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Review

Recent Advances in Metal-Catalyzed Alkyl–Boron (C(sp³)-C(sp²)) Suzuki-Miyaura Cross-Couplings

Janwa El-Maiss ^{1,†}, Tharwat Mohy El Dine ^{2,†}, Chung-Shin Lu ³, Iyad Karamé ⁴, Ali Kanj ⁴, Kyriaki Polychronopoulou ^{5,6,*} and Janah Shaya ^{7,8,*}

¹ Université d'Orléans, Institut de Chimie Organique et Analytique, Pole Chimie, Rue de Chartres, 45000 Orléans, France; janwa.el-maiss@univ-orleans.fr

² Institut des Biomolécules Max Mousseron (IBMM), UMR 5247, École nationale supérieure de chimie de Montpellier (ENSCM), 240 Avenue du Professeur Emile Jeanbrau, 34090 Montpellier, France; Tharwat.Mohy-El-Dine@enscm.fr

³ Department of General Education, National Taichung University of Science and Technology, Taichung 404, Taiwan; cslu6@nutc.edu.tw

⁴ Laboratory of Catalysis Organometallic and Materials (LCOM), Depart. of Chemistry, Faculty of Science I, Lebanese University-Hariri Campus, Hadath, Lebanon; iyad.karameh@ul.edu.lb (I.K.); kani@ul.edu.lb (A.K.)

⁵ Department of Mechanical Engineering, Khalifa University of Science and Technology, Abu Dhabi, P.O. Box 127788, UAE

⁶ Center for Catalysis and Separation, Khalifa University of Science and Technology, Abu Dhabi, P.O. Box 127788, UAE

⁷ College of Arts and Sciences, Khalifa University, Abu Dhabi, P.O. Box 127788, UAE

⁸ College of Medicine and Health Sciences, Khalifa University, Abu Dhabi, P.O. Box 127788, UAE

* Correspondence: kyriaki.polychrono@ku.ac.ae (K.P.); shaya.janah@ku.ac.ae (J.S.)

† J.E.-M. and T.M.E.D. contributed equally to this work and shall be considered Co-First authors.

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Abstract: Boron chemistry has evolved to become one of the most diverse and applied fields in organic synthesis and catalysis. Various valuable reactions such as hydroborylations and Suzuki–Miyaura cross-couplings (SMCs) are now considered as indispensable methods in the synthetic toolbox of researchers in academia and industry. The development of novel sterically- and electronically-demanding C(sp³)-Boron reagents and their subsequent metal-catalyzed cross-couplings attracts strong attention and serves in turn to expedite the wheel of innovative applications of otherwise challenging organic adducts in different fields. This review describes the significant progress in the utilization of classical and novel C(sp³)-B reagents (9-BBN and 9-MeO-9-BBN, trifluoroboronates, alkylboranes, alkylboronic acids, MIDA, etc.) as coupling partners in challenging metal-catalyzed C(sp³)-C(sp²) cross-coupling reactions, such as B-alkyl SMCs after 2001.

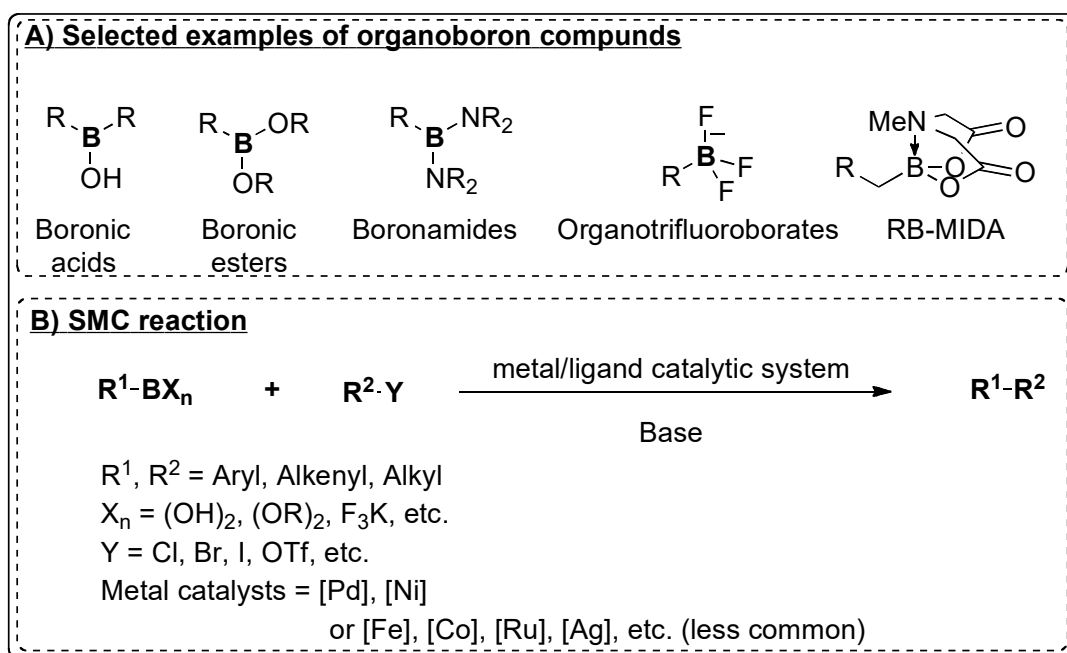
Keywords: Suzuki–Miyaura cross-couplings; C(sp³)-C(sp²); alkylboron reagents; metal catalysis

1. Introduction

Boron is a peculiar metalloid with fascinating chemical complexity. The unusual properties of boron stem from its three valence electrons, which can be easily torn away, favoring metallicity and making it electron-deficient, yet sufficiently localized and tightly bound to the nucleus, consequently allowing the insulating states to emerge [1]. Boron compounds have been intensively investigated for energy storage applications, particularly due to the relatively low atomic mass of boron (10.811 ± 0.007 amu). The energy-related uses of boron compounds range from high-energy fuels for advanced aircrafts to boron–nitrogen–hydrogen compounds as hydrogen storage materials for fuel cells [2]. The rich

pioneering research on boron resulted in the consecutive awarding of two Nobel Prizes in chemistry in 1976 and 1979 [3,4].

Organoboron compounds (e.g., boronic acids, boronic esters and boronamides) generally comprise at least one carbon–boron (C–B) bond (Scheme 1A) [5–8]. Organoboron compounds were initially used in organic synthesis 60 years ago [9,10]. Ever since, chemistries involving such compounds continued to advance until these reagents have become one of the most diverse, widely studied and applied families in catalysis and organic synthesis [10,11]. Currently, they are engaged in numerous classic and important reactions such as hydroborations and Suzuki–Miyaura cross-couplings (SMCs), among others [8]. The SMC reaction generally involves the conjoining of an organoboron reagent and an organic halide or pseudohalide in the presence of palladium (or other relevant metal/ligand) as a catalyst and a base for the activation of the boron compound (Scheme 1B) [5–7,12]. Organoboron compounds have also found several applications in pharmaceuticals where boron-based drugs exemplify a novel class of molecules for several biomedical applications as molecular imaging agents (optical/nuclear imaging) and neutron capture therapy agents (BNCT), as well as therapeutic agents (anticancer, antiviral, antibacterial, etc.) [13]. Likewise, the utility and ubiquity of boron-based compounds have bolstered the development of agricultural and material sciences [14,15]. Organoborane polymers have been investigated as electrolytes for batteries, electro-active materials, and supported Lewis acid catalysts [16,17].



Scheme 1. (A) Examples of organoboron compounds, (B) Suzuki–Miyaura cross-coupling reaction.

Metal catalysis has had a major impact on numerous research fields from energy, biomass, environmental and water purification to synthesis of otherwise challenging and even inaccessible materials and medicinal adducts [18–30]. In line, the intensive research in metal catalysis has led to significant progress in borylation of primary $C(\text{sp}^3)\text{--H}$ bonds of unfunctionalized hydrocarbons, allowing access to a variety of $C(\text{sp}^3)\text{--B}$ reagents and consequent breakthroughs in $C(\text{sp}^3)\text{--C}(\text{sp}, \text{sp}^2, \text{sp}^3)$ cross-couplings. Comprehensive work has been done on the development of an efficient $\text{sp}^2\text{--sp}^2$ SMC; however, there have been far fewer reports on $\text{sp}^3\text{--sp}^2$ or $\text{sp}^3\text{--sp}^3$ variants [31–38]. Among the different hybridized boron reagents employed in SMCs (e.g., aryl, heteroaryl, and vinylboronic acids and esters), the use of organoboron compounds with alkyl groups (sp^3 carbon) was severely limited in these coupling reactions due to competitive side reactions [39,40]. Organometallic compounds that are metalated at sp^3 carbon atoms and especially containing β -hydrogen atoms give rise to alkyl–palladium complexes that

are susceptible to β -hydride elimination rather than reductive elimination [41]. Furthermore, although boronic acids are relatively stable at ambient temperature and can be isolated by chromatography and crystallization, they favor other side reactions such as protodeboronation under SMC conditions [42]. The undesired decomposition pathways in sp^3 -boron couplings are mostly circumvented by using tetrahedral boronates (e.g., potassium trifluoroborates (RBF_3K) and N-methyliminodiacetyl boronates (RB-[MIDA]; Scheme 1A) or stoichiometric loadings of palladium catalysts. On the other hand, the use of alkylborane (B-alkyl-9-borabicyclo [3.3.1]nonane: B-alkyl-9-BBN) in sp^3 SMCs suffers from isolation difficulties, lack of atom economy, air sensitivity and functional group tolerance (e.g., to ketones). Trialkylboranes (R_3B) have also been employed in SMCs [43,44].

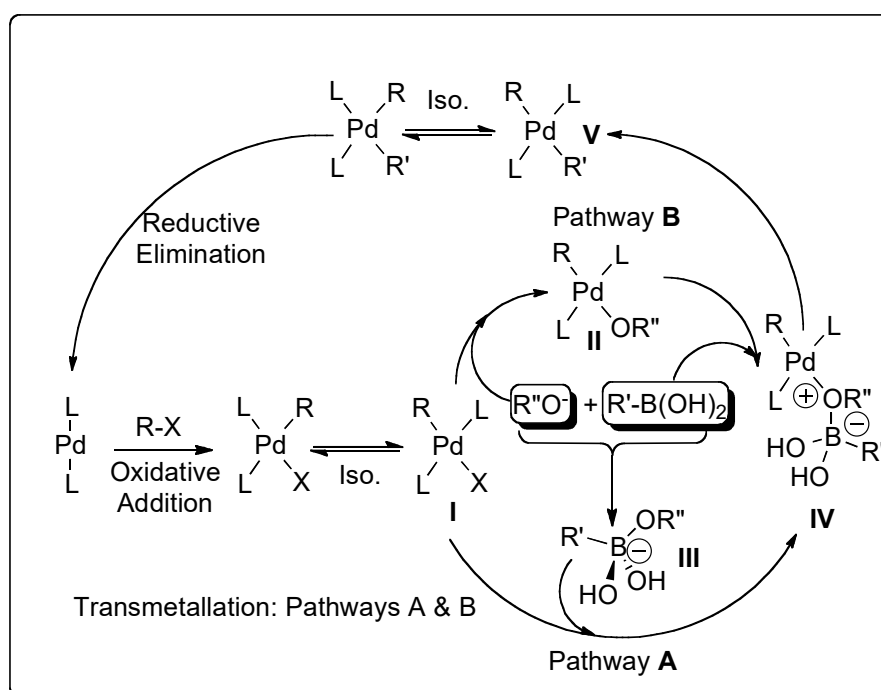
The alkyl-alkyl SMCs (sp^3 - sp^3) were recently reviewed in 2017 [45]. Hence, we will focus here on the recent development in cross-coupling reactions using sp^3 -boron reagents and $C(sp^2)$ -reagents. One class of the sp^3 - sp^2 SMC is commonly known as *B-alkyl Suzuki-Miyaura cross-coupling*. It is distinguished from the other SMCs in that this cross-coupling occurs between an alkyl borane and an aryl or vinyl halide, triflate or enol phosphate. Generally, the most reactive partners for B-alkyl SMC are unhindered electron-rich organoboranes and electron-deficient coupling partners (halides or triflates). Notably, this type of coupling is highly affected by all the reaction parameters including the type of organoborane, base, solvent and metal catalyst, and the nature of the halide partner. The effects of these parameters were detailed in the review by Danishefsky et al. on B-alkyl SMC in 2001 [33]. This work will thus summarize the $C(sp^3)$ - $C(sp^2)$ cross-couplings covering the more recent progress in this area after 2001. The advances in stereospecific sp^3 - sp^2 SMCs will be out of the scope of this highlight. However, it is worth noting that different versions that proceed with either retention or inversion of configuration have been well established [46,47]. Acyl SMC (acid halides, anhydrides, amides, esters), decarbonylative SMC and Liebeskind-Srogl cross-couplings are also not covered here and were recently reviewed in the literature extensively [48–52].

2. Suzuki-Miyaura Cross-Coupling (SMC)

As mentioned in the introduction, SMC is the conjoining of an organoboron reagent and an organic halide or pseudohalide in the presence of palladium (or other relevant metal) as a catalyst and a base for the activation of the boron compound (Scheme 1B) [5–7]. The efficiency of palladium has contributed to the ever-accelerating advances in catalysis, where coupling reactions, including SMC ones, are nowadays performed at ppb (parts per billion) molar catalyst loadings [53]. Nickel has also proved to have an efficient catalytic activity for SMC as the expensive palladium catalysts [54,55]. The high reactivity of nickel was revealed with difficult substrates such as aryl chlorides/mesyates, whose coupling reactions do not proceed easily with conventional Pd catalysis. In addition to being inexpensive, nickel catalysts can be more easily removed from the reaction mixtures while their economic practicality eliminates the need to recycle them [56]. Other metal catalytic systems have been investigated in SMC reactions such as Fe, Co, Ru, Cu, Ag, etc. However, their applications are by far less than Pd and Ni catalysts [56–58].

Since its discovery in 1979 [59], the Suzuki-Miyaura reaction has arguably become one of the most widely-applied, simple and versatile transition metal-catalyzed methods used for the construction of C–C bonds [60]. The general catalytic cycle is similar to other metal-catalyzed cross-couplings starting with an oxidative addition followed by a transmetalation and ending with a reductive elimination (Scheme 2). Transmetalation or the activation of the boron reagent makes Suzuki-Miyaura coupling different than other transition-metal cross-couplings processes. Mechanistic investigations were able to illustrate the role of each reagent in the reaction medium in addition to the metal. Some insights are now well established such as the necessity of sigma-rich electron-donor ligands, protic solvents and the base [61,62]; other mechanistic insights are still active areas of research including the activation way of boron in presence of the base. Two main analysis routes can be outlined as can be seen in Scheme 2: A) Boronate pathway: tetracoordinate nucleophilic boronate species **III** is generated *in situ* and substitutes the halide ligand of the Pd intermediate **I** issued from the oxidative addition, followed

by the elimination of $B(OH)_2OR$ from the resulting intermediate **IV** to transfer the organic moiety to palladium species **V**. B) Oxo-palladium pathway: the RO^- substitute ligand X on the palladium center leading to oxo-palladium **II** which acts as a nucleophile toward the boronic acid species, generating the tetracoordinate species **IV**. Ambiguity occurs since inorganic bases in aqueous or alcohol solvents, generating the required alkoxy or hydroxy ligands, are commonly employed in the SMC, to accelerate either pathway **A** or **B**. However, all DFT (Density Functional Theory) studies and ES-MS (Electrospray Ionization-Mass Spectrometry) investigations [63,64], where boronate species were observed and not oxo-palladium ones [65–67], support pathway **A**. Studies defending the suggestion of pathway **B** consist of kinetic analysis and experimental observations of the lack of activities in some cases in the presence of organic Lewis bases or lithium salts of boronic species. The group of Maseras claimed that while pathway **A** and pathway **B** are competitive, the first has lower energy barriers than the second [68]. Therefore, the boronate pathway (**A**) is faster. Additionally, they stated that their theoretical report is consistent with the experimental observations they reproduced [63].



Scheme 2. General mechanism of Suzuki–Miyaura cross-coupling.

Further investigation is needed to conclude which pathway is the actual one, or whether both exist in a competitive manner in each catalytic cycle. One point supporting pathway **A** can still be considered here. The formation of oxo palladium **II** is less favored in the case where the palladium center is electron-rich (bearing a good sigma donor and weak π acceptor ligands), which is more likely to react with a weaker nucleophile like boronate $[R-B(OH)_3]^-$ rather than with a strong nucleophile, such as hydroxy or alkoxy groups.

The success of the SMC method originates from its high regio- and stereo-selectivity, extremely low catalytic loadings, and the exceptionally mild reaction conditions. The employed conditions are compatible with aqueous and heterogeneous media and tolerate steric hindrance and a wide range of functional groups. In addition, the readily available organoboron reagents and the versatile developed methods that permit access to challenging boron-functionalized adducts as well as the easy incorporation of nontransferable boron ligands have contributed to the appeal of SMC reactions. Most boron starting materials are thermally stable and inert to oxygen, water and related solvents. In general, they are relatively non-toxic and environmentally benign, and so are their by-products. Thus, they can be handled and separated easily from the reaction mixtures [69–72]. These unique

features have allowed researchers to utilize SMC in a great variety of applications from development of polymeric materials to total synthesis of complex natural products. SMCs also constitute an important tool in medicinal chemistry, in production of fine chemicals and innovative materials as organic-light emitting diodes and in large-scale syntheses of pharmaceuticals [73–75]. Several reviews and textbooks have been dedicated to the applications of SMCs. Our review will only highlight a few examples of target molecules in Section 9. The relevant reports of $C(sp^3)–C(sp^2)$ cross-couplings are summarized in Table 1 (*reaction partners and conditions*) in order of the respective sections where they are discussed.

Table 1. General summary of the relevant reports of $C(sp^3)–C(sp^2)$ cross-couplings in this review.

Boron Reagent	Substrate	Reaction Conditions (General)	Reference	Section and Scheme
B-alkyl-9-BBN and trialkylboranes	Aryl iodides	$PdCl_2(dppf)$, NaOH, THF, reflux, 16 h	76	3;3A
Alkylboranes	Aryl bromides and iodides	$PdCl_2(dppf)$, NaOH, THF, 65 °C	77–79	3;3B
B-alkyl-9-BBN and boronic acids	Aryl halides	$Pd(OAc)_2$, SPhos, $K_3PO_4 \cdot H_2O$, THF or toluene	80	3;3C
B-benzyl-9-BBN	Chloroenynes	$Pd(PPh_3)_4$, Cs_2CO_3 , water, 60 °C, 12 h	81	3;4
B-alkyl-9-BBN	$C_{Ar}-O$ electrophiles	$Ni(COD)_2$, iPr_2O , Cs_2CO_3 , iPr_2O , 110 °C, 12 h	85	3;5A
B-alkyl-9-BBN	Aromatic and alkenyl ethers	$Ni(COD)_2$, PCy_3 , base, iPr_2O , 110 °C	86	3;5B,C
1,3-dienes and 9-BBN	Aryl halides	$Pd(dppf)Cl_2$ or $Pd(dppb)Cl_2$, NaOH, THF, 40 or 65 °C	87	3;6
B-alkyl-9-BBN	β -triflyl enones	$Pd(dppf)Cl_2$, Cs_2CO_3 , DMF:THF:H ₂ O, 60 °C, 16 h	88	3;7A
9-BBN derivatives of L-aspartic acid	Halogenated pyridine	$Pd(PPh_3)_4$, K_3PO_4 (aq.), THF, 50 °C, 2 h	89	3;7B
Alkyl organoboron reagents	Aromatic esters	$Ni(COD)_2$, dcyep, CsF, toluene, 150 °C	91	3; 8A
Alkyl organoboron reagents	Aroyl fluorides	$Ni(COD)_2$, dppe, CsF, toluene/hexane, 140 °C	92	3;8B
Potassium alkyltrifluoroborates	Aryl halides/triflates and vinyl triflates	$PdCl_2(dppf) \cdot CH_2Cl_2$, Cs_2CO_3 , THF:H ₂ O, reflux, 6–72 h	44,94	4;9B
Tertiary trifluoroborate salts	Aryl and heteroaryl chlorides and bromides	CatacXium-A-Pd G3, Cs_2CO_3 , tol/water, 90 °C, 18 h	99	4;9C
Secondary alkyl β -trifluoroboratoketones and -esters	Aryl Bromides	$Ir[dFCF_3ppy]_2(bpy)PF_6$, $NiCl_2 \cdot dme$, dtbbpy, Cs_2CO_3 , 2,6-lutidine, 1,4-dioxane, $h\nu$	10	4;10A
α -alkoxyalkyl- and α -acyloxyalkyltrifluoroborates	Aryl bromides	$Ir[dFCF_3ppy]_2(bpy)PF_6$, $Ni(COD)_2$, dtbbpy, K_2HPO_4 , dioxane, $h\nu$	101	4;10B
Tertiary organotrifluoroborates reagents	Aryl bromides	$Ir[dFCF_3ppy]_2(bpy)PF_6$, $Ni(TMHD)_2$ or $Ni(dtbbpy)(H_2O)_4Cl_2$, K_2HPO_4 or Na_2CO_3 , no additive or $ZnBr_2$, dioxane/DMA or DMA, $h\nu$, 12–72 h	102	4;10C
Trialkylboranes	Aryl bromides	$PdCl_2(dppf)$, THF, reflux, 2–6 h	105,106	5;11B
NHC-boranes complexes	Aryl halides and triflates	[Pd], Ligand, tol-H ₂ O or THF-H ₂ O, heat or microwave	107	5;11C
Trialkyl- and triaryl-boranes (generated <i>in situ</i>)	Alkenyl and aryl halides	$Pd(OAc)_2$, $n-BuAd_2P$ or RuPhos, K_3PO_4 , tol-H ₂ O, 100 °C	108	5;11D
<i>n</i> -alkylboronic acids	Alkenyl and aryl halides or triflates	$PdCl_2(dppf)$, K_2CO_3 , Ag_2O , THF, 80 °C, 6–10 h	112	6;12A
<i>n</i> -alkylboronic acids	Alkenyl halides	$PdCl(C_3H_5)dppb$, Cs_2CO_3 , toluene or xylene, 100–130 °C, 20 h	113	6;12B
Primary and secondary alkylboronic acids	2-bromoalken-3-ol derivatives	$Pd(OAc)_2$, LB-Phos.HBF ₄ , K_2CO_3 , toluene, 110 °C, 3–27 h	114	6;12C

Table 1. Cont.

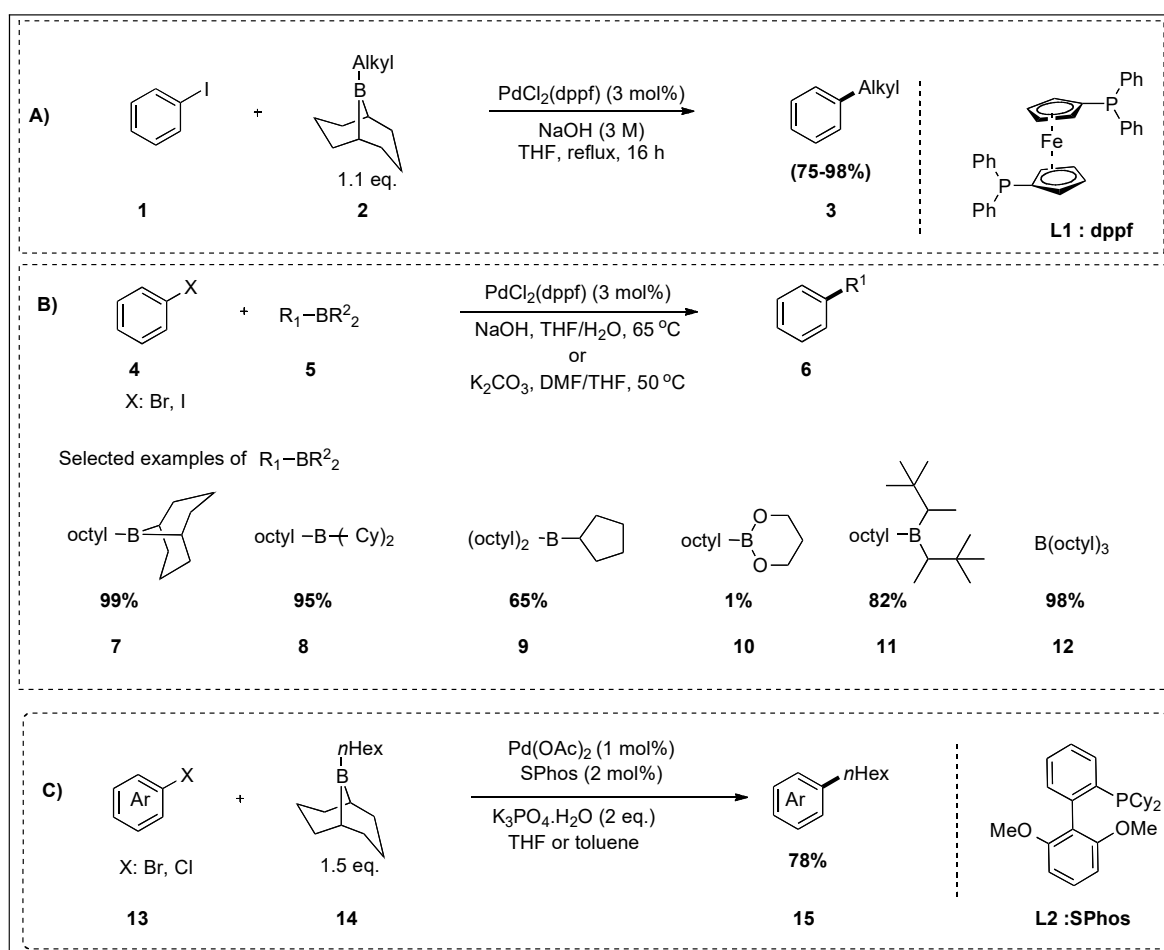
Boron Reagent	Substrate	Reaction Conditions (General)	Reference	Section and Scheme
Cyclic secondary alkylboronic acids	di-ortho-substituted arylhalides	Pd(OAc) ₂ , AntPhos, K ₃ PO ₄ , toluene, 110 °C, 12–24 h	115	6;12D
Acyclic secondary alkylboronic acids	Aryl and alkenyl triflates	[Pd(cinnamyl)Cl] ₂ , Ligand, K ₃ PO ₄ ·H ₂ O, toluene, 110 °C, 12 h	116	6;12E
Boronic esters	Aryl methyl ethers bearing ortho-carbonyls	RuH ₂ (CO)(PPh ₃) ₃ , toluene, 110 °C	117	7;13A
MIDA boronates	Aryl and heteroaryl bromides	PdCl ₂ (dppf)·CH ₂ Cl ₂ , Cs ₂ CO ₃ , THF:H ₂ O, 80 °C, 24–48 h	43	7;14
Alkyl iodide and 9-MeO-9BBN (tBuLi for <i>in situ</i> generation)	Alkenyl bromide	Pd(OAc) ₂ , Aphos-Y	126	8;15B
OBBD derivatives	Aryl Bromide	Pd(dtbpf)Cl ₂ , Et ₃ N or K ₃ PO ₄ , TPGS-750-M/H ₂ O 45 °C, Ar, 16–21 h	127	8;15D

3. First Reports of B-alkyl SMC and Methods Employing 9-BBN Derivatives

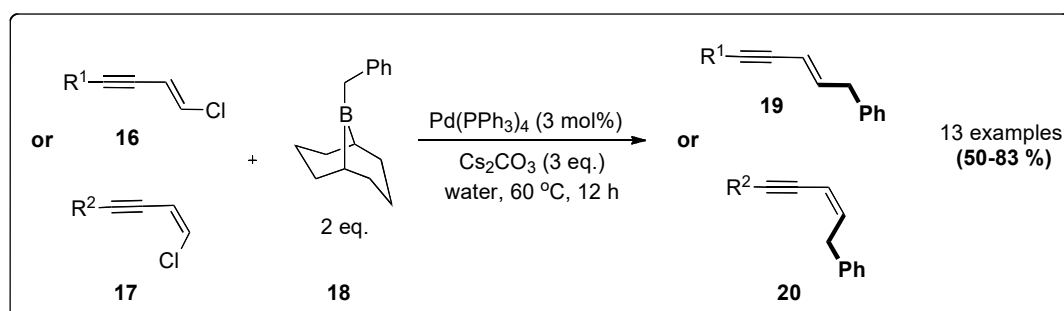
The alkylboron cross-coupling was disclosed in 1986 by Suzuki and Miyaura using B-alkyl-9-BBN **2** or trialkylboranes (R₃B) in the presence of PdCl₂(dppf) and a base (sodium hydroxide or methoxide) (Scheme 3A). The reaction proceeded readily providing alkylated arenes **3** and alkenes in excellent yields of 75%–98%. On the other hand, no coupling was observed when sec-butylboranes were used [76]. In 1989, the same group revealed the reactivity of different alkyl boranes **5** in B-alkyl SMC (Scheme 3B). Pinacolborane **10** was almost unreactive (1% yield), while 9-BBN derivatives **7** showed the highest efficiencies (e.g., 99%). Thus, functionalized alkenes, arenes and cycloalkenes were synthesized via a hydroboration-coupling sequence of 9-BBN derivatives with haloalkenes or haloarenes **4** (inter- and intramolecular). Good yields of geometrically pure alkenes and arenes were afforded from the performed reactions with a variety of functionalities on either coupling partner. The reaction could also be carried out using K₂CO₃ instead of NaOH with base-sensitive compounds [77–79].

In 2004, the group of Buchwald reported the design of a new ligand with tuned steric and electronic properties. The phosphane ligand incorporated two methoxy groups on one of phenyls (**L2**, Scheme 3C). The oxygen lone pairs increase the electron density on the biaryl and participate in stabilizing the Pd complex. Simultaneously, the MeO groups increase the steric bulk and prevent cyclometalation. This as-designed ligand aimed to serve as a universal catalyst for cross-coupling and C–H activation reactions. It was later commercialized under the name of SPhos, and became a basic ligand in today's catalysis toolbox. The ligand demonstrated a wide scope and stability with aryl boronic acids. It was also efficient for coupling of B-alkyl-9-BBN derivatives **14** (and boronic acids) using K₃PO₄·H₂O as an essential base (vs. lower conversions with anhydrous bases) (Scheme 3C). The scope involved challenging aryl halides as 3-dimethylamino-2-bromoanisole and aryl chlorides [80].

In 2013, Wu et al. developed a SMC between B-benzyl-9-BBN **18** and chloroenynes **16** and **17** to synthesize a vast array of 1,5-diphenylpent-3-en-1-yne derivatives **19** and **20** in good yields and full control on the E/Z selectivity using Pd(PPh₃)₄ and Cs₂CO₃ in pure water (Scheme 4) [81]. The conditions tolerated substrates bearing several electron-donating and withdrawing groups. It is worth remarking that these derivatives are known for their anti-inflammatory activity and can be isolated from plants, but only in minor quantities.

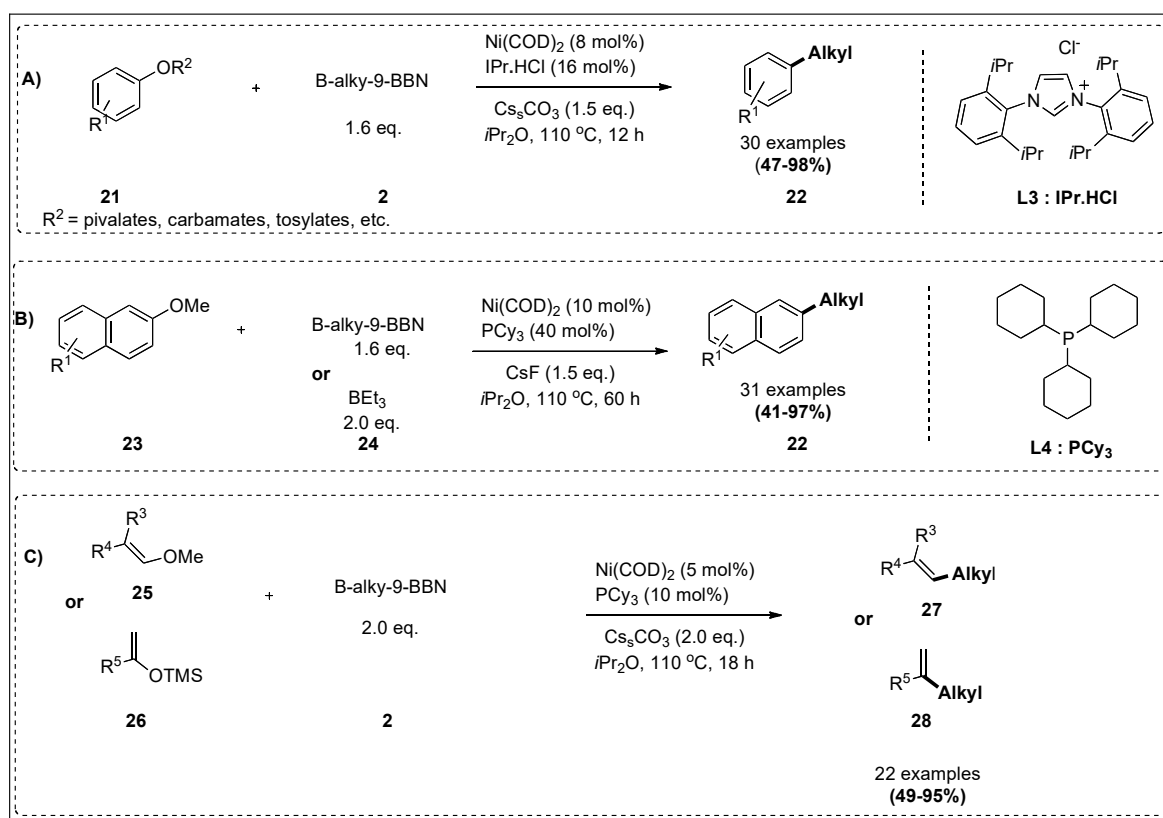


Scheme 3. First reports of B-alkyl Suzuki–Miyaura cross-coupling (A–C) and the reactivity of alkylboranes (C).



Scheme 4. B-alkyl SMC of chloroenynes.

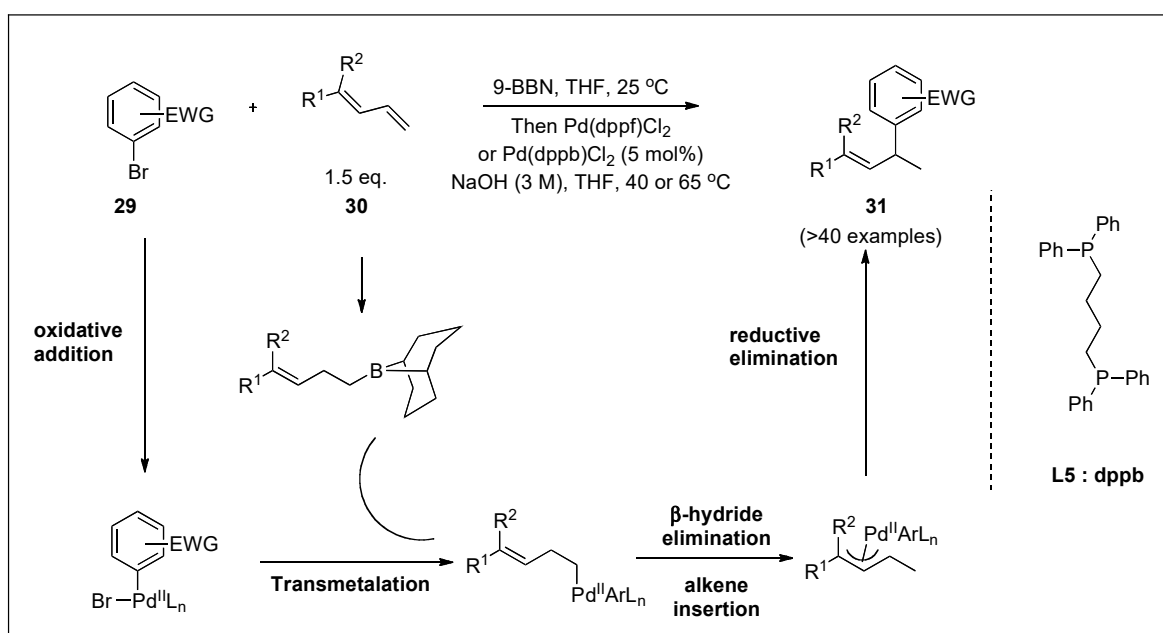
C–O electrophiles represent attractive alternatives to halides. However, research on cross-couplings of aryl methyl ethers was delayed by the perception that they can be challenging coupling counterparts in comparison to other protected phenol electrophiles such as aryl pivalates, sulfonates and carbamates. Indeed, the activation energy for effecting C–OMe bond cleavage is significantly higher, with OMe being more difficult to separate from the group and more reluctant to oxidative addition. It is noteworthy that C–O electrophiles cross-couplings are predominantly conducted with nickel catalysis, as can be seen in Scheme 5, which depicts the work of the Rueping group in this regard. This demonstrates the higher activity of Ni with such challenging substrates [82–84].



Scheme 5. Ni-catalyzed alkylation of $\text{C}_{\text{Ar}}\text{-O}$ electrophiles (including aromatic methyl ethers) (A,B) and methyl enol ethers (C).

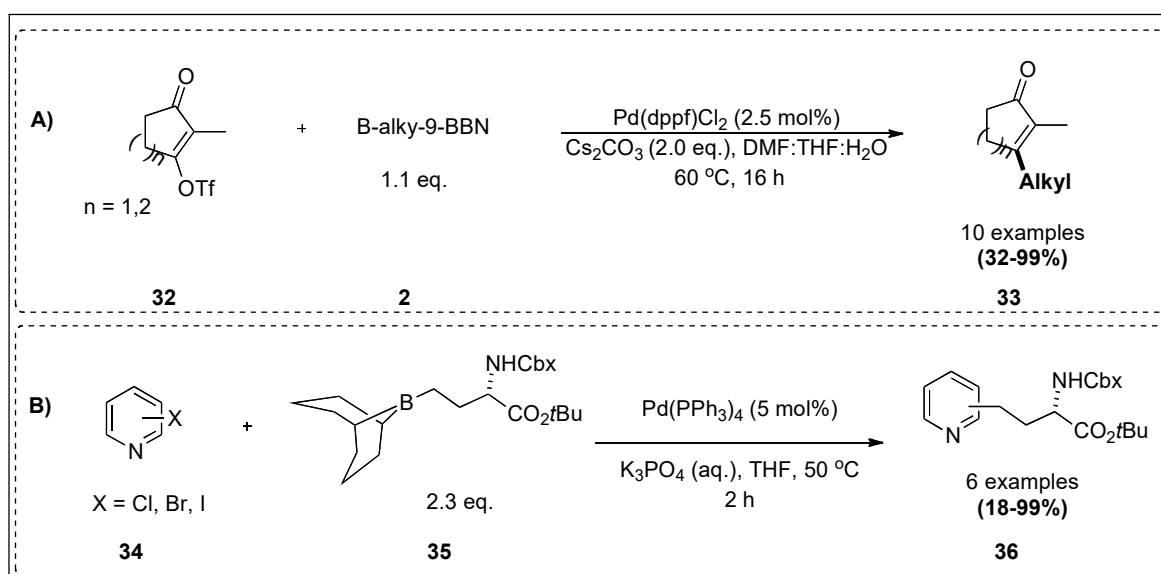
In 2016, Rueping et al. utilized the B-alkyl-9-BBN **2** to report an efficient nickel-catalyzed alkylation of $\text{C}_{\text{Ar}}\text{-O}$ electrophiles **21** (pivalates, carbonates, carbamates, sulphamates and tosylates). The optimal conditions involved Ni(COD)_2 , a IPr·HCl ligand and Cs_2CO_3 in diisopropyl ether (Scheme 5A). This new protocol was tolerant to numerous synthetically important functional groups of phenol pivalates and alkylboranes circumventing the restriction of β -hydride elimination [85]. Soon after, the same group described the use of the first alkylation of polycyclic aromatic methyl ethers **23** and methyl enol ethers **25** and **26** (Scheme 5B,C), which involves the cleavage of the highly inert $\text{C}(\text{sp}^2)\text{-OMe}$ bonds, using alkylboron reagents with broad functional group tolerance. As expected, the choice of the base and the ligand is critical in C–O bond-cleaving reactions. Thus, the conditions described for $\text{C}_{\text{Ar}}\text{-O}$ electrophiles were not successful, and the optimal conditions necessitated the replacement of the IPr·HCl ligand with PCy₃. Cs_2CO_3 was mostly used in couplings of alkenyl ethers, while both CsF and Cs_2CO_3 could be used in the case of aromatic methyl ethers. The reaction performed better with a Ni/L ratio of 1:4 instead of 1:2, and a prolonged reaction time of 60 h instead of 12 h. The optimal conditions for these novel transformations are summarized in Scheme 5 [86].

In 2018, Zhang et al. reported a hydroboration/Pd-catalyzed migrative SMC of 1,3-dienes **30** with electron-deficient aryl halides **29** (Scheme 6) with a wide scope (>40 examples). This method allows the use of primary homoallylic alkylboranes in the direct synthesis of branched allylarenes. The selectivity of the branched versus linear coupling was found to be tuned by the choice of the ligand. The branch-selective coupling was found to be favored by the more electron-rich bidentate ligand with a larger ligand–metal–ligand (bite) angle (i.e., L5: dppb). Their report involved preliminary mechanistic studies, showing a palladium migration in the formation of allyl palladium species. The migration proceeded via a sequence of β -hydride elimination and an alkene reinsertion partially involving an alkene dissociation/association process (Scheme 6) [87].



Scheme 6. Hydroboration/Pd-catalyzed migrative SMC of 1,3-dienes aryl halides.

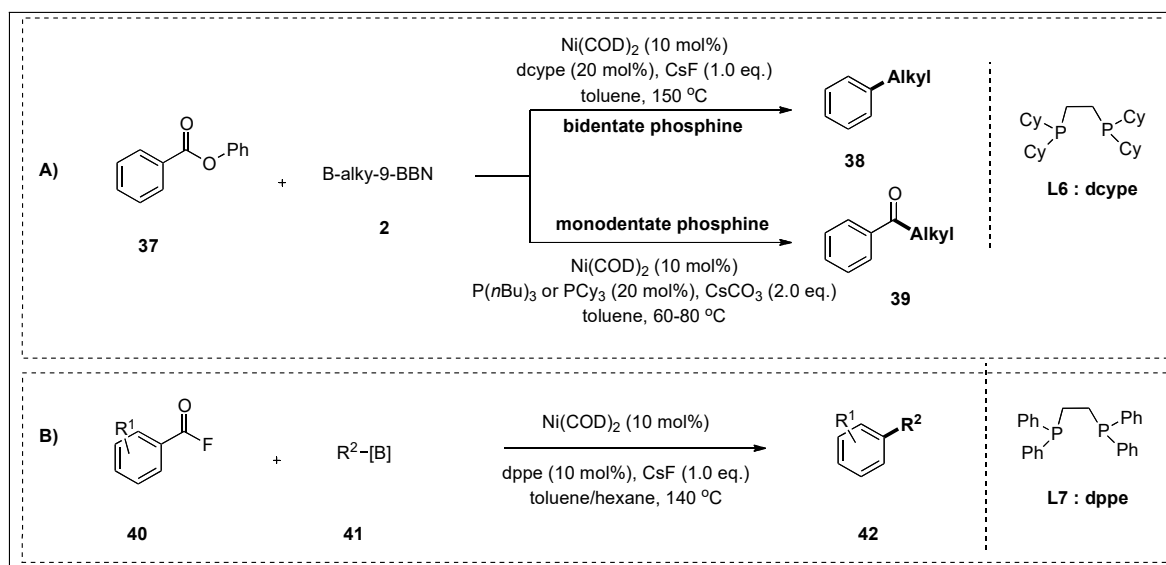
Very recently, Newhouse et al. described the use of β -triflyl enones **32** as efficient coupling partners in a mild B-alkyl SMC (Pd(dppf)Cl_2 (2.5 mol%), Cs_2CO_3 (2 eq.)), and tolerant of sensitive functional groups (Scheme 7A). The more stable triflate to light and chromatography, in comparison to halogenated analogs, were used to establish challenging cyclic α,β -disubstituted enones **33** with good to excellent yields (10 examples) [88]. In parallel, Usuki et al. reported an SMC between halogenated pyridines **34** and a borated L-aspartic acid derivative (9-BBN) **35** using $\text{Pd(PPh}_3)_4$ (5 mol%) and $\text{K}_3\text{PO}_4(\text{aq.})$ in THF (Scheme 7B). The experimental yield gave insight on the reactivity order of halogen substituents and position, which was found to be as follows: $\text{Br} > \text{I} \gg \text{Cl}$ and $\text{C3} > \text{C2}, \text{C4}$ [89].



Scheme 7. Latest reports of SMCs using 9BBN (A and B).

Although decarbonylative and acyl cross-coupling reactions are not covered in this review [48–52,90], it is worth mentioning two very recent novel reports from the groups of Rueping and Nishihara. Rueping et al. (Scheme 8A) described an elegant ligand-controlled and site-selective

nickel catalyzed SMC with aromatic esters **37** and alkyl organoboron reagents (majorly 9-BBN **2** and 6 examples with triethylboron). Ester substrates **37** were transformed into alkylated arenes **38** and ketone products **39** simply by switching the ligand from bidentate phosphine (**L6**: dcype) to monodentate phosphine ($P(nBu)_3$ or PCy_3). The regioselectivity was rationalized by DFT studies and the reported method has shown broad tolerance to functional groups and a wide substrate scope. The reaction was tested successfully on a large scale (1 g) using a cheaper $NiCl_2$ catalyst [91]. The group of Nishihara reported an elegant nickel-catalyzed decarbonylative C–F bond alkylation of aryl fluorides **40**; the conditions are depicted in Scheme 8B [92].

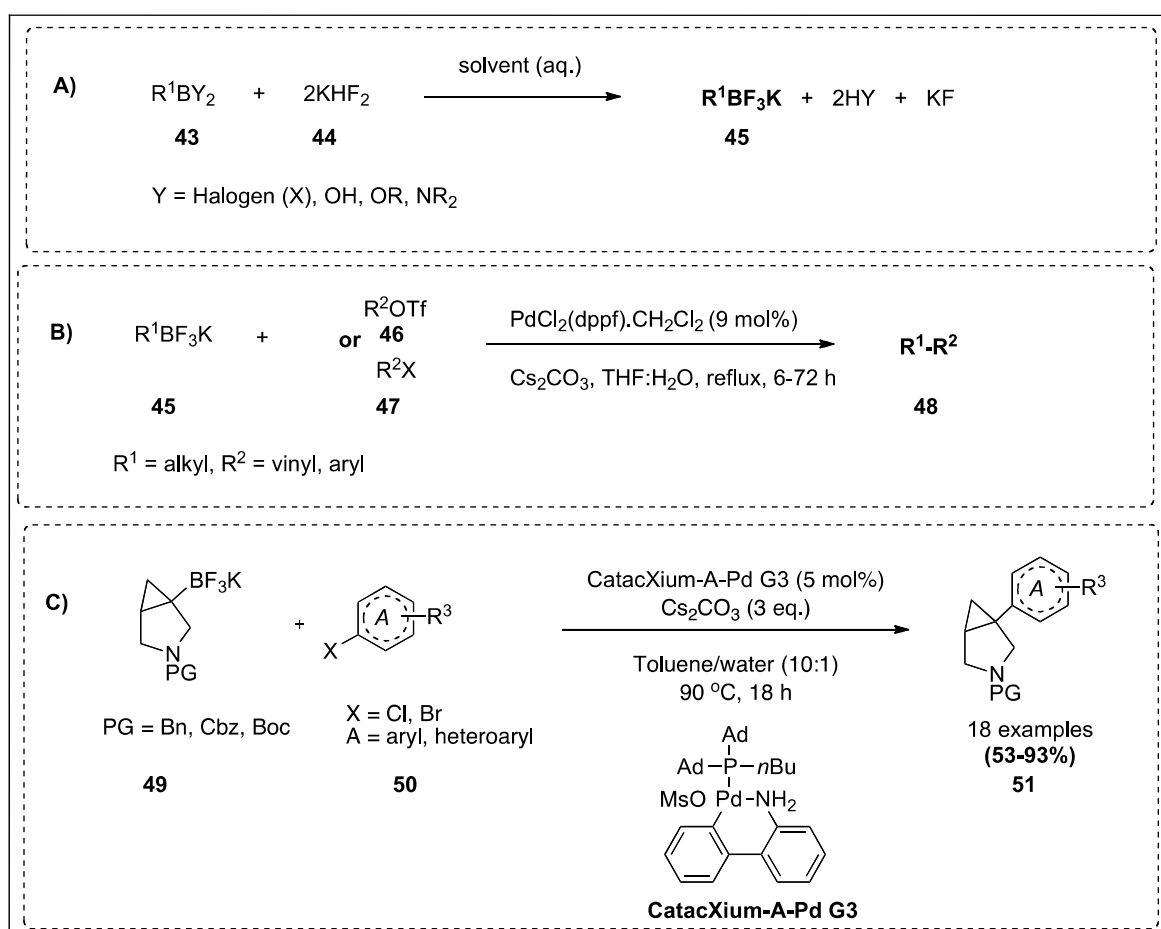


Scheme 8. Novel decarbonylative cross-coupling reactions with alkylboranes (**A** and **B**).

4. Organotrifluoroborates in sp^3 – sp^2 SMCs

The tetracoordinate nature of the boron in organotrifluoroborates fortified by strong boron–fluorine bonds has been found to inhibit the undesirable reactions typical of trivalent organoborons. All of these complexes are crystalline solids and stable in water and under air; thus they can be stored on the shelf indefinitely. Besides, the manipulation of remote functional groups within the organotrifluoroborates is feasible while retaining the valuable C–B bond. Borates (RBF_3K) **45** can be easily prepared on a large scale by the addition of inexpensive fluoride source (KHF_2) **44** to a variety of organoboron intermediates **43**, such as boronic acids/esters, organodihaloboranes and organodiaminoboranes (Scheme 9A) [93].

Molander and coworkers were the first to use potassium alkyltrifluoroborates **45** as coupling partners with aryl halides/triflates and vinyl triflates **46/47** using $PdCl_2(dppf)\cdot CH_2Cl_2$ as the catalyst in THF– H_2O and Cs_2CO_3 as the base (Scheme 9B). Two successive reports in 2001 and 2003 studied the scope of this B–alkyl SMC, reporting more than 50 examples with acceptable to very good yields, hence revealing a potential general method to a wide range of functionalities [44,94]. Later, the same group used microscale parallel experimentation to describe the first comprehensive study of the coupling of secondary alkylborons (organotrifluoroborates) and aryl chlorides (and bromides), elaborating different catalytic systems for this purpose. Their results demonstrated a ligand-dependent β -hydride elimination/reinsertion mechanism in the cross-couplings of hindered partners, which can result in isomeric products of coupled products [34]. The use of trifluoroborates in SMC was validated by numerous publications that appeared thereafter and was reviewed many times by different research groups, as the one by Molander in 2015 [79,95–98].

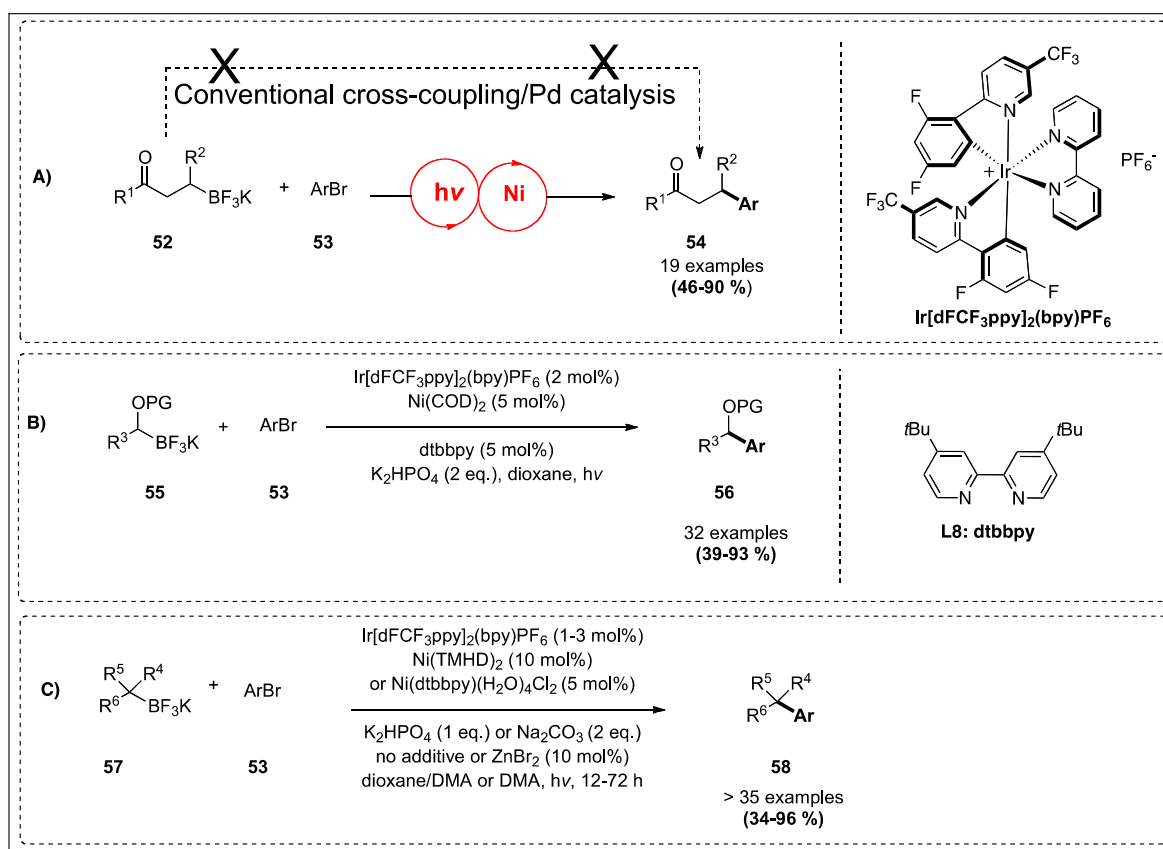


Scheme 9. Alkyltrifluoroborates salts: General synthesis and first report in sp³–sp² SMC (A and B); Pd-catalyzed SMC report of Harris et al. (C).

Harris et al. recently reported a Pd-catalyzed SMC reaction with tertiary trifluoroborate salts **49** to synthesize 1-heteroaryl-3-azabicyclo[3.1.0]hexanes **51**, an interesting scaffold in medicinal studies with limited synthetic approaches. The SMC protocol was compatible with a range of aryl and heteroaryl chlorides and bromides **50** (Scheme 9C) [99]. The optimized conditions involved CatacXium-A-Pd-G3, Cs₂CO₃ in toluene/water and were applied in synthesis of 18 examples with good to excellent yields.

The group of Molander, after their review [98], has extended the scope of sp²–sp³ cross-couplings to fluoroborates that show recalcitrance to Pd-catalyzed classical couplings via dual catalysis (Scheme 10). The first comprised the coupling of aryl bromides **53** to secondary alkyl β-trifluoroborato ketones and -esters **52** using Ir-based photoredox/nickel dual catalysis (Scheme 10A). This dual catalysis relies on a single-electron transmetalation and provides a complementary toolbox to the classical couplings that are based on two-electron processes. The oxidative fragmentation in the dual catalysis activates the organometallic reagent into its corresponding alkyl radical, which is then readily intercepted by the nickel catalyst mediating the formation of the C–C bond formation with the aryl halide partner. Their optimized conditions consisted of a catalytic system of Ir[dFCF₃ppy]₂(bpy)PF₆ photocatalyst (2.5 mol%), NiCl₂-dme (2.5 mol%), dtbbpy (2.5 mol%), Cs₂CO₃ (0.5 eq.) and 2,6-lutidine (0.5 eq.) in 1,4-dioxane, tolerating various functionalities in addition to sterically and electronically diverse coupling partners (Scheme 10A) [100]. The second report described a photoredox/nickel dual catalysis alternative approach to the protecting-group-independent cross-coupling of α-alkoxyalkyl- and α-acyloxyalkyltrifluoroborates **55** with aryl (and heteroaryl) bromides **53**, which can also be achieved by palladium catalysis. This method was compatible with various functional groups and N,N-diisopropylcarbamoyl, pivaloyl and benzyl protecting groups (Scheme 10B) [101]. Their

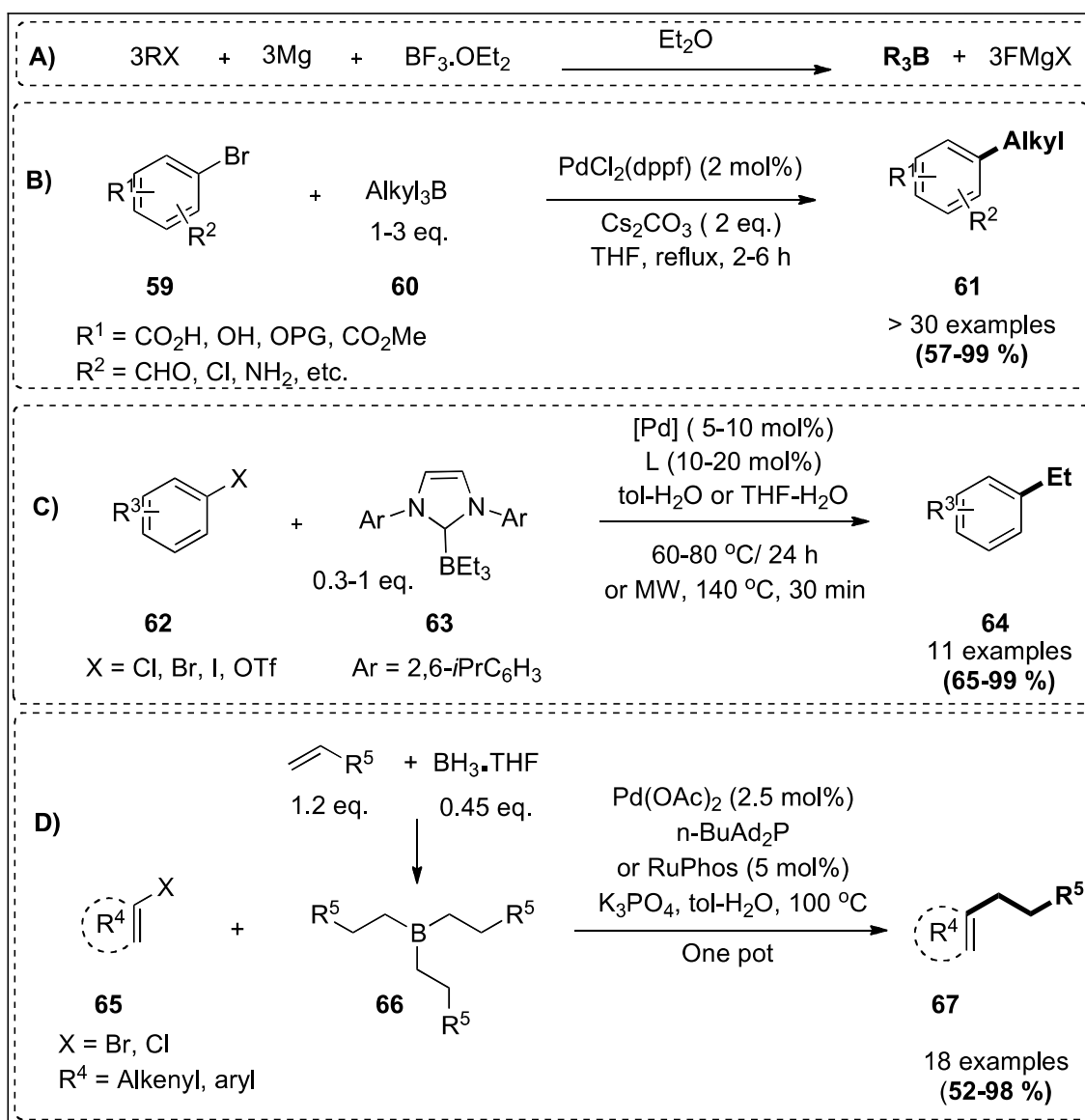
third dual catalysis report (Scheme 10C) contributed to the construction of sterically demanding quaternary centers **58**, an area that is not yet comprehensive and suffers from the absence of general methodologies and the copious limitations of the currently used metal-catalyzed methods. Various tertiary organotrifluoroborates reagents **57** were coupled using different conditions and light intensities, which were found to be crucial depending on the nature of the substituents (e.g., bridged versus acyclic). The scope of the coupled aryl bromides **53** in this method was limited to electron-poor and electron-neutral systems [102].



Scheme 10. Photoredox/metal dual catalysis of organotrifluoroborates by the Molander group (A–C).

5. Other Alkylboranes in sp^3 – sp^2 SMCs

Tri-*n*-alkylboranes (R_3B) can be easily prepared by the reaction of Grignard reagents with boron trifluoride etherate (Scheme 11A) [103]. The use of this class of boranes in B–alkyl SMC was sporadically reported in the literature, probably due to their flammable nature and sensitivity to oxygen, as well as the inefficiency of the transfer of all three alkyl groups from the boron center [104]. In 2009, Wang et al. published optimization studies that presented efficient and chemoselective Pd-catalyzed direct SMCs of trialkylboranes **60** with bromoarenes **59** in the presence of unmasked acidic or basic functions using the weak base Cs_2CO_3 under mild non-aqueous conditions (Scheme 11B). The conditions tolerated carbonyl reagents, chlorinated derivatives, nitriles and unprotected and base-labile Piv- and TBS-protected phenols with more than 30 examples incorporating primary alkyls, and especially lower *n*-alkyls such as ethyl groups [105,106].



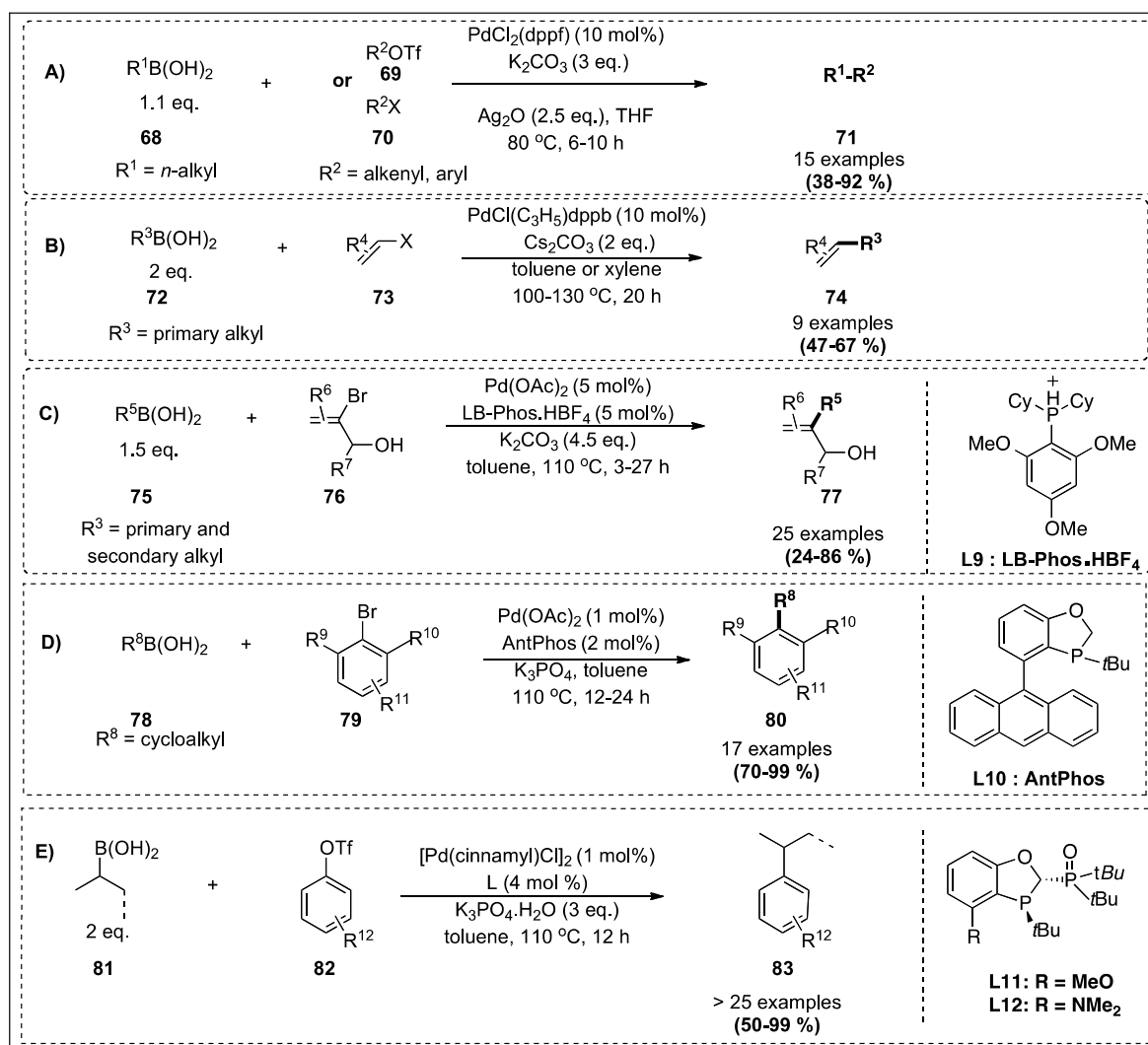
Scheme 11. Synthesis of alkylboranes (A and D) and their uses as coupling partners in $\text{sp}^3\text{-sp}^2$ SMCs (A–D).

Lacôte et al. developed the efficient transfer of all three groups of trialkyl- and triaryl-boranes (0.3–1 eq. instead of 1–3 eq.) in SMC in good yields under base-free conditions, achieving the activation by using N-heterocyclic carbenes (i.e., **63** in Scheme 11C). The $\text{C}(\text{sp}^2)\text{-C}(\text{sp}^3)$ scope involved the NHC–borane complexes **63** with aryl chlorides, bromides, iodides and triflates **62** in 11 examples (65%–99%) using $\text{PdCl}_2(\text{dppf})$ or $\text{Pd}(\text{OAc})_2$ with a ligand (XPhos or RuPhos) under microwave irradiation or classical heating [107]. In 2015, Li et al. described a general, atom-economic methodology that uses peralkyl and peraryl groups of unactivated symmetrical triaryl- and trialkyl-boranes **66** in SMC (Scheme 11D). The hydroboration of terminal alkenes was carried out *in situ*, and the corresponding trialkylboranes **66** were coupled with alkenyl and aryl halides **65** in a one-pot fashion. The method was compatible with a variety of functional groups and heterocycles [108].

6. Alkylboronic Acids in $\text{sp}^3\text{-sp}^2$ SMCs

Alkylboronic acids ($\text{R}(\text{BOH})_2$), like their aryl analogs, exist in equilibrium with their trimeric cyclic anhydrides—boroxines, which also proved to be efficient coupling partners in SMCs [109]. Thus,

the determination of the concentration of boroxine vs. boronic acid in the catalytic reaction can be difficult, requiring the employment of excess boronic acid to ensure the completion of the reaction [110]. Gibbs et al. were among the first to use alkylboronic acids as coupling partners with alkenyl triflates in 1995 [111]. The group of Falck widened the scope by reporting an efficient Ag(I)-promoted SMC of *n*-alkylboronic acids **68** (Scheme 12A) [112].



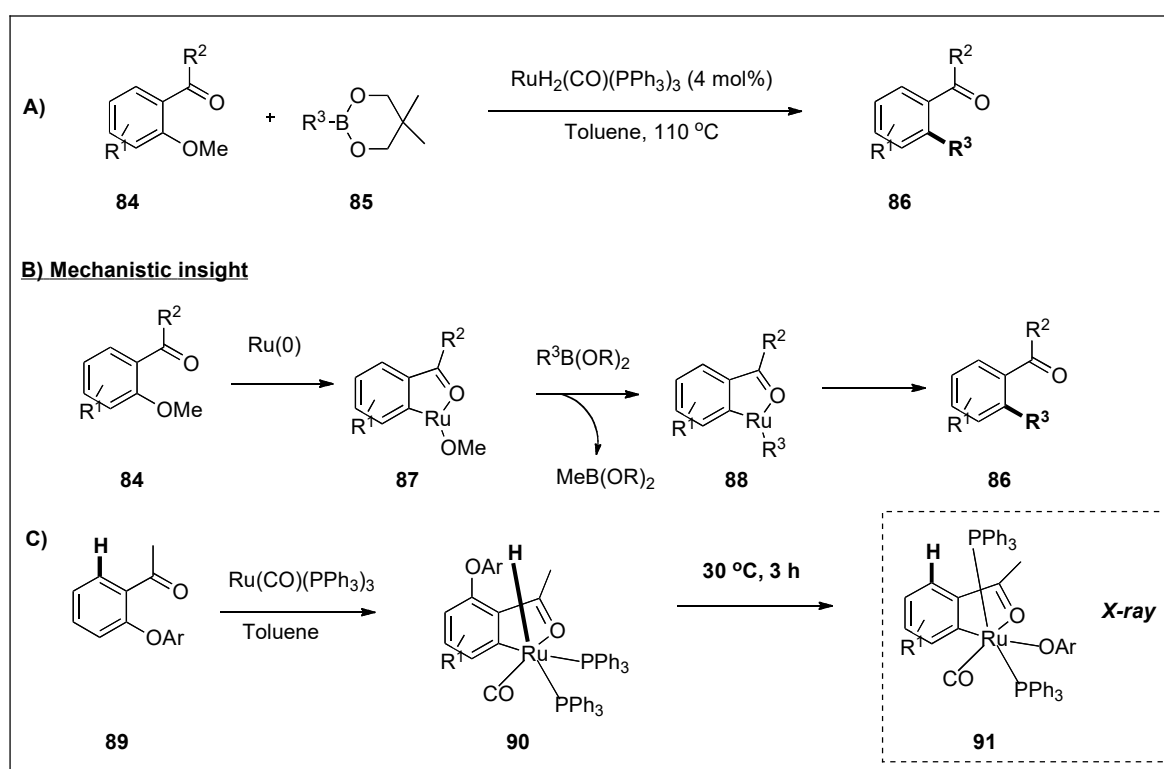
Scheme 12. Alkylboronic acids as coupling partners in sp^3 – sp^2 SMCs (A–E).

The progress of utilizing alkylboronic acids was reviewed in 2008 [110]. Next, the SMC of primary alkylboronic acids **72** with alkenyl halides **73** was reported using air-stable catalyst $PdCl(C_3H_5)(dppb)$ and Cs_2CO_3 , and toluene or xylene as solvents (Scheme 12B) [113]. In 2012, Ma et al. used $Pd(OAc)_2$ with K_2CO_3 and an air-stable monophosphine HBF₄ salt (**L9**: LB-Phos.HBF₄) as an efficient ligand to couple primary and secondary alkylboronic acids **75** with 2-bromoalken-3-ol derivatives **76** (Scheme 12C) [114]. In 2014, Tang et al. revealed a sterically demanding aryl–alkyl SMC between di-ortho-substituted arylhalides **79** and (secondary) cycloalkylboronic acids **78** using a highly reactive Pd-AntPhos catalyst that allowed to reduce the β -hydride elimination (Scheme 12D). The method comprised a scope of sterically hindered substituted aryl compounds, including highly substituted benzene, naphthalene and anthracene derivatives [115]. The same group described the cross-coupling between aryl/alkenyl triflates **82** and acyclic secondary alkylboronic acids **81** in good to excellent yields (Scheme 12E). The employment of sterically bulky P=P=O ligands (**L11/12**) was found to be critical to achieve the

chemoselectivity by inhibiting the isomerization of the secondary alkyl coupling partner (e.g., *i*Pr vs. *n*Pr) and to obtain high yields [116].

7. Boronic Esters and MIDA Boronates in sp^3 - sp^2 SMCs

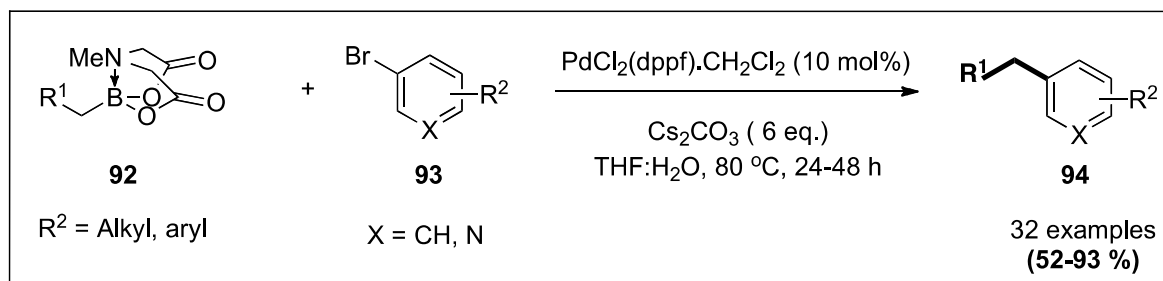
Prior to the work of Rueping on more general cross-coupling methods of challenging C–O electrophiles with organoboron reagents, a robust Ru-catalyzed SMC of aryl methyl ethers **84** with boronic esters **85** was elegantly revealed by chelation assistance (Scheme 13A) [84,117]. Aromatic ketones **84** where the carbonyl is located in an ortho position were reported to assist in the cleavage of C–OMe bonds. Neopentyl boronates **85** were the most reactive among all the tested boronic esters. The conditions were employed to couple aryl, alkenyl and even alkyl boronates with the same efficiency by using a $RuH_2(CO)(PPh_3)_3$ catalytic system. The C–OMe bond-cleavage was facilitated by the coordination of the carbonyl group to the Ru center, in an analogous mechanistic scenario to C–H activation (Scheme 13B). The suggested chelation-assisted mechanism was later supported by the isolation of the oxidative addition complex of an aryl C–O bond using low-valent Ru complexes **91** (Scheme 13C) [84,118,119]. The C–O bond-cleavage occurred at high temperatures (thermodynamic control) as compared to the C–H functionalization that rapidly took place at room temperature (Scheme 13C). The Ru-catalyzed SMC of aryl methyl ethers remained restricted to the presence of an ortho directing group to the reactive site [84,118,119]. The reported more general Ni-catalyzed coupling version of aryl methyl ether without directing group involved aryl boranes, and did not involve a scope of alkyl boranes [84,117–120].



Scheme 13. Chelation-assisted Ru-catalyzed sp^3 - sp^2 SMCs of C–OMe electrophiles (A) and mechanistic insight (B,C).

Inspired by the pioneering work of Wrackmeyer on protected boronic acids by iminodiacetic acids [121], the groups of Burke, Yudin and others developed the use of *N*-methyliminodiacetic acid (MIDA) boronates **92** in direct and iterative SMC reactions [122–124]. In addition to stability and compatibility with chromatography, the advantage of MIDA boronates is their mild hydrolysis to

liberate the corresponding boronic acids compared to the harsh conditions needed in the case of sterically bulky boronic esters. This class found various applications in synthesis, and the efficient iterative assembly of the MIDA building blocks was recently reviewed in 2015 [122]. A direct SMC between MIDA boronates **92** and aryl and heteroaryl bromides **93** is presented in Scheme 14 [43].



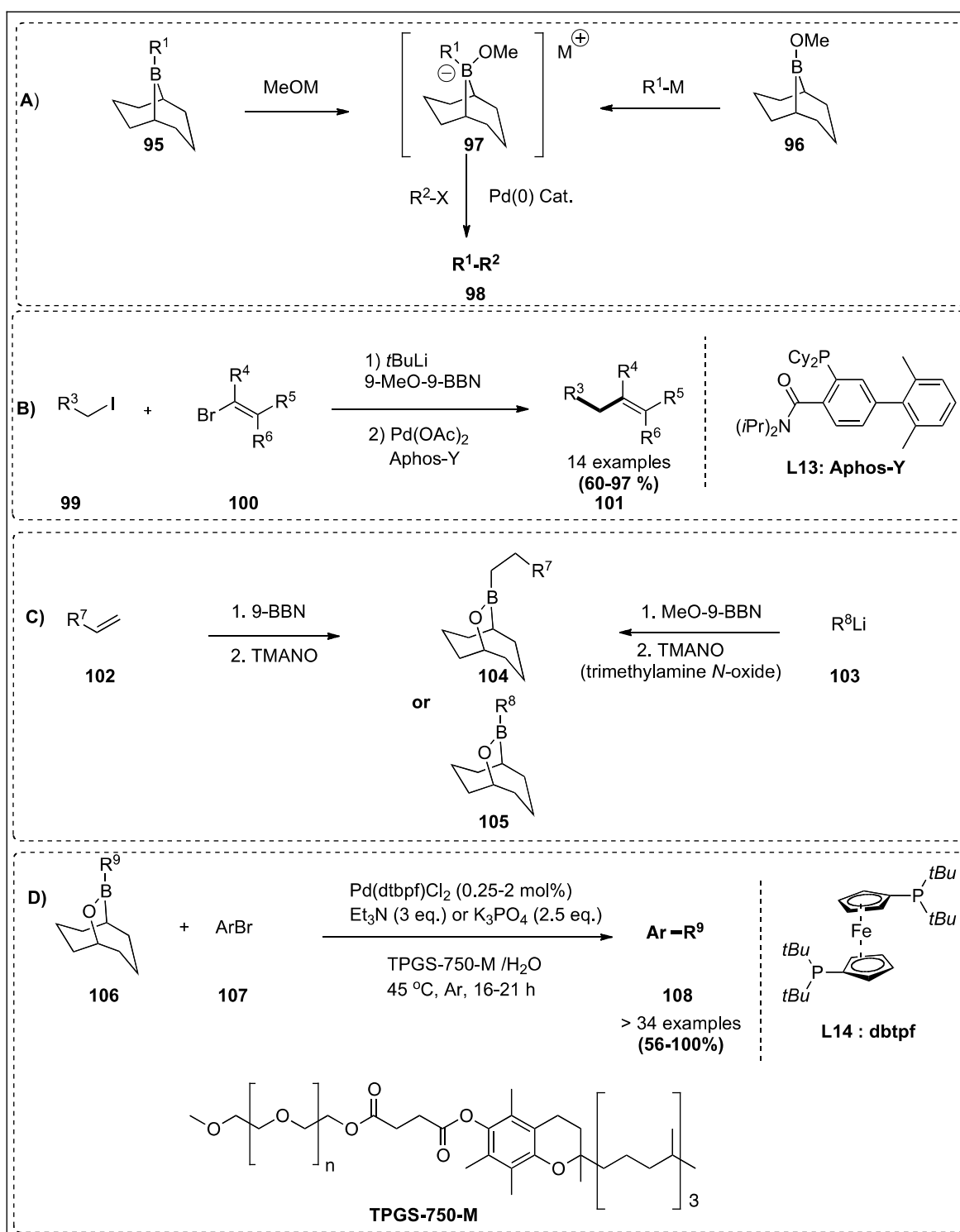
Scheme 14. $\text{sp}^3\text{-sp}^2$ SMCs using N-methyliminodiacetic acid (MIDA) boronates.

8. B-Alkyl SMCs Using BBN Variants (9-MeO-9-BBN and OBBD Derivatives)

The basic set-up of the SMC has essentially stayed similar for decades. However, the ‘9-MeO-9-BBN variant’ is one of the alternative formats for this transformation that has permitted advanced applications of the $\text{sp}^3\text{-sp}^2$ coupling process (Scheme 15A,B). This method is distinguished by the absence of the essential base that acts as a promoter in the classical SMC version. Rather, the R-M (sp^3 , sp^2 , or sp) is first intercepted with 9-MeO-9-BBN, resulting in the corresponding borinate complex **97**, which then passes the R-group onto an organopalladium complex generated *in situ* as the electrophilic partner (Scheme 15A). The 9-MeO-9-BBN variant was reviewed by Seidel and Fürstner in 2011 [125]. In 2013, Dai et al. reported a 9-MeO-9-BBN variant methodology, depicted in Scheme 15B, using $\text{Pd}(\text{OAc})_2$ and a hemilabile P,O-ligand, Aphos-Y **L13** under mild reaction conditions ($\text{K}_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$, THF/H₂O, rt) coupling the alkyl iodide **99** and the alkenyl bromide **100**. This new process serves as an improvement of the Johnson protocol, which generally employs two ligands (dppf and Ph_3As) and two organic solvents (THF and DMF) in the SMC step in the total synthesis of structurally complex natural products, by using one ligand (**L13**, Aphos-Y) and one organic solvent (THF) [126].

OBBD (B-alkyl-9-oxa-10-borabicyclo[3.3.2]decane) derivatives **104/105** represent another variant of 9-BBN (Scheme 15C,D). OBBD reagents **104/105** were used successfully to perform B-Alkyl SMC under mild aqueous micellar catalysis conditions. The straightforward preparation of OBBD **104/105** is shown in Scheme 15C.

OBBD derivatives showed similar reactivity to 9-BBN reagents in SMCs, with the advantage of increased stability and isolable nature. The optimized SMC conditions (Scheme 15D) comprised dtbpf **L14** as the supporting ligand, which allows the reaction to be run at a catalyst loading as low as 0.25 mol% (i.e., 2500 ppm). The optimization was carried out in aqueous surfactant media, with TPGS-750-M as the preferred amphiphile and Et_3N or K_3PO_4 as the base. The substrate scope **108** was shown by more than 34 examples with good to excellent yields (56%–100%). Lower yields were observed with steric hindrance next to the boronate group, and the conditions were limited on secondary OBBD reagents (even upon using 9-BBN derivatives instead). The synthetic utility of this methodology was demonstrated by a four-step one-pot synthesis and a successful recycling of the reaction medium [127].

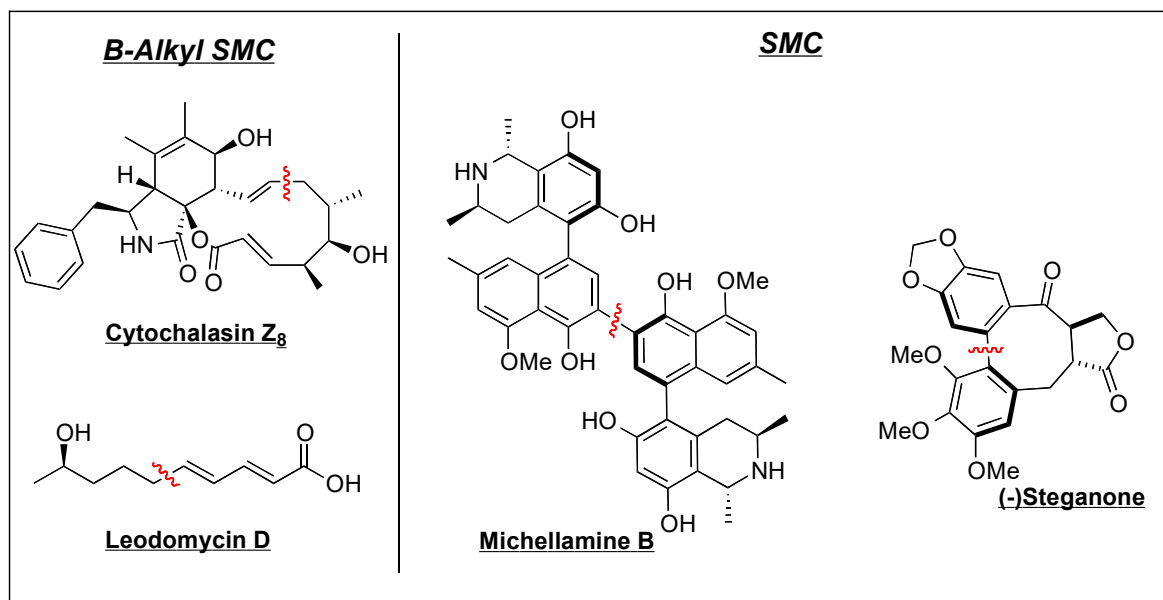


Scheme 15. B-alkyl SMCs using BBN variants (9-MeO-9-BBN (A,B) and OBBD derivatives (C,D)).

9. Selected Examples of Applications of SMCs and B-alkyl SMC in the Synthesis of Target Molecules

It is rare nowadays to find a total synthesis that does not involve at least a cross-coupling reaction, and in particular, a Suzuki–Miyaura reagent [6]. The use of SMC in total synthesis has been extensively reviewed by Heravi et al. [128,129].

B-alkyl SMC, in particular, was likewise applied in the synthesis of beneficial products [130–132]. Two examples are shown in Scheme 16: **Cytochalasin Z₈** and **Ieodomycin D**, which belong to the family of secondary fungal metabolite with a wide range of biological activities that target cytoskeletal processes [133–135]. Scheme 16 also includes examples of complex molecules that were achieved by synthetic routes involving SMCs with C(sp²)-B reagents; namely **Michellamine** (an anti-HIV viral replication receptor) and **(-)-steganone** (an antileukemic lignan precursor) [136,137].



Scheme 16. Examples of drugs and active molecules whose total synthesis involved SMC.

10. Conclusion

The present review focused on the use of C(sp³)-organoboranes as cross-coupling partners in metal-catalyzed C(sp³)-C(sp²) cross-couplings, such as B-alkyl Suzuki-Miyaura reactions. Indeed, metal-catalyzed cross-coupling reactions have become mature tools in organic synthesis. Nevertheless, C(sp³)-C cross-couplings are far less reported than other C-C coupling reactions. Furthermore, this field is largely dominated by using organic halides or pseudohalides as coupling partners. C-O-Alkyl electrophiles remain an area of research that is attracting strong attention. Undoubtedly, the progress made in the syntheses of stable and isolable sp³-boron reagents is impacting the development of C(sp³)-C(sp²) cross-couplings of the Suzuki-Miyaura type. The attention given to dual and photocatalysis is also strongly contributing to the furnishing of a toolbox that can achieve active adducts, which impact all fields of research and industry and cannot be otherwise obtained.

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