Photoinduced Deborylative C-C Bond Formation

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Abstract

In the last decade, photoredox catalysis serves as a most exciting topic in organic chemistry, because photoredox catalysts can provide unique and environmentally friendly processes of organic synthesis. Visible light sources are readily available, eco-friendly, highly abundant, and as well as sustainable. Mild reaction conditions are used for the construction of diverse C-C bonds. On the other hand, the organoboron compounds are stable, commercially available and well-suited precursors for the photocatalytic transformations. In the last decade, photoredox catalysis with organoboron compounds has unlocked unprecedented reactivities in synthetic organic chemistry. This mini-review documented several smooth and efficient methodologies for the development of C-C bonds *via* deborylation in the presence of visible light.

Keywords: photoredox, boronic acid, radical, 1,4-addition, photocatalyst.

1. Introduction

Organoboron chemistry has been extensively used in organic synthesis due to its easy commercial availability, bench stability, and non-toxicity.[1] Boronic acid and its derivatives are important synthons for bioactive compounds, light-harvesting materials, and more.[2] Many of them are commercially available, and a handful of procedures have been reported that allow the synthesis of the non-commercial ones. The reactivity of the organoboron compounds originated from the presence of a vacant orbital in the boron atom. A nucleophile can attack the empty 'p' orbital of the boron center for the formation of the boronate complex, which makes the C-B bond weaker. In the presence of a suitable photosensitizer, the C-B bong got cleaved to generate free radicals, which participate in diverse synthetic transformations.[3]

Photoredox catalysis has been in the spotlight of synthetic organic chemistry due to its diverse application in accessing a large number of C-C and C-heteroatom bonds under mild and sustainable reaction conditions.[4] A plethora of methods has been developed for the generation of radicals *via* the cleavage of C-X, C-H, C-O, C-N, and other bonds.[5] Also, there have been a large number of inorganic and organic-based photosensitizers evolved for a variety of synthetic transformations.[6] Due to the low bond energy of C-B bonds, there have been a large number of deborylative transformations developed under photoredox catalysis which goes *via a* radical mechanism. The stability of organoboron compounds depends on the groups attached to the trivalent boron compounds.[7] Other than a few exceptions the boronic

acid, esters, and their triflouroboroate salts are bench stable.[8] Various methods have been reported for activation of the C-B bond to generate radical species from corresponding boronic acids, esters, and the triflouroborate salts.[9] Previous review article in this area does not cover this important topic. This review will summarize their development in a chronological manner.
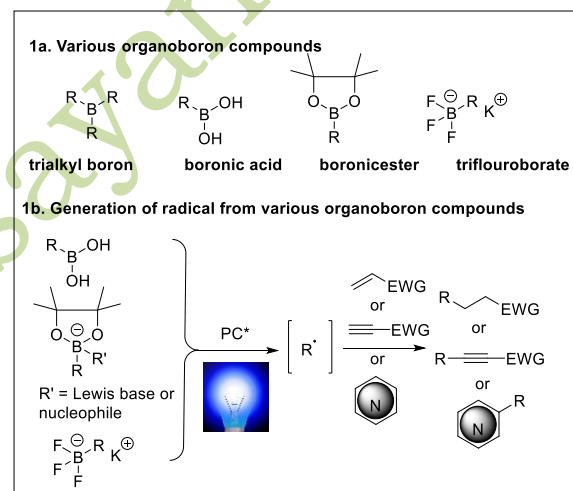
2. Deboranative C-C bond formation *via* radical generation from boronic acid:

Deborylative C-C bond formation is always a demanding protocol due to its versatility in organic synthesis. But in some cases, the harsh reaction condition was found to be disadvantageous; lowering the functional group compatibility and enantioselectivity. On the other side, photocatalysis is a greener approach to conduct those reactions. Hence, the implementation of the photo-catalysis to deborylative transformations further widens the adaptability of these protocols. On the other hand, the generation of carbon-centered radicals is more facile under the photocatalytic condition. Organoboron species are important radical precursors due to their less toxicity, stability, easy availability, and versatile functional group tolerance.[10]

It is well known that the Minisci reaction is a breakthrough achievement in the organic synthesis for the successive alkylation of heteroarene. Previously, the
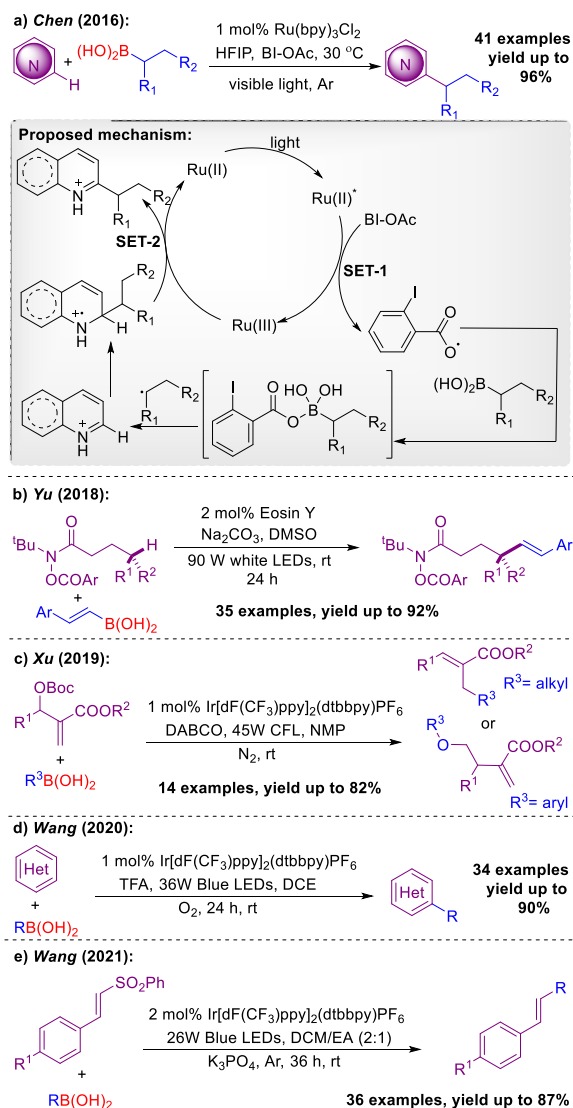
Scheme 2: Deboranative C-C bond formation using boronic acid

DiRocco group and MacMillan group reported the photoredox driven C-H alkylation of N-containing heteroarenes using peroxides and phenol as an alkylating precursor respectively.[11] Later on, the Chen group modified this approach by the involvement of alkyl boronic acids as an alkylating reagent (Scheme 2a).[12] It has a remarkable application for the functionalization of natural products like-quinine, camptothecin, caffeine, etc. The author already pointed out that the BI-OAc oxidant could be effectively initiated a radical cycle in presence of Ru(bpy)$_3$Cl$_2$ catalyst in HFIP solvent. The proposed mechanistic approach begins through a SET process between excited Ru(II)* species and oxidant to give a benziodoxole radical which reacts with alkyl boronic acids to form an alkyl radical. The free-radical adds to the N-containing heteroarene to form α-complex. Then the Ru(III) species oxidizes the α-complex to afford the desired alkylated products. The C-C bond formation in the amide
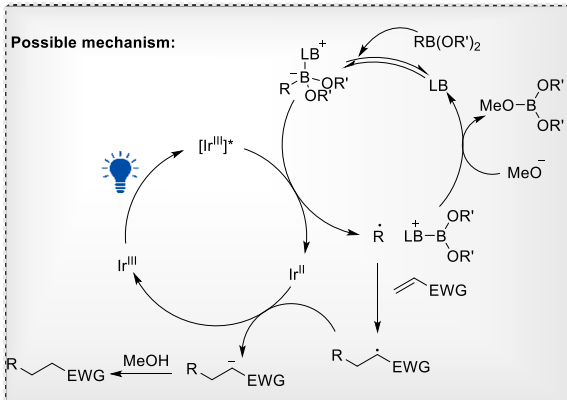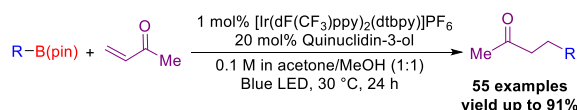
system was explored by the Yu group in the year 2018 (Scheme 2b).[13] Selective vinylation of the γ- C(Sp^3)-H of the hydroxamic acid derivatives could be achieved successfully using 2 mol% eosin Y (an organic photoredox catalyst) in presence of 90 W blue LEDs. The excited state of the photocatalyst reduced the hydroxamic acid derivative through a single electron transfer process into an amidyl radical and carboxylate anion. The generating amidyl radical forms a 1°/2°/3° radical *via* 1,5 H transfer and successively adds to the alkenyl boronic acid derivatives to form a new C-centred radical. Later the newly formed radical upon oxidation affords the cationic species and subsequent deboronation provides the desired C(Sp^3)-C(Sp^2) coupled product. The use of Na$_2$CO$_3$ as a base in DMSO solvent was found to be suitable in this reaction. After that, in 2019, the Xu group prepared a variety of α,β-unsaturated compounds using Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ as a photocatalyst (Scheme 2c).[14] Later on, in 2020, a Minisci-type C-H alkylation was documented by the Wang group under blue LEDs irradiation using 1°/2° alkyl boronic acids as a radical precursor (Scheme 2d).[15] Here, the O$_2$ acts as an oxidant to activate the organoboronic acid to form a nucleophilic radical species, which coordinates with the protonated electron-deficient N-heteroaryl species to afford the desired alkylated product. Further, the same group explored the alkenylation reaction using the substituted *trans*-phenyl vinylsulfone system. A variety of cyclic and acyclic boronic acid derivates were well tolerated under the optimum reaction condition affording the desired product with a moderate *E/Z* selectivity (Scheme 2e).[16]

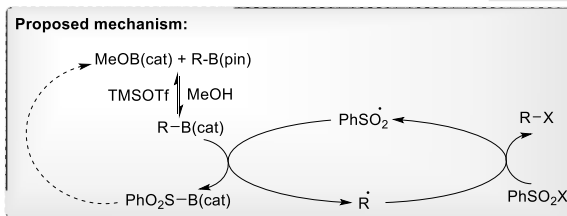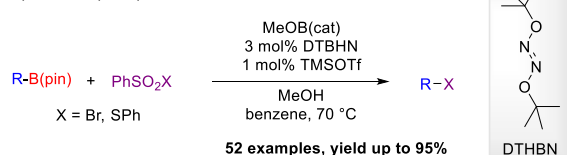## 3. Deboranative C-C bond formation *via* radical generation from boronic ester:

Pinacol boronic esters do not form radicals directly. They form radicals either *via* the formation of Lewis acid-base adduct or boronate complex or transesterification. Ley group showed that in the presence of a Lewis base and [Ir(dF(CF$_3$)ppy)$_2$(dtbpy)]PF$_6$ as a photoredox catalyst under blue light irradiation, the pinacol boronic esters could generate radicals (Scheme 3a).[17] Here, first the Lewis base, Quinuclidin-3-ol forms an adduct with the pinacol boronic ester that further undergoes a single electron transfer in presence of excited [Ir^{III}]* and generates the radical. The radical further reacts with electron-deficient alkene and forms a new radical intermediate. Now, the reduction of the radical intermediate by Ir^{II} followed by protonolysis by methanol, forms the final desired product and regenerates the photocatalyst. This protocol also works well with other Lewis bases like DMAP, PPh$_3$. However, this group has also shown that pyridine-like Lewis base can also activate the boronic esters and reported dual iridium- and nickel-catalyzed C(Sp^2)–C(Sp^3) coupling using boronic esters and cyano heteroarenes under flow conditions.[18]

Recently, the Renaud group reported the *in situ* generations of alkylboronic catechol esters by boron-transesterification with a substoichiometric amount of catechol methyl borate (MeO-Bcat) that telescoped onto a
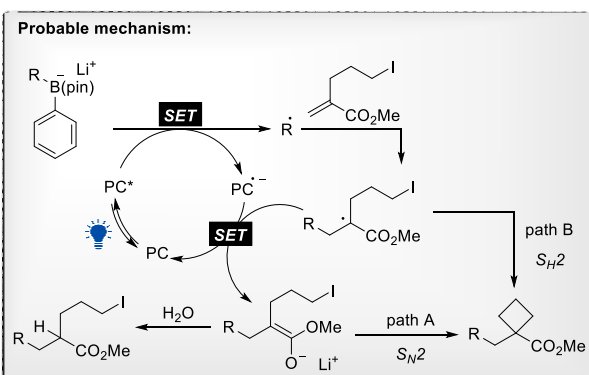
a) *Ley* **(2017):**

R−B(pin) + [acryl ketone] →

1 mol% [Ir(dF(CF$_3$)ppy)$_2$(dtbpy)]PF$_6$
20 mol% Quinuclidin-3-ol
0.1 M in acetone/MeOH (1:1)
Blue LED, 30 °C, 24 h

→ Me—C(=O)—CH$_2$CH$_2$—R

55 examples yield up to 91%

Possible mechanism:

RB(OR')$_2$ LB
[Ir^{III}]*   MeO−B(OR')   OR'
MeO$^-$
Ir^{III} Ir^{II}
R· + LB−B(OR')$_2$$^+$
EWG
R—CH$_2$CH$_2$—EWG ← (MeOH) ← R—CH$_2$—EWG$^-$ ← R—CH$_2$—EWG·

b) *Renaud* **(2020):**

R-B(pin) + PhSO$_2$X
X = Br, SPh

MeOB(cat)
3 mol% DTBHN
1 mol% TMSOTf
─────────────
MeOH
benzene, 70 °C

→ R−X

52 examples, yield up to 95%

DTHBN

Proposed mechanism:

MeOB(cat) + R-B(pin)
TMSOTf ⇵ MeOH
R−B(cat)
PhSO$_2$·   R−X
PhO$_2$S−B(cat)   R·   PhSO$_2$X

Scheme 3: Deboranative C-C bond formation using boronic ester

a) *Aggarwal* **(2019):**

R^2,R^1,R^3—B(pin) + [iodo ester]

PhLi, THF, 1 h
0 °C to rt
then
5 mol% 4CzIPN
blue LEDs, rt
DMSO, 20 h

→ R^2,R^1,R^3—(cyclobutane)—CO$_2$Me

39 examples yield up to 90%

Probable mechanism:

R—B(pin)—Li$^+$ (Ph)
SET
R·   CO$_2$Me
PC*   PC·$^-$
SET
R—CH$_2$CH$_2$—·CO$_2$Me (with I)
path B S$_H$2
PC
R—CH$_2$—H—CO$_2$Me ← H$_2$O ← R—C(OMe)=... O$^-$ Li$^+$
path A S$_N$2 → R—(cyclobutane)—CO$_2$Me

b) *Aggarwal* **(2019):**

R^1—Bpin, R^2,R^3—Bpin + [alkene]—R^4

ArLi, THF
then
5 mol% 4CzIPN
blue LEDs, 35 °C
^{t}BuOH, MeCN, 16 h

→ R^1—Bpin, R^2,R^3—CH$_2$CH$_2$—R^4

25 examples yield up to 98%

Possible mechanism:

R—B(pin)$_2$ ArLi   [Ar—Li$^+$ / R—B(pin)$_2$]
R—·—B(pin) ⇌ R—B(pin)—·
PC*   PC·$^-$
R—CH(B(pin))—CH$_2$—EWG·
PC
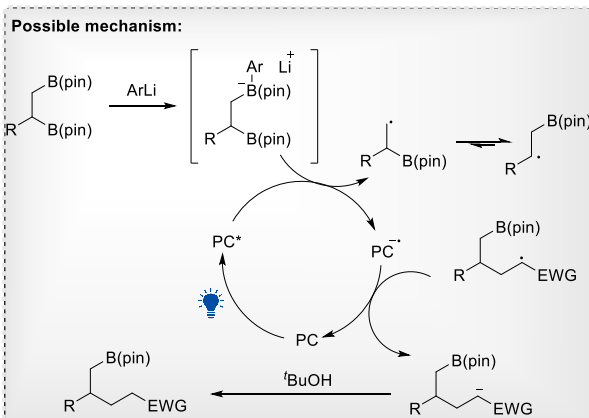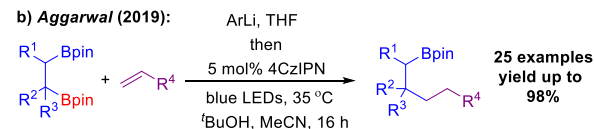R—CH(B(pin))—CH$_2$CH$_2$—EWG ← ^{t}BuOH ← R—CH(B(pin))—CH$_2$CH$_2$—EWG$^-$

Scheme 4: Deboranative C-C bond formation using boronic ester

wide array of radical chain processes (Scheme 3b).[19] Here, the *in situ* generated catechol boronic ester generates the radical in the presence of a radical initiator di-*tert*-butylhyponitrile that further reacts with various electrophiles like iodides, bromides, chlorides, and thioethers to yield the desired product.

On the other hand, the Aggarwal group showed that pinacol boronic esters could generate radicals *via* boronate complex formation. They reported the formation of boronate complex by phenyl lithium, which generates radicals in the presence of organic photocatalyst, like 4CzIPN under blue light irradiation (Scheme 4a).[20] In the presence of blue light, the photocatalyst (PC) gets excited and generates PC*, which undergoes a single electron transfer and generates the alkyl radical. Now, these radical intermediates form the anionic intermediate through a second SET, which undergoes a S$_N$2 reaction to give the desired product. However, they also proposed that the radical intermediate can undergo nucleohomolytic substitution (S$_H$2) to generate the desired cyclobutane product. Later on, the same group showed the versatility of the boryl migration strategy for diverse C-C bond-forming reactions. Photocatalytic 1,2-boron shift of the β-boryl radical from 1,2-bis-boronic esters enables access to a wide array of functionalized boronic esters along

with highly diastereoselective fragmentation and transannular cyclization reactions (Scheme 4b).[21] Mechanistically, single electron transfer between the primary boronate complex and the excited state photocatalyst gives rise to a primary alkyl radical along with the loss of arylboronic ester. Subsequent 1,2-boryl migration provides a thermodynamically favored secondary radical, which reacts with an electron-deficient alkene. Single electron reduction of the alkyl radical intermediate by the reduced state photocatalyst followed by a protonation furnishes the corresponding product.

4. Deboronative C-C bond formation *via* radical generation from trifluroborate:

4.a. Radical addition to C(Sp^2), C(Sp) centers

Later on, in 2017, the Xu group introduced the C-H functionalization of the pyridine-N-oxides (Scheme 5a).[22] The author explained the C-2 alkylation route simply by

incorporating the potassium alkyltrifluoroborate and pyridine N-oxide as a model precursor. The use of 2 mol% $Ru(bpy)_3(PF_6)_2$ catalyst with BI-OAc as an oxidant under blue LEDs irradiation was proved as a fruitful catalytic condition to furnish the desired product. Arene ring substituted with Ether, amide, CF_3, fluoro, chloro, etc is well tolerated under the reaction conditions. Similarly, triflouroborates carrying sensitive functional groups were well accommodated.

Later on, in 2017, the Molander group extended the versatility and the scope of the reaction in the C-H functionalization of the heteroarenes (Scheme 5b).[23] The mesityl acridinium photocatalysts are suitable to develop the alkyl radical from the corresponding alkyl-trifluoroborates. The alkyl radical reacts with the protonated heteroarene to furnish the cationic radical intermediate. Abstraction of H-atom by sulfate-radical anion of the intermediate affords the alkylation of heteroarene *via* rearomatization. Here 5 mol% MesAcr photocatalyst, $K_2S_2O_8$ oxidant in MeCN/H_2O mixed solvent at 23 ^{o}C using 26 W CFL as a light source were identified as an optimal condition. Further, in the same year, the Molander group documented the arylation of heteroarene using 2-trifluoroborato-4-chromanones as a potent reaction partner in the presence of MesAcr photocatalyst (Scheme 5c).[24]
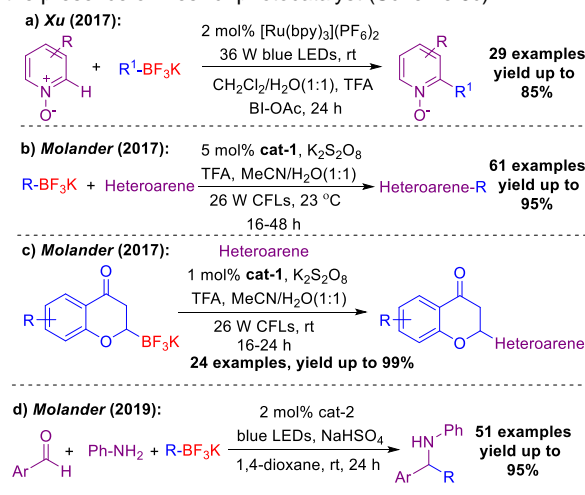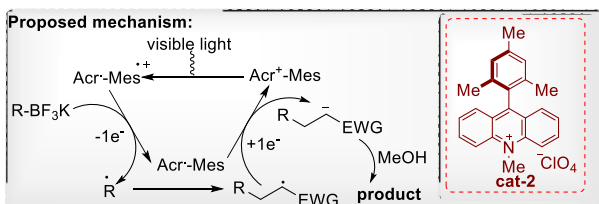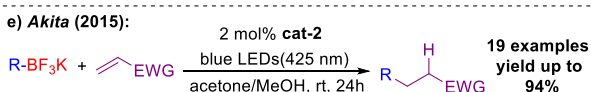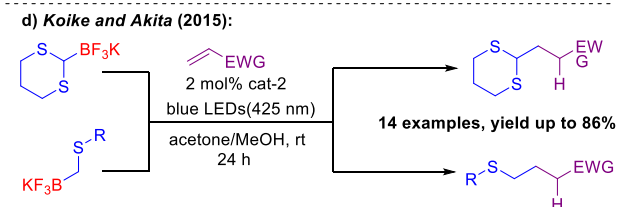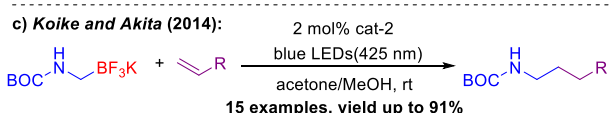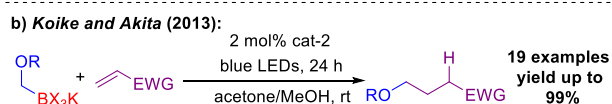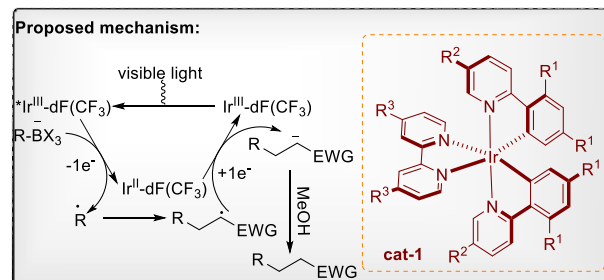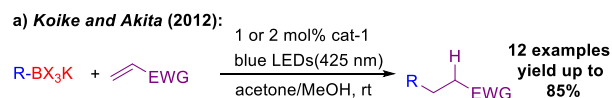

Scheme 5: Deborylative 1,2-addition

Further, in 2019, the author described the multicomponent Petasis reaction involving aldehydes, potassium alkyltrifluoroborates, and aniline as novel reaction partners using 2 mol% [Ir{dF(CF$_3$)ppy}$_2$(bpy)]PF$_6$ (Scheme 5d).[25] A diverse variety of substituted anilines, aldehydes, and potassium alkyltrifluoroborate reacted well to provide the desired products in excellent yields.

Photocatalysts are easily available, highly abundant, and sustainable. Oxidative transformation using photocatalysis under visible light irradiation is highly desirable. The Koike and Akita group explored various unique approaches that led to the oxidation of different organoboron compounds using photoredox catalysis under visible light irradiation. In 2012, the author established a new strategy to oxidize the alkyl/aryl/benzyl trifluoroborates using
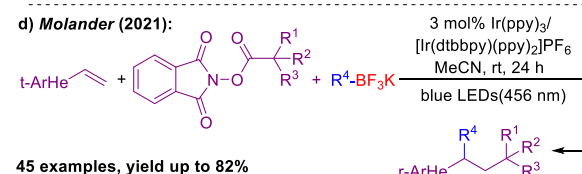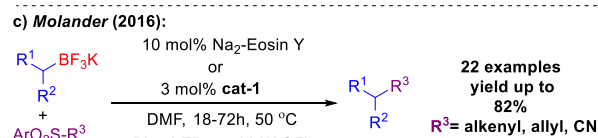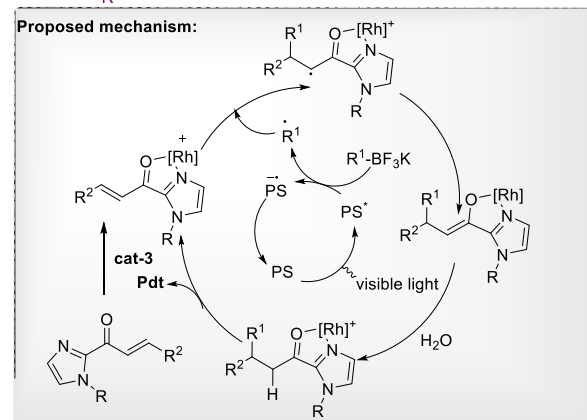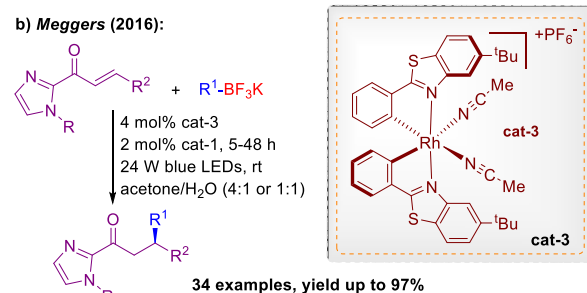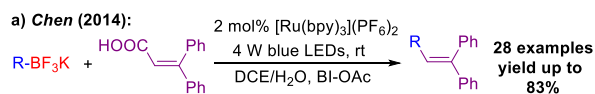
1 mol% Ir-dF(CF$_3$) upon irradiation by blue LEDs in acetone/MeOH solvent (Scheme 6a).[26] The author developed a visible-light-induced single electron transfer process to generate the alkyl/aryl/benzyl radicals from organoborates. At first, excitation of the initial photocatalyst was carried by irradiation of visible light. Then, single electron transfer from alkyl/aryl/benzyl trifluroborates formed radical species and the catalyst itself was reduced. Subsequently, the radicals add to the olefin-containing electron-withdrawing group resulting in C-C bond formation between them with good to excellent yields. Further, in 2013 the author came up with a new idea choosing alkoxymethyltrifluroborates as a reaction precursor (Scheme 6b).[27] The author explained the hydroalkoxy methylation of electron-deficient olefins under the same reaction condition using the same mechanistic approach. After that, the authors expanded their thoughts towards the hydroaminomethylation of electron-deficient alkenes *via* deborylation involving the boc-protected aminomethyltrifluoroborates in the presence of 2 or 5 mol% Ir-photocatalyst (Scheme 6c).[28] The mixed acetone/EtOH solvent was found to be best for this reaction under irradiation by blue LEDs. Bulky substituted on olefin moieties and enamides, aromatic alkenes participated in the reaction smoothly, but styrene exhibited low yields of desired coupled product. The authors adopted the same visible-light-driven SET process to illustrate the mechanistic pathway of the hydroaminomethylation reaction.

After that in 2015, the author documented the oxidation of alkyl/aryl-thioalkyltrifluoroborates using the Ir-photocatalyst under visible light irradiation *via* deboronation (Scheme 6d).[29] The author applied the visible-light-induced SET process to develop the α-thioalkyl radical which reacts with electron-deficient alkenes resulting in an alkyl/aryl-thioalkylated product. This method is useful to access the diverse variety of alkyl sulphide derivatives. However, the development of a transition metal-free condition makes this approaches unique, versatile, and inexpensive. The use of an organic photoredox catalyst is a beneficial addition in terms of eco-friendly and green chemistry. In the year 2015, the Akita group introduced 9-mesityl-10-methylacridinium perchlorate as an organic photoredox catalyst for the first time (Scheme 6e).[30] The photoresponsive excited state of the catalyst pursues a role of an oxidant and facilitates oxidative transformation. The author was enlightened on the organic radical generation pathway from potassium alkyltrifluoroborate using the 9-mesityl-10-methylacridinium perchlorate photocatalyst in acetone/water solvent at room temperature under blue LEDs irradiation. Here the electron-withdrawing group substituted alkene used as a potent coupling partner to obtain the C-C coupled product. From the mechanism; it is revealed that an organic catalyst under photo-irradiation converts into an electron transfer state which drives the generation of carbon-centered radicals from organoborates *via* oxidative transformation. The resulting alkyl radical reacts with olefin moieties to generate a new radical intermediate which takes part in reduction to provide a carbanion intermediate and lastly upon protonation by solvent affords the desired products.

a) *Koike and Akita* (2012):

R-BX$_3$K + =EWG → (1 or 2 mol% cat-1, blue LEDs(425 nm), acetone/MeOH, rt) → R—EWG (H) — **12 examples yield up to 85%**

Proposed mechanism:

visible light

*Ir^{III}-dF(CF$_3$) ← Ir^{III}-dF(CF$_3$)
R-BX$_3^-$
-1e$^-$
Ir^{II}-dF(CF$_3$) → +1e$^-$
R• → R—EWG → R—EWG (MeOH) → R—EWG

cat-1

b) *Koike and Akita* (2013):

OR—BX$_3$K + =EWG → (2 mol% cat-2, blue LEDs, 24 h, acetone/MeOH, rt) → RO—EWG (H) — **19 examples yield up to 99%**

c) *Koike and Akita* (2014):

BOC—NH—BF$_3$K + =R → (2 mol% cat-2, blue LEDs(425 nm), acetone/MeOH, rt) → BOC—NH—R — **15 examples, yield up to 91%**

d) *Koike and Akita* (2015):

(dithiane)-BF$_3$K, =EWG (2 mol% cat-2, blue LEDs(425 nm), acetone/MeOH, rt, 24 h) → (dithiane)—EWG (H) ; R-S—KF$_3$B → R-S—EWG (H) — **14 examples, yield up to 86%**

e) *Akita* (2015):

R-BF$_3$K + =EWG → (2 mol% **cat-2**, blue LEDs(425 nm), acetone/MeOH, rt, 24h) → R—EWG (H) — **19 examples yield up to 94%**

Proposed mechanism:

visible light

Acr•-Mes ← Acr$^+$-Mes
R-BF$_3$K
-1e$^-$
Acr•-Mes → +1e$^-$
R• → R—EWG → R—EWG (MeOH) → **product**

cat-2

Scheme 6: Deborylative 1,4-addition

a) *Chen* (2014):

R-BF$_3$K + HOOC—(Ph)(Ph) → (2 mol% [Ru(bpy)$_3$](PF$_6$)$_2$, 4 W blue LEDs, rt, DCE/H$_2$O, BI-OAc) → R—(Ph)(Ph) — **28 examples yield up to 83%**

b) *Meggers* (2016):

(N-imidazole acyl alkene)-R^2 + R^1-BF$_3$K → (4 mol% cat-3, 2 mol% cat-1, 5-48 h, 24 W blue LEDs, rt, acetone/H$_2$O (4:1 or 1:1)) → product with R^1, R^2

cat-3 (+PF$_6^-$), ^{t}Bu

34 examples, yield up to 97%

Proposed mechanism:

cat-3 Pdt
visible light
H$_2$O
PS, PS*, PS$^-$
R^1-BF$_3$K

c) *Molander* (2016):

R^1(R^2)—BF$_3$K + ArO$_2$S-R^3 → (10 mol% Na$_2$-Eosin Y or 3 mol% cat-1, DMF, 18-72h, 50 °C, Blue LEDs or 26 W CFLs) → R^1(R^2)—R^3 — **22 examples yield up to 82%, R^3= alkenyl, allyl, CN**

d) *Molander* (2021):

t-ArHe= + (phthalimide-O—C(=O)—C(R^1)(R^2)(R^3)) + R^4-BF$_3$K → (3 mol% Ir(ppy)$_3$/ [Ir(dtbbpy)(ppy)$_2$]PF$_6$, MeCN, rt, 24 h, blue LEDs(456 nm)) → r-ArHe—R^4(R^1)(R^2)(R^3)

45 examples, yield up to 82%

**Scheme 7: Deborylative 1,4-addition**

In the same year, the Chen group got involved designing a synthetic methodology using potassium alkyltrifluoroborate using Ru(bpy)$_3$(PF$_6$)$_2$ catalyst in DCE/H$_2$O solvent under blue LEDs irradiation (scheme 7a).[31] Here BI-OH played the role of oxidant. Further applying organotrifluoroborates as a radical precursor for the addition of alkyl radicals to the α,β-unsaturated acyl imidazole was demonstrated by the Meggers group (Scheme 7b).[32] Here, both chiral Lewis acid catalyst and photocatalyst were employed to achieve the 1,4-addition product with high enantioselectivity.

α,β-unsaturated *N*-acyl pyrazole substrates worked well under the optimum conditions. The mechanistic study reveals that the Rh center effectively coordinates with the *N*-atom of imidazole and the O atom of the acyl group generating the product with high enantioselectivity. After that, in 2016, the Molander group reported a synthetic route to allylic amine and alkyl nitrile derivatives using 10 mol% Na$_2$-Eosin Y dye or 3 mol% mesityl acridinium as an organic photocatalyst respectively (Scheme 7c).[33] A wide variety of potassium alkyltrifluoroborates underwent coupling reaction with the substituted alkenyl and allylic sulfones, tosyl cyanides in DMF solvent under blue LEDs irradiation. The mechanistic studies disclosed that the reaction follows a radical addition-elimination route to afford the C-C coupled products with satisfactory yields. Next, the author invented a pioneering approach following the photochemical radical/polar crossover pathway (Scheme 7d).[34] Here, alkyl N-(acyloxy) phthalimide esters and organotrifuloroborates were identified as an

appropriate reaction partners under the optimum reaction condition. 3 mol% Ir(ppy)$_3$ or [Ir(dtbbpy)(ppy)$_2$]PF$_6$ in MeCN solvent at room temperature for 24 h under blue LEDs irradiation were signified as an effective optimal condition to obtain the 1,2-dicarbofunctionalizations of olefin moieties with good to excellent yields.
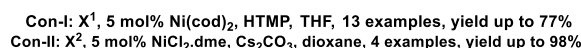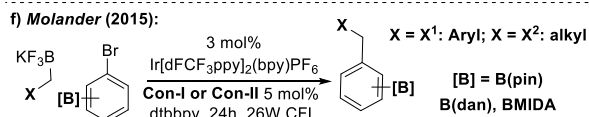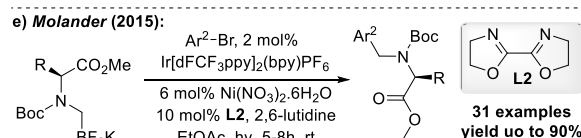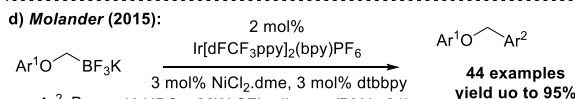

a) *Koike and Akita* (2013):

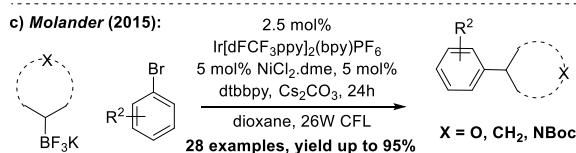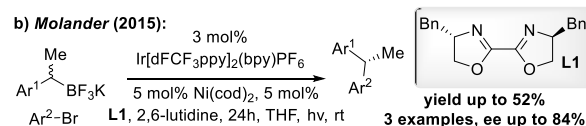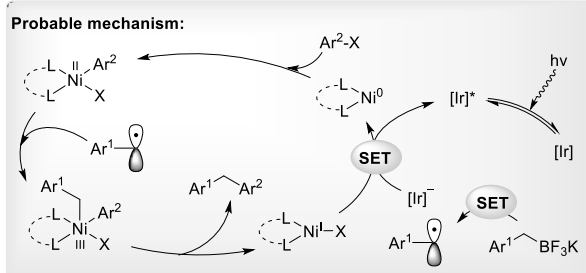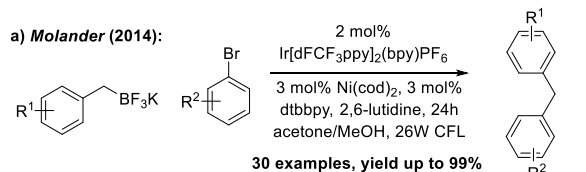**b) *Chen* (2014):**

Proposed mechanism:
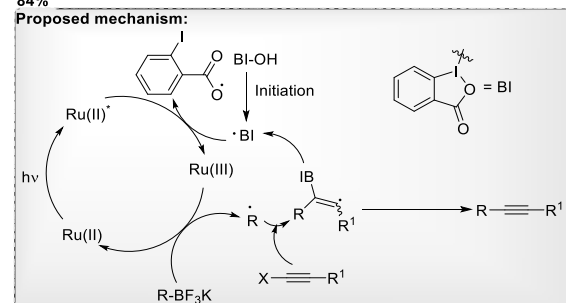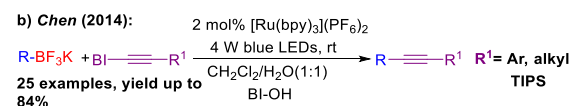
Scheme 8: other transformation of radical generation from trifluoroborate

Next, the Koike and Akita group invented a new method to form the C(Sp^2)-C(Sp^3) bond by employing vinyltrifluoroborates as a starting material for the reaction (Scheme 8a).[36] The use of 5 mol% [Ru(bpy)$_3$](PF$_6$)$_2$ photoredox catalyst with Togni's reagent in methanol under irradiation of the blue LEDs afforded the desired trifluoromethyl substituted alkene derivatives with excellent *E/Z* selectivity and satisfying yields. Methoxy, bromo, carbamoyl, fluoro, and carbonitrile substituted *E*-styrylborates and heteroaryl substituted vinyl borates furnished the desired products under this optimum condition. Further in 2014, the Chen group implemented a novel strategy to form the C(Sp^3)-C(Sp) bond by introducing 1°,2°, and 3° potassium alkyltrifluoroborate and boronic acids as a reaction precursor. The author used 2 mol% Ru(bpy)$_3$(PF$_6$)$_2$ with BI-OH as a photoredox catalyst and blue LEDs as a visible light source (Scheme 8b).[37] Based on mechanistic studies we find out that initially the catalyst is excited and undergoes oxidation by benziodoxole radical; then Ru(III) catalytic intermediate oxidizes the potassium trifluoroborate to generate the alkyl radical. Next, the alkyl radical does α-addition to BI-alkyne and generates the desired alkyl, aryl and silyl substituted alkyne with excellent yields. Lastly, the benziodoxole radical itself converts into *ortho*-iodobenzoic acid and oxidizes the excited Ru^{2+} species.

4.b. Dual catalyst based cross-coupling

Deborylative cross-coupling is always a demanding protocol due to its versatility in the organic synthesis field. But in some cases, the harsh reaction condition was found to be disadvantageous lowering the functional group compatibility and enantioselectivity. On the other side photocatalysis is a greener approach for supplying the activation energy to catalyze the reaction. Hence, the implementation of the

a) *Molander* (2014):

30 examples, yield up to 99%

Probable mechanism:

b) *Molander* (2015):

yield up to 52%
3 examples, ee up to 84%

c) *Molander* (2015):

X = O, CH$_2$, NBoc

28 examples, yield up to 95%

d) *Molander* (2015):

44 examples yield uo to 95%

e) *Molander* (2015):

31 examples yield uo to 90%

f) *Molander* (2015):

X = X^1: Aryl; X = X^2: alkyl

[B] = B(pin) B(dan), BMIDA

Con-I: X^1, 5 mol% Ni(cod)$_2$, HTMP, THF, 13 examples, yield up to 77%
Con-II: X^2, 5 mol% NiCl$_2$.dme, Cs$_2$CO$_3$, dioxane, 4 examples, yield up to 98%

Scheme 9: Dual catalyst based cross-coupling

photo-catalytic deborylative transformation widens the scope.[38]

Based on this concept the Molander group developed a pioneer work in this arena. The author engaged a dual catalyst approach for the organoboron-mediated cross-coupling encompassing a single electron *trans*-metalation mode (Scheme 9a).[39] A variety of nickel salts was engaged as the center metal for the cross-coupling catalytic cycle whereas the Ir-based catalyst was for maintaining the

photocatalytic cycle under visible light irradiation. Here both the catalytic cycle are cooperative in nature. Next, the author engage secondary trifluoroborates as the coupling partner. Here the use of chiral Ni-catalyst leads to the chiral product formation (Scheme 9b). A detailed DFT study[40] indicates that the nickel comprises the 0, I, II and III oxidation state in the course of the reaction and maintain the oxidative addition and reductive elimination steps. Here first the Ir-photocat absorb the photon from the visible light and promoted to its excited state which captures one C-B bond electron from the organoborate salt resulting the heterolytic cleavage of C-B bond and generating the alkyl radical. In the other catalytic cycle the Ni^0 species 1st undergoes the oxidative addition followed by a reversible addition to the alkyl radical which in situ generate the Ni^{III} species. Next the Ni^{III} species takes part in reductive elimination resulting in the desired product and the Ni^I species. Now, the Ni^I species get converted to the Ni^0 by taking one electron from the reduced Ir-specie maintaining the catalytic cycle.

Further, a series of 2° cyclic as well as acyclic potassium trifluroborates (Scheme 9c)[41] were coupled with various arylic/heterolycic bromides resulting in the desired product in good to excellent yield. However, various α-alkoxy (Scheme 9d)[42] and α-amino[43] (Scheme 9e) methyltrifluoroborates can also be coupled with heteroaryl and aryl bromides under the optimized reaction condition. Further, the author demonstrated, the reactivity difference among the boron moieties based on the connectivity. It has been found that when the trifluoroborate salt is directly connected to the $C(Sp^2)$ carbon that found to be unreactive while the aryl bromide takes part in the reaction *via* the dehalogenetive pathway (Scheme 9f).[44] Hence various aryl bromides having $B(OH)_2$, B(dan), BMIDA moieties take part in the reaction without any interruption. However, to simplify the purification all the product was oxidized and isolated in the corresponding alcohol form. Further, the trifluromethyl group was incorporated by using this cross-coupling method using suitable α-trifluromethyl-trifluroborate salt (Scheme 10a).[45] Under the optimized reaction condition the α-trifluromethyl-trifluroborate underwent smooth deborylative cross coupling resulting in the desired product. Of note, while the α-alkoxy methyltrifluoroborates were reacted with various acyl chlorides, it underwent smooth dehalogenetive carbonylation under the optimization condition (Scheme 10b).[46] Here the acyl chloride takes part in the oxidative addition with the nickel intermediate following the general pathway.

This chemistry was further extended to β-trifluoroboratoamides, ester, ketones, which were successfully coupled with the aryl halides[47] (Scheme 10c). Recently the author also extended this approach with tertiary potassium alkyltrifluoroborate (Scheme 10d).[48] A combination of a catalytic amount of $ZnBr_2$ and bulkier tetramethylheptanedione ligand combination were required for efficient conversation. Further with the continuation of the Molandar approach with the nickel-based dual catalyst mediated transformation, another cyclic meso-anhydrides desymmetrization protocol was developed by the Doyle group (Scheme 10e).[49] Surprisingly, not only the Ir-based photocatalysts, but various organphotocatalysts can also catalyze the reaction. Here 2 mol% 4CzIPN was found to be

optimal for the heterolytic C-B bond cleavage. Further, a
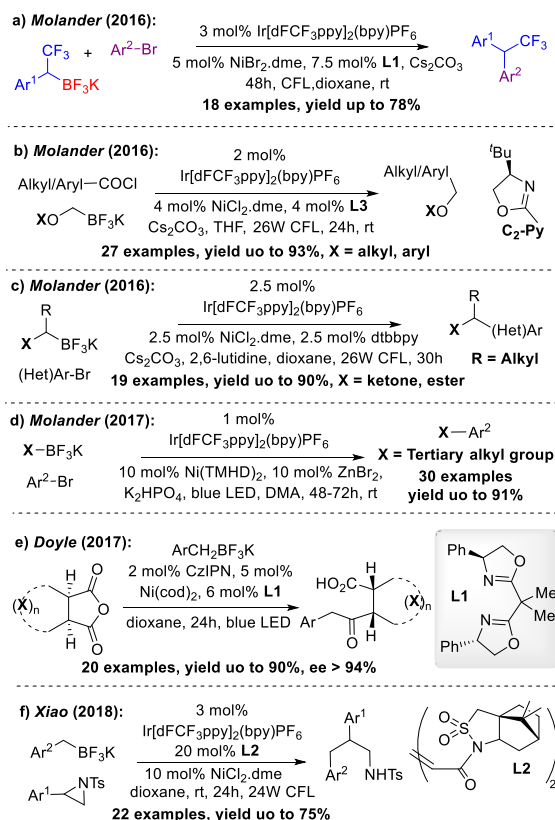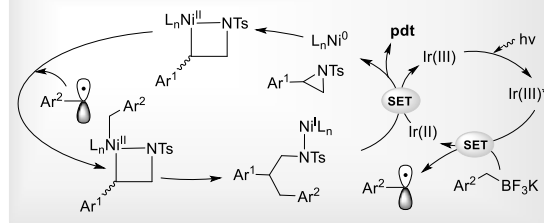
Scheme 10: Dual catalyst based cross-coupling

combination of 5 mol% $Ni(cod)_2$ along with 6 mol% chiral ligands (**L2**) leads to the desired product with excellent ee. Here the oxidative addition occurs in the acyl C-O bond by the Ni(0) species and the rest pathway is similar as described in the Molander group work. Later, the Xiao group also shows that the nickel can also easily undergoes oxidative addition across the C-N bond (Scheme 10f).[50] A variety of N-substituted aziridines were engaged for the cross-coupling in which the oxidative addition to aziridine generates a four-membered Ni^{II} intermediate which next coupled with the in situ generates benzylic radical followed by reductive elimination to the desired product.

5. Conclusion

In conclusion, photo-induced deborylative transformation has been widely used for the construction of C-C bonds with good yields. Visible light sources are readily accessible, inexpensive, and eco-friendly. Under visible light

irradiation, the C-C coupled product formation is a breakthrough innovation in the field of organic synthesis to achieve a wide variety of unique transformations. The capability to form different C-C coupled products by using readily available, cheaper, non-toxic organoboron compounds makes this method widespread for the synthesis of different bioactive molecules and natural products. Despite several developments, there is a need for the generation of conditions for easy access to free radicals from boronic acid using cheap organophotocatalysts. There are still several challenges which need to be conqueror; for activation of boronic esters organolithium was needed to form boronate complex which reduces the scope of this reaction. Recently EDA complxes are used for the radical generation instead of photosensitizers, which will allow to carryout the experiments in absence of any photocatalyst. Also, the scope of C-C bond formation using organoboron compounds needs to be expanded to satisfy the demand in organic synthesis.

6. Acknowledgements

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Suparna Mondal was born in West Bengal, India, in 1997. She completed her B.Sc from Kazi Nazrul University in 2019 and her M.Sc from the Indian Institute of Technology Kharagpur in chemistry in 2021. She completed her M.Sc project under the guidance of Dr. Rajashri Samanta. Recently, she started her r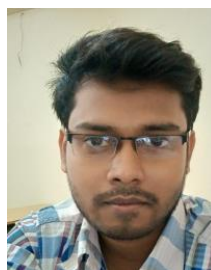esearch work under the supervision of Dr. Santanu Panda. Her research interest focuses on the synthesis and reactivities of organoboron.

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