Cross-Coupling Reaction of Oxazoles

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Abstract: The metal-catalyzed cross-coupling reaction of oxazoles is discussed in this review. Initially, preparation of metallated oxazoles (oxazole-M) and halo- and trifloyloxazoles (oxazole-X) is outlined. After that, comprehensive examples of Negishi, Stille, Suzuki-Miyaura, and Sonogashira reactions at each three position in oxazoles (C-2, C-4, and C-5) are detailed with showing both types of reactions [route A (reaction of oxazol-M and Ar-X) and route B (reaction of oxazole-X and Ar-M)].

Key Words: Oxazoles, cross-coupling, Negishi reaction, Stille reaction, Suzuki-Miyaura reaction, Sonogashira reaction.

1. INTRODUCTION

Oxazoles, (Fig. (**1**)), are recognized as an important class of heterocyclic compounds due to the appearance in the areas of natural product chemistry, medicinal chemistry, agricultural chemistry, and material science. Because of their fascinating utility, many procedures for their preparations and reactions have been reported and reviewed [1]. One of the reliable methods to synthesize the functionalized oxazoles is introduction of the substituents into the oxazole ring using a transition metal-catalyzed cross-coupling reaction. The metal-catalyzed cross-coupling reaction between organometals (RM) and organic electrophiles (R'X) is undoubtedly defined as a powerful carbon-carbon bond forming reaction. Especially, Negishi (M=Zn, Al, Zr) [2], Stille (M=Sn) [3], Suzuki-Miyaura (M=B) [4], and Sonogashira (R=alkyne) [5] reactions have been utilized for various organic syntheses from lab to pilot scale. In terms of the cross-coupling reaction of the oxazoles, as well as other heterocycles there has been a great progress in recent years [6]. As depicted in Scheme (**1**), to execute the cross-coupling reaction of the oxazoles, researchers generally take into account two possible alternative methods, I) the reaction between metallated oxazole and aryl electrophile (route A) and II) the reaction between oxazolyl electrophile and metallated arene (route B). Regarding easy availability of starting materials and the efficiency of the reaction, they would choose the appropriate method. This review will focus on the metal-catalyzed cross-coupling reactions of the oxazoles including Negishi, Stille, Suzuki-Miyaura, and Sonogashira reactions, where we will discuss both types of reactions (routes A and B) at each three reactive position (C-2, C-4, and C-5).

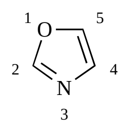
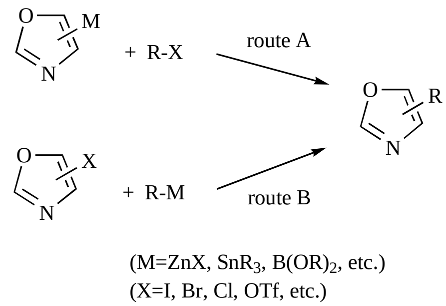


Fig. (1).



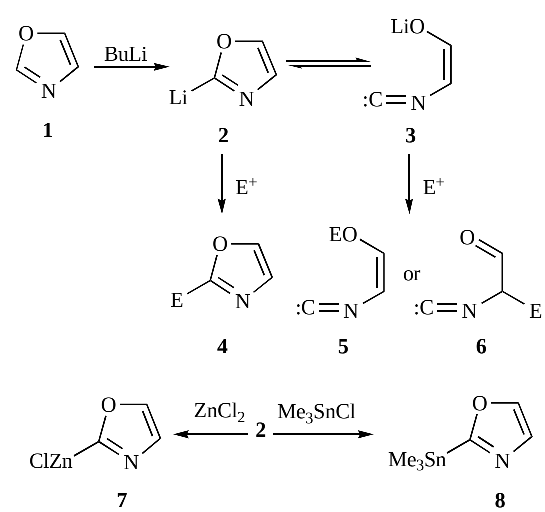
Scheme 1.

2. PREPARATION OF SUBSTRATES FOR THE CROSS-COUPLING REACTION

2-1. Preparation of Metallated Oxazoles [oxazole-M, M=ZnX, SnR_3, $B(OR)_2$]

2-1-1. 2-Metallated oxazoles

Since the acidity at the C-2 position is the highest [C(2)-H>C(5)-H>C(4)-H], lithiation of oxazole (**1**) with *n*-BuLi gives 2-lithiooxazole **2** as shown in Scheme (**2**) [7]. It is well-studied that since **2** exists in equilibrium with the acyclic lithium enolate **3**, depending on the additional electrophile (E^+) the resulting product forms as one of three pos-



Scheme 2.

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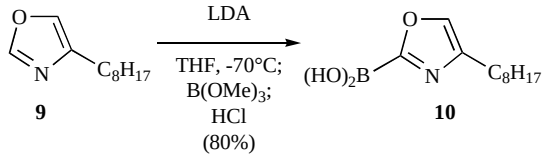
sible regioisomers (oxazole **4**, enol ether **5**, or isonitrile **6**) [8, 9]. Although the addition of TMSCl produced acyclic silyl enol ether [9], in the case of $ZnCl_2$ or Me_3SnCl as an electrophile, the 2-metallated oxazole derivatives (**7** and **8**) were produced owing to their high carbophilicity and low oxophilicity [10, 11].

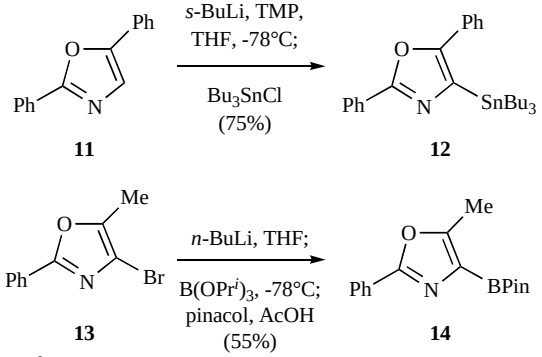
Some groups failed to prepare the oxazol-2-ylboronic acid derivatives probably due to instability of the resulting boronic acid [12, 13]. Only one example can be found in a Japanese patent [14], in which 4-octyloxazol-2-ylboronic acid (**10**) was successfully synthesized from the corresponding oxazole **9** with LDA and $B(OMe)_3$ in 80% yield, (Scheme (**3**)).



Scheme 3.

2-1-2. 4-Metallated oxazoles

Nucleophilic reaction of 4-lithiooxazoles normally gives the 4-substituted oxazoles with rare exceptions [15]. Thus, lithiation of 2,5-diphenyloxazole (**11**) by LiTMP followed by addition of Bu_3SnCl furnished a 75% yield of oxazol-4-ylstannane **12**, Scheme (**4**) [16]. Our group reported borylation of 4-bromooxazole **13** gave boronate **14** in 55% yield [17]. Palladium-catalyzed borylation and stannylation of 4-halo- and 4-trifloyloxazoles were also disclosed [17, 18].



Scheme 4.

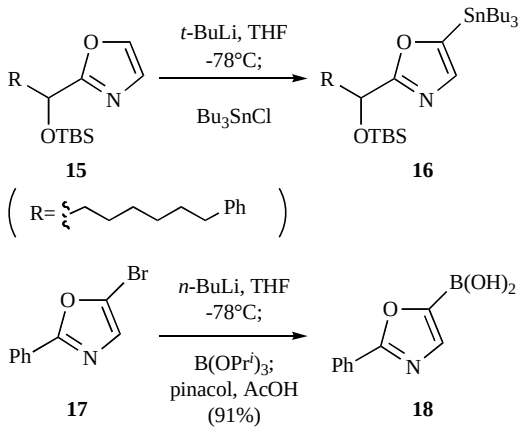
2-1-3. 5-Metallated oxazoles

Because the C-5 proton is the second acidic position, lithiation of the C-2 substituted oxazoles occurs at the C-5-position by treatment with BuLi. Exposure of the resulting 5-lithiooxazoles, which can be also derived by halogen-metal exchange reaction of 5-halooxazoles, to Bu_3SnCl and $B(OPr^i)_3$ gave rise to organotin and organoboron compounds, respectively, (Scheme (**5**)) [19, 20].

2-2. Preparation of Halo- and Trifloyloxazoles (oxazole-X, X=halogen, OTf)

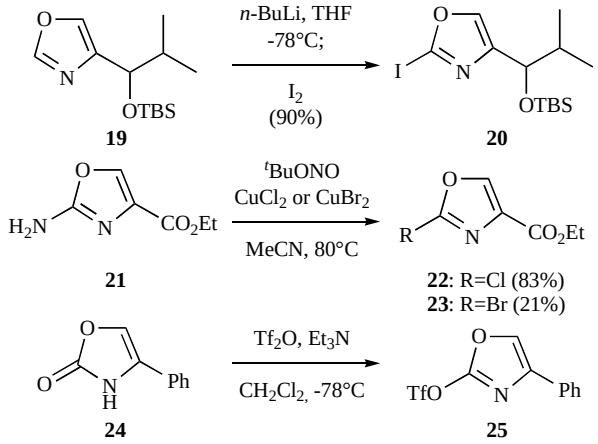
2-2-1. 2-Halo- and 2-trifloyloxazoles

Barrett *et al.* reported that 2-iodooxazole **20** was obtained by lithiation and iodination of oxazole **19**, (Scheme (**6**)) [18].



Scheme 5.

Sandmeyer reaction of 2-aminooxazole **21** furnished 2-chloro and 2-bromooxazole derivatives (**22** and **23**) through a nitrosamine intermediate [*t*-BuONO and cupper salt ($CuBr_2$ or $CuCl_2$)] [21]. The yield of chlorination is high (83%), but the yield of bromination is very low (21%). Addition of Tf_2O and 2,6-lutidine to 2-oxazolone **24** offered 2-trifloyloxazole **25** [13].



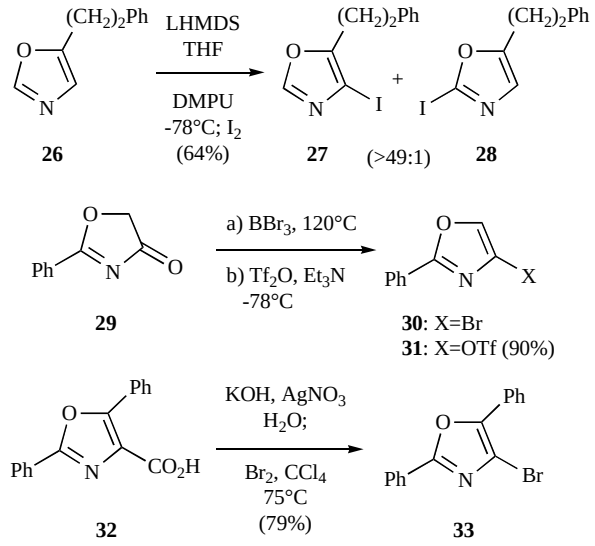
Scheme 6.

2-2-2. 4-Halo- and 4-trifloyloxazoles

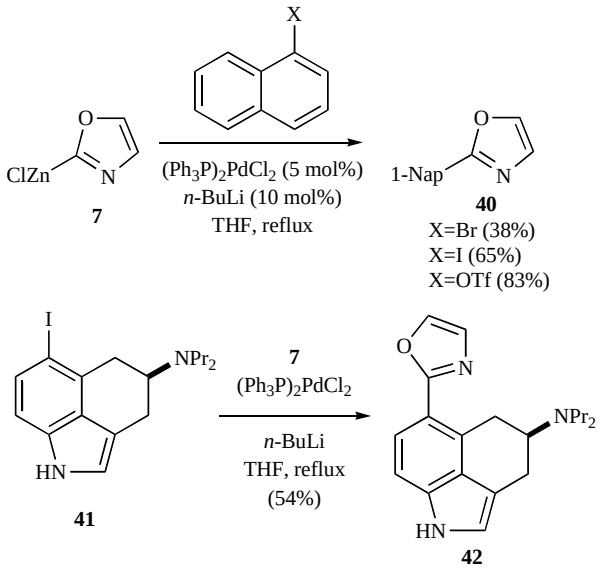
Vedejs *et al.* exploited the regioselective iodination at the C-4 position. Thus, treatment of a premixture of 5-substituted oxazole **26** and DMPU with LiHMDS, followed by addition of 1,2-diiodoethane predominantly produced 4-iodooxazole **27** in 64% yield with high regisoselectivity, (Scheme (**7**)) [22]. The key issue was executing the reaction in THF-DMPU, which prompted generation of an iodo-isonitrile intermediate such as **6** and then formation on **27**. Without DMPU 2-iodooxazole **28** was mainly produced. 4-Bromo-2-phenyloxazole **30** was obtained by heating of 2-phenyl-4-oxazolone (**29**) with BBr_3 [23]. Subjection of carboxylic acid **32** to Hunsdiecker reaction gave 4-bromooxazole **33** in 79% yield [21]. 4-Trifloyloxazole **31** was produced from **29** in 90% yield through the action of Tf_2O and Et_3N [24].

2-2-3. 5-Halo- and 5-trifloyloxazoles

Electrophilic bromination is prone to occur at the C-5 position. Some selective brominations are shown in Scheme



Scheme 7.



Scheme 9.

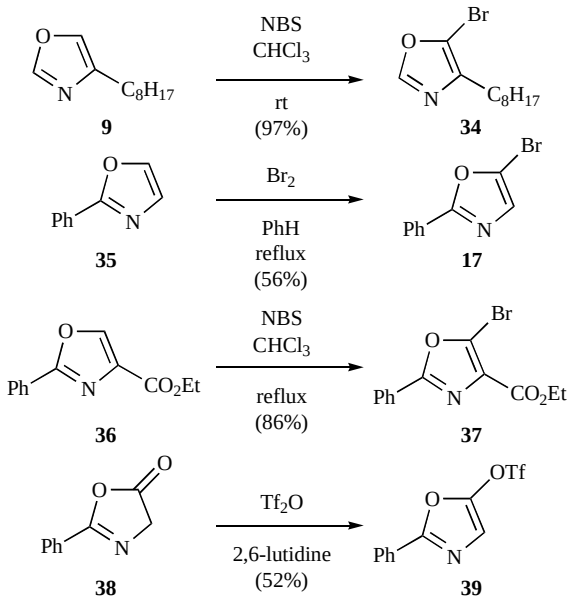
(**8**). Bromination of 4-octyloxazole (**9**), 2-phenyloxazole (**35**), and the 2,4-disubstituted oxazole **36** with brominating reagents such as Br_2 and NBS yielded 5-bromooxazoles (**34**, **17**, and **37**) with high regioselectivity [14, 21, 25]. 2-Phenyl-5-trifloyloxazole (**39**) was produced in 52% yield from 2-phenyl-5-oxazolone (**38**) by the addition of Tf_2O and 2,6-lutidine [26].

3. CROSS-COUPLING REACTION OF OXAZOLES

3-1. Negishi Coupling

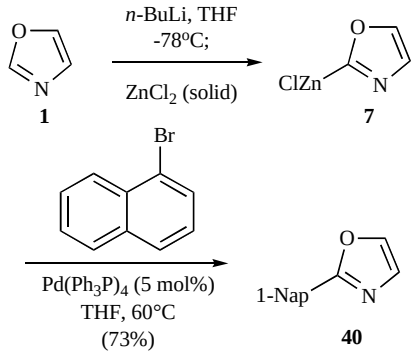
3-1-1. Reaction of oxazol-2-ylzinc reagents

The first appearance of Negishi coupling of oxazoles was the reaction of 5-phenyloxazol-2-ylzinc chloride with iodobenzene in the presence of palladium catalyst [$(Ph_3P)_2PdCl_2$ and DIBAL], producing 2,5-diphenyloxazole in 69% by Hughes *et al.* [27]. After that, Anderson *et al.* precisely explored the reaction condition of oxazol-2-ylzinc reagent **7** with several aryl halides, Scheme (**9**) [28]. The most effective catalytic system was a combination of $(Ph_3P)_2PdCl_2$ (5mol%) and *n*-BuLi (10mol%). The order of the reactivity of electrophiles is Ar-OTf>Ar-I>Ar-Br. They applied this optimized method to the synthesis of the oxazole-containing partial ergot alkaloid **42** [12]. Compared with the corresponding Stille reaction (11%), the yield was improved to 54% yield. Vedejs *et al.* utilized Negishi coupling for the bis-oxazole synthesis [22].



Scheme 8.

As shown in Scheme (**10**), Reeder *et al.* demonstrated an improved and scalable (kilo-gram scale) procedure [29]. They found that the use of solid $ZnCl_2$ in place of an ether solution of $ZnCl_2$ dramatically enhanced the reactivity of oxazol-2-ylzinc reagent **7**, which was allowed to react with 1-bromonaphthalene to produce **40** in the improved yield (73%). Unfortunately, Ar-Cl was not suitable for the reaction.

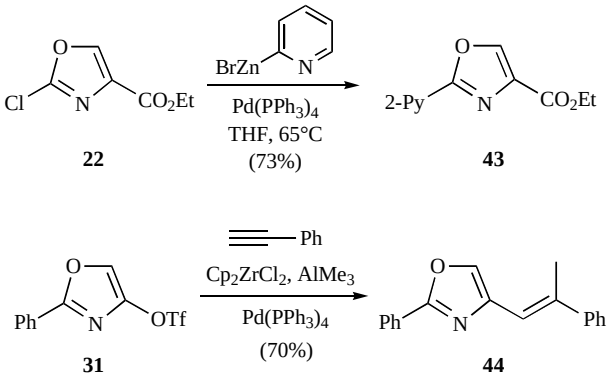


Scheme 10.

3-1-2. Reaction of halo- and trifloyloxazoles with organozinc(aluminum) reagents

Hodgetts *et al.* examined Negishi reaction of haloxazoles (**22**, **33**, and **37**) with 2-pyridylzinc bromide [21]. Under the same reaction condition [$Pd(PPh_3)_4$, THF, 65°C], all reac-

tions cleanly proceeded to produce the 2-pyridyl, 4-pyridyl and 5-pyriyloxazole derivatives in around 70% yield, (Scheme (**11**)). Carboalumination of phenylacetylene (Cp_2ZrCl_2 and $AlMe_3$) followed by the palladium-catalyzed reaction with 4-trifloyloxazole **31** yielded (*E*)-alkenyloxazole **44** in 70% yield [24].



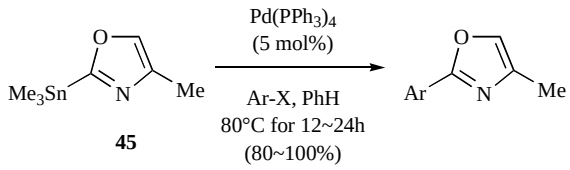
22 **43** **31** **44**

Scheme 11.

3-2. Stille Coupling

3-2-1. Reaction of oxazol-2-ylstannanes

Dondoni *et al.* first reported the synthesis of oxazol-2-ylstannane **45** from 4-methyloxazole with BuLi and Me_3SnCl and utilized **45** for the cross-coupling reaction [11]. Subjection of **45** and several aryl halides including iodobenzene, 4-bromoacetophenone, 3-bromopyridine, and 2-bromonaphthalene to a catalytic amount of $Pd(PPh_3)_4$ in benzene led to the formation of 2-aryloxazoles in high yields, (Scheme (**12**)). After their report, other groups have proved the efficiency of oxazol-2-ylstannanes to synthesize the 2-substituted oxazole derivatives [30, 31].



45

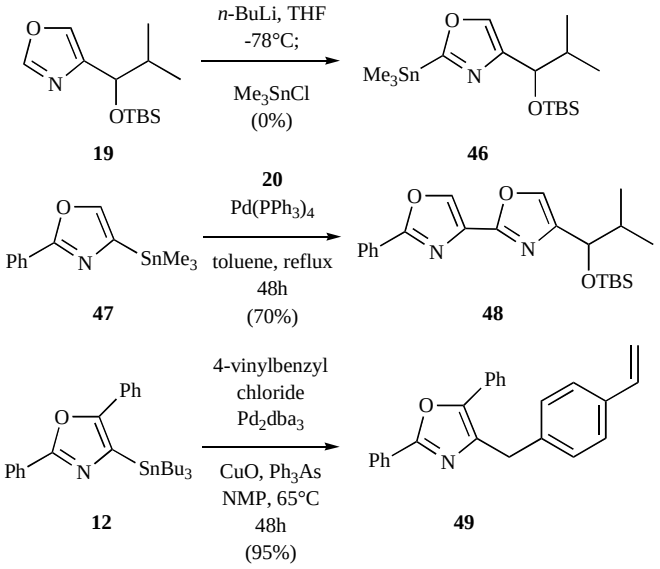
Scheme 12.

3-2-2. Reaction of oxazol-4-ylstannanes

While Dondoni succeeded in synthesizing **45**, Barrett *et al.* failed to obtain oxazol-2-ylstannane **46** from **19**, (Scheme (**13**)) [18]. As an alternative route for the synthesis of hennoxazole, oxazol-4-ylstannane **47**, derived from **31** *via* the palladium-catalyzed stannylation, was treated with 2-iodooxazole **20** in the presence of $Pd(PPh_3)_4$ to generate bisoxazole **48** in 70% yield. Sutherland *et al.* carefully optimized the reaction condition of oxazol-4-ylstannane **12** with 4-vinylbenzyl chloride [16]. They found that the addition of a stoichiometric amount of CuO enhanced the reaction rate and the yield increased from 57 to 95%.

3-2-3. Reaction of oxazol-5-ylstannanes

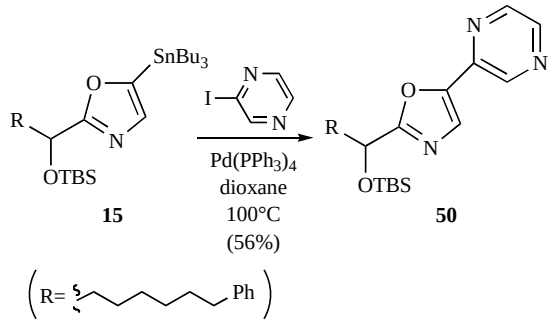
It is reported that the reaction of oxazol-5-ylstannane **16** with 2-iodopyrazine proceeded well in the presence of



19 **20** **46** **47** **48** **12** **49**

Scheme 13.

$Pd(PPh_3)_4$ to furnish the 2,5-disubstituted oxazole **50**, a fatty acid amide hydrolase inhibitor, (Scheme (**14**)) [19].



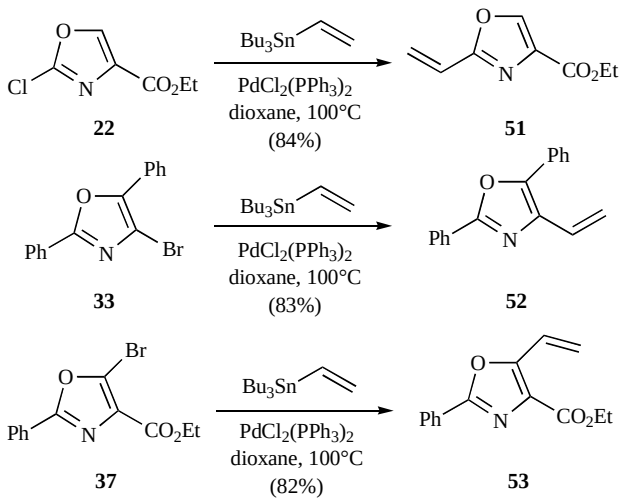
15 **50**

Scheme 14.

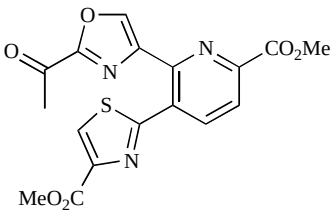
3-2-4. Reaction of halo- and trifloyloxazoles with organostannanes

Hodgetts *et al.* demonstrated that the reaction of 2-, 4-, and 5-halooxazoles (**22**, **33**, and **37**) with vinylstannane proceeded upon the same reaction condition [$PdCl_2(PPh_3)_2$, dioxane, 100°C] to give the coupling products in about 80% yield, (Scheme (**15**)) [21].

Since many natural products contain the 2,4-disubstituted oxazole moiety [32], several researchers have reported the synthesis of these biological active 2,4-disubstituted oxazoles *via* Stille reaction. In the synthesis of dimethyl sulfomycinamate (**54**), (Fig. (**2**)), a thiopeptide antibiotic, Kelly *et al.* planned construction of the oxazolyl-pyridine bond by Stille coupling [26, 33]. As a model study, they fulfilled this task by the reaction of 4-trifloyloxazole **55** and 2-pyridinylstannane, leading to the formation of oxazolylpyridine **56** in good yield, (Scheme (**16**)). In extending this research, they were interested in the reactivity of 5-trifloyloxazole **39**. However, they could not obtain any coupling product from **39** because of decomposition of **39** to **38** under the reaction condition.

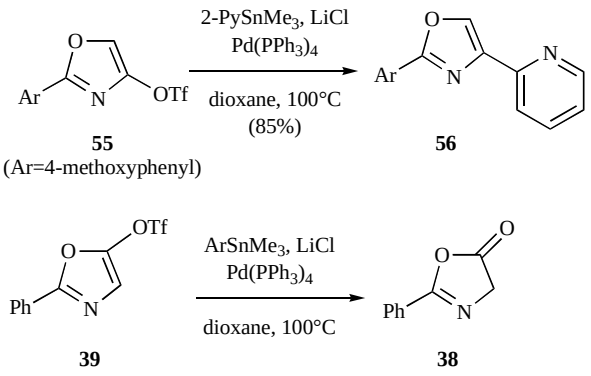


Scheme 15.



dimethyl sulfomycinamate (**54**)

Fig. (2).



Scheme 16.

Harran *et al.* implemented Stille reaction between 5-bromooxazole **57** and vinylstannane in the presence of $PdCl_2(MeCN)_2$ to produce the desired coupling product **58** in their initial efforts for diazonamide synthesis, (Scheme (**17**)) [34].

In phorboxazole A synthesis, Smith's group demonstrated an excellent coupling reaction using complex substrates [35]. They elaborated a carbon-carbon bond of the 4-vinyloxazole moiety in **61** by the reaction of 4-trifloyloxazole **59** and vinylstannane **60**, (Scheme (**18**)). While they obtained a low yield (20%) of the desired product in the case of using Pd_2dba_3 as a catalyst, after extensive exploration they eventually found the appropriate condition [$Pd(PPh_3)_4$ and excess LiCl in dioxane], producing a 72% yield of **61**. In addition, several other groups also reported Stille reaction of halo- and trifloyloxaozles to synthesize the valuable compounds [36-38].

3-3. Suzuki-Miyaura Coupling

3-3-1. Reaction of oxazol-2-ylboranes

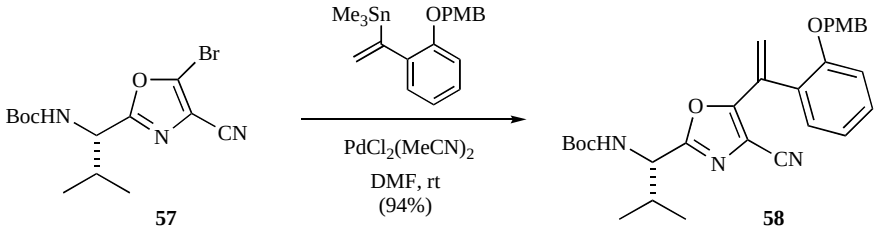
Only one example of oxazol-2-ylboronic acid **10** has been disclosed, which was allowed to react with 5-bromooxazole **34** under the normal reaction condition [$Pd(PPh_3)_4$, Na_2CO_3, THF] to afford bis-oxazole **62**, (Scheme (**19**)) [14]. Repeating two-step procedure (bromination at the C-5 position with NBS and coupling reaction with **10**) four times gave rise to hexakis-oxazole **63**.

3-3-2. Reaction of oxazol-4-ylboranes

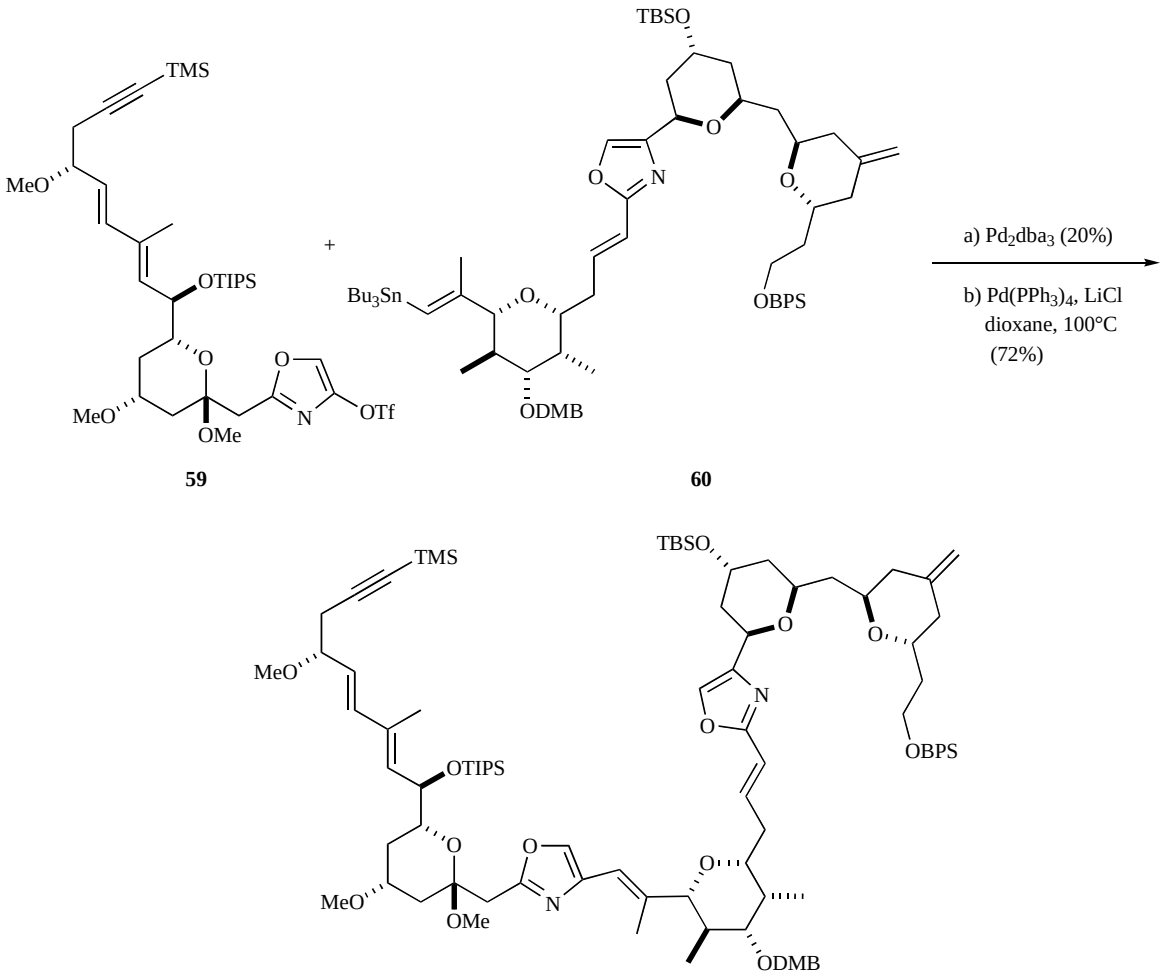
Our group has reported that the palladium catalyzed reaction of oxazol-4-ylboronates such as **14** with a wide variety of aryl halides gave rise to 4-(hetero)aryloxazoles under the normal reaction condition [$Pd(PPh_3)_4$, K_2CO_3, DMF, 100°C] in moderate to good yields [17]. By applying this method, we examined the synthesis of the hexakis-oxazole moiety in telomestatin (**64**), a natural telomerase inhibitor, (Fig. (**3**)). We have developed a two-step iterative method for C2-C4' linked poly-oxazole synthesis including TBS-iodine exchange reaction and Suzuki-Miyaura cross-coupling reaction with the common boronate **65**, where we efficiently achieved a short synthesis of tris-, tetrakis- pentakis- and hexakis-oxazoles (**66**, **69**, **67**, and **70**), Scheme (**20**) [39]. Greaney *et al.* also examined to generate oxazol-4-ylboronates, which were used *in situ* for the microwave-accelerated Suzuki-Miyaura reaction [$PdCl_2(PPh_3)_2$, K_2CO_3, dioxane, μw, 150°C] [13].

3-3-3. Reaction of oxazol-5-ylboranes

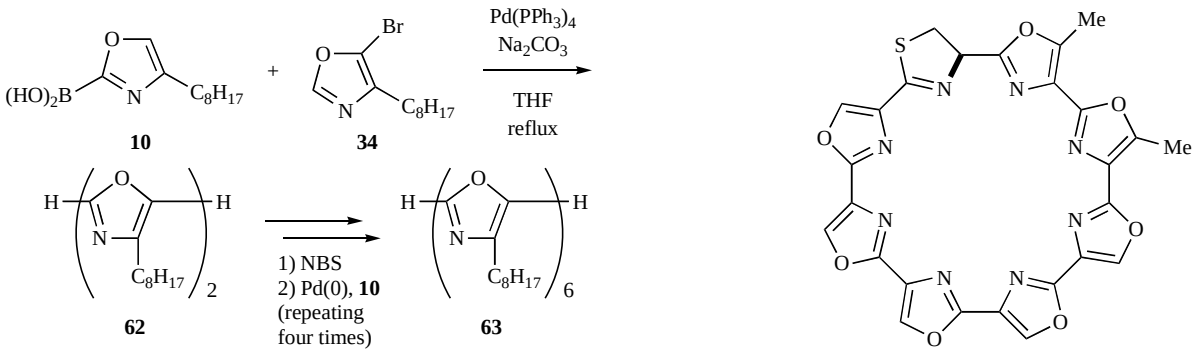
We observed that oxazol-5-ylboronic acid **18** is stable under Ar at 0°C for a prolonged time, however, **18** is gradually decomposed under an aqueous and/or basic condition to give the protodeborylated product. Due to its chemical instability we required to find the adequate reaction condition for **18** [20]. After extensive investigations, we found under the optimal condition [$Pd_2(dba)_3$ (5 mol%), P(*t*-Bu)$_3$ (15 mol%),



Scheme 17.



Scheme 18.



Scheme 19.

telomestatin (**64**)

Fig. (3).

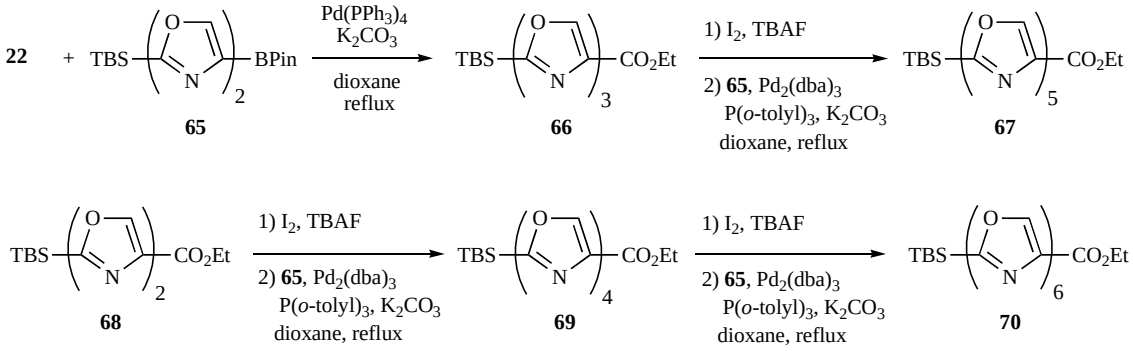
Na_2CO_3 (3 eq.), DMF, 100°C], the reaction of **18** with several aryl halides proceeded to give 5-aryloxazoles, (Scheme (**21**)).

3-3-4. Reaction of halo- and trifloyloxazoles with organoboranes

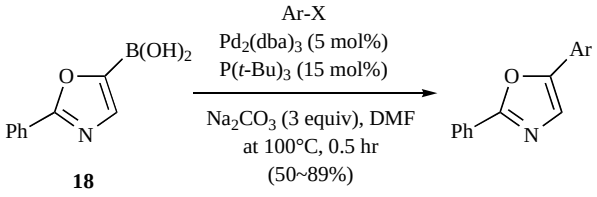
Hodgetts *et al.* examined the reaction of the halogenated oxazoles (**22**, **33**, and **37**) with phenylboronic acid upon the same condition [$Pd(PPh_3)_4$, aq. K_2CO_3, 90°C] in Scheme (**22**) [21]. Greaney *et al.* also disclosed a carefully optimization of the reaction of 2-phenyl-4-trifloyloxazoel **31** with several arylboronic acids, in which microwave heating was a key process to perform the reaction [13]. They also attempted the coupling reaction of 2-trifloyloxazole **25** in the same manner, but **25** was quite unstable and decomposed immediately at high temperature. Other groups also utilized Suzuki reaction to synthesize the biological active compounds [37, 40-42].

3-4. Sonogashira Coupling

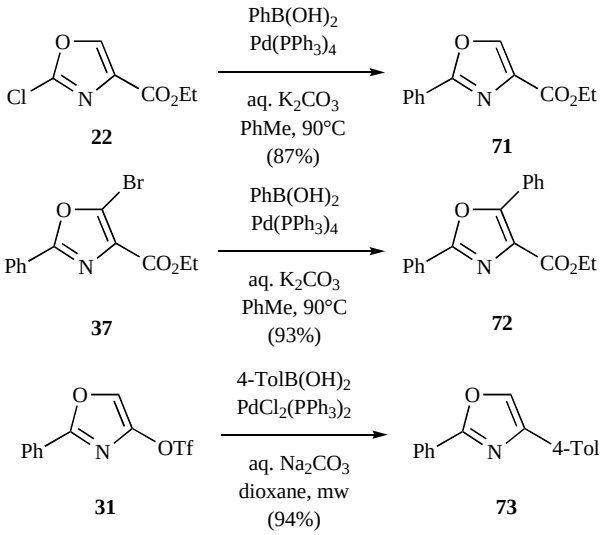
Yamanaka *et al.* first reported the Sonogashira coupling of oxazoles in 1987 [43]. 4-Bromo-2-methyl-5-phenyloxa-



Scheme 20.



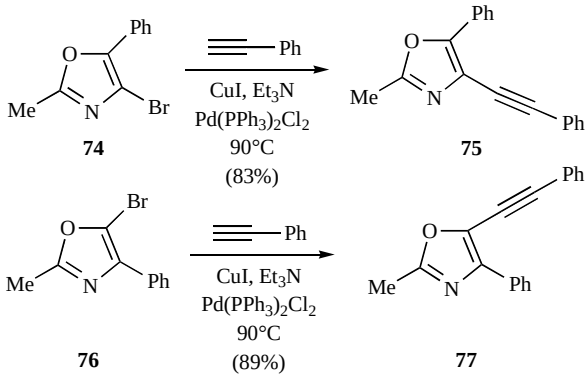
Scheme 21.



Scheme 22.

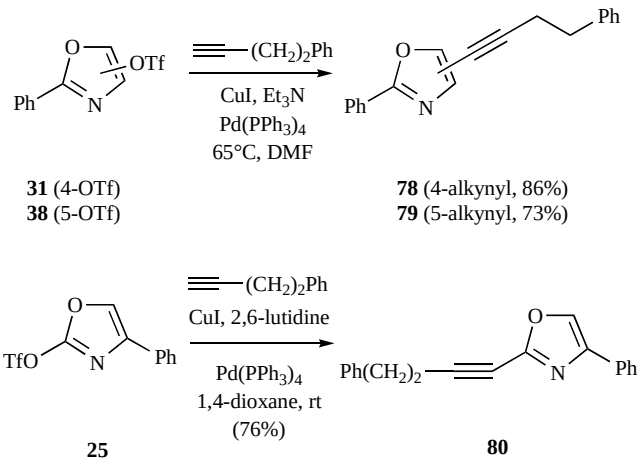
zole (**74**) and 5-Bromo-2-methyl-4-phenyloxazole (**76**) were allowed to react with phenylacetylene in the presence of CuI, Et_3N and $Pd(PPh_3)_2Cl_2$, leading the coupling products (**75** and **77**) in 83 and 89% yield, respectively, (Scheme (**23**)).

Panek *et al.* carefully investigated the reaction condition of 2-, 4- and 5-trifloyloxazoles (**25**, **31**, and **38**) as shown in Scheme (**24**) [44]. Heating around 65°C and the choice of copper salt are essential to complete the reaction. The order of the reactivity is CuI>CuBr>$(MeCN)_4CuPF_4$≅CuCl. Under the optimal condition [CuI, Et_3N, $Pd(PPh_3)_4$, DMF at 65°C, 24h], the reaction of **31** and **38** proceeded cleanly without any detection of the side product such as a homodimer of acetylene. However, subjection of 2-trifloyloxazole **25** to this condition yielded only 2-oxazolone **24**. Since this same phenomenon was observed as stirring of **25** with Et_3N at room temperature, they were prompted to screen the reaction conditions. After exploring several amines, they finally dis-



Scheme 23.

covered the appropriate amine, 2,6-lutidine. Under the improved condition [5 mol% of $Pd(PPh_3)_4$, 10% of CuI, 5 eq. of 2,6-lutidine, 0.1 M in 1,4-dioxane at room temperature), **25** was cleanly converted to the desired product **80** in 76% yield. They applied this condition to synthesize leucascandrolide A [45, 46]. As well as other cross-coupling reactions, Hodgetts *et al.* demonstrated the Sonogashira reaction of the halogenated oxazoles (**22**, **33**, and **37**) with phenylacetylene [21]. While the 4- and 5-phenylethynyloxazole derivatives were cleanly obtained in nearly 80% yield under the same condition [$Pd(PPh_3)_2Cl_2$, CuI, Et_3N, 80°C], the reaction of 2-chlorooxazole derivative **22** gave no coupling product.



Scheme 24.

CONCLUSIONS

The transition-metal-catalyzed cross-coupling reactions (Negishi, Stille, Suzuki-Miyaura, and Sonogashira reactions) of oxazoles are reviewed in this article. All cross-coupling reactions have been reported in recent two decades. While some difficulties still remain in this area, it is obvious to say that considerable progress in chemistry of oxazoles has been made with these cross-coupling reactions.

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Received: February 10, 2008 **Revised: February 25, 2008** **Accepted: February 25, 2008**