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Divergent Synthesis of Oxindolylidene Acetates and Spirooxindolopyrrolidones from Arynes

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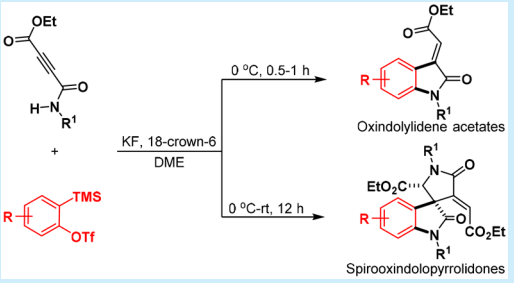
Supporting Information

ABSTRACT: A novel process for the preparation of various (*E*)-oxindolylidene acetates using arynes and carbamoylpropiolates has been developed. The utility of this protocol is also further extended to the one-pot synthesis of complex spirooxindolopyrrolidones. This method provides a milder and transition-metal-free access to both of the target scaffolds in moderate to good yields.



Diverse functional groups, intriguing structure, and a broad range of biological activities make the oxindole scaffold containing compounds a fascinating target for chemists.[1] Among oxindoles, oxindolylidene acetates and their derivatives are versatile substrates. They have been used in the synthesis of drugs, bioactive molecules, and natural products (Figure 1).[2]

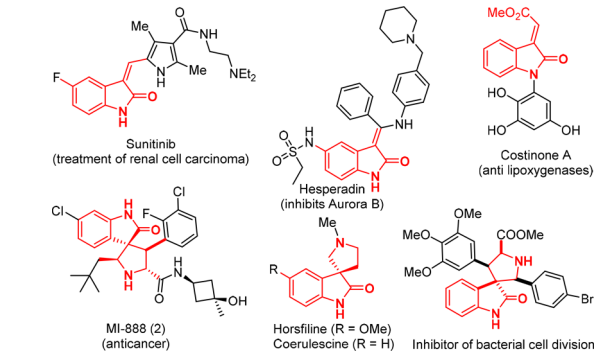
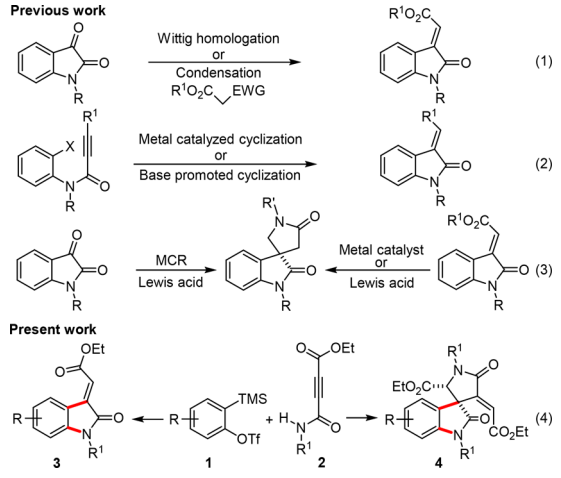


Figure 1. Representative drugs and natural products.

A literature survey disclosed that various methods for the synthesis of the 3-ylideneoxindole core have been developed, but they have their virtues and shortcomings.[3] Conventionally, they are synthesized from isatin by Wittig homologation[3l,q] or by condensation[3i] with active methylene compounds (Scheme 1, eq 1). Few reports demonstrated the synthesis of 3-ylideneoxindoles by transition-metal-catalyzed[3c,m] or base-promoted[3b] cyclization methods starting from the corresponding substituted propiolamides (Scheme 1, eq 2).

Spirooxindoles are also well-recognized scaffolds that have received much attention from the scientific community due to their unique biological and pharmaceutical properties as well as challenging structural architecture (Figure 1).[4] Several methods

Scheme 1. Previous and Present Work



are known for the construction of spirooxindolopyrrolidone derivatives,[5] but often they are synthesized either from isatin or from 3-ylideneoxindoles, which demand transition-metal or organocatalysts and, in some cases, harsh reaction conditions (Scheme 1, eq 3). In view of the importance of oxindole scaffolds, their synthesis using a general and mild protocol is of enduring interest to industry and academia. Recently, Mehta et al. reported spiroannulation of oxindoles with arynes to obtain cyclopentanone fused spirooxindoles.[6] However, to date, the synthesis of oxindolylidene acetates and spirooxindolopyrrolidones using aryne chemistry has not been explored.

Over the past decade, aryne chemistry has evolved as a versatile synthetic tool for organic chemists.[7] Owing to their high

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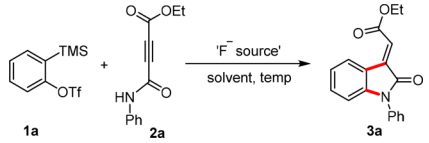
reactivity as an electrophile and easy accessibility, they have been used in the development of several methodologies[7] and total synthesis of natural products.[8] Our group has been involved in the development of expedient methodologies using arynes.[9] Intrigued by the recent advances in the construction of nitrogen containing heterocyclic cores,[10] such as isatins, indoles, quinazolinones, and carbazoles from aryne, we endeavored to develop a milder and metal-free process for the synthesis of 3-ylideneoxindole acetates and spirooxindolopyrrolidones using aryne chemistry.

To develop an efficient protocol for the synthesis of oxindolylidene acetates, we examined the possibility of double functionalization of arynes via the formation of carbon−nitrogen and carbon−carbon bonds. The reaction of aryne precursor **1a** with phenyl carbamoylpropiolate **2a**[11] in the presence of CsF in acetonitrile was performed at 0 °C to room temperature (Table 1, entry 1). However, we did not observe any product formation.

Table 1. Optimization to Obtain Oxindolylidene Acetates[a−d]



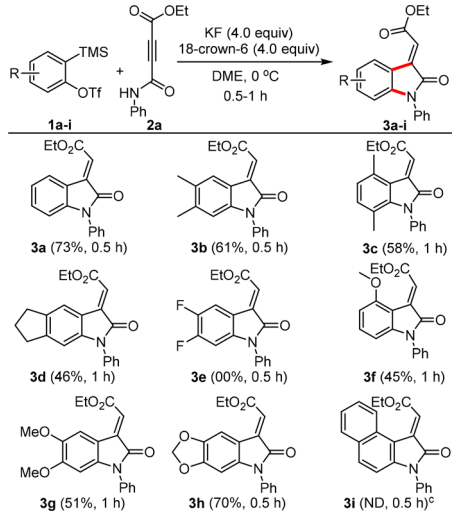
entry	**1a**/**2a** (equiv)	F^- source (equiv)	solvent/temp (°C)	time (h)	yield (%)
1	1:1	CsF (1.5)	ACN/0 to rt	2	–
2	1:1	CsF (1.5)	DME/0 to rt	2	–
3	1:1	CsF (1.5)	THF/0 to rt	2	–
4	1:1	CsF (1.5)	DME/0 to rt	2	–
5	1:1	KF (1.5)	ACN/0 to rt	0.5−2	trace/–
6	1:1	KF (1.5)	toluene/0	0.5	20
7	2:1	KF (3.0)	DME/0	0.5	51
8	2:1	KF (3.0)	THF/0	0.5	50
9	2:1	KF (3.0)	DME/−5	0.5	50
10	2:1	TBAF (2.0)	THF/0 to rt	0.5−3	–
11	2:1	TBAT (2.0)	THF/0 to rt	0.5−3	–
12	3:1	KF (4.0)	THF/0	0.5	70
13	**3:1**	**KF (4.0)**	**DME/0**	**0.5**	**73**
14	3:1	KF (4.0)	DME/−5	0.5	73
15	3:1	KF (4.0)	DME/rt	0.5	<10

[a]Selected entries. [b]Reactions were performed on a 50 mg scale of **2a** in a solvent (2.0 mL). [c]Isolated yield. [d]Equivalent quantity of 18-crown-6 was used with KF.

After several permutations and combinations (Table 1, entries 2−15) the best yield for the desired compound **3a** was obtained when the reaction was performed using 3.0 equiv of aryne precursor, KF, and 18-crown-6 ether in DME solvent at 0 °C (Table 1, entry 13). The *E*-configuration of **3a** was confirmed by literature comparison.[3q]

To establish the generality and scope of the reaction, a variety of aryne precursors **1a−i** were reacted with phenyl carbamoylpropiolate **2a** under the optimized conditions. As outlined in Scheme 2, the reaction worked smoothly with aryne precursors **1b−d** having alkyl substitution to furnish the corresponding oxindolylidene acetates **3b−d** in good to moderate yields. Notably, the aryne precursor **1c** having the alkyl substitution near the reaction center also provided the desired compound **3c** in 58% yield, which suggests that the steric hindrance has no effect on the reaction. The difluoro-substituted aryne precursor **1e**, however, failed to give the corresponding compound **3e**. The

Scheme 2. Oxindolylidene Acetates from Various Arynes[a,b]

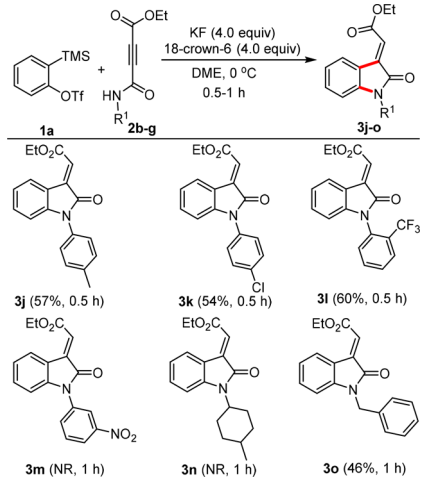


[a]Reaction conditions: **1a−i** (0.345 mmol, 3.0 equiv), **2a** (0.115 mmol, 25 mg, 1.0 equiv), KF (4.0 equiv) and 18-crown-6 ether (4.0 equiv) in DME (1.0 mL). [b]Isolated yield. [c]ND: yield not determined.

aryne precursors **1f−h** having electron-releasing groups at different positions delivered the expected products **3f−h** in moderate to good yields. Remarkably, the unsymmetrically substituted aryne precursor **1f** endowed the respective compound **3f** as a single regioisomer because of the strong electronic and steric effects of the methoxy group. The naphthyl aryne precursor **1i** also furnished the corresponding oxindolylidene acetate **3i**, but due to its labile nature it could not be purified. ^{1}H NMR and HRMS of the crude product clearly indicates the formation of **3i**.

We also studied the scope of the protocol with various carbamoylpropiolates. Carbamoylpropiolates **2a−g** were synthesized from the corresponding isocyanates.[11] They reacted smoothly with aryne precursor **1a** and delivered the corresponding oxindolylidene acetates in moderate to good yields (Scheme 3). Carbamoylpropiolates **2b** and **2c** bearing alkyl and halo

Scheme 3. Substrate Scope of Carbamoylpropiolates[a,b]



[a]Reaction conditions: **1a** (3.0 equiv), **2b−g** (25 mg, 1.0 equiv), KF (4.0 equiv) and 18-crown-6 ether (4.0 equiv) in DME (1.0 mL). [b]Isolated yield. NR = no reaction.

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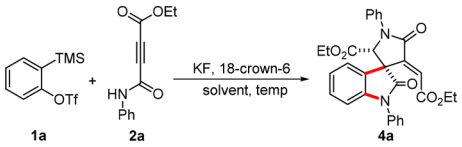
groups, respectively, at the C4-position of the aryl moiety provided products **3j** and **3k**, respectively, in moderate yields. Gratifyingly, carbamoylpropiolate **2d** having an $-CF_3$ group at the C2-position of the aryl moiety was well tolerated, leading to the desired product **3l** in good yield. We did not observe products **3m** and **3n** from the corresponding carbamoylpropiolates **2e** and **2f**. However, *N*-benzyl-substituted carbamoylpropiolate **2g** afforded the corresponding oxindolylidene acetate **3o** in moderate yield.

Further experimentation and detailed analysis of the optimized reaction conditions (Table 1, entry 13) indicated that this protocol can generate spirooxindolopyrrolidone **4a** (Table 2). In

Table 2. Optimization To Obtain Spiro Products[a–d]



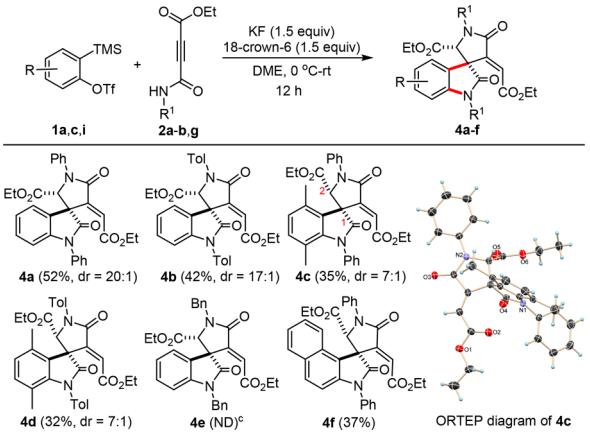
entry	**1a**/**2a** (equiv)	KF (equiv)	temp (°C)	yield (%)
1	3.0:1.0	2.5	0-rt	21
2	1.8:1.0	2.5	0-rt	37
3	1.5:1.0	2.5	0-rt	35
4	1.8:1.0	2.5	rt	13
5	1.0:1.0	2.5	0-rt	19
6	1.0:2.0	2.5	0-rt	21
7	**1.0:3.0**	**1.5**	**0-rt**	**52**
8	1.0:5.0	1.5	0-rt	41
9	1.0:5.0	2.5	0-rt	46

[a]Selected entries. [b]Reactions were performed on a 25 mg scale of **2a** in DME solvent (1.0 mL), 12 h. [c]Isolated yield. [d]Equivalent quantity of 18-crown-6 ether was added.

this context, we performed the reaction of **1a** with **2a** at 0 °C using our optimized reaction conditions, and the reaction mixture was then allowed to attain room temperature gradually (Table 2, entry 1). When the reaction was continued for comparatively longer time, we observed the formation of a new product, spirooxindolopyrrolidone **4a**. To improve the yield of **4a**, we screened various parameters, and the selected results (Table 2, entries 2–9) indicate that the best yield of the product **4a** was obtained when the reaction was performed using **2a** (3.0 equiv) and **1a** (1.0 equiv) in the presence of KF and 18-crown-6 ether in DME at 0 °C to room temperature (Table 2, entry 7). The structure of **4a** was confirmed by spectroscopic analysis and by comparison of the NMR data with structurally similar compounds reported in the literature.[5c,l]

After finding the optimal condition for spirooxindolopyrrolidones, we examined the substrate scope (Scheme 4). Aryne precursor **1a** reacted smoothly with both carbamoylpropiolates **2a** and **2b** to furnish the corresponding spiro products **4a** and **4b** in moderate yields. Notably, aryne precursor **1c** bearing alkyl substitution near the reaction center was well tolerated to provide the spirooxindolopyrrolidones **4c** and **4d** in moderate yields. The single-crystal X-ray diffraction data obtained for the spiro product **4c** confirmed the structure and 1,2-*cis* relative configuration between the ester and amide group as well as the presence of *E*-olefin. A complex mixture was observed, along with the expected compound **4e**, when *N*-benzyl-substituted carbamoylpropiolate **2g** was reacted with the aryne precusor **1a**. ^{1}H NMR and HRMS indicate the formation of **4e**. Naphthyl aryne precursor **1i** on treatment with carbamoylpropiolate **2a**

Scheme 4. Spirooxindolopyrrolidones Substrate Scope[a,b]



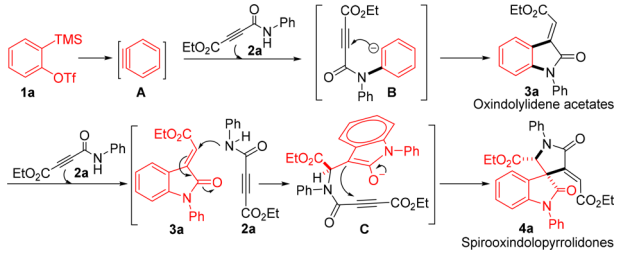
[a]Reaction conditions: **1** (1.0 equiv), **2** (25 mg, 3.0 equiv), KF (1.5 equiv), and 18-crown-6 ether (1.5 equiv) in DME (1.0 mL). [b]Isolated yield. [c]ND: yield not determined.

furnished the expected product **4f** in moderate yield. It is a mixture of regio- and diastereromers. The isolation of stable product **4f** indirectly confirms the formation of product **3i** (Scheme 2) in the reaction mixture.

Potassium fluoride mediated dimerization (see the Supporting Information) or oligomerization of carbamoylpropiolate and high tenacity of products **4** to react with nucleophiles could be the reasons behind the moderate yields (Scheme 4).

On the basis of the literature precedence and our experience in the field of aryne chemistry, a plausible mechanism for the developed protocol is depicted in Scheme 5. The aryne species **A**

Scheme 5. Plausible Mechanism



was trapped by a nucleophile carbamoylpropiolate **2a** and formed the intermediate **B**. Subsequently, intramolecular Michael addition provides the cyclized product oxindolylidene acetate **3a**. Furthermore, nucleophilic attack of another molecule of carbamoylpropiolate **2a** on the product **3a** at the most electrophilic carbon[5l] generates intermediate **C**, which upon cyclization provides spirooxindolopyrrolidone **4a**.

In summary, we have demonstrated an efficient and facile route to access pharmacologically important and versatile building blocks, "oxindolylidene acetates". The process is also optimized to obtain spirooxindolopyrrolidones, a common scaffold found in drugs, natural products, and bioactive molecules. This transition-metal-free one-pot approach provides varyingly substituted oxindole scaffolds from the easily available carbamoylpropiolates and aryne precursors. The diversity-oriented protocol developed herein has a good functional group tolerance, which will be useful in generating a focused library of oxindolylidene or spirooxindole congeners for SAR studies. Presently, we are working on the application of this

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protocol in the total syntheses of related drugs and natural products.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b03661.

Experimental procedures, and spectroscopic data of all new compounds (PDF)

Accession Codes

CCDC 1825703 contains 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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