Chapter 2

Unusual Allylpalladium Carboxylate Complexes: Identification of the Resting State of Catalytic Enantioselective Decarboxylative Allylic Alkylation Reactions of Ketones

2.1 Introduction

Our previous mechanistic investigations into the palladium-catalyzed decarboxylative asymmetric allylic alkylation of ketones enolates focused primarily on DFT simulation and product analysis under various conditions.[1] While these studies proved to be significantly informative, they did not create a complete mechanistic picture that could explain all of the experimentally observed results.[2] To this effect we sought to gain further experimental insight into this chemistry by studying the active catalytic reactions by NMR.

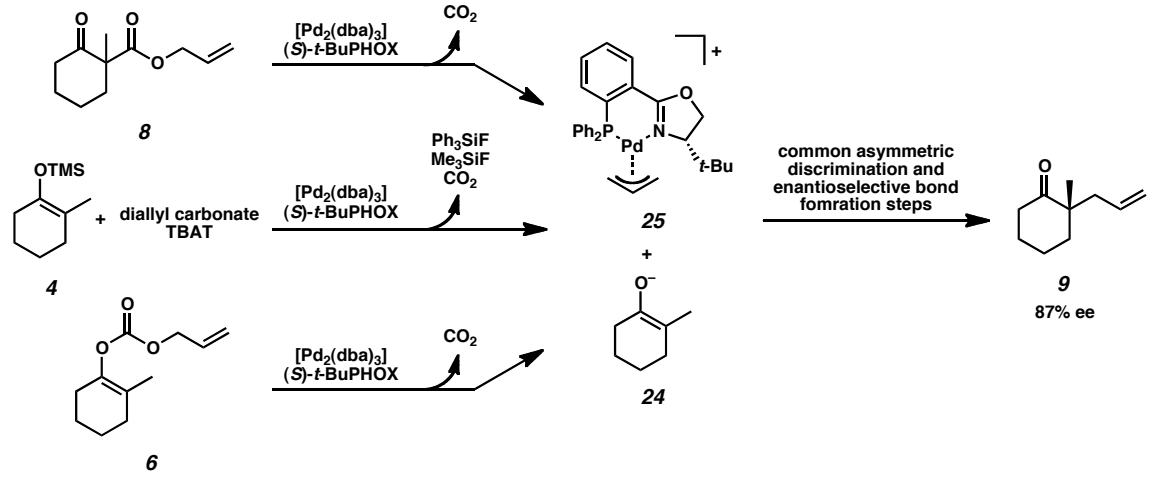
2.2 Observing the Reaction by ^{31}P NMR

2.2.1 ^{31}P NMR Studies of Allyl Enol Carbonates and Allyl β-Keto Ester Reactions

The phosphorous atom found in the PHOX ligand makes the allylic alkylation reaction a natural candidate for monitoring by ^{31}P NMR. As all three substrate classes are understood to have a common underlying mechanism,[2] species visible by ^{31}P NMR across

all three variants of the reaction represent potential key intermediates for this transformation (Scheme 2.1 on page 24). To this effect, the reactions of allyl enol carbonate **6**, allyl β-ketoester **8**, and silyl enol ether **4** were monitored and compared by ^{31}P NMR.

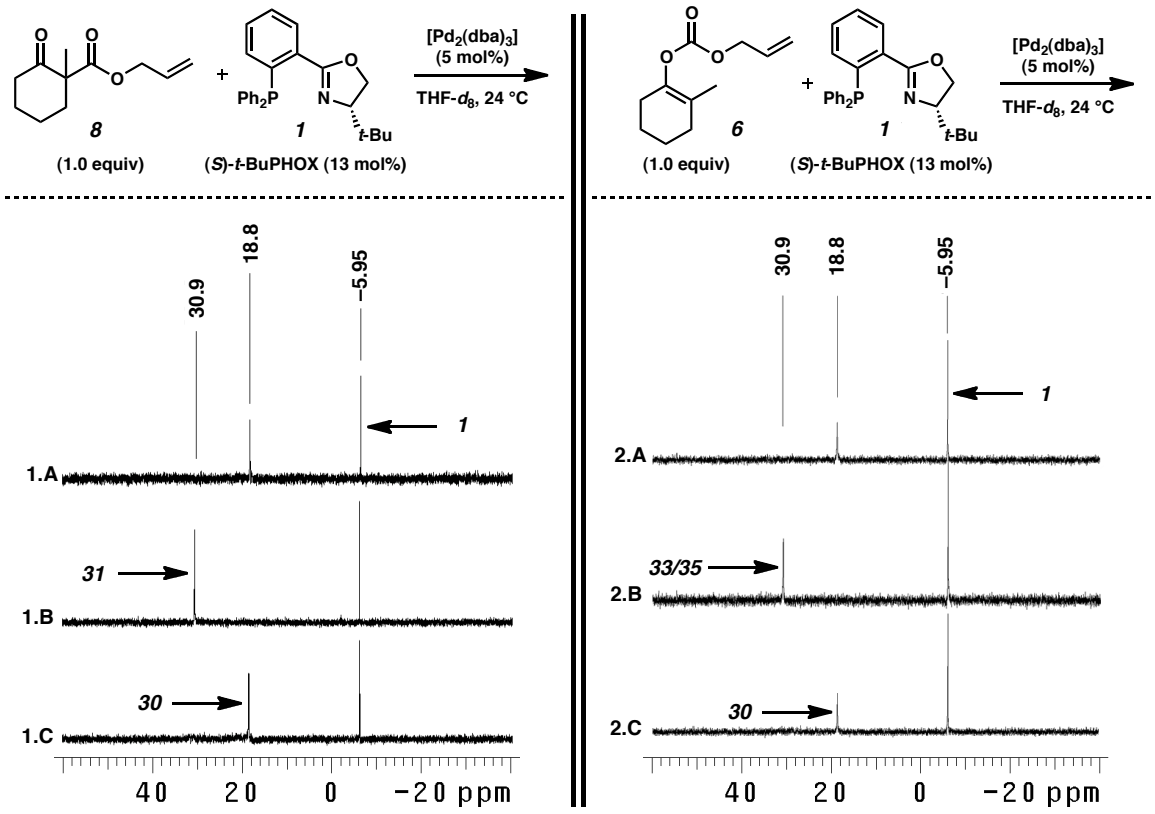
Scheme 2.1. Asymmetric and Bond-Forming Events Are Understood to be Common to All Three Substrate Classes.



Reactions of allyl enol carbonate **6** and allyl β-ketoester **8** appear nearly identical by ^{31}P NMR. The combination of (*S*)-*t*-BuPHOX ligand **1** (δ = –5.95 ppm) with $[Pd_2(dba)_3]$ in a 2.6:1 ratio at room temperature for 30 minutes, as specified in our standard alkylation procedure,[3] led to a single new phosphorous resonance at δ = 18.8 ppm (Spectra **1.A** and **2.A**, in Figure 2.1 on page 25). The addition of β-ketoester **8** or allyl enol carbonate **6** resulted in the complete disappearance of the resonance at δ = 18.8 ppm and produced a single long-lived resonance at δ = 30.9 ppm (Spectra **1.B** and **2.B**, in Figure 2.1). As these reactions neared completion, the long-lived intermediates seen at δ = 30.9 ppm slowly reverted to the initial resonance at δ = 18.8 ppm (Spectra **1.C** and **2.C**, in Figure 2.1). Complete consumption of β-ketoester **8** and allyl enol carbonate **6** was

observed by TLC for these reactions approximately at the time when the resonance at δ = 18.8 ppm began to reappear.

Figure 2.1. ^{31}P NMR Studies of Allylic Alkylation With β-Ketoester and Enol Carbonate Substrates



NMR tube reactions were run on a 63–66 μmol scale. Spectra **1.A** and **2.A** were obtained after mixing [$Pd_2(dba)_3$] and (*S*)-*t*-BuPHOX in solution for 30 minutes. Spectrum **1.B** was obtained immediately after adding allyl β-ketoester **8** to the solution pictured in spectrum **1.A**. Spectrum **2.B** was obtained immediately after adding allyl enol carbonate **6** to the solution pictured in Spectrum **2.A**. Spectra **1.C** and **2.C** were obtained 30 minutes after substrates **8** and **6** could no longer be observed by TLC in their respective reactions.

2.2.2 ^{31}P NMR Studies of Silyl Enol Ether Reactions

The allylic alkylation reaction of silyl enol ether **4** by ^{31}P NMR bore many similarities to the NMR reactions of allyl β-ketoester **8** and allyl enol carbonate **6**. Starting from the resonance at δ = 18.8 ppm formed during precomplexation (Spectrum

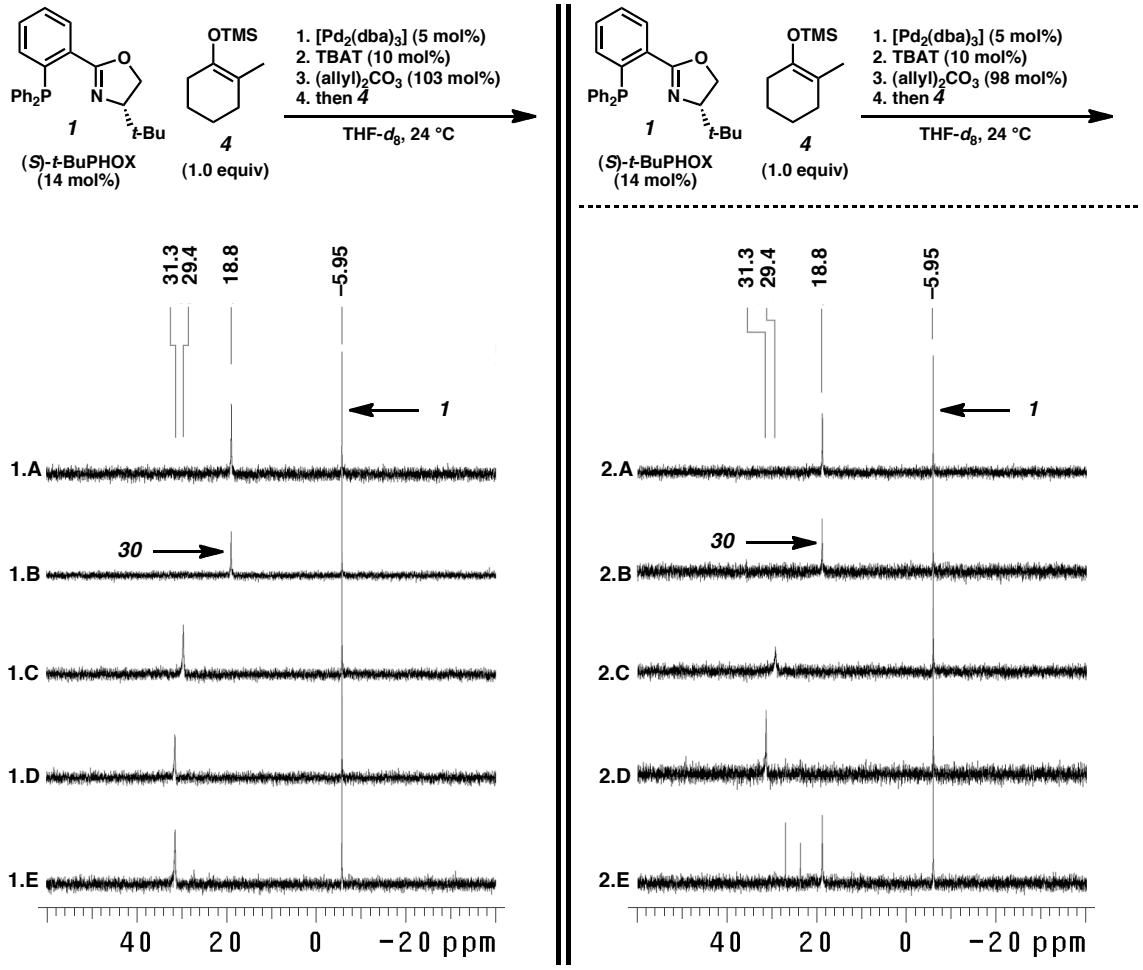
1.A, in Figure 2.2 on page 27), addition of 1 equivalent of TBAT[4] produced no new resonances (Spectrum **1.B**, in Figure 2.2). This suggests that TBAT does not appreciably interact with the palladium catalyst. Subsequent addition of 10.6 equivalents of diallyl carbonate, an allyl electrophile, resulted in the complete disappearance of the resonance at δ = 18.8 ppm and produced a new shift at δ = 29.4 ppm (Spectrum **1.C**, in Figure 2.2). Addition of 10.3 equivalents of silyl enol ether **4** appeared to shift the resonance at δ = 29.4 ppm to δ = 31.3 ppm (Spectrum **1.D**, in Figure 2.2). The resonance at δ = 31.3 ppm remained even after the reaction completed, as determined by the disappearance of silyl enol ether **4** via TLC (Spectrum **1.E**, in Figure 2.2).[5]

One of the most notable differences between the silyl enol ether and both the allyl enol carbonate and allyl β-ketoester reactions, is that the catalyst does not revert to the species responsible for the resonance at δ = 18.8 ppm when the reaction is completed. As per the original conditions,[3a] the NMR experiment with silyl enol ether **4** was performed with a slight excess of diallyl carbonate relative to silyl enol ether **4** (103 and 100 mol% respectively). This means that the silyl enol ether variant of the reaction differs from the other two by the presence of excess allyl electrophile relative to enolate nucleophile. This suggested that this persistent resonance at δ = 31.3 ppm may be a palladium(II) allyl species derived from allyl acetate.

To confirm this hypothesis, the NMR experiment with silyl enol ether **4** was performed again but with less diallyl carbonate then enol ether **4** (98 and 100 mol%, respectively). For the main course of this reaction (Spectra **2.A** to **2.D**, in Figure 2.2) the spectra obtained were effectively identical to the other reaction with silyl enol ether **4** under the standard conditions (Spectra **1.A** to **1.D** left, in Figure 2.2) Gratifyingly,

however, this reaction did show reversion to the resonance at δ = 18.8 ppm upon completion (Spectra **2.E**, in Figure 2.2) as observed for the allyl enol carbonate and allyl β-ketoester variants of the reaction (Spectra **1.C** and **2.C**, in Figure 2.1 on page 25). Some oxidative decomposition was observed for this reaction (resonances at δ = 27.2 and 23.6 ppm, representing 11% and 10% of total phosphorus integration, respectively, in Spectra **2.E**, in Figure 2.2).[6]

Figure 2.2. ^{31}P NMR Studies of Allylic Alkylation With Silyl Enol Ether Substrates



NMR tube reactions were run on a 67–68 μmol scale. Spectra **1.A** and **2.A** were obtained after mixing [$Pd_2(dba)_3$] and (*S*)-*t*-BuPHOX in solution for 30 minutes. Spectra **1.B** and **2.B** were obtained after adding TBAT to the solutions pictured in **1.A** and **2.A**, respectively. Spectra **1.C** and **2.C** were obtained after adding diallyl carbonate to the solutions pictured in **1.B** and **2.B**, respectively. Spectra **1.D** and **2.D** were obtained after adding silyl enol ether **4** to the solutions pictured in **1.C** and **2.C**, respectively. Spectra

1.E and **2.E** were obtained 30 minutes after silyl enol ether **4** could no longer be observed by TLC for the reactions initiated in **1.D** and **2.D**, respectively. In spectrum **2.E** the two extra resonances found downfield of δ = 20 ppm are most likely oxidative decomposition products.[6]

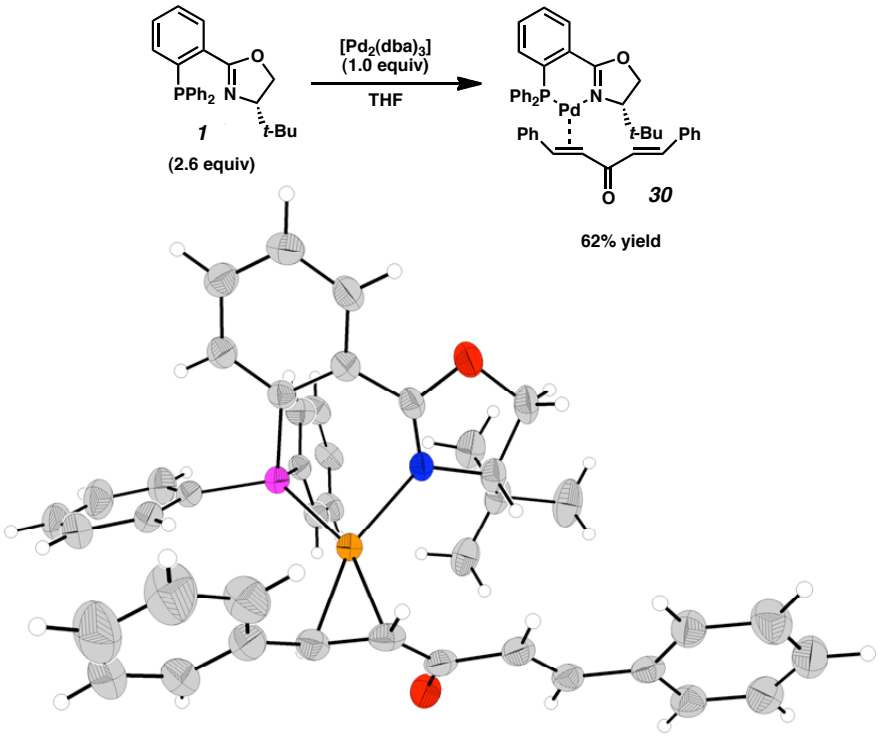
Integrating relative to the free PHOX ligand at δ = –5.95 ppm suggests that the sum of the species represented at δ = 18.8, 29.4, and 31.3 ppm for the silyl enol ether variant and δ = 18.8 and 30.9 ppm for the allyl enol carbonate and allyl β-ketoester varients are constant throughout the course of their respective reactions. As a result, any other PHOX-ligand-containing species that might form during the course of these reactions must be present in quantities too small to be observed by ^{31}P NMR. The yield and *ee* of the allylic alkylation product **9** was obtained for each of the NMR reactions and gave results consistent with the standard conditions when run on a similar scale.

2.3 Isolation and Characterization of Intermediates

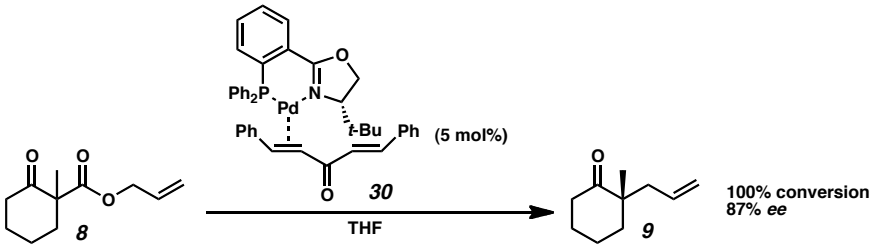
2.3.1 Olefin Complex ***30***

Olefin complex **30** was synthesized and isolated using reaction-like conditions to combine (*S*)-*t*-BuPHOX ligand **1** and [$Pd_2(dba)_3$] in THF (Scheme 2.2 on page 29). [{(*S*)-*t*-BuPHOX}Pd(dba)] **30** was fully characterized including single-crystal X-ray diffraction, and in solution was found to have a ^{31}P resonance of δ = 18.8 ppm, matching the resonance found at the start of the reaction. Isolated samples of **30** were found to be competent for catalyzing the asymmetric allylic alkylation reaction, and gave results analogous to those observed for the standard reaction procedure (Scheme 2.3 on page 29). Based on these properties [{(*S*)-*t*-BuPHOX}Pd(dba)] **30** appears to be the initial catalytic species formed in our, and other related, allylic alkylation systems.[3,7a,f]

Scheme 2.2. Isolation and X-Ray Structure of Initial Catalyst Complex ***30***



Scheme 2.3. Decarboxylative Asymmetric Allylic Alkylation Catalyzed by Isolated Complex ***30***



2.3.2 Carboxylate ***31***

As the few apparent intermediates observed by NMR during the course of these reactions were long-lived singular species, the possibility was explored for the isolation of these species directly from the reaction. Initial efforts revealed that the apparent stability of these intermediates was largely illusory, and their seeming robustness under reaction conditions is the result of a steady-state equilibrium. Under reaction conditions, these intermediates decompose at a rate equivalent to their regeneration from the

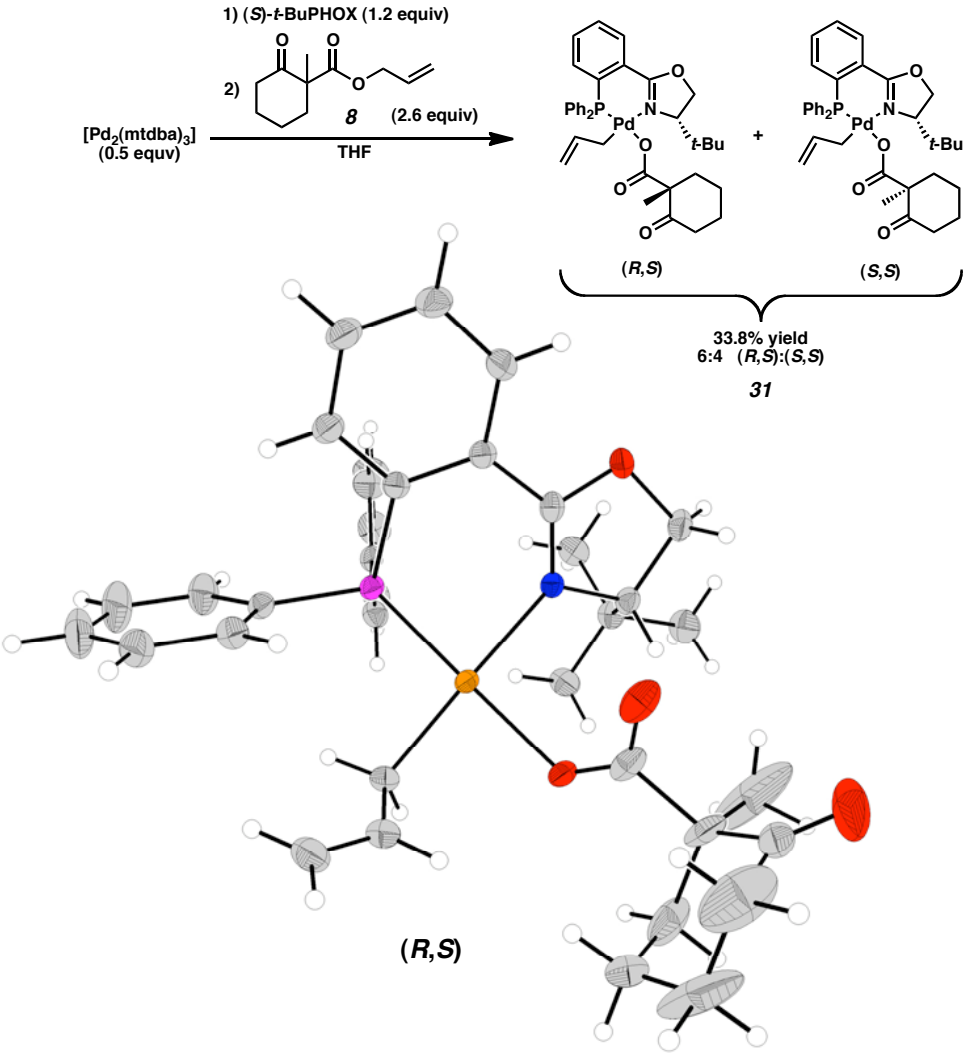
remaining reservoir of substrate. In the absence of excess substrate all of these species were found to be thermally unstable and short lived at room temperature, both in solution and as solvent-free solids. Even at reduced temperatures these species were also found to be sensitive to air and moisture.

However, at –36 °C in a nitrogen glove box, palladium allyl carboxylate **31** could be isolated from reaction-like conditions following the addition of allyl β-ketoester **8** as a substrate (Scheme 2.4 on page 31). This species was identified as the important intermediate corresponding to the ^{31}P NMR resonance at δ = 30.9 ppm (Figure 2.1 on page 25). Interestingly, initial isolates of carboxylate **31**, which were impure, visibly expelled a gas (presumably CO_2) in the solid state and effervesced when submerged in a liquid. By using [Pd_2(mtdba)$_3$], a version of [Pd_2(dba)$_3$] modified to be more amenable toward use in organometallic synthesis,[8] crystals of superior stability that contained carboxylate **31** in high purity were obtained. This allowed for the complete characterization of carboxylate **31** as a mixture of diastereomers resulting from the use of racemic β-ketoester **8** in its synthesis (Scheme 2.4 on page 31).

The structure of complex **31**, as determined in solution by NMR techniques[9] and in the solid state by single-crystal X-ray diffraction, is rather uncommon. Complex **31** is a square-planar 16-electron species with a β-ketocarboxylate ligand *trans* to the phosphorus atom of the PHOX ligand and a σ-bound monohapto η^1-allyl ligand *trans* to the nitrogen atom. Not only is the crystal structure of palladium carboxylate **31** the first example in the Cambridge Structural Database (CCDC) of a palladium species with a β-ketocarboxylate ligand, but it is also the first X-ray crystal structure of a transition-metal complex with a non-chelating carboxylate ligand *cis* to a σ-bound allyl group.[10,11,12] By

contrast, the analogous PF_6 salt of [{(*S*)-*t*-BuPHOX}Pd(η^3-allyl)] (**25**) displays an η^3-π-allyl bonding mode in both the solid state[1c,13] and solution,[13] as do related compounds.[14]

*Scheme 2.4. Isolation and X-Ray Structure of Palladium Carboxylate **31**[15]*

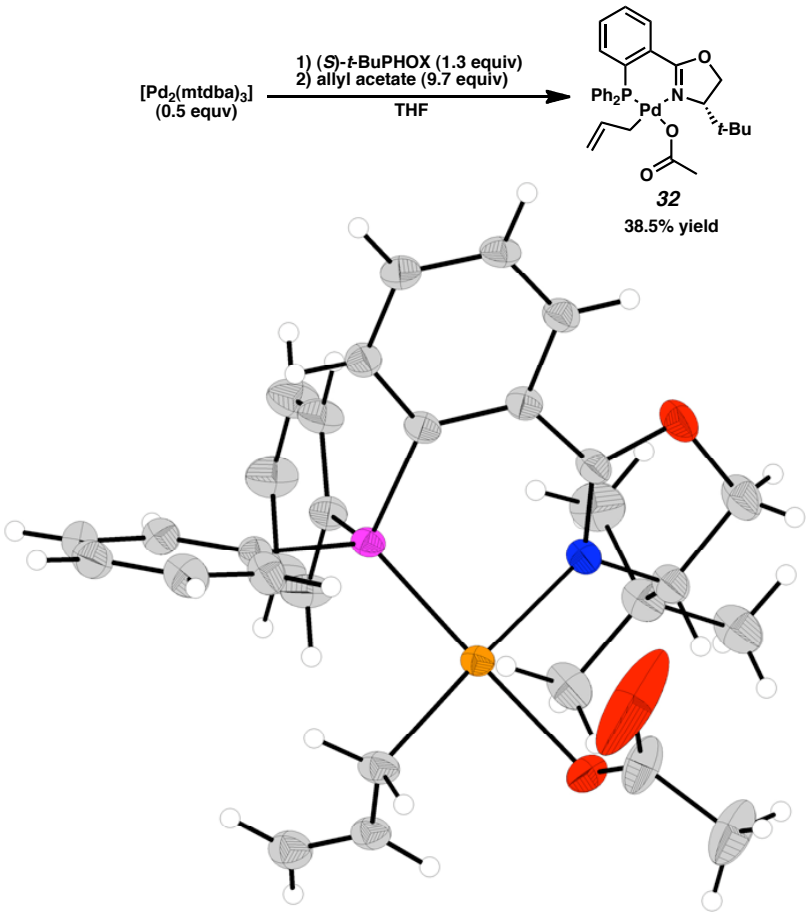


The presence of the β-ketocarboxylate ligand derived directly from deallylation of allyl β-ketoester **8** reveals that this complex must form after oxidative addition of the substrate, but prior to decarboxylation. Because **31** is the only observable species during the course of the catalytic reaction, we concluded that **31** is the catalyst's resting state and thus the rate-determining step for the allylic alkylation of allyl β-ketoester substrates is decarboxylation. This conclusion is consistent with the kinetics data for the overall

reaction, which shows a first-order dependence on catalyst and a zero-order dependence on the substrate concentration.[2,1c] Decarboxylation has also been proposed as the rate-determining step for related palladium-catalyzed decarboxylative alkylation reactions.[16]

Despite the enormous number of transition-metal-catalyzed reactions involving allylic acetates and carbonates, a simple square planer transition metal species representing the canonical oxidative-addition adduct of allyl acetate and $L_nM(0)$ had not been reported prior to our work. With this in mind, and noting that intermediate **31** is basically an elaborated derivative of such a fundamental species, we synthesized the parent neutral [{(*S*)-*t*-BuPHOX}Pd(η-1)(OAc) complex **32** by the same means (Scheme 2.5 on page 33). The structure of complex **32**, a four-coordinate Pd(II) square-planar species in which the phosphorus atom and the acetate group have a *trans* relationship, is similar to that of carboxylate **31**. Together the structure and properties of palladium allyl carboxylates **32** and **31** may have implications not only for immediately related decarboxylative allylic alkylation reactions,[7,17] but also for palladium-catalyzed allylic oxidation,[18,19] palladium-catalyzed 1,4-diacetoxylation,[18,20] and late-transition-metal-catalyzed decarboxylative reactions in general.

Scheme 2.5. Synthesis and X-Ray Structure of Canonical Palladium Allyl Acetate Complex ***32***[21]

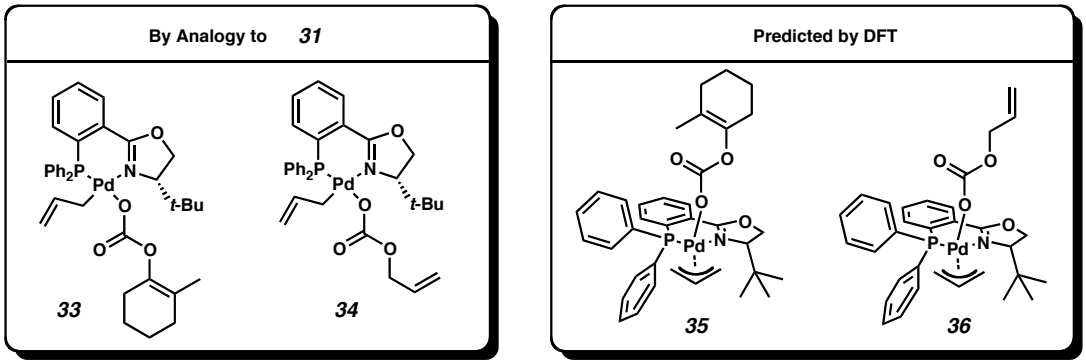


2.3.3 The Carbonate Complexes

This still leaves questions about the structures of the equivalent intermediates seen by ^{31}P NMR at δ = 30.9 ppm for the decarboxylative allylic alkylation of allyl enol carbonate **6** and at 29.4 and 31.3 ppm for silyl enol ether **4**. None of these species exhibits a ^{31}P NMR spectrum similar to that of the corresponding π-allyl cation **25** (δ = 23.5 and 22.5 ppm for the *exo* and *endo* η-3 allyl conformers of **25**, respectively). Instead, the phosphorous resonances and means of formation for these intermediates is closer to palladium carboxylates **31** and **32**.

By analogy to carboxylates **31** and **32,** the uncharacterized intermediates of the carbonate-based reactions are postulated to be palladium (II) allyl carbonate species with associated carbonate ligands. While the similarity of these intermediates to palladium allyl carboxylate **31** suggests that they may be palladium carbonates **33** and **34** (Figure 2.3 left, on page 34), DFT calculation predicts a tetragonal pyramidal structure with an η^3 allyl ligand and an apically coordinated carbonate ligand (carbonates **35** and **36** in Figure 2.3 right).[1a] Similar neutral palladium η^3 allyl complexes with tetragonal pyramidal structures are known in the literature.[22]

Figure 2.3. Estimated Structures for Carbonate Intermediates



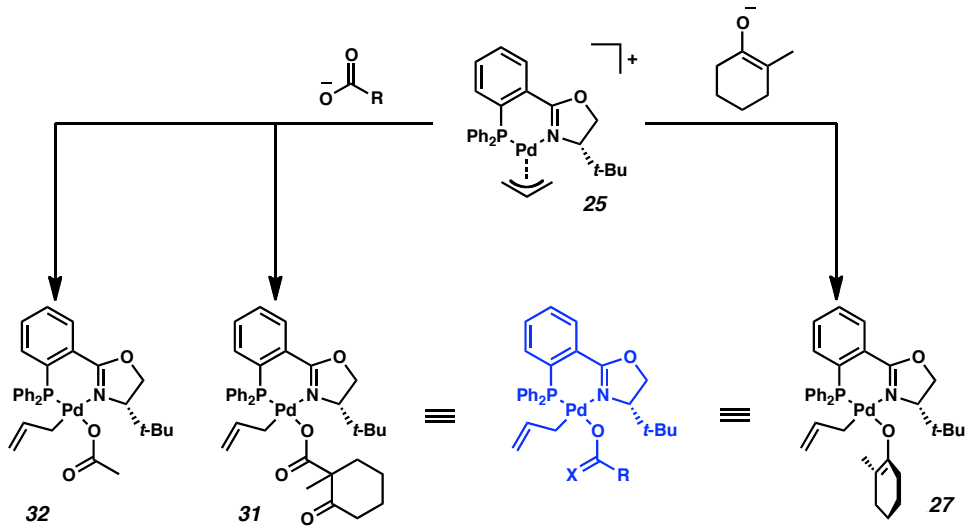
2.4 Role and Significance of the Intermediates

*2.4.1 Analogy to Putative Key Palladium Intermediate **27***

Notably the arrangement and hybridization of the allyl and carboxylate ligands in palladium carboxylates **31** and **32** are similar to that of the palladium allyl enolate intermediate **27** (Scheme 2.6 on page 35). This is significant as enolate **27** is believed to be the key intermediate preceding the doubly vinylogous reductive elimination that represents the key bond-forming step for this reaction. While the reality of palladium carboxylate species **31** and **32** does not assure the existence of palladium enolate **27** or its

role as a key reaction intermediate, they do lend credence to the proposed structure for enolate **27** by setting structural precedents in this system. Furthermore, the solution behavior of complexes **31** and **32** demonstrates that even fairly weak nucleophiles are capable of displacing one end of the η^3-allyl ligand in this system and binding to the palladium center.[2,13]

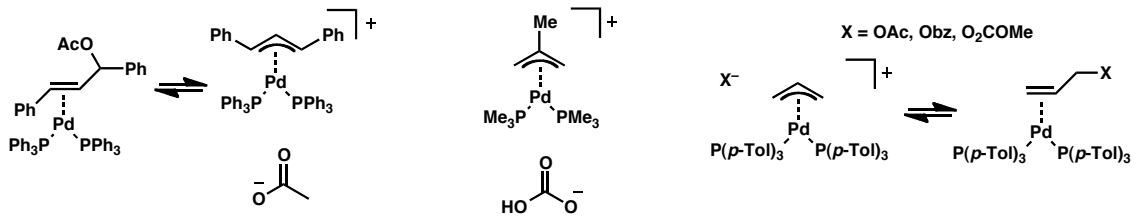
*Scheme 2.6. Underlying Structural and Chemical Similarity between **31**, **32**, and **27***



This is significant, as almost all the palladium-catalyzed asymmetric allylic alkylation systems that are understood to function by an outer-sphere mechanism remain unable to demonstrate compounds isolable from reaction-like conditions that possess structures similar to carboxylates **31** and **32**. Instead, palladium-catalyzed allylic alkylation systems that function by an outer-sphere mechanism tend to produce allylic esters and allyl-carbonate-derived species that exist as either apparent η-2 olefin complexes,[23] or as palladium π-allyl cations (Figure 2.4 on page 36).[24] As a result, the high degree of similarity between palladium enolate **27** and palladium carboxylates **31** and **32** does lend credence to the key calculated palladium allyl enol structure **27** and its mechanistic role. It is possible that palladium allyl carboxylate complexes like **31** and **32**

represent the best isolable model systems by which the key intermediate **27** may be experimentally studied.

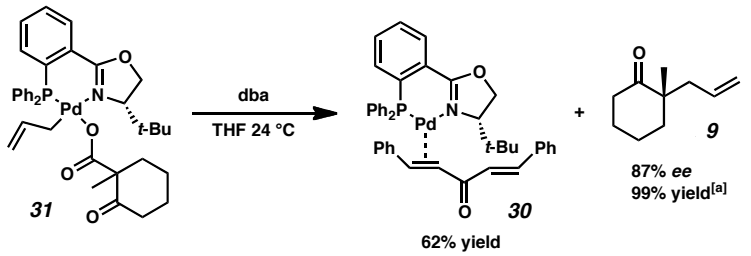
Figure 2.4. Select Examples of Typical Palladium Allyl Carboxylate and Carbonate Species Found in the Literature[23a,e,24e]



*2.4.2 The Function of Complexes **30** and **31** in the Catalytic Cycle*

To examine the role of carboxylate **31** in the catalytic cycle, it was subjected to reaction-like conditions in THF at 24 °C in the presence of free dba ligand, and the reaction was followed by ^{31}P NMR. The half-life of carboxylate **31** was measured to be 7.3 min under these conditions, and after 40 minutes **31** could no longer be detected by NMR. During this time, the resonance at δ = 18.8 ppm in the ^{31}P NMR, seen at the end of the catalytic reaction, appeared, and after 40 minutes, became the only observable ^{31}P resonance. Both allylic alkylation product **9** (99% yield, 87% *ee*) and [{(*S*)-*t*-BuPHOX}Pd(dba)] **30** (62% yield), were obtained from this reaction (Scheme 2.7 on page 37). This reaction demonstrates that complex **30** is regenerated at the end of an allylic alkylation reaction, making it the catalyst's resting state in the absence of allyl electrophiles.

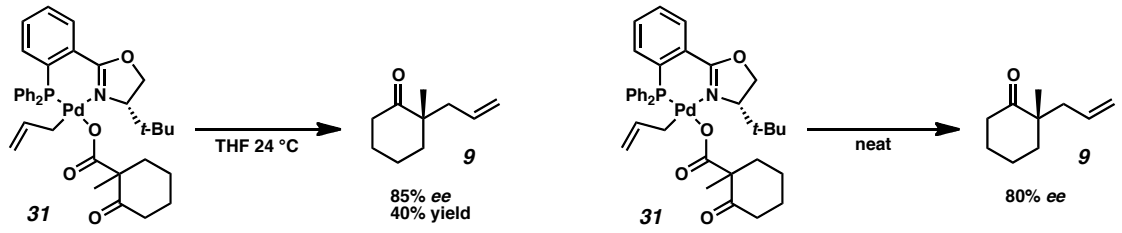
*Scheme 2.7. Thermal Decomposition of **31** in the Presence of Free dba Ligand in THF*



The yield of **30** and **9** are from two different runs. In the first run, only **30** was isolated, and in the second run only the yield and *ee* of **9** was assayed. [a] GC yield relative to internal standard (tridecane)

To determine if carboxylate **31** was part of the catalytic cycle or just an unproductive resting state, its decomposition was monitored in the absence of the dba ligand both in THF and neat. In THF solution at 24 °C in the absence of dba, allyl carboxylate **31** decomposes to give an increasingly complex mixture of phosphorous containing species by ^{31}P NMR, none of which can be observed during the course of the catalytic reaction. Under these conditions, allylic alkylation product **9** appears to be the only metal or phosphine-free product formed in the reaction, and **9** can be isolated with 85% *ee* from solution (Scheme 2.8 on page 37). Most telling is that the neat thermal decomposition of crystalline carboxylate **31** in a nitrogen glove box at ambient temperature still yielded ketone **9** as the major organic product, albeit with slightly reduced enantioinduction (80% *ee*).

*Scheme 2.8. Thermal Decomposition of **31** Without dba in THF and Neat*



2.5 Conclusions

The ^{31}P NMR investigations of the palladium-catalyzed decarboxylative allylic alkylation reaction reveal long-lived singular intermediates for all three substrate variants of the methodology. The only two NMR detectable intermediates from the allyl β-ketoester variant of the methodology, dba complex **30** and carboxylate complex **31**, have been isolated and fully characterized. Carboxylate complex **31** represents the resting state of the catalyst for the allyl β-ketoester variant of the reaction while it is running and proves that decarboxylation is rate limiting. The dba complex **30**, is the initial catalytic species generated in the precomplexation of PHOX ligand **1** and $[Pd_2(dba)_3]$. The dba complex **30** is also the catalyst's resting state in the absence of allyl electrophiles like allyl enol carbonates, allyl β-ketoesters, and diallyl carbonate. As a result, dba complex **30** will regenerate under reaction conditions when these species become fully consumed.

Carboxylate complex **31** and its parent **32** represent exceptionally rare examples of isolated transition metal complexes with a non-chelating carboxylate ligand *cis* to an η^1-allyl ligand. However, many such species may actually play a prevalent role in an array of catalytic processes. Similar intermediates to carboxylate **31**, such as carbonates **34**/**36** and **33**/**35**, are expected for the allyl enol carbonate and silyl enol ether variants of the reaction, respectively. Finally, carboxylate complexes **31** and **32** lend credence to the existence and proposed structure of putative palladium enolate **27**, which is believed to be the key intermediate for this allylic alkylation system. All the intermediates observable by ^{31}P NMR appear to be part of the pre-decarboxylation phase of the mechanism, and thus not part of the universal underlying allylic alkylation mechanism that is expected to be common for all three reaction variants as previously simulated by DFT.[1,2]

2.6 Experimental Procedures

2.6.1 Materials and Methods

Unless otherwise stated, reactions were performed in flame-dried glassware under an argon atmosphere using dry, deoxygenated solvents. Unless otherwise stated, solvents were purchased from Fisher Scientific, dried by passage through an activated alumina column under ultra high purity (UHP) argon, and either stored under UHP argon or stored over 4Å molecular sieves in a nitrogen glove-box after drying. Solvents stored over molecular sieves were filtered under a nitrogen atmosphere immediately before use to remove sieve dust. Petroleum ether was obtained from Fisher Scientific and is defined here as petroleum fractions that boil from 36–60 °C. The NMR solvents $CDCl_3$ and $THF_{d\text{-}8}$ were purchased from Cambridge Isotope Laboratories and used as received. $THF_{d\text{-}8}$ was purchased as 1 or 0.75 mL ampoules, which were only used in a nitrogen glove box to exclude water. All filtrations performed in a glove box or otherwise associated directly or indirectly with inorganic or organometallic complexes were performed exclusively with scintillated glass Buchner funnels or using 2.4 mm GF/A Whatman glass microfiber filter paper. Unless otherwise stated, all starting materials were purchased from Sigma-Aldrich or Alfa Aesar, and used as received. Tetrabutylammonium difluorotriphenylsilicate (TBAT) was purchased from Sigma-Aldrich and azeotropically dried five times from acetonitrile, backfilled with argon and then stored in a nitrogen glove box until immediately prior to use. Tris(dibenzylideneacetone)dipalladium(0) [$Pd_2(dba)_3$] and $PdCl_2$ were purchased from

Strem and stored in either a desiccator or a nitrogen glove box until immediately before use. 1-Methyl-2-oxo-cyclohexanecarboxylic acid allyl ester (β-ketoester **8**),[25] trimethyl(2-methylcyclohex-1-enyloxy)silane (**4**),[3b] allyl 2-methylcyclohex-1-enyl carbonate (**6**),[3b] and (*S*)-*t*-BuPHOX ligand (**1**) [3b,26] were prepared by known methods. Reaction temperatures were controlled by an IKAmag temperature modulator. Thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F254 precoated plates (0.25 mm). SiliCycle® SiliaFlash® P60 Academic Silica Gel (particle size 40–63 μm; pore diameter 60 Å), was used for flash chromatography. ^{1}H, ^{13}C, ^{31}P, and ^{19}F NMR spectra were recorded on a Varian Inova 600 (at 600 MHz and 150 MHz for ^{1}H and ^{13}C, respectively), a Varian Inova 500 (at 500 MHz and 125 MHz for ^{1}H and ^{13}C, respectively), or a Varian Mercury 300 (at 300 MH, 75 MHz, 121.4 MHz, and 282 MHz for ^{1}H, ^{13}C, ^{31}P, and ^{19}F, respectively). ^{1}H NMR spectra are reported relative to residual $CHCl_3$ (δ 7.26)[27] or to the downfield proton in residual $THF_{d\text{-}7}$ (δ 3.58).[27] Data for ^{1}H NMR spectra are reported as follows: chemical shift (δ ppm) (multiplicity,[1] coupling constant (Hz),[2] integration). Multiplicities are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet, comp. m = complex multiplet, app. = apparent, br. = broad. ^{13}C NMR spectra are reported relative to $CDCl_3$ (δ 77.16)[27] or to the downfield carbon in $THF_{d\text{-}8}$ (δ 67.21).[27] ^{31}P NMR spectra are reported relative to

[1] In many cases hyperfine coupling could be observed but was not resolved enough that its splitting pattern could be determined. In such cases the larger coupling is calculated and the relevant multiplicities are indicated but terminated with m (multiplet) to signify the unresolved hyperfine coupling. For example (tm, J = 7.2 Hz, 1H) indicates a triplet of 7.2 Hz, with irresolvable hyperfine coupling. This is done in place of reporting the entire resonance as a multiplet for the purpose of reproducibility on lower field strength NMR spectrometers where only the larger calculable splitting(s) will be observed.

[2] When a lower case subscript is shown with the coupling constant, it indicates what type of splitting the constant is associated with in splitting patterns that consist of different multiplicities of coupling. For example (td, J_t = 5.0 Hz, J_d = 3.3 Hz, 1H) indicates that the triplet splitting has a 5.0 Hz coupling constant and the doublet has a 3.3 Hz coupling constant.

H_3PO_4 (δ 0.00) as an external standard consisting of 85% neat phosphoric acid or to free (*S*)-*t*-BuPHOX ligand (δ –5.95) as either an internal or external standard in $THF_{d\text{-}8}$. ^{19}F NMR spectra are reported relative to $CFCl_3$ (δ 0.00) as an external standard. Analytical achiral gas chromatography (GC) was performed with an Agilent 6850 GC utilizing a DB-WAX (30 m x 0.25 mm) column (1.0 mL/min carrier gas flow). Analytical chiral GC was performed with an Agilent 6850 GC utilizing a G-TA (30 m x 0.25 mm) column (1.0 mL/min carrier gas flow). Optical rotations were measured with a Jasco P-1010 polarimeter at 589 nm. IR spectra were recorded on a Perkin Elmer Paragon 1000 spectrometer and are reported in frequency of absorption (cm^{-1}). High-resolution mass spectra were obtained from the Caltech Mass Spectral Facility or on an Agilent 6200 Series Time-of-Flight LC/MS/TOF system. Melting points were determined on a Thomas-Hoover melting point apparatus and are uncorrected. Boiling points are measured directly during distillation and are uncorrected. Crystallographic analyses were performed at the California Institute of Technology Beckman Institute X-Ray Crystallography Laboratory. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, and copies can be obtained upon request, free of charge, by quoting the publication citation and the deposition numbers provided with the structures below.

2.6.2 ^{31}P NMR Studies

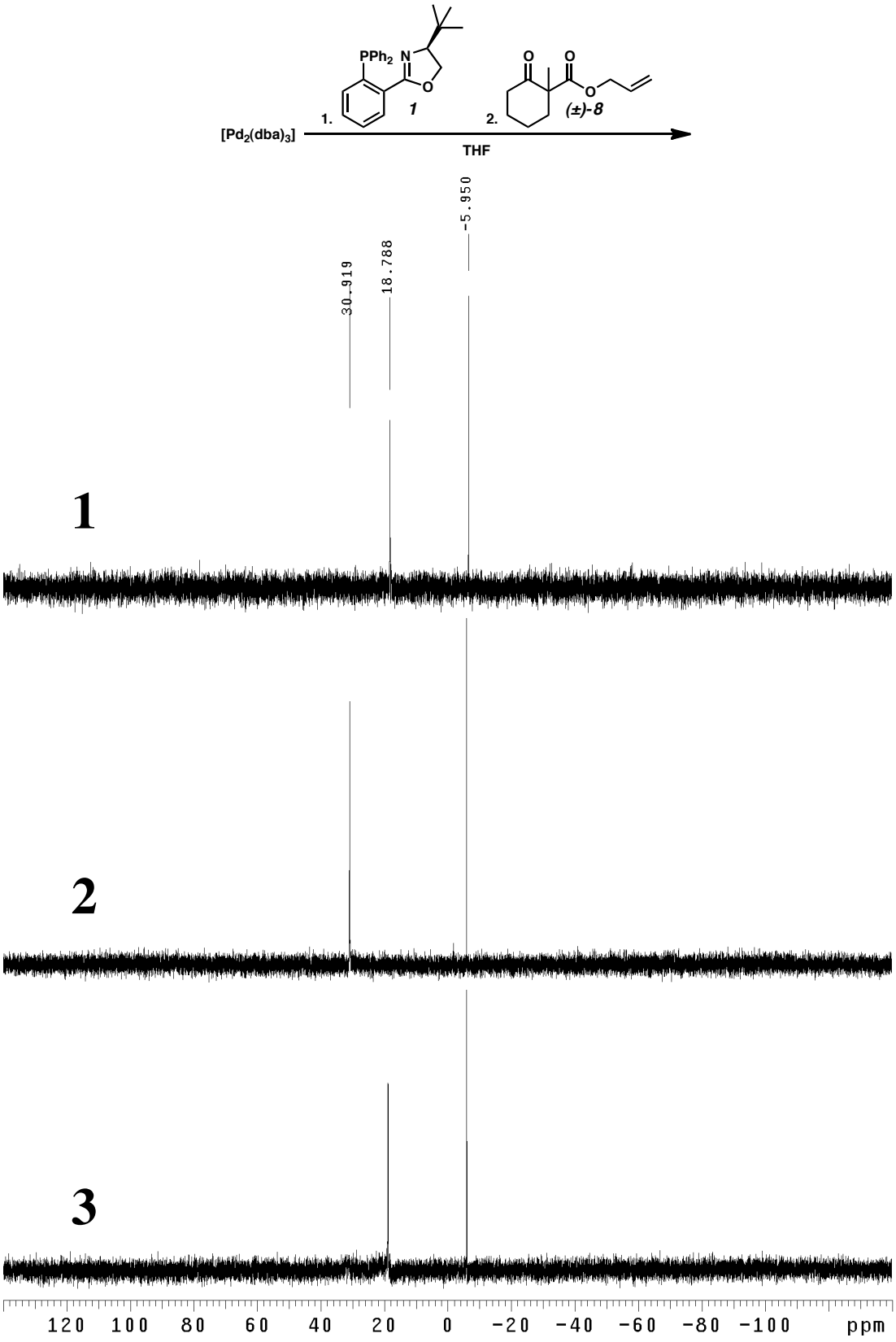
2.6.2.1 General Notes and Procedures

For NMR studies of the various allylic alkylation procedures, the reaction was followed by TLC. Due to air sensitivity, TLCs were taken either by cycling the NMR tube into a nitrogen glove box and taking an aliquot, or by connecting the NMR tube through its septum to an argon line with a needle while sampling the solution with a second needle and TLC spotter under slight argon overpressure. The most common product of air exposure was the phosphine oxide of (*S*)-*t*-BuPHOX ligand (the experimental procedure section contains characterization data for (*S*)-*t*-BuPHOX oxide for reference.)

2.6.2.2 The Decarboxylative Allylic Alkylation of β-Ketoester 8 Monitored by ^{31}P NMR

In a nitrogen atmosphere glove box [$Pd_2(dba)_3$] (3.0 mg, 3.3 μmol, 1 equiv) was placed in a 1 dram vial. (*S*)-*t*-Bu-PHOX ligand (**1**) (3.3 mg, 8.5 μmol, 2.6 equiv) was weighed in a second 1 dram vial. THF (1 mL) was filtered through a pipette with glass filter paper directly into the vial containing the (*S*)-*t*-Bu-PHOX ligand (**1**). The solution was mixed manually by pipette until all the material had dissolved, forming a clear colorless solution. The solution was then moved by pipette to the vial containing [$Pd_2(dba)_3$]. This solution was mixed manually by pipette for 1 min during which time a dark red-purple solution formed that then lightened to a dark but richly orange color. This solution was then filtered through a pipette filter with glass filter paper directly into an NMR tube, separating a bright, richly orange filtrate from a black amorphous precipitate presumed to be colloidal Pd(0) particles. The NMR tube was then sealed with

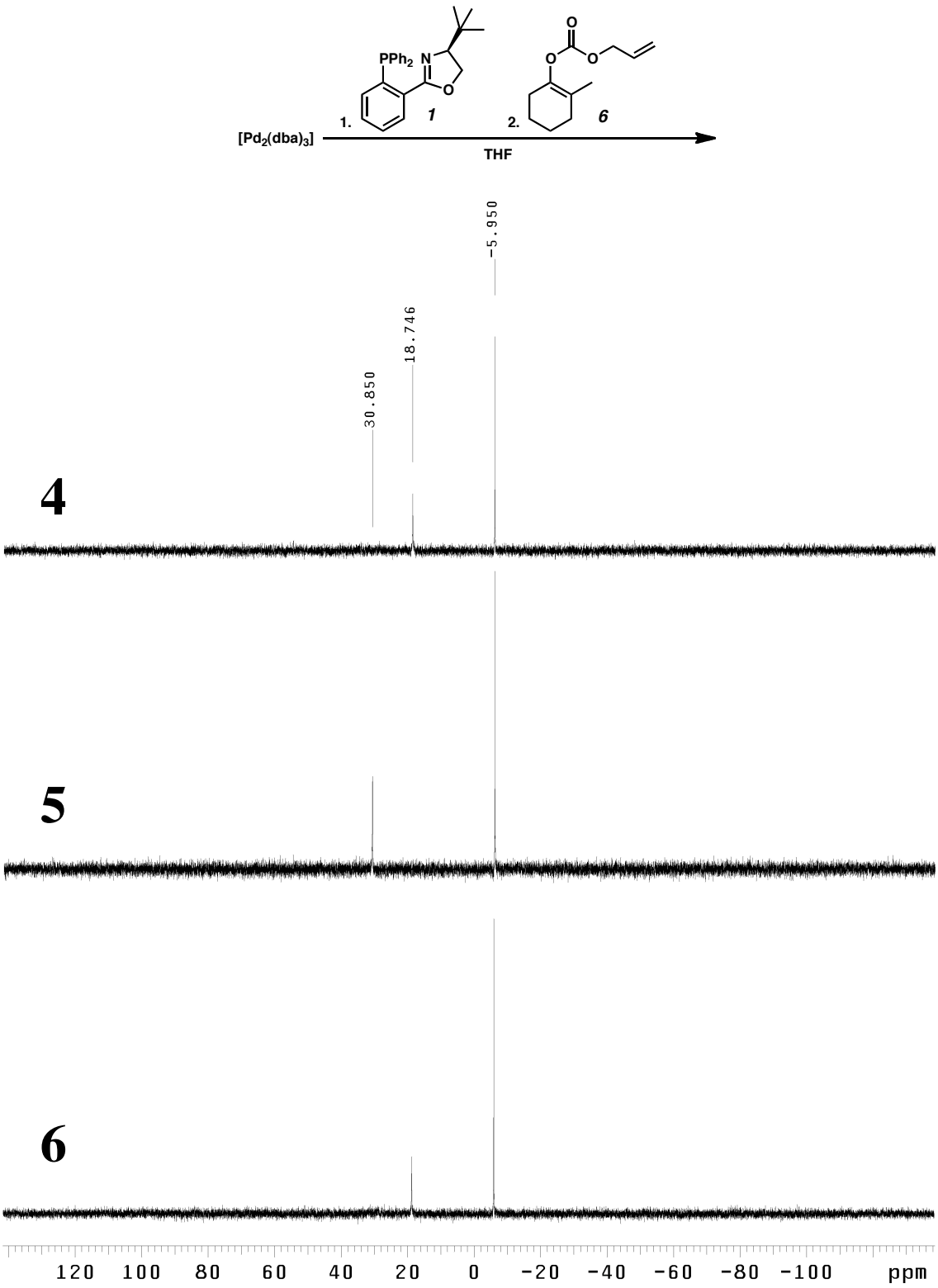
a septum and removed from the glove box. NMR spectrum #1 was taken at this time. Neat 1-methyl-2-oxo-cyclohexanecarboxylic acid allyl ester (β-ketoester **8**) (12.3 mg, 62.8 μmol, 19.1 equiv) was added to the NMR tube via a 25 μL Hamilton syringe in a single portion. The NMR tube was shaken vigorously for 30 s, and the solution quickly changed color from a rich orange to a lighter yellow-green. NMR spectrum #2 was taken at this time. The NMR tube was then placed in an oil bath regulated at 24 °C and warmed for 3 h, which was 20 min longer than it took for the solution's color to change from a light yellow-green to a rich orange and 30 minutes after allyl β-ketoester **8** could no longer be observed by TLC. NMR spectrum #3 was taken at this time.


PPh2
N
O
1
1.
2.
O
O
O
(±)-8
[Pd2(dba)3]
THF
-5.950
18.788
30.919
1
2
3
120 100 80 60 40 20 0 -20 -40 -60 -80 -100 ppm

2.6.2.3 The Decarboxylative Allylic Alkylation of Allyl 2-methylcyclohex-1-enyl carbonate (6) Monitored by ^{31}P NMR

In a nitrogen glove box (S)-t-BuPHOX ligand (3.3 mg, 8.5 μmol, 1.3 equiv) was weighed into a half-dram vial. $[Pd_2(dba)_3]$ (2.9 mg, 3.2 μmol, 0.5 equiv) was weighed into a second half-dram vial. Anhydrous THF (1 mL) was filtered through a pipette filter with glass filter paper into the half-dram vial containing the PHOX ligand. The solution was mixed manually via pipette for a little less than 1 min until all material had dissolved. The resulting solution was transferred via pipette and added as a single portion to the half-dram vial containing the $[Pd_2(dba)_3]$. The resulting solution was mixed manually via pipette for 2 min during which time it turned a dark purple-brown. The solution was left to stand and mix via diffusion for 30 min during which time it turned an orange color. The solution was filtered though a pipette with glass filter paper to separate a bright orange solution from a small amount of black precipitate presumed to be aggregated palladium(0) metal. The NMR tube was sealed with a septum and removed from the glove box. NMR spectrum #4 was taken at this time. Allyl 2-methylcyclohex-1-enyl carbonate (**6**) (12.9 mg, 65.7 μmol, 10.3 equiv) was added in a single portion via a syringe. The tube was fully inverted and righted causing an abrupt color change from a rich orange color to a light yellow-green solution. NMR spectrum #5 was taken at this time. The NMR tube was left to stand for 3 h at 24 °C during which time the solution turned orange, and 30 minutes after allyl enol carbonate **6** could no longer be observed by TLC. NMR spectrum #6 was taken at this time. The solution was concentrated under a jet of nitrogen to a small amount of yellow solution. Chromatography was preformed in a pipette column on silica eluting with 5→10% Et_2O in petroleum ether affording 2-allyl-2-methylcyclohexanone (87.4% *ee* [assay: GC, G-TA

column {100 °C isothermal for 30 min}, major enantiomer (S) Ret. Time = 14.897 min, minor enantiomer (R) Ret. Time = 17.313 min], clear colorless oil).



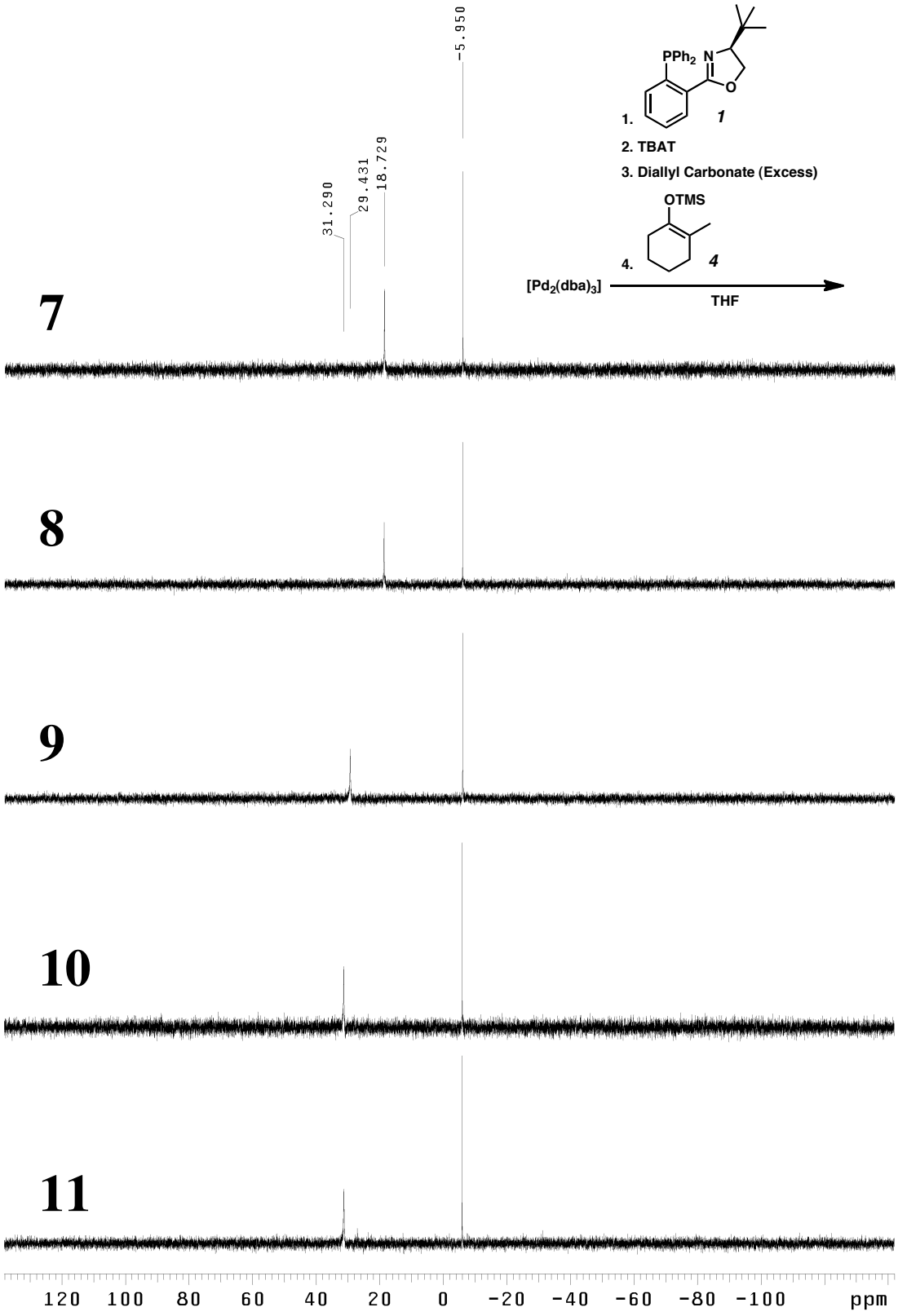
2.6.2.4 The Decarboxylative Allylic Alkylation of Trimethyl(2-methylcyclohex-1-enyloxy)silane (4) Monitored by ^{31}P NMR (standard alkylation procedure)

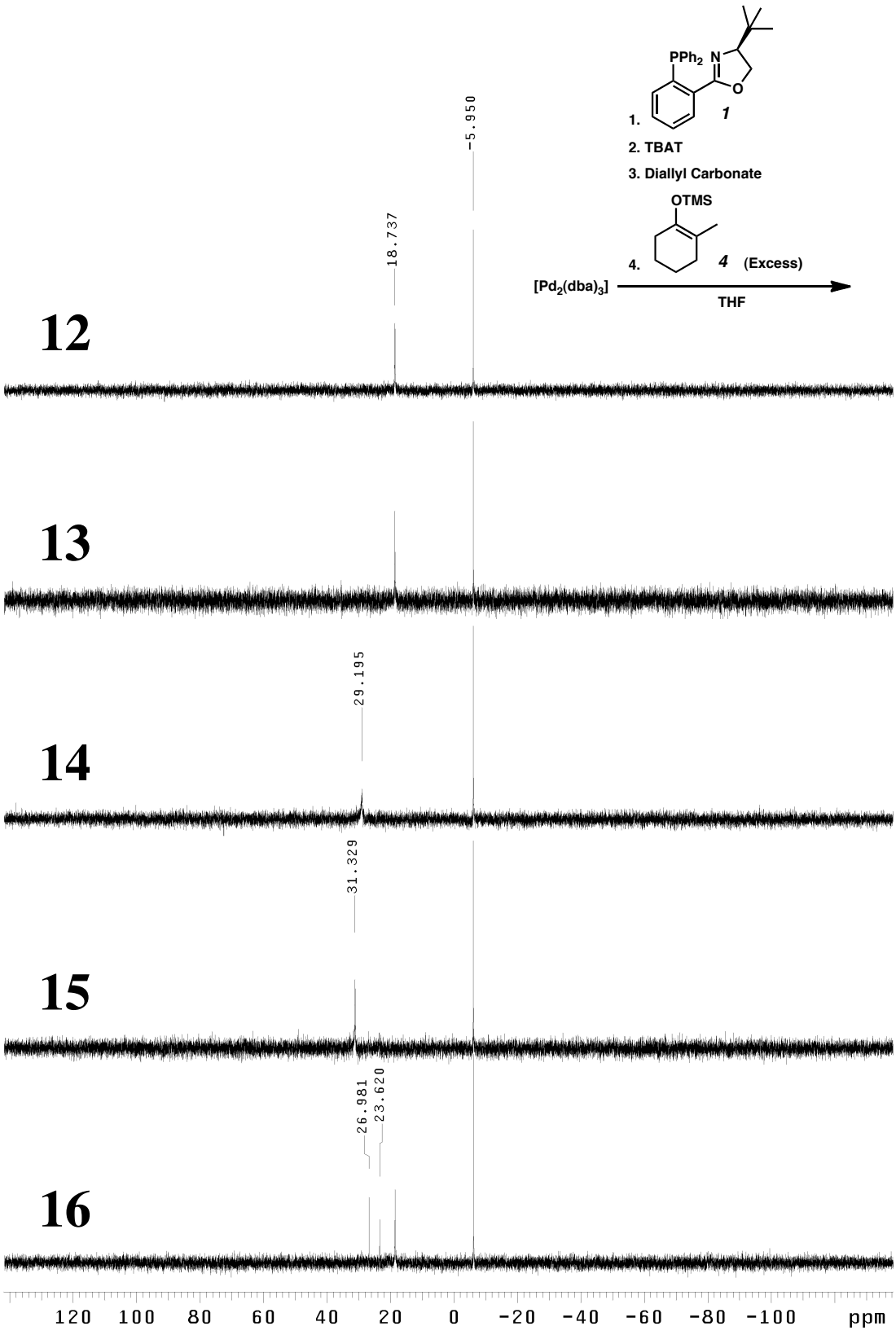
In a nitrogen glove box (S)-t-BuPHOX ligand (3.5 mg, 9.0 μmol, 1.4 equiv) was weighed into a half-dram vial. $[Pd_2(dba)_3]$ (3.0 mg, 3.3 μmol, 0.5 equiv) was weighed into a second half-dram vial. Anhydrous THF (1 mL) was added into the half-dram vial containing the PHOX ligand. The solution was mixed manually via pipette for 1 min until all of the solids had dissolved. The resulting solution was added to the half-dram vial containing the $[Pd_2(dba)_3]$ via pipette in a single portion. The resulting solution was mixed manually via pipette for 2 min during which time it turned a dark purple-brown. The solution was left to stand and mix via diffusion for 30 min during which time it turned an orange color. The solution was filtered though a pipette with glass filter paper to separate a bright orange solution from a small amount of black precipitate presumed to be aggregated palladium(0) metal. The NMR tube was sealed with a septum and removed from the glove box. NMR spectrum #7 was taken at this time. The NMR tube was the cycled back into the glove box. TBAT (3.6 mg, 6.7 μmol, 1 equiv) was weighed into a half-dram vial in the glove box. The contents of the NMR tube were emptied into the half-dram vial. The solution was mixed manually by pipette for 1 min until all the material had dissolved. The resulting solution was returned to the NMR tube, which was resealed with a septum and removed from the glove box. NMR spectrum #8 was taken at this time. Diallyl carbonate (10 μL, 9.9 mg, 69.7 μmol, 10.6 equiv) was added via a syringe in one portion. The NMR tube was inverted once resulting in a rapid color change from a rich orange to a light yellow-green. NMR spectrum #9 was taken at this time. Trimethyl(2-methylcyclohex-1-enyloxy)silane (**4**) (12.5 mg, 67.8 μmol, 10.3 equiv) was added via a syringe in one portion. NMR spectrum #10 was taken at this

time. The NMR tube was left to stand for 10 h at 24 °C during which time the solution turned orange. NMR spectrum #11 was taken at this time. The solution was then concentrated under a jet of nitrogen to a small amount of yellow oil. Chromatography was preformed on a pipette column on silica eluting with 5→10% Et_2O in petroleum ether affording 2-allyl-2-methylcyclohexanone (84.5% *ee* [assay: GC, G-TA column {100 °C isothermal for 30 min}, major enantiomer (S) Ret. Time = 14.897 min, minor enantiomer (R) Ret. Time = 17.313 min], clear colorless oil).

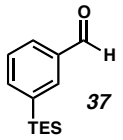
2.6.2.5 The Decarboxylative Allylic Alkylation of Trimethyl(2-methylcyclohex-1-enyloxy)silane (4) Monitored by ^{31}P NMR (excess nucleophile)

The procedure above was repeated with the following changes: Diallyl carbonate (9.0 μL, 8.9 mg, 62.7 μmol, 9.8 equiv), Trimethyl(2-methylcyclohex-1-enyloxy)silane (**4**) (12.4 mg, 67.2 μmol, 10.5 equiv). NMR spectra 12 to 16 were taken at the equivalent intervals to NMR spectra 7 to 11. The *ee* was 84.9% as measured by GC.


-5.950
31.290
29.431
18.729
PPh2
N
O
1.
1
2. TBAT
3. Diallyl Carbonate (Excess)
OTMS
4.
4
[Pd2(dba)3]
THF
7
8
9
10
11
120 100 80 60 40 20 0 -20 -40 -60 -80 -100 ppm


PPh2
N
O
1
1.
2. TBAT
3. Diallyl Carbonate
OTMS
4.
4
(Excess)
[Pd2(dba)3]
THF
-5.950
18.737
29.195
31.329
26.981
23.620
12
13
14
15
16
120 100 80 60 40 20 0 -20 -40 -60 -80 -100 ppm

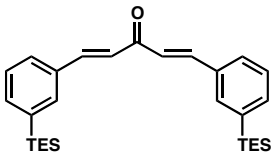
2.6.3 Synthesis of $[Pd_2(mtdba)_3]$



37

3-(Triethylsilyl)benzaldehyde (37): Anhydrous THF (160 mL) was added to a 250 mL 14/20 round-bottom flask with a stir bar. To this solution was added 3-bromobenzaldehyde diethylacetal (8.0 mL, 10 g, 39 mmol) via syringe. The solution was cooled to –78 °C and *n*-BuLi (2.5 M solution in hexanes, 36 mL, 90 mmol, 2.3 equiv) was added dropwise to the cooled stirring solution via syringe over 45 min. The solution was left to stir at –78 °C for 2 h. Triethylsilylchloride (7.6 mL, 6.8 g, 45 mmol, 1.2 equiv) was added via syringe over 15 min. The solution was stirred for 3 h at –78 °C, and allowed to warm to and maintain room temperature over 8 h. The solution was quenched with aq HCl (2 N, 90 mL) and diluted with diethyl ether (45 mL). The phases were spererated. The aq phase was extracted with diethyl ether (2 x 25 mL). The organic phases were merged, washed with aq saturated sodium chloride (1 x 100 mL), dried over magnesium sulfate, filtered with dichloromethane, and concentrated in vacuo. The resulting liquid was diluted with THF (6 mL), acetic acid (15 mL), and water (4 mL), and stirred for 3 h. The solution was slowly and carefully quenched with saturated aq sodium bicarbonate (100 mL) causing the rapid evolution of gas. The solution was diluted with diethyl ether (30 mL), and the phases were separated. The aq phase was extracted with diethyl ether (2 x 25 mL). The organic phases were washed with saturated aq sodium chloride (1 x 50 mL), dried over sodium sulfate, filtered with ethyl acetate, and concentrated in vacuo. The resulting yellow oil was bulb-to-bulb distilled on a kugelrohr at 0.3 torr and 130–180 °C using a 25 mL bulb before the final collection bulb to help

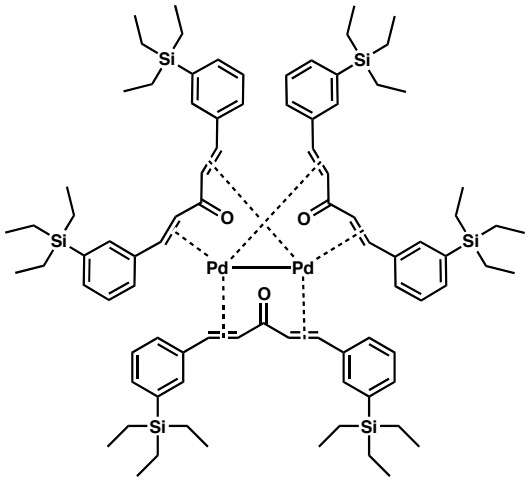
fractionate the distillate. Volatile impurities were removed from the distillate in a kugelrohr distillation at 0.2 torr and 15–85 °C affording 3-(triethylsilyl)benzaldehyde (**37**) (4.86 g, 56.5% yield, faintly colored clear oil). TLC (R_f 0.65, 5% diethyl ether in petroleum ether, observed by UV). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.03 (s, 1H), 7.98 (s, 1H), 7.85 (ddd, *J* = 7.6, 1.5, 1.5 Hz, 1H), 7.75 (ddd, *J* = 7.3, 1.2, 1.2 Hz, 1H), 7.52 (dd, *J* = 7.6, 7.3 Hz, 1H), 0.97 (t, *J* = 7.8 Hz, 9H), 0.85 (qm, *J* = 7.8 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.1, 140.4, 139.1, 135.73, 135.70, 130.2, 128.5, 7.5 (br. s), 3.3; IR (neat film, NaCl) 2955, 2910, 2876, 2808, 2716, 1700, 1586, 1572, 1458, 1415, 1370, 1263, 1238, 1205, 1170, 1123, 1106, 1010, 891, 864, 790, 734, 720, 696 cm^{-1}; HRMS (LC/MS TOF, Multi Mode: APCI/ESI) *m/z* calc'd for $C_{13}H_{21}OSi$ [M + H]$^+$: 221.1356, found: 221.1361.



38

1,5-Bis-[3-(triethylsilyl)phenyl]penta-1,4-dien-3-one, (mtdba) (38): To a 250 mL Erlenmeyer flask with a stir bar were added sodium hydroxide (1.92 g, 48.0 mmol, 5.4 equiv) and water (20 mL). Stirring was started, and once all the sodium hydroxide had dissolved, ethanol (200 proof, 34 mL) was added. The solution was cooled to 0 °C, and 3-(triethylsilyl)benzaldehyde (**37**) (4.08 g, 18.5 mmol, 2.04 equiv) was added dropwise over 5 min. Acetone (650 μL, 514 mg, 8.85 mmol) was added dropwise to the cooled stirring solution over 2 min. The solution was stirred for 5 min at 0 °C, and the cold bath was removed and the solution was stirred at room temperature for 9 h. The solution was diluted with water (25 mL) and hexanes (50 mL). The aq phase was

extracted with hexanes (2 x 25 mL) and 1:1 hexanes:diethyl ether (2 x 25 mL). The organic phases were washed with water (2 x 25 mL) and saturated aq sodium chloride (50 mL). The organic phases were then dried with magnesium sulfate, filtered with dichloromethane, and concentrated in vacuo. Chromatography was performed with 0.5%→5% Et_2O in petroleum ether on silica gel to afford 1,5-bis-[3-(triethylsilyl)phenyl]penta-1,4-dien-3-one (**38**) (54.4% yield, bright yellow-green waxy solid). TLC (R_f 0.41, 5% ether in petroleum ether, observed by UV and stained with anisaldehyde [orange]); mp 72.5–74.5 °C;[28] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 16.0 Hz, 2H), 7.70 (s, 2H), 7.65 (d, *J* = 7.7 Hz, 2H), 7.53 (d, *J* = 7.3 Hz, 2H), 7.41 (dd, *J* = 7.7, 7.3 Hz, 2H), 7.10 (d, *J* = 16.0 Hz, 2H), 0.98 (t, *J* = 7.8 Hz, 18H), 0.83 (qm, *J* = 7.9 Hz, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.2, 144.0, 138.8, 136.6, 134.9, 134.1, 128.39, 128.35, 125.4, 7.6, 3.4; IR (neat film, NaCl) 3047, 2954, 2909, 2874, 1652, 1619, 1456, 1415, 1394, 1323, 1237, 1187, 1096, 1010, 875, 793, 769, 735, 720 cm^{-1}; HRMS (LC/MS TOF, Multi Mode: APCI/ESI) *m/z* calc'd for $C_{29}H_{43}OSi_2$ $[M + H]^+$: 463.28524, found: 463.28502.



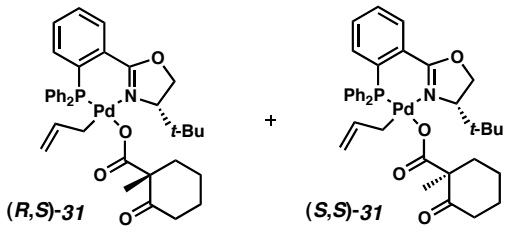
39

Tris{1,5-bis-[3-(triethylsilyl)phenyl]penta-1,4-dien-3-one}dipalladium(0), [Pd_2(mtdba)$_3$] (39):[29] 1,5-Bis-[3-(triethylsilyl)phenyl]penta-1,4-dien-3-one (**38**) (1.70 g, 3.67 mmol, 3.4 equiv) and sodium acetate (1.48 g, 18.0 mmol, 16.7 equiv) were added neat to a flame-dried 100 mL round-bottom flask with a stirbar. The flask was sparged with argon. Dry methanol (44 mL) was added via syringe. Stirring was started, and the solution was heated to 58 °C in an oil bath. Palladium(II) dichloride (382.6 mg, 2.158 mmol, 2 equiv) was added to the heated stirring solution in one portion. The solution was left to stir for about 5 min until it turned a dark purple-brown color. The temperature was reduced to 40 °C, and the solution was left to stir for 2 h. The solution was filtered on a 60 mL frit, and the solid was rinsed with methanol (2 x 15 mL) and then water (2 x 25 mL). The dark purple powder was collected, dissolved in hexanes (15 mL) and was filtered on a frit rinsing with hexanes (25 mL). The filtrate was diluted with ethanol (100 mL, 200 proof), methanol (100 mL), and cooled to –20 °C in a freezer for 36 h forming crystals.[30] Crystals were recovered by filtration on a 30 mL frit and were rinsed with methanol (30 mL) yielding a first crop of tris{1,5-bis-[3-(triethylsilyl)phenyl]penta-1,4-dien-3-one}dipalladium(0) [Pd_2(mtdba)$_3$] (**39**) (62.9% yield, dark purple crystalline

flakes). The filtrate was concentrated in vacuo, redissolved in hexanes (2 mL), diluted with ethanol (5 mL, 200 proof), then methanol (5 mL) and left to crystallize in a –20 °C freezer. After 36 h, crystals formed. The second crop of crystals were recovered by filtration on a 15 mL frit, then were washed with methanol (4 x 5 mL) and then ethanol[31] (10 x 8 mL) yielding a second crop of tris{1,5-bis-[3-(triethylsilyl)phenyl]penta-1,4-dien-3-one}dipalladium(0) [$Pd_2(mtdba)_3$] (**39**) (9.7% yield, 72.6% yield total, dark-purple crystalline flakes). mp 194 °C (decomposition); ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C) δ 7.68–7.79 (comp. m, 3H), 7.76 (d, *J* = 15.8 Hz, 0.3H), 7.69 (br. s, 0.35H), 7.63 (dm, *J* = 7.9 Hz, 0.18H), 7.58 (d, *J* = 7.3 Hz, 0.2H), 7.51–7.37 (comp. m, 3.73H), 7.34–7.12 (comp. m, 4.56H), 7.11–7.00 (comp. m, 1.54H), 6.88 (br. s, 1H), 6.79–6.61 (m, 5.34H), 6.61–648 (m, 2H), 6.15 (d, *J* = 14.0 Hz 1H), 6.07 (br. s, 0.67H), 5.95 (d, *J* = 9.7 Hz, 2H), 5.67 (br. s, 1H), 5.52–5.38 (comp. m, 1.77H), 5.38–5.20 (comp. m, 2.25H), 5.09 (d, *J* = 12.6 Hz, 1H), 4.94 (app. t, *J* = 12.8 Hz, 1.42), 4.88 (br. s, 0.91 H),[32] 1.15–0.94 (m, 54H), 0.94–0.70 (m, 36H); ^{13}C NMR (150 MHz, $CDCl_3$, –10 °C) δ 188.9, 184.6, 182.6, 181.6, 180.8, 144.0, 142.0, 138.96, 138.92, 138.7, 138.6, 138.5, 138.4, 138.1, 138.0, 137.6, 137.4, 137.1, 137.0, 136.7 136.1, 135.8, 135.2, 135.0, 134.7 134.5, 134.4, 134.05, 133.95, 133.71, 133.70, 133.35, 133.34, 133.31, 133.0, 128.5, 128.3, 128.1, 112.4 (br. s), 110.8, 110.2 (br. s), 97.7 (br. s), 96.8 (br. s), 94.3 (br. s), 91.4 (br. s), 89.2 (br. s), 85.7 (br. s), 84.4 (br. s), 84.1 (br. s), 7.71, 7.68, 7.67, 7.654, 7.647, 7.5, 3.4, 3.32, 3.28, 3.26, 3.24, 3.23, 3.1; IR (neat film, NaCl) 3080, 3045, 3023, 2954, 2909, 2875, 1621, 1585, 1570, 1544, 1464, 1416, 1386, 1323, 1297, 1239, 1186, 1120, 1082, 1010, 975, 911, 877, 861, 791, 736, 720, 686, 611 cm^{-1}; IR (Fluorolube® mull, CaF_2) 3076, 3041, 3020, 2950, 2906, 2872, 1620, 1586, 1568, 1544, 1455, 1415, 1385 cm^{-1}; HRMS (high field FAB, 2-

nitrophenyl octyl ether) *m/z* calc'd for $C_{87}H_{126}O_3Pd_2Si_6$ $[M]^+$: 1601.6505, found: 1601.6477.

2.6.4 Synthesis, Handling, and Characterization Methods for Intermediate 1:



2.6.4.1 Synthesis

Complexes (*R*,*S*)-31 and (*S*,*S*)-31: In a glove box with a nitrogen atmosphere, (*S*)-*t*-BuPHOX ligand (**1**) (148.8 mg, 384.0 mmol, 1.24 equiv) was added to a 20 mL scintillation vial. $[Pd_2(mtdba)_3]$ (**39**) (248.9 mg, 155.4 mmol, 0.5 equiv) was weighed into a 1 dram vial.[8] Anhydrous THF (1 mL) was added to the 20 mL vial containing (*S*)-*t*-BuPHOX lignad (**1**). The 20 mL scintillation vial was swirled manually until all the (*S*)-*t*-BuPHOX ligand (**1**) had dissolved. Anhydrous THF (3 x 1 mL) was added into the 1 dram vial containing $[Pd_2(mtdba)_3]$ (**39**), each portion was mixed manually by pipette and then added dropwise to the solution of (*S*)-*t*-BuPHOX ligand (**1**) in the 20 mL scintillation vial. The solution was swirled manually by hand for 1 min, and then left to stand and mix by diffusion for 1.5 h. The solution was cooled to –36 °C in a freezer in the glove box. Once cooled, the solution was then moved to a precooled aluminum block at –36°C in the glove box. Then, 1-methyl-2-oxo-cyclohexanecarboxylic acid allyl ester (β-ketoester **2**) (157 mg, 800 mmol, 2.57 equiv) was added via a syringe in a single portion. The solution was stirred manually for 1 min while cold, and moved to a –36 °C

freezer in the glove box. The reaction was left to stand for 10 min in the freezer. The solution was then diluted with hexanes (12 mL) that had been precooled to –20 °C, and then the mixture was concentrated in vacuo in a –20 °C freezer in the glove box to roughly 10 mL. The solution was moved in 2 mL portions to another 20 mL scintillation vial in a precooled aluminum block at –36 °C where each portion was individually triturated with hexanes (5 mL) that had been precooled to –20 °C, then the supernatant was decanted via pipette. Solvent was removed from the precipitated material in vacuo at –20 °C in a freezer in the glove box to afford a mixture of complexes (*S*,*S*)- **31** and (*R*,*S*)- **31** (72.4 mg, 33.8% yield, bright yellow powder). ^{1}H NMR (600 MHz, $THF_{d\text{-}8}$, –28 °C) δ 8.19 (app. br. t, *J* = 3.5 Hz, 1H), 7.69 (app. t, *J* = 7.5 Hz, 1H), 7.62 (app. t, *J* = 7.2 Hz, 1H), 7.59–7.46 (comp. m, 8H), 7.25 (app. t. *J* = 9.0 Hz, 2H), 7.03 (app. t. *J* = 8.8 Hz, 1H), 6.23 (br. s, 1H), 5.11 (s, 1H), 4.57 (d, *J* = 9.7 Hz, 1H), 4.55–4.47 (m, 1H), 4.47 (br. s, 1H), 4.40-4.23 (comp. m, 2H), 3.06 (br. s, 0.35H), 2.94–2.85 (br. m, 1H), 2.86–2.77 (m, 0.65H), 2.48 (dd, *J* = 14.0, 13.8 Hz, 1H), 2.17 (d, *J* = 13.2 Hz, 0.35H), 2.11 (d, *J* = 12.9 Hz, 0.65H), 1.97–1.85 (m, 1H), 1.84–1.70 (m, 1H), 1.63–1.38 (m, 1H), 1.38–1.45 (m, 1H), 1.33–1.18 (m, 1.3H), 1.14 (s, 1.95H), 1.11 (s, 1.05H), 0.92–0.87 (m 0.35H), 0.69 (s, 9H); ^{13}C NMR (150 MHz, $THF_{d\text{-}8}$, –28 °C) δ 210.3, 210.2, 176.7, 176.6, 163.6, 143.8 (app. br. s), 135.8, 134.9 (d, J_{CP} = 11.0 Hz), 134.7 (d, J_{CP} = 12.2 Hz), 133.7 (d, J_{CP} = 6.6 Hz), 133.4 (d, J_{CP} = 7.7 Hz), 132.4 (d, J_{CP} = 9.4 Hz), 132.1, 131.4, 131.08, 131.02, 130.7, 130.45, 130.37, 130.04, 129.97, 129.9, 129.8, 129.3, 129.0. 106.3 (app. br. s), 70.3, 68.1, 67.9, 67.8, 59.4, 41.85, 41.81, 40.6, 40.5, 35.1, 29.2 (app. br. s), 28.9, 28.7, 25.9, 25.8, 25.7, 24.55, 24.48, 23.0, 22.9; ^{31}P NMR (121.4 MHz, $THF_{d\text{-}8}$, 24 °C) δ 30.9; ^{31}P NMR (121.4 MHz, $THF_{d\text{-}8}$, –20 °C) δ 30.8; IR (neat film, NaCl) 3065, 2956, 2930,

2858, 1708, 1662, 1623, 1613, 1571, 1483, 1465, 1437, 1372, 1346, 1313, 1243, 1166, 1142, 1117, 1099, 1062, 1029, 959, 900, 876, 848, 814, 781, 696, 675 cm^{-1}; IR (Fluorolube® mull, CaF_2) 3076, 3055, 3016, 2959, 2934, 2924, 2874, 2853, 1711, 1634, 1616, 1604, 1568, 1480, 1465, 1448, 1433, 1373 cm^{-1}; HRMS (FAB, 2-nitrophenyl octyl ether) *m/z* calc'd for $C_{28}H_{31}NOPPd$ $[M - C_8H_{11}O_3]^+$: 534.1178, found: 534.1187; X-ray quality crystals were grown by partially dissolving freshly synthesized intermediate **31** in cold (–20 °C) THF using the undissolved material to act as a nucleation site for crystals, and then the solution was layered with cold hexanes (–20 °C). Diethyl ether was added dropwise until most of the finer precipitation on the boundary between the layers had redissolved and layer diffusion was allowed to progress at –36 °C in a glove box freezer.

2.6.4.2 Handling and Characterization Methods for Complexes (*S,S*)-31 and (*R,S*)-31

Due to the instability of complexes (*S*,*S*)-**31** and (*R*,*S*)-**31**, basic handling and the acquisition of characterization data often required special procedures to achieve good reproducible results. These procedures are outlined here.

General Handling Notes: All glassware and metalware were precooled to –36 °C in a freezer for 1 h before being allowed to come into contact with complexes (*S*,*S*)-**31** and (*R*,*S*)-**31**. If during operation, glassware or metalware warmed to the point that it was just barely perceptibly cool through triple gloves, it was returned to the –36 °C freezer for at least 20 min before being used again. All solvents that came in contact with complexes (*S*,*S*)-**31** and (*R*,*S*)-**31** were precooled to either –36 °C or –20 °C in a freezer as indicated. Complexes (*S*,*S*)-**31** and (*R*,*S*)-**31** were only ever exposed to argon or nitrogen atmospheres; even as a solvent-free crystalline solid at subzero temperatures

these complexes appear to react with air and possibly moisture. Decomposition of these complexes by poor handling could be readily determined by indicative color change. Healthy samples of the complexes are a bright yellow, reminiscent of a classic highlighter pen. Air exposure leads to an orange color change while minimal thermal decomposition leads to a more subtle color change resulting in a yellow-beige hue. In cases where some decomposition had occurred, samples could be partially recovered with tolerable, but not analytical, purity by manually excising incorrectly colored regions using precooled implements. Such recovered samples are unfit for NMR or IR characterization, but give consistent results when used in reactions. Samples of complexes (*S*,*S*)-**31** and (*R*,*S*)-**31** store well as a desolvated solid at –36 °C in a glove box freezer for months, but do eventually show signs of decomposition by ^{1}H NMR.

Thin-Film IR on NaCl plates: In a glove box, a few milligrams of the diastereomeric mixture of complexes (*S*,*S*)-**31** and (*R*,*S*)-**31** were added to a half-dram vial in an aluminum block that had been precooled to –36 °C in a freezer. The sample was dissolved in minimal anhydrous THF that had been precooled to –36 °C in a freezer, and then the solution was carefully deposited via a pipette on a NaCl IR plate that had been precooled to –36 °C in a freezer. The IR plate was quickly moved into a small desiccator inside the glove box, and the desiccator was inserted into a –20 °C freezer in the glove box. A vacuum hose was connected to the desiccator inside the glove box in the –20 °C freezer, and a gentle vacuum was applied reducing the solution on the IR plate to a thin yellow-green film over 5 h. The thin film was then sandwiched between a second NaCl IR plate that had been precooled to –36 °C. The fine gap between the two plates was sealed over with Parafilm®, and the sealed plates were returned to the

desiccator in a –20 °C freezer for 20 min. The desiccator was sealed, quickly removed from the glove box, and then partially submerged in a bucket of powdered dry ice that was carried to the spectrometer. The sealed plates were removed from the desiccator whereupon they quickly frosted over. A Kimwipe® was used to vigorously polish both exterior faces of the two-plate sandwich until they were just barely warm enough that they did not readily frost over (roughly 1 min), but that the sample in between the two plates was still cold. The two-plate sandwich was then inserted into the spectrometer just above a fresh dish full of anhydrous $CaCl_2$ and a rushing stream of nitrogen. It is recommended that new or otherwise valuable NaCl plates not be used for this procedure as they are left opaque and lightly pitted by the unavoidable quick frosting and polishing.

Fluorolube® mull IR on CaF_2 plates: In a glove box, a small amount of partially frozen Fluorolube® was spread thinly with a spatula across the center of a CaF_2 IR plate that had been precooled to –36 °C in a freezer. A few milligrams of the mixture of complexes (*S*,*S*)-**1** and (*R*,*S*)-**1** were added on top of the Fluorolube® film as a powder. The powder and Fluorolube® film were then sandwiched between a second CaF_2 IR plate that had been precooled to –36 °C in a freezer, and the materials were mulled briskly between the two cold IR plates for 1 min. The plates were sealed, moved cold to the spectrometer and spectra were taken as per the procedure for the thin film IR on NaCl plates above. Unlike NaCl plates, CaF_2 plates seem unblemished by their unavoidable exposure to frost and polishing in this procedure.

NMR Spectra (^{1}H, ^{13}C, ^{31}P): In a glove box with a nitrogen atmosphere, roughly 20 mg of the mixture of complexes (*S*,*S*)-**31** and (*R*,*S*)-**31** were added to a half-dram vial in an aluminum block, both of which had been precooled to –36 °C. A fresh ampule of

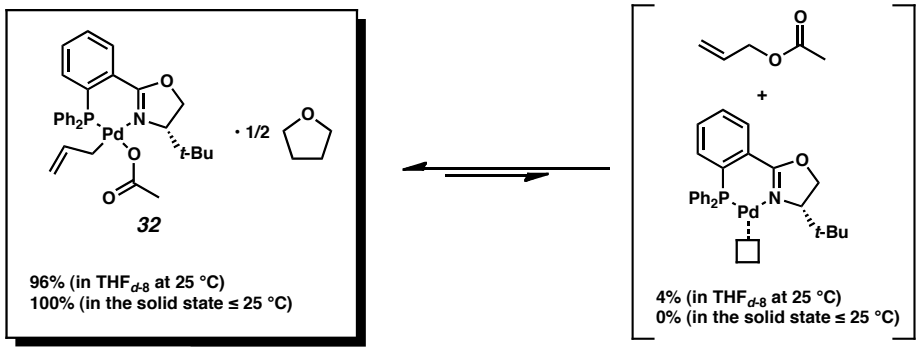
$THF_{d\text{-}8}$ that had been precooled to –36 °C was opened, and 0.75 mL of $THF_{d\text{-}8}$ was used portion-wise to dissolve the material and move it into an NMR tube that had been precooled to –36 °C. The tube was quickly sealed with a plastic cap and removed from the glove box, where it was immediately submerged to within a few centimeters of its top in powdered dry ice in a dewar. The dewar was carried to the spectrometer, which was then cooled to the desired temperature before quickly removing the NMR tube from the dry ice and inserting it into the instrument. Phosphorus spectra obtained at reduced temperatures could not be directly referenced to phosphoric acid as outlined in the Materials and Methods section due to the relatively high freezing point of the phosphoric acid standard. Instead, subzero ^{31}P NMR spectra were referenced to free (*S*)-*t*-BuPHOX ligand (δ –5.95) used as either an internal or external standard in $THF_{d\text{-}8}$. The reported 24 °C ^{31}P NMR spectrum was recorded by generating the mixture of intermediates (*S*,*S*)-**31** and (*R*,*S*)-**31** in situ as outlined in the section on NMR experiments in this supporting information (Page 5).

2.6.4.3 Effervescent Crystals

Synthesis: In a nitrogen glove box (*S*)-*t*-BuPHOX ligand (**1**) (96.7 mg, 250 μmol, 1.3 equiv) followed by $[Pd_2(dba)_3]$ (86.2 mg, 94.1 μmol, 0.5 equiv) were added, neat, into a 20 mL scintillation vial. Anhydrous THF (8 mL) was filtered through a pipette with glass filter paper directly into the 20 mL scintillation vial. The solution was mixed manually by pipette for two minutes, and then left to stand and mix by diffusion for 20 min. During this time an initially dark red-purple solution formed, which then lightened to a dark, rich, orange color. The solution was filtered through a pipette with glass filter paper into five separate 1 dram vials evenly (1.6 mL each). This filtration

separated a rich orange filtrate from a black precipitate presumed to be aggregated palladium(0) metal. The vials were sealed with plastic screw caps and removed from the box. On the bench, the vials were individually opened, and β-ketoester **8** (210 mg, 1.07 mmol, 28.5 equiv), was added by syringe to each vial, after which they were resealed. The vials were then swirled manually for 5 seconds, during which time the solution underwent a rapid color change from a rich orange to a lighter yellow green. The vials were left to stand and mix by diffusion for an additional 10 min. Each vial was then opened and inserted into a 20 mL scintillation vial containing 5 mL of hexanes for vapor diffusion. The atmosphere of each two-vial apparatus was gently displaced with a flow of argon from a hose, and then the 20 mL vial was sealed tightly with a plastic screw cap. These self-contained vapor diffusion apparatus were left to slowly crystallize at –20 °C in a freezer for a week. During this time the inner vials begin to grow one of two crystal forms, clear colorless fine feathery needles or clear colorless large glassy blocks. The formation of colored crystals results from impurities or improper handling. The type of crystal form often varies from vial to vial, but is usually homogeneous within a given vial. Only the clear colorless large glassy blocks show visible signs of effervescence, though various characterization methods (HRMS and partial crystal structure) suggest that both crystal forms are predominantly composed of intermediate **31**, and both can be thermally decomposed to yield 2-allyl-2-methylcyclohexanone with reproducible and reasonably high enantioinduction.

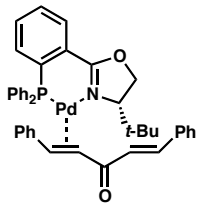
2.6.5 Synthesis and Characterization of Other New Molecules



Allyl Acetate Complex 32, half THF adduct:[33] In a nitrogen glove box (*S*)-*t*-BuPHOX ligand (**3**) (75.6 mg, 195 μmol, 1.3 equiv) was weighed into a 20 mL scintillation vial. $[Pd_2(mtdba)_3]$ (**39**) (120.2 mg, 75.06 μmol, 0.5 equiv) was weighed into a 1 dram vial. Anhydrous THF (0.5 mL) was added to the 20 mL scintillation vial, which was swirled manually for 30 s until all of the (*S*)-*t*-BuPHOX ligand (**1**) had dissolved. Anhydrous THF (3 x 0.5 mL) was added to the 1 dram vial containing $[Pd_2(mtdba)_3]$ (**39**). The solution in the 1 dram vial was mixed manually by pipette resulting in the formation of a dark purple solution, which was added dropwise to the solution in the 20 mL scintillation vial containing (*S*)-*t*-BuPHOX ligand (**1**). The resulting solution in the 20 mL scintillation vial was swirled manually for 1 min, and then left to stand and mix by diffusion for 1.5 h, during which time the solution turned from a dark purple to a rich orange color. Allyl acetate (146 mg, 1.46 mmol, 9.7 equiv) was added in one portion via syringe. The solution was swirled manually for 1 min then left to stand for 20 min, during which time its color lightened slightly to a yellow-orange. The solution was then carefully layered with hexanes (18 mL) and allyl acetate (200 μL) and left to crystallize via layer diffusion in a –20 °C freezer in the glove box resulting in

the formation of small yellow-green crystal clusters and powder. This mixture of crystals and powder was redissolved in THF (3 x 0.5 mL) and filtered through a pipette filter with glass filter paper into a 1 dram vial to separate a yellow-orange solution from a small amount of gray material. The solution was then layered with hexanes (0.5 mL) causing the solution to become cloudy with precipitate. Diethyl ether (1 mL) was added to the solution carefully, so as not to disturb the interface between the two layers, and was added until most of the finer suspended precipitate had dissolved, leaving two distinct homogenous layers. The vial was then left in a –36 °C freezer to crystallize via layer diffusion. The mother liquor was decanted, the crystals were powdered, washed with hexanes (1 x 5 mL), and azeotroped with hexanes (1 x 5 mL), before being dried in vacuo affording complex **32** as a half THF adduct (34.3 mg, 38.5% yield, yellow green powder). mp 128–131 °C (decomp); ^{1}H NMR (500 MHz, $THF_{d\text{-}8}$) δ 8.18 (ddd, J_{HP} = 4.0 Hz, J = 7.9 Hz, 1.1 Hz, 1H), 7.64 (app. tt, J = 7.7, 1.3 Hz, 1H) 7.56–7.40 (comp. m, 9H), 7.32–7.26 (m, 2H) , 7.04 (ddd, J_{HP} = 1.2 Hz, J = 10.0, 7.8, 1H), 6.19 (ddddd, J_{HP} = 1.7 Hz, J = 11.6, 11.1, 10.8, 10.2 Hz, 1H), 4.56–4.39 (comp. m, 3.7H), 4.39–4.31 (m, 1H), 3.64–3.59 (m, 2H), 2.75 (br. s, 1H), 1.99–1.84 (comp. m, 1.3 H), 1.80 (s, 3H), 1.79–1.75 (m, 2H), 0.72 (s, 9H); ^{13}C NMR (125 MHz, $THF_{d\text{-}8}$) δ 174.8, 163.5 (d, J_{CP} = 2.7 Hz), 144.1 (app. br. s), 135.9 (d, J_{CP} = 1.8 Hz), 134.96 (d, J_{CP} = 10.1 Hz), 134.86 (d, J_{CP} = 11.5 Hz), 133.2 (d, J_{CP} = 10.1 Hz), 133.1 (d, J_{CP} = 8.3 Hz), 132.2 (d, J_{CP} = 1.5 Hz), 132.1 (d, J_{CP} = 2.3 Hz), 131.9 (d, J_{CP} = 35.9 Hz), 131.7 (d, J_{CP} = 2.8 Hz), 131.5 (d, J_{CP} = 30.4 Hz), 130.9 (d, J_{CP} = 12.4 Hz), 130.3 (d, J_{CP} = 50.6 Hz), 129.8 (d, J_{CP} = 11.0 Hz), 129.6 (d, J_{CP} = 11.0 Hz), 106.0 (app. br. s), 75.4, 70.3, 68.4, 35.1, 30.1 (app. br. s.), 26.5, 26.1, 24.9 ; ^{31}P NMR (121.4 MHz, $THF_{d\text{-}8}$) δ 31.1; IR (neat film, NaCl) 3059, 2962, 2869, 1632, 1606,

1581, 1482, 1436, 1372, 1321, 1244, 1213, 1192, 1144, 1115, 1099, 1063, 1058, 1028, 958, 928, 876, 781, 747, 730, 708; IR (Fluorolube® mull, CaF_2) 3066, 2958, 2909, 2867, 1637, 1609, 1580, 1565, 1481, 1436, 1372; HRMS (FAB, 2-nitrophenyl octyl ether) *m/z* calc'd for $C_{30}H_{35}O_3NPPd$ $[M + H]^+$: 594.1390, found: 594.1393. X-ray quality crystals were obtained by layering a concentrated THF solution of complex **7** with hexanes. Diethyl ether was added dropwise until most of the finer precipitation on the boundary between the layers had redissolved. Allyl acetate (≈ 10 μL per 30 mg of **32**) was added for stability, and layer diffusion was allowed to progress at – 36 °C in a freezer in a nitrogen glove box.

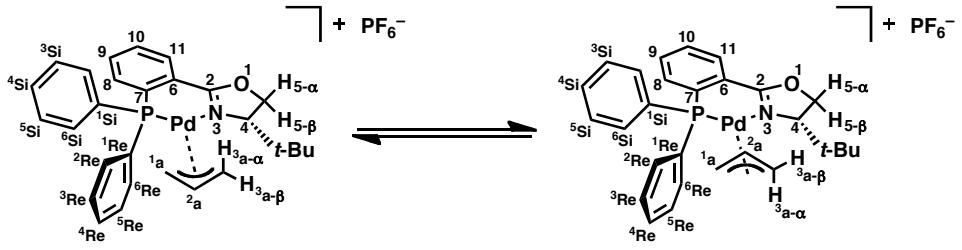


30

[{(*S*)-*t*-BuPHOX}Pd(dba)] precatalyst 30:[34] In a nitrogen glove box (*S*)-*t*-BuPHOX ligand (**1**) (323.4 mg, 830.4 μmol, 2.5 equiv) and $[Pd_2(dba)_3]$ (302.4 mg, 330 μmol, 1 equiv) were weighed directly into a 100 mL round bottom flask with a stirbar, neat, in the order specified. Anhydrous THF (70 mL) was filtered through a pipette filter with glass filter paper and added to the flask. Stirring was started and the solution quickly became a dark red-purple color. The solution was left to stir for 8 h, turning a dark orange color with a small amount of black precipitate. The solution was filtered through a 15 mL frit separating an intensely orange-red solution from a thick silting of insoluble black powder presumed to be particulate Pd(0). The solution was concentrated in vacuo to a thin foamy red film. Minimal diethyl ether (pipette filtered, 5 x 1.2 mL) was used to

dissolve the film and transfer it to a 50 mL round-bottom flask. An orange-red powder started to precipitate from the ethereal solution in the new flask. The ether solution was layered with 20 mL of hexanes, and then cooled to –36 °C in a glove box freezer. The solution was filtered on a 30 mL frit, separating a bright orange fluffy solid from a bright orange filtrate. The orange solid was rinsed with hexanes until the filtrate was almost clear (20 x 5 mL). The material was subsequently recrystallized from diethyl ether layered with hexanes, followed by a second recrystalization using toluene layered with hexanes. The solids were rinsed with 1:1 toluene/hexanes, diethyl ether, and then 1:1 Et_2O/hexanes. The material was dissolved in THF and layered with hexanes and left to precipitate at –36 °C in a glove box freezer. The resulting light yellow solution was decanted, and the solids rinsed with hexanes (2 x 3 mL). This THF/hexanes precipitation and hexanes wash was repeated four times. The material was then azeotroped in hexanes (4 x 5 mL) and dried in vacuo for 16 h to afford precatalyst **30** (300 mg, 62.2%, yellow powder). mp 144.5–147 °C; ^{1}H NMR (500 MHz, $THF_{d\text{-}8}$) δ 8.18 (br. s. 0.07H), 8.12–8.01 (m, 0.89H), 7.76–7.66 (comp. m, 0.19H), 7.61 (br. s. 0.23H), 7.53 (d, *J* = 7.3 Hz, 1.43H), 7.51–6.95 (m, 17.57H) 6.87 (br. s, 4H), 6.68 (br. s, 0.15H), 6.53 (app. t, *J* = 8.7 Hz, 1.48H), 5.04 (br. s, 0.09H), 4.89 (m, 0.73H), 4.76 (s, 0.08H), 4.63 (app. dd, *J* = 9.3, 9.0 Hz, 0.75H), 4.53 (br. s, 0.14H), 4.30 (m, 1.07H), 4.23–4.13 (m, 0.77H), 4.05 (app. dd, *J* = 9.5, 9.3 Hz, 0.75H), 4.01 (br. s, 0.2 Hz, 0.2H), 2.49 (s, 0.02H), 2.48–2.44 (comp. m, 0.04H), 2.04 (s, 0.1H), 1.37–1.26 (m, 0.24H), 0.82 (br. s, 8H), 0.42 (br. s, 1H); ^{13}C NMR (125 MHz, $THF_{d\text{-}8}$) δ 184.2, 164.6, 146.4, 143.2, 138.2, 137.4 (br. s), 136.1, 135.8, 135.6, 135.3, 135.1, 134.83, 134.75, 134.5, 134.2, 134.1, 133.4, 133.3, 132.7, 131.3, 131.2, 131.1, 130.78, 130.77, 130.6, 130.3, 129.8, 129.6, 129.5, 129.4, 129.3, 129.2, 129.1,

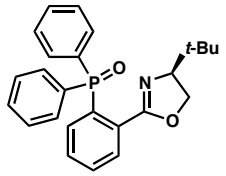
128.8, 128.3, 127.4 (br. s), 126.8, 125.9, 124.2, 80.2 (br. s), 79.9 (br. s), 69.5 (br. s), 68.9, 68.1, 58.3 (br. s), 35.5, 30.5; ^{31}P NMR (121.4 MHz, $THF_{d\text{-}8}$) δ 21.26 (0.1P), 18.97 (0.9P); IR (neat film, NaCl) 3055, 2958, 2867, 1638, 1622, 1581, 1568, 1496, 1472, 1435, 1359, 1332, 1310, 1280, 1239, 1202, 1141, 1108, 1095, 1068, 1054, 1028, 998, 967, 920, 862, 761, 747 cm^{-1}; IR (Fluorolube® mull, CaF_2) 3055, 3009, 2953, 2867, 1638, 1618, 1597, 1568, 1578, 1493, 1466, 1448, 1433, 1359 cm^{-1}; HRMS (FAB, 2-nitrophenyl octyl ether) *m/z* calc'd for $C_{42}H_{41}PPdO_2N$ $[M + H]^+$: 728.1910, found: 728.1925. X-ray quality crystals were grown from THF via successive layer diffusion in a glove box with Et_2O at –20 °C to form seed crystals, and then hexanes at –20 °C.



***exo*-25** ***endo*-25**

[({*S*}-*t*BuPHOX)Pd(allyl)]PF_6 Salt and 1/2 EtOH adduct (25 PF_6^-): The hexaflourophosphate salt of complex **25** was prepared using Zehnder's method[35] with (*S*)-*t*-BuPHOX ligand (**1**) to afford a quantitative yield of rapidly interconverting *exo* and *endo* allyl isomers (ca. 60/40 in $CDCl_3$, 67/33 in $THF_{d\text{-}8}$ as the 1/2 EtOH adduct, and 44/56 in the solid state crystallized from EtOH as a 1/2 EtOH adduct) as a light yellow powder; mp (1/2 EtOH adduct) 152–154 °C (decomp.); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.30 (app. ddd, *J* = 7.7, 4.1, 1.1 Hz, 0.6H), 8.24 (app. ddd, *J* = 7.7, 4.4, 1.1 Hz, 0.4H), 7.74–7.42 (comp. m, 8H), 7.39–7.11 (comp. m, 4H), 7.04–6.87 (comp. m, 1H), 5.96–5.82 (m, 0.4H), 5.82–5.67 (m, 0.6H), 4.96–4.86 (comp. m, 1H), 4.68 (app. q, *J* = 9.9 Hz, 1H),

4.49 (app. dt, J_d = 11.3 Hz, J_t = 3.9 Hz, 1H), 4.19 (app. dt, J_d = 11.3 Hz, J_t = 4.4 Hz, 1H), 4.03 (app. dd, J = 14.3, 9.4 Hz, 0.6H), 3.63–3.48 (comp. m, 1H), 3.32 (app. d, J = 6.6 Hz, 0.4H), 3.16 (app. d, J = 12.7 Hz, 0.4H), 2.77 (app. d, J = 12.1 Hz, 0.6H), 0.64 (s, 3.5 H), 0.56 (s, 5.5 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.9–164.8 (3 peaks), 134.9, 134.8, 134.0–133.3 (7 peaks), 132.9–132.6 (4 peaks), 132.2–132.1 (3 peaks), 131.8 (app. d, J = 2.3 Hz), 130.2–128.8 (13 peaks), 128.5–127.8 (5 peaks), 127.3, 122.4 (app. d, J = 6.0 Hz), 122.4, 83.3–79.4 (6 peaks), 69.8, 69.7, 58.6, 54.1, 54.0, 34.3, 25.2; ^{31}P NMR (121.4 MHz, $CDCl_3$) δ 23.2 (s, 0.6P), 22.2 (s, 0.4P), –143.4 (septet, J_{PF} = 711.0 Hz, 1P); ^{31}P NMR (121.4 MHz, $THF_{d\text{-}8}$) δ 23.5 (s, 0.67P), 22.5 (s, 0.33P), –143.8 (septet, J_{PF} = 710.4 Hz, 1P); ^{19}F NMR (242 MHz, $CDCl_3$) δ –73.7 (d, J_{FP} = 712.6 Hz); IR (Neat Film from $CDCl_3$, NaCl) 3062, 2964, 2872, 2271, 1971, 1899, 1826, 1621, 1584, 1568, 1482, 1437, 1372, 1315, 1249, 1211, 1145, 1121, 1100, 1060, 1028, 958, 913, 836, 778, 732, 697, 678 cm^{-1}; HRMS (FAB, 3-nitrobenzyl alcohol) m/z calc'd for $C_{28}H_{31}ONPPd$ $[M–PF_6]^+$: 534.1178, found 534.1182; Anal. calcd for $C_{29}H_{34}F_6NO_{1.5}P_2Pd$ (1/2 EtOH adduct): C, 49.55; H, 4.88; N, 1.99; O, 3.41. Found: C, 49.48; H, 4.82; N, 1.97; O, 3.67. $[\alpha]_D^{27.1}$ +256.6 (*c* 3.72, CH_2Cl_2). X-ray quality crystals were grown from the slow cooling of a hot and concentrated EtOH solution. See CCDC deposition number: 245187 or Appendix 2 for X-ray structural data of this compound.



i

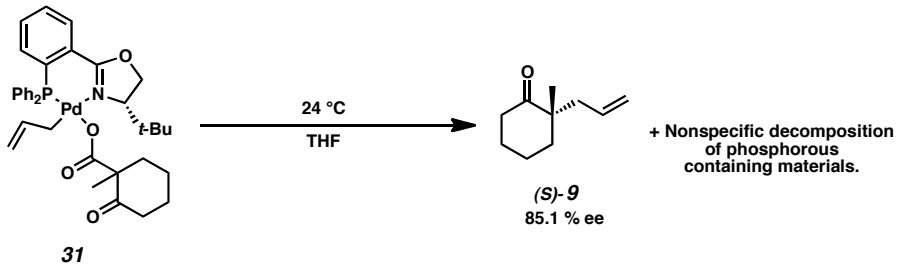
(*S*)-*t*-BuPHOX Oxide (i): To a solution of (*S*)-*t*-BuPHOX ligand (**1**) (150 mg, 0.387 mmol, 1 equiv) in THF (2.5 mL) was added a 5% aqueous H_2O_2 solution (1.94 mL). After 15 min the reaction mixture was diluted with EtOAc (5 mL) and brine (5 mL), washed with 10% aqueous Na_2CO_3 (5 mL) and brine (5 mL), dried with magnesium sulfate, and filtered. Chromatography was performed with 5% methanol in dichloromethane on silica gel to afford (*S*)-*t*-BuPHOX oxide (**i**) (149.3 mg, 96% yield, white foam). TLC (R_f 0.20, 3% methanol in dichloromethane); ^{1}H, NMR (300 MHz, $CDCl_3$) δ 7.95 (ddd, J = 7.5, 3.9, 1.2 Hz, 1H), 7.81–7.33 (comp. m, 7H), 7.52–7.31 (comp. m, 7H), 3.84 (dd, J = 8.1, 8.1 Hz, 1H), 3.57, (dd, J = 9.9 Hz, J = 9.9 Hz, 1H), 3.41 (dd, J = 9.9 Hz, 8.4 Hz, 1H), 0.77 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.1, 135.0 (d, J_{CP} = 10.1 Hz), 133.7 (d, J_{CP} = 107.1 Hz), 133.3 (d, J_{CP} = 11.7 Hz), 138.2 (app. dd, J_{CP} = 12.3, 1.4 Hz), 75.9, 68.8, 33.6, 25.8; ^{31}P NMR (121.4 MHz, $CDCl_3$) δ 30.3; ^{31}P NMR (121.4 MHz, $THF_{d\text{-}8}$) δ 27.2;[36] IR (Neat Film, NaCl) 3057, 2957, 2903, 2868, 2217, 1664, 1589, 1565, 1477, 1438, 1356, 1337, 1307, 1248, 1201, 1119, 1108, 1067, 1028, 963, 930, 905 cm^{-1}; HRMS (FAB) *m*/*z* calc'd for $C_{25}H_{27}O_2NP$ $[M]^+$: 404.1779, found 404.1799; $[\alpha]_D^{27.6}$ –69.3 (*c* 1.96, CH_2Cl_2).

*2.6.6 Controlled Thermal Decomposition of Intermediate **31***

2.6.6.1 Controlled Thermal Decomposition of Intermediate 31 in the Absence of dba Ligand in Solution (THF)

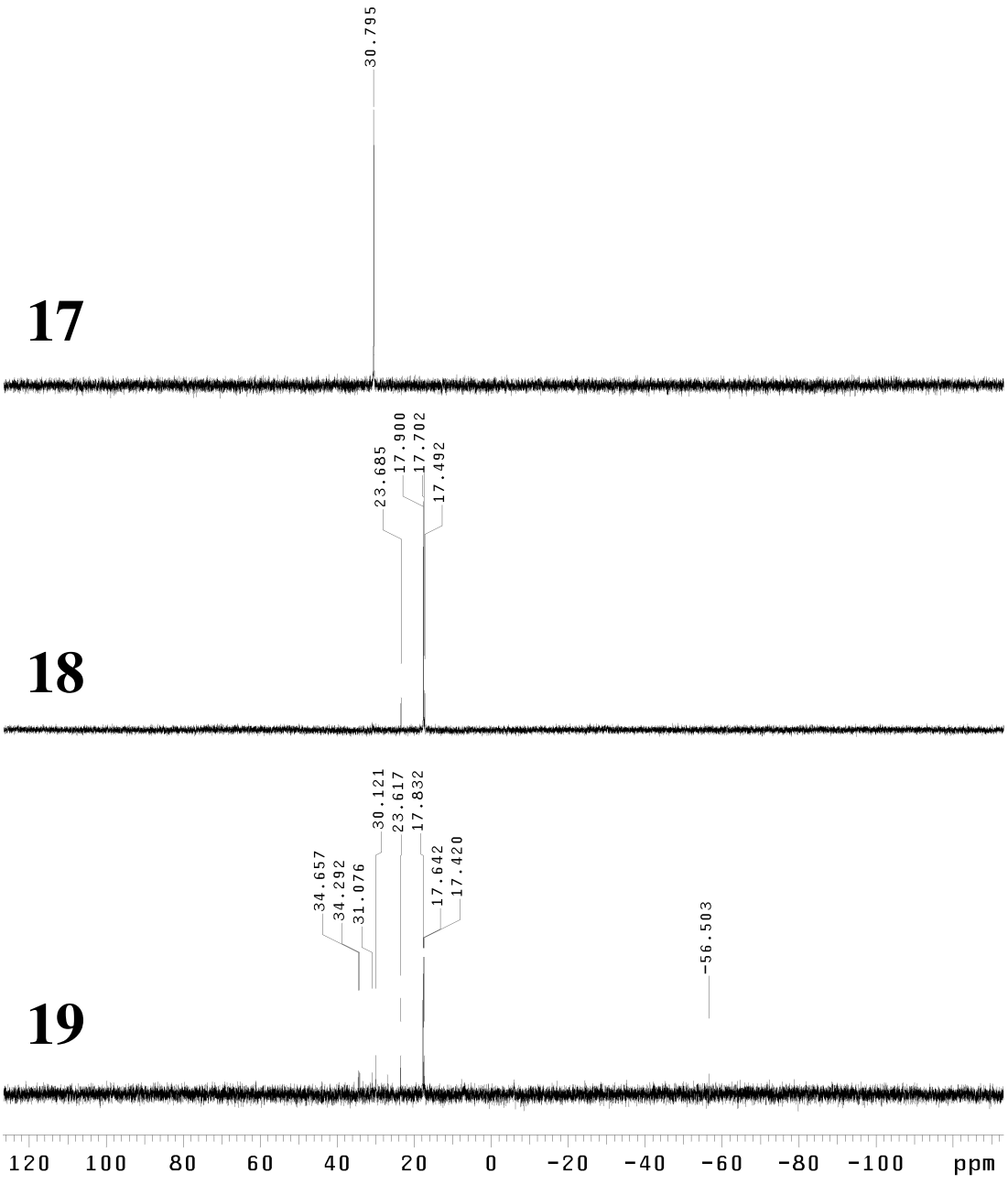
Until the sample left the glove box, all of the following operations were performed in a cold aluminum block with implements and containers [such as the half-dram vial and NMR tube] that had been precooled to –36°C in a glove box freezer. In a nitrogen glove box, intermediate **31** (22.8 mg, 33.0 μmol, 1 equiv) was weighed into a half-dram vial. A 1 mL ampule of $THF_{d\text{-}8}$ that had been precooled to –36°C in a glove box freezer was opened, and its contents were used to dissolve the sample of intermediate **31** and transfer it to an NMR tube. The NMR tube was tightly sealed with a plastic cap, and was then cooled again to –36 °C in a glove box freezer for 20 min. The NMR tube was then quickly removed from the glove box and immediately submerged in powdered dry ice. The NMR probe was precooled to –20 °C while the NMR tube was still submerged in dry ice. The NMR tube was removed from the dry ice, quickly inserted into the precooled spectrometer, and NMR spectrum #17 was taken at –20 °C. The NMR tube was then allowed to sit at 24 °C outside the spectrometer for 30 minutes, during which time the solution turned from light yellow-green to a light orange color. After the 30 min spent outside the spectrometer, the NMR tube was resubmerged in dry ice until NMR spectrum #18 was taken with the probe regulated at 24 °C, showing trace amounts of intermediate **31** left. The NMR tube was left to sit outside the spectrometer at 24 °C for 2 h during which time the solution began to turn from light orange to dark red-purple. NMR spectrum #19 was taken at 24 °C at this time revealing complete consumption of intermediate **31**. The NMR tube was cycled into a nitrogen glove box and the solution

was concentrated in vacuo to a dark purple semisolid. The semisolid was rinsed with hexanes, and this wash was saved. Attempts to separate the semisolid into its constituent compounds were unsuccessful. The hexane wash was removed from the box and concentrated in vacuo to a dark brown semisolid. Chromatography was performed with 5% ether in petroleum ether to afford (*S*)-2-allyl-2-methylcyclohexanone **9** (2.0 mg, 40% yield, 85.1% *ee* [assay: GC, G-TA column {100 °C isothermal for 30 min}, major enantiomer (*S*) ret. time = 14.897 min, minor enantiomer (*R*) ret. time = 17.313 min], clear colorless oil).


Ph2P
Pd
N
O
t-Bu
O
O
O
24 °C
THF
O
+ Nonspecific decomposition of phosphorous containing materials.

31

(S)-9
85.1 % ee


30.795
17
23.685
17.900
17.702
17.492
18
30.121
23.617
17.832
34.657
34.292
31.076
17.642
17.420
-56.503
19
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
ppm

2.6.6.2 Controlled Thermal Decomposition of Intermediate 31 in the Presence of dba Ligand in Solution (THF) (Isolation of Complex 30 Only)

Until the sample left the glove box, all of the following operations were performed in a cold aluminum block with implements and containers, such as the half-dram vial and NMR tube, that had been precooled to –36°C in a glove box freezer. Intermediate **31** (11.3 mg, 16.4 μmol, 1 equiv) was weighed into a half-dram vial. Dibenzylideneacetone (9.6 mg, 46 μmol, 2.8 equiv) was added to the half-dram vial. A 1 mL ampule of $THF_{d\text{-}8}$ that had been precooled to –36 °C in a glove box freezer was opened and the contents were added to the half-dram vial. The resulting solution was mixed manually by pipette for 1 min until all the solids had dissolved forming a yellow solution. The solution was transferred to an NMR tube via pipette. The NMR tube was sealed with an appropriately sized septum, quickly removed from the glove box, and submerged in dry ice to within two inches of its cap. An initial NMR was taken at –20 °C revealing intermediate **31** as the only detectable phosphorous-containing compound.[3] The tube was left to sit at 24 °C for 40 min, after which time a ^{31}P NMR spectrum indicated complete conversion to precatalyst complex **30** as the only detectable phosphorous-containing compound. The NMR tube was cycled back into a nitrogen glove box, where its contents were moved to a 1 dram vial and concentrated in vacuo to roughly 50 μL of thick red-orange oil. The oil was triturated with hexanes (1 mL) and the resulting mixture was filtered in a pipette with glass filter paper. The solids were rinsed with hexanes (12 x 0.5 mL) and these washes were merged and saved. The solids were rinsed with additional hexanes (10 x 1 mL) and these washes were not saved. The saved hexane washes were left to stand for 20 min, during which time yellow-orange

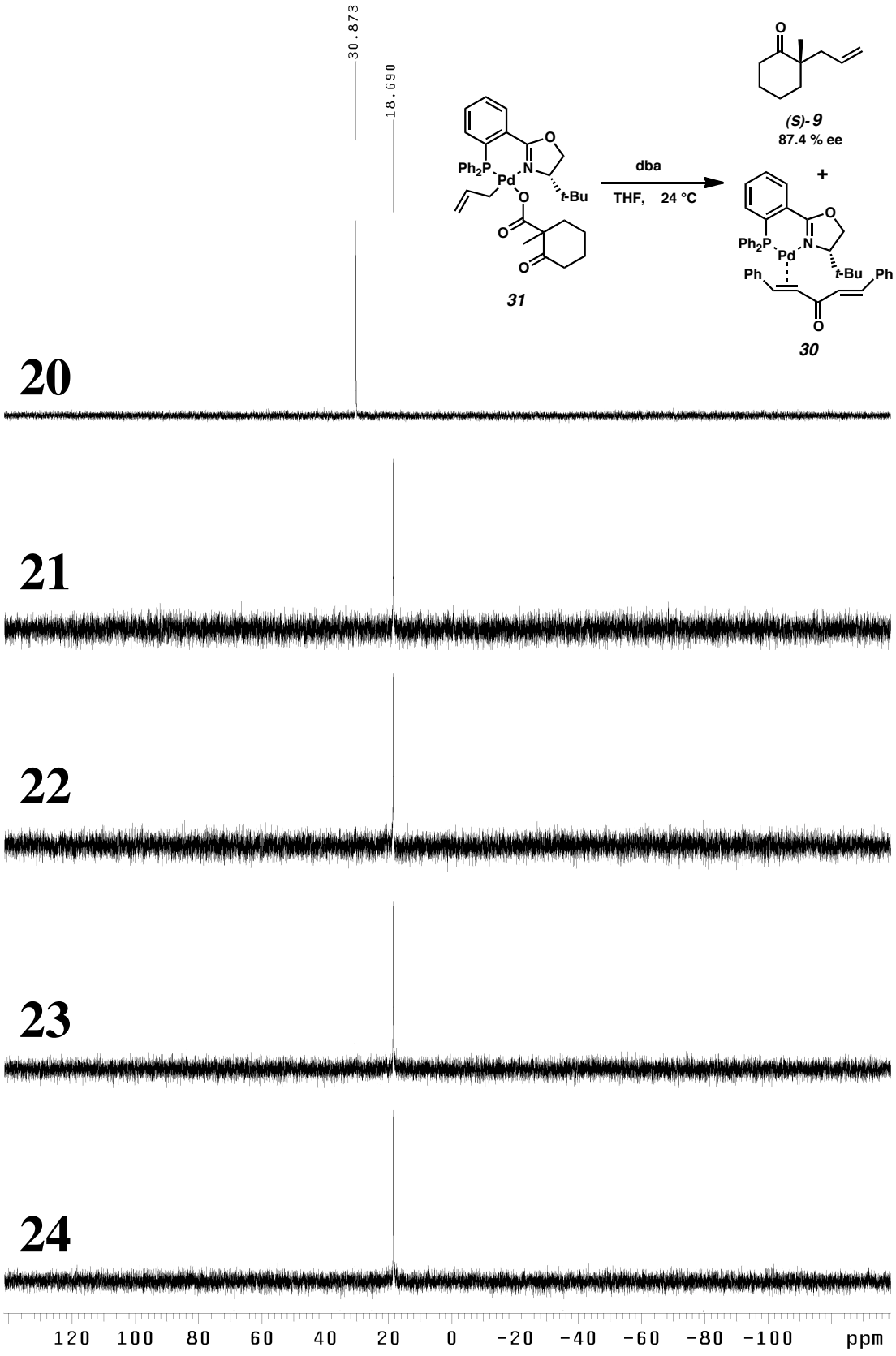
[3] See the following procedure for representative spectra.

material began to crystallize and precipitate. These precipitated solids were then filtered in a pipette with glass filter paper. All of the samples of the precipitated red-orange material were dissolved in minimal THF, merged, and filtered through a pipette with glass filter paper into a 20 mL scintillation vial. The solution was concentrated in vacuo to a thin red film. This film was washed with diethyl ether (1 mL) and hexanes (2 x 1 mL). The remaining solids were azeotroped once from diethyl ether and twice from hexanes to afford precatlyst complex **5** (7.1 mg, 62% yield, yellow powder).

2.6.6.3 Controlled Thermal Decomposition of Intermediate 31 in the Presence of dba Ligand in Solution (THF) (Isolation of 2-allyl-2-methylcylcohexanone 9 Only)

Until the sample left the glove box, all of the following operations were performed in cold aluminum block with implements and containers, such as a half-dram vial and NMR tube, that had been precooled to –36°C in a glove box freezer before use. Dibenzylideneacetone (3.3 mg, 16 μmol, 1.5 equiv) was weighed into a 1 dram vial. Intermediate **31** (7.3 mg, 11 μmol, 1 equiv) was weighed into a separate half-dram vial. Anhydrous THF that had been precooled to –36 °C in the glove box freezer was added into the 1 dram vial containing the dibenzylideneacetone. The solution was mixed manually via pipette for roughly 10 s until all the material had dissolved resulting in the formation of a yellow solution. The solution was transferred via pipette to the half-dram vial containing intermediate **31**, where it was mixed manually via pipette for 10 s until all the material had dissolved, resulting in the formation of a yellow-green solution. The NMR tube was sealed with a septum, quickly removed from the glove box, and submerged in dry ice to within two inches of its top. NMR spectrum # 20 was taken at this time with the probe precooled to –20 °C. The NMR tube was then left to stand at 24

°C. After 17 min at 24 °C NMR spectrum #21 was taken. After 22 min, NMR spectrum #22 was taken. After 30.5 min, NMR spectrum #23 was taken. After 40 min, NMR spectrum #24 was taken indicating complete conversion to precatalyst **30** as the only detectable phosphorous-containing compound. Tridecane (4.0 μL, 3.0 mg, 16 μmol, 1.5 equiv) was added via a 10 μL Hamilton syringe. The solution was concentrated under a jet of nitrogen to roughly 100 μL of viscous orange oil. The oil was triturated with 0.5 mL of diethyl ether and the resulting mixture was filtered through a pipette filter with a 3 cm plug of dry silica gel. The materials were eluted with diethyl ether separating a faintly pink solution from red/orange insoluble solids. The filtrate afforded 2-allyl-2-methyl-cyclohexanone (**9**) (99% GC yield [DB-WAX column {60 °C initial temp for 10 min, then ramp 5 °C/min for 36 min to 240 °C, hold at 240 °C for 12 min}, ret. time of tridecane = 13.243 min, ret. time 2-allyl-2-methylcyclohexanone = 18.399 min], 87.4% *ee* [assay: GC, G-TA column {100 °C isothermal for 30 min}, major enantiomer (*S*) ret. time = 14.897 min, minor enantiomer (*R*) ret. time = 17.313 min]).


30.873
18.690
dba
THF, 24 °C
(S)-9
87.4 % ee
31
30
20
21
22
23
24
120 100 80 60 40 20 0 -20 -40 -60 -80 -100 ppm

*2.6.7 Rate Constant and Half-Life of Complex **31** at 24 °C in THF*

Data were extracted from spectra 21 to 23 of the above reaction. Data point one at 18 min (spectrum #21) was set to time = 0 min for the sake of the regression plot. Data from NMR spectrum #20 were omitted as the spectrum was taken at a different temperature.

Raw Data:

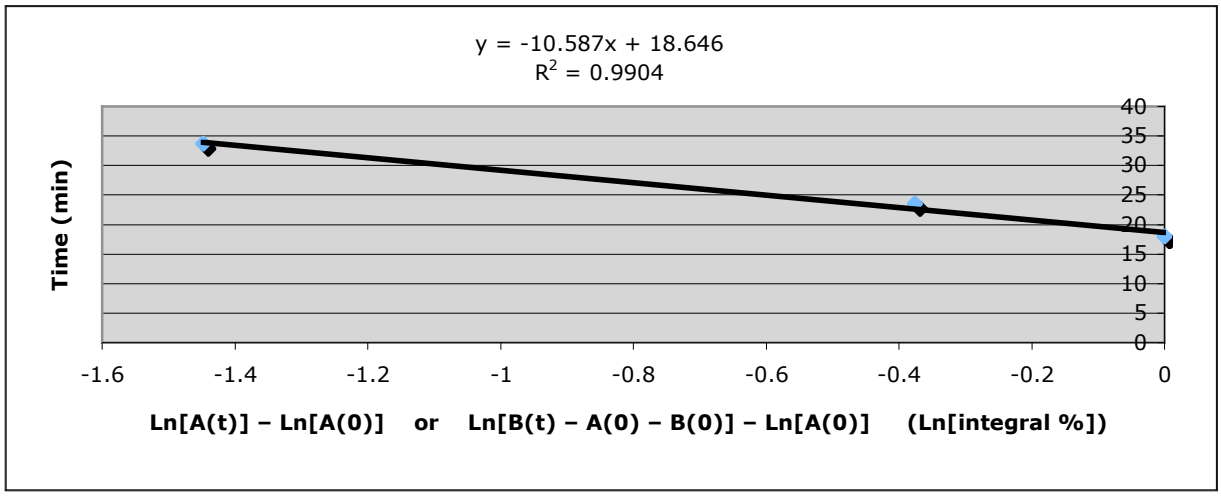
Data Point	Intermediate **31** (integral)	Complex **30** (integral)	Time (min)		Complex **30** Adjusted* (integral)
1 (spectrum 21)	0.37	1	17-19	(18)	1.1111
2 (spectrum 22)	0.23	1	22-25	(23.5)	1.1111
3 (spectrum 23)	0.07	1.01	30.5-37	(33.75)	1.1222

[*] The adjusted value of the major resonance for complex **30** is used instead of attempting to integrate both the major and minor resonances for complex **30**, as the minor resonance's contribution is so small that its integration is highly affected by baseline noise giving a poor plot fit. The adjusted integral value for complex **30** is determined by taking the integral value of the major ^{31}P resonance for complex **30** and dividing it by its relative fraction to the total integral, 0.9. See the ^{31}P NMR characterization data for complex **30** in this experimental section or its ^{31}P NMR spectrum reproduced in Appendix 1 for more data on the multiple ^{31}P resonances for complex **30**.

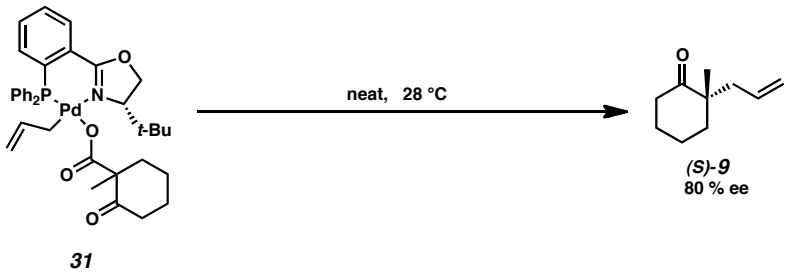
Derived Data:

Data Point	Intermediate **31** (% ^{31}P) = A(t)	Complex **30** (% ^{31}P) = B(t)	Ln[A(t)] – Ln[A(0)]	Ln[B(t) – A(0) – B(0)] – Ln[A(0)]
1	0.249812	0.75019	0	0
2	0.171499	0.82850	-0.37612	-0.37612
3	0.058714	0.94129	-1.44803	-1.44803

Linear Regression Plot:



=> Rate constant, k = 1/x = –9.45 x 10^{-2} min^{-1} or –1.58 x 10^{-4} s^{-1} at 24 °C
=> Half-life = [ln(0.5) / k] = 7.34 min at 24 °C



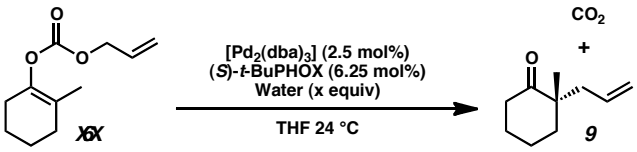
31

2.6.7.1 Controlled Thermal Decomposition of Intermediate 31 in the Solid State

In a nitrogen glove box, intermediate **31** (15 mg, 22 μmol, 1 equiv) was added to a 20 mL scintillation vial. The vial was tightly sealed, and then left to stand at ambient glove box temperature (28 °C). After 36 h the decomposed material, now black in color, was moved to the bench where it was partially dissolved by pulverization under diethyl ether (5 x 1 mL) with manual grinding by a stainless steel spatula. The resulting heterogeneous mixture was filtered through a pipette filter with a 2 inch plug of silica gel that had been prewetted/packed with diethyl ether, separating a dark maroon filtrate from a black insoluble solid. The filtrate was concentrated under a jet of nitrogen to a dark maroon oil with some small darkly colored crystalline masses. Chromatography was

performed on a pipette column eluting with 5% diethyl ether in petroleum ether affording 2-allyl-2-methylcyclohexanone (**9**) (80% *ee* [assay: GC, G-TA column {100 °C isothermal for 30 minutes}, major enantiomer (*S*) ret. time = 14.897 min, minor enantiomer (*R*) ret. time = 17.313 min], clear colorless oil).

2.6.8 Water Tolerance Experiments



Water (equiv)	Yield[a]	ee[b]
0	99.9%	88.5%
0.55	99.6%	86.7%
1.6	88.1%	83.8%
8.3	70.3%	60.9%
17	66.8%	48.8%
33	67.9%	40.5%

Data reported is the average of three trials. [a] GC yield relative to internal standard (tridecane). [b] Enantiomeric excess measured by chiral GC.

Complete Table of Runs:

Water (L, equiv)	Time (h)	GC Conversion (%)	GC Yield (%)	ee (%)
0.0 μL = 0 equiv	1.5	100 %	100.5 %	88.5 %
""	1.0	100 %	101.6 %	88.4 %
""	1.0	100 %	97.2 %	88.7 %
Averaged =	*1.2*	*100 %*	*99.9 %*	*88.5 %*
1.0 μL = 0.55 equiv	1.5	100 %	100.6 %	86.6 %
""	0.5	100 %	103.0 %	87.0 %
""	0.5	100 %	95.4 %	86.6 %
Averaged =	*0.8*	*100 %*	*99.6 %*	*86.7 %*
3.0 μL = 1.6 equiv	0.75	100 %	88.5 %	83.6 %
""	0.5	100 %	87.4 %	83.9 %
""	0.5	100 %	88.3 %	84.0 %
Averaged =	*0.6*	*100 %*	*88.1 %*	*83.8 %*

15 μL = 8.3 equiv	0.75	100 %	75.3 %	60.3 %
“”	0.5	100 %	70.8 %	62.4 %
“”	0.5	100 %	70.3 %	59.9 %
Averaged =	*0.6*	*100 %*	*70.3 %*	*60.9%*
30 μL = 17 equiv	0.75	100 %	67.8 %	50.4 %
“”	0.75	100 %	65.6 %	48.7 %
“”	0.75	100 %	66.9 %	47.4 %
Averaged =	*0.75*	*100 %*	*66.8 %*	*48.4 %*
60 μL = 33 equiv	1.5	100 %	64.3 %	40.4 %
“”	1.0	100 %	73.5 %	40.0 %
“”	6.0	78.2 %	(66.0 %)*	41.0 %
Averaged =	*2.8*	*92.7 %*	*67.9 %*	*40.5 %*

[*] Based on conversion. The uncorrected yield was 51.6%.

General Procedure: A 1 dram vial equipped with a magnetic stir bar was flame dried under vacuum. After cooling under dry argon, [$Pd_2(dba)_3$] (4.6 mg, 0.005 mmol, 0.05 equiv) and (*S*)-*t*-BuPHOX ligand (**31**) (0.0125 mmol, 0.125 equiv) were added. After the flask was flushed with argon, THF (3.0 mL) was added and the contents were stirred at 25 °C for 30 min. Tridecane (12.25 μL), water, and then carbonic acid allyl ester 2-methyl-cyclohex-1-enylmethyl ester (**6**) (19.6 mg, 0.1 mmol, 1.0 equiv) were added by syringe in the given order. When the reaction was complete by TLC, the reaction mixture was diluted with hexanes (5 mL), filtered through a small plug of silica gel and analyzed by GC. A GC yield was determined on DB-WAX column (70 °C initial temp, 5 °C/min ramp to 180 °C), tridecane ret. time = 7.000 min, ketone **9** ret. time = 12.309 min, carbonate **6** ret. Time = 17.771 min. Enantiopurity was determined by GC on a GT-A column (100°C isothermal for 30 min) major enantiomer (*S*) ret. time = 14.897 min, minor enantiomer (*R*) ret. time = 17.313 min.

(1) (a) Keith, J. A. *Computational Insight into Homogeneous Organopalladium Catalysis*, Ph.D. Thesis, California Institute of Technology, Pasadena, CA, **2008**. (b) Behenna, D. C. *Progress Toward the Synthesis of (+)-Zoanthenol and The Development of an Asymmetric Tsuji Allylation Reaction*, Ph.D. Thesis, California Institute of Technology, Pasadena, CA, **2007**. (c) Keith, J. A.; Behenna, D. C.; Mohr, J. T.; Ma, S.; Marinescu, S. C.; Oxgaard, J.; Stoltz, B. M. Goddard, W. A., III. *J. Am. Chem. Soc.* **2007**, *129*, 11876–11877.

(2) For a thorough discussion, see: Chapter 1.

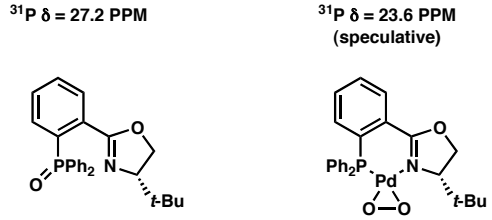
(3) (a) Mohr, J. T.; Behenna, D. C.; Harned, A. M.; Stoltz, B. M. *Angew. Chem., Int. Ed.* **2005**, *44*, 6924–6927. (b) Behenna, D. C. ; B. M. Stoltz, B. M. *J. Am. Chem. Soc.* **2004**, *126*, 15044–15045.

(4) TBAT (Tetrabutylammonium difluorotriphenylsilicate) is a dry fluoride source used to activate silyl enol ether **4** for allylic alkylation, as specified in the original allylic alkylation conditions, see reference 3b.

(5) It is possible that the resonances at δ = 31.3 and 29.4 ppm correspond to the same carbonate complex (such as **34** or **36**). The carboxylate species **31** and **32** and the π-allyl cation **25** are all extremely fluxional in solution (see Chapter 3), and are thus strongly effected by solution conditions. If this is also true of the carbonate complex initially observed at δ = 29.4 ppm, then the sudden change in solution upon the addition of silyl enol ether **4** and its reaction with TBAT might be more then enough to shift the carboxylate complex 2 ppm to the resonance found at δ = 31.3 ppm. Consistent with this hypothesis is that the resonance at δ = 31.3 ppm lasts beyond the end of the reaction when there is excess diallyl carbonate, but this species reverts to the dba complex **30** at the end of the reaction when there is excess silyl enol ether. This is consistent with both resonances δ = 29.4 and 31.3 ppm being some form of palladium carbonate complex, and is strongly suggestive that neither resonance corresponds to a palladium enolate complex like **27**.

(6) The decarboxylative asymmetric allylic alkylation reaction is very sensitive to oxygen, and many NMR experiment runs show some oxidative decomposition by their completion in spite of precautions to exclude air. The resonance at $\delta \approx 27$ ppm (see reference 36) is the phosphine oxide of the PHOX ligand **i**, and a common oxidative decomposition product (see the experimental procedures section of this chapter for complete characterization of **i**). The resonance at $\delta \approx$ 23.6 ppm is as of yet unidentified, but it seems to appear before the formation of PHOX oxide **i** when oxidation begins to occur and then slowly disappear over time. It is tentatively postulated that δ = 23.6 ppm may correspond to μ-peroxo palladium species **ii**. This highly speculative assignment is based off of analogy to other palladium systems that react directly with O_2 to form oxidizing species,

see: Konnick, M. M.; Guzei, L. A.; Stahl, S. S. *J. Am. Chem. Soc.* **2004**, *126*, 10212–10213 and references therein.



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(8) It should be noted that the use of this custom [$Pd_X(dba)_Y$] derivative in this reaction was not arbitrarily decided upon. Most common [$Pd_X(dba)_Y$] derivatives were tried in this reaction first, including: [$Pd_2(dba)_3$], "[$Pd(dba)_2$]", [$Pd(pmdba)_2$], and [$Pd_2(dmdba)_3$]. The problem with most other dba ligands is that they are comparably crystalline and have similar solubility to palladium complexes **31** and **32**. As complexes **31**, and **32** need to be purified by recrystalization, this results in prohibitive purification issues. The mtdba ligand, however was designed for use in organometallic synthesis by being completely non-crystalline (it does not crystallize but can be congealed into a waxy amorphous solid), and by having enhanced solubility in strongly apolar solvents like hexanes and pentanes, which do not appreciably dissolve most palladium(II) complexes such as **31**, and **32**. Not only do these properties make mtdba easy to separate from complexes **31**, and **32**, but palladium(0) byproducts and unreacted palladium(0) species, such as [{(*S*)-*t*-BuPHOX}Pd(mtdba)], have a tendency to bind with mtdba, which enhances the solubility of these specices in organic solvents and makes them easier to separate from the intended palladium(II) products as well.

(9) For a thorough analysis of the solution structures and behavior of complexes **25** **31**, and **32**, see: chapter 3.

(10) Chelating ligands with a carboxylate functionality bound to a metal *cis* to an η-1 allyl group behave very differently from non-chelating carboxylate ligands in the same arrangement. Notably, chelated carboxylate complexes tend to be relatively stable and inert compared to the corresponding monodentate species. Generally the chelated complexes exhibit practically none of the fluxion solution behavior found for complexes like **25**, **31**, and **32**, as discussed in Chapter 3. For a recent and highly relevant example of a chelating carboxylate ligand *cis* to an η-1 allyl,

and a short discussion of its solution behavior and relative stability, see reference 11.

(11) Wencel, J.; Laurent, I.; Toupet, L.; Crévisy, C.; Mauduit, M. *Organometallics*, **2010**, *29*, 1530–1533.

(12) Transition metal complexes with a carboxylate ligand *trans* to a σ-bound allyl group typically are relatively simple to synthesize and are generally more stable due to the *trans* arrangement of these two ligands, which prevents various potential mechanisms of decarboxylation such as doubly vinylogous reductive elimination. This is also true for metal complexes that adopt geometries that do not put these two ligands roughly with in 90° of one another, such as linear complexes. Such allyl acetate transition metal complexes are noticeably less rare. In contrast, reported examples of transition-metal complexes with a non-chelating carboxylate ligand *cis* to a σ-bound allyl group are limited to a single ruthenium complex and a single rhodium complex, neither of which have a crystal structure among their other characterization data; see: (b) Planas, J. G.; Marumo, T.; Ichikawa, Y.; Hirano, M.; Komiya, S. *J. Mol. Catal. A* **1999**, *147*, 137–154. (c) M. J. Payne, D. J. Cole-Hamilton, *J. Chem. Soc. Dalton Trans.* **1997**, 3167–3176.

(13) See Chapter 3 for a through discussion.

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(15) The crystal structure of palladium carboxylate **31** exists as a superposition of the two diastereomers resulting from the use of racemic β-ketoester **31** (≈ 6:4 d.r. found in the crystal structure). The structure depicted in Scheme 2.4 corresponds to the (*R*,*S*) major diastereomer only.

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(21) The crystal structure of **32** contains 4 discrete rotamers of the complex per unit cell. Scheme 2.5 depicts only one of the rotamers found in the unit cell.

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(28) The material becomes soft and relaxes noticeably above 68 °C but does not actually change states until the given range.

(29) $[Pd_2(mtdba)_3]$ is highly dynamic in solution giving the observed intricate NMR spectra with fractional resonance integrations. This dynamic nature has been reported for all published $[Pd_x(dba)_y]$ derivatives as of this writing. For some select examples see: Fairlamb, I. J. S.; Kapdi, A. R.; Lee, A. F. *Org. Lett.* **2004**, *6*, 4435-4438.

(30) The solution of the crude complex in hexanes is immiscible with methanol and no crystallization or precipitation occurs even on the interface between the two phases. By adding ethanol first, the methanol becomes miscible and the resulting ternary solvent system becomes ideal for crystallization at lower temperatures.

(31) The second crop of crystals often formed with an amorphous white or off-white solid. This amorphous solid is weakly soluble in ethanol and is the reason for the recommended ethanol washes of the second crystal crop.

(32) This resonance overlaps significantly with the triplet immediately down field of it. The reported integrations were estimated from the combined integration of these two resonances of 2.33H.

(33) It should be noted that while palladium allyl acetate **32** does not appear prone to the thermal decarboxylation mechanism that causes palladium carboxylate **31** to decompose near and above room temperature, **32** is still thermally unstable in roughly the same temperature range. The rate of thermal decomposition for **32**, however is considerably slower then **31**. Unlike **31**, **32** can be worked with at room temperature for hours at a time without any noticeable decomposition, but **32** must still be stored cold (≈ –36 °C or lower) if it is to be kept for more then a day or so without beginning to decompose. Thermal decomposition for **32** was

found to be slower in the solid state than in solution. Decomposition of **32** is visibly obvious as the complex undergoes a color change from a light yellow green to a darker orange and then brown as it decays. While the thermal decomposition pathway for **32** is unknown and unstudied, it is hypothesized to start with loss of allyl acetate from the complex via reductive elimination. The resulting 14 electron [{(*S*)-*t*-BuPHOX}Pd(0)] species then presumably has many options for farther chemical transformations by which it can undergo non-specific decomposition.

(34) Complex **30** exists as a mixture of dba rotomers in solution. For a study of relevant palladium dba complexes, see: Herrmann, W. A.; Thiel, W. R.; Broßmer, C.; Öfele, K.; Priermeier, T.; Scherer, W. *J. Organomet. Chem.* **1993**, *461*, 51-61.

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(36) Experimentally this resonance appears to be highly sensitive to solution conditions and has been seen to drift significantly (often up to half a ppm) during the course of a reaction.