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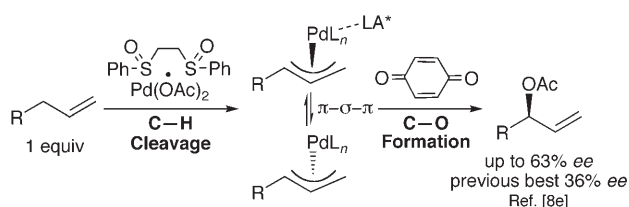
A Chiral Lewis Acid Strategy for Enantioselective Allylic C–H Oxidation**

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C–H oxidation reactions have the potential to significantly streamline synthetic processes. However, to be useful for the synthesis of complex molecules, these reactions must proceed with high levels of chemo-, regio-, and stereoselectivity. Chiral bisoxazoline/copper-catalyzed systems have shown promising levels of asymmetric induction in the enantioselective allylic C–H esterification of symmetrical, cyclic olefins. Application of these systems to complex substrates is limited by a lack of chemo- and regioselectivity as well as the need to use a large excess of reactant (4 to 10 equiv).[1] A direct allylic C–H oxidation route would significantly increase the efficiency of producing chiral allylic esters; their syntheses generally require lengthy sequences of functional-group manipulations from preoxidized materials.[2,3]

We have recently reported a collection of mild, highly regio- and chemoselective, allylic C–H esterification[4] and amination[5] reactions of α-olefins, and have demonstrated their utility in streamlining the synthesis of complex molecules.[6] These allylic oxidation reactions are catalyzed by Pd[II] systems with weakly coordinating sulfoxide and quinone ligands that are poorly suited for effecting asymmetric induction.[7] Herein we disclose a novel chiral Lewis acid strategy for generating an asymmetric environment about a metal center in electrophilic, oxidative reactions that do not tolerate strongly coordinating ligands. In our approach a chiral Lewis acid is used which selectively interacts with an organopalladium intermediate to accelerate and induce asymmetry in the C–O bond-forming step. Significantly, by using this strategy we have achieved the highest enantioselection observed to date for the allylic C–H oxidation of terminal olefins (Scheme 1).[8] This system represents the first example of asymmetric induction from an organometallic intermediate that is effected by a chiral Lewis acid, as well as a

Scheme 1. Chiral Lewis acid (LA*) strategy for enantioselection in serial ligand catalysis.

rare example of catalytic enantioselective C–H activation by palladium.[9]

Conventional approaches toward asymmetric organometallic reactions make use of strongly coordinating chiral ligands. The oxidation of terminal olefins using **1** to give branched allylic compounds has been demonstrated to proceed by a serial ligand catalysis mechanism in which weakly coordinating bis(sulfoxide) and 1,4-benzoquinone (BQ) ligands sequentially interact with the Pd center to promote the C–H bond-cleavage and C–O bond-forming steps, respectively. (Scheme 1).[4b] In theory, a chiral variant of either ligand could lead to enantioenriched products. All attempts to use chiral sulfoxides have been unsuccessful in effecting asymmetric induction. Experiments with *cis*-[1-D]-1-decene reveal that this ineffectiveness is due to rapid π-σ-π isomerization of the [(π-allyl)Pd] intermediate, which scrambles any chiral information imparted during the C–H cleavage step (Scheme 1, and see the Supporting Information). We therefore set out to identify a viable alternative strategy for enantioselective C–O bond formation. Traditional methods for asymmetric [(π-allyl)Pd] functionalization, such as the introduction of chiral phosphine ligands, are not compatible with electrophilic, oxidative C–H activation conditions. In addition, functionalization ligand BQ is impractical for covalent chiral modification, as large amounts are required for optimal reactivity. Collectively, these considerations suggest that this organometallic reaction is not readily amenable to asymmetric induction through the use of a chiral ligand.

Lewis acid co-catalysts have been demonstrated to accelerate bond-forming reactions from organometallic intermediates.[10] We postulated that a chiral Lewis acid co-catalyst could be used to both accelerate and influence the stereochemical outcome of C–O bond formation via a [(π-allyl)Pd(BQ)] intermediate. Specifically, we envisioned that coordination of an oxophilic, chiral Lewis acid to the carbonyl group of BQ would increase the π acidity of the metal ligand, thus accelerating C–O bond formation while transmitting chiral information to the metal center. This approach would afford enantioenrichment despite background reactivity.

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We began by examining chiral Lewis acids that are known to catalyze highly enantioselective reactions by single-point binding to Lewis basic carbonyl groups. Of the catalysts evaluated (see the Supporting Information), commercially available [(salen)Cr^{III}Cl] complex (**2**)[11] gave the only measurable enantioselectivity for the process, albeit with diminished conversion and regioselectivity (Table 1, entry 1 vs 2).

Table 1: Discovery and optimization of enantioselective Lewis acid mediated C−H bond oxidation.

Entry	LA	Conv. [%][a]	Yield [%][b]	B:L	ee [%][c]
1[d]	–	90	71	>30:1	0
2[d]	2	15	7	1.2:1	32
3[d]	3	84	74	9.3:1	9
4[e]	2	42	35	1.1:1	32
5[e]	3	94	86	4.6:1	54
6	3	100	93	5.1:1	57
7	4	78	71	2.0:1	31
8[f]	3	17	2	–	–
9[g]	3	10	0	–	–

[a] As compared to nitrobenzene as an internal standard. [b] Yield was determined by GC and is an average of at least two runs. [c] The ee values were determined by GC analysis on a chiral stationary phase. (see the Supporting Information). [d] AcOH (4 equiv), dioxane (0.33 M), 45°C, 24 h. [e] Dioxane (2 M), 24 h. [f] 2,6-Dimethylbenzoquinone (2 equiv). [g] No palladium catalyst (**1**). B = branched, L = linear, M.S. = molecular sieves.

Analysis of several counterions for the Cr^{III} metal center revealed that [(salen)Cr^{III}F] (**3**) gave better conversion and regioselectivity, although enantioselectivity was reduced (Table 1, entry 3). Increasing the concentration of the reaction, lowering the number of equivalents of acetic acid, and decreasing the temperature resulted in a significant enhancement in enantioselectivity for the reaction with **3** (Table 1, entry 5). Further optimization resulted in a system that afforded 57% ee with excellent yield and good regioselectivity (Table 1, entry 6).

The scope and functional-group tolerance of this system were evaluated. The absolute stereochemistry of the allylic stereocenter that is formed when using (R,R)-**3** as the catalyst was determined to be R, while (S,S)-**3** afforded the S-configured product (Table 2, entries 1 and 2; see the Supporting Information). Gratifyingly, the functional-group tolerance of this system matched that of the original bis(sulfoxide)/Pd^{II} methodology, with tolerance for esters, amides, a wide variety of protected alcohols, and even a free alcohol (Table 2, entries 3–9). As steric bulk was brought closer to the allylic position, a modest variation in enantioselectivity and a more significant change in the regioselectivity were observed

**Table 2:** Preliminary investigation of the scope of the enantioselective allylic C−H oxidation.

Entry	Product	Yield [%][a] (brsm)[b]	B:L	ee [%][c]
1		92	5.3:1	59
2[d]		92	5.3:1	−59
3	n = 7	89	4.8:1	57
4	n = 2	69 (73)	4.6:1	50
5		81 (88)	4.4:1	54
6	R = TBDPS	84 (90)	4.4:1	63
7	R = H	83	4.4:1	50
8	R = THP	91	3.6:1	49
9	R = Bn	90	4.3:1	45
10[e]		78 (83)	1.5:1	62

[a] Yields of isolated allylic oxidation products (1.0 mmol substrate) are an average of at least three experiments. [b] Yield is based on recovered starting material. [c] The ee values were determined by GC analysis on a chiral stationary phase. (see the Supporting Information). [d] The (S,S)-**3** catalyst was used. [e] 72 h. Bn = benzyl, cHex = cyclohexyl, TBDPS = tert-butyldiphenylsilyl, THP = tetrahydropyranyl.

(Table 2, entry 3 vs 4, entry 1 vs 10). To the best of our knowledge these results represent the highest enantioselectivity observed for the allylic C−H oxidation of terminal olefins.[8a,e]

Pairing this asymmetric branched allylic acetoxylation with enzymatic resolution affords streamlined routes to highly enantioenriched allylic acetates in high yields. Conventional routes to chiral bisoxygenated compounds such as **5** (Scheme 2) require protection/deprotection sequences and oxidation-state manipulations to generate racemic precursors, which can undergo kinetic resolution to give a maximum of 50% yield.[12] Alternatively, beginning with a commercially available monooxygenated hydrocarbon (undecenoic acid), **5** can be generated rapidly in 97% ee and in 42% overall yield (in 3 steps and without functional-group manipulation) through a chiral allylic C−H oxidation/enzymatic resolution sequence (Scheme 2).

Mechanistic studies were carried out to investigate the role of [(salen)Cr^{III}F] (**3**) in the product-forming steps of the catalytic cycle (namely C−H cleavage and C−O bond formation; Scheme 1). Studies with stoichiometric amounts of undecene and bis(sulfoxide)/Pd(OAc)$_2$ catalyst **1** indicate that the rate of C−H cleavage to form the π-allyl palladium acetate dimer is unaffected by **3** (see the Supporting Information). Moreover, functionalization in the absence of BQ does not occur. Consistent with the role of BQ as a ligand for promoting functionalization, sterically hindered 2,6-dime-

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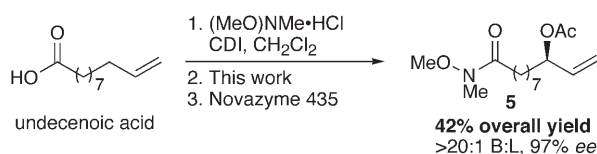
Scheme 2. Streamlined generation of chiral allylic acetates. CDI = 1,1'-carbonyldiimidazole.

thylbenzoquinone gave only a trace amount of product in the catalytic reaction (Table 1, entry 8).

We envisioned three mechanistic scenarios (Scheme 3) that are likely to effect the observed asymmetric induction during the C−O bond-forming step: **I**: coordination of
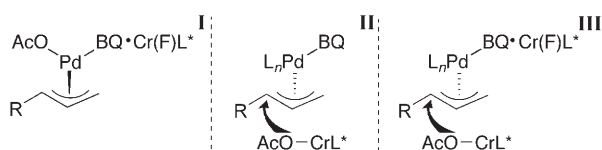
Scheme 3. Proposed modes of action for chromium Lewis acid: **I**: reductive elimination of acetate by a [L*Cr(BQ)]-activated π-allyl palladium complex; **II**: delivery of an acetate group from [L*Cr(OAc)] to [(π-allyl)Pd(BQ)L] complex; **III**: delivery of an acetate group from [L*Cr(OAc)] to an activated L*Cr(BQ)−Pd(π-allyl). L = ligand, L* = chiral ligand.

[(salen)Cr^{III}F] (**3**) to BQ to promote and control the facial selectivity in the reductive elimination of acetate from a [(π-allyl)Pd(BQ)OAc] intermediate, **II**: delivery of an acetate group to a [(π-allyl)Pd(BQ)L] intermediate from [(salen)-Cr^{III}OAc] (**4**), or **III**: activation of a [(π-allyl)Pd(BQ)] intermediate by [(salen)Cr^{III}F] (**3**) with a concurrent delivery of acetate from [(salen)Cr^{III}OAc] (**4**).[10,13,14] To test these hypotheses, reductive elimination from the synthetic π-allyl palladium acetate dimer **6** was evaluated in terms of reaction rates and selectivities. This study was carried out under conditions that mimic the reaction of a monomeric π-allyl palladium intermediate during one catalytic cycle (see the Supporting Information). As hypothesized, the addition of Lewis acid co-catalyst [(salen)Cr^{III}F] (**3**) led to a 10-fold increase in the rate of functionalization relative to reaction conditions that were otherwise identical but lacked **3** (Table 3, entry 1 vs 2). Moreover, the branched allylic acetate was furnished with comparable enantio- and regioselectivities to those obtained under catalytic conditions (Table 3, entry 2 vs Table 1, entry 6). As noted above, functionalization does not occur with **3** in the absence of BQ (Table 3, entry 3).

To evaluate mechanistic scenario **II**, which invokes counterion exchange to give [(salen)Cr^{III}OAc] (**4**; Scheme 3), we independently synthesized **4** and examined its reactivity under both catalytic and stoichiometric conditions. Enantio- and regioselectivity as well as conversion are significantly diminished by using **4** relative to **3** under both catalytic and stoichiometric reaction conditions (Table 1, entry 7 vs 6, Table 3, entry 4 vs 2).[15] These results are inconsistent with asymmetric induction arising exclusively through the delivery of an acetate group by **4** (Scheme 3, scenario **II**), while they

Table 3: Effects of catalysts **3** and **4** on the functionalization of a π-allyl palladium acetate dimer.[a]

Entry	LA	k_{rel}[b]	Yield [%][c]	B:L	ee [%][d]
1	–	1.0	20	> 20:1	–
2	(R,R)-**3**	9.7	85	5.2:1	55
3[e]	(R,R)-**3**	–	0	–	–
4	(R,R)-**4**	3.8	41	2.2:1	29

[a] Mock catalytic conditions; EtOAc (0.2 M), AcOH (11 equiv), BQ (20 equiv), RT, (molarity and equivalents are relative to Pd). [b] Rate and selectivity determined by GC analysis and was compared to a standard curve using nitrobenzene as an internal standard (see the Supporting Information). [c] Determined by GC analysis on a chiral stationary phase. [d] The ee values were determined by GC analysis with a chiral β-cyclodextrin stationary phase. [e] No BQ added.

are most consistent with a **3**·BQ-promoted functionalization (Scheme 3, scenario **I**). However, at this time we cannot rule out a dual activation mechanism in which **4** delivers the acetate nucleophile to a [(π-allyl)Pd(BQ)·**3**] electrophilic intermediate (Scheme 3, scenario **III**).

In conclusion, we have reported a heterobimetallic Pd^{II}/bis(sulfoxide)/Cr^{III}(salen) system for the asymmetric allylic C−H oxidation of terminal olefins that proceeds with the highest levels of enantioselectivity reported to date.[16] These materials can be further enantioenriched through enzymatic resolution to rapidly furnish optically pure building blocks in high yields. To the best of our knowledge, this represents the first report of the interaction of a chiral Lewis acid co-catalyst with an organometallic intermediate that influences the stereochemical outcome of a catalytic process. We anticipate that this novel strategy will find widespread use in other electrophilic, oxidative transition-metal-catalyzed processes that are not amenable to asymmetric induction by using conventional chiral ligands.

Experimental Section

General procedure for branched asymmetric allylic acetoxylation (Table 3): A vial (2 mL, borosilicate) was charged with the substrate (1.0 mmol), AcOH (1.1 equiv, 63 μL), and EtOAc (200 μL). The liquid was then transferred to a vial (8 mL, borosilicate) containing 1,2-bis(phenylsulfinyl)ethanepalladium(II) acetate (**1**; 10 mol%, 0.10 mmol, 50 mg) (1R,2R)-(−)-[1,2-cyclohexanediamino-N,N'-bis(3,5-di-tert-butylsalicylidene)]chromium(III) fluorine (R,R)-**3**; 10 mol%, 0.10 mmol, 61.6 mg), 1,4-benzoquinone (2 equiv, 2.0 mmol, 216 mg), activated molecular sieves (4 Å bead; ca. 30 mg), and a teflon stir bar. After carefully stirring the reaction mixture for 48 h at room temperature, the mixture was diluted with EtOAc (3 mL), transferred into a separatory funnel, and diluted with hexanes (200 mL). The organic layer was washed with saturated aq NaHSO$_3$ (1 × 50 mL) and 5% aq K$_2$CO$_3$ (2 × 50 mL). **Caution: CO$_2$ is evolved when the aqueous solutions are combined**. The combined aqueous layers were back-extracted with hexanes (100 mL). The combined organic layers were dried (MgSO$_4$), filtered, and concentrated in vacuo. The resulting oil was redissolved in hexanes (50 mL)

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and extracted again with 5% aq K_2CO_3 (3×10 mL) to remove residual hydroquinone. The organic layer was again dried ($MgSO_4$), filtered, and concentrated in vacuo to afford a mixture of allylic oxidation products and any remaining starting material from which the conversion, yield, and B:L ratio were determined (by ^{1}H NMR spectroscopy). The *ee* values were determined by GC analysis on a chiral stationary phase. (see the Supporting Information).

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