ANNULATION OF 2-ALKYNYLBENZAMIDES: THE VERSATILE CHEMICAL COMPOUNDS

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Abstract. *2-Alkynylbenzamides as versatile substrates have been widely used as precursors for the synthesis of nitrogen and oxygen atoms containing heterocycles. The focus of this mini-review is on the introduction of 2-alkynylaniline and its derivatives in the synthesis of five-, six-, and seven-membered heterocycles including indoles, fused indoles, isoindolinones, benzoisofurans, isochromens, isocoumarins, isoquinolines, isoquinolinones, quinolones, and azepinones.*

Contents

1. Introduction

The annulation reaction of alkynyl containing compounds has been frequently utilized in synthetic strategies as an intriguing technique for the production of various heterocyclic backbones.[1-4] Literature surveys shows some critical review article discussing about application of alkynyl structures in synthetic routes. He *et al.* published a critical evaluation of 2-alkynylbenzaldoximes reactivity in the synthesis of nitrogen-including heterocycles in 2014.[5] Moreover, siloxyalkynes were considered a class of reactive substances in organic synthesis.[6] In 2018, the role of 2-alkynylarylaldehydes were examined in heterocyclization reactions and described the mechanisms that result in the production of the target products were described.[7] Furthermore, electrochemical intramolecular and intermolecular cyclization of different alkynes has also been studied.[8]

2-Alkynylbenzamides are also useful building blocks for the annulation processes that lead to a variety of heterocycles. Since multifunctional substrates can be produced and employed for the formation of precursors and structures having diverse functional groups, greatly increasing attentions have been focused on the cyclization potency of these compounds, through noble processes.[9-11] Tautomerization of 2-alkynylbenzamide provides three reactive sites on its structure (Figure 1): 1) alkyne group which plays the main role in cyclization reactions, 2) oxygen atom of amide moiety which can form benzofuran and isochromene cores, 3) nitrogen atom of amide moiety which is cyclised to indole, isoindolinone, and isoquinolinone cores. By the use of additional chemical compounds and reagents, other types of heterocyclic structures are formed which are discussed in this mini-review.

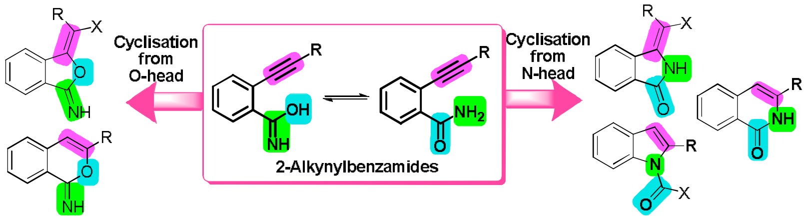
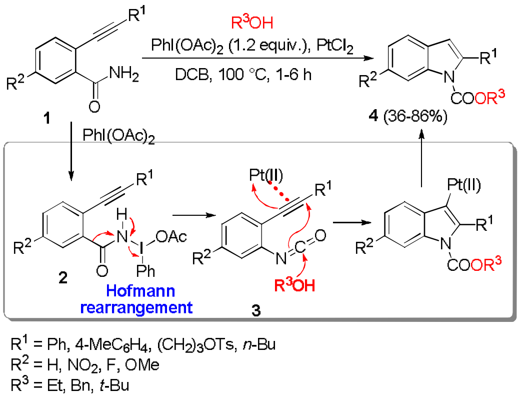


Figure 1. The effect of 2-alkynylbenzamides' functional groups in cyclization reaction.

2. Annulation reaction of 2-alkynylbenzamides

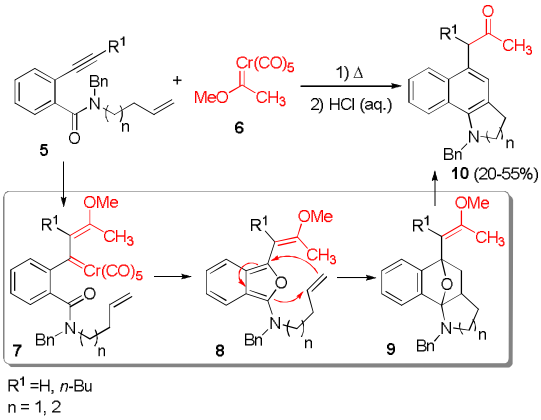
2.1. Synthesis of five-membered heterocycles

The Pt(II)-catalyzed reaction of 2-alkynylbenzamides **1** with alcohols in dichlorobenzene (DCB) as solvent led to the formation of indole carbamates (Scheme 1). This synthesis probably started from the reaction of **1** with $PhI(OAc)_2$ to give adduct **2** which undergoes Hofmann-type rearrangement. Nucleophilic addition of alcohol to the formed isocyanate intermediate **3** affords the target product **4**. The main achievement of this synthesis is its scope that can be diversified by the use of various amides and different alcohols, Wittig reagents, and amines, as nucleophiles to obtain carbamates, ureas, and carbamoyl-stabilized ylides of indoles and isoquinolines.



Scheme 1. Synthesis of indole carbamates.

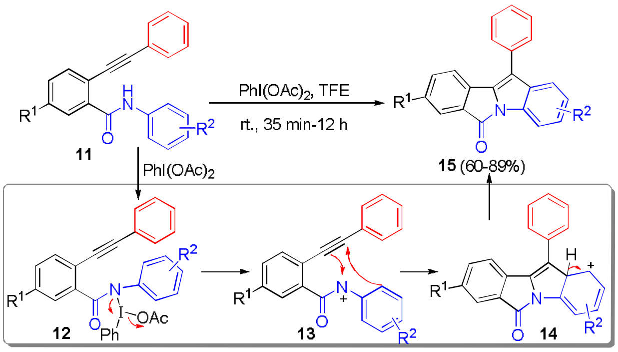
Coupling reaction of 2-alkynylbenzamides **5** with Fischer carbene **6**[12,13] gives tetrahydrobenzo[*g*]quinoline or tetrahydrobenzo[*h*]indole compounds **10**. The progress of this reaction relies on the sequential cascade coupling reaction furnishing **7**, intramolecular Diels-Alder reaction to give intermediate **8**, and finally dehydration of **9** in acidic medium to achieve the target product **10** (Scheme 2).[14]



Scheme 2. Synthesis of tetrahydro benzo[*g*]quinoline and benzo[*h*]indole compounds.

A $PhI(OAc)_2$-promoted intramolecular oxidative cyclization reaction was designed to produce 11-phenyl-6*H*-isoindolo[2,1-*a*]indol-6-ones **15**. Starting from *N*-aryl-2-(1-phenylethynyl)benzamides **11**, $PhI(OAc)_2$ gives its *N*-iodoamido species **12** which releases acetic acid, phenyl iodide, and nitrenium ion **13**.

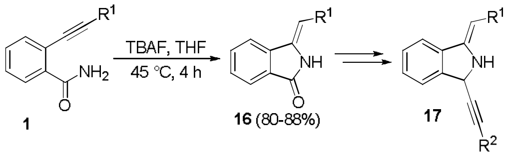
Intramolecular cascade cyclization of the latter followed by aromatization of **14** leads to the formation of target product **15** in good to high yields (Scheme 3).[15]



R^1 = H, NO$_2$
R^2 = 4-Et, 3,4-Me$_2$, 2,4-Me$_2$, 2,6-Me$_2$, 3-OMe, 4-Cl

Scheme 3. Synthesis of isoindolo[2,1-*a*]indol-6-ones.

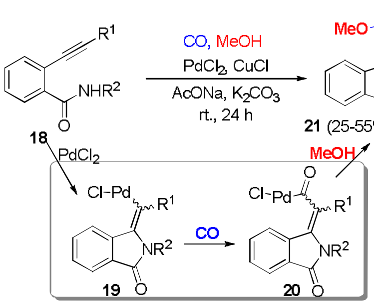
1*H*-Isoindole derivatives **16** were efficiently preprared through intramolecular cyclization of 2-alkynylbenzamides **1** in the presence of tetra-*n*-butylammonium fluoride (TBAF). Then, products **16** were tolerated two-step modification reactions to achieve isoindoles **17** (Scheme 4).[16]



R^1 = H, Ph, 4-MeOC$_6$H$_4$, 4-NCC$_6$H$_4$
R^4 = Ph, TIPS, 4-MeOC$_6$H$_4$, 4-NCC$_6$H$_4$

Scheme 4. Synthesis of 1*H*-isoindole.

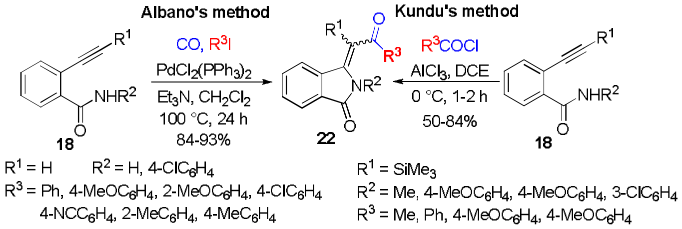
The Pd-catalyzed sequential cyclization/carbonylation of 2-alkynylbenzamides **18** with carbon monoxide and methanol gave 3-alkylidenisoindolinones **21** (Scheme 5). The progress of reaction started from Pd-promoted cyclization of 2-alkynylbenzamides **18** furnishing Pd-containing intermediate **19**. The latter reacts with carbon monoxide to generate acylpalladium species **20**. Nucleophilic attack of methanol to this intermediate leads to the target product **21**, while Pd(0) is oxidized in the presence of Cu(I).[17]



R^1 = Ph, Bu
R^2 = H, Me

Scheme 5. Synthesis of 3-alkylidenisoindolinones.

2-Alkynylbenzamides **18** can be converted to 3-alkylideneisoindolin-1-ones **22** *via* two reported methods (Scheme 6). The method described by Albano *et al.* includes cyclocarbonylative Sonogashira reaction of **18** with aryl iodide under CO pressure in the presence of $PdCl_2(PPh_3)_2$ as catalyst; this reaction showed high stereoselectivity toward *E*-isomer.[18] The method developed by Kundu and Khan suggests the use of acyl chlorides through Friedel-Crafts acylation and cyclization to five *Z*-3-alkylideneisoindolin-1-ones.[19]

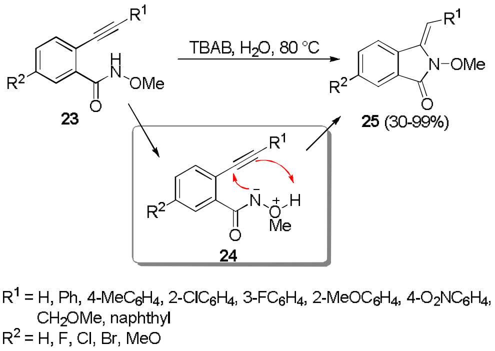


R^1 = H R^2 = H, 4-ClC_6H_4
R^3 = Ph, 4-$MeOC_6H_4$, 2-$MeOC_6H_4$, 4-ClC_6H_4
4-NCC_6H_4, 2-MeC_6H_4, 4-MeC_6H_4

R^1 = $SiMe_3$
R^2 = Me, 4-$MeOC_6H_4$, 4-$MeOC_6H_4$, 3-ClC_6H_4
R^3 = Me, Ph, 4-$MeOC_6H_4$, 4-$MeOC_6H_4$

Scheme 6. Synthesis of 3-alkylideneisoindolin-1-ones.

N-Methoxy-2-alkynylbenzamides **23** was converted to *N*-methoxyisoindolinones **25** in the presence of phase tranfer catalyst tetrabutylammonium bromide (TBAB). In this reaction, a hydrogen migration occurred from NH to methoxy furnishing intermediate **24** and the target product is formed from 5-*exo* cyclization reaction (Scheme 7).



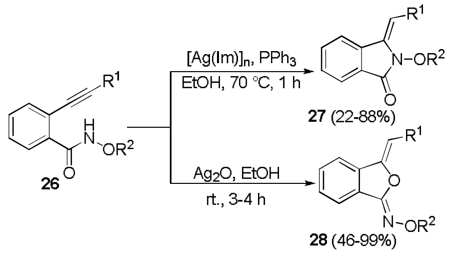
R^1 = H, Ph, 4-MeC_6H_4, 2-ClC_6H_4, 3-FC_6H_4, 2-$MeOC_6H_4$, 4-$O_2NC_6H_4$,
CH_2OMe, naphthyl
R^2 = H, F, Cl, Br, MeO

Scheme 7. Synthesis of *N*-methoxyisoindolinones.

Some products were obtained as pure *Z*-isomer, while the other ones were a mixture of *Z*/*E* isomers with higher percentage of *Z*. By replacing methoxy with OAc, aryl, alkyl, and hydrogen, no favorable product was obtained.[20] *N*-Alkyl-2-alkynylbenzamides was also examined in this reaction furnishing *N*-alkylisoindolinones in the presence of $CuCl_2$ as catalyst and carbonate as base,[21,22] or $Pd(OAc)_2$.[23] Kanazawa and Tereda used P_4-*t*-Bu (shown in Scheme 9) as an organic superbase catalyst to control *Z*/*E* regioselectivity of the product.[24] Bantreil *et al.* found that silver imidazolate polymer, [Ag(Im)]n, in the presence of PPh_3 can regioselectively convert *N*-alkoxy-2-alkynylbenzamides **26** to the corresponding *N*-alkoxyisoindolinones **27**; while catalyzing the reaction with Ag_2O led to the occurance of cycloisomerization furnishing isobenzofuran-1-one oximes **28** (Scheme 8).[25]

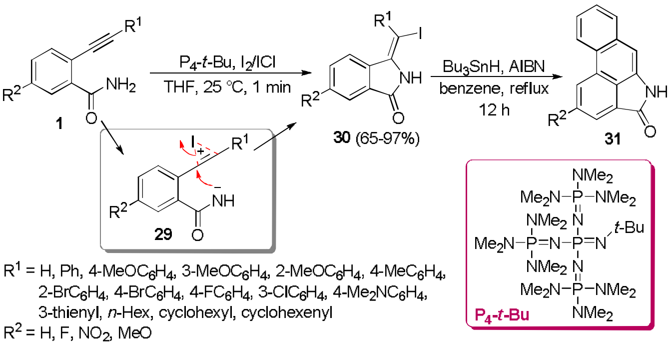
Iodoaminocyclization of compound **1** was promoted by phosphazene superbase P_4-*t*-Bu passing from intermediate **29** to access *Z*-geometry of 3-alkylidenisoindolinones **30** in good to excellent yields.[26] Then the products was used as substrate for the preparation of natural product aristolactams **31** (Scheme 9).[26,27] Synthesis of product **30** was also examined in the presence of *n*-BuLi and I_2/ICl and the yields were moderate to high (41-94%).[28]

3-Hydroxyisoindolin-1-ones **35** were synthesized through metal-free hydroxylhydrative aza-cyclization of 2-alkynylbenzamides **18** by the use of TBAB, oxone, 1,4-dioxane, and moisture. This reaction passes from radical intermediates of Br$^•$ and 1,4-dioxane to give intermediate **32**. Again Br$^•$ attacks regioselectively to the latter furnishing dibromide radical **33** which is converted to hydroxylated adduct **34**. Target product **35** is formed *via* final hydrolysis process (Scheme 10).[29]



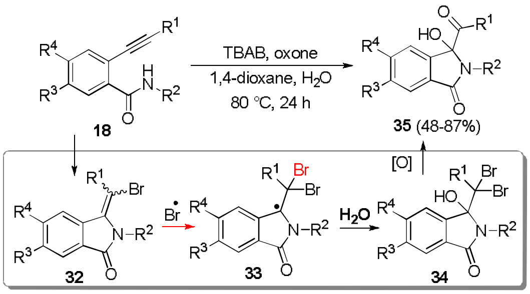
R^1 = H, Ph, 4-MeC$_6$H$_4$, CH$_2$OMe, CH(OH)Me, CH$_2$OH, TMS, *n*-Bu
R^2 = Me, Bn

Scheme 8. Silver-catalyzed reaction of *N*-alkoxy-2-alkynylbenzamides.



R^1 = H, Ph, 4-MeOC$_6$H$_4$, 3-MeOC$_6$H$_4$, 2-MeOC$_6$H$_4$, 4-MeC$_6$H$_4$, 2-BrC$_6$H$_4$, 4-BrC$_6$H$_4$, 4-FC$_6$H$_4$, 3-ClC$_6$H$_4$, 4-Me$_2$NC$_6$H$_4$, 3-thienyl, *n*-Hex, cyclohexyl, cyclohexenyl
R^2 = H, F, NO$_2$, MeO

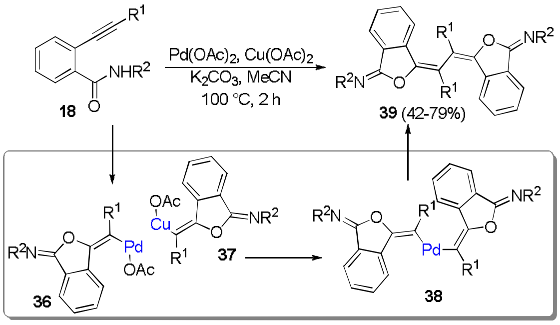
Scheme 9. Synthesis of *Z*-geometry of 3-alkylidenisoindolinones.



R^1 = H, Ph, 4-MeC$_6$H$_4$, 2-ClC$_6$H$_4$, 4-FC$_6$H$_4$, 2-thienyl
R^3 = H, F, Cl, Br, MeO R^4 = H, Me

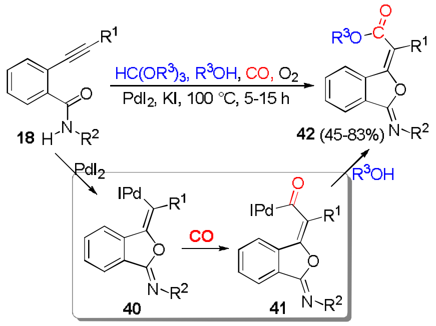
Scheme 10. Synthesis of 3-hydroxyisoindolin-1-ones.

Athough 2-alkynylbenzamides could be converted to isoindolinones through nucleophilic addition from its nitrogen atom head, they can also annulated from oxygen atom of the carbonyl group depending on the reaction conditions and the nature of employed nucleophile; examples of such *O*-cyclization are described in the following. A Pd (OAc)$_2$/Cu(OAc)$_2$ co-catalyzed 5-*exo-dig* oxy-cyclizative dimerization of 2-alkynylbenzamides **18** was performed to give bis-iminobenzoisofurans **39**. This reaction occurs *via* transmetalation between vinylpalladium **36** and vinyl-Cu(II) **37** intermediates furnishing adduct **38** which upon reductive elimination gives Pd(0) and the cyclizative dimer **39** (Scheme 11).[30]



Scheme 11. Synthesis of bis-iminobenzoisofurans.

Upon Pd(II)-catalyzed oxidative carbonylation conditions, annulated intermediate **40** is formed from **18** and subsequently gives adduct **41** by carbon monoxide insertion. An external alcohol, methanol or ethanol, then attacks the carbonyl group as nucleophile to give isobenzofuran-1(3*H*)-imine **42** together with Pd(0) and HI. (Scheme 12).[31] Pd(0) is finally oxidized back to Pd(II) by the action of the external oxidant (molecular oxygen). In this reaction, trialkyl orthoformate plays a vital role as dehydrating agent to avoid the hydrolysis of intermediates.



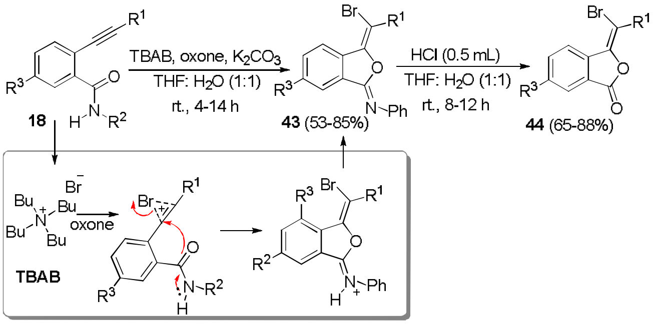
R^1 = H, Ph, *n*-Bu, cyclohexyl
R^2 = Ph, *n*-Bu, *t*-Bu
R^3 = Me, Et

Scheme 12. Synthesis of isobenzofuran-1(3*H*)-imines.

TBAB can promote 5-*exo-dig* oxy-cyclization of 2-alkynylbenzamides **18** in the presence of oxone under basic medium to give isobenzofuran-1-imines **43**. This reaction proceeds through the formation of bromonium cation and cyclization of substrate from oxygen atom.[32] Upon hydrolysis of **43**, isobenzofurans **44** are formed (Scheme 13).[33] Iodide derivatives of these structures were also synthesized in the presence of TBAI.[34,35] Chloride derivatives were prepared by the use of $CuCl_2$ and NCS.[36] Electrochemical approach assisted 5-*exo-dig* oxy-cyclization of 2-alkynylbenzamides **18** was also examined in the presence of cheap sodium halide and good results were obtained with no stoichiometric amounts of oxidants and metal catalyst.[37]

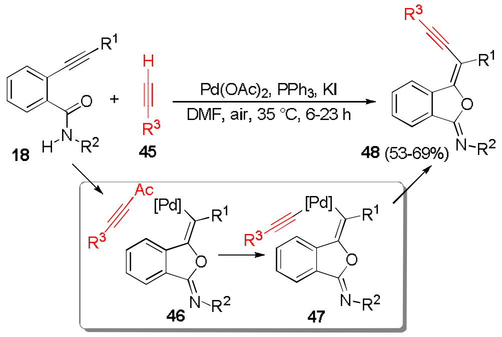
By treating 2-alkynylbenzamides **18** with terminal alkynes **45** in the presence of Pd(II)-catalytic system, a cascade 5-exo *O*-cyclization/Sonogashira coupling takes place through intermediates **46** and **47**, respectively. The result of this reaction is the formation of alkynyl isobenzofuran-1-imines **48** in moderate yields (Scheme 14).[38] Madich *et al.* replaced acrylates with alkynes to construct carbonyl-substituted 3-allylideneisobenzofuran-1-imines.[39-41]

In the Pd(II)-catalyzed cross-coupling reaction of *N,N*-dialkyl-2-alkynylanilines **49** with 2-alkynylbenzamides **18**, a series of isobenzofuran substituted indole structures **53** was prepared (Scheme 15). The reaction mechanism proposed by the author consists in the *anti* aminopalladation (5-*endo-dig*) of substrate **49** to yield **50**, followed by regio- and chemoselective *anti*-5-*exo*-*dig* oxypalladation of the latter to give **51**. *N*-Demethylation through nucleophilic attack of anions followed by reductive elimination from intermediate **52** gives the target product **53**. Cu(II) acts as oxidizing agent to convert Pd(0) to Pd(II).[42]



R^1 = Ph, 4-MeC_6H_4, 3-MeC_6H_4, 4-$MeOC_6H_4$, 2-$MeOC_6H_4$, 4-FC_6H_4, 4-ClC_6H_4, 1-cyclohexyenyl, 2-thiophenyl, *n*-Bu, *t*-Bu, $(CH_2)_2OH$
R^2 = Me, Ph, Bn, allyl, *n*-Bu, *t*-Bu, *n*-$C_{11}H_{13}$
R^3 = H, Me, F, Cl, Br

Scheme 13. Synthesis of isobenzofuran-1-imines and isobenzofurans.



R^1 = H, Ph, *n*-Hex, 4-$MeO_2CC_6H_4$, 4-$MeOC_6H_4$,
R^2 = Ph, *n*-Bu, Bn, 4-$MeOC_6H_4$, 4-ClC_6H_4
R^3 = Ph, 4-$MeOC_6H_4$, cyclohexyl, *n*-Hex, 3-thienyl

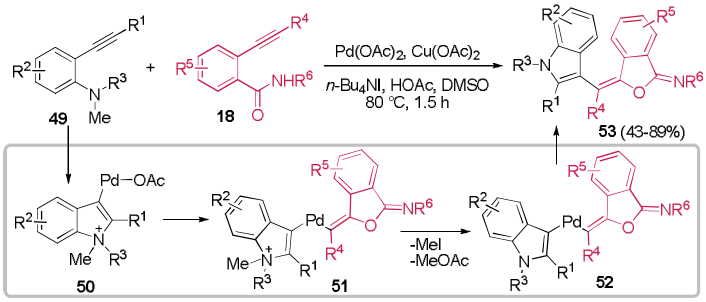
Scheme 14. Synthesis of alkynyl isobenzofuran-1-imines.

2.2. Synthesis of six-membered heterocycles

The 6-*endo*-*dig* *oxy*-cyclization of *N*-phenyl-2-alkynylbenzamides **18** was catalyzed by TBAB and oxone to access functionalized isochromen-1-imines **57**. This reaction is started from formation of bromonium cation **54**, followed by regioselectively 5-*exo*-*dig* *oxy*-cyclization to give intermediate **55**. Protonation of the latter and its rearrangements lead to ring expansion *via* 1.2-oxygen shift and formation of intermediate **56**. Removal of Br group gives rise to the target product **57** (Scheme 16).[43]

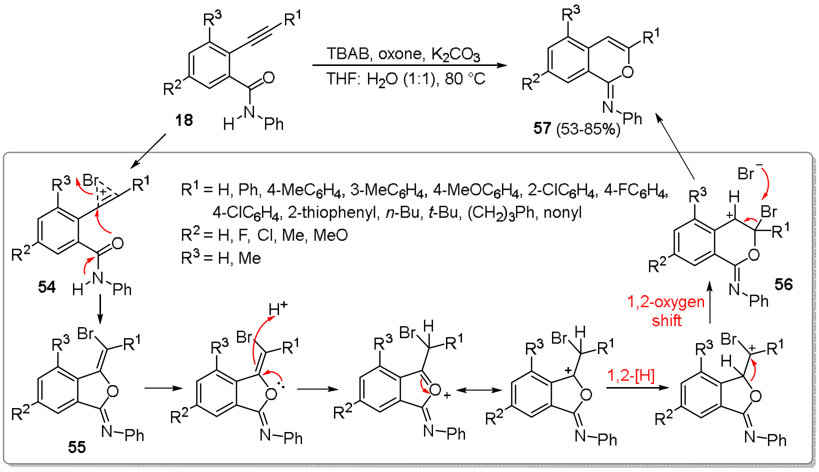
Minami developed this reaction starting from 2-alkynylbenzamides and used diaryliodonium salts as alkylating agent to achieve *N*-aryl-2-alkynylbenzamides. Cocurrent cocatalysis of this reaction by CuBr promoted the substrate annulation to give products **57**.[44] Neto *et al.* expanded this reaction to access 4-organochalcogenyl-1*H*-isochromen-1-imines through $FeCl_3$-catalyzed reaction of compound **18** with diorganyl dichalcogenides.[45]

In another research, compounds **18** were treated with allyl bromide in the presence of Pd(0) as catalyst and *N*,*N*-diisopropylethylamine (DIPEA) as base. The formation of 4-allylisochromen-1-imines **60** was highly regioselective through 6-*endo*-cyclization of intermediate **58** and C–C coupling reaction passing from adduct **59** (Scheme 17).[46] This reaction was also catalyzed by $Cu(TFA)_2$ and the yield of products was good to high (52-90%).[47] Madich *et al.* replaced acrylaldehyde with allyl bromide and catalyzed the reaction by $PdCl_2$ to achieve 4-(butan-2-one)-isochromen-1-imines; the yields were good to excellent (76-97%).[48] Hydrolysis of compound **60** under acidic condition leads to the formation of 4-allyl substituted isocoumarins showing PDE4 inhibitor activities.[49]



R^1 = Ph, 4-MeC_6H_4, 4-FC_6H_4, *n*-Hex, $CH_2CH_2CONHPh$
R^2 = H, 5-Me, 6-Cl, 6-OMe (in indole ring)
R^3 = Me, *n*-Pentyl
R^4 = Ph, 4-MeC_6H_4, 4-FC_6H_4
R^5 = H, 7-Me, 7-MeO, 6-Cl, 6-Me, 5-Cl, 5-MeO (in isobenzofuran ring)
R^6 = Bn, *n*-Pr, *n*-Bu, *i*-Bu

Scheme 15. Synthesis of isobenzofuran substituted indole structures.

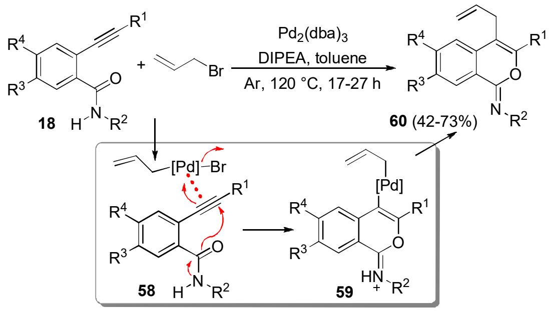


R^1 = H, Ph, 4-MeC_6H_4, 3-MeC_6H_4, 4-$MeOC_6H_4$, 2-ClC_6H_4, 4-FC_6H_4, 4-ClC_6H_4, 2-thiophenyl, *n*-Bu, *t*-Bu, $(CH_2)_3Ph$, nonyl
R^2 = H, F, Cl, Me, MeO
R^3 = H, Me

Scheme 16. Synthesis of isochromen-1-imines.

Microwave-assisted 6-*endo*-cyclization/hydrolysis of 2-alkynylbenzamides **1** was promoted by triflic acid (TFA) to obtain isocoumarins **61** (Scheme 18). This methodology could be applied to a variety of 1,2-alkynyl-carboxamides, including 3-(ethynyl)indole-2-carboxamides, piperanol tethered benzamides, and 3-ethynylnaphthalene-2-carboxamides.[50] Inspired by this method, Vong *et al.* designed a 2-alkynylbenzamide prodrug for the gold-triggered release of secondary amine including drug under physiological conditions.[51]

1-Aminoisoquinolines **65** can be produced through annulation of 2-alkynylbenzamides **18** in the presence of the Au(III)/$AgSbF_6$ catalytic system to give intermediate **62**. Nucleophilic addition of ammonia, obtained from ammonium acetate, to the latter led to the ring opening of intermediate **63**. Finally, intramolecular addition of secondary amino group of **64** to carbonyl furnishes enamine after dehydration process (Scheme 19).[52,53]

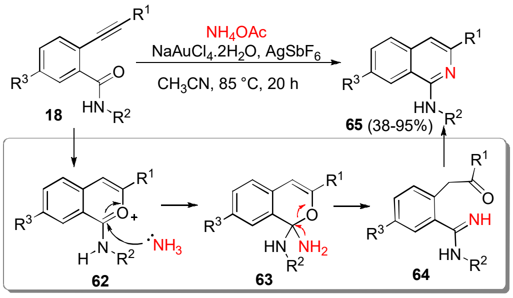


R^1 = Ph, 4-MeOC$_6$H$_4$, *n*-Hex
R^2 = Ph, *n*-Bu, 4-MeOC$_6$H$_4$
R^3 = H, MeO, Cl
R^4 = H, MeO

Scheme 17. Synthesis of 4-allyl-isochromen-1-imines.

R^1 = H, Ph, 4-MeOC$_6$H$_4$, 4-MeOC$_6$H$_4$, 3-FC$_6$H$_4$, Et, Me, *n*-Bu
R^2 = H, MeO R^3 = H, MeO, F R^4 = H, NO$_2$

Scheme 18. Synthesis of isocoumarins.

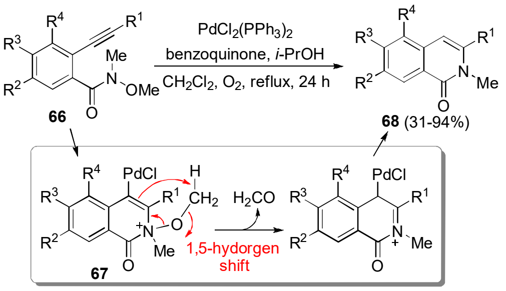


R^1 = Ph, 4-MeO$_2$CC$_6$H$_4$, 4-MeOC$_6$H$_4$, 4-F$_3$CC$_6$H$_4$ *n*-Hex, thienyl, 1-cyclohexen, (CH$_2$)$_3$CN, (CH$_2$)$_{12}$CH$_3$, *t*-Bu, naphthyl
R^2 = H, Ph, *n*-Bu, *n*-Pr
R^3 = H, MeO, Cl R^4 = H, MeO

Scheme 19. Synthesis of 1-aminoisoquinolines.

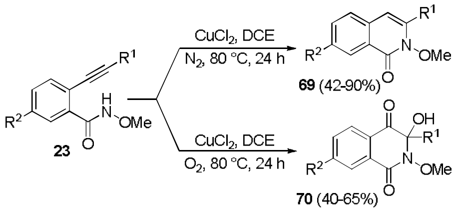
Jithunsa *et al.* synthesized isoquinolinone compounds **68** through a Pd(II)-catalyzed cyclization of *N*-alkoxy-*N*-methyl-2-alkynylbenzamides **66** (Scheme 20). Deuterium-labeling studies showed that the formation of product **68** occurred through the formation of intermediate **67** followed by 1,5-hydrogen shift and elimination of formaldehyde.[54]

Liu *et al.* found that by replacing *N*-alkoxy-2-alkynylbenzamides with compounds **23**, and with the use of CuCl$_2$ as catalyst under inert atmosphere, *N*-alkoxyisoquinolinones **69** are formed, while 3-hydroxylisoquinolin-1,4-diones **70** are obtained under air (Scheme 21).[55] Yang *et al.* reported the highly efficient synthesis of compound **70** using PhI(OCOCF$_3$)$_2$ under metal-free medium of MeCN/H$_2$O.[56]



R^1 = n-Bu, cyclohexyl, Ph, 4-FC_6H_4, 4-MeC_6H_4, 4-$MeOC_6H_4$
R^2 = H, Me, MeO, F, Cl
R^3 = H, Cl, F R^4 = H, Me

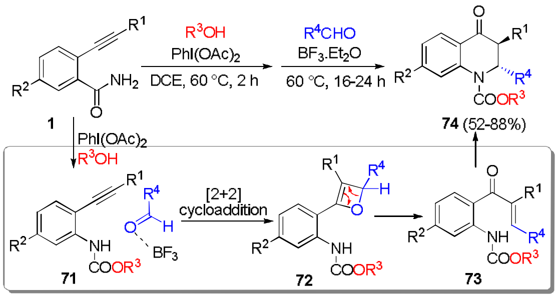
Scheme 20. Synthesis of isoquinolinones.



R^1 = Ph, 2-ClC_6H_4, 4-ClC_6H_4, 4-FC_6H_4, 3-FC_6H_4, 4-$O_2NC_6H_4$
2-$MeOC_6H_4$, 4-$MeOC_6H_4$, 4-MeC_6H_4, 2-naphthyl, 2-thiophenyl
R^2 = H, Br, Cl, F, OMe, Me

Scheme 21. Synthesis of *N*-methoxy isoquinolinones and 3-hydroxylisoquinolin-1,4-diones.

Inspired by their previous research achievement as shown in Scheme 1, Okamoto *et al.* designed a one-pot synthetic route starting from the reaction of compound **1** with alcohol and $PhI(OAc)_2$ followed by the treatment of carbamate intermediate **71** with aldehyde to give 4-quinolones **74**. In the second step of this reaction, BF_3 catalyzes [2+2]-cycloaddition of C≡C to C=O furnishing oxetene **72**. Heat-promoted rearrangement of the latter gives α,β-unsaturated carbonyl intermediate **73** which is annulated to the target product **74** in the presence of BF_3 (Scheme 22). Both aromatic and aliphatic alcohols and aldehydes gave good results.[57]

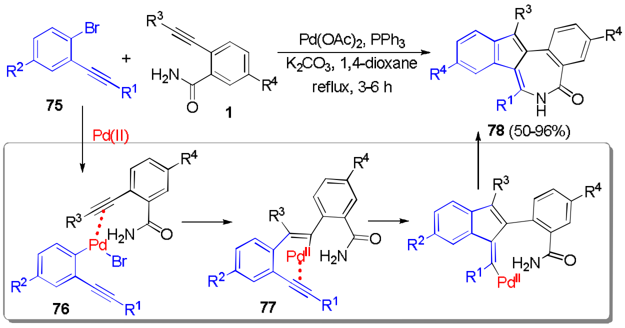


R^1 = H, Ph, n-Bu
R^2 = H, NO_2, F, OMe
R^3 = Et, Bn, t-Bu
R^4 = Cyclohexyl, n-Hex,Ph, 2-MeC_6H_4, 3-MeC_6H_4,
4-MeC_6H_4, 4-NCC_6H_4, 4-FC_6H_4, 4-$O_2NC_6H_4$

Scheme 22. Synthesis of 4-quinolones.

2.3. Synthesis of seven-membered heterocycles

Luo and Wu developed a Pd(II)-catalyzed synthetic route for the production of indeno[1,2-*c*]azepin-3(2*H*)-ones **78**. In the presence of catalytic Pd(II), 2-alkynylbromobenzenes **75** would form intermediate **76** which interacts with the triple bond of 2-alkynylbenzamides **1** to give adduct **77**. The second C≡C insertion occurs intramolecularly followed by C-N bond formation to afford the target fused heterocyle **78** in good to excellet yields (Scheme 23).[58]



R^1 = Ph, 4-MeC_6H_4, 4-$MeOC_6H_4$, 4-ClC_6H_4, *n*-Bu
R^2 = H, F, MeO
R^3 = Ph, 4-MeC_6H_4, 4-$MeOC_6H_4$, 4-ClC_6H_4, *n*-Bu
R^4 = H, Me, Cl

Scheme 23. Synthesis of indeno[1,2-*c*]azepin-3(2*H*)-ones.

3. Conclusions

We have reviewed herein the recent development for the production of nitrogen and oxygen atoms containing heterocyclic structures starting from 2-alkynylbenzamides through various cascade reactions. Since intramolecular cyclization can be provoked by the type of the employed catalyst, the cascade reactions of cycloaddition, nucleophilic reaction, and rearrangement could be expected. These introduced methodologies for the preparation of heterocycles can be extensively employed in the design of libraries of bioactive compounds.

References

1. Kardile, R. D.; Chao, T. H.; Cheng, M. J.; Liu, R. S. *Angew. Chem. Int. Ed.* **2020**, *59*, 10396-10400.
2. Xu, M.-Y.; Wang, C.; Jiang, W.-T.; Xiao, B. *Adv. Synth. Catal.* **2020**, *362*, 1706-1711.
3. Wang, L.; Jiang, F.; Gao, X.; Wang, W.; Wu, Y.; Guo, H.; Zheng, B. *Adv. Synth. Catal.* **2021**, *363*, 2066-2070.
4. Liu, X.-Y.; Liu, Y.-L.; Chen, L. *Adv. Synth. Catal.* **2020**, *362*, 5170-5195.
5. He, L.; Nie, H.; Qiu, G.; Gao, Y.; Wu, J. *Org. Biomol. Chem.* **2014**, *12*, 9045-9053.
6. Qian, H.; Zhao, W.; Sun, J. *Chem. Rec.* **2014**, *14*, 1070-1085.
7. Li, L.; Huang, D.; Shi, C.; Yan, G. *Adv. Synth. Catal.* **2019**, *361*, 1958-1984.
8. Sun, K.; Lei, J.; Liu, Y.; Liu, B.; Chen, N. *Adv. Synth. Catal.* **2020**, *362*, 3709-3726.
9. Fathi Vavsari, V.; Ziarani, G. M. *Chem. Heterocycl. Compnd.* **2018**, *54*, 317-319.
10. Golmohammadi, F.; Balalaie, S.; Fathi Vavsari, V.; Anwar, M. U.; Al-Harrasi, A. *J. Org. Chem.* **2020**, *85*, 13141-13152.
11. Fathi Vavsari, V.; Balalaie, S. *Chem. Heterocycl. Compnd.* **2020**, *56*, 404-407.
12. Barluenga, J.; Santamaría, J.; Tomás, M. *Chem. Rev.* **2004**, *104*, 2259-2284.
13. Doetz, K. H.; Stendel Jr, J. *Chem. Rev.* **2009**, *109*, 3227-3274.
14. Ghorai, B. K.; Herndon, J. W. *Organometallics* **2003**, *22*, 3951-3957.
15. Dev, K.; Maurya, R. *RSC Adv.* **2015**, *5*, 13102-13106.
16. Fillmore, B. C.; Price, J.; Dean, R.; Brown, A. A.; Decken, A.; Eisler, S. *ACS Omega* **2020**, *5*, 22914-22925.
17. Kondo, Y.; Shiga, F.; Murata, N.; Sakamoto, T.; Yamanaka, H. *Tetrahedron* **1994**, *50*, 11803-11812.
18. Albano, G.; Giuntini, S.; Aronica, L. A. *J. Org. Chem.* **2020**, *85*, 10022-10034.
19. Kundu, N. G.; Khan, M. W. *Tetrahedron Lett.* **1997**, *38*, 6937-6940.
20. Renzhia, L.; Min, Y.; Guanyinsheng, Q.; Lianpeng, Z.; Yuchao, W.; Jin, L. *Chin. J. Org. Chem.* **2020**, *40*, 2071-2077.

21. Mancuso, R.; Pomelli, C. S.; Raut, D. S.; Marino, N.; Giofrè, S. V.; Romeo, R.; Sartini, S.; Chiappe, C.; Gabriele, B. *ChemistrySelect* **2017**, *2*, 894-899.
22. Tan, J.; Tong, Y.; Chen, Z. *ChemistrySelect* **2018**, *3*, 3886-3890.
23. Kundu, N. G.; Khan, M. W. *Tetrahedron* **2000**, *56*, 4777-4792.
24. Kanazawa, C.; Terada, M. *Chem. Asian J.* **2009**, *4*, 1668-1672.
25. Bantreil, X.; Bourderioux, A. l.; Mateo, P.; Hagerman, C. E.; Selkti, M.; Brachet, E.; Belmont, P. *Org. Lett.* **2016**, *18*, 4814-4817.
26. Mehta, S.; Brahmchari, D. *J. Org. Chem.* **2019**, *84*, 5492-5503.
27. Fathi Vavsari, V.; Balalaie, S. *Curr. Org. Chem.* **2017**, *21*, 1393-1426.
28. Brahmchari, D.; Verma, A. K.; Mehta, S. *J. Org. Chem.* **2018**, *83*, 3339-3347.
29. Liu, R.; Yang, M.; Xie, W.; Dong, W.; Zhou, H.; Yadav, S.; Potkin, V. I.; Qiu, G. *J. Org. Chem.* **2020**, *85*, 5312-5320.
30. Yao, B.; Jaccoud, C.; Wang, Q.; Zhu, J. *Chem. Eur. J.* **2012**, *18*, 5864-5868.
31. Mancuso, R.; Ziccarelli, I.; Armentano, D.; Marino, N.; Giofre, S. V.; Gabriele, B. *J. Org. Chem.* **2014**, *79*, 3506-3518.
32. Chinta, B. S.; Sanapa, H.; Vasikarla, K. P.; Baire, B. *Org. Biomol. Chem.* **2018**, *16*, 3947-3951.
33. Wang, R.-X.; Yuan, S.-T.; Liu, J.-B.; Wu, J.; Qiu, G. *Org. Biomol. Chem.* **2018**, *16*, 4501-4508.
34. Wang, Y.-H.; Liu, J.-B.; Ouyang, B.; Zhou, H.; Qiu, G. *Tetrahedron* **2018**, *74*, 4429-4434.
35. Schlemmer, C.; Andernach, L.; Schollmeyer, D.; Straub, B. F.; Opatz, T. *J. Org. Chem.* **2012**, *77*, 10118-10124.
36. Jithunsa, M.; Ueda, M.; Miyata, O. *Org. Lett.* **2011**, *13*, 518-521.
37. Bhargava Reddy, M.; Peri, R.; Bhagavathiachari, M.; Anandhan, R. *Org. Biomol. Chem.* **2021**, *19*,6792-6796.
38. Cruz, F.; Vaz, B.; Vilar, U.; Ortega, A.; Madich, Y.; Alvarez, R.; Aurrecoechea, J. M. *Organometallics* **2018**, *37*, 3813-3826.
39. Madich, Y.; Álvarez, R.; Aurrecoechea, J. M. *Eur. J. Org. Chem.* **2014**, *2014*, 6263-6271.
40. Okamoto, N.; Takeda, K.; Yanada, R. *J. Org. Chem.* **2010**, *75*, 7615-7625.
41. Okamoto, N. *J. Pharm. Soc. Jpn.* **2013**, *133*, 879-887.
42. Yao, B.; Wang, Q.; Zhu, J. *Angew. Chem. Int. Ed.* **2013**, *125*, 13230-13234.
43. Wang, Y.-H.; Ouyang, B.; Qiu, G.; Zhou, H.; Liu, J.-B. *Org. Biomol. Chem.* **2019**, *17*, 4335-4341.
44. Minami, H.; Sueda, T.; Okamoto, N.; Miwa, Y.; Ishikura, M.; Yanada, R. *Eur. J. Org. Chem.* **2016**, *2016*, 541-548.
45. Neto, J. S. S.; Back, D. F.; Zeni, G. *Eur. J. Org. Chem.* **2015**, *2015*, 1583-1590.
46. Álvarez, R.; Vilar, U.; Madich, Y.; Aurrecoechea, J. M. *Org. Biomol. Chem.* **2017**, *15*, 8594-8605.
47. Wang, R.-X.; Fang, Z.; Qiu, G.; Xie, W.; Liu, J.-B. *Synthesis* **2019**, *51*, 4048-4065.
48. Madich, Y.; Álvarez, R.; Aurrecoechea, J. M. *Eur. J. Org. Chem.* **2015**, *2015*, 6298-6305.
49 Thirupataiah, B.; Mounika, G.; Reddy, G. S.; Kumar, J. S.; Hossain, K. A.; Medishetti, R.; Samarpita, S.; Rasool, M.; Mudgal, J.; Mathew, J. E.; Shenoy, G. G.; Rao, C. M.; Chatti, K.; Parsa, K. V. L.; Pal, M. *Eur. J. Med. Chem.* **2021**, *221*, 113514.
50. Praveen, C.; Dheenkumar, P.; Perumal, P. *J. Chem. Sci.* **2013**, *125*, 71-83.
51. Vong, K.; Yamamoto, T.; Chang, T.-c.; Tanaka, K. *Chem. Sci.* **2020**, *11*, 10928-10933.
52. Long, Y.; She, Z.; Liu, X.; Chen, Y. *J. Org. Chem.* **2013**, *78*, 2579-2588.
53. Yang, W.; Du, Y.; Yi, F.; Cai, M. *J. Chem. Res.* **2021**, *45*, 34-41.
54. Jithunsa, M.; Ueda, M.; Aoi, N.; Sugita, S.; Miyoshi, T.; Miyata, O. *Synlett* **2013**, *24*, 475-478.
55. Liu, R.; Li, M.; Xie, W.; Zhou, H.; Zhang, Y.; Qiu, G. *J. Org. Chem.* **2019**, *84*, 11763-11773.
56. Yang, C.; Zhang, X.; Zhang-Negrerie, D.; Du, Y.; Zhao, K. *J. Org. Chem.* **2015**, *80*, 5320-5328.
57. Okamoto, N.; Takeda, K.; Ishikura, M.; Yanada, R. *J. Org. Chem.* **2011**, *76*, 9139-9143.
58. Luo, Y.; Wu, J. *Chem. Commun.* **2011**, *47*, 11137-11139.