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Review

Chemistry of Group 13 Element-Transition Metal Linkage - the Platinum- and Palladium-Catalyzed Reactions of (Alkoxo)diborons

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Abstract

The metal-catalyzed borylation of alkenes, alkynes, and organic electrophiles with B-B compounds was developed for the synthesis of organoboronic esters from simple organic substrates. The platinum(0)-catalyzed additions of bis(pinacolato)diboron to alkenes and alkynes stereoselectively yielded *cis*-bis(boryl)alkanes or *cis*-bis(boryl)alkenes. The addition of diboron to 1,3-dienes with a platinum(0) complex afforded a new access to the *cis*-1,4-bis(boryl)butene derivatives which are a versatile reagent for diastereoselective allylboration of carbonyl compounds. The cross-coupling reactions of diborons with aryl and vinyl halides or triflates, and allyl chlorides or acetates was found to yield aryl-, vinyl-, and allylboronates in high yields in the presence of a base and a palladium catalyst, which provides the first one-step procedure for the synthesis of organoboronic esters from organic electrophiles under mild conditions. The mechanisms and the synthetic applications of these reactions are discussed.

Keywords: metal-catalyzed reaction, diboron(4), palladium, platinum, rhodium, cross-coupling, diboration, organoboron compound

1. Introduction

Recently, a range of transition metal-boryl compounds have extensively studied [1-4] since these compounds have proposed as key intermediates in various catalytic reactions of group 13 elements including the metal-catalyzed hydroboration [5] and diboration [6, 7] of alkenes and alkynes. The representative metal-boryl complexes reported in oxidative addition of boron reagents to low valent transition metals are summarized in Scheme 1. Halocatecholborane ($XBO_2C_6H_4$, X=Cl, Br) adds to $Pt(C_2H_4)(PPh_3)_2$ at room temperature giving *trans*-platinum(II) complexes (**1**) [8]. Oxidative addition of diboron ($X_2B\text{-}BX_2$, X=halogen, OR) to $Pt(PPh_3)_4$ or $Pt(C_2H_4)(PPh_3)_2$ (**2**) [9-11], $Rh(Me)(PMe_3)_4$ (**4** and **5**) [12], and to other low valent metals such as Ir(I) [13], Co(0) [14], and Cp_2W [15] yield various metal-boryl complexes. The addition of catecholborane to Ir(I) or Rh(I) affords a key intermediate for catalytic hydroboration (**6**) [16]. The synthesis, characterization, bonding, and reactivity of these catalytically important species are recently reviewed [1-4]. In addition, theoretical studies for M-B bond and its role in the proposed catalytic cycles have also been studied [17-19].

In this work, particular attention will be given to the synthesis of organoboronic esters *via* the addition and cross-coupling reactions of diborons catalyzed by a transition metal complex. Much attention has been recently focused on organoboronic acids and their esters due to their practical usefulness for synthetic organic reactions [20, 21],

molecular recognition such as host-guest compounds [22], and neutron capture therapy on treatment of malignant melanoma and brain tumor [23]; however, new development in their preparations is very few. The methods now available are based on the reaction of trialkyl borates with Grignard or lithium reagents (transmetalation) or hydroboration of alkenes and alkynes with HBX_2 (X=halogen, alkoxy). The addition and cross-coupling reaction of metal-boryl reagents are an alternative and convenient protocol which has been extensively studied for disilanes [24] and distannanes [25], but the related reactions of B-B compounds have not been reported previously. Since (alkoxy)diborons are thermally stable and easily handled in air, the reagent can be useful as a reagent for the boration of alkenes, alkynes, and organic electrophiles.

2. Synthesis of diborons

Diboron tetrachloride (Cl_2B-BCl_2) obtained by an electric discharge reduction of boron trichloride ignites in air and undergoes a decomposition into boron trichloride and colored solid materials at room temperature [26]. On the other hand, tetra(amido)- and tetra(alkoxo)diboron dramatically enhance the stability of the B-B species. Tetra(dimethylamido)diboron (**7**) is available in large quantity by the Wurtz coupling of bromo- or chloroborane with sodium or potassium in refluxing toluene (Scheme 2) [27]. The reaction of **7** with an alcohol or a diol leads to various alkoxo-derivatives of diboron (**8**) [28-30]. Two diborons, **8b** and **8c**, are now commercially available. Although the reactions of bis(pinacolato)diboron (**8b**) [29] have been extensively studied due to its high stability to air and moisture, distillation, and chromatography over silica gel, similar reactions can be anticipated for other diborons, e.g., tetra(methoxo)diboron (**8a**) [28] and bis(catecholato)diboron (**8c**) [30].

3. Addition reaction of diborons

The addition of diboron tetrahalides B_2X_4 (X=F, Cl, Br) to unsaturated hydrocarbons, first discovered by Schlesinger in 1954, is an attractive and straightforward method to introduce boryl groups into organic molecules, but the synthetic use has been severely limited because of instability and availability of the reagents [31]. On the other hand, amido **7** and alkoxo derivatives of diboron **8a-c** are rather stable, but the compounds are quite inert to ionic reactions due to the low Lewis acidity of the boron centers conjugated with hetero atoms and a high B-B bond energy [19]. Fortunately, the B-B bonds oxidatively add to a low-valent transition metal with B-B bond cleavage, thus allowing the catalyzed transfer of B-B bond to unsaturated organic substrates [6, 7].

3-1. Diboration of alkynes

The diboration of alkynes is efficiently catalyzed by a platinum(0) complex such as $Pt(PPh_3)_4$, $Pt(C_2H_4)(PPh_3)_2$ or $Pt(CO)_2(PPh_3)_2$ (3 mol%) yielding *cis*-1,2-diborylalkenes in high yields (Scheme 3) [9, 32]. Other metal complexes, such as $PtCl_2(PPh_3)_2$, $Pd(PPh_3)_4$, $Pd(OAc)_2$/isocyanide, and $RhCl(PPh_3)_3$ are ineffective. Platinum(0) complexes similarly catalyze the addition of other (alkoxo)diborons, **8a** [9] and **8c** [10, 11], but reaction of (amido)diborn **7** is very slow even at 120 °C. There are no large differences in the yields and the reaction rates between internal and terminal alkynes and the reaction is available with various functional groups. The carbon-carbon double bond, chloro, epoxy, ester, cyano, and ketone carbonyl groups remained intact during the diboration of the carbon-carbon triple bonds.

Monitoring of the reaction mixture of **8b** and $Pt(PPh_3)_4$ by multinuclear NMR spectroscopies reveals the formation of a new Pt(II) species which shows reasonable thermal stability for isolation and are characteristic of phosphines *cis*-coordinated to a platinum(II) center. A single crystal of **9** consists of a distorted square-planar coordination geometry for the Pt atom containing two *cis* boryl and phosphine ligands where the significant bond angles are ∠P(1)-Pt-P(2) (102.65°) and ∠B(1)-Pt-B(2) (75.3°) (Scheme 4) [9]. Treatment of **9** with 1-octyne yields 1,2-bis(boryl)octene as the sole product, in consistent with the catalytic cycle shown in Scheme 5 [9-11]. The cycle involves (a) oxidative addition of diboron (**8**) to Pt(0) giving *cis*-B-Pt-B complex (**10**), (b) insertion of alkene or alkyne into B-Pt bond, and (c) reductive elimination of product to regenerate Pt(0) complex. The catalyst activity significantly decreases in the presence of added PPh_3 suggests that phosphine dissociation (**10→11**) is a critical step in the catalytic cycle. A theoretical study based on the B3LYP density functional method also supports the oxidative addition-insertion sequence [17-19].

The transformations of 1,2-bis(boryl)-1-alkenes provides a method for regio- and stereoselective synthesis of 1-alkenylboranes because they have potential reactivity difference between two C-B bonds. The regioselective cross-coupling reaction at terminal C-B bond are shown in Scheme 6 [33]. Although the reaction accompanies with a double-coupling product at both C-B bonds (5-10%), high terminal-selectivity over 99% are readily achieved in each cases. The two-step procedures is synthetically equivalent to carboboration of alkynes. Thus, 1-alkenylboronates thus obtained couples with another organic halide to provide an regio- and stereodefined trisubstituted alkene (Scheme 7) [33]. The utility of stepwise double-coupling procedure is demonstrated in the parallel synthesis of Tamoxifen and derivatives on solid support (Scheme 8) [34].

Using this strategy, each position about the ethylene core is modified by the appropriate choice of alkyne, aryl halide, and cleavage conditions.

3-2. Diboration of alkenes, 1,3-dienes, and allenes

The phosphine-based platinum(0) catalysts failed to add diboron to alkenes due to high coordination ability of phosphine over alkene double bond, but platinum(0) complexes without phosphine ligand such as $Pt(dba)_2$ [35] and $Pt(cod)_2$ [36] are an excellent catalyst allowing the alkene insertion into B-Pt bond under mild conditions. The diboration of aliphatic and aromatic terminal alkenes takes place at 50 °C or even at room temperature. The reaction is significantly slow for disubstituted alkenes and cyclic alkenes, but cyclic alkenes having an internal strain afford the *cis*-diboration products in high yields (Scheme 9) [35]. A phosphine-gold(I) complex [37] and a zwitter ionic rhodium complex [38] catalyze the diboration of styrene derivatives. Asymmetric diboration of styrene derivatives is demonstrated by using chiral diboron compounds (Scheme 10) [35b]. The diphenylethanediol derivative achieves 60%d.e., whereas a low diastereoselectivity is resulted in the tartarate derivative.

Methylenecyclopropane and its derivatives are of interest as the substrate for the transition metal-catalyzed addition reactions due to their high and unique reactivities originating from the strained structure. Palladium-catalyzed silylcyanation, hydrocarbonation, and hydroamination give the products derived from the distal bond cleavage of the cyclopropane ring, whereas the proximal ring-opening products are observed in the palladium-catalyzed hydrostannation and the rhodium-catalyzed hydrosilylation. The platinum-catalyzed reaction of diboron (**8b**) to methylenecyclopropanes affords 2,4-bis(boryl)-1-butenes through the proximal bond

cleavage of the cyclopropane ring (Scheme 11) [39]. The catalytic cycle may involve insertion of methylenecyclopropane into the B-Pt bond of **9**, followed by rearrangement to a homoallylplatinum(II) species. The selective formation of *cis*-isomers for bicyclic methylenecyclopropane suggested a four-centered cyclic transition state for the ring-opening rearrangement. The results suggest that terminal-alkene insertion into Pt-B bond gives a primary alkyl-platinum intermediate for both platinum-phosphine and platinum-dba catalysts.

The addition of diboron to 1,3-dienes affords various allylic boron compounds which dramatically changes the products and selectivities depending on ligand of Pt(0) catalysts. $Pt(PPh_3)_4$ yield *cis*-1,4-addition products as the sole product for the representative aliphatic and alicyclic dienes (Scheme 12) [40]. The reaction suggests the mechanism involving a S-*cis* coordination of diene to **9** by displacing two phosphines, the insertion of a diene to B-Pt bond giving *anti*-π-allyl(boryl)platinum(II) , and the reductive elimination at the less-substituted terminal carbon [40, 41].

Interestingly, the change of the catalyst to $Pt(dba)_2$ results in dimerization of diene before the addition of the diboron (Scheme 13) [40]. Isoprene provides an 1,8-addition product having (E,E) configuration and a symmetrical structure derived from the head-to-head coupling. Such dimerization *via* the stepwise insertion process can be well catalyzed by a phosphine-free platinum complex since the generation of a coordinately unsaturated π-allylplatinum(II) species allows further coordination of a diene.

On the other hand, $Pt(dba)_2$ directs the 1,2-addition to certain conjugated dienes, whereas the 1,4-addition through the π-allylplatinum(II) intermediate is an energetically more favorable process. The 1,4-addition to 1,3-pentadiene with $Pt(PPh_3)_4$ is consistent with the results shown in Scheme 12, but the same reaction with $Pt(dba)_2$ exceptionally

produces an 1,2-addition product (Scheme 13) [35].

The diboration of allenes yielding another group of allylboron derivatives are summarized in Scheme 15 [42]. The addition has a strong tendency to occur at the internal double bond, but steric hindrance in both allenes and phosphine ligands forces the addition towards the terminal double bond. Thus, the reaction of monosubstituted allenes with a less bulky ligand PPh_3 preferentially produces the internal adducts (**14a**) and the bulky and electron-donating ligand $(c\text{-Hex})_3P$ affords the terminal adducts (**14b**) for 1,1-disubstituted allenes. The *cis*-**14b** is selectively obtained for 1,2-heptadiene ($R^1=C_4H_9$, $R^2=H$) by way of addition from the less-hindered side of the terminal double bond.

The ready availability of various allylic boronates *via* the diboration of allenes now offers a new route to substituted homoallyl alcohols (Scheme 16) [42]. A sequence of allylboration of aldehydes and the cross-coupling with organic halides provides homoallylic alcohols.

The diboration of enones with diboron provides a (*Z*)-enolates (**15**) when using a platinum(0) catalyst such as $Pt(C_2H_4)(PPh_3)_2$ [43a] at 80 °C or $Pt(dba)_2$ [43b] at room temperature (Scheme 17). The hydrolysis of the boron-enolate intermediates with water gives b-borylketones in high yields, the conversion of which is synthetically equivalent to 1,4-addition of a boryl anion to enones. The diboration of a,b-unsaturated esters and nitriles affords similar products.

The rhodium-catalyzed addition of diboron (**8c**) to keteimines affords N-borylenamines and catecholborane (HBcat) *via* a sequence of oxidative addition of **8c** to Rh(I), insertion of imine into Rh-B bond, and finally b-hydride elimination. Analogous catalyzed reaction of HBcat in THF yields multiply borated products

(Scheme 18) [44].

4. Cross-coupling reaction of diborons

The transition metal-catalyzed cross-coupling reaction of disilanes [24] and distannanes [25] is an elegant method for the synthesis of organosilicone and -tin compounds directly from organic electrophiles, but the lack of suitable boron nucleophiles has limited this protocol for boron compounds. However, tetra(alkoxo)diborons **8** act as the boron-nucleophile in the presence of a base in the palladium-catalyzed cross-coupling reaction of organic electrophiles. More recently, pinacolborane $(Me_4C_2O_2)BH$ is also found to be an excellent boron-nucleophile for the palladium-catalyzed coupling reaction in the presence of triethylamine [45].

4-1. Aryl and vinyl electrophiles

The cross-coupling reaction of diborons with organic halides and triflates proceeds in the presence of base and a palladium catalyst (Scheme 19) [46, 47]. The use of $PdCl_2$(dppf) and KOAc in DMSO or DMF is found to be the best combination for aryl halides because stronger bases, such as K_3PO_4 and K_2CO_3, prompts the further reaction of **7** with bromobenzene, resulting in contamination of a substantial amount of biphenyl (36-60% yields) [46]. The coupling of triflates is carried out in dioxane in the presence of an additional dppf ligand [47]. Arylboronic acid syntheses using Grignard or lithium reagents need the protection of functional groups sensitive to these reagents, but the present reaction is available with various functional groups, e.g., CO_2Me, COMe, NO_2 and CN. Arylboronic acids having an electron-donating group, such as *p*-NMe_2 and *p*-OMe, are synthesized from the corresponding iodides, but aryl bromides or triflates

give good results for *p*-CO_2Me, *p*-COMe, *p*-NO_2, and *p*-CN derivatives because the electron-withdrawing substituents enhance the rate of coupling. However, all attempts at the synthesis of 2-pyridyl-, 2-thiophenyl-, and 2-furylboronate are unsuccessful since such C-B bond adjacent to a hetero atom is highly sensitive to protodeboronation.

The presence of a base such as KOAc is critical for the coupling reaction of diborons. The quantitative formation of *trans*-PhPd(OAc)$(PPh_3)_2$ (**17**) is observed when *trans*-PhPdBr$(PPh_3)_2$ (**16**) is treated with excess of KOAc, which exhibits high reactivity toward diboron **8b** giving a coupling product at room temperature, whereas no reaction is observed between **8b** and **16** (Scheme 20) [46]. High reactivity of the oxo-palladium complexes for the transmetalation with organoboron compounds can be attributed to both the high reactivity of the Pd-O bond which consists of a soft acid and a hard base combination, and the high oxophilicity of the boron center. The catalytic cycles based on these observations is outlined in Scheme 21, which involves the formation of (acetoxo)palladium(II) species **17** prior to transmetalation with diboron.

Both $Pd(PPh_3)_4$ and $PdCl_2$(dppf) catalyze the coupling reaction of diboron, but the reaction suffers from the coupling with phosphine-bound aryls when using $Pd(PPh_3)_4$ as the catalyst (Scheme 22) [46]. The contamination of such unexpected by-product, arising from the coupling with a phenyl group on triphenylphosphine (**19→20**) [48], is observed on the reaction of electron-rich haloarenes such as (4-methoxy)- and (4-dimethylamino)bromobenzene, though it is very small amount in electron-deficient haloarenes. The aryl exchange occurs before transmetalation; thus, the slow transmetalation due to steric and electronic reasons results in increasing the coupling of phosphine-bound aryls.

The synthesis of L-(4-boronophenyl)alanine (L-BPA) by this protocol is shown in

Scheme 22 [49, 50]. Although pinacol esters is thermally stable and inert to water and oxygen, thus allowing the handling without special precautions, they strongly resist the hydrolysis to arylboronic acids. Alternatively, the 1,3-diphenylpropanediol ester (**22**) is used to deprotect the diol moiety by catalytic hydrogenolysis.

The direct preparation of arylboronic esters from aryl halides or triflates now allows a one-pot, two-step procedure for the synthesis of unsymmetrical biaryls (Scheme 24) [47]. The synthesis of unsymmetrical biaryls is readily carried out in a same flask when the first coupling of the triflate with diboron **8b** is followed by the next reaction with another triflate. The protocol offers a direct and efficient method for the synthesis of the boronic ester on solid-phase which hitherto met with little success using classical methodology. A solid-phase boronate is quantitatively obtained by treating the a polymer-bound iodoarenes with the diboron (Schemes 24 and 25) [51]. The next coupling with haloarenes furnishes various biaryls. The robot synthesis or the parallel synthesis on the surface of resin is the topic of further accounts of this research [51c].

The palladium-catalyzed coupling reaction of (**8b**) and 1-alkenyl halides or triflates provides a one-step procedure for the synthesis of 1-alkenylboronic esters from vinyl electrophiles (Scheme 27) [52, 53]. The coupling using a palladium catalyst and KOAc suffers from the formation of an inseparable mixture of several products including the Heck coupling products, the homocoupling product of haloalkenes along with the desired coupling. The selective coupling to 1-alkenylboronats undergoes in the presence of a solid PhOK suspended in toluene. The reaction provides an alternative synthetic procedure for various vinylboronic esters, which are not available by conventional hydroboration of alkynes [52].

4-2. Allyl and benzyl electrophiles

Allylboron compounds are valuable reagents in organic synthesis, addition of which to the carbon-oxygen or the carbon-nitrogen double bond diastereoselectively provides homoallylic alcohols or amines *via* a chair-like six-membered cyclic transition state. Allylboron compounds are now accessible by the transmetalation of allyllithiums or allylmagnesiums to the boron, but the palladium-catalyzed cross-coupling reaction of diboron **8b** with allyl acetates or chlorides regio- and stereoselectively affords the allylboronic esters under neutral conditions (Scheme 28) [54, 55]. The reaction with allyl acetates proceeds under neutral conditions because their oxidative addition directly produces an (acetoxo)palladium(II) species (**17**) active for transmetalation (Schemes 20 and 21), but the presence of a base is critical for allyl chlorides [55].

All (*E*)- and (*Z*)-cinnamyl acetate, chloride, and its secondary alcohol derivative afford an (*E*)-cinnamylboronate. The borylation of prenyl acetate results in low yields, but the corresponding tertiary derivative is used for the same purpose because the boron atom exclusively bonds to its primary carbon. The coupling at the less hindered terminal carbon and the formation of thermally stable (*E*)-allylboronates *via* the isomerization of *anti*-π-allylpalladiums to the more stable *syn*-complexes is similar to other palladium-catalyzed coupling reactions of allyl electrophiles.

Intramolecular addition of allylmetal reagents to carbonyl substrates is a powerful tool for the synthesis of cyclic homoallyl alcohols with high regio- and stereoselectivity, but the corresponding reaction of allylboranes has not been well developed mainly due to the lack of a general method for the synthesis of allylboronates having a carbonyl group. The palladium(0)-catalyzed cross-coupling reaction of diboron **8b** provides an efficient and convenient access to variously functionalized allyboranes (Scheme 29)

[56]. A variety of 5-5, 6-5, and 7-5 *cis*-fused alcohols are stereoselectively synthesized from cyclic β-ketoesters (**25**) or diketone (**27**) *via* a cross-coupling/intramolecular allylboration sequence.

The coupling with benzyl halides is carried out under similar conditions used for allyl chlorides (Scheme 30) [57]. The selective coupling is achieved by using a tris(*p*-methoxy)phosphine complex because the slow reaction catalyzed by $Pd(PPh_3)_4$ accompanies with the formation of benzyl acetate.

5. Catalyzed reaction of other metal-boryl compounds

The related metal-catalyzed reactions of Si-B [58] and Sn-B [59] compounds have been also extensively studied. However, a part of them are recently reviewed [7a] and will be further discussed by other members of this research group.

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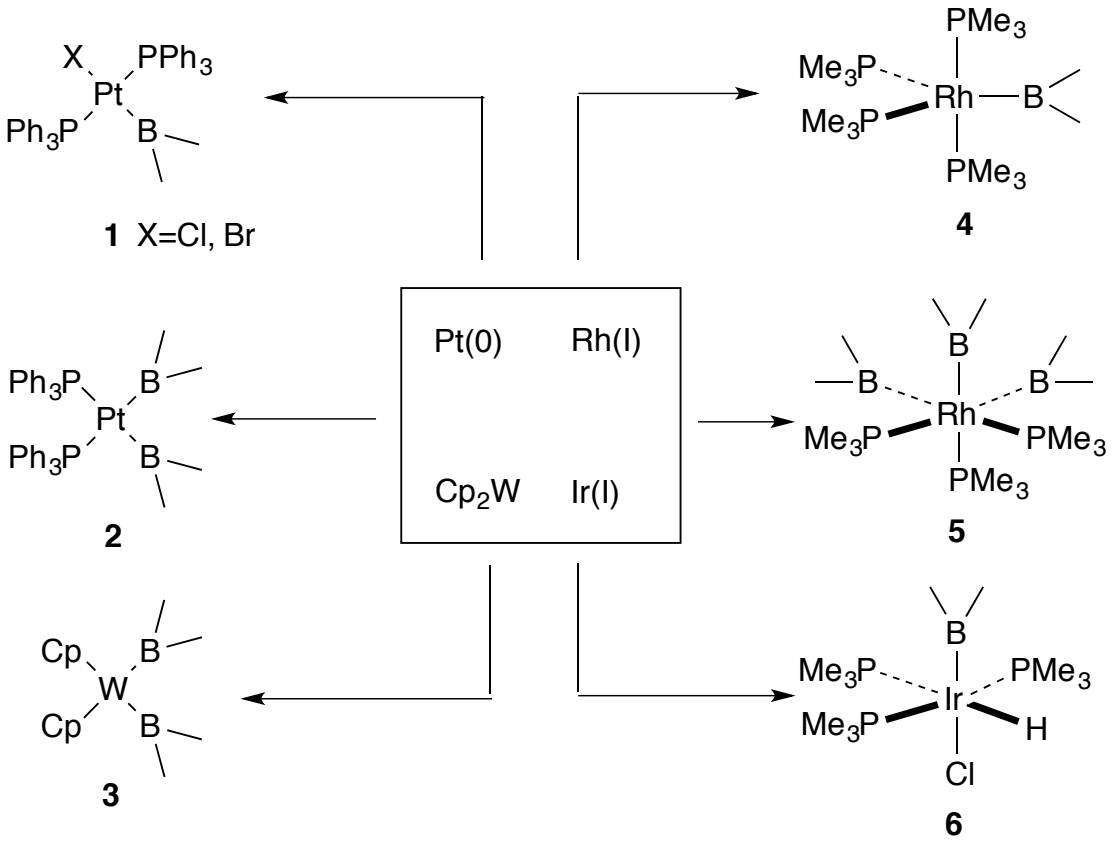
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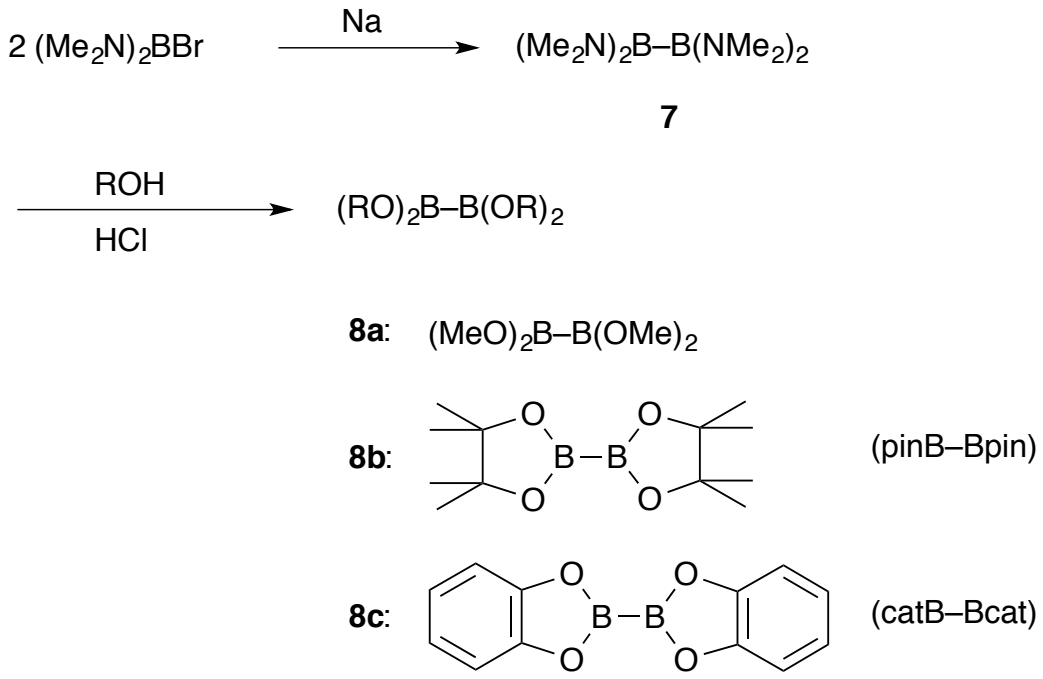
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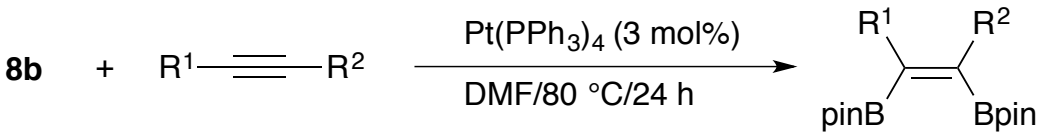
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Scheme 1. Synthesis of Metal-Boryl Complexes *via* Oxidative Addition

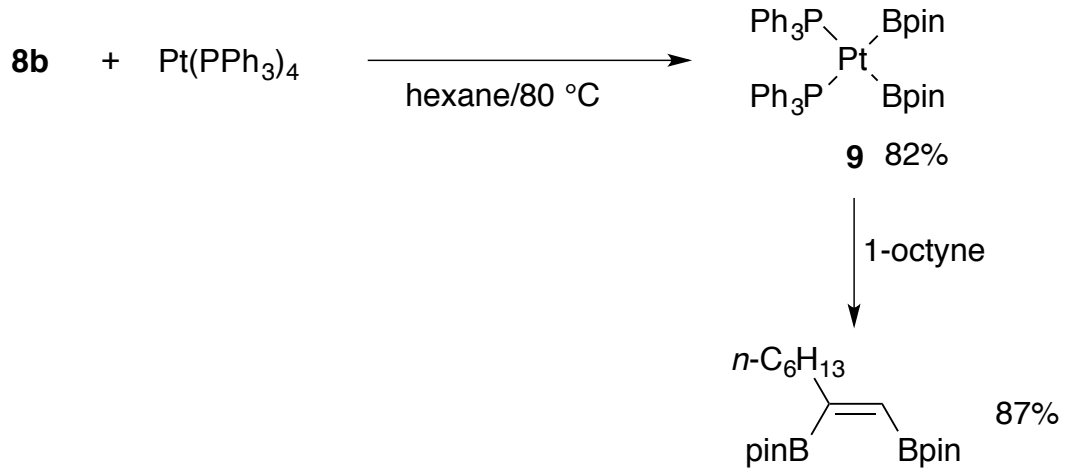


Scheme 2. Synthesis of diboron(4) cpompounds

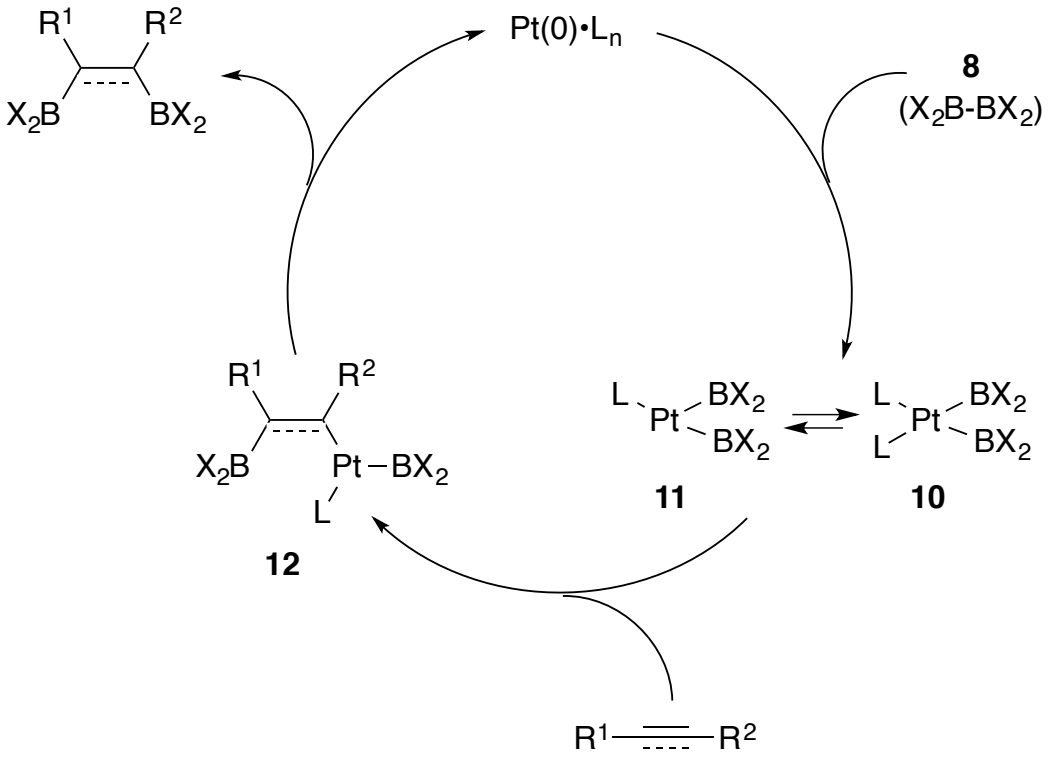


R^1	R^2	yield/%
n-C_8H_{17}	H	86
Ph	H	79 (120 °C)
n-C_3H_7	n-C_3H_7	86
Ph	Ph	79
CH_2=CH$(CH_2)_4$	H	85
NC$(CH_2)_3$	H	79
$MeO_2C(CH_2)_4$	H	89

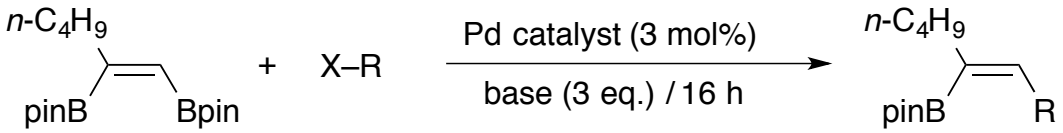
Scheme 3. Diboration of alkynes.

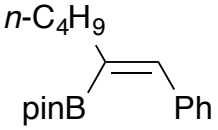
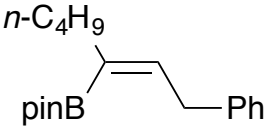
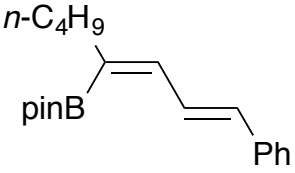
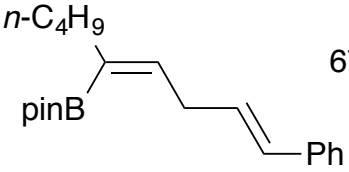


Scheme 4. Oxidative addition and insertion of diborons

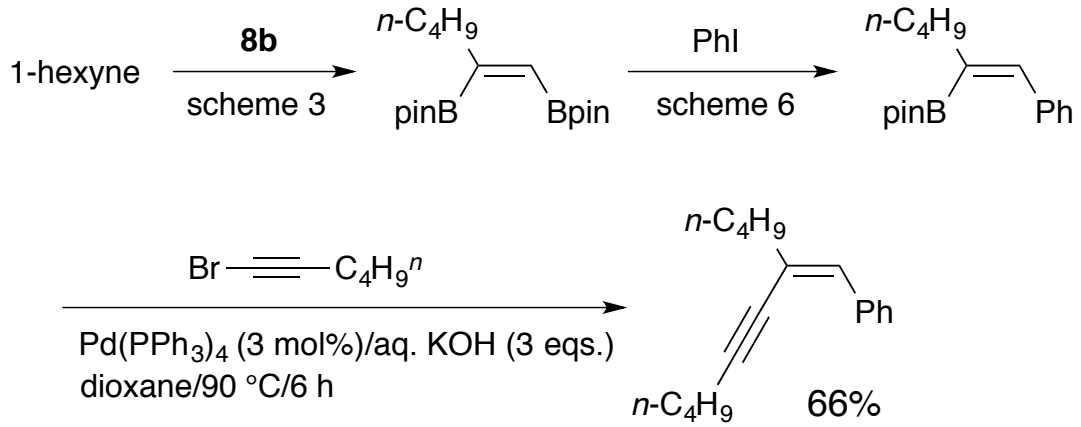


Scheme 5. Catalytic cycle for diboration of alkenes and alkynes

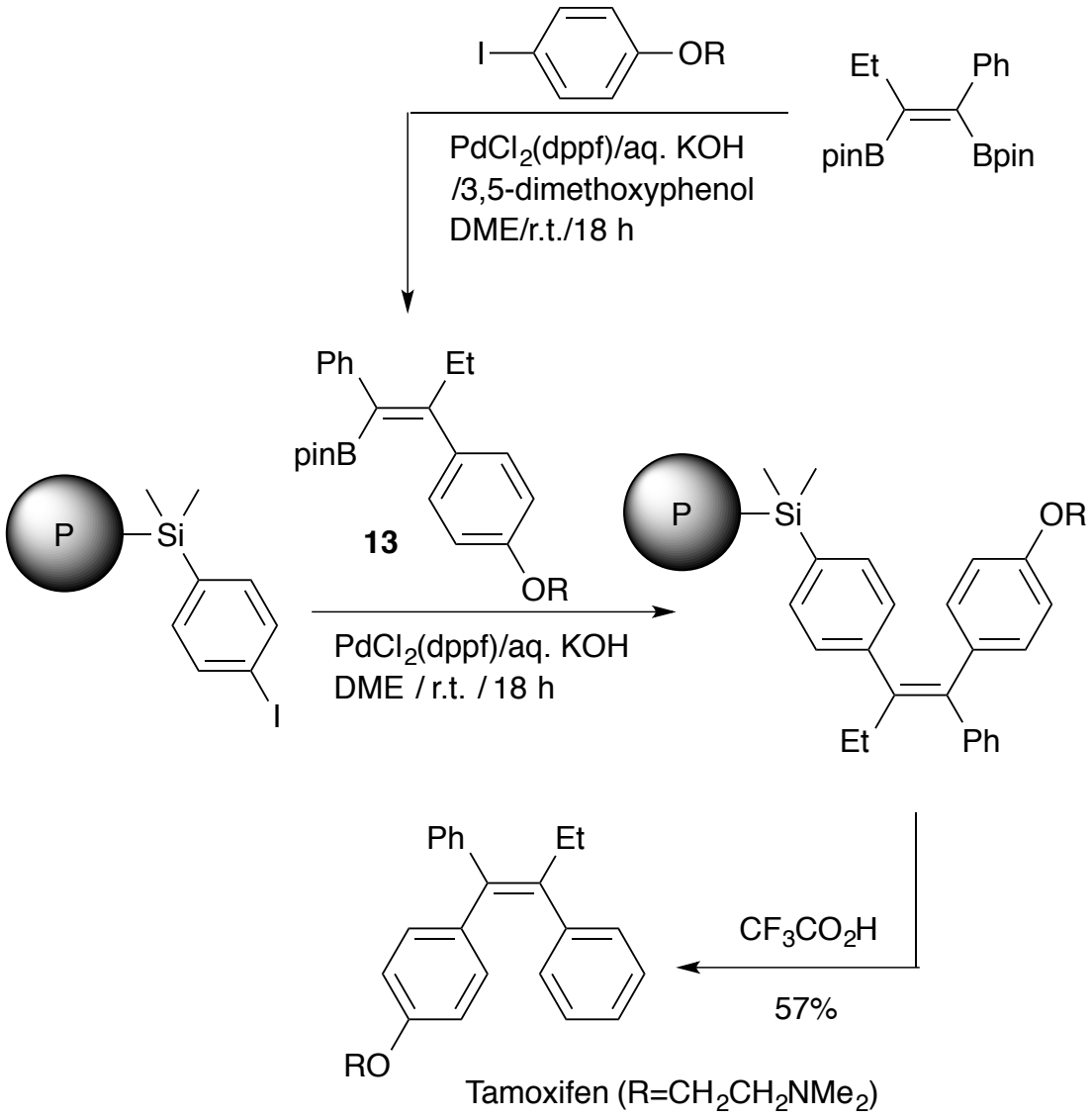


X–R	conditions	product	yield (%)
BrPh	$PdCl_2$(dppf) K_2CO_3 DMF 80 °C		79
$ClCH_2Ph$	$PdCl_2$(dppf) K_2CO_3 DMF 80 °C		82
(*E*)-BrCH=CHPh	$Pd(PPh_3)_4$ aq. KOH DME 70 °C		72
(*E*)-$ClCH_2CH$=CHPh	$PdCl_2$(dppf) K_3PO_4 dioxane 80 °C		67

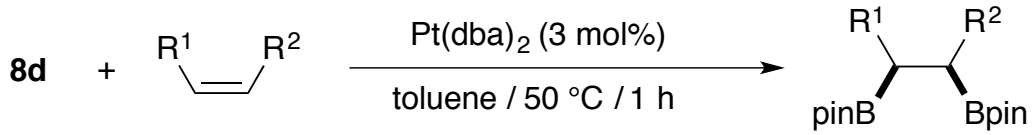
Scheme 6. Synthesis of (*E*)-(1-organo-1-alkenyl)boranes



Scheme 7. Trisubstituted alkenes *via* a diboration-coupling sequence

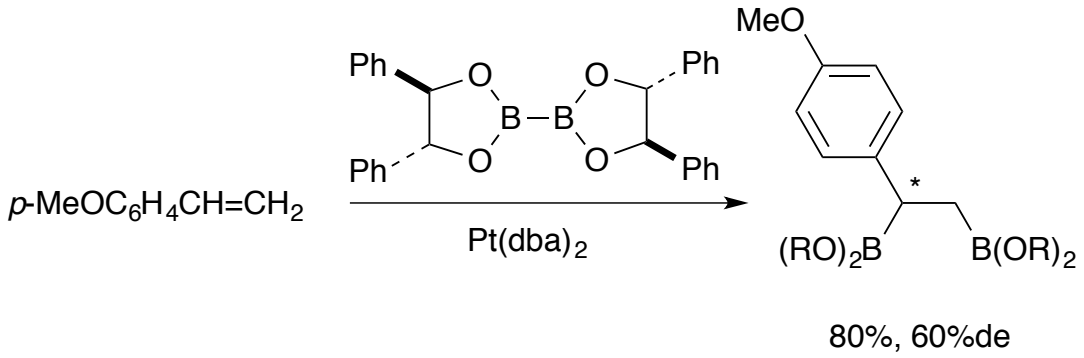


Scheme 8. Solid-phase Synthesis of tamoxifen

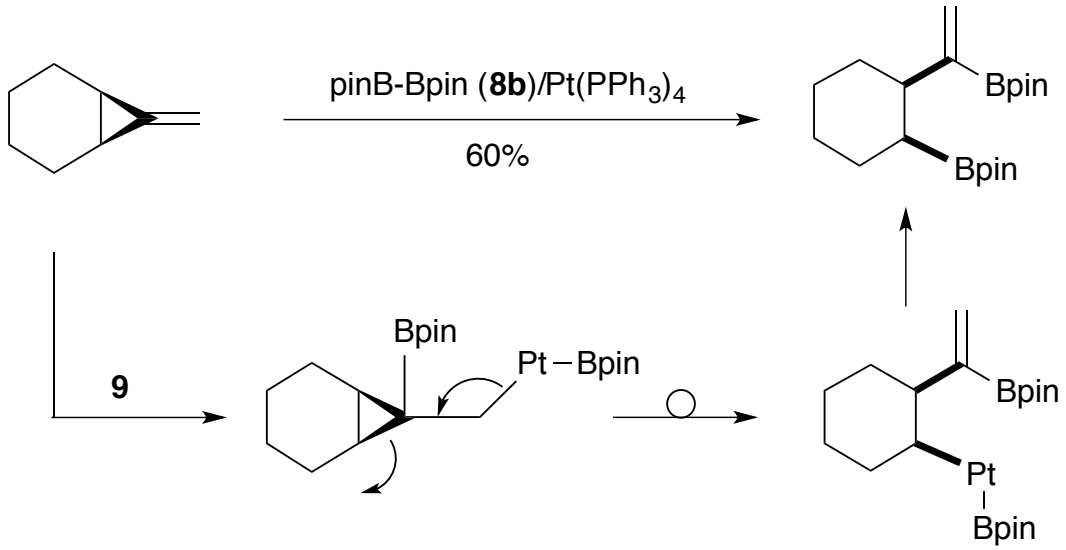


alkene	yield (%)
1-decene (1.5 eqs)	82
styrene (1.5 eqs)	86
$NCCH_2CH=CH_2$ (3 eqs)	70
$CH_3COCH_2CH_2CH=CH_2$ (3 eqs)	70
cyclopentene (1.5 eqs)	85
cyclohexene (1.5 eqs)	0
norbornene (3 eqs.)	85

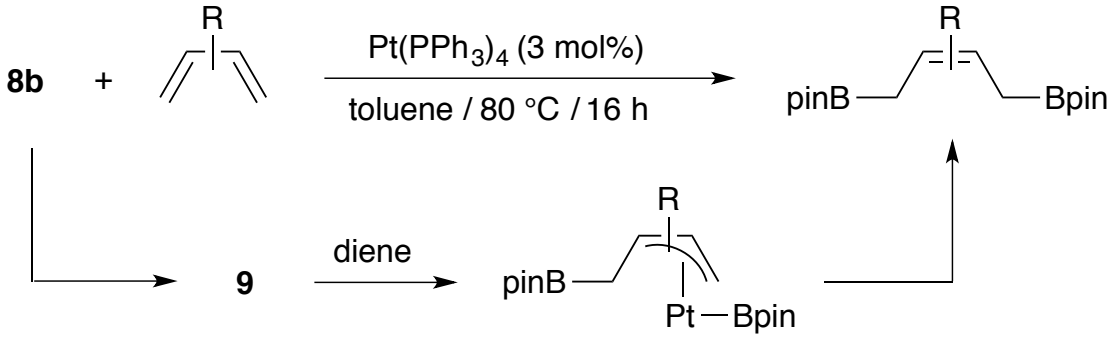
Scheme 9. Diboration of alkenes



Schene 10. Asymmetric diboration

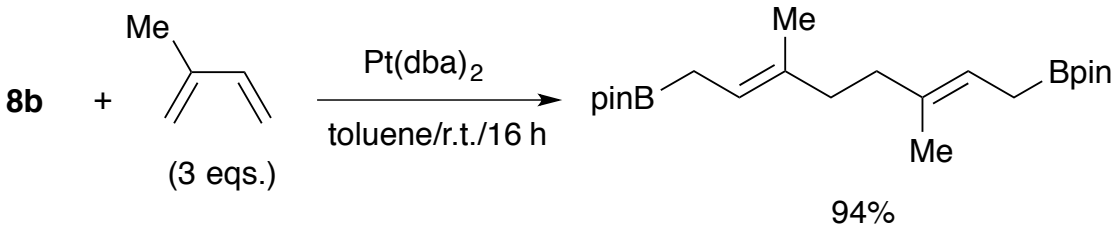


Scheme 11. Diboration of methylenecyclopropanes

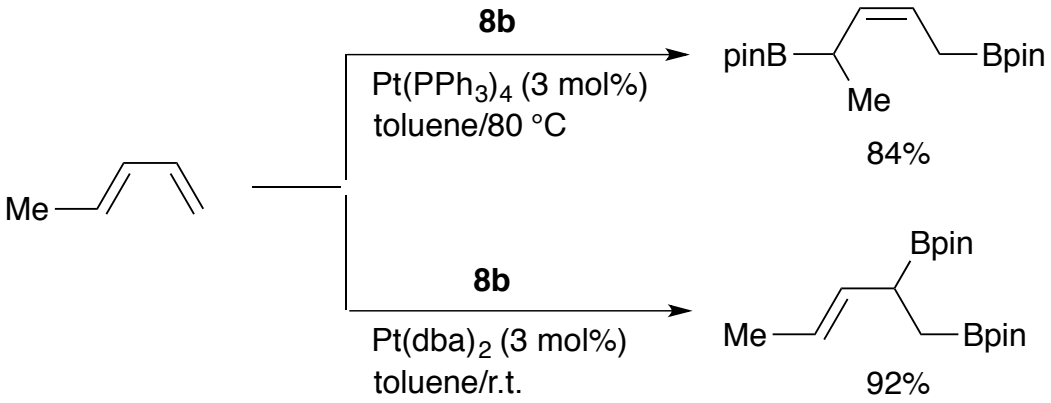


1,3-diene	yield (%)
1,3-butadiene (1.5 eqs)	95
isoprene (1.5 eqs)	93
2,3-dimethyl-1,3-butadiene (1.5 eqs)	91
1,3-pentadiene (4.5 eqs)	84
1,3-cyclohexadiene (1.5 eqs)	91

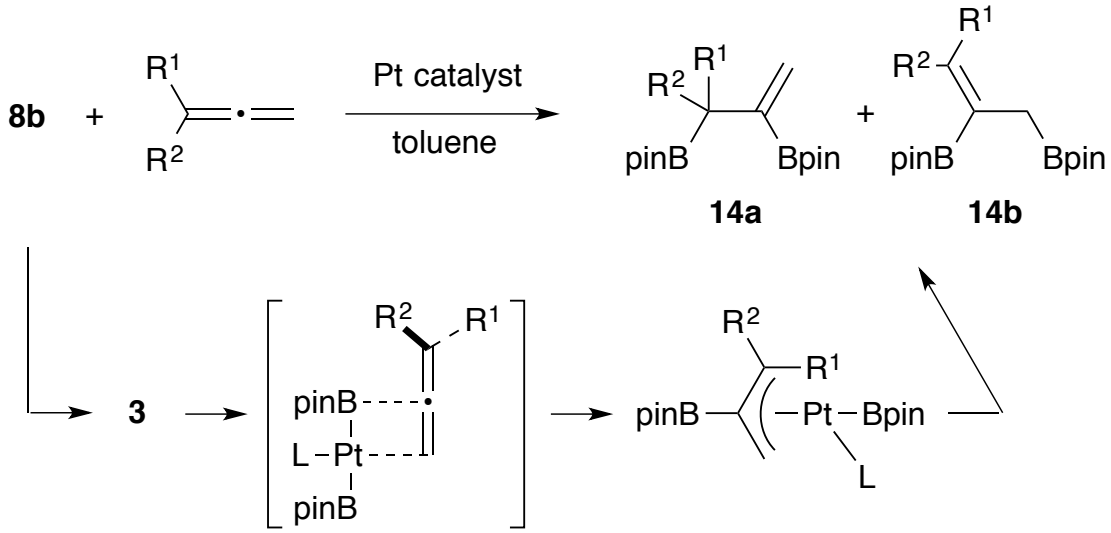
Scheme 12. Diboration of 1,3-dienes



Scheme 13. 1,8-Diboration of 1,3-dienes

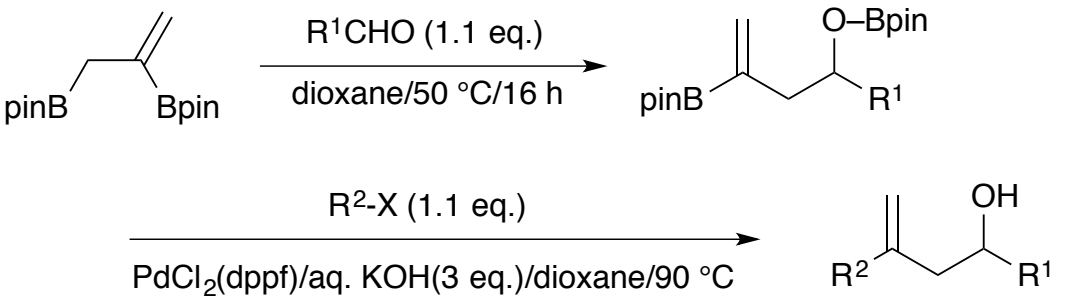


Scheme 14. 1,2- and 1,4-Diboration of 1,3-dienes



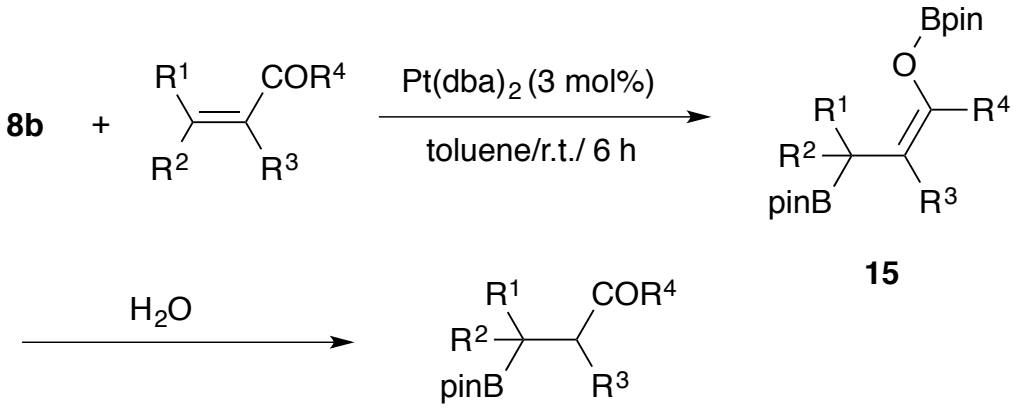
allene and product		$Pt(PPh_3)_4$/80 °C		$Pt(dba)_2$-$P(Cy)_3$/50 °C	
R^1=	R^2=	yield (%)	**14a**:**14b**	yield (%)	**14a**:**14b**
H	H	99	—	99	—
n-C_4H_9	H	97	94:6	90	84:16
Me	Me	98	24:76	99	2:98
MeO	H	81	0:100	85	0:100

Scheme 15. Diboration of allenes



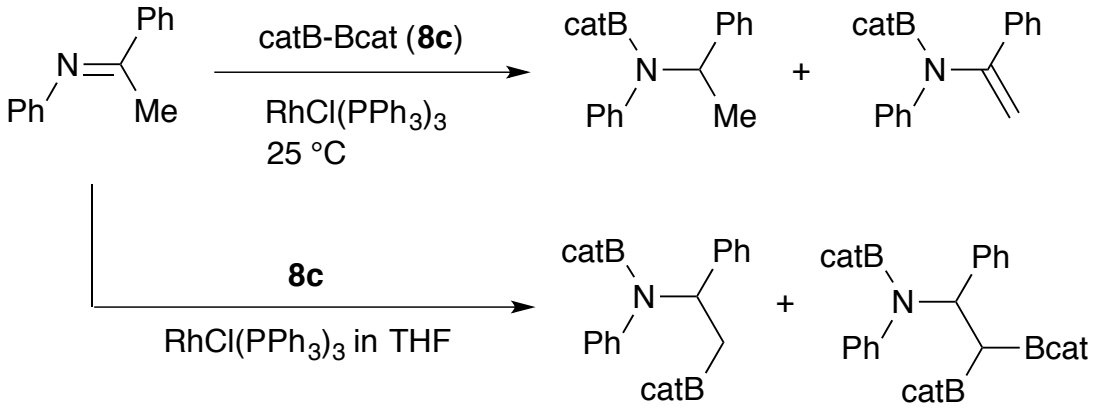
R^1CHO	R^2-X	yield (%)
PhCHO	PhI	75
n-$C_5H_{11}CHO$	PhI	62
PhCHO	$PhCH_2Cl$	61
PhCHO	(*E*)-n-$C_6H_{13}CH{=}CHI$	65

Scheme 16. Synthesis of homoallylic alcohols

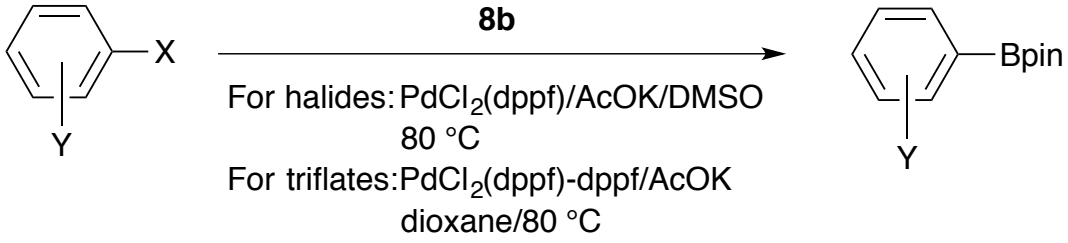


R^1	R^2	R^3	R^4	yield/%
H	H	H	CH_3	88
H	H	CH_3	CH_3	64
CH_3	H	H	CH_3	72
Ph	H	H	CH_3	90
2-cyclopentenone				88
2-cyclohexenone				61

Scheme 17. Diboration of α,β-unsaturated ketones.

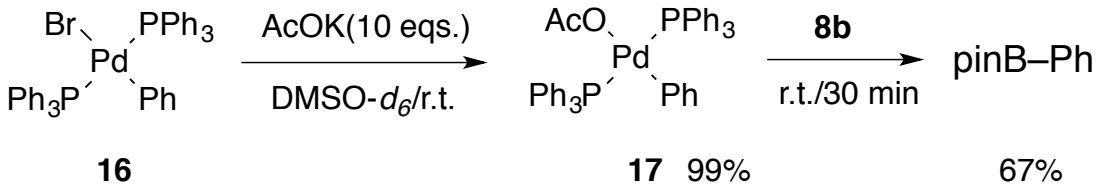


Scheme 18. Boration of imines

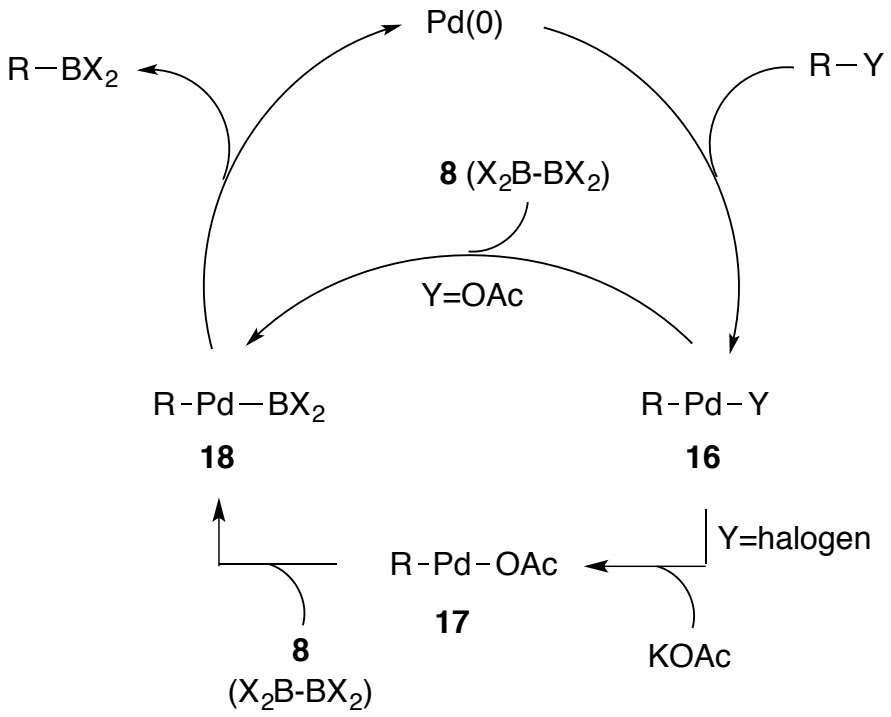


ArX (Ar=)	ArX (X=)	yield/%
p-NCC_6H_4	Br	76
	OTf	75
p-$CH_3COC_6H_4$	Br	80
	OTf	92
p-$MeOC_6H_4$	I	82
	OTf	93
p-BrC_6H_4	I	71
2,4,6-$Me_3C_6H_2$	Br	86
3-bromoquinoline		84
3-iodobenzothiophene		60

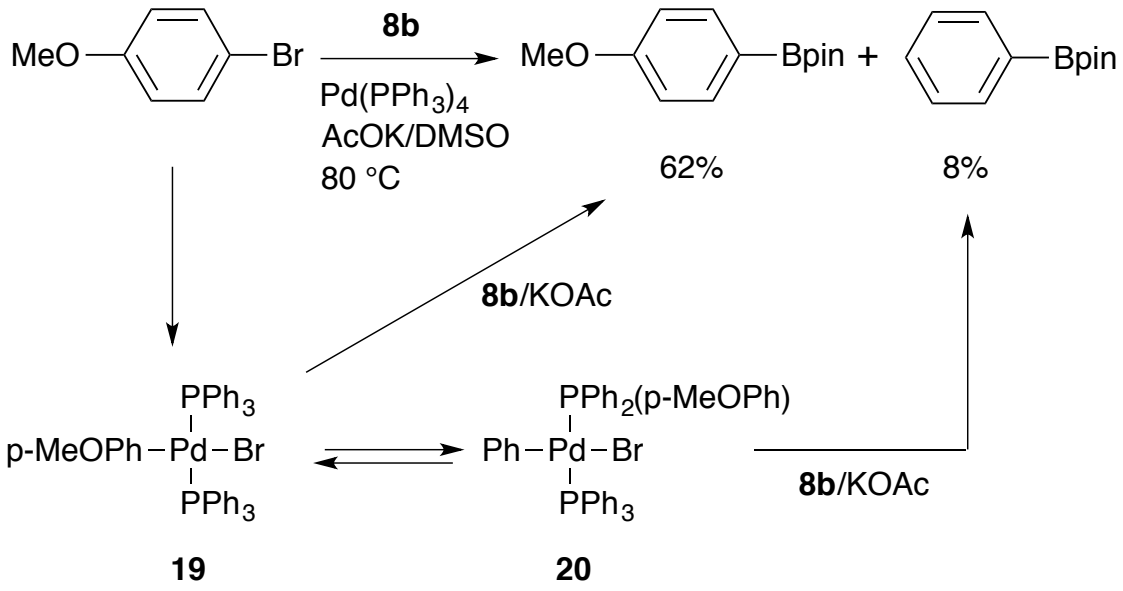
Scheme 19. Borylation of aryl electrophiles.



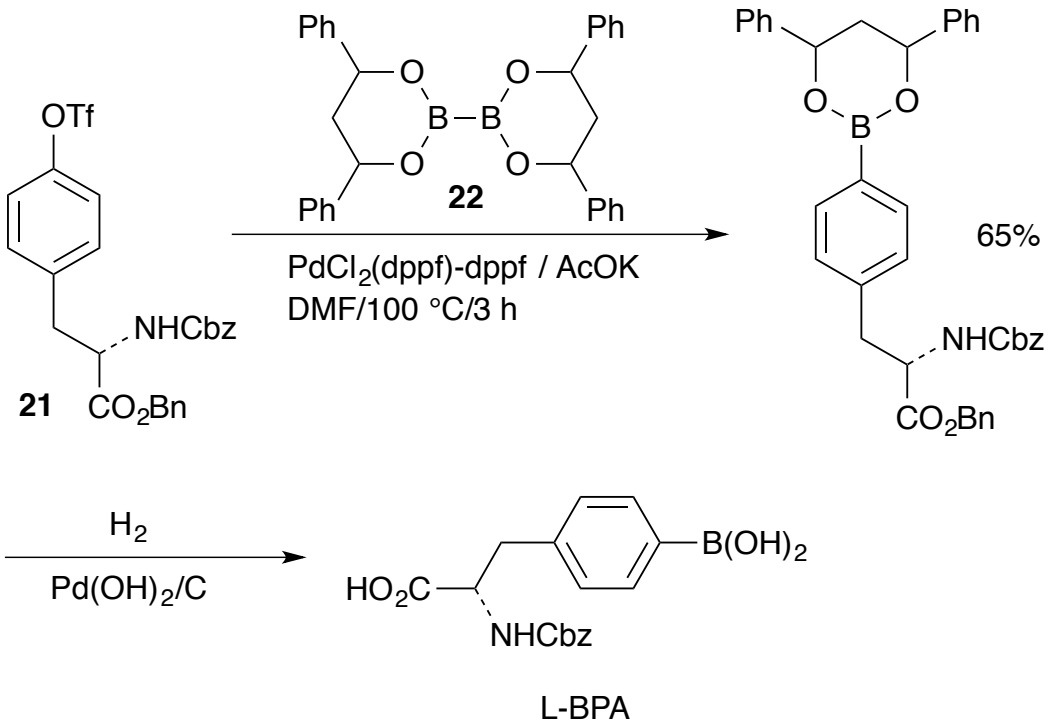
Scheme 20. (Acetoxo)palladium(II) intermediate for transmetalation



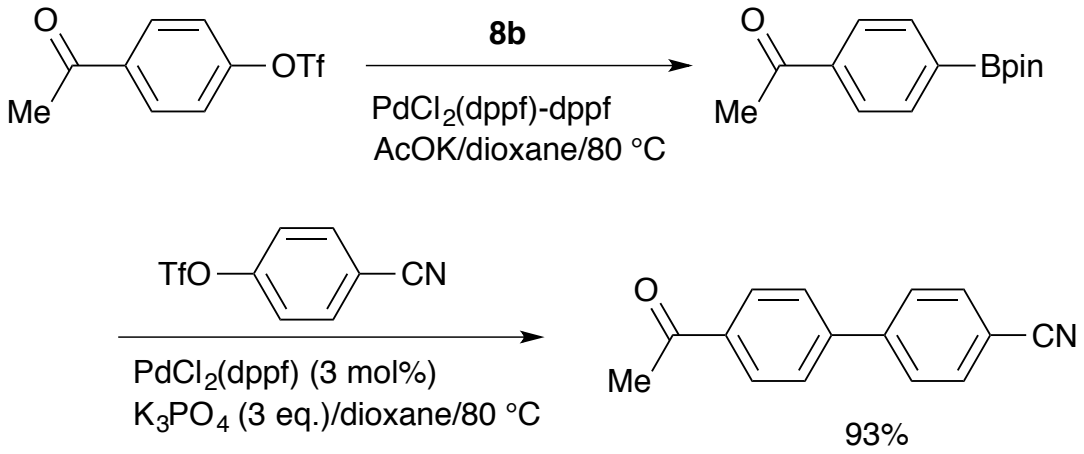
Scheme 21. Catalytic cycle for cross-coupling of diborons



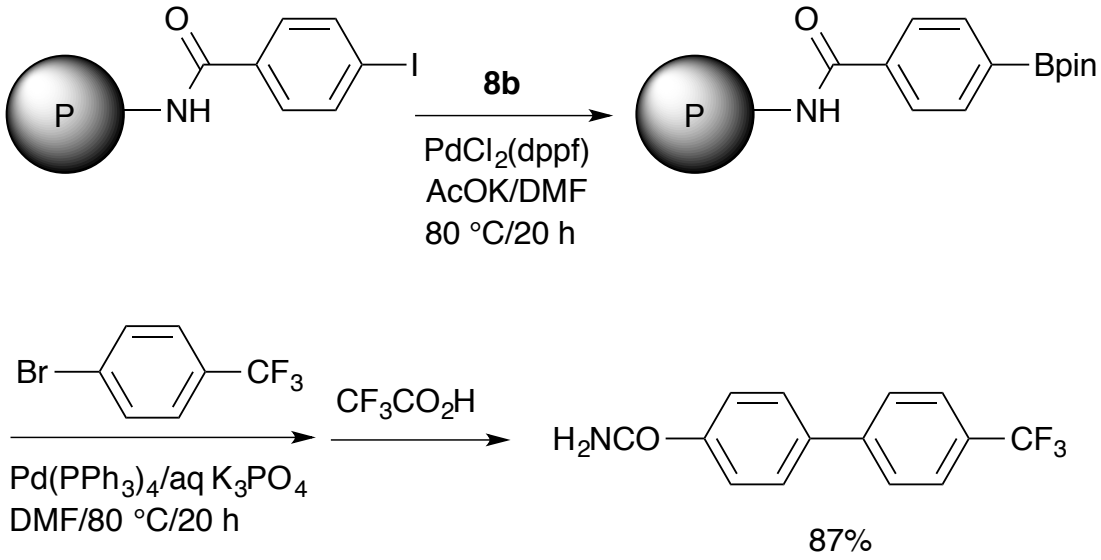
Scheme 22. Coupling with a phosphine-bound aryls



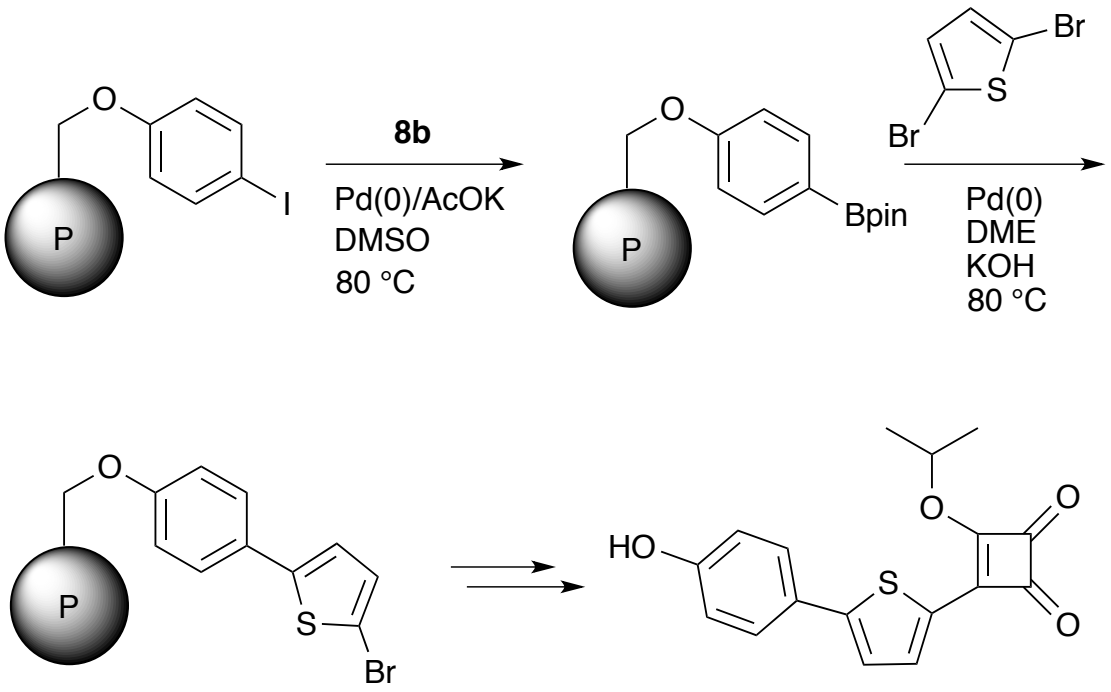
Scheme 23. Synthesis of L-BPA



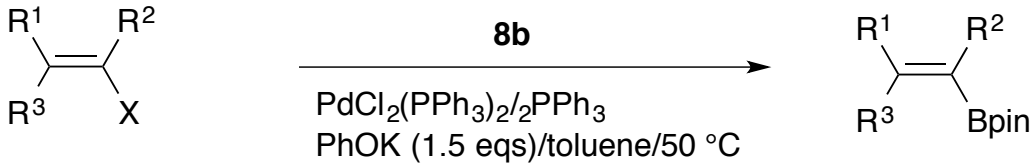
Scheme 24. One-pot synthesis of biaryls



Scheme 25. Solid-phase synthesis of biaryls



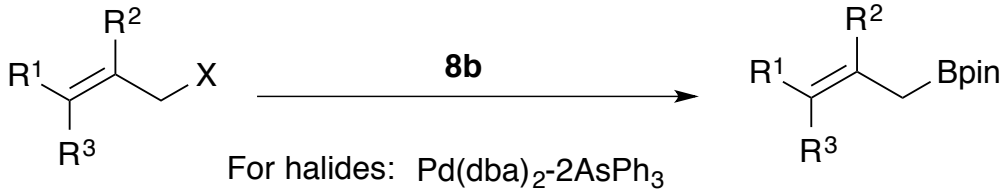
Scheme 26. Cyclobutenediones on solid support



X=Br, OTf

R^1	R^2	R^3	X	yield/%
H	n-C_8H_{17}	H	Br	69
H	Ph	H	Br	88
H	$NC(CH_2)_3$	H	Br	85
H	H	n-C_8H_{17}	Br	74
- $(CH_2)_4$ -		H	Br	99
- $(CH_2)_4$ -		H	OTf	88

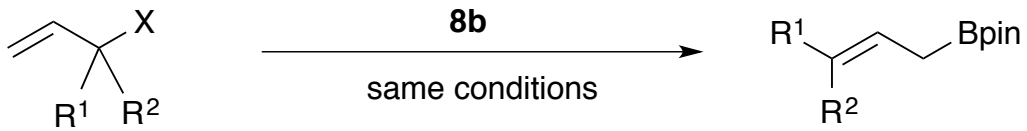
Scheme 27. Borylation of vinyl electrophiles



23

For halides: $Pd(dba)_2$-$2AsPh_3$
AcOK/toluene/50 °C
For acetates: $Pd(dba)_2$/DMSO/50 °C

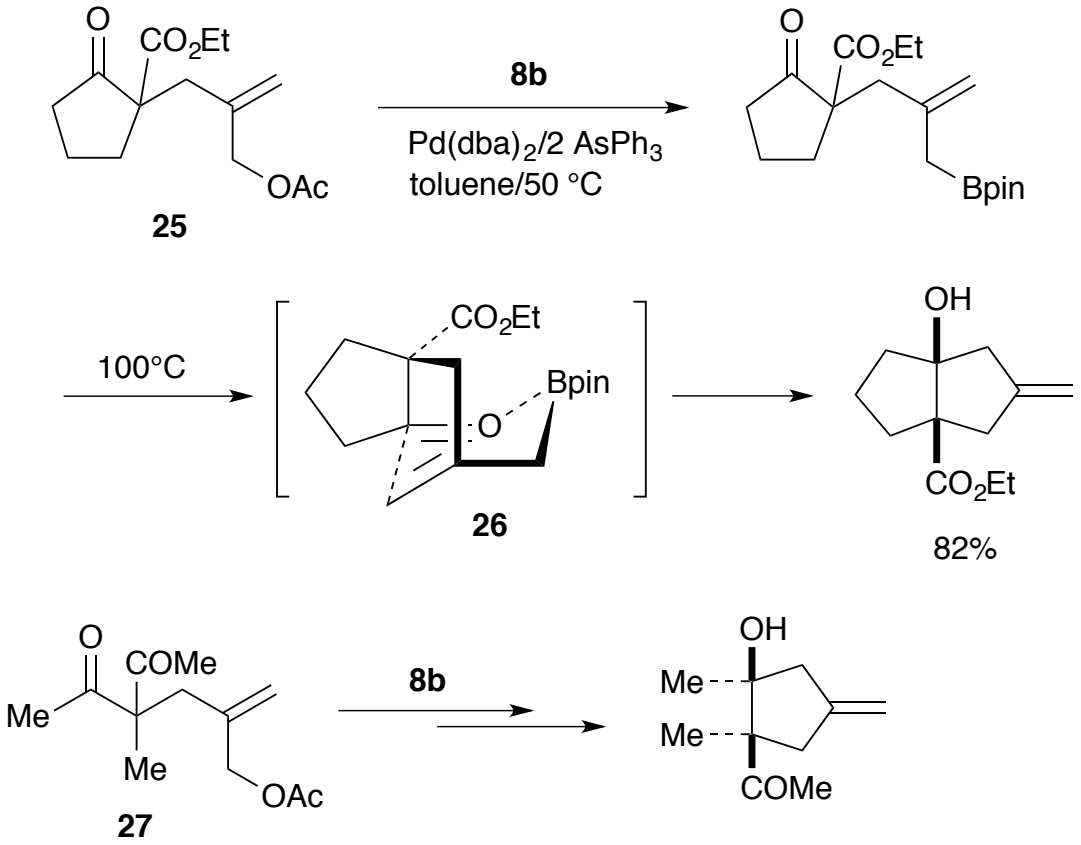
R^1	R^2	R^3	X	time/h	yield/%
Ph	H	H	Cl	10	70
Ph	H	H	OAc	26	73
H	Ph	H	Cl	5	71
H	Ph	H	OAc	16	89
Me	H	Me	Cl	5	78
Me	H	Me	OAc	60	24
3-chlorocyclohexene				5	70
3-acetoxycyclohexene				60	4



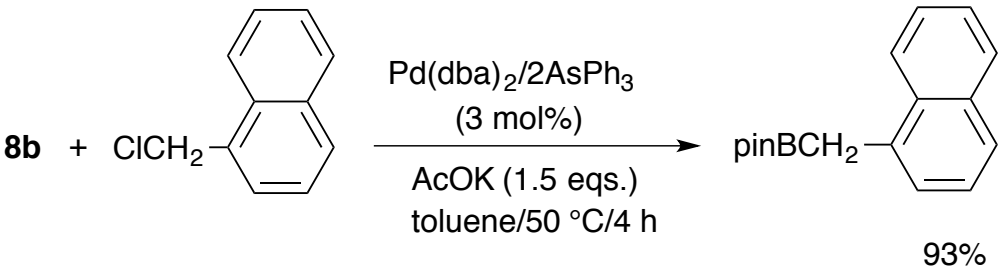
24

R^1	R^2	X	time/h	yield/%
Ph	H	Cl	10	64
Ph	H	OAc	16	83
Me	Me	OAc	16	83

Scheme 28. Borylation of allylic electrophiles.



Scheme 29. Homoallyl alcohols *via* intramolecular allylboration



Scheme 30. Cross-coupling with benzyl chlorides