Palladium(0)-Catalyzed Synthesis of Chiral Ene-allenes Using Alkenyl Trifluoroborates

Gary A. Molander,* Erin M. Sommers, and Sharon R. Baker

Roy and Diana Vagelos Laboratories, Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6323

gmolandr@sas.upenn.edu

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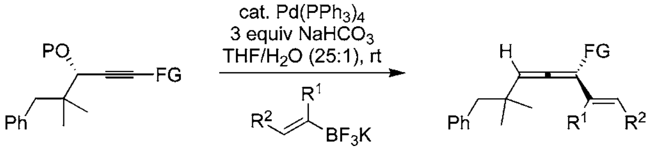

Enantioenriched allenes serve as chiral transfer reagents, making them attractive synthetic targets. Herein, the synthesis of enantioenriched allenes utilizing a Pd(0)-catalyzed cross-coupling reaction of propargylic carbonates and phosphates with alkenyl trifluoroborates is reported. Di-, tri-, and tetrasubstituted allenes were synthesized in moderate to high optical yields. Several racemic allenes possessing various functional groups were also synthesized.

Introduction

Allenes are becoming increasingly important as synthetic targets, both in natural products and in other biologically active compounds.[1] Moreover, chiral allenes with appropriate substitution are uniquely powerful intermediates for organic synthesis, translating axial chirality to central chirality.[2] For these reasons, our laboratory seeks to develop methods for the efficient, stereoselective synthesis of enantiomerically enriched allenes. Previously, the synthesis of chiral nonracemic allenes by cationic chromium(III) catalysis has been reported.[3] However, this method possesses several drawbacks. Not only must substrates remain unfunctionalized, but a bulky *tert*-butyldimethylsilanoxy group serves as the leaving group, generating wasteful byproducts. In an effort to avoid these complications, a milder, more atom economical synthesis of enantioenriched allenes was desired.

Although a myriad of allene syntheses exist,[4] few are achieved in high ee.[5] S$_N$2′-type reactions on optically active propargylic derivatives involving organocuprates are the most common and convenient methods for generating enantioenriched allenes.[5] Although chiral nonracemic propargylic alcohols are easily synthesized either by reduction of the conjugated alkynones[6] or from the asymmetric addition of alkynylmetallics to aldehydes,[7] organocuprate methods suffer from some major drawbacks, including racemization of the product allenes under the reaction conditions.[8] Attempts have been made to remedy this problem (e.g., utilizing mixed organocuprates, additives, and different leaving groups), but a general approach to the synthesis of optically active allenes remains elusive.

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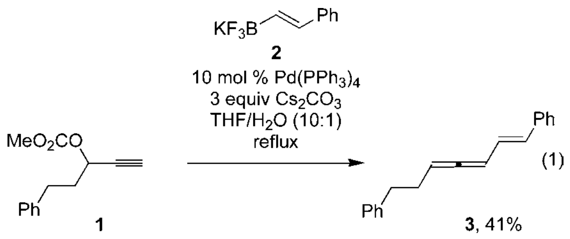
Easy access to enantioenriched substrates, mild reaction conditions, and atom economy make cross-coupling routes to form allenes extraordinarily attractive.[9] Despite these favorable attributes, few general methods have been developed. Arylations using organozinc reagents have been reported with varying success.[10] Depending on the substrate, *anti* selectivity ranges from 4:1 to complete stereoselectivity, and sterically unbiased internal and terminal propargylic substrates consistently yield allenes with less than 90% ee. The analogous Suzuki−Miyaura coupling reaction with boronic acids yielded an allene with complete transfer of chirality in the sole case reported.[11] Likewise, one example has been reported where a 4-aryl-2,3-allenol was formed with complete retention of stereochemistry when a propargylic oxirane undergoes the cross coupling reaction with an aryl boronic acid.[12] Although other aryl-,[11] alkynyl-,[13] alkenyl-,[14] and alkylzincs[10a] as well as analogous organoboron reagents have been used as coupling partners in racemic reactions, the scope of the reactions has not been extensively explored. Thus, the opportunity to refine this transformation exists. Because only one example of a cross-coupling type reaction with an alkenyl organoboron has been reported,[14] alkenyl trifluoroborates as coupling partners served as a place to begin the studies described herein.

Potassium organotrifluoroborate salts have many attractive properties compared to other organoboron compounds.[15] They are monomeric, air-stable solids that generate nontoxic byproducts. This paper details the synthesis of allenes by Pd(0)-catalyzed cross-coupling of alkenyl trifluoroborates and propargylic carbonates. The functional group scope of the reaction is also presented. Additionally, the stereoselectivity of the reaction with propargylic phosphates is probed.

Results and Discussion

Optimization of Reaction Conditions for Propargylic Carbonates and Exploration of Substrate Scope. Initially, using $Pd(PPh_3)_4$ as a catalyst and Cs_2CO_3 as a base in THF/H_2O[16] yielded 41% of the desired racemic ene-allene **3** from **1** (eq 1). Encouraged by this initial result, the reaction was optimized for palladium source, catalyst loading, base, solvent, and isolation conditions (Table 1). The yields given are quantitative GC yields using an internal standard and are based on complete consumption of the starting material. A comparison of different Pd catalysts proved that our original choice of $Pd(PPh_3)_4$ was indeed correct (Table 1, entry 3). The reaction does not proceed in the absence of a Pd(0) catalyst. After determining $Pd(PPh_3)_4$ to be the appropriate catalyst, several bases were screened. Entries 4−8 (Table 1) depict the results of changing the base. Inexpensive $NaHCO_3$ proved to be the most efficient base. Using $NaHCO_3$, the catalyst loading was lowered. Entries 9 and 10 (Table 1) display these results. A 10-fold decrease in catalyst loading from 10 to 1 mol % created only a 10% decrease in yield (entries 6 and 9), although the reaction time was longer with less catalyst. However, lowering the catalyst loading to only 0.5 mol % on this reaction scale not only lengthened the reaction time but also decreased the yield (entry 10). Therefore, 1 mol % was chosen as the optimum catalyst loading on the reaction scale employed. It should be noted that up to 10 mol % was used in subsequent reactions to achieve the desired reaction efficiency and high yields. The final reaction parameter explored was the solvent. EtOH, DMSO, and THF without water were all tried. EtOH led to deprotection of **1** to yield only the free alcohol and no allene product. No reaction was observed in DMSO or THF without water. Despite the necessity of water, the water content could be lowered to 25:1 (THF/H_2O) without observing any decrease in yield or reaction rate.



1 **3**, 41%

TABLE 1. Optimization of Reaction Conditions

$$\mathbf{1} \xrightarrow[\text{reflux}]{\substack{\mathbf{2},\ \text{Pd(0)} \\ \text{3 equiv base} \\ \text{THF/H}_2\text{O (10:1)}}} \mathbf{3}$$

entry	catalyst, ligand	base	time, h	% GC yield
1	$PdCl_2(dppf)\bullet CH_2Cl_2$ (10 mol %)	Cs_2CO_3	2	starting material
2	$Pd(OAc)_2$, 2 PPh_3 (10 mol %)	Cs_2CO_3	2	14[a]
3	$Pd(PPh_3)_4$ (10 mol %)	Cs_2CO_3	2	41[a]
4	$Pd(PPh_3)_4$ (10 mol %)	Cs_2CO_3	2	93
5	$Pd(PPh_3)_4$ (10 mol %)	K_2CO_3	7	66
6	$Pd(PPh_3)_4$ (10 mol %)	$NaHCO_3$	2	100
7	$Pd(PPh_3)_4$ (10 mol %)	*i*-Pr_2NH	4	61
8	$Pd(PPh_3)_4$ (10 mol %)	none	24	0
9	$Pd(PPh_3)_4$ (1 mol %)	$NaHCO_3$	3	90
10	$Pd(PPh_3)_4$ (0.5 mol %)	$NaHCO_3$	4.5	58

[a] Isolated yields.

One more aspect of the reaction optimization bears mention. The palladium byproducts present appeared to polymerize/degrade the allene product. Very low isolated yields were obtained initially. To eliminate this problem, methods were investigated to remove the offending palladium from solution as quickly as possible upon completion of the reaction. Addition of adsorbent carbon black (Darco) followed by a period of stirring exhibited a marked increase in isolated yield (e.g., 41−

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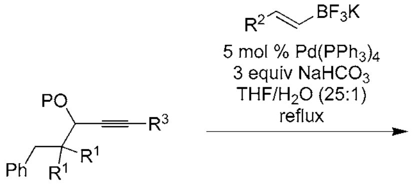
TABLE 2. Exploration of Substrate Scope



entry	substrate	R^1	R^2	P	R^3	product yield (%)
1	**4**	Me	Ph, **2**	CO_2Me	C_8H_{17}	**5**, 84
2	**1**	H	Ph, **2**	CO_2Me	H	**3**, 70
3	**6**	H	H, **7**	$P(O)(OEt)_2$	$(CH_2)_3CN$	**8**, 56
4	**9**	Me	Ph, **2**	CO_2Me	$(CH_2)_3CN$	**10**, 76
5	**9**	Me	H, **7**	CO_2Me	$(CH_2)_3CN$	**11**, 71
6	**12**	Me	H, **7**	CO_2Me	$(CH_2)_4OH$	**13**, 63
7	**14**	H	H, **7**	CO_2Me	$(CH_2)_3Cl$	**15**, 47
8	**16**	Me	H, **7**	CO_2Me	$(CH_2)_4N(Bn)_2$	**17**, 53
9	**18**	Me	H, **7**	CO_2Me	$(CH_2)_3CHO$	**19**, 19
10	**20**	H	H, **7**	CO_2Me	$(CH_2)_4OTBS$	**21**, 74
11	**22**	H	H, **7**	$P(O)(OEt)_2$	$(CH_2)_4OTBS$	**21**, 44
12	**23**	Me	$(CH_2)_3Cl$, **24**	CO_2Me	H	**25**, 69
13	**26**	Me	H, **7**	CO_2Me	$(CH_2)_4SPh$	**27**, 73
14	**28**	H	C_8H_{17}, **29**	CO_2Me	$(CH_2)_3SO_2Ph$	**30**, 60
15	**31**	H	C_8H_{17}, **29**	CO_2Me	TMS	**32**, 17[a]

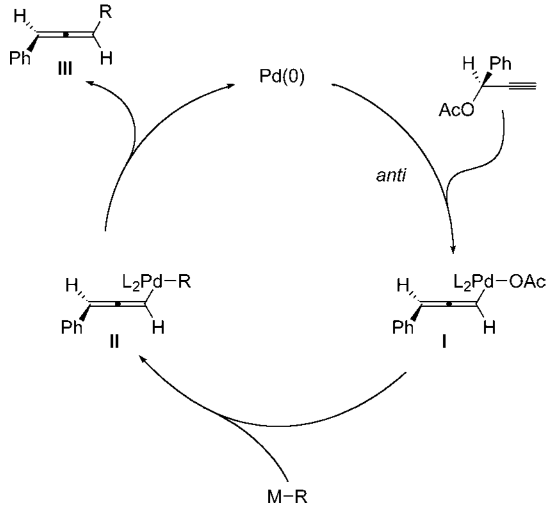
[a] Product **32**; R^3 = H.

70% yield). It became standard practice to open the reactions to air and quench with Darco for all subsequent reactions. Except for the initial results (eq 1 and Table 1, entries 2 and 3), the yields reported herein reflect this workup protocol.

After optimizing the reaction parameters, the functional group tolerance was explored. The results are presented in Table 2. Many functional groups were compatible with the reaction conditions. For example, nitrile, naked and protected alcohol, amine, chloride, and sulfur-containing substrates tolerated the reaction conditions, producing racemic ene-allenes in moderate to good yields. Aldehyde **18** was the exception, producing only 19% of the allene. The basic conditions necessary for the reaction may have led to aldol products or polymerization, lowering the yield. The moderate yields of the remaining substrates can be explained by the above-mentioned workup protocol. The Darco necessary to achieve reasonable yields may also sequester the product. Excessive solvent washes of the Darco will release the problematic palladium. As discussed below, phosphates were thermally unstable, highlighted by the results in entries 3 and 11. Unlike their carbonate counterparts (entries 5 and 10, respectively), the phosphates suffered from lower yields. To synthesize an allene capped with a trimethylsilyl group, **31** was subjected to the reaction conditions. Instead of isolating the desired TMS-substituted allene, a small amount (17%) of deprotected product was observed. The alkynyl-TMS might be readily deprotected under the basic reaction conditions, or the fluorine-containing trifluoroborate byproducts may have removed TMS from the alkyne or allene. More robust silyl protecting groups were not explored.

Probing the Stereospecificity of the Reaction: Optimization and Application. Based on previous literature reports of similar transformations, the substitution step was anticipated to proceed with inversion to generate allenyl-Pd **I** (Scheme 1), while the transmetalation/reductive elimination steps would occur with retention of configuration to yield an allene product **III** with overall *anti* substitution.[2b] Therefore, an enantioenriched substrate should lead to an enantioenriched allene product. Carbonate (*R*)-**1** was subjected to the optimized reaction conditions (eq 2). Disappointingly, the product was nearly racemic.

SCHEME 1. Mechanism of Pd(0)-Catalyzed Cross-Coupling Reaction To Form Allenes



$$(R)\text{-}\mathbf{1}\ \xrightarrow[\text{reflux}]{\substack{\mathbf{2},\ 3\ \text{mol}\ \%\ Pd(PPh_3)_4 \\ 3\ \text{equiv}\ NaHCO_3 \\ THF/H_2O\ (25:1)}}\ (S)\text{-}\mathbf{3} \qquad (2)$$

96% ee 71%, 13% ee

At this juncture, the literature was searched for examples of palladium-catalyzed racemization of allenes. To the best of our knowledge, palladium has been shown to racemize allenes by three mechanisms. In the first mechanism, allenes can be racemized through the η^1-allenylpalladium(II) to η^1-propargylpalladium(II) interconversion (Scheme 2).[17] When the Pd

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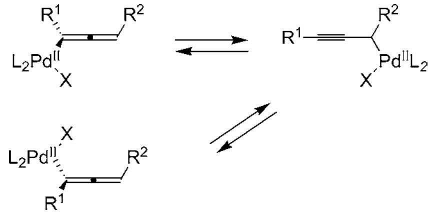
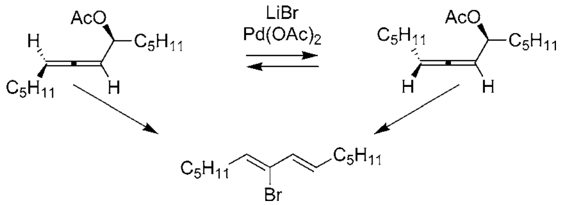
[17] Mikami, K.; Yoshida, A. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 858−860.

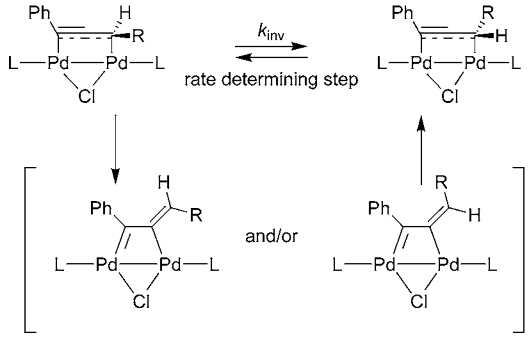
SCHEME 2. Possible Mechanism for Racemization of Allenes via Propargylic/Allenyl Pd Intermediate



SCHEME 3. Racemization of Allenes with Pd(II) and LiBr via a Bromopalladation/Elimination Sequence



SCHEME 4. Racemization of Allenyl−Pd Intermediate via a Bimetallic Complex



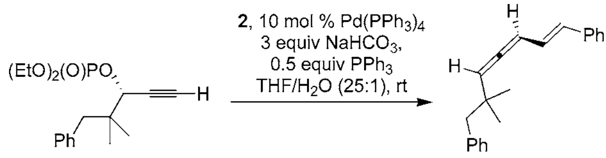
occupies the propargylic position, free rotation can occur, resulting in racemization. This mechanism proved beneficial for Mikami and co-workers in their report of a dynamic kinetic protonation of intermediate allenylmetals.[17]

By the second mechanism (Scheme 3), enantioenriched allenes are racemized by $Pd(OAc)_2$-catalyzed bromopalladation/LiBr elimination.[18]

In the third case, Ogoshi and co-workers postulated that an enantioenriched η^1-allenylpalladium(II) species will racemize over time due to the generation of a configurationally labile μ-η^3-allenyl/propargyldipalladium complex under normal catalytic conditions (Scheme 4). Racemization was accelerated in the presence of oxygen and decreased when as little as 10 mol % of PPh_3 was added to the reaction.[19]

The reaction conditions were manipulated to maximize the enantioselectivity based on these three mechanisms. Unfortunately, success was limited. Palladium catalysts on solid supports were used to generate single-site catalysis and to circumvent the formation of potential bimetallic intermediates (Scheme 4). Reactions using $Pd(PPh_3)_4$ on polystyrene, FibreCat 1029, and FibreCat 1031 exhibited a decreased reaction rate or no reaction, and any product isolated was racemic. Yoshida suggests that water assists formation of the bimetallic species (Scheme 4).[12] To eliminate water, other alcoholic solvents, such as *tert*-amyl and *sec*-butyl alcohol were used. Unfortunately, these solvents completely inhibited the reaction. Water was introduced using hydrated bases: $KF{\cdot}2H_2O$, $CsOH{\cdot}H_2O$, and $Na_2CO_3{\cdot}H_2O$ in THF led to the formation of racemic allenes. Mimicking Ogoshi's work, excess PPh_3 was added to the reaction. Except for noticeably slowing the reaction, only a moderate rise in ee was observed when the substrate was fully consumed. Other metal catalysts (Ni, Rh, and Cu) were employed with no success.

In a final bid to raise the ee, different leaving groups were examined. The acetate leaving group led to racemic product at a slower reaction rate than the propargylic carbonate. The slower reaction can be explained by the fact that the acetate anion acts as a ligand for palladium, retarding the rate-determining transmetalation step and thereby decreasing the reaction rate.[20] When an enantioenriched phosphate was subjected to the reaction conditions (eq 3), not only was there a rise in ee, but the reaction could be conducted at room temperature instead of at reflux. At this juncture, the catalyst/ligand combinations were screened again using a propargylic phosphate. An array of reactions using $PdCl_2$, $Pd(PhCN)_2Cl_2$, $Pd(MeCN)_2Cl_2$, $Pd(OAc)_2$, Pd_2dba_3, and $[Pd(allyl)Cl]_2$ as catalysts and Ph_3As, $(2\text{-furyl})_3P$, dppe, dppb, and dppf as ligands were conducted. Each catalyst/ligand combination yielded products that were racemic. $Pd(PPh_3)_4$ remained the most viable catalyst for this transformation. Again different metals, bases, solvents, and additives were investigated to raise the ee; however, no additional headway was made. Under the countless reaction conditions tried, the ee of **34** was initially high; however, (*S*)-**33** failed to be fully consumed before racemization occurred.



(*S*)-**33**, 88% ee (*R*)-**34**, 49% ee (3)

These empirical observations prompted an investigation into the nature of the racemization. We proposed that there was an initial rapid formation of allene possessing high ee followed by a prolonged period in which little to no additional product was formed and racemization of the product occurred. This idea was confirmed by examining the conversion versus the racemization of the product at several temperatures (Table 3).

As predicted, the ee decreased over time while the production of product tapered off. At room temperature the racemization was rapid, occurring within 2 min, while the reaction reached completion after 1 h. Lowering the temperature was beneficial to both the conversion and ee, but a similar trend was observed. Because of a difficult analytical separation of the enantiomers of **34**, another trifluoroborate was examined to corroborate the trend. Table 4 indicates the results of using vinyl trifluoroborate **7**. Unlike the reaction with **2**, the reaction was complete within 30 s, but the same loss of ee was observed over time.

These results confirmed the hypothesis that the newly formed ene-allenes sequester the palladium, perhaps via initial coordination shown in Figure 1, and undergo racemization, effectively shutting down the desired coupling reaction. Alkenes with electron withdrawing substituents are better ligands for palladium based on back-bonding into the empty π^* orbital.[21]

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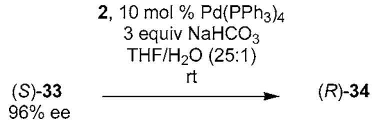
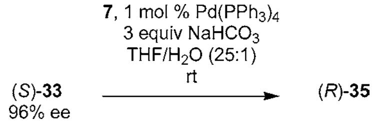
TABLE 3. Time vs Conversion and % ee Using 2



entry	*T*, °C	time, min	conversion,[a] %	ee, %
1	rt	0.5	54	67
2	rt	2.5	73	0
3	rt	5	80	0
4	rt	12	88	0
5	rt	60	99	0
6	0	5	80	85
7	0	22	93	76
8	−15	5	92	80
9	−15	60	95	59
10	−40	15	90	74

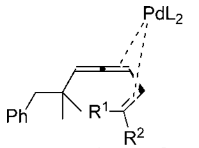
[a] Conversion based on quantitative GC analysis of starting material consumption.

TABLE 4. Time vs Conversion and % ee Using 7



entry	time, min	conversion,[a] %	ee, %
1	0.5	> 99	98
2	1	> 99	92
3	3	> 99	78
4	4	> 99	76
5	5	> 99	50

[a] Conversion based on quantitative GC analysis of starting material consumption.

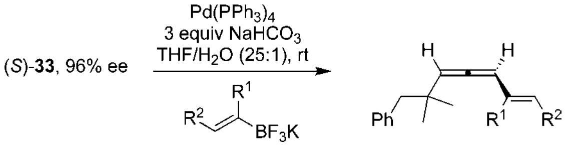


34 R^1 = H, R^2 = Ph
35 R^1 = R^2 = H

FIGURE 1. Possible coordination of Pd(0) with ene-allenes **34** and **35**.

Because the phenyl group is more electronegative than a hydrogen substituent,[22] allene **34** was a better ligand for Pd(0) than **35**, explaining the slower turnover and more rapid racemization of **34**. Additionally, the phenyl substituent may further coordinate to the metal center, increasing its affinity. Initially, high ee's suggest that the first and third racemization mechanisms (Schemes 2 and 4) are not operating. If racemization occurred at the allenyl-Pd intermediate, any product formed would be racemic because racemization must necessarily occur before the transmetalation/reductive elimination step. Therefore, the Pd(II) racemization mechanism remains a possibility with $NaOP(O)(OEt)_2$ or $NaHCO_3$ playing the role of LiBr; however, no experimental evidence for this proposal has been gathered. Furthermore, this mechanism seems unlikely due to the weakly nucleophilic character of the phosphate and bicarbonate anions compared to bromide in the reported example.

TABLE 5. Synthesis of Enantioenriched Ene-allenes



entry	trifluoroborate	catalyst, mol %	time, min	product, yield (%)	% ee
1	R^1, R^2 = H, **7**	2	1.75	**35**, 80	94
2	R^1 = Me, R^2 = H, **36**	2	10	**37**, 52	76
3	R^1 = H, R^2 = Ph, **2**	10	2	**34**, 42	32
4	R^1 = H, R^2 = $(CH_2)_3CN$, **38**	10	20	**39**, 45[a]	87
5	**38**	5	20	**39**, 53[a]	91

[a] Yield based on recovered starting material.

To expand the scope of the asymmetric reaction, several classes of alkenyl trifluoroborates were subjected to the reaction conditions. The results are displayed in Table 5 and reflect the optimized result for each trifluoroborate. (*S*)-**33** reacted with vinyl trifluoroborate (**7**) to produce (*R*)-**35** in 80% yield and 94% ee (Table 5, entry 1). The less substituted trifluoroborates produced allenes possessing high ee (Table 5, entries 1 and 4). Conversely, the more substituted potassium 1-methyl-1-vinyl trifluoroborate (**36**) resulted in a poorer yield of **37**, with a moderate loss of ee. Ironically, our test trifluoroborate **2** led to **5** in the poorest yield and ee (Table 5, entry 3).[23] In the case of the 1,2-disubstituted trifluoroborate **38**, the reaction time was extended to increase the conversion. This extra time negatively impacted the ee of the reaction (Table 5, entry 4), but loss of ee was alleviated to some degree by decreasing the catalyst loading (Table 5, entry 5).

In addition to different classes of alkenyl trifluoroborates, substrates possessing different substitution patterns were subjected to the reaction conditions. Equations 4 and 5 illustrate the formation of enantioenriched tri- and tetrasubstituted allenes. In the case of **40**, the reaction must be heated to reflux for reasonable conversion to **41**. However, phosphates were thermally unstable at higher temperatures, resulting in a lower yield. Additionally, a high reaction temperature negatively impacted the ee. In contrast, the tetrasubstituted allene **43** was formed in moderate yield with high retention of ee. Although **42** was more sterically encumbered than **40**, the phosphate was poised to be a much better leaving group because of its benzylic, propargylic, and tertiary character. Therefore, the reaction was performed at room temperature. Because the synthesis of chiral nonracemic tertiary propargylic alcohols has recently been reported,[24] this method is a convenient way to generate tetrasubstituted allenes in high ee.

As a last area of interest, other classes of trifluoroborates, such as aryl, alkynyl, or alkyl were subjected to the reaction conditions optimized for alkenyl trifluoroborates. Unfortunately, only an aryl trifluoroborate coupled to generate an allene under these conditions (eq 6). Interestingly, aryl allenes appear to be more resistant to racemization. After 40 min at reflux, **45** was isolated in 80% ee. This result correlates with Yoshida's successful coupling of an aryl boronic acid and a carbonate at

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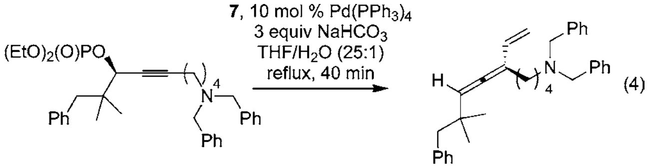
[22] Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry, Part A: Structure and Mechanism*, 4th ed.; Kluwer Academic/Plenum Publishers: New York, 2000; p 17.

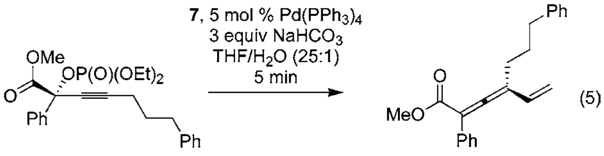
[23] The apparent discrepancy between Table 2, entry 2, and Table 5, entry 3, can be attributed to the different isolation procedures. Table 2 results are based on GC and HPLC analysis of aliquots from the same reaction. Table 5 results were generated from isolated material.

[24] Jiang, B.; Chen, Z.; Tang, X. *Org. Lett.* **2002**, *4*, 3451−3453.



40, > 99% ee

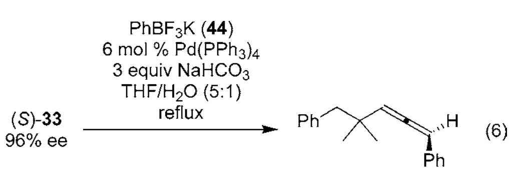
41, 54%, 32% ee



42, 74% ee

43 48%, 72% ee

100 °C.[12] Alkynyl and alkyl trifluoroborate coupling partners did not yield any coupled product upon workup. In the case of the alkyl coupling, almost complete decomposition of the starting material was observed after 2 h at reflux.



45, 26%, 80% ee

Conclusions

Ene-allenes were synthesized in low to high enantiomeric excess depending on the trifluoroborate coupling partner and product formed. To the best of our knowledge, this report marks the first time that ene-allenes have been synthesized asymmetrically. Based on experimental observation of stunted conversion and rampant loss of ee over time, we propose that racemization occurs after the allene is formed by an unknown mechanism. Rapid racemization of electron-poor ene-allene products (i.e., alkenes bearing a phenyl substituent) further supports this proposal because these compounds serve as better ligands for palladium than ene-allenes bearing hydrogen or methylene substituents. In addition to synthesizing enantioenriched di-, tri-, and tetrasubstituted allenes, functional group tolerance was exhaustively examined. Despite the poor yield of an aldehyde and the loss of a TMS protecting group, all other cases (nitrile, alcohol, silyl ether, amine, thioether, and sulfone) provided moderate to good yields of allenes. Although alkynyl and alkyl trifluoroborates failed to couple under the reaction conditions, a chiral nonracemic aryl allene was synthesized in 83% optical yield. Furthermore, a reproducible workup procedure to remove the rogue palladium was devised. The continued development of methods for the synthesis of enantioenriched allenes is ongoing in our laboratory.

Experimental Section

Cross-Coupling Reaction To Form Enantioenriched Allenes: Method A. The alkenyl trifluoroborate, $Pd(PPh_3)_4$, and $NaHCO_3$ were combined in a round-bottom flask. The flask was evacuated and refilled with nitrogen, and THF (3 mL) and H_2O (200 μL) were added. In a separate flask, the propargyl phosphate was degassed by evacuation or by the freeze/pump/thaw method and refilled with nitrogen. The substrate was then dissolved in THF (1 mL). The substrate solution was transferred via cannula into the catalyst solution. The flask containing the substrate was washed with THF (1 mL), which was also transferred to the reaction mixture. The reaction time was calculated beginning with the first drop of substrate transferred. At the completion of the reaction, Darco was added and the flask was left uncapped. After being stirred for 30 min to 1 h, the mixture was filtered through a short plug of Celite to remove the Darco. The plug was washed with Et_2O. The solution was transferred to a separatory funnel where the organic layer was washed three times with brine (1 mL each time). The ethereal layer was dried with $MgSO_4$, filtered, and concentrated. The crude product was then purified via column chromatography with appropriate conditions for each allene product (see the Supporting Information).

Cross-Coupling Reaction To Form Racemic Allenes from Carbonates/Phosphates: Method B. The alkenyl trifluoroborate, $Pd(PPh_3)_4$, and $NaHCO_3$ were combined in a round-bottom flask with a sidearm. The flask was fitted with a reflux condenser and was evacuated and refilled with nitrogen, and THF (3 mL) and H_2O (200 μL) were added. In a separate flask, the propargyl carbonate/phosphate was degassed by evacuation or by the freeze/pump/thaw method and refilled with nitrogen. The substrate was then dissolved in THF (1 mL). The substrate solution was transferred via cannula into the catalyst solution. The flask containing the substrate was washed with THF (1 mL), which was also transferred to the reaction mixture. The reaction was then heated to reflux. At the completion of the reaction, Darco was added and the flask was left uncapped. After being stirred for 30 min to 1 h, the mixture was filtered through a short plug of Celite to remove the Darco. The plug was washed with Et_2O. The solution was transferred to a separatory funnel where the organic layer was washed three times with brine (1 mL each time). The ethereal layer was dried with $MgSO_4$, filtered, and concentrated. The crude product was then purified via column chromatography under the appropriate conditions for each allene product (see the Supporting Information).

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Supporting Information Available: Experimental details and structural data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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