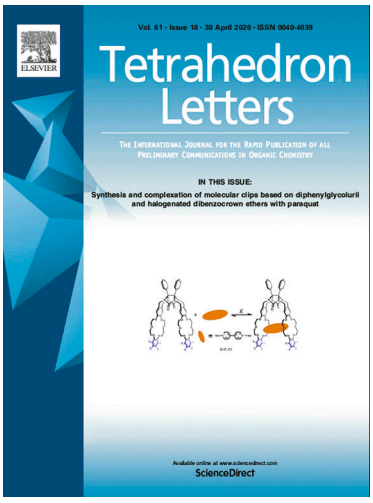
Journal Pre-proofs



Pyridinium Triflate Catalyzed Intramolecular Alkyne-Carbonyl Metathesis Reaction of *O*-Propargylated 2-Hydroxyarylaldehydes

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PII: S0040-4039(20)31168-0
DOI: https://doi.org/10.1016/j.tetlet.2020.152657
Reference: TETL 152657

To appear in: *Tetrahedron Letters*

Received Date: 5 October 2020
Revised Date: 4 November 2020
Accepted Date: 8 November 2020

Please cite this article as: Kumar Saini, M., Singh Korawat, H., Kant Verma, S., Basak, A.K., Pyridinium Triflate Catalyzed Intramolecular Alkyne-Carbonyl Metathesis Reaction of *O*-Propargylated 2-Hydroxyarylaldehydes, *Tetrahedron Letters* (2020), doi: https://doi.org/10.1016/j.tetlet.2020.152657

Pyridinium Triflate Catalyzed Intramolecular Alkyne-Carbonyl Metathesis Reaction of *O*-Propargylated 2-Hydroxyarylaldehydes

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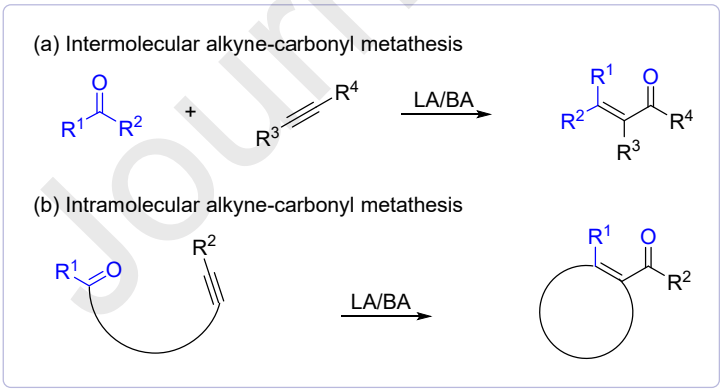
Abstract: 3,5-dibromopridinium trifluoromethanesulfonate catalyzes the intramolecular alkyne-carbonyl metathesis reaction of a variety of *O*-propargylated 2-hydroxyarylaldehydes and ketones bearing alkyl, aryl and heteroaryl substituted internal alkynes to provide various 3-(hetero)aroyl 2*H*-chromenes in high yields.

Introduction: Over the last two decades, alkyne-carbonyl metathesis (ACM) reaction has emerged as a powerful tool for the stereoselective synthesis of α,β-unsaturated ketones utilizing an alkyne (mostly internal alkyne) and a carbonyl compound (aldehyde/ketone).[1] The general reaction is shown in Scheme 1. The ACM reaction is considered as a viable and atom-economic alternative to the classical Wittig olefination and has been extensively utilized for the synthesis of biologically active natural products.[2] While the intermolecular version of the reaction provides direct access to the synthetically useful acyclic α,β-unsaturated ketones, the intermolecular version has widely been demonstrated as a unique strategy for annulation reactions which delivers ring systems difficult-to-synthesize or nearly impossible to synthesize by other known synthetic methods.[3] This aspect of the intermolecular alkyne-carbonyl metathesis reaction has been continuing attracting interest of synthetic organic chemists worldwide. The ACM reaction



Scheme 1: General scheme for alkyne-carbonyl metathesis reaction

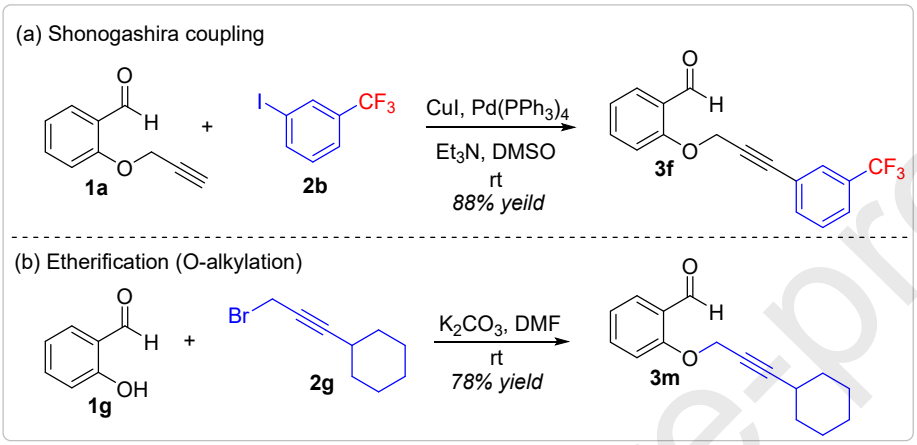
is usually catalyzed by σ-electrophilic Lewis acids[4] (LA) such as $BF_3.OEt_2$, $FeCl_3$, $Sc(OTf)_3$, $In(OTf)_3$, $Mg(OTf)_2$, $Sn(OTf)_2$, $Zn(OTf)_2$, SbF_5, π-electrophilic Lewis acids[5] ($AgSbF_6$, AgOTf,

$AuCl_3$), combination of Lewis acid with alcohol[6] and Bronsted acids[7] (BA) such as TfOH, CF_3CO_2H, HBF_4, etc. In addition, Barluenga reagent in combination with HBF_4 (Py_2IBF_4-HBF_4) has also been reported as an efficient catalyst for the intra- and intermolecular ACM reaction.[8]

On the other hand, pyridinium salts are commonly utilized as mild, neutral and environmentally benign organocatalyst for various transformations such as acetal formation and cleavage,[9] H_2O_2 mediated oxidation of sulfide to sulfoxide[10] and aziridination of olefins.[11] Pyridinium p-toluenesulfonate (PPTS) is a suitable catalyst for deprotection of silyl ethers or tetrahydropyranyl ethers when a substrate is not compatible to stronger acid catalysts. It is also a commonly used catalyst for the preparation of acetals and ketals from aldehydes and ketones. In addition to these reports, very recently Kancharla et al. showed that 2,4,6-tri-*tert*-butylpyridinium chloride acts an efficient catalyst for highly stereoselective glycosylation reactions of glycals.[12] However, despite these reports, to the best of our knowledge, alkyne-carbonyl metathesis reaction catalyzed by an organocatalyst, in particular, readily available pyridinium salts has not been reported in the literatures.

Among the various intramolecular versions, alkyne-carbonyl metathesis reactions of internal alkyne-tethered 2-hydroxyarylaldehydes have recently gained significant research interest due to the important biological activities associated with the products derived thereof. Although examples (mostly single example) of this intramolecular reaction were scattered in the literature,[5a,7a] in 2011, Jana and co-workers carried out extensive work and demonstrated that internal alkyne-tethered 2-hydroxyarylaldehydes can be converted into the corresponding 3-aroyl 2*H*-chromenes in high yields using 15 mol% $FeCl_3$ in refluxing CH_3CN (12 examples, 45-89% yields).[13] Later on, Saito et al. utilized Py_2IBF_4-HBF_4 catalytic system for the intramolecular ACM reaction (4 examples, 50-80% yields).[8] Das and co-workers showed that stoichiometric amount (1.2 eq) of $BF_3.OEt_3$ in trifluoroethanol promote the intramolecular metathesis reaction to generate 3-aroyl 2*H*-chromenes in excellent yields at rt (13 examples, 90-97% yields).[14] Adding to these development, in a very recent report, Ramesh et at. utilized acidic deep eutectic solvent (choline chloride:p-toluene sulfonic acid) as a promoter for this useful transformation (13 examples, 29-92% yields).[15] However, these reported methods have certain drawbacks such as use of transition metal based catalyst, use of stoichiometric amount of Lewis acid and use of special solvents which limits their wide applicability, practicality and environmental compatibity. Moreover, all these reports are restricted to the substrates containing aryl and alkyl-

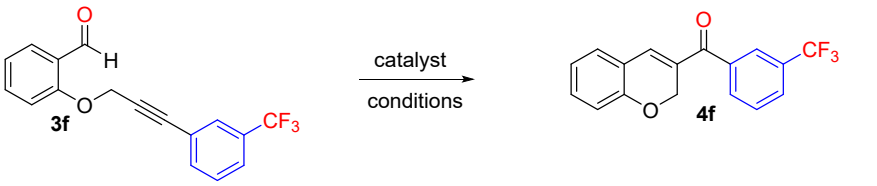
substituted internal alkynes. To the best of our knowledge, there is no report for this intramolecular alkyne-carbonyl metathesis reaction of substrates bearing a heteroaryl substituted internal alkynes. Herein, we disclose our results of the intramolecular alkyne-carbonyl metathesis reaction of a fairly large number of *O*-propargylated 2-hydroxyarylaldehydes bearing aryl, alkyl and heteroaryl substituted internal alkynes using 30 mol% 3,5-dibromopyridinium triflate as the organocatalyst in MeOH at 80 °C.

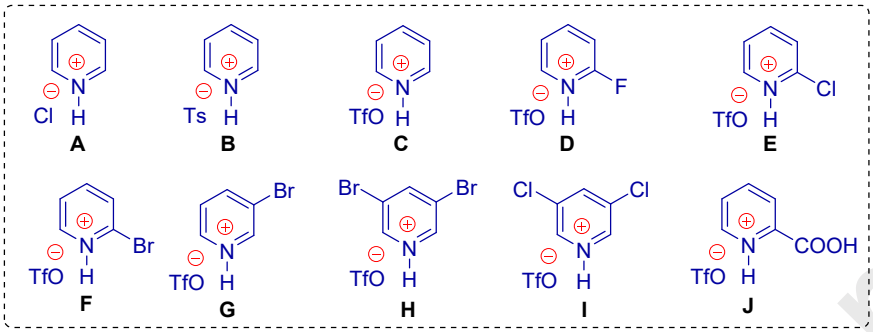


Scheme 2: Synthesis of *O*-propargylated benzaldehydes bearing internal alkyne

We began our investigation with 2-propargyloxybenzaldehyde **3f** which was prepared in two steps from commercially available starting materials (Scheme 2a). Initially, 2-propargyloxybenzaldehyde **3f** was treated with 10 mol% hydrochloride salt **A** in DCM at rt. However, no detectable transformation was observed. Upon heating at 60 °C in a sealed tube for 24 h, formation of trace amount of product was observed. To our disappointment, pyridinium salts **B** and **C** also provided similar results in DCM at 60 °C (entries c-d, Table 1). However, when we tested the intramolecular metathesis reaction using 10 mol% pyridinium triflate salt **C** in MeOH at 60 °C, we observed approximately 20% conversion after 24 h (entry e, Table 1). Carrying out the reaction at 80 °C for 24 h led to 30% conversion (entry f, Table 1). Using 30 mol% of catalyst **C**, a moderate conversion (45%) was observed (entry g, Table 1). While the catalyst **C** exhibited lower activity in EtOH and ^{i}PrOH, its activity in HFIP was comparable to that in MeOH (entries h-j, Table 1). Next, screening of triflate salts of halogenated pyridines were examined as the catalyst in MeOH at 80 °C. Triflate salts derived from 2-fluoropyridine and 2-chloropyridine provided inferior results when compared to that of 2-bromopyridine (entries k-m, Table 1). Pyridinium salt **G** provided encouraging results (entry n, Table 1). When the triflate salt **H** derived from 3,5-dibromopyridine

Table 1: Optimization study



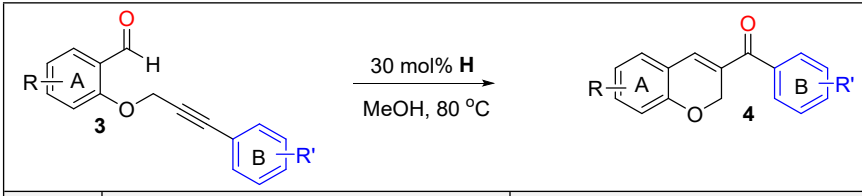


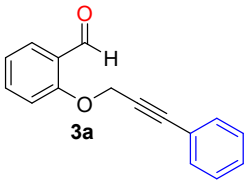
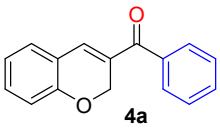
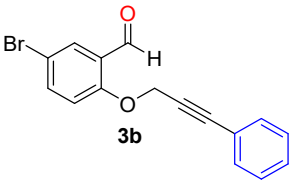
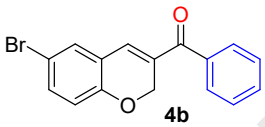
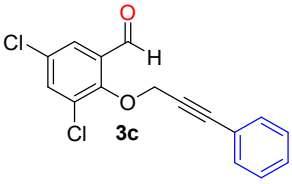
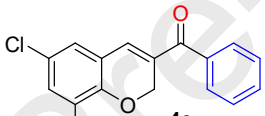
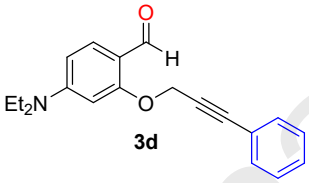
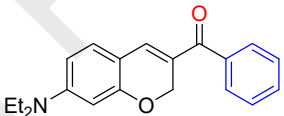
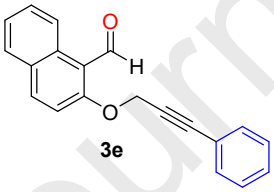
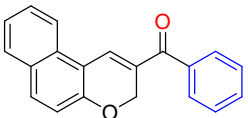
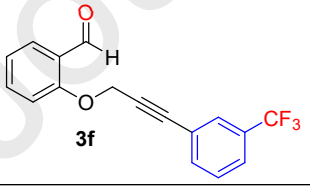
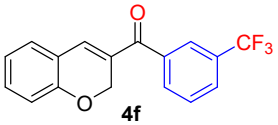
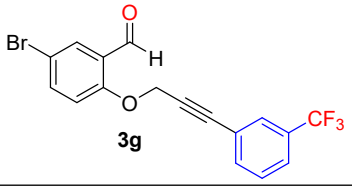
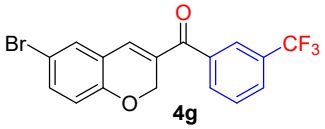
entry	catalyst	conditions[a]	yield (%)
a	10 mol% **A**	DCM, rt, 24 h	NR
b	10 mol% **A**	DCM, 60 °C, 24 h	trace
c	10 mol% **B**	DCM, 60 °C, 24 h	trace
d	10 mol% **C**	DCM, 60 °C, 24 h	trace
e	10 mol% **C**	MeOH, 60 °C, 24 h	14 %
f	10 mol% **C**	MeOH, 80 °C, 24 h	22%
g	30 mol% **C**	MeOH, 80 °C, 24 h	36%
h	30 mol% **C**	EtOH, 80 °C, 24 h	24%
i	30 mol% **C**	^{i}PrOH, 80 °C, 24 h	18%
j	30 mol% **C**	HFIP, 80 °C, 24 h	34%
k	30 mol% **D**	MeOH, 80 °C, 24 h	18%
l	30 mol% **E**	MeOH, 80 °C, 24 h	23%
m	30 mol% **F**	MeOH, 80 °C, 24 h	45%
n	30 mol% **G**	MeOH, 80 °C, 24 h	60%
o	30 mol% **H**	MeOH, 80 °C, 20 h	85%
p	30 mol% **I**	MeOH, 80 °C, 24 h	67%
q	30 mol% **J**	MeOH, 80 °C, 24 h	62%
r	30 mol% **H**	H_2O, 80 °C, 24 h	NR

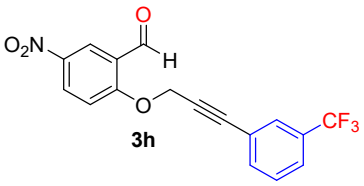
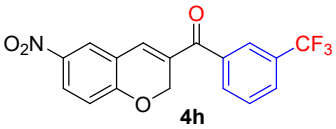
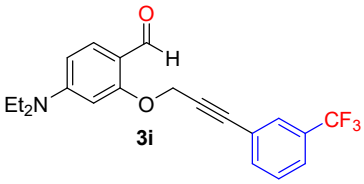
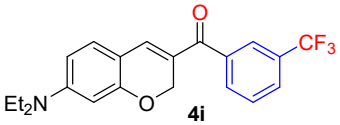
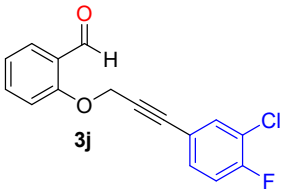
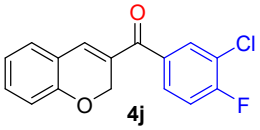
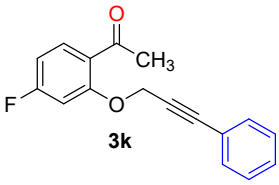
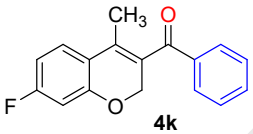
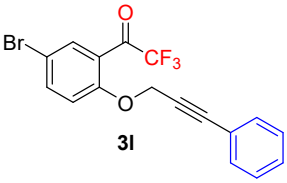
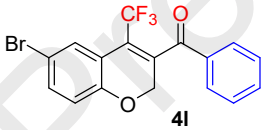
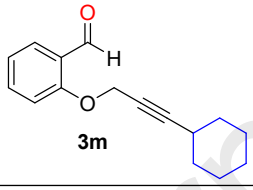
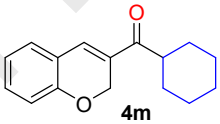
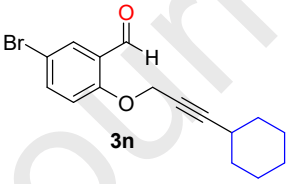
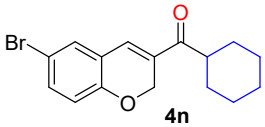
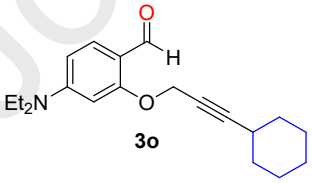
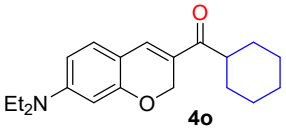
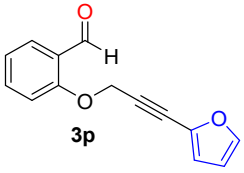
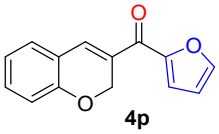
[a]All reactions were carried out in 0.20 mmol scale in appropriate solvent in 0.2M concentration; NR = no reaction.

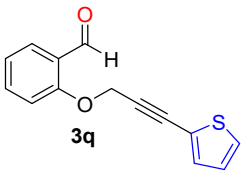
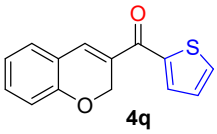
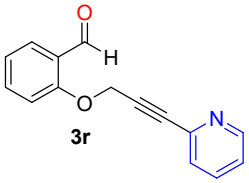
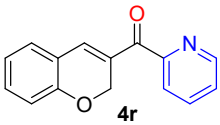
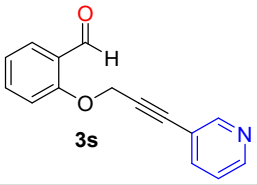
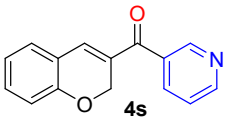
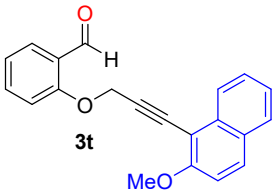
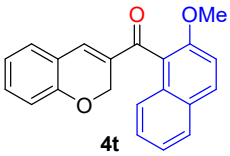
was used as the catalyst, complete conversion took place within 20 h and product **4f** was obtained in 85% yield (entry o, Table 1). Catalyst **I** provided inferior results when compared with catalyst **H** (entry p, Table 1). Interestingly, triflate salt of 2-picolinic acid also worked as catalyst albeit in lower efficiency (entry q, Table 1). It is important to mention that no reaction

Table 2: Synthesis of 3-(hetero)aroyl 2*H*-chromenes



entry	2-propargyloxyarylaldehyde **3**	3-(hetero)aroyl 2*H*-chromene **4**
a	 **3a**	 **4a** 80 °C, 24 h, 89%
b	 **3b**	 **4b** 80 °C, 16 h, 90%
c	 **3c**	 **4c** 80, 16 h, 92%
d	 **3d**	 **4d** 80 °C, 36 h, 84%
e	 **3e**	 **4e** 80 °C, 24 h, 91%
f	 **3f**	 **4f** 80 °C, 20 h, 85%
g	 **3g**	 **4g** 80 °C, 24 h, 92%

h	 **3h**	 **4h** 80 °C, 18 h, 86%
i	 **3i**	 **4i** 80 °C, 36 h, 84%
j	 **3j**	 **4j** 100 °C, 24 h, 82%
k	 **3k**	 **4k** 60 °C, 24 h, 62%
l	 **3l**	 **4l** 60 °C, 12 h, 58%
m	 **3m**	 **4m** 90 °C, 12 h, 68%[b]
n	 **3n**	 **4n** 90 °C, 12 h, 72%[b]
o	 **3o**	 **4o** 90 °C, 24 h, 64%[c]
p	 **3p**	 **4p** 80 °C, 8 h, 84%

q	 **3q**	 **4q** 80 °C, 10 h, 88%
r	 **3r**	 **4r** 150 °C, 12 h, (35)[c]
s	 **3s**	 **4s** 150 °C, 16 h, (42)[d]
t	 **3t**	 **4t** 80 °C, 24 h, 80%

[a]All reactions were carried out in 0.25 mmol scale using 1.0 eq of **3**, 30 mol% of catalyst **H**, in MeOH (0.2 M); [b]reaction was carried out in DCM-MeOH (1:1); [c]NMR yield (40% conversion); [d]NMR yield (45% conversion).

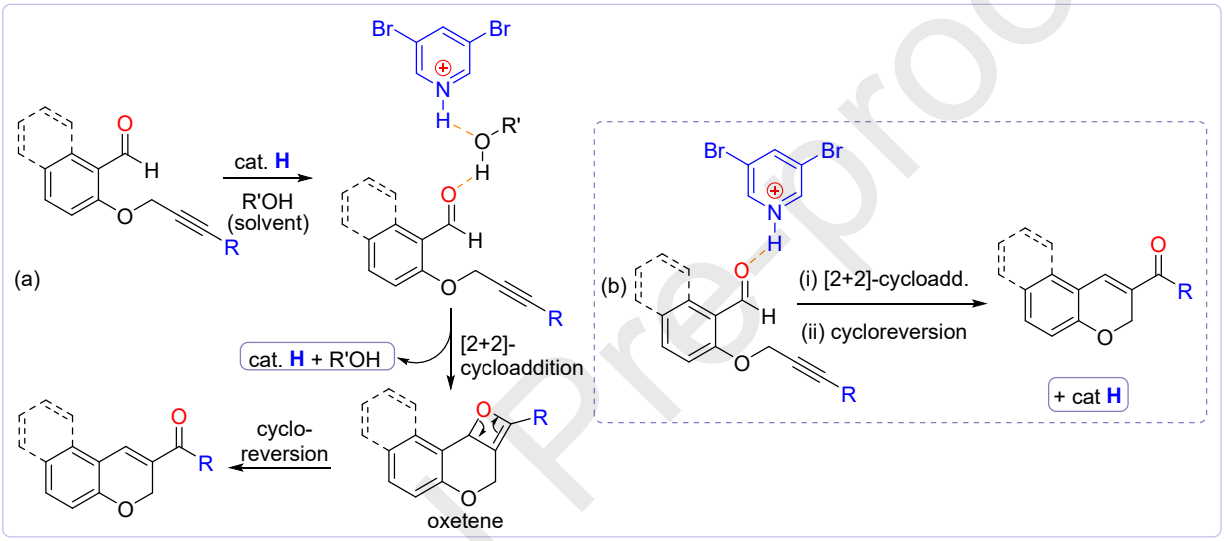
was observed in water at 80 °C possibly due to the insolubility of the starting material in water (entry r, Table 1).

Identifying pyridinium salt **H** as an efficient catalyst for the high yielding conversion of **3f** to **4f**, we next sought to evaluate the scopes of this catalytic transformation. A series of 2-propargyloxybenzaldehydes bearing (hetero)aryl and alky substituted internal alkynes were synthesized following reported procedures. As shown in Scheme 2, a wide variety of *O*-propargylated 2-hydroxyarylaldehydes bearing internal alkynes can be synthesized via complementary methods, viz. Sonogashira coupling and *O*-alkylation. In addition, the trifluoromethyl ketone containing *O*-propargylated compound **3l** can be synthesized in two steps (see the supplementary information, page S6) from compound **3b**. As shown in Table 2, the alkyne-carbonyl metathesis reaction of 2-propargyloxybenzaldehydes bearing phenyl and 3-(trifluoromethyl)phenyl substituted internal alkynes underwent smooth metathesis reaction furnishing 3-aroyl 2*H*-chromenes in very high yields (entries a-i, Table 2). Due to the presence of two strong electronegative halogen atoms (F, Cl) in aryl ring B, substrate **3j** required elevated

temperature (100 °C) for the alkyne-carbonyl metathesis reaction to furnish 2*H*-chromene **4j** in 82% yields (entry j, Table 2). Substrates bearing electron-withdrawing groups on the aryl ring A showed better reactivity than those having strong electron-releasing group on the aryl ring A. Substrates bearing methyl ketone as well as trifluoromethyl ketone exhibited lower reactivity when compared to the substrates containing aldehydic group. The lower reactivity of these substrates could be attributed to the steric and electronic effects exerted by the methyl and trifluoromethyl groups in the transition state of the cycloaddition reaction. Nevertheless, synthetically useful yields of the corresponding 3-aroyl 2*H*-chromenes were obtained by carrying out the reactions at 60 °C (entries k-l, Table 2). Unlike phenyl substituted 2-propargyloxybenzaldehydes, the cyclohexyl substituted substrates exhibited lower reactivity towards the metathesis reaction. However, good yields of the products were obtained by carrying out the reaction at 90 °C (entries m-o, Table 2). Next, the scopes of heteroaryl substituted 2-propargyloxybenzaldehydes were evaluated under the optimized reaction conditions. Electron-rich heteroaryl (furan, thiophene) substituted 2-propargyloxybenzaldehydes underwent smooth reaction at 80 °C in short reaction time to provide the corresponding 3-(hetero)aroyl 2*H*-chromenes in high yields (entries p-q, Table 2). On the contrary, 2- and 3-pyridyl substituted 2-propargyloxybenzaldehydes failed to undergo metathesis reaction at 80 °C. However, approximately 40% conversion took place when these substrates were heated with 1.0 eq. of catalyst **H** in MeOH at 150 °C (entries r-s, Table 2). Unfortunately, despite our best efforts, the pyridyl products could not be separated from the starting materials to obtain a sample for recording analytical data. It would be interesting to see the reactivity of the substrates containing pyridine *N*-oxide which may exhibit better reactivity towards the metathesis reaction. It is worth mentioning that substrate **3t** bearing 2-methoxynaphthyl substituted alkyne also underwent metathesis reaction to provide 2*H*-chromene **4t** in high yield (80%). Due to the extended conjugation, all the synthesized 3-(hetero)aryl 2*H*-chromenes could be visualized under long UV (354 nm) at which 2-propargyloxybenzaldehydes usually do not show any absorption.

The mechanistic hypothesis of the pyridinium triflate catalyzed ACM reaction is outlined in Scheme 3a. Pyridinium triflate **H** activates an alcohol molecule (solvent) via intermolecular hydrogen bonding between the H-atom of pyridinium salt and O-atom of the alcohol molecule. The H-atom of the alcohol molecule, in turn, activates the carbonyl group via intermolecular H-bonding towards the intramolecular [2+2]-cycloaddition reaction leading to the oxetene

intermediate and release of the pyridinium catalyst. Formal (2+2)-cycloreversion of the unstable oxetene intermediate leads to the 3-aroyl 2*H*-chromene with complete regioselectivity. Direct activation of the carbonyl group by the pyridinium salt, as shown in Scheme 3b, is also considerable in aprotic solvent (such as 1,2-dichloroethane). However, substrate activation by the catalyst in aprotic solvent is less effective. For example, with catalyst **H** at 100 °C for 24 h, 2-propargyloxybenzaldehyde **3j** underwent complete conversion in MeOH whereas only approximately 60% conversions was observed in 1,2-dichloroethane. Recent literature reports by Kancharla and co-workers[12] further supports our catalytic hypothesis in MeOH (solvent).



Scheme 3: Plausible mechanism of the pyridinium salt catalyzed ACM reaction.

Conclusion: In summary, the intramolecular alkyne-carbonyl metathesis reaction of 2-propargyloxyarylaldehydes containing (hetero)aryl and alkyl substituted internal alkynes catalyzed by 3,5-dibromopyridinium triflate in MeOH has been demonstrated. The mild reaction conditions are amenable to several functional groups (NO_2, NEt_2, CF_3, enones) and provide a wide variety of novel 3-(hetero)aroyl 2*H*-chromenes in good yields. 2-Pyridyl and 3-pyridyl substituted 2-propargyloxybenzaldehydes exhibited poor reactivity under the standard reaction conditions. It would be interesting to examine the reactivity of the substrates bearing pyridine *N*-oxide substituted internal alkynes. The intramolecular alkyne-carbonyl metathesis reaction may provide interesting results in the presence of a pyridine based bifunctional organocatalyst.[16] We will investigate on these in our future work.

Notes: Authors declare no competing financial interest.

Acknowledgement: Research grants from Council of Scientific and Industrial Research, New Delhi (Grant No. 02(0346)/19/EMR-II) is gratefully acknowledged. MKS thanks CSIR, New Delhi for a research fellowship. HSK and SKV thank UGC, New Delhi for research fellowships.

Associated content:

The Supplementary Information is available (Experimental procedures, analytical data and copies of ^{1}H & ^{13}C NMR spectra).

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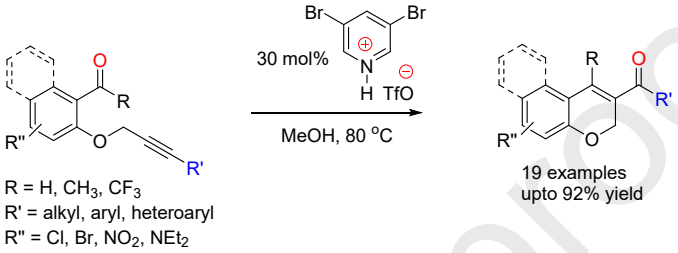
Graphical Abstract

Pyridinium Triflate Catalyzed Intramolecular Alkyne-Carbonyl Metathesis Reaction of *O*-Propargylated 2-Hydroxyarylaldehydes

Manoj Kumar Saini, Harshita Singh Korawat, Shashi Kant Verma, Ashok K. Basak*



- Organocatalyzed alkyne-carbonyl metathesis reaction
- Activation via hydrogen bonding
- Broad substrate scope
- High yielding reactions