JOC The Journal of Organic Chemistry

Note

pubs.acs.org/joc

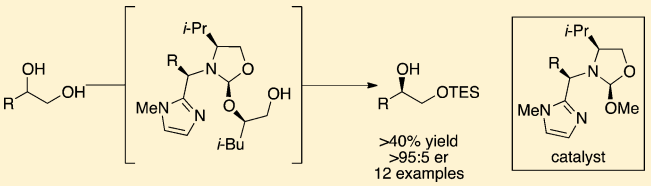
Resolution of Terminal 1,2-Diols via Silyl Transfer

Xixi Sun, Amanda D. Worthy, and Kian L. Tan*

Boston College, 2609 Beacon Street, Chestnut Hill, Massachusetts 02467-3860, United States

Supporting Information

ABSTRACT: Through kinetic analysis and optimization, we report an improved resolution of terminal 1,2-diols via asymmetric silyl transfer. Because the reaction is a regiodivergent resolution, the monoprotected product could be isolated in excess of 95:5 er and 40% yield. The described method offers a means of chemically differentiating a terminal 1,2-diol with concomitant resolution of the enantiomers.

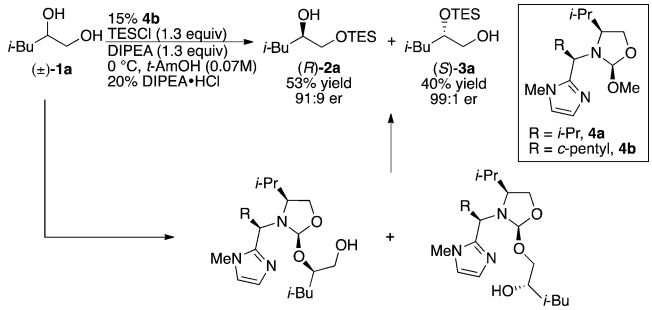


Terminal 1,2-diols have been shown to be practical building blocks in the synthesis of biologically relevant compounds.[1,2] Based on the synthetic value of these compounds, several metal-catalyzed methods have been explored for their asymmetric synthesis including hydrolytic kinetic resolution of epoxides,[3−5] as well as diboration/oxidation[6−8] and dihydroxylation[2,9] of terminal olefins. An alternative approach to the synthesis of enantiopure terminal 1,2-diols is through kinetic resolution via electrophile transfer.[10−12] The robust nature and chemical orthogonality of silyl protecting groups[13−15] has made asymmetric silyl transfer particularly synthetically valuable in the resolution of alcohols. Early work by Ishikawa demonstrated that chiral guanidine catalysts successfully promote the resolution of indanol via silyl transfer.[16] Subsequently, both metal[17−20] and nonmetal catalysts[21−27] have been found to effectively promote enantio- and stereoselective silyl transfer to alcohols.

Recently, Hoveyda and Snapper disclosed the kinetic resolution of 1,2-diols via silylation with an organic catalyst.[22] The same groups[23] and our group[26] reported a highly effective regiodivergent resolution of 1,2-diols. In a regiodivergent resolution of a racemic mixture (RRM),[28−31] the enantiomers of the starting material are preferentially converted into constitutionally isomeric products. The advantage of the regiodivergent RRM over a traditional kinetic resolution is that it is generally easier to obtain the products of the transformation in both high yield and enantioselectivity. The net effect is that in a single step the regiodivergent resolution resolves the enantiomers and generates a synthetically more valuable product. For example, using catalysts **4a** and **4b**, we demonstrated that the regiodivergent resolution of terminal 1,2-diols is an efficient means of accessing enantiopure products with the silyl-protected secondary hydroxyl (Scheme 1). In this transformation, we resolve the enantiomers and simultaneously chemically differentiate the primary and secondary hydroxyls.

A unique feature of catalysts **4a** and **4b** is their ability to reversibly and covalently bond with organic molecules, which is in part responsible for the protection of the inherently less reactive secondary hydroxyl (Scheme 1). Organic catalysts and metal-binding ligands that use reversible covalent bonding have

Scheme 1. Regiodivergent kinetic resolution of terminal 1,2-diol



seen a resurgence over the past decade as a means of controlling selectivity in a range of reactions.[32−40] The majority of this effort has focused on using reversible covalent bonding to control site and regioselectivity, whereas less progress has been made in the area of enantioselective catalysis.[41−44] In this article, we re-evaluate the reaction conditions of our original divergent resolution in order to provide a practical method for obtaining enantioenriched terminal 1,2-diols in which the primary hydroxyl is silylated.

In our initial publication on the regiodivergent RRM, we found using 15% of **4b** that the secondary protected product **3a** formed in 40% yield and 99:1 er, while the primary protected product **2a** formed in a more modest 91:9 er (Scheme 1). In an effort to improve the catalyst performance, we monitored the conversion and selectivity of the reaction at a reduced catalyst loading (10% **4b**, Figure 1). To our surprise, the enantioselectivity for both **2a** and **3a** increases with time under these suboptimal conditions; moreover, the rate of reaction appears to accelerate over time (Figure 1). A potential explanation for the increasing enantioselectivity is that at low conversion the catalyzed reaction could be limited by the rate of the exchange between catalyst **4b** and **1a**, which allows for unselective background silylation to be competitive. As the

Received: June 18, 2013
Published: October 2, 2013

dx.doi.org/10.1021/jo4012909 | J. Org. Chem. 2013, 78, 10494−10499

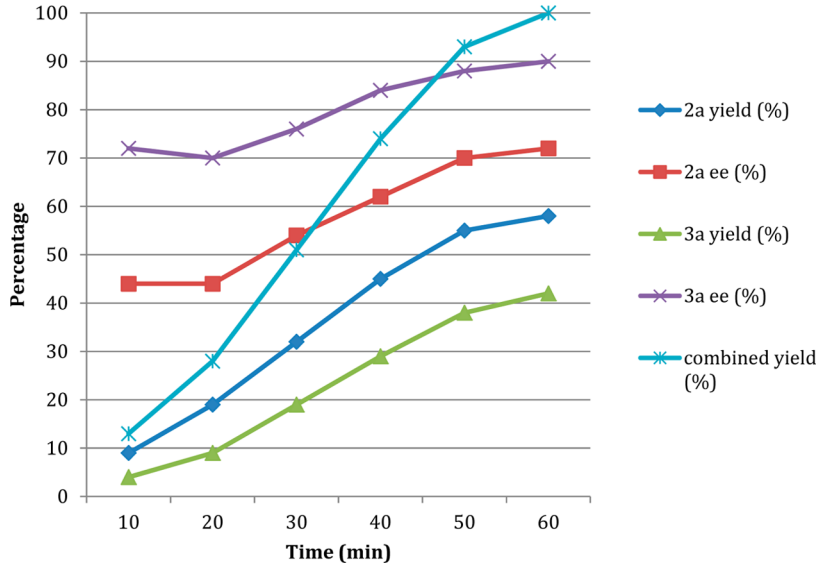


Figure 1. Reaction time course at 0 °C with a single addition of TESCl.

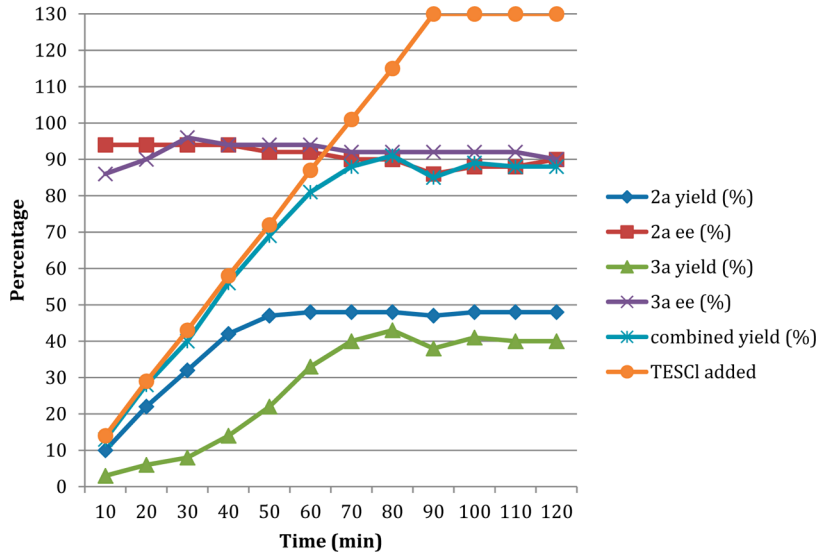


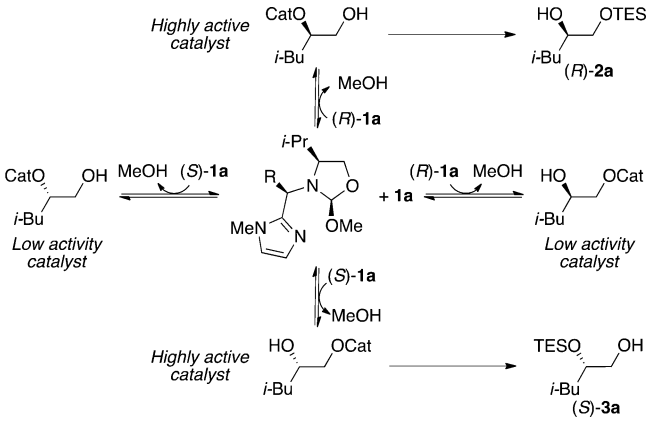
Figure 2. Reaction time course at room temperature with a syringe pump addition of TESCl.

reaction progresses, the concentration of silyl chloride decreases, slowing the silylation step; moreover, acid is generated in the reaction, which catalyzes the exchange reaction. To test this hypothesis, we monitored the reaction while adding the silyl chloride at a rate such that conversion and silyl chloride addition were matched, thus limiting the amount of excess electrophile in solution (Figure 2). In addition, we found that performing the reaction at room temperature provided the optimal results. Under these conditions, the formation of **2a** proceeds in 97:3 er at low conversion (10 min) with a small decrease in er (94.5:5.5) after 110 min. The conversion to **3a** still shows a small increase in enantioselectivity at the beginning of the reaction, but the effect is considerably smaller and the final product is formed in high enantioselectivity (96:4 er). Based on the time course, the formation of **3a** clearly accelerates as the reaction progresses. In Figure 2, we have drawn a simplified version of the kinetics model; notably, we have only shown the pathways for the major products formed ((*R*)-**2a** and (*S*)-**3a**). Furthermore, we have not included the equilibria for product bound to catalyst even though these equilibria are present. The rapid formation of (*R*)-**2a** is consistent with the primary alcohol being the inherently more reactive alcohol and the substrate being stereochemically matched to the catalyst. The accelerated formation of **3a** as the reaction progresses can be rationalized by considering that the majority of **3a** is the *S* enantiomer (er = 96:4). Therefore, any catalyst bound to (*R*)-**1a**, through either the primary or secondary alcohol, is lowering the concentration of catalyst bound to (*S*)-**1a**, effectively inhibiting the formation of (*S*)-**3a**. The formation of (*R*)-**3a** is likely slow because of a mismatched relationship between the catalyst and (*R*)-**1a**. Therefore, as (*R*)-**1a** is converted to (*R*)-**2a** (where the primary hydroxyl is silylated), this increases the concentration of catalyst bound to (*S*)-**1a**, thereby accelerating the rate of formation of (*S*)-**3a** (Scheme 2).

Analysis of the time course suggests that to obtain the optimal yield and enantioselectivity of **2a** approximately 0.7 equiv of TESCl is required. With this in mind, we examined the substrate scope of the regiodivergent resolution with the aim of obtaining **2a** in high yield and enantioselectivity. To improve

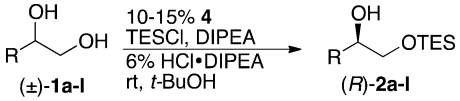
dx.doi.org/10.1021/jo4012909 | *J. Org. Chem.* 2013, 78, 10494−10499

Scheme 2. Kinetic Model for Formation of (*S*)-3a



the operational practicality, we employed a portionwise addition of the silyl chloride rather than a syringe pump addition. Under these conditions, **2a** was formed in 46% yield and 96.5:3.5 er (Table 1, entry 1), matching the time course data. As a note of comparison, a traditional kinetic resolution catalyst would need to operate with a selectivity factor (s) of 67 to obtain similar yield and enantioselectivity of **2a**.

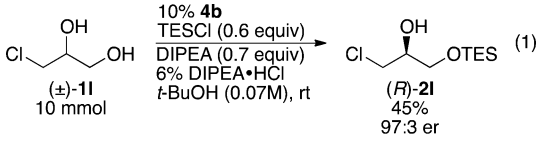
Table 1. Kinetic Resolution of 1,2-Diols



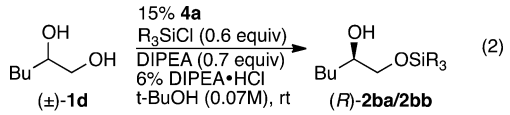
entry	R	catalyst	yield 2 (%)[g]	er 2 (%)
1[a]	$-CH_2CH(CH_3)_2$ (a)	10% **4b**	46	96.5:3.5
2[b]	$-(CH_2)_3CH_3$ (b)	10% **4a**	44	96:4
3	−Cy (c)	10% **4b**	47	96:4
4[c]	−*t*-Bu (d)	15% **4b**	43	95.5:4.5
5[d]	$-CH_3$ (e)	15% **4b**	37	94:6
6[a]	$-CH_2Ph$ (f)	10% **4b**	41	96:4
7[b]	$-CH_2OBn$ (g)	15% **4a**	40	95:5
8[e]	$-CH_2OPh$ (h)	15% **4a**	36	94.5:5.5
9[a]	$-CH{=}CH_2$ (i)	15% **4b**	41	89:11
10[f]	−Ph (j)	15% **4b**	39	95.5:4.5
11[a]	$-CH_2Br$ (k)	10% **4b**	40	97.5:2.5
12[a]	$-CH_2Cl$ (l)	10% **4b**	41	97.5:2.5

[a]0.70 equiv of TESCl and 0.80 equiv of DIPEA were used. [b]0.60 equiv of TESCl and 0.70 equiv of DIPEA were used. [c]0.60 equiv of TESCl and 0.70 equiv of DIPEA were used; *t*-amyl-OH was used as solvent, and reaction was run at 4 °C for 2 h. [d]0.80 equiv of TESCl and 0.90 equiv of DIPEA were used. [e]0.70 equiv of TESCl and 0.80 equiv of DIPEA were used; reaction time was 2 h. [f]0.50 equiv of TESCl and 0.60 equiv of DIPEA were used; *t*-amyl-OH was used as solvent. [g]Isolated yields.

Under these modified conditions, the substrate scope was examined, and in general, the primary protected products (**2**) were isolated in synthetically practical levels of enantioselectivity (>95:5 er) and yields ≥40% (Table 1). In these cases, groups both small (R = *n*-Bu, Table 1, entry 2) and large (R = *t*-Bu, Table 1, entry 4) provide the desired products in high yield and enantioselectivity. For Table 1, the majority of substrates undergo a regiodivergent resolution; however, the conditions are run such that only a minimal amount of **3** is formed during the reaction. One substrate that did not undergo a regiodivergent resolution was substrate **1d** (R = *t*-Bu); in this case, the product with the secondary hydroxyl protected (**3d**) was never observed even with excess silyl chloride. Even though a regiodivergent kinetic resolution does not occur with **1d**, a traditional kinetic resolution provides **2d** in 43% yield and 95.5:4.5 er (s = 44, Table 1, entry 4). The substrates with the lowest enantioselectivities and yields were **2e** and **2i**, which have the smallest R substituents (R = Me and vinyl, Table 1, entries 5 and 9). A benzyl-protected glycerol derivative also functions in the reaction, yielding the differentially protected triol in 40% yield and 95:5 er (Table 1, entry 7). Under the reaction conditions, halogen-containing substrates, both Cl and Br, provide the highest stereoselectivities of the silylated products while maintaining excellent yields (Table 1, entries 11 and 12). As further evidence of the practicality of the reaction, we performed a larger scale reaction. Using 10 mmol of **1l** (R = CH_2Cl), the resolution produced **2l** in 45% yield and 97:3 er (eq 1), consistent with the smaller scale reaction.



Having explored the substrate scope of the resolution to form the primary protected products, we next investigated the range of silyl groups that could be transferred enantioselectively. By employing more bulky silylating agents, it was discovered that the product with the secondary hydroxyl protected (**3**) does not form in appreciable quantities. Consequently, reactions with the larger silylating agents undergo traditional kinetic resolutions rather than the regiodivergent RRMs. Using TBSCl in the resolution of 1,2-hexanediol provides (*R*)-**2** in 45% yield and 89:11 er (s = 15). Increasing the steric bulk of the silyating reagent to TIPSCl provides a significant increase in s factor to 45, allowing the product to be isolated in 40% yield and 96:4 er, comparable to the results with TESCl (eq 2).



TBSCl: yield= 45%, er= 89:11, s= 15

TIPSCl: yield= 40%, er= 96:4, s= 45

We have demonstrated that a catalyst that uses reversible covalent bonding is effective at the resolution of 1,2-diols. By monitoring the reaction kinetics, we were able to improve the yield and selectivity of the reaction while also gaining insight into the mechanism of the reaction. We believe the above method will be a practical means of accessing enantiopure terminal 1,2-diols in which the hydroxyls have been chemically differentiated.

EXPERIMENTAL SECTION

General Considerations. Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. Lithium reagents were titrated against 2-pentanol using 1,10-phenanthroline as the indicator. All experiments were performed in oven or flame-dried glassware under an atmosphere of nitrogen or argon using standard syringe and cannula techniques, except where otherwise noted. All reactions were run with dry, degassed solvents dispensed from a glass contour solvent purification system. *tert*-Amyl

dx.doi.org/10.1021/jo4012909 | J. Org. Chem. 2013, 78, 10494−10499

alcohol and *tert*-butanol were distilled over CaH_2 and stored over 3 Å molecular sieves in a drybox under a nitrogen atmosphere. Deuterated solvents were stored over 3 Å molecular sieves. C_6D_6 was degassed by three successive freeze−pump−thaw cycles and stored over 3 Å molecular sieves in a drybox under a nitrogen atmosphere. Column chromatography was performed using and automatic purification system prepacked columns. All NMR chemical shifts are reported in ppm relative to residual solvent for ^1H and ^{13}C NMR. Coupling constants are reported in Hz. All IR spectra values are reported in cm^{-1}. High-resolution mass spectra (HRMS) were taken using a TOF analyzer.

The following compounds were made according to literature procedure: 1-benzyloxy-2,3-propanediol,[45] 4-methylpentane-1,2-diol,[26] 1-cyclohexylethane-1,2-diol,[26] 3-phenylpropane-1,2-diol,[26] **4a**,[25] **4b**.[26]

Reaction Time Course at 0 °C with a Single Addition of TESCl (Figure 1). In a drybox, a solution of diol **1a** (24 mg, 0.20 mmol), catalyst **4b** (6.2 mg, 0.02 mmol, 10 mol %), and *N*,*N*-diisopropylethylamine hydrochloride (2.0 mg, 1.2×10^{-2} mmol, 6 mol %) in anhydrous *tert*-butanol (3 mL) was prepared in an oven-dried glass reaction vial. A solution of 1,3,5-trimethoxybenzene as internal standard (50 μL, 2.0×10^{-2} mmol, 10 mol %, 0.40 M in $CDCl_3$) was added. The reaction was brought out of the drybox and was stirred at 4 °C for 15 min. *N*,*N*-Diisopropylethylamine (49 μL, 0.28 mmol, 1.4 equiv) was added, followed by addition of chlorotriethylsilane (44 μL, 0.26 mmol, 1.2 equiv). The reaction was stirred at room temperature for 1 h. Aliquots (0.5 mL) were taken at every 10 min. Methanol (5 μL) was added to quench the aliquot. The solvent was removed under reduced pressure. Chiral GLC analysis of the crude mixture afforded the yield and selectivity. Chiral GLC Analysis (Beta Dex 120 (30 m × 0.15 mm × 0.25 mm film thickness), 90 °C for 135 min, 20 °C/min to 160 °C, 160 °C for 20 min, 20 °C/min to 180 °C, 180 °C for 20 min, 15 psi, $t_{(S)\text{-}2a}$ = 96.2 min, $t_{(R)\text{-}2a}$ = 97.4 min, $t_{(S)\text{-}3a}$ = 104.2 min, $t_{(R)\text{-}3a}$ = 110.9 min, $t_{standard}$ = 143.7 min), response factors ((*S*)-**2a** = 0.59, (*R*)-**2a** = 0.59, (*S*)-**3a** = 0.66, (*R*)-**3a** = 0.66, standard = 1.0).

Reaction Time Course at Room Temperature with a Syringe Pump Addition of TESCl (Figure 2). In a drybox, a solution of diol **1a** (240 mg, 2.0 mmol), catalyst **4b** (61 mg, 0.20 mmol, 10 mol %), and *N*,*N*-diisopropylethylamine hydrochloride (20 mg, 0.12 mmol, 6 mol %) in anhydrous *tert*-butanol (30 mL) was prepared in an oven-dried glass reaction vial. The solution brought out of the drybox, and a solution of 1,3,5-trimethoxybenzene as internal standard (0.50 mL, 0.20 mmol, 10 mol %, 0.40 M in $CDCl_3$) was added. The reaction was stirred at room temperature for 15 min. *N*,*N*-Diisopropylethylamine (490 μL, 2.8 mmol, 1.4 equiv) was added, followed by addition of chlorotriethylsilane (440 μL, 2.6 mmol, 1.2 equiv) in 2 mL of THF via syringe pump over 1.5 h. The reaction was stirred at room temperature for 2 h. Aliquots (0.5 mL) were taken every at 10 min. Methanol (5 μL) was added to quench the aliquot. The solvent was removed under reduced pressure. Chiral GLC analysis of the crude mixture afforded the yield and selectivity.

General Procedure for Kinetic Resolution of Terminal 1,2-Diols. In a drybox, a solution of diol substrate (1.0 mmol), catalyst **4b** (31 mg, 0.10 mmol, 10 mol %), and *N*,*N*-diisopropylethylamine hydrochloride (10 mg, 6.0×10^{-2} mmol, 6 mol %) in anhydrous *tert*-butanol (15 mL) was prepared in an oven-dried glass reaction vial. The reaction was brought out of the drybox and was stirred at room temperature for 15 min. *N*,*N*-Diisopropylethylamine (120 μL, 0.70 mmol, 0.70 equiv) was added, followed by addition of chlorotriethylsilane (100 μL, 0.60 mmol, 0.60 equiv) in four portions every 15 min (dropwise addition was performed for each portion added). The reaction was stirred at room temperature for 1 h (starting from the first addition of chlorotriethylsilane). Methanol (150 μL) was added to quench the reaction. The solvent was removed under reduced pressure, and flash column chromatography (hexanes/EtOAc = 60:1) afforded pure product. Chiral GLC or HPLC analysis of the product afforded the selectivity.

*(R)-4-Methyl-1-((triethylsilyl)oxy)pentan-2-ol (**2a**, Table 1, entry 1).* The general procedure was followed using 10 mol % of catalyst **4b**, 0.80 equiv of *N*,*N*-diisopropylethylamine, and 0.70 equiv of chlorotriethylsilane to yield product as colorless oil (run 1: 108 mg, 46%, er = 96.5:3.5; run 2: 46%, er = 96:4): chiral GLC analysis (Beta Dex 120 (30 m × 0.15 mm × 0.25 mm film thickness), 95 °C for 90 min, 20 °C/min to 180 °C, 180 °C for 20 min, 15 psi, t_{rminor} = 74.4 min, t_{rmajor} = 74.8 min); ^1H NMR ($CDCl_3$, 500 MHz) δ 3.71 (ddd, 1H, *J* = 16.4, 7.8, 3.2), 3.58 (dd, 1H, *J* = 9.8, 3.2), 3.33 (dd, 1H, *J* = 9.8, 7.8), 2.40 (d, 1H, *J* = 3.2), 1.74−1.82 (m, 1H), 1.36 (ddd, 1H, *J* = 14.2, 8.8, 5.9), 1.11 (ddd, 1H, *J* = 13.5, 8.5, 4.2), 0.95 (t, 9H, *J* = 7.8), 0.92 (d, 3H, *J* = 6.6), 0.90 (d, 3H, *J* = 6.6), 0.60 (q, 6H, *J* = 7.8); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 70.3, 67.6, 42.0, 24.8, 23.6, 22.4, 6.9, 4.6; IR 2954, 2912, 2876, 1096, 1049, 1004, 789, 726 cm^{-1}; HRMS (ESI+) calcd for $C_{12}H_{28}O_2NaSi$ $[M + Na]^+$ 255.1751, found 255.1763; $[\alpha]_D^{20}$ = −1.9 (*c* = 1.0, CH_2Cl_2, *l* = 50 mm).

*(R)-1-((Triethylsilyl)oxy)hexan-2-ol (**2b**, Table 1, entry 2).* The general procedure was followed using 10 mol % of catalyst **4a**, 0.70 equiv of *N*,*N*-diisopropylethylamine, and 0.60 equiv of chlorotriethylsilane to yield product as colorless oil (run 1: 101 mg, 43%, er = 96:4; run 2: 44%, er = 95.5:4.5): chiral GLC analysis (Beta Dex 120 (30 m × 0.15 mm × 0.25 mm film thickness), 95 °C for 120 min, 20 °C/min to 180 °C, 180 °C for 20 min, 15 psi, t_{rminor} = 102.5 min, t_{rmajor} = 103.4 min); ^1H NMR ($CDCl_3$, 500 MHz) δ 3.59−3.64 (m, 2H), 3.36 (dt, 1H, *J* = 2.0, 8.8), 2.44 (d, 1H, *J* = 3.2), 1.22−1.45 (m, 6H), 0.94 (t, 9H, *J* = 7.8), 0.89 (t, 3H, *J* = 7.1), 0.60 (q, 6H, *J* = 7.8); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 72.1, 67.2, 32.7, 28.0, 23.0, 14.2, 6.9, 4.6; IR 2955 cm^{-1}; HRMS (ESI+) calcd for $C_{12}H_{28}O_2NaSi$ $[M + Na]^+$ 255.1751, found 255.1745; $[\alpha]_D^{20}$ = −3.2 (*c* = 1.0, CH_2Cl_2, *l* = 50 mm).

*(R)-1-Cyclohexyl-2-((triethylsilyl)oxy)ethanol (**2c**, Table 1, entry 3).* The general procedure was followed using 10 mol % of catalyst **4b**, 0.70 equiv of *N*,*N*-diisopropylethylamine, and 0.60 equiv of chlorotriethylsilane to yield product as colorless oil (run 1: 123 mg, 48%, er = 95:5; run 2: 46%, er = 96.5:3.5). Chiral GC analysis (Gamma Dex 120 (30 m × 0.25 mm × 0.25 μm film thickness), 115 °C for 180 min, 20 °C/min to 180 °C, 180 °C for 20 min, 15 psi, t_{rmajor} = 172.2 min, t_{rminor} = 169.5 min); ^1H NMR ($CDCl_3$, 500 MHz) δ 0.59 (q, 6H, *J* = 7.8), 0.94 (t, 9H, *J* = 7.8), 0.98−1.06 (m, 2H), 1.10−1.25 (m, 3H), 1.33−1.40 (m, 1H), 1.57−1.65 (m, 2H), 1.69−1.75 (m, 2H), 1.87−1.91 (m, 1H), 2.48 (d, 1H, *J* = 2.9), 3.34−3.38 (m, 1H), 3.44 (dd, 1H, *J* = 9.8, 8.3), 3.67 (dd, 1H, *J* = 9.8, 3.2); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 4.6, 6.9, 26.3, 26.4, 26.7, 29.0, 29.1, 40.7, 65.2, 76.0; IR 2921, 2875, 2852, 1450, 1112, 1079, 1004, 817, 726 cm^{-1}; HRMS (ESI+) calcd for $C_{14}H_{30}O_2NaSi$ $[M + Na]^+$ 281.1907, found 281.1915; $[\alpha]_D^{20}$ = −7.4 (*c* = 1.0, CH_2Cl_2, *l* = 50 mm).

*(R)-3,3-Dimethyl-1-((triethylsilyl)oxy)butan-2-ol (**2d**, Table 1, entry 4).* The general procedure was followed using 15 mol % of catalyst **4b**, 0.70 equiv of *N*,*N*-diisopropylethylamine, 0.60 equiv of chlorotriethylsilane, and *t*-amyl-OH as solvent. Reaction was run at 4 °C for 2 h to yield product as colorless oil (run 1: 104 mg, 45%, er = 96:4; run 2: 42%, er = 95.5:4.5): chiral GLC analysis (Gamma Dex 120 (30 m × 0.15 mm × 0.25 mm film thickness), 95 °C for 120 min, 20 °C/min to 180 °C, 180 °C for 20 min, 15 psi, t_{rminor} = 43.7 min, t_{rmajor} = 45.0 min); ^1H NMR ($CDCl_3$, 500 MHz) δ 3.69 (dd, 1H, *J* = 9.8, 3.2), 3.43 (t, 1H, *J* = 9.3), 3.30 (ddd, 1H, *J* = 9.0, 3.2, 2.0), 2.65 (d, 1H, *J* = 2.2), 0.95 (t, 9H, *J* = 8.1), 0.90 (s, 9H), 0.60 (q, 6H, *J* = 8.1); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 78.9, 63.5, 33.4, 26.2, 6.9, 4.6; IR 2954, 2912, 2877, 1460, 1108, 1067, 1003, 817, 726 cm^{-1}; HRMS (ESI+) calcd for $C_{12}H_{29}O_2Si$: $[M + H]^+$ 233.1937, found 233.1940; $[\alpha]_D^{20}$ = −21.2 (*c* = 1.0, CH_2Cl_2, *l* = 50 mm).

*(R)-1-((Triethylsilyl)oxy)propan-2-ol (**2e**, Table 1, entry 5).* The general procedure was followed using 15 mol % of catalyst **4b**, 0.90 equiv of *N*,*N*-diisopropylethylamine, and 0.80 equiv of chlorotriethylsilane to yield product as colorless oil (run 1: 72 mg, 36%, er = 94.5:5.5; run 2: 38%, er = 93.5:6.5): chiral GLC analysis (Beta Dex 120 (30 m × 0.15 mm × 0.25 mm film thickness), 80 °C for 45 min, 20 °C/min to 180 °C, 180 °C for 20 min, 15 psi, t_{rminor} = 35.4 min, t_{rmajor} = 36.5 min); ^1H NMR ($CDCl_3$, 500 MHz) δ 3.77−3.84 (m, 1H), 3.57 (dd, 1H, *J* = 9.8, 3.4), 3.32 (dd, 1H, *J* = 9.8, 7.8), 2.48 (d, 1H, 3.0), 1.10 (d, 3H, *J* = 6.4), 0.94 (t, 9H, *J* = 7.8), 0.60 (q, 6H, *J* = 7.8); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 68.4, 68.2, 18.4, 6.9, 4.6; IR 2955, 2911, 2877, 1459, 1239, 1087, 1006, 801, 724 cm^{-1}; HRMS (ESI+) calcd for $C_9H_{22}O_2NaSi$ $[M + Na]^+$ 213.1281, found 213,1271; $[\alpha]_D^{20}$ = −11.2 (*c* = 1.0, CH_2Cl_2, *l* = 50 mm).

dx.doi.org/10.1021/jo4012909 | J. Org. Chem. 2013, 78, 10494−10499

*(R)-1-Phenyl-3-((triethylsilyl)oxy)propan-2-ol (**2f**, Table 1, entry 6).* The general procedure was followed using 10 mol % of catalyst **4b**, 0.80 equiv of *N*,*N*-diisopropylethylamine, and 0.70 equiv of chlorotriethylsilane to yield product as a colorless oil (run 1: 107 mg, 41%, er = 96:4; run 2: 40%, er = 96:4): chiral HPLC analysis (OD-H, hexanes/*i*PrOH = 98/2, 1.0 mL/min, 220 nm, t_{rmajor} = 5.51 min and t_{rminor} = 6.12 min); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.27−7.30 (m, 2H), 7.18−7.22 (m, 3H), 3.85−3.90 (m, 1H), 3.60 (dd, 1H, *J* = 10.0, 3.7), 3.46 (dd, 1H, *J* = 9.8, 6.8), 2.78 (dd, 1H, *J* = 13.7, 7.1), 2.74 (dd, 1H, *J* = 13.7, 6.4), 2.42 (d, 1H, *J* = 3.9), 0.94 (t, 9H, *J* = 7.8), 0.59 (q, 6H, *J* = 7.8); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 138.5, 129.5, 128.6, 126.5, 73.0, 66.2, 39.8, 6.9, 4.6; IR 2953, 2911, 2876, 1239, 1111, 1031, 792, 727, 698 cm^{-1}; HRMS (ESI+) calcd for $C_{15}H_{26}O_2NaSi$ $[M + Na]^+$ 289.1594, found 289.1600; $[\alpha]_D^{20}$ = +3.2 (*c* = 1.0, CH_2Cl_2, *l* = 50 mm).

*(R)-1-(Benzyloxy)-3-((triethylsilyl)oxy)propan-2-ol (**2g**, Table 1, entry 7).* The general procedure was followed using 15 mol % of catalyst **4a**, 0.70 equiv of *N*,*N*-diisopropylethylamine, and 0.60 equiv of chlorotriethylsilane to yield product as colorless oil (run 1: 122 mg, 41%, er = 95:5; run 2: 40%, er = 95:5): chiral HPLC analysis (OD-H, hexanes/*i*PrOH = 95/5, 1.0 mL/min, 220 nm, t_{rminor} = 7.12 min and t_{rmajor} = 8.19 min); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.26−7.35 (m, 5H), 4.54 (s, 2H), 3.82−3.87 (m, 1H), 3.66 (dd, 1H, *J* = 10.0, 4.9), 3.62 (dd, 1H, *J* = 10.0, 5.9), 3.53 (dd, 1H, *J* = 9.5, 4.9), 3.49 (dd, 1H, *J* = 9.5, 5.9), 2.48 (d, 1H, *J* = 4.9), 0.94 (t, 9H, *J* = 7.8), 0.59 (q, 6H, *J* = 7.8); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 138.4, 128.6, 128.0, 127.9, 73.7, 71.3, 71.0, 64.0, 6.9, 4.6; IR 2953, 2910, 2875. 1089, 1004, 804, 728, 696 cm^{-1}; HRMS (ESI+) calcd for $C_{16}H_{28}O_3NaSi$ $[M + Na]^+$ 319.1700, found 319.1697; $[\alpha]_D^{20}$ = −1.1 (*c* = 1.0, CH_2Cl_2, *l* = 50 mm).

*(R)-1-Phenoxy-3-((triethylsilyl)oxy)propan-2-ol (**2h**, Table 1, entry 8).* The general procedure was followed using 15 mol % of catalyst **4a**, 0.80 equiv of *N*,*N*-diisopropylethylamine, and 0.70 equiv of chlorotriethylsilane. The reaction was stirred for 2 h to yield product as colorless oil (run 1: 98 mg, 35%, er = 95:5; run 2: 37%, er = 94:6): chiral HPLC analysis (OD-H, hexanes/*i*PrOH = 90/10, 1.0 mL/min, 220 nm, t_{rminor} = 5.11 min and t_{rmajor} = 10.66 min); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.25−7.28 (m, 2H), 6.92−6.96 (m, 1H), 6.89−6.91 (m, 2H), 3.99−4.05 (m, 3H), 3.78 (dd, 1H, *J* = 10.3, 4.6), 3.74 (dd, 1H, *J* = 10.3, 5.1), 2.55 (d, 1H, *J* = 5.1), 0.94 (t, 9H, *J* = 7.8), 0.61 (q, 6H, *J* = 7.8); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 158.9, 129.7, 121.2, 114.8, 70.5, 68.7, 63.7, 6.9, 4.6; IR 2953, 2876, 1599, 1495, 1458, 1242, 1079, 1043, 1005, 802, 745, 727, 689 cm^{-1}; HRMS (ESI+) calcd for $C_{15}H_{26}O_3NaSi$ $[M + Na]^+$ 305.1543, found 305.1552; $[\alpha]_D^{20}$ = +1.2 (*c* = 1.0, CH_2Cl_2, *l* = 50 mm).

*(R)-1-((Triethylsilyl)oxy)but-3-en-2-ol (**2i**, Table 1, entry 9).* The general procedure was followed using 15 mol % of catalyst **4b**, 0.80 equiv of *N*,*N*-diisopropylethylamine, and 0.70 equiv of chlorotriethylsilane to yield product as colorless oil (run 1: 84 mg, 42%, er = 89:11; run 2: 40%, er = 89:11): chiral GLC analysis (Beta Dex 120 (30 m × 0.15 mm × 0.25 mm film thickness), 90 °C for 50 min, 20 °C/min to 180 °C, 180 °C for 20 min, 15 psi, t_{rminor} = 42.9 min, t_{rmajor} = 44.6 min); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.80 (ddd, 1H, *J* = 17.1, 10.5, 5.6), 5.33 (dt, 1H, *J* = 17.4, 1.5), 5.17 (dt, 1H, 10.5, 1.5), 4.13−4.18 (m, 1H), 3.64 (dd, 1H, *J* = 10.0, 3.7), 3.42 (dd, 1H, *J* = 10.0, 7.8), 2.57 (d, 1H, 3.4), 0.95 (t, 9H, *J* = 7.8), 0.60 (q, 6H, *J* = 7.8); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 136.8, 116.7, 73.3, 66.9, 6.9, 4.6; IR 2955, 2912, 2877, 1238, 1102, 1004, 923, 795, 725 cm^{-1}; HRMS (ESI+) calcd for $C_{10}H_{22}O_2NaSi$ $[M + Na]^+$ 225.1281, found 225.1285; $[\alpha]_D^{20}$ = +0.3 (*c* = 1.0, CH_2Cl_2, *l* = 50 mm).

*(R)-1-Phenyl-2-((triethylsilyl)oxy)ethanol (**2j**, Table 1, entry 10).* The general procedure was followed using 15 mol % of catalyst **4b**, 0.60 equiv of *N*,*N*-diisopropylethylamine, 0.50 equiv of chlorotriethylsilane, and *t*-amyl-OH as solvent to yield product as colorless oil (run 1: 96 mg, 38%, er = 96:4; run 2: 39%, er = 95:5): chiral HPLC analysis (OD-H, hexanes/iPrOH = 95/5, 1.0 mL/min, 220 nm, t_{rminor} = 4.84 min and t_{rmajor} = 5.56 min); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.31−7.37 (m, 4H), 7.25−7.28 (m, 1H), 4.74 (dt, 1H, *J* = 8.3, 3.2), 3.75 (dd, 1H, *J* = 10.3, 3.7), 3.52 (dd, 1H, *J* = 10.0, 9.0), 2.97 (d, 1H, *J* = 2.2), 0.95 (t, 9H, *J* = 8.1), 0.61 (q, 6H, *J* = 8.1); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 104.5, 128.5, 128.0, 126.4, 74.6, 68.8, 6.9, 4.6; IR 2954, 2911, 2876, 1454, 1103, 1062, 1004, 727, 698, 532 cm^{-1}; HRMS (ESI+) calcd for $C_{14}H_{23}OSi$ $[M - OH]^+$ 235.1518, found 235.1523; $[\alpha]_D^{20}$ = −26.2 (*c* = 1.0, CH_2Cl_2, *l* = 50 mm).

*(S)-1-Bromo-3-((triethylsilyl)oxy)propan-2-ol (**2k**, Table 1, entry 11).* The general procedure was followed using 10 mol % of catalyst **4b**, 0.80 equiv of *N*,*N*-diisopropylethylamine, and 0.70 equiv of chlorotriethylsilane to yield product as colorless oil (run 1: 110 mg, 41%, er = 97.5:2.5; run 2: 40%, er = 97.5:2.5): chiral GLC analysis (Gamma Dex 120 (30 m × 0.15 mm × 0.25 mm film thickness), 110 °C for 160 min, 20 °C/min to 180 °C, 180 °C for 20 min, 15 psi, t_{rminor} = 73.6 min, t_{rmajor} = 74.8 min); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.83 (ddd, 1H, *J* = 16.4, 6.1, 4.9), 3.72 (dd, 1H, *J* = 10.0, 4.6), 3.68 (dd, 1H, *J* = 10.0, 4.9), 3.41−3.49 (m, 2H), 2.56 (d, 1H, J = 6.4), 0.93−0.96 (m, 9H), 0.61 (q, 6H, J = 7.8); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 71.3, 64.0, 34.7, 6.9, 4.5; IR 2955, 2876, 1459, 1240, 1108, 1006, 799, 727, 671 cm^{-1}; HRMS (ESI+) calcd for $C_9H_{22}BrO_2Si$ $[M + H]^+$ 269.0572, found 269.0576; $[\alpha]_D^{20}$ = −1.0 (*c* = 1.0, CH_2Cl_2, *l* = 50 mm).

*(S)-1-Chloro-3-((triethylsilyl)oxy)propan-2-ol (**2l**, Table 1, entry 12).* The general procedure was followed using 10 mol % of catalyst **4b**, 0.80 equiv of *N*,*N*-diisopropylethylamine, and 0.70 equiv of chlorotriethylsilane to yield product as colorless oil (run 1: 94 mg, 42%, er = 97.5:2.5; run 2: 40%, er = 97.5:2.5): chiral GLC analysis (Gamma Dex 120 (30 m × 0.15 mm × 0.25 mm film thickness), 110 °C for 50 min, 20 °C/min to 180 °C, 180 °C for 20 min, 15 psi, t_{rminor} = 44.3 min, t_{rmajor} = 45.0 min); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.80−3.86 (m, 1H), 3.66−3.72 (m, 2H), 3.54−3.61 (m, 2H), 2.54 (d, 1H, *J* = 6.4), 0.93−0.96 (m, 9H), 0.61 (q, 6H, *J* = 8.1); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 71.6, 63.3, 45.6, 6.9, 4.5; IR 3425, 2955, 2877, 1459, 1240, 1111, 1006, 804, 740 cm^{-1}; HRMS (ESI+) calcd for $C_9H_{22}ClO_2Si$ $[M + H]^+$ 225.1070, found 225.1078; $[\alpha]_D^{20}$ = −2.5 (*c* = 1.1, CH_2Cl_2, *l* = 50 mm).

Large Scale Experiment (eq 1). In a drybox, a solution of 3-chloropropane-1,2-diol (1.1 g, 10 mmol), catalyst **4b** (310 mg, 1.0 mmol, 10 mol %), and *N*,*N*-diisopropylethylamine hydrochloride (99 mg, 0.60 mmol, 6 mol %) in anhydrous *tert*-butanol (150 mL) was prepared in an oven-dried 250 mL round-bottom flask. The reaction was brought out of the drybox and was stirred at room temperature for 45 min. *N*,*N*-Diisopropylethylamine (1.4 mL, 8.0 mmol) was added, followed by addition of chlorotriethylsilane (1.2 mL, 7.0 mmol) in four portions every 15 min (dropwise addition was performed for each portion added). The reaction was stirred at room temperature for 1 h (starting from the first addition of chlorotriethylsilane). Methanol (1.5 mL) was added to quench the reaction. The solvent was removed under reduced pressure, and flash column chromatography (hexanes/EtOAc = 60:1) afforded pure product as colorless oil (940 mg, 45%, er = 97:3).

Kinetic Resolution Using *tert*-Butyldimethylsilyl Chloride (eq 2). In a drybox, a solution of hexane-1,2-diol (120 mg, 1.0 mmol), catalyst **4a** (42 mg, 0.15 mmol, 15 mol %), and *N*,*N*-diisopropylethylamine hydrochloride (10 mg, 0.060 mmol, 6 mol %) in anhydrous *tert*-butanol (15 mL) was prepared in an oven-dried glass reaction vial. The reaction was brought out of the drybox and was stirred at room temperature for 45 min. *N*,*N*-Diisopropylethylamine (140 μL, 0.80 mmol) was added, followed by addition of *tert*-butyldimethylsilyl chloride (110 mg, 0.70 mmol). The reaction was stirred at 4 °C for 24 h. Methanol (150 μL) was added to quench the reaction. The solvent was removed under reduced pressure, and flash column chromatography (hexanes/EtOAc = 60:1) afforded pure product as colorless oil (run 1: 106 mg, 46%, er = 89:11; run 2: 101 mg, 43%, er = 89:11): chiral GLC analysis (Beta Dex 120 (30 m × 0.15 mm × 0.25 mm film thickness), 95 °C for 80 min, 20 °C/min to 180 °C, 180 °C for 20 min, 15 psi, t_{rminor} = 56.9 min, t_{rmajor} = 57.8 min).

*(R)-1-((tert-Butyldimethylsilyl)oxy)hexan-2-ol (**2ba**):* ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.59−3.63 (m, 2H), 3.37 (dd, 1H, *J* = 10.5, 8.3), 2.38 (d, 1H, *J* = 3.4), 1.24−1.43 (m, 6H), 0.86−0.90 (m, 12H), 0.05 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 72.1, 67.5, 32.7, 28.0, 26.1, 23.0, 18.5, 14.2, −5.1, −5.2; IR 2955, 2929, 2858, 1463, 1254, 1098, 835, 775 cm^{-1}; HRMS (ESI+) calcd for $C_{12}H_{29}O_2Si$ $[M + H]^+$

dx.doi.org/10.1021/jo4012909 | J. Org. Chem. 2013, 78, 10494−10499

233.1937, found 233.1938; $[\alpha]_D^{20}$ = −4.6 (*c* = 1.0, CH_2Cl_2, *l* = 50 mm).

Kinetic Resolution Using Triisopropylsilyl Chloride (eq 2). In a drybox, a solution of hexane-1,2-diol (120 mg, 1.0 mmol), catalyst **4a** (42 mg, 0.15 mmol, 15 mol %), and *N*,*N*-diisopropylethylamine hydrochloride (10 mg, 0.060 mmol, 6 mol %) in anhydrous *tert*-butanol (15 mL) was prepared in an oven-dried glass reaction vial. The reaction was brought out of the drybox and was stirred at room temperature for 45 min. *N*,*N*-Diisopropylethylamine (140 μL, 0.80 mmol) was added, followed by addition of triisopropylsilyl chloride (150 μL, 0.70 mmol). The reaction was stirred at 4 °C for 48 h. Methanol (150 μL) was added to quench the reaction. The solvent was removed under reduced pressure, Flash column chromatography (hexanes/EtOAc = 60:1) afforded pure product as colorless oil (run 1: 115 mg, 42%, er = 95:5; run 2: 105 mg, 38%, er = 97:3): chiral GLC analysis (Gamma Dex 120 (30 m × 0.15 mm × 0.25 mm film thickness), 110 °C for 150 min, 20 °C/min to 180 °C, 180 °C for 20 min, 15 psi, t_{rminor} = 137.4 min, t_{rmajor} = 140.7 min).

*(R)-1-((Triisopropylsilyl)oxy)hexan-2-ol (**2bb**):* ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.64 (dd, 1H, *J* = 9.5, 3.2), 3.56−3.61 (m, 1H), 3.40 (dd, 1H, *J* = 9.5, 7.6), 2.47 (d, 1H, 3.2), 1.25−1.39 (m, 6H), 0.95−1.07 (m, 21H), 0.84 (m, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 72.2, 67.8, 32.7, 28.0, 23.0, 18.2, 14.2, 12.1; IR 2940, 2865, 1463, 1103, 882, 797, 681, 660 cm^{-1}; HRMS (ESI+) calcd for $C_{15}H_{35}O_2Si$ $[M + H]^+$ 275.2406, found 275.2415; $[\alpha]_D^{20}$ = −4.2 (*c* = 1.0, CH_2Cl_2, *l* = 50 mm).

■ ASSOCIATED CONTENT

Supporting Information

^{1}H and ^{13}C NMR spectra for the products. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: kian.tan@novartis.com.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the Alfred P. Sloan Foundation (K.L.T.), LaMattina Fellowship (X.S. and A.D.W.), NSF (CHE-1150393), and NIGMS (RO1GM087581) for funding of this project. Mass spectrometry instrumentation at Boston College is supported by funding from the NSF (DBI-0619576).

■ REFERENCES

(1) Hanson, R. M. *Chem. Rev.* **1991**, *91*, 437.
(2) Kolb, H. C.; Vannieuwenhze, M. S.; Sharpless, K. B. *Chem. Rev.* **1994**, *94*, 2483.
(3) White, D. E.; Jacobsen, E. N. *Tetrahedron: Asymmetry* **2003**, *14*, 3633.
(4) Schaus, S. E.; Brandes, B. D.; Larrow, J. F.; Tokunaga, M.; Hansen, K. B.; Gould, A. E.; Furrow, M. E.; Jacobsen, E. N. *J. Am. Chem. Soc.* **2002**, *124*, 1307.
(5) Tokunaga, M.; Larrow, J. F.; Kakiuchi, F.; Jacobsen, E. N. *Science* **1997**, *277*, 936.
(6) Kliman, L. T.; Mlynarski, S. N.; Morken, J. P. *J. Am. Chem. Soc.* **2009**, *131*, 13210.
(7) Lee, Y.; Jang, H.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2009**, *131*, 18234.
(8) Morgan, J. B.; Miller, S. P.; Morken, J. P. *J. Am. Chem. Soc.* **2003**, *125*, 8702.
(9) Jacobsen, E. N.; Marko, I.; Mungall, W. S.; Schroder, G.; Sharpless, K. B. *J. Am. Chem. Soc.* **1988**, *110*, 1968.
(10) Diaz-de-Villegas, M. D.; Galvez, J. A.; Badorrey, R.; Lopez-Ram-de-Viu, M. P. *Chem.—Eur. J.* **2012**, *18*, 13920.
(11) Muller, C. E.; Schreiner, P. R. *Angew. Chem., Int. Ed.* **2011**, *50*, 6012.
(12) Voituriez, A.; Panossian, A.; Fleury-Bregeot, N.; Retailleau, P.; Marinetti, A. *Adv. Synth. Catal.* **2009**, *351*, 1968.
(13) Wuts, P. G. M.; Greene, T. W. *Protective Groups in Organic Synthesis*, 4th ed.; Wiley-Interscience: New York, 2007.
(14) Kocienski, P. *Protecting Groups*, 3rd ed.; Thieme: Stuttgart, 2005.
(15) Nelson, T. D.; Crouch, R. D. *Synthesis* **1996**, 1031.
(16) Isobe, T.; Fukuda, K.; Araki, Y.; Ishikawa, T. *Chem. Commun.* **2001**, 243.
(17) Rendler, S.; Auer, G.; Oestreich, M. *Angew. Chem., Int. Ed.* **2005**, *44*, 7620.
(18) Weickgenannt, A.; Mewald, M.; Muesmann, T. W. T.; Oestreich, M. *Angew. Chem., Int. Ed.* **2010**, *49*, 2223.
(19) Weickgenannt, A.; Mewald, M.; Oestreich, M. *Org. Biomol. Chem.* **2010**, *8*, 1497.
(20) Takeichi, T.; Kuriyama, M.; Onomura, O. *Tetrahedron Lett.* **2011**, *52*, 6646.
(21) Zhao, Y.; Rodrigo, J.; Hoveyda, A. H.; Snapper, M. L. *Nature* **2006**, *443*, 67.
(22) Zhao, Y.; Mitra, A. W.; Hoveyda, A. H.; Snapper, M. L. *Angew. Chem., Int. Ed.* **2007**, *46*, 8471.
(23) Rodrigo, J. M.; Zhao, Y.; Hoveyda, A. H.; Snapper, M. L. *Org. Lett.* **2011**, *13*, 3778.
(24) Sheppard, C. I.; Taylor, J. L.; Wiskur, S. L. *Org. Lett.* **2011**, *13*, 3794.
(25) Sun, X. X.; Worthy, A. D.; Tan, K. L. *Angew. Chem., Int. Ed.* **2011**, *50*, 8167.
(26) Worthy, A. D.; Sun, X. X.; Tan, K. L. *J. Am. Chem. Soc.* **2012**, *134*, 7321.
(27) You, Z.; Hoveyda, A. H.; Snapper, M. L. *Angew. Chem., Int. Ed.* **2009**, *48*, 547.
(28) Miller, L. C.; Sarpong, R. *Chem. Soc. Rev.* **2011**, *40*, 4550.
(29) Kumar, R. R.; Kagan, H. B. *Adv. Synth. Catal.* **2010**, *352*, 231.
(30) Vedejs, E.; Jure, M. *Angew. Chem., Int. Ed.* **2005**, *44*, 3974.
(31) Wu, B.; Parquette, J. R.; RajanBabu, T. V. *Science* **2009**, *326*, 1662.
(32) Tan, K. L. *ACS Catal.* **2011**, *1*, 877.
(33) Rousseau, G.; Breit, B. *Angew. Chem., Int. Ed.* **2011**, *50*, 2450.
(34) Park, Y. J.; Park, J. W.; Jun, C. H. *Acc. Chem. Res.* **2008**, *41*, 222.
(35) Taylor, M. S.; Beale, T. M. *Org. Lett.* **2013**, *15*, 1358.
(36) Lee, D.; Williamson, C. L.; Chan, L. N.; Taylor, M. S. *J. Am. Chem. Soc.* **2012**, *134*, 8260.
(37) Chan, L. N.; Taylor, M. S. *Org. Lett.* **2011**, *13*, 3090.
(38) Gouliaras, C.; Lee, D.; Chan, L. N.; Taylor, M. S. *J. Am. Chem. Soc.* **2011**, *133*, 13926.
(39) Lee, D.; Taylor, M. S. *J. Am. Chem. Soc.* **2011**, *133*, 3724.
(40) Lee, D.; Taylor, M. S. *Synthesis* **2012**, *44*, 3421.
(41) Worthy, A. D.; Joe, C. L.; Lightburn, T. E.; Tan, K. L. *J. Am. Chem. Soc.* **2010**, *132*, 14757.
(42) MacDonald, M. J.; Hesp, C. R.; Schipper, D. J.; Pesant, M.; Beauchemin, A. M. *Chem.—Eur. J.* **2013**, *19*, 2597.
(43) Guimond, N.; MacDonald, M. J.; Lemieux, V.; Beauchemin, A. M. *J. Am. Chem. Soc.* **2012**, *134*, 16571.
(44) MacDonald, M. J.; Schipper, D. J.; Ng, P. J.; Moran, J.; Beauchemin, A. M. *J. Am. Chem. Soc.* **2011**, *133*, 20100.
(45) Tsujigami, T.; Sugai, T.; Ohta, H. *Tetrahedron: Asymmetry* **2001**, *12*, 2543.