Synthesis J. Yu et al. Short Review

Recent Developments on Denitrogenative Functionalization of Benzotriazoles

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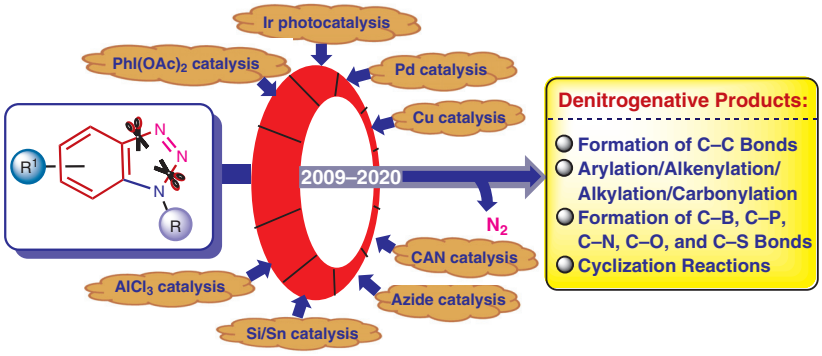
This manuscript is dedicated to the memory of the late Prof. Rolf Huisgen for his notable contributions on triazole chemistry.



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Abstract Benzotriazoles are employed as useful synthons in organic synthesis, and due to their unique structural motif, they are able to undergo denitrogenation during the construction of new bonds. Various methods for the functionalization of benzotriazoles as precursors of *ortho*-amino arenediazoniums have recently been developed that involve transition-metal-catalyzed coupling reactions, mainly via cyclization, borylation, alkenylation, alkylation, carbonylation and the formation of carbon–heteroatom bonds. In this short review, we primarily focus on the recent applications of benzotriazoles in organic chemistry that proceed via a denitrogenative process, and the mechanisms are also discussed.

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2 Common Synthetic Routes Allowing Easy Access to Benzotriazole Derivatives
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Key words benzotriazoles, BtRC, ring cleavage, coupling reactions, denitrogenative functionalization

1 Introduction

1,2,3-Triazoles represent an important class of heterocyclic compounds of significant biological relevance.[1,2] Owing to their unique structural motif, they readily undergo ring–chain isomerization via a Dimroth-type equilibrium to form diazonium or diazo species (Scheme 1, a). In the past decades, numerous novel reactions have been explored on the basis of this unique reactivity. Among these, much progress has been made on the transition-metal-catalyzed diazo reactions of *N*-sulfonyl-substituted 1,2,3-triazoles (Scheme 1, b), which can act as an alternative source of a diazo synthon.[3] Rhodium catalysts have shown high efficacy for this transformation. However, the ring-opening of relatively stable benzotriazoles occurs under harsh conditions, such as thermolysis and photolysis,[4] which for decades has led to poor development.

Transition-metal-catalyzed cross-coupling reactions have emerged as a powerful tool for the construction of carbon–carbon and carbon–heteroatom bonds in organic synthesis,[5] and the application of this strategy to the ring cleavage of benzotriazoles would be of significant value for the synthesis of various nitrogen-containing compounds known for their wide range of pharmacological activities (Scheme 1, c). In 2009, Nakamura and co-workers reported the palladium-catalyzed [3+2]-cycloaddition of *N*-aroylbenzotriazoles with internal alkynes via a denitrogenative process for the synthesis of indole derivatives.[6] This pioneering work encouraged several investigations in the following years into the transition-metal-catalyzed denitrogenative reactions of benzotriazole derivatives as synthetic precursors of *ortho*-amino arenediazoniums, which exhibit fascinating chemistry leading to pharmacologically relevant scaffolds **II**–**XV**, as depicted in Scheme 2. For instance, the transition-metal-catalyzed intermolecular cyclizations of benzotriazoles have been achieved through unsaturated hydrocarbons as coupling partners, such as internal and terminal alkynes, 1,3-dienes, allenes, *N*-allenamides, etc.[6–13] On the other hand, intramolecular cyclizations for the synthesis of benzothiazoles and benzoxazoles have been recently reported by the Tiwari group.[14–21]

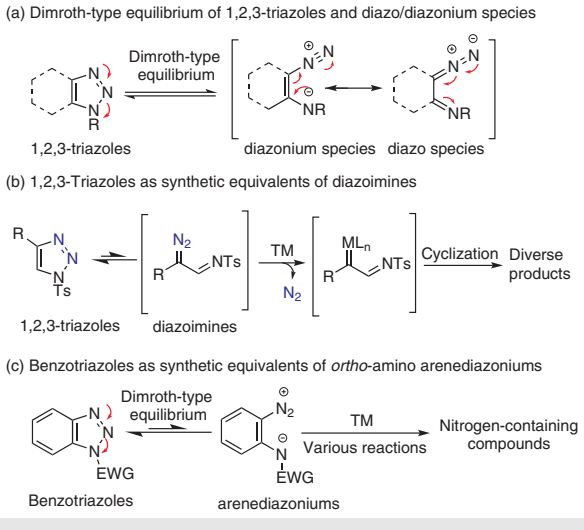
Jie Yu (from left to right) was born in Zhejiang, P. R. of China, in 1999. She obtained her B.Sc. from Lishui University. Her current research interests focus on the transition-metal-catalyzed activation of inert chemical bonds and green synthetic chemistry.

Anoop Shyam Singh was born in Varanasi, Uttar Pradesh, India, in 1986. He obtained his M.Sc. in chemistry (specializing in organic chemistry, 2010) from U. P. College Autonomous Institution, Varanasi, India. He passed his Common Entrance Test (CET, 2012), his Graduate Aptitude Test in Engineering (GATE-2013), and his National Eligibility Test Lectureship (NET, 2013) before beginning his doctoral research. He completed his Ph.D. in 2018 on the 'Development of Novel Synthetic Methodology through Benzotriazole Ring Cleavage' under the guidance of Dr. V. K. Tiwari at the Department of Chemistry at Banaras Hindu University, Varanasi, India. Dr Anoop Singh has contributed significantly to about 20 publications and several book chapters of international repute.

Guobing Yan was born in Jiangxi, P. R. of China, in 1975. He obtained his B.Sc. from Jinggangshan Normal University, his M.Sc. from Suzhou University, and his Ph.D. from Tongji University in 2010. He spent two years between 2008 and 2009 as a visiting student at Professor Jianbo Wang's laboratory at Peking University. In 2013, he joined Professor Guangbin Dong's group at the University of Texas at Austin as a visiting professor and then returned to Lishui University in 2014. Since 2016 he has been a professor at Lishui University. His current research interests focus on the transition-metal-catalyzed activation of inert chemical bonds and green synthetic chemistry.

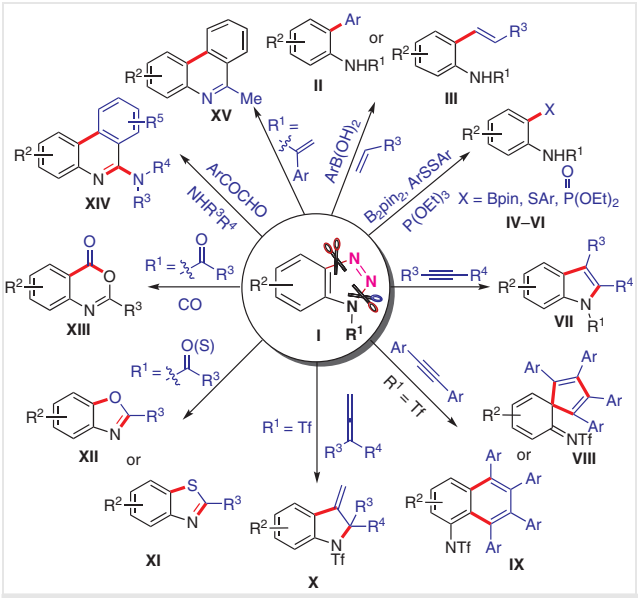
Jian Yu was born in 1979, in Jilin, P. R. of China. He obtained his B.Sc. from Jilin Institute of Technology and his M.Sc. from Changchun University of Technology (China). He joined Lishui University as a lecturer in 2005. His current research interests focus on transition-metal-catalyzed tandem reactions and green synthetic chemistry.

Vinod Kumar Tiwari was born in 1976 in Bihar, India. After completing his M.Sc. at Banaras Hindu University (BHU) in 1998, he passed his CSIR-UGC-NET, GATE, and SET exams, and then undertook doctoral research at the CSIR-Central Drug Research Institute, Lucknow, India (mentor: Dr R. P. Tripathi). This was followed by postdoctoral studies at the University of Florida, USA (mentor: Prof. Alan R. Katritzky), the University of California-Davis, USA (mentor: Prof. Xi Chen), and Universitat Konstanz, Germany (mentor: Prof. Richard R. Schmidt). He was offered the post of lecturer at Bundelkhand University, Jhansi (2004–2005) before being appointed as an Associate Professor of Organic Chemistry at Banaras Hindu University (BHU), India in 2005. With more than 21 years of research and 17 years of teaching experience, Dr. Tiwari has supervised 12 Ph.D. theses (seven are working at present) and has contributed significantly to 142 peer-reviewed publications, several patents and invited book chapters. His research has been recognized with many prestigious honors/awards/medals by the Indian Chemical Society, the Chemical Research Society of India, the Indian Science Congress Association, the Indian Council of Chemists, the UP-Council of Science and Technology, the Association of Carbohydrate Chemists & Technologists of India, Holkar Science College-Indore, and Banaras Hindu University. He has successfully completed 7 major research projects and delivered over 160 invited lectures in India and abroad. His current research focuses on various aspects of carbohydrate chemistry, click chemistry in glycosciences and the development of novel synthetic methodology including benzotriazole ring cleavage (BtRC).



Scheme 1 Ring-opening chemistry of 1,2,3-triazoles and benzotriazoles

In addition, classical cross-coupling reactions of benzotriazoles can also occur under transition-metal catalysis, such as arylation, alkenylation, alkylation and carbonylation.[9,22–24] Tang's group recently presented an overview of the ring-opening chemistry of 1,2,3-benzotriazoles leading to biologically relevant heterocycles and *ortho*-amino arene derivatives via a Dimroth-type equilibrium.[24] Similar to arenediazonium salts, benzotriazoles can be used as precursors of aryl radicals and the radical-coupling reactions take place under the initiation of a free radical for the construction of carbon–carbon and carbon–heteroatom bonds.[23–26]

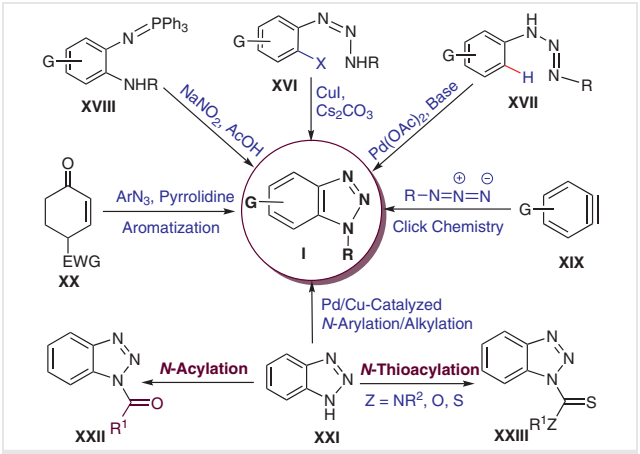


Scheme 2 The denitrogenative reactions of benzotriazoles **I** leading to various biologically relevant molecules **II–XV**

In this short review, we mainly focus on the denitrogenative functionalization of benzotriazoles, their scope in organic synthesis and their mechanisms (Scheme 2). We sincerely hope that this review will serve as a useful reference for chemists interested in benzotriazole chemistry, particularly benzotriazole ring cleavage (BtRC) methodology, and in discovering new transformations in organic synthesis.

2 Common Synthetic Routes Allowing Easy Access to Benzotriazole Derivatives

A range of diverse *N*1-substituted benzotriazoles **I** was prepared in good to high yields through routine intramolecular *N*-arylation of *o*-chloro-1,2,3-benzotriazenes **XVI** (obtained from *o*-chloroaniline via diazotization followed by coupling with amines) when treated in the presence of CuI/Cs_2CO_3 in refluxing DMF (Scheme 3).[27a,b] Similar expeditious Buchwald–Hartwig-type chemistry was further devised under palladium catalysis [$Pd(OAc)_2$/Cs_2CO_3].[27c] Another fascinating way to furnish the desired *N*1-arylbenzotriazoles **I** was successfully established through C–H activation of aryl triazines **XVII** followed by intramolecular amination under palladium catalysis.[27d,e] On the other hand, in presence of $NaNO_2$ and acetic acid at 0 °C, *o*-(arylamino)arylaminophosphoranes **XVIII** underwent cyclocondensation and furnished high yields of the corresponding *N*1-arylbenzotriazoles within 5–20 minutes.[27f] Alternatively, the [3+2]-cycloaddition reaction of benzyne derivatives **XIX** with various organic azides under click conditions (CuI/base) successfully afforded high yields of the respective *N*1-substituted benzotriazoles **I**.[27g–i] Likewise, [3+2]-cycloaddition of cyclohexenones **XX** with a variety of aryl azides in the presence of a catalytic amount of pyrrolidine followed by 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ)-mediated oxidative aromatization under one-pot conditions afforded high yields of *N*1-arylbenzotriazoles **I**.[27j] Interestingly, the reaction of (*Z*)-1-aryl-3-hexen-1,5-diynes with sodium azide can further deliver high yields of *N*1-benzotriazoles.[27k,l] Moreover, simple and straightforward routes for the *N*H-arylation of benzotriazole **XXI** under copper or palladium catalysis are frequently utilized for the synthesis of functionalized NH-benzotriazoles **I**.[27m–p]



Scheme 3 Common routes for the synthesis of benzotriazoles and their derivatives

Over the past few decades, *N*-acylbenzotriazoles and thioacylbenzotriazoles have been employed as very useful synthons in a number of *N*-, *C*-, *S*- and *O*-acylation reactions to develop many pharmacologically active molecules.[4c] There are several well-established protocols for the *N*-acylation of benzotriazoles. As the very first example, a carboxylic acid can be activated by means of thionyl chloride and subsequently reacts with benzotriazole in anhydrous dichloromethane at room temperature to furnish the corresponding *N*-acylbenzotriazoles **XXII** in high to excellent yields.[28a] Other notable examples of the *N*-acylation of benzotriazoles include the reactions of carboxylic acids with NBS/PPh_3/BtH (BtH = benzotriazole) in dry dichloromethane at 0 °C,[28b] I_2/PPh_3/Et_3N/BtH,[28c] RSO_2Bt/Et_3N/BtH in THF under refluxing conditions,[28d,e] TsCl/Et_3N/DMAP/BtH in dichloromethane,[28f] 2,4,6-trichloro-1,3,5-triazine (TCT)/BtH in the presence of Et_3N in an organic solvent,[28g] $NaHCO_3$ in an aqueous medium,[28h] trichloroisocyanuric acid/PPh_3/BtH in dichloromethane,[28i] *N*-propanephosphonic acid anhydride (T_3P@)/pyridine in DMF at room temperature,[28j] and 2,2′-dipyridylsulfide/Ph_3P/BtH in dichloromethane.[28k] *N*-Thioacylbenzotriazoles **XXIII** (ROCSBt or RSCSBt) were obtained in excellent yields simply by reacting alcohols or thiols with bis(1-benzotriazolyl)methanethione (BtCSBt) in

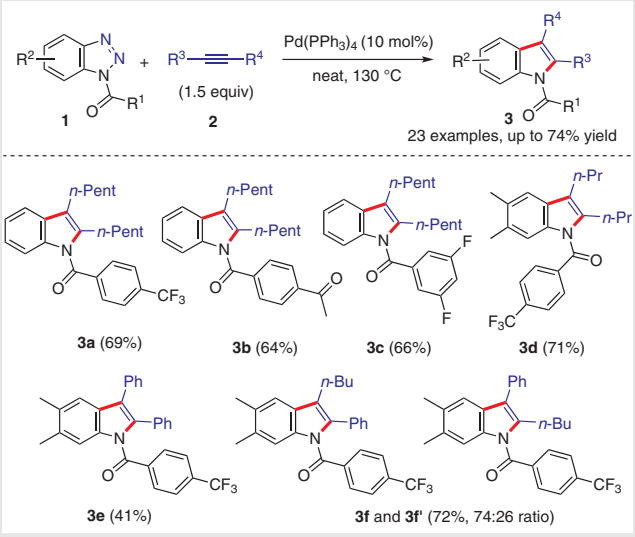
the presence of a suitable base. However, the reactions of secondary amines (R_2NH) with bis(1-benzotriazolyl)methanethione furnished the respective *N*-thioacylbenzotriazoles (R_2NCSBt) in excellent yields in 30 minutes even in the absence of a base (Scheme 3).[14,15]

3 Formation of C–C Bonds

3.1 Cyclization Reactions

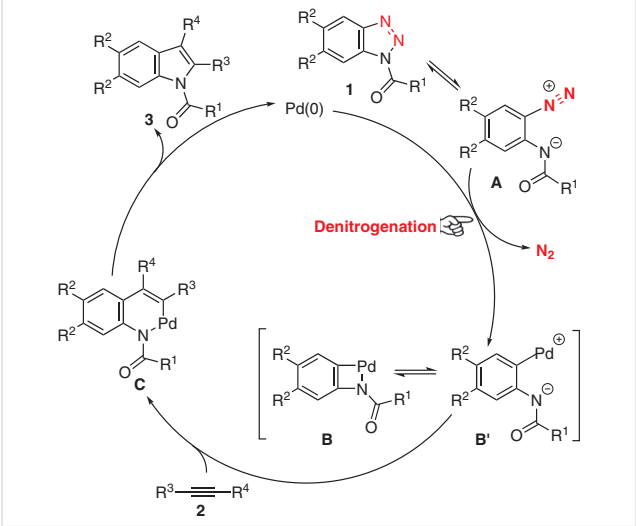
Nitrogen-containing fused heterocycles are widely found in natural products and pharmaceuticals.[29] Significant efforts have been devoted to the development of new synthetic methods for their preparation because of their important biological and physiological activities. Among these methods, cyclization and cycloaddition reactions have been established as the most useful transformations.[30] In recent years, benzotriazole derivatives have been employed in inter- and intramolecular cyclizations via a denitrogenative process for the synthesis of various nitrogen-containing fused heterocycles.[6–20]

In 2009, Nakamura and co-workers reported a novel route for the palladium-catalyzed denitrogenative [3+2]-cycloaddition of *N*-aroylbenzotriazoles **1** with internal alkynes **2** for the construction of biologically relevant indole derivatives **3** (Scheme 4).[6] Notable advantages of this novel protocol include a simple, solvent- and base-free experimental procedure, mild reaction conditions, easy separation of the product, the release of molecular nitrogen gas as the sole by-product and satisfactory reaction yields. Although terminal alkynes were not compatible with this transformation, a broad substrate scope with respect to the benzotriazole was tolerated. In addition, the reaction exhibited good regioselectivity for asymmetric alkyne substrates, in which a bulkier substituent was located at the C-2 position of the indole ring. From the results, it was evident that benzotriazoles could be used efficiently as synthetic equivalents of 2-haloanilides or *ortho*-amino arenediazoniums in metal-catalyzed coupling reactions.



Scheme 4 Pd-catalyzed cycloaddition of benzotriazoles with internal alkynes

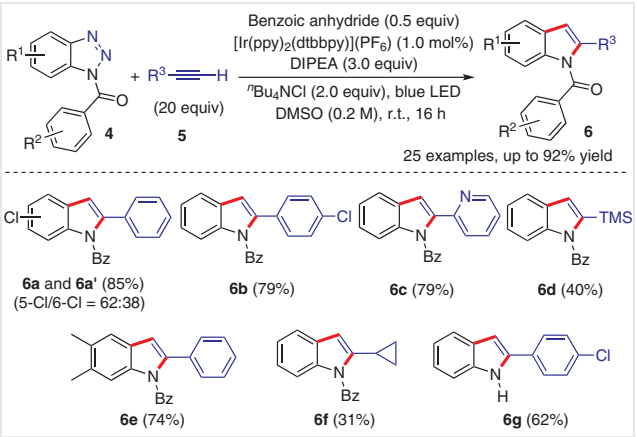
A plausible mechanism was proposed by the authors and is depicted in Scheme 5.[6] Initially, under the thermal conditions, benzotriazoles **1** can undergo ring–chain isomerization via a Dimroth-type equilibrium (see Scheme 1, a) to afford 2-iminobenzenediazoniums **A**, followed by oxidative insertion of the Pd(0) species to give Pd(II) intermediate **B** or **B′**. Subsequently, insertion of the internal alkyne **2** into the carbon–palladium bond generated the palladacyclic species **C**. Finally, reductive elimination took place to give the desired indoles **3** as the sole products, along with the Pd(0) species to complete the catalytic cycle. Both a high reaction temperature and a strong electron-withdrawing group on the nitrogen atom are crucial for opening of the triazole ring.



Scheme 5 A plausible mechanism

In 2017, Glorius and co-workers developed the Ir-catalyzed denitrogenative [3+2]-cycloaddition of aroylbenzotriazoles **4** with terminal alkynes **5** under irradiation with visible light (Scheme 6).[7] This protocol represents an important complement to Nakamura's work.[6] The reaction exhibited a broad substrate scope, excellent functional group tolerance and high regioselectivity for the synthesis of 2-substituted indoles **6** in moderate to good yields. Notably, deprotected indoles could be obtained with substrates possessing a strongly electron-withdrawing trifluoromethyl group on the benzoyl fragment, which provides a valuable approach for the synthesis of 2-aryl-substituted in-

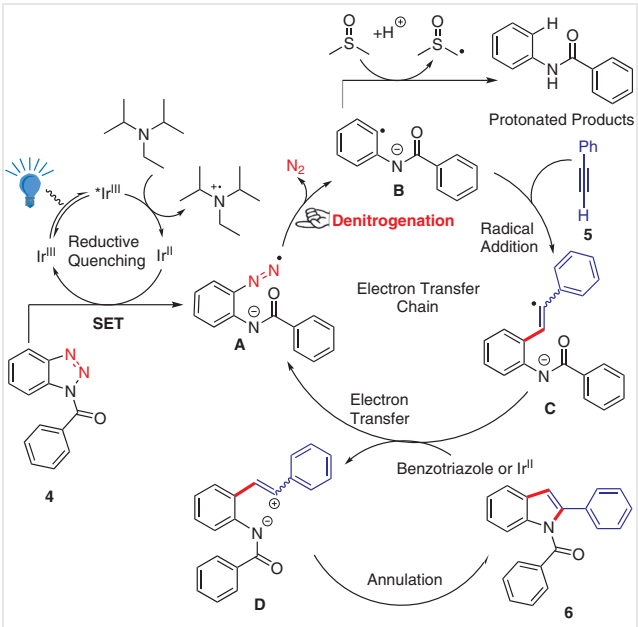
doles without additional deprotection steps. However, internal alkynes were not compatible with this transformation.



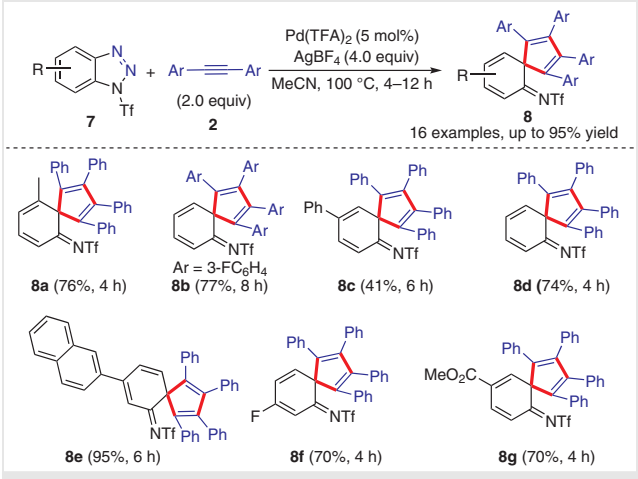
Scheme 6 Ir-catalyzed cycloaddition of benzotriazoles with terminal alkynes

On the basis of their investigation of the mechanism, Glorius proposed a radical pathway for this Ir-catalyzed cycloaddition of benzotriazoles with terminal alkynes (Scheme 7).[7] Initially, the excited-state Ir(III)* catalyst, generated upon irradiation with blue light, was reduced by the tertiary amine (DIPEA) via a single-electron transfer process to afford the amine radical cation and the highly reducing Ir(II) catalyst. Subsequently, single-electron transfer between the Ir(II) catalyst and the benzotriazole took place to regenerate the Ir(III) catalyst and produce radical anion **A**. This was followed by release of nitrogen gas to produce aryl radical **B**. On the one hand, the protonated by-product could be obtained by hydrogen abstraction from the solvent. On the other hand, the addition of aryl radical **B** to the triple bond of the alkyne occurred to give the stabilized radical intermediate **C**, which could be oxidized by another molecule of benzotriazole or by the Ir(II) catalyst to afford the zwitterionic intermediate **D**. Finally, intramolecular cyclization gave the desired product **6**.

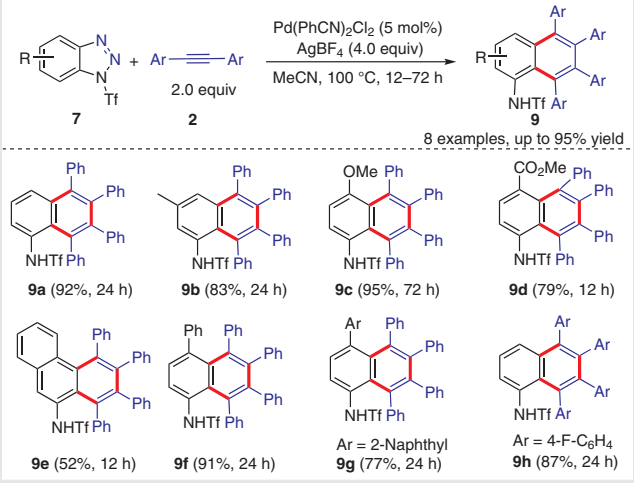
In 2018, Tang and co-workers reported novel denitrogenative [2+2+1]- and [2+2+2]-cycloadditions of benzotriazoles **7** with internal alkynes **2** catalyzed by palladium catalysts (Schemes 8 and 9).[8] The multiply functionalized 5,6-spiro bicycles **8** and naphthylamines **9** could be obtained by controlling the conditions of the reactions of benzotriazoles **7** with the internal alkynes **2** under selective catalysis with $Pd(TFA)_2$ (5 mol%)/$AgBF_4$ (4.0 equiv) or $Pd(PhCN)_2Cl_2$ (5 mol%)/$AgBF_4$ (4.0 equiv), respectively. Notably, it was found that the 5,6-spiro bicycles **8** could gradually convert into naphthylamines **9** via a ring-expansion process at high temperature. Different from previous work,[6,7] indole derivatives could not be obtained under these conditions, which might be attributed to the introduction of a more electron-deficient substituent (Tf) on the nitrogen atom of the benzotriazole and $AgBF_4$ stabilizing the arenediazonium species. A broad range of benzotriazole and internal alkyne substrates were suitable for these reactions. Interestingly, the alkenylation products could be obtained with terminal alkynes (see Section 3.2).



Scheme 7 A possible mechanism



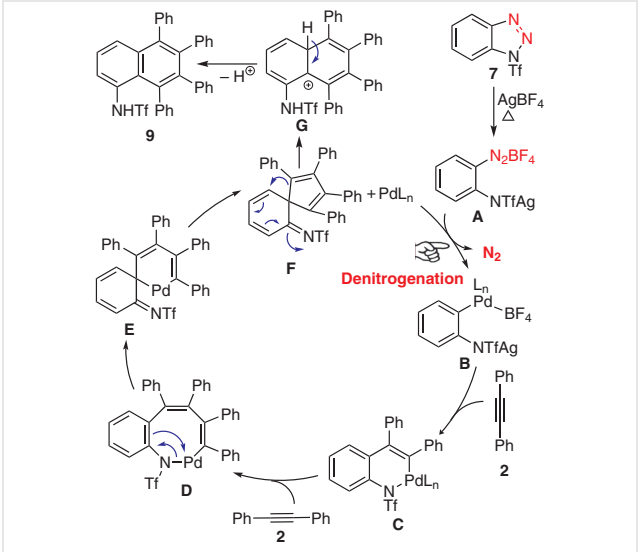
Scheme 8 Pd-catalyzed [2+2+1]-cycloaddition of benzotriazoles with internal alkynes



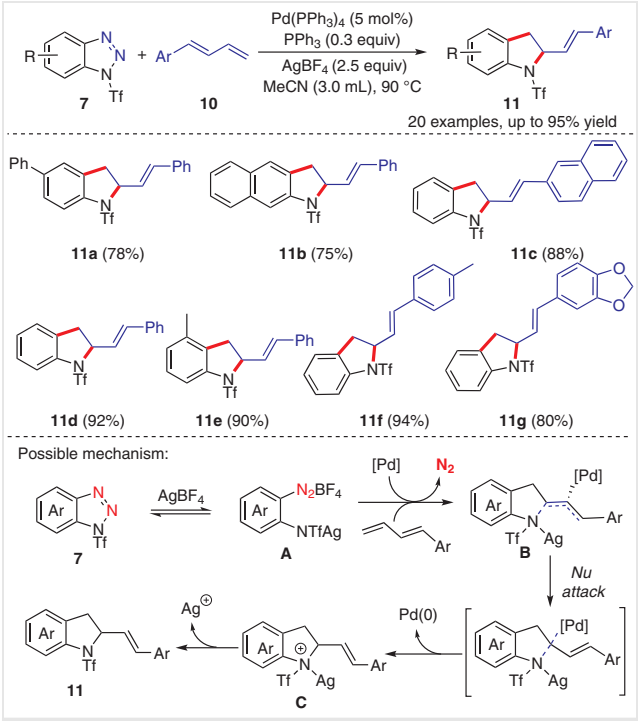
Scheme 9 Pd-catalyzed [2+2+2]-cycloaddition of benzotriazoles with internal alkynes

A plausible mechanism has been proposed for these reactions (Scheme 10). Firstly, benzotriazole **7** underwent ring opening under the thermal conditions to generate the arenediazonium tetrafluoroborate **A**, followed by oxidative addition with the Pd(0) catalyst to afford the Pd(II) complex **B**. Subsequently, insertion of the internal alkyne into carbon–palladium bond produced the palladacycle species **C**. Due to the highly electron-deficient nature of the nitrogen atom, the direct reductive elimination process to give indole products was largely inhibited at this stage. Thus, intermediate **D** was generated by a second insertion of another internal alkyne. Next, a 1,3-shift of the metal center in intermediate **D** occurred to give the six-membered palladacycle species **E**, which was followed by reductive elimination to afford the 5,6-spiro bicycle product **F**. At a high temperature, the 5,6-spiro bicycle readily underwent ring expansion to generate the thermodynamically more stable naphthylamine **9**.

The same group has also developed a novel method for the synthesis of indolines **11** of biological interest through the [3+2]-cycloaddition of benzotriazoles **7** with 1,3-dienes **10** as the coupling partners by using $Pd(PPh_3)_4$ (5 mol%)/PPh_3 (0.3 equiv) in the presence of $AgBF_4$ (2.5 equiv) in MeCN at 90 °C (Scheme 11).[9] The reactions proceeded smoothly to yield the corresponding indoline products **11** in good to excellent yields. Additionally, this catalytic system exhibited a broad substrate scope and excellent functional group tolerance. An investigation of the mechanism suggested that the highly electrophilic nature of the π-allylpalladium species **B** readily underwent intramolecular *N*-allylation instead of β-H elimination.



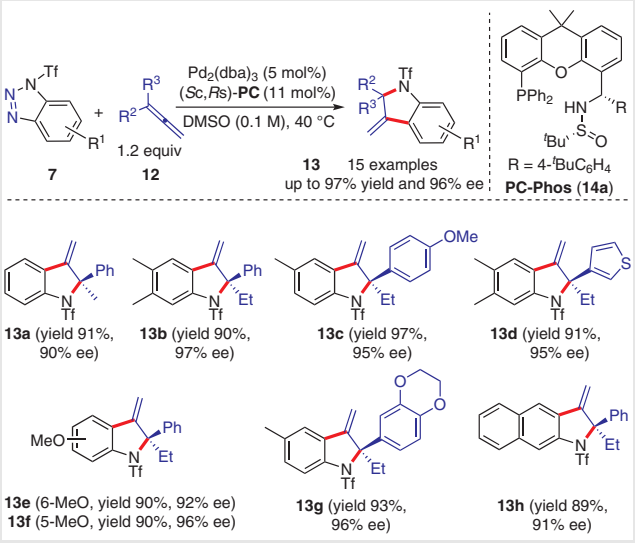
Scheme 10 Tang's mechanism for the denitrogenative cycloaddition of Tf-substituted benzotriazoles (BtTf) with internal alkynes under palladium catalysis



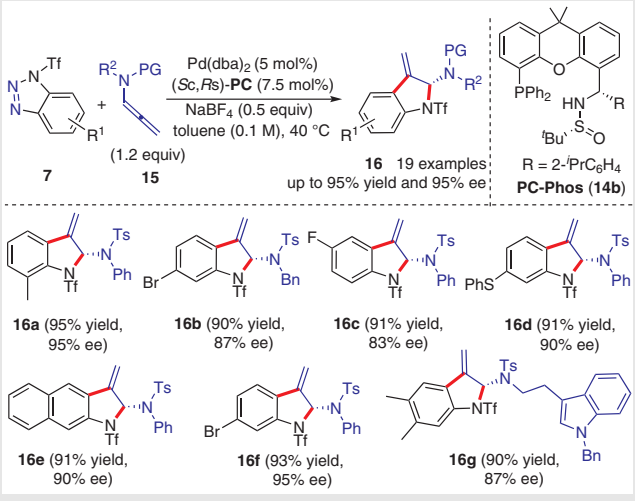
Scheme 11 Pd-catalyzed [3+2]-cycloaddition of benzotriazoles with 1,3-dienes leading to the respective indolines through denitrogenative functionalization of benzotriazoles

More recently, Zhang and co-workers developed the enantioselective palladium-catalyzed intermolecular denitrogenative cyclization reaction of benzotriazoles **7** separately with allenes **12** and *N*-allenamides **15** using the chiral sulfinamidephosphine-type ligand **14a** or **14b** (Schemes 12 and

13).[10] Optically active 3-methyleneindolines **13** and **16** could be obtained in excellent yields and with high to excellent enantioselectivity (ee values up to 96%) by utilizing the same protocol. The advantages of the reaction were a broad substrate scope, mild reaction conditions without a base, and high regio- and enantioselectivity. In addition, a gram-scale reaction also provided a high yield and ee value under the standard conditions. Furthermore, 3-methyleneindolines **16** could be oxidized to give the corresponding chiral ketones in good yields. These features make this reaction extremely useful and practical.

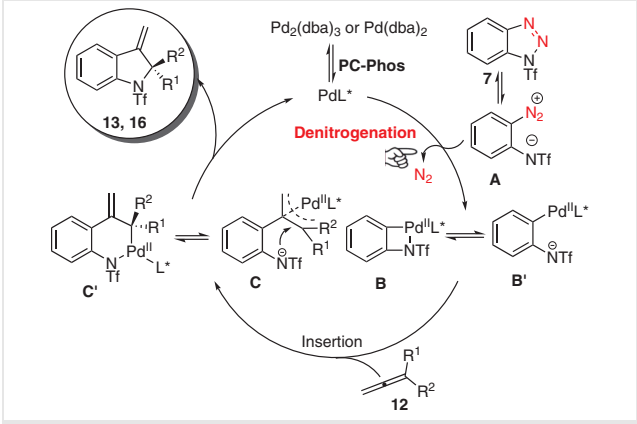


Scheme 12 Pd-catalyzed [3+2]-cycloaddition of benzotriazoles with allenes in the presence of chiral sulfinamidephosphine-type ligand **14a** leading to optically active 3-methyleneindolines



Scheme 13 Pd-catalyzed [3+2]-cycloaddition of benzotriazoles with *N*-allenamides in the presence of chiral sulfinamidephosphine-type ligand **14b** leading to chiral 3-methyleneindolines

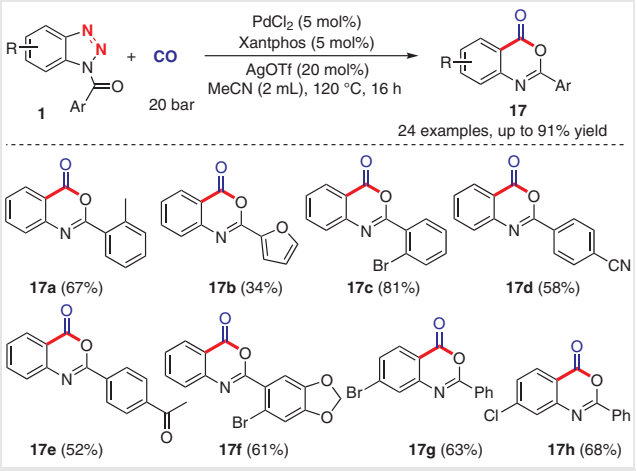
For the mechanism (Scheme 14), under thermal conditions, benzotriazoles **7** readily undergo ring–chain isomerization via a Dimroth-type equilibrium to form the arenediazonium **A**, which is followed by oxidative addition of the Pd(0) catalyst and extrusion of molecular nitrogen gas to afford intermediate **B** or **B′**. Subsequently, the insertion of allenes **12** or *N*-allenamides **15** into the carbon–palladium bond generates a π-allylpalladium complex **C** or **C′**. Finally, intramolecular allylic substitution can occur to produce the cyclization products **13** or **16**, along with release of the palladium catalyst to complete the catalytic cycle.



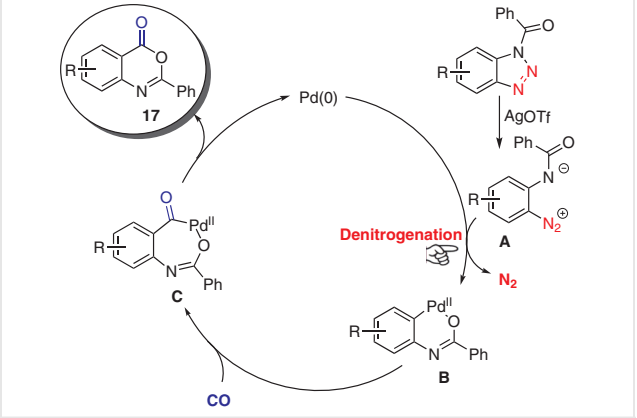
Scheme 14 BtRC mediated by a sulfinamidephosphine-type ligand followed by reaction with allenes leading to the corresponding chiral 3-methyleneindolines

In addition to these unsaturated hydrocarbons, carbon monoxide was also employed in the cyclization of acyl-substituted benzotriazoles. In 2017, Wu and co-workers developed a novel carbonylative activation of benzotriazoles **1** with a silver and palladium bimetallic catalyst system (Scheme 15).[11] The reaction gave the corresponding heterocycles **17** in moderate to good yields with excellent functional group tolerance under neutral conditions. A series of biologically relevant benzoxazinones **17** could be efficiently obtained in good yields by utilizing this simple procedure.

A possible mechanism for the reaction as put forward by the authors is depicted in Scheme 16. Initially, arenediazonium intermediate **A** was generated from *N*-acylbenzotriazole **1** in the presence of the silver salt under thermal conditions. Subsequently, oxidative addition of the formed arenediazonium with the Pd(0) catalyst took place to produce the organopalladium complex **B**, which was followed by coordination and insertion of CO to afford the seven-membered intermediate **C**. Finally, reductive elimination occurred to deliver the desired cyclized product **17**, along with the active Pd(0) species to finish the catalytic cycle.

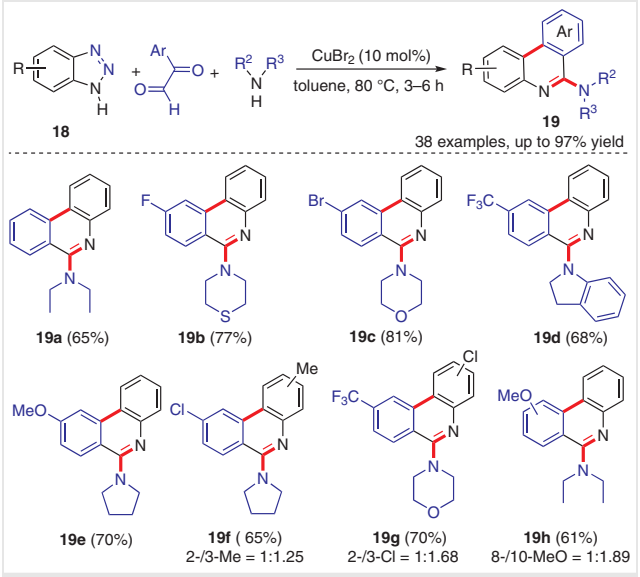


Scheme 15 Pd-catalyzed carbonylative cyclization of benzotriazoles with carbon monoxide



Scheme 16 Wu's mechanism for the Pd-catalyzed carbonylative cyclization of benzotriazoles with CO

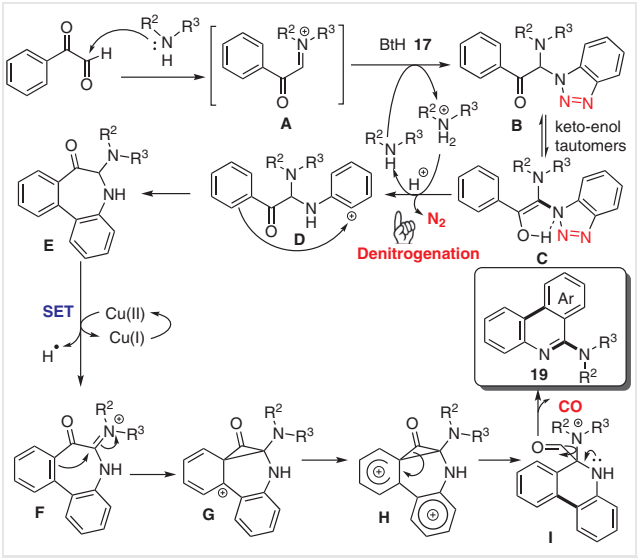
Ahmed and co-workers were the first to develop the copper-catalyzed three-component denitrogenative cyclization of benzotriazole derivatives **18**, 2-oxoaldehydes and secondary amines under mild conditions (Scheme 17).[12] This protocol provides a simple and practical procedure for the synthesis of various phenanthridines **19** from readily available and inexpensive starting materials. Numerous functional groups were tolerated in this reaction. However, *ortho*-substituted 2-oxoaldehydes were not suitable for this reaction and monosubstituted benzotriazoles provided a pair of isomers with similar regioselectivity.



Scheme 17 Cu-catalyzed three-component denitrogenative cyclization reactions of benzotriazoles

Based on their investigations, the authors proposed a plausible mechanism as depicted in Scheme 18. Initially, the reaction of the 2-oxoaldehyde with the secondary amine generated 2-oxoiminium ion **A**. Under a basic environment, benzotriazole derivative **18**, acting as a nucleophilic reagent, attacks the 2-oxoiminium ion **A** to afford α,α-diamino carbonyl adduct **B** or its enolic form **C**. This is followed by the release of nitrogen gas to produce the reactive aryl electrophilic species **D** via a five-membered hydrogen-bonded intermediate. Subsequently, electrophilic substitution occurred to give the cyclic product **E**, which immediately produced a second iminium ion **F** under the oxidative conditions. Finally, sequential rearrangement and decarbonylation occurred to give the cyclized product **19**.

A number of denitrogenative functionalizations of benzotriazole derivatives have been accomplished through various methods, mainly under thermal (pyrolysis) or photoirradiation (photolysis) conditions, as discussed in this section. A representative application of denitrogenative functionalization of benzotriazole **20** involves the synthesis of clausenawalline D (**21b**) (Scheme 19). The Burgess group explored the photoinduced Graebe–Ullmann-type reaction that proceeded smoothly to afford a variety of biologically relevant carbazole alkaloids.[31] The reaction involves the photolysis of benzotriazole **20** via cleavage of the benzotriazole ring to afford the diradical species **A**, which immediately rearranges into species **B**. Recombination then gives heterocycle **C** as an intermediate. Finally, the cyclized intermediate **C** can undergo aromatization to afford clausenawalline D (**21b**) in addition to carbazole **21a**.



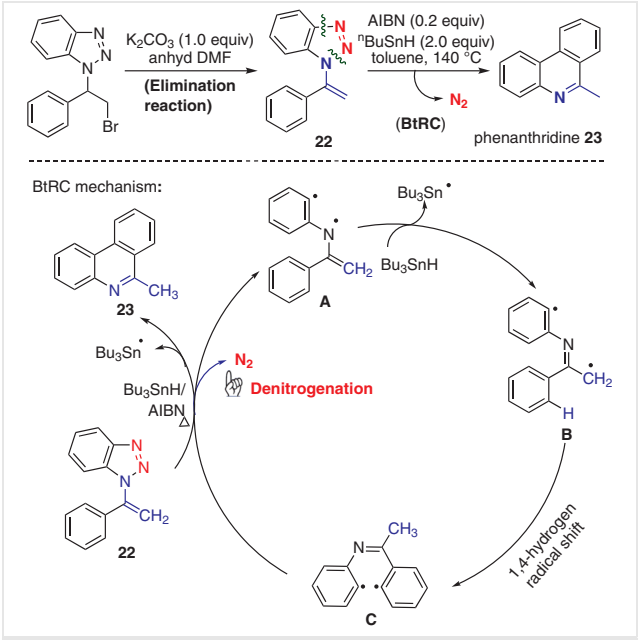
Scheme 18 Ahmad's concept on Cu-catalyzed three-component denitrogenative functionalization benzotriazoles leading to respective phenanthridines **19**

Very recently, Tiwari's group extended their established BtRC methodology for the synthesis of phenanthridine **23** via free-radical benzotriazole ring cleavage of 1-(1-phenylvinyl)-1*H*-benzotriazole (**22**).[21] This was achieved by treating compound **22** with 2.0 equivalents of ^{n}BuSnH in the presence of 0.2 equivalents of AIBN as a radical initiator in sealed tube. The 2-cyanoprop-2-yl radical generated from AIBN rapidly reacts with $^{n}Bu_3SnH$ to produce a tin radical, which then reacts with the vinylic group of 1-(1-phenylethenyl)-1*H*-1,2,3-benzotriazole (**22**) leading to cleavage of the N–N bond. The removal of molecular nitrogen initially results in the radical **A**, which on subsequent rearrangement gives biradical **B**. This species undergoes a 1,4-hydrogen radical shift involving the other phenyl ring leading to the generation of two phenyl radical centers (**C**). Both phenyl radicals then participate in a cyclization to give the phenanthridine **23** (Scheme 20). The yield of the reaction product needs to be improved and further investigations in this direction are ongoing in our laboratory.

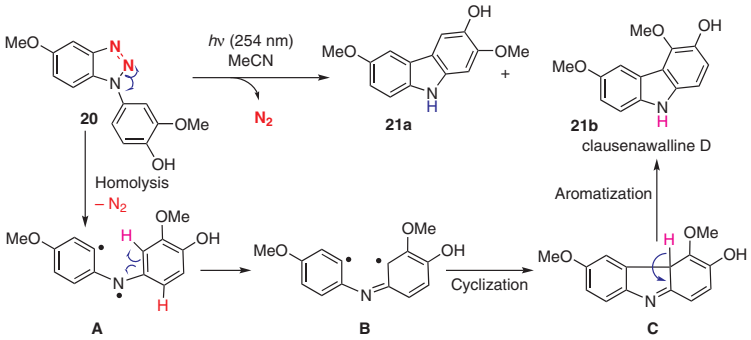
3.2 Arylation, Alkenylation, Alkylation and Carbonylation Reactions

Transition-metal-catalyzed cross-coupling reactions have emerged as a powerful tool for the construction of carbon–carbon bonds. Over the years, various coupling partners have been developed for this purpose, such as organic (pseudo)halides, organometallic reagents, (hetero)aromatic compounds, etc.[32] Recently, benzotriazoles were utilized as the synthetic precursors of *ortho*-amino arenediazonium salts for the formation of carbon–carbon bonds in transition-metal-catalyzed cross-coupling reactions, mainly involving arylation, alkenylation, alkylation and carbonylation.

Organoboronic acids represent versatile building blocks in organic synthesis[33] and have found wide applications in transition-metal-catalyzed cross-coupling reactions.[5a,34] In 2017, Tang and co-workers reported the palladium-catalyzed denitrogenative Suzuki and carbonylative Suzuki

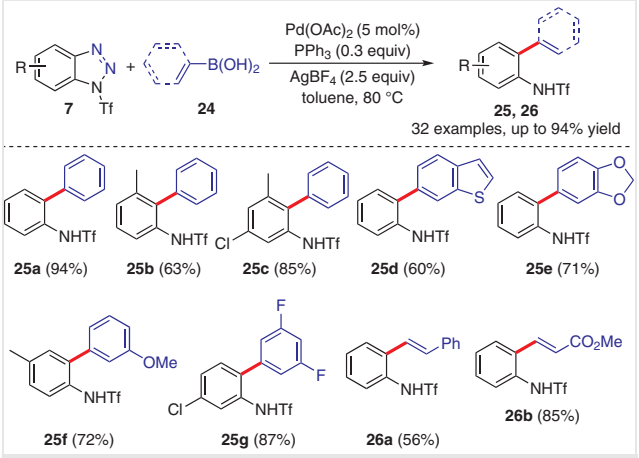


Scheme 20 Application of 1-(2-bromo-1-phenylethyl)-1*H*-benzotriazole for the systematic formation of phenanthridine **23** via a free-radical reaction pathway

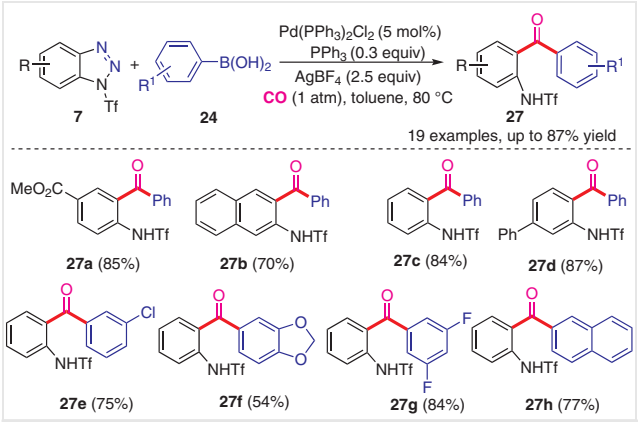


Scheme 19 Synthesis of clausenawalline D (**21b**) via Graebe–Ullmann-type denitrogenative functionalization of BtAr (BtAr = *N*1-aryl benzotriazole)

coupling reactions of benzotriazoles **7** with boronic acids **24** under mild conditions (Schemes 21 and 22),[24] which provided not only the corresponding *ortho*-amino biaryls **25** and styrenes **26**, but also biaryl ketone derivatives **27**. This catalytic system exhibited broad substrate scope with respect to both the coupling partners and gave good yields of the products. A range of electron-donating and electron-withdrawing substituents was tolerated in the reaction. Notably, for the carbonylative reactions, vinyl boronic acids failed to give the desired products under the standard conditions. In addition, the application of this strategy for the synthesis of bioactive natural products and drugs showed that the reaction had potential value in the field of pharmaceutical chemistry.

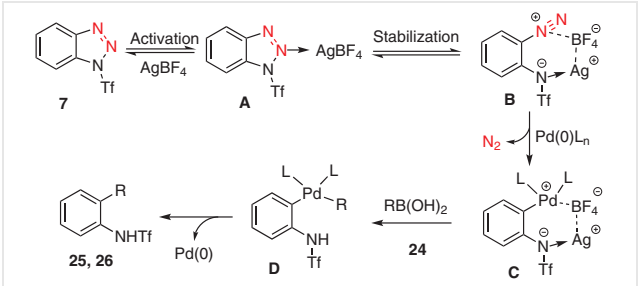


Scheme 21 Pd-catalyzed arylation and alkenylation of benzotriazoles with boronic acids



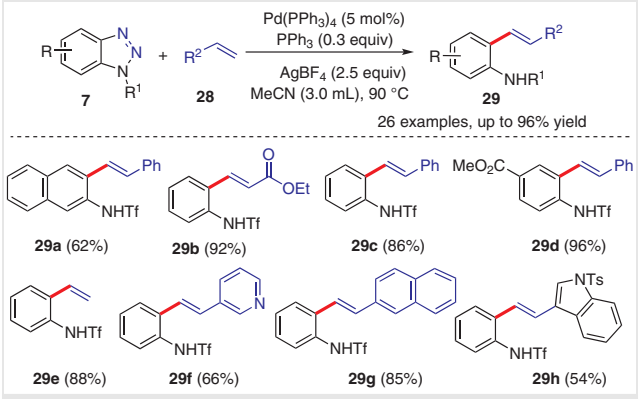
Scheme 22 Pd-catalyzed carbonylation of benzotriazoles with boronic acids and carbon monoxide

For the mechanism shown in Scheme 23, $AgBF_4$ was used as the additive and coordinated with a nitrogen to activate the N1–N2 bond of the triazole ring. This resulted in cleavage of the ring to afford the stabilized ring-opened intermediate **B** through the formation of an arenediazonium tetrafluoroborate. Subsequently, oxidative addition with the Pd(0) catalyst occurred to give the organopalladium complex **C** along with the release of nitrogen gas. Subsequent transmetalation with the organoboronic acid generated complex **D**. Finally, reductive elimination occurred to furnish the desired coupling products.



Scheme 23 Tang's mechanism for the denitrogenative Pd-catalyzed arylation and alkenylation of benzotriazoles with boronic acids

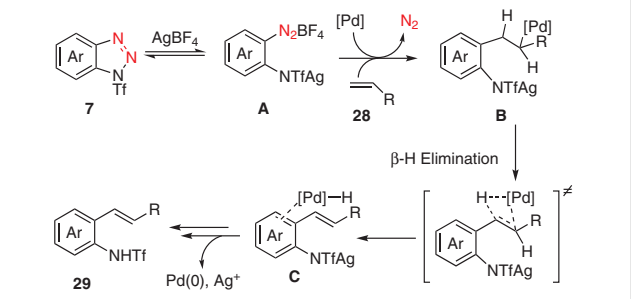
In the same year, Tang's group extended further the denitrogenative alkenylation of benzotriazoles with a diverse range of alkenes under similar palladium catalysis, making the route more general at the same time (Scheme 24).[9] A series of functional groups on the aryl moiety of benzotriazoles **7** was tolerated and gave the corresponding *ortho*-amino styrene products **29** in good to excellent yields. In addition, various alkenes were compatible with this reaction, such as styrenes, ethylene and ethyl acrylate. However, the desired products could not be obtained with aliphatic substrates and internal alkenes. Notably, for 1,3-diene substrates, the reaction provided the [3+2]-cycloaddition products, which have been already discussed in Section 2.1.



Scheme 24 Pd-catalyzed alkenylation of benzotriazoles with alkenes

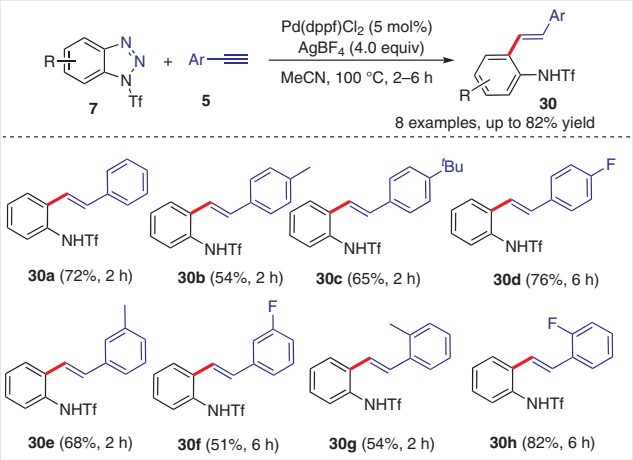
A similar mechanism for the reaction was proposed (Scheme 25). Initially, in the presence of $AgBF_4$, the ring opening of benzotriazole **7** generated the *ortho*-amino arenediazonium salt **A** through a Dimroth-type equilibrium. Sequential oxidative addition with the Pd(0) catalyst and migratory insertion of the alkene occurred to afford the

Pd(II) complex **B**. Finally, β-hydride elimination led to the Heck-type reaction products **29** via intermediate **C**, along with Pd(0) to complete the catalytic cycle.



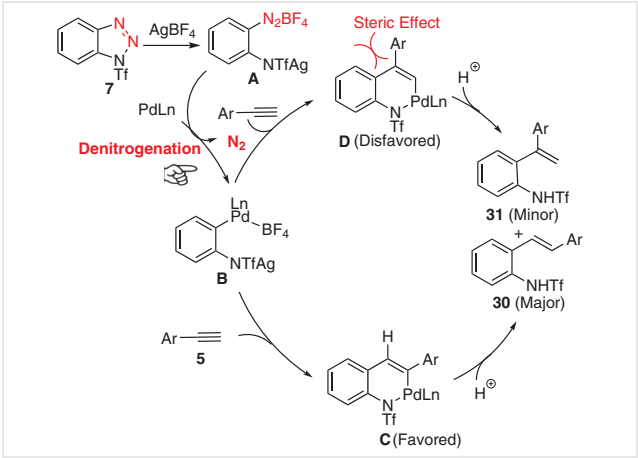
Scheme 25 Mechanistic denitrogenative route via Pd-catalyzed alkenylation of benzotriazoles with boronic acids to give Heck-type products

Interestingly, Tang's group extended their investigations and reported the palladium-catalyzed alkenylation of benzotriazoles **7** with terminal alkynes **5** (Scheme 26).[8] Although a broad range of terminal alkynes was compatible with this reaction to afford the *ortho*-amino styrene derivatives **30** (as the major products) along with 1,1-disubstituted styrenes **31** (as minor products, see Scheme 27) in moderate to good yields, compared with alkenes, terminal alkynes are more expensive and are not as easy to obtain. Of course, this reaction provides another method for the synthesis of styrene derivatives using terminal alkynes as alkenylation reagents.



Scheme 26 Pd-catalyzed alkenylation of benzotriazoles with terminal alkynes

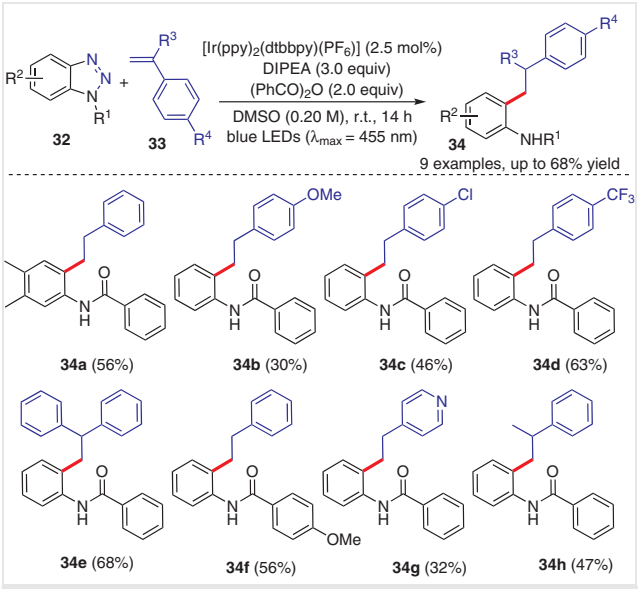
Compared with the previous cyclization of internal and terminal alkynes,[6–8] a different mechanism was proposed for the alkenylation reaction (Scheme 27). Two regioisomers, **C** and **D**, could be generated via the insertion of terminal alkynes, followed by protonation to afford the major product. However, the formation of 1,1-disubstituted styrene products is disfavored due to steric effects. In addition, the insertion of a second alkyne did not occur under the current conditions, which could be attributed to the easier protonation in the presence of the proton source generated in situ from the solvent.



Scheme 27 Possible mechanism for the Pd-catalyzed alkenylation of benzotriazoles with terminal alkynes

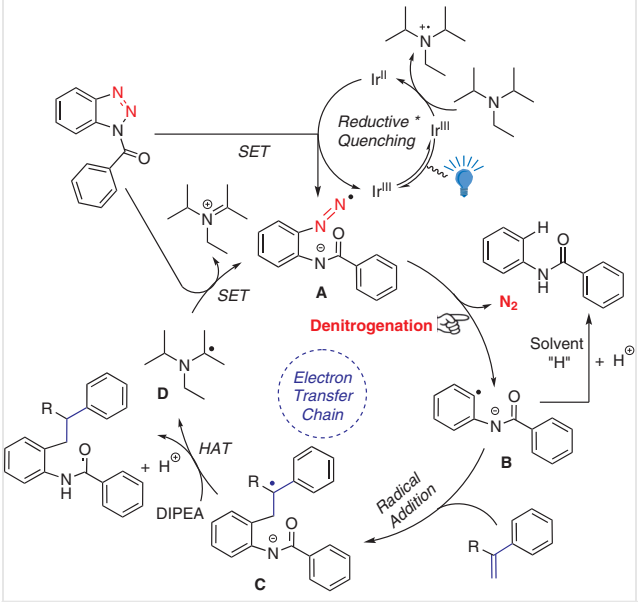
In 2017, Glorius and co-workers reported a novel visible-light-promoted alkylation of benzotriazoles **32** with styrenes **33** via a denitrogenative route to give *ortho*-alkylated *N*-arylbenzamide derivatives **34** (Scheme 28).[25] Various styrenes with electron-withdrawing and electron-donating substituents could react to provide the alkylated products in moderate to good yields, whereas a few examples of substituted benzotriazoles underwent the reaction smoothly. However, aliphatic alkenes were not suitable coupling partners, which could be attributed to them being relatively poor radical acceptors.

A plausible mechanism was proposed for the reaction as depicted in Scheme 29. Under irradiation with visible light, the excited photocatalyst underwent a single-electron transfer (SET) with the reductive quencher (DIPEA), resulting in the generation of an amine radical cation and a highly reactive Ir(II) species. Subsequently, a second single-electron transfer between the benzotriazole and Ir(II) species took place to produce species **A**, along with regeneration of the Ir(III) catalyst, which immediately extruded molecular nitrogen to give the aryl radical **B**. Subsequently, the addition of aryl radical **B** to the carbon–carbon bond of the styrene gave the stabilized radical intermediate **C**. Finally, the abstraction of hydrogen could occur from the reductive quencher (DIPEA) or its radical cation through the adoption of hydrogen atom transfer (HAT) in a photocatalytic approach to afford the *ortho*-alkylated benzamide products along with amino radical intermediate **D**, which could further reduce another molecule of the benzotriazole by serving as a potential single-electron donor to complete the catalytic cycle.[25] The adoption of hydrogen atom transfer in a photocatalytic approach often results in an excited catalyst



Scheme 28 Visible-light-promoted denitrogenative alkylation of benzotriazoles with styrenes

for the activation of substrates and offers outstanding opportunities for the synthesis of wide range of molecules by enabling the straightforward activation of R–H bonds (for example, R = C, Si, S) in the reagents.

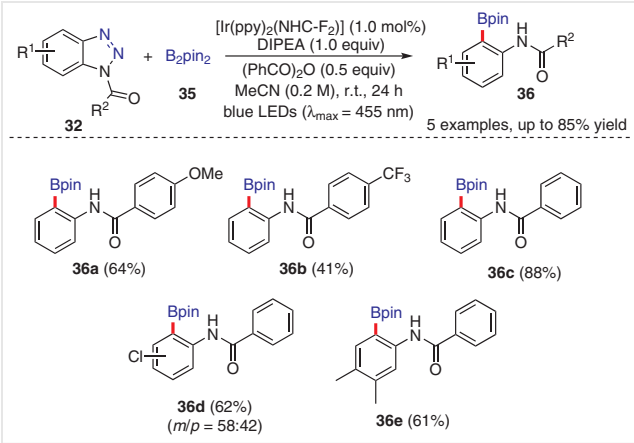


Scheme 29 A possible mechanism for the visible-light-promoted alkylation of *N*1-(benzoyl)benzotriazoles with styrenes via a denitrogenative BtRC route

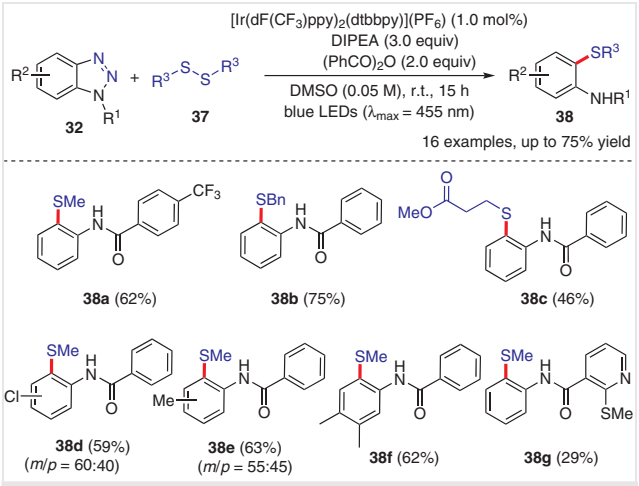
4 Carbon–Heteroatom Bond Formation

The formation of carbon–heteroatom bonds is one of the fundamental transformations in organic synthesis. Transition-metal-catalyzed cross-coupling reactions have been established as powerful tools for the construction of carbon–heteroatom bonds.[5a,34,35] Among these, radical oxidative coupling has been the subject of intense research in organic synthesis in recent years.[36]

In 2017, Glorius and co-workers reported novel visible-light-promoted methods for the borylation and thiolation of benzotriazoles via denitrogenative routes to give *ortho*-functionalized *N*-arylbenzamide derivatives **36** and **38** (Schemes 30 and 31).[25] The reactions tolerated electron-donating and electron-deficient substituents on either the benzotriazole core or the benzoyl fragment. Although there are only a few examples of the borylation reaction, a variety of functional groups and additives were tolerated. In addition, for the thiolation, various alkyl disulfides **37** were compatible with this transformation, but aryl disulfides failed to afford the thiolation products. The mechanism for the borylation and thiolation is similar to that of the alkylation shown in Scheme 29.

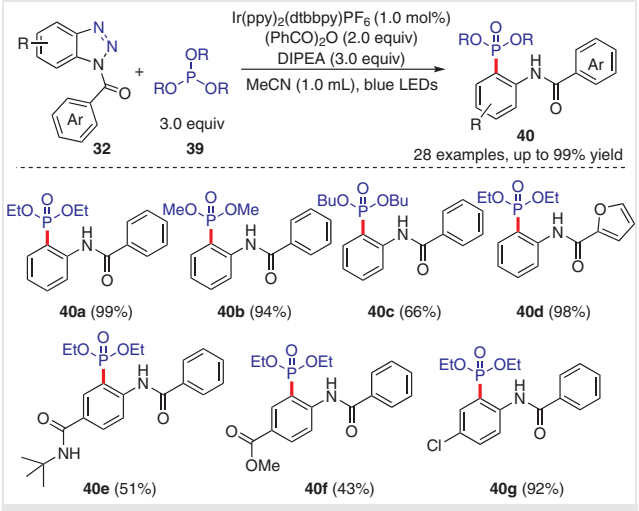


Scheme 30 Visible-light-promoted borylation of benzotriazoles with B_2pin_2



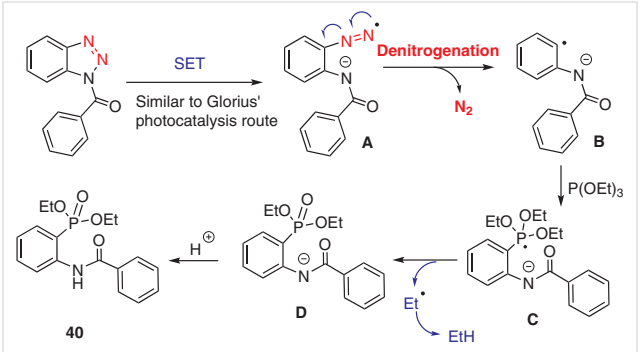
Scheme 31 Visible-light-promoted thiolation of benzotriazoles with alkyl disulfides

More recently, Yang and co-workers developed the visible-light-induced denitrogenative phosphorylation of benzotriazoles with phosphites under mild conditions (Scheme 32).[26] A series of *ortho*-phosphorylated *N*-arylbenzamides was obtained in good to excellent yields. In addition, this reaction exhibited excellent functional group tolerance. Various trialkyl phosphites were suitable for the reaction and steric hindrance due to the phosphites had an important effect on the product yields. However, the desired products could not be obtained when triphenyl phosphite was used as the phosphorylation agent. Furthermore, a gram-scale reaction performed under the standard conditions gave a good yield of the expected product, which demonstrates the utility of this new protocol.



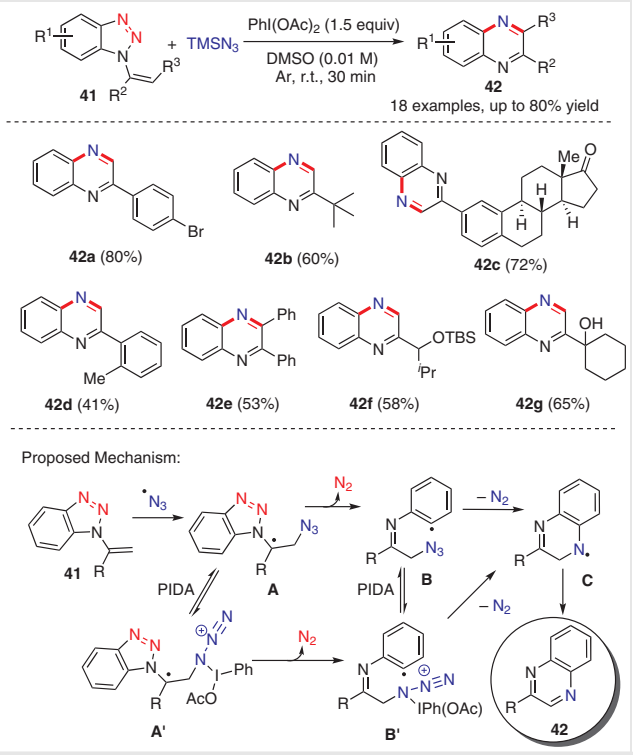
Scheme 32 Visible-light-induced phosphorylation of benzotriazoles with phosphites

For the mechanism of the reaction shown in Scheme 33, the benzotriazole could be reduced by the highly reactive Ir(II) species to give the ring-opened radical anion **A** through a single-electron transfer process, along with regeneration of the Ir(III) catalyst. Subsequently, the radical anion **A** readily underwent denitrogenation to afford aryl radical anion **B**, from which two pathways were possible, the abstraction of hydrogen leading to the by-product of *N*-phenylbenzamide, or reaction with the trialkyl phosphite to afford the unstable phosphoranyl radical anion **C**. The rapid release of an ethyl radical from species **C** could then generate the intermediate anion **D**. Finally, the phosphorylation products **40** could be obtained by protonation .



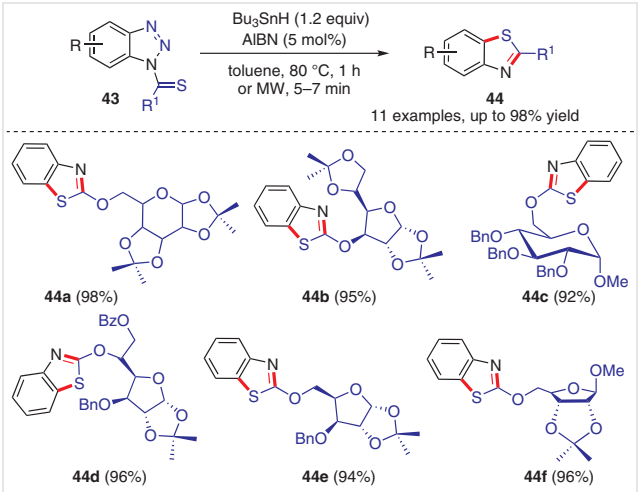
Scheme 33 A possible mechanism for the visible-light-induced denitrogenative phosphorylation

Free-radical cyclization is an important method for the synthesis of heterocyclic compounds.[30,36b,37] Recently, Shi and co-workers developed a novel approach for the ring opening of benzotriazoles via radical addition to *N*-vinylbenzotriazoles **41** under mild conditions (Scheme 34).[13] The reaction exhibited excellent chemoselectivity by controlling the precursors of the azide radical for the selective synthesis of quinoxaline or nitrile compounds. A series of substituted quinoxalines could be obtained in moderate to good yields by using $TMSN_3$ as the azide radical precursor. In addition, a wide scope of functional groups on both aromatic and aliphatic *N*-vinylbenzotriazoles was suitable for this reaction. For the mechanism, the formation of quinoxalines was relatively simple through the sequential release of nitrogen gas. In the presence of $PhI(OAc)_2$, an azide radical generated in situ from $TMSN_3$ could be trapped by the *N*-vinylbenzotriazole to afford radical intermediate **A** or **A′**. Subsequently, ring opening of the triazole could lead to the formation of aryl radical **B** or **B′**, followed by the release of another molecule of nitrogen gas to produce nitrogen-centered radical **C**. Finally, the desired products **42** were obtained under oxidative conditions.

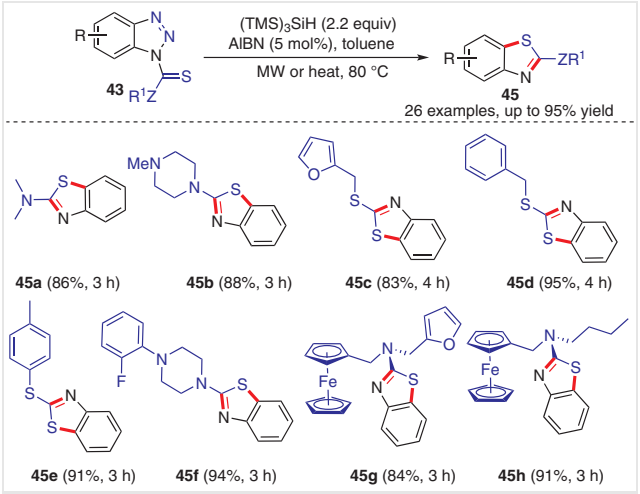


Scheme 34 The synthesis of quinoxalines through radical addition to *N*-vinylbenzotriazoles with $TMSN_3$

The intramolecular cyclization of benzotriazole derivatives via a denitrogenative process has also been reported for the synthesis of benzothiazoles and benzoxazoles. Tiwari's group has performed significant research in this field.[14–21] In 2013, we developed a novel protocol for the synthesis of various benzothiazole glycoconjugates from protected carbohydrates through intramolecular cyclization (Scheme 35).[14] This reaction underwent free radical β-scission of the N–N bond of the benzotriazole ring by treatment with a stannane under heating or microwave irradiation. The advantages of this methodology, such as the short reaction time, mild conditions, simple work-up, good yields and excellent functional group tolerance, highlight its potential applications. In order to avoid the use of the toxic stannane for the radical cyclization, $(TMS)_3SiH$ was utilized as a radical reducing agent for the synthesis of diverse 2-N/S/C-substituted benzothiazoles via ring cleavage of the benzotriazole in the presence of AIBN (Scheme 36).[15]

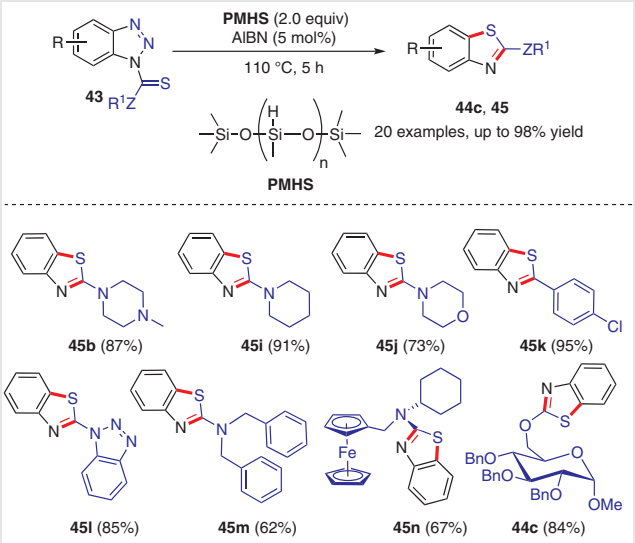


Scheme 35 Intramolecular cyclization of benzotriazole derivatives using a stannane as the radical reducing agent



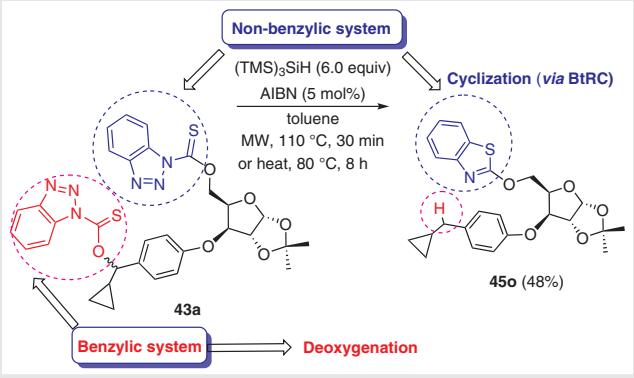
Scheme 36 Intramolecular cyclization of benzotriazole derivatives using $(TMS)_3SiH$ as a radical reducing agent

These reactions tolerated a series of functional groups and a wide scope of substrates was compatible leading to high yields of the corresponding products. More recently, we developed a green and efficient modification of this process for the synthesis of benzothiazoles using polymethylhydrosiloxane (PMHS) as the radical reducing agent, instead of Bu_3SnH and $(TMS)_3SiH$ (Scheme 37).[16,17] The use of the silicone industry by-product polymethylhydrosiloxane (PMHS) makes the process cost-effective, more practical and greener than the previous BtRC methods as PMHS is a non-toxic and biodegradable industrial waste.



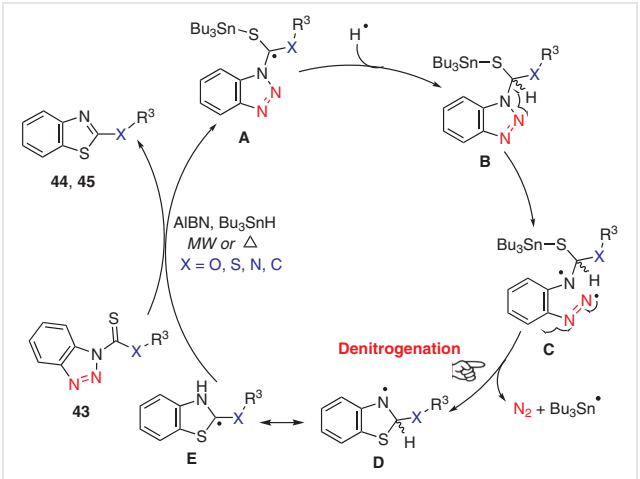
Scheme 37 Intramolecular cyclizations of benzotriazole derivatives using PMHS as the radical reducing agent

Furthermore, benzyloxythioacylbenzotriazoles (ROCSBt), comprising a thiocarbonyl benzotriazole residue at the non-benzylic end, when treated with Bu_3SnH or silanes in refluxing toluene undergo anticipated free radical β-scission of the C–O bond in compound **43o** instead of the N–N bond (as a part of denitrogenative functionalization), and thus result in the formation of deoxy compound **45o** (Scheme 38).[19] Similar reactions under microwave irradiation required shorter reaction times than those under conventional heating conditions. Hence this method can be considered as being regioselective for the required deoxygenation of benzylic alcohols, simply with the aid of bis(1-benzotriazolyl)methanethione in addition to relatively non-toxic $(TMS)_3SiH$ as an adequate alternative to Bu_3SnH.



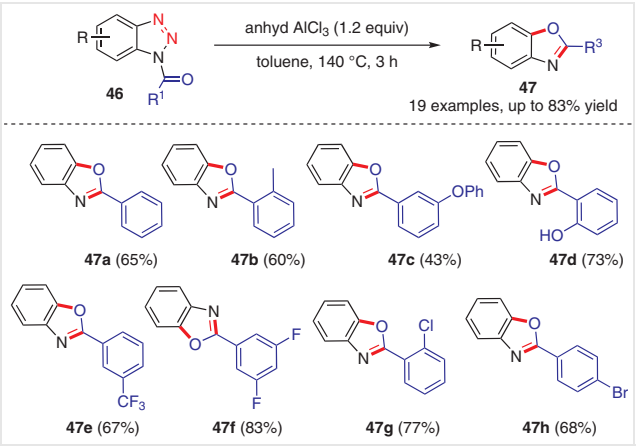
Scheme 38 Deoxygenation vs denitrogenative cyclization of benzylic/non-benzylic alcohols using bis(1-benzotriazolyl)methanethione

A mechanism for the radical cyclization has been proposed (Scheme 39). Initially, on heating in the presence of AIBN, homolytic cleavage of tributylstannane generates a stannyl radical, which adds to the thiocarbonyl of the benzotriazole to afford radical intermediate **A**. Subsequently, a hydrogen radical is rapidly captured to furnish intermediate **B**, in which β-scission of the N–N bond of the benzotriazole ring leads to the formation of biradical intermediate **C**. Next, the release of nitrogen gas produced resonance stabilized aryl radical intermediate **D** or **E**. Finally, the desired products **44** and **45** are obtained via a thermodynamically favorable and thermally induced oxidation process.



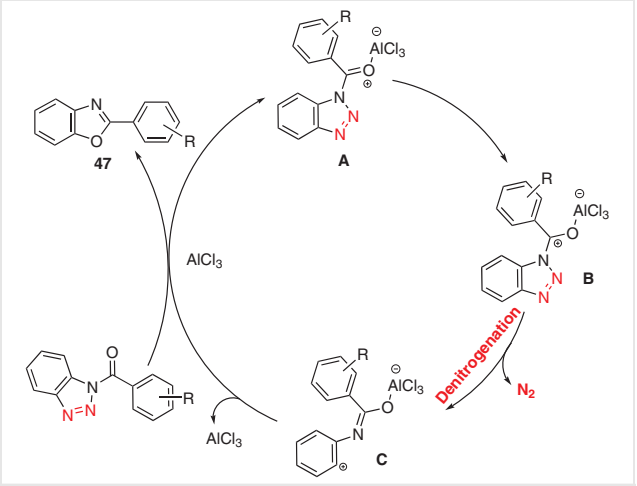
Scheme 39 Possible mechanism for the BtRC of thioacylbenzotriazole **43** leading to the respective benzothiazoles **44** and **45**

In 2017, Tiwari's group further developed the Lewis acid mediated cyclization of *N*-acylbenzotriazoles for the synthesis of benzoxazoles via a ring-opening process (Scheme 40).[18] Although a high temperature was required, the reaction gave good yields of products **47** and employed an inexpensive and easily available catalyst under mild conditions. In addition, both electron-withdrawing and electron-donating substituents on the aromatic ring could be tolerated in this transformation. Importantly, a gram-scale reaction could be achieved under the standard conditions with no adverse effect on the yield. Notably, the reaction underwent the traditional Friedel–Crafts acylation to afford the corresponding ketones in excellent yields for the substrates of aliphatic *N*-acylbenzoxazoles. Indeed, this novel protocol provides a simple and practical access to a variety of benzoxazoles.



Scheme 40 $AlCl_3$-mediated cyclization of *N*-acylbenzotriazoles for the synthesis of benzoxazoles

A plausible mechanism for the reaction was proposed (Scheme 41). Initially, coordination of the carbonyl with the Lewis acid $AlCl_3$ generates intermediate **A**, which is followed by a charge transfer process to afford carbocation intermediate **B** by stabilization of the aryl ring. Subsequently, the release of one molecule of nitrogen gas produces the stabilized intermediate **C** through an extended π-conjugative interaction, which involves delocalization of the positive charge over the aryl ring and carbonyl functionality. Finally, cyclization is achieved to deliver the corresponding cyclized oxazole products **47**.

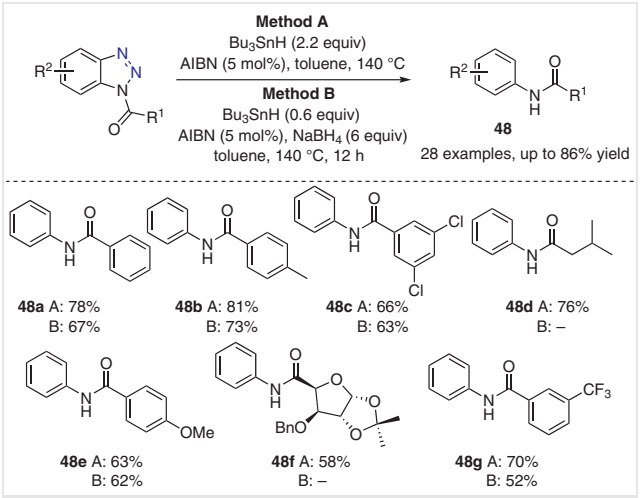


Scheme 41 Possible mechanism for the Lewis acid catalyzed BtRC of acylbenzotriazoles leading to the corresponding benzoxazoles **47**

5 Miscellaneous Denitrogenative Functionalization

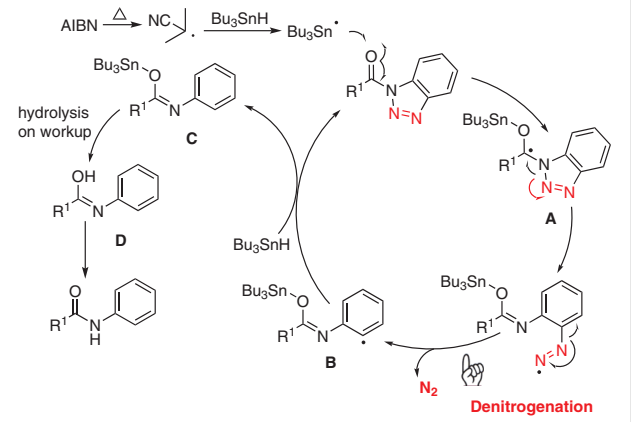
In fact, during the described ring-opening reactions of benzotriazoles for the formation of carbon–carbon and carbon–heteroatom bonds, by-products, such as *ortho*-protonated products, were often detected. That is to say, after ring-opening of the triazole ring, the corresponding intermediates can easily capture protons from the solvent or other additives. Therefore, in order to avoid the formation of by-products, aprotic or anhydrous solvents were often used in these types of reactions. Different from previous reactions, various amides could be prepared through using this strategy of protonation of intermediates.

In 2017, Tiwari's group developed a novel *n*-Bu_3SnH/AIBN-mediated ring-opening method for the synthesis of amides from *N*-acylbenzotriazoles via a radical pathway (Scheme 42).[20] Various aryl- and alkyl-carbonylbenzotriazoles were compatible with this transformation and the corresponding amides could be obtained in high yields. In addition, a series of functional groups was tolerated. Furthermore, the use of $NaBH_4$ as a reactant improved the reaction by reduction of the tin dimer to regenerate *n*-Bu_3SnH, which reduced the amount of *n*-Bu_3SnH required.



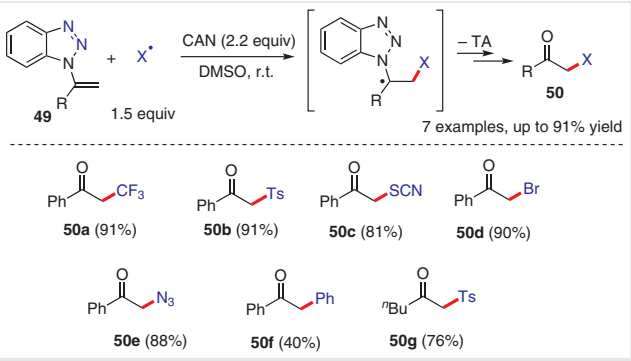
Scheme 42 Synthesis of amides from *N*-acylbenzotriazoles mediated by Bu_3SnH and AIBN

Sequential reductive cleavage and evolution of molecular nitrogen gas are included in the mechanism shown in Scheme 43. Initially, under heating conditions, the 2-cyanoprop-2-yl radical generated from AIBN rapidly reacted with Bu_3SnH to give a tin radical. Subsequently, radical intermediate **A** could be formed through attack of the tin radical on the carbonyl group of the *N*-acylbenzotriazole. The release of molecular nitrogen then occurred to afford radical intermediate **B**, which could capture a hydrogen radical from Bu_3SnH to produce intermediate **C** along with regeneration of the tin radical. Finally, hydrolysis delivered intermediate **D**, which rearranged into the final product.



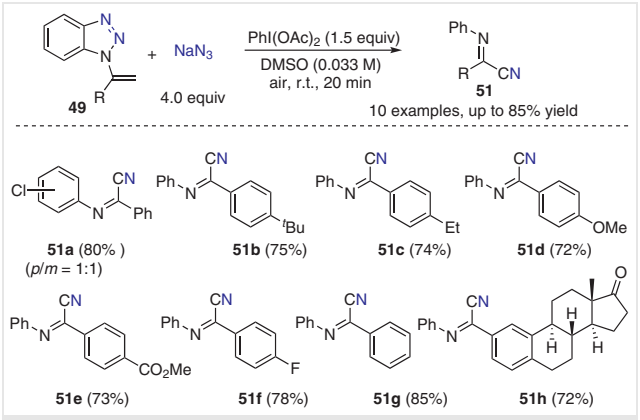
Scheme 43 Possible mechanism for the cleavage of acylbenzotriazoles to the corresponding amides under free-radical conditions

The type of reaction is closely related to the substituents on the nitrogen atom of the benzotriazoles. Specifically, *N*-vinylbenzotriazole substrates could be used as the acceptor of the free radical, readily undergoing radical addition. In 2015, Shi and co-workers reported radical addition to a vinyltriazole for the preparation of α-substituted ketones using cerium ammonium nitrate (CAN) as the oxidant (Scheme 44).[13] A series of radical precursors were compatible with this reaction and led to the corresponding products in good yields. In addition, a less reactive aliphatic vinyltriazole also gave the desired product in 76% yield. This reaction opens a new possibility to synthesize various α-substituted ketones from *N*-vinylbenzotriazoles using triazole as a leaving group.



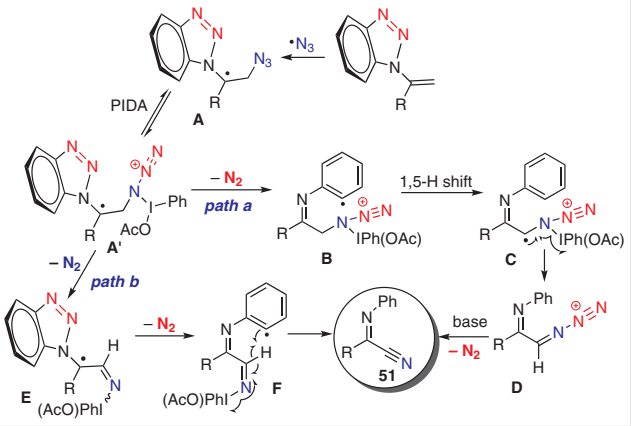
Scheme 44 CAN-mediated radical addition to of *N*-vinylbenzotriazoles

During the investigation of this reaction, Shi also described the denitrogenative functionalization of *N*-vinylbenzotriazoles by using NaN_3 as the precursor of an azide radical for the selective synthesis of nitriles in the presence of $PhI(OAc)_2$ (Scheme 45).[13] Relatively higher yields could be obtained with more polar DMSO as the solvent, in which the relatively high solubility of NaN_3 could accelerate the formation of the nitrile compounds. This reaction worked smoothly with α-aromatic-substituted *N*-vinylbenzotriazoles and tolerated a series of functional groups of different electronic nature. However, α-aliphatic-substituted *N*-vinylbenzotriazoles were not suitable for this transformation. Notably, the use of $TMSN_3$ as the azide radical precursor afforded the corresponding cyclization products as has already been discussed in Section 4 (see Scheme 34).



Scheme 45 $PhI(OAc)_2$-mediated radical addition of *N*-vinylbenzotriazoles

The mechanism is shown in Scheme 46. In the presence of $PhI(OAc)_2$ (PIDA), addition of the azide radical, generated in situ from $TMSN_3$, to the carbon–carbon double bond of the *N*-vinylbenzotriazole occurs to afford radical intermediate **A** or **A′**. Two possible pathways of sequential denitrogenation were included in the next steps. In path a, ring opening of the triazole occurs initially followed by the release of molecular nitrogen to afford intermediate **B**. Subsequently, a 1,5-H shift leads to intermediate **C**, which can provide intermediate **D** through a single-electron transfer process. Finally, the nitrile product is obtained by release of another molecule of nitrogen gas. In path b, the emission of nitrogen gas from the azide unit occurs first to give intermediate **E**, followed by ring opening of the triazole to produce intermediate **F**. Finally, a single-electron transfer process delivers the desired product.



Scheme 46 Possible mechanisms for the $PhI(OAc)_2$-mediated radical addition to *N*-vinylbenzotriazoles

6 Conclusion and Perspective

To summarize, we have presented a critical overview on the functionalization of benzotriazoles via denitrogenative processes. As we know, triazoles readily undergo ring–chain isomerization through a Dimroth-type equilibrium to form the diazonium or diazo species. Owing to its unique structural motif, the use of 1,2,3-triazoles as diazo precursors has been investigated in transition-metal-catalyzed coupling reactions, whereas the reactions of this heterocyclic skeleton as a precursor of diazonium salts have only been developed in recent years. Therefore, this short review focuses on the formation of carbon–carbon and carbon–heteroatom bonds by using benzotriazoles as the synthetic precursors of *ortho*-amino arenediazoniums, and mainly involving cyclization, arylation, alkenylation, alkylation, carbonylation, borylation, thiolation and phosphorylation. Gathering mechanistic insights could help us to understand the nature of the ring-opening and subsequent functionalization. Although significant progress has been made in this area of research, there are still some major challenges that need to be addressed, such as the limitations of the substrate scope with respect to both coupling partners.

To overcome these central challenges, the most important development will be to extend the substrate scope and the reaction types. On the one hand, with regards to the previously developed transition-metal-catalyzed coupling reactions of diazonium salts, additional novel reactions will be explored for the functionalization of benzotriazoles. On the other hand, the radical strategy opens up a new approach for the denitrogenative functionalization of benzotriazoles under visible light conditions. Thus, various radical precursors should be explored for radical coupling with benzotriazoles. Of course, changing the substituents on the nitrogen atom of the benzotriazoles may lead to some new reactions. As a consequence, new achievements in benzotriazole chemistry are expected to appear in the near future.

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