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Selective Monoacylation of Diols and Asymmetric Desymmetrization of Dialkyl *meso*-Tartrates Using 2-Pyridyl Esters as Acylating Agents and Metal Carboxylates as Catalysts

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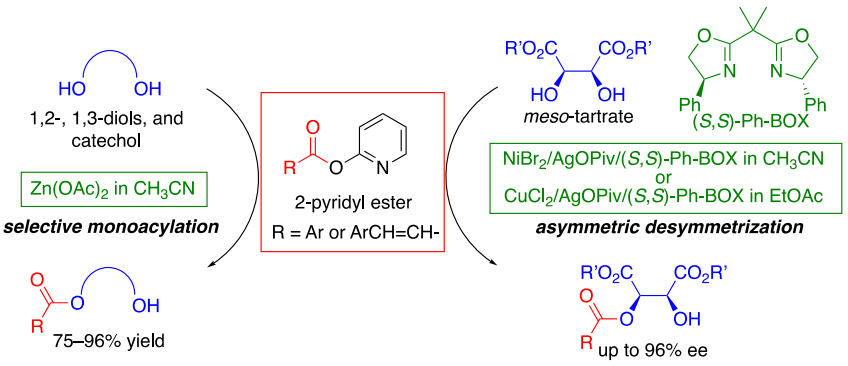


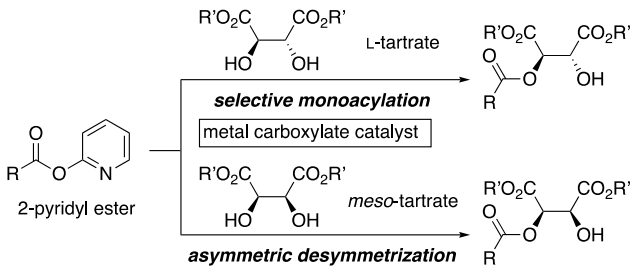
ABSTRACT: With 2-pyridyl benzoates as acylating agents and $Zn(OAc)_2$ as catalyst, 1,2- and 1,3-diols, and catechol were selectively monoacylated. Furthermore, the highly enantioselective desymmetrization of *meso*-tartrates was achieved for the first time utilizing 2-pyridyl esters and $NiBr_2$/AgOPiv/Ph-BOX in CH_3CN or $CuCl_2$/AgOPiv/Ph-BOX in EtOAc catalyst systems (up to 96% ee). The latter catalyst system was also effective for the kinetic resolution of dibenzyl *dl*-tartrate.

The asymmetric non-enzymatic mono-functionalization of *dl*- or *meso*-diols by acylation, sulfonylation, alkylation, oxidation, and the like is useful for the preparation of optically active, functionalized alcohols.[1] For enantioselective acylations, a variety of chiral organocatalysts have been developed, beginning with the introduction of chiral phosphines by Vedejs[2] and (*S*)-proline-derived diamines by Oriyama.[3] More recently, Mandai and Suga *et al.* reported binaphthyl-based chiral 4-aminopyridines for reactions of *dl*- or *meso*-diols with acid anhydrides.[4] Several metal catalyst systems have also been developed for asymmetric mono-

functionalization.[5] For example, Matsumura and Onomura *et al.* introduced Cu(II)/chiral bis(oxazoline) ligand (BOX) catalysts for the reactions of diols with acyl chlorides, isocyanates, or sulfonyl chlorides.[6] Niu *et al.* recently developed a Cu(I)/borinic acid dual catalyst system for asymmetric monopropargylation.[7] However, enantioselective mono-functionalization of dialkyl tartrates has not yet been successful. In the acylation of dialkyl tartrates, diacylation often becomes prominent, presumably because of the high acidity of the hydroxy groups.[6a,8]

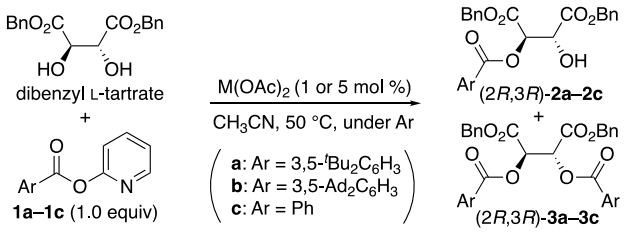
We have been interested in monoacylation of dibenzyl L-tartrate for preparation of *O*-monoacyltartaric acids (MATs), effective organocatalysts for the enantioselective conjugate addition of boronic acids or diborons to enones.[9] The reaction of this tartrate with aroyl chlorides and tertiary amines or with the corresponding benzoic acids and condensation agents usually furnishes considerable amounts of diaroylated products (10–20%) along with the desired monoacylated tartrates (40–70%). Therefore, we have focused on the use of 2-pyridyl esters as acylating agents, because these can be activated by suitable metal salts such as copper bromide without using additional bases.[10–12] Here we report the selective monoacylation of diols and asymmetric desymmetrization of dialkyl tartrates with 2-pyridyl esters using metal carboxylates as catalysts (Scheme 1).

Scheme 1. Selective Acylation of Tartrates with 2-Pyridyl Esters as Acylating Agents (This Work).



Initially, we investigated the reaction of dibenzyl L-tartrate with 2-pyridyl 3,5-di(*tert*-butyl)benzoate (**1a**) in the presence of various fourth-period transition metal salts (1 mol%) in CH_3CN at 50 °C (Table 1). The reaction did not take place in the absence of the catalyst. Screening of metal salts revealed that the desired monoacylated product (2*R*,3*R*)-**2a** was selectively obtained with cobalt, nickel, copper, and zinc acetates (entries 1–4). We chose metal acetates considering ability of the acetate anion as a proton shuttle.[13] Zinc acetate (5 mol%) provided the highest yield (entry 5) and was also effective for monoacylation with bulkier 3,5-di(1-adamantyl)benzoate **1b** (entry 6) and smaller benzoate **1c** (entry 7). The reaction of **1b** was performed in toluene instead of acetonitrile, because **1b** was more soluble in toluene. The reaction was feasible even in a polar, Lewis basic solvent, DMF (**2b**: 81%, **3b**: 1%). Products **2a** and **2b** are precursors of the MAT catalysts, which we have prepared by conventional methods in moderate yields (73% and 43%, respectively).[9a,c]

Table 1. Monoacylation of L-Tartrate with Metal Acetates

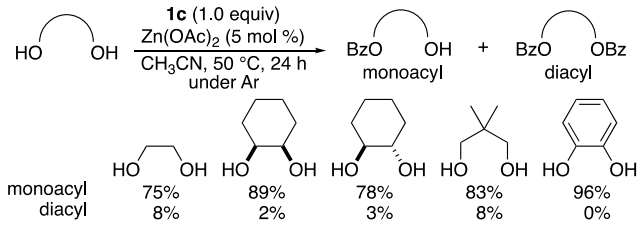


entry	**1**	$M(OAc)_2$	time (h)	**2** (%)[a]	**3** (%)[a]
1[b]	**1a**	$Co(OAc)_2•4H_2O$	15	60	2
2[b]	**1a**	$Ni(OAc)_2•4H_2O$	15	70	0
3[b]	**1a**	$Cu(OAc)_2$	15	79	5
4[b]	**1a**	$Zn(OAc)_2$	15	93	1
5[c]	**1a**	$Zn(OAc)_2$	15	96	1
6[c,d]	**1b**	$Zn(OAc)_2$	24	85	1
7[c]	**1c**	$Zn(OAc)_2$	15	86	2

[a]Isolated yields. [b]With metal salt (1 mol%). [c]With metal salt (5 mol%). [d]In toluene instead of CH_3CN.

Using 2-pyridyl benzoate (**1c**) and zinc acetate (5 mol%), several 1,2- and 1,3-diols, and catechol were monobenzoylated with good selectivity (Scheme 2). Catechol showed especially high reactivity. Competitive reactions between catechol and resorcinol or hydroquinone resulted in the exclusive formation of catechol monobenzoate.[14]

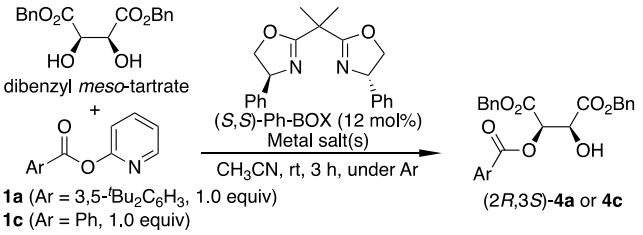
Scheme 2. Selective Monobenzoylation of Diols and Catechol.



We then focused on the asymmetric desymmetrization of dibenzyl *meso*-tartrate with 2-pyridyl ester **1a** in CH_3CN at rt using (*S*,*S*)-Ph-BOX as chiral ligand (Table 2). Among the metal acetates that were effective for the monoacylation of dibenzyl L-tartrate (entries 1–4), nickel acetate was found to give monoacylated product (2*R*,3*S*)-**4a** with the most promising enantioselectivity (entry 2). Use of $Ni(acac)_2•4H_2O$ in place of $Ni(OAc)_2•4H_2O$ resulted in low yield and selectivity (entry 5). Other nickel salts, i.e., chloride, bromide, perchlorate, and hydroxide, did not promote the reaction at all. Other chiral bis(oxazoline) ligands[15] and *N*,*N'*-dibenzyl (1*R*,2*R*)-cyclohexane-1,2-diamine[16] were tested instead of Ph-BOX, but lower selectivities were observed.[14] Nickel acetate/Ph-BOX (entry 2) was also effective for the desymmetrization with simple pyridyl benzoate **1c** (entry 6). Considering the possibility that the acetate anion plays a vital role in the catalytic activity and selectivity, not only as a ligand on the metal but also as a proton shuttle,[13] the introduction of carboxylates other than acetate was investigated. $NiCl_2$ or $NiBr_2$ (10 mol%) was treated with several silver carboxylates (10 or 20 mol%), and the resulting mixture was used as the catalyst solution (entries 7–

12). $NiCl_2$/silver pivalate (AgOPiv) (1:2), $NiBr_2$/AgOPiv (1:1), and $NiBr_2$/silver 1-adamantanecarboxylate (AgOCOAd) (1:1) were found to improve the enantioselectivity (entries 8, 9, and 12), whereas silver benzoate was ineffective, presumably due to the low basicity of the benzoate anion (entry 11).

Table 2. Screening of Asymmetric Metal Catalysts for Desymmetrization of Dibenzyl *meso*-Tartrate



1a (Ar = 3,5-^{t}Bu$_2$C$_6$H$_3$, 1.0 equiv)
1c (Ar = Ph, 1.0 equiv)

(2*R*,3*S*)-**4a** or **4c**

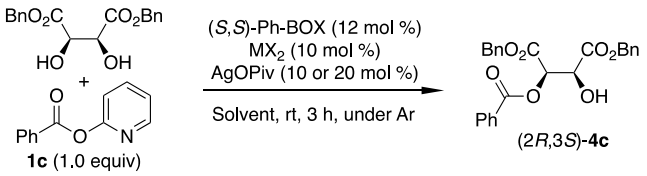
entry	1	Metal Salt(s) (mol%)	**4** (%)[a]	ee (%)[b]
1	1a	$Co(OAc)_2{\cdot}4H_2O$ (10)	81	37
2	1a	$Ni(OAc)_2{\cdot}4H_2O$ (10)	84	77
3	1a	$Cu(OAc)_2$ (10)	52	35
4	1a	$Zn(OAc)_2{\cdot}$ (10)	41	4
5	1a	$Ni(acac)_2{\cdot}4H_2O$ (10)	17	6
6	1c	$Ni(OAc)_2{\cdot}4H_2O$ (10)	84	72
7	1c	$NiCl_2$ (10) + AgOPiv (10)	35	60
8	1c	$NiCl_2$ (10) + AgOPiv (20)	91	81
9	1c	$NiBr_2$ (10) + AgOPiv (10)	88	83
10	1c	$NiBr_2$ (10) + AgOPiv (20)	88	79
11	1c	$NiBr_2$ (10) + AgOBz (10)	37	78
12	1c	$NiBr_2$ (10) + AgOCOAd (10)	74	85

[a]Isolated yield. [b]Determined by HPLC analysis.

We next examined the combination of other metal halides and AgOPiv (Table 3). Although the reaction scarcely proceeded with $CuCl_2$ or AgOPiv alone (entries 1 and 2), good yield and enantioselectivity were obtained with the combination of $CuCl_2$ and AgOPiv (10 mol% each) (entry 3). The use of two equivalents of AgOPiv relative to $CuCl_2$ lowered both the reactivity and selectivity (entry 4). The combination of AgOPiv with $CuBr_2$ or other metal chlorides, $CoCl_2$ and $ZnCl_2$, gave inferior results (entries 5–7). To our delight, the enantioselectivity was remarkably improved from 88% ee to 96% ee when EtOAc was used as solvent instead of CH_3CN (entry 8).[17] The effect of EtOAc was unexpectedly found, in an attempt to recovery and reuse a copper catalyst with EtOAc. To the best of our knowledge, this is the first successful example of highly enantioselective desymmetrization of *meso*-tartrates. Use of either $CuCl_2$/Ph-BOX or $Cu(OAc)_2$/Ph-BOX in EtOAc was ineffective (entries 9 and 10). However, a combination of $CuCl_2$ and $Cu(OAc)_2$ (5 mol% each) provided a good result (entry 11). These results indicate that the presence of both chloride and carboxylate anions is important to show high catalytic activity and selectivity (*see below*).

The migration of the acyl group causes racemization of the monoacylated *meso*-diols in the presence of a metal catalyst and a base.[6c,d] However, almost no racemization occurred under the reaction conditions in entry 8 of Table 3, because (2*R*,3*S*)-**4c** was obtained in 94% ee after a longer reaction time (24 h). This result may be ascribed to the low basicity of the 2-hydroxypyridine (2-pyridone) byproduct (pK_a of the conjugate acid: 0.75).[18]

Table 3. Effect of Combination of Metal Halides and Carboxylates on Desymmetrization of Dibenzyl *meso*-Tartrate

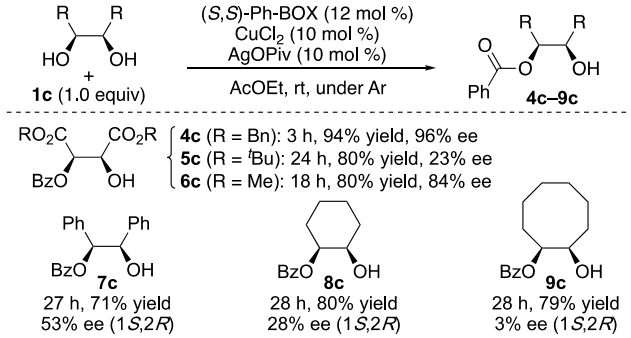


entry	MX_2	AgOPiv (mol%)	solvent	**4c** (%)[a]	ee (%)[b]
1	$CuCl_2$	0	CH_3CN	7	69
2	–	10	CH_3CN	18	8
3	$CuCl_2$	10	CH_3CN	85	88
4	$CuCl_2$	20	CH_3CN	62	5
5	$CuBr_2$	10	CH_3CN	61	63
6	$CoCl_2$	10	CH_3CN	81	49
7	$ZnCl_2$	10	CH_3CN	34	44
8	$CuCl_2$	10	EtOAc	94	96
9	$CuCl_2$	0	EtOAc	4	56
10	$Cu(OAc)_2$	0	EtOAc	61	27
11	$CuCl_2$ $Cu(OAc)_2$[c]	0	EtOAc	90	84

[a]Isolated yield. [b]Determined by HPLC analysis. [c]5 mol% each.

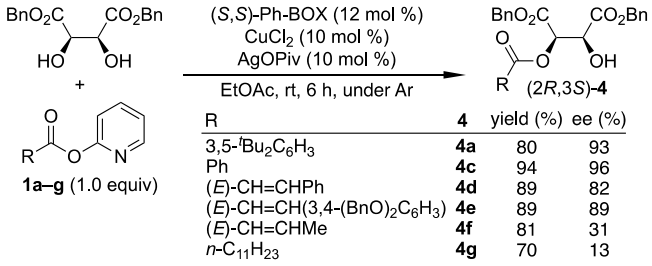
With an effective catalyst system [$CuCl_2$/AgOPiv/Ph-BOX (1:1:1.2) in EtOAc] in hand, the asymmetric acylation of other *meso*-1,2-diols was investigated (Scheme 3). The size of the ester groups of the *meso*-tartrate was found to be crucial. While the di-*tert*-butyl ester resulted in low enantioselectivity (product **5c**), the dimethyl ester provided good selectivity (product **6c**). *meso*-Hydrobenzoin, *cis*-1,2-cyclohexanediol, and *cis*-1,2-cyclooctanediol showed lower reactivity and selectivity than the tartrates (products **7c**–**9c**).[19] The more reactive *meso*-1,2-diol tended to give higher selectivity. Diols with sufficiently acidic hydroxy groups and moderate steric hindrance may give high selectivity *via* a tight transition state in the acylation step.

Scheme 3. Asymmetric Desymmetrization of *meso*-1,2-Diols.



Next, various pyridyl esters were evaluated for the reaction with dibenzyl *meso*-tartrate (Scheme 4). 3,5-Di(*tert*-butyl)benzoate **1a** afforded the corresponding monobenzoate **4a** with high enantioselectivity, as did simple unsubstituted benzoate **1c**.[20] Good enantioselectivities were observed for the reactions with cinnamates **1d** and **1e** (products **4d** and **4e**), whereas crotonate **1f** and laurate **1g** resulted in low selectivities (products **4f** and **4g**). The planarity and size of the acyl group might be important in discriminating between the hydroxy groups. Product **4e** can be a synthetic precursor of the optically active *meso* analogue of caftaric acid[21] and is expected to have biological activity.

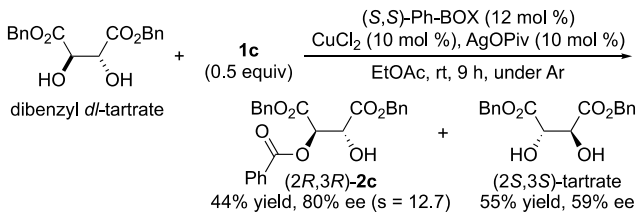
Scheme 4. Asymmetric Desymmetrization of Dibenzyl *meso*-Tartrate with Various 2-Pyridyl Esters.



R	4	yield (%)	ee (%)
3,5-^{t}Bu$_2$C$_6$H$_3$	**4a**	80	93
Ph	**4c**	94	96
(*E*)-CH=CHPh	**4d**	89	82
(*E*)-CH=CH(3,4-(BnO)$_2$C$_6$H$_3$)	**4e**	89	89
(*E*)-CH=CHMe	**4f**	81	31
n-C$_{11}$H$_{23}$	**4g**	70	13

The asymmetric kinetic resolution of dibenzyl *dl*-tartrate with **1c** was investigated using the $CuCl_2$/AgOPiv/Ph-BOX (1:1:1.2) catalyst in EtOAc (Scheme 5). The (*R*,*R*)-isomer was selectively monobenzoylated with good selectivity, indicating a preference for the (*R*)-configured hydroxy group regardless of the relative configuration of the tartrate.

Scheme 5. Kinetic Resolution of *dl*-Tartrate



We speculate that the catalytically active species is a mononuclear copper(II) monochloride monocarboxylate complex, according to the following experimental results. First, a 1:1 mixture of $CuCl_2$/(*S*,*S*)-Ph-BOX and $Cu(OAc)_2$/(*S*,*S*)-Ph-BOX complexes (5 mol% each) gave a higher yield and enantioselectivity (90% yield, 84% ee) for the desymmetrization of dibenzyl *meso*-tartrate with **1c** in EtOAc than either complex (see Table 3, entries 9–11). Second, the IR spectrum of this $CuCl_2$/$Cu(OAc)_2$-mixed complex showed a characteristic absoption of $\nu_{C=O}$ at 1604 cm^{-1}, which was not observed in the spectrum of either complex.[14] In addition, the IR spectrum of $CuCl_2$/AgOPiv/Ph-BOX showed an absorption at 1586 cm^{-1} similar to that of the $CuCl_2$/$Cu(OAc)_2$-mixed complex. These data support an equilibrium between copper dichloride, dicarboxylate, and monochloride monocarboxylate complexes. In fact, a 2:1 mixture of $CuCl_2$/(*S*,*S*)-Ph-BOX and $Cu(OAc)_2$/(*S*,*S*)-Ph-BOX complexes (10 and 5 mol%, respectively) afforded higher enantioselectivity (92% ee) than the 1:1 mixture (84% ee).[14] This result is consistent with the existence of an equilibrium and the fact that the $CuCl_2$/(*S*,*S*)-Ph-BOX complex shows lower activity but higher enantioselectivity than the $Cu(OAc)_2$/(*S*,*S*)-Ph-BOX complex. Third, a linear relationship between the enantiomeric excess of the Ph-BOX and that of product **4c** was observed for the $CuCl_2$/AgOPiv/Ph-BOX-catalyzed reaction of dibenzyl *meso*-tartrate with **1c** in AcOEt, suggesting that the enantioselective catalyst contains one Ph-BOX ligand.[14,22] Further mechanistic studies and improvement of the catalytic activity are now under investigation.

In conclusion, we have demonstrated that several 1,2- and 1,3-diols, and catechol can be monoacylated using 2-pyridyl benzoates as acylating agents and zinc acetate as catalyst. Furthermore, the asymmetric desymmetrization of *meso*-tartrates with high enantioselectivity was achieved for the first time utilizing 2-pyridyl esters and a $NiBr_2$/AgOPiv/Ph-BOX catalyst in CH_3CN or $CuCl_2$/AgOPiv/Ph-BOX catalyst in EtOAc. The latter catalyst system was also applicable to the kinetic resolution of dibenzyl *dl*-tartrate. Further improvement and application to other mono-functionalizations of diols or polyols are currently in progress.

EXPERIMENTAL SECTION

General Methods. Melting points (mp) were uncorrected. ^1H and $^{13}C\{^1H\}$ NMR spectra were measured in $CDCl_3$ with 400 or 500 MHz spectrometer. Tetramethylsilane (TMS) (δ = 0 ppm) and $CDCl_3$ (δ = 77.0 ppm) served as internal standards for ^1H and ^{13}C NMR, respectively. Infrared spectra were recorded on an FT-IR spectrometer. High-resolution mass spectra were recorded on an ESI-TOF mass spectrometer or a double-focusing magnetic-sector mass analyzer operating in a FAB or EI mode. Thin-layer chromatography (TLC) was visualized with UV light, phosphomolybdic acid and/or anisaldehyde. Column chromatography was performed using silica gel (spherical, neutral, 63−210 nm), silica gel (neutral, 40-63 μm), or aluminum oxide (neutral, activity I, 63-200 μm). The reactions under anhydrous conditions were carried out using oven, and heating gun-dried glassware with a rubber septum and a magnetic stirring bar under argon atmosphere.

Preparation of Dialkyl meso-Tartrates.

Dibenzyl *meso*-tartrate. The title compound was prepared following the procedure for dibenzyl L-tartrate.[23] To a stirred solution of *meso*-tartaric acid (6.66 mmol, 1000 mg) in toluene (20 mL) was added benzyl alcohol (20.0 mmol, 2.1 mL), *p*-toluenesulfonic acid monohydrate (0.083 mmol, 15.8 mg). The resulting mixture was refluxed with an oil bath, using a water separator, until all the water separated. Toluene and benzyl alcohol ware evaporated under reduced pressure and the reaction residue was recrystallized from Et_2O to give the product (1.48 g, 64%). TLC: R_f 0.53 (Hex/EtOAc = 1:1, stained blue with phosphomolybdic acid). Mp: 107–108 °C. IR (KBr, cm^{-1}) 3436, 3376, 3034, 2976, 2887, 1753, 1728, 1498, 1455, 1379, 1351, 1260, 1235, 1125, 1091, 1026. ^1H NMR ($CDCl_3$) δ 7.34-7.30 (m, 6H), 7.25-7.22 (m, 4H) 5.07 (d, J = 12.1 Hz, 4H), 5.00 (d, J = 12.1 Hz, 4H) 4.61 (d, J = 4.6 Hz, 2H), 3.52 (s, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 170.8, 134.5, 128.6, 128.5, 72.9, 67.9. HRMS (ESI+): Calcd for $C_{18}H_{18}O_6Na$ ($M+Na^+$) 353.1001, found 353.0997.

Di-*tert*-butyl *meso*-tartrate. The title compound was prepared following the procedure for di-*tert*-butyl L-tartrate.[21c] *meso*-Tartaric acid (5 mmol, 750.5 mg) in acetyl chloride (4.8 mL) was refluxed with an oil bath under an argon atmosphere for 48 h. The reaction mixture was cooled to rt and concentrated in vacuo to give the crude diacetyl *meso*-tartaric anhydride, which was used in the next step without further purification. The crude diacetyl *meso*-tartaric anhydride was dissolved in acetone (5.3 mL) followed by the addition of water (0.18 mL, 10 mmol). The mixture was stirred at rt for 12 h. After concentration, the residue was recrystallized from Hex/EtOAc (3:1) to give diacetyl *meso*-tartaric acid (408.1 mg, 35%). A mixture of anhydrous $MgSO_4$ (1.56 g) and conc. sulfuric acid (0.2 mL) in dry CH_2Cl_2 (47 mL) were stirred for 15 min. Diacetyl *meso*-tartaric acid (1.73 mmol, 404.0 mg) and dry *tert*-butyl alcohol (16.3 mmol, 1.55 mL) were added to the mixture. After being stirred at rt for 3 days, the mixture was poured into sat. aqueous $NaHCO_3$ solution (40 mL) and stirred until the $MgSO_4$ dissolved. The mixture was extracted with CH_2Cl_2, washed with brine, dried with $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (CH_2Cl_2) to give diacetyl di-*tert*-butyl *meso*-tartrate (357.7 mg, 60%). Powdered potassium hydroxide (11.2 mg, 0.2 mmol) was added to a solution of diacetyl di-*tert*-butyl *meso*-tartrate (342.2 mg, 0.99 mmol) in methanol (2.5 mL) and the mixture was stirred at rt. After 1 h, the mixture was concentrated in vacuo and purified by column chromatography on silica gel (Hex/EtOAc = 3:1) to give di-*tert*-butyl *meso*-tartrate (151.9 mg, 58%) as a white solid.

***O,O'*-Diacetyl *meso*-tartaric anhydride.** ^{1}H NMR ($CDCl_3$) δ 5.53 (s, 2H), 2.20 (s, 6H).

***O,O'*-Diacetyl *meso*-tartaric acid.** ^{1}H NMR (DMSO) δ 5.75 (s, 2H), 2.21 (s, 6H).

***O,O'*-Diacetyl di-*tert*-butyl *meso*-tartrate.** TLC: R_f 0.64 (Hex/EtOAc = 3:1, stained blue with phosphomolybdic acid). ^{1}H NMR: ($CDCl_3$) δ 5.43 (s, 2H), 2.17 (s, 6H), 1.49 (s, 18H).

Di-*tert*-butyl *meso*-tartrate. TLC: R_f 0.33 (Hex/EtOAc = 3:1, stained blue with phosphomolybdic acid). Mp: 94–96 °C. IR (KBr, cm^{-1}) 3407, 2983, 1752, 1369, 1239, 1159, 1105. ^{1}H NMR ($CDCl_3$) δ 4.40 (d, J = 5.2 Hz, 2H), 3.41 (d, J = 5.2 Hz, 2H), 1.49 (s, 18H). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 170.4, 83.5, 73.4, 28.0. HRMS (ESI+): Calcd for $C_{12}H_{22}O_6Na$ ($M+Na^+$) 285.1314, found 285.1308.

Dimethyl *meso*-tartrate. The title compound was prepared following the procedure for dimethyl L-tartrate.[24] To a stirred solution of *meso*-tartaric acid (0.5 mmol, 75.0 mg) in anhydrous methanol (0.1 mL) was slowly added thionyl chloride (2.5 mmol, 0.18 mL) at 0 °C with an ice bath. After being stirred at 0 °C for 1 h, the mixture was refluxed with an oil bath for 3 h. The hydrogen chloride and methanol were removed under reduced pressure. After addition of water, the mixture was extracted with EtOAc (3 × 20 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and concentrated. The residue was purified by column chromatography on silica gel (Hex/EtOAc = 1:1) to give the product (28.3 mg, 32%). TLC: R_f 0.11 (Hex/EtOAc = 1:1, stained blue with phosphomolybdic acid). Mp: 114–115 °C. IR (KBr, cm^{-1}) 3397, 3330, 2963, 1755, 1440, 1259, 1209, 1103, 1017, 974. ^{1}H NMR ($CDCl_3$) δ 4.58 (s, 2H), 3.82 (s, 6H), 3.15 (brs, 2H). ^{13}C NMR ($CDCl_3$) δ 171.4, 72.9, 52.9. HRMS (ESI+): Calcd for $C_6H_{10}O_6Na$ ($M+Na^+$) 201.0375, found 201.0371.

Preparation of Pyridyl Esters 1a–g

Pyridin-2-yl 3,5-di-*tert*-butylbenzoate (1a). Under an argon atmosphere, a 100-mL round-bottom flask was charged with 3,5-di-*tert*-butylbenzoic acid (5 mmol, 1.17 g), 2-hydroxypyridine (5 mmol, 0.48 g), DMAP (0.5 mmol 61.2 mg), and dry CH_2Cl_2 (20 mL). Then EDC•HCl (5.5 mmol, 1.05 g) was added and the mixture was stirred at rt for 23 h. The solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel (CH_2Cl_2) to give the product (1.38 g, 88%). TLC: R_f 0.60 (Hex/EtOAc = 3:1, detected by UV absorption). Mp: 107–109 °C. IR (KBr, cm^{-1}) 3477, 3063, 2961, 2907, 2869, 1798, 1743, 1591, 1471, 1436, 1364, 1310, 1249, 1134, 1090. ^{1}H NMR ($CDCl_3$) δ 8.47 (dd, J = 5.2, 1.8 Hz, 1H), 8.09 (d, J = 1.8 Hz, 2H), 7.84 (dt, J = 8.0, 1.8 Hz, 1H), 7.72 (t, J =

1.8 Hz, 1H), 7.26 (dd, *J* = 8.0, 5.2 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 1.38 (s, 18H). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 165.6, 158.4, 151.3, 148.6, 139.4, 128.4, 128.0, 124.6, 121.9, 116.8, 34.9, 31.3. HRMS (ESI+): Calcd for $C_{20}H_{25}NO_2Na$ ($M+Na^+$) 334.1783, found 334.1782.

Pyridin-2-yl 3,5-di(1-adamantyl)benzoate (1b). Under an argon atmosphere, a 100-mL round-bottom flask was charged with 3,5-di(1-adamanthyl)benzoic acid (3 mmol, 1.17 g), 2-hydroxypyridine (3 mmol, 0.29 g), DMAP (0.3 mmol 36.7 mg), and dry toluene (15 mL). Then EDC•HCl (3.3 mmol, 0.63 g) was added and the mixture was stirred at rt for 72 h. The solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel (CH_2Cl_2) to give the product (1.00 g, 71%). TLC: R_f 0.64 (Hex/EtOAc = 3:1, detected by UV absorption). Mp: 216–218 °C. IR (KBr, cm^{-1}) 2901, 2846, 1744, 1590, 1433, 1287, 1194, 1178, 1097, 1042. ^1H NMR ($CDCl_3$) δ 8.47 (dd, *J* = 5.2, 1.7 Hz, 1H), 8.06 (d, *J* = 1.5 Hz, 2H), 7.84 (t, *J* = 8.0, 1.7 Hz, 1H), 7.66 (t, *J* = 1.5 Hz, 1H), 7.26 (dd, *J* = 8.0, 5.2 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 1H), 2.15-2.09 (br, 6H), 2.01-1.94 (br, 12H), 1.84-1.74 (m, 12H). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 165.6, 158.4, 151.4, 148.6, 139.4, 128.4, 127.3, 124.4, 121.9, 116.9, 43.1, 36.6, 36.5, 28.9. HRMS (ESI+): Calcd for $C_{32}H_{37}NO_2Na$ ($M+Na^+$) 490.2722, found 490.2741.

Pyridin-2-yl benzoate (1c).[25] Under an argon atmosphere, benzoyl chloride (10 mmol, 951.0 mg) was added to a stirred solution of 2-hydroxypyridine (10 mmol, 0.95 mg), DMAP (0.1 mmol, 12.2 mg), and Et_3N (10 mmol, 1.01 g) in Et_2O (20 mL) at 0 °C with an ice bath. The mixture was warmed to rt and stirred for 17.5 h. The mixture was washed with water (10 mL) and saturated $NaHCO_3$ aq. (10 mL) twice. The organic layer was dried over anhydrous $MgSO_4$, filtrate, and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (Hex/EtOAc = 3:1) to give the product (1.83 g, 87%). TLC: R_f 0.40 (Hex/EtOAc = 3:1, detected by UV absorption). ^1H NMR ($CDCl_3$) δ 8.47 (dd, *J* = 5.0, 1.8 Hz, 1H), 8.24 (dd, *J* = 7.3, 1.4 Hz, 2H), 7.85 (dt, *J* = 7.8, 1.8 Hz, 1H), 7.65 (tt, *J* = 7.3, 1.4 Hz, 1H), 7.52 (t, *J* = 7.8 Hz, 2H), 7.28 (dd, *J* = 7.8, 5.0 Hz, 1H), 7.22 (d, *J* = 7.8 Hz, 1H).

Pyridin-2-yl cinnamate (1d). Under an argon atmosphere, a 30-mL round-bottom flask was charged with *trans*-cinnamic acid (2 mmol, 296.3 mg), 2-hydroxypyridine (2 mmol, 190.2 mg), DMAP (0.2 mmol, 24.4 mg), and dry CH_2Cl_2 (8 mL). Then EDC•HCl (2.1 mmol, 402.6 mg) was added and the mixture was stirred at rt for 4 h. The solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel (Hex/EtOAc = 7:1) to give the product (238.0 mg, 66%). TLC: R_f 0.42 (Hex/EtOAc = 3:1, detected by UV absorption).

Mp: 80–82 °C. IR (KBr, cm^{-1}) 3061, 3027, 1721, 1637, 1592, 1497, 1471, 1449, 1430, 1308, 1280, 1192, 1133. ^1H NMR ($CDCl_3$) δ 8.42 (dd, *J* = 5.2, 1.7 Hz, 1H), 7.91 (d, *J* = 16.1 Hz, 1H), 7.78 (dt, *J* = 8.1, 1.7 Hz, 1H), 7.41-7.39 (m, 2H), 7.44-7.36 (m, 3H) 7.21 (dd, *J* = 8.0, 5.2 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 1H), 6.64 (d, *J* = 16.1 Hz, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 164.6, 157.8, 148.4, 147.1, 139.2, 133.8, 130.7, 128.8, 128.2, 121.8, 116.7, 116.3.

HRMS (ESI+): Calcd for $C_{14}H_{11}NO_2Na$ ($M+Na^+$) 248.0687, found 248.0681.

Pyridin-2-yl 3,4-dibenzyloxycinnamate (1e). To a stirred solution of 3,4-dibenzyloxycinnamic acid (0.2 mmol, 72.1 mg) and DMF (0.01 mmol, 0.8 μL) in CH_2Cl_2 (0.5 mL) was added dropwise oxalyl chloride (0.3 mmol, 25.8 μL) at 0 °C under an argon atmosphere. After being stirred at rt for 4 h, the mixture was concentrated under reduced pressure to give the crude 3,4-dibenzyloxycinnamoyl chloride, which was used in the next step without further purification. The crude 3,4-dibenzyloxycinnamoyl chloride was added to a mixture of 2-hydroxypyridine (0.2 mmol, 19.0 mg) and Et_3N (0.2 mmol 27.9 μL) in Et_2O (1 mL) at 0 °C with an ice bath under an argon atmosphere. The resulting mixture was warmed to rt and stirred for 15 h. The mixture was diluted with CH_2Cl_2, washed with water, and dried over Na_2SO_4. After filtration and concentration, the residue was quickly purified by column chromatography on aluminum oxide (Hex/CH_2Cl_2 = 1:1 to CH_2Cl_2 only) to give the product (55.7 mg, 64%). TLC: R_f 0.25 (CH_2Cl_2, stained blue with phosphomolybdic acid). Mp: 105–107 °C. IR (KBr, cm^{-1}) 3063, 3029, 2935, 1729, 1630, 1597, 1508, 1470, 1454, 1431, 1385, 1303, 1274, 1224, 1209, 1124. ^1H NMR ($CDCl_3$) δ 8.42 (dd, *J* = 5.2, 1.8 Hz, 1H), 7.79 (d, *J* = 15.6 Hz, 1H), 7.78 (dt, *J* = 8.0, 1.8, 1H), 7.46-7.43 (m, 4H), 7.38-7.35 (m, 4H), 7.31 (tt, *J* = 7.5, 2.3 Hz, 2H) 7.21 (dd, *J* = 8.0, 5.2 Hz, 1H), 7.16 (d, *J* = 8.0 Hz, 1H) 7.16 (d, *J* = 2.3 Hz, 1H), 7.11 (dd, *J* = 8.0, 1.7 Hz, 1H), 6.93 (d, *J* = 8.0 Hz, 1H), 6.42 (d, *J* = 15.6 Hz, 1H), 5.20 (s, 2H), 5.19 (s, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 164.9, 158.0, 151.4, 148.8, 148.5, 147.0, 139.3, 136.7, 136.5, 128.5, 127.9, 127.3, 127.2, 127.1, 123.3, 121.8, 116.5, 114.5, 114.0, 113.7, 71.2, 70.8. HRMS (ESI+): Calcd for $C_{28}H_{23}NO_4Na$ ($M+Na^+$) 460.1519, found 460.1512.

Pyridin-2-yl crotonate (1f). Under an argon atmosphere, a 30-mL round-bottom flask was charged with crotonic acid (2 mmol, 172.9 mg), 2-hydroxypyridine (2 mmol, 190.2 mg), DMAP (0.2 mmol 24.4 mg), and dry CH_2Cl_2 (8 mL). Then EDC•HCl (2.1 mmol, 402.6 mg) was added and the mixture was stirred at rt for 15 h. The mixture was washed with sat. aqueous $NaHCO_3$. The organic layer was dried over Na_2SO_4, filtrated, and concentrated. The residue was purified by column chromatography on silica gel (Hex/EtOAc = 10:1) to give the product (95.9 mg, 29%). TLC: R_f 0.50 (Hex/EtOAc = 3:1, detected by UV absorption). IR (film on NaCl, cm^{-1}) 3060, 1739, 1656, 1592, 1469, 1433,

1201, 1152, 1100, 976. ^{1}H NMR ($CDCl_3$) δ 8.41 (dd, *J* = 5.2, 1.7 Hz, 1H), 7.79 (dt, *J* = 8.0, 1.7 Hz, 1H), 7.21 (dq, *J* = 15.6, 6.9 Hz, 1H) 7.19 (dd, *J* = 8.0, 5.2 Hz, 1H), 7.12 (d, *J* = 8.0 Hz, 1H), 6.04 (dq, *J* = 15.6, 1.7 Hz, 1H), 1.97 (dd, *J* = 6.9, 1.7 Hz, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 164.2, 158.0, 148.5, 147.9, 139.3, 121.8, 121.7, 116.5, 18.2. HRMS (ESI+): Calcd for $C_9H_9NO_2Na$ (M+Na+) 186.0525, found 186.0534.

Pyridin-2-yl dodecanoate (1g). Under an argon atmosphere, a 30-mL round-bottom flask was charged with lauric acid (2 mmol, 400.6 mg), 2-hydroxypyridine (2 mmol, 190.2 mg), DMAP (0.2 mmol 24.4 mg) and dry CH_2Cl_2 (10 mL). Then EDC•HCl (2.1 mmol, 402.6 mg) was added and the mixture was stirred at rt for 3 h. The solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel deactivated by water (SiO_2/H_2O = 10:1, Hex/CH_2Cl_2 = 2:1) to give the product (384.7 mg, 69%). TLC: R_f 0.64 (Hex/EtOAc = 3:1, detected by UV absorption). Mp: 44–46 °C. IR (KBr, cm^{-1}) 2923, 2851, 1766, 1715, 1656, 1621, 1543, 1470, 1434, 1212, 1188, 1137, 1109. ^{1}H NMR ($CDCl_3$) δ 8.41 (dd, *J* = 5.2, 1.8 Hz, 1H), 7.78 (dt, *J* = 7.5, 1.8 Hz, 1H), 7.22 (dd, *J* = 7.5, 5.2 Hz, 1H), 7.07 (d, *J* = 7.5 Hz, 1H), 2.61 (t, *J* = 7.5 Hz, 2H), 1.77 (quint, *J* = 7.5 Hz, 2H), 1.46-1.20 (m, 16H), 0.88 (t, *J* = 6.9 Hz, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 171.9, 158.0, 148.6, 139.4, 121.9, 116.4, 34.4, 31.9, 29.6, 29.4, 29.3, 29.2, 29.0, 24.7, 22.6, 14.1. HRMS (ESI+): Calcd for $C_{17}H_{27}O_2NNa$ ($M+Na^+$) 300.1940, found 300.1944.

General Procedure A for Selective Monoacylation of Diols with Metal Acetate. Under argon atmosphere, a 20-mL, screw-top test tube was charged with a 2-pyridyl ester (0.1 mmol, 31.1 mg) and a diol (0.1 mmol), and CH_3CN (0.5 mL). A metal acetate (5 mol%) was added to the mixture. After being stirred at 50 °C with an oil bath for the indicated time, the resulting mixture was passed through silica gel (0.5 g) in a Pasture pipette with EtOAc to remove catalyst. The eluent was concentrated under reduced pressure and the residue was purified by column chromatography (SiO_2 3.0 g, Hex/EtOAc = 5:1) to give the monoacylated product.

***O*-3,5-Di-*tert*-butylbenzoyl dibenzyl (2*R*,3*R*)-tartrate (2a).**[9a] According to General Procedure A, the reaction of 2-pyridyl ester **1a** (0.1 mmol, 31.1 mg) and dibenzyl L-tartrate (33.0 mg) with $Zn(OAc)_2$ (0.9 mg, 5 mol%) at 50 °C for 15 h gave monoacylated product **2a** (50.8 mg, 93% yield) and diacylated product **3a** (1.8 mg, 1% yield). TLC: R_f 0.47 (Hex/EtOAc = 3:1, stained blue with phosphomolybdic acid). ^{1}H NMR ($CDCl_3$) δ 7.81 (s, 2H), 7.65 (s, 1H), 7.40-7.06 (m, 10H), 5.66 (d, *J* = 1.8 Hz, 1H), 5.28 (s, 2H), 5.24 (d, *J* = 12.4 Hz, 1H), 5.13 (d, *J* = 12.4 Hz, 1H), 4.92 (d, *J* = 1.8 Hz, 1H) 3.38 (brs, 1H) 1.34 (s, 18H).

***O,O*'-Bis(3,5-di-*tert*-butylbenzoyl) dibenzyl (2*R*,3*R*)-tartrate (3a).**[26] TLC: R_f 0.82 (Hex/EtOAc = 3:1, stained blue with phosphomolybdic acid). ^{1}H NMR ($CDCl_3$) δ 7.90 (d, *J* = 1.8 Hz, 4H), 7.66 (t, *J* = 1.8 Hz, 2H), 7.24-7.15 (m, 4H), 7.15-7.01 (m, 6H), 6.06 (s, 2H), 5.23 (d, *J* = 12.4 Hz), 5.12 (d, *J* = 12.4 Hz, 2H) 1.33 (s, 36H).

***O*-3,5-Di(1-adamantyl)benzoyl dibenzyl (2*R*,3*R*)-tartrate (2b).**[9c] According to General Procedure A, the reaction of 2-pyridyl ester **1b** (0.1 mmol, 46.8 mg) and dibenzyl L-tartrate (0.1 mmol, 33.0 mg) with $Zn(OAc)_2$ (0.9 mg, 5 mol%) at 50 °C for 24 h gave monoacyl product **2b** (59.8 mg, 85% yield). TLC: R_f0.26 (Hex/CH_2Cl_2 = 1:2, stained blue with phosphomolybdic acid). ^{1}H NMR ($CDCl_3$) δ 7.78 (d, *J* = 1.8 Hz, 2H), 7.61 (t, *J* = 1.8 Hz, 1H), 7.38-7.04 (m, 10H), 5.70 (d, *J* = 2.3 Hz, 1H), 5.24 (d, *J* = 11.9 Hz, 2H), 5.13 (d, *J* = 11.9 Hz, 2H), 4.92 (d, *J* = 2.3 Hz, 1H), 3.38 (brs, 1H), 2.08-2.01 (br, 6H), 1.99-1.89 (m, 12H), 1.87-1.71 (m, 12H).

***O*-Benzoyl dibenzyl (2*R*,3*R*)-tartrate (2c).**[27] According to General Procedure A, the reaction of 2-pyridyl ester **1c** (0.1 mmol, 19.9 mg) and dibenzyl L-tartrate (0.1 mmol, 33.0 mg) with $Zn(OAc)_2$ (0.9 mg, 5 mol%) at 50 °C for 15 h gave monoacyl product **2c** (37.2 mg, 86% yield). TLC: R_f0.33 (Hex/EtOAc= 3:1, stained blue with phosphomolybdic acid). ^{1}H NMR ($CDCl_3$) δ 7.93 (d, *J* = 7.4 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.41 (t, *J* = 7.4 Hz, 2H), 7.37-7.07 (m, 10H), 5.49 (d, *J* = 2.3 Hz, 1H), 5.24 (d, *J* = 11.9 Hz, 2H), 5.12 (d, *J* = 11.9 Hz, 2H), 4.91 (d, *J* = 2.3 Hz, 1H), 3.34 (brs, 1H).

2-Hydroxyethyl benzoate.[28] According to General Procedure A, the reaction of 2-pyridyl ester **1c** (0.1 mmol 19.9 mg) and ethylene glycol (0.1 mmol, 6.2 mg) with $Zn(OAc)_2$ (0.9 mg, 5 mol%) at 50 °C for 24 h gave the product (24.9 mg, 75% yield). TLC: R_f0.22 (Hex/EtOAc= 3:1, detected by UV absorption). ^{1}H NMR ($CDCl_3$) δ 8.07 (d, *J* = 7.3 Hz, 2H), 7.57 (t, *J* = 7.3 Hz, 1H), 7.45 (t, *J* = 7.3 Hz, 2H), 4.47 (t, *J* = 4.6 Hz, 2H), 3.96 (t, *J* = 4.6 Hz, 2H). 2.17 (brs, 1H).

***cis*-2-Hydroxycyclohexyl benzoate.**[29] According to General Procedure A, the reaction of 2-pyridyl ester **1c** (0.2 mmol, 39.8 mg) and *cis*-1,2-cyclohexanediol (0.2 mmol, 23.2 mg) with $Zn(OAc)_2$ (1.8 mg, 5 mol%) at 50 °C for 24 h gave the product (39.3 mg, 89% yield). TLC: R_f 0.39 (Hex/EtOAc= 3:1, stained blue with phosphomolybdic acid). ^{1}H NMR ($CDCl_3$) δ 8.07 (dd, *J* = 8.0, 1.2 Hz, 2H), 7.58 (tt, *J* = 8.0, 1.2 Hz, 1H), 7.46 (t, *J* = 8.0 Hz, 2H), 5.23 (dt, *J* = 7.5, 2.9 Hz, 1H), 3.97 (dt, *J* = 7.5, 2.9 Hz, 1H), 2.14-2.00 (m, 2H), 1.89-1.66 (m, 5H), 1.51-1.38 (m, 2H).

***trans*-2-Hydroxycyclohexyl benzoate.**[27] According to General Procedure A, the reaction of 2-pyridyl ester **1c** (0.2 mmol, 39.8 mg) and *trans*-1,2-cyclohexanediol (0.2 mmol, 23.2 mg) with $Zn(OAc)_2$ (1.8 mg, 5 mol%) at 50 °C for 24 h gave the product (34.5 mg, 78% yield). TLC: R_f 0.33 (Hex/EtOAc= 3:1, stained blue with phosphomolybdic acid). ^{1}H NMR ($CDCl_3$): δ 8.05 (dd, *J* = 7.8, 1.4 Hz, 2H), 7.56 (tt, *J* = 7.8, 1.4 Hz, 1H), 7.48-7.42 (t, *J* = 7.8 Hz, 2H), 4.91-4.71 (m, 1H), 3.80-3.60 (m, 1H), 3.00 (brs, 1H), 2.20-2.05 (m, 2H), 1.85-1.63 (m, 2H), 1.50-1.213 (m, 4H).

3-Hydroxy-2,2-dimethylpropyl benzoate.[8d] According to General Procedure A, the reaction of 2-pyridyl ester **1c** (0.1 mmol, 19.9 mg) and neopentyl glycol (0.1 mmol, 10.4 mg) with $Zn(OAc)_2$ (0.9 mg, 5 mol%) at 50 °C for 24 h gave the product (17.2 mg, 83% yield). TLC: R_f 0.42 (Hex/EtOAc= 3:1, stained blue with phosphomolybdic acid). ^{1}H NMR ($CDCl_3$) δ 8.05 (dd, *J* = 7.3, 1.4 Hz, 2H), 7.58 (tt, *J* = 7.3, 1.4 Hz, 1H), 7.45 (dt, *J* = 7.3, 1.4 Hz, 2H), 4.19 (s, 2H), 3.39 (s, 2H), 2.81 (brs, 1H) 1.02 (s, 6H).

2-Hydroxyphenyl benzoate.[8d] According to General Procedure A, the reaction of 2-pyridyl ester **1c** (0.2 mmol, 39.8 mg) and catechol (0.2 mmol, 22.0 mg) with $Zn(OAc)_2$ (1.8 mg, 5 mol%) at 50 °C for 24 h gave the product (41.1 mg, 96% yield). TLC: R_f0.47 (Hex/EtOAc= 3:1, stained blue with phosphomolybdic acid). ^{1}H NMR δ 8.06 (d, *J* = 7.8 Hz, 2H), 7.53 (t, *J* = 7.8 Hz, 1H), 7.41-7.33 (m, 4H), 7.30-7.19 (m, 2H), 5.51 (brs, 1H).

General Procedure B for Asymmetric Desymmetrization of Dialkyl meso-Tartrates Using $CuCl_2$/AgOPiv/(S,S)-Ph-BOX. A mixture of $CuCl_2$ (0.01 mmol, 1.3 mg) and (*S*,*S*)-Ph-BOX (0.012 mmol, 4.0 mg) in EtOAc (0.5 mL) was stirred at rt for 10 min under argon atmosphere. Silver pivalate (AgOPiv)[30] (0.01 mmol, 2.1 mg) was added, and the mixture was further stirred at rt for 30 min. A pyridyl ester (0.1 mmol) and a dialkyl *meso*-tartrate (0.1 mmol) were then added to the catalyst solution. The resulting mixture was stirred at rt for the indicated time with monitoring by TLC analysis and passed through silica gel (0.5 g) in a Pasture pipette with EtOAc to remove catalyst. The eluent was evaporated under reduced pressure and the residue was purified by column chromatography (SiO_2 3.0 g, Hex/EtOAc = 5:1) to give the product.

***O*-3,5-Di-*tert*-butylbenzoyl dibenzyl (2*R*,3*S*)-tartrate (4a).** According to General Procedure B, the reaction of 2-pyridyl ester **1a** (0.3 mmol, 93.4 mg) and dibenzyl *meso*-tartrate (0.3 mmol, 99.1 mg) for 3 h gave product (2*R*,3*S*)-**4a** (130.4 mg, 80% yield, 93% ee). TLC: R_f 0.47 (Hex/EtOAc = 3:1, stained blue with phosphomolybdic acid). $[\alpha]_D^{26}$

−19.9 (*c* 1.0, $CHCl_3$) for 93% ee. IR (film on NaCl, cm^{-1}) 3500, 2963, 1732, 1217, 774, 741. ^1H NMR ($CDCl_3$) δ 7.91 (d, *J* = 1.8 Hz, 2H), 7.66 (t, *J* = 1.8 Hz, 1H) 7.31-7.28 (m, 8H), 7.23-7.20 (m, 2H), 5.80 (d, *J* = 2.3 Hz, 1H), 5.22 (d, *J* = 12.0 Hz, 1H), 5.11 (d, *J* = 12.0 Hz, 1H), 5.09 (d, *J* = 13.8 Hz, 1H), 5.02 (d, *J* = 13.8 Hz, 1H), 4.85 (d, *J* = 2.3 Hz, 1H), 3.37 (brs, 1H), 1.34 (s, 18H). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 170.9, 166.3, 166.1, 151.2, 134.8, 134.3, 128.7, 128.6, 128.5, 128.5, 128.4, 128.3, 128.2, 127.9, 124.2, 74.1, 70.8, 68.4, 67.5, 34.9, 31.3. HRMS (ESI+): Calcd for $C_{33}H_{38}O_7Na$ ($M+Na^+$) 569.2515, found 569.2501. HPLC (Daicel Chiralpak AD-H, Hex/^{i}PrOH = 9:1, 1.0 mL/min, 254 nm) t_R = 6.3 min (1*S*, 2*R*), 7.0 min (1*R*, 2*S*).

***O*-Benzoyl dibenzyl (2*R*,3*S*)-tartrate (4c).** According to General Procedure B, the reaction of 2-pyridyl ester **1c** (0.1 mmol, 19.9 mg) and dibenzyl *meso*-tartrate (0.1 mmol, 33.0 mg) for 6 h gave product (2*R*,3*S*)-**4c** (40.8 mg, 94% yield, 96% ee). TLC: R_f 0.25 (Hex/EtOAc = 3:1 stained blue with phosphomolybdic acid). $[\alpha]_D^{25}$ −5.1 (*c* 1.0, $CHCl_3$) for 96% ee. IR (film on NaCl, cm^{-1}) 3487, 1731, 1275, 1216, 1117, 752, 713. ^1H NMR ($CDCl_3$) δ 7.96 (d, *J* = 7.8 Hz, 2H), 7.58 (t, *J* = 7.8 Hz, 1H), 7.41 (t, *J* = 7.8 Hz, 2H), 7.33-7.22 (m, 10H), 5.81 (d, *J* = 2.3 Hz, 1H), 5.15 (d, *J* =11.8 Hz, 1H), 5.13 (d, *J* = 11.8 Hz, 1H), 5.12 (d, *J* = 11.9 Hz, 1H), 5.06 (d, *J* = 11.9 Hz, 1H), 4.84 (m, 1H), 3.28 (brs, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 170.7, 166.1, 165.4, 134.8, 134.3, 133.6, 130.0, 128.8, 128.8, 128.6, 128.5, 128.4, 74.0, 70.7, 68.5, 67.6. HRMS (ESI+): Calcd for $C_{25}H_{22}O_7Na$ (M+Na+) 457.1263, found 457.1282. HPLC (Daicel Chiralpak AD-H, Hex/^{i}PrOH = 9:1, 1.0 mL/min, 254 nm) t_R = 28.1 min (1*S*, 2*R*), 29.0 min (1*R*, 2*S*).

***O*-Benzoyl di-*tert*-butyl (2*R*,3*S*)-tartrate (5c).** According to General Procedure B, the reaction of 2-pyridyl ester **1c** (0.3 mmol, 59.8 mg) and di-*tert*-butyl *meso*-tartrate (0.3 mmol, 78.7 mg) for 24 h gave product (2*R*,3*S*)-**5c** (88.4 mg, 80% yield, 23% ee). TLC: R_f 0.50 (Hex/EtOAc = 3:1, stained blue with phosphomolybdic acid). $[\alpha]_D^{25}$ −7.7 (*c* 1.0, $CHCl_3$) for 23% ee. IR (film on NaCl, cm^{-1}) 3491, 2980, 2935, 1731, 1454, 1395, 1370, 1245, 1156, 1116, 712. ^1H NMR ($CDCl_3$) δ 8.07 (dd, *J* = 7.5, 1.2 Hz, 2H), 7.60 (tt, *J* = 7.5, 1.2 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 2H), 5.56 (d, *J* = 1.8 Hz, 1H), 4.60 (dd, *J* = 5.8, 1.8 Hz, 1H), 3.43 (d, *J* = 5.8 Hz, 1H), 1.54 (s, 9H), 1.49 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 170.2, 165.5, 165.0, 133.4, 129.9, 129.1, 128.3, 84.4, 83.1, 75.0, 70.9, 28.1, 28.0. HRMS (ESI+): Calcd for $C_{19}H_{26}O_7Na$ ($M+Na^+$) 389.1576, found 389.1593. HPLC (Daicel Chiralpak AD, Hex/^{i}PrOH = 9:1, 1.0 mL/min, 254 nm) t_R = 6.4 min (1*S*, 2*R*), 8.9 min (1*R*, 2*S*).

***O*-Benzoyl dimethyl (2*R*,3*S*)-tartrate (6c).** According to General Procedure B, the reaction of 2-pyridyl ester **1c** (0.15 mmol, 29.9 mg) and dimethyl *meso*-tartrate (0.15 mmol, 26.7 mg) for 18 h gave product (2*R*,3*S*)-**6c** (34.0 mg, 80% yield, 84% ee). TLC: R_f 0.19 (Hex/EtOAc = 3:1, stained blue with phosphomolybdic acid). $[\alpha]_D^{26}$ +4.5 (*c* 1.0, $CHCl_3$) for 80% ee. IR (film on NaCl, cm^{-1}) 3481, 2956, 1731, 1453, 1239, 1116, 1026, 714. ^1H NMR ($CDCl_3$) δ 8.08 (dd, *J* = 8.2, 1.4 Hz, 2H), 7.63-7.58 (tt, *J* = 8.2, 1.4 Hz, 1H), 7.47 (t, *J* = 8.2 Hz, 2H), 5.79 (d, *J* = 2.3 Hz, 1H), 4.78 (dd, *J* = 6.0, 2.3 Hz, 1H), 3.90 (s, 3H), 3.80 (s, 3H), 3.31 (d, *J* = 6.0 Hz, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 171.3, 166.9, 165.4, 133.7, 130.0, 128.8, 128.5, 74.1, 70.8, 53.4, 52.8. HRMS (ESI+): Calcd for $C_{13}H_{14}O_7Na$ ($M+Na^+$) 305.0637, found 305.0651. HPLC (Daicel Chiralpak AD, Hex/^{i}PrOH = 4:1, 1.0 mL/min, 254 nm) t_R = 8.3 min (1*S*, 2*R*), 9.3 min (1*R*, 2*S*).

(1*S*,2*R*)-2-Hydroxy-1,2-diphenylethyl benzoate (7c).[6a] According to General Procedure B, the reaction of 2-pyridyl ester **1c** (0.3 mmol, 59.8 mg) and (1*S*,2*R*)-hydrobenzoin (0.3 mmol, 64.3 mg) for 27 h gave product (1*S*,2*R*)-**7c** (67.9 mg, 71% yield, 53% ee). TLC: R_f 0.28 (CH_2Cl_2, stained blue with phosphomolybdic acid). ^1H NMR ($CDCl_3$): δ 8.01 (dd, *J* = 7.5, 1.7 Hz, 2H), 7.56 (tt, *J* = 7.5, 1.7 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.35-7.27 (m, 10H), 6.16 (d, *J* = 5.8 Hz, 1H), 5.15 (dd, *J* = 5.8, 3.4 Hz, 1H) 2.23 (d, *J* = 3.4 Hz, 1H). HPLC (Daicel Chiralpak OJ, Hex/^{i}PrOH = 4:1, 1.0 mL/min, 254 nm) t_R = 11.5 min (1*S*, 2*R*), 17.9 min (1*R*, 2*S*).

(1*S*, 2*R*)-2-Hydroxycyclohexyl benzoate (8c).[31] According to General Procedure B, the reaction of 2-pyridyl ester **1c** (0.3 mmol, 59.8 mg) and *cis*-cyclohexane-1,2-diol (0.3 mmol, 34.8 mg) for 28 h gave product (1*S*,2*R*)-**8c** (52.8 mg, 80% yield, 28% ee). TLC: R_f 0.33 (CH_2Cl_2, stained blue with phosphomolybdic acid). ^1H NMR ($CDCl_3$) δ 8.07 (dd, *J* = 8.0, 1.2 Hz, 2H), 7.58 (tt, *J* = 8.0, 1.2 Hz, 1H), 7.46 (t, *J* = 8.0 Hz, 2H), 5.23 (dt, *J* = 7.5, 2.9 Hz, 1H), 3.97 (dt, *J* = 7.5, 2.9 Hz, 1H), 2.14-2.00 (m, 2H), 1.89-1.66 (m, 5H), 1.51-1.38 (m, 2H). HPLC (Daicel Chiralpak AS-H, Hex/^{i}PrOH = 9:1, 0.8 mL/min, 254 nm) t_R = 9.9 min (1*S*, 2*R*), 20.0 min (1*R*, 2*S*).

(1*S*, 2*R*)-2-Hydroxycyclooctyl benzoate (9c).[31] According to General Procedure B, the reaction of 2-pyridyl ester **1c** (0.3 mmol, 59.8 mg) and *cis*-cyclooctane-1,2-diol (0.3 mmol, 43.3 mg) for 28 h gave product (1*S*,2*R*)-**9c** (68.1 mg, 79% yield, 3% ee). TLC: R_f 0.19 (CH_2Cl_2, stained blue with phosphomolybdic acid). ^1H NMR ($CDCl_3$): δ 8.05 (dd, *J* = 8.0, 1.7 Hz, 2H), 7.58 (tt, *J* = 8.0, 1.7 Hz, 1H), 7.46 (t, *J* = 8.0 Hz, 2H), 5.33 (dt, *J* = 4.6, 2.3 Hz, 1H), 4.13-4.08 (m, 1H), 2.21 (brs), 1.96-1.51 (m, 12H). HPLC (Daicel Chiralpak AS-H, Hex/^{i}PrOH = 1:1, 0.8 mL/min, 254 nm) t_R = 9.3 min (1*S*, 2*R*), 14.4 min (1*R*, 2*S*).

***O*-Cinnamoyl dibenzyl (2*R*,3*S*)-tartrate (4d).** According to General Procedure B, the reaction of 2-pyridyl ester **1d** (67.6 mg) and dibenzyl *meso*-tartrate (99.1 mg) for 6 h gave product (2*R*,3*S*)-**4d** (122.5 mg, 89% yield, 82% ee). TLC: R_f 0.53 (Hex/EtOAc = 3:1, stained blue with phosphomolybdic acid). $[\alpha]_D^{26}$ −39.3 (*c* 1.0, $CHCl_3$) for 82% ee. IR (film on NaCl, cm^{-1}) 3478, 3033, 2959, 1728, 1636, 1497, 1452, 1201, 1158. ^1H NMR ($CDCl_3$) δ 7.72 (d, *J* = 16.0 Hz, 1H), 7.51-7.49 (m, 2H), 7.40-7.37 (m, 3H), 7.34-7.24 (m, 10H), 6.46 (d, *J* = 16.0 Hz, 1H), 5.73 (dd, *J* = 2.3, 1.2 Hz, 1H), 5.15 (d, *J* = 12.0 Hz, 1H), 5.12 (s, 1H), 5.09 (s, 1H), 5.06 (d, *J* = 12.0 Hz, 1H), 4.80-4.71 (m, 1H), 3.36 (brs, *J* = 6.0 Hz, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 170.6, 166.2, 165.6, 146.7, 134.7, 134.4, 134.0, 130.6, 128.9, 128.7, 128.6, 128.5, 128.4, 128.3, 116.4, 73.6, 70.7, 68.4, 67.6. HRMS (ESI+): Calcd for $C_{27}H_{24}O_7Na$ ($M+Na^+$) 483.1420, found 483.1441. HPLC (Daicel Chiralpak AD, Hex/^{i}PrOH = 4:1, 1.0 mL/min, 254 nm) t_R = 17.4 min (1*S*, 2*R*), 23.6 min (1*R*, 2*S*).

***O*-3,4-Dibenzyloxycinnamoyl dibenzyl (2*R*,3*S*)-tartrate (4e).** According to General Procedure B, the reaction of 2-pyridyl ester **1e** (0.13 mmol, 55.7 mg) and dibenzyl *meso*-tartrate (0.13 mmol, 42.9 mg) for 6 h gave product (2*R*,3*S*)-**4e** (57.0 mg, 89% yield, 89% ee). TLC: R_f 0.08 (Hex/Et_2O = 2:1 stained blue with phosphomolybdic acid). $[\alpha]_D^{25}$ −29.0 (*c* 0.98, $CHCl_3$) for 72% ee. IR (film on NaCl, cm^{-1}) 3481, 3064, 3033, 2950, 1731, 1632, 1597, 1509, 1455, 1433, 1265, 1137, 1024, 738, 697. ^1H NMR ($CDCl_3$) δ 7.61 (d, *J* = 16.1 Hz, 1H), 7.46 (d, *J* = 6.9 Hz, 2H), 7.44 (d, *J* = 6.9 Hz, 2H), 7.37 (t, *J* = 6.9 Hz, 2H), 7.37 (t, *J* = 6.9 Hz, 2H), 7.31 (m, 10H), 7.26-7.24 (m, 2H), 7.12 (d, *J* = 1.8 Hz, 1H), 7.06 (dd, *J* = 8.0, 1.8 Hz, 1H), 6.92 (d, *J* = 8.0 Hz, 1H), 6.29 (d, *J* = 16.1 Hz, 1H), 5.71 (d, *J* = 2.3 Hz, 1H), 5.19 (s, 2H), 5.17 (s, 2H), 5.15 (d, *J* = 12.0 Hz, 1H), 5.09 (d, *J* =12.1 Hz, 1H), 5.09 (d, *J* = 12.0 Hz, 1H), 5.05 (d, *J* = 12.1 Hz, 1H), 4.74 (dd, *J* = 5.2, 2.3 Hz, 1H), 3.27 (d, *J* = 5.2 Hz, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 170.7, 166.3, 165.9, 151.3, 148.9, 146.5, 136.8, 136.6, 134.7, 134.4, 128.7, 128.7, 128.6, 128.5, 128.5, 127.9, 127.5, 127.3, 127.1, 123.4, 114.2, 114.1, 113.7, 73.5, 70.7, 71.3, 70.9, 68.4, 67.6. HRMS (ESI+): Calcd for $C_{41}H_{36}O_9Na$ ($M+Na^+$) 695.2252, found 695.2249. HPLC (Daicel Chiralpak AS-H, Hex/^{i}PrOH = 1:2, 0.6 mL/min, 254 nm) t_R = 43.2 min (1*R*, 2*S*), 62.8 min (1*S*, 2*R*).

***O*-Crotonoyl dibenzyl (2*R*,3*S*)-tartrate (4f).** According to General Procedure B, the reaction of 2-pyridyl ester **1f** (0.13 mmol, 21.9 mg) and dibenzyl *meso*-tartrate (0.13 mmol, 44.3 mg) for 6 h gave product (2*R*,3*S*)-**4f** (43.2 mg, 81% yield, 31% ee). TLC: R_f 0.25 (Hex/EtOAc = 3:1 stained blue with phosphomolybdic acid). $[\alpha]_D^{25}$ −2.9 (*c* 1.05, $CHCl_3$) for 13% ee. IR (film on NaCl, cm^{-1}) 3487, 3065, 3034, 2952, 1732, 1655, 1498, 1171, 1106, 968, 836, 742, 698. ^1H

NMR ($CDCl_3$) δ 7.34-7.31 (m, 6H), 7.29-7.28 (m, 2H), 7.25-7.23 (m, 2H), 7.03-6.95 (dq, *J* = 15.5, 6.9 Hz, 1H), 5.88 (dd, *J* = 15.5, 1.7 Hz, 1H), 5.64 (d, *J* = 2.3 Hz, 1H), 5.12 (d, *J* = 12.0 Hz, 1H), 5.09 (s, 1H), 5.07 (s, 1H), 5.03 (d, *J* = 12.0, 1H), 4.71 (dd, *J* = 5.2, 2.3 Hz, 1H), 3.25 (m, 1H), 1.88 (dd, *J* = 6.9, 1.7 Hz, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 170.6, 166.2, 165.0, 147.1, 134.8, 134.4, 128.7, 128.7, 128.5, 128.5, 128.4, 121.3, 73.3, 70.7, 68.3, 67.5, 18.1. HRMS (ESI+): Calcd for $C_{22}H_{22}O_7Na$ ($M+Na^+$) 421.1258, found 421.1242. HPLC (Daicel Chiralpak AD, Hex/^{i}PrOH = 4:1, 1.0 mL/min, 254 nm) t_R = 8.6 min (1*S*, 2*R*), 10.5 min (1*R*, 2*S*).

***O*-Dodecanoyl dibenzyl (2*R*,3*S*)-tartrate (4g).** According to General Procedure B, the reaction of 2-pyridyl ester **1g** (0.1 mmol, 27.7 mg) and dibenzyl *meso*-tartrate (0.1 mmol, 33.0 mg) for 6 h gave product (2*R*,3*S*)-**4g** (35.7 mg, 70% yield, 13% ee). TLC: R_f 0.53 (Hex/EtOAc = 3:1 stained blue with phosphomolybdic acid). $[\alpha]_D^{25}$ +1.1 (*c* 1.0, $CHCl_3$) for 13% ee. IR (film on NaCl, cm^{-1}) 3489, 2925, 2854, 1750, 1457, 1214, 750, 697. ^1H NMR ($CDCl_3$) δ 7.34-7.31 (m, 6H), 7.28-7.22 (m, 4H), 5.59 (d, *J* = 2.3 Hz, 1H), 5.13 (d, *J* = 12.1 Hz, 1H), 5.08 (d, *J* = 12.1 Hz, 1H), 5.07 (d, *J* = 12.1 Hz, 1H) 5.01 (d, *J* = 12.1 Hz, 1H), 4.68 (d, *J* = 2.3 Hz, 1H), 3.26 (brs, 1H), 2.42-2.31 (m, 2H), 1.63-1.56 (m, 2H), 1.34-1.20 (m, 16H), 0.88 (t, *J* = 6.9 Hz, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 172.7, 170.6, 166.2, 134.7, 134.3, 128.7, 128.7, 128.6, 128.5, 128.4, 73.3, 70.6, 68.4, 67.6, 33.8, 31.9, 29.6, 29.4, 29.3, 29.2, 29.0, 24.7, 22.7, 14.1. HRMS (ESI+): Calcd for $C_{30}H_{40}O_7Na$ ($M+Na^+$) 535.2672, found 535.2655. HPLC (Daicel Chiralpak AD, Hex/^{i}PrOH = 9:1, 1.0 mL/min, 220 nm) t_R = 9.2 min (1*S*, 2*R*), 10.3 min (1*R*, 2*S*).

Kinetic Resolution of Dibenzyl *dl*-Tartrate. A mixture of $CuCl_2$ (0.03 mmol, 4 mg) and (*S*,*S*)-Ph-BOX (0.036 mmol, 12.0 mg) in EtOAc (1.5 mL) was stirred at rt for 10 min under argon atmosphere. Silver pivalate (AgOPiv)[30] (0.03 mmol, 6.3 mg) was added, and the mixture was further stirred at rt for 30 min. 2-Pyridyl ester **1c** (0.15 mmol) and a dibenzyl *dl*-tartrate (0.3 mmol) were then added to the catalyst solution. The resulting mixture was stirred at rt for 9 h with monitoring by TLC analysis and passed through silica gel (0.5 g) in a Pasture pipette with EtOAc to remove catalyst. The eluent was evaporated under reduced pressure. The residue was purified by column chromatography (SiO_2 3.0 g, Hex/EtOAc = 5:1) to give (2*R*,3*R*)-**2c** (57.0 mg, 44% yield, 80% ee) and unreacted dibenzyl (2*S*,3*S*)-tartrate (54.0 mg, 55% yield, 59% ee).

***O*-Benzoyl dibenzyl (2*R*,3*R*)-tartrate (2c).**[27] TLC: R_f 0.28 (Hex/EtOAc = 3:1 stained blue with phosphomolybdic acid). HPLC (Daicel Chiralcel OD-H, Hex/^{i}PrOH = 9:1, 1.0 mL/min, 254 nm) t_R = 21.3 min (1*R*,2*R*), 26.4 min (1*S*,2*S*). The absolute configuration was determined according to the fact that dibenzyl (2*S*,3*S*)-tartrate was recovered mainly.

Dibenzyl (2*S*,3*S*)-tartrate.[23] TLC: R_f 0.17 (Hex/EtOAc = 3:1 stained blue with phosphomolybdic acid). ^{1}H NMR ($CDCl_3$) δ 7.41-7.30 (m, 10H), 5.29 (d, *J* = 12.0 Hz, 2H), 5.25 (d, *J* = 12.0 Hz, 2H), 4.61 (d, J = 6.9 Hz, 2H), 3.18 (d, *J* = 6.9 Hz, 2H). HPLC (Daicel Chiralpak AD, Hex/^{i}PrOH = 1:1, 1.0 mL/min, 220 nm) t_R = 10.4 min (1*S*,2*S*), 11.6 min (1*R*,2*R*). The absolute configuration was determined by comparison with the HPLC data of the commercially available dibenzyl (2*R*,3*R*)-tartrate.

ASSOCIATED CONTENT

Supporting Information

Competitive reactions between catechol and other phenols, tables for optimization of reaction conditions, determination of the absolute configuration of **4a**, experiments toward elucidation of catalytically active species, ^{1}H and ^{13}C NMR spectra of new compounds, and HPLC traces of optically active compounds (PDF). This Supporting Information is available free of charge on the ACS Publications website at DOI:

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