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Metal free C-3 chalcogenation (sulfenylation and selenylation) of 4*H*-pyrido[1,2-*a*]pyrimidin-4-ones[†]

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An expeditious metal free C-3 chalcogenation of 4*H*-pyrido[1,2-a]pyrimidin-4-one has been devised to synthesize diversely orchestrated 3-ArS/ArSe derivatives in high yields (up to 95%). This operationally simple reaction proceeds under mild reaction conditions, can be executed in gram scale, and also highlights broad functional group tolerance. Preliminary experimental investigation suggests a radical mechanistic pathway for these transformations.

Organosulfur species and derivatives thereof, have garnered a prominent position in contemporary organic synthesis.¹ They also have widespread applications in pharmaceuticals, bioactive compounds and polymer materials.² In addition, carbonselenium-carbon skeletons are high value core structures for their extensive use as therapeutically active agents, such as antioxidant, antihypertensive, antimicrobial, antibacterial, antiviral, anticancer agents etc.3 Moreover, organoselenium species have been identified as non-toxic compounds.⁴ Some of the biologically active C-S/C-Se linkage containing scaffolds is outlined in Fig. 1. Consequently, numerous efforts have been devoted to develop facile and reliable methods for the installation of a sulfenyl/selenyl group into organic frameworks.5 Apart from the cross-coupling approach, an alternative protocol for the transition-metal-catalyzed C-S bond formation via C-H bond functionalization has been established, which is known as a sulfenylation reaction.⁶ In this reaction, aryl sulfonyl hydrazides,7 arylsulfonyl chlorides,8 sulfinic acids,9 and sodium sulfinates¹⁰, thiols¹¹ are mostly used as the sulfenylating agents. Although, these methods are advantageous, certain limitations comprising the use of metal catalyst and toxic reagents still persist. Complete removal of trace amounts of transition-metal residues from the anticipated bioactive products is quite challenging task, and this contamination of a transition metal also inhibits the sustainable development.12 Despite these accomplishments, development of an efficient and practical method for transition-metal-free C-S/Se bond forming reactions using thiols/diselenide as the sulfenylation/selenation reagent is an attractive and synthetically desirable.

On the other hand, *N*-fused bicyclic heterocycles¹³ has received enormous interest from synthetic chemists as well as medicinal researchers due to their profound impact in agrochemicals, pharmaceuticals and material sciences.¹⁴ In this family, 4H-pyrido[1,2-a]pyrimidin-4-one (Fig. 1) exhibits versatile biological activities,15 such as CXCR3 antagonism,16 HLE inhibition,17 MexAB-OprM specific efflux pump inhibition,18 potent 5-HT6 antagonists,19 and acetylcholinesterase inhibition.20 Meanwhile, Pd catalyzed direct arylation and alkenylation of 4H-pyrido[1,2-a]pyrimidin-4-one through C-H bond functionalization has already been reported in the literature.21 Rather, only a single report for the insertion of -SAr group in 4*H*-pyrido[1,2-*a*]pyrimidin-4-one molecule using sulfonyl hydrazides as thiol surrogates is documented by Wang et al.22 Nevertheless, this protocol is effective at elevated temperature. Based on our research interests on the structural diversification of heterocyclic scaffolds, we recently reported different methodologies for the metal free direct C-H bond functionalization.²³ Herein, we envisaged to disclose a straightforward and efficient protocol of sulfenylation/selenylation for 4H-pyrido[1,2-a]pyrimidin-4-one in the presence of iodine under mild conditions. Pleasingly, several thiols/organodiselenides are smoothly coupled with 4H-pyrido[1,2*a*]pyrimidin-4-one and furnished the desired anticipated products in good to excellent yields (Scheme 1).

We commenced our studies with the optimization of the sulfenylation reaction where 2-phenyl-4*H*-pyrido[1,2-*a*]pyrimidin-4-one (**1a**) and thiophenol were used as a model coupling partner



Fig. 1 Representative examples of some biologically active 4*H*-pyrido [1,2-*a*]pyrimidin-4-one and diarylsulfide/diselenide scaffold.

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Scheme 1 Previous approaches and the present route of C–H bond functionalization of 4*H*-pyrido[1,2-*a*]pyrimidin-4-ones.

(Table 1). Initial attempts to couple them, using NaI and TBHP (as oxidant) in DMSO as a solvent at 100 °C remained unfruitful (Table 1, entry 1). No improvement was observed even after switching the solvent from DMSO to acetonitrile (Table 1; entry 2). However, yield of the expected product **2a** was raised to 50% upon using TBAI/ $K_2S_2O_8$ in water (Table 1; entry 3). The reaction efficiency was further enhanced using one equiv. of TBAI in MeCN at 70 °C (Table

1; entry 4). Subsequently, several others inexpensive and readily available iodine/iodide additives were screened under aerobic condition (Table 1; entries 5-9). Delightedly, one equiv. of iodine provided the desired thiolated product 2a in excellent (91%) yield at 70 °C (entry 5), after 12 h, while other forms of iodine additives were unable to promote this transformation effectively (Table 1; entries 6-9). It is noteworthy that except TBHP all others oxidant appears to be redundant in this reaction (Table 1; entries 10-13). Lowering the reaction temperature (50 °C and 30 °C) had a detrimental result on the reaction outcome (Table 1; entries 14-15). Notably, in absence of potassium persulfate, no desired product was detected in TLC, indicating that the oxidant has a decisive role for this sulfenylation reaction (Table 1; entry 16). Interestingly, consistent with our previous observation (Table 1; entry 5), using of 50 mol% of iodine also afforded the 92% yield of thiolated derivative 2a (Table 1; entry 17). Other solvents were inefficient to provide decent yields (Table 1; entries 18-22). So it is evident from the optimization table that a combination of 50 mol% of iodine and $K_2S_2O_8$ (2 equiv.) as an oxidant in MeCN at 70 °C was found to be optimal for the sulfenylation reaction of 2-phenyl-4H-pyrido 1,2a pyrimidin-4-one, which resulted in the formation of the corresponding 3-ArS derivative 2a in excellent yield (92%) after 12 h (Table 1, entry 17).

$ \begin{array}{c} $	ant, temp, solvent
1a	2a

Entry	Reagent (equiv.)	Oxidant (equiv.)	Temperature (°C)	Solvent (ml)	Time (h)	$\operatorname{Yield}^{b}(\%)$
1	NaI (3)	TBHP (3)	100	DMSO	24	NR
2	NaI (3)	TBHP (3)	100	CH ₃ CN	24	NR
3	TBAI (2)	$K_2S_2O_8(2)$	70	H_2O	24	50
4	TBAI (1)	$K_2S_2O_8(2)$	70	CH_3CN	12	67
5	$I_2(1)$	$K_2 S_2 O_8 (2)$	70	CH ₃ CN	12	91
6	KI (1)	$K_2S_2O_8(2)$	70	CH ₃ CN	12	NR
7	NaI (1)	$K_2 S_2 O_8 (2)$	70	CH ₃ CN	12	NR
8	$NH_4I(1)$	$K_2S_2O_8(2)$	70	CH ₃ CN	12	60
9	NIS (1)	$K_2S_2O_8(2)$	70	CH ₃ CN	12	63
10	$I_2(1)$	TBHP (2)	70	CH ₃ CN	12	85
11	$I_2(1)$	DTBP (2)	70	CH ₃ CN	12	NR
12	$I_{2}(1)$	TBPB (2)	70	CH ₃ CN	12	NR
13	$I_2(1)$	$H_2O_2(2)$	70	CH ₃ CN	12	71
14	$I_{2}(1)$	$K_2S_2O_8(2)$	50	CH ₃ CN	12	53
15	$I_2(1)$	$K_2S_2O_8(2)$	30	CH ₃ CN	12	NR
16	$I_{2}(1)$		70	CH ₃ CN	12	NR
17	I ₂ (50 mol%)	$K_2S_2O_8(2)$	70	CH ₃ CN	12	92
18	I_2 (50 mol%)	$K_2S_2O_8(2)$	70	Toluene	12	35
19	I ₂ (50 mol%)	$K_2S_2O_8(2)$	70	Dioxane	12	41
20	I_2 (50 mol%)	$K_2S_2O_8(2)$	70	DCE	12	66
21	I_2 (50 mol%)	$K_2S_2O_8(2)$	70	EtOH	12	81
22	I ₂ (50 mol%)	$K_2S_2O_8(2)$	70	DMF	12	NR

^{*a*} Reaction condition: 2-phenyl substituted 4*H*-pyrido[1,2-*a*]pyrimidin-4-ones (0.125 mmol, 1 equiv.), benzene thiol (0.1875 mmol, 1.5 equiv.), inducer (equiv./mol%), solvent (2 ml), oxidant (3 equiv.). ^{*b*} Isolated yields based on the reactants **1a**, the reaction was run for 12–24 h.

Having assimilated the robust reaction conditions for the C-S coupling of 4*H*-pyrido[1,2-*a*]pyrimidin-4-one, we sought to explore the scope and general applicability of this protocol (Table 2). A variety of 2-substituted-4*H*-pyrido[1,2-*a*]pyrimidin-4one was treated with a broad range of thiols, and the corresponding results are represented in Table 2. Satisfyingly, both electron-rich (-OMe, -Me) and electron-deficient (-F, -Cl, -Br) groups bearing benzene thiols reacted smoothly with 2-phenyl-4H-pyrido[1,2-a]pyrimidin-4-one, affording the desired 3-sulfenylated derivatives in good to excellent yields (Scheme 1; entries 2b-2h). Noticeably, a crucial effect in the product yield was surveyed with the substituents present at the benzene thiol. 4-Methoxybenzene thiol furnished much lower yield of the corresponding coupled product (2b), compared to electronwithdrawing group, probably due to the generation of a more stable dimer [disulphide]. However, the yield of the anticipated product [2b] could further be enhanced upon/on using stoichiometric amount of catalyst (I_2) . To our delight, maximum productivity of the product was obtained in the case of Fsubstituted benzenethiol compare to the other halogens. Notably, ortho bromo-substituted benzene thiol delivered in a higher yield of the corresponding product (2h) than the

Table 2 Scope of different substituted 4H-pyrido[1,2-a]pyrimidin-4ones and thiol derivatives for I₂ mediated sulfenylation^{*a*}



corresponding chloro derivative (2c). 2,5-Dimethylbenzene thiol was endured under the current reaction conditions to provide 88% yield of 2e. Importantly, the bulkier naphthalene thiol also effectively participated in this transformation to give 82% yield of the C-S coupled product (2g). For adorning the synthetic potentiality further, we investigated the reactivity of various thiols with diverse 4H-pyrido [1,2-a] pyrimidin-4-one. Employment of both electron-neutral (-Me) and electron-deficient (-Cl) functional group substituted parent scaffold provided synthetically useful yields of the desired sulfenylated products with a wide spectrum of benzene thiols (entries 2i-2p). In this context, a suitable choice of benzene thiols is also important, since electronic bias plays a pivotal role in this transformation (entries 2i-2p). Comparatively, a higher yield of the desired ArS derivatives was always obtained in the presence of an electronwithdrawing group (-F, -Cl) at the para position of benzene thiol (entries 2k, 2m, 2n and 2p). Exposure of 2-alkyl substituted 4H-pyrido[1,2-a]pyrimidin-4-one with thiophenol and 4-chlorothiophenol was also fruitful to give intended products in acceptable yields (entries 2q and 2r). Unfortunately, benzyl thiol, 1-pentane thiol and heterocyclic congener of thiol (2mercapto benzimidazole) did not respond under the optimal reaction conditions (entries 2s, 2t and 2u). Especially, upscale synthesis of 2a was also achieved, illuminating potential capabilities to assemble specialized 3-ArS substituted 4H-pyrido-[1,2-a]pyrimidin-4-ones. It was remarkable that PhSSPh was also amenable instead of PhSH with this catalytic system.



Table 3 Scope of different substituted 4H-pyrido[1,2-a]pyrimidin-4-ones and diselenides derivatives for I₂ mediated selenylation^{*a*}

^{*a*} Reaction condition: substituted 4*H*-pyrido[1,2-*a*]pyrimidin-4-ones (0.125 mmol, 1 equiv.), thiol (0.1875 mmol, 1.5 equiv.), I_2 (50 mol%), MeCN (2 ml), $K_2S_2O_8$ (2 equiv.). ^{*b*} Isolated yields based on the reactants **1**, the reaction was run for 12 h. ^{*c*} Yield at 1 g scale. ^{*d*} PhSSPh was used instead of PhSH. ^{*e*} 1 equiv. of I_2 was used.

^{*a*} Reaction condition: various 4*H*-pyrido[1,2-*a*]pyrimidin-4-ones (0.125 mmol, 1 equiv.), organo diselenides (0.1875 mmol, 1.5 equiv.), I₂ (50 mol%), MeCN (2 ml), K₂S₂O₈ (2 equiv.). ^{*b*} Isolated yields based on the reactants 1, the reaction was run for 12 h. ^{*c*} 1 equiv. of I₂ was used.





To comprehend the plausible reaction mechanism, we executed the sulfenylation reaction under inert atmosphere (N_2) and isolated 76% yield of the desired product 2a (Scheme 2; eqn (1)). This observation revealed that aerial oxygen was not only the sole oxidant for this transformation. Additionally, the reaction of 2-phenyl-4*H*-pyrido[1,2-*a*]pyrimidin-4-one and iodine in presence potassium persulfate did not afford the corresponding iodo derivative (Scheme 2; eqn (2)). The result unambiguously confirmed that iodinated derivative of 4*H*-pyrido[1,2-*a*]pyrimidin-4-one was not involved in the catalytic cycle. Furthermore, the presence of stoichiometric amount of radical scavengers (TEMPO, BHT and 1,1-diphenyl ethylene) inhibited





the reactivity, refuting the involvement of non-radical pathway in the reaction mechanism (Scheme 2; eqn (3) and (4)). In addition, we have trapped the *in situ* generated radical intermediate (PhSe[•]) and isolated the compound **4** in reasonable yield (Scheme 2; eqn (4)).

On the basis of these findings and previous literature reports,²⁴ a plausible mechanistic pathway is elaborated in Scheme 3. Presumably, this sulfenylation/selenylation strategy involve an initial generation of the thiyl radical or selenyl radical species **A** ('SY/'SeY, Y = R) in presence of persulfate $(S_2O_8^{2-})$ or sulfate radical anion $(SO_4^{\cdot-})$. Subsequently, the reactive sulphur/selenyl radical intermediates **A** coupled with 2-phenyl-4*H*-pyrido[1,2-*a*]pyrimidin-4-one substrate leading to a formation of next intermediate **1ab**. Then, it underwent further oxidation by sulfate radical anion *via* a SET mechanism to generate a cationic intermediate **1ac** which could be stabilized by resonance to **1ac'**. Lastly, the final coupled product (**2a/3a**) was formed with the liberation of H₂ species.

In summary, we have developed an efficient and straightforward transformative tool for regioselective chalcogenation of 4Hpyrido[1,2-*a*]pyrimidin-4-one under mild conditions. The protocol tolerated diverse common organic functional groups and resulted in good to excellent yields of the desired sulfenylated/selenylated products. Our methodology is operationally simple, regioselective, scalable and avoid the use any expensive metal catalyst. This present protocol opens a new avenue for the direct and convenient chalcogenation of 4H-pyrido[1,2-*a*]pyrimidin-4-one. Further, C–H bond functionalization reactions on 4H-pyrido[1,2-*a*]pyrimidin-4-one are currently underway in our laboratory and these observations will be forthcoming.

Conflicts of interest

There are no conflicts to declare.

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