Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Determination of Enantiomeric Excess and Diastereomeric Excess via Optical Methods. Application to α-alkyl- β-hydroxy-carboxylic acids.

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1. General Procedure

All materials used in the synthesis of each compound and related tests were purchased from Sigma-Aldrich Chemical Co., Acros Organics, etc. and used without further purification. Solvents (Hexanes, Ethyl Acetate, MeOH and MeCN) were of reagent grade or HPLC grade quality and purchased from Fischer Scientific. NMR solvents (CD_3OD) were purchased from Cambridge Isotope Laboratories

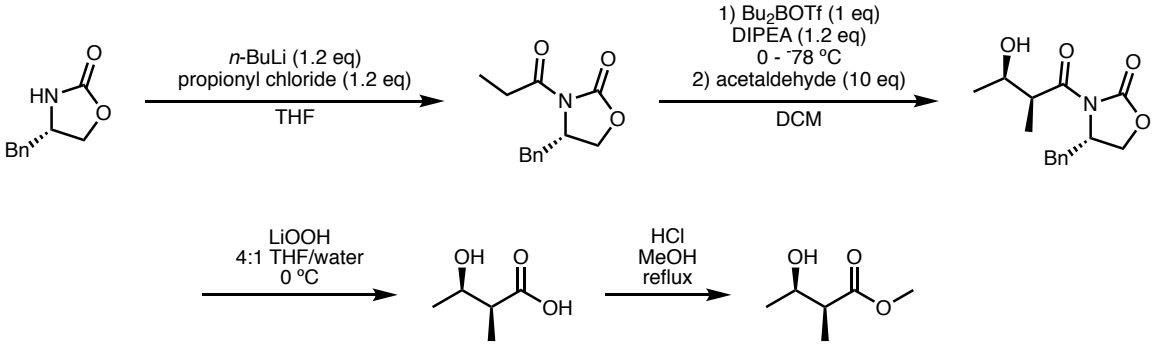
NMR spectra were taken on a Bruker AVANCE III 500 MHz NMR spectrometer.

TLC analyses were carried out using Silica TLC Plates Backing 20 by 20 cm sheet UV active at 254 nm.

Liquid Chomatography/Mass Spectrometry data was recorded on an Agilent Technologies 6120 Single Quadrapole or 6130 Single Quadrapole interfaced with an Agilent 1200 series liquid chromatography system equipped with a diode-array detector. Resulting spectra were analyzed using Agilent LC/MSD ChemStation. All liquid chromatographs were run as 5-95% gradient elution (MeOH/Water or MeCN/Water) over 15 minutes.

2. Experimental

2.1 Substrate Synthesis



Scheme S1. General synthetic route for the synthesis of the *threo*- enantiomers.

(S)-4-benzyl-3-propionyloxazolidin-2-one

n-BuLi (9.5 mL, 2.5 M in hexanes) was added to a stirring solution of (*S*)-4-benzyloxazolidin-2-one (4 g, 22.57 mmol, 1 eq.) in anhydrous THF at -79 ºC. This solution was allowed to stir for 20 minutes. At this point, propionyl chloride (2.15 mL, 24.8 mmol, 1.1 eq.) was added dropwise over a period of 15 minutes. After 2.5 hours at -79 ºC, the solution was warmed to room temperature and quenched with 50 mL of sat. ammonium chloride. The THF was removed in vacuo. DCM was added to the remaining mixture and the organic layer was washed with a 5% NaOH solution. The aqueous layer was extracted with DCM (3 x 100 mL). The combined organic layers were washed with brine and dried over $MgSO_4$ and filtered. The solvent was removed in vacuo and the crude residue was purified by silica gel chromatography (1:1 Hex/EtOAc) to yield the pure product (4.77g, 90.7%). ^{1}H-NMR (400 mHz, $CDCl_3$) ð 1.22 (t, 3H), 2.76–2.82 (m, 1H), 2.90–3.05 (m, 2H), 3.31 (dd, 1H), 4.16–4.23 (m, 2H), 4.66–4.70 (m, 1H), 7.19-7.23 (m, 2H), 7.27-7.36 (m, 3H). Characterization of the compound agreed with literature data. [55]

(S)-4-benzyl-3-((2S,3R)-3-hydroxy-2-methylbutanoyl)oxazolidin-2-one

(*S*)-4- benzyl-3-propionyloxazolidin-2-one (4.77 g, 20.5 mmol, 1 eq.) in anhydrous DCM was cooled to 0 ºC. Dibutyl boron triflate (22.5 mL, 1 M DCM, 1 eq.) was added to the stirring solution followed by dropwise addition of diisopropylethylamine (4.29 mL, 24.6 mmol, 1.2 eq.). This solution was cooled to -79 ºC and acetaldehyde (11.51 mL, 205 mmol, 10 eq.) was added via a cannula. The solution was stirred for 30 minutes at -79 ºC and then 2 hours at 0 ºC. pH=7.4 phosphate buffer (28.7 mL) and MeOH (70.9 mL) were added to the reaction mixture at 0 ºC followed by dropwise addition of 2:1 MeOH:30% H_2O_2 (aq.) (47 mL). After 1.5 hours of stirring, the organics were removed in vacuo. The remaining material was suspended in 5% HCO_3 and the product was extracted with DCM (3 x 150 mL). The combined organic layers were washed with 5% HCO_3 and then brine. The organic layer was dried over $MgSO_4$, filtered and concentrated in vacuo to yield a yellow oil. The crude oil was purified by silica gel chromatography (3:1 Hex/EtOAc) to give product (4.12 g, 72.6%). 1H-NMR (400 mHz, CDCl3) ð 1.23 (d, 3H), 1.28 (d, 3H), 2.76–2.82 (m, 1H), 2.93 (br s, 1H), 3.26 (dd, 1H), 3.75 (dq, 1H), 4.16–4.23 (m, 3H), 4.65–4.69 (m, 1H), 7.18-7.22 (m, 2H), 7.26-7.36 (m, 3H). Characterization of the compound agreed with literature data.[55]

(2S,3R)-3-hydroxy-2-methylbutanoic acid

The aldol product (*S*)-4-benzyl-3-((2*S*,3*R*)-3-hydroxy-2-methylbutanoyl)oxazolidin-2-one (3.12 g, 11.26 mmol, 1 eq.) was dissolved in 225 mL of 3:1 THF/H_2O and cooled to 0 ºC. To this stirring solution, 30% H_2O_2 (aq) (10.2 mL, 8 eq) was added dropwise followed by addition of crushed LiOH (0.54 g, 22.52 mmol, 2 eq.). The solution was stirred at 0 ºC and warmed to room temperature overnight. A 10% excess of Na_2SO_3 was added to neutralize excess peroxide for 1 hour. The THF was removed in vacuo and the remaining material was suspended in 5% $NaHCO_3$. This mixture was extracted with DCM (3 x 50 mL). The combined DCM layer was back extracted once with DI H_2O. The combined aqueous layers were cooled to 0 ºC and acidified to pH=1 with 6N HCl. The aqueous layer was extracted with EtOAc (10x50 mL). The combined organic layer was dried over $MgSO_4$, filtered and concentrated in vacuo to yield a clear oil (1.05

g, 76%). This product was used without further purification. 1H-NMR (400 mHz, CDCl3) ð 1.18-1.21 (d, 3H), 1.21- 1.23 (d, 3H), 2.53-2.6 (dq, 1H), 4.07-4.15 (m, 1H). Characterization of the compound agreed with literature data.[55]

Methyl (2S,3R)-3-hydroxy-2-methylbutanoate

(2*S*,3*R*)-3-hydroxy-2- methylbutanoic acid (200 mg, 1.69 mmol, 1 eq.) was dissolved in 18 mL of anhydrous MeOH and 6 mL of concentrated HCl was added. The mixture was stirred at reflux for four hours. Water was added to neutralize the reaction and the product was extracted with DCM (3 x 25mL). The combined organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated in vacuo to yield a yellow oil. The crude product was purified by silica gel chromatography (1:1 Hex/EtOAc) to yield a pale-yellow oil (40 mg, 18%). 1H-NMR (400 mHz, CDCl3) ð 1.17-1.185 (d, 3H), 1.19-1.2 (d, 3H), 2.49-2.56 (dq, 1 H), 3.71 (s, 3 H), 4.05-4.1 (dq, 1H). Characterization of the compound agreed with literature data.[55]

(R)-4-benzyl-3-propionyloxazolidin-2-one

This compound was prepared following the same procedure as (*S*)-4-benzyl-3-propionyloxazolidin-2-one with the exception that (*R*)-4-benzyloxazolidin-2-one was substituted for (*S*)-4-benzyloxazolidin-2-one (2.4 g, 90.2%). 1H-NMR (400 mHz, CDCl3) ð 1.22 (t, 3H), 2.76–2.82 (m, 1H), 2.90–3.05 (m, 2H), 3.31 (dd, 1H), 4.16–4.23 (m, 2H), 4.66–4.70 (m, 1H), 7.19-7.23 (m, 2H), 7.27-7.36 (m, 3H). Characterization of the compound agreed with literature data.[55]

(R)-4-benzyl-3-((2R,3S)-3-hydroxy-2-methylbutanoyl)oxazolidin-2-one

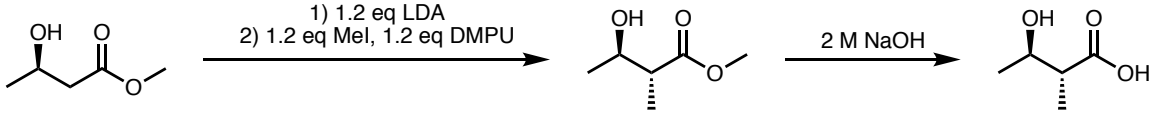
This compound was prepared following the same procedure as (*S*)-4-benzyl-3-((2*R*,3*S*)-3-hydroxy-2-methylbutanoyl)oxazolidin-2-one (2.5 g, 87.1%). 1H-NMR (400 mHz, CDCl3) ð 1.23 (d, 3H), 1.28 (d, 3H), 2.76–2.82 (m, 1H), 2.93 (br s, 1H), 3.26 (dd, 1H), 3.75 (dq, 1H), 4.16–4.23 (m, 3H), 4.65–4.69 (m, 1H), 7.18-7.22 (m, 2H), 7.26-7.36 (m, 3H). Characterization of the compound agreed with literature data.[55]

(2R,3S)-3-hydroxy-2-methylbutanoic acid

This compound was prepared following the same procedure as (2*S*,3*R*)-3-hydroxy-2-methylbutanoic acid with the exception that (*R*)-4-benzyl-3-((2*R*,3*S*)-3-hydroxy-2-methylbutanoyl)oxazolidin-2-one was used instead of (*S*)-4-benzyl-3-((2*S*,3*R*)-3-hydroxy-2-methylbutanoyl)oxazolidin-2-one (1.01 g, 96%). 1H-NMR (400 mHz, CDCl3) ð 1.18-1.21 (d, 3H), 1.21-1.23 (d, 3H), 2.53-2.6 (dq, 1H), 4.07-4.15 (m, 1H). Characterization of the compound agreed with literature data.[55]

Methyl (2R,3S)-3-hydroxy-2-methylbutanoate

This compound was prepared following the same procedure as methyl (2*S*,3*R*)-3-hydroxy-2-methylbutanoate with the exception that (2*R*,3*S*)-3-hydroxy-2-methylbutanoic acid was used instead of (2*S*,3*R*)-3-hydroxy-2-methylbutanoic acid (178 mg, 40%). 1H-NMR (400 mHz, CDCl3) ð 1.17-1.185 (d, 3H), 1.19-1.2 (d, 3H), 2.49-2.56 (dq, 1 H), 3.71 (s, 3 H), 4.05-4.1 (dq, 1H). Characterization of the compound agreed with literature data.[55]



Scheme S2. General synthetic route for the synthesis of the *erythro*- enantiomers.

Methyl (2R,3R)-3-hydroxy-2-methylbutanoate

n-BuLi (8 mL, 2.5 M in hexanes) was added to a solution of diisopropylamine (8 mL, 22 mmol, 2.3 eq.) in 50 mL anhydrous THF under an Ar atmosphere at -79 ºC and the solution was stirred for 30 minutes. The solution was warmed to 0 ºC and stirred for an additional 30 minutes. The solution was cooled to -79 ºC and methyl (*R*)-3-hydroxybutanoate (0.95 mL, 9.6 mmol, 1 eq.) added dropwise over 15 minutes. MeI

(0.62 mL, 9.9 mmol, 1.03 eq.) and DMPU (3.4 mL, 28.12 mmol, 2.92 eq) were added and the solution was stirred for 30 minutes at -79 ºC. The solution was warmed to -40 ºC and stirred for 1.5 hours. The reaction was warmed to room temperature and quenched with 50 mL sat. ammonium chloride. The organic layers were separated, and the aqueous phase was extracted with EtOAc (3 x 50 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated in vacuo. The crude product was purified by silica gel chromatography (10:1 Hex/EtOAc) to give pure product (854 mg, 68%). 1H-NMR (400 mHz, CDCl3) ð 1.1.6-1.18 (d, 3H), 1.19-1.21 (d, 3H), 2.41-2.48 (pent., 1 H), 2.55-2.65 (br s, 1H), 3.7 (s, 3H), 3.83-3.9 (pent., 1 H). Characterization of the compound agreed with literature data.[56]

(2R,3R)-3-hydroxy-2-methylbutanoic acid

Methyl (2*R*,3*R*)-3-hydroxy-2- methylbutanoate (51.1 mg, 0.384 mmol, 1 eq.) was dissolved in 250 µL of 2M NaOH and stirred 24 hours at room temperature. The solution was neutralized with water, cooled to 0 ºC and acidified to pH=1 with 6N HCl. The product was extracted with ethyl acetate (10 x2 mL). The combined organic layer was dried over $MgSO_4$, filtered and concentrated in vacuo to yield a clear oil (30 mg, 66%). This product was used without further purification. 1H-NMR (400 mHz, CDCl3) ð 1.21-1.24 (d, 3H), 1.24-1.27 (d, 3H), 2.46- 2.56 (m, 1H), 3.9-3.96 (pent., 1 H). Characterization of the compound agreed with literature data.[56]

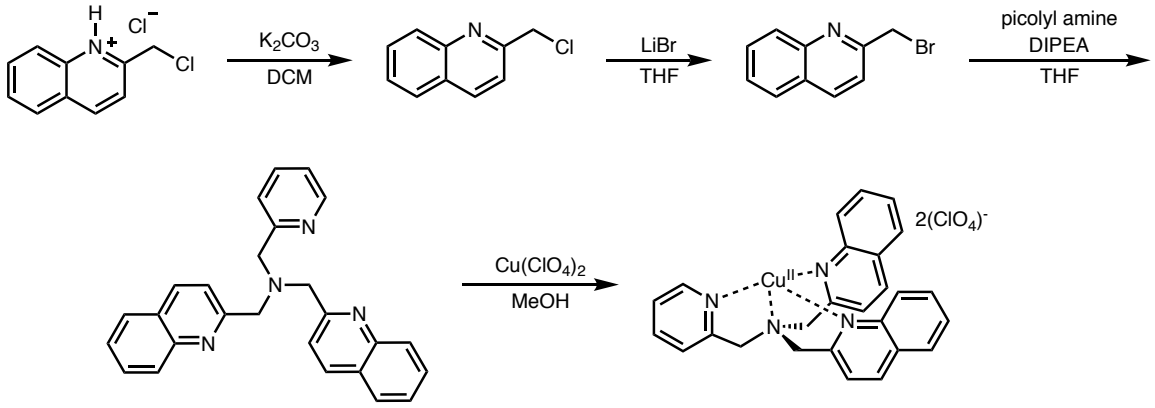
Methyl (2S,3S)-3-hydroxy-2-methylbutanoate

This compound was prepared following the same procedure as that of methyl (2*R*,3*R*)-3-hydroxy-2-methylbutanoate with the exception that (*S*)-3-hydroxybutanoate was substituted for (*R*)-3-hydroxybutanoate (650 mg, 52%). 1H-NMR (400 mHz, CDCl3) ð 1.1.6-1.18 (d, 3H), 1.19-1.21 (d, 3H), 2.41-2.48 (pent., 1 H), 2.55-2.65 (br s, 1H), 3.7 (s, 3H), 3.83-3.9 (pent., 1 H). Characterization of the compound agreed with literature data.[56]

(2S,3S)-3-hydroxy-2-methylbutanoic acid

This compound was prepared following the same procedure as that of (2*R*,3*R*)-3-hydroxy-2-methylbutanoic acid with the exception that methyl (2*S*,3*S*)-3-hydroxy-2-methylbutanoate was used instead of methyl (2*R*,3*R*)-3-hydroxy-2-methylbutanoate (25 mg, 56%). 1H-NMR (400 mHz, CDCl3) ð 1.21-1.24 (d, 3H), 1.24-1.27 (d, 3H), 2.46-2.56 (m, 1H), 3.9-3.96 (pent., 1 H). Characterization of the compound agreed with literature data.[56]

2.2 Sensor Synthesis



Scheme S1. Synthetic route to [(BQPA)$Cu^{II}(ClO_4)^2$].

2-(chloromethyl)quinoline

2-(chloromethyl)quinoline hydrochloride (1.8 g, 8.41 mmol, 1 eq.) was suspended in a solution containing 175 mL of 4:3 DCM/H_2O. K_2CO_3 (1.9 g, 12.6 mmol, 1.5 eq) was added in one portion and the solution was stirred for 1 hour. The layers were separated, and the organic layer was dried over $MgSO_4$, filtered and removed in vacuo. This product was used without further purification (quant.). 1H-NMR (400 mHz, CDCl3) ð 4.84 (s, 3H), 7.52-7.63 (m, 2H), 7.7-7.76 (m, 1 H), 7.8-7.84 (m, 1H), 8.05-8.09 (d, 1H), 8.16-8.19 (d, 1H). Characterization of the compound agreed with literature data.[57]

2-(bromomethyl)quinoline

2-(chloromethyl)quinoline (1.2, 6.7 mmol, 1 eq) and LiBr (7.28 g, 84.1 mmol, 10 eq.) were added to 75 mL of anhydrous THF and refluxed for 24 hours. The solution was cooled to room temperature and 75 mL of H_2O was added. The phases were separated, and the aqueous phase was extracted with ether (2 x 50mL). The combined organic layer was dried over $MgSO_4$, filtered and concentrated in vacuo. This product was used without further purification (quant.). 1H-NMR (400 mHz, CDCl3) ð 4.71 (s, 3H), 7.52-7.63 (m, 2H), 7.7-7.76 (m, 1 H), 7.8-7.84 (m, 1H), 8.05-8.09 (d, 1H), 8.16-8.19 (d, 1H). Characterization of the compound agreed with literature data.[57]

1-(pyridin-2-yl)-N,N-bis(quinolin-2-ylmethyl)methanamine [BQPA]

2- (bromomethyl)quinoline (2.62 g, 11.8 mmol, 2 eq) and DIPEA (4.11 mL, 23.6 mmol, 4 eq.) were added to 50 mL of anhydrous THF. Picolyl amine (0.608 mL, 5.9 mmol, 1 eq) was added dropwise and the solution was stirred for three days at room temperature. The THF was removed in vacuo and the crude residue was recrystallized from diethyl ether to give the pure product as a pale yellow solid (600 mg, 28.7%). 1H-NMR (400 mHz, CDCl3) ð 3.95 (s, 2H), 4.05 (s, 4H), 7.10-7.15 (m, 1H), 7.45-7.51 (m, 2H), 7.56-7.69 (m, 5H), 7.71-7.79 (m, 4H), 8.01-8.06 (d, 2H), 8.09-8.13 (d, 1H), 8.5-8.54 (d, 1H). Characterization of the compound agreed with literature data.[57]

[Cu(BQPA)](ClO$_4$)$_2$

BQPA (200 mg, 0.5 mmol, 1 eq.) was dissolved in 10 mL anhydrous MeOH. $Cu(ClO_4)2$ (0.185 g, 0.5 mmol, 1 eq.) was dissolved in 10 mL anhydrous MeOH and added dropwise to the stirring solution of BQPA. This solution was stirred for 10 minutes and 50 mL of diethyl ether were added and stirred for an additional hour. The solid precipitate was filtered via vacuum filtration to isolate the product as a dark green solid (200 mg, 61.5%). ESI MS: m/z 497.9 Cu(BQPA)-formate adduct; calculated 498.11. Characterization of the compound agreed with literature data.[40]

2.3 Spectroscopic Studies

General Procedure for Alcohol Assembly Formation

To a stirred solution of 3-methyl-pyridine-2-carboxaldehyde or 2-pyridinecarboxaldehyde or 3-*o*-tolyl-pyridine-2-carboxaldehyde (35 mM, 1 eq.), dipicolylamine (42 mM, 1.2 eq.), 4-(2-chloroethyl)morpholine hydrochloride (35mM, 1 eq.), and zinc (II) triflate (35 mM, 1 eq.), was added methyl 3-hydroxy-2-methylbutanoate (175 mM, 5 eq.). Activated 3Å molecular sieves were added and the mixture was stirred overnight at room temperature. Assembly formation was characterized by ^{1}H-NMR. The percent yield and diastereomeric ratio (*dr*) of the desired hemiaminal ether product was calculated using integrals from the ^{1}H-NMR. The diastereomeric ratio of the desired hemiaminal ether complex was determined from two peaks in the NMR spectrum in the region of 5.0 – 6.0 ppm for each stereoisomer of methyl 3-hydroxy-2-methylbutanoate. The yield of the desired hemiaminal ether complex was determined using the integrals corresponding to the diastereomers of the hemiaminal ether complex, the integral from the hemiaminal complex corresponding to water incorporation, and the integral corresponding to residual 3-methyl-pyridine-2-carboxaldehyde or 2-pyridinecarboxaldehyde or 3-*o*-tolyl-pyridine-2-carboxaldehyde.

Alcohol Assembly CD Analysis

The CD spectra were gathered using diluted solutions of assembly at 25 ºC (1.75 mM 3-methyl-2-pyridinecarboxaldehyde, 1 mm cell). CD spectra were recorded from 220 – 300 nm with a scan speed of 200 nm/min, and 1 second response time. The CD spectrum for each sample was accumulated 3 times.

General Procedure for Preparation of Chiral Carboxylate Samples for CD Analysis

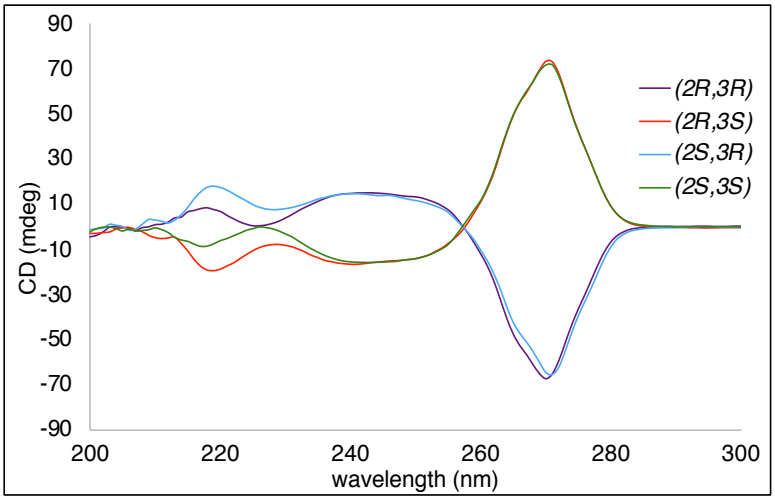
All solutions were prepared using 20 mM HEPES buffer (3:1 CH_3CN/H_2O, pH=7.4) as the solvent. A 10 mL stock solution of $[Cu(BQPA)](ClO_4)_2$ was prepared (74.6 mg, 0.114 mmol) in buffer. A 10 mL stock solution was prepared for all four chiral carboxylates (5.91 mg, 0.05 mmol). Each point of the titration was

prepared as a separate solution containing [Cu(BQPA)]$(ClO_4)_2$ (43.8 µL, 0.5 mM) and the indicated amount of chiral carboxylate (400 µL, 2 mM) to obtain the appropriate *ee*.

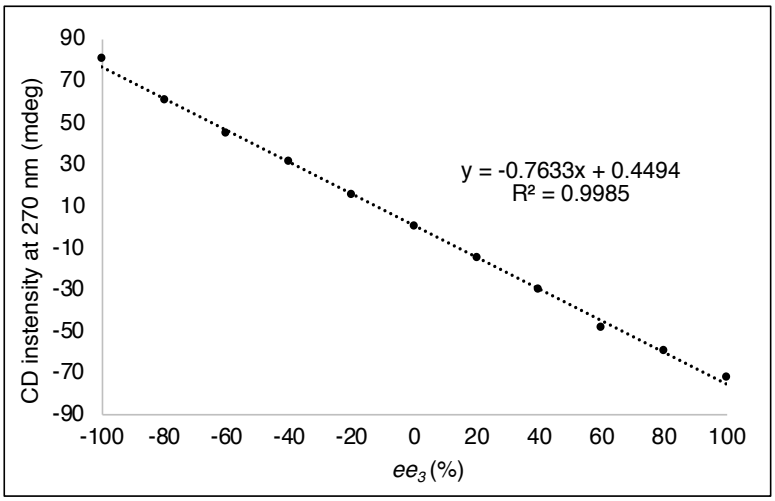
Chiral Carboxylate CD Analysis

The CD spectra were recorded at 25 ºC in a 1 mm cell. CD spectra were gathered for a range of *ee* (-100 – 100%) to create calibration curves. CD spectra were gathered from 220 – 255 nm with a scan speed of 200 nm/min, and 1 second response time. The CD spectrum for each sample was accumulated 3 times.

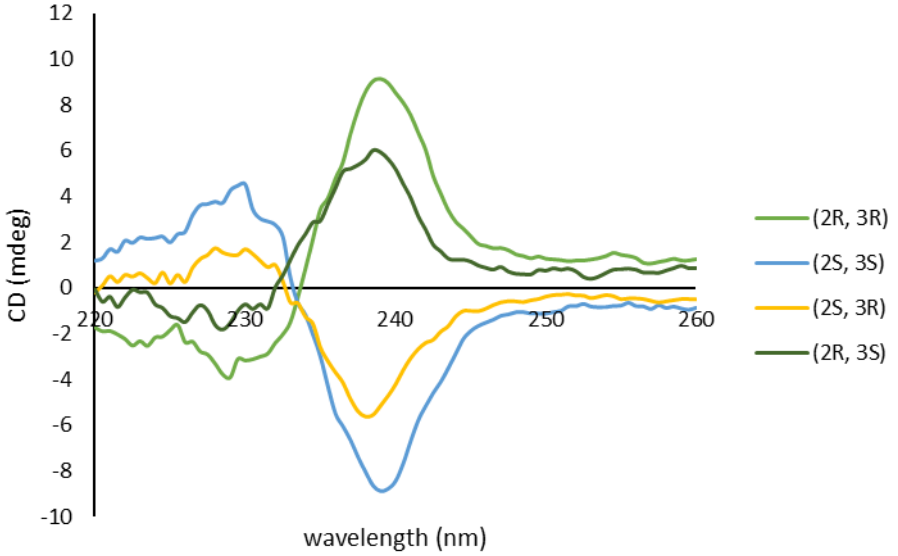
3. CD Data



SI Figure 1. ECCD signals for the four stereoisomers of methyl-3-hydroxy-2-methylbutanoate with dipicolylamine, 3-methyl-2-pyridinecarboxaldehyde, 4-(2-chloroethyl)morpholine hydrochloride, and $Zn(OTf)_2$. The ECCD spectra were recorded in CH_3CN at 25 °C (1.75 mM 3-methyl-2-pyridinecarboxaldehyde, 8.75 mM 2-methyl-3-hydroxybutyic methyl ester, 1 mm cell).

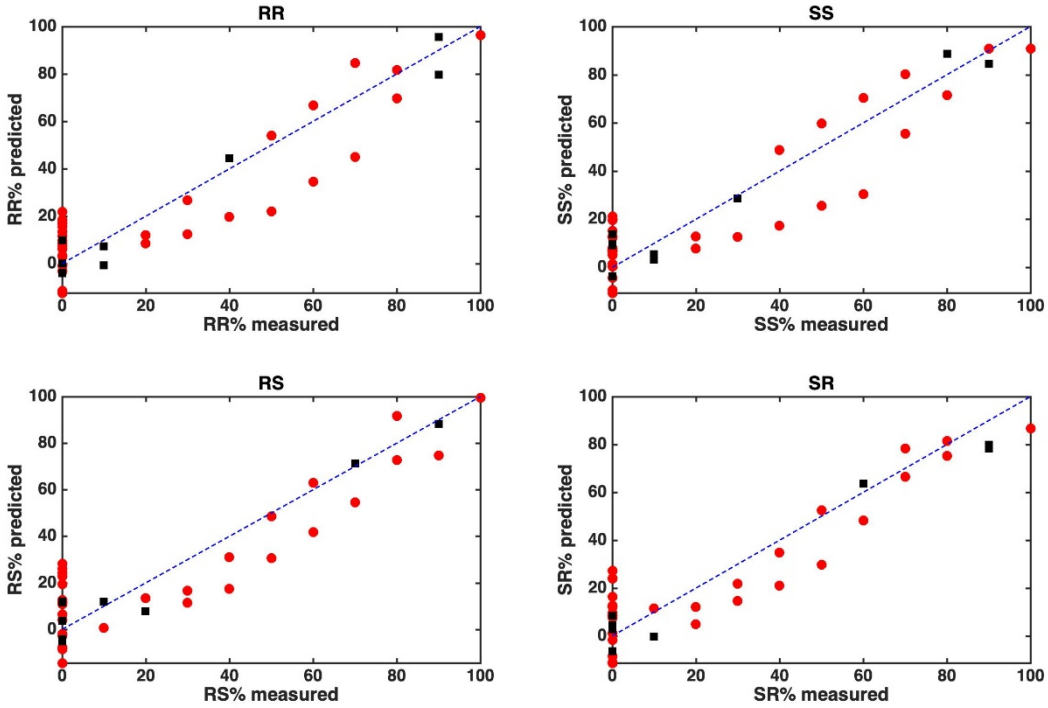


SI Figure 2. ECCD signals for the four stereoisomers of methyl-3-hydroxy-2-methylbutanoate with dipicolylamine, 3-methyl-2-pyridinecarboxaldehyde, 4-(2-chloroethyl)morpholine hydrochloride, and $Zn(OTf)_2$. The ECCD spectra were recorded in CH_3CN at 25 °C (1.75 mM 3-methyl-2-pyridinecarboxaldehyde, 8.75 mM 2-methyl-3-hydroxybutyic methyl ester, 1 mm cell).

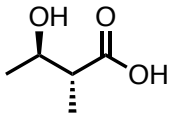
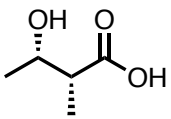
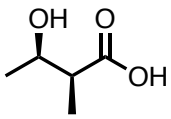
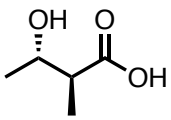


SI Figure 3. CD spectra for the Cu (II) host **13** with the four stereoisomeric carboxylic acids (**10**). The CD spectra were recorded in HEPES buffer (pH = 7.4) in 3:1 CH_3CN:H_2O at 25 ºC (0.5 mM 2, 2 mM 4, 1 mm cell).

4. PLSR Code and Results



SI Figure 4. Plots with training dataset (red circles) and test dataset (black squares) for each of the stereoisomers of 3-hydroxy-2-methylbutanoic acid

	 2R, 3R			 2R, 3S			 2S, 3R			 2S, 3S		
Trial	**Actual**	**Obs.**	**Error**	**Actual**	**Obs.**	**Error**	**Actual**	**Obs.**	**Error**	**Actual**	**Obs.**	**Error**
1	0.00	-3.93	3.93	10.00	11.75	-1.75	90.00	78.38	11.62	0.00	13.79	-13.79
2	0.00	0.01	-0.01	90.00	88.30	1.70	0.00	8.43	-8.43	10.00	3.26	6.74
3	0.00	-4.03	4.03	70.00	71.25	-1.25	0.00	4.04	-4.04	30.00	28.74	1.26
4	0.00	9.92	-9.92	20.00	7.86	12.14	0.00	-6.44	6.44	80.00	88.66	-8.66
5	10.00	-0.67	10.67	0.00	11.63	-11.63	90.00	79.82	10.18	0.00	9.22	-9.22
6	40.00	44.36	-4.36	0.00	-4.23	4.23	60.00	63.60	-3.60	0.00	-3.72	3.72
7	90.00	95.50	-5.50	0.00	-5.06	5.06	10.00	-0.23	10.23	0.00	9.80	-9.80
8	10.00	7.29	2.71	0.00	3.66	-3.66	0.00	4.58	-4.58	90.00	84.48	5.52
9	90.00	79.74	10.26	0.00	11.99	-11.99	0.00	2.79	-2.79	10.00	5.48	4.52

SI Table 1. KPLS model predictions for each of the four stereoisomers. Values are in % composition.

Code

```
%% Loads the data
load eedata

%% Builds the model and validates it on the test set
opt=kpls_cv('options');
opt.LVmax=15;
opt.kernelpar=[0.0001 0.0003162 0.0005 0.001 0.003162 0.005 0.01 0.03162 0.05 0.1];

m2=kpls_cv(Xmb(mm1,:), Yca(mm1,:), opt);
p2=kpls_pred(Xmb(tt1,:), Yca(tt1,:), m2.OptModel);

%% Plots the results
   eel={'RR', 'SS', 'RS', 'SR'};



   figure('units', 'normalized', 'position',[0.05 0.05 0.8 0.8])
   for i=1:4,
      subplot(2,2,i),
      plot(Yca(mm1,i), m2.OptModel.Ypred(:,i), 'or', 'markerfacecolor', 'r', 'markersize', 10),
      hold on
      plot(Yca(tt1,i), p2.Ypred(:,i), 'sk', 'markerfacecolor' ,'k', 'markersize', 10),
      plot([0 100], [0 100], '--b', 'linewidth', 1.5)
      axis tight
      set(gca, 'fontsize', 18, 'fontweight', 'bold', 'linewidth', 2)
      xlabel([eel{i}, '% measured'])
      ylabel([eel{i}, '% predicted'])
      title(eel{i}, 'fontsize', 20)
   end
```