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Visible Light-Induced Thiocyanation of Enaminone C-H Bond to Access Polyfunctionalized Alkenes and Thiocyano Chromones

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ABSTRACT: The visible light induced C-H bond thiocyanation on the α-site of tertiary enaminones has been realized under metal-free, photocatalytic conditions in the presence of Rose Bengal, which enables the synthesis of thiocyanated alkene derivatives and chromones using NH_4SCN as the thiocyano source under an aerobic atmosphere. In addition, employing $Ru(bpy)_3Cl_2·6H_2O$ as photocatalyst switches the reaction pathway to provide NH_2-functionalized thiocyanated enamines via the difunctionalization process consisting of C-H bond thiocyanation and vinyl C-N bond transamination.

INTRODUCTION

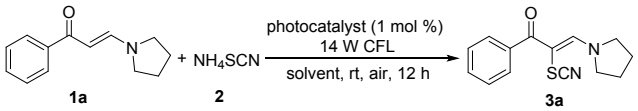
Organic thiocyanates are moieties possessing enriched biological and pharmaceutical activities in both synthesized and naturally occurring molecules.[1] Moreover, the enriched reactivity of the thiocyano group also endows organic thiocyanates with widespread application as building blocks in organic synthesis.[2] Although different strategies on organic thiocyanate synthesis have been known with efficiency,[3] the thiocyanation reaction employing low cost reagents such as $Fe(SCN)_3$, KSCN, NH_4SCN, TMSCNS, *etc* as the thiocyano sources constitutes one major option for the atom economical C-S bond formation.[4] Inarguably, the direct thiocyanation of the stable C-H bond is among the most favorable route because such method allows the synthesis of organic thiocyanates using those prevalently available C-H bond donors. During the past decade, a plethora of catalytic methods have been successfully developed for the direct thiocyanation of both stable C(sp^2)-H[5] and C(sp^3)-H[6] bonds, which provides rapid access to divergent thiocyanated molecules. Despite these notable advances, most of the successful examples on the C(sp^2)-H bond thiocyanation takes place on aromatic system. On the other hand, much less transformations of such type on the equally pivotal alkenyl C(sp^2)-H bond are known. In this regard, devising catalytic methods enabling alkene C(sp^2)-H bond thiocyanation is highly urgent for the sake of providing facile methods synthesizing structurally diverse alkenyl thiocyanates.

Enaminones are a class of functionalized alkenes derivative featured with easy access, ideal stability and highly versatile reactivity.[7]Among the various reported reaction pathways in enaminones, the direct cross coupling of the alkenyl C-H bond has in recent years gained extensive attention. For example, the intramolecular C-H arylation of enaminones is a reliable method for indole synthesis under different catalytic conditions.[8] In addition, the intermolecular arylations on the enaminone C-H bond have been also realized via noble metal catalysis.[9] Noteworthy, the functionalization on the same C-H bond under transition metal-free has been recently found to be applicable in forging new C-heteroatom bonds. Specifically, the enaminone C-H acyloxyation and oxygenation,[10] amination,[11] sulfenylation/aryl selenylation and annulative alkyl thiolation,[12] sulfonylation,[13] as well as the elemental sulfur-based double C-H thiolation[14] have been consequently reported. Amazingly, as a valuable functional structure, the SCN group has not yet been successfully installed to enaminones. Based on our longstanding interest in enaminone-based organic synthesis, we report herein the first transition metal-free synthesis of α-thiocyano enaminones through visible light induced thiocyanation of the enaminone C-H bond, wherein Rose Bengal (RB) is employed as a low cost and nonmetal photocatalyst.[15]

RESULTS AND DISCUSSION

We started the investigation on the reaction of enaminone **1a** with ammonium thiocyanate **2**. At first, several non-metal photocatalysts, including Eosin Y, Eosin B and RB were tentatively employed with the visible light irradiation of 14W compact fluorescent lamp (CFL). We observed that RB could catalyze the C-H thiocyanation of **1a** to provide product **3a** with excellent yield in only 1% loading (entries 1-3, Table 1). Control experiments revealed that the photocatalyst and visible light irradiation were both mandatory (Table 1, entry 4-5). Later on, a series of organic solvents with different polarities, such as dioxane, acetone, MeCN and DMF were utilized as the reaction medium, respectively (entries 6-9, Table 1), and THF was found as the most favorable medium. At last, the decrease on the loading of ammonium thiocyanate **2** was not favored, as lower yield of **3a** was provided (entry 10, Table 1).

Table 1 Optimization on the reaction condition[a]



1a **2** **3a**

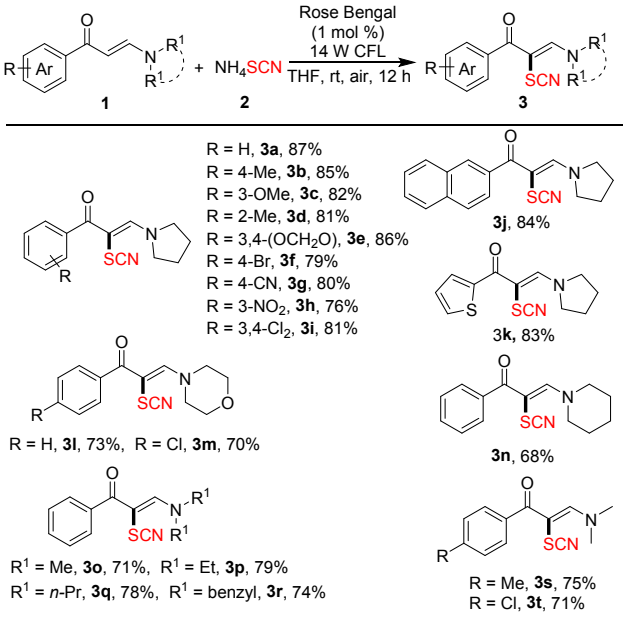
entry	catalyst	solvent	yield (%)[b]
1	Eosin Y	THF	21
2	Eosin B	THF	17
3	Rose Bengal	THF	87
4	-	THF	trace
5[c]	Rose Bengal	THF	0

6	Rose Bengal	dioxane	52
7	Rose Bengal	acetone	37
8	Rose Bengal	MeCN	45
9	Rose Bengal	DMF	0
10[d]	Rose Bengal	THF	74

[a]General Conditions: **1a** (0.2 mmol), **2** (0.4 mmol), catalyst (1 mol %), and 2 mL solvent, stirred for 12 h at rt under air with 14 W CFL irradiation. [b]Yield of isolated product based on **1a**. [c]Reaction in dark atmosphere. [d]Reaction with 1.1 equiv of **2**.

Later, the generality of this photocatalytic thiocyanation reaction was investigated, and the results are summarized in Scheme 1. It was observed that this reaction tolerated a broad array of functional groups of different features in the phenyl ring of **1**. The enaminone substrates containing electron donating and electron withdrawing groups participated in the synthesis of corresponding products **3** with good to excellent yields (**3a-3i**, Scheme 1). The reactions employing enaminone **1a** indicated that the electron withdrawing effect in the phenyl ring was negative to the reaction by affording thiocyanated products with slightly lower yield (**3f-3i**, Scheme 1). On the other hand, the reactions employing morpholine (**3l** and **3m**, Scheme 1) piperidine (**3n**, Scheme 1) and acylic alkyl (**3o-3t**, Scheme 1) functionalized enaminones were found to give related products with lower yield than those using **1a**. Besides the reactions employing phenyl-based aryl enaminones, a notable point was that the naphthyl and heteroaryl functionalized enaminones also smoothly reacted with NH_4SCN to provide products **3j** and **3k** with excellent yields. However, NH or NH_2 functionalized enaminones were not able to undergo this transformation under the present conditions. In addition, the (E)-4-(dimethylamino)but-3-en-2-one, an alkyl-based enaminone was not thiocyanated with the present catalytic method.

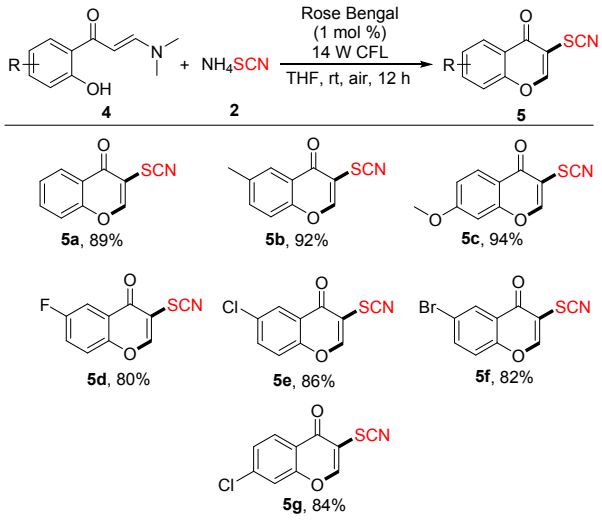
Scheme 1 Scope of the thiocyanation reaction of tertiary enaminones[a,b]



[a]General Conditions: enominone **1** (0.2 mmol), NH_4SCN **2** (0.4 mmol), RB (0.002 mmol) in THF (2 mL), stirred with 14 W CFL irradiation at room temperature for 12h. [b]Yield of isolated product based on **1**.

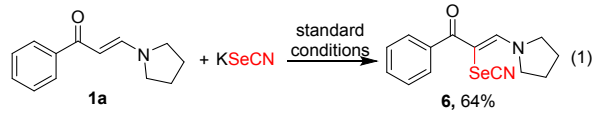
Inspired by the satisfactory results acquired from the direct C-H thiocyanation of tertiary enaminones **1**, we assumed that this transformation could be employed in designing cascade reaction to synthesis thiocyanated molecules of higher structural divergence. Consequently, the *N,N*-dimethyl enaminones **4** with o-hydroxylphenyl substructure were selected to react with **2**, expecting that the 3-thiocyanated chromones of type **5** would be synthesized by combing this newly developed C-H thiocyanation and the chromone annulation featured with enaminones **4**. To our delight, under the standard conditions of visible light irradiation, the thiocyanated chromones **5** were afforded with generally excellent yield regardless the electronic property of the substituent in the phenyl ring of **4** (**5a-5g**, Scheme 2). In addition, when (*E*)-1-(2-hydroxyphenyl)-3-morpholinoprop-2-en-1-one, an enaminone with different *N,N*-disubstitution was employed with NH_4SCN under the catalytic conditions, the product **5a** was provided with 80% yield.

Scheme 2 Synthesis of thiocyano chromones by C-H thiocyanation[a,b]



[a]General Conditions: enaminone **4** (0.2 mmol), NH_4SCN **2** (0.4 mmol), Rose Bengal (0.002 mmol) in THF (2 mL), stirred with 14 W CFL irradiation at room temperature for 12 h. [b]Yield of isolated product based on **4**.

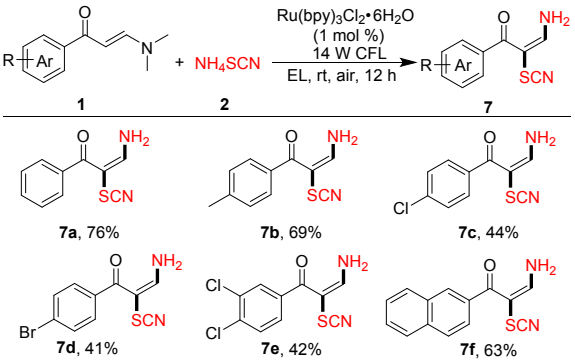
Interestingly, the analogous C-H selenocyanation on enaminone **1a** was found also highly practical by utilizing the commercially available KSeCN as coupling reagent under the standard reaction conditions (Eq 1). Another entry employing enaminone **1s**, however, did not provide the expected selenocyanated product.



During further investigation on the reaction, we also noticed an interesting difunctionalization reaction forming thiocyano and NH_2-functionalized alkenes **7** by using $Ru(bpy)_3Cl_2{\cdot}6H_2O$ as the photoredox catalyst (See Scheme 3).[16] Therefore, brief optimization on the reaction employing different media was conducted on the reaction providing **7a**. While the entries employing MeCN, dioxane and DMF did not provide this product, the entry employing ethyl lactate (EL) gave **7a** with 76% yield in the presence of 1 mol% $Ru(bpy)_3Cl_2{\cdot}6H_2O$, while the same reaction in MeCN, DMF, EtOH or dioxane did not take place.

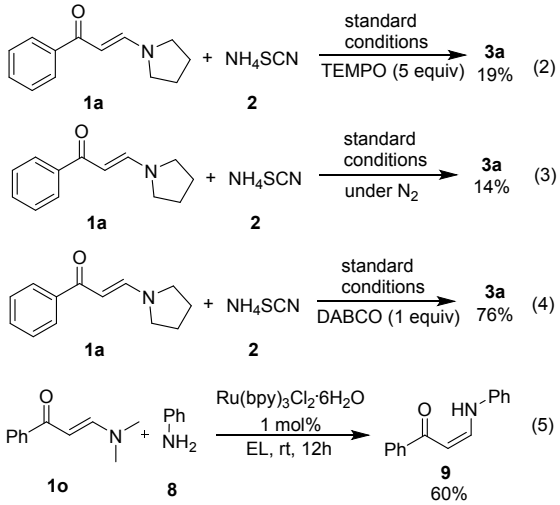
Thus, the scope on this enaminone difunctionalization involving the C-H bond thiocyanation and the C-N bond amination was examined. As outlined in Scheme 3, the polyfunctionalized alkenes **7** were practically synthesized with moderate to good yield under the irradiation of visible light in the presence of $Ru(bpy)_3Cl_2·6H_2O$. The selectivity in providing only *Z*-alkene derivatives could be attributed to the stabilization effect resulting from the presence of intramolecular hydrogen bond in **7**. The good results using the bio-mass feedstock EL as reaction medium constituted additional advantage of this synthetic method.

Scheme 3 Photocatalytic difunctionalization of enaminones[a,b]



[a]General conditions: enominone **1** (0.2 mmol), NH_4SCN (0.4 mmol), $Ru(bpy)_3Cl_2·6H_2O$ (0.002 mmol) in 2 mL EL, stirred with 14 W CFL irradiation at room temperature for 12h. [b]Yield of isolated product based on **1** was reported.

To gain possible information on the reaction process, several control entries on the model reaction were executed. First, the inhibition of TEMPO to the reaction supported that the reaction took place via a free radical process (Eq 2). In addition, the very low yield of product **3a** in the reaction under N_2 confirmed the indispensable role of molecular oxygen (Eq 3). Finally, the yield of **3a** was not evidently undermined in the reaction conducted in the presence of DABCO, indicating against the involvement of singlet oxygen (Eq 4).[17]



To further explore the interaction of RB with substrates, the fluorescence quenching experiments of of RB with enaminone **1a** and NH_4SCN **2** were investigated, respectively. The results indicated that NH_4SCN evidently quenching the fluorescence emission of excited RB because the regularly diminished fluorescence emission intensity occurred following the increased concentration of NH_4SCN (Fig. 1). This tendency was also visual in the corresponding Stern-Volmer plots (Fig. 2). On the contrary, such quenching effect was not observed in corresponding experiments using enaminone **1o** (R = H, R^1 = Me, see SI).

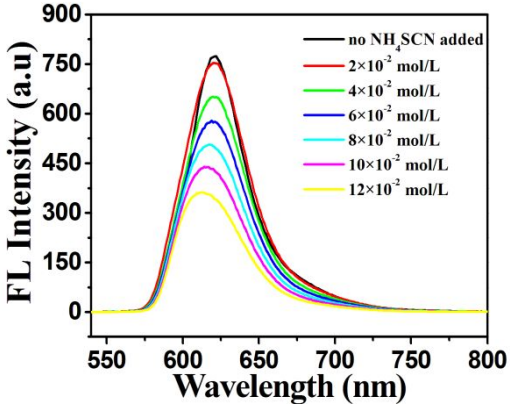


Figure 1 Quenching of RB fluorescence emission with NH_4SCN

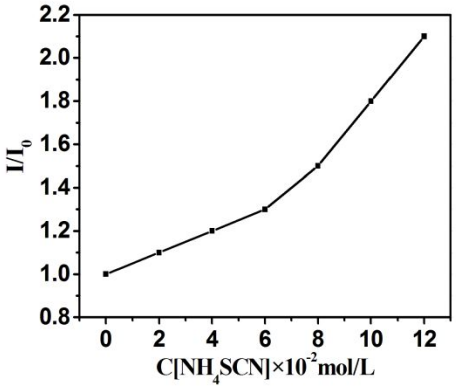
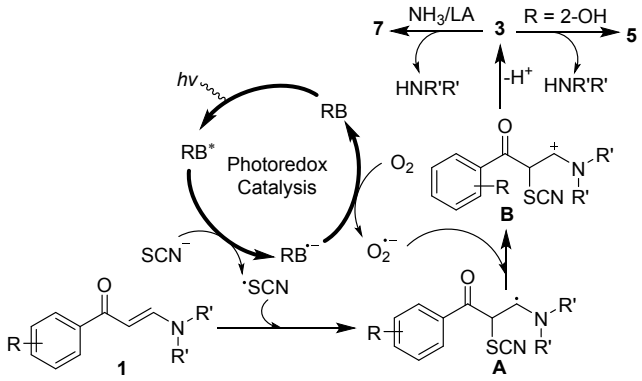


Figure 2 Stern-Volmer plot. I_0 is the inherent fluorescence intensity of RB. *I* Is the fluorescence intensity of RB in the presence of NH_4SCN.

According to the product structures as well as the results obtained from control experiments, the mechanism for the C-H thiocyanation reaction was proposed. As shown in Scheme 4, the reactions may start from the quenching of NH_4SCN to the excited RB* species generated from the visible light irradiation to RB catalyst, which gives rise to ˙SCN free radical.[5j] The simultaneously formed $RB^{\bullet-}$ can be regenerated to RB by the oxidation of molecular oxidation. Subsequently, the addition of the ˙SCN to the C=C double bond in **1** gives rise to free radical intermediate **A**. The site selectivity of the addition transformation is determined by the better stability of free radical **A** with the adjacent electron donating amino group. By means of oxidation from the superoxide radical ion—generated during the RB regeneration, free radical **A** is transformed into the carbon cation intermediate **B**. The deprotonation on **B** then yields thiocyanated product **3**. When *o*-hydroxylphenyl functionalized enaminones are used as substrates, the featured intramolecular annulation successively takes place to give thiocyanated chromones **5**. In addition, when Ru-catalyst is employed, a transamination between the tertiary enaminones and the ammonium is promoted to form products **7**, wherein the Ru-catalyst may act also as Lewis acid (LA) catalyst. In fact, although the transamination of ammonium with tertiary enaminone was hard, we carried out the typical

Lewis acid-catalyzed transamination between tertiary enaminone and aniline[18] in the presence of the $Ru(bpy)_3Cl_2{\cdot}6H_2O$ without CFL irradiation, which provided the expected *NH*-enaminone with good yield (Eq 5), supporting the function of this catalyst as Lewis acid.

Scheme 4 The postulated reaction mechanism



CONCLUSION

In conclusion, we have realized herein the first vinyl C-H bond thiocyanation reaction of tertiary enaminones by metal-free photocatalysis. Besides providing a simple and efficient approach toward the synthesis of thiocyanated alkene derivatives, the switchable synthesis of even more divergent organic thiocyanates, including thiocyanated chromones and the polyfunctionalized alkenes containing primary amino and thiocyano groups has been achieved by simply modifying the substrate structure or the photocatalyst species.

EXPERIMENTAL SECTION

General experimental information. All experiments were carried out under air atmosphere with the irradiation of 14W CFL lamp (OSRAM Ltd., MUN-DULCOM20WSIN01BK, Bulb shape- Standard). The enaminones **1** and **4** were synthesized following literature procedure in 2 mmol scale.[18b,19] Known compounds synthesized by the literature methods have been confirmed by comparing reported characterization data. Characterization data for those newly synthesized substrates by these methods were shown below (see SI for their chemical structures). Other chemicals and solvents used in our experiments were obtained from commercial sources and used directly without further treatment. The ^1H and ^{13}C NMR spectra were recorded in 400 MHz apparatus in $CDCl_3$. The frequencies for ^1H NMR and ^{13}C NMR test were 400 MHz and 100 MHz, respectively. The chemical shifts were reported in ppm with TMS as internal standard. Melting points were tested in X-4A instrument without correcting the temperature. The HRMS data for all new products were obtained under ESI model in a mass spectrometer equipped with TOF analyzer.

(*E*)-3-(Pyrrolidin-1-yl)-1-(*p*-tolyl)prop-2-en-1-one (**1b**).[20] Yield 71%, 305 mg; ^1H NMR (400 MHz, $CDCl_3$): δ 8.07-7.96 (m, 1 H), 7.81 (d, *J* = 7.8 Hz, 2 H), 7.21 (d, *J* = 7.8 Hz, 2 H), 5.68 (d, *J* = 12.2 Hz, 1 H), 3.27 (brs, 4 H), 2.38 (s, 3 H), 2.06-1.88 (m, 4 H).

(*E*)-1-(3-Methoxyphenyl)-3-(pyrrolidin-1-yl)prop-2-en-1-one (**1c**). Yield 67%, 309 mg; mp 82-83 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.12-7.98 (m, 1 H), 7.47 (d, *J* = 7.0 Hz, 2 H), 7.55-7.42 (m, 2 H), 7.08-6.93 (m, 1 H), 5.67 (d, *J* = 12.0 Hz, 1 H), 3.87 (s, 3 H), 3.29 (brs, 4 H), 2.12-1.88 (m, 4H); $13C\{^1H\}$ NMR (100 MHz, CDCl3): δ 188.1, 159.6, 150.1, 142.2, 129.0, 120.0, 117.1, 112.3, 93.2, 55.4, 52.4, 47.0, 25.2; HRMS Calcd for $C_{14}H_{18}NO_2^+$ $[M + H]^+$ 232.1332, found 232.1333.

(*E*)-3-(Pyrrolidin-1-yl)-1-(*o*-tolyl)prop-2-en-1-one (**1d**). Yield 57%, 245 mg; yellow liquid; ^1H NMR (400 MHz, $CDCl_3$): δ 7.50-6.99 (m, 5 H), 5.32 (d, *J* = 12.0 Hz, 1 H), 3.22 (brs, 4 H), 2.41 (s, 3 H), 2.06-1.88 (m, 4 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 194.1, 150.9, 142.1, 135.3, 130.6, 128.5, 127.1, 125.2, 99.0, 52.3, 46.9, 25.2, 25.1, 19.8; HRMS Calcd for $C_{14}H_{18}NO^+$ $[M + H]^+$ 216.1383, found 216.1384.

(*E*)-1-(Benzo[d][1,3]dioxol-5-yl)-3-(pyrrolidin-1-yl)prop-2-en-1-one (**1e**). Yield 53%, 260 mg; mp 144-145 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.03-7.93 (m, 1 H), 7.54-7.41 (m, 2 H), 6.88-6.74 (m, 1 H), 6.00 (s, 2 H), 5.61 (d, *J* = 12.0 Hz, 1 H), 3.26 (brs, 4 H), 2.08-1.89 (m, 4 H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 186.7, 149.6, 147.6, 135.2, 122.5, 107.9, 107.6, 101.4, 92.5, 52.3, 47.0, 25.2; HRMS Calcd for $C_{14}H_{16}NO_3^+$ $[M + H]^+$ 246.1125, found 246.1121.

(*E*)-1-(4-Bromophenyl)-3-(pyrrolidin-1-yl)prop-2-en-1-one (**1f**). Yield 64%, 357 mg; mp 122-123 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.08-7.97 (m, 1 H), 7.78 (d, *J* = 8.2 Hz, 2 H), 7.54 (d, *J* = 8.4 Hz, 2 H), 5.62 (d, *J* = 12.0 Hz, 1 H), 3.28 (brs, 4 H), 2.08-1.90 (m, 4 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ187.0, 150.3, 139.4, 131.3, 129.2, 125.3, 92.5, 52.5, 47.1, 25.2; HRMS Cald for $C_{13}H_{15}BrNO^+$ $[M + H]^+$ 280.0332, found 280.0335.

(*E*)-4-(3-(Pyrrolidin-1-yl)acryloyl)benzonitrile (**1g**). Yield 61%, 276 mg; mp 128-129 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.08-7.88 (m, 3 H), 7.67 (d, *J* = 7.8 Hz, 2 H), 5.59 (d, *J* = 11.6 Hz, 1 H), 3.27 (brs, 4 H), 2.10-1.90 (m, 4 H).$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 186.1, 150.8, 144.4, 132.0, 128.0, 118.7, 113.8, 92.6, 52.6, 47.2, 25.2, 25.1; HRMS Cald for $C_{14}H_{15}N_2O^+$ $[M + H]^+$ 227.1179, found 227.1178.

(*E*)-1-(3-Nitrophenyl)-3-(pyrrolidin-1-yl)prop-2-en-1-one (**1h**). Yield 70%, 344 mg; mp 95-96 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.70 (s, 1 H), 8.34-8.23 (m, 2 H), 8.14-8.05 (m, 1 H), 7.60 (t, *J* = 7.8 Hz, 1H), 5.68 (d, *J* = 12.0 Hz, 1 H), 3.35 (brs, 4 H), 2.12-1.96 (m, 4H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 185.1, 150.9, 148.1, 142.1, 133.4, 129.2, 125.2, 122.3, 92.1, 52.7, 47.3, 25.2, 25.2; HRMS Cald for $C_{13}H_{15}N_2O_3^+$ $[M + H]^+$ 247.1077, found 247.1079.

(*E*)-1-(3,4-Dichlorophenyl)-3-(pyrrolidin-1-yl)prop-2-en-1-one (**1i**). Yield 63%, 339 mg; mp 85-86 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.12-7.88 (m, 2 H), 7.79-7.67 (m, 1 H), 7.53-7.41 (m, 1 H), 5.59 (d, *J* = 12.0 Hz, 1 H), 3.30 (brs, 4 H), 2.11-1.92 (m, 4 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 185.3, 150.6, 140.4, 134.8, 132.4, 130.1, 129.5, 126.7, 92.2, 52.6, 47.2, 25.2, 25.2; HRMS Cald for $C_{13}H_{14}Cl_2NO^+$ $[M + H]^+$ 270.0447, found 270.0449.

(*E*)-1-(Naphthalen-2-yl)-3-(pyrrolidin-1-yl)prop-2-en-1-one (**1j**). Yield 72%, 361 mg; mp 106-107 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.42 (s, 1 H), 8.15-7.82 (m, 5 H), 7.61-7.43 (m, 2 H), 5.85 (d, *J* = 12.0 Hz, 1 H), 3.33 (brs, 4 H), 2.10-1.87 (m, 4 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 188.2, 150.0, 137.9, 134.7, 132.8, 129.2, 127.8, 127.7, 127.6, 127.1, 126.2, 124.7, 93.2, 52.4, 47.1, 25.2; HRMS Cald for $C_{17}H_{18}NO^+$ $[M + H]^+$ 252.1383, found 252.1382.

(*E*)-3-(Pyrrolidin-1-yl)-1-(thiophen-2-yl)prop-2-en-1-one (**1k**). Yield 59%, 244 mg; mp 114-115 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, *J* = 12.0 Hz, 1 H), 7.68-7.44 (m, 2 H), 7.14-7.02 (m, 1 H), 5.60 (d, *J* = 12.0 Hz, 1 H), 3.28 (brs, 4 H), 2.08-1.90 (m, 4 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 180.6, 149.3,

147.6, 130.1, 128.3, 127.5, 92.5, 52.4, 47.0, 25.2; HRMS Cald for $C_{11}H_{14}NOS^+$ $[M + H]^+$ 208.0791, found 208.0790.

(*E*)-1-Phenyl-3-(piperidin-1-yl)prop-2-en-1-one (**1n**).[10b] Yield 70%, 299 mg; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94-7.76 (m, 3 H), 7.42 (d, *J* = 7.0 Hz, 3 H), 5.84 (d, *J* = 11.0 Hz, 1 H), 3.37 (s, 4 H), 1.67 (s, 6 H).

(*E*)-3-(Dimethylamino)-1-phenylprop-2-en-1-one (**1s**).[21] Yield 62%, 218 mg; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, *J* = 8.0 Hz, 2 H), 7.86-7.76 (m, 1 H), 7.43 (d, *J* = 8.0 Hz, 3 H), 5.73 (d, *J* = 13.2 Hz, 1 H), 3.14 (s, 3 H), 2.93 (s, 3 H).

(*E*)-3-(Dimethylamino)-1-(*p*-tolyl)prop-2-en-1-one (**1t**).[21] Yield 52%, 196 mg; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93–7.75 (m, 3 H), 7.22 (d, *J* = 8.0 Hz, 2 H), 5.73 (d, *J* = 12.0 Hz, 1 H), 3.12 (s, 3 H), 2.93 (s, 3 H), 2.40 (s, 3 H).

(*E*)-1-(4-chlorophenyl)-3-(dimethylamino)prop-2-en-1-one (**1u**).[21] Yield 65%, 272 mg; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99–7.71 (m, 3 H), 7.38 (d, *J* = 8.4 Hz, 2 H), 5.67 (d, *J* = 12.8 Hz, 1 H), 3.16 (s, 3 H), 2.93 (s, 3 H).

(*E*)-1-(4-Bromophenyl)-3-(dimethylamino)prop-2-en-1-one (**1v**).[10b] Yield 65%, 329 mg; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89-7.72 (m, 3 H), 7.55 (d, *J* = 7.4 Hz, 2 H), 5.67 (d, *J* = 12.0 Hz, 1 H), 3.17 (s, 3 H), 2.94 (s, 3 H).

(*E*)-1-(3,4-Dichlorophenyl)-3-(dimethylamino)prop-2-en-1-one (**1w**). Yield 73%, 354 mg; mp 92-93 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (s, 1 H), 7.88-7.80 (m, 1 H), 7.74 (d, *J* = 8.0 Hz, 1 H), 7.49 (d, *J* = 8.4 Hz, 1 H), 5.63 (d, *J* = 12.8 Hz, 1 H), 3.19 (s, 3 H), 2.96 (s, 3 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 185.6, 154.9, 140.3, 134.9, 132.4, 130.1, 129.5, 126.7, 91.3, 45.2, 37.4; HRMS Calcd for $C_{11}H_{12}Cl_2NO^+$ $[M + H]^+$ 244.0290, found 244.0293.

(*E*)-3-(dimethylamino)-1-(naphthalen-2-yl)prop-2-en-1-one (**1x**).[21] Yield 61%, 274 mg; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.42 (s, 1 H), 8.08–7.81 (m, 5 H), 7.53 (s, 2 H), 5.89 (d, *J* = 12.4 Hz, 1 H), 3.14 (s, 3 H), 2.97 (s, 3 H).

(*E*)-3-(Dimethylamino)-1-(2-hydroxyphenyl)prop-2-en-1-one (**4a**).[22] Yield 75%, 286 mg; ^{1}H NMR (400 MHz, $CDCl_3$): δ 13.98 (s, 1H), 7.95-7.84 (m, 1 H), 7.71 (d, *J* = 8.0 Hz, 1 H), 7.45–7.32 (m, 1 H), 6.95 (d, *J* = 8.0 Hz, 1 H), 6.87–6.79 (m, 1 H), 5.79 (d, *J* = 12.0 Hz, 1 H), 3.20 (s, 3 H), 2.98 (s, 3 H).

(*E*)-3-(Dimethylamino)-1-(2-hydroxy-5-methylphenyl)prop-2-en-1-one (**4b**).[22] Yield 69%, 282 mg; ^{1}H NMR (400 MHz, $CDCl_3$): δ 13.77 (s, 1 H), 7.96-7.79 (m, 1 H), 7.49 (s, 1 H), 7.18 (d, *J* = 7.2 Hz, 1 H), 6.85 (d, *J* = 8.4 Hz, 1 H), 5.78 (d, *J* = 12.0 Hz, 1 H), 3.19 (s, 3 H), 2.99 (s, 3 H), 2.31 (s, 3 H).

(*E*)-3-(Dimethylamino)-1-(2-hydroxy-4-methoxyphenyl) prop-2-en-1-one (**4c**).[22] Yield 63%, 278 mg; ^{1}H NMR (400 MHz, $CDCl_3$): δ 14.50 (s, 1 H), 7.99-7.71 (m, 1 H), 7.62 (d, *J* = 8.8 Hz, 1 H), 6.55-6.23 (m, 2 H), 5.69 (d, *J* = 12.8 Hz, 1 H), 3.82 (s, 3 H), 3.17 (s, 3 H), 2.95 (s, 3 H).

(*E*)-3-(Dimethylamino)-1-(5-fluoro-2-hydroxyphenyl)prop-2-en-1-one (**4d**).[22] Yield 60%, 251 mg; ^{1}H NMR (400 MHz,$CDCl_3$): δ 13.70 (s, 1 H), 8.07–7.77 (m, 1 H), 7.37 (s, 1 H), 7.09 (s, 1 H), 6.90 (s, 1 H), 5.67 (d, *J* = 12.0 Hz, 1 H), 3.22 (s, 3 H), 2.99 (s, 3 H).

(*E*)-1-(5-Chloro-2-hydroxyphenyl)-3-(dimethylamino)prop-2-en-1-one (**4e**).[22] Yield 63%, 283 mg; ^{1}H NMR (400 MHz, $CDCl_3$): δ 13.94 (s, 1H), 7.98–7.83 (m, 1 H), 7.64 (s, 1 H), 7.30 (d, *J* = 7.6 Hz, 1 H), 6.89 (d, *J* = 8.8 Hz, 1 H), 5.69 (d, *J* = 12.0 Hz, 1 H), 3.22 (s, 1 H), 3.00 (s, 1 H).

(*E*)-1-(5-Bromo-2-hydroxyphenyl)-3-(dimethylamino)prop-2-en-1-one (**4f**).[22] Yield 64%, 344 mg; ^{1}H NMR (400 MHz, $CDCl_3$): δ 13.97 (s, 1 H), 7.97–7.85 (m, 1 H), 7.78 (s, 1 H), 7.43 (d, *J* = 8.4 Hz, 1 H), 6.85 (d, *J* = 8.4 Hz, 1 H), 5.68 (d, *J* = 13.6 Hz, 1 H), 3.22 (s, 3 H), 3.01 (s, 3 H).

(*E*)-1-(4-Chloro-2-hydroxyphenyl)-3-(dimethylamino)prop-2-en-1-one (**4g**).[23] Yield 58%, 260 mg; ^{1}H NMR (400 MHz, $CDCl_3$): δ 14.30 (s, 1 H), 7.95–7.82 (m, 1 H), 7.61 (d, *J* = 8.8 Hz, 1 H), 6.94 (s, 1 H), 6.79 (d, *J* = 7.2 Hz, 1 H), 5.69 (d, *J* = 12.0 Hz, 1 H), 3.20 (s, 3 H), 2.98 (s, 3 H).

General procedure for the synthesis of products 3 and 6. To a 25 mL round-bottom flask were added enaminone **1** (0.2 mmol), NH_4SCN or KSeCN (0.4 mmol), RB (0.002 mmol) and THF (2 mL). The mixture was then stirred at room temperature for 12h with the irradiation of 14 W CFL (distance bulb−vessel approximately 5 cm) under air atmosphere (TLC). Upon on completion, 5 mL water was added to the flask, and the resulting mixture was extracted with ethyl acetate (3 × 8 mL). The organic phases were collected and dried with anhydrous Na_2SO_4. After filtration, the resulting solution was employed under reduced pressure to remove the solvent. The acquired residue was subjected to flash silica gel column chromatography to provide pure products by the elution with mixed petroleum ether/ethyl acetate (v/v = 3 : 1).

(*Z*)-1-Phenyl-3-(pyrrolidin-1-yl)-2-thiocyanatoprop-2-en-1-one (**3a**). Yield 87%, 45.0 mg; R_f = 0.2; yellow solid; mp 90-91 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (s, 1 H), 7.48-7.41 (m, 5 H), 4.09 (brs, 2 H), 3.57 (brs, 2 H), 2.08-1.94 (m, 4 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 192.5, 155.3, 140.0, 130.3, 128.3, 128.0, 113.7, 87.8, 56.3, 49.5, 26.2, 24.0; ESI-HRMS Calcd for $C_{14}H_{14}N_2NaOS$ $[M + Na]^+$ 281.0719, found 281.0731.

(*Z*)-3-(Pyrrolidin-1-yl)-2-thiocyanato-1-(*p*-tolyl)prop-2-en-1-one (**3b**). Yield 85%, 46.2 mg; R_f = 0.3; yellow solid; mp 118-119 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (s, 1 H), 7.42 (d, *J* = 7.5 Hz, 2 H), 7.22 (d, *J* = 7.7 Hz, 2 H), 4.10 (brs, 2 H), 3.59 (brs, 2 H), 2.40 (s, 3 H), 2.00 (brs, 4 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 192.4, 155.1, 140.7, 137.0, 128.9, 128.3, 113.9, 87.7, 56.3, 49.4, 26.1, 23.9, 21.5; ESI-HRMS Calcd for $C_{15}H_{16}N_2NaOS$ $[M + Na]^+$ 295.0876, found 295.0866.

(*Z*)-1-(3-Methoxyphenyl)-3-(pyrrolidin-1-yl)-2-thiocyanatoprop-2-en-1-one (**3c**). Yield 82%, 47.1 mg; R_f = 0.2; yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (s, 1 H), 7.26-7.20 (m, 1 H), 6.97-6.91 (m, 3 H), 4.03 (brs, 2 H), 3.77 (s, 3 H), 3.52 (brs, 2 H), 2.02-1.88 (m, 4 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 192.4, 159.5, 155.3, 141.3, 129.3, 120.3, 116.5, 113.8, 113.0, 87.7, 56.3, 55.4, 49.8, 26.2, 24.2; ESI-HRMS Calcd for $C_{15}H_{16}N_2NaO_2S$ $[M + Na]^+$ 311.0825, found 311.0836.

(*Z*)-3-(Pyrrolidin-1-yl)-2-thiocyanato-1-(*o*-tolyl)prop-2-en-1-one (**3d**). Yield 81%, 44.1 mg; R_f = 0.3; yellow solid; mp 105-106 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (s, 1 H), 7.28-7.10 (m, 4 H), 4.04 (brs, 2 H), 3.49 (brs, 2 H), 2.25 (s, 3 H), 2.05 (brs, 2 H), 1.87 (brs, 2 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 193.4, 154.9, 140.2, 134.9, 130.6, 128.9, 126.5, 125.5, 113.4, 89.0, 56.3, 49.5, 26.1, 23.9, 19.2; ESI-HRMS Calcd for $C_{15}H_{16}N_2NaOS$ $[M + Na]^+$ 295.0876, found 295.0882.

(*Z*)-1-(Benzo[d][1,3]dioxol-5-yl)-3-(pyrrolidin-1-yl)-2-thiocyanatoprop-2-en-1-one (**3e**). Yield 86%, 52.0 mg; R_f = 0.8; yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (s, 1 H), 7.06-7.03 (m, 2 H), 6.82 (d, *J* = 7.8 Hz, 1 H), 6.02 (s, 2 H), 4.06 (brs, 2 H), 3.65 (brs, 2 H), 2.02 (s, 4 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 191.2, 155.0, 149.7, 147.6, 133.7, 123.3, 113.8, 109.0, 107.8, 101.5, 87.4, 56.0, 49.7, 25.9, 24.4; ESI-HRMS Calcd for $C_{15}H_{14}N_2NaO_3S$ $[M + Na]^+$ 325.0617, found 325.0629.

(*Z*)-1-(4-Bromophenyl)-3-(pyrrolidin-1-yl)-2-thiocyanatoprop-2-en-1-one (**3f**). Yield 79%, 53.1 mg; R_f = 0.3; yellow solid; mp 118-119 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (s, 1 H), 7.54 (d, *J* = 8.3 Hz, 2 H), 7.37 (d, *J* = 8.3 Hz, 2 H), 4.08 (brs, 2 H), 3.60 (brs, 2 H), 2.09-1.94 (m, 4 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 191.3, 155.1, 138.8, 131.5, 129.7, 124.7, 113.6, 87.3, 56.4, 49.6, 26.2, 24.0; ESI-HRMS Calcd for $C_{14}H_{13}BrN_2NaOS$ $[M + Na]^+$ 358.9824, found 358.9810.

(*Z*)-4-(3-(Pyrrolidin-1-yl)-2-thiocyanatoacryloyl)benzonitrile (**3g**). Yield 80%, 45.3 mg; R_f = 0.1; yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (s, 1 H), 7.65 (d, *J* = 8.1 Hz, 2 H), 7.52 (d, *J* = 8.0 Hz, 2 H), 4.06 (brs, 2 H), 3.59 (brs, 2 H), 2.07-1.90 (m, 4 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 191.1, 155.0, 144.4, 132.2, 128.3, 118.2, 113.7, 113.3, 86.7, 56.6, 49.7, 26.2, 24.0; ESI-HRMS Calcd for $C_{15}H_{13}N_3NaOS$ $[M + Na]^+$ 306.0672, found 306.0672.

(*Z*)-1-(3-Nitrophenyl)-3-(pyrrolidin-1-yl)-2-thiocyanatoprop-2-en-1-one (**3h**). Yield 76%, 46.1 mg; R_f = 0.2; yellow solid; mp 125-126 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32-8.29 (m, 2 H), 7.93 (s, 1 H), 7.86 (d, *J* = 7.6 Hz, 1 H), 7.64 (t, *J* = 7.9 Hz, 1 H), 4.14 (brs, 2 H), 3.68 (brs, 2 H), 2.15-1.98 (m, 4 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 190.1, 155.1, 147.9, 141.6, 133.7, 129.6, 124.8, 122.6, 113.2, 86.5, 56.6, 49.8, 26.2, 24.0; ESI-HRMS Calcd for $C_{14}H_{13}N_3NaO_3S$ $[M + Na]^+$ 326.0570, found 326.0579.

(*Z*)-1-(3,4-Dichlorophenyl)-3-(pyrrolidin-1-yl)-2-thiocyanatoprop-2-en-1-one (**3i**). Yield 81%, 53.0 mg; R_f = 0.3; yellow solid; mp 111-112 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (s, 1 H), 7.58 (s, 1 H), 7.50 (d, *J* = 8.2 Hz, 1 H), 7.33 (d, *J* = 7.6 Hz, 1 H), 4.10 (brs, 2 H), 3.64 (brs, 2 H), 2.12-1.96 (m, 4 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 189.9, 155.2, 139.8, 134.5, 132.7, 130.4, 129.9, 127.2, 113.3, 87.1, 56.5, 49.8, 26.2, 24.0; ESI-HRMS Calcd for $C_{14}H_{12}Cl_2N_2NaOS$ $[M + Na]^+$ 348.9940, found 348.9947.

(*Z*)-1-(Naphthalen-2-yl)-3-(pyrrolidin-1-yl)-2-thiocyanatoprop-2-en-1-one (**3j**). Yield 84%, 51.7 mg; R_f = 0.3; yellow solid; mp 125-126 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (s, 1 H), 7.91-7.86 (m, 4 H), 7.62-7.52 (m, 3 H), 4.08 (brs, 2 H), 3.53 (brs, 2 H), 2.05-1.91 (m, 4 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 192.4, 155.3, 137.3, 134.1, 132.5, 128.7, 128.2, 128.1, 127.8, 127.3, 126.7, 125.3, 113.8, 87.9, 55.9, 49.5, 26.1, 23.9; ESI-HRMS Calcd for $C_{18}H_{16}N_2NaOS$ $[M + Na]^+$ 331.0876, found 331.0874.

(*Z*)-3-(Pyrrolidin-1-yl)-2-thiocyanato-1-(thiophen-2-yl)prop-2-en-1-one (**3k**). Yield 83%, 43.7 mg; R_f = 0.3; yellow solid; mp 123-124 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (s, 1 H), 7.68 (s, 1 H), 7.57-7.56 (m, 1 H), 7.10 (s, 1 H), 4.09 (brs, 2 H), 3.72 (brs, 2 H), 2.05 (brs, 4 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 182.6, 154.9, 143.1, 131.5, 131.3, 127.2, 113.7, 85.7, 56.3, 49.7, 26.1, 24.1; ESI-HRMS Calcd for $C_{12}H_{12}N_2NaOS_2$ $[M + Na]^+$ 287.0283, found 287.0275.

(*Z*)-3-Morpholino-1-phenyl-2-thiocyanatoprop-2-en-1-one (**3l**). Yield 73%, 40.0 mg; R_f = 0.4; yellow solid; mp 122-123 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (s, 1 H), 7.52-7.41 (m, 5 H), 3.92 (brs, 4 H), 3.85-3.83 (m, 4 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 193.0, 156.1, 139.4, 130.7, 128.4, 128.1, 112.2, 87.5, 67.1, 66.8, 52.1; ESI-HRMS Calcd for $C_{14}H_{15}N_2O_2S$ $[M + H]^+$ 275.0849, found 275.0860.

(*Z*)-1-(4-Chlorophenyl)-3-morpholino-2-thiocyanatoprop-2-en-1-one (**3m**). Yield 70%, 43.2 mg; R_f = 0.4; yellow solid; mp 134-135 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (s, 1 H), 7.46 (d, *J* = 8.3 Hz, 2 H), 7.40 (d, *J* = 8.3 Hz, 2 H), 3.93 (brs, 4 H), 3.85-3.84 (m, 4 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 191.7, 156.0, 137.8, 136.8, 129.5, 128.6, 112.0, 87.0, 66.8, 52.0; ESI-HRMS Calcd for $C_{14}H_{13}ClN_2NaO_2S$ $[M + Na]^+$ 331.0278, found 331.0277.

(*Z*)-1-Phenyl-3-(piperidin-1-yl)-2-thiocyanatoprop-2-en-1-one (**3n**). Yield 68%, 37.0 mg; R_f = 0.5; yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (s, 1 H), 7.51-7.40 (m, 5 H), 3.85 (brs, 4 H), 1.76 (s, 6 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 193.2, 156.3, 140.0, 130.3, 128.3, 128.0, 112.7, 85.9, 26.7, 23.9; ESI-HRMS Calcd for $C_{15}H_{17}N_2OS$ $[M + H]^+$ 273.1056, found 273.1059.

(*Z*)-3-(Dimethylamino)-1-phenyl-2-thiocyanatoprop-2-en-1-one (**3o**). Yield 71%, 33.0 mg; R_f = 0.4; yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (s, 1 H), 7.50-7.40 (m, 5 H), 3.38 (brs, 6 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 192.9, 158.5, 139.8, 130.4, 128.3, 128.1, 113.4, 87.5; ESI-HRMS Calcd for $C_{12}H_{12}N_2NaOS$ $[M + Na]^+$ 255.0563, found 255.0562.

(*Z*)-3-(Diethylamino)-1-phenyl-2-thiocyanatoprop-2-en-1-one (**3p**). Yield 79%, 41.1 mg; R_f = 0.3; yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (s, 1 H), 7.48-7.40 (m, 5 H), 3.82 (brs, 2 H), 3,43 (brs, 2 H), 1.29 (s, 6 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 192.8, 156.6, 140.1, 130.3, 128.3, 128.0, 112.8, 86.5, 53.6, 44.1, 14.4; ESI-HRMS Calcd for $C_{14}H_{17}N_2OS$ $[M + H]^+$ 261.1056, found 261.1057.

(*Z*)-3-(Dipropylamino)-1-phenyl-2-thiocyanatoprop-2-en-1-one (**3q**). Yield 78%, 45.0 mg; R_f = 0.5; yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (s, 1 H), 7.48-7.39 (m, 5 H), 3.78 (brs, 2 H), 3.22 (brs, 2 H), 1.69 (s, 4 H), 0.95 (s, 6 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 192.8, 157.1, 140.0, 130.3, 128.2, 128.0, 112.7, 86.5, 61.3, 50.8, 22.2, 10.8; ESI-HRMS Calcd for $C_{16}H_{21}N_2OS$ $[M + H]^+$ 289.1369, found 289.1383.

(*Z*)-3-(Ddibenzylamino)-1-phenyl-2-thiocyanatoprop-2-en-1-one (**3r**). Yield 74%, 57.0 mg; R_f = 0.5; yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (s, 1 H), 7.46-7.34 (m, 11 H), 7.17 (d, *J* = 6.9 Hz, 4 H), 4.77 (brs, 4 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 192.9, 157.8, 139.6, 134.5, 130.5, 129.3, 128.6, 128.4, 128.2, 127.6, 112.3, 88.8; ESI-HRMS Calcd for $C_{24}H_{20}N_2NaOS$ $[M + Na]^+$ 407.1189, found 407.1170.

(*Z*)-3-(Dimethylamino)-2-thiocyanato-1-(*p*-tolyl)prop-2-en-1-one (**3s**). Yield 75%, 36.9 mg; R_f = 0.7; yellow solid; mp 92-93 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (s, 1 H), 7.41 (d, *J* = 7.9 Hz, 2 H), 7.22 (d, *J* = 7.8 Hz, 2 H), 3.37 (brs, 6 H), 2.39 (s, 3 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 192.8, 158.3, 140.9, 136.9, 128.9, 128.3, 113.4, 87.4, 21.5; ESI-HRMS Calcd for $C_{13}H_{14}N_2NaOS$ $[M + Na]^+$ 269.0719, found 269.0718.

(*Z*)-1-(4-Chlorophenyl)-3-(dimethylamino)-2-thiocyanatoprop-2-en-1-one (**3t**). Yield 71%, 37.8 mg; R_f = 0.2; yellow solid; mp 85-86 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (s, 1 H), 7.45 (d, *J* = 8.4 Hz, 2 H), 7.39 (d, *J* = 8.4 Hz, 2 H), 3.39 (brs, 6 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 191.6, 158.3, 138.2, 136.5, 129.5, 128.5, 113.2, 87.0; ESI-HRMS Calcd for $C_{12}H_{11}ClN_2NaOS$ $[M + Na]^+$ 289.0173, found 289.0174.

(*Z*)-1-Phenyl-3-(pyrrolidin-1-yl)-2-selenocyanatoprop-2-en-1-one (**6**). Yield 64%, 39.1 mg; R_f = 0.3; yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (s, 1 H), 7.52-7.41 (m, 5 H), 3.84 (brs, 4 H), 2.03 (s, 4 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 192.7, 155.6, 140.1, 130.3, 128.3, 128.2, 104.2, 89.0, 25.1, 24.9; ESI-HRMS Calcd for $C_{14}H_{15}N_2OSe$ $[M + H]^+$ 307.0344, found 307.0342.

Synthesis of 3o in 1 mmol scale. To a 25 mL round bottom flask were charged with enaminone **1o** (1 mmol), NH_2SCN (2 mmol), RB (0.01 mmol) and THF (5 mL). The mixture was stirred at room temperature with the irradiation of 14 W CFL (distance bulb−vessel approximately 5 cm) for 12h under air atmosphere. Successively, 10 mL water was added to the flask, and the resulting mixture was extracted with ethyl acetate (3 × 10 mL). The subsequent operation following equivalent 0.2 mmol scale experiment provided product **3o** with 57% yield (133 mg).

General procedure for the synthesis of 3-thiocyanated chromenones 5. To a 25 mL round-bottom flask were added *o*-hydroxyaryl enaminone **4** (0.2 mmol), NH_4SCN (0.4 mmol), RB (0.002 mmol) and THF (2 mL). The mixture was then stirred at room temperature for 12h with the irradiation of 14 W CFL (distance bulb−vessel approximately 5 cm) under air atmosphere (TLC). Upon on completion, 5 mL water was added to the flask, and the resulting mixture was extracted with ethyl acetate (3 × 8 mL). The organic phases were collected dried with anhydrous Na_2SO_4. After filtration, the resulting solution was employed to reduced pressure to remove the solvent. The acquired residue was subjected to flash silica gel column chromatography to provide pure products by the elution with mixed petroleum ether/ethyl acetate (v/v = 10 : 1).

3-Thiocyanato-4*H*-chromen-4-one (**5a**).[5c] Yield 89%, 36.0 mg; R_f = 0.2; yellow solid; mp 150-151 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.35 (s, 1 H), 8.25 (d, *J* = 7.9 Hz, 1 H), 7.79 (t, *J* = 7.8 Hz, 1 H), 7.56-7.51 (m, 2 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 173.0, 156.3, 155.4, 135.0, 126.7, 126.1, 122.7, 118.4, 112.6, 108.9.

6-Methyl-3-thiocyanato-4*H*-chromen-4-one (**5b**).[5c] Yield 92%, 39.8 mg; R_f = 0.3; yellow solid; mp 134-135 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (s, 1 H), 8.00 (s, 1 H), 7.59-7.57 (m, 1 H), 7.44 (d, *J* = 8.6 Hz, 1 H), 2.48 (s, 3 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 173.0, 155.5, 154.6, 137.0, 136.2, 125.3, 122.4, 118.2, 112.1, 109.1, 21.0.

7-Methoxy-3-thiocyanato-4*H*-chromen-4-one (**5c**). Yield 94%, 43.8 mg; R_f = 0.2; yellow solid; mp 159-160 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (s, 1 H), 8.13 (d, *J* = 9.0 Hz, 1 H), 7.07-7.04 (m, 1 H), 6.90 (d, *J* = 2.2 Hz, 1 H), 3.94 (s, 3 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 172.2, 165.0, 158.3, 154.5, 127.5, 116.4, 116.0, 112.7, 109.1, 100.5, 56.1; ESI-HRMS Calcd for $C_{11}H_8NO_3S$ $[M + H]^+$ 234.0219, found 234.0219.

6-Fluoro-3-thiocyanato-4*H*-chromen-4-one (**5d**).[5c] Yield 80%, 35.4 mg; R_f = 0.2; yellow solid; mp 164-165 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.38 (s, 1 H), 7.88-7.86 (m, 1 H), 7.61-7.49 (m, 2 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 172.3, 158.9 (d, *J* = 244 Hz), 155.8, 152.6, 123.9 (d, *J* = 8.5 Hz), 123.5 (d, *J* = 24.2 Hz), 120.8 (d, *J* = 7.7 Hz), 112.1, 111.2 (d, *J* = 24.2 Hz), 108.7.

6-Chloro-3-thiocyanato-4*H*-chromen-4-one (**5e**).[5c] Yield 86%, 40.8 mg; R_f = 0.2; yellow solid; mp 185-186 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.35 (s, 1 H), 8.19 (d, *J* = 2.4 Hz, 1 H), 7.74-7.71 (m, 1 H), 7.53 (d, *J* = 9.0 Hz, 1 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 171.9, 155.4, 154.7, 135.3, 132.8,125.4, 123.5, 120.2, 112.9, 108.6.

6-Bromo-3-thiocyanato-4*H*-chromen-4-one (**5f**).[5c] Yield 82%, 46.1 mg; R_f = 0.4; yellow solid; mp 189-190 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.36-8.34 (m, 2 H), 7.87-7.85 (m, 1 H), 7.46 (d, *J* = 8.9 Hz, 1 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 171.8, 155.3, 155.1, 138.0, 128.7, 123.8, 120.3, 120.2, 113.0, 108.5.

7-Chloro-3-thiocyanato-4*H*-chromen-4-one (**5g**).[5c] Yield 84%, 39.8 mg; R_f = 0.3; yellow solid; mp 178-179 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31 (s, 1 H), 8.19 (d, *J* = 8.2 Hz, 1 H), 7.57 (s, 1 H), 7.49 (d, *J* = 8.1 Hz, 1 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 172.2, 156.4, 155.1, 141.3, 127.6, 127.5, 121.1, 118.5, 113.3, 108.6.

General procedure for the enaminone difunctionalized providing products 7. To a 25 mL round-bottom flask were charged with enaminone **2** (0.2 mmol), NH_4SCN **2** (0.4 mmol), $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (0.002 mmol) and EL (2 mL). The mixture was stirred with the irradiation of 14 W CFL for 12 h under air atmosphere (TLC). Upon completion, 5 mL of water was added to the flask, and the resulting mixture was extracted with ethyl acetate (3 × 8 mL). The combined organic phases were collected and washed with small amount of water for several times. After drying with anhydrous Na_2SO_4 and filtration, the solvent was removed from the solution at reduced pressure. The resulting residue was subjected to flash silica gel column chromatography to provide pure products by employing mixed petroleum ether/ethyl acetate (v/v = 3 : 1) as eluent.

(*E*)-3-Amino-1-phenyl-2-thiocyanatoprop-2-en-1-one (**7a**). Yield 76%, 31 mg; R_f = 0.3; yellow solid; mp 160-161 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.24-8.20 (m, 2 H), 7.69-7.63 (m, 1 H), 7.51-7.45 (m, 5 H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): 189.9, 159.0, 140.1, 130.8, 128.8, 128.3, 112.7, 90.0; ESI-HRMS Calcd for $C_{10}H_8N_2NaOS$ $[M + Na]^+$ 227.0250, found 227.0244.

(*E*)-3-Amino-2-thiocyanato-1-(p-tolyl)prop-2-en-1-one (**7b**). Yield 69%, 30.2 mg; R_f = 0.3; yellow solid; mp 142-143 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.20-8.16 (m, 2 H), 7.69-7.63 (m, 1 H), 7.36 (d, *J* = 8.0 Hz, 2 H), 7.27 (d, *J* = 7.9 Hz, 2 H), 2.36 (s, 3 H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): 189.7, 158.7, 140.7, 137.2, 129.3, 128.5, 112.7, 89.9, 21.4; ESI-HRMS Calcd for $C_{11}H_{11}N_2OS$ $[M + H]^+$ 219.0587, found 219.0586.

(*E*)-3-Amino-1-(4-chlorophenyl)-2-thiocyanatoprop-2-en-1-one (**7c**). Yield 44%, 21.0 mg; R_f = 0.2; yellow solid; mp 147-148 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.31-8.27 (m, 2 H), 7.71-7.65 (m, 1 H), 7.50 (q, *J* = 8.6 Hz, 4 H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): 188.7, 159.1, 138.8, 135.5, 130.3, 128.9, 112.6, 89.8; ESI-HRMS Calcd for $C_{10}H_8ClN_2OS$ $[M + H]^+$ 239.0040, found 239.0038.

(*E*)-3-Amino-1-(4-bromophenyl)-2-thiocyanatoprop-2-en-1-one (**7d**). Yield 41%, 23.1 mg; R_f = 0.2; yellow solid; mp 158-159 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.31-8.26 (m, 2 H), 7.71-7.65 (m, 3 H), 7.41 (d, J = 8.4 Hz, 2 H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): 188.8, 159.1, 139.2, 131.8, 130.5, 124.3, 112.6, 89.8; ESI-HRMS Calcd for $C_{10}H_8BrN_2OS$ $[M + H]^+$ 282.9535, found 282.9530.

(*E*)-3-Amino-1-(3,4-dichlorophenyl)-2-thiocyanatoprop-2-en-1-one (**7e**). Yield 42%, 23.0 mg; R_f = 0.2; yellow solid; mp 158-159 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.43-8.36 (m, 2 H), 7.78-7.71 (m, 3 H), 7.44 (d, *J* = 9.8 Hz, 1 H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): 187.3, 159.5, 140.6, 133.4, 131.7, 131.1, 130.2, 128.6, 112.5, 89.7; ESI-HRMS Calcd for $C_{10}H_7Cl_2N_2OS$ $[M + H]^+$ 272.9651, found 272.9645.

(*E*)-3-Amino-1-(naphthalen-2-yl)-2-thiocyanatoprop-2-en-1-one (**7f**). Yield 63%, 32.0 mg; R_f = 0.1; yellow solid; mp 178-179 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.27-8.25 (m, 2 H), 8.06-7.97 (m, 4 H), 7.81-7.75 (m, 1 H), 7.63-7.56 (m, 3 H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): 189.8, 159.2, 137.3, 134.1, 132.5, 129.1, 128.5, 128.2, 128.1, 127.8, 127.2, 125.7, 112.7, 90.2; ESI-HRMS Calcd for $C_{14}H_{11}N_2OS$ $[M + H]^+$ 255.0587, found 255.0583.

The transamination reaction between enaminone 1d and aniline with $Ru(bpy)_3Cl_2·6H_2O$. Enaminone **1d** (0.2 mmol), aniline **8** (0.2 mmol) and $Ru(bpy)_3Cl_2·6H_2O$ (0.002 mmol) were mixed with EL (2 mL) in the 25 mL round bottom flask, and the mixture was stirred at room temperature for 12h without CFL irradiation. After pouring water (10 mL) into the vessel to quench the reaction, the resulting mixture was extracted with ethyl acetate (3 × 8 mL). The subsequent treatment following known procedures[18a] gave pure product **9**.

ASSOCIATED CONTENT

Supporting Information.

The Supporting Information is available free of charge on the ACS Pulicationss website at DOI:

Details on the fluorescent quenching experiments, ^1H and ^{13}C NMR spectra of all products.

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Notes

The authors declare no competing financial interest.

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REFERENCES

1 (a) Dean, L. J.; Prinsep, M. R. The chemistry and chemical ecology of nudibranchs. *Nat. Prod. Rep.* **2017**, *34*, 1359-1390. (b) Elhalem, E.; Bailey, B. N.; Docampo, R.; Ujváry, I.; Szajnman, S. H.; Rodriguez, J. B. Design, synthesis, and biological evaluation of aryloxyethyl thiocyanate derivatives against trypanosoma cruzi. *J. Med. Chem.* **2002**, *45*, 3984-3999. (c) Dutta, S.; Abe, H.; Aoyagi, S.; Kibayashi, C.; Gates, K. S. DNA damage by fasicularin. *J. Am. Chem. Soc.* **2005**, *127*, 15004-15005. (d) Capon, R. J.; Skene, C.; Liu, E. H.-T.; Lacey, E.; Gill, J. H.; Heiland, K.; Friedel, T. The isolation and synthesis of novel nematocidal dithiocyanates from an australian marine sponge, oceanapia sp. *J. Org. Chem.* **2001**, *66*, 7765-7769.

2 (a) Brown, S. P.; Smith, A. B., III Peptide/Protein stapling and unstapling: introduction of s-tetrazine, photochemical release, and regeneration of the peptide/protein. *J. Am. Chem. Soc.* **2015**, *137*, 4034-4037. (b) Bayarmagnai, B.; Matheis, C.; Jouvin, K.; Goossen, L. J. Synthesis of difluoromethyl thioethers from difluoromethyl trimethylsilane and organothiocyanates generated in situ. *Angew. Chem., Int. Ed.* **2015**, *54*, 5753-5756. (c) Li, L.; Ganesh, M.; Seidel, D. Catalytic enantioselective synthesis of α,β-diamino acid derivatives. *J. Am. Chem. Soc.* **2009**, *131*, 11648-11649. (d) Chen, B.; Guo, S.; Guo, X.; Zhang, G.; Yu, Y. Selective access to 4-substituted 2-aminothiazoles and 4-substituted 5-thiocyano-2-aminothiazoles from vinyl azides and potassium thiocyanate switched by palladium and iron catalysts. *Org. Lett.* **2015**, *17*, 4698-4701. (e) Lei, W.-L.; Wang, T.; Feng, K.-W.; Wu, L.-Z.; Liu, Q. Visible-light-driven synthesis of 4-alkyl/aryl-2-aminothiazoles promoted by in situ generated copper photocatalyst. *ACS Catal.* **2017**, *7*, 7941-7945. (f) D'hooghe, M.; Waterinckx, A.; De Kimpe, N. A novel entry toward 2-imino-1,3-thiazolidines and 2-imino-1,3-thiazolines by ring transformation of 2-(thiocyanomethyl)aziridines. *J. Org. Chem.* **2005**, *70*, 227-232. (g) Zhen, L.; Yuan, K.; Li, X.; Zhang, C.; Yang, J.; Fan, H.; Jiang, L. Cascade reaction of propargyl amines with $AgSCF_3$, as well as one-pot reaction of propargyl amines, $AgSCF_3$, and di-tert-butyl peroxide: access to allenyl thiocyanates and allenyl trifluoromethylthioethers. *Org. Lett.* **2018**, *20*, 3109-3113.

3 (a) Yu, J.-T.; Teng, F.; Cheng, J. The construction of X–CN (X=N, S, O) bonds. *Adv. Synth. Catal.* **2017**, *359*, 26-38. (b) Guo, W.; Tan, W.; Zhao, M.; Zheng, L.; Tao, K.; Chen, D.; Fan, X. Direct photocatalytic S–H bond cyanation with green "CN" source. *J. Org. Chem.* **2018**, *83*, 6580-6588. (c) Zhu, D.; Chang, D.; Shi, L. Transition-metal-free cross-coupling of thioethers with aryl(cyano)iodonium triflates: a facile and efficient method for the one-pot synthesis of thiocyanates. *Chem. Commun.* **2015**, *51*, 7180-7183. (d) Teng, F.; Yu, J.-T.; Yang, H.; Jiang, Y.; Cheng, J. Copper-catalyzed cyanation of disulfides by azobisisobutyronitrile leading to thiocyanates. *Chem. Commun.* **2014**, *50*, 12139-12141. (e) Frei, R.; Courant, T.; Wodrich, M. D.; Waser, J. General and practical formation of thiocyanates from thiols. *Chem.-Eur. J.* **2015**, *21*, 2662-2668. (f) Liang, Z.; Wang, F.; Chen, P.; Liu, G. Copper-catalyzed intermolecular trifluoromethylthiocyanation of alkenes: convenient access to CF_3-containing alkyl thiocyanates. *Org. Lett.* **2015**, *17*, 2438-2441. (g) Yang, X.; She, Y.; Chong, Y.; Zhai, H.; Zhu, H.; Chen, B.; Huang, G.; Yan, R. Iodothiocyanation/nitration of allenes with potassium thiocyanate/silver nitrite and iodine. *Adv. Synth. Catal* **2016**, *358*, 3130-3134.

4 For a review and selected examples, see: (a) Castanheiro, T.; Suffert, J.; Donnard, M.; Gulea, M. Recent advances in the chemistry of organic thiocyanates. *Chem. Soc. Rev.* **2016**, *45*, 494-505. (b) Jiang, G.; Zhu, C.; Li, J.; Wu, W.; Jiang, H. Silver‐catalyzed regio‐ and stereoselective thiocyanation of haloalkynes: access to (Z)-vinyl thiocyanates. *Adv. Synth. Catal.* **2017**, *359*, 1208-1212. (c) Dwivedi, V.; Rajesh, M.; Kumar, R.; Kant, R.; Reddy, M. S. A stereoselective thiocyanate conjugate addition to electron deficient alkynes and concomitant cyclization to N,S-heterocycles. *Chem. Commun.* **2017**, *53*, 11060-11063. (d) Sun, N.; Che, L.; Mo, W.; Hu, B.; Shen, Z.; Hu, X. A mild copper-catalyzed aerobic oxidative thiocyanation of arylboronic acids with TMSNCS. *Org. Biomol. Chem.* **2015**, *13*, 691-696. (e) Wu, C.; Lu, L.-H.; Peng, A.-Z.; Jia, G.-K.; Peng, C.; Cao, Z.; Tang, Z.; He, W.; Xu, X. Ultrasound-promoted Brønsted acid ionic liquid-catalyzed hydrothiocyanation of activated alkynes under minimal solvent conditions. *Green Chem.* **2018**, *20*, 3683-3688. (f) Pan, F.; Li, X.-L.; Chen, X.-M.; Shu, C.; Ruan, P.-P.; Shen, C.-H.; Lu, X.; Ye, L.-W. Catalytic ynamide oxidation strategy for the preparation of α-functionalized amides. *ACS Catal.* **2016**, *6*, 6055-6062. (g) Tao, Z.; Li, C.-K.; Zhang, P.-Z.; Shoberu, A.; Zou, J.-P.; Zhang, W. Phosphinoyl radical-initiated 1,2-bifunctional thiocyanodiphenylphosphinoylation of alkenes. *J. Org. Chem.* **2018**, *83*, 2418-2424. (h) Modi, A.; Ali, W.; Patel, B. K. Organocatalytic regioselective concomitant thiocyanation and acylation of oxiranes using aroyl isothiocyanates. *Org. Lett.* **2017**, *19*, 432-435. (i) Yang, H.; Duan, X.-H.; Zhao, J.-F.; Guo, L.-N. Transition-metal-free tandem radical thiocyanooxygenation of olefinic amides: a new route to SCN-containing heterocycles. *Org. Lett.* **2015**, *17*, 1998-2001.

5 (a) Jiang, H.; Yu, W.; Tang, X.; Li, J.; Wan, W. Copper-catalyzed aerobic oxidative regioselective thiocyanation of aromatics and heteroaromatics. *J. Org. Chem.* **2017**, *82*, 9312-9320. (b) Zhang, H.; Wei, Q.; Wei, S.; Qu, J.; Wang, B. Highly efficient and practical thiocyanation of imidazopyridines using an N-chlorosuccinimide /NaSCN combination. *Eur. J. Org. Chem.* **2016**, 3373-3379. (c) Zhang, X.-Z.; Ge, D.-L.; Chen, S.-Y.; Yu, X.-Q. A catalyst-free approach to 3-thiocyanato-4H-chromen-4-ones. *RSC Adv.* **2016**, *6*, 66320-66323. (d) Wang, C.; Wang, Z.; Wang, L.; Chen, Q.; He, M. Catalytic thiourea promoted electrophilic thiocyanation of indoles and aromatic amines with NCS/NH_4SCN. *Chin. J. Chem.* **2016**, *34*, 1081-1085. (e) Ren, Y.-L.; Wang, W.; Zhao, B.; Tian, Z.; Zhao, S.; Wang, J.; Li, F. Nitrogen dioxide catalyzed oxidative thiocyanation of arenes with ambient air as the terminal oxidant. *ChemCatChem* **2016**, *8*, 3361-3366. (f) Chen, Q.; Lei, Y.; Wang, Y.; Wang, C.; Wang, Y.; Xu, Z.; Wang, H.; Wang, R. Direct thiocyanation of ketene dithioacetals under transition-metal-free conditions. *Org. Chem. Front.* **2017**, *4*,

369-372. (g) Khalili, D. Graphene oxide: a promising carbocatalyst for the regioselective thiocyanation of aromatic amines, phenols, anisols and enolizable ketones by hydrogen peroxide/KSCN in water. *New. J. Chem.* **2016**, *40*, 2547-2553. (h) Yang, D.; Yan, K.; Wei, W.; Li, G.; Lu, S.; Zhao, C.; Tian, L.; Wang, H. Catalyst-Free Regioselective C-3 Thiocyanation of Imidazopyridines. *J. Org. Chem.* **2015**, *80*, 11073-11079. (i) Mitra, S.; Ghosh, M.; Mishra, S.; Hajra, A. Metal-free thiocyanation of imidazoheterocycles through visible light photoredox catalysis. *J. Org. Chem.* **2015**, *80*, 8275-8281. (j) Fan, W.; Yang, Q.; Xu, F.; Li, P. A visible-light-promoted aerobic metal-free C-3 thiocyanation of indoles. *J. Org. Chem.* **2014**, *79*, 10588-10592. (k) Ichake, S. S.; Rajawinslin, R. R.; Kavala, V.; Villuri, B. K.; Yang, H.-T.; Kuo, C.-W.; Yao, C.-F. N-Bromosuccinimide - mediated thiocyanation of cyclohexene - fused isoxazoline N-oxides. *Asian J. Org. Chem.* **2016**, *5*, 343-352. (l) Zhang, W.; Tang, J.; Yu, W.; Huang, Q.; Fu, Y.; Kuang, G.; Pan, C.; Yu, G. Visible light-driven C-3 functionalization of indoles over conjugated microporous polymers. *ACS Catal.* **2018**, *8*, 8084-8091.

6 (a) Chen, Y.; Wang, S.; Jiang, Q.; Cheng, C.; Xiao, X.; Zhu, G. Palladium-catalyzed site-selective sp^3 C–H bond thiocyanation of 2-aminofurans. *J. Org. Chem.* **2018**, *83*, 716-722. (b) Qiu, J.; Wu, D.; Karmaker, P. G.; Yin, H.; Chen, F.-X. Enantioselective organocatalyzed direct α-thiocyanation of cyclic β-ketoesters by N-thiocyanatophthalimide. *Org. Lett.* **2018**, *20*, 1600-1603. (c) Wu, D.; Qiu, J.; Karmaker, P. G.; Yin, H.; Chen, F.-X. N-Thiocyanatosaccharin: a "sweet" electrophilic thiocyanation reagent and the synthetic applications. *J. Org. Chem.* **2018**, *83*, 1576-1583. (d) Liang, S.; Zeng, C.-C.; Tian, H.-Y.; Sun, B.-G.; Luo, X.-G.; Ren, F.-Z. Redox active sodium iodide/recyclable heterogeneous solid acid: an efficient dual catalytic system for electrochemically oxidative α-C–H thiocyanation and sulfenylation of ketones. *Adv. Synth. Catal.* **2018**, *360*, 1444-1452. (e) Kang, L.-S.; Luo, M.-H.; Lam, C. M.; Hu, L.-M.; Little, R. D.; Zeng, C.-C. Electrochemical C–H functionalization and subsequent C–S and C–N bond formation: paired electrosynthesis of 3-amino-2-thiocyanato-α,β-unsaturated carbonyl derivatives mediated by bromide ions. *Green Chem.* **2016**, *18*, 3767-3774. (f) Yuan, P.-F.; Zhang, Q.-B.; Jin, X.-L.; Lei, W.-L.; Wu, L.-Z.; Liu, Q. Visible-light-promoted aerobic metal-free aminothiocyanation of activated ketones. *Green Chem.* **2018**, *20*, 5464-6468.

7 For reviews, see: (a) Stanovnik, B.; Svete, J. Synthesis of heterocycles from alkyl 3-(dimethylamino)propenoates and related enaminones. *Chem. Rev.* **2004**, *104*, 2433-2480. (b) Wan, J.-P.; Gao, Y. Domino reactions based on combinatorial bond transformations in electron - deficient tertiary enamines. *Chem. Rec.* **2016**, *16*, 1164-1177. (c) Elassar, A.-Z. A.; El-Khair, A. A. Recent developments in the chemistry of enaminones. *Tetrahedron* **2003**, *59*, 8463-8480.

8 (a) Würtz, S.; Rakshit, S.; Neumann, J. J.; Dröge, T.; Glorius, F. Palladium - catalyzed oxidative cyclization of N-aryl enamines: from anilines to indoles. *Angew. Chem. Int. Ed.* **2008**, *47*, 7230-7233. (b) Bernini, R.; Fabrizi, G.; Sferrazza, A.; Cacchi, S. Copper-catalyzed C-C bond formation through C-H functionalization: synthesis of multisubstituted indoles from N-aryl Enaminones. *Angew. Chem. Int. Ed.* **2009**, *48*, 8078-8081. (c) Zoller, J.; Fabry, D. C.; Ronge, M. A.; Rueping, M. Synthesis of indoles using visible light: photoredox catalysis for palladium - catalyzed C-H activation. *Angew. Chem. Int. Ed.* **2014**, *53*, 13264-13268. (d) Yu, W.; Du, Y.; Zhao, K. PIDA-mediated oxidative C−C bond formation: novel synthesis of indoles from n-aryl enamines. *Org. Lett.* **2009**, *11*, 2417-2420. (e) Tang, S.; Gao, X.; Lei, A. Electrocatalytic intramolecular oxidative annulation of N-aryl enamines into substituted indoles mediated by iodides. *Chem. Commun.* **2017**, *53*, 3354-3356.

9 (a) Ge, H.; Niphakis, M. J.; Georg, G. I. Palladium(II)-catalyzed direct arylation of enaminones using organotrifluoroborates. *J. Am. Chem. Soc.* **2008**, *130*, 3708-3709. (b) Xiang, H.; Zhao, Q.; Tan, Z.; Xiao, J.; Xia, P.; Wang, C.; Yang, C.; Chen, X.; Yang, H. Visible-light-driven, radical-triggered tandem cyclization of o-hydroxyaryl enaminones: facile access to 3-CF_2/CF_3-containing chromones. *Org. Lett.* **2017**, *19*, 146-149. (c) Hu, W.; Zheng, J.; Li, L.; Wan, W.; Liu, H.; Jiang, H. Palladium-catalyzed intermolecular oxidative coupling reactions of (Z)-enamines with isocyanides through selective β-C(sp^2)-H and/or C=C bond cleavage. *Chin. J. Chem.* **2018**, *36*, 712-715.

10 (a) Guo, Y.; Xiang, Y.; Wei, L.; Wan, J.-P. Thermoinduced free-radical C–H acyloxylation of tertiary enaminones: catalyst-free synthesis of acyloxyl chromones and enaminones. *Org. Lett.* **2018**, *20*, 3971-3974. (b) Wang, F.; Sun, W.; Wang, Y.; Jiang, Y.; Loh, T.-P. Highly site-selective metal-free C–H acyloxylation of stable enamines. *Org. Lett.* **2018**, *20*, 1256-1260. (c) Liu, X.; Cheng, R.; Zhao, F.; Zhang-Negrerie, D.; Du, Y.; Zhao, K. Direct β-acyloxylation of enamines via PhIO-mediated intermolecular oxidative C–O bond formation and its application to the synthesis of oxazoles. *Org. Lett.* **2012**, *14*, 5480-5483. (d) Yuan, J.; Zhang, Q.; Yu, M.; Huang, P.; Zhang, R.; Dong, D. Phenyliodine(III) diacetate mediated oxidative cyclization of 1-alkenoyl-1-carbamoyl cycloalkanes: access to spiro-fused dihydrofuran-3(2H)-ones. *Org. Lett.* **2015**, *17*, 5012-5015.

11 (a) Yuan, Y.; Hou, W.; Zhang-Negrerie, D.; Zhao, K. Du, Y. Direct oxidative coupling of enamines and electron-deficient amines: TBAI/TBHP-mediated synthesis of substituted diaminoalkenes under metal-free conditions. *Org. Lett.* **2014**, *16*, 5410-5413. (b) Zheng, C.; Wang, Y.; Fan, R. Iodine(III)-Mediated oxidative cross-coupling of enamines and propargylamines under metal-free conditions: an alternative way to prepare highly substituted 3-pyrrolines. *Org. Lett.* **2015**, *17*, 916-919.

12 (a) Wan, J.-P.; Zhong, S.; Xie, L.; Cao, X.; Liu, Y.; Wei, L. KIO_3-catalyzed aerobic cross-coupling reactions of enaminones and thiophenols: synthesis of polyfunctionalized alkenes by metal-free C–H sulfenylation. *Org. Lett.* **2016**, *18*, 584-587. (b) Sun, J.; Zhang-Negrerie, D.; Du, Y. Oxidative coupling of enamines and disulfides via tetrabutylammonium iodide/tert - butyl hydroperoxide - mediated intermolecular oxidative C(sp^2)-S bond formation under transition metal-free conditions. *Adv. Synth. Catal.* **2016**, *358*, 2035-2040. (c) Siddaraju, Y.; Probhu, K. R. Iodine-catalyzed cross dehydrogenative coupling reaction: sulfenylation of enaminones using dimethyl sulfoxide as an oxidant. *J. Org. Chem.* **2017**, *82*, 3084-3093. (d) Rafique, J.; Saba, S.; Schneider, A. R.; Franco, M. S.; Silva, S. M.; Braga, A. L. Metal- and solvent-free approach to access 3-Se/S-chromones from the cyclization of enaminones in the presence of dichalcogenides catalyzed by KIO_3. *ACS Omega* **2017**, *2*, 2280-2290. (e) Gao, Y.; Hu, C.; Wen, C.; Wan, J.-P. Tunable synthesis of disulfide-functionalized enaminones and 1,4-thiazines via the reactions of enaminones and β-aminoethanethiol. *ACS Omega* **2017**, *2*, 7784-7789. (f) Wan, J.-P.; Cao, S.; Hu, C.; Wen, C. Iodine - catalyzed, ethyl-lactate - mediated synthesis of 1,4 - benzothiazines via metal-free cascade enaminone transamination and C−H sulfenylation. *Asian J. Org. Chem.* **2018**, *7*, 328-331.

13 Wan, J.-P.; Zhong, S.; Guo, Y.; Wei, L. Iodine-mediated domino c(sp2) - h sulfonylation/annulation of enaminones and sulfonyl hydrazines for the synthesis of 3 - sulfonyl chromones. *Eur. J. Org. Chem.* **2017**, 4401-4404.

14 Gao, Y.; Wei, L.; Liu, Y.; Wan, J.-P. Iodine-mediated synthesis of sulfur-bridged enaminones and chromones via double C(sp^2)–H thiolation. *Org. Biomol. Chem.* **2017**, *15*, 4631-4634.

15 For selected recent references on metal-free photocatalytic reactions, see: (a) Romero, N. A.; Nicewicz, D. A. Organic photoredox catalysis. *Chem. Rev.* **2016**, *116*, 10075-10166. (b) Liu, Q.; Wu, L.-Z. Recent advances in visible-light-driven organic reactions. *Nat. Sci. Rev.* **2017**, *4*, 359-380. (c) Xie, J.; Jin, H.; Xu, P.; Zhu, C. When C–H bond functionalization meets visible-light photoredox catalysis. *Tetrahedron Lett.* **2014**, *55*, 36-48. (d) Hering, T.; Meyer, U.; König, B. Photocatalytic anion oxidation and applications in organic synthesis. *J. Org. Chem.* **2016**, *81*, 6927-6936. (e) Wei, W.; Bao, P.; Yue, H.; Liu, S.; Wang, L.; Li, Y.; Yang, D. Visible-light-enabled construction of thiocarbamates from isocyanides, thiols, and water at room temperature. *Org. Lett.* **2018**, *20*, 5291-5295. (f) Wei, W.; Cui, H.; Yue, H.; Yang, D. Visible-light-enabled oxyazidation of

alkenes leading to α-azidoketones in air. *Green Chem.* **2018**, *20*, 3197-3202. (g) Pan, Y.; Kee, C. W.; Chen, L.; Tan, C.-H. Dehydrogenative coupling reactions catalysed by Rose Bengal using visible light irradiation. *Green Chem.* **2011**, *13*, 2682-2685. (h) Ding, X.; Dong, C.-L.; Guan, Z.; He, Y.-H. Visible - light - promoted alkylation of indoles with tertiary amines by the oxidation of a sp^3 C-H bond. *Adv. Synth. Catal.* **2018**, *360*, 762-767. (i) Yan, D.-M.; Zhao, Q.-Q.; Rao, L.; Chen, J.-R.; Xiao, W.-J. Eosin Y as a Redox Catalyst and Photosensitizer for Sequential Benzylic C−H Amination and Oxidation. *Chem. Eur. J.* **2018**, *24*, 16895-16901.

16 For reviews on the Ru-complex-based photocatalysis, see: (a) Prier, C. K.; Rankic, D. A.; MacMillan, D. W. C. Visible light photoredox catalysis with transition metal complexes: applications in organic synthesis. *Chem. Rev.* **2013**, *113*, 5322-5363. (b) Chen, J.-R.; Hu, X.-Q.; Lu, L.-Q.; Xiao, W.-J. Visible light photoredox-controlled reactions of N-radicals and radical ions. *Chem. Soc. Rev.* **2016**, *45*, 2044-2056. (c) Chen, J.-R.; Hu, X.-Q.; Lu, L.-Q.; Xiao, W.-J. Exploration of Visible-Light Photocatalysis in Heterocycle Synthesis and Functionalization: Reaction Design and Beyond. *Acc. Chem. Res.* **2016**, 49, 1911-1923. (d) Xi, Y.; Yi, H.; Lei, A. Synthetic applications of photoredox catalysis with visible light. *Org. Biomol. Chem.* **2013**, *11*, 2387-2403. (e) Koike, T.; Akita, M. Visible-light radical reaction designed by Ru- and Ir-based photoredox catalysis. *Inorg. Chem. Front.* **2014**, *1*, 562-576.

17 Keshari, T.; Yadav, V. K.; Srivastava, V. P.; Yadav, L. D. S. Visible light organophotoredox catalysis: a general approach to β-keto sulfoxidation of alkenes. *Green Chem.* **2014**, *16*, 3986-3992.

18 The Lewis acid and EL are both positive for the transamiantion of tertiary enaminones: (a) Liu, Y.; Zhou, R.; Wan, J.-P. Water-promoted synthesis of enaminones: mechanism investigation and application in multicomponent reactions. *Synth. Commun.* **2013**, *43*, 2475-2483. (b) Gao, Y.; Liu, Y.; Wei, L.; Wan, J.-P. Synthesis of enaminones containing diverse N,N-disubstitution via simple transamination: a study with sustainable catalyst-free operation. *Res. Chem. Intermed.* **2017**, *43*, 5547-5555.

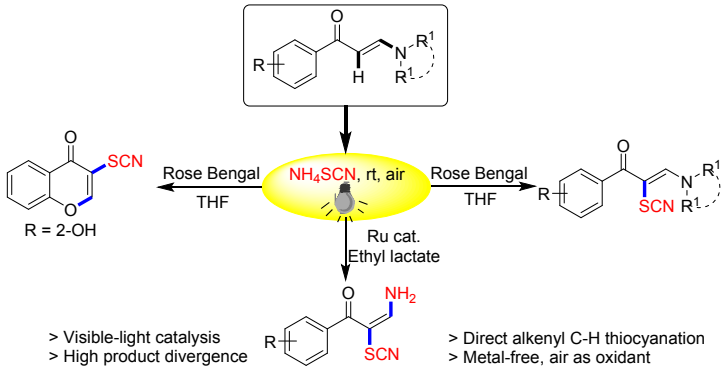
19 EL-Taweel, F. M. A. A.; Elnagdi, M. H. Studies with enaminones: synthesis of new coumarin-3-yl azoles, coumarin-3-yl azines, coumarin-3-yl azoloazines, coumarin-3-yl pyrone and coumarin-2-yl benzo[b]Furans. *J. Heterocyclic Chem.* **2001**, *38*, 981-984.

20 Kashima, C.; Tajima, T.; Omote, Y. The preparation and nucleophilic reaction of 3,3-di(1-azolyl)-2-alken-1-ones, precursors of acetylketene derivatives. *J. Heterocyclic Chem.* **1984**, *21*, 133-137.

21 Kumar, D.; Kommi, D. N.; Chopra, P.; Ansari, M. I.; Chakraborti, A. K. L-Proline-Catalyzed Activation of Methyl Ketones or Active Methylene Compounds and DMF-DMA for Syntheses of (2E)-3-Dimethylamino-2propen-1-ones. *Eur. J. Org. Chem.* **2012**, 6407-6413.

22 Akram, M. O.; Bera, S.; Patil, N. A facile strategy for accessing 3-alkynylchromones through gold-catalyzed alkynylation/cyclization of o-hydroxyarylenaminones. *Chem. Commun.* **2016**, *52*, 12306-12309.

23 Gammill, R. B. A New and Efficient Synthesis of 3-Halogenated 4H-1-Benzopyran-4-ones. *Synthesis* **1979**, 901-903.


R
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SCN
R1
Ru cat.
Ethyl lactate
NH2
O
R
SCN
> Visible-light catalysis
> High product divergence
> Direct alkenyl C-H thiocyanation
> Metal-free, air as oxidant