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RECENT ADVANCES IN SYNTHETIC TRANSFORMATIONS WITH ROBUST YET REACTIVE B(DAN) MOIETY

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Abstract – Recent advances in the direct B(dan)-installing reactions (dan = naphthalene-1,8-diaminato) into organic frameworks by utilizing (pin)B–B(dan) or H–B(dan) as a B(dan) source, and the direct cross-coupling of dan-substituted organoboron compounds therefrom are described.

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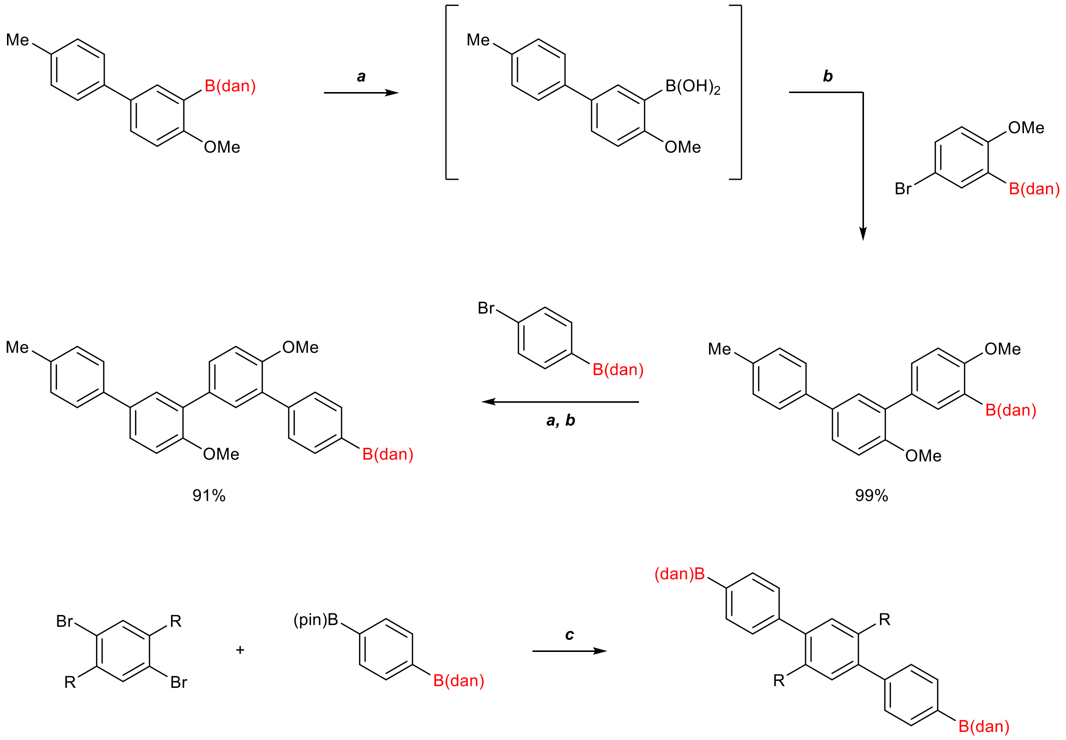
1. INTRODUCTION

Organoboronic acids [R–B$(OH)_2$][1] and esters such as R–B(pin) (pin = pinacolato) [2-5] and R–B(neop) (neop = neopentyl glycolato) [6-7] have been the linchpin in the boron-based synthetic organic chemistry,[8-10] where their boron Lewis acidity strongly affects reactivity and stereoselectivity in various carbon–carbon and carbon–heteroatom bond-forming reactions. In addition, the Lewis acidity often has an impact on stability of organoboron compounds.[11-17] Hence diminishing the inherent Lewis acidity arising from the empty p orbital by introducing suitable substituents on the boron center leads to a drastic change in the properties and behavior of corresponding organoboron compounds. A naphthalene-1,8-diaminato moiety (dan) is the representative substituent for the boron Lewis acidity-diminishment, because a dan-substituted boryl group [B(dan)] can form nearly ideal B(sp^2)-hybridized orbital derived from its planar six-membered ring structure with effective electron-donation to the empty p orbital from adjacent nitrogen atoms.[18,19] The diminished Lewis acidity leads to robust property of dan-substituted organoboron compounds [R–B(dan)], and the most typical synthetic utilization of them is iterative Suzuki–Miyaura coupling (SMC) developed by Suginome in 2007,[20,21] where the carbon–B(dan) bonds stay completely intact even under strongly basic aqueous conditions (Scheme 1). As shown in Figure 1, the number of papers related to B(dan) has been on a rise in the last decade, which shows a growing recognition towards the synthetic utility of R–B(dan).



Reaction conditions: (a) H_2SO_4 aq. or HCl aq., THF, rt; (b) Pd[P(tBu)$_3$]$_2$ (2 mol%), CsF, THF, 60 °C.
(c) Pd[P(tBu)$_3$]$_2$ (2 mol%), NaOH aq., 1,4-dioxane, H_2O, 60 °C, 4 h.
Scheme 1

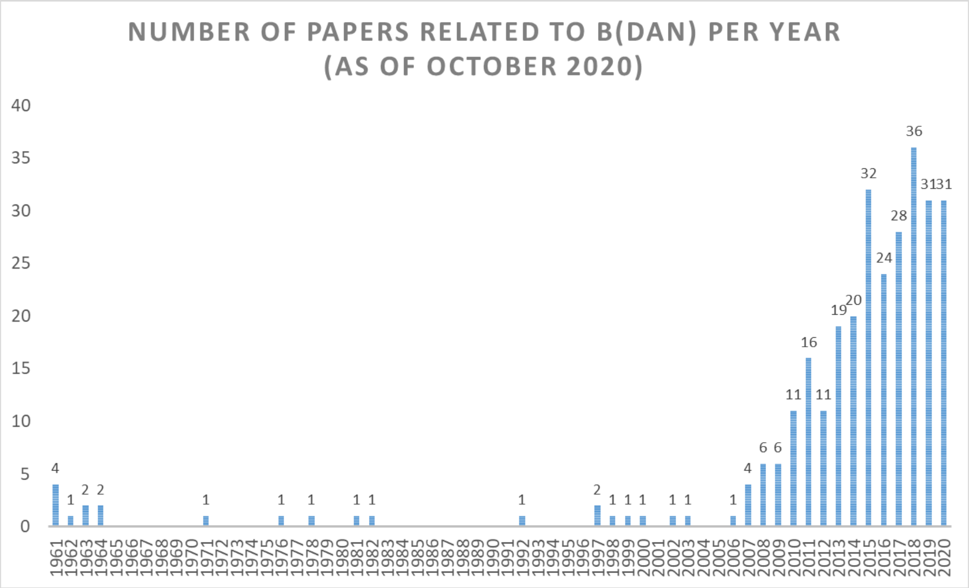
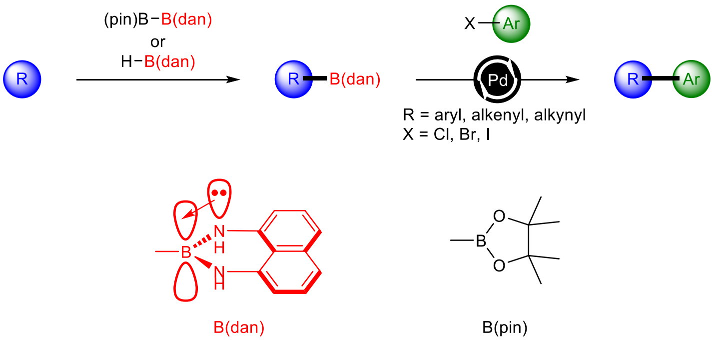


Figure 1

This review aims to summarize recent advances[22-24] in synthetic methods of accessing diverse R–B(dan), especially focusing on direct installation of a B(dan) moiety into organic frameworks by use of a diboron [(pin)B–B(dan)] and a borane [H–B(dan)] as a B(dan) source. Moreover, construction of carbon–carbon bonds based upon direct SMC with R–B(dan), which were believed to be totally inert toward SMC until recently, is also described (Scheme 2).

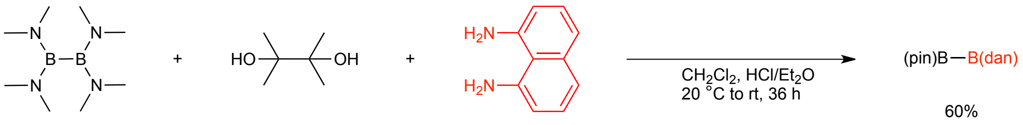


Scheme 2

2. SYNTHESIS OF B(DAN)-INSTALLING REAGENTS

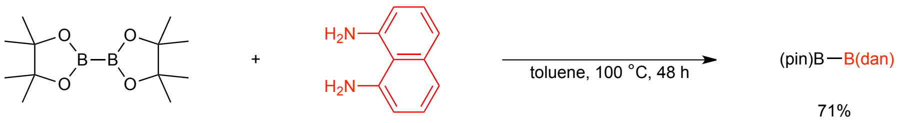
2-1. (pin)B–B(dan)

In 2010, Suginome reported the first synthesis of an unsymmetrical diboron, (pin)B–B(dan), from tetrakis(dimethylamino)diboron, 1,8-diaminonaphthalene and pinacol in the presence of hydrogen chloride (Scheme 3).[25]



Scheme 3

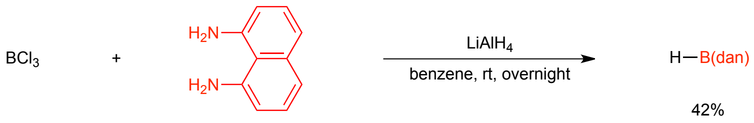
Yoshida developed the modified synthesis of (pin)B–B(dan) using readily available (pin)B–B(pin) and 1,8-diaminonaphthalene, in which one of the pin moieties was selectively substituted (Scheme 4).[26,27]



Scheme 4

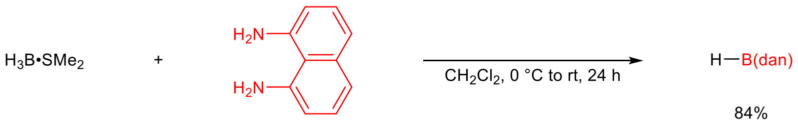
2-2. H–B(dan)

dan-Substituted borane, H–B(dan), was first synthesized by Caserio in 1961 by the reaction of boron trichloride and 1,8-diaminonaphthalene, followed by treatment of the resulting Cl–B(dan) with $LiAlH_4$ (Scheme 5).[28]

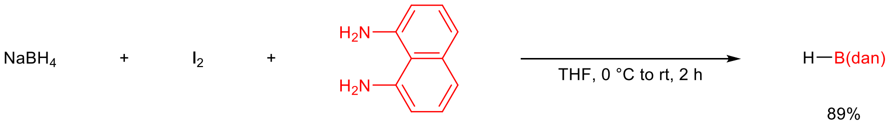


Scheme 5

Direct synthesis of H–B(dan) was achieved by dehydrogenative coupling with BH_3•SMe_2 as a boron source (Scheme 6),[29] and Tsuchimoto developed a practical approach to H–B(dan) by employing $NaBH_4$ (Scheme 7).[30]



Scheme 6



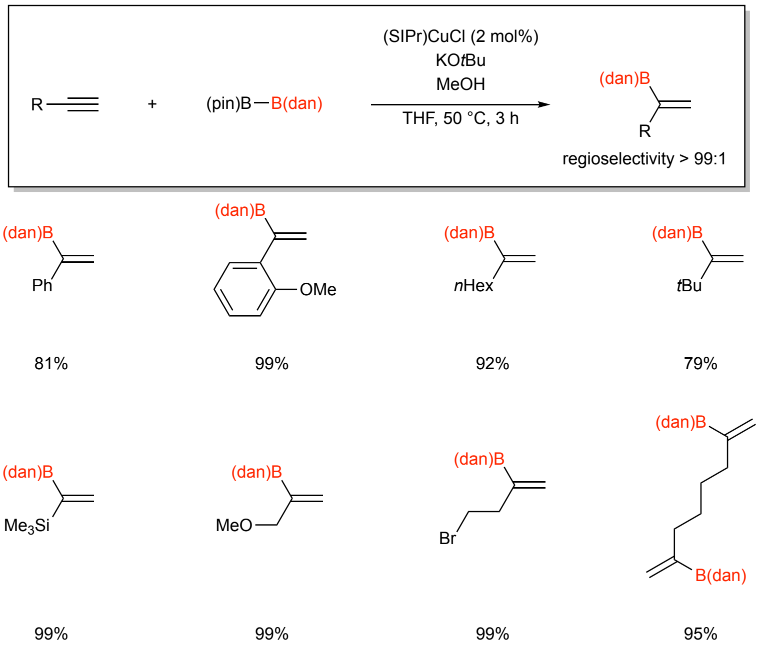
Scheme 7

3. B(DAN)-INSTALLING REACTIONS WITH (PIN)B–B(DAN)

3-1. Monoborylation including addition to unsaturated carbon–carbon bonds

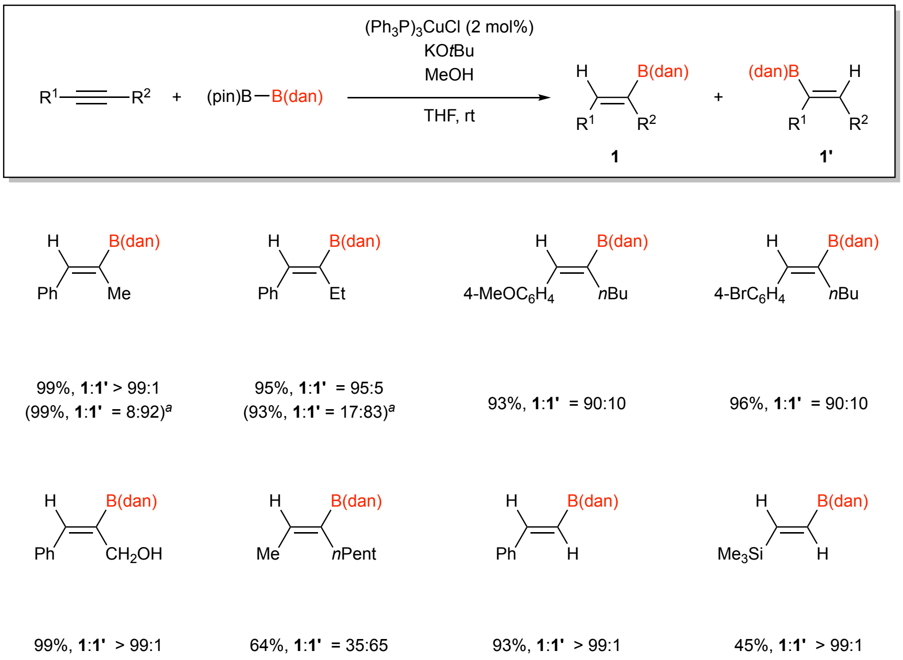
3-1-1. Hydroboration and related reactions

In 2014, Yoshida first disclosed that (pin)B–B(dan) underwent chemoselective σ-bond metathesis with a copper catalyst to generate a dan-substituted borylcopper species, which served as a key catalytic intermediate for the B(dan)-installing three-component hydroboration of terminal alkynes with a bulky *N*-heterocyclic carbene (SIPr) ligand and MeOH as a proton source (Scheme 8).[26] It should be noted that the B(dan) moiety is exclusively attachable to the internal carbons to provide Markovnikov-type branched alkenylboron compounds efficiently, being in stark contrast to the *anti*-Markovnikov regioselectivity observed in the usual hydroboration.[31]



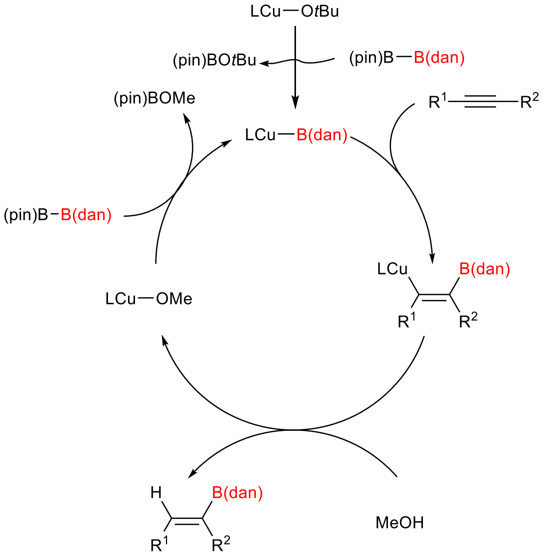
Scheme 8

Internal alkynes were also found to be hydroborated in regio- and stereoselective manners under the copper catalysis; alkyl(aryl)alkynes accepted the B(dan)-addition at the geminal position to the alkyl group in the presence of $(Ph_3P)_3CuCl$, whereas the reaction with (SIPr)CuCl resulted in the inverse regioselectivity (Scheme 9).[32] Furthermore, phenylacetylene and (trimethylsilyl)acetylene could be converted into the respective linear alkenylboron compounds with $(Ph_3P)_3CuCl$, verifying that the choice of ligands as well as the diminished boron-Lewis acidity is the key to achieving Markovnikov selectivity.



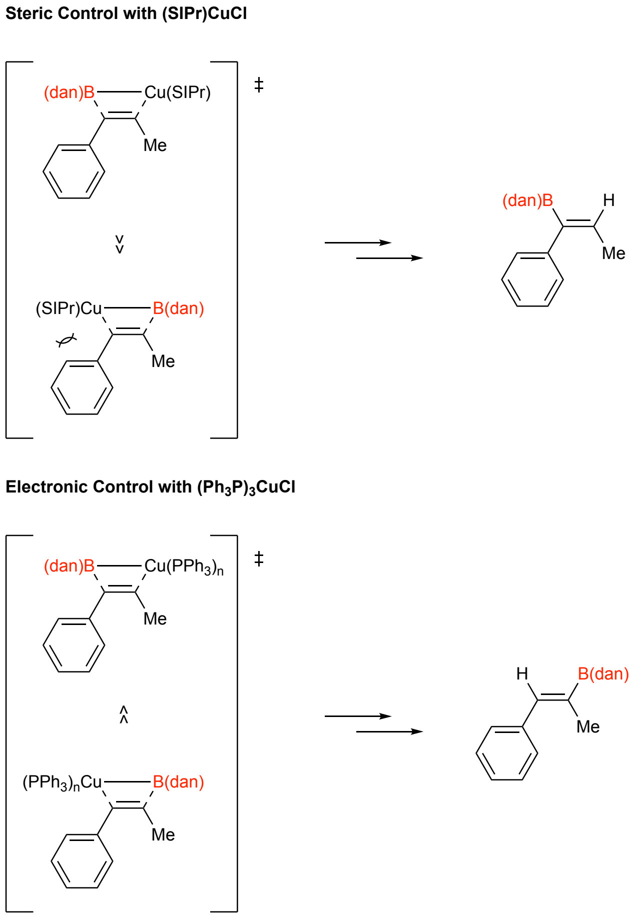
[a] (SIPr)CuCl was used instead of $(Ph_3P)_3CuCl$, 50 °C instead of rt.

Scheme 9

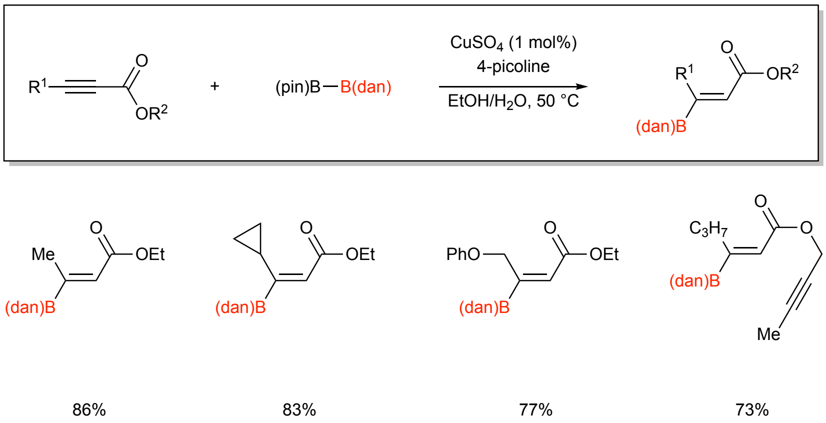


Scheme 10

A catalytic cycle of the hydroboration would be commenced by exclusive formation of a dan-substituted borylcopper species, Cu–B(dan), which can be rationally explained by selective interaction between the Lewis acidic B(pin) moiety of (pin)B–B(dan) and the alkoxy moiety of Cu–OR in σ-bond metathesis step (Scheme 10). Subsequent insertion of an alkyne into the Cu–B(dan) bond (borylcupration) which generates a borylalkenylcopper species followed by protonation with MeOH provides the hydroboration product with regeneration of Cu–OR. The orientation of Cu–B(dan) in the borylcupration step governs the regioselectivity; in the case with (SIPr)CuCl, this should be controlled by steric repulsion between a substituent on alkynes and the bulkier copper moiety, which results in the introduction of the B(dan) moiety into a sterically hindered position of alkyne (Scheme 11). In contrast, the less sterically congested copper moiety in $(Ph_3P)_n$Cu–B(dan) should be apt to be added to the α position of the aryl group according to the electronic directing effect of the aryl group of alkyl(aryl)alkynes.



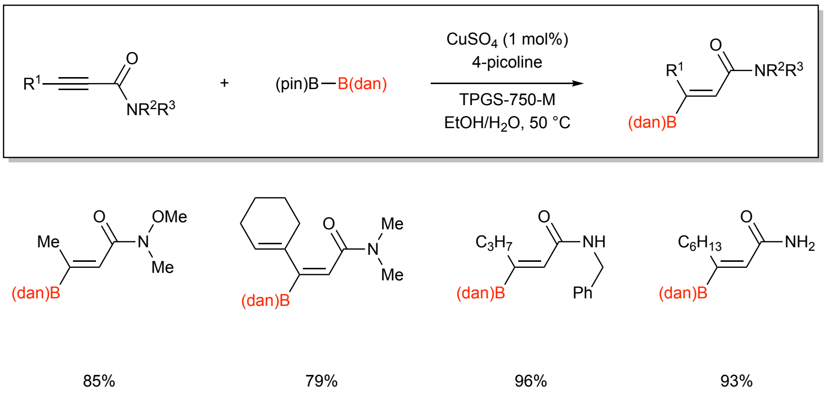
Scheme 11



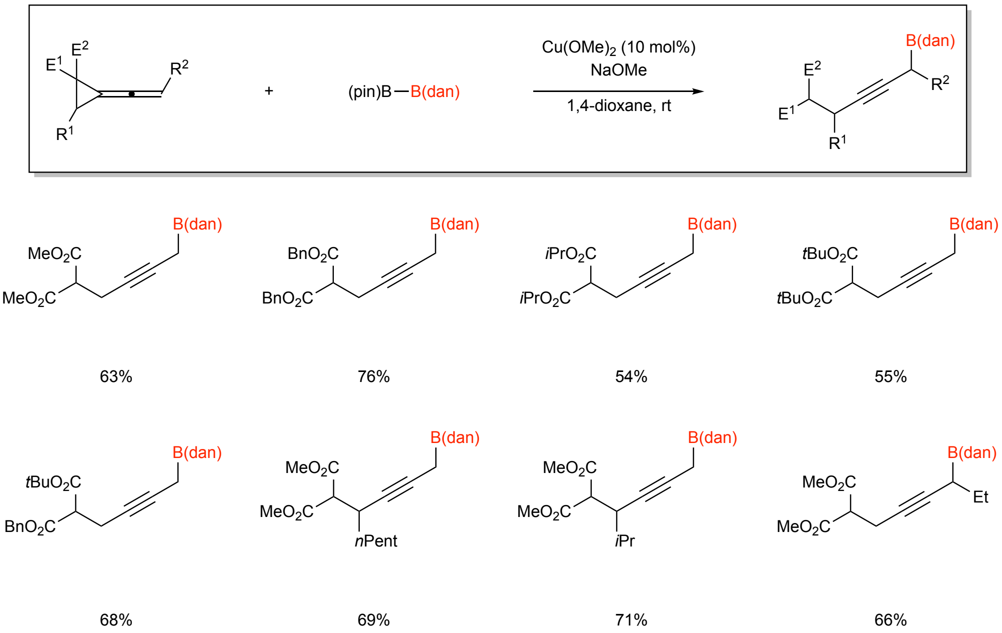
Scheme 12

Similar B(dan)-installing *syn*-hydroboration of alkynoates and alkynamides under Cu(II) catalysis was reported by Santos, in which the B(dan) moiety was regioselectively attached to the β-position (Scheme 12 and 13).[33]

Vinylidene cyclopropanes bearing electron-withdrawing groups could also participate in the copper-catalyzed B(dan)-installation at the terminal carbon of the allene moieties to afford propargylboron compounds (Scheme 14).[34]

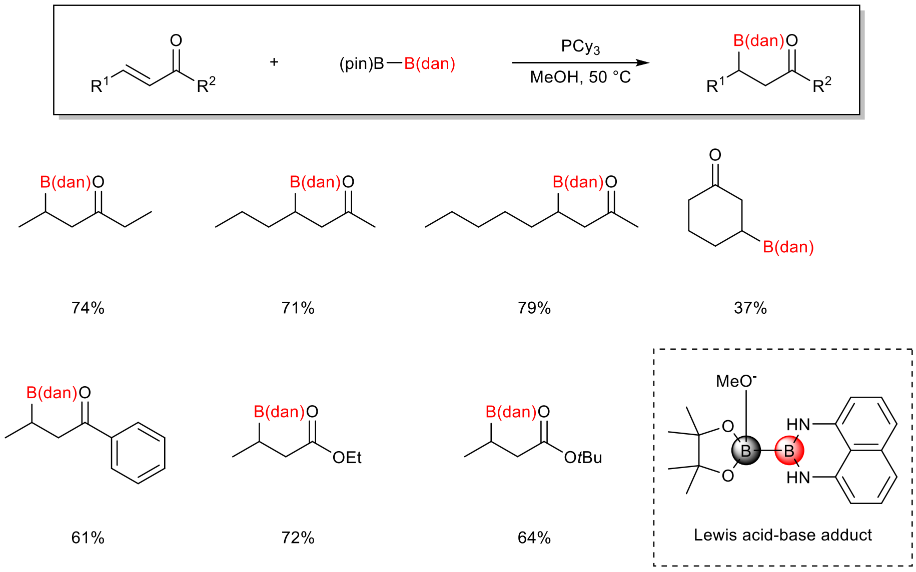


Scheme 13



Scheme 14

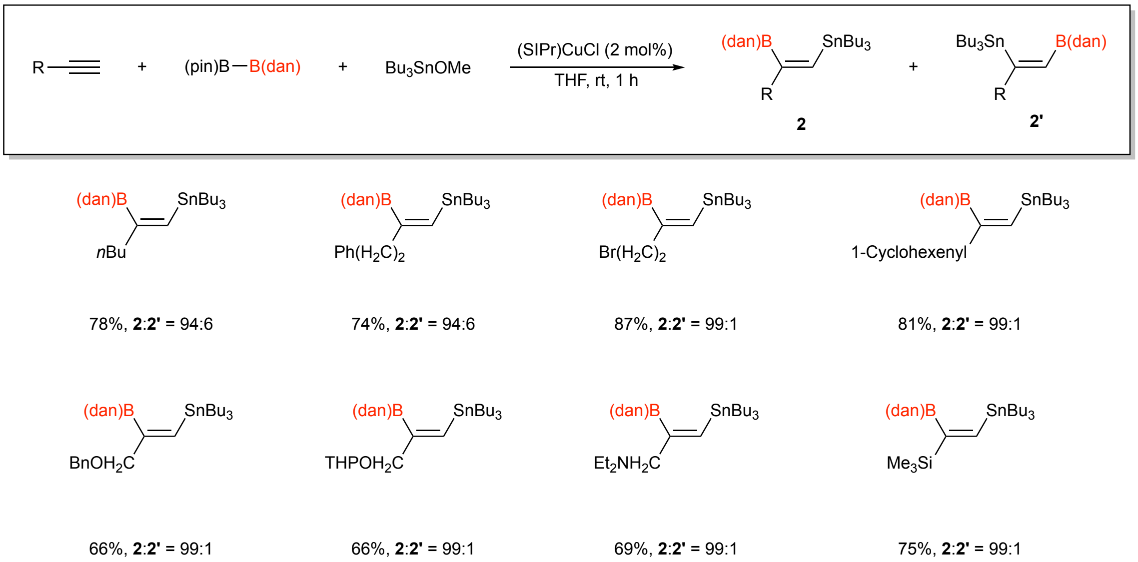
In 2014, Fernández demonstrated that (pin)B–B(dan) could be activated in a site-selective fashion under transition metal-free conditions. Thus, treatment of α,β-unsaturated carbonyl compounds with PCy_3 in methanol led to B(dan)-selective conjugate addition, where in situ-generated methoxide attacked more Lewis acidic B(pin) site to give $[MeO\rightarrow B(pin)–B(dan)]^-$ intermediate (Scheme 15).[35]



Scheme 15

3-1-2. Borylstannylation

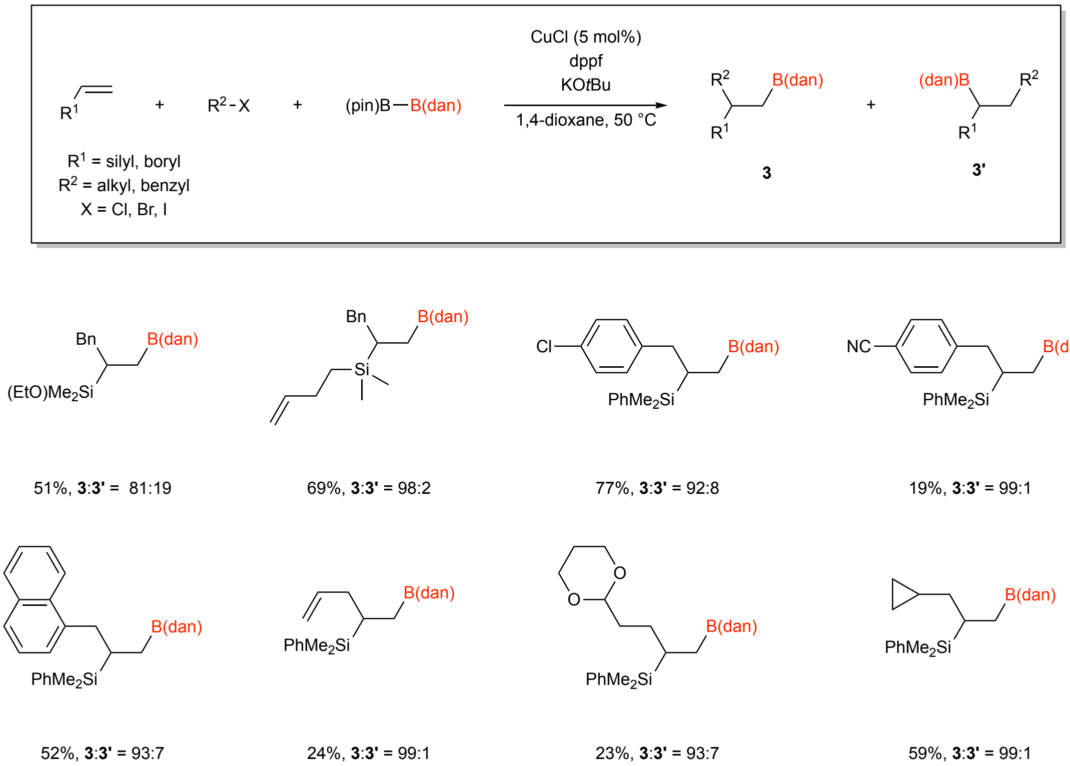
The use of a tin alkoxide as a third-component allowed copper-catalyzed three-component borylstannylation of terminal alkynes to proceed regio- and stereoselectively, giving *syn*-*vic*-boryl(stannyl)alkenes (Scheme 16).[36] It is worthy of note that the boron moieties were installed into an internal carbon of terminal alkynes, being in marked contrast to well-established terminal selectivity in the previous borylstannylations.[37-39]



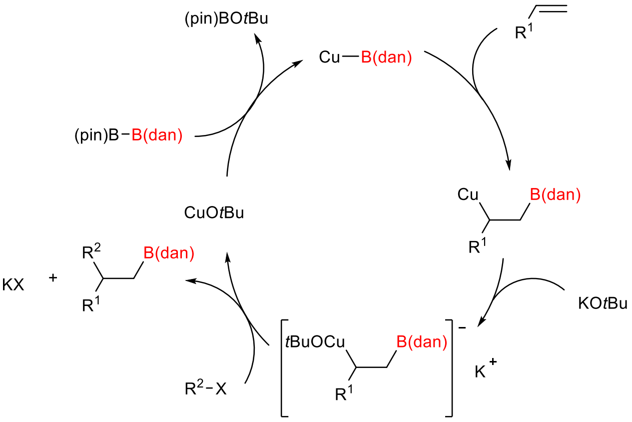
Scheme 16

3-1-3. Carboboration

Three-component B(dan)-installing carboboration with (pin)B–B(dan) was first developed by Yoshida; silyl and borylalkenes facilely underwent the reaction with alkyl halides in the presence of a dppf–CuCl catalyst, resulting in the simultaneous formation of C–B and C–C bonds (Scheme 17).[40]

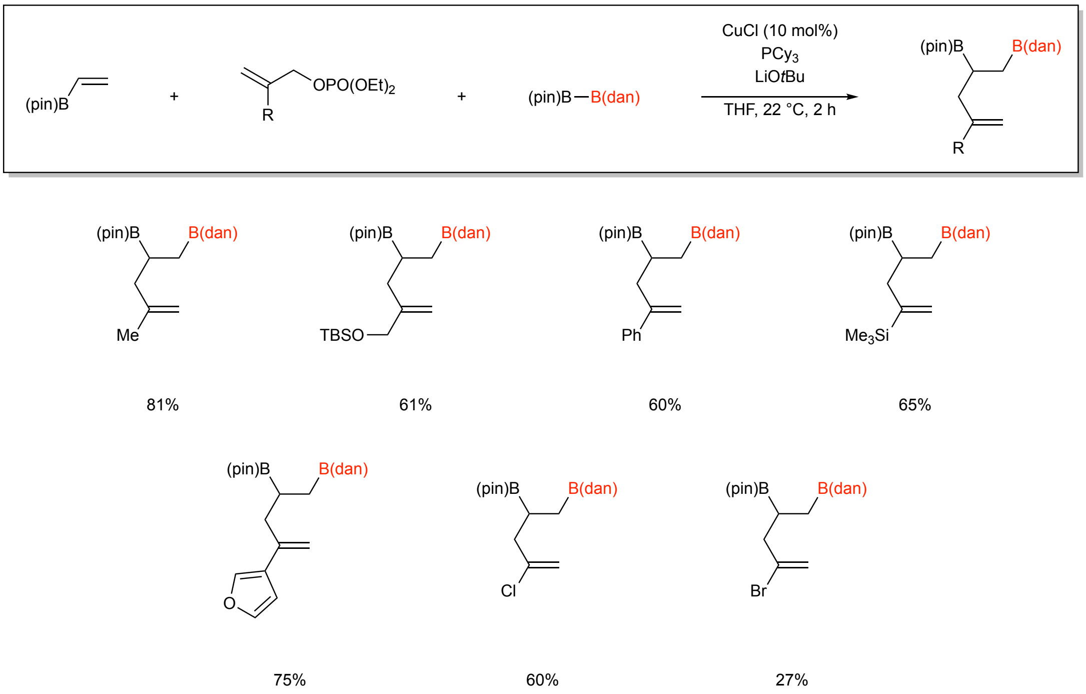


Scheme 17

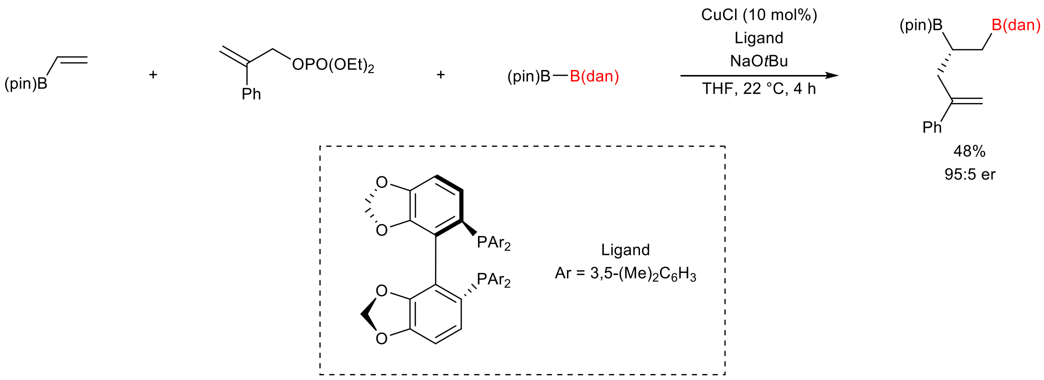


Scheme 18

As is the case of the above hydroboration (Scheme 10), Cu–B(dan) is a key intermediate in this carboboration (Scheme 18). After insertion of an alkene into the Cu–B bond, an alkylcopper species thus generated accepts coordination of an alkoxide to form an alkylcuprate species, which is finally captured by a carbon electrophile to give the product.



Scheme 19

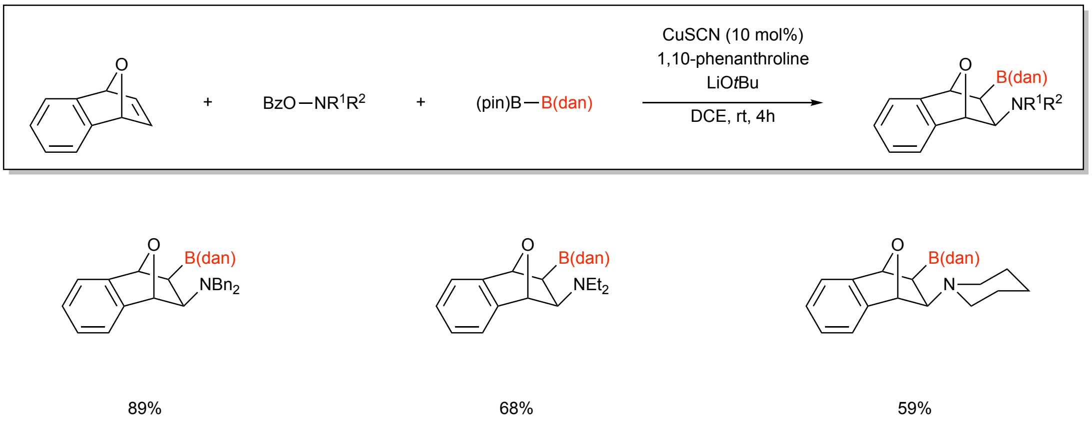


Scheme 20

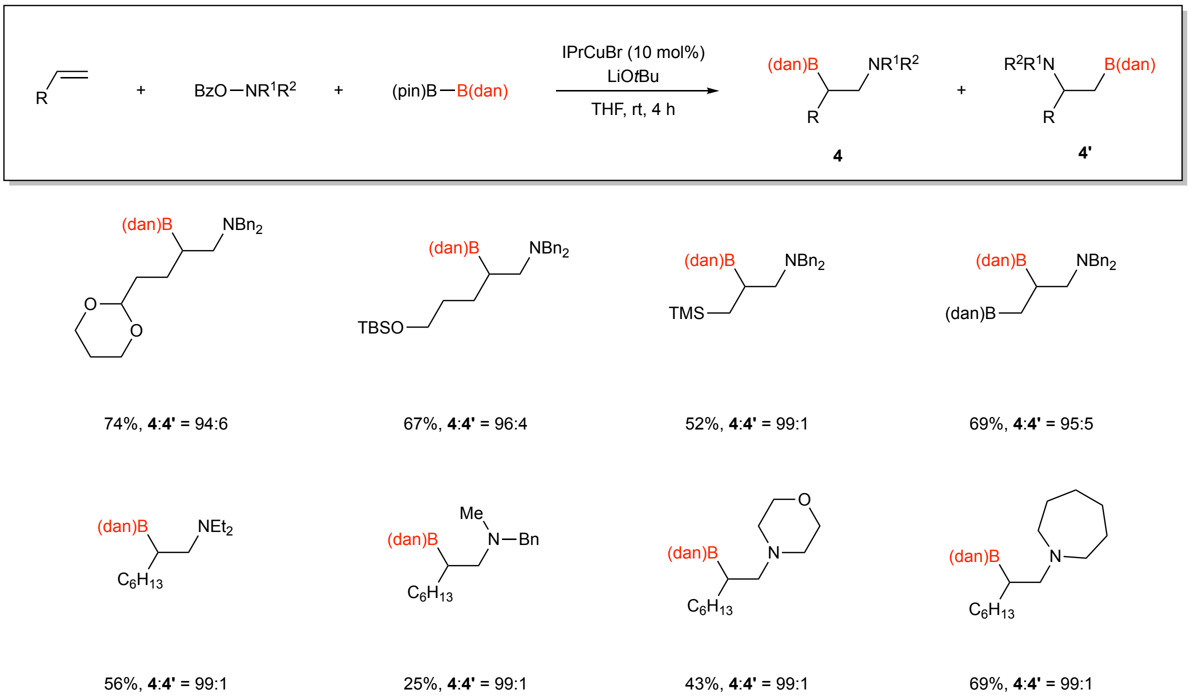
Similar carboboration with allyl phosphates as a carbon electrophile was also reported (Scheme 19),[41] and this reaction was extended to enantioselective version by use of a chiral bisphosphine ligand (Scheme 20).

3-1-4. Aminoboration

B(dan)-installing aminoboration was developed by Hirano and Miura, and bicyclic alkenes including oxa- and azabenzonorbornadienes were transformable into the respective products stereoselectively without the formation of ring-opened side-products (Scheme 21).[42]



Scheme 21



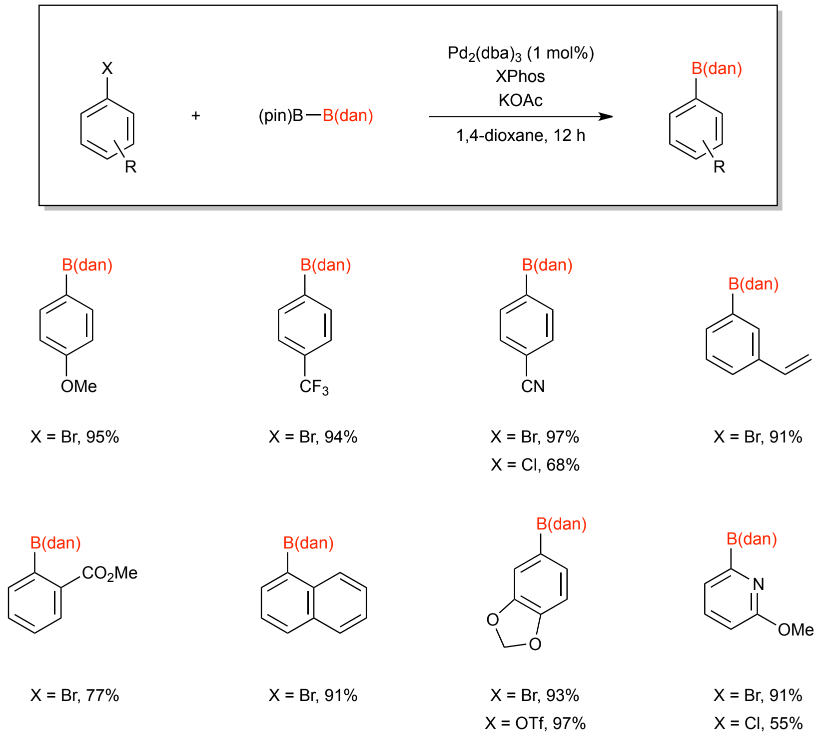
Scheme 22

Aliphatic terminal alkenes could also undergo the copper-catalyzed aminoboration, where the B(dan) moieties were regioselectively attached to an internal carbon (Scheme 22).[43]

3-2. Monoborylation including substitution

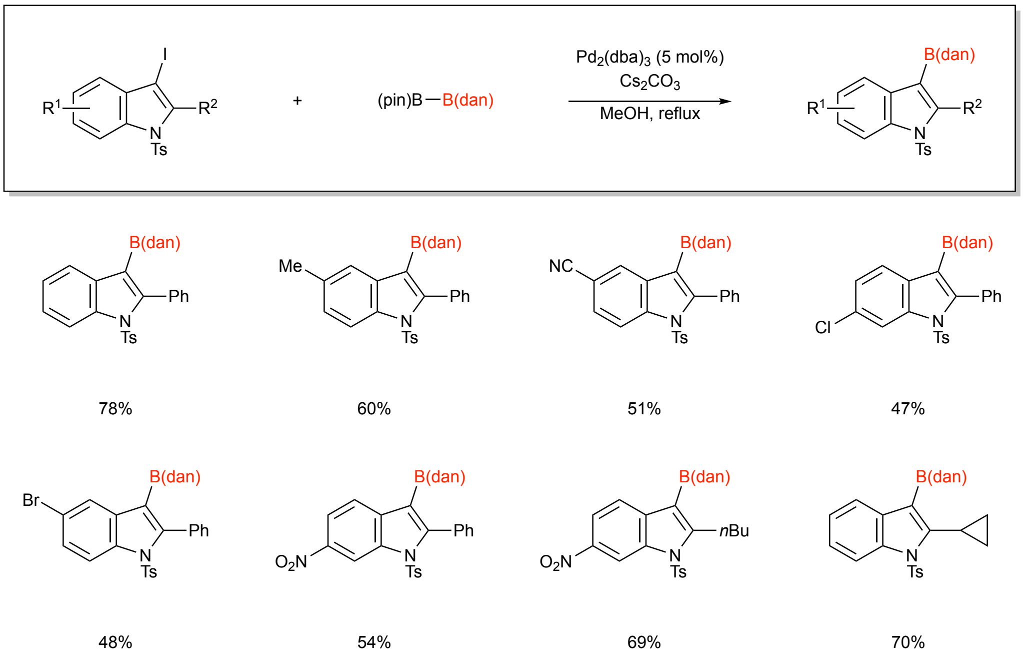
3-2-1. Borylation of carbon–halogen (pseudohalogen) bonds

Li reported on palladium-catalyzed Miyaura–Ishiyama-type borylation of aryl halides using (pin)B–B(dan) in 2015 (Scheme 23).[44] The reaction proceeds through the sole transfer of the B(dan) moiety to furnish various aryl–B(dan) in high yields.

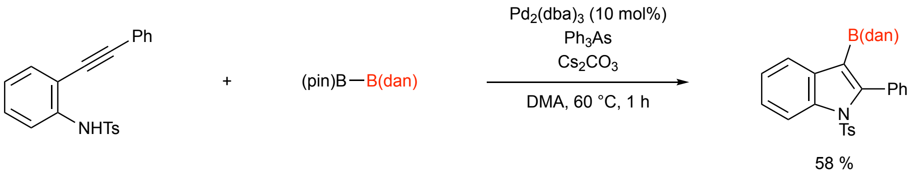


Scheme 23

Similar B(dan)-installation into indole skeletons was achieved with 3-iodoindoles under ligand-free palladium catalysis (Scheme 24).[45] In addition, the authors developed a direct approach to a B(dan)-containing indole via borylative cyclization as shown in Scheme 25. Its catalytic cycle may be similar to that of the borylative cyclization with (pin)B–B(pin).[46]

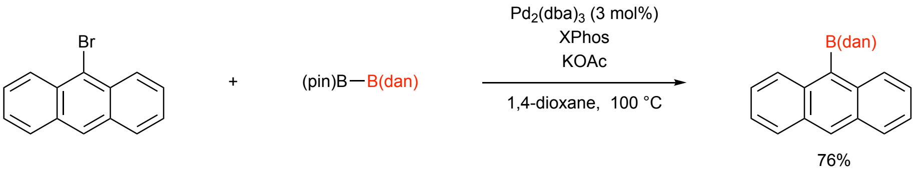


Scheme 24

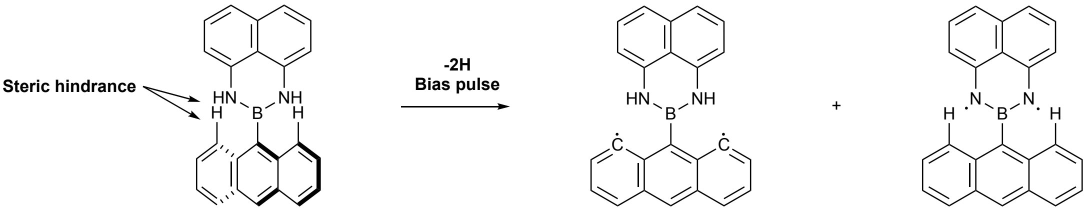


Scheme 25

Majzik and Fernández applied the Li's method to the conversion of 9-bromoanthracene to produce B(dan)-containing anthracene in 76% yield (Scheme 26).[47] They verified the original nonplanar structure of this molecule with atomic force microscopy (AFM), and succeeded in the planarization of the skeleton by removing H atoms (Scheme 27).

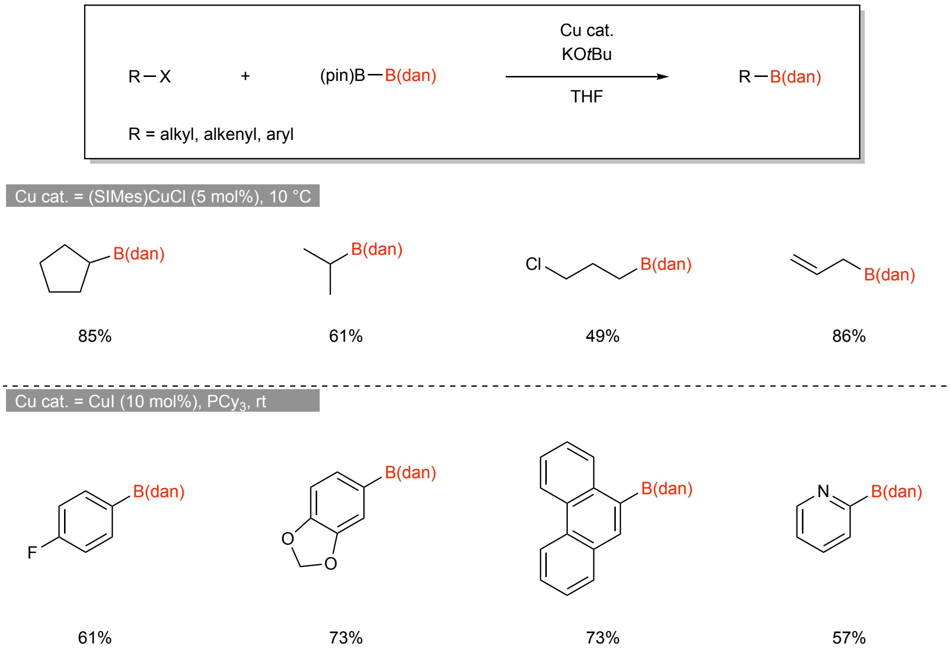


Scheme 26

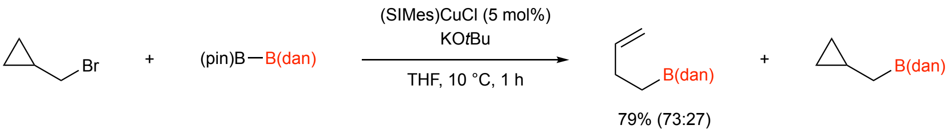


Scheme 27

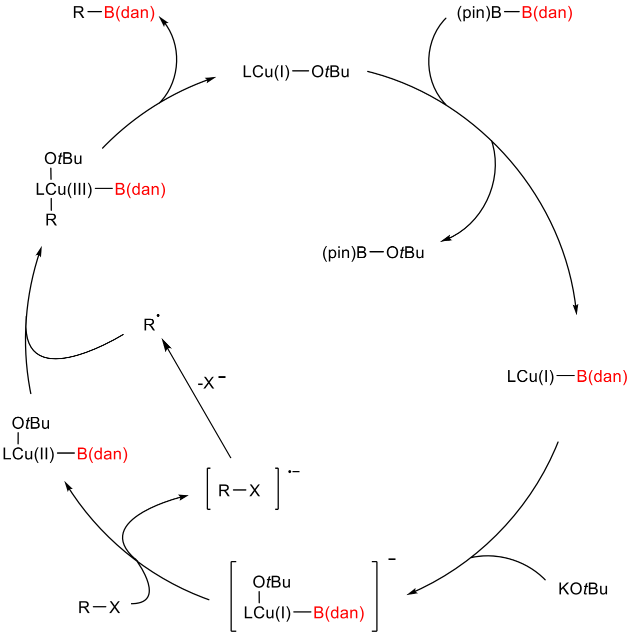
Borylative substitution of organic halides with (pin)B–B(dan) was found to be also feasible with a copper catalyst; a variety of alkyl, alkenyl, aryl and heteroaryl halides were smoothly coupled with (pin)B–B(dan) to give the respective R–B(dan) in high yields (Scheme 28).[48] Especially, it should be noted that 2-pyridyl–B(dan) obtained by this reaction shows excellent stability toward aqueous work-up and isolation by Florisil column chromatography, being in stark contrast to the well-known instability of its $B(OH)_2$- and B(pin)-counterparts.[49] Formation of a ring-opened product in the reaction of cyclopropylmethyl bromide would imply that one-electron transfer process is involved in the reaction pathway (Scheme 29), and a proposed catalytic cycle is shown in Scheme 30. A dan-substituted boryl-copper species first accepts coordination of KO*t*Bu to form an electron-rich borylcuprate, which should act as a one-electron reductant to organic halides. Subsequent elimination of X^- from the resulting radical anion species generates a radical, which is then combined with [*t*BuO–Cu(II)–B(dan)] to give a Cu(III) complex. Finally, R–B(dan) is generated from the Cu(III) complex through reductive elimination with regenerating a Cu–O*t*Bu complex.



Scheme 28

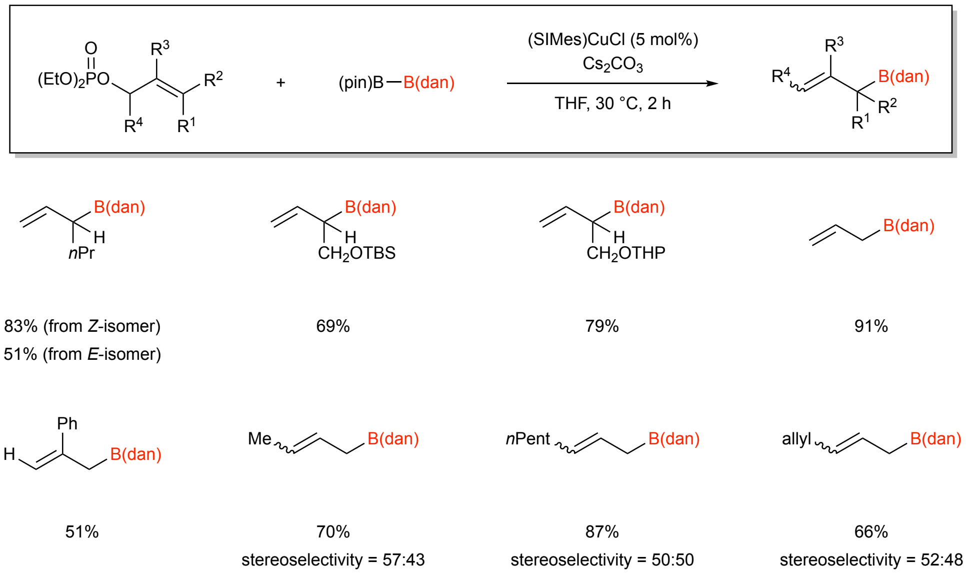


Scheme 29

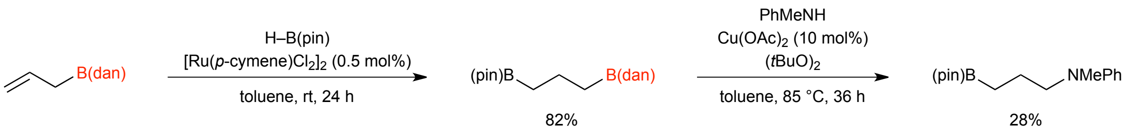


Scheme 30

γ-Selective B(dan)-installing allylic borylation of allylic phosphates was also reported to occur in the presence of a copper catalyst, affording diverse allyl–B(dan) in a straightforward manner (Scheme 31).[50] The allyl–B(dan) thus obtained could be transformed into a 1,3-diborylpropane by hydroboration with H–B(pin), and it should be noted that its B(dan) moiety was selectivity convertible into a nitrogen functionality by copper-catalyzed Chan–Lam–Evans-type coupling, leaving the C–B(pin) bond intact (Scheme 32). Although the yield still remains to be improved, the reaction has demonstrated first that a C–B(dan) bond can become more reactive under certain conditions, being in marked contrast to its inertness toward SMC because of the diminished Lewis acidity.

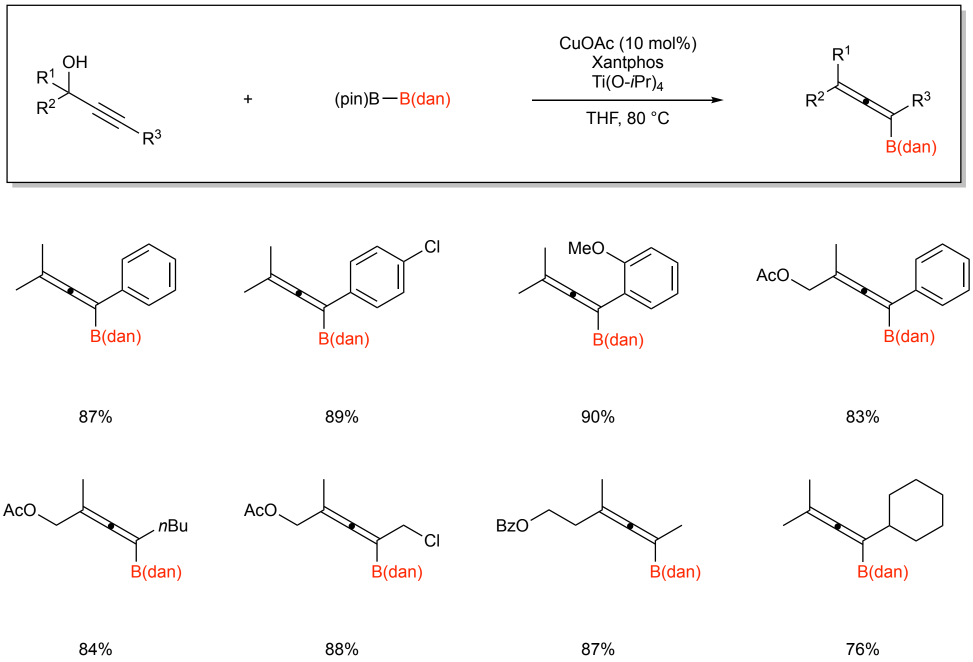


Scheme 31

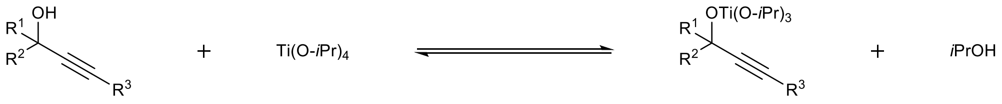


Scheme 32

Copper-catalyzed borylative substitution with (pin)B–B(dan) was further extended to propargylic alcohols to give allenyl–B(dan) via S_N2'-type reaction (Scheme 33).[51] Addition of Ti(O-*i*Pr)$_4$ is indispensable for the reaction to proceed, which can activate a hydroxy group of poor leaving ability as shown in Scheme 34.

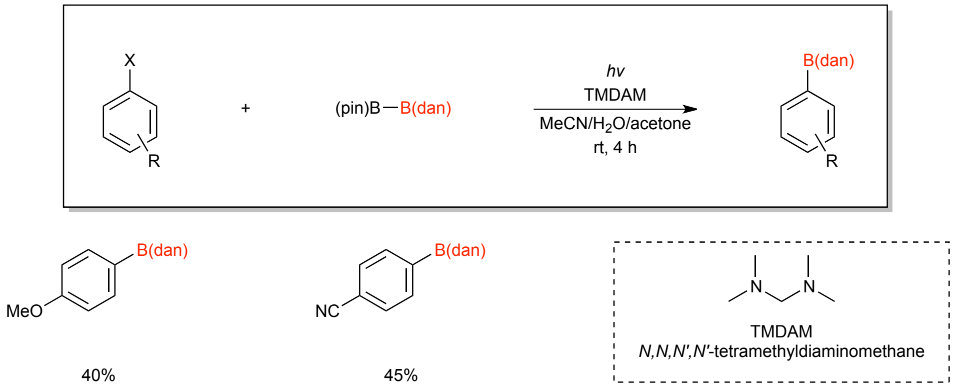


Scheme 33



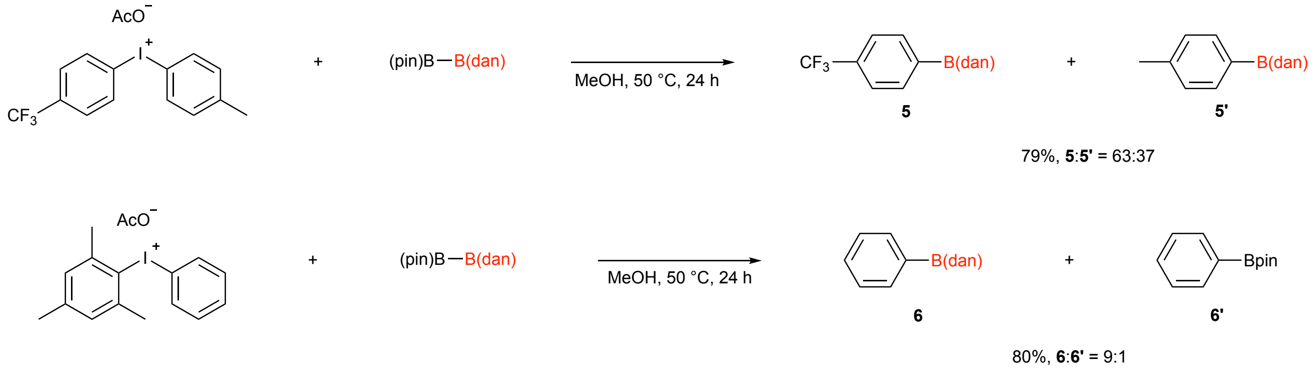
Scheme 34

Transition metal-free borylation of aryl iodides under photo-irradiation conditions was developed by Li (Scheme 35).[52] In the reaction with (pin)B–B(dan), the B(dan) moiety was selectively transferable into the aromatic frameworks, although the yields were moderate.



Scheme 35

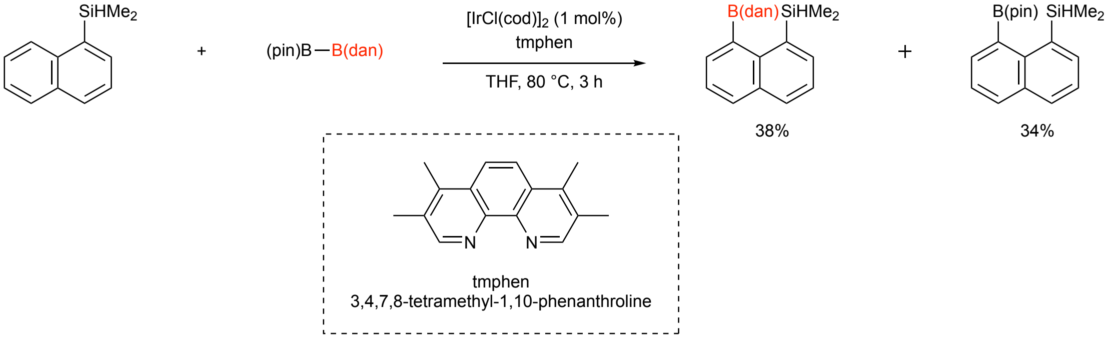
Diaryliodonium salts were also demonstrated to serve as carbon electrophiles in transition metal-free B(dan)-installation with (pin)B–B(dan) (Scheme 36).[53] Site-selective coupling with unsymmetrical mesityl(phenyl)iodonium salt was possible to afford Ph–B(dan), whereas the reaction of a diaryliodonium salt with different electronic characters without steric bias led to the formation of a mixture of two products.



Scheme 36

3-2-2. Borylation of carbon–hydrogen bonds

Hosoya reported on iridium-catalyzed silane-directed *peri*-C–H borylation using 1-(dimethylsilyl)naphthalene (Scheme 37),[54] however the use of (pin)B–B(dan) gave Ar–B(dan) and Ar–B(pin) in nearly 1:1 ratio.

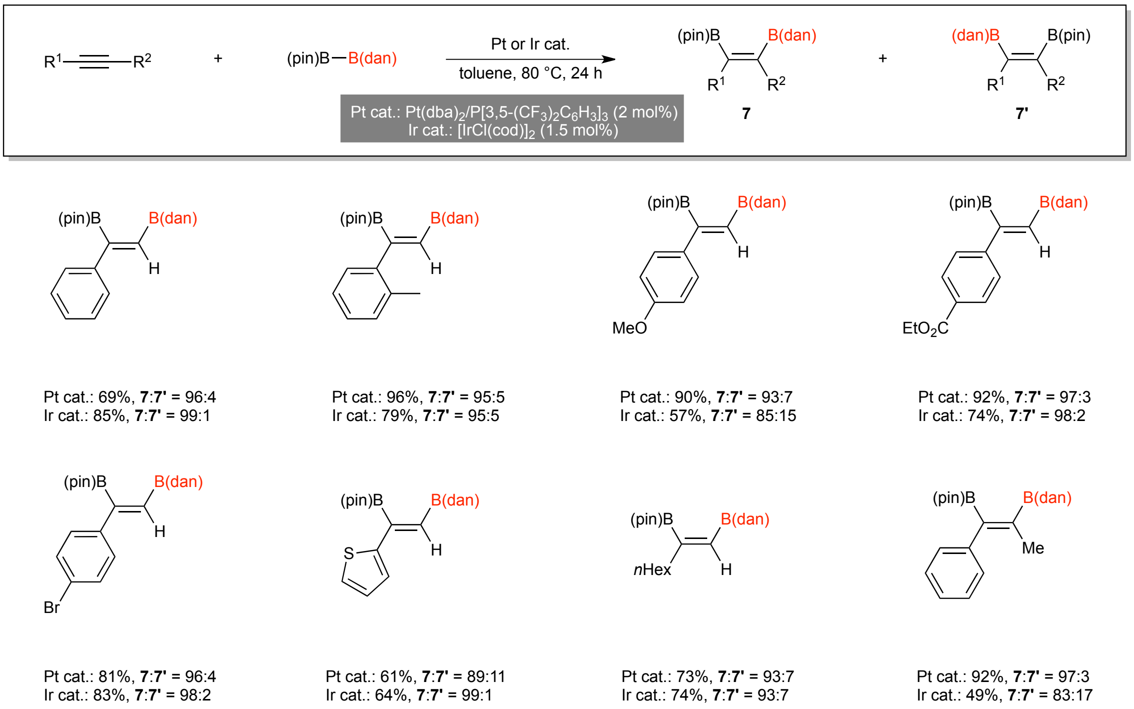


Scheme 37

3-3. Diborylation

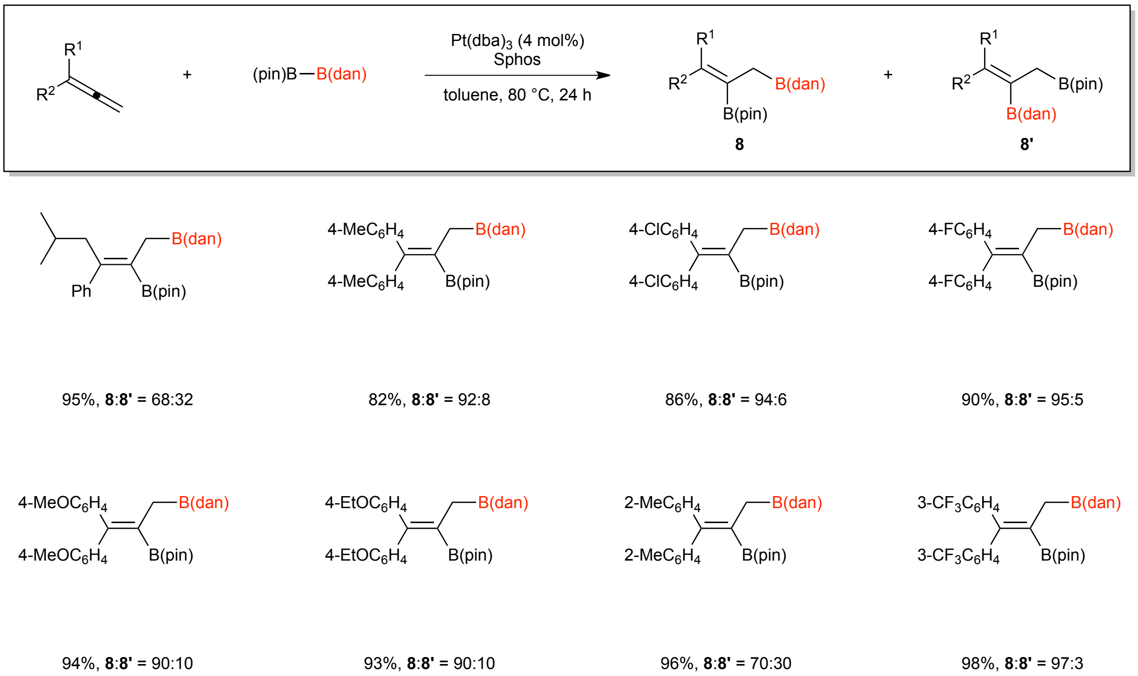
3-3-1. 1,2-Diborylation

In 2010, Suginome disclosed that the boron–boron bond of (pin)B–B(dan) was added across a carbon–carbon triple bond of terminal alkynes under platinum or iridium catalysis, leading to the synthesis of *vic*-diborylated alkenes with the regioselective B(dan)-attachment to the terminal carbons (Scheme 38).[25]



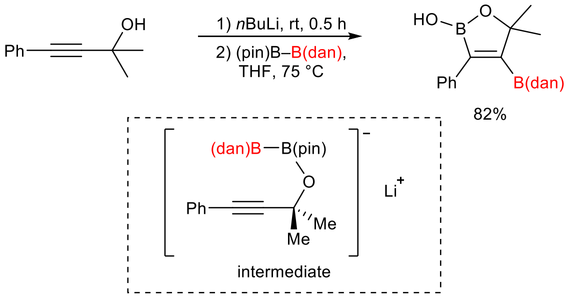
Scheme 38

The platinum-catalyzed 1,2-diborylation with (pin)B–B(dan) was also applicable to 1,1-disubstituted allenes, in which the B(dan) moiety was installed into a terminal carbon in a regioselective fashion (Scheme 39).[55]



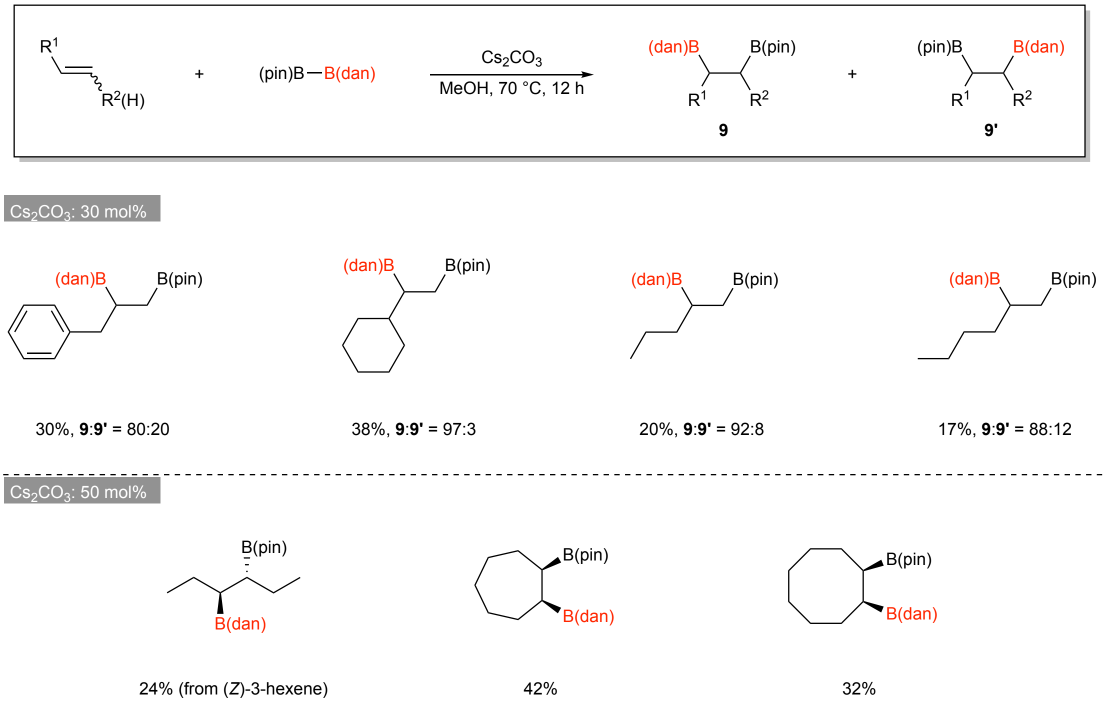
Scheme 39

The first *trans*-selective diborylation reaction of alkynes was achieved by Hirano and Uchiyama. The presence of a directing alkoxide functionality generated in situ from propargyl alcohols and *n*-BuLi is the key to the successful transformation, and the use of (pin)B–B(dan) resulted in the sole formation of the product via selective interaction of an alkoxide and the Lewis acidic B(pin) moiety (Scheme 40).[56]



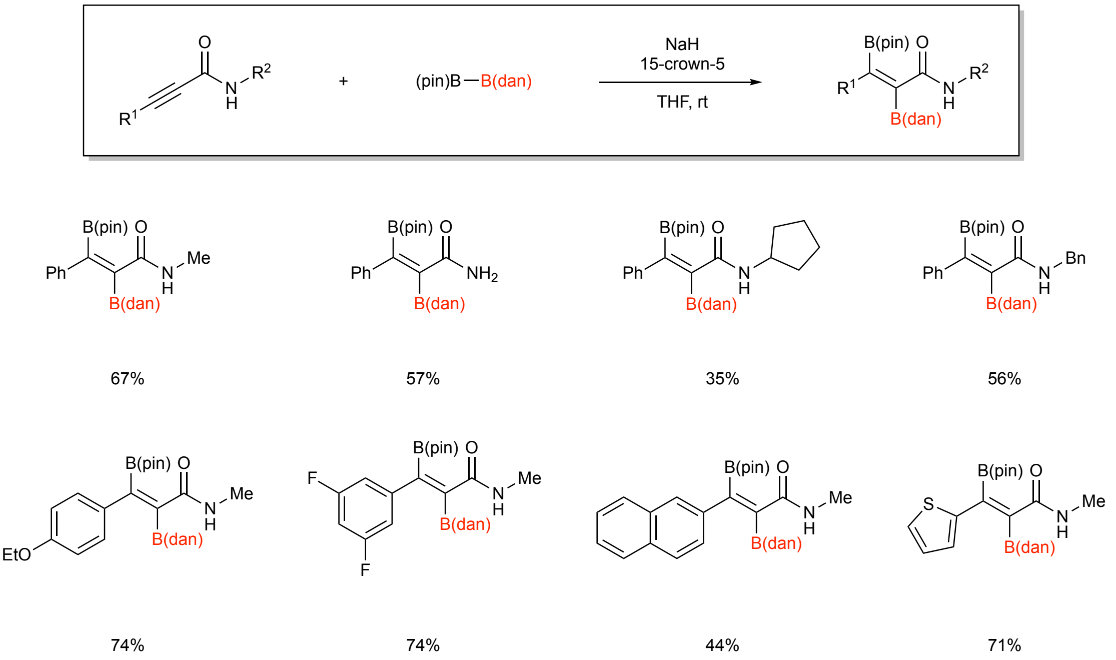
Scheme 40

Fernández demonstrated that even electronically unbiased alkenes could undergo transition metal-free base-promoted 1,2-diborylation with (pin)B–B(dan): the B(dan) moiety was regioselectively installed into an internal carbon of terminal alkenes, and *syn*-addition of the diboron occurred with internal alkenes (Scheme 41).[57]

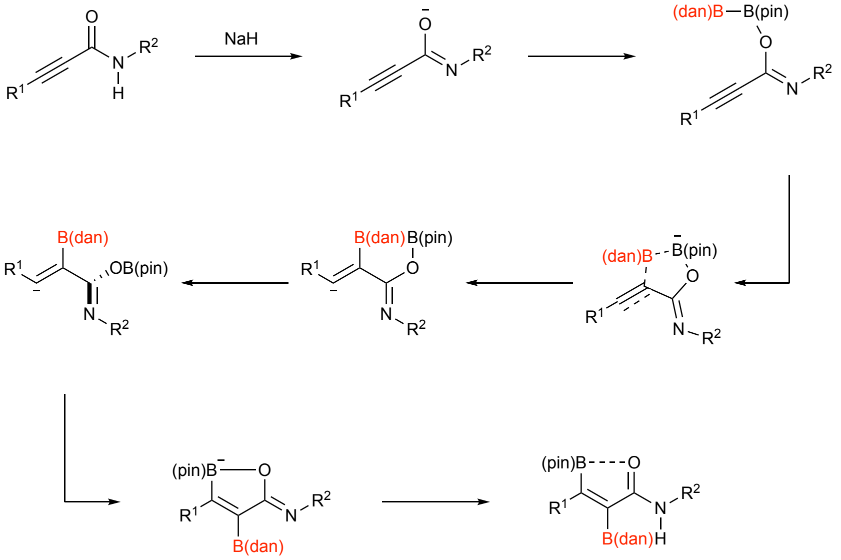


Scheme 41

A similar base-promoted diborylation of alkynamides was reported by Santos, in which (pin)B–B(dan) was added across the carbon–carbon triple bond in *trans* fashion with B(dan) attachment at the β-position (Scheme 42).[58] This regioselectivity was rationally explained by preferential activation of the B(pin) moiety by a Lewis basic site arising from deprotonation of alkynamides with sodium hydride (Scheme 43).

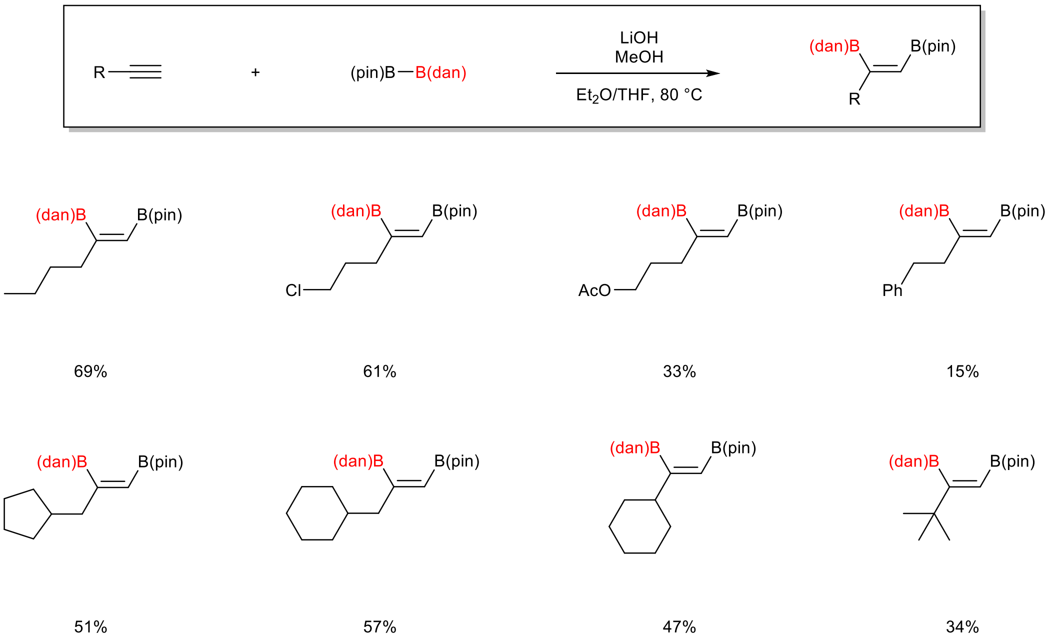


Scheme 42



Scheme 43

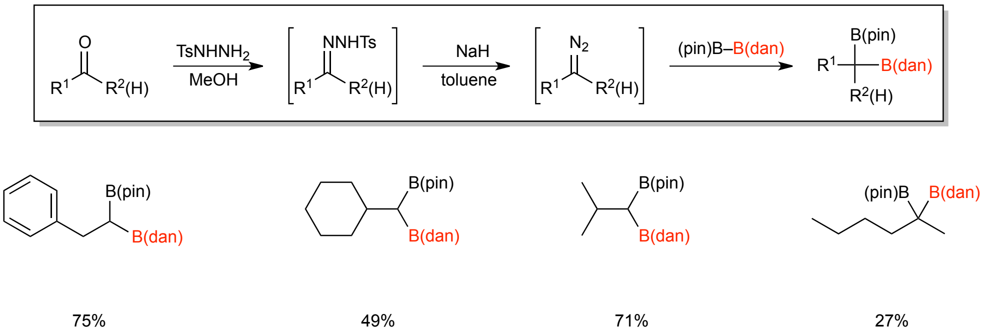
Base-promoted *syn*-1,2-diborylation of terminal alkynes with (pin)B–B(dan) was also found to proceed by use of LiOH and a stoichiometric amount of MeOH. Of note is that the B(dan) moiety was regioselectively installed into an internal carbon, being in sharp contrast to the transition metal-catalyzed version (Scheme 44).[59]



Scheme 44

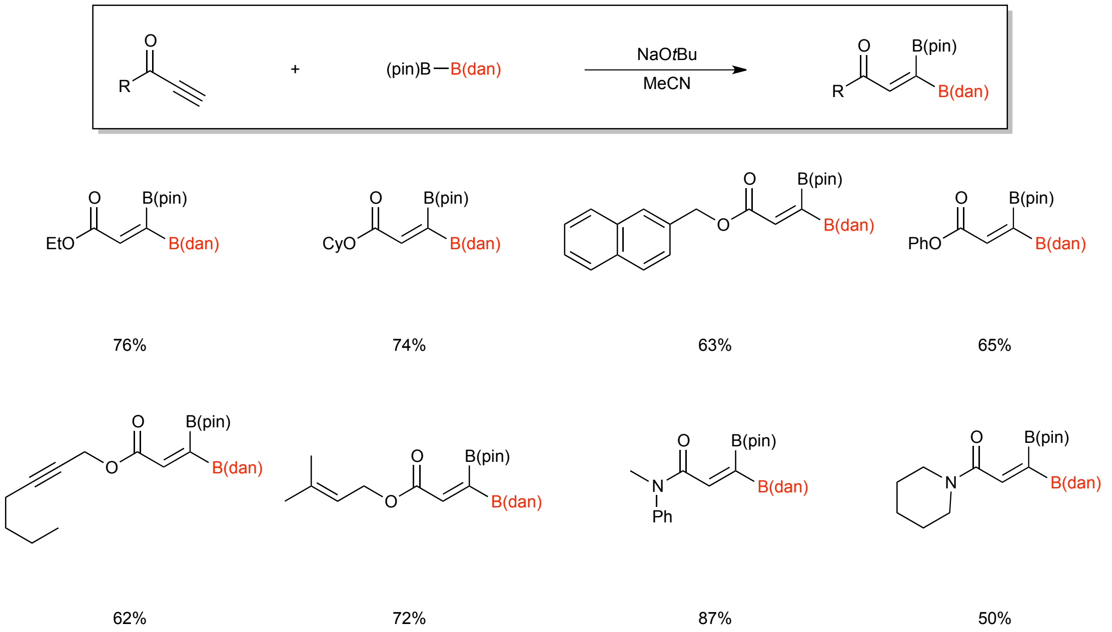
3-3-2. 1,1-Diborylation

In 2015, Fernández disclosed that tosylhydrazone-derived carbenoids were inserted into (pin)B–B(dan) to give 1,1-diborylation products under transition metal-free conditions (Scheme 45).[60]



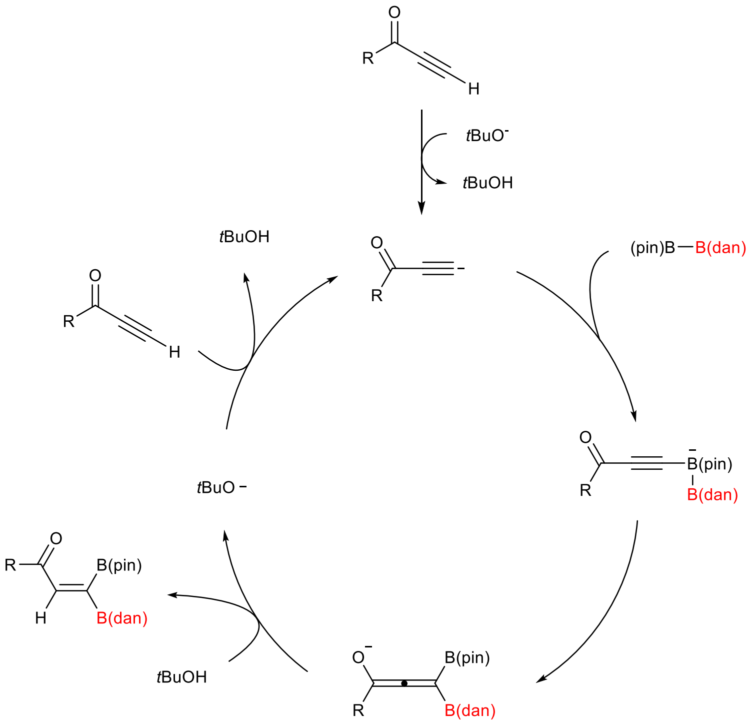
Scheme 45

Terminal alkynoates and alkynamides were reported to undergo 1,1-diborylation in the presence of NaO*t*Bu, affording *gem*-diborylated α,β-undaturated carbonyl compounds whose B(dan) moieties were connected to the *trans* position to the carbonyl group (Scheme 46).[61]



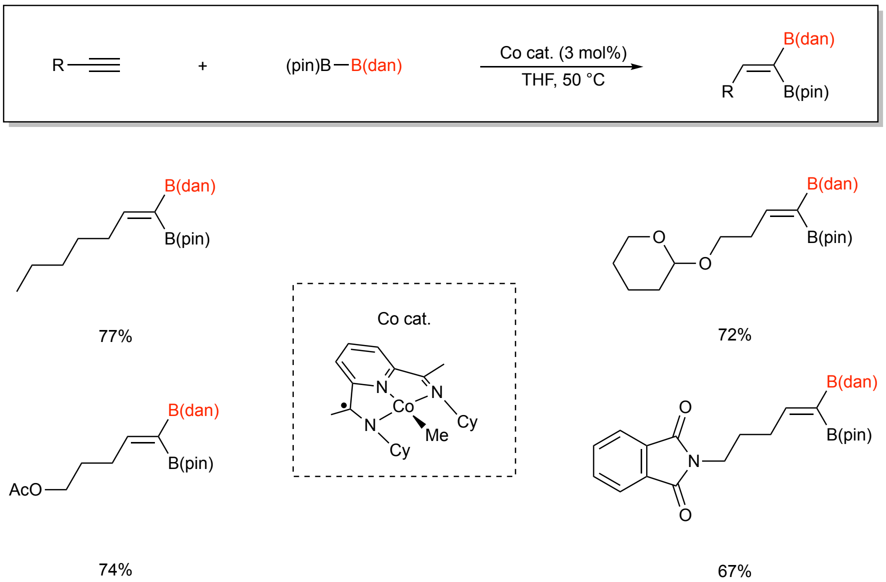
Scheme 46

As shown in Scheme 47, deprotonation of an alkyne by NaO*t*Bu, which generates an acetylide, triggers the reaction. The resulting acetylide attacks chemoselectively a B(pin) moiety of (pin)B–B(dan) to form a borate intermediate, which then undergoes 1,2-migration of a B(dan) moiety. Finally, an allenolate intermediate was protonated to give a 1,1-diborylalkene.

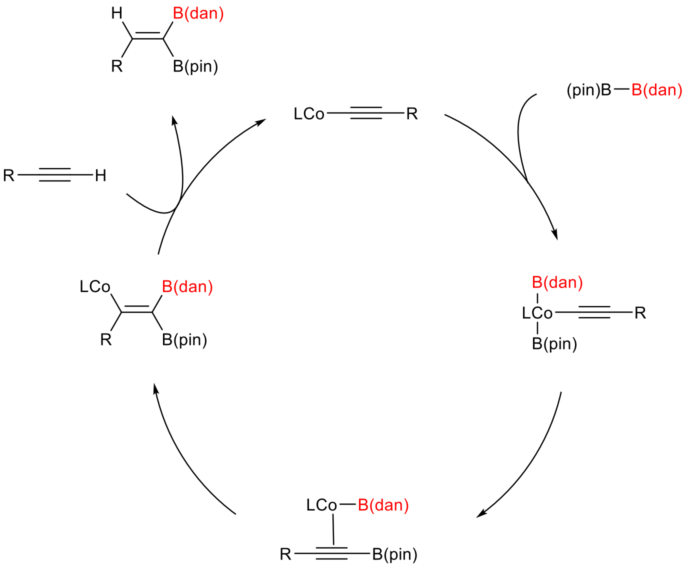


Scheme 47

Chirik reported on cobalt-catalyzed 1,1-diborylation of terminal alkynes with (pin)B–B(dan). The B(dan) moieties were installed into a *trans* position to a substituent on alkynes (Scheme 48),[62] and the authors proposed a catalytic cycle involving formation of a cobalt acetylide and an alkynyl–B(pin), and subsequent regioselective borylcobaltation.



Scheme 48



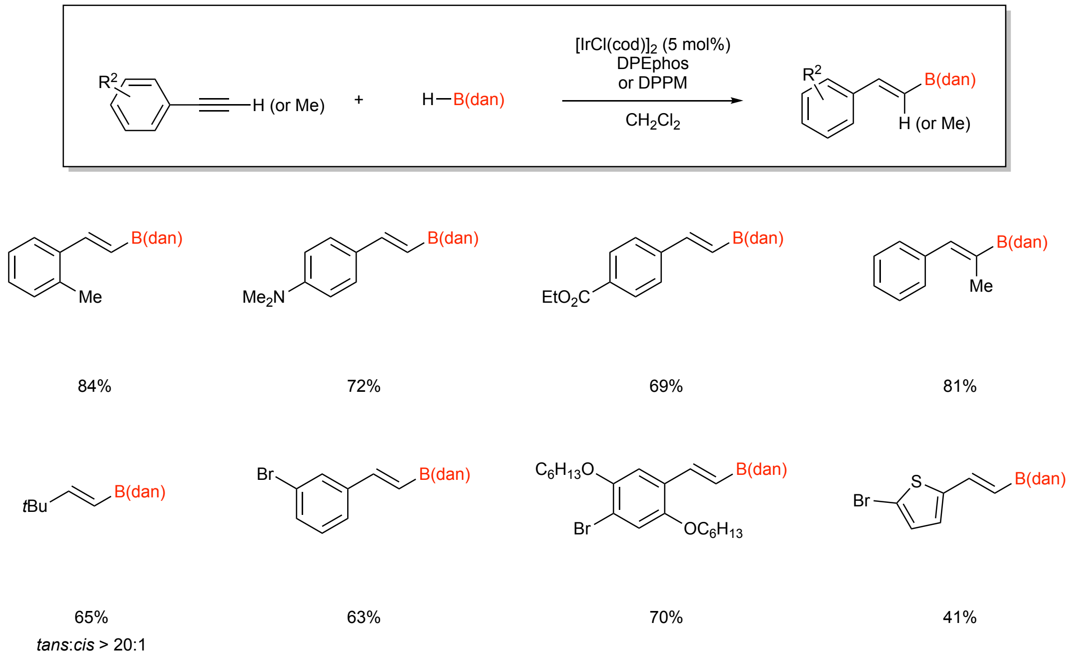
Scheme 49

4. B(DAN)-INSTALLING REACTIONS WITH H–B(DAN)

4-1. Monoborylation including addition to unsaturated carbon–carbon bonds

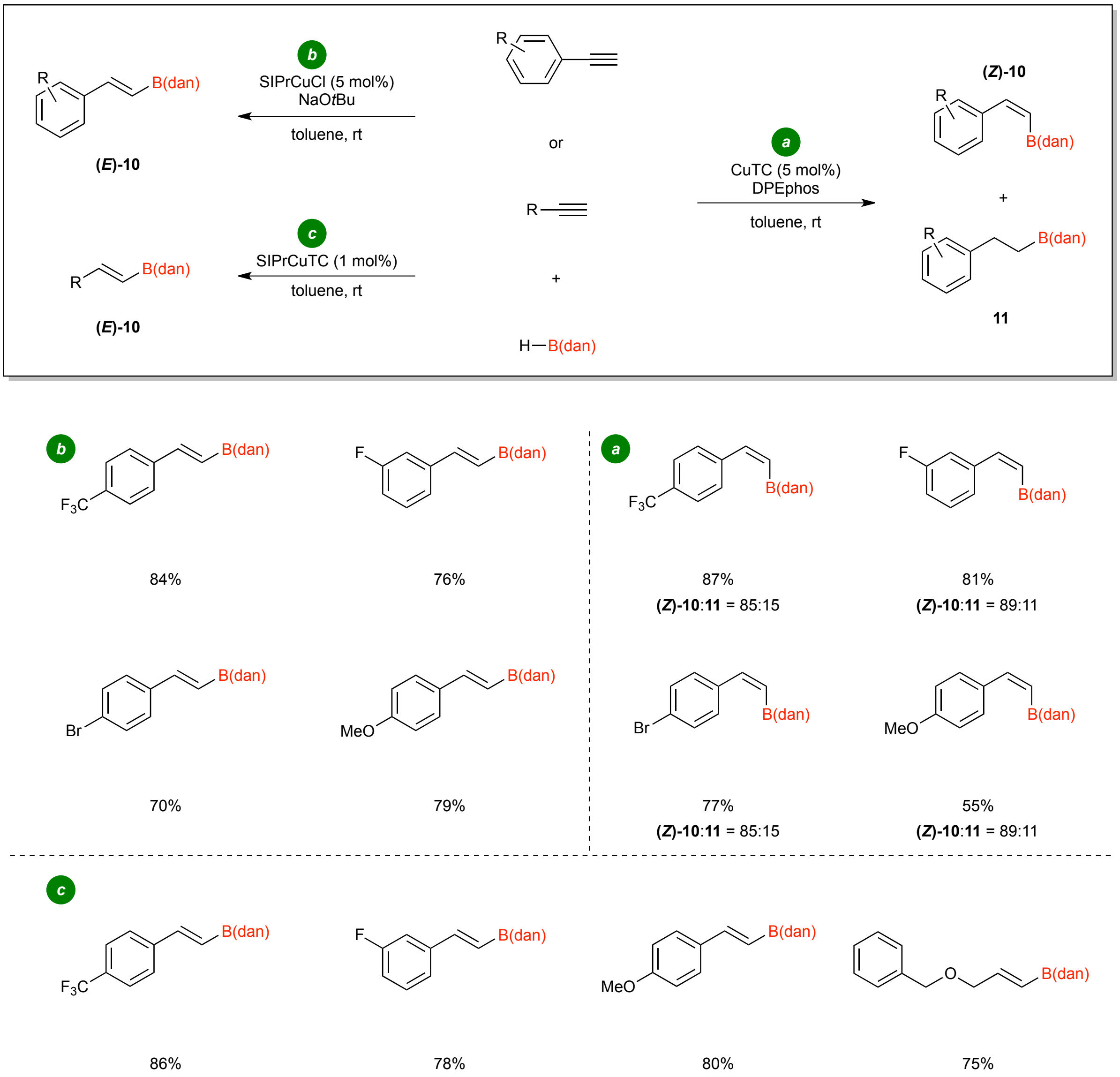
4-1-1. Hydroboration

Suginome disclosed that H–B(dan) could participate in iridium-catalyzed hydroboration of terminal and internal alkynes to afford linear (*E*)-alkenyl–B(dan) in a stereoselective manner (Scheme 50).[63]

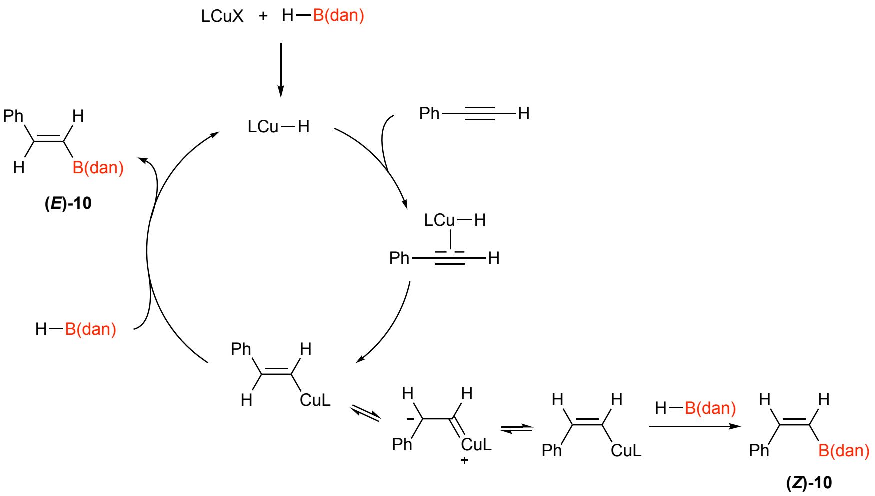


Scheme 50

Hydroboration of terminal alkynes with H–B(dan) turned out to smoothly proceed under copper catalysis (Scheme 51).[64] Stereodivergent character of the reaction, depending on a ligand employed, is worthy of note: (*E*)-stereoselectivity was observed by use of an NHC (SIPr), while the reaction with DPEphos preferentially provided (*Z*)-isomers. A copper hydride formed by σ-bond metathesis between H–B(dan) and a copper catalyst accepts insertion of an alkyne to give a vinylcopper species, and this can isomerize via a zwitterionic carbene–copper intermediate, leading to the formation of (*E*)- or (*Z*)-product (Scheme 52).[65]

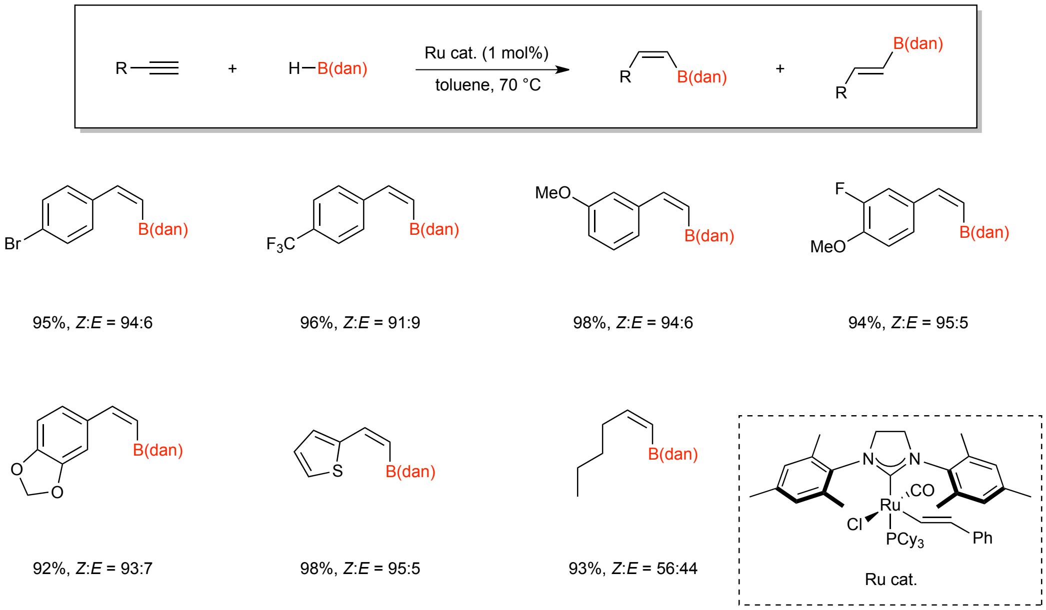


Scheme 51

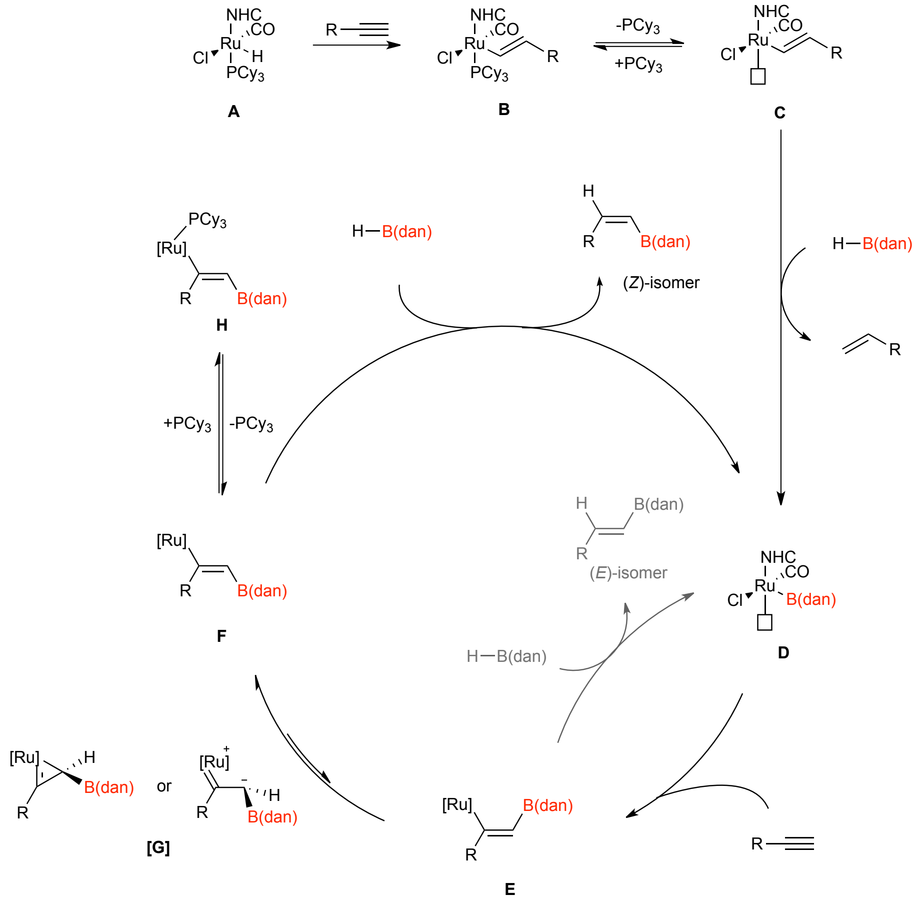


Scheme 52

Ruthenium-catalyzed *trans*-hydroboration of terminal alkynes was developed by Mutoh and Saito in 2019, that provided convenient route to (*Z*)-alkenyl–B(dan) (Scheme 53).[66]



Scheme 53



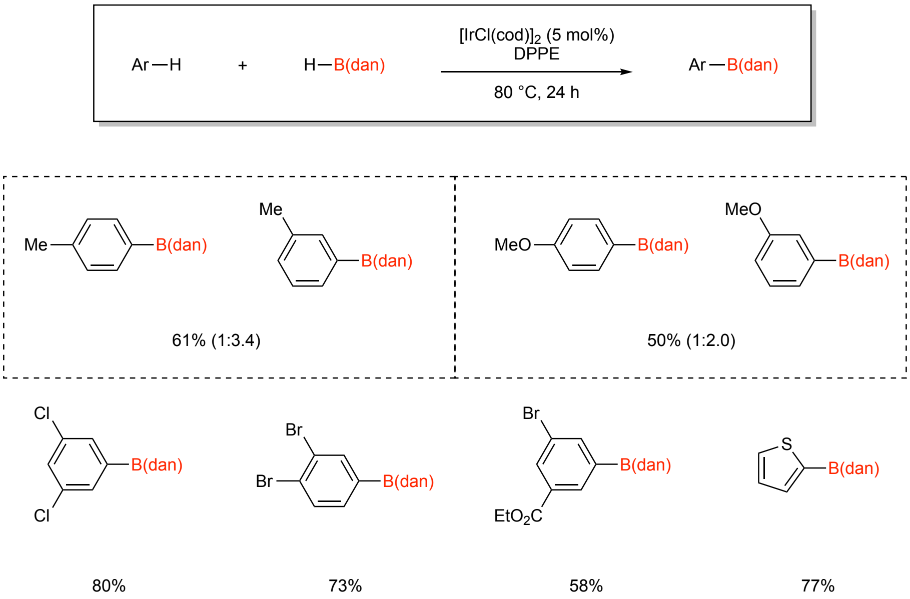
Scheme 54

A terminal alkyne inserts into the Ru−H bond of hydrido complex A to afford styryl complex B, which liberates PCy_3 (Scheme 54). Then the resulting complex (C) undergoes σ-bond metathesis with H−B(dan) to give boryl complex D and styrene. Migratory insertion of another terminal alkyne into the Ru−B bond of D would generate borylethenyl complex E which isomerizes rapidly to form F via a zwitterionic species or a metallacyclopropene intermediate (G), and F is the major isomer in most examples which should be in equilibrium between a potential catalytic resting state H. Finally, F could react with H−B(dan) to afford (*Z*)-isomer with regeneration of D.

4-2. Monoborylation including substitution

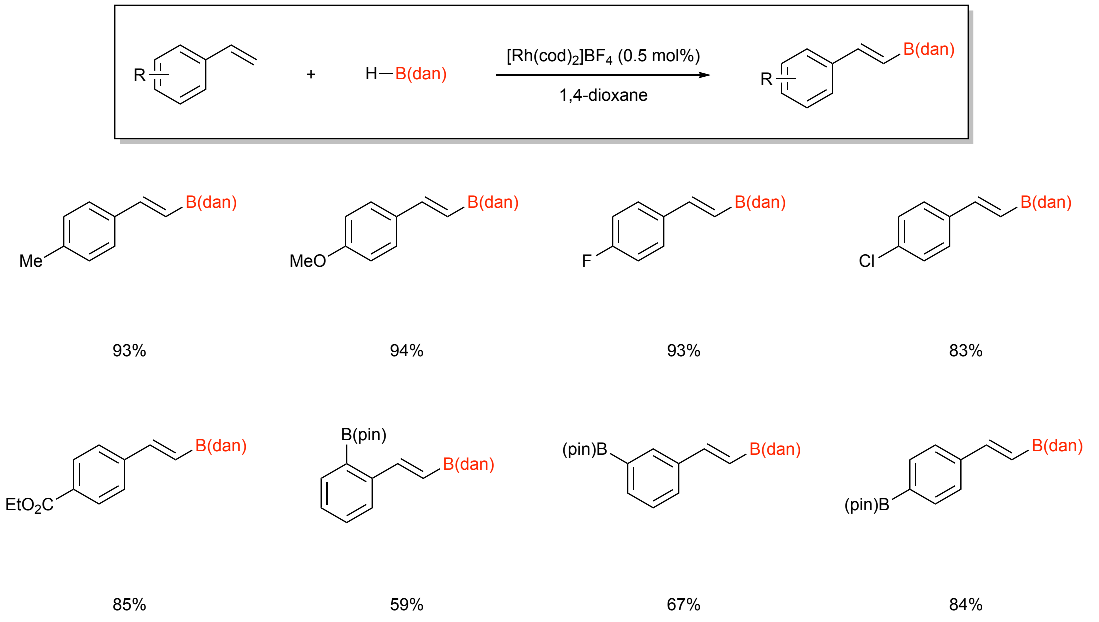
4-2-1. Borylation of carbon–hydrogen bonds

Dehydrogenative direct C(aryl)–H borylation of arenes with H–B(dan) was efficiently promoted by a DPPE-coordinated iridium catalyst, giving a variety of Ar–B(dan). As is the case of the usual Hartwig–Miyaura borylation,[67-69] the B(dan) moiety was regioselectively installed into a less sterically hindered position (Scheme 55).[29]

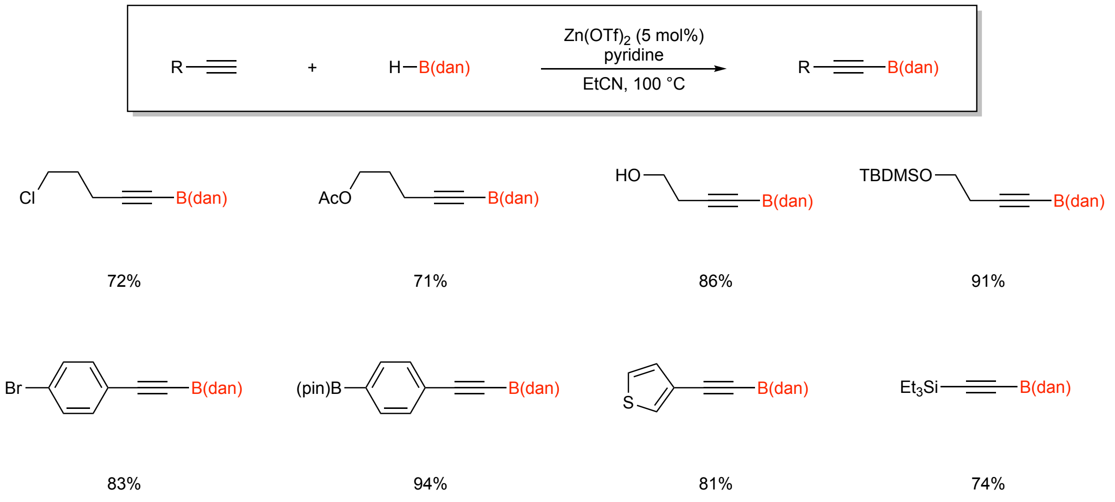


Scheme 55

Styrene derivatives were also convertible into (*E*)-β-borylstyrenes stereoselectively by cationic rhodium-catalyzed dehydrogenative borylation with H–B(dan) (Scheme 56).[70]

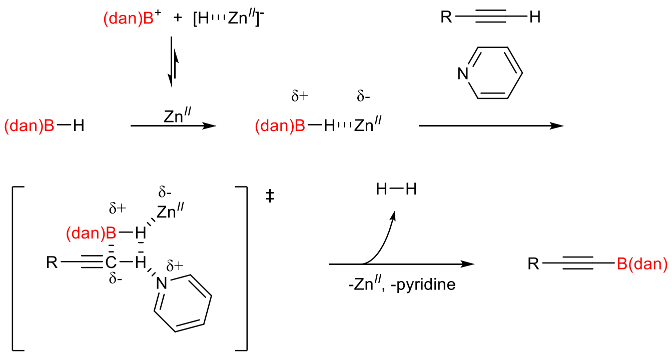


Scheme 56



Scheme 57

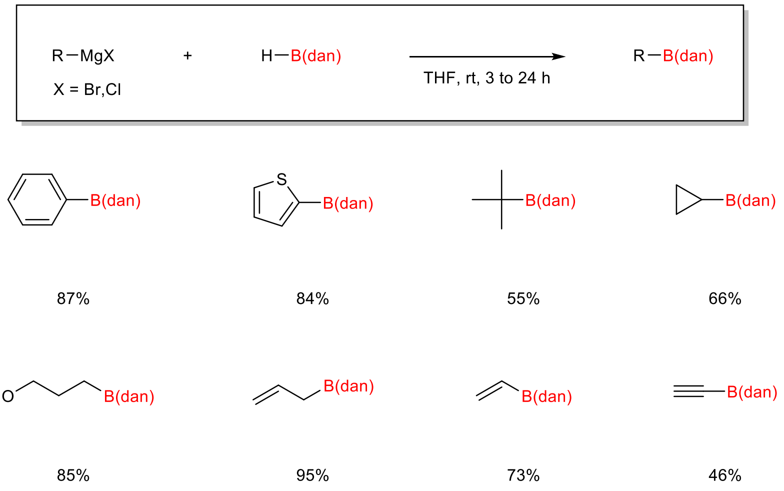
Tsuchimoto demonstrated that Lewis acidic $Zn(OTf)_2$ efficiently catalyzed dehydrogenative borylation of terminal alkynes with H–B(dan) to afford various alkynyl–B(dan) in a straightforward manner (Scheme 57).[71] Addition of pyridine is necessary for achieving high catalytic performance, and a proposed pathway is depicted in Scheme 58. Activation of a H–B(dan) bond by $Zn(OTf)_2$ leads to the formation of boron cationic species and zinc hydride. On the other hand, pyridine would interact with a terminal alkyne to produce an acetylide-like species. Accordingly, an electrophilic boron species should react with a nucleophilic acetylide species to give an alkynyl–B(dan) with release of hydrogen gas.



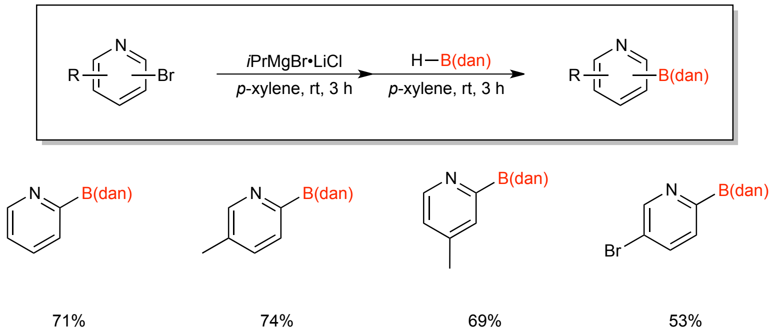
Scheme 58

4-2-2. Borylation using H–B(dan) as a B(dan) electrophile

Yoshida recently reported that H–B(dan) served as a B(dan) electrophile, despite its highly diminished boron-Lewis acidity; a variety of Grignard reagents having a C(sp, sp^2 or sp^3)–MgX bond were found to be readily transformable into R–B(dan) under transition metal-free conditions via nucleophilic substitution at the boron center (Scheme 59).[72] Furthermore, diverse 2-pyridyl–B(dan) were accessible as stable compounds according to a modified protocol by use of Turbo Grignard reagent (Scheme 60).



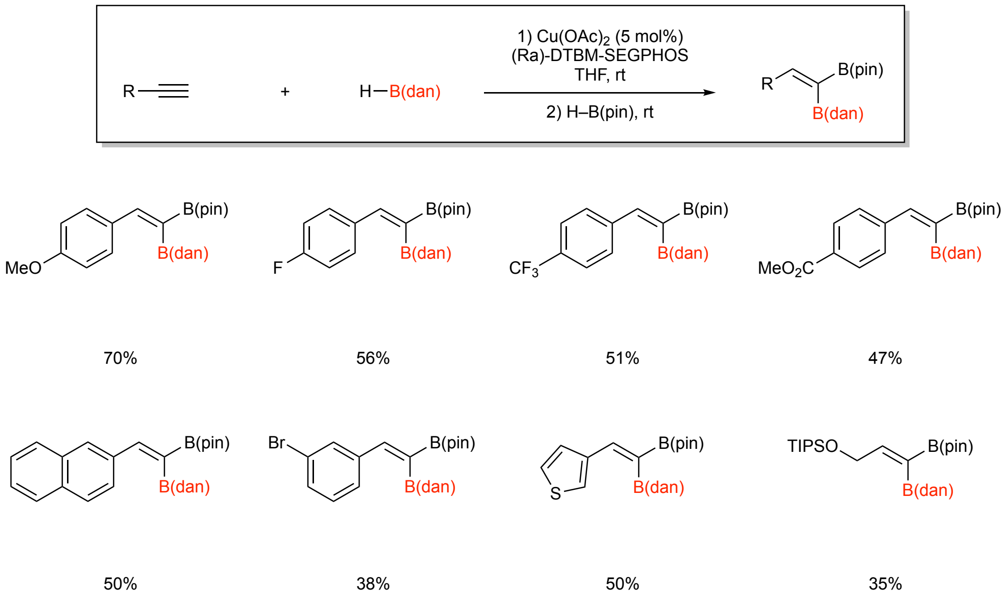
Scheme 59



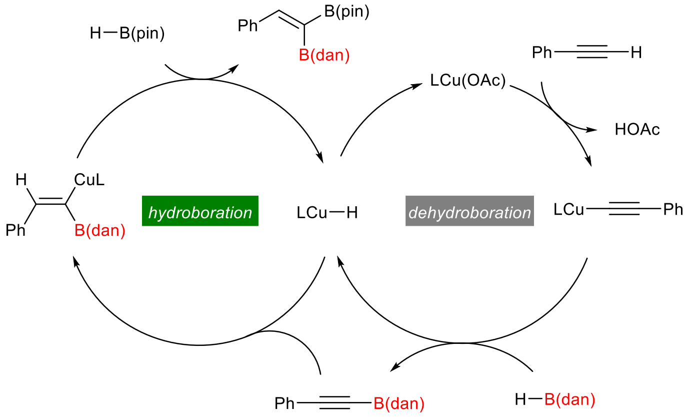
Scheme 60

4-3. Diborylation

Three-component 1,1-diborylation of terminal alkynes with H–B(dan) and H–B(pin) was achieved in one-pot under copper catalysis; a terminal carbon of alkynes accepted addition of B(dan) and B(pin) moieties with stereoselective B(dan)-attachment to the *cis* position to the substituents (Scheme 61).[73] The tandem process involves dehydrogenative borylation of a terminal alkyne with H–B(dan), followed by hydroboration of the generated alkynyl–B(dan) with H–B(pin) (Scheme 62).



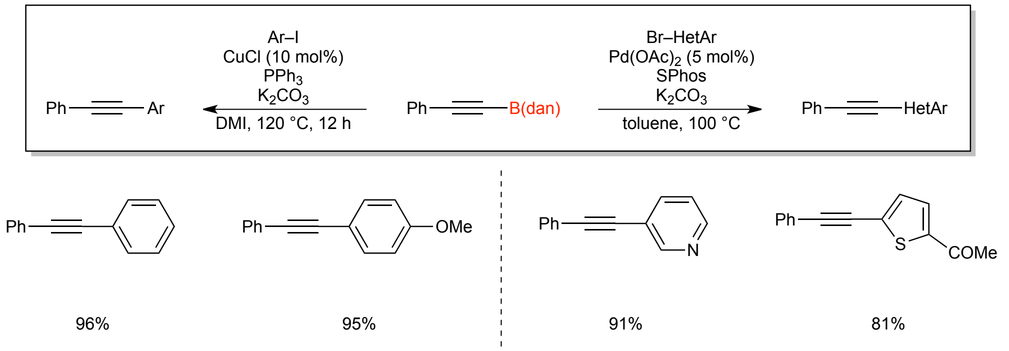
Scheme 61



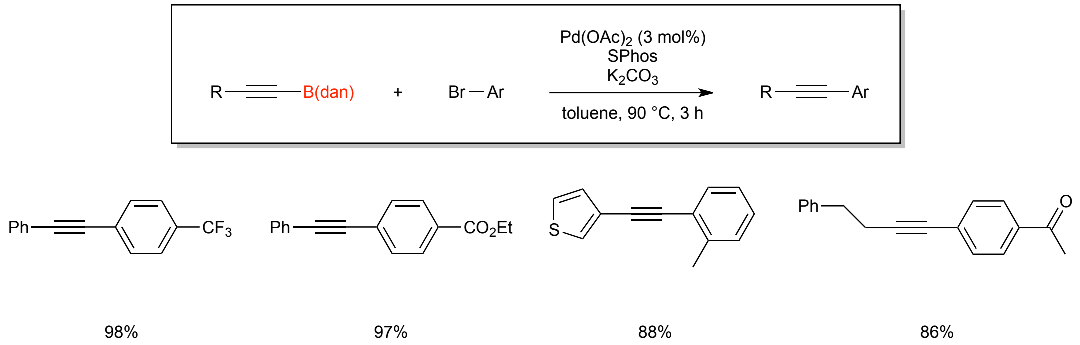
Scheme 62

5. DIRECT CROSS-COUPLING WITH R–B(DAN)

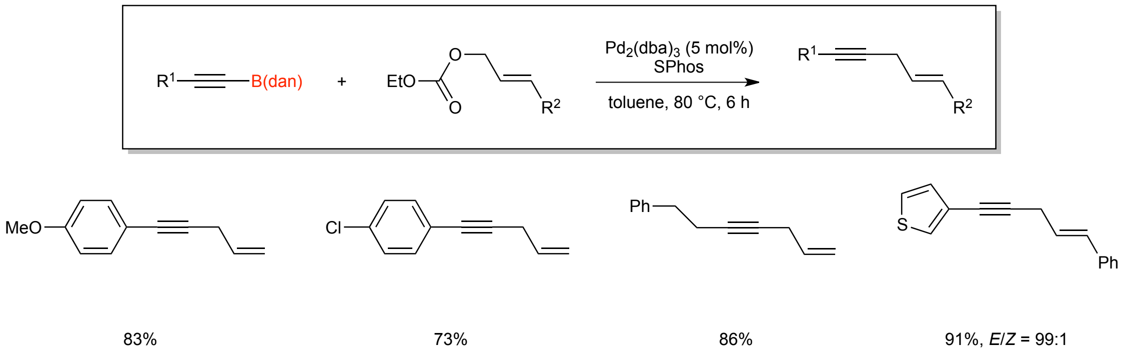
A variety of dan-substituted organoboron compounds, R–B(dan), have become accessible straightforwardly by the above-described B(dan)-installing reactions with (pin)B–B(dan) or H–B(dan). The diminished Lewis acidity of the B(dan) leads to unique reactivity/stereoselectivity in the borylations, and marked stability of organoboron compounds obtained therefrom. The resulting C–B(dan) bonds, on the other hand, were recognized to be unusable for the SMC until recently, owing to their inert properties toward transmetalation as depicted in the introduction section. Therefore, development of direct ways of activating the C–B(dan) bonds with overcoming their strongly diminished boron-Lewis acidity, which would result in new boron-based C–C and C–heteroatom bond-forming reactions, is a challenging subject in synthetic organic chemistry.



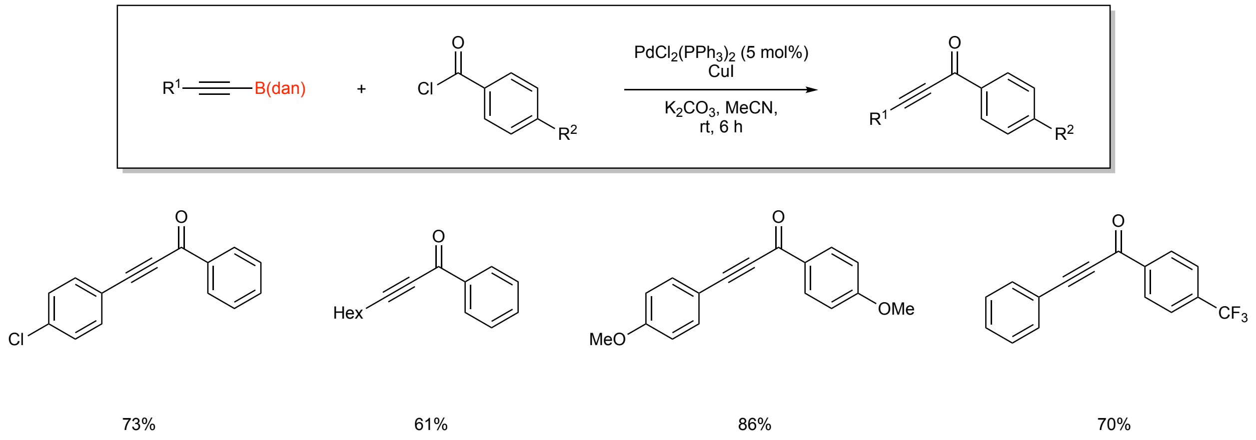
Scheme 63



Scheme 64

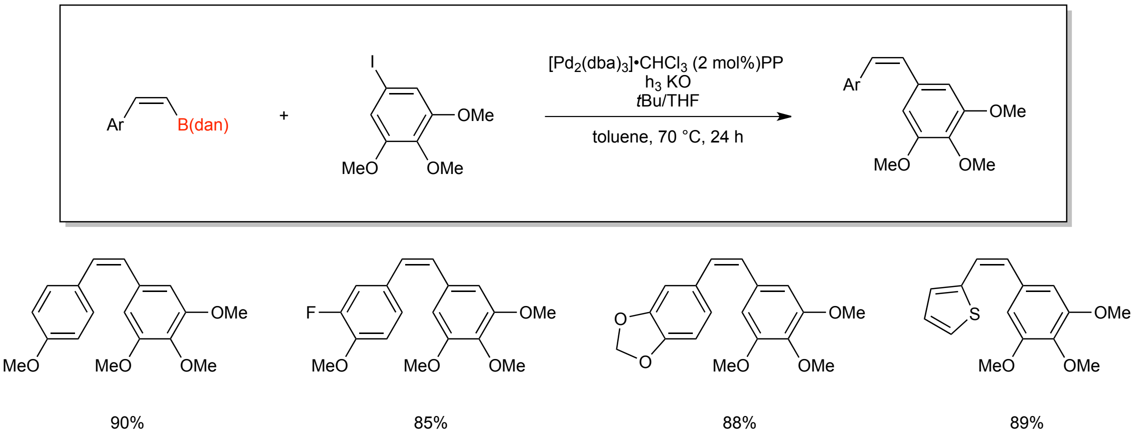


Scheme 65



Scheme 66

After a preliminary work on the direct SMC of aryl halides with alkynyl–B(dan) in 2015, Tsuchimoto thoroughly demonstrated that the C(sp)–B(dan) bonds were efficiently convertible into C(sp)–C bonds by the palladium-catalyzed direct SMC with various carbon electrophiles including aryl halides, allyl carbonates and acid chlorides (Schemes 63–66).[30,71]

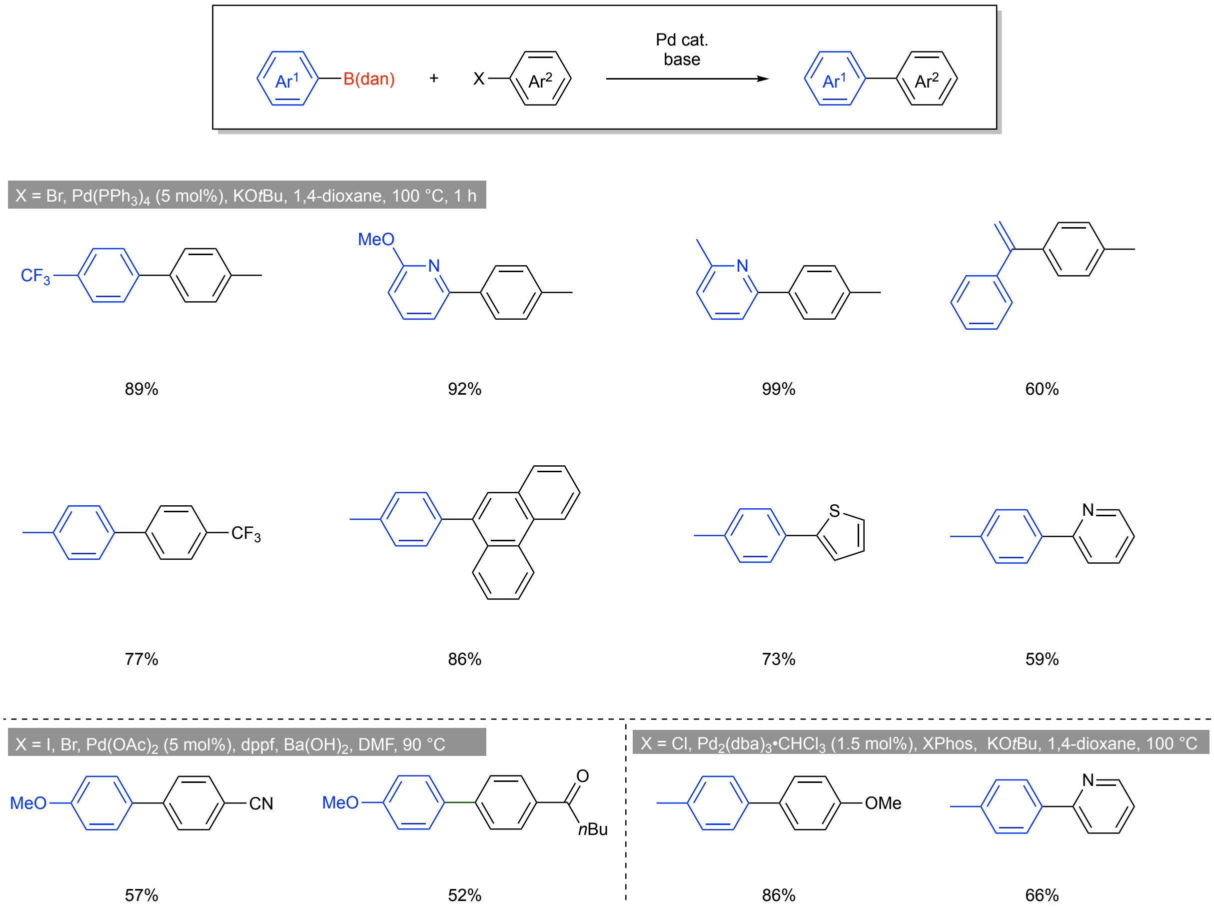


Scheme 67

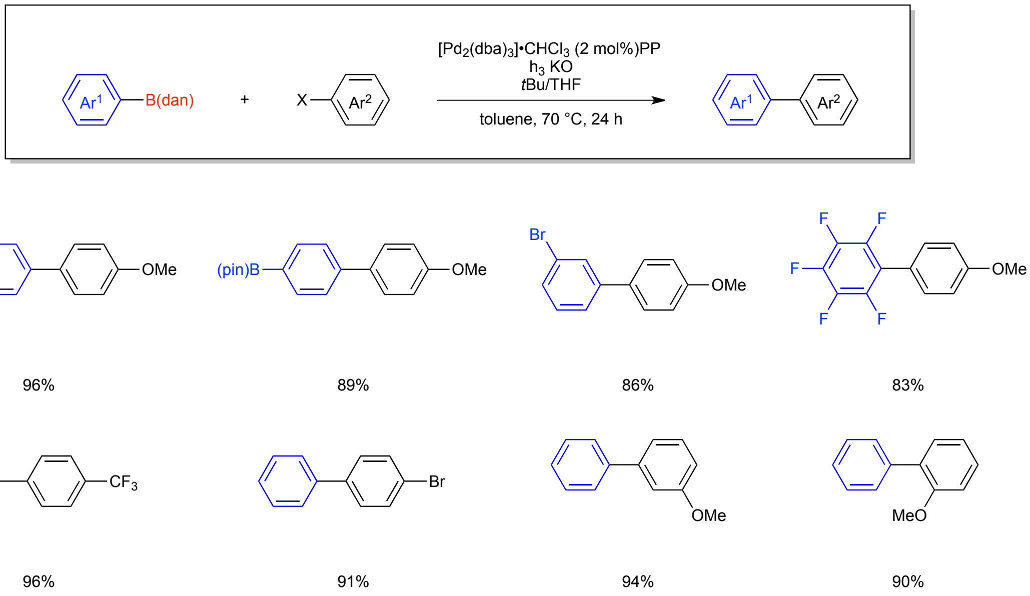
Mutoh and Saito reported that (*Z*)-alkenyl–B(dan), prepared by the ruthenium-catalyzed *trans*-hydroboration (Scheme 53), could participate in the direct SMC by use of KO*t*Bu as a base (Scheme 67).[66]

Around the same time, Yoshida and Tsuchimoto achieved the direct SMC with diverse aryl–B(dan), demonstrating even robust C(aryl)–B(dan) bonds could be smoothly activated without acidic deprotection (Scheme 68).[74] The use of KO*t*Bu as a base under anhydrous conditions is also the key to the successful reaction, and ^{11}B NMR experiments revealed that a transmetalation-active borate species was generated only with KO*t*Bu. Synthetic significance of this method was demonstrated by the smooth SMC with

2-pyridyl–B(dan), which provides convenient and effective solution to “2-pyridyl problem” in the conventional SMC.[49]

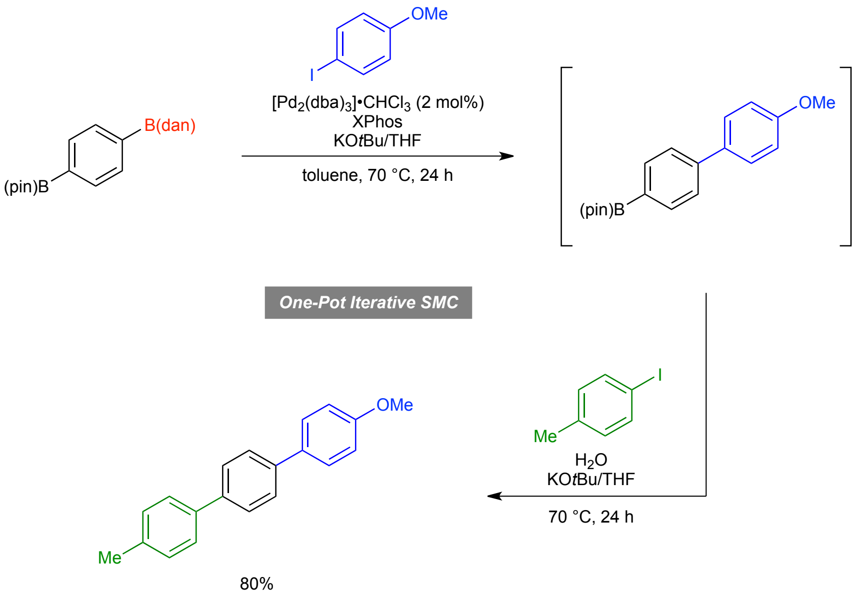


Scheme 68

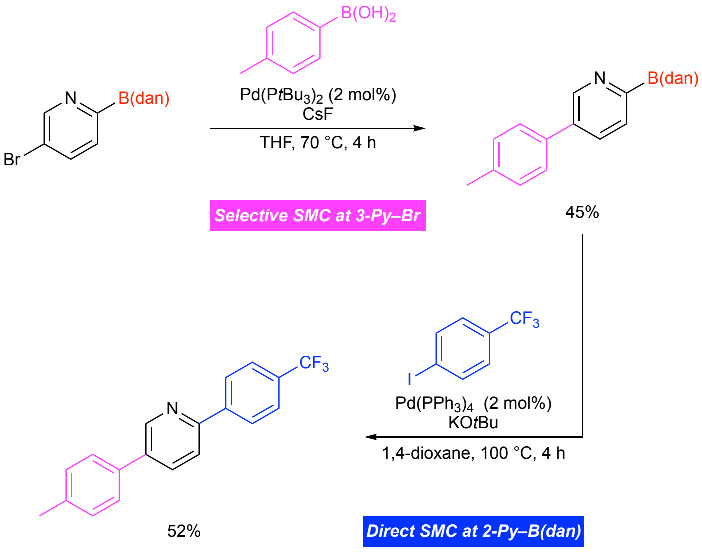


Scheme 69

A quite similar SMC was also reported by Mutoh and Saito. In particular, they succeeded in one-pot sequential SMC, where a B(dan) moiety was first coupled with a B(pin) moiety remaining intact (Schemes 69 and 70).[75] In addition to similar ^{11}B NMR experiments as above, they succeeded in determining a molecular structure of a transmetalation-active borate species by a single-crystal X-ray diffraction study. Moreover, Yoshida achieved the iterative SMC with 5-bromo-2-pyridyl–B(dan), obtained by their Grignard reagent–H–B(dan) reaction (Scheme 60), which demonstrated the synthetic significance of this direct SMC (Scheme 71).[72]



Scheme 70



Scheme 71

6. CONCLUSION

The growing synthetic organic chemistry with dan-substituted organoboron compounds has been thoroughly described. A variety of B(dan)-installing reactions have been developed by use of (pin)B–B(dan) or H–B(dan) to provide convenient and straightforward access to diverse R–B(dan) with unique stereoselectivity and reactivity arising from the highly diminished boron-Lewis acidity. The resulting C–B(dan) bonds, which were believed to be totally inert toward SMC, has now become convertible directly into C–C bonds without acidic deprotection, which would open the door to new direct catalytic C–C and C–heteroatom bond-forming reactions with R–B(dan).

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