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Palladacyclic Imidazoline−Naphthalene Complexes: Synthesis and Catalytic Performance in Pd(II)-Catalyzed Enantioselective Reactions of Allylic Trichloroacetimidates

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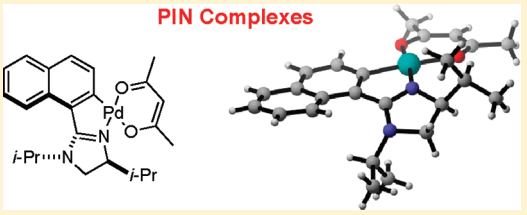
Supporting Information

ABSTRACT: A new family of air- and moisture-stable enantiopure *C,N*-palladacycles (PIN-acac complexes) were prepared in good overall yield in three steps from 2-iodo-1-naphthoic acid and enantiopure *β*-amino alcohols. Three of these PIN complexes were characterized by single-crystal X-ray analysis. As anticipated, the naphthalene and imidazoline rings of PIN-acac complexes **18a** and **18b** were canted significantly from planarity and projected the imidazoline substituents R^1 and R^2 on opposite faces of the palladium square plane. Fifteen PIN complexes were evaluated as catalysts for the rearrangement of prochiral (*E*)-allylic trichloroacetimidate **19** (eq 2) and the S_N2' allylic substitution of acetic acid with prochiral (*Z*)-allylic trichloroacetimidate **23**. Although these complexes were kinetically poor catalysts for the Overman rearrangement, they were good catalysts for the allylic substitution reaction, providing branched allylic esters in high yield. However, enantioselectivities were low to moderate and significantly less than that realized with palladacyclic complexes of the COP family. Computational studies support an *anti*-acetoxypalladation/*syn*-deoxypalladation mechanism analogous to that observed with COP catalysts. The computational study further suggests that optimizing steric influence in the vicinity of the carbon ligand of a chiral *C,N*-palladacycle, rather than near the nitrogen heterocycle, is the direction to pursue in future development of improved enantioselective catalysts of this motif.



INTRODUCTION

Enantioselective allylic substitution reactions are an essential class of catalytic asymmetric processes that are used to prepare a wide variety of enantioenriched chiral organic molecules.[1] For a number of years, we have been engaged in the development of catalytic enantioselective transformations of allylic substrates that employ palladium(II) complexes.[2] Among these are allylic alkylation reactions of trichloroacetimidate derivatives of prochiral 2-alken-1-ols with carboxylic acid[3] and phenol[3c,4] nucleophiles (Figure 1). These reactions take place with extraordinarily high branched-to-linear ratios (>100:1) and have been shown to not proceed via η^3-allylpalladium(0) intermediates.[3c] Of the many palladium(II) complexes investigated for the reaction of (*Z*)-allylic trichloroacetimidates **1** with carboxylic acids and phenols, the commercially available catalysts $[(R_p,S \text{ and } S_p,R)\text{-COP-OAc}]_2$[5] (**5** and *ent*-**5**) were found to be optimal. For the transformation of (*E*)-allylic trichloroacetimidates **4** to branched allylic phenols **3**, the di-*μ*-amidate dipalladium complexes $[(R_p,S \text{ and } S_p,R)\text{-COP-NHCOCCl}_3]_2$ (**6** and *ent*-**6**) are preferred because they are kinetically poor catalysts for the competing allylic rearrangement to form 3-trichloroacetamido-1-alkenes.[4b]

Since our initial disclosure in 1997,[6] a wide variety of palladium(II) complexes have been evaluated as catalysts for various transformations of allylic imidates.[7] Among these, palladacyclic catalysts,[8] in particular *C,N*-palladacycles such as the COP (**5** and **6**)[5] and FOP complexes (e.g., **7**)[9] and related complexes such as **8** developed by Peters[10] have proven to be of particular value. A structural feature of the *C,N*-palladacycle catalyst motifs **5**−**8** that is believed to be important for achieving high levels of enantioselectivity is the projection of steric bulk both above and below the palladium square-plane coordination sphere. Sterically differentiating the faces of the palladium square plane is thought to control which prochiral face of the coordinated alkene is activated in the enantiodetermining step. As a result, most enantioselective palladacycle catalysts rely on a planar chiral design to place steric elements perpendicular to the cyclopalladated ring.[11] However, methods for preparing nonracemic planar-chiral palladacycles are multistep, typically requiring diastereoselective cyclopalladation of an auxiliary-appended metallocene or resolution of a racemic complex.[12] Consequently, this structural moiety adds complexity to catalyst synthesis and limits the accessibility of analogues.

With the aforementioned considerations in mind, we have explored the *C,N*-palladacyclic imidazoline naphthalene (PIN) catalyst motif **9** (Figure 2). The modular nature of this bidentate palladacycle, derived from a naphthalene and an easily modified imidazoline ring, should allow rapid access to an array of catalyst structures. Moreover, both the steric and electronic environment around the metal center can be systemically altered by variation of the imidazoline substituents (R^1, R^2, and R^3), the aromatic carbon ligand, and the ancillary ligands (L) on palladium. Of central importance, we envisioned

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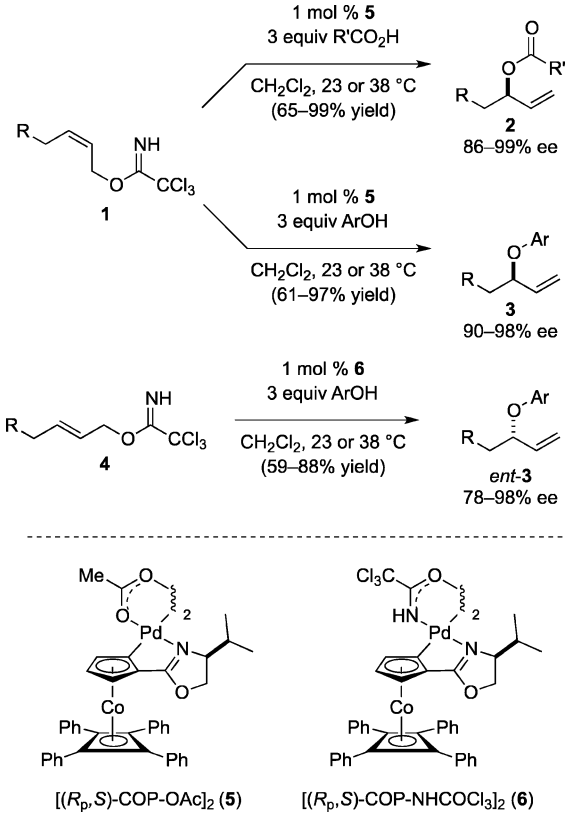


Figure 1. Enantioselective reactions of allylic trichloroacetimidates catalyzed by COP complexes **5** and **6**.

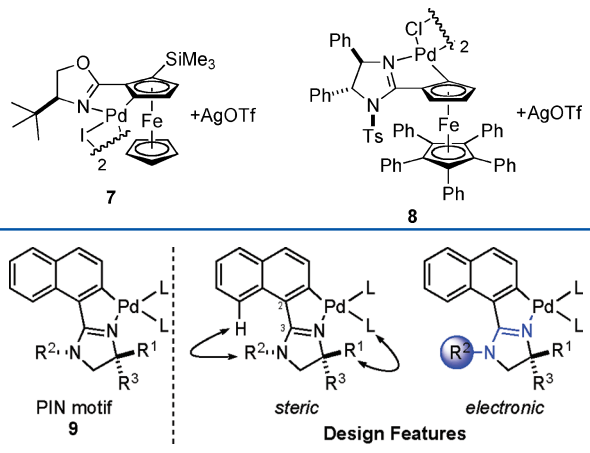


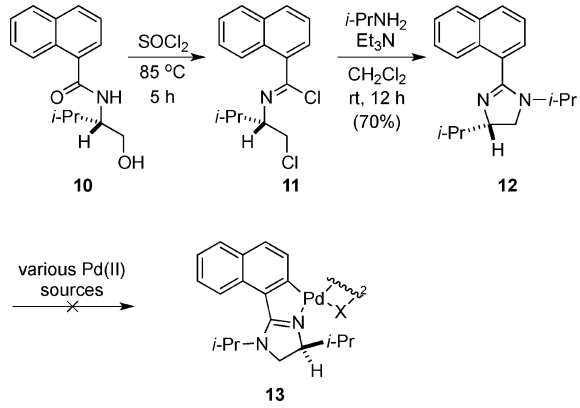
Figure 2. Design of the palladacycle imidazoline–naphthalene (PIN) catalyst motif.

creating an adjustable element of chirality by perturbation of the steric interaction between the naphthalene ring and imidazoline substituent R^2. This approach would capitalize on two potential steric contacts: (1) the interaction between R^1 and R^3 and the ancillary palladium ligands L and (2) the interaction between R^2 and the *peri*-C–H bond of the naphthalene ring. When R^1 and R^2 are large (and R^3 small), these steric interactions should result in the cyclopalladated complex being nonplanar, with the naphthalene and imidazoline rings canted out of plane and the substituents R^1 and R^2 oriented in an anti fashion. Furthermore, we anticipated that the nitrogen substituent R^2 would provide a handle to tune the basicity of the donating nitrogen atom, allowing easy adjustment of the electronic properties of the palladium center.[13] In this article, we report the preparation and structural characterization of a family of PIN complexes **9** and an evaluation of their performance as catalysts for the enantioselective transformation of (*Z*)-allylic trichloroacetimidates **1** to branched allylic esters **2** and phenols **3**.

RESULTS AND DISCUSSION

Synthesis of PIN Complexes. Nitrogen-directed carbopalladation of an aromatic ring is the most direct route to *C,N*-palladacycles;[8,14] therefore, we began our investigation by exploring the C–H activation of imidazoline **12** with various Pd(II) electrophiles (Scheme 1). Starting from (*S*)-valinol-derived *β*-hydroxyamide **10**, enantiopure 1-naphthylimidazoline **12** was prepared by a conventional sequence that began by the conversion of amide **10** to imidoyl chloride **11** by reaction with $SOCl_2$ at 85 °C.[15] After evaporation of excess $SOCl_2$ under reduced pressure, crude **11** was allowed to react with 1.1 equiv of isopropylamine in 5:1 CH_2Cl_2–Et_3N at room temperature. This two-step sequence provided imidazoline **12** in 70% yield and >98% ee.[16] However, attempted reaction of **12** with stoichiometric amounts of various Pd(II) electrophiles under common cyclopalladation conditions did not generate palladacycle **13**.[8] For example, attempted cyclopalladation of **12** with $Pd(OAc)_2$ in refluxing acetic acid[5] resulted in decomposition of the imidazoline and formation of palladium black, whereas attempted reaction at ambient temperature afforded a dark, intractable reaction mixture. Attempted cyclopalladation of imidazoline **12** using $Pd(OAc)_2$, Na_2PdCl_4, or $PdCl_2(MeCN)_2$ under both neutral and basic reaction conditions either returned **12** or resulted in decomposition. We reasoned that the desired cyclopalladation reaction was complicated by the steric strain associated with bringing the naphthyl and imidazoline rings into the near coplanar orientation required to promote C–H activation.

Scheme 1. Attempted Synthesis of PIN Complexes by Direct Cyclopalladation



The inability to cyclopalladate imidazoline **12** led us to explore forming palladacyclic PIN complexes by the oxidative addition of Pd(0) with halogen-containing precursors. Accordingly, 1-cyanonaphthalene (**14**) was deprotonated at low temperature with lithium 2,2,6,6-tetramethylpiperide and the resultant aryllithium species was quenched with I_2 as reported by Fraser to give 1-cyano-2-iodonaphthalene (Scheme 2).[17] Hydrolysis of this crude product in refluxing HOAc containing concentrated H_2SO_4 yielded the primary aryl amide, which was

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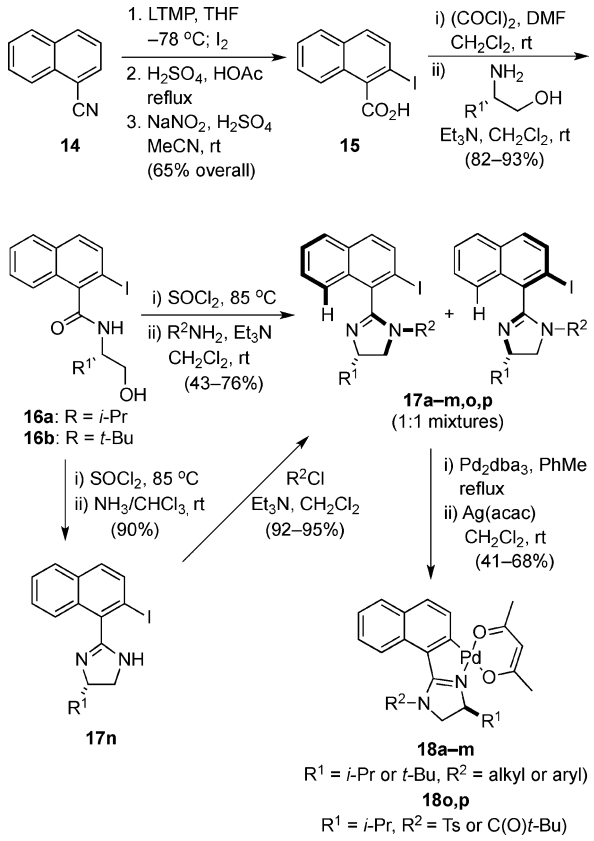
Scheme 2. Synthesis of (*S*)-PIN-acac Complexes 18



subsequently dissolved in MeCN and treated with excess $NaNO_2$ and 70% H_2SO_4 at room temperature to provide 2-iodo-1-naphthoic acid (**15**).[18] This three step sequence was preformed routinely on 5−10 g scales without purification of intermediates to give iodoacid **15** in 65% overall yield after recrystallization. Conversion of **15** to the corresponding acid chloride and subsequent reaction with either (*S*)-valinol or (*S*)-*tert*-leucinol gave respectively *β*-hydroxyamides **16a** (R^1 = *i*-Pr) and **16b** (R^1 = *t*-Bu) in high yields as colorless solids after recrystallization.

Hydroxy amides **16a,b** were converted in 43−76% yield to imidazolines **17a−m** by the two-step sequence utilized to prepare imidazoline **12** (Scheme 2, Table 1). In addition, imidazolines **17o** (R^2 = Ts) and **17p** (R^2 = CO*t*-Bu) were prepared in good yield from N−H imidazoline **17n** by reaction with TsCl or pivaloyl chloride at room temperature. With the exception of imidazoline **17n**, these products were 1:1 mixtures of atropisomers.[19]

Having developed an efficient route to imidazolines **17**, several conditions for promoting their conversion to palladacycles were explored. The optimal condition was found to be reaction of the imidazoline with 0.5 equiv of Pd_2dba_3 in refluxing toluene,[20] which furnished iodide-bridged palladacyclic products as yellow-orange solids. NMR analysis showed that these products were mixtures of head-to-head and head-to-tail isomers. Separation of these dimeric complexes was complicated by their decomposition upon exposure to silica gel. As a result, the crude mixtures of iodide-bridged dimers were allowed to react with silver acetylacetonate in CH_2Cl_2 at room temperature to give (*S*)-PIN-acac complexes **18a−m,o−p** as pale yellow solids in 41−68% yield (Table 1). Alternatively, the acetylacetonate complexes could be prepared in comparable

Table 1. Prepartion of (*S*)-PIN-acac Complexes 18 from Imidazoline Precursors 17

entry	17	R^1	R^2	18	yield (%)[a]
1	**17a**	*i*-Pr	*i*-Pr	**18a**	70
2	**17b**	*t*-Bu	*i*-Pr	**18b**	68
3[b]	**17c**	*i*-Pr	CH_2Ph	**18c**	53
4[b]	**17d**	*i*-Pr	$CH(Ph)_2$	**18d**	62
5[b]	**17e**	*i*-Pr	Cy	**18e**	57
6	**17f**	*i*-Pr	*t*-Bu	**18f**	68
7[b]	**17g**	*t*-Bu	*t*-Bu	**18g**	41
8	**17h**	*t*-Bu	1-adamantyl	**18h**	63
9	**17i**	*i*-Pr	Ph	**18i**	72
10[b]	**17j**	*t*-Bu	Ph	**18j**	52
11[b]	**17k**	*i*-Pr	*p*-$OMeC_6H_4$	**18k**	54
12[b]	**17l**	*i*-Pr	*p*-$CF_3C_6H_4$	**18l**	58
13[b]	**17m**	*i*-Pr	mesityl	**18m**	65
14	**17o**	*i*-Pr	Ts	**18o**	64
15	**17p**	*i*-Pr	C(O)*t*-Bu	**18p**	50

[a]Isolated yield. [b]Prepared directly from amides **16a,b** without purification of the imidazoline intermediate. Reflects overall isolated yield (3 steps).

overall yields directly from amides **16a,b** without purification of the labile imidazoline ligand. These monomeric complexes displayed a high degree of stability, withstanding silica gel chromatography and prolonged exposure to air and moisture at room temperature. Palladacycles **18** were generally more soluble in common organic solvents such as Et_2O and toluene than COP complexes **5** and **6**. Analysis of the NMR spectra of (*S*)-PIN-acac complexes **18** revealed that most were produced as single stereoisomers; the exception was (*S*)-PIN-acac complex **18h** (R^2 = 1-adamantyl), which was isolated in 41% yield as a ∼1:1 mixture of inseparable stereoisomers.

Structural Properties of PIN-acac Complexes. Two PIN-acac complexes having alkyl substituents, **18a** (R^1 = R^2 = *i*-Pr) and **18b** (R^1 = *t*-Bu, R^2 = *i*-Pr), provided single crystals suitable for X-ray diffraction by slow evaporation from solutions of 10% CH_2Cl_2−cyclohexane. Palladacycle **18a** crystallizes in the orthorhombic space group $P2_12_12_1$, whereas palladacycle **18b** crystallizes in the monoclinic space group $P2_1$. Representations of their X-ray models are shown in Figure 3. The bond lengths and angles involving the atoms coordinated to palladium are nearly identical in the two complexes, with the ligands about palladium being approximately square-planar (Table 2). Bond lengths and angles involving Pd, the coordinated imidazoline nitrogen atom N(1), and the cyclometalated carbon C(1) are similar to those found in other *C,N*-palladacycles.[8b] The Pd−O bond lengths of the acetylacetonate ligand are longer for the bond trans to carbon [Pd−O(2) bond length: **18a**, 2.0796(11) Å; **18b**, 2.0848(13) Å] than that trans to nitrogen [Pd−O(1) bond length: **18a**, 2.0122(11) Å; **18b**, 2.0050(14) Å], consistent with a larger trans influence for the anionic naphthyl ligand.

As we had anticipated, the imidazoline and naphthalene fragments are twisted out of plane in the X-ray models of PIN-acac complexes **18a** and **18b**, with the two alkyl substituents on opposite sides of the palladium square plane. The torsion angles around the C(2)−C(3) bond provide a measure of the degree to which the imidazoline substituents would be expected to influence coordination of an alkene *π*-bond to the Pd(II) center. This angle is 18.1° for diisopropyl complex **18a** and slightly larger, 24.6°, for the isopropyl/*tert*-butyl complex **18b**.

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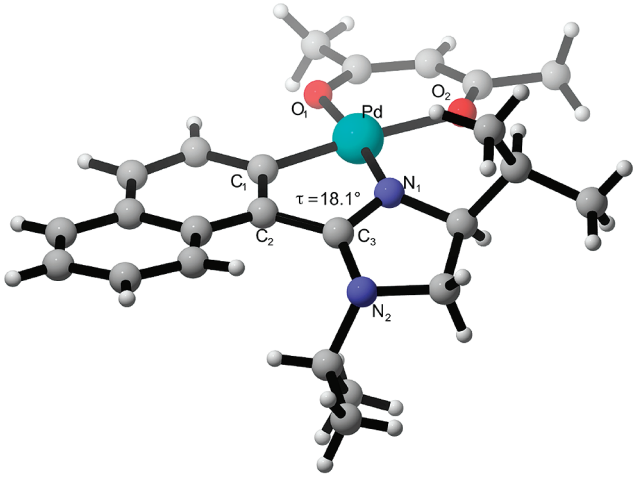
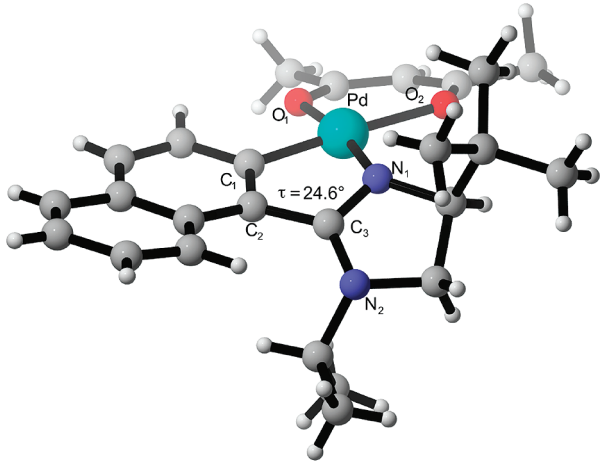


18a: R^1 = *i*-Pr, R^2 = *i*-Pr

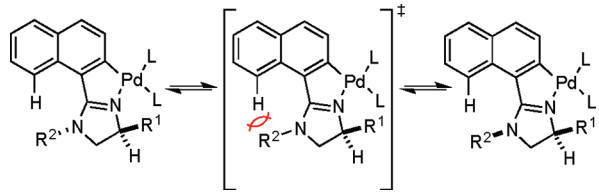


18b: R^1 = *t*-Bu, R^2 = *i*-Pr

Figure 3. X-ray models of (*S*)-PIN-acac complexes **18a** and **18b**.

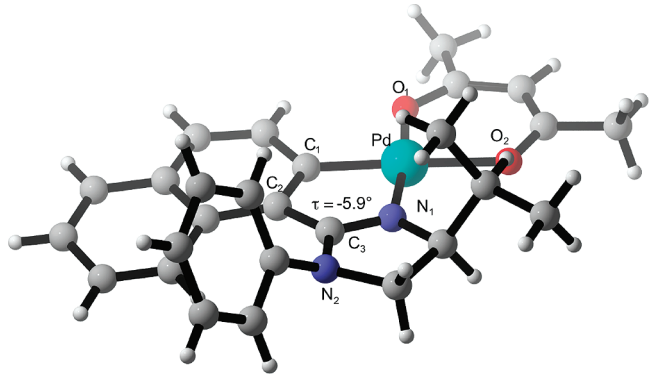
Although the imidazoline substituents of PIN-acac complexes **18a** and **18b** reside on opposite sides of the palladium square plane in the solid state, the configurational stability of the *N*-isopropyl substituent in solution was less certain (Scheme 3). Inversion at this site, which would require bringing the bulky isopropyl substituent into an unfavorable coplanar orientation with the naphthalene ring, could result in both alkyl substituents residing on the same face of the palladium square plane. The configurational stability of **18a** in solution was examined by variable temperature ^{1}H NMR from −80 to 110 °C.[21] Within this temperature range, the ^{1}H NMR spectrum of **18a** was unchanged. This observation, and DFT calculations

Scheme 3. Nitrogen Inversion of PIN Complexes



(b3-lyp/def2-TZVP) that estimate the barrier to be <15 kcal/mol,[22,23] are consistent with the N(2) nitrogen stereocenter undergoing rapid inversion at room temperature.

The structural features and catalytic properties of PIN-acac complex **18i** in which R^2 is phenyl and R^1 isopropyl are quite different than those of complexes **18a** and **18b**. The X-ray model of complex **18i** (Figure 4) shows that the geometry



18i: R^1 = *i*-Pr, R^2 = Ph

Figure 4. X-ray structure of (*S*)-PIN-acac complex **18i**.

around the palladium center is approximately square planar with the bond lengths and angles involving the palladium atom being quite similar to those of complexes **18a** and **18b** (Table 2). However, the imidazoline substituents reside on the same face of the palladium coordination sphere and N(2) is nearly sp^3 hybridized. The overall shape of this complex is quite flat, with the torsion angle around the C(2)−C(3) bond being −5.9°.[24] The phenyl substituent is twisted perpendicular to the imidazoline ring, thus minimizing destabilizing steric interactions when the naphthalene and imidazoline fragments are oriented nearly coplanar.[22]

Catalytic Performance of PIN-acac Complexes. (*S*)-PIN-acac complexes **18** were examined as enantioselective catalysts for the [3,3]-rearrangement and allylic substitution reactions of allylic trichloroacetimidates. Initial investigations were carried out with complex **18a**, which was found to be a poor catalyst for the rearrangement of (*E*)-allylic imidate **19**.

Table 2. Selected Bond Lengths and Bond Angles for Three PIN-acac Complexes and COP-hexafluoroacetylacetonate

	bond length (Å)				bond angle (deg)		dihedral angle (deg)
complex	Pd−C	Pd−N	Pd−O(1)[a]	Pd−O(2)[b]	C−Pd−N	O−Pd−O	τ[c]
18a	1.9800(16)	1.9970(13)	2.0122(11)	2.0769(11)	80.74(6)	92.48(5)	18.11(18)
18b	1.9693(16)	2.0262(16)	2.0050(14)	2.0848(13)	80.97(7)	92.72(5)	24.6(3)
18i	1.964(2)	1.9817(18)	2.0186(16)	2.0791(17)	79.65(8)	91.55(7)	−5.9(4)
(R_p,*S*)-COP-hfacac[d]	1.962	2.026	2.020	2.102	80.78	92.76	n/a

[a]The Pd−O(1) bond is trans to the Pd−N bond. [b]The Pd−O(2) bond is trans to the Pd−C bond. [c]The dihedral angle C(1)−C(2)−C(3)−N(1). [d]Crystalographic data for the COP hexafluoroacetylacetonate complex (COD 4021070) is available from the Crystallographic Open Database.

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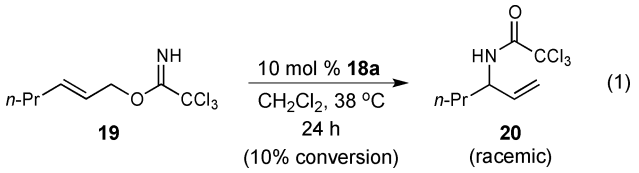
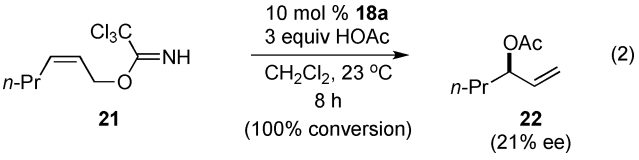
For example, after 24 h, allylic trichloroacetamide **20** was formed in only 10% yield when **19** was exposed to 10 mol % of **18a** (1.0 M substrate concentration) at 38 °C, with the bulk of the starting allylic imidate remaining unchanged (eq 1).



In contrast, PIN-acac complexes proved to be kinetically excellent catalysts for the allylic esterification reaction. Initial experiments were again conducted with complex **18a**, which at 10 mol % transformed (*Z*)-allylic trichloroacetimidate **21** cleanly to branched allylic acetate **22** within 8 h at room temperature (eq 2). This reaction proceeded with no detectable



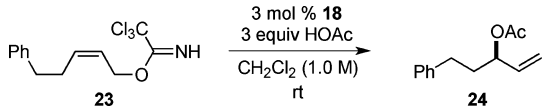
formation of rearrangement product **20**; however, allylic acetate **22** was produced in only 21% ee. Attempts to improve enantioselectivity by carrying out the reaction at 0 °C resulted only in prolonged reaction times without any improvement in enantioselectivity. In addition, changes in the solvent had only a small influence on catalytic efficiency or enantioselectivity (yield of **22**, reaction time at 23 °C, ee): CH_2Cl_2 (95%, 8 h, 21%) ≈ MeCN (92%, 8 h, 20%) > toluene (88%, 10 h, 10%) > Et_2O (94%, 16 h, 20%) ≈ THF (94%, 18 h, 18%).

These initial experiments indicated that PIN-acac complexes might be useful catalysts for enantioselective allylic esterification of (*Z*)-allylic trichloroacetimidates if stereoinduction could be improved by modification of the imidazoline substituents. Accordingly, our small library of PIN catalysts was surveyed for the enantioselective conversion of (*Z*)-allylic trichloroacetimidate **23** to 3-acetoxy-5-phenyl-1-pentene (**24**) (Table 3).

Several trends in the data summarized in Table 3 are apparent. Palladacycles containing bulky alkyl substituents on the imidazoline nitrogen (**18a**–**h**) provided 3-acetoxy-1-pentene (**24**) in excellent yields (70–95%) and moderate enantioselectivities (25–57% ee). Increasing the size of the R^1 substituent from *i*-Pr to *t*-Bu translated into only a marginal increase in enantioselectivity (Table 3, entries 1 and 2), whereas increasing the size of the imidazoline nitrogen substituent R^2 proved to be more critical to the stereochemical outcome (Table 3, entries 3–7). The most effective R^2 substituent was *t*-Bu, with PIN catalysts **18f** and **18g** providing acetate **24** in 48% and 57% ee, respectively (Table 3, entries 6 and 7). Notably, catalyst **18g** (R^1 = *t*-Bu, R^2 = *t*-Bu), which is expected to have the largest degree of angular torsion around the C(2)–C(3) bond, provided the highest level of enantioselectivity among the PIN complexes screened (Table 3, entry 7). However, catalytic rate was somewhat lower with this catalyst, with a reaction time of 48 h being required to give acetate **24** in high yield. It is not surprising that complex **18h**, which was used as a 1:1 mixture of atropisomers, provided acetate **24** in low ee only (Table 3, entry 8). PIN complexes having *N*-aryl substituents (Table 3, entries 9–13) displayed useful catalytic activity but provided the allylic acetate product in low to moderate ee. The most enantioselective *N*-aryl PIN variant was **18m** (R^1 = *t*-Bu, R^2 = Mes), which gave allylic acetate **24** in 90% yield and 42% ee (Table 3, entry 13). PIN catalysts **18o**–**p**, bearing an electron-withdrawing substituent on the imidazoline nitrogen, gave product **24** in low ee and exhibited only marginal improvement in reaction rate relative to **18a**–**m** (Table 3, entries 14 and 15).

This catalyst survey showed that PIN-acac complexes are useful catalysts for the addition of carboxylic acid nucleophiles

Table 3. Survey of (*S*)-PIN-acac Complexes for the Catalytic Asymmetric Synthesis of Branched Allylic Acetates



entry	catalyst	R^1	R^2	time (h)	yield (%)[a]	ee (%)[b]
1	**18a**	*i*-Pr	*i*-Pr	18	95	28
2	**18b**	*t*-Bu	*i*-Pr	18	96	34
3	**18c**	*i*-Pr	CH_2Ph	18	93	30
4	**18d**	*i*-Pr	$CH(Ph)_2$	18	90	38
5	**18e**	*i*-Pr	Cy	18	95	25
6	**18f**	*i*-Pr	*t*-Bu	24	96	48
7	**18g**	*t*-Bu	*t*-Bu	48	95	57
8[c,d]	**18h**	*t*-Bu	1-adamantyl	18	65	28
9	**18i**	*i*-Pr	Ph	18	97	20
10	**18j**	*t*-Bu	Ph	18	96	23
11	**18k**	*i*-Pr	*p*-$OMeC_6H_4$	18	94	18
12	**18l**	*i*-Pr	*p*-$CF_3C_6H_4$	18	96	21
13	**18m**	*i*-Pr	mesityl	36	90	42
14	**18o**	*i*-Pr	Ts	12	90	16
15	**18p**	*i*-Pr	C(O)*t*-Bu	18	91	10
16[e]	$[COP\text{-}OAc]_2$ (**5**)			16	88	91

[a]Duplicate experiments (±3%). [b]Determined by GC analysis of duplicate experiments (±2%). [c]Complex **18h** was used as a 1:1 mixture of atropisomers. [d]The remaining mass was imidate **23**. [e]Catalyst loading of 5 was 1.5 mol % (3 mol % Pd).

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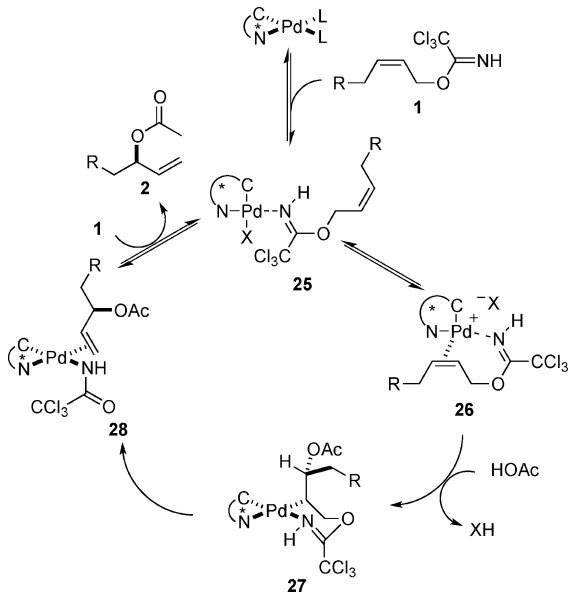
to allylic trichloroacetimidates, with catalytic rates being similar to those of COP catalyst **5** (Table 3, entry 16). Unfortunately, the enantioselectivity achieved with PIN catalysts **18** is significantly lower than that realized with COP catalyst **5**.

Computational Modeling. To gain insight into what features of the PIN complex architecture might be modified to increase enantioselectivity of these catalysts, computational modeling was undertaken. The structural relationship between the *C,N*-palladacycle portions of the PIN and COP catalyst structures and their comparable reactivity suggests that they might operate by a common mechanism. We have recently reported a detailed computational study of the addition of carboxylic acid nucleophiles to (*Z*)-allylic trichloroacetimidates using COP catalyst **5**.[3c] The proposed catalytic cycle, which involves antarafacial S_N2' addition of acetic acid to the double bond, is summarized in Scheme 4.[25] On the basis of

Scheme 4. Proposed Catalytic Cycle for the Pd(II)-Catalyzed Conversion of (*Z*)-Allylic Trichloroacetimidates (1) to Enantioenriched Allylic Esters (2)



experimental observations and computational experiments, this earlier study concluded that (1) oxypalladation (**26** → **27**) is the rate- and enantio-determining step; (2) bidentate coordination of the allylic trichloroacetimidate to the palladacycle catalyst (e.g., intermediate **26**) is favored over other coordination modes; and (3) there is a preference for the alkene π-bond to coordinate cis to the Pd−C σ-bond of the palladacycle.[3c] This latter observation is consistent with our mechanistic investigations of the COP-catalyzed [3,3]-rearrangement of (*E*)-allylic trichloroacetimidates[26] and with the strong trans influence observed for d^8 square-planar Pd(II) complexes.[27] The current analysis thus focused on the interactions between the imidate substrate, acetate nucleophile, and *C,N*-palladacycle framework in the oxypalladation step.

In order to gain a better understanding of diastereoselection induced by the chiral PIN catalyst architecture, the oxypalladation step (Scheme 4, **26** → **27**) was studied computationally. Calculations modeled the addition of HOAc to the trichloroacetimidate derivative of (*Z*)-2-butene-1-ol using complex **18a** as a catalyst.[28−31] The previously reported enantiodetermining transition-state structure for the reaction of acetic acid with (*Z*)-2-butenyl trichloroacetimidate catalyzed by COP complex **5** was used as the starting geometry for calculations of PIN transition-state structures **29**−**32**.[3c] The results of this computational study are depicted in Figure 5. In transition-state structures **29** and **30**, the reacting allylic C−C π-bond is positioned cis to the Pd−C(1) bond, consistent with the predicted preferred coordination geometry of the imidate (e.g., **26**, Scheme 4). Conversely, in transition-state structures **31** and **32**, the C−C π-bond is coordinated trans to the palladacycle Pd−C(1) bond. Transition-state structures **29** and **31** would afford the observed major *R*-enantiomer of the allylic acetate product, whereas the transition-state structures **30** and **32** would produce the minor *S*-enantiomer. Of the four transition structures, **29** was found to have both the lowest activation energy ($\Delta E^{\ddagger}$ = 4.2 kcal/mol) and the lowest relative energy ($\Delta\Delta E^{\ddagger}$). Structures **31** and **32** having the C−C π-bond coordinated trans to the carbon of the palladacycle are calculated to be 4.0 and 5.4 kcal/mol higher in energy than the corresponding cis complexes. Transition-state structure **30**, which has the imidate nitrogen coordinated trans to the Pd−C(1) bond and leads to the formation of the minor enantiomer, is calculated to be only 0.2 kcal/mol higher in energy than the low energy transition-state structure **29**.

Several additional observations from the computational study warrant comment. In low energy transition-state structures **29** and **30**, nucleophilic attack on the activated C−C double bond takes place next to C(19) of the naphthalene ligand. Thus, the enantiodetermining event is occurring relatively far away from the chiral environment provided by the imidazoline substituents R^1 and R^2. The small energy difference ($\Delta\Delta E^{\ddagger}$ = 0.2 kcal/mol) between the transition-state structures **29** (*Re* face addition) and **30** (*Si* face addition) is consistent with the observed low level of enantioselectivity realized with PIN complex **18a**. Although variation of R^1 and R^2 can undoubtedly lead to increased torsion around the C(2)−C(3) bond, which would place these groups in somewhat closer proximity to the reacting C−C π-system, it is doubtful that the N(2) substituent could be positioned in a way to effect a high degree of energy separation between transition-state structures **29** and **30**. Our computational analysis suggests that the most useful approach to optimizing the PIN catalyst structure would be by appending functionality at C(19) of the naphthalene backbone.

CONCLUSION

In summary, a new family of enantiopure *C,N*-palladacycles (PIN-acac complexes **18**) were developed and evaluated as asymmetric catalysts for the reaction of allylic trichloroacetimidates with external nonmetal bound nucleophiles. These air- and moisture-stable complexes were formed in good overall yield in three steps from 2-iodo-1-naphthoic acid (**15**) and β-amino alcohols. Three PIN complexes were characterized by single-crystal X-ray analysis. As anticipated, the naphthalene and imidazoline rings of PIN-acac complexes **18a** and **18b** were canted significantly from planarity and projected the imidazoline substituents R^1 and R^2 on opposite faces of the palladium square plane. Although these PIN palladacycles displayed useful levels of catalytic activity for the allylic substitution of prochiral allylic trichloroacetimidates with carboxylic acid nucleophiles and exclusively provided branched allylic esters in high yield, enantioselectivities were low to moderate. Nonetheless, the accessible and easily varied naphthalene−imidazoline ligands described here may be useful for the synthesis of related

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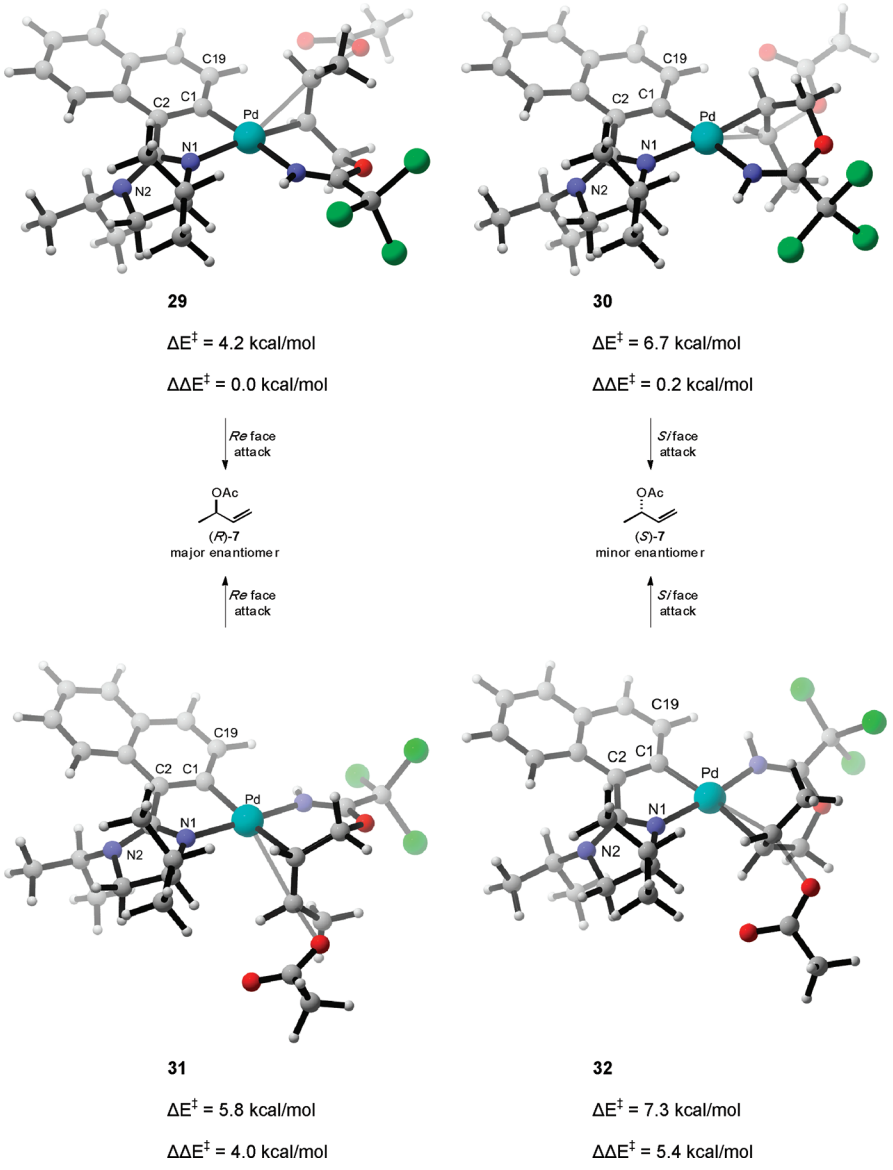

Figure 5. Relative energies of four isomeric transition-state structures for oxypalladation using PIN complex **18a**.

enantiopure axial chiral cyclometalated complexes that might find future applications in asymmetric catalysis.

The experimental and computational results presented here reinforce our previous conclusions with COP catalysts that the alkene π-bond of an allylic imidate substrate is preferentially coordinated cis to the carbon ligand of the palladacycle[3c,26] with attack of an external nucleophile occurring from the least-sterically hindered face in this quadrant. This study further suggests that optimizing steric influence in the vicinity of the carbon ligand of a chiral *C,N*-palladacycle, rather than near the nitrogen heterocycle, is the direction to pursue in future development of improved enantioselective catalysts in this area.

EXPERIMENTAL SECTION

General Procedure for the Synthesis of β-Hydroxyamides. Preparation of (*S*)-*N*-(1-Hydroxy-3-methylbutan-2-yl)-2-iodonaphthalene-1-carboxamide (16a). Carboxylic acid **15** (6.00 g, 20.1 mmol) was suspended in CH_2Cl_2 (100 mL) and rapidly stirred. Oxalyl chloride (3.6 mL, 40 mmol) and a catalytic amount of DMF (~0.02 mL) were added dropwise at rt (***Caution!*** *Gas evolved*), and the resultant suspension was stirred until it became homogeneous (approximately 2 h). The reaction mixture was then concentrated under reduced pressure, and the resulting yellow residue was dissolved in CH_2Cl_2 (50 mL) and transferred by cannula to a solution of (*S*)-valinol (2.07 g, 21.1 mmol) and Et_3N (8.5 mL, 61 mmol) in CH_2Cl_2 (150 mL) maintained at 0 °C. The reaction mixture was allowed to warm to rt over 16 h. The reaction then was diluted with CH_2Cl_2 (150 mL) and washed successively with 1 M HCl (2 × 250 mL), 1 M NaOH (2 × 250 mL), and brine. The organic layer was dried with anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting brown residue was recrystallized from $CHCl_3$ to afford **16a** (6.55 g, 17.1 mmol, 85%) as a tan solid: mp 132−136 °C; $[\alpha]_D^{24}$ = +11.2, $[\alpha]_{577}^{24}$ = +12.1, $[\alpha]_{546}^{24}$ = +12.9, $[\alpha]_{435}^{24}$ = +15.3, $[\alpha]_{405}^{24}$ = +17.4, (*c* = 0.2, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ 7.87 (q, *J* = 3.0, 1H), 7.80−7.76 (m, 2H), 7.52−7.47 (m, 3H), 6.07 (d, *J* = 8.3, 1H), 4.07−4.01 (m, 1H), 3.93−3.91 (m, 1H), 3.81−3.79 (m, 1H), 2.50 (br s, 1H), 1.97 (octet, *J* = 6.8, 1H), 1.04 (d, *J* = 6.8, 3H), 1.03 (d, *J* = 6.8, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, 298 K) δ 170.3 (C), 141.0 (C), 135.2 (CH), 132.5 (C), 131.2 (C), 130.4 (CH), 128.2 (CH), 127.9 (CH), 127.0 (CH), 125.2 (CH), 91.2 (C), 63.6 (CH_2), 57.8 (CH), 29.0 (CH), 19.8 (CH_3), 19.3 (CH_3); IR (thin film) 3406, 2960, 1732, 1076 cm^{-1}; HRMS (ESI) *m*/*z*, 406.0271 (406.0280 calcd for $C_{16}H_{18}NINaO_2$, $(M + Na)^+$).

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(*S*)-*N*-(1-Hydroxy-3,3-dimethyl-2-yl)-2-iodonaphthalene-1-carboxamide (16b). Prepared following the general procedure used to prepare **16a**. The crude residue was recrystallized from $CHCl_3$ to afford amide **16b** (2.48 g, 6.24 mmol, 93%) as a light brown solid: mp 71−75 °C; $[\alpha]_D^{23} = -10.3$, $[\alpha]_{577}^{23} = -11.2$, $[\alpha]_{546}^{23} = -13.3$, $[\alpha]_{435}^{23} = -24.6$, ($c$ = 0.83, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ 8.01 (br s, 1H), 7.83 (d, J = 8.5, 2H), 7.58 (d, J = 8.4, 1H), 7.55−7.53 (m, 2H), 6.02 (d, J = 8.2, 1H), 4.22 (ddd, J = 9.8, 6.8, 3.0, 1H), 4.10 (dd, J = 11.0, 2.4, 1H), 5.38 (m, 1H), 2.48 (br s, 1H), 1.10 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$, 298 K) δ 170.6 (C), 141.2 (C), 135.2 (CH), 132.5 (C), 131.3 (C), 130.4 (CH), 128.2 (CH), 127.9 (CH), 127.0 (CH), 125.3 (CH), 91.2 (C), 63.1 (CH), 60.5 (CH_2), 33.8 (C), 27.5 (CH_3); IR (thin film) 3395, 3278, 3058, 2960, 1746 cm^{-1}; HRMS (ESI) m/z, 398.0625 (398.0619 calcd for $C_{17}H_{21}INO_2$, $(M + H)^+$).

General Procedure for the Synthesis of Imidazolines.[32] Preparation of (*S*)-1,4-Diisopropyl-2-(naphthalene-1-yl)-4,5-dihydro-1*H*-imidazole (12). Amide **10** (0.518 g, 2.00 mmol) was dissolved in freshly distilled $SOCl_2$ (0.73 mL, 10 mmol), and the solution was warmed to 85 °C. After 5 h, the reaction was cooled to rt, diluted with toluene (10 mL), and concentrated under reduced pressure. The unpurified chloroalkylimidoyl chloride was dissolved in CH_2Cl_2 (5 mL), and any insoluble impurities were removed by filtration. The resulting solution was treated with a solution of Et_3N (0.83 mL, 6.0 mmol) and isopropylamine (0.18 mL, 2.2 mmol) in CH_2Cl_2 (2 mL) at rt. The reaction mixture was maintained at rt for 12 h, then stirred with 2 M NaOH (20 mL) for 30 min. The organic layer was separated, and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organics were dried with anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting yellow residue was purified by column chromatography (silica gel, 8:1:1 hexanes/Et_2O/Et_3N)[33] to afford imidazoline **12** (0.392 g, 1.40 mmol, 70%) as a colorless foam: $[\alpha]_D^{24} = -37.0$, $[\alpha]_{577}^{24} = -38.9$, $[\alpha]_{546}^{24} = -42.6$, $[\alpha]_{435}^{24} = -72.4$, $[\alpha]_{405}^{24} = -85.7$, ($c$ = 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ 8.34 (d, J = 8.3, 1H), 7.95 (d, J = 8.0, 1H), 7.88 (d, J = 7.9, 1H), 7.65 (d, J = 7.9, 1H), 7.56−7.54 (m, 2H), 7.48 (dd, J = 8.0, 7.3, 1H), 6.18 (d, J = 8.7, 1H), 4.11−4.08 (m, 1H), 3.94−3.91 (m, 1H), 3.86 (m, 1H), 2.51 (br s, 1H), 2.05 (septet, J = 7.0, 1H), 1.10 (d, J = 6.8, 3H), 1.09 (d, J = 6.8, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, 298 K) δ 170.6 (C), 134.7 (CH), 133.7 (CH), 130.6 (C), 130.1 (CH), 128.3 (CH), 127.2 (C), 126.5 (CH), 125.4 (CH), 124.8 (C), 124.7 (CH), 64.0 (CH), 57.6 (CH_2), 29.2 (CH), 19.7 (CH_3), 19.0 (CH_3); IR (thin film) 3296, 3060, 3051, 2931, 1623 cm^{-1}; HRMS (ESI) m/z, 281.2021 (281.2018 calcd for $C_{19}H_{25}N_2$, $(M + H)^+$).

The following compounds were prepared in identical fashion from **16a** or **16b** employing 1.1 equiv of the appropriate alkyl/aryl primary amine.

(*S*)-2-(2-Iodonaphthalen-1-yl)-1,4-diisopropyl-4,5-dihydro-1*H*-imidazole (17a). Following the general procedure, the crude residue was purified by column chromatography (silica gel, 6:3:1 hexane/Et_2O/Et_3N) to afford **17a** (0.463 g, 1.14 mmol, 76%) as a yellow foam. The product was characterized as a 1:1 mixture of atropisomers: ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ 7.90−7.89 (m, 2H), 7.87 (dd, J = 8.7, 1.7, 2H), 7.80−7.78 (m, 2H), 7.56 (d, J = 8.7, 2H), 7.52−7.47 (m, 4H), 4.13 (dt, J = 11.0, 6.3, 1H), 4.05 (dt, J = 10.6, 3.1, 1H), 3.65−3.60 (m, 2H), 3.35−3.31 (m, 2H), 3.18 (sextet, J = 6.7, 2H), 2.00 (sextet, J = 6.5, 2H), 1.24 (d, J = 6.6, 3H), 1.23 (d, J = 6.6, 3H), 1.16 (d, J = 6.7, 3H), 1.13 (d, J = 6.7, 3H), 1.08 (d, J = 6.6, 3H), 1.07 (d, J = 6.7, 3H), 0.96 (d, J = 6.6, 3H), 0.93 (d, J = 6.6, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, 298 K) δ 163.30 (C), 163.26 (C), 135.7 (CH), 135.6 (CH), 132.9 (C), 132.7 (C), 132.6 (C), 132.5 (C), 130.2 (CH), 128.1 (CH), 128.0 (CH), 127.3 (CH), 127.2 (CH), 126.7 (CH), 126.6 (CH), 125.8 (CH), 96.3 (C), 95.9 (C), 71.2 (CH), 70.9 (CH), 46.34 (CH), 46.31 (CH), 45.6 (CH_2), 45.1 (CH_2), 33.8 (CH), 33.7 (CH), 21.7 (CH_3), 21.5 (CH_3), 20.8 (CH_3), 20.7 (CH_3), 19.9 (CH_3), 19.4 (CH_3), 18.9 (CH_3); IR (thin film) 3040, 2952, 1712, 1624, cm^{-1}; HRMS (ESI) m/z, 429.0811 (429.0804 calcd for $C_{19}H_{23}IN_2Na$, $(M + Na)^+$).

(*S*)-4-*tert*-Butyl-2-(2-iodonaphthalen-1-yl)-1-isopropyl-4,5-dihydro-1*H*-imidazole (17b). Following the general procedure, the crude residue was purified by column chromatography (silica gel, 7:2:1 hexane/Et_2O/Et_3N) to afford **17b** (0.379 g, 0.902 mmol, 43%) as an orange film. The product was characterized as a 1:1 mixture of atropisomers: ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ 7.92−7.89 (m, 2H), 7.86 (app dd, J = 8.7, 2.8, 2H), 7.80−7.77 (m, 2H), 7.55 (app dd, J = 8.7, 2.6, 2H), 7.50−7.46 (m, 4H), 4.08 (t, J = 11.4, 2H), 3.54 (dt, J = 9.5, 4.3, 2H), 3.42−3.36 (m, 2H), 3.19 (sextet, J = 6.4, 2H), 1.22−1.21 (m, 6H), 1.10 (s, 9H), 1.09 (s, 9H), 0.96 (d, J = 6.6, 3H), 0.92 (d, J = 6.5, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, 298 K) δ 163.43 (C), 163.41 (C), 135.82 (C), 135.80 (C), 135.7 (CH), 135.6 (CH), 133.1 (C), 132.8 (C), 132.6 (C), 132.5 (C), 130.14 (CH), 130.11 (CH), 128.13 (CH), 128.0 (CH), 127.3 (CH), 127.1 (CH), 126.7 (CH), 126.6 (CH), 126.0 (CH), 125.9 (CH), 96.6 (C), 95.6 (C), 74.88 (CH), 74.86 (CH), 46.42 (CH), 46.36 (CH), 43.7 (CH_2), 43.5 (CH_2), 34.7 (C), 34.3 (C), 27.2 (CH_3), 26.6 (CH_3), 22.1 (CH_3), 21.7 (CH_3), 20.5 (CH_3), 20.4 (CH_3); IR (thin film) 3051, 2990, 1661, 1235, cm^{-1}; HRMS (ESI) m/z, 443.0970 (443.0960 calcd for $C_{20}H_{25}IN_2Na$, $(M + Na)^+$)

(*S*)-1-*tert*-Butyl-2-(2-iodonaphthalen-1-yl)-4-isopropyl-4,5-dihydro-1*H*-imidazole (17f). Following the general procedure, the crude residue was purified by column chromatography (silica gel, 8:1:1 hexane/Et_2O/Et_3N) to afford **17f** (0.274 g, 0.652 mmol, 71%) as a yellow paste. The product was characterized as a 1:1 mixture of atropisomers: ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ 7.88−7.86 (m, 2H), 7.80 (d, J = 5.3, 1H), 7.78 (d, J = 5.4, 1H), 7.75−7.71 (m, 2H), 7.49−7.43 (m, 6H), 3.96 (dt, J = 11.0, 6.3, 1H), 3.86 (dt, J = 10.8, 7.3, 1H), 3.74 (app ddd, J = 11.0, 9.3, 6.3, 2H), 3.45 (app q, J = 9.3, 2H), 1.97 (m, 2H), 1.12 (d, J = 6.7, 3H), 1.07 (d, J = 6.8, 3H), 1.04−1.02 (m, 24H); ^{13}C NMR (125 MHz, $CDCl_3$, 298 K) δ 162.8 (C), 162.6 (C), 139.0 (C), 138.98 (C), 135.7 (CH), 135.6 (CH), 133.5 (C), 132.8 (C), 132.5 (C), 132.4 (C), 129.6 (CH), 128.0 (CH), 127.9 (CH), 127.0 (CH), 126.9 (CH), 126.7 (CH), 126.4 (CH), 97.8 (C), 96.7 (C), 69.9 (CH), 69.7 (CH), 54.5 (C), 50.6 (CH_2), 50.0 (CH_2), 33.6 (CH), 33.4 (CH), 29.4 (CH_3), 29.2 (CH_3), 19.9 (CH_3), 19.5 (CH_3), 19.4 (CH_3), 18.8 (CH_3); IR (thin film) 3059, 2980, 1655, 1241 cm^{-1}; HRMS (ESI) m/z, 421.1143 (421.1141 calcd for $C_{20}H_{26}IN_2$, $(M + H)^+$).

(*S*)-1,4-Di-*tert*-butyl-2-(2-iodonaphthalen-1-yl)-4,5-dihydro-1*H*-imidazole (17g). Following the general procedure, the crude residue was purified by column chromatography (silica gel, 8:2:1 hexane/Et_2O/Et_3N) to afford **17g** (0.504 g, 1.16 mmol, 75%) as a yellow film. The product was characterized as a 1:1 mixture of atropisomers: ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ 7.89−7.88 (m, 2H), 7.79 (t, J = 8.5, 2H), 7.72 (m, 1H), 7.71 (d, J = 9.0, 1H), 7.49−7.43 (m, 6H), 3.93 (t, J = 11.8, 2H), 3.68 (t, J = 9.3, 1H), 3.66 (t, J = 8.7, 1H), 3.51−3.47 (m, 2H), 1.10 (s, 9H), 1.04 (s, 9H), 1.03 (s, 9H), 1.01 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$, 298 K) δ 163.0 (C), 162.9 (C), 139.13 (C), 139.08 (C), 135.9 (CH), 135.6 (CH), 133.9 (C), 132.7 (C), 132.6 (C), 132.4 (C), 129.7 (CH), 129.6 (CH), 128.1 (CH), 127.8 (CH), 127.0 (CH), 126.84 (CH), 126.80 (CH), 126.7 (CH), 126.5 (CH), 98.3 (C), 96.1 (C), 73.5 (CH), 73.5 (CH), 54.7 (C), 54.6 (C), 48.8 (CH_2), 48.6 (CH_2), 34.7 (C), 34.3 (C), 29.5 (CH_3), 29.1 (CH_3), 27.2 (CH_3), 26.6 (CH_3); IR (thin film) 2989, 2908, 1648, 1211, 1023 cm^{-1}; HRMS (ESI) m/z, 435.1294 (435.1297 calcd for $C_{21}H_{28}IN_2$, $(M + H)^+$).

(*S*)-4-*tert*-Butyl-2-(2-iodonaphthalen-1-yl)-1-(1-adamantyl)-4,5-dihydro-1*H*-imidazole (17h). Following the general procedure, the crude residue was purified by column chromatography (silica gel, 8:1:1 hexane/Et_2O/Et_3N) to afford **17h** (0.155 g, 0.302 mmol, 60%) as a colorless foam. The product was characterized as a 1:1 mixture of atropisomers: ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ 7.93−7.89 (m, 2H), 7.81 (t, J = 8.6, 2H), 7.79−7.76 (m, 2H), 7.50−7.46 (m, 6H), 3.93 (t, J = 11.8, 1H), 3.92 (t, J = 11.6, 1H), 3.75−3.69 (m, 2H), 3.60−3.56 (m, 2H), 1.85−1.84 (m, 6H), 1.73−1.67 (m, 12H), 1.50−1.38 (m, 8H), 1.09 (s, 9H), 1.06 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$, 298 K) δ 162.48 (C), 139.7 (C), 135.8 (CH), 135.6 (CH), 134.0 (C), 132.9 (C), 132.6 (C), 132.4 (C), 129.53 (CH), 129.50 (CH), 128.0 (CH), 127.8 (CH), 127.0 (CH), 126.9 (CH), 126.82 (CH), 126.80 (CH), 126.41 (CH), 126.39 (CH), 98.2 (C), 96.2 (C), 73.30 (CH), 73.28 (CH), 55.74 (C), 55.69 (C), 41.5 (CH_2), 41.1

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(CH_2), 36.07 (CH_2), 36.06 (CH_2), 34.8 (C), 34.4 (C), 27.2 (CH_3), 26.6 (CH_3); IR (thin film) 3056, 2994, 2852, 1590, 1260, 1242 cm^{-1}; HRMS (ESI) *m/z*, 513.1748 (513.1767 calcd for $C_{27}H_{34}IN_2$, $(M + H)^+$).

(*S*)-2-(2-Iodonaphthalen-1-yl)-4-isopropyl-1-phenyl-4,5-dihydro-1*H*-imidazole (17i). Following the general procedure, the crude residue was purified by column chromatography (silica gel, 8:1:1 hexane/Et_2O/Et_3N) to afford **17i** (0.355 g, 0.806 mmol, 69%) as an orange foam. The product was characterized as a ~1.4:1 mixture of atropisomers. The compound contains some minor impurities but was used directly in the next step, as decomposition was observed during purification attempts: ^1H NMR (500 MHz, $CDCl_3$, 298 K) δ 8.02 (dd, J = 8.0, 2.8, 1H), 7.83−7.80 (m, 5H), 7.79 (d, J = 8.3, 1H), 7.73−7.53 (m, 4H), 7.01−6.96 (m, 3H), 6.83−6.80 (m, 3H), 6.62 (d, J = 8.4, 1H), 6.57−6.55 (m, 3H), 4.26−4.20 (m, 2H), 4.05−4.00 (m, 2H), 3.91 (d, J = 6.2, 1H), 2.17 (septet, J = 6.8, 1H), 2.12 (septet, J = 6.5, 1H), 1.16 (d, J = 6.7, 3H), 1.15 (d, J = 6.7, 3H), 1.12 (d, J = 6.5, 3H), 1.11 (d, J = 6.5, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, 298 K) δ 160.3 (C), 160.2 (C), 140.4 (C), 140.2 (C), 135.7 (CH), 135.6 (CH), 135.5 (C), 135.2 (C), 133.6 (C), 132.9 (CH), 132.7 (CH), 132.5 (C), 130.1 (CH), 129.5 (CH), 128.7 (CH), 128.1 (CH), 128.0 (CH), 127.9 (CH), 127.3 (CH), 127.2 (CH), 126.7 (CH), 126.6 (CH), 125.9 (CH), 125.3 (CH), 122.3 (CH), 122.2 (CH), 118.3 (CH), 118.2 (CH), 97.0 (C), 96.4 (C), 70.8 (CH), 70.6 (CH), 53.4 (CH_2), 53.1 (CH_2), 33.2 (CH), 33.0 (CH), 20.0 (CH_3), 19.4 (CH_3), 19.2 (CH_3), 19.1 (CH_3); IR (thin film) 3061, 2995, 1675, 1238 cm^{-1}; HRMS (ESI) *m/z*, 463.0650 (463.0647 calcd for $C_{22}H_{21}IN_2Na$, $(M + Na)^+$).

(*S*)-2-(2-Iodonaphthalen-1-yl)-4-isopropyl-4,5-dihydro-1*H*-imidazole (17n). The general procedure was followed with the exception that the unpurified chloroalkylimidoyl chloride was suspended in a saturated solution of NH_3 in $CHCl_3$ (15 mL) at rt. The crude residue was purified by column chromatography (silica gel, 6:3:1 hexane/Et_2O/Et_3N) to afford **17n** (0.379 g, 1.04 mmol, 90%) as a colorless solid: mp 159−163 °C; $[\alpha]_D^{24}$ = −12.8, $[\alpha]_{577}^{24}$ = −13.6, $[\alpha]_{546}^{24}$ = −15.9, $[\alpha]_{435}^{24}$ = −30.4, $[\alpha]_{405}^{24}$ = −36.9, (c = 1.0, CH_2Cl_2); ^1H NMR (500 MHz, $CDCl_3$, 330 K) δ 7.96 (m, 1H), 7.84 (d, J = 8.6, 1 H), 7.87 (m, 1H), 7.55 (d, J = 8.6, 1H), 7.41−7.40 (m, 2H), 4.82 (br s, 1H), 3.97 (m, 2 H), 3.66 (br s, 1H), 2.00−1.99 (m, 1H), 1.10 (d, J = 6.0, 3H), 1.05 (d, J = 6.3, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, 298 K) δ 164.3 (C), 136.0 (C), 135.2, (CH), 132.6 (C), 132.5 (C), 130.4 (CH), 127.9 (CH), 127.5 (CH), 126.8 (CH), 125.8 (CH), 94.8 (C), 33.1 (CH), 29.8 (CH_2), 19.7 (CH_3), 19.1 (CH_3); IR (thin film) 3142, 3064, 2955, 2869, 1610, 1504 cm^{-1}; HRMS (ESI) *m/z*, 365.0511 (365.0515 calcd for $C_{16}H_{18}IN_2$, $(M + H)^+$).

Preparation of (*S*)-2-(2-Iodonaphthalen-1-yl)-4-isopropyl-1-tosyl-4,5-dihydro-1*H*-imidazole (17o). A solution of **17n** (0.150 g, 0.441 mmol) and Et_3N (0.18 mL, 1.3 mmol) in CH_2Cl_2 (2 mL) was cooled to 0 °C. A solution of TsCl (0.100 g, 0.534 mmol) in CH_2Cl_2 (1 mL) was added, and the reaction was allowed to warm to rt. After 16 h, the reaction was diluted with CH_2Cl_2 (25 mL) and washed with saturated aqueous $NaHCO_3$ (2 × 20 mL). The organic layer was separated, dried with anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure to afford **17o** (0.217 g, 0.419 mmol, 95%) as a colorless foam. No purification was necessary. The product was characterized as a 1:1 mixture of atropisomers: ^1H NMR (500 MHz, $CDCl_3$, 298 K) δ 7.87−7.79 (m, 4H), 7.63 (d, J = 8.7, 2H), 7.57−7.54 (m, 2H), 7.50−7.46 (m, 2H), 7.35 (app t, J = 7.6, 2 H), 7.30−7.25 (m, 4H), 7.19−7.14 (m, 1H), 7.08 (app d, J = 8.0, 3H), 4.23−4.09 (m, 4H), 3.89−3.85 (m, 2H), 2.38 (s, 3H), 2.37 (s, 3H), 2.06 (septet, J = 6.7, 1H), 2.02 (septet, J = 6.9, 1H), 1.16 (d, J = 6.7, 3H), 1.16−1.05 (m, 9H); ^{13}C NMR (125 MHz, $CDCl_3$, 298 K) δ 156.1 (C), 156.0 (C), 144.4 (C), 144.3 (C), 135.5 (C), 135.3 (C), 135.2 (CH), 135.2 (CH), 133.8 (C), 133.7 (C), 133.0 (C), 132.8 (C), 132.2 (C), 132.2 (C), 130.9 (CH), 129.5 (CH), 129.5 (CH), 129.1 (CH), 128.3 (CH), 128.2 (CH), 128.1 (CH), 127.8 (CH), 127.7 (CH), 127.2 (CH), 126.52 (CH), 126.49 (CH), 125.6 (CH), 125.5 (CH), 97.6 (C), 97.2 (C), 71.7 (CH), 71.4 (CH), 51.4 (CH_2), 50.9 (CH_2), 33.2 (CH), 33.0 (CH), 21.7 (CH_3), 21.6 (CH_3), 19.7 (CH_3), 19.4 (CH_3), 19.1 (CH_3), 18.9 (CH_3); IR (thin film) 3058, 2959, 2872, 1640, 1360 cm^{-1}; HRMS (ESI) *m/z*, 519.0610 (519.0605 calcd for $C_{23}H_{24}IN_2O_2S$, $(M + H)^+$).

(*S*)-1-(2-(2-Iodonaphthalen-1-yl)-4-isopropyl-4,5-1*H*-imidazol-1-yl)-2,2-dimethylpropan-1-one (17p). Prepared by the procedure used to prepare **17o** using 1.1 equiv of pivaloyl chloride as the electrophile. The crude residue was purified by column chromatography (silica gel, 9:1:1 hexane/Et_2O/Et_3N) to furnish **17p** (0.182 g, 0.406 mmol, 92%) as a yellow foam. The product was characterized as a 1:1 mixture of atropisomers: ^1H NMR (500 MHz, $CDCl_3$, 298 K) δ 7.80−7.77 (m, 4H), 7.75−7.73 (m, 2H), 7.53 (d, J = 8.6, 2H), 7.48−7.46 (m, 2H), 4.33−4.21 (m, 4H), 4.07 (dd, J = 8.6, 5.6, 1H), 3.94 (t, J = 9.4, 1H), 2.14−2.06 (m, 2H), 1.31−1.30 (m, 18H), 1.81 (app t, J = 6.9, 6H), 1.14−1.20 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$, 298 K) δ 174.8 (C), 174.7 (C), 160.8 (C), 160.7 (C), 137.9 (C), 137.7 (C), 135.0 (CH), 134.9 (CH), 132.7 (C), 132.6 (C), 132.5 (C), 132.4 (C), 129.74 (CH), 129.67 (CH), 128.4 (CH), 128.3 (CH), 127.3 (CH), 127.2 (CH), 126.4 (CH), 126.3 (CH), 125.7 (CH), 125.4 (CH), 94.1 (C), 93.5 (C), 73.6 (CH), 73.4 (CH), 50.7 (CH_2), 50.2 (CH_2), 40.4 (C), 33.0 (CH), 32.7 (CH), 27.6 (CH_3), 27.5 (CH_3), 19.7 (CH_3), 19.3 (CH_3), 19.2 (CH_3); IR (thin film) 3056, 2960, 2872, 1668, 1334 cm^{-1}; HRMS (ESI) *m/z*, 449.1089 (449.1092 calcd for $C_{21}H_{26}IN_2O$, $(M + H)^+$).

General Procedure for the Synthesis of (*S*)-PIN-acac Complexes from Imidazolines 17. Preparation of Acetylacetonato{(*S*)-2-[2-(1-isopropyl)-4-isopropyl)-4,5-dihydro-1*H*-imidazyl]-naphthyl-*C*,*N*}palladium(II) (18a). Imidazoline **17a** (0.406 g, 1.00 mmol) and Pd_2dba_3 (0.458 g, 0.500 mmol) were dissolved in toluene (3 mL), and the resulting dark red solution was heated to 120 °C. After 12 h, the reaction mixture was concentrated under reduced pressure to furnish a labile mixture of iodine-bridged palladacycle dimers, as a dark brown residue.

The residue prepared above was dissolved in CH_2Cl_2 (5 mL), and silver acetylacetonate (0.217 g, 1.05 mmol) was added in a single portion. The resulting black suspension was stirred at rt for 4 h, then filtered through a pad of Celite. The filter cake was washed with CH_2Cl_2 (50 mL), and the filtrate was concentrated to afford a yellow residue. The crude product was purified by column chromatography (silica gel, 10:1 hexanes/acetone) to afford palladacycle **18a** (0.339 g, 0.70 mmol, 70%) as a yellow solid: mp 150−152 °C; $[\alpha]_D^{24}$ +22.7, $[\alpha]_{577}^{24}$ +23.1, $[\alpha]_{546}^{24}$ +24.2, $[\alpha]_{435}^{24}$ +25.5, $[\alpha]_{435}^{24}$ +28.1 (c = 0.2, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$, 298 K) δ 7.85 (d, J = 8.4, 2H), 7.77 (d, J = 8.0, 1H), 7.63 (d, J = 8.4, 1H), 7.39 (t, J = 7.4, 1H), 7.30 (t, J = 7.4, 1H), 5.35 (s, 1H), 4.34 (septet, J = 6.6, 1H), 4.12 (ddd, J = 10.5, 8.0, 5.1, 1H), 3.59 (t, J = 10.5, 1H), 3.36 (dd, J = 10.5, 8.0, 1H), 2.50−2.49 (m, 1H), 2.07 (s, 3H), 1.95 (s, 3H), 1.25 (d, J = 6.7, 3H), 1.01 (d, J = 6.7, 3H), 0.95 (d, J = 7.0, 3H), 0.91 (d, J = 7.0, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, 298 K) δ 188.0 (C), 186.1 (C), 176.8 (C), 156.0 (C), 132.0 (C), 129.7 (C), 129.6 (C), 129.1 (CH), 129.0 (CH), 128.8 (CH), 125.7 (CH), 123.6 (CH), 123.5 (CH), 100.3 (CH), 67.5 (CH), 50.5 (CH_2), 43.9 (CH), 30.9 (CH), 29.8 (CH_3), 27.9 (CH_3), 27.7 (CH_3), 21.0 (CH_3), 18.9 (CH_3), 18.7 (CH_3), 15.8 (CH_3); IR (thin film) 3053, 2960, 1572, 1514, 1263 cm^{-1}; HRMS (ESI) *m/z*, 507.1242 (507.1249 calcd for $C_{24}H_{30}N_2O_2PdNa$, $(M + Na)^+$). Anal. Calcd for $C_{24}H_{30}N_2O_2Pd$: C, 59.44; H, 6.24; N, 5.78. Found: C, 59.29; H, 6.22; N, 5.76.

The following compounds were prepared in identical fashion from the corresponding imidazoline.

Acetylacetonato{(*S*)-2-[2-(1-isopropyl)-4-*tert*-butyl-4,5,-dihydro-1*H*-imidazyl]-naphthyl-*C*,*N*}palladium(II) (18b). Following the general procedure, the crude product was purified by column chromatography (silica gel, 10:1 hexanes/acetone) to afford palladacycle **18b** (0.220 g, 0.441 mmol, 68%) as a yellow solid: mp 123−126 °C; $[\alpha]_D^{24}$ −22.6, $[\alpha]_{577}^{24}$ −22.9, $[\alpha]_{546}^{24}$ −24.7, $[\alpha]_{435}^{24}$ −30.1, $[\alpha]_{435}^{24}$ −36.3 (c = 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$, 298 K) δ 7.86 (d, J = 8.4, 1H), 7.81 (d, J = 8.1, 1H), 7.72 (d, J = 8.4, 1H), 7.65 (d, J = 8.1, 1H), 7.41 (dt, J = 6.8, 1.2, 1H), 7.35 (dt, J = 6.8, 1.2, 1H), 5.38 (s, 1H), 4.47 (septet, J = 6.6, 1H), 3.84 (dd, J = 10.6, 3.8, 1H), 3.73 (t, J = 10.6, 1H), 3.49 (dd, J = 10.6, 3.8, 1H), 2.10 (s, 3H), 2.00 (s, 1H), 2.06 (s, 3H), 1.34 (d, J = 6.6, 3H), 1.01 (s, 9H), 0.99 (d, J = 6.6, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, 298 K) δ 187.9 (C), 185.9 (C), 176.5 (C), 153.6 (C), 132.0 (C), 130.2 (C), 129.4 (C), 129.2 (CH), 128.6 (CH), 128.5 (CH), 125.7 (CH), 123.7 (CH), 123.5

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(CH), 100.2 (CH), 69.6 (CH), 49.7 (CH), 45.3 (CH_2), 36.1 (C), 28.0 (CH_3), 27.6 (CH_3), 25.7 (CH_3), 21.1 (CH_3), 18.3 (CH_3); IR (thin film) 3111, 2901, 2780, 1761, 1654, 1031 cm^{-1}; HRMS (ESI) *m/z*, 521.1405 (521.1406 calcd for $C_{25}H_{32}N_2O_2PdNa$, $(M + Na)^+$). Anal. Calcd for $C_{25}H_{32}N_2O_2Pd$: C, 60.18; H, 6.46; N, 5.61. Found: C, 59.98; H, 6.48; N, 5.59.

Acetylacetonato{(*S*)-2-[2-(1-*tert*-butyl)-4-isopropyl-4,5,-dihydro-1*H*-imidazyl]-naphthyl-*C*,*N*}palladium(II) (18f). Following the general procedure, the crude product was purified by column chromatography (silica gel, 9:1 hexanes/acetone) to afford palladacycle **18f** (0.230 g, 0.461 mmol, 68%) as a yellow solid: mp 148−151 °C; $[\alpha]_D^{24}$ +43.7, $[\alpha]_{577}^{24}$ +44.1, $[\alpha]_{546}^{24}$ +44.8, $[\alpha]_{435}^{24}$ +47.5, $[\alpha]_{435}^{24}$ +51.2 (*c* = 0.1, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$, 298 K) δ 8.64 (d, *J* = 8.4, 1H), 7.99 (d, *J* = 8.4, 1H), 7.79 (d, *J* = 8.2, 1H), 7.66 (d, *J* = 8.4, 1H), 7.41 (t, *J* = 8.2, 1H), 7.35 (d, *J* = 8.2, 1H), 5.54 (s, 1H), 4.20 (ddd, *J* = 12.1, 7.4, 4.8, 1H), 3.67 (dd, *J* = 12.7, 7.5, 1H), 3.42 (t, *J* = 12.1, 1H), 2.98−2.96 (m, 1H), 2.12 (s, 3H), 2.04 (s, 3H), 1.35 (s, 9H), 1.01 (d, *J* = 7.1, 3H), 0.89 (d, *J* = 7.1, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, 298 K) δ 188.1 (C), 186.0 (C), 179.7 (C), 154.8 (C), 133.7 (C), 132.0 (C), 131.7 (C), 128.6 (CH), 128.5 (CH), 128.4 (CH), 125.4 (CH), 124.7 (CH), 123.5 (CH), 100.3 (CH), 67.9 (CH), 61.6 (CH_2), 47.4 (C), 28.9 (CH_3), 28.4 (CH), 27.9 (CH_3), 27.7 (CH_3), 19.1 (CH_3), 15.3 (CH_3); IR (thin film) 3051, 2968, 2933, 1729, 1582, 1264 cm^{-1}; HRMS (ESI) *m/z*, 499.1582 (499.1578 calcd for $C_{25}H_{33}N_2O_2Pd$, $(M + H)^+$). Anal. Calcd for $C_{25}H_{32}N_2O_2Pd$: C, 60.18; H, 6.46; N, 5.61. Found: C, 60.09; H, 6.47; N, 5.60.

Acetylacetonato{(*S*)-2-[2-(1-1-adamantyl)-4-*tert*-butyl-4,5,-dihydro-1*H*-imidazyl]-naphthyl-*C*,*N*}palladium(II) (18h). Following the general procedure, the crude product was purified by column chromatography (silica gel, 15:1 hexanes/acetone) to afford palladacycle **18h** (0.186 g, 0.315 mmol, 63%) as a yellow solid. The resulting compound was an inseparable 1:1 mixture of isomers: mp 89−92 °C; ^1H NMR (500 MHz, toluene-d_8, 298 K) δ 9.09 (d, *J* = 8.4, 1H), 8.51 (d, *J* = 8.4, 1H), 8.23 (d, *J* = 8.3, 1H), 8.13 (d, *J* = 8.5, 1H), 7.61 (d, *J* = 8.2, 1H), 7.54 (d, *J* = 8.3, 1H), 7.53 (d, *J* = 8.4, 1H), 7.52 (d, *J* = 8.3, 1H), 7.47 (t, *J* = 7.0, 1H), 7.39−7.36 (m, 2H), 7.20 (m, 1H), 5.24 (s, 1H), 5.21 (s, 1H), 4.01 (dd, *J* = 10.1, 7.0, 1H), 3.95 (t, *J* = 9.3, 1H), 3.86 (dd, *J* = 13.0, 10.3, 1H), 3.77 (dd, *J* = 13.0, 7.0, 1H), 3.51 (app t, *J* = 11.4, 1H), 3.12 (dd, *J* = 11.5, 8.3, 1H), 2.16−2.06 (m, 8H), 1.98−1.95 (m, 2H), 1.94−1.91 (m, 4H), 1.90−1.84 (m, 13H), 1.78−1.74 (m, 2H), 1.73 (s, 1H), 1.67 (s, 3H), 1.60 (s, 3H), 1.00 (s, 9H), 0.99 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$, 298 K) δ 188.1 (C), 188.0 (C), 185.9 (C), 185.7 (C), 177.6 (C), 165.4 (C), 151.5 (C), 147.3 (C), 134.8 (C), 132.4 (C), 131.9 (C), 131.8 (C), 131.7 (C), 129.0 (C), 128.4 (CH), 127.9 (CH), 127.7 (CH), 127.3 (CH), 127.1 (CH), 126.4 (CH), 125.7 (CH), 125.6 (CH), 124.9 (CH), 124.4 (CH), 124.3 (CH), 123.4 (CH), 78.8 (CH), 70.3 (CH), 67.9 (CH_2), 62.5 (CH_2), 53.0 (CH_2), 47.1 (CH_2), 42.3 (CH_2), 40.5 (CH_2), 35.95 (CH_2), 35.90 (CH_2), 34.4 (C), 30.2 (CH_3), 29.81 (CH_3), 29.77 (C), 28.3 (CH), 28.0 (CH), 27.62 (CH), 27.55 (CH), 26.5 (CH_3), 26.2 (CH_3); IR (thin film) 3092, 2898, 1701, 1594, 1234 cm^{-1}; HRMS (ESI) *m/z*, 591.2197 (591.2203 calcd for $C_{32}H_{41}N_2O_2Pd$, $(M + H)^+$). Anal. Calcd for $C_{32}H_{40}N_2O_2Pd$: C, 65.02; H, 6.82; N, 4.74. Found: C, 65.18; H, 6.81; N, 4.73.

Acetylacetonato{(*S*)-2-[2-(1-phenyl)-4-isopropyl-4,5,-dihydro-1*H*-imidazyl]-naphthyl-*C*,*N*}palladium(II) (18i). Following the general procedure, the crude product was purified by column chromatography (silica gel, 9:1 hexanes/acetone) to afford palladacycle **18i** (0.618 g, 1.19 mmol, 72%) as a yellow solid: mp 182−185 °C; $[\alpha]_D^{24}$ +96.6, $[\alpha]_{577}^{24}$ +102.7, $[\alpha]_{546}^{24}$ +109.8, $[\alpha]_{435}^{24}$ +114.3 (*c* = 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$, 298 K) δ 7.91 (d, *J* = 8.4, 1H), 7.65−7.62 (m, 2H), 7.35 (d, *J* = 8.6, 1H), 7.11−7.07 (m, 3H), 6.98 (t, *J* = 7.4, 1H), 6.87 (d, *J* = 7.4, 2H), 6.82 (t, *J* = 7.4, 1H), 5.39 (s, 1H), 4.28−4.22 (m, 2H), 3.92 (app d, *J* = 5.9, 1H), 2.63−2.59 (m, 1H), 2.10 (s, 3H), 1.98 (s, 3H), 0.92 (d, *J* = 7.1, 3H), 0.84 (d, *J* = 7.1, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, 298 K) δ 188.0 (C), 186.4 (C), 172.4 (C), 157.9 (C), 144.7 (C), 132.0 (C), 130.0 (CH), 129.5 (C), 129.2 (CH), 128.9 (C), 128.7 (CH), 128.6 (CH), 125.1 (CH), 124.6 (CH), 124.2 (CH), 123.3 (CH), 122.8 (CH), 100.4 (CH), 66.3 (CH), 55.0 (CH_2), 29.3 (CH), 27.9 (CH_3), 27.8 $(CH)_3$, 18.9 (CH_3), 15.3 (CH_3); IR (thin film) 3434, 3053, 2960, 1572, 1514, 1263 cm^{-1}; HRMS (ESI) *m/z*, 541.1080 (541.1083 calcd for $C_{27}H_{28}N_2O_2PdNa$, $(M + Na)^+$). Anal. Calcd for $C_{27}H_{28}N_2O_2Pd$: C, 62.49; H, 5.44; N, 5.40. Found: C, 62.33; H, 5.42; N, 5.42.

Acetylacetonato{(*S*)-2-[2-(1-tosyl)-4-isopropyl-4,5,-dihydro-1*H*-imidazyl]-naphthyl-*C*,*N*}palladium(II) (18o). Following the general procedure, the crude product was purified by column chromatography (silica gel, 5:1 hexanes/acetone) to afford palladacycle **18o** (0.184 g, 0.309 mmol, 64%) as a orange solid: mp 162−166 °C; $[\alpha]_D^{24}$ +41.2, $[\alpha]_{577}^{24}$ +43.4, $[\alpha]_{546}^{24}$ +56.7, $[\alpha]_{435}^{24}$ +64.3 (*c* = 1.1, CH_2Cl_2); ^1H NMR (500 MHz, $CDCl_3$, 298 K) δ 8.62 (d, *J* = 8.5, 1H), 7.88 (d, *J* = 8.4, 1H), 7.76 (d, *J* = 8.1, 1H), 7.74 (d, *J* = 8.4, 3H), 7.47 (t, *J* = 8.1, 1H), 7.39−7.36 (m, 3H), 5.40 (s, 1H), 3.95 (dd, *J* = 12.6, 7.7, 1H), 3.18−3.13 (m, 1H), 2.50−2.47 (m, 1H), 2.15 (s, 3H), 2.08 (s, 3H), 1.92 (s, 3H), 0.78 (d, *J* = 6.8, 6H); ^{13}C NMR (125 MHz, $CDCl_3$, 298 K) δ 188.1 (C), 186.2 (C), 171.6 (C), 158.2 (C), 145.6 (C), 133.1 (C), 132.2 (C), 131.8 (C), 131.0 (CH), 130.0 (C), 128.6 (CH), 128.5 (CH), 127.8 (CH), 125.8 (CH), 125.6 (CH), 124.3 (CH), 100.4 (CH), 67.1 (CH), 49.0 (CH_2), 28.8 (CH_3), 27.7 (CH), 27.6 (CH_3), 21.9 (CH_3), 18.7 (CH_3), 14.8 (CH_3); IR (thin film) 3061, 2944, 1642, 1579, 1241 cm^{-1}; HRMS (ESI) *m/z*, 619.0857 (619.0859 calcd for $C_{28}H_{30}N_2O_4PdSNa$, $(M + Na)^+$). Anal. Calcd for $C_{28}H_{30}N_2O_4PdS$: C, 56.33; H, 5.06; N, 4.69. Found: C, 56.55; H, 5.04; N, 4.68.

Acetylacetonato{(*S*)-2-[2-(1-pivoloyl)-4-isopropyl-4,5,-dihydro-1*H*-imidazyl]-naphthyl-*C*,*N*}palladium(II) (18p). Following the general procedure, the crude product was purified by column chromatography (silica gel, 19:1→5:1 hexanes/acetone) to afford palladacycle **18p** (0.147 g, 0.279 mmol, 50%) as a yellow solid: mp 131−136 °C (decomp); $[\alpha]_D^{24}$ +111.2, $[\alpha]_{577}^{24}$ +112.4, $[\alpha]_{546}^{24}$ +115.2, $[\alpha]_{435}^{24}$ +118.8 (*c* = 1.5, CH_2Cl_2); ^1H NMR (500 MHz, $CDCl_3$, 298 K) δ 7.90 (d, *J* = 8.3, 1H), 7.81 (br s, 1H), 7.74 (d, *J* = 8.4, 1H), 7.61 (d, *J* = 4.3, 1H), 7.34−7.28 (m, 2H), 5.41 (s, 1H), 4.14 (br s, 1H), 4.08−4.06 (m, 2H), 2.29 (br s, 1H), 2.12 (s, 3H), 2.00 (s, 3H), 1.44 (s, 9H), 1.04 (d, *J* = 6.7, 3H), 0.83 (d, *J* = 5.2, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, 298 K) δ 187.9 (C), 186.4 (C), 180.3 (C), 173.7 (C), 131.9 (C), 130.1 (C), 130.0 (CH), 129.8 (C), 129.0 (CH), 128.8 (C), 128.2 (CH), 125.4 (CH), 123.5 (CH), 100.3 (CH), 47.8 (CH), 40.8 (CH_2), 28.7 (C), 28.2 (CH_3), 27.8 (CH_3), 27.7 (CH_3), 25.4 (CH), 19.6 (CH_3), 15.1 (CH_3); IR (thin film) 3072, 2955, 1729, 1629, 1252 cm^{-1}; HRMS (ESI) *m/z*, 549.1352 (549.1345 calcd for $C_{26}H_{32}N_2O_3PdNa$, $(M + Na)^+$). Anal. Calcd for $C_{26}H_{32}N_2O_3Pd$: C, 59.26; H, 6.12; N, 5.32. Found: C, 59.33; H, 6.14; N, 5.31.

General Procedure for the Synthesis of (*S*)-PIN-acac Complexes Directly from Amide 16. Preparation of Acetylacetonato{(*S*)-2-[2-(1-benzyl)-4-isopropyl-4,5,-dihydro-1*H*-imidazyl]-naphthyl-*C*,*N*}palladium(II) (18c). Amide **16a** (0.350 g, 0.913 mmol) was dissolved in freshly distilled $SOCl_2$ (0.33 mL, 4.6 mmol), and the resulting solution was heated to 85 °C. After 5 h, the reaction was diluted with toluene (15 mL) and concentrated under reduced pressure to afford the crude chloroalkylimidoyl chloride. The residue was dissolved in CH_2Cl_2 (2 mL) and treated with a solution of benzylamine (0.11 mL, 1.0 mmol) and Et_3N (0.38 mL, 2.7 mmol) in CH_2Cl_2 (2 mL). The reaction was maintained at rt for 6 h and then stirred with 2 M NaOH (10 mL) for 20 min. The organic layer was separated and flushed through a small pad of silica gel. The filter cake was washed with 1:1 Et_2O/hexane (50 mL), and the combined organics were concentrated under reduced pressure to afford the corresponding imidazoline as an orange foam of sufficient purity to be used in the next step.

The imidazoline ligand prepared above was dissolved in toluene (2 mL), and Pd_2dba_3 (0.418 g, 0.457 mmol) was added in a single portion. The resulting red solution was heated to 120 °C. After 16 h, the reaction was concentrated under reduced pressure. The resulting solid was immediately dissolved in CH_2Cl_2 (4 mL), and silver acetylacetonate (0.207 g, 1.00 mmol) was added in a single portion. The resulting black suspension was stirred at rt overnight then filtered through a pad of Celite. The filter cake was washed with CH_2Cl_2 (50 mL), and the filtrate was concentrated to afford a yellow residue. The crude product was purified by column chromatography (silica gel, 10:1

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hexanes/acetone) to afford palladacycle **18c** (0.258 g, 0.484 mmol, 53%) as a yellow solid: mp 122−128 °C (decomp); $[\alpha]_D^{24}$ −110.3, $[\alpha]_{577}^{24}$ −110.9, $[\alpha]_{546}^{24}$ −112.7, $[\alpha]_{435}^{24}$ −114.4, $[\alpha]_{435}^{24}$ −118.6 (c = 1.2, CH_2Cl_2); ^{1}H NMR (500 MHz, toluene-d_8, 298 K) δ 8.20 (d, J = 8.4, 1H), 7.89 (d, J = 8.1, 1H), 7.56 (d, J = 7.8, 1H), 7.51 (d, J = 8.4, 1H), 7.11−7.08 (m, 5H), 7.07−7.01 (m, 2H), 5.24 (s, 1H), 4.39 (d, J = 16.3, 1H), 4.11 (d, J = 16.3, 1H), 4.02−4.00 (m, 1H), 3.22−3.19 (m, 1H), 3.09 (t, J = 10.8, 1H), 2.54−2.51 (m, 1H), 1.92 (s, 3H), 1.84 (s, 3H), 0.88 (d, J = 6.8, 3H), 0.83 (d, J = 7.0, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, 298 K) δ 188.0 (C), 186.2 (C), 177.0 (C), 157.0 (C), 136.9 (C), 132.0 (C), 129.6 (C), 129.3 (CH), 129.2 (CH), 129.0 (CH), 128.9 (CH), 127.6 (CH), 127.1 (CH), 125.9 (CH), 123.6 (CH), 100.3 (CH), 67.1 (CH), 56.5 (CH_2), 52.2 (CH_2), 30.4 (CH), 27.9 (CH_3), 27.7 (CH_3), 18.7 (CH_3), 15.8 (CH_3); IR (thin film) 3072, 3019, 2951, 1668, 1592, 1255 cm^{-1}; HRMS (ESI) m/z, 555.1236 (555.1251 calcd for $C_{28}H_{30}N_2O_2PdNa$, $(M + Na)^+$). Anal. Calcd for $C_{28}H_{30}N_2O_2Pd$: C, 63.10; H, 5.67; N, 5.26. Found: C, 62.90; H, 5.68; N, 5.27.

The following compounds were prepared in identical fashion from amides **16a** or **16b** without purification of the intermediate imidazoline.

Acetylacetonato{(*S*)-2-[2-(1-benzhydryl)-4-isopropyl-4,5,-dihydro-1*H*-imidazyl]-naphthyl-*C*,*N*}palladium(II) (18d). Following the general procedure, the crude product was purified by column chromatography (silica gel, 12:1 hexanes/acetone) to afford palladacycle **18d** (0.195 g, 0.320 mmol, 62%) as a yellow solid: mp 197−201 °C; $[\alpha]_D^{24}$ +12.7, $[\alpha]_{577}^{24}$ +12.9, $[\alpha]_{546}^{24}$ +14.1, $[\alpha]_{435}^{24}$ +18.6, $[\alpha]_{435}^{24}$ +19.9 (c = 1.3, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ 8.02 (d, J = 8.3, 1H), 7.84 (d, J = 8.1, 1H), 7.81 (d, J = 8.6, 1H), 7.77 (d, J = 8.4, 1H), 7.52−7.49 (m, 2H), 7.45 (d, J = 7.1, 1H), 7.37−7.32 (m, 4H), 7.26 (t, J = 8.1, 1H), 7.03−7.01 (m, 2H), 6.97 (t, J = 7.1, 1H), 6.61 (s, 1H), 5.44 (s, 1H), 3.85−3.81 (m, 1H), 3.65 (dd, J = 10.5, 7.9, 1H), 3.84 (t, J = 10.5, 1H), 2.59−2.55 (m, 1H), 2.18 (s, 3H), 2.00 (s, 3H), 0.93−0.89 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$, 298 K) δ 188.1 (C), 186.1 (C), 176.8 (C), 156.9 (C), 139.1 (C), 138.9 (C), 131.9 (C), 129.8 (C), 129.5 (CH), 129.4 (C), 129.1 (CH), 128.8 (CH), 128.7 (CH), 128.6 (CH), 128.3 (CH), 128.0 (CH), 127.5 (CH), 125.8 (CH), 124.0 (CH), 123.7 (CH), 100.3 (CH), 67.6 (CH), 67.2 (CH), 46.4 (CH_2), 30.0 (CH), 27.9 (CH_3), 27.7 (CH_3), 18.7 (CH_3), 15.5 (CH_3); IR (thin film) 3058, 3029, 2960, 1768, 1582, 1264 cm^{-1}; HRMS (ESI) m/z, 609.1740 (609.1733 calcd for $C_{34}H_{35}N_2O_2Pd$, $(M + H)^+$). Anal. Calcd for $C_{34}H_{34}N_2O_2Pd$: C, 67.05; H, 5.63; N, 4.60. Found: C, 66.89; H, 5.64; N, 4.59.

Acetylacetonato{(*S*)-2-[2-(1-cyclohexyl)-4-isopropyl-4,5,-dihydro-1*H*-imidazyl]-naphthyl-*C*,*N*}palladium(II) (18e). Following the general procedure, the crude product was purified by column chromatography (silica gel, 15:1 hexanes/acetone) to afford palladacycle **18e** (0.134 g, 0.255 mmol, 57%) as a orange solid: mp 187−190 °C; $[\alpha]_D^{24}$ −71.7, $[\alpha]_{577}^{24}$ −72.9, $[\alpha]_{546}^{24}$ −74.1, $[\alpha]_{435}^{24}$ −78.6, $[\alpha]_{435}^{24}$ −82.4 (c = 1.5, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ 7.89 (d, J = 8.5, 1H), 7.85 (d, J = 8.5, 1H), 7.80 (d, J = 7.7, 1H), 7.64 (d, J = 8.3, 1H), 7.40 (dt, J = 6.8, 1.3, 1H), 7.33 (dt, J = 6.9, 1.1, 1H), 5.37 (s, 1H), 4.13 (ddd, J = 8.0, 4.5, 1.3, 1H), 3.96−3.90 (m, 1H), 3.67 (t, J = 10.6, 1H), 3.42 (dd, J = 10.6, 8.0, 1H), 2.57−2.51 (m, 1H), 2.09 (s, 3H), 1.98 (s, 3H), 1.85−1.80 (m, 1H), 1.66−1.63 (m, 1H), 1.56−1.47 (m, 5H), 1.23−1.14 (m, 2H), 0.97 (d, J = 7.0, 3H), 0.93 (d, J = 6.8, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, 298 K) δ 187.9 (C), 186.1 (C), 176.5 (C), 155.9 (C), 132.1 (C), 129.8 (C), 129.6 (C), 129.1 (CH), 128.9 (CH), 128.8 (CH), 125.5 (CH), 123.6 (CH), 123.5 (CH), 100.2 (CH), 67.6 (CH), 58.7 (CH), 45.2 (CH_2), 31.9 (CH_2), 30.8 (CH), 29.5 (CH_2), 27.9 (CH_3), 27.7 (CH_3), 25.9 (CH_2), 25.4 (CH_2), 25.3 (CH_2), 18.7 (CH_3), 15.8 (CH_3); IR (thin film) 3045, 2950, 1718, 1612, 1258 cm^{-1}; HRMS (ESI) m/z, 547.1568 (547.1564 calcd for $C_{27}H_{34}N_2O_2PdNa$, $(M + Na)^+$). Anal. Calcd for $C_{27}H_{34}N_2O_2Pd$: C, 61.77; H, 6.53; N, 5.34. Found: C, 61.84; H, 6.54; N, 5.33.

Acetylacetonato{(*S*)-2-[2-(1-*tert*-butyl)-4-*tert*-butyl-4,5,-dihydro-1*H*-imidazyl]-naphthyl-*C*,*N*}palladium(II) (18g). Following the general procedure, the crude product was purified by column chromatography (silica gel, 10:1 hexanes/acetone) to afford palladacycle **18g** (72 mg, 0.14 mmol, 41%) as a yellow film: mp 123−126 °C; $[\alpha]_D^{24}$ −82.4, $[\alpha]_{577}^{24}$ −83.3, $[\alpha]_{546}^{24}$ −85.1, $[\alpha]_{435}^{24}$ −89.6 (c = 0.5, CH_2Cl_2); ^{1}H NMR (500 MHz, toluene-d_8, 298 K) δ 8.36 (d, J = 8.4, 1H), 8.23 (d, J = 8.4, 1H), 7.53 (d, J = 8.4, 1H), 7.47 (d, J = 8.4, 1H), 7.18 (t, J = 7.0, 1H), 7.10 (t, J = 7.0, 1H), 5.24 (s, 1H), 3.91 (dd, J = 9.6, 7.8, 1H), 3.28 (dd, J = 11.4, 9.6, 1H), 3.15 (dd, J = 11.4, 7.8, 1H), 1.92 (s, 3H), 1.87 (s, 3H), 0.97 (s, 9H), 0.95 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$, 298 K) δ 188.0 (C), 185.7 (C), 177.8 (C), 151.5 (C), 134.3 (C), 131.8 (C), 131.6 (C), 128.5 (CH), 127.9 (CH), 127.7 (CH), 125.6 (CH), 124.5 (CH), 123.4 (CH), 100.2 (CH), 70.0 (CH), 61.1 (C), 49.1 (CH_2), 35.8 (C), 29.8 (CH_3), 28.9 (CH_3), 27.5 (CH_3), 26.0 (CH_3); IR (thin film) 3101, 2979, 1690, 1584 cm^{-1}; HRMS (ESI) m/z, 535.1549 (535.1553 calcd for $C_{26}H_{34}N_2O_2PdNa$, $(M + Na)^+$). Anal. Calcd for $C_{26}H_{34}N_2O_2Pd$: C, 60.88; H, 6.68; N, 5.46. Found: C, 60.84; H, 6.70; N, 5.45.

Acetylacetonato{(*S*)-2-[2-(1-phenyl)-4-*tert*-butyl-4,5,-dihydro-1*H*-imidazyl]-naphthyl-*C*,*N*}palladium(II) (18j). Following the general procedure, the crude product was purified by column chromatography (silica gel, 10:1 hexanes/acetone) to afford palladacycle **18j** (0.119 g, 0.223 mmol, 52%) as a yellow film: mp 98−101 °C (decomp); $[\alpha]_D^{24}$ −8.4, $[\alpha]_{577}^{24}$ −8.9, $[\alpha]_{546}^{24}$ −10.7, $[\alpha]_{435}^{24}$ −15.3, $[\alpha]_{405}^{24}$ −17.7 (c = 1.9, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ 7.92 (d, J = 8.3, 1H), 7.65 (t, J = 8.8, 2H), 7.30 (d, J = 8.3, 1H), 7.11−7.09 (m, 3H), 7.04 (t, J = 8.1, 2H), 7.02 (br s, 1H), 6.84 (t, J = 6.84, 1H), 5.41 (s, 1H), 4.31 (dd, J = 10.1, 3.0, 1H), 4.04 (dd, J = 10.6, 3.0, 1H), 3.92 (t, J = 10.1, 1H), 2.13 (s, 3H), 2.01 (s, 3H), 1.10 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$, 298 K) δ 187.9 (C), 186.1 (C), 173.4 (C), 156.2 (C), 144.4 (C), 131.9 (C), 129.8 (C), 129.5 (CH), 129.3 (C), 128.7 (CH), 128.6 (CH), 128.4 (CH), 125.5 (CH), 125.0 (CH), 124.4 (CH), 123.9 (CH), 123.3 (CH), 100.3 (CH), 69.1 (CH), 57.5 (CH_2), 36.1 (C), 28.0 (CH_3), 27.7 (CH_3), 26.0 (CH_3); IR (thin film) 3444, 3063, 2961, 1562, 1513, 1260 cm^{-1}; HRMS (ESI) m/z, 533.1423 (533.1420 calcd for $C_{28}H_{31}N_2O_2Pd$, $(M + H)^+$). Anal. Calcd for $C_{28}H_{30}N_2O_2Pd$: C, 63.10; H, 5.67; N, 5.26. Found: C, 63.19; H, 5.68; N, 5.26.

Acetylacetonato{(*S*)-2-[2-(1-(4-methoxyphenyl))-4-isopropyl-4,5,-dihydro-1*H*-imidazyl]-naphthyl-*C*,*N*}palladium(II) (18k). Following the general procedure, the crude product was purified by column chromatography (silica gel, 5:1 toluene/CH_2Cl_2) to afford palladacycle **18k** (51 mg, 0.09 mmol, 54%) as a yellow film: $[\alpha]_D^{24}$ +34.4, $[\alpha]_{577}^{24}$ +35.1, $[\alpha]_{546}^{24}$ +35.9, $[\alpha]_{435}^{24}$ +42.3, $[\alpha]_{405}^{24}$ +45.1 (c = 0.9, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ 7.92 (d, J = 8.4, 1H), 7.66 (t, J = 8.6, 2H), 7.42 (d, J = 8.8, 1H), 7.11 (t, J = 7.4, 1H), 6.90−6.85 (m, 3H), 6.66 (d, J = 8.8, 1H), 5.41 (s, 1H), 4.24−4.20 (m, 2H), 3.89 (dd, J = 9.5, 4.2, 1H), 3.70 (s, 3H), 2.66−2.58 (m, 1H), 2.13 (s, 3H), 2.00 (s, 3H), 0.95 (d, J = 7.0, 3H), 0.90 (d, J = 7.0, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, 298 K) δ 188.0 (C), 186.3 (C), 172.7 (C), 157.7 (C), 156.7 (C), 138.1 (C), 131.9 (C), 129.8 (CH), 129.5 (C), 129.0 (C), 128.8 (CH), 128.7 (CH), 128.5 (CH), 128.5 (CH), 125.1 (CH), 124.3 (CH), 124.2 (CH), 123.3 (CH), 114.4 (CH), 100.3 (CH), 66.3 (CH), 55.5 (CH_3), 29.5 (CH_2), 27.9 (CH_3), 27.8 (CH_3), 18.9 (CH_3), 15.4 (CH_3); IR (thin film) 3092, 2958, 1662, 1510, 1248 cm^{-1}; HRMS (ESI) m/z, 549.1376 (549.1370 calcd for $C_{28}H_{31}N_2O_3Pd$, $(M + H)^+$). Anal. Calcd for $C_{28}H_{30}N_2O_3Pd$: C, 61.26; H, 5.51; N, 5.10. Found: C, 61.21; H, 5.49; N, 5.10.

Acetylacetonato{(*S*)-2-[2-(1-(3,4,5-trifluorophenyl))-4-isopropyl-4,5,-dihydro-1*H*-imidazyl]-naphthyl-*C*,*N*}palladium(II) (18l). Following the general procedure, the crude product was purified by column chromatography (silica gel, 8:1 toluene/CH_2Cl_2) to afford palladacycle **18l** (0.107 g, 0.187 mmol, 58%) as a colorless solid: mp 210−214 °C; $[\alpha]_D^{24}$ +68.4, $[\alpha]_{577}^{24}$ +69.1, $[\alpha]_{546}^{24}$ +71.3, $[\alpha]_{435}^{24}$ +78.9, $[\alpha]_{405}^{24}$ +83.2 (c = 1.5, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ 7.94 (d, J = 8.4, 1H), 7.73 (d, J = 8.3, 1H), 7.70 (d, J = 8.4, 1H), 7.35 (d, J = 8.6, 1H), 7.21 (t, J = 7.6, 1H), 7.03 (t, J = 8.0, 1H), 6.55−6.52 (m, 2H), 5.42 (s, 1H), 4.31−4.28 (m, 1H), 4.23 (t, J = 10.8, 1H), 3.87 (dd, J = 9.6, 4.3, 1H), 2.69−2.64 (m, 1H), 2.14 (s, 3H), 2.01 (s, 3H), 0.96 (d, J = 7.0, 3H), 0.84 (d, J = 6.8, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, 298 K) δ 188.1 (C), 186.4 (C), 171.5 (C), 158.9 (C), 151.2 (d, J = 249 Hz, C), 140.3 (app s, C), 136.8 (d, J = 248 Hz, C), 132.1 (C), 130.6 (CH), 129.2 (CH), 128.8 (C), 128.7 (CH), 128.4

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(C), 125.8 (CH), 123.7 (CH), 123.4 (CH), 107.2 (CH), 107.0 (CH), 100.5 (CH), 66.5 (CH), 55.0 (CH_2), 29.0 (CH), 27.9 (CH_3), 27.7 (CH_3), 19.0 (CH_3), 15.2 (CH_3); IR (thin film) 3071, 2955, 1622, 1533, 1241 cm^{-1}; HRMS (ESI) *m*/*z*, 595.0801 (595.0811 calcd for $C_{27}H_{25}F_3N_2O_2PdNa$, $(M + Na)^+$). Anal. Calcd for $C_{27}H_{25}F_3N_2O_2Pd$: C, 56.60; H, 4.40; N, 4.89. Found: C, 56.71; H, 4.41; N, 4.88.

Acetylacetonato{(*S*)-2-[2-(1-mesityl)-4-isopropyl-4,5,-dihydro-1*H*-imidazyl]-naphthyl-*C*,*N*}palladium(II) (18m). Following the general procedure, the crude product was purified by column chromatography (silica gel, 10:1 hexanes/acetone) to afford palladacycle **18m** (0.190 g, 0.339 mmol, 65%) as a yellow solid: mp 134−139 °C; $[\alpha]_D^{24}$ +32.6, $[\alpha]_{577}^{24}$ +32.9, $[\alpha]_{546}^{24}$ +33.7, $[\alpha]_{435}^{23}$ +38.9 (*c* = 0.1, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$, 298 K) δ 7.88 (d, *J* = 8.4, 1H), 7.59 (d, *J* = 8.1, 1H), 7.57 (d, *J* = 8.4, 1H), 7.05−7.02 (m, 2H), 6.94 (s, 1H), 6.74 (t, *J* = 8.1, 1H), 6.54 (s, 1H), 5.38 (s, 1H), 4.28 (dt, *J* = 10.4, 5.5, 1H), 3.95 (dd, *J* = 10.4, 5.7, 1H), 3.63 (t, *J* = 10.4, 1H), 2.54−2.48 (m, 1H), 2.44 (s, 3H), 2.17 (s, 3H), 2.09 (s, 3H), 1.98 (s, 3H), 1.79 (s, 3H), 1.03 (d, *J* = 6.8, 3H), 1.00 (d, *J* = 6.8, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, 298 K) δ 188.1 (C), 186.3 (C), 174.8 (C), 138.7 (C), 137.4 (C), 135.40 (C), 135.36 (C), 131.8 (C), 130.8 (C), 130.4 (CH), 129.6 (CH), 129.4 (CH), 128.73 (C), 128.70 (CH), 128.4 (CH), 124.2 (CH), 123.3 (CH), 123.1 (CH), 100.4 (C), 66.2 (CH), 54.4 (CH_2), 30.9 (CH), 28.0 (CH_3), 27.8 (CH_3), 20.9 (CH_3), 18.9 (CH_3), 18.7 (CH_3), 18.3 (CH_3), 15.9 (CH_3); IR (thin film) 2958, 2920, 1584, 1398, 1264 cm^{-1}; HRMS (ESI) *m*/*z*, 583.1560 (583.1564 calcd for $C_{30}H_{34}N_2O_2PdNa$, $(M + Na)^+$). Anal. Calcd for $C_{30}H_{34}N_2O_2Pd$: C, 64.23; H, 6.11; N, 4.99. Found: C, 64.30; H, 6.13; N, 4.98.

General Procedure for the PIN-Catalyzed Synthesis of Enantiomerically Enriched 3-Acyloxy-1-alkenes. Preparation of 3-Acetoxy-5-phenyl-1-pentene (24). Palladacycle **18a** (0.9 mg, 0.02 mmol, 3 mol %) was added in a single portion to a solution of allylic trichloroacetimidate **23** (0.200 g, 0.652 mmol), acetic acid (0.11 mL, 2.0 mmol), in CH_2Cl_2 (0.65 mL). The reaction was sealed under an inert atmosphere (N_2 or Ar) and maintained at rt. After 18 h, the reaction mixture was concentrated under reduced pressure and purified by chromatography (silica gel, 95:5 pentane/Et_2O) to afford allylic acetate **24** (0.126 g, 0.619 mmol, 95%) as a colorless oil. Enantiomeric excess was determined by GC using a chiral stationary phase [*T* = 130 °C, hold 40 min; ramp 5 to 180 °C, hold 40 min; *S* (minor) enantiomer t_R = 28.12 min, *R* (major) enantiomer t_R = 30.09 min; 28% ee]. Spectral data was identical in all respects to previously reported values.[8c]

Preparation of 2-Iodo-1-naphthoic Acid (15).[17,18] A solution of *n*-BuLi (2.5 M, hexane, 34.5 mL) was added dropwise over 1 h to a solution of 2,2,6,6-tetramethylpiperidine (12.20 g, 86.35 mmol) in THF (300 mL) maintained at 0 °C. After 30 min, the reaction mixture was cooled to −78 °C, and a solution of 1-cyanonaphthalene (**14**, 12.57 g, 82.03 mmol) in THF (25 mL) was added dropwise over 30 min. The resulting dark solution was maintained at −78 °C for 2 h. A solution of I_2 (21.92 g, 86.35 mmol) in THF (250 mL) was added dropwise via addition funnel over 2 h. The reaction mixture was maintained at −78 °C for 2 h and then allowed warm to rt overnight. The reaction mixture was quenched with H_2O (400 mL), and the resulting mixture was extracted with EtOAc (2 × 250 mL). The combined organics were washed successively with saturated aqueous $Na_2S_2O_3$ (3 × 300 mL), 1 M HCl (3 × 300 mL), and brine (1 × 300 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude residue was recrystallized from $CHCl_3$/heptane to afford 2-iodo-1-cyanonaphthalene (21.45 g, 76.85 mmol, 89%) as a tan solid. Spectral data was identical in all respects to previously reported values.[17]

2-Iodo-1-cyanonaphthalene (5.00 g, 17.9 mmol) was suspended in a solution of water (60 mL) and glacial acetic acid (120 mL). The suspension was cooled to 0 °C, and concentrated H_2SO_4 (100 mL) was slowly added dropwise such that the internal temperature was maintained between 45−50 °C. The resulting brown solution was heated to 120 °C. After 16 h, the reaction mixture was cooled to rt and poured into ice water (300 mL). The resulting slurry was extracted with EtOAc (3 × 100 mL), and the combined organic extracts were washed with 3 M NaOH (3 × 150 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated under reduced pressure to afford a brown paste. The residue was digested in toluene (300 mL) and concentrated under reduced pressure to remove residual AcOH and water. This process was repeated (1−3 times) until a light brown solid formed. The crude solid was recrystallized from MeCN to afford 2-iodonaphthalene-1-carboxamide (5.05 g, 17.0 mmol, 95%) as a tan solid in sufficient purity to be used in the next step. This solid (5.05 g, 17.0 mmol) was dissolved in MeCN (10.0 mL) with external heating. A chilled solution of aqueous H_2SO_4 (70% (w/w), 100 mL) was added, and the resulting solution was maintained at rt. $NaNO_2$ (11.7 g, 170 mmol) was added to the reaction mixture in five equal portions over 1 h. Gas evolution and a color change to red-brown were accompanied by the formation of a precipitate. The resulting suspension was protected from light and stirred at rt. After 16 h, the mixture was diluted with water (100 mL) and extracted with CH_2Cl_2 (3 × 100 mL). The combined organic extracts were washed with 2 M NaOH (3 × 100 mL). The pH of the combined aqueous extracts was adjusted to ∼3 with 2 M HCl. The resulting cloudy suspension was extracted with CH_2Cl_2 (3 × 50 mL). The combined organics were dried over Na_2SO_4, filtered, and concentrated under reduced pressure to afford **15** (3.90 g, 13.1 mmol, 77%) as a tan solid. Spectral data was identical in all respects to previously reported values.[18]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

VT-NMR experiments for PIN complexes **18a** and **18i**, details of computational studies, X-ray data for **18a**, **18b**, and **18i**, ^1H and ^{13}C NMR data for new compounds, and copies of enantioselective GC traces used to determine enantiomeric purity (77 pages). 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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