Kinetic Resolution of Secondary Alcohols by NHC-Catalyzed Oxidative Esterification

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Received 18 March 2011

Dedicated to Prof. Dieter Hoppe on the occasion of his 70th birthday

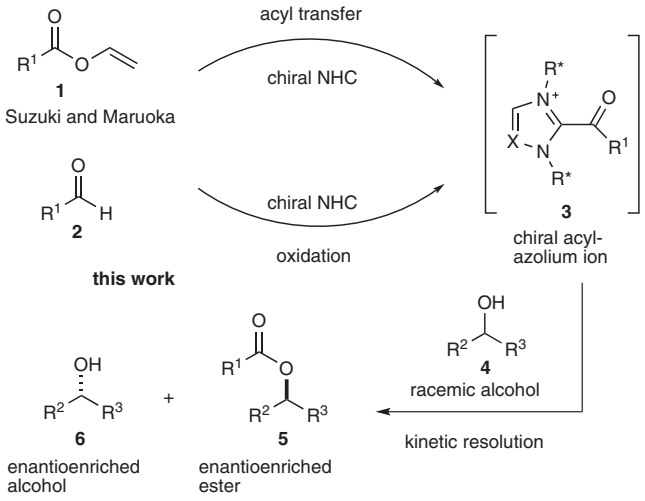
Abstract: Kinetic resolution of racemic secondary alcohols by oxidative esterification using carbene catalysis is described. Good to moderate selectivity has been achieved. N-Heterocyclic carbenes (NHCs) were systematically varied and several aldehydes were included in this study as acyl donors. As an oxidant, a readily available bisquinone-type system was used.

Key words: carbene catalysis, kinetic resolution, oxidative esterification, secondary alcohols, acylazolium ions

In recent years, a large number of catalysts based on small organic molecules have been prepared and successfully applied in a variety of transformations rendering the field 'organocatalysis'[1,2] one of the hottest areas in asymmetric catalysis. Along this line, N-heterocyclic carbenes (NHCs)[3] have become prominent candidates which allow catalyzation of a broad range of useful asymmetric transformations including the benzoin condensation,[4] the Stetter reaction,[5] conjugate umpolung or homoenolate reactions,[6] redox processes[7,8] and acyl-transfer reactions.[9]

The development of nonenzymatic catalysts for the kinetic resolution of racemic alcohols has been intensively investigated over the last decade;[10] however, the use of chiral NHCs in this context has not been well explored. Suzuki and co-workers reported the first example of a chiral NHC-catalyzed kinetic resolution of various 1-arylethanols.[11a] Their strategy is based on the generation of a chiral acylazolium ion[12] **3** by acyl transfer from a vinyl acetate **1** to a chiral NHC, and subsequent stereoselective acylation of the racemic alcohol **4** (Scheme 1).[13] The same approach was later used by Maruoka and co-workers who found that high selectivities can be achieved by using bulky vinyl esters.[11b]

We have recently explored the biomimetic oxidation of aldehydes by oxidative NHC catalysis applying external organic oxidants. Our efforts culminated in novel mild esterification, amidation and azidation protocols.[14] Based on these results, we envisioned the use of chiral acylazolium ions of type **3**, generated from the corresponding aldehydes **2** by oxidative NHC catalysis, as asymmetric acylating reagents for the kinetic resolution of chiral secondary alcohols (Scheme 1). To our knowledge, kinetic resolution by the acylation of racemic alcohols using an oxidative esterification approach has not been reported.[15]



Scheme 1 Catalytic generation and use of acylazolium ions as asymmetric acylating reagents

For optimization studies we chose the resolution of 1-(1-naphthyl)ethanol (**4a**) using cinnamaldehyde (**2a**) in combination with various chiral carbene precursors **7**–**13** as a test system (Figure 1, Table 1). The aldehyde **2a** (1 equiv) was reacted with an excess of racemic alcohol **4a** (3 equiv) in the presence of the triazolium salt (5 mol%), 1,8-diazabicyclo[5.4.0]undec-7-ene (10 mol%) and bisquinone oxidant **14**[16] in tetrahydrofuran as a solvent (Table 1). In contrast to most studies on kinetic resolutions where reactions using 1 equivalent of alcohol are stopped at lower conversions, esterifications were allowed to go to maximum conversion at room temperature (2 to 12 hours depending on the activity of the NHC). Ester **15a** was readily isolated and the enantiomeric excess (ee) was determined by chiral HPLC. This ee value cannot be used for calculation of the stereoselectivity factor (*S*-value) since reactions were not conducted under pseudo-first-order conditions in alcohol; however, the ee measured can be taken as a good estimate for the evaluation of the efficiency of the given NHC for the kinetic resolution of alcohol **4a**. For the most efficient system, we also ran reactions under pseudo-first-order conditions (large excess of alcohol, see below).

SYNTHESIS 2011, No. 12, pp 1974–1983
Advanced online publication: 06.05.2011
DOI: 10.1055/s-0030-1260030; Art ID: C30511SS

With catalyst **7**,[17] the ester **15a** was isolated in 84% yield and 14% ee within 2 hours (Table 1, entry 1). We found that the selectivity increased when switching from the *tert*-butyldimethylsilyl to the bulkier *tert*-butyldiphenylsilyl ether **8** (36% ee, 88% yield; Table 1, entry 2). The *S*-enantiomer was formed in excess.[18] Selectivity with bifunctional catalysts (i.e., **9**, **10**[19] and **11**[19]) was unsatisfactory (Table 1, entries 3–5) indicating that the additional functional group on the carbene does not influence selectivity to a large extent. Chiral amino alcohol derived triazolium salt **12**[20] provided a moderate selectivity (30% ee; Table 1, entry 6), whereas electron-deficient catalyst **13**[21] was found to be inefficient in the oxidative esterification under the applied conditions (Table 1, entry 7). Further optimization studies were conducted using catalyst **8**. We found that by lowering reaction temperature, and by using a stoichiometric amount of base, both ee and yield increased (Table 1, entries 8 and 9).

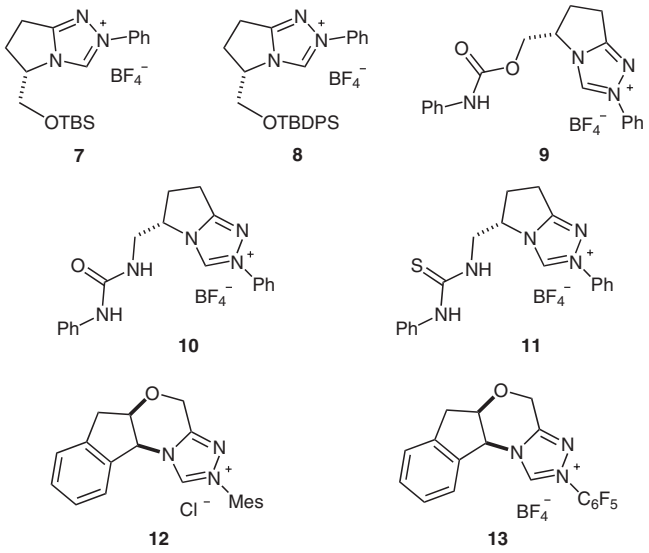
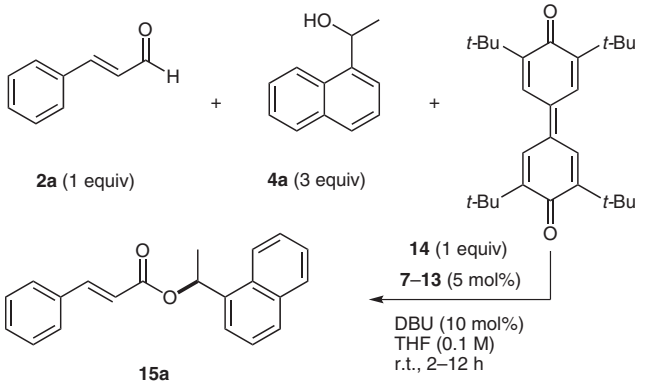


Figure 1 Chiral carbene precursors used for kinetic resolution

Table 1 Kinetic Resolution of 1-(1-Naphthyl)ethanol (**4a**) Using Various Carbene Precursors



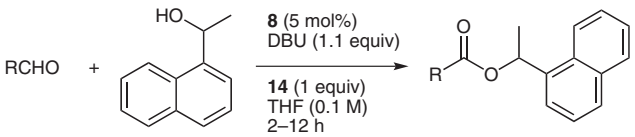
Entry	Catalyst	Time (h)	Yield[a] (%) of ester **15a**	ee[b] (%) of ester **15a**
1	**7**	2	84	14
2	**8**	2	88	36
3	**9**	6	72	7
4	**10**	6	85	24
5	**11**	6	80	14
6	**12**	6	78	30[c]
7	**13**	12	<5	n.d.[d]
8[e]	**8**	6	81	50
9[e,f]	**8**	6	98	52

[a] Isolated yield.
[b] Enantiomeric excess of the isolated product was determined using chiral HPLC. The absolute configuration of the major enantiomer was determined by comparing the HPLC retention time with that of an authentic sample.
[c] The other enantiomer was obtained as the major isomer.
[d] n.d. = not determined.
[e] Reaction performed at –20 °C.
[f] Using 1.1 equivalents of DBU.

We next studied the effect of the structure of the aldehyde on the kinetic resolution of alcohol **4a** using triazolium salt **8** as a precatalyst under the optimized reaction conditions to give esters **15b–i** and **16a** (Table 2). Electron-rich cinnamaldehyde derivative **2b** was found to be a good acyl donor at –20 °C and ester **15b** was isolated in 71% yield with 59% ee (Table 2, entry 1). Aliphatic enal **2c** delivered ester **15c** with moderate ee (Table 2, entry 2). Oxidative esterifications with benzaldehyde derivatives were performed at room temperature since they reacted very slowly at –20 °C (Table 2, entry 3). *para*-Substituted electron-poor aldehydes **2d** and **2e** showed moderate to low selectivity in the kinetic resolution of alcohol **4a** (Table 2, entries 4 and 5). With 2-bromobenzaldehyde (**2f**), the ester **15f** was isolated with a good selectivity (60% ee; Table 2, entry 6), whereas 2-methylbenzaldehyde (**2g**) provided a moderate result (37% ee; Table 2, entry 7). 3-Chlorobenzaldehyde (**2h**) and 2-naphthaldehyde (**2i**) showed similar activity and the products were isolated with moderate ee (Table 2, entries 8 and 9). As a summary of these screenings, we can state that α,β-unsaturated aldehydes are more reactive than the aromatic aldehydes for steric reasons, and best selectivity at room temperature was achieved with 2-bromobenzaldehyde.

To study the effect of the alcohol structure on the reaction, four different alcohols were reacted by oxidative esterification with cinnamaldehyde using catalyst **8** (Table 3). With 1-(2-naphthyl)ethanol (**4b**) at –20 °C, the ester **17b** was isolated in 73% yield with 43% ee (Table 3, entry 1). This selectivity is slightly lower than the selectivity obtained with 1-(1-naphthyl)ethanol (**4a**) (cf. Table 1, entry 8). The bulky aromatic naphthyl substituent is important for enantiotopic differentiation since 1-phenylethanol (**4c**) provided the ester **17c** with significantly lower selectivity (Table 3, entry 2). As expected, changing the electronic environment of the alcohol moiety by adding an electron-donating substituent at the *ortho* position did not lead to

Table 2 Kinetic Resolution of 1-(1-Naphthyl)ethanol (**4a**) Using Various Aldehydes



2b–j **4a** (3 equiv) **15b–i**, **16a**

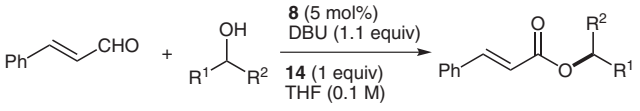
Entry	R	Conditions	Ester	Yield[a] (%)	ee[b] (%)
1	4-$MeOC_6H_4CH$=CH	–20 °C, 12 h	**15b**	71	59
2	*i*-PrCH=CH	–20 °C, 12 h	**15c**	61	35
3	4-$MeO_2CC_6H_4$	–20 °C, 12 h	**15d**	<5	n.d.[c]
4	4-$MeO_2CC_6H_4$	r.t., 2 h	**15d**	51	38
5	4-$O_2NC_6H_4$	r.t., 2 h	**15e**	67	14
6	2-BrC_6H_4	r.t., 12 h	**15f**	65	60
7	2-MeC_6H_4	r.t., 12 h	**15g**	59	37
8	3-ClC_6H_4	r.t., 12 h	**15h**	67	42
9	2-naphthyl	r.t., 12 h	**15i**	68	41
10	2-pyridyl	r.t., 2 h	**16a**	92	0

[a] Isolated yield.
[b] Enantiomeric excess of the isolated product was determined using chiral HPLC. The absolute configuration of the major isomer was not assigned.
[c] n.d. = not determined.

an increase in the selectivity (Table 3, entry 3), and also an increase in the size of the alkyl substituent of the secondary alcohol [see cyclohexyl(phenyl)methanol (**4e**); Table 3, entry 4] did not influence the reaction outcome to a large extent.

Interestingly, pyridine-2-carbaldehyde (**2j**), which turned out to deliver an inefficient acylazolium ion for kinetic resolution in combination with catalyst **8** (see Table 2, entry 10), showed higher selectivity in combination with carbene precursor **13** in the kinetic resolution of 1-(1-naphthyl)ethanol (57% ee; Table 4, entry 1). For this particular system, the ee was further increased when toluene was used as a solvent (63% ee; Table 4, entry 2). We therefore decided to test the resolution of other alcohols using aldehyde **2j** and catalyst **13** (Table 4); however, as for the aldehyde **2a**/catalyst **8** couple, for 1-(2-methoxyphenyl)ethanol (**4d**), and also for 1-phenylpropan-1-ol (**4f**), significantly lower selectivity was obtained (Table 4, entries 3 and 4). By increasing the steric bulk in the alcohol moiety, a slightly better resolution was achieved (Table 4, entry 5). The difficult kinetic resolution of diarylmethanols occurred with low selectivity (Table 4, entries 6–8).

Table 3 Kinetic Resolution of Various Alcohols by NHC-Catalyzed Cinnamoylation

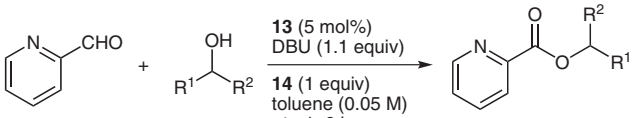


2a **4b–e** (3 equiv) **17b–e**

Entry	R^2	R^3	Conditions	Ester	Yield[a] (%)	ee[b] (%)
1	2-naphthyl	Me	–20 °C, 12 h	**17b**	73	43
2	Ph	Me	r.t., 6 h	**17c**	56	10
3	2-$MeOC_6H_4$	Me	r.t., 12 h	**17d**	59	10
4	Ph	Cy	–20 °C, 12 h	**17e**	50	19

[a] Isolated yield.
[b] Enantiomeric excess of the isolated product was determined using chiral HPLC. The absolute configuration was assigned by analogy to **15a**.

Table 4 Kinetic Resolution of Various Alcohols Using Pyridine-2-carbaldehyde (**2j**) as the Acyl Source



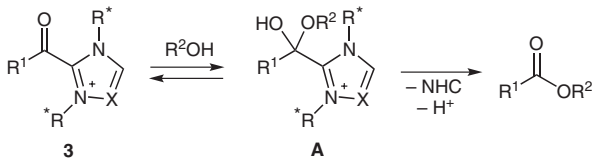
2j **4** (3 equiv) **16**

Entry	R^2	R^3	Time (h)	Ester	Yield[a] (%)	ee[b] (%)
1[c]	1-naphthyl	Me	1	**16a**	76	57
2	1-naphthyl	Me	3	**16a**	80	63
3	2-$MeOC_6H_4$	Me	4	**16d**	78	15
4	Ph	Et	4	**16f**	83	20
5	Ph	*t*-Bu	4	**16g**	40	30
6	2-BrC_6H_4	Ph	2	**16h**	87	35
7	2-MeC_6H_4	Ph	3	**16i**	77	11
8	1-naphthyl	Ph	6	**16j**	50	7

[a] Isolated yield.
[b] Enantiomeric excess of the isolated product was determined using chiral HPLC. For **16a**, the absolute configuration of the major isomer is *S* and was determined by comparing the HPLC retention time with that of an authentic sample. For the other products, the absolute configuration was not assigned.
[c] Reaction conducted in THF.

The mechanism of the acylation of a secondary alcohol with a chiral acylazolium ion **3** is a two-step process (Scheme 2). The alcohol first reacts with ion **3** to give adduct **A**. This step is likely reversible.[22] Moreover, we have shown by DFT calculations that free carbenes activate alcohols by strong hydrogen-bonding interactions.[14b] Hence, a second carbene is probably involved in adduct formation. The rate-determining step might be the fragmentation of **A** to liberate the carbene and the product ester.[22] Considering the effect of the free carbene on adduct formation and the pre-equilibrium, the equation (Equation 1) suggested by Kagan and Fiaud that is usually

applied for calculation of the *S*-value should not be valid (C = conversion, ee = enantiomeric excess of the product).[23]



Scheme 2 Suggested mechanism

$$S = \frac{\ln[1 - C(1 + ee)]}{\ln[1 - C(1 - ee)]}$$

Equation 1

Indeed, running the reaction of aldehyde **2b** with 1-(1-naphthyl)ethanol (**4a**, 1 equiv) at –20 °C until 20% conversion provided ester **15b** with 48% ee. According to equation 1 this leads to an *S*-value of 3.2 which is significantly lower than expected based on the experiment using 3 equivalents of alcohol (not pseudo first order) described in Table 2 (entry 1, 59% ee at 71% conversion; assuming pseudo first order in alcohol, this would lead to an *S*-value of 3.9). We therefore repeated experiments with an even larger excess of racemic alcohol **4a** while keeping the aldehyde concentration constant. When a large excess of the alcohol is used, reaction occurs under pseudo-first-order conditions with respect to the alcohol and the ee of the product ester, irrespective of the conversion, reflects the *S*-value. With 10 equivalents of *rac*-**4a** at 92% conversion, the ester was isolated with 68% ee (*S*-value = 5.3); with 15 equivalents the ee further increased to 73% (*S*-value = 6.4), and with 25 equivalents the ee was raised to 76% (*S*-value = 7.3). No further increase in selectivity was observed when the amount of alcohol was increased to 50 equivalents. Hence, in these systems the selectivity factor *S* varies as a function of the initial alcohol concentration and the best selectivities are obtained by using a large excess of the alcohol under pseudo-first-order conditions.

In conclusion, we have presented an application of oxidative esterification for the kinetic resolution of secondary alcohols employing various chiral carbenes. The key intermediate chiral acylazolium ion is generated oxidatively by using an aldehyde as the acyl source. Although the selectivities are currently moderate, we expect that further modification of the carbene structure will lead to the development of an efficient catalyst for the kinetic resolution using our oxidative esterification protocol.

All reactions were carried out in heat-gun-dried glassware under an argon atmosphere. THF was freshly distilled from potassium under argon. All other solvents and reagents, including alcohols **4e**,[24] **4h**[25] and **4j**,[26] were purified according to standard procedures or were used as received from Aldrich, Acros, ABCR or Fluka. 1,3-Dimethyltriazolium iodide[27] was used to prepare racemic samples. ^{1}H and ^{13}C NMR spectroscopy was conducted on a Bruker DPX 300 instrument at 300 K. For flash column chromatography, Merck or Fluka silica gel 60 (40–63 μm) was used at approximately 0.4 bar. Infrared spectra were recorded on a Varian FT-IR 3100 Excalibur or a Shimadzu FTIR 8400S spectrophotometer. Mass spectra were recorded on a Bruker Daltonics MicroTOF (ESI) instrument. A Hewlett Packard Binary Pump System with a Hewlett Packard Series 1100 ChemStation for LC was used for HPLC analysis. The column, eluent and retention times used for the determination of enantiomer ratios are given with the details of the relevant experiment. Full characterization is provided for previously unknown compounds.

Preparation of the Chiral Triazolium Salts 8 and 9

(*S*)-5-[(*tert*-Butyldiphenylsilyloxy)methyl]-2-phenyl-6,7-dihydro-5*H*-pyrrolo[2,1-*c*][1,2,4]triazol-2-ium Tetrafluoroborate (8)

Trimethyloxonium tetrafluoroborate (320 mg, 2.2 mmol) was added to a soln of (*S*)-5-[(*tert*-butyldiphenylsilyloxy)methyl]pyrrolidin-2-one[28] (0.7 g, 2.0 mmol) in CH_2Cl_2 (8 mL) at r.t. and the mixture was stirred overnight. Then, phenylhydrazine (238 mg, 2.2 mmol) was added and the mixture was allowed to stir at r.t. for 12 h. The solvent was removed under reduced pressure; the product was used without further purification. Trimethyl orthoformate (20 mL) was added and the mixture was refluxed for an additional 12 h. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (CH_2Cl_2–MeOH, 50:1) to afford **8** as a yellow solid; yield: 904 mg (83%).

FTIR (neat): 3132, 3073, 2957, 2934, 2889, 2859, 2360, 1684, 1590, 1470, 1429, 1391, 1106, 1053, 1026, 857, 824, 762, 745, 703, 688 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.43 (s, 1 H), 7.66–7.58 (m, 2 H), 7.50–7.43 (m, 3 H), 7.43–7.34 (m, 3 H), 7.30–7.22 (m, 3 H), 7.22–7.09 (m, 4 H), 5.08–5.04 (m, 1 H), 4.35–4.26 (m, 1 H), 3.97–3.88 (m, 1 H), 3.26–3.05 (m, 2 H), 3.01–2.83 (m, 1 H), 2.77–2.63 (m, 1 H), 0.92 (s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 163.2, 136.4, 135.6, 135.5, 135.4, 132.3, 132.0, 130.8, 130.4, 130.4, 130.2, 128.2, 128.1, 120.8, 64.8, 62.2, 29.7, 27.0, 22.4, 19.2.

HRMS (ESI): *m*/*z* [M]$^+$ calcd for $C_{28}H_{32}N_3OSi$: 454.2309; found: 454.2303.

(*S*)-(5-Oxopyrrolidin-2-yl)methyl Phenylcarbamate

Phenyl isocyanate (655 mg, 5.5 mmol) and a catalytic amount of pyridine were added to a soln of (*S*)-5-(hydroxymethyl)pyrrolidin-2-one (575 mg, 5.0 mmol) in THF (20 mL) at r.t. The resulting mixture was refluxed for 24 h. Solvent was removed under reduced pressure and the crude product was purified by column chromatography (MTBE–MeOH, 20:1) to afford the title compound as a white solid; yield: 602 mg (52%).

FTIR (neat): 3300, 2225, 1714, 1655, 1236, 727 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.02 (s, 1 H), 7.57 (s, 1 H), 7.44–7.28 (m, 2 H), 7.25–7.13 (m, 2 H), 7.01–6.89 (m, 1 H), 4.14–4.09 (m, 1 H), 3.95–3.75 (m, 2 H), 2.37–1.99 (m, 3 H), 1.76–1.58 (m, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 179.0, 153.5, 138.2, 129.0, 123.3, 118.8, 67.5, 53.5, 30.0, 22.8.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{12}H_{14}N_2O_3Na$: 257.0897; found: 257.0892.

(*S*)-2-Phenyl-5-[(phenylcarbamoyloxy)methyl]-6,7-dihydro-5*H*-pyrrolo[2,1-*c*][1,2,4]triazol-2-ium Tetrafluoroborate (9)

A flame-dried 25-mL round-bottom Schlenk flask was charged with (*S*)-(5-oxopyrrolidin-2-yl)methyl phenylcarbamate (234 mg, 1.0 mmol) and CH_2Cl_2 (8 mL). Trimethyloxonium tetrafluoroborate

(163 mg, 1.1 mmol) was added and the mixture was stirred at r.t. overnight. Then, phenylhydrazine (119 mg, 1.1 mmol) was added and the mixture was allowed to stir at r.t. for 24 h. The solvent was removed under reduced pressure; the product was used without further purification. MeOH (1 mL) and trimethyl orthoformate (10 mL) were added and the mixture was refluxed for an additional 24 h. The solvent was removed under reduced pressure. Crystallization from hot MeOH afforded **9** as a colorless crystalline solid; yield: 200 mg (47%).

FTIR (neat): 3382, 3152, 2361, 1738, 1595, 1540, 1214, 1074, 1022, 761 cm^{-1}.

^1H NMR (300 MHz, CD_3CN): δ = 9.80 (s, 1 H), 8.03 (s, 1 H), 7.88–7.77 (m, 2 H), 7.74–7.59 (m, 3 H), 7.52–7.40 (m, 2 H), 7.38–7.25 (m, 2 H), 7.14–7.03 (m, 1 H), 5.15–4.99 (m, 1 H), 4.68 (dd, *J* = 11.8, 3.4 Hz, 1 H), 4.22 (dd, *J* = 11.8, 8.3 Hz, 1 H), 3.41–3.16 (m, 2 H), 3.10–2.95 (m, 1 H), 2.71–2.57 (m, 1 H).

^{13}C NMR (75 MHz, CD_3CN): δ = 164.1, 153.6, 139.4, 138.5, 136.7, 132.1, 131.3, 130.1, 124.4, 122.4, 119.6, 65.2, 60.9, 30.1, 22.3.

HRMS (ESI): *m*/*z* $[M]^+$ calcd for $C_{19}H_{19}N_4O_2$: 335.1503; found: 335.1512.

Procedure for the Catalyst Screening Experiments (Table 1)

DBU (10 mol%) was added to a soln of a chiral triazolium salt **7**–**13** (5 mol%) in THF (0.1 M) under argon atmosphere. The mixture was stirred for 5 min, then 1-(1-naphthyl)ethanol (**4a**, 3.0 equiv) and 3,3′,5,5′-tetra-*tert*-butyldiphenoquinone (**14**, 1.0 equiv) were added. After the mixture was stirred for 5 min, (*E*)-cinnamaldehyde (**2a**, 1 equiv) was added. The resulting solution was stirred at r.t. for 2–6 h. The solvent was removed under reduced pressure and the residue was purified by flash silica gel column chromatography (pentane–Et_2O, 50:1 to 20:1).

General Procedure (GP I) for the Kinetic Resolution of Secondary Alcohols Using Catalyst 8 (Tables 2 and 3)

DBU (10 mol% or 1.1 equiv) was added to a soln of triazolium salt **8** (5 mol%) in THF (0.1 M) under argon atmosphere. The mixture was stirred for 5 min, then an alcohol **4a**–**e** (3.0 equiv) and 3,3′,5,5′-tetra-*tert*-butyldiphenoquinone (**14**, 1.0 equiv) were added. After the mixture was stirred for 5 min, an aldehyde **2a**–**j** (1 equiv) was added at r.t. or –20 °C. The resulting solution was stirred for 2–12 h at that temperature. The solvent was removed under reduced pressure and the residue was purified by flash silica gel column chromatography (pentane–Et_2O).

1-(1-Naphthyl)ethyl (*E*)-Cinnamate (15a)

According to GP I with (*E*)-cinnamaldehyde (**2a**; 66 mg, 0.5 mmol), DBU (83 mg, 0.55 mmol), catalyst **8** (13.5 mg, 25 μmol), 1-(1-naphthyl)ethanol (**4a**; 258 mg, 1.5 mmol) and 3,3′,5,5′-tetra-*tert*-butyldiphenoquinone (**14**; 205 mg, 500 μmol) in THF (5.0 mL) at –20 °C for 6 h and silica gel chromatography (pentane–Et_2O, 50:1 to 20:1) to afford **15a** as a light yellow solid; yield: 148 mg (98%).

FTIR (neat): 3415, 3055, 2980, 2935, 2361, 2340, 1714, 1639, 1338, 1317, 1167, 1074, 1005, 798, 768 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.17 (d, *J* = 8.5 Hz, 1 H), 7.90 (d, *J* = 9.5 Hz, 1 H), 7.83 (d, *J* = 8.2 Hz, 1 H), 7.76 (d, *J* = 16.0 Hz, 1 H), 7.69 (d, *J* = 6.8 Hz, 1 H), 7.62–7.46 (m, 5 H), 7.44–7.34 (m, 3 H), 6.81 (q, *J* = 6.6 Hz, 1 H), 6.54 (d, *J* = 16.0 Hz, 1 H), 1.81 (d, *J* = 6.6 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.4, 145.2, 137.6, 134.6, 134.0, 130.5, 130.4, 129.0, 129.0, 128.6, 128.2, 126.5, 125.8, 125.5, 123.4, 118.5, 69.7, 30.5, 21.9.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{21}H_{18}O_2Na$: 325.1199; found: 325.1195.

The enantiomeric excess (52%) was determined by chiral HPLC; column: Chiralcel OD-H; solvent: cyclohexane–*i*-PrOH (99.5:0.5); flow: 1.0 mL/min; major enantiomer t_R = 17.6 min, minor enantiomer t_R = 33.6 min. The absolute configuration of the major enantiomer was determined by comparing the HPLC retention time with that of an authentic sample.

1-(1-Naphthyl)ethyl (*E*)-3-(4-Methoxyphenyl)acrylate (15b)

According to GP I with (*E*)-3-(4-methoxyphenyl)acrylaldehyde (**2b**; 41 mg, 0.25 mmol), DBU (42 mg, 0.28 mmol), catalyst **8** (6.8 mg, 12.5 μmol), 1-(1-naphthyl)ethanol (**4a**; 129 mg, 750 μmol) and 3,3′,5,5′-tetra-*tert*-butyldiphenoquinone (**14**; 102 mg, 250 μmol) in THF (2.5 mL) at –20 °C for 12 h and silica gel chromatography (pentane–Et_2O, 9:1) to afford **15b** as a light yellow solid; yield: 59 mg (71%).

FTIR (neat): 2977, 1703, 1600, 1509, 1249, 1157, 1032, 780 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.17 (d, *J* = 8.3 Hz, 1 H), 7.93–7.86 (m, 1 H), 7.82 (d, *J* = 8.2 Hz, 1 H), 7.75–7.67 (m, 2 H), 7.60–7.45 (m, 5 H), 6.90 (d, *J* = 8.8 Hz, 2 H), 6.80 (q, *J* = 6.5 Hz, 1 H), 6.41 (d, *J* = 15.9 Hz, 1 H), 3.83 (s, 3 H), 1.80 (d, *J* = 6.6 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.5, 161.4, 144.7, 137.6, 133.9, 130.4, 129.7, 128.9, 128.4, 127.2, 126.3, 125.6, 125.4, 123.3, 123.2, 115.8, 114.3, 69.3, 55.3, 21.7.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{22}H_{20}O_3Na$: 355.1305; found: 355.1308.

The enantiomeric excess (59%) was determined by chiral HPLC; column: Chiralpak AD-H; solvent: cyclohexane–*i*-PrOH (99.0:1.0); flow: 1.0 mL/min; major enantiomer t_R = 45.7 min, minor enantiomer t_R = 26.2 min. The absolute configuration of the major enantiomer was not assigned.

1-(1-Naphthyl)ethyl (*E*)-4-Methylpent-2-enoate (15c)

According to GP I with (*E*)-4-methylpent-2-enal (**2c**; 25 mg, 0.25 mmol), DBU (42 mg, 0.28 mmol), catalyst **8** (6.8 mg, 12.5 μmol), 1-(1-naphthyl)ethanol (**4a**; 129 mg, 750 μmol) and 3,3′,5,5′-tetra-*tert*-butyldiphenoquinone (**14**; 102 mg, 250 μmol) in THF (2.5 mL) at –20 °C for 12 h and silica gel chromatography (pentane–Et_2O, 100:1 to 20:1) to afford **15c** as a light yellow oil; yield: 41 mg (61%).

FTIR (neat): 2963, 1715, 1650, 1455, 1263, 1166, 1065, 980, 781 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.13 (d, *J* = 8.3 Hz, 1 H), 7.91–7.84 (m, 1 H), 7.81 (d, *J* = 8.2 Hz, 1 H), 7.64 (d, *J* = 7.0 Hz, 1 H), 7.59– 7.43 (m, 3 H), 7.02 (dd, *J* = 15.7, 6.5 Hz, 1 H), 6.73 (q, *J* = 6.6 Hz, 1 H), 5.86 (dd, *J* = 15.7, 1.4 Hz, 1 H), 2.47 (dqd, *J* = 13.7, 6.8, 1.4 Hz, 1 H), 1.74 (d, *J* = 6.6 Hz, 3 H), 1.07 (d, *J* = 6.8 Hz, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.3, 155.9, 137.6, 133.8, 130.3, 128.8, 128.4, 126.2, 125.6, 125.3, 123.3, 123.2, 118.7, 69.2, 30.9, 21.7, 21.2.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{18}H_{20}O_2Na$: 291.1356; found: 291.1363.

The enantiomeric excess (35%) was determined by chiral HPLC; column: Chiralpak AD-H; solvent: cyclohexane–*i*-PrOH (99.5:0.5); flow: 1.0 mL/min; major enantiomer t_R = 10.7 min, minor enantiomer t_R = 7.2 min. The absolute configuration of the major enantiomer was not assigned.

Methyl 1-(1-Naphthyl)ethyl Terephthalate (15d)

According to GP I with methyl 4-formylbenzoate (**2d**; 82 mg, 0.5 mmol), DBU (83 mg, 0.55 mmol), catalyst **8** (13.5 mg, 25 μmol), 1-(1-naphthyl)ethanol (**4a**; 258 mg, 1.5 mmol) and 3,3′,5,5′-tetra-*tert*-butyldiphenoquinone (**14**; 205 mg, 500 μmol) in THF (5.0 mL) at

r.t. for 2 h and silica gel chromatography (pentane–Et_2O, 50:1 to 20:1) to afford **15d** as a light yellow solid; yield: 85 mg (51%).

FTIR (neat): 3422, 2954, 2937, 2392, 2294, 1716, 1597, 1577, 1442, 1275, 1113, 1099, 1070, 800, 778, 730 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.30–8.05 (m, 5 H), 7.95–7.78 (m, 2 H), 7.70 (d, *J* = 6.9 Hz, 1 H), 7.61–7.42 (m, 3 H), 6.90 (q, *J* = 6.6 Hz, 1 H), 3.95 (s, 3 H), 1.86 (d, *J* = 6.6 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.4, 165.2, 137.3, 134.4, 134.1, 134.0, 130.4, 129.8, 129.7, 129.1, 128.8, 126.6, 125.9, 125.5, 123.5, 123.3, 71.0, 52.5, 22.0.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{21}H_{18}O_4Na$: 357.1097; found: 357.1090.

The enantiomeric excess (38%) was determined by chiral HPLC; column: Chiralpak AD-H; solvent: cyclohexane–*i*-PrOH (99.5:0.5); flow: 1.0 mL/min; major enantiomer t_R = 17.9 min, minor enantiomer t_R = 19.6 min. The absolute configuration of the major enantiomer was not assigned.

1-(1-Naphthyl)ethyl 4-Nitrobenzoate (15e)

According to GP I with 4-nitrobenzaldehyde (**2e**; 76 mg, 0.5 mmol), DBU (83 mg, 0.55 mmol), catalyst **8** (13.5 mg, 25 μmol), 1-(1-naphthyl)ethanol (**4a**; 258 mg, 1.5 mmol) and 3,3′,5,5′-tetra-*tert*-butyldiphenoquinone (**14**; 205 mg, 500 μmol) in THF (5.0 mL) at r.t. for 2 h and silica gel chromatography (pentane–Et_2O, 50:1 to 20:1) to afford **15e** as a yellow oil; yield: 108 mg (67%).

FTIR (neat): 3054, 2985, 2389, 2349, 2280, 1720, 1604, 1525, 1268, 1101, 777, 718 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.31–8.22 (m, 4 H), 8.18 (d, *J* = 8.4 Hz, 1 H), 7.94–7.81 (m, 2 H), 7.70 (d, *J* = 6.9 Hz, 1 H), 7.62–7.47 (m, 3 H), 6.93 (q, *J* = 6.6 Hz, 1 H), 1.90 (d, *J* = 6.6 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.1, 150.7, 136.9, 136.0, 134.0, 131.0, 129.2, 129.0, 126.7, 126.0, 125.5, 123.7, 123.5, 123.1, 71.6, 21.9.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{19}H_{15}NO_4Na$: 344.0893; found: 344.0889.

The enantiomeric excess (14%) was determined by chiral HPLC; column: Chiralpak AD-H; solvent: cyclohexane–*i*-PrOH (99.5:0.5); flow: 1.0 mL/min; major enantiomer t_R = 16.4 min, minor enantiomer t_R = 14.5 min. The absolute configuration of the major enantiomer was not assigned.

1-(1-Naphthyl)ethyl 2-Bromobenzoate (15f)

According to GP I with 2-bromobenzaldehyde (**2f**; 46.3 mg, 0.25 mmol), DBU (42 mg, 0.28 mmol), catalyst **8** (6.8 mg, 12.5 μmol), 1-(1-naphthyl)ethanol (**4a**; 129 mg, 750 μmol) and 3,3′,5,5′-tetra-*tert*-butyldiphenoquinone (**14**; 102 mg, 250 μmol) in THF (2.5 mL) at r.t. for 12 h and silica gel chromatography (pentane–Et_2O, 100:1 to 50:1) to afford **15f** as a viscous yellow oil; yield: 58 mg (65%).

FTIR (neat): 3057, 1725, 1591, 1437, 1250, 1112, 1034, 746 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.12 (d, *J* = 8.4 Hz, 1 H), 7.82 (d, *J* = 8.3 Hz, 1 H), 7.79–7.71 (m, 2 H), 7.66 (d, *J* = 7.1 Hz, 1 H), 7.63–7.57 (m, 1 H), 7.55–7.37 (m, 3 H), 7.32–7.17 (m, 2 H), 6.87 (q, *J* = 6.6 Hz, 1 H), 1.81 (d, *J* = 6.6 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.5, 137.0, 134.3, 133.8, 132.5, 132.4, 131.3, 130.3, 128.9, 128.6, 127.1, 126.4, 125.7, 125.4, 123.5, 123.2, 121.7, 71.1, 21.7.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{19}H_{15}BrO_2Na$: 377.0148; found: 377.0153.

The enantiomeric excess (60%) was determined by chiral HPLC; column: Chiralpak AD-H; solvent: cyclohexane–*i*-PrOH (99.5:0.5); flow: 1.0 mL/min; major enantiomer t_R = 10.3 min, minor enantiomer t_R = 7.1 min. The absolute configuration of the major enantiomer was not assigned.

1-(1-Naphthyl)ethyl 2-Methylbenzoate (15g)

According to GP I with 2-methylbenzaldehyde (**2g**; 30 mg, 0.25 mmol), DBU (42 mg, 0.28 mmol), catalyst **8** (6.8 mg, 12.5 μmol), 1-(1-naphthyl)ethanol (**4a**; 129 mg, 750 μmol) and 3,3′,5,5′-tetra-*tert*-butyldiphenoquinone (**14**; 102 mg, 250 μmol) in THF (2.5 mL) at r.t. for 12 h and silica gel chromatography (pentane–Et_2O, 100:1 to 50:1) to afford **15g** as a yellow oil; yield: 43 mg (59%).

FTIR (neat): 2977, 1702, 1598, 1448, 1248, 1071, 862, 740 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.18 (d, *J* = 8.4 Hz, 1 H), 7.99 (d, *J* = 7.6 Hz, 1 H), 7.87 (d, *J* = 7.9 Hz, 1 H), 7.80 (d, *J* = 8.2 Hz, 1 H), 7.69 (d, *J* = 7.1 Hz, 1 H), 7.59–7.43 (m, 3 H), 7.38 (t, *J* = 7.4 Hz, 1 H), 7.24 (t, *J* = 7.2 Hz, 2 H), 6.89 (q, *J* = 6.6 Hz, 1 H), 2.59 (s, 3 H), 1.83 (d, *J* = 6.6 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.8, 140.3, 137.6, 133.9, 131.9, 131.7, 130.6, 130.3, 129.9, 128.9, 128.4, 126.3, 125.7, 125.7, 125.4, 123.2, 123.2, 69.9, 21.9, 21.7.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{20}H_{18}O_2Na$: 313.1199; found: 313.1202.

The enantiomeric excess (37%) was determined by chiral HPLC; column: Chiralpak AD-H; solvent: cyclohexane–*i*-PrOH (99.5:0.5); flow: 1.0 mL/min; major enantiomer t_R = 7.0 min, minor enantiomer t_R = 5.4 min. The absolute configuration of the major enantiomer was not assigned.

1-(1-Naphthyl)ethyl 3-Chlorobenzoate (15h)

According to GP I with 3-chlorobenzaldehyde (**2h**; 35 mg, 0.25 mmol), DBU (42 mg, 0.28 mmol), catalyst **8** (6.8 mg, 12.5 μmol), 1-(1-naphthyl)ethanol (**4a**; 129 mg, 750 μmol) and 3,3′,5,5′-tetra-*tert*-butyldiphenoquinone (**14**; 102 mg, 250 μmol) in THF (2.5 mL) at r.t. for 12 h and silica gel chromatography (pentane–Et_2O, 100:1 to 50:1) to afford **15h** as a yellow oil; yield: 52 mg (67%).

FTIR (neat): 3064, 1719, 1576, 1426, 1254, 1125, 1072, 902, 743, 630 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.18 (d, *J* = 8.3 Hz, 1 H), 8.09 (s, 1 H), 8.00 (d, *J* = 7.8 Hz, 1 H), 7.90 (d, *J* = 7.9 Hz, 1 H), 7.84 (d, *J* = 8.2 Hz, 1 H), 7.70 (d, *J* = 7.1 Hz, 1 H), 7.62–7.46 (m, 4 H), 7.38 (t, *J* = 7.9 Hz, 1 H), 6.91 (q, *J* = 6.6 Hz, 1 H), 1.86 (d, *J* = 6.6 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.6, 137.2, 134.5, 133.9, 133.0, 132.2, 130.3, 129.7, 129.7, 129.0, 128.6, 127.8, 126.4, 125.7, 125.4, 123.3, 123.1, 70.7, 21.8.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{19}H_{15}ClO_2Na$: 333.0653; found: 333.0654.

The enantiomeric excess (42%) was determined by chiral HPLC; column: Chiralpak AD-H; solvent: cyclohexane–*i*-PrOH (99.5:0.5); flow: 1.0 mL/min; major enantiomer t_R = 8.3 min, minor enantiomer t_R = 7.1 min. The absolute configuration of the major enantiomer was not assigned.

1-(1-Naphthyl)ethyl 2-Naphthoate (15i)

According to GP I with 2-naphthaldehyde (**2i**; 39 mg, 0.25 mmol), DBU (42 mg, 0.28 mmol), catalyst **8** (6.8 mg, 12.5 μmol), 1-(1-naphthyl)ethanol (**4a**; 129 mg, 750 μmol) and 3,3′,5,5′-tetra-*tert*-butyldiphenoquinone (**14**; 102 mg, 250 μmol) in THF (2.5 mL) at r.t. for 12 h and silica gel chromatography (pentane–Et_2O, 50:1 to 20:1) to afford **15i** as a light yellow solid; yield: 55 mg (68%).

FTIR (neat): 3050, 1712, 1628, 1507, 1445, 1355, 1271, 1222, 1086, 977, 766 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.69 (s, 1 H), 8.25 (d, *J* = 8.4 Hz, 1 H), 8.14 (dd, *J* = 8.6, 1.5 Hz, 1 H), 7.97 (d, *J* = 7.7 Hz, 1 H), 7.93–

7.86 (m, 3 H), 7.84 (d, *J* = 8.3 Hz, 1 H), 7.78 (d, *J* = 7.0 Hz, 1 H), 7.63–7.47 (m, 5 H), 6.97 (q, *J* = 6.5 Hz, 1 H), 1.91 (d, *J* = 6.6 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.0, 137.6, 135.6, 133.9, 132.5, 131.2, 130.4, 129.4, 128.9, 128.5, 128.2, 128.2, 127.8, 126.6, 126.4, 125.7, 125.4, 125.4, 123.3, 123.3, 70.4, 21.9.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{23}H_{18}O_2Na$: 349.1199; found: 349.1200.

The enantiomeric excess (41%) was determined by chiral HPLC; column: Chiralcel OD-H; solvent: cyclohexane–*i*-PrOH (99.5:0.5); flow: 1.0 mL/min; major enantiomer t_R = 11.7 min, minor enantiomer t_R = 15.6 min. The absolute configuration of the major enantiomer was not assigned.

1-(2-Naphthyl)ethyl (*E*)-Cinnamate (17b)

According to GP I with (*E*)-cinnamaldehyde (**2a**; 33 mg, 0.25 mmol), DBU (42 mg, 0.28 mmol), catalyst **8** (6.8 mg, 12.5 μmol), 1-(2-naphthyl)ethanol (**4b**; 129 mg, 750 μmol) and 3,3′,5,5′-tetra-*tert*-butyldiphenoquinone (**14**; 102 mg, 250 μmol) in THF (2.5 mL) at –20 °C for 12 h and silica gel chromatography (pentane–Et_2O, 100:1 to 20:1) to afford **17b** as a yellow oil; yield: 55 mg (73%).

FTIR (neat): 3056, 2981, 1710, 1636, 1500, 1449, 1307, 1268, 1168, 1062, 984, 861 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.91–7.82 (m, 4 H), 7.78–7.70 (m, 1 H), 7.59–7.46 (m, 5 H), 7.42–7.36 (m, 3 H), 6.53 (d, *J* = 16.0 Hz, 1 H), 6.21 (q, *J* = 6.6 Hz, 1 H), 1.72 (d, *J* = 6.6 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.2, 144.9, 139.1, 134.5, 133.2, 133.1, 130.3, 128.9, 128.4, 128.1, 128.0, 127.7, 126.2, 126.0, 125.0, 124.1, 118.4, 72.5, 22.2.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{21}H_{18}O_2Na$: 325.1199; found: 325.1198.

The enantiomeric excess (43%) was determined by chiral HPLC; column: Chiralpak AD-H; solvent: cyclohexane–*i*-PrOH (99.5:0.5); flow: 1.0 mL/min; major enantiomer t_R = 39.2 min, minor enantiomer t_R = 17.2 min. The absolute configuration of the major enantiomer was determined by analogy to **15a**.

1-Phenylethyl (*E*)-Cinnamate (17c)

According to GP I with (*E*)-cinnamaldehyde (**2a**; 66 mg, 0.5 mmol), DBU (83 mg, 0.55 mmol), catalyst **8** (13.5 mg, 25 μmol), 1-phenylethanol (**4c**; 183 mg, 1.5 mmol) and 3,3′,5,5′-tetra-*tert*-butyldiphenoquinone (**14**; 205 mg, 500 μmol) in THF (5.0 mL) at r.t. for 6 h and silica gel chromatography (pentane–Et_2O, 50:1 to 20:1) to afford **17c** as a yellow oil; yield: 71 mg (56%).

The physical data are in agreement with those reported in the literature.[29]

The enantiomeric excess (10%) was determined by chiral HPLC; column: Chiralcel OD-H; solvent: cyclohexane–*i*-PrOH (99.5:0.5); flow: 1.0 mL/min; major enantiomer t_R = 9.7 min, minor enantiomer t_R = 27.9 min. The absolute configuration of the major enantiomer was determined by analogy to **15a**.

1-(2-Methoxyphenyl)ethyl (*E*)-Cinnamate (17d)

According to GP I with (*E*)-cinnamaldehyde (**2a**; 66 mg, 0.5 mmol), DBU (83 mg, 0.55 mmol), catalyst **8** (13.5 mg, 25 μmol), 1-(2-methoxyphenyl)ethanol (**4d**; 228 mg, 1.5 mmol) and 3,3′,5,5′-tetra-*tert*-butyldiphenoquinone (**14**; 205 mg, 500 μmol) in THF (5.0 mL) at r.t. for 12 h and silica gel chromatography (pentane–Et_2O, 50:1 to 20:1) to afford **17d** as a yellow oil; yield: 83 mg (59%).

FTIR (neat): 3061, 3031, 2982, 2937, 2838, 2252, 1709, 1638, 1494, 1451, 1245, 1172, 1065, 755, 733, 632 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.63 (d, *J* = 16.0 Hz, 1 H), 7.50–7.39 (m, 2 H), 7.38–7.25 (m, 4 H), 7.23–7.13 (m, 1 H), 6.89 (m, 1 H), 6.79 (d, *J* = 8.2 Hz, 1 H), 6.42 (d, *J* = 16.0 Hz, 1 H), 6.30 (q, *J* = 6.5 Hz, 1 H), 3.76 (s, 3 H), 1.48 (d, *J* = 6.5 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.2, 156.2, 144.7, 134.7, 130.6, 130.3, 129.0, 128.7, 128.2, 126.0, 120.8, 118.8, 110.7, 67.5, 55.6, 21.35.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{18}H_{18}O_3Na$: 305.1148; found: 305.1148.

The enantiomeric excess (10%) was determined by chiral HPLC; column: Chiralcel OD-H; solvent: cyclohexane–*i*-PrOH (99.5:0.5); flow: 1.0 mL/min; major enantiomer t_R = 18.2 min, minor enantiomer t_R = 22.7 min. The absolute configuration of the major enantiomer was determined by analogy to **15a**.

Cyclohexyl(phenyl)methyl (*E*)-Cinnamate (17e)

According to GP I with (*E*)-cinnamaldehyde (**2a**; 33 mg, 0.25 mmol), DBU (42 mg, 0.28 mmol), catalyst **8** (6.8 mg, 12.5 μmol), cyclohexyl(phenyl)methanol (**4e**; 143 mg, 750 μmol) and 3,3′,5,5′-tetra-*tert*-butyldiphenoquinone (**14**; 102 mg, 250 μmol) in THF (2.5 mL) at –20 °C for 12 h and silica gel chromatography (pentane–Et_2O, 100:1 to 20:1) to afford **17e** as a yellow oil; yield: 40 mg (50%).

FTIR (neat): 2929, 2855, 1712, 1638, 1450, 1310, 1273, 1077, 990, 863, 762 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.68 (d, *J* = 16.0 Hz, 1 H), 7.55–7.27 (m, 10 H), 6.49 (d, *J* = 16.0 Hz, 1 H), 5.63 (d, *J* = 7.7 Hz, 1 H), 1.98–1.59 (m, 5 H), 1.51–1.36 (m, 1 H), 1.32–0.85 (m, 5 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.3, 144.7, 139.8, 134.5, 131.6, 130.2, 129.4, 128.8, 128.2, 128.1, 127.7, 127.1, 118.5, 80.4, 43.1, 35.2, 29.1, 29.0, 26.3, 25.9, 25.9.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{22}H_{24}O_2Na$: 343.1699; found: 343.1694.

The enantiomeric excess (19%) was determined by chiral HPLC; column: Chiralcel OD-H; solvent: cyclohexane–*i*-PrOH (99.5:0.5); flow: 1.0 mL/min; major enantiomer t_R = 20.2 min, minor enantiomer t_R = 11.7 min. The absolute configuration of the major enantiomer was determined by analogy to **15a**.

General Procedure (GP II) for the Kinetic Resolution of Secondary Alcohols Using Catalyst 13 (Table 4)

DBU (1.1 equiv) was added to a soln of triazolium salt **13** (5 mol%) in toluene (0.05 M) under argon atmosphere. The mixture was stirred for 5 min, then an alcohol **4** (3.0 equiv) and 3,3′,5,5′-tetra-*tert*-butyldiphenoquinone (**14**, 1.0 equiv) were added. After the mixture was stirred for 5 min, aldehyde **2j** (1 equiv) was added at r.t. The resulting solution was stirred for 1–6 h at that temperature. The solvent was removed under reduced pressure and the residue was purified by flash silica gel column chromatography [pentane–methyl *tert*-butyl ether (MTBE)].

1-(1-Naphthyl)ethyl Picolinate (16a)

According to GP II with pyridine-2-carbaldehyde (**2j**; 27 mg, 0.25 mmol), DBU (42 mg, 0.28 mmol), catalyst **13** (5.8 mg, 12.5 μmol), 1-(1-naphthyl)ethanol (**4a**; 129 mg, 750 μmol) and 3,3′,5,5′-tetra-*tert*-butyldiphenoquinone (**14**; 102 mg, 250 μmol) in toluene (5.0 mL) at r.t. for 3 h and silica gel chromatography (pentane–MTBE, 2:1) to afford **16a** as a pale yellow oil; yield: 56 mg (80%).

FTIR (neat): 3056, 1720, 1583, 1512, 1441, 1298, 1241, 1129, 1075, 998, 781, 740 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.85–8.75 (m, 1 H), 8.20 (d, *J* = 8.4 Hz, 1 H), 8.13 (d, *J* = 7.8 Hz, 1 H), 7.92–7.72 (m, 4 H), 7.60–7.41 (m, 4 H), 6.98 (q, *J* = 6.6 Hz, 1 H), 1.90 (d, *J* = 6.6 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.4, 150.0, 148.3, 137.1, 136.9, 133.8, 130.3, 128.9, 128.6, 126.8, 126.4, 125.7, 125.4, 125.2, 123.4, 123.1, 71.1, 21.7.

HRMS (ESI): *m/z* [M + Na]$^+$ calcd for $C_{18}H_{15}NO_2Na$: 300.0995; found: 300.0987.

The enantiomeric excess (63%) was determined by chiral HPLC; column: Chiralcel OD-H; solvent: cyclohexane–*i*-PrOH (98:2); flow: 1.0 mL/min; major enantiomer t_R = 18.7 min, minor enantiomer t_R = 14.5 min. The absolute configuration of the major enantiomer was determined by comparing the HPLC retention time with that of an authentic sample.

1-(2-Methoxyphenyl)ethyl Picolinate (16d)

According to GP II with pyridine-2-carbaldehyde (**2j**; 27 mg, 0.25 mmol), DBU (42 mg, 0.28 mmol), catalyst **13** (5.8 mg, 12.5 μmol), 1-(2-methoxyphenyl)ethanol (**4d**; 114 mg, 750 μmol) and 3,3′,5,5′-tetra-*tert*-butyldiphenoquinone (**14**; 102 mg, 250 μmol) in toluene (5.0 mL) at r.t. for 4 h and silica gel chromatography (pentane–MTBE, 2:1) to afford **16d** as a colorless oil; yield: 50 mg (78%).

FTIR (neat): 2982, 1722, 1590, 1453, 1293, 1244, 1134, 1059, 866, 752 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.80 (d, *J* = 4.7 Hz, 1 H), 8.14 (d, *J* = 7.8 Hz, 1 H), 7.83 (td, *J* = 7.7, 1.3 Hz, 1 H), 7.52 (d, *J* = 7.5 Hz, 1 H), 7.47 (dd, *J* = 7.5, 4.9 Hz, 1 H), 7.30–7.22 (m, 1 H), 6.96 (t, *J* = 7.5 Hz, 1 H), 6.89 (d, *J* = 8.2 Hz, 1 H), 6.57 (q, *J* = 6.5 Hz, 1 H), 3.86 (s, 3 H), 1.68 (d, *J* = 6.5 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.2, 156.1, 149.9, 148.5, 136.9, 130.1, 128.7, 126.7, 126.0, 125.1, 120.7, 110.6, 68.9, 55.5, 21.2.

HRMS (ESI): *m/z* [M + Na]$^+$ calcd for $C_{15}H_{15}NO_3Na$: 280.0944; found: 280.0955.

The enantiomeric excess (15%) was determined by chiral HPLC; column: Chiralcel OD-H; solvent: cyclohexane–*i*-PrOH (98:2); flow: 1.0 mL/min; major enantiomer t_R = 21.0 min, minor enantiomer t_R = 13.3 min. The absolute configuration of the major enantiomer was not assigned.

1-Phenylpropyl Picolinate (16f)

According to GP II with pyridine-2-carbaldehyde (**2j**; 27 mg, 0.25 mmol), DBU (42 mg, 0.28 mmol), catalyst **13** (5.8 mg, 12.5 μmol), 1-phenylpropan-1-ol (**4f**; 102 mg, 750 μmol) and 3,3′,5,5′-tetra-*tert*-butyldiphenoquinone (**14**; 102 mg, 250 μmol) in toluene (5.0 mL) at r.t. for 4 h and silica gel chromatography (pentane–MTBE, 2:1) to afford **16f** as a yellow oil; yield: 50 mg (83%).

FTIR (neat): 2969, 1722, 1582, 1444, 1304, 1132, 1083, 896, 751, 702 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.79–8.74 (m, 1 H), 8.10 (dd, *J* = 7.8, 0.9 Hz, 1 H), 7.79 (td, *J* = 7.7, 1.7 Hz, 1 H), 7.48–7.40 (m, 3 H), 7.37–7.23 (m, 3 H), 5.97 (t, *J* = 7.0 Hz, 1 H), 2.22–2.07 (m, 1 H), 2.06–1.91 (m, 1 H), 0.95 (t, *J* = 7.4 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.5, 149.9, 148.4, 140.1, 136.9, 128.4, 127.9, 126.7, 126.7, 125.1, 78.9, 29.3, 10.1.

HRMS (ESI): *m/z* [M + Na]$^+$ calcd for $C_{15}H_{15}NO_2Na$: 264.0995; found: 264.0991.

The enantiomeric excess (20%) was determined by chiral HPLC; column: Chiralcel OD-H; solvent: cyclohexane–*i*-PrOH (98:2); flow: 1.0 mL/min; major enantiomer t_R = 9.4 min, minor enantiomer t_R = 12.8 min. The absolute configuration of the major enantiomer was not assigned.

2,2-Dimethyl-1-phenylpropyl Picolinate (16g)

According to GP II with pyridine-2-carbaldehyde (**2j**; 27 mg, 0.25 mmol), DBU (42 mg, 0.28 mmol), catalyst **13** (5.8 mg, 12.5 μmol), 2,2-dimethyl-1-phenylpropan-1-ol (**4g**; 123 mg, 750 μmol) and 3,3′,5,5′-tetra-*tert*-butyldiphenoquinone (**14**; 102 mg, 250 μmol) in toluene (5.0 mL) at r.t. for 4 h and silica gel chromatography (pentane–MTBE, 2:1) to afford **16g** as a white solid; yield: 27 mg (40%).

FTIR (neat): 2962, 1727, 1580, 1443, 1286, 1239, 1128, 1037, 975, 739, 698 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.77 (d, *J* = 4.3 Hz, 1 H), 8.13 (d, *J* = 7.8 Hz, 1 H), 7.83 (td, *J* = 7.7, 1.5 Hz, 1 H), 7.44 (dd, *J* = 6.9, 5.0 Hz, 1 H), 7.41–7.33 (m, 2 H), 7.33–7.20 (m, 3 H), 5.82 (s, 1 H), 1.02 (s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.0, 150.1, 148.5, 138.1, 136.9, 127.8, 127.6, 126.6, 124.9, 84.1, 35.5, 26.2.

HRMS (ESI): *m/z* [M + Na]$^+$ calcd for $C_{17}H_{19}NO_2Na$: 292.1308; found: 292.1302.

The enantiomeric excess (30%) was determined by chiral HPLC; column: Chiralcel OD-H; solvent: cyclohexane–*i*-PrOH (98:2); flow: 1.0 mL/min; major enantiomer t_R = 5.9 min, minor enantiomer t_R = 9.2 min. The absolute configuration of the major enantiomer was not assigned.

(2-Bromophenyl)(phenyl)methyl Picolinate (16h)

According to GP II with pyridine-2-carbaldehyde (**2j**; 27 mg, 0.25 mmol), DBU (42 mg, 0.28 mmol), catalyst **13** (5.8 mg, 12.5 μmol), (2-bromophenyl)(phenyl)methanol (**4h**; 200 mg, 750 μmol) and 3,3′,5,5′-tetra-*tert*-butyldiphenoquinone (**14**; 102 mg, 250 μmol) in toluene (5.0 mL) at r.t. for 2 h and silica gel chromatography (pentane–MTBE, 2:1) to afford **16h** as a colorless oil; yield: 80 mg (87%).

FTIR (neat): 3060, 1722, 1580, 1439, 1289, 1240, 1118, 1033, 968, 749, 701 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.79 (d, *J* = 5.3 Hz, 1 H), 8.17 (d, *J* = 7.8 Hz, 1 H), 7.84 (t, *J* = 7.7 Hz, 1 H), 7.65 (d, *J* = 7.8 Hz, 1 H), 7.59 (d, *J* = 8.0 Hz, 1 H), 7.53–7.41 (m, 4 H), 7.41–7.27 (m, 4 H), 7.18 (t, *J* = 7.7 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 163.9, 150.0, 148.0, 139.1, 138.3, 136.9, 133.1, 129.5, 128.8, 128.5, 128.2, 127.8, 127.7, 126.9, 125.34, 123.2, 77.1, 27.0.

HRMS (ESI): *m/z* [M + Na]$^+$ calcd for $C_{19}H_{14}BrNO_2Na$: 390.0100; found: 390.0099.

The enantiomeric excess (35%) was determined by chiral HPLC; column: Chiralcel OD-H; solvent: cyclohexane–*i*-PrOH (98:2); flow: 1.0 mL/min; major enantiomer t_R = 12.6 min, minor enantiomer t_R = 9.3 min. The absolute configuration of the major enantiomer was not assigned.

Phenyl(2-tolyl)methyl Picolinate (16i)

According to GP II with pyridine-2-carbaldehyde (**2j**; 27 mg, 0.25 mmol), DBU (42 mg, 0.28 mmol), catalyst **13** (5.8 mg, 12.5 μmol), phenyl(2-tolyl)methanol (**4i**; 149 mg, 750 μmol) and 3,3′,5,5′-tetra-*tert*-butyldiphenoquinone (**14**; 102 mg, 250 μmol) in toluene (5.0 mL) at r.t. for 3 h and silica gel chromatography (pentane–MTBE, 2:1) to afford **16i** as a colorless oil; yield: 58 mg (77%).

FTIR (neat): 3058, 1722, 1582, 1450, 1298, 1243, 1125, 964, 748 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.73–8.70 (m, 1 H), 8.09 (d, *J* = 7.8 Hz, 1 H), 7.74 (td, *J* = 7.8, 1.7 Hz, 1 H), 7.48 (dd, *J* = 5.1, 3.9 Hz, 1 H), 7.41–7.08 (m, 10 H), 2.30 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.1, 150.1, 148.2, 139.0, 137.7, 136.8, 135.9, 130.6, 128.5, 128.0, 128.0, 127.7, 127.2, 126.8, 126.1, 125.2, 75.6, 19.5.

HRMS (ESI): *m/z* [M + Na]$^+$ calcd for $C_{20}H_{17}NO_2Na$: 326.1151; found: 326.1158.

The enantiomeric excess (11%) was determined by chiral HPLC; column: Chiralcel OD-H; solvent: cyclohexane–*i*-PrOH (98:2); flow: 1.0 mL/min; major enantiomer t_R = 10.5 min, minor enantiomer t_R = 8.7 min. The absolute configuration of the major enantiomer was not assigned.

1-Naphthyl(phenyl)methyl Picolinate (16j)

According to GP II with pyridine-2-carbaldehyde (**2j**; 27 mg, 0.25 mmol), DBU (42 mg, 0.28 mmol), catalyst **13** (5.8 mg, 12.5 µmol), 1-naphthyl(phenyl)methanol (**4j**; 176 mg, 750 µmol) and 3,3′,5,5′-tetra-*tert*-butyldiphenoquinone (**14**; 102 mg, 250 µmol) in toluene (5.0 mL) at r.t. for 6 h and silica gel chromatography (pentane–MTBE, 2:1) to afford **16j** as an orange solid; yield: 43 mg (50%).

FTIR (neat): 3054, 1722, 1586, 1514, 1443, 1293, 1239, 1119, 956, 743, 699 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.72 (m, 1 H), 8.10 (d, *J* = 7.8 Hz, 1 H), 8.03 (dd, *J* = 6.2, 3.5 Hz, 1 H), 7.88 (s, 1 H), 7.84–7.64 (m, 4 H), 7.47–7.34 (m, 6 H), 7.31–7.16 (m, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.2, 150.1, 148.1, 139.4, 136.9, 134.9, 133.9, 130.8, 129.1, 128.8, 128.5, 128.1, 127.6, 126.9, 126.4, 125.9, 125.7, 125.3, 125.2, 124.0, 75.8.

HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{23}H_{17}NO_2Na$: 362.1151; found: 362.1152.

The enantiomeric excess (7%) was determined by chiral HPLC; column: Chiralpak AD-H; solvent: cyclohexane–*i*-PrOH (98:2); flow: 1.0 mL/min; major enantiomer t_R = 16.3 min, minor enantiomer t_R = 27.0 min. The absolute configuration of the major enantiomer was not assigned.

Acknowledgment

We thank the DFG for funding this project within the priority program ‘organocatalysis’ and the NRW Graduate School of Chemistry for providing a scholarship to A.B.

References

(1) (a) Berkessel, A.; Gröger, H. *Asymmetric Organocatalysis: From Biomimetic Concepts to Applications in Asymmetric Synthesis*; Wiley-VCH: Weinheim, **2005**. (b) Dalko, P. I. *Enantioselective Organocatalysis: Reactions and Experimental Procedures*; Wiley-VCH: Weinheim, **2007**.

(2) For recent reviews on organocatalysis, see: (a) Valero, G.; Companyo, X.; Bravo, N.; Alba, A.-N. R.; Moyano, A.; Rios, R. *Synlett* **2010**, 1883. (b) Zhang, Z. G.; Schreiner, P. R. *Chem. Soc. Rev.* **2009**, *38*, 1187. (c) Dondoni, A.; Massi, A. *Angew. Chem. Int. Ed.* **2008**, *47*, 4638. (d) Pellissier, H. *Tetrahedron* **2007**, *63*, 9267.

(3) For recent reviews on NHC-catalyzed transformations, see: (a) Nair, V.; Vellalath, S.; Babu, B. P. *Chem. Soc. Rev.* **2008**, *37*, 2691. (b) Enders, D.; Niemeier, O.; Henseler, A. *Chem. Rev.* **2007**, *107*, 5606. (c) Marion, N.; Díez-González, S.; Nolan, S. P. *Angew. Chem. Int. Ed.* **2007**, *46*, 2988. (d) Zeitler, K. *Angew. Chem. Int. Ed.* **2005**, *44*, 7506.

(4) (a) Lathrop, S. P.; Rovis, T. *J. Am. Chem. Soc.* **2009**, *131*, 13628. (b) Enders, D.; Henseler, A. *Adv. Synth. Catal.* **2009**, *351*, 1749.

(5) (a) DiRocco, D. A.; Oberg, K. M.; Dalton, D. M.; Rovis, T. *J. Am. Chem. Soc.* **2009**, *131*, 10872. (b) Li, Y.; Shi, F.-Q.; He, Q.-L.; You, S.-L. *Org. Lett.* **2009**, *11*, 3182.

(6) (a) Burstein, C.; Glorius, F. *Angew. Chem. Int. Ed.* **2004**, *43*, 6205. (b) Sohn, S. S.; Rosen, E. L.; Bode, J. W. *J. Am. Chem. Soc.* **2004**, *126*, 14370.

(7) For selected examples of NHC-catalyzed esterifications using internal redox reactions, see: (a) Zeitler, K.; Rose, C. A. *J. Org. Chem.* **2009**, *74*, 1759. (b) Chow, K. Y.-K.; Bode, J. W. *J. Am. Chem. Soc.* **2004**, *126*, 8126. (c) Reynolds, N. T.; Read de Alaniz, J.; Rovis, T. *J. Am. Chem. Soc.* **2004**, *126*, 9518. (d) Grasa, G. A.; Güveli, T.; Singh, R.; Nolan, S. P. *J. Org. Chem.* **2003**, *68*, 2812.

(8) For NHC-catalyzed oxidative esterifications using an external oxidant, see: (a) Maki, B. E.; Chan, A.; Phillips, E. M.; Scheidt, K. A. *Tetrahedron* **2009**, *65*, 3102. (b) Noonan, C.; Baragwanath, L.; Connon, S. J. *Tetrahedron Lett.* **2008**, *49*, 4003. (c) Miyashita, A.; Suzuki, Y.; Nagasaki, I.; Ishiguro, C.; Iwamoto, K.-I.; Higashino, T. *Chem. Pharm. Bull.* **1997**, *45*, 1254. (d) Tam, S. W.; Jimenez, L.; Diederich, F. *J. Am. Chem. Soc.* **1992**, *114*, 1503.

(9) (a) Campbell, C. D.; Duguet, N.; Gallagher, K. A.; Thomson, J. E.; Lindsay, A. G.; O'Donoghue, A. C.; Smith, A. D. *Chem. Commun.* **2008**, 3528. (b) Thomson, J. E.; Rix, K.; Smith, A. D. *Org. Lett.* **2006**, *8*, 3785.

(10) For selected examples of the nonenzymatic kinetic resolution of alcohols, see: (a) Hu, B.; Meng, M.; Wang, Z.; Du, W.; Fossey, J. S.; Hu, X.; Deng, W.-P. *J. Am. Chem. Soc.* **2010**, *132*, 17041. (b) Rendler, S.; Plefka, O.; Karatas, B.; Auer, G.; Fröhlich, R.; Mück-Lichtenfeld, C.; Grimme, S.; Oestreich, M. *Chem. Eur. J.* **2008**, *14*, 11512. (c) Vedejs, E.; Jure, M. *Angew. Chem. Int. Ed.* **2005**, *44*, 3974. (d) Miller, S. J. *Acc. Chem. Res.* **2004**, *37*, 601.

(11) (a) Suzuki, Y.; Yamauchi, K.; Muramatsu, K.; Sato, M. *Chem Commun.* **2004**, 2770. (b) Kano, T.; Sasaki, K.; Maruoka, K. *Org. Lett.* **2005**, *7*, 1347.

(12) For recent reports involving acylazolium ions, see: (a) De Sarkar, S.; Studer, A. *Angew. Chem. Int. Ed.* **2010**, *49*, 9266; *Angew. Chem.* **2010**, *122*, 9452. (b) Zhu, Z. Q.; Xiao, J. C. *Adv. Synth. Catal.* **2010**, *352*, 2455. (c) Kaeobamrung, J.; Mahatthananchai, J.; Zheng, P.; Bode, J. W. *J. Am. Chem. Soc.* **2010**, *132*, 8810. (d) Ryan, S. J.; Candish, L.; Lupton, D. W. *J. Am. Chem. Soc.* **2009**, *131*, 14176.

(13) For NHC-catalyzed transesterifications, see: (a) Grasa, G. A.; Güveli, T.; Singh, R.; Nolan, S. P. *J. Org. Chem.* **2003**, *68*, 2812. (b) Nyce, G. W.; Lamboy, J. A.; Connor, E. F.; Waymouth, R. M.; Hedrick, J. L. *Org. Lett.* **2002**, *4*, 3587.

(14) (a) De Sarkar, S.; Studer, A. *Org. Lett.* **2010**, *12*, 1992. (b) De Sarkar, S.; Grimme, S.; Studer, A. *J. Am. Chem. Soc.* **2010**, *132*, 1190. (c) Guin, J.; De Sarkar, S.; Grimme, S.; Studer, A. *Angew. Chem. Int. Ed.* **2008**, *47*, 8727; *Angew. Chem.* **2008**, *120*, 8855.

(15) Scheidt and co-workers reported the desymmetrization of *meso*-diols using oxidative carbene catalysis; see ref. 8a.

(16) Bisquinone **14** is readily prepared by treatment of 2,6-di-*tert*-butylphenol (Aldrich US$37.50/1 kg) with O_2; see: Kharasch, M. S.; Joshi, B. S. *J. Org. Chem.* **1957**, *22*, 1439.

(17) Enders, D.; Niemeier, O.; Balensiefer, T. *Angew. Chem. Int. Ed.* **2006**, *45*, 1463.

(18) The absolute configuration of the major enantiomer of **15a** formed using catalyst **8** was determined by comparing the HPLC retention time with that of an authentic sample.

(19) Brand, J. P.; Siles, J. I. O.; Waser, J. *Synlett* **2010**, 881.

(20) Struble, J. R.; Bode, J. W. *Org. Synth.* **2010**, *87*, 362.

(21) Vora, H. U.; Lathrop, S. P.; Reynolds, N. T.; Kerr, M. S.; deAlaniz, J. R.; Rovis, T. *Org. Synth.* **2010**, *87*, 350.

(22) Mahatthananchai, J.; Zheng, P.; Bode, J. W. *Angew. Chem. Int. Ed.* **2011**, *50*, 1673.

(23) Kagan, H. B.; Fiaud, J. C. *Top. Stereochem.* **1988**, *18*, 249.

(24) Tietze, L. F.; Kinzel, T.; Wolfram, T. *Chem. Eur. J.* **2009**, *15*, 6199.

(25) Luo, Y.; Herndon, J. W.; Cervantes-Lee, F. *J. Am. Chem. Soc.* **2003**, *125*, 12720.
(26) Ryu, E.-H.; Cho, H. K.; Zhao, Y. *Org. Lett.* **2007**, *9*, 5147.
(27) Belletire, J. L.; Bills, R. A.; Shackelford, S. A. *Synth. Commun.* **2008**, *38*, 738.
(28) Enders, D.; Han, J.; Henseler, A. *Chem. Commun.* **2008**, 3989.
(29) Chênevert, R.; Pelchat, N.; Morin, P. *Tetrahedron: Asymmetry* **2009**, *20*, 1191.