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Synthesis of dihydro-[1,3]oxazino[4,3-a] isoindole and tetrahydroisoquinoline through $Cu(OTf)_2$-catalyzed reactions of *N*-acyliminium ions with ynamides

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ABSTRACT

An efficient approach to access functionalized dihydro-[1,3]oxazino[4,3-a] isoindole and tetrahydroisoquinoline skeletons has been developed through the addition-cyclization process of ynamides **8** with *N*-acyliminium ions generated from *N,O*-acetals **6,7**. The reactions were conducted under the catalysis of $Cu(OTf)_2$, and a number of functionalized dihydro-[1,3]oxazino[4,3-a] isoindoles **9a-9y** and tetrahydroisoquinolines **10a-10g, 11a-11p** were generated in 48–98% yields. When chiral ynamides **8n-8u** were used, optically pure products **11a-11p** could be obtained with good to excellent yields and diastereoselectivities.

Discovery of efficient methodology to access skeletons for pharmaceutical use is one of the most important research areas in synthetic chemistry [1]. Nitrogen-containing heterocycles, due to wide existence in nature, are valuable subunits in these fields [2]. As a prime instance (Fig. 1), substituted isoindoline and tetrahydroisoquinoline (THIQ) skeletons **1** and **2** [3,4], the key frameworks of several pharmacologically interesting molecules and clinical drugs, have received intensive attention in recent years. Emetine (**3**) exhibits antiprotozoic activity [5] and is used in the treatment of lymphatic leukemia [6]. In addition, its close structural analogue, tubulosine, shows potent antitumor activity [7]. So far, tremendous efforts have been devoted to the construction of functionalized isoindoline skeleton **1** or tetrahydroisoquinoline scaffold **2**, and several important methods have been established. However, drug-like fragments like dihydro-[1,3]oxazino[4,3-a] isoindole **4** and tetrahydroisoquinoline skeletons **5** are rarely investigated [8].

N-Acyliminium ions [9], acting as important organic synthetic intermediates, are widely used in the formation of C—C and C–heteroatom bonds [10], mostly through intermolecular addition and intramolecular cyclization [11] with various nucleophilic reagents. For examples, Hiemstra and Speckamp group achieved a synthetic method to oxazinones through the intermolecular reactions of *N*-alkoxycarbonyliminium ions with propargyltrimethylsilane (Fig. 2, 1) [12a]. Recently, Maruoka group established a BF_3-catalyzed process to form the same skeleton through the reactions of Boc-protected aminals with alkynes (Fig. 2, 2) [12b]. Ynamides, known as nitrogen-substituted alkynes with an electron-withdrawing group at the nitrogen atom, have undoubtedly become one of the most popular synthons due to their high reactivity and high regio- and stereoselectivity [13]. As a result, they have been successfully applied in the syntheses of many important skeletons in the past decade [14–21]. In recent years, we studied various nucleophilic reactions of *N*-acyliminium ions, and established facile approaches to pyrido or pyrrolo[1,2-c][1,3]oxazin-1-ones and 3,4-dihydro-1,3-oxazin-2-ones by reacting with alkynes or ynamides (Fig. 2, 3-4) [22]. On the basis of our continuous efforts in *N, O*-acetals and ynamides, we envisioned that the iminium ions derived from the *N, O*-acetals **6** and **7** [22f] could undergo a nucleophilic addition-cyclization process with ynamides **8** [22a,b] to give substituted dihydro-[1,3]oxazino[4,3-a] isoindole and tetrahydroisoquinoline skeletons, respectively (Fig. 2, 5).

Our investigation started with the reaction of *N,O*-acetal **6a** with ynamide **8a**. When the mixture of **6a** and **8a** was stirred without any Lewis acid at room temperature, no desired product was afforded (Table 1, entry 1). The treatment with TMSOTf or BF_3OEt_2 at −78 °C ~ −45 °C for 2 h could lead to the desired product **9a** in 45% and 70% yield, respectively (Table 1, entries 2–3). Unfortunately, the reaction became complicated at room temperature. In

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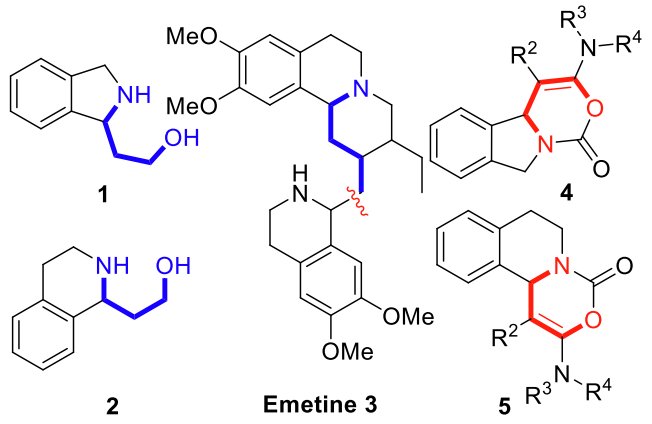


Fig. 1. Several structures of privileged azacycles and corresponding benzo heterocycles.

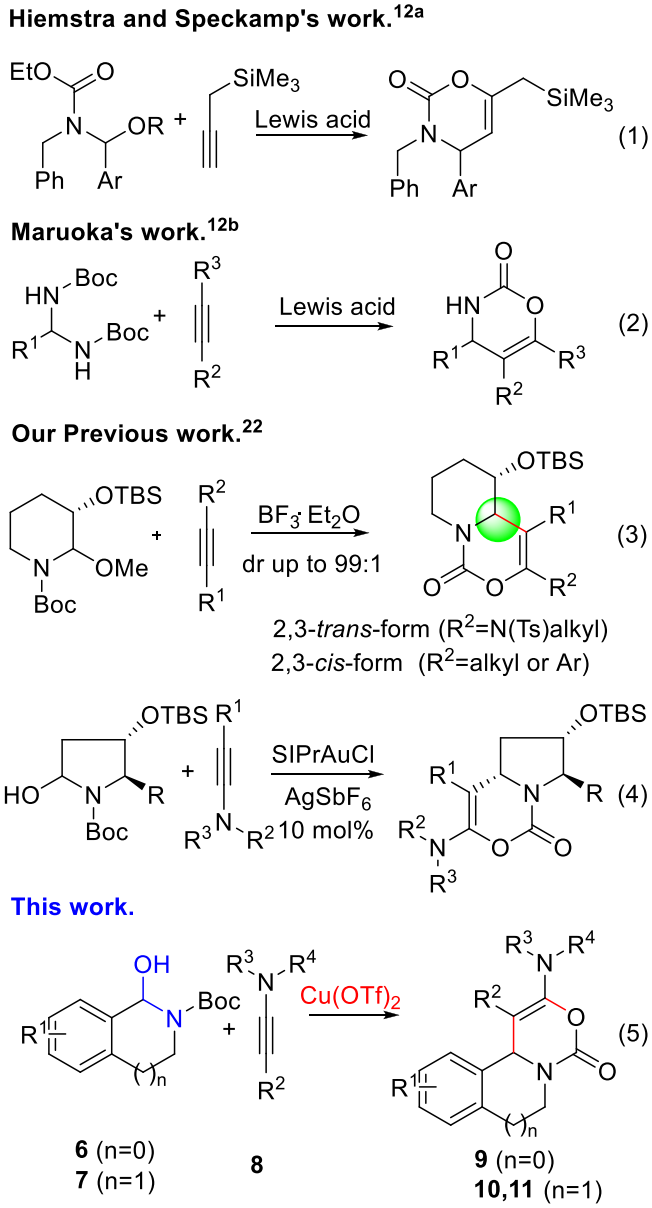
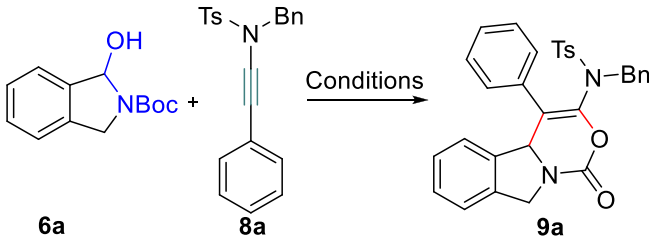


Fig. 2. Lewis Acid-promoted nucleophilic addition-cyclization of *N, O*-acetals with ynamides.

Table 1
Optimization of reaction conditions.



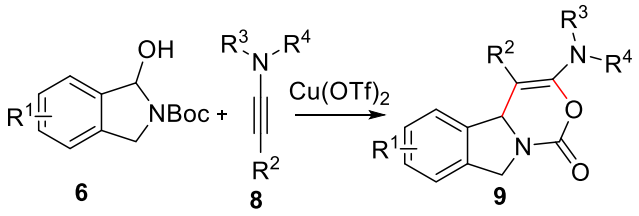
Entries[a]	LA (equiv.)	Temp/°C	Solvent	Y%(**9a**) [b]
1	–	rt	DCM	NR
2	TMSOTf (1.0)	−78 to −45	DCM	45
3	BF_3OEt_2 (1.0)	−78 to −45	DCM	70
4	$AuCl_3$ (0.1)	rt	DCM	23
5	$AgSbF_6$ (0.1)	rt	DCM	<10
6	SIPrAuCl (0.1)	rt	DCM	34
7	SIPrAuCl/$AgSbF_6$ (0.1)	rt	DCM	37
8	PPh_3AuCl/$AgNTf_2$ (0.1)	rt	DCM	26
9	PPh_3AuCl/$AgSbF_6$ (0.1)	rt	DCM	31
10	$Cu(OTf)_2$ (0.1)	rt	DCM	54
11	$Cu(OTf)_2$ (0.2)	rt	DCM	73
12	$Cu(OTf)_2$ (0.5)	rt	DCM	40
13	$CuSO_4$ (0.2)	rt	DCM	NR
14	$CuCl_2$ (0.2)	rt	DCM	22
15	$CuBr_2$ (0.2)	rt	DCM	20
16	$Cu(OTf)_2$ (0.2)	rt	DCE	62
17	$Cu(OTf)_2$ (0.2)	rt	THF	18
18	$Cu(OTf)_2$ (0.2)	rt	Toluene	Trace

[a] The reaction was performed with **6a** (0.5 mmol), **8a** (0.6 mmol) and catalyst in dry solvent (3 mL) at assigned reaction temperature for 2 h under Ar atmosphere.
[b] Isolated yield; NR = no reaction.

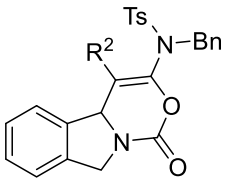
order to improve the yield under mild reaction conditions, various metal Lewis acids were screened. $AuCl_3$, $AgSbF_6$, SIPrAuCl, SIPrAuCl/$AgSbF_6$, PPh_3AuCl/$AgNTf_2$, PPh_3AuCl/$AgSbF_6$ could afford the desired product, albeit with low yield (<10~31%, Table 1, entries 4–9). Delightfully, $Cu(OTf)_2$ could lead to the desired product **9a** in 54% yield (Table 1, entry 10). When the use of $Cu(OTf)_2$ was increased to 0.2 equivalent, the yield could be significantly improved to 73% (Table 1, entry 11). Further increasing the use of $Cu(OTf)_2$ to 0.5 equivalent led to the erosion of yield to 40% (Table 1, entry 12). Other copper salts, like $CuSO_4$, $CuCl_2$ and $CuBr_2$ did not result in any satisfactory yield. Different reaction solvents including DCE, THF, toluene were also examined. Among them, DCE led to moderate yield of **9a** (62%, Table 1, entry 16), while THF gave much lower yield of **9a** and toluene was not suitable for this transformation at all (Table 1, entries 17 and 18).

Next, we turned to investigate the scope and limitation of such cyclization of *N,O*-acetals **6a-6e** with ynamides **8a-8l** (Table 2). A variety of substitutions at the acetylene phenyl ring and nitrogen of ynamides **8a-8l** were investigated. TsNBn-type ynamides with different *para*-substituted (methyl, methoxyl and halogen) aryls were surveyed under the optimal conditions, as summarized in Table 2. In general, all these substituted aryl TsNBn ynamides (**8b-8g**) could smoothly react with *N, O*-acetals **6a**, affording the desired products **9b-9g** in moderate yields. Thiophene substituted TsNBn ynamide **8h** was also a suitable substrate for this cyclization reaction, leading to the desired products **9h** in 62% yield. When Bn group in ynamides was replaced with different aryl, alkyl, allyl groups, the corresponding derivatives **8i-8l** also worked well to give the desired **9i-9l** in moderate yields. Different substitutions at the isoindole ring were also investigated. 5-Chloro-substituted isoindole *N, O*-acetal **6b** could smoothly react with ynamides **8a-8l**, affording the desired products **9m-9u** in 66–87% yields. 6-bromo, 4-bromo, 6-methoxy isoindole *N, O*-acetals **6c-6e** were also

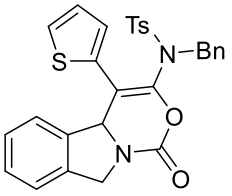
Table 2
The reactions of *N,O*-acetals **6a-6e** with Ynamides **8a-8l**.[a-b]



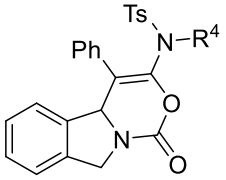
6 **8** **9**



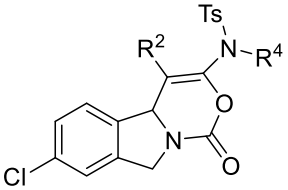
9a, R^2 = Ph, 73%
9b, R^2 = 4-MeC_6H_4, 64%
9c, R^2 = 4-FC_6H_4, 63%
9d, R^2 = 4-$MeOC_6H_4$, 68%
9e, R^2 = 4-ClC_6H_4, 67%
9f, R^2 = 4-BrC_6H_4, 81%
9g, R^2 = 2-$MeOC_6H_4$, 78%



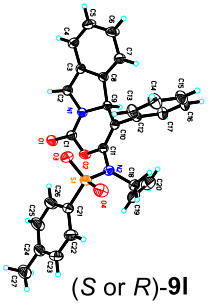
9h, 62%



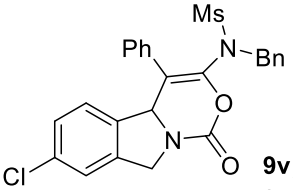
9i, R^4 = Me, 60%
9j, R^4 = *n*-C_4H_9, 63%
9k, R^4 = Ph, 48%
9l, R^4 = Allyl, 68%



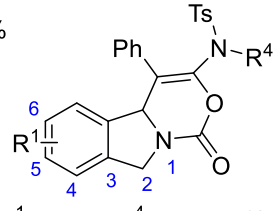
9m, R^2 = Ph, R^4 = Bn, 68%
9n, R^2 = 4-MeC_6H_4, R^4 = Bn, 74%
9o, R^2 = 4-FC_6H_4, R^4 = Bn, 83%
9p, R^2 = 4-$MeOC_6H_4$, R^4 = Bn, 87%
9q, R^2 = 4-ClC_6H_4, R^4 = Bn, 83%
9r, R^2 = Ph, R^4 = Me, 66%
9s, R^2 = Ph, R^4 = *n*-C_4H_9, 70%
9t, R^2 = Ph, R^4 = Ph, 77%
9u, R^2 = Ph, R^4 = Allyl, 84%



(*S* or *R*)-**9l**



9y, 61%



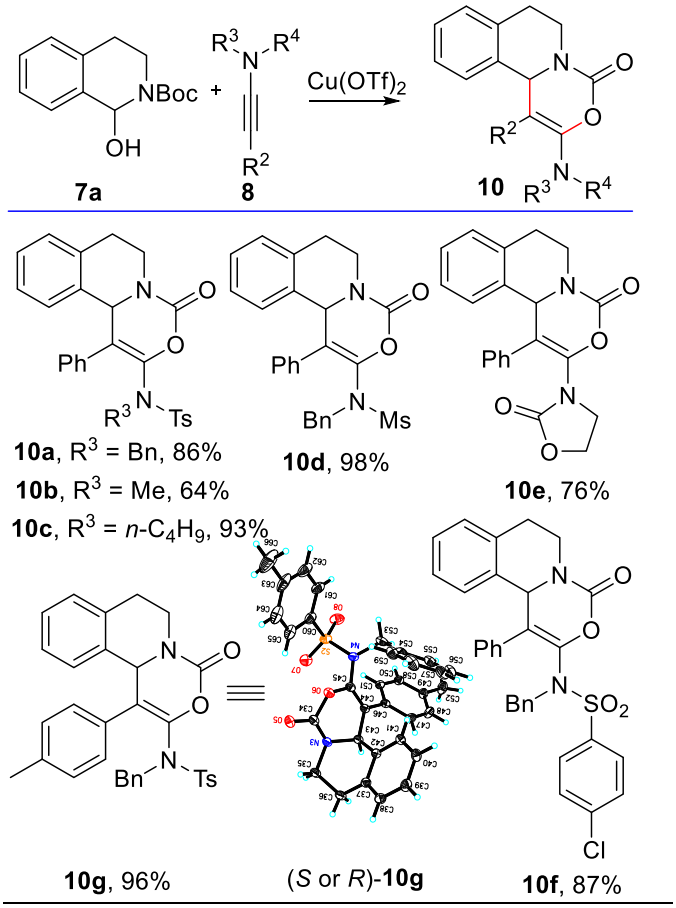
9v, R^1 = 6-Br, R^4 = Bn, 64%
9w, R^1 = 4-Br, R^4 = Bn, 86%
9x, R^1 = 6-MeO, R^4 = Ph, 64%

[a] The reaction was performed with **6** (0.5 mmol), **8** (0.6 mmol) and $Cu(OTf)_2$ (0.1 mmol) in dry DCM (3 mL) under Ar atmosphere at room temperature for 2 h.
[b] Isolated yield.

suitable substrates for this cyclization reaction, and the desired products **9v-9x** could be obtained in 64–86% yields. In addition, the replacement of Ts group in ynamides with Ms also gave positive results under the optimal conditions, and the desired products **9y** was obtained in 61% yield. The chemical structures of **9a-9y** were unambiguously confirmed based on the X-ray crystallographic analysis of compound **9l** (see the Supporting Information) [23].

After the successful cyclization of isoindole *N, O*-acetals **6a-6e** with ynamides **8a-8l** to produce a variety of substituted dihydro-[1,3]oxazino[4,3-a] isoindoles, we turned our attention to investigate the reaction of tetrahydroisoquinoline *N, O*-acetal **7a** with

Table 3
The reactions of *N,O*-acetal **7a** with Ynamides **8a-8g.**[a-b]

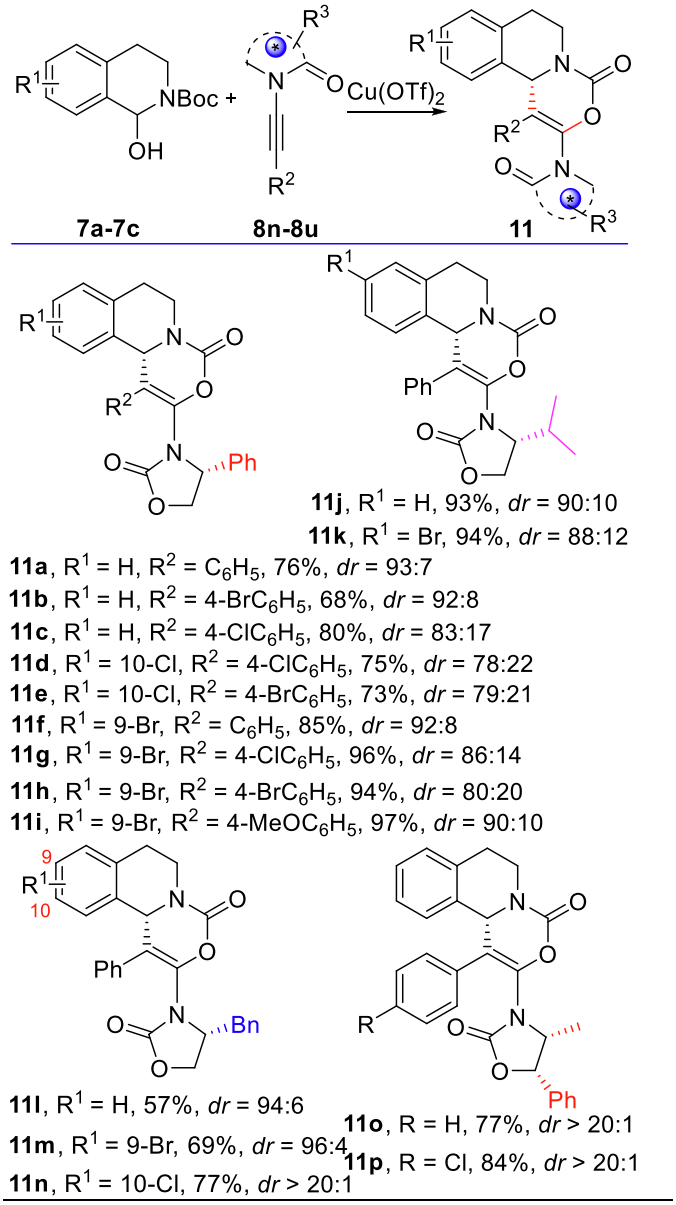


[a] The reaction was performed with **7a** (0.5 mmol), **8** (0.6 mmol) and $Cu(OTf)_2$ (0.1 mmol) in dry DCM (3 mL) under Ar atmosphere at room temperature for 2 h.
[b] Isolated yield.

ynamides in order to achieve dihydro-[1,3]oxazino[4,3-a] tetrahydroisoquinoline skeleton (Table 3). To our delight, Bn, Me, *n*-C_4H_9-NTs ynamides **8a-8c** could react with *N, O*-acetal **7a**, affording the desired dihydro-[1,3]oxazino[4,3-a] tetrahydroisoquinolines **10a-10c** in 86%, 64%, 93% yields, respectively. The replacement of Ts group in ynamides with Ms and 4-$ClC_6H_4SO_2$ also gave positive results under the optimal conditions, and the desired products **10d** and **10f** were obtained in 98% and 87% yields, respectively. Notably, oxazolidinone substituted ynamide **8m** could also afford the desired product **10e** in moderate yield. In addition, the replacement of phenyl group in ynamide **10a** with 4-Me-phenyl also worked well to give the desired products **10g** in 96% yield. The chemical structures of **10a-10g** were unambiguously confirmed based on the X-ray crystallographic analysis of compound **10g** (see the Supporting Information) [24].

Motivated by the successful reaction with oxazolidinone ynamide **8m**, we further explored the use of several chiral oxazolidinone ynamides. As summarized in Table 4, when optically pure phenyloxazolidinone and isopropyloxazolidinone ynamides were used, the desired products **11a-11k** were successfully obtained in 68%–97% yields, albeit with moderatate diastereoselectivities. Interestingly, chiral benzyloxazolidinone and (4*R*,5*S*)-4-methyl-5-phenyloxazolidinone ynamides could afford the desired products **11l-11p** in 57%-84% yields, along with excellent diastereoselectivities (up to dr > 20:1).

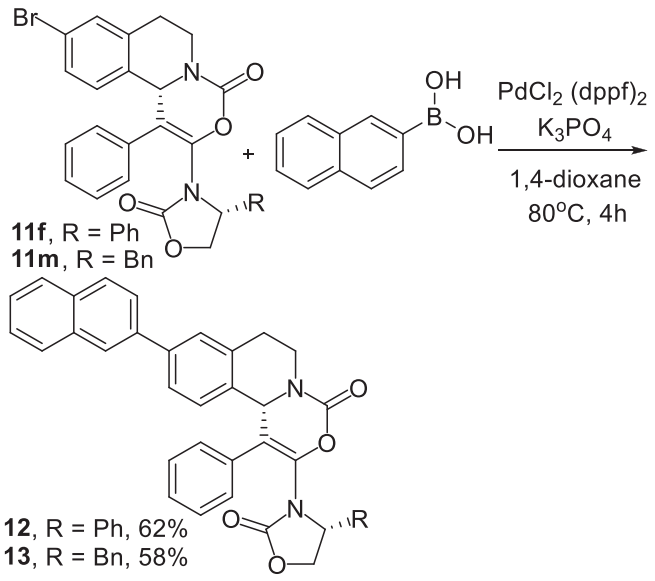
Table 4
The reactions of *N,O*-acetals **7** with Ynamides **8n-8u.**[a-b]



[a] The reaction was performed with **7a-7c** (0.5 mmol), **8n-8u** (0.6 mmol) and Cu $(OTf)_2$ (0.1 mmol) in dry DCM (3 mL) under Ar atmosphere at room temperature for 2 h.
[b] Isolated yield.
[c] dr was determined by HPLC.

To determine the relative configuration by crystals, we tried to introduce a large group. Dihydro-[1,3]oxazino[4,3-a] tetrahydroisoquinolin **11f** and **11m** were coupled with 2-naphthaleneboronic acid, under standard Suzuki-Miyaura conditions [$PdCl_2$ $(dppf)_2/K_3PO_4$], smoothly afforded products **12** and **13** in 62% and 58% yields (Scheme 1) [25]. Unfortunately, both products obtained were foam solids and failed for crystallization.

The ECD calculations were used to assign the absolute configuration of **12**. As shown in Fig. 3, the experimental ECD curve of **12** was in good agreement with the calculated one for M336-*S*. Therefore, the absolute configurations of the new stereogenic centers for **11a-11p** were determined as S [26].



Scheme 1. Suzuki-Miyaura coupling reaction of **11f** and **11 m** with boronic acid.

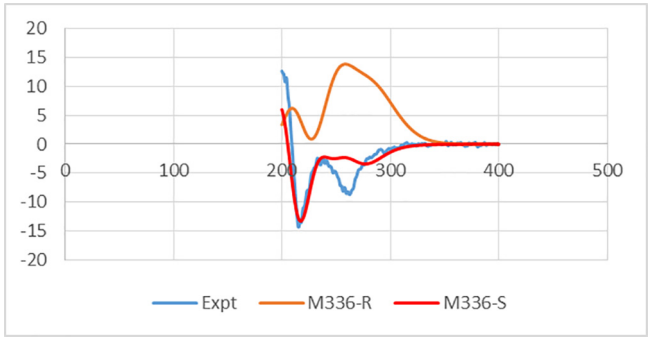


Fig. 3. Experimental and calculated ECD spectra of **12** in acetonitrile.

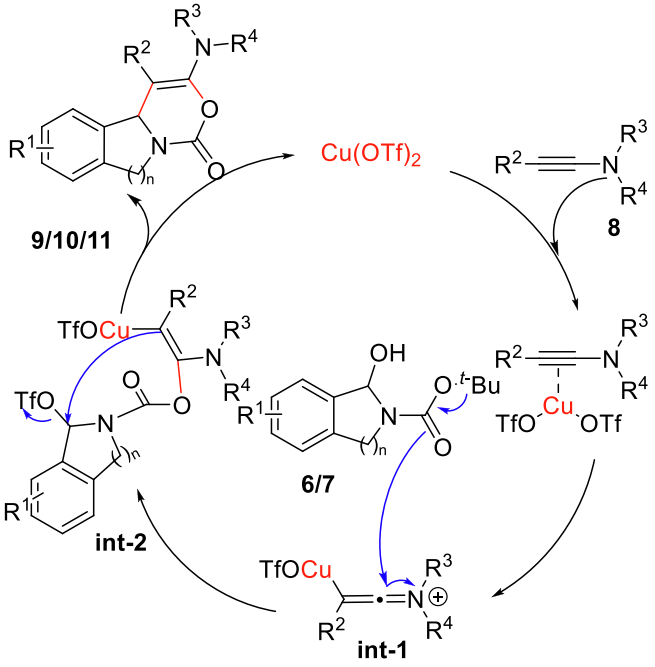


Fig. 4. Proposed mechanism for $Cu(OTf)_2$-catalyzed nucleophilic addition-cyclization process.

A plausible mechanism for this $Cu(OTf)_2$-catalyzed nucleophilic addition-cyclization process was illustrated in Fig. 4 on the basis of our obtained experimental results and the precedent ynamide chemistry [27]. First, the triple bond in ynamide **8** was activated by copper (II) triflate. Then, the resulting vinyl Cu(II) intermediate **int-1** was attacked by **6/7** through the cleavage of *t*-butyl group to give **int-2**, in which an intramolecular cyclization occurred to form the desired product **9/10/11**.

In summary, we established a novel and efficient approach for the synthesis of functionalized dihydro-[1,3]oxazino[4,3-a] isoindole **9a-9y** and tetrahydroisoquinoline **10a-10g, 11a-11p**. Both isoindole *N, O*-acetals **6** and tetrahydroisoquinoline *N, O*-acetals **7** proved to be suitable dipolarophiles for such a $Cu(OTf)_2$-catalyzed nucleophilic addition-cyclization process. As a result, a number of functionalized dihydro-[1,3]oxazino[4,3-a] isoindole **9a-9y** and tetrahydroisoquinoline **10a-10g, 11a-11p** were achieved in moderate to good yields (48–98%). In addition, the chiral ynamides **8n-8u** could lead to optically pure products **11a-11p** with moderate to excellent yields and diastereoselectivities.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tetlet.2021.152873.

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