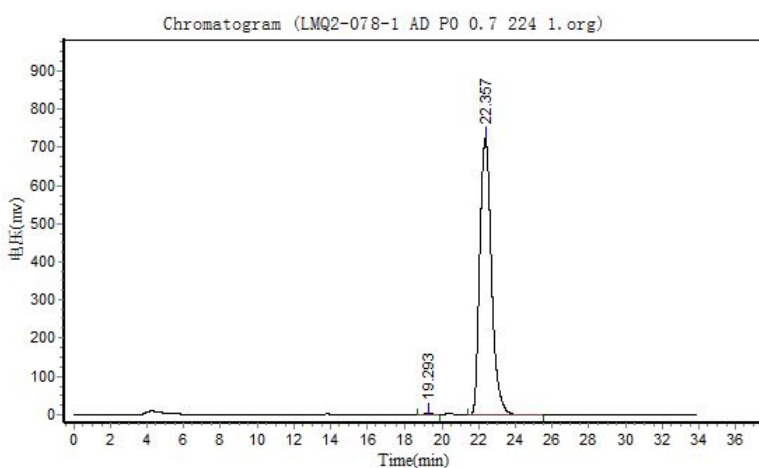
White solid, 44 mg, 86% yield, 99% ee. $[\alpha]_D^{20} = +2.3$ (c 1.29, CHCl₃). ¹H NMR (300 MHz, CDCl₃) δ 7.21 (s, 4H), 4.65 and 4.62 (AB q, $J = 8.7$ Hz, 1H), 2.36 (s, 3H), 2.17-1.90 (m, 2H), 1.36-1.01 (m, 2H), 0.88 (t, $J = 7.3$ Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 138.59, 137.07, 130.04, 125.40, 80.06, 68.74, 42.57, 21.34, 17.58, 14.23. HRMS (EI) for C₁₂H₁₇NO₃S: calcd 255.0929, found 255.0935.

HPLC: Chiralcel AD-H column (250 mm); detected at 224 nm; hexane/*i*-propanol = 90/10; flow = 0.7 mL/min; Retention time: 19.3 min, 22.4 min (major).



Results

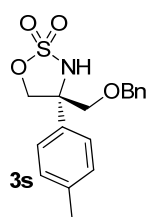
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		19.490	414350.875	15565262.000	49.7769
2		22.707	397936.844	15704768.000	50.2231
Total			812287.719	31270030.000	100.0000



Results

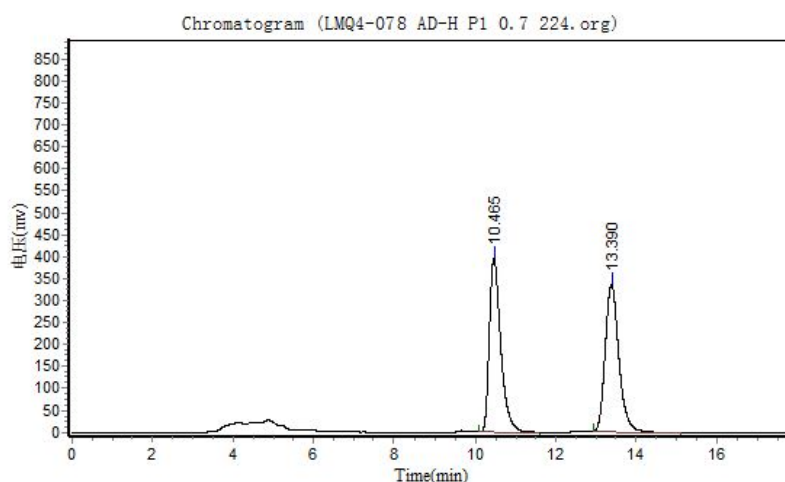
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		19.293	4952.352	152580.000	0.4738
2		22.357	723614.875	32048788.000	99.5262
Total			728567.227	32201368.000	100.0000

(S)-4-((benzyloxy)methyl)-4-(p-tolyl)-1,2,3-oxathiazolidine 2,2-dioxide (3s)



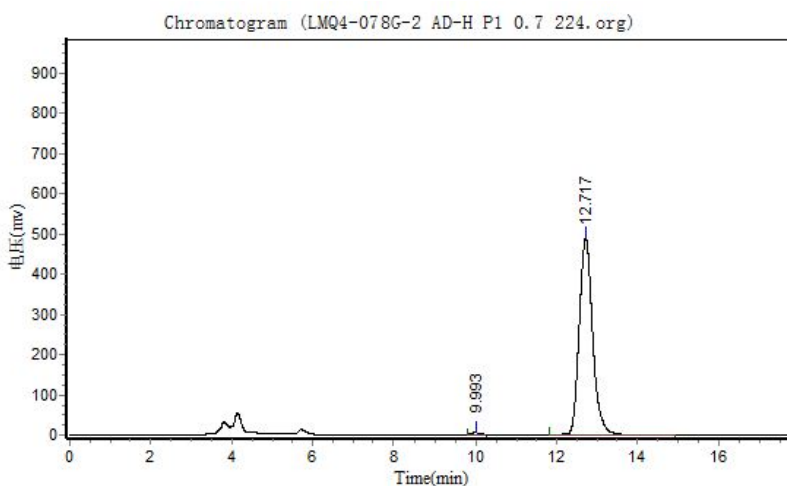
Colorless oil, 66 mg, 99% yield, 99% ee. $[\alpha]_D^{20} = +11.5$ (c 1.50, CHCl_3). ^1H NMR (300 MHz, CDCl_3) δ 7.41-7.14 (m, 9H), 5.17 (s, 1H), 4.81 and 4.63 (AB q, $J = 8.4$ Hz, 1H), 4.61-4.52 (m, 2H), 3.65 and 3.58 (AB q, $J = 10.1$ Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 139.02, 136.83, 135.44, 129.95, 129.06, 128.68, 128.20, 125.91, 76.73, 73.83, 72.31, 68.08, 21.36. HRMS (ESI) for $\text{C}_{17}\text{H}_{18}\text{NO}_4\text{S}$ $[\text{M}-\text{H}]^-$: calcd 332.0962, found 332.0966.

HPLC: Chiralcel AD-H column (250 mm); detected at 224 nm; hexane/*i*-propanol = 80/20; flow = 0.7 mL/min; Retention time: 10.0 min, 12.7 min(major).



Results

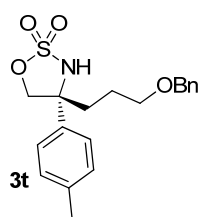
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.465	394392.719	7811705.500	49.2315
2		13.390	337977.750	8055585.000	50.7685
Total			732370.469	15867290.500	100.0000



Results

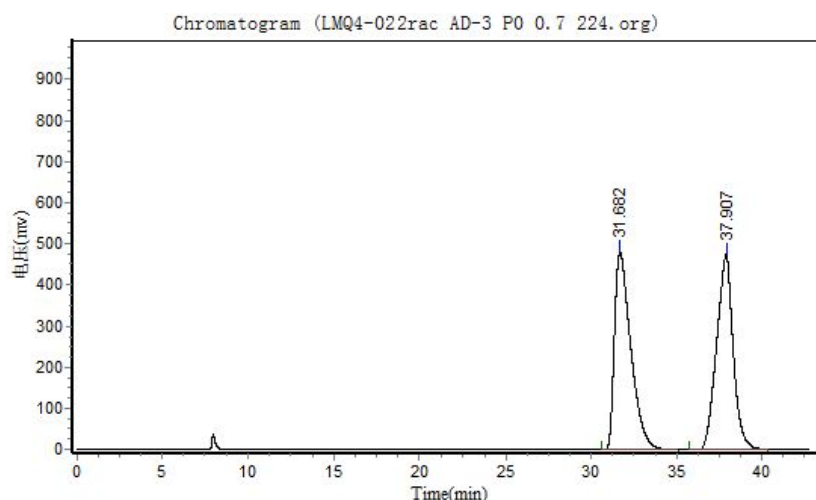
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		9.993	5040.129	70378.797	0.6212
2		12.717	488636.281	11258985.000	99.3788
Total			493676.410	11329363.797	100.0000

(R)-4-(3-(benzyloxy)propyl)-4-(p-tolyl)-1,2,3-oxathiazolidine 2,2-dioxide (3t)



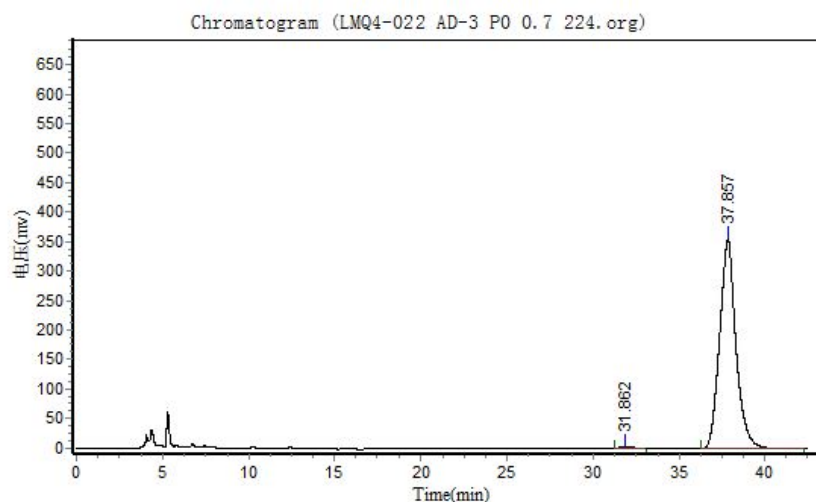
White solid, 45 mg, 62% yield, 99% ee. $[\alpha]_D^{20} = +11.3$ (c 1.49, CHCl_3). ^1H NMR (300 MHz, CDCl_3) δ 7.41-7.27 (m, 5H), 7.26-7.14 (m, 4H), 6.29 (s, 1H), 4.60-4.42 (m, 4H), 3.49-3.34 (m, 2H), 2.34 (s, 3H), 2.28-2.15 (m, 2H), 1.64-1.39 (m, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 138.25, 137.77, 137.62, 129.95, 128.88, 128.37, 128.33, 125.65, 79.88, 73.67, 69.64, 68.18, 37.81, 24.33, 21.30. HRMS (ESI) for $\text{C}_{19}\text{H}_{22}\text{NO}_4\text{S}$ $[\text{M}-\text{H}]^-$: calcd 360.1275, found 360.1276.

HPLC: Chiralcel AD-3 column (250 mm); detected at 224 nm; hexane/*i*-propanol = 90/10; flow = 0.7 mL/min; Retention time: 31.9 min, 37.9 min (major).



Results

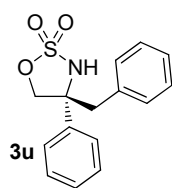
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		31.682	478894.344	31932802.000	49.8660
2		37.907	474080.719	32104422.000	50.1340
Total			952975.063	64037224.000	100.0000



Results

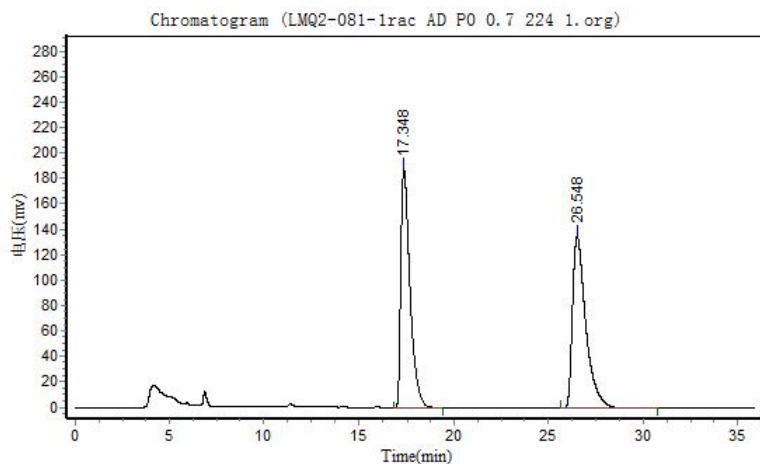
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		31.862	3254.331	168981.203	0.7153
2		37.857	355126.094	23455498.000	99.2847
Total			358380.425	23624479.203	100.0000

(R)-4-benzyl-4-phenyl-1,2,3-oxathiazolidine 2,2-dioxide (3u)^[2]



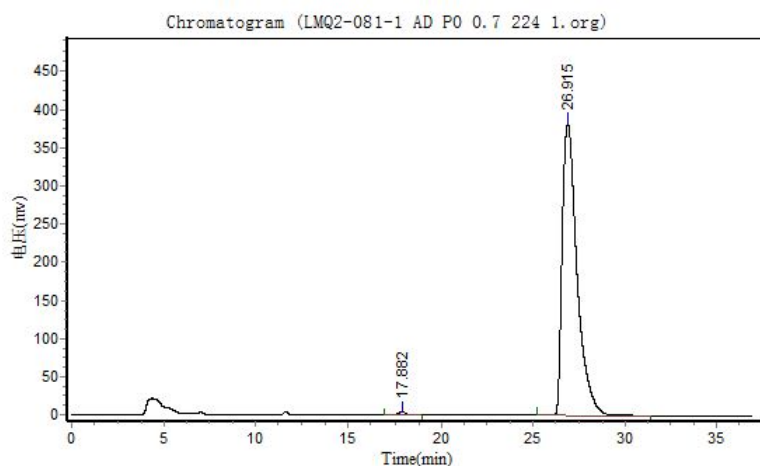
Yellowoil, 44 mg, 75% yield, 99% ee. $[\alpha]_D^{20} +18.4$ (c 1.34, CHCl₃). ¹H NMR (300 MHz, CDCl₃) δ 7.43-7.31 (m, 3H), 7.25-7.14 (m, 3H), 7.10-7.07 (m, 2H), 6.78 (d, J = 6.6 Hz, 2H), 4.76 (s, 1H), 4.86 and 4.63 (AB q, J = 8.7 Hz, 1H), 3.44 and 3.35 (AB q, J = 13.6 Hz, 1H).

HPLC: Chiralcel AD-H column (250 mm); detected at 224 nm; hexane/*i*-propanol = 90/10; flow = 0.7 mL/min; Retention time: 17.9 min, 26.9 min (major).



Results

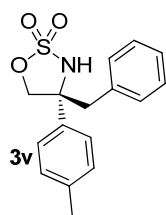
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		17.348	187199.984	6352679.500	48.9770
2		26.548	134739.156	6618053.000	51.0230
Total			321939.141	12970732.500	100.0000



Results

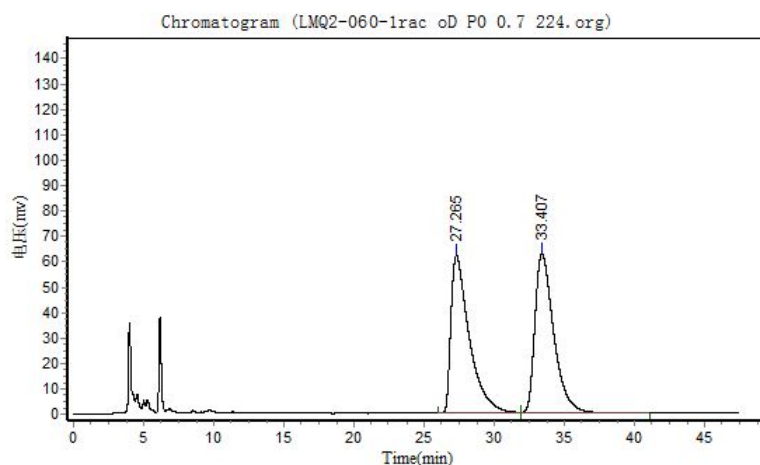
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		17.882	5067.948	155104.594	0.7182
2		26.915	381957.219	21440742.000	99.2818
Total			387025.167	21595846.594	100.0000

(R)-4-benzyl-4-(p-tolyl)-1,2,3-oxathiazolidine 2,2-dioxide (3v)



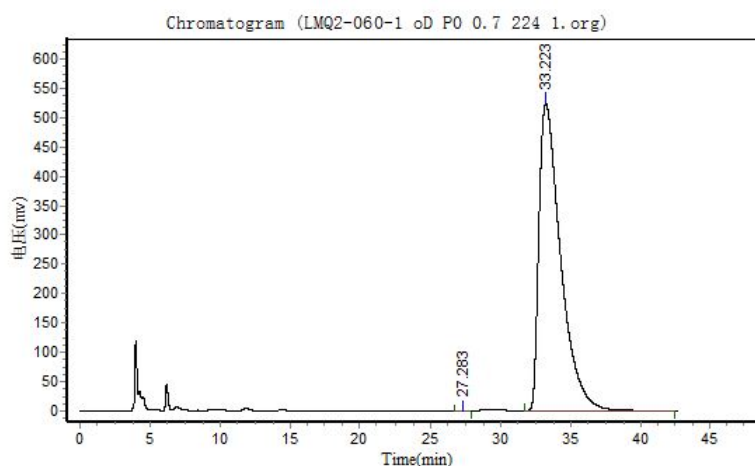
White solid, 50 mg, 83% yield, 99% ee. $[\alpha]_D^{20} = +31.6$ (c 1.23, CHCl_3). ^1H NMR (300 MHz, CDCl_3) δ 7.25-7.10 (m, 5H), 6.97 (d, $J = 8.1$ Hz, 2H), 6.81 (d, $J = 6.3$ Hz, 2H), 4.67 (s, 1H), 4.83 and 4.59 (AB q, $J = 8.7$ Hz, 1H), 3.42 and 3.33 (AB q, $J = 13.5$ Hz, 1H), 2.36 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 138.83, 136.42, 134.02, 130.89, 129.94, 128.84, 127.95, 125.50, 78.49, 68.73, 45.82, 21.43. HRMS (EI) for $\text{C}_{16}\text{H}_{17}\text{NO}_3\text{S}$: calcd 303.0929, found 303.0940.

HPLC: Chiralcel OD-H column (250 mm); detected at 224 nm; hexane/*i*-propanol = 90/10; flow = 0.7 mL/min; Retention time: 27.3 min, 33.2 min (major).



Results

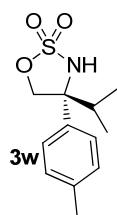
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		27.265	62083.105	5713334.000	49.1712
2		33.407	62792.207	5905929.000	50.8288
Total			124875.313	11619263.000	100.0000



Results

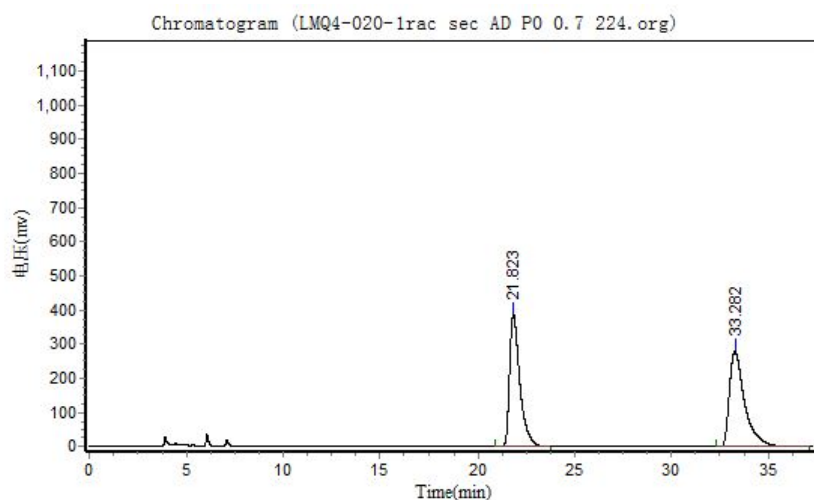
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		27.283	137.190	5639.180	0.0100
2		33.223	524042.625	56466440.000	99.9900
Total			524179.815	56472079.180	100.0000

(R)-4-isopropyl-4-(p-tolyl)-1,2,3-oxathiazolidine 2,2-dioxide (3w)



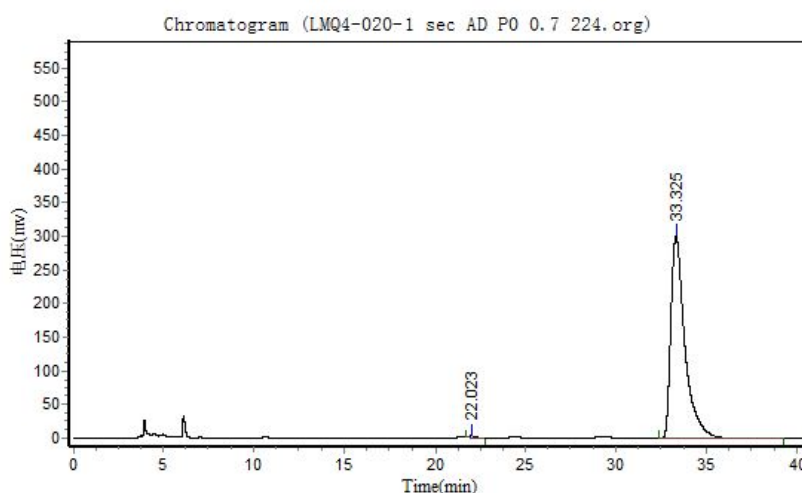
White solid, 14 mg, 28% yield, 99% ee. $[\alpha]_D^{20} = +19.2$ (c 1.02, CHCl_3). ^1H NMR (300 MHz, CDCl_3) δ 7.24-7.09 (m, 4H), 4.78 and 4.67 (AB q, $J = 8.8$ Hz, 1H), 4.62 (s, 1H), 2.38-2.29 (m, 1H), 2.36 (s, 3H), 1.00 (d, $J = 6.7$ Hz, 3H), 0.80 (d, $J = 6.8$ Hz, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 138.49, 135.65, 129.65, 126.22, 78.45, 71.70, 36.48, 21.34, 17.82, 17.25. HRMS (EI) for $\text{C}_{12}\text{H}_{17}\text{NO}_3\text{S}$: calcd 255.0929, found: 255.0926.

HPLC: Chiralcel AD-H column (250 mm); detected at 224 nm; hexane/*i*-propanol = 90/10; flow = 0.7 mL/min; Retention time: 22.0 min, 33.3 min (major).



Results

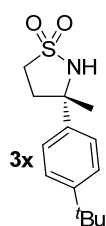
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		21.823	386030.375	14272104.000	48.3318
2		33.282	276833.875	15257350.000	51.6682
Total			662864.250	29529454.000	100.0000



Results

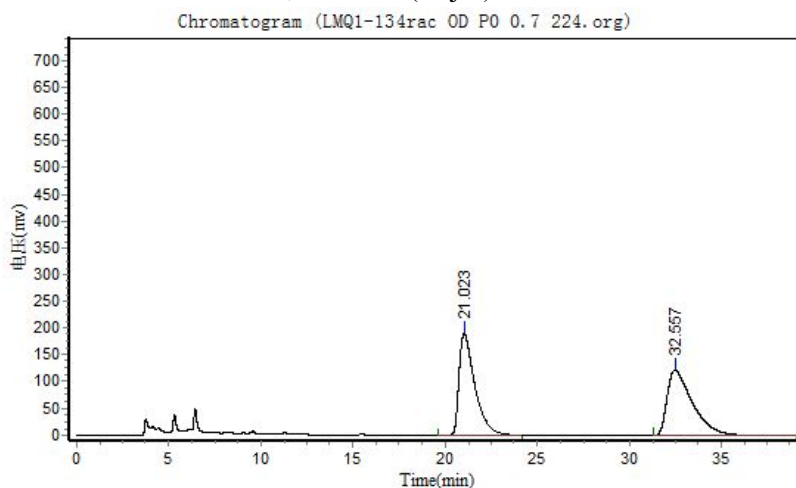
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		22.023	2277.574	57271.902	0.3515
2		33.325	300858.938	16235728.000	99.6485
Total			303136.511	16292999.902	100.0000

(S)-3-(4-(tert-butyl)phenyl)-3-methylisothiazolidine 1,1-dioxide (3x)



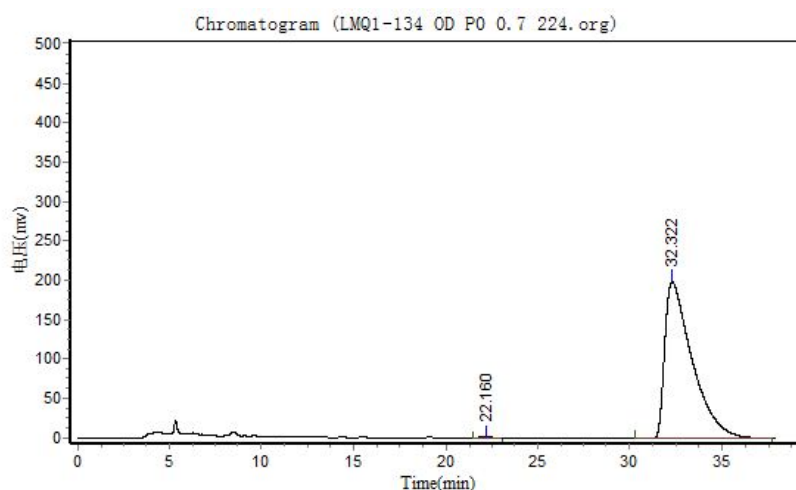
White solid, 27 mg, 50% yield, 99% ee. $[\alpha]_D^{20} = -18.4$ (c 1.30, CHCl_3). ^1H NMR (300 MHz, CDCl_3) δ 7.49-7.32 (m, 4H), 4.36 (s, 1H), 3.36-3.10 (m, 2H), 2.75-2.50 (m, 2H), 1.73 (s, 3H), 1.32 (s, 9H). ^{13}C NMR (151 MHz, CDCl_3) δ 150.98, 142.14, 126.07, 124.87, 62.98, 48.01, 38.59, 34.81, 31.61, 30.35. HRMS (EI) for $\text{C}_{14}\text{H}_{21}\text{NO}_2\text{S}$: calcd 267.1293, found 267.1297.

HPLC: Chiralcel OD-H column (250 mm); detected at 224 nm; hexane/*i*-propanol = 90/10; flow = 0.7 mL/min; Retention time: 22.2 min, 32.3 min (major).



Results

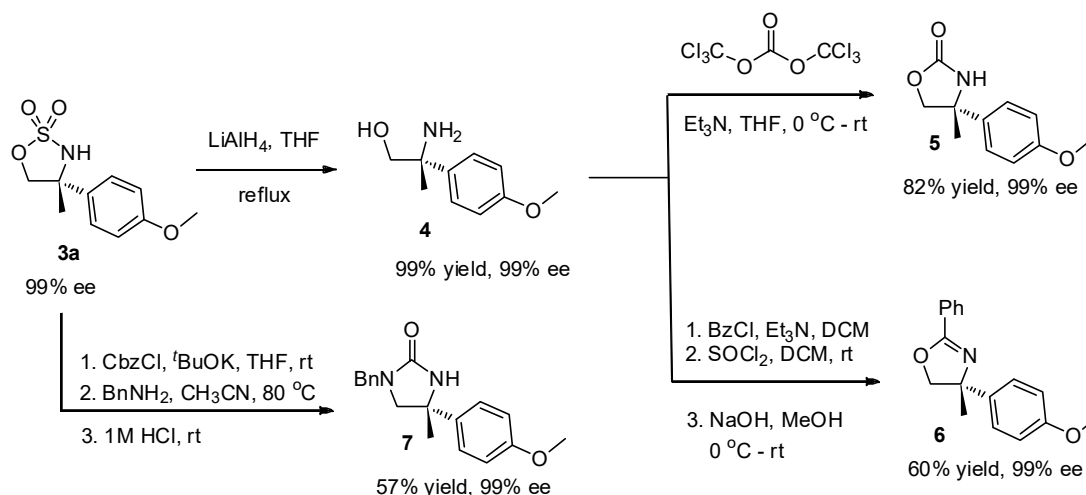
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		21.023	189514.688	11473882.000	49.6275
2		32.557	121706.953	11646122.000	50.3725
Total			311221.641	23120004.000	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		22.160	1478.077	74025.984	0.3580
2		32.322	198756.125	20605962.000	99.6420
Total			200234.202	20679987.984	100.0000

4. Derivatizations of the arylation product **3a**



(R)-2-amino-2-(4-methoxyphenyl)propan-1-ol (4): To a suspension of lithium aluminum hydride (30.4 mg, 0.8 mmol) in THF (1 mL), a solution of **3a** (48.7 mg, 0.2 mmol, 99% ee) in THF (1 mL) was added dropwise. After refluxing for 6 h, the mixture was cooled to room temperature and quenched with ice water. Then 10% NaOH was added. The aqueous layer was extracted with EtOAc three times, and the combined organic layers were dried and concentrated to provide the crude product without purification.

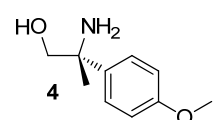
(R)-4-(4-methoxyphenyl)-4-methyloxazolidin-2-one (5): To a solution of **4** (36.2 mg, 0.2 mmol, 1 equiv) in dry THF, triphosgene (71.2 mg, 0.24 mmol, 1.2 equiv) was added slowly at 0°C . The resulting mixture was allowed to stir at the same temperature for 10 min followed by addition of Et_3N (97 μL , 70.8 mg, 0.7 mmol, 3.5 equiv). The reaction mixture then stirred for additional 3 h at room temperature. After completion of reaction, the reaction mixture was added to ice and extracted with ethyl acetate. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was then purified by flash chromatography on silica gel using petroleum ether/ethyl acetate to obtain product **5** in 82% yield.

(R)-4-(4-methoxyphenyl)-4-methyl-2-phenyl-4,5-dihydrooxazole (6): To a solution of **4** (36.2 mg, 0.2 mmol, 1 equiv) and triethylamine (0.72 mmol, 0.1 mL, 3.6 equiv) in DCM (1 mL) at 0°C was added benzoyl chloride (0.22 mmol, 25 μL , 1.1 equiv). The reaction was stirred at room temperature for 12 h. After removal of solvent, the crude product was dissolved in DCM (1 mL) and SOCl_2 was added (0.9 mmol, 65 μL , 4.5 equiv) at 0°C . The mixture was then warmed to room temperature and stirred for 12 h. The residue SOCl_2 was removed under reduced pressure and saturated NaHCO_3 (8 mL) was added. The mixture was extracted with DCM (10 mL $\times$ 3) and the combined organic layer was dried over sodium sulfate. After removal of DCM, methanol (1 mL) and NaOH solution (1 mL, 2 M in water) were added to the residue and stirred at room

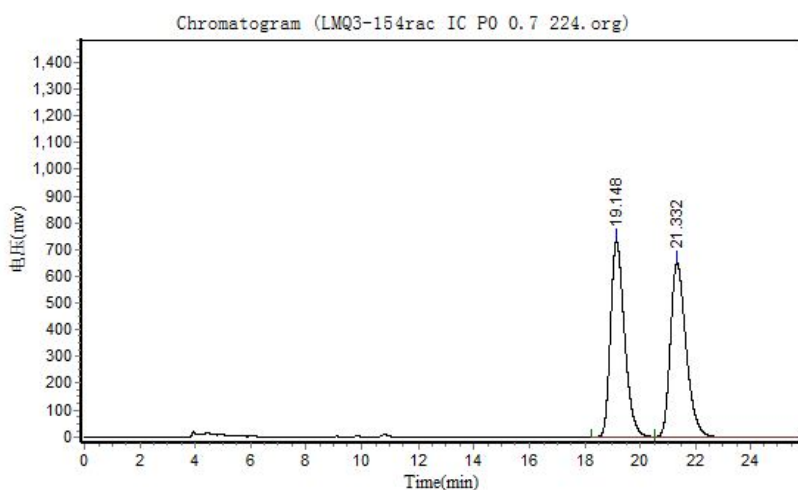
temperature for 12 h. After completion, the methanol was removed by rotary evaporation and the residue was extracted with DCM (10 mL×3). The organic layer dried over anhydrous magnesium sulfate and the residue was then purified by silica gel column chromatography to afford the product **6** in 60% yield.

(R)-1-benzyl-4-(4-methoxyphenyl)-4-methylimidazolidin-2-one (7): A round-bottom flask was charged with a solution of *t*-BuOK (33.7 mg, 0.3 mmol, 1.5 equiv) and cyclic sulfamidate **3a** (48.7 mg, 0.2 mmol, 1 equiv) in THF (1 mL) and purged with N₂, stirred at room temperature for 1h. Benzyl chloroformate (70 µL, 0.5 mmol, 2.5 equiv) was then added slowly and stirred at room temperature for 2 h. The reaction was quenched with H₂O (8 mL) and extracted with EtOAc. The organic phase was washed with brine (10 mL), dried over Na₂SO₄, filtered and concentrated. The crude product was purified by silica gel chromatography (hexanes/EtOAc = 8/1) to provide Cbz-protected cyclic sulfamidate. A round-bottom flask was charged with protected cyclic sulfamidate, MeCN (1 mL) and purged with N₂. Benzyl amine (31 µL, 0.28 mmol, 1.5 equiv) was added and the reaction was heated to 80 °C and stirred for 28 h. The reaction was cooled, diluted with EtOAc (1 mL), 1 M HCl (1 mL) was added and the mixture was stirred at room temperature for 2 h. The organic layer was separated, washed with 1 M NaOH (1 mL), dried over Na₂SO₄, filtered and concentrated. The crude product was purified by silica gel chromatography to afford the product **7** in 57 % yield.

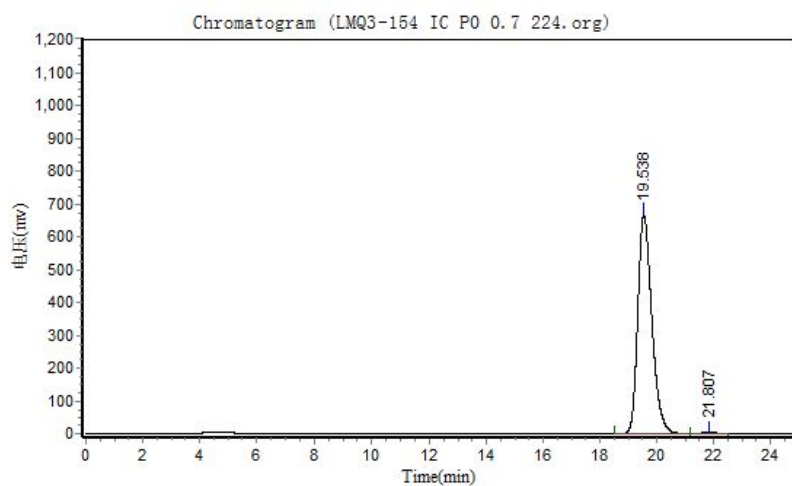
(R)-4-(4-methoxyphenyl)-4-methyloxazolidin-2-one (4)

 White solid, 36 mg, 99% yield, 99% ee. $[\alpha]_D^{20} = -11.9$ (c 0.60, CHCl_3). ^1H NMR (300 MHz, CDCl_3) δ 7.44-7.31 (m, 2H), 6.95-6.82 (m, 2H), 3.80 (s, 3H), 3.57 (q, $J = 10.7$ Hz, 2H), 2.16 (s, 3H), 1.44 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 158.73, 138.63, 126.79, 114.11, 72.14, 56.23, 55.60, 27.47. HRMS (ESI) for $\text{C}_{10}\text{H}_{16}\text{NO}_2$ $[\text{M}+\text{H}]^+$: calcd 182.1176, found 182.1179.

HPLC: Chiralcel IC column (250 mm); detected at 224 nm; hexane/*i*-propanol = 90/10; flow = 0.7 mL/min; Retention time: 19.5 min (major), 21.8 min.

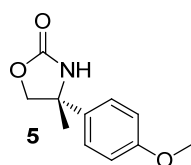


Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		19.148	733261.000	25646036.000	49.9887
2		21.332	651373.750	25657668.000	50.0113
Total			1384634.750	51303704.000	100.0000



Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		19.538	666527.750	22804594.000	99.3579
2		21.807	3992.485	147378.016	0.6421
Total			670520.235	22951972.016	100.0000

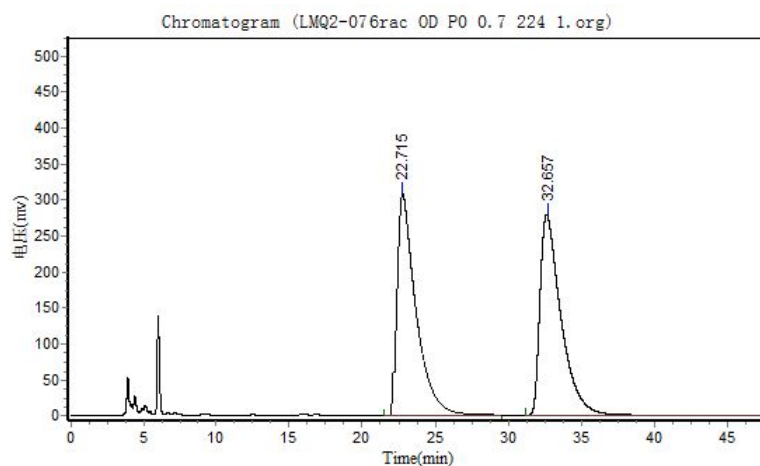
(R)-4-(4-methoxyphenyl)-4-methyloxazolidin-2-one (5)



Yellow solid, 34 mg, 82% yield, 99% ee. $[\alpha]_D^{20} = -65.8$ (c 1.22, CHCl_3). ^1H NMR (300 MHz, CDCl_3) δ 7.31 (d, $J = 8.6$ Hz, 2H), 6.91 (d, $J = 8.7$ Hz, 2H), 5.56 (s, 1H), 4.34 and 4.29 (AB q, $J = 8.3$ Hz, 1H), 3.82 (s, 3H), 1.75 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 159.58, 159.29, 135.66, 126.35, 114.59, 78.74, 60.26, 55.70, 27.74. HRMS (EI) for $\text{C}_{11}\text{H}_{13}\text{NO}_3$: calcd 207.0890, found

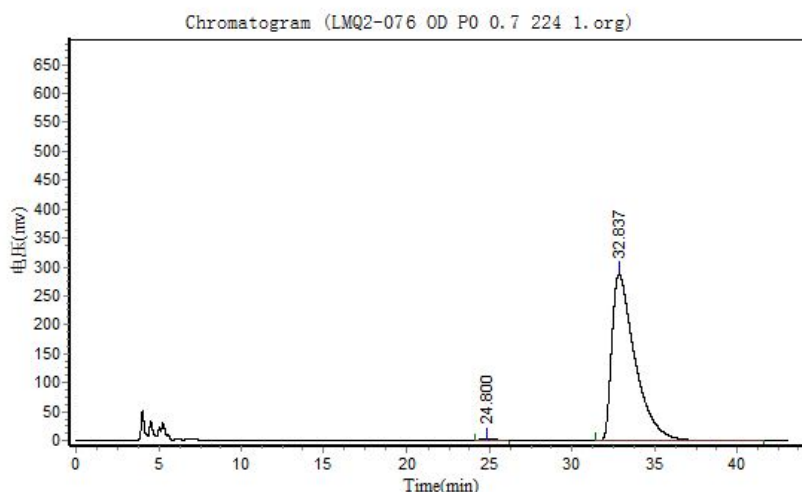
207.0895.

HPLC: Chiralcel OD-H column (250 mm); detected at 224 nm; hexane/*i*-propanol = 90/10; flow = 0.7 mL/min; Retention time: 24.8 min, 32.8 min (major).



Results

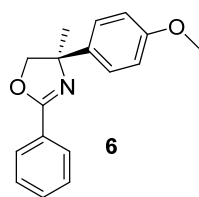
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		22.715	308507.406	27431616.000	49.4101
2		32.657	278425.969	28086594.000	50.5899
Total			586933.375	55518210.000	100.0000



Results

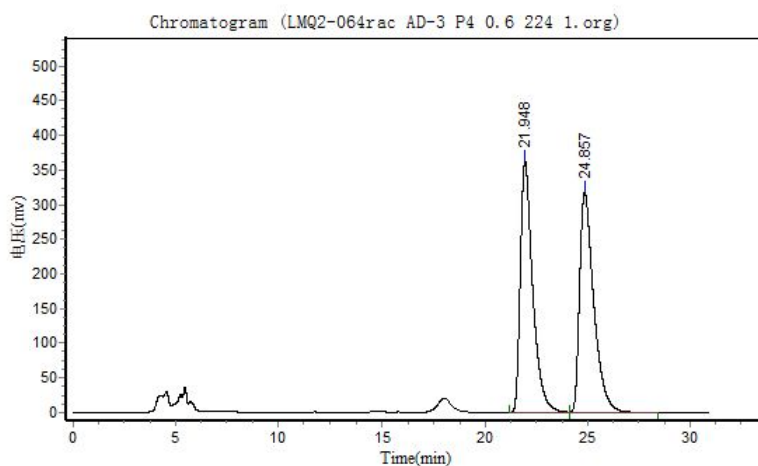
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		24.800	3274.011	213299.094	0.7467
2		32.837	288065.844	28350550.000	99.2533
Total			291339.855	28563849.094	100.0000

(R)-4-(4-methoxyphenyl)-4-methyl-2-phenyl-4,5-dihydrooxazole (6)



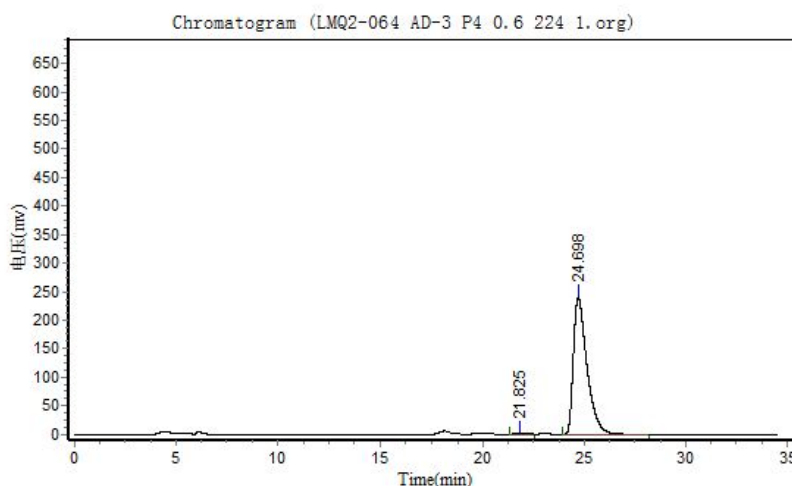
Yellow solid, 32 mg, 72% yield, 99% ee. $[\alpha]_D^{20} = -86.6$ (c 1.29, CHCl_3). ^1H NMR (300 MHz, CDCl_3) δ 8.08-7.99 (m, 2H), 7.55-7.30 (m, 5H), 6.92-6.83 (m, 2H), 4.42 and 4.37 (AB q, $J = 8.1$ Hz, 1H), 3.79 (s, 3H), 1.70 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 163.10, 158.80, 139.45, 131.69, 128.74, 128.66, 128.28, 126.81, 114.11, 80.80, 72.89, 55.61, 29.34. HRMS (EI) for $\text{C}_{17}\text{H}_{17}\text{NO}_2$: calcd 267.1254, found 267.1248.

HPLC: Chiralcel AD-3 column (250 mm); detected at 224 nm; hexane/*i*-propanol = 99/1; flow = 0.6 mL/min; Retention time: 21.8 min, 24.7 min (major).



Results

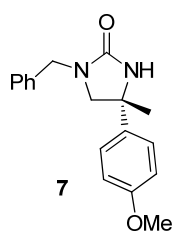
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		21.948	362250.313	15195291.000	49.9683
2		24.857	316773.219	15214596.000	50.0317
Total			679023.531	30409887.000	100.0000



Results

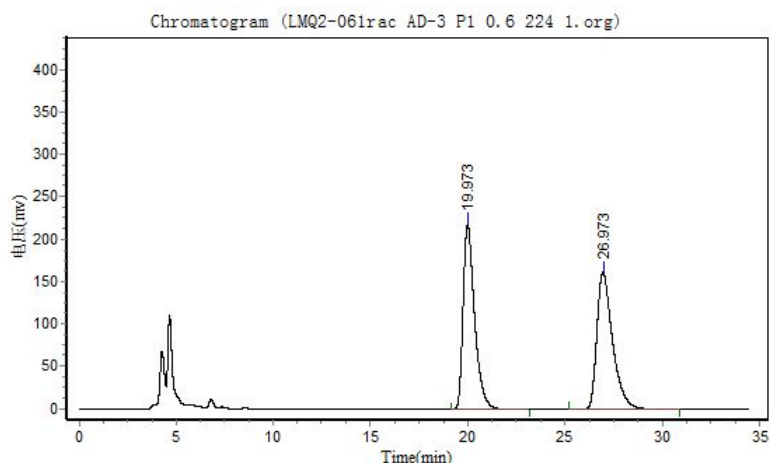
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		21.825	2574.166	83370.000	0.7424
2		24.698	240192.969	11146730.000	99.2576
Total			242767.134	11230100.000	100.0000

(R)-1-benzyl-4-(4-methoxyphenyl)-4-methylimidazolidin-2-one (7)



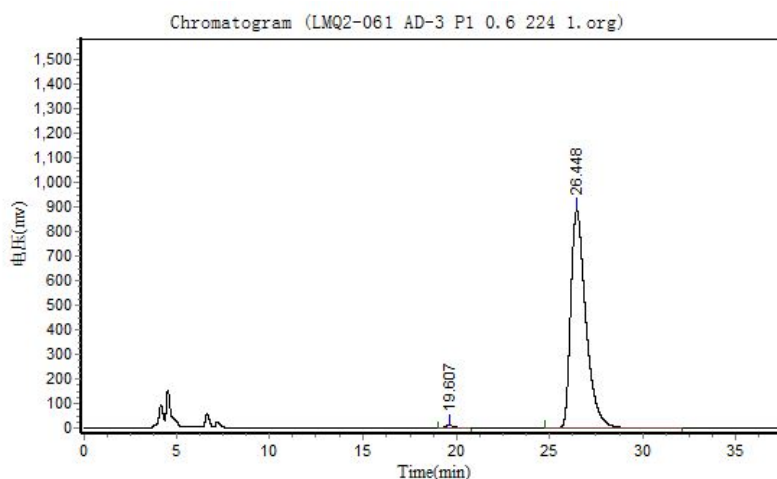
Whitesolid, 34 mg, 57% yield, 99% ee. $[\alpha]_D^{20} = +17.0$ (c 1.27, CHCl_3). ^1H NMR (300 MHz, CDCl_3) δ 7.41-7.16 (m, 7H), 6.86 (d, $J = 8.1$ Hz, 2H), 5.06 (s, 1H), 4.51 and 4.29 (AB q, $J = 15.0$ Hz, 1H), 3.79 (s, 3H), 3.30 and 3.26 (AB q, $J = 8.7$ Hz, 1H), 1.62 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 161.23, 159.08, 138.02, 137.30, 128.95, 128.27, 127.77, 126.31, 114.25, 59.43, 57.13, 55.63, 47.65, 28.73. HRMS (EI) for $\text{C}_{18}\text{H}_{20}\text{N}_2\text{O}_2$: calcd 296.1519, found 296.1522.

HPLC: Chiralcel AD-3 column (250 mm); detected at 224 nm; hexane/*i*-propanol = 80/20; flow = 0.6 mL/min; Retention time: 19.6 min, 26.4 min (major).



Results

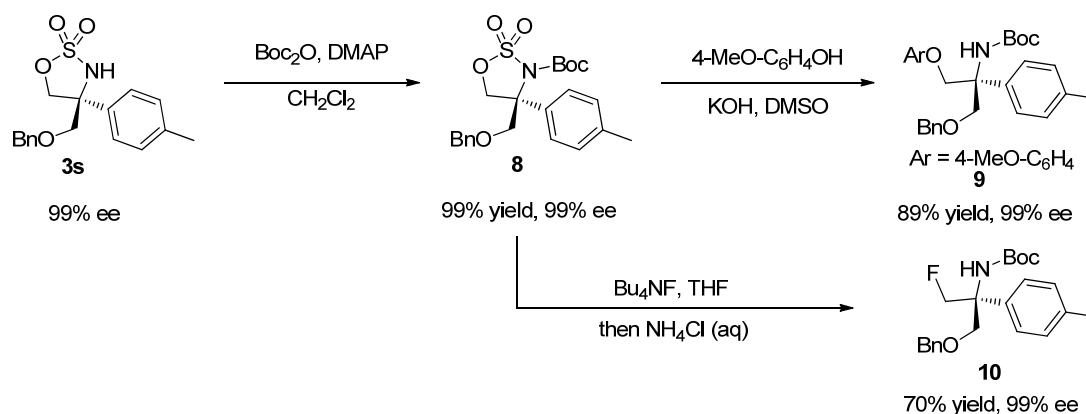
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		19.973	218326.688	9014210.000	49.7029
2		26.973	161868.578	9121995.000	50.2972
Total			380195.266	18136205.000	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		19.607	10126.016	377914.031	0.7494
2		26.448	886395.813	50051092.000	99.2506
Total			896521.828	50429006.031	100.0000

5. Transformations of **3s** into highly functionalized α -tertiary amines.

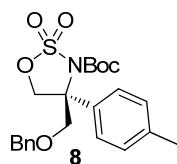


(S)-tert-butyl 4-((benzyloxy)methyl)-4-(p-tolyl)-1,2,3-oxathiazolidine-3-carboxylate 2,2-dioxide (8): To a solution of **3s** (66.7 mg, 0.20 mmol, 99% ee) and 4-dimethyl aminopyridine (5 mg, 0.04 mmol) in CH₂Cl₂ (1.0 mL) was added di-*tert*-butyldicarbonate (87.3 mg, 0.4 mmol), and the mixture was stirred at room temperature overnight. The mixture was concentrated on a rotary evaporator and the residue was subjected to flash column chromatography on silica gel with hexane/ethyl acetate (20/1) to give **8** in 99% yield.

(S)-tert-butyl (1-(benzyloxy)-3-(4-methoxyphenoxy)-2-(p-tolyl)propan-2-yl)carbamate (9): To a solution of **8** (86.7 mg, 0.2 mmol, 99% ee) and 4-methoxyphenol (49.7 mg, 0.4 mmol) in dimethyl sulfoxide (1.0 mL) was added 8 M KOH (aq) (50 μ L, 0.4 mmol), and the mixture was stirred at room temperature for 15 h. Aqueous NH₄Cl solution was added to the mixture and it was extracted with diethyl ether. The organic extracts were washed with H₂O and brine, dried over Na₂SO₄, filtered, and concentrated on a rotary evaporator, the residue was subjected to flash column chromatography on silica gel with hexane/ethyl acetate (20:1) to give **9** in 89% yield.

(S)-tert-butyl (1-(benzyloxy)-3-fluoro-2-(p-tolyl)propan-2-yl)carbamate (10): To a solution of **8** (86.7 mg, 0.2 mmol, 99% ee) and tetrabutylammonium fluoride (49.7 mg, 0.4 mmol) in THF (1 mL), the mixture was stirred at 60 °C for 16 h. Aqueous NH₄Cl solution was added to the mixture, and it was stirred at room temperature for 2 h. The mixture was extracted with diethyl ether, and the extracts were washed with H₂O and brine, dried over Na₂SO₄, filtered, and concentrated on a rotary evaporator. The residue was subjected to preparative TLC on silica gel with hexane/ethyl acetate (20:1) to give **10** in 70% yield.

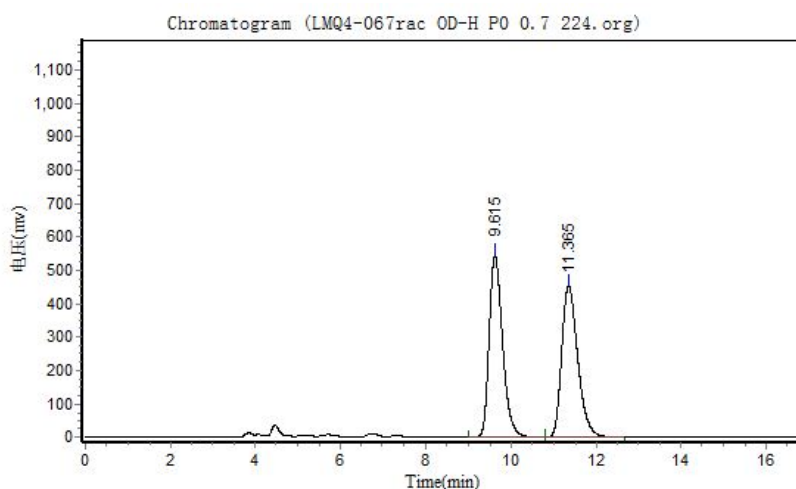
(S)-tert-butyl
2,2-dioxide (8)



4-((benzyloxy)methyl)-4-(p-tolyl)-1,2,3-oxathiazolidine-3-carboxylate

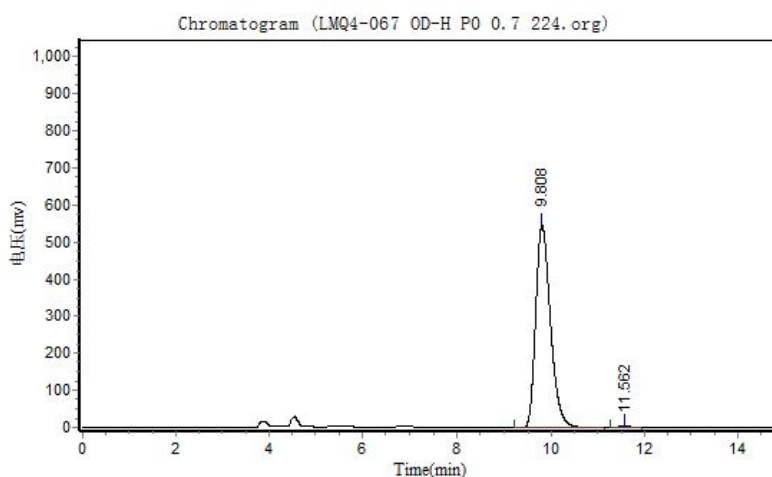
Colorless oil, 86 mg, 99% yield, 99% ee. $[\alpha]_D^{20} = -17.4$ (c 1.23, CHCl_3). ^1H NMR (300 MHz, CDCl_3) δ 7.41-7.30 (m, 7H), 7.19 (d, $J = 8.1$ Hz, 2H), 4.94 (d, $J = 9.2$ Hz, 1H), 4.76-4.58 (m, 2H), 4.42 (d, $J = 9.2$ Hz, 1H), 4.24 and 4.11 (AB q, $J = 9.6$ Hz, 1H), 2.34 (s, 3H), 1.37 (s, 9H). ^{13}C NMR (126 MHz, CDCl_3) δ 148.42, 138.92, 137.52, 135.34, 129.97, 128.90, 128.35, 127.99, 125.95, 85.67, 74.39, 73.96, 70.53, 68.44, 28.13, 21.35. HRMS (ESI) for $\text{C}_{22}\text{H}_{27}\text{NNaO}_6\text{S}$ $[\text{M}+\text{Na}]^+$: calcd 456.1451, found 456.1463.

HPLC: Chiralcel OD-H column (250 mm); detected at 224 nm; hexane/*i*-propanol = 90/10; flow = 0.7 mL/min; Retention time: 9.8 min (major), 11.6 min.



Results

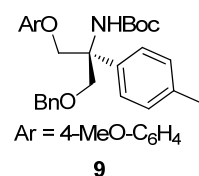
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		9.615	543809.500	11988674.000	50.0230
2		11.365	453820.406	11977657.000	49.9770
Total			997629.906	23966331.000	100.0000



Results

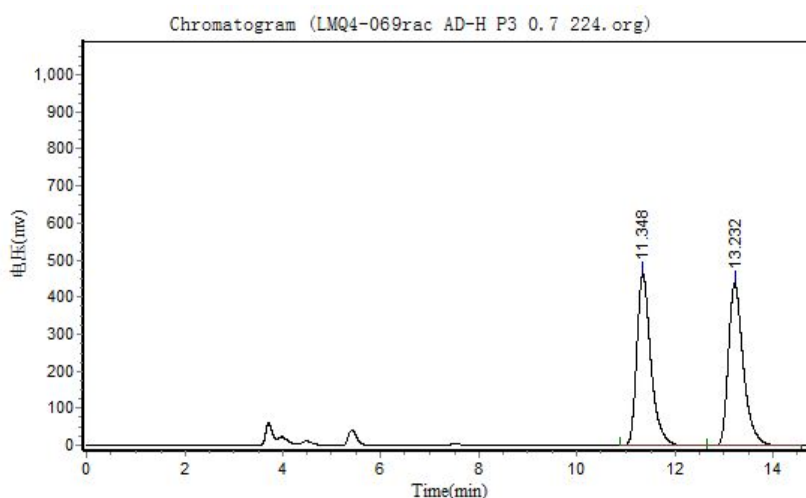
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		9.808	544848.500	12014352.000	99.4489
2		11.562	3178.489	66575.445	0.5511
Total			548026.989	12080927.445	100.0000

(S)-tert-butyl (1-(benzyloxy)-3-(4-methoxyphenoxy)-2-(p-tolyl)propan-2-yl)carbamate (9)



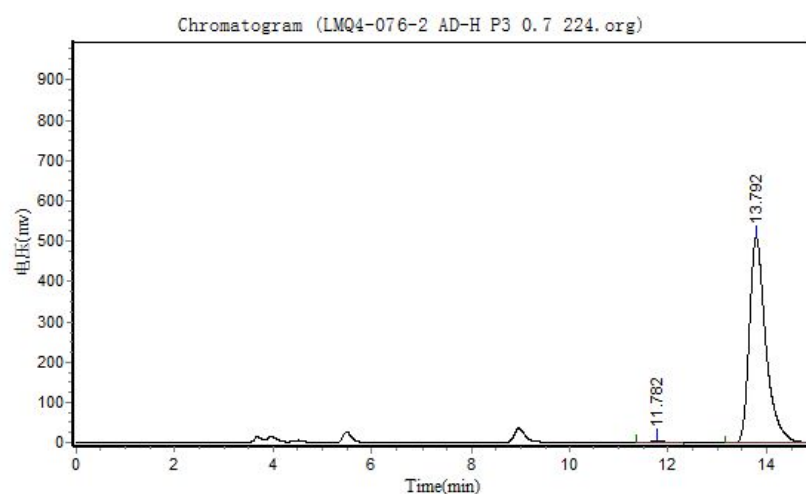
Colorless oil, 85 mg, 89% yield, 99% ee. $[\alpha]_D^{20} = -3.4$ (c 1.33, CHCl₃). ¹H NMR (300 MHz, CDCl₃) δ 7.41 (d, $J = 8.2$ Hz, 2H), 7.33-7.18 (m, 5H), 7.12 (d, $J = 8.1$ Hz, 2H), 6.91-6.75 (m, 4H), 5.54 (s, 1H), 4.54-4.51 (m, 3H), 4.26 (d, $J = 8.7$ Hz, 1H), 4.07 (d, $J = 9.3$ Hz, 1H), 3.84 (d, $J = 8.6$ Hz, 1H), 3.75 (s, 3H), 2.31 (s, 3H), 1.35 (s, 9H). ¹³C NMR (126 MHz, CDCl₃) δ 154.97, 154.41, 153.05, 138.57, 138.29, 137.05, 129.19, 128.63, 127.90, 126.53, 116.20, 114.91, 79.77, 73.68, 73.40, 71.36, 60.80, 56.02, 28.57, 21.31. HRMS (ESI) for C₂₉H₃₆NO₅ [M+H]⁺: calcd 478.2588, found 478.2597.

HPLC: Chiralcel AD-H column (250 mm); detected at 224 nm; hexane/*i*-propanol = 95/5; flow = 0.7 mL/min; Retention time: 11.8 min, 13.8 min (major).



Results

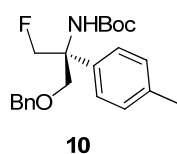
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.348	463267.906	9279575.000	49.7030
2		13.232	437230.938	9390480.000	50.2970
Total			900498.844	18670055.000	100.0000



Results

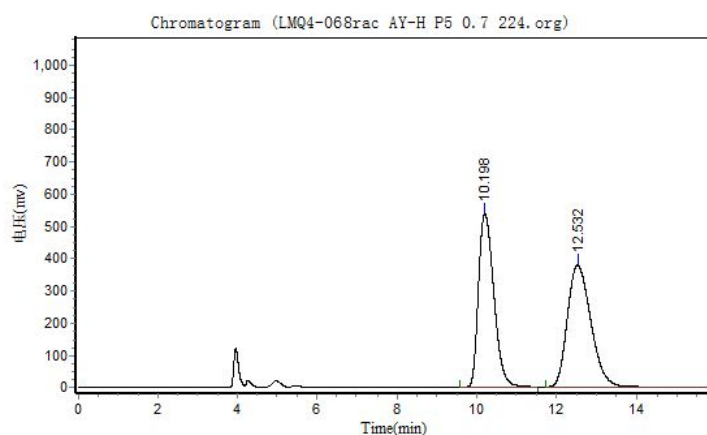
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.782	3806.104	75606.898	0.6338
2		13.792	509613.594	11853336.000	99.3662
Total			513419.698	11928942.898	100.0000

(S)-tert-butyl (1-(benzyloxy)-3-fluoro-2-(p-tolyl)propan-2-yl)carbamate (10)

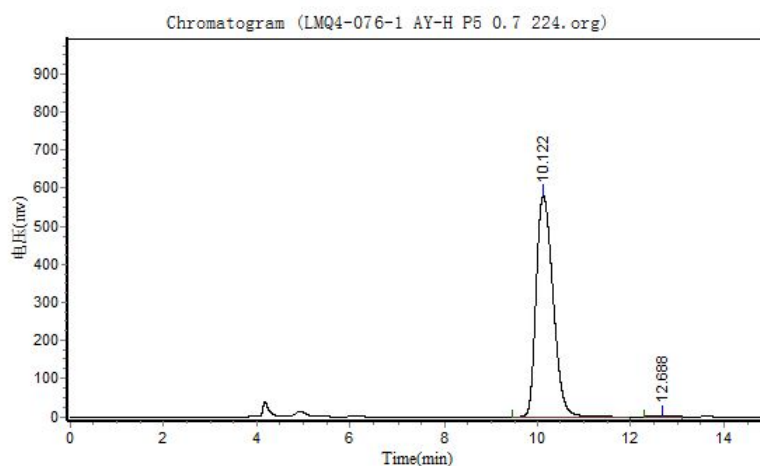


Colorless oil, 53 mg, 70% yield, 99% ee. $[\alpha]_D^{20} = +0.3$ (c 1.58, CHCl_3). ^1H NMR (300 MHz, CDCl_3) δ 7.34-7.25 (m, 7H), 7.13 (d, $J = 8.0$ Hz, 2H), 5.39 (s, 1H), 5.12-4.73 (m, 2H), 4.61-4.42 (m, 2H), 3.86 (d, $J = 9.3$ Hz, 1H), 3.66 (d, $J = 8.0$ Hz, 1H), 2.32 (s, 3H), 1.34 (s, 9H). ^{13}C NMR (126 MHz, CDCl_3) δ 154.85, 138.00, 137.38, 129.36, 128.74, 128.10, 127.93, 126.21, 85.34, 83.92, 80.01, 73.79, 73.30, 70.27, 60.63 (d, $J_{\text{CF}} = 17.5$), 28.53, 21.31. HRMS (ESI) for $\text{C}_{22}\text{H}_{28}\text{FNNaO}_3$ $[\text{M}+\text{Na}]^+$: calcd 396.1945, found 396.1944.

HPLC: Chiralcel AD-3 column (250 mm); detected at 224 nm; hexane/*i*-propanol = 97/3; flow = 0.7 mL/min; Retention time: 10.1 min (major), 12.7 min.



Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.198	539937.250	14641696.000	48.0898
2		12.532	380007.563	15804860.000	51.9102
Total			919944.813	30446556.000	100.0000



Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.122	580057.438	14698411.000	99.2651
2		12.688	3777.741	108813.703	0.7349
Total			583835.178	14807224.703	100.0000

Ref:

[1]: Y.-J. Chen, Y.-H. Chen, C.-G. Feng and G.-Q. Lin, *Org. Lett.*, 2014, **16**, 3400.

[2]: S. Chang and E. E. Lee, *Synthesis*, 2010, **14**, 2361.

6. Copies of ^1H NMR and ^{13}C NMR spectra of products

