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Carbonylation of *cis*-Disubstituted Epoxides to *trans*-β-Lactones: Catalysts Displaying Steric and Contrasteric Regioselectivity

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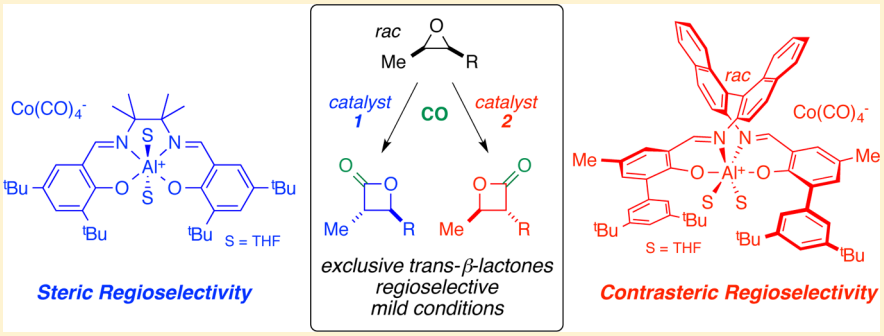
Supporting Information



ABSTRACT: *trans*-β-Lactones are a versatile and useful class of compounds, but reliable methods for their direct synthesis are still limited. Addressing this problem, we present herein two catalysts for the regioselective carbonylation of *cis*-disubstituted epoxides. The two catalysts show high activities and opposing regioselectivities so that either one of the two possible β-lactone regioisomers can be obtained selectively.

INTRODUCTION

β-Lactones represent a valuable class of organic compounds due to their occurrence in natural products,[1] their ability to serve as monomers in the synthesis of polyesters,[2] and their versatility as synthetic intermediates.[3,4] The latter part is based on the high inherent reactivity of β-lactones and often used in the synthesis of aldol-type products.[5] *trans*-β-Lactones in racemic or enantioenriched form are particularly valuable for this purpose because the resulting *anti*-aldol products are often less readily available than their *syn*-counterparts when using traditional aldol chemistry.[6] Unfortunately, not many methods are currently available to make *trans*-β-lactones stereoselectively in a direct and economical fashion (Figure 1).[3a,7,8] Typical routes include the cyclization of aldol products or (formal) [2 + 2] cycloadditions of ketenes with aldehydes. Although the latter approach is very direct, only a few selective catalytic systems have been described for this transformation. Elegant contributions to this field were recently made by Peters and co-workers[9a−c] as well as Calter and co-workers.[9d]

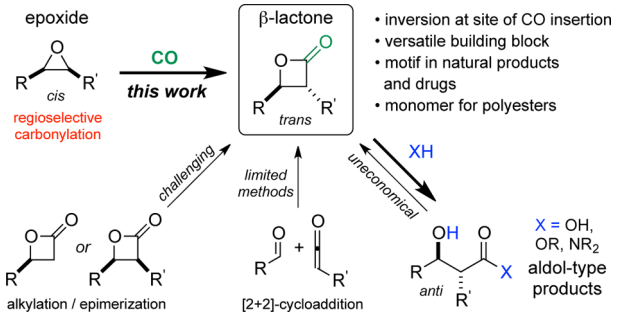


Figure 1. Common approaches to *trans*-β-lactones and regioselective epoxide carbonylation as a versatile alternative.

Carbonylation of epoxides using catalysts of the form [Lewis acid]$^+$[Co(CO)$_4$]$^-$ has recently emerged as a reliable direct approach to β-lactones when using terminal or symmetrically 2,3-disubstituted epoxides as substrates.[10,11] Unsymmetrically *cis*- or *trans*-disubstituted epoxides, however, are prone to giving mixtures of regioisomeric β-lactones.[11] Presumably, an indiscriminate S_N2-ring opening reaction of the cobaltate nucleophile in the case of electronically or sterically unbiased substrates causes these mixtures (Scheme 1). This is a general problem associated with this class of epoxides.[12]

Our group recently addressed part of this challenge by introducing two new catalysts that could carbonylate racemic and enantioenriched *trans*-disubstituted epoxides to the corresponding *cis*-β-lactones with high and opposing regioselectivities.[13] This method would be of significant value if it could be adapted to the regioselective production of *trans*-β-lactones from the corresponding *cis*-epoxides because of the *anti*-aldol-type products resulting from them. In addition, almost all naturally occurring β-lactones display a *trans*-configuration.[14] Previously reported carbonylation catalysts usually show unsatisfactory regioselectivities with *cis*-epoxides,[15]

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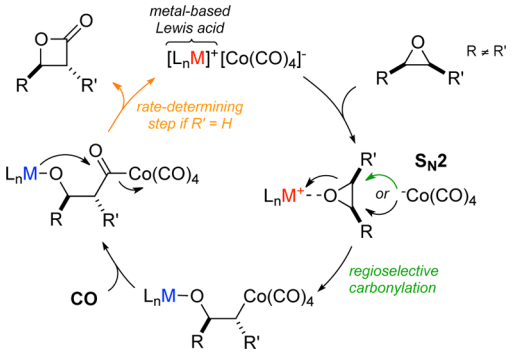
Scheme 1. Simplified Mechanism of Epoxide Carbonylation[a]



[a]For a more detailed discussion, see reference 10d.

which necessitated the design of new carbonylation catalysts. Herein, we report how previously gained mechanistic insight led to a catalyst that shows good activity and high contrasteric regioselectivity in the carbonylation of *cis*-disubstituted epoxides. A carbonylation catalyst selectively yielding the steric carbonylation product is reported as well.

RESULTS AND DISCUSSION

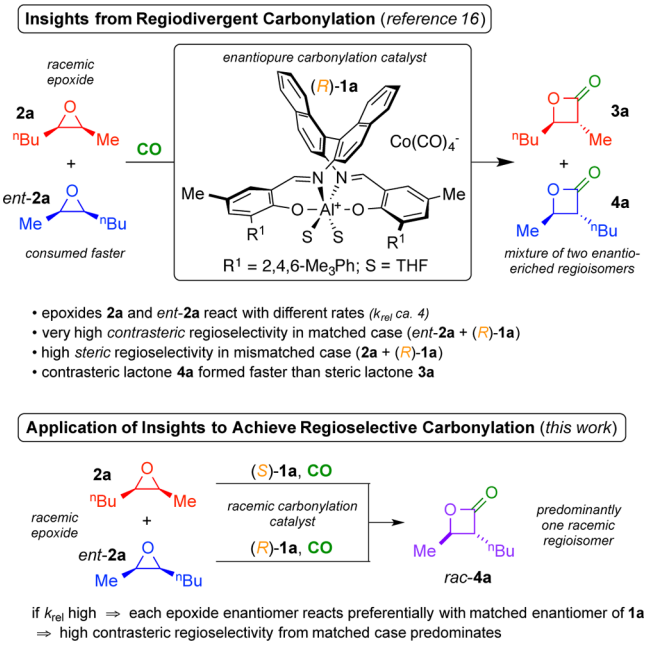
The development of the contrasteric carbonylation catalyst was based on insight gained during our investigation of the regiodivergent carbonylation of *cis*-2,3-disubstituted epoxides.[16] In this process, an enantiopure carbonylation catalyst such as (*R*)-**1a** transforms a racemic *cis*-2,3-disubstituted epoxide *rac*-**2** into a mixture of two regioisomeric β-lactones **3** and **4**, both of which are highly enantioenriched (Scheme 2, top part).

While following the regiodivergent carbonylation of racemic *cis*-2,3-heptene oxide (*rac*-**2a**) in detail, we made the unusual observation that incorporation of CO was kinetically more facile at the methine carbon of the epoxide that was seemingly more sterically hindered.[16] In the case of racemic **2a**, this meant that the 3-butyl-4-methyl-substituted β-lactone **4a**, and not the 4-butyl-3-methyl isomer **3a**, was the predominant lactone species at low levels of epoxide conversion. Indeed, when reacting only the kinetically preferred enantiomer of *cis*-2,3-heptene oxide (*ent*-**2a**) with (*R*)-**1a**, i.e., the matched case between substrate and catalyst, a high contrasteric selectivity (41:1) was observed.[16] The mismatched case, i.e., **2a** reacting with (*R*)-**1a**, on the other hand, produced a reduced selectivity (8:1) in favor of the steric product.

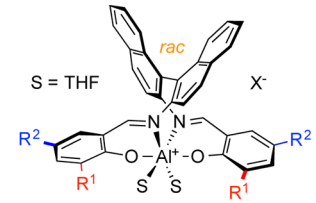
Based on this information, we proposed that the use of *rac*-**1a** instead of (*R*)-**1a** would induce formation of mainly one regioisomer of the β-lactone, albeit in racemic form (Scheme 2, bottom part). In order to be successful, each enantiomer of the catalyst must react only with its matched enantiomer of the epoxide; i.e., the catalyst must show an appreciable k_{rel},[17] and the matched enantiomer of the epoxide must be carbonylated with high regioselectivity. Only then would one expect predominant formation of only one of the two regioisomers of the β-lactone.[18] Given the previous insight, these conditions were seemingly met if catalyst *rac*-**1a** were used in the carbonylation of racemic *cis*-2,3-heptene oxide (*rac*-**2a**).

A test reaction using *rac*-**1a** and *rac*-**2a** showed that the contrasteric β-lactone product *rac*-**4a** was indeed formed preferentially (Scheme 3). The observed selectivity of 4.0:1

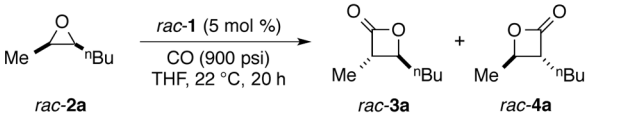
Scheme 2. Observations Made during the Study of Regiodivergent Carbonylation of *cis*-Epoxides and the Implied Possibility of Regioselective Carbonylation



Scheme 3. Evaluation of Catalysts for the Carbonylation of *cis*-Disubstituted Epoxide *rac*-2a with Contrasteric Selectivity



	R^1	R^2
rac-**1a**	2,4,6-Me_3Ph	Me
rac-**1b**	2,6-Me_2Ph	2,6-Me_2Ph
rac-**1c**	3,5-$^t Bu_2$Ph	Me



catalyst	solvent	product ratio
rac-**1a**	THF	1 : 4.0
rac-**1b**	THF	1 : 1.9
rac-**1c**	THF	1 : 11.5
rac-**1c**	1,4-dioxane	1 : 24.0

correlates very well with the very high contrasteric regioselectivity and the k_{rel} of ca. 4 that were determined previously for this reaction (vide supra). With the goal of increasing the selectivity further, previously reported catalyst *rac*-**1b**[16] was also tested in the same reaction (Scheme 3). Although this catalyst showed a slightly lower contrasteric regioselectivity when reacting (*R*)-**1b** with enantiopure *ent*-**2a** (24.6:1),[19] we theorized that the increased steric bulk of the Lewis acid part might significantly increase the k_{rel} value. Unfortunately, the opposite case was true. The observed low regioselectivity of 1.9:1 is most likely the result of the reduced regioselectivity in the matched case in combination with a lower k_{rel} value. Extensive experimentation eventually revealed catalyst *rac*-**1c** to be the most suitable catalyst for the carbonylation of *cis*-disubstituted epoxides with contrasteric regioselectivity so far (Scheme 3). This catalyst most likely retains the high regioselectivity observed with **1a** and **b** in the

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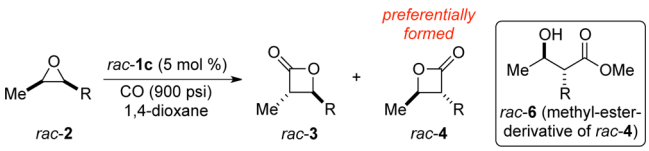
matched case,[20] so that the improved outcome of the reaction can be attributed to a superior k_{rel} value.

Moreover, changing the solvent from THF to 1,4-dioxane further improved the observed selectivity from 11.5:1 to 24.0:1. Structurally related ethereal solvents such as tetrahydropyran and diethyl ether also showed markedly different results in terms of selectivity and activity.[19] This observation underlines the importance of the previously determined interaction between solvent and carbonylation catalysts of the type [Lewis acid]$^+$[Co(CO)$_4$]$^-$.[10d] However, the specific effect of solvent structure on regioselectivity is not understood at this point.

With a competent contrasteric catalyst in hand, the scope of this regioselective carbonylation reaction was investigated (Table 1). Selective formation of lactones *rac*-**4** using catalyst

Table 1. Regioselective Carbonylation of Racemic *Cis*-Disubstituted Epoxides 2 Yielding *β*-Lactones *rac*-4 Using Catalyst *rac*-1c[a]



entry	R (epoxide)	ratio[b] 3:4	product	yield (%)
1	Et (*rac*-**2b**)	1:10.1	*rac*-**6b**	70
2	^{n}Pr (*rac*-**2c**)	1:15.7	*rac*-**6c**	77
3	^{n}Bu (*rac*-**2a**)	1:24.0	*rac*-(**3a** + **4a**)	69
4	^{n}Pent (*rac*-**2d**)	1:24.0	*rac*-(**3d** + **4d**)	74
5	^{n}Hex (*rac*-**2e**)	1:19.0	*rac*-(**3e** + **4e**)	72
6[c]	^{n}Bu (**2a**)	1:24.0	**3a** + **4a**	>95[d]
7	CH_2Cy (*rac*-**2f**)	1:4.9	*rac*-(**3f** + **4f**)	83[d]
8	CH_2Ph (*rac*-**2g**)	1:1.3	*rac*-(**3g** + **4g**)	18[d]
9	$(CH_2)_2$Ph (*rac*-**2h**)	1:32.3	*rac*-**6h**	83
10	$(CH_2)_2{}^i$Pr (*rac*-**2i**)	1:19.0	*rac*-**6i**	78
11	$(CH_2)_2$OTBS (*rac*-**2j**)	1:24.0	*rac*-**6j**	81
12	$(CH_2)_3$OTBS (*rac*-**2k**)	1:13.3	*rac*-**6k**	80
13	$(CH_2)_3$OAc (*rac*-**2l**)	1:10.1	*rac*-(**3l** + **4l**)	82

[a]Reaction conditions: [*rac*-**2**] = 0.5 M, 22 °C, 20 h. [b]Determined by ^{1}H NMR analysis of crude reaction mixture. [c](2*S*,3*R*)-heptene oxide (99% ee) was used. [d]Percent conversion to *β*-lactone (^{1}H NMR analysis). All reactions gave full conversion (GC or ^{1}H NMR analysis), except for *rac*-**2f**,**g**. Catalyst *rac*-**1c** was prepared in situ (L_nAlCl (*rac*-**5c**) + NaCo(CO)$_4$).

rac-**1c** proceeded extremely well, with ratios in favor of *rac*-**4** exceeding 10.0:1 for nearly all *cis*-epoxides *rac*-**2** tested. Even *rac*-**2b**, an epoxide with sterically very similar substituents, gave a very good selectivity of 10.1:1 (entry 1). Slightly better ratios were achieved with epoxides bearing longer alkyl chains (entries 2−5). It is worth noting that catalyst *rac*-**1c** did not show much variance in selectivity as the length of the linear alkyl chain in the substituent R was altered, the only exception being *rac*-**2b**. Furthermore, *rac*-**1c** carbonylated enantioenriched epoxides such as **2a** with equally high regioselectivity (entry 6). Given the availability of enantioenriched epoxides,[21] this makes for a convenient entry into enantioenriched *β*-lactones and aldol-type products. Epoxides with additional steric hindrance in R also underwent regioselective carbonylation reactions with *rac*-**1c** and still yielded the contrasteric lactone *rac*-**4** preferentially (entries 7−13). Interestingly, the selectivities observed with these epoxides were comparable to those achieved with the less hindered epoxides *rac*-**2a**−**e**, and even ratios as high as 32.3:1 and 24.0:1 (entries 9 and 11) were obtained. The only limitation arose when steric bulk was situated very close to the epoxide (entries 7 and 8). Nevertheless, the observed ratios of 4.9:1 and 1.3:1 in favor of lactones *rac*-**4f** and **g**, respectively, are still good given how sterically shielded the corresponding methine carbons are from nucleophilic attack. This fact is also reflected in the high selectivity with which lactones *rac*-**3f** and **g** are formed when using a carbonylation catalyst with steric selectivity (vide infra, Table 4). Lastly, *cis*-epoxides with sterically very similar substituents such as racemic *cis*-3,4-octene oxide were carbonylated with low regioselectivity by *rac*-**1c**.[22]

The two resulting lactones *rac*-**3** and **4** could generally not be separated quantitatively from one another using flash column chromatography. Therefore, the resulting *trans*-*β*-lactones were isolated as mixtures in good yields, except for those derived from the sterically encumbered epoxides *rac*-**2f** and **g**. However, ring opening of lactones *rac*-**3** and **4** to the corresponding aldol-type methyl esters by quenching the reaction with MeOH/NaOMe allowed for facile separation of the two regioisomers. Equally good yields were obtained using this approach, which is shown for a selected range of epoxides in Table 1 (entries 1 and 2 and 9−12).

Catalyst *rac*-**1c** most likely operates under the mechanism proposed in Scheme 1. However, this mechanism was elucidated for carbonylation catalysts bearing salen ligands coordinating in a *trans*- instead of *cis*-*α*-fashion and with terminal instead of internal epoxides as substrates. These changes may seem minor but could influence which step in the catalytic cycle becomes rate-determining. In the case of terminal epoxides, ring-closing to the lactone is thought to be rate-determining (cf. Scheme 1) and all prior steps to be fully reversible. It seems unlikely that this also holds for internal epoxides because then the observed regioselectivity would be the result of thermodynamic instead of kinetic control. Given the conformational flexibility of a ring-opened epoxide, the ligand would have a hard time discriminating between the two regioisomeric species effectively. A more likely scenario is that the nucleophilic attack of the cobaltate anion on the internal epoxide, once it has coordinated to the Lewis acid, has become the rate- and selectivity-determining step in this reaction.

Given the success of the Lewis acid moiety of catalyst **1c** in inducing contrasteric ring opening of *cis*-epoxides, the use of a different nucleophile was explored. The use of chloride instead of [Co(CO)$_4$]$^-$ as the anion, and thus the synthesis of vicinally disubstituted chlorohydrins, seemed particularly attractive because they are important functional groups,[23] yet methods for their regioselective synthesis are scarce.[24] Moreover, compounds of the type [L$_n$Al]-Cl, which are commonly used as precursors in the synthesis of carbonylation catalysts, seemed ideal catalysts for the regioselective formation of chlorohydrins. Indeed, complex *rac*-**5c**, the precursor to *rac*-**1c** (Scheme 3), turned out to be a selective and active catalytic system. Addition of 2,4,6-trimethylpyridine hydrochloride as a mild surrogate for hydrochloric acid led to complete conversion of assorted *cis*-epoxides in the presence of *rac*-**5c** (Table 2). In the absence of *rac*-**5c**, only negligible amounts of conversion were detected.[19]

The observed contrasteric selectivity with preferential formation of chlorohydrins *rac*-**8** is consistent with the results obtained with *rac*-**1c** in Table 1. Interestingly, contrasteric selectivity is also observed in the absence of *rac*-**5c** or when

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Table 2. Regioselective Formation of Chlorohydrins *rac*-8 from Racemic *Cis*-Disubstituted Epoxides 2 Using Catalyst *rac*-5c[a]

entry	R (epoxide)	ratio 7:8	product	yield (%)
1	^{n}Bu (*rac*-**2a**)	1:6.7[b]	*rac*-**8a**	68
2	^{n}Hex (*rac*-**2e**)	1:6.1[c]	*rac*-**8e**	77
3[d]	CH_2Ph (*rac*-**2g**)	1:2.8[c]	*rac*-**8g**	55
4	$(CH_2)_2Ph$ (*rac*-**2h**)	1:4.9[c]	*rac*-**8h**	75
5	$(CH_2)_2{}^{i}Pr$ (*rac*-**2i**)	1:6.7[b]	*rac*-**8i**	68

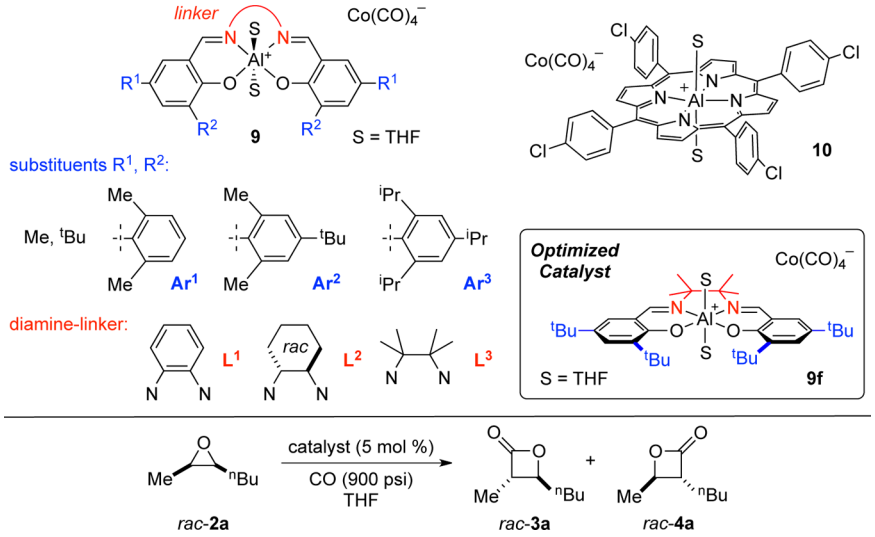
[a]Reaction conditions: [*rac*-**2**] = 0.5 M, 22 °C, 48 h. [b]Determined by GC analysis of crude reaction mixture. [c]Determined by ^{1}H NMR analysis of crude reaction mixture. [d]7.5 mol % *rac*-**5c** used. All reactions gave full conversion (GC or ^{1}H NMR analysis). See the Supporting Information for additional tables concerning control experiments and solvent optimization.

opening the epoxide directly using hydrochloric acid in diethyl ether.[19] However, the selectivities obtained in those cases are significantly less when compared to the results with *rac*-**5c**. Ratios in favor of *rac*-**8** exceeded 6.0:1 for epoxides with linear or branched alkyl chains as substituent R when using *rac*-**5c** (entries 1, 2, and 5). However, regioselectivity dropped in cases where the steric bulk was located too close to the epoxy group (entry 3) or became too large (entry 4). Nonetheless, all chlorohydrins were readily isolated in good yields.

Having established a good methodology to access the contrasteric β-lactone product *rac*-**4**, it now seemed sensible to find a catalyst that would selectively produce the steric regioisomer. The resulting β-lactones *rac*-**3** would give rise to potentially useful propionate aldol-type motifs commonly found in natural products synthesis.[25] Because of the recent success of salen-based complexes with *trans*-geometry in the regioselective carbonylation of *trans*-epoxides,[13] we hoped that the salen framework could be modified to yield a catalyst with steric selectivity for *cis*-epoxides. To this end, a variety of salen-based carbonylation catalysts were synthesized and screened for the selective synthesis of *rac*-**3a** starting from epoxide *rac*-**2a** (Table 3).

Test reactions using literature-known catalysts **9a**–**c** already yielded good conversions and selectivities for lactone *rac*-**3a** (entries 1–3). Interestingly, the use of chromium as Lewis acidic metal ion produced a more active yet less selective catalyst in comparison to the aluminum-based system (entries 1 and 2) and, thus, was not pursued further. Introduction of bulky aryl substituents in position *ortho* to the phenol moiety (substituent R^2) showed no benefit in terms of selectivity

Table 3. Evaluation of Catalysts for the Carbonylation of *Cis*-Disubstituted Epoxide *rac*-2a with Steric Selectivity[a]



entry	linker	R^1	R^2	catalyst	ratio[b] **3a**:**4a**	conv[b] (%)
1	L^1	^{t}Bu	^{t}Bu	**9a**	3.0:1	74
2[c]	L^1	^{t}Bu	^{t}Bu	**9b**	2.1:1	95
3	L^2	^{t}Bu	^{t}Bu	*rac*-**9c**	2.7:1	72
4	L^2	Me	Ar^1	*rac*-**9d**	1.6:1	74
5	L^2	Me	Ar^2	*rac*-**9e**	3.0:1	72[d]
6	L^3	^{t}Bu	^{t}Bu	**9f**	3.3:1	>95
7	L^3	^{t}Bu	Me	**9g**	2.0:1	>95
8	L^3	Me	Me	**9h**	2.1:1	>95
9	L^3	Me	H	**9i**	2.1:1	>95
10	L^3	Ar^3	^{t}Bu	**9j**	2.1:1	>95
11[e]				**10**	2.9:1	>95

[a]Reaction conditions: [*rac*-**2a**] = 0.5 M, 22 °C, 20 h. [b]Conversion to lactone and ratio of regioisomers determined by GC or ^{1}H NMR analysis of crude reaction mixture. [c]Cr^{3+} used as the Lewis acidic metal ion. [d]The remainder was 3-heptanone. [e]2 mol % of **10** was used. All catalysts except **9a**–**c** and **10** were prepared in situ (L_nAlCl + $NaCo(CO)_4$).

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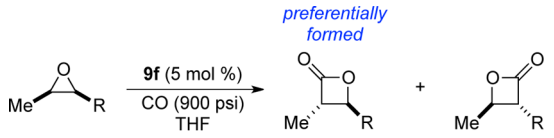
(entries 4 and 5). Changing the diamine linker to 2,3-dimethylbutane-2,3-diamine (L^3) preserved the good steric regioselectivity observed with linkers L^1 and L^2 and further increased the activity of the catalytic system (catalyst **9f**, entry 6). Keeping linker L^3 but reducing the steric size of substituents R^1 and R^2 had no beneficial effect in terms of selectivity (entries 7−9). Installation of a very bulky substituent in position R^1 also brought no further advantage (entry 10). Consequently, **9f** was the catalyst of choice for selective production of lactone *rac*-**3a** from *rac*-**2a**. Lastly, it should be noted that porphyrin catalyst **10** also displayed good activity and steric selectivity (entry 11). However, modifications of this framework were not pursued further.

When using catalyst **9f** in the carbonylation of a variety of racemic *cis*-epoxides, selectivities of >3.0:1 in favor of lactone *rac*-**3** were usually observed (Table 4). As with catalyst *rac*-**1c**,

Table 4. Regioselective Carbonylation of *Cis*-Disubstituted Epoxides *rac*-2 Yielding *β*-Lactones *rac*-3 Using Catalyst 9f[a]



rac-**2** *rac*-**3** *rac*-**4**

entry	R (epoxide)	ratio[b] **3**:**4**	product	yield (%)
1	Et (*rac*-**2b**)	3.2:1	*rac*-(**3b** + **4b**)	66
2[c]	^{n}Pr (*rac*-**2c**)	2.9:1	*rac*-(**3c** + **4c**)	62
3	^{n}Bu (*rac*-**2a**)	3.3:1	*rac*-(**3a** + **4a**)	80
4	^{n}Pent (*rac*-**2d**)	3.8:1	*rac*-(**3d** + **4d**)	74
5	^{n}Hex (*rac*-**2e**)	3.5:1	*rac*-(**3e** + **4e**)	91
6	CH_2Cy (*rac*-**2f**)	5.7:1	*rac*-(**3f** + **4f**)	88
7[c]	CH_2Ph (*rac*-**2g**)	19.0:1	*rac*-(**3g** + **4g**)	90
8[c]	$(CH_2)_2Ph$ (*rac*-**2h**)	3.5:1	*rac*-(**3h** + **4h**)	86
9	$(CH_2)_2{}^iPr$ (*rac*-**2i**)	3.3:1	*rac*-(**3i** + **4i**)	90
10[c]	$(CH_2)_2OTBS$ (*rac*-**2j**)	4.0:1	*rac*-(**3j** + **4j**)	87
11	$(CH_2)_3OTBS$ (*rac*-**2k**)	2.7:1	*rac*-(**3k** + **4k**)	92

[a]Reaction conditions: [*rac*-**2**] = 0.5 M, 22 °C, 20 h. [b]Determined by ^{1}H NMR analysis of crude reaction mixture. [c]7.5 mol % of **9f** used. All reactions gave full conversion (GC or ^{1}H NMR analysis).

epoxides with linear alkyl chains as substituent R showed good selectivities in the range of 2.9 to 3.8:1 irrespective of the length of the alkyl chain (entries 1−5). In the case of epoxides with sterically more demanding substituents R, one would predict an increase in selectivity due to a stronger inherent steric bias. Indeed, such additional bias benefited selectivity as long as it was situated close to the epoxide (entries 6 and 7). Distancing it further away, however, lessened the influence quickly (entries 8−11), and the obtained selectivities resembled those achieved with epoxides *rac*-**2a**−**e**. Interestingly, epoxides *rac*-**2f** and **g** gave very different ratios of *rac*-**3** and **4** despite their structural similarity. As before, the resulting *trans*-*β*-lactones were isolated as mixtures in good yields due to the inseparability of the regioisomeric products.

From a mechanistic viewpoint, the arguments made during the discussion of catalyst *rac*-**1c** should also apply to **9f**. Although catalyst **9f** most likely displays *trans*-coordination of the salen ligand, it seems unlikely that good regioselectivities could be obtained if the ring-closing step were still the rate-determining step with internal epoxides. As before, it seems more probable that ring opening of the epoxide is the rate-limiting step with these substrates.

CONCLUSION

Two new catalysts, *rac*-**1c** and **9f**, were introduced for the regioselective carbonylation of racemic and enantioenriched *cis*-2,3-disubstituted epoxides **2**. The development of *rac*-**1c**, which shows contrasteric selectivity, was based on insight gained previously from our study of the regiodivergent carbonylation of *cis*-disubstituted epoxides.[16] On the other hand, catalyst **9f** displayed steric regioselectivity, and its development was based on our previous work on the regioselective carbonylation of *trans*-disubstituted epoxides.[13] Because of the opposing regiopreference of *rac*-**1c** and **9f**, either one of the two regioisomeric *trans*-*β*-lactones *rac*-**3** and *rac*-**4** could be accessed in high yield and selectivity. Furthermore, ring opening of *rac*-**3** and **4** using a one-pot procedure gave rise to *anti*-aldol-type compounds that were readily separable by column chromatography. Lastly, a structurally related catalyst *rac*-**5c** was applied to the regioselective synthesis of vicinally disubstituted chlorohydrins *rac*-**8** from *cis*-epoxides *rac*-**2**. This transformation also proceeded with synthetically useful yields and contrasteric selectivity. It was surmised that the regioselective carbonylation of *cis*-disubstituted epoxides follows the previously determined mechanism. However, the occurrence of regioselectivity was rationalized better by assuming that ring opening of the epoxide is the rate-determining step with these substrates.

EXPERIMENTAL SECTION

See the Supporting Information for general considerations, methods, and materials used.

The following compounds were prepared according to literature procedures: *rac*-(2*R*,3*S*)-2-ethyl-3-methyloxirane (*rac*-**2b**),[16] *rac*-(2*R*,3*S*)-2-methyl-3-propyloxirane (*rac*-**2c**),[16] *rac*-(2*R*,3*S*)-2-butyl-3-methyloxirane (*rac*-**2a**),[26] (2*R*,3*S*)-2-butyl-3-methyloxirane (**2a**),[16] *rac*-(2*R*,3*S*)-2-butyl-3-ethyloxirane,[27] *rac*-(2*R*,3*S*)-2-methyl-3-pentyloxirane (*rac*-**2d**),[16] *rac*-(2*R*,3*S*)-2-hexyl-3-methyloxirane (*rac*-**2e**),[16] *rac*-(2*R*,3*S*)-2-isopentyl-3-methyloxirane (*rac*-**2i**),[16] *rac*-*tert*-butyldimethyl-(3-((2*R*,3*S*)-3-methyloxiran-2-yl)propoxy)silane (*rac*-**2k**),[16] *rac*-3-((2*R*,3*S*)-3-methyloxiran-2-yl)propyl acetate (*rac*-**2l**),[28] *rac*-MesBinamAlCl (*rac*-**5a**, precursor to *rac*-**1a**, *rac*-MesBinam = *rac*-3,3″-(([1,1′-binaphthalene]-2,2′-diylbis(azanylylidene))bis(methanylylidene))bis-(2′,4′,5,6′-tetramethyl-[1,1′-biphenyl]-2-olate)),[16] *rac*-Xyl$_2$BinamAlCl (*rac*-**5b**, precursor to *rac*-**1b**, *rac*-Xyl$_2$Binam = *rac*-5′,5″-((1**E**,1′**E**)-([1,1′-binaphthalene]-2,2′-diylbis(azanylylidene))bis(methanylylidene))bis(2,2″,6,6″-tetramethyl[1,1′:3′,1″-terphenyl]-4′-olate),[16] [salphAl(THF)$_2$]$^+$[Co(CO)$_4$]$^-$ (**9a**, salph =6,6′-((1*E*,1′*E*)-(1,2-phenylenebis(azanylylidene))bis(methanylylidene))bis(2,4-di-*tert*-butylphenolate)),[10a] [salphCr(THF)$_2$]$^+$[Co(CO)$_4$]$^-$ (**9b**),[10c] *rac*-[salcyAl(THF)$_2$]$^+$[Co(CO)$_4$]$^-$ (*rac*-**9c**, salcy = *N*,*N*′-*bis*(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamine),[29] *rac*-3,3″-((1*E*,1′*E*)-((1*S*,2*S*)-cyclohexane-1,2-diylbis(azanylylidene))bis(methanylylidene))bis(2′,5,6′-trimethyl-[1,1′-biphenyl]-2-olate)aluminum chloride (precursor to *rac*-**9d**),[13] *rac*-3,3″-((1*E*,1′*E*)-((1*S*,2*S*)-cyclohexane-1,2-diylbis(azanylylidene))bis(methanylylidene))bis(4′-*tert*-butyl-2′,5,6′-trimethyl-[1,1′-biphenyl]-2-olate)aluminum chloride (precursor to *rac*-**9e**),[13] 6,6′-((1*E*,1′*E*)-((2,3-dimethylbutane-2,3-diyl)bis-(azanylylidene))bis(methanylylidene))bis(2,4-di-*tert*-butylphenolate) aluminum chloride (precursor to **9f**),[13] [ClTPPAl(THF)$_2$]$^+$[Co-(CO)$_4$]$^-$ (**10**, ClTPP = *meso*-tetra(4-chlorophenyl)porphyrinato),[30] 3′,5′-di-*tert*-butyl-2-hydroxy-5-methyl-[1,1′-biphenyl]-3-carbaldehyde,[31] 5-*tert*-butyl-2-hydroxy-3-methylbenzaldehyde,[32] 4-bromo-2-(*tert*-butyl)phenol,[33] 2,3-dimethylbutane-2,3-diamine,[34] NaCo-(CO)$_4$,[35] (*Z*)-*tert*-butyldimethyl(pent-3-en-1-yloxy)silane,[36] (*Z*)-but-2-en-1-ylbenzene,[37] (*Z*)-1-phenyl-3-pentene,[38] and 2,4,6-trimethylpyridine hydrochloride.[39]

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General Procedure A: Epoxidation of Alkenes to Epoxides Using *m*-CPBA. *m*-Chloroperoxybenzoic acid (*m*-CPBA, ≤77%) was added in portions at 0 °C to a solution of the corresponding alkene in DCM, and the resulting mixture was stirred at the same temperature until TLC analysis indicated complete consumption of the alkene. After excess *m*-CPBA was destroyed by addition of aqueous $NaHSO_3$ at 0 °C, the reaction mixture was filtered and the organic phase washed with $NaHCO_3$ (satd, aq, 3×), dried with sodium sulfate, filtered, and concentrated under reduced pressure. The residue was purified via either distillation or flash column chromatography.

General Procedure B: Assembly of Salen Compounds via Imine Condensation. The appropriate salicylaldehyde derivative was mixed under air with either methanol or ethanol at the indicated temperature. The appropriate diamine was added and the reaction mixture stirred at the same temperature for the time indicated. The reaction mixture was allowed to reach 22 °C, and the resulting precipitate was isolated by filtration, followed by washings with small amounts of cold methanol or ethanol to give the corresponding salen-compound after drying in vacuo at 80 °C.

General Procedure C: Metalation of Salen Compounds Using Et_2AlCl. The appropriate salen compound was dissolved in the indicated amount of DCM and cooled to 0 °C. Et_2AlCl (1.0 M, hexanes, pyrophoric) was added in one portion under vigorous stirring at 0 °C, and the resulting solution was stirred at 22 °C for 12 h. The resulting metal complex was then isolated as indicated.

General Procedure D: Regioselective Carbonylation of *cis*-Epoxides Using Catalyst 9f. In a glovebox, a 2 fluid dram glass vial equipped with a Teflon-coated magnetic stir bar was charged with catalyst **9f** and THF. The vial was then placed in a custom-made six-well high-pressure reactor[40] which itself was placed in a glovebox freezer at −34 °C for 30 min. The appropriate epoxide (also cooled to −34 °C) was then added to the vial and the reactor removed from the freezer, subsequently sealed, taken out of the glovebox, placed in a well-ventilated hood, and pressurized with carbon monoxide (900 psi). It is important to keep the temperature of the reactor below 0 °C once it is removed from the freezer to minimize isomerization of the epoxide to ketone products. The reactor was then sealed again, placed in a 22 °C water bath, and stirred for the time indicated. The reactor was carefully vented in a well-ventilated hood, the crude reaction mixture concentrated under reduced pressure, and the product isolated as indicated.

General Procedure E: Regioselective Carbonylation of Epoxides with in Situ Formation of Catalyst *rac*-1c. In a glovebox, a 2 fluid dram glass vial equipped with a Teflon-coated magnetic stir bar was charged with $NaCo(CO)_4$, 1,4-dioxane, and the precursor to *rac*-**1c**, compound *rac*-**5c**. The vial was then placed in a custom-made 6-well high-pressure reactor,[40] which itself was placed in a glovebox freezer at −34 °C for 30 min. The appropriate epoxide (also cooled to −34 °C) was added to the vial and the reactor removed from the freezer, subsequently sealed, taken out of the glovebox, placed in a well-ventilated hood and pressurized with carbon monoxide (900 psi). It is important to keep the temperature of the reactor below 0 °C once it is removed from the freezer to minimize isomerization of the epoxide to ketone products. The reactor was then sealed again, placed in a 22 °C water bath, and stirred for the time indicated. The reactor was carefully vented in a well-ventilated hood, the crude reaction mixture concentrated under reduced pressure, and the product isolated as indicated.

Please note: In the case of substrates *rac*-**2b**, *rac*-**2c**, *rac*-**2h**, *rac*-**2i**, *rac*-**2j**, and *rac*-**2k**, the general procedure was slightly altered: The reactor was carefully vented in a well-ventilated hood, and the crude reaction mixture was treated with methanol and sodium methoxide, stirred for 5 min at 22 °C, and then concentrated under reduced pressure. The product was then isolated as indicated.

General Procedure F: Regioselective Chlorohydrin Formation Using Catalyst *rac*-5c. In a glovebox, a 2 fluid dram glass vial equipped with a Teflon-coated magnetic stir bar was charged with catalyst *rac*-**5c**, 2,4,6-trimethylpyridine hydrochloride, THF, and the appropriate epoxide. The vial was sealed with a Teflon-coated cap, and the reaction mixture stirred at 22 °C for 48 h. The crude reaction mixture was concentrated under reduced pressure and the product isolated as indicated.

*rac-(2R,3S)-2-(Cyclohexylmethyl)-3-methyloxirane (rac-**2f**).* Methyllithium (1.6 M, Et_2O, 21.5 mL, 34.4 mmol) was added dropwise at −78 °C to a solution of prop-2-yn-1-ylcyclohexane (3.81 g, 31.2 mmol) in THF (55 mL), and the resulting solution was stirred at −78 °C for 0.5 h. Methyl iodide (10.5 g, 74.0 mmol) was added dropwise at −78 °C, the reaction mixture was slowly warmed to 22 °C and stirred for 12 h. $NaHCO_3$ (satd, aq) was added and the aqueous phase extracted with pentane. The combined organic layers were dried with sodium sulfate, filtered, and concentrated under reduced pressure. THF (14 mL) was added to the residue and the resulting solution degassed by two freeze−pump−thaw cycles. The solution was then added to a solution of 9-BBN (0.5 M, THF, 72 mL, 36 mmol) at 0 °C, and the resulting reaction mixture was stirred at 22 °C until TLC analysis indicated complete disappearance of the alkyne. Methanol (1.0 mL) was added followed by glacial acetic acid (20.0 mg) as a solution in methanol (2.6 mL) and the resulting mixture stirred for 2 h at 22 °C. Pentane was added, followed by controlled addition of NaOH (1 M, aq, 40 mL) and H_2O_2 (30%, aq, 20 mL) under ice cooling. The aqueous layer was extracted with pentane, and the combined organic layers were washed with $NaHCO_3$ (aq, satd), dried with sodium sulfate, filtered, and concentrated under reduced pressure. The crude product was filtered through a plug of silica gel using pentane, and the filtrates were concentrated under reduced pressure.

Following general procedure A, the residue was reacted with *m*-CPBA (9.00 g) in DCM (40 mL) to give *rac*-**2f** (1.12 g, 23%) as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.02 (dtd, J = 5.3, 4.3 Hz, 1H), 2.94 (td, J = 6.0, 4.2 Hz, 1H), 1.79−1.62 (m, 5H), 1.51−1.33 (m, 3H), 1.30−1.08 (m, 3H), 1.25 (d, J = 5.5 Hz, 3H), 1.04−0.89 (m, 2H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 56.0, 52.7, 36.2, 35.0, 33.8, 33.3, 26.6, 26.41, 26.38, 13.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{10}H_{19}O$ 155.1430, found 155.1443.

*rac-(2R,3S)-2-Benzyl-3-methyloxirane (rac-**2g**).* Following general procedure A, (*Z*)-but-2-en-1-ylbenzene[37] (0.446 g, 3.37 mmol) was reacted with *m*-CPBA (0.960 g) in DCM (17 mL) to give *rac*-**2g** (0.390 g, 78%) as a colorless liquid. The analytical data were in accordance with that reported in the literature.[41] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35−7.31 (m, 2H), 7.27−7.23 (m, 3H), 3.18−3.11 (m, 2H), 2.94 (dd, J = 14.7, 5.8 Hz, 1H), 2.79 (dd, J = 14.7, 6.3 Hz, 1H), 1.41 (d, J = 5.4 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 137.9, 128.9, 128.7, 126.6, 57.4, 53.0, 34.2, 13.6.

*rac-(2R,3S)-2-Methyl-3-phenethyloxirane (rac-**2h**).* Following general procedure A, (*Z*)-1-phenyl-3-pentene[38] (2.71 g, 18.5 mmol) was reacted with *m*-CPBA (5.50 g) in DCM (45 mL) to give *rac*-**2h** (2.19 g, 73%) as a colorless liquid. The analytical data were in accordance with that reported in the literature.[38] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31−7.28 (m, 2H), 7.22−7.18 (m, 3H), 3.04 (qd, J = 5.5, 4.2 Hz, 1H), 2.95 (td, J = 6.3, 4.3 Hz, 1H), 2.85 (ddd, J = 14.6, 9.2, 5.8 Hz, 1H), 2.74 (ddd, J = 13.9, 8.9, 7.4 Hz, 1H), 1.93−1.69 (m, 2H), 1.19 (d, J = 5.5 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 141.5, 128.55, 128.55, 126.2, 56.6, 53.0, 32.8, 29.6, 13.3.

*rac-tert-Butyldimethyl(2-((2R,3S)-3-methyloxiran-2-yl)ethoxy)-silane (rac-**2j**).* Following general procedure A, (*Z*)-*tert*-butyldimethyl-(pent-3-en-1-yloxy)silane[36] (2.74 g, 13.7 mmol) was reacted with *m*-CPBA (4.10 g) in DCM (35 mL) to give *rac*-**2j** (2.34 g, 79%) as a colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.80−3.75 (m, 2H), 3.09−3.03 (m, 2H), 1.82−1.63 (m, 2H), 1.26 (d, J = 5.4 Hz, 3H), 0.89 (s, 9H), 0.05 (s, 6H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 60.6, 54.8, 52.7, 31.2, 26.1, 18.5, 13.6, −5.2. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{11}H_{24}NaO_2Si$ 239.1438, found 239.1445.

*5-tert-Butyl-4-hydroxy-2′,4′,6′-triisopropyl[1,1′-biphenyl]-3-carbaldehyde (**11**).* 4-Bromo-2-*tert*-butylphenol[33] (1.6 g, 7.0 mmol) was added in small portions to a mixture of sodium hydride (95%, dry, 0.23 g, 9.6 mmol) and THF (7 mL) at 0 °C, followed by stirring at 22 °C for 10 min. $Pd(OAc)_2$ (Strem, 0.107 g, 0.351 mmol) was added, followed by 2,4,6-triisopropylphenylmagnesium bromide (0.5 M, THF, 30 mL, 15 mmol), and the resulting mixture was refluxed for 12 h. Upon cooling to 0 °C, H_2O was carefully added to destroy residual Grignard reagent and sodium hydride. HCl (2 M, aq) was

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added followed by Celite, and the resulting mixture was filtered through a pad of Celite. The resulting phases were separated, and the aqueous phase was extracted with Et_2O (3×). The combined organic layers were washed with brine, dried with sodium sulfate, filtered, and concentrated under reduced pressure. The resulting residue was subjected to flash column chromatography. The isolated product (1.88 g) was contaminated with approximately 5% of 2-*tert*-butylphenol and was used without further purification in the next step. ^{1}H NMR data for the main component, 3-*tert*-butyl-2′,4′,6′-triisopropyl[1,1′-biphenyl]-4-ol, are provided. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.06 (s, 1H), 7.05 (s, 2H), 6.88−6.85 (m, 1H), 6.68 (d, J = 7.9 Hz, 1H), 4.72 (s, 1H), 2.94 (p, J = 6.9 Hz, 1H), 2.70−2.50 (m, 2H), 1.41 (d, J = 1.3 Hz, 9H), 1.31 (d, J = 6.9 Hz, 6H), 1.09 (d, J = 6.7 Hz, 6H), 1.07 (d, J = 6.8 Hz, 6H).

Methylmagnesium bromide (3 M, Et_2O, 2.2 mL, 6.6 mmol) was added slowly to 3-*tert*-butyl-2′,4′,6′-triisopropyl[1,1′-biphenyl]-4-ol (1.88 g, ca. 5 mmol) in THF (13 mL) at 0 °C. After the mixture was warmed to 22 °C, toluene (26 mL), triethylamine (1.3 mL, 9.3 mmol), and paraformaldehyde (0.42 g, 14 mmol) were added, and the resulting reaction mixture was stirred at 80 °C for 12 h. After the mixture was cooled to 0 °C, H_2O and then HCl (2 M, aq) were added, and the resulting phases were separated. The aqueous phase was extracted with Et_2O (3×). The combined organic layers were washed with brine, dried with sodium sulfate, filtered, and concentrated under reduced pressure. The residue was subjected to flash column chromatography followed by recrystallization from methanol to give **11** (1.32 g, 50% over two steps) as an off-color solid. Mp: 144−143 °C (methanol). ^{1}H NMR (500 MHz, $CDCl_3$): δ 11.80 (s, 1H), 9.87 (s, 1H), 7.36 (d, J = 2.2 Hz, 1H), 7.22 (d, J = 2.1 Hz, 1H), 7.08 (s, 2H), 2.96 (hept, J = 6.9 Hz, 1H), 2.61 (hept, J = 6.9 Hz, 2H), 1.43 (s, 9H), 1.32 (d, J = 6.9 Hz, 6H), 1.12 (d, J = 6.9 Hz, 6H), 1.09 (d, J = 6.9 Hz, 6H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 197.4, 160.0, 148.4, 147.1, 137.9, 136.3, 135.9, 132.4, 131.6, 120.9, 120.4, 35.1, 34.5, 30.5, 29.55, 29.55, 24.5, 24.23, 24.20. HRMS (EI-quadrupole) m/z: [M]$^+$ calcd for $C_{26}H_{36}O_2$ 380.2715, found 380.2709.

*2,2′-((1E,1′E)-((2,3-Dimethylbutane-2,3-diyl)bis(azanylylidene))bis(methanylylidene))bis(4-methylphenol) (**12**).* Following general procedure B, 2-hydroxy-5-methylbenzaldehyde (204 mg, 1.50 mmol), 2,3-dimethylbutane-2,3-diamine[34] (87.0 mg, 0.749 mmol), and methanol (4.5 mL) were mixed, and then the mixture was stirred at 70 °C for 11 h. Following filtration and drying in vacuo, **12** (189 mg, 72%) was obtained as a yellow powder. Mp: 198−199 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 13.81 (s, 2H), 8.32 (s, 2H), 7.11 (dd, J = 8.3, 2.2 Hz, 2H), 7.06 (d, J = 2.3 Hz, 2H), 6.85 (d, J = 8.3 Hz, 2H), 2.28 (s, 6H), 1.37 (s, 12H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 161.7, 159.3, 133.1, 131.9, 127.6, 118.7, 116.9, 65.3, 23.2, 20.5. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{22}H_{29}N_2O_2$ 353.2224, found 353.2225.

*6,6′-((1E,1′E)-((2,3-Dimethylbutane-2,3-diyl)bis(azanylylidene))bis(methanylylidene))bis(2,4-dimethylphenol) (**13**).* Following general procedure B, 2-hydroxy-3,5-dimethylbenzaldehyde (225 mg, 1.50 mmol), 2,3-dimethylbutane-2,3-diamine[34] (87.0 mg, 0.749 mmol), and methanol (4.5 mL) were mixed and then stirred at 70 °C for 12 h. Following filtration and drying in vacuo, **13** (228 mg, 80%) was obtained as a yellow powder. Mp: 178−179 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 14.07 (s, 2H), 8.33 (s, 2H), 7.01 (s, 2H), 6.92 (s, 2H), 2.26 (s, 12H), 1.39 (s, 12H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 161.9, 157.7, 134.4, 129.5, 127.0, 125.8, 117.9, 65.2, 23.3, 20.5, 15.6. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{24}H_{33}N_2O_2$ 381.2537, found 381.2538.

*6,6′-((1E,1′E)-((2,3-Dimethylbutane-2,3-diyl)bis(azanylylidene))bis(methanylylidene))bis(4-tert-butyl-2-methylphenol) (**14**).* Following general procedure B, 5-*tert*-butyl-2-hydroxy-3-methylbenzaldehyde[32] (384 mg, 2.00 mmol), 2,3-dimethylbutane-2,3-diamine[34] (116 mg, 0.998 mmol), and methanol (6.0 mL) were mixed and then stirred at 70 °C for 8 h. Following filtration and drying in vacuo, **14** (362 mg, 78%) was obtained as a yellow powder. Mp: 171−173 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 14.1 (s, 2H), 8.40 (s, 2H), 7.23 (s, 2H), 7.12 (s, 2H), 2.30 (s, 6H), 1.40 (s, 12H), 1.31 (s, 18H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 162.2, 157.7, 140.7, 130.9, 125.8, 125.4, 117.5, 65.2, 34.0, 31.6, 23.3, 15.9. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{30}H_{45}N_2O_2$ 465.3476, found 465.3471.

*5,5″-((1E,1′E)-((2,3-Dimethylbutane-2,3-diyl)bis(azanylylidene))bis(methanylylidene))bis(3-tert-butyl-2′,4′,6′-triisopropyl[1,1′-biphenyl]-4-ol) (**15**).* Following general procedure B, **11** (381 mg, 1.00 mmol), 2,3-dimethylbutane-2,3-diamine[34] (58 mg, 0.50 mmol), and methanol (15 mL) were mixed and then stirred at 70 °C for 12 h. Following filtration and drying in vacuo, **15** (319 mg, 76%) was obtained as a yellow powder. Mp: >200 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 14.51 (s, 2H), 8.45 (s, 2H), 7.14 (d, J = 2.1 Hz, 2H), 7.08 (s, 4H), 6.97 (d, J = 2.1 Hz, 2H), 2.97 (hept, J = 6.9 Hz, 2H), 2.70 (hept, J = 6.8 Hz, 4H), 1.47 (s, 12H), 1.45 (s, 18H), 1.33 (d, J = 6.9 Hz, 12H), 1.13 (d, J = 6.9 Hz, 12H), 1.09 (d, J = 6.8 Hz, 12H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 162.5, 159.4, 147.8, 147.2, 137.1, 136.9, 131.5, 130.6, 129.9, 120.7, 118.5, 65.4, 35.1, 34.4, 30.4, 29.7, 24.7, 24.3, 23.5. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{58}H_{85}N_2O_2$ 841.6606, found 841.6605.

*3,3″-((1E,1′E)-([1,1′-Binaphthalene]-2,2′-diylbis(azanylylidene))bis(methanylylidene))bis(3′,5′-di-tert-butyl-5-methyl[1,1′-biphenyl]-2-ol) (**16**).* 3′,5′-Di-*tert*-butyl-2-hydroxy-5-methyl[1,1′-biphenyl]-3-carbaldehyde[31] (324 mg, 0.999 mmol), racemic [1,1′-binaphthalene]-2,2′-diamine (142 mg, 0.499 mmol), and ethanol (8 mL) were mixed and then refluxed for 12 h. After the reaction mixture was allowed to reach 22 °C, the resulting precipitate was isolated by filtration and washed with a small amount of ethanol and finally pentane to give **16** (372 mg, 83%) as a powder of orange color. Mp: 196−198 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.36 (s, 2H), 8.62 (s, 2H), 8.01 (d, J = 8.8 Hz, 2H), 7.89 (d, J = 8.2 Hz, 2H), 7.56 (d, J = 8.8 Hz, 2H), 7.38 (dt, J = 8.1, 4.0 Hz, 2H), 7.33 (t, J = 1.8 Hz, 2H), 7.26 (d, J = 1.8 Hz, 2H), 7.22 (d, J = 3.2 Hz, 2H), 7.14 (d, J = 2.1 Hz, 2H), 6.92 (d, J = 2.2 Hz, 2H), 2.24 (s, 6H), 1.35 (s, 36H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 162.6, 156.2, 150.0, 144.4, 136.6, 135.0, 133.4, 132.5, 131.6, 130.09, 130.05, 129.3, 128.3, 127.6, 127.0, 126.6, 125.8, 123.8, 121.0, 119.4, 117.3, 35.0, 31.8, 20.5. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{64}H_{69}N_2O_2$ 897.5354, Found 897.5382.

*6,6′-((1E,1′E)-((2,3-Dimethylbutane-2,3-diyl)bis(azanylylidene))bis(methanylylidene))bis(4-tert-butyl-2-methylphenolate)aluminum Chloride (**17**, Precursor to **9g**).* Following general procedure C, Et_2AlCl (1.0 M, hexanes, 950 μL, 0.950 mmol) was added to **14** (360 mg, 0.775 mmol) in DCM (5.0 mL). After the solution was stirred at 22 °C, the volatiles were removed in vacuo. The residue was broken up and dried in vacuo at 80 °C for 1 h to give **17** (276 mg, 68%) as a yellow powder. Mp: >200 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.45 (s, 2H), 7.42 (d, J = 1.5 Hz, 2H), 7.10 (d, J = 2.6 Hz, 2H), 2.39 (s, 6H), 1.55 (s, 6H), 1.34 (s, 6H), 1.31 (s, 18H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 167.1, 162.3, 139.3, 135.0, 130.4, 126.7, 117.5, 66.3, 34.0, 31.5, 25.8, 24.4, 16.4. HRMS (ESI-TOF) m/z: [M − Cl]$^+$ Calcd for $C_{30}H_{42}AlN_2O_2$ 489.3056, found 489.3065.

*6,6′-((1E,1′E)-((2,3-Dimethylbutane-2,3-diyl)bis(azanylylidene))bis(methanylylidene))bis(2,4-dimethylphenolate)aluminum Chloride (**18**, Precursor to **9h**).* Following general procedure C, Et_2AlCl (1.0 M, hexanes, 750 μL, 0.750 mmol) was added to **13** (228 mg, 0.599 mmol) in DCM (4.0 mL). After the solution was stirred at 22 °C, the volatiles were removed in vacuo. The residue was broken up and dried in vacuo at 80 °C for 1 h to give **18** (193 mg, 73%) as a yellow powder. Mp: >200 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.40 (s, 2H), 7.20 (s, 2H), 6.95 (s, 2H), 2.36 (s, 6H), 2.26 (s, 6H), 1.54 (s, 6H), 1.33 (s, 6H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 166.8, 162.2, 138.3, 130.7, 130.4, 125.8, 118.1, 66.3, 25.7, 24.3, 20.4, 16.0. HRMS (ESI-TOF) m/z: [M − Cl]$^+$ calcd for $C_{24}H_{30}AlN_2O_2$ 405.2117, found 405.2122.

*2,2′-((1E,1′E)-((2,3-Dimethylbutane-2,3-diyl)bis(azanylylidene))bis(methanylylidene))bis(4-methylphenolate)aluminum Chloride (**19**, Precursor to **9i**).* Following general procedure C, Et_2AlCl (1.0 M, hexanes, 650 μL, 0.650 mmol) was added to **12** (188 mg, 0.533 mmol) in DCM (4.0 mL). After the solution was stirred at 22 °C, the volatiles were removed in vacuo. The residue was broken up and dried in vacuo at 80 °C for 1 h to give **19** (170 mg, 78%) as a yellow powder. Mp: >200 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.43 (s, 2H), 7.28 (dd, J = 8.7, 2.4 Hz, 2H), 7.15−7.11 (m, 2H), 7.10 (s, 1H), 7.08 (s, 1H), 2.28 (s, 6H), 1.55 (s, 6H), 1.32 (s, 6H). ^{13}C{^{1}H} NMR (126

MHz, $CDCl_3$): δ 166.9, 163.4, 137.9, 133.1, 126.6, 122.6, 118.8, 66.5, 25.6, 24.4, 20.3. HRMS (ESI-TOF) *m/z*: $[M - Cl]^+$ calcd for $C_{22}H_{26}AlN_2O_2$ 377.1804, found 377.1813.

*5,5″-((1E,1′E)-((2,3-Dimethylbutane-2,3-diyl)bis(azanylylidene))bis(methanylylidene))bis(3-tert-butyl-2′,4′,6′-triisopropyl[1,1′-biphenyl]-4-olate)aluminum Chloride (**20**, Precursor to **9j**).* Following general procedure C, Et_2AlCl (1.0 M, hexanes, 650 μL, 0.650 mmol) was added to a suspension of **15** (281 mg, 0.334 mmol) in DCM (7.0 mL). After the solution was stirred at 22 °C, the volatiles were removed in vacuo. The residue was broken up and dried in vacuo at 80 °C for 1 h to give **20** (254 mg, 84%) as a yellow powder. Mp: >200 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 8.44 (s, 2H), 7.33 (d, *J* = 2.3 Hz, 2H), 7.09 (d, *J* = 4.8 Hz, 4H), 6.99 (d, *J* = 2.2 Hz, 2H), 2.97 (hept, *J* = 6.9 Hz, 2H), 2.79 (p, *J* = 6.9 Hz, 2H), 2.78 (p, *J* = 6.9 Hz, 2H), 1.61 (s, 6H), 1.58 (s, 18H), 1.41 (s, 6H), 1.34 (d, *J* = 6.9 Hz, 12H), 1.17 (d, *J* = 6.9 Hz, 6H), 1.16 (d, *J* = 6.9 Hz, 6H), 1.12 (d, *J* = 6.8 Hz, 6H), 1.10 (d, *J* = 6.8 Hz, 6H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 167.6, 163.6, 147.9, 147.6, 147.2, 141.4, 136.8, 135.7, 132.3, 129.0, 120.8, 120.6, 119.3, 66.4, 35.7, 34.4, 30.5, 30.4, 30.0, 25.8, 24.79, 24.77, 24.6, 24.33, 24.32, 24.27, 24.25. HRMS (ESI-TOF) *m/z*: $[M - Cl]^+$ calcd for $C_{58}H_{82}AlN_2O_2$ 865.6186, found 865.6186.

*3,3″-((1E,1′E)-([1,1′-Binaphthalene]-2,2′-diylbis(azanylylidene))bis(methanylylidene))bis(3′,5′-di-tert-butyl-5-methyl[1,1′-biphenyl]-2-olate)aluminum Chloride (rac-**5c**, Precursor to rac-**1c**).* Following general procedure C, Et_2AlCl (1.0 M, hexanes, 950 μL, 0.950 mmol) was added to a solution of **16** (774 mg, 0.863 mmol) in DCM (8.0 mL) at 0 °C. After being stirred at 22 °C for 12 h, approximately half of the solvent was removed in vacuo. The remainder was cooled to 0 °C, and the precipitate isolated by filtration. The solid, still kept at 0 °C, was washed with cold DCM, then cold pentane, and subsequently dried in vacuo at 80 °C for 1 h to give *rac*-**5c** (549 mg, 66%) as a yellow powder. Mp: >200 °C. ^1H NMR (500 MHz, $CDCl_3$, −55 °C): δ 8.20 (s, 1H), 7.96 (s, 1H), 7.82 (d, *J* = 8.7 Hz, 1H), 7.76 (d, *J* = 8.3 Hz, 1H), 7.69−7.67 (m, 2H), 7.62 (s, 2H), 7.57 (d, *J* = 8.6 Hz, 1H), 7.30 (t, *J* = 7.7 Hz, 1H), 7.27−7.24 (m, 2H), 7.21 (s, 1H), 7.13 (s, 1H), 7.11−7.03 (m, 4H), 6.98−6.95 (m, 3H), 6.86 (d, *J* = 8.7 Hz, 1H), 6.67 (s, 2H), 1.99 (s, 3H), 1.97 (s, 3H), 1.01 (s, 18H), 0.83 (s, 18H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, −55 °C): δ 174.1, 168.9, 162.8, 159.3, 149.5, 149.4, 144.2, 143.9, 140.8, 138.9, 136.6, 136.5, 134.0, 133.2, 133.0, 132.45, 132.40, 132.3, 131.8, 131.7, 130.5, 129.4, 128.6, 128.4, 127.2, 127.0, 126.9, 126.8, 126.5, 126.28, 126.25, 126.23, 126.0, 125.9, 125.8, 125.24, 125.22, 124.9, 124.48, 124.45, 124.12, 124.05, 120.6, 120.2, 119.3, 118.7, 34.9, 34.6, 31.5, 31.2, 20.5, 20.4. HRMS (ESI-TOF) *m/z*: $[M - Cl]^+$ calcd for $C_{64}H_{66}AlN_2O_2$ 921.4934, found 921.4906.

*6,6′-((1E,1′E)-((2,3-Dimethylbutane-2,3-diyl)bis(azanylylidene))bis(methanylylidene))bis(2,4-di-tert-butylphenolate)aluminum Cobaltate (**9f**).* $NaCo(CO)_4$[35] (33.4 mg, 0.172 mmol), 6,6′-((1*E*,1′*E*)-((2,3-dimethylbutane-2,3-diyl)bis(azanylylidene))bis(methanylylidene))bis(2,4-di-*tert*-butylphenolate)aluminum chloride[13] (100 mg, 0.164 mmol), and THF (2.5 mL) were mixed and stirred for 12 h at 22 °C. The reaction mixture was filtered through a 0.45 μm Teflon syringe filter and the filtrate carefully layered with hexane and then placed in a freezer at −34 °C for a day. The resulting crystals were isolated by filtration, washed with hexanes, and then dried in vacuo to give **9f** (118 mg, 81%) as yellow crystals. ^1H NMR (400 MHz, C_6D_6): δ 8.75 (s, 2H), 7.87 (d, *J* = 2.6 Hz, 2H), 7.78 (d, *J* = 2.5 Hz, 2H), 3.47−3.23 (m, 8H, THF), 1.65 (s, 18H), 1.43 (s, 18H), 1.18 (s, 12H), 1.20−1.15 (m, 8H, THF). $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6 + THF-d_8, (1:1, v/v)): δ 171.0, 162.4, 139.4, 132.2, 130.5, 128.2, 119.9, 67.9 (THF), 67.6, 35.8, 34.5, 31.5, 29.8, 26.3, 25.9 (THF). IR (neat, cm^{-1}): 1862.1 $\nu_{(C=O)}$. Anal. Calcd for $C_{48}H_{70}AlCoN_2O_8$: C, 64.85; H, 7.94; N, 3.15. Found: C, 65.00; H, 8.18; N, 3.02.

*rac-(3R,4R)-4-Butyl-3-methyloxetan-2-one (rac-**3a**) and rac-(3R,4R)-3-Butyl-4-methyloxetan-2-one (rac-**4a**).* General procedure D was followed using **9f** (13.3 mg, 0.0150 mmol, 4.93 mol %), THF (0.6 mL), and *rac*-**2a** (34.7 mg, 0.304 mmol). After being stirred at 22 °C for 20 h, the crude reaction mixture was subjected to flash column chromatography to give a mixture of *rac*-**3a** and *rac*-**4a** (34.7 mg, 80%) as a colorless oil. Analytical data for *rac*-**3a**[9a] and *rac*-**4a**[16] have previously been reported. ^1H NMR (400 MHz, $CDCl_3$): δ 4.38 (qd, *J* = 6.1, 4.0 Hz, 1H, **4a**), 4.15 (ddd, *J* = 7.2, 6.3, 4.0 Hz, 1H, **3a**), 3.20 (qd, *J* = 7.5, 4.0 Hz, 1H, **3a**), 3.17−3.12 (m, 1H, **4a**), 1.90−1.68 (m, 2H + 2H, **3a** + **4a**), 1.53 (d, *J* = 6.1 Hz, 3H, **4a**), 1.37 (d, *J* = 7.5 Hz, 3H, **3a**), 1.48−1.26 (m, 4H + 4H, **3a** + **4a**), 0.93−0.88 (m, 3H + 3H, **3a** + **4a**). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 172.2 (**3a**), 171.5 (**4a**), 79.7 (**3a**), 74.7 (**4a**), 57.7 (**4a**), 50.8 (**3a**), 33.9 (**3a**), 29.1 (**4a**), 27.5 (**4a**), 27.2 (**3a**), 22.5 (**4a**), 22.4 (**3a**), 20.4 (**4a**), 14.0 (**3a**), 13.9 (**4a**), 12.6 (**3a**).

*rac-(3R,4R)-4-Ethyl-3-methyloxetan-2-one (rac-**3b**) and rac-(3R,4R)-4-Methyl-3-propyloxetan-2-one (rac-**4b**).* General procedure D was followed using **9f** (18.6 mg, 0.0209 mmol, 7.21 mol %), THF (0.6 mL), and *rac*-**2b** (25.0 mg, 0.290 mmol). After being stirred at 22 °C for 20 h, the crude reaction mixture was subjected to bulb-to-bulb distillation to give a mixture of *rac*-**3b** and *rac*-**4b** (22.0 mg, 66%) as a yellow oil. Analytical data for *rac*-**3b**[9a] and *rac*-**4b**[42] have previously been reported. ^1H NMR (400 MHz, $CDCl_3$): δ 4.41 (qd, *J* = 6.1, 4.0 Hz, 1H, **4b**), 4.13 (td, *J* = 6.6, 4.0 Hz, 1H, **3b**), 3.22 (qd, *J* = 7.5, 4.0 Hz, 1H, **3b**), 3.13 (ddd, *J* = 8.4, 6.7, 4.0 Hz, 1H, **4b**), 1.94−1.73 (m, 4H), 1.55 (d, *J* = 6.1 Hz, 3H, **4b**), 1.39 (d, *J* = 7.5 Hz, 3H, **3b**), 1.03 (t, *J* = 7.5 Hz, 3H, **3b**), 1.00 (t, *J* = 7.6 Hz, 3H, **4b**). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 172.1 (**3b**), 171.2 (**4b**), 80.6 (**3b**), 74.2 (**4b**), 59.0 (**4b**), 50.4 (**3b**), 27.3 (**3b**), 21.0 (**4b**), 20.4 (**4b**), 12.7 (**3b**), 11.2 (**4b**), 9.1 (**3b**).

*rac-(3R,4R)-3-Methyl-4-propyloxetan-2-one (rac-**3c**) and rac-(3R,4R)-3-Ethyl-4-methyloxetan-2-one (rac-**4c**).* General procedure D was followed using **9f** (18.6 mg, 0.0209 mmol, 6.74 mol %), THF (0.6 mL), and *rac*-**3c** (31.0 mg, 0.310 mmol). After being stirred at 22 °C for 20 h, the crude reaction mixture was subjected to flash column chromatography to give a mixture of *rac*-**3c** and *rac*-**4c** (22.0 mg, 66%) as a yellow oil. Analytical data for *rac*-**3c**[9a] and *rac*-**4c**[43] have previously been reported. ^1H NMR (300 MHz, $CDCl_3$): δ 4.40 (qd, *J* = 6.1, 3.9 Hz, 1H, **4c**), 4.18 (ddd, *J* = 7.3, 6.2, 4.0 Hz, 1H, **3c**), 3.24−3.14 (m, 2H), 1.89−1.78 (m, 2H), 1.76−1.65 (m, 2H), 1.55 (d, *J* = 6.1 Hz, 3H, **4c**), 1.50−1.34 (m, 4H), 1.38 (d, *J* = 7.5 Hz, 3H, **3c**), 0.98 (t, *J* = 7.5 Hz, 3H, **3c**), 0.95 (t, *J* = 7.3 Hz, 3H, **4c**). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 172.2 (**3c**), 171.4 (**4c**), 79.5 (**3c**), 74.7 (**4c**), 57.5 (**4c**), 50.8 (**3c**), 36.2 (**3c**), 29.8 (**4c**), 20.4 (**4c**), 20.3 (**4c**), 18.5 (**3c**), 13.80 (**3c**), 13.79 (**4c**), 12.6 (**3c**).

*rac-(3R,4R)-3-Methyl-4-pentyloxetan-2-one (rac-**3d**) and rac-(3R,4R)-4-Methyl-3-pentyloxetan-2-one (rac-**4d**).* General procedure D was followed using **9f** (17.8 mg, 0.0200 mmol, 6.58 mol %), THF (0.6 mL), and *rac*-**2d** (39.0 mg, 0.304 mmol). After being stirred at 22 °C for 20 h, the crude reaction mixture was subjected to flash column chromatography to give a mixture of *rac*-**3d** and *rac*-**4d** (35.2 mg, 74%) as a colorless oil. Analytical data for *rac*-**3d**[44] and *rac*-**4d**[16] have previously been reported. ^1H NMR (400 MHz, $CDCl_3$): δ 4.38 (qd, *J* = 6.1, 3.9 Hz, 1H, **4d**), 4.16 (td, *J* = 6.7, 4.0 Hz, 1H, **3d**), 3.20 (qd, *J* = 7.6, 4.0 Hz, 1H, **3d**), 3.16 (ddd, *J* = 8.9, 6.5, 3.9 Hz, 1H, **4d**), 1.89−1.79 (m, 2H), 1.78−1.6 (m, 2H), 1.54 (d, *J* = 6.0 Hz, 3H, **4d**), 1.48−1.24 (m, 12H), 1.38 (d, *J* = 7.5 Hz, 3H, **3d**), 0.90−0.86 (m, 6H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 172.2 (**3d**), 171.5 (**4d**), 79.7 (**3d**), 74.8 (**4d**), 57.7 (**4d**), 50.8 (**3d**), 34.2 (**3d**), 31.50 (**4d**), 31.46 (**3d**), 27.7 (**4d**), 26.6 (**4d**), 24.7 (**3d**), 22.54 (**3d**), 22.46 (**4d**), 20.4 (**4d**), 14.04 (**4d**), 14.02 (**3d**), 12.6 (**3d**).

*rac-(3R,4R)-4-Hexyl-3-methyloxetan-2-one (rac-**3e**) and rac-(3R,4R)-3-Hexyl-4-methyloxetan-2-one (rac-**4e**).* General procedure D was followed using **9f** (13.3 mg, 0.0150 mmol, 5.02 mol %), THF (0.6 mL), and *rac*-**2e** (42.5 mg, 0.299 mmol). After being stirred at 22 °C for 20 h, the crude reaction mixture was subjected to flash column chromatography to give a mixture of *rac*-**3e** and *rac*-**4e** (48.3 mg, 95%) as a colorless oil. Analytical data for *rac*-**3e**[45] and *rac*-**4e**[16] have previously been reported. ^1H NMR (300 MHz, $CDCl_3$): δ 4.38 (qd, *J* = 6.1, 4.0 Hz, 1H, **4e**), 4.15 (td, *J* = 6.6, 3.9 Hz, 1H, **3e**), 3.20 (qd, *J* = 7.5, 4.0 Hz, 1H, **3e**), 3.14 (ddd, *J* = 8.9, 6.5, 3.9 Hz, 1H, **4e**), 1.88−1.78 (m. 2H), 1.78−1.65 (m. 2H), 1.54 (d, *J* = 6.1 Hz, 3H), 1.47−1.21 (m, 16H), 1.37 (d, *J* = 7.6 Hz, 3H), 0.89−0.85 (m, 6H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 172.2 (**3e**), 171.5 (**4e**), 79.7 (**3e**), 74.7 (**4e**), 57.7 (**4e**), 50.8 (**3e**), 34.2 (**3e**), 31.7 (**3e**), 31.6 (**4e**), 29.00 (**4e**), 28.96

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(**3e**), 27.8 (**4e**), 26.9 (**4e**), 25.0 (**3e**), 22.60 (**4e**), 22.57 (**3e**), 20.4 (**4e**), 14.11 (**4e**), 14.11 (**3e**), 12.6 (**3e**).

*rac-(3R,4R)-4-(Cyclohexylmethyl)-3-methyloxetan-2-one (rac-**3f**) and rac-(3R,4R)-3-(Cyclohexylmethyl)-4-methyloxetan-2-one (rac-**4f**).* General procedure D was followed using **9f** (8.9 mg, 0.010 mmol, 5.0 mol %), THF (0.4 mL), and *rac*-**2f** (31.0 mg, 0.201 mmol). After being stirred at 22 °C for 20 h, the crude reaction mixture was subjected to flash column chromatography to give a mixture of *rac*-**3f** and *rac*-**4f** (32.3 mg, 88%) as a colorless oil. Only analytical data for *rac*-**3f** are provided: ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.28−4.23 (m, 1H), 3.23−3.14 (m, 1H), 1.83−1.53 (m, 7H), 1.39 (d, J = 7.6 Hz, 3H), 1.50−1.34 (m, 1H), 1.32−1.12 (m, 3H), 1.08−0.89 (m, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 172.3, 78.4, 51.3, 42.0, 34.9, 33.5, 33.1, 26.4, 26.2, 26.1, 12.6. IR (neat, cm^{-1}): 1817.8 $\nu_{(C=O)}$. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{11}H_{19}O_2$ 183.1380, found 183.1390.

*rac-(3R,4R)-4-Benzyl-3-methyloxetan-2-one (rac-**3g**) and rac-(3R,4R)-3-Benzyl-4-methyloxetan-2-one (rac-**4g**).* General procedure D was followed using **9f** (13.2 mg, 0.0148 mmol, 7.33 mol %), THF (0.4 mL), and *rac*-**2g** (30.0 mg, 0.202 mmol). After being stirred at 22 °C for 21 h, the crude reaction mixture was subjected to flash column chromatography to give a mixture of *rac*-**3g** and *rac*-**4g** (31.8 mg, 90%) as a colorless oil. Only analytical data for *rac*-**3g** are provided. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36−7.27 (m, 3H), 7.23−7.20 (m, 2H), 4.40 (td, J = 6.5, 4.0 Hz, 1H), 3.33 (qd, J = 7.5, 4.0 Hz, 1H), 3.20 (dd, J = 14.2, 6.4 Hz, 1H), 3.04 (dd, J = 14.3, 6.5 Hz, 1H), 1.30 (d, J = 7.6 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 171.6, 135.3, 129.2, 128.9, 127.3, 79.0, 50.5, 40.1, 12.5. IR (neat, cm^{-1}): 1816.1 $\nu_{(C=O)}$. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{11}H_{13}O_2$ 177.0910, found 177.0919.

*rac-(3R,4R)-3-Methyl-4-phenethyloxetan-2-one (rac-**3h**) and rac-(3R,4R)-4-Methyl-3-phenethyloxetan-2-one (rac-**4h**).* General procedure D was followed using **9f** (13.2 mg, 0.0149 mmol, 7.30 mol %), THF (0.4 mL), and *rac*-**2h** (33.1 mg, 0.204 mmol). After being stirred at 22 °C for 20 h, the crude reaction mixture was subjected to flash column chromatography to give a mixture of *rac*-**3h** and *rac*-**4h** (33.5 mg, 86%) as a colorless oil. Analytical data for *rac*-**3h** have previously been reported in the literature.[46] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33−7.30 (m, 2H + 2H, **3h** + **4h**), 7.25−7.19 (m, 3H + 3H, **3h** + **4h**), 4.32 (qd, J = 6.1, 3.9 Hz, 1H, **4h**), 4.17 (ddd, J = 7.7, 5.8, 3.9 Hz, 1H, **3h**), 3.20 (qd, J = 7.5, 4.0 Hz, 1H, **3h**), 3.15 (ddd, J = 9.1, 6.5, 4.0 Hz, 1H, **4h**), 2.83 (ddd, J = 14.2, 8.8, 5.5 Hz, 1H + 1H, **3h** + **4h**), 2.71 (dt, J = 13.9, 8.0 Hz, 1H + 1H, **3h** + **4h**), 2.23−2.16 (m, 1H + 1H, **3h** + **4h**), 2.12−2.05 (m, 1H + 1H, **3h** + **4h**), 1.43 (d, J = 6.1 Hz, 3H, **4h**), 1.33 (d, J = 7.6 Hz, 3H, **3h**). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 171.9 (**3h**), 171.2 (**4h**), 140.2 (**4h**), 140.1 (**3h**), 128.67 (**3h**), 128.66 (**4h**), 128.5 (**4h**), 128.4 (**3h**), 126.5 (**4h**), 126.4 (**3h**), 78.7 (**3h**), 75.0 (**4h**), 56.8 (**4h**), 50.9 (**3h**), 35.8 (**3h**), 33.1 (**4h**), 31.3 (**3h**), 29.5 (**4h**), 20.1 (**4h**), 12.5 (**3h**). IR (neat, cm^{-1}): 1815.5 $\nu_{(C=O)}$. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{12}H_{15}O_2$ 191.1067, found 191.1080.

*rac-(3R,4R)-4-Isopentyl-3-methyloxetan-2-one (rac-**3i**) and rac-(3R,4R)-3-Isopentyl-4-methyloxetan-2-one (rac-**4i**).* General procedure D was followed using **9f** (13.2 mg, 0.0149 mmol, 5.16 mol %), THF (0.6 mL), and *rac*-**2i** (37.0 mg, 0.289 mmol). After being stirred at 22 °C for 20 h, the crude reaction mixture was subjected to flash column chromatography to give a mixture of *rac*-**3i** and *rac*-**4i** (40.9 mg, 91%) as a colorless oil. Analytical data for *rac*-**3i** and *rac*-**4i** have previously been reported in the literature.[16] ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.39 (qd, J = 6.1, 3.9 Hz, 1H, **4i**), 4.13 (td, J = 6.7, 4.0 Hz, 1H, **3i**), 3.21 (qd, J = 7.5, 4.0 Hz, 1H, **3i**), 3.12 (ddd, J = 8.9, 6.5, 3.9 Hz, 1H, **4i**), 1.88−1.80 (m, 2H), 1.78−1.69 (m, 2H), 1.62−1.51 (m, 2H), 1.55 (d, J = 6.2 Hz, 3H, **4i**), 1.38 (d, J = 7.5 Hz, 3H, **3i**), 1.35−1.28 (m, 2H), 1.25−1.16 (m, 2H), 0.90 (d, J = 6.6 Hz, 6H, **4i**), 0.89 (d, J = 6.6 Hz, 6H, **3i**). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 172.2 (**3i**), 171.5 (**4i**), 79.9 (**3i**), 74.7 (**4i**), 57.8 (**4i**), 50.8 (**3i**), 35.9 (**4i**), 33.9 (**3i**), 32.2 (**3i**), 27.92 (**4i**), 27.86 (**3i**), 25.7 (**4i**), 22.51 (**3i**), 22.48 (**3i**), 22.45 (**4i**), 22.45 (**4i**), 20.47 (**4i**), 12.7 (**3i**).

*rac-(3R,4R)-4-(2-((tert-Butyldimethylsilyl)oxy)ethyl)-3-methyloxetan-2-one (rac-**3j**) and rac-(3R,4R)-3-(2-((tert-Butyldimethylsilyl)oxy)ethyl)-4-methyloxetan-2-one (rac-**4j**).* General procedure D was followed using **9f** (13.2 mg, 0.0149 mmol, 7.49 mol %), THF (0.4 mL), and *rac*-**2j** (43.0 mg, 0.199 mmol). After being stirred at 22 °C for 21 h, the crude reaction mixture was subjected to flash column chromatography to give a mixture of *rac*-**3j** and *rac*-**4j** (44.6 mg, 92%) as a colorless oil. Analytical data for *rac*-**3j** have previously been reported in the literature.[46] ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.52 (qd, J = 6.1, 4.0 Hz, 1H, **4j**), 4.32 (td, J = 6.6, 4.0 Hz, 1H, **3j**), 3.79−3.70 (m, 2H, **3j**), 3.71−3.65 (m, 2H, **4j**), 3.35 (qd, J = 7.6, 4.0 Hz, 1H, **3j**), 3.28 (ddd, J = 9.5, 5.4, 4.0 Hz, 1H, **4j**), 2.07−1.91 (m, 2H + 2H, **3j** + **4j**), 1.55 (d, J = 6.1 Hz, 3H, **4j**), 1.39 (d, J = 7.6 Hz, 3H, **3j**), 0.88 (s, 9H + 9H, **3j** + **4j**), 0.05 (s, 6H + 6H, **3j** + **4j**). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 172.3 (**3j**), 171.5 (**4j**), 77.6 (**3j**), 75.5 (**4j**), 61.0 (**4j**), 59.1 (**3j**), 55.6 (**4j**), 51.1 (**3j**), 37.0 (**3j**), 30.9 (**4j**), 25.98 (**4j**), 25.97 (**3j**), 25.97 (**4j**), 20.3 (**4j**), 18.4 (**3j**), 12.5 (**3j**), −5.37 (**4j**), −5.38 (**3j**). IR (neat, cm^{-1}): 1823.2 $\nu_{(C=O)}$. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{12}H_{25}O_3Si$ 245.1567, found 245.1564.

*rac-(3R,4R)-4-(3-((tert-Butyldimethylsilyl)oxy)propyl)-3-methyloxetan-2-one (rac-**3k**) and rac-(3R,4R)-3-(3-((tert-Butyldimethylsilyl)oxy)propyl)-4-methyloxetan-2-one (rac-**4k**).* General procedure D was followed using **9f** (8.9 mg, 0.010 mmol, 5.0 mol %), THF (0.4 mL), and *rac*-**2k** (46.0 mg, 0.200 mmol). After being stirred at 22 °C for 21 h, the crude reaction mixture was subjected to flash column chromatography to give a mixture of *rac*-**3k** and *rac*-**4k** (44.9 mg, 87%) as a colorless oil. Analytical data for *rac*-**3k** have previously been reported in the literature.[47] ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.40 (qd, J = 6.1, 3.9 Hz, 1H, **4k**), 4.22 (td, J = 6.8, 4.0 Hz 1H, **3k**), 3.68−3.61 (m, 2H + 2H, **3k** + **4k**), 3.25−3.18 (m, 1H + 1H, **3k** + **4k**), 1.93−1.78 (m, 2H + 2H, **3k** + **4k**), 1.70−1.53 (m, 2H + 2H, **3k** + **4k**), 1.54 (d, J = 6.1 Hz, 3H, **4k**), 1.38 (d, J = 7.6 Hz, 3H, **3k**), 0.88 (s, 9H + 9H, **3k** + **4k**), 0.04 (s, 6H + 6H, **3k** + **4k**). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 172.1 (**3k**), 171.3 (**4k**), 79.6 (**3k**), 74.8 (**4k**), 62.35 (**3k**), 62.34 (**4k**), 57.4 (**4k**), 50.9 (**3k**), 31.0 (**3k**), 29.9 (**4k**), 28.2 (**3k**), 26.03 (**4k**), 26.03 (**3k**), 24.5 (**4k**), 20.4 (**4k**), 18.42 (**3k**), 18.42 (**4k**), 12.7 (**3k**), −5.23 (**3k**), −5.23 (**4k**). IR (neat, cm^{-1}): 1822.7 $\nu_{(C=O)}$. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{13}H_{27}O_3Si$ 259.1724, found 259.1724.

*rac-3-((2R,3R)-2-Methyl-4-oxooxetan-3-yl)propyl Acetate (rac-**3l**) and rac-3-((2R,3R)-3-Methyl-4-oxooxetan-2-yl)propyl Acetate (rac-**4l**).* General procedure E was followed using *rac*-**5c** (14.4 mg, 0.0150 mmol, 5.00 mol %), 1,4-dioxane (0.3 mL), $NaCo(CO)_4$ (3.0 mg, 0.015 mmol, 5.0 mol %), and *rac*-**3l** (1.00 M, 1,4-dioxane, 300 μL, 0.300 mmol). After the solution was stirred at 22 °C for 20 h, the reactor was carefully vented in a well-ventilated hood. The crude reaction mixture was concentrated under reduced pressure and then subjected to flash column chromatography to give a mixture of *rac*-**3l** and *rac*-**4l** (46.0 mg, 82%) as a colorless oil. Only analytical data for *rac*-**4l** are provided. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.38 (qd, J = 6.1, 4.0 Hz, 1H), 4.05 (t, J = 6.1 Hz, 2H), 3.18 (td, J = 7.5, 4.0 Hz, 1H), 2.01 (s, 3H), 1.90−1.64 (m, 4H), 1.53 (d, J = 6.1 Hz, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 171.0, 170.8, 74.5, 63.5, 57.0, 26.0, 24.4, 21.0, 20.3. IR (neat, cm^{-1}): 1810.0 $\nu_{(C=O,\ lactone)}$, 1732.7 $\nu_{(C=O,\ ester)}$. HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_9H_{14}NaO_4$ 209.0784, found 209.0795.

*rac-(2R,3R)-Methyl 2-ethyl-3-hydroxybutanoate (rac-**6b**).* General procedure E was followed using *rac*-**5c** (14.3 mg, 0.0149 mmol, 5.02 mol %), $NaCo(CO)_4$ (3.3 mg, 0.017 mmol, 5.7 mol %), 1,4-dioxane (0.3 mL), and *rac*-**2b** (0.990 M, 1,4-dioxane, 300 μL, 0.297 mmol). After the solution was stirred at 22 °C for 21 h, the reactor was carefully vented in a well-ventilated hood. The crude reaction mixture was treated with methanol (0.4 mL) and sodium methoxide (ca. 20.0 mg, ca. 0.370 mmol), stirred for 5 min at 22 °C, and then concentrated under reduced pressure. The residue was subjected to flash column chromatography to give *rac*-**6b** (30.3 mg, 70%) as a colorless oil. The analytical data were in accordance with those reported in the literature.[48] ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.91 (q, J = 5.5 Hz, 1H), 3.70 (d, J = 0.6 Hz, 3H), 2.55 (d, J = 5.5 Hz, 1H), 2.31 (dt, J = 8.7, 6.1 Hz, 1H), 1.73−1.59 (m, 2H), 1.21 (d, J = 6.3 Hz, 3H), 0.90 (t, J = 7.5 Hz, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 176.0, 68.2, 54.4, 51.7, 22.7, 21.6, 11.8.

*rac-(R)-Methyl 2-((R)-1-Hydroxyethyl)pentanoate (rac-**6c**).* General procedure E was followed using *rac*-**5c** (14.4 mg, 0.0150 mmol,

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5.07 mol %), 1,4-dioxane (0.3 mL), $NaCo(CO)_4$ (3.0 mg, 0.015 mmol, 5.1 mol %), and *rac*-**2c** (0.988 M, 1,4-dioxane, 300 μL, 0.296 mmol). After the solution was stirred at 22 °C for 20 h, the reactor was carefully vented in a well-ventilated hood. The crude reaction mixture was treated with methanol (0.4 mL) and sodium methoxide (ca. 20.0 mg, ca. 0.370 mmol), stirred for 5 min at 22 °C, and then concentrated under reduced pressure. The residue was subjected to flash column chromatography to give *rac*-**6c** (36.4 mg, 77%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.88 (h, *J* = 6.8 Hz, 1H), 3.69 (s, 3H), 2.57 (d, *J* = 7.1 Hz, 1H), 2.38 (dt, *J* = 9.3, 5.7 Hz, 1H), 1.70−1.45 (m, 2H), 1.29 (h, *J* = 7.3 Hz, 2H), 1.21 (d, *J* = 6.3 Hz, 3H), 0.89 (t, *J* = 7.3 Hz, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 176.1, 68.5, 52.7, 51.7, 31.7, 21.7, 20.7, 14.1. IR (neat, cm^{-1}): 1735.3 $\nu_{(C=O)}$. HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ calcd for $C_8H_{16}NaO_3$ 183.0992, found 183.0998.

*rac-(2R,3R)-Methyl 3-Hydroxy-2-phenethylbutanoate (rac-**6h**).* General procedure E was followed using *rac*-**5c** (14.4 mg, 0.0150 mmol, 5.26 mol %), 1,4-dioxane (0.3 mL), $NaCo(CO)_4$ (3.0 mg, 0.015 mmol, 5.3 mol %), and *rac*-**2h** (0.950 M, 1,4-dioxane, 300 μL, 0.285 mmol). After the solution was stirred at 22 °C for 22 h, the reactor was carefully vented in a well-ventilated hood. The crude reaction mixture was treated with methanol (0.4 mL) and sodium methoxide (ca. 20.0 mg, ca. 0.370 mmol), stirred for 5 min at 22 °C, and then concentrated under reduced pressure. The residue was subjected to flash column chromatography to give *rac*-**6h** (52.6 mg, 83%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31−7.26 (m, 2H), 7.21−7.17 (m, 3H), 3.94 (p, *J* = 6.4 Hz, 1H), 3.73 (s, 3H), 2.70−2.55 (m, 3H), 2.45 (dddd, *J* = 9.4, 5.7, 4.8, 0.8 Hz, 1H), 2.09−1.99 (m, 1H), 1.90 (dddd, *J* = 14.0, 9.7, 6.9, 4.9 Hz, 1H), 1.22 (d, *J* = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 175.7, 141.3, 128.50, 128.48, 126.1, 68.5, 52.3, 51.7, 33.6, 31.1, 21.6. IR (neat, cm^{-1}): 1736.8 $\nu_{(C=O)}$. HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ calcd for $C_{13}H_{18}NaO_3$ 245.1148, found 245.1155.

*rac-(R)-Methyl 2-((R)-1-Hydroxyethyl)-5-methylhexanoate (rac-**6i**).* General procedure E was followed using *rac*-**5c** (14.4 mg, 0.0150 mmol, 5.00 mol %), 1,4-dioxane (0.3 mL), $NaCo(CO)_4$ (3.0 mg, 0.015 mmol, 5.0 mol %), and *rac*-**2i** (1.00 M, 1,4-dioxane, 300 μL, 0.300 mmol). After the solution was stirred at 22 °C for 20 h, the reactor was carefully vented in a well-ventilated hood. The crude reaction mixture was treated with methanol (0.4 mL) and sodium methoxide (ca. 20.0 mg, ca. 0.370 mmol), stirred for 5 min at 22 °C, and then concentrated under reduced pressure. The residue was subjected to flash column chromatography to give *rac*-**6i** (44.1 mg, 78%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.89 (p, *J* = 6.3 Hz, 1H), 3.69 (s, 3H), 2.54 (s, 1H), 2.33 (ddd, *J* = 9.3, 6.2, 5.2 Hz, 1H), 1.69−1.45 (m, 3H), 1.20 (d, *J* = 6.3 Hz, 3H), 1.22−1.04 (m, 2H), 0.86 (d, *J* = 3.1 Hz, 3H), 0.84 (d, *J* = 3.1 Hz, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 176.2, 68.5, 53.1, 51.7, 36.5, 28.2, 27.4, 22.7, 22.4, 21.7. IR (neat, cm^{-1}): 1736.2 $\nu_{(C=O)}$. HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ calcd for $C_{10}H_{20}NaO_3$ 211.1305, found 211.1317.

*rac-(R)-Methyl 4-((tert-Butyldimethylsilyl)oxy)-2-((R)-1-hydroxyethyl)butanoate (rac-**6j**).* General procedure E was followed using *rac*-**5c** (14.4 mg, 0.0150 mmol, 5.02 mol %), 1,4-dioxane (0.3 mL), $NaCo(CO)_4$ (3.0 mg, 0.015 mmol, 5.0 mol %), and *rac*-**2j** (0.998 M, 1,4-dioxane, 300 μL, 0.299 mmol). After the solution was stirred at 22 °C for 20 h, the reactor was carefully vented in a well-ventilated hood. The crude reaction mixture was treated with methanol (0.4 mL) and sodium methoxide (ca. 20.0 mg, ca. 0.370 mmol), stirred for 5 min at 22 °C, and then concentrated under reduced pressure. The residue was subjected to flash column chromatography to give *rac*-**6j** (66.7 mg, 81%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.97−3.89 (m, 1H), 3.69 (s, 3H), 3.67 (dt, *J* = 11.6, 5.7 Hz, 1H), 3.58 (ddd, *J* = 10.4, 7.5, 5.2 Hz, 1H), 2.79 (d, *J* = 7.5 Hz, 1H), 2.60 (dt, *J* = 8.4, 5.4 Hz, 1H), 1.95−1.78 (m, 2H), 1.22 (d, *J* = 6.4 Hz, 3H), 0.87 (s, 9H), 0.02 (s, 6H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 175.7, 68.3, 61.2, 51.7, 49.5, 32.1, 26.0, 21.5, 18.4, −5.4, −5.3. IR (neat, cm^{-1}): 1735.0 $\nu_{(C=O)}$. HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ calcd for $C_{13}H_{29}O_4Si$ 277.1830, found 277.1837.

*rac-(R)-Methyl 5-((tert-Butyldimethylsilyl)oxy)-2-((R)-1-hydroxyethyl)pentanoate (rac-**6k**).* General procedure E was followed using *rac*-**5c** (14.4 mg, 0.0150 mmol, 5.05 mol %), 1,4-dioxane (0.3 mL), $NaCo(CO)_4$ (3.0 mg, 0.015 mmol, 5.1 mol %), and *rac*-**2k** (0.991 M, 1,4-dioxane, 300 μL, 0.297 mmol). After the solution was stirred at 22 °C for 21 h, the reactor was carefully vented in a well-ventilated hood. The crude reaction mixture was treated with methanol (0.4 mL) and sodium methoxide (ca. 20.0 mg, ca. 0.370 mmol), stirred for 5 min at 22 °C, and then concentrated under reduced pressure. The residue was subjected to flash column chromatography to give *rac*-**6k** (69.7 mg, 80%) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.92 (h, *J* = 6.4 Hz, 1H), 3.70 (s, 3H), 3.59 (t, *J* = 6.2 Hz, 2H), 2.49 (d, *J* = 6.9 Hz, 1H), 2.40 (dt, *J* = 8.0, 6.4 Hz, 1H), 1.71−1.64 (m, 2H), 1.52−1.46 (m, 2H), 1.22 (d, *J* = 6.4 Hz, 3H), 0.87 (s, 9H), 0.03 (s, 6H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 176.1, 68.6, 62.7, 52.6, 51.7, 30.5, 26.1, 25.9, 21.7, 18.4, −5.2. IR (neat, cm^{-1}): 1737.0 $\nu_{(C=O)}$. HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ calcd for $C_{14}H_{31}O_4Si$ 291.1986, found 291.2000.

*rac-(2R,3R)-3-Chloroheptan-2-ol (rac-**8a**).* General procedure F was followed using *rac*-**5c** (14.8 mg, 0.0155 mmol, 5.20 mol %), THF (0.6 mL), 2,4,6-trimethylpyridine hydrochloride (52.3 mg, 0.332 mmol), and *rac*-**2a** (34.0 mg, 0.298 mmol). The crude reaction mixture was subjected to bulb-to-bulb distillation to give *rac*-**8a** (30.5 mg, 68%) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.86−3.80 (m, 2H), 2.06 (d, *J* = 5.9 Hz, 1H), 1.84−1.71 (m, 2H), 1.58−1.49 (m, 1H), 1.45−1.25 (m, 3H), 1.28 (d, *J* = 6.0 Hz, 3H), 0.92 (t, *J* = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 70.7, 70.5, 34.5, 28.8, 22.4, 20.5, 14.1. Anal. Calcd for $C_7H_{15}ClO$: C, 55.81; H, 10.04; Cl, 23.53. Found: C, 55.61; H, 9.98; Cl, 23.48. No molecular ion peak was observed when performing EI-MS or ESI-MS analysis; consequently, no HRMS data were acquired.

*rac-(2R,3R)-3-Chlorononan-2-ol (rac-**8e**).* General procedure F was followed using *rac*-**5c** (14.3 mg, 0.0149 mmol, 5.03 mol %), THF (0.6 mL), 2,4,6-trimethylpyridine hydrochloride (52.0 mg, 0.330 mmol), and *rac*-**2e** (42.3 mg, 0.297 mmol). The crude reaction mixture was subjected to flash column chromatography to give *rac*-**8e** (40.8 mg, 77%) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.85−3.79 (m, 2H), 2.09 (d, *J* = 5.7 Hz, 1H), 1.83−1.70 (m, 2H), 1.59−1.51 (m, 1H), 1.46−1.23 (m, 7H), 1.27 (d, *J* = 5.8 Hz, 3H), 0.90−0.87 (m, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 70.7, 70.5, 34.7, 31.8, 28.9, 26.7, 22.7, 20.5, 14.2. Anal. Calcd for $C_9H_{19}ClO$: C, 60.49; H, 10.72; Cl, 19.84. Found: C, 60.32; H, 10.66; Cl, 19.74. No molecular ion peak was observed when performing EI-MS or ESI-MS analysis; consequently, no HRMS data were acquired.

*rac-(2R,3R)-3-Chloro-4-phenylbutan-2-ol (rac-**8g**).* General procedure F was followed using *rac*-**5c** (21.5 mg, 0.0225 mmol, 7.50 mol %), THF (0.6 mL), 2,4,6-trimethylpyridine hydrochloride (52.0 mg, 0.330 mmol), and *rac*-**2g** (44.5 mg, 0.300 mmol). The crude reaction mixture was subjected to flash column chromatography to give *rac*-**8g** (30.7 mg, 55%) as a colorless oil. The analytical data were in accordance with that reported in the literature.[49] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35−7.31 (m, 2H), 7.28−7.25 (m, 3H), 4.05 (ddd, *J* = 8.2, 6.5, 3.2 Hz, 1H), 3.91−3.84 (m, 1H), 3.23 (dd, *J* = 14.0, 6.5 Hz, 1H), 3.07 (dd, *J* = 14.0, 8.1 Hz, 1H), 1.97 (d, *J* = 8.1 Hz, 1H), 1.32 (d, *J* = 6.3 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 137.8, 129.5, 128.7, 127.0, 70.1, 68.6, 41.3, 21.1.

*rac-(2R,3R)-3-Chloro-5-phenylpentan-2-ol (rac-**8h**).* General procedure F was followed using *rac*-**5c** (14.4 mg, 0.0150 mmol, 4.95 mol %), THF (0.6 mL), 2,4,6-trimethylpyridine hydrochloride (52.0 mg, 0.330 mmol), and *rac*-**2h** (49.2 mg, 0.303 mmol). The crude reaction mixture was subjected to flash column chromatography to give *rac*-**8h** (45.1 mg, 75%) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33−7.30 (m, 2H), 7.23−7.21 (m, 3H), 3.88−3.82 (m, 1H), 3.79 (ddd, *J* = 7.9, 6.1, 4.5 Hz, 1H), 2.94 (dt, *J* = 13.8, 6.9 Hz, 1H), 2.77 (dt, *J* = 13.9, 8.2 Hz, 1H), 2.13−2.08 (m, 3H), 1.27 (d, *J* = 6.3 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 140.9, 128.64, 128.64, 126.3, 70.6, 69.3, 36.3, 32.8, 20.4. Anal. Calcd for $C_{11}H_{15}ClO$: C, 66.49; H, 7.61; Cl, 17.84. Found: C, 66.49; H, 7.67; Cl, 17.92. No molecular ion peak was observed when performing EI-MS or ESI-MS analysis; consequently, no HRMS data were acquired.

*rac-(2R,3R)-3-Chloro-6-methylheptan-2-ol (rac-**8i**).* General procedure F was followed using *rac*-**5c** (14.3 mg, 0.0149 mmol, 5.03 mol %), THF (0.6 mL), 2,4,6-trimethylpyridine hydrochloride (52.0 mg,

0.330 mmol), and *rac*-**2i** (38.0 mg, 0.296 mmol). The crude reaction mixture was subjected to flash column chromatography to give *rac*-**8i** (33.1 mg, 68%) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.87−3.79 (m, 2H), 2.05 (d, J = 6.2 Hz, 1H), 1.86−1.70 (m, 2H), 1.62−1.51 (m, 1H), 1.44 (dddd, J = 13.1, 10.7, 7.2, 4.7 Hz, 1H), 1.35−1.25 (m, 1H), 1.28 (d, J = 6.1 Hz, 3H), 0.90 (t, J = 6.6 Hz, 6H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 71.1, 70.5, 35.8, 32.7, 27.9, 22.9, 22.4, 20.5. Anal. Calcd for $C_8H_{17}ClO$: C, 58.35; H, 10.41; Cl, 21.53. Found: C, 58.49; H, 10.50; Cl, 21.62. No molecular ion peak was observed when performing EI-MS or ESI-MS analysis; consequently, no HRMS data were acquired.

■ ASSOCIATED CONTENT

Supporting Information

Additional tables concerning control reactions and catalyst optimization; copies of ^{1}H and ^{13}C{^{1}H} NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(19) See the Supporting Information for more details.

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