

Electronic Supplementary Information

Dynamic kinetic asymmetric transformations of β -halo- α -keto esters by *N,N'*-dioxide/Ni(II)-catalyzed carbonyl-ene reaction

Wen Liu, Weidi Cao,* Haipeng Hu, Lili Lin and Xiaoming Feng*

Key Laboratory of Green Chemistry & Technology, Ministry of Education, College of Chemistry,
Sichuan University, Chengdu 610064, P. R. China.

E-mail: wdcao@scu.edu.cn, xmfeng@scu.edu.cn; Fax: +86 28 85418249

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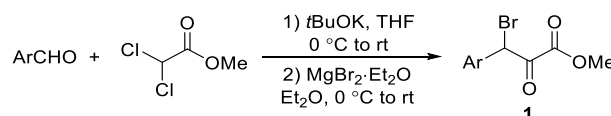
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1. General remarks

Unless otherwise noted, all commercially available compounds were used without further purification. CH₂Cl₂ was distilled from CaH₂. Enantiomeric excesses (ee) were determined by HPLC analysis using the corresponding commercial chiral column as stated in the experimental procedures at 23 °C with UV detector at 254 or 210 nm. ¹H NMR and ¹³C{¹H} NMR were recorded on a Bruker AMX-400 spectrometer in CDCl₃. Data for ¹H NMR are reported as follows: chemical shift in reference to residual CHCl₃ at 7.26 ppm (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, td = triplet of doublets, m = multiplet), coupling constants (*J*) are in Hertz (Hz), and integration. Data for ¹³C{¹H} NMR are reported in terms of chemical shift in reference to the CDCl₃ solvent signal (77.16 ppm). ¹⁹F{¹H} NMR spectra were collected on commercial instruments (376 MHz) with complete proton decoupling. HRMS was recorded on a commercial apparatus (ESI Source). The chiral HPLC methods were calibrated with the corresponding racemic mixtures. Optical rotations were measured at 589 nm on a Rudolph Autopol V automatic polarimeter and are reported as follows: [α]_D^T (c g/100 mL, in solvent).

2. General procedure for chiral *N,N'*-dioxide and substrates preparation

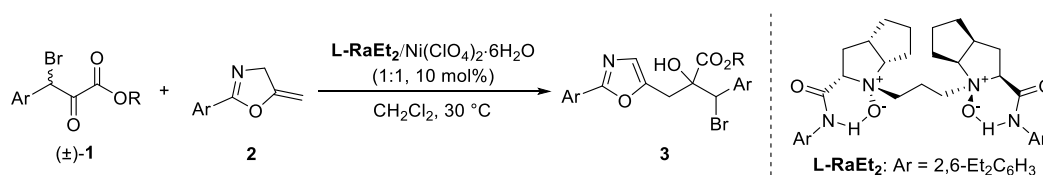
The *N,N'*-dioxide chiral ligands were synthesized according to the same procedure published on the literatures.¹⁻³



The substrate **1** were synthesized according to the general procedure reported in the literature.⁴ A 100 mL oven-dried flask was charged with benzaldehyde (2.04 mL, 20 mmol, 1 equiv), methyl dichloroacetate (2.69 mL, 26 mmol, 1.3 equiv) and THF (40 mL). To the resulting suspension was added *t*BuOK (2.92g, 26 mmol, 1.3 equiv) stepwise at 0 °C, and the resulting wine mixture was warmed to room temperature and stirred for another 18 h. After the addition of Et₂O (30 mL) and H₂O (20 mL), the resulting mixture was extracted with Et₂O (3×30 mL). The combined organic layer was washed with H₂O, brine, dried over Na₂SO₄, and concentrated under reduced pressure to give the crude epoxide product. The crude epoxide product was used in the next step without further purification.

The crude epoxide product was dissolved in Et₂O (60 mL) and cooled to 0 °C followed by the addition of MgBr₂·Et₂O (5.16 g, 20 mmol, 1 equiv) in one portion. Then the mixture was warmed to room temperature and stirred for an additional 2 h. After addition of Et₂O (20 mL) and H₂O (20 mL), the resulting mixture was extracted with Et₂O (3×20 mL). The combined organic layer was washed with H₂O, brine, dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 15/1).

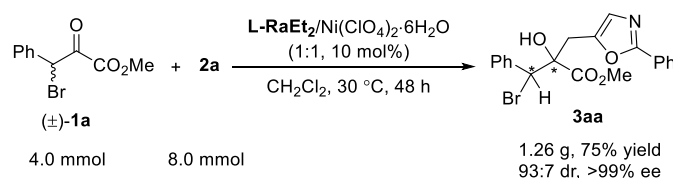
3. General procedure for the carbonyl-ene reaction



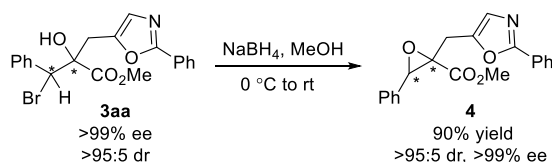
An oven-dried test tube was charged with **L-RaEt₂** (0.01 mmol, 10 mol%), Ni(ClO₄)₂·6H₂O (0.01 mmol, 10 mol%), β-halo-α-keto ester **1** (0.1 mmol, 1.0 equiv) and CH₂Cl₂ (1.0 mL). The solution was stirred at 30 °C for 30 min followed by the addition of 5-methyleneoxazolines **2** (0.2 mmol, 2.0 equiv). Then, the reaction mixture was stirred at the same temperature for another 48 h. Finally, the residue was purified by flash chromatography on silica gel (eluent: petroleum ether/EtOAc = 4/1) to afford the desired product **3**.

The racemic products were prepared with the same procedure of the catalytic asymmetric reaction, using racemic ligand (±)-**L-PiPr₂** instead of chiral ligand **L-RaEt₂**.

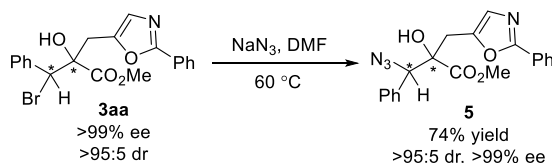
4. Typical procedure for scale-up reaction and transformations of the product



An oven-dried 100 mL round bottom flask was charged with **L-RaEt₂** (0.4 mmol, 256 mg, 10 mol%), Ni(ClO₄)₂·6H₂O (0.4 mmol, 144 mg, 10 mol%), **1a** (4.0 mmol, 1.028 g) and CH₂Cl₂ (40.0 mL). This solution was stirred at 30 °C for 30 min followed by the addition of 5-methyleneoxazolines **2a** (8.0 mmol, 1.272 g). Then the reaction mixture was stirred at the same temperature for another 48 h before it was directly purified by flash chromatography on silica gel (eluent: petroleum ether/EtOAc = 4/1) to afford the desired product **3aa** in 75% yield with >99 % ee.



In a dried tube, the compounds **3aa** (0.1 mmol) was dissolved in 1.0 mL MeOH at 0 °C. Subsequently, NaBH₄ (0.4 mmol, 4 equiv) was added at 0 °C and the reaction stirred at rt for 24 h. The mixture was quenched with H₂O and extracted with EtOAc. The organic layer was dried (Na₂SO₄) and concentrated under reduced pressure. Purification by flash chromatography (eluent: petroleum ether/EtOAc = 4/1) furnished the corresponding product **4** in 30.1 mg (90% yield, >95:5 dr and >99% ee).



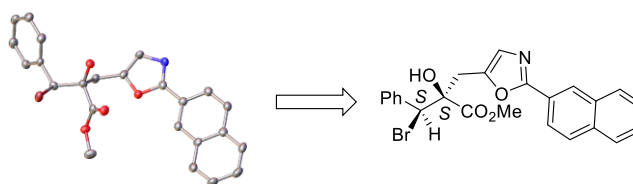
In a dried tube, the compounds **3aa** (0.1 mmol) was dissolved in 1.0 mL DMF. Subsequently, NaN₃

(0.5 mmol, 5 equiv) was added and the reaction stirred at 60 °C for 48 h. The mixture was allowed to cool down to rt, quenched with H₂O and extracted with EtOAc. The organic layer was dried (Na₂SO₄) and concentrated under reduced pressure. Purification by flash chromatography (eluent: petroleum ether/EtOAc = 4/1) furnished the corresponding product **5** in 28.0 mg (74% yield, >95:5 dr and >99% ee).

5. Determination of absolute configuration and the X-ray structure of **3ah**

The absolute configuration of the optically active product **3ah** was determined to be (2*S*, 3*S*) by X-ray crystal analysis.

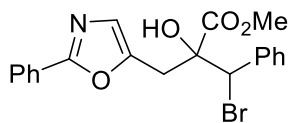
The single crystal of **3ah** was obtained from mixed solvents of CH₂Cl₂ and petroleum ether. CCDC 1561469 contains the supplementary crystallographic data which can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.



6. References

- [1] Y. H. Wen, X. Huang, J. L. Huang, Y. Xiong, B. Qin and X. M. Feng, *Synlett*, 2005, 2445.
- [2] J. L. Huang, X. H. Liu, Y. H. Wen, B. Qin and X. M. Feng, *J. Org. Chem.*, 2007, **72**, 204.
- [3] Z. P. Yu, X. H. Liu, Z. H. Dong, M. S. Xie and X. M. Feng, *Angew. Chem., Int. Ed.*, 2008, **47**, 1308.
- [4] V. A. Mamedov, E. A. Berdnikov, S. Tsuboi, H. Hamamoto, T. Komiyama, E. A. Gorbunova, A. T. Gubaidullin and I. A. Litvinova, *Russ. Chem. Bull.*, 2006, **55**, 1455.

7. Characterization of the products



Methyl 3-bromo-2-hydroxy-3-phenyl-2-((2-phenyloxazol-5-yl)methyl)propanoate (3aa):

White solid in 89% yield, dr =93:7, m.p. = 138 – 141 °C, $[\alpha]_D^{29} = +127.9$ ($c = 0.61$, in CH_2Cl_2).

HPLC: Chiralcel IA, hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, $\lambda = 254$ nm, $t_{r1} = 14.56$ min (major enantiomer of major diastereoisomer), $t_{r2} = 15.85$ min (major enantiomer of minor diastereoisomer), $t_{r3} = 17.07$ min (major enantiomer of minor diastereoisomer), $t_{r4} = 27.96$ min (minor enantiomer of minor diastereoisomer), ee (major diastereoisomer) = 99%.

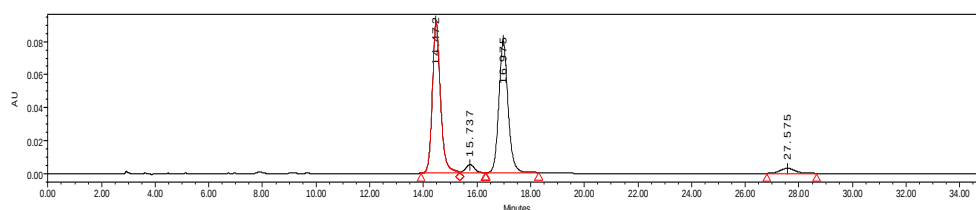
^1H NMR (400 MHz, CDCl_3) δ 7.94 – 7.92 (m, 2H), 7.64 – 7.62 (m, 2H), 7.42 – 7.37 (m, 6H), 6.86 (s, 1H), 5.33 (s, 1H), 4.02 (s, 1H), 3.89 (s, 3H), 3.12 (d, $J = 15.2$ Hz, 1H), 2.68 (d, $J = 15.2$ Hz, 1H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 173.1, 161.4, 146.5, 136.4, 130.3, 129.8, 129.3, 128.8, 128.6, 127.4, 126.8, 126.1, 79.8, 57.7, 53.8, 33.7.

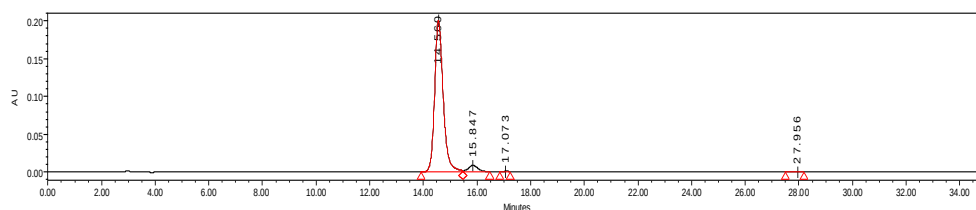
HRMS (ESI-TOF) Calculated for $\text{C}_{20}\text{H}_{18}^{78.9183}\text{BrNO}_4$ ($[\text{M}] + \text{H}^+$) = 416.0492, Found 416.0496.

HRMS (ESI-TOF) Calculated for $\text{C}_{20}\text{H}_{18}^{80.9163}\text{BrNO}_4$ ($[\text{M}] + \text{H}^+$) = 418.0472, Found 418.0479.

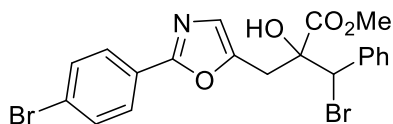
IR (film): 3504, 3055, 2916, 1745, 1259, 1124, 721, 694 cm^{-1} .



	Retention Time	Area	% Area
1	14.472	1933083	47.25
2	15.737	119570	2.92
3	16.975	1919504	46.92
4	27.575	119044	2.91



	Retention time	Area	% Area
1	14.560	4419045	95.21
2	15.847	214885	4.63
3	17.073	5534	0.12
4	27.956	2043	0.04



Methyl 3-bromo-2-((2-(4-bromophenyl)oxazol-5-yl)methyl)-2-hydroxy-3-phenylpropanoate (3ab)

White solid in 82% yield, dr = 94:6, m.p. = 139 – 143 °C, $[\alpha]^{27}_D = +104.5$ ($c = 0.57$, in CH_2Cl_2).

HPLC: Chiralcel IA, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, $\lambda = 254$ nm, t_r (major) = 12.47 min, t_r (minor) = 16.29 min, ee (major diastereoisomer) = 99%.

^1H NMR (400 MHz, CDCl_3) δ 7.81 – 7.76 (m, 2H), 7.65 – 7.60 (m, 2H), 7.58 – 7.53 (m, 2H), 7.38 (m, 3H), 6.86 (s, 1H), 5.32 (s, 1H), 3.97 (d, $J = 1.2$ Hz, 1H), 3.89 (s, 3H), 3.11 (d, $J = 15.2$ Hz, 1H), 2.68 (dd, $J = 15.2, 0.8$ Hz, 1H).

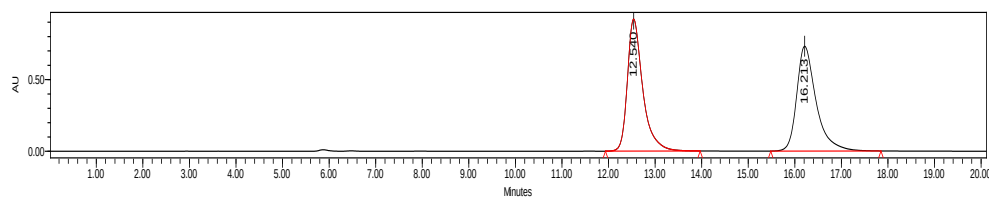
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 173.1, 146.9, 136.4, 132.0, 129.8, 129.3, 128.6, 127.6, 126.9, 126.3, 124.7, 79.8, 57.7, 53.8, 33.7.

HRMS (ESI-TOF) Calculated for $\text{C}_{20}\text{H}_{17}^{78.9183}\text{Br}_2\text{NO}_4$ ($[\text{M}] + \text{H}^+$) = 493.9597, Found 493.9698.

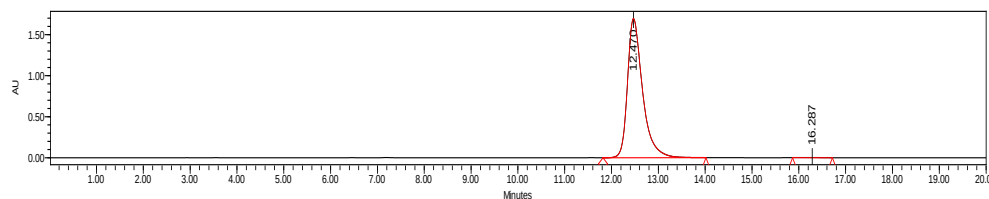
HRMS (ESI-TOF) Calculated for $\text{C}_{20}\text{H}_{17}^{78.9183}\text{Br}^{80.9163}\text{BrNO}_4$ ($[\text{M}] + \text{H}^+$) = 495.9577, Found 495.9579.

HRMS (ESI-TOF) Calculated for $\text{C}_{20}\text{H}_{17}^{80.9163}\text{Br}_2\text{NO}_4$ ($[\text{M}] + \text{H}^+$) = 497.9556, Found 497.9557.

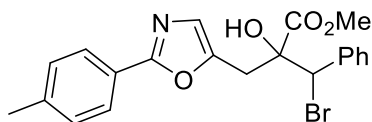
IR (film): 3510, 2920, 1749, 1483, 1257, 1124, 732, 698 cm^{-1} .



	Retention Time	Area	% Area
1	12.540	21087755	49.98
2	16.213	21104777	50.02



	Retention Time	Area	% Area
1	12.470	37756925	99.89
2	16.287	41144	0.11



Methyl 3-bromo-2-hydroxy-3-phenyl-2-((2-(p-tolyl)oxazol-5-yl)methyl)propanoate (3ac):

White solid in 77% yield, dr = 94:6, m.p. = 141 – 144 °C, $[\alpha]_D^{27} = +133.5$ ($c = 0.50$, in CH_2Cl_2).

HPLC: Chiralcel IA, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, $\lambda = 254$ nm, t_r (major) = 10.53 min, t_r (minor) = 13.09 min, ee (major diastereoisomer) = 99%.

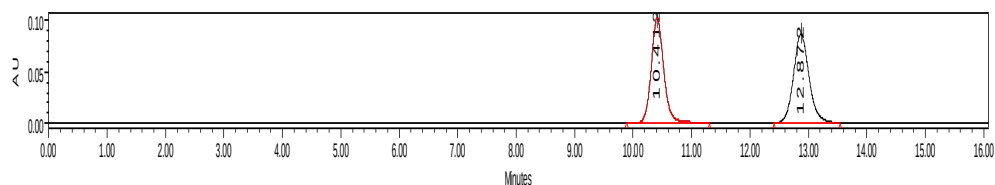
^1H NMR (400 MHz, CDCl_3) δ 7.82 (d, $J = 8.0$ Hz, 2H), 7.63 (m, 2H), 7.42 – 7.35 (m, 3H), 7.22 (d, $J = 8.0$ Hz, 2H), 6.84 (s, 1H), 5.33 (s, 1H), 3.94 (s, 1H), 3.89 (d, $J = 1.2$ Hz, 3H), 3.11 (d, $J = 15.2$ Hz, 1H), 2.67 (d, $J = 14.8$ Hz, 1H), 2.38 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 173.1, 161.6, 146.1, 140.5, 136.5, 129.8, 129.5, 129.3, 128.6, 126.7, 126.1, 124.7, 79.8, 57.8, 53.7, 33.7, 21.5.

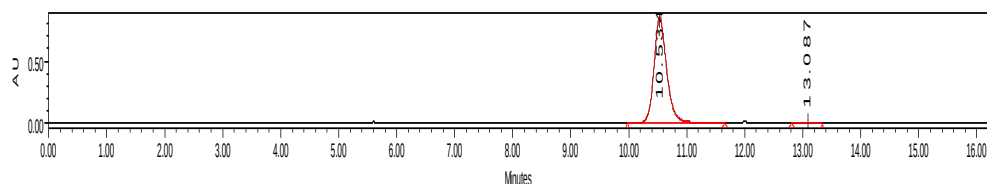
HRMS (ESI-TOF) Calculated for $\text{C}_{21}\text{H}_{20}^{78,9183}\text{BrNO}_4$ ($[\text{M}] + \text{H}^+$) = 430.0648, Found 430.0652.

HRMS (ESI-TOF) Calculated for $\text{C}_{21}\text{H}_{20}^{80,9163}\text{BrNO}_4$ ($[\text{M}] + \text{H}^+$) = 432.0628, Found 432.0638.

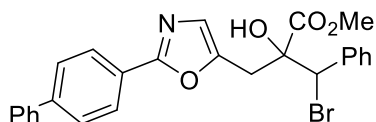
IR (film): 3487, 2955, 2929, 1749, 1433, 1263, 1124, 837, 702 cm^{-1} .



	Retention Time	Area	% Area
1	10.412	1529615	48.81
2	12.872	1604076	51.19



	Retention Time	Area	% Area
1	10.534	13133475	99.61
2	13.087	51259	0.39



Methyl 2-((2-([1,1'-biphenyl]-4-yl)oxazol-5-yl)methyl)-3-bromo-2-hydroxy-3-phenylpropanoate (3ad):

White solid in 64% yield, dr = 94:6, m.p. = 176 – 180 °C, $[\alpha]_D^{27} = +116.6$ ($c = 0.61$, in CH_2Cl_2).

HPLC: Chiralcel IC, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, $\lambda = 254$ nm, $t_{r1} = 9.58$ min (major enantiomer of minor diastereoisomer), $t_{r2} = 16.41$ min (minor enantiomer of minor diastereoisomer), $t_{r3} = 18.41$ min (major enantiomer of major diastereoisomer), $t_{r4} = 27.04$ min (minor enantiomer of major diastereoisomer), ee (major diastereoisomer) = 99%.

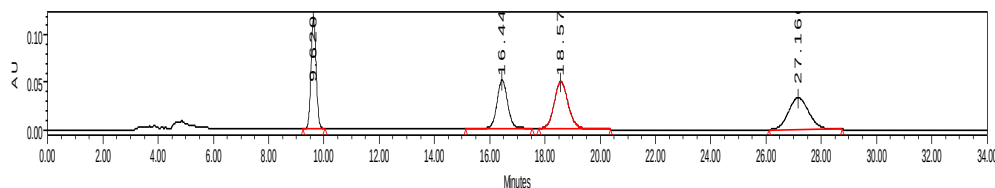
^1H NMR (400 MHz, CDCl_3) δ 8.02 – 7.97 (m, 2H), 7.68 – 7.60 (m, 6H), 7.48 – 7.34 (m, 6H), 6.89 (s, 1H), 5.34 (s, 1H), 3.97 (d, $J = 0.8$ Hz, 1H), 3.91 (s, 3H), 3.14 (d, $J = 14.8$ Hz, 1H), 2.70 (dd, $J = 15.2, 0.8$ Hz, 1H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 173.1, 161.3, 146.6, 142.9, 140.1, 136.5, 129.8, 129.3, 128.9, 128.6, 127.9, 127.4, 127.1, 126.9, 126.6, 126.2, 79.8, 57.8, 53.8, 33.8.

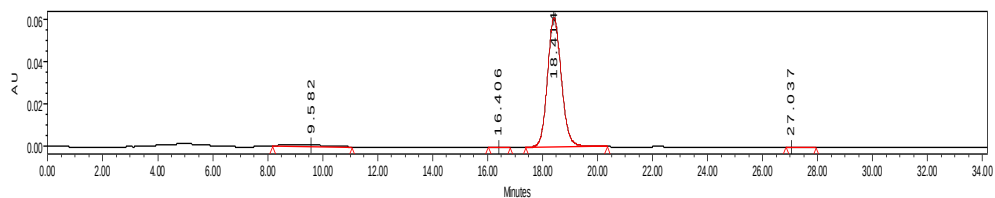
HRMS (ESI-TOF) Calculated for $\text{C}_{26}\text{H}_{22}^{78,9183}\text{BrNO}_4$ ($[\text{M}]+\text{H}^+$) = 492.0805, Found 492.0805.

HRMS (ESI-TOF) Calculated for $\text{C}_{26}\text{H}_{22}^{80,9163}\text{BrNO}_4$ ($[\text{M}]+\text{H}^+$) = 494.0785, Found 494.0786.

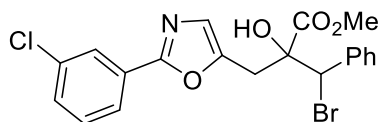
IR (film): 3504, 2958, 2927, 1735, 1450, 1257, 1124, 736 cm^{-1} .



	Retention Time	Area	% Area
1	9.620	1504102	23.67
2	16.448	1357937	21.37
3	18.572	1746522	27.49
4	27.166	1745353	27.47



	Retention Time	Area	% Area
1	9.582	78414	3.50
2	16.406	1211	0.05
3	18.414	2162560	96.44
4	27.037	276	0.01



Methyl 3-bromo-2-((2-(3-chlorophenyl)oxazol-5-yl)methyl)-2-hydroxy-3-phenylpropanoate (3ae):

Colorless oil in 98% yield, dr = 92:8, $[\alpha]_D^{27} = +120.9$ ($c = 0.62$, in CH_2Cl_2).

HPLC: Chiralcel IA, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, $\lambda = 254$ nm, t_r (major) = 8.14 min, t_r (minor) = 9.90 min, ee (major diastereoisomer) = 99%.

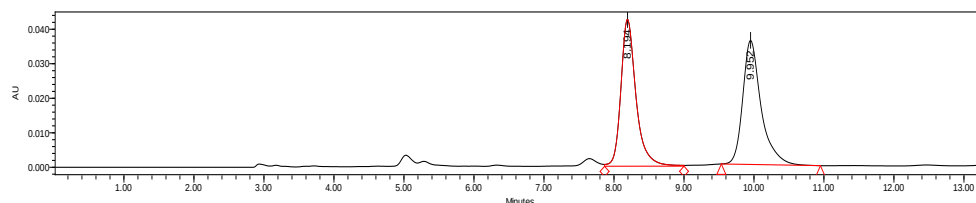
^1H NMR (400 MHz, CDCl_3) δ 7.93 – 7.89 (m, 1H), 7.81 (dt, $J = 7.2, 1.6$ Hz, 1H), 7.65 – 7.60 (m, 2H), 7.40 – 7.36 (m, 5H), 6.87 (s, 1H), 5.32 (s, 1H), 3.98 (d, $J = 1.2$ Hz, 1H), 3.91 (s, 3H), 3.12 (d, $J = 14.8$ Hz, 1H), 2.69 (dd, $J = 15.2, 0.2$ Hz, 1H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 173.1, 160.0, 147.1, 136.4, 134.9, 130.2, 130.1, 129.8, 129.3, 129.0, 128.6, 127.0, 126.2, 124.1, 79.8, 57.7, 53.8, 33.6.

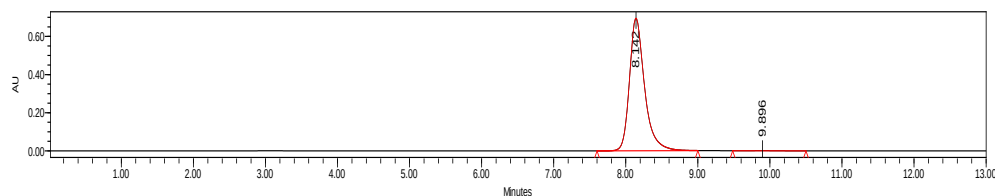
HRMS (ESI-TOF) Calculated for $\text{C}_{20}\text{H}_{17}^{78.9183}\text{BrClINO}_4$ ($[\text{M}+\text{H}^+]$) = 450.0102, Found 450.0109.

HRMS (ESI-TOF) Calculated for $\text{C}_{20}\text{H}_{17}^{80.9163}\text{BrClINO}_4$ ($[\text{M}+\text{H}^+]$) = 452.0082, Found 452.0084.

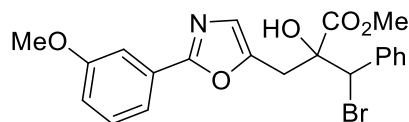
IR (film): 3506, 2927, 1745, 1433, 1259, 1219, 1120, 729 cm^{-1} .



	Retention Time	Area	% Area
1	8.194	638208	49.37
2	9.952	654388	50.63



	Retention Time	Area	% Area
1	8.142	10083841	99.85
2	9.896	15192	0.15



Methyl 3-bromo-2-hydroxy-2-((2-(3-methoxyphenyl)oxazol-5-yl)methyl)-3-phenylpropanoate (3af):

White solid in 81% yield, dr = 94:6, m.p. = 104 – 106 °C, $[\alpha]_D^{27} = +128.2$ ($c = 0.52$, in CH_2Cl_2).

HPLC: Chiralcel IA, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, $\lambda = 254$ nm, t_r (major) = 9.33 min, t_r (minor) = 10.93 min, ee (major diastereoisomer) = 99%.

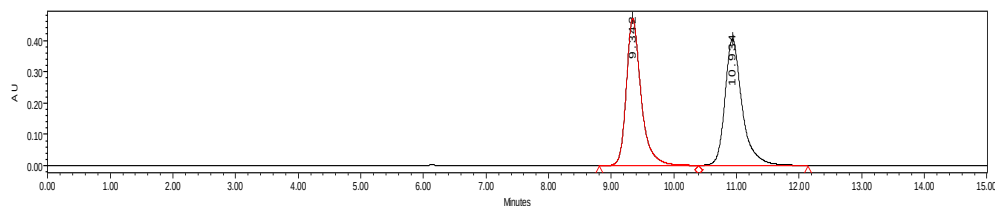
^1H NMR (400 MHz, CDCl_3) δ 7.66 – 7.60 (m, 2H), 7.53 – 7.49 (m, 1H), 7.47 (m, 1H), 7.42 – 7.35 (m, 3H), 7.33 (t, $J = 8.0$ Hz, 1H), 6.97 (m, 1H), 6.86 (s, 1H), 5.33 (s, 1H), 3.95 (s, 1H), 3.90 (s, 3H), 3.85 (s, 3H), 3.12 (d, $J = 14.8$ Hz, 1H), 2.69 (d, $J = 15.2$ Hz, 1H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 173.1, 161.3, 159.8, 146.6, 136.4, 129.9, 129.8, 129.8, 129.3, 128.6, 128.5, 126.8, 118.5, 116.8, 110.8, 79.8, 57.7, 55.4, 53.8, 33.7.

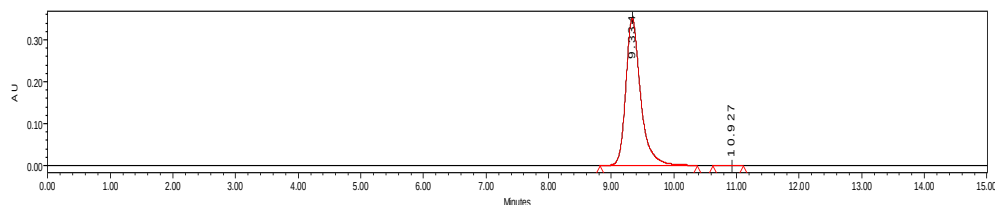
HRMS (ESI-TOF) Calculated for $\text{C}_{21}\text{H}_{20}^{78.9183}\text{BrNO}_5$ ($[\text{M}] + \text{H}^+$) = 446.0598, Found 446.0600.

HRMS (ESI-TOF) Calculated for $\text{C}_{21}\text{H}_{20}^{80.9163}\text{BrNO}_5$ ($[\text{M}] + \text{H}^+$) = 448.0577, Found 448.0579.

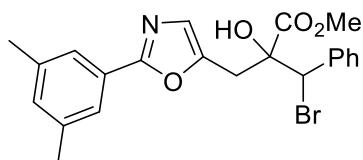
IR (film): 3506, 2951, 1749, 1467, 1263, 1124, 842, 736, 690 cm^{-1} .



	Retention time	Area	% Area
1	9.342	7711445	49.96
2	10.934	7722328	50.04



	Retention time	Area	Area%
1	9.334	5744193	99.91
2	10.927	5218	0.09



Methyl 3-bromo-2-((2-(3,5-dimethylphenyl)oxazol-5-yl)methyl)-2-hydroxy-3-phenylpropanoate (3ag):

Colorless oil in 94% yield, dr = 93:7, $[\alpha]_D^{27} = +105.3$ ($c = 0.36$, in CH_2Cl_2).

HPLC: Chiralcel IA, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, $\lambda = 254$ nm, t_r (major) = 6.39 min, t_r (minor) = 7.41 min, ee (major diastereoisomer) = 99%.

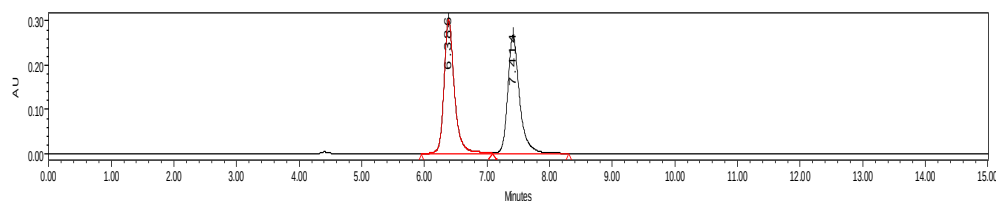
^1H NMR (400 MHz, CDCl_3) δ 7.63 (m, 2H), 7.58 – 7.53 (m, 2H), 7.42 – 7.35 (m, 3H), 7.07 – 7.02 (m, 1H), 6.84 (s, 1H), 5.33 (s, 1H), 3.97 (d, $J = 1.2$ Hz, 1H), 3.89 (s, 3H), 3.11 (d, $J = 15.2$ Hz, 1H), 2.68 (dd, $J = 15.2, 0.8$ Hz, 1H), 2.34 (s, 6H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 173.1, 161.7, 146.3, 138.4, 136.5, 132.0, 129.8, 129.3, 128.6, 127.1, 126.6, 123.9, 79.9, 57.8, 53.7, 33.8, 21.3.

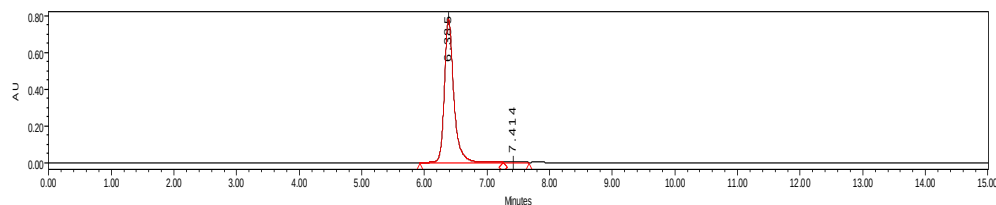
HRMS (ESI-TOF) Calculated for $\text{C}_{22}\text{H}_{22}^{78.9183}\text{BrNO}_4$ ($[\text{M}] + \text{H}^+$) = 444.0805, Found 444.0811.

HRMS (ESI-TOF) Calculated for $\text{C}_{22}\text{H}_{22}^{80.9163}\text{BrNO}_4$ ($[\text{M}] + \text{H}^+$) = 446.0785, Found 446.0793.

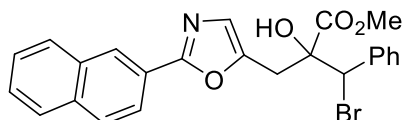
IR (film): 3510, 2951, 2924, 1749, 1552, 1450, 1257, 1120, 736, 694 cm^{-1} .



	Retention Time	Area	% Area
1	6.386	3500198	50.14
2	7.414	3480147	49.86



	Retention Time	Area	% Area
1	6.385	8121873	99.79
2	7.414	17138	0.21



Methyl 3-bromo-2-hydroxy-2-((2-(naphthalen-2-yl)oxazol-5-yl)methyl)-3-phenylpropanoate (3ah):

White solid in 82% yield, dr = 93:7, m.p. = 171 – 173 °C, $[\alpha]_D^{27} = +120.9$ ($c = 0.64$, in CH_2Cl_2).

HPLC: Chiralcel IA, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, $\lambda = 254$ nm, $t_{r1} = 13.29$ min (major enantiomer of major diastereoisomer), $t_{r2} = 17.22$ min (major enantiomer of minor diastereoisomer), $t_{r3} = 18.23$ min (minor enantiomer of major diastereoisomer), $t_{r4} = 20.17$ min (minor enantiomer of minor diastereoisomer), ee (major diastereoisomer) = 99%.

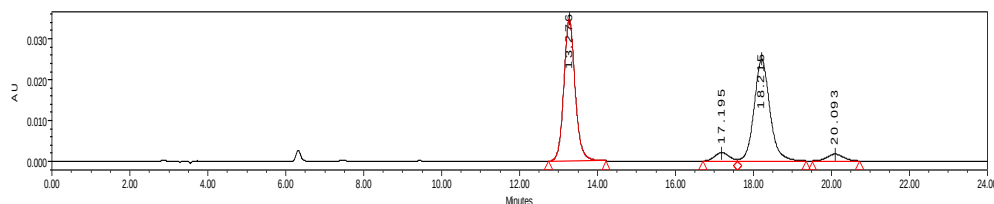
^1H NMR (400 MHz, CDCl_3) δ 8.42 (s, 1H), 8.02 (m, 1H), 7.92 – 7.80 (m, 3H), 7.68 – 7.60 (m, 2H), 7.55 – 7.47 (m, 2H), 7.40 (m, 3H), 6.92 (s, 1H), 5.35 (d, $J = 0.8$ Hz, 1H), 3.99 (s, 1H), 3.92 (d, $J = 1.2$ Hz, 3H), 3.17 (d, $J = 15.2$ Hz, 1H), 2.73 (d, $J = 14.8$ Hz, 1H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 173.1, 161.6, 146.8, 136.5, 134.1, 133.0, 129.8, 129.3, 128.6, 128.6, 127.9, 127.2, 127.0, 126.8, 126.0, 124.6, 123.1, 79.9, 57.8, 53.8, 33.8.

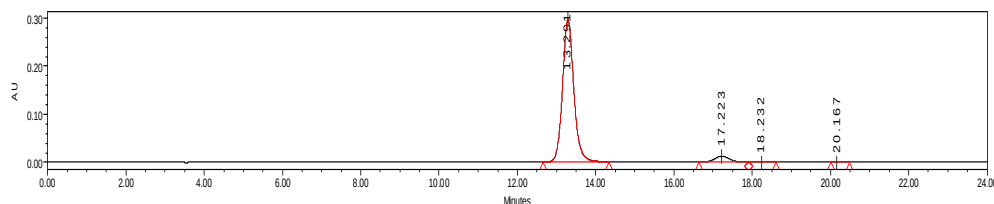
HRMS (ESI-TOF) Calculated for $\text{C}_{24}\text{H}_{20}^{78.9183}\text{BrNO}_4$ ($[\text{M}] + \text{H}^+$) = 466.0648, Found 466.0654.

HRMS (ESI-TOF) Calculated for $\text{C}_{24}\text{H}_{20}^{80.9163}\text{BrNO}_4$ ($[\text{M}] + \text{H}^+$) = 468.0628, Found 468.0620.

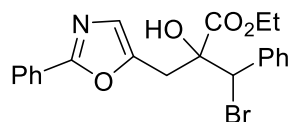
IR (film): 3487, 3062, 2947, 1745, 1448, 1263, 1120, 756 cm^{-1} .



	Retention time	Area	Area%
1	13.276	698249	46.75
2	17.195	53114	3.56
3	18.215	694984	46.53
4	20.093	47172	3.16



	Retention time	Area	Area%
1	13.291	5981646	94.16
2	17.223	344768	5.43
3	18.232	24561	0.39
4	20.167	1668	0.03



Ethyl 3-bromo-2-hydroxy-3-phenyl-2-((2-phenyloxazol-5-yl)methyl)propanoate (3ba):

White solid in 69% yield, dr = 92:8, m.p. = 43 – 46 °C, $[\alpha]_D^{29} = +113.0$ ($c = 0.46$, in CH_2Cl_2).

HPLC: Chiralcel IC, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, $\lambda = 254$ nm, $t_{r1} = 10.95$ min (minor enantiomer of minor diastereoisomer), $t_{r2} = 13.96$ min (major enantiomer of major diastereoisomer), $t_{r3} = 16.50$ min (minor enantiomer of major diastereoisomer), $t_{r4} = 42.50$ min (major enantiomer of minor diastereoisomer), ee (major diastereoisomer) = 99%.

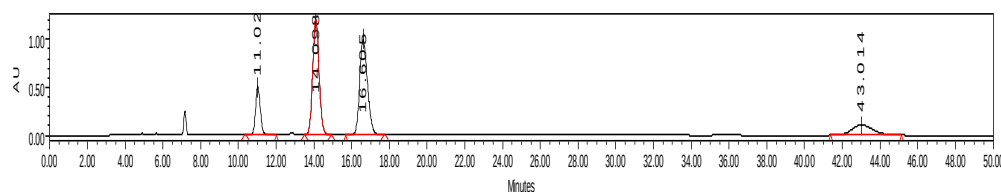
^1H NMR (400 MHz, CDCl_3) δ 7.99 – 7.89 (m, 2H), 7.69 – 7.60 (m, 2H), 7.45 – 7.34 (m, 6H), 6.87 (s, 1H), 5.33 (s, 1H), 4.35 (m, 2H), 3.97 (d, $J = 1.2$ Hz, 1H), 3.12 (d, $J = 15.2$ Hz, 1H), 2.69 (dd, $J = 15.2$, 0.8 Hz, 1H), 1.34 (t, $J = 7.2$ Hz, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 172.6, 161.3, 146.6, 136.6, 130.2, 129.8, 129.3, 128.8, 128.6, 127.4, 126.8, 126.1, 79.5, 63.3, 57.8, 33.7, 14.2.

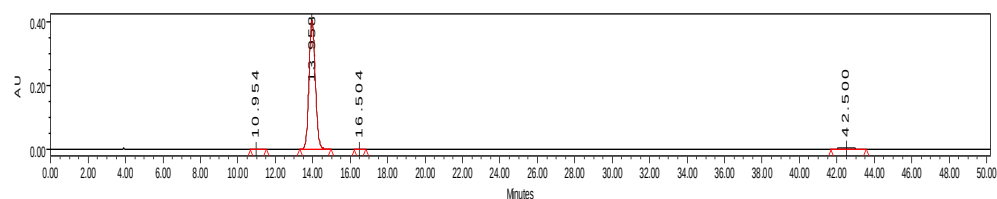
HRMS (ESI-TOF) Calculated for $\text{C}_{21}\text{H}_{20}^{78.9183}\text{BrNO}_4$ ($[\text{M}]+\text{H}^+$) = 430.0648, Found 430.0648.

HRMS (ESI-TOF) Calculated for $\text{C}_{21}\text{H}_{20}^{80.9163}\text{BrNO}_4$ ($[\text{M}]+\text{H}^+$) = 432.0628, Found 432.0629.

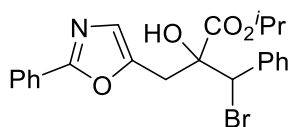
IR (film): 3506, 3059, 2933, 1739, 1249, 1128, 713, 698 cm^{-1} .



	Retention Time	Area	% Area
1	11.027	8868885	11.91
2	14.098	28469421	38.22
3	16.605	28707486	38.54
4	43.014	8443764	11.34



	Retention Time	Area	% Area
1	10.954	5692	0.06
2	13.958	9431518	96.80
3	16.504	16859	0.17
4	42.500	289291	2.97



Isopropyl 3-bromo-2-hydroxy-3-phenyl-2-((2-phenyloxazol-5-yl)methyl)propanoate (3ca):

White solid in 83% yield, dr = 92:8, m.p. = 130 – 132 °C, $[\alpha]_D^{29} = +115.2$ ($c = 0.64$, in CH_2Cl_2).

HPLC: Chiralcel IC, hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, $\lambda = 254$ nm, $t_{r1} = 16.04$ min (major enantiomer of minor diastereoisomer), $t_{r2} = 24.28$ min (major enantiomer of major diastereoisomer), $t_{r3} = 27.26$ min (minor enantiomer of major diastereoisomer), $t_{r4} = 66.92$ min (minor enantiomer of minor diastereoisomer), ee (major diastereoisomer) = 99%.

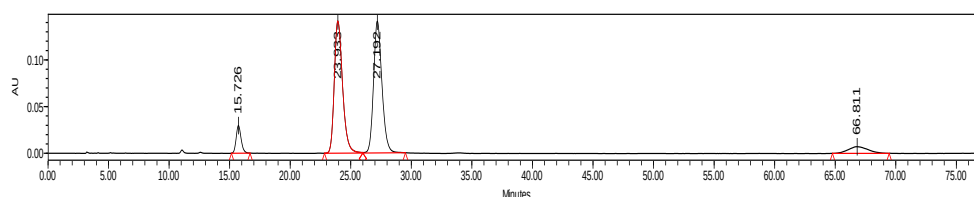
^1H NMR (400 MHz, CDCl_3) δ 7.95 – 7.92 (m, 2H), 7.67 – 7.64 (m, 2H), 7.43 – 7.37 (m, 6H), 6.88 (s, 1H), 5.31 (s, 1H), 5.120 – 5.10 (m, 1H). 4.00 (d, $J = 1.2$ Hz, 1H), 3.20 – 3.01 (d, $J = 15.2$ Hz, 1H), 2.69 (dd, $J = 15.2, 0.8$ Hz, 1H), 1.33 (d, $J = 3.6$ Hz, 3H), 1.31 (d, $J = 3.2$ Hz, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 172.0, 161.3, 146.7, 136.6, 130.2, 129.8, 129.2, 128.7, 128.6, 127.4, 126.8, 126.1, 79.3, 71.5, 57.8, 33.6, 21.8, 21.6.

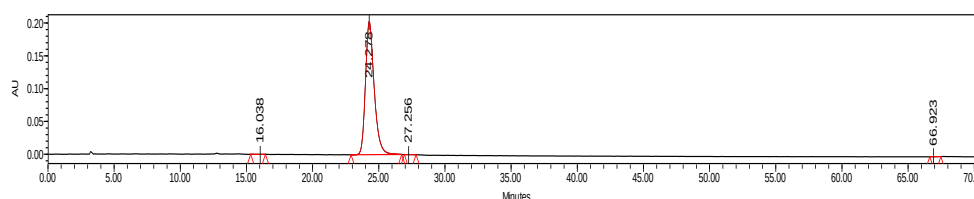
HRMS (ESI-TOF) Calculated for $\text{C}_{22}\text{H}_{22}^{78.9183}\text{BrNO}_4$ ($[\text{M}] + \text{H}^+$) = 444.0805, Found 444.0806.

HRMS (ESI-TOF) Calculated for $\text{C}_{22}\text{H}_{22}^{80.9163}\text{BrNO}_4$ ($[\text{M}] + \text{H}^+$) = 446.0785, Found 446.0785.

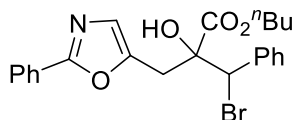
IR (film): 3500, 2985, 2933, 1739, 1257, 1103, 702 cm^{-1} .



	Retention Time	Area	% Area
1	15.726	842022	5.56
2	23.933	6715566	44.32
3	27.192	6785225	44.78
4	66.811	810514	5.35



	Retention Time	Area	% Area
1	16.038	5418	0.06
2	24.278	9278864	99.90
3	27.256	3543	0.04
4	66.923	665	0.01



Butyl 3-bromo-2-hydroxy-3-phenyl-2-((2-phenyloxazol-5-yl)methyl)propanoate (3da):

Colorless oil in 78% yield, dr = 93:7, $[\alpha]_D^{29} = +103.2$ ($c = 0.50$, in CH_2Cl_2).

HPLC: Chiralcel IC, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, $\lambda = 254$ nm, $t_{r1} = 9.37$ min (minor enantiomer of minor diastereoisomer), $t_{r2} = 12.20$ min (major enantiomer of major diastereoisomer), $t_{r3} = 15.03$ min (minor enantiomer of major diastereoisomer), $t_{r4} = 32.84$ min (major enantiomer of minor diastereoisomer), ee (major diastereoisomer) = 99%.

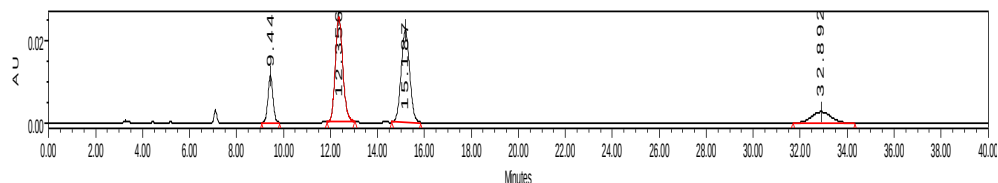
^1H NMR (400 MHz, CDCl_3) δ 7.99 – 7.89 (m, 2H), 7.69 – 7.61 (m, 2H), 7.45 – 7.34 (m, 6H), 6.87 (s, 1H), 5.32 (s, 1H), 4.36 – 4.16 (m, 2H), 3.97 (d, $J = 1.2$ Hz, 1H), 3.12 (d, $J = 15.2$ Hz, 1H), 2.70 (dd, $J = 15.2, 0.8$ Hz, 1H), 1.75 – 1.61 (m, 2H), 1.47 – 1.31 (m, 2H), 0.91 (t, $J = 7.2$ Hz, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 172.7, 161.3, 146.6, 136.6, 130.2, 129.8, 129.3, 128.7, 128.6, 127.4, 126.8, 126.1, 79.6, 67.1, 57.8, 33.7, 30.5, 19.1, 13.6.

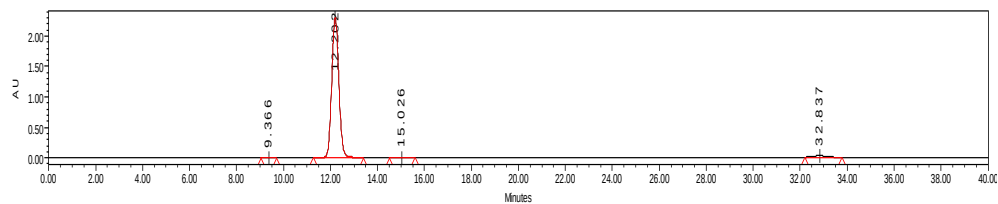
HRMS (ESI-TOF) Calculated for $\text{C}_{23}\text{H}_{24}^{78.9183}\text{BrNO}_4$ ($[\text{M}] + \text{H}^+$) = 458.0961, Found 458.0965.

HRMS (ESI-TOF) Calculated for $\text{C}_{23}\text{H}_{24}^{80.9163}\text{BrNO}_4$ ($[\text{M}] + \text{H}^+$) = 460.0941, Found 460.0950.

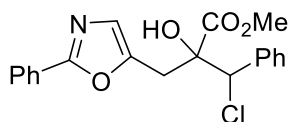
IR (film): 3564, 3059, 2927, 1743, 1489, 1259, 1120, 704 cm^{-1} .



	Retention Time	Area	% Area
1	9.443	167888	11.47
2	12.356	567046	38.73
3	15.187	565982	38.66
4	32.892	163054	11.14



	Retention Time	Area	% Area
1	9.366	54143	0.11
2	12.202	48194384	96.89
3	15.026	219296	0.44
3	32.837	1275056	2.56



Methyl 3-chloro-2-hydroxy-3-phenyl-2-((2-phenyloxazol-5-yl)methyl)propanoate (3ea):

Colorless oil in 78% yield, dr = 75:25, $[\alpha]_D^{26} = +89.0$ ($c = 0.24$, in CH_2Cl_2).

HPLC: Chiralcel IC, hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, $\lambda = 254$ nm, t_r (major) = 28.84 min, t_r (minor) = 37.15 min, ee (major diastereoisomer) = 99%.

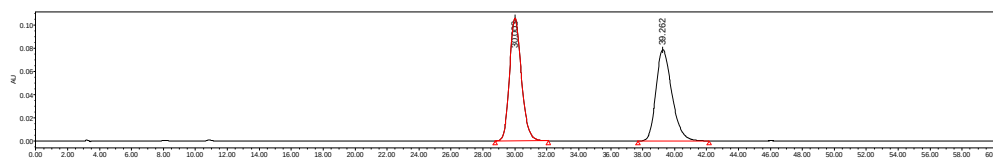
^1H NMR (400 MHz, CDCl_3) δ 7.95 – 7.92 (m, 2H), 7.60 – 7.57 (m, 2H), 7.43 – 7.40 (m, 6H), 6.87 (s, 1H), 5.24 (s, 1H), 3.91 (s, 3H), 3.84 (s, 1H), 3.14 (d, $J = 15.2$ Hz, 1H), 2.65 (d, $J = 15.2$ Hz, 1H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 173.0, 161.4, 146.5, 135.7, 130.3, 129.4, 129.3, 128.8, 128.5, 127.4, 126.8, 126.1, 79.8, 66.1, 53.7, 33.8.

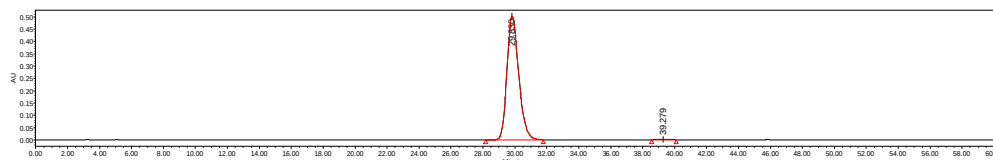
HRMS (ESI-TOF) Calculated for $\text{C}_{20}\text{H}_{18}^{34.9689}\text{ClNO}_4$ ($[\text{M}] + \text{H}^+$) = 372.0997, Found 372.1000

HRMS (ESI-TOF) Calculated for $\text{C}_{20}\text{H}_{18}^{36.9659}\text{ClNO}_4$ ($[\text{M}] + \text{H}^+$) = 374.0968, Found 374.0972

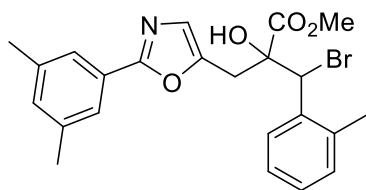
IR (film): 3514, 3066, 2929, 1749, 1552, 1458, 1259, 1120, 711 cm^{-1} .



	Retention Time	Area	% Area
1	30.003	5477415	50.04
2	39.262	5467821	49.96



	Retention Time	Area	% Area
1	29.830	25755781	99.51
2	39.279	126582	0.49



Methyl 3-bromo-2-((2-(3,5-dimethylphenyl)oxazol-5-yl)methyl)-2-hydroxy-3-(o-tolyl)propanoate (3fg):

Colorless oil in 84% yield, dr = 90:10, $[\alpha]_D^{27} = +63.1$ ($c = 0.68$, in CH_2Cl_2).

HPLC: Chiralcel IC, hexane/*i*-PrOH = 70/30, flow rate 1.0 mL/min, $\lambda = 254$ nm, t_r (major) = 11.59 min, t_r (minor) = 14.28 min, ee (major diastereoisomer) = 99%.

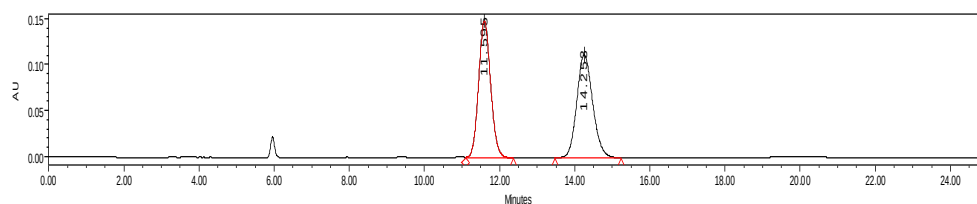
^1H NMR (400 MHz, CDCl_3) δ 8.08 (d, $J = 8.0$ Hz, 1H), 7.56 (s, 2H), 7.30 – 7.26 (m, 1H), 7.25 – 7.22 (m, 1H), 7.18 – 7.16 (m, 1H), 7.05 (s, 1H), 6.84 (s, 1H), 5.70 (s, 1H), 4.03 (s, 1H), 3.92 (d, $J = 1.2$ Hz, 3H), 3.10 (d, $J = 15.2$ Hz, 1H), 2.82 (d, $J = 14.8$ Hz, 1H), 2.47 (s, 3H), 2.34 (s, 6H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 173.3, 161.7, 146.2, 138.4, 135.6, 135.2, 132.0, 130.7, 130.4, 129.0, 127.1, 127.0, 126.7, 123.9, 80.4, 53.8, 52.6, 33.1, 21.3, 19.9.

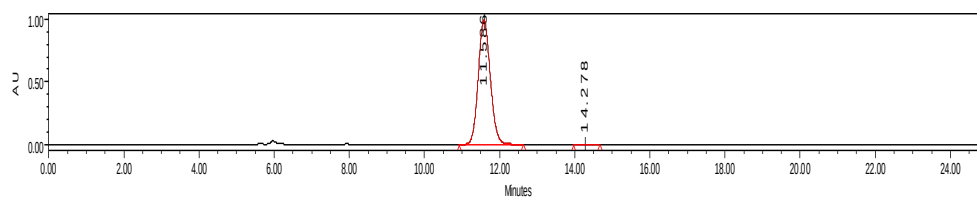
HRMS (ESI-TOF) Calculated for $\text{C}_{23}\text{H}_{24}^{78.9183}\text{BrNO}_4$ ($[\text{M}] + \text{H}^+$) = 458.0961, Found 458.0971.

HRMS (ESI-TOF) Calculated for $\text{C}_{23}\text{H}_{24}^{80.9163}\text{BrNO}_4$ ($[\text{M}] + \text{H}^+$) = 460.0941, Found 460.0941.

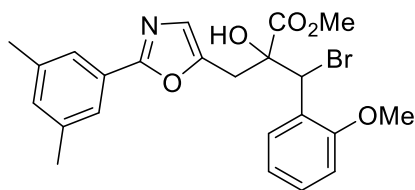
IR (film): 3500, 2958, 2920, 1757, 1458, 1259, 1128, 736 cm^{-1} .



	Retention time	Area	Area%
1	11.595	3327756	50.20
2	14.253	3300586	49.80



	Retention time	Area	Area%
1	11.586	22102843	99.91
2	14.278	19996	0.09



Methyl 3-bromo-2-((2-(3,5-dimethylphenyl)oxazol-5-yl)methyl)-2-hydroxy-3-(2-methoxyphenyl)propanoate (3gg):

Colorless oil in 77% yield, dr = 94:6, $[\alpha]_D^{27} = +32.3$ ($c = 0.82$, in CH_2Cl_2).

HPLC: Daicel chiralpakLux 5u Cellulose-2, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, $\lambda = 254$ nm, t_r (minor) = 9.23 min, t_r (major) = 11.30 min, ee (major diastereoisomer) = 99%.

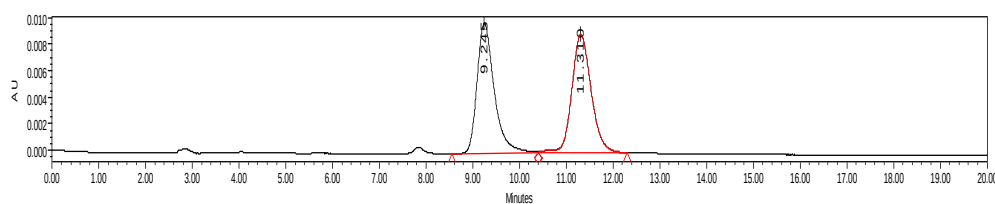
^1H NMR (400 MHz, CDCl_3) δ 7.94 (dd, $J = 8.0, 1.6$ Hz, 1H), 7.56 (s, 2H), 7.35 – 7.28 (m, 1H), 7.08 – 7.00 (m, 2H), 6.89 (dd, $J = 8.4, 0.8$ Hz, 1H), 6.84 (s, 1H), 6.09 (s, 1H), 3.97 – 3.93 (m, 1H), 3.91 (s, 3H), 3.91 (s, 3H), 3.23 (dd, $J = 15.2, 1.2$ Hz, 1H), 2.69 (dd, $J = 15.2, 0.8$ Hz, 1H), 2.34 (s, 6H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 173.4, 161.7, 156.0, 146.7, 138.4, 132.5, 131.9, 130.2, 126.5, 124.7, 123.9, 121.2, 110.4, 80.3, 55.8, 53.6, 49.7, 32.8, 21.2.

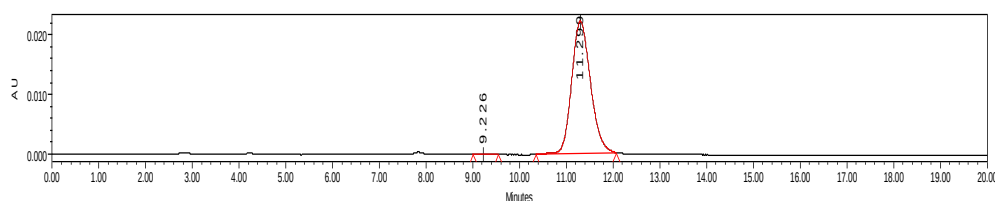
HRMS (ESI-TOF) Calculated for $\text{C}_{23}\text{H}_{24}^{78.9183}\text{BrNO}_5$ ($[\text{M}] + \text{H}^+$) = 474.0911, Found 474.0915.

HRMS (ESI-TOF) Calculated for $\text{C}_{23}\text{H}_{24}^{80.9163}\text{BrNO}_5$ ($[\text{M}] + \text{H}^+$) = 476.0890, Found 476.0890.

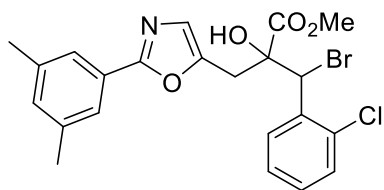
IR (film): 3514, 2958, 2924, 1757, 1492, 1263, 1136, 754 cm^{-1} .



	Retention time	Area	Area%
1	9.245	252438	49.42
2	11.310	258323	50.58



	Retention time	Area	Area%
1	9.226	1007	0.16
2	11.299	620183	99.84



Methyl 3-bromo-3-(2-chlorophenyl)-2-((2-(3,5-dimethylphenyl)oxazol-5-yl)methyl)-2-hydroxypropanoate (3hg):

Yellow oil in 78% yield, dr = 90:10, $[\alpha]_D^{27} = +58.3$ ($c = 0.78$, in CH_2Cl_2).

HPLC: Daicel chiralpakLux 5u Cellulose-2, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, $\lambda = 254$ nm, t_r (minor) = 7.46 min, t_r (major) = 8.87 min, ee (major diastereoisomer) = 99%.

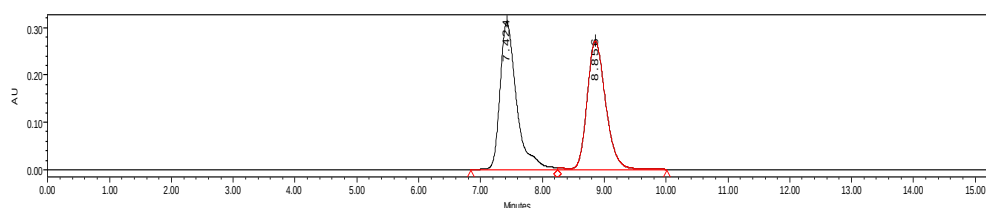
^1H NMR (400 MHz, CDCl_3) δ 8.10 (dd, $J = 7.6, 1.6$ Hz, 1H), 7.56 (s, 2H), 7.40 – 7.26 (m, 3H), 7.05 (s, 1H), 6.85 (s, 1H), 6.05 (s, 1H), 4.05 (s, 1H), 3.93 (s, 3H), 3.30 (d, $J = 15.2$ Hz, 1H), 2.68 (d, $J = 14.8$ Hz, 1H), 2.34 (s, 6H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 173.0, 161.8, 146.1, 138.4, 134.4, 133.1, 132.0, 130.3, 129.2, 127.6, 127.1, 126.7, 123.9, 80.1, 53.9, 51.5, 32.8, 21.2.

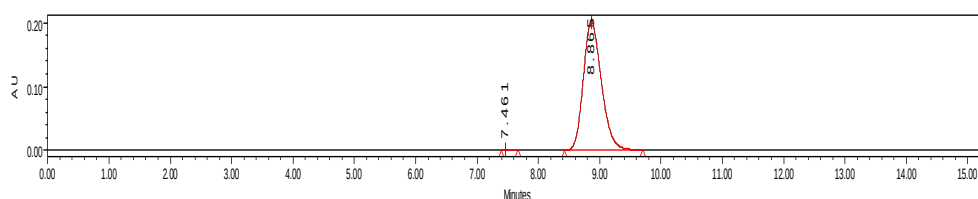
HRMS (ESI-TOF) Calculated for $\text{C}_{22}\text{H}_{21}^{78.9183}\text{BrClINO}_4$ ($[\text{M}] + \text{H}^+$) = 478.0415, Found 478.0424.

HRMS (ESI-TOF) Calculated for $\text{C}_{22}\text{H}_{21}^{80.9163}\text{BrClINO}_4$ ($[\text{M}] + \text{H}^+$) = 480.0395, Found 480.0400.

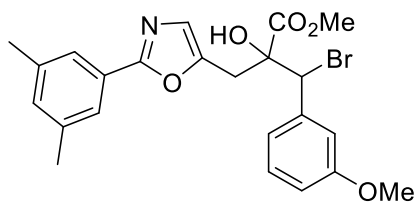
IR (film): 3506, 2958, 2924, 1757, 1548, 1471, 1259, 1124, 742 cm^{-1} .



	Retention time	Area	Area%
1	7.424	5777128	50.62
2	8.856	5635286	49.38



	Retention time	Area	Area%
1	7.461	953	0.02
2	8.865	4122036	99.98



Methyl 3-bromo-2-((2-(3,5-dimethylphenyl)oxazol-5-yl)methyl)-2-hydroxy-3-(3-methoxyphenyl)propanoate (3ig):

White solid in 89% yield, dr > 95:5, m.p. = 160 – 163 °C, $[\alpha]_D^{27} = +106.8$ ($c = 0.80$, in CH_2Cl_2).

HPLC: Chiralcel IC, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, $\lambda = 254$ nm, t_r (major) = 22.27 min, t_r (minor) = 33.97 min, ee (major diastereoisomer) = 99%.

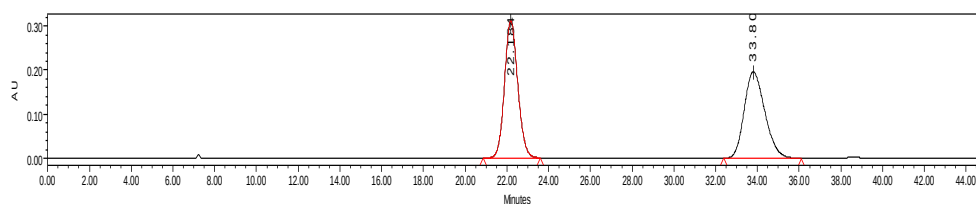
^1H NMR (400 MHz, CDCl_3) δ 7.56 (s, 2H), 7.27 – 7.31 (m, 1H), 7.24 – 7.16 (m, 2H), 7.05 (s, 1H), 6.91 (dd, $J = 4.4, 2.4$ Hz, 1H), 6.85 (s, 1H), 5.29 (s, 1H), 3.93 (s, 1H), 3.89 (s, 3H), 3.84 (s, 3H), 3.12 (d, $J = 15.2$ Hz, 1H), 2.73 (d, $J = 14.8$ Hz, 1H), 2.35 (s, 6H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 173.1, 161.7, 159.5, 146.3, 138.4, 137.8, 132.0, 129.5, 127.1, 126.6, 123.9, 122.0, 115.6, 114.8, 79.8, 57.6, 55.3, 53.7, 33.7, 21.3, 21.2.

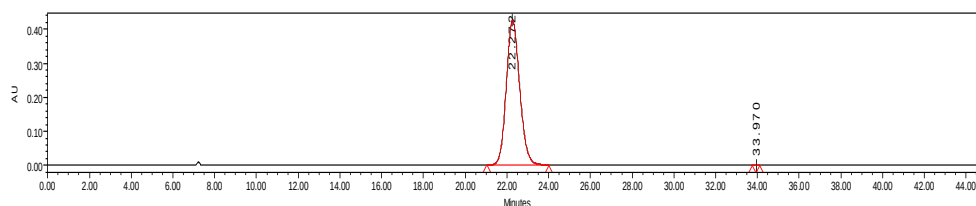
HRMS (ESI-TOF) Calculated for $\text{C}_{23}\text{H}_{24}^{78.9183}\text{BrNO}_5$ ($[\text{M}] + \text{H}^+$) = 474.0911, Found 474.0914.

HRMS (ESI-TOF) Calculated for $\text{C}_{23}\text{H}_{24}^{80.9163}\text{BrNO}_5$ ($[\text{M}] + \text{H}^+$) = 476.0890, Found 476.0894.

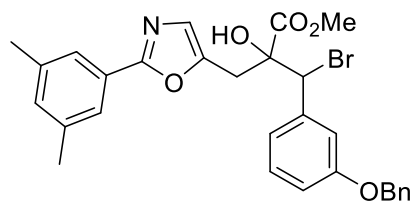
IR (film): 3496, 2958, 2916, 1753, 1444, 1253, 1128, 736 cm^{-1} .



	Retention time	Area	Area%
1	22.184	13736347	50.42
2	33.803	13506872	49.58



	Retention time	Area	Area%
1	22.272	18993987	100.00
2	33.970	455	0.00



Methyl 3-(3-(benzyloxy)phenyl)-3-bromo-2-((2-(3,5-dimethylphenyl)oxazol-5-yl)methyl)-2-hydroxypropanoate (3jg)

Colorless oil in 93% yield, dr = 94:6, $[\alpha]_D^{29} = +96.4$ ($c = 0.92$, in CH_2Cl_2).

HPLC: Daicel chiralpakLux 5u Cellulose-2, hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, $\lambda = 254$ nm, t_r (minor) = 19.10 min, t_r (major) = 23.06 min, ee (major diastereoisomer) = 99%.

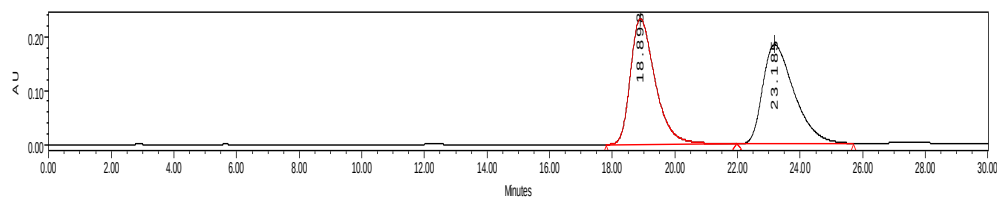
^1H NMR (400 MHz, CDCl_3) δ 7.56 (s, 2H), 7.45 (d, $J = 7.2$ Hz, 2H), 7.41 – 7.35 (m, 2H), 7.35 – 7.26 (m, 3H), 7.18 (d, $J = 7.6$ Hz, 1H), 7.05 (s, 1H), 6.98 (dd, $J = 8.4, 2.4$ Hz, 1H), 6.84 (s, 1H), 5.29 (s, 1H), 5.09 (s, 2H), 3.95 – 3.88 (m, 1H), 3.88 (s, 3H), 3.08 (d, $J = 14.8$ Hz, 1H), 2.69 (d, $J = 14.8$ Hz, 1H), 2.34 (s, 6H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 173.1, 161.7, 158.7, 146.3, 138.4, 137.8, 136.7, 132.0, 129.5, 128.6, 128.1, 127.7, 127.1, 126.6, 123.9, 122.3, 116.4, 115.9, 79.8, 70.1, 57.6, 53.7, 33.7, 21.3.

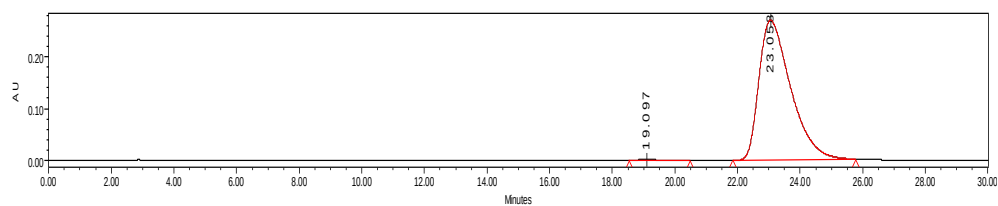
HRMS (ESI-TOF) Calculated for $\text{C}_{29}\text{H}_{28}^{78.9183}\text{BrNO}_5$ ($[\text{M}] + \text{H}^+$) = 550.1224, Found 550.1225.

HRMS (ESI-TOF) Calculated for $\text{C}_{29}\text{H}_{28}^{80.9163}\text{BrNO}_5$ ($[\text{M}] + \text{H}^+$) = 552.1203, Found 552.1207.

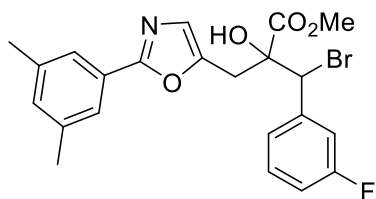
IR (film): 3506, 2958, 2924, 1753, 1485, 1253, 1128, 1037, 736 cm^{-1} .



	Retention Time	Area	% Area
1	18.898	12813396	49.98
2	23.185	12824816	50.02



	Retention Time	Area	% Area
1	19.097	78657	0.41
2	23.058	18990298	99.59



Methyl 3-bromo-2-((2-(3, 5-dimethylphenyl)oxazol-5-yl)methyl)-3-(3-fluorophenyl)-2-hydroxypropanoate (3kg):

Colorless oil in 83% yield, dr = 94:6, $[\alpha]_D^{27} = +88.2$ ($c = 0.79$, in CH_2Cl_2).

HPLC: Daicel chiralpakLux 5u Cellulose-2, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, $\lambda = 254$ nm, t_r (minor) = 9.36 min, t_r (major) = 12.28 min, ee (major diastereoisomer) = 99%.

^1H NMR (400 MHz, CDCl_3) δ 7.56 (s, 2H), 7.48 – 7.40 (m, 1H), 7.35 (m, 2H), 7.11 – 7.03 (m, 2H), 6.85 (s, 1H), 5.29 (s, 1H), 4.00 (s, 1H), 3.90 (d, $J = 1.2$ Hz, 3H), 3.11 (d, $J = 14.8$ Hz, 1H), 2.70 (d, $J = 14.8$ Hz, 1H), 2.35 (s, 6H).

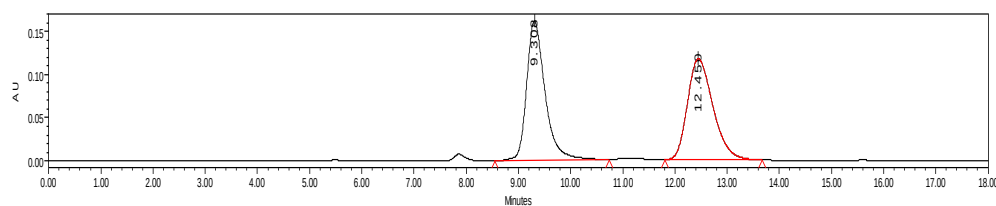
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 172.9, 162.5 (d, $J = 246.0$ Hz), 161.8, 146.1, 138.8 (d, $J = 8.0$ Hz), 138.4, 132.1, 130.0 (d, $J = 8.0$ Hz), 127.1, 126.7, 125.4 (d, $J = 3.0$ Hz), 123.9, 117.1 (d, $J = 23.0$ Hz), 116.4 (d, $J = 21.0$ Hz), 79.7, 56.4, 53.8 (d, $J = 2.0$ Hz), 33.7, 21.2.

$^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CDCl_3) δ -111.7 (s, 1F).

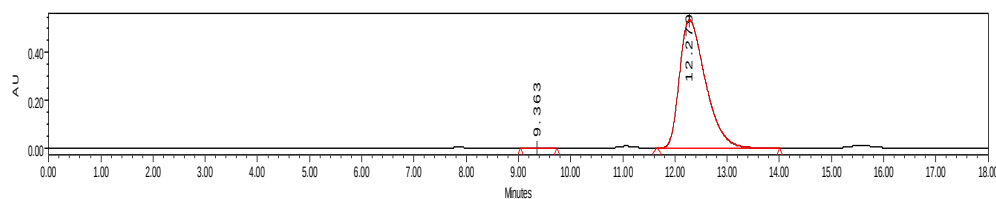
HRMS (ESI-TOF) Calculated for $\text{C}_{22}\text{H}_{21}^{78.9183}\text{BrFNO}_4$ ($[\text{M}] + \text{H}^+$) = 462.0711, Found 462.0719.

HRMS (ESI-TOF) Calculated for $\text{C}_{22}\text{H}_{21}^{80.9163}\text{BrFNO}_4$ ($[\text{M}] + \text{H}^+$) = 464.0690, Found 464.0700.

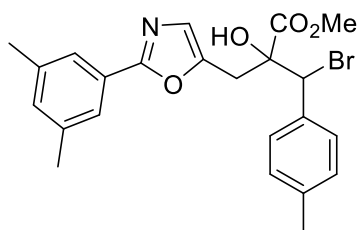
IR (film): 3500, 2964, 2920, 1749, 1489, 1236, 1124, 773 cm^{-1} .



	Retention Time	Area	% Area
1	9.308	3973624	50.00
2	12.450	3973191	50.00



	Retention Time	Area	% Area
1	9.363	27336	0.15
2	12.279	18632946	99.85



Methyl 3-bromo-2-((2-(3,5-dimethylphenyl)oxazol-5-yl)methyl)-2-hydroxy-3-(p-tolyl)propanoate (3lg):

White solid in 96% yield, dr = 94:6, m.p. = 135 – 138 °C, $[\alpha]_D^{27} = +109.7$ ($c = 0.71$, in CH_2Cl_2).

HPLC: Chiralcel ODH, hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, $\lambda = 254$ nm, t_r (major) = 10.93 min, t_r (minor) = 19.62 min, ee (major diastereoisomer) = 99%.

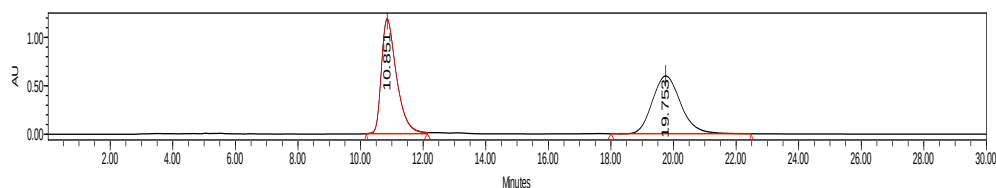
^1H NMR (400 MHz, CDCl_3) δ 7.58 – 7.48 (m, 4H), 7.18 (d, $J = 7.6$ Hz, 2H), 7.05 (s, 1H), 6.84 (d, $J = 1.2$ Hz, 1H), 5.32 (s, 1H), 3.94 (s, 1H), 3.89 (d, $J = 0.8$ Hz, 3H), 3.10 (d, $J = 14.8$ Hz, 1H), 2.70 (d, $J = 15.2$ Hz, 1H), 2.36 (s, 3H), 2.34 (s, 6H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 173.2, 161.7, 146.4, 139.3, 138.4, 133.5, 132.0, 129.6, 129.3, 127.2, 126.6, 123.9, 80.0, 58.0, 57.9, 53.7, 33.7, 21.3.

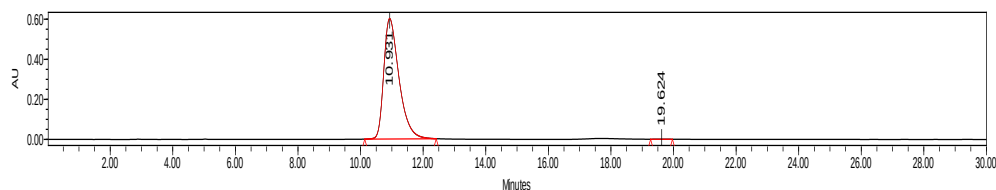
HRMS (ESI-TOF) Calculated for $\text{C}_{23}\text{H}_{24}^{78,9183}\text{BrNO}_4$ ($[\text{M}] + \text{H}^+$) = 458.0961, Found 458.0963.

HRMS (ESI-TOF) Calculated for $\text{C}_{23}\text{H}_{24}^{80,9163}\text{BrNO}_4$ ($[\text{M}] + \text{H}^+$) = 460.0941, Found 460.0941.

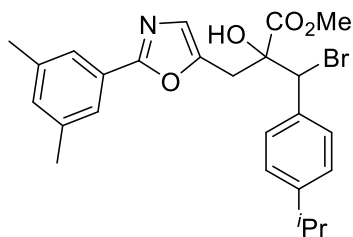
IR (film): 3506, 2962, 2920, 1745, 1436, 1263, 1128, 738 cm^{-1} .



	Retention Time	Area	% Area
1	10.851	39790835	51.43
2	19.753	37581439	48.57



	Retention Time	Area	% Area
1	10.931	20287461	99.97
2	19.624	5964	0.03



Methyl 3-bromo-2-((2-(3,5-dimethylphenyl)oxazol-5-yl)methyl)-2-hydroxy-3-(4-isopropylphenyl)propanoate (3mg):

White solid in 95% yield, dr = 93:7, m.p. = 133 – 136 °C, $[\alpha]_D^{27} = +101.8$ ($c = 0.87$, in CH_2Cl_2).

HPLC: Daicel chiralpakLux 5u Cellulose-2, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, $\lambda = 254$ nm, t_r (minor) = 6.35 min, t_r (major) = 7.20 min, ee (major diastereoisomer) = 99%.

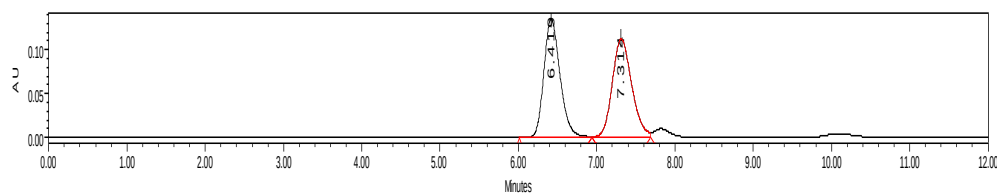
^1H NMR (400 MHz, CDCl_3) δ 7.56 – 7.53 (m, 4H), 7.25 (s, 1H), 7.23 (s, 1H), 7.05 (s, 1H), 6.85 (s, 1H), 5.33 (s, 1H), 3.94 (s, 1H), 3.89 (d, $J = 0.8$ Hz, 3H), 3.10 (d, $J = 15.2$ Hz, 1H), 2.98 – 2.86 (m, 1H), 2.70 (d, $J = 15.2$ Hz, 1H), 2.34 (s, 6H), 1.26 (dd, $J = 6.8, 1.2$ Hz, 6H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 173.2, 161.7, 150.1, 146.4, 138.4, 133.7, 132.0, 129.7, 127.2, 126.7, 126.6, 123.9, 80.0, 58.0, 53.6, 33.9, 33.8, 23.9, 23.8, 21.3.

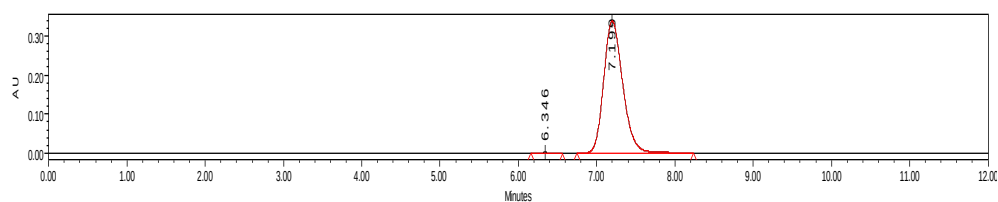
HRMS (ESI-TOF) Calculated for $\text{C}_{25}\text{H}_{28}^{78,9183}\text{BrNO}_4$ ($[\text{M}] + \text{H}^+$) = 486.1274, Found 486.1280.

HRMS (ESI-TOF) Calculated for $\text{C}_{25}\text{H}_{28}^{80,9163}\text{BrNO}_4$ ($[\text{M}] + \text{H}^+$) = 488.1254, Found 488.1263.

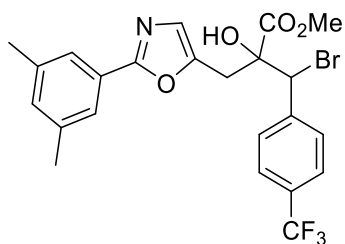
IR (film): 3506, 2964, 2929, 1753, 1450, 1263, 1132, 742 cm^{-1} .



	Retention time	Area	Area%
1	6.419	1946332	50.06
2	7.314	1941660	49.94



	Retention time	Area	Area%
1	6.346	20430	0.36
2	7.199	5726309	99.64



Methyl 3-bromo-2-((2-(3,5-dimethylphenyl)oxazol-5-yl)methyl)-2-hydroxy-3-(4-(trifluoromethyl)phenyl)propanoate (3ng):

White solid in 69% yield, dr = 82:18, m.p. = 170 – 174 °C, $[\alpha]_D^{27} = +115.7$ ($c = 0.78$, in CH_2Cl_2).

HPLC: Daicel chiralpakLux 5u Cellulose-2, hexane/*i*-PrOH = 85/15, flow rate 1.0 mL/min, $\lambda = 254$ nm, $t_{r1} = 7.75$ min (minor enantiomer of major diastereoisomer), $t_{r2} = 8.49$ min (major enantiomer of major diastereoisomer), $t_{r3} = 10.68$ min (minor enantiomer of minor diastereoisomer), $t_{r4} = 17.63$ min (major enantiomer of minor diastereoisomer), ee (major diastereoisomer) = 99%.

^1H NMR (400 MHz, CDCl_3) δ 7.77 (d, $J = 8.0$ Hz, 2H, major), 7.65 (d, $J = 8.0$ Hz, 2H, major), 7.61 – 7.51 (m, 2H), 7.06 (s, 1H), 6.99 (s, 1H, minor), 6.84 (s, 1H, major), 5.34 (s, 1H, major), 5.30 (s, 1H, minor), 4.08 (s, 1H, major), 3.91 (d, $J = 0.8$ Hz, 3H, major), 3.74 (s, 1H, minor), 3.65 (d, $J = 0.8$ Hz, 1H, minor), 3.37 (d, $J = 15.2$ Hz, 1H, minor), 3.12 (d, $J = 15.2$ Hz, 1H), 2.65 (d, $J = 15.2$ Hz, 1H), 2.34 (s, 6H).

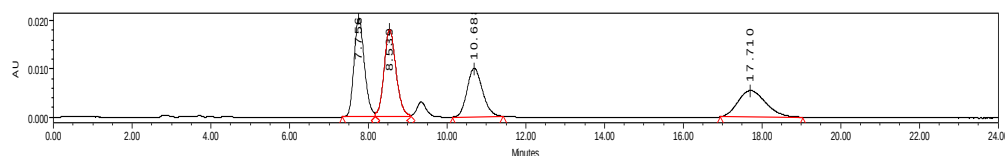
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 172.8, 161.9, 145.9, 138.4, 132.1, 130.3, 129.5, 127.0, 126.8, 126.6 (q, $J = 103.7$ Hz), 123.9, 79.6, 56.0, 53.9, 33.8, 21.2.

$^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CDCl_3) δ -62.8 (s, 3F).

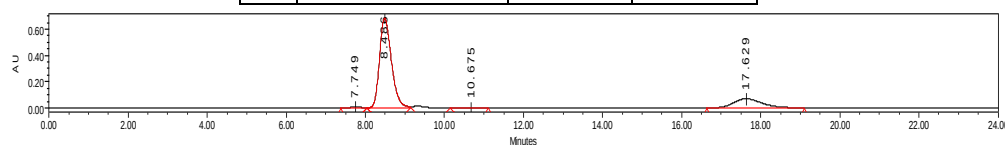
HRMS (ESI-TOF) Calculated for $\text{C}_{23}\text{H}_{21}^{78,9183}\text{BrF}_3\text{NO}_4$ ($[\text{M}+\text{H}^+]$) = 512.0679, Found 512.0685.

HRMS (ESI-TOF) Calculated for $\text{C}_{23}\text{H}_{21}^{80,9163}\text{BrF}_3\text{NO}_4$ ($[\text{M}+\text{H}^+]$) = 514.0658, Found 514.0667.

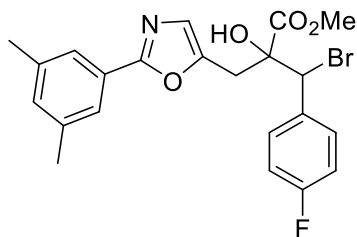
IR (film): 3475, 2962, 2927, 1749, 1554, 1419, 1328, 1124, 860 cm^{-1} .



	Retention Time	Area	% Area
1	7.756	375080	28.83
2	8.539	383102	29.44
3	10.688	274161	21.07
4	17.710	268834	20.66



	Retention Time	Area	% Area
1	7.749	111490	0.62
2	8.486	14287807	79.95
3	10.675	44947	0.25
4	17.629	3427011	19.18



Methyl 3-bromo-2-((2-(3,5-dimethylphenyl)oxazol-5-yl)methyl)-3-(4-fluorophenyl)-2-hydroxypropanoate (3og):

White solid in 84% yield, dr = 89:11, m.p. = 108 – 112 °C, $[\alpha]_D^{27} = +96.6$ ($c = 0.71$, in CH_2Cl_2).

HPLC: Daicel chiralpakLux 5u Cellulose-2, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, $\lambda = 254$ nm, $t_{r1} = 8.75$ min (major enantiomer of major diastereoisomer), $t_{r2} = 9.50$ min (minor enantiomer of major diastereoisomer), $t_{r3} = 11.16$ min (minor enantiomer of minor diastereoisomer), $t_{r4} = 17.33$ min (major enantiomer of minor diastereoisomer), ee (major diastereoisomer) = 99%.

^1H NMR (400 MHz, CDCl_3) δ 7.65 – 7.61 (m, 2H), 7.58 – 7.56 (m, 2H), 7.10 – 7.05 (m, 3H), 6.84 (s, 1H), 5.32 (s, 1H), 3.99 (s, 1H), 3.90 (s, 3H), 3.10 (d, $J = 15.2$, 1H), 2.67 (d, $J = 14.8$ Hz, 1H), 2.35 (s, 6H).

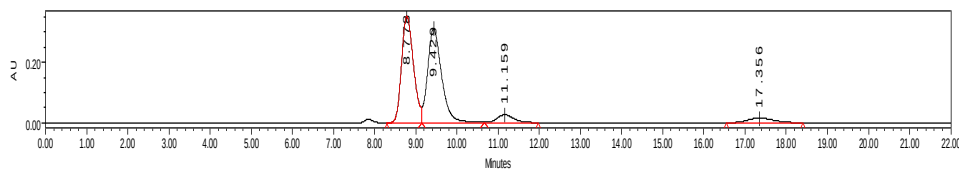
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 173.0, 164.3, 161.8, 146.1, 138.4, 132.5 (d, $J = 3.0$ Hz), 132.0, 131.7, 131.6, 127.1, 126.7, 123.9, 115.6 (d, $J = 22.0$ Hz), 79.9, 56.7, 53.8 (d, $J = 2.0$ Hz), 33.8, 21.3.

$^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CDCl_3) δ -111.7 (s, 1F).

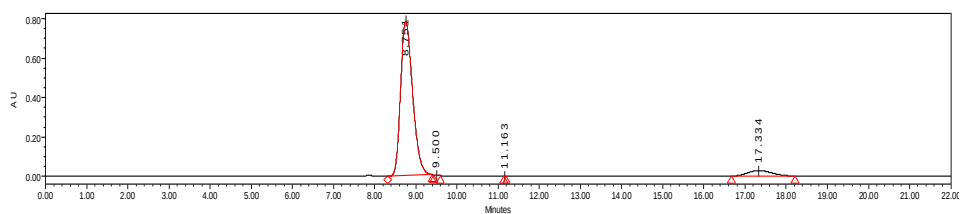
HRMS (ESI-TOF) Calculated for $\text{C}_{22}\text{H}_{21}^{78.9183}\text{BrFNO}_4$ ($[\text{M}]+\text{H}^+$) = 462.0711, Found 462.0713.

HRMS (ESI-TOF) Calculated for $\text{C}_{22}\text{H}_{21}^{80.9163}\text{BrFNO}_4$ ($[\text{M}]+\text{H}^+$) = 464.0690, Found 464.0695.

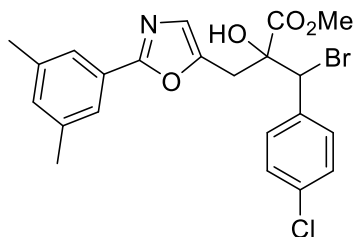
IR (film): 3500, 2958, 2920, 1757, 1448, 1232, 1166, 736 cm^{-1} .



	Retention Time	Area	% Area
1	8.778	7057844	44.55
2	9.429	7359602	46.46
3	11.159	731462	4.62
4	17.356	693395	4.38



	Retention Time	Area	% Area
1	8.751	15761852	92.88
2	9.500	1515	0.01
3	11.163	12	0.00
4	17.334	1206814	7.11



Methyl 3-bromo-3-(4-chlorophenyl)-2-((2-(3,5-dimethylphenyl)oxazol-5-yl)methyl)-2-hydroxypropanoate (3pg):

White solid in 69% yield, dr = 89:11, m.p. = 130 – 134 °C, $[\alpha]_D^{27} = +110.6$ ($c = 0.71$, in CH_2Cl_2).

HPLC: Chiralcel IC, hexane/*i*-PrOH = 70/30, flow rate 1.0 mL/min, $\lambda = 254$ nm, $t_{r1} = 5.95$ min (minor enantiomer of minor diastereoisomer), $t_{r2} = 10.29$ min (major enantiomer of major diastereoisomer), $t_{r3} = 16.16$ min (minor enantiomer of major diastereoisomer), $t_{r4} = 28.23$ min (major enantiomer of minor diastereoisomer), ee (major diastereoisomer) = 99%.

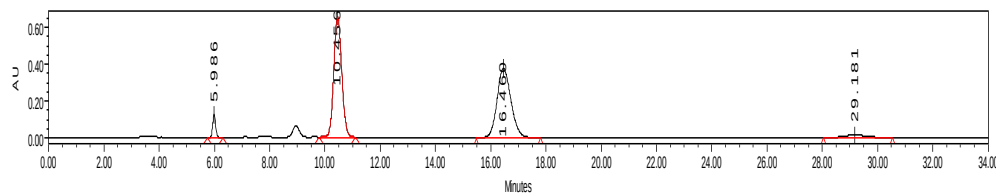
^1H NMR (400 MHz, CDCl_3) δ 7.59 – 7.55 (m, 4H), 7.38 – 7.35 (m, 2H), 7.06 (s, 1H), 6.84 (s, 1H), 5.29 (s, 1H), 3.92 (s, 1H), 3.90 (s, 3H), 3.10 (d, $J = 15.2$ Hz, 1H), 2.68 (d, $J = 15.2$ Hz, 1H), 2.35 (s, 6H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 172.9, 161.8, 146.0, 138.4, 135.2, 135.1, 132.0, 131.1, 128.8, 127.1, 126.7, 123.9, 79.7, 56.5, 53.8, 33.7, 21.3.

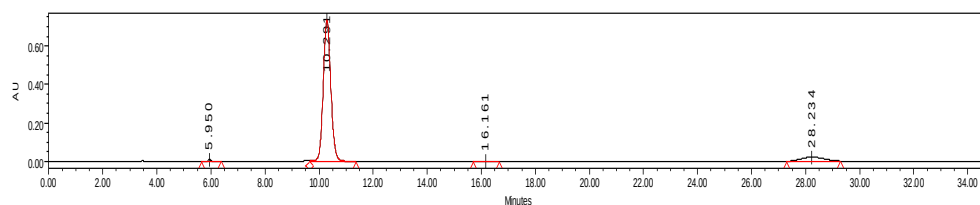
HRMS (ESI-TOF) Calculated for $\text{C}_{22}\text{H}_{21}^{78.9183}\text{BrClINO}_4$ ($[\text{M}] + \text{H}^+$) = 478.0415, Found 478.0416.

HRMS (ESI-TOF) Calculated for $\text{C}_{22}\text{H}_{21}^{80.9163}\text{BrClINO}_4$ ($[\text{M}] + \text{H}^+$) = 480.0395, Found 480.0392.

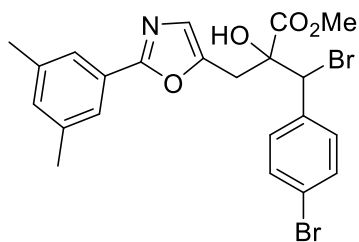
IR (film): 3506, 2958, 2927, 1757, 1489, 1233, 1128, 738 cm^{-1} .



	Retention time	Area	Area%
1	5.986	972573	3.42
2	10.456	13331147	46.83
3	16.460	13208467	46.40
4	29.181	956325	3.36



	Retention time	Area	Area%
1	5.950	88154	0.56
2	10.291	14346439	91.09
3	16.161	54521	0.35
4	28.234	1260616	8.00



Methyl 3-bromo-3-(4-bromophenyl)-2-((2-(3,5-dimethylphenyl)oxazol-5-yl)methyl)-2-hydroxypropanoate (3qg):

White solid in 81% yield, dr = 88:12, m.p. = 126 – 128 °C, $[\alpha]_D^{27} = +94.0$ ($c = 0.75$, in CH_2Cl_2).

HPLC: Chiralcel IC, hexane/*i*-PrOH = 70/30, flow rate 1.0 mL/min, $\lambda = 254$ nm, $t_{r1} = 10.24$ min (minor enantiomer of minor diastereoisomer), $t_{r2} = 11.31$ min (major enantiomer of major diastereoisomer), $t_{r3} = 17.43$ min (minor enantiomer of major diastereoisomer), $t_{r4} = 34.61$ min (major enantiomer of minor diastereoisomer), ee (major diastereoisomer) = 99%.

^1H NMR (400 MHz, CDCl_3) δ 7.55 (s, 2H), 7.52 (s, 4H), 7.06 (s, 1H), 6.84 (s, 1H), 5.27 (s, 1H), 3.99 (s, 1H), 3.90 (d, $J = 0.8$ Hz, 3H), 3.09 (d, $J = 15.2$ Hz, 1H), 2.67 (d, $J = 15.2$ Hz, 1H), 2.35 (s, 6H).

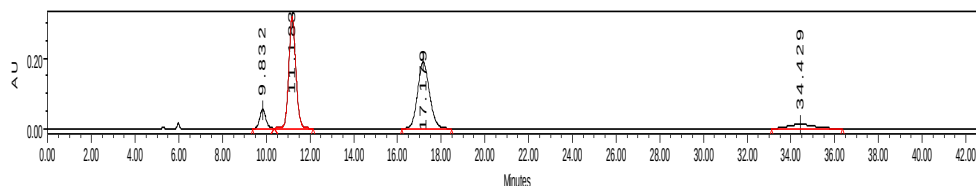
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 172.9, 161.8, 146.0, 138.4, 135.6, 132.0, 131.8, 131.4, 127.1, 126.7, 123.9, 123.5, 79.7, 56.5, 53.8, 33.7, 21.3.

HRMS (ESI-TOF) Calculated for $\text{C}_{22}\text{H}_{21}^{78,9183}\text{Br}_2\text{NO}_4$ ($[\text{M}] + \text{H}^+$) = 521.9910, Found 521.9912.

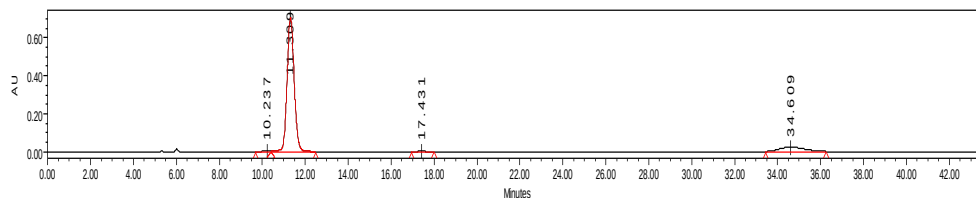
HRMS (ESI-TOF) Calculated for $\text{C}_{22}\text{H}_{21}^{78,9183}\text{Br}^{80,9163}\text{BrNO}_4$ ($[\text{M}] + \text{H}^+$) = 523.9890, Found 523.9891.

HRMS (ESI-TOF) Calculated for $\text{C}_{22}\text{H}_{21}^{80,9163}\text{Br}_2\text{NO}_4$ ($[\text{M}] + \text{H}^+$) = 525.9869, Found 525.9871.

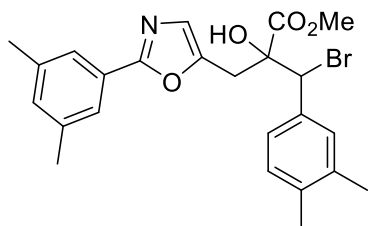
IR (film): 3504, 2958, 2916, 1753, 1548, 1440, 1263, 1124, 746 cm^{-1} .



	Retention Time	Area	% Area
1	9.832	1074004	6.58
2	11.183	7165405	43.92
3	17.179	7118342	43.63
4	34.429	958017	5.87



	Retention Time	Area	% Area
1	10.237	87824	0.48
2	11.309	16316781	89.09
3	17.431	60655	0.33
4	34.609	1848773	10.09



Methyl 3-bromo-3-(3,4-dimethylphenyl)-2-((2-(3,5-dimethylphenyl)oxazol-5-yl)methyl)-2-hydroxypropanoate (3rg)

Colorless oil in 96% yield, dr > 95:5, $[\alpha]_D^{27} = +107.1$ ($c = 0.94$, in CH_2Cl_2).

HPLC: Daicel chiralpakLux 5u Cellulose-2, hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, $\lambda = 254$ nm, t_r (minor) = 12.67 min, t_r (major) = 14.53 min, ee (major diastereoisomer) = 99%.

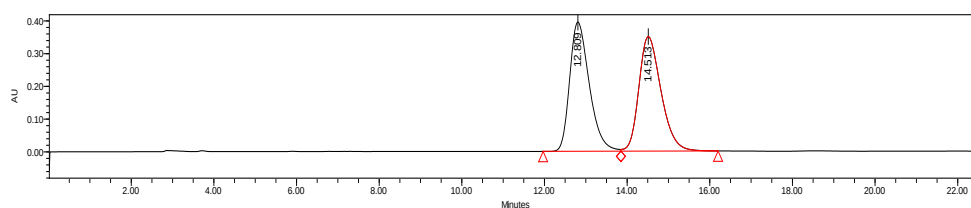
^1H NMR (400 MHz, CDCl_3) δ 7.56 (s, 2H), 7.44 – 7.33 (m, 2H), 7.13 (d, $J = 7.6$ Hz, 1H), 7.05 (s, 1H), 6.85 (s, 1H), 5.30 (s, 1H), 3.92 (s, 1H), 3.88 (s, 3H), 3.10 (d, $J = 15.2$ Hz, 1H), 2.72 (d, $J = 15.2$ Hz, 1H), 2.34 (s, 6H), 2.28 (s, 3H), 2.26 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 173.3, 161.7, 146.5, 138.4, 138.0, 136.8, 133.9, 132.0, 130.8, 129.8, 127.2, 126.6, 123.9, 79.9, 58.2, 53.7, 33.7, 21.3, 19.9, 19.6.

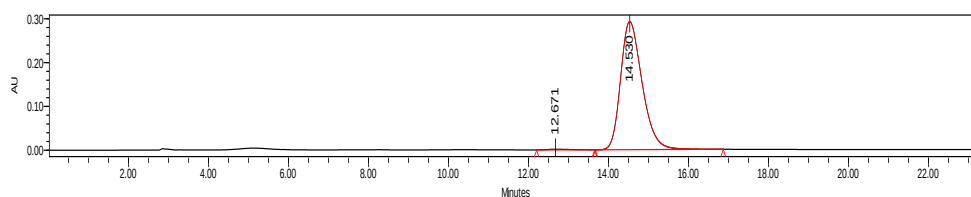
HRMS (ESI-TOF) Calculated for $\text{C}_{24}\text{H}_{26}^{78,9183}\text{BrNO}_4$ ($[\text{M}] + \text{H}^+$) = 472.1118, Found 472.1125.

HRMS (ESI-TOF) Calculated for $\text{C}_{24}\text{H}_{26}^{80,9163}\text{BrNO}_4$ ($[\text{M}] + \text{H}^+$) = 474.1098, Found 474.1090.

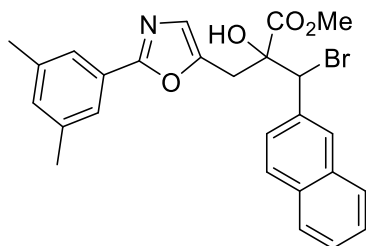
IR (film): 3506, 2916, 1757, 1440, 1236, 1120, 738 cm^{-1} .



	Retention Time	Area	% Area
1	12.809	12995448	49.95
2	14.513	13021048	50.05



	Retention Time	Area	% Area
1	12.671	50825	0.46
2	14.530	10903382	99.54



Methyl 3-bromo-2-((2-(3,5-dimethylphenyl)oxazol-5-yl)methyl)-2-hydroxy-3-(naphthalen-2-yl)propanoate (3sg)

Yellow oil in 91% yield, $dr > 95:5$, $[\alpha]_D^{27} = +109.0$ ($c = 0.89$, in CH_2Cl_2).

HPLC: Daicel chiralpakLux 5u Cellulose-2, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, $\lambda = 254$ nm, t_r (major) = 10.65 min, t_r (minor) = 13.09 min, ee (major diastereoisomer) = 99%.

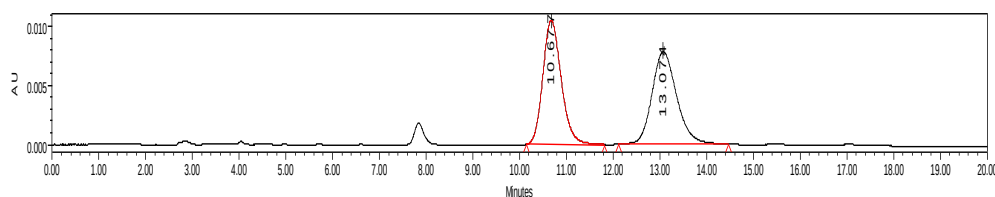
1H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.89 – 7.81 (m, 4H), 7.57 – 7.48 (m, 4H), 7.04 (s, 1H), 6.82 (s, 1H), 5.52 (s, 1H), 4.05 (s, 1H), 3.92 (s, 3H), 3.17 (d, $J = 15.2$ Hz, 1H), 2.70 (d, $J = 14.8$ Hz, 1H), 2.33 (s, 6H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 173.2, 161.7, 146.3, 138.4, 133.9, 133.6, 132.7, 132.0, 128.9, 128.7, 128.2, 127.8, 127.1, 127.0, 126.6, 126.6, 123.9, 80.0, 58.2, 53.8, 33.9, 21.3.

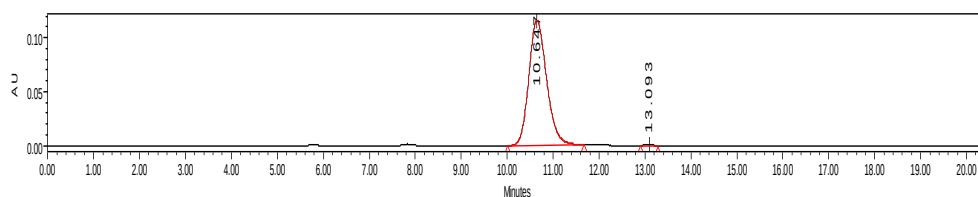
HRMS (ESI-TOF) Calculated for $C_{26}H_{24}^{78.9183}BrNO_4$ ($[M]+H^+$) = 494.0961, Found 494.0966.

HRMS (ESI-TOF) Calculated for $C_{26}H_{24}^{80.9163}BrNO_4$ ($[M]+H^+$) = 496.0941, Found 496.0949.

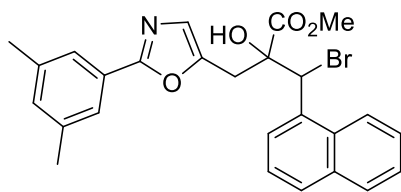
IR (film): 3506, 3066, 2927, 1753, 1448, 1259, 1128, 746 cm^{-1} .



	Retention time	Area	Area%
1	10.677	287731	49.97
2	13.074	288080	50.03



	Retention time	Area	Area%
1	10.647	3127854	99.97
2	13.093	819	0.03



Methyl 3-bromo-2-((2-(3,5-dimethylphenyl)oxazol-5-yl)methyl)-2-hydroxy-3-(naphthalen-1-yl)propanoate (3tg)

Yellow oil in 92% yield, dr = 86:14, $[\alpha]_D^{27} = -22.0$ ($c = 0.67$, in CH_2Cl_2).

HPLC: Chiralcel IB, hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, $\lambda = 254$ nm, $t_{r1} = 10.15$ min (major enantiomer of minor diastereoisomer), $t_{r2} = 10.83$ min (major enantiomer of major diastereoisomer), $t_{r3} = 18.43$ min (minor enantiomer of minor diastereoisomer), $t_{r4} = 19.75$ min (minor enantiomer of major diastereoisomer), ee (major diastereoisomer) = 99%.

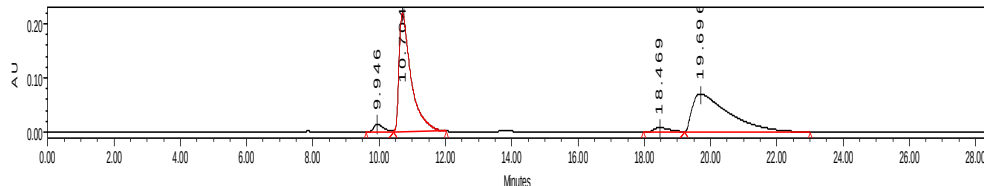
^1H NMR (400 MHz, CDCl_3) δ 8.39 (d, $J = 7.6$ Hz, 1H), 8.16 (d, $J = 8.8$ Hz, 1H), 7.90 (dd, $J = 14.0$, 8.0 Hz, 2H), 7.66 – 7.61 (m, 1H), 7.59 – 7.52 (m, 2H), 7.52 (s, 2H), 7.03 (s, 1H), 6.80 (s, 1H), 6.40 (s, 1H), 4.14 (s, 1H), 3.96 (d, $J = 1.2$ Hz, 3H), 3.17 (d, $J = 15.2$ Hz, 1H), 2.75 (d, $J = 15.2$ Hz, 1H), 2.33 (s, 6H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 173.4, 161.7, 146.2, 138.4, 133.6, 132.3, 132.0, 131.0, 129.8, 129.7, 129.4, 127.1, 127.1, 126.7, 125.9, 125.8, 123.9, 121.9, 80.7, 53.9, 51.2, 33.4, 21.2.

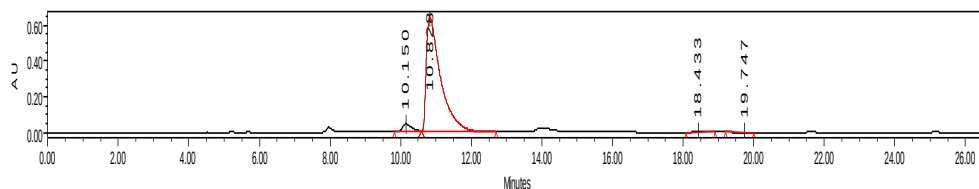
HRMS (ESI-TOF) Calculated for $\text{C}_{26}\text{H}_{24}^{78.9183}\text{BrNO}_4$ ($[\text{M}] + \text{H}^+$) = 494.0961, Found 494.0961.

HRMS (ESI-TOF) Calculated for $\text{C}_{26}\text{H}_{24}^{80.9163}\text{BrNO}_4$ ($[\text{M}] + \text{H}^+$) = 496.0941, Found 496.0944.

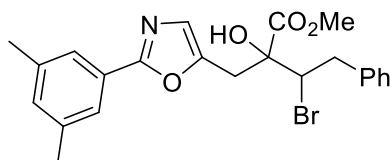
IR (film): 3504, 3062, 2958, 1745, 1552, 1444, 1271, 1124, 794 cm^{-1} .



	Retention time	Area	Area%
1	9.946	301226	2.59
2	10.704	5522723	47.47
3	18.469	307209	2.64
4	19.696	5503147	47.30



	Retention time	Area	Area%
1	10.150	910843	4.73
2	10.828	18339876	95.15
3	18.433	22469	0.12
4	19.747	1357	0.01



Methyl 3-bromo-2-((2-(3,5-dimethylphenyl)oxazol-5-yl)methyl)-2-hydroxy-4-phenylbutanoate (3ug)

Colorless oil in 70% yield, dr = 67:33, $[\alpha]_D^{29} = +96.4$ ($c = 0.92$, in CH_2Cl_2).

HPLC: Chiralcel IC, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, $\lambda = 254$ nm, $t_{r1} = 13.21$ min (minor enantiomer of major diastereoisomer), $t_{r2} = 17.96$ min (minor enantiomer of minor diastereoisomer), $t_{r3} = 21.07$ min (major enantiomer of minor diastereoisomer), $t_{r4} = 25.14$ min (major enantiomer of major diastereoisomer), ee (major diastereoisomer) = 99%.

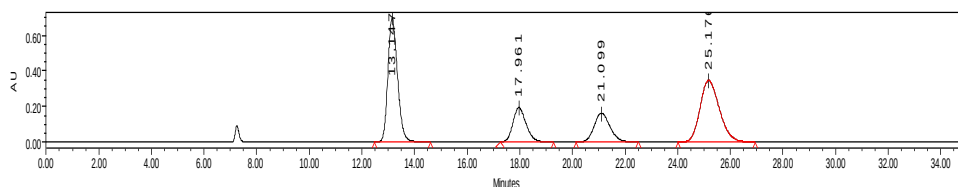
(Diastereoisomer mixture) **^1H NMR** (400 MHz, CDCl_3) δ 7.61 – 7.60 (m, 2H), 7.38 – 7.17 (m, 5H), 7.07 (s, 1H), 6.98 (s, 0.6H, major), 6.97 (s, 0.3H, minor), 4.56 – 4.51 (m, 1H), 3.82 (s, 1H, minor), 3.79 (s, 0.3H, major), 3.75 (s, 2H, minor), 3.69 (s, 0.6H, major), 3.60 – 3.51 (m, 1H), 3.35 – 3.33 (m, 1H), 3.29 – 3.19 (m, 1H), 3.16 – 3.10 (m, 1H), 2.36 (s, 6H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 172.9, 172.6, 162.0, 146.4, 146.3, 138.5, 137.9, 137.7, 132.1, 132.1, 129.3, 129.2, 128.6, 128.5, 127.1, 127.1, 126.9, 126.8, 125.5, 124.2, 124.0, 123.9, 79.7, 79.0, 60.8, 60.4, 53.5, 53.4, 40.7, 38.3, 36.4, 33.3, 21.3.

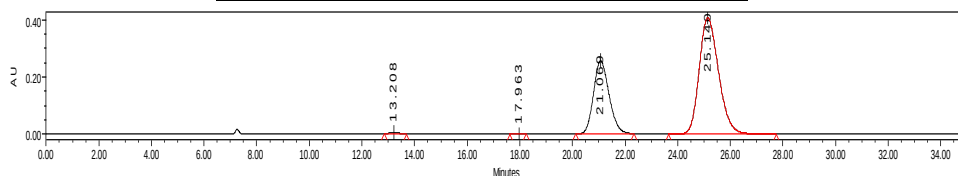
HRMS (ESI-TOF) Calculated for $\text{C}_{23}\text{H}_{24}^{78,9183}\text{BrNO}_4$ ($[\text{M}] + \text{H}^+$) = 458.0961, Found 458.0963.

HRMS (ESI-TOF) Calculated for $\text{C}_{23}\text{H}_{24}^{80,9163}\text{BrNO}_4$ ($[\text{M}] + \text{H}^+$) = 460.0941, Found 460.0944.

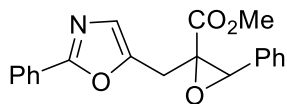
IR (film): 3518, 2958, 2920, 1745, 1450, 1267, 1118, 738 cm^{-1} .



	Retention Time	Area	% Area
1	13.147	17575715	36.01
2	17.961	6761560	13.85
3	21.099	6819413	13.97
4	25.176	17650431	36.16



	Retention Time	Area	% Area
1	13.208	150044	0.48
2	17.963	10746	0.03
3	21.069	10519336	33.47
4	25.140	20751936	66.02



Methyl 3-phenyl-2-((2-phenyloxazol-5-yl)methyl)oxirane-2-carboxylate (4)

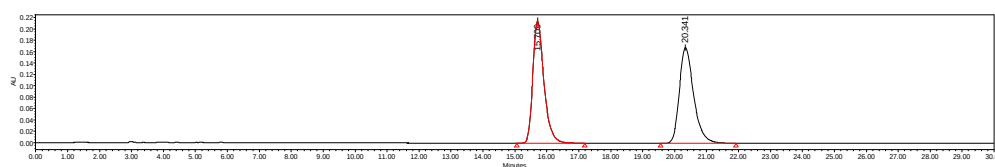
Colorless oil in 90% yield, dr > 95:5, $[\alpha]_D^{26} = +36.8$ ($c = 0.59$, in CH_2Cl_2).

HPLC: Chiralcel IA, hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, $\lambda = 254$ nm, t_r (major) = 15.70 min, t_r (minor) = 20.40 min, ee (major diastereoisomer) = 99%.

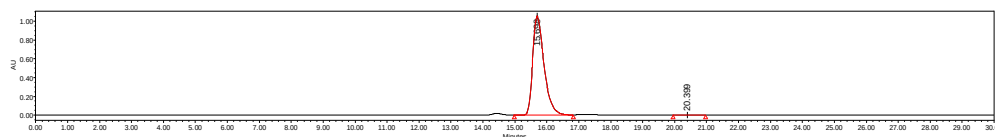
^1H NMR (400 MHz, CDCl_3) δ 8.04 – 8.01 (m, 2H), 7.46 – 7.45 (m, 3H), 7.38 – 7.31 (m, 5H), 7.08 (s, 1H), 4.16 (s, 1H), 3.79 (d, $J = 16.0$ Hz, 1H), 3.49 (s, 3H), 3.23 (d, $J = 16.0$ Hz, 1H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 167.6, 161.7, 146.5, 132.7, 130.3, 128.8, 128.6, 128.2, 127.4, 126.5, 126.3, 126.2, 64.2, 62.5, 52.2, 30.1.

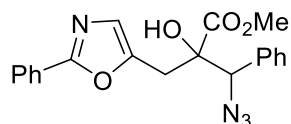
HRMS (ESI-TOF) Calculated for $\text{C}_{20}\text{H}_{17}\text{NO}_4$ ($[\text{M}] + \text{H}^+$) = 336.1230, Found 336.1227.



	Retention time	Area	Area%
1	15.709	5211898	49.97
2	20.341	5218686	50.03



	Retention time	Area	Area%
1	15.698	25989536	99.63
2	20.399	96931	0.37



Methyl 3-bromo-2-hydroxy-3-phenyl-2-((2-phenyloxazol-5-yl)methyl)propanoate (5)

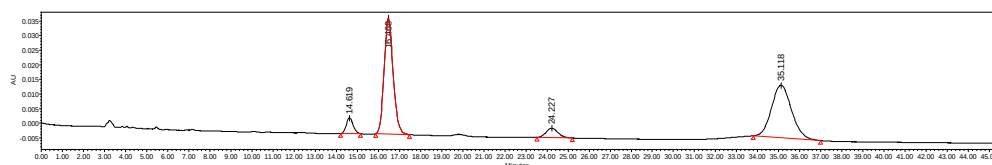
Colorless oil in 74% yield, dr > 95:5, $[\alpha]_D^{26} = +126.6$ ($c = 0.48$, in CH_2Cl_2).

HPLC: Chiralcel IC, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, $\lambda = 254$ nm, $t_{r1} = 14.54$ min, $t_{r2} = 16.31$ min, $t_{r3} = 24.00$ min, $t_{r4} = 34.71$ min, ee (major diastereoisomer) = 99%.

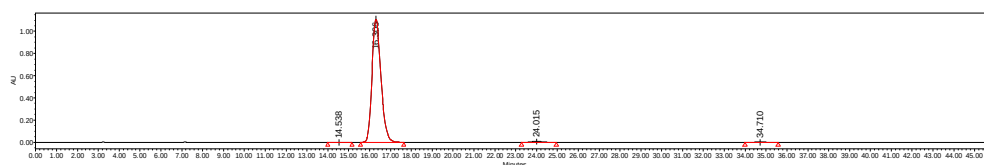
^1H NMR (400 MHz, CDCl_3) δ 7.94 – 7.92 (m, 2H), 7.55 – 7.53 (m, 2H), 7.46 – 7.41 (m, 6H), 6.86 (s, 1H), 4.83 (s, 1H), 3.90 (s, 3H), 3.67 (s, 1H), 3.12 (d, $J = 16.0$ Hz, 1H), 3.71 (d, $J = 16.0$ Hz, 1H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 173.6, 161.4, 146.5, 133.5, 130.2, 129.5, 128.8, 128.8, 127.4, 126.8, 126.1, 79.0, 70.1, 53.6, 33.1.

HRMS (ESI-TOF) Calculated for $\text{C}_{20}\text{H}_{18}\text{N}_4\text{O}_4$ ($[\text{M}] + \text{H}^+$) = 379.1401, Found 379.1402.



	Retention time	Area	Area%
1	14.619	122247	4.66
2	16.468	1181173	45.01
3	24.227	127141	4.85
4	35.118	1193475	45.48



	Retention time	Area	Area%
1	14.538	7545	0.02
2	16.306	33034164	98.43
3	24.015	368407	1.10
4	34.710	150702	0.45

8. Copies of NMR spectra for products

