Research Article

Chemical Review and Letters
journal homepage: www.chemrevlett.com
ISSN (online): 2645-4947 (print) 2676-7279

Recent progress on the borylation of organosulfur compounds *via* C−S activation

Ahmed Mohamed Kmkm[1], Maha mohammed Tawfiq[2], Hiba Mushtaq[3], Evan Abdulkareem Mahmood[4,*], Dheyaa Flayih Hasan[5], Hala Bahair[6]

[1] *Al-Zahrawi University College, Iraq*
[2] *Department of Optics Techniques, health and medical techniques college, Alnoor University, Mosul, Iraq*
[3] *Gilgamesh Ahliya University, Baghdad, Iraq*
[4] *Medical Laboratory Sciences Department, College of Health Sciences, University of Human Development, Sulaymaniyah, Iraq*
[5] *College of Health and Medical Technology, National University of Science and Technology, Dhi Qar, 64001, Iraq*
[6] *Medical technical college, Al-Farahidi University, Iraq*

ARTICLE INFO

Article history:
Received 3 May 2024
Received in revised form 19 June 2024
Accepted 20 June 2024
Available online 24 June 2024

Keywords:
Organosulfur compounds,
boronic esters, borylation, desulfurative functionalization, C-S bond, C-B bond

ABSTRACT

In this review, we intend to summarize the recent developments in the field of desulfurative borylation of organosulfur compounds since the initial discovery. Depending on the type of starting materials, the review has been divided into six major sections: desulfurative borylation of (i) sulfides; (ii) sulfonium salts; (iii) sodium arylsulfinates, (iv) sulfoxides, (v) sulfones; and (vi) dibenzothiophenes.

1. Introduction

Cross-coupling is the remarkable organic chemistry reactions that extensively chemists have been worked [1]. As one of the most important and versatile classes of reagents, aryl boronic acids/esters play prominent roles in modern organic synthesis and serves as a precursor for various cross-coupling reactions, most notably the Suzuki-Miyaura reaction [1, 2]. More significantly, this class of organoboron compounds also exhibit a wide range of biological activities (*e.g.*, anticancer, antibacterial, antiviral activities) [3-5] and can even be used as sensors and delivery systems [6]. Considering the above facts, borylation is undoubtedly one of the most important transformations in organic chemistry, but usually employs hazardous and toxic halides and pseudohalides [7]. In order to address sustainable development and green strategies, synthetic chemists have devoted considerable effort to the discovery and development of convenient and less toxic alternative electrophilic reagents [8]. In this regard, desulfurative borylation of organosulfur compounds has recently received considerable attention as a new concept for the construction of aryl boronic ester derivatives. This strategy allows a single-step synthesis of diverse aryl boronic esters from various easily available and less toxic aromatic organosulfur compounds such as sulfides, sulfones, sulfoxides, sulfonium salts, sodium arylsulfinates, and dibenzothiophenes, through the cleavage of C-S bond (Fig. 1). Although several interesting review articles have covered some aspects in desulfurative functionalization reactions [9], a review that covers a comprehensive list of the

---

* Corresponding author; e-mail: eva.mahmood@uhd.edu.iq
https://doi.org/10.22034/crl.2024.460832.1347

existing literature on desulfurative borylation reactions is not yet available. In connection with our recent review articles on organosulfur chemistry [10] and new methodologies in organic synthesis [11], herein, we will try to summarize the recent progress and developments on this appealing research arena by hoping that it will inspire and stimulate further research on the topic.

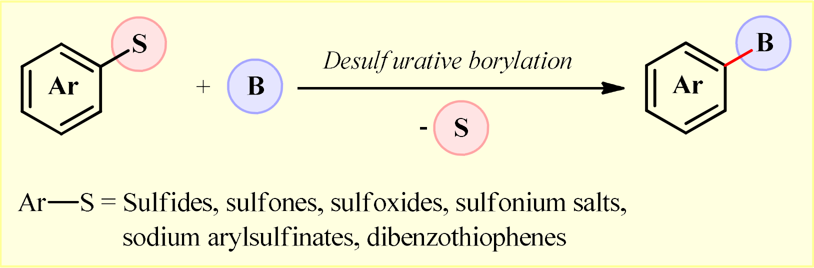
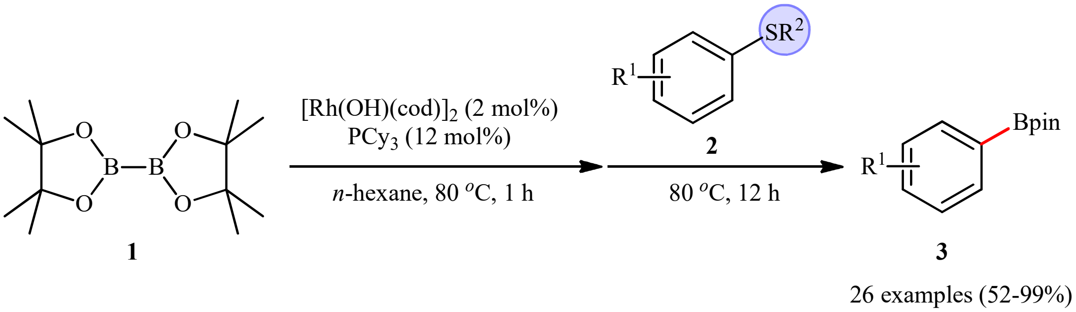


Fig. 1. Desulfurative borylation of aromatic organosulfur compounds.

2. Borylation of sulfides

Sulfides were used for C–B bond formation *via* Rh-catalyzed desulfanylative coupling with diborons by Hosoya and co-workers for the first time [12]. In this case, a mixture of the rhodium source ([Rh(OH)(cod)]$_2$), ligand [tricyclohexylphosphine (PCy$_3$)] and bis(pinacolato)diboron (B$_2$pin$_2$; **1**) was stirred in hexane at 80 °C for 1 h, and then alkyl aryl sulfides **2** were added to initiate the cross-coupling reaction. Under the optimal conditions, the borylation occurred *via* selective fission of the aromatic C−S bond and the target arylboronic acid pinacol esters **3** were obtained in moderate to quantitative yields (Scheme 1). However, diphenylsulfane did not work well under these conditions and therefore no other diaryl sulfides were examined in the protocol. The reaction mechanism is proposed as shown in Scheme 2. Initially, preheating of the mixture of [Rh(OH)(cod)]$_2$, PCy$_3$ and B$_2$pin$_2$ generates the borylrhodium(I) species **A**. Then, oxidative addition of the $C_{(aryl)}$–S bond in alkyl aryl sulfide **2** to the Rh metal center of species **A** followed by reductive elimination results in observed product **3** and methylthiorhodium(I) species **B**. The low-valent methylthiorhodium(I) species **B** then undergoes transmetalation with B$_2$pin$_2$ to regenerate the active borylrhodium(I) species **A**.

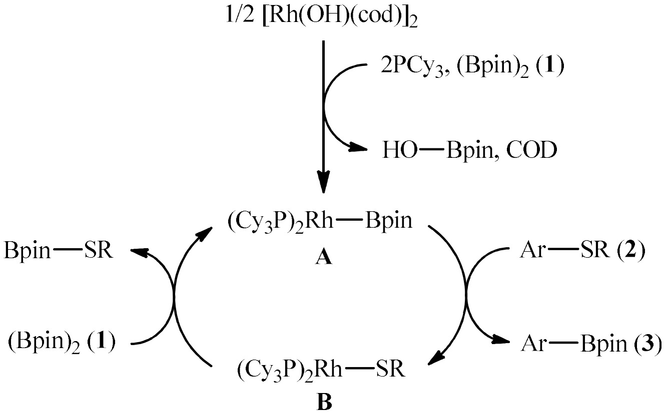


R^1= H, 4-Me, 4-Ph, 4-OMe, 4-OBn, 4-F, 4-CO$_2$, 4-OCOMe, 4-OMOM, 4-OTIPS, 4-CH$_2$CO$_2$Me, 4-Bpin, 4-OTs, 4-N(BOc)(Me), 4-N(Me)(Ac), 4-(4-morpholinyl), 4-(4-NBoc-piperazinyl), 4-(3-thienyl), 4-(3-(1-SO$_2$Ph)-indolyl), 3-OMe, 2-Ph, 2-Bpin, 2,3-(CH=CH)$_2$
R^2= Me, Et, ^{i}Pr, Bn

Scheme 1. Hosoya's synthesis of arylboronic acid pinacol esters **3**.

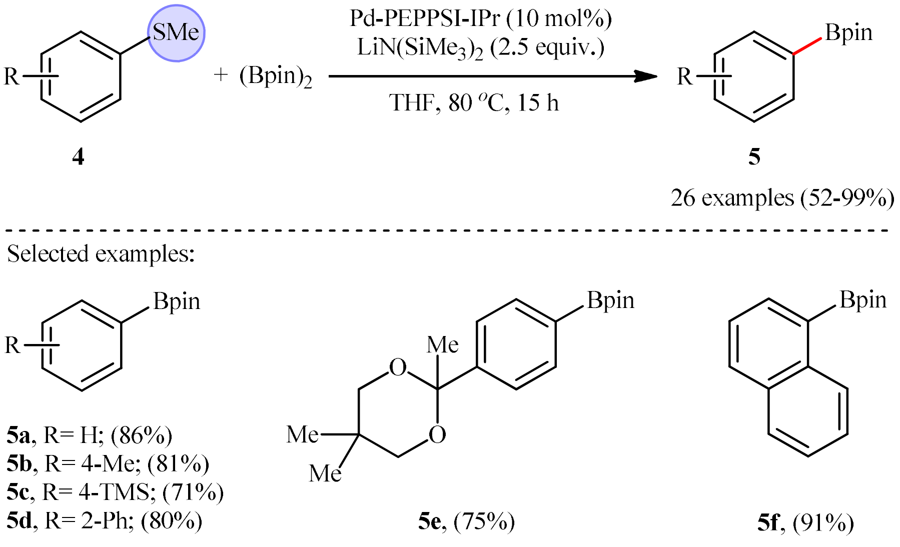
Concurrently, by means of the same strategy and using the Pd–PEPPSI–IPr ([1,3-bis(2,6-diisopropylphenyl) imidazol-2-ylidene] (3-chloropyridyl) palladium (II) dichloride) catalyst in the presence of LiN(SiMe$_3$)$_2$, Yorimitsu and co-workers were able to synthesize a large library of arylboronic acid pinacol esters **5** from the corresponding methyl aryl sulfides **4** (Scheme 3) [13].

Apart from methylsulfanyl, other alkylsulfanyl groups such as ethylsulfanyl and dodecylsulfanyl groups can also be used as the leaving groups in this protocol. However, the results showed that longer alkyl chains were inferior to methylsulfanyl as leaving groups probably because of their more electron-donating character. Interestingly, a 180% yield of arylboronate product was obtained when diphenyl sulfide was used as a substrate.



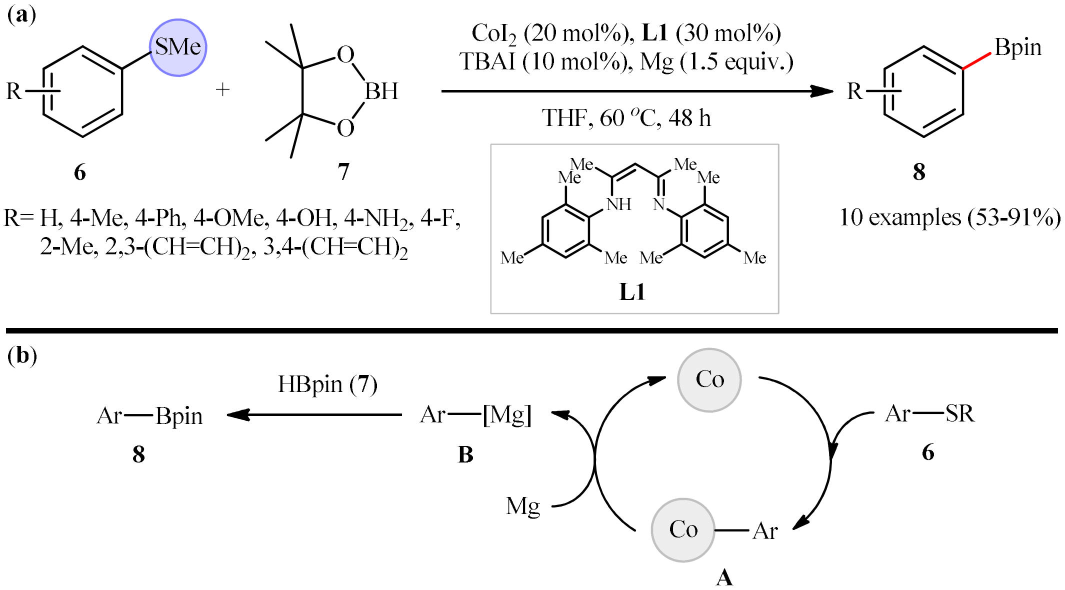
Scheme 2. The proposed mechanism for the formation of arylboronic acid pinacol esters **3**.

This result suggests that the leaving benzenethiolate species should undergo the second borylation with another equivalent of B$_2$pin$_2$. Unfortunately, replacing B$_2$pin$_2$ with some other diboron reagents [*e.g.*, bis(neopentyl glycolato)diboron, bis(hexylene glycolato)diboron, bis-(catecholato)diboron] led to lower yields or even no desired product at all. Four years later, Yamanaka and Kuninobu along with their co-workers unraveled that when the same reaction was performed in the presence of a catalytic amount of [Ir(OMe)(cod)]$_2$ and 5-phenyl-2 2'-bipyridine ligand, *ortho*-selective C−H borylation took place and the respective 2-borylthioanisoles were produced in moderate to high yields [14].



Scheme 3. Yorimitsu's synthesis of arylboronic acid pinacol esters **5**.

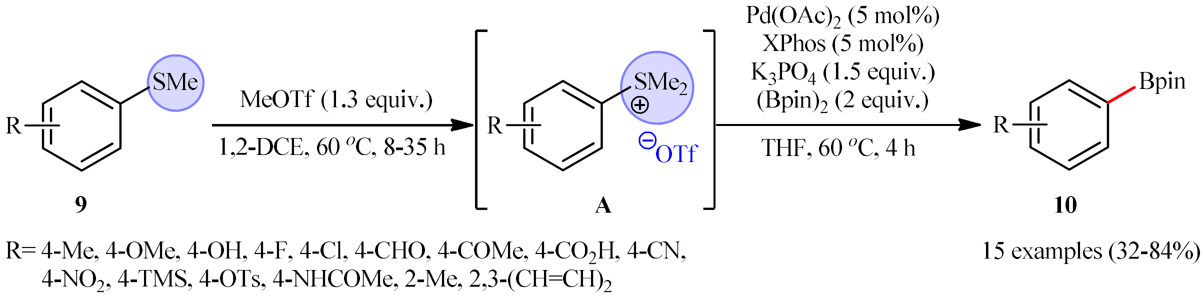
Following these works, Seo, Lee, and co-workers disclosed that using the CoI$_2$/**L1**/TBAI/Mg catalytic system, the reaction of thioanisoles **6** and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (HBpin, **7**) proceeded smoothly in THF at 50 °C to afford arylboronic acid pinacol esters **8** in fair to excellent yields (Scheme 4a) [15]. Mechanistic studies suggest that a Grignard reagent is generated as an intermediate *via* a C−S bond activation process, which subsequently trapped with HBpin electrophile (Scheme 4b).



Scheme 4. (a) Seo-Lee's synthesis of arylboronic acid pinacol esters **8**; (b) plausible mechanism for the formation of arylboronates **8**.

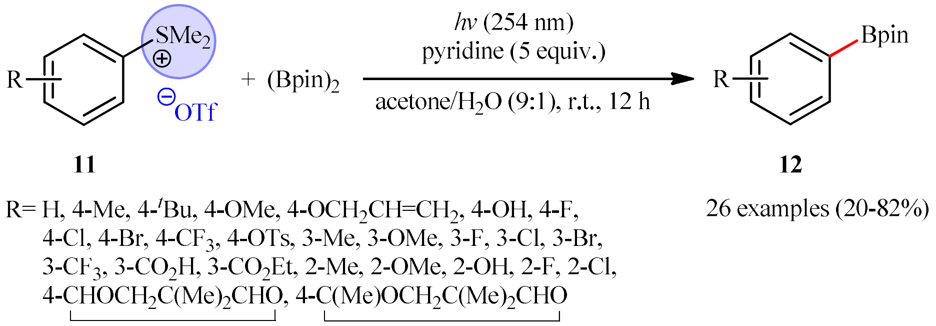
3. Borylation of sulfonium salts

In 2018, Yorimitsu and co-workers published one of the earliest reports on the desulfurative borylation of aryl sulfonium salts using the merge of $Pd(OAc)_2$ and XPhos with K_3PO_4 as the catalytic system [16]. They showed that the treatment of various aryl methyl sulfides **9** with methyl triflate (MeOTf) in 1,2-DCE, resulted in the formation of the corresponding aryl sulfoniums **A** through methylation. After removal of all volatiles, addition of the catalytic mixture and B_2pin_2, and subsequent heating at 60 °C gave the desired arylboronate esters **10** in moderate to high yields, ranging from 32% to 84% (Scheme 5). Owing to the mild reaction conditions, a wide range of functional groups such as fluoro, chloro, cyano, nitro, trimethylsilyl, ester, ether, amide, ketone, and aldehyde functionalities were well tolerated. In order to extend the substrate scope of the protocol, the authors subjected a series of aryl dodecyl sulfides to the same reaction conditions. Interestingly, aryl dodecyl sulfide derivatives afforded the expected arylboronate ester products in better yields than the corresponding aryl methyl sulfides. They explained this observation by more solubility and more reluctantly of aryl(dodecyl)methylsulfoniums to demethylation than aryldimethylsulfoniums.

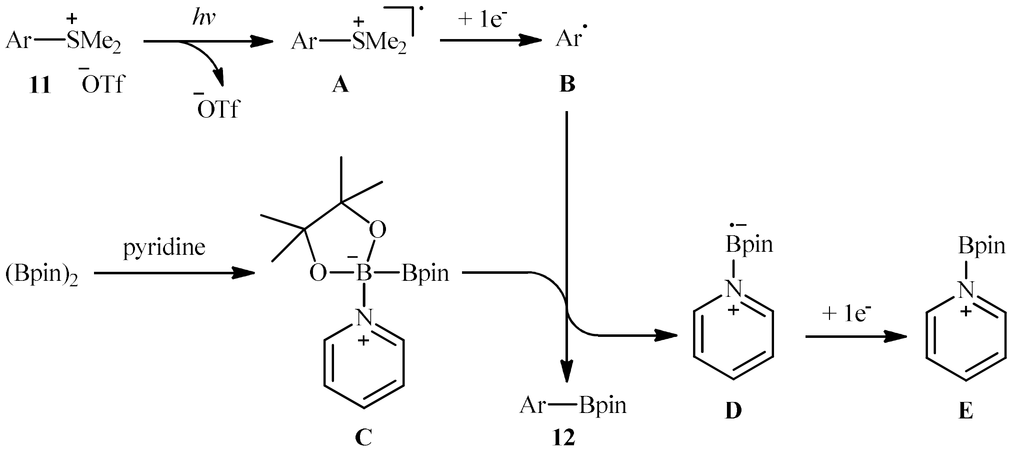


Scheme 5. Yorimitsu's synthesis of arylboronate esters **10**.

Subsequently, Gao, Du, Tang and co-workers developed an alternative desulfurative borylation of aryl sulfonium salts under transition-metal-free, photo-irradiation conditions [17]. Thus, in the presence of 5.0 equiv of pyridine, the reaction of various aryldimethylsulfonium sults **11** with B_2pin_2 at room temperature under irradiation of ultraviolet (UV) light, furnished the corresponding arylboronate esters **12** within 12 h (Scheme 6). Unfortunately, this synthetic strategy was not applicable to benzyl and alkyl sulfonium salts, as they were rapidly decomposed. The authors suggested mechanism for this C–B bond forming reaction is depicted in Scheme 7. The transformation may start with the photoexcitation of aryl sulfonium **11** to form an excited state species **A**, which after cleavage of the activated C(sp^2)−S bond *via* a reductive single electron transfer (SET) process affords the key aryl-radical **B**. Concurrently, nucleophilic addition of pyridine to the boron center of B_2Pin_2 leads to the formation of a hereroleptic complex **C**. Thereafter, the reaction complex **C** with aryl-radical **B** through a boron transfer process affords the desired product **12** and a pyridine-complexed boryl-radical **D**. Finally, the open-shell intermediate **D** converts to the corresponding pyridinium **E** through a SET oxidative process.

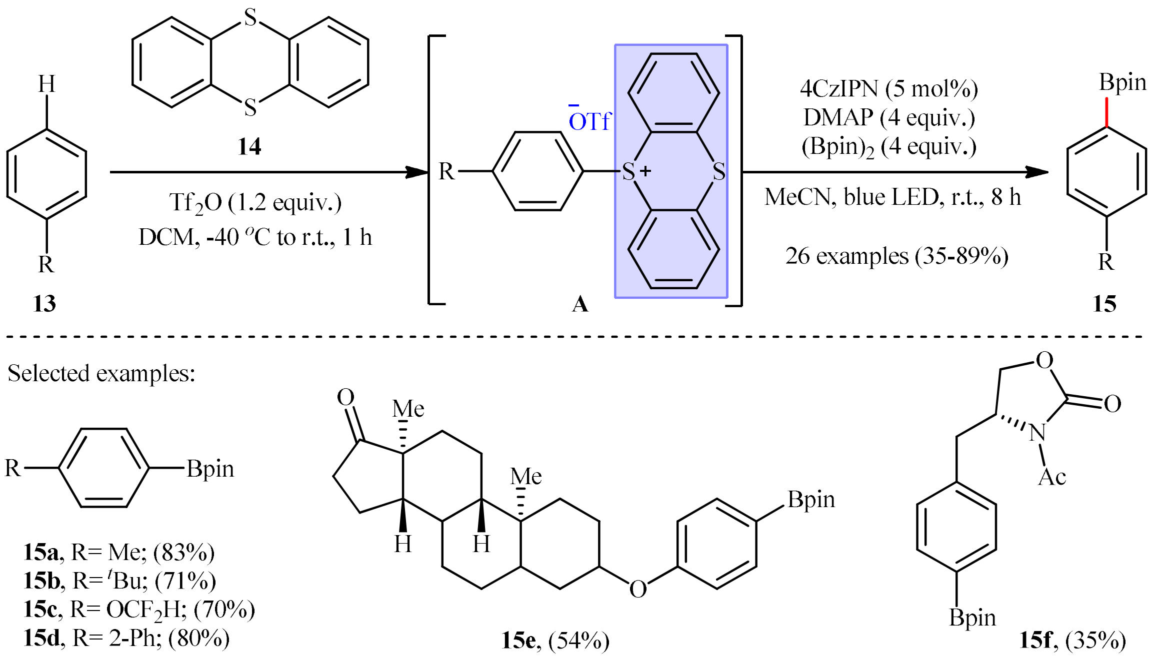


Scheme 6. Photoinduced, transition-metal-free borylation of aryldimethylsulfonium sults **11** with B_2pin_2.



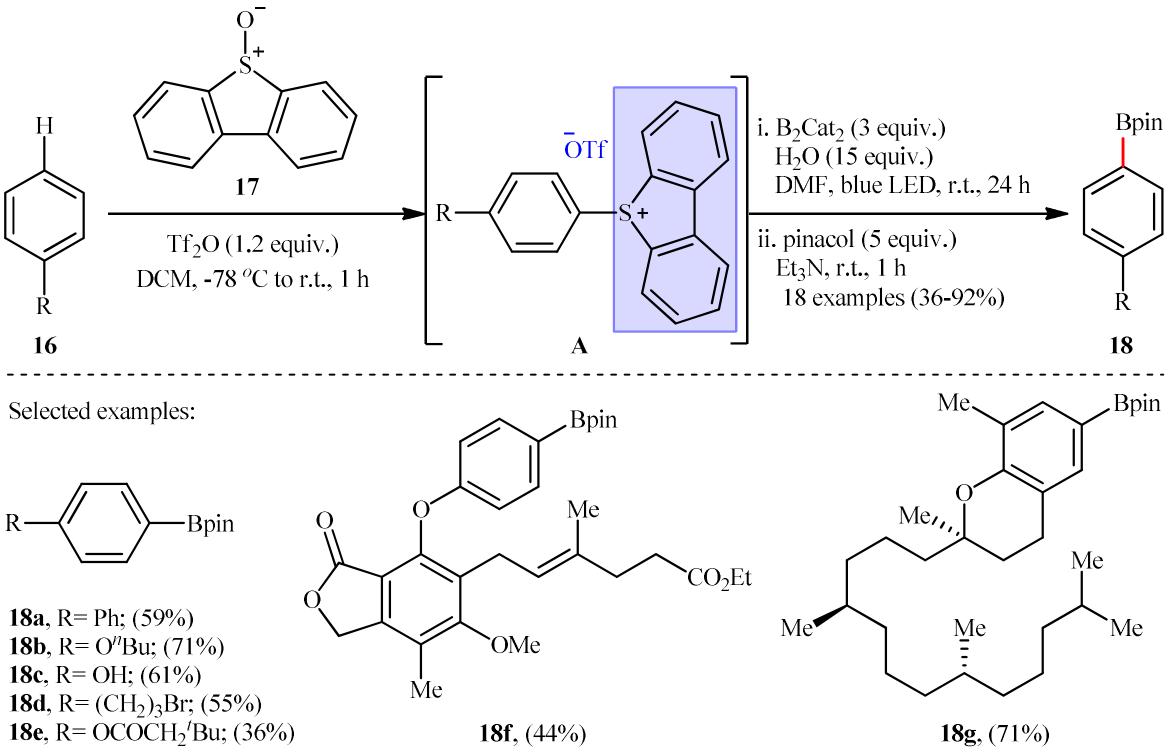
Scheme 7. Proposed mechanism for the reaction in Scheme 6.

In 2020, Peng and Wang developed an interesting photocatalyzed *para*-selective borylation of monosubstituted arenes **13** enabled by thianthrenation of arenes to provide the desired arylboronate esters **15** (Scheme 8) [18]. Aryl thianthrenium salts **A** were generated *in situ* in a regioselective manner by mixing arenes **13** with thianthrene **14** under mild conditions, followed by 4CzIPN-catalyzed borylation of these reactive intermediates with B_2Pin_2 *via* cleavage of the C–S bond. This strategy was compatible with electron-rich arenes and complex bioactive molecules, demonstrating its versatility for late-stage functionalization of drug molecules. However, when electron-poor substrates (*e.g.*, acetophenone, methyl benzoate) were employed under the optimal reaction conditions, only trace amounts of the desired products were obtained. In a related study, Ritter and co-workers disclosed an example of arylboronate ester synthesis through the light-mediated borylation of the corresponding aryl thianthrenium tetrafluoroborate [19].



Scheme 8. Peng-Wang's synthesis of arylboronate esters **15**.

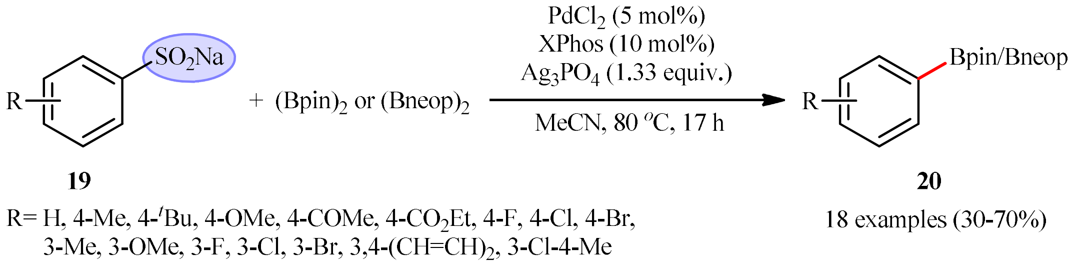
Subsequently, the Rueping group reported a similar photochemical *para*-selective C−H borylation of arenes **16** *via* dibenzothiophenation using dibenzothiophene-*S*-oxide **17**, followed by complexation with B_2cat_2 under the photochemical conditions and borylation of *in situ* generated electron donor-acceptor (EDA) complex with B_2Pin_2 (Scheme 9) [20]. The reaction showed excellent functional group tolerance and also successfully applied in the late stage borylation of complex natural product derivatives, such as estrone and vitamin E.



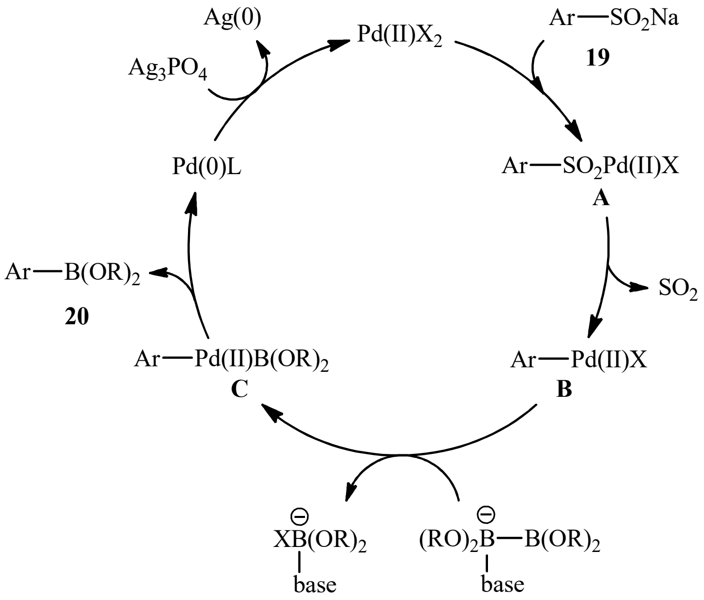
Scheme 9. Rueping's synthesis of arylboronate esters **18**.

4. Borylation of sodium arylsulfinates

The first and only example of the desulfitative borylation of sodium arylsulfinates with diborons has been reported by Qiu-Ye and co-workers in 2021 [21], when sodium arylsulfinates **19** underwent borylation with bis(pinacolato)diboron or bis(neopentylglycolato)diboron in the presence of $PdCl_2$/XPhos/Ag_3PO_4 combination as the catalytic system to form the respective arylboronates **20** (Scheme 10). Both electron-donating and electron-withdrawing groups were compatible with the transformation, affording the expected products in modest to good yields. However, *ortho*-substituted arylsulfinates were not compatible with the current protocol, presumably due to the steric hindrance. Regarding the influence of diborons, the reactions using B_2pin_2 afforded better yields compared to those used B_2neop_2 as the diboron source. In order to demonstrate the synthetic applicability and practicality of their borylation methodology, the authors also studied the possibility of synthesizing biaryl derivatives through the cascade borylation/Suzuki-Miyaura coupling process. Thus, a library of biaryl products were effectively synthesized in moderate yields through the tandem Pd-catalyzed Suzuki-Miyaura cross-coupling reaction of a series of crude borylation products with corresponding aryl halides. A possible mechanism for this borylation reaction is illustrated in Scheme 11. The reaction starts with the generation of palladium arylsulfinate **A** through the ligand exchange of the *in situ* formed Pd(II) complex with the sodium arylsulfinate **19**. Subsequently, this intermediate undergoes SO_2 extrusion to give intermediate **B**, which after transmetalation affords palladium species **C**. Finally, reductive elimination of this complex **C** leads to the formation of final product **20** and Pd(0), which the later can be oxidized *in situ* by Ag(I) salt to regenerate the active Pd(II) species.



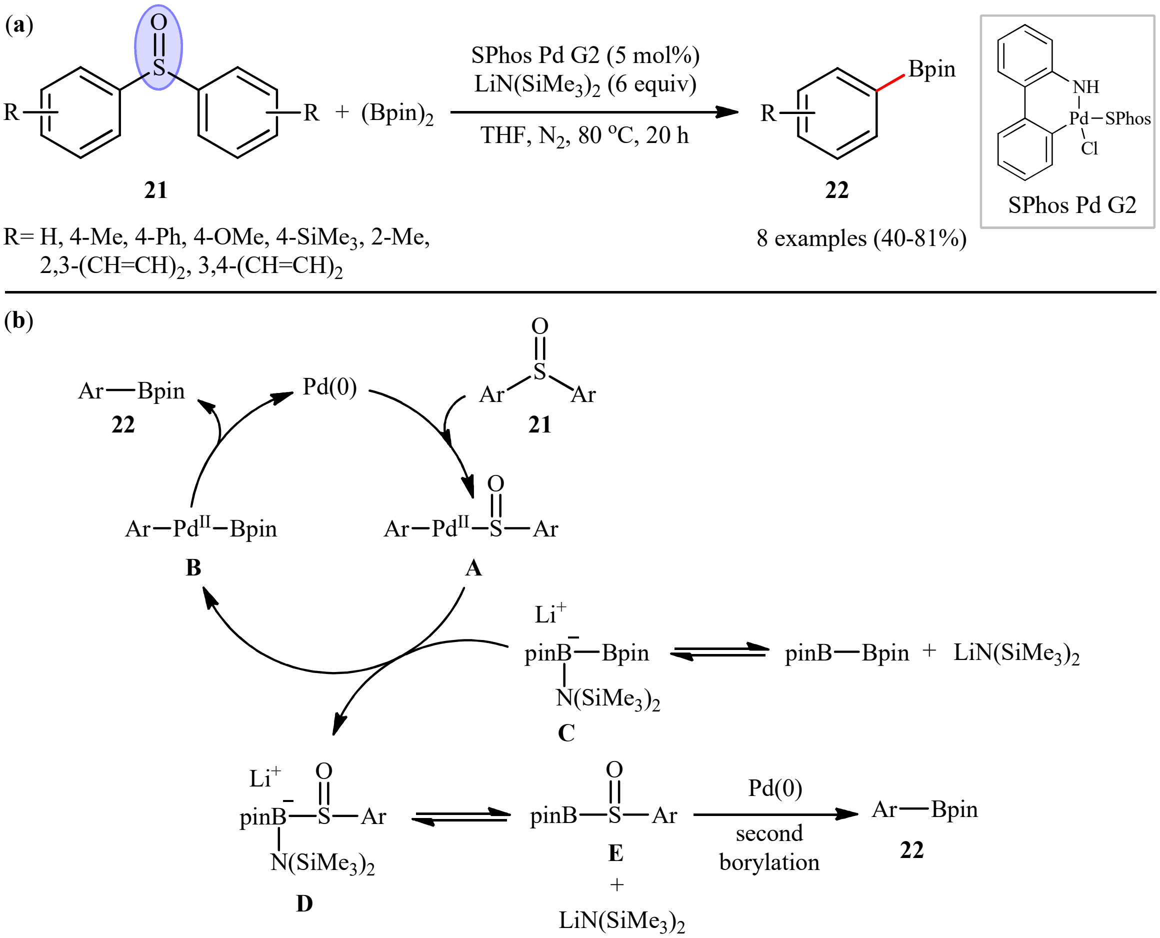
Scheme 10. Pd-catalyzed desulfitative borylation of sodium arylsulfinates **19** with diborons.



Scheme 11. Plausible mechanism for the reaction in Scheme 10.

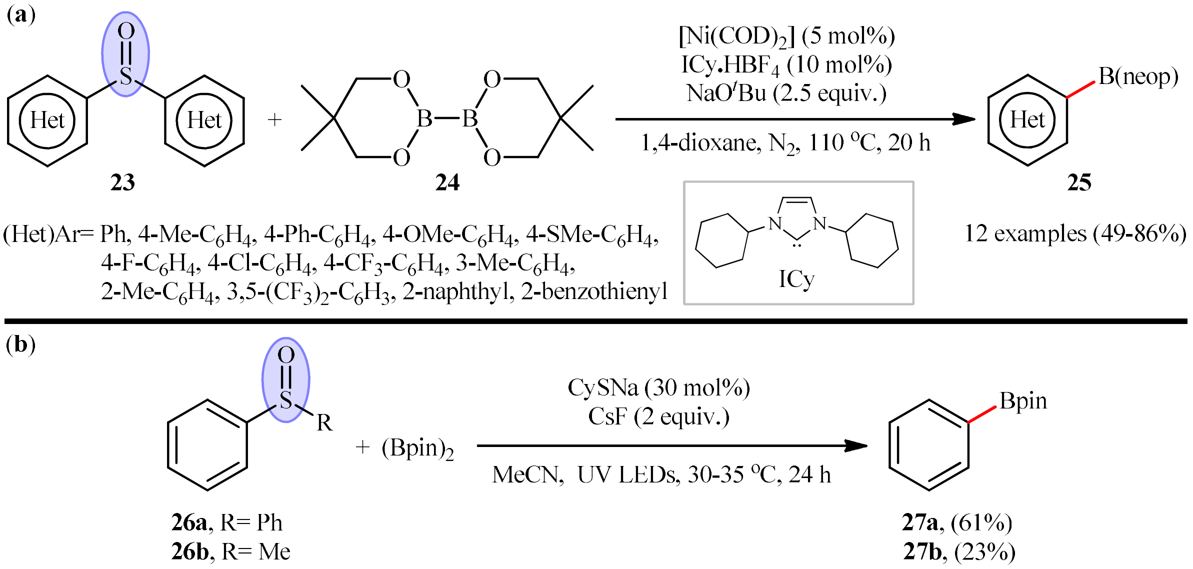
5. Borylation of sulfoxides

Following the early study by Hayashi [22], in 2017, Yorimitsu and co-workers reported the first general protocol for the synthesis of aryl boronic esters **22** *via* desulfurative coupling of diaryl sulfoxides **21** with B_2pin_2 catalyzed by a phosphine-ligated palladium catalyst, SPhos Pd G2 (Scheme 12a) [23]. The reactions were performed in refluxing THF at a catalyst loading of 5 mol%. Generally high yields were achieved when electron-rich diaryl sulfoxides were used; however, electron-poor diaryl sulfoxides were not suitable coupling partners under these conditions, resulting in low yields. Instead of diaryl sulfoxides, methyl phenyl sulfoxide was reluctant to undergo the borylation, and afforded only 12% NMR yield although it was fully consumed. Under similar conditions, the borylation with B_2nep_2 proceeded sluggishly resulting in poor yield of final products. The plausible reaction mechanism for this borylation is shown in Scheme 12b. It consists of the following key steps: (i) initial formation of arylpalladium(II) intermediate **A** *via* oxidative addition of diaryl sulfoxide **21** to the palladium(0) species; (ii) boryl transfer from highly reactive borate complex **C** to intermediate **A** to form borate species **B**; (iii) reductive elimination of intermediate **B** to generate the desired product **22** and borate species **D**; (iv) dissociation of **D** into the boryl sulfenate **E** and $LiN(SiMe_3)_2$; (v) initiation of the second catalytic borylation with boryl sulfenate **E** and another molecule of B_2pin_2.

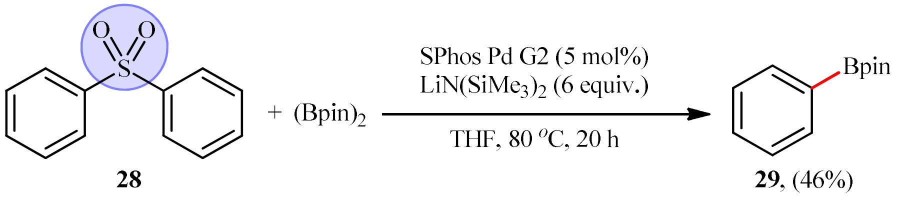


Scheme 12. (a) Pd-catalyzed double borylation of diaryl sulfoxides **21** with B_2pin_2; (b) Mechanism proposed to explain the formation of aryl boronic esters **22**.

Subsequently, in a related method, Marder and co-workers disclosed the efficient coupling between di(hetero) aryl sulfoxides **23** and bis (neopentylglycolato) diboron (B_2nep_2; **24**) catalyzed by $[Ni(COD)_2]$ in the presence of $ICy{\cdot}HBF_4$ (ICy=1,3-dicyclohexylimidazolin-2-ylidene) ligand (Scheme 13a) [24]. The reaction provides an efficient method to convert sulfoxides into boronic acid neopentyl glycol esters **25**. The method is characterized by excellent functional group tolerance in that functionalities, such as methoxy, thiomethyl, fluoro, chloro groups, and even trifluoromethyl group are well compatible under this catalyst system, demonstrating the generality of the protocol. However, sterically-hindered substrates, such as bis(1,3,5-trimethylphenyl) sulfoxide are not compatible with this reaction. Considering the failure when utilizing sterically-hindered substrates, the authors nicely extended their methodology to regioselective borylation of unsymmetrical diaryl sulfoxides by means of steric bias. Thus, a panel of 10 (hetero)aryl boronic esters were synthesized in moderate-to-good yields from corresponding 2,6-dimethylphenyl aryl sulfoxides and B_2nep_2 under the standard conditions. Concurrently, König's research team informed a metal-free protocol for desulfurative borylation of sulfoxides **26** with B_2pin_2 using the merge of 30 mol% of sodium cyclohexanethiolate (CySNa) with 2 equiv. CsF under irradiation with a 385–390 nm LED at 30-35 °C (Scheme 13b) [25].



Scheme 13. (a) Ni-catalyzed desulfurative borylation of di(hetero)aryl sulfoxides **23** with B_2neop_2; (b) photo-induced borylation of di(hetero)aryl sulfoxides **26** reported by König.



Scheme 14. Pd-catalyzed borylation of diphenyl sulfone **28**.

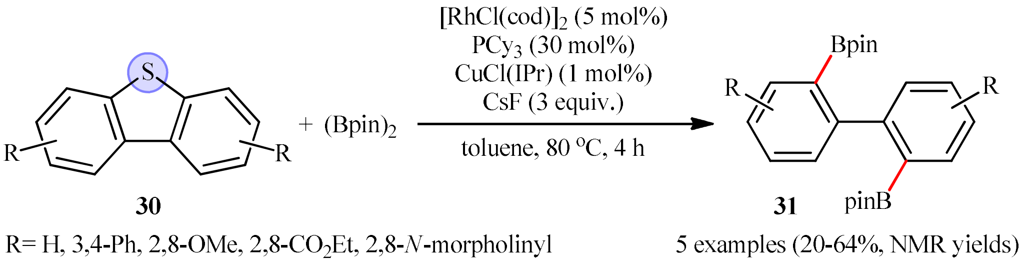
6. Borylation of Sulfones

Although desulfonative borylation of alkyl/benzyl sulfones has been well established [26-29], reports on desulfonative borylation of aryl sulfones are very scarce. To the best of our knowledge, only one example of such a reaction was reported in the literature till date. In 2017, in the same paper describing Pd-catalyzed double borylation of diaryl sulfoxides with diborons [23], Yorimitsu's research group also utilized the same catalytic system towards the desulfonative borylation of diphenyl sulfone **28** with B_2pin_2 and obtained the respective borylated product **29** in 46% yield (Scheme 14). Unfortunately, after about seven years of this report, the scope and limitations of this page of aryl boronic acid synthesis have not yet been investigated.

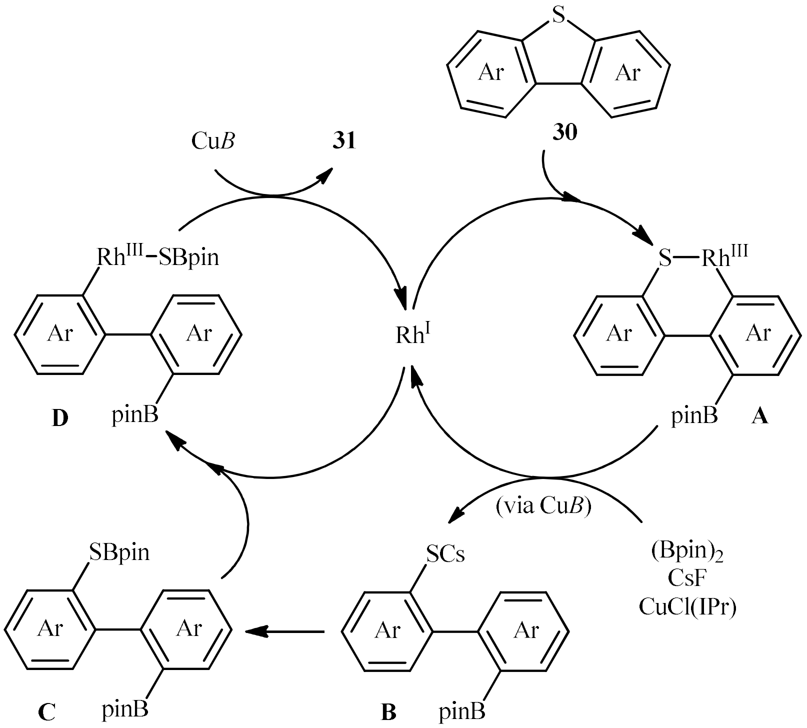
7. Borylation of dibenzothiophenes

In 2017, Yorimitsu and co-workers reported an elegant bimetallic Rh/Cu-catalyzed ring-opening diborylation of dibenzothiophenes with diboron through aromatic metamorphosis to access 2,2′-diborylbiaryl compounds [30]. They disclosed that in the presence of 5 mol % $[Rh(cod)Cl]_2$, 1 mol%

CuCl(IPr), and 3 equiv. of CsF, dibenzothiophene derivatives **30** underwent a couple of sequential borylation reactions with B_2pin_2 to afford the corresponding 2,2′-diborylbiaryls **31** in up to 49% yields (Scheme 15). This process involved the cleavage of two C–S bonds and the subsequent formation of two C–B bonds. As a proof-of-principle, 2,2′-diborylbiphenyl was converted into a series of 6,6-disubstituted fulvene derivatives through two-fold Pd-catalyzed cross-coupling reactions with gem-dibromoethylenes, and dibenzofuran *via* the formal Cu-mediated replacement of the sulfur atom of 2,2′-diborylbiphenyl with an oxygen atom under basic conditions. According to the authors proposed mechanism (Scheme 16), thiarhodacycle **A** might be the key intermediate for this transformation.

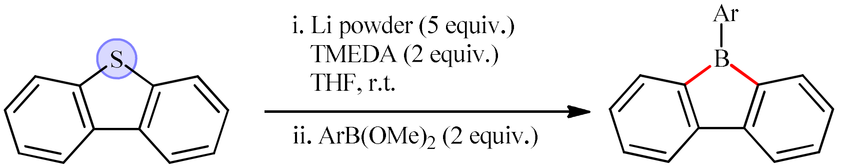


Scheme 15. Yorimitsu's synthesis of 2,2′-diborylbiaryls **31**.



Scheme 16. Mechanistic proposal for the formation of 2,2′-diborylbiaryls **31**.

Four years later, the same research group unraveled the preparation of borole **33** through the desulfurative dilithiation of dibenzothiophene **32** with lithium powder under basic condition, followed by trapping of 2,2’-dilithiobiphenyl intermediate with dimethyl (2,4,6-triisopropylphenyl)boronate (Scheme 17) [31].



32

33, Ar= 2,4,6-(^{i}Pr)-C_6H_2 (51%)

Scheme 17. Yorimitsu's synthesis of borole **33**.

8. Conclusion

This review highlights the recent progress and development on desulfurative borylation of aromatic organosulfur compounds. This new approach may serve as a complementary methodology for construction of aryl boronic ester derivatives which conventionally rely on the use on toxic aryl (pseudo)halides. Although considerable successes have been achieved so far in this area, additional development of novel borylating agents and further investigation of scope and limitation of existing methods is highly warranted.

Acknowledgment
Authors are grateful to the Researchers Supporting Project (ANUI2024M111), Alnoor University, Mosul, Iraq

References

[1] (a) W. Xu, D. Guo, A.G. Ebadi, M. Toughani, E. Vessally, Transition-metal catalyzed carboxylation of organoboron compounds with CO_2. J. CO_2 Util., 45 (2021) 101403; (b) L. Hao, G. Ding, D.A. Deming, Q. Zhang, Recent advances in green synthesis of functionalized phenols from aromatic boronic compounds. Eur. J. Org. Chem, (2019) 7307-7321; (c) F. Behmagham, M.A. Mustafa, S.K. Saraswat, K.A. Khalaf, M. Kaur, P. Ghildiyal, E. Vessally, Recent investigations into deborylative (thio-/seleno-) cyanation of aryl boronic acids. RSC Adv., 14 (2024) 9184-9199; (d) M. R. J. Sarvestani, N. Mert, E. Vessally, Cross-dehydrogenative coupling of aldehydes with N-hydroxyimides: An efficient and straightforward route to N-hydroxyimides esters, J. Chem. Lett. 1 (2020) 93-102. 10.22034/jchemlett.2020.120304; (e) J. Khayitov et. al, Transition metal-catalyzed carbonylative coupling of aryl/alkyl halides with thiols: A straightforward, *Chem. Rev. Lett.* 7 (2024) 333-345. 10.22034/crl.2024.448261.1311; (f) E. A. Mahmood, B. Azizi, S. Majedi, Decarboxylative cyanation and azidation of carboxylic acids: An overview, Chem. Rev. Lett. 3 (2020) 2-8. 10.22034/crl.2020.219565.1036.

[2] A.J. Lennox, G.C. Lloyd-Jones, Selection of boron reagents for Suzuki–Miyaura coupling. Chem. Soc. Rev., 43 (2014) 412-443.

[3] G.F.S. Fernandes, W.A. Denny, J.L. Dos Santos, Boron in drug design: Recent advances in the development of new therapeutic agents. Eur. J. Med. Chem., 179 (2019) 791-804.

[4] J. Plescia, N. Moitessier, Design and discovery of boronic acid drugs. Eur. J. Med. Chem., 195 (2020) 112270.

[5] M.P. Silva, L. Saraiva, M. Pinto, M.E. Sousa, Boronic acids and their derivatives in medicinal chemistry: synthesis and biological applications. Molecules, 25 (2020) 4323.

[6] (a) T. Zhang, X. Chen, C. Xiao, X. Zhuang, X. Chen, Synthesis of a phenylboronic ester-linked PEG-lipid conjugate for ROS-responsive drug delivery. Polym. Chem., 8 (2017) 6209-6216; (b) Y. Zhang, P. He, X. Liu, H. Yang, H. Zhang, C. Xiao, X. Chen, A PEGylated alternating copolymer with oxidation-sensitive phenylboronic ester pendants for anticancer drug delivery. Biomater. Sci., 7 (2019) 3898-3905.

[7] W.K. Chow, O.Y. Yuen, P.Y. Choy, C.M. So, C.P. Lau, W.T. Wong, F.Y. Kwong, A decade advancement of transition metal-catalyzed borylation of aryl halides and sulfonates. RSC Adv., 3 (2013) 12518-12539.

[8] (a) L. Xu, G. Wang, S. Zhang, H. Wang, L. Wang, L. Liu, J. Jiao, P. Li, Recent advances in catalytic C− H borylation reactions. Tetrahedron, 73 (2017) 7123-7157; (b) Y.M. Tian, X.N. Guo, H. Braunschweig, U. Radius, T.B. Marder, Photoinduced borylation for the synthesis of organoboron compounds: focus review. Chem. Rev., 121 (2021) 3561-3597; (c) S. Daliran, A.R. Oveisi, Y. Peng, A. López-Magano, M. Khajeh, et. al, Metal–organic framework (MOF)- covalent-organic framework (COF)-, and porous-organic polymers (POP)-catalyzed selective C–H bond activation and functionalization reactions, Chem. Soc. Rev. 51 (2022)7810-7882.

[9] (a) L. Wang, W. He, Z. Yu, Transition-metal mediated carbon–sulfur bond activation and transformations. Chem. Soc. Rev., 42 (2013) 599-621; (b) J. Lou, Q. Wang, P. Wu, H. Wang, Y.G. Zhou, Z. Yu, Transition-metal mediated carbon–sulfur bond activation and transformations: an update. Chem. Soc. Rev., 49 (2020) 4307-4359; (c) J. Corpas, S.H. Kim-Lee, P. Mauleón, R.G. Arrayás, J.C. Carretero, Beyond classical sulfone chemistry: metal-and photocatalytic approaches for C–S bond functionalization of sulfones. Chem. Soc. Rev., 51 (2022) 6774-6823; (d) K. Yang, Q. Li, Z.Y. Li, X. Sun, Transition-metal-free C–S bond cleavage and

transformation of organosulfur compounds. Chemical Communications. Chem. Commun., 59 (2023) 5343-5364.

[10] A. K. O. Aldulaimi, A. H. Hussein, M. J. Mohammed, H. R. Saud, H. Bahair, F. Shahimi, Direct hydroxyazidation of alkenes: A viable strategy for the synthesis of β-azido alcohols, . Chem. Rev. Lett. 7 (2024) 53-64.10.22034/crl.2024.430494.1270

[11] (a) .C. Y. Hsu, A. K. O. Aldulaimi, H. Bahair, A. H. Adhab, S. K. Saraswat, Hydrazinosulfonylation of aryl electrophiles: a straightforward approach for the synthesis of aryl N-aminosulfonamides, *RSC adv.* 13(27) (2023) 18546-18560; (b) A. K. Obaid Aldulaimi; E. A. Mahmood; E. Vessally, Sulfaguanidines: A new class of carbonic anhydrase inhibitors, *Med Med Chem,* 1 (2024) 2-9. 10.22034/medmedchem.2024.198914

[12] Y. Uetake, T. Niwa, T. Hosoya, Rhodium-catalyzed *ipso*-borylation of alkylthioarenes *via* C–S bond cleavage. Org. Lett., 18 (2016) 2758-2761.

[13] M. Bhanuchandra, A. Baralle, S. Otsuka, K. Nogi, H. Yorimitsu, A. Osuka, Palladium-catalyzed *ipso*-borylation of aryl sulfides with diborons. Org. Lett., 18 (2016) 2966-2969.

[14] J. Zeng, M. Naito, T. Torigoe, M. Yamanaka, Y. Kuninobu, Iridium-catalyzed *ortho*-C–H borylation of thioanisole derivatives using bipyridine-type ligand. Org. Lett., 22 (2020) 3485-3489.

[15] E. Pietrasiak, S. Ha, S. Jeon, J. Jeong, J. Lee, J. Seo, E. Lee, Cobalt-catalyzed formation of Grignard reagents via C–O or C–S bond activation. J. Org. Chem., 87 (2022) 8380-8389.

[16] H. Minami, S. Otsuka, K. Nogi, H. Yorimitsu, Palladium-catalyzed borylation of aryl sulfoniums with diborons. ACS Catal., 8 (2018) 579-583.

[17] C. Huang, J. Feng, R. Ma, S. Fang, T. Lu, W. Tang, D. Du, J. Gao, Redox-neutral borylation of aryl sulfonium salts via C–S activation enabled by light. Org. Lett., 21 (2019) 9688-9692.

[18] J. Wu, Z. Wang, X.Y. Chen, Y. Wu, D. Wang, Q. Peng, P. Wang, Para-selective borylation of monosubstituted benzenes using a transient mediator. Sci. China Chem., 63 (2020) 336-340.

[19] F. Berger, M.B. Plutschack, J. Riegger, W. Yu, S. Speicher, M. Ho, N. Frank, T. Ritter, Site-selective and versatile aromatic C−H functionalization by thianthrenation. Nature, 567 (2019) 223-228.

[20] B. Li, K. Wang, H. Yue, A. Drichel, J. Lin, Z. Su, M. Rueping, Catalyst-free C(sp^2)-H borylation through aryl radical generation from thiophenium salts *via* electron donor–acceptor complex formation. Org. Lett., 24 (2022) 7434-7439.

[21] D. Qiu, S. Li, G. Yue, J. Mao, B. Xu, X. Yuan, F. Ye, Synthesis of arylboronates via the Pd-catalyzed desulfitative coupling reaction of sodium arylsulfinates with bis(pinacolato) diboron. Tetrahedron Lett., 85 (2021) 153478.

[22] T. Shimada, Y.H. Cho, T. Hayashi, Nickel-catalyzed asymmetric grignard cross-coupling of dinaphthothiophene giving axially chiral 1,1'-binaphthyls. J. Am. Chem. Soc., 124 (2002) 13396-13397.

[23] H. Saito, K. Nogi, H. Yorimitsu, Palladium-catalyzed double borylation of diaryl sulfoxides with diboron. Synthesis, 49 (2017) 4769-4774.

[24] M. Huang, Z. Wu, J. Krebs, A. Friedrich, X. Luo, S.A. Westcott, U. Radius, T.B. Marder, Ni-catalyzed borylation of aryl sulfoxides. Chem. Eur. J., 27 (2021) 8149-8158.

[25] S. Wang, H. Wang, B. König, Photo-induced thiolate catalytic activation of inert C$_{aryl}$-hetero bonds for radical borylation. Chem, 7 (2021) 1653-1665.

[26] Y. Maekawa, Z.T. Ariki, M. Nambo, C.M. Crudden, Pyridine-catalyzed desulfonative borylation of benzyl sulfones. Org. Biomol. Chem., 17 (2019) 7300-7303.

[27] M. Huang, J. Hu, I. Krummenacher, A. Friedrich, H. Braunschweig, S.A. Westcott, U. Radius, T.B. Marder, Base-mediated radical borylation of alkyl sulfones. Chem. Eur. J., 28 (2022) 202103866.

[28] M. Huang, M. Tang, J. Hu, S.A. Westcott, U. Radius, T.B. Marder, Cu-mediated vs. Cu-free selective borylation of aryl alkyl sulfones. Chem. Commun., 58 (2022) 395-398.

[29] L. Tang, G. Lv, F. Jia, R. Zhao, X. Wang, Q. Zhou, Visible light-driven eosin Y-catalyzed Suzuki-type sulfonylation. Adv. Synth. Catal., 366 (2024) 70-76.

[30] H. Saito, K. Nogi, H. Yorimitsu, Rh/Cu-cocatalyzed ring-opening diborylation of dibenzothiophenes for aromatic metamorphosis *via* diborylbiaryls. Chem. Lett., 46 (2017) 1122-1125.

[31] A. Kaga, H. Iida, S. Tsuchiya, H. Saito, K. Nakano, H. Yorimitsu, Aromatic metamorphosis of thiophenes by means of desulfurative dilithiation. Chem. Eur. J., 27 (2021) 4567-4572.