Tetrahedron Letters 51 (2010) 2247–2250

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

PIDA-mediated synthesis of oxazoles through oxidative cycloisomerization of propargylamides

Akio Saito *, Asami Matsumoto, Yuji Hanzawa *

Laboratory of Organic Reaction Chemistry, Showa Pharmaceutical University, 3-3165 Higashi-tamagawagakuen, Machida, Tokyo 194-8543, Japan

ARTICLE INFO

Article history:
Received 26 January 2010
Revised 16 February 2010
Accepted 18 February 2010
Available online 21 February 2010

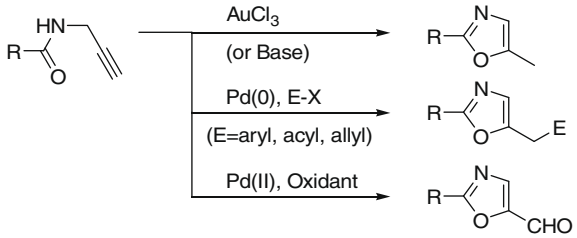
ABSTRACT

PIDA [phenyliodine(III) diacetate] in AcOH or AcOH-HFIP (hexafluoroisopropanol) efficiently promotes the formation of 2,5-disubstituted oxazoles via the oxidative cycloisomerization of propargylamide derivatives.

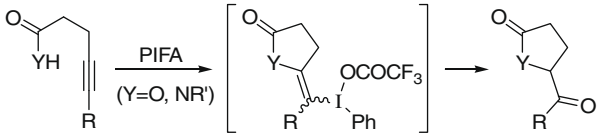
Since oxazole nucleus has found widespread applications in the fields of medicinal chemistry and synthetic chemistry,[1,2] many strategies have been developed for the construction of oxazole nucleus.[3] In the construction of oxazole nucleus, the cycloisomerization of propargylamides provides us with a straightforward approach to the synthesis of 2,5-disubsituted oxazole compounds (Scheme 1). Although the cycloisomerization of propargylamides under basic reaction conditions has been used so far,[4] the alternative procedure catalyzed by $AuCl_3$ has been reported.[5] Pd-catalyzed reaction of propargylamides with aryl iodides, acyl chloride, or allyl reagent leads to the oxazoles with the incorporation of aryl, acyl, or allyl groups into the side chain at 5-position by the tandem cycloisomerization-coupling reaction.[6,7] Recently, the oxidative cycloisomerization of propargylamides under Pd-catalyzed conditions was reported for the preparation of 5-oxazole-carbaldehydes.[8] Thus, a novel and efficient procedure for the construction of oxazole nucleus has remained an attractive goal.

Hypervalent iodine compounds have received much attention as oxidants due to their low toxicity, mild reactivity, high stability, easy handling, and so on.[9] In particular, phenyliodine(III) diacetate (PIDA) and phenyliodine(III) bis(trifluoroacetate) (PIFA) are very useful not only as oxidants in the metal-catalyzed oxidative addition of carbon or hetero atom nucleophiles to alkyne compounds[10] but also as promoters in the oxidation of alkynes to carboxylic acids,[11] α-hydroxy or α-acyloxy ketones,[12] alkynyliodonium salts,[13] and so on.[14–16] PIFA also promotes the intramolecular oxidative amidation or carboxylation of 4-alkynylamide or 4-alkynyl-carboxylic acid derivatives (Scheme 2).[17] As a part of our study on the synthesis of heterocycles from propargylamine compounds,[7,18] we are prompted to attempt the oxidative cycloisomerization of propargylamides. In this Letter, we describe the PIDA-mediated formation of the oxazolylmethyl acetate derivatives from propargylamides.

The evaluation of solvents was conducted for the oxidative cycloisomerization reaction of propargylamide **1a** with phenyliodine(III) diacetate (PIDA, 1.5 equiv) as shown in Table 1. It turned out that fluorinated alcohols were very important for the smooth formation of oxazolylmethyl acetate **2a** (entries 1–7), and thus, the use of hexafluoroisopropanol (HFIP) gave **2a** in 54% yield at room temperature within 6 h (entry 1). In trifluoroethanol (TFE) or MeOH, ether compound **4a** or **5a** was obtained with the formation of **2a** (entries 2 and 6). Although the oxidative cycloisomerization of **1a** in AcOH proceeded slowly (90 °C, 22 h), the isolated yield of **2a** was improved up to 86% (entry 9).[19] The addition of AcOH (5 equiv) was also effective for the reaction of **1a** in HFIP, and **2a** was isolated in 81% yield at room temperature for 20 h (entry 10).[20]



Scheme 1. Synthesis of oxazoles from *N*-propargylamides.

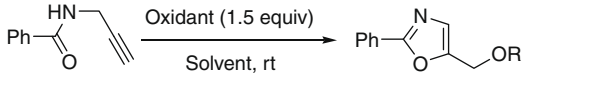


Scheme 2. Oxidative amidation or carboxylation.

* Corresponding authors. Tel.: +81 (0) 42 721 1571; fax: +81 (0) 42 721 1569.
E-mail addresses: akio-sai@ac.shoyaku.ac.jp (A. Saito), hanzaway@ac.shoyaku.ac.jp (Y. Hanzawa).

0040-4039/$ - see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2010.02.096

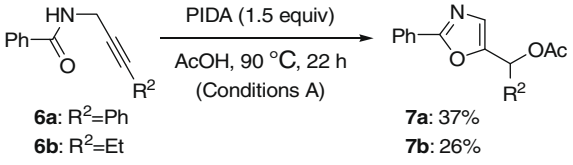
Table 1
Optimization for the oxidative cycloisomerization of **1a**



Entry	Oxidant	Solvent	(h)	**2a**[a] (%)	**1a**[a] (%)
1	PIDA	HFIP	6	54	0
2[b]	PIDA	TFE	6	19	63
3	PIDA	CH_2Cl_2	6	12	44
4	PIDA	THF	23	0	50
5	PIDA	MeCN	23	0	87
6[c]	PIDA	MeOH	23	8	65
7	PIDA	H_2O	23	5	58
8	PIDA	AcOH	23	25	74
9[d]	PIDA	AcOH	22	91 (86)	0
10[e]	PIDA	HFIP	20	78 (81)	0
11	PIFA	HFIP	3	**3a** 35	0
12	PIFA	TFE	22	**3a** 36	0
13	PIFA	CH_2Cl_2	18	**3a** 76	0

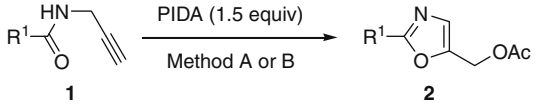
[a] Yields were determined by ^{1}H NMR analysis. Yield in the parenthesis is the isolated yield.
[b] **4a** was detected in 7% yield.
[c] **5a** was detected in 21% yield.
[d] Temp: 90 °C.
[e] Additive: 5 equiv AcOH.

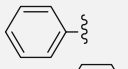
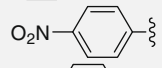
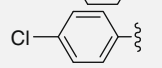
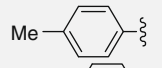
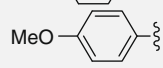
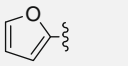
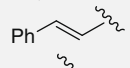
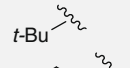
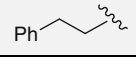
Next, the scope of substrates **1** having the various acyl groups under the PIDA (1.5 equiv)-mediated conditions A (solvent: AcOH, temp: 90 °C) or B (solvent: HFIP, additive: 5 equiv AcOH, temp: rt) is shown in Table 2. Both the conditions could be applied to the oxidative cycloisomerization of not only aromatic amides **1a–g** but also aliphatic amides **1h–i**, and the corresponding oxazoles **2a–i** were obtained. In some cases, the conditions A brought about the superior results to the conditions B (entries 9, 11, and 17). Furthermore, the conditions A could be applied to the reaction of internal alkynes **6a** (R^2 = Ph) and **6b** (R^2 = Et) (Scheme 3). It should



Scheme 3. The oxidative cycloisomerization of internal alkynes **6**.

Table 2
The oxidative cycloisomerization of various propargylamides **1**

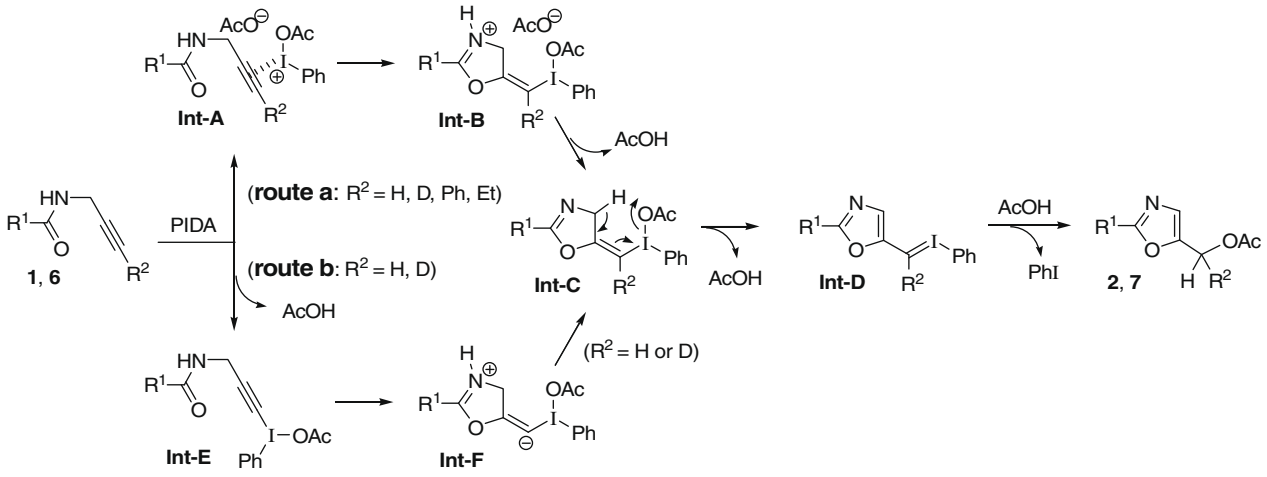


Entry	R^1	**1**	Conditions[a]	/(h)	**2**[b] (%)	
1		**1a**	A	22	**2a**	86
2			B	20	**2a**	81
3		**1b**	A	22	**2b**	92
4			B	23	**2b**	88
5		**1c**	A	22	**2c**	81
6			B	24	**2c**	80
7		**1d**	A	22	**2d**	84
8			B	24	**2d**	86
9		**1e**	A	22	**2e**	83
10			B	24	**2e**	66
11		**1f**	A	45	**2f**	71
12			B	47	**2f**	53
13		**1g**	A	21	**2g**	73
14			B	12	**2g**	78
15		**1h**	A	22	**2h**	86
16			B	24	**2h**	88
17		**1i**	A	34	**2i**	67
18			B	24	**2i**	25

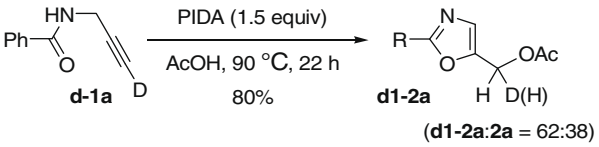
[a] Conditions A: solvent; AcOH, temp; 90 °C. Conditions B: solvent; HFIP, additive; AcOH (5 equiv), temp; rt.
[b] Isolated yield.

be mentioned that phenyliodine(III) bis(trifluoroacetate) (PIFA, 1.5 equiv) in CH_2Cl_2, which worked well for the formation of **3a** (Table 1, entry 13), did not yield good results in reactions of other substrates.

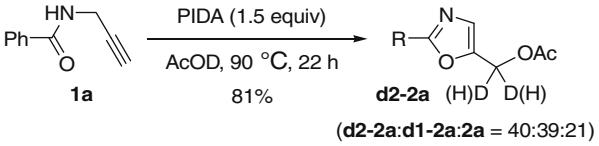
On the basis of these observations and the previous report about the PIFA-mediated cyclization of 4-alkynylamides,[17b,21] the present formation of oxazole would consist of (i) the cyclization of **Int-A** through the activation of the triple bond by PIDA, (ii) the formation of **Int-D**[12e] by the proton transfer of **Int-B** and the subsequent isomerization of **Int-C**, and (iii) the substitution of phenyliodonium group in **Int-D** by AcOH (Scheme 4). This is supported by the reaction of internal alkynes (Scheme 3) or the reaction of the deuterated **d-1a** (Scheme 5). Thus, the treatment of **d-1a** with PIDA (1.5 equiv) in AcOH brought about the mono-deuterated oxazole **d1-2a** with the undeuterated **2a** in 80% yield (**d1-2a**/**2a** = 62:38,



Scheme 4. A possible mechanism.



Scheme 5. The oxidative cycloisomerization of **1a**–**D**.



Scheme 6. The oxidative cycloisomerization of **1a** in AcOD.

Scheme 5). It is suggested that the oxazole **d1**-**2a** was derived from the route **a** shown in Scheme 4. The formation of the undeuterated **2a** shown in Scheme 5 would be a result of an intervention of the route **b** shown in Scheme 4.

The reaction of **1a** with PIDA (1.5 equiv) in AcOD afforded a mixture of di-deuterated, mono-deuterated, and undeuterated oxazoles (**d2**-**2a**/**d1**-**2a**/**2a** = 40:39:21, Scheme 6).[22] On the other hand, regardless of the addition of PIDA, the treatment of undeuterated **2a** in AcOD did not yield deuterated **2a**. A similar observation has been reported in the PIDA-mediated oxidation of terminal alkyne compounds to α-acetoxy ketones.[12e] It has been proposed that the incorporation of acetoxy groups into the ketones proceeds via the alkynyliodonium intermediate like the **Int**-**E** shown in Scheme 4.[12] Thus, the di-deuterated compound shown in Scheme 6 was derived from the deuteration of **Int**-**F** and **Int**-**D** by AcOD.[12e]

In conclusion, we have demonstrated the facile preparation of the oxazolylmethyl acetate derivatives through the oxidative cycloisomerization of propargylamides with PIDA. A plausible mechanism for the present formation of oxazole was proposed. Particularly, in reactions of terminal alkyne substrates, we suggested that the two routes (routes **a** and **b** shown in Scheme 4) were involved in deuterium labeling experiments. The present procedure would shed new light on the convenient approach for the preparation of oxazole compounds. Synthetic applications and detailed mechanistic studies of the present reaction are underway.

Acknowledgments

This work was supported by Grant-in-Aid for Young Scientists (B), MEXT Japan (No. 21790024). A generous donation of HFIP by Central Glass Co., Ltd is gratefully acknowledged.

References and notes

1. (a) Turchi, I. J.; Dewar, M. J. S. *Chem. Rev.* **1975**, *75*, 389; (b) Wasserman, H. H.; McCarthy, K. E.; Prowse, K. S. *Chem. Rev.* **1986**, *75*, 845; (c) Wipf, P. *Chem. Rev.* **1995**, *95*, 2115; (d) Jin, Z. *Nat. Prod. Rep.* **2003**, *20*, 584; (e) Jin, Z. *Nat. Prod. Rep.* **2009**, *26*, 382; (f) Palmer, D. C.. In *Oxazoles: Synthesis, Reactions, and Spectroscopy, Part A*; John Wiley & Sons: Hoboken, NJ, 2003; Vol. 60, (g) Palmer, D. C.. In *Oxazoles: Synthesis, Reactions and Spectroscopy, Part B*; John Wiley & Sons: Hoboken, NJ, 2004; Vol. 60,.
2. (a) Dalvie, D. K.; Kalgutkar, A. S.; Khojasteh- Bakht, S. C.; Obach, R. S.; O'Donnell, J. P. *Chem. Res. Toxicol.* **2002**, *15*, 269; (b) McGovern, S. L.; Caselli, E.; Grigorieff, N.; Shoichet, B. K. *J. Med. Chem.* **2002**, *45*, 1712; (c) Murcia-Soler, M.; Perez-Gimenez, F.; Garcia-March, F. J.; Salabert-Salvador, M. T.; Diaz-Villanueva, W.; Castro-Bleda, M. J.; Villanueva-Pareja, A. *J. Chem. Inf. Comput. Sci.* **2004**, *44*, 1031.
3. For recent examples: (a) Xia, M. *J. Chem. Res., Synop.* **2000**, 382; (b) Milton, M. D.; Inada, Y.; Nishibayashi, Y.; Uemura, S. *Chem. Commun.* **2004**, 2712; (c) Hashmi, A. S. K.; Rudolph, M.; Schymura, S.; Visus, J.; Frey, W. *Eur. J. Org. Chem.* **2006**, 4905; (d) Ueda, S.; Nagasawa, H. *Angew. Chem., Int. Ed.* **2008**, *47*, 6411; (e) Xia, Q.; Ganem, B. *Org. Lett.* **2002**, *4*, 1631; (f) Mihara, H.; Xu, Y.; Shepherd, E.; Matsunaga, S.; Shibasaki, M. *J. Am. Chem. Soc.* **2009**, *131*, 8384.
4. (a) Eloy, F.; Deryckere, A. *Chim. Ther.* **1973**, 437; (b) Nilsson, B. M.; Hacksell, U. *J. Heterocycl. Chem.* **1989**, *26*, 269; (c) Freedman, J.; Huber, E. W. *J. Heterocycl. Chem.* **1990**, *27*, 343; (d) Nilsson, B. M.; Vargas, H. M.; Ringdahl, B.; Hacksell, U. *J. Med. Chem.* **1992**, *35*, 285; (e) Wipf, P.; Rahman, L. T.; Rector, S. R. *J. Org. Chem.* **1998**, *63*, 7132; (f) Clark, D. C.; Travis, D. A. *Bioorg. Med. Chem.* **2001**, *9*, 2857; (g) Coqueron, P.-Y.; Didier, C.; Ciufolini, M. A. *Angew. Chem., Int. Ed.* **2003**, *42*, 1411; (h) Zhang, J.; Polishchuk, E. A.; Chen, J.; Ciufolini, M. A. *J. Org. Chem.* **2009**, *74*, 9140.
5. Hashmi, A. S. K.; Weyrauch, J. P.; Frey, W.; Bats, J. W. *Org. Lett.* **2004**, *6*, 4391.
6. Incorporation of aryl groups: (a) Arcadi, A.; Cacchi, S.; Cascia, L.; Fabrizi, G.; Marinelli, F. *Org. Lett.* **2001**, *3*, 2501; Incorporation of acyl groups: (b) Merkul, E.; Müller, T. J. J. *Chem. Commun.* **2006**, 4817; (c) Bacchi, A.; Costa, M.; Gabriele, B.; Pelizzi, G.; Salerno, G. *J. Org. Chem.* **2002**, *67*, 4450.
7. We recently found the tandem cycloisomerization–allylation reaction of propargylamides with allyl reagents catalyzed by Pd(0). See, Saito, A.; Iimura, K.; Hanzawa, Y. *Tetrahedron Lett.* **2010**, *51*, 1471.
8. Beccalli, E. M.; Borsini, E.; Broggini, G.; Palmisano, G.; Sottocornola, S. *J. Org. Chem.* **2008**, *73*, 4746.
9. Recent reviews: (a) Dohi, T.; Kita, Y. *Chem. Commun.* **2009**, 2073; (b) Uyanik, M.; Ishihara, K. *Chem. Commun.* **2009**, 202086; (c) Zhdankin, V. V.; Stang, P. J. *Chem. Rev.* **2008**, *108*, 5299; (d) Ciufolini, M. A.; Braun, N. A.; Canesi, S.; Ousmer, M.; Chang, J.; Chai, D. *Synthesis* **2007**, *24*, 3759; (e) Wirth, T. *Angew. Chem., Int. Ed.* **2005**, *44*, 3656; (f) Zhdankin, V. V.; Stang, P. J. *Chem. Rev.* **2002**, *102*, 2523.
10. Pd-catalyzed oxidative cyclizations of enynes: (a) Tong, X.; Beller, M.; Tse, M. K. *J. Am. Chem. Soc.* **2007**, *129*, 4906; (b) Welbes, L. L.; Lyons, T. W.; Cychosz, K. A.; Sanford, M. S. *J. Am. Chem. Soc.* **2007**, *129*, 5836; (c) Tsujihara, T.; Takenaka, K.; Onitsuka, K.; Hatanaka, M.; Sasai, H. *J. Am. Chem. Soc.* **2009**, *131*, 3452; Pd-catalyzed oxidative cyclization of alkynyl-enone: (d) Tello-Aburto, R.; Harned, A. M. *Org. Lett.* **2009**, *11*, 3998; Pd-catalyzed oxidative arylation of *N*-phenylpropiolamides: (e) Tang, S.; Peng, P.; Pi, S.-F.; Liang, Y.; Wang, N.-X.; Li, J.-H. *Org. Lett.* **2008**, *10*, 1179; (f) Tang, S.; Peng, P.; Zhong, P.; Li, J.-H. *J. Org. Chem.* **2008**, *73*, 5476; Dimerization of terminal alkynes: (g) Yan, J.; Lin, F.; Yang, Z. *Synthesis* **2007**, 1301; (h) Yan, J.; Wu, J.; Jin, H. *J. Organomet. Chem.* **2007**, *692*, 3636; (i) Zhu, M.; Jin, J. C.; Tong, J. Y. *J. Chem. Res.* **2008**, 218; Rh-catalyzed metallonitrene/alkyne metathesis: (j) Thornton, A. R.; Blakey, S. B. *J. Am. Chem. Soc.* **2008**, *130*, 5020; (k) Thornton, A. R.; Martin, V. I.; Blakey, S. B. *J. Am. Chem. Soc.* **2009**, *131*, 2434.
11. Oxidative cleavage of alkynes: (a) Moriarty, R. M.; Penmasta, R.; Awasthi, A. K.; Prakash, I. *J. Org. Chem.* **1988**, *53*, 6124; Oxidative rearrangement of alkynes: (b) Moriarty, R. M.; Vaid, R. K.; Duncan, M. P.; Vaid, B. K. *Tetrahedron Lett.* **1987**, *28*, 2845.
12. (a) Tamura, Y.; Yakura, T.; Haruta, J.; Kita, Y. *Tetrahedron Lett.* **1985**, *26*, 3837; (b) Kita, Y.; Yakura, T.; Terashi, H.; Haruta, J.; Tamura, Y. *Chem. Pharm. Bull.* **1989**, *37*, 891; (c) Ochiai, M.; Kunishima, M.; Fuji, K.; Nagao, Y. *J. Org. Chem.* **1989**, *54*, 4038; (d) Robertson, J.; Dallimore, J. W. P.; Meo, P. *Org. Lett.* **2004**, *6*, 3857; (e) Mo, D.-L.; Dai, L.-X.; Hou, X.-L. *Tetrahedron Lett.* **2009**, *50*, 5578; (f) Koser, G. F.; Chen, X.; Chen, K.; Sun, G. *Tetrahedron Lett.* **1993**, *34*, 779; (g) Moriarty, R. M.; Condeiu, C.; Tao, A.; Prakash, O. *Tetrahedron Lett.* **1997**, *38*, 2401.
13. (a) Stang, P. J.; Boehshar, M.; Wingert, H.; Kitamura, T. *J. Am. Chem. Soc.* **1988**, *110*, 3272; (b) Lodaya, J. S.; Koser, G. F. *J. Org. Chem.* **1990**, *55*, 1513; (c) Kitamura, T.; Lee, C. H.; Taniguchi, H.; Matsumoto, M.; Sano, Y. *J. Org. Chem.* **1994**, *59*, 8053; (d) Kitamura, T.; Kotani, M.; Fujiwara, Y. *Synthesis* **1998**, 1416; (e) Zhdankin, V. V.; Persichini, P. J., III; Cui, R.; Jin, Y. *Synlett* **2000**, 719–721; (f) Huang, X.; Zhu, Q. *Tetrahedron Lett.* **2001**, *42*, 6373; (g) Koumbis, A. E.; Kyzas, C. M.; Savva, A.; Varvoglis, A. *Molecules* **2005**, *10*, 1340; (h) Yoshida, M.; Osafune, K.; Hara, S. *Synthesis* **2007**, 1542; Iodoalkynes: (i) Yan, J.; Li, J.; Cheng, D. *Synlett* **2007**, 2442.
14. Formations of haloalkenes: (a) Kitamura, T.; Furuki, R.; Taniguchi, H.; Stang, P. J. *Tetrahedron Lett.* **1990**, *31*, 703; (b) Muraki, T.; Yokoyama, M.; Togo, H. *J. Org. Chem.* **2000**, *65*, 4679; (c) Das, B.; Srinivas, Y.; Sudhakar, C.; Damodar, K.; Narender, R. *Synth. Commun.* **2009**, *39*, 220; See, (d) Moriarty, R. M.; Vaid, R. K.; Duncan, M. P. *Synth. Commun.* **1987**, *17*, 703.
15. Ring expansions of alkynyl cycloalkanols: (a) Bovonsombat, P.; McNelis, E. *Tetrahedron* **1993**, *49*, 1525; (b) Bovonsombat, P.; McNelis, E. *Tetrahedron Lett.* **1993**, *34*, 4277; (c) Bovonsombat, P.; McNelis, E. *Tetrahedron Lett.* **1994**, *35*, 6431; (d) Djuardi, E.; Bovonsombat, P.; McNelis, E. *Tetrahedron* **1994**, *50*, 11793; (e) Bovonsombat, P.; McNelis, E. *Synth. Commun.* **1995**, *25*, 1223; (f) Herault, X.; McNelis, E. *Tetrahedron* **1996**, *52*, 10267; (g) Chen, J.-M.; Huang, X. *Synthesis* **2004**, 2459.
16. Reactions of propargylsilanes or -stannanes (a) Ochiai, M.; Ito, T.; Takaoka, Y.; Masaki, Y. *J. Am. Chem. Soc.* **1991**, *113*, 1319; (b) Ochiai, M.; Ito, T.; Masaki, Y. *J. Chem. Soc., Chem. Commun.* **1992**, 15; (c) Gately, D. A.; Luther, T. A.; Norton, J. R.; Miller, M. M.; Anderson, O. P. *J. Org. Chem.* **1992**, *57*, 6496; (d) Ochiai, M.; Ito, T. *J. Org. Chem.* **1995**, *60*, 2274.
17. (a) Serna, S.; Tellitu, I.; Dominguez, E.; Moreno, I.; SanMartin, R. *Org. Lett.* **2005**, *7*, 3073; (b) Tellitu, I.; Serna, S.; Herrero, M. T.; Moreno, I.; Dominguez, E.; SanMartin, R. *J. Org. Chem.* **2007**, *72*, 1526; (c) Gao, M.; Wang, D.-X.; Zheng, Q.-Y.; Huang, Z.-T.; Wang, M.-Xi. *J. Org. Chem.* **2007**, *72*, 6060; (d) Tellitu, I.; Serna, S.; Dominguez, E. *ARKIVOC* **2010**, 7.
18. Synthesis of indole compounds from *N*-propargylanilines: (a) Saito, A.; Kanno, A.; Hanzawa, Y. *Angew. Chem., Int. Ed.* **2007**, *46*, 3931; (b) Saito, A.; Oda, S.; Fukaya, H.; Hanzawa, Y. *J. Org. Chem.* **2009**, *74*, 1517; Synthesis of pyrrole

compounds from *N*-propargyl β-enaminones: (c) Saito, A.; Konishi, T.; Hanzawa, Y. *Org. Lett.* **2010**, *12*, 372.

19. *Representative procedure for the preparation of oxazolylmethyl acetate derivatives in AcOH (conditions A)*: $PhI(OAc)_2$ (193 mg, 0.6 mmol) was added to a solution of propargylamide **1a** (63.6 mg, 0.4 mmol) in AcOH (2.0 mL), and the reaction mixture was stirred at 90 °C for 22 h. The mixture was diluted with ether and satd $NaHCO_3$ aq was added. The aqueous solution was extracted with ether and the combined organic layer was dried with $MgSO_4$. After concentration of the filtrate to dryness and purification of the residue by silica gel column chromatography (hexane/AcOEt = 80:20) gave oxazolylmethyl acetate **2a** (74.5 mg, 86%) as a white solid. Mp 143 °C. IR (KBr) ν cm^{-1}: 1735. ^1H NMR (300 MHz, $CDCl_3$) δ; 2.08 (s, 3H), 5.14 (s, 2H), 7.19 (s, 1H), 7.42–7.44 (m, 3H), 8.01–8.04 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ; 20.7, 55.6, 126.4, 127.1, 128.6, 128.7, 130.5, 146.5, 162.4, 170.3. FAB-LM *m*/*z*: 218 (M^++1). FAB-HM Calcd for $C_{12}H_{12}NO_3$: 218.0817, Found: 218.0817. Anal. Calcd for $C_{12}H_{11}NO_3$: C, 66.35; H, 5.10; N, 6.45. Found: C, 66.03; H, 5.21; N, 6.30.
20. *Representative procedure for the preparation of oxazolylmethyl acetate derivatives in HFIP (conditions B)*: $PhI(OAc)_2$ (193 mg, 0.6 mmol) and AcOH (114 μL, 2.0 mmol) were added to a solution of propargylamide **1a** (63.6 mg, 0.4 mmol) in HFIP (2.0 mL), and the reaction mixture was stirred at room temperature for 20 h. The mixture was diluted with ether and filtered through a short alumina column. After concentration of the filtrate to dryness, purification of the residue by silica gel column chromatography (hexane/AcOEt = 80:20) gave oxazolylmethyl acetate **2a** (70.1 mg, 81%) as a white solid.
21. See, oxidative cyclization of *cis*-2-en-4-yn-1-ones mediated by 2-iodoxybenzoic acid (IBX): Du, X.; Chen, H.; Liu, Y. *Chem. Eur. J.* **2008**, *14*, 9495.
22. In the absence of PIDA, the treatment of **1a** in AcOD did not bring about H–D exchange reaction of terminal alkyne moiety of **1a**.