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Catalyst-Controlled Regioselective Synthesis of Benzotriazlolodiazepin-7-ones and Benzotriazolodiazocin-8-ones

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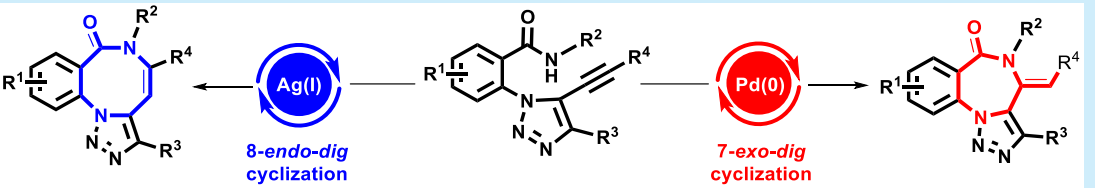
Supporting Information



ABSTRACT: A catalyst-controlled highly chemoselective and regioselective intramolecular cycloamidation of triazol-1-ylbenzamides toward the synthesis of scarcely known heterocycles is reported. In the presence of a palladium catalyst, this cycloisomerization reaction afforded substituted benzotriazlolodiazepin-7-ones via intramolecular insertion of a palladium into C−C triple bond in a 7-*exo*-dig way. Alternatively, the use of a silver catalyst in the reaction produced substituted benzotriazolodiazocin-8-ones in a highly regioselective manner through 8-*endo*-dig intramolecular ring closure.

Medium-sized ring systems are prevalent in various natural products and therapeutic compounds.[1] Among them, 1,4-benzodiazepines and 1,4-benzodiazepin-5-ones show interesting biological properties. For example, anthramycin shows antitumor activity by inhibition of DNA and RNA synthesis in mammalian cells.[2] Estazolam is used for insomnia-associated anxiety disorder, because of its anxiolytic action.[3]

Moreover, CNS depressant Triazolam displays sedative activity and is used for the treatment of insomnia.[4] Amaryllidaceae alkaloid Buflavine exhibits antiserotonin activity.[5] Liver X receptors (LXR) regulates cholesterol, lipid, and glucose metabolism, and dibenz[*b*,*f*]azocin-6-one shows LXR-agonistic activity toward both subtypes LXRα and LXRβ.[6] A potent and orally active antagonist SM-406 is an apoptosis inducer that inhibits cancer cell growth in clinical development[7] (see Figure 1).

Even though both seven- and eight-membered fused heterocycles exhibit interesting bioactivities, their preparation is a challenging task. The difficulty in accessing these medium-sized rings can be attributed to enthalpically unfavorable transition states that are due to transannular interaction and obstruction of ring closure by several entropic factors (see Figure 2).[8]

Various methods have been developed for the synthesis of medium-sized rings, such as ring-closing metathesis,[9] ring expansion,[10] radical cyclization,[11] intramolecular cyclization,[12] and electrophilic cyclization.[13] In particular, intramolecular cycloamidation of alkynes has been poorly explored. In this context, Zhang et al. reported gold-catalyzed 7-*endo*-*dig* cyclization of phenylacetamides for the synthesis of 3-benzazepinone.[14] Swamy and co-workers demonstrated ruthenium-catalyzed synthesis of isoquinolinones through intramolecular amide-alkyne annulation.[15] Yang and colleagues developed PIFA-mediated intramolecular cyclization, followed by oxidative hydroxylation of 1-alkynyl benzamides for the construction of 3-hydroxy-2,3-dihydroisoquinoline-1,4-dione.[16]

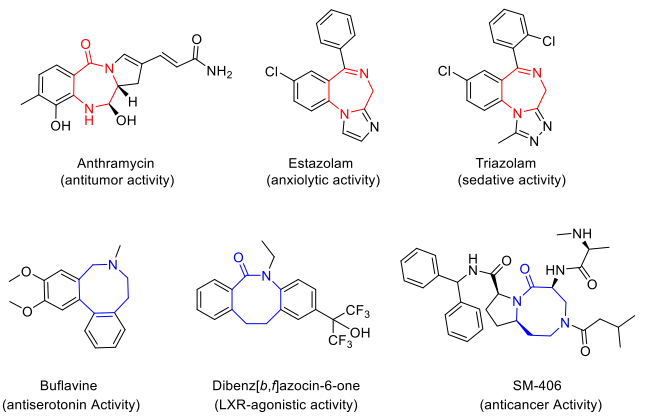


Figure 1. Biologically active 1,4-benzodiazepines and 1,4-benzodiazepin-5-ones.

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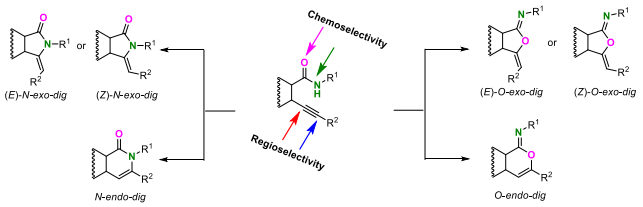
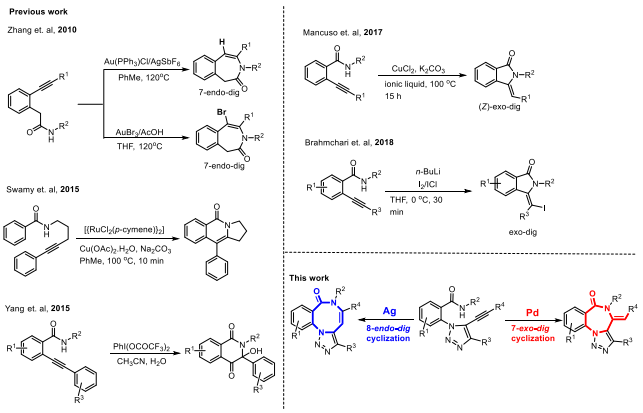


Figure 2. Intramolecular hydroamidation—a challenging task.

Copper-catalyzed cycloisomerization of 2-alkynyl benzamides in the presence of ionic liquid to produce (*Z*)-3-alkylideneisoindolinones was reported by Mancuso et al.[17] Recently, Brahmchari and co-workers achieved the synthesis of isoindolin-1-ones through iodoaminocyclization of 2-alkynylbenzamides by *n*-BuLi-I_2/ICl.[18] In most of the cases, reaction conditions have been tuned to afford either *exo*-dig- or *endo*-dig-products, and, in many cases, afforded a mixture. Because of the ambident nature of amides resulting in *O*-nucleophile and *N*-nucleophile, and the availability of two electrophilic sites at the alkyne bond in the same system, the chemoselectivity and regioselectivity scenario is intricate[19] (see Scheme 1). In this context, a chemoselective- and regioselective-controlled approach by merely changing a metal catalyst in intramolecular cycloamidation is a powerful tool to synthesize medium-sized ring compounds.

Scheme 1. Intramolecular Cycloamidation for the Synthesis of Fused Heterocycles



Herein, we report an unprecedented Ag- and Pd-mediated chemoselective and regioselective cyclization of triazol-1-ylbenzamides for the synthesis of seven- and eight-membered triazole-fused heterocycles.

The required triazol-1-yl benzamides **1** were prepared by modifying the previously reported procedure in the literature.[20] With the required precursor amides **1** in hand, we chose benzamide **1a** as a model substrate to study the intramolecular cyclization with various bases and metal catalysts (see Table S1 in the Supporting Information (SI)). Accordingly, when **1a** was treated with 3 equiv of DBU in a sealed tube at 110 °C for 16 h, a mixture of benzylidene diazepin-6-one **2a** and triazolo[1,5-*a*][1,5]diazocin-7(6*H*)-one **3a**, in yields of 62% and 37%, respectively (Table S1, entry 2), was isolated. The proton NMR of **2a** and **3a** showed a singlet at 6.57 and 6.68 ppm, corresponding to the C═C−H proton. Finally, the absolute structures of **2a** and **3a** were confirmed by single-crystal X-ray analysis (Figure 3). The ORTEP diagram of **2a** exhibited that the seven-membered ring adopted a boat conformation, whereas structure of **3a** is present in chair conformation. Next, we attempted to synthesize **2a** and **3a** in a regiodivergent and chemodivergent manner through the assistance of various metal catalysts and found that Pd and Ag catalysts could be crucial in achieving the desired goal. We then examined a series of Pd catalysts to tune the regioselectivity of the cyclization of **1a** toward the formation of **2a**.

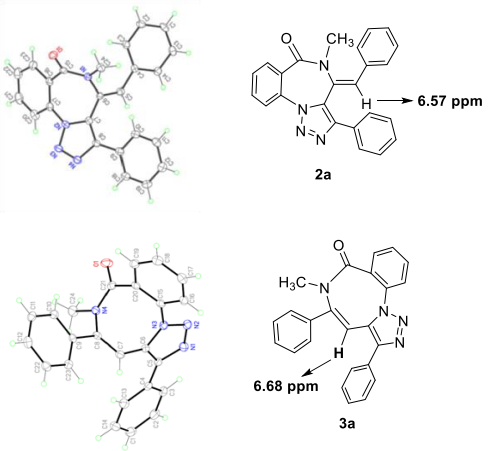


Figure 3. ORTEP diagram of **2a** and **3a**. (Atomic displacement ellipsoids are drawn at the 50% probability level.)

Evaluation of solvents revealed their significant influence on the reaction and CH_3CN was found to be the best choice. Accordingly, treatment of **1a** with 10 mol % of $Pd(PPh_3)_4$, 3 equiv of K_2CO_3 in CH_3CN in sealed tube at 110 °C for 16 h furnished the desired seven-membered product **2a**, which was resulted from 7-*exo*-dig cyclization in 82% yield (Table 1, entries 1−5). Switching to other bases such as Et_3N and KOH was futile (Table 1, entries 6 and 7). The screening of Pd(II) catalysts in the absence of a base did not afford any product, whereas poor regioselectivity was observed in the presence of K_2CO_3 (Table 1, entries 8−10). The combination of $Pd(OAc)_2$ and a small monodentate phosphine ligand P(*o*-tol)$_3$ provided the **2a** and **3a** in 51% and 49% yields, respectively (Table 1, entry 11). Ligand-based Pd(II) catalysts were less effective (Table 1, entries 12−15).

With the optimized conditions in hand, scope of this regioselective 7-*exo*-dig cyclohydroamidation reaction for the synthesis of **2** was investigated in CH_3CN (5 mL) using 10 mol % of $Pd(PPh_3)_4$, 3 equiv of K_2CO_3 at 110 °C in sealed tube for 16 h (see Table 2).

Various 4-substituted triazol-1-ylbenzamides (**1**) with electron-withdrawing and electron-donating groups afforded desired products in excellent yields. Moreover, the substrate **1n**, prepared from 3-amino-2-naphthoic acid, provided the corresponding product **2n** in 84% yield. A wide range of alkynes having alkyl, aryl and heteroaryl substituents (R^2 and R^3) on aromatic ring were successfully participated in the reaction. Amines having aliphatic and aromatic substituents (R^2) successfully participated in the reaction to yield corresponding products in excellent yields.

Having realized the regioselective synthesis of benzotriazolodiazepin-7-ones **2**, we next examined the 8-*endo*-dig cyclization of triazol-1-ylbenzamide **1** toward synthesis of benzotriazolodiazocin-8-ones **3**. Recently, silver(I) salts became prevalent reagents for the cycloisomerization reactions, because of their mild Lewis acidity and carbophilicity.[21] In

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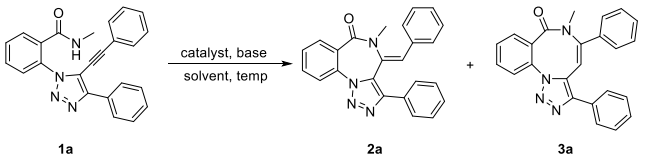
Table 1. Optimization Study on Pd-Catalyzed Regioselective Cyclization of Triazolobenzamide 1a[a]



entry	catalyst	base	solvent	time (h)	Yield[b] (%) 2	3
1[c]	$Pd(PPh_3)_4$	K_2CO_3	toluene	16	–	trace
2[d]	$Pd(PPh_3)_4$	K_2CO_3	DCE	16	–	trace
3[e]	$Pd(PPh_3)_4$	K_2CO_3	MeOH	16	–	–
4[e]	$Pd(PPh_3)_4$	K_2CO_3	THF	16	–	–
5	$Pd(PPh_3)_4$	K_2CO_3	CH_3CN	16	82	18
6	$Pd(PPh_3)_4$	Et_3N	CH_3CN	16	–	–
7	$Pd(PPh_3)_4$	KOH	CH_3CN	16	–	–
8	$PdCl_2$	–	CH_3CN	16	–	–
9	$Pd(TFA)_2$	–	CH_3CN	16	–	–
10	$Pd(TFA)_2$	K_2CO_3	CH_3CN	24	57	43
11[f]	$Pd(OAc)_2$	K_2CO_3	CH_3CN	24	51	49
12	$(CH_3CN)_2PdCl_2$	K_2CO_3	CH_3CN	24	39	61
13	$(CH_3CN)_2PdCl_2$	K_2CO_3	CH_3CN	24	48	52
14[g]	$(CH_3CN)_2PdCl_2$	K_2CO_3	CH_3CN	16	29	71
15	$PdCl_2(PPh_3)_2$	K_2CO_3	CH_3CN	48	52	48

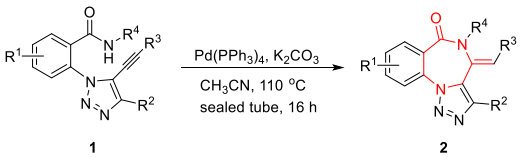
[a]Reaction conditions: **1a** (1 equiv), catalyst (10 mol %), base (3 equiv), CH_3CN (5 mL), 110 °C. [b]Isolated yield. [c]At 130 °C. [d]At 100 °C. [e]At 80 °C. [f]$P(o\text{-tol})_3$ (5 mol %) was used as a ligand. [g]5 mol % $(CH_3CN)_2PdCl_2$ was used.

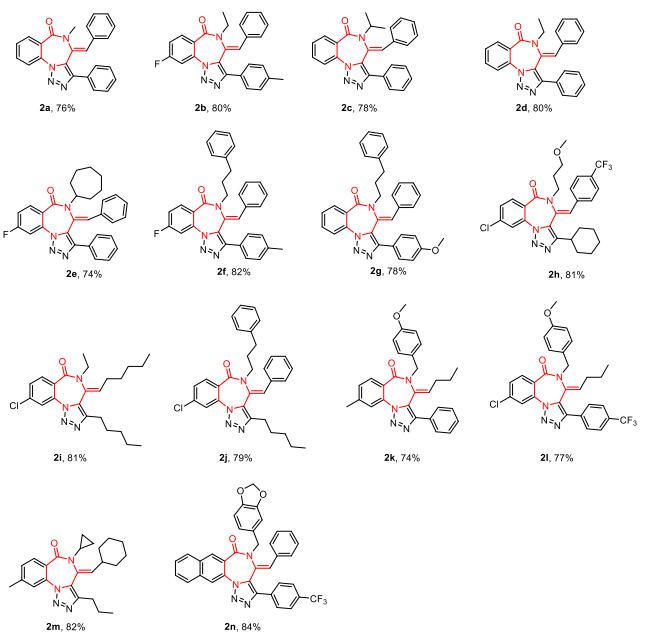
view of that, AgOTf was selected as a catalyst of choice. Initially, treatment of **1a** with 10 mol % of AgOTf, 3 equiv of DBU in CH_3CN at 110 °C in a sealed tube for 16 h did not provide anticipated selectivity of the product **3a** (Table 3, entry 1). Use of other bases such as Et_3N and KOH were ineffective and **1a** was recovered (Table 3, entries 2 and 3). Employment of Cs_2CO_3 gave a disappointing result (Table 3, entry 4). To our delight, when **1a** was treated with 10 mol % of AgOTf and 3 equiv of K_2CO_3 in CH_3CN at 110 °C in a sealed tube for 16 h, desired compound **3a** was obtained in 81% yield (Table 3, entry 5). Further evaluation of solvents revealed that CH_3CN was the best choice (Table 3, entries 6–8). Subsequent screening of other Ag catalysts either failed to catalyzed the annulation or was ineffective in delivering the anticipated regioselectivity (Table 3, entries 9–13).

We next performed substrate scope evaluation under optimized conditions (10 mol % of AgOTf, 3 equiv of K_2CO_3 in CH_3CN, 110 °C, sealed tube, 16 h) for the synthesis of benzotriazolodiazocin-8-ones **3** (see Table 4). The substitution group, either electron-donating or electron-withdrawing on the aromatic ring of triazol-1-ylbenzamides **1**, had little influence on the cyclization, and all the reactions underwent smooth transformation to afford benzotriazolodiazocin-8-ones **3** in excellent yields. In addition, the terminal alkyl and aryl acetylenes were successfully involved in the reaction and corresponding products were obtained in excellent yield.

On the basis of previous reports and experimental observations, a plausible mechanism for Pd- and Ag-catalyzed regioselective synthesis of benzotriazolodiazepin-7-ones (**2**) and benzotriazolodiazepin-7-ones (**3**) is proposed in Schemes 2 and 3.

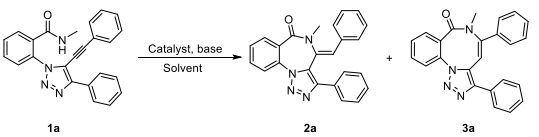
Table 2. Substrate Scope of Benzotriazlolodiazepin-7-ones (2)[a]





[a]Reaction conditions: **1a** (1 equiv), catalyst (10 mol %), base (3 equiv), CH_3CN (5 mL), sealed tube, 16 h. In each case less than 15% of **3** were observed.

Table 3. Optimization Study on Ag-Catalyzed Regioselective Cyclization of 1a[a]



entry	catalyst	base	solvent	temperature (°C)	Yield[b] (%) 2a	3a
1	AgOTf	DBU	CH_3CN	110	58	41
2	AgOTf	Et_3N	CH_3CN	110	–	–
3	AgOTf	KOH	CH_3CN	110	–	–
4	AgOTf	Cs_2CO_3	CH_3CN	110	62	37
5	AgOTf	K_2CO_3	CH_3CN	110	19	81
6	AgOTf	K_2CO_3	MeOH	80	53	47
7	AgOTf	K_2CO_3	THF	80	–	–
8	AgOTf	K_2CO_3	DCE	100	–	–
9	CF_3COOAg	K_2CO_3	CH_3CN	110	47	53
10	$AgSbF_6$	K_2CO_3	CH_3CN	110	64	35
11	AgI	K_2CO_3	CH_3CN	110	71	28
12	AgOAc	K_2CO_3	CH_3CN	110	55	44
13	$AgNO_3$	K_2CO_3	CH_3CN	110	–	–

[a]Reaction conditions: **1a** (1 equiv), catalyst (10 mol %), base (3 equiv), CH_3CN (5 mL), sealed tube, 16 h. [b]Isolated yield.

In the case of palladium-catalyzed reactions, a low ligated $Pd(0)L_2$ generated from $Pd(PPh_3)_4$ activates the N–H bond

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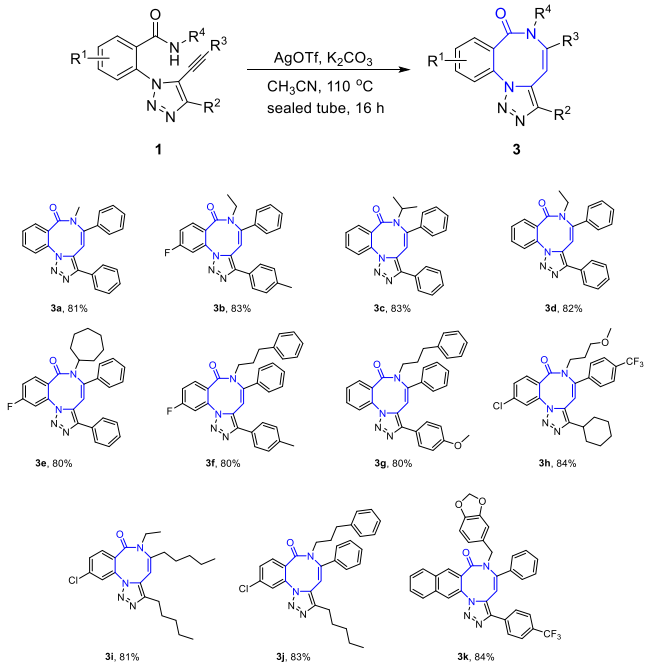
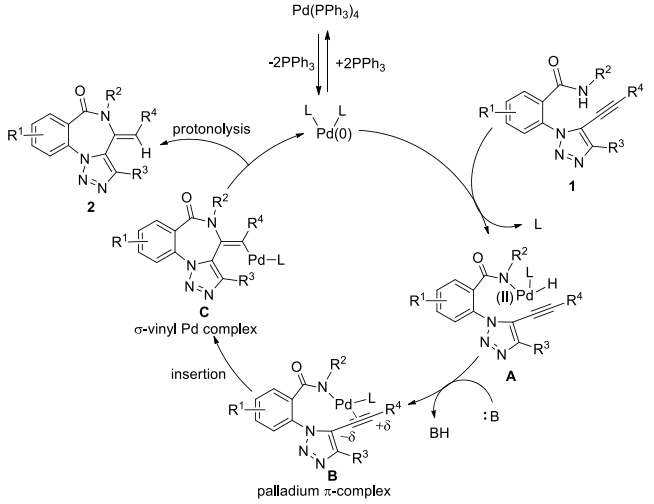
Table 4. Substrate Scope of Benzotriazolodiazocin-8-ones (3)[a]



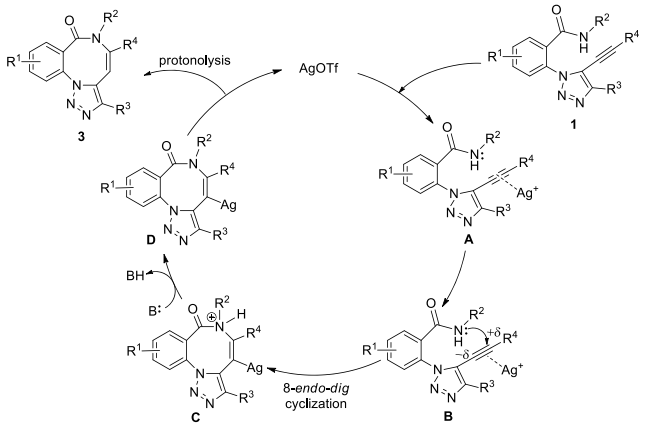
[a]Reaction conditions: **1a** (1 equiv), AgOTf (10 mol %), K_2CO_3 (3 equiv), CH_3CN (5 mL). In each case less than 15% of **2** were observed.

Scheme 2. A Plausible Mechanism for the Synthesis of Benzotriazlolodiazepin-7-ones (2)



to form the intermediate **A**.[22,23] Abstraction of proton by a base and subsequent coordination of palladium with alkyne results in palladium π-complex **B**. In the next step, regioselective intramolecular insertion of a palladium into C−C triple bond and deprotonation gives σ-vinyl Pd complex **C**. Finally, protonolysis of the C−Pd bond yields product **2**.[24] In the case of Ag-catalyzed cycloisomerization of **1**, the reaction proceeds through activation of C−C triple bond by carbophilic AgOTf via coordination to form Ag-alkyne π-complex **A**. Subsequent anti-*endo*-dig intramolecular nucleophilic attack by a lone pair of electrons from the N atom on activated triple bond and deprotonation by a base provides **D**. Finally, protonolysis of the C−Ag bond affords 8-*endo*-dig

Scheme 3. A Plausible Mechanism for the Synthesis of Benzotriazlolodiazepin-8-ones (3)



product **3**. The regioselective anti-*endo*-dig attack by amide nitrogen can be explained by the induced polarization of the triple bond, because of the presence of an electron-withdrawing group at one of the alkyne carbons.

The electron-deficient triazole moiety renders a partial positive charge on β-carbon. This localization of charges assists endo-dig cyclization.[25] Chemoselectivity could be rationalized on the basis of Pearson's principle of hard and soft acids and bases. In view of that, activated triple bond from the Ag(I)-π complex is a soft Lewis acid in nature which would prefer to react with amide nitrogen, compared to more electronegative hard oxygen atom of amide through soft−soft interaction.[26]

In conclusion, catalyst-based switch of regioselectivity in intramolecular cycloamidation of triazol-1-ylbenzamides has been developed. The use of palladium catalyst selectively gave benzotriazlolodiazepin-7-ones resulting from regioselective insertion of a palladium into C−C triple bond while 8-*endo*-*dig* cyclization leads to benzotriazolodiazocin-8-ones when silver catalyst was used. All the products were obtained in excellent yields with high regioselectivity and chemoselectivity. Investigation on mechanistic details regarding a complete switch in regioselectivity by the utilization of either Pd or Ag catalyst is now underway in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.9b04162.

Experimental procedure, characterization, and spectral data of compounds **1a**, **2a**−**2n**, and **3a**−**3k** (PDF)

Accession Codes

CCDC 1953172 and 1953178 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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