ORGANIC CHEMISTRY FRONTIERS

CCS 中国化学会 CHINESE CHEMICAL SOCIETY

SIOC

ROYAL SOCIETY OF CHEMISTRY

Iodine-Catalyzed Cyclization-Allylation of *N*-Allyl-2-alkynylanilines via Iodocyclization-Rearrangement-Deiodination Sequence

Journal:	*Organic Chemistry Frontiers*
Manuscript ID	QO-RES-02-2023-000315.R1
Article Type:	Research Article
Date Submitted by the Author:	29-Apr-2023
Complete List of Authors:	Tubata, Sae; Tokyo University of Agriculture and Technology, Division of Applied Chemistry, Institute of Engineering Tsubouchi, Akira; Tokyo University of Agriculture and Technology, Applied Chemistry Saito, Akio; Tokyo University of Agriculture and Technology, Division of Applied Chemistry, Institute of Engineering

ARTICLE

Iodine-catalyzed cyclization-allylation of *N*-allyl-2-alkynylanilines via iodocyclization-rearrangement-deiodination sequence†

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

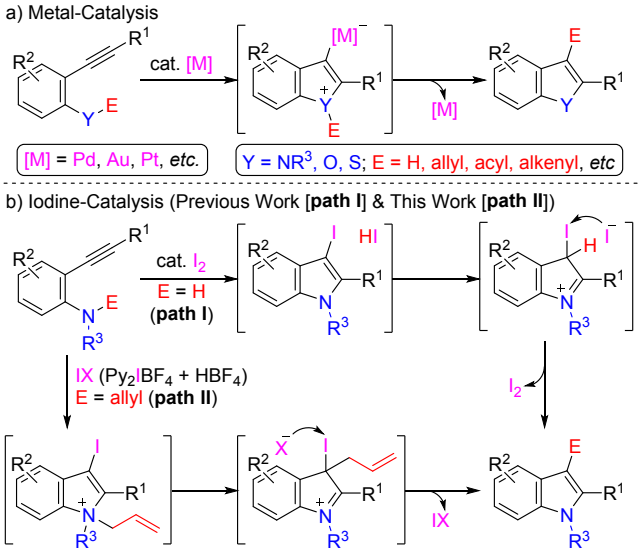
Sae Tsubata,[a] Akira Tsubouchi,[a] and Akio Saito*[a]

From the viewpoint of green and sustainable chemistry, metal-free cyclization-functionalization reactions of *o*-alkynylanilines methods have been developed recently. However, the applicable substrates are limited because these methods require different activation modes from those by transition metal catalysts. Herein, we report a metal-free cyclization-allylation reaction of *o*-alkynylanilines catalyzed by iodine(I) species via carbo-deiodination of iodocyclized intermediates involving rearrangement of allyl groups, which is the similar mechanism to transition metal-catalysis. This method represents the first iodine-catalysis via carbo-deiodination with rearrangement of functional groups.

Introduction

Since indoles are heterocycles widely found in nature and widely applied in chemistry, biology, and materials science, a variety of methods for the construction of indoles have been developed.[1] Among them, the transition metal-catalyzed cyclization of *o*-alkynylanilines provides one of the facile and powerful synthetic methods of substituted indoles. The catalytic reaction generally proceeds via the activation of triple bond by π-acidic metal complexes and the subsequent proto-demetallation of cyclized intermediates (Scheme 1a, Y = NR, E = H).[2] This method can be applied to cyclization-functionalization reactions of *N*,*N*-disubstituted *o*-alkynylanilines, which produce indoles with the migration of various substituents on the nitrogen to the 3-position (Y = NR, E = allyl,[3] acyl,[4] alkenyl,[5] *etc*[6,7]), as well as the reactions of the oxygen[3b,g,5b] and sulfur analogues (Y = O and S).[8] Recently, the metal-free reactions of *N*,*N*-disubstituted *o*-alkynylanilines with the 1,3-migration of carbon-based functional groups have been developed from the viewpoint of green and sustainable chemistry.[9] However, the applicable substrates are limited because these methods are triggered by the interaction of tetrabutylammonium fluoride catalyst with silyl group,[9a] acid-mediated enamine to iminium ion conversion[9b] or radical addition to ynamides.[9c] Thus, the metal-free cyclization-functionalization reactions of *N*,*N*-disubstituted *o*-alkynylanilines remains challenging.

In recent years, iodine-based catalysts have gained increasing popularity in metal-free transformation reactions due to their benefits such as low toxicity, inexpensiveness and transition-metal-like reactivity. In addition to hypervalent iodine[10] and (hypo)iodite catalysts[11] *in situ* generated from iodine-based precatalysts and oxidants, these catalysts include halogen-bonding-based catalysts as a σ-electrophilic Lewis acid[12] and activation catalysts for the donor of functional groups.[13]



Scheme 1. Cyclization of *o*-alkynylanilines.

On the other hand, as part of our research on the synthesis of heterocycles through the activation of alkynes by iodine-based catalyst,[14] we recently reported a molecular iodine-catalyzed cyclization of *o*-alkynylanilines (Scheme 1b, path I).[14d] In this reaction, molecular iodine promotes the iodocyclization of the substrates and then the byproduct HI causes proto-deiodination of the iodocyclized intermediates, thereby giving rise to indoles along with the regeneration of molecular iodine. However, such an iodine catalysis including redox processes

[a] Division of Applied Chemistry, Institute of Engineering, Tokyo University of Agriculture and Technology, 2-24-16 Naka-cho, Koganei, Tokyo 184-8588, Japan. E-mail: akio-sai@cc.tuat.ac.jp

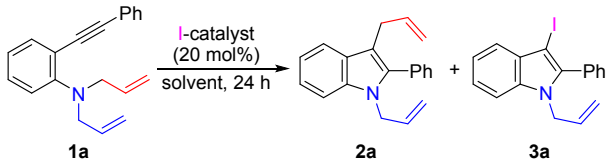
†Electronic Supplementary Information (ESI) available: experimental procedures, characterisation data for new compounds. For ESI or other electronic format see DOI: 10.1039/x0xx00000x

without any terminal oxidants are very rare examples.[15] Moreover, although iodine-mediated cyclization reactions of *o*-alkynylanilines via carbo-deiodination processes have been known,[16] the catalytic method for these reactions have not been achieved. Herein, we report a metal-free cyclization-allylation reaction of *o*-alkynylanilines catalyzed by iodine(I) species *in situ* derived from Barluenga's reagent (Py_2IBF_4, Py = pyridine) and $HBF_4{\cdot}OEt_2$,[17] in which iodocyclized intermediates would undergo carbo-deiodination involving rearrangement of allyl groups (Scheme 1b, path II).

Results and discussion

Based on the molecular iodine-catalyzed cyclization of *o*-alkynylanilines (Scheme 1b, path I),[14d] iodine catalysts were initially evaluated in the formation of 3-allylindole **2a** from *N*,*N*-diallyl-*o*-alkynylaniline **1a** (Table 1). We envisioned that the iodine catalyst would cause the iodocyclization of **1a** to produce **2a** along with the regeneration of the iodine catalyst via the aza-Claisen rearrangement reaction and subsequent deiodination (Scheme 1b, path II).

Table 1. Optimization of conditions.



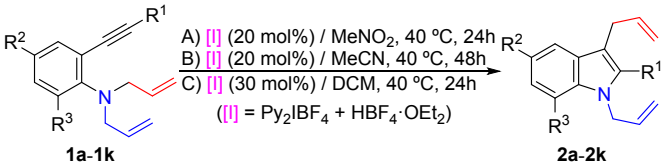
Entry	Catalyst	Solvent	(ºC)	Yields[a] or recovery[a] (%)		
				2a	**3a**	**1a**
1	I_2	$MeNO_2$	60	41	4	6
2	NIS	$MeNO_2$	60	33	ND[b]	49
3	ICl	$MeNO_2$	60	48	trace	0
4	Py_2IBF_4	$MeNO_2$	60	50	trace	0
5[c]	Py_2IBF_4	$MeNO_2$	40	69	6	0
6[c]	Py_2IBF_4	MeCN	40	38	4	42
7[c,d]	Py_2IBF_4	MeCN	40	66	5	9
8[c]	Py_2IBF_4	DCE	40	45	5	44
9[c,d]	Py_2IBF_4	DCM	40	40	4	30
10[e]	Py_2IBF_4	DCM	40	54[f]	10	19

[a] Determined by ^{1}H NMR analysis using an internal standard. [b] Not determined. [c] Addtive: $HBF_4{\cdot}OEt_2$ (20 mol%). [d] Time: 48 h. [e] Py_2IBF_4 and $HBF_4{\cdot}OEt_2$: 30 mol% each. [f] Isolated yield: 53%.

As expected, **1a** was treated with molecular iodine (20 mol%) in $MeNO_2$ to give the desired **2a** (41%) at 60 ºC for 24 h (Table 1, entry 1). However, *N*-iodosuccinimide (NIS) resulted in a lower yield of **2a** (33%) and a significant recovery of **1a** (49%) probably due to the relatively high nucleophilicity of the succinimide anion, which promotes the deallylation reaction of the iodocyclized intermediate before the aza-Claisen rearrangement reaction. Hence, ICl and Barluenga's reagent having lower nucleophilic counter anions gave relatively good results (entries 3 and 4). Furthermore, Barluenga's reagent pretreated with $HBF_4{\cdot}OEt_2$[17] improved the yield of **2a** up to 69% at 40 ºC (entry 5). Among the attempted solvent (entries 5-10 and ESI), MeCN gave the similar result (**2a**: 66%) to $MeNO_2$ albeit taking for 48 h (entry 7). Unfortunately, the obtained **2a** was difficult to separate from a byproduct of undetermined structure. On the other hand, the formation of the byproduct was not observed in DCM (entry 8). Therefore, we examined the conditions thoroughly in DCM and found that it was better to increase the amount of catalyst (entry 10) rather than to extend the reaction time (entry 9). When 30 mol% of catalyst was used in DCM, **2a** was isolated in 53% yield (entry 10).

Next, the cyclization-allylation reactions of *o*-alkynylanilines **1** were investigated using iodine species (20-30 mol%) generated from Barluenga's reagent and $HBF_4{\cdot}OEt_2$ in $MeNO_2$ (method **A**), MeCN (method **B**) or DCM (method **C**), which gave relatively good results. As shown in Table 2, method **C** was found to show equal or better results than methods **A** and **B** in some cases (**1b**, **1d**, **1f** and **1i**-**1k**) as well as to allow the proper purification of **2** in all cases.

Table 2. Effect of substituents on alkynes or aromatic rings.



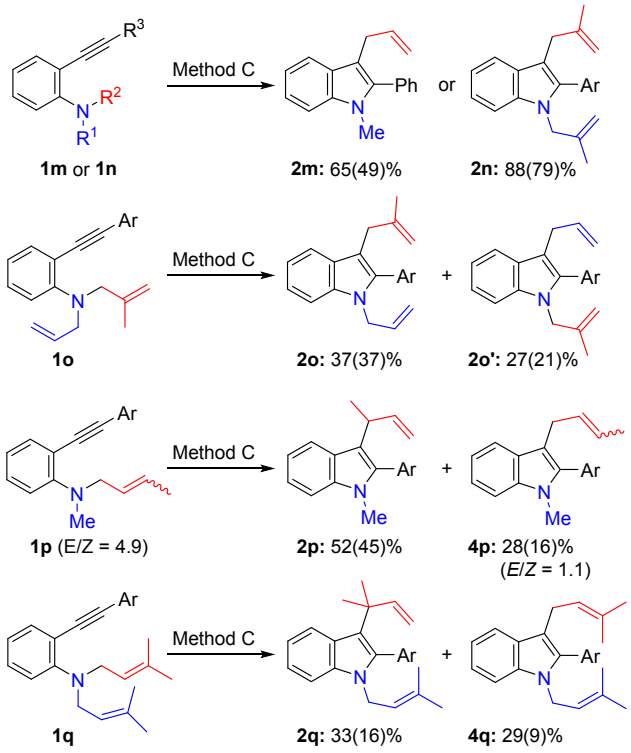
1	R^1	R^2	R^3	**2**[a] (%)		
				A	**B**	**C**
1a	Ph	H	H	69	66	54 (53)
1b	4-MeC_6H_4	H	H	63	69	68 (58)
1c	4-$MeOC_6H_4$	H	H	73	82	71 (60)
1d	4-$CF_3C_6H_4$	H	H	27	33	35 (31)
1e	4-ClC_6H_4	H	H	66	59	39 (39)
1f	3-ClC_6H_4	H	H	35	32	36 (26)
1g	2-ClC_6H_4	H	H	<5	<5	<5
1h	2-$MeOC_6H_4$	H	H	74	87	77 (58)
1i	^{n}Bu	H	H	74	75	87 (62)
1j	^{i}Pr	H	H	66	62	65 (47)
1k	Ph	Me	H	64	56	64 (61)
1l	Ph	Me	Me	ND[b]	75	90 (67)

[a] Determined by ^{1}H NMR analysis using an internal standard. Values in parentheses show isolated yields. [b] Not determined.

Among the attempted substrates with various substituents of the alkynes (Table 2), the electron-rich aryl-substituted **1b**, **1c**, **1h** and the alkyl-substituted **1i**, **1j** afforded the corresponding products in good yields. On the other hand, in cases of the electron-deficient aryl-substituted **1d**-**1g**, the product yields were relatively low. Particularly, the *o*-chlorophenyl-substituted **1g** was hardly converted into **2g**. In addition, the ^{t}Bu-subsituted substrate gave a complex mixture. Thus, it is suggested that the present reaction is greatly affected by steric factors as well as the electron density of the alkynes. It should be mentioned that **2k** and **2l** having substituents at the *ortho*- and *para*-positions of aniline moiety were formed in good yields.

As for the migration ability of the substituents on nitrogen of *o*-alkynylanilines **1m**-**1q** (Scheme 2), allyl and crotyl groups underwent the rearrangement prior to methyl group, as in

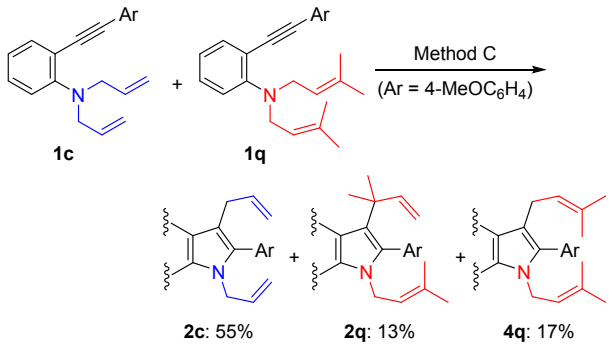
products **2m** and **2p**. However, the rearrangement of allyl groups competed with that of methallyl group, as in products **2o** and **2o'**. Note that, in the case of methallyl group, the desired products were obtained from the 4-methoxyphenyl-substituted *o*-alkynylanilines **1n** and **1o**, which have a high electron density in the alkyne moiety, while the corresponding phenyl compounds were not converted at all. These results imply that iodine species would probably undergo competitive coordination of alkyne and alkene to retard the iodocyclization step. Interestingly, the reactions of crotyl compound **1p** and prenyl compound **1q** produced [1,3] adducts **4p** and **4q** along with [3,3] adducts **2p** and **2q**.



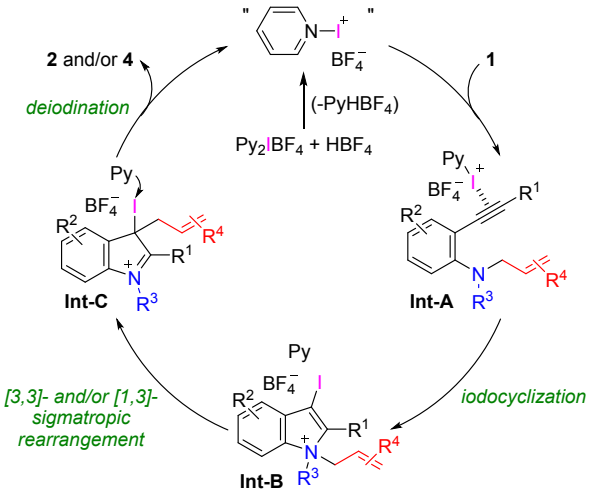
Scheme 2. Effect of substituents on nitrogen (Ar = 4-$MeOC_6H_4$, Values in parentheses show isolated yields).

To obtain mechanistic insight into the migration process of allyl groups, we attempted crossover experiments using **1c** and **1q**. As shown in Scheme 3, a 1:1 mixture of **1c** and **1q** was treated with the iodine species (30 mol% based on total amount of **1c** and **1q**) generated from Barluenga's reagent and $HBF_4{\cdot}OEt_2$ in DCM (method **C**) to give **2c**, **2q** and **4q** in 55% (based on amount of **1c**), 13% and 17% (based on amount of **1q**) yields, respectively. Notably, the molecular ion peak (*m/z*: 331.19) of the crossover products was not detected even in the GC-MS analysis of the above reaction mixture. Thus, the migration of allyl groups was suggested to be the intramolecular reaction.

On the basis of the above results and previous reports of iodine-mediated/catalyzed cyclization of *o*-alkynylanilines,[14d,15-17] a proposed mechanism for the iodine(I)-catalyzed cyclization-allylation reactions of *o*-alkynylanilines **1** is shown in Scheme 4. Initially, the generated iodine catalyst "$PyIBF_4$" derived from Barluenga's reagent and $HBF_4{\cdot}OEt_2$ activates the triple bond of **1** (**INT-A**) to form an iodocyclized intermediate **INT-B**. And then, **INT-B** is converted into **INT-C** via [3,3]- and/or [1,3]-sigmatropic rearrangement reactions. Finally, deiodination of **INT-C** with pyridine (and/or BF_4 anion) afford the products **2** and/or **4** along with the regeneration of the iodine catalyst. When the *γ*-position of the allyl group, such as the crotyl or prenyl group, is relatively bulky, the [1,3] rearrangement of the tight iodinated indole-allyl cation complex[18] is expected to proceed along with the [3,3] rearrangement due to steric hindrance with the indole 3-position (Figure 1).



Scheme 3. Crossover experiments using **1c** and **1q**.



Scheme 4. Proposed mechanism.

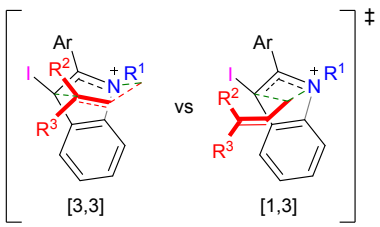


Figure 1. [3,3]- and/or [1,3]-sigmatropic rearrangement of **1p** or **1q** (Ar = 4-MeOC$_6$H$_4$; R^1 = Me or CH$_2$CH=CMe$_2$; R^2, R^3 = Me or H).

Conclusions

In conclusion, we have developed a metal-free cyclization-allylation reaction of *o*-alkynylanilines catalyzed by iodine(I) species *in situ* derived from Barluenga's reagent and HBF$_4$·OEt$_2$. On the basis of experimental data including control experiments, we proposed that the reaction proceeds via iodocyclization of the substrates followed by [3,3] and [1,3] sigmatropic rearrangement of cyclized intermediates. This work represents the first report of iodine-catalysis via carbo-deiodination with rearrangement of functional groups, and provides the metal-free and powerful method for the construction of indole skeleton with introduction of allylic functional groups. Studies on other cyclization-functionalization of *o*-alkynylanilines and their analogues catalyzed by iodine species are underway.

Experimental

Representative procedure for conversion of 1a into 2a.

After Barluenga's reagent (55.9 mg, 0.15 mmol) was treated with HBF$_4$·OEt$_2$ (24.4 mg, 0.15 mmol) in CH$_2$Cl$_2$ (1.3 mL) at 0 ºC for 15 min, a solution of **1a** (137.5 mg, 0.5 mmol) in CH$_2$Cl$_2$ (2.5 mL) was added at 0 ºC. After being stirred at 40 ºC for 24 h, the reaction mixture was quenched with sat. NaHCO$_3$ aq. and 20 wt% Na$_2$S$_2$O$_3$ aq., and exacted with AcOEt. The organic layer was dried over MgSO$_4$ and concentrated in vacuo to dryness. The yield of **2a** was determined to be 59% by ^{1}H NMR analysis of the residue using MeCN as an internal standard. Then, the residue was purified by medium pressure liquid chromatography (MPLC) on silica gel modified with amino groups (hexane only) and by MPLC on silica gel modified with octadecylsilyl (ODS) groups (MeCN:H$_2$O = 9:1) in turn to give **2a** (72.9 mg, 53%).

Author Contributions

Conceptualization, A.S.; data curation, all; formal analysis, all; funding acquisition, A.S.; investigation, S.T. and A.T.; methodology, S.T. and A.T.; project administration, A.S.; resources, A.S.; supervision, A.S.; validation, S.T. and A.T.; visualization, S.T. and A.T.; writing—original draft preparation, A.S.; writing—review and editing, A.T. and A.S.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported partly by JST CREST (No. JPMJCR19R2), Shiono Wellness Foundation and The Sumitomo Foundation.

Notes and references

1 (*a*) S. Cacchi and G. Fabrizi, Update 1 of: Synthesis and Functionalization of Indoles through Palladium-Catalyzed Reactions, *Chem. Rev.*, 2011, **111**, PR215–PR283; (*b*) T. Guo, F. Huang, L. Yu and Z. Yu, Indole Synthesis through Transition Metal-Catalyzed C–H Activation, *Tetrahedron Lett.*, 2015, **56**, 296–302; (*c*) S. W. Youn and T. Y. Ko, Metal-Catalyzed Synthesis of Substituted Indoles, *Asian J. Org. Chem.*, 2018, **7**, 1467–1487; (*d*) S. Sahu, A. Banerjee, S. Kundu, A. Bhattacharyya and M. S. Maji, Synthesis of Functionalized Indoles via Cascade Benzannulation Strategies: A Decade's Overview, *Org. Biomol. Chem.*, 2022, **20**, 3029–3042.

2 (*a*) S. Cacchi, V. Carnicelli and F. Marinelli, Palladium-Catalysed Cyclization of 2-Alkynylanilines to 2-Substituted Indoles under An Acidic Two-Phase System, *J. Organomet. Chem.*, 1994, **475**, 289–296; (*b*) A. Arcadi, G. Bianchi and F. Marinelli, Gold(III)-Catalyzed Annulation of 2-Alkynylanilines: A Mild and Efficient Synthesis of Indoles and 3-Haloindoles, *Synthesis*, 2004, 610–618; (*c*) X. Li, A. R. Chianese, T. Vogel and R. H. Crabtree, Intramolecular Alkyne Hydroalkoxylation and Hydroamination Catalyzed by Iridium Hydrides, *Org. Lett.*, 2005, **7**, 5437–5440; (*d*) K. Hiroya, S. Itoh and T. Sakamoto, Mild and Efficient Cyclization Reaction of 2-Ethynylaniline Derivatives to Indoles in Aqueous Medium, *Tetrahedron*, 2005, **61**, 10958–10964; (*e*) N. Sakai, K. Annaka and T. Konakahara, InBr$_3$-Catalyzed Intramolecular Cyclization of 2-Alkynylanilines Leading to Polysubstituted Indole and Its Application to One-Pot Synthesis of An Amino Acid Precursor, *Tetrahedron Lett.*, 2006, **47**, 631–634; (*f*) T. Kurisaki, T. Naniwa, H. Yamamoto, H. Imagawa and M. Nishizawa, Hg(OTf)$_2$-Catalyzed Cycloisomerization of 2-Ethynylaniline Derivatives Leading to Indoles, *Tetrahedron Lett.*, 2007, **48**, 1871–1874; (*g*) M. T. Herrero, J. D. de Sarralde, R. SanMartin, L. Bravo, E. Domínguez, Cesium Carbonate-Promoted Hydroamidation of Alkynes: Enamides, Indoles and the Effect of Iron(III) Chloride, *Adv. Synth. Catal.*, 2012, **354**, 3054–3064.

3 (*a*) S. Cacchi, G. Fabrizi and P. Pace, Palladium-Catalyzed Cyclization of *o*-Alkynyltrifluoroacetanilides with Allyl Esters. A Regioselective Synthesis of 3-Allylindoles, *J. Org. Chem.*, 1998, **63**, 1001–1011; (*b*) A. Fürstner and P. W. Davies, Heterocycles by PtCl$_2$-Catalyzed Intramolecular Carboalkoxylation or Carboamination of Alkynes, *J. Am. Chem. Soc.*, 2005, **127**, 15024–15025; (*c*) C. Wu, F. Zhao, Y. Du, L. Zhao, L. Chen, J. Wang and H. Liu, Highly Selective Intramolecular Addition of C–N and S–N Bonds to Alkynes Catalyzed by Palladium: A Practical Access to Two Distinct Functional Indoles, *RSC Adv.*, 2016, **6**, 70682–70690; (*d*) T. Mino, T. Yamaoka, K. Watanabe, C. Masuda, S. Kasano, Y. Yoshida, R. Takita, Y. Kasashima and M. Sakamoto, Synthesis of 3‐Allylindoles via Annulation of *N*‐Allyl-2-ethynylaniline Derivatives Using a P,Olefin Type Ligand/Pd(0) Catalyst, *J. Org. Chem.*, 2022, **87**, 7365−7377; (*e*) P.-Y. Chiang, Y.-C. Lin, Y. Wang and Y.-H. Liu, Aza-Claisen Rearrangement in the Cyclization Reactions of Nitrogen-Containing Enynes via Ruthenium Vinylidene Complexes, *Organometallics*, 2010, **29**, 5776–5782; (*f*) K. C. Majumdar, S. Hazra and B. Roy, Gold-Catalyzed Heteroannulation and Allyl Migration: Synthesis of Highly Functionalized Indole Derivatives, *Tetrahedron Lett.*, 2011, **52**, 6697–6701; (*g*) M.-G. Rong, T.-Z. Qin, and W. Zi, Rhenium-Catalyzed Intramolecular Carboalkoxylation and Carboamination of Alkynes for the Synthesis of C3-Substituted Benzofurans and Indoles, *Org. Lett.*, 2019, **21**, 5421–5425.

4 (*a*) T. Shimada, I. Nakamura and Y. Yamamoto, Intramolecular C-N Bond Addition of Amides to Alkynes Using Platinum Catalyst, *J. Am. Chem. Soc.*, 2004, **126**, 10546–10547; (*b*) I. Nakamura, Y. Sato and M. Terada, Platinum-Catalyzed

Dehydroalkoxylation-Cyclization Cascade via N-O Bond Cleavage, *J. Am. Chem. Soc.*, 2009, **131**, 4198–4199; (*c*) C.-Y. Wu, M. Hu, Y. Liu, R.-J. Song, Y. Lei, B.-X. Tang, R.-J. Li and J.-H. Li, Ruthenium-Catalyzed Annulation of Alkynes with Amides via Formyl Translocation, *Chem. Commun.*, 2012, **48**, 3197–3199; (*d*) F. Zhao, D. Zhang, Y. Nian, L. Zhang, W. Yang and H. Liu, Palladium-Catalyzed Difunctionalization of Alkynes via C–N and S–N Cleavages: A Versatile Approach to Highly Functional Indoles, *Org. Lett.*, 2014, **16**, 5124–5127.

5 (*a*) C. H. Oh, S. Karmakar, H. S. Park, Y. C. Ahn and J. W. Kim, Domino Process in Silver-Catalyzed Reactions of *N*-Arylformimidates and Active Methylene Compounds Involving Cycloisomerization and 1,3-Alkenyl Shift, *J. Am. Chem. Soc.*, 2010, **132**, 1792–1793; (*b*) S. D. Tambe, N. Iqbal and E. J. Cho, Nickel-Catalyzed *trans*-Carboamination across Internal Alkynes to Access Multifunctionalized Indoles, *Org. Lett.*, 2020, **22**, 8550–8554.

6 Other carbon-based functional groups: (*a*) X. Zeng, R. Kinjo, B. Donnadieu and G. Bertrand, Serendipitous Discovery of the Catalytic Hydroammoniumation and Methylamination of Alkynes, *Angew. Chem. Int. Ed.*, 2010, **49**, 942–945; (*b*) Y. Tokimizu, S. Oishi, N. Fujii and H. Ohno, Gold-Catalyzed Cascade Cyclization of 2-Alkynyl-*N*-propargylanilines by Rearrangement of a Propargyl Group, *Angew. Chem. Int. Ed.*, 2015, **54**, 7862–7866; (*c*) Z.-Y. Liao, P.-Y. Liao and T.-C. Chien, CuI-Catalyzed Intramolecular Aminocyanation of Terminal Alkynes in *N*-(2-Ethynylphenyl)-*N*-sulfonylcyanamides via Cu–Vinylidene Intermediates, *Chem. Commun.*, 2016, **52**, 14404–14407; (*d*) J. He, Y. Yu, P. Guo, X. Liu, B. Zhu and H. Cao, Palladium-Catalyzed C-N Bond Formation: A Straightforward Alkoxymethylation Process for the Synthesis of the C1 and C3-Dialkoxy Indoles, *ChemistrySelect*, 2020, **5**, 15148–15152.

7 Boryl or sulfonyl group: (*a*) E. Chong and S. A. Blum, Aminoboration: Addition of B–N σ Bonds across C–C π Bonds, *J. Am. Chem. Soc.*, 2015, **137**, 10144–10147; (*b*) I. Nakamura, U. Yamagishi, D. Song, S. Konta and Y. Yamamoto, Gold- and Indium-Catalyzed Synthesis of 3- and 6-Sulfonylindoles from *ortho*-Alkynyl-*N*-sulfonylanilines, *Angew. Chem. Int. Ed.*, 2007, **46**, 2284–2287; (*c*) see also ref. 3*c*.

8 I. Nakamura, T. Sato, M. Terada and Y. Yamamoto, Gold-Catalyzed Cyclization of (*ortho*-Alkynylphenylthio)silanes: Intramolecular Capture of the Vinyl-Au Intermediate by the Silicon Electrophile, *Org. Lett.*, 2007, **9**, 4081–4083.

9 (*a*) A. De Nisi, S. Sierra, M. Ferrara, M. Monari and M. Bandini, TBAF Catalyzed One-pot Synthesis of Allenyl-indoles, *Org. Chem. Front.*, 2017, **4**, 1849–1853; (*b*) M. Mandal and R. Balamurugan, TfOH-Promoted Synthesis of Indoles and Benzofurans Involving Cyclative Transposition of Vinyl Ketone, *Chem. Commun.*, 2022, **58**, 9778–9781; (*c*) M. R. Mutra and J.-J. Wang, Photoinduced Ynamide Structural Reshuffling and Functionalization, *Nat. Commun.*, 2022, **13**, 2345.

10 (*a*) A. Yoshimura and V. V. Zhdankin, Advances in Synthetic Applications of Hypervalent Iodine Compounds, *Chem. Rev.*, 2016, **116**, 3328–3435; (*b*) A. Claraz and G. Masson, Asymmetric Iodine Catalysis-Mediated Enantioselective Oxidative Transformations, *Org. Biomol. Chem.*, 2018, **16**, 5386–5402.

11 (*a*) M. Uyanik and K. Ishihara, Catalysis with In Situ-Generated (Hypo)iodite Ions for Oxidative Coupling Reactions, *ChemCatChem*, 2012, **4**, 177–185; (*b*) R. Chen, J. Chen, J. Zhang and X. Wan, Combination of Tetrabutylammonium Iodide (TBAI) with *tert*-Butyl Hydroperoxide (TBHP): An Efficient Transition-Metal-Free System to Construct Various Chemical Bonds, *Chem. Rec.*, 2018, **18**, 1292–1305.

12 (*a*) D. Bulfield and S. M. Huber, Halogen Bonding in Organic Synthesis and Organocatalysis, *Chem. Eur. J.*, 2016, **22**, 14434–14450; (*b*) M. Breugst and D. von der Heiden, Mechanisms in Iodine Catalysis, *Chem. Eur. J.*, 2018, **24**, 9187–9199; (*c*) Y. Kobayashi and Y. Takemoto, Reactions Catalyzed by 2-Halogenated Azolium Salts: From Halogen-Bond Donors to Brønsted-Acidic Salts, *Synlett*, 2020, **31**, 772–783; (*d*) see also, K. Murai, K. Tateishi and Akio Saito, Barluenga's Reagent with HBF_4 as An Efficient Catalyst for Alkyne-Carbonyl Metathesis of Unactivated Alkynes, *Org. Biomol. Chem.*, 2016, **14**, 10352–10356.

13 (*a*) K. Kiyokawa and S. Minakata, Iodine-Based Reagents in Oxidative Amination and Oxygenation, *Synlett*, 2020, **31**, 845–855 and the references cited therein; (*b*) S. Minakata, H. Miwa, K. Yamamoto, A. Hirayama and S. Okumura, Diastereodivergent Intermolecular 1,2-Diamination of Unactivated Alkenes Enabled by Iodine Catalysis, *J. Am. Chem. Soc.*, 2021, **143**, 4112–4118; (*c*) S. Aich, R. Nandi, N. Chatterjee, K. S. Gayen, S. Pala and D. K. Maiti, Catalytic I2-Moist DMSO-Mediated Synthesis of Valuable *α*-Amidohydroxyketones and Unsymmetrical *gem*-Bisamides from Benzimidates, *Org. Biomol. Chem.*, 2023, **21**, 2524–2530; (*d*) Y. Shinomoto, A. Yoshimura, H. Shimizu, M. Yamazaki, V. V. Zhdankin, A. Saito, Tetra-*n*-butylammonium Iodide Catalyzed C–H Azidation of Aldehydes with Thermally Stable Azidobenziodoxolone, *Org. Lett.*, 2015, **17**, 5212–5215 and the references cited therein.

14 (*a*) A. Saito, Hypervalent Iodine-mediated/Catalyzed Oxidative Cycloisomerization/Annulation of Alkynes for Metal-free Synthesis of Oxazoles, *Cur. Org. Chem.*, 2020, **24**, 2048–2069 and the references cited therein; (*b*) S. Takahashi, Y. Umakoshi, K. Nakayama, Y. Okada, V. V. Zhdankin, A. Yoshimura and A. Saito, Fluorocyclization of *N*-Propargyl Carboxamides by λ^3-Iodane Catalysts with Coordinating Substituents. *Adv. Synth. Catal.*, 2020, **362**, 2997–3003; (*c*) Y. Umakoshi, Y. Takemoto, A. Tsubouchi, V. V. Zhdankin, A. Yoshimura and A. Saito, Dehydrogenative Cycloisomerization/Arylation Sequence of *N*-Propargyl Carboxamides with Arenes by Iodine(III)-Catalysis, *Adv. Synth. Catal.*, 2022, **364**, 2053–2059; (*d*) Y. Takeda, R. Kajihara, N. Kobayashi, K. Noguchi and A. Saito, Molecular-Iodine-Catalyzed Cyclization of 2-Alkynylanilines via Iodocyclization-Protodeiodination Sequence, *Org. Lett.*, 2017, **19**, 6744–6747.

15 W.-C. Lee, H.-C. Shen, W.-P. Hu, W.-S. Lo, C. Murali, J. K. Vandavasi and J.-J. Wang, Iodine-Catalyzed, Stereo- and Regioselective Synthesis of 4-Arylidine-4*H*-benzo[*d*][1,3]oxazines and their Applications for the Synthesis of Quinazoline 3-Oxides, *Adv. Synth. Catal.*, 2012, **354**, 2218–2228.

16 (*a*) C.-C. Chen, S.-C. Yang and M.-J. Wu, Iodine-Mediated Cascade Cyclization of Enediynes to Iodinated Benzo[*a*]carbazoles, *J. Org. Chem.*, 2011, **76**, 10269–10274; (*b*) H. Song, Y. Liu and Q. Wang, Cascade Electrophilic Iodocyclization: Efficient Preparation of 4-Iodomethyl Substituted Tetrahydro-*β*-carbolines and Formal Synthesis of Oxopropaline G, *Org. Lett.*, 2013, **15**, 3274–3277.

17 (*a*) J. Barluenga, M. Trincado, E. Rubio and J. M. González, IPy_2BF_4-Promoted Intramolecular Addition of Masked and Unmasked Anilines to Alkynes: Direct Assembly of 3-Iodoindole Cores, *Angew. Chem. Int. Ed.*, 2003, **42**, 2406–2409; (*b*) X.-L. Cui and R. S. Brown, Mechanistic Evaluation of the Halocyclization of 4-Penten-1-ol by Some Bis(2-substituted pyridine) and Bis(2,6-disubstituted pyridine)bromonium Triflates, *J. Org. Chem.*, 2000, **65**, 5653–5658.

18 C. G. Nasveschuk and T. Rovis, The [1, 3] O-to-C Rearrangement: Opportunities for Stereoselective Synthesis, *Org. Biomol. Chem.*, 2008, **6**, 240–254.